JOC The Journal of Organic Chemistry
Cite This: J. Org. Chem. 2018, 83, 11359−11368
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pubs.acs.org/joc

Synthesis of Halogenated Anilines by Treatment of *N,N*-Dialkylaniline *N*-Oxides with Thionyl Halides

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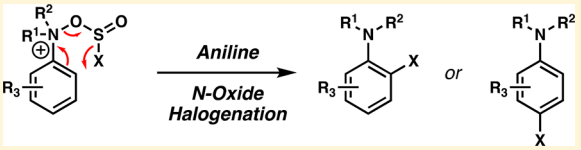
Supporting Information

ABSTRACT: The special reactivity of *N,N*-dialkylaniline *N*-oxides allows practical and convenient access to electron-rich aryl halides. A complementary pair of reaction protocols allow for the selective *para*-bromination or *ortho*-chlorination of *N,N*-dialkylanilines in up to 69% isolated yield. The generation of a diverse array of halogenated anilines is made possible by a temporary oxidation level increase of *N,N*-dialkylanilines to the corresponding *N,N*-dialkylaniline *N*-oxides and the excision of the resultant weak *N*−*O* bond via treatment with thionyl bromide or thionyl chloride at low temperature.

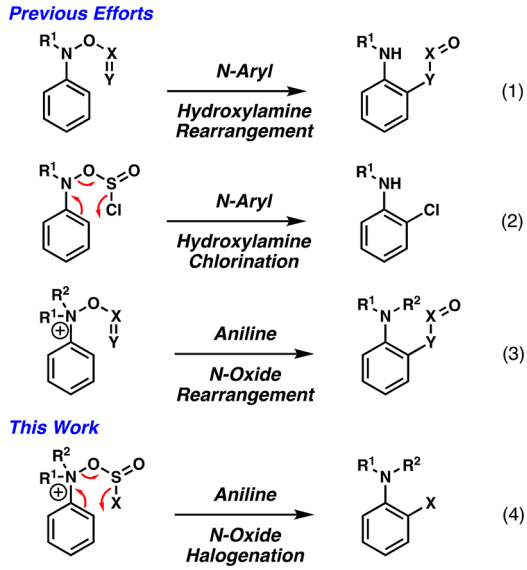


Halogenated aromatic rings are ubiquitous in various disciplines of the organic chemistry field. Aryl halides are critically important synthetic building blocks for use in cross-coupling chemistries,[1] lithium−halogen exchange reactions,[2] and classical Grignard reactions.[3] Collectively, these methods represent some of the most highly utilized means of constructing carbon−carbon bonds in synthesis. Aryl halides are also common substructures in synthetic and naturally occurring biologically active molecules and constitute some end-user industrial materials as well.[4] Classical methods of preparing aryl halides (e.g., electrophilic aromatic substitution) are prone to complications in electron-rich settings;[5,6] aniline and phenol substrates are highly reactive toward electrophilic halogenation reagents, often compromising the regioselectivity or stoichiometry of the resultant reactions.[7] Thus, new synthetic methods for the regioselective halogenation of electron-rich aromatics are of high utility in synthetic organic chemistry.

We have a longstanding interest in the manipulations of anilines at elevated oxidation levels (Scheme 1).[8] The functionalization of anilines by group transfer is known at the *N*-arylhydroxylamine oxidation level (Scheme 1, eqs 1 and 2),[9] and a small number of examples of *ortho*-chlorination reactions have been reported on that platform (Scheme 1, eq 3).[10] We report here the practical and convenient syntheses of 2-chloro-*N,N*-dialkylanilines and 4-bromo-*N,N*-dialkylanilines as part of our ongoing interests in the reactivity of aniline *N*-oxides (Scheme 1, eq 4). In our previous work, we demonstrated that *N,N*-dimethylaniline *N*-oxides can be acylated with a variety of electrophiles, and the resultant *O*-acylated materials can undergo a group transfer event by which a variety of C−O, C−N, and C−C bonds are generated.[8a] The materials so derived constitute a diverse array of useful materials that are otherwise unavailable by traditional synthetic methods (e.g., electrophilic aromatic substitution). The mechanistic pathways of these group-transfer events are ambiguous; possibilities include [3,3]-sigmatropic rearrangements in which the N−O bond is excised as a C−X bond is formed or stepwise processes in which the N−O bond is excised homolytically followed by a radical recombination in which the C−X bond is formed. We envisioned that monohalogenation of the aniline platform could be achieved by treatment of aniline *N*-oxides with thionyl halides or phosphorus oxyhalides; transfer of the halogen atom would result in expulsion of sulfur dioxide or metaphosphoryl halide.

We quickly determined that treatment of the aniline *N*-oxide **1a** with phosphorus oxychloride could generate the corresponding aryl chloride but only in trace yields. However, treatment of aniline *N*-oxide **1a** with thionyl halides in dichloromethane followed by base cleanly afforded the

Scheme 1. Aniline Functionalization by Group Transfer

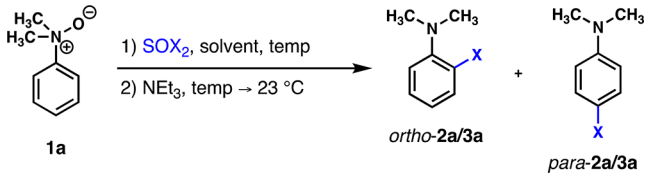


Received: June 25, 2018
Published: July 26, 2018

DOI: 10.1021/acs.joc.8b01590
J. Org. Chem. 2018, 83, 11359−11368

corresponding aryl halides at low temperature (Table 1, entry 1). For example, treatment of *N*,*N*-dimethylaniline *N*-oxide **1a**

Table 1. Optimization of the *N*,*N*-Dimethylaniline *N*-Oxide Halogenation Reactions[a]



entry	solvent	temp (°C)	X = Br, yield (4-Br) (%)	X = Cl, yield (2-Cl/4-Cl) (%)
1	CH_2Cl_2	−78	31	25 (4.3:1)
2	CH_2Cl_2	−40	26	22 (4.0:1)
3	CH_2Cl_2	−85	13	15 (6.6:1)
4	Et_2O	−78	27	20 (3.6:1)
5	THF	−78	55	35 (4.0:1)
6[b]	THF	−78	53	49 (4.9:1)

[a]Yields of isolated products; reactions were performed on a 0.7 mmol scale. Addition of SOX_2 was followed by stirring at the indicated temperature for 4 h. [b]Addition of SOX_2 was divided into two portions (0.5 equiv, followed by 0.5 equiv after 2 h).

with 1 equiv of thionyl bromide in dichloromethane at −78 °C for 4 h followed by addition of 4 equiv of triethylamine and warming to room temperature afforded the corresponding 4-bromo-*N*,*N*-dimethylaniline **2a** in 31% yield after an aqueous workup. The regioisomeric aryl chloride **3a** could be obtained in 25% yield by treatment of **1a** with thionyl chloride under otherwise identical conditions (Table 1, entry 1). Isolated yields were diminished when the reaction temperature was warmed above or cooled below −78 °C (Table 1, entries 2 and 3). Unlike our previous work with aniline *N*-oxides, we found the halogenation reactions to be highly sensitive to solvent. Reactions conducted in tetrahydrofuran were routinely more efficient; treatment of **1a** with thionyl halides in THF at −78 °C followed by addition of 4 equiv of triethylamine and warming to room temperature afforded a 55% yield of the aryl bromide **2a** and a 35% yield of the aryl chloride **3a** (Table 1, entry 5). Interestingly, addition of 1 equiv of thionyl chloride in two portions over a period of 4 h under otherwise identical reaction conditions markedly improved the isolated yield of the aryl chloride **3a** (49%, Table 1, entry 6). No such advantage was apparent for reactions with thionyl bromide. Most interestingly, we found the halogenation reactions to be highly regioselective; treatment of *N*,*N*-dimethylaniline *N*-oxides with thionyl bromide results in the corresponding 4-bromo-*N*,*N*-dimethylanilines exclusively, while treatment with thionyl chloride results in predominately the corresponding 2-chloro-*N*,*N*-dimethylanilines (3.6−6.6:1 2-chloro/4-chloro).

Utilizing our optimized reaction conditions, we generated a variety of halogenated anilines, and we found the selectivity profiles to be general. Treatment of diversely substituted *N*,*N*-dialkylaniline *N*-oxides (including *N*,*N*-dimethyl-1-naphthylamine *N*-oxide, and *N*-methyl-tetrahydroquinoline *N*-oxide) with thionyl bromide under the optimized reaction conditions routinely afforded 4-bromo-*N*,*N*-dialkylanilines **2a**−**t** (including 4-bromo-*N*,*N*-dimethyl-1-naphthylamine **2d** and 7-bromo-*N*-methyltetrahydroquinoline **2t**) in up to 69% yield (Table 2). In all cases, we observed no evidence for the formation of the corresponding 2-bromo-substituted equivalents; however, if we blocked that position by subjecting 4-substituted substrates to our reaction conditions, we could observe 2-bromo-substituted products in reduced yields (Table 2, **2k**−**o**).

Treatment of a similar set of *N*,*N*-dialkylaniline *N*-oxides (including *N*,*N*-dimethyl-1-naphthylamine *N*-oxide and *N*-methyl-tetrahydroquinoline *N*-oxide) with thionyl chloride under the optimized reaction conditions routinely afforded 2-chloro-*N*,*N*-dialkylanilines **3a**−**j** (including 2-chloro-*N*,*N*-dimethyl-1-naphthylamine **3d** and 9-chloro-*N*-methyl-tetrahydroquinoline **3o**) in up to 65% yield with up to 6.7:1 (2-Cl/4-Cl) selectivity (Table 3), though some 2-substituted anilines are problematic in chlorination reactions (e.g., **3k**).

Together, these reactions comprise a complementary set of synthetic tools to access regioselectively monohalogenated anilines that are otherwise difficult to obtain. The elevated reactivity of aniline *N*-oxides allowed us to overcome the difficulties described in the chlorination of the equivalent *N*-arylhydroxylamines. In contrast to the few reported examples of halogenation of *N*-arylhydroxylamines, and consistent with our prior work,[8] these halogenation reactions are general and conducted at low temperature, which renders the reactions more amenable to sensitive substrates. However, the elevated reactivity of aniline *N*-oxides comes at the cost of mechanistic ambiguity. The manipulations described above employing *N*-arylhydroxylamines almost certainly proceed by [3,3]-sigmatropic rearrangement pathways;[9−11] however, reactions with aniline *N*-oxides may proceed by multiple mechanisms. While the 2-haloaniline products are consistent with a sigmatropic rearrangement, the 4-haloaniline products must arise by a radical pathway or a nucleophilic aromatic substitution-type mechanism. We conducted bromination reactions in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) under otherwise identical conditions in order to probe the involvement of radical species. We observed no significant change in the isolated yield of 4-bromoaniline product; for example, treatment of **1a** with 1 equiv of thionyl bromide and 20 mol % of BHT in tetrahydrofuran at −78 °C for 4 h, followed by treatment with triethylamine (4 equiv), afforded the 4-bromo-*N*,*N*-dimethylaniline **2a** in 55% yield (cf. Table 2, 55% yield). Analogous experiments with other radical traps or tool compounds such as (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl (TEMPO) afforded no conclusive data. Interestingly, bromination reactions conducted in the presence of LiCl additives and chlorination reactions conducted in the presence of LiBr additives result in scrambled halogenation products. These results are consistent with simple halogen exchange of the reagent, halogen exchange with intermediates such as those shown in Scheme 1, eq 4, or the involvement of nucleophilic aromatic substitution-type mechanisms. Efforts to fully elucidate the mechanistic pathway of these reactions is still underway but in any case, the synthetic building blocks available by these methods are widely utilized for a myriad of applications in synthetic organic chemistry.

The special reactivity of *N*,*N*-dialkylaniline *N*-oxides allows for the efficient, controlled, and regioselective halogenation of aromatic systems without exogenous activation of halogen sources, Lewis acids, or other exotic reagents. We are working to further probe the mechanisms of these transformations, and exploit further chemistries enabled by the weak *N*−*O* bond within aniline *N*-oxides.

DOI: 10.1021/acs.joc.8b01590
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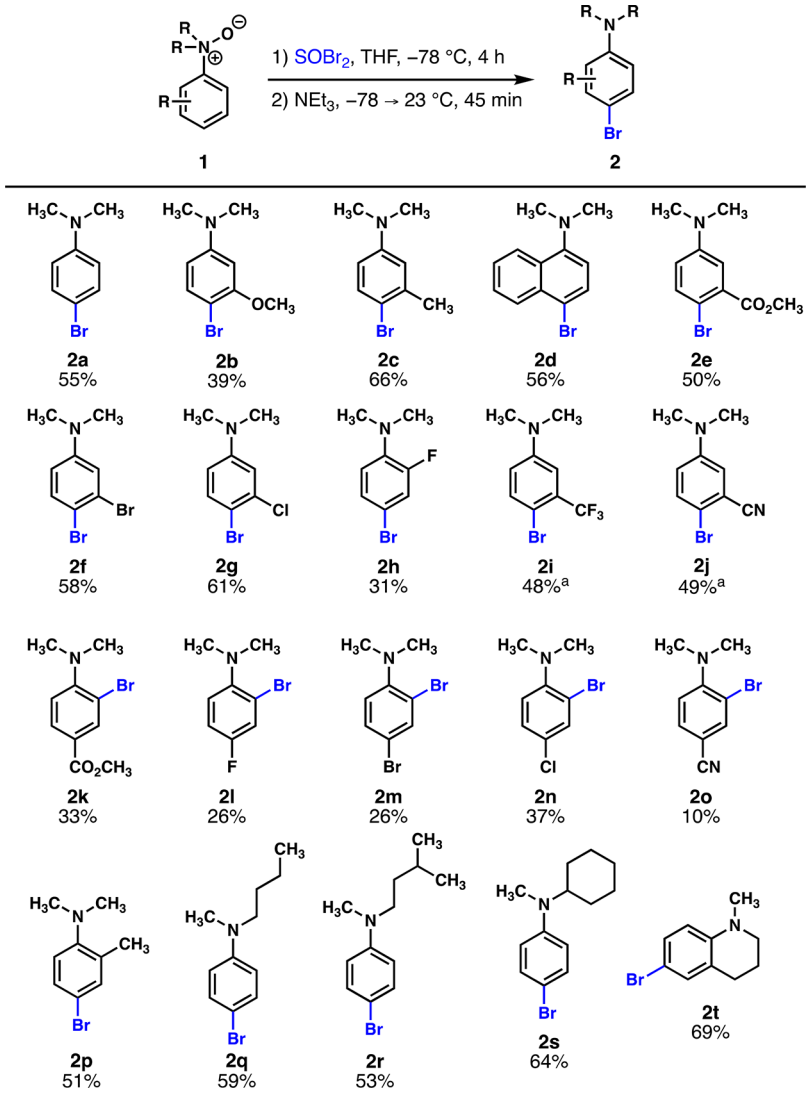
Table 2. Selective 4-Bromination of Substituted *N,N*-Dialkylaniline *N*-Oxides[a]



[a]Yields of isolated products; reactions were performed on a 0.7 mmol scale. [b]Reaction conducted in dichloromethane as solvent.

EXPERIMENTAL SECTION

General Information. Commercial reagents and solvents were used as received with the following exceptions. Triethylamine, dichloromethane, ethyl ether, dimethyl sulfoxide, tetrahydrofuran, hexane, toluene, *N,N*-dimethylformamide, and benzene were purified by the method of Pangborn et al.[12] Thionyl chloride ($SOCl_2$) was purified by distillation over calcium hydride prior to use. Thionyl bromide was used without further purification. All reactions were performed in single-neck oven- or flame-dried round-bottom flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at or below 35 °C at 10 Torr (diaphragm vacuum pump) unless otherwise noted. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV400 CryoPlatform QNP or Bruker AVIII600 SMART NMR spectrometers at 23 °C. Proton chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26, C_6HD_5: δ 7.16). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$: δ 77.16, C_6D_6: δ 128.06). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), integration, and coupling constant (J) in hertz (Hz). Accurate mass measurements were obtained using an Agilent 1100 quaternary LC system coupled to an Agilent 6210 LC/MSD-TOF fitted with an ESI or an APCI source, or Thermo Q-Exactive Orbitrap using electrospray ionization (ESI) or a Waters GCT Premier spectrometer using chemical ionization (CI). Compounds were isolated using flash column chromatography[13] with silica gel (60-Å pore size, 40−63 μm, standard grade, Silicycle) or basic alumina (60-Å pore size, 50−200 μm, Brockmann I, Acros Organics). Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with silica gel (0.25 mm, 60-Å pore size, 5−20 μm, Silicycle) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV), then were stained by submersion in aqueous ceric ammonium molybdate solution (CAM), ethanolic phosphomolybdic acid solution (PMA), acidic ethanolic *p*-anisaldehyde solution (anisaldehyde), or aqueous potassium permanganate solution ($KMnO_4$), followed by brief heating on a hot plate (215 °C, 10−15 s).

General Procedure for the Formation of *N,N*-Dimethylanilines. 1-(*N,N*-Dimethylamino)naphthalene *N*-oxide (**4d**), 4-methoxy-*N,N*-dimethylaniline *N*-oxide (**4p**), and 4-methyl-*N,N*-dimethylaniline *N*-oxide (**4q**) were obtained using the procedure of Lewis et al.[8] All other anilines were obtained using the following procedure modified from Chandrasekharam et al.[14]

DOI: 10.1021/acs.joc.8b01590
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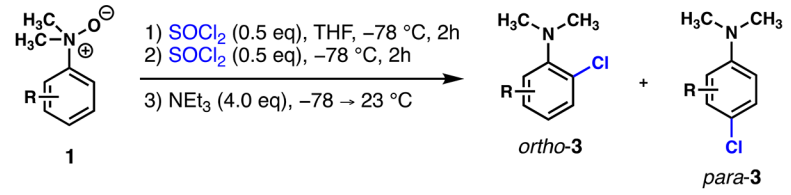
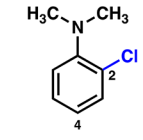
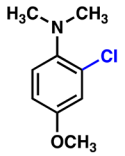
Table 3. Selective 2-Chlorination of Substituted *N,N*-Dialkylaniline *N*-Oxides[a]

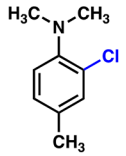




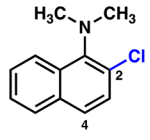
3a
49%, 4.9:1
(2-Cl:4-Cl)



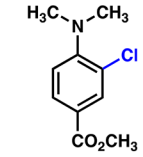
3b
61%



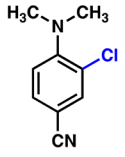
3c
41%



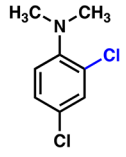
3d
60%, 6.7:1
(2-Cl:4-Cl)



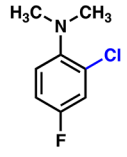
3e
40%



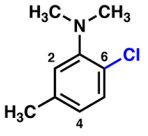
3f
33%



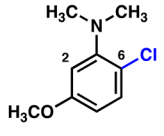
3g
55%



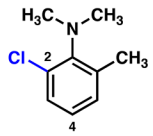
3h
30%



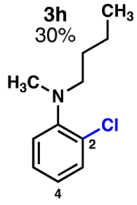
3i
54%, 2.9:1.5:1
(6-Cl:2-Cl:4-Cl)



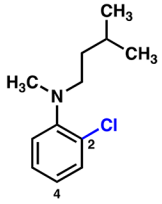
3j
43%, 4.8:1
(6-Cl:2-Cl)



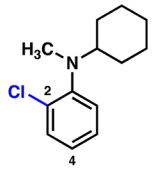
3k
19%, 1.3:1
(2-Cl:4-Cl)



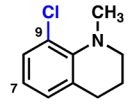
3l
55%, 2.9:1
(2-Cl:4-Cl)



3m
59%, 2.8:1
(2-Cl:4-Cl)



3n
65%, 4.9:1
(2-Cl:4-Cl)



3o
61%, 2.1:1
(9-Cl:7-Cl)

[a]Yields of isolated products; reactions were performed on a 0.7 mmol scale.

Glacial acetic acid (7.3 mL, 130 mmol, 5.4 equiv) was added dropwise to a mixture of 3-methoxyaniline (3.0 g, 24 mmol, 1 equiv), paraformaldehyde (3.9 g, 130 mmol, 5.4 equiv), and sodium cyanoborohydride (7.9 g, 130 mmol, 5.4 equiv) in tetrahydrofuran (100 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (100 mL) and diethyl ether (40 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed sequentially with water (2 × 60 mL) and saturated aqueous sodium chloride solution (3 × 40 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 5% ethyl acetate−hexanes, grading to 10% ethyl acetate−hexanes) to afford **4b** as a yellow oil (2.8 g, 18 mmol, 77% yield).

*3-Methoxy-N,N-dimethylaniline (**4b**).* TLC 10% ethyl acetate−hexanes, R_f = 0.40 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (t, J = 8.1 Hz, 1H), 6.37 (dd, J_1 = 8.3, J_2 = 2.3 Hz, 1H), 6.30 (m, 2H), 3.80 (s, 3H), 2.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7, 152.1, 129.8, 105.8, 101.4, 99.2, 55.2, 40.7. HRMS: ESI$^+$ [M + H]$^+$ calcd for $C_9H_{14}ON$ 152.1075, found 152.1071.

*3-Methyl-N,N-dimethylaniline (**4c**).* Obtained as a yellow oil (2.8 g, 75%). TLC 10% ethyl acetate−hexanes, R_f = 0.59 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (m, 1H), 6.59 (m, 3H), 2.95 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.9, 138.8, 129.0, 117.7, 113.6, 110.0, 40.8, 22.0. HRMS: ESI$^+$ [M + H]$^+$ calcd for $C_9H_{14}N$ 136.1126, found 136.1122.

*Methyl 3-N,N-Dimethylaminobenzoate (**4e**).* Obtained as a yellow oil (3.1 g, 87%). TLC 10% ethyl acetate−hexanes, R_f = 0.27 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41−7.36 (m, 2H), 7.29 (m, 1H), 6.90 (m, 1H), 3.90 (s, 3H), 2.99 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.9, 150.5, 130.9, 129.1, 117.6, 116.8, 113.3, 52.2, 40.7. HRMS: ESI$^+$ [M + H]$^+$ calcd for $C_{10}H_{14}O_2N$ 180.1025, found 180.1018.

*3-Bromo-N,N-dimethylaniline (**4f**).* Obtained as an orange-yellow oil (3.2 g, 92%). TLC 10% ethyl acetate−hexanes, R_f = 0.53 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (t, J = 8.0 Hz, 1H), 6.83 (m, 2H), 6.63 (m, 1H), 2.94 (s, 6H). ^{13}C NMR (101 MHz,

DOI: 10.1021/acs.joc.8b01590
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$CDCl_3$) δ: 151.7, 130.3, 123.5, 119.1, 115.1, 111.0, 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NBr$ 200.0075, found 200.0071.

*3-Chloro-N,N-dimethylaniline (**4g**).* Obtained as a yellow oil (2.50 g, 68%). TLC 10% ethyl acetate−hexanes, R_f = 0.56 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (m, 1H), 6.69 (m, 2H), 6.59 (dd, J_1 = 8.5, J_2 = 2.4 Hz, 1H), 2.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.6, 135.1, 130.1, 116.2, 112.3, 110.5, 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NCl$ 156.0580, found 156.0575.

*2-Fluoro-N,N-dimethylaniline (**4h**).* Obtained as a red-orange oil (2.9 g, 77%). TLC 10% ethyl acetate−hexanes, R_f = 0.49 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08−6.98 (m, 2H), 6.95−6.84 (m, 2H), 2.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.3 (d, J = 245.1 Hz), 140.9 (d, J = 8.6 Hz), 124.4 (d, J = 3.6 Hz), 121.3 (d, J = 7.8 Hz), 118.4 (d, J = 3.4 Hz), 116.2 (d, J = 20.9 Hz), 43.0 (d, J = 4.0 Hz). HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NF$ 140.0876, found 140.0869.

*3-(Trifluoromethyl)-N,N-dimethylaniline (**4i**).* Obtained as a yellow oil (2.3 g, 65%). TLC 10% ethyl acetate−hexanes, R_f = 0.51 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.89 (m, 1H), 6.85 (dd, J_1 = 8.4 Hz, J_2 = 2.7 Hz, 1H), 3.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.5, 131.4 (q, J = 31.4 Hz), 129.5, 124.7 (q, J = 272.4 Hz), 115.2 (d, J = 1.5 Hz), 112.7 (q, J = 3.9 Hz), 108.5 (q, J = 4.0 Hz), 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}NF_3$ 190.0844, found 190.0834.

*3-(N,N-Dimethylamino)benzonitrile (**4j**).* Obtained as a yellow oil (3.5 g, 95%). TLC 10% ethyl acetate−hexanes, R_f = 0.28 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (m, 1H), 6.95 (m, 1H), 6.88 (m, 2H), 2.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3, 129.8, 119.9, 119.5, 116.3, 114.8, 112.8, 40.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}N_2$ 147.0922, found 147.0917.

*Methyl 4-N,N-Dimethylaminobenzoate (**4k**).* Obtained as a white solid (2.4 g, 63%). Mp: 93−95 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.25 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.7 Hz, 2H), 3.86 (d, J = 0.8 Hz, 3H), 3.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.8, 153.4, 131.4, 116.9, 110.8, 51.7, 40.2. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{14}O_2N$ 180.1025, found 180.1012.

*4-Fluoro-N,N-dimethylaniline (**4l**).* Obtained as a yellow solid (2.9 g, 77%). Mp: 34−35 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.34 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.95 (m, 2H), 6.68 (m, 2H), 2.90 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.70 (d, J = 235.1 Hz), 147.61 (d, J = 1.8 Hz), 115.50 (d, J = 22.0 Hz), 114.04 (d, J = 7.4 Hz), 41.53. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NF$ 140.0876, found 140.0869.

*4-Bromo-N,N-dimethylaniline (**4m**).* Obtained as a white solid (3.2 g, 90%). Mp: 29−31 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.45 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, J = 9.1 Hz, 2H), 6.59 (d, J = 9.1 Hz, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.6, 131.8, 114.2, 108.6, 40.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NBr$ 200.0075, found 200.0070.

*4-Chloro-N,N-dimethylaniline (**4n**).* Obtained as a white solid (3.0 g, 83%). Mp: 30−32 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.57 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, J = 9.1 Hz, 2H), 6.64 (d, J = 9.1 Hz, 2H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.3, 128.9, 121.5, 113.7, 40.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NCl$ 156.0580, found 156.0577.

*4-(N,N-Dimethylamino)benzonitrile (**4o**).* Obtained as an orange-brown solid (2.4 g, 65%). Mp: 72−74 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.29 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.5, 133.5, 120.9, 111.5, 97.4, 40.1. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}N_2$ 147.0922, found 147.0917.

*2-Methyl-N,N-dimethylaniline (**4p**).* Obtained as a yellow oil (2.5 g, 65%). TLC 10% ethyl acetate−hexanes, R_f = 0.65 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.13 (m, 2H), 7.07−7.02 (m, 1H), 6.96 (td, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H), 2.71 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 132.2, 131.2, 126.5, 122.6, 118.4, 44.3, 18.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{14}N$ 136.1126, found 136.1120.

Procedures for the Formation of *N*-Alkyl-*N*-methylanilines. Asymmetric anilines were obtained using the following procedure modified from Chandrasekharam et al.[12]

*N-Butyl-N-methylaniline (**4q**).* Glacial acetic acid (4.8 mL, 84 mmol, 3.0 equiv) was added dropwise to a mixture of *N*-methylaniline (3.0 g, 28 mmol, 1 equiv), butyraldehyde (7.6 mL, 84 mmol, 3.0 equiv), and sodium cyanoborohydride (5.3 g, 84 mmol, 3.0 equiv) in tetrahydrofuran (100 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (100 mL) and diethyl ether (40 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed sequentially with water (2 × 60 mL) and saturated aqueous sodium chloride solution (3 × 40 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 1% ethyl acetate−hexanes, grading to 5% ethyl acetate−hexanes) to afford **4q** as a yellow oil (2.3 g, 14 mmol, 50% yield). TLC 10% ethyl acetate−hexanes, R_f = 0.75 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.19 (m, 2H), 6.76−6.64 (m, 3H), 3.37−3.27 (m, 2H), 2.93 (s, 3H), 1.57 (m, 2H), 1.36 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 129.2, 115.8, 112.1, 52.6, 38.4, 28.9, 20.5, 14.2. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{11}H_{18}Nr$ 164.1439, found 164.1433.

*N-Isopentyl-N-methylaniline (**4r**).* Glacial acetic acid (4.8 mL, 84 mmol, 3.0 equiv) was added dropwise to a mixture of *N*-methylaniline (3.0 g, 28 mmol, 1 equiv), isovaleraldehyde (9.2 mL, 84 mmol, 3.0 equiv), and sodium cyanoborohydride (5.3 g, 84 mmol, 3.0 equiv) in tetrahydrofuran (100 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (100 mL) and diethyl ether (40 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed sequentially with water (2 × 60 mL) and saturated aqueous sodium chloride solution (3 × 40 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 1% ethyl acetate−hexanes, grading to 5% ethyl acetate−hexanes) to afford **4r** as a yellow oil (2.2 g, 12 mmol, 43% yield). TLC 10% ethyl acetate−hexanes, R_f = 0.80 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.20 (m, 2H), 6.69 (m, 3H), 3.37−3.29 (m, 2H), 2.92 (s, 3H), 1.61 (m, 1H), 1.46 (m, 2H), 0.96 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 129.3, 115.9, 112.2, 51.1, 38.3, 35.1, 26.3, 22.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{20}N$ 178.1596, found 178.1589.

*N-Cyclohexyl-N-methylaniline (**4s**).* Glacial acetic acid (9.2 mL, 160 mmol, 5.0 equiv) was added dropwise to a mixture of aniline (3.0 g, 32 mmol, 1 equiv), cyclohexanone (16.6 mL, 178 mmol, 5.6 equiv), and sodium cyanoborohydride (10.1 g, 161 mmol, 5.0 equiv) in tetrahydrofuran (100 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (100 mL) and diethyl ether (40 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed sequentially with water (2 × 60 mL) and saturated aqueous sodium chloride solution (3 × 40 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 5% ethyl acetate−hexanes, grading to 10% ethyl acetate−hexanes) to afford **5s** as a yellow oil (2.7 g, 15 mmol, 47% yield). TLC 10% ethyl acetate−hexanes, R_f = 0.59 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (dd, J_1 = 8.4 Hz, J_2 = 7.4 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.62−6.57 (m, 2H), 3.52 (s, 1H), 3.27 (m, 1H), 2.07 (m, 2H), 1.77 (m, 2H), 1.70−1.62 (m, 1H), 1.45−1.31 (m, 2H), 1.29−1.09

DOI: 10.1021/acs.joc.8b01590
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(m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 129.4, 116.9, 113.2, 51.8, 33.6, 26.1, 25.2. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{18}N$ 176.1439, found 176.1430.

Glacial acetic acid (1.6 mL, 28 mmol, 4.9 equiv) was added dropwise to a mixture of **5s** (1.0 g, 5.7 mmol, 1 equiv), paraformaldehyde (0.86 g, 29 mmol, 5.1 equiv), and sodium cyanoborohydride (1.8 g, 29 mmol, 5.1 equiv) in tetrahydrofuran (30 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (30 mL) and diethyl ether (20 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed sequentially with water (2 × 30 mL) and saturated aqueous sodium chloride solution (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 5% ethyl acetate−hexanes, grading to 10% ethyl acetate−hexanes) to afford **4s** as a yellow oil (0.69 g, 3.6 mmol, 64% yield). TLC 10% ethyl acetate−hexanes, R_f = 0.61 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.20 (m, 2H), 6.78 (d, J = 8.6 Hz, 2H), 6.71−6.66 (m, 1H), 3.61−3.53 (m, 1H), 2.78 (s, 3H), 1.87−1.75 (m, 4H), 1.69 (d, J = 13.0 Hz, 1H), 1.53−1.29 (m, 5H), 1.19−1.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.27, 129.21, 116.29, 113.21, 58.21, 31.28, 30.17, 26.34, 26.07. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{13}H_{20}N$ 190.1596, found 190.1589.

*N-Methyl-1,2,3,4-tetrahydroquinoline (**4t**).* Glacial acetic acid (6.6 mL, 120 mmol, 5.1 equiv) was added dropwise to a mixture of 1,2,3,4-tetrahydroquinoline (3.0 g, 22 mmol, 1 equiv), paraformaldehyde (3.48 g, 120 mmol, 5.1 equiv), and sodium cyanoborohydride (7.3 g, 120 mmol, 5.1 equiv) in tetrahydrofuran (100 mL) at 23 °C. The resultant mixture was heated to 50 °C and stirred at that temperature for 18 h. The reaction mixture was cooled to 23 °C and then was partitioned between saturated aqueous sodium bicarbonate solution (100 mL) and diethyl ether (40 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed sequentially with water (2 × 60 mL) and saturated aqueous sodium chloride solution (3 × 40 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with 5% ethyl acetate−hexanes, grading to 10% ethyl acetate−hexanes) to afford **4t** as a yellow oil (2.5 g, 17 mmol, 76% yield). TLC 10% ethyl acetate−hexanes, R_f = 0.71 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (t, J = 7.7 Hz, 1H), 6.98−6.94 (m, 1H), 6.61 (m, 2H), 3.27−3.18 (m, 2H), 2.89 (s, 3H), 2.78 (t, J = 6.4 Hz, 2H), 1.99 (p, J = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 128.9, 127.2, 123.0, 116.3, 111.1, 51.4, 39.3, 27.9, 22.6. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{14}N$ 148.1126, found 148.1117.

General Procedure for the Oxidation of *N,N*-Dialkylanilines. *N,N*-Dimethylaniline *N*-oxide (**1a**), 3-methoxy-*N,N*-dimethylaniline *N*-oxide (**1b**), 3-methyl-*N,N*-dimethylaniline *N*-oxide (**1c**), 1-(*N,N*-dimethylamino)naphthalene *N*-oxide (**1d**), methyl 3-(*N,N*-dimethylamino)benzoate (**1e**), 4-fluoro-*N,N*-dimethylaniline *N*-oxide (**1l**), 4-chloro-*N,N*-dimethylaniline *N*-oxide (**1n**), 4-methoxy-*N,N*-dimethylaniline *N*-oxide (**1u**), and 4-methyl-*N,N*-dimethylaniline *N*-oxide (**1v**) were previously synthesized and reported by Lewis et al.[8] All other *N,N*-dimethylaniline *N*-oxides were synthesized using the same procedure. A solution of 3-bromo-*N,N*-dimethylaniline **4f** (1.0 g, 5.0 mmol) in dichloromethane (25 mL) was added dropwise to a solution of *m*-CPBA (77%, 0.99 g, 6.0 mmol, 1.2 equiv) in dichloromethane (25 mL each) at 23 °C. The resultant solution was allowed to stir at 23 °C for 60 min. The solution was concentrated in vacuo to give a crude product, which was further purified using flash chromatography (basic alumina, starting with dichloromethane grading to 2% methanol−dichloromethane) to yield 3-bromo-*N,N*-dimethylaniline *N*-oxide **1f** (0.68 g, 63%) as a white solid.

*3-Bromo-N,N-dimethylaniline N-Oxide (**1f**).* Mp: 117−119 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (m, 1H), 7.87 (m, 1H), 7.55 (m, 1H), 7.34 (t, J = 8.1 Hz, 1H), 3.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.8, 132.3, 130.5, 124.1, 123.0, 118.8, 63.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}ONBr$ 216.0024, found 216.0017.

*3-Chloro-N,N-dimethylaniline N-Oxide (**1g**).* Obtained as a tan solid (0.99 g, 90%). Mp: 115−117 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (m, 1H), 7.80 (m, 1H), 7.45−7.35 (m, 2H), 3.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.8, 135.2, 130.2, 129.4, 121.3, 118.2, 63.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}ONCl$ 172.0529, found 172.0521.

*2-Fluoro-N,N-dimethylaniline N-Oxide (**1h**).* Obtained as a orange-brown solid (0.96 g, 84%). Mp: 75−77 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (m, 1H), 7.42 (m, 1H), 7.32 (m, 1H), 7.15 (m, 1H), 3.65 (d, J = 1.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.5 (d, J = 246.3 Hz), 141.3 (d, J = 9.9 Hz), 131.4 (d, J = 7.8 Hz), 125.3 (d, J = 3.6 Hz), 125.0, 116.5 (d, J = 22.5 Hz), 62.5 (d, J = 5.7 Hz). HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}ONF$ 156.0825, found 156.0817.

*3-(Trifluoromethyl)-N,N-dimethylaniline N-Oxide (**1i**).* Obtained as a white solid (0.86 g, 79%). Mp: 131−132 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (m, 1H), 8.18 (m, 1H), 7.70 (m, 1H), 7.62 (m, 2H), 3.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.3, 131.9 (q, J = 33.3 Hz), 130.0, 126.1 (q, J = 3.6 Hz), 123.5, 123.4 (q, J = 272.7 Hz), 117.9 (q, J = 3.8 Hz), 63.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}ONF_3$: 206.0793, found 206.0786.

*3-(N,N-Dimethylamino)benzonitrile N-Oxide (**1j**).* Obtained as a white solid (0.85 g, 77%). Mp: 140−142 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (m, 1H), 8.25 (m, 1H), 7.72 (m, 1H), 7.62 (t, J = 8.0 Hz, 1H), 3.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.5, 132.9, 130.3, 124.8, 124.5, 117.6, 113.6, 63.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}ON_2$ 163.0871, found 163.0863.

*N-Methyl 4-(N,N-Dimethylamino)benzoate N-Oxide (**1k**).* Obtained as a white solid (0.64 g, 58%). Mp: 145−146 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, J = 8.9 Hz, 2H), 8.09 (d, J = 8.9 Hz, 2H), 3.94 (s, 3H), 3.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9, 158.2, 131.0, 130.8, 120.5, 63.6, 52.6. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{14}O_3N$ 196.0974, found 196.0966.

*4-Bromo-N,N-dimethylaniline N-Oxide (**1m**).* Obtained as a white solid (0.78 g, 71%). Mp: 158−160 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 9.0 Hz, 2H), 3.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.8, 132.3, 123.0, 122.1, 63.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}ONBr$ 216.0024, found 216.0016.

*4-(N,N-Dimethylamino)benzonitrile N-Oxide (**1o**).* Obtained as a white solid (0.76 g, 69%). Mp: 139−140 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J = 8.9 Hz, 2H), 7.80 (d, J = 9.0 Hz, 2H), 3.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.2, 133.4, 121.6, 117.6, 113.5, 63.6. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{11}ON_2$: 163.0871, found 163.0863.

*2-Methyl-N,N-dimethylaniline N-Oxide (**1p**).* Obtained as a yellow solid (0.39 g, 68%). Mp: 69−71 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29−8.24 (m, 1H), 7.30−7.23 (m, 3H), 3.65 (s, 6H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 134.1, 130.0, 129.2, 127.1, 120.9, 61.8, 22.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{14}ON$ 152.1075, found 152.1066.

*N-Butyl-N-dimethylaniline N-Oxide (**1q**).* Obtained as a yellow solid (0.44 g, 79%). TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93−7.88 (m, 2H), 7.49−7.43 (m, 2H), 7.40−7.36 (m, 1H), 3.68−3.56 (m, 2H), 3.52 (s, 3H), 1.96−1.85 (m, 2H), 1.26 (dddd, J = 17.1, 10.0, 4.1, 2.0 Hz, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 129.1, 128.7, 121.0, 73.5, 62.4, 25.6, 20.0, 14.0. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{11}H_{18}ON$ 180.1388, found 180.1377.

DOI: 10.1021/acs.joc.8b01590
J. Org. Chem. 2018, 83, 11359−11368

*N-Isopentyl-N-dimethylaniline N-Oxide (**1r**).* Obtained as a yellow solid (0.38 g, 79%). TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92−7.87 (m, 2H), 7.49−7.43 (m, 2H), 7.41−7.36 (m, 1H), 3.63 (m, 2H), 3.52 (s, 3H), 1.94−1.77 (m, 2H), 1.54 (m, 2H), 1.17 (m, 1H), 0.85 (dd, J = 13.5, 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 129.1, 128.7, 121.0, 72.4, 62.4, 32.0, 26.3, 22.7, 22.6. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{20}ON$ 194.1545, found 194.1535.

*N-Cyclohexyl-N-dimethylaniline N-Oxide (**1s**).* Obtained as a yellow solid (0.36 g, 66%). TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89−7.84 (m, 2H), 7.43 (td, J = 7.3, 6.6, 1.4 Hz, 2H), 7.38−7.33 (m, 1H), 3.46 (s, 3H), 3.39 (m, 1H), 2.24−2.19 (m, 1H), 1.91 (m, 1H), 1.76 (m, 2H), 1.63−1.54 (m, 2H), 1.33−1.20 (m, 2H), 1.18−1.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 128.8, 128.5, 121.5, 79.7, 57.5, 26.7, 26.6, 25.5, 25.4, 25.1. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{13}H_{20}ON$ 206.1545, found 206.1534.

*N-Methyl-1,2,3,4-tetrahydroquinoline N-Oxide (**1t**).* Obtained as a tan solid (0.32 g, 57%). Mp: 118−120 °C. TLC 20% ethyl acetate−hexanes, R_f = 0.00 (UV, $KMnO_4$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.15 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.35−7.31 (m, 1H), 7.24 (dt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.12 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 3.87−3.80 (m, 2H), 3.53 (s, 3H), 3.03−2.96 (m, 1H), 2.90 (m, 1H), 2.48 (m, 1H), 2.17−2.09 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.96, 129.51, 128.64, 128.36, 128.14, 122.09, 69.50, 62.46, 26.23, 19.85. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{14}ON$ 164.1075, found 164.1065.

General Procedure for the Reaction of *N,N*-Dialkylaniline *N*-Oxides with $SOBr_2$. Thionyl bromide (54 μL, 0.70 mmol, 1.0 equiv) was added dropwise to solution of the *N,N*-dimethylaniline *N*-oxide (96 mg, 0.70 mmol, 1 equiv) in tetrahydrofuran (4 mL) at −78 °C. The resultant mixture was stirred at −78 °C for 4 h, whereupon triethylamine (365 μL, 2.80 mmol, 4.0 equiv) was added. The cooling bath was removed, and the resultant mixture was allowed to warm to 23 °C and was stirred at that temperature for 45 min. The resultant mixture was diluted with saturated aqueous sodium bicarbonate solution (4 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with hexanes, grading to 1% ethyl acetate−hexanes) to afford **2a** as a white solid (77 mg, 0.38 mmol, 55% yield).

*4-Bromo-N,N-dimethylaniline (**2a**).* Mp: 29−31 °C. TLC: 10% ethyl acetate−hexanes, R_f = 0.45 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, J = 9.1 Hz, 2H), 6.59 (d, J = 9.1 Hz, 2H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.6, 131.8, 114.2, 108.6, 40.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NBr$ 200.0075, found 200.0069.

*4-Bromo-3-methoxy-N,N-dimethylaniline (**2b**).* Obtained as a tan solid (65 mg, 39%). Mp: 67−68 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.55 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 8.7 Hz, 1H), 6.25 (d, J = 2.8 Hz, 1H), 6.21 (dd, J_1 = 8.7, J_2 = 2.8 Hz, 1H), 3.89 (s, 3H), 2.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 151.4, 133.1, 106.2, 98.0, 97.2, 56.1, 40.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}ONBr$ 230.0181, found 230.0175.

*4-Bromo-3-methyl-N,N-dimethylaniline (**2c**).* Obtained as a white solid (103 mg, 66%). Mp: 51−53 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.41 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J = 8.8 Hz, 1H), 6.59 (d, J = 3.1 Hz, 1H), 6.44 (dd, J_1 = 8.8, J_2 = 3.1 Hz, 1H), 2.91 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.0, 138.0, 132.5, 115.0, 112.0, 111.5, 40.8, 23.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NBr$ 214.0231, found 214.0225.

*4-Bromo-1-(N,N-dimethylamino)naphthalene (**2d**).* Obtained as a yellow oil (85 mg, 56%). TLC 10% ethyl acetate−hexanes, R_f = 0.46 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.29−8.17 (m, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.56 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 2.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.1, 132.9, 130.2, 129.7, 127.7, 127.2, 126.0, 124.7, 116.5, 114.8, 45.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{13}NBr$ 250.0231, found 250.0225.

*Methyl 2-Bromo-5-(N,N-dimethylamino)benzoate (**2e**).* Obtained as a yellow oil (91 mg, 50%). TLC 10% ethyl acetate−hexanes, R_f = 0.26 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J = 8.9 Hz, 1H), 7.06 (d, J = 3.2 Hz, 1H), 6.65 (dd, J_1 = 8.9, J_2 = 3.2 Hz, 1H), 3.92 (s, 3H), 2.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.6, 149.4, 134.5, 132.3, 116.5, 114.6, 106.9, 52.5, 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{13}O_2NBr$ 258.0130, found 258.0135.

*3,4-Dibromo-N,N-dimethylaniline (**2f**).* Obtained as a white solid (109 mg, 58%). Mp: 64−65 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.47 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 3.0 Hz, 1H), 6.50 (dd, J_1 = 9.0, J_2 = 3.0 Hz, 1H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.4, 133.4, 125.2, 116.9, 112.9, 110.0, 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBr_2$ 277.9180, found 277.9185.

*4-Bromo-3-chloro-N,N-dimethylaniline (**2g**).* Obtained as a white solid (101 mg, 61%). Mp: 48−49 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.50 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 3.0 Hz, 1H), 6.46 (dd, J_1 = 9.0, J_2 = 3.0 Hz, 1H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.5, 134.7, 133.5, 113.7, 112.3, 107.7, 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBrCl$ 233.9685, found 233.9690.

*4-Bromo-2-fluoro-N,N-dimethylaniline (**2h**).* Obtained as a yellow oil (49 mg, 31%). TLC 10% ethyl acetate−hexanes, R_f = 0.55 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.15 (m, 2H), 6.75 (m, 1H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.8 (d, J = 249.9 Hz), 140.2 (d, J = 8.5 Hz), 127.3 (d, J = 3.6 Hz), 119.5 (d, J = 40.4 Hz), 119.4 (d, J = 12.2 Hz), 112.0 (d, J = 9.4 Hz), 42.8 (d, J = 4.2 Hz). HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBrF$: 217.9980, found 217.9984.

*4-Bromo-3-(trifluoromethyl)-N,N-dimethylaniline (**2i**).* Obtained as a yellow oil (92 mg, 48%). TLC 10% ethyl acetate−hexanes, R_f = 0.47 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J = 2.4 Hz, 1H), 7.38 (dd, J_1 = 8.6, J_2 = 2.3 Hz, 1H), 6.96 (d, J = 8.6 Hz, 1H), 2.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.2, 135.2, 130.1 (q, J = 30.4 Hz), 123.3 (q, J = 273.5 Hz), 116.1, 111.2 (q, J = 5.8 Hz), 104.5 (q, J = 1.9 Hz), 40.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{10}NBrF_3$ 267.9949, found 267.9952.

*2-Bromo-5-(N,N-dimethylamino)benzonitrile (**2j**).* Obtained as a white solid (77 mg, 49%). Mp: 70−72 °C. TLC 5% ethyl acetate−hexanes, R_f = 0.21 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J = 9.1 Hz, 1H), 6.87 (d, J = 3.2 Hz, 1H), 6.73 (dd, J_1 = 9.1, J_2 = 3.2 Hz, 1H), 2.97 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.2, 133.3, 118.2, 117.6, 116.9, 115.7, 109.9, 40.4. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{10}N_2Br$ 225.0027, found 225.0020.

*Methyl 3-Bromo-4-(N,N-dimethylamino)benzoate (**2k**).* Obtained as a yellow oil (60 mg, 33%). TLC 10% ethyl acetate−hexanes, R_f = 0.57 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J = 2.0 Hz, 1H), 7.89 (dd, J_1 = 8.5, J_2 = 2.0 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 3.87 (s, 3H), 2.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 155.8, 135.7, 129.7, 124.5, 119.3, 116.9, 52.2, 43.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{13}O_2NBr$ 258.0130, found 258.0123.

*2-Bromo-4-fluoro-N,N-dimethylaniline (**2l**).* Obtained as a yellow oil (39 mg, 26%). TLC 10% ethyl acetate−hexanes, R_f = 0.56 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (dd, J_1 = 8.1, J_2 = 2.9 Hz, 1H), 7.06 (m, 1H), 6.99 (m, 1H), 2.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.3 (d, J = 245.5 Hz), 148.4 (d, J = 3.0 Hz), 121.1 (d, J = 8.5 Hz), 120.9 (d, J = 25.0 Hz), 119.7 (d, J = 9.5 Hz), 114.8 (d, J = 21.6 Hz), 44.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBrF$ 217.9981, found 217.9981.

*2,4-Dibromo-N,N-dimethylaniline (**2m**).* Obtained as a yellow oil (51 mg, 26%). TLC 10% ethyl acetate−hexanes, R_f = 0.62 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 2.4 Hz, 1H), 7.36 (dd, J_1 = 8.6, J_2 = 2.3 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 2.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.2, 136.1, 131.1, 121.7, 119.8, 115.4, 44.2. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBr_2$ 279.9180, found 279.9158.

*2-Bromo-4-chloro-N,N-dimethylaniline (**2n**).* Obtained as a yellow oil (58 mg, 37%). TLC 10% ethyl acetate−hexanes, R_f = 0.54 (UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 2.5 Hz, 1H), 7.23 (dd, J_1 = 8.6, J_2 = 2.4 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H),

DOI: 10.1021/acs.joc.8b01590
J. Org. Chem. 2018, 83, 11359−11368

2.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.8, 133.4, 128.2, 128.2, 121.2, 119.5, 44.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NBrCl$ 233.9685, found 233.9680.

*3-Bromo-4-(N,N-dimethylamino)benzonitrile (**2o**).* Obtained as a yellow oil (20 mg, 10%). TLC 5% ethyl acetate−hexanes, R_f = 0.23 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 2.0 Hz, 1H), 7.51 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 2.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.7, 137.8, 132.1, 119.9, 118.3, 116.6, 105.4, 43.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{10}N_2Br$ 225.0027, found 225.0030.

*4-Bromo-2-methyl-N,N-dimethylaniline (**2p**).* Obtained as a yellow oil (77 mg, 51%). TLC 10% ethyl acetate−hexanes, R_f = 0.63 (UV, $KMnO_4$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (d, J = 2.1 Hz, 1H), 7.24 (dd, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 2.67 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 134.5, 133.8, 129.3, 120.2, 115.2, 44.2, 18.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NBr$ 214.0231, found 214.0222.

*4-Bromo-N-butyl-N-dimethylaniline (**2q**).* Obtained as a yellow oil (100 mg, 59%). TLC 10% ethyl acetate−hexanes, R_f = 0.71 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 9.2 Hz, 2H), 6.54 (d, J = 9.0 Hz, 2H), 3.30−3.24 (m, 2H), 2.89 (s, 3H), 1.58−1.48 (m, 2H), 1.34 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 131.8, 113.7, 107.6, 52.6, 38.5, 28.8, 20.4, 14.1. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{11}H_{17}NBr$ 242.0544, found 242.0534.

*4-Bromo-N-isopentyl-N-dimethylaniline (**2r**).* Obtained as a yellow oil (96 mg, 53%). TLC 10% ethyl acetate−hexanes, R_f = 0.74 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 9.3 Hz, 2H), 6.54 (d, J = 9.1 Hz, 2H), 3.32−3.25 (m, 2H), 2.88 (s, 3H), 1.65−1.51 (m, 2H), 1.46−1.38 (m, 2H), 0.94 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 131.9, 113.8, 107.7, 51.1, 38.4, 35.0, 26.3, 22.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{19}NBr$ 256.0701, found 256.0690.

*4-Bromo-N-cyclohexyl-N-dimethylaniline (**2s**).* Obtained as a yellow solid (120 mg, 64%). Mp: 45−47 °C. TLC 10% ethyl acetate−hexanes, R_f = 0.68 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 9.3 Hz, 2H), 6.63 (d, J = 9.1 Hz, 2H), 3.49 (m, 1H), 2.73 (s, 3H), 1.87−1.80 (m, 2H), 1.79−1.67 (m, 3H), 1.47−1.31 (m, 4H), 1.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 131.8, 114.7, 107.9, 58.3, 31.3, 30.1, 26.3, 26.0. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{13}H_{19}NBr$ 268.0701, found 268.0689.

*7-Bromo-N-methyl-1,2,3,4-tetrahydroquinoline (**2t**).* Obtained as a yellow oil (110 mg, 69%). TLC 10% ethyl acetate−hexanes, R_f = 0.59 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, J_1 = 8.7 Hz, J_2 = 2.5 Hz, 1H), 7.06−7.03 (m, 1H), 6.43 (d, J = 8.7 Hz, 1H), 3.23−3.17 (m, 2H), 2.85 (s, 3H), 2.73 (t, J = 6.5 Hz, 2H), 1.98−1.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.8, 131.2, 129.7, 125.0, 112.5, 107.8, 51.2, 39.2, 27.8, 22.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{13}NBr$ 226.0231, found 226.0221.

General Procedure for the Reaction of *N,N*-Dialkylanilines *N*-Oxides with $SOCl_2$. A solution of thionyl chloride (52 μL, 0.70 mmol, 1.0 equiv) in tetrahydrofuran (1 mL) was added dropwise in two portions over a period of 2 h to a solution of the *N,N*-dimethylaniline *N*-oxide (96 mg, 0.703 mmol, 1 equiv) in tetrahydrofuran (3 mL) at −78 °C. The resultant mixture was stirred at −78 °C for 4 h, whereupon triethylamine (365 μL, 2.80 mmol, 4.00 equiv) was added. The cooling bath was removed, and the resultant mixture was allowed to warm to 23 °C and stirred at that temperature for 45 min. The resultant mixture was diluted with saturated aqueous sodium bicarbonate solution (4 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the dried solution was concentrated. The resultant oily residue was purified by flash column chromatography (silica gel, starting with hexanes, grading to 1% ethyl acetate−hexanes) to afford **3a** as a yellow oil (isolated as a mix of regioisomers, 4.9:1 (2-Cl:4-Cl), asterisk denotes minor peaks, 53 mg, 0.34 mmol, 49%).

*2-Chloro-N,N-dimethylaniline (**3a**).* TLC 10% ethyl acetate−hexanes, R_f = 0.57 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (dd, J_1 = 7.9, J_2 = 1.6 Hz, 1H), 7.22 (dt, J_1 = 8.1, J_2 = 1.6 Hz, 1H), 7.17* (d, J = 9.1 Hz, 2H), 7.08 (dd, J_1 = 8.1, J_2 = 1.6 Hz, 1H), 6.95 (dt, J_1 = 7.9, J_2 = 1.6 Hz, 1H), 6.64* (d, J = 9.1 Hz, 2H), 2.93* (s, 6H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.5, 149.3*, 130.8, 130.4, 128.9*, 128.4, 127.5, 123.3, 120.1*, 113.7*, 43.9, 40.8*. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{11}NCl$ 156.0580, found 156.0570.

*2-Chloro-4-methoxy-N,N-dimethylaniline (**3b**).* Obtained as a yellow oil (79 mg, 61%). TLC 10% ethyl acetate−hexanes, R_f = 0.38 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 2.9 Hz, 1H), 6.78 (dd, J_1 = 8.8, J_2 = 2.9 Hz, 1H), 3.77 (s, 3H), 2.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.6, 144.0, 129.5, 120.8, 116.1, 113.1, 55.8, 44.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}ONCl$ 186.0686, found 186.0685.

*2-Chloro-4-methyl-N,N-dimethylaniline (**3c**).* Obtained as a yellow oil (49 mg, 41%). TLC 10% ethyl acetate−hexanes, R_f = 0.56 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, J = 1.9 Hz, 1H), 7.02−6.95 (m, 2H), 2.78 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.0, 133.3, 131.2, 128.2, 128.1, 119.9, 44.2, 20.5. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NCl$ 170.0737, found 170.0729.

*2-Chloro-1-(N,N-dimethylamino)naphthalene (**3d**, 4-Cl Regioisomer also Isolated).* Obtained as a colorless oil (75 mg, 52%). TLC 10% ethyl acetate−hexanes, R_f = 0.87 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (m, 1H), 7.80 (m, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.50 (m, 2H), 7.37 (d, J = 8.8 Hz, 1H), 3.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.4, 133.9, 133.3, 130.4, 128.6, 128.0, 126.6, 126.5, 126.1, 124.6, 42.9. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{13}NCl$ 206.0737, found 206.0727. *4-Chloro-1-(N,N-dimethylamino)naphthalene.* Obtained as a yellow oil (11 mg, 8%). TLC 10% ethyl acetate−hexanes, R_f = 0.47 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (m, 2H), 7.62−7.51 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 2.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3, 131.7, 130.0, 126.9, 126.0, 126.0, 126.0, 125.0, 124.7, 114.2, 45.4. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{13}NCl$ 206.0737, found 206.0728.

*Methyl 3-Chloro-4-(N,N-dimethylamino)benzoate (**3e**).* Obtained as a yellow oil (61 mg, 40%). TLC 10% ethyl acetate−hexanes, R_f = 0.41 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J = 2.1 Hz, 1H), 7.86 (dd, J_1 = 8.5, J_2 = 2.1 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 3.89 (s, 3H), 2.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.2, 154.3, 132.5, 129.1, 126.5, 123.9, 118.8, 52.2, 43.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{13}O_2NCl$: 214.0635, found 214.0625.

*3-Chloro-4-(N,N-dimethylamino)benzonitrile (**3f**).* Obtained as a yellow oil (42 mg, 33%). TLC 10% ethyl acetate−hexanes, R_f = 0.22 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J = 2.0 Hz, 1H), 7.46 (dd, J_1 = 8.5, J_2 = 2.0 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 2.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.1, 134.5, 131.6, 126.5, 119.4, 118.5, 104.5, 43.1. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{10}N_2Cl$ 181.0533, found 181.0530.

*2,4-Dichloro-N,N-dimethylaniline (**3g**).* Obtained as a yellow oil (73 mg, 55%). TLC 10% ethyl acetate−hexanes, R_f = 0.54 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 2.4 Hz, 1H), 7.17 (dd, J_1 = 8.6, J_2 = 2.5 Hz, 1H), 6.98 (d, J = 8.7 Hz, 1H), 2.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.3, 130.4, 128.9, 127.7, 127.5, 120.8, 43.9. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NCl_2$ 190.0190, found 190.0183.

*2-Chloro-4-fluoro-N,N-dimethylaniline (**3h**).* Obtained as a yellow oil (37 mg, 30%). TLC 10% ethyl acetate−hexanes, R_f = 0.57 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (m, 1H), 7.03 (m, 1H), 6.93 (m, 1H), 2.76 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.1 (d, J = 244.3 Hz), 147.0 (d, J = 3.1 Hz), 129.2 (d, J = 10.3 Hz), 120.8 (d, J = 8.7 Hz), 117.9 (d, J = 25.3 Hz), 114.1 (d, J = 21.5 Hz), 44.2. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_8H_{10}NClF$ 174.0486, found 174.0478.

*6-Chloro-3-methyl-N,N-dimethylaniline (**3i**).* Obtained as a yellow oil (isolated as a mixture of regioisomers, (5.3:3.7:1 (6-Cl:2-Cl:4-Cl), asterisk denotes 2-Cl, plus denotes 4-Cl, 57 mg, 47%). TLC 10% ethyl acetate−hexanes, R_f = 0.64−54 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, J = 8.0 Hz, 1H), 7.16$^+$ (d, J = 8.8 Hz, 1H), 7.11* (t, J = 7.7 Hz, 1H), 6.94* (m, 2H), 6.87 (d, J = 2.0 Hz, 1H), 6.76 (dd,

DOI: 10.1021/acs.joc.8b01590
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J_1 = 8.0, J_2 = 1.7 Hz, 1H), 6.58$^+$ (d, J = 3.1 Hz, 1H), 6.50$^+$ (dd, J_1 = 8.8, J_2 = 3.1 Hz, 1H), 2.91$^+$ (s, 6H), 2.80 (s, 6H), 2.79* (s, 6H), 2.39* (s, 3H), 2.33$^+$ (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.9*, 150.1, 149.4$^+$, 137.8*, 137.4, 136.2$^+$, 130.4, 129.3$^+$, 128.9*, 126.6*, 125.2, 125.1*, 124.1, 122.1$^+$, 120.9, 117.7*, 115.0$^+$, 111.6$^+$, 44.2*, 44.0, 40.9$^+$, 21.3, 21.1*, 20.7$^+$. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NCl$ 170.0737, found 170.0733. *4-Chloro-3-methyl-N,N-dimethylaniline.* Obtained as a yellow oil (8 mg, 7%). TLC 10% ethyl acetate−hexanes, R_f = 0.54 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 3.0 Hz, 1H), 6.50 (dd, J_1 = 8.8, J_2 = 3.1 Hz, 1H), 2.91 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.5, 136.2, 129.3, 122.1, 115.0, 111.6, 40.9, 20.7. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NCl$ 170.0737, found 170.0733.

6-Chloro-3-methoxy-N,N-dimethylaniline (**3j**). Obtained as a yellow oil (isolated as a mixture of regioisomers, 4.9:1 (6-Cl/4-Cl), asterisk denotes minor peaks, 55 mg, 43%). TLC 10% ethyl acetate−hexanes, R_f = 0.46 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, J = 8.7 Hz, 1H), 7.17* (t, J = 8.2 Hz, 1H), 6.74* (dd, J_1 = 8.2, J_2 = 1.3 Hz, 1H), 6.65* (dd, J_1 = 8.3, J_2 = 1.3 Hz, 1H), 6.62 (d, J = 2.9 Hz, 1H), 6.49 (dd, J_1 = 8.7 Hz, J_2 = 2.9 Hz, 1H), 3.90* (s, 1H), 3.79 (s, 3H), 2.81* (s, 1H), 2.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.1, 156.2*, 152.1*, 151.4, 131.0, 127.1*, 119.8, 116.5*, 112.4* 107.5, 107.0, 106.3*, 56.4*, 55.6, 44.1*, 43.8. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}ONCl$ 186.0686, found 186.0683.

2-Chloro-6-methyl-N,N-dimethylaniline (**3k**). Obtained as a yellow oil (isolated as mixture of regioisomers, 1.3:1 (6-Cl:4-Cl), asterisk denotes minor peaks, 23 mg, 19%). TLC 10% ethyl acetate−hexanes, R_f = 0.89 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, J = 6.8 Hz, 1H), 7.13* (d, J = 2.0 Hz, 1H), 7.10* (dd, J_1 = 8.4, J_2 = 2.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.93* (d, J = 8.4 Hz, 1H), 2.70 (s, 6H), 2.67* (s, 6H), 2.34 (s, 3H), 2.30* (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7*, 151.3, 134.0, 132.1, 131.2*, 130.8, 127.4*, 126.4*, 126.2, 122.5*, 119.6, 118.3*, 44.3*, 44.2, 18.4*, 18.3. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_9H_{13}NCl$ 170.0737, found 170.0727.

2-Chloro-N-butyl-N-dimethylaniline (**3l**). Obtained as a yellow oil (isolated as a mixture of regioisomers, 2.9:1 (6-Cl:2-Cl), asterisk denotes minor peaks, 77 mg, 55%). TLC 10% ethyl acetate−hexanes, R_f = 0.70 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.22 (td, J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H), 7.17* (d, J = 9.1 Hz, 2H), 7.09 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 6.96 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 6.61* (d, J = 9.1 Hz, 2H), 3.33−3.27* (m, 2H), 3.07−3.00 (m, 2H), 2.92* (s, 3H), 2.80 (s, 3H), 1.62−1.51* (m, 2H), 1.62−1.51 (m, 2H),1.41−1.28* (m, 2H), 1.41−1.28 (m, 2H), 0.95* (m, 3H), 0.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 148.0*, 130.7, 129.0, 129.0*, 127.3, 123.2*, 121.3, 120.6*, 113.2*, 55.8, 52.7*, 40.9, 38.6*, 29.5, 28.8*, 20.5*, 20.4, 14.2, 14.1*. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{11}H_{17}NCl$ 198.1050, found 198.1040.

2-Chloro-N-isopentyl-N-dimethylaniline (**3m**). Obtained as a yellow oil (isolated as a mixture of regioisomers, 2.8:1 (6-Cl:2-Cl), asterisk denotes minor peaks, 89 mg, 59%). TLC 10% ethyl acetate−hexanes, R_f = 0.75 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.22−7.17 (m, 1H), 7.15* (d, J = 9.1 Hz, 2H), 7.07 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 6.93 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 6.59* (d, J = 9.1 Hz, 2H), 3.32−3.26* (m, 2H), 3.05−2.99 (m, 2H), 2.89* (s, 3H), 2.77 (s, 3H), 1.62−1.52* (m, 1H), 1.62−1.52 (m, 1H), 1.50−1.39* (m, 2H), 1.50−1.39 (m, 2H), 0.94* (d, J = 6.6 Hz, 6H), 0.90 (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 147.9*, 130.7, 129.0, 129.0*, 127.3, 123.2, 121.3, 120.6*, 113.3*, 54.4, 51.2*, 41.0, 38.4*, 36.2, 35.0*, 26.4, 26.3*, 22.9, 22.8*. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{12}H_{19}NCl$ 212.1206, found 212.1196.

2-Chloro-N-cyclohexyl-N-dimethylaniline (**3n**). Obtained as a yellow oil (isolated as a mixture of regioisomers, 4.9:1 (6-Cl:2-Cl), asterisk denotes minor peaks, 103 mg, 65%). TLC 10% ethyl acetate−hexanes, R_f = 0.82 (UV, $KMnO_4$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.19−7.16 (m, 1H), 7.15* (d, J = 9.0 Hz, 2H), 7.07 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 6.91 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 6.68* (d, J = 9.1 Hz, 2H), 3.52−3.46* (m, 1H), 3.14 (m, 1H), 2.74* (s, 3H), 2.71 (s, 3H), 1.84 (m, 1H), 1.87−1.73 (m, 3H), 1.69* (m, 1H), 1.65−1.58* (m, 3H), 1.45 (m, 3H), 1.39−1.30* (m, 3H), 1.29−1.20 (m, 3H), 1.11* (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 148.8*, 130.7, 129.4, 129.2*, 128.9*, 127.0, 123.0, 122.7, 114.3*, 61.6, 58.5*, 33.8, 31.4*, 30.1*, 29.2, 26.3*, 26.2, 26.1, 26.0*. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{13}H_{19}NCl$ 224.1206, found 224.1195.

9-Chloro-N-methyl-1,2,3,4-tetrahydroquinoline (**3o**). Obtained as a yellow oil (isolated as a mixture of regioisomers, 2.1:1 (9-Cl:7-Cl), asterisk denotes minor peaks, 78 mg, 61%). TLC 20% ethyl acetate−hexanes, R_f = 0.64 (UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18−7.15 (m, 1H), 7.01−6.98* (m, 1H), 6.97−6.94 (m, 1H), 6.91* (dt, J_1 = 2.4 Hz, J_2 = 1.0 Hz, 1H), 6.83 (t, J = 7.7 Hz, 1H), 6.48* (d, J = 8.7 Hz, 1H), 3.22−3.18* (m, 1H), 3.16−3.12 (m, 1H), 2.88* (s, 3H), 2.86 (s, 3H), 2.80 (t, J = 6.7 Hz, 2H), 2.73* (t, J = 6.6 Hz, 2H), 1.98−1.92* (m, 2H), 1.88−1.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.0*, 145.4*, 131.4, 128.4 (2 resonances), 128.3, 128.0, 127.7*, 126.7*, 124.5*, 122.2, 120.7*, 112.0, 52.1, 51.2*, 42.9, 39.3*, 28.0, 27.8*, 22.3*, 17.1. HRMS: ESI$^+$ $[M + H]^+$ calcd for $C_{10}H_{13}NCl$ 182.0737, found 182.0728.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01590.

^{1}H and ^{13}C NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The University of Delaware (UD), the American Chemical Society Petroleum Research Fund (ACS PRF 54452-ND1), and the National Science Foundation (NSF CHE-1664954) are gratefully acknowledged for financial support. Spectral data were acquired at UD on instruments obtained with the assistance of NSF and NIH funding (NSF CHE0421224, CHE0840401, CHE1229234, CHE1048367; NIH S10 OD016267-01, S10 RR026962-01, P20GM104316, P30GM110758).

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