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Palladium-Catalyzed Synthesis of *N,N*-Dimethylanilines via Buchwald–Hartwig Amination of (Hetero)aryl Triflates

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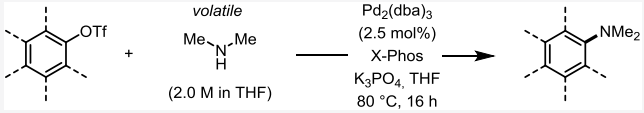
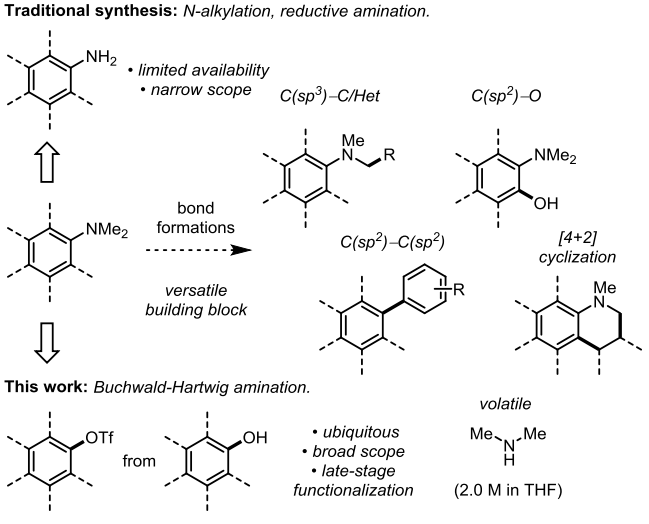
ABSTRACT: This work delineates the synthesis of *N,N*-dimethylaniline derivatives from dimethylamines and aryl triflates. The palladium-catalyzed C–N bond formation proceeds in excellent yields, using an unsophisticated catalytic system, a mild base, and triflates as electrophiles, which are readily available from inexpensive phenols. *N,N*-Dimethylanilines are multifunctional reaction partners and represent useful but underutilized building blocks in organic synthesis.



INTRODUCTION

The structural elucidation of *N,N*-dimethylaniline was reported as early as 1850.[1] However, its application was confined to specific areas, such as the synthesis of triarylmethane dyes[2] or as a promotor in the curing of polymers.[3] Over the past decades, the extended synthetic value of *N,N*-dimethylaniline derivatives has been re-evaluated and studies on the modification and utilization of this compound class have been reported with increasing frequency. The possibility of the global derivatization around the core structure turns *N,N*-dimethylaniline into a versatile building block in organic synthesis (Scheme 1). The activating nature of the *N,N*-dimethylamine group allows for the diverse decoration of the arene.[4−8] Furthermore, the unique redox activity of alkylamines can be exploited for C(sp^3)–C and C(sp^3)–heteroatom bond formations.[9,10] This reaction palette was recently extended by reports on the utilization of *N,N*-dimethylanilines as electrophiles in cross-coupling reactions.[11] Irrespective of these developments, the synthesis of this structural motif is less advanced. The main access to *N,N*-dimethylanilines is granted through *N*-alkylation[11,12] or reductive amination with formaldehyde.[6,13] Both synthetic routes start from aniline derivatives, which are of limited availability and otherwise difficult to access. The Buchwald–Hartwig amination grants the most expedient possibility for C(sp^2)–N bond construction via palladium-catalyzed coupling of amines with aryl halides.[14−17] Notably, this reaction is most reliable for the arylation of cyclic amines.[18,19] The free rotation of the N–C bond in acyclic amines on the contrary can set the stage for β-hydride elimination, resulting in a palladium-hydride species, causing undesired proto-(pseudo)-dehalogenation of the electrophile. In 2009, Buchwald and co-workers published a method for the *N,N*-dimethylamination of aryl chlorides.[20] In their study, a preactivated palladium catalyst and LiHMDS at 130 °C were used. However, aryl chlorides are less abundant and rarely suited for late-stage functionalization and thus are often replaced by more accessible pseudohalides such as sulfonates.[21] Other related experiments for dimethylamination were conducted under even harsher conditions at 160 °C or in more specialized catalytic systems.[22,23] The utilization of *N,N*-dimethylamine (boiling point, 7 °C; 10 atm at 80 °C) and other gaseous amines under these conditions is not desirable and could be problematic without appropriate equipment.[24]

Scheme 1. Synthesis and Derivatization Possibilities of *N,N*-Dimethylaniline



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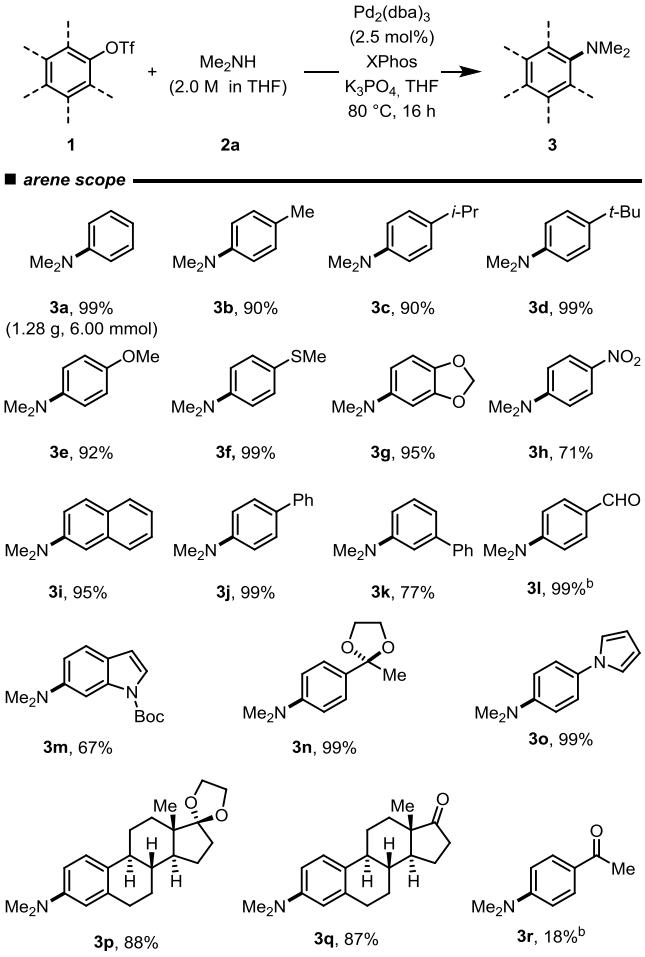
RESULTS AND DISCUSSION

Herein, we report the scope and limitations of the Buchwald–Hartwig amination of aryl triflates with *N,N*-dimethylamine using a simple catalytic system, $Pd_2(dba)_3$ (2.5 mol %), K_3PO_4 (1.2 equiv), in tetrahydrofuran (THF, 0.5 M), and XPhos (7.5 mol %) at 80 °C. For the optimization, we utilized *tert*-butylbenzene triflate and dimethylamine as a 2.0 M solution in THF. Several solvents, ligands, and (in)organic bases were tested. Alternatively, the use of different ligands and solvents such as SPhos, RuPhos, and *t*BuXPhos or dioxane, *n*-hexane, and MeCN showed no deterioration in yield.[25]

With the optimized reaction conditions in hand, the scope of the palladium-catalyzed amination was evaluated and the reaction was applied to a range of aryl triflates (Scheme 2).

Scheme 2. Palladium-Catalyzed *N,N*-Dimethylamination of Various Aryl Triflates

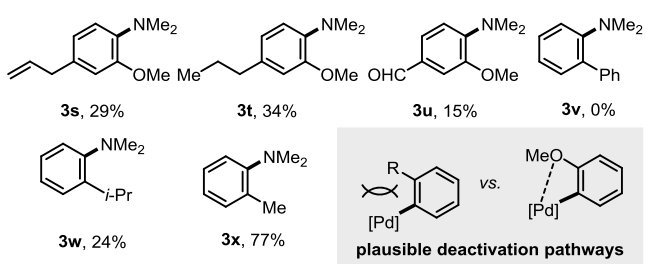


[a]Reaction conditions: **1** (0.5 mmol), **2a** (2.0 mmol, 2.0 M in THF), $Pd_2(dba)_3$ (2.5 mol %), XPhos (7.5 mol %), K_3PO_4 (0.6 mmol), THF (1 mL), 80 °C, 16 h. [b]Acetal cleavage during workup.

The reaction is compatible with a broad range of electronically diverse aryl triflates, yielding electron-neutral (**3a**), electron-rich (**3b–f**), and electron-deficient dimethylanilines (**3h**). Furthermore, bicyclic (**3i**), metasubstitution (**3k**), and heterocyclic products (**3o**) could be obtained in this reaction. Functional groups such as ether, thioether, acetal, and nitro groups are well tolerated. Carbonyl functionalities could be used only in the case of the Boc-protected indole (**3m**) and estrogen (**3q**). The structure of the estrogen derivative (**3q**) was confirmed by X-ray crystallography (see the Supporting Information: Figure S1). However, in the case of acetophenone (**3n**) and benzaldehyde (**3l**), this functionality had to be acetal-protected to circumvent undesired side reactions.

More demanding *ortho*-substituted aryl triflates proved to be more challenging (Scheme 3). If the starting material had a coordinative character at the *ortho*-position, as in the vanillin (**3u**) or eugenol (**3s–t**) derivatives bearing *ortho*-methoxy groups, the reaction proceeded in poor yields. Likewise, the presence of a phenyl substituent in the *ortho*-position led to no observable product formation. In this case, no conversion of the diphenyl triflate was detected. In contrast, the conversion of aryl triflates with a methyl group proceeded in a moderate yield (**3x**). These experimental results suggest that a coordinative character of the substrate may inhibit the reaction through complexation or steric repulsion.

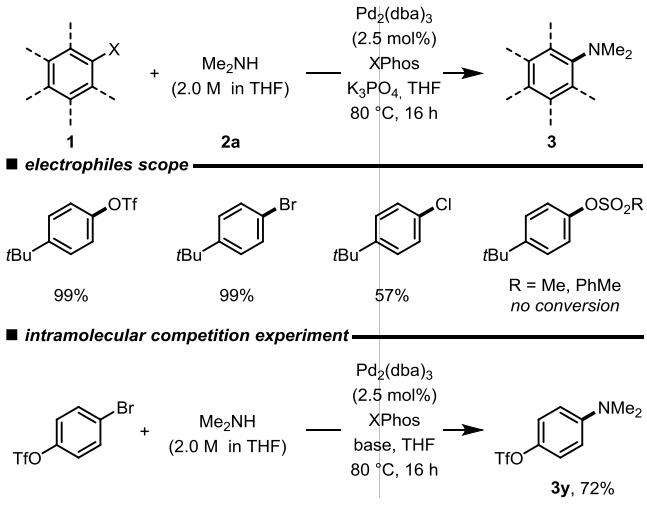
Scheme 3. Challenging Substrates for the Palladium-Catalyzed *N,N*-Dimethylamination of Various Aryl Triflates



[a]Reaction conditions: **1** (0.5 mmol), **2a** (2.0 mmol, 2.0 M in THF), $Pd_2(dba)_3$ (2.5 mol %), XPhos (7.5 mol %), K_3PO_4 (0.6 mmol), THF (1 mL), 80 °C, 16 h.

To assess the possible extension of the reaction scope toward other electrophiles, different aryl (pseudo)halides were tested under the optimized conditions. Aryl bromides and aryl triflates showed excellent yields under these conditions (Scheme 4). Aryl chloride can also be used but does not lead to the complete conversion of the starting material. Less activated sulfonates such as mesylates or tosylates are not

Scheme 4. Comparison of Different Electrophiles and Intramolecular Competition Experiments



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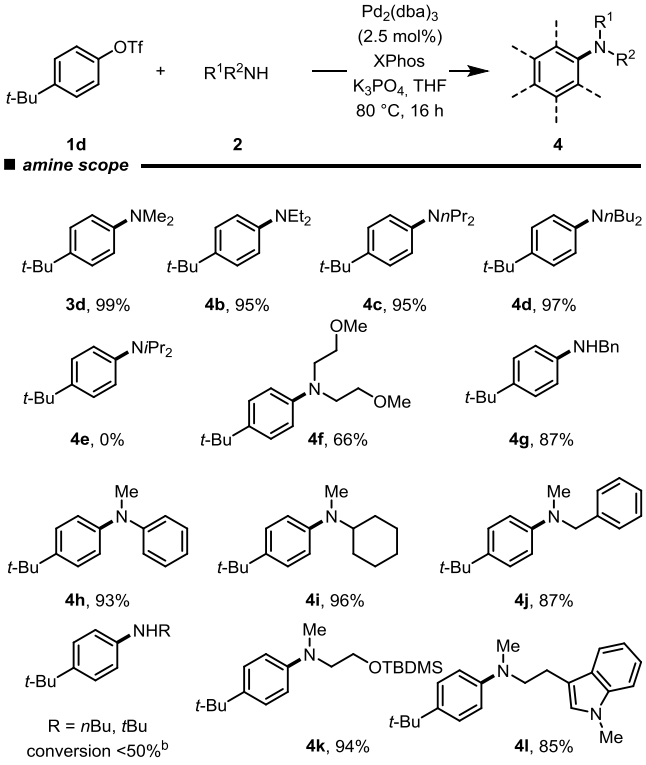
J. Org. Chem. XXXX, XXX, XXX–XXX

suitable under these conditions. An intramolecular competition reaction confirmed that the aryl bromine bond is more activated compared to the sulfonate bond. Noteworthily, the triflate functionality remained intact and could be utilized in a subsequent coupling reaction.

The scope of the amine component is similarly wide (Scheme 5) and includes electronically rich alkylamines (**4a**–**d**), an aniline (**4h**), a benzylamine (**4j**), a silyl-containing functional group (**4k**), an ether moiety (**4f**), and an indole derivative (**4l**). Branched alkyl chains, with an increased tendency to β-hydride elimination, did not show any product formation under the applied conditions (**4e**). However, a similarly branched but cyclic amine (**4i**) could easily be converted. Primary amines were poor substrates under these conditions. The only exception was benzylamine (**4g**) in 89% isolated yield.

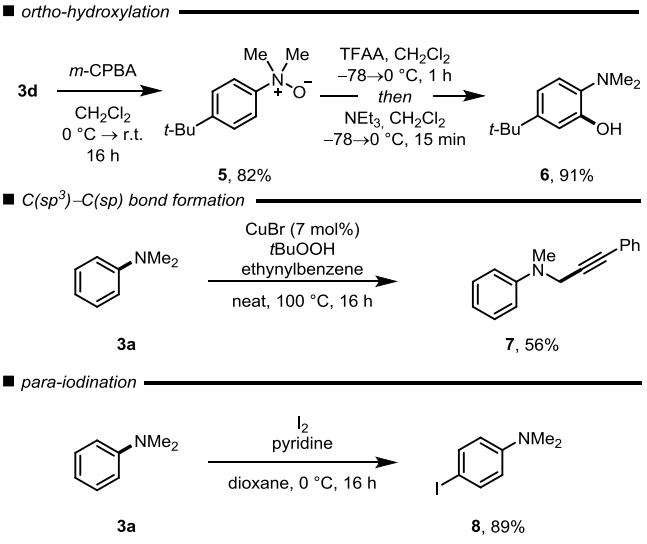
Scheme 5. Palladium-Catalyzed Arylation of Acyclic Alkylamines



[a]Reaction conditions: **1d** (0.5 mmol), **2** (2.0 mmol, 2.0 M in THF), $Pd_2(dba)_3$ (2.5 mol %), XPhos (7.5 mol %), K_3PO_4 (1.2 mol), THF (1 mL), 80 °C, 16 h. [b]According to gas chromatography–mass spectrometry (GC–MS).

To further assess the utility of dimethylamination, we performed synthetic manipulations around the core structure of the products. For example, *para-tert*-butyl dimethylaniline (**3d**) was readily oxidized with *m*-CPBA to produce the corresponding *N*-oxide (**5**) in 83% yield (Scheme 6). This *N*-oxidized compound can be converted into the ortho-substituted phenol in 91% yield.[7] Also, dimethylaniline (**3a**) smoothly underwent an alkynyl–methyl bond formation in the presence of the CuBr catalyst under oxidative conditions in 57% yield.[9] *para*-Iodination via electrophilic aromatic substitution with iodine delivered 4-iodo dimethylaniline **8** in 89% yield under mild conditions.[8]

Scheme 6. Derivatization of *N,N*-Dimethylanilines



In conclusion, we reported the convenient synthesis of *N,N*-dimethylaniline derivatives from dimethylamines and aryl triflates. The presented method shows a wide reaction scope and good chemoselectivity under mild reaction conditions. We want to emphasize that *N,N*-dimethylanilines are multifunctional reaction partners. By granting easy access to this substance class, we hope to aid future research efforts toward the functionalization of these building blocks.

EXPERIMENTAL SECTION

General Remarks. Unless otherwise noted, all reactions were carried out under an inert atmosphere using argon. All chemicals were purchased from commercial suppliers and used as received. Dry *n*-hexanes, acetonitrile (MeCN), and tetrahydrofuran (THF) were obtained by passing commercially available anhydrous, oxygen-free HPLC-grade solvents through activated alumina columns using an MBRAUN solvent purification system. Analytical thin-layer chromatography (TLC) was performed on MERCK silica gel 60 F254 aluminum plates. Visualization was accomplished with UV light and/or potassium permanganate ($KMnO_4$) or cerium ammonium molybdate stain (CAM). Retention factor (R_f) values reported were measured using a 5 × 2 cm^2 TLC plate in a developing chamber containing the solvent system described. Flash column chromatography was performed using Silica 60 M from Macherey-Nagel (SiO_2, 40–63 μm particle size, 230–400 mesh). Mass spectrometry (MS) and NMR spectroscopy were performed by the LIKAT analytic department. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 (400 MHz, ^1H; 100 MHz, ^{13}C) or Bruker 300 (300 MHz, ^1H; 75 MHz, ^{13}C) MHz spectrometers. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ^1H; 77.16 ppm, ^{13}C) or residual dimethyl sulfoxide (δ = 2.50 ppm, ^1H; 39.5 ppm, ^{13}C). Chemical shifts are reported in parts per million (ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants J are reported in hertz (Hz). Electron impact (EI^+) spectra were recorded at 70 eV using methane as the carrier gas, with a time-of-flight (TOF) mass analyzer. Electrospray ionization (ESI^+) spectra were recorded using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100). High-resolution mass spectra were recorded using WATERS Xevo G2-XS Tof ESI-TOF LC/MS spectrometers or Thermo Fisher Scientific Finnigan MAT95XP EI GC/MS. Infrared spectra were recorded neat on a PERKIN-ELMER BX FT-IR spectrometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T), m (medium, 34–66% T), w (weak, 67–100% T), and br (broad). Melting points of solids, compounds

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J. Org. Chem. XXXX, XXX, XXX–XXX

that solidified after chromatography, were measured on a Büchi B-540 melting point apparatus and are uncorrected. X-ray data were collected on a Bruker Kappa APEX II Duo and a Bruker D8 QUEST diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations.

General Procedure A: Synthesis of Aryl Sulfonates. The following procedure was carried out in air. The selected phenol (1−5 mmol) and the base (2.0 equiv) were transferred into a 25 mL flask and dissolved in CH_2Cl_2 (1.0 M). The flask was sealed with a septum and cooled to −78 °C. Afterward, trifluoromethanesulfonic anhydride (1.2 equiv) was added via a syringe dropwise over a period of 5 min. Overnight (approximately 16 h), the reaction mixture was allowed to warm to ambient temperature and quenched with water. The mixture was extracted three times with CH_2Cl_2 and dried over Na_2SO_4. The crude product was purified with column chromatography to furnish the desired aryl sulfonate.

General Procedure B: Synthesis of *N,N*-Dimethylaniline Substrates. All reactions were carried out in septum-sealed 4 mL vials. Subsequently, $Pd_2(dba)_3$ (2.5 mol %), XPhos (1.5 equiv of the metal), K_3PO_4 (1.2 equiv), and the appropriate trifluoromethanesulfonate (0.5 mmol) were added and the vial was sealed. The reaction vessel was back-filled with argon three times. Afterward, 1 mL of THF was added and the suspension was stirred at 80 °C in a block of aluminum. After 5 min, a dimethylamine solution (2 M THF, 1 mL) was added through the septum in one portion. After 16 h, the reaction mixture was quenched with water and extracted three times with CH_2Cl_2. The organic layer was analyzed via GC−MS. After a positive result, the solvent was removed in vacuo (500 mbar) and the desired dimethylaniline was purified with column chromatography. To avoid a loss of yields due to the volatility of the desired amines, the fraction was treated with a HCl solution (2.0 M in diethyl ether) to form the corresponding hydrochloride salts.

General Procedure C: Arylation of Nonvolatile Alkylamines. All reactions were carried out in septum-sealed 4 mL vials. Subsequently, $Pd_2(dba)_3$ (2.5 mol %), XPhos (1.5 equiv of the metal), K_3PO_4 (1.2 equiv), 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (0.5 mmol), and the appropriate amine (2−4 equiv) were added and the vial was sealed. The reaction vessel was back-filled with argon three times. Afterward, 1 mL of THF was added and the suspension was stirred at 80 °C in a block of aluminum. After 16 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2 three times. The organic layer was analyzed via GC−MS and TLC. After a positive result, the solvent was removed in vacuo (500 mbar) and the desired dimethylaniline was purified with column chromatography. To avoid a loss of yields due to the volatility of the desired amines, the fraction was treated with a HCl solution (2.0 M in diethyl ether) to form the corresponding hydrochloride salts.

*Phenyl Trifluoromethanesulfonate (**1a**).* Following general procedure A, the use of 2.13 mmol phenol at 0 °C instead of −78 °C with triethylamine as the base afforded the title compound **1a** (365 mg, 1.61 mmol, 76%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.45 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.27 (m, 3H), 7.24−7.15 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.8, 130.4, 128.5, 121.5, 118.9 (q, J = 320.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.96. MS (EI): m/z (relative intensity) 226 (19), 96 (12), 93 (28), 69 (100), 65 (95), 64 (16), 63 (18), 50 (10), 48 (12), 39 (58), 38 (11). HRMS (EI, m/z): calcd for $C_7H_5O_3F_3S$ $[M]^+$ 225.9906, found 225.9905. IR (ATR, neat, cm^{-1}): 1603 (w), 1587 (w), 1487 (m), 1459 (w), 1420 (s), 1287 (w), 1249 (m), 1203 (s), 1175 (m), 1129 (s), 1073 (w), 1024 (w), 912 (m), 879 (s), 826 (w), 779 (m), 764 (s), 735 (m), 685 (m), 621 (m), 600 (s), 567 (m), 515 (s), 475 (m), 405 (w). The analytical data is in accordance with that reported in the literature.[26]

*N,N-Dimethylaniline Hydrochloride (**3a**·HCl).* Following general procedure B, the use of phenyl trifluoromethanesulfonate afforded the title compound **3a** (78 mg, 0.496 mmol, 99%) as a colorless waxy solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). R_f = 0.15 (*n*-pentane, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.05 (s, 1H), 7.81−7.62 (m, 2H), 7.46−7.28 (m, 2H), 3.10 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.7, 130.3, 130.1, 120.7, 46.4. MS (EI): m/z (relative intensity) 121 (71), 120 (100), 105 (12), 104 (13), 77 (22), 51 (11). HRMS (ESI-TOF, m/z): calcd for $C_8H_{11}N$ $[M + H]^+$ 122.0969, found 122.0969. IR (ATR, neat, cm^{-1}): 3045 (w), 3012 (w), 2952 (w), 2929 (w), 2853 (w), 2629 (w), 2529 (w), 2495 (m), 2381 (s), 2127 (w), 1598 (m), 1494 (s), 1468 (m), 1421 (m), 1403 (w), 1345 (w), 1326 (w), 1196 (m), 1185 (w), 1158 (w), 1136 (m), 1127 (m), 1079 (w), 1063 (w), 1026 (w), 995 (m), 928 (w), 899 (m), 853 (w), 764 (s), 696 (s), 616 (w), 575 (m), 542 (s), 480 (w).

*p-Tolyl Trifluoromethanesulfonate (**1b**).* Following general procedure A, the use of *p*-cresol (9.25 mmol) at 0 °C instead of −78 °C with NEt_3 as the base afforded the title compound **1b** (2.18 g, 9.07 mmol, 98%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.36 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.20 (m, 2H), 7.18−7.12 (m, 2H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 147.6, 138.5, 130.7, 121.0, 118.8 (q, J = 320.7 Hz), 20.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.91. MS (EI): m/z (relative intensity) 240 (65), 175 (11), 107 (100), 91 (12), 79 (24), 78 (14), 77 (60), 69 (18), 51 (11). HRMS (EI, m/z): calcd for $C_8H_{11}N$ $[M]^+$ 240.0063, found 240.0061. IR (ATR, neat, cm^{-1}): 1600 (w), 1501 (m), 1420 (s), 1249 (m), 1203 (s), 1178 (m), 1132 (s), 1044 (w), 1018 (w), 938 (w), 881 (s), 821 (s), 770 (w), 714 (w), 691 (m), 639 (m), 606 (s), 583 (m), 561 (w), 542 (w), 502 (s), 485 (m), 417 (w). The analytical data is in accordance with that reported in the literature.[26]

*N,N-4-Trimethylaniline Hydrochloride (**3b**·HCl).* Following general procedure B, the use of *p*-tolyl trifluoromethanesulfonate (**1b**) afforded the title compound **3b** (78 mg, 0.454 mmol, 90%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). R_f = 0.20 (*n*-pentane, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.86 (s, 1H), 7.60 (d, J = 6.1 Hz, 2H), 7.21−7.09 (m, 2H), 3.09 (s, 6H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 140.2, 130.7, 120.4, 46.5, 20.9. MS (EI): m/z (relative intensity) 135 (66), 134 (100), 119 (14), 118 (14), 91 (18). HRMS (EI, m/z): calcd for $C_9H_{13}N$ $[M]^+$ 135.1046, found 135.1046. IR (ATR, neat, cm^{-1}): 3031 (w), 2922 (w), 2627 (w), 2536 (w), 2498 (w), 2422 (m), 2405 (m), 1611 (w), 1501 (s), 1485 (s), 1462 (m), 1440 (m), 1423 (m), 1362 (w), 1267 (w), 1249 (s), 1231 (m), 1173 (m), 1128 (m), 1094 (w), 1027 (s), 987 (m), 944 (w), 919 (s), 878 (w), 854 (m), 815 (m), 724 (w), 697 (w), 634 (s), 554 (w), 448 (m), 423 (m). The analytical data is in accordance with that reported in the literature.[27]

*4-Isopropylphenyl Trifluoromethanesulfonate (**1c**).* Following general procedure A, the use of 2 mmol 4-isopropylphenol at 0 °C instead of −78 °C and pyridine as the base afforded the title compound **1c** (389 mg, 1.45 mmol 72%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.50 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.26 (m, 2H), 7.22−7.16 (m, 2H), 2.95 (sept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.5, 147.8, 128.3, 121.2, 118.9 (q, J = 320.7 Hz), 33.8, 24.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.95. MS (EI): m/z (relative intensity) 268 (48), 254 (11), 253 (100), 135 (42), 107 (29), 103 (32), 92 (14), 91 (60), 79 (13), 77 (16), 69 (23), 65 (16). HRMS (EI, m/z): calcd for $C_{10}H_{11}O_3F_3S_1$ $[M]^+$ 268.0376, found 268.0375. IR (ATR, neat, cm^{-1}): 2966 (s), 2933 (s), 2876 (s), 1597 (s), 1502 (s), 1465 (s), 1419 (s), 1367 (s), 1339 (s), 1302 (s), 1281 (s), 1249 (s), 1204 (s), 1181 (s), 1134 (s), 1057 (s), 1017 (s), 942 (s), 883 (s), 837 (s), 787 (s), 763 (s), 730 (s), 684 (s), 637 (s), 608 (s), 588 (s), 564 (s), 537 (s), 511 (s), 472 (w).

*4-Isopropyl-N,N-dimethylaniline Hydrochloride (**3c**·HCl).* Following general procedure B, the use of 0.524 mmol 4-isopropylphenyl trifluoromethanesulfonate (**1c**) afforded the title compound **3c** (94 mg, 0.457 mmol, 90%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). R_f = 0.17 (*n*-pentane, UV) free base; ^{1}H NMR (300

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J. Org. Chem. XXXX, XXX, XXX−XXX

MHz, $CDCl_3$) δ 14.22 (s, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.14 (s, 6H), 2.91 (sept, J = 7.1 Hz, 1H), 1.20 (d, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 151.4, 140.5, 128.5, 120.6, 46.7, 33.9, 23.8. MS (EI): m/z (relative intensity) 163 (29), 149 (11), 148 (100). HRMS (EI, m/z): calcd for $C_{11}H_{17}N$ $[M + H]^+$ 164.1439, found 164.1442. IR (ATR, neat, cm^{-1}): 3408 (w), 3006 (w), 2957 (m), 2932 (w), 2869 (w), 2492 (w), 2296 (s), 1940 (w), 1810 (w), 1662 (w), 1600 (w), 1511 (s), 1482 (s), 1461 (m), 1413 (m), 1384 (w), 1363 (w), 1311 (w), 1287 (w), 1251 (w), 1190 (m), 1133 (m), 1057 (m), 1019 (m), 1000 (m), 963 (w), 900 (m), 848 (s), 834 (s), 740 (w), 677 (w), 638 (w), 582 (s), 557 (m), 456 (w), 410 (w). The analytical data is in accordance with that reported in the literature.[28]

*4-(tert-Butyl)phenyl Trifluoromethanesulfonate (**1d**).* Following general procedure A, the use of 20 mmol 4-(*tert*-butyl)phenol at 0 °C instead of −78 °C with pyridine as the base afforded the title compound **1d** (5.65 g, 19.24 mmol, 96%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.40 (*n*-pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.49−7.41 (m, 2H), 7.22−7.16 (m, 2H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 151.8, 147.6, 127.3, 120.8, 118.9 (q, J = 320.7 Hz), 34.9, 31.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.97. MS (EI): m/z (relative intensity) 282 (11), 269 (10), 268 (15), 267 (100), 175 (17), 134 (12), 109 (11), 106 (10), 79 (10), 78 (10), 77 (13), 41 (13). HRMS (EI) m/z calcd for $C_{11}H_{13}O_3F_3S_1^+$ $[M]^+$ 282.0532, found 282.0530. IR (ATR, neat, cm^{-1}): 2966 (w), 2909 (w), 2873 (w), 1648 (w), 1596 (w), 1504 (m), 1466 (w), 1422 (s), 1366 (w), 1310 (w), 1268 (w), 1249 (m), 1205 (s), 1138 (s), 1111 (m), 1015 (m), 942 (w), 886 (s), 837 (s), 780 (m), 756 (m), 730 (m), 664 (m), 637 (m), 609 (s), 582 (m), 552 (m), 531 (m), 509 (s), 414 (m). The analytical data is in accordance with that reported in the literature.[26]

*4-(tert-Butyl)-N,N-dimethylaniline Hydrochloride (**3d**·HCl).* Following general procedure B, the use of 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (**1d**) afforded the title compound **3d** (106 mg, 0.497 mmol, 99%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). To demonstrate the practical use of the method as a synthetic tool, this synthesis was also carried out in a 50 mL septum-sealed round-bottom flask (1.28 g, 6.00 mmol, 99%) R_f = 0.21 (*n*-pentane, UV) free base; ^1H NMR (300 MHz, $CDCl_3$) δ 14.14 (s, 1H), 7.69−7.62 (m, 2H), 7.46−7.39 (m, 2H), 3.13 (s, 6H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 153.4, 140.3, 127.3, 120.2, 46.4, 34.8, 31.1. MS (EI): m/z (relative intensity) 177 (24), 163 (13), 162 (100), 147 (15). HRMS (ESI-TOF, m/z): calcd for $C_{12}H_{19}N$ $[M + H]^+$ 178.1595, found 178.1598. IR (ATR, neat, cm^{-1}): 3020 (w), 2957 (m), 2901 (w), 2865 (w), 2488 (w), 2351 (m), 1599 (w), 1513 (m), 1484 (m), 1451 (m), 1417 (w), 1396 (w), 1362 (w), 1269 (w), 1205 (w), 1188 (w), 1143 (m), 1120 (w), 1018 (w), 991 (m), 898 (m), 837 (m), 741 (w), 656 (w), 573 (s), 544 (w), 461 (w). The analytical data is in accordance with that reported in the literature.[29]

*4-Methoxyphenyl Trifluoromethanesulfonate (**1e**).* Following general procedure A, the use of 4-methoxyphenol (2.00 mmol) at 0 °C instead of −78 °C and triethylamine as the base afforded the title compound **1e** (456 mg, 1.78 mmol, 89%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.13 (*n*-pentane, UV); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24−7.16 (m, 2H), 6.96−6.88 (m, 2H), 3.81 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2, 143.2, 122.5, 118.9 (q, J = 320.9 Hz), 115.2, 55.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.87. MS (EI): m/z (relative intensity) 256 (13), 123 (100), 95 (37), 69 (27). HRMS (EI, m/z): calcd for $C_{20}H_{26}O_3$ $[M + H]^+$ 256.0012, found 256.0005. IR (ATR, neat, cm^{-1}): 2953 (w), 2843 (w), 1597 (w), 1501 (s), 1465 (w), 1417 (s), 1300 (w), 1248 (m), 1203 (s), 1168 (s), 1133 (s), 1105 (m), 1032 (m), 1008 (m), 928 (w), 881 (s), 832 (s), 808 (s), 769 (w), 721 (w), 694 (m), 636 (m), 606 (s), 561 (m), 518 (s), 503 (m), 469 (m). The analytical data is in accordance with that reported in the literature.[26]

*4-Methoxy-N,N-dimethylaniline Hydrochloride (**3e**·HCl).* Following general procedure B, the use of 4-methoxyphenyl trifluoromethanesulfonate (**1e**, 0.33 mmol) afforded the title compound **3e** (57 mg, 0.30 mmol, 92%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1) and treatment with HCl (2.0 M in Et_2O). R_f = 0.27 (*n*-pentane/EtOAc = 10:1) free base; ^1H NMR (300 MHz, $CDCl_3$) δ 14.07 (s, 1H), 7.72−7.63 (m, 2H), 6.92−6.84 (m, 2H), 3.74 (s, 3H), 3.10 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.3, 135.6, 122.1, 115.4, 55.7, 46.9. MS (EI): m/z (relative intensity) 151 (56), 136 (100), 108 (11). HRMS (EI, m/z): calcd for $C_{14}H_{16}N$ $[M + H]^+$ 152.1075, found 152.1078. IR (ATR, neat, cm^{-1}): 3126 (w), 3074 (w), 3056 (w), 3006 (w), 2974 (w), 2943 (w), 2913 (w), 2844 (w), 2621 (w), 2531 (w), 2498 (m), 2427 (m), 2407 (m), 2150 (w), 2120 (w), 2036 (w), 1954 (w), 1921 (w), 1885 (w), 1700 (w), 1616 (w), 1605 (m), 1519 (s), 1492 (m), 1458 (s), 1447 (m), 1425 (w), 1404 (w), 1314 (m), 1266 (s), 1242 (m), 1181 (s), 1158 (m), 1141 (m), 1119 (m), 1023 (s), 995 (m), 979 (m), 900 (m), 849 (s), 823 (m), 813 (m), 724 (w), 700 (m), 636 (w), 565 (s), 552 (s), 486 (w), 438 (w), 418 (w). The analytical data is in accordance with that reported in the literature.[27]

*4-Methoxyphenyl Trifluoromethanesulfonate (**1f**).* Following general procedure A, the use of 4-(methylthio)phenol (4.00 mmol) and $NEtiPr_2$ as the base afforded the title compound **1f** (0.981 g, 3.60 mmol, 90%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1, UV). R_f = 0.35 (*n*-pentane/EtOAc = 50:1, UV); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32−7.26 (m, 1H), 7.24−7.17 (m, 1H), 2.50 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 147.0, 139.9, 127.6, 121.8, 118.8 (d, J = 320.9 Hz), 15.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.89. MS (EI): m/z (relative intensity) 272 (33), 139 (100), 111 (14), 69 (1). HRMS (EI, m/z): calcd for $C_8H_7O_3F_3S_2$ $[M]^+$ 271.9783, found 271.9790. IR (ATR, neat, cm^{-1}): 2178 (w), 2152 (w), 1983 (w), 1486 (m), 1418 (m), 1399 (m), 1248 (w), 1201 (s), 1183 (m), 1131 (s), 1090 (m), 1011 (m), 970 (w), 944 (w), 885 (s), 828 (s), 782 (m), 756 (m), 720 (w), 648 (w), 632 (m), 604 (s), 575 (m), 556 (w), 525 (m), 490 (m), 472 (w), 456 (m), 437 (w), 427 (w), 420 (m), 401 (m). The analytical data is in accordance with that reported in the literature.[30]

*N,N-Dimethyl-4-(methylthio)aniline Hydrochloride (**3f**·HCl).* Following general procedure B, the use of 4-(methylthio)phenyl trifluoromethanesulfonate afforded the title compound **3f** (100 mg, 0.492 mmol, 99%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 50:1) and treatment with 2 M HCl in Et_2O. R_f = 0.29 (*n*-pentane/EtOAc = 50:1, UV) free base; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70−7.63 (m, 2H), 7.25−7.18 (m, 2H), 3.11 (s, 6H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.0, 139.5, 127.2, 121.2, 46.6, 15.3. MS (EI): m/z (relative intensity) 167 (68), 153 (12), 152 (100), 136 (19), 119 (13), 108 (16), 77 (11), 69 (17), 63 (12), 51 (12), 47 (23), 45 (37), 42 (22). HRMS (EI, m/z): calcd for $C_8H_7O_3F_3S_2$ $[M]^+$ 167.0763, found 167.0757. IR (ATR, neat, cm^{-1}): 3482 (w), 3042 (w), 3008 (w), 2974 (w), 2914(w), 2535 (w), 2497 (m), 2394 (s), 1925 (w), 1656 (w), 1590 (w), 1486 (s), 1464 (m), 1426 (m), 1395 (m), 1321 (w), 1286 (w), 1187 (m), 1157 (w), 1138 (m), 1096 (m), 1016 (w), 992 (m), 981 (w), 956 (m), 897 (m), 825 (s), 776 (w), 715 (w), 635 (w), 539 (s), 520 (m), 413 (w). The analytical data is in accordance with that reported in the literature.[31]

*4-Acetylphenyl Trifluoromethanesulfonate (**1g**).* Following general procedure A, the use of benzo[*d*][1,3]dioxol-5-ol (4.00 mmol) and pyridine as the base afforded the title compound **1g** (1.01 g, 3.74 mmol, 93%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.34 (*n*-pentane/EtOAc = 50:1, UV); ^1H NMR (300 MHz, $CDCl_3$) δ 6.83−6.71 (m, 3H), 6.03 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 148.7, 147.6, 143.6, 118.9 (q, J = 320.8 Hz), 114.5, 108.3, 103.5, 102.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.84. MS (EI): m/z (relative intensity) 270 (19), 137 (100), 107 (43), 79 (44), 69 (64), 53 (35), 51 (20), 50 (14). HRMS (EI, m/z): calcd for $C_8H_5O_5F_3S_1$ $[M]^+$ 269.9804, found 269.9806. IR (ATR, neat, cm^{-1}): 2908 (w), 1638 (w), 1610 (w), 1505 (m), 1481 (s), 1418 (s), 1366 (w), 1245 (s), 1202 (s), 1163 (m), 1136 (s), 1108 (s), 1087 (s), 1036 (s), 940 (s), 928 (s), 859 (s), 843 (s), 804 (s), 772 (w), 733 (m), 713 (m), 652 (m), 606 (s), 589 (s), 559 (m), 534 (w), 504 (s), 452 (m), 426 (m). The analytical data is in accordance with that reported in the literature.[30]

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J. Org. Chem. XXXX, XXX, XXX−XXX

*N,N-Dimethylbenzo[d][1,3]dioxol-5-amine Hydrochloride (**3g**·HCl).* Following general procedure B, the use of benzo[*d*][1,3]-dioxol-5-yl trifluoromethanesulfonate **1g** (0.529 mmol) afforded the title compound **3g** (103 mg, 0.501 mmol, 95%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1) and treatment with 2 M HCl in Et_2O. R_f = 0.4 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.48 (s, 1H), 7.31 (dd, J = 8.4, 2.4 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 6.05 (s, 2H), 3.12 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.1, 148.9, 136.9, 114.6, 109.1, 102.6, 102.0, 47.0. MS (EI): m/z (relative intensity) 166 (10), 165 (100), 164 (61), 149 (14), 136 (12), 107 (13), 92 (37), 82 (13), 65 (11). HRMS (EI, m/z): calcd for $C_9H_{11}O_2N$ $[M]^+$ 165.0784, found 165.0782. IR (ATR, neat, cm^{-1}): 3031 (w), 2923 (w), 2536 (w), 2498 (w), 2422 (m), 2405 (m), 1651 (w), 1612 (w), 1501 (s), 1462 (m), 1440 (m), 1423 (m), 1362 (w), 1267 (w), 1249 (s), 1231 (m), 1173 (m), 1129 (m), 1094 (m), 1028 (s), 987 (m), 944 (w), 919 (s), 878 (w), 854 (m), 815 (m), 762 (w), 723 (w), 696 (w), 634 (s), 554 (w), 528 (w), 479 (w), 447 (m), 422 (m). The analytical data is in accordance with that reported in the literature.[32]

*4-Nitrophenyl Trifluoromethanesulfonate (**1h**).* Following general procedure A, the use of 4-nitrophenol (3.59 mmol) and pyridine as the base afforded the title compound **1h** (940 mg, 3.47 mmol, 96%) as a clear white solid after purification via column chromatography (pure *n*-pentane). R_f = 0.24 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42−8.29 (m, 2H), 7.56−7.41 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.1, 147.1, 126.0, 122.5, 118.6 (q, J = 320.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.73. MS (EI): m/z (relative intensity) 271 (62), 177 (41), 161 (16), 149 (18), 95 (59), 92 (21), 75 (11), 69 (100), 64 (37), 63 (43), 62 (11), 38 (11), 30 (25). HRMS (EI, m/z): calcd for $C_7H_4O_5NF_3S$ $[M]^+$ 270.9757, found 270.9752. IR (ATR, neat, cm^{-1}): 3124 (w), 1622 (w), 1589 (w), 1534 (s), 1485 (m), 1420 (s), 1381 (w), 1347 (s), 1318 (w), 1291 (w), 1250 (m), 1210 (s), 1174 (m), 1129 (s), 1011 (m), 892 (s), 859 (s), 779 (m), 757 (m), 740 (s), 689 (m), 629 (m), 608 (s), 572 (s), 524 (s), 472 (m), 444 (s).

*N,N-Dimethyl-4-nitroaniline Hydrochloride (**3h**·HCl).* Following general procedure B, the use of 4-nitrophenyl trifluoromethanesulfonate (**1h**) afforded the title compound **3h** (65 mg, 0.391 mmol, 71%, free base) as a yellow crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1). R_f = 0.20 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14−8.03 (m, 2H), 6.63−6.53 (m, 2H), 3.09 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.2, 136.8, 126.1, 110.2, 40.3. MS (EI): m/z (relative intensity) 166 (63), 165 (15), 136 (57), 120 (15), 119 (26), 118 (20), 108 (15), 105 (19), 104 (21), 92 (11), 91 (11), 79 (15), 78 (18), 77 (39), 76 (17), 65 (18), 64 (12), 63 (17), 51 (19), 50 (22), 46 (47), 42 (52), 39 (14), 30 (100). HRMS (EI, m/z): calcd for $C_9H_{11}O_2N$ $[M]^+$ 166.0737, found 166.0736. IR (ATR, neat, cm^{-1}): 2918 (w), 1915 (w), 1580 (s), 1526 (m), 1481 (s), 1449 (m), 1382 (w), 1284 (s), 1231 (s), 1196 (s), 1112 (s), 1066 (s), 938 (m), 819 (s), 748 (s), 695 (s), 629 (m), 604 (m), 539 (s), 505 (s), 491 (s). The analytical data is in accordance with that reported in the literature.[27]

*Naphthalen-2-yl Trifluoromethanesulfonate (**1i**).* Following general procedure A, the use of naphthalen-2-ol (4.00 mmol) and pyridine as the base afforded the title compound **1i** (1.00 g, 3.62 mmol, 91%) as a clear colorless oil after purification via column chromatography (*n*-pentane). R_f = 0.50 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.83 (m, 3H), 7.78 (d, J = 2.5 Hz, 1H), 7.65−7.53 (m, 2H), 7.39 (dd, J = 9.0, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.2, 133.4, 132.5, 130.7, 128.1, 128.0, 127.7, 127.3, 119.6, 119.3, 119.0 (q, J = 320.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.82. MS (EI): m/z (relative intensity) 276 (41), 143 (42), 115 (100). HRMS (EI, m/z): calcd for $C_{11}H_7O_3F_3S$ $[M]^+$ 276.0063, found 276.0061. IR (ATR, neat, cm^{-1}): 3063 (w), 1633 (w), 1600 (w), 1582 (w), 1511 (w), 1461 (w), 1419 (s), 1356 (w), 1250 (m), 1233 (m), 1201 (s), 1135 (s), 1104 (s), 955 (s), 911 (s), 884 (m), 859 (s), 831 (s), 807 (s), 766 (m), 748 (s), 697 (m), 643 (s), 620 (m), 603 (s), 577 (m), 542 (w), 522 (w), 495 (s), 471 (s), 430 (m). The analytical data is in accordance with that reported in the literature.[33]

*N,N-Dimethylnaphthalen-2-amine Hydrochloride (**3i**·HCl).* Following general procedure B, the use of naphthalen-2-yl trifluoromethanesulfonate (**1i**) afforded the title compound **3i** (102 mg, 0.491 mmol, 95%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with 2 M HCl in Et_2O. R_f = 0.13 (*n*-pentane, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.49 (s, 1H), 8.34 (d, J = 2.4 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.90−7.79 (m, 2H), 7.76 (dd, J = 8.9, 2.4 Hz, 1H), 7.59−7.44 (m, 2H), 3.25 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.9, 133.2, 132.8, 131.2, 128.4, 128.0, 127.9, 120.2, 117.4, 46.7. MS (EI): m/z (relative intensity) 172 (12), 171 (100), 170 (87), 155 (19), 128 (27), 127 (24), 77 (11). HRMS (ESI-TOF, m/z): calcd for $C_{12}H_{13}N$ $[M + H]^+$ 172.1126, found 172.1126. IR (ATR, neat, cm^{-1}): 3465 (w), 3405 (w), 3011 (w), 2506 (w), 2305 (m), 1634 (w), 1603 (w), 1515 (m), 1486 (m), 1470 (m), 1422 (w), 1361 (w), 1271 (w), 1181 (m), 1135 (m), 1109 (m), 990 (w), 954 (m), 922 (w), 909 (w), 870 (m), 843 (m), 816 (s), 755 (s), 693 (w), 655 (m), 616 (w), 566 (m), 545 (m), 483 (s), 474 (s). The analytical data is in accordance with that reported in the literature.[34]

*[1,1′-Biphenyl]-4-trifluoromethanesulfonate (**1j**).* Following general procedure A, the use of [1,1′-biphenyl]-4-ol (2.10 mmol) at 0 °C instead of −78 °C and triethylamine as the base afforded the title compound **1j** (0.510 g, 1.69 mmol, 80%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.36 (*n*-pentane, UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.62 (m, 2H), 7.61−7.54 (m, 2H), 7.52−7.40 (m, 3H), 7.40−7.32 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.1, 141.8, 139.4, 129.1, 129.0, 128.2, 127.3, 121.8, 118.9 (q, J = 320.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.79. MS (EI): m/z (relative intensity) 302 (46), 170 (13), 169 (100), 141 (51), 139 (13), 115 (36). HRMS (EI, m/z): calcd for $C_{13}H_9F_3O_3S$ $[M + H]^+$ 302.0219, found 302.0225. IR (ATR, neat, cm^{-1}): 3061 (w), 1595 (w), 1483 (m), 1454 (w), 1425 (s), 1342 (s), 1250 (m), 1213 (s), 1179 (m), 1226 (s), 1016 (m), 1006 (m), 945 (w), 876 (m), 844 (s), 787 (m), 758 (s), 720 (m), 687 (s), 640 (m), 599 (m), 569 (s), 541 (m), 513 (s), 475 (m), 419 (m). The analytical data is in accordance with that reported in the literature.[33]

*N,N-Dimethyl-[1,1′-biphenyl]-4-amine Hydrochloride (**3j**·HCl).* Following general procedure B, the use of [1,1′-biphenyl]-4-yl trifluoromethanesulfonate (**1j**) afforded the title compound **3j** (122 mg, 0.522 mmol, 99%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 50:1) and treatment with 2 M HCl in Et_2O. R_f = 0.38 (*n*-pentane/EtOAc = 20:1, UV) free base; m.p. = 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.49 (s, 1H), 7.85 (ddd, J = 8.8, 2.5, 2.1 Hz, 2H), 7.66 (dt, J = 9.0, 2.1 Hz, 2H), 7.53−7.47 (m, 2H), 7.47−7.32 (m, 3H), 3.21 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.3, 141.9, 139.0, 129.1, 129.1, 128.4, 127.2, 121.2, 46.6. MS (EI): m/z (relative intensity) 198 (16), 197 (100), 196 (78), 181 (14), 180 (10), 153 (12), 152 (21), 98 (13). HRMS (ESI-TOF, m/z): calcd for $C_{14}H_{16}N$ $[M + H]^+$ 198.1283, found 198.1283. IR (ATR, neat, cm^{-1}): 3505 (w), 3367 (w), 3014 (w), 2957 (w), 2548 (w), 2498 (w), 2453 (w), 1631 (w), 1599 (w), 1577 (w), 1522 (w), 1484 (m), 1441 (w), 1418 (w), 1396 (w), 1337 (w), 1273 (w), 1246 (w), 1211 (w), 1186 (w), 1154 (w), 1137 (m), 1077 (w), 1062 (w), 1041 (w), 1019 (w), 1005 (w), 994 (w), 899 (w), 837 (m), 765 (s), 720 (m), 691 (s), 638 (w), 583 (m), 557 (m), 503 (s). The analytical data is in accordance with that reported in the literature.[35]

*[1,1′-Biphenyl]-3-yl Trifluoromethanesulfonate (**1k**).* Following general procedure A, the use of [1,1′-biphenyl]-3-ol (2.94 mmol) and pyridine as the base afforded the title compound **1k** (0.886 g, 2.93 mmol, 80%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.29 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.57 (m, 3H), 7.57−7.41 (m, 6H), 7.29 (dd, J = 8.3, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.2, 144.1, 139.1, 130.6, 128.5, 127.3, 127.2, 120.1, 119.9, 118.9 (q, J = 320.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.83. MS (EI): m/z (relative intensity) 303 (11), 302 (74), 238 (12), 141 (100), 115 (37), 66 (14). HRMS (EI, m/z): calcd for $C_{13}H_9O_3F_3S_2$ $[M]^+$

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J. Org. Chem. XXXX, XXX, XXX−XXX

302.0224, found 302.0219. IR (ATR, neat, cm^{-1}): 3067 (w), 3037 (w), 1608 (w), 1571 (w), 1477 (m), 1418 (s), 1244 (m), 1204 (s), 1126 (s), 1087 (w), 1048 (w), 1025 (w), 1000 (w), 897 (s), 806 (s), 755 (s), 690 (s), 613 (m), 599 (s), 574 (s), 511 (s), 452 (w), 420 (w). The analytical data is in accordance with that reported in the literature.[36]

*N,N-Dimethyl-[1,1′-biphenyl]-3-amine Hydrochloride (**3k**·HCl).* Following general procedure B, the use of [1,1′-biphenyl]-3-yl trifluoromethanesulfonate (**1k**) afforded the title compound **3k** (70 mg, 0.408 mmol, 77%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1). R_f = 0.22 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.42 (s, 1H), 7.99 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.59−7.47 (m, 3H), 7.45−7.30 (m, 3H), 3.20 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 143.9, 143.5, 138.8, 130.9, 129.1, 128.8, 128.5, 127.2, 119.4, 119.3, 46.6. MS (EI): *m*/*z* (relative intensity) 197 (94), 196 (100), 153 (12), 152 (22), 98 (12). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{14}H_{15}N$ $[M + H]^+$ 198.1283, found 198.1283. IR (ATR, neat, cm^{-1}): 3017 (w), 2925 (w), 2852 (w), 2496 (w), 2380 (m), 1609 (w), 1594 (w), 1573 (w), 1514 (w), 1480 (m), 1462 (m), 1442 (m), 1419 (w), 1403 (w), 1321 (w), 1294 (w), 1270 (w), 1192 (m), 1156 (w), 1135 (m), 1096 (w), 1073 (w), 1052 (w), 1025 (w), 995 (m), 913 (m), 803 (m), 757 (s), 696 (s), 634 (m), 614 (w), 585 (m), 527 (w), 489 (w), 464 (w). The analytical data is in accordance with that reported in the literature.[37]

*4-(1,3-Dioxolan-2-yl)-N,N-dimethylaniline (**3l**).* Following general procedure B, the use of 4-(1,3-dioxolan-2-yl)phenyl trifluoromethanesulfonate (**1l**, 523 mmol) afforded the title compound **3l** (77 mg, 0.516 mmol, 99%, free base) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1). R_f = 0.16 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.79−7.65 (m, 2H), 6.77−6.60 (m, 2H), 3.13−2.99 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 190.3, 154.3, 132.0, 125.1, 111.0, 40.1. MS (EI): *m*/*z* (relative intensity) 149 (80), 148 (100), 132 (11), 77 (52). HRMS (ESI-TOF, *m*/*z*): calcd for $C_9H_{11}NO$ $[M + H]^+$ 150.0919, found 150.0921. IR (ATR, neat, cm^{-1}): 2918 (w), 2795 (w), 2713 (w), 1656 (w), 1589 (m), 1546 (m), 1529 (m), 1459 (w), 1431 (w), 1367 (m), 1311 (w), 1230 (s), 1161 (m), 1065 (m), 999 (w), 937 (w), 824 (m), 811 (s), 726 (m), 632 (w), 594 (m), 508 (m), 472 (w). The analytical data is in accordance with that reported in the literature.[38]

*tert-Butyl 6-(((Trifluoromethyl)sulfonyl)oxy)-1H-indole-1-carboxylate (**1m**).* Following general procedure A, the use of *tert*-butyl 6-hydroxy-1*H*-indole-1-carboxylate (2.23 mmol) and pyridine as the base afforded the title compound **1m** (675 mg, 1.85 mmol, 82%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.50 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.69 (d, J = 3.8 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.15 (dd, J = 8.6, 2.4 Hz, 1H), 6.59 (dd, J = 3.7, 0.8 Hz, 1H), 1.69 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.1, 146.6, 134.8, 130.2, 128.0, 121.8, 118.9 (d, J = 320.9 Hz), 116.0, 108.9, 106.9, 84.8, 28.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.82. MS (EI): *m*/*z* (relative intensity) 365 (7), 309 (22), 292 (13), 265 (17), 200 (7), 176 (18), 132 (80), 104 (12), 103 (13), 69 (15), 57 (100), 41 (20). HRMS (EI, *m*/*z*): calcd for $C_{14}H_{14}O_5NF_3S$ $[M]^+$ 187.1235, found 187.1236. IR (ATR, neat, cm^{-1}): 2982 (w), 1738 (s), 1616 (w), 1534 (w), 1470 (w), 1445 (m), 1420 (s), 1372 (m), 1334 (s), 1291 (w), 1244 (s), 1202 (s), 1139 (s), 1121 (s), 1074 (m), 1040 (w), 1024 (m), 932 (s), 880 (s), 836 (s), 814 (s), 789 (m), 762 (m), 739 (w), 723 (m), 661 (w), 622 (m), 598 (s), 576 (m), 500 (s), 432 (m). The analytical data is in accordance with that reported in the literature.[39]

*tert-Butyl 6-(Dimethylamino)-1H-indole-1-carboxylate (**3m**).* Following general procedure B, the use of *tert*-butyl 6-(((trifluoromethyl)sulfonyl)oxy)-1*H*-indole-1-carboxylate (**1m**) afforded the title compound **3m** (89 mg, 0.342 mmol, 67%, free base) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1). R_f = 0.36 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.46 = 7.32 (m, 2H), 6.80 (dd, J = 8.6, 2.3 Hz, 1H), 6.50 = 6.38 (m, 1H), 3.02 (s, 6H), 1.68 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.2, 149.1, 137.0, 123.6, 121.8, 121.1, 110.7, 107.3, 99.7, 83.1, 41.7, 28.4. MS (EI): *m*/*z* (relative intensity) 260 (20), 205 (13), 204 (100), 160 (46), 159 (61), 176 (18), 132 (80), 104 (12), 103 (13), 69 (15), 57 (100), 41 (20). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{15}H_{20}N_2O_2$ $[M + H]^+$ 261.1603, found 261.1598. IR (ATR, neat, cm^{-1}): 2977 (w), 2930 (w), 2799 (w), 1724 (s), 1619 (m), 1575 (w), 1531 (m), 1500 (m), 1461 (w), 1440 (m), 1380 (s), 1368 (m), 1333 (s), 1288 (m), 1248 (s), 1222 (m), 1184 (m), 1161 (s), 1144 (s), 1132 (s), 1075 (m), 1038 (m), 1018 (s), 962 (s), 895 (m), 846 (s), 795 (m), 768 (s), 755 (m), 705 (m), 634 (m), 614 (m), 575 (m), 469 (w), 442 (w).

*N,N-Dimethyl-4-(2-methyl-1,3-dioxolan-2-yl)aniline (**3n**).* Following general procedure B, the use of 4-(2-methyl-1,3-dioxolan-2-yl)phenyl trifluoromethanesulfonate (0.447 mmol) afforded the title compound **3n** (93 mg, 0.446 mmol, 99%, free base) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.18 (*n*-pentane/EtOAc = 20:1, UV) free base; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.22 (m, 2H), 6.63−6.58 (m, 2H), 3.99−3.84 (m, 2H), 3.77−3.63 (m, 2H), 2.85 (s, 6H), 1.56 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.1, 129.9, 125.1, 111.1, 108.0, 63.3, 39.5, 26.6. MS (EI): *m*/*z* (relative intensity) 207 (20), 193 (12), 192 (100), 148 (52). HRMS (ESI-TOF, *m*/*z*): calcd for $C_9H_{13}N$ $[M + H]^+$ 208.1337, found 208.1339. IR (ATR, neat, cm^{-1}): 2995 (w), 2943 (w), 2890 (w), 2801 (w), 1611 (m), 1519 (m), 1445 (w), 1426 (w), 1373 (w), 1344 (m), 1257 (w), 1221 (m), 1198 (m), 1182 (s), 1137 (m), 1100 (m), 1078 (m), 1028 (s), 947 (m), 888 (m), 861 (s), 817 (s), 761 (w), 694 (w), 621 (w), 604 (w), 568 (m), 523 (m), 505 (m).

*4-(1H-Pyrrol-1-yl)phenyl Trifluoromethanesulfonate (**1o**).* Following general procedure A, the use of benzo[*d*][1,3]dioxol-5-ol (3.14 mmol) and pyridine as the base afforded the title compound **1o** (350 mg, 1.20 mmol, 38%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.08 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.40 (m, 2H), 7.41−7.30 (m, 2H), 7.11−7.03 (m, 2H), 6.43−6.35 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 146.7, 140.6, 122.7, 121.7, 119.3, 118.8 (q, J = 320.9 Hz), 111.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.69. MS (EI): *m*/*z* (relative intensity) 291 (46), 159 (12), 158 (100), 130 (38), 103 (15), 77 (20), 69 (12) 69(18). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{14}H_{15}N$ $[M + H]^+$ 292.0255, found 292.0251. IR (ATR, neat, cm^{-1}): 3137 (w), 3094 (w), 1603 (w), 1514 (s), 1425 (s), 1412 (s), 1329 (m), 1250 (m), 1207 (s), 1191 (s), 1133 (s), 1070 (s), 1012 (m), 938 (w), 921 (w), 881 (s), 832 (s), 781 (m), 753 (m), 723 (s), 645 (m), 632 (m), 604 (s), 571 (s), 527 (s), 503 (s), 441 (m). The analytical data is in accordance with that reported in the literature.[40]

*N,N-Dimethyl-4-(1H-pyrrol-1-yl)aniline Hydrochloride (**3o**·HCl).* Following general procedure B, the use of 4-(1*H*-pyrrol-1-yl)phenyl trifluoromethanesulfonate (**1o**) afforded the title compound **3o** (111 mg, 0.498 mmol, 99%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1) and treatment with 2 M HCl in Et_2O. R_f = 0.44 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.34 (br. s, 1H), 7.87 (d, J = 8.9 Hz, 2H), 7.54−7.41 (m, 2H), 7.12−7.00 (m, 2H), 6.40−6.29 (m, 2H), 3.20 (s, 6H), 2.02 (br. s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 141.8, 139.7, 122.4, 121.5, 119.1, 111.7, 46.7. MS (EI): *m*/*z* (relative intensity) 187 (13), 186 (100), 185 (44), 171 (32), 170 (26), 143 (12), 115 (16). HRMS (EI, *m*/*z*): calcd for $C_{12}H_{14}N_2$ $[M]^+$ 187.1235, found 187.1236. IR (ATR, neat, cm^{-1}): 3479 (w), 3410 (w), 3054 (w), 3011 (w), 2498 (w), 2347 (w), 1612 (w), 1523 (m), 1489 (w), 1473 (w), 1413 (w), 1329 (m), 1253 (w), 1203 (w), 1188 (w), 1159 (w), 1141 (m), 1123 (w), 1074 (w), 1060 (w), 1013 (w), 996 (w), 919 (w), 899 (w), 869 (w), 851 (w), 830 (m), 770 (w), 733 (s), 638 (w), 608 (w), 548 (m), 510 (m), 484 (m). The analytical data is in accordance with that reported in the literature.[41]

*(8R,9S,13S)-13-Methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[Cyclopenta[a]phenanthrene-17,2′-[1,3]dioxolan]-3-yl Trifluoromethanesulfonate (**1p**).* Following general procedure A, the use of carbonyl-protected estrogen (3.28 mmol) and NEt_3 as the base

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J. Org. Chem. XXXX, XXX, XXX−XXX

afforded the title compound **1p** (1.44 g, 3.23 mmol, 99%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.70 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 1H), 7.01 (dd, J = 8.6, 2.8 Hz, 1H), 6.96 (d, J = 2.7 Hz, 1H), 4.01−3.83 (m, 4H), 2.92−2.84 (m, 2H), 2.38−2.18 (m, 2H), 2.09−1.71 (m, 5H), 1.70−1.22 (m, 6H), 0.88 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.6, 141.1, 139.7, 127.3, 121.2, 119.4, 118.9 (q, J = 320.7 Hz), 118.2, 65.4, 64.7, 49.4, 46.1, 43.9, 38.6, 34.3, 30.7, 29.6, 26.7, 26.0, 22.5, 14.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.97. MS (EI): m/z (relative intensity) 446 (6), 384 (15), 99 (100), 86 (12), 84 (10), 28 (35). HRMS (EI, m/z): calcd for $C_{21}H_{25}O_5F_3S_1[M]^+$ 446.1369, found 446.1370. IR (ATR, neat, cm^{-1}): 2973 (w), 2938 (w), 2872 (w), 1739 (w), 1606 (w), 1583 (w), 1489 (m), 1456 (w), 1418 (s), 1381 (w), 1339 (w), 1308 (w), 1274 (w), 1248 (m), 1204 (s), 1182 (m), 1163 (m), 1139 (s), 1118 (s), 1105 (m), 1075 (w), 1060 (m), 1044 (m), 1032 (m), 1013 (m), 984 (w), 963 (m), 948 (m), 915 (s), 882 (m), 849 (m), 836 (m), 818 (m), 780 (m), 765 (w), 751 (w), 718 (w), 704 (w), 657 (w), 603 (s), 565 (m), 548 (w), 535 (w), 511 (m), 491 (w), 477 (w), 453 (w), 422 (w), 404 (w). The analytical data is in accordance with that reported in the literature.[42]

*(8R,9S,13S,14S)-N,N,13-Trimethyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro [Cyclopenta[a]phenanthrene-17,2′-[1,3]dioxolan]-3-amine (**3p**).* Following general procedure B, the use of (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,-15,16-decahydrospiro [cyclopenta[*a*]phenanthrene-17,2′-[1,3]dioxolan]-3-yl trifluoromethanesulfonate (**1p**, 0.365 mmol) afforded the title compound **3p** (110 mg, 0.322 mmol, 88%, free base) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 4:1). R_f = 0.08 (*n*-pentane/EtOAc = 8:1, UV) free base; m.p. = 90.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.64 (d, J = 7.4 Hz, 1H), 6.53 (s, 1H), 4.02−3.84 (m, 4H), 2.91 (s, 6H), 2.89−2.77 (m, 2H), 2.37−2.17 (m, 2H), 2.09−1.98 (m, 1H), 1.94−1.71 (m, 4H), 1.69−1.59 (m, 1H), 1.57−1.26 (m, 5H), 0.88 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.5, 126.2, 119.6, 113.7, 111.4, 77.4, 65.4, 64.7, 49.5, 46.4, 43.7, 41.3, 39.4, 34.4, 30.9, 30.2, 27.3, 26.3, 22.5, 14.5. MS (EI): m/z (relative intensity) 341 (49), 240 (17), 186 (12), 172 (19), 158 (17), 129 (12), 99 (100), 86 (14), 55 (15), 43 (16). HRMS (EI, m/z): calcd for $C_{20}H_{26}O_3[M]^+$ 341.2349, found 341.2368. IR (ATR, neat, cm^{-1}): 2972 (w), 2921 (m), 2870 (m), 2808 (m), 1610 (m), 1561 (w), 1509 (s), 1469 (m), 1458 (m), 1436 (m), 1409 (w), 1376 (m), 1354 (m), 1337 (m), 1299 (m), 1275 (m), 1224 (s), 1195 (m), 1180 (m), 1157 (s), 1120 (s), 1103 (s), 1074 (m), 1059 (s), 1045 (s), 1031 (s), 1010 (m), 1001 (m), 985 (m), 955 (s), 934 (m), 918 (m), 884 (m), 856 (m), 836 (m), 803 (m), 773 (s), 747 (m), 713 (m), 696 (m), 650 (m), 629 (m), 587 (m), 572 (m), 525 (m), 511 (m), 483 (m), 443 (m), 420 (m), 406 (m).

*(8R,9S,13S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl Trifluoromethanesulfonate (**1q**).* Following general procedure A, the use of estrogen (3.70 mmol) and NEt_3 as the base afforded the title compound **1q** (1.46 g, 19.24 mmol, 98%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 5:1). R_f = 0.30 (*n*-pentane/EtOAc = 5:1, UV); m.p. = 91.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 1H), 7.03 (dd, J = 8.6, 2.8 Hz, 1H), 6.99 (d, J = 2.6 Hz, 1H), 2.94 (dd, J = 8.7, 4.3 Hz, 2H), 2.59−2.46 (m, 1H), 2.45−2.36 (m, 1H), 2.30 (td, J = 10.4, 9.9, 4.1 Hz, 1H), 2.23−1.91 (m, 4H), 1.73−1.38 (m, 6H), 0.92 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 220.5, 147.7, 140.4, 139.4, 127.3, 121.4, 118.9 (q, J = 320.8 Hz), 118.4, 50.5, 48.0, 44.2, 37.9, 35.9, 31.6, 29.5, 26.2, 25.8, 21.7, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.97. MS (EI): m/z (relative intensity) 402 (60), 358 (35), 345 (22), 292 (11), 251 (17), 225 (22), 213 (35), 185 (14), 157 (17), 129 (24), 128 (23), 115 (39), 91 (22), 69 (100), 55 (24), 41 (24). HRMS (EI, m/z): calcd for $C_{21}H_{25}O_5F_3S_1[M]^+$ 402.1107, found 402.1105. IR (ATR, neat, cm^{-1}): 2966 (w), 2931 (w), 2869 (w), 1736 (s), 1604 (w), 1488 (w), 1455 (w), 1418 (s), 1405 (m), 1373 (w), 1338 (w), 1275 (w), 1249 (m), 1207 (s), 1137 (s), 1085 (m), 1054 (m), 1007 (m), 983 (w), 951 (w), 916 (s), 901 (m), 879 (m), 848 (m), 836 (s), 820 (m), 785 (m), 766 (w), 723 (w), 714 (w), 702 (m), 654 (w), 639 (w), 620 (m), 605 (s), 578 (m), 548 (m), 506 (m), 487 (w), 475 (w), 443 (m). The analytical data is in accordance with that reported in the literature.[43]

*(8R,9S,13S,14S)-3-(Dimethylamino)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]-phenanthren-17-one (**3q**).* Following general procedure B, the use of (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (**1q**, 0.532 mmol) afforded the title compound **3q** (87%, 138 mg, 0.463 mmol, free base) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.44 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.7 Hz, 1H), 6.63 (dd, J = 8.6, 2.8 Hz, 1H), 6.52 (d, J = 2.8 Hz, 1H), 2.98−2.88 (m, 7H), 2.59−1.89 (m, 7H), 1.74−1.37 (m, 6H), 1.28 (s, 1H), 0.92 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 221.2, 149.0, 137.0, 128.3, 126.0, 113.2, 111.1, 50.4, 48.1, 44.0, 40.9, 38.6, 35.9, 31.7, 30.0, 26.8, 26.0, 21.6, 13.9. MS (EI): m/z (relative intensity) 298 (22), 297 (100), 296 (12), 212 (20), 173 (38), 172 (12). HRMS (EI, m/z): calcd for $C_{20}H_{27}NO$ $[M]^+$ 298.2171, found 298.2167. IR (ATR, neat, cm^{-1}): 2972 (w), 2921 (m), 2870 (m), 2808 (m), 1610 (m), 1561 (w), 1509 (s), 1469 (m), 1458 (m), 1436 (m), 1409 (w), 1376 (m), 1354 (m), 1337 (m), 1299 (m), 1275 (m), 1224 (s), 1195 (m), 1180 (m), 1157 (s), 1120 (s), 1103 (s), 1074 (m), 1059 (s), 1045 (s), 1031 (s), 1010 (m), 1001 (m), 985 (m), 955 (s), 934 (m), 918 (m), 884 (m), 856 (m), 836 (m), 803 (m), 773 (s), 747 (m), 713 (m), 696 (m), 650 (m), 629 (m), 587 (m), 572 (m), 525 (m), 511 (m), 483 (m), 443 (m), 420 (m), 406 (m). Crystal data of **3q** (CCDC1981523): $C_{20}H_{27}NO$, M = 297.42, orthorhombic, space group $P2_12_12_1$, a = 8.2340(2), b = 12.4121(4), c = 16.2533(5) Å, V = 1661.11(8) Å^3, T = 150(2) K, Z = 4, 9416 reflections measured, 2923 independent reflections (R_{int} = 0.0317), final R values ($I > 2\sigma(I)$): R_1 = 0.0442, wR_2 = 0.1217, final R values (all data): R_1 = 0.0453, wR_2 = 0.1234, 202 parameters.

*4-Acetylphenyl Trifluoromethanesulfonate (**1r**).* Following general procedure A, the use of 1-(4-hydroxyphenyl)ethan-1-one (11.02 mmol) at 0 °C instead of −78 °C and triethylamine as the base afforded the title compound **1r** (2.82 g, 10.51 mmol, 95%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 5:1). R_f = 0.27 (*n*-pentane/EtOAc = 5:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 2.61 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.1, 152.5, 136.9, 130.6, 121.7, 118.7 (q, J = 320.8 Hz), 26.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.03 (dd, J = 10.0, 4.8 Hz). MS (EI): m/z (relative intensity) 268 (17), 253 (100), 95 (12). HRMS (EI, m/z): calcd for $C_9H_7O_4F_3S$ $[M]^+$ 268.0012, found 268.0005. IR (ATR, neat, cm^{-1}): 1690 (m), 1594 (w), 1497 (w), 1423 (m), 1409 (m), 1360 (w), 1301 (w), 1263 (m), 1250 (m), 1205 (s), 1132 (s), 1077 (w), 1014 (w), 960 (w), 879 (s), 842 (s), 787 (m), 762 (w), 672 (m), 632 (m), 607 (s), 585 (s), 571 (m), 524 (m), 471 (w), 422 (w).

*1-(4-(Dimethylamino)phenyl)ethan-1-one Hydrochloride (**3r**·HCl).* Following general procedure B, the use of 4-formyl-2-methoxyphenyl trifluoromethanesulfonate (**1r**) afforded the title compound **3r** (15 mg, 0.092 mmol, 18%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1) and treatment with 2 M HCl in Et_2O. R_f = 0.20 (*n*-pentane/EtOAc = 5:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94−7.84 (m, 1H), 6.73−6.59 (m, 1H), 3.07 (s, 3H), 2.52 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.4, 153.4, 130.5, 125.4, 110.7, 40.1, 26.0. MS (EI): m/z (relative intensity) 163 (30), 148 (100), 118 (10), 104 (12), 91 (11), 78 (10), 77 (23), 74 (13), 63 (13), 51 (13), 50 (11), 43 (29), 42 (39). HRMS (ESI-TOF, m/z): calcd for $C_{10}H_{13}NO$ $[M + H]^+$ 164.1075, found 164.1075. IR (ATR, neat, cm^{-1}): 2901 (w), 2822 (w), 2651 (w), 1649 (m), 1586 (m), 1547 (w), 1522 (w), 1429 (m), 1413 (m), 1356 (m), 1313 (m), 1282 (m), 1229 (m), 1187 (m), 1130 (m), 1067 (m), 1018 (m), 943 (m), 814 (s), 654 (m), 592 (m), 560 (m), 498 (m). The analytical data is in accordance with that reported in the literature.[44]

*4-Allyl-2-methoxyphenyl Trifluoromethanesulfonate (**1s**).* Following general procedure A, the use of 4-allyl-2-methoxyphenol (3.50 mmol) and 2,6-dimethylpyridine as the base afforded the title compound **1s** (830 mg, 2.67 mmol, 76%) as a colorless oil after

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J. Org. Chem. XXXX, XXX, XXX−XXX

purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.45 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) 7.14 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.07−5.80 (m, 1H), 5.21−5.04 (m, 2H), 3.90 (s, 3H), 3.40 (d, *J* = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 151.3, 142.0, 137.2, 136.4, 122.2, 120.9, 118.9 (q, *J* = 320.5 Hz), 116.9, 113.5, 56.2, 40.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.00. MS (EI): *m*/*z* (relative intensity) 296 (34), 164 (11), 163 (100), 107 (19), 105 (12), 103 (40), 91 (38), 79 (16), 77 (19), 69 (19), 65 (13), 41 (18), 39 (10). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{11}H_{11}O_4F_3S$ $[M]^+$ 296.0325, found 296.0318. IR (ATR, neat, cm^{-1}): 3082 (w), 3012 (w), 2980 (w), 2944 (w), 2916 (w), 2847 (w), 1640 (w), 1606 (m), 1503 (m), 1465 (w), 1417 (s), 1291 (w), 1270 (m), 1248 (m), 1201 (s), 1175 (m), 1137 (s), 1105 (s), 1032 (m), 995 (w), 903 (m), 873 (s), 815 (m), 774 (w), 751 (m), 708 (m), 616 (s), 571 (m), 546 (w), 500 (s), 456 (w). The analytical data is in accordance with that reported in the literature.[45]

*4-Allyl-2-methoxy-N,N-dimethylaniline Hydrochloride (**3s**·HCl).* Following general procedure B, the use of 4-allyl-2-methoxyphenyl trifluoromethanesulfonate (**1s**, 0.526 mmol) afforded the title compound **3s** (35 mg, 0.154 mmol, 29%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1) and treatment with 2 M HCl in Et_2O. R_f = 0.36 (*n*-pentane/EtOAc = 20:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.76 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.77 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.94−5.75 (m, 1H), 5.03 (dd, *J* = 8.3, 1.5 Hz, 1H), 3.92 (s, 3H), 3.33 (d, *J* = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.3, 144.1, 135.9, 128.4, 123.7, 121.7, 117.1, 113.3, 56.0, 44.8, 40.00. MS (EI): *m*/*z* (relative intensity) 192 (13), 191 (100), 177 (10), 176 (81), 174 (11), 160 (13), 91 (10), 42 (24). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{12}H_{17}NO$ $[M]^+$ 192.1388, found 192.1393.

*2-Methoxy-4-propylphenyl Trifluoromethanesulfonate (**1t**).* Following general procedure A, the use of 2-methoxy-4-propylphenol (3.17 mmol) and pyridine as the base afforded the title compound **1t** (830 mg, 2.78 mmol, 88%) as a colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.45 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.89 (s, 3H), 2.67−2.54 (m, 2H), 1.87−1.51 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 151.0, 144.5, 136.8, 121.9, 120.6, 118.8 (q, *J* = 320.4 Hz), 113.2, 56.0, 37.9, 24.4, 13.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.13. MS (EI): *m*/*z* (relative intensity) 298 (25), 166 (11), 165 (100), 109 (11), 107 (10), 105 (11), 95 (27), 79 (10), 77 (19), 69 (15), 65 (10), 43 (20). HRMS (EI, *m*/*z*): calcd for $C_{11}H_{13}O_4F_3S$ $[M]^+$ 298.0481, found 298.0484. IR (ATR, neat, cm^{-1}): 2964 (w), 2937 (w), 2874 (w), 1605 (m), 1504 (m), 1465 (w), 1417 (s), 1291 (m), 1268 (m), 1248 (m), 1202 (s), 1179 (s), 1138 (s), 1107 (s), 1032 (m), 936 (w), 876 (s), 815 (m), 788 (w), 740 (m), 704 (w), 612 (s), 546 (w), 504 (s), 458 (s). The analytical data is in accordance with that reported in the literature.[46]

*2-Methoxy-N,N-dimethyl-4-propylaniline Hydrochloride (**3t**·HCl).* Following general procedure B, the use of 2-methoxy-4-propylphenyl trifluoromethanesulfonate (**1t**) afforded the title compound **3t** (40 mg, 0.170 mmol, 34%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1) and treatment with 2 M HCl in Et_2O. R_f = 0.40 (*n*-pentane/EtOAc = 20:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 6.74 (dd, *J* = 8.1, 1.6 Hz, 1H), 3.91 (s, 3H), 2.58−2.44 (m, 2H), 3.17 (s, 7H), 2.56−2.48 (m, 2H), 1.65−1.48 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.1, 146.7, 127.9, 123.5, 121.4, 113.2, 55.9, 44.7, 37.9, 24.3, 13.7. MS (EI): *m*/*z* (relative intensity) 193 (49), 178 (23), 165 (11), 164 (100), 149 (16), 134 (15). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{12}H_{19}NO$ $[M]^+$ 194.1545, found 194.1548.

*4-Formyl-2-methoxyphenyl Trifluoromethanesulfonate (**1u**).* Following general procedure A, the use of 2-methoxy-4-propylphenol (3.17 mmol) and pyridine as the base afforded the title compound **1u** (1.080 g, 3.80 mmol, 76%) as a colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.33 (*n*-pentane/EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.58−7.54 (m, 1H), 7.53−7.45 (m, 1H), 7.40 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.99 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 190.4, 152.2, 142.7, 136.8, 124.1, 123.2, 118.7 (q, *J* = 320.5 Hz), 111.8, 56.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.79. MS (EI): *m*/*z* (relative intensity) 284 (77), 151 (100), 95 (71), 80 (14), 79 (29), 77 (36), 69 (32), 67 (15), 65 (22), 52 (17), 51 (28), 50 (11). HRMS (EI, *m*/*z*): calcd for $C_9H_7O_5F_{3S}$ $[M]^+$ 283.9961, found 283.9964. IR (ATR, neat, cm^{-1}): 2857 (w), 2842 (w), 2736 (w), 1704 (m), 1605 (m), 1499 (m), 1466 (w), 1420 (s), 1388 (m), 1318 (w), 1278 (m), 1248 (m), 1203 (s), 1134 (s), 1101 (s), 1027 (m), 957 (w), 931 (w), 868 (s), 820 (m), 778 (m), 733 (m), 711 (m), 611 (s), 590 (s), 569 (m), 539 (m), 509 (m), 467 (m), 451 (m). The analytical data is in accordance with that reported in the literature.[47]

*4-(Dimethylamino)-3-methoxybenzaldehyde Hydrochloride (**3u**·HCl).* Following general procedure B, the use of 4-formyl-2-methoxyphenyl trifluoromethanesulfonate (**1u**) afforded the title compound **3u** (16 mg, 0.074 mmol, 15%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 5:1) and treatment with 2 M HCl in Et_2O. R_f = 0.26 (*n*-pentane/EtOAc = 5:1) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.40 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 2.95 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 191.0, 151.8, 126.9, 116.7, 109.3, 77.4, 55.8, 42.8, 29.8. MS (EI): *m*/*z* (relative intensity) 180 (11), 179 (100), 178 (14), 164 (67), 162 (20), 148 (20), 108 (10), 92 (14), 65 (13), 42 (19). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{12}H_{13}NO_2$ $[M]^+$ 180.1024, found 180.1026. The analytical data is in accordance with that reported in the literature.[48]

*[1,1′-Biphenyl]-2-yl Trifluoromethanesulfonate (**1v**).* Following general procedure A, the use of [1,1′-biphenyl]-2-ol (2.94 mmol) and pyridine as the base afforded the title compound **1v** (875 mg, 2.89 mmol, 95%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.55 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.41 (m, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.9, 135.6, 132.0, 129.4, 129.0, 128.6, 128.5, 128.4, 122.1, 118.4 (q, *J* = 320.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.09. MS (EI): *m*/*z* (relative intensity) 302 (47), 170 (13), 169 (100), 141 (33), 139 (14), 115 (29). HRMS (EI, *m*/*z*): calcd for $C_{13}H_9O_3F_3S$ $[M]^+$ 302.0219, found 302.0221. IR (ATR, neat, cm^{-1}): 3066 (w), 3035 (w), 1504 (w), 1476 (m), 1419 (s), 1360 (w), 1246 (m), 1202 (m), 1135 (s), 1099 (s), 1076 (w), 1046 (m), 1011 (w), 948 (w), 881 (s), 783 (s), 763 (s), 751 (s), 731 (s), 697 (s), 646 (m), 624 (s), 593 (s), 570 (s), 462 (m), 436 (m). The analytical data is in accordance with that reported in the literature.[36]

*2-Isopropylphenyl Trifluoromethanesulfonate (**1w**).* Following general procedure A, the use of 2-isopropylphenol (7.34 mmol) with pyridine as the base afforded the title compound **1r** (1.96 g, 7.34 mmol, 99%) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.35 (*n*-pentane/EtOAc = 50:1, UV); ^{1}H NMR (300 MHz, chloroform-d) δ 7.45−7.39 (m, 1H), 7.38−7.30 (m, 1H), 7.29−7.22 (m, 2H), 3.33 (hept, J = 6.9 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.15, 141.23, 128.60, 127.83, 127.42, 121.18, 118.67 (q, *J* = 319.9 Hz), 27.12, 23.04. ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.07. MS (EI): *m*/*z* (relative intensity) 268 (81), 254 (10), 253 (100), 135 (27), 134 (14), 120 (48), 119 (21), 118 (15), 107 (43), 103 (36), 95 (23), 92 (11), 91 (74), 77 (20), 69 (23), 65 (15), 39 (11). HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}O_3F_3S$ $[M]^+$ 268.0376, found 268.0370. The analytical data is in accordance with that reported in the literature.[49]

*2-Isopropyl-N,N-dimethylaniline Hydrochloride (**3w**·HCl).* Following general procedure B, the use of 2-isopropylphenyl trifluoromethanesulfonate (**1w**) afforded the title compound **3w** (24 mg, 0.120 mmol, 24%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 10:1) and treatment with 2 M HCl in Et_2O. R_f = 0.54 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (400 MHz, chloroform-d) δ 7.29 (m, 1H), 7.21−7.13 (m, 2H), 7.10 (m, 1H), 3.58 (hept, *J* = 6.9 Hz, 1H), 2.71 (s, 6H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.97, 144.28, 126.57, 126.30, 124.05, 119.72, 45.95, 26.75, 24.30. MS (EI): *m*/*z*

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J. Org. Chem. XXXX, XXX, XXX−XXX

(relative intensity) 163 (71), 162 (11), 149 (13), 148 (100), 134 (18), 133 (45), 132 (34), 118 (38), 117 (20), 91 (11), 77 (12). HRMS (ESI-TOF, m/z): calcd for $C_{11}H_{17}N$ $[M + H]^+$ 164.1439, found 164.1440. The analytical data is in accordance with that reported in the literature.[7]

*o-Tolyl Trifluoromethanesulfonate (**1x**).* Following general procedure A, the use of *o*-cresol (9.25 mmol) at 0 °C instead of −78 °C with triethylamine as the base afforded the title compound **1x** (1.97 g, 8.18 mmol, 88%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.52 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.8, 1.9 Hz, 2H), 7.33 (dd, J = 8.7, 1.8 Hz, 2H), 2.57 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 196.1, 152.5, 136.9, 130.6, 121.6, 118.7 (q, J = 320.7 Hz), 26.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.03. MS (EI): m/z (relative intensity) 240 (58), 107 (100), 91 (12), 79 (24), 78 (14), 77 (60), 69 (18), 51 (11). HRMS (ESI-TOF, m/z): calcd for $C_{12}H_{13}NO_2$ $[M]^+$ 240.006, found 240.006. IR (ATR, neat, cm^{-1}): 1582 (w), 1491 (w), 1462 (w), 1417 (s), 1293 (w), 1249 (m), 1203 (s), 1136 (s), 1086 (s), 1043 (w), 990 (w), 942 (w), 887 (s), 800 (s), 760 (s), 726 (w), 702 (m), 646 (m), 626 (m), 602 (s), 572 (m), 546 (w), 520 (s), 493 (m), 442 (m). The analytical data is in accordance with that reported in the literature.[50]

*N,N,2-Trimethylaniline Hydrochloride (**3x**·HCl).* Following general procedure B, the use of *o*-tolyl trifluoromethanesulfonate (**1x**) afforded the title compound **3x** (70 mg, 0.408 mmol, 77%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1) and treatment with 2 M HCl in Et_2O. R_f = 0.24 (*n*-pentane/EtOAc = 20:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.00 (s, 1H), 7.62−7.45 (m, 1H), 7.36−7.23 (m, 3H), 3.23 (s, 6H), 2.84−2.63 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 141.0, 133.3, 133., 130.1, 128.1, 120.0, 46.6, 19.3. MS (EI): m/z (relative intensity) 135 (100), 134 (87), 120 (73), 119 (13), 118 (34), 104 (20), 91 (37), 77 (12), 67 (10), 65 (20). HRMS (ESI-TOF, m/z): calcd for $C_9H_{13}N$ $[M + H]^+$ 136.1126, found 136.1126. IR (ATR, neat, cm^{-1}): 3378 (w), 3038 (w), 2954 (w), 2495 (m), 2442 (m), 1995 (w), 1813 (w), 1495 (m), 1461 (s), 1381 (s), 1210 (w), 1180 (m), 1140 (m), 1116 (m), 1098 (m), 1051 (m), 983 (m), 895 (m), 804 (w), 770 (s), 715 (s), 597 (s), 556 (m), 499 (m), 455 (s). The analytical data is in accordance with that reported in the literature.[51]

*4-(tert-Butyl)-N,N-diethylaniline Hydrochloride (**4b**·HCl).* Following general procedure B, the use of 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (**1d**) and diethylamine solution (2 M THF, 1 mL) afforded the title compound **4b** (116 mg, 0.480 mmol, 95%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with 2 M HCl in Et_2O. R_f = 0.67 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.68−3.20 (m, 4H), 1.24 (s, 9H), 1.17 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.4, 134.4, 127.1, 122.4, 53.5, 34.8, 31.1, 10.3. MS (EI): m/z (relative intensity) 205 (22), 191 (15), 190 (100). HRMS (EI, m/z): calcd for $C_{14}H_{23}N$ $[M]^+$ 205.1825, found 205.1831. IR (ATR, neat, cm^{-1}): 2950 (m), 2863 (w), 2330 (m), 1736 (w), 1596 (w), 1509 (m), 1462 (m), 1381 (m), 1373 (m), 1327 (w), 1307 (w), 1264 (m), 1191 (w), 1157 (m), 1122 (m), 1107 (w), 1066 (w), 1026 (m), 1011 (m), 926 (w), 875 (w), 853 (s), 838 (m), 799 (w), 767 (w), 740 (w), 650 (w), 593 (s), 542 (m), 516 (w), 480 (w), 455 (w). The analytical data is in accordance with that reported in the literature.[52]

*4-(tert-Butyl)-N,N-dipropylaniline Hydrochloride (**4c**·HCl).* Following general procedure B, the use of 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (**1d**) and dipropylamine solution (2 M THF, 1 mL) afforded the title compound **4c** (132 mg, 0.489 mmol, 95%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with 2 M HCl in Et_2O. R_f = 0.76 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.46 (s, 1H), 7.52 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 3.40−3.20 (m, 2H), 3.16−2.96 (m, 2H), 1.99−1.77 (m, 2H), 1.18 (s, 9H), 1.27−1.09 (m, 2H), 0.74 (t, J = 7.4 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 153.4, 135.6, 127.2, 122.2, 60.4, 34.9, 31.3, 18.3, 11.0. MS (EI): m/z (relative intensity) 233 (20), 218 (14), 205 (16), 204 (100), 162 (18), 146 (10). HRMS (EI, m/z): calcd for $C_{16}H_{27}N$ $[M]^+$ 233.2168, found 233.2136. IR (ATR, neat, cm^{-1}): 3042 (w), 2960 (s), 2933 (s), 2874 (m), 2848 (m), 2542 (w), 2421 (m), 1607 (w), 1570 (w), 1516 (m), 1461 (m), 1446 (m), 1398 (w), 1380 (w), 1361 (w), 1338 (w), 1315 (w), 1268 (m), 1193 (w), 1159 (w), 1110 (w), 1070 (w), 1054 (w), 1025 (w), 997 (s), 969 (w), 875 (w), 847 (s), 783 (w), 761 (m), 740 (m), 700 (w), 652 (w), 603 (s), 589 (w), 544 (w), 516 (w), 506 (w), 480 (w), 462 (w), 425 (w), 411 (w).

*4-(tert-Butyl)-N,N-dibutylaniline Hydrochloride (**4d**·HCl).* Following general procedure C, using 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (**1d**) and dibutylamine solution (2 M THF, 1 mL) afforded the title compound **4d** (150 mg, 0.504 mmol, 97%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with 2 M HCl in Et_2O. R_f = 0.79 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.53 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 3.52−3.30 (m, 2H), 3.27−3.07 (m, 2H), 2.05−1.82 (m, 2H), 1.26 (d, J = 0.6 Hz, 6H), 1.24−1.09 (m, 1H), 0.79 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 148.5, 130.8, 122.4, 117.3, 53.9, 30.1, 26.4, 21.7, 15.1, 8.7. MS (EI): m/z (relative intensity) 261 (25), 246 (15), 219 (16), 218 (100), 176 (43), 162 (12), 146 (10). HRMS (EI, m/z): calcd for $C_{16}H_{27}N$ $[M]^+$ 261.2451, found 261.2452. IR (ATR, neat, cm^{-1}): 3040 (w), 2961 (s), 2935 (m), 2871 (m), 2656 (w), 2402 (m), 1599 (w), 1515 (m), 1463 (m), 1430 (m), 1402 (w), 1379 (w), 1364 (w), 1339 (w), 1316 (w), 1267 (m), 1236 (w), 1202 (w), 1183 (w), 1160 (w), 1127 (w), 1108 (w), 1018 (w), 987 (w), 966 (w), 949 (w), 936 (w), 876 (w), 848 (s), 793 (w), 767 (w), 742 (w), 652 (w), 636 (w), 602 (s), 551 (w), 461 (w). The analytical data is in accordance with that reported in the literature.[49]

*tert-Butyl 3-(2-((tert-Butoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate Hydrochloride (**4f**·HCl).* Following general procedure C, the use of bis(2-methoxyethyl)amine (1.05 mmol) afforded the title compound **4f** (100 mg, 0.331 mmol, 65%) as a red oil after purification via column chromatography (*n*-pentane/EtOAc = 10:1) and treatment with HCl (2.0 M in Et2O). R_f = 0.34 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.11 (m, 2H), 6.86−6.49 (m, 2H), 3.56 (s, 8H), 3.36 (s, 6H), 1.30 (s, 9H). Free base. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 126.1, 126.1, 113.6, 111.8, 70.1, 59.0, 51.3, 33.8, 31.6. Free base. MS (EI): m/z (relative intensity) 265 (11), 221 (16), 220 (100), 59 (20). HRMS (EI, m/z): calcd for $C_{16}H_{27}NO_2$ $[M + H]^+$ 266.2120, found 266.2121. IR (ATR, neat, cm^{-1}): 3405 (w), 2958 (m), 2873 (w), 2373 (w), 1614 (w), 1519 (s), 1460 (m), 1393 (w), 1363 (m), 1269 (m), 1196 (m), 1113 (s), 1016 (m), 959 (w), 925 (w), 813 (m), 548 (m), 463 (w).

*N-Benzyl-4-(tert-butyl)aniline Hydrochloride (**4g**·HCl).* Following general procedure C, the use of benzylamine (0.999 mmol) afforded the title compound **4g** (123 mg, 0.446 mmol, 87%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 20:1) and treatment with HCl (2.0 M in Et_2O). R_f = 0.45 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 2H), 7.43−7.36 (m, 2H), 7.33−7.26 (m, 3H), 7.25−7.19 (m, 2H), 4.29 (s, 2H), 1.25 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.5, 131.7, 131.1, 129.6, 129.3, 128.6, 126.6, 123.4, 56.0, 34.7, 31.2. MS (EI): m/z (relative intensity) 239 (31), 225 (18), 224 (100), 91 (47). HRMS (EI, m/z): calcd for $C_{17}H_{21}N$ $[M]^+$ 240.1752, found 240.1753. IR (ATR, neat, cm^{-1}): 3061 (w), 3005 (w), 2960 (w), 2855 (w), 2658 (w), 2604 (w), 2520 (m), 2384 (w), 1509 (m), 1476 (w), 1447 (w), 1416 (m), 1388 (w), 1362 (w), 1321 (w), 1269 (w), 1229 (w), 1205 (w), 1188 (w), 1127 (w), 1108 (w), 1032 (w), 1018 (w), 976 (m), 956 (w), 926 (w), 876 (w), 833 (m), 750 (s), 703 (s), 678 (w), 639 (w), 590 (w), 558 (s), 496 (m), 470 (w), 435 (w), 406 (s). The analytical data is in accordance with that reported in the literature.[53]

*4-(tert-Butyl)-N-methyl-N-phenylaniline Hydrochloride (**4h**·HCl).* Following general procedure C, the use of *N*-methylaniline (0.784 mmol) afforded the title compound **4h** (131 mg, 0.475 mmol, 93%)

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J. Org. Chem. XXXX, XXX, XXX−XXX

as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). R_f = 0.70 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.27 (m, 4H), 7.13−7.02 (m, 4H), 7.00−6.92 (m, 1H), 3.37 (d, J = 0.6 Hz, 3H), 1.40 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.3, 146.5, 144.9, 129.1, 126.2, 121.3, 120.3, 119.1, 40.3, 34.3, 31.6. MS (EI): *m*/*z* (relative intensity) 239 (33), 225 (17), 224 (100). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{17}H_{21}N$ $[M]^+$ 240.1752, found 240.1755. IR (ATR, neat, cm^{-1}): 3035 (w), 2959 (m), 2902 (w), 2866 (w), 2809 (w), 1594 (s), 1511 (s), 1494 (s), 1393 (w), 1362 (m), 1340 (m), 1267 (m), 1254 (m), 1200 (w), 1132 (m), 1087 (w), 1067 (w), 1026 (w), 991 (w), 870 (w), 823 (m), 746 (s), 693 (s), 593 (m), 542 (m), 483 (w), 408 (w). The analytical data is in accordance with that reported in the literature.[54]

*4-(tert-Butyl)-N,N-dibutylaniline Hydrochloride (**4i**·HCl).* Following general procedure C, the use of *N*-methylcyclohexanamine (0.765 mmol) afforded the title compound **4i** (138 mg, 0.504 mmol, 96%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 50:1) and treatment with HCl (2.0 M in Et_2O). R_f = 0.58 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.59 (s, 1H), 7.68−7.54 (m, 2H), 7.43 (d, J = 8.3 Hz, 2H), 3.37−3.19 (m, 1H), 3.10 (d, J = 4.9 Hz, 3H), 2.36−2.22 (m, 1H), 1.94−1.46 (m, 6H), 1.30−1.25 (m, 9H), 1.33−1.00 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 153.2, 137.5, 126.9, 122.2, 68.4, 41.2, 34.8, 31.1, 27.9, 27.7, 25.0, 24.5. MS (EI): *m*/*z* (relative intensity) 245 (41), 230 (29), 203 (15), 202 (100), 174 (13), 148 (13), 146 (29), 144 (11), 132 (13), 91 (10), 55 (17), 42 (10), 41 (17). HRMS (EI, *m*/*z*): calcd for $C_{17}H_{27}N$ $[M]^+$ 246.2222, found 246.2225 IR (ATR, neat, cm^{-1}): 3036 (w), 2942 (w), 2859 (w), 2304 (m), 1513 (m), 1466 (m), 1452 (m), 1414 (w), 1364 (w), 1311 (w), 1272 (w), 1204 (w), 1165 (w), 1140 (w), 1111 (m), 1093 (w), 1058 (w), 1011 (m), 927 (w), 903 (m), 857 (s), 795 (w), 679 (w), 637 (w), 594 (s), 556 (m), 434 (w). The analytical data is in accordance with that reported in the literature.[49]

*N-Benzyl-4-(tert-butyl)-N-methylaniline Hydrochloride (**4j**·HCl).* Following general procedure C, the use of *N*-methylbenzylamine (0.770 mmol) afforded the title compound **4j** (126 mg, 0.504 mmol, 87%) as a white crystalline solid after purification via column chromatography (pure *n*-pentane) and treatment with HCl (2.0 M in Et_2O). R_f = 0.61 (*n*-pentane/EtOAc = 10:1, UV) free base; NMR (300 MHz, $CDCl_3$) δ 7.46−7.38 (m, 2H), 7.37−7.30 (m, 4H), 7.31−7.17 (m, 4H), 4.53 (s, 2H), 3.16 (s, 3H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 131.5, 129.8, 128.7, 127.0, 126.8, 122.3, 121.5, 63.8, 43.0, 34.8, 31.1. MS (EI): *m*/*z* (relative intensity) 253 (31), 239 (18), 238 (90), 146 (19), 91 (100), 65 (15). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{18}H_{23}N$ $[M + H]^+$ 254.1908, found 254.1913. IR (ATR, neat, cm^{-1}): 2957 (w), 2400 (w), 1511 (w), 1455 (w), 1403 (m), 1363 (w), 1268 (w), 1242 (w), 1215 (w), 1152 (w), 1132 (w), 1117 (w), 1012 (w), 936 (w), 909 (w), 845 (m), 830 (w), 779 (w), 749 (s), 700 (s), 653 (w), 633 (w), 608 (m), 573 (s), 543 (w), 512 (w). The analytical data is in accordance with that reported in the literature.[55]

*4-(tert-Butyl)-N-(2-((tert-butyldimethylsilyl)oxy)ethyl)-N-methylaniline (**4k**).* Following general procedure C, with *N*-methylbenzylamine (0.908 mmol) afforded the title compound **4k** (160 mg, 0.504 mmol, 94%, free base) as a yellow oil after purification via column chromatography (*n*-pentane/EtOAc = 50:1). R_f = 0.70 (*n*-pentane/EtOAc = 10:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.20 (m, 2H), 6.67 (d, J = 8.3 Hz, 2H), 3.78 (t, J = 6.5 Hz, 2H), 3.44 (t, J = 6.5 Hz, 2H), 2.97 (s, 3H), 1.30 (s, 9H), 0.90 (s, 9H), 0.05 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 125.9, 111.6, 60.6, 55.1, 39.1, 33.7, 31.6, 25.9, 18.3, −5.3. MS (EI): *m*/*z* (relative intensity) 321 (16), 177 (18), 176 (100). HRMS (EI, *m*/*z*): calcd for $C_{19}H_{35}NOSi$ $[M]^+$ 321.2482, found 321.2481. IR (ATR, neat, cm^{-1}): 2953 (w), 2857 (w), 1614 (w), 1519 (s), 1462 (w), 1362 (m), 1250 (m), 1205 (m), 1097 (s), 1006 (w), 987 (w), 927 (w), 834 (s), 810 (s), 774 (s), 731 (w), 664 (w), 551 (w).

*N-Methyl-2-(1-methyl-1H-indol-3-yl)ethan-1-amine (**2l**): tert-Butyl 3-(2-((tert-Butoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate (**S2l-1**).* A solution of tryptamine hydrochloride (993 mg, 6.20 mmol, 1.0 equiv), 4-dimethylaminopyridine (1.55 g, 12.69 mmol, 2.0 equiv), and di-*tert*-butyl dicarbonate (2.90 g, 13.29 mmol, 2.1 equiv) in acetonitrile (20 mL) was stirred at rt under argon. After 16 h, water was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (*n*-pentane/EtOAc = 10:1), yielding the title compound **S2l-1** (1.11 g, 3.08 mmol, 50%). R_f = 0.24 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 7.58−7.50 (m, 1H), 7.42 (s, 1H), 7.32 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.30−7.18 (m, 1H), 4.66 (s, 1H), 3.46 (q, J = 6.7 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 1.67 (s, 9H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 155.9, 149.7, 135.6, 130.5, 124.5, 123.2, 122.5, 119.0, 117.8, 115.3, 83.5, 79.3, 40.2, 28.4, 28.2, 25.6. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{28}N_2O_4$ $[M + Na]^+$ 383.1941, found 383.1952. HRMS (EI, *m*/*z*): calcd for $C_{20}H_{28}N_2O_4$ $[M]^+$ 360.2044, found 360.2041. IR (ATR, neat, cm^{-1}): 3410 (w), 2979 (w), 2934 (w), 1808 (w), 1713 (m), 1510 (w), 1477 (w), 1453 (m), 1369 (s), 1308 (m), 1251 (s), 1211 (m), 1157 (s), 1114 (s), 1061 (s), 1017 (m), 956 (w), 844 (m), 768 (m), 745 (s), 663 (w), 592 (w), 521 (w), 462 (w), 424 (w). The analytical data is in accordance with that reported in the literature.[56]

*tert-Butyl (2-(1H-Indol-3-yl)ethyl)carbamate (**S2l-2**).* A solution of di-*tert*-butyl dicarbonate (6.13 g, 28.09 mmol, 3.0 equiv) in 1,4-dioxane (5 mL) was added to a mixture of tryptamine (1.52 g, 9.47 mmol, 1.0 equiv) and triethylamine (2.84 g, 28.09 mmol, 3.0 equiv) in 1,4-dioxane (10 mL), and the reaction mixture was stirred at rt. After 16 h, water was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (*n*-pentane/EtOAc =5:1), yielding the title compound **S2l-2** (1.55 g, 5.94 mmol, 63%). Additionally, **S2l-1** was reisolated in 37% yield. R_f = 0.10 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.99 (s, 1H), 4.67 (s, 1H), 3.47 (s, 2H), 2.96 (t, J = 6.8 Hz, 2H), 1.48 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2, 136.5, 127.4, 122.1, 119.4, 118.9, 113.0, 111.3, 79.3, 41.1, 28.5, 25.9. MS (EI): *m*/*z* (relative intensity) 260 (6), 143 (32), 131 (14), 130 (100), 103 (10), 77 (14), 59 (12), 57 (43), 41 (28), 39 (11), 29 (13). HRMS (EI, *m*/*z*): calcd for $C_{15}H_{20}N_2O_2$ $[M]^+$ 260.1519, found 260.1516. IR (ATR, neat, cm^{-1}): 3434 (w), 3313 (m), 3062 (w), 3002 (w), 2974 (w), 2936 (w), 1686 (s), 1619 (w), 1521 (s), 1452 (m), 1436 (w), 1390 (m), 1366 (s), 1351 (m), 1284 (m), 1270 (m), 1248 (m), 1229 (m), 1163 (s), 1131 (m), 1107 (m), 1079 (m), 1038 (m), 1008 (w), 954 (m), 867 (m), 809 (m), 773 (m), 736 (s), 684 (m), 623 (m), 588 (m), 562 (m), 492 (s), 465 (m), 419 (s). The analytical data is in accordance with that reported in the literature.[57]

*tert-Butyl (2-(1-Methyl-1H-indol-3-yl)ethyl)carbamate (**S2l-3**).* A solution of *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)carbamate (1.00 g, 3.85 mmol, 1.0 equiv) in DMF (5 mL) was added dropwise to a stirred mixture of mineral-oil-suspended NaH (169 mg, 4.04 mmol, 60 wt %, 1.05 equiv) in DMF (5 mL) at −30 °C. The reaction mixture was allowed to warm to room temperature over the period of 1 h. Afterward, the reaction mixture was cooled again to −30 °C and MeI (598mg, 4.21 mmol, 1.09 equiv) was added dropwise. After 16 h, water was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, yielding the title compound **S2l-3** (1.03 g, 3.76 mmol, 98%). R_f = 0.25 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 1H), 7.36−7.19 (m, 2H), 7.19−7.07 (m, 1H), 6.89 (s, 1H), 4.67 (s, 1H), 3.75 (s, 3H), 3.60−3.33 (m, 2H), 3.07−2.79 (m, 2H), 1.46 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.1, 137.2, 127.9, 126.9, 121.7, 119.0, 118.9, 111.6, 109.3, 79.2, 41.2, 32.7, 28.5, 25.8. MS (EI): *m*/*z* (relative intensity) 274 (16), 157 (26), 145 (13), 144 (100). HRMS (EI, *m*/*z*): calcd for $C_{16}H_{22}N_2O_2$ $[M]^+$ 274.1676, found 274.1676. IR (ATR, neat, cm^{-1}): 3351 (w), 2974 (w), 2930

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J. Org. Chem. XXXX, XXX, XXX−XXX

(w), 1691 (s), 1615 (w), 1505 (m), 1473 (m), 1390 (m), 1364 (m), 1326 (m), 1246 (s), 1158 (s), 1071 (w), 1048 (w), 1012 (w), 958 (w), 869 (w), 780 (w), 736 (s), 602 (w), 541 (w), 462 (w), 427 (m). The analytical data is in accordance with that reported in the literature.[58]

*N-Methyl-2-(1-methyl-1H-indol-3-yl)ethan-1-amine (**2l**).* A solution of *tert*-butyl (2-(1-methyl-1*H*-indol-3-yl)ethyl)carbamate (**S2l-3**, 750 mg, 2.73 mmol) in THF (5.0 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (1.08 g, 28.4 mmol, 10 equiv) in THF (10 mL) at −78 °C. The reaction mixture was then heated to 50 °C. After 16 h, water was added, and the mixture was filtered through a small pad of Celite. The aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (*n*-pentane/EtOAc = 10:1), yielding the title compound **2l** (366 mg, 1.94 mmol, 71%). R_f = 0.31 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.28−7.20 (m, 1H), 7.17−7.08 (m, 1H), 6.91 (s, 1H), 3.75 (s, 3H), 3.04−2.97 (m, 2H), 2.97−2.89 (m, 2H), 2.46 (s, 3H), 2.12 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.2, 127.9, 126.9, 121.7, 119.1, 118.8, 112.4, 109.3, 52.2, 36.3, 32.7, 25.5. MS (EI): m/z (relative intensity) 188 (4), 146 (12), 145 (88), 144 (100), 129 (10), 128 (13), 115 (17), 102 (15), 77 (17), 44 (67). HRMS (EI, m/z): calcd for $C_{12}H_{26}N_2$ $[M]^+$ 188.1308, found 188.1308. IR (ATR, neat, cm^{-1}): 3052 (w), 2927 (w), 2842 (w), 2787 (w), 1614 (w), 1552 (w), 1470 (m), 1442 (w), 1424 (w), 1376 (m), 1325 (m), 1248 (w), 1154 (w), 1129 (m), 1064 (w), 1011 (w), 922 (w), 734 (s), 663 (w), 601 (w), 564 (w), 426 (m). The analytical data is in accordance with that reported in the literature.

Following general procedure C, the use of 0.781 mmol *N*-methyl-2-(1-methyl-1*H*-indol-3-yl)ethan-1-amine (**2l**) afforded the title compound **4l** (141 mg, 0.440 mmol, 85%, free base) as a clear colorless oil after purification via column chromatography (*n*-pentane/EtOAc = 20:1). R_f = 0.24 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.9 Hz, 3H), 7.28 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.17 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H), 6.91 (s, 1H), 6.81 (d, J = 8.0 Hz, 2H), 3.78 (s, 3H), 3.71−3.59 (m, 2H), 3.06 (dd, J = 9.8, 6.0 Hz, 2H), 3.00 (s, 3H), 1.36 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.2, 128.0, 126.7, 126.2, 121.7, 119.0, 118.9, 112.5, 112.1, 109.4, 54.1, 38.6, 33.9, 32.7, 31.7, 22.4. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{28}N_2$ $[M + H]^+$ 321.2331, found 321.2333. IR (ATR, neat, cm^{-1}): 3050 (w), 2951 (m), 2864 (w), 1613 (m), 1518 (s), 1472 (m), 1424 (w), 1361 (m), 1325 (m), 1298 (w), 1270 (m), 1247 (m), 1225 (w), 1203 (m), 1184 (m), 1156 (w), 1128 (w), 1100 (w), 1063 (w), 1012 (w), 956 (w), 812 (s), 734 (s), 630 (w), 607 (w), 550 (m), 498 (w).

*4-Bromophenyl Trifluoromethanesulfonate (**1y**).* Following general procedure A, the use of 4-bromophenol (3.03 mmol) at 0 °C instead of −78 °C and triethylamine as the base afforded the title compound **1y** (0.635 g, 2.08 mmol, 69%) as a clear colorless oil after purification via column chromatography (pure *n*-pentane). R_f = 0.78 (*n*-pentane, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.52 (m, 2H), 7.20−7.13 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.6, 133.5, 123.2, 122.2, 118.8 (q, J = 320.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.71. MS (EI): m/z (relative intensity) 306 (82), 304 (79), 242 (29), 242 (30), 173 (98), 171 (100), 145 (92), 143 (17), 119 (16), 117 (17), 92 (22), 69 (59), 64 (36), 63 (59), 62 (14), 38 (14). HRMS (EI, m/z): calcd for $C_7H_4O_3BrF_3S$ $[M]^+$ 303.9011, found 303.9011. IR (ATR, neat, cm^{-1}): 1480 (m), 1423 (s), 1400 (m), 1296 (w), 1250 (m), 1205 (s), 1173 (m), 1134 (s), 1099 (m), 1069 (s), 1012 (s), 939 (w), 877 (s), 829 (s), 779 (m), 748 (s), 700 (w), 639 (m), 627 (m), 602 (s), 572 (m), 522 (s), 483 (s), 422 (m). The analytical data is in accordance with that reported in the literature.[59]

*4-(Dimethylamino)phenyl Trifluoromethanesulfonate Hydrochloride (**3y**·HCl).* Following general procedure B, the use of 4-bromophenyl trifluoromethanesulfonate (**1y**, 0.502 mmol) afforded the title compound **3y** (110 mg, 0.36 mmol, 72%) as a white crystalline solid after purification via column chromatography (*n*-pentane/EtOAc = 50:1) and treatment with HCl (2.0 M in Et_2O). R_f = 0.16 (*n*-pentane/EtOAc = 50:1, UV) free base; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.16 (s, 1H), 8.04−7.94 (m, 2H), 7.48−7.37 (m, 2H), 3.20 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.6, 142.7, 123.7, 123.4, 118.6 (q, J = 320.9 Hz), 46.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.60. MS (EI): m/z (relative intensity) 269 (5), 136 (100), 108 (16), 69 (33), 67 (12), 66 (12), 65 (19), 42 (10). HRMS (ESI-TOF, m/z): calcd for C_9H_{10} F_3NO_3S $[M]^+$ 270.041, found 270.041. IR (ATR, neat, cm^{-1}): 3019 (w), 2489 (w), 2355 (m), 1619 (w), 1504 (m), 1451 (w), 1415 (s), 1326 (w), 1237 (m), 1202 (s), 1130 (s), 1017 (m), 990 (m), 881 (s), 850 (s), 794 (m), 767 (m), 734 (w), 691 (w), 624 (s), 581 (s), 556 (m), 536 (s), 515 (m), 488 (m), 415 (w).

*4-(tert-Butyl)phenyl 4-Methylbenzenesulfonate (**S1y-1**).* Following general procedure A, the use of 4-(*tert*-butyl)phenol (20 mmol) at 0 °C instead of −78 °C and NEt_3 as the base and 4-methylbenzenesulfonyl chloride as the sulfonating agent afforded the title compound **S1y-1** (5.63 g, 18.5 mmol, 92%) as a white solid after purification via column chromatography (pure *n*-pentane). R_f = 0.51 (*n*-pentane/EtOAc = 18:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75−7.69 (m, 2H), 7.32 (t, J = 0.7 Hz, 1H), 7.31−7.28 (m, 2H), 7.26 (s, 1H), 6.92−6.86 (m, 2H), 2.45 (d, J = 0.8 Hz, 3H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.2, 147.4, 145.3, 132.9, 129.8, 128.6, 126.6, 121.8, 34.7, 31.4, 21.8. MS (EI): m/z (relative intensity) 304 (25), 290 (18), 289 (100), 155 (26), 109 (10), 91 (54), 65 (12). HRMS (EI, m/z): calcd for $C_{17}H_{20}O_3S$ $[M]^+$ 304.1128, found 304.1131. IR (ATR, neat, cm^{-1}): 3062 (w), 2962 (w), 2868 (w), 1596 (w), 1504 (m), 1475 (w), 1457 (w), 1395 (w), 1363 (s), 1307 (w), 1297 (w), 1266 (w), 1202 (m), 1178 (s), 1156 (s), 1112 (w), 1092 (s), 1040 (w), 1017 (m), 963 (w), 948 (w), 924 (w), 866 (s), 846 (s), 835 (s), 817 (s), 759 (s), 734 (m), 705 (w), 682 (s), 649 (m), 584 (s), 552 (s), 543 (s), 531 (s), 430 (w).

*4-(tert-Butyl)phenyl Methanesulfonate (**S1y-2**).* Following general procedure A, the use of 4-(*tert*-butyl)phenol (20 mmol) at 0 °C instead of −78 °C with NEt_3 as the base and 4-methylbenzenesulfonyl chloride as the sulfonating agent afforded the title compound **S1y-2** (5.63 g, 18.49 mmol, 92%) as a white solid after purification via column chromatography (*n*-pentane/EtOAc = 18:1). R_f = 0.26 (*n*-pentane/EtOAc = 18:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.39 (m, 2H), 7.23−7.17 (m, 2H), 3.11 (s, 3H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.5, 147.0, 126.9, 121.4, 37.2, 34.6, 31.3. MS (EI): m/z (relative intensity) 228 (19), 214 (10), 213 (100), 135 (44). HRMS (EI, m/z): calcd for $C_{11}H_{16}O_3S$ $[M]^+$ 228.0815, found 228.0813. IR (ATR, neat, cm^{-1}): 3030 (w), 3014 (w), 2962 (w), 2952 (w), 2936 (w), 2906 (w), 2870 (w), 1591 (w), 1501 (m), 1478 (w), 1466 (w), 1411 (w), 1396 (w), 1352 (s), 1337 (s), 1267 (w), 1204 (m), 1174 (m), 1153 (s), 1108 (m), 1015 (w), 969 (s), 947 (w), 924 (w), 870 (s), 851 (s), 836 (s), 822 (m), 790 (s), 741 (w), 726 (m), 656 (w), 639 (w), 573 (s), 530 (s), 509 (s), 471 (w), 431 (w), 404 (m).

*4-(tert-Butyl)-N,N-dimethylaniline Oxide (**5**).* 4-(*tert*-Butyl)-*N*,*N*-dimethylaniline (**3d**) (539 mg, 2.52 mmol) was dissolved in CH_2Cl_2 (0.5 M) and cooled to 0 °C. Afterward, *meta*-chloroperoxybenzoic acid (70%, 1.0 equiv) was added in one portion and the mixture was allowed to warm to room temperature. After 16 h, the reaction mixture was quenched with a saturated K_2CO_3 solution and extracted three times with CH_2Cl_2. The removal of the solvent afforded the title compound **5** (400 mg, 2.07 mmol, 82%) as a white crystalline solid. R_f = 0.00 (EtOAc, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78−7.71 (m, 2H), 7.38−7.32 (m, 2H), 3.47 (s, 6H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.0, 151.6, 126.0, 119.4, 63.1, 34.6, 31.2. MS (EI): m/z (relative intensity) 193 (44), 179 (13), 178 (100), 148 (23), 147 (44), 146 (29), 132 (17), 118 (10). HRMS (ESI-TOF, m/z): calcd for $C_{12}H_{19}NO$ $[M + H]^+$ 194.1545, found 194.1541. IR (ATR, neat, cm^{-1}): 3391 (w), 3129 (w), 3058 (w), 3021 (w), 2952 (m), 2902 (w), 2865 (w), 1654 (w), 1560 (w), 1503 (w), 1463 (w), 1401 (w), 1362 (w), 1267 (w), 1249 (w), 1186 (w), 1138 (w), 1101 (w), 1012 (w), 971 (m), 875 (m), 838 (s), 760 (w), 749 (w), 709 (m), 636 (m), 584 (s), 546 (w), 508 (m), 461 (w), 422 (w).

*5-(tert-Butyl)-2-(dimethylamino)phenol (**6**).* 4-(*tert*-Butyl)-*N*,*N*-dimethylaniline oxide (**5**, 96mg, 0.5 mmol) was dissolved in

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J. Org. Chem. XXXX, XXX, XXX−XXX

CH_2Cl_2 (5 mL, 0.1 M) and cooled to −78 °C. Afterward, trifluoroacetic anhydride was added dropwise via a syringe over a period of 15 min. The resultant solution was stirred for 1 h, whereupon triethylamine (150 mg, 3.00 equiv) was added. Subsequently, the mixture was allowed to warm to room temperature and quenched with a saturated $NaHCO_3$ solution. Afterward, the aqueous phase was extracted with DCM. The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated in vacuum. The crude product was further purified with column chromatography (*n*-pentane/EtOAc = 20:1), yielding the title compound **6** (88 mg, 0.455 mmol, 91%). R_f = 0.38 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H), 6.89 (dd, J = 8.3, 2.2 Hz, 1H), 2.65 (s, 6H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.0, 149.5, 137.9, 120.1, 116.8, 111.4, 45.4, 34.6, 31.5. MS (EI): *m*/*z* (relative intensity) 193 (34), 179 (12), 178 (100). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{12}H_{19}NO$ $[M + H]^+$ 194.1545, found 194.1550. IR (ATR, neat, cm^{-1}): 3053 (w), 2957 (s), 2867 (m), 2834 (m), 2791 (m), 1746 (w), 1568 (m), 1503 (s), 1478 (m), 1454 (m), 1441 (m), 1430 (m), 1393 (w), 1363 (w), 1308 (m), 1288 (s), 1271 (s), 1236 (m), 1202 (s), 1168 (s), 1125 (s), 1087 (m), 1035 (m), 1024 (m), 947 (s), 917 (s), 873 (m), 809 (s), 724 (s), 648 (s), 543 (w), 510 (m), 497 (m), 459 (m), 439 (m), 416 (s).

*N-Methyl-N-(3-phenylprop-2-yn-1-yl)aniline (**7**).* A mixture of CuBr (40.0 mg, 0.28 mmol, 7.0 mol %), *N*,*N*-dimethylaniline (974 mg, 8.0 mmol, 2.0 equiv), phenylacetylene (412 mg, 4.0 mmol, 1.0 equiv), and *tert*-butyl hydroperoxide (0.8 mL, 5−6 M in decane) was heated under argon to 100 °C in an oil bath. After 16 h, water was added, and the aqueous phase was extracted with DCM. The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated in vacuum. The crude product was further purified with column chromatography, yielding the title compound **7** (469 mg, 2.26 mmol, 56%). R_f = 0.57 (*n*-pentane/EtOAc = 10:1, UV); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.39 (m, 2H), 7.38−7.28 (m, 5H), 7.02−6.92 (m, 2H), 6.87 (td, J = 7.3, 1.3 Hz, 1H), 4.30 (d, J = 1.2 Hz, 2H), 3.15−3.03 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.4, 131.8, 129.1, 128.2, 128.1, 123.1, 118.2, 114.4, 85.1, 84.2, 43.4, 38.8. MS (EI): *m*/*z* (relative intensity) 222 (15), 221 (93), 220 (91), 144 (18), 116 (11), 115 (100), 104 (14), 89 (13), 77 (25). HRMS (EI, *m*/*z*): calcd for $C_{16}H_{14}N$ $[M]^+$ 221.1199, found 221.1192. IR (ATR, neat, cm^{-1}): 3057 (w), 1597 (s), 1503 (m), 1489 (m), 1442 (w), 1423 (w), 1365 (w), 1333 (m), 1241 (w), 1200 (w), 1110 (w), 1029 (w), 995 (m), 920 (m), 867 (w), 750 (s), 687 (s), 597 (m), 526 (m), 489 (w), 446 (m).

*4-Iodo-N,N-dimethylaniline (**8**).* *N*,*N*-Dimethylaniline (**3a**, 122 mg, 1.00 mmol) was dissolved in 1,4-dioxane (5 mL) and pyridine (5 mL), and the mixture was cooled to 0 °C. Iodine (761 mg, 3 mmol, 3.0 equiv) was add in one portion. After 2 h, water was added, and the aqueous phase was extracted with DCM. The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated in vacuum. The crude product was further purified with column chromatography (*n*-pentane/EtOAc = 20:1), yielding the title compound **8** (220 mg, 0.89 mmol, 89%). R_f = 0.29 (*n*-pentane/EtOAc = 20:1, UV); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.42 (m, 1H), 6.55−6.44 (m, 1H), 2.92 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.0, 137.6, 114.7, 77.5, 40.4. MS (EI): *m*/*z* (relative intensity) 247 (100), 246 (54), 119 (15), 77 (11). HRMS (EI, *m*/*z*): calcd for C_8H_9NI $[M]^+$ 245.9774, found 245.9773. IR (ATR, neat, cm^{-1}): 2881 (w), 2800 (w), 1868 (w), 1733 (w), 1582 (w), 1443 (m), 1346 (m), 1312 (m), 1227 (m), 1191 (m), 1164 (m), 1125 (m), 1062 (m), 983 (w), 943 (w), 799 (s), 743 (m), 691 (m), 566 (w), 505 (s), 476 (m). The analytical data is in accordance with that reported in the literature.[27]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c00491.

Reaction optimization, experimental procedures, analytical data with ^{1}H and ^{13}C NMR spectra, and X-ray crystallography data (PDF)

X-ray crystallographic structure of compound **3q** (CCDC1981523); these data are provided free of charge by The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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