Simple Procedures for the Preparation of 1,3,5-Substituted 2,4,6-Trimethoxybenzenes

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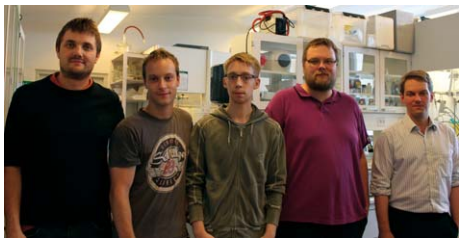
Abstract: We describe straightforward protocols for the preparation of a number of 1,3,5-substituted 2,4,6-trimethoxybenzenes. A two-step procedure for the preparation of a 1,3,5-*tris*-methylamino-2,4,6-trimethoxybenzene and further synthetic elaboration of this key substrate to yield a triamide, a tricarbamate and three different triureas is described. We also present a computational (DFT) study that investigates the different possible conformations of the overcrowded benzene substrate and a single-crystal X-ray structure of one of the key intermediates.

Key words: supramolecular chemistry, tripodal receptors, ureas, amides, overcrowded aromatics

The subtle interplay between rigidity and flexibility makes the design of receptors in supramolecular chemistry complex and sometimes unpredictable.[1] Preorganization has proven a reliable strategy in receptor design, but this is only truly effective if there is a good fit with the binding partner. A particularly popular and simple scaffold that relies on preorganization is the 1,3,5-substituted 2,4,6-triethylbenzene scaffold.[2] Receptors based on this scaffold have the unique feature that the three ethyl substituents predominantly orient themselves towards one side of the central benzene ring, while the three other substituents point towards the other side of the benzene ring.[3] This feature has been used extensively in the preparation of receptors for a wide range of guest molecules.[2] The central benzene ring can potentially engage in the molecular recognition events. This has inspired a renewed interest in the preparation of tripodal structures with alternative substitution patterns on the central benzene ring. This opens up new opportunities for fine-tuning the binding properties of these privileged receptor structures. A strategy to improve the binding properties of the tripodal receptors is to modify the electronic properties of the benzene ring by changing the three ethyl substituents to three methoxy substituents.[4] This subtle change in design (three CH_2 groups substituted for three oxygens) appears to provide less preorganized structures, presumably because three almost aligned O–Me dipoles in a completely alternating structure would not be favorable, and receptors based on this design would need other favorable interactions to outweigh this effect.[5] Here we describe reliable synthetic protocols for the preparation of a series of 1,3,5-*tris*-substituted 2,4,6-trimethoxybenzenes. We also quantify, by means of DFT calculations, the relative energetics of the different conformations of the 1,3,5-substituted 2,4,6-trimethoxybenzenes.



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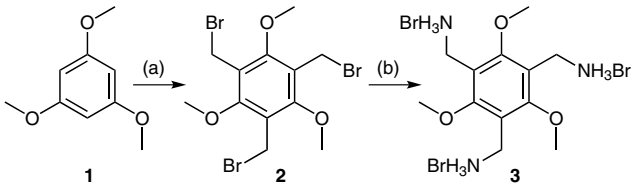
Bromomethylation of 1,3,5-trimethoxybenzene (**1**) was performed using a modified literature procedure.[6,7] Treatment of 1,3,5-trimethoxybenzene with paraformaldehyde and HBr in AcOH for three hours at 85 °C in a sealed container yielded the *tris*-bromomethylated product (**2**) in 49% yield. This procedure reliably yields >10 g of **2** as a white solid material. The transformation into the *tris*-methylamino compound (**3**) proceeded smoothly by dissolving **2** in liquid ammonia in a sealed bomb at room temperature for 18 hours. When optimized, this transformation proceeded in quantitative yield. Simple evaporation of the ammonia, addition of water and filtration yielded after concentration in vacuo the *tris*-hydrobromide as a pale yellow solid (Scheme 1).[8] This protocol was concentration dependent and a concentration of the tribromide of 0.1 gram per 40 mL ammonia proved to be the optimal conditions to avoid side reactions.

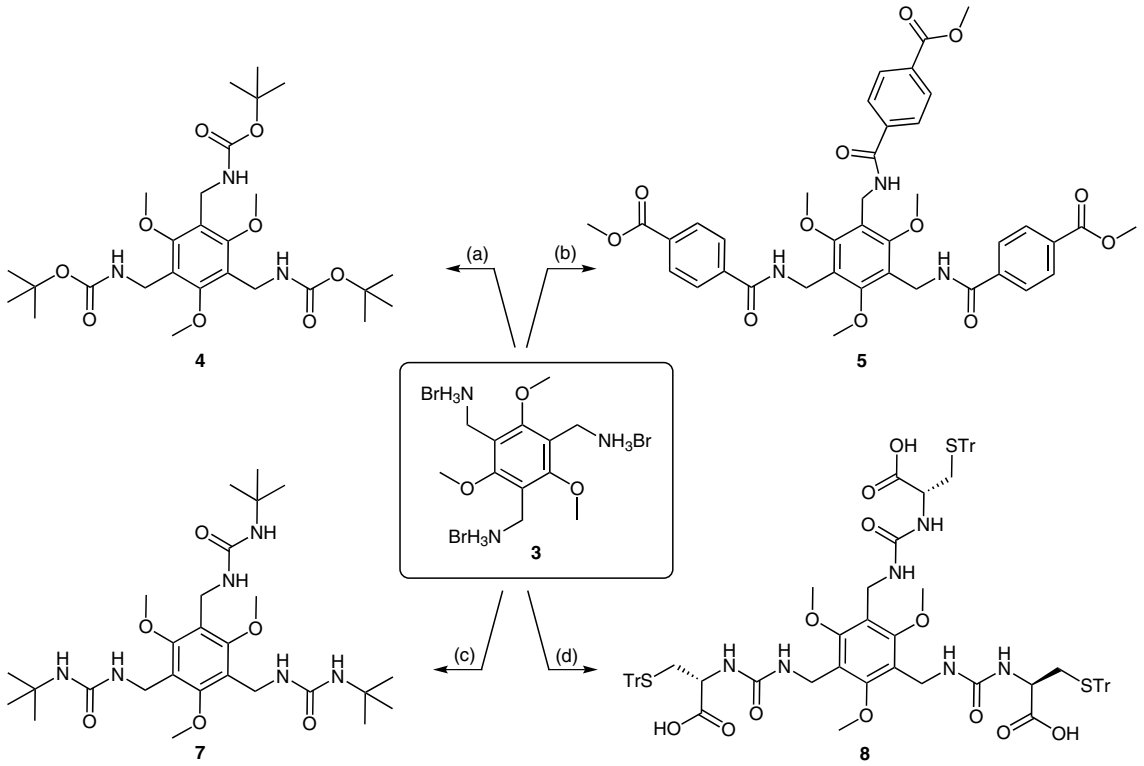


Scheme 1 Synthesis of 1,3,5-*tris*-methylamino-2,4,6-trimethoxybenzene (**3**). *Reagents and conditions*: (a) paraformaldehyde, 33% HBr in AcOH, sealed vessel, 49%; (b) NH_3, sealed vessel, >98%.

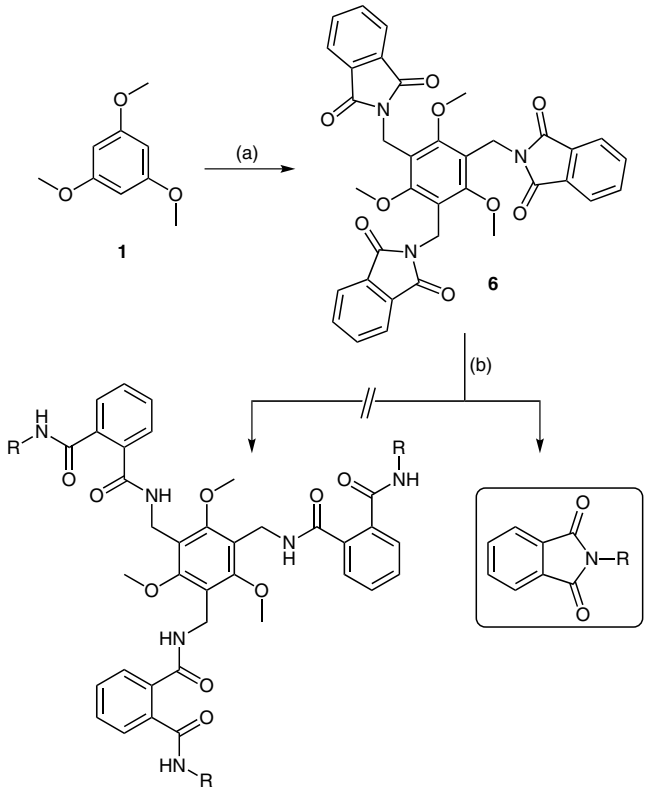
With the triamine in hand, we explored the possibilities for functionalization via simple amide coupling reaction and by carbamate formation. The formation of the tris(*tert*-butyl)carbamate (Boc) compound **4** (Scheme 2) was effective by treatment with di-*tert*-butyl dicarbonate in dioxane and water, and was easily purified by column chromatography.[9] The yield was moderate but acceptable due to the three-fold reaction (above 60% yield per carbamate formation) and easy purification protocol. We also developed conditions for the preparation of an amide, **5**, by coupling of the triamine and terephthalic acid monomethyl ester and a coupling reagent (either Me_3P/I_2 or PYBOP) in CH_2Cl_2.[10] This material was also purified by chromatography on silica revealing 66% of the triamide.

Formation of amides was also attempted by an alternative route. 1,3,5-Trimethoxybenzene gave, via reaction with *N*-(hydroxymethyl)phthalimide, the triphthalimide **6**[11] and ways of opening the phthalimide functionalities by reaction with amines as described by Gali et al. were attempted (Scheme 3).[12] However, the isolated product in these attempts was the *N*-alkyl-substituted phthalimide of the amine.

Another functionality derived from amines is the urea group which has been widely used in the design of hosts towards hydrogen bond accepting guests.[1] We studied convenient ways of converting the triamine **3** into triurea derivatives, and it was found that reaction between **3** and *tert*-butylisocyanate under mild conditions gave the desired triurea derivative **7**.[13] The binding properties of this compound were studied by NMR in chloroform, and the host showed a modest affinity towards chloride ions (see Supporting Information).



Scheme 2 Functionalization of the triamine **3** to carbamates, amides, and ureas. *Reagents and conditions*: (a) Boc_2O; (b) Me_3P, I_2, terephthalic acid monomethyl ester; (c) *tert*-butylisocyanate; (d) (i) 1,1′-carbonyldiimidazole; (ii) *S*-tritylcysteine (protected cysteine).



Scheme 3 Alternative attempts to functionalize triamine **3** with amides. *Reagents and conditions*: (a) *N*-hydroxymethylphthalimide, boron triflouride etherate; (b) RNH_2.

We studied ways to urea functionalize the triamine **3** without the need of isocyanate reagents. The compound 1,1′-carbonyldiimidazole has previously been used as an urea activating reagent by formation of an activated imidazole urea intermediate which can be reacted with a second amine giving the unsymmetrical urea.[14] This activation method is particularly challenging with a substrate containing multiple amine functionalities because reactions between activated and non-activated amines at the early stages of the activation process can give rise to unwanted urea side products. We studied this triple activation step carefully, and under optimized conditions it was found that complete triple activation could be achieved. The optimized conditions were found by following the progress of reaction for every ten minutes using ^{13}C NMR spectroscopy directly on the reaction mixture. Even in the non-deuterated reaction mixture the carbon signal originating from the methoxy CH_3 group was easily identified and could be monitored during the activation (Figure 1). As the triamine began to react with the activation reagent the overall symmetry of **3** was broken and therefore the signal split up. After 60 minutes of reaction a single signal was again obtained indicating that the overall symmetry had been reestablished due to complete activation. After complete activation, trityl-protected cysteine was added to the mixture to give the desired unsymmetrical triurea compound **8**.[15]

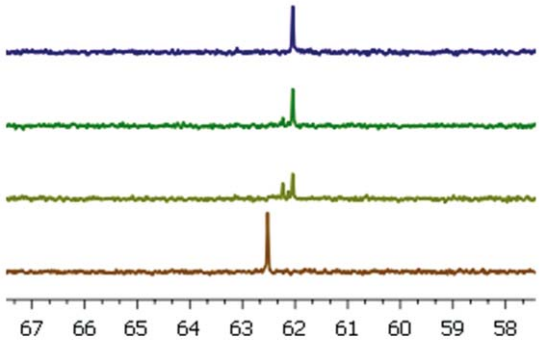
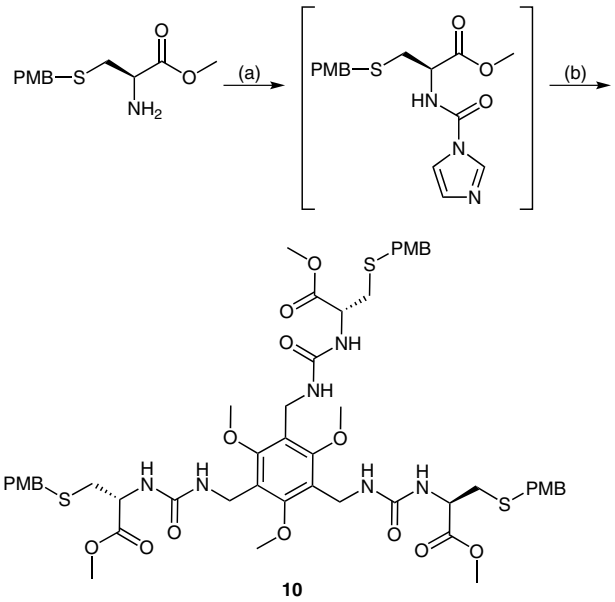


Figure 1 Part of the ^{13}C NMR spectra of the reaction mixture for the activation of triamine **3** with 1,1′-carbonyldiimidazole after different reaction times. From below, the spectra were recorded after 0, 10, 20, and 60 minutes.

The final step was most efficient when aliphatic amines were used. When 3-aminobenzoic acid was reacted with the triactivated triamine the desired triurea, **9**, was isolated in 21% yield even after optimization with respect to reaction temperature and choice of added base.[16]

The activation towards urea formation can also be carried out by activating the amine that is coupled to the central benzene core. This was illustrated by activation of the methyl ester of PMB-protected cysteine followed by reaction with the triamine **3** to give the desired triurea compound **10** (Scheme 4).[17]



Scheme 4 Alternative activation order in the urea formation of triamine **3**. *Reagents and conditions*: (a) 1,1′-carbonyldiimidazole; (b) **3** and imidazole.

To gain insights into the level of preorganization of the 1,3,5-*tris*-substituted 2,4,6-trimethoxybenzenes, we carried out a study combining single-crystal X-ray structure determination and DFT calculations. In Figure 2 the sin-

gle-crystal X-ray structure of the tribromide **2** is illustrated, showing the co-crystallization of two different conformers of **2**. When the isolated crystals were dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy the spectrum did not show separated signals for both conformers. This indicates that the energy barrier for conformer conversion is sufficiently low to make the conformer-exchange process fast on the chemical shift time scale.

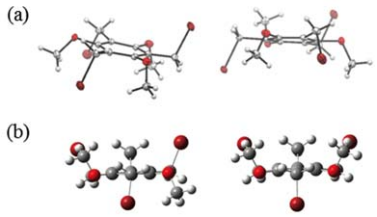


Figure 2 (a) Crystal structure of the tribromide **2** showing the co-crystallization of two conformers.[18] (b) B3LYP/6-31G(d) geometry optimized structures of the same conformers.

Gas-phase structure optimization and energy calculations of ten possible conformers of **2** (see Supporting Information) using DFT calculations indicate that these two co-crystallizing conformers are among the three lowest energy structures. The most stable conformer was found to have all substituents located on the same plane of the benzene ring, and the highest energy structure was found to have the substituents placed alternating.

We did not succeed in obtaining crystals of sufficient quality for single-crystal X-ray determination of any of the nitrogen-containing tripodal structures. NMR data, however, was obtained and showed a number of signals only possible if either the alternating conformer or the conformer with all substituents on the same side of the benzene ring were formed exclusively or if the conformer-exchange process is fast on the chemical shift time scale.

In summary, we have presented a straightforward two-step protocol for the preparation of 1,3,5-*tris*-methylamino-2,4,6-trimethoxybenzene. We have shown how this key substrate can be transformed into tricarbamates, triamides, and triureas. Despite the preorganization of these 1,3,5-*tris*-substituted 2,4,6-trimethoxybenzenes towards an alternating conformation appears to be less than that in the triethyl substrates, we are optimistic regarding the future use of these structures in the design of supramolecular receptors.[4b]

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(7) **1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene** (**2**): 1,3,5-Trimethoxybenzene (10.0 g, 59.5 mmol) and paraformaldehyde (11.0 g, 366 mmol) were suspended in 33% HBr in AcOH (85 mL) in a sealed stainless steel reaction vessel. The mixture was stirred for 3 h at 85 °C. After cooling to 25 °C CH_2Cl_2 (200 mL) was added, the phases were separated, and the organic phase was washed with H_2O (3 × 75 mL). The CH_2Cl_2 phase was filtered through silica (Ø = 50 mm, h = 60 mm) and the column was flushed with further CH_2Cl_2 (2 × 150 mL). The solvent was removed in vacuo, and the resulting yellow oil was dissolved in a mixture of 2-propanol (100 mL) and CH_2Cl_2 (100 mL). White crystals were obtained by reducing the volume of the solution to 50 mL and the precipitates were filtered off and washed with 2-propanol. Yield: 13.0 g (49%); mp 125–126 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.60 (s, 6 H), 4.14 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 123.5, 62.9, 22.7. HRMS: *m/z* $[M + NH_4]^+$ calcd for $C_{12}H_{19}O_3NBr_3^+$: 461.8910; found: 461.8924.

(8) **(2,4,6-Trimethoxybenzene-1,3,5-triyl)trimethanamine Hydrobromide** (**3**): 1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene (401 mg, 0.898 mmol) and liquid NH_3 (160 mL) were stirred at 25 °C for 18 h in a sealed reaction vessel. The ammonia was removed by evaporation, and the residue was dissolved in H_2O (30 mL) and filtered. Concentration in vacuo gave a colorless solid. Yield: 437 mg (98%); mp 176 °C (dec.). ^1H NMR (500 MHz, D_2O): δ = 4.33 (s, 6 H), 3.92 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 118.1, 63.0, 33.2. HRMS: *m/z* [2 M + H] calcd for $C_{24}H_{43}N_6O_6^+$: 511.3239; found: 511.3239.

(9) **Tri-*tert*-butyl [(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tricarbamate** (**4**): The tribromide **2** (1.80 g, 4.02 mmol) was dissolved in THF–EtOH (100 mL; 1:1) and concentrated aq NH_3 (80 mL) was added. The reaction mixture was stirred for 14 h whereafter the solvent was removed in vacuo. The residue was dissolved in dioxane–H_2O (70 mL, 1:1) and NaOH (0.80 g, 20 mmol) was added. Boc_2O (5.76 g, 26 mmol) in dioxane (20 mL) was slowly added at 0 °C and the reaction was stirred for an hour at 0 °C and 5 h at 25 °C. H_2O was added and the solution was extracted with CH_2Cl_2 (3 × 60 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The product was further purified by dry column chromatography (Ø = 60 mm, h = 50 mm, heptane with 0.1% Et_3N to EtOAc with 0.1% Et_3N with 5% gradient), followed by

recrystallization from heptane. Yield: 0.517 g (23%); mp 93.5–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.12 (s, 3 H), 4.39 (d, 6 H), 3.81 (s, 9 H), 1.44 (s, 27 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 155.1, 122.6, 79.1, 62.4, 34.8, 28.6. HRMS: *m/z* [M + Na]$^+$ calcd for $C_{27}H_{45}N_3O_9Na^+$: 578.3048; found: 578.3069.

(10) **Trimethyl 4,4′,4′′-[{[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris(azanediyl)}tris(carbonyl)]tribenzoate** (**5**): Iodine (458 mg, 1.81 mmol) was added to an ice-cooled solution of trimethyl phosphite (0.213 mL, 1.81 mmol) in CH_2Cl_2 (40 mL). When all the iodine had dissolved, terephthalic acid monomethyl ester (325 mg, 1.81 mmol) and Et_3N (1.12 mL, 8.03 mmol) were added and the solution was stirred for 20 min under continued cooling. The triamide **3** (200 mg, 0.401 mmol) was added and the mixture was stirred for 10 min at 0 °C and for 3 h at 25 °C. Sat. $NaHCO_3$ was added and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The organic phase was washed with 2 M HCl (2 × 50 mL) and brine (50 mL), dried over Na_2SO_4, and filtered. The product was further purified by dry column chromatography (Ø = 40 mm, h = 40 mm, CH_2Cl_2 to 12% MeOH in CH_2Cl_2 with 1.5% gradient). Yield: 0.31 g (66%); mp 212–213 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.60 (t, *J* = 4.8 Hz, 3 H), 7.94–8.02 (m, 12 H), 4.58 (d, *J* = 4.8 Hz, 6 H), 3.88 (s, 9 H), 3.83 (s, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 165.69, 165.21, 158.98, 138.58, 131.60, 128.98, 127.75, 121.01, 62.17, 52.33, 33.92. HRMS: *m/z* [M + H]$^+$ calcd for $C_{39}H_{40}N_3O_{12}^+$: 742.2607; found: 742.2613.

(11) **2,2′,2′′-[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris(isoindoline-1,3-dione)** (**6**): 1,3,5-Trimethoxybenzene (500 mg, 2.97 mmol) and *N*-hydroxymethylphthalimide (1.65 g, 9.31 mmol) were dissolved in boron triflouride etherate (25 mL) by gentle heating. Afterwards the solution was stirred at 25 °C for 3 h. The reaction mixture was poured into an ice–sodium acetate mixture (100 g/15 g) and stirred for an hour. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phase was washed with H_2O (50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The product was further purified by dry column chromatography (Ø = 40 mm, h = 40 mm, toluene to 15% MeCN in toluene with 3% gradient). Yield: 0.31 g (16%); mp 223–224 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.65–7.78 (m, 12 H), 4.77 (s, 6 H), 3.73 (s, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.24, 158.18, 134.22, 131.30, 122.73, 119.02, 61.82, 32.27. HRMS: *m/z* [M + H]$^+$ calcd for $C_{36}H_{28}N_3O_9^+$: 646.1820; found: 646.1794.

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(13) **1,1′,1′′-[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris[3-(*tert*-butyl)urea]** (**7**): The triamine **3** (200 mg, 0.402 mmol) was suspended in CH_2Cl_2–Et_3N (50 mL, 9:1) and *tert*-butylisocyanate (318 mg, 3.21 mmol) was added. The reaction mixture was stirred for 3 d at 25 °C. The volatiles were removed in vacuo and the residues were redissolved in CH_2Cl_2 (75 mL) and washed with 1 M hydrochloric acid (2 × 30 mL) and brine. The product was further purified by preparative HPLC, to yield 58% yield of a white solid; mp 275 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.83 (s, 3 H), 5.71 (t, *J* = 5.3 Hz, 3 H), 4.20 (d, *J* = 5.3 Hz, 6 H), 3.73 (s, 9 H), 1.20 (s, 27 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 157.80, 156.82, 122.90, 62.00, 48.93, 32.64, 29.31. HRMS: *m/z* [M + H]$^+$ calcd for $C_{27}H_{49}N_6O_6^+$: 553.3708; found: 553.3717.

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(15) **2,2′,2′′-{[{[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris(azanediyl)}tris(carbonyl)]tris-(azanediyl)}tris[3-(tritylthio)propanoic Acid] (8)**: The triamine **3** (100 mg, 0.200 mmol) was dissolved in DMF (10 mL) and a solution of 1,1′-carbonyldiimidazole (100.9 mg, 0.622 mmol) in MeCN (10 mL) was added. The reaction mixture was stirred for an hour and *S*-tritylcysteine (233.5 mg, 0.643 mmol) and Et_3N (0.142 mL, 1 mmol) were added. The reaction mixture was stirred overnight whereafter the volatiles were removed. The residue was redissolved in $CHCl_3$ and washed with 0.5 M HCl (3 × 50 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The product was further purified by preparative HPLC to give a white solid material. Yield: 121 mg (45%); mp 177–179 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.70 (s, 3 H), 7.17–7.40 (m, 45 H), 6.42 (d, *J* = 8.3 Hz, 3 H), 6.30 (t, *J* = 5.4 Hz, 3 H), 4.25 (d, *J* = 5.4 Hz, 6 H), 4.20 (ddd, *J* = 8.3, 6.8, 5.1 Hz, 3 H), 3.72 (s, 9 H), 2.41 (dd, *J* = 11.7, 6.8 Hz, 3 H), 2.33 (dd, *J* = 11.7, 5.1 Hz, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 172.60, 158.04, 156.69, 144.16, 129.00, 128.03, 126.78, 122.54, 65.80, 62.13, 51.60, 34.31, 33.03. HRMS: *m/z* [M + H]$^+$ calcd for $C_{81}H_{79}N_6O_{12}S_3^+$: 1423.4913; found: 1423.4884.

(16) **3,3′,3′′-{[{[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris(azanediyl)}tris(carbonyl)]tris-(azanediyl)}tribenzoic Acid (9)**: The triamine **3** (202 mg, 0.406 mmol) was dissolved in DMF (20 mL) and a solution of 1,1′-carbonyldiimidazole (3.1 equiv, 204 mg, 1.26 mmol) in MeCN (20 mL) was added. The reaction mixture was stirred for an hour at r.t. 3-Aminobenzoic acid (3.2 equiv, 178 mg, 1.30 mmol), Et_3N (21.2 equiv, 1.2 mL, 8.6 mmol) and DMAP (0.1 equiv, 5.1 mg, 0.042 mmol) were added and the reaction mixture was stirred for 3 d. Thereafter, the reaction mixture was poured into an ice-cold solution of 2 M HCl, the precipitate was filtered off and dried in vacuo. Finally, the crude product was washed once with 2 M NaOH (20 mL), reacidified with 2 M HCl, filtered and dried in vacuo. Yield: 62.9 mg (21%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.24 (s, 3 H), 8.06 (s, 3 H), 7.58 (d, *J* = 7.7 Hz, 3 H), 7.44 (d, *J* = 7.7 Hz, 3 H), 7.31 (t, *J* = 7.7 Hz, 3 H), 6.57 (s, 3 H), 4.38 (s, 6 H), 3.84 (s, 9 H). ^{13}C NMR (125 MHz, DMSO): δ = 167.36, 158.22, 154.79, 140.90, 131.19, 128.78, 122.34, 121.73, 121.48, 118.00, 62.37, 32.98. HRMS: *m/z* [M + H]$^+$ calcd for $C_{36}H_{37}N_6O_{12}^+$: 745.2464; found: 745.2489.

(17) **Trimethyl 2,2′,2′′-{[{[(2,4,6-Trimethoxybenzene-1,3,5-triyl)tris(methylene)]tris(azanediyl)}tris(carbonyl)]tris-(azanediyl)}tris{3-[(4-methoxybenzyl)thio]propanoate} (10)**: The PMB-protected cysteine (234 mg, 0.830 mmol) was dissolved in DMF (20 mL) and a solution of 1,1′-carbonyldiimidazole (143.1 mg, 0.883 mmol) in MeCN (20 mL) was added. The mixture was stirred for 30 min and the triamine **3** (100 mg, 0.201 mmol) and imidazole (136 mg, 2.00 mmol) were added. The reaction mixture was stirred overnight whereafter the volatiles were removed. The residues were redissolved in CH_2Cl_2 (80 mL) and washed with 0.5 M HCl (3 × 50 mL) and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was further purified by dry column chromatography (Ø = 40 mm, h = 40 mm, CH_2Cl_2 to 5% MeOH in CH_2Cl_2 with 0.5% gradient) to yield a white solid. Yield: 65 mg (28%); mp 195 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.19 (d, *J* = 8.7 Hz, 6 H), 6.86 (d, *J* = 8.7 Hz, 6 H), 6.52 (d, *J* = 8.2 Hz, 3 H), 6.32 (t, *J* = 5.3 Hz, 3 H), 4.38–4.49 (m, 3 H), 4.27 (d, *J* = 5.3 Hz, 6 H), 3.74 (s, 9 H), 3.72 (s, 9 H), 3.67 (s, 6 H), 3.61 (s, 9 H), 2.71 (dd, *J* = 13.6, 5.3 Hz, 3 H), 2.65 (dd, *J* = 13.6, 6.8 Hz, 3 H). ^{13}C NMR (125

MHz, DMSO-d_6): δ = 172.14, 158.16, 158.05, 156.72, 129.95, 129.79, 122.47, 113.73, 62.10, 55.00, 52.41, 51.91, 34.79, 33.07, 33.00. HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{51}H_{67}N_6O_{15}S_3^+$: 1099.3821; found: 1099.3853.

(18) $C_{12}H_{15}Br_3N_3$; M = 446.97; monoclinic; a = 9.9840(8) Å, b = 16.845(2) Å, c = 18.806(2) Å, α = 90°, β = 112.224(8)°, γ = 90°; V = 2927.8(5) Å^3; T = 122 K; space group $P2_1/c$; Z = 8; $\mu(Mo–K_\alpha)$ = 0.07 mm^{-1}; 94511 reflections measured, 11105 independent reflections (R_{int} = 0.112). The final R_1 values were 0.039 [$F^2 > 2\sigma(F^2)$]. The final R_1 values were 0.0688 (all data). The final $wR(F^2)$ (all data) values were 0.110. The goodness of fit on F^2 was 1.163. The structure of the tribromide **2** has been submitted to the Cambridge Crystallographic Data Centre (CCDC) as CCDC 947822.

