Anion receptors based on 7,7'-diamido-2,2'-diindolylmethane

Paweł Dydioa,b, Tomasz Zieliński,a, Janusz Jurczaka,b

a Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
b Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

Supporting information

Contents

SYNTHESIS S2

GENERAL REMARKS S2
3-METHYL-7-NITRO-1H-INDOLE (4) S2
1,1-BIS-(3-METHYL-7-NITRO-1H-INDOL-2-YL)-PROPANE (5) S2
1,1-BIS-(7-AMINO-3-METHYL-1H-INDOL-2-YL)-PROPANE (6) S3

GENERAL PROCEDURE FOR PREPARATION OF THE LIGANDS 1A-C S4
1,1-BIS-(7-BUTYRYLAMINO-3-METHYL-1H-INDOL-2-YL)-PROPANE (1A) S4
1,1-BIS-(7-BENZOYLAMINO-3-METHYL-1H-INDOL-2-YL)-PROPANE (1B) S4
1,1-BIS-(3-METHYL-7-(1H-PYRROLE-2-CARBOXYL)-AMINO-1H-INDOL-2-YL)-PROPANE (1C) S5

BINDING STUDIES S6

GENERAL COMMENTS S6
1H NMR TITRATION EXPERIMENTS S6
1H NMR JOB PLOT EXPERIMENTS S6

CRYSTAL DATA S12

NMR SPECTRA S16

LIGAND 1A S16
LIGAND 1B S18
LIGAND 1C S20
COMPOUND 4 S21
COMPOUND 5 S22
COMPOUND 6 S23
Synthesis

General remarks
All precursors for syntheses were obtained from Aldrich or Fluka and were used without further purification. The flash chromatography was carried out using Merck Kieselgel 60 (63–100 μm mesh size), TLC was carried out on Merck Kieselgel F254 plates.

3-Methyl-7-nitro-1H-indole (4)

1,2-dinitrobenzene (2.8 g, 16.7 mmol) was dissolved in dry THF (75 ml) in a two-neck flask equipped with a thermometer and a dropping funnel. The resulting mixture was cooled down to -60°C and stirred under inert atmosphere. Then the 0.5M solution of 1-propenylmagnesiumbromide in THF (100 ml, 50 mmol) was added dropwise slowly enough to keep the temperature between -60°C and -50°C (which took about 1 hour). After addition of the Gringard’s reagent, the reaction mixture was stirred at -60°C for the next 4 hours and then the reaction was quenched with ammonium chloride (6g) in water (70 ml). THF was removed in vacuo from the solution, and the remaining water phase was extracted with CHCl₃. The CHCl₃ portions were combined, dried over MgSO₄, and the solvent was evaporated. The product was purified by column chromatography on silica gel, with hexane : ethyl acetate (99 : 1) mixture as an eluent. The product was crystallized from hexane : ethyl acetate mixture yielding 1.1 g (37%) of the methylnitroindole 4 as yellow crystals, m.p. 138-140°C.

\[ ^1H \text{ NMR} \ (200 \text{ MHz, CDCl}_3) \delta = 9.57 \ (bs, 1H, N\text{-H}), \ 8.07 \ (d, 1H, J_1 = 8.0 \text{ Hz}), \ 7.83 \ (d, 1H, J_1 = 7.8 \text{ Hz}), \ 7.11 \ (t, 1H, J_1 = 7.8 \text{ Hz}), \ 7.07 \ (s, 1H), \ 2.29 \ (s, 3H, CH}_3); \]

\[ ^13C \text{ NMR} \ (50 \text{ MHz, CDCl}_3) \delta = 132.2, \ 129.6, \ 126.9, \ 123.9, \ 119.1, \ 118.4, \ 113.1, \ 9.4; \]

HR ESI calcd. for C₉H₈N₂O₂Na [M+Na]^+: 199.0478, found: 199.04845;
Elemental analysis (%) calcd. for C₉H₈N₂O₂: C 61.36, H 4.58, N 15.90, found: C 61.10, H 4.45, N 15.87.

1,1-Bis-(3-methyl-7-nitro-1H-indol-2-yl)-propane (5)

Well powdered 3-methyl-7-nitro-1H-indole (4) (176mg, 1mmol) and propionaldehyde (0.22ml, 3mmol) were suspended in
concentrated HCl (10ml), and heated at 100°C over 2 hours in a sealable tube. After cooling down, the suspension was carefully poured into Na₂CO₃(sat) (20ml) and CHCl₃ was added to dissolve the precipitate formed. The layers were separated and the remaining water phase was extracted with CHCl₃. The CHCl₃ extracts were combined, washed with water, dried over MgSO₄, and evaporated. The product was further purified by column chromatography on silica gel, with hexane : ethyl acetate (gradient: 99:1 to 95:5 ) mixture as an eluent, followed by crystallization from hexane : ethyl acetate mixture yielding 137mg (70%) of the desired compound 5, m.p. 198-200°C.

**1H NMR** (200 MHz, CDCl₃) δ = 9.72 (bs, 2H, NH), 8.09 (d, 2H, J₁ = 8.1 Hz), 7.84 (d, 2H, J₁ = 7.8 Hz), 7.17 (t, 2H, J₁ = 8.2 Hz), 4.56 (t, 1H, J₁ = 8.2Hz), 2.37 (m, 2H, CH₂), 2.34 (s, 6H, CH₃), 1.08 (t, 3H, J₁ = 7.2 Hz, CH₃CH₂);  

**13C NMR** (50 MHz, CDCl₃) δ = 136.5, 133.1, 132.5, 128.9, 126.3, 118.8, 109.5, 37.1, 26.4, 12.4, 8.7;  

**HR EI** calcd. for C₂₁H₂₀N₄O₄ M⁺: 392.14846, found: 392.14746;  

**Elemental analysis** (%) calcd. for C₂₁H₂₀N₄O₄: C 64.28, H 5.14, N 14.28, found: C 64.16, H 5.13, N 14.15.

1,1-bis(-7-amino-3-methyl-1H-indol-2-yl)-propane (6)  

1,1-Bis(-3-methyl-7-nitro-1H-indol-2-yl)-propane (5) (392mg, 1 mmol) was dissolved in methanol (20 ml) and 5% palladium on charcoal was added (0.1g). The reaction mixture was vigorously stirred under hydrogen atmosphere. The progress of the reaction was monitored on TLC, and after completion (about one hour), the catalyst was filtered off on Celite®. The solvent was evaporated, and the crude amine 6 was immediately used in a subsequent reaction with the appropriate acetic chloride assuming a complete transformation of substrate 5 into the desired amine 6.

**1H NMR** (200 MHz, CDCl₃) δ = 8.18 (bs, 2H, NH-indole), 7.07 (d, 2H, J₁ = 8.0 Hz), 6.92 (t, 2H, J₁ = 7.6 Hz), 6.42 (d, 2H, JII = 7.0 Hz), 4.23 (t, 1H, JII = 7.6Hz), 3.17 (bs, 4H, N H₂), 2.23 (s, 6H, CH₃), 2.09 (m, 2H, CH₂), 0.95 (t, 3H, J₁ = 7.2 Hz, CH₃CH₂).
**General Procedure for Preparation of the Ligands 1a-c**

Triethylamine was added (0.42ml, 3mmol) to the cooled (0˚C) solution of crude diamine 6 (1mmol) in dry CH₂Cl₂ (60ml). Subsequently, appropriate acid chloride was added slowly dropwise to the stirred solution under Ar atmosphere. Afterwards, the cooling bath was removed and the stirring was continued overnight. The organic layer was washed with NaHCO₃(sat.) (2•50 ml), water (50ml), dried over MgSO₄, and then the solvent was evaporated. The crude product was purified by column chromatography on silica gel, with CH₂Cl₂ : methanol (250:1) mixture as an eluent.

**1,1-bis-(7-butyrylamino-3-methyl-1H-indol-2-yl)-propane (1a)**

Butanoic acid chloride (0.26ml, 2.5mmol) was used as the acyl reagent, yielding 0.412g (87%) of product, which was recrystallized from hot ethyl acetate giving colorless crystals, m.p. 242-243˚C.

**¹H NMR** (500 MHz, DMSO) δ = 10.16 (bs, 2H, NH-indole), 9.66 (bs, 2H, NH), 7.43 (d, 2H, J₁ = 7.5 Hz), 7.16 (d, 2H, J₁ = 7.8 Hz), 6.90 (t, 2H, J₂ = 7.7 Hz), 4.46 (t, 1H, J₁ = 8.0Hz, CHCH₂CH₃), 2.38 (t, 4H, J₁ = 7.4 Hz, COCH₂), 2.20 (m, 2H, CHCH₂CH₃), 2.16 (s, 6H, CH₃), 1.66 (m, 4H, COCH₂CH₂), 0.94 (t, 6H, J₁ = 7.4 Hz, COCH₂CH₂CH₃), 0.92 (t, 3H, J₁ = 7.4 Hz, CHCH₂CH₃);

**¹³C NMR** (50 MHz, DMSO) δ = 171.5, 135.7, 130.8, 127.1, 123.1, 118.9, 114.1, 112.7, 107.0, 36.6, 27.0, 19.1, 14.1, 12.6, 9.0;

**HR ESI** calcd. for C₂₉H₳₆N₄O₂Na [M+Na]⁺: 495.27305, found: 495.27522;

**Elemental analysis (%)** calcd. for (C₂₉H₳₆N₄O₂)₄·CH₃CO₂C₂H₅: C 72.84, H 7.74, N 11.33, found: C 72.85, H 7.96, N 11.52.

**1,1-Bis-(7-benzoylamino-3-methyl-1H-indol-2-yl)-propane (1b)**

Benzoyl chloride (0.29ml, 2.5mmol) was used as the acyl reagent, yielding 0.500g (92%) of product, which was recrystallized from ethyl acetate – hexane mixture giving off-white powder, m.p. 270˚C (decomp).

(4·Ligands 1a·Ethyl acetate – as observed on ¹H NMR spectra)
**1H NMR** (500 MHz, DMSO) δ = 10.23 (bs, 2H, NH-indole), 10.06 (bs, 2H, NH), 7.94 (d, 4H, J₁ = 7.4 Hz), 7.58 (t, 2H, J₁ = 7.4 Hz), 7.48 (t, 4H, J₁ = 7.7 Hz), 7.37 (d, 2H, J₁ = 7.5 Hz), 7.26 (d, 2H, J₁ = 7.8 Hz), 6.96 (t, 2H, J₁ = 7.7 Hz), 4.50 (t, 1H, J₁ = 8.0 Hz, CHCH₂CH₃), 2.23 (s, 6H, CH₃), 2.20 (m, 2H, CHCH₂CH₃), 0.91 (t, 3H, J₁ = 7.2 Hz, CHCH₂CH₃);

**13C NMR** (50 MHz, DMSO) δ = 166.1, 136.1, 135.5, 131.8, 130.8, 128.8, 128.3, 123.2, 118.8, 115.4, 115.2, 106.8, 79.6, 36.5, 27.0, 12.7, 9.1;

**HR ESI** calcd. for C₃₅H₃₂N₄O₂Na [M+Na]⁺: 563.24175, found: 563.24443;

**Elemental analysis** (%) calcd. for C₃₅H₃₂N₄O₂·H₂O: C 75.24, H 6.13, N 10.03, found: C 75.03, H 6.66, N 10.26.

**1,1-Bis-(3-methyl-7-(1H-pyrrole-2-carboxyl)-amino-1H-indol-2-yl)-propane (1c)**

1H-pyrrole-2-carboxylic acid chloride (0.58g, 4.5mmol) in dry CH₂Cl₂ (20 ml) was used as an acyl reagent. Larger amount of triethylamine (0.81ml, 10mmol) was employed. 0.410g (79%) of product was obtained, which was crystallized from hot ethyl acetate – hexane mixture giving off-white powder, m.p. 135°C (decomp).

**1H NMR** (500 MHz, DMSO) δ = 11.62 (bs, 2H, NH-pyrrole), 10.28 (bs, 2H, NH-indole), 9.59 (bs, 2H, NΗ), 7.25 (d, 2H, J₁ = 7.5 Hz), 7.22 (d, 2H, J₁ = 7.7 Hz), 7.06 (m, 2H), 6.96 (m, 2H), 6.93 (d, 2H, J₁ = 7.7 Hz), 6.17 (dt, 2H, J₁ = 3.7 Hz, J₂ = 2.4 Hz), 4.50 (t, 1H, J₁ = 8.1 Hz, CHCH₂CH₃), 2.23 (s, 6H, CH₃), 2.21 (m, 2H, CHCH₂CH₃), 0.91 (t, 3H, J₁ = 7.3 Hz, CHCH₂CH₃);

**13C NMR** (125 MHz, DMSO) δ = 159.3, 135.7, 130.2, 128.7, 126.1, 122.5, 122.2, 118.3, 115.0, 114.4, 111.6, 108.8, 106.2, 35.8, 26.2, 12.2, 8.5;

**HR ESI** calcd. for C₃₁H₃₀N₆O₂Na [M+Na]⁺: 541.23225, found: 541.23049;

**Elemental analysis** (%) calcd. for (C₃₁H₃₀N₆O₂)₂·H₂O: C 70.57, H 5.92, N 15.93, found: C 70.95, H 6.17, N 15.21.

---

**ii** Monohydrate as observed X-ray structure
Binding studies

General comments
As the source of anions, commercially available tetrabutylammonium salts were used which were pre-dried overnight under high vacuum at 60°C. Distilled water was added to the commercially available DMSO-\textit{d}_6 of 99.9% isotopic purity (purchased from ARMAR AG) to obtain the appropriate water concentration.

$^1$H NMR titration experiments
The ligand solution (concentration about $1.5 \cdot 10^{-2} \text{ M}$, details are given in Tables S1-S4) was titrated in the NMR tubes with the solution of the respective tetrabutylammonium salt in ligand aliquots (salt concentration about 0.1-0.2 M). 14-18 data points were recorded. The binding constants were calculated from the changes in chemical shifts of ligand protons. Nonlinear curve fitting for 1:1 binding model was carried out with the Origin program. The binding constants K and the asymptotic change in chemical shift $\Delta \delta_{\text{max}}$ were chosen as the free parameters for fitting.

$^1$H NMR Job plot experiments
0.40ml of the ligand solution (C about $2 \cdot 10^{-2} \text{ M}$) was titrated in the NMR tubes with aliquots (50μl) of the equimolar solution of the respective tetrabutylammonium salt, to the point of 1 : 1 ligand : anion ratio. Similarly, the anion solution was titrated with the ligand solution. 17 data points were recorded, which were used to obtain the Job plot.
Table S1. The details of $^1$H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand 1a

<table>
<thead>
<tr>
<th>Anion</th>
<th>L [mol·dm$^{-3}$]</th>
<th>A [mol·dm$^{-3}$]</th>
<th>K [M$^{-1}$]</th>
<th>$\Delta \delta_{\text{max}}$[ppm]</th>
<th>L [mol·dm$^{-3}$]</th>
<th>A [mol·dm$^{-3}$]</th>
<th>K [M$^{-1}$]</th>
<th>$\Delta \delta_{\text{max}}$[ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^-$</td>
<td>0.014608</td>
<td>0.22078</td>
<td>20.1 ± 0.2</td>
<td>21.5 ± 1.1</td>
<td>0.014440</td>
<td>0.21406</td>
<td>12.5 ± 0.8</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.013800</td>
<td>0.22491</td>
<td>470 ± 4</td>
<td>-</td>
<td>0.014472</td>
<td>0.21478</td>
<td>244 ± 24</td>
<td>145 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhCOO$^-$</td>
<td>0.010098</td>
<td>0.07396</td>
<td>&gt; 10 000</td>
<td>&gt; 10 000</td>
<td>0.011755</td>
<td>0.094172</td>
<td>1884 ± 47</td>
<td>2061 ± 44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>0.01088</td>
<td>0.07221</td>
<td>&gt; 10 000</td>
<td>&gt; 10 000</td>
<td>0.011268</td>
<td>0.100252</td>
<td>&gt; 10 000</td>
<td>2.52 (NH$_{\text{amde}}$)</td>
</tr>
</tbody>
</table>

$^1$H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.

1H NMR titration curves

1H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.
Table S2. The details of $^1$H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand 1a

<table>
<thead>
<tr>
<th>Ligand</th>
<th>[mol·dm$^{-3}$]</th>
<th>[mol·dm$^{-3}$]</th>
<th>K [M$^{-1}$]</th>
<th>$\Delta\delta_{\text{max}}$ [ppm]</th>
<th>[mol·dm$^{-3}$]</th>
<th>[mol·dm$^{-3}$]</th>
<th>K [M$^{-1}$]</th>
<th>$\Delta\delta_{\text{max}}$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>DMSO-$d_6$ + 10% H$_2$O</td>
<td>DMSO-$d_6$ + 25% H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anion</td>
<td>L</td>
<td>A</td>
<td>K</td>
<td></td>
<td>L</td>
<td>A</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.013174</td>
<td>0.101716</td>
<td>585 ± 8</td>
<td>2.35 (NH$_{\text{ind.}}$)</td>
<td>0.012870</td>
<td>0.088522</td>
<td>211 ± 11</td>
<td>2.11 (NH$_{\text{ind.}}$)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.010527</td>
<td>0.100527</td>
<td>537 ± 19</td>
<td>0.55 (NH$_{\text{amide}}$)</td>
<td>0.010657</td>
<td>0.088522</td>
<td>206 ± 11</td>
<td>1.17 (NH$_{\text{amide}}$)</td>
</tr>
<tr>
<td>PhCOO$^-$</td>
<td>0.012711</td>
<td>0.101716</td>
<td>5644±397</td>
<td>2.46 (NH$_{\text{ind.}}$)</td>
<td>0.012870</td>
<td>0.088522</td>
<td>211 ± 11</td>
<td>2.11 (NH$_{\text{ind.}}$)</td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>0.012711</td>
<td>0.100527</td>
<td>5981±355</td>
<td>1.50 (NH$_{\text{amide}}$)</td>
<td>0.012870</td>
<td>0.088522</td>
<td>206 ± 11</td>
<td>1.17 (NH$_{\text{amide}}$)</td>
</tr>
</tbody>
</table>

$^1$H NMR titration curves

$^1$H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.
Table S3. The details of $^1$H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand 1b

<table>
<thead>
<tr>
<th>Ligand</th>
<th><img src="image" alt="Ligand Structure" /></th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMSO-$d_6$ + 0.5% H$_2$O</th>
<th>DMSO-$d_6$ + 5% H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>L [mol·dm$^{-3}$]</td>
<td>A [mol·dm$^{-3}$]</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.016321</td>
<td>0.199893</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.014682</td>
<td>0.213520</td>
</tr>
<tr>
<td>PhCOO$^-$</td>
<td>0.010419</td>
<td>0.070163</td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>0.010419</td>
<td>0.074015</td>
</tr>
</tbody>
</table>

$^1$H NMR shifts of the indole (●) and amide NH (x) signals upon addition of various anions salts.
Table S4. The details of $^1$H NMR titration experiments: concentrations used, titration curves and the results of data fitting, for ligand 1c

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Solvent DMSO-$d_6$ + 0.5% H$_2$O</th>
<th>Solvent DMSO-$d_6$ + 5% H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L$ [mol·dm$^{-3}$]</td>
<td>$A$ [mol·dm$^{-3}$]</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.015761</td>
<td>0.201625</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.018086</td>
<td>0.226384</td>
</tr>
<tr>
<td>PhCO$_2$-$^-$</td>
<td>0.009483</td>
<td>0.074793</td>
</tr>
<tr>
<td>H$_2$PO$_4$-$^-$</td>
<td>0.008900</td>
<td>0.074186</td>
</tr>
</tbody>
</table>

$^1$H NMR shifts of the indole (●), pyrrole (Δ) and amide NH (x) signals upon addition of various anions salts.

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2009
Table S5. Job plots of ligand 1a and various anions in DMSO-$d_6$ + 5% H$_2$O.
Crystal data

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw. Crystallographic data (excluding structure factors) for the structures discussed in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

All measurements of crystal were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. The crystals were positioned at 62 mm from the CCD camera. 1200 frames were measured at 0.5°/1° intervals (for the chloride complex/for the benzoate complex and the free ligand structures, respectively) with a counting time of 10, 22, and 21 sec (for the chloride complex of 1c, the benzoate complex of 1a, and monohydrate of 1b, respectively). The data were corrected for Lorentz and polarization effects. Empirical correction for absorption was applied. Data reduction and analysis were carried out with the Oxford Diffraction programs.

The structure was solved by direct methods and refined using SHELXL. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The F_o^2 > 2σ (F_o^2) criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F.

Crystal data for 1a•TBAPhCOO: CCDC number 725837. C52H77N5O4, M = 836.19, Triclinic, P-1, a = 13.4563(10) Å, b = 13.7844(11) Å, c = 27.517(2) Å, α = 101.614(7)°, β = 100.781(7)°, γ = 94.217(6)°, V = 4878.4(7) Å^3, T = 100(2) K, Z = 4, μ(Mo-Kα) = 0.072 mm^-1, 88056 reflections measured, 21275 unique (R(int) = 0.0403) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F^2) = 0.0423 and wR2(F^2) = 0.0940, for all data: R1(F^2) = 0.1028 and wR2(F^2) = 0.10062. Three disordered carbon atoms were refined with isotropic temperature factors due to low occupancy (below 20%). All hydrogen atoms were located geometrically and their position and temperature factors were not refined except eight ones engaged in hydrogen bonds. Scattering factors were taken from Tables

S12

Diffraction grade crystal was obtained by slow diffusion of water and slow evaporation of a DMSO solution of the ligand 1a in the presence of excess tetrabutylammonium benzoate.

Crystal data for 1b*H2O: **CCDC** number 707058. C35H34N4O3, M = 558.66, Monoclinic, P21/c, a = 14.5822(6) Å, b = 13.6329(5) Å, c = 15.4897(5) Å, α = 90°, β = 112.956(4) °, γ = 90°, V = 2835.45(18) Å³, T = 110(2) K, Z = 4, μ(Mo-Kα) = 0.085 mm⁻¹, 26227 reflections measured, 6833 unique (R(int) = 0.0207) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F²) = 0.0361 and wR2(F²)= 0.0868, for all data: R1(F²)= 0.0599 and wR2(F²)= 0.0906. All hydrogen atoms were located geometrically. Positions and temperature factors of most of them were not refined. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.

Diffraction grade crystal was obtained by slow evaporation of an acetone - water solution of the ligand 1b.

Crystal data for 1c*TBA-Cl: **CCDC** number 707057. C47H66ClN7O2, M = 796.52, Triclinic, P-1, a = 10.7982(7) Å, b = 20.0727(13) Å, c = 22.7848(14) Å, α = 65.331(6)°, β = 80.937(5)°, γ = 86.475(5)°, V = 4431.8(5) Å³, T = 100(2) K, Z = 4, μ(Mo-Kα) = 0.132 mm⁻¹, 84109 reflections measured, 21476 unique (R(int) = 0.0372) which were used in all calculations. The final R indices [I>2σ(I)]: R1(F²) = 0.0406 and wR2(F²) = 0.0951, for all data: R1(F²) = 0.0839 and wR2(F²) = 0.1038. All hydrogen atoms were located geometrically and their positions and temperature factors were not refined except those atoms engaged in hydrogen bonds. Hydrogen atoms of the methyl groups (C21A, C33A, C21B, C33B) are disordered, and they are refined in two positions (AFIX 123). Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.

Diffraction grade crystal was obtained by slow diffusion of pentane to a solution of ligand 1c in C2H4Cl2 – ethyl acetate mix in the presence of excess tetrabutylammonium chloride.
Figure S1. Different views of crystal structures of a) the benzoate complex of 1a; b) 1b·H₂O; and c) the chloride complex of 1c; some parts omitted for clarity.
Figure S2. ORTEP presentation of two forms of the benzoate complex of ligand 1a.

Figure S3. ORTEP presentation of the ligand 1b*H2O.

Figure S4. ORTEP presentation of two forms of the chloride complex of the ligand 1c.
NMR SPECTRA

*Ligand 1a*

$^1$H NMR (500 MHz, DMSO)

**COSY** (500 MHz, DMSO)
**NOESY (500 MHz, DMSO)**

![NOESY spectrum](image)

**$^{13}$C NMR (200 MHz, DMSO)**

![$^{13}$C NMR spectrum](image)
**Ligand 1b**

$^1$H NMR (500 MHz, DMSO)

**COSY (500 MHz, DMSO)**
**NOESY (500 MHz, DMSO)**

![NOESY spectrum]

**$^{13}$C NMR (200 MHz, DMSO)**

![13C NMR spectrum]
**Ligand 1c**

$^{1}H$ NMR (500 MHz, DMSO)

$^{13}C$ NMR (500 MHz, DMSO)
**Compound 4**

$^1\text{H NMR}$ (200 MHz, CDCl$_3$)

$^{13}\text{C NMR}$ (200 MHz, CDCl$_3$)
**Compound 5**

\[^1\text{H NMR (200 MHz, CDCl}_3\text{)}\]

\[^{13}\text{C NMR (200 MHz, CDCl}_3\text{)}\]
**Compound 6**

$^1$H NMR (200 MHz, CDCl$_3$)

![NMR spectrum image]