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Supporting Information

Regioselective Reactivity of an Asymmetric Tetravalent Di[dihydroxotin(IV)] Bis-porphyrin Host Driven by Hydrogen-Bond Templation

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General Experimental Considerations.

Melting points were recorded on a Reichert melting point stage and are uncorrected. Infrared spectra were recorded on a SHIMADZU FTIR-8400S Fourier transform infrared spectrophotometer, as solutions in chloroform. Intensity abbreviations used are: w, weak; m, medium; s, strong. Ultravioletvisible spectra were routinely recorded on a Cary 5E UV-Vis-NIR spectrophotometer in ethanol free chloroform that was deacidified by filtration through a column of alumina.

^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) and signals are quoted in ppm relative to the residual protiated solvent peak.[1] The two dimensional NMR spectra discussed were recorded on the same instrument using standard Bruker pulse programs. Temperature was controlled using a Bruker B-VT 2000 variable temperature unit. ^{119}Sn NMR (149 MHz) chemical shifts are quoted relative to external dihydroxo[5,10,15,20-tetrakis-(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) (^{119}Sn = -569.2)[2] Deuteriated chloroform was dried and deacidified by filtration through a plug of anhydrous potassium carbonate and activated neutral alumina prior to use. Other deuteriated solvents were used as received. Signals are recorded in terms of chemical shift (in ppm), relative integral, multiplicity, coupling constants (in Hz) and assignment, in that order. The following abbreviations for multiplicity are used: s, singlet; d, doublet; app t, apparent triplet; m, multiplet; br, broad. For accurate volume measurements solvents were delivered by Hamilton microlitre syringe.

Homonuclear 2D NMR experiments (dqf-COSY, NOESY, ROESY) were typically run using a 90° pulse of 7.75 μs and a relaxation delay of 3.0 s over a spectral width of 8000 Hz using 2048 data points, giving an acquisition time of 0.12 s. Experiments were acquired over 512 increments each with 24 accumulated scans. Linear prediction of 128 t_1 data points and zero filling were applied prior to transformation, giving a 4k x 4k data matrix. Shifted sinebell window functions were applied in both dimensions. Mixing times for NOESY experiments were varied from 400 to 800 ms; ROESY experiments were carried out using mixing times ranging from 200 to 400 ms.

Heteronuclear 2D experiments (^{1}H-^{13}C HMBC, ^{1}H-^{13}C HSQC, ^{1}H-^{119}Sn HMQC) employed parameters for the ^{1}H (acquisition) dimension as described for homonuclear experiments. For ^{1}H-^{13}C experiments the ^{13}C dimension utilised a 90° pulse of 12 μs, with 512 increments collected over a

spectral width of 22000 Hz with 24 scans accumulated for each increment. Data collection was optimised for coupling constants of 125 Hz (HSQC) and 8 Hz (HMBC). Data was linear predicted in the ^{13}C dimension over 128 points, and a squared sinebell function applied. An exponential line broadening of 2 Hz was applied to the acquisition dimension and zero filling was employed in both dimensions to give a 4k x 4k data matrix. ^{1}H-^{119}Sn HMQC experiments utilised a ^{119}Sn 90° pulse of 15 μs, with 64 increments collected over a spectral width of 1500 Hz with 24 scans accumulated for each increment. Data collection was optimised according to the coupling constant to the central ^{119}Sn nucleus and data was zero filled in both dimensions to give a 4k x 1k data matrix.

Electrospray ionisation (ESI) were recorded on a ThermoQuest Finnigan LCQ DECA instrument. High resolution electrospray ionization Fourier transform ion cyclotron resonance (HR-ESI-FT/ICR) spectra were acquired at the Research School of Chemistry, Australian National University on a Bruker Daltonics BioAPEX II FT/ICR mass spectrometer equipped with a 4.7 Tesla MAGNEX superconducting magnet and an Analytica external ESI source.

Column chromatography was routinely carried out using the gravity feed column technique on Merck silica gel Type 9385 (230-400 mesh). Analytical thin layer chromatography (TLC) analyses were performed on Merck silica gel 60 F254 precoated sheets (0.2 mm). Alumina refers to Merck aluminium oxide 90 active neutral I, type 1077.

Solvents and reagents were purified using standard techniques.[3] All commercial solvents were routinely distilled prior to use. Light petroleum refers to the fraction of b.p. 60-80 °C. Where solvent mixtures were used, proportions are given by volume.

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) for dizinc(II) asymmetric bis-porphyrin **3**.

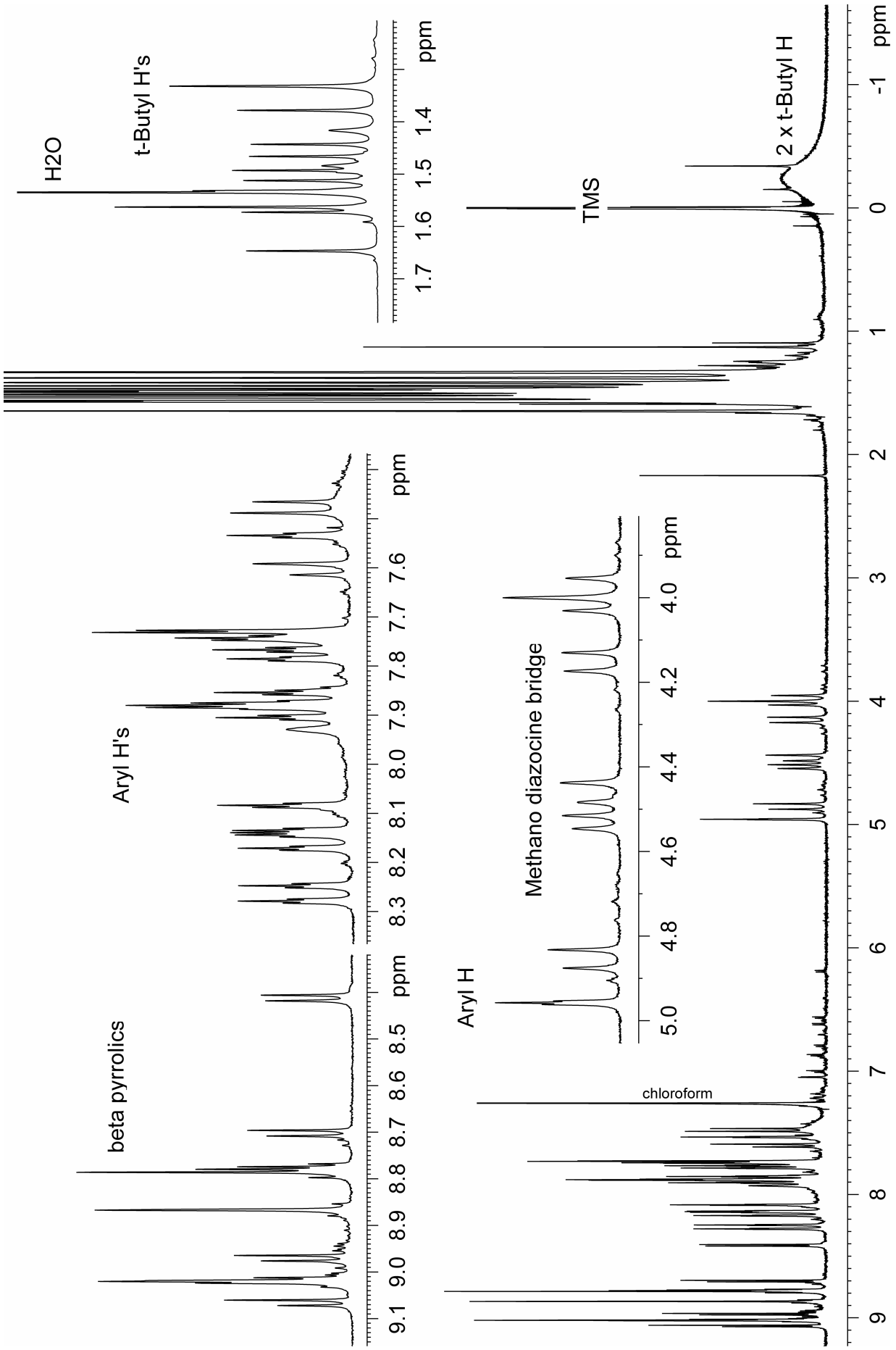


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) for free-base asymmetric bis-porphyrin **4**.

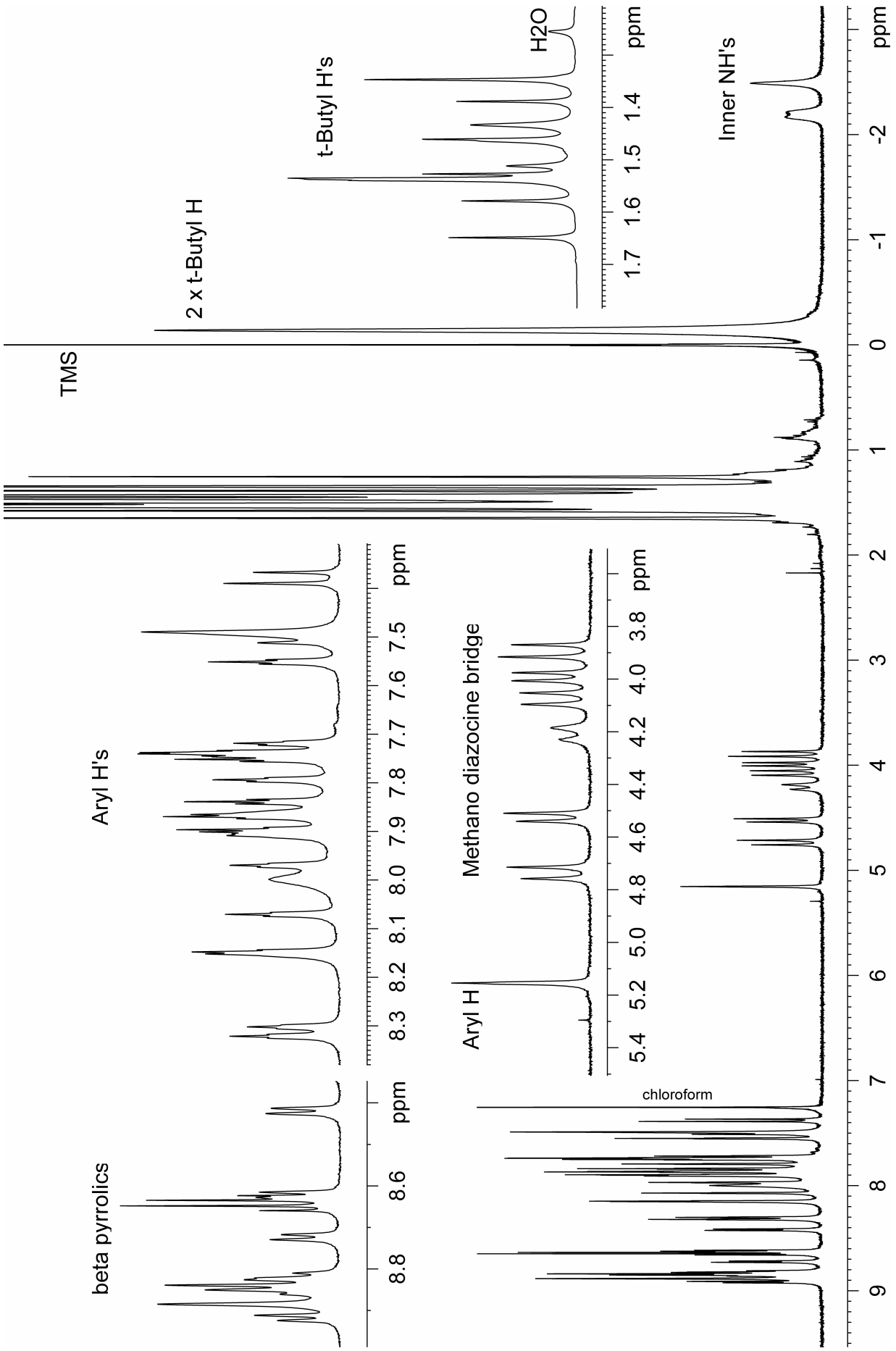


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) for di[dihydroxotin(IV)] asymmetric bis-porphyrin, host **5**.

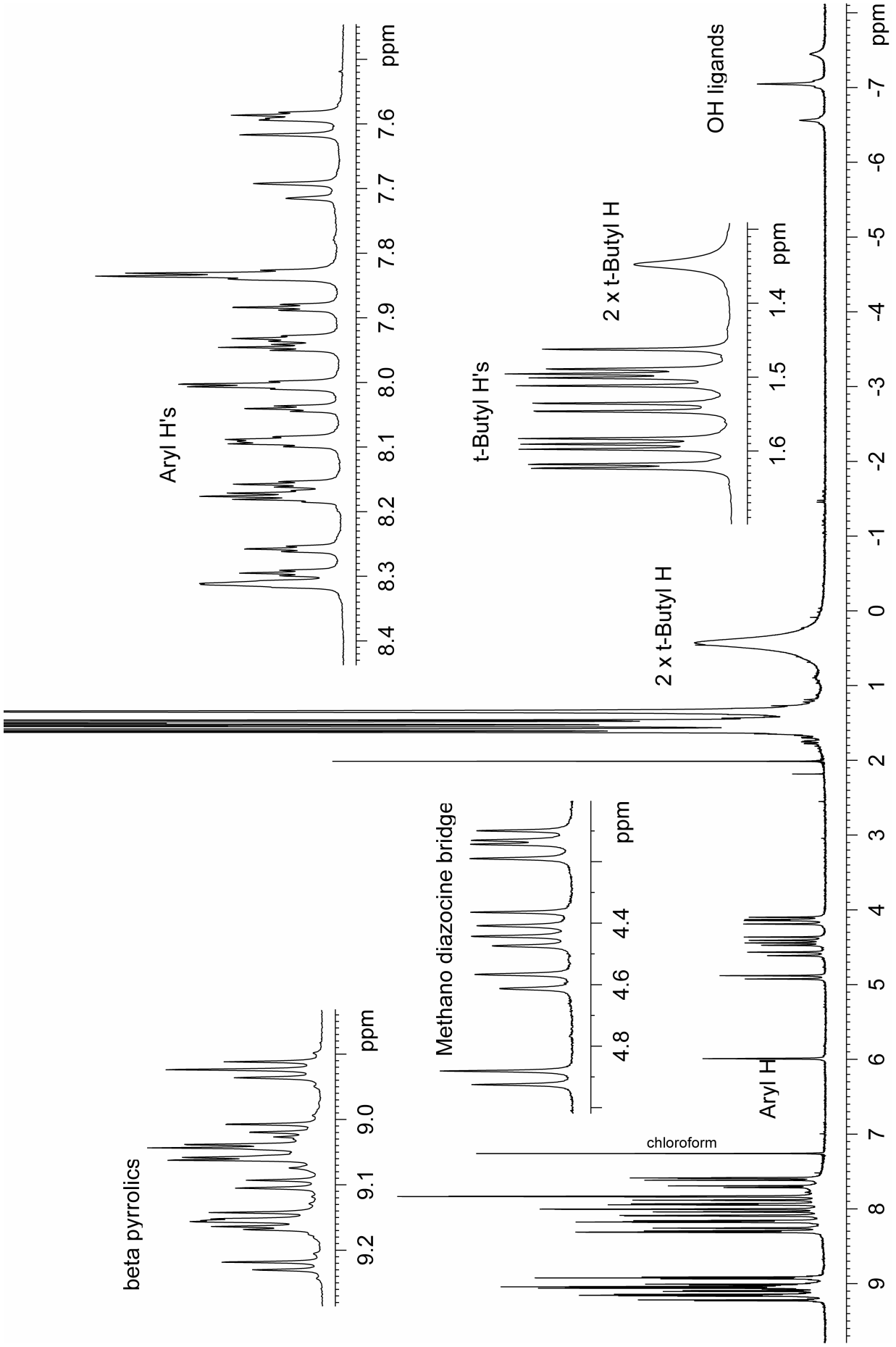


Figure S4. Free-base asymmetric Tröger's base bis-porphyrin **4**.

MS (HR-ESI-FT/ICR): found $[M + 2H]^{2+}$ 1148.2740. $C_{161}H_{192}N_{12} + 2H^+$ requires 1148.2785.

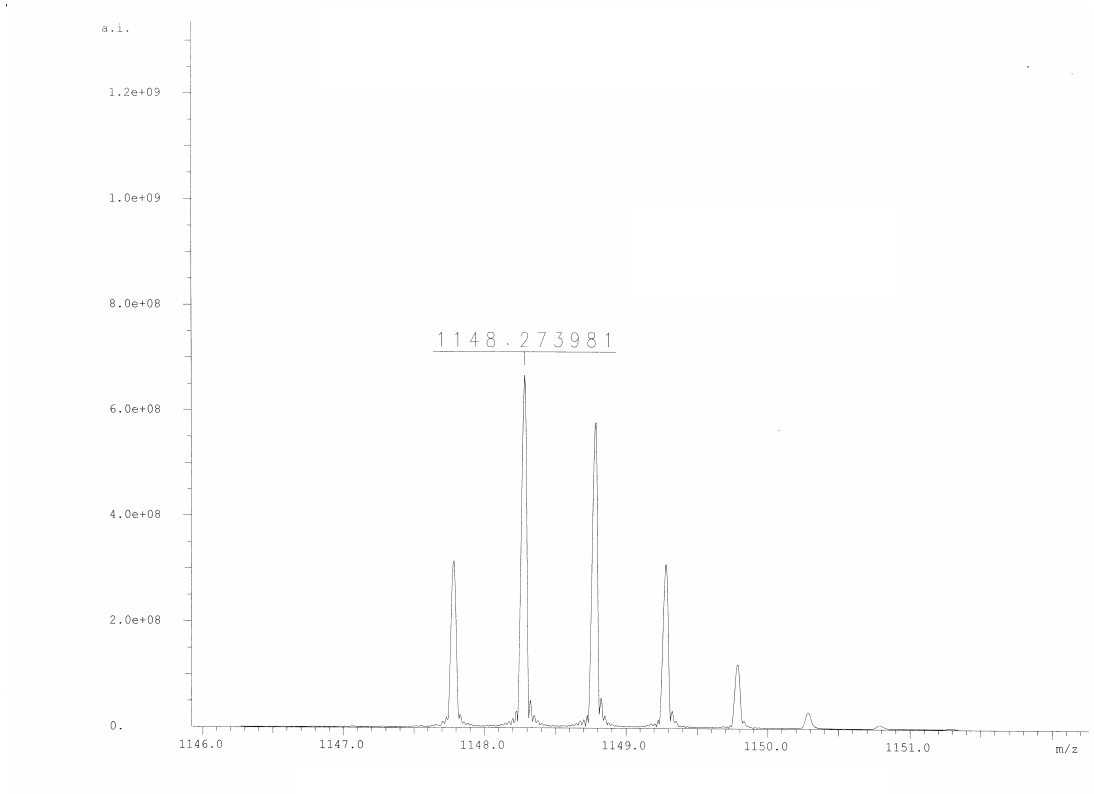
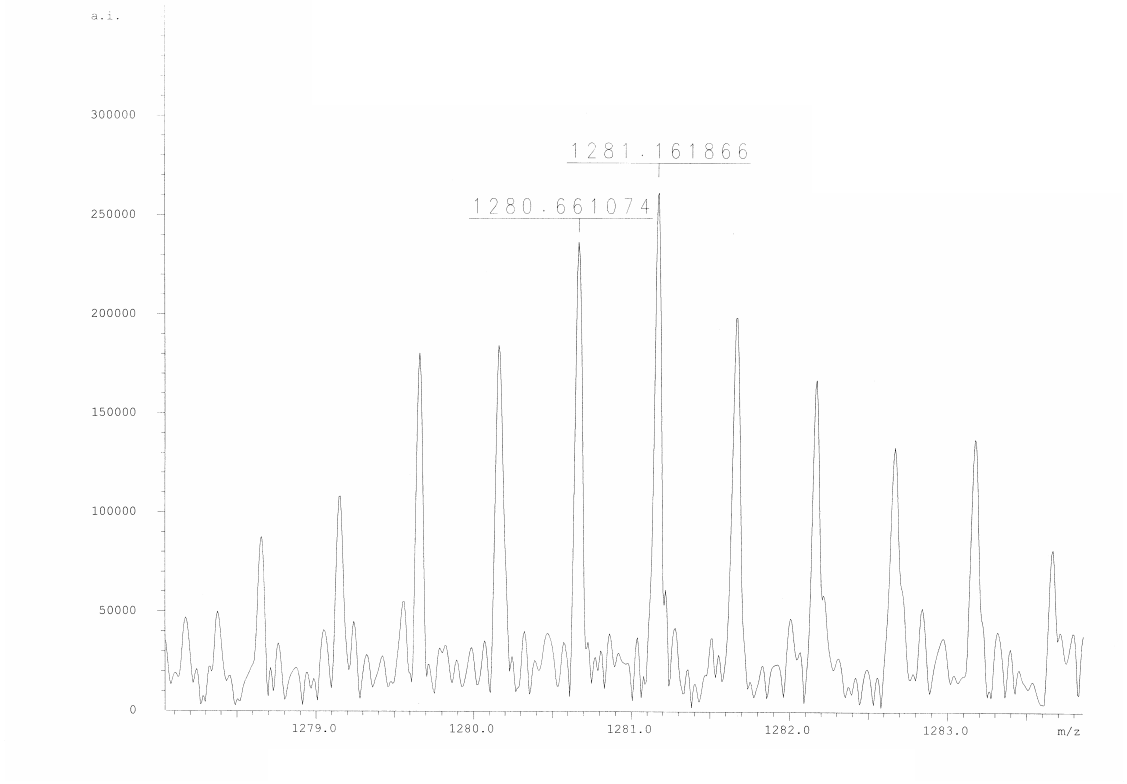


Figure S5. Di[dihydroxotin(IV)] asymmetric Tröger's base bis-porphyrin, host **5**.

MS (HR-ESI-FT/ICR): found $[M - 2OH]^{2+}$ 1281.1619. $C_{161}H_{190}N_{12}O_2Sn_2$ (2+) requires 1281.1614.



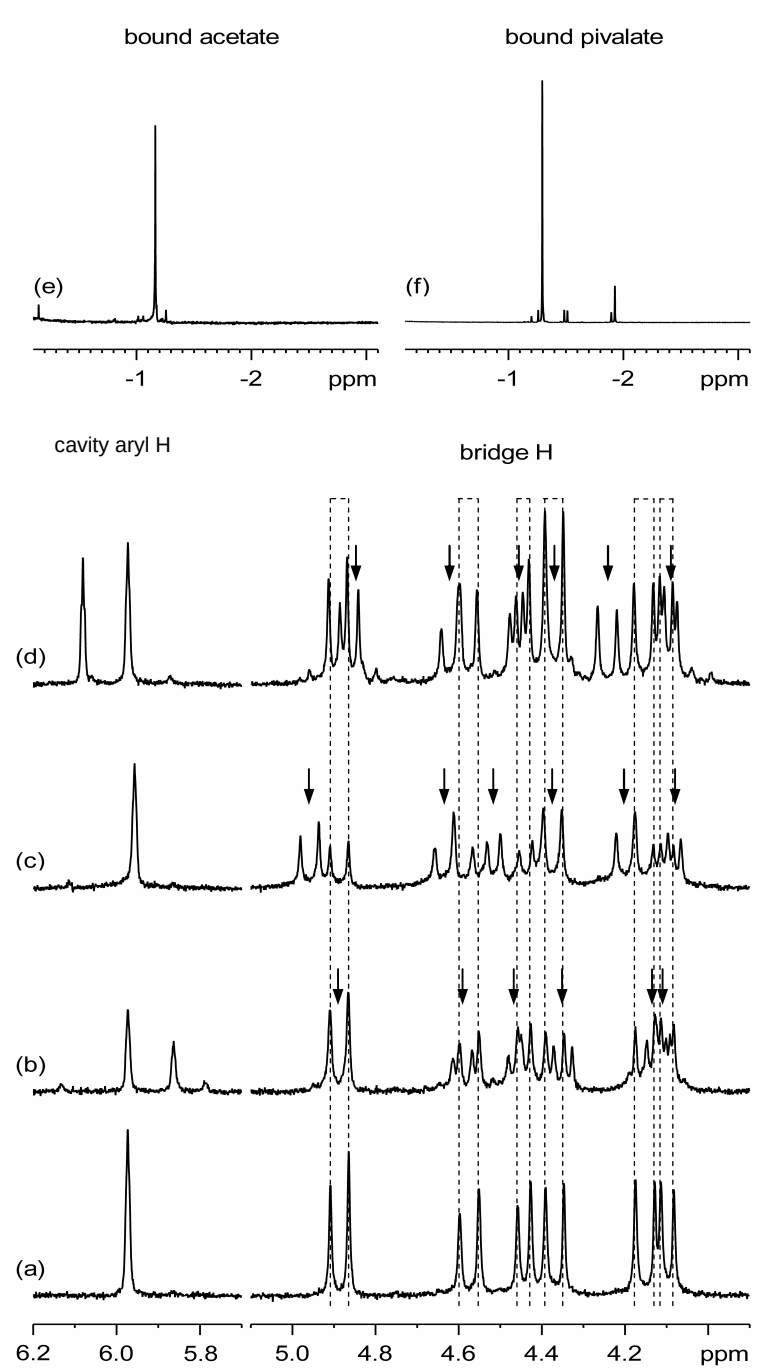


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) showing responses in the methanodiazocine bridge protons and the "cavity aryl proton" signal of **5** (a) to the binding of 0.6 mole equivalents formate **6** (b), acetate **7** (c) and pivalate **8** (d). Note the development of one major new "cavity aryl proton" signal [these aryl signals are coincident for the monoacetate complex in (c)] and the appearance of six new doublets (indicated by arrows) in the bridge region. Signals for residual **5** are indicated by the dashed lines. Expansions of the regions for bound acetate **7** and pivalate **8** are shown in (e) and (f). Bound **6** is indistinguishable beneath the ^{t}Bu signals of the host.

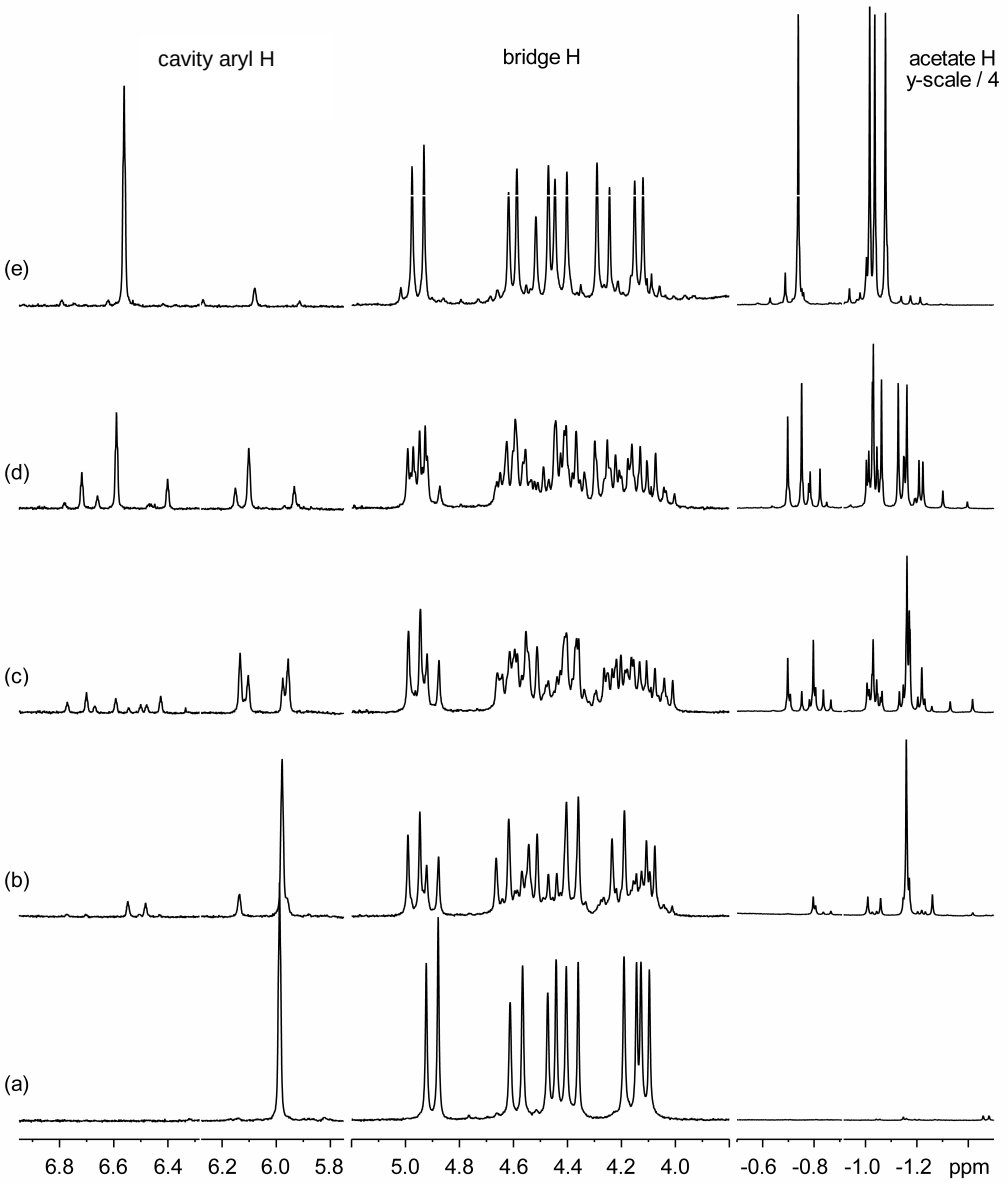


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) showing the response of the "cavity aryl proton", the methanodiazocine bridge region and the bound acetate region to titration of host **5** with acetic acid **7**. (a) **5**. Note six doublets in the bridge region. (b) **5** + 0.95 mole equivalents (eq) **7**. Spectrum shows a 70% yield of one new dihydroxo – hydroxo-acetato complex. (c) **5** + 2.0 eq **7**. Spectrum complicates dramatically. (d) **5** + 3.0 eq **7**. (e) **5** + 6.0 eq **7**. Spectrum simplifies to a single di(diacetato) complex. Note six doublets in the bridge region and four bound acetate signals.

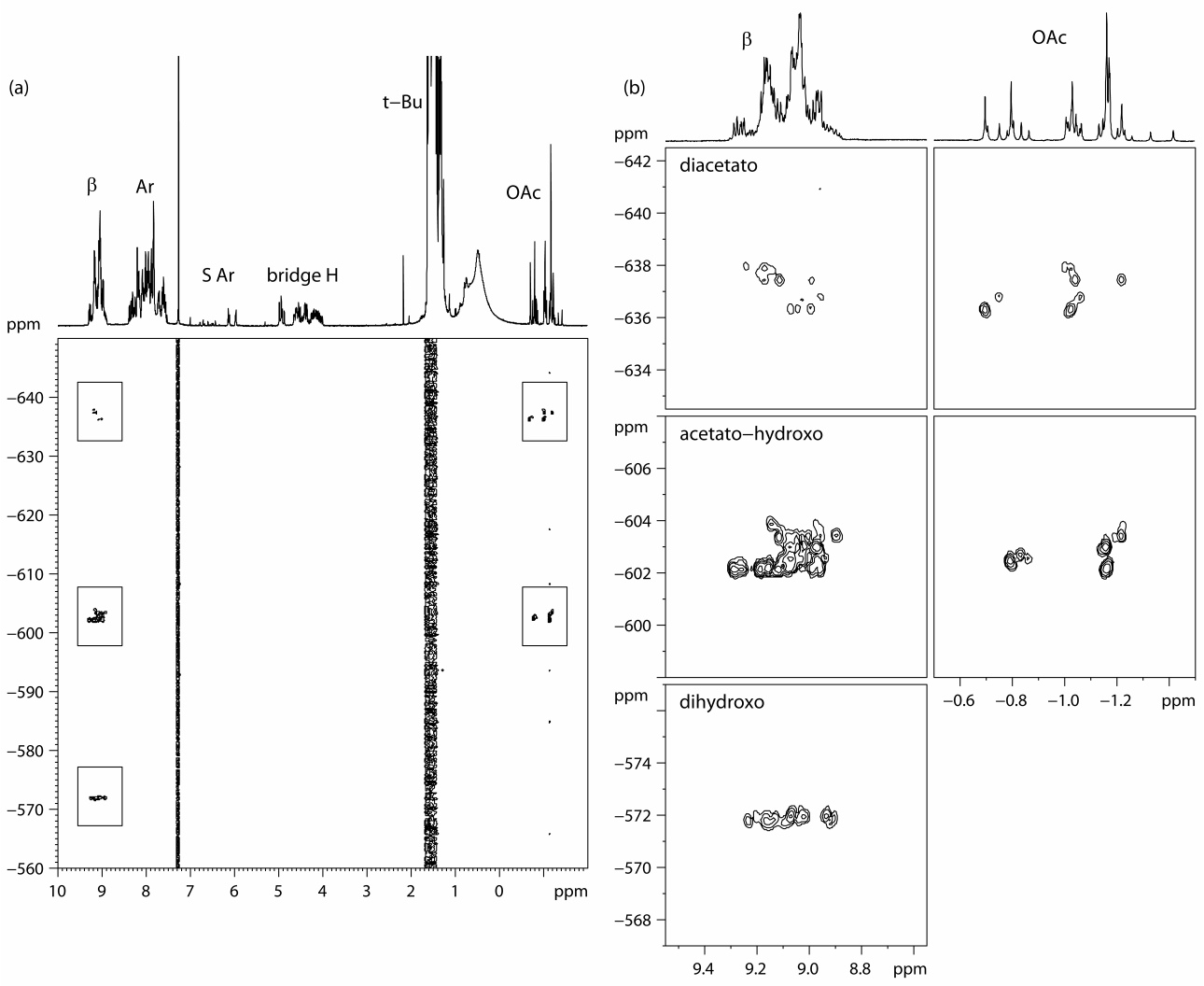


Figure S8. $^{1}H^{119}Sn$ HMQC ($CDCl_3$, 300 K) for complexes generated by the addition of 2.0 mole equivalents acetic acid **7** to **5**. (See Figure S7(c)) Note the random binding of the second equivalent of **7**. (a) Full spectrum. The sample is comprised of complexes possessing dihydroxotin(IV) nuclei (δ ^{119}Sn ~–572 ppm), many acetato-hydroxotin(IV) nuclei (δ ^{119}Sn –602 to –604 ppm) and diacetatotin(IV) nuclei (δ^{119}Sn –636 to –638 ppm). (b) Expansion of boxed signals.

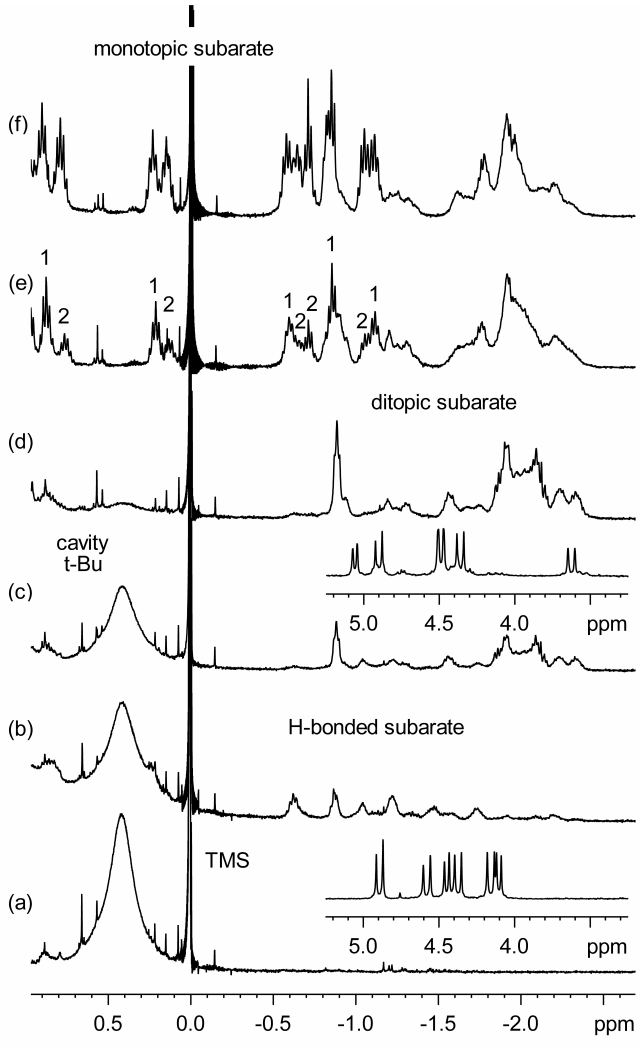


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) showing the binding of subaric acid **12** to host **5**. (a) Host **5**. Inset shows methanodiazocine bridge region, six doublets of a single complex. (b) Host **5** + 0.5 mole equivalent (eq) **12**, 30 min. Signals due to ditopic H-bonded 1:1 host **5** – **12** complex. (c) Host **5** + 0.5 eq **12**, 17 h, near complete 1:1 ditopic tin(IV) – carboxylate binding. (d) Host **5** + 1.0 eq **12**, 17 h, complete 1:1 ditopic tin(IV) – carboxylate binding. Inset (c) shows methanodiazocine bridge region, six doublets of a single ditopically bound subarate – host **5** complex. (e) Host **5** + 2.0 eq **12**, 1 h. A higher yield of one of the two possible products of ligand exchange forms, signals denoted 1 and 2. (f) Host **5** + 3.0 eq **12**, 10 h. Complete 3:1 host **5** – **12** complex formation. Note development of second set of externally bound subarate signals. The C-7-methylene for external subarate is obscured beneath the ^{t}Bu signals.

References

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512-7515.

[2] M. J. Crossley, P. Thordarson and R. A.-S. Wu, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2294-2302.

[3] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, **1988**, p. 391.