Supporting Information

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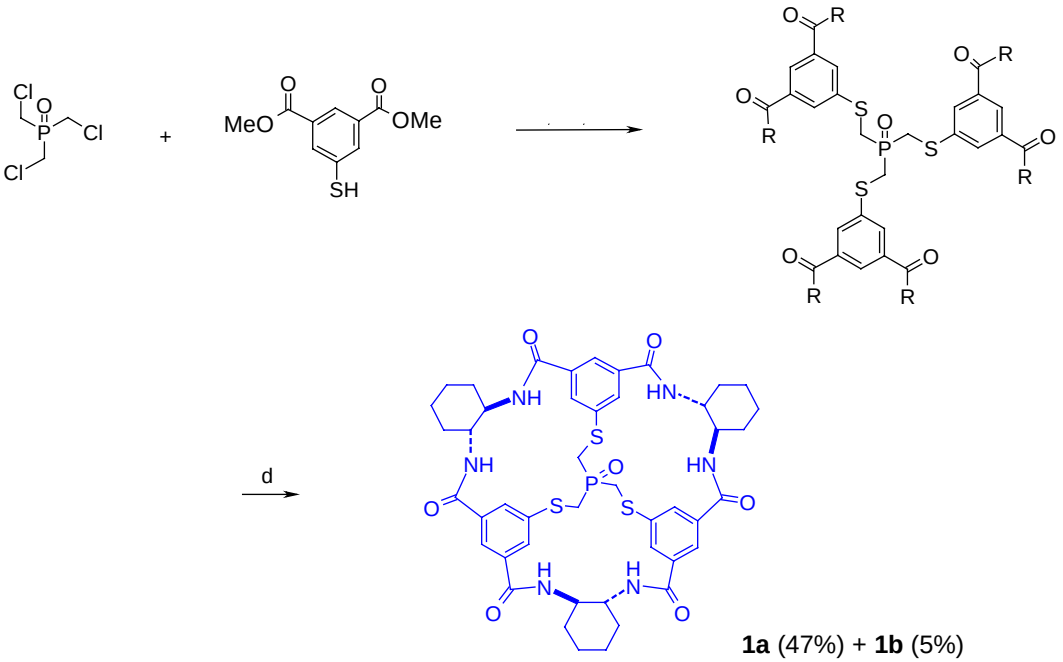
Figure SI1. Synthesis of **1a** and **1b**



(a) DIPEA, THF (78%) (b) 1N NaOH, THF/MeOH/H_2O, and HCl (95%). (c) C_6F_5OH, EDC, CH_2Cl_2 (57%). (d) (1*R*,*2R*)-diaminocyclohexane, DIPEA, THF.

Hexakis ester

To a solution of tris(chloromethyl)phosphine oxide (150 mg, 0.77 mmol) and dimethyl 5-mercaptoisophtalate (990 mg, 3.1 mmol) in 10 ml of THF was added 1 ml of DIPEA. The reaction mixture was stirred at rt for 10 h. The organic solvent was evaporated *in vacuo*. The resulting mixture was diluted water (100 ml) and extracted three times with CH_2Cl_2. The organic extracts were washed with water and then with brine. Drying and solvent evaporation were followed by column chromatography (EtOAc/hexane(2/1,v/v), CH_2Cl_2, and CH_2Cl_2/MeOH(10/1)) to give 0.46 g (78 %) of hexakis ester as a white solid: mp 149 - 149.5 ^oC; IR (KBr) 2954, 1728, 1580, 1314, 1246, 1144 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 8.40 (s, 3H), 8.13 (s, 6H), 3.95 (s, 9H), 3.53 (d, 6H, J = 9.0 Hz);

^{13}C NMR (300 MHz, $CDCl_3$) 165.6, 136.4, 134.1, 129.5, 120.2, 53.0, 29.3; HR FAB-MS (mNBA) *m*/*e* calcd for $C_{33}H_{33}O_{13}PS_3$ $[M+H]^+$ 765.0899, found 765.0899.

Hexakis acid

To a solution of hexakis ester (400 mg, 0.52 mmol) in 20 ml of THF/MeOH/H_2O (5/3/1,v/v) was added 1N aqueous NaOH solution (4.2 ml). The resulting solution was stirred at rt for 6 h and concentrated to 1/5 volume *in vaccuo*. The residue was triturated with 50 ml of 1N aqueous HCl solution. The resulting solid was filtered to give 0.34 g (95 %) of hexakis acid as a white solid: mp >> 250 ^{o}C (decomp.); ^{1}H NMR (DMSO-d_6) 8.21 (s, 3H), 8.09 (s, 6H), 3.78 (d, 6H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$) 166.8, 137.9, 133.1, 132.8, 29.5; HR FAB-MS (mNBA) *m*/*e* calcd for $C_{27}H_{22}O_{13}PS_3$ $[M+H]^+$ 680.9960, found 680.9936

Hexakis(pentafluorophenyl) ester

To a solution of hexaki sacid (300 mg, 0.44 mmol) and EDC (0.68 g, 3.5 mmol) in 20 ml of CH_2Cl_2 was added C_6F_5OH (0.65 g, 3.5 mmol). The resulting solution was stirred at rt for 10 h. The reaction mixture was concentrated to 10 ml. The concentrated reaction mixture was purified with column chromatography (EtOAc/hexane,1/2, v/v) to give 0.42 g (57 %) of the desired product as a white solid: mp 207-208 ^{o}C; IR (KBr) 2962, 1768, 1521, 1285, 1185, 1149 cm^{-1}; ^{1}H NMR ($CDCl_3$) 8.83 (s, 3H), 8.56 (s, 6H), 3.70 (d, J = 8.4 Hz, 6H); ^{13}C NMR ($CDCl_3$) 161.1, 143.2, 142.0, 140.0, 138.2, 136.7, 136.4, 131.3, 129.5, 125, 29.4; FAB-MS (mNBA) *m*/*e* calcd for $C_{63}H_{15}F_{30}O_{13}PS_3$ $[M]^+$ 1677, found 1677.

Macrocyclic receptor

To a solution of hexakis(pentafluorophenyl) ester (100 mg, 0.059 mmol) and DIPEA (1 mL) in 50 ml of THF was added 10 ml solution of (1*R*, 2*R*)-diaminocyclohexane (20 mg, 0.18 mmol) in THF at rt for 12 h via syringe pump. The solution was stirred for an additional 12 h. The organic solvent was evaporated in vacuo. The concentrated reaction mixture was purified with flash chromatograph (CH_2Cl_2/MeOH, 20/1, v/v) to give 25.4 mg (47 %) of **1a** and 2.6 mg (5%) of **1b** as white solids.

1a: mp >> 300 ^{o}C (decomp.); ^{1}H NMR ($CDCl_3$/CD_3OD, 10/1, v/v) 8.28 (s, 3H), 7.98 (s, 3 H), 7.96 (d, J = 7.9 Hz, 3H), 7.53 (s, 3 H), 7.47 (d, J = 7.9 Hz, 3H), 4.20 (dd, 3 H, J = 6.7, 15.6 Hz, 3H), 4.18 (m, 3H), 3.80 (m, 3H), 2.48 (d, J = 15.6 Hz, 3 H), 2.19 (m, 6H), 2.05 (m, 6H), 1.85 ~ 1.43 (m,12H); ^{13}C NMR ($CDCl_3$/CD_3OD, 10/1, v/v) 171.0, 170.1, 139,9, 138.0, 137.3, 136.5, 135.1, 128.5, 74.4, 59.8, 57.7, 56.7, 36.2, 35.9, 32.2,

31.4, 29.4, 29.0; FAB-MS (mNBA) *m/e* calcd for $C_{45}H_{51}O_7N_6PS_3$ $[M+1]^+$ 915, found 915; HR FAB-MS (mNBA) m/e calcd for $C_{45}H_{51}O_7N_6PS_3$ $[M+1]^+$ 915.2719, found $[M+H]^+$ 915.2787.

1b: mp >> 250 °C (decomp.); ^{1}H NMR ($CDCl_3$/CD_3OD, 10/1, v/v) 8.16 (s, 3H, Ar*H*), 7.99 (broad, 6 H, Ar*H*, CON*H*), 7.63 (d, J = 9 Hz, 3H, Ar*H*), 7.58 (s, 3 H, ArH), 4.12 (m, 3 H), 3.78(m, 3H), 3.00 (dd, 3 H, J = 9.9, 14.7 Hz, 3H), 1.98 (m, 6H), 1.79 (m, 6H), 1.54 ~ 1.17 (m, 12H); FAB-MS (mNBA) *m/e* calcd for $C_{45}H_{51}O_7N_6PS_3$ $[M+1]^+$ 915, found 915; HR FAB-MS (mNBA) m/e calcd for $C_{45}H_{51}O_7N_6PS_3$ $[M+1]^+$ 915.2719, found $[M+H]^+$ 915.2791.

Figure SI2. ^{1}H NMR spectrum of **1a** in 10% MeOH-*d*$_4$ in $CDCl_3$.

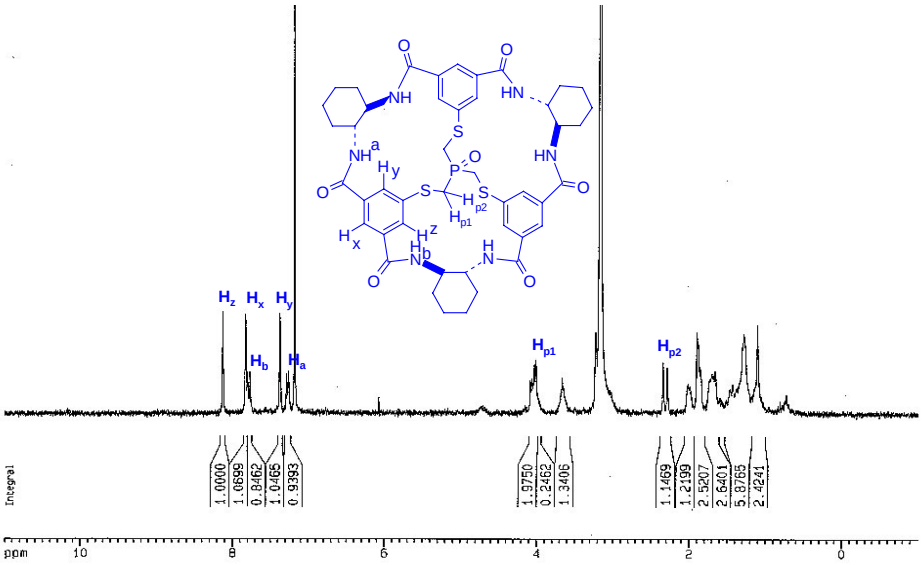


Table SI1. The chemical shift of the ^{31}P NMR for **1a** and **1b** upon addition of the guest (ppm)

	1a	**1b**	Hexakis-ester
No guest	32.5	45.4	43.2
$Ph_2SnCl_2 \rightarrow NH_4^+$	32.6 →36.8		
$tBuNH_3^+$	33.0	50.9	44.2

Figure SI3. ^{31}P NMR spectra of (a) the reaction mixture (**1a**, **1b** and uncyclized product), (b) after addition of *t*-$BuNH_3^+$ to the reaction mixture, (c) **1b** + **1a**, (d) **1a**. The peak at –6 ppm corresponds to PPh_3 (external reference) and the peak at 41.5 ppm corresponds to the uncylized product.

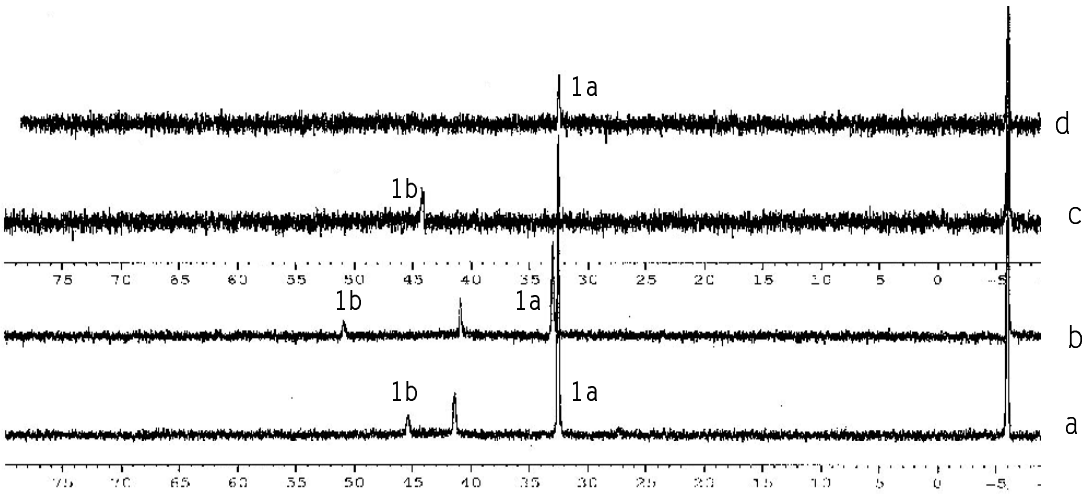
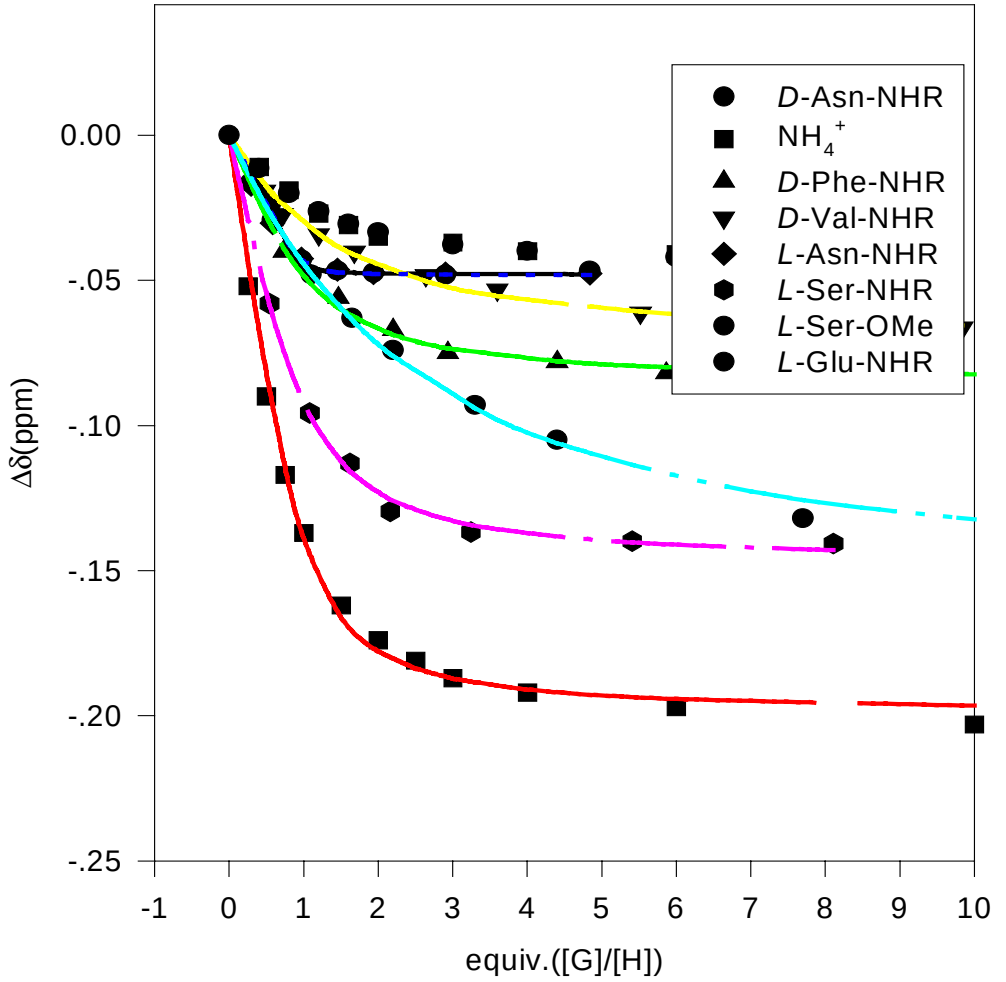
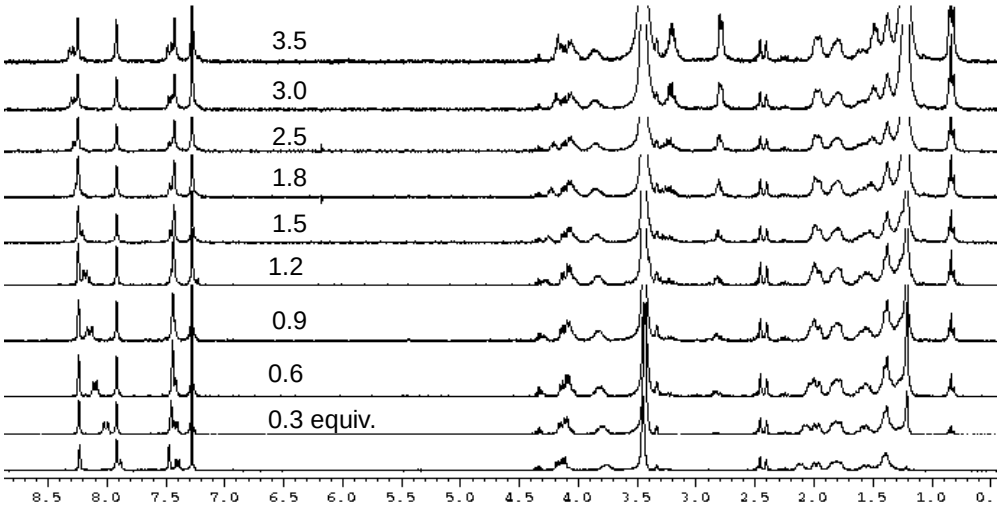


Figure SI4. Titration curves for **1a** vs ammonium derivatives (R = dodecyl).



conc of host = 3 mM, Conc. of guest stock solution = 25~150 mM
counter anion = $CF_3CO_2^-$ in $CDCl_3/CD_3OD$(v/v, 10/1). R=dedecyl

Figure SI5. Stacked plot for ^{1}H NMR titration of **1a** with *L*-Asn-NHR.



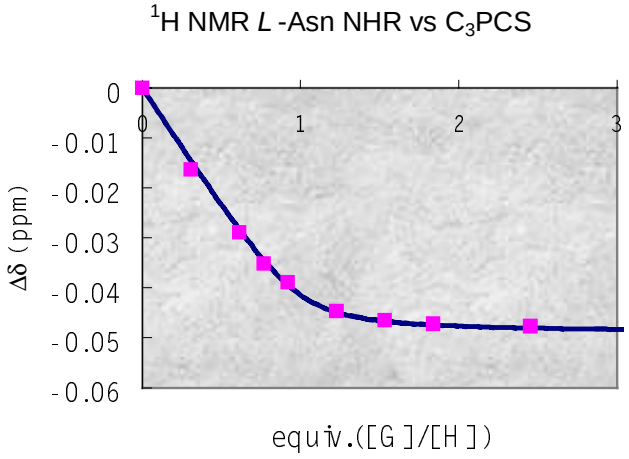
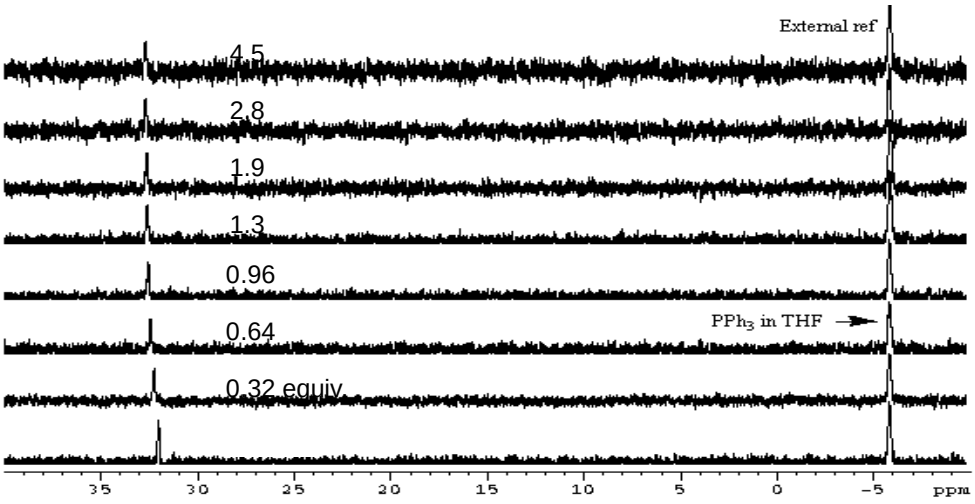


Figure SI6. Stacked plot for ^{31}P NMR titration of **1a** with *L*-Asn-NHR.



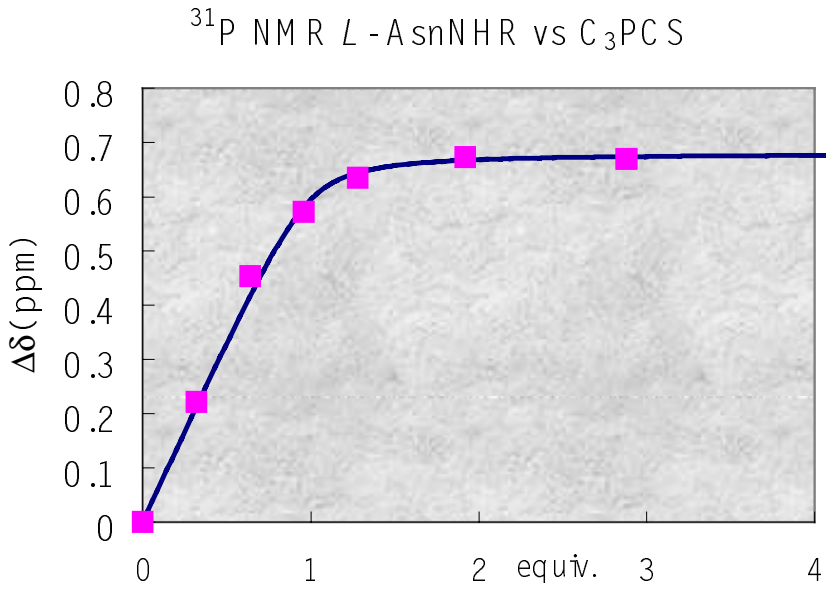


Figure SI7. Job plot for **1a** and D-Asn-NHR.

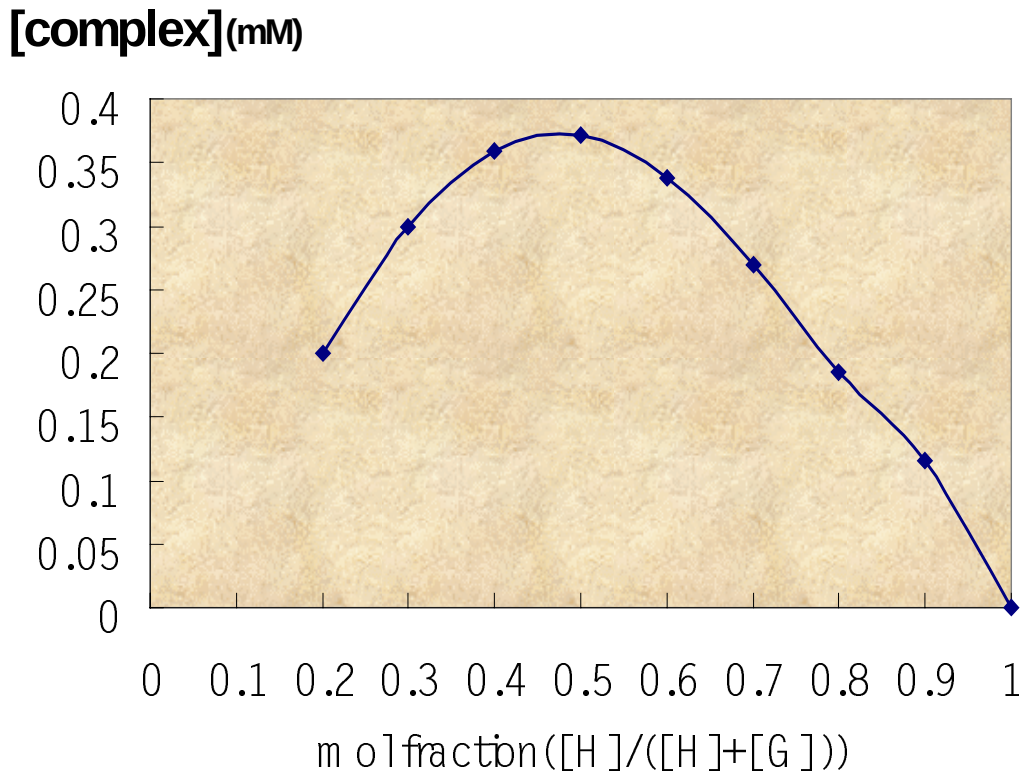
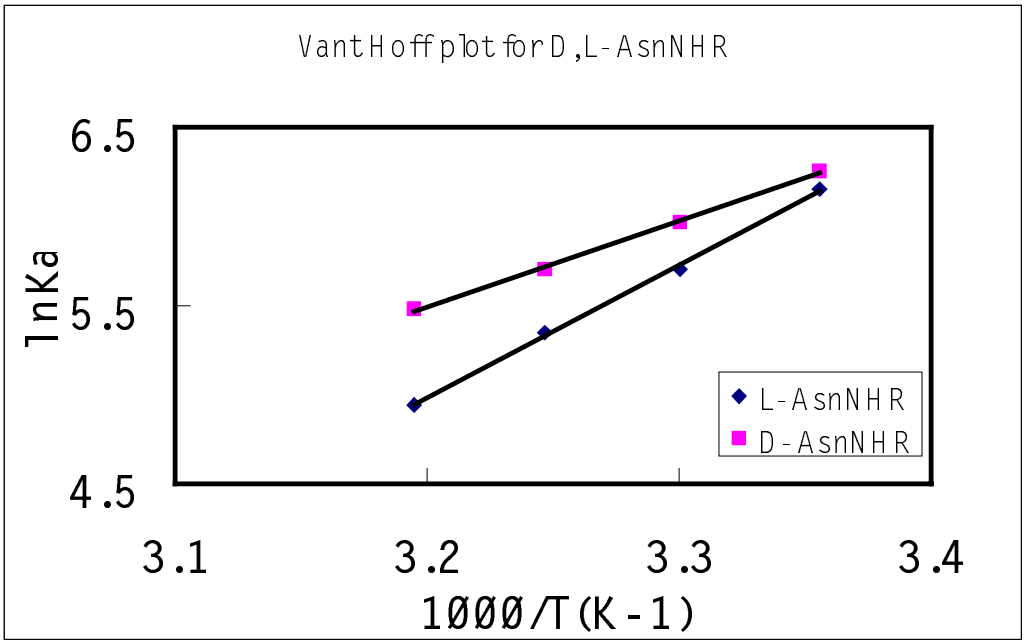


Figure SI8. Van't Hoff plot for *D, L*-AsnNHR in $CD_3OD/CDCl_3$ (1:4, v/v)



Solvent: $CD_3OD/CDCl_3$ (1:4, v/v), [**1a**] = 3 mM. Guest stock solution = 32.5 mM.

	L	**D**
slope	**7.445**	**4.820**
H (kcal/mol)	**-14.79**	**-9.58**
intercept	**-18.84**	**-9.93**
S ($calK^{-1}mol^{-1}$)	**-37.4**	**-19.7**
G(300K) (kcal/mol)	**-3.56**	**-3.66**