

## **Supporting Information-Experimental Details**

### **Cobalt-Catalyzed Intramolecular C–H Amination with Arylsulfonyl Azides**

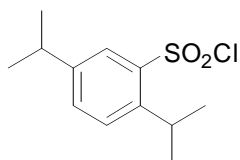
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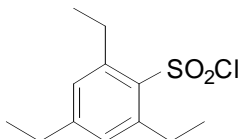
**General Considerations.** All intramolecular C-H amidation reactions were performed under nitrogen in oven-dried glassware following standard Schlenk techniques. 5 Å molecular sieves were dried in a vacuum oven prior to use. Chlorobenzene and dichloromethane were dried over calcium hydride under nitrogen and freshly distilled before use, and toluene was distilled under nitrogen from sodium benzophenone ketyl. 2,4,6-Triisopropylbenzenesulfonyl azide was purchased from Alfa Aesar and used without further purification. Substituted benzenes and sulfonyl chlorides were purchased from commercial sources and used without further purification. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60Å, 230-400 mesh, 32-63µm). <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Varian Inova400 (400 MHz) or a Varian Inova500 (500MHz) instrument with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HRMS data was obtained on an Agilent 1100 LC/MS ESI/TOF mass spectrometer.

**Note on Safety:** Careful control experiments showed the arylsulfonyl azides reported in this work were stable under the conditions used. But it should be noted that some of the azide compounds may be explosive and should be handled with great care.

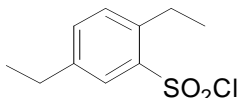
**General Procedure for the Synthesis of Sulfonyl Chlorides<sup>1</sup>:** A round bottom flask was purged with N<sub>2</sub> and charged with the substituted benzene and chloroform (2.0 ml/mmol sub. benzene). The resulting solution was cooled in an ice bath to 0 °C. Chlorosulfonic acid (4.5 eq) was added to the flask via a syringe over 10 minutes and was stirred under N<sub>2</sub> atmosphere until the reaction was complete (monitored by TLC/developed in I<sub>2</sub> – approximately 3-4 hrs). Upon reaction completion, the mixture was carefully poured over crushed ice and the aqueous layer was extracted with chloroform (3 x 5 ml). The combined organic layers were then washed with brine (10 ml), dried over sodium sulfate, and concentrated by rotary evaporation to give the crude product. The resulting oil was then purified by flash column chromatography (9:1, hexanes: ethyl acetate).



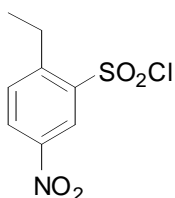
**2, 5-Diisopropylbenzene-1-sulfonyl chloride<sup>2</sup>** was obtained from 1,4-diisopropylbenzene using the general procedure as a white solid in 96% yield (1.25 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.52 (m, 2H), 4.02 (sept, *J* = 6.8 Hz, 1H), 2.97 (sept, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 6H), 1.29 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.4, 146.4, 142.0, 133.6, 128.8, 126.1, 33.7, 28.7, 23.7, 23.6. IR (neat, cm<sup>-1</sup>): 2963, 1490, 1362, 1167.



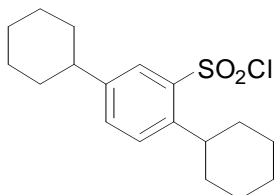
**2,4,6-Triethylbenzene-1-sulfonyl chloride** was obtained from 1,3,5-triethylbenzene using the general procedure as a yellow oil in 99% yield (778 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.0 (s, 2H), 3.15 (q,  $J = 7.2$  Hz, 4H), 2.66 (q,  $J = 7.2$  Hz, 2H), 1.32 (m, 6H), 1.26 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.5, 145.7, 139.5, 129.7, 28.5, 28.3, 16.1, 14.7. IR (neat,  $\text{cm}^{-1}$ ): 2969, 1595, 1366, 1184, 1172.



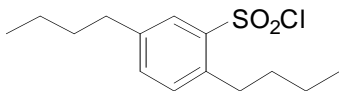
**2,5-Diethylbenzene-1-sulfonyl chloride** was obtained from 1,4-diethylbenzene using the general procedure as colorless oil in 94% yield (1.64 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 1.2$  Hz, 1H), 7.48 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.38 (d,  $J = 8.0$ , 1H), 3.16 (q,  $J = 7.2$  Hz, 2H), 2.71 (q,  $J = 7.6$  Hz, 2H), 1.34 (t,  $J = 7.2$  Hz, 3H), 1.27 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.0, 142.5, 141.1, 134.9, 131.5, 127.9, 28.1, 25.35, 15.23, 15.02. IR (neat,  $\text{cm}^{-1}$ ): 2968, 1366, 1172.



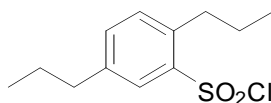
**2-Ethyl-5-nitrobenzene-1-sulfonyl chloride**<sup>3</sup> was obtained from 1-ethyl-4-nitrobenzene using the literature procedure as tan oil in 83% yield (1.37 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (d,  $J = 2.0$  Hz, 1H), 8.50 (dd,  $J = 2.0, 8.0$  Hz, 1H), 7.71 (d,  $J = 8.4$  Hz, 1H), 3.31 (q,  $J = 7.2$  Hz, 2H), 1.42 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.1, 145.8, 143.4, 132.9, 129.2, 124.3, 26.0, 14.7. IR (neat,  $\text{cm}^{-1}$ ): 3108, 1526, 1347.



**2,5-Dicyclohexylbenzene-1-sulfonyl chloride**<sup>1b</sup> was obtained from 1,4-dicyclohexylbenzene using the general procedure as a white solid in 98% yield (1.37 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (s, 1H), 7.48 (m, 2H), 3.65-3.58 (m, 1H), 2.56-2.53 (m, 1H), 1.94-1.74 (m, 10H), 1.56-1.26 (m, 10H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.5, 145.1, 142.1, 133.8, 129.5, 126.5, 43.9, 39.3, 34.0, 33.9, 26.6, 26.0, 25.8. IR (neat,  $\text{cm}^{-1}$ ): 2924, 2850, 1448, 1361, 1163. HRMS (ESI): Calcd. for  $\text{C}_{18}\text{H}_{29}\text{NClO}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  358.1602, Found 358.1625.

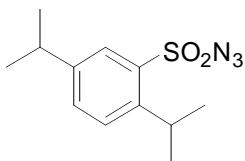


**2,5-Dibutylbenzene-1-sulfonyl chloride** was obtained from 1,4-dibutylbenzene using the general procedure as colorless oil in 81% yield (2.45 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 1.6 Hz, 1H), 7.43 (dd,  $J$  = 1.6, 8.0 Hz, 1H), 7.34 (d,  $J$  = 8.0 Hz, 1H), 3.08 (t,  $J$  = 8.0 Hz, 2H), 2.66 (t,  $J$  = 7.6 Hz, 2H), 1.69 (m, 2H), 1.61 (m, 2H), 1.47 (sextet,  $J$  = 7.6 Hz, 2H), 1.36 (sextet,  $J$  = 7.6 Hz, 2H), 0.97 (t,  $J$  = 7.6 Hz, 3H), 0.94 (t,  $J$  = 7.6 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.5, 141.8, 140.0, 135.2, 132.1, 128.4, 34.9, 33.1, 32.0, 22.7, 22.2, 13.8. IR (neat,  $\text{cm}^{-1}$ ): 2957, 2931, 1370, 1174. HRMS (ESI): Calcd. for  $\text{C}_{14}\text{H}_{25}\text{NClO}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  306.1295, Found 306.1287.



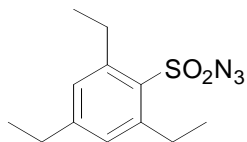
**2,5-Dipropylbenzene-1-sulfonyl chloride** was obtained from 1,4-dipropylbenzene using the general procedure as colorless oil in 91% yield (2.93 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 1.6 Hz, 1H), 7.43 (dd,  $J$  = 1.6, 8.0 Hz, 1H), 7.35 (d,  $J$  = 8.0 Hz, 1H), 3.06 (t,  $J$  = 8 Hz, 2H), 2.64 (t,  $J$  = 7.6 Hz, 2H), 1.74 (q,  $J$  = 8.0 Hz, 2H), 1.66 (q,  $J$  = 7.6 Hz, 2H), 1.04 (t,  $J$  = 7.6 Hz, 3H), 0.95 (t,  $J$  = 7.6 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.8, 141.8, 139.8, 135.4, 132.37, 128.7, 37.4, 34.4, 24.4, 24.3, 14.3, 13.8. IR (neat,  $\text{cm}^{-1}$ ): 2962, 1369, 1174.

**General Procedure for the Synthesis of Sulfonyl Azides<sup>1b</sup>:** A solution of the sulfonyl chloride (1-10 mmol) in water: acetone (1:1, 6 ml/mmol) was stirred in a round bottom flask and cooled in an ice bath to 0 °C for 15-20 minutes. Sodium azide (1.5 eq) was added in portions to the sulfonyl chloride mixture and the reaction was monitored by TLC to completion (typically 2-5 hrs). After the reaction was complete, the flask underwent rotary evaporation until the acetone was removed. The crude product was extracted from the water using ethyl acetate or dichloromethane (3 x 5 ml/mmol). It was then washed with brine (10 ml/mmol), dried over sodium sulfate, and concentrated by rotary evaporation. The resulting oil was then purified by flash column chromatography (9:1, hexanes: ethyl acetate). The fractions containing product were collected and concentrated by rotary evaporation to afford the pure compound.

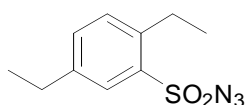


**2,5-Diisopropylbenzene-1-sulfonyl azide (1b)**, Table 2, Entry 2) was obtained from 2,5-diisopropylbenzene-1-sulfonyl chloride using the general procedure as a white solid in 98% yield (603 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23 (s, 1H), 7.50 (m, 2H), 3.70 (sept,  $J$  = 6.8 Hz, 1H), 2.97 (sept,  $J$  = 6.8 Hz, 1H), 1.30-1.27 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.2, 146.8, 135.6, 133.1, 128.5, 126.9, 33.6, 29.3, 24.0, 23.6. IR

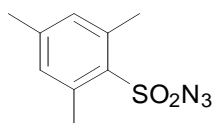
(neat,  $\text{cm}^{-1}$ ): 2964, 2123, 1361, 1161. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{21}\text{NN}_3\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  285.1385, Found 285.1379.



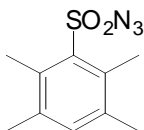
**2,4,6-Triethylbenzene-1-sulfonyl azide (1c)**, Table 2, Entry 3) was obtained from 2,4,6-triethylbenzene-1-sulfonyl chloride using the general procedure as colorless oil in 95% yield (487 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.0 (s, 2H), 3.02 (q,  $J = 7.2$  Hz, 4H), 2.62 (q,  $J = 7.6$  Hz, 2H), 1.27-1.20 (m, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 146.3, 132.4, 129.6, 28.5, 28.3, 16.7, 14.7. IR (neat,  $\text{cm}^{-1}$ ): 2968, 2119, 1597, 1363, 1162. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{21}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  285.1385, Found 285.1373.



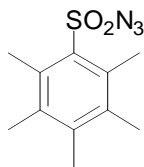
**2,5-Diethylbenzene-1-sulfonyl azide (1d)**, Table 2, Entry 4) was obtained from 2,5-diethylbenzene-1-sulfonyl chloride using the general procedure as colorless oil in 94% yield (481 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83 (d,  $J = 1.6$  Hz, 1H), 7.44 (dd,  $J = 1.2, 7.6$  Hz, 1H), 7.35 (d,  $J = 8.0$  Hz, 1H), 2.98 (q,  $J = 7.6$  Hz, 2H), 2.69 (q,  $J = 7.6$  Hz, 2H), 1.28 (t,  $J = 7.6$  Hz, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.8, 141.6, 136.1, 134.3, 131.3, 128.5, 28.19, 25.6, 15.3, 15.2. IR (neat,  $\text{cm}^{-1}$ ): 2970, 2123, 1363, 1164, 1190. HRMS (ESI): Calcd. for  $\text{C}_9\text{H}_{17}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  243.0916, Found 243.0915.



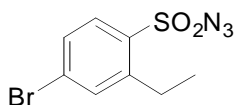
**2,4,6-Trimethylbenzene-1-sulfonyl azide<sup>1b,4</sup> (1e)**, Table 2, Entry 5) was obtained from 2,4,6-trimethylbenzene-1-sulfonyl chloride using the general procedure as a tan oil in 93% yield (480 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.01 (s, 2H), 2.66 (s, 6H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.5, 139.8, 133.1, 132.0, 22.67, 21.03. IR (neat,  $\text{cm}^{-1}$ ): 2980, 2120, 1601, 1363, 1188, 1163.



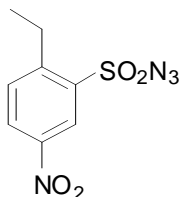
**2,3,5,6-Tetramethylbenzene-1-sulfonyl azide<sup>1b</sup> (1f)**, Table 2, Entry 6) was obtained from 2,3,5,6-tetramethylbenzene-1-sulfonyl chloride using the general procedure as a white solid in 84% yield (1.73 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23 (s, 1H), 2.56 (s, 6H), 2.30 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.3, 137.7, 136.4, 135.7, 20.84, 17.87. IR (neat,  $\text{cm}^{-1}$ ): 2920, 2119, 1349, 1157. HRMS (ESI): Calcd. for  $\text{C}_{10}\text{H}_{17}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  257.1072, Found 257.1070.



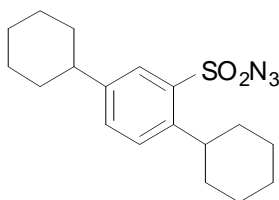
**2,3,4,5,6-Pentamethylbenzene-1-sulfonyl azide (1g)**, Table 2, Entry 7) was obtained from 2,3,4,5,6-pentamethylbenzene-1-sulfonyl chloride using the general procedure as a white solid in 98% yield (2.02 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.59 (s, 6H), 2.31 (s, 3H), 2.27 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.8, 135.5, 135.3, 134.9, 19.01, 17.97, 17.00. IR (neat,  $\text{cm}^{-1}$ ): 2927, 2121, 1348, 1152. HRMS (ESI): Calcd. for  $\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  271.1229, Found 271.1227.



**4-Bromo-2-ethylbenzene-1-sulfonyl azide (1h)**, Table 2, Entry 8) was obtained from 4-bromo-2-ethylbenzene-1-sulfonyl chloride using the general procedure as a white solid in 98% yield (486 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J = 8.0$  Hz, 1H), 7.61 (d,  $J = 2.0$  Hz, 1H), 7.53 (dd,  $J = 2.0, 8.0$  Hz, 1H), 3.01 (q,  $J = 7.2$  Hz, 2H), 1.32 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.4, 135.4, 134.3, 130.8, 130.1, 129.6, 25.97, 14.88. IR (neat,  $\text{cm}^{-1}$ ): 2979, 2126, 1579, 1364, 1164.

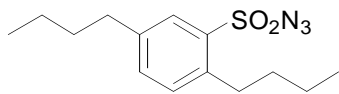


**2-Ethyl-5-nitrobenzene-1-sulfonyl azide (1i)**, Table 2, Entry 9) was obtained from 2-ethyl-5-nitrobenzene-1-sulfonyl chloride using the general procedure as a yellow solid in 92% yield (472 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (d,  $J = 2.4$  Hz, 1H), 8.46 (dd,  $J = 2.4, 8.8$  Hz, 1H), 7.68 (d,  $J = 8.4$  Hz, 1H), 3.15 (q,  $J = 7.6$  Hz, 2H), 1.38 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.6, 145.8, 138.1, 132.6, 128.8, 124.6, 26.43, 14.84. IR (neat,  $\text{cm}^{-1}$ ): 2972, 2141, 1522, 1349, 1168.

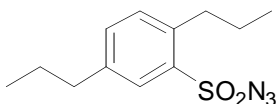


**2,5-Dicyclohexylbenzene-1-sulfonyl azide<sup>1b</sup> (1j)**, Table 2, Entry 10) was obtained from 2,5-dicyclohexylbenzene-1-sulfonyl chloride using the general procedure as a white solid in 99% yield (502 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (s, 1H), 7.45 (m, 2H), 3.28 (m, 1H), 2.56 (m, 1H), 1.83 (m, 10H), 1.34 (m, 10H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.3, 145.5, 135.8, 133.2, 129.2, 127.4, 43.85, 40.01, 34.31, 34.10, 26.66, 26.62, 26.00,

25.87. IR (neat,  $\text{cm}^{-1}$ ): 2924, 2852, 2122, 1364, 1164. HRMS (ESI): Calcd. for  $\text{C}_{18}\text{H}_{29}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  365.2011, Found 365.2005.

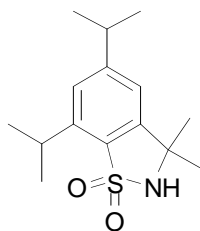


**2,5-Dibutylbenzene-1-sulfonyl azide (1k)**, Table 3, Entries 1–3) was obtained from 2,5-dibutylbenzene-1-sulfonyl chloride using the general procedure as colorless oil in 98% yield (1.00 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83 (s, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.32 (d,  $J = 8.0$  Hz, 1H), 2.92 (t,  $J = 8.0$  Hz, 2H), 2.64 (t,  $J = 8.0$  Hz, 2H), 1.67–1.52 (m, 4H), 1.47–1.39 (m, 2H), 1.38–1.29 (m, 2H), 0.95–0.90 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.5, 140.4, 136.1, 134.6, 131.9, 129.1, 34.89, 33.48, 33.23, 32.40, 22.79, 22.22, 13.86, 13.82. IR (neat,  $\text{cm}^{-1}$ ): 2958, 2931, 2872, 2123, 1367, 1165. HRMS (ESI): Calcd. for  $\text{C}_{14}\text{H}_{25}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  313.1698, Found 313.1689.

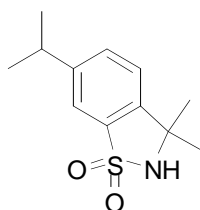


**2,5-Dipropylbenzene-1-sulfonyl azide (1l)**, Table 3, Entries 4–9) was obtained from 2,5-dipropylbenzene-1-sulfonyl chloride using the general procedure as colorless oil in 78% yield (803 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83 (s, 1H), 7.41 (d,  $J = 7.6$  Hz, 1H), 7.34 (d,  $J = 8.0$  Hz, 1H), 2.92 (t,  $J = 7.6$  Hz, 2H), 2.64 (t,  $J = 7.2$  Hz, 2H), 1.73–1.63 (m, 4H), 1.02 (t,  $J = 7.6$  Hz, 3H), 0.95 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.3, 140.2, 136.1, 134.7, 131.9, 129.1, 37.18, 34.60, 24.49, 24.21, 14.10, 13.61. IR (neat,  $\text{cm}^{-1}$ ): 2962, 2933, 2123, 1365, 1165. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{21}\text{N}_4\text{O}_2\text{S}$  ( $[\text{M}+\text{NH}_4]^+$ )  $m/z$  285.1385, Found 285.1379.

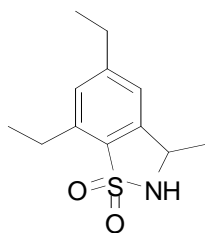
**General Procedure for Intramolecular C-H Amidation.** An oven dried Schlenk tube, that was previously evacuated and backfilled with nitrogen gas, was charged with azide (if solid, 0.2 mmol), catalyst (0.004 mmol), and 5 Å MS (100 mg). The Schlenk tube was then evacuated and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and 0.5 ml of solvent was added followed by azide (if liquid, 0.2 mmol) and the remaining solvent (total 1 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The Schlenk tube was then placed in an oil bath for the desired time and temperature. Following completion of the reaction, the reaction mixture was concentrated and purified by dry loading the sample on a Teledyne flash chromatography instrument running a gradient solvent system of 100:0 (hexanes: ethyl acetate) to 50:50 (hexanes: ethyl acetate). The fractions containing product were collected and concentrated by rotary evaporation to afford the pure compound.



**2a** (Table 2, Entry 1) was synthesized by the general procedure from 2,4,6-triisopropylbenzene-1-sulfonyl azide (**1a**) as a tan solid in 96% yield (54.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.21 (s, 1H), 6.98 (s, 1H), 4.68 (s, 1H), 3.60 (heptet,  $J = 6.8$  Hz, 1H), 2.97 (heptet,  $J = 6.8$  Hz, 1H), 1.62 (s, 6H), 1.34 (d,  $J = 6.8$  Hz, 6H), 1.26 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.4, 146.7, 145.2, 130.8, 124.2, 117.7, 59.72, 34.58, 29.81, 29.38, 23.81, 23.51. IR (neat,  $\text{cm}^{-1}$ ): 3244, 2960, 2922, 2865, 1598, 1459, 1382, 1295, 1172, 1151, 1129. HRMS (ESI): Calcd. for  $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{SNa}$  ( $[\text{M}+\text{Na}]^+$ )  $m/z$  304.13417, Found 304.13441.

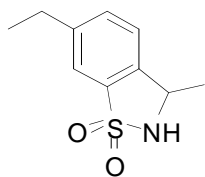


**2b**<sup>5</sup> (Table 2, Entry 2) was synthesized by the general procedure from 2,5-diisopropylbenzene-1-sulfonyl azide (**1b**) as a tan solid in 94% yield (45.0 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (s, 1H), 7.47 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 1H), 4.61 (s, 1H), 3.00 (heptet,  $J = 7.2$  Hz, 1H), 1.63 (s, 6H), 1.27 (d,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.5, 143.5, 135.1, 132.1, 122.5, 118.4, 60.62, 33.95, 29.68, 23.71. IR (neat,  $\text{cm}^{-1}$ ): 3240, 2965, 2930, 2899, 2871, 1486, 1463, 1382, 1302, 1277, 1158, 1143, 1122, 1073. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ )  $m/z$  240.10528, Found 240.10532.

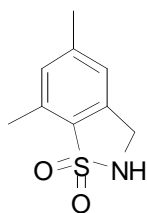


**2c** (Table 2, Entry 3) was synthesized by the general procedure from 2,4,6-triethylbenzene-1-sulfonyl azide (**1c**) as a tan oil in 90% yield (43.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.11 (s, 1H), 6.96 (s, 1H), 4.68 (m, 1H), 4.64 (m, 1H), 2.98 (q,  $J = 7.6$  Hz, 2H), 2.70 (q,  $J = 7.6$  Hz, 2H), 1.57 (d,  $J = 6.8$  Hz, 3H), 1.33 (t,  $J = 7.6$  Hz, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 142.4, 140.1, 131.3, 128.6, 120.2, 52.64, 28.99, 24.62, 21.55, 15.36, 14.57. IR (neat,  $\text{cm}^{-1}$ ): 3251, 2976, 2935, 2875, 1600, 1459, 1374, 1279, 1174, 1146. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ )  $m/z$  240.10528, Found 240.10416.

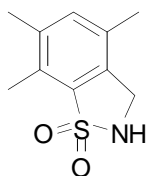




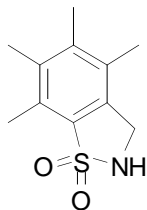
**2d<sup>6</sup>** (Table 2, Entry 4) was synthesized by the general procedure from 2,5-diethylbenzene-1-sulfonyl azide (**1d**) as a tan oil in 91% yield (38.6 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.57 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 4.81 (s, 1H), 4.78-4.70 (m, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.2, 139.3, 135.7, 133.5, 123.8, 120.1, 53.40, 28.77, 21.75, 15.46. IR (neat, cm<sup>-1</sup>): 3256, 2932, 1489, 1455, 1417, 1372, 1282, 1211, 1150. HRMS (ESI): Calcd. for C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>) *m/z* 212.07398, Found 212.07422.



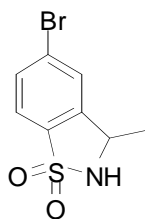
**2e<sup>1b</sup>** (Table 2, Entry 5) was synthesized by the general procedure from 2,4,6-trimethylbenzene-1-sulfonyl azide (**1e**) as a tan solid in 96% yield (38.1 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.04 (s, 1H), 6.94 (s, 1H), 4.87 (s, 1H), 4.42 (d, *J* = 5.2 Hz, 2H), 2.56 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 144.0, 137.2, 133.9, 131.5, 131.3, 122.2, 45.06, 21.44, 16.78. IR (neat, cm<sup>-1</sup>): 3236, 2957, 2920, 1594, 1447, 1379, 1281, 1170, 1146. HRMS (ESI): Calcd. for C<sub>9</sub>H<sub>12</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>) *m/z* 198.05833, Found 198.05891.



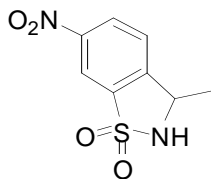
**2f<sup>1b</sup>** (Table 2, Entry 6) was synthesized by the general procedure from 2,3,5,6-tetramethylbenzene-1-sulfonyl azide (**1f**) as a tan solid in 91% yield (38.5 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.15 (s, 1H), 4.79 (s, 1H), 4.32 (d, *J* = 5.2 Hz, 2H), 2.49 (s, 3H), 2.29 (s, 3H), 2.19 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO): δ 140.0, 136.1, 133.1, 132.1, 129.6, 127.5, 43.40, 16.16, 15.34, 14.37, 14.27. IR (neat, cm<sup>-1</sup>): 3269, 2959, 2929, 2858, 1727, 1490, 1460, 1382, 1268, 1138, 1072, 1038. HRMS (ESI): Calcd. for C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>) *m/z* 212.07398, Found 212.07460.



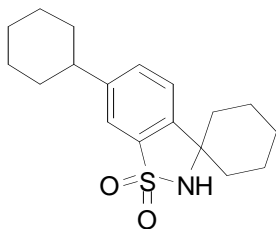
**2g** (Table 2, Entry 7) was synthesized by the general procedure from 2,3,4,5,6-pentamethylbenzene-1-sulfonyl azide (**1g**) as a tan solid in 95% yield (42.6 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.89 (s, 1H), 4.33 (d, *J* = 5.2 Hz, 2H), 2.53 (s, 3H), 2.25 (s, 3H), 2.36 (s, 3H), 2.12 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO): δ 137.5, 134.8, 134.5, 133.6, 131.2, 127.9, 42.81, 18.38, 16.35, 13.13. IR (neat, cm<sup>-1</sup>): 3250, 2957, 2929, 2871, 1728, 1458, 1378, 1272, 1200, 1148, 1072, 1036. HRMS (ESI): Calcd. for C<sub>11</sub>H<sub>16</sub>NO<sub>2</sub>S ([M+H]<sup>+</sup>) *m/z* 226.08963, Found 226.08941.



**2h** (Table 2, Entry 8) was synthesized by the general procedure from 4-bromo-2-ethylbenzene-1-sulfonyl azide (**1h**) as a tan solid in 93% yield (48.9 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.65-7.59 (m, 2H), 7.53 (s, 1H), 4.96 (s, 1H), 4.78-4.71 (m, 1H), 1.60 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.8, 134.6, 132.5, 127.8, 127.2, 122.5, 52.91, 21.15. IR (neat, cm<sup>-1</sup>): 3268, 2966, 2924, 2871, 1727, 1572, 1459, 1389, 1320, 1284, 1193, 1165, 1138, 1073. HRMS (ESI): Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>SBr ([M+NH<sub>4</sub>]<sup>+</sup>) *m/z* 278.97974, Found 278.97988.

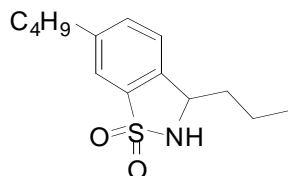


**2i** (Table 2, Entry 9) was synthesized by the general procedure from 2-ethyl-5-nitrobenzene-1-sulfonyl azide (**1i**) as a tan solid in 99% yield (45.2 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.60 (d, *J* = 1.6 Hz, 1H), 8.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 4.91 (s, 1H), 4.87 (m, 1H), 1.69 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.5, 147.7, 137.5, 128.1, 125.3, 117.4, 53.32, 21.40. IR (neat, cm<sup>-1</sup>): 3243, 1600, 1529, 1351, 1282, 1162, 1137, 1094, 1049, 1025. HRMS (ESI): Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub>S ([M+NH<sub>4</sub>]<sup>+</sup>) *m/z* 246.05430, Found 246.05436.



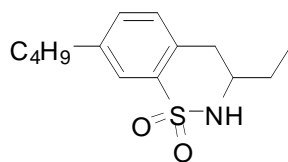
**2j** (Table 2, Entry 10) was synthesized by the general procedure from 2,5-dicyclohexylbenzene-1-sulfonyl azide (**1j**) as a tan solid in 87% yield (55.4 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (s, 1H), 7.42 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 4.67 (s, 1H), 2.59-2.46 (m, 1H), 1.85-1.73 (m, 12H), 1.63-1.53 (m, 2H), 1.44-1.21 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 149.8, 143.6, 135.3, 132.3, 122.7, 118.9,

63.47, 44.24, 37.75, 34.21, 26.63, 25.89, 24.78, 22.55. IR (neat,  $\text{cm}^{-1}$ ): 3268, 2928, 2851, 1728, 1447, 1384, 1296, 1268, 1164, 1137, 1072. HRMS (ESI): Calcd. for  $\text{C}_{18}\text{H}_{26}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ )  $m/z$  320.16788, Found 320.16886.



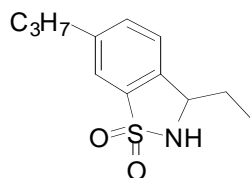
(See note 7 for a description of isolation and characterization)

**2k**<sup>7</sup> (Table 3, Entries 1–3) was synthesized by the general procedure from 2,5-dibutylbenzene-1-sulfonyl azide (**1k**) as tan oil. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.27 (d,  $J = 7.6$  Hz, 1H), 4.66–4.60 (m, 2H), 2.70 (t,  $J = 7.6$  Hz, 2H), 1.95–1.90 (m, 1H), 1.77–1.70 (m, 1H), 1.62 (m, 2H), 1.52–1.44 (m, 2H), 1.36 (sext,  $J = 7.2$  Hz, 2H), 0.98 (t,  $J = 7.2$  Hz, 3H), 0.95 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 137.9, 135.5, 133.6, 123.7, 120.5, 57.51, 37.69, 35.23, 33.23, 22.19, 13.82, 13.71. IR (neat,  $\text{cm}^{-1}$ ): 3259, 2958, 2931, 2872, 1489, 1465, 1381, 1287, 1152, 1107. HRMS (ESI): Calcd. for  $\text{C}_{14}\text{H}_{22}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ )  $m/z$  268.13658, Found 268.13665.



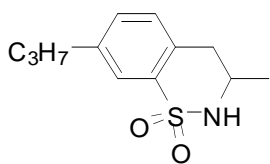
(See note 7 for a description of isolation and characterization)

**3k**<sup>7</sup> (Table 3, Entries 1–3) was synthesized by the general procedure from 2,5-dibutylbenzene-1-sulfonyl azide (**1k**) as tan oil. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (s, 1H), 7.25–7.23 (m, 1H), 7.10 (d,  $J = 8.0$  Hz, 1H), 4.17 (d,  $J = 11.6$  Hz, 1H), 3.82–3.73 (m, 1H), 2.91 (dd,  $J = 16.8, 4.0$  Hz, 1H), 2.76–2.72 (m, 1H), 2.61 (t,  $J = 8.0$  Hz, 2H), 1.70–1.64 (m, 2H), 1.62–1.55 (m, 2H), 1.36–1.30 (m, 2H), 1.05 (t,  $J = 7.2$  Hz, 3H), 0.90 (t,  $J = 7.2$  Hz, 3H).



(See note 7 for a description of isolation and characterization)

**2l**<sup>7</sup> (Table 3, Entries 4–9) was synthesized by the general procedure from 2,5-dipropylbenzene-1-sulfonyl azide (**1l**) as tan oil. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (s, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.27 (d,  $J = 8.4$  Hz, 1H), 4.62 (m, 2H), 2.68 (t,  $J = 7.6$  Hz, 2H), 2.05–2.00 (m, 1H), 1.83–1.78 (m, 1H), 1.67 (sext,  $J = 7.6$  Hz, 2H), 1.03 (t,  $J = 7.2$  Hz, 3H), 0.95 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6, 137.5, 135.7, 133.6, 123.7, 120.6, 58.85, 37.56, 28.72, 24.22, 13.66, 9.88. IR (neat,  $\text{cm}^{-1}$ ): 3272, 2964, 2931, 2872, 1489, 1458, 1379, 1281, 1151, 1094, 1049. HRMS (ESI): Calcd. for  $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ )  $m/z$  240.10528, Found 240.10521.



(See note 7 for a description of isolation and characterization)

**31**<sup>7</sup> (Table 3, Entries 4–9) was synthesized by the general procedure from 2,5-dipropylbenzene-1-sulfonyl azide (**11**) as tan oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 (s, 1H), 7.25-7.20 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.41 (d, *J* = 11.2 Hz 1H), 4.03-3.94 (m, 1H), 2.89 (dd, *J* = 17.2, 3.6 Hz, 1H), 2.72 (dd, *J* = 17.2, 11.2Hz, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.69-1.59 (m, 2H), 1.35 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

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- 7) Extensive efforts were made to attempt the separation of the 5-membered from 6-membered ring products. However, we were only able to isolate a small fraction of the pure 5-membered ring products in both of the cases, which allowed for NMR assignments and determination of the 5- to 6-membered ring product ratios by integration from <sup>1</sup>H NMR spectra of 5- and 6-membered ring product mixtures.