Electronic Supplementary Material (ESI) for Chemical Communications

Solvent Effects on the Molecular Recognition of Anions

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Experimental

General. All reactants and reagents including $(Ph_3P)_2NCl$ and Bu_4NX (X = Cl, OAc, NO_3, H_2PO_4, and HSO_4) were bought from Sigma–Aldrich. Tetrahydrofuran was dried by refluxing it over sodium metal under argon and subsequently was distilled. TLC analyses were performed on precoated (250 mm) silica gel 60 F-254 plates (Merck) and were visualized by staining with $KMnO_4$ or with a hand–held UV lamp. Diol **1** was synthesized as previously reported.[S1] All deuterated solvents were purchased from Cambridge Isotope Laboratories and used from freshly opened bottles except for $CDCl_3$ and CD_3CN which were dried over activated 3 Å molecular sieves for several days. Proton NMR spectra were recorded on Varian VI-500 and VI-300 MHz instruments at different temperatures as indicated, and the resulting chemical shifts are reported in parts per million (δ) relative to the residual solvent peak. For ^{13}C spectra the residual acetonitrile signal at 1.39 ppm was used whereas for ^{19}F an external reference sample of $CFCl_3$ was set to 0.00 ppm. A Bruker BioTOF II electrospray ionization–time of flight mass spectrometer with polyethylene glycol 400 as an internal standard was used to obtain an exact mass measurement of **2**.

Binding Constant Determinations. Dilute solutions of **1** and **2** (2.5 mM) were titrated with anions salts (30-100 mM) at different temperatures. The changes in the chemical shifts of the hydroxyl groups in **1** and **2** were followed and nonlinear plots of the titration data (i.e., Δδ versus the concentration of the guest) were fit to a 1:1 binding equation using the Solver add–on program to Microsoft Excel 2010 to obtain the binding constants.[17] Representative data for both hosts are given in the supporting information.

meso-1,1,1,6,6,6-Hexafluoro-2,5-diphenylhexane-2,5-diol *(***2***).* A dry two–necked round bottomed flask was equipped with a magnetic stirring bar, a reflux condenser with an argon inlet, and a rubber septum. The flask was charged with 0.95 g (4.0 mmol) of 1,4-diphenylbutane-1,4-dione dissolved in 5 ml of monoglyme and cooled to 0 °C. Trifluoromethyl(trimethyl-silane) (1.85 g, 13.0 mmol) and a catalytic amount of CsF (0.012g, 0.10 mmol) were added sequentially with stirring and then the bath temperature was allowed to rise to room temperature before heating the reaction mixture at 60 °C for 3 h. The solvent was removed at reduced pressure and then 5 ml of THF was added to the residue. Tetrabutylammonium fluoride (12 ml of a 1 M solution in THF) was added dropwise and the resulting solution was stirred at room temperature for 2 h. Volatile compounds were removed at reduced pressure and the product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and concentrated under vacuum to give the diol in a 2:1 (meso : dl) diastereomeric ratio. Purification and separation of the diastereomers was carried out via column chromatography (1:5 diethyl ether/pentane) to give 0.55 g (35%) of the meso diol as a white solid. The diastereomeric assignment was based upon chiral HPLC since the two enantiomers of the dl-diol were separated on a Chiralcel OD column (15:85 *i*-PrOH/hexane) whereas the meso diol only affords a single peak. ^{1}H NMR (300 MHZ, CD_3CN) δ 1.60 (2H, dd, J = 13.8 and 4.0 Hz), 2.30 (2H, dd, J = 13.8 and 4.5 Hz), 4.41 (2H, br s), 7.46 (6H, m), 7.59 (4H, d, J = 7.2 Hz). ^{13}C NMR (75 MHZ, CD_3CN) δ 29.1, 77.8 (q, J = 28.2 Hz), 127.3 (CF_3, q, J = 284 Hz), 128.0, 129.7, 129.9, 137.7. ^{19}F-NMR (282 MHz, CD_3CN) δ -81.2. IR (ATR source) 3537 (OH), 3405 (OH, br). HRMS-ESI: calc for $C_{18}H_{15}F_6O_2^-$ (M - H)$^-$ 377.0982, found 377.0979.

S1 A. Shokri, X. B. Wang and S. R. Kass, *J. Am. Chem. Soc.* 2013, **135**, 9525.

Figure S1. Non-linear plot for the binding of **1** with Bu_4NCl in $CDCl_3$ at room temperature.

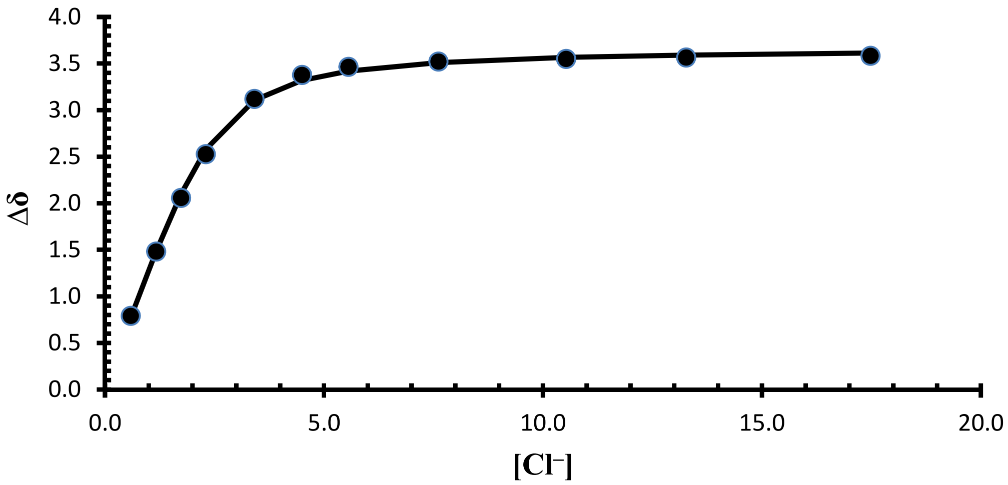


Table S1. Titration data for Bu_4NCl binding to **1** in $CDCl_3$.[1]

μL (Cl^- added)	[Cl^-]	[**1**]	δ (OH)	Δδ	%bound
0	0.0	2.50	2.562	0.000	0.0
5	0.58	2.49	3.354	0.792	22.1
10	1.16	2.47	4.044	1.482	41.4
15	1.73	2.46	4.619	2.057	57.4
20	2.30	2.44	5.090	2.528	70.5
30	3.41	2.41	5.683	3.121	87.1
40	4.49	2.39	5.940	3.378	94.3
50	5.56	2.36	6.026	3.464	96.7
70	7.61	2.31	6.083	3.521	98.2
100	10.53	2.24	6.111	3.549	99.0
130	13.27	2.17	6.126	3.564	99.4
180	17.48	2.06	6.146	3.584	100

[1] Chemical shifts and concentrations are given in ppm and mM, respectively. The chloride solution was 100 mM and the NMR initially contained 0.85 ml of a 2.5 mM solution of **1**.

Figure S2. Non-linear plot for the binding of **2** with Bu_4NCl in $CDCl_3$ at room temperature.

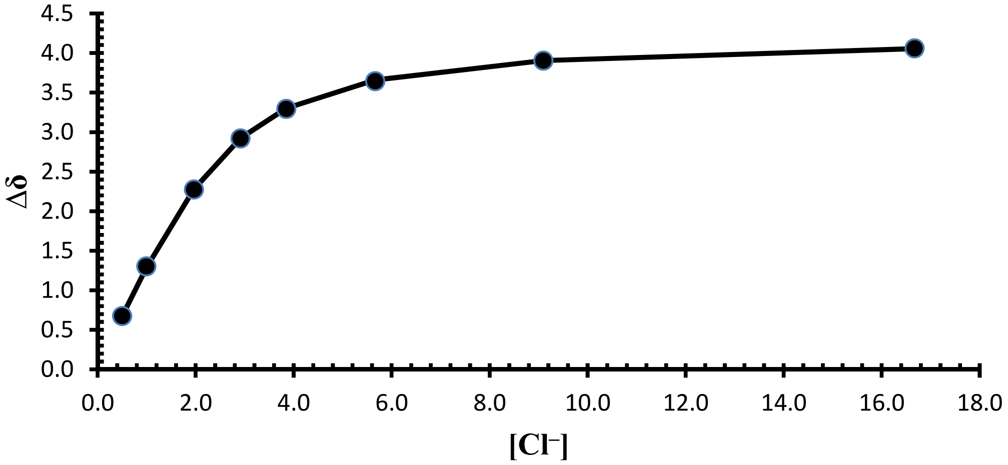


Table S2. Titration data for Bu_4NCl binding to **1** in $CDCl_3$.[1]

μL (Cl^- added)	[Cl^-]	[**2**]	δ (OH)	Δδ	%bound
0	0.0	2.50	2.395	0.000	0.0
5	0.50	2.49	3.072	0.677	16.1
10	0.99	2.47	3.699	1.304	31.0
20	1.96	2.45	4.671	2.276	54.1
30	2.91	2.43	5.316	2.921	69.4
40	3.85	2.40	5.691	3.296	78.4
60	5.66	2.36	6.040	3.645	86.6
100	9.09	2.27	6.300	3.905	92.8
200	16.66	2.08	6.456	4.061	96.5

[1] Chemical shifts and concentrations are given in ppm and mM, respectively. The chloride solution was 100 mM and the NMR initially contained 0.85 ml of a 2.5 mM solution of **1**.

Figure S3. Van't Hoff plot of complex formation of **1** with Cl^- at three different temperatures.

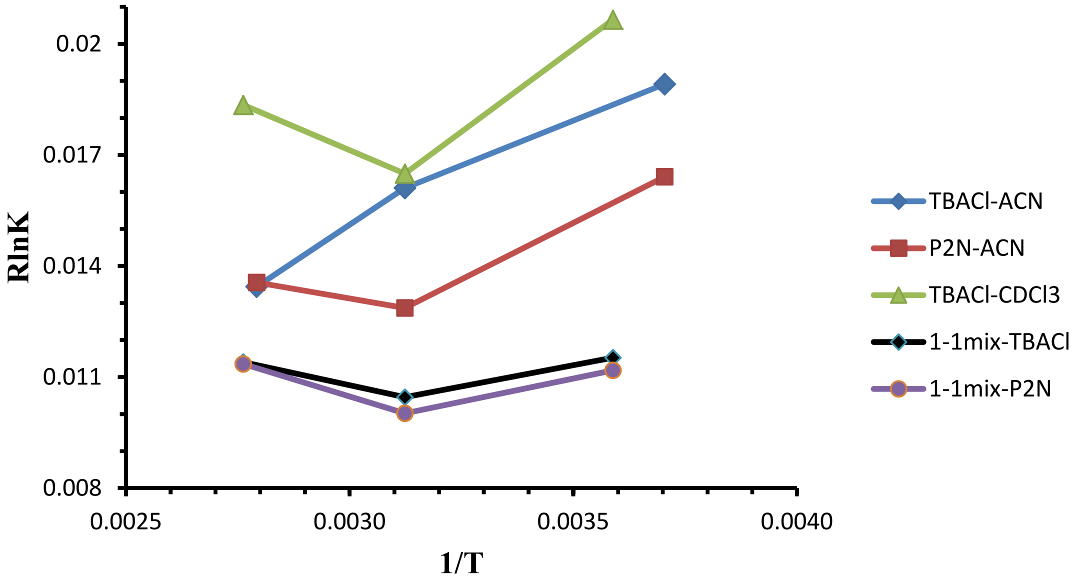
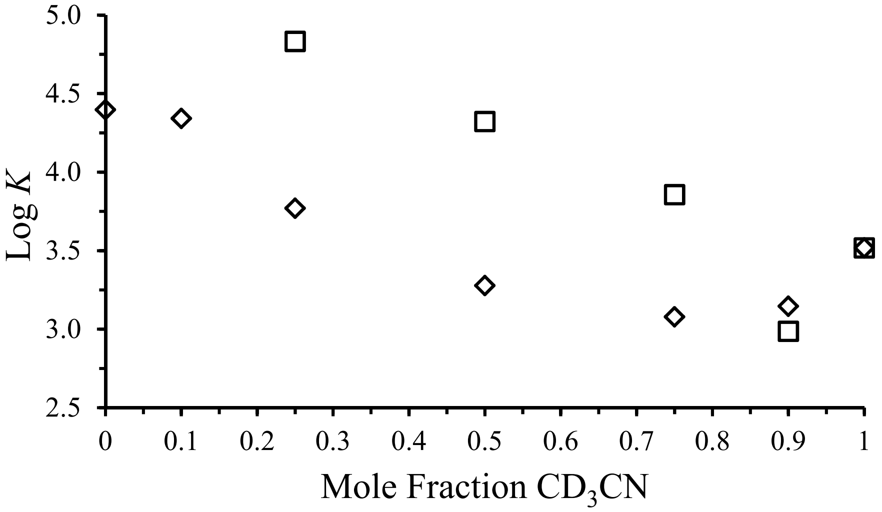
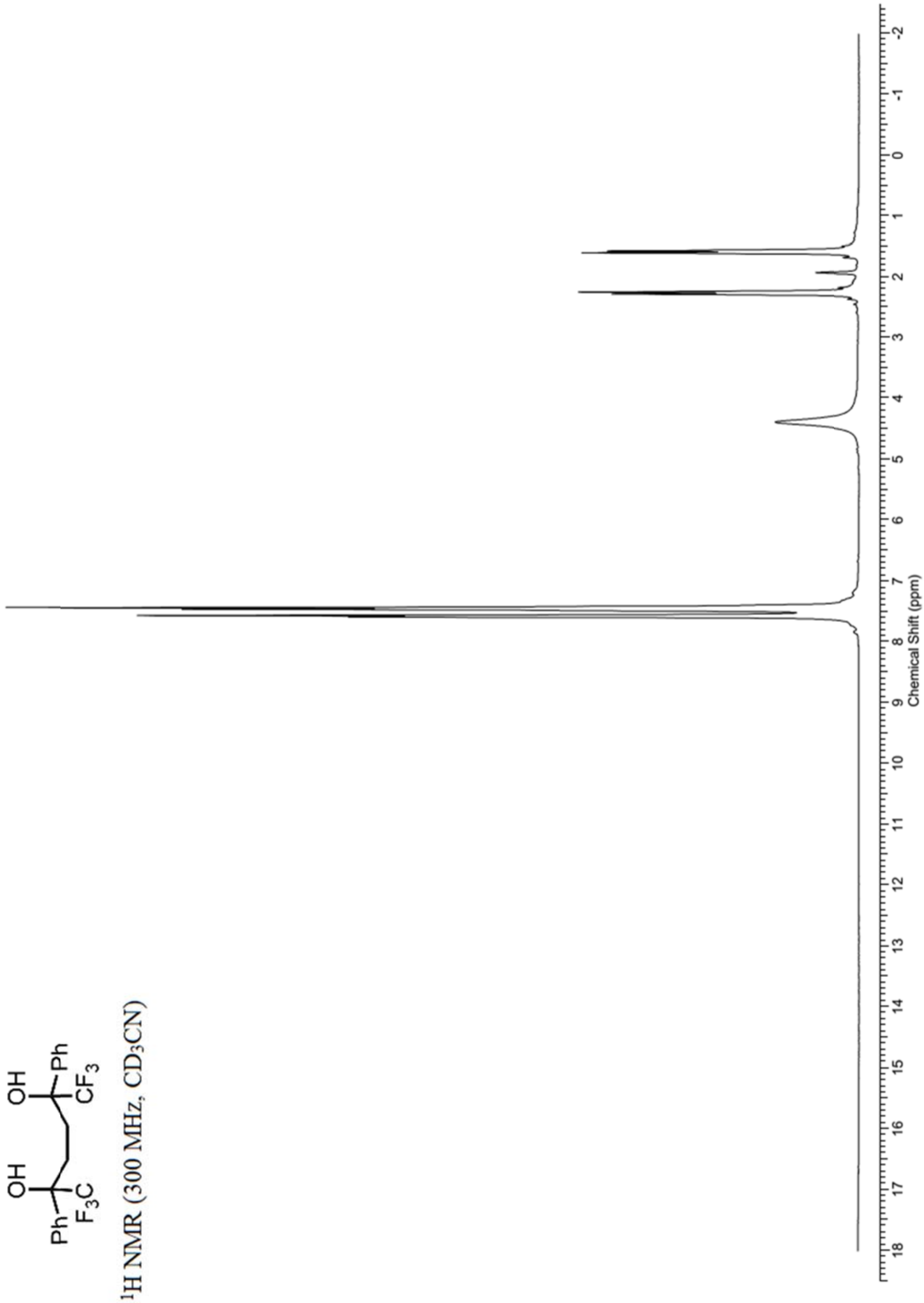
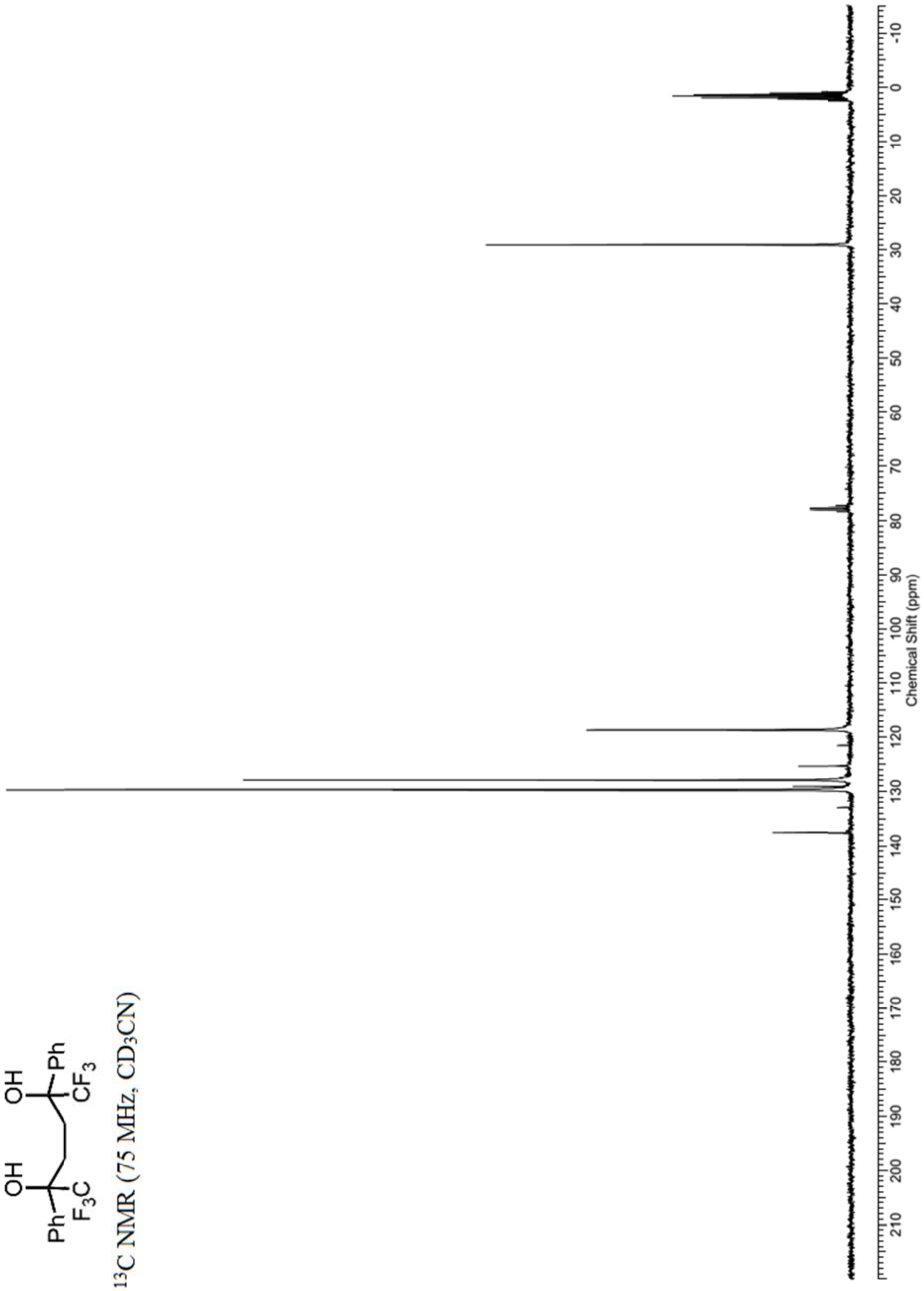


Figure S4. A logarithmic plot of the binding constants of **1** with Bu_4NCl versus the mole fraction of $CD_3CN–CD_2Cl_2$ (diamonds) and $CD_3CN–C_6D_5CD_3$ (squares) mixtures.

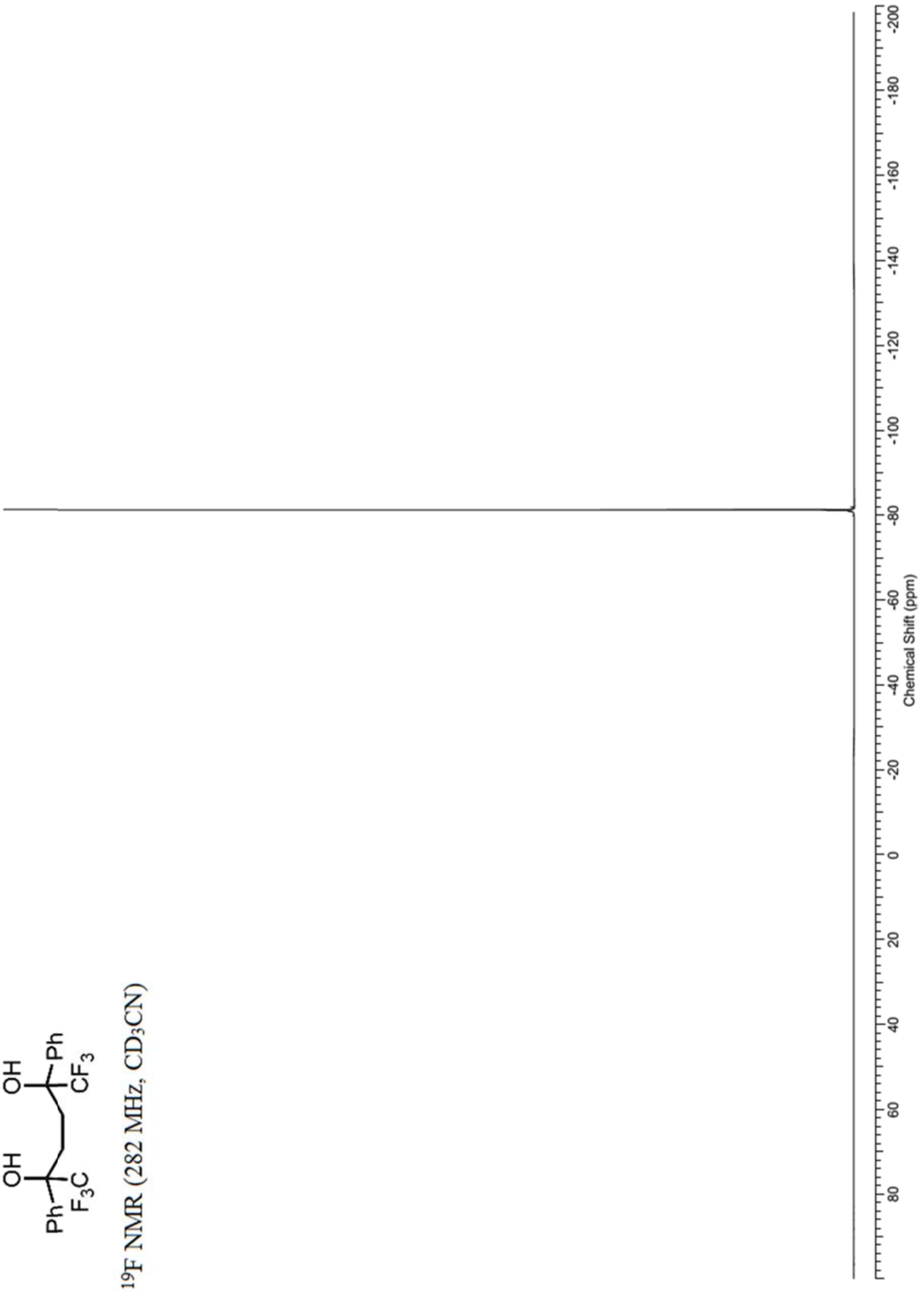




^{1}H NMR (300 MHz, CD$_3$CN)



^{13}C NMR (75 MHz, CD_3CN)



^{19}F NMR (282 MHz, CD_3CN)