Electronic Supplementary Material (ESI) for Catalysis Science and Technology

Supporting Information

Supramolecularly Controlled Surface Activity of an Amphiphilic Ligand. Application to Aqueous Biphasic Hydroformylation of Higher Olefins

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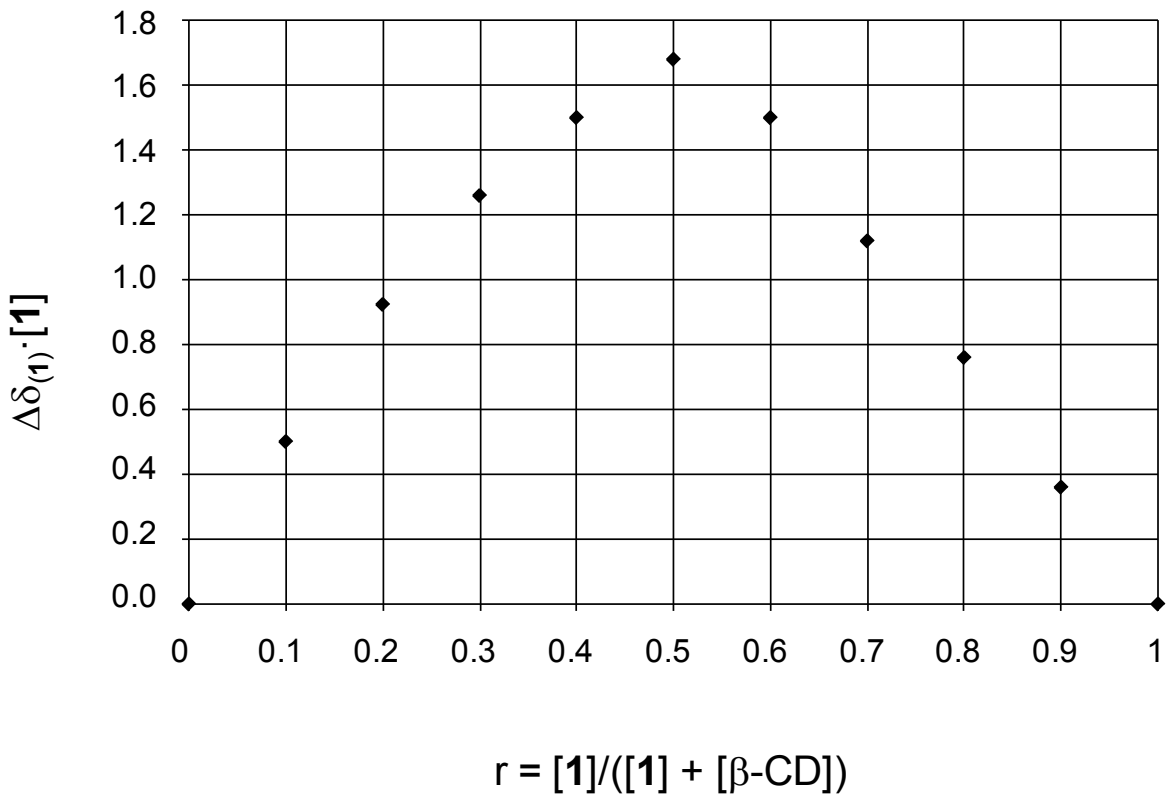
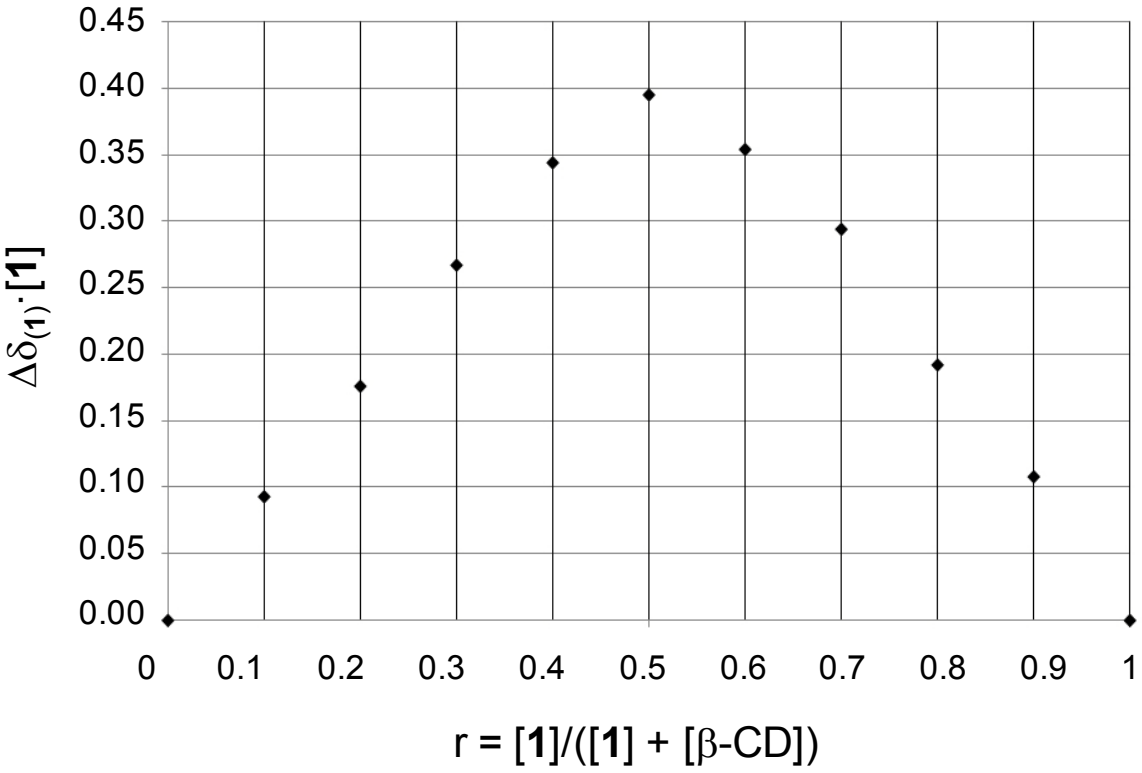
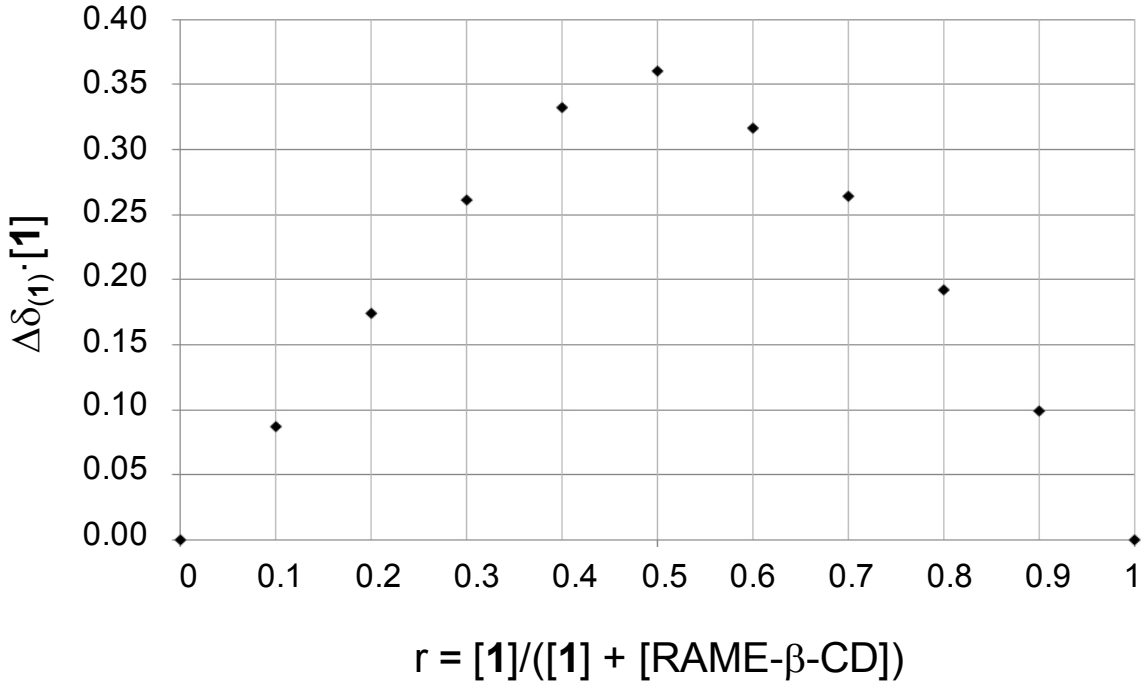
S1. The sodium salt of the trisulfonated triphenylphosphane (TPPTS)



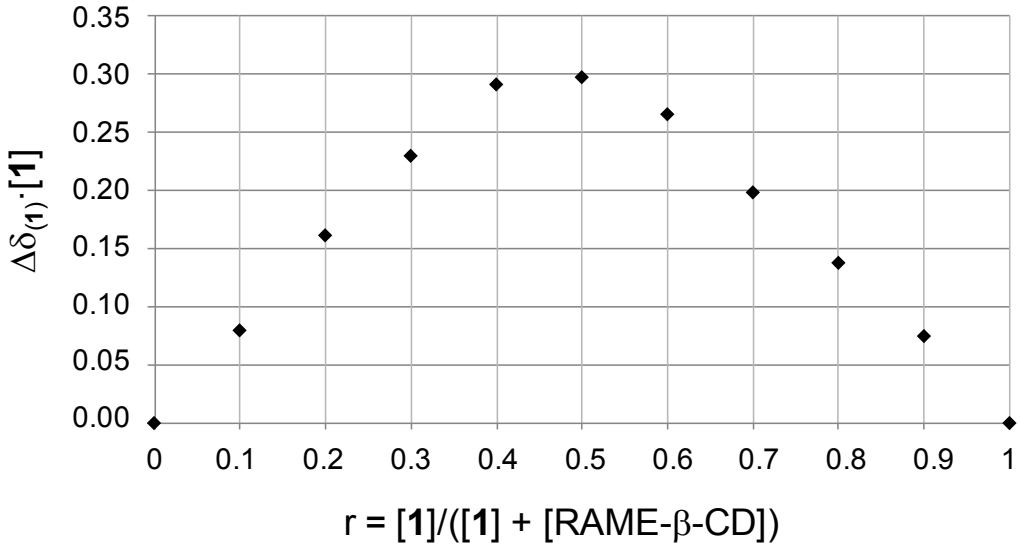
S2. Continuous variation plot (Job plot) derived from chemical shift variations of the phosphorous signal on ^{31}P NMR spectra of β-CD/**1** mixtures in D_2O at 25 °C. The total concentration of species is 10 mM.



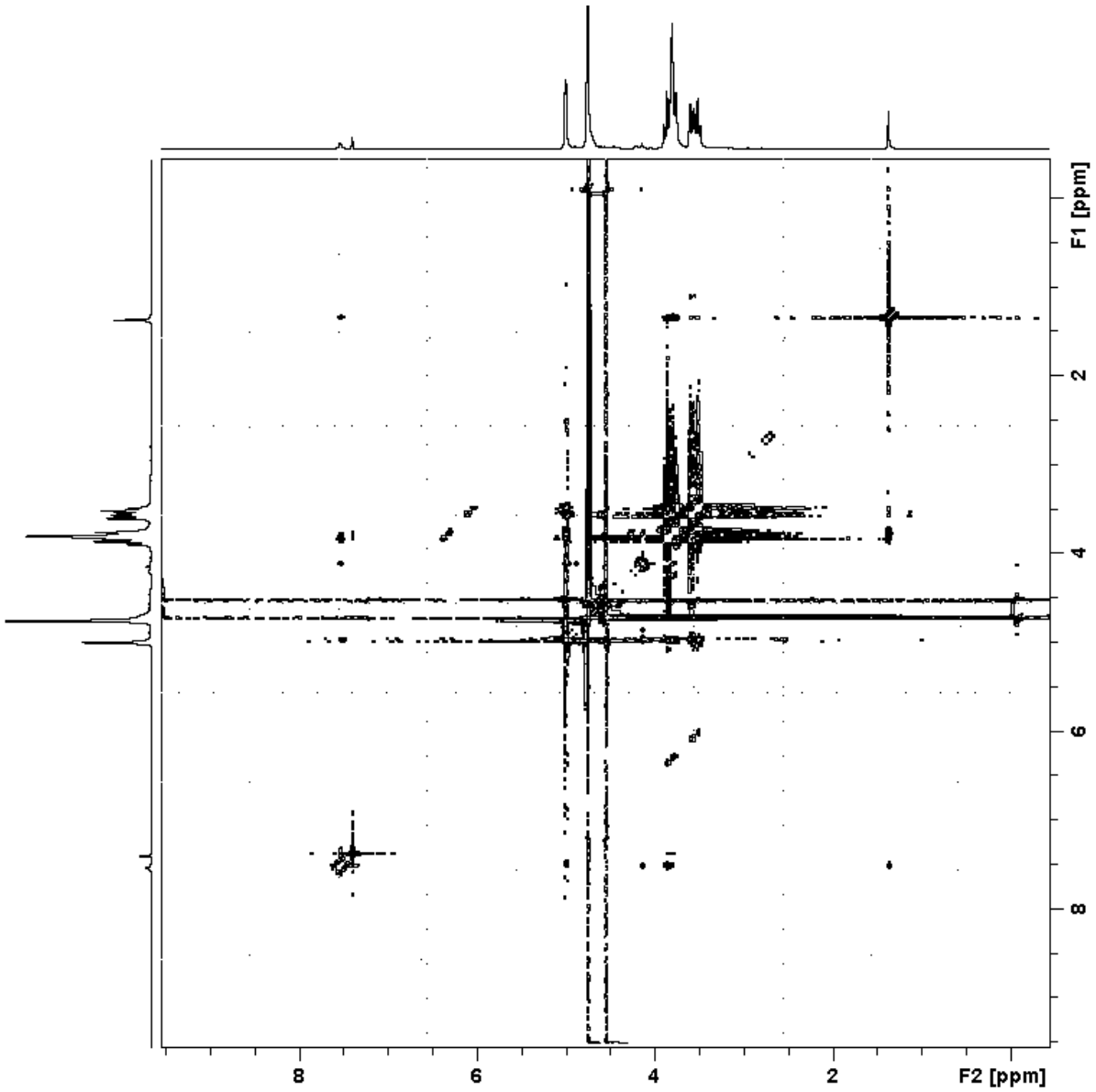
S3. Continuous variation plot (Job plot) derived from chemical shift variations of the *t*Bu signal on ^{1}H NMR spectra of β-CD/**1** mixtures in D_2O at 80 °C. The total concentration of species is 10 mM.



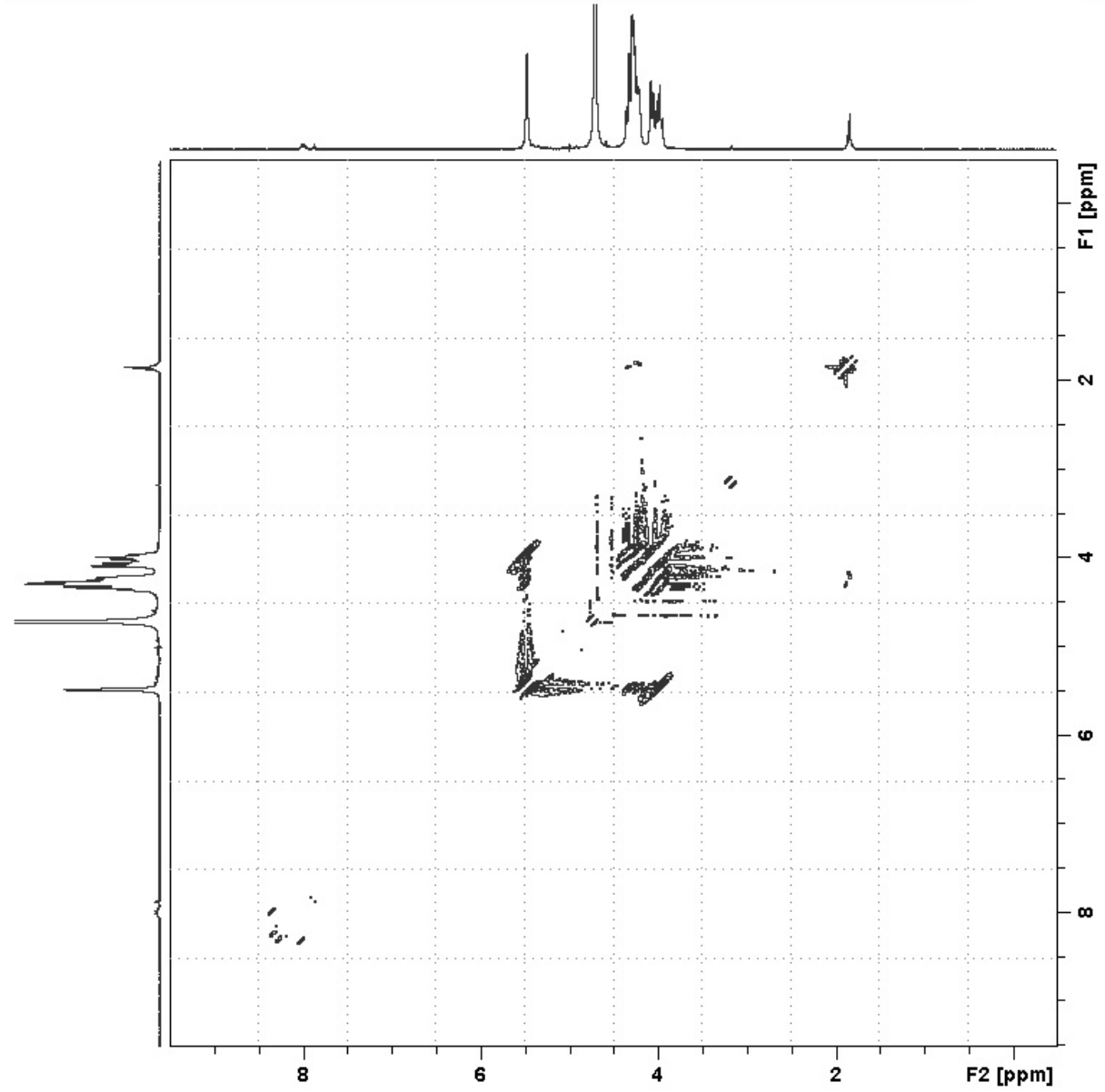
S4. Continuous variation plot (Job plot) derived from chemical shift variations of the *t*Bu signal on ^{1}H NMR spectra of RAME-β-CD/**1** mixtures in D_2O at 25 °C. The total concentration of species is 10 mM.



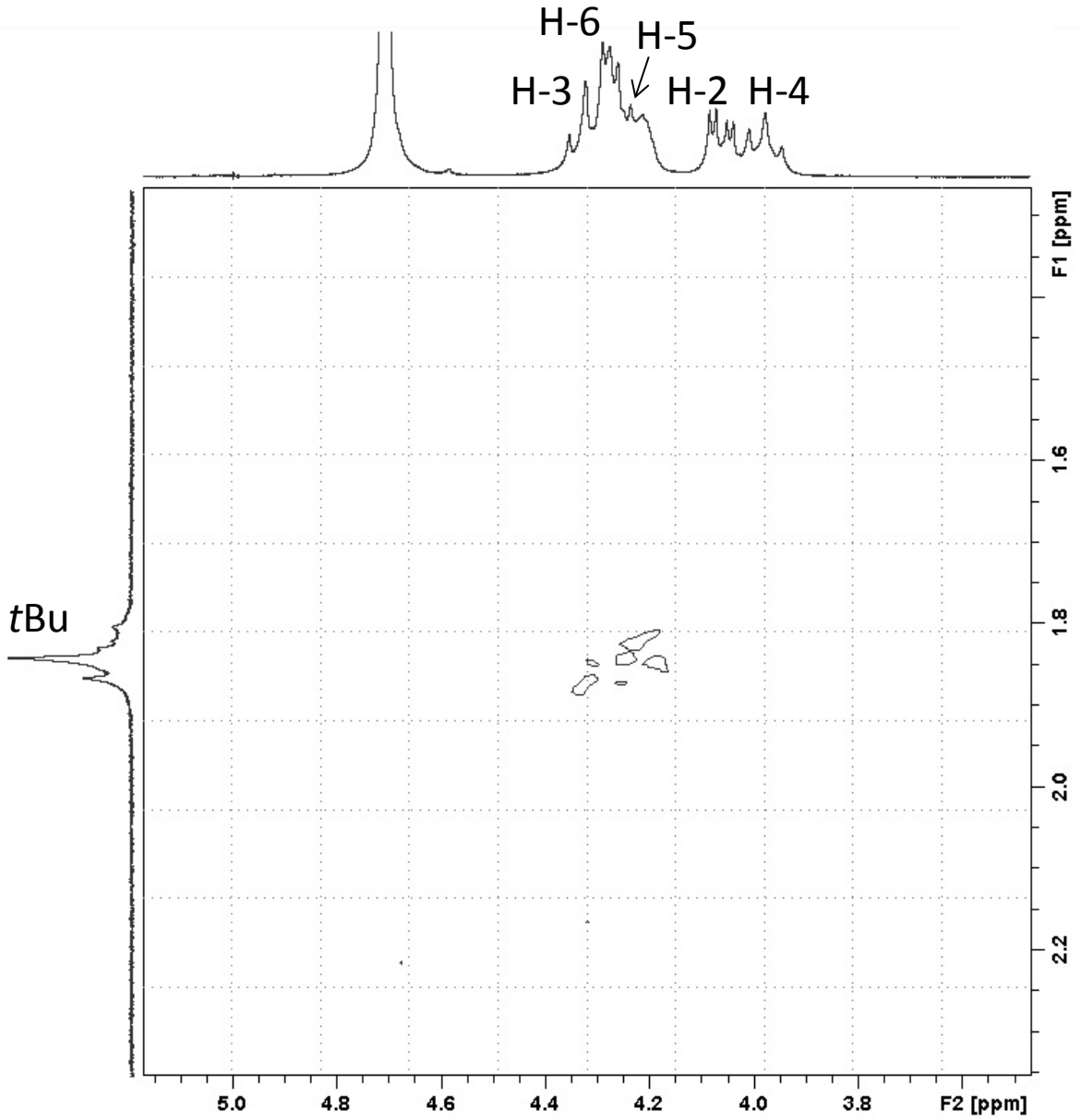
S5. Continuous variation plot (Job plot) derived from chemical shift variations of the *t*Bu protons signal on ^{1}H NMR spectra of RAME-β-CD/**1** mixtures in D_2O at 80 °C. The total concentration of species is 10 mM.



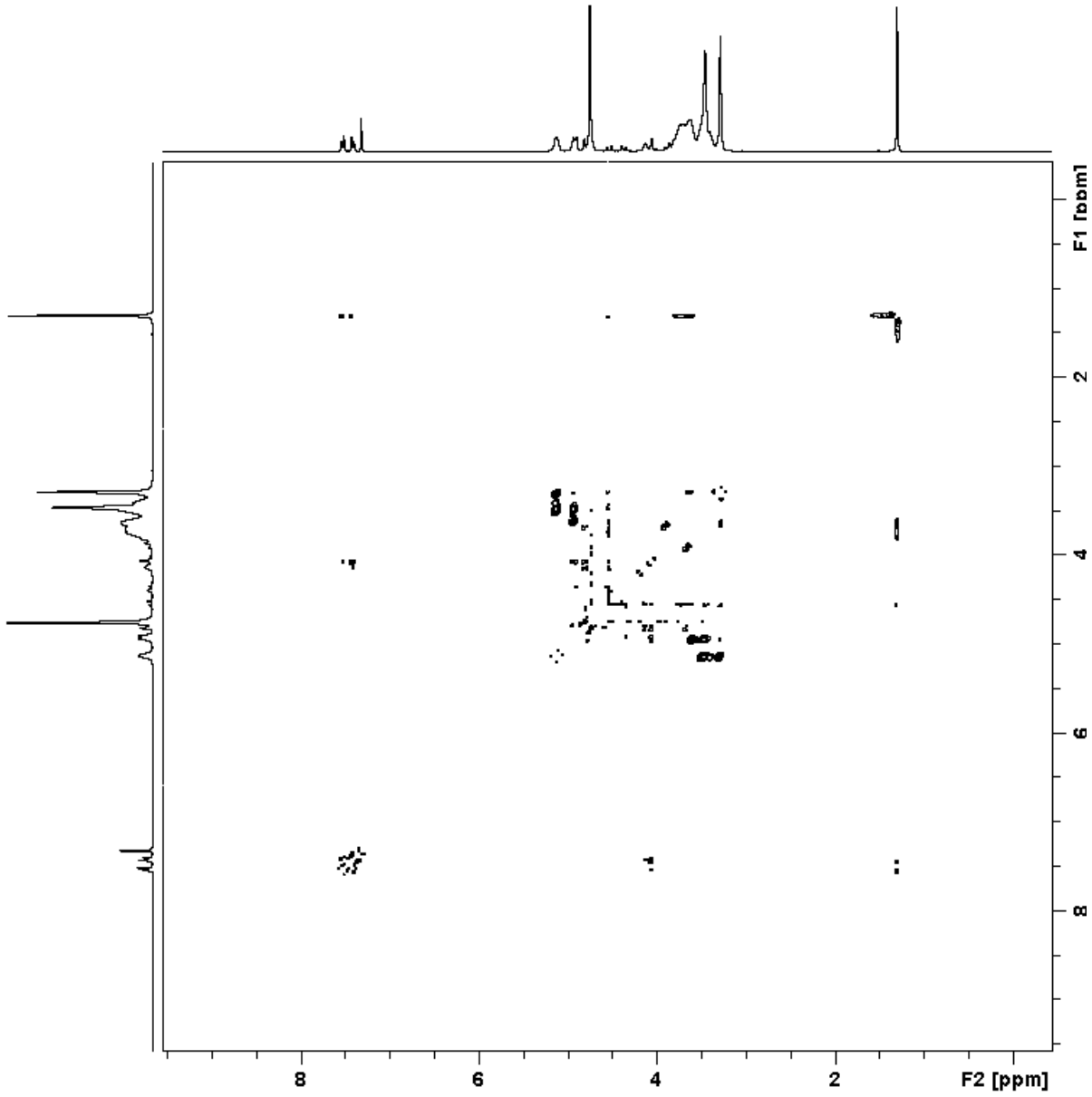
S6. 2D T-ROESY NMR spectrum of an equimolar mixture of native β-CD and **1** (10 mM/10 mM) at room temperature in D_2O (mixing time = 300 ms).



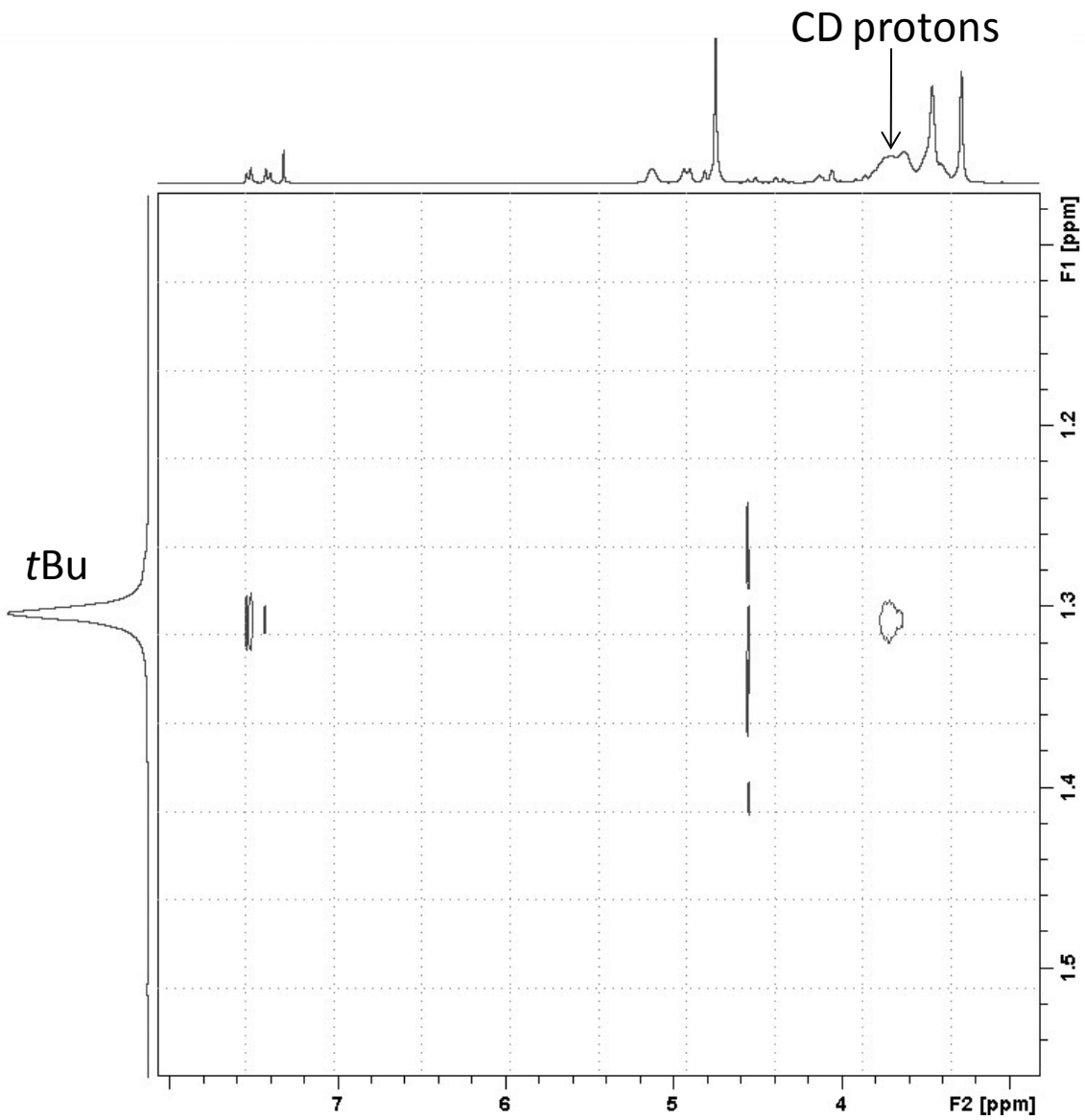
S7. 2D T-ROESY NMR spectrum of an equimolar mixture of native β-CD and **1** (10 mM/10 mM) at 80 °C in D_2O (mixing time = 300 ms).



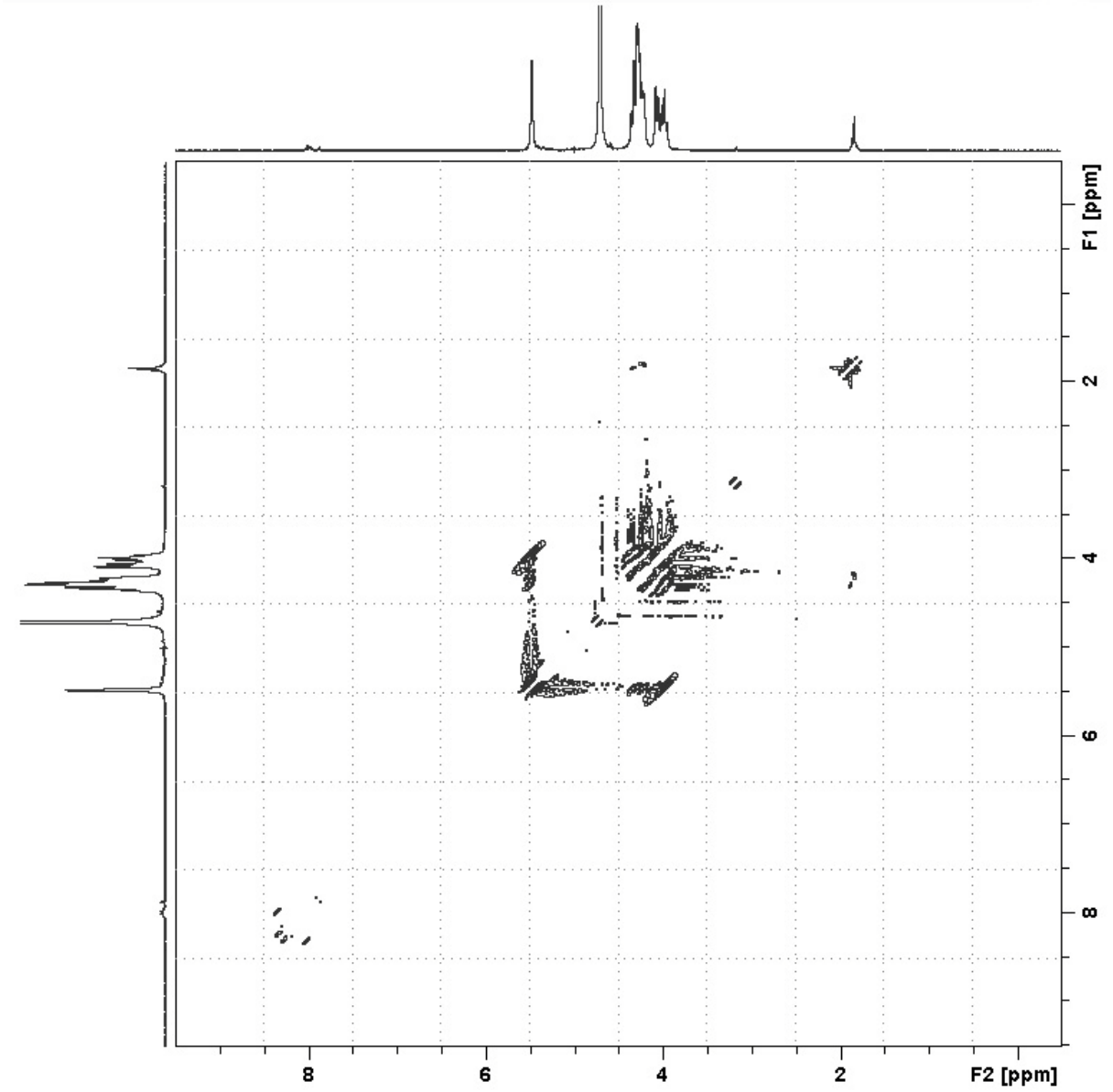
S8. Zoom of S6 on dipolar contacts between the *tert*-Bu protons of **1** and the H-3, H-5 and H-6 CD protons of native β-CD.



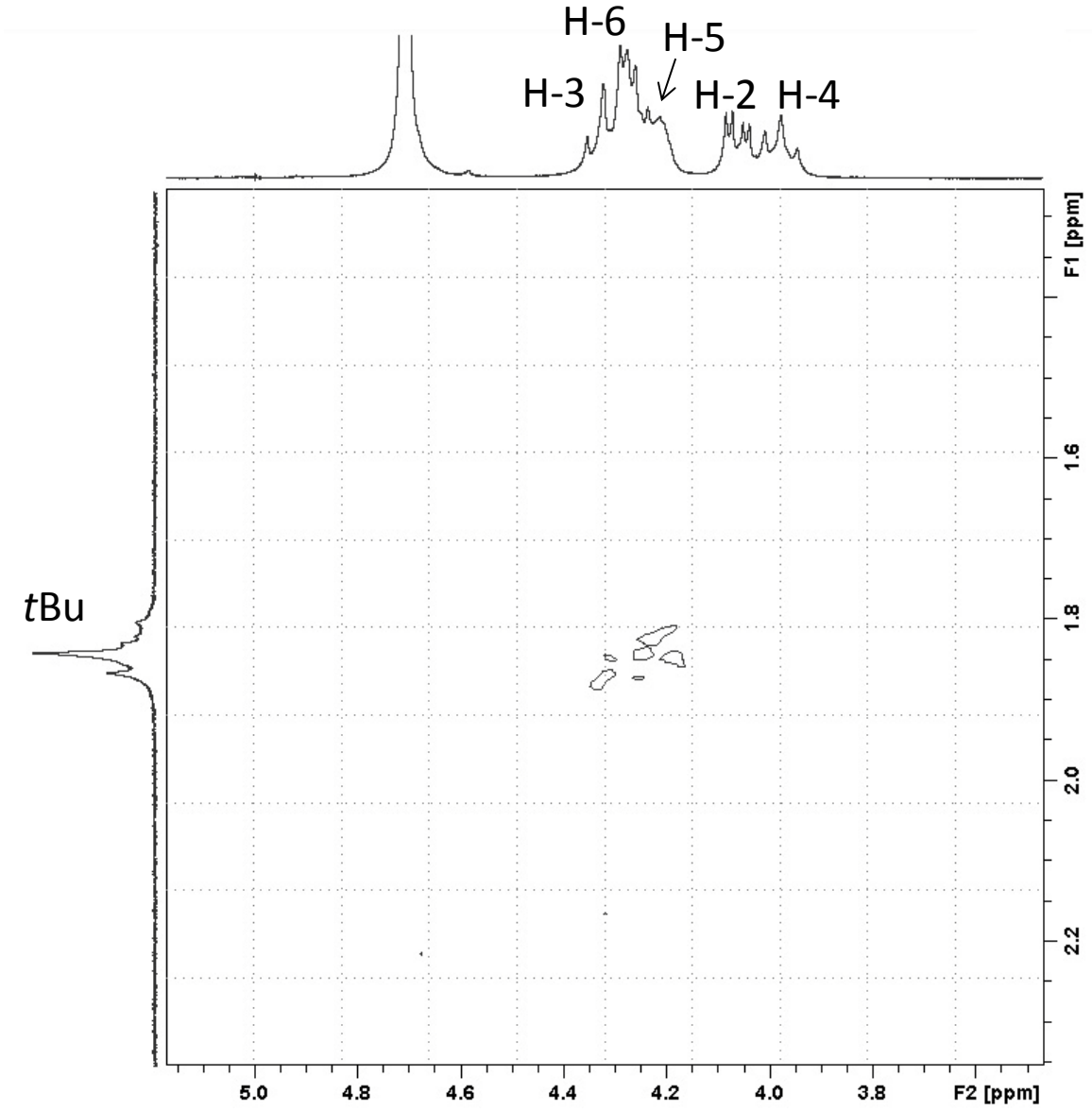
S9. 2D T-ROESY NMR spectrum of an equimolar mixture of RAME-β-CD and **1** (10 mM/10 mM) at room temperature in D_2O (mixing time = 300 ms).



S10. Zoom of S8 on dipolar contacts between the *t*Bu protons of **1** and CD protons H-3, H-5 and H-6.



S11. 2D T-ROESY NMR spectrum of an equimolar mixture of RAME-β-CD and **1** (10 mM/10 mM) at 80 °C in D_2O (mixing time = 300 ms).

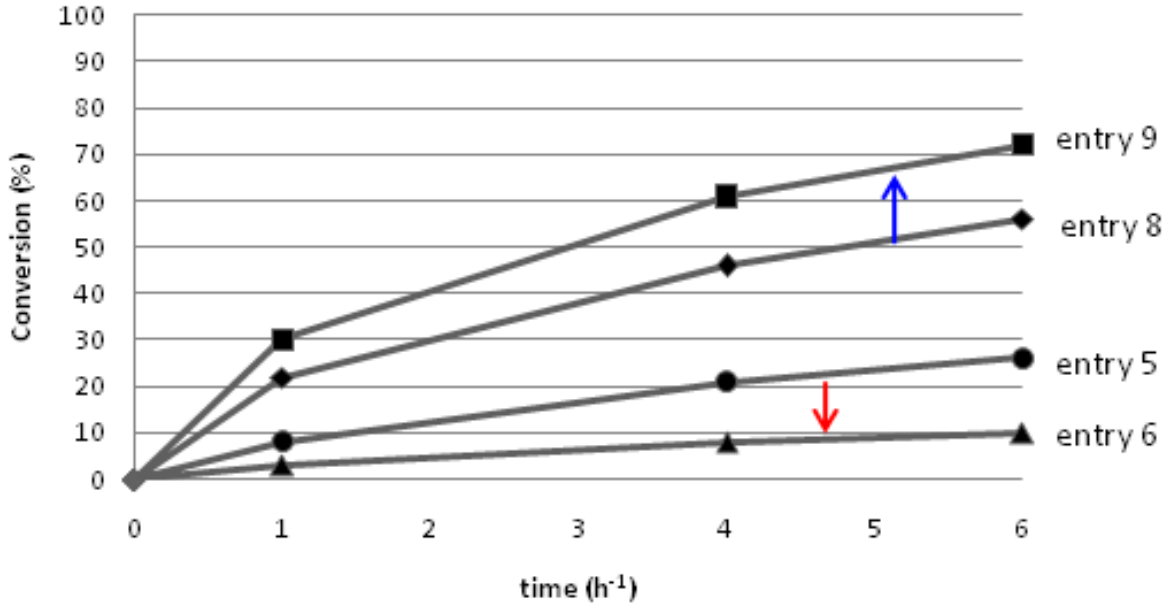


S12. Zoom of S10 on dipolar contacts between the *t*Bu protons of **1** and CD protons H-3, H-5 and H-6.

S13. Determination of the phosphane basicity

Phosphane selenides were synthesized by stirring overnight at room temperature excess selenium (10 equiv.) with **1** (250 mg) in absolute ethanol (15 mL) under nitrogen. The resulting mixture was directly analyzed by $^{31}P\{^{1}H\}$ NMR without any purification. NMR spectra exhibit the presence of phosphane selenides characterized by a singlet with two satellites due to only 7.6% of active selenium isotope (^{77}Se) in NMR spectroscopy. The upfield phosphorus signal (-83.09 ppm) was characteristic of the PTA phosphorus atom. The first order phosphorus-selenium coupling constants ($^{1}J_{P\text{-}Se}$) of the Se=**1** selenide allowed for the estimation of the basicity of **1**. The higher the $^{1}J_{P\text{-}Se}$ value, the lower the basicity. Ligand **1** ($^{1}J_{P\text{-}Se}$ = 814.6 Hz) was thus more basic than the previously synthesized CD non-interacting phosphane *N*-Bz-PTA (Scheme 1) for which a $^{1}J_{P\text{-}Se}$ = 817.7 Hz constant was determined.

S14. Reaction profiles of entries 5, 6, 8 and 9.



Experimental conditions: $Rh(acac)(CO)_2$ (4.07×10^{-2} mmol), water-soluble ligand (0.21 mmol), cyclodextrin (0.48 mmol), H_2O (11.5 mL), 1-alkene (20.35 mmol), 1500 rpm, CO/H_2 (1/1): 50 bar, 6 h. Entry 5: 80 °C without CD; Entry 6: 80 °C with RAME-β-CD; Entry 8: 100 °C without CD; Entry 9: 100 °C with RAME-β-CD.

The reaction profiles of these four relevant experiments highlight the poisoning effect of RAME-β-CD at 80 °C (red arrow) and the increase in activity observed at 100 °C (blue arrow).