SUPPORTING INFORMATION

Recognition of Primary Amines in Water by a Zinc Funnel Complex Based on Calix[6]arene†

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MATERIALS. Solvents and chemicals were of reagent grade and were used without purification. Calixarene 1 was synthesized according to ref. 1. HRMS were performed at the Institut de Chimie des Substances Naturelles, France. MS (ESI) analyses were obtained with a ThermoFinnigen LCQ Advantage spectrometer using methanol as solvent. NMR spectra were recorded on a Bruker ARX250 MHz spectrometer or an Advance 500 spectrometer. The pD values of the solutions were corrected considering pD = pHread + 0.4 at 25°C. IR spectra were obtained with a Perkin-Elmer Spectrum on FTIR spectrometer equipped with a MIRacleTM single reflection horizontal ATR unit (germanium crystal). The standard deviation $\sigma$ of each calculated value “g” ($K$, $K'$, $pK_{aeff}$, $\Delta H$, $\Delta S$) was calculated based on the following formula:

$$\sigma_{n-1} = \sqrt{\frac{\sum (g_i - \bar{g})^2}{n-1}}$$

with: $\bar{g} = \frac{1}{n} \sum g_i$, where $n$ is the number of independent experiments.

Ion-exchange resin
"Dowex 1*2-100 ion-exchange resin", Aldrich: 21,737-9 [60267-37-0]
0.6 equiv./mL ie. 4.8 mequiv./g
"Dowex 1*2-100 ion-exchange resin" (1 g) was treated by 50 mL of a 1M solution of nitric acid. After 15 min stirring (on rotary evaporator without any heating or vacuum), the resin was filtered (fritté n°3) and washed with water until the solution filtered reached neutral pH. This protocol was repeated twice.

1/ SYNTHESIS

Propargyltrimethylammonium hexafluorophosphate

![Propargyltrimethylammonium hexafluorophosphate](image)

Propargyltrimethylammonium hexafluorophosphate was obtained from the previously described propargyltrimethylammonium bromide,2 by a simple counter-ion exchange based on the following procedure: a solution of potassium hexafluorophosphate (7.94 g, 43.2 mmol) in water was added to the solid propargyltrimethylammonium bromide (14.4 mmol). The

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mixture was stirred for 30 min. The obtained precipitate was filtered, washed with water and ether to yield compound 2 in 83% yield (2.90 g).

\(^1\text{H NMR (250 MHz, CD}_3\text{CN, 300 K)}: \delta (\text{ppm}) = 3.11 (\text{HCCCH}_2\text{N}^+(\text{CH}_3)_3, \text{s, 9H}), 3.21 (\text{HCCCH}_2\text{N}^+(\text{CH}_3)_3, \text{t, } J = 2.5 \text{ Hz, 1H}), 4.11 (\text{HCCCH}_2\text{N}^+(\text{CH}_3)_3, \text{d, } J = 2.5 \text{ Hz, 2H}).\\

\text{Calixarene 3}

To a solution of \(L^{(N_3)_3} \text{I (65 mg, 0.052 mmol)}\) in CH\(_3\text{CN/H}_2\text{O (3.5 mL/1 mL)}\) were added 4.2 equivalents of propargyl trimethylammonium hexafluorophosphate \(2 (53 \text{ mg, 0.22 mmol})\) and 1.5 equivalents of 2,6-lutidine (9 \(\mu\text{L, 0.078 mmol}\)). Argon was bubbled through the solution, then 0.6 equivalent of \([\text{Cu(CH}_3\text{CN)}_4.]\text{PF}_6\] (11.6 mg, 0.031 mmol) were added. The reaction mixture was refluxed for 64 h. An IR spectrum of one reaction sample revealed the presence of starting material. Argon was bubbled at RT through the reaction mixture. After adding 0.6 equivalent of \([\text{Cu(CH}_3\text{CN)}_4.]\text{PF}_6\] (11.6 mg, 0.031 mmol) and 1.5 equivalents of 2,6-lutidine (9 \(\mu\text{L, 0.078 mmol}\)), the reaction mixture was refluxed for additional 24 h and monitored by IR (ATR method): the reaction was stopped as soon as the 2100 cm\(^{-1}\) band (N\(_3\)) fully disappeared.

The mixture was cooled to RT, water (7 mL) and 2 drops of NH\(_4\)OH (20% aqueous) were added. The obtained precipitate was collected by filtration and dissolved in acetone/methanol (20 mL/10 mL). 540 mg of ion-exchange resin were added. The mixture was gently stirred at RT mechanically for 15 minutes, then filtered. The resin was rinsed with MeOH. The filtrate was concentrated and yielded, after drying under vacuum, 69 mg of \(3\) as a tan solid (yield = 86% from \(1\)).

The IR (ATR) spectra indicated the disappearance of the PF\(_6\)\(^-\) band at 843 cm\(^{-1}\).
\(^1H\) NMR (250 MHz, CD\(_3\)CN, Zn(ClO\(_4\))\(_2\).6H\(_2\)O excess, 300 K): \(\delta\) (ppm): 1.38 (t-Bu, s, 27H), 3.03 (N+Me\(_3\), s, 27H), 3.63 (OCH\(_3\), s, 9H), 3.72 (NCH\(_3\), s, 9H), 3.63-3.73 (ArCH\(_2\), m, 6H), 3.69 (ArCH\(_2\), d, \(J = 14\) Hz, 6H), 4.58 (CH\(_2\)N+Me\(_3\), s, 6H), 5.12 (CH\(_2\)Im, br s, 6H), 6.56 (H\(_{\text{triazole}}\), s, 6H), 6.95 (H\(_{\text{Im}}\), d, \(J = 1.8\) Hz, 3H), 7.44 (H\(_{\text{Ar-Bu}}\), s, 6H), 7.46 (H\(_{\text{Im}}\), d, \(J = 1.8\) Hz, 3H), 7.87 (H\(_{\text{triazoles}}\), br s, 3H).

\(^13C\) NMR (125 MHz, CD\(_3\)CN, Zn(ClO\(_4\))\(_2\).6H\(_2\)O excess, 300 K): \(\delta\) (ppm): 31.5, 32.1, 35.4, 53.7, 53.9, 54.0, 61.4, 61.6, 65.3, 119.6, 125.3, 127.3, 128.5, 13.5, 132.6, 133.7, 137.3, 137.8, 148.3, 149.5, 155.7, 156.6.

IR (ATR): \(\nu\) (cm\(^{-1}\)) = 3454.0 (br), 2959.6, 1641.6, 1479.9, 1339.6 (NO\(_3^-\)), 1231.3, 1186.8, 110.0, 1050.5, 1001.5, 976.0, 897.6, 760.1

ESI-MS (MeOH) m/z: 515.6 (calcd for [M]\(^{3+}\) 515.6); 386.8 (calcd for [M+H]\(^{4+}\) 386.9).

HRMS (TOF ES+) 1607.9234 (calcd for [M\(^{3+}\)+NO\(_3^-\)]\(^{2+}\) 1607.9282.

2/ Characterization in Organic Solvents

The \(^1H\) NMR spectra of compound 3 in organic solvents such as MeCN, DMSO were extremely broad and uninterpretable, even at high T. Such a behavior is typical of calix[6]arenes with three bulky groups at one rim and three other bulky groups at the opposite rim on different aromatic units. This is due to slow conformational motions of the calixarene core on the NMR time scale. As for a closely related calixarene bearing three imidazole and three triazole substituents,\(^1\) coordination to Zn(II) was then used to rigidify the calixarene core and obtain a nice spectrum with sharp resonances. Therefore, full characterisation of ligand 3 has been performed in the presence of Zn(II) as the corresponding tetrahedral dicationic complex depicted above as compound 4.

When a stoechiometric amount of [Zn(OH\(_2\))\(_6\)](ClO\(_4\))\(_2\) was added, sharp resonances due to the rigidification of calix[6]arene core upon complexation appeared (Figure S1). The resonances corresponding to the imidazolyl protons are split into two peaks (6.95 and 7.46 ppm), in agreement with zinc complexation. The chemical shift of the OMe groups (3.72 ppm) shows that they point away from the cavity. These observations account for the formation of a monometallic zinc complex 4 with zinc cation being coordinated to the imidazole units and to a solvent molecule (CD\(_3\)CN) that is included in the calixarene cavity. When additional amounts of [Zn(OH\(_2\))\(_6\)](ClO\(_4\))\(_2\) (up to 3 equiv.) were added, no significant changes were
observed. In contrast to the previously reported tris(imidazolyl)calixarenes bearing neutral triazole derivatives at their large rim,\textsuperscript{1} no coordination of a second metal center on the triazole units could be detected, even in the presence of a large excess of Zn(II). Indeed, in the case of the ligand 3, coordination of the triazole units must be hindered by charge repulsion because of the proximity to positively-charged trimethylammonium substituents. Finally, when calixarene 3 in the presence of one equivalent of Zn(NO$_3$)$_2$.6H$_2$O was dissolved in a mixture of deuterated acetonitrile/methanol (4:1, 1.6 mM), addition of water up to 20% v/v could be achieved without affecting the observation of characteristic chemical shifts of the complex by $^1$H NMR.

**Figure S1:** $^1$H NMR (250 MHz, CD$_3$CN, Zn(ClO$_4$)$_2$.6H$_2$O excess, 300 K); w = water, s = solvent.
3/ Gradual Addition of Water

When the complexation to calixarene 3 was performed with Zn(NO$_3$)$_2$.6H$_2$O, a similar signature was obtained, attesting to the formation of the same dicationic complex. The nitrate complex revealed soluble and stable in a mixture of deuterated acetonitrile/methanol (4:1, at 1.6 mM), and addition of water up to 20% v/v did not affect the $^1$H NMR signature, thereby attesting to the stability of the complex in such a mixed organic-aqueous medium.

0.729 $\mu$mol of ligand 3 and 0.729 $\mu$mol of Zn(NO$_3$)$_2$.6H$_2$O were dissolved in 400 $\mu$L of CD$_3$CN and 100 $\mu$L of MeOD. $^1$H NMR 250 MHz spectra were recorded after each addition of D$_2$O.
**Figure S3:** $^1$H NMR spectrum (250 MHz) of compound 3 from bottom to top 1) after addition of one equivalent of Zn(NO$_3$)$_2.6$H$_2$O in CD$_3$CN/MeOD (400 μL: 100 μL), 2) after addition of 50 μL of D$_2$O, 3) after addition of 100 μL of D$_2$O, 4) after addition of 200 μL of D$_2$O.

**4/ NMR-CHARACTERIZATION OF THE TERNARY COMPLEX OBTAINED WITH HEPTYLAMINE IN DEUTERATED WATER**
Figure S4: $^1$H NMR (top) and COSY (bottom) of the ternary complex (D$_2$O, 500 MHz, 300K, [3] = 3.3 mM, in the presence of 3 equiv. Zn(NO$_3$)$_2$.6H$_2$O and 15 equiv. of heptylamine).

$^1$H NMR (500 MHz, D$_2$O, 300 K): $\delta$ (ppm) : -1.43 (CH$_2$(3) heptylamine in, m, 2H), -1.14 (CH$_2$(2 and 4) heptylamine in, m, 4H), -1.07 (CH$_2$(5) heptylamine in, m, 2H), -0.52 (CH$_2$(6) heptylamine in, m, 2H), 0.04 (CH$_3$(7) heptylamine in, t, $J$ = 6.5 Hz, 3H), 0.92 (CH$_3$(7) heptylamine out, t, $J$ = 7.5 Hz), 1.01 (CH$_2$(1) heptylamine in, m, 2H), 1.30-1.43 (CH$_2$(3–6)
heptylamine out, m), 1.44 (tBu, s, 27H), 1.71 (CH$_2$(2) heptylamine out, q, $J = 7.0$ Hz), 3.04 (CH$_2$(1) heptylamine out, t, $J = 8.0$ Hz), 3.15 (N$\text{Me}_3$, s, 27H), 3.76 (OCH$_3$, s, 9H), 3.80 (ArCH$_2$, d, $J = 15$ Hz, 6H), 3.94 (NCH$_3$, s, 9H), 4.71 (CH$_2$N$\text{Me}_3$, s, 6H), 5.59 (CH$_2$Im, br s, 6H), 7.04 (H$_{\text{Artria}}$, s, 6H), 7.17 (H$_{\text{Im}}$, d, $J = 1.5$ Hz, 3H), 7.67 (H$_{\text{Ar-Bu}}$, s, 6H), 7.70 (H$_{\text{Im}}$, d, $J = 1.5$ Hz, 3H), 8.43 (H$_{\text{triazole}}$, s, 3H).

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5/ pH-DEPENDANCE

Protometric measurements

Solutions containing ligand 3 at a concentration of $10^{-3}$ mol.L$^{-1}$ were prepared by dissolving the solid compounds in the presence of an excess of nitric acid (10 eq), they are then neutralized by KOH (0.05M).

The ionic strength was kept constant ($I = 0.1$) by addition of potassium nitrate (Prolabo) of the highest purity (> 99%). The titrating solutions of carbonate-free base KOH 0.05M and nitric acid 0.1 M were prepared from standardized 1 M solutions (Prolabo). All solutions were prepared with glass-distilled, de-ionized water and degassed by argon saturation in order to remove all dissolved CO$_2$.

Protometric titrations were carried out with an automatic titrator composed of a microprocessor burette Metrohm Dosimat 665 and a pH-meter Metrohm 713 connected to a computer. The combined type “U” glass electrode used has a very low alkaline error. The titration was fully automated. All measurements were performed within a thermoregulated cell at 25 °C under an argon stream to avoid the dissolution of carbon dioxide. For a classical
titration, a total of 120 to 150 points (volume of titrant, pH) was taken. All equilibrium measurements were carried out in 5.00 mL sample volumes with magnetic stirring. The ionic strength was adjusted to 0.1 with sodium chloride. A HNO₃ solution at exactly 10⁻² M was used to calibrate the electrode. The electrode slope was checked by titration with a HNO₃ solution, and no correction was necessary in the pH range 2 at 12. The ionic product of water was determined under these conditions (pKw = 13.75) and used in the calculations.

The protonation constants of the ligands were determined from the refinements of neutralisation curves with the general computation program PROTAF.³

**Optimal pH determination**

A solution of calixarene 3 in D₂O ([3] = 2.9 mM) in the presence of 1 equiv. of Zn(NO₃)₂·6H₂O and 3 equiv. of heptylamine was prepared and nitric acid was added until pD reaches a starting value of 5.9. Aliquots of a NaOD solution (10.8 mg in 1 mL D₂O) were gradually added to this solution and pD values and ¹H NMR spectra were recorded after each addition. The integration value of one of the encapsulated amine signal in comparison with a reference peak (acetone) was evaluated at different pD by gradual addition of NaOD.

6/ **DETERMINATION OF AFFINITY CONSTANT**

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**Figure S5:** $^1$H NMR (500 MHz, D$_2$O) of calixarene 3 in D$_2$O ([3] = 5.9 mM) with Zn(NO$_3$)$_2$.6H$_2$O (1 equiv.) and heptylamine (1 equiv.) at 300 K, pD = 7.44.

The formation constant $K$ and $K_{pH}$ of the ternary complex can be defined in the following equilibrium:

$$
\text{Zn}^{2+} + 3^{3+} + \text{RNH}_3^+ + \text{H}_2\text{O} \leftrightarrow [\text{Zn}(3)(\text{RNH}_2)^{2+} + \text{H}_3\text{O}^+] \quad (1)
$$

$$
K = K_{\text{eff}} = \frac{[[\text{Zn}(3)(\text{RNH}_2)^{2+}][\text{H}_3\text{O}^+]]}{[\text{Zn}^{2+}][3^{3+}][\text{RNH}_3^+]}
$$

and

$$
K_{pH} = \frac{[[\text{Zn}(3)(\text{RNH}_2)^{2+}]]}{[\text{Zn}^{2+}][3^{3+}][\text{RNH}_3^+]}
$$

From the above spectrum:

$$
\rho = \frac{[\text{Zn}(3)(\text{RNH}_2)^{2+}]}{[\text{RNH}_2]_{\text{free}}} = 0.16 \Rightarrow [\text{Zn}(3)(\text{RNH}_2)^{2+}] = \rho C_0/(1+\rho) = 0.814 \text{ mM}
$$

$\Rightarrow K = K_{\text{eff}} = 2.25.10^{-4} \text{ mol}^{-1}.\text{L} \Rightarrow pK_{\text{eff}} = 3.7$

and $K_{pH,7.44} = 6184 \text{ mol}^2.\text{L}^2$

From another experiment:

$^1$H NMR (500 MHz, D$_2$O) of calixarene 3 in D$_2$O ([3] = 5.9 mM) with Zn(NO$_3$)$_2$.6H$_2$O (1 equiv.) and heptylamine (1.5 equiv.) at 300 K, pD = 7.86.

$$
\rho = \frac{[\text{Zn}(3)(\text{RNH}_2)^{2+}]}{[\text{RNH}_2]_{\text{free}}} = 0.1075 \Rightarrow [\text{Zn}(3)(\text{RNH}_2)^{2+}] = \rho C_0/(1+\rho) = 0.859 \text{ mM}
$$

$\Rightarrow K = K_{\text{eff}} = 5.84.10^{-5} \text{ mol}^{-1}.\text{L} \Rightarrow pK_{\text{eff}} = 4.2$

$K_{pH,7.86} = 4232 \text{ mol}^2.\text{L}^2$

These calculations were repeated four times, on four different experiments. The obtained average values of $pK_{\text{eff}}$ is $4.0 \pm 0.3$. 

S-11
7/ AMINE RECEPTOR

**DimethylDOPA**

Ligand 3 (2 mg, 1.3 μmol) was dissolved in D₂O (400 μL). To this solution were added Zn(NO₃)₂·6H₂O (1.3 μmol, 29 μL of a solution containing 6.5 mg of Zn(NO₃)₂·6H₂O in 500 μL D₂O) and dimethylDOPA (3.9 μmol, 25.5 μL of a solution containing 5.5 mg of dimethylDOPA in 200 μL MeOD).

The ¹H NMR spectrum in D₂O of the ternary complex observed in the presence of dimethyldopamine is presented in Figure S6. As observed with heptylamine, it displays characteristic resonances of a dicationic C₃ symmetric complex where the zinc ion is coordinated to the three imidazole groups and to the amine substrate. Addition of only 1 equiv. of dimethyldopamine was enough to detect the NMR signature of the ternary complex. Further addition of dimethyldopamine led to an increase in ternary complex formation. In the absence of buffer and with C = 2.5 mM of calixarene 3 and Zn(II), the maximal amount of ternary complex was observed when 3 equivalents of dimethyldopamine were added. Under these conditions, around 60% of calixarene was effective as amine-receptor.
Figure S6: $^1$H NMR (500 MHz, D$_2$O, 300 K) of ligand 3 (C = 3.25 mM) with one equivalent of Zn(NO$_3$)$_2$.6H$_2$O and 3 equivalents of dimethylDOPA (blue-framed signals: dimethylDOPA out, red-framed signals: dimethylDOPA in)

$^1$H NMR (500 MHz, D$_2$O, 300 K): δ (ppm): 0.30 (CH$_2$(2) dimethylDOPA in, t, $J = 9$ Hz, 2H), 1.42 (tBu and CH$_2$(1) dimethylDOPA in, br s, 29H), 2.88 (OCH$_3$ dimethylDOPA in, 6H), 2.97 (br s, CH$_2$(2) dimethylDOPA out), 3.10 (N$^+$Me$_3$, s, 27H), 3.20 (OCH$_3$ dimethylDOPA in), 3.30 (CH$_2$(1) dimethylDOPA out, br s), 3.74 (OCH$_3$, 9H), 3.88 (OCH$_3$ dimethylDOPA out), 3.94 (NCH$_3$, s, 9H), 4.15 (H(5) dimethylDOPA in, d, $J = 8.0$ Hz, 1H), 4.45 (CH$_2$N$^+$Me$_3$, s, 6H), 4.59 (H(4’) dimethylDOPA in, s, 1H), 4.68 (H(4) dimethylDOPA in, d, $J = 8.0$ Hz, 1H), 6.95 (H(5) dimethylDOPA out, d, $J = 8.0$ Hz), 7.02 (H(4’) dimethylDOPA out, s), 7.07 (d, H(4 ) dimethylDOPA out, $J = 8.0$ Hz), 7.22 (H$_{Im}$, d, $J = 1.5$ Hz, 3H), 7.67 (H$_{Ar-tBu}$ br s, 6H), 7.73 (H$_{Im}$ d, $J = 1.5$ Hz, 3H), 7.94 (H$_{triazole}$, s, 3H).
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Tryptamine

Ligand 3 (1 μmol) was dissolved in D₂O (350 μL). To this solution were added Zn(NO₃)₂·6H₂O (1 μmol) and tryptamine (1 μmol, 6.5 μL of a solution containing 7.2 mg of tryptamine in 300 μL MeOD).
Figure S7: $^1$H NMR (500 MHz, D$_2$O, 300 K) of ligand 3 (C = 2.85 mM) with Zn(NO$_3$)$_2$.6H$_2$O (1 equiv.) and tryptamine (1 equiv.) (blue-framed signals: tryptamine out, red-framed signals: tryptamine in).

$^1$H NMR (500 MHz, D$_2$O, 300 K): δ (ppm): 0.34 (CH$_2$ (2) tryptamine in, t, $J = 8.0$ Hz, 2H), 1.42 (tBu and CH$_2$ (1) tryptamine in, s, 29H), 3.03 (N$^+$Me$_3$, s, 27H), 3.22 (CH$_2$(2) tryptamine out, br s), 3.38 (CH$_2$(1) tryptamine out, br s), 3.76 (OCH$_3$, s, 9H), 3.79 (CH$_2$Ar, d, $J = 16$ Hz, 6H), 3.95 (NCH$_3$, s, 9H), 4.24 (CH$_2$N$^+$Me$_3$, s, 6H), 4.47 (H (4) tryptamine in, s, 1H), 5.16 (H (5) tryptamine in, d, $J = 7.5$ Hz, 1H), 5.69 (CH$_2$Im, br s, 6H), 5.94 (H (6) tryptamine in, t, $J = 7.5$ Hz, 1H), 6.18 (H (7) tryptamine in, d, $J = 8.0$ Hz, 1H), 6.57 (H (7) tryptamine in, t, $J = 7.0$ Hz, 1H), 6.91 (H$_{ArTriaz}$ br s, 6H), 7.20 (H$_{im}$, d, $J = 1.5$ Hz, 3H), 7.23 (H (6) tryptamine out, t, $J = 7.0$ Hz), 7.27 (s, H Triazole, 3H), 7.32 (H (7) tryptamine out, t, $J = 7.5$ Hz), 7.35 (H (4) tryptamine out, s), 7.58 (H(5) tryptamine out, d, $J = 7.5$ Hz), 7.67 (H$_{Ar-Bu}$, s, 6H), 7.73 (H$_{im}$ and H (7) tryptamine out, d).

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**Tyramine**

Ligand 3 (1 μmol) was dissolved in D₂O (400 μL, C = 2.5 mM). To this solution were added Zn(NO₃)₂·6H₂O (1 μmol) and chlorhydrate salt of tyramine (1 μmol, 10.8 μL of a solution containing 2.7 mg of chlorhydrate salt of tyramine in 320 μL D₂O). pD value of the solution was recorded and reached 7.94.
Figure S8: $^1$H NMR (500 MHz, D$_2$O, 300 K) of ligand 3 (C = 2.5 mM) with Zn(NO$_3$)$_2$.6H$_2$O (1 equiv.) and chlorhydrate salt of tyramine (1 equiv.) (blue-framed signals: tyramine out, red-framed signals: tyramine in).

$^1$H NMR (500 MHz, D$_2$O, 300 K): $\delta$ (ppm): 0.21 (CH$_2$ (2) tyramine in, m, 2H), 1.45 (tBu and CH$_2$(1) tyramine in, s, 29H), 2.98 (CH$_2$(2) tyramine out, t, $J = 7.0$ Hz), 3.13 (N$^+\text{Me}_3$, s, 27H), 3.28 (CH$_2$(1) tyramine out, m), 3.77 (OCH$_3$, s, 9H), 3.80 (CH$_2$Ar, br s, 6H), 3.95 (NCH$_3$, s, 9H), 4.38 (H(5) tyramine in, d, $J = 7.5$ Hz, 2H), 4.60 (CH$_2$N$^+\text{Me}_3$, s, 6H), 4.91 (H(4) tyramine in, d, $J = 7.5$ Hz, 2H), 6.95 (H(5) tyramine out, d, $J = 8.0$ Hz), 7.22 (H$_{\text{Im}}$, br s, 3H), 7.26 (H(4) tyramine out, d, $J = 8.0$ Hz), 7.69 (H$_{\text{Ar-Bu}}$, br s, 6H), 7.73 (H$_{\text{Im}}$, s, 3H), 7.80 (s, 3H, H$_{\text{Triazole}}$).

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