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Chemoselective C-Benzylation of Unprotected Anilines with Benzyl Alcohols Using Re_2O_7 Catalyst

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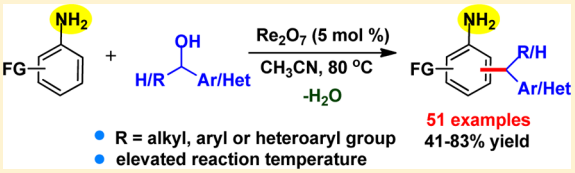
Supporting Information

ABSTRACT: An unprecedented dehydrative C−C bond formation between unprotected anilines with benzyl alcohols is disclosed. Re_2O_7 catalyst (5 mol %) at elevated reaction temperature (80 °C) provided *C*-benzylanilines with high to excellent yields and with good chemoselectivities (over N-alkylation). A probable mechanism has been proposed based on mechanistic studies.



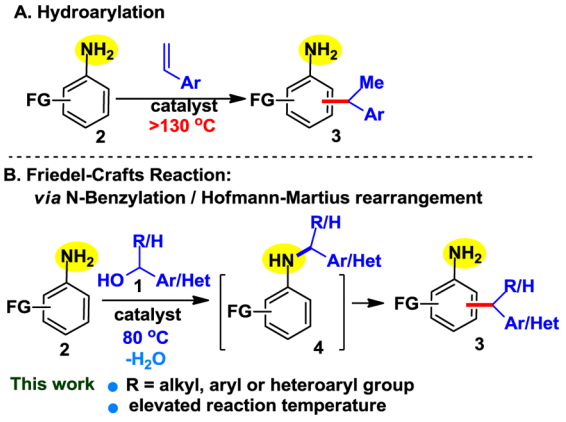
INTRODUCTION

Benzyl-substituted anilines represent the recurring precursors for the synthesis of many complex molecular architectures and bioactive molecules with pharmaceutical relevance.[1] Anilines containing *ortho*-chiral alkyl substituents are being used as chiral building blocks for the preparation of various chiral ligands.[2] The amine functionality of benzylanilines could easily be converted to various functional groups.[3] Despite the versatile importance of such substituted anilines, their viable synthetic protocols are extremely rare to date.[4,5] The pioneering synthesis of such *C*-benzylanilines has been accomplished *via* hydroarylation of anilines with styrenes by Beller,[4a] Ackermann,[4b] Bergman,[4c] Coates,[4d] Peris,[4e] and Li[4f] (Scheme 1A). Nevertheless, in many cases the requirement of harsh reaction conditions and very limited substrate scope has been realized.

Friedel−Crafts (FC) alkylation reactions are among the most efficient processes for critical C−C bond formation from unactivated aromatic C−H bonds.[6] Despite the tremendous advancement in such FC benzylation reactions, arenes bearing unprotected amine (aniline **1**) usually provide only the N-alkylated anilines (**4**, Scheme 1B).[7] This is due to the strong deactivation of the aromatic ring of aniline toward electrophilic substitution *via* the coordination of Lewis acid with the amine (aniline)[8] or the buffering effect of anilines with Brönsted acids.[9] In recent times, the direct use of benzyl alcohols as electrophiles instead of corresponding toxic alkyl halides has been a rapidly developing trend in organic synthesis[10] and eventually has been adopted for FC benzylation as well.[11] Therefore, development of a mild catalytic method for the synthesis of such *C*-benzylanilines (**3**) *via* dehydrative coupling of unprotected anilines and benzyl alcohols would synthetically be an attractive strategy for the synthesis of *C*-benzylanilines.

We envisioned that condensation of alcohol **1** and aniline **2** ultimately would lead to benzylated aniline **3** *via* the formation of *N*-alkylaniline **4**, followed by the Hofmann−Martius rearrangement[12] as illustrated in Scheme 1B. Although the *C*-alkylanilines are more stable (thermodynamically controlled product) compared to *N*-alkylanilines (kinetically controlled product), the real obstruction to this strategy is the deamination of **4** (second step, Scheme 1B). Therefore, such instances are very rare, the only report being by Pullarkat, Leung, and co-workers on the corresponding allylation of anilines using Pd and Cu catalysts.[13] Recently, the higher oxophilicity of oxo-rhenium complexes enabled their use as efficient catalysts for direct dehydrative C−O, C−N, and C−C bond formation from π-activated alcohols.[14,15b] Such efficiency of oxo-rhenium complexes triggered us to explore the direct FC alkylation of anilines with benzyl alcohols. Nevertheless, the oxo-rhenium complexes in higher oxidation states have gained considerable attention as ecologically benign catalysts for numerous organic reactions due to their mild reactivity, low toxicity, and air-/moisture-tolerant nature.[14−16]

Scheme 1. C-Benzylation of Anilines



RESULTS AND DISCUSSION

Our investigations began with a survey of different catalysts as shown in Table 1. In the reaction of 1,1-diaryl methanol (**1a**)

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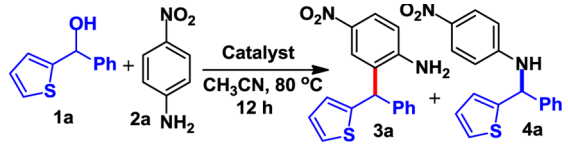
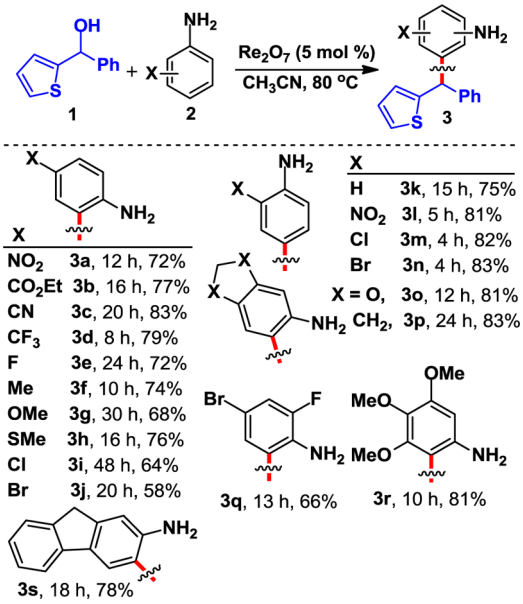
Table 1. Optimization of the Friedel–Crafts Benzylation of Aniline



Entry	Catalyst (5 mol %)	Conversions[a]	3a:4a[a]
1	$Cu(OTf)_2$	80	42:58
2	$AgSbF_6$	100	1:99
3	AgOTf	91	1:99
4	$Yb(OTf)_3$	83	4:96
5	$Ce(OTf)_3$	100	3:97
6	$Sc(OTf)_3$	100	22:78
7	$In(OTf)_3$	64	65:35
8	Re_2O_7	100 (74)[b]	95:05
9	*p*-Tol-SO_3H (*p*TSA)	88	9:91
10	CF_3CO_2H (TFA)	90	1:99

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.12 mmol, 1.2 equiv). The conversions and the ratio was determined by ^1H NMR spectroscopy of the reaction mixture using anisole as internal standard. [b]In parentheses is the isolated yield.

Table 2. Friedel–Crafts Benzylation of Anilines: Variation of Anilines[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol, 1.2 equiv), Re_2O_7 (5 mol %), CH_3CN (2 mL), 80 °C. [b]Isolated yield.

and 4-nitroaniline (**2a**) in acetonitrile as solvent using various Lewis acid catalysts such as $Cu(OTf)_2$, $AgSbF_6$, AgOTf, $Yb(OTf)_3$, $Ce(OTf)_3$, $Sc(OTf)_3$, and $In(OTf)_3$, the formation of the desired C-alkylated product (**3a**) was absent or less compared to N-alkylated product (**4**) (entries 1–7, respectively). Brönsted acids such as *p*-toluene sulfonic acid (*p*TSA) and trifluoroacetic acid (TFA) displayed similar reaction scenarios (entries 9– and 10, respectively). Remarkably, using Re_2O_7 catalyst under similar reaction conditions, the desired C-alkylated product **3a** was formed almost quantitatively and also with excellent chemoselectivity (entry 8). Instead of acetonitrile (with **3a**:**4a** = 95:5), other solvents such as toluene (4:96), 1,4-dioxane (44:56), nitromethane (92:8), methanol (61:39), trifuoroethanol (93:7), and dichloromethane (39:61) are not superior for the current process to provide **3a** with high chemoselectivity (over **4a**).

The optimized reaction conditions proved to be effective for a wide range of substituted anilines, including those with electron-rich as well as electron-deficient substituents (see Table 2). Various mono-, di-, or tri-substituted anilines, with *ortho*, *meta*, and *para* substitution patterns, furnished the desired products in good yields (**3a**–**3s**). Interestingly, the regioselective formation of only *p*-benzylanilines (**3k**–**n**) was observed from anilines with the *para*-position being vacant. Notably, the slower rate is observed for *ortho*-benzylated products compared to *para*-benzylated ones (for example, the cases such as **3a** vs **3l**, **3i** vs **3m**, and **3j** vs **3n**); the slower rate is mainly attributable to the effect of steric hindrance at the *ortho*-position. Gratifyingly, the electron-deficient anilines with substituents such as 4-NO_2-, 4-EtO_2C-, 4-CN-, 4-F_3C-, and 4-F-, which are considered to be prototypically deactivated anilines and usually provide N-alkylated products on alkylation,[4] also provided the corresponding *C*-benzylanilines in good yields (**3a**–**e**, respectively).

To broaden the substrate scope, we carried out the reaction of various aryl-heteroaryl as well as diaryl alcohols with substituted anilines (see Table 3). Various combinations of heteroaryl- and aryl-containing alcohols condensed with *para* or *ortho* Cl-aniline to provide the corresponding *C*-benzylanilines (**6a**–**i**) in good yields. Condensation of 1,1-diaryl methanols with anilines is also equally effective for the synthesis of corresponding *C*-benzylanilines (**6j**–**o**).

To our excitement, even the monoaryl-containing secondary alcohols reacted smoothly with anilines at similar reaction conditions. For examples, various 2-thiophene-containing secondary alcohols provided the corresponding *C*-benzylanilines (**6q**–**s**) in good yields. The corresponding 1-furanyl-1-ethyl methanol also gave *C*-benzylanilines (**6t**). These examples directly reflect the advantage of current strategy over the hydroarylation processes where the styrenes provided only methyl substitution on the benzylic position of anilines.[4]

Further, primary aryl or heteroaryl methanols, where the Hofmann–Martius rearrangement process is challenging, have also been utilized successively as electrophiles for the current process. In this context, heteroaryl-containing primary alcohols such as 2-thiophenylmethan-1-ol and 2-pyrrolylmethan-1-ol as well as methoxy benzyl alcohols provided the corresponding C-alkylated anilines with somewhat acceptable yields (**6u**–**x**, Table 3), even under similar reaction conditions, except in a few cases where increase in the reaction temperature was required (**6t**–**x**).

Interestingly, even lower loading of Re_2O_7 catalyst (1.5 mol %) at 60 °C is sufficient to activate the corresponding substituted allyl and propargyl alcohols to provide the corresponding 2-substituted anilines from anilines in excellent chemoselectivity as well as good yields (**8a**–**h**), as shown in Table 4. Notably, the anilines with electron-deficient substituents such as 4-NO_2-, 4-EtO_2C-, 4-CN-, 4-F_3C-, and 4-F- also provided the corresponding *C*-allylanilines in good yields (**8a**–**e**, respectively). This result represented a major advancement over the previous protocol reported by Pullarkat, Leung, and co-workers[13] where 4-NO_2- and 4-EtO_2C-anilines provided the corresponding *N*-allylanilines only. Notably, to the

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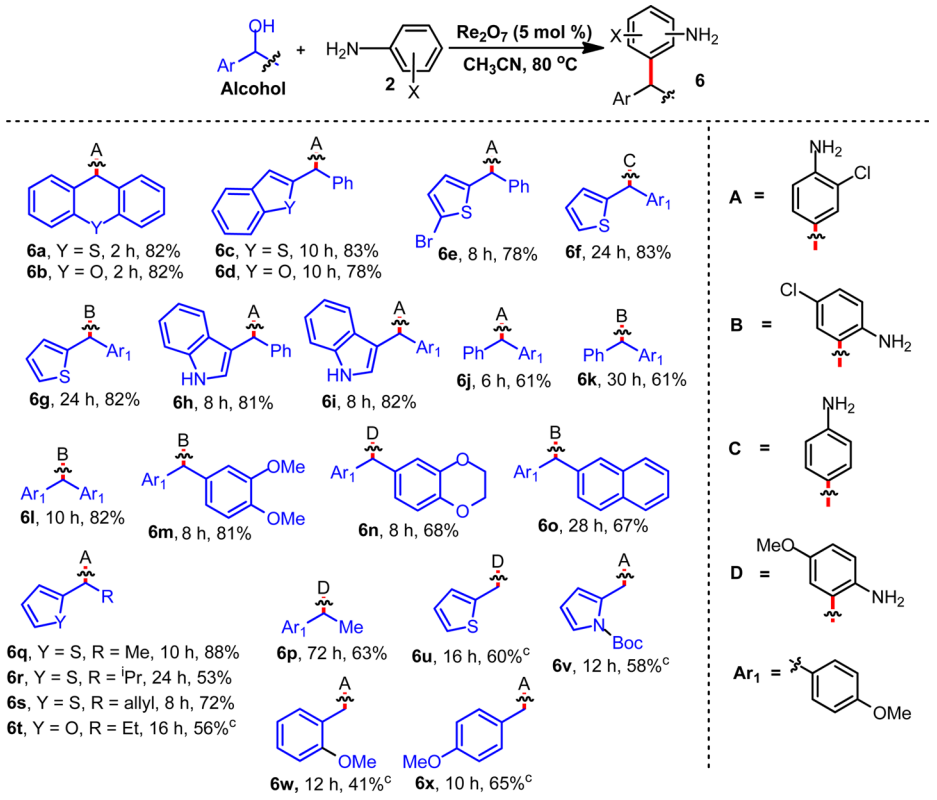
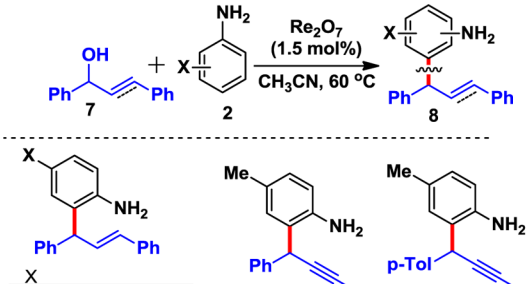
Table 3. Friedel–Crafts Benzylation of Anilines: Variation of Alcohols[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol, 1.2 equiv), Re_2O_7 (5 mol %), CH_3CN (2 mL), 80 °C. [b]Isolated yield after column chromatography. [c]Reaction was performed at 100 °C using 5 mol % Re_2O_7.

Table 4. Friedel–Crafts Allylation and Propargylation of Anilines[a,b]



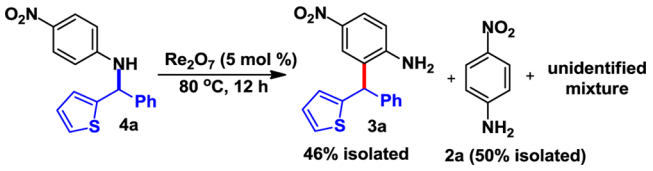
X		
NO_2	**8a**,12 h, 78%	
CO_2Et	**8b**, 8 h, 72%	
CN	**8c**, 15 h, 65%	
CF_3	**8d**, 24 h, 68%	
F	**8e**, 18 h, 75%	
Me	**8f**, 10 h, 73%	

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol, 1.2 equiv), Re_2O_7 (1.5 mol %), CH_3CN (2 mL), 60 °C. [b]Isolated yield after column chromatography. [c]5 mol % catalyst was used in $MeNO_2$ as solvent.

best of our knowledge this is the first report of C-propargylation of anilines using substituted propargyl alcohol.

To gain insight into the reaction mechanism of the current benzylation of anilines using Re_2O_7 as catalyst, *N*-benzylaniline **4a** was treated under our standard reaction conditions using Re_2O_7 catalyst (5 mol %) (Scheme 2). As expected, the formation of *C*-benzylaniline **3a** was clearly observed. Here, the reduced isolated yield of **3a** in comparison to the same in Table 2 is probably because of the excess use of nucleophile, 4-nitroaniline, in Table 2. Also, because of the poor

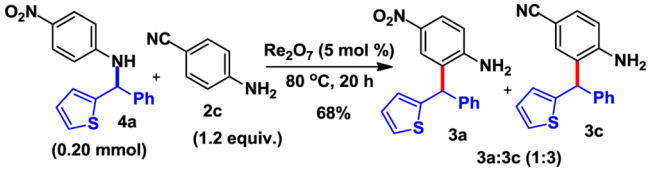
Scheme 2. Stepwise Reaction Pathway



nucleophilicity of 4-nitroaniline (**2a**), the *in situ* formed corresponding benzylic carbocation (generated from **4a**) undergoes partial decomposition to provide an unidentified complex mixture, whereas 4-nitroaniline (**2a**) remained unreactive.

To understand whether the current rearrangements proceed through an inter- or intramolecular pathway, the following crossover experiment was performed (Scheme 3). The treatment of *N*-benzylaniline (**4a**) in the presence of 4-cyanoaniline (**2c**), an alternative Friedel–Crafts coupling partner, under our specified reaction conditions using 5 mol % Re_2O_7, a mixture of *C*-benzylanilines (**3a** and **3c**) was obtained. This indicates the dissociative reversible nature of this rearrangement and the formation of a carbocation intermediate.

Scheme 3. Crossover Experiment



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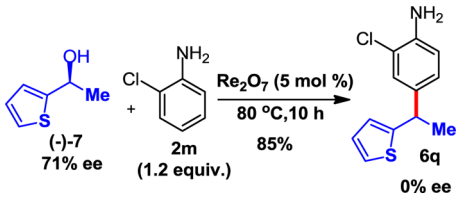
As shown in Scheme 4, an enantiorich benzyl alcohol (−)-7 with 71% ee was treated with aniline **2m** under our optimized

Scheme 4. Friedel−Crafts Benzylation of Aniline of Chiral Benzyl Alcohol



reaction conditions, and the racemic *C*-benzylaniline **6q** was obtained. This result also suggests the formation of a carbocationic intermediate (S_N1-like mechanism) from chiral alcohol (−)-7 during the reaction process.

To gain further insight into the mechanism of this Re_2O_7 catalysis, the reaction between benzyl alcohol **1a** and 4-nitroaniline (**2a**) was monitored by ^1H NMR spectroscopy. In the ^1H NMR spectra of benzyl alcohol **1a**, *N*-benzylaniline **4a**, and *C*-benzylaniline **3a** taken in acetonitrile-d_3, the distinguishable signal of benzylic CH proton appeared at δ = 6.02, 6.01−5.95, and 5.70 ppm, respectively. As shown in Figure 1, the monitoring of the reaction between **1a** and **2a** in acetonitrile-d_3 at 80 °C revealed that immediately after the mixing (at 0 min) of **1a** and **2a**, the only signal observed cleanly was for

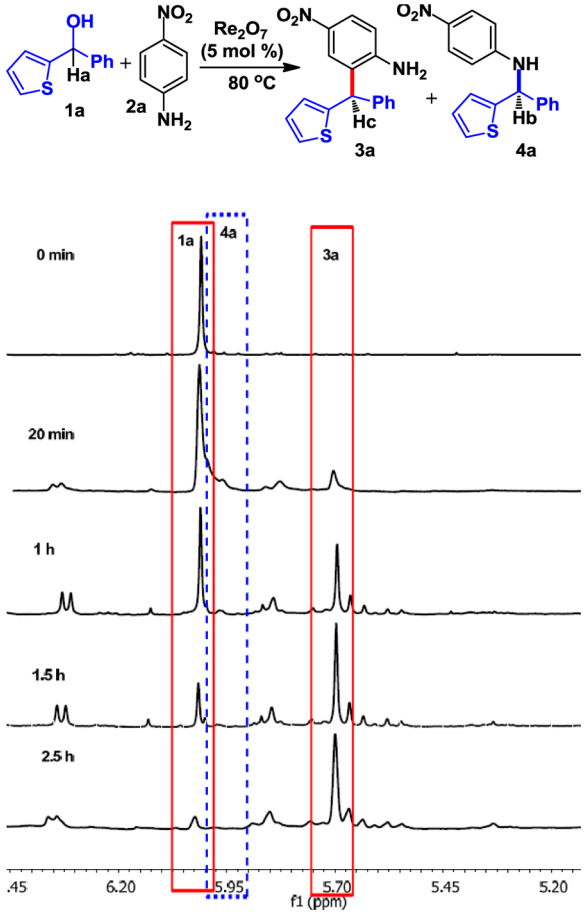
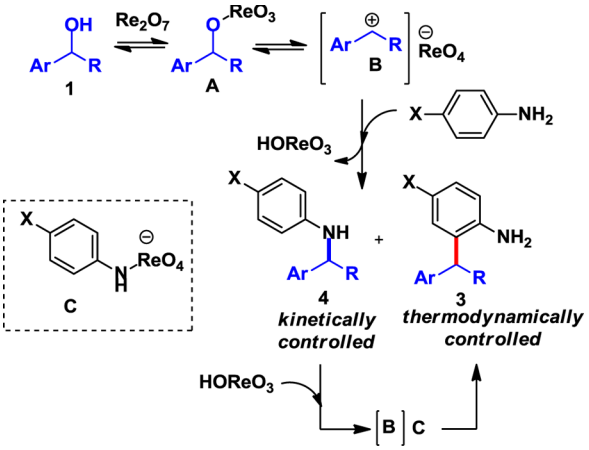


Figure 1. Monitoring the gradual change in the concentrations of the C−N and C−C products by ^1H NMR spectra at 80 °C.

corresponding **1a**. After 20 min, the signal for **4a** appeared along with a small signal of low intensity at δ = 5.70 ppm corresponding to the formation of **3a**; this reflects that the formation of **4a** is faster compared to the formation of **3a**. Eventually, the concentration of **3a** started increasing in parallel with the decreasing concentration of **1a**. Finally, the spectra obtained is for the product **3a** exclusively.

Based on the above studies, the proposed mechanism for the current benzylation of anilines is depicted below (Scheme 5).

Scheme 5. Proposed Mechanism



The strong oxophilicity[14d] of Re_2O_7 enabled the formation of carbocation **B**, which simultaneously is trapped to give N-alkylation product **4** (a kinetically controlled product) as well as C-alkylation product **3** (a thermodynamically controlled product) with anilines. Further activation of *N*-alkyl product by Re_2O_7 again generated the carbocation **B** and followed the previous reaction cycle. This also indicates that oxo-rhenium complexes could be an efficient catalyst for the activation of a π-activated C−N bond.

CONCLUSION

In conclusion, a catalytic approach for the synthesis of highly substituted *C*-benzylanilines has been developed using unprotected anilines and aryl and/or heteroaryl alcohols with Re_2O_7 as catalyst under an open-flask reaction condition. This offers a significant advantage over the previous protocols for the synthesis of *C*-benzylanilines. Excellent chemoselective formation of C-alkylated over N-alkylated products were observed. The mechanistic studies revealed that the probable formation of *N*-alkylanilines followed by Martius rearrangement to provide *C*-alkylanilines as well as the dehydrative formation of *C*-alkylanilines occurred. Further developments of catalytic reactions where anilines are directly used as substrate are our current focus.

EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were used as supplied commercially. Commercial Re_2O_7, ranging in color from yellow to brown-black, was stored in a desiccator over $CaCl_2$. Reactions were conducted in open atmosphere. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated Science silica gel EM 60-F254 plates. Visualization was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde, or $KMnO_4$ solution followed by heating. Melting points are uncorrected. ^1H NMR spectra were acquired on a 400 MHz spectrometer, and chemical shifts are reported relative to the residual

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solvent peak. ^{13}C NMR spectra were acquired on a 100 MHz spectrometer, and chemical shifts are reported in ppm relative to the residual solvent peak. Unless noted, NMR spectra were acquired in $CDCl_3$; individual peaks are reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant in hertz. All IR spectra were obtained as neat films, and selected absorbances are reported in cm^{-1}. Low resolution (LR) and high-resolution (HR) data were acquired using either a Daltonics Micro TOF-Q-II Mass Spectrometer or a GC Q-TOF Mass Spectrometer or by GC−MS (EI 70 eV) using DB-5 column.

Standard Procedure for the Synthesis of Benzyl Anilines. To a stirred solution of alcohol (0.5 mmol) and aniline (0.6 mmol) in CH_3CN (2.0 mL), in a round-bottom flask attached to a reflux condenser, was added Re_2O_7 (5 mol %). Unless otherwise noted, the reaction was stirred at 80 °C for the given time in Schemes 2 and 3. The reaction was quenched with the addition of brine solution (2 mL), followed by extraction with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the crude residue was purified by flash column chromatography (EtOAc/hexane) on silica gel.

Characterization Data. 4-Nitro-2-(phenyl(thiophen-2-yl)-methyl)aniline (3a). 0.111 g, 72% yield; R_f = 0.30 (20:80 = EtOAc/*n*-hexane); dark solid; mp 150−155 °C; FT-IR (neat) 3480, 3383, 3247, 3065, 2924, 1627, 1602, 1580, 1488,1452, 1434, 1301, 1155, 1094, 915, 829, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.8, 2.4 Hz, 1H), 7.74 (d, J = 2.4 Hz, 1H), 7.37−7.30 (m, 3H), 7.27 (dd, J = 5.2, 0.8 Hz, 1H), 7.19 (d, J = 7.2 Hz, 2H), 6.97 (dd, J = 5.2, 3.6 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 5.56 (s, 1H), 4.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 144.3, 140.5, 139.4, 129.1, 128.6, 127.8, 127.7, 127.17, 127.14, 125.9, 125.6, 124.6, 114.9, 47.2; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}N_2O_2S$ 311.0854, found 311.0846.

Ethyl 4-Amino-3-(phenyl(thiophen-2-yl)methyl)benzoate (3b). 0.130 g, 77% yield; R_f = 0.36 (20:80 = EtOAc/*n*-hexane); white solid; mp 130−135 °C; FT-IR (neat) 3406, 3359, 3068, 2982, 2357, 1694, 1605, 1505, 1392, 1285, 1238, 1150, 1110, 1029, 836, 770, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 (d, J = 1.6 Hz, 1H), 7.31 (d, J = 7.2 Hz, 2H), 7.28 (d, J = 6.8 Hz, 1H), 7.23 (dd, J = 5.2, 1.2 Hz, 2H), 7.20 (s, 1H), 6.95 (dd, J = 4.8, 3.2 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 5.60 (s, 1H), 4.24 (q, J = 6.8 Hz, 2H), 3.94 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 148.6, 145.5, 141.5, 131.4, 129.9, 128.83, 128.81, 127.6, 127.3, 126.9, 126.8, 125.1, 120.3, 115.3, 60.3, 47.4, 14.3; HRMS-GC (EI, m/z) $[M]^+$ calculated for $C_{20}H_{19}NO_2S$ 337.1136, found 337.1109.

4-Amino-3-(phenyl(thiophen-2-yl)methyl)benzonitrile (3c). 0.120 g, 83% yield; R_f = 0.24 (20:80 = EtOAc/*n*-hexane); dark solid; mp 135−140 °C; FT-IR (neat) 3477, 3375, 3059, 2952, 2365, 2218, 1627, 1603, 1503, 1452, 1306, 1210, 1156, 1110, 1077, 1038, 908, 826, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 4H), 7.26−7.24 (m, 1H), 7.16 (d, J = 6.8 Hz, 2H), 7.04 (d, J = 1.2 Hz, 1H), 6.96 (dd, J = 5.2, 3.6 Hz, 1H), 6.70 (d, J = 3.2 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.54 (s, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 144.5, 140.7, 133.5, 132.1, 129.0, 128.7, 128.6, 127.7, 127.1, 127.0, 125.5, 120.2, 115.8, 100.5, 46.9; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{15}N_2S$ 291.0956, found 291.0956.

2-(Phenyl(thiophen-2-yl)methyl)-4-(trifluoromethyl)aniline (3d). 0.132 g, 79% yield; R_f = 0.24 (10:90 = EtOAc/hexane); brown solid; mp 80−85 °C; FT-IR (neat) 3470, 3388, 3065, 2924, 2852, 1628, 1509, 1452, 1434, 1328, 1303, 1246, 1151, 1112, 1078, 910, 826, 744, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.36 (m, 3H), 7.35−7.32 (m, 1H), 7.29 (dd, J = 5.2, 1.0 Hz, 1H), 7.25 (d, J = 1.5 Hz, 1H), 7.23 (s, 1H), 7.09 (d, J = 1.5 Hz, 1H), 7.01 (dd, J = 5.5, 3.5 Hz, 1H), 6.76−6.75 (m, 1H), 6.74 (d, J = 8.3 Hz, 1H), 5.66 (s, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 145.2, 141.2, 128.90, 128.8, 128.4, 127.5, 127.0, four signals: 126.46, 126.43, 126.40, 126.30 (q, J = 3 Hz), 125.34, four signals: 125.20, 125.16, 125.13, and 125.10 (q, J = 3 Hz), two signals: 125.84 and 123.69 (d, J = 268 Hz), four signals: 120.73, 120.47, 120.21, and 119.96 (q, J = 26 Hz), 115.7, 47.2; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{15}F_3NS$ 334.0877, found 334.0873.

4-Fluoro-2-(phenyl(thiophen-2-yl)methyl)aniline (3e). 0.102 g, 72% yield; R_f = 0.33 (10:90 = EtOAc/hexane); brown solid; mp 70−75 °C; FT-IR (neat) 3446, 3362, 3062, 2923, 1625, 1495, 1451, 1432, 1258, 1230, 1197, 1144, 1076, 1030, 961, 881, 816, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H), 7.29 (d, J = 6.8 Hz, 1H), 7.24 (dd, J = 5.2, 1.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 2H), 6.96 (dd, J = 5.2, 3.6 Hz, 1H), 6.81 (td, J = 8.3, 2.9 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.61 (dd, J = 8.4, 4.8 Hz, 1H), 6.56 (dd, J = 10.0, 2.8 Hz, 1H), 5.65 (s, 1H), 3.38 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ two signals: 157.7 and 155.4 (d, J = 2.34 Hz), 145.7, 141.7, two signals: 140.10 and 140.08 (d, J = 2 Hz), two signals: 131.0 and 130.9 (d, J = 6 Hz), two signals: 128.87 and 128.84 (d, J = 3 Hz), 127.3, two signals: 126.92 and 126.86 (d, J = 6 Hz), 125.1, two signals: 117.28 and 117.21 (d, J = 7 Hz), two signals: 116.1 and 115.8 (d, J = 24 Hz), two signals: 114.32 and 114.09 (d, J = 23 Hz), 47.2; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}FNS$ 284.0909, found 284.0894.

4-Methyl-2-(phenyl(thiophen-2-yl)methyl)aniline (3f). 0.103 g, 74% yield; R_f = 0.32 (10:90 = EtOAc/*n*-hexane); brown solid; mp 75−80 °C; FT-IR (neat) 3435, 3361, 3026, 2921, 2859, 2363, 1732, 1626, 1505, 1452, 1266, 1156, 1076, 1040, 817, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 7.24 (d, J = 6.4 Hz, 3H), 6.97 (dd, J = 5.2, 3.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 3.2 Hz, 1H), 6.65 (s, 1H), 6.61 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 3.40 (br s, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 142.5, 141.6, 129.7, 129.3, 128.9, 128.6, 128.3, 128.0, 127.0, 126.7, 126.6, 124.8, 116.6, 47.2, 20.8; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{18}NS$ 280.1160 , found 280.1135.

4-Methoxy-2-(phenyl(thiophen-2-yl)methyl)aniline (3g). 0.100 g, 68% yield; R_f = 0.40 (20:80 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3426, 3355, 3062, 3026, 2998, 2928, 2853, 2831, 1608, 1497, 1452, 1403, 1322, 1277, 1227, 1155, 1130, 1075, 816 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.39 (m, 2H), 7.28−7.25 (m, 1H), 7.22 (d, J = 5.6 Hz, 3H), 6.94 (dd, J = 4.8, 3.6 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.68 (dd, J = 8.4, 2.8 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 6.45 (dJ = 2.4 Hz, 1H), 5.69 (s, 1H), 3.64 (s, 3H), 3.00 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 146.3, 142.2, 137.6, 131.1, 128.9, 128.7, 127.1, 126.79, 126.75, 124.9, 117.5, 115.9, 112.4, 55.5, 47.3; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{18}NOS$ 296.1109, found 296.1100.

4-(Methylthio)-2-(phenyl(thiophen-2-yl)methyl)aniline (3h). 0.118 g, 76% yield; R_f = 0.34 (20:80 = EtOAc/*n*-hexane); brown solid; mp 70−75 °C; FT-IR (neat) 3437, 3365, 3025, 2917, 1621, 1488, 1451, 1435, 1405, 1310, 1282, 1229, 1148, 1110, 1030, 968, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.23−7.19 (m, 3H), 7.10 (dd, J = 8.0, 2.0 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 5.62 (s, 1H), 3.50 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 142.7, 141.9, 130.5, 129.9, 128.98, 128.90, 128.7, 127.2, 126.8, 126.2, 125.0, 117.0, 47.2, 18.3; HRMS (ESI, m/z) $[M]^+$ calculated for $C_{18}H_{17}NS_2$ 311.0802, found 311.0811.

4-Chloro-2-(phenyl(thiophen-2-yl)methyl)aniline (3i). 0.096 g, 64% yield; R_f = 0.43 (20:80 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3447, 3369, 3061, 3026, 2918, 1622, 1488, 1451, 1413, 1283, 1230, 1142, 1076, 1030, 905, 815, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 3H), 7.23 (dd, J = 5.2, 1.2 Hz, 1H), 7.18 (d, J = 6.8 Hz, 2H), 7.04 (dd, J = 8.4, 2.4 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 5.61 (s, 1H), 3.67 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.3, 141.5, 130.9, 129.0, 128.84, 128.84, 127.7, 127.3, 126.92, 126.90, 125.2, 123.9, 117.7, 47.1; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}ClNS$ 300.0614, found 300.0595.

4-Bromo-2-(phenyl(thiophen-2-yl)methyl)aniline (3j). 0.099 g, 58% yield; R_f = 0.32 (10:90 = EtOAc/hexane); brown liquid; FT-IR (neat) 3446, 3370, 3025, 1621, 1485, 1451, 1408, 1282, 1075, 894, 814, 745, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 2H), 7.29−7.27 (m, 1H), 7.23 (d, J = 0.8 Hz, 1H), 7.20−7.16 (m, 3H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 5.59 (s, 1H), 3.52 (s, 2H); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 145.4, 143.2, 141.5, 131.8, 131.1, 130.6, 128.85, 128.83, 127.3, 126.92, 126.90, 125.2, 117.9, 110.8, 47.1; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}BrNS$ 344.0109, found 344.0106.

4-(Phenyl(thiophen-2-yl)methyl)aniline (3k). 0.99 g, 75% yield; R_f = 0.34 (05:95 = EtOAc/hexane); brown liquid; FT-IR (neat) 3448, 3370, 3219, 3060, 1621, 1513, 1493, 1451, 1435, 1279, 1228, 1181, 1107, 1076, 819, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.2 Hz, 2H), 7.23−7.21 (m, 3H), 7.19 (dd, J = 5.2, 1.4 Hz, 1H), 7.00 (d, J = 8.3 Hz, 2H), 6.93 (dd, J = 5.2, 3.6 Hz, 1H), 6.69 (d, J = 3.2 Hz, 1H), 6.62 (d, J = 8.4 Hz, 2H), 5.58 (s, 1H), 3.59 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 145.0, 144.4, 134.0, 129.7, 128.8, 128.3, 126.55, 126.54, 126.1, 124.3, 115.1, 51.4; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{16}NS$ 266.1003, found 266.1019.

4-Nitro-2-(phenyl(thiophen-2-yl)methyl)aniline (3l). 0.126 g, 81% yield; R_f = 0.30 (10:90 = EtOAc/hexane); yellow solid; mp 130−140 °C; FT-IR (neat) 3485, 3383, 3245, 3065, 2928, 1627, 1602, 1575, 1488, 1477, 1434, 1301, 1155, 1099, 915, 829, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 1.9 Hz, 1H), 7.31 (t, J = 7.2 Hz, 2H), 7.26 (s, 1H), 7.21 (dd, J = 10.6, 4.6 Hz, 4H), 6.94 (dd, J = 5.1, 3.6 Hz, 1H), 6.71 (dd, J = 20.2, 6.0 Hz, 2H), 6.07 (s, 2H), 5.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 143.5, 142.9, 136.3, 132.9, 131.8, 128.65, 128.65, 127.0, 126.7, 126.4, 125.6, 124.9, 119.0, 50.8; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}N_2O_2S$ 311.0854, found 311.0846

2-Chloro-4-(phenyl(thiophen-2-yl)methyl)aniline (3m). 0.123 g, 82% yield; R_f = 0.30 (05:95 = EtOAc/*n*-hexane); light yellow liquid; FT-IR (neat) 3474, 3382, 3061, 3026, 1621, 1505, 1311, 1075, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.20 (6H), 7.14 (s, 1H), 7.02−6.92 (2H), 6.77−6.68 (2H), 5.59 (s, 1H), 4.02 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.7, 141.5, 134.8, 129.5, 128.7, 128.4, 128.1, 126.7, 126.6, 126.3, 124.6, 119.2, 115.7, 51.1; HR-MS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}ClNS$ 300.0614, found 300.0602.

2-Bromo-4-(phenyl(thiophen-2-yl)methyl)aniline (3n). 0.142 g, 83% yield; R_f = 0.32 (05:95 = EtOAc/hexane); clear liquid; FT-IR (neat) 3472, 3379, 3203, 3061, 3025, 2922, 2871, 2622, 1950, 1618, 1501, 1487, 1451, 1309, 1276, 1229, 1190, 1158, 1108, 1036, 893, 746, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, J = 7.3 Hz, 2H), 7.28−7.23 (m, 2H), 7.22−7.19 (m, J = 2.1 Hz, 3H), 6.97−6.92 (m, 2H), 6.68 (dd, J = 8.12, 1.76 Hz, 2H), 5.55 (s, 1H), 4.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.7, 142.7, 135.2, 132.6, 128.8, 128.7, 128.4, 126.8, 126.6, 126.3, 124.6, 115.6, 109.2, 51.0; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{17}H_{15}BrNS$ 344.0109, found 344.0074.

6-(Phenyl(thiophen-2-yl)methyl)benzo[*d*][1,3]dioxol-5-amine (3o). 0.125 g, 81% yield; R_f = 0.22 (05:95 = EtOAc/hexane); yellow solid; mp 132−138 °C; FT-IR (neat) 3433, 3360, 3064, 2888, 2360, 1620, 1496, 1484, 1442, 1269, 1229, 1185, 1163, 1039, 934, 877, 829, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.21 (s, 2H), 7.20 (s, 1H), 6.95 (dd, J = 4.8, 3.6 Hz, 1H), 6.72 (d, J = 3.2 Hz, 1H), 6.34 (s, 1H), 6.28 (s, 1H), 5.82 (d, J = 1.2 Hz, 2H), 5.62 (s, 1H), 3.33 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 142.6, 140.5, 138.6, 128.8, 128.7, 127.0, 126.8, 126.6, 124.9, 121.9, 109.4, 100.6, 98.6, 46.8; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{16}NO_2S$ 310.0902, found 310.0870.

6-(Phenyl(thiophen-2-yl)methyl)-2,3-dihydro-1*H*-inden-5-amine (3p). 0.127 g, 83% yield; R_f = 0.33 (05:95 = EtOAc/hexane); brown solid; mp 80−85 °C; FT-IR (neat)3445, 3361, 3026, 2931, 2859, 2363, 1732, 1626, 1505, 1452, 1266, 1216, 1076, 1045, 777, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 14.0, 7.2 Hz, 3H), 7.25 (dd, J = 13.2, 5.6 Hz, 3H), 6.97 (t, J = 3.6 Hz, 1H), 6.75 (s, 1H), 6.69 (s, 1H), 6.61 (s, 1H), 5.70 (s, 1H), 3.41 (br s, 2H), 2.85 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 7.2 Hz, 2H), 2.07−2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 143.8, 142.9, 142.4, 134.6, 129.0, 128.6, 127.6, 126.9, 126.7, 126.6, 124.8, 124.7, 112.6, 47.3, 32.8, 32.3, 25.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{20}H_{20}NS$ 306.1316, found 306.1330.

4-Bromo-2-fluoro-6-(phenyl(thiophen-2-yl)methyl)aniline (3q). 0.119 g, 66% yield; R_f = 0.31 (05:95 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3452, 3376, 3061, 2924, 2363, 1624, 1475, 1425, 1267, 1228, 1078, 967, 871, 853, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.29 (d, J = 6.8 Hz, 1H), 7.24 (dd, J = 4.8, 0.8 Hz, 1H), 7.18 (d, J = 6.8 Hz, 2H), 7.10 (dd, J = 10, 2.4 Hz, 1H), 6.95 (dd, J = 4.8, 3.6 Hz, 1H), 6.71 (dd, J = 3.2, 2.0 Hz, 2H), 5.62 (s, 1H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ two signals: 152.99 and 150.57 (d, J = 242 Hz), 144.85, 141.02, two signals: 132.81 and 132.78 (d, J = 3 Hz), two signals: 131.98, and 131.85 (d, J = 13 Hz), two signals: 129.20 and 128.43 (d, J = 77 Hz), 128.95, 128.74, 127.56, two signals: 127.34 and 127.31 (d, J = 3 Hz), two signals: 126.99 and 126.98 (d, J = 1 Hz), 125.40, two signals: 117.19 and 116.97 (d, J = 22 Hz), two signals: 108.99 and 108.89 (d, J = 10 Hz), 47.07; HRMS (ESI, m/z) $[M - H]^+$ calculated for $C_{17}H_{12}BrFNS$ 359.9858, found 359.9859.

3,4,5-Trimethoxy-2-(phenyl(thiophen-2-yl)methyl)aniline (3r). 0.144 g, 81% yield; R_f = 0.33 (20:80 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3436, 3357, 2935, 2838, 2116, 1623, 1604, 1495, 1455, 1360, 1299, 1196, 1117, 1033, 998, 823, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.28 (m, 4H), 7.23 (d, J = 7.2 Hz, 1H), 7.20 (dd, J = 5.2, 0.8 Hz, 1H), 6.93 (dd, J = 5.2, 3.6 Hz, 1H), 6.87 (d, J = 3.6 Hz, 1H), 6.24 (s, 1H), 5.99 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.68 (s, 3H), 3.36 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 152.4, 146.8, 142.4, 141.6, 134.7, 128.4, 128.3, 126.6, 126.5, 126.2, 124.5, 114.5, 96.9, 61.1, 61.0, 55.6, 41.9; HRMS (EI, m/z) $[M + H]^+$ calculated for $C_{20}H_{22}NO_3S$ 356.1320, found 356.1341.

3-(Phenyl(thiophen-2-yl)methyl)-9*H*-fluoren-2-amine (3s). 0.138 g, 78% yield; R_f = 0.42 (10:90 = EtOAc/hexane); brown solid; mp 125−130 °C; FT-IR (neat) 3441, 3367, 3060, 2868, 2326, 1625, 1454, 1429, 1281, 1027, 852, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.2 Hz, 2H), 7.37−7.33 (m, 2H), 7.31−7.25 (m, 5H), 7.23 (s, 1H), 7.17 (td, J = 7.6, 0.8 Hz, 1H), 6.99 (dd, J = 4.8, 3.6 Hz, 1H), 6.87 (s, 1H), 6.78 (d, J = 3.6 Hz, 1H), 5.76 (s, 1H), 3.80 (s, 2H), 3.59 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 143.5, 143.4, 142.5, 142.4, 142.2, 133.2, 129.0, 128.7, 128.3, 127.1, 126.85, 126.83, 126.5, 125.1, 124.9, 124.7, 120.7, 118.7, 113.1, 47.4, 36.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{24}H_{20}NS$ 354.1316, found 354.1324.

2-Chloro-4-(9*H*-thioxanthen-9-yl)aniline (6a). 0.132 g, 82% yield; R_f = 0.29 (10:90 = EtOAc/hexane); white solid; mp 138−143 °C FT-IR (neat) 3446, 3384, 3314, 2918, 2368, 1618, 1498, 1292, 1162, 943, 825, 796, 740, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 6.8 Hz, 2H), 7.24−7.21 (m, 4H), 6.85 (s, 1H), 6.68−6.63 (dd, J = 7.6, 0.8 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 5.18 (s, 1H), 3.86 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.2, 133.1, 131.8, 129.4, 128.6, 127.2, 127.1, 126.9, 126.6, 119.1, 115.5, 52.0; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{19}H_{15}ClNS$ 324.0614, found 324.0587.

2-Chloro-4-(9*H*-xanthen-9-yl)aniline (6b). 0.126 g, 82% yield; R_f = 0.27 (10:90 = EtOAc/hexane); white solid; mp 140−143 °C FT-IR (neat) 3446, 3384, 3314, 2900, 2378, 1638, 1498, 1292, 1162, 943, 825, 796, 750, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 2H), 7.10 (dd, J = 7.8, 2.4 Hz, 2H), 7.06 (s, 1H), 7.02 (d, J = 7.6 Hz, 2H), 6.95 (t, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 5.09 (s, 1H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 141.5, 137.6, 129.7, 129.1, 127.9, 127.7, 124.3, 123.2, 119.3, 116.6, 116.1, 43.3; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{19}H_{15}ClNO$ 308.0842, found 308.0824.

4-(Benzo[*b*]thiophen-2-yl(phenyl)methyl)-2-chloroaniline (6c). 0.145 g, 83% yield; R_f = 0.28 (10:90 = EtOAc/hexane); colorless liquid; FT-IR (neat) 3477, 3382, 3030, 2955, 2361, 2325, 1611, 1505, 1456, 1307, 1255, 1166, 1103, 1075, 962, 813, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.36−7.32 (m, 3H), 7.30−7.26 (m, 4H), 7.17 (s, 1H), 6.98 (dd, J = 8.4, 1.6 Hz, 1H), 6.89 (s, 1H), 6.71 (d, J = 8.4 Hz, 1H), 5.61 (s, 1H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.9, 141.7, 140.0, 139.7, 133.9, 129.7, 128.9, 128.5, 128.3, 127.0, 124.2, 123.9, 123.3, 123.1, 122.2, 119.2, 115.8, 51.8; GC-HRMS (EI, m/z) $[M]^+$ calculated for $C_{21}H_{16}ClNS$ 349.0692, found 349.0698.

4-(Benzofuran-2-yl(phenyl)methyl)-2-chloroaniline (6d). 0.130 g, 78% yield; R_f = 0.32 (10:90 = EtOAc/hexane); light yellow

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liquid; FT-IR (neat) 3479, 3384, 3030, 2925, 2360, 2325, 1622, 1505, 1456, 1307, 1255, 1164, 1103, 1073, 962, 813, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 4H), 7.17 (d, J = 2.0 Hz, 1H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.33 (s, 1H), 5.50 (s, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 155.1, 141.8, 141.0, 131.9, 129.6, 128.8, 128.6, 128.4, 128.2, 127.0, 123.8, 122.6, 120.7, 119.3, 115.9, 111.2, 105.6, 50.2; GC-HRMS (EI, m/z) $[M]^+$ calculated for $C_{21}H_{16}ClNO$ 333.0920, found 333.0928.

4-((5-Bromothiophen-2-yl)(phenyl)methyl)-2-chloroaniline (6e). 0.147 g, 78% yield; R_f = 0.33 (10:90 = EtOAc/hexane); yellow liquid; FT-IR (neat) 3385, 3347, 3026, 2359, 1618, 1501, 1450, 1311, 1212, 1157, 1047, 963, 886, 797, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.24 (d, J = 4.8 Hz, 1H), 7.17 (d, J = 7.2 Hz, 2H), 7.06 (d, J = 2 Hz, 1H), 6.88 (dd, J = 8, 2.0 Hz, 1H), 6.86 (d, J = 3.6 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.41 (dd, J = 3.6, 0.8 Hz, 1H), 5.42 (s, 1H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 142.8, 141.7, 133.9, 129.5, 129.4, 128.6, 128.5, 128.0, 127.0, 126.5, 119.2, 115.7, 111.0, 51.3; GC-HRMS (EI, m/z) $[M]^+$ calculated for $C_{17}H_{13}BrClNS$ 376.9641, found 376.9644.

4-((4-Methoxyphenyl)(thiophen-2-yl)methyl)aniline (6f). 0.122 g, 83% yield; R_f = 0.25 (20:80 = EtOAc/hexane); orange solid; mp 105–110 °C; FT-IR (neat) 3444, 3368, 2925, 2854, 2361, 1618, 1458, 1246, 1176, 1108, 1031, 822, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 4.8, 0.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.93 (dd, J = 4.8, 3.6 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 8.4 Hz, 2H), 5.54 (s, 1H), 3.79 (s, 3H), 3.59 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.4, 145.0, 136.7, 134.3, 129.7, 129.6, 126.5, 125.9, 124.2, 115.1, 113.7, 55.2, 50.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{18}NOS$ 296.1109, found 296.1123.

4-Chloro-2-((4-methoxyphenyl)(thiophen-2-yl)methyl)-aniline (6g). 0.135 g, 82% yield; R_f = 0.34 (20:80 = EtOAc/hexane); yellow liquid; FT-IR (neat) 3445, 3369, 3001, 2959, 2931, 2836, 1621, 1583, 1509, 1488, 1440, 1413, 1248, 1178, 1142, 1033, 907, 838, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.2, 1.2 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.03 (dd, J = 8.4, 2.4 Hz, 1H), 6.94 (dd, J = 5.2, 3.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 2.0 Hz, 1H), 6.69 (d, J = 3.6 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.55 (s, 1H), 3.79 (s, 3H), 3.36 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 146.0, 142.5, 133.5, 131.1, 129.8, 128.9, 127.6, 126.9, 126.6, 125.1, 123.7, 117.5, 114.2, 55.2, 46.3; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{18}H_{17}ClNOS$ 330.0719, found 330.0729.

4-((1*H*-Indol-3-yl)(phenyl)methyl)-2-chloroaniline (6h). 0.134 g, 81% yield; R_f = 0.20 (20:80 = EtOAc/hexane); pink liquid; FT-IR (neat) 3419, 3056, 3024, 1620, 1501, 1455, 1094, 742, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.33–7.26 (m, 6H), 7.21–7.16 (m, 3H), 7.03 (t, J = 7.2 Hz, 1H), 6.94 (dd, J = 8.0, 1.2 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 6.53 (s, 1H), 5.57 (s, 1H), 3.93 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.1, 136.7, 135.2, 129.6, 128.9, 128.4, 128.3, 126.9, 126.3, 124.1, 122.1, 119.9, 119.8, 119.4, 119.3, 115.9, 111.1, 47.8; HR-MS (ESI, m/z) $[M + H]^+$ calculated for $C_{21}H_{18}ClN_2$ 333.1159, found 333.1141.

4-((1*H*-Indol-3-yl)(4-methoxyphenyl)methyl)-2-chloroaniline (6i). 0.148 g, 82% yield; R_f = 0.30 (20:80 = EtOAc/hexane); reddish brown solid; mp 67–69 °C; FT-IR (neat) 3416, 3380, 1619, 1508, 1245, 1032, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.29 (dd, J = 11.2, 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.8 Hz, 3H), 7.03 (t, J = 7.2 Hz, 1H), 6.94 (dd, J = 8.2, 1.8 Hz, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 1.3 Hz, 1H), 5.52 (s, 1H), 3.93 (br s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 141.0, 136.7, 136.2, 135.6, 129.8, 129.5, 128.2, 126.9, 123.9, 122.1, 120.1, 119.9, 119.3, 119.2, 115.9, 113.7, 111.1, 55.2, 46.9; HR-MS (ESI, m/z) $[M + H]^+$ calculated for $C_{22}H_{20}ClN_2O$ 363.1264, found 363.1260.

2-Chloro-4-((4-methoxyphenyl)(phenyl)methyl)aniline (6j). 0.098 g, 61% yield; R_f = 0.2 (10:90 = EtOAc/*n*-hexane); yellow liquid; FT-IR (neat) 3472, 3379, 1621, 1507, 1247, 1032, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.30 (t, J = 7.2 Hz, 2H), 7.29–7.22 (1H), 7.14 (d, J = 7.2 Hz, 2H), 7.10–7.00 (3H), 6.94–6.82 (3H), 6.71 (d, J = 8 Hz, 1H), 5.41 (s, 1H), 4.00 (bs, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.2, 141.1, 136.0, 135.4, 130.2, 130.0, 129.2, 128.6, 128.3, 126.3, 119.2, 115.8, 113.7, 55.2, 54.9; HRMS (ESI, m/z) $[M + Na]^+$ calculated for $C_{20}H_{19}ClNO$ 324.1155, found 324.1155.

4-Chloro-2-((4-methoxyphenyl)(phenyl)methyl)aniline (6k). 0.098 g, 61% yield; R_f = 0.43 (10:90 = EtOAc/*n*-hexane); light yellow liquid; FT-IR (neat) 3504, 3411, 3081, 3028, 1635, 1598, 1492, 1462, 1325, 1281, 1244, 1174, 1112, 1072, 1030, 973, 852, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.26–7.22 (m, 1H), 7.09 (d, J = 6.8 Hz, 2H), 7.04–7.00 (m, 3H), 6.84 (d, J = 8.4 Hz, 2H), 6.61–6.59 (2H), 5.36 (s, 1H), 3.79 (s, 3H), 3.45 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 142.7, 142.0, 133.6, 131.2, 130.3, 129.6, 129.34, 128.7, 127.2, 126.9, 123.5, 117.3, 114.1, 55.2, 51.3; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{20}H_{19}ClNO$ 324.1155, found 324.1151.

2-(Bis(4-methoxyphenyl)methyl)-4-chloroaniline (6l). 0.145 g, 82% yield; R_f = 0.37 (10:90 = EtOAc/hexane); brown liquid; FT-IR (neat) 3449, 3371, 3001, 2955, 2836, 1610, 1582, 1509, 1488, 1464, 1411, 1302, 1282, 1247, 1177, 1141, 1111, 1033, 909, 873, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 8.4 Hz, 5H), 6.84 (d, J = 8.4 Hz, 4H), 6.62 (d, J = 2.0 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 5.31 (s, 1H), 3.78 (s, 6H), 3.41 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 142.7, 134.0, 131.5, 130.3, 129.5, 127.2, 123.4, 117.3, 114.1, 55.2, 50.5; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{21}H_{21}ClNO_2$ 354.1261, found 354.1257.

4-Chloro-2-((3,4-dimethoxyphenyl)(4-methoxyphenyl)-methyl)aniline (6m). 0.155 g, 81% yield; R_f = 0.38 (40:60 = EtOAc/hexane); brown solid; mp 50–55 °C; FT-IR (neat) 3447, 3368, 3000, 2934, 2835, 1609, 1509, 1489, 1464, 1412, 1248, 1177, 1139, 1110, 1028, 954, 907, 814, 782, 757, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.4 Hz, 3H), 6.83 (d, J = 88 Hz, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.62 (dd, J = 13.2, 2.0 Hz, 2H), 6.56 (d, J = 8.4 Hz, 2H), 5.28 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.43 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 149.1, 147.8, 142.9, 134.5, 133.8, 131.4, 130.2, 129.4, 127.2, 123.3, 121.3, 117.2, 114.1, 112.6, 111.1, 55.86, 55.86, 55.2, 50.9; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{22}H_{22}ClNNaO_3$ 406.1186, found 406.1180.

2-((2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)(4-methoxyphenyl)-methyl)-4-methoxyaniline (6n). 0.128 g, 68% yield; R_f = 0.26 (20:80 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3428, 3358, 2984, 2934, 2835, 2364, 1737, 1610, 1509, 1465, 1401, 1370, 1328, 1248, 1158, 1117, 1063, 1037, 892, 837, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.76 (2H), 6.63–6.56 (m, 3H), 6.30 (s, 1H), 5.32 (s, 1H), 4.21 (s, 4H), 3.77 (s, 3H), 3.62 (s, 3H). 3.44 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.9, 143.4, 142.2, 137.3, 135.9, 134.4, 131.9, 130.3, 122.4, 118.1, 117.2, 116.7, 114.8, 113.9, 111.6, 64.33, 64.31, 55.5, 55.2, 50.7; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{23}H_{24}NO_4$ 378.1705, found 378.1686.

4-Chloro-2-((4-methoxyphenyl)(naphthalen-2-yl)methyl)-aniline (6o). 0.125 g, 67% yield; R_f = 0.37 (20:80 = EtOAc/hexane); yellowish oil; FT-IR (neat) 3448, 3371, 3054, 2931, 2835, 2366, 1621, 1610, 1508, 1488, 1412, 1301, 1248, 1178, 1143, 1109, 1033, 961, 909, 818, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83–7.80 (m, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.72–7.70 (m, 1H), 7.46–7.44 (m, 3H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H), 7.06 (d, J = 8.8 Hz, 3H), 6.86 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 2.4 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 5.53 (s, 1H), 3.80 (s, 3H), 3.55 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.6, 139.5, 133.49, 133.43, 132.4, 131.1, 130.5, 129.7, 128.4, 127.9, 127.8, 127.65, 127.60, 127.4, 126.2, 125.9, 123.7, 117.5, 114.1, 55.2, 51.4; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{24}H_{21}ClNO$ 374.1312, found 374.1290.

4-Methoxy-2-(1-(4-methoxyphenyl)ethyl)aniline (6p).[4c–f] 0.081 g, 63% yield; R_f = 0.21 (20:80 = EtOAc/hexane); dark brown semi solid; FT-IR (neat) 3514, 3411, 3083, 3029, 1635, 1598, 1492, 1462, 1325, 1281, 1244, 1174, 1112, 1078, 1030, 973, 890, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 2.8 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.73–6.69 (1H), 6.65 (dd, J =

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8.4, 2.8 Hz, 1H), 4.10 (q, J = 7.2 Hz, 1H), 3.99−3.22 (broad, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.8, 137.1, 135.8, 133.4, 128.4, 118.1, 114.17, 114.11, 111.5, 55.6, 55.2, 39.3, 21.9; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{16}H_{20}NO_2$ 258.1494, found 258.1474.

2-Chloro-4-(1-(thiophen-2-yl)ethyl)aniline (6q). 0.104 g, 88% yield; R_f = 0.37 (10:90 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3464, 3379, 2967, 2932, 2878, 1888, 1620, 1504, 1454, 1415, 1312, 1281, 1230, 1152, 1045, 870, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 1.6 Hz, 1H), 7.16 (dd, J = 5.2, 0.8 Hz, 1H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 6.94 (dd, J = 5.2, 3.6 Hz, 1H), 6.81 (d, J = 3.2 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 4.24 (q, J = 7.1 Hz, 1H), 4.01 (br s, 2H), 1.67 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 141.3, 137.2, 128.1, 126.65, 126.62, 123.6, 123.5, 119.3, 116.0, 39.7, 23.4; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{12}H_{13}ClNS$ 238.0457, found 238.0471.

2-Chloro-4-(2-methyl-1-(thiophen-2-yl)propyl)aniline (6r). 0.070 g, 53% yield; R_f = 0.40 (05:95 = EtOAc/hexane); brown liquid; FT-IR (neat) 3475, 3384, 3028, 2958, 2928, 2870, 2365, 1622, 1505, 1467, 1418, 1386, 1367, 1310, 1282, 1196, 1159, 1045, 948, 882, 853, 818, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 1.6 Hz, 1H), 7.10 (d, J = 5.2 Hz, 1H), 6.99 (dd, J = 8.4, 2.0 Hz, 1H), 6.88 (dd, J = 4.8, 3.6 Hz, 1H), 6.84 (d, J = 2.8 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 3.91 (s, 2H), 3.59 (d, J = 9.6 Hz, 1H), 2.32−2.23 (m, 1H), 0.93 (d, J = 6.4 Hz, 3H), 0.84 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.1, 135.3, 128.8, 127.2, 126.4, 123.8, 123.2, 119.1, 115.9, 54.4, 34.2, 21.8, 21.4; GC-HRMS (EI, m/z) $[M]^+$ calculated for $C_{14}H_{16}ClNS$ 265.0692, found 265.0692.

2-Chloro-4-(1-(thiophen-2-yl)but-3-en-1-yl)aniline (6s). 0.095 g, 72% yield; R_f = 0.32 (10:90 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3472, 3382, 3076, 2919, 2848, 1616, 1504, 1428, 1310, 1200, 1156, 1044, 989, 914, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 4.0, 2.0 Hz, 2H), 6.95 (dd, J = 8.4, 2.0 Hz, 1H), 6.91 (dd, J = 4.8, 3.2 Hz, 1H), 6.81 (d, J = 3.2 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.76−5.65 (m, 1H), 5.04 (dd, J = 17.2, 1.6 Hz, 1H), 4.98 (dd, J = 10.4, 0.8 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.95 (br s, 2H), 2.86−2.78 (m, 1H), 2.75−2.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.4, 136.1, 135.1, 128.5, 127.0, 126.5, 123.8, 123.6, 119.2, 116.8, 115.9, 45.7, 41.5; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{14}H_{14}ClNS$ 264.0614, found 264.0596.

2-Chloro-4-(1-(furan-2-yl)propyl)aniline (6t). 0.066 g, 56% yield; R_f = 0.42 (10:90 = EtOAc/hexane); light yellow liquid; IR (neat) 3475, 3385, 2964, 2931, 2874, 1623, 1505, 1458, 1419, 1310, 1147, 1046, 1010, 939, 884, 806 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 0.8 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 8.4, 2.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.27 (dd, J = 2.8, 2.0 Hz, 1H), 6.03 (d, J = 3.2 Hz, 1H), 3.93 (br s, 2H), 3.68 (t, J = 7.6 Hz, 1H), 2.10−2.01 (m, 1H), 1.88−1.77 (m, 1H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 141.3, 141.2, 133.7, 128.6, 127.1, 119.2, 115.9, 109.9, 105.1, 46.0, 27.7, 12.3; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{13}H_{15}ClNO$ 236.0842, found 236.0838.

4-Methoxy-2-(thiophen-2-ylmethyl)aniline (6u). 0.066 g, 60% yield; R_f = 0.34 (20:80 = EtOAc/hexane); brown solid; mp 50−55 °C; FT-IR (neat) 3445, 3369, 3001, 2959, 2931, 2836, 1621, 1583, 1509, 1488, 1440, 1413, 1248, 1178, 1142, 1033, 907, 838, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 5.2, 0.8 Hz, 1H), 6.91 (dd, J = 5.2, 3.6 Hz, 1H), 6.80 (dd, J = 3.2, 0.8 Hz, 1H), 6.72 (1H), 6.68 (d, J = 2.8 Hz, 1H), 6.64(1H), 4.04 (s, 2H), 3.74 (s, 3H), 3.20 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 142.6, 137.9, 126.9, 126.6, 125.1, 124.2, 117.4, 116.2, 113.2, 55.7, 32.7; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{12}H_{14}NOS$ 220.0796, found 220.0791.

***tert*-Butyl 2-(4-Amino-3-chlorobenzyl)-1*H*-pyrrole-1-carboxylate (6v).** 0.089 g, 58% yield; R_f = 0.35 (10:90 = EtOAc/hexane); clear liquid; FT-IR (neat) 3474, 3381, 2980, 2932, 1738, 1624, 1505, 1457, 1406, 1370, 1324, 1258, 1234, 1159, 1123, 1061, 1013, 931, 893, 847 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 3.2, 2.0 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 6.87 (dd, J = 8.0, 1.6 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.06 (t, J = 3.6 Hz, 1H), 5.76 (d, J = 0.8 Hz, 1H), 4.07 (s, 2H), 3.93 (br s, 2H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 140.9, 134.5, 130.7, 129.5, 128.1, 121.3, 119.1, 115.8, 112.9, 109.9, 83.5, 33.9, 27.9; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{16}H_{20}ClN_2O_2$ 307.1213, found 307.1205.

2-Chloro-4-(2-methoxybenzyl)aniline (6w). 0.051 g, 41% yield; R_f = 0.25 (10:90 = EtOAc/hexane); light brown liquid; FT-IR (neat) 3504, 3421, 3081, 3028, 1635, 1588, 1492, 1462, 1366, 1281, 1244, 1174, 1155, 1072, 1040, 973, 852, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, J = 8.0, 1.6 Hz, 1H), 7.09 (d, J = 1.6 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 6.90 (dd, J = 8.4, 1.6 Hz, 1H), 6.85 (dd, J = 7.6, 2.4 Hz, 2H), 6.66 (d, J = 8.0 Hz, 1H), 3.89 (br s, 2H), 3.83 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 140.7, 132.0, 130.1, 129.69, 129.63, 128.2, 127.4, 120.5, 119.2, 115.8, 110.4, 55.3, 34.7; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{14}H_{15}ClNO$: 248.0842, found 248.0853.

2-Chloro-4-(4-methoxybenzyl)aniline (6x). 0.081 g, 65% yield; R_f = 0.31 (10:90 = EtOAc/hexane); light brown liquid; FT-IR (neat) 3504, 3411, 3081, 3028, 1635, 1598, 1492, 1462, 1325, 1281, 1244, 1174, 1112, 1072, 1030, 973, 852, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09−7.05 (m, 3H), 6.87 (dd, J = 8.0, 1.6 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.4 Hz, 1H), 3.82 (br s, 2H), 3.79 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 140.9, 133.3, 132.6, 129.7, 129.5, 128.0, 119.3, 116.0, 113.9, 55.2, 39.8; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{14}H_{15}ClNO$ 248.0842, found 248.0853.

***(E)*-2-(1,3-Diphenylallyl)-4-nitroaniline (8a).** 0.129 g, 78% yield; R_f = 0.20 (10:90 = EtOAc/hexane); yellow liquid; FT-IR (neat) 3485, 3387, 1626, 1490, 1302, 972 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.00 (2H), 7.55−7.20 (10H), 6.75−6.60 (2H), 6.37 (d, J = 16 Hz, 1H), 4.85 (d, J = 7.2 Hz, 1H), 4.33 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 140.0, 139.3, 136.5, 132.8, 129.3, 129.2, 128.6, 128.5, 127.8, 127.5, 126.7, 126.5, 125.8, 124.6, 114.9, 49.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_2$ 331.1447, found 331.1445.

***(E)*-Ethyl 4-Amino-3-(1,3-diphenylallyl)benzoate (8b).** 0.128 g, 71% yield; R_f = 0.30 (10:90 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3476, 3375, 1693, 1624, 1603, 1279, 1106, 1027, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.75 (2H), 7.55−7.15 (10H), 6.85−6.70 (2H), 6.36 (d, J = 16 Hz, 1H), 4.87 (d, J = 7.2 Hz, 1H), 4.33 (q, J = 6.8 Hz, 2H), 3.97 (bs, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.7, 141.1, 137.0, 132.0, 131.5, 131.3, 130.4, 129.8, 128.9, 128.6, 128.5, 127.5, 127.1, 126.7, 126.4, 120.3, 115.3, 113.7, 60.4, 49.8, 14.4; LRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{24}H_{24}NO_2$ 358.1807, found 358.1832.

***(E)*-4-Amino-3-(1,3-diphenylallyl)benzonitrile (8c).**[13a] 0.111 g, 65% yield; R_f = 0.37 (20:80 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3480, 3377, 3060, 3028, 2217, 1733, 1626, 1602, 1504, 1450, 1424, 1307, 1266, 1210, 1161, 1030, 973, 745, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (9H), 7.26−7.20 (3H), 6.65 (d, J = 8.4 Hz, 1H), 6.58 (dd, J = 16.0, 7.2 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 4.79 (d, J = 6.8 Hz, 1H), 4.07 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.2, 136.5, 133.4, 132.6, 132.0, 129.5, 129.1, 128.68, 128.66, 127.8, 127.7, 127.4, 126.4, 120.3, 115.8, 100.6, 49.2; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{22}H_{19}N_2$ 311.1548, found 311.1524.

***(E)*-2-(1,3-Diphenylallyl)-4-(trifluoromethyl)aniline (8d).**[13a] 0.120 g, 68% yield; R_f = 0.3 (10:90 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3476, 3391, 2925, 1627, 1328, 1111, 746, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.22 (12H), 6.80−6.66 (2H), 6.39 (dd, J = 0.8 Hz and 16 Hz, 1H), 4.92 (d, J = 6.8 Hz, 1H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 140.8, 136.8, 132.3, 130.1, 129.0, 128.7, 128.6, 127.7, 127.4, 127.2, 126.5, 126.3 (q, J = 3.7 Hz), 125.0 (q, J = 3.7 Hz), 120.3 (q, J = 32.2 Hz), 115.7, 49.7; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{22}H_{19}F_3N$ 354.1470, found 354.1495.

***(E)*-2-(1,3-Diphenylallyl)-4-fluoroaniline (8e).**[13a] 0.114 g, 75% yield; R_f = 0.30 (10:90 = EtOAc/hexane); light yellow liquid; FT-IR (neat) 3437, 3367, 1625, 1496, 1257, 964 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.15 (10H), 6.85−6.65 (2H), 6.63−6.50 (2H), 6.26 (dd, J = 0.8 and 16 Hz, 1H), 4.84 (d, J = 6.8 Hz, 1H), 3.39 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8 and 155.4 (d, J = 235 Hz), 141.1, 140.3, 140.2, 136.9, 132.0, 130.6, 130.0, and 129.9 (d, J = 6.3

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Hz), 128.9, 128.8, 128.6, 127.6, 127.1, 126.4, 117.3, and 117.2 (d, J = 7.6 Hz), 115.9 and 115.7 (d, J = 23.2 Hz), 114.0 and 113.8 (d, J = 22.1 Hz), 49.4; HR-MS (ESI, m/z) $[M + H]^+$ calculated for $C_{21}H_{19}NF$ 304.1496, found 304.1486.

(*E*)-2-(1,3-Diphenylallyl)-4-methylaniline (8f).[13a] 0.109 g, 73% yield; R_f = 0.2 (2:98 = EtOAc/hexane); orange liquid; FT-IR (neat) 3436, 3362, 3025, 1623, 1503, 1449, 1281, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.12 (10H), 6.99 (s, 2H), 6.76 (dd, J = 7.2 and 16 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.36 (d, J = 16 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 3.48 (bs, 2H), 2.31 (s, 3H), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.7, 137.2, 131.6, 131.4, 129.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 127.4, 126.8, 126.4, 116.7, 49.6, 20.7; HR-MS (ESI, m/z) $[M + H]^+$ calculated for $C_{22}H_{22}N$ 300.1752, found 300.1764.

2-(1,3-Diphenylprop-2-yn-1-yl)-4-methylaniline (8g). 0.107 g, 72% yield; R_f = 0.34 (10:90 = EtOAc/hexane); dark brown liquid; FT-IR (neat) 3436, 3367, 3025, 2922, 2857, 1624, 1601, 1505, 1491, 1449, 1279, 1155, 1071, 1029, 915, 815, 756, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 4H), 7.35−7.31 (m,2H), 7.29−7.26 (m,4H), 7.08 (s, 1H), 6.93 (dd, J = 8.0, 1.6 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 3.48 (br s, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.6, 131.7, 130.1, 128.8, 128.7, 128.3, 128.2, 128.0, 127.9, 127.1, 125.8, 123.3, 117.1, 88.9, 85.1, 40.1, 20.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{24}H_{24}N$ 326.1909, found 326.1922.

2-(1,3-Di-*p*-tolylprop-2-yn-1-yl)-4-methylaniline (8h). 0.097 g, 60% yield; R_f = 0.32 (10:90 = EtOAc/hexane); yellowish brown liquid; FT-IR (neat) 3437, 3364, 3025, 2919, 2852, 2361, 1627, 1607, 1509, 1455, 1414, 1266, 1208, 1181, 1111, 1021, 816, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 4H), 7.13−7.07 (m, 5H), 6.92 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 5.19 (s, 1H), 3.62 (br s, 2H), 2.32 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.6, 131.6, 130.1, 129.3, 128.9, 128.6, 127.8, 120.3, 120.2, 117.3, 88.3, 85.0, 39.8, 21.4, 21.0, 20.6; HRMS (ESI, m/z) $[M + H]^+$ calculated for $C_{24}H_{24}N$ 326.1909, found 326.1922.

(*S*)-1-(Thiophen-2-yl)ethanol [(−)-7].[17] This chiral alcohol was prepared according to the reported ketone reduction protocol using CBS-catalyst.[18] Procedure: To a borane-methylsulfide complex (BMS) solution (0.19 mL, 1.2 mmol) was added (*R*)-MeCBS in toluene (0.1 mL of 1.0 M, 0.1 mmol). After stirring the BMS/MeCBS reaction mixture for 10 min, 2-acetylthiophenone (0.252 g, 2.0 mmol) in THF (2 mL) was then slowly added to the reaction flask at 0 °C over 30 min. After completing the addition of 2-acetylthiophenone, the reaction solution was allowed to stir for 10 min before being quenched with a solution of HCl in H_2O (1 mL of 2 M, 2 mmol). Diethyl ether (5 mL) was added, and the organic phase was washed with saturated aqueous solutions of $NaHCO_3$ (3 × 1.5 mL) and KCl (3 × 1 mL). The organic phase was then dried over Na_2SO_4 and then was evaporated in vacuo. The crude was purified by flash column chromatography on silica gel using *n*-hexane/ethyl acetate (95:5) as solvent to afford (−)-7: 0.109 g, 85% yield; R_f = 0.21 (10:90 = EtOAc/hexane); volatile brown oil; FT-IR (neat) 3340, 3025, 2919, 1515, 1200, 1181, 1111, 1021, 816, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 4.8, 1.2 Hz, 1H), 6.97−6.92 (m, 2H), 5.11 (q, J = 6.4 Hz, 1H), 2.07 (br s, 1H), 1.58 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 126.6, 124.4, 123.2, 66.2, 25.2; LRMS (ESI, m/z) $[M + Na]^+$ calculated for C_6H_8NaOS 151.0194, found 151.1124; $[\alpha]^{20}_D$ = −7.0 (c 0.20, $CHCl_3$, 71% ee).

The enantiomeric ratio was determined by HPLC analysis using Phenomenex Lux 5u cellulose-1 column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 27.61 min (major), t_R = 25.45 min (minor).

2-Chloro-4-(1-(thiophen-2-yl)ethyl)aniline (6q). The enantiomeric ratio was determined by HPLC analysis using Diacel Chiralpak IC-3 column, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 20.43 min, t_R = 16.88 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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