**Conformational NMR Study of Bistriazolyl Anion Receptors**

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***Supplementary materials***

## 1. Synthesis details

*Synthesis of compound **1***

To a solution of 96 mg 2,6-diazidopyridine[1] in dry THF (5 ml) was added 0.14 ml N-Boc-propargylamine, 44.7 mg $[(CH_3CN)_4Cu]PF_6$ and 0.03 ml $Et_3N$ and the reaction mixture was stirred at 50°C for 3 h. The solvent was removed under vacuum and the crude product was purified by column chromatography ($SiO_2$, EtOAc).

The obtained product (0.244 g) was suspended in 4 N HCl in dioxane (2 ml) and stirred at room temperature for 2h. Then the solvent was removed under vacuum. In another flask a mixture of 0.21 ml *tert*-pentylamine and 348 mg CDI in 5 ml dry DMSO was stirred for 4 h at room temperature. The resulting mixture was together with 0.15 ml $Et_3N$ added to the first flask and the reaction mixture was stirred for 16 h at room temperature. The reaction mixture was diluted with 50 ml water and extracted with DCM (3 x 50 ml). The combined organic layers were washed with distilled $H_2O$ (3 x 100 ml), dried over $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by column chromatography ($SiO_2$, DCM + 7% MeOH) to afford **1** (0.159 g).

*Synthesis of compound **2***

A mixture of 62 mg 4,6-dichloro-2-(propylthio)pyrimidine[1], 38 mg $NaN_3$ and 9 mg tetra-*n*-butylammonium bromide in 1 ml THF was stirred at 50°C for 3 h. Then 109.4 mg N-Boc-propargylamine, 13.9 mg $CuSO_4.5H_2O$, 22.1 mg sodium ascorbate, 1 ml *tert*-butanol and 0.5 ml $H_2O$ were added and the resulting reaction mixture was stirred at 50°C for 2 h. Subsequently, the reaction mixture was extracted with DCM (3 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under vacuum. The crude product was purified by column chromatography ($SiO_2$, DCM + 2% MeOH).

4 N HCl in dioxane (2 ml) was added to the obtained product (109 mg) at 0 °C and the resulting solution was stirred for 30 min at room temperature. The solvent was removed under vacuum and then the obtained product was redissolved in 5ml DCM. Subsequently, 0.09 ml butyl isothiocyanate and 0.2 ml $Et_3N$ were added and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed under vacuum and the crude product was purified by column chromatography ($SiO_2$, DCM + 4% MeOH) to afford **2** (0.085 g).

## 2. Binding constants of receptor 2

The binding constants of the receptors **1** and **2** were determined by $^1$H NMR titrations with the tetra-*n*-butylammonium salts of the anions in acetonitrile. The data was fitted to a 1:1 binding model as confirmed by Job plot analysis and the anion binding constants were calculated with HypNMR[2]. For receptor **1** binding constants 1050 $M^{-1}$ for chloride and 490 $M^{-1}$ for bromide were obtained, as already published[1]. The binding constants obtained for receptor **2** are summarized in Table S1.

**Table S1.** Stability constants ($\log(K_a)$) of receptor **2** determined by $^1$H NMR titrations with the tetra-*n*-butylammonium salts of the anions in acetonitrile (400 MHz, 298 K, [**2**] = 2 mM).

| **Anion** | **Chloride** | **Bromide** | **Nitrate** | **Bisulfate** | **Acetate** | **Benzoate** |
|---|---|---|---|---|---|---|
| **1**[1] | 3.02 ± 0.03 | 2.69 ± 0.02 | - | - | - | - |
| **2** | 2.24 ± 0.07 | 1.91 ± 0.01 | 1.35 ± 0.01 | 1.73 ± 0.03 | 3.12 ± 0.02 | 2.99 ± 0.03 |

## 3. 2D NOESY NMR spectra

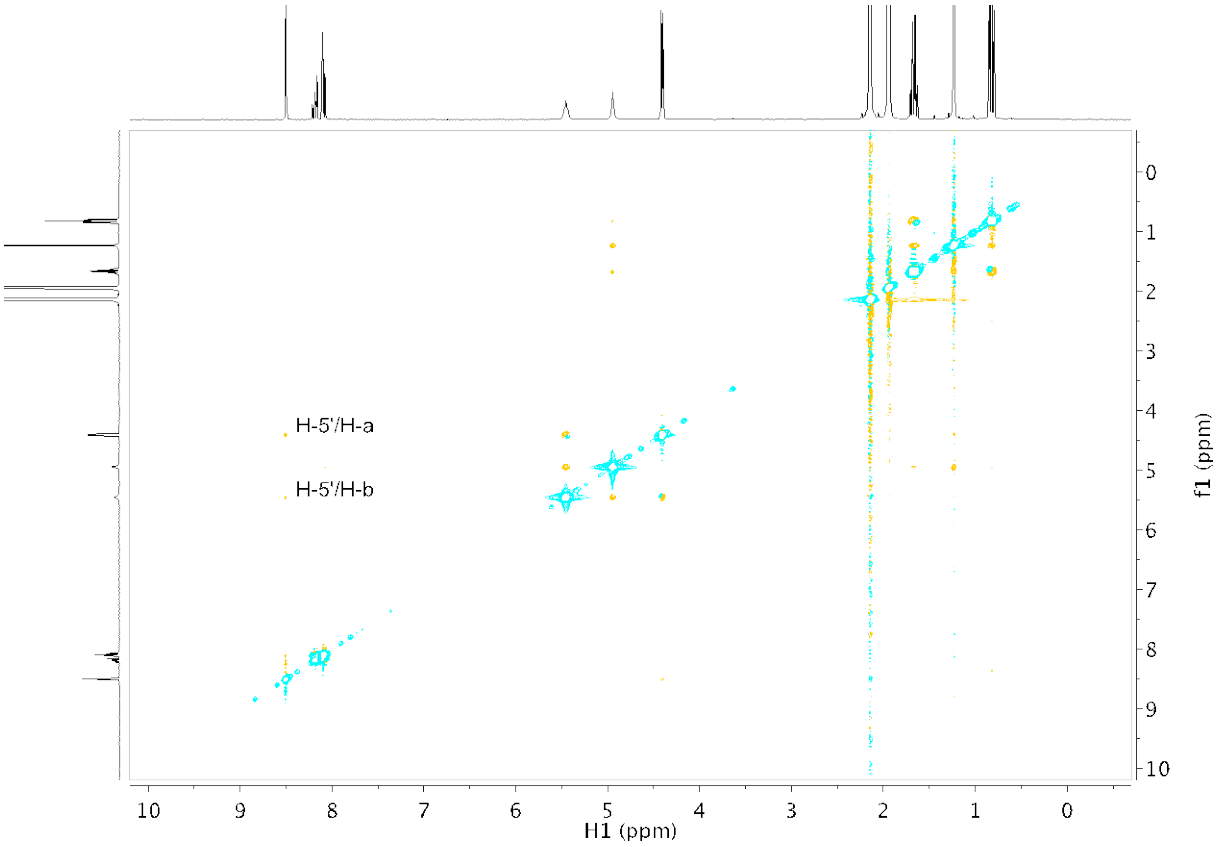


**Figure S1.** 2D NOESY NMR spectra of **1** in acetonitrile-$d_3$ at 298 K using mixing time 200 ms. The key NOESY correlations are noted according to atom numbering.

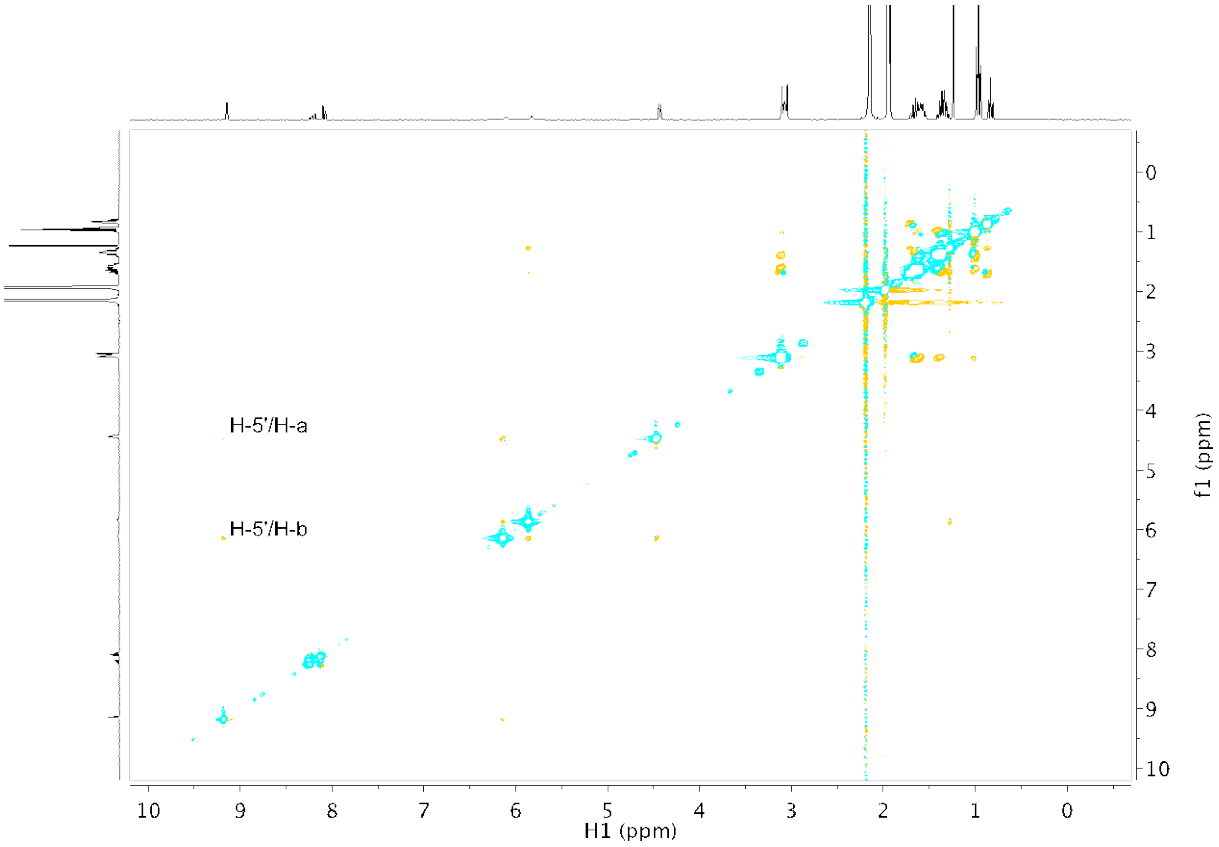


**Figure S2.** 2D NOESY NMR spectra of **1** in the presence of 1 eq. of chloride anions in acetonitrile-$d_3$ at 298 K using mixing time 200 ms. The key NOESY correlations are noted according to atom numbering.

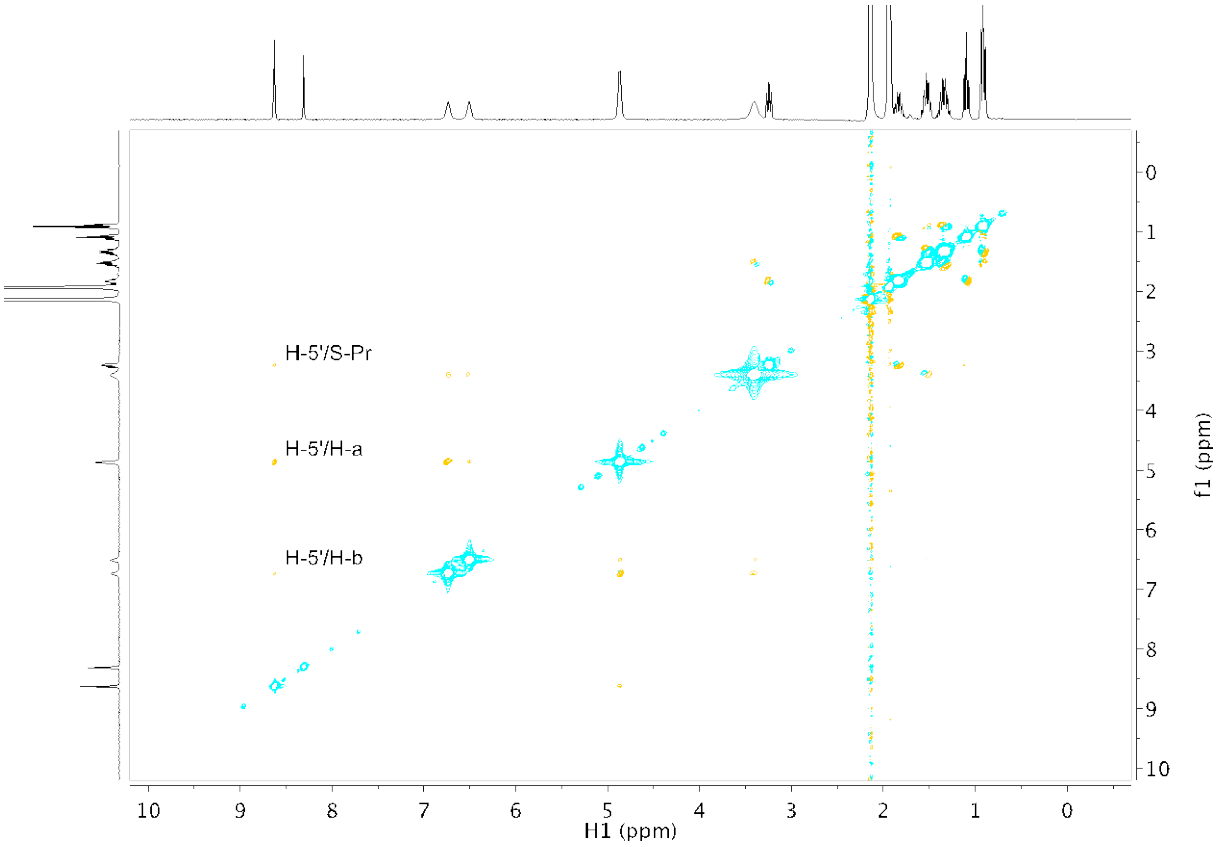


**Figure S3.** 2D NOESY NMR spectra of **2** in acetonitrile-$d_3$ at 298 K using mixing time 200 ms. The key NOESY correlations are noted according to atom numbering. S-Pr denotes propylsulfanyl group.

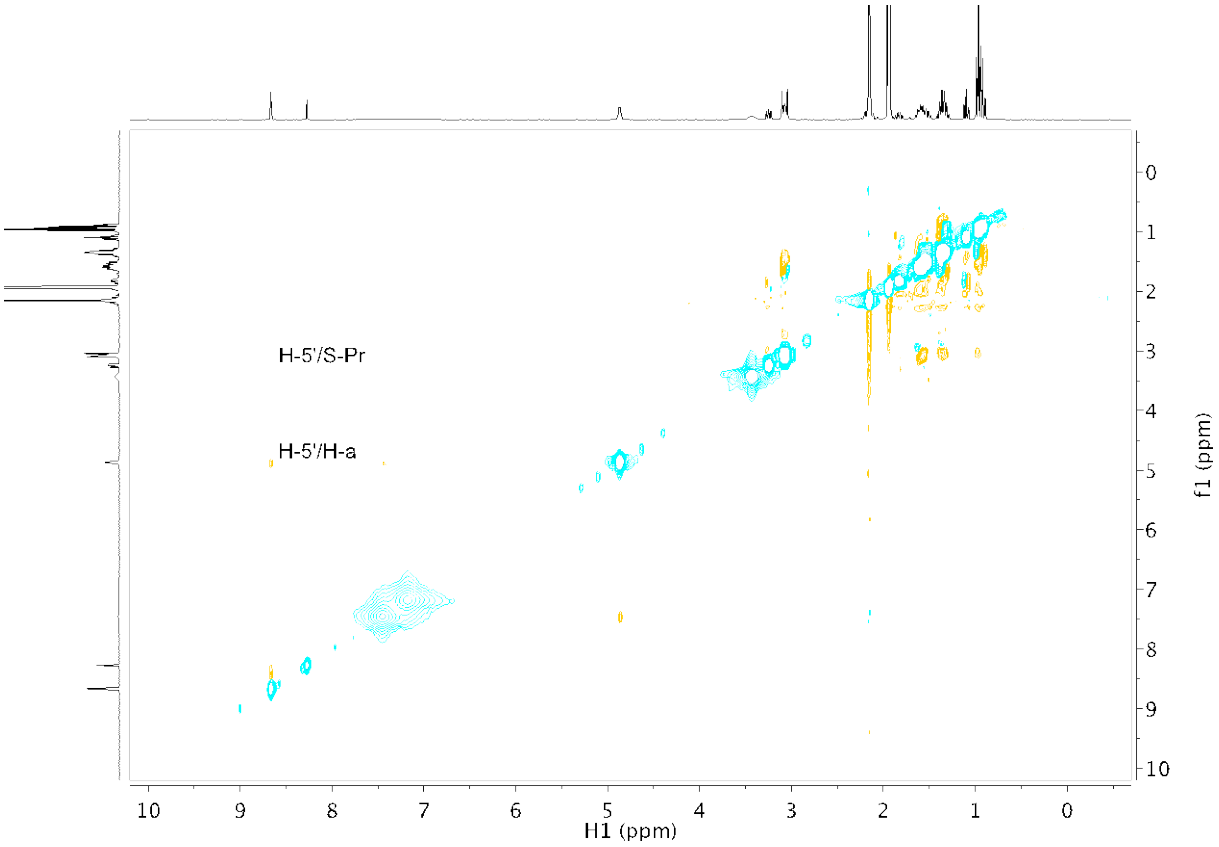


**Figure S4.** 2D NOESY NMR spectra of **2** in the presence of 1 eq. of chloride anions in acetonitrile-$d_3$ at 298 K using mixing time 200 ms. The key NOESY correlations are noted according to atom numbering. S-Pr denotes propylsulfanyl group.

## 4. References

1. T. Merckx, P. Verwilst, W. Dehaen, *Tetrahedron Lett.* **2013**, *54*, 4237-4240.
2. C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi, A. Vacca, *Anal. Biochem.* **1995**, *231*, 374-382.