Supporting Information 2: 
Quantitative analysis of zero-field splitting parameter distributions in Gd(III) complexes

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2. NMR spectra.
Unless otherwise stated, reactions were performed under ambient atmosphere using solvents and reagents as commercially received, except THF (HPLC grade) which was distilled from sodium/benzophenone prior to use. Gd-DOTA (2) was commercially obtained. If inert atmosphere was needed, argon was used that was passed through anhydrous CaCl₂ prior to use. The solvents used for extraction and chromatography were of technical grade and were distilled prior to their use. For the preparation of the aqueous solutions, deionized water was used. Semi-saturated aqueous solution of NaHCO₃ was prepared by mixing a saturated aqueous solution of NaHCO₃ with an aliquot of water. The proton-exchange resin (Dowex® 50WX4 hydrogen form, Sigma-Aldrich, 91 g) was subsequently washed with THF (3 × 200 mL), EtOH (2 × 100 mL), H₂O (2 × 150 mL), and EtOH (200 mL) and then dried over P₂O₅ at ~0.05 mbar for 5 days to obtain a purified and dry proton-exchange resin (30 g).

The temperatures given for the reactions refer to the bath temperature. Solvents were removed at a bath temperature of about 40 °C and reduced pressure. The products were dried at room temperature at ~0.05 mbar. The pH/pD values of the solutions were determined using pH indicator strips (resolution: 0.3 pH or 0.5 pH).

Column chromatography was carried out on silica gel 60 (0.035 − 0.070 mm) applying slight pressure with argon gas. In the procedures reported below, the size of the column is given as diameter × length. Unless otherwise stated, the material was loaded onto the column dissolved in a small quantity of the eluent. Analytical thin layer chromatography (TLC) was performed on silica gel 60 containing fluorescent indicator F254. The solid support for the silica gel layer was aluminum foil. The compound spots were detected with UV light of λ = 254 nm. The compositions of solvent mixtures are given in volume ratios.

For centrifugation, a centrifuge with a relative centrifugal force of 6500rpm/4000g was used.

NMR spectra were recorded at room temperature. NMR spectra were calibrated using the solvent signal as an internal standard [CDCl₃: δ (1H) = 7.25, δ (13C) = 77.0; DMSO-d₆: δ (1H) = 2.49, δ (13C) = 39.5; CD₃OD: δ (1H) = 3.31, δ (13C) = 49.0; D₂O: δ (1H) = 4.79]. For ¹³C NMR experiments in D₂O, a drop of MeOH was added as the internal standard [δ (¹³C)MeOH = 49.5]. Signal assignments are supported by DEPT-135, COSY, HMBC, and HMQC experiments.

ESI MS spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik) equipped with a standard ESI source. Accurate MS experiments were performed using a FT-ICR mass spectrometer APEX III (Bruker Daltonik) interfaced to an external...
ESI ion source.

**Synthesis of Gd-NO3Pic (1)**

The procedures reported by Huang et al.\(^1\) and by Storr et al.\(^2\) for the synthesis of mesylate 17 and the procedure reported by Gateau et al.\(^3\) for the syntheses of Et\(_3\)NO3Pic (ethyl analogon of Me\(_3\)NO3Pic (19)) and Gd-NO3Pic (1) were the basis for our work. We applied some modifications.

**Methyl 6-(hydroxymethyl)picolinate (16).** This reaction was performed under argon. NaBH\(_4\) (1.02 g, 26.9 mmol) was added portionwise within 10 min to a suspension of dimethyl pyridine-2,6-dicarboxylate (15) (3.00 g, 15.4 mmol) in MeOH (100 mL) under cooling with an ice water bath (caution: gas evolution). During the adding of NaBH\(_4\) the colorless suspension turned into a slightly pink solution. The solution was stirred, while still in the cooling bath, for 10 min. Then, the cooling bath was removed and the solution was stirred at room temperature for 165 min. During the stirring the color of the solution changed from pinkish to colorless. Under cooling with an ice water bath, hydrochloric acid (37 wt.%, 4 mL) was added to lower the pH of the solution from 9 to 2, upon which a colorless precipitate formed. The solvent of the suspension was removed. The residual colorless solid was dissolved in water (20 mL). A saturated aqueous solution of NaHCO\(_3\) (28 mL) was added to rise the pH of the solution to 8 (caution: vigorous gas evolution). The aqueous solution was extracted with CH\(_2\)Cl\(_2\) (3 × 40 mL). The combined organic phases were dried over Na\(_2\)SO\(_4\), the suspension was filtered, and the solvent of the filtrate was removed. Column chromatography (3.5 cm × 32 cm, CH\(_2\)Cl\(_2\)/MeOH 10:1) of the residual colorless solid (2.35 g) gave methyl 6-(hydroxymethyl)picolinate (16) (1.84 g, 71%; \(R_f = 0.50\)) as a
colorless solid and dimethyl pyridine-2,6-dicarboxylate (15) (417 mg, 14%; \( R_f = 0.78 \)) as a colorless solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.02 \) (d, \( ^3J = 7.7 \) Hz, 1H, H\(_{Ar}\) para to CH\(_2\)OH), 7.85 (apparent t, \( ^3J = 7.7 \) Hz, \( ^3J = 7.8 \) Hz, 1H, H\(_{Ar}\) meta to CH\(_2\)OH), 7.53 (d, \( ^3J = 7.8 \) Hz, 1H, H\(_{Ar}\) ortho to CH\(_2\)OH), 4.86 (s, 2H, CH\(_2\)), 3.98 (s, 3H, CH\(_3\)), 2.99 (s br, 1H, OH). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 165.5 \) (C=O), 160.1 (C\(_{Ar}\)CH\(_2\)OH), 146.9 (C\(_{Ar}\)C=O), 137.8 (C\(_{Ar}\)H meta to CH\(_2\)OH), 124.0 (C\(_{Ar}\)H ortho to CH\(_2\)OH), 123.9 (C\(_{Ar}\)H para to CH\(_2\)OH), 64.5 (CH\(_2\)), 52.9 (CH\(_3\)). MS (ESI): \( m/z = 189.9 \) [M + Na]\(^+\).

**Mesylate 17.** This reaction was performed in dried glassware under argon. Triethylamine (2.0 mL, 14.4 mmol) and MsCl (0.6 mL, 7.8 mmol) were added successively to a solution of methyl 6-(hydroxymethyl)picolinate (16) (760 mg, 4.55 mmol) in dry CH\(_2\)Cl\(_2\) (50 mL) under cooling with an ice water bath. The yellow solution was stirred, while still in the cooling bath, for 2 h, during which time the color of the solution changed to dark yellow. The dark yellow solution was poured into a mixture of semi-saturated aqueous solution of NaHCO\(_3\) (50 mL). The organic phase was separated, and the aqueous phase was extracted with CH\(_2\)Cl\(_2\) (3 \( \times \) 25 mL). The combined organic phases were washed with semi-saturated aqueous NaHCO\(_3\) solution (2 \( \times \) 20 mL) and dried over MgSO\(_4\). The suspension was filtered, and the solvents of the filtrate were removed. Column chromatography (3.0 cm \( \times \) 32 cm, CH\(_2\)Cl\(_2\)/Et\(_2\)O 1:1) of the residual beige solid (1.15 g) gave mesylate 17 (783 mg, 70%; \( R_f = 0.33 \)) as a colorless solid. Because of the poor solubility in CH\(_2\)Cl\(_2\)/Et\(_2\)O 1:1, the beige solid was loaded onto the column dissolved in a small quantity of CH\(_2\)Cl\(_2\). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.10 \) (d, \( ^3J = 7.8 \) Hz, 1H, H\(_{Ar}\) para to CH\(_2\)OMs), 7.92 (t, \( ^3J = 7.8 \) Hz, 1H, H\(_{Ar}\) meta to CH\(_2\)OMs), 7.68 (d, \( ^3J = 7.8 \) Hz, 1H, H\(_{Ar}\) ortho to CH\(_2\)OMs), 5.42 (s, 2H, CH\(_2\)), 3.99 (s, 3H, OCH\(_3\)), 3.14 (s, 3H, OMs). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 165.1 \) (C=O), 154.4 (C\(_{Ar}\)CH\(_2\)), 147.7 (C\(_{Ar}\)C=O), 138.3 (C\(_{Ar}\)H meta to CH\(_2\)OMs), 125.2 (C\(_{Ar}\)H ortho to CH\(_2\)OMs), 124.9 (C\(_{Ar}\)H para to CH\(_2\)OMs), 70.9 (CH\(_2\)), 53.0 (OCH\(_3\)), 38.0 (O\(_3\)SCH\(_3\)). MS (ESI): \( m/z = 267.9 \) [M + Na]\(^+\).

**Me\(_3\)NO\(_3\)Pic (19).** A solution of mesylate 17 (233 mg, 0.95 mmol) in acetonitrile (2 mL) was added dropwise to a suspension of 1,4,7-triazacyclononane trihydrochloride (18) (77 mg, 0.32 mmol) and K\(_2\)CO\(_3\) (266 mg, 1.92 mmol) in acetonitrile (15 mL). This suspension was heated to reflux (oil bath temperature 96 °C) for 22.5 h. The pale yellow suspension was filtered. The solvent of the filtrate was removed. The residual yellow oil (212 mg) was dissolved in CH\(_2\)Cl\(_2\) (20 ml) and this solution was washed with semi-saturated aqueous NaHCO\(_3\) solution (2 \( \times \) 10 mL) and dried over Na\(_2\)SO\(_4\). The suspension was filtered and the solvents were removed giving Me\(_3\)NO\(_3\)Pic (19) (101 mg, 56%) as a yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.99 \) (d, \( ^3J = 7.7 \) Hz, 3H, H\(_{Ar}\) para to CH\(_2\)N), 7.80 (apparent t, \( ^3J = 7.7 \) Hz, \( ^3J = 7.5 \) Hz, 3H, H\(_{Ar}\) meta to CH\(_2\)N), 7.76 (d, \( ^3J = 7.5 \) Hz, 3H, H\(_{Ar}\) ortho to CH\(_2\)N),
3.97 (s, 9H, OCH₃), 3.94 (s, 6H, ArCH₂), 2.88 (s, 12H, CH₂CH₂). ¹³C NMR (125 MHz, CDCl₃): δ = 165.9 (C=O), 161.4 (CArCH₂N), 147.2 (CArC=O), 137.2 (CArH meta to CH₂N), 126.3 (CArH ortho to CH₂N), 123.5 (CArH para to CH₂N), 64.7 (ArCH₂), 56.1 (CH₂CH₂), 52.9 (OCH₃). MS (ESI): m/z = 599.2 [M + Na]+, 577.2 [M + H]+.

[Na₃NO₃Pic]•3 NaCl•x H₂O (20). Me₃NO₃Pic (19) (94 mg, 163 μmol) was dissolved in EtOH (2 mL) and water (1.5 mL). An aqueous NaOH solution (2 M, 0.5 mL, 1.0 mmol) was added and the yellow solution was stirred at room temperature for 31.5 h. Aqueous hydrochloric acid (2 M, 0.25 mL, 0.5 mmol) was added to lower the pH of the solution to 11.5. Removal of the solvents gave [Na₃NO₃Pic]•3 NaCl•x H₂O (20) (124 mg, containing 131 μmol of the structural motif [NO₃Pic]³⁻ as determined by quantitative ¹H NMR spectroscopy;⁴,⁵ yield 80%) as a pale yellow solid. ¹H NMR (500 MHz, D₂O): δ = 7.85 (t, 3J = 7.7 Hz, 3H, HAr meta to CH₂N), 7.79 (d, 3J = 7.7 Hz, 3H, HAr para to CH₂N), 7.40 (d, 3J = 7.7 Hz, 3H, HAr ortho to CH₂N), 3.85 (s, 6H, ArCH₂), 2.87 (s, 12H, CH₂CH₂). ¹³C NMR (125 MHz, D₂O): δ = 173.7 (C=O), 157.2 (CArCH₂N), 154.1 (CArC=O), 139.1 (CArH meta to CH₂N), 126.7 (CArH ortho to CH₂N), 123.3 (CArH para to CH₂N), 62.3 (ArCH₂), 52.6 (CH₂CH₂). MS (ESI): m/z = 601.1 [Na₃NO₃Pic + H]+, 623.1 [Na₃NO₃Pic + Na]+.

Gd-NO₃Pic (1). A solution of [Na₃NO₃Pic]•3 NaCl•x H₂O (20) in D₂O (150 μL, containing 3.89 μmol of the structural motif [NO₃Pic]³⁻) was mixed with a solution of GdCl₃ in D₂O (50 mM, 74 μL, 3.70 μmol). The resulting solution was diluted with D₂O (to a total volume of 778 μL) to obtain a 5 mM solution of Gd-NO₃Pic (1) in D₂O containing NaCl. The pD of the solution was 7.5. MS (ESI): m/z = 712.1 [M + Na]+.

Synthesis of Gd-maleimide-DOTA (3)

Gd-maleimide-DOTA (3). A solution of GdCl₃ in D₂O (0.1 M, 46.3 μL, 4.63 μmol) was added to a solution of maleimide-H₃DOTA (21) (purity 94 wt.% as determined with quantitative ¹H NMR spectroscopy, 4.049 mg, 4.84 μmol) in D₂O (500 μL). A solution of NaOD in D₂O (0.10 M, 250 μL, 25 μmol) was added to rise the pD of the solution to 8.2. The solution was diluted with D₂O (233.3 μL) to obtain a 4.5 mM solution of Gd-maleimide-DOTA (3) in D₂O. MS (ESI): m/z = 704.2 [M + Na]+.
Synthesis of R-(Gd-PyMTA) (4)

![Diagram of Synthesis of R-(Gd-PyMTA) (4)]

The syntheses of iodo-H$_4$PyMTA • n TFA (22), iodo-(Gd-PyMTA) (4a), and MOMethynyl-H$_n$NamPyMTA (23) were reported in our previous work.$^{4,6,7}$

**MOMethynyl-(Gd-PyMTA) (4b).** A solution of GdCl$_3$ in D$_2$O (0.1 M, 331.1 μL, 33.11 μmol) was added to a solution of MOMethynyl-H$_n$NamPyMTA (23) in D$_2$O (1743 μL, containing 34.85 μmol of the structural motif [MOMethynyl-PyMTA]$^{4-}$ as determined by quantitative $^1$H NMR spectroscopy$^4,5$). The solution was diluted with D$_2$O (1411 μL) to obtain a 10.0 mM solution of MOMethynyl-(Gd-PyMTA) (4b). A part of the obtained solution (100 μL) was mixed with a solution of NaOD in D$_2$O (0.10 M, 33 μL, 3.3 μmol), a solution of NaCl in D$_2$O (0.10 M, 37 μL), and D$_2$O (330 μL) to obtain a 2.0 mM solution of MOMethynyl-(Gd-PyMTA) (4b) in D$_2$O containing NaCl. The pD of the solution was 8.2. MS (ESI): $m/z = 590.9$ [M$^+$].

Synthesis of Gd-TAHA (5)

![Diagram of Synthesis of Gd-TAHA (5)]

The synthesis of H$_6$TAHA • n TFA (24) was reported in our previous work.$^6$

**Gd-TAHA (5).** H$_6$TAHA • n TFA (24) (10.053 mg, containing 15.63 μmol of the structural motif H$_6$TAHA) was dissolved in D$_2$O (600 μL). A part of the obtained solution (100 μL, containing 2.60 μmol of the structural motif [TAHA]$^{6-}$) was mixed with a solution of GdCl$_3$ • 6
H₂O in D₂O (0.05 M, 49 μL, 2.45 μmol). A solution of NaOD in D₂O (0.10 M, 130 μL, 13 μmol) was added to raise the pH of the solution to 6.5. The solution was diluted with D₂O (to a total volume of 520 μL) to obtain a 5.0 mM solution of Gd-TAHA (5) in D₂O containing Na(O₂CCF₃). MS (ESI): m/z = 680.9 [M + 2 H]+.

**Synthesis of iodo-(Gd-PCTA-[12]) (6)**

The strategy reported by Ferroud et al.⁸ for the synthesis of Gd-PCTA-[12] with a substituent in meta position of the pyridine ring was applied to synthesize iodo-(Gd-PCTA-[12]) (6). The procedure reported by Favre-Réguillon et al.⁹ for the nosylation of 1,4,7-triazahexane and the procedures reported by Ferroud et al.⁸ for the synthesis of dinosylate 29, diamine 30 and PCTA-[12] were the basis for our work. We applied some modifications. The synthesis of mesylate 31 was reported in our previous work.⁴ For nosylation of diethylenetriamine (25) the procedure reported by Favre-Réguillon et al.⁹ for the threefold nosylation of was applied. However, we isolated only the dinosylation product in form of the salt 1,7-dinosyl-1,4,7-triazahexane • NsOH (27). Obviously, hydrolysis of 2-nitrobenzenesulfonyl chloride (NsCl) (26) was competing with N-nosylation.

For denosylation p-toluenethiol was used instead of benzenethiol because of the toxicity of the latter.

**1,7-Dinosyl-1,4,7-triazahexane•NsOH (27).** A solution of 2-nitrobenzenesulfonyl chloride (NsCl) (26) (30.9 g, 140 mmol) in THF (300 mL) was added dropwise within 2 h to a suspension of diethylenetriamine (25) (4.4 mL, 41 mmol) and NaHCO₃ (23.7 g, 282 mmol) in THF (300 mL) under cooling with an ice water bath, during which time the color of the suspension changed to yellow. The cooling bath was removed and the suspension was stirred at room temperature for 69 h. The suspension was filtered. The solvent of the filtrate was removed. The residual orange brown solid was recrystallized twice in CH₂Cl₂ (140 mL,
1,7-Dinolsyl-1,4,7-triazaheptane•NsOH (27) (8.45 g, 68%) was obtained as pale brown solid. 1H NMR (500 MHz, DMSO-d6): δ = 8.68 (br s, 2H, H2N+), 8.32 (t, J = 5.7 Hz, 2H, NsNH), 7.84 (m, 1H, H Ar of NsO- ortho to NO2), 7.56 (m, 2H, H Ar of NsO- para to NO2 and H Ar of NsO- para to SO3-), 7.50 (m, 1H, H Ar of NsO- ortho SO3-), 7.91 (m, 4H, H Ar of NsNs para to NO2 and H Ar of NsNs para to SO3NH), 8.02 (m, 4H, H Ar of NsO- para to NO2 and H Ar of NsO- para to SO3-), 7.91 (m, 4H, H Ar of NsNs para to NO2 and H Ar of NsNs para to SO3NH), 7.84 (m, 1H, H Ar of NsO- ortho to NO2), 7.56 (m, 2H, H Ar of NsO- para to NO2 and H Ar of NsO- para to SO3-), 7.50 (m, 1H, H Ar of NsO- ortho SO3-), 3.18 (apparent q, J = 6 Hz, 4H, NsNHCH2CH2), 3.07 (apparent pent, J = 6 Hz, 4H, NsNHCH2CH2). 13C NMR (125 MHz, DMSO-d6): δ = 147.8 (CArNO2 of NsO-), 147.7 (CArNO2 of NsNs), 134.5 (CArH of NsO- ortho to NO2), 124.7 (CArH of NsO- para to NO2), 122.3 (CArH of NsO- para to SO3-), 130.0 (CArH of NsO- ortho to NO2), 129.0 (CArH of NsO- ortho to SO3), 131.8 (CArSO2N), 129.6 (CArH of NsNs para to NO2), 133.4 (CArSO2N), 130.7 (CArH of NsO- para to NO2), 131.8 (CArH of NsO- para to SO3), 46.5 (CH2CH2NHNss), 39.0 (CH2CH2NHNss). MS (ESI): m/z = 496.1 [1,7-dinosyl-1,4,7-triazaheptane + Na]+, 474.1 [1,7-dinosyl-1,4,7-triazaheptane + H]++. 

Dinosylate 29. Tert-butyl bromoacetate (28) (3.8 mL, 26 mmol) was added dropwise within 5 min to a suspension of 1,7-dinosyl1,4,7-triazaheptane•NsOH (27) (2.01 g, 2.97 mmol) and K2CO3 (17.5 g, 127 mmol) in acetonitrile (100 mL). This suspension was heated to reflux for 2 h and then stirred at room temperature for 17 h. The suspension was filtered. The solvent of the filtrate was removed. Column chromatography (7.0 cm × 30 cm, ethyl acetate/n-hexane 1:1) of the residual yellow oil gave dinosylate 29 (1.44 g, 59%; Rf = 0.26) as a viscous yellow oil. 1H NMR (500 MHz, CDCl3): δ = 8.07 (m, 2H, H Ar ortho to NO2), 7.66 (m, 4H, H Ar para to NO2 and H Ar para to SO3N), 7.57 (m, 2H, H Ar ortho to SO3N), 4.15 (s, 4H, NsNCH2CO2tBu), 3.45 (t, J = 6.9 Hz, 4H, NsNCH2CH2), 3.23 (s, 2H, (CH2)2NCH2CO2tBu), 2.86 (t, J = 6.9 Hz, 4H, NsNCH2CH2), 1.43 (s, 9H, (CH2)2NCH2CO2tBu), 1.33 (s, 18H, NsNCH2CO2tBu). 13C NMR (125 MHz, CDCl3): δ = 170.2 ((CH2)2NCH2CO2Bu), 167.8 (NsNCH2CO2Bu), 147.9 (CArNO2), 133.4 (CArH para to NO2), 133.3 (CArSO2N), 131.8 (CArH para to SO3N), 130.9 (CArH ortho to NO2), 123.9 (CArH ortho to SO3N), 82.2 (NsNCH2CO2CH3), 81.4 ((CH2)2NCH2CO2CH3), 56.2 ((CH2)2NCH2CO2Bu), 53.1 (NsNCH2CH2), 49.4 (NsNCH2CO2Bu), 46.7 (NsNCH2CH2), 28.1 ((CH2)2NCH2CO2C(CH3)3), 27.8 (NsNCH2CO2C(CH3)3). MS (ESI): m/z = 838.4 [M + Na]++, 816.4 [M + H]++. 

Amine 30. A solution of p-toluenethiol (189 mg, 1.52 mmol) in DMF (1.4 mL) was added to a suspension of dinosylate 29 (200 mg, 0.25 mmol) and Na2CO3 (317 mg, 3.00 mmol) in DMF (5 mL). This black-yellow suspension was stirred at 50 °C for 5 h. After 4 h the color of the solution turned into yellow. The suspension was stirred at room temperature for another 19.5 h. The solvent of the reaction mixture was removed at reduced pressure. Et2O (15 mL) was added to the yellow residue and the ethereal solution was washed with
water (3 × 5 mL). Removal of the solvents gave a yellow viscous oil. The components of this oil were separated by column chromatography (4.5 cm × 6 cm). Eluting first with pentane/Et\textsubscript{2}O 10:1 gave a mixture of (2-nitrophenyl)(p-toly)sulfane (\(R_f\) (pentane/Et\textsubscript{2}O 10:1) = 0.36) and 1,2-di-p-tolylidisulfane (\(R_f\) (pentane/Et\textsubscript{2}O 10:1) = 0.83). Then, the eluent was changed to THF, and amine \textbf{30} (93 mg, 85%; \(R_f\) (pentane/Et\textsubscript{2}O 10:1) = 0, \(R_f\) (THF) = 0.90) was obtained as a yellow-orange oil. \(^1\)H NMR of amine \textbf{30} (500 MHz, CDCl\textsubscript{3}): \(\delta = 3.32\) (s, 2H, (CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}\textit{tBu}), 3.29 (s, 4H, HNCH\textsubscript{2}CO\textsubscript{2}\textit{tBu}), 2.79 (t, \(\textit{J} = 6.0\) Hz, 4H each, NHCH\textsubscript{2}CH\textsubscript{2}), 2.65 (t, \(\textit{J} = 6.0\) Hz, 4H each, NHCH\textsubscript{2}CH\textsubscript{2}), 1.44 (s, 18H, HNCH\textsubscript{2}CO\textsubscript{2}(CH\textsubscript{3})\textsubscript{3}), 1.43 (s, 9H, (CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3}). \(^{13}\)C NMR of amine \textbf{30} (125 MHz, CDCl\textsubscript{3}): \(\delta = 171.6\) (HNCH\textsubscript{2}CO\textsubscript{2}\textit{tBu}), 170.9 ((CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}Bu), 80.9 (HNCH\textsubscript{2}CO\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3}), 80.8 ((CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}Bu), 55.7 ((CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}Bu), 54.1 (NHCH\textsubscript{2}CH\textsubscript{2}), 51.6 (HNCH\textsubscript{2}CO\textsubscript{2}Bu), 47.3 (NHCH\textsubscript{2}CH\textsubscript{2}), 28.2 ((CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3}), 28.1 (HNCH\textsubscript{2}CO\textsubscript{2}C(CH\textsubscript{3})\textsubscript{3}). MS of amine \textbf{30} (ESI) \(m/z\): 468.4 [M + Na]\(^+\), 446.4 [M + H]\(^+\). \(^1\)H NMR of (2-nitrophenyl)(p-toly)sulfane (500 MHz, CDCl\textsubscript{3}): \(\delta = 8.21\) (dd, \(\textit{J} = 1.5\) Hz, \(\textit{J} = 8.2\) Hz, HAr ortho to NO\textsubscript{2}), 7.46 (half of an AA'XX' spin system, 2H, HAr meta to CH\textsubscript{3}), 7.31 (apparent td, \(\textit{J} = 1.5\) Hz, \(\textit{J} = 7.2\) Hz, \(\textit{J} = 8.5\) Hz, HAr para to S), 7.28 (half of an AA'XX' spin system, 2H, HAr ortho to CH\textsubscript{3}), 7.18 (apparent td, \(\textit{J} = 1.3\) Hz, \(\textit{J} = 7.2\) Hz, \(\textit{J} = 8.4\) Hz, HAr para to NO\textsubscript{2}), 6.84 (dd, \(\textit{J} = 1.3\) Hz, \(\textit{J} = 8.3\) Hz, HAr ortho to S), 2.42 (s, 3H, CH\textsubscript{3}). \(^1\)H NMR 1,2-di-p-tolylidisulfane (500 MHz, CDCl\textsubscript{3}): \(\delta = 7.38\) (half of an AA'XX' spin system, 4H, HAr ortho to CH\textsubscript{3}), 7.10 (half of an AA'XX' spin system, 4H, HAr ortho to CH\textsubscript{3}), 2.31 (s, 6H, CH\textsubscript{3}).

\textbf{4-iodo-PCTA-[12] tert-butyl ester (32).} Mesylate \textbf{31} (99 mg, 0.24 mmol) was added to a solution of amine \textbf{30} (105 mg, 0.24 mmol) and triethylamine (328 \(\mu\)L, 2.37 mmol) in acetonitrile (10 mL). The yellow solution was stirred at room temperature for 46.5 h. The solvents were removed. The residual yellow solid was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the resulting solution was washed with H\textsubscript{2}O (5 \(\times\) 7 mL). The washing was performed in a centrifuge tube: The CH\textsubscript{2}Cl\textsubscript{2} phase and the aqueous phase were mixed well. Centrifugation of the resulting yellow emulsion at 9000 rpm for 2 min separated the mixture into two phases, a yellow CH\textsubscript{2}Cl\textsubscript{2} phase and a colorless aqueous phase. The aqueous phase was removed with the help of a glass pipette. The solvent of the CH\textsubscript{2}Cl\textsubscript{2} phase was removed. Centrifugal thin layer chromatography using a chromatotron (stationary phase: aluminiumoxid 60 neutral F254; layer thickness: 2 mm; plate diameter: 24 cm; eluent: THF; the separation on the plate was monitored using UV light with \(\lambda = 254\) nm) of the residual yellow oil (97 mg) gave 4-iodo-PCTA-[12] tert-butyl ester (32) (19 mg, 12%; \(R_f = 0.59\)) contaminated with a small amount of unidentified components. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 7.54\) (s, 2H, HAr), 3.94 (s, 4H, ArCH\textsubscript{2}), 3.41 (s, 4H, ArCH\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}Bu), 3.12 (s br, 2H, (CH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{2}CO\textsubscript{2}Bu), 2.78 (m, 4H, ArCH\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}), 2.62 (m, 4H, ArCH\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}), 1.47 (s, 18H,
ArCH$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$, 1.41 (s, 9H, (CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 170.7 ((CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$Bu), 170.6 (ArCH$_2$NCH$_2$CO$_2$Bu), 158.7 (CArCH$_2$), 131.4 (CArH), 106.5 (CArI), 81.1 (ArCH$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$), 80.8 ((CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$), 59.8 (CArCH$_2$), 58.2 (ArCH$_2$NCH$_2$CO$_2$Bu), 57.5 ((CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$Bu), 50.2 (ArCH$_2$NCH$_2$CH$_2$), 50.1 (ArCH$_2$NCH$_2$CH$_2$), 28.2 (ArCH$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$), 28.1 ((CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$C(CH$_3$)$_3$). MS (ESI) m/z: 697.3 [M+Na]$^+$, 675.3 [M+H]$^+$.  

4-Iodo-PCTA-[12]•n TFA (33). 4-Iodo-PCTA-[12] tert-butyl ester (32) (15 mg, ca. 22 $\mu$mol), as it had been received in the experiment described above, was dissolved in trifluoroacetic acid (TFA) (1 mL) and the resulting orange solution was stirred at room temperature for 1 h. The volatile components were removed at room temperature by lowering the pressure to 10 mbar. The residue was dissolved in TFA (1 mL) and the resulting orange solution was stirred at room temperature for 1 h. The solution was concentrated at room temperature at reduced pressure. The residual solution was added dropwise to Et$_2$O (3 mL), whereupon a colorless solid precipitated. The precipitate was separated via centrifugation (9000 rpm, 1 min), washed with Et$_2$O, and dried at reduced pressure. 4-Iodo-PCTA-[12]•n TFA (33) (12 mg) contaminated with a small amount of unidentified components was obtained as a colorless solid. $^1$H NMR (500 MHz, D$_2$O): $\delta$ = 7.92 (s, 2H, ArH), 4.79 (s, covered by the signal of H$_2$O; evidence comes from HMQC and HMBC NMR spectra, ArCH$_2$), 4.19 (s, 4H, ArCH$_2$NCH$_2$CO$_2$H), 3.62 (s, 2H, (CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$H), 3.53 (s br, 4H, ArCH$_2$NCH$_2$CH$_2$), 2.97 (s br, 4H, ArCH$_2$NCH$_2$CH$_2$). $^{13}$C NMR (125 MHz, D$_2$O): $\delta$ = 175.3 ((CH$_2$CH$_2$)$_2$NCH$_2$CO$_2$H), 170.0 (ArCH$_2$NCH$_2$CO$_2$H), 163.6 (q, $^2$J = 35.6 Hz, CO$_2$H of TFA), 151.3 (CArCH$_2$), 132.3 (CArH), 116.9 (q, $^1$J = 291.8 Hz, CF$_3$ of TFA), 109.5 (CArI), 59.4 (CArCH$_2$), 57.8 (ArCH$_2$NCH$_2$CO$_2$H), 55.3 ((CH$_2$CH$_2$)$_2$NCH$_2$COOH), 55.1 (ArCH$_2$NCH$_2$CH$_2$), 51.7 (ArCH$_2$NCH$_2$CH$_2$). MS (ESI, positive) m/z: 507.2 [M + H]$^+$. MS (ESI, negative) m/z: 619.1 [M + CF$_3$COO]$^-$, 505.1 [M - H]$^-$.

Iodo-(Gd-PCTA-[12]) (6). 4-Iodo-PCTA-[12]•n TFA (33) was used as obtained in the experiment described above. A solution of GdCl$_3$ in D$_2$O (50 mM, 129.7 $\mu$L, 6.486 $\mu$mol) was added into a solution of 4-Iodo-PCTA-[12]•n TFA (33) in D$_2$O (500 $\mu$L, containing 6.83 $\mu$mol of the structural motif [4-Iodo-PCTA-[12]]$^3$ as determined by quantitative $^1$H NMR spectroscopy$^4,5$) as determined by quantitative $^1$H NMR spectroscopy$^4,5$) as determined by quantitative $^1$H NMR spectroscopy$^4,5$). A solution of NaOD in D$_2$O (0.1 M, 425.6 $\mu$L, 42.56 $\mu$mol) was added to increase the pD to 9.0. The solution was diluted with D$_2$O (to a total volume of 1365.6 $\mu$L) to obtain a 5.0 mM solution of iodo-(Gd-PCTA-[12]) (6) in D$_2$O. Accurate MS (ESI): m/z calcd for [M + Na]$^+$ C$_{17}$H$_{20}$GdIn$_4$O$_8$Na$,^+$, 683.95607; found, 683.95601.
Synthesis of Gd-PyDTTA (7)

The procedure reported by Williams et al.\textsuperscript{10} for the synthesis of bromide 36 and the procedure reported by Bridger et al.\textsuperscript{11} for the synthesis of PyDTTA ester 38 were the basis for our work. We applied some modifications.

**Alcohol 35.** Tert-butyl bromoacetate (28) (1.3 mL, 8.92 mmol) was added dropwise to a suspension of 2-aminoethanol (34) (250 μL, 4.14 mmol) and NaHCO\textsubscript{3} (784 mg, 9.33 mmol) in DMF (10 mL) cooled with an ice water bath. The suspension was stirred, while still in the cooling bath, for 1.5 h. Then, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 21.5 h. After removal of the solvent, the colorless residue was dissolved in a mixture of Et\textsubscript{2}O (25 mL), saturated aqueous solution of NaHCO\textsubscript{3} (15 mL), and H\textsubscript{2}O (10 mL). The phases were separated. The organic phase was washed with a saturated aqueous solution of NaHCO\textsubscript{3} (3 × 10 mL). The aqueous phase was extracted with Et\textsubscript{2}O (3 × 20 mL). The combined organic phases were dried over Na\textsubscript{2}SO\textsubscript{4}. The suspension was filtered and the solvent of the filtrate was removed giving alcohol 35 (957 mg, 80%) as a colorless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta = 3.77 \text{ (t, } \text{ } 3J = 5.6 \text{ Hz, } 1\text{H, OH}), 3.51 \text{ (apparent q, } 3J \sim 5 \text{ Hz, } 2\text{H, HOCH}_2\text{), 3.42 (s, } 4\text{H, CH}_2\text{CO), 2.87 (t, } 3J = 5.0 \text{ Hz, } 2\text{H, HOCH}_2\text{CH}_2\text{), 1.45 (s, } 18\text{H, CH}_3\text{).} \textsuperscript{13}C \text{ NMR (125 MHz, CDCl}_3\text{): } \delta = 171.5 \text{ (C=O), 81.5 (C(\text{CH}_3}_3\text{), 59.3 (HOCH}_2\text{), 57.0 (HOCH}_2\text{CH}_2\text{), 56.6 (CH}_2\text{CO), 28.1 (CH}_3\text{). MS (ESI): } m/z = 312.2 \text{ [M + Na}^+\text{], 290.2 [M + H}^+\text{].}

**Bromide 36.** PPh\textsubscript{3} (2.51 g, 9.56 mmol) was added in portions within 5 min to a solution of alcohol 35 (2.49 g, 8.61 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (25 mL). The resulting solution was cooled with an ice water bath and then N-bromosuccinimide (1.71 g, 9.60 mmol) was added in portions within 5 min maintaining the cooling. During this addition the color of the solution changed to yellow. The reaction mixture was stirred, while still in the cooling bath, for 1.7 h. The volatile components were removed at reduced pressure. Et\textsubscript{2}O (45 mL) was added to the
residual yellow oil, whereupon a yellow solid precipitated. The yellow solid was removed through filtration and the solvent of the filtrate was removed. Column chromatography (5.0 cm × 22 cm, CH₂Cl₂/Et₂O 1:1) of the residual yellow oil (2.52 g) gave bromide 36 (1.12 g, 37%; \(R_f = 0.9\)) contaminated with a small amount of unidentified components as a yellow oil. \(^1H\) NMR (500 MHz, CDCl₃): \(δ = 3.46\) (s, 4H, CH₂CO), 3.42 (t, \(^3J = 7.0\) Hz, 2H, BrCH₂CH₂), 2.96 (t, \(^3J = 7.0\) Hz, 1H, BrCH₂CH₂), 1.44 (s, 18H, CH₃). \(^13C\) NMR (125 MHz, CDCl₃): \(δ = 170.5\) (C=O), 81.3 (CMe₃), 56.6 (BrCH₂CH₂), 56.5 (CH₂CO), 30.3 (BrCH₂), 28.1 (CH₃). MS (ESI): \(m/z = 374.2\) [M + Na]⁺, 352.2 [M + H]⁺.

**PyDTTA tert-butyl ester (38).** A suspension of bromide 36 (1.00 g, 2.84 mmol; as obtained in the experiment described above), 2-picolyamine (37) (968 μL, 946 μmol) and K₂CO₃ (3.98 g, 28.8 mmol) in acetonitrile (35 mL) was stirred under reflux for 24 h. The solvent was removed at reduced pressure. The residue was dissolved in Et₂O (15 mL) and H₂O (20 mL). The organic phase was separated, and the aqueous phase was extracted with Et₂O (5 × 10 mL). The combined organic phases were dried over Na₂SO₄ and filtered, and the solvents were removed. Column chromatography (3.5 cm × 39.5 cm, CH₂Cl₂/MeOH 10:1) of the residual oil (850 mg) gave PyDTTA tert-butyl ester (38) (339 mg, 55%; \(R_f = 0.25\)) as a yellow oil and bromide 36 (229 mg, 23%; \(R_f = 0.86\)) as a yellow oil. \(^1H\) NMR (500 MHz, CD₂Cl₂); *marks slightly broadened signals: \(δ = 8.49^*\) (d, \(^3J = 4.2\) Hz, 1H, Hₐ ortho to N), 7.68* (t-like, \(^3J = 7.6\) Hz, 1H, Hₐ para to N), 7.52* (d, \(^3J = 6.0\) Hz, 1H, Hₐ ortho to CH₂), 7.19* (t-like, \(^3J = 6.0\) Hz, 1H, Hₐ para to CH₂), 4.10 (broad s, 2H, ArCH₂), 3.97 (very broad s, ArCH₂), 3.38 (s, 8H, CH₂CO), 2.93 (broad s, 8H, CH₂CH₂), 1.42 (s, 36H, CH₃). \(^1H\) NMR (500 MHz, CDCl₃): \(δ = 8.49\) (slightly broadened d, \(^3J = 4.2\) Hz, 1H, Hₐ ortho to N), 7.65 (broad t, \(^3J = 7.0\) Hz, 1H, Hₐ para to N), 7.53 (broad s, 1H, Hₐ ortho to CH₂), 7.16 (broad s, 1H, Hₐ para to CH₂), 3.97 (very broad s, ArCH₂), 3.40 (s, 8H, CH₂CO), 2.96 (broad s, 8H, CH₂CH₂), 1.40 (s, 36H, CH₃). \(^13C\) NMR (125 MHz, CDCl₃): 170.6 (C=O), 170.1 (Cₐ CH₂), 148.9 (Cₐ-H ortho to N), 136.7 (Cₐ para to N), 123.6 (Cₐ ortho to CH₂), 122.4 (Cₐ para to CH₂), 81.1 (CMe₃), 55.9 (CH₂CO), 52.9 (CH₃CH₂), 50.7 (ArCH₂), 28.1 (CH₃). MS (ESI): \(m/z = 651.5\) [M + H]⁺.

**PyDTTA•x TFA (39).** PyDTTA tert-butyl ester (38) (301 mg, 462 μmol), was dissolved in TFA (15 mL) and the dark yellow solution was stirred at room temperature for 1 h. The volatile components were removed at room temperature by lowering the pressure to 10 mbar, giving a brown oil. This oil was dissolved in TFA (15 mL) and the yellow orange solution was stirred at room temperature for 1 h. The solution was concentrated by removing the volatile components at reduced pressure. This concentrated solution was added dropwise into Et₂O (13 mL), whereupon a beige solid precipitated. The precipitate was separated via centrifugation (9000 rpm, 1 min) and dissolved in H₂O (5 mL). Removal of the solvent through freeze-drying provided a brown solid (209 mg) containing PyDTTA•x.
TFA (39) (228 μmol of the structural motif [PyDTTA]4−; yield: 49%) and ca. 6 mol% of an unidentified component, as was quantified by quantitative ¹H NMR spectroscopy.¹⁴ ¹H NMR (500 MHz, D₂O): δ = 8.74 (d, J = 5.9 Hz, 1H, HAr ortho to N), 8.56 (dt, J = 8.0 Hz, 4J = 1.1 Hz, 1H, HAr para to N), 8.07 (d, J = 8.0 Hz, 1H, HAr ortho to CH₂), 7.99 (t-like, J = 7.5 Hz, 1H, HAr para to CH₂), 4.18 (s, 2H, ArCH₂), 4.03 (s, 8H, CH₂CO), 3.55 and 3.07 (2t, J = 6.7 Hz, 4H each, CH₂CH₂). ¹³C NMR (125 MHz, D₂O): 169.5 (C=O), 163.5 (q, J = 35.8 Hz, C=O of TFA), 152.4 (CArCH₂), 148.2 (CArH para to N), 142.6 (CArH ortho to N), 128.1 (CAr ortho to CH₂), 127.2 (CAr para to CH₂), 116.9 (q, J = 291.8 Hz, CF₃ of TFA), 56.6 (CH₂CO), 55.0 (ArCH₂), 53.2 and 48.6 (CH₂CH₂). MS (ESI): m/z = 427.2 [M + H]⁺.

Gd-PyDTTA (7). A solution of GdCl₃•6 H₂O in D₂O (0.05 M, 87.8 μL, 4.39 μmol) was added to a solution of PyDTTA•x TFA 39 (125 μL, contains 4.63 μmol of the structural motif [PyDTTA]⁺ as determined by quantitative ¹H NMR spectroscopy). A solution of NaOD in D₂O (0.10 M, 390.8 μL, 39.08 μmol) was added to rise the pD of the solution to 7. The pale yellow solution was diluted with D₂O (to a total volume of 925 μL) to obtain a 5.0 mM solution of Gd-PyDTTA (7) in D₂O containing Na(O₂CCF₃). MS (ESI): m/z = 579.9 [M - Na]⁻.
Figure SII-1: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of methyl 6-(hydroxymethyl)picolinate (16).
Figure SII-2: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of methyl 6-(hydroxymethyl)picolinate (16).
Figure SII-3: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of methyl 6-(hydroxymethyl)picolinate (16).
Figure SII-4: HMQC spectrum (500 MHz/125 MHz, CDCl₃) of methyl 6-(hydroxymethyl)picolinate (16).
Figure SII-5: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of mesylate 17.
Figure SII-6: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of mesylate 17.
Figure SII-7: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of mesylate 17.
Figure SII-8: HMQC spectrum (500 MHz/125 MHz, CDCl3) of mesylate 17.
Figure SII-9: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of NO3Pic methyl ester 19.
Figure SII-10: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of NO3Pic methyl ester 19.
Figure SII-11: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of NO3Pic methyl ester 19.
Figure SII-12: HMQC spectrum (500 MHz/125 MHz, CDCl₃) of NO₃Pic methyl ester 19.
Figure SII-13: $^1$H NMR spectrum (500 MHz, D$_2$O) of [Na$_3$NO$_3$Pic]•3 NaCl•x H$_2$O (20).
Figure SII-14: $^{13}$C NMR spectrum (125 MHz, D$_2$O) of [Na$_3$NO$_3$Pic]$^\cdot$3NaCl$^\cdot$xH$_2$O. A drop of MeOH was added as reference for the chemical shift.
Figure SII-15: $^{13}$C DEPT 135 NMR spectrum (125 MHz, D$_2$O) of [Na$_3$NO$_3$Pic]$\cdot$3 NaCl$\cdot$x H$_2$O. A drop of MeOH was added as reference for the chemical shift.
Figure SII-16: HMQC spectrum (500 MHz/125 MHz, D$_2$O) of [Na$_3$NO$_3$Pic]$^*$-3 NaCl$^*$x H$_2$O. A drop of MeOH was added as reference for the chemical shift.
Figure SII-17: $^1$H NMR spectrum (500 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazaheptane·NsOH (27).
Figure SII-18: $^{13}$C NMR spectrum (125 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazaheptane-NsOH (27).
Figure SII-19: $^{13}$C DEPT 135 NMR spectrum (125 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazasheptane-NsOH (27).
Figure SII-20: COSY NMR spectrum (500 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazahexane-NsOH (27).
Figure SII-21: HMQC NMR spectrum (500 MHz, 125 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazahexane-NsOH (27).
Figure SII-22: HMBC NMR spectrum (500 MHz, 125 MHz, DMSO-d$_6$) of 1,7-dinosyl-1,4,7-triazaheptane•NsOH (27).
Figure SII-23: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of dinosylate 29. *Signals of ethyl acetate.
Figure SII-24: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of dinosylate 29. *Signals of ethyl acetate.
Figure SII-25: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of dinosylate 29. *Signals of ethyl acetate.
Figure SII-26: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl3) of dinosylate 29.
Figure SII-27: HMBC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of dinosylate 29.
Figure SII-28: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of amine 30.
Figure SII-29: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of amine 30.
Figure SII-30: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of amine 30.
Figure SII-31: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of amine 30.
Figure SII-32: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of 4-iodo-PCTA tert-butyl ester (32) contaminated with unidentified component(s).
Figure SII-33: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 4-iodo-PCTA tert-butyl ester (32) contaminated with unidentified component(s).
Figure SII-34: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of 4-iodo-PCTA tert-butyl ester (32) contaminated with unidentified component(s).
Figure SII-35: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of 4-iodo-PCTA tert-butyl ester (32) contaminated with unidentified component(s).
Figure SII-36: HMBC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of 4-iodo-PCTA tert-butyl ester (32) contaminated with unidentified component(s).
Figure SII-37: $^1$H NMR spectrum (500 MHz, D$_2$O) of 4-iodo-PCTA-$n$ TFA (33) contaminated with unidentified component(s).

Overlapped with the signal of H$_2$O, evidenced by the cross signal in the HMQC and HMBC spectra.
Figure SII-38: $^{13}$C NMR spectrum (125 MHz, D$_2$O) of 4-Iodo-PCTA-n TFA (33) contaminated with unidentified component(s).
Figure SII-39: HMOC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of 4-Iodo-PCTA•n TFA (33) contaminated with unidentified component(s).
Figure SII-40: HMBC NMR spectrum (500 MHz, 125 MHz, CDCl3) of 4-Iodo-PCTA-n TFA (33) contaminated with unidentified component(s).
Figure SII-41: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of alcohol 35.
Figure SII-42: $^{13}$C NMR spectrum (125 MHz, CDCl₃) of alcohol 35.
Figure SII-43: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of alcohol 35.
Figure SII-44: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl₃) of alcohol 35.
Figure SII-45: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of bromide 36.
Figure SII-46: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of bromide 36.
Figure SII-47: $^{13}$C DEPT 135 NMR spectrum (125 MHz, CDCl$_3$) of bromide 36.
Figure SII-48: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl3) of bromide 36.
Figure SII-49: $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$) of PyDTTA tert butyl ester (38).
Figure SII-50: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of PyDTTA tert butyl ester (38).
Figure SII-51: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of PyDTTA tert butyl ester (38).
Figure SII-52: HMQC NMR spectrum (500 MHz, 125 MHz, CDCl3) of PyDTTA tert butyl ester (38).
Figure SII-53: $^1$H NMR spectrum (500 MHz, D$_2$O) of PyDTTA PyDTTA• x TFA (39) contaminated with unidentified component(s)
Figure SII-54: $^{13}$C NMR spectrum (500 MHz, D$_2$O) of PyDTTA PyDTTAX TFA (39) contaminated with unidentified component(s).
Figure SII-55: $^{13}$C DEPT 135 NMR spectrum (500 MHz, D$_2$O) of PyDTTA $\times$ TFA (39) contaminated with unidentified component(s).
Figure SII-56: HMQC NMR spectrum (500 MHz, 125 MHz, D₂O) of PyDTTA PyDTTA• x TFA (39) contaminated with unidentified component(s).
References