Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Binding of the terephthalate dianion by di- tri- and tetrathiourea functionalised fused [*3*] and [*5*] polynorbornane based hosts

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Nomenclature – Von-Baeyer numbering system:

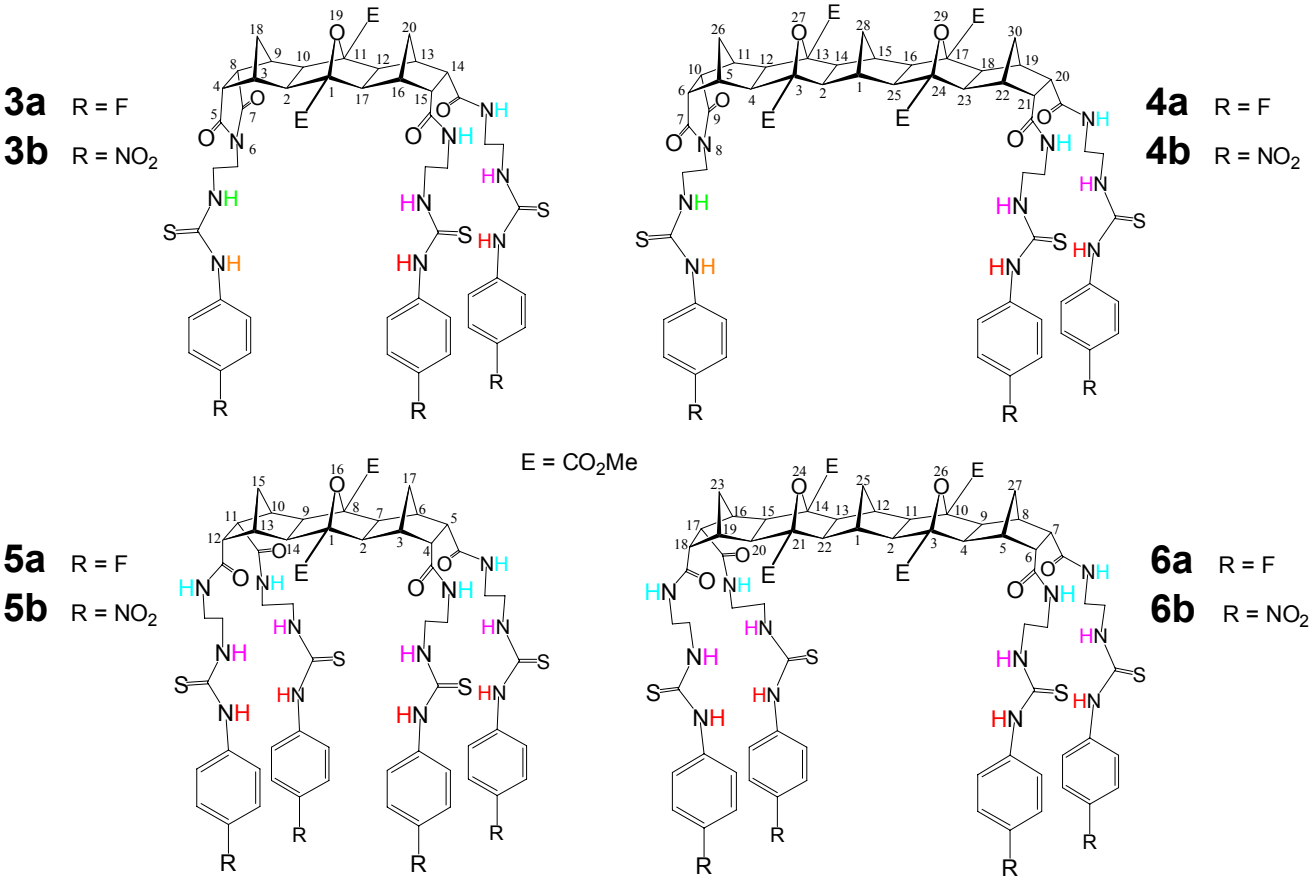

Figure S1 The numbering system employed for naming compounds **3a,b**–**6a,b**.

Specific syntheses:

Epoxide synthesis

Dimethyl (1α,2β,6β,7α) 8,9-di[(*tert*butoxycarbonylamino)ethylcarboximido] 4-oxatetracyclo [5.2.1.$0^{2,6}$.$0^{3,5}$] deca-8-ene-3,5-dicarboxylate 10

Prepared according to standard two step protocol; *Step 1*: 5,6-di[(*tert*butoxycarbonylamino) ethylcarboximido] bicyclo [2.2.1] hepta-2,5-diene **9**[12] (1.487 g, 3.201 mmol), DMAD (0.50 ml, 4.1 mmol) and $RuH_2(CO)(PPh_3)_3$ (150 mg, 0.163 mmol) in THF (10 ml) at 90 °C for 21 h to yield (1.823 g, 3.005 mmol, 94%) the cyclobutene diester as a light tan solid following chromatographic purification (EtOAc, R_f = 0.35); mp 77.8–80.2 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 1.18 (1 H, d, J = 8.8 Hz, H9), 1.37 (18 H, s, 2 × C(CH_3)$_3$) 1.52 (1 H, d, J = 9.2 Hz, H9), 2.84 (2 H, s, H2,5), 3.06 (4 H, t, J = 5.1 Hz, 2 × CH_2NHCO), 3.19 (2 H, s, H1,6), 3.20 (4 H, s, 2 × CH_2NHCOO), 3.75 (6 H, s, 2 × COOCH_3), 6.87 (2 H, s, 2 × N*H*COO) and 9.18 (2 H, s, 2 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.8, 38.0, 42.7, 45.1, 52.5, 78.2, 129.3, 132.0, 143.5, 145.9, 156.3, 161.8 and 164.1; HRMS: m/z = 607.29458 $[M + H]^+$, $C_{29}H_{43}N_4O_{10}$ requires 607.29737.

Step 2: The above diester (2.001 g, 3.297 mmol) was epoxidised with TBHP (1.14M, 3.5 ml, 4.0 mmol) and KO^{t}Bu (93 mg, 0.83 mmol) in dry THF (250 ml) for 15 h. Column chromatography (EtOAc, R_f = 0.28) afforded **10** (1.124 g, 1.805 mmol, 55%) as a white powder; mp 81.1–85.3 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 1.24 (2 H, s, H2,6), 1.36 (18 H, s, 2 × C(CH_3)$_3$), 1.59 (1 H, d, J = 9.2 Hz, H10), 1.82 (1 H, d, J = 9.9 Hz, H10), 3.05 (4 H, t, J = 5.1 Hz, 2 × CH_2NHCO), 3.16 (4 H, t, J = 5.1 Hz, , 2 × CH_2NHCOO), 3.63 (2 H, s, H1,7), 3.75 (6 H, s, 2 × COOCH_3), 6.86 (2 H, s, 2 × N*H*COO) and 9.15 (2 H, s, 2 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.8, 45.9, 49.9, 53.3, 66.2, 78.2, 129.3, 132.0, 132.7, 147.0, 156.3, 164.0, 164.3; HRMS: m/z = 623.29641 $[M + H]^+$, $C_{29}H_{43}N_4O_{11}$ requires 623.29228.

Dimethyl (1α,2β,6β,7α) 4-oxatetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]deca-8-ene-3,5-dicarboxylate 12

In this case the initial step was a [2 + 2] cycloaddition; *Step 1*: both quadricyclane (2.001 g, 21.71 mmol) and DMAD (2.6 ml, 21.17 mmol) were added neat to a pressure vessel containing a magnetic stirrer. Following heating with stirring at 100 °C for 72 h, TLC analysis indicated the formation of a single major product. The crude reaction mixture was seperated by column chromatography (10% EtOAc/Pet Sp, R_f = 0.33) to provide dimethyl (1α,2β,5β,6α) tricyclo [4.2.1.$0^{2,5}$] nona-3,7-diene-3,4-dicarboxylate **11** as a viscous clear oil in high yield (4.578 g, 19.54 mmol, 92%); δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.26 (2 H, q, J = 9.2 Hz, H9), 2.46 (2 H, s, H1,6), 2.60 (2 H, s, H2,5), 3.69 (6 H, s, 2 × COOCH_3) and 6.08 (2 H, s, H7,8); δ_C(270 MHz; $CDCl_3$; Me_4Si) 38.3, 39.6, 44.2, 51.8, 136.0, 145.1 and 161.7; HRMS: m/z = 235.09774 $[M + H]^+$, $C_{13}H_{15}O_4$ requires 235.09649.

Step 2: Diester **11** (3.202 g, 13.66 mmol) was epoxidised with TBHP (1.14M, 13.5 ml, 15.39 mmol) and KO^{t}Bu (400 mg, 3.56 mmol) in dry THF (250 ml) for 48 h. Column chromatography (10% EtOAc/Pet Sp, R_f = 0.27) gave **12** (2.322 g, 9.279 mmol, 68%) as a white crystalline solid; mp 101.2–102.9 °C; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.52 (1 H, d, J = 9.9 Hz, H10), 1.77 (1 H, d, J = 9.9 Hz, H10), 2.27 (2 H, s, H1,7), 3.22 (2 H, s, H2,6), 3.79 (6 H, s, 2 × COOCH_3) and 6.15 (2 H, s, H8,9); δ_C(270 MHz; $CDCl_3$; Me_4Si) 41.8, 49.0, 52.8, 66.8, 76.8, 137.6 and 164.9; HRMS: m/z = 251.09267 $[M + H]^+$, $C_{13}H_{15}O_5$ requires 251.09140.

Tetramethyl (1α,2β,6β,7α,8β,12β) 4,10-dioxahexacyclo [5.5.1.$0^{2,6}$.$0^{3,5}$.$0^{8,12}$.$0^{9,11}$] trideca-3,5,9,11-tetra-carboxylate 13[8a]

Prepared according to standard two step protocol; *Step 1*: the above epoxide **12** (1.124 g, 4.494 mmol), DMAD (0.70 ml, 5.7 mmol) and $RuH_2(CO)(PPh_3)_3$ (421 mg, 0.459 mmol) in THF (12 ml) at 90 °C for 21 h to yield (1.621 g, 4.134 mmol, 92%) the cyclobutene diester as an off-white powder solid following chromatographic purification (25% EtOAc/Pet Sp, R_f = 0.31); mp 144.6–149.3 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 1.44 (1 H, d, J = 9.5 Hz, H12), 1.79 (1 H, d, J = 9.9 Hz, H12), 2.32 (2 H, s, H1,7), 2.71 (2 H, s, H8,11), 3.25 (2 H, s, H2,6), 3.75 (6 H, s, 2 × COOCH_3) and 3.80 (6 H, s, 2 × COOCH_3); δ_C(270 MHz; d_6-DMSO; Me_4Si) 23.8, 28.5, 31.9, 36.4, 46.2, 48.8, 52.4, 142.7, 161.8 and 164.1; HRMS: m/z = 393.12021 $[M + H]^+$, $C_{19}H_{21}O_9$ requires 393.11856.

Step 2: The above diester (1.237 g, 3.155 mmol) was epoxidised with TBHP (1.14M, 3.3 ml, 3.8 mmol) and KO^{t}Bu (91 mg, 0.81 mmol) in dry THF (150 ml) for 18 h. Recrystallisation of the crude solid (25% EtOAc/Pet Sp, R_f = 0.44) gave **13**[8a] (734 mg, 1.80 mmol, 57%) as a white powder; mp 191.2–194.9 °C; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.89 (2 H, s, H13), 2.25 (4 H, s, H2,6,8,12); 3.28 (2 H, s, H1,7) and 3.81 (12

H, s, 4 × COOCH_3); δ_C(270 MHz; $CDCl_3$; Me_4Si) 28.6, 36.5, 48.9, 52.9, 64.4 and 164.3; HRMS: *m*/*z* = 409.10746 $[M + H]^+$, $C_{19}H_{21}O_{10}$ requires 409.11352.

ACE reaction

Dimethyl (2β,3α,4α,8α,9α,10β,12β,13α,16α,17β) 6-*tert*butoxycarbonylaminoethyl-6-aza-19-oxa-5,7-dioxo-heptacyclo[9.6.1.$1^{3,9}$.$1^{13,16}$.$0^{2,10}$.$0^{4,8}$.$0^{12,17}$]icosa-14-ene-1,11-dicarboxylate 15

Coupling of epoxide **12** (2.243 mg, 8.963 mmol) and norbornene **7**[8a] (2.715 g, 8.867 mmol) at 150 °C in THF (5 ml) for 70 h provided **15** (1.621 g, 2.912 mmol, 33%) as a white powder following column chromatography (75% EtOAc/Pet Sp, R_f = 0.37); mp 116.7–120.5 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.83 (1 H, d, *J* = 8.2 Hz, H20), 1.18 (1 H, d, *J* = 7.6 Hz, H18), 1.36 (9 H, s, C(CH_3)$_3$), 2.00 (2 H, s, H2,10), 2.16 (2 H, s, H13,16), 2.20 (1 H, d, *J* = 7.5 Hz, H20), 2.36 (1 H, d, *J* = 8.8 Hz, H18), 2.39 (2 H, s, H3,9), 2.53 (2 H, s, H12,17), 3.01 (2 H, s, H4,8), 3.03 (2 H, s, CH_2NH), 3.44 (2 H, t, *J* = 5.7 Hz, NCH_2), 3.81 (6 H, s, 2 × COOCH_3), 6.12 (2 H, s, H14,15) and 6.59 (1 H, t *J* = 5.5 Hz, N*H*); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.7, 37.7, 37.9, 38.5, 40.73, 41.9, 44.0, 48.2, 50.9, 52.7, 53.3, 78.4, 88.9, 139.4, 156.1, 169.1 and 177.4; HRMS: *m*/*z* = 595.22491 $[M + K]^+$, $C_{29}H_{36}N_2O_9K$ requires 595.20524.

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α,16β,18β,19α,22α,23β,25β) 8-*tert*butoxycarbonyl-aminoethyl-20,21-di[(*tert*butoxycarbonylamino) ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxoundeca-cyclo [13.10.1.1^{3,13}.1^{5,11}.1^{17,24}. 1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}] triaconta-20-ene-3,13,17,24-tetracarboxylate 16

Equimolar amounts of epoxide **10** (1.613 g, 2.591 mmol) and [*3*]polynorbornene **15** (1.552 g, 2.789 mmol) were heated (150 °C) in THF (4 ml) for 66 h. Column chromatography (EtOAc, R_f = 0.25) resulted in **16** (2.041 g, 1.731 mmol, 67%) as a white solid; mp 184.9–189.8 °C; ; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.84 (1 H, d, *J* = 8.2 Hz, H30), 1.02 (1 H, d, *J* = 8.3 Hz, H26), 1.37 (18 H, s, 2 × C(CH_3)$_3$), 1.40 (9 H, s, 1 × C(CH_3)$_3$), 1.63 (2 H, br s, H28), 1.71 (2 H, s, H1,15), 1.82 (2 H, s, H16,25), 1.92 (2 H, s, H4,12), 1.99 (2 H, s, H2,14), 2.03 (1 H, s, H30), 2.08 (1 H, s, H26), 2.19 (2 H, s, H19,22), 2.25 (2 H, s, H18,23), 2.34 (2 H, s, H5,11), 2.97 (12 H, br m, 2 × CH_2NHCO 3 × CH_2NHCOO, H6,10), 3.50 (2 H, s, NCH_2), 3.73 (6 H, s, 2 × COOCH_3), 3.78 (6 H, s, 2 × COOCH_3), 6.35 (1 H, s, 1 × N*H*COO) 6.80 (2 H, s, 2 × N*H*COO), 8.74 (2 H, s, 2 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.6, 28.7, 37.6, 37.9, 40.6, 42.4, 47.7, 48.2, 50.9, 52.5, 52.7, 54.1, 54.6, 78.3, 78.5, 78.8, 88.8, 89.8, 90.0, 92.5, 147.6, 147.9, 156.0, 156.3, 163.9, 168.5, 168.9 and 177.4; HRMS: *m*/*z* = 1179.53434 $[M + H]^+$, $C_{58}H_{79}N_6O_{20}$ requires 1179.53437.

Dimethyl (2β,3α,6α,7β,9β,10α,13α,14β) 4,5,11,12-tetra[(*tert*butoxycarbonylamino)ethylcarboxamido]-16-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}] heptadeca-4,11-diene-1,8-dicarboxylate 17

Equimolar amounts of epoxide **10** (570 mg, 0.915 mmol) and norbornene **9**[12] (425 mg, 0.915 mmol) were heated (150 °C) in THF (5 ml) for 45 h. Column chromatography (5% EtOH/EtOAc, R_f = 0.35) afforded **17** (753 mg, 0.693 76%) as an off-white powder; mp 121.9–124.1 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 1.09 (2 H, d, *J* = 8.2 Hz, H15,17), 1.36 (36 H, s, 4 × C(CH_3)$_3$), 2.27 (2 H, d, *J* = 8.6 Hz, H15,17), 2.33 (4 H, s, H3,6,10,13), 3.03 (8 H, br s, 4 × CH_2NHCO), 3.16 (12 H, br s, 4 × CH_2NHCOO, H2,7,9,14), 3.87 (6 H, s, 2 × COOCH_3), 6.83 (4 H, s, 4 × N*H*COO) and 8.78 (4 H, s, 4 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.4, 28.7, 47.8, 52.9, 54.3, 78.3, 87.9, 129.3, 132.0, 148.0, 156.3, 163.9 and 168.8; HRMS: *m*/*z* = 1087.55588 $[M + H]^+$, $C_{52}H_{79}N_8O_{17}$ requires 1087.55577.

Tetramethyl (1α,2β,4β,5α,8α,9β,11β,12α,13β,15β,16α,19α,20β,22β) 6,7,17,18-tetra[(*tert*butoxycarbonyl-amino)ethyl carboxamido]-24,26-dioxadecacyclo[10.10.1.1^{3,10}.1^{5,8}.1^{14,21} .1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]heptacosa-6,17-diene-3,10,14,21-tetracarboxylate 18

Coupling of bis epoxide **13**[8a] (520 mg, 1.27 mmol) with two equivalents of norbornene **9**[12] (1.300 g, 280 mmol) at 150 °C in THF (9 ml) for 49 h resulted in **18** (1.112 g, 0.83 mmol, 65%) as a white solid following column chromatography (5% EtOH/EtOAc, R_f = 0.33); mp 174.9–178.5 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 1.01 (2 H, d, *J* = 7.9 Hz, H23,27), 1.37 (36 H, s, 4 × C(CH_3)$_3$), 1.68 (2 H, s, H25), 1.91 (2 H, s, H1,12), 2.04 (4 H, s, H2,11,13,22), 2.20 (2 H, d, *J* = 8.2 Hz, H23,27), 2.25 (4 H, s, H5,8,16,19), 3.04 (8 H, t, *J* = 5.3 Hz, 4 × CH_2NHCO), 3.09 (4 H, s, H4,9,15,20), 3.14 (8 H, t, *J* = 5.2 Hz, 4 × CH_2NHCOO), 3.82 (12 H, s, 4 × COOCH_3), 6.83 (4 H, s, 4 × N*H*COO) and 8.78 (4 H, s, 4 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.8, 29.6, 47.9, 52.8, 54.0, 54.8, 78.3, 88.9, 147.8, 156.3, 163.9 and 168.9; HRMS: *m*/*z* = 1337.64001 $[M + H]^+$, $C_{65}H_{93}N_8O_{22}$ requires 1337.63989.

Hydrogenation

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α, 16β,18β,19α,20α,21α,22α,23β,25β) 8-*tert*butoxy-carbonylaminoethyl-20β,21β-di[(*tert*butoxycarbonylamino)ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxo undeca-cyclo[13.10.1.1^{3,13}.1^{5,11}.1^{17,24}. 1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}]triaconta-3,13,17,24-tetracarboxylate

The [*5*]polynorbornene **16** (1.100 g, 0.9329 mmol) underwent hydrogenation in EtOH (30 ml) for 48 h, purification by flash chromatography (10% EtOH/EtOAc, R_f = 0.36) resulted in the 3-*armed* [*5*]polynorbornane scaffold (1.063 g, 0.9000 mmol, 96%) as a white solid; mp 190.6–194.1 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.79 (1 H, d, *J* = 8.4 Hz, H30), 1.11 (1 H, d, *J* = 8.6 Hz, H26), 1.37 (18 H, s, 2 × C(C*H*$_3$)$_3$), 1.41 (9 H, s, 1 × C(C*H*$_3$)$_3$), 1.62 (2 H, br s, H28), 1.71 (2 H, s, H1,15), 1.73 (2 H, s, H16,25), 1.96 (2 H, s, H4,12), 2.00 (2 H, s, H2,14), 2.02 (1 H, s, H30), 2.10 (2 H, s, H19,22), 2.21 (1 H, s, H26), 2.33 (2 H, s, H5,11), 2.59 (2 H, s, H20,21), 2.74 (2 H, s, H18,23), 2.97 (12 H, br s, 2 × C*H*$_2$NHCO 3 × C*H*$_2$NHCOO, H6,10), 3.53 (2 H, s, NC*H*$_2$), 3.72 (6 H, s, 2 × COOC*H*$_3$), 3.77 (6 H, s, 2 × COOC*H*$_3$), 6.46 (1 H, s, 1 × N*H*COO) 6.57 (2 H, s, 2 × N*H*COO), 7.60 (2 H, s, 2 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.6, 28.8, 34.6, 37.8, 38.8, 39.4, 40.8, 43.1, 46.8, 48.2, 50.1, 50.7, 52.4, 52.7, 54.0, 54.6, 78.2, 78.7, 89.9, 90.0, 90.2, 156.0, 156.1, 168.9, 169.4, 171.6, 171.8 and 177.4; HRMS: *m*/*z* = 1181.55071 [M + H]$^+$, $C_{58}H_{81}N_6O_{20}$ requires 1181.55002.

Dimethyl (2β,3α,4α,5α,6α,7β,9β,10α,11α,12α,13α,14β) 4β,5β,11β,12β-tetra[(*tert*butoxycarbonylamino)ethyl carboxamido]-16-oxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-1,8-dicarboxylate

The [*3*]polynorbornadiene **17** (1.923 g, 1.769 mmol) was subject to hydrogenation conditions in EtOH (30 ml) for 48 h, column chromatography (10% EtOH/EtOAc, R_f = 0.20) resulted in the 4-*armed* [*3*]polynorbornane scaffold being isolated (1.660 mg, 1.521 mmol, 86%) as a white powder; mp 157.8–163.8 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.78 (2 H, d, *J* = 9.2 Hz, H15,17), 1.37 (36 H, s, 4 × C(C*H*$_3$)$_3$), 2.11 (4 H, s, H3,6,10,13), 2.23 (2 H, d, *J* = 8.9 Hz, H15,17), 2.59 (4 H, s, H4,5,11,12), 2.75 (4 H, s, H2,7,9,14), 2.98 (16 H, br s, 8 × C*H*$_2$NH), 3.72 (6 H, s, 2 × COOC*H*$_3$), 6.57 (4 H, s, 4 × N*H*COO) and 7.57 (4 H, s, 4 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.8, 34.9, 43.3, 46.9, 49.8, 52.2, 78.2, 90.7, 156.1, 169.8 and 171.7; HRMS: *m*/*z* = 1113.57982 [M + H]$^+$, $C_{52}H_{83}N_8O_{17}$ requires 1113.56901.

Tetramethyl (1α,2β,4β,5α,6α,7α,8α,9β,11β,12α,13β,15β,16α,17α,18α,19α,20β,22β) 6β,7β,17β,18β-tetra [(*tert*butoxycarbonylamino)ethylcarboxamido]-24,26-dioxadecacyclo [10.10.1.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9} .0^{13,22}.0^{15,20}] heptacosa-3,10,14,21-tetracarboxylate

The [*5*]polynorbornadiene **18** (2.100 g, 1.570 mmol) underwent hydrogenation in EtOH (20 ml) for 48 h, flash chromatography (10% EtOH/EtOAc, R_f = 0.19) afforded the 4-*armed* [*5*]polynorbornane scaffold (1.288 g, 0.9601 mmol, 61%) as a white solid; mp 196.2–203.1 °C; ; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.80 (2 H, d, *J* = 7.9 Hz, H23,27), 1.37 (36 H, s, 4 × C(C*H*$_3$)$_3$), 1.64 (2 H, s, H25) 1.76 (2H, s, H1,12), 2.02 (4 H, s, H2,11,13,22), 2.10 (4 H, s, H5,8,16,19), 2.11 (2 H, d, *J* = 8.2 Hz, H23,27), 2.60 (4 H, s, H6,7,17,18), 2.71 (4 H, s, H4,9,15,20), 3.00 (16 H, br s, 8 × C*H*$_2$NH), 3.74 (12 H, s, 4 × COOC*H*$_3$), 6.57 (4 H, s, 4 × N*H*COO) and 7.63 (4 H, s, 4 × N*H*CO); δ_C(270 MHz; d_6-DMSO; Me_4Si) 28.8, 29.6, 34.6, 43.2, 46.9, 50.3, 52.4, 54.9, 78.2, 90.1, 156.1, 169.5 and 171.8; HRMS: *m*/*z* = 1363.65314 [M + Na]$^+$, $C_{65}H_{96}N_8O_{22}Na$ requires 1363.65335.

Boc deprotection and isothiocyanate coupling

Dimethyl (2β,3α,4α,8α,9α,10β,12β,13α,14α,15α,16α,17β) 6-(4-nitrophenylthioureido)ethyl-14β,15β-di[(4-nitrophenylthioureido)ethylcarboximido]-6-aza-19-oxa-5,7-dioxoheptacyclo [9.6.1.1^{3,9}.1^{13,16}.0^{2,10}.0^{4,8}.0^{12,17}] icosa-1,11-dicarboxylate 3b

Dimethyl (2β,3α,4α,8α,9α,10β,12β,13α,14α,15α,16α,17β) 6-*tert*butoxycarbonylaminoethyl-14β,15β-di-[(*tert*butoxycarbonylamino) ethylcarboximido]-6-aza-19-oxa-5,7-dioxoheptacyclo [9.6.1.1^{3,9}.1^{13,16}.0^{2,10}.0^{4,8} .0^{12,17}] icosa-1,11-dicarboxylate (850 mg, 0.913 mmol) was deprotected (10 ml, 20% TFA/DCM) in 2 h to give the free triamine which was subsequently coupled with 4-nitrophenylisothiocyanate (494 mg, 2.74 mmol) and DIPEA (1.4 ml, 8.0 mmol) in $CHCl_3$ (15 ml) for 20 h. The resultant dark yellow crude product was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.37) to yield host **3b** (763 mg, 0.651 mmol, 71%) as a bright yellow powder; mp 194.6–198.1 °C; found: C, 51.9; H, 4.9; N, 14.1%. $C_{51}H_{54}N_{12}O_{15}S_3$ requires C, 52.3; H, 4.7; N, 14.4%; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.86 (1 H, d, *J* = 9.0 Hz, H20), 1.19 (1 H, d, *J* = 9.3 Hz, H18), 1.87 (2 H, s, H2,10), 2.16 (2 H, s, H13,16), 2.22 (1 H, d, *J* = 8.5 Hz, H20), 2.37 (1 H,

d, *J* = 10.0 Hz, H18), 2.40 (2 H, s, H3,9), 2.66 (2 H, s, H14,15), 2.87 (2 H, s, H12,17), 3.06 (2 H, s, H4,8), 3.21 (6 H, s, 1 × CH_2NHCS, 2 × CH_2NHCO), 3.53 (4 H, s, 2 × CH_2NHCS), 3.66 (2 H, s, NCH_2), 3.76 (6 H, s, 2 × COOCH_3), 7.71 (4 H, s, 2 × ArC*H*CNH, 2 × CO*N*H), 7.83 (4 H, d, *J* = 8.3 Hz, 4 × ArC*H*CNH), 8.18 (6 H, d, *J* = 6.9 Hz, 6 × ArC*H*CNO$_2$), 8.24 (2 H, s, 2 × CH$_2$N*H*CS), 8.29 (1 H, s, 1 × CH$_2$N*H*CS), 10.18 (1 H, s, 1 × ArN*H*) and 10.20 (2 H, s, 2 × ArN*H*); δ_C(270 MHz; d_6-DMSO; Me$_4$Si) 35.6, 38.0, 38.4, 38.5, 41.6, 42.3, 43.6, 44.6, 47.2, 48.9, 50.0, 51.1, 53.1, 90.3, 121.5, 122.2, 125.5, 142.8, 143.2, 146.8, 147.2, 169.4, 172.4, 178.0, 181.2 and 181.6; HRMS: *m*/*z* = 1171.29865 [M + H]$^+$, $C_{51}H_{55}N_{12}O_{15}S_3$ requires 1171.30665.

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α,16β,18β,19α,20α,21α,22α,23β,25β) 8-(4-fluorophenylthioureido) ethyl-20β,21β-di[(4-fluorophenylthioureido)ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxoundecacyclo[13.10.1.1^{3,13}.1^{5,11}.1^{17,24}. 1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}]triaconta-3,13,17,24-tetracarboxylate 4a

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α,16β,18β,19α,20α,21α,22α,23β,25β) 8-*tert*butoxycarbonylaminoethyl-20β,21β-di[(*tert*butoxycarbonylamino) ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxoundecacyclo [13.10.1.1^{3,13}.1^{5,11}.1^{17,24}.1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}] triaconta-3,13,17,24-tetracarboxylate (370 mg, 0.313 mmol) was deprotected (10 ml, 20% TFA/DCM) in 3 h to yield the free triamine, following coupling with 4-fluorophenylisothiocyanate (158 mg, 1.03 mmol) and DIPEA (0.5 ml, 2.9 mmol) in $CHCl_3$ (10 ml) for 18 h, the resultant crude off-white product was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.46) resulting in host **4a** (359 mg, 0.268 mmol, 85%) as a white powder; mp 192.2–196.0 °C; found: C, 57.0; H, 5.1; N, 9.5%. $C_{64}H_{68}N_9O_{14}F_3S_3$ requires C, 57.3; H, 5.1; N, 9.4%; δ_H(270 MHz; d_6-DMSO; Me$_4$Si) 0.82 (1 H, d, *J* = 8.9 Hz, H30), 1.16 (1 H, d, *J* = 8.8 Hz, H26), 1.59 (1 H, s, H28), 1.64 (1 H, s, H28), 1.73 (2 H, s, H1,15), 1.89 (2 H, s, H2,14), 1.91 (2 H, s, H4,12), 1.99 (2 H, s, H16,25), 2.15 (3 H, s, H19,22,30), 2.27 (1 H, d, *J* = 10.1 Hz, H26), 2.36 (2 H, s, H5,11), 2.63 (2 H, s, H20,21), 2.80 (2 H, s, H18,23), 2.99 (2 H, s, H6,10), 3.17 (4 H, s, 2 × CH_2NHCO), 3.50 (4 H, s, 2 × CH_2NHCS), 3.59 (2 H, s, 1 × CH_2NHCS), 3.66 (2 H, s, NCH_2), 3.74 (6 H, s, 2 × COOCH_3), 3.78 (6 H, s, 2 × COOCH_3), 7.14 (4 H, q, *J* = 8.7 Hz, 4 × ArC*H*CF), 7.31 (6 H, m, 6 × ArC*H*CNH), 7.42 (2 H, s, 2 × ArC*H*CF), 7.66 (3 H, s, 1 × CH$_2$N*H*CS, 2 × CON*H*), 7.71 (2 H, s, 2 × CH$_2$N*H*CS) and 9.57 (3 H, s, 3 × ArN*H*); δ_C(270 MHz; d_6-DMSO; Me$_4$Si) 29.5, 35.2, 37.9, 38.7, 40.5, 40.9, 42.6, 43.5, 47.2 48.7, 50.5, 51.2, 52.8, 53.1, 54.8, 55.1, 90.3, 90.5, 116.0, 116.2, 126.6, 127.4, 135.8, 136.4, 159.9, 160.3, 169.2, 169.7, 172.4, 177.9, 181.7 and 181.8; HRMS: *m*/*z* = 1340.40758 [M + H]$^+$, $C_{64}H_{69}N_9O_{14}F_3S_3$ requires 1340.40727.

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α,16β,18β,19α,20α,21α,22α,23β,25β) 8-(4-nitrophenylthioureido) ethyl-20β,21β-di[(4-nitrophenylthioureido)ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxoundecacyclo[13.10.1.1^{3,13}.1^{5,11}.1^{17,24}. 1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}]triaconta-3,13,17,24-tetracarboxylate 4b

Tetramethyl (1α,2β,4β,5α,6α,10α,11α,12β,14β,15α,16β,18β,19α,20α,21α,22α,23β,25β) 8-*tert*butoxycarbonylaminoethyl-20β,21β-di[(*tert*butoxycarbonylamino) ethylcarboximido]-8-aza-27,29-dioxa-7,9-dioxoundecacyclo [13.10.1.1^{3,13}.1^{5,11}.1^{17,24}.1^{19,22}.0^{2,14}.0^{4,12}.0^{6,10}.0^{16,25}.0^{18,23}] triaconta-3,13,17,24-tetracarboxylate (650 mg, 0.550 mmol) was deprotected (10 ml, 20% TFA/DCM) in 3 h to give the free triamine which underwent coupling with 4-nitrophenylisothiocyanate (327 mg, 1.81 mmol) and DIPEA (0.9 ml, 5.2 mmol) in $CHCl_3$ (20 ml) for 18 h. The resultant dark yellow crude solid was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.34) to produce host **6b** (638 mg, 0.449 mmol, 82%) as a bright yellow powder; mp 195.3–199.7 °C; δ_H(270 MHz; d_6-DMSO; Me$_4$Si) 0.80 (1 H, d, *J* = 8.8 Hz, H30), 1.12 (1 H, d, *J* = 8.9 Hz, H26), 1.59 (1 H, s, H28), 1.62 (1 H, s, H28), 1.72 (2 H, s, H1,15), 1.88 (2 H, s, H16,25), 1.94 (2 H, s, H4,12), 2.03 (2 H, s, H2,14), 2.14 (3 H, s, H19,22,30), 2.67 (1 H, d, *J* = 10.0 Hz, H26), 2.36 (2 H, s, H5,11), 2.64 (2 H, s, H20,21), 2.79 (2 H, s, H18,23), 3.01 (2 H, s, H6,10), 3.21 (4 H, s, 2 × CH_2NHCO), 3.53 (4 H, s, 1 × CH_2NHCS), 3.62 (2 H, s, 1 × CH_2NHCS), 3.68 (2 H, s, NCH_2), 3.71 (6 H, s, 2 × COOCH_3), 3.77 (6 H, s, 2 × COOCH_3), 7.72 (2 H, s, 2 × CO*N*H), 7.82 (4 H, d, *J* = 7.2 Hz, 4 × ArC*H*CNH), 8.16 (8 H, m, 2 × ArC*H*CNH, 6 × ArC*H*CNO$_2$), 8.55 (3 H, s, 3 × CH$_2$N*H*CS) and 10.51 (3 H, s, 3 × ArN*H*); δ_C(270 MHz; d_6-DMSO; Me$_4$Si) 29.4, 35.3, 37.9, 38.0, 38.2, 40.8, 41.2, 42.6, 43.5, 47.2 48.7, 50.5, 51.2, 52.8, 53.1, 54.8, 55.1, 90.3, 90.5, 121.2, 121.7, 125.3, 142.6, 142.9, 147.1, 147.4, 169.2, 169.7, 172.4, 177.8, 181.2 and 181.5; HRMS: *m*/*z* = 1421.39104 [M + H]$^+$, $C_{64}H_{69}N_{12}O_{20}S_3$ requires 1421.39077.

Dimethyl (2β,3α,4α,5α,6α,7β,9β,10α,11α,12α,13α,14β) 4β,5β,11β,12β-tetra[(4-fluorophenylthioureido)ethyl carboxamido]-16-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}] heptadeca-1,8-dicarboxylate 5a

Dimethyl (2β,3α,4α,5α,6α,7β,9β,10α,11α,12α,13α,14β) 4β,5β,11β,12β-tetra[(*tert*butoxycarbonylamino) ethylcarboxamido]-16-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}] heptadeca-1,8-dicarboxylate (820 mg, 0.751

mmol) was deprotected (10 ml, 20% TFA/DCM) in 4 h to yield the free tetraamine which was subsequently coupled with 4-fluorophenylisothiocyanate (507 mg, 3.31 mmol) and DIPEA (1.6 ml, 9.2 mmol) in $CHCl_3$ (20 ml) for 26 h. The resultant off-white crude solid was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.50) to give host **5a** (782 mg, 0.600 mmol, 80%) as a white powder; mp 184.6–188.2 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.82 (2 H, d, J = 8.3 Hz, H15,17), 2.16 (4 H, s, H3,6,10,13), 2.25 (2 H, d J = 7.6 Hz, H15,17), 2.63 (4 H, s, H4,5,11,12), 2.86 (4 H, s, H2,7,9,14), 3.17 (8 H, s, 4 × CH_2NHCO), 3.50 (8 H, s, 4 × CH_2NHCS), 3.73 (6 H, s, 2 × COOCH_3), 7.13 (8 H, t, J = 6.9 Hz, 8 × ArCHCF), 7.39 (8 H, t, J = 6.7 Hz, 8 × ArCHCNH), 7.69 (8 H, br s, 4 × CONH, 4 × CH_2NHCS) and 9.58 (4 H, s, 4 × ArNH); δ_C(270 MHz; d_6-DMSO; Me_4Si) 35.1, 38.5, 43.3, 44.0, 46.9, 49.8, 52.4, 90.7, 115.7, 126.2, 136.1, 159.4, 169.6, 172.0 and 181.5; HRMS: m/z = 1303.39788 $[M + H]^+$, $C_{60}H_{67}N_{12}O_9F_4S_4$ requires 1303.39674.

Dimethyl (2β,3α,4α,5α,6α,7β,9β,10α,11α,12α,13α,14β) 4β,5β,11β,12β-tetra[(4-nitrophenylthioureido)ethyl carboxamido]-16-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}] heptadeca-1,8-dicarboxylate 5b

Dimethyl (2β,3α,4α,5α,6α,7β,9β,10α,11α,12α,13α,14β) 4β,5β,11β,12β-tetra[(*tert*butoxycarbonylamino) ethylcarboxamido]-16-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}] heptadeca-1,8-dicarboxylate (800 mg, 0.733 mmol) was deprotected (10 ml, 20% TFA/DCM) in 4 h to give the free tetraamine, following coupling with 4-nitrophenylisothiocyanate (581 mg, 3.22 mmol) and DIPEA (1.6 ml, 9.2 mmol) in (20 ml) $CHCl_3$ for 26 h, the resultant dark yellow crude product was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.26) to yield host **5b** (935 mg, 0.662 mmol, 90%) as a bright yellow powder; mp 187.7–192.1 °C; found: C, 50.5; H, 4.9; N, 15.4%. $C_{60}H_{66}N_{16}O_{17}S_4$ requires C, 51.0; H, 4.7; N, 15.9%; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.82 (2 H, d, J = 8.2 Hz, H15,17), 2.18 (4 H, s, H3,6,10,13), 2.26 (2 H, d J = 7.7 Hz, H15,17), 2.66 (4 H, s, H4,5,11,12), 2.88 (4 H, s, H2,7,9,14), 3.21 (8 H, s, 4 × CH_2NHCO), 3.54 (8 H, s, 4 × CH_2NHCS), 3.74 (6 H, s, 2 × COOCH_3), 7.80 (8 H, t, J = 8.3 Hz, 8 × ArCHCNO$_2$), 8.12 (8 H, t, J = 8.8 Hz, 8 × ArCHCNH), 7.77 (4 H, s, 4 × CONH), 8.24 (4 H, s, 4 × CH_2NHCS) and 10.29 (4 H, s, 4 × ArNH); δ_C(270 MHz; d_6-DMSO; Me_4Si) 35.3, 38.4, 43.3, 44.3, 47.2, 50.2, 52.7, 90.1, 121.2, 125.3, 142.6, 147.3, 170.2, 172.6 and 181.1; HRMS: m/z = 1411.36385 $[M + H]^+$, $C_{60}H_{67}N_{16}O_{17}S_4$ requires 1411.37474.

Tetramethyl (1α,2β,4β,5α,6α,7α,8α,9β,11β,12α,13β,15β,16α,17α,18α,19α,20β,22β) 6β,7β,17β,18β-tetra[(4-fluorophenylthioureido)ethylcarboxamido]-24,26-dioxadecacyclo [10.10.1.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] hepta-cosa-3,10,14,21-tetracarboxylate 6a

Tetramethyl (1α,2β,4β,5α,6α,7α,8α,9β,11β,12α,13β,15β,16α,17α,18α,19α,20β,22β) 6β,7β,17β,18β-tetra [(*tert*butoxycarbonylamino)ethylcarboxamido]-24,26-dioxadecacyclo [10.10.1.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] heptacosa-3,10,14,21-tetracarboxylate (820 mg, 0.611 mmol) was deprotected (10 ml, 20% TFA/DCM) in 4 h to yield the free tetraamine which underwent coupling with 4-fluorophenylisothiocyanate (412 mg, 2.69 mmol) and DIPEA (1.3 ml, 7.5 mmol) in $CHCl_3$ (20 ml) for 46 h. The resultant off-white crude solid was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.38) resulting in host **6a** (908 mg, 0.584 mmol, 96%) as a white powder; mp 209.9–215.5 °C; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.82 (2 H, d, J = 8.1 Hz, H23,27), 1.64 (2 H, s, H25), 1.75 (2 H, s, H1,12), 1.93 (4 H, s, H2,11,13,22) 2.14 (4 H, s, H5,8,16,19), 2.16 (2 H, d, J = 7.5 Hz, H23,27), 2.63 (4 H, s, H6,7,17,18), 2.80 (4 H, s, H4,9,15,20), 3.17 (8 H, s, 4 × CH_2NHCO), 3.50 (8 H, s, 4 × CH_2NHCS), 3.74 (12 H, s, 4 × COOCH_3), 7.14 (8 H, t, J = 8.8 Hz, 8 × ArCHCF), 7.41 (8 H, t, J = 8.5 Hz, 8 × ArCHCNH), 7.68 (4 H, s, 4 × CONH), 7.72 (4 H, s, 4 × CH_2NHCS) and 9.58 (4 H, s, 4 × ArNH); δ_C(270 MHz; d_6-DMSO; Me_4Si) 27.8, 35.3, 38.8, 40.1, 43.5, 44.5, 47.2, 50.5, 52.8, 55.2, 90.5, 116.1, 126.5, 136.4, 159.9, 169.8, 172.3 and 181.7; HRMS: m/z = 1553.48067 $[M + H]^+$, $C_{73}H_{81}N_{12}O_{14}F_4S_4$ requires 1553.48087.

Tetramethyl (1α,2β,4β,5α,6α,7α,8α,9β,11β,12α,13β,15β,16α,17α,18α,19α,20β,22β) 6β,7β,17β,18β-tetra[(4-nitrophenylthioureido)ethylcarboxamido]-24,26-dioxadecacyclo [10.10.1.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] heptacosa-3,10,14,21-tetracarboxylate 6b

Tetramethyl (1α,2β,4β,5α,6α,7α,8α,9β,11β,12α,13β,15β,16α,17α,18α,19α,20β,22β) 6β,7β,17β,18β-tetra [(*tert*butoxycarbonylamino)ethylcarboxamido]-24,26-dioxadecacyclo [10.10.1.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] heptacosa-3,10,14,21-tetracarboxylate (870 mg, 0.649 mmol) was deprotected (10 ml, 20% TFA/DCM) in 4 h to give the free tetraamine which was subsequently coupled with 4-nitrophenylisothiocyanate (514 mg, 2.85 mmol) and DIPEA (1.4 ml, 8.0 mmol) in $CHCl_3$ (20 ml) for 46 h. The resultant dark yellow crude solid was purified by column chromatography (10% EtOH/EtOAc, R_f = 0.24) to produce host **6b** (796 mg, 0.479 mmol, 74%) as a bright yellow powder; mp 218.8–223.1 °C; found: C, 52.7; H, 4.9; N, 12.9%. $C_{73}H_{80}N_{16}O_{22}S_4$ requires C, 52.8; H, 4.9; N, 13.5%; δ_H(270 MHz; d_6-DMSO; Me_4Si) 0.84 (2 H, d, J = 8.2 Hz, H23,27), 1.65 (2 H, s, H25), 1.74 (2 H, s, H1,12), 1.96 (4 H, s, H2,11,13,22) 2.16 (4 H, s, H5,8,16,19), 2.18 (2 H, d, J = 7.6 Hz, H23,27), 2.65 (4 H, s, H6,7,17,18), 2.83 (4 H, s, H4,9,15,20), 3.23 (8 H, s, 4 × CH_2NHCO), 3.53 (8 H, s, 4 × CH_2NHCS), 3.72 (12 H, s, 4 ×

COOCH_3), 7.71 (4 H, s, 4 × CONH), 7.80 (8 H, d, J = 8.1 Hz, 8 × ArCHCNO$_2$), 8.17 (8 H, d, J = 9.0 Hz, 8 × ArCHCNH), 8.22 (4 H, s, 4 × CH$_2$NHCS) and 10.21 (4 H, s, 4 × ArNH); δ_C(270 MHz; d_6-DMSO; Me$_4$Si) 29.3, 35.3, 38.2, 41.4, 43.5, 44.6, 47.3, 50.5, 52.9, 55.2, 90.6, 121.4, 125.4, 142.8, 147.2, 169.8, 172.5 and 181.2; HRMS: m/z = 1661.46487 $[M + H]^+$, $C_{73}H_{81}N_{16}O_{22}S_4$ requires 1661.45887.

Stack plots of ^{1}H NMR titration spectra in d_6-DMSO:

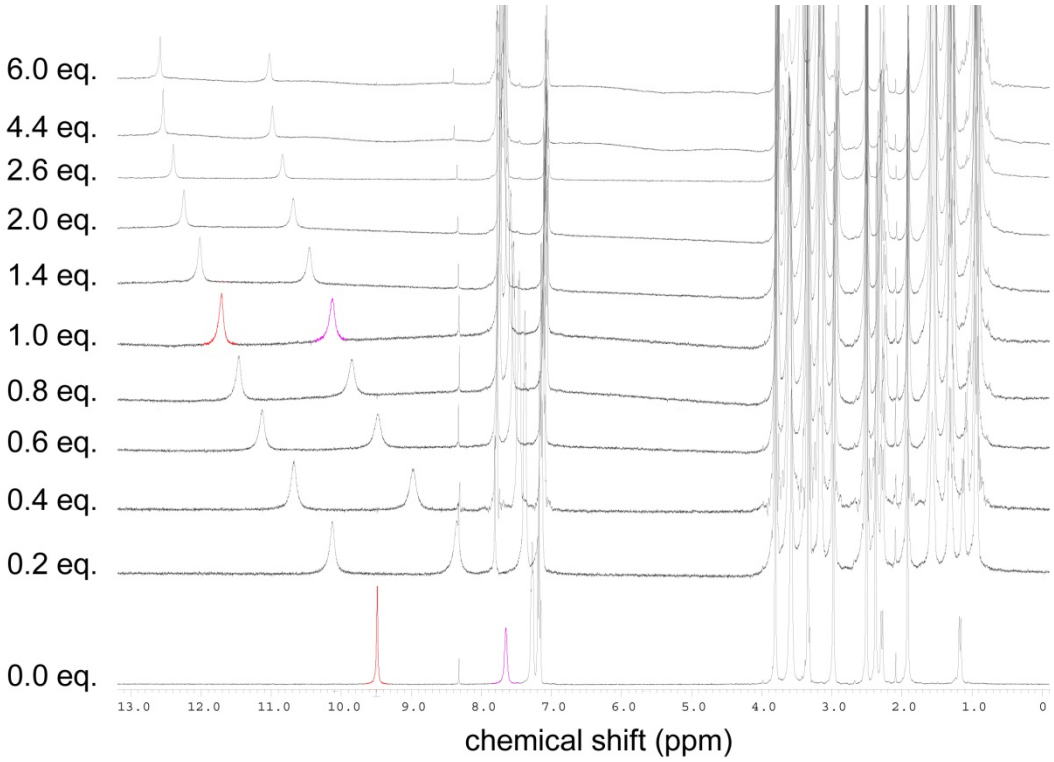

Figure S2 Host **1a**, $[H]_i$ = 1.00 × 10^{-3} M.

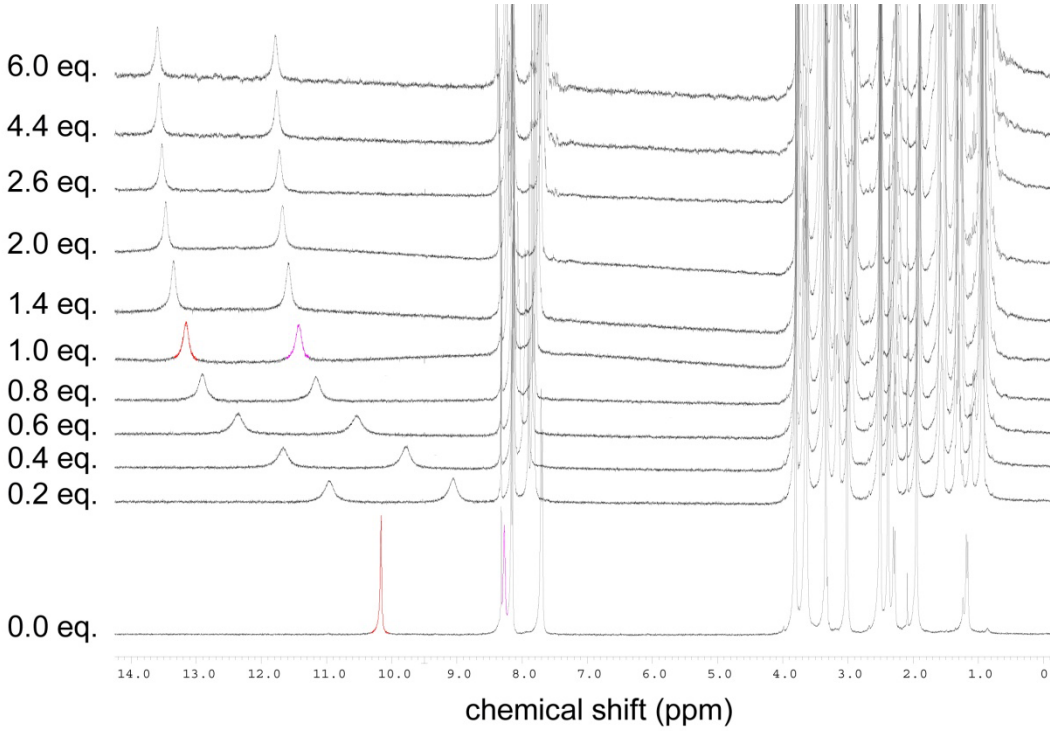

Figure S3 Host **1b**, $[H]_i = 1.00 \times 10^{-3}$ M.

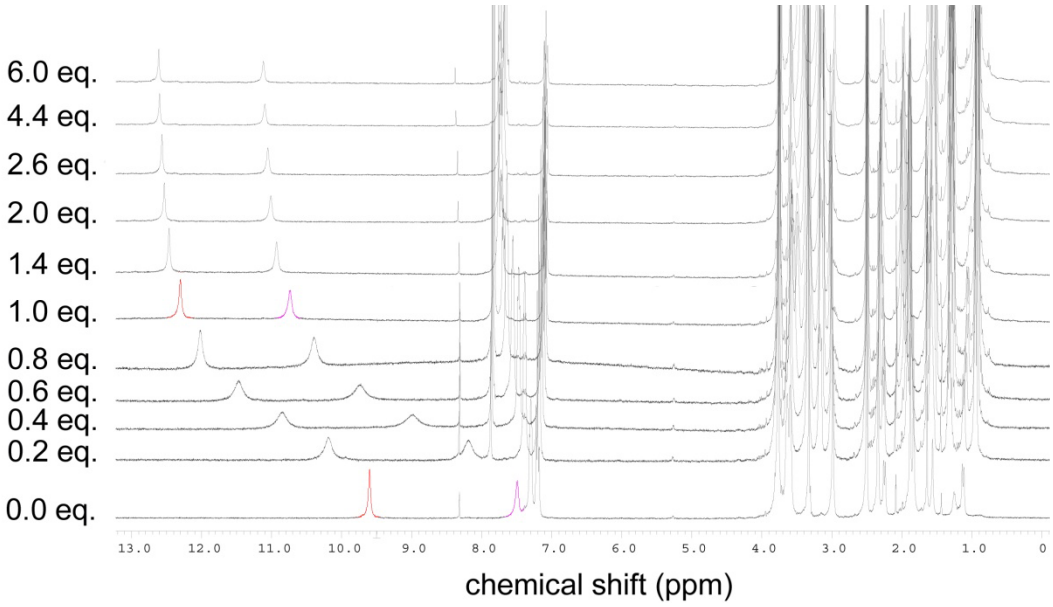

Figure S4 Host **2a**, $[H]_i = 1.00 \times 10^{-3}$ M.

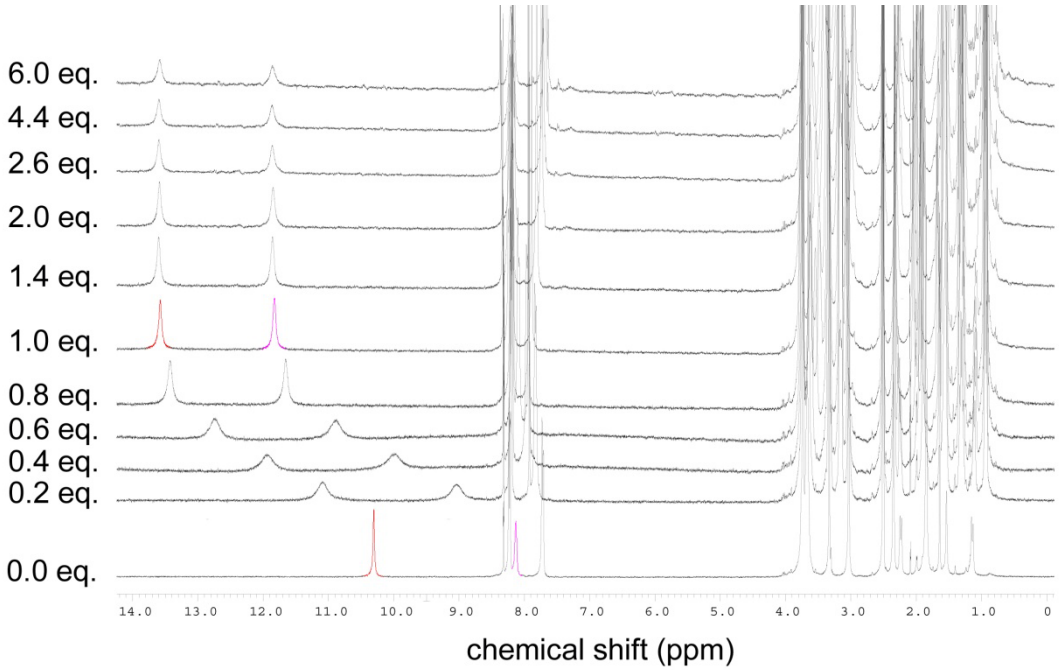

Figure S5 Host **2b**, $[H]_i = 1.00 \times 10^{-3}$ M.

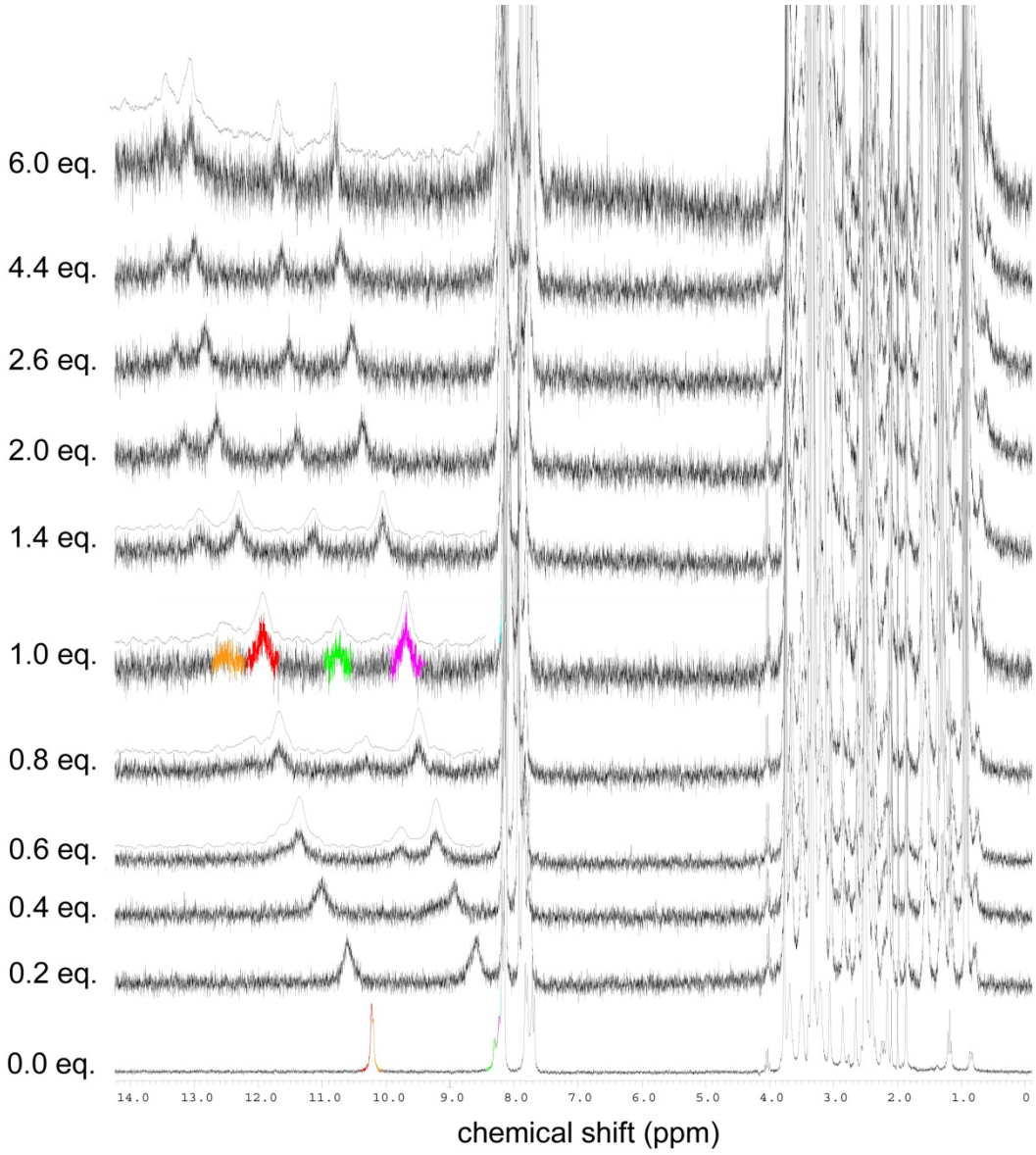

Figure S6 Host **3a**, $[H]_i = 2.51 \times 10^{-3}$ M.

Note: a smoothing function was used to distinguish absolute values and is shown as a faint trace above each original spectrum.

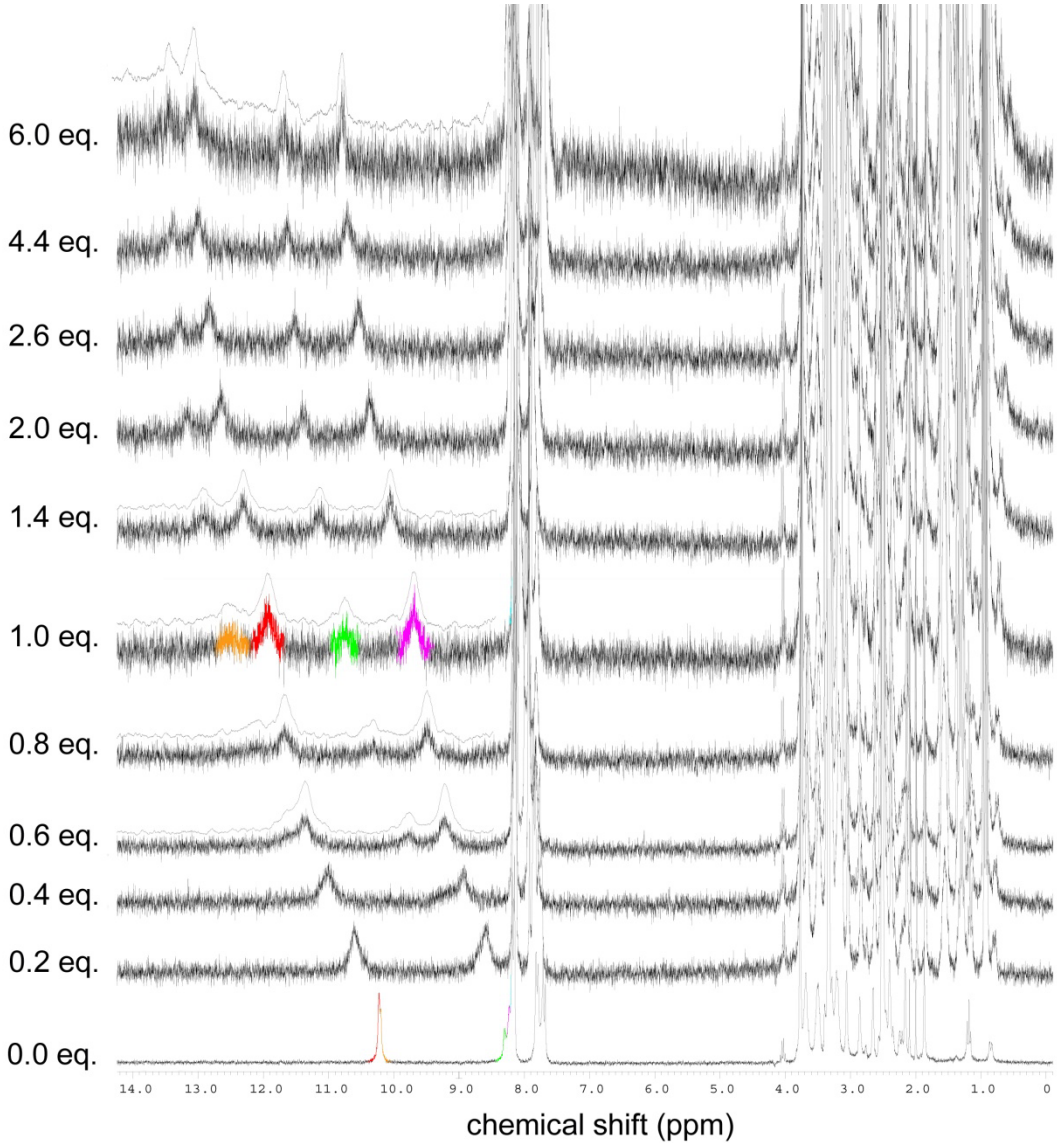

Figure S7 Host **3b**, $[H]_i = 2.50 \times 10^{-3}$ M.

Note: a smoothing function was used to distinguish absolute values and is shown as a faint trace above each original spectrum.

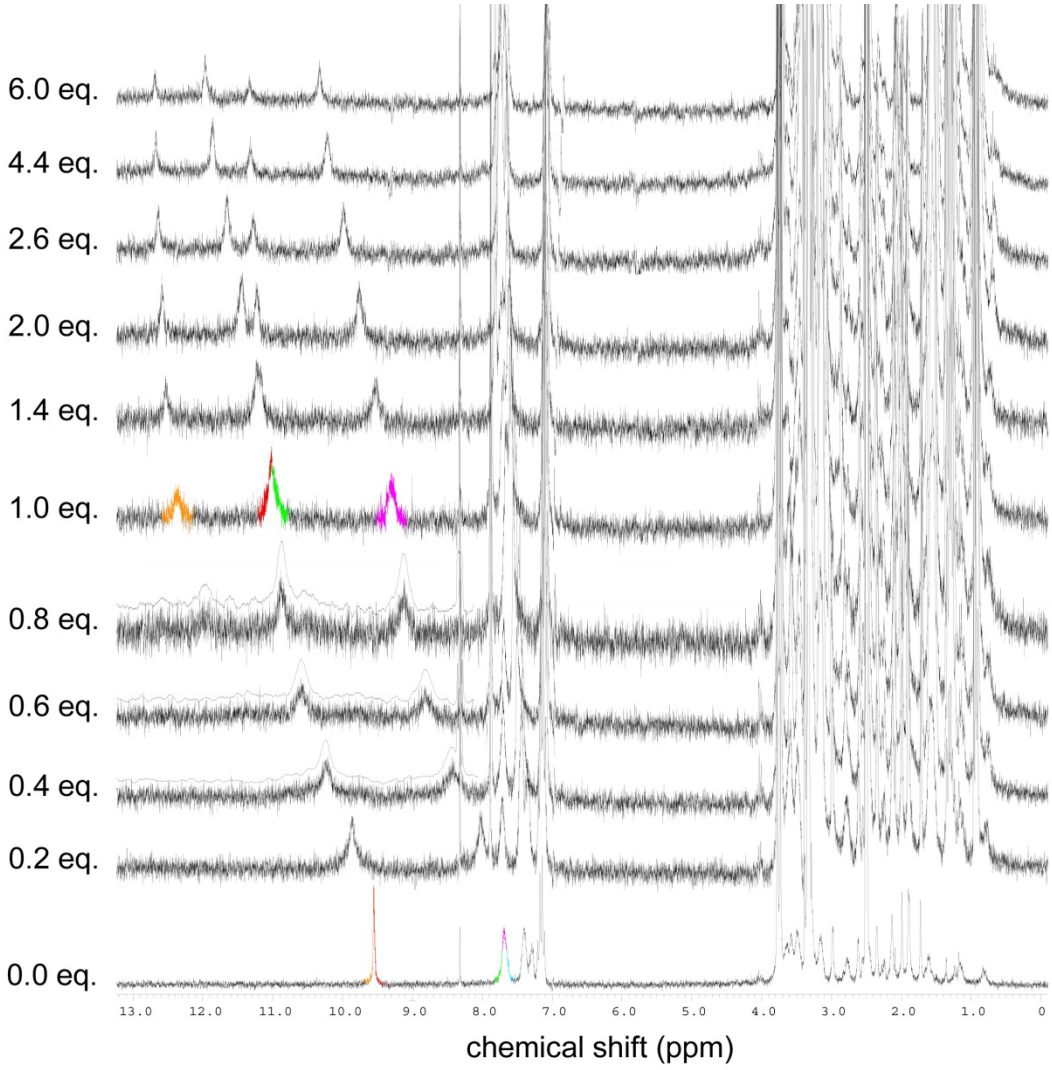

Figure S8 Host **4a**, $[H]_i = 2.50 \times 10^{-3}$ M.

Note: a smoothing function was used to distinguish absolute values and is shown as a faint trace above each original spectrum.

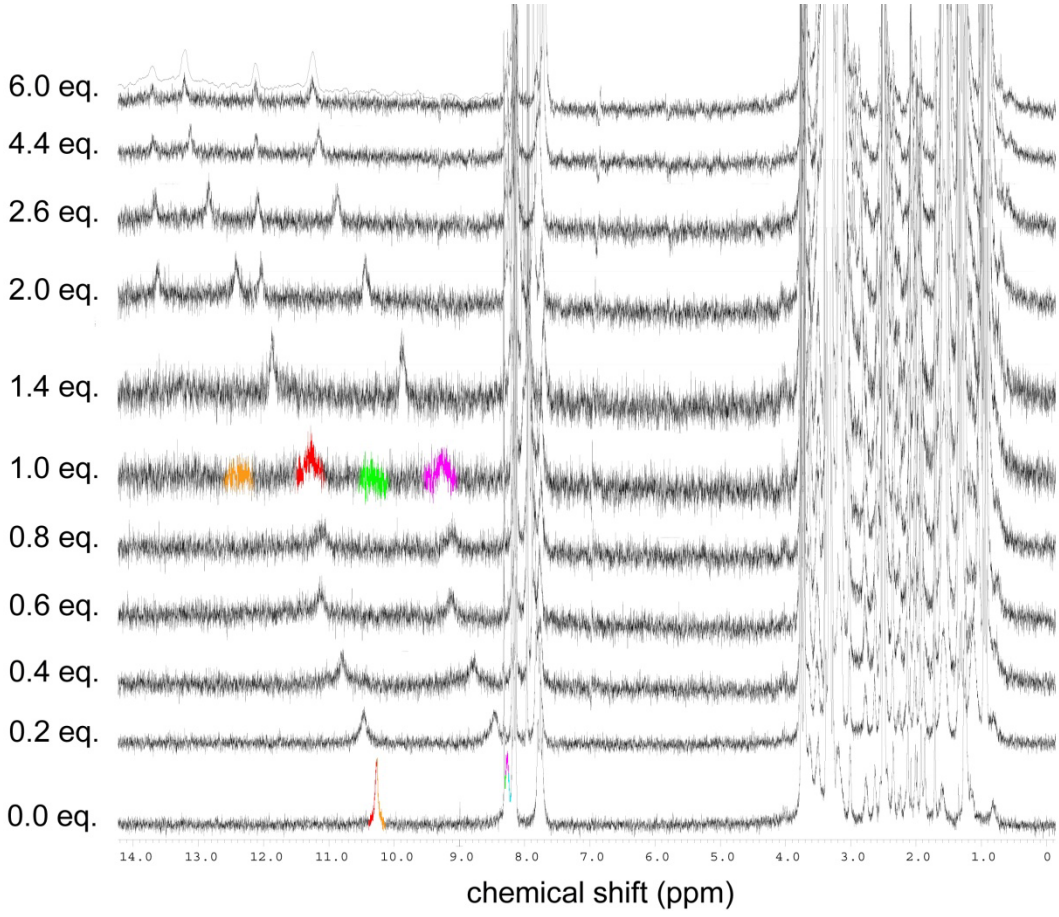

Figure S9 Host **4b**, $[H]_i = 2.50 \times 10^{-3}$ M.

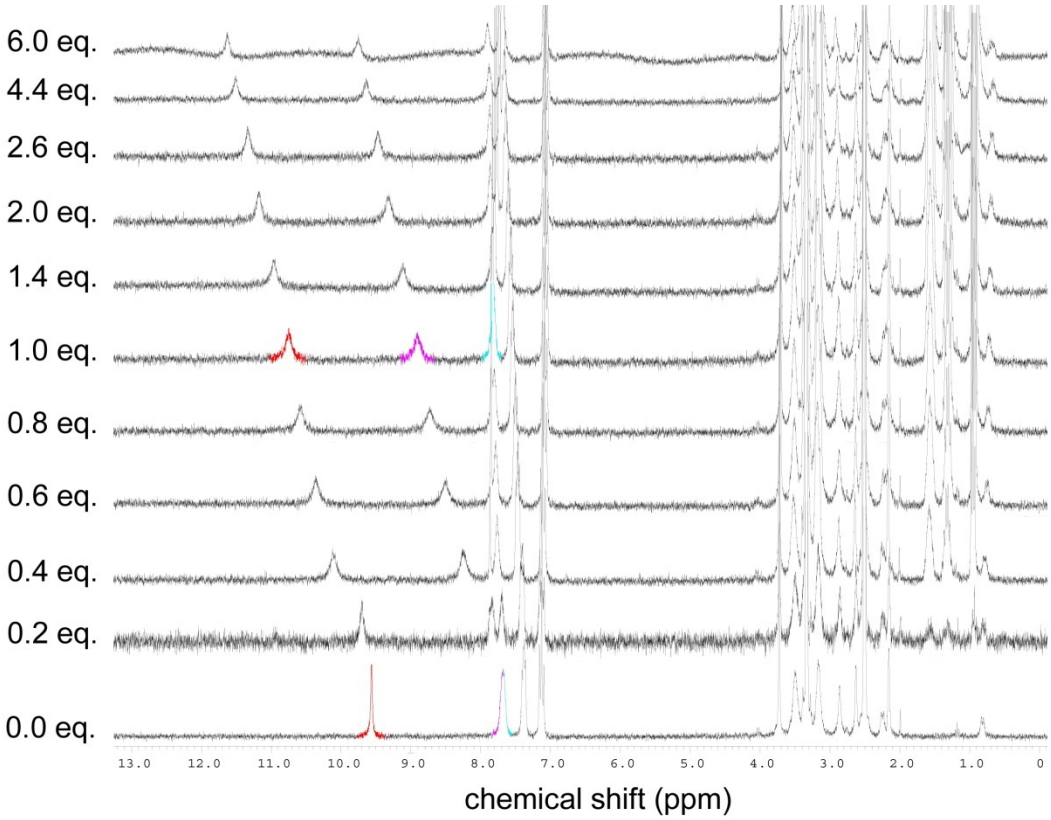

Figure S10 Host **5a**, $[H]_i = 2.51 \times 10^{-3}$ M.

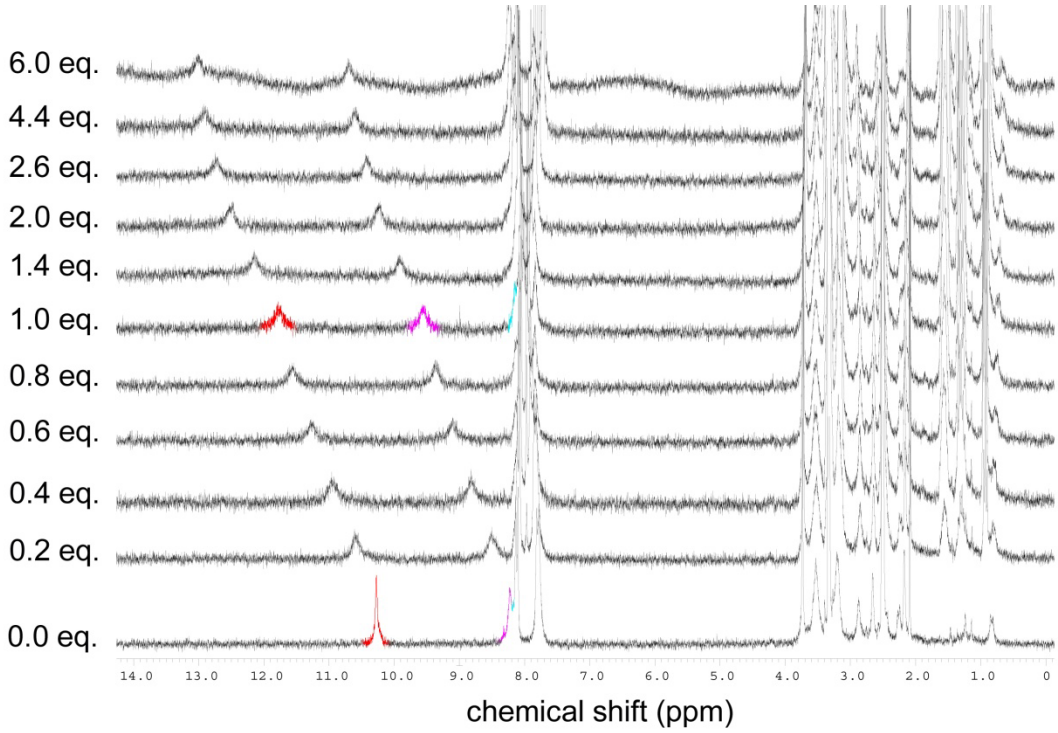

Figure S11 Host **5b**, $[H]_i = 2.50 \times 10^{-3}$ M.

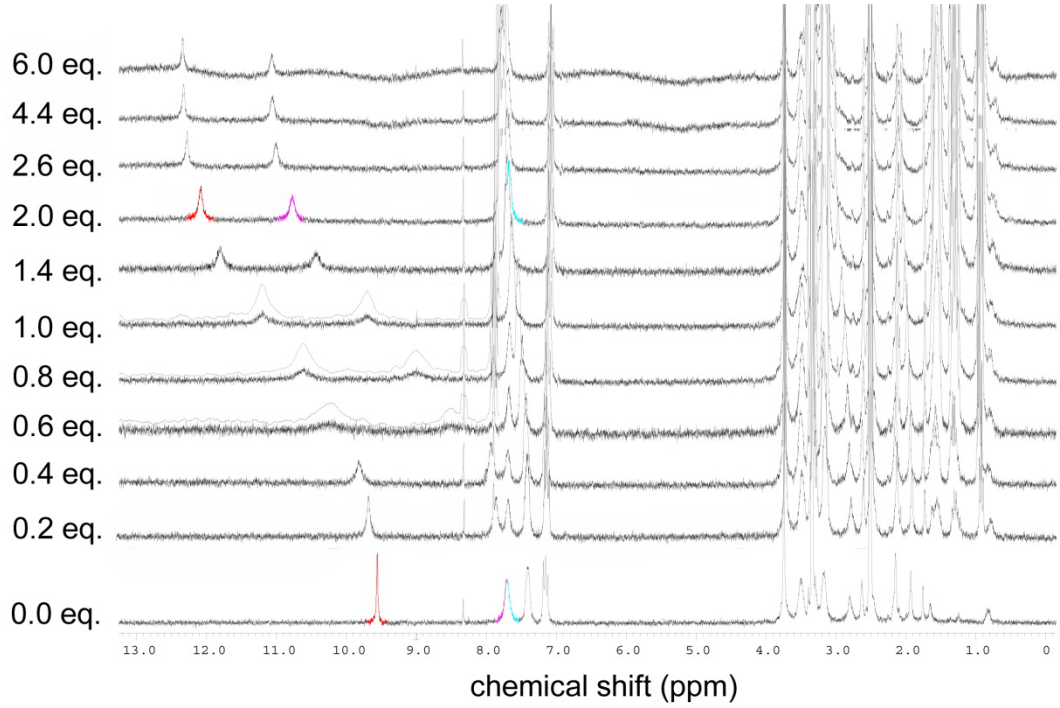

Figure S12 Host **6a**, $[H]_i = 2.50 \times 10^{-3}$ M.

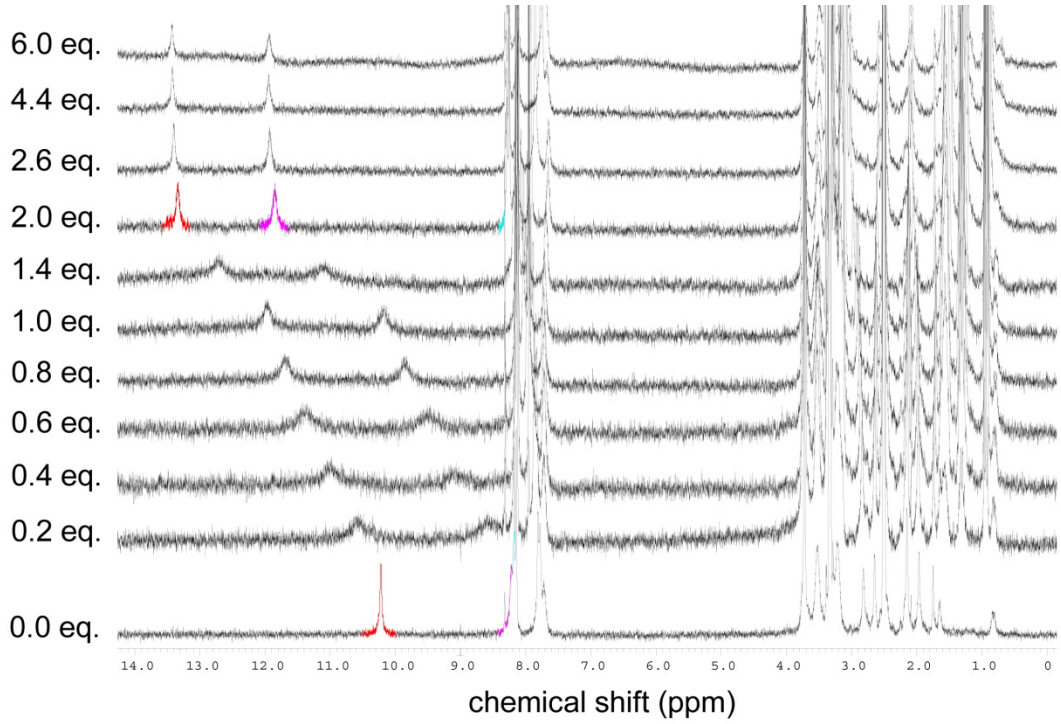

Figure S13 Host **6b**, $[H]_i = 2.50 \times 10^{-3}$ M.

Titration isotherms – Internal framework C-H protons of hosts 2 (H2,14,16,28), 4(H2,14,16,25) and 6(H2,11,13,22) when binding terephthalate^{2-}:

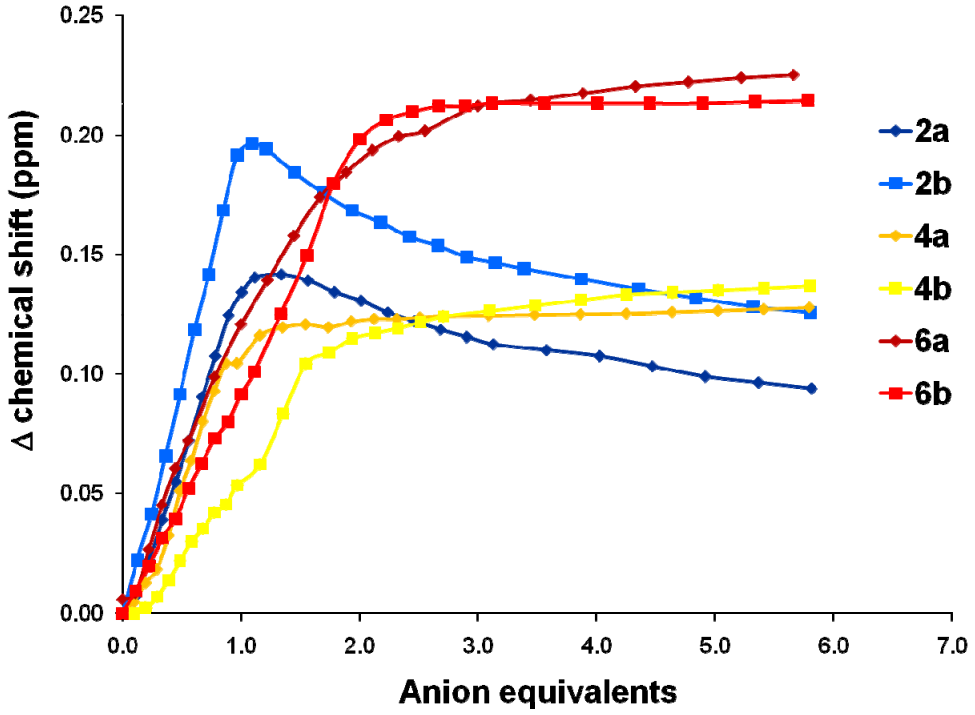

Figure S14 Binding isotherms of the internal framework C–H protons for hosts **2**, **4** and **6**.