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Copper-catalyzed Regioselective Hydroaminations of Allylic Sulfones With Aromatic Amines

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The highly regioselective copper-catalyzed hydroaminations of terminal or γ-substituted allylic sulfones with aromatic amines is described. The combination of an *N*-heterocyclic carbene-copper complex and KO*t*-Bu plays an important role in promoting selective amination under mild reaction conditions. This catalytic reaction tolerates a wide range of functional groups and enables the efficient syntheses of new and versatile functionalized β-amino sulfones in high yields (up to 98%) with >98% regioselectivity.

Keywords: Allyl sulfones, Aromatic amines, Copper catalyst, Hydroamination, Regioselectivity

Introduction

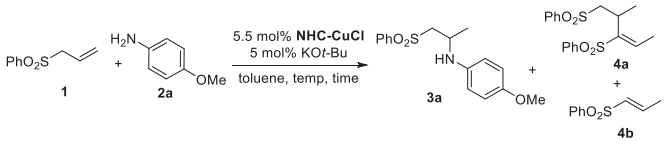
The direct addition of a nitrogen–hydrogen bond across a carbon–carbon double bond is one of the most powerful carbon–nitrogen bond forming processes due to its simplicity and atom economy.[1] Nitrogen-containing compounds play significant roles in medicinal and organic chemistry as valuable building blocks and synthetically useful intermediates.[2] Therefore, a number of catalytic systems for the mild and efficient syntheses of various amines through hydroamination or aza-Michael addition have been intensively studied. In particular, the direct intermolecular addition of an aromatic amine to an alkene is a useful and attractive way of synthesizing a functionalized *N*-alkyl aromatic amine from readily accessible alkene substrates but is challenging in that regioselectivity should be controlled and aromatic amines are less nucleophilic.[3] Among various catalysts that promote direct intermolecular addition reactions of arylamines to alkenes, copper, which is readily available, relatively inexpensive, and easy-to-handle, is a promising candidate for efficient and practical amination reactions. In the past decade, copper-based catalysts have been used to improve reactivity and regio-, chemo-, and stereo-control under mild reaction conditions.[4] For example, the Cu-catalyzed intermolecular additions of anilines to highly activated α,β-unsaturated carbonyl compounds with copper(II) triflate as the Lewis acid catalyst have been reported by Yamazaki and coworkers.[5] Copper(II) triflate has also been used to intermolecularly hydroaminate arylalkenes with sulfonamides, but this amination reaction is thought to be catalyzed by Brønsted acids accidently produced under the reaction conditions, rather than a copper catalyst.[6] Gunnoe and coworkers reported that a copper(I) amido complex coordinated to an *N*-heterocyclic carbene (NHC) ligand catalyzes the additions of anilines to terminal alkenes with high regioselectivities.[7] In a recent study, Zhang and coworkers reported that a copper catalyst promoted the regioselective intermolecular hydroaminations of terminal vinylarenes with arylamines in the presence of visible light.[8] Despite recent advances related to highly efficient and selective Cu-catalyzed additions of aromatic amines to alkenes, most reactions are limited in substrate scope to terminal alkenes.

We recently reported that copper catalysts using phosphine- or NHC-based CuCl and KO*t*-Bu enhance reactivity to promote the intermolecular additions of anilines or heterocycles to 1,2-disubstituted alkenes, including α,β-unsaturated carbonyls, α,β-unsaturated sulfones, 1-sulfonyl-1,3-dienes, and arylalkenes, while also controlling regio- and stereoselectivities, to afford versatile functionalized amines in a highly efficient manner.[9] To further develop copper catalysts that widely promote the aminations of a broad range of alkenes, we devised the copper-catalyzed hydroaminations of aromatic amines with readily accessible β,γ-unsaturated sulfones as alternatives to β-substituted β-amino sulfones. Hence, herein we report that NHC-CuCl and KO*t*-Bu catalyze the additions of aromatic amines selectively at the β-positions of β,γ-unsaturated sulfones. This catalytic process facilitates access to new and versatile β-amino sulfones that can be functionalized using a variety of synthetic transformations and used in the syntheses of biologically active molecules.[10]

Results and Discussion

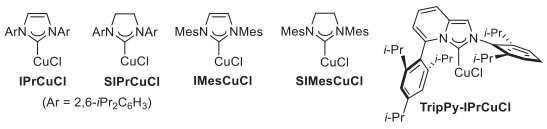
We initially evaluated the ability of an NHC-based copper catalyst to promote the amination of allyl phenyl sulfone (**1**) with *p*-anisidine (**2a**), the results of which are presented in Table 1. When **1** was treated with **2a** in the presence of 5.5 mol % **IPrCuCl** and 5 mol % KO*t*-Bu at ambient temperature, the reaction proceeded regioselectively to afford the desired aminated product **3a** in 75% yield (entry 1).

Table 1. Optimizing the reaction conditions.[a]

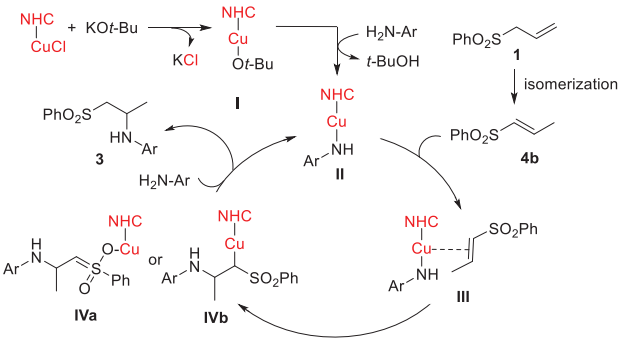


entry	NHC-CuCl	KO*t*-Bu	Temp (°C)	Time (h)	Conv (%)[b]	3a:4a:4b (%)[b]
1	**IPrCuCl**	5	22	15	75	75:<2:<2
2	**SIPrCuCl**	5	22	15	87	70:16:<2
3	**IMesCuCl**	5	22	15	>98	86:14:<2
4	**SIMesCuCl**	5	22	15	>98	86:14:<2
5	**TripPy-IPr-CuCl**	5	22	15	89	47:<2:37
6	**IPrCuCl**	5	40	15	>98	>98:<2:<2
7	**IPrCuCl**	5	40	5	71	68:<2:3
8	No	no	40	15	<2	<2
9	**IPrCuCl**	0	40	15	<2	<2
10	No	5	40	15	>98	<2:30:<2
11	CuCl	5	40	15	<2	<2

[a] Reaction conditions: allyl phenyl sulfone (**1**, 0.30 mmol), *p*-anisidine (**2a**, 0.36 mmol), **NHCCuCl** (5.5 mol %), KO*t*-Bu (5 mol %), toluene (1.0 M) under N_2.
[b] Determined by ^{1}H NMR spectroscopy against 1,3,5-trimethoxybenzene as the internal standard.



While various NHC–CuCl complexes, such as **SIPrCuCl**, **IMesCuCl**, and **SIMesCuCl**, also catalyzed amination, non-negligible amounts of the dimerized side product **4a** was obtained (14–16%, entries 2–4). The reaction of **1** with **2a** catalyzed by sterically demanding **TripPy-IPr-CuCl** was less efficient, providing the desired product **3a** in 47% yield along with vinyl sulfone **4b** (entry 5). After optimizing the reaction temperature and time, **3a** was obtained in >98% yield with >98% regioselectivity using the **IPrCuCl** catalyst under the reaction conditions described in entry 6. The results summarized in entries 8–11 show that the NHC ligand plays an important role in promoting the addition of anisidine **2a** to allyl sulfone **1**, with KO*t*-Bu also essential for amination. In the absence of the NHC-CuCl catalyst, the reaction of **1** with **2a** proceeded to completion in the presence of 5 mol % KO*t*-Bu, but the desired product was not obtained (<2% of **3a**); instead, **1** was observed to decompose and also form 30% of the dimerized product **4a** (entry 10). The dimerized product **4a** is possibly formed by the conjugate addition of allyl sulfone **1** to vinyl sulfone **4b**, which was formed by the base-promoted isomerization of allyl sulfone **1** with KO*t*-Bu or arylamide.[11] When allyl sulfone **1** was treated with 5.5 mol % **IPrCuCl** and 5 mol % KO*t*-Bu at room temperature in the absence of anisidine

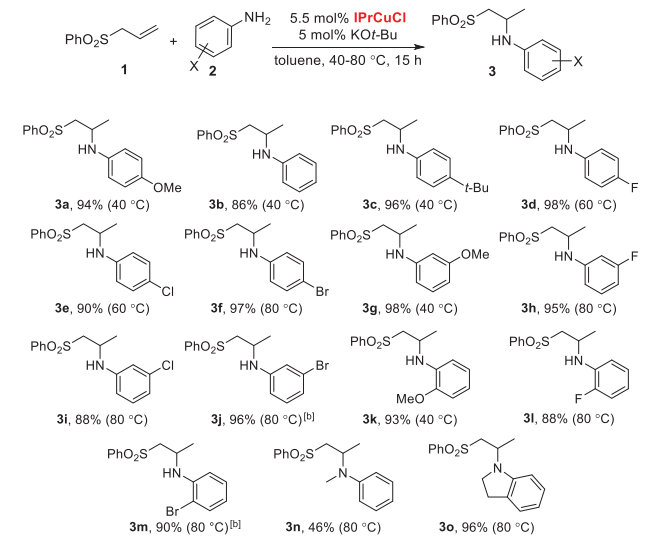


Scheme 1. Plausible mechanism for the Cu-catalyzed amination reaction.

2a, **1** predominantly dimerized to give **4a** in 80% yield (90% conv., 10% **4b**). This result reveals that the NHC-CuO*t*-Bu complex also promotes the isomerization of allyl sulfone **1** to vinyl sulfone **4b**, resulting in dimerization. Therefore, **4a** is formed during tedious catalytic aminations (entries 2–4).

Based on our studies and reports by the Gunnoe group,[7b,9d,12] we assume that NHC-Cu-NHAr complex **II** derived from ligand exchange between *in situ* generated

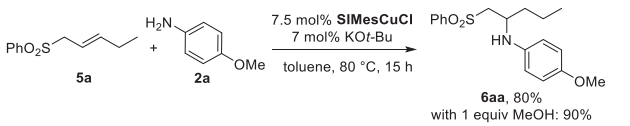
Table 2. Cu-catalyzed hydroaminations of allyl sulfone **1** with various aromatic amines.[a]



[a] Reaction conditions: allyl phenyl sulfone (**1**, 0.30 mmol), aniline **2** (0.36 mmol), **IPrCuCl** (5.5 mol %), KO*t*-Bu (5 mol %), toluene (1.0 M) under N_2. Yields of isolated products.
[b] **SIMesCuCl** was used.

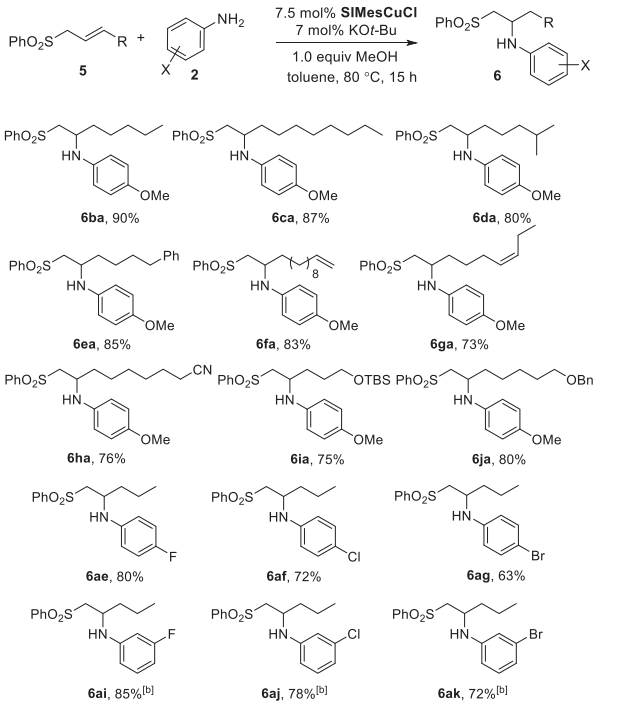
NHC-CuO*t*-Bu **I** and anisidine acts as the main catalytic species (Scheme 1). After NHC-Cu-NHAr **II** coordinates to the vinyl sulfone intermediate **4b**, obtained from isomerization of allyl sulfone **1** promoted by **I** or **II**, copper complex **II** activated by the electron-donating NHC ligand inserts into vinyl sulfone **4b**. As a result, intermediate **IVb**, which has a C─N bond at the β-position and a Cu─C bond at the α-position with respect to the sulfonyl group, or intermediate **IVa** bearing a Cu─O bond, is generated. The reaction of **IVa** or **IVb** with aniline releases protonated product **3** and regenerates copper-amino complex **II**.

With the optimized reaction conditions in hand, we next explored the scope of the substituent on the aromatic amine. A variety of arylamines effectively and selectively added to the β-position of allyl sulfone **1** in the presence of 5.5 mol % of the NHC-Cu catalyst and 5 mol % KO*t*-Bu, as summarized in Table 2. These Cu-catalyzed aminations successfully provided a broad range of β-substituted β-amino sulfones in high yields and excellent regioselectivities. The reaction of **1** with aniline **2b** gave the desired product **3b** in 86% yield, and arylamines, including those substituted with methoxy, *tert*-butyl, fluoro, chloro, or bromo substituents at their *para*, *meta*, and *ortho* positions, were well tolerated, to afford the corresponding β-amino sulfones **3a**–**3m** in yields of 86–98%. Notably, the reaction temperature needed to be raised to 60 °C or 80 °C to more efficiently add several anilines (*i.e.*, 62% of **3d** at 40 °C vs. 98% at 60 °C). In addition, the yield of the desired product was improved when **1** was aminated with



Scheme 2. Cu-catalyzed hydroaminations of γ-substituted allyl sulfone **5a** with anisidine **2a**.

Table 3. Cu-catalyzed hydroamination reactions of γ-substituted allylic sulfones with arylamines.[a]



[a] Reaction conditions: allylic sulfone (**5**, 0.30 mmol), aniline **2** (0.36 mmol), **SIMesCuCl** (7.5 mol %), KO*t*-Bu (7 mol %), toluene (1.0 M) under N_2. Yields of isolated products.
[b] 7.5 mol % Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) and CuCl were used.

o- or *m*-bromoaniline using the less sterically demanding **SIMesCuCl** catalyst (*i.e.*, 70% of **3m** with **IPrCuCl** vs. 90% with **SIMesCuCl**). The catalytic reaction involving *N*-methylaniline (**2n**) was sluggish under the optimized conditions, affording the desired product **3n** in 46% yield along with 40% of the dimerized side product **4a**. Dihydroindole **2o** also participated well in this amination reaction to give the corresponding amine in excellent yield; this amine serves as a valuable building block for the syntheses of biologically active molecules.[13]

We subsequently turned our attention to γ-substituted allyl sulfones bearing a variety of functional groups. As shown in Scheme 2, **SIMesCuCl** more effectively catalyzes the amination of the more sterically demanding γ-substituted allyl sulfone **5a** with anisidine **2a**, to afford

the desired product **6aa** in 80% yield (60% yield with **IPrCuCl**). We noted that the yield of the aminated product **6aa** could be improved to 90% by adding 1 equiv. of MeOH. We believe that MeOH promotes the regeneration of the Cu-amido complex **II** through the efficient reaction with copper intermediate **IV**.[9b,14]

Various disubstituted allyl sulfones and arylamines were catalytically aminated, as summarized in Table 3. Substrates **5b**–**5e** containing *n*-butyl, *n*-heptyl, isopentyl, and phenylpropyl groups at the γ-position of allyl sulfone were highly efficient and provided the corresponding amines **6ba**–**6ea** in high yields (80–90%) and excellent regioselectivities under the established reaction conditions. This catalytic copper amination tolerates synthetically valuable functional groups, such as alkenes, nitriles, silyl ethers, and benzyl ethers; new functionalized β-amino sulfones **6fa**–**6ja** were obtained in yields of 73–83%. Arylamines substituted with fluoro, chloro, and bromo groups at their *meta* or *para* positions were also smoothly aminated with γ-substituted allyl sulfone **5a**, to give aminated products **6ae**–**6ak** in yields of 63–85%. We noted that the phosphine-based copper catalyst formed using a combination of 7.5 mol % Xantphos and CuCl was more effective in reactions involving **5a** with *meta*-substituted anilines **2i**–**k** (*i.e.*, 85% yield vs. 68% yield with **SIMesCuCl**).

Conclusion

A broad range of new and versatile functionalized β-amino sulfones was synthesized by the Cu-catalyzed hydroaminations of easily accessible β,γ-unsaturated sulfones with aromatic amines. Reactions catalyzed by an *N*-heterocyclic carbene-copper complex and KO*t*-Bu proceeded successfully with excellent regioselectivities under mild reaction conditions. This catalytic transformation features good functional group tolerance, good substrate scope, and the use of readily available allylic sulfones and catalysts. The syntheses of valuable amines through the Cu-catalyzed hydroaminations of other nucleophiles are currently in progress.

Experimental Section

General Information. Infrared (IR) spectra were recorded on the wavenumber (cm^{-1}) scale on a ABB MB3000 FT-IR spectrophotometer. Bands are characterized as strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts are reported in ppm relative to the solvent resonance of tetramethylsilane as the internal standard ($CDCl_3$: δ 7.27 ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on the abovementioned spectrometer with complete proton decoupling. Chemical shifts are reported in ppm (relative to TMS) and were referenced against $CDCl_3$ (δ 77.00) as the internal standard. High-resolution mass spectrometry (HRMS) was performed at the Korea Basic Science Institute using 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. Potassium *tert*-butoxide was purchased from the Sigma-Aldrich corporation and used as received. All work-up and purification procedures were carried out using reagent grade solvents in air. A variety of NHC–CuCl complexes[15] and allyl sulfones[16] were prepared according to reported experimental procedures.

Representative Experimental Procedure for the Cu-Catalyzed Hydroamination of an β,γ-Unsaturated Sulfone With an Aromatic Amine

4-Methoxy*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline (3a). IPr-CuCl (8.1 mg, 17 × 10^{-3} mmol), KO*t*-Bu (1.7 mg, 15 × 10^{-3} mmol) and 4-methoxyaniline (44 mg, 0.36 mmol) were added to a 4-mL vial charged with a magnetic bar in glove box. The vial was sealed with a cap and was removed from the glove box. The vial was purged with N_2 gas for 5 min, after which toluene (0.2 mL) was added. The solution was allowed to premix for 30 min and a solution of (allylsulfonyl)benzene (**1**, 55 mg, 0.30 mmol) in toluene (0.1 mL) was added to the mixture, which was allowed to stir at 40 °C for 15 h. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (EtOAc:hexanes = 1:3) to afford the desired **3a** (86 mg, 0.28 mmol, 94%) as a brown solid. mp. 69–70 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90 (d, J = 7.3 Hz, 2H), 7.66 (tt, J = 7.3, 1.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 6.72 (dt, J = 9.2, 3.0 Hz, 2H), 6.44 (dt, J = 9.2, 3.0 Hz, 2H), 3.95–3.87 (m, 1H), 3.74 (s, 3H), 3.43 (br s, 1H), 3.41 (dd, J = 14.2, 4.1 Hz, 1H), 3.05 (dd, J = 14.2, 7.8 Hz, 1H), 1.43 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.7. 139.7, 139.4, 133.7, 129.3, 127.8, 115.1, 114.9, 60.7, 55.6, 45.5, 21.2; **IR** (neat): 3387 (w), 2955 (w), 1512 (s), 1443 (m), 1288 (s), 1234 (s), 1134 (s), 1034 (m), 810 (m), 748 (s) cm^{-1}; **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_3S$ 306.1164, Found 306.1164.

(E)-(2-Methylpent-3-ene-1,3-diyldisulfonyl)dibenzene (4a). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.86 (dd, J = 7.3, 0.9 Hz, 2H), 7.76 (d, J = 7.3 Hz, 2H), 7.71–7.67 (m, 1H), 7.63–7.56 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 6.96 (q, J = 7.3 Hz, 1H), 3.48–3.42 (m, 1H), 3.37 (d, J = 7.3 Hz, 2H), 1.94 (d, J = 7.3 Hz, 3H), 1.23 (d, J = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.8, 140.1, 139.5, 139.1, 133.8, 133.2, 129.3, 129.1, 127.8, 127.7, 60.1, 27.7, 18.6, 14.5; **IR** (neat): 3063 (w), 2986 (w), 2939 (w), 2361 (s), 1450 (w), 1296 (s), 1149 (s), 1088 (m), 733 (s), 697 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_4S_2$ 365.0881, Found 365.0881.

(E)-(Prop-1-en-1-ylsulfonyl)benzene (4b). **^{1}H NMR** ($CDCl_3$, 400 MHz)[17]: δ 7.89 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.05–6.96 (m, 1H), 6.36 (dq, J = 14.9, 1.6 Hz, 1H), 1.94 (dd, J = 7.3, 1.8 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.6, 140.4, 133.2, 131.6, 129.1, 127.4, 17.3.

N-*(1-(Phenylsulfonyl)propan-2-yl)aniline (3b).* Compound **3b** was synthesized in 86% yield (71 mg, 0.26 mmol) as a light orange solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). mp 79–80 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.92 (dd, J = 8.2, 1.1 Hz, 2H), 7.67 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 8.2 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 8.2 Hz, 2H), 4.03–3.99 (m, 1H), 3.69 (brs, 1H), 3.43 (dd, J = 14.2, 4.1 Hz, 1H), 3.08 (dd, J = 14.2, 7.3 Hz, 1H), 1.47 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 145.4, 139.7, 133.8, 129.4, 129.3, 127.9, 118.1, 113.2, 60.7, 44.4, 21.3; **IR** (neat): 2978 (w), 2885 (w), 2854 (w), 2381 (m), 2330 (m), 1605 (s), 1504 (s), 1304 (s), 1149 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{18}NO_2S$ 276.1058, Found 276.1058 Supporting Information.

4-(*tert*-Butyl)-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3c). Compound **3c** was synthesized in 96% yield (95 mg, 0.29 mmol) as a light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:5). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.93 (dd, J = 7.2, 1.4 Hz, 2H), 7.68 (t, J = 6.9 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.17 (dd, J = 8.7, 1.4 Hz, 2H), 6.41 (dd, J = 8.7, 1.4 Hz, 2H), 4.04–3.96 (m, 1H), 3.61 (br s, 1H), 3.46 (dd, J = 14.2, 4.1 Hz, 1H), 3.06 (ddd, J = 14.1, 7.9, 1.4 Hz, 1H), 1.47 (d, J = 6.4 Hz, 3H), 1.28 (d, J = 1.4 Hz, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 143.0, 140.9, 139.7, 133.8, 129.3, 127.9, 126.2, 112.9, 60.8, 44.5, 33.8, 31.4, 21.4; **IR** (neat): 3371 (w), 2970 (m), 2870 (m), 2361 (s), 1612 (m), 1520 (s), 1450 (w), 1304 (s), 1257 (w), 1142 (s), 1088 (w), 825 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{26}NO_2S$ 332.1684, Found 332.1685.

4-Fluoro-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3d). Compound **3d** was synthesized in 98% yield (86 mg, 0.29 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:5). mp 96–97 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 6.9 Hz, 2H), 7.66 (tt, J = 7.4, 1.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 6.83 (t, J = 8.7 Hz, 2H), 6.41–6.36 (m, 2H), 3.95–3.88 (m, 1H), 3.53 (br s, 1H), 3.37 (dd, J = 14.2, 4.1 Hz, 1H), 3.08 (dd, J = 14.2, 7.3 Hz, 1H), 1.42 (d, J = 1.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 156.0 (d, J = 118 Hz), 141.9, 139.6, 133.8, 129.3, 127.8, 115.8 (d, J = 11.1 Hz), 114.2 (d, J = 3.9 Hz), 60.6, 45.1, 21.2; **IR** (neat): 3425 (m), 2924 (w), 1612 (w), 1512 (s), 1296 (s), 1211 (s), 1142 (s), 1080 (m), 818 (s), 748 (s), 687 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}FNO_2S$ 294.0964, Found 294.0964.

4-Chloro-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3e). Compound **3e** was synthesized in 90% yield (83 mg, 0.27 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:5). mp 113–114 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0, 1.1 Hz, 2H), 7.67 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.36 (d, J = 8.7 Hz, 2H), 3.98–3.90 (m, 1H), 3.76 (br s, 1H), 3.36 (dd, J = 14.2, 4.6 Hz, 1H), 3.09 (dd, J = 14.2, 7.3 Hz, 1H), 1.44 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.1, 139.5, 133.9, 129.3, 129.2, 127.9, 122.7, 114.3, 60.6, 44.6, 21.2; **IR** (neat): 3387 (m), 2962 (w), 2932 (w), 1597 (s), 1497 (s), 1450 (w), 1396 (w), 1296 (s), 1134 (s), 1080 (m), 887 (m), 810 (s), 741 (s), 679 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO_2S$ 310.0669, Found 310.0669.

4-Bromo-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3f). Compound **3f** was synthesized in 97% yield (103 mg, 0.29 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 114–115 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0, 1.1 Hz, 2H), 7.68 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 6.30 (d, J = 8.7 Hz, 2H), 3.98–3.90 (m, 1H), 3.79 (br s, 1H), 3.36 (dd, J = 14.2, 4.6 Hz, 1H), 3.08 (dd, J = 14.2, 7.3 Hz, 1H), 1.44 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.5, 139.4, 133.9, 132.1, 129.4, 127.8, 114.6, 109.7, 60.5, 44.4, 21.2; **IR** (neat): 3433 (w), 2978 (w), 2924 (w), 1589 (m), 1497 (s), 1396 (w), 1296 (s), 1257 (m), 1142 (s), 1080 (s), 995 (w), 802 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}BrNO_2S$ 354.0163, Found 354.0161.

3-Methoxy-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3g). Compound **3g** was synthesized in 98% yield (90 mg, 0.29 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 55–56 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 7.7 Hz, 2H), 7.67 (tt, J = 7.0, 1.3 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 8.2 Hz, 1H), 6.32 (dd, J = 8.3 Hz, 1H), 6.12–6.07 (m, 2H), 4.21 (br s, 1H), 4.05–3.98 (m, 1H), 3.76 (s, 3H), 3.46 (dd, J = 14.2, 4.1 Hz, 1H), 3.10 (dd, J = 14.2, 7.8 Hz, 1H), 1.47 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 160.8, 146.9, 139.6, 133.7, 130.1, 129.3, 127.8, 105.9, 103.5, 99.0, 60.7, 55.0, 44.3, 21.2; **IR** (neat): 3387 (m), 2970 (w), 1597 (s), 1288 (m), 1211 (m), 1072 (w), 748 (s), 679 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_3S$ 306.1164, Found 306.1164.

3-Fluoro-N-(1-(phenylsulfonyl)propan-2-yl)aniline (3h). Compound **3h** was synthesized in 95% yield (84 mg, 0.29 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). mp 50–51 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90 (dd, J = 8.2, 1.4 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.3 Hz, 2H), 7.05 (td, J = 8.2, 6.4 Hz, 1H), 6.38 (td, J = 8.3, 2.5 Hz, 1H), 6.20 (dd, J = 8.0, 2.5 Hz, 1H), 6.06 (dt, J = 11.6, 2.5 Hz, 1H), 3.92 (br s, 2H), 3.39 (dd, J = 14.2, 2.7 Hz, 1H), 3.11 (dd, J = 14.2, 6.9 Hz, 1H),

1.44 (d, J = 5.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 163.9 (d, J = 243.8 Hz), 147.3 (d, J = 10.6 Hz), 139.3, 133.9, 130.5 (d, J = 9.6 Hz), 129.4, 127.8, 108.8 (d, J = 1.9 Hz), 104.4 (d, J = 21.2 Hz), 99.7 (d, J = 25.0 Hz), 60.6, 44.4, 21.1; **IR** (neat): 2998 (w), 2885 (w), 2854 (w), 2368 (m), 2330 (m), 1620 (s), 1520 (m), 1497 (m), 1296 (s), 1149 (s), 1080 (m), 849 (m), 756 (m) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}FNO_2S$ 294.0964, Found 294.0963.

***3-Chloro*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3i).** Compound **3i** was synthesized in 88% yield (82 mg, 0.26 mmol) as a light pink solid. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:4). mp 76–77 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 7.3 Hz, 2H), 7.67 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.66 (dd, J = 7.8, 1.8 Hz, 1H), 6.32 (t, J = 8.2 Hz, 2H), 3.93–3.88 (m, 2H), 3.38 (dd, J = 14.4, 3.9 Hz, 1H), 3.10 (dd, J = 14.2, 6.0 Hz, 1H), 1.43 (d, J = 6.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.7, 139.3, 134.9, 133.9, 130.3, 129.4, 127.8, 117.8, 112.6, 111.2, 60.5, 44.3, 21.0; **IR** (neat): 3394 (w), 2854 (w), 2361 (s), 2330 (s), 1597 (m), 1497 (m), 1296 (m), 1142 (s), 1080 (w), 741 (m) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO_2S$ 310.0669, Found 310.0670.

***3-Bromo*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3j).** Compound **3j** was synthesized in 96% yield (102 mg, 0.29 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 8.2 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.53 (s, 1H), 6.35 (dd, J = 8.2, 2.3 Hz, 1H), 3.90 (m, 2H), 3.38 (dd, J = 14.4, 4.3 Hz, 1H), 3.11 (dd, J = 14.2, 6.9 Hz, 1H), 1.43 (d, J = 5.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.8, 139.3, 133.9, 130.7, 129.4, 127.8, 123.2, 120.7, 115.6, 111.6, 60.5, 44.3, 21.0; **IR** (neat): 3387 (m), 2978 (m), 2870 (w), 2368 (w), 2330 (w), 1597 (s), 1504 (m), 1481 (m), 1296 (s), 1142 (s), 1080 (m), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}BrNO_2S$ 354.0163, Found 354.0164.

***2-Methoxy*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3k).** Compound **3k** was synthesized in 93% yield (85 mg, 0.28 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 53–54 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 6.9 Hz, 2H), 7.67 (tt, J = 7.3 Hz, 1.6 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 6.81–6.68 (m, 3H), 6.38 (d, J = 7.8 Hz, 1H), 4.45 (br s, 1H), 4.07–4.00 (m, 1H), 3.80 (s, 3H), 3.49 (dd, J = 14.2, 3.7 Hz, 1H), 3.07 (dd, J = 14.2, 8.2 Hz, 1H), 1.52 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.8, 139.7, 135.2, 133.7, 129.2, 127.9, 121.2, 117.2, 109.9, 109.6, 60.8, 55.2, 43.7, 21.4; **IR** (neat): 3425 (w), 2978 (w), 2353 (w), 1520 (m), 1458 (m), 1304 (m), 1250 (m), 1227 (m), 1142 (m), 1028 (m), 741 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_3S$ 306.1164, Found 306.1164.

***2-Fluoro*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3l).** Compound **3l** was synthesized in 88% yield (77 mg, 0.26 mmol) as white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). mp 62–63 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91 (dd, J = 8.5, 1.1 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.3 Hz, 2H), 6.97–6.91 (m, 2H), 6.64 (tdd, J = 7.7, 4.9, 1.6 Hz, 1H), 6.49 (td, J = 8.5, 1.4 Hz, 1H), 4.07–4.03 (m, 1H), 3.88 (d, J = 6.4 Hz, 1H), 3.42 (dd, J = 14.2, 3.7 Hz, 1H), 3.11 (dd, J = 14.2, 7.8 Hz, 1H), 1.49 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.4 (d, J = 151.4, Hz), 139.6, 134.0, 133.8, 129.3, 127.8, 124.7 (d, J = 3.8 Hz), 117.4 (d, J = 6.7 Hz), 114.7 (d, J = 18.3 Hz), 112.1 (d, J = 2.9 Hz), 60.8, 44.0, 21.3; **IR** (neat): 3394 (w), 2986 (w), 2361 (s), 1620 (m), 1520 (s), 1450 (m), 1304 (s), 1142 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}FNO_2S$ 294.0964, Found 294.0964.

***2-Bromo*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3m).** Compound **3m** was synthesized in 90% yield (95 mg, 0.27 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 7.8 Hz, 2H), 7.65 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.38 (dd, J = 7.8, 1.4 Hz, 1H), 7.10 (td, J = 7.8, 0.9 Hz, 1H), 6.57 (t, J = 7.8 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 4.24 (br s, 1H), 4.10–4.06 (m, 1H), 3.39 (dd, J = 14.2, 3.7 Hz, 1H), 3.10 (dd, J = 14.2, 7.8 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.2, 139.5, 133.8, 132.7, 129.3, 128.6, 127.8, 118.4, 111.3, 109.9, 60.8, 44.1, 21.3; **IR** (neat): 2978 (w), 2854 (w), 2381 (m), 2322 (m), 1597 (m), 1512 (s), 1450 (m), 1304 (s), 1142 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}BrNO_2S$ 354.0163, Found 354.0163.

***N-Methyl*-N-*(1-(phenylsulfonyl)propan-2-yl)aniline* (3n).** Compound **3n** was synthesized in 46% yield (40 mg, 0.14 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:4). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.3 Hz, 2H), 7.21 (dd, J = 8.9, 7.1 Hz, 2H), 6.77 (t, J = 7.1 Hz, 1H), 6.70 (d, J = 8.2 Hz, 2H), 4.57 (sext, J = 6.8 Hz, 1H), 3.46 (dd, J = 14.6, 6.9 Hz, 1H), 3.20 (dd, J = 14.4, 6.6 Hz, 1H), 2.37 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.7, 139.6, 133.5, 129.2, 129.0, 127.9, 118.0, 114.0, 59.2, 49.8, 30.0, 17.3; **IR** (neat): 3063 (w), 2978 (m), 2924 (m), 2870 (m), 1597 (s), 1504 (s), 1450 (m), 1389 (m), 1304 (s), 1142 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{19}NNaO_2S$ 312.1034, Found 312.1034.

***1-(1-(Phenylsulfonyl)propan-2-yl)indoline* (3o).** Compound **3o** was synthesized in 96% yield (87 mg, 0.29 mmol) as a brown oil. The crude product was purified

using silica gel column chromatography (EtOAc:hexanes = 1:4 with 1% Et_3N). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.3Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.03–6.99 (m, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 7.8 Hz, 1H), 4.27 (sext, J = 6.7 Hz, 1H), 3.41–3.29 (m, 2H), 3.16 (dd, J = 14.2, 7.3 Hz, 1H), 2.95–2.79 (m, 2H), 2.63 (ddd, J = 15.6, 9.1, 6.9 Hz, 1H), 1.39 (d, J = 6.9 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 149.4, 139.9, 133.5, 129.8, 129.1, 127.9, 127.4, 124.5, 118.0, 107.1, 58.5, 46.3, 46.0, 27.9, 17.0; **IR** (neat): 3055 (w), 2978 (m), 2932 (m), 2854 (m), 1605 (s), 1489 (s), 1450 (m), 1396 (m), 1304 (s), 1257 (s), 1142 (s), 1080 (s), 741 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{19}NNaO_2S$ 324.1034, Found 324.1033.

4-Methoxy*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6aa). Compound **6aa** was synthesized in 90% yield (90 mg, 0.27 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 106–107 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.3 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.55–7.51 (m, 2H), 6.72 (d, J = 8.9 Hz, 2H), 6.43 (d, J = 8.9 Hz, 2H), 3.84–3.80 (m, 1H), 3.74 (s, 3H), 3.40 (br s, 1H), 3.34 (dd, J = 14.2, 4.6 Hz, 1H), 3.14 (dd, J = 14.2, 6.9 Hz, 1H), 1.94–1.86 (m, 1H), 1.62–1.53 (m, 1H), 1.50–1.34 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.4, 140.0, 139.9, 133.6, 129.2, 127.6, 114.9, 114.7, 59.4, 55.7, 49.6, 37.2, 19.0, 13.7; **IR** (neat): 3394 (w), 3009 (w), 2947 (w), 1520 (s), 1450 (m), 1296 (s), 1234 (s), 1142 (s), 1080 (m), 1034 (m), 810 (m), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{23}NNaO_3S$ 356.1296, Found 356.1298.

4-Methoxy*-N-*(1-(phenylsulfonyl)heptan-2-yl)aniline (6ba). Compound **6ba** was synthesized in 90% yield (98 mg, 0.27 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 57–58 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.56–7.52 (m, 2H), 6.73 (d, J = 8.7 Hz, 2H), 6.44 (d, J = 8.7 Hz, 2H), 3.78 (br s, 1H), 3.74 (s, 3H), 3.51 (br s, 1H), 3.34 (dd, J = 14.3, 4.3 Hz, 1H), 3.15 (dd, J = 14.3, 6.4 Hz, 1H), 1.97–1.88 (m, 1H), 1.63–1.54 (m, 1H), 1.45–1.35 (m, 2H), 1.35–1.25 (m, 4H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ152.5, 139.9, 139.9, 133.7, 129.2, 127.9, 115.0, 114.9, 59.4, 55.7, 50.0, 35.1, 31.5, 25.5, 22.5, 14.0; **IR** (neat): 3402 (m), 3032 (w), 2932 (m), 1520 (s), 1450 (m), 1296 (s), 1250 (s), 1134 (s), 1080 (m), 1034 (m), 810 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{28}NO_3S$ 362.1790, Found 362.1787.

4-Methoxy*-N-*(1-(phenylsulfonyl)decan-2-yl)aniline (6ca). Compound **6ca** was synthesized in 87% yield (105 mg, 0.26 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 54–55 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.54–7.51 (m, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.42 (d, J = 8.5 Hz, 2H), 3.78 (s, 1H), 3.73 (s, 3H), 3.43 (br s, 1H), 3.33 (dd, J = 14.2, 4.1 Hz, 1H), 3.14 (dd, J = 14.2, 6.9 Hz, 1H), 1.94–1.86 (m, 1H), 1.60–1.53 (m, 1H), 1.43–1.26 (m, 12H), 0.89 (t, J = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.3, 140.0, 139.9, 133.6, 129.1, 127.8, 114.9, 114.6, 59.4, 55.6, 49.8, 35.1, 31.7, 29.3, 29.2, 29.1, 25.7, 22.5, 14.0; **IR** (neat): 3364 (w), 2916 (w), 2847 (w), 1512 (s), 1458 (m), 1304 (s), 1242 (s), 1142 (s), 1088 (m), 1041 (m), 825 (s), 741 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{34}NO_3S$ 404.2259, Found 404.2256.

4-Methoxy*-N-*(6-methyl-1-(phenylsulfonyl)heptan-2-yl) aniline (6da). Compound **6da** was synthesized in 80% yield (90 mg, 0.24 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 83–84 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 8.7 Hz, 2H), 3.82–3.76 (m, 1H), 3.74 (s, 3H), 3.36 (br s, 1H), 3.34 (d, J = 14.3, 4.3 Hz, 1H), 3.14 (dd, J = 14.2, 6.9 Hz, 1H), 1.94–1.86 (m, 1H), 1.61–1.43 (m, 3H), 1.41–1.30 (m, 1H), 1.20–1.13 (m, 2H), 0.86 (d, J = 6.4 Hz, 3H), 0.85(d, J = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ.152.4, 140.0, 139.9, 133.6, 129.2, 127.8, 114.9, 114.7, 59.4, 55.7, 50.0, 38.5, 35.4, 27.8, 23.6, 22.5, 22.4; **IR** (neat): 2955 (w), 2908 (w), 2870 (w), 2253 (w), 1512 (m), 1304 (m), 1242 (m), 1149 (m), 910 (s), 733 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{30}NO_3S$ 376.1946, Found 376.1948.

4-Methoxy*-N-*(6-phenyl-1-(phenylsulfonyl)hexan-2-yl)aniline (6ea). Compound **6ea** was synthesized in 85% yield (108 mg, 0.26 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 76–77 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.23–7.18 (m, 3H), 6.75 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), 3.85–3.79 (m, 1H), 3.76 (s, 3H), 3.45 (br s, 1H), 3.35 (dd, J = 14.2, 4.1 Hz, 1H), 3.15 (dd, J = 14.2, 6.9 Hz, 1H), 2.62 (t, J = 7.5 Hz, 2H), 2.04–1.95 (m, 1H), 1.70–1.59 (m, 3H), 1.57–1.39 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.4, 142.1. 139.9, 139.8, 133.6, 129.2, 128.3, 128.2, 127.7, 125.6, 114.9, 114.7, 59.3, 55.6, 49.8, 35.5, 34.8, 30.9, 25.3; **IR** (neat): 3109 (w), 2970 (w), 1589 (w), 1497 (w), 1450 (w), 1304 (s), 1142 (s), 1088 (m), 972 (s), 895 (m), 741 (s), 687 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_3S$ 424.1946, Found 424.1945.

(Z)-4-Methoxy*-N-*(1-(phenylsulfonyl)trideca-2,12-dien-2-yl)aniline (6fa). Compound **6fa** was synthesized in 83% yield (110 mg, 0.25 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 76–77 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 6.9 Hz, 2H), 7.65 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 9.1 Hz, 2H), 6.44 (d, J = 8.7 Hz, 2H), 5.82 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.00 (dq, J = 17.0, 1.8 Hz, 1H), 4.94 (dt, J = 10.2, 1.1 Hz, 1H), 3.82–3.77 (m, 1H),

3.74 (s, 3H), 3.48 (br s, 1H), 3.34 (dd, J = 14.2, 4.6 Hz, 1H), 3.15 (dd, J = 14.2, 6.9 Hz, 1H), 2.07–2.02 (m, 2H), 1.92 (ddt, J = 14.2, 9.7, 5.2 Hz, 1H), 1.63–1.53 (m, 1H), 1.44–1.34 (m, 4H), 1.26 (s, 10H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.5, 139.9, 139.9, 139.2, 133.6, 129.2, 127.9, 114.9, 114.8, 114.1, 99.9, 59.4, 55.7, 50.0, 35.1, 33.7, 29.4, 29.4, 29.3, 29.1, 28.9, 25.8; **IR** (neat): 3387 (w), 2924 (s), 2854 (m), 1512 (s), 1450 (m), 1304 (s), 1242 (s), 1142 (s), 1041 (m), 910 (s), 825 (m), 733 (s); **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{38}NO_3S$ 444.2572, Found 444.2571.

(Z)-4-Methoxy*-N-*(1-(phenylsulfonyl)non-6-en-2-yl)aniline (6ga). Compound **6ga** was synthesized in 73% yield (85 mg, 0.22 mmol) as an orange solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 55–56 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 8.7 Hz, 2H), 5.42–5.35 (m, 1H), 5.31–5.25 (m, 1H), 3.83–3.77 (m, 1H), 3.75 (s, 3H), 3.36 (br s, 1H), 3.34 (dd, J = 14.2, 4.6 Hz, 1H), 3.14 (dd, J = 14.4, 6.6 Hz, 1H), 2.07–1.90 (m, 5H), 1.63–1.40 (m, 3H), 0.95 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.5, 140.0, 139.9, 133.7, 132.3, 129.2, 128.2, 127.9, 115.0, 114.8, 59.5, 55.7, 50.0, 34.8, 26.7, 25.9, 20.5, 14.3; **IR** (neat): 3394 (w), 2924 (w), 2862 (w), 1690 (w), 1512 (s), 1450 (m), 1288 (s), 1242 (s), 1142 (s), 1080 (m), 1034 (s), 964 (w), 810 (s), 741 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{30}NO_3S$ 388.1946, Found 388.1946.

8-((4-Methoxyphenyl)amino)-9-(phenylsulfonyl)nonanenitrile (6ha). Compound **6ha** was synthesized in 76% yield (91 mg, 0.23 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.86 (dd, J = 8.5 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 6.42 (d, J = 9.1 Hz, 2H), 3.83–3.77 (m, 1H), 3.73 (s, 3H), 3.43 (br s, 1H), 3.33 (dd, J = 14.2, 4.1 Hz, 1H), 3.11 (dd, J = 14.2, 7.3 Hz, 1H), 2.32 (t, J = 7.1 Hz, 2H), 2.01–1.92 (m, 1H), 1.66–1.53 (m, 3H), 1.51–1.25 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.3, 139.8, 139.6, 133.7, 129.2, 127.7, 119.8, 114.8, 114.5, 59.1, 55.5, 49.5, 34.9, 28.3, 25.4, 25.0, 16.9; **IR** (neat): 3379 (w), 2978 (m), 2932 (m), 2862 (m), 1512 (s), 1450 (m), 1389 (w), 1304 (s), 1242 (s), 1142 (s), 1080 (w), 1041 (m), 825 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{29}N_2O_3S$ 401.1899, Found 401.1897.

N-*(5-((tert-Butyldimethylsilyl)oxy)-1-(phenylsulfonyl)pentan-2-yl)-4-methoxyaniline (6ia)*. Compound **6ia** was synthesized in 75% yield (104 mg, 0.22 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 8.7 Hz, 2H), 3.82 (br s, 1H), 3.75 (s, 3H), 3.63–3.60 (m, 3H), 3.35 (dd, J = 14.6, 4.6 Hz, 1H), 3.17 (dd, J = 14.2, 6.9 Hz, 1H), 2.04–1.97 (m, 1H), 1.73–1.58 (m, 3H), 0.90 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.0, 137.4, 137.1, 133.7, 133.5, 129.3, 127.9, 115.0, 62.6, 55.7, 44.2, 29.0, 25.9, 20.9, 18.3, 17.8, −5.3; **IR** (neat): 3379 (w), 2932 (m), 2862 (m), 2361 (s), 1512 (s), 1450 (w), 1304 (m), 1250 (s), 1149 (s), 1119 (s), 1041 (w), 833 (s), 779 (m) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{38}NO_4SSi$ 464.2291, Found 464.2289.

N-*(7-(Benzyloxy)-1-(phenylsulfonyl)heptan-2-yl)-4-methoxyaniline (6ja)*. Compound **6ja** was synthesized in 80% yield (112 mg, 0.24 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (dd, J = 8.5, 1.1 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.36–7.34 (m, 4H), 7.31-7.28 (m, 1H), 6.73 (d, J = 8.7 Hz, 2H), 6.42 (d, J = 9.1 Hz, 2H), 4.51 (s, 2H), 3.82-3.76 (m, 1H), 3.75 (s, 3H), 3.46 (t, J = 6.4 Hz, 2H), 3.39 (s, 1H), 3.33 (dd, J = 14.2, 4.1 Hz, 1H), 3.12 (dd, J = 14.2, 6.9 Hz, 1H), 2.00-1.92 (m, 1H), 1.65–1.53 (m, 3H), 1.51–1.37 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 152.3, 139.9, 139.7, 138.5, 133.7, 129.2, 128.3, 127.8, 127.5, 127.4, 114.8, 114.6, 72.8, 70.1, 49.2, 55.6, 49.7, 35.1, 29.5, 25.9, 25.6; **IR** (neat): 3387 (w), 2978 (m), 2932 (m), 2862 (m), 2361 (s), 1512 (s), 1450 (m), 1381 (w), 1304 (s), 1242 (s), 1142 (s), 1034 (m), 825 (m), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{34}NO_4S$ 468.2209, Found 468.2209.

4-Fluoro*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6ae). Compound **6ae** was synthesized in 80% yield (77 mg, 0.24 mmol) as an orange solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 78–79 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.86–7.83 (m, 2H), 7.64–7.60 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 6.82–6.78 (m, 2H), 6.38–6.35 (m, 2H), 3.82–3.76 (m, 1H), 3.57 (br s, 1H), 3.29 (dd, J = 14.2, 4.6 Hz, 1H), 3.14 (dd, J = 14.2, 6.4 Hz, 1H), 1.90–1.81 (m, 1H), 1.60–1.47 (m, 1H), 1.45–1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 155.9 (d, J = 236 Hz), 142.4, 139.8, 133.7, 129.2, 127.8, 115.8 (d, J = 23.1 Hz), 114.0 (d, J = 6.7 Hz), 59.4, 49.4, 37.3, 19.0, 13.7; **IR** (neat): 3387 (w), 2962 (w), 2932 (w), 1612 (w), 1520 (s), 1450 (w), 1296 (s), 1219 (m), 1134 (s), 1080 (s), 887 (w), 810 (s), 741 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}FNO_2S$ 322.1277, Found 322.1277.

4-Chloro*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6af). Compound **6af** was synthesized in 72% yield (73 mg, 0.22 mmol) as an orange solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 96–97 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.86 (dd, J = 8.2, 1.4 Hz, 2H), 7.65 (tt, J = 7.3, 1.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.35 (d, J = 9.1 Hz, 2H), 3.86–3.80 (m, 1H), 3.68 (br s, 1H), 3.30 (dd, J = 14.6, 4.6 Hz, 1H), 3.17 (dd, J = 14.2, 6.9 Hz, 1H), 1.90–1.85 (m, 1H), 1.59–1.52 (m, 1H), 1.47–1.35 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$,

100 MHz): δ 144.7, 139.7, 133.8, 129.3, 129.1, 127.8, 122.3, 114.1, 59.5, 48.8, 37.2, 19.0, 13.7; **IR** (neat): 3433 (w), 2924 (w), 1597 (s), 1497 (s), 1396 (w), 1296 (s), 1257 (w), 1142 (s), 1080 (s), 802 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}ClNO_2S$ 338.0982, Found 338.0984.

4-Bromo*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6ag). Compound **6ag** was synthesized in 63% yield (72 mg, 0.19 mmol) as a light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.2 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.3 Hz, 2H), 7.20 (dd, J = 8.9, 1.1 Hz, 2H), 6.31 (dd, J = 8.7, 0.9 Hz, 2H), 3.87–3.80 (m, 1H), 3.67 (br s, 1H), 3.30 (dd, J = 14.2, 3.7 Hz, 1H), 3.17 (dd, J = 14.2, 6.4 Hz, 1H), 1.92–1.88 (m, 1H), 1.61–1.56 (m, 1H), 1.46–1.36 (m, 2H), 0.92 (td, J = 7.3, 0.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 145.1, 139.8, 133.8, 132.1, 129.3, 127.9, 114.6, 109.6, 59.5, 48.9, 37.3, 19.0, 13.7; **IR** (neat): 3387 (w), 2970 (m), 2870 (m), 2361 (m), 1690 (s), 1597 (s), 1489 (s), 1443 (m), 1304 (s), 1142 (s), 1080 (w), 1018 (w), 818 (s), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{20}BrNNaO_2S$ 404.0296, Found 404.0297.

3-Fluoro*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6ai). Compound **6ai** was synthesized in 85% yield (82 mg, 0.26 mmol) as a light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc: hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.8 Hz, 2H), 7.66 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.04 (td, J = 8.1, 6.6 Hz, 1H), 6.38 (td, J = 8.3, 2.5 Hz, 1H), 6.21 (dd, J = 8.2, 2.7 Hz, 1H), 6.06 (dt, J = 11.4, 2.5 Hz, 1H), 3.86–3.75 (m, 2H), 3.33 (dd, J = 14.2, 4.6 Hz, 1H), 3.19 (dd, J = 14.2, 6.4 Hz, 1H), 1.95–1.87 (m, 1H), 1.63–1.54 (m, 1H), 1.50–1.33 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 164.0 (d, J = 243.8 Hz), 147.8 (d, J = 10.6 Hz), 139.6, 133.8, 130.5 (d, J = 10.6 Hz), 129.3, 127.9, 108.8 (d, J = 2.0 Hz), 104.4 (d, J = 22.2 Hz), 99.7 (d, J = 25.0 Hz), 59.5, 48.8, 37.2, 19.0, 13.7; **IR** (neat): 3379 (w), 2970 (m), 2870 (m), 2361 (m), 1620 (s), 1497 (m), 1450 (m), 1304 (s), 1149 (s), 1088 (w), 841 (m), 756 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}FNO_2S$ 322.1277, Found 322.1274.

3-Chloro*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6aj). Compound **6aj** was synthesized in 78% yield (79 mg, 0.23 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 7.3 Hz, 2H), 7.66 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.66 (dd, J = 8.0, 2.1 Hz, 1H), 6.36–6.31 (m, 2H), 3.86–3.80 (m, 1H), 3.72 (br s, 1H), 3.33 (dd, J = 14.2, 4.6 Hz, 1H), 3.20 (dd, J = 14.2, 6.9 Hz, 1H), 1.98–1.87 (m, 1H), 1.63–1.53 (m, 1H), 1.49–1.32 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.3, 139.6, 135.1, 133.9, 130.4, 129.4, 127.8, 117.8, 112.7, 111.2, 59.5, 48.7, 37.2, 19.0, 13.7; **IR** (neat): 3387 (w), 2970 (m), 2870 (m), 2338 (w), 1597 (s), 1481 (s), 1389 (w), 1304 (s), 1142 (s), 1080 (m), 841 (m), 748 (s) cm^{-1}; **HRMS** (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}ClNO_2S$ 338.0982, Found 338.0983.

3-Bromo*-N-*(1-(phenylsulfonyl)pentan-2-yl)aniline (6ak). Compound **6ak** was synthesized in 72% yield (82 mg, 0.22 mmol) as a brown oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 6.9 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 8.0 Hz, 1H), 6.81 (dd, J = 7.3, 0.9 Hz, 1H), 6.53 (t, J = 2.1 Hz, 1H), 6.36 (dd, J = 8.2, 2.3 Hz, 1H), 3.85–3.80 (m, 1H), 3.74 (br s, 1H), 3.32 (dd, J = 14.2, 4.6 Hz, 1H), 3.19 (dd, J = 14.2, 6.4 Hz, 1H), 1.95–1.86 (m, 1H), 1.61–1.53 (m, 1H), 1.50–1.34 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.4, 139.6, 133.8, 130.7, 129.3, 127.8, 123.3, 120.7, 115.6, 111.6, 59.5, 48.7, 37.1, 19.0, 13.7; **IR** (neat): 3379 (w), 2970 (m), 2870 (m), 2353 (w), 1597 (s), 1474 (m), 1304 (s), 1142 (s), 1080 (m), 987 (w), 841 (m), 748 (s) cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}BrNO_2S$ 382.0476, Found 382.0475.

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Conflict of interest

The authors declare no competing financial interests.

Supporting Information

Additional supporting information (^{1}H NMR and ^{13}C NMR spectra for all products) is available in the online version of this article.

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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