# Unexpected Discovery of Calcium Cryptates with Exceptional Stability

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## Supplementary Information

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# 1. Materials and Methods

## General

NMR spectra were recorded on a Bruker AVII+400 spectrometer ($^1H$: 400.0 MHz, $^{13}C$: 100.6 MHz, $^{19}F$: 376.5 MHz) using $CD_3OD$ (≥ 99.8% D) or $D_2O$ (99.9% D) as the solvent. $H_4DOTA$ (Chematech), NaOD (40 wt.% in $D_2O$, Sigma-Aldrich), $Ca(OTf)_2$ (min. 99 %, Alfa Aesar), $La(OTf)_3$ (98 %, abcr) and $Lu(OTf)_3$ (98 %, Sigma-Aldrich) were obtained from commercial suppliers and used as received. $Na_2CaDOTA$ was synthesized as described in ref. S1.

## RP-HPLC

RP-HPLC was performed using Lichrospher RP-18e columns (Merck, preparative: 250 mm × 10 mm, 10 µm particle size; analytical: 125 mm × 4 mm, 5 µm particle size) on a Knauer AZURA P6.1L system. The purity of the isolated fractions was checked by analytical runs. Flow rates of 3.0 $mL \cdot min^{-1}$ and 1.0 $mL \cdot min^{-1}$ were used for preparative and analytical runs, respectively. The substances were detected by UV absorption at 300 nm.
Mobile phases (both preparative and analytical):
A: $H_2O$ (+1% $CF_3COOH$, v/v); B: $CH_3CN$ (HPLC gradient grade)

Gradient:

| min | %A | %B |
|---|---|---|
| 0 | 85 | 15 |
| 5 | 85 | 15 |
| 19 | 45 | 55 |
| 25 | 45 | 55 |
| 40 | 85 | 15 |
| 50 | 85 | 15 |

# 2. Synthetic Procedures and Analytical Data

## Serendipitous discovery 3-Ca($CF_3COO^-$)

The sodium cryptate **1-Na** was synthesized as described previously and “purified” (see manuscript text) by silica gel chromatography.[S2] Upon reacting the material with $LnCl_3 \cdot 6\ H_2O$ (Ln = Eu, Nd) in boiling $CH_3CN$ and purification via preparative RP-HPLC as described previously, two major products were isolated (Figure S1, reaction with $EuCl_3 \cdot 6\ H_2O$ is shown).[S2,S3] Subsequent experiments revealed that transformation of **1-Na** to **3-Ca** also occurred under those conditions without the addition of any lanthanoid salt. The yield of **3-Ca** varied drastically from batch to batch indicating strong fluctuations in the $Ca^{2+}$ content of the material. Through various control experiments, the purification via silica gel was determined to be the source of the calcium contamination.

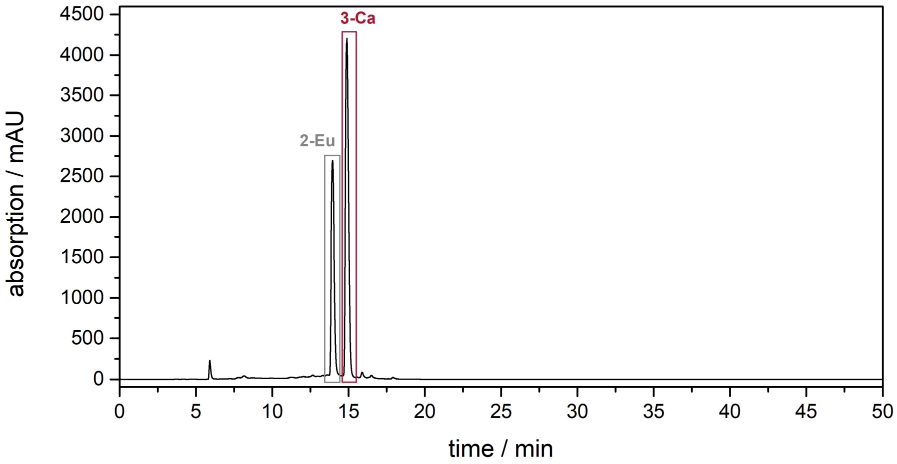


**Figure S1.** Preparative RP-HPLC (Lichrospher- RP-18e, 250 mm × 10 mm - 10 µm, 3 mL·min$^{-1}$ flow, $H_2O$+1% $CF_3COOH/CH_3CN$) of the purification of **2-Eu** showing the desired product (grey rectangle) and the "byproduct" **3-Ca** (red rectangle).

Analytical properties of **3-Ca**($CF_3COO^-$):

$^1$H NMR (400 MHz, $CD_3OD$): δ = 8.12 - 8.19 (m, 6 H), 8.10 (dd, *J* = 8.0, 2.0 Hz, 2 H), 8.06 (dd, *J* = 7.9, 1.9 Hz, 2 H), 7.92 - 8.01 (m, 6 H), 7.72 (dd, *J* = 6.4, 2.2 Hz, 2 H), 4.42 (d, *J* = 12.7 Hz, 2 H), 4.33 (d, *J* = 12.2 Hz, 2 H), 4.04 (d, *J* = 14.2 Hz, 2 H), 3.92 (d, *J* = 14.2 Hz, 2 H), 3.82 (d, *J* = 12.3 Hz, 2 H), 3.74 (d, *J* = 12.7 Hz, 2 H) ppm.

$^{13}$C NMR (100.6 MHz, $CD_3OD$): δ = 159.1, 157.3, 149.6, 149.2, 145.5, 142.2, 133.3, 132.9, 132.4, 132.2, 130.4, 129.2, 127.4, 124.5, 121.6, 62.5, 56.8, 56.6 ppm.

$^{19}$F NMR (376.5 MHz, $CD_3OD$): δ = –77.0 ppm.

HR-MS (ESI, pos. mode): m/z (%, assignment, $\Delta m_{rel}$) = 339.10032 (100, [**3-Ca**]$^{2+}$, 0.21 ppm), 661.22728 (26, [**1-Na**]$^+$, 1.4 ppm) , 791.18488 (12, [**3-Ca** + $CF_3COO$]$^+$, 1.5 ppm).

Anal. Calcd. (Found) for [**3-Ca**]$(CF_3CO_2)_2 \cdot 2\ CF_3CO_2H \cdot 3\ H_2O$ = $C_{44}H_{38}CaF_{12}N_8O_{15}$ ($M_r$ = 1186.89): C, 44.53 (44.21); H, 3.23 (3.33); N, 9.44 (9.60).

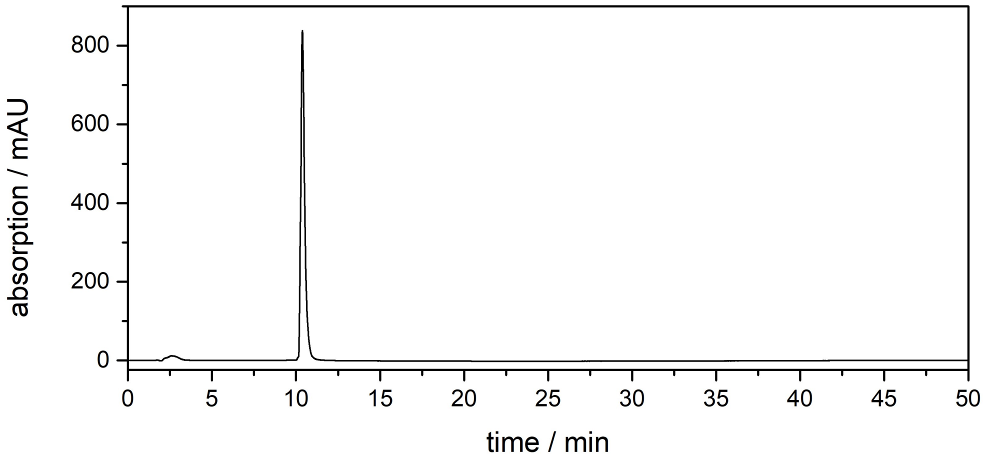
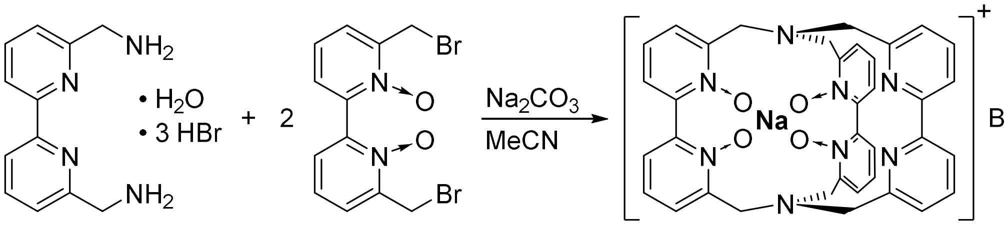


**Figure S2.** Analytical RP-HPLC (Lichrospher- RP-18e, 125 mm × 4 mm - 5 µm, 1 mL·min$^{-1}$ flow, $H_2O$+1% $CF_3COOH/CH_3CN$) of isolated **3-Ca** ($CF_3COO^-$) from the reaction described above.

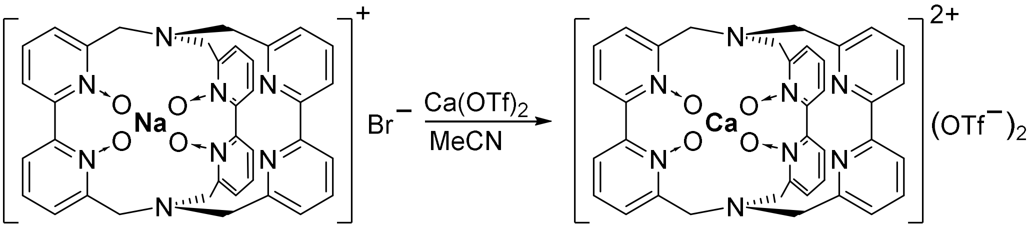
## Optimized synthesis of 3-Ca($^-$OTf)



A suspension of 6,6′-bis(aminomethyl)-2,2′-bipyridine trihydrobromide hydrate[S4] (150 mg, 316 µmol, 1.0 equiv.), 6,6′-bis(bromomethyl)-2,2′-bipyridine-*N*,*N*′-dioxide[S5] (236 mg, 631 µmol, 2.0 equivs.) and $Na_2CO_3$ (334 mg, 3.15 mmol, 10.0 equivs.) in $CH_3CN$ (300 mL, HPLC grade) was heated under reflux (100 °C bath temperature) for 21 h. Heating was discontinued, the hot solution was filtered, and all volatiles were removed from the filtrate *in vacuo*. Column chromatography (activated neutral aluminium oxide 90, activity I, $CH_2Cl_2/CH_3OH$ 25:1) yielded **1-Na** (Ca-free) as colorless, iridescent platelets (134 mg, 186 µmol, 57 %).

To ensure that this material is indeed free of undesired $Ca^{2+}$, 10 mg were dissolved in $CH_3CN$ (10 mL) and heated under reflux (100 °C bath temperature) for 48 h. The solvent was removed *in vacuo*. No sign of conversion into **3-Ca** was observed by TLC control or NMR spectroscopy proving that no free $Ca^{2+}$ was present in this material.

The analytical properties match those obtained previously.[S2]
TLC: $R_f$ = 0.25 (neutral $Al_2O_3$, $CH_2Cl_2/CH_3OH$ 25:1, UV detection).



**1-Na** (Ca-free, 40 mg, 54.0 µmol, 1.0 equiv.) and Ca(OTf)$_2$ (18.3 mg, 54.1 µmol, 1.0 equiv.) were dissolved in $CH_3CN$ (20 mL) and heated under reflux (100 °C bath temperature). Shortly after reaching boiling temperature, a fine, colorless precipitate began to form. The reaction mixture was heated for 20 h, additional Ca(OTf)$_2$ (9.4 mg, 27.8 µmol, 0.5 equivs.) was added, and heating was continued for 8 h. The heating bath was removed, and the hot solution was filtered over a PTFE filter (0.2 µm pore size). All volatiles were removed from the filtrate *in vacuo* yielding a colorless solid, which was subjected to column chromatography (activated neutral aluminium oxide 90, activity I, $CH_2Cl_2$/$CH_3OH$ 9:1). The product was obtained as a colorless solid (36.5 mg, 37.4 µmol, 69 %).

$^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 8.10 - 8.20 (m, 8 H), 8.07 (dd, *J* = 7.9, 1.9 Hz, 2 H), 7.93 - 8.01 (m, 6 H), 7.74 (dd, *J* = 6.7, 1.8 Hz, 2 H), 4.42 (d, *J* = 12.7 Hz, 2 H), 4.33 (d, *J* = 12.3 Hz, 2 H), 4.04 (d, *J* = 14.2 Hz, 2 H), 3.95 (d, *J* = 14.2 Hz, 2 H), 3.86 (d, *J* = 12.3 Hz, 2 H), 3.78 (d, *J* = 12.8 Hz, 2 H) ppm.

$^{13}$C NMR (100.6 MHz, $CD_3OD$): $\delta$ = 159.0, 157.2, 149.4, 149.1, 145.3, 142.1, 133.2, 132.7, 132.3, 132.1, 130.2, 129.0, 127.3, 124.4, 121.4, 62.4, 56.6, 56.4 ppm.

$^{19}$F NMR (376.5 MHz, $CD_3OD$): $\delta$ = –80.0 ppm.

MS (ESI, pos. mode): m/z (%) = 339.08 (100, [**3-Ca**]$^{2+}$).

TLC: $R_f$ = 0.25 (neutral $Al_2O_3$, $CH_2Cl_2$/MeOH 9:1, UV detection).

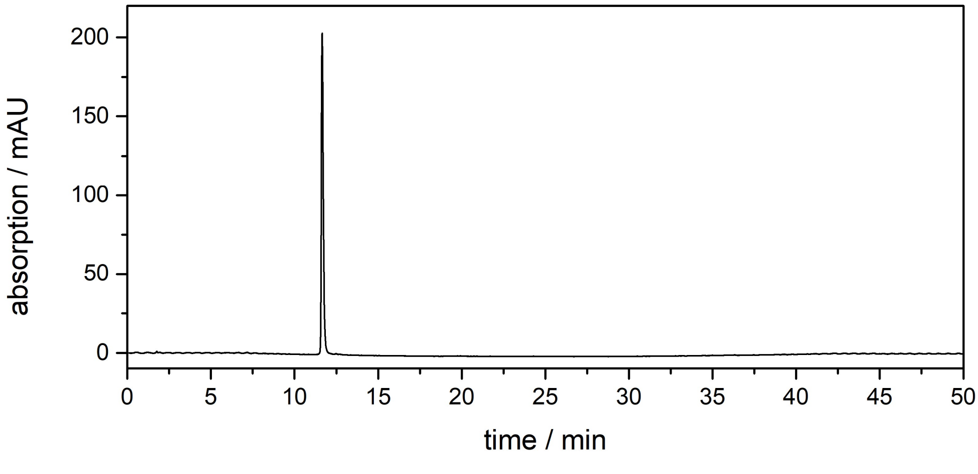


**Figure S3.** Analytical RP-HPLC (Lichrospher- RP-18e, 125 mm × 4 mm - 5 µm, 1 mL·min$^{-1}$ flow, $H_2O$+1% $CF_3COOH$/$CH_3CN$) of directly synthesized **3-Ca** ($^-$OTf).

## 3. Single Crystal X-ray Diffraction

Single crystals of **3-Ca**($CF_3COO^-$) were obtained by slow evaporation of a dichloromethane solution at room temperature, those of **3-Ca**($^-$OTf) were obtained by layering a methanol solution with diethyl ether. X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated Mo $K_\alpha$ radiation or a Bruker APEX II Duo diffractometer with a Mo IμS microfocus tube and a TRIUMPH monochromator. The programs used were Bruker's APEX2 v2011.8-0, including SADABS for absorption correction and SAINT for data reduction.[S6] The structure was solved within the Wingx (Version 2018.3) package[S7] using direct methods (SHELXT[S8a] and SIR2014[S8b]) and expanded using Fourier techniques (SHELXL-2018).[S8a,S9] All non-hydrogen atoms were refined isotropically. The hydrogen atoms attached to carbon atoms were positioned geometrically but not refined. All hydrogens were constrained to ride on their parent carbon atoms. $U_{iso}(H)$ values were set at 1.2 times $U_{eq}(C)$.

**Table S1.** Selected crystallographic data for **3-Ca** ($CF_3COO^-$) and **3-Ca** ($^-$OTf).

| Compound | **3-Ca** ($CF_3COO^-$) | **3-Ca** ($^-$OTf) |
|---|---|---|
| Empirical formula | $C_{40}H_{30}CaF_6N_8O_8$ | $C_{38}H_{30}CaF_6N_8O_{10}S_2$ |
| $M_r$ [g mol$^{-1}$] | 904.80 | 976.90 |
| Crystal appearance | colorless block | colorless prism |
| T [K] | 100(2) | 100(2) |
| $\lambda$ [Å] | 0.71073 (Mo $K_\alpha$) | 0.71073 (Mo $K_\alpha$) |
| Crystal system | monoclinic | monoclinic |
| Space group | C2/c | C2/c |
| Z | 4 | 4 |
| a [Å] | 27.4699(11) | 27.2841(9) |
| b [Å] | 9.5594(4) | 9.7632(3) |
| c [Å] | 18.4011(7) | 17.9917(5) |
| $\beta$ [°] | 129.344(2) | 127.373(1) |
| V [Å$^3$] | 3736.9(3) | 3808.7(2) |
| $D_{calc}$ [g cm$^{-3}$] | 1.608 | 1.704 |
| $\mu$ [mm$^{-1}$] | 0.267 | 0.378 |
| F(000) | 1856 | 2000 |
| Crystal size [mm × mm × mm] | 0.24 × 0.21 × 0.20 | 0.22 × 0.19 × 0.17 |
| $\theta$ range [°] | 2.22-28.98 | 3.04-29.70 |
| Limitting indices | $-37 \leq h \leq 37$<br>$-12 \leq k \leq 12$<br>$-23 \leq l \leq 24$ | $-36 \leq h \leq 38$<br>$-11 \leq k \leq 13$<br>$-25 \leq l \leq 25$ |
| Collected refl. | 26677 | 14347 |
| Independent refl. | 4883 | 5370 |
| Absorption corr. | empirical | empirical |
| Transm. (max., min.) | 0.746, 0.650 | 0.746, 0.699 |
| Parameters/restraints | 285 / 0 | 294 / 0 |
| $R_1$ [$I > 2\sigma(I)$]$^a$ | 0.1028 | 0.0438 |
| $wR_2$ [$I > 2\sigma(I)$]$^b$ | 0.2560 | 0.1211 |
| $R_1$ (all data)$^a$ | 0.1415 | 0.0492 |
| $wR_2$ (all data)$^b$ | 0.2847 | 0.1175 |
| GOF on $F^2$ | 0.970 | 1.054 |
| $\Delta\rho_{max,min}$ [e Å$^{-3}$] | 2.836 /-1.121 | 1.356 /-0.521 |

[a] $R_1$ factor definition: $R_1 = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|$

[b] $wR_2$ factor definition: $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)]^{1/2}$. Weighting scheme: $w = 1 / [\sigma^2(F_0)^2 + (np)^2]$, $p = [F_0^2 + 2 F_c^2] / 3$

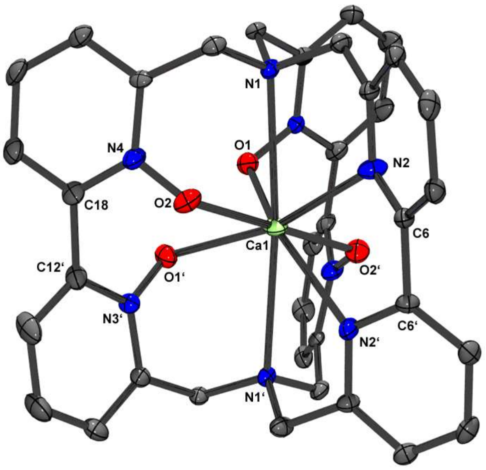


**Figure S4.** Thermal ellipsoid plot for the dicationic calcium complex in **3-Ca**(CF$_3$COO$^-$) (Ortep 3 for Windows,[S10] 50% probability level). The trifluoroacetate counterions and hydrogen atoms in the cryptate are omitted for clarity.

Interatomic distances [Å]: Ca1-N1 2.828(3), Ca1-N1' 2.828(3), Ca1-N2 2.702(4), Ca1-N2' 2.702(4), Ca1-O1 2.381(3), Ca1-O1' 2.381(3), Ca1-O2 2.306(3), Ca1-O2' 2.306(3). Angles [°]: O2-Ca1-O2' 179.15(17), O2-Ca1-O1 108.74(11), O2-Ca1-O1' 72.01(11), O1-Ca1-O1' 65.35(15), O2-Ca1-N2 85.48(11), O2-Ca1-N2' 93.79(11), O1-Ca1-N2 121.46(10), O1-Ca1-N2' 157.26(10), N2-Ca1-N2' 61.85(15), O2-Ca1-N1 71.12(10); O2-Ca1-N1' 108.94(10), O1-Ca1-N1 68.30(10), O1-Ca1-N1' 104.67(10), N2-Ca1-N1 63.63(10), N2-Ca1-N1' 124.25(10). Dihedral angles [°]: N4-C18-C12'-N3' 58.2, N2-C6-C6'-N2' 37.5.

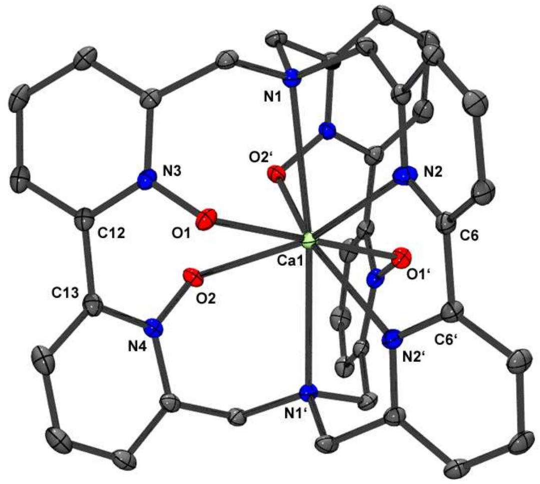


**Figure S5.** Thermal ellipsoid plot for the dicationic calcium complex in **3-Ca**($^-$OTf) (Ortep 3 for Windows,[S10] 50% probability level). The triflate counterions and hydrogen atoms in the cryptate are omitted for clarity.

Interatomic distances [Å]: Ca1-N1 2.8329(13), Ca1-N1' 2.8329(13), Ca1-N2 2.6451(15), Ca1-N2' 2.6451(15), Ca1-O2’ 2.4096(13), Ca1-O2 2.4096(13), Ca1-O1 2.3205(12), Ca1-O1' 2.3205(12). Angles [°]: O1-Ca1-O1' 178.61(6), O1-Ca1-O2' 106.89(4), O1-Ca1-O2 71.88(4), O2'-Ca1-O2 64.70(6), O1-Ca1-N2 85.67(4), O1-Ca1-N2' 95.52(4), O2'-Ca1-N2 121.45(4), O2'-Ca1-N2' 157.33(4), N2-Ca1-N2' 62.50(6), O1-Ca1-N1 71.23(4); O1-Ca1-N1' 108.65(4), O2'-Ca1-N1 66.98(4), O2'-Ca1-N1' 104.53(4), N2-Ca1-N1 63.94(4), N2-Ca1-N1' 125.53(4). Dihedral angles [°]: N3-C12-C13-N4 61.2, N2-C6-C6'-N2' 26.9.

# 4. Competition Experiments

## 4.1 3-Ca vs. DOTA$^{4-}$

For **3-Ca**($^{-}$OTf), competition experiments with three different ratios **3-Ca**/**DOTA**$^{4-}$ were performed. In a 5 ml volumetric flask, $H_4$DOTA · 1.5 $H_2O$ (431.4 mg, 1.00 mmol) was dissolved in dilute NaOD in $D_2O$ (0.4 wt%, 2.0 mL). Concentrated NaOD in $D_2O$ (40 wt% NaOD, 280 µL, 410 mg, 4.00 mmol NaOD) was added and the flask was filled with $D_2O$/NaOD (0.4 wt% NaOD). The pD of this solution was determined to be 14±0.2 using a glass electrode in combination with a Ag/AgCl reference electrode. Appropriate amounts of **3-Ca**($^{-}$OTf) were dissolved in the $Na_4$DOTA/NaOD/$D_2O$ mixture (500 µL) prepared above. The resulting clear, colorless solution was filtered through a syringe filter (PTFE, pore size 0.2 µm) into a quartz NMR tube (Qtz500-5-7, Deutero GmbH). In order to obtain a signal of constant integral for each experiment, a sealed capillary tube filled with a reference compound (MeO$^{t}$Bu in $CD_3OD$) was inserted into the tube before each measurement and was removed immediately after the measurement. For each competition experiment, NMR spectra were recorded immediately after mixing of the compounds (< 30 min at r.t. before the first spectrum was recorded) and after the specified intervals of heating at 100 °C. At the end of each experiment, the activity of the solution with respect to rapid complexation of free $Ca^{2+}$ was demonstrated by addition of the appropriate amounts of 1 M $Ca(OTf)_2$ in $D_2O$. Relative concentrations of the reactants **3-Ca** and **DOTA**$^{4-}$ in the solutions determined by integration are given below for each set of experiments.

Note: The acquisition of the spectra after the final additon of $Ca(OTf)_2$ were complicated by precipitation of $Ca(OD)_2$ and Ca[CaDOTA].

Experiment 1 (see Figure S6): Molar ratio of reactants **3-Ca**/**DOTA**$^{4-}$ = 1.2 to 1
Experiment 2 (see Figure S7): Molar ratio of reactants **3-Ca**/**DOTA**$^{4-}$ = 1 to 16
Experiment 3 (see Figure S8): Molar ratio of reactants **3-Ca**/**DOTA**$^{4-}$ = 1 to 77

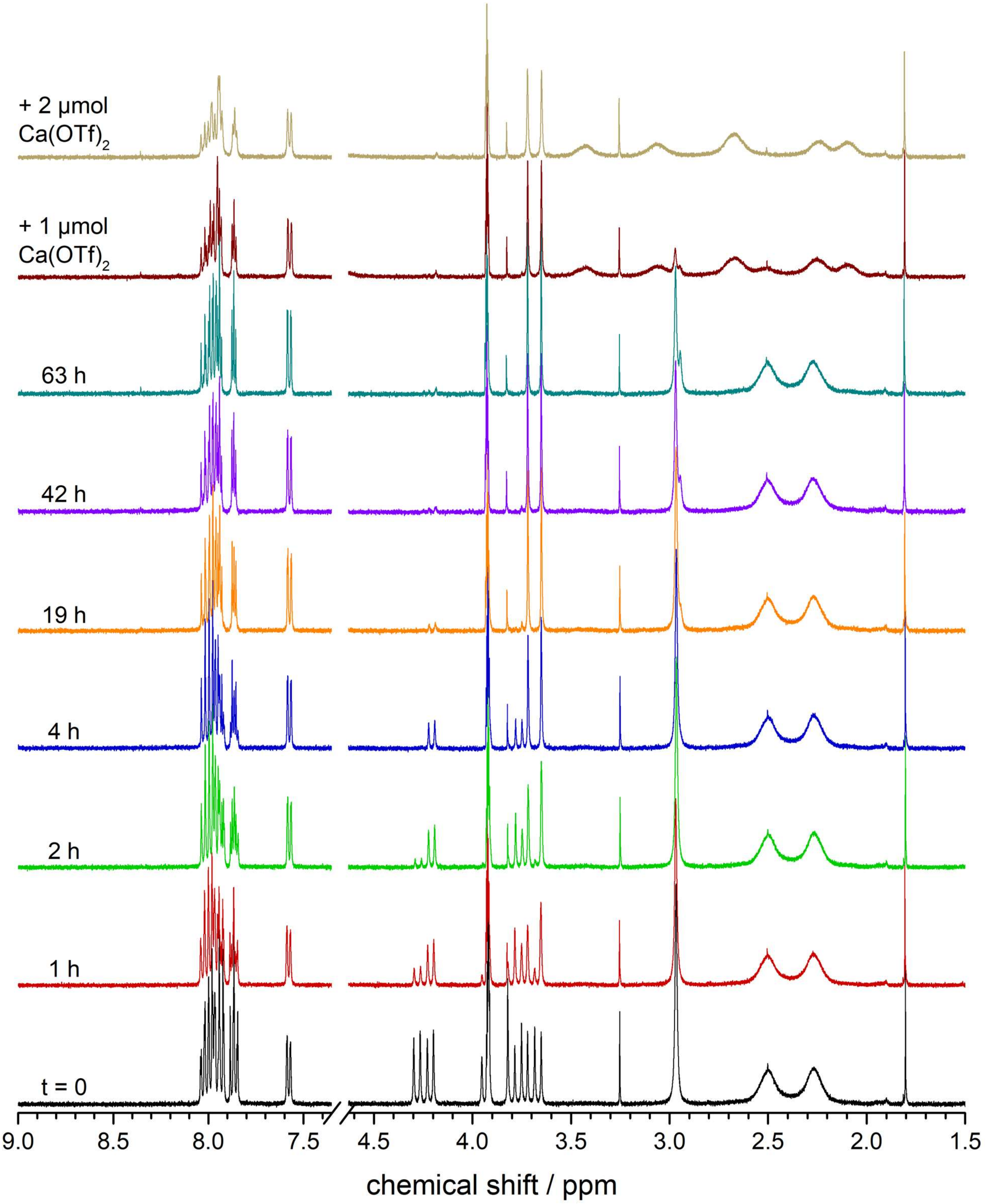


**Figure S6.** $^1$H NMR spectra (NaOD/$D_2O$, 400 MHz) of competition experiment 1 described above (**3-Ca**/**DOTA$^{4-}$** = 1.2 to 1).

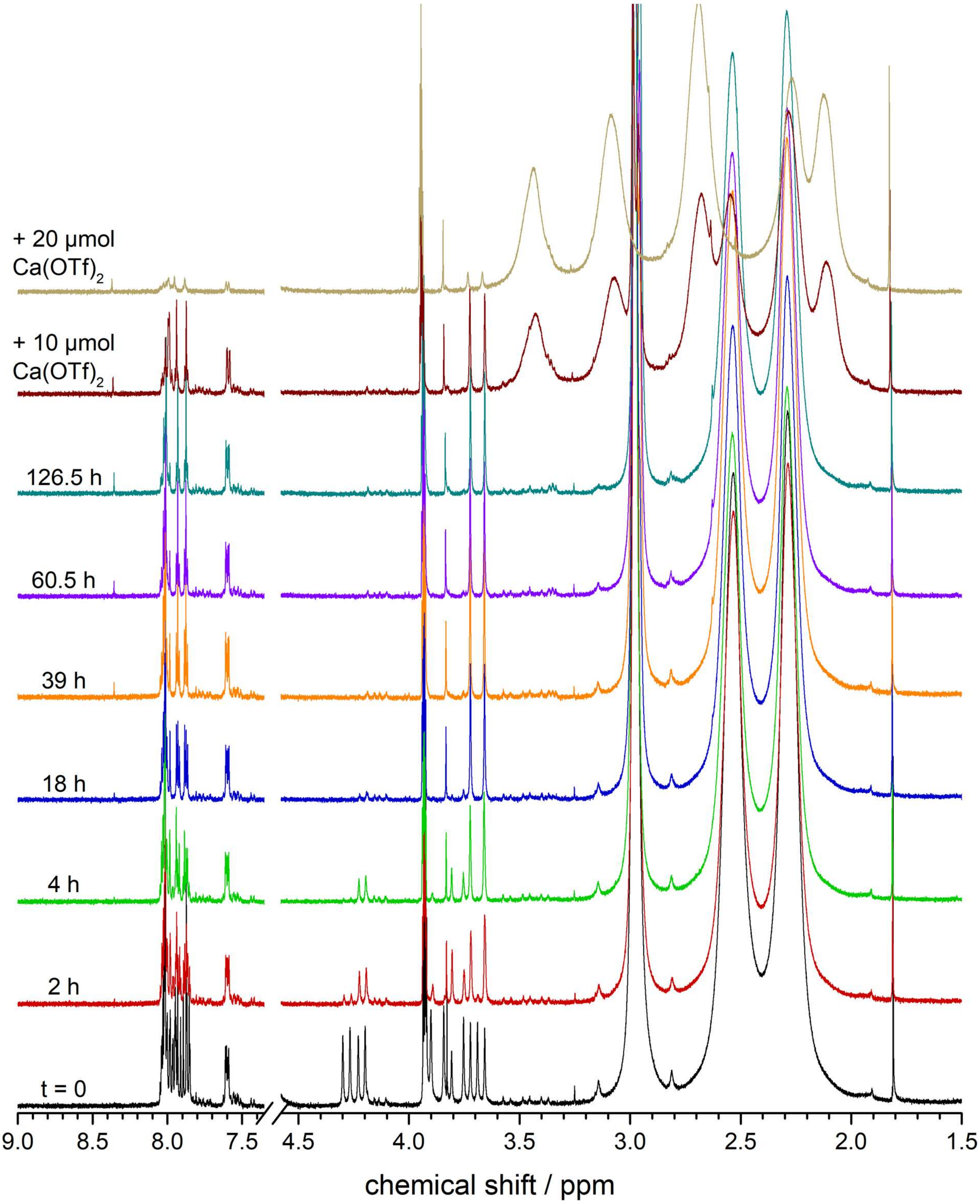


**Figure S7.** $^1$H NMR spectra (NaOD/$D_2O$, 400 MHz) of competition experiment 2 described above (**3-Ca**/**DOTA$^{4-}$** = 1 to 16). Remark: The small peak growing in over time at ca. 8.35 ppm is an unknown impurity in commercial $H_4$DOTA.

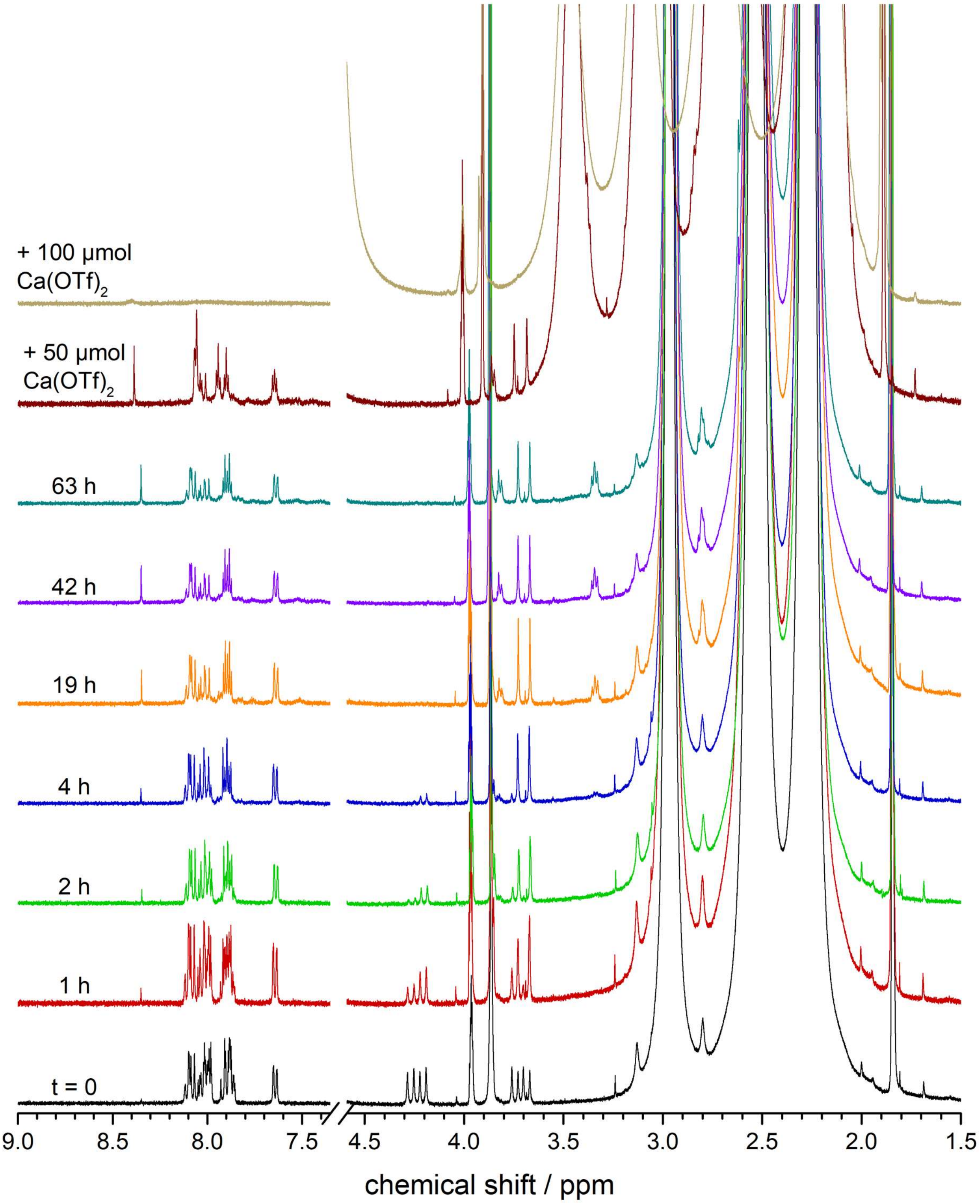


**Figure S8.** $^1$H NMR spectra (NaOD/$D_2O$, 400 MHz) of competition experiment 3 described above (**3-Ca**/**DOTA$^{4-}$** = 1 to 77). Remark: The small peak growing in over time at ca. 8.35 ppm is an unknown impurity in commercial $H_4$DOTA.

### 4.2 1-Na vs. $[Ca(DOTA)]^{2-}$

In a 5 mL volumetric flask, $Na_2[CaDOTA] \cdot H_2O$ (27.2 mg, 53.9 µmol) was dissolved in $D_2O$. 11 µL of 0.4wt% NaOD in $D_2O$ were added and the flask was filled with $D_2O$. The pD of this solution was determined to be 8.0±0.2 using a glass electrode in combination with a Ag/AgCl reference electrode. **1-Na** (Ca-free, 4.0 mg, 5.4 µmol, 1.0 equiv.) was dissolved in the solution of $Na_2[CaDOTA]$ (500 µL, 1.0 equiv.) prepared above resulting in a 1:1 mixture of the two reactants. The mixture was heated at 100°C (bath temperature). After 380 h, analytical RP-HPLC was used to detect and quantify **3-Ca** (Figure S9).

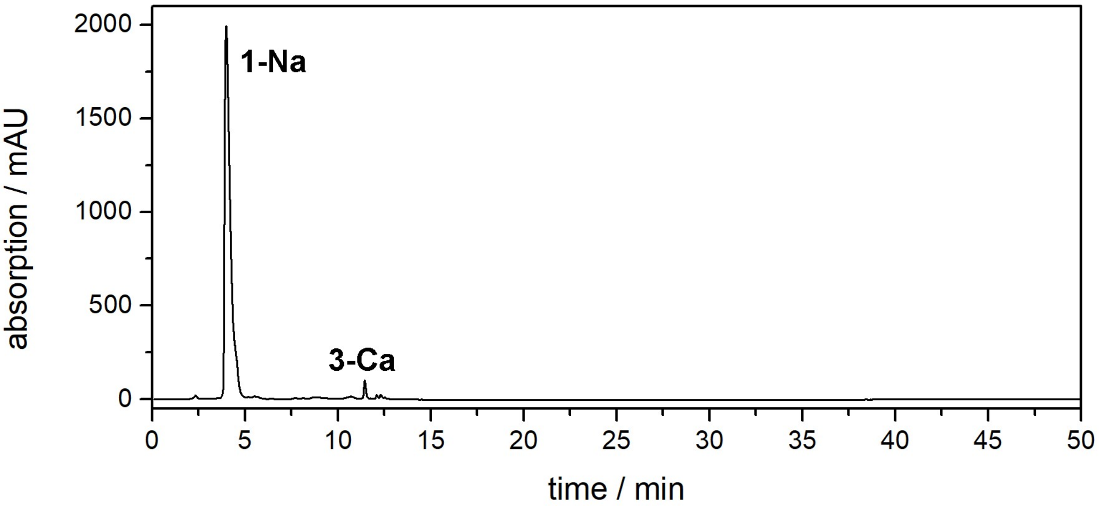


**Figure S9.** Competition **1-Na** vs. $[Ca(DOTA)]^{2-}$ after 380 h at 100°C in $D_2O$: Analytical RP-HPLC trace (Lichrospher- RP-18e, 125 mm × 4 mm - 5 µm, 1 $mL\cdot min^{-1}$ flow, $H_2O$+1% $CF_3COOH/CH_3CN$).

## 4.3 1-Na + $Ca(OTf)_2$ + $Ln(OTf)_3$ (Ln = La, Lu)

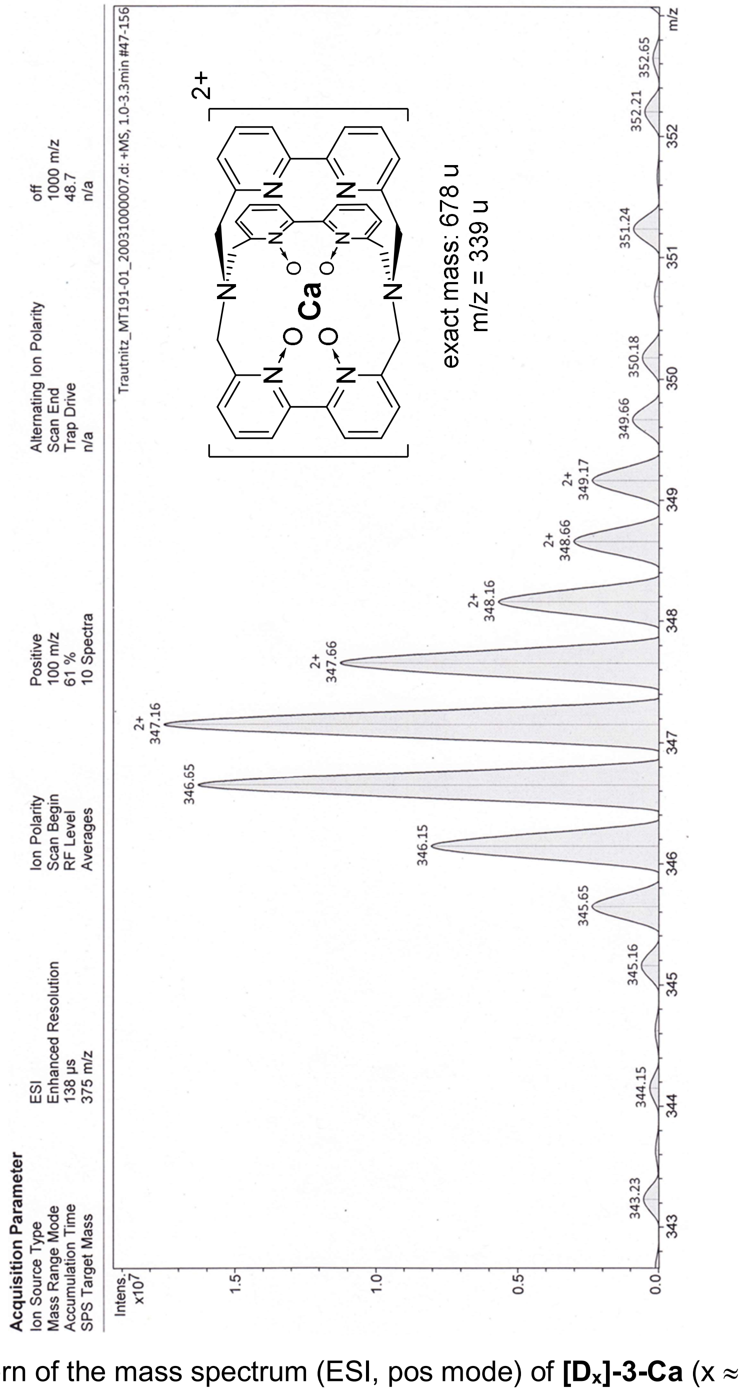
**1-Na** (Ca-free, 15.0 mg, 20.2 µmol, 1.0 equiv.), $Ca(OTf)_2$ (13.8 mg, 40.4 µmol, 2.0 equivs.) and $La(OTf)_3$ (30.3 mg, 40.4 µmol, 2.0 equivs.) were dissolved in $CH_3CN$ (15 mL, HPLC grade). The mixture was heated under reflux (bath temperature 100 °C) for 3h 40 min, cooled to room temperature and the solvent was removed under reduced pressure. The remaining colorless solid was thoroughly homogenized. A sample was taken, dissolved in $D_2O$, and a $^1H$ NMR spectrum was recorded which showed the exclusive formation of **3-Ca** and no sign of **2-La**.

**1-Na** (Ca-free, 5.0 mg, 6.75 µmol, 1.0 equiv.), $Ca(OTf)_2$ (4.6 mg, 13.5 µmol, 2.0 equivs.) and $Lu(OTf)_3$ (10.8 mg, 13.5 µmol, 2.0 equivs.) were dissolved in $CH_3CN$ (5 mL, HPLC grade). The mixture was heated under reflux (bath temperature 100 °C) for 15 min, cooled to room temperature and the solvent was removed under reduced pressure. The colorless solid was thoroughly homogenized. A sample was taken, dissolved in $D_2O$ and an NMR spectrum was recorded. The relative amounts of **3-Ca** and **2-Lu** were determined by integration of the cleanly separated doublets at 7.58 (**3-Ca**) and 7.70 (**2-Lu**) ppm. Based on this evaluation, a product ratio **3-Ca**/**2-Lu** of 97:3 was found.

## 4.4 3-Ca + $Lu(OTf)_3$

**3-Ca**($^-$OTf) (5.0 mg, 5.1 µmol, 1.0 equiv.) and $Lu(OTf)_3$ (40.1 mg, 50.1 µmol, 10.0 equivs.) were dissolved in $CH_3CN$ (10 mL, HPLC grade) and heated under reflux (bath temperature 100 °C). After selected heating intervals, samples were taken and the solvent was removed. The colourless residue was dissolved in $D_2O$ and a $^1H$ NMR spectrum was recorded. The last spectrum was recorded after 8 days of heating and none of the spectra showed any sign of formation of **2-Lu**.

# 5. Deuteration of 3-Ca during the Competition Experiments



**Acquisition Parameter**

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Mass Range Mode Enhanced Resolution
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SPS Target Mass 375 m/z
Ion Polarity Positive
Scan Begin 100 m/z
RF Level 61 %
Averages 10 Spectra
Alternating Ion Polarity off
Scan End 1000 m/z
Trap Drive 48.7
n/a n/a

Trautnitz_MT191-01_20031000007.d: +MS, 1.0-3.3min #47-156

**Figure S10.** Isotope pattern of the mass spectrum (ESI, pos mode) of **[D$_x$]-3-Ca** (x ≈14-17).

# 6. References

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