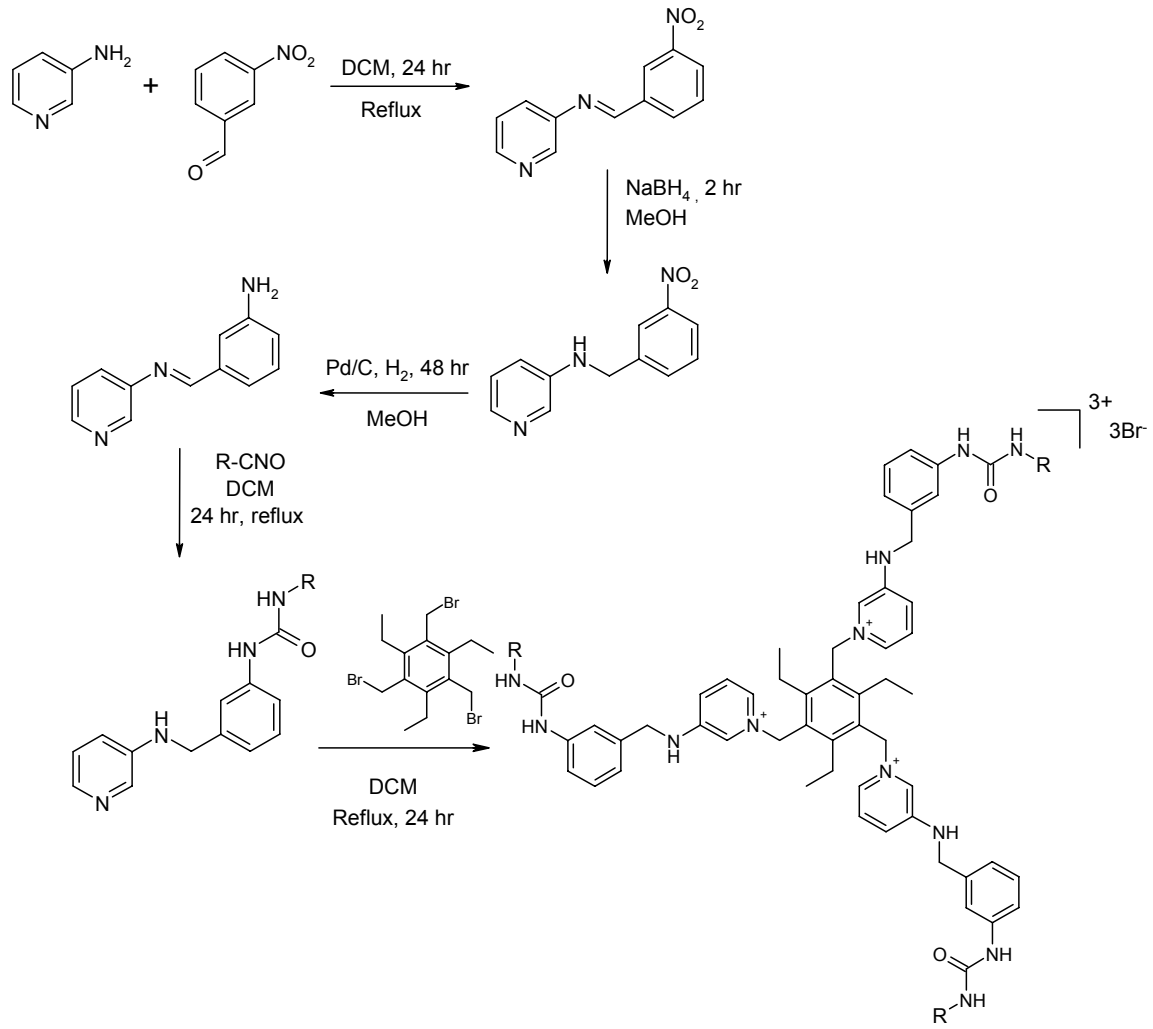
# Supplementary data

## Contents



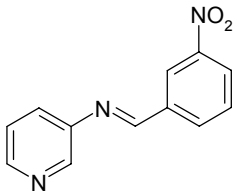

**Scheme 1:** Synthesis of the new receptor.

**Materials and Synthesis.** All purchased starting materials were of commercial quality and were used without further purification. Solvents were used as obtained unless mentioned otherwise. Dichloromethane was dried using a calcium hydride still and methanol was dried using $Al/I_2$. Reactions were carried out under air unless specifically mentioned, although no air sensitivity was observed for any of the products obtained.

**Analyses.** $^{1}H$ and $^{13}C$ NMR spectra were run at room temperature using a Bruker AV-400 spectrometer, operating at 400 and 100 MHz respectively. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as an internal reference. Coupling constants (J) are reported in Hertz (Hz). Multiplicities are

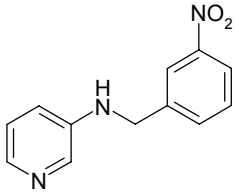
reported as singlet (s), doublet (d), doublet of doublets (dd), doublets of doublets of doublets (ddd), multiplets (m) or broad signals (b). Mass spectra were run at using a Micromass Autospec operating in EI or ES mode at the University of Durham or a Jeol AX505W in FAB mode in a thioglycerol or nitrobenzyl matrix. Micro-analyses for C, H and N were recorded at either the University of Durham or the University of North London. IR spectra were collected on a Perkin-Elmer Paragon 100 FT-IR spectrometer as nujol mulls. Peaks are reported in wavenumbers ($cm^{-1}$) and are described as weak (w), medium (m) and strong (s).

## (3-Nitro-benzylidene)-pyridin-3-yl-amine



3-Aminopyridine (0.47 g, 5.00 mmol) and 3-nitrobenzaldehyde (0.75 g, 4.90 mmol) were dissolved in dichloromethane (50 ml). The solution was placed under reflux for 24 hours. After this time the mixture was left to cool before filtering (to remove protonated 3-aminopyridine). The solvent was removed under reduced pressure to yield a pure, orange solid (0.90 g, 3.97 mmol, 81 %). $^{1}$H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.71 (1H, t, J = 1.8, ArH); 8.50 (1H, s, CH); 8.47 (2H, m, ArH); 8.30 (1H, ddd, J = 8.0, 2.3, 1.1, ArH); 8.20 (1H, m, ArH); 7.63 (1H, t, J = 7.8, ArH); 7.50 (1H, ddd, J = 8.2, 2.4, 1.9, ArH); 7.30 (1H, dd, J = 8.0, 4.8, ArH). $^{13}$C{$^{1}$H}-NMR ($CDCl_3$, 100 MHz, δ / ppm): 158.9, 148.8, 148.0, 146.7, 142.6, 137.4, 134.3, 129.9, 127.9, 126.1, 123.8, 123.7. EI-MS: *m/z* = 227 $[M]^+$. Anal: Calculated for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49 % Found: C, 63.14; H, 4.02; N, 18.29 %. IR (ν / $cm^{-1}$): 1535 (s), 1738 (s)

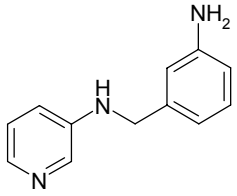
## (3-Nitro-benzyl)-pyridin-3-yl-amine



(3-Nitro-benzylidene)-pyridin-3-yl-amine (0.26 g, 1.15 mmol) was dissolved in methanol (75 ml) in a 250 ml flask (as a precaution due to effervescence during the reaction). To this solution was carefully added an excess of $NaBH_4$ (0.22 g, 5.87 mmol) with constant stirring. Once all of the borohydride had been added the solution was left stirring for a further two hours. After this time, any remaining borohydride was neutralised with hydrochloric acid. The product was then extracted into dichloromethane. The DCM solution was dried over magnesium sulphate and the solvent was removed under reduced pressure to yield the pure product as a yellow solid (0.22 g, 0.94 mmol, 82 %). $^{1}$H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.15 (1H, br, ArH); 8.04 (1H, d, J = 8.0, ArH); 7.99 (1H, d, J = 2.8, ArH); 7.90 (1H, dd, J =

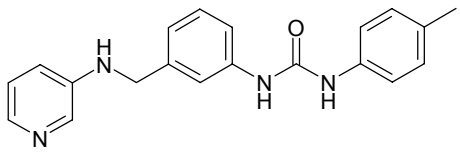
4.6, 1.0, ArH); 7.62 (1H, d, J = 7.6, ArH), 7.44 (1H, t, J = 7.8, ArH), 7.00 (1H, dd, J = 8.4, 4.8, ArH); 6.78 (1H, ddd, J = 8.4, 2.8, 1.2, ArH); 4.61 (1H, b, NH); 4.41 (2H, s, $CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100 MHz, δ / ppm): 148.7, 143.5, 141.1, 139.2, 135.9, 133.1, 129.8, 123.9, 122.1, 119.0, 47.1. EI-MS: *m/z* = 229 $[M]^+$ Anal: Calculated for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33 % Found: C, 62.73; H, 4.89; N, 18.49 %. IR (ν / $cm^{-1}$): 1530 (s), 3250 (w).

### (3-Amino-benzyl)-pyridin-3-yl-amine



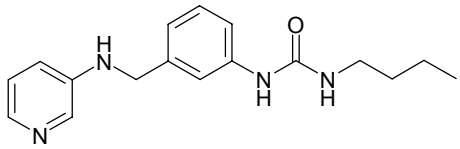

(3-Nitro-benzyl)-pyridin-3-yl-amine (3.14 g, 13.71 mmol) was dissolved in methanol (75 ml). To this solution was added 1 % equivalent of 10 % Pd/C catalyst (1 % w.r.t moles of (3-Nitro-benzyl)-pyridin-3-yl-amine and Pd). The mixture was stirred for 48 hours in a hydrogen atmosphere under a slight initial pressure. After this time the catalyst was removed by filtration through celite. The solvent was removed under reduced pressure to yield the product as a brown oil (2.57 g, 12.91 mmol, 94 %) which was found to be suitable for use in subsequent reactions without further purification. $^1H$-NMR (DMSO-$d_6$, 400 MHz, δ / ppm, J / Hz): 7.96 (1H, d, J = 2.2, ArH); 7.73 (1H, d, J = 4.4, ArH), 7.02 (1H, dd, J = 8.2, 4.5, ArH); 6.96 (1H, t, J = 7.7, ArH); 6.85 (1H, d, J = 8.1, ArH); 6.56 (1H, s, ArH); 6.49 (1H, d, J = 7.4, ArH); 6.43 (2H, m, ArH & NH) 5.04 (2H, b, $NH_2$)**;** 4.12 (2H, d, J = 5.7, $CH_2$). $^{13}C\{^1H\}$-NMR (DMSO-$d_6$, 100 MHz, δ / ppm): 136.6, 135.4, 128.8, 123.5, 119.7, 117.6, 114.6, 112.5, 112.4, 46.3. EI-MS: *m/z* = 199 $[M]^+$ Anal: Calculated for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58; N, 21.09 %. Found: C, 71.78; H, 6.44; N, 21.54 %. IR (ν / $cm^{-1}$): 3192 (w), 3400 (m).

### 1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-*p*-tolyl-urea



(3-Nitro-benzyl)-pyridin-3-yl-amine (2.37 g, 11.90 mmol) and *p*-tolylisocyanate (1.59 g, 11.93 mmol) were dissolved in dry dichloromethane (75 ml). The resulting solution was placed under reflux for 24 hours, during which time a precipitate formed. The mixture was cooled and the precipitate was collected by filtration and washed with dichloromethane. The solid was found to be the desired product, with some isocyanate contaminant (3.70 g, 11.10 mmol, 93 %). $^{1}$H-NMR (DMSO-$d_6$, 400 MHz, δ / ppm, J / Hz): 8.65 (1H, s, NH); 8.50 (1H, s, NH); 8.47 (1H, d, J = 2.4, ArH); 8.38 (2H, m, ArH); 7.66 (1H, m, ArH); 7.31 – 7.39 (6H, m, ArH); 7.19 (1H, t, J = 8.0, NH), 7.06 (3H, m, ArH); 6.83 (1H, d, J = 7.8, ArH); 4.95 (2H, b, $CH_2$); 2.23 (3H, s, $CH_3$). $^{13}$C{$^{1}$H}-NMR (DMSO-$d_6$, 100 MHz, δ / ppm): 154.8, 152.4, 148.3, 146.6, 139.9, 138.8, 137.1, 134.4, 131.2, 130.6, 129.1, 128.7, 124.0, 120.8, 120.5, 118.3, 117.0, 116.7, 52.2, 20.3. EI-MS: *m/z* = 332 $[M]^+$. Anal: Calculated for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.85 %. Found: C, 71.23; H, 5.79; N, 15.34 %. IR (ν / $cm^{-1}$): 1684(s), 3266 (m), 3329 (m).

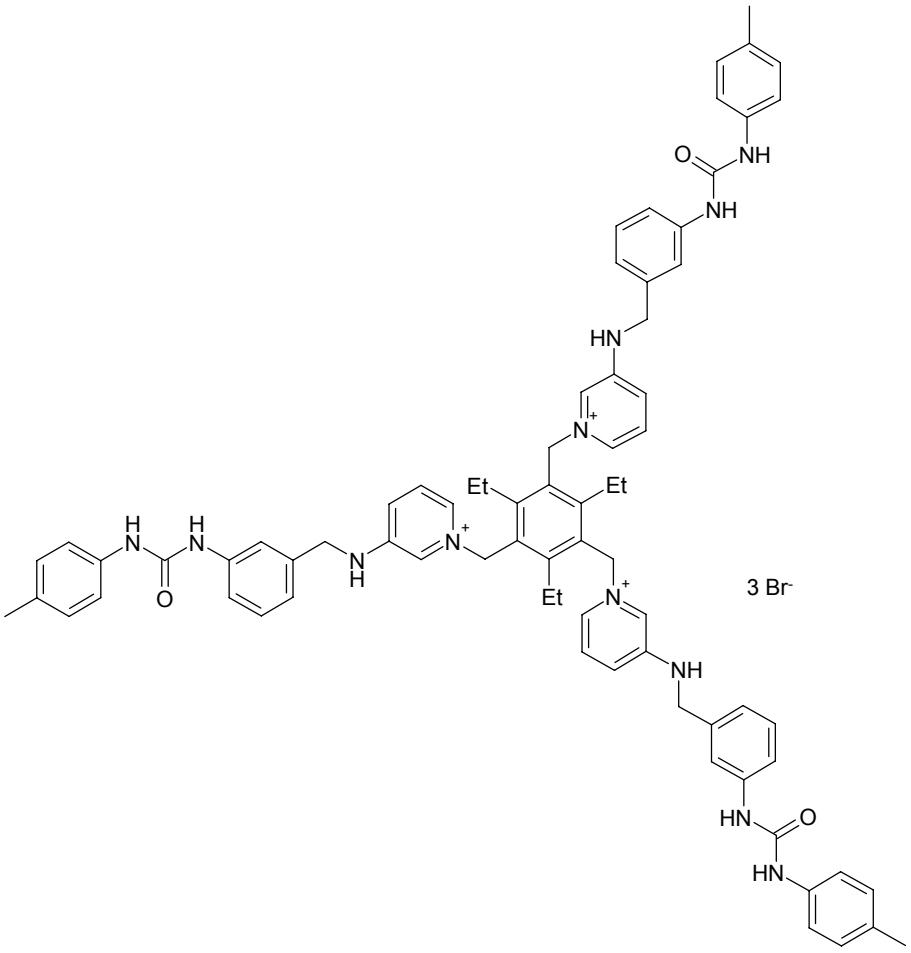
**1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-butyl-urea**




(3-Nitro-benzyl)-pyridin-3-yl-amine (3.62 g, 18.19 mmol) and *n*-butylisocyanate (1.81 g, 18.28 mmol) were dissolved in dry dichloromethane (75 ml). The resulting solution was placed under reflux for 24 hours. After this time the reaction mixture was cooled and the solvent was removed under reduced pressure to yield a crude, brown oil. The oil was re-dissolved in dichloromethane (50 ml) and placed in a freezer (-30 °C) for three days. After this time a pale beige precipitate was collected by filtration and washed with cold dichloromethane to yield the desired pure product (1.61 g, 5.39 mmol, 30 %). $^{1}$H-NMR (DMSO-$d_6$, 400 MHz, δ / ppm, J / Hz): 8.37 (1H, s, NH); 7.96 (1H, d, J = 2.8, ArH); 7.73 (1H, d, J = 4.4, ArH); 7.31 (2H, m, ArH); 7.16 (1H, t, J = 7.8, ArH); 7.03 (1H, dd, J = 8.4, 4.8, ArH); 6.85 (2H, m, ArH); 6.49 (1H, t, J = 6.0, NH); 6.06 (1H, t, J = 5.6, NH); 4.22 (2H, d, J = 6.0, $CH_2$); 3.06 (2H, m, $CH_2$); 1.38 (2H, m, $CH_2$); 1.29 (2H, m, $CH_2$); 0.88 (3H, t, J = 7.4, $CH_3$). $^{13}$C{$^{1}$H}-NMR (DMSO-$d_6$, 100 MHz, δ / ppm): 155.8, 145.4, 141.4, 140.8, 137.5, 136.1, 129.3, 124.2, 120.4, 118.3, 116.7, 46.8, 32.6, 20.2, 14.4. EI-MS: *m/z* = 298

$[M]^+$. Anal: Calculated for $C_{17}H_{22}N_4O$: C, 68.43; H, 7.43; N, 18.78 %. Found: C, 67.74; H, 7.41; N, 18.42 %. IR ($\nu$ / $cm^{-1}$): 1638 (s), 3256 (w), 3331 (w).

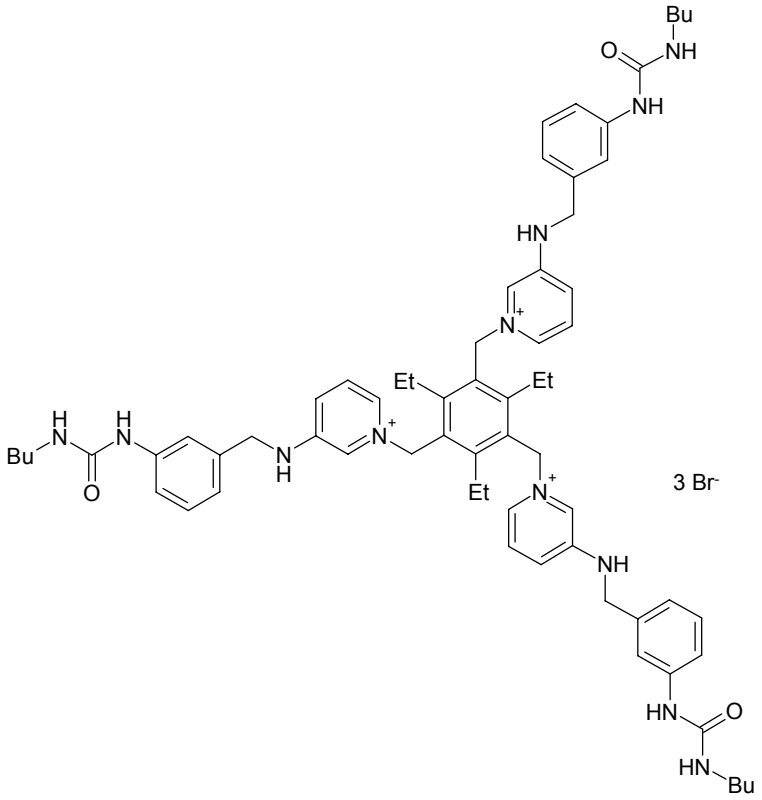
**Tris(1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-*p*-tolyl-urea), Bromide Salt**




1,3,5-tris(bromomethyl)-2,4,6-triethyl benzene[1] (0.30 g, 0.68 mmol) and 1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-*p*-tolyl-urea (0.68 g, 2.05 mmol) were dissolved in THF (50 ml) and the resulting solution was placed under reflux. The solution was observed to turn cloudy within 30 minutes, but was left for 24 hours to ensure the reaction went to completeness. The solution was cooled and filtered to yield the desired product (0.87 g, 0.59 mmol, 88 %). $^1$H-NMR (DMSO-$d_6$, 400 MHz, $\delta$ / ppm, J / Hz): 8.98 (3H, s, NH); 8.89 (3H, s, NH); 8.24 (3H, s, ArH); 8.10 (3H, d, J = 4.4, NH); 8.01 (3H, b, ArH); 7.74 (3H, dd, J = 8.6, 6.0, ArH); 7.64 (3H, d, J = 8.4, ArH); 7.53 (3H, s, ArH); 7.32 (9H, m, ArH); 7.21 (3H, t, J = 7.8, ArH); 7.07 (6H, d, J = 8.3, ArH); 6.93 (3H, d, J = 7.4, ArH); 5.86 (6H, s, $CH_2$); 4.38 (6H, d, J = 4.4, $CH_2$); 2.61 (6H, b, $CH_2$); 1.75 (6H, m, $CH_2$); 0.72 (6H, b, $CH_2$). $ES^+$-MS: *m/z* = 1357 $[M-Br]^+$,

639 $[M-2Br]^+$. Anal: Calculated for $C_{75}H_{81}N_{12}O_3Br_3$: C, 62.59; H, 5.63; N, 11.68 %. Found: C, 62.98; H, 5.68; N, 11.26 %.

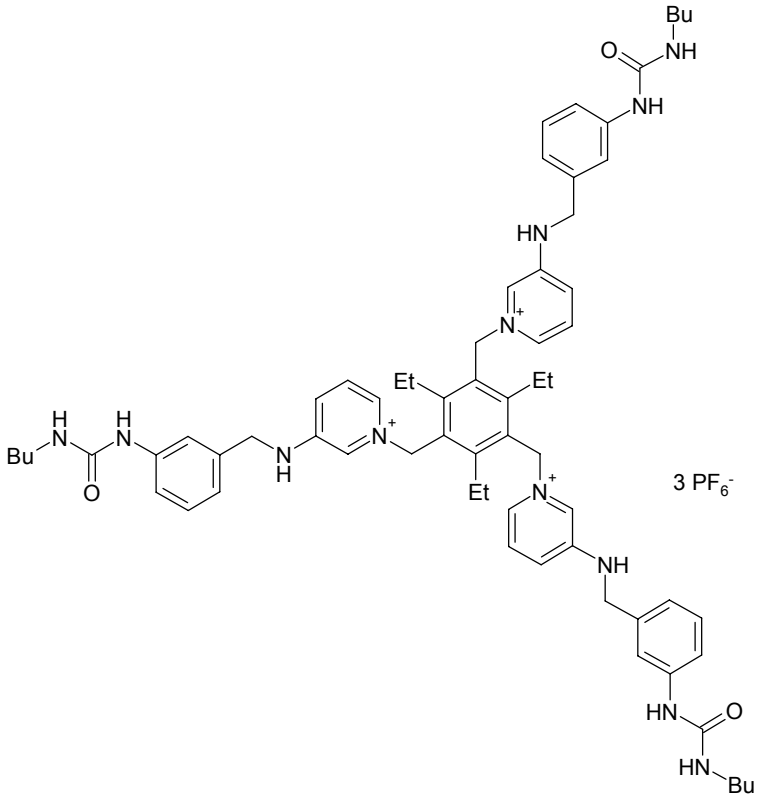
**Tris(1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-butyl-urea), Bromide Salt**




1,3,5-tris(bromomethyl)-2,4,6-triethyl benzene[1] (0.16 g, 0.35 mmol) and 1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-butyl-urea (0.32 g, 1.06 mmol) were dissolved in dichloromethane (50 ml) and the resulting solution was placed under reflux for 24 hours. During this time an oily, insoluble yellow product was observed to form. The mixture was allowed to cool and the product formed a solid layer on the bottom of the flask. The remaining solvent was poured out and the product left to dry. The resulting glassy substance was found to be the desired product, pure expect for some residual DCM (0.37 g, 0.28 mmol, 79 %). $^1$H-NMR (DMSO-$d_6$, 400 MHz, δ / ppm, J / Hz): 8.69 (3H, s, ArH); 8.25 (3H, b, NH); 8.14 (3H, d, J = 5.2, ArH); 8.02 (3H, b, ArH), 7.75 (3H, dd, J = 8.4, 5.6, ArH); 7.62 (3H, d, J = 8.4, ArH), 7.46 (3H, b, ArH); 7.25 (3H, d, J = 8.0, ArH); 7.13 (3H, t, J = 7.6, ArH); 6.83 (3H, d, J = 7.6, ArH); 6.32 (3H, t, J = 5.6, NH); 5.85 (6H, b, $CH_2$); 4.34 (6H, d, J = 5.2, $CH_2$); 3.05 (6H, dd, J = 12.0, 6.0, $CH_2$); 2.59 (6H, b, $CH_2$); 1.37 (6H, m, $CH_2$); 1.28 (6H, m, $CH_2$); 0.87 (9H, t, J = 7.2, $CH_3$); 0.72 (9H, t, J = 6.5, $CH_3$). $^{13}$C{$^1$H}-NMR (DMSO-$d_6$, 100 MHz, δ / ppm): 155.2, 149.3, 147.9, 141.0, 137.7, 130.5, 128.7, 128.2, 128.1, 126.5, 125.9,

119.7, 116.5, 116.4, 57.1, 54.8, 45.8, 31.8, 23.4, 19.5, 14.7, 13.6. $ES^+$-MS: *m/z* = 1255 $[M\text{-}Br]^+$, 587 $[M\text{-}2Br]^{2+}$, 365 $[M\text{-}3Br]^{3+}$. Anal: Calculated for $C_{66}H_{87}N_{12}O_3Br_3$: C, 59.33; H, 6.52; N, 12.58 %. Found: C, 57.05; H, 6.56; N, 12.19 %. IR ($\nu$ / $cm^{-1}$): 1673 (s), 3192 (w).

## Tris(1-[3-(Pyridin-3-ylaminomethyl)-phenyl]-3-butyl-urea), Hexafluorophosphate Salt




The bromide salt **7·15**-3Br (0.25 g, 0.19 mmol) was dissolved in methanol with an excess of $KPF_6$ (0.34 g, 1.87 mmol) in methanol (50 ml). The resulting solution was left to stir for 6 hours. After this time the organic product was extracted into dichloromethane (20 ml), using water (20 ml) to promote separation. The organic layer was removed and to solvent evaporated under reduced pressure to yield a green product (0.17 g, 0.11 mmol, 58 %). $^1$H-NMR (DMSO-$d_6$, 400 MHz, δ / ppm, J / Hz): 8.44 (3H, s, ArH); 8.04 (3H, s, NH); 7.84 (3H, d, J = 5.2, ArH); 7.79 – 7.66 (4H, m, ArH) 7.54 (3H, b, ArH); 7.18 (6H, m, ArH); 6.83 (3H, b, ArH); 6.12 (3H, t, J = 5.5, NH); 5.81 (6H, b, $CH_2$); 4.34 (6H, d, J = 5.1, $CH_2$); 3.06 (6H, dd, J = 12.4, 6.4, $CH_2$); 2.61 (6H, b, $CH_2$); 1.38 (6H, m, $CH_2$); 1.30 (6H, m, $CH_2$); 0.88 (9H, t, J = 8.1, $CH_3$); 0.65 (9H, b, $CH_3$). $^{13}C\{^1H\}$-NMR (DMSO-$d_6$, 100 MHz, δ / ppm): 155.5, 149.7, 148.2, 141.3, 138.0, 129.2, 128.8, 120.2, 117.1, 116.8, 57.4, 46.3, 32.2, 19.8, 15.0,

14.0. $ES^+$-MS: *m/z* = 1385 $[M\text{-}PF_6]^+$, 620 $[M\text{-}2PF_6]^{2+}$, 365 $[M\text{-}3PF_6]^{3+}$. Anal: Calculated for $C_{66}H_{87}N_{12}O_3P_3F_{18}$: C, 51.76; H, 5.69; N, 10.98 %. Found: C, 51.11; H, 5.73; N, 10.66 %. IR ($\nu$ / $cm^{-1}$): 844 (s), 1665 (s), 3196 (w), 3300 (w), 3426 (s).

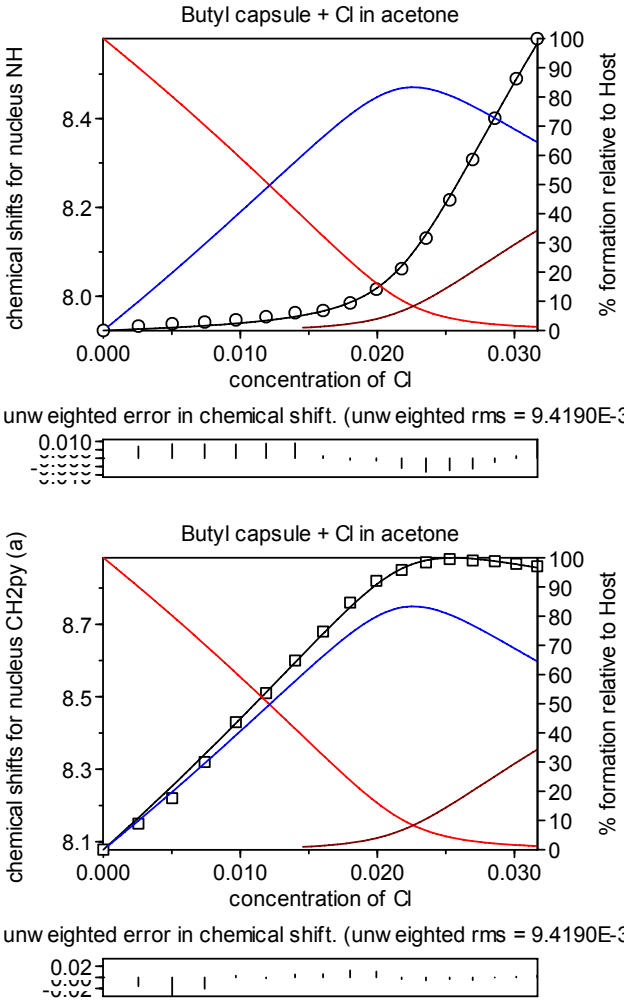
**NMR Experiments**

## $^1$H NMR Titration Experiments

$^1$H NMR titration experiments were carried out at room temperature using either a Bruker AV-500 spectrometer operating at 500 MHz or a Varian Mercury 400-BB operating at 400 MHz. All chemical shifts are reported in ppm relative to TMS as an internal reference. A solution of the host species of known concentration, typically 0.02 M, was made up in an NMR tube using the appropriate deuterated solvent (0.5 ml) with TMS added. Solutions of the anions, as tetrabutylammonium salts, were made up in volumetric flasks (2 ml) with a concentration five times greater than that of the host. The guest solution was typically added in 10 μl aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously.

## Variable Temperature (VT) $^1$H NMR Experiments

$^1$H VT-NMR experiments were conducted using a Bruker AV-400 spectrometer operating at 400 MHz. Spectra were run in acetone-$d_6$ with TMS as an internal reference. An initial spectrum was run at room temperature before reducing the temperature in 10 K steps to 183 K. The temperature was allowed to equilibrate at each temperature before collection of the spectra. Guest anions were added as the tetrabutylammonium salts.




## Computational Supporting Information

*Detailed description of computational work*

Density functional theory has been shown to be able to accurately model hydrogen-bonded structures when non-local, gradient corrected, exchange-correlation functionals (e.g., B3LYP) are used in conjunction with appropriate basis sets (i.e., including diffuse functions).[2, 3] Results in agreement with correlated *ab initio* methods, such as MP2 and CCSD for example, can be obtained with a significant reduction in the computational cost, opening up the possibility of obtaining structural information on large supramolecular complexes containing hydrogen bonds. In particular many recent studies have involved the application of DFT to nucleic acid base-pair chemistry.[4, 5] Of particular relevance to the current study is work by Zheng

*et al.* in which it was found that the B3LYP functional gives reliable minima for chloride hydrogen-bonded tri-s-triazine complexes, and π–π stacking complexes of polynitrogen anions with tri-s-triazine.[6]

*References for Supplementary information*

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