

Supporting Information for:

**Solid-State Examination of Conformationally Diverse  
Sulfonamide Receptors Based on  
Bis(2-anilinoethynyl)pyridine, -Bipyridine and -Thiophene**

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## Experimental Procedures

**General methods:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Varian Inova 500 ( $^1\text{H}$  500.10 MHz,  $^{13}\text{C}$  125.75 MHz) spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard ( $\text{CDCl}_3$ :  $^1\text{H}$  7.26 ppm,  $^{13}\text{C}$  77.0 ppm). UV-Vis spectra were recorded using a Hewlett-Packard 8453 spectrophotometer and extinction coefficients are expressed in  $\text{M}^{-1}\text{cm}^{-1}$ . Mass spectra were recorded using an Agilent 1100 Series LC/MSD, high resolution mass spectra were acquired using a Waters LCT Premier ESI-MS in positive mode in MeCN solvent. Melting points were determined with a Meltemp II apparatus or a TA Instruments DSC 2920 Modulated DSC. THF,  $\text{Et}_3\text{N}$ , and  $\text{CH}_2\text{Cl}_2$  were distilled from either potassium or  $\text{CaH}_2$  prior to use. All chemicals were of reagent grade and used as obtained from manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230-400 mesh). Precoated silica gel plates (Sorbent Technology,  $\text{UV}_{254}$ , 200  $\mu\text{m}$ , 5  $\times$  20 cm) were used for analytical thin-layer chromatography. Dianilines **13** and **16** and ethynylarene **14** were prepared as previously reported.<sup>1-3</sup>

**General procedure for sulfonamide formation:** A solution of dianiline (1 equiv) and sulfonyl chloride (5 equiv) in pyridine (10-15 mM) was stirred for 3 h under a static  $\text{N}_2$  atmosphere. Following concentration in vacuo, the crude oil was filtered through a 2.5 cm silica plug and then chromatographed on silica gel.

**4-Bromophenylsulfonamide 9.** Dianiline **13** (100 mg, 0.24 mmol) was reacted with 4-bromobenzenesulfonyl chloride according to the general procedure. Purification by chromatography (5:2 hexanes:EtOAc) followed by recrystallization by diffusion (hexanes:EtOAc) afforded **7** (183 mg, 89%) as colorless crystals. Mp: 152-154  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (t,  $J = 7.9$  Hz, 1H), 7.73 (d,  $J = 8.6$  Hz, 4H), 7.61 (br s, 2H), 7.55 –

7.48 (m, 8H), 7.44 (d,  $J = 7.8$  Hz, 2H), 7.40 (dd,  $J = 8.6$  Hz, 2.3 Hz, 2H), 1.29 (s, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.38, 142.81, 138.56, 137.06, 135.34, 132.26, 129.66, 128.90, 128.18, 128.05, 126.35, 121.50, 113.50, 93.22, 85.57, 34.46, 31.11; UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 243 (64,000), 291 (29,100), 342 (19,900) nm; IR (neat):  $\nu$  3178, 2963, 2873, 2214, 1498, 1170  $\text{cm}^{-1}$ ; MS (CI pos):  $m/z$  (%) 863 ( $\text{M}^+ + 6$ , 24), 862 ( $\text{M}^+ + 5$ , 61), 861 ( $\text{M}^+ + 4$ , 42), 860 ( $\text{M}^+ + 3$ , 100), 859 ( $\text{M}^+ + 2$ , 21), 858 ( $\text{MH}^+$ , 49); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{41}\text{H}_{38}\text{Br}_2\text{N}_3\text{O}_4\text{S}_2$  858.0670, found 858.0713.

**Sulfonimide 10.** Dianiline **13** (100 mg, 0.24 mmol) was reacted with 3,5-bis(trifluoromethyl)benzenesulfonyl chloride according to the general procedure. Purification by chromatography (2:1  $\text{CH}_2\text{Cl}_2$ :hexanes) afforded **8** (212 mg, 58%) as a crystalline colorless solid. Recrystallization by diffusion (hexanes: $\text{CH}_2\text{Cl}_2$ ) afforded white needles. Mp: 88-90  $^\circ\text{C}$ .;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.41 (s, 8H), 8.08 (s, 4H), 7.82 (br s, 2H), 7.56 (dd,  $J = 8.5$ , 2.5 Hz, 2H), 7.48 (br s, 1H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.10 (br s, 2H), 1.39 (s, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.45, 142.21, 141.72, 136.34, 132.98 (q,  $J = 35$  Hz), 132.13, 131.68, 131.23, 129.22 (q,  $J = 3.9$  Hz), 127.82, 127.00, 124.59, 122.18 (q,  $J = 274$  Hz), 92.47, 85.14, 35.22, 31.00; IR (neat):  $\nu$  2961, 2902, 2873, 2219, 1279, 1181  $\text{cm}^{-1}$ ; MS (CI pos):  $m/z$  (%) 1528 ( $\text{M}^+ + 2\text{H}$ , 41), 1527 ( $\text{MH}^+$ , 75), 1526 ( $\text{M}^+$ , 100); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{61}\text{H}_{39}\text{F}_{24}\text{N}_3\text{O}_8\text{S}_4$ : 1525.1237, found 1525.1251.

**Dianiline 15.** A suspension of ethynylarene **14** (500 mg, 2 mmol) and  $\text{K}_2\text{CO}_3$  (5 equiv) in MeOH (20 mL) and  $\text{Et}_2\text{O}$  (10 mL) was stirred at rt and monitored by TLC until reaction completion (15-30 min). The solution was diluted with  $\text{Et}_2\text{O}$  and washed with water and brine. The organic layer was dried over  $\text{MgSO}_4$  and concentrated in vacuo. Without further purification, the residue was dissolved in THF (10 mL) and added dropwise over a period of 12 h to a stirred, deoxygenated suspension of 2,5-dibromothiophene (225 mg, 0.93 mmol),  $\text{Pd}(\text{PPh}_3)_4$

(231 mg, 0.2 mmol), and CuI (76 mg, 0.4 mmol) in THF (50 mL) and *i*-Pr<sub>2</sub>NH (50 mL) at 45 °C. After an additional 3 h, the suspension was concentrated and filtered through a 2.5 cm silica plug (CH<sub>2</sub>Cl<sub>2</sub>). Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) afforded **15** (297 mg, 75%) as a bright yellow, crystalline solid. Mp: 144-145 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.36 (d, *J* = 2.3 Hz, 2H), 7.20 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.14 (s, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 4.14 (br s, 4H), 1.29 (s, 18H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 145.55, 140.97, 131.49, 128.67, 127.65, 124.58, 114.40, 106.74, 91.28, 86.78, 33.94, 31.37; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε) 230 (62,000), 323 (25,200), 378 (37,000) nm; IR (neat): ν 3473, 3376, 2961, 2906, 2866, 2193, 1499 cm<sup>-1</sup>; MS (CI pos) *m/z* (%): 498 (M<sup>+</sup>+THF, 100), 428 (M<sup>+</sup>+2, 18), 427 (MH<sup>+</sup>, 53); HRMS (ESI): *m/z*: calcd for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>S: 426.2130, found 426.2138.

**Sulfonamide 11.** Dianiline **15** (90 mg, 0.2 mmol) was reacted with *p*-toluenesulfonyl chloride according to the general procedure. Chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) afforded **11** (123 mg, 82%) as a pale yellow solid. Mp: 89-91 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 8.3 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 2.3 Hz, 2H), 7.36 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.16 (s, 2H), 6.97 (s, 2H), 2.39 (s, 6H), 1.28 (s, 18H).; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 148.03, 144.05, 136.29, 135.03, 132.49, 129.69, 129.00, 127.68, 127.24, 124.13, 120.92, 113.76, 89.59, 87.42, 34.45, 31.16, 21.64; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε) 230 (71,000), 287 (31,000), 357 (37,200) nm; IR (neat): ν 3248, 2921, 2870, 2852, 2198, 1162 cm<sup>-1</sup>; MS (CI pos) *m/z* (%): 807 (M<sup>+</sup>+THF, 16), 737 (M<sup>+</sup>+2, 21), 736 (MH<sup>+</sup>, 37), 735 (M<sup>+</sup>, 71), 595 (100), 580 (89); HRMS (ESI): *m/z*: calcd for C<sub>42</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>: 735.2385, found 735.2357.

**Sulfonamide 12.** Dianiline **16** (25 mg, 0.05 mmol) was reacted with *p*-toluenesulfonyl chloride according to the general procedure. Chromatography on silica gel (3:1 hexanes:EtOAc) afforded **12** (38 mg, 53%) as a pale yellow solid. Recrystallization by diffusion (hexanes:EtOAc) afforded colorless crystals. Mp: 251-252 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.59 (d, *J* = 8.0 Hz,

2H), 7.90 (t,  $J = 7.7$  Hz, 2H), 7.77 (d,  $J = 8.0$  Hz, 4H), 7.57 (d,  $J = 8.6$  Hz, 2H), 7.51 (d,  $J = 7.6$  Hz, 2H), 7.48 (d,  $J = 2.3$  Hz, 2H), 7.42 (s, 2H), 7.38 (dd,  $J = 8.7, 2.3$  Hz, 2H), 7.15 (d,  $J = 8.0$  Hz, 4H), 2.31 (s, 6H), 1.29 (s, 18H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.86, 147.77, 143.85, 141.95, 137.44, 136.36, 135.74, 129.54, 129.18, 127.75, 127.40, 127.29, 121.15, 120.63, 113.34, 94.77, 84.26, 34.40, 31.13, 21.52; UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 236 (96,000), 291 (56,000), 315 (46,100) nm; IR (neat):  $\nu$  3313, 2961, 2902, 2866, 2213, 1558, 1165  $\text{cm}^{-1}$ ; MS (CI pos)  $m/z$  (%): 809 ( $\text{M}^{+}+2$ , 29), 808 ( $\text{MH}^+$ , 63), 807 ( $\text{M}^+$ , 100); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{48}\text{H}_{47}\text{N}_4\text{O}_4\text{S}_2$ : 807.3039, found 807.3019.

## References

1. Engle, J. M.; Lakshminarayanan, P. S.; Carroll, C. N.; Zakharov, L. N.; Haley, M. M.; Johnson, D. W. *Cryst. Growth Des.* **2011**, *11*, 5144–5152.
2. Gavette, J. V.; Mills, N. S.; Zakharov, L. N.; Johnson II, C. A.; Johnson, D. W.; Haley, M. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 10270–10274.
3. (a) Wan, W. B.; Haley, M. M. *J. Org. Chem.* **2001**, *66*, 3893–3901. (b) Kimball, D. B.; Weakley, T. J. R.; Haley, M. M. *J. Org. Chem.* **2002**, *67*, 6395–6405.

# NMR Spectra









