Supporting Information
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Efficient Ligand-free Copper Catalyzed N-arylation of Sulfonamides

Supporting Information

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Supporting Information

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General Methods

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Flash chromatography was performed using Merck silica gel 60 with AR grade solvents. Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Bruker Avance DPX 400 spectrophotometer (CDCl$_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as $\delta$ in units of parts per million (ppm) downfield from SiMe$_4$ ($\delta$ 0.0) and relative to the signal of chloroform-$d$ ($\delta$ 7.2600, singlet). Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as $\delta$ in units of parts per million (ppm) downfield from SiMe$_4$ ($\delta$ 0.0) and relative to the signal of chloroform-$d$ ($\delta$ 77.03, triplet). Elemental analysis was performed on vario MICRO CUBE CHNS. The N-arylated products are all known compounds that exhibited spectroscopic data identical to those reported in the literature$^{1-17}$ except for 4f, 4i, 4j, 4k, 4l, 4n.

All reagents were purchased from commercial supplier and were used without any purification. CuI (Sigma Aldrich, 99.99% purity) was purchased from Sigma Aldrich.

General procedure for N-arylation of aliphatic amines

A mixture of CuI (Sigma-Aldrich, 99.99% purity, 0.0735 mmol) and Cs$_2$CO$_3$ (2.94 mmol) was dissolved in (0.75 mL) dimethylformamide (DMF). Following the addition of aryl halide (2.21 mmol) and sulfonamide (1.47 mmol), the reaction vial was sealed. The reaction mixture was stirred under air in a closed system at 135 °C for 24 h, then the heterogeneous mixture was cooled to RT and diluted with dichloromethane. The resulting solution was directly filtered through a pad of Celite. The combined organic extracts were dried with anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography to afford the N-arylated product. The identity and purity of the products was confirmed by $^1$H and $^{13}$C NMR spectroscopic analysis.
**1H and 13C NMR data of N-arylated products**

**4-Methyl-N-phenyl-benzencesulfonamide**¹,²,³ (3a). Following the general procedure using p-toluenesulfonamide (0.252 g, 1.47 mmol) and iodobenzene (0.328 mL, 2.94 mmol) provided 314 mg (86% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

![Structure of 4-Methyl-N-phenyl-benzencesulfonamide](image)

**1H NMR (400 MHz, CDCl₃):** δ 7.70 (d, J=8.3 Hz, 2H), 7.22-7.18 (m, 4H), 7.11-7.06 (m, 3H), 2.34 (s, 3H).

**13C NMR (100 MHz, CDCl₃):** δ 143.8, 136.7, 136.0, 129.6, 129.2, 127.3, 125.1, 121.3, 21.5.

Anal. Calcd for C₁₃H₁₃NO₂S: C, 63.13; H, 5.30; N, 5.66; S, 12.97. Found: C, 62.68; H, 5.29; N, 5.53; S, 12.72.

**N-(2-Methoxy-phenyl)-4-methyl-benzencesulfonamide**¹ (3b). Following the general procedure using p-toluenesulfonamide (0.252 g, 1.47 mmol) and 2-iodoanisole (0.287 mL, 2.21 mmol) provided 101 mg (25% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

![Structure of N-(2-Methoxy-phenyl)-4-methyl-benzencesulfonamide](image)

**1H NMR (400 MHz, CDCl₃):** δ 7.64 (d, J=8.3 Hz, 2H), 7.50 (d, J=7.9, 1H), 7.18 (d, J=8.1, 2H), 7.02-7.00 (m, 2H), 6.88 (t, 1H), 6.74 (d, J=1.0, 1H), 3.64 (s, 3H), 2.35 (s, 3H).

**13C NMR (100 MHz, CDCl₃):** δ 149.8, 143.9, 136.6, 129.6, 127.6, 126.4, 125.6, 121.4, 121.3, 110.9, 55.9, 21.8.

Anal. Calcd for C₁₄H₁₅NO₃S: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 61.61; H, 5.55; N, 4.44; S, 10.47.

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N-(2-Chloro-phenyl)-4-methyl-benzenesulfonamide$^4$ (3c). Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 2-chloro-iodobenzene (0.269 mL, 2.21 mmol) provided 300 mg (72% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67-7.64 (m, 3H), 7.26-7.21 (m, 4H), 7.04 (t, $J$=4.6 Hz, 1H), 6.95 (s, 1H), 2.38 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.0, 135.7, 133.3, 130.0, 129.2, 127.7, 127.1, 125.6, 124.9, 122.2, 21.4. Anal. Calcd for C$_{13}$H$_{12}$ClNO$_2$: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 56.47; H, 4.56; N, 4.71; S, 10.96.

4-Methyl-N-$m$-tolyl-benzenesulfonamide$^5$ (3d). Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 3-iodotoluene (0.282 mL, 2.21 mmol) provided 292 mg (76% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J$=8.2 Hz, 2H), 7.42 (bs, 1H), 7.20 (d, $J$=8.1 Hz, 2H), 7.08 (t, $J$ = 7.8 Hz, 1H), 6.93-6.87 (m, 3H), 2.35 (s, 3H), 2.24 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.7, 139.2, 136.6, 136.1, 129.6, 129.0, 127.3, 125.9, 121.9, 118.1, 21.9, 21.8.

N-(3-Chloro-phenyl)-4-methyl-benzenesulfonamide$^6$ (3e). Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 3-chloro-iodobenzene (0.273 mL, 2.21 mmol) provided 270 mg (65% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.
1H NMR (400 MHz, CDCl₃): δ 7.72 (d, J=8.2 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H), 7.15-7.11 (m, 2H), 7.04 (d, J=4.2 Hz, 1H), 6.98 (d, J=4.3 Hz, 1H), 2.38 (s, 3H).

13C NMR (100 MHz, CDCl₃): δ 144.3, 137.9, 135.7, 134.9, 130.3, 129.7, 127.4, 125.1, 120.9, 118.9, 21.5.

Anal. Calcd for C₁₃H₁₂ClNO₂S: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.31; H, 4.24; N, 4.78; S, 11.55.

4-Methyl-N-(3-trifluoromethyl-phenyl)-benzenesulfonamide⁷ (3f). Following the general procedure using p-toluenesulfonamide (0.252 g, 1.47 mmol) and 3-iodobenzotrifluoride (0.318 mL, 2.21 mmol) provided 340 mg (73% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

1H NMR (400 MHz, CDCl₃): δ 7.68-7.66 (m, 2H), 7.37-7.36 (m, 2H), 7.30-7.24 (m, 5H), 2.39 (s, 3H).

13C NMR (100 MHz, CDCl₃): δ 144.5, 137.3, 135.6, 132.0, 131.7, 130.0, 129.9, 127.3, 124.1, 121.8, 117.7, 21.6.

Anal. Calcd for C₁₄H₁₂F₃NO₂S: C, 53.33; H, 3.84; N, 4.44; S, 10.17. Found: C, 53.45; H, 3.81; N, 4.34; S, 10.07.

4-Methyl-N-(4-nitro-phenyl)-benzenesulfonamide (3g). Following the general procedure using p-toluenesulfonamide (0.252 g, 1.47 mmol) and 1-iodo-3-nitrobenzene (0.549g, 2.21 mmol) provided 269 mg (63% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.
$\text{H-NMR (400 MHz, CDCl}_3\text{): }\delta 7.96-7.94 (m, 1H), 7.88 (s, 1H), 7.71 (d, J=8.2 Hz, 2H), 7.49-7.40 (m, 2H), 7.31-7.21 (m, 2H), 6.91 (s, 1H), 2.40 (s, 3H)$.


$\text{N-(4-Methoxy-phenyl)-4-methyl-benzenesulfonamide}^8 (3\text{h})$. Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 4-iodo-anisole (0.516 g, 2.21 mmol) provided 303 mg (74% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

$\text{N-(4-Fluoro-phenyl)-4-methyl-benzenesulfonamide}^9 (3\text{i})$. Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 4-fluoriodobenzene (0.254 ml, 2.21 mmol) provided 312 mg (80% yield) of the coupling product as a brown oil after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.64 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.07-7.04 (m, 2H), 6.93-6.89 (m, 2H), 2.38 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.8, 159.4, 144.0, 135.7, 132.4, 129.7, 127.4, 124.5, 124.4, 116.4, 115.9, 29.7.
Anal. Calcd for C$_{13}$H$_{12}$FNO$_2$S: C, 58.85; H, 4.56; N, 5.80; S, 12.09. Found: C, 59.28; H, 4.59; N, 5.08; S, 12.31.

**N-(4-Chloro-phenyl)-4-methyl-benzenesulfonamide** $^8$ (3j). Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 4-chloroiodobenzene (0.526 g, 2.21 mmol) provided 175 mg (42% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J = 8.3$ Hz, 2H), 7.25-7.18 (m, 4H), 7.05-7.03 (m, 2H), 2.39 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.2, 135.7, 135.2, 130.8, 129.4, 129.1, 127.6, 122.9, 21.5.
Anal. Calcd for C$_{13}$H$_{12}$ClNO$_2$S: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.50; H, 4.22; N, 4.71; S, 11.06.

**N-(4-Bromo-phenyl)-4-methyl-benzenesulfonamide** $^8$ (3k). Following the general procedure using $p$-toluenesulfonamide (0.252 g, 1.47 mmol) and 4-bromo-iodobenzene (0.624 g, 2.21 mmol) provided 251 mg (52% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.
4-Methyl-N-(4-trifluoromethyl-phenyl)-benzenesulfonamide\textsuperscript{8} (3l). Following the general procedure using \textit{p}-toluenesulfonamide (0.252 g, 1.47 mmol) and 4-iodo-benzotrifluoride (0.324 mL, 2.21 mmol) provided 324 mg (70\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (85:15 hexane/ethyl acetate) of the crude oil.

\[ \text{S H O}\]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{Br} \]

\[ ^{1}\text{H-NMR (400 MHz, CDCl}_{3} \right) \delta 7.65 (d, J=8.4 \text{ Hz}, 2H), 7.34 (d, J=8.8 \text{ Hz}, 2H), 7.24 (d, J=8.1 \text{ Hz}, 2H), 6.96 (d, J=8.8 \text{ Hz}, 2H), 2.39 (s, 3H). \]

\[ ^{13}\text{C-NMR (100 MHz, CDCl}_{3} \right) \delta 143.9, 138.0, 135.4, 132.1, 129.5, 127.0, 122.8, 118.2, 21.3. \]

\textit{N}-Phenyl-benzenesulfonamide\textsuperscript{1,10} (4a). Following the general procedure using benzenesulfonamide (0.231g, 1.47 mmol) and iodobenzene (0.246 mL, 2.21 mmol) provided 293 mg (86\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\[ \text{S H O}\]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{C F}_{3} \]
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 7.76-7.74\ (m, 2H),\ 7.56-7.52\ (m, 1H),\ 7.46-7.42\ (m, 2H),\ 7.31-7.21\ (m, 2H),\ 7.15-7.06\ (m, 1H),\ 7.06-7.04\ (m, 2H),\ 6.38\ (s, 1H)\).

\textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 139.0,\ 136.5,\ 133.0,\ 129.2,\ 129.0,\ 127.3,\ 125.3,\ 121.6\).

Anal. Calcd for C\textsubscript{12}H\textsubscript{11}NO\textsubscript{2}S: C, 61.78; H, 4.75; N, 6.00; S, 13.74. Found: C, 61.49; H, 4.69; N, 5.73; S, 13.58.

\textbf{N-m-Tolyl-benzenesulfonamide\textsuperscript{11} (4b).\ }Following the general procedure using benzenesulfonamide (0.231g, 1.47 mmol) and 3-iodotoluene (0.282 mL, 2.21 mmol) provided 260 mg (71\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure1}
\caption{Structure of N-m-Tolyl-benzenesulfonamide (4b).}
\end{figure}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 7.75\ (d, \textit{J}= 8.8\ Hz, 2H),\ 7.53\ (t, \textit{J}= 3.7\ Hz, 1H),\ 7.44\ (t, \textit{J}=7.7\ Hz, 2H),\ 7.10\ (t, \textit{J}= 3.9\ Hz, 1H),\ 6.94-6.86\ (m, 3H),\ 6.40\ (s, 1H),\ 2.27\ (s, 3H)\).

\textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 155.8,\ 139.4,\ 136.2,\ 133.0,\ 129.1,\ 129.0,\ 127.2,\ 126.4,\ 122.5,\ 118.8,\ 21.3\).

Anal. Calcd for C\textsubscript{13}H\textsubscript{13}NO\textsubscript{2}S: C, 63.13; H, 5.30; N, 5.66; S, 12.97. Found: C, 63.71; H, 5.20; N, 5.49; S, 13.36.

\textbf{N-(3-Chloro-phenyl)-benzenesulfonamide\textsuperscript{12} (4c).\ }Following the general procedure using benzenesulfonamide (0.231g, 1.47 mmol) and 3-chloro-iodobenzene (0.273 mL, 2.21 mmol) provided 322 mg (82\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure2}
\caption{Structure of N-(3-Chloro-phenyl)-benzenesulfonamide (4c).}
\end{figure}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 7.84\ (d, \textit{J}=7.5\ Hz, 2H),\ 7.57\ (t, \textit{J}=7.5\ Hz, 1H),\ 7.48\ (t, \textit{J}=7.7\ Hz, 2H),\ 7.27-7.14\ (m, 2H),\ 7.09-7.06\ (m, 1H),\ 7.01-6.99\ (m, 1H)\).

\textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\ 138.7,\ 137.7,\ 134.4,\ 133.4,\ 130.4,\ 129.2,\ 127.4,\ 125.4,\ 121.1,\ 119.1\).

Anal. Calcd for C\textsubscript{12}H\textsubscript{10}ClNO\textsubscript{2}S: C, 53.83; H, 3.76; N, 5.23; S, 11.98. Found: C, 54.04; H, 3.81; N, 5.04; S, 11.39.
Naphthalene-2-sulfonic acid phenylamide\(^{13}\) (4d). Following the general procedure using naphthalene-2-sulfonamide (0.104 g, 0.5 mmol) and iodobenzene (0.084 mL, 0.75 mmol) provided 109 mg (77% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\[
\begin{align*}
\text{Naphthalene-2-sulfonic acid phenylamide} & \\
\text{Following the general procedure using naphthalene-2-sulfonamide (0.104 g, 0.5 mmol) and iodobenzene (0.084 mL, 0.75 mmol) provided 109 mg (77\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.}
\end{align*}
\]

\(^{1}\text{H NMR (400 MHz, CDCl}_3\): } \delta 8.37 (s, 1H), 7.87 (t, J=8.7 Hz, 3H), 7.77 (d, J=8.7 Hz, 1H), 7.64-7.55 (m, 2H), 7.26-7.19 (m, 2H), 7.19-7.04 (m, 4H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\): } \delta 136.4, 136.0, 134.9, 132.0, 129.4, 129.4, 129.3, 128.9, 128.9, 127.9, 127.5, 125.5, 122.3, 121.8.

Anal. Calcd for C\(_{16}\)H\(_{13}\)NO\(_2\)S: C, 67.82; H, 4.62; N, 4.94; S, 11.32. Found: C, 67.46; H, 4.63; N, 4.83; S, 11.28.

Naphthalene-2-sulfonic acid m-tolylamide\(^{14}\) (4e). Following the general procedure using naphthalene-2-sulfonamide (0.104 g, 0.5 mmol) and 3-iodotoluene (0.096 mL, 0.75 mmol) provided 125 mg (84% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\[
\begin{align*}
\text{Naphthalene-2-sulfonic acid m-tolylamide} & \\
\text{Following the general procedure using naphthalene-2-sulfonamide (0.104 g, 0.5 mmol) and 3-iodotoluene (0.096 mL, 0.75 mmol) provided 125 mg (84\% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.}
\end{align*}
\]

\(^{1}\text{H NMR (400 MHz, CDCl}_3\): } \delta 8.42 (s, 1H), 7.85-7.77 (m, 5H), 7.56-7.47 (m, 2H), 7.05-6.96 (m, 3H), 6.82 (d, J=7.3 Hz, 1H), 2.17 (s, 3H).

\(^{13}\text{C NMR (100 MHz, CDCl}_3\): } \delta 139.2, 136.4, 136.0, 134.8, 132.0, 129.2, 129.0, 128.9, 128.8, 128.8, 127.8, 127.3, 126.0, 122.3, 122.0, 118.2, 21.2.

Naphthalene-2-sulfonic acid (3-chloro-phenyl)-amide (4f). Following the general procedure using naphthalene-2-sulfonamide (0.104 g, 0.5 mmol) and 3-chloro-iodobenzene (0.093 mL, 0.75
mmol) provided 137 mg (86% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

1H NMR (400 MHz, CDCl₃): δ 8.45 (s, 1H), 7.87-7.81 (m, 4H), 7.61-7.52 (m, 2H), 7.22 (s, 1H), 7.09-6.97 (m, 3H).

13C NMR (100 MHz, CDCl₃): δ 138.1, 135.8, 135.3, 135.2, 132.3, 130.6, 130.0, 129.6, 129.4, 129.3, 128.2, 127.9, 125.5, 122.3, 121.2, 119.2.

Anal. Calcd for C₁₁₆H₁₂ClNO₂S: C, 60.47; H, 3.81; N, 4.41; S, 10.09. Found: C, 59.69; H, 3.99; N, 4.21; S, 9.31.

2-Methyl-N-phenyl-benzenesulfonamide15 (4g). Following the general procedure using o-toluenesulfonamide (0.252g , 1.47 mmol) and iodobenzene (0.246 mL, 2.21 mmol) provided 277 mg (76% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

1H NMR (400 MHz, CDCl₃): δ 7.95 (d, J=8.2 Hz, 1H), 7.43 (t, J= 8.1 Hz, 1H), 7.31-7.19 (m, 4H), 7.08 (t, J=7.9 Hz, 1H), 7.01-6.99 (m, 2H), 6.50 (s, 1H), 2.65 (s, 3H).

13C NMR (400 MHz, CDCl₃): δ 137.4, 137.2, 136.4, 133.1, 132.6, 130.0, 129.4, 126.3, 125.0, 120.6, 20.4.


2-Methyl-N-m-tolyl-benzenesulfonamide16 (4h). Following the general procedure using o-toluenesulfonamide (0.252g , 1.47 mmol) and 3-iodotoluene (0.282 mL, 2.21 mmol) provided 305 mg (79% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.
1H NMR (400 MHz, CDCl3): δ 7.96 (d, J=7.6 Hz, 1H), 7.43 (t, J= 7.6 Hz, 1H), 7.29-7.26 (m, 2H), 7.08 (t, J=7.8 Hz, 1H), 6.88 (d, J=7.6 Hz, 1H), 6.82 (s, 1H), 6.79 (d, J=8.0 Hz, 1H), 6.52 (s, 1H), 2.65 (s, 3H), 2.25 (s, 3H).

13C NMR (400 MHz, CDCl3): δ 139.3, 137.5, 137.2, 136.4, 133.1, 132.6, 130.0, 129.1, 126.2, 125.7, 121.1, 117.4, 21.3, 20.4.

Anal. Calcd for C14H15NO2S: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 64.74; H, 5.67; N, 5.29; S, 12.09.

N-(3-Chloro-phenyl)-2-methyl-benzenesulfonamide (4i). Following the general procedure using o-toluenesulfonyl chloride (0.252g, 1.47 mmol) and 3-chloro-iodobenzene (0.273 mL, 2.21 mmol) provided 364 mg (88% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

1H NMR (400 MHz, CDCl3): δ 7.98 (d, J=9.3 Hz, 1Hz), 7.46 (t, J=7.0 Hz, 1H), 7.33-7.21 (m, 2H), 7.14 (t, J=7.9 Hz, 1H), 7.05-7.02 (m, 2H), 6.91-6.89 (m, 1H), 6.58 (s, 1H), 2.66 (s, 3H).

13C NMR (400 MHz, CDCl3): δ 137.8, 137.3, 136.9, 134.8, 133.4, 132.8, 130.3, 129.8, 126.4, 124.6, 119.7, 117.7, 20.3.

Anal. Calcd for C13H12ClNO2S: C, 55.42; H, 4.29; N, 4.97; S, 11.38. Found: C, 55.67; H, 4.25; N, 4.83; S, 11.11.

4-Fluoro-2-methyl-N-phenyl-benzenesulfonamide (4j). Following the general procedure using 4-fluoro-2-methylbenzene sulfonamide (0.095g, 0.5 mmol) and iodobenzene (0.084 ml, 0.75 mmol) provided 97 mg (73% yield) of the coupling product as a brown oil after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.
1H-NMR (400 MHz, CDCl3) δ 7.98-7.95 (m, 1H), 7.26-7.21 (m, 2H), 7.12-7.10 (m, 1H), 7.01-6.95 (m, 4H), 6.60 (s, 1H), 2.63 (s, 3H).

13C-NMR (100 MHz, CDCl3) δ 166.2, 163.6, 140.9, 140.8, 136.3, 133.3, 133.2, 132.8, 129.4, 125.0, 120.5, 119.5, 119.3, 113.3, 113.1, 20.5.

4-Fluoro-2-methyl-N-m-tolyl-benzenesulphonamide (4k). Following the general procedure using 4-fluoro-2-methylbenzene sulphonamide (0.095g, 0.5 mmol) and 3-iodotoluene (0.096 mL, 0.75 mmol) provided 116 mg (83% yield) of the coupling product as a brown oil after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

1H NMR (400 MHz, CDCl3): δ 7.99-7.95 (m, 1H), 7.10 (t, J=4.0 Hz, 1H), 6.97-6.92 (m, 4H), 6.82-6.78 (m, 2H), 6.45 (s, 1H), 2.64 (s, 3H), 2.26 (s, 3H).

13C NMR (100 MHz, CDCl3): δ 166.2, 163.7, 140.8, 140.7, 139.5, 136.1, 133.4, 133.0, 132.9, 129.2, 126.0, 121.3, 119.6, 119.3, 117.6, 113.3, 113.1, 21.3, 20.6.

Anal. Calcd for C14H14FNO2S: C, 60.20; H, 5.05; N, 5.01; S, 11.48. Found: C, 60.40; H, 4.88; N, 4.82; S, 11.64.

N-(3-Chloro-phenyl)-4-fluoro-2-methyl-benzenesulphonamide (4l). Following the general procedure using 4-fluoro-2-methylbenzene sulphonamide (0.095g, 0.5 mmol) and 3-chloroiodobenzene (0.093 mL, 0.75 mmol) provided 120 mg (80% yield) of the coupling product as a brown oil after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.
\[ \text{N-4-Chloro-3-Tolyl-4-trifluoromethyl-benzenesulfonamide} \ (4m). \]

Following the general procedure using 4-trifluoromethyl-benzenesulfonamide (0.113 g, 0.5 mmol) and 3-iodotoluene (0.096 mL, 0.75 mmol) provided 127 mg (81% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.

\[ \text{N-(3-Chloro-phenyl)-4-trifluoromethyl-benzenesulfonamide} \ (4n). \]

Following the general procedure using 4-trifluoromethyl-benzenesulfonamide (0.113 g, 0.5 mmol) and 3-chloroiodobenzene (0.093 mL, 0.75 mmol) provided 124 mg (74% yield) of the coupling product as a yellowish solid after purification by flash chromatography (80:20 hexane/ethyl acetate) of the crude oil.
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J=8.2\) Hz, 2H), 7.74 (d, \(J=8.4\) Hz, 2H), 7.23-7.18 (m, 1H), 7.15-7.13 (m, 2H), 6.97-6.95 (m, 1H), 6.68 (s, 1H).

\(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 142.2, 137.0, 135.2, 135.1, 134.9, 130.6, 127.7, 126.5, 126.0, 121.7, 119.4.

Anal. Calcd for C\(_{13}\)H\(_9\)ClF\(_3\)NO\(_2\)S: C, 46.51; H, 2.70; N, 4.17; S, 9.55. Found: C, 47.11; H, 2.67; N, 4.03; S, 9.79.
References

$^1$H NMR and $^{13}$C NMR spectroscopic data for \(N\)-arylated compounds

4-Methyl-\(N\)-phenyl-benzenesulfonamide (3a)
N-(2-Methoxy-phenyl)-4-methyl-benzenesulfonamide (3b)
N-(2-Chloro-phenyl)-4-methyl-benzenesulfonamide (3c)
4-Methyl-N-m-tolyl-benzenesulfonamide (3d)
**N-(3-Chloro-phenyl)-4-methyl-benzenesulfonamide (3e)**
4-Methyl-N-(3-trifluoromethyl-phenyl)-benzenesulfonamide (3f)
4-Methyl-N-(4-nitro-phenyl)-benzenesulfonamide (3g)
N-(4-Methoxy-phenyl)-4-methyl-benzenesulfonamide (3h)
N-(4-Fluoro-phenyl)-4-methyl-benzenesulfonamide (3i)
N-(4-Chloro-phenyl)-4-methyl-benzenesulfonamide (3j)
N-(4-Bromo-phenyl)-4-methyl-benzenesulfonamide (3k)
4-Methyl-N-(4-trifluoromethyl-phenyl)-benzenesulfonamide (3l)
N-Phenyl-benzenesulfonamide (4a)
N-m-Tolyl-benzenesulfonamide (4b)
N-(3-Chloro-phenyl)-benzenesulfonamide (4c)
Naphthalene-2-sulfonic acid phenylamide (4d)
Naphthalene-2-sulfonic acid \textit{m}-tolylamide (4e)
Naphthalene-2-sulfonic acid (3-chloro-phenyl)-amide (4f)
2-Methyl-N-phenyl-benzenesulfonamide (4g)
2-Methyl-N-m-tolyl-benzenesulfonamide (4h)
N-(3-Chloro-phenyl)-2-methyl-benzenesulfonamide (4i)
4-Fluoro-2-methyl-N-phenyl-benzenesulfonamide (4j)
4-Fluoro-2-methyl-N-m-tolyl-benzenesulfonamide (4k)
N-(3-Chloro-phenyl)-4-fluoro-2-methyl-benzenesulfonamide (4l)
N-m-Tolyl-4-trifluoromethyl-benzenesulfonamide (4m)
N-(3-Chloro-phenyl)-4-trifluoromethyl-benzenesulfonamide (4n)