

## Supplementary Information

### Size matters—strong binding of the terephthalate dianion by thiourea functionalised fused $[n]$ polynorbornane hosts

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#### Experimental

**General:** NMR spectra were collected on either a JEOL EX 270 MHz FT-NMR spectrometer (Tokyo, Japan), or a JEOL EX 400 MHz FT-NMR spectrometer (Tokyo, Japan) where indicated. UV-Vis spectra were measured using a Varian Cary Eclipse 300 Bio, UV-Visible spectrophotometer. HRMS was performed with an Agilent 6210 LC/MSD TOF instrument using CH<sub>3</sub>CN as the mobile phase. Melting points were determined on a digital Electrothermal® 9200 (UK) heated-block melting point apparatus and are uncorrected. Microanalysis was performed by Chemical and Microanalytical Services Pty Ltd, Belmont, Geelong, 3216. TLC was performed using Merck 60 F254 aluminium backed silica plates. Visualisation employed a UVP Mineralight 254 NM UV lamp or an oxidising dip containing KMnO<sub>4</sub> (1.0 g), K<sub>2</sub>CO<sub>3</sub> (1.0 g) and H<sub>2</sub>O (100 mL). Flash chromatography was performed using Merck Kieselgel 60 (70–230 mesh). General reagents were analytical grade and used as supplied unless otherwise stated. Peptide coupling agents and isothiocyanates were supplied by Aldrich Chemical Co.

#### Syntheses:

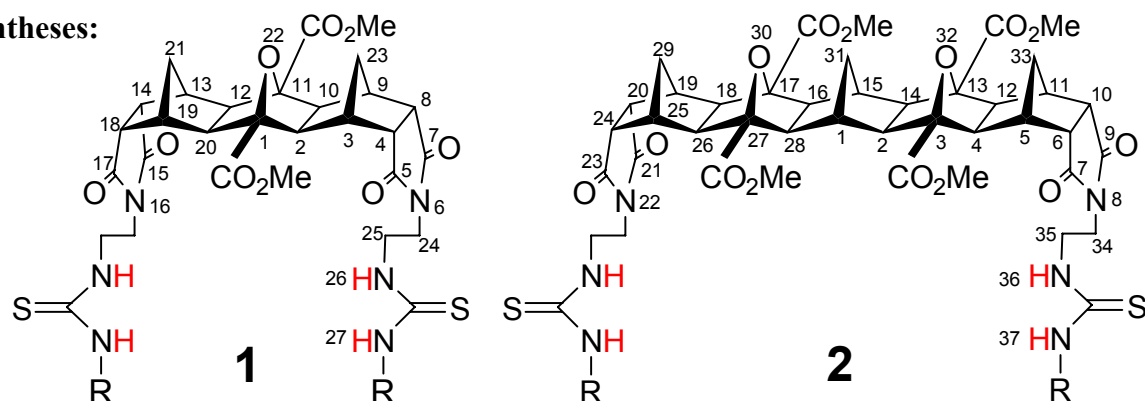


Fig. 1 Numbering system for [3] and [5] polynorbornane frameworks

#### *endo*-norborn-5-ene-2,3-anhydride 3

Freshly distilled cyclopentadiene (11.6 ml, 0.220 mol) was gradually added to an ice cold solution of maleic anhydride (21.614 g, 0.220 mol) in 1:1 ethyl acetate/petroleum spirits (160 ml). This mixture was stirred on ice until a white precipitate formed (1/2 h), the solution was

then heated (~ 80 °C) to dissolve the crude product, then left to recrystallise overnight. The recrystallised product was filtered and washed with petroleum spirits (~ 20 ml) to yield the desired compound (29.284 g, 81.1 %) as a white crystalline solid; mp 153.8–155.4 °C;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>; TMS) 1.55 (1H, d,  $J$  = 9.2 Hz, CH<sub>2</sub>), 1.76 (1H, d,  $J$  = 8.9 Hz, CH<sub>2</sub>), 3.49 (2H, s, CHCH<sub>2</sub>), 3.57 (2H, s, CHCHCH<sub>2</sub>) and 6.29 (2H, s, CH=CH);  $\delta_{\text{C}}$ (270 MHz; CDCl<sub>3</sub>; TMS) 46.19, 47.15, 52.83, 135.61 and 171.35;  $m/z$  (HRMS) 165.0539 ([M + H]<sup>+</sup>. C<sub>9</sub>H<sub>9</sub>O<sub>3</sub> requires 165.0552).

### **2-(*tert*-butoxycarbonylamino)ethylamine<sup>15</sup>**

A solution of di-*tert*-butyldicarbonate (5.154 g, 23.62 mmol) in 1,4-dioxane (5 ml) was prepared and added dropwise over thirty minutes to a solution of ethylene diamine (5.0 ml, 74.6 mmol) in 1,4-dioxane (45 ml). This reaction mixture was then allowed to stir at room temperature for 4 hours during which a white precipitate formed. The suspension was filtered and the filtrate concentrated under reduced pressure to afford (3.675 g, 97.1 %) a clear oil;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>; TMS) 1.35 (9 H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.69 (2 H, q,  $J$  5.5, CH<sub>2</sub>NH<sub>2</sub>), 3.08 (2 H, q,  $J$  5.8, CH<sub>2</sub>NH) and 5.12 (1 H, br s, NH);  $\delta_{\text{C}}$ (270 MHz; CDCl<sub>3</sub>; TMS) 28.42, 41.89, 43.43, 44.85 and 156.30;  $m/z$  (HRMS) 161.1155 ([M + H]<sup>+</sup>. C<sub>7</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> requires 161.1290).

### **(1 $\alpha$ ,2 $\alpha$ ,6 $\alpha$ ,7 $\alpha$ )-4-(2'-*tert*-Butoxycarbonylaminoethyl)-4-azatricyclo[5.2.1.0<sup>2,6</sup>]deca-8-ene-3,5-dione 4**

Both *endo*-norborn-5-ene-2,3-anhydride **3** (3.591 g, 21.87 mmol) and 2-(*tert*-butoxycarbonylamino)ethylamine (3.501 g, 21.85 mmol) were added to a pressure vessel containing a stirrer bar and CHCl<sub>3</sub> (10 ml). Following heating at 120 °C for 12 h, the crude solution was allowed to cool, whereupon TLC analysis indicated the formation of two new products. The major product was isolated using flash chromatography (50 % ethyl acetate/petroleum spirits, R<sub>f</sub> = 0.57) to yield the desired compound (5.416 g, 80.9 %) as a white crystalline solid; mp 125.2–127.5 °C;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>; TMS) 1.40 (9H, s, <sup>t</sup>Bu), 1.52 (1H, d,  $J$  = 8.8 Hz, CHCH<sub>2</sub>), 1.71 (1H, d,  $J$  = 9.0 Hz, CHCH<sub>2</sub>), 3.21 (2H, m, NHCH<sub>2</sub>), 3.24 (2H, s, CH<sub>2</sub>CH), 3.36 (2H, s, CH<sub>2</sub>CHCH), 3.47 (2H, m, NCH<sub>2</sub>), 4.65 (1H, br s, NH) and 6.08 (2H, s, CH=CH);  $\delta_{\text{C}}$ (400 MHz; CDCl<sub>3</sub>; TMS) 28.43, 37.86, 39.04, 44.99, 45.88, 52.28, 79.89, 134.55, 155.78 and 177.91;  $m/z$  (HRMS) 307.1569 ([M + H]<sup>+</sup>. C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub> requires 307.1658).

### **Dimethyl (1 $\alpha$ ,2 $\alpha$ ,6 $\alpha$ ,7 $\alpha$ ,8 $\beta$ ,11 $\beta$ )-4-(2'-*tert*-butoxycarbonylaminoethyl)-4-azatetracyclo[5.4.1.0<sup>2,6</sup>.0<sup>8,11</sup>]dodeca-9-ene-3,5-dione-9,10-dicarboxylate**

Freshly distilled dimethyl acetylenedicarboxylate (2.5 ml, 20 mmol) was added to a pressure vessel containing **4** (5.000 g, 16.33 mmol) and carbonyldihydridotris(triphenylphosphine) ruthenium(II) catalyst (400 mg, 0.436 mmol) in dry THF (20 ml). The reaction mixture was subsequently stirred at 70 °C for 72 h before TLC analysis indicated the consumption of the majority of starting materials. Following cooling, the reaction mixture was filtered (Whatman No. 1) and the solvent removed under reduced pressure. The remaining crude black material was subject to column chromatography (50 % ethyl acetate/petroleum spirits, R<sub>f</sub> = 0.26) to yield the required compound (6.262 g, 85.54 %) as a white powder; mp 153.8–154.7 °C;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; TMS) 1.37 (9H, s, <sup>t</sup>Bu), 1.47 (2H, d,  $J$  = 11.6 Hz, CHCH<sub>2</sub>), 1.74 (2H, d,  $J$  = 11.6 Hz, CHCH<sub>2</sub>), 2.79 (2H, s, C=CCH), 2.83 (2H, s, CH<sub>2</sub>CH), 3.22 (2H, s, CH<sub>2</sub>CHCH), 3.33 (2H, m, NHCH<sub>2</sub>), 3.61 (2H, m, NCH<sub>2</sub>), 3.76 (6H, s, CH<sub>3</sub>) and 4.70 (1H, br s, NH);  $\delta_{\text{C}}$ (400 MHz; CDCl<sub>3</sub>; TMS) 27.87, 33.74, 35.47, 37.79, 38.42, 41.95, 47.03, 51.52, 79.01,

140.69, 155.76, 160.12 and 176.51;  $m/z$  (HRMS) 449.1903 ( $[M + H]^+$ ).  $C_{22}H_{29}N_2O_8$  requires 449.1924).

**Dimethyl (1 $\alpha$ ,2 $\alpha$ ,6 $\alpha$ ,7 $\alpha$ ,8 $\alpha$ ,9 $\alpha$ ,11 $\beta$ ,12 $\beta$ )-4-(2'-*tert*butoxycarbonylaminoethyl)-4-aza-10-oxapentacyclo[5.5.1.0<sup>2,6</sup>.0<sup>8,12</sup>.0<sup>9,11</sup>]tridecane-3,5-dione-9,11-dicarboxylate 5**

A nitrogen-flushed solution of dimethyl (1 $\alpha$ ,2 $\alpha$ ,6 $\alpha$ ,7 $\alpha$ ,8 $\beta$ ,11 $\beta$ )-4-(2'-*tert*-butoxycarbonyl aminoethyl)-4-azatetracyclo [5.4.1.0<sup>2,6</sup>.0<sup>8,11</sup>]dodeca-9-ene-3,5-dione-9,10-dicarboxylate (1.197 g, 2.670 mmol) in dry THF (150 ml) was cooled to 0 °C in an ice bath before *tert*-butyl hydroperoxide (1.14 M) was added (3.0 ml, 3.42 mmol) by syringe. Following rapid stirring for 10 min, potassium *tert*butoxide (80 mg, 0.71 mmol) was added in a single portion, after another 10 min of stirring the ice bath was removed and the solution allowed to stir overnight. Once complete (28 h), 10 % aqueous sodium thiosulfate solution (20 ml) was added and the mixture stirred for a further 30 min. The resultant two-phase mixture was then concentrated to approx. 1/3 of its volume and extracted with  $CHCl_3$  (3  $\times$  50 ml), the organics were combined, dried ( $MgSO_4$ ), filtered and evaporated under reduced pressure. The crude off-white solid obtained was purified by column chromatography (50 % ethyl acetate/petroleum spirits,  $R_f$  = 0.22) resulting in the desired compound (854 mg, 68.9 %) as a white solid; mp 190.8–192.2 °C;  $\delta_H$ (270 MHz;  $CDCl_3$ ; TMS) 1.39 (9H, s, <sup>t</sup>Bu), 1.72 (2H, d,  $J$  = 11.5 Hz,  $CHCH_2$ ), 2.12 (2H, d,  $J$  = 11.5 Hz,  $CHCH_2$ ), 2.37 (2H, s, CCH), 3.17 (2H, s,  $CH_2CH$ ), 3.27 (2H, m,  $NHCH_2$ ), 3.29 (2H, s,  $CH_2CHCH$ ), 3.55 (2H, m,  $NCH_2$ ), 3.79 (6H, s,  $CH_3$ ) and 4.68 (1H, br s,  $NH$ );  $\delta_C$ (400 MHz;  $CDCl_3$ ; TMS) 27.85, 34.24, 36.40, 38.56, 38.72, 45.63, 47.11, 52.47, 79.05, 141.23, 155.49, 163.31 and 176.21;  $m/z$  (HRMS) 465.1862 ( $[M + H]^+$ ).  $C_{22}H_{29}N_2O_9$  requires 465.1873).

**Dimethyl (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\alpha$ ,8 $\alpha$ ,9 $\alpha$ ,10 $\beta$ ,11 $\alpha$ ,12 $\beta$ ,13 $\alpha$ ,14 $\alpha$ ,18 $\alpha$ ,19 $\alpha$ ,20 $\beta$ )-6-16-(2',2''-di-*tert*-butoxycarbamatoethyl)-6,16-diaza-22-oxaocyclo[9.9.1<sup>1,11</sup>.1<sup>3,9</sup>.1<sup>13,19</sup>.0<sup>2,10</sup>.0<sup>4,8</sup>.0<sup>12,20</sup>.0<sup>14,18</sup>]tricosane-5,7,15,17-tetraone-1,11-dicarboxylate 6**

Epoxide **5** (400 mg, 0.862 mmol), alkene **4** (264 mg, 0.862 mmol) and  $CH_2Cl_2$  (2.0 ml) were added to a pressure vessel containing a stirrer bar. The vessel was sealed and heated at 140 °C with stirring for 24 h. The resultant crude mixture was evaporated to dryness and subject to flash chromatography using gradient elution (50–100 % ethyl acetate/petroleum spirits,  $R_f$  = 0.57, ethyl acetate) to provide the coupled product (387 mg, 58.3 %) as a white powder; mp 130.6–139.9 °C (slow decomposition);  $\delta_H$ (270 MHz; DMSO; TMS) 1.17 (2H, d,  $J$  = 9.6 Hz, H21,23), 1.36 (18H, s, <sup>t</sup>Bu), 1.92 (4H, s, H2,10,12,20), 2.29 (2H, d,  $J$  = 9.6 Hz, H21,23), 2.38 (4H, s, H3,9,13,19), 2.98 (4H, s, H4,8,14,18), 3.39 (8H, br s, H24,25), 3.80 (6H, s,  $CH_3$ ), 6.83 (2H, t,  $J$  = 6.0 Hz,  $NH$ );  $\delta_C$ (400 MHz; DMSO; TMS) 28.77, 29.55, 37.42, 37.69, 38.50, 48.10, 50.36, 53.02, 78.37, 90.15, 156.15, 168.39 and 177.34;  $m/z$  (HRMS) 771.3394 ( $[M + H]^+$ ).  $C_{38}H_{51}N_4O_{13}$  requires 771.3453).

**Dimethyl (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\alpha$ ,8 $\alpha$ ,9 $\alpha$ ,10 $\beta$ ,11 $\alpha$ ,12 $\beta$ ,13 $\alpha$ ,14 $\alpha$ ,18 $\alpha$ ,19 $\alpha$ ,20 $\beta$ )-6-16-bis((2',2''-di-(4'''fluorophenyl)thiourea)ethyl)-6,16-diaza-22-oxaocyclo[9.9.1<sup>1,11</sup>.1<sup>3,9</sup>.1<sup>13,19</sup>.0<sup>2,10</sup>.0<sup>4,8</sup>.0<sup>12,20</sup>.0<sup>14,18</sup>]tricosane-5,7,15,17-tetraone-1,11-dicarboxylate 1a**

The Boc protected framework **6** (400 mg, 0.519 mmol) was stirred in a solution of 20 % TFA/ $CH_2Cl_2$  (5.0 ml) at room temperature for 4 h. TLC indicated complete deprotection by this time, so the excess solvent and TFA were removed under reduced pressure to yield the free amine **7** as an off-white solid. This material was used directly in the following step;

CHCl<sub>3</sub> (3.0 ml), diisopropylethylamine (0.36 ml, 2.1 mmol), and 4-fluorophenylisothiocyanate (159 mg, 1.038 mmol) were added to the amine **7** in a round bottomed flask equipped with a stirrer bar. The subsequent reaction mixture was stirred at room temperature for 23 h before being evaporated to dryness under reduced pressure. The crude product was purified using flash chromatography (ethyl acetate, R<sub>f</sub> = 0.45) to afford **1a** as a white powder (380 mg, 83.5 %); mp > 350 °C; (Found: C, 57.3; H, 4.8; N, 9.2. C<sub>42</sub>H<sub>42</sub>F<sub>2</sub>N<sub>6</sub>O<sub>9</sub>S<sub>2</sub> requires C, 57.5; H, 4.8; N, 9.5 %); δ<sub>H</sub>(400 MHz; DMSO; TMS) 1.17 (2H, d, *J* = 9.6 Hz, H<sub>21,23</sub>), 1.92 (4H, s, H<sub>2,10,12,20</sub>), 2.29 (2H, d, *J* = 9.6 Hz, H<sub>21,23</sub>), 2.38 (4H, s, H<sub>3,9,13,19</sub>), 2.98 (4H, s, H<sub>4,8,14,18</sub>), 3.58 (8H, br s, H<sub>24,25</sub>), 3.80 (6H, s, CH<sub>3</sub>), 7.17 (4H, t, *J* = 8.8 Hz, ArCHCNH), 7.28 (4H, t, *J* = 8.8 Hz, ArCHCF), 7.66 (2H, br s, H<sub>26</sub>) and 9.49 (2H, s, H<sub>27</sub>); δ<sub>C</sub>(400 MHz; DMSO; TMS) 37.93, 38.65, 40.81, 42.31, 48.61, 50.78, 53.41, 116.34, 127.65, 135.57, 159.23, 161.64, 168.83, 177.93 and 181.72; *m/z* (HRMS) 877.2515 ([M + H]<sup>+</sup>. C<sub>42</sub>H<sub>43</sub>N<sub>6</sub>O<sub>9</sub>S<sub>2</sub>F<sub>2</sub> requires 877.2501).

**Dimethyl (1α,2β,3α,4α,8α,9α,10β,11α,12β,13α,14α,18α,19α,20β)-6-16-bis((2',2''-di-(4''''nitrophenyl)thiourea)ethyl)-6,16-diaza-22-oxaocyclo[9.9.1<sup>1,11</sup>.1<sup>3,9</sup>.1<sup>13,19</sup>.0<sup>2,10</sup>.0<sup>4,8</sup>.0<sup>12,20</sup>.0<sup>14,18</sup>]tricosane-5,7,15,17-tetraone-1,11-dicarboxylate **1b****

As for **1a**, using: Boc protected framework **6** (600 mg, 0.779 mmol), and 20 % TFA/CH<sub>2</sub>Cl<sub>2</sub> (6.0 ml) for deprotection, followed by diisopropylethylamine (0.54 ml, 3.1 mmol) and 4-nitrophenylisothiocyanate (281 mg, 1.56 mmol) in CHCl<sub>3</sub> (4.0 ml) to afford **1b** as a yellow crystalline solid (0.492 mg, 67.8 %) following chromatographic purification (ethyl acetate, R<sub>f</sub> = 0.46); mp > 204.8 °C (slow decomposition with evolution of gas bubbles); δ<sub>H</sub>(400 MHz; DMSO; TMS) 1.17 (2H, d, *J* = 9.8 Hz, H<sub>21,23</sub>), 1.95 (4H, s, H<sub>2,10,12,20</sub>), 2.29 (2H, d, *J* = 9.6 Hz, H<sub>21,23</sub>), 2.38 (4H, s, H<sub>3,9,13,19</sub>), 3.01 (4H, s, H<sub>4,8,14,18</sub>), 3.64 (8H, br s, H<sub>24,25</sub>), 3.80 (6H, s, CH<sub>3</sub>), 7.71 (4H, d, *J* = 9.0 Hz, ArCHCNH), 8.15 (4H, d, *J* = 8.6 Hz, ArCHCNO<sub>2</sub>), 8.29 (2H, br s, H<sub>26</sub>) and 10.20 (2H, s, H<sub>27</sub>); δ<sub>C</sub>(400 MHz; DMSO; TMS) 37.50, 37.75, 40.81, 41.75, 48.21, 50.33, 53.03, 90.19, 121.58, 125.05, 142.59, 146.41, 168.44, 177.53 and 181.02; *m/z* (HRMS) 931.2380 ([M + H]<sup>+</sup> C<sub>42</sub>H<sub>43</sub>N<sub>8</sub>O<sub>13</sub>S<sub>2</sub> requires 931.2391).

**Tetramethyl tetracyclo[4.4.1.0<sup>2,5</sup>.0<sup>7,10</sup>]undeca-3,8-diene-3,4,8,9-tetracarboxylate**

In a similar fashion to the synthesis of the alkene diester above, freshly distilled dimethyl acetylenedicarboxylate (3.0 ml, 24 mmol) was added to a pressure vessel containing a stirrer bar, norborna-2,5-diene (1.047 g, 11.36 mmol), carbonyldihydridotris(triphenylphosphine) ruthenium(II) catalyst (0.999 g, 1.088 mmol) and dry THF (5 ml). The reaction vessel was wrapped in foil to exclude light, then the mixture stirred at 70 °C for 24 h before TLC analysis indicated the formation of a new product. Following cooling, the reaction mixture was filtered (Whatman No. 1) and the solvent removed under reduced pressure. The remaining crude black material was subject to column chromatography (25 % ethyl acetate/petroleum spirits, R<sub>f</sub> = 0.28) to yield the required compound (1.430 g, 33.43 %) as a white powder; mp 141.1–142.8 °C; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>; TMS) 1.34 (2H, s, CH<sub>2</sub>), 2.39 (2H, s, CH<sub>2</sub>CH); 2.73 (4H, s, CH<sub>2</sub>CHCH) and 3.75 (12H, s, CH<sub>3</sub>); δ<sub>C</sub>(400 MHz; CDCl<sub>3</sub>; TMS) 23.65, 31.77, 46.12, 52.01, 142.46 and 161.27; *m/z* (HRMS) 377.0967 ([M + H]<sup>+</sup>. C<sub>19</sub>H<sub>21</sub>O<sub>8</sub> requires 377.1236).

**Tetramethyl 4,10-dioxahexacyclo[5.5.1.0<sup>2,6</sup>.0<sup>3,5</sup>.0<sup>8,12</sup>.0<sup>9,11</sup>]tridecane-3,5,9,11-tetracarboxylate 8**

The method employed was analogous to that for epoxide **5** using: tetramethyl tetracyclo[4.4.1.0<sup>2,5</sup>.0<sup>7,10</sup>]undeca-3,8-diene-3,4,8,9-tetracarboxylate (1.500 g, 3.986 mmol), *tert*-butyl hydroperoxide (1.14 M, 7.7 ml, 8.8 mmol), potassium *tert*butoxide (224 mg, 2.00 mmol) and dry THF (200 ml). After 15 h, 10 % aqueous sodium thiosulfate solution (20 ml) was added and the mixture stirred for a further 30 min. The resultant two-phase mixture was then concentrated to approx. 1/3 of its volume and extracted with CHCl<sub>3</sub> (4 × 40 ml), the organics were combined, dried (MgSO<sub>4</sub>), filtered and evaporated under reduced pressure. The crude off-white solid obtained was purified by recrystallisation (25 % ethyl acetate/petroleum spirits, R<sub>f</sub> = 0.44) resulting in the desired compound (884 mg, 54.3 %) as a white powder; mp 191.2–194.9 °C; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>; TMS) 1.89 (2H, s, CH<sub>2</sub>), 2.25 (4H, s, CH<sub>2</sub>CHCH), 3.28 (2H, s, CH<sub>2</sub>CH) and 3.81 (12H, s, CH<sub>3</sub>); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; TMS) 28.60, 36.53, 48.92, 52.92, 64.41 and 164.32; *m/z* (HRMS) 409.1074 ([M + H]<sup>+</sup>. C<sub>19</sub>H<sub>21</sub>O<sub>10</sub> requires 409.1135).

**Tetramethyl (1α,2β,3α,4β,5α,6α,10α,11α,12β,13α,14β,15α,16β,17α,18β,19α,20α,24α,25α,26β,27α,28β)-8,22-(2',2''-di-*tert*-butoxycarbamatoethyl)-8,22-diaza-30,32-dioxadodecacyclo[13.13.1<sup>1,15</sup>.1<sup>3,13</sup>.1<sup>5,11</sup>.1<sup>17,27</sup>.1<sup>19,25</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>.0<sup>16,28</sup>.0<sup>18,26</sup>.0<sup>20,24</sup>]tritriacontane-7,9,21,23-tetraone-3,13,17,27-tetracarboxylate 9**

As for **6** using: epoxide **8** (500 mg, 1.22 mmol), alkene **4** (750 mg, 2.45 mmol) and THF (2.0 ml) at 140 °C for 41 h. The resultant crude mixture was evaporated to dryness and subject to flash chromatography (ethyl acetate, R<sub>f</sub> = 0.52) to provide the coupled product (805 mg, 64.4 %) as a white powder; mp >170 °C (slow decomposition); δ<sub>H</sub>(270 MHz; DMSO; TMS) 1.16 (2H, d, *J* = 10.4 Hz, H8), 1.46 (18H, s, <sup>t</sup>Bu), 1.75 (2H, s, H1); 1.95 (2H, s, H2), 2.01 (4H, s, H5), 2.04 (4H, s, H3), 2.49 (2H, d, *J* = 10.0 Hz, H8), 2.55 (4H, s, H6), 2.93 (4H, s, H7), 3.73 (8H, br s, H9,10), 3.79 (12H, s, CH<sub>3</sub>), 5.21 (2H, s, NH); δ<sub>C</sub>(270 MHz; CDCl<sub>3</sub>; TMS) 22.61, 29.42, 37.63, 38.09, 40.18, 40.84, 41.15, 48.37, 50.86, 52.75, 54.31, 78.46, 89.92, 156.27, 168.79 and 177.63; *m/z* (HRMS) 1021.4286 ([M + H]<sup>+</sup>. C<sub>51</sub>H<sub>65</sub>N<sub>4</sub>O<sub>18</sub> requires 1021.4294).

**Tetramethyl (1α,2β,3α,4β,5α,6α,10α,11α,12β,13α,14β,15α,16β,17α,18β,19α,20α,24α,25α,26β,27α,28β)-8,22-bis((2',2''-di(4''-fluorophenyl)thiourea)ethyl)-8,22-diaza-30,32-dioxadodecacyclo[13.13.1<sup>1,15</sup>.1<sup>3,13</sup>.1<sup>5,11</sup>.1<sup>17,27</sup>.1<sup>19,25</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>.0<sup>16,28</sup>.0<sup>18,26</sup>.0<sup>20,24</sup>]tritriacontane-7,9,21,23-tetraone-3,13,17,27-tetracarboxylate 2a**

As for **1a**, using: [5]polynorbornane framework **9** (672 mg, 0.658 mmol), and 20 % TFA/CH<sub>2</sub>Cl<sub>2</sub> (8.0 ml) for deprotection, followed by diisopropylethylamine (0.69 ml, 3.9 mmol) and 4-fluorophenylisothiocyanate (202 mg, 1.32 mmol) in CHCl<sub>3</sub> (10 ml) to afford **2a** as a white crystalline solid (0.684 mg, 92.2 %) following recrystallisation (ethyl acetate, R<sub>f</sub> = 0.38); mp > 216.3 °C (slow decomposition with evolution of gas bubbles); (Found: C, 58.1; H, 5.0; N, 7.1. C<sub>55</sub>H<sub>56</sub>F<sub>2</sub>N<sub>6</sub>O<sub>14</sub>S<sub>2</sub> requires C, 58.6; H, 5.0; N, 7.5 %); δ<sub>H</sub>(270 MHz; DMSO; TMS) 1.12 (2H, d, *J* = 9.7 Hz, H29,33), 1.56 (2H, s, H31); 1.64 (2H, s, H1,15), 1.83 (4H, s, H4,12,18,26), 1.88 (4H, s, H2,14,16,28), 2.25 (2H, d, *J* = 9.5 Hz, H29,33), 2.34 (4H, s, H5,11,19,25), 2.98 (4H, s, H6,10,20,24), 3.63 (8H, br s, H34,35), 3.76 (12H, s, CH<sub>3</sub>), 7.20 (4H, t, *J* = 8.8 Hz, ArCHCF), 7.28 (4H, t, *J* = 8.6 Hz, ArCHCNH), 7.48 (2H, br s, H36), 9.60 (2H, s, H37); δ<sub>C</sub>(400 MHz; DMSO; TMS) 29.44, 37.56, 37.99, 40.10, 40.87, 41.08, 48.28, 50.81, 52.75, 54.27, 89.88, 116.02, 127.20, 135.22, 159.65, 168.74, 177.59, and 181.34; *m/z* (HRMS) 1127.3502 ([M + H]<sup>+</sup>. C<sub>55</sub>H<sub>57</sub>N<sub>6</sub>O<sub>14</sub>S<sub>2</sub>F<sub>2</sub> requires 1127.3342).

**Tetramethyl (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,5 $\alpha$ ,6 $\alpha$ ,10 $\alpha$ ,11 $\alpha$ ,12 $\beta$ ,13 $\alpha$ ,14 $\beta$ ,15 $\alpha$ ,16 $\beta$ ,17 $\alpha$ ,18 $\beta$ ,19 $\alpha$ ,20 $\alpha$ ,24 $\alpha$ ,25 $\alpha$ ,26 $\beta$ ,27 $\alpha$ ,28 $\beta$ )-8,22-bis((2',2''-di(4'''nitrophenyl)thiourea)ethyl)-8,22-diaza-30,32-dioxadodecacyclo[13.13.1<sup>1,15</sup>.1<sup>3,13</sup>.1<sup>5,11</sup>.1<sup>17,27</sup>.1<sup>19,25</sup>.0<sup>2,14</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>.0<sup>16,28</sup>.0<sup>18,26</sup>.0<sup>20,24</sup>]tritriacontane-7,9,21,23-tetraone-3,13,17,27-tetracarboxylate **2b****

As for **1a**, using: [5]polynorbornane framework **9** (761 mg, 0.745 mmol), and 20 % TFA/CH<sub>2</sub>Cl<sub>2</sub> (10.0 ml) for deprotection, followed by diisopropylethylamine (0.78 ml, 4.5 mmol) and 4-nitrophenylisothiocyanate (269 mg, 1.49 mmol) in CHCl<sub>3</sub> (15 ml) to afford **2b** as a yellow crystalline solid (0.832 mg, 94.5 %) following chromatographic purification (ethyl acetate, R<sub>f</sub> = 0.40); mp > 224.8 °C (slow decomposition with evolution of gas bubbles);  $\delta_{\text{H}}$ (270 MHz; DMSO; TMS) 1.14 (2H, d,  $J$  = 9.7 Hz, H29,33), 1.53 (2H, s, H31); 1.64 (2H, s, H1,15), 1.84 (8H, s, H2,4,12,14,16,18,26,28), 2.23 (2H, d,  $J$  = 8.8 Hz, H29,33), 2.34 (4H, s, H5,11,19,25), 3.03 (4H, s, H6,10,20,24), 3.66 (8H, br s, H34,35), 3.73 (12H, s, CH<sub>3</sub>), 7.72 (4H, d,  $J$  = 9.2 Hz, ArCHCNH), 8.14 (2H, br s, H36), 8.23 (4H, d,  $J$  = 9.2 Hz, ArCHCNO<sub>2</sub>), 10.32 (2H, br s, H37);  $\delta_{\text{C}}$ (400 MHz; DMSO; TMS) 29.28, 37.47, 37.59, 40.09, 40.86, 43.07, 48.26, 50.91, 52.75, 54.40, 89.80, 121.54, 125.20, 142.88, 146.34, 168.61, 177.64, and 181.05;  $m/z$  (HRMS) 1181.3341 ([M + H]<sup>+</sup>. C<sub>55</sub>H<sub>57</sub>N<sub>8</sub>O<sub>18</sub>S<sub>2</sub> requires 1181.3232).

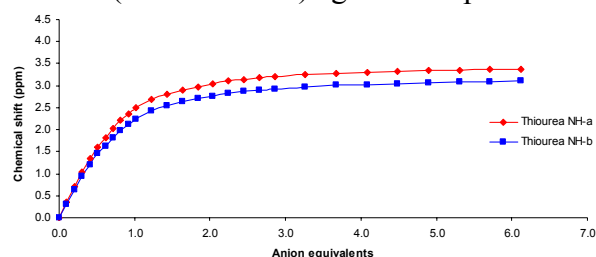
**Tetrabutylammonium terephthalate**

One equivalent of terephthalic acid (150 mg, 0.903 mmol) was stirred in two equivalents of tetrabutylammonium hydroxide in MeOH (1.0 M, 1.8 ml, 1.8 mmol) for 48 hours. Excess MeOH was then removed under reduced pressure, complete dryness was obtained by heating (70 °C) the crude white solid under vacuum for 2 days to yield (568 mg, 96.9 %) a white powder; mp 98.2–102.1 °C;  $\delta_{\text{H}}$ (400 MHz; DMSO; TMS) 0.93 (24 H, t,  $J$  6.5, CH<sub>3</sub>), 1.30 (16 H, sextet,  $J$  7.2, CH<sub>2</sub>CH<sub>3</sub>); 1.57 (16 H, q,  $J$  7.2, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 3.17 (16 H, t,  $J$  7.8, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) and 7.62 (4 H, d,  $J$  1.7, Ar-CH);  $\delta_{\text{C}}$ (400 MHz; DMSO; TMS) 14.06, 19.78, 23.65, 58.13, 128.06, 142.28 and 169.15.

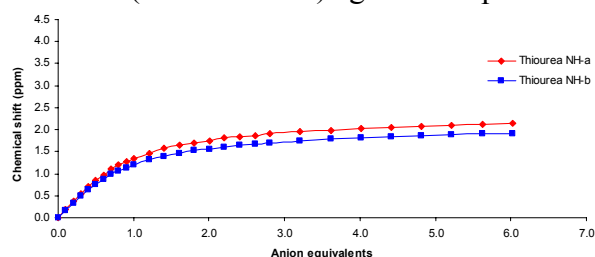
**Binding Studies:**

**<sup>1</sup>H NMR binding assays in *d*<sub>6</sub>-DMSO**

Host **1a** (1.25 × 10<sup>-2</sup> M) against terephthalate

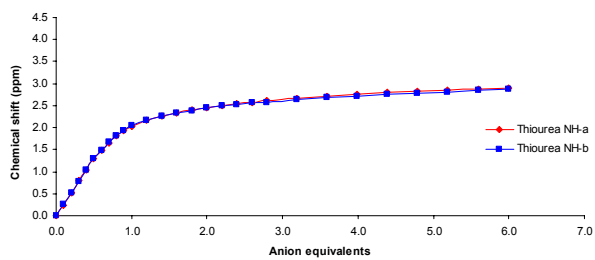
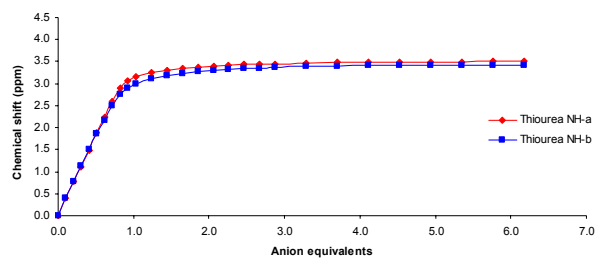


Host **1a** (1.00 × 10<sup>-3</sup> M) against terephthalate



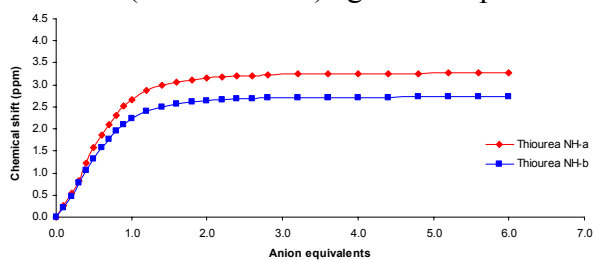
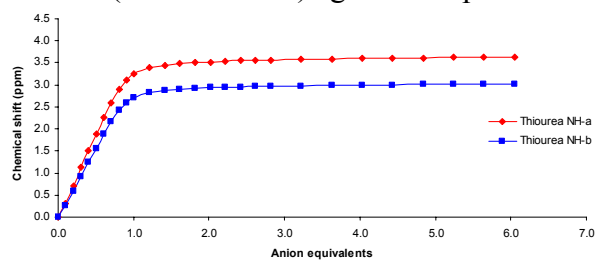
Host **1b** (1.24 × 10<sup>-2</sup> M) against terephthalate

Host **1b** (1.00 × 10<sup>-3</sup> M) against terephthalate



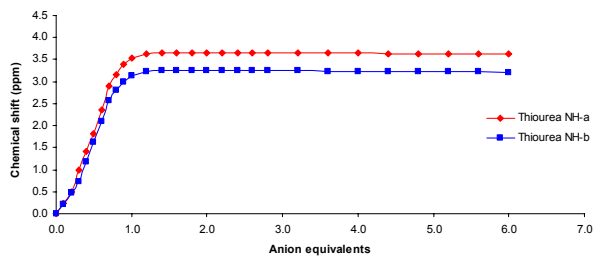
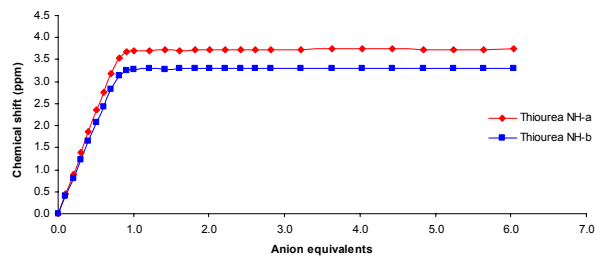
Host **2a** ( $1.26 \times 10^{-2}$  M) against terephthalate

Host **2a** ( $1.00 \times 10^{-3}$  M) against terephthalate



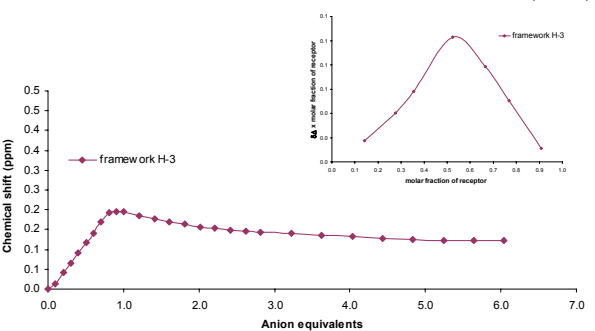
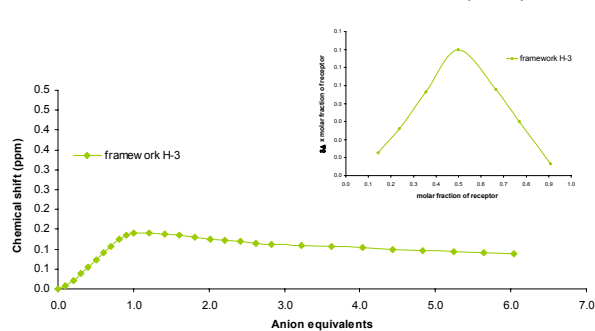
Host **2b** ( $1.26 \times 10^{-2}$  M) against terephthalate

Host **2b** ( $1.00 \times 10^{-3}$  M) against terephthalate



Framework internal-H shifts for **2a** (H-3)

Framework internal-H shifts for **2b** (H-3)

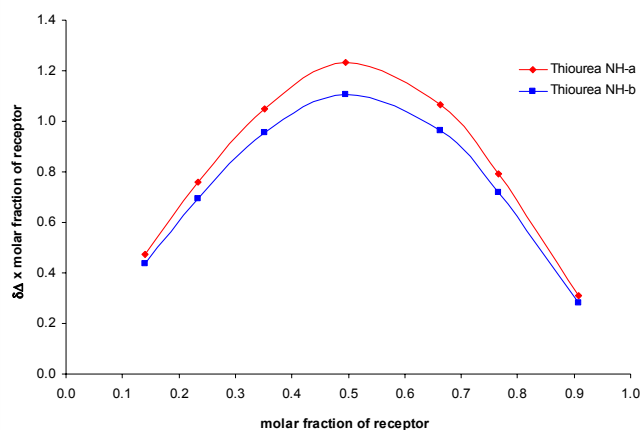
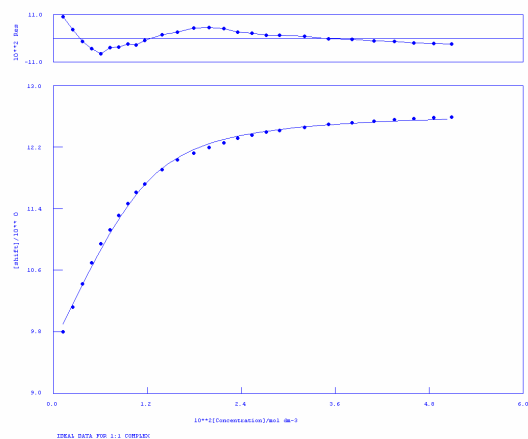


### $^1\text{H}$ NMR fit plots (WinEQNMR) and job plots

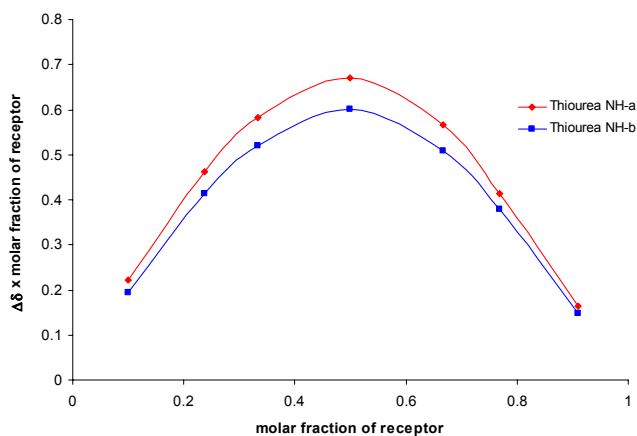
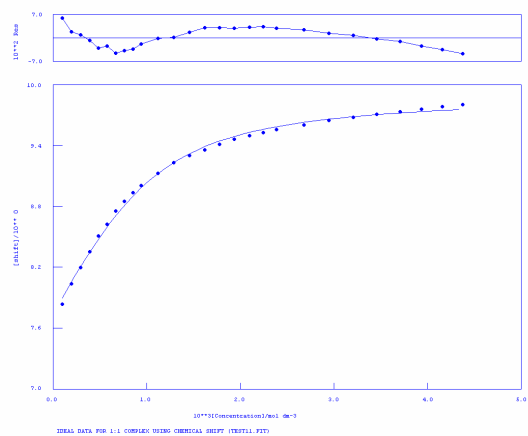
Host **1a** ( $1.25 \times 10^{-2}$  M) against terephthalate (1:1 model)

$K = 550.886$  Error = 39.09 (7.10 %)

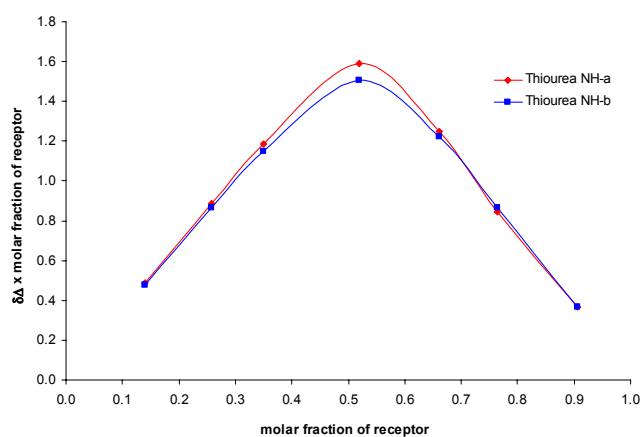
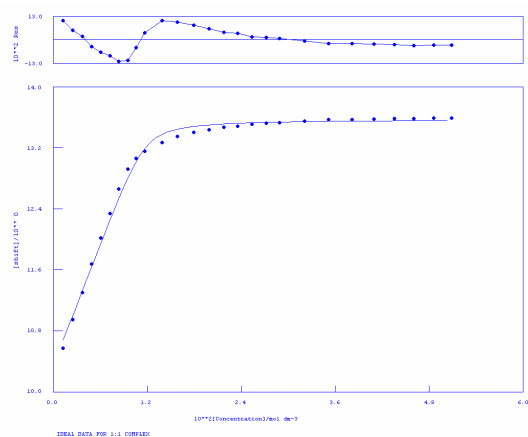
$\log K = 2.74$



Host **1a** ( $1.00 \times 10^{-3}$  M) against terephthalate (1:1 model)  
 $K = 3293.21$  Error = 211.7 (6.43 %)  
 $\log K = 3.52$

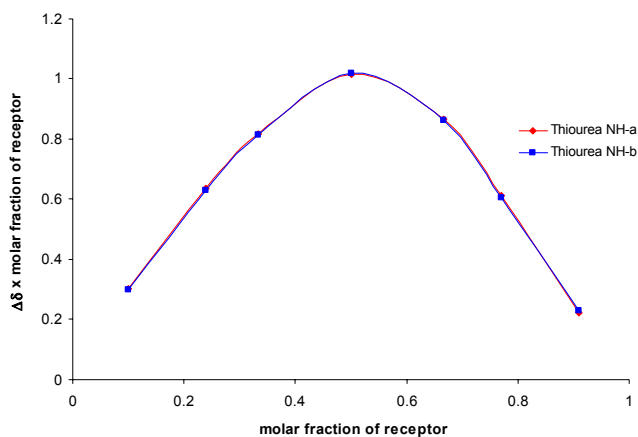
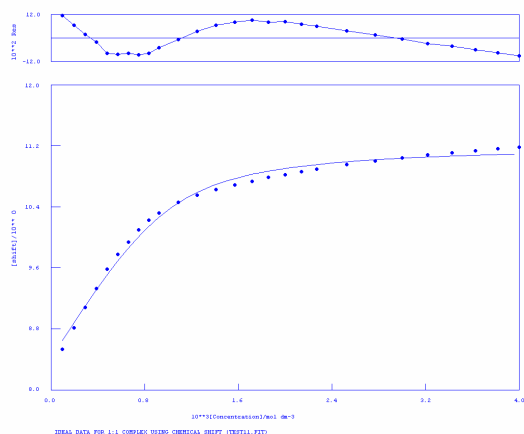


Host **1b** ( $1.24 \times 10^{-2}$  M) against terephthalate (1:1 model)  
 $K = 4514.22$  Error = 917.8 (20.3 %)  
 $\log K = 3.65$



Host **1b** ( $1.00 \times 10^{-3}$  M) against terephthalate (1:1 model)  
 $K = 6239.04$  Error = 854.1 (13.69 %)  
 $\log K = 3.80$

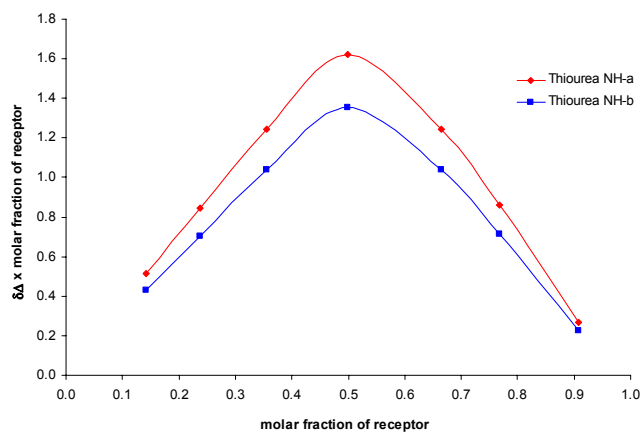
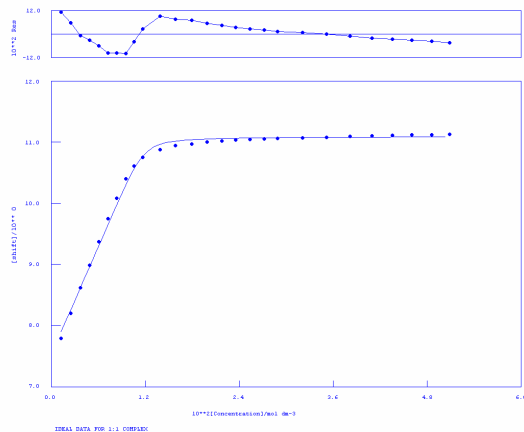




Host **2a** ( $1.26 \times 10^{-2}$  M) against terephthalate (1:1 model)

$K = 9504.11$  Error = 2756 (29.0 %)

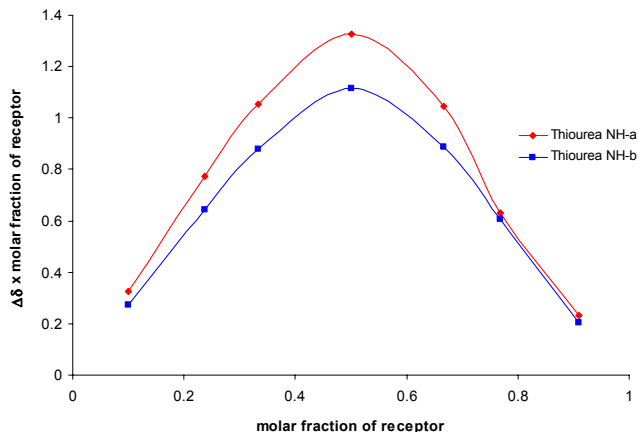
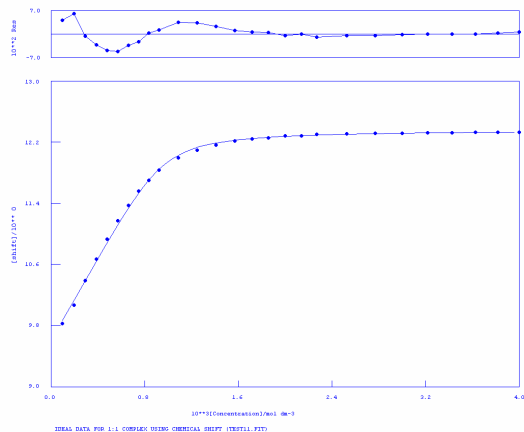
$\log K = 3.98$



Host **2a** ( $1.00 \times 10^{-3}$  M) against terephthalate (1:1 model)

$K = 25078.4$  Error = 1966 (7.84 %)

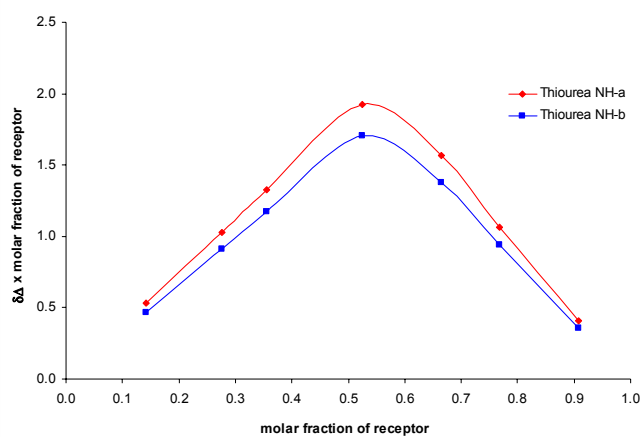
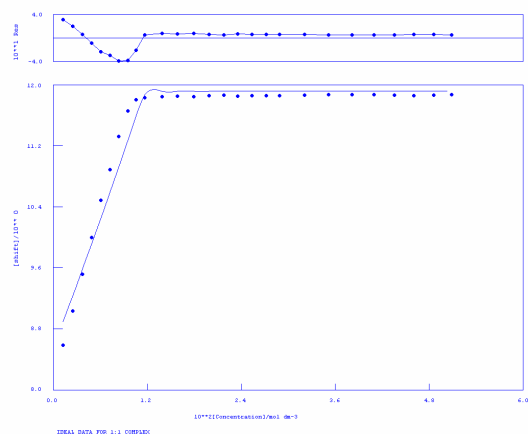
$\log K = 4.40$



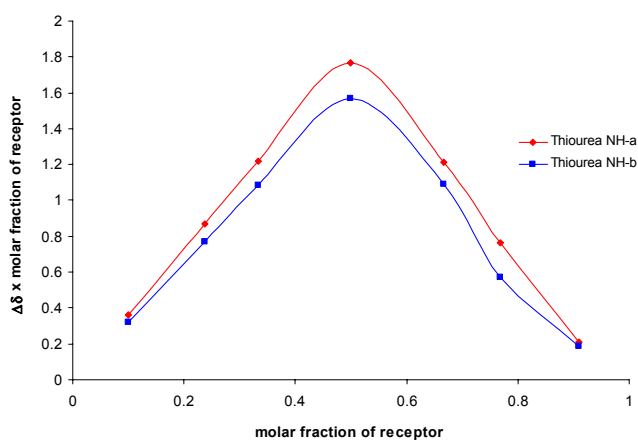
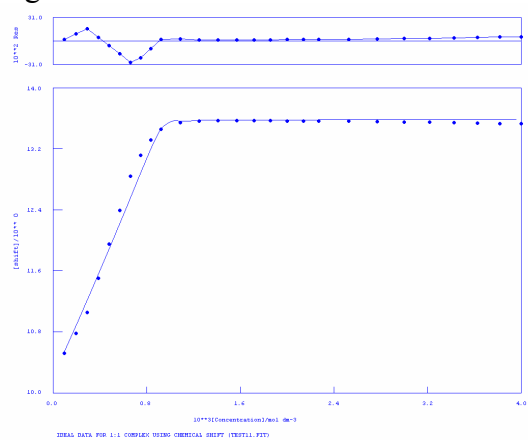
Host **2b** ( $1.26 \times 10^{-2}$  M) against terephthalate (1:1 model)

$K = 549589$  Error = 160900 (29.3 %)

$\log K = 5.74$

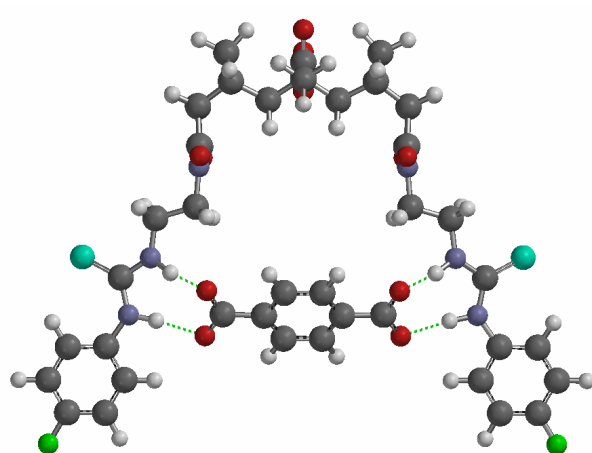


Host **2b** ( $1.00 \times 10^{-3}$  M) against terephthalate (1:1 model)  
 $K = 1042210$  Error = 84220 (8.08 %)  
 $\log K = 6.02$

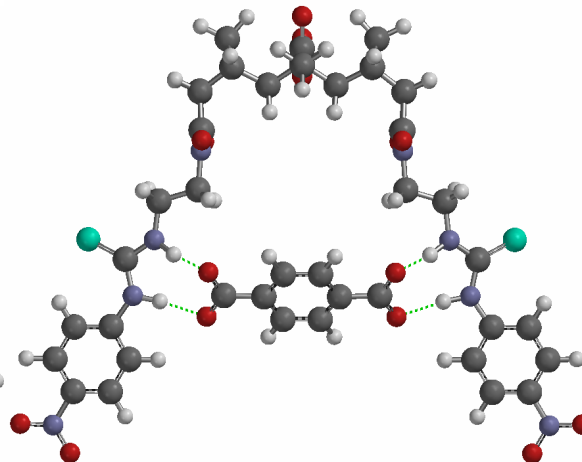


## Energy minimised molecular models

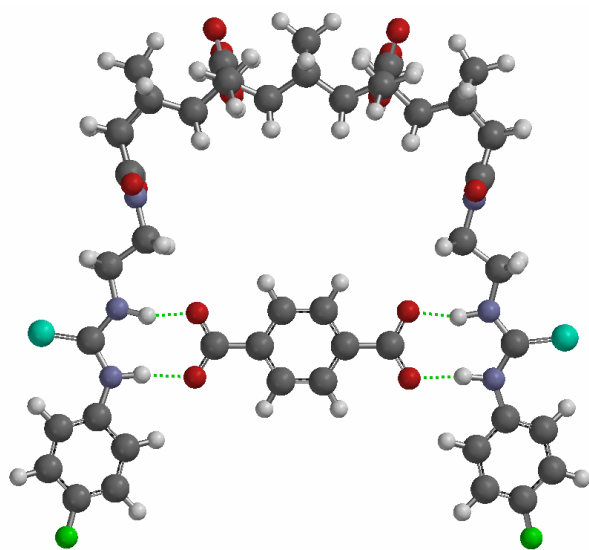
Host **1a** and terephthalate



Host **1b** and terephthalate



Host **2a** and terephthalate



Host **2b** and terephthalate

