Pergamon

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Tetrahedron 59 (2003) 4303–4308

TETRAHEDRON

Synthesis of a new and versatile macrocyclic NADH model

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Received 20 January 2003; revised 24 March 2003; accepted 16 April 2003

Abstract—A new macrocyclic NADH model **1** has been designed and synthesised. The new model consists of the same subunits as previously reported models. However, the present model is designed as such that the pyridine nitrogen of the nicotinamide units are not incorporated in the macrocyclic framework. Thus, properties such as solubility can easily be varied by alkylation with an appropriate agent. The macrocyclic framework was prepared in 7 steps. Methylation of the pyridine nitrogens followed by reduction gave the desired model. This model compound was found to reduce methyl benzoylformate stereoselectively in good yield with 48% enantiomeric excess. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The coenzyme nicotinamide adenine dinucleotide (NAD^+/NADH) is the most common redox reagent in biological systems, used by hundreds of different enzymes. In the enzymatic reductions of ketones, one of the two diastereotopic hydrogens on the dihydropyridine ring of NADH is transferred stereoselectively to the substrate.[1] The high performances generally obtained in these reductions have intrigued organic chemists. Since the initial report by Ohno and co-workers on asymmetric reduction using an NADH model,[2] there have been many different approaches to NADH mimicking.[3–5] Most of these model reactions have been studied in acetonitrile. However, hydride transfer is much faster in more polar solvents such as water.[6] Furthermore, very few examples have been concerned with the catalytic use of NADH models. This is reasonable, since biomimetic oxidations and reductions usually require completely different reaction conditions such as solvent. A water soluble NADH reducing agent could overcome this problem. Herein is reported the development of a synthetic route towards water soluble NADH models.

We have previously reported the results from studies of NADH models of the type represented by **2** (Fig. 1). It was shown that the oxidised form of **2** was able to form complexes with derivatives of benzoic acid such as the dianions of terephthalic and isophthalic acid in water.[7] In these complexes, the guests were intercalated between the aromatic spacers of **2**, showing that the cavity is large enough to encapsulate a substrate. Compound **2** was also tested as a reducing agent and was able to reduce methyl benzoylformate to the corresponding alcohol in 81% enantiomeric excess.[8] The goal was then to use **2** in a catalytic cycle by taking advantage of the four nicotinamide units that are incorporated in the model. By reduction of only one or two nicotinamide units the model should still be water soluble and capable of reducing a substrate. The initial experiments showed that it was not possible to control the different redox levels of **2**, so this route to a water soluble redox reagent had to be abandoned. Instead, compound **1** was designed, which has a similar macrocyclic framework to **2** (Fig. 1). The only difference is that the dihydropyridine rings are incorporated into the macrocycle at the 3,5-positions instead of the 1,3-positions. This modification has several advantages, one being a greater stability towards basic conditions and nucleophiles. The bond between the pyridine nitrogen and the methylene group in **2** is easily broken, thus interrupting the cyclic structure, and this bond is absent in **1**. The modification also benefits from a greater versatility, since the pyridine nitrogen is 'liberated'. Properties such as solubility and perhaps redox potential can readily be changed by attaching the appropriate functional groups to the pyridine nitrogen.

2. Results and discussions

2.1. Synthesis

The synthetic pathway of the previous models was rather straightforward where nitrogen–carbon bonds were formed in virtually every step and no modifications prior to condensation were necessary.[8] The synthesis of the new model compound required a totally different strategy, where the formation of a carbon–carbon bond resulting in a methylene group bridging two aromatic rings was the most challenging task. There are basically two synthetic routes to

Keywords: NADH model; macrocycle; reductions; stereoselectivity.

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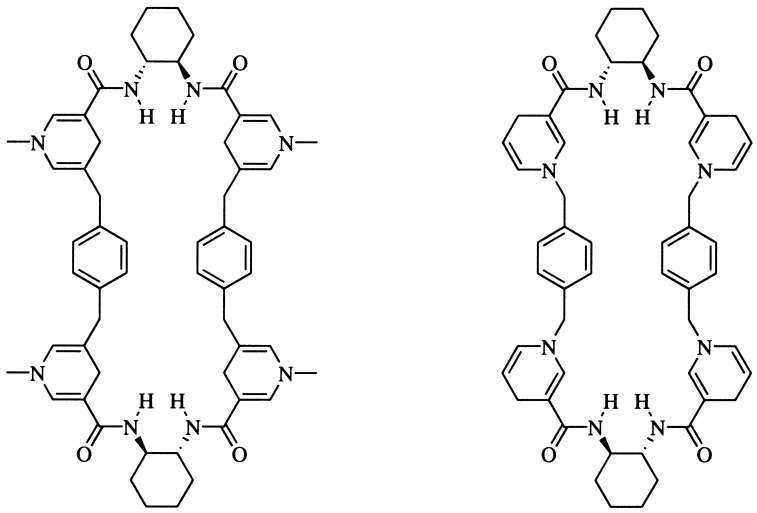
0040–4020/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0040-4020(03)00626-4



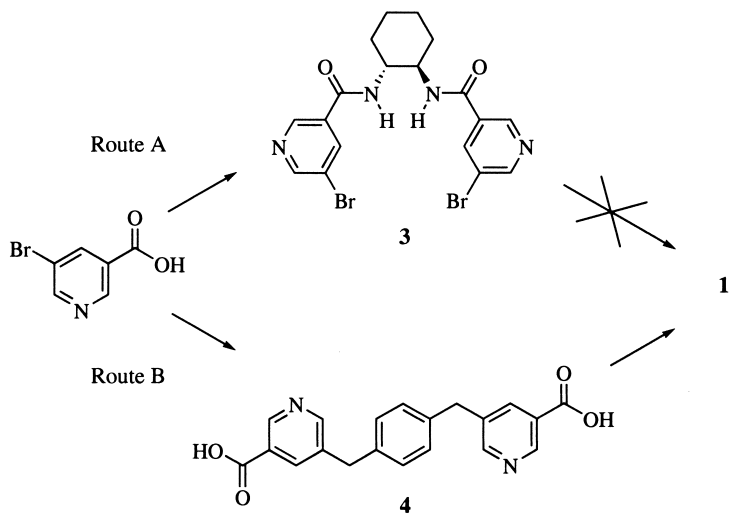
1 **2**

Figure 1. The current NADH model **1** and a previously reported model **2**.

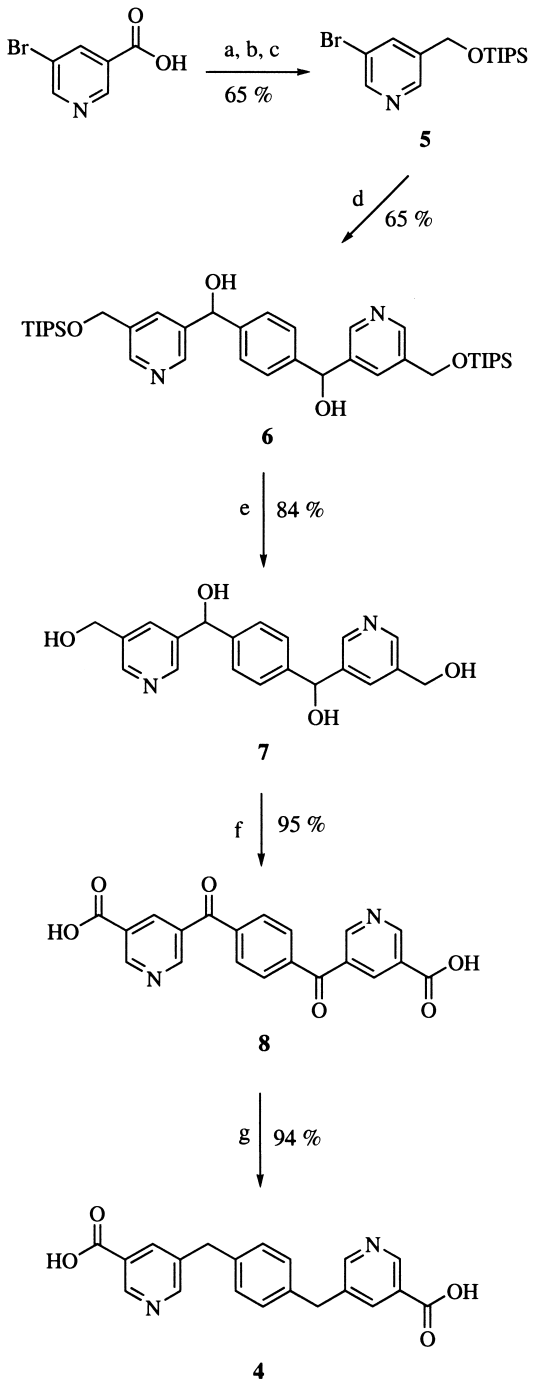
macrocycle **1**, both using commercially available 5-bromonicotinic acid as the starting point, as outlined in Scheme 1.

Route A was first explored, where the first step was to condense 2 equiv. of 5-bromonicotinic acid with enantiomerically pure (1*R*,2*R*)-*trans*-diaminocyclohexane via the acid chloride prepared in situ, which gave **3** in good yield. An attempt was then made to use **3**, after stannylation, in a palladium-catalysed Stille coupling. For this purpose, **3** was converted to the corresponding distannane by lithiation of **3** using *n*-BuLi followed by addition of tributyltin chloride. Stille coupling of the distannane with 1,4-bis(bromomethyl)benzene would then give the main cyclic structure of **1**. However, the coupling failed and so did attempts with other benzyl halides. Other strategies to modify **3** in order to synthesise **1** also failed, either because of low yields or purification problems. Therefore, route A was abandoned and route B was pursued instead. The synthesis using route B is outlined in Scheme 2.

The crucial step was the connection of 2 equiv. of a pyridine derivative to an aromatic spacer. The most straightforward method for the connection is through lithiation followed by the addition of an electrophile. However, using this method, an electrophile such as 1,4-bis(halomethyl)benzene has to be precluded, since it does not mix well with strong bases such as lithium reagents. Electrophiles containing carbonyl groups are more suitable in this case, which means that the methylene groups bridging the pyridine rings and the aromatic spacer in **4** cannot be obtained in a direct manner. Furthermore, the metalated analogue of 5-bromonicotinic acid was a very poor nucleophile. Lithiation of 5-bromonicotinic acid using 2 equiv. of *n*-BuLi followed by addition of an electrophile only gave nicotinic acid after quenching with water. Quenching the lithiated species using D_2O gave 5-deuterio-nicotinic acid, proving that self-quenching is not a factor. Converting the acid to the corresponding pyridyloxazoline and treating it in the same way did not lead to reaction with an electrophile either. It seems like the reactivity of lithiated pyridine rings is highly dependent on its substituents. An electron withdrawing group on the already electron poor pyridine ring seems to decrease the reactivity markedly, even with a mildly



Scheme 1. Two synthetic routes to **1**, starting from 5-bromonicotinic acid.



Scheme 2. *Reagents and conditions*: (a) Et_3N, methyl chloroformate, toluene, rt. (b) $LiAlH_4$, THF, −78°C. (c) Imidazole, TIPS-Cl, DMF, rt. (d) *n*-BuLi, terephthaldialdehyde, THF, −100°C. (e) Bu_4NF, THF, −20°C. (f) Na_2CO_3, $KMnO_4$, H_2O, rt. (g) H_2NNH_2, KOH, ethylene glycol, reflux.

deactivating group such as a carboxylate group. It has actually been shown that pyridyloxazolines can act as electrophiles when treated with organolithium or Grignard reagents.[9] Instead, the bromonicotinic acid was reduced and *O*-TIPS-protected to give *O*-TIPS-5-bromopyridine-3-methanol (**5**). Lithiation of this species followed by addition of terephthaldialdehyde worked nicely and gave compound **6** in 65% yield.

The diacid can now be obtained from **6** through a series of transformations. Deprotection using TBAF had to be performed at low temperature (−20°C) to get the tetraol **7** in good yield. Reoxidation of the terminal alcohols back to carboxylic acids using $KMnO_4$ as the oxidising agent also converted the methine alcohols to carbonyl groups to give **8**, which was reduced through Wolff–Kishner reduction to give the desired diacid **4** in 89% yield from tetraol **7**.

The macrocycle **9** could be obtained from **4** and (1*R*,2*R*)-1,2-transdiaminocyclohexane. This could be carried out either in a 'one-pot' procedure using **4** and the diamine in 1:1 stoichiometry, or via compound **10**, as outlined in Scheme 3. The latter procedure gave a higher yield and the product was also easier to purify. The amide-forming reactions were initially performed via the acid chloride prepared in situ, but the use of the coupling reagents TBTU and HOBt reduced the reactions times considerably.

Alkylation followed by reduction would give the NADH model **1** (Scheme 4). Since the macrocycle **9** and the by-products had very low solubility in organic solvents, the crude product of **9** was alkylated using methyl iodide. Disappointingly though, the alkylated analogues were not readily soluble either. However, the iodide counter-ions could be exchanged for chloride ions using an ion-exchange resin and the chloride salts were readily soluble in methanol and water. The crude product was then purified by a similar method used by Geuder et al. for the purification of polypyridinium salts.[10] Flash chromatography with MeOH/NH_4Cl (aq. 25%) 4:1 as eluent followed by size exclusion chromatography for the separation of the model compound from ammonium chloride gave **11**. Reduction using basic sodium dithionite gave the final product **1**.

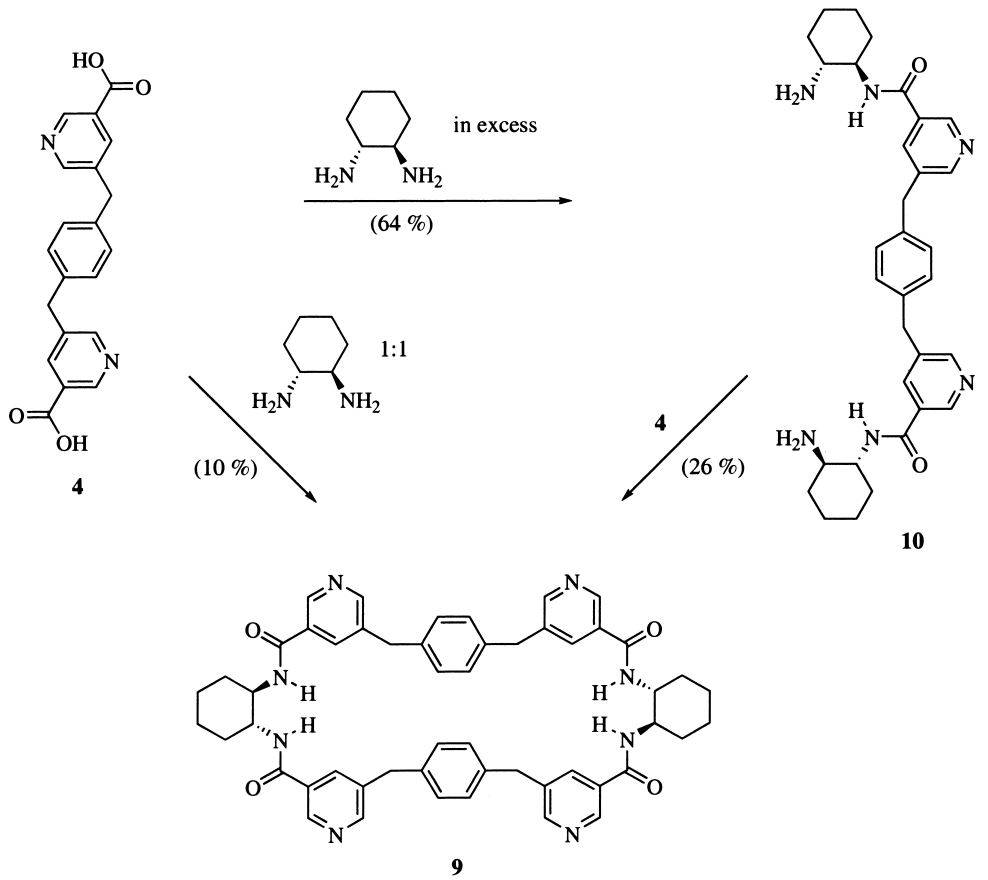
2.2. Reductions

A limited number of reductions were performed using **1** as the reducing agent. The results are summarised in Table 1 together with results previously obtained for **2**.[8]

The reductions were carried out in methylene chloride using Mg^{2+} as a co-catalyst. The results show that NADH model **1** can reduce methyl benzoylformate stereoselectively and in good yields. The NADH models **1** and **2** seem to be similar as reducing agents. The same enantiomer (*R*-mandelate) of the resulting alcohol is obtained upon reduction and in similar enantiomeric excess. A more extensive study of the reduction properties of **2** showed that the selectivity and the reactivity were dependent on the magnesium ion concentration and the temperature. The enantiomeric excess varied from 15 to 81% depending on the conditions. These variations were attributed to a rather flexible structure of **2**. Furthermore, the cavity of **2** is large enough to encapsulate a substrate, which in apolar solvents leads to poor discrimination between the two faces of the dihydropyridine rings and affects the selectivity negatively. Since the macrocyclic structure of **1** is similar, it is most likely that these arguments are valid for **1** as well.

3. Conclusions

A new and versatile NADH model **1** has been synthesised. It was shown that **1** could function as a stereoselective

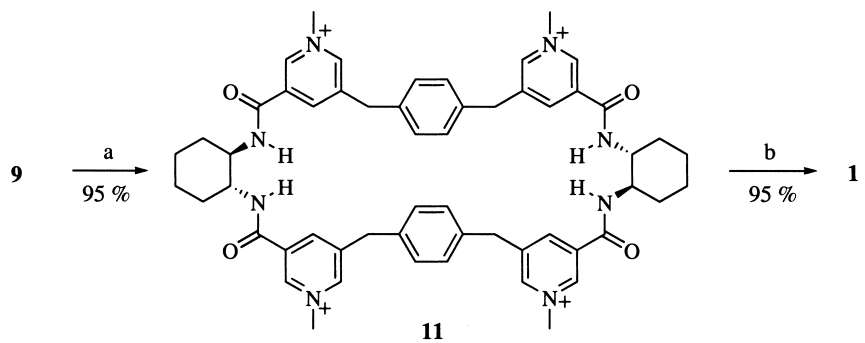


Scheme 3. Two pathways for the synthesis of the macrocycle **9**.

Table 1. Reductions using **1** and **2**

Entry	Substrate	Reducing agent	Ratio[a] Mg^{2+}/model	e.e. (%)[b]	Yield (%)[c]
1	Methyl benzoylformate	**1**	1.25	48	100 (2 days)
2	Methyl benzoylformate	**2**	1.25	54	100 (1 day)
3	Methyl benzoylformate	**1**	4	28	100 (12 h)
4	Methyl benzoylformate	**2**	4	30	100 (4.5 h)

The reactions were carried out in methylene chloride at room temperature. Model/substrate 1:1.
[a] Magnesium was added in the form of $Mg(ClO_4)_2$.
[b] Determined via capillary gas chromatography. The *R*-isomer was in enantiomeric excess for all entries.
[c] Isolated yields.



Scheme 4. NADH model **1** is obtained from **9** by alkylation followed by reduction.

reducing agent and the results indicated that it had similar reduction properties as the previously reported model **2**. The developed synthetic route can be used for preparing NADH models with different properties such as solubility. Using the macrocyclic precursor **9** as a starting point, a certain property can be fine-tuned by alkylation with the appropriate agent. An investigation towards a NADH model which is water soluble both in its reduced and oxidised state is underway and will be reported in due time.

4. Experimental

4.1. Materials

The reactions were carried out with oven-dried equipment. Methylene chloride was dried by distillation from calcium hydride under nitrogen. THF was dried by distillation from sodium/benzophenone under nitrogen. Dried solvents were used immediately after distillation. Commercial grade (peptide-grade) DMF was used. Commercially available reagents were used without further purification.

4.2. Methods

Thin-layer chromatography was performed on silica gel Plate (Merck, silica gel 60 F_{254}). Flash chromatography was performed using silica gel (Matrex, LC 60 Å/35–70 μm). Size-exclusion chromatography was performed using Sephadex LH-20 in methanol. ^{1}H (400 MHz)- and ^{13}C (100.6 MHz) NMR spectra were recorded at 293 K on a Varian UNITY-400 NMR spectrometer with $CDCl_3$, DMSO-d_6 or methanol-d_4 as solvents with tetramethylsilane as internal standard. IR spectra were recorded on an FT-IR instrument, Perkin–Elmer 1600. Mass spectra were recorded on a VG ZabSpec instrument. Positive FAB-MS (matrix 3-nitrobenzyl alcohol) and positive ESI-MS were the methods used. Capillary gas chromatography was performed using a Varian 3300 gas chromatograph equipped with a silicone fused silica column (column i.d. 0.32 mm, column length 30 m). Optical rotations were measured on a Perkin–Elmer 241 polarimeter using a 1 dm cell with a total volume of 1 mL. The enantiomeric excess was measured using a Hewlett–Packard 5890 gas chromatograph equipped with a β-cyclodextrin based column (Chrompack, CP-Chirasil-dex CB, column i.d. 0.25 mm, column length 25 m).

4.2.1. *O*-(Triisopropylsilyl)-5-bromopyridine-3-methanol (5). To a suspension of 5-bromonicotinic acid (6.0 g, 29.7 mmol) in toluene, Et_3N (4.4 mL, 31.5 mmol) was added at room temperature. After the carboxylic acid was dissolved, methyl chloroformate (2.42 mL, 31.3 mmol) was added to the solution and the mixture was stirred for 1.5 h at room temperature. Precipitated Et_3N·HCl was filtered off and the filtrate was evaporated to dryness to give a mixed anhydride, which was immediately used in the next step. A solution of the mixed anhydride in anhydrous THF (50 mL) was added dropwise to a slurry of $LiAlH_4$ (1.19 g, 31.3 mmol) in anhydrous THF (20 mL) under argon at −78°C and the mixture was stirred for 1.5 h at the same temperature. It was then poured into 5% aq NaOH solution (70 mL) and the mixture was passed through celite. The aqueous layer was extracted with EtOAc (3×50 mL) and the organic layers were dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure to give crude 5-bromopyridine-3-methanol, which was used in the next step without purification. To a solution of 5-bromopyridine-3-methanol (4.15 g, 22.1 mmol) in DMF (20 mL) was added, under argon, imidazole (3.31 g, 48.6 mmol) followed by triisopropylsilyl chloride (TIPS-Cl) (5.67 mL, 26.5 mmol). After stirring for 24 h at room temperature the reaction mixture was evaporated to dryness. Purification by flash chromatography (silica gel, pentane/EtOAc, 9:1) gave **5** as a colourless oil (6.66 g, 65% overall). ^{1}H NMR ($CDCl_3$): δ 1.08 (d, 18H, J=4.3 Hz), 1.19 (m, 3H), 4.84 (s, 2H), 7.86 (s, 1H), 8.50 (s, 1H), 8.57 (s, 1H). ^{13}C NMR: δ 11.9, 18.0, 62.2, 136.3, 138.8, 145.5, 149.2, 154.0. HRMS: m/z calcd for $C_{15}H_{27}NSiOBr$ ($[M+H]^+$) 344.105, found 344.108.

4.2.2. Compound 6. To a stirred solution of *O*-(triisopropylsilyl)-5-bromopyridine-3-methanol (3.52 g, 10.2 mmol) in anhydrous THF (60 mL) under argon was added *n*-BuLi (4.4 mL, 2.45 M in hexane, 10.76 mmol) at −100°C. The solution was stirred for 15 min and terephthaldialdehyde (0.76 g, 5.64 mmol) dissolved in anhydrous THF (25 mL) was added at the same temperature. The mixture was allowed to slowly warm to room temperature (6 h) before H_2O (60 mL) was added. The aqueous layer was extracted with EtOAc (3×50 mL) and the combined organic layers were dried (Na_2SO_4), filtered and evaporated. Purification by flash chromatography (silica gel, EtOAc) gave **6** as a white solid (2.22 g, 65%). ^{1}H NMR ($CDCl_3$): δ 1.03 (d, 36H, J=4.3 Hz), 1.13 (m, 6H), 4.79 (s, 4H), 5.77 (s, 2H), 7.27 (s, 4H), 7.67 (s, 2H), 8.16 (s, 2H), 8.39 (s, 2H). ^{13}C NMR: δ 11.9, 18.0, 62.8, 73.5, 127.0, 132.0, 136.7, 139. 1, 143.1, 146.0, 146.2. HRMS: m/z calcd for $C_{38}H_{61}N_2O_4Si_2$ ($[M+H]^+$) 665.417, found 665.419. IR (KBr): 1107, 1464, 2865, 2942, 3156.

4.2.3. Compound 7. A sample of **6** (2.14 g, 3.22 mmol) was dissolved in anhydrous THF (35 mL) under argon. Bu_4NF (8.05 mmol, 8.05 mL of a 1.0 M solution in THF) was added at −20°C and the mixture was stirred at the same temperature for 9 h. The solvent was evaporated and the crude product was purified by flash chromatography (silica gel, EtOAc/methanol, 1:1) to give **7** as a white solid (0.95 g, 84%). ^{1}H NMR (DMSO-d_6): δ 4.47 (d, 4H, J=3.5 Hz), 5.30 (tr, 2H, J=3.5 Hz), 5.74 (s, 2H), 6.02 (s, 2H), 7.34 (s, 4H), 7.66 (s, 2H), 8.34 (s, 2H), 8.45 (s, 2H). ^{13}C NMR: δ 60.8, 72.2, 126.3, 132.1, 137.4, 140.6, 144.0, 146.4, 146.8. HRMS: m/z calcd for $C_{20}H_{21}N_2O_4$ ($[M+H]^+$) 353.150, found 353.152. IR (KBr): 1027, 1036, 1436, 2858, 3338.

4.2.4. Compound 8. To a mixture of **7** (0.77 g, 2.21 mmol) in 10% aq. Na_2CO_3 solution (11.5 mL) was added $KMnO_4$ (1.66 g, 10.5 mmol) dissolved in water (80 mL). The mixture was stirred at room temperature for 4 h and was then passed through celite to eliminate MnO_2. The solution was neutralised with HCl (2 M) to pH 4 and the resulting precipitate was collected to give **8** as a white solid (0.79 g, 95%). ^{1}H NMR (DMSO-d_6): δ 7.98 (s, 4H), 8.51 (s, 2H), 9.12 (s, 2H), 9.29 (s, 2H). ^{13}C NMR: δ 126.4, 129.2, 129.7, 131.8, 137.8, 139.2, 153.0, 165.3, 193.1. HRMS: m/z calcd for $C_{20}H_{13}N_2O_6$ ($[M+H]^+$) 377.077, found 377.077. IR (KBr): 1252, 1661, 1718, 3060.

4.2.5. Compound 4. To a mixture of **8** (1.20 g, 3.19 mmol) in ethylene glycol (7 mL) was added hydrazine hydrate (1.55 mL, 31.9 mmol) and KOH (38.3 mmol, 2.15 g). The solution was heated under reflux for 1.5 h. Volatile material was distilled off until the internal temperature reached 180°C and the solution was heated again under reflux for 45 min. After cooling water was added and the solution was neutralised with HCl (2 M) to pH 4. The resulting precipitate was collected to give **4** as a white solid. The filtrate was evaporated and a second crop was obtained by ion-exchange chromatography (Isolute SCX-3) to give 1.04 g (94%) of **4** as a white solid. ^{1}H NMR (DMSO-d_6): δ 4.01 (s, 4H), 7.22 (s, 4H), 8.05 (s, 2H), 8.68 (s, 2H), 8.88 (s, 2H). ^{13}C NMR: δ 37.4, 127.3, 129.3, 136.8, 137.1, 138.4, 148.3, 153.2, 166.6. HRMS: *m/z* calcd for $C_{20}H_{17}N_2O_4$ ($[M+H]^+$) 349.119, found 349.119. IR (KBr): 1208, 1716, 3056.

4.2.6. Compound 10. To a stirred mixture of **4** (85 mg, 0.24 mmol) in DMF (20 mL) under argon was added TBTU (172 mg, 0.54 mmol) and HOBt (66 mg, 0.48 mmol). After the dicarboxylic acid was dissolved, (1*R*,2*R*)-(−)-1,2-transdiaminocyclohexane (167 mg, 1.47 mmol) was added and the solution was stirred over night at room temperature. The solvent was evaporated and the crude product was purified by flash chromatography (silica gel, gradient from EtOAc/methanol 1:1 to methanol/Et_3N, 99:1), which gave **10** in 84 mg (64%) as a white solid. ^{1}H NMR (methanol-d_4): δ 1.33 (m, broad, 8H), 1.75 (m, broad, 4H), 1.97 (m, broad, 4H), 2.64 (m, 2H), 3.71 (m, 2H), 4.04 (s, 4H), 7.20 (s, 4H), 8.10 (s, 2H), 8.54 (s, 2H), 8.83 (s, 2H). ^{13}C NMR: δ 26.0, 26.2, 33.0, 35.3, 39.1, 55.1, 57.4, 130.4, 132.1, 137.3, 138.9, 139.4, 147.0, 152.7, 168.0. HRMS: *m/z* calcd for $C_{32}H_{41}N_6O_2$ ($[M+H]^+$) 541.329, found 541.327. IR (KBr): 1326, 1543, 1642, 2931, 3278.

4.2.7. Compound 11. To a stirred mixture of **4** (122 mg, 0.35 mmol) in DMF (100 mL) under argon was added TBTU (247 mg, 0.77 mmol) and HOBt (107 mg, 0.70 mmol). After the dicarboxylic acid was dissolved, a sample of **10** (189 mg, 0.35 mmol) dissolved in DMF (15 mL) was added and the solution was stirred over night at room temperature. The solvent was evaporated and acetonitrile (40 mL) was added. The resulting precipitate was collected to give crude **9**, which was used in the next step without purification. To a stirred mixture of **9** in DMF (5 mL) was methyl iodide (3 mL) and the mixture was stirred under argon for seven days at room temperature. The solvent was evaporated and the resulting iodide salt was converted to the chloride salt using ion-exchange chromatography (Amberlite IRA-400 (Cl)) with methanol as eluent. The solvent was evaporated and the crude product was purified by flash chromatography (silica gel, methanol/NH_4Cl (25% aq.), 4:1) followed by size exclusion chromatography with methanol as eluent to give **11** in 92 mg (25%). ^{1}H NMR (methanol-d_4): δ 1.43 (m, broad, 4H), 1.66 (m, broad, 4H), 1.87 (m, broad, 4H), 2.05 (m, broad, 4H), 4.02 (m, 4H) 4.18 (s, 8H), 4.41 (s, 12H), 7.30 (s, 8H), 8.52 (s, 4H), 9.00 (s, 4H), 9.03 (s, 4H). ^{13}C NMR: δ 25.8, 32.5, 38.6, 49.3, 55.7, 131.2, 135.6, 137.9, 143.7, 144.2, 144.5, 147.9, 163.3. HRMS: *m/z* calcd for $C_{56}H_{64}N_8O_4Cl_2$ (M^{2+}) 491.221, found 491.225. IR (KBr): 1560, 1664, 2933, 3386.

4.2.8. Compound 1. Sodium dithionite (182 mg, 1.04 mmol) and sodium carbonate (111 mg, 1.04 mmol) dissolved in water (2 mL) were added to deaerated solution of **11** (55 mg, 0.052 mmol) in water (2 mL). The mixture was stirred for 16 h at room temperature. The solvent was evaporated and **1** was dissolved in chloroform, filtered to remove inorganic salts and concentrated to give **1** in 45 mg (95%) as a red solid. ^{1}H NMR ($CDCl_3$): δ 1.3 (m, broad, 4H), 1.73 (m, broad, 4H), 1.81 (m, broad, 4H), 2.11 (m, broad, 4H), 2.88 (s, 12H), 2.90 (m(overlapping), 8H), 3.06 (d, 4H, *J*=9.5 Hz), 3.16 (d, 4H, *J*=9.5 Hz), 3.65 (m, 4H), 5.48 (s, 4H), 5.87 (d, broad, 4H), 6.75 (s, 4H), 7.13 (s, 8H).

4.3. General procedure for reductions

A 10 mL round-bottomed flask was charged with magnesium perchlorate and the model compound (80–100 μmol), sealed with a rubber septum, and flushed with argon. Freshly distilled methylene chloride (2.5–3 mL) was added via syringe and the mixture was stirred for 1–2 h, whereupon the substrate was added via syringe. The flask was kept in the dark and the reaction mixture was stirred under argon. The reaction was quenched by adding 7–8 mL of water. The aqueous phase was extracted with methylene chloride (3×10 mL) and the combined organic phases were dried over Na_2SO_4, filtered and concentrated. The optical rotation was measured to determine the enantiomer in excess and the enantiomeric excess was measured using capillary GC.

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