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# Copper-Catalyzed Aza-Michael Addition of Aromatic Amines or Aromatic Aza-Heterocycles to α,β-Unsaturated Olefins

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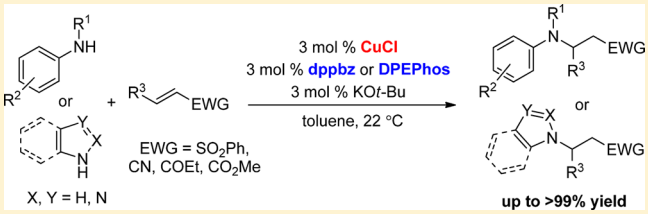
Supporting Information

**ABSTRACT:** A highly efficient and mild Cu-catalyzed conjugate addition reaction of aromatic amines and aromatic aza-heterocycles to α,β-unsaturated olefins is described. The transformation is promoted by 3−7 mol % of a Cu complex generated in situ from a mixture of inexpensive CuCl, a readily available phosphine or imidazolium salt, and KO*t*-Bu at ambient temperature. A wide range of β-amino sulfone, β-amino nitrile, and β-amino carbonyl compounds is efficiently and selectively synthesized in high yields (62−99%).




## INTRODUCTION

The development of synthetic approaches to β-amino sulfone, β-amino nitrile, and β-amino carbonyl compounds bearing aromatic amine or aromatic aza-heterocycle substituents has received great attention because of its numerous synthetic applications to diverse natural products, drugs, and functional materials.[1] The direct addition of (hetero)aryl amines to α,β-unsaturated olefins (aza-Michael reaction) is one of the simplest and most effective strategies to prepare β-amino carbonyls with high atom economy from readily available starting materials.[2] Traditionally, aza-Michael reactions proceed under strongly acidic or basic conditions; however, several challenging issues remain.[3] For example, high temperatures and long reaction times are required. Such reactions exhibit poor compatibility with various substrate functional groups and generate side products, e.g., polymeric compounds, due to the use of a strong base. Furthermore, these methods are limited in substrate scope to aliphatic amine additions. In order to overcome these limitations, a variety of Lewis acid metal catalysts, including early- and late-transition metals as well as lanthanides, have been intensively developed and used to efficiently catalyze the conjugate addition of aromatic amines to electron-deficient olefins under mild conditions.[4−6] Despite great advances in metal-catalyzed aza-Michael additions, there are still shortcomings for their practical utility; namely, the use of expensive precious metals, the use of air- and moisture-sensitive metal catalysts, and the less efficiency for the addition of less nucleophilic aryl amines or aza-heterocycles vs aliphatic amine addition. Over the past decades, reaction conditions using ionic liquids or water as solvents have been successfully developed and partially addressed the above-described drawbacks.[7,8]

Among the numerous protocols involving aza-Michael additions, copper-catalyzed processes are particularly attractive due to ease of handling, the use of environmentally benign and low cost copper salts, and mild reaction conditions. Although Cu-catalyzed Michael additions of carbon-based nucleophiles to α,β-unsaturated alkenes for the formation of carbon−carbon bonds are well studied,[9] the corresponding aza-Michael addition of (hetero)aromatic amines has received less attention.[10] In most previous studies, a Cu catalyst such as $Cu(OTf)_2$ has been used as a Lewis acid to activate an alkene by increasing its electrophilicity.[10] In contrast, Cu-catalyzed systems using an electron-donating ligand to activate an amine by enhancing its nucleophilicity are rare.[11] One example was reported by Gunnoe and co-workers: the well-defined copper amido complex **L13**, coordinated to an electron-rich *N*-heterocyclic carbene (NHC) ligand,[12] catalyzes the conjugate addition of aniline to activated olefins, affording the desired β-amino carbonyls under mild conditions [Scheme 1 (a)].[11] However, several synthetic steps are required for the preparation of the catalyst NHC-Cu-NHPh **L13**, and glovebox techniques are required for the overall process as the catalyst is highly air- and moisture-sensitive. Additionally, the transformations were only carried out in $C_6D_6$ solvent without isolation of products; the substrate scope was not examined in detail. Therefore, there is still a need for a more practical and synthetically useful method for the synthesis of β-aryl amine- or β-aza-heterocycle-substituted sulfone, nitrile, and carbonyl compounds.

Herein we describe a highly efficient and mild Cu-catalyzed aza-Michael addition of various weak nucleophilic aromatic amines and aza-heterocycles to α,β-unsaturated olefins. The use of inexpensive CuCl, commercially available phosphine or imidazolium salts, and KO*t*-Bu to generate a Cu-amido catalyst in situ is an attractive feature of this method, and the catalytic transformation can be performed on a benchtop without the use of glovebox techniques. A broad range of (hetero)aryl amine substrates including aniline, indole, carbazole, pyrrole,

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**Scheme 1. Cu-Catalyzed Aza-Michael Additions of Aromatic Amines**

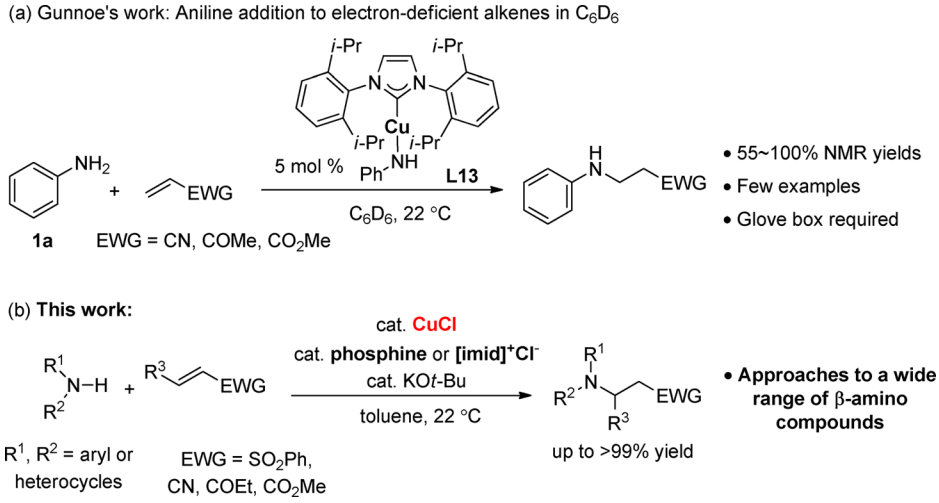
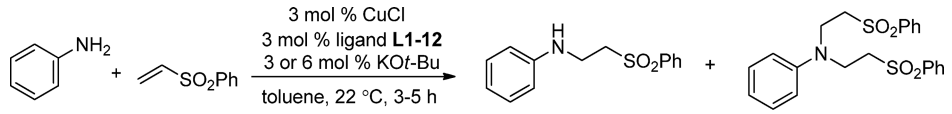



**Table 1. Optimization of the Cu-Catalyzed Aza-Michael Addition Reaction of Aniline 1a to Alkenyl Sulfone 2**[a]




**1a** **2** **3a** **4a**

| entry | ligands | CuCl (mol %) | KO*t*-Bu (mol %) | time (h) | yield (%)[b] | **3a**:**4**[b] |
|---|---|---|---|---|---|---|
| 1 | **L1** | 3 | 6 | 3 | 82 | 76:6 |
| 2 | **L1** | 3 | 6 | 5 | >98 | 89:11 |
| 3 | **L2** | 3 | 6 | 5 | 95 | 95:0 |
| 4 | **L3** | 3 | 6 | 3 | >98 | 97:3 |
| 5 | **L4** | 3 | 3 | 3 | 76 | 73:3 |
| 6 | **L5** | 3 | 3 | 3 | 66 | 63:3 |
| 7 | **L6** | 3 | 3 | 3 | 98 | 83:15 |
| 8 | **L7** | 3 | 3 | 3 | >98 | 89:11 |
| 9 | **L8** | 3 | 3 | 3 | >98 | 76:24 |
| 10 | **L9** | 3 | 3 | 3 | 76 | 76:0 |
| 11 | **L10** | 3 | 3 | 3 | >98 | >98:<2 |
| 12 | **L11** | 3 | 3 | 3 | >98 | >98:<2 |
| 13 | **L12** | 3 | 3 | 3 | >98 | >98:<2 |
| 14 | **L10** | 3 | 0 | 3 | <2 | <2 |
| 15 | **L10** | 0 | 0 | 3 | <2 | <2 |
| 16 | no | 3 | 3 | 3 | <2 | <2 |
| 17 | no | 0 | 3 | 3 | <2 | <2 |
| 18 | no | 3 | 0 | 3 | <2 | <2 |

[a]Reaction conditions: aniline **1a** (0.60 mmol), vinyl sulfone **2** (0.50 mmol), CuCl (0.015 mmol), ligand (0.015 mmol), KO*t*-Bu (0.015 mmol), toluene (1.5 mL) under $N_2$. [b]Determined by $^1$H NMR spectrum analysis using 1,3,5-trimethoxybenzene as an internal standard.

imidazole, pyrazole, and triazole derivatives is converted to the desired *β*-amino compounds with a catalyst loading of 3−7 mol % at ambient temperature and in isolated yields of up to >99%.

## RESULTS AND DISCUSSION

We began by examining the ability of *N*-heterocyclic carbene- or phosphine-based copper catalysts to promote the aza-Michael addition of aniline (**1a**) to phenyl vinyl sulfone (**2**). Inspired by previous studies of NHC-Cu-NHPh **L13** (Scheme 1), we investigated catalytic conjugate additions using a copper complex generated in situ from air- and moisture stable and readily available imidazolium salts, CuCl, and KO*t*-Bu without the use of glovebox techniques (entries 1−4 in Table 1). When 3 mol % of imidazolinium salt **L1** and CuCl in the presence of 6 mol % KO*t*-Bu were used, the reaction of 1.2 equiv of **1a** at room temperature proceeded to full conversion in 5 h, providing the desired product **3a**; however, the undesired dialkylated product **4a** was also obtained in 11% yield (entry 2). Amination using the more sterically demanding ligand **L2** afforded only the desired product **3a** with 95% conversion (entry 3). Use of 3 mol % of the cyclohexyl-substituted imidazolium salt **L3** led to complete conversion in 3 h; however, 3% of the undesired product **4a** was also formed (entry 4). In order to search for a more efficient catalytic system, various phosphine-based ligands were examined (entries 5−13). As shown in entries 5−13 of Table 1, the copper catalyst coordinated with bidentate phosphine ligands (**L6**−**L12** in Figure 1)[13] was more reactive than that with



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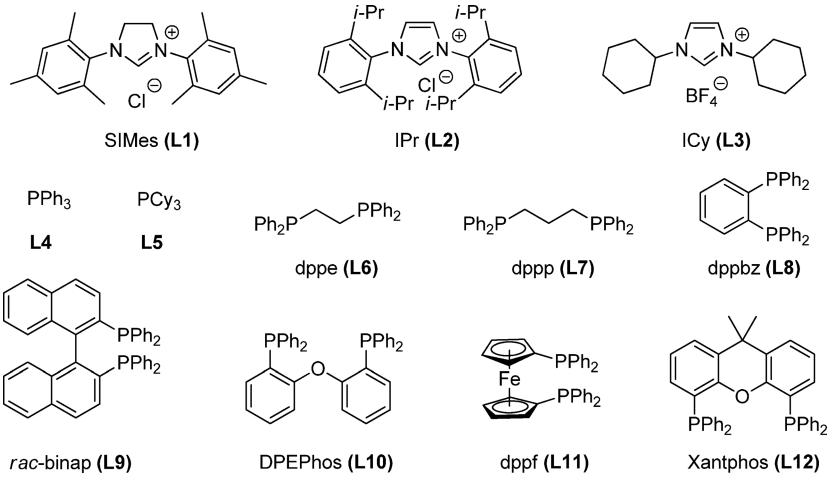
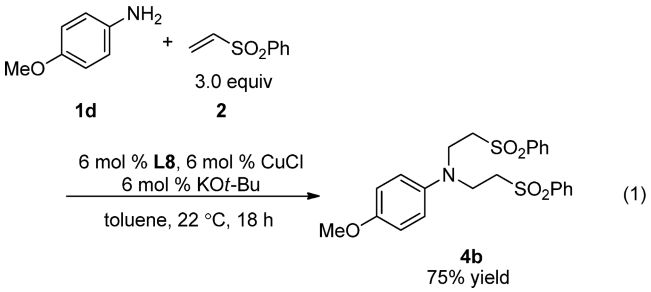



**Figure 1.** Various ligands studied for conjugate addition reactions.

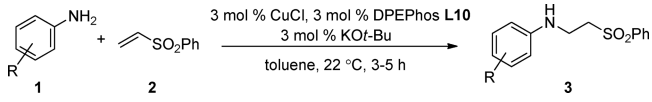
monodentate phosphines (**L4** and **L5** in Figure 1), affording **3a** with higher conversion (up to >98% vs 66−77%). In addition, bidentate phosphine ligands with a larger bite angle such as binap **L9**, DPEPhos **L10**, dppf **L11** and Xantphos **L12** were more selective for the formation of the monoaminated product **3a** (>98:<2) than dppe **L6**, dppp **L7** and dppbz **L8** (76:24−89:11).[14] These results are consistent with the proposal that an NHC-Cu catalyst with a more sterically demanding ligand is more selective for monoamination. It was noteworthy that the use of 3 equiv of phenyl vinyl sulfone with 6 mol % CuCl and the ligand dppbz provided the dialkylated amine product **4b** in 75% yield (eq 1). Entries 14−18 of Table 1 indicate that CuCl,

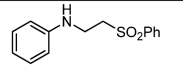
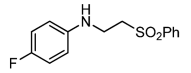
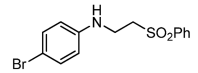
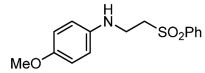
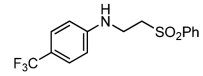
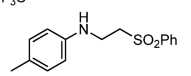
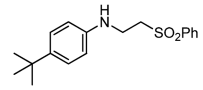
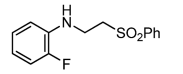
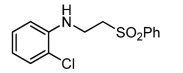
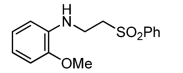
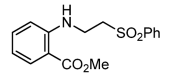
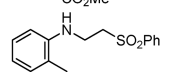



an electron-donating ligand, and KO*t*-Bu are required to promote aniline addition to phenyl vinyl sulfone (**2**). When 3 mol % of CuCl and DPEPhos in the absence of KO*t*-Bu were used, no reaction was observed (entry 14). Additionally, without phosphine ligand or Cu salt, amination did not proceed (<2% conversion, entries 15−18). Based on these results, it can be postulated that a CuO*t*-Bu intermediate complexed with an electron-donating bidentate phosphine ligand is generated and subsequently reacts with aniline to form a phosphine-Cu-amido complex in situ as the catalytic species. Electron-donating ligands appear to enhance the nucleophilic attack of aromatic amines toward electron deficient alkenes.[15] Finally, we selected DPEPhos **L10** as the optimal ligand for the conjugate addition of anilines to **2**, taking into account the cost and efficiency of bidentate phosphines as summarized in entries 7−13.

The Cu-catalyzed aza-Michael addition reaction can be successfully performed with a variety of anilines, as shown in Table 2. All transformations were selective and efficient: >98% conversion was observed in 3−6 h using a combination of 3 mol % CuCl and DPEPhos **L10** with KO*t*-Bu, affording only monoaminated products in excellent yield (90−99%). The additions were carried out in toluene at ambient temperature. Catalytic reactions of **2** with anilines including a fluoro-, chloro-, and bromo-substituent in the *para*- or *ortho*-position

**Table 2. Cu-Catalyzed Aza-Michael Addition Reactions of Various Anilines**[a]




| entry | products | | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 |  | **3a** | 3 | 99 |
| 2 |  | **3b** | 3 | 98 |
| 3 |  | **3c** | 4 | 97 |
| 4 |  | **3d** | 3 | >99 |
| 5 |  | **3e** | 5 | 98 |
| 6 |  | **3f** | 3 | 90 |
| 7 |  | **3g** | 3 | 93 |
| 8 |  | **3h** | 6 | >99 |
| 9 |  | **3i** | 3 | 99 |
| 10 |  | **3j** | 3 | 98 |
| 11 |  | **3k** | 5 | 96 |
| 12 |  | **3l** | 5 | 99 |

[a]Reaction conditions: aniline **1** (0.60 mmol), vinyl sulfone **2** (0.50 mmol), CuCl (3 mol %), DPEPhos (**L10**, 3 mol %), KO*t*-Bu (3 mol %), toluene (1.5 mL) under $N_2$. [b]Yields of the isolated products.



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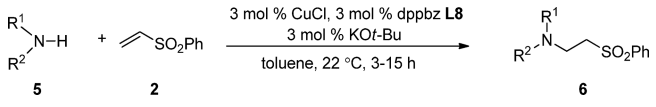
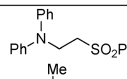
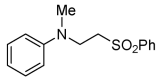
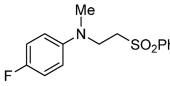
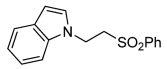
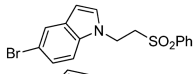
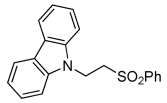
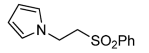
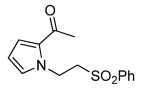
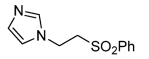
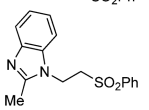
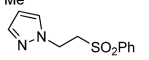
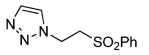
were highly efficient and afforded the desired products **3b,c** and **3h–i** in more than 97% yield (entries 2–3 and 8–9). Neither electron-donating (methoxy, methyl, *tert*-butyl) nor electron-withdrawing ($CF_3$, $CO_2Me$) groups in the *para*- or *ortho*-position of the aryl ring affected the high reactivity observed (90–99% yields, entries 4–7 and 10–12).[16] When the sterically demanding aniline **1l** was used, the corresponding aminated product **3l** was obtained in 99% yield (entry 12).

We next explored Cu-catalyzed aza-Michael addition reactions of a wide range of readily available *N*-substituted aromatic amines and aza-heterocycles such as methyl aniline, indole, carbazole, pyrrole, imidazole, pyrazole, and triazole derivatives. As the data in Table 3 illustrate, dppbz **L8** is more

**Table 3. Cu-Catalyzed Aza-Michael Addition Reactions with Substituted Aromatic Amines**[a]




5 2 6

| entry | products | | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 |  | **6a** | 3 | 92 |
| 2 |  | **6b** | 3 | 94 |
| 3 |  | **6c** | 3 | 96 |
| 4 |  | **6d** | 3 | 98 |
| 5 |  | **6e** | 3 | 94 |
| 6 |  | **6f** | 3 | 98 |
| 7 |  | **6g** | 3 | 84 |
| 8 |  | **6h** | 5 | 98 |
| 9 |  | **6i** | 3 | >99 |
| 10 |  | **6j** | 5 | >99 |
| 11[c] |  | **6k** | 15 | 90 |
| 12 |  | **6l** | 15 | 54 |

[a]Reaction conditions: **5** (0.60 mmol), vinyl sulfone **2** (0.50 mmol), CuCl (3 mol %), dppbz (**L8**, 3 mol %), KO*t*-Bu (3 mol %), toluene (1.5 mL) under $N_2$. [b]Yields of the isolated products. [c]6 mol % of dppbz (**L8**, 0.030 mmol) used.

effective than DPEPhos **L10** as a ligand for promoting additions of *N*-substituted anilines or aza-heterocycles to **2**. For example, when 3 mol % of CuCl and DPEPhos **L10** were used in the reaction of diphenyl amine (**5a**), only 10% of the aminated product **6a** was observed (vs 92% yield with dppbz **L8**, entry 1). Therefore, dppbz **L8** was selected as the optimal ligand for this class of amine additions. Additions of *N*-methyl anilines to **2** proceeded to >98% conversion in 3 h to give the desired products **6b,c** in 94–96% yields (entries 2–3). As the data in entries 4–10 in Table 3 indicate that $\beta$-amino sulfones bearing indole, pyrrole and imidazole substituents **6d–j**, which are among the most useful building-blocks for biologically active molecules, were produced efficiently and selectively from the corresponding amines in high yields (up to >99%, entries 4–10). Cu-catalyzed additions of pyrazole **5k** and triazole **5l** showed less efficiency; a longer reaction time (15 h vs 3 h) and higher catalyst loading (6 mol % vs 3 mol %) for reaction of **5k** was required (entries 11–12).

A more sterically demanding disubstituted alkene can also be applied to copper-catalyzed aza-Michael additions. As illustrated in Scheme 2, indole **5d** was successfully added to alkene **7a** in the presence of 5 mol % of CuCl and **L3**, affording the desired $\beta$-amino sulfone **8a** in 99% yield. On the other hand, reactions of anisidine **1d** or imidazole **5i** with a disubstituted alkene **7a** were much more sluggish than that with **2** (entry 4 in Table 2 and entry 9 in Table 3); with 7 mol % of CuCl and **L3** for 15 h, the products **8b,c** were obtained in moderate yields (68–75%). A phenyl-substituted alkene **7b** also underwent catalytic amination to give the corresponding amine **8d** in 62% yield. Development of more effective ligands is required to promote amine additions to sterically hindered olefins.

Additional attributes of our new Cu-catalyzed aza-Michael reaction are illustrated by the synthesis of a wide range of $\beta$-amino nitrile and $\beta$-amino carbonyl compounds **10a–k**. As shown in Table 4, various $\alpha,\beta$-unsaturated alkenes bearing a nitrile, ester or ketone group undergo conjugate additions of anilines in the presence of 7 mol % CuCl and **L1** or **L2**, affording the corresponding amine products with high efficiency. When acrylonitrile (**9a**) was reacted with anilines, the $\beta$-amino nitriles **10a–f** were obtained in high yields (84–95%, entries 1–6) within 15 h. Additions of anilines to methyl acrylate (**9b**) were less efficient, resulting in lower yields of the desired products **10g,h** (70–73% yields, entries 7–8). In the case of aza-Michael addition involving pent-1-en-3-one (**9c**), >98% conversion was observed within 1 h, albeit in moderate yields (75–89%) due to the generation of unidentified side products (entries 9–11).

## CONCLUSIONS

In summary, we have developed efficient and mild Cu-catalyzed aza-Michael addition reactions of less nucleophilic aromatic amines or aza-heterocycles to $\alpha,\beta$-unsaturated olefins. A readily available electron-donating phosphine or NHC-based ligand, complexed to an inexpensive copper salt, plays a crucial role in enhancing the nucleophilic addition of aromatic amines or aza-heterocycles to alkenes. The catalytic protocols enable the synthesis of a broad range of new $\beta$-amino sulfone, $\beta$-amino nitrile, and $\beta$-amino carbonyl compounds including aniline, indole, carbazole, pyrrole, imidazole, pyrazole, and triazole derivatives in high yields these represent a less well-studied category of substrates for catalytic conjugate addition. Further efforts will be directed toward expansion of substrate scope to more sterically demanding olefins and development of Cu-catalyzed enantioselective amination.

## EXPERIMENTAL SECTION

**General Methods.** Infrared (IR) spectra were recorded in reciprocal centimeters ($cm^{-1}$). Bands are characterized as broad (br), strong (s), medium (m), and weak (w). $^1H$ NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal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**Scheme 2. Cu-Catalyzed Aza-Michael Addition Reactions to Disubstituted Olefin 7**

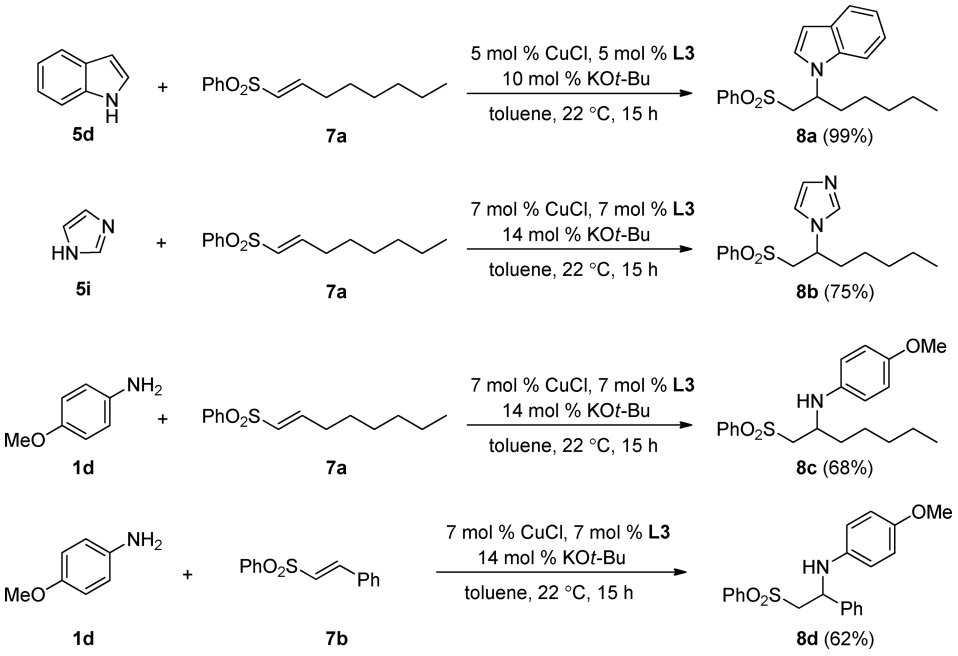
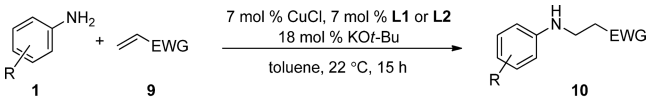
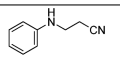
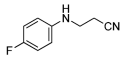
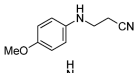
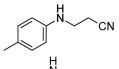
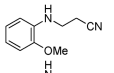
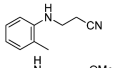
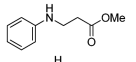
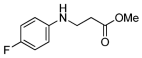
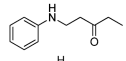
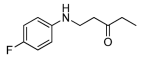
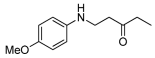



**Table 4. Cu-Catalyzed Aza-Michael Addition of Anilines to Various α,β-Unsaturated Olefins**[a]




EWG = CN **9a**, $CO_2Me$ **9b**, COEt **9c**

| entry | ligand | products | | time (h) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **L2** |  | **10a** | 15 | 94 |
| 2 | **L2** |  | **10b** | 15 | 95 |
| 3 | **L2** |  | **10c** | 15 | 94 |
| 4 | **L2** |  | **10d** | 15 | 84 |
| 5 | **L1** |  | **10e** | 15 | 93 |
| 6 | **L1** |  | **10f** | 15 | 89 |
| 7 | **L2** |  | **10g** | 15 | 70 |
| 8 | **L2** |  | **10h** | 15 | 73 |
| 9 | **L2** |  | **10i** | 0.5 | 81 |
| 10 | **L2** |  | **10j** | 1 | 89 |
| 11 | **L2** |  | **10k** | 0.5 | 75 |

[a]Reaction conditions: aniline **1** (0.50 mmol), olefin **9** (0.75 mmol), CuCl (7 mol %), ligand (**L1** or **L2**, 7 mol %), KO*t*-Bu (18 mol %), toluene (1.5 mL) under $N_2$. [b]Yields of the isolated products.

standard ($CDCl_3$ $\delta$ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. $^{13}C$ NMR spectra were recorded on a 100 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$ $\delta$ 77.26 ppm). High-resolution mass spectra (HRMS) were obtained using an electron ionization (EI) or an electrospray ionization (ESI) time-of-flight mass spectrometer. Unless otherwise noted, all reactions were carried out with distilled solvents under an atmosphere of dry $N_2$ in oven-dried (130 °C) glassware. Toluene was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All workup and purification procedures were carried out with reagent grade solvents in air.

**Representative Experimental Procedures for Cu-Catalyzed Aza-Michael Addition of Aromatic Amines or Aza-Heterocycles to α,β-Unsaturated Olefins.** *General Procedure A.* CuCl (1.50 mg, 0.0150 mmol), DPEphos **L10** (8.10 mg, 0.0150 mmol) and KO*t*-Bu (1.70 mg, 0.0150 mmol) were added to a vial (8 mL) charged with a magnetic bar, which was purged by $N_2$ gas. After purging for 5 min, toluene (0.8 mL) and aniline (**1a**) (55.0 μL, 0.600 mmol) were added to the mixture and allowed to premix for 10 min. And then a solution of phenyl vinyl sulfone (**2**) (84.1 mg, 0.500 mmol) in toluene (0.7 mL) was added to the reaction solution, which was allowed to stir at room temperature for 3 h. After that time, reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (1 mL) and washed with EtOAc (3 × 3 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexanes:EtOAc = 5:1) to afford the desired aminated product **3a** (130 mg, 0.497 mmol, 99% yield) as a white solid.

*General Procedure B.* CuCl (1.50 mg, 0.0150 mmol), ICy **L3** (4.80 mg, 0.0150 mmol) and KO*t*-Bu (3.40 mg, 0.0300 mmol) were added to a vial (8 mL) charged with a magnetic bar, which was purged by $N_2$ gas. After purging for 5 min, toluene (0.8 mL) was added and allowed to premix for 30 min. And then aniline (**1a**) (55.0 μL, 0.600 mmol) was added to the mixture, which was allowed to stir for further 20 min. A solution of phenyl vinyl sulfone (**2**) (84.1 mg, 0.500 mmol) in toluene (0.7 mL) was added to the reaction solution and it was allowed to stir at room temperature for 3 h. After that time, reaction was quenched with a saturated aqueous solution of $NH_4Cl$ (1 mL) and washed with EtOAc (3 × 3 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexanes:EtOAc = 5:1) to afford the desired aminated product **3a** (127 mg, 0.485 mmol, 97% yield) as a white solid.

*N-(2-(Phenylsulfonyl)ethyl)aniline (**3a**).* This compound has been previously reported and spectra data match described.[3d] $^1H$ NMR



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($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.4 Hz, 2H), 7.69 (dd, $J$ = 7.4, 7.4 Hz, 1H), 7.58 (dd, $J$ = 7.4, 7.4 Hz, 2H), 7.18 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.76 (dd, $J$ = 7.6, 7.6 Hz, 1H), 6.54 (d, $J$ = 7.6 Hz, 2H), 4.19 (br s, 1H), 3.59 (t, $J$ = 6.3 Hz, 2H), 3.37 (t, $J$ = 6.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 146.4, 138.8, 133.9, 129.3, 129.2, 127.7, 118.1, 112.8, 54.4, 37.3.

*4-Fluoro-N-(2(phenylsulfonyl)ethyl)aniline (**3b**).* Compound **3b** was synthesized according to general procedure A using 4-fluoroaniline (**1b**) to obtain as a light yellow white solid in 98% yield (137 mg, 0.490 mmol). mp 105−106 °C; IR (neat) 3387 (s), 2926 (s), 2846 (s), 1516 (s), 1316 (s), 1288 (s), 1140 (s), 1083 (s), 821 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.91 (d, $J$ = 7.6 Hz, 2H), 7.68 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.58 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.87 (m, 2H), 6.48 (m, 2H), 4.13 (br s, 1H), 3.55 (t, $J$ = 6.2 Hz, 2H), 3.35 (t, $J$ = 6.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 156.2 (d, $J$ = 235.9 Hz), 142.8, 138.9, 134.0, 129.4, 127.8, 115.8 (d, $J$ = 22.3 Hz), 114.0 (d, $J$ = 7.4 Hz), 54.4, 38.1; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{14}H_{14}FNO_2S$ 279.0729, Found 279.0736.

*4-Bromo-N-(2-(phenylsulfonyl)ethyl)aniline (**3c**).* Compound **3c** was synthesized according to general procedure A using 4-bromoaniline (**1c**) to obtain as a white solid in 97% yield (165 mg, 0.485 mmol). This compound has been previously reported and spectra data match described.[17] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.92 (d, $J$ = 7.5 Hz, 2H), 7.70 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.60 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.25 (d, $J$ = 8.8 Hz, 2H), 6.42 (d, $J$ = 8.8 Hz, 2H), 4.25 (br s, 1H), 3.60 (t, $J$ = 6.1 Hz, 2H), 3.38 (t, $J$ = 6.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 145.6, 138.9. 134.1, 132.1, 129.5, 127.9, 114.6, 110.1, 54.5, 37.6.

*4-Methoxy-N-(2-(phenylsulfonyl)ethyl)aniline (**3d**).* Compound **3d** was synthesized according to general procedure A using *p*-anisidine (**1d**) to obtain as a brown solid in >99% yield (145 mg, 0.498 mmol). This compound has been previously reported and spectra data match described.[17] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.5 Hz, 2H), 7.69 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz 2H), 6.77 (d, $J$ = 8.5 Hz, 2H), 6.53 (d, $J$ = 8.5 Hz, 2H), 3.91 (br s, 1H), 3.75 (s, 3H), 3.56 (t, $J$ = 5.8 Hz, 2H), 3.35 (t, $J$ = 5.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 152.9, 140.5, 139.1, 134.0, 129.5, 128.0, 115.0, 114.8, 55.6, 54.7, 38.7.

*N-(2-(Phenylsulfonyl)ethyl)-4-(trifluoromethyl)aniline (**3e**).* Compound **3e** was synthesized according to general procedure A using 4-(trifluoromethyl)aniline (**1e**) to obtain as a white solid in 98% yield (161 mg, 0.489 mmol). mp 142−143 °C; IR (neat) 3382 (s), 3058 (w), 2955 (m), 2830 (w), 2361 (w), 1611 (s), 1519 (s), 1265 (s), 1142 (s), 1084 (s), 829 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.7 Hz, 2H), 7.71 (dd, $J$ = 7.7, 7.7 Hz, 1H), 7.60 (dd, $J$ = 7.7, 7.7 Hz, 2H), 7.40 (d, $J$ = 8.5 Hz, 2H), 6.55 (d, $J$ = 8.5 Hz, 2H), 4.60 (t, $J$ = 6.1 1H), 3.64 (dt, $J$ = 6.1, 6.1 Hz, 2H), 3.38 (t, $J$ = 6.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 149.1, 138.8, 134.2, 129.6, 127.9, 126.7 (q, $J$ = 3.9 Hz), 124.7 (q, $J$ = 270.6 Hz), 119.8 (q, $J$ = 32.5 Hz), 112.1, 54.4, 37.1; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{15}H_{14}F_3NO_2S$ 329.0697, Found 329.0694.

*4-Methyl-N-(2-(phenylsulfonyl)ethyl)aniline (**3f**).* Compound **3f** was synthesized according to general procedure A using *p*-toluidine (**1f**) as a white solid in 90% yield (124 mg, 0.450 mmol). This compound has been previously reported and spectra data match described.[17] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.5 Hz, 2H), 7.69 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 2H), 6.99 (d, $J$ = 8.0 Hz, 2H), 6.47 (d, $J$ = 8.0 Hz, 2H), 4.06 (br s, 1H), 3.59 (t, $J$ = 6.1 Hz, 2H), 3.37 (t, $J$ = 6.1 Hz, 2H), 2.24 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 144.1, 139.1, 134.0, 129.9, 129.5, 128.0, 127.8, 113.4, 54.7, 38.0, 20.2.

*4-(tert-Butyl)-N-(2-(phenylsulfonyl)ethyl)aniline (**3g**).* Compound **3g** was synthesized according to general procedure A using 4-*tert*-butylaniline (**1g**) to obtain as a white solid in 93% yield (148 mg, 0.466 mmol). mp 107−108 °C; IR (neat) 3382 (s), 3058 (w), 2954 (m), 2832 (w), 2359 (w), 1611 (s), 1519 (s), 1265 (s), 1141 (s), 1083 (s), 830 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.95 (d, $J$ = 7.5 Hz, 2H), 7.70 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.22 (d, $J$ = 8.7 Hz, 2H), 6.52 (d, $J$ = 8.7 Hz, 2H), 4.12 (br s, 1H), 3.59 (t, $J$ = 6.4 Hz, 2H), 3.39 (t, $J$ = 6.4 Hz, 2H), 1.30 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 144.0, 141.0, 138.9, 133.9, 129.4, 127.8, 126.1, 112.7, 54.6, 37.6, 33.6, 31.3; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{18}H_{23}NO_2S$ 317.1449, Found 317.1431.

*2-Fluoro-N-(2-(phenylsulfonyl)ethyl)aniline (**3h**).* Compound **3h** was synthesized according to general procedure A using 2-fluoroaniline (**1h**) to obtain as a white solid in >99% yield (139 mg, 0.498 mmol). mp 67−68 °C; IR (neat) 3410 (s), 2927 (s), 1619 (s), 1520 (s), 1449 (s), 1288 (s), 1137 (s), 1079 (s), 806 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.6 Hz, 2H), 7.69 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.58 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.99−6.93 (m, 2H), 6.67 (dd, $J$ = 7.4, 7.4 Hz, 1H), 6.58 (dd, $J$ = 8.3, 8.3 Hz, 1H) 4.34 (br s, 1H), 3.64 (dt, $J$ = 6.3, 6.3 Hz, 2H), 3.40 (t, $J$ = 6.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 151.6 (d, $J$ = 239.2 Hz), 138.8, 134.9 (d, $J$ = 11.6 Hz), 133.9, 129.4, 127.8, 124.5 (d, $J$ = 4.7 Hz), 117.5, 114.6 (d, $J$ = 19 Hz), 111.7, 54.5, 37.0; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{14}H_{14}FNO_2S$ 279.0729; Found 279.0723.

*2-Chloro-N-(2-(phenylsulfonyl)ethyl)aniline (**3i**).* Compound **3i** was synthesized according to general procedure A using 2-chloroaniline (**1i**) to obtain as yellow liquid in 99% yield (147 mg, 0.497 mmol). IR (neat) 3399 (m), 3066 (w), 2981 (w), 2360 (m), 1732 (s), 1596 (s), 1511 (s), 1295 (s), 1140 (s), 1082 (s), 736 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.95 (d, $J$ = 7.6 Hz, 2H), 7.69 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.59 (dd, $J$ = 7.6, 7.6 Hz, 2H), 7.25 (d, $J$ = 7.7 Hz, 1H), 7.12 (dd, $J$ = 7.7, 7.7 Hz, 1H), 6.67 (dd, $J$ = 7.7, 7.7 Hz, 1H), 6.54 (d, $J$ = 7.7, 7.7 Hz, 1H), 4.72 (br s, 1H), 3.67 (dt, $J$ = 6.5, 6.5 Hz, 2H), 3.42 (t, $J$ = 6.5 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 142.5, 139.0, 134.1, 129.5, 129.5, 128.0, 127.8, 119.7, 118.2, 110.7, 54.7, 37.2; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{14}H_{14}ClNO_2S$ 295.0434, Found 295.0415.

*2-Methoxy-N-(2-(phenylsulfonyl)ethyl)aniline (**3j**).* Compound **3j** was synthesized according to general procedure A using *o*-anisidine (**1j**) to obtain as a white solid in 98% yield (143 mg, 0.490 mmol). This compound has been previously reported and spectra data match described.[17] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.94 (d, $J$ = 7.5 Hz, 2H), 7.68 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.58 (dd, $J$ = 7.5, 7.5 Hz, 2H), 6.83 (dd, $J$ = 7.6, 7.6 Hz, 1H), 6.76 (d, $J$ = 7.6 Hz, 1H), 6.70 (dd, $J$ = 7.6, 7.6 Hz, 1H), 6.47 (d, $J$ = 7.6 Hz, 1H), 4.57 (s, 1H), 3.81 (br s, 3H), 3.63 (t, $J$ = 6.6 Hz, 2H), 3.41 (t, $J$ = 6.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 147.2, 139.2, 136.4, 133.8, 129.4, 127.9, 121.1, 117.4, 109.7, 109.5, 55.3, 54.8, 37.1.

*Methyl 2-((2-(phenylsulfonyl)ethyl)amino)benzoate (**3k**).* Compound **3k** was synthesized according to general procedure A using methyl anthranilate (**1k**) to obtain as a white solid in 96% yield (154 mg, 0.482 mmol). mp 88−89 °C; IR (neat) 3359 (s), 2357 (w), 1678 (s), 1577 (s), 1516 (s), 1439 (s), 1231 (s), 1141 (s), 1080 (s), 992 (m), 753 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.92 (d, $J$ = 7.6 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.84 (d, $J$ = 7.6 Hz, 1H), 7.65 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.55 (dd, $J$ = 7.6, 7.6 Hz, 2H), 7.33 (dd, $J$ = 8.0, 8.0 Hz, 1H), 6.62 (dd, $J$ = 8.0, 8.0 Hz, 1H), 6.55 (d, $J$ = 8.3 Hz, 1H), 3.82 (br s, 3H), 3.68 (dt, $J$ = 6.9, 5.8 Hz, 2H), 3.41 (t, $J$ = 6.9 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 168.7, 149.4, 139.0, 134.7, 133.8, 131.8, 129.3, 127.91, 115.5, 110.8, 110.4, 54.4, 51.5, 36.3; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{16}H_{17}NO_4S$ 319.0878, Found 319.0884.

*2-Methyl-N-(2-(phenylsulfonyl)ethyl)aniline (**3l**).* Compound **3l** was synthesized according to general procedure A using *o*-toluidine (**1l**) to obtain as a yellow solid in 99% yield (136 mg, 0.494 mmol). This compound has been previously reported and spectra data match described.[17] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.95 (d, $J$ = 7.5 Hz, 2H), 7.70 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.14−7.08 (m, 2H), 6.72 (dd, $J$ = 7.2, 7.2 Hz, 1H), 6.50 (d, $J$ = 7.8 Hz, 1H), 4.21 (br s, 1H), 3.65 (t, $J$ = 5.9 Hz, 2H), 3.44 (t, $J$ = 5.9 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 144.6, 138.8, 133.9, 130.3, 129.4, 127.8, 127.0, 122.7, 117.7, 109.2, 54.6, 37.3, 17.1.

*N,N-Bis(2-(phenylsulfonyl)ethyl)aniline (**4a**).* Compound **4a** was synthesized according to general procedure A using aniline (**1a**) to obtain as a white solid. mp 158−159 °C; IR (neat) 3066 (w), 2958 (w), 2925 (m), 2853 (m), 2360 (m), 2337 (m), 1866 (w), 1702 (m), 1650 (m), 1557 (m), 1508 (s), 1456 (m), 1364 (m), 1303 (m), 1145 (s), 1084 (m), 992 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.90 (d, $J$ = 7.5 Hz, 4H), 7.69 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.17 (dd, $J$ = 7.7, 7.7 Hz, 2H), 6.78 (dd, $J$ = 7.7, 7.7 Hz, 1H), 6.46 (d, $J$ = 7.7 Hz, 2H), 3.71 (t, $J$ = 7.2 Hz, 4H), 3.28 (t, $J$ = 7.2 Hz,


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4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 145.1, 139.4, 134.0, 129.9, 129.5, 127.9, 118.8, 113.2, 52.9, 45.0; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{22}H_{23}NO_4S_2$ 429.1068, Found 429.1067.

*4-Methoxy-N,N-bis(2-(phenylsulfonyl)ethyl)aniline (**4b**).* Compound **4b** was synthesized according to general procedure A using *p*-anisidine (**1d**, 49.3 mg, 0.400 mmol) to obtain as a yellow solid in 75% yield (139 mg, 0.302 mmol). mp 118−119 °C; IR (neat) 3066 (w), 2928 (m), 2359 (m), 1584 (m), 1512 (s), 1446 (s), 1296 (s), 1145 (s), 1083 (s), 817 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.78 (d, $J$ = 7.5 Hz, 4H), 7.68 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.58 (dd, $J$ = 7.5, 7.5 Hz, 4H), 6.74 (d, $J$ = 8.8 Hz, 2H), 6.49 (d, $J$ = 8.8 Hz, 2H), 3.74 (s, 3H), 3.56 (t, $J$ = 6.7 Hz, 4H), 3.19 (t, $J$ = 6.7 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 153.7, 139.2, 139.1, 133.8, 129.3, 127.7, 117.2, 114.9, 55.41, 52.8, 46.0; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{23}H_{26}NO_5S_2$ 460.1252, Found 460.1251.

*N-Phenyl-N-(2-(phenylsulfonyl)ethyl)aniline (**6a**).* Compound **6a** was synthesized according to general procedure A using diphenylamine (**5a**) to obtain as a white solid in 92% yield (155 mg, 0.460 mmol). mp 124−125 °C; IR (neat) 3066 (s), 2924 (s), 1947 (w), 1600 (s), 1500 (s), 1318 (s), 1311 (s), 994 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.93 (d, $J$ = 7.4 Hz, 2H), 7.70 (dd, $J$ = 7.4, 7.4 Hz, 1H), 7.59 (dd, $J$ = 7.4, 7.4 Hz, 2H), 7.24 (dd, $J$ = 7.3, 7.3 Hz, 4H), 6.98 (dd, $J$ = 7.3, 7.3 Hz, 2H), 6.86 (d, $J$ = 7.3 Hz, 4H), 4.17 (t, $J$ = 7.6 Hz, 2H), 3.44 (t, $J$ = 7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 146.6, 139.3, 134.0, 129.6, 129.5, 127.9, 122.2, 120.8, 52.7, 45.5; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{20}H_{19}NO_2S$ 337.1136, Found 337.1127.

*N-Methyl-N-(2-(phenylsulfonyl)ethyl)aniline (**6b**).* Compound **6b** was synthesized according to general procedure A using *N*-methylaniline (**5b**) to obtain as a white solid in 94% yield (129 mg, 0.470 mmol). mp 77−78 °C; IR (neat) 3062 (s), 2917 (s), 1921 (w), 1600 (s), 1504 (s), 1446 (s), 1361 (s), 1307 (s), 1242 (s), 1180 (s), 1145 (s), 1087 (s), 991 (m), 860 (w), 806 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.94 (d, $J$ = 7.5 Hz, 2H), 7.69 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.22 (dd, $J$ = 7.3, 7.3 Hz, 2H), 6.75 (dd, $J$ = 7.3, 7.3 Hz, 1H), 6.60 (d, $J$ = 7.3 Hz, 2H), 3.83 (t, $J$ = 7.4 Hz, 2H), 3.33 (t, $J$ = 7.4 Hz, 2H), 2.88 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 147.6, 139.2, 133.8, 129.3, 129.3, 127.7, 117.4, 112.4, 51.7, 45.8, 38.1; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{15}H_{17}NO_2S$ 275.0980, Found 275.0971.

*4-Fluoro-N-methyl-N-(2-(phenylsulfonyl)ethyl)aniline (**6c**).* Compound **6c** was synthesized according to general procedure A using 4-fluoro-*N*-methylaniline (**5c**) to obtain as a white solid in 96% yield (141 mg, 0.481 mmol). mp 98−99 °C; IR (neat) 3064 (s), 2962 (s), 2828 (m), 1855 (w), 1608 (s), 1518 (s), 1447 (s), 1365 (s), 1298 (s), 1086 (s), 1019 (m), 945 (m), 811 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.92 (d, $J$ = 7.4 Hz, 2H), 7.69 (dd, $J$ = 7.4, 7.4 Hz, 1H), 7.59 (dd, $J$ = 7.4, 7.4 Hz, 2H), 6.91 (dd, $J$ = 8.8, 8.8 Hz, 2H) 6.53 (dd, $J$ = 8.8, 8.8 Hz, 2H), 3.78 (t, $J$ = 7.4 Hz, 2H), 3.28 (t, $J$ = 7.4 Hz, 2H), 2.81 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 156.0 (d, $J$ = 236.7 Hz), 144.3 (d, $J$ = 1.6 Hz), 139.3, 133.9, 129.4, 127.8, 115.9 (d, $J$ = 22.4 Hz), 114.1 (d, $J$ = 7.5 Hz), 51.7, 46.6, 38.7; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{15}H_{16}FNO_2S$ 293.0886, Found 293.0882.

*1-(2-(Phenylsulfonyl)ethyl)-1H-indole (**6d**).* Compound **6d** was synthesized according to general procedure A using indole (**5d**) to obtain as a white solid in 98% yield (140 mg, 0.490 mmol). This compound has been previously reported and spectra data match described.[18] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.88 (d, $J$ = 7.4 Hz, 2H), 7.65 (dd, $J$ = 7.4, 7.4 Hz, 1H), 7.59−7.52 (m, 3H), 7.22−7.16 (m, 2H), 7.11 (dd, $J$ = 7.8, 7.8 Hz, 1H), 7.00 (d, $J$ = 3.2 Hz, 1H), 6.45 (d, $J$ = 3.2 Hz, 1H), 4.61 (t, $J$ = 7.4 Hz, 2H) 3.56 (t, $J$ = 7.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 138.7, 135.3, 133.9, 129.3, 128.7, 127.6, 127.3, 121.9, 121.2, 119.8, 108.6, 102.4, 55.2, 39.6.

*5-Bromo-1-(2-(phenylsulfonyl)ethyl)-1H-indole (**6e**).* Compound **6e** was synthesized according to general procedure A using 5-bromoindole (**5e**) to obtain as a white solid in 94% yield (171 mg, 0.469 mmol). mp 158−159 °C; IR (neat) 3054 (m), 2966 (m), 1971 (w), 1904 (w), 1849 (w), 1743 (w), 1469 (s), 1447 (s), 1302 (s), 1144 (s), 1086 (s), 871 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.84 (d, $J$ = 7.5 Hz, 2H), 7.69 (d, $J$ = 1.5 Hz, 1H), 7.65 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.53 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.30−7.24 (m, 1H), 7.06 (d, $J$ = 8.7 Hz, 1H), 7.00 (d, $J$ = 3.2 Hz, 1H), 6.37 (d, $J$ = 3.2 Hz, 1H), 4.59 (t, $J$ = 7.2 Hz, 2H), 3.54 (t, $J$ = 7.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 138.8, 134.2, 134.1, 130.5, 129.5, 128.6, 127.7, 124.9, 123.8, 113.3, 110.2, 102.2, 55.3, 39.9; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{16}H_{14}BrNO_2S$ 362.9929, Found 362.9903.

*9-(2-(Phenylsulfonyl)ethyl)-9H-carbazole (**6f**).* Compound **6f** was synthesized according to general procedure A using carbazole (**5f**) to obtain as a white solid in 98% yield (165 mg, 0.492 mmol). mp 162−163 °C; IR (neat) 3062 (m), 2968 (m), 1596 (m), 1485 (s), 1450 (s), 1307 (s), 1234 (m), 1176 (m), 1141 (s), 1087 (m), 1002 (m), 914 (m), 817 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.03 (d, $J$ = 7.8 Hz, 2H), 7.84 (d, $J$ = 7.4 Hz, 2H), 7.62 (dd, $J$ = 7.4, 7.4 Hz, 1H), 7.50−7.43 (m, 4H), 7.29−7.22 (m, 4H), 4.79 (t, $J$ = 7.6 Hz, 2H), 3.58 (t, $J$ = 7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 139.5, 138.7, 134.0, 129.4, 127.6, 126.1, 123.3, 120.6, 119.8, 108.2, 53.5, 36.4; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{20}H_{18}NO_2S$ 336.1058, Found 336.1056.

*1-(2-(Phenylsulfonyl)ethyl)-1H-pyrrole (**6g**).* Compound **6g** was synthesized according to general procedure A using pyrrole (**5g**) to obtain as a white solid in 84% yield (99.0 mg, 0.421 mmol). This compound has been previously reported and spectra data match described.[19] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.90 (d, $J$ = 7.3 Hz, 2H), 7.69 (dd, $J$ = 7.3, 7.3 Hz, 1H), 7.58 (dd, $J$ = 7.3, 7.3 Hz, 2H), 6.57 (d, $J$ = 1.4 Hz, 2H), 6.10 (d, $J$ = 1.4 Hz, 2H), 4.34 (t, $J$ = 7.8 Hz, 2H), 3.53 (t, $J$ = 7.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 139.0, 134.2, 129.6, 127.9, 120.4, 109.3, 57.2, 42.7.

*1-(1-(2-(Phenylsulfonyl)ethyl)-1H-pyrrol-2-yl)ethanone (**6h**).* Compound **6h** was synthesized according to general procedure A using 2-acetylpyrrole (**5h**) to obtain as a white solid in 98% yield (136 mg, 0.490 mmol). mp 94−95 °C; IR (neat) 3112 (m), 3062 (m), 2985 (m), 2931 (m), 1647 (s), 1531 (m), 1307 (s), 1245 (m), 1153 (s), 1087 (s), 1026 (m), 945 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.85 (d, $J$ = 7.6 Hz, 2H), 7.64 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.54 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.94 (m, 1H), 6.90−6.88 (m, 1H), 6.13−6.11 (m, 1H), 4.65 (t, $J$ = 6.7 Hz, 2H) 3.65 (t, $J$ = 6.7 Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 188.5, 139.4, 133.8, 131.5, 129.9, 129.3, 127.7, 121.2, 108.8, 56.2, 43.8, 26.9; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{14}H_{15}NO_3S$ 277.0773, Found 277.0768.

*1-(2-(Phenylsulfonyl)ethyl)-1H-imidazole (**6i**).* Compound **6i** was synthesized according to general procedure A using imidazole (**5i**) to obtain as a white solid in >99% yield (118 mg, 0.499 mmol). This compound has been previously reported and spectra data match described.[20] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.88 (d, $J$ = 7.5 Hz, 2H), 7.70 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.59 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.44 (br s, 1H), 7.01 (br s, 1H), 6.85 (br s, 1H), 4.43 (t, $J$ = 7.3 Hz, 2H), 3.54 (t, $J$ = 7.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 138.7, 137.2, 134.4, 130.4, 129.7, 127.8, 118.4, 56.6, 40.2.

*2-Methyl-1-(2-(phenylsulfonyl)ethyl)-1H-benzo[d]imidazole (**6j**).* Compound **6j** was synthesized according to general procedure A using 2-methyl-1*H*-benzo[*d*]imidazole (**5j**) to obtain as a white solid in >99% yield (150 mg, 0.499 mmol). mp 178−179 °C; IR (neat) 3061 (m), 3001 (m), 2981 (m), 2939 (m), 1616 (m), 1515 (s), 1458 (s), 1404 (s), 1361 (s), 1307 (s), 1234 (m), 1145 (s), 1083 (m), 1010 (m), 914 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.85 (d, $J$ = 7.7 Hz, 2H), 7.70−7.58 (m, 2H), 7.53 (dd, $J$ = 7.7, 7.7 Hz, 2H), 7.25−7.14 (m, 2H), 7.14−7.07 (m, 1H), 4.57 (t, $J$ = 7.5 Hz, 2H), 3.53 (t, $J$ = 7.5 Hz, 2H), 2.57 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 151.1, 142.7, 138.4, 134.3, 134.1, 129.6, 127.6, 122.5, 122.4, 119.5, 108.4, 54.3, 37.1, 13.6; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{16}H_{16}N_2O_2S$ 300.0932, Found 300.0903.

*1-(2-(Phenylsulfonyl)ethyl)-1H-pyrazole (**6k**).* Compound **6k** was synthesized according to general procedure A using pyrazole (**5k**) to obtain as a white solid in 90% yield (106 mg, 0.449 mmol). mp 122−123 °C; IR (neat) 3117 (s), 2973 (s), 2915 (s), 2360 (m), 1445 (s), 1396 (s), 1296 (s), 1149 (s), 1084 (s), 998 (s), 963 (s), 809(s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.85 (d, $J$ = 7.5 Hz, 2H), 7.65 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.54 (dd, $J$ = 7.5, 7.5 Hz, 2H), 7.40 (d, $J$ = 4.4 Hz, 2H), 6.18 (s, 1H), 4.56 (t, $J$ = 7.0 Hz, 2H), 3.74 (t, $J$ = 7.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 139.9, 138.7, 133.7, 129.8, 129.1,


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127.5, 105.6, 55.2, 45.0; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2S$ 237.0698, Found 237.0694.

*1-(2-(Phenylsulfonyl)ethyl)-1H-1,2,3-trizole (**6l**).* Compound **6l** was synthesized according to general procedure A using 1*H*-1,2,3-triazole (**5l**) to obtain as a white solid in 54% yield (64.0 mg, 0.270 mmol). mp 122−123 °C; IR (neat) 3121 (w), 3004 (w), 2360 (m), 1446 (s), 1295 (s), 1149 (s), 1133 (s), 1083 (s), 999 (s), 802 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.87 (d, $J$ = 7.6 Hz, 2H), 7.70 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.65 (d, $J$ = 5.1 Hz, 2H), 7.58 (dd, $J$ = 7.6, 7.6 Hz, 2H), 4.84 (t, $J$ = 6.9 Hz, 2H), 3.78 (t, $J$ = 6.9 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 138.6, 134.4, 134.0, 129.6, 127.8, 124.4, 55.4, 43.3; HRMS (EI) $m/z$ $[M]^+$ Calcd for $C_{10}H_{11}N_3O_2S$ 237.0572, Found 237.0559.

*1-(1-(Phenylsulfonyl)octan-2-yl)-1H-indole (**8a**).* Compound **8a** was synthesized according to general procedure B using alkene **7** (0.120 mmol) to obtain as colorless liquid in 99% yield (44.0 mg, 0.119 mmol). IR (neat) 3749 (w), 2963 (w), 2916 (m), 2858 (w), 2364 (w), 2339 (w), 1453 (m), 1305 (m), 1138 (s), 1081 (w), 914 (w), 786 (w), 728 (s), 695 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.59−7.52 (m, 3H), 7.46 (dd, $J$ = 8.3, 8.3 Hz, 1H), 7.33−7.19 (m, 3H), 7.12 (dd, $J$ = 7.3, 7.4 Hz, 1H), 6.91 (d, $J$ = 3.4 Hz, 1H), 6.36 (d, $J$ = 3.1 Hz, 1H), 5.04−4.94 (m, 1H), 3.81 (dd, $J$ = 14.6, 7.5 Hz, 1H), 3.62 (dd, $J$ = 14.9, 5.4 Hz, 1H), 2.15−1.99 (m, 2H), 1.46−1.12 (m, 8H), 1.11−0.99 (m, 1H), 0.87 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 138.9, 135.7, 133.3, 128.8, 128.6 127.3, 123.9, 121.8, 121.0 119.8, 109.6, 103.0, 61.0, 51.6, 35.3, 31.3, 28.5, 25.7, 22.3, 12.8; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{22}H_{28}NO_2S$ 370.1841, Found 370.1835.

*1-(1-(Phenylsulfonyl)octan-2-yl)-1H-imidazole (**8b**).* Compound **8b** was synthesized according to general procedure B using alkene **7** (0.120 mmol) to obtain as colorless oil in 75% yield (28.8 mg, 0.0899 mmol). IR (neat) 3747 (w), 2956 (w), 2930 (m), 2862 (w), 2354 (w), 2341 (w), 1505 (m), 1454 (w), 1299 (m), 1222 (w), 1142 (s), 1081 (m), 903 (w), 730 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.69 (d, $J$ = 7.6 Hz, 2H), 7.60 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.47 (dd, $J$ = 7.6, 7.6 Hz, 2H), 7.37 (s, 1H) 6.87 (br s, 1H), 6.66 (br s, 1H), 4.71−4.58 (m, 1H), 3.60 (dd, $J$ = 14.8, 8.2 Hz, 1H), 3.49 (dd, $J$ = 14.7, 4.4 Hz, 1H), 1.98−1.84 (m, 1H), 1.83−1.67 (m, 1H), 1.35−1.10 (m, 7H), 1.10−0.94 (m, 1H), 0.84 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 139.2, 136.8, 134.0, 130.4, 129.4, 127.5, 115.8, 61.4, 53.0, 36.1, 31.3, 28.3, 25.4, 22.3, 13.8; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{17}H_{25}N_2O_2S$ 321.1637, Found 321.1631.

*4-Methoxy-N-(1-(phenylsulfonyl)octan-2-yl)aniline (**8c**).* Compound **8c** was synthesized according to general procedure B using alkene **7a** (0.120 mmol) to obtain as a brown solid in 68% yield (30.6 mg, 0.0815 mmol). mp 76−77 °C; IR (neat) 3394 (w), 2950 (w), 2947 (w), 2924 (m), 2375 (w), 1508 (s), 1439 (w), 1285 (m), 1242 (s), 1139 (s), 1075 (w), 1027 (m), 812 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.88 (d, $J$ = 7.6 Hz, 2H), 7.66 (dd, $J$ = 7.6, 7.6 Hz, 1H), 7.55 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.73 (d, $J$ = 8.8 Hz, 2H) 6.43 (d, $J$ = 8.8 Hz, 2H), 3.83−3.76 (m, 1H), 3.75 (s, 3H), 3.36 (br s, 1H), 3.34 (dd, $J$ = 14.4, 4.4 Hz, 1H), 3.14 (dd, $J$ = 14.3, 7.0 Hz, 1H), 1.98−1.87 (m, 1H), 1.64−1.53 (m, 1H), 1.49−1.40 (m, 1H), 1.33−1.22 (m, 7H), 0.88 (t, $J$ = 6.6 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 152.6, 140.2, 140.1, 133.7, 129.3, 128.0, 115.1, 114.9, 59.5, 55.8, 50.0, 35.2, 31.6, 29.0, 25.7, 22.5, 13.9; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{21}H_{30}NO_3S$ 376.1946, Found 376.1940.

*4-Methoxy-N-(1-phenyl-2-(phenylsulfonyl)ethyl)aniline (**8d**).* Compound **8d** was synthesized according to general procedure B using alkene **7b** (0.120 mmol) to obtain as a brown solid in 62% yield (27.3 mg, 0.0744 mmol). mp 135−136 °C; IR (neat) 3394 (m), 2938 (w), 2825 (w), 1518 (s), 1454 (m), 1404 (w), 1290 (s), 1239 (s), 1133 (s), 1079 (w), 1027 (m), 809 (m), 736 (s), 695 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.88 (d, $J$ = 7.3 Hz, 2H), 7.65 (dd, $J$ = 7.3, 7.3 Hz, 1H), 7.53 (dd, $J$ = 7.3, 7.3 Hz, 2H), 7.38−7.19 (m, 5H), 6.68 (d, $J$ = 8.0 Hz, 2H), 6.44 (d, $J$ = 8.0 Hz, 2H), 4.75−4.55 (m, 2H), 3.71 (s, 3H), 3.51 (dd, $J$ = 14.3, 10.1 Hz, 1H), 3.42 (dd, $J$ = 9.8, 2.4 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 152.8, 141.2, 140.6, 139.1, 134.0, 129.4, 129.1, 128.2, 128.0, 126.3, 115.5, 114.7, 62.5, 55.6, 55.1; HRMS (ESI) $m/z$ $[M + H]^+$ Calcd for $C_{21}H_{22}NO_3S$ 368.1320, Found 368.1321.

*3-(Phenylamino)propanenitrile (**10a**).* Compound **10a** was synthesized according to general procedure B using aniline (**1a**) to obtain as a white solid in 94% yield (68.5 mg, 0.469 mmol). This compound has been previously reported and spectra data match described.[6g] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.23 (dd, $J$ = 7.6, 7.6 Hz, 2H), 6.80 (dd, $J$ = 7.6, 7.6 Hz, 1H), 6.64 (d, $J$ = 7.6, 7.6 Hz, 2H), 4.00 (br s, 1H), 3.53 (t, $J$ = 6.5 Hz, 2H), 2.65 (t, $J$ = 6.5 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 146.1, 129.5, 118.6, 118.2, 113.0, 39.6, 17.9.

*3-((4-Fluorophenyl)amino)propanenitrile (**10b**).* Compound **10b** was synthesized according to general procedure B using 4-fluoroaniline (**1b**) to obtain as white liquid in 95% yield (78.0 mg, 0.475 mmol). This compound has been previously reported and spectra data match described.[21] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 6.96−6.90 (m, 2H), 6.57 (m, 2H), 3.92 (br s, 1H), 3.47 (dt, $J$ = 6.5, 6.5 Hz, 2H), 2.63 (t, $J$ = 6.5 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 156.2 (d, $J$ = 235.9 Hz), 142.5, 118.2, 115.8 (d, $J$ = 22.3 Hz), 113.9 (d, $J$ = 7.4 Hz), 40.1, 17.8.

*3-((4-Methoxyphenyl)amino)propanenitrile (**10c**).* Compound **10c** was synthesized according to general procedure B using *p*-anisidine (**1d**) to obtain as a yellow solid in 94% yield (82.9 mg, 0.470 mmol). This compound has been previously reported and spectra data match described.[6g] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 6.81 (d, $J$ = 8.7 Hz, 2H), 6.60 (d, $J$ = 8.7 Hz, 2H), 3.76 (s, 4H), 3.43 (t, $J$ = 6.3 Hz, 2H), 2.58 (t, $J$ = 6.3 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 152.7, 140.2, 118.3, 114.9, 114.5, 55.4, 40.5, 17.8.

*3-(p-Tolylamino)propanenitrile (**10d**).* Compound **10d** was synthesized according to general procedure B using *p*-toluidine (**1f**) to obtain as a white solid in 84% yield (67.6 mg, 0.422 mmol). This compound has been previously reported and spectra data match described.[6g] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.04 (d, $J$ = 8.7 Hz, 2H). 6.56 (d, $J$ = 8.7 Hz, 2H), 3.85 (br s, 1H), 3.51 (t, $J$ = 6.5 Hz, 2H), 2.63 (t, $J$ = 6.5 Hz, 2H), 2.26 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 143.8, 130.0, 128.1, 118.2, 113.3, 40.1, 20.2, 18.0.

*3-((2-Methoxyphenyl)amino)propanenitrile (**10e**).* Compound **10e** was synthesized according to general procedure B using aniline (**1j**) as a yellow solid in 93% yield (81.9 mg, 0.465 mmol). This compound has been previously reported and spectra data match described.[6g] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 6.94−6.88 (m, 1H), 6.83 (dd, $J$ = 7.8, 1.3 Hz, 1H), 6.76 (ddd, $J$ = 7.8, 7.8, 1.3 Hz, 1H), 6.59 (dd, $J$ = 7.8, 1.3 Hz, 1H), 4.58 (br s, 1H), 3.87 (s, 3H), 3.55 (dt, $J$ = 6.7, 6.7 Hz, 2H), 2.65 (t, $J$ = 6.7 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 147.1, 136.1, 121.2, 118.2, 117.3, 109.8, 109.6, 55.3, 39.4, 17.9.

*3-(o-Tolylamino)propanenitrile (**10f**).* Compound **10f** was synthesized according to general procedure B using *o*-toluidine (**1l**) as a white solid in 89% yield (71.6 mg, 0.447 mmol). This compound has been previously reported and spectra data match described.[6g] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.17 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.12 (d, $J$ = 7.5 Hz, 1H), 6.75 (dd, $J$ = 7.5, 7.5 Hz, 1H), 6.59 (d, $J$ = 7.5 Hz, 1H), 3.88 (br s, 1H), 3.60 (t, $J$ = 6.4 Hz, 2H), 2.68 (t, $J$ = 6.4 Hz, 2H), 2.19 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 144.0, 130.6, 127.1, 122.8, 118.2, 118.1, 109.5, 39.5, 18.0, 17.2.

*Methyl 3-(phenylamino)propanoate (**10g**).* Compound **10g** was synthesized according to general procedure B using aniline (**1a**) to obtain as a yellow solid in 70% yield (62.4 mg, 0.348 mmol). This compound has been previously reported and spectra data match described.[21] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.23 (dd, $J$ = 8.0, 7.4 Hz, 2H), 6.77 (dd, $J$ = 7.4, 7.4 Hz, 2H), 6.67 (d, $J$ = 8.0 Hz, 1H), 4.09 (br s, 1H), 3.74 (s, 3H), 3.49 (t, $J$ = 6.4 Hz, 2H), 2.65 (t, $J$ = 6.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 172.7, 147.5, 129.1, 117.5, 112.8, 51.4, 39.1, 33.4.

*Methyl 3-((4-fluorophenyl)amino)propanoate (**10h**).* Compound **10h** was synthesized according to general procedure B using 4-fluoroaniline (**1b**) to obtain as a yellow solid in 73% yield (72.0 mg, 0.365 mmol). This compound has been previously reported and spectra data match described.[7] $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 6.87 (dd, $J$ = 8.7, 8.7 Hz, 2H), 6.55−6.52 (m, 2H), 3.96 (br s, 1H), 3.67 (s, 3H), 3.38 (t, $J$ = 6.3 Hz, 2H), 2.58 (t, $J$ = 6.3 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 172.8, 156.1 (d, $J$ = 235.1 Hz), 143.9, 115.7 (d, $J$ = 22.3 Hz), 114.0 (d, $J$ = 6.6 Hz), 51.7, 40.0, 33.5.



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*1-(Phenylamino)pentan-3-one (10i).* Compound **10i** was synthesized according to general procedure B using aniline (**1a**) as a white solid in 81% yield (71.8 mg, 0.405 mmol). This compound has been previously reported and spectra data match described.[3c] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.18 (dd, $J$ = 7.3, 7.3 Hz, 2H), 6.72 (dd, $J$ = 7.3, 7.3 Hz, 2H), 6.62 (d, $J$ = 7.3 Hz, 1H), 4.00 (br s, 1H), 3.44 (t, $J$ = 6.1 Hz, 2H), 2.73 (t, $J$ = 6.1 Hz, 2H), 2.45 (q, $J$ = 7.3 Hz, 2H), 1.06 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 210.9, 147.6, 129.2, 117.5, 112.9, 41.0, 38.2, 36.1, 7.4.

*1-((4-Fluorophenyl)amino)pentan-3-one (10j).* Compound **10j** was synthesized according to general procedure B using aniline (**1b**) to obtain as a white solid in 89% yield (86.9 mg, 0.445 mmol). mp 66−67 °C; IR (neat) 3371 (s), 3051 (w), 2977 (m), 2927 (s), 2360 (m), 1705 (s), 1508 (s), 1385 (s), 1206 (s), 1103 (s), 987 (m), 810 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 6.88 (dd, $J$ = 8.7, 8.7 Hz, 2H), 6.55 (dd, $J$ = 8.7, 8.7 Hz, 2H), 3.88 (br s, 1H), 3.37 (t, $J$ = 6.1 Hz, 2H), 2.71 (t, $J$ = 6.1 Hz, 2H), 2.45 (q, $J$ = 7.3 Hz, 2H), 1.06 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 210.9, 155.9 (d, $J$ = 235.0 Hz), 144.1, 115.6 (d, $J$ = 22.4 Hz), 114.0 (d, $J$ = 1.5 Hz), 41.0, 39.1, 36.2, 7.5; HRMS (EI) $m/z$ [M]$^+$ Calcd for $C_{11}H_{14}FNO$ 195.1059, Found 195.1047.

*1-((4-Methoxyphenyl)amino)penta-3-one (10k).* Compound **10k** was synthesized according to general procedure B using *p*-anisidine (**1d**) to obtain as a white solid in 75% yield (77.7 mg, 0.375 mmol). This compound has been previously reported and spectra data match described.[22] $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 6.78 (dd, $J$ = 8.8, 8.8 Hz, 2H), 6.59 (d, $J$ = 8.8 Hz, 2H), 3.75 (s, 4H), 3.37 (t, $J$ = 6.1 Hz, 2H), 2.71 (t, $J$ = 6.1 Hz, 2H), 2.44 (q, $J$ = 7.3 Hz, 2H), 1.06 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 211.0, 152.3, 141.9, 114.9, 114.5, 55.6, 41.2, 39.5, 36.2, 7.5.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00341.

$^1$H NMR and $^{13}$C NMR spectra for all products. (PDF)

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### Notes

The authors declare no competing financial interest.

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