Promoting helicity in carbohydrate-containing foldamers through long-range hydrogen bonds

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General: All solvents and reagents were purchased from commercial sources and used without further purification, except for dichloromethane, which was distilled under Ar stream over CaH2. Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-isothiocyanato-β-D-glucopyranoside,1 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate,2 and 2,3,4-tri-O-acetyl-β-D-xylopyranosyl isothiocyanate1a,3 were prepared according to described procedures. Optical rotations were measured at 20 ºC in 1-cm or 1-dm tubes on a Perkin-Elmer 141 MC polarimeter. 1H (and 13C NMR) spectra were recorded at 500 (125.7) MHz with a Bruker 500 DRX instrument. 2D COSY, 1D TOCSY, HMQC and HSQC experiments were used to assist on NMR assignments. Thin-layer chromatography (TLC) was carried out on aluminium sheets coated with Kieselgel 60 F254 (E. Merck), with visualisation by UV light and by charring with 10% H2SO4. Column chromatography was carried out on Silica Gel 60 (E. Merck, 230-400 mesh). FAB mass spectra were obtained with a Kratos MS-80 RFA instrument. The operating conditions were the following: the primary beam consisted of Xe atoms with a maximum energy of 8 keV; the samples were dissolved in thioglycerol, and the positive ions were separated and accelerated over a potential of 7 keV; NaI was added as cationizing agent. In the CIMS spectra, isobutene was added as the reactive gas (500 mA, 8 kV). Elemental analyses were performed at the Instituto de Investigaciones Químicas (Sevilla, Spain).
General procedure for the preparation of monotopic benzylthioureas (1a-c):
To a solution of the corresponding sugar derived isothiocyanate (0.51 mmol) and Et$_3$N (0.46 mmol, 0.9 eq) in CH$_2$Cl$_2$ (5 mL) was added benzylamine hydrochloride (0.46 mmol, 0.9 eq). The mixture was stirred at room temperature until completion (TLC) and concentrated. The resulting residue was chromatographed with the indicated eluent to give the thiourea adduct.

$N'$-Benzyl-2,3,4-tri-$O$-acetyl-$\beta$-D-xylopyranosylthiourea (1a): Reaction time: 5 min. Column chromatography, eluent 1:3 → 2:3 EtOAc-petroleum ether. Yield: 189 mg (97%); $R_f$ = 0.61 (1:1 EtOAc-petroleum ether); $[\alpha]_D = +1.2$ (c 0.8, CH$_2$Cl$_2$); UV (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 256 nm ($\varepsilon_{\text{mm}}$ 13.3); $^1$H NMR (500 MHz, CDCl$_3$, 313 K): $\delta$ = 7.31-7.24 (m, 5 H, Ar), 6.66 (bs, 2 H, NH, N’H), 5.63 (t, 1 H, $J_{1,2,3} = J_{4,5a} = 5.7$ Hz, $J_{4,5b} = 9.3$ Hz, H-3), 4.95 (td, 1 H, $J_{1,2} = J_{1,\text{NH}} = 9.3$ Hz, H-1), 5.29 (t, 1 H, H-2), 4.62 (bs, 2 H, ArCH$_2$), 4.02 (dd, 1 H, $J_{5a,5b} = 11.0$ Hz, H-5a), 3.41 (dd, 1 H, H-5b), 1.99, 1.96 (2 s, 9 H, 3 MeCO); $^1$H NMR (500 MHz, CDCl$_3$, 218 K, rotamer Z,Z): $\delta$ = 7.33-7.17 (m, 5 H, Ar), 6.93 (m, 2 H, NH, N’H), 5.78 (t, 1 H, $J_{1,2} = J_{1,\text{NH}} = 9.2$ Hz, H-1), 5.34 (t, 1 H, H-2, 4.75 (dd, 1 H, $\delta_{\text{H,H}} = 13.9$ Hz, $J_{\text{ArCH}_a,\text{N’H}} = 4.1$ Hz, ArCH$_a$), 4.56 (dd, 1 H, $J_{\text{ArCH}_b,\text{N’H}} = 3.7$ Hz, ArCH$_b$), 4.05 (dd, 1 H, $J_{5a,5b} = 10.9$ Hz, H-5a), 3.46 (t, 1 H, H-5b), 2.18-1.84 (m, 3 MeCO); 13C NMR (125.7 MHz, CDCl$_3$, 313 K): $\delta$ = 182.5 (CS), 171.4-169.7 (CO), 128.9-127.7 (Ar), 83.3 (C-1), 72.2 (C-3), 70.9 (C-2), 69.1 (C-4), 64.1 (C-5), 48.7 (ArCH$_2$), 20.6 (MeCO); CIMS: $m/z$ 425 ([M + H]$^+$). Anal. Calcd for C$_{19}$H$_{24}$N$_2$O$_7$S: C, 53.76; H, 5.70; N, 6.60. Found: C, 54.07; H, 5.50; N, 6.67.

$N'$-Benzyl-2,3,4,6-tetra-$O$-acetyl-$\beta$-D-glucopyranosylthiourea (1b): Reaction time: 5 h. Column chromatography, eluent 1:1 EtOAc-petroleum ether. Yield: 175 mg (77%); $R_f$ = 0.36 (1:1 EtOAc-petroleum ether); $[\alpha]_D = +3.9$ (c 1.0, CHCl$_3$); UV (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 256 nm ($\varepsilon_{\text{mm}}$ 13.7); $^1$H NMR (500 MHz, CDCl$_3$, 313 K): $\delta$ = 7.34-7.26 (m, 5 H, Ar), 6.35 (d, 1 H, $J_{\text{NH,1}} = 7.9$ Hz, NH), 6.20 (bs, 1 H, N’H), 5.62 (t, 1 H, $J_{1,2} = 9.4$ Hz, H-1), 5.33 (t, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3), 5.03 (t, 1 H, $J_{4,5} = 9.4$ Hz, H-4), 4.26 (m, 2 H, ArCH$_a$, ArCH$_b$), 3.97 (dd, 1 H, $J_{5a,5b} = 11.0$ Hz, H-5a), 3.40 (t, 1 H, H-5b), 2.18-1.84 (m, 3 MeCO); $^1$C NMR (125.7 MHz, CDCl$_3$, 313 K): $\delta$ = 182.5 (CS), 171.4-169.7 (CO), 128.9-127.7 (Ar), 83.3 (C-1), 72.2 (C-3), 70.9 (C-2), 69.1 (C-4), 64.1 (C-5), 48.7 (ArCH$_2$), 20.6 (MeCO); CIMS: $m/z$ 425 ([M + H]$^+$). Anal. Calcd for C$_{19}$H$_{24}$N$_2$O$_7$S: C, 53.76; H, 5.70; N, 6.60. Found: C, 54.07; H, 5.50; N, 6.67.
4.93 (t, 1 H, H-2), 4.62 (bs, 2 H, ArCH₂), 4.26 (dd, 1 H, J₆₅,₆₆ = 12.4 Hz, J₅₆₆ = 5.0 Hz, H-6a), 4.09 (dd, 1 H, J₅₆₆ = 2.3 Hz, H-6b), 3.83 (ddd, 1 H, H-5), 2.02-1.99 (3 s, 12 H, 4 MeCO); ¹H NMR (500 MHz, CDCl₃, 215 K, rotamer Z,Z): δ = 7.38-7.19 (m, 5 H, Ar), 7.05 (bs, 1 H, N’H), 6.86 (d, 1 H, J₉₈,₁ = 9.3 Hz, NH), 5.81 (t, 1 H, J₂₃ = 9.3 Hz, H-3), 5.14 (t, 1 H, J₄₅ = 9.3 Hz, H-4), 4.98 (t, 1 H, H-2), 4.68 (dd, 1 H, J₁₂,₁ = 14.8 Hz, J₂₃,₄ = 4.4 Hz, ArCH₂), 4.64 (m, 1 H, ArCH₂), 4.30 (m, 1 H, H-6a), 3.83 (m, 1 H, H-5), 3.82 (da, 1 H, J₆₅,₆₆ = 12.7 Hz, H-6b), 2.05-1.92 (m, 12 H, 4 MeCO); ¹H NMR (500 MHz, CDCl₃, 218 K, rotamer Z,E): δ = 7.38-7.19 (m, 5 H, Ar), 7.05 (bs, 1 H, N’H), 6.70 (d, 1 H, J₉₈,₁ = 9.5 Hz, NH), 5.54 (t, 1 H, J₁₂ = 9.5 Hz, H-1), 5.34 (t, 1 H, J₂₃ = J₃₄ = 9.5 Hz, H-3), 5.06 (t, 1 H, J₄₅ = 9.5 Hz, H-4), 4.91 (t, 1 H, H-2), 4.30 (m, 1 H, H-6a), 4.23 (dd, 1 H, J₂₃,₁ = 14.2 Hz, J₃₄,₅ = 5.1 Hz, ArCH₂), 4.13 (dd, 1 H, J₆₅,₆₆ = 5.2 Hz, ArCH₂), 3.99 (bd, 1 H, J₆₅,₆₆ = 12.0 Hz, H-6b), 3.81 (m, 1 H, H-5), 2.05-1.92 (m, 12 H, 4 MeCO); ¹³C NMR (125.7 MHz, CDCl₃, 323 K): δ = 183.7 (CS), 171.3-169.5 (CO), 137.0-127.8 (Ar), 83.1 (C-1), 73.7 (C-3), 72.9 (C-5), 71.0 (C-2), 68.7 (C-4), 61.9 (C-6), 48.7 (ArCH₂), 20.6-20.4 (MeCO); CIMS: m/z 497 ([M + H]⁺). Anal. Calcd for C₂₂H₂₈N₂O₉S: C, 53.22; H, 5.68; N, 5.64. Found: C, 53.31; H, 5.38; N, 5.57.

Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-(N’-benzylthioureido)-β-D-glucopyranoside (1c): Reaction time: 5 h. Column chromatography, eluent 1:1 EtOAc-petroleum ether). Yield: 213 mg (99%); Rf = 0.60 (2:1 EtOAc-petroleum ether); [α]D = +13.9 (c 1.0, CH₂Cl₂); UV (CH₂Cl₂): λₘₐₓ 252 nm (εₘₐₓ 12.4); ¹H NMR (500 MHz, CDCl₃, 313 K): δ = 7.32-7.26 (m, 5 H, Ar), 6.56 (t, 1 H, J₆₅,₆₆ = 9.0 Hz, NH), 6.14 (bs, 1 H, N’H), 5.14 (t, 1 H, J₂₃ = J₃₄ = 9.6 Hz, H-3), 4.82 (dd, 1 H, J₁₂ = 8.0 Hz, H-2), 4.77 (t, 1 H, J₄₅ = 9.5 Hz, H-4), 4.59 (bs, 2 H, ArCH₂), 4.33 (d, 1 H, H-1), 3.92 (ddd, 1 H, J₆₅,₆₆ = 13.4 Hz, J₅₆₅,₆₆ = 4.7 Hz, H-6a), 3.63 (ddd, 1 H, J₅₆₅,₆₆ = 6.1 Hz, H-5), 3.60 (dd, 1 H, H-6b), 3.31 (s, 3 H, OMe), 2.03-1.96 (3 s, 9 H, 3 MeCO); ¹H NMR (500 MHz, CDCl₃, 223 K, rotamer Z,E): δ = 7.42-7.24 (m, 5 H, Ar), 7.10 (bs, 1 H, N’H), 5.92 (bs, 1 H, NH), 5.07 (t, 1 H, J₂₃ = J₃₄ = 9.5 Hz, H-3), 4.70 (t, 1 H, J₁₂ = 9.5 Hz, H-2), 4.50 (t, 1 H, J₄₅ = 9.5 Hz, H-4), 4.36 (m, 2 H, ArCH₂), 4.16 (d, 1 H, H-1), 3.96 (dd, 1 H, J₆₅,₆₆ = 13.5 Hz, J₅₆₅,₆₆ = 5.5 Hz, H-6a), 3.64 (dt, 1 H, J₅₆₅,₆₆ = 6.0 Hz, H-6b), 3.54 (ddd, 1 H, H-5), 3.22 (s, 3 H, OMe), 2.06-1.95 (m, 9 H, 3 MeCO); ¹H NMR (500 MHz, CDCl₃, 223 K, rotamer E,Z): δ = 7.42-7.24 (m, 5 H, Ar), 7.07 (bs, 1 H, NH), 6.99 (bs, 1 H, N’H), 5.19 (t, 1 H, J₂₃ = J₃₄ = 9.5 Hz, H-3), 5.00 (t, 1 H, J₄₅ = 9.5 Hz, H-4), 4.87 (dd, 1
H, \( J_{1,2} = 9.5 \text{ Hz, H-2} \), 4.83 (m, 1 H, ArCHa), 4.62 (dd, 1 H, \(^2J_{H,H} = 14.5 \text{ Hz, J}_{\text{ArCHb, N'H}} = 3.5 \text{ Hz, ArCHb}} \), 4.30 (d, 1 H, H-1), 3.58 (m, 1 H, H-5), 3.39 (dd, 1 H, \( J_{6a,6b} = 13.4 \text{ Hz, H-6a} \)), 3.30 (dd, 1 H, H-6b), 3.03 (s, 3 H, OMe), 2.06-1.95 (m, 9 H, 3 MeCO); \(^1H\) NMR (500 MHz, CDCl\(_3\), 223 K, rotamer ZZ) \( \delta = 7.42-7.24 \text{ (m, 5 H, Ar), 7.06 (bs, 1 H, N'H), 6.87 (bs, 1 H, NH), 5.17 (t, 1 H, \( J_{2,3} = J_{3,4} = 9.5 \text{ Hz, H-3} \)), 4.89 (t, 1 H, \( J_{4,5} = 9.5 \text{ Hz, H-4} \)), 4.87 (t, 1 H, \( J_{1,2} = 9.5 \text{ Hz, H-2} \)), 4.83 (m, 1 H, ArCHa), 4.67 (m, 1 H, ArCHb), 4.34 (d, 1 H, H-1), 4.04 (da, 1 H, \( J_{6a,6b} = 13.4 \text{ Hz, H-6a} \)), 3.80 (m, 1 H, H-5), 3.76 (bd, 1 H, H-6b), 3.43 (s, 3 H, OMe), 2.06-1.95 (m, 9 H, 3 MeCO); \(^13C\) NMR (125.7 MHz, CDCl\(_3\), 313 K): \( \delta = 183.3 \text{ (CS), 170.0-169.4 (CO), 136.7-127.4 (Ar), 101.7 (C-1), 72.7 (C-5), 72.6 (C-3), 71.2 (C-2), 69.3 (C-4), 57.0 (OMe), 48.4 (ArCH_2), 45.1 (C-6), 20.7-20.5 (MeCO); FABMS: m/z 491 ([M + Na])\(^+\), 469 ([M + H])\(^+\). Anal. Calcd for C\(_{21}\)H\(_{28}\)N\(_2\)O\(_8\)S: C, 53.83; H, 6.02; N, 5.98. Found: C, 53.69; H, 5.94; N, 5.79.

**General procedure for the preparation of ditopic m-xylylene bis(thioureas) (2a-c):** To a solution of the corresponding sugar derived isothiocyanate (0.36 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added 1,3-bis(aminomethyl)benzene (0.18 mmol). The mixture was stirred at room temperature until completion (TLC) and concentrated. The resulting residue was chromatographed with the indicated eluent to give the bis(thiourea) adduct.

**1,3-Bis-[N\(^\prime\)-\((2,3,4\text{-tri-}O\text{-acetyl-}\beta\text{-}D\text{-xylopyranosyl})\text{thioureidomethyl\]benzene (2a):**

Reaction time: 10 min. Column chromatography, eluent 1:1 → 2:1 EtOAc-petroleum ether. Yield: 77.6 mg (56%); \( R_f = 0.47 \) (2:1 EtOAc-petroleum ether); \([\alpha]_D = -23.0 \) (c 0.8, CH\(_2\)Cl\(_2\)); UV (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} 255 \text{ nm (} \varepsilon_{\text{max}} 31.5\text{); } \)\(^1H\) NMR (500 MHz, CDCl\(_3\), 313 K): \( \delta = 7.26-6.99 \text{ (m, 4 H, Ar), 7.09 (bs, 2 H, NH), 6.88 (bs, 2 H, N'H), 5.70 (t, 2 H, \( J_{1,2} = J_{1,\text{N'H}} = 9.4 \text{ Hz, H-1} \)), 5.31 (t, 2 H, \( J_{2,3} = J_{3,4} = 9.4 \text{ Hz, H-3} \)), 4.96 (ddd, 2 H, \( J_{4,5b} = 11.0 \text{ Hz, J}_{4,5a} = 5.7 \text{ Hz, H-4} \)), 4.94 (t, 2 H, H-2), 4.62 (bs, 4 H, ArCH\(_2\)), 4.01 (dd, 2 H, \( J_{5a,5b} = 11.0 \text{ Hz, H-5a} \)), 3.42 (t, 2 H, H-5b), 2.02-1.96 (3 s, 18 H, 6 MeCO); \(^13C\) NMR (125.7 MHz, CDCl\(_3\), 313 K): \( \delta = 183.6 \text{ (CS), 171.7-169.7 (CO), 129.2-126.2 (Ar), 83.3 (C-1), 72.3 (C-3), 71.4 (C-2), 69.0 (C-4), 64.2 (C-5), 48.2 (ArCH\(_2\)), 20.6 (MeCO); CIMS: m/z 771 ([M + H])\(^+\). Anal. Calcd for C\(_{32}\)H\(_{28}\)N\(_2\)O\(_8\)S: C, 53.82; H, 6.02; N, 5.98. Found: C, 53.69; H, 5.94; N, 5.79.

**1,3-Bis-[N\(^\prime\)-\((methyl \ 2,3,4\text{-tri-}O\text{-acetyl-}\beta\text{-}D\text{-glucopyranosid-6-yl})\text{thioureidomethyl\]benzene (2c).**

Time of reaction: 5 min; column chromatography, eluent 2:1 EtOAc-petroleum ether → EtOAc; Yield: 137 mg (89%); \( R_f = 0.45 \) (4:1 EtOAc-petroleum ether); \([\alpha]_D = +0.3 \) (c 1.0, CH\(_2\)Cl\(_2\)); UV (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} 251 \text{ nm (} \varepsilon_{\text{max}} 20.6\text{); } \)\(^1H\) NMR (500 MHz, CDCl\(_3\), 323 K): \( \delta = 7.38-7.28 \text{ (m, 4 H, Ar), 7.03 (bs, 2 H, NH), 6.28 (bs, 2 H, N'H), 5.07 (t, 2 H, \( J_{2,3} = J_{3,4} = 9.5 \text{ Hz, H-3} \)), 4.76 (m, 2 H, ArCH\(_a\)),

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4.62 (m, 4 H, H-2, ArCH\textsubscript{b}), 4.50 (m, 2 H, H-4), 4.31 (d, 2 H, J\textsubscript{1,2} = 8.0 Hz, H-1), 4.09 (m, 2 H, H-6a), 3.68 (m, 2 H, H-6b), 3.56 (m, 2 H, J=J\textsubscript{4,5} = 9.5 Hz, H-5), 3.40 (s, 6 H, OMe), 2.04-1.95 (3 s, 18 H, 6 MeCO); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 223 K, P-helix): δ = 7.45-7.24 (m, 4 H, Ar), 7.33 (bs, 2 H, NH), 7.12 (m, 2 H, N’H), 5.41 (dd, 2 H, J\textsubscript{H,H} = 15.5 Hz, J\textsubscript{ArCH\textsubscript{a},NH} = 5.0 Hz, ArCH\textsubscript{a}), 4.93 (t, 2 H, J\textsubscript{2,3} = J\textsubscript{3,4} = 10.0 Hz, H-3), 4.68 (m, 2 H, ArCH\textsubscript{b}), 4.46 (dd, 2 H, J\textsubscript{6a,6b} = 17.0 Hz, J\textsubscript{5,6a} = 7.0 Hz, H-6a), 4.36 (dd, 2 H, J\textsubscript{5,6b} = 3.5 Hz, H-6b), 4.13 (d, 2 H, J\textsubscript{1,2} = 10.0 Hz, H-1), 4.05 (t, 2 H, H-2), 3.81 (t, 2 H, H-4), 3.47 (ddd, 2 H, H-5), 3.47-3.40 (s, 6 H, OMe), 2.09-1.98 (3 s, 18 H, 6 MeCO); \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}, 323 K): δ = 183.6 (CS), 170.1-169.6 (CO), 138.2-124.4 (Ar), 101.8 (C-1), 72.8 (C-3), 72.6 (C-5), 71.4 (C-2), 68.6 (C-4), 57.2 (OMe), 47.6 (ArCH\textsubscript{2}), 44.4 (C-6), 20.9-20.4 (MeCO); FABMS: m/z 881 ([M + Na] +), 859 ([M + H] +).

Anal. Calcd for C\textsubscript{36}H\textsubscript{50}N\textsubscript{4}O\textsubscript{16}S\textsubscript{2}: C, 50.34; H, 5.87; N, 6.52. Found: C, 50.13; H, 5.66; N, 6.43.

1,3-Bis-\[N’-(2,3,4,6-tetra-O-acetyl-\beta-D-glucopyranosyl)thioureidomethyl\]benzene (2e): Time of reaction: 20 min; column chromatography, eluent 1:1 EtOAc-petroleum ether; Yield: 89 mg (54%); R\textsubscript{f} = 0.35 (1:1 EtOAc-petroleum ether); [α]\textsubscript{D} = +2.2 (c 1.1, CH\textsubscript{2}Cl\textsubscript{2}); UV (CH\textsubscript{2}Cl\textsubscript{2}): λ\textsubscript{max} 254 nm (ε\textsubscript{MM} 35.3); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 313 K): δ = 8.40 (bs, 2 H, NH), 7.26 (t, 1 H, J\textsubscript{H,H} = 7.6 Hz, Ar), 7.13 (d, 2 H, J\textsubscript{H,H} = 7.6 Hz, Ar), 6.90 (s, 1 H, Ar), 6.85 (d, 2 H, J\textsuperscript{N’H,1} = 9.0 Hz, N’H), 5.78 (t, 2 H, J\textsubscript{1,2} = 9.0 Hz, H-1), 5.36 (t, 2 H, J\textsubscript{2,3} = J\textsubscript{3,4} = 9.0 Hz, H-3), 5.35 (m, 2 H, ArCH\textsubscript{a}), 5.17 (t, 1 H, J\textsubscript{4,5} = 9.0 Hz, H-4), 5.10 (m, 2 H, H-6a), 5.06 (t, 1 H, H-2), 4.35 (d, 2 H, J\textsubscript{H,H} = 15.6 Hz, ArCH\textsubscript{b}), 3.87 (ddd, 1 H, J\textsubscript{5,6a} = 8.6 Hz, J\textsubscript{5,6b} = 2.3 Hz, H-5), 3.81 (dd, 1 H, J\textsubscript{6a,6b} = 11.0 Hz, H-6b), 2.06-2.01 (4 s, 24 H, 8 MeCO); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 223 K, P-helix): δ = 8.47 (bs, 2 H, NH), 7.24-6.70 (m, 4 H, Ar), 6.99 (d, 2 H, J\textsuperscript{N’H,1} = 9.3 Hz, N’H), 5.72 (t, 2 H, J\textsubscript{1,2} = 9.3 Hz, H-1), 5.33 (t, 2 H, J\textsubscript{2,3} = J\textsubscript{3,4} = 9.3 Hz, H-3), 5.23 (m, 2 H, ArCH\textsubscript{a}), 5.13 (t, 1 H, J\textsubscript{4,5} = 9.3 Hz, H-4), 5.08 (m, 2 H, H-6a), 5.00 (t, 1 H, H-2), 4.39 (bd, 2 H, J\textsubscript{H,H} = 14.4 Hz, ArCH\textsubscript{b}), 3.82 (bt, 1 H, J\textsubscript{5,6a} = 9.3 Hz, H-5), 3.75 (bd, 1 H, J\textsubscript{6a,6b} = 11.6 Hz, H-6b), 2.18-1.87 (4 s, 24 H, 8 MeCO); \textsuperscript{13}C
NMR (125.7 MHz, CDCl$_3$, 313 K): $\delta = 185.1$ (CS), 170.4-168.9 (CO), 138.5-125.5 (Ar), 82.7 (C-1), 74.6 (C-5), 73.9 (C-3), 71.1 (C-2), 69.4 (C-4), 62.0 (C-6), 47.1 (ArCH$_2$), 21.0-20.2 (MeCO); FABMS: $m/z$ 937 ([M + Na$^+$]). Anal. Calcd for C$_{38}$H$_{50}$N$_4$O$_{18}$S$_2$: C, 49.88; H, 5.51; N, 6.12. Found: C, 49.61; H, 5.30; N, 6.03.

**Titration experiment:** The association constants ($K_{as}$) were determined in CDCl$_3$ at 298 K by measuring the proton chemical shift changes of solutions of the corresponding receptor upon increasing amounts of tetrabutilammonium benzoate as the guest. In a typical titration experiment, a 5 mM solution of host in CDCl$_3$ was prepared, a 500-µL aliquot was transferred to a 5-mm NMR tube, and the initial NMR spectrum was recorded. A solution (25-50 mM) of the guest in the previous host solution was prepared and then added via microsyringe initially in 10 µL portions. These amounts were increased until 90-100% complexation of the host. The $^1$H NMR spectrum of each solution was recorded and the chemical shift of the diagnostic signals obtained at 10-15 different host-guest concentration ratios were used in an iterative least-squares fitting procedure.

**Job’s Plots:** Stock solutions of host and guest were prepared (5 mM each) and mixed into 5-mm NMR tubes to give the following volume ratios: 6:0, 5:1, 4:2, 3:3, 2.5:3.5, 2:4, 1.5:4.5, 1:5. $^1$H NMR spectra of all samples were obtained and the concentration of complex ([C]) for each solution was determined from the equation

$$[C] = [H]_0(\delta_{obs} - \delta_0)/(\delta_{max} - \delta_0)$$

**References**


**Figure S1.** Variable temperature $^1$H NMR spectra for 1a (500 MHz, CDCl$_3$).

**Figure S2.** Variable temperature $^1$H NMR spectra for 2a (500 MHz, CDCl$_3$).
Figure S3. Variable temperature $^1$H NMR spectra for $1b$ (500 MHz, CDCl$_3$).

Figure S4. Variable temperature $^1$H NMR spectra for $2b$ (500 MHz, CDCl$_3$).
Figure S5. Variable temperature $^1$H NMR spectra for 1c (500 MHz, CDCl$_3$).

Figure S6. Variable temperature $^1$H NMR spectra for 2c (500 MHz, CDCl$_3$). The Notation A and B in the upper spectrum correspond to the $P$- and $M$-helices, respectively.