Supporting Information for

Sequential Self-assembly of Iron Structures in Water

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Experimental Methods

4,4'-Diaminobiphenyl ether-2,2'-disulfonic acid (B) was prepared following literature procedure.[1] Complexes **1**[2] and **3**[3] were prepared as described in the literature.

Simultaneous preparation of 1, 2 and 3. Tris(2-ethylamino)amine **A** (1.46 mg, 10.0 μmol), 4,4'-diaminobiphenyl ether-2,2'-disulfonic acid **B** (4.5 mg, 80%, balance water, 6.6 μmol), 4,4'-diaminobiphenyl-2,2'-disulfonic acid **C** (4.6 mg, 75%, balance water, 6.6 μmol), sodium bicarbonate (5.0 mg, 60 μmol), $FeSO_4{\cdot}7H_2O$ (6.5 mg, 23.3 μmol) and 2-formyl pyridine (6.7 μL, 70 μmol) were dissolved in D_2O (0.75 mL) in a Teflon-capped NMR tube, and the solution was then degassed with three vacuum / N_2 cycles. The sealed tube was heated in an oil bath to 323 K and left to react for 8 h, at which point ^1H NMR spectra corresponded to a mixture of **1**, **2** and **3** (Figure S1d). No further evolution was noted following heating to 323 K for 24 h.

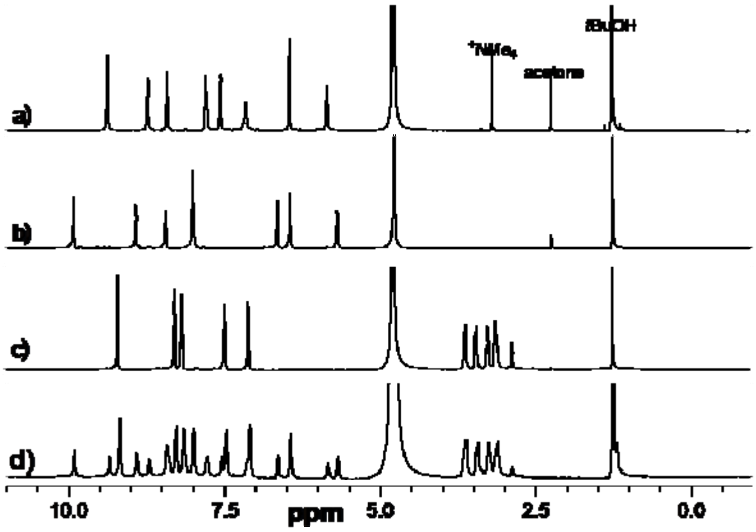

Figure S1. ^1H NMR spectra of a) cage **3**; b) helicate **2**; c) complex **1** and d) all three structures generated together.

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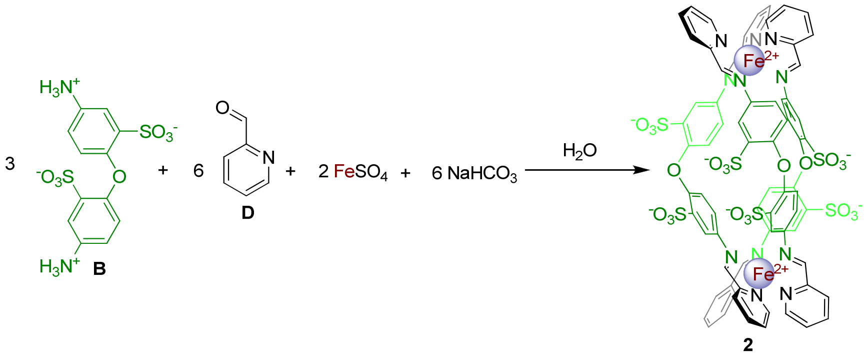
[1] J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita and K.-I. Okamoto, *Macromolecules* 2002, **35**, 9022.

[2] M. A. Hoselton, L. J. Wilson and R. S. Drago, *J. Am. Chem. Soc.* 1975, **97**, 1722.

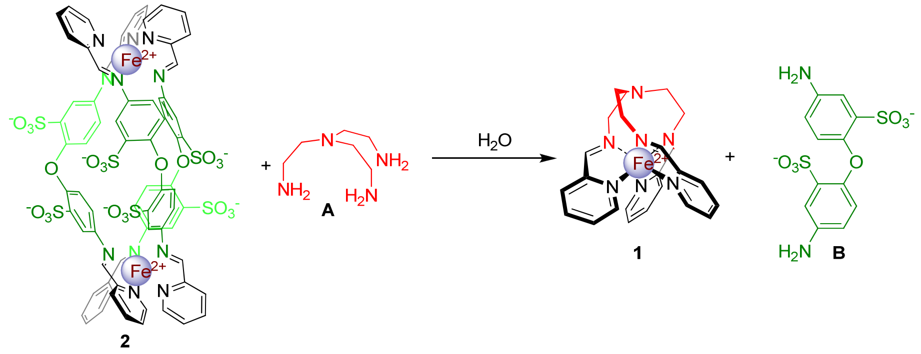
[3] P. Mal, D. Schultz, K. Beyeh, K. Rissanen and J. R. Nitschke, *Angew. Chem. Int. Ed.* 2008, **47**, 8297.

Preparation of Complex 2. To a 50 mL Schlenk flask containing degassed water (12 mL) and a stir-bar were added 4,4'-diaminobiphenyl ether-2,2'-disulfonic acid **B** (450 mg, 80%, balance water, 1.0 mmol), 2-formylpyridine **D** (214 mg, 2.0 mmol), sodium bicarbonate (168 mg, 2.0 mmol), and iron(II) sulfate heptahydrate (186 mg, 0.67 mmol). All starting materials dissolved, giving a dark purple solution. The flask was sealed and the atmosphere was purified of dioxygen by three evacuation / argon fill cycles. The reaction was stirred for 14 h at 323 K. The product was then isolated as a dark purple microcrystalline material by slow vapor diffusion of acetone into the aqueous solution of **2**; isolated yield 601 mg (97%); ^{1}H NMR (500 MHz, 300 K, D_2O, referenced to methyls of 2-methyl-2-propanol at 1.24 ppm as internal standard): δ = 9.90 (s, 6 H, imine), 8.91 (d, J = 7.6 Hz, 6 H, 3-pyridine), 8.42 (t, J = 7.6 Hz, 6 H, 4-pyridine), 8.03-7.93 (m, 12 H, 4-, 5-pyridine), 6.63 (d, J = 9.0 Hz, 6 H, 6,6'-benzidine), 6.42 (d, J = 2.0 Hz, 6 H, 3,3'-benzidine), 5.66 (dd, J = 9.0, 2.0 Hz, 6 H, 5,5'-benzidine); ^{13}C NMR (125 MHz, 300 K, D_2O, referenced to the methyl groups of 2-methyl-2-propanol at 30.29 ppm as internal standard): δ = 175.1, 157.3, 156.9, 156.0, 148.0, 140.8, 135.4, 133.8, 132.7, 126.6, 123.6, 123.3; ESI-MS: m/z = -559.1 ($[\mathbf{L}+\mathrm{Na}^+]^-$), -860.2 ($[\mathbf{2}]^{2-} \equiv [\mathbf{L}_3\mathbf{Fe}_2]^{2-}$).



Scheme S1. Preparation of complex **2**.

Reaction of 2 and A to give 1 and B. D_2O (0.5 mL), **2** (4.0 mg, 2.2 μmol) and **A** (0.86 mg, 5.8 μmol) were loaded into a Teflon-capped NMR tube, and the solution was degassed with three vacuum / N_2 cycles. The sealed tube was heated in an oil bath to 323 K, and reaction progress was monitored by NMR (Figure S2). The appearance was noted of ^{1}H resonances corresponding to **A**, free 4,4'-diaminobiphenyl ether-2,2'-disulfonate (**B**). The reaction had reached completion after 72 h at 323 K.



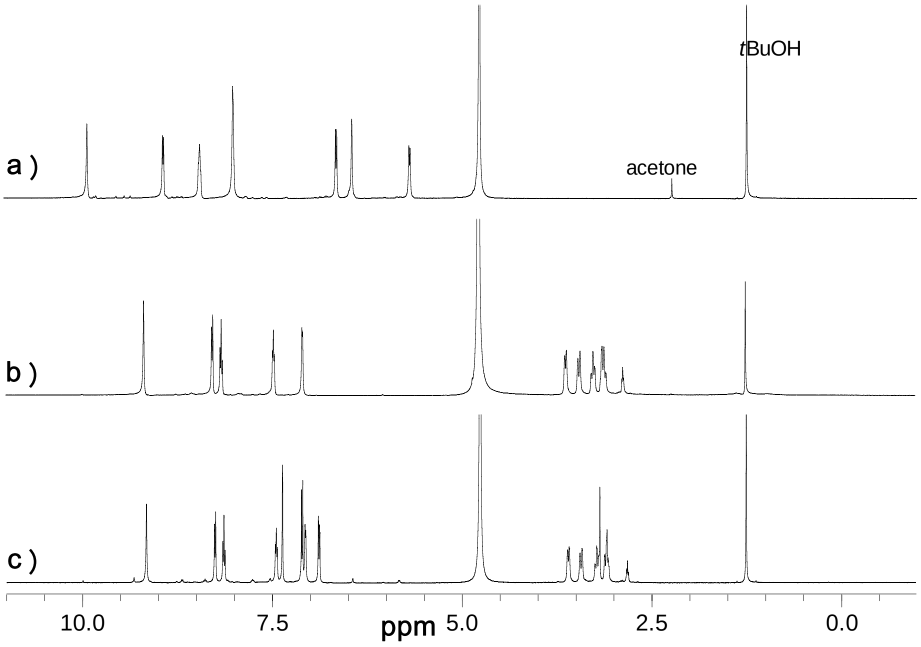
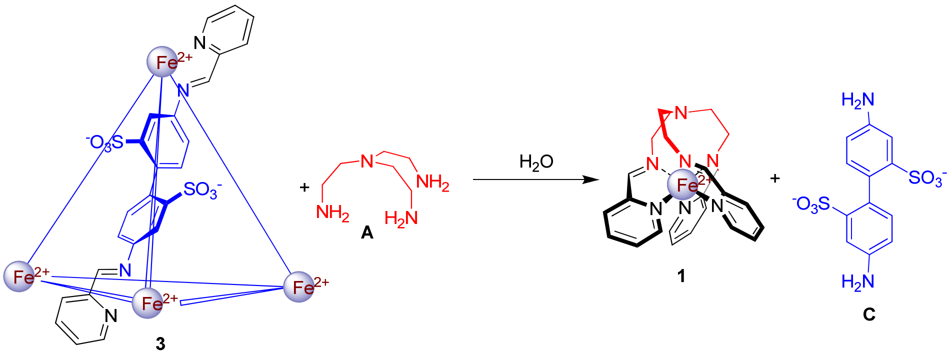


Figure S2. ^{1}H NMR spectra for the conversion of **2** into **1**: a) **2**; b) **1**; c) mixture of **2** with **A** (2.6 equiv.) after 72 h at 323 K.

Conversion of 3 into 1 by reaction with A. As noted in our previous study,[3] the reaction of **3** with **A** yielded **1** quantitatively after 120 h at 323 K.



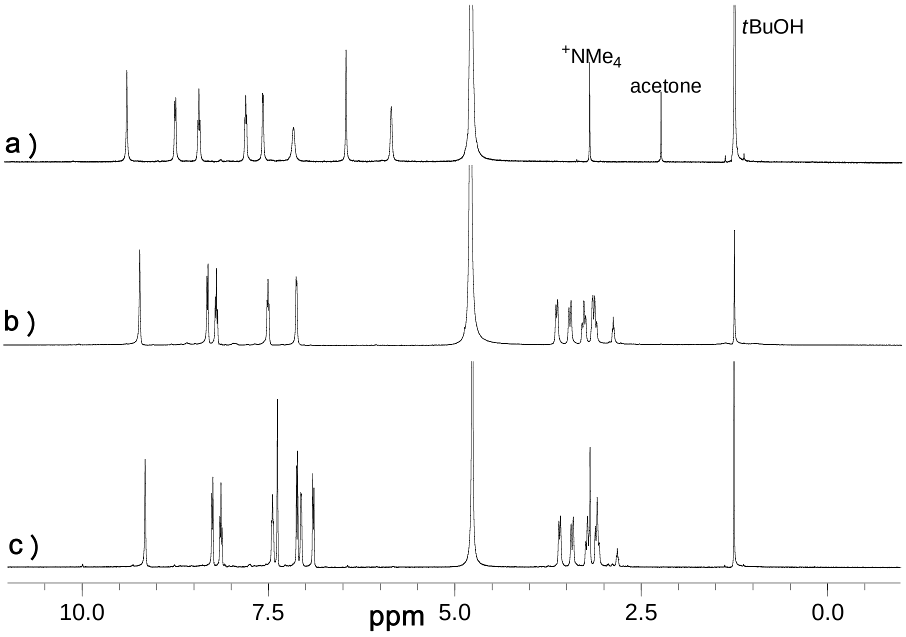
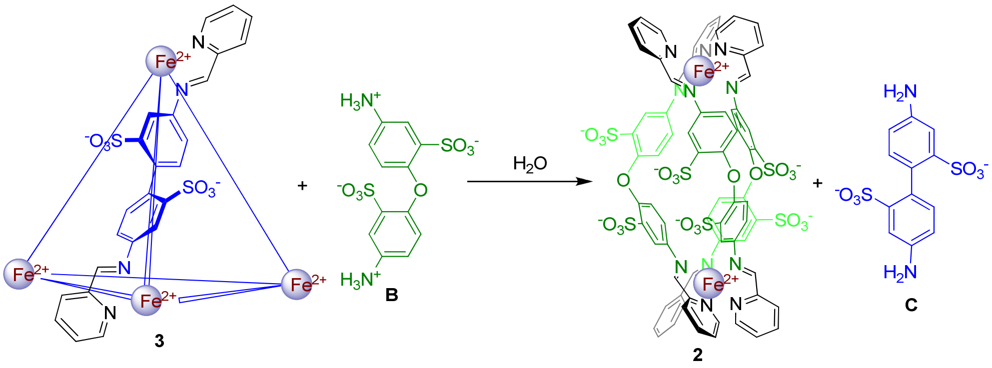


Figure S3. ^{1}H NMR spectra for the conversion of **3** into **1**: a) **3**; b) **1**; c) mixture of **3** with **A** (6.0 equiv.) after 120 h at 323 K.

Conversion of 3 into 2 by reaction with B. 3 (4.0 mg, 0.94 μmol), D_2O (0.5 mL), 4,4'-diaminobiphenyl ether-2,2'-disulfonate **B** (4.0 mg, 80%, balance water, 8.9 μmol) and $NaHCO_3$ (1.5 mg. 17.9 μmol) were loaded into a Teflon-capped NMR tube and the solution was degassed with three vacuum / N_2 cycles. The sealed tube was heated in an oil bath to 323K for 84 h, and reaction progress was monitored by NMR (Figure S4).



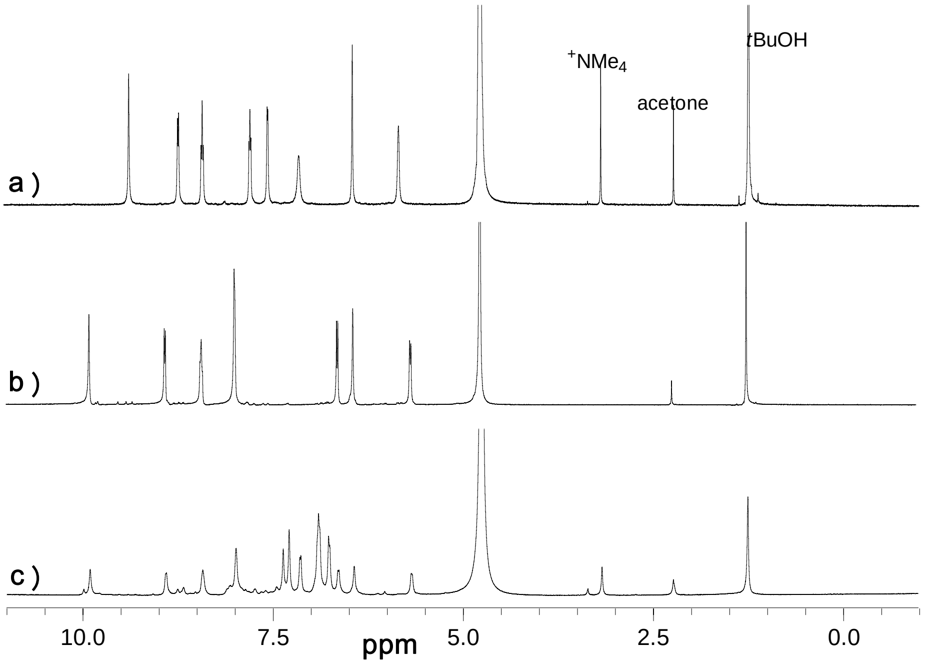
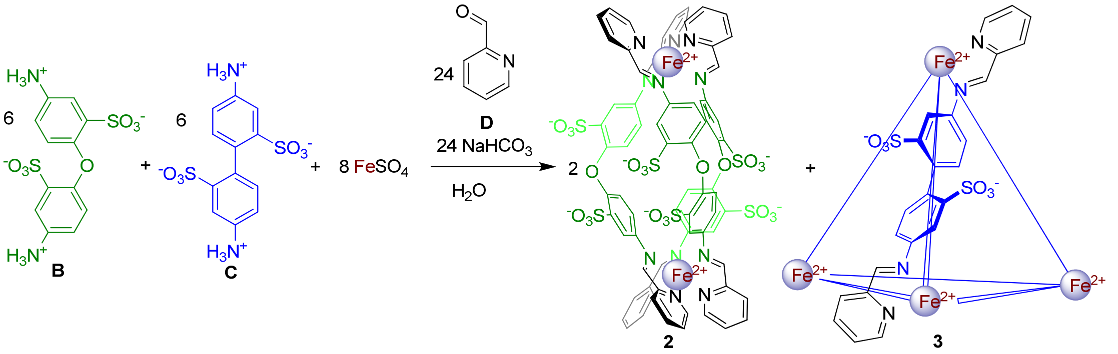


Figure S4. ^1H NMR spectra for the conversion of **3** into **2**: a) **3**; b) **2**; c) mixture of **3** with **B** (9.5 equiv.) after 84 h at 323 K.

Simultaneous preparation of 2 and 3. 4,4’-Diaminobiphenyl ether-2,2’-disulfonic acid **B** (4.5 mg, 80%, balance water, 10.0 µmol), 4,4’-diaminobiphenyl-2,2’-disulfonic acid **C** (4.6 mg, 75%, balance water, 10 µmol), sodium bicarbonate (3.4 mg, 40 µmol), $FeSO_4$ (3.7 mg, 13.3 µmol), 2-formyl pyridine **D** (4.3 mg, 40 µmol) were dissolved in D_2O (0.5 mL) in a Teflon-capped NMR tube, then the solution was degassed with three vacuum / N_2 cycles. The sealed tube was heated in an oil bath to 323 K for 8 h and reaction progress was monitored by NMR (Figure S5).



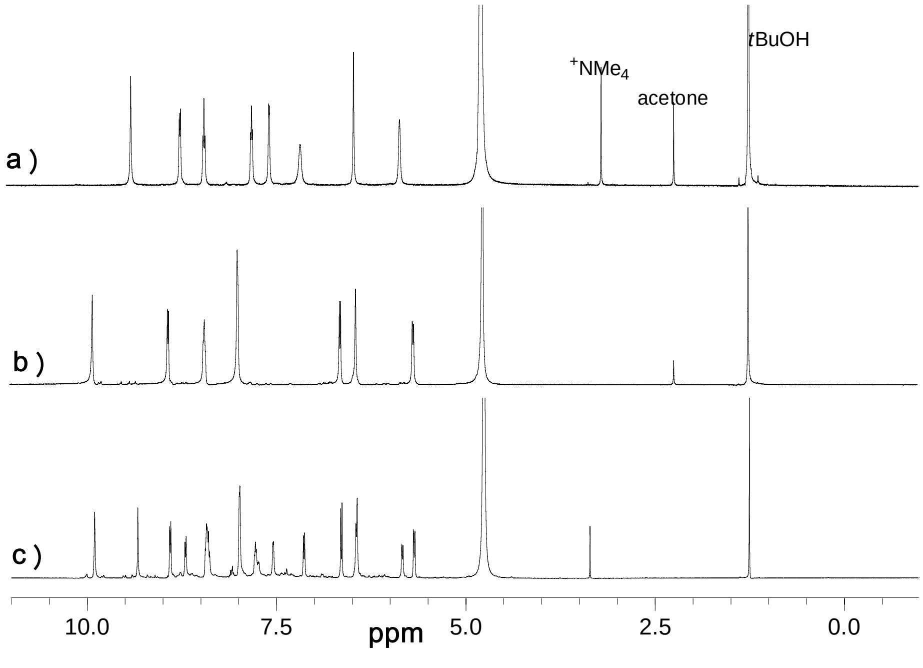
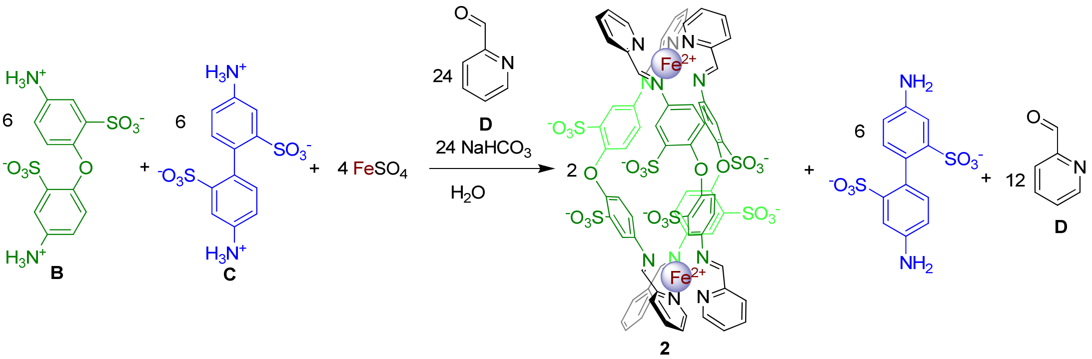


Figure S5. ^1H NMR spectra for the preparation of **2** and **3**: a) **3**; b) **2**; c) the mixture of **2** and **3**.

Selective preparation of 2 from a mixture of B and C when iron(II) is the limiting reagent. 4,4’-Diaminobiphenyl ether-2,2’-disulfonic acid **B** (4.5 mg, 80%, balance water, 10.0 µmol), 4,4’-diaminobiphenyl-2,2’-disulfonic acid **C** (4.6 mg, 75%, balance water, 10 µmol), Sodium bicarbonate (3.4 mg, 40 µmol), $FeSO_4$ (1.9 mg, 6.67 µmol), 2-formyl pyridine (4.3 mg, 40 µmol) were dissolved in D_2O (0.5 mL) in a Teflon-capped NMR tube, then the solution was degassed with three vacuum / N_2 cycles. The sealed tube was heated in an oil bath to 323 K for 8 h and reaction progress was monitored by NMR (Figure S6).



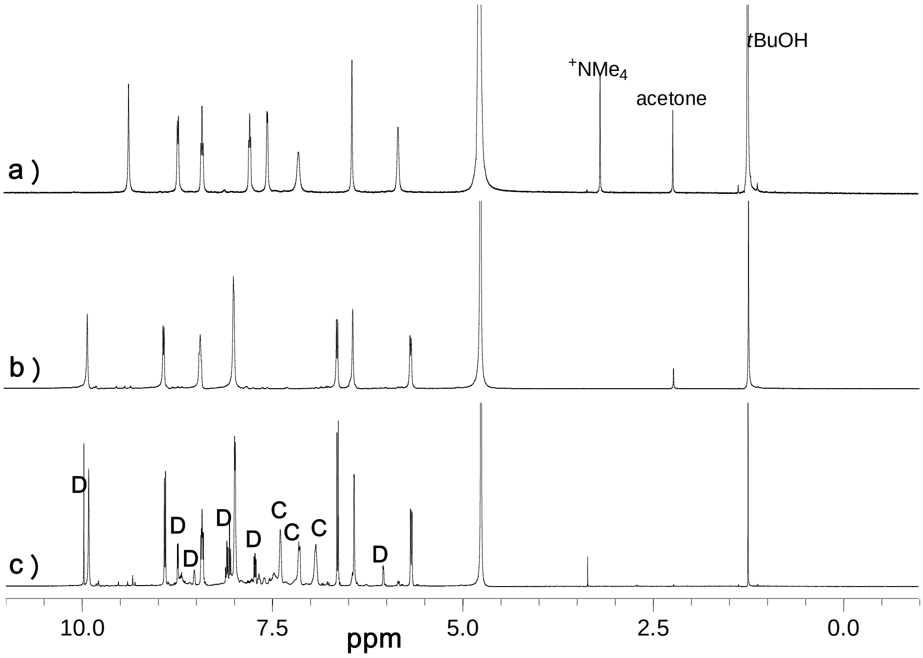


Figure S6. ^{1}H NMR spectra for the selective preparation of **2** from a mixture of **B** and **C**: a) **3** b) **2**; c) **2** in presence of **C** and excess 2-formyl pyridine **D**.

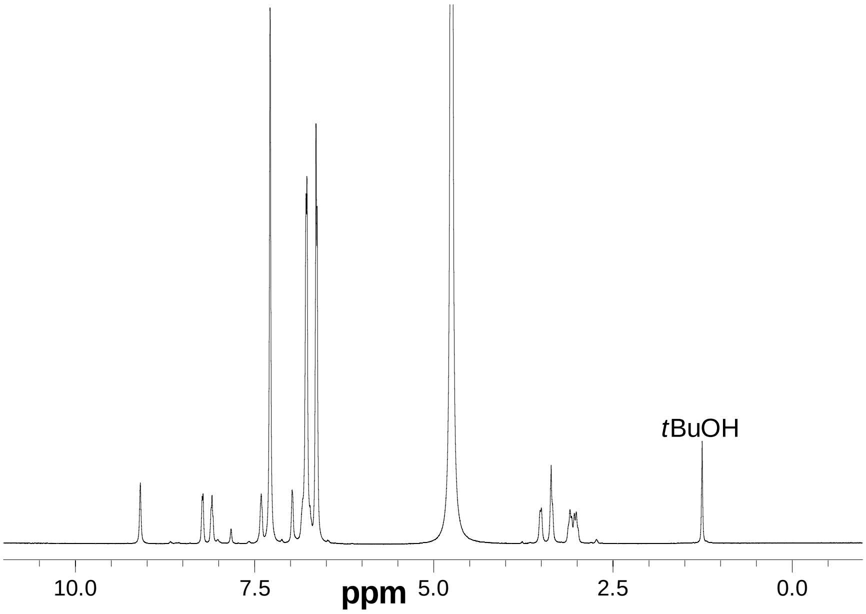


Figure S7. Unchanged ^{1}H NMR spectrum of **1** (10.0 μmol) in D_2O (0.5 mL) solution with **B** (45 mg, 80%, balance water, 100.0 μmol, 10.0 equiv) and $NaHCO_3$ (18.5 mg, 220 μmol) following 32 h at 323 K.

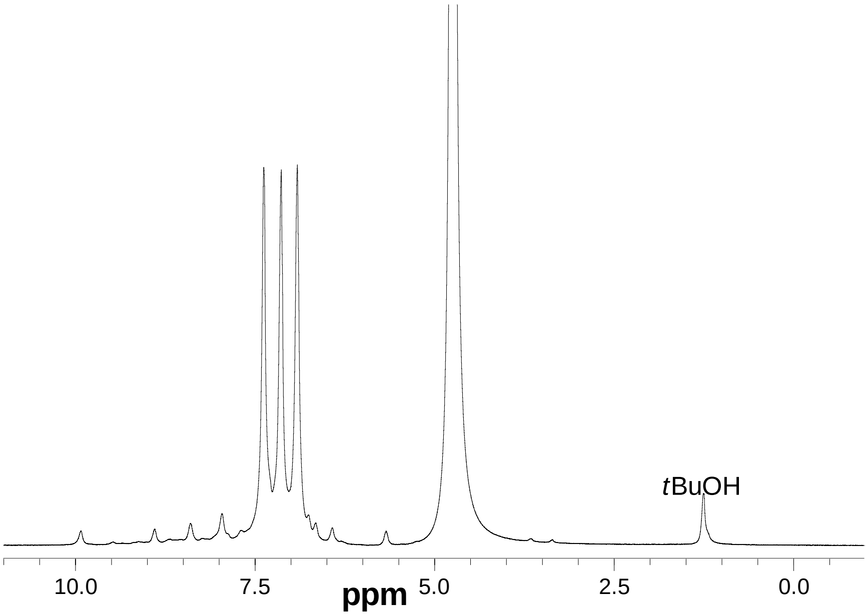


Figure S8. Unchanged ^{1}H NMR spectrum of **2** (10.0 μmol) in D_2O (0.5 mL) solution with **C** (46 mg, 75%, balance water, 100.0 μmol, 10.0 equiv) and $NaHCO_3$ (18.5 mg, 220 μmol) following 32 h at 323 K.