# An Extended Cavitand with an Introverted Carboxylic Acid

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## Supporting Information

## 1. General Information

Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. Commercially available guests were obtained from Aldrich Chemical Company, St. Louis, MO and were used as received. $^1$H, and $^{13}$C were recorded on a Bruker DRX-600 spectrometer with a 5mm QNP probe. Proton ($^1$H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ = 0), and referenced internally with respect to the monoprotio solvent impurity. Molecular modeling (semi-empirical calculations) was carried out using the PM3 force field as implemented by Spartan. Anhydrous solvents were purified by passing through a commercial solvent drying system (SG Water, Inc., Andover, NH).

## 2. Synthesis

Compounds **1**[1] and Kemp's triacid anhydride acid chloride[2] were prepared according to literature procedures.

**Diamino compound 2:** 500 mg (0.25 mmol) of dinitro compound **1** was dissolved in 40 mL of THF. To the solution was added 1 g of Raney nickel that was prewashed with THF. The mixture was placed in a hydrogenation bomb and charged with 1200 psi of $H_2$. After stirring at room temperature for 24 hours, the solvent was evaporated under reduced pressure. The diamine was used for the next reaction without further purification. $^1$H

NMR (600 MHz, acetone-$d_6$) δ 9.43 (s, 2H), 9.14 (s, 2H), 8.68 (s, 2H), 7.82 (br, 4H), 7.70 (s, 2H), 7.65 (s, 2H), 7.42 (s, 2H), 7.10 (s, 2H), 5.75 (br, 2H), 4,86 (br, 2H), 4.30 (t, 3H), 4,26 (t, 1H), 1.99 ~ 2.54 (br, 28H), 0.85~1.62 (br, 94H). ;

**Extended introverted acid 3:** A tube was charged with **2** (450 mg, 0.24 mmol, 1.0 eq) and Kemp's triacid chloride anhydride (75 mg, 0.29 mmol, 1.2 eq) in *p*-xylene (6 mL) and $Et_3N$ (0.10 mL, 0.72 mmol, 3.0 eq). After flushing with argon it was sealed. On stirring for 30 min at room temperature, the tube was immersed in an oil bath pre-heated to 135 °C. After overnight stirring, the tube was cooled to ambient temperature. The reaction mixture was filtered through a pad of cotton, and concentrated in vacuum to give brown solid material. The residue was dissolved in $CH_2Cl_2$ (40 mL) and to this solution was added 1 N HCl aq (10 mL). The mixture was transferred into a separatory funnel, and the organic phase was washed with 1 N HCl aq. (10 mL), dried over $Na_2SO_4$, filtered, and concentrated in vacuum to give brown crude solid (445 mg). Purification by column chromatography (100 g silica gel, $CH_2Cl_2$/EtOAc=1/0~4/1~1/1) afforded **3** (200 mg, 0.095 mmol, 40%) as an off-white powder, melting point (mp), >200°C (decomposition).

$\delta_H$ (600 MHz, $CDCl_3$) 9.71 (s, 1H), 9.06 (s, 1H), 8.87 (s, 1H), 8.62 (s, 1H), 8.16 (s, 1H), 7.89 (s, 1H), 7.78 (s, 2H), 7.74 (s, 2H), 7.66 (s, 1H), 7.55 (s, 1H), 7.42 (s, 1H), 7.33 (d, *J* 10.5,2 H), 7.20 (m, 8 H), 7.16 (s, 2H), 5.75 (t, *J* = 9, 1H), 5.70 (t, *J* = 9, 1H), 5.66 (t, *J* = 9, 1H), 5.59 (t, *J* = 9, 1H), 2.78 (d, *J* = 14, 1H), 2.72 (d, *J* = 14, 1H), 2.35 (m, 20H), 2.00 (m, 2H), 1.61 (s, 3H), 1.49 – 1.19 (m, 90H), 1.07 (m, 6H), 1.00 (t, *J* = 7, 3H), 0.97 (t, *J* = 7, 3H), 0.90 (t, *J* = 7, 3H).

$\delta_C$ (151 MHz, $CDCl_3$) 176.49, 176.48, 176.21, 175.01, 174.61, 174.26, 173.98, 173.63, 172.94, 163.59, 157.67, 156.23, 156.00, 155.38, 155.31, 154.87, 153.28, 153.20, 153.04, 152.99, 151.87, 151.53, 150.89, 150.07, 145.65, 138.61, 138.49, 136.89, 136.64, 136.40, 136.36, 136.25, 136.11, 136.01, 133.54, 129.05, 128.57, 128.46, 127.63, 124.90, 124.44, 124.22, 124.09, 123.79, 123.42, 122.21, 118.95, 118.36, 118.21, 117.54, 117.29, 117.06, 113.48, 47.81, 47.15, 44.97, 43.57, 42.85, 42.35, 37.06, 36.07, 34.76, 34.55, 34.43, 34.21, 34.17, 33.79, 32.82, 32.49, 32.08, 31.49, 31.35, 30.9- 30.29(many peaks are overlapped), 28.9- 28.8 (many peaks are overlapped), 26.54, 25.69, 23.57, 15.00, 10.97, 10.77, 10.48, 10.13. HRMS (ESI, *m/z*, $MH^+$) Calcd For C128H164N10O17: 2114.2348. Found: 2114.2381.

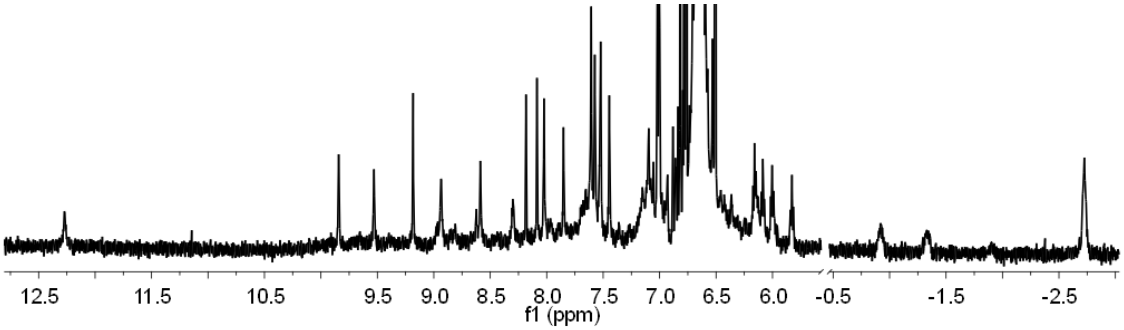

**Figure S1**. $^1$H NMR spectrum (600 MHz) of extended introverted acid **3** in mesitylene-$d_{12}$ at 300 K.

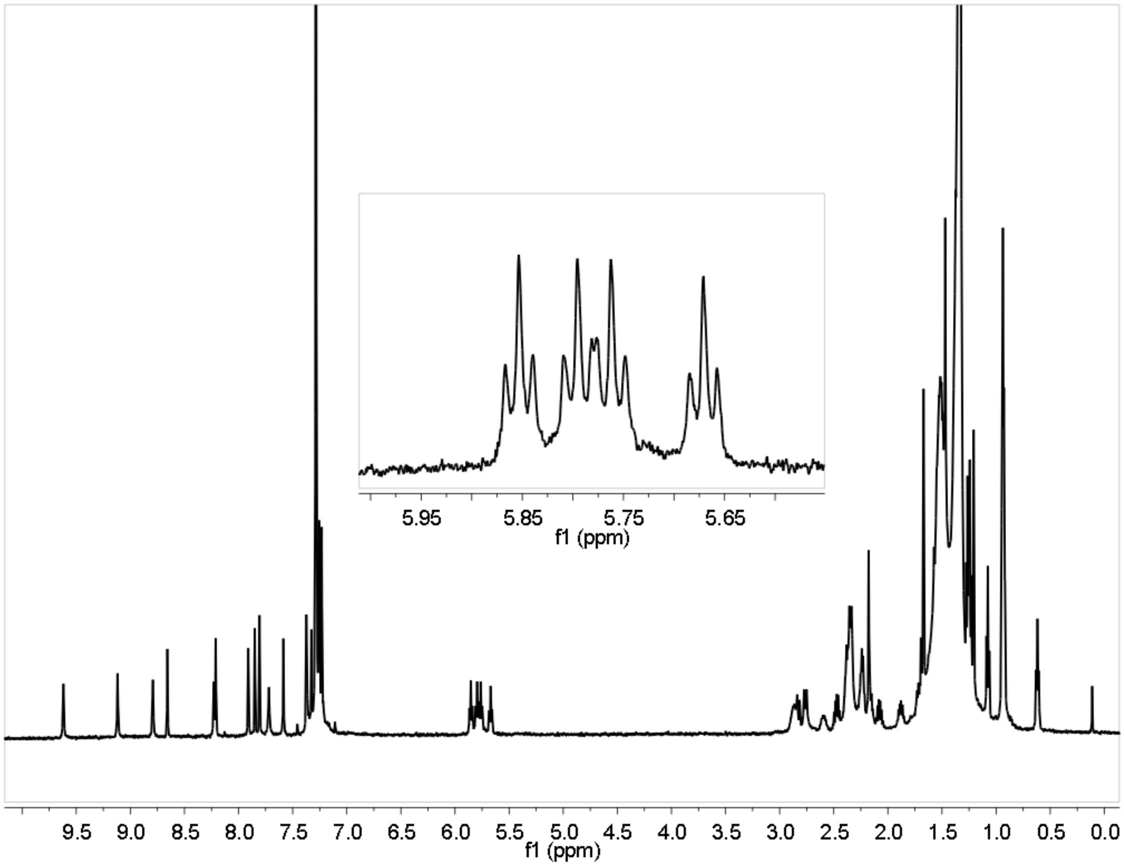

**Figure S2**. $^1$H NMR spectrum (600 MHz) of extended introverted acid **3** in $CDCl_3$ at 300 K.

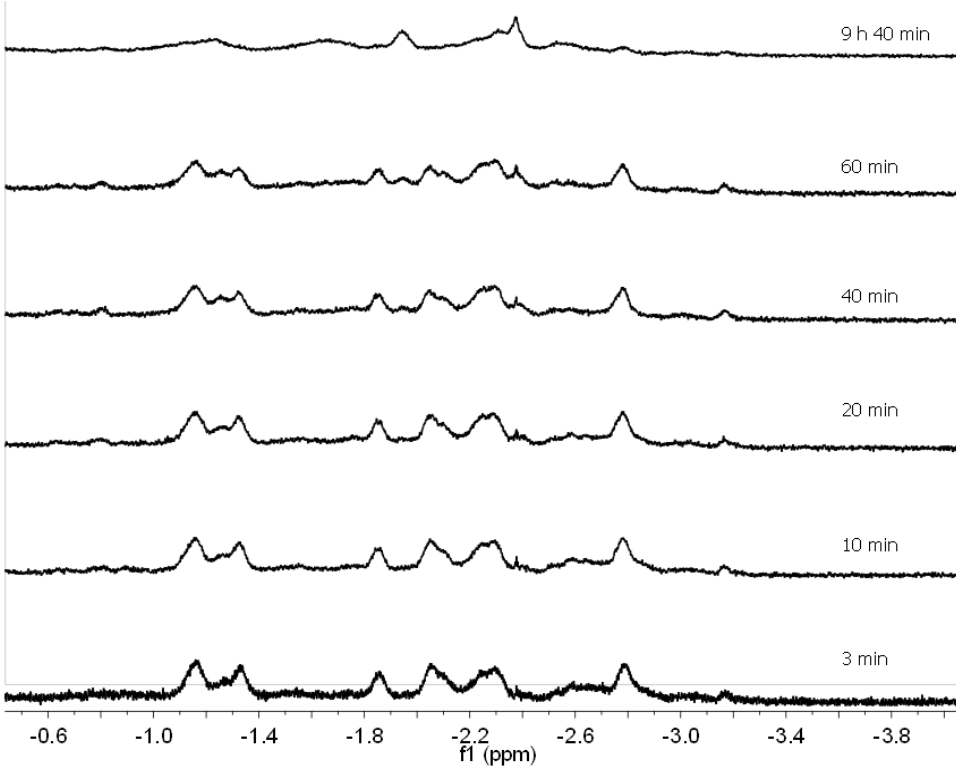

**Figure S3**. $^1$H NMR (600 MHz, mesitylene-$d_{12}$, 300 K) spectra of extended introverted acid **3** and cyclohexylisocyanide.

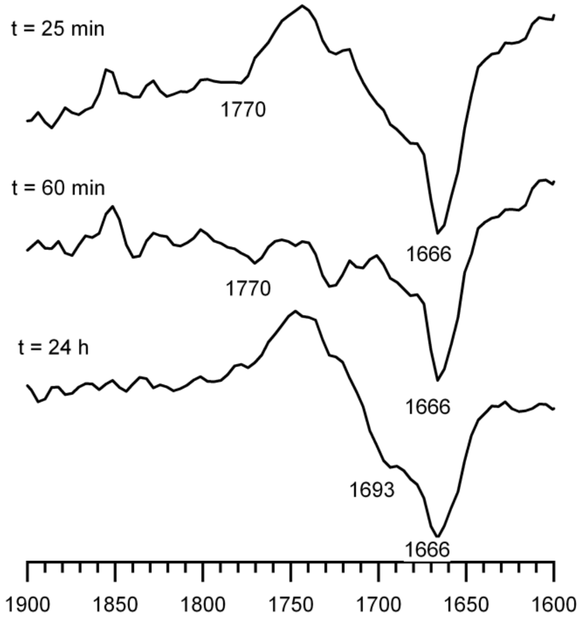

**Figure S4**. IR spectrum of extended introverted acid **3** and cyclohexylisocyanide.

1 S. Xiao, D. Ajami, and J. Rebek, Jr., *J. Org. Chemistry*, 2009, **11**, 3163.

2 Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Parris, K.; Williams, K.; Rebek, J., Jr., *J. Am. Chem. Soc.* 1989**, 111**, 1082-90.