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New Macrocycles with Planar Chirality—Synthesis and Determination of Absolute Configurations

Jarosław Kalisiak,[a] Paweł Skowronek,[b] Jacek Gawroński,[b] and Janusz Jurczak*[a, c]

Abstract: A versatile system for preparing macrocyclic compounds with planar chirality is presented. In this system chiral diazacoronands are synthesized readily from lariat-type diesters **13** and **14** and unsymmetrical diamines **7, 8, 12, 15**, and **16** under non-high-dilution conditions. The title compounds were subjected to structural analysis by X-ray crystallography and circular dichroism spectroscopy, and absolute configurations for two representative examples (compounds **2** and **3**) were assigned by molecular modeling. The correctness of the theoretical approach was verified by the crystallographic results obtained experimentally.

Keywords: chirality · circular dichroism · configuration determination · macrocycles · supramolecular chemistry

Introduction

Chiral recognition is one of the most important and fascinating areas in supramolecular chemistry.[1] Over the last few decades, large numbers of chiral macrocyclic receptors have been synthesized and subjected to host–guest investigations. Most of these have a center[2] and/or an axis[3] as a chiral element, but less attention has been paid to receptors possessing planar chirality. This is probably because planar chiral macrocyclic compounds are based mostly on small, rigid cyclophane backbones with smaller numbers of donor atoms[4] and, although suitable for construction of ligands for asymmetric synthesis,[5] they are completely inefficient in supramolecular applications. Among numerous examples of artificial receptors, only a few of those possessing planar chirality possess a larger macroring structure with donor atoms.[6] Therefore, the synthesis of efficient receptors with planar chirality requires certain limitations to be overcome: 1) the size of the macroring, and 2) the presence of the donor groups and/or atoms in the macroring structure.

[a] Dr. J. Kalisiak, Prof. J. Jurczak
Institute of Organic Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01–224 Warsaw (Poland)
Fax: (+48) 22-632-66-81
E-mail: jurczak@icho.edu.pl

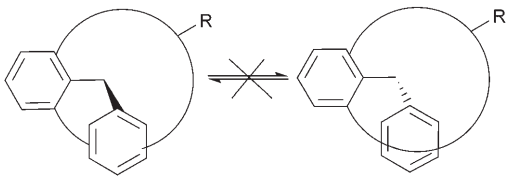
[b] Dr. P. Skowronek, Prof. J. Gawroński
Department of Chemistry, A. Mickiewicz University
Grunwaldzka 6, 61–780 Poznań (Poland)

[c] Prof. J. Jurczak
Department of Chemistry, University of Warsaw
Pasteura 1, 02–093 Warsaw (Poland)

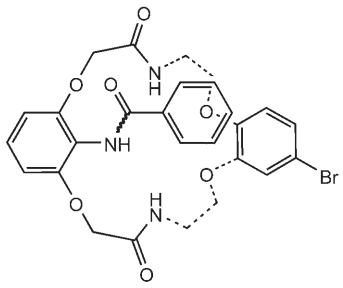
In our studies of the synthesis of macrocyclic compounds, we have applied the double amidation reaction, in which dimethyl α,ω-dicarboxylates are treated with primary α,ω-diamines. The great advantage of our approach is the presence of the amide groups, which exhibit dual complexing character (C=O and N or NH), thereby enabling amide-based molecular receptors to bind metal[7] and ammonium cations,[8] neutral organic molecules,[9] and anionic species.[10] The designed planar chiral system has two essential requirements: 1) the presence of the large intraannular group that cannot go through the macroring plane easily, with the effect that the top and bottom sides of the molecule are different, and 2) the presence of a group that breaks the symmetry of the molecule (Scheme 1).

In accordance with these rules, we recently presented the synthesis and chiro-optical properties of four representative macrocyclic compounds.[11] Racemic compounds **1**–**4** were resolved into enantiomers by conducting chiral HPLC, and their high enantiomeric stability, sufficient for potential supramolecular applications, was corroborated.

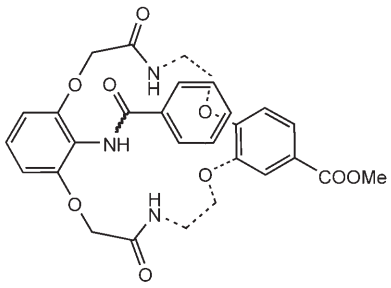
Here, we present further studies relating to the synthesis of diazacoronands with planar chirality from different α,ω-



Scheme 1. Representation of planar chirality in macrocyclic compounds.



1 (19%)



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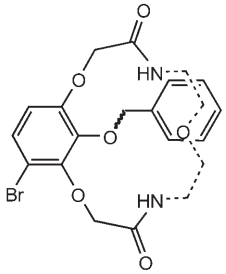
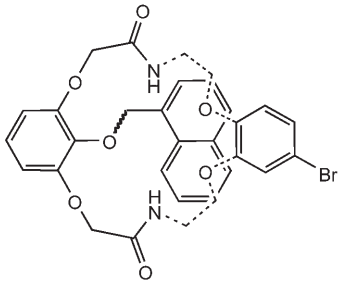


3 (72%)



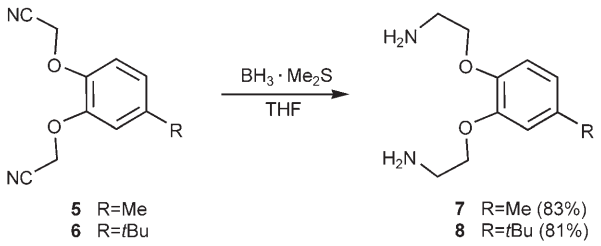
4 (15%)

diamine building blocks. Structural features of the title compounds were also investigated, including their absolute configurations, by X-ray diffraction and circular dichroism (CD) spectroscopy. In the latter case, the CD spectra for the minimum-energy conformers of macrocycles **2** and **3** were calculated by using the semiempirical ZINDO/S method and the absolute configurations were assigned by comparing the experimentally observed and the calculated CD spectra.

Results and Discussion

Synthesis of macrocycles: For the preparation of diazacoronands with planar chirality, the double amidation reaction was applied. In this reaction, introduced by Tabushi[12] and developed in our laboratories,[13] dimethyl α,ω-dicarboxylates are treated with primary α,ω-diamines in the presence of base [MeO^- or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)] under non-high-dilution conditions. The initial stage in the synthesis of chiral diazacoronands was the preparation of the appropriate unsymmetrical building blocks. According to our previous experience, we decided to synthesize the unsymmetrical α,ω-diamines from appropriate α,ω-dinitrile precursors. Alkyl functions (Me and *t*Bu) were used as groups to break symmetry, and the corresponding compounds **5**[14] and **6**[15] were reduced smoothly with borane dimethylsulfide complex (BMS) to give the corresponding α,ω-diamines **7** and **8** in good yields (Scheme 2).

Another interesting and suitable precursor for the preparation of an appropriate α,ω-diamine seems to be 2,3-dihydroxypyridine (**9**), because its tautomeric analogue 3-hydroxypyridinone can bind trivalent cations, such as indium and gallium,[16] and its complexes are used for medical purposes.[17] It is known that direct alkylation of hydroxypyridines may yield either *N*-alkylpyridones or alkoxypyridines, due to tautomeric equilibrium.[18] In our case, the main tautomeric form was 3-hydroxy-1*H*-pyridin-2-one (**10**), and its elongation with chloroacetonitrile gave the



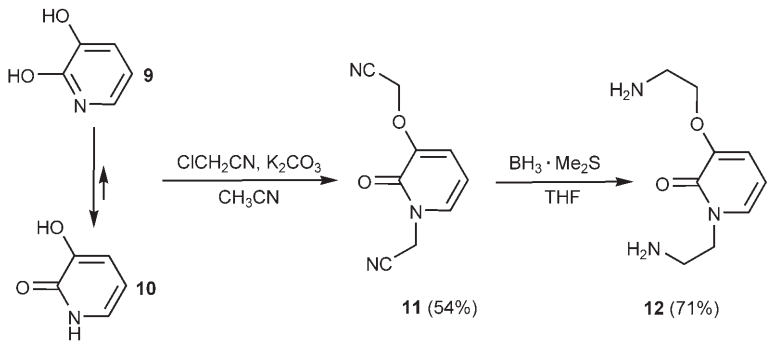
5 R=Me
6 R=*t*Bu

7 R=Me (83%)
8 R=*t*Bu (81%)

Scheme 2. Synthesis of unsymmetrical α,ω-diamines **7** and **8**.

α,ω-dinitrile **11**, which was subsequently reduced with BMS to give the desired diamine **12** (Scheme 3).

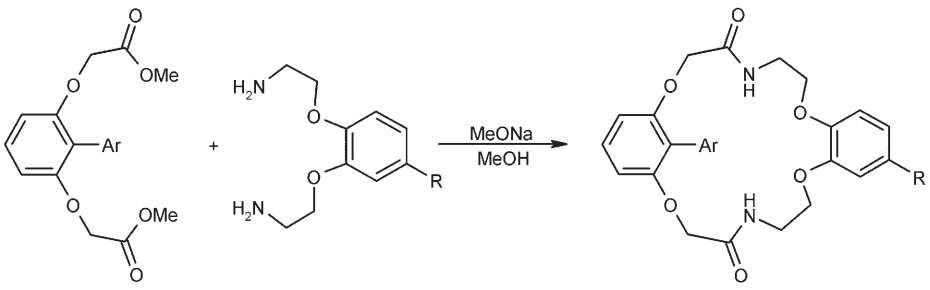
The synthesis of chiral diazacoronands was carried out as shown in Scheme 4, with the appropriate diesters **13**[11a] and **14**,[11b] and the unsymmetrical diamines **7** and **8**, and also **15** and **16**.[11b] These latter two possess a bromine atom and an ester group, respectively, which are susceptible to further modification.



11 (54%)

12 (71%)

Scheme 3. Synthesis of unsymmetrical α,ω-diamine **12**.



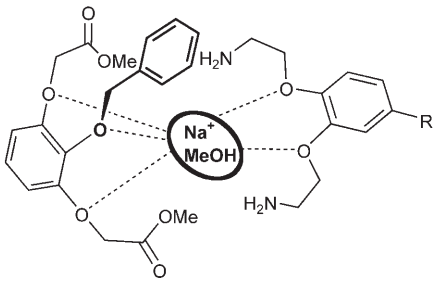
13 Ar=OCH_2Ph
14 Ar=NHCOPh

7 R=Me
8 R=*t*Bu
15 R=Br
16 R=COOMe

17 Ar=OCH_2Ph R=Me (16%)
18 Ar=OCH_2Ph R=*t*Bu (22%)
19 Ar=OCH_2Ph R=Br (38%)
20 Ar=OCH_2Ph R=COOMe (10%)
21 Ar=NHCOPh R=Me (13%)
22 Ar=NHCOPh R=*t*Bu (15%)

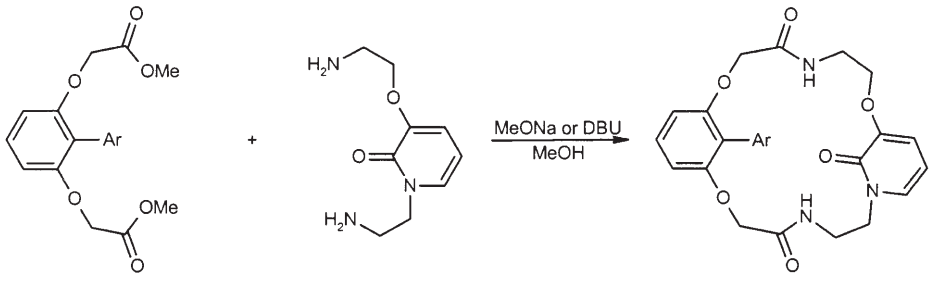
Scheme 4. Synthesis of diazacoronands possessing planar chirality.

In general, the cyclization step proceeded smoothly and the macrocyclic products were isolated in moderate yields of 10–38%. The lowest yield was obtained for derivative **20**, containing the ester group, presumably due to autocondensation of the diamine **16**. Surprisingly, the yields observed for the *O*-benzyl derivatives (**17**–**20**) were higher than those for their *N*-benzoyl analogues (**1** and **2, 21** and **22**), probably due to an additional contribution from the benzyloxy oxygen atom, during the macrocyclization step, to the interaction between the substrates and a template molecule, which could be methanol and/or a sodium cation (Scheme 5).



Scheme 5.

As discussed above, another unsymmetrical building block employed in the synthesis of planar chiral receptors was the pyridin-2-one derivative **12**, which was subjected to macrocyclization with diesters **13** and **14**. In this case, the results obtained with DBU as base were better than those with MeONa (Scheme 6).



13 Ar=OCH_2Ph
14 Ar=NHCOPh

12

23 Ar=OCH_2Ph (DBU-28%), (MeONa-8%)
24 Ar=NHCOPh (DBU-23%), (MeONa-7%)

Scheme 6. Synthesis of chiral diazacoronands containing the pyridin-2-one moiety.

X-ray studies: The synthesized diazacoronands crystallized readily under diffusive conditions and single crystals suitable for X-ray analysis were obtained for compounds **1**–**3, 19** and **20**, and **23**.

The solid-state conformation of *rac*-**1** shows a U-shaped arrangement of the macroring with both aromatic rings almost parallel. Two bromine atoms were detected with a half occupation (Figure 1). The intraannular group in compound **1** is turned away from the macroring and participates in two intramolecular hydrogen bonds with the amide group protons.

To examine the influence on the diazacoronand structure of substitution of the bromine atom (in derivative **1**) by the ester group, single crystals of compound **2** were obtained. Unfortunately, these included solvent molecules (MeOH) and underwent destruction immediately upon removal from the crystallization vial. X-ray measurements performed at low temperature allowed merely an estimation of the structure of compound **2** with a large parameter $R1 = 0.18$; nevertheless, the structures of both diazacoronands **1** and **2** show significant similarity (Figure 2).

Enantiomers of diazacoronand **3** were obtained in a sufficient quantity and their crystallization, performed in a methanol/pentane diffusive system, gave single crystals suitable for X-ray investigation (Figure 3). Structural analysis of the enantiomer (+)-(R_p)-**3** reveals typical intramolecular hydrogen bonds, also observed in the *N*-benzoyl derivative **1**. The presence of the heavy bromine atom in the structure allowed the absolute configuration to be determined with a reliable Flack parameter of −0.016(7).[19]

The structure of diazacoronand **19**, containing a bromine atom, also shows intramolecular hydrogen bonds between the oxygen atom of the benzyloxy function and the protons of the amide groups (Figure 4). Additionally, a π–π-type interaction between a side arm and the bromobenzene unit is

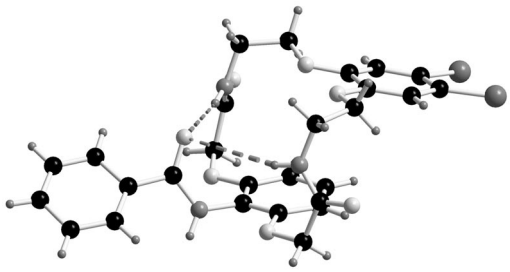


Figure 1. X-ray structure analysis of the diazacoronand *rac*-**1**.

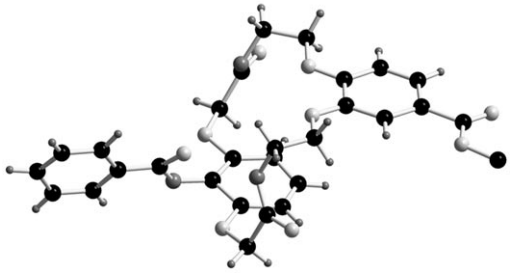


Figure 2. X-ray structure analysis of the diazacoronand *rac*-**2**.

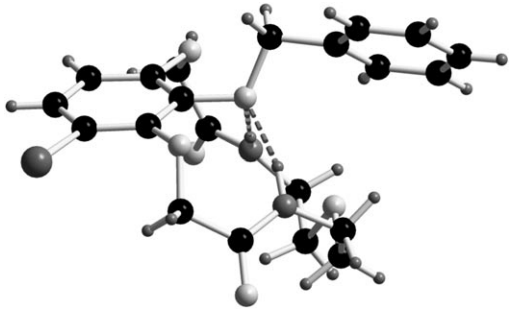


Figure 3. X-ray structure analysis of the diazacoronand (+)-(R_p)-**3**.

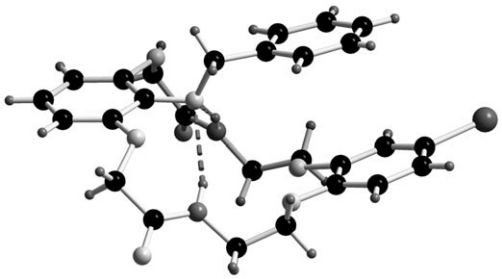


Figure 4. X-ray structure analysis of the diazacoronand *rac*-**19**.

observed, and is probably responsible for the relatively high synthetic yield (38%) of compound **19**.

In the case of diazacoronand **20**, with an ester function, structural investigation revealed only a few changes from compound **19**. Although the same type of hydrogen bonding was observed, the benzyloxy group was directed outside the macroring and no π–π-type interaction was detected (Figure 5).

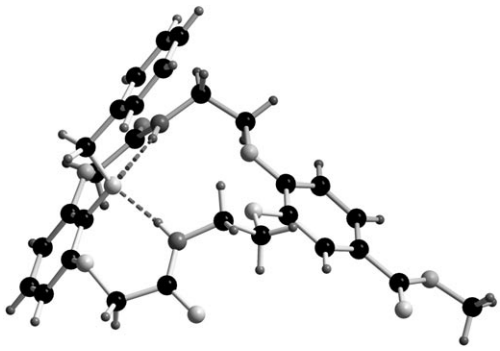


Figure 5. X-ray structure analysis of the diazacoronand *rac*-**20**.

The results obtained for compound **23**, however, revealed a completely different arrangement from the other *O*-benzyl derivatives **3**, and **19** and **20**. The benzene ring is almost parallel to the pyridin-2-one moiety, and the intraannular group is perpendicular to the macroring structure and does not form hydrogen bonds with amide function, as in the cases of **3**, and **19** and **20** (Figure 6).

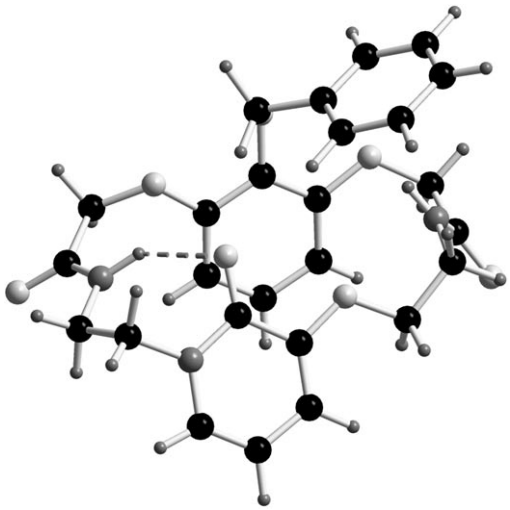
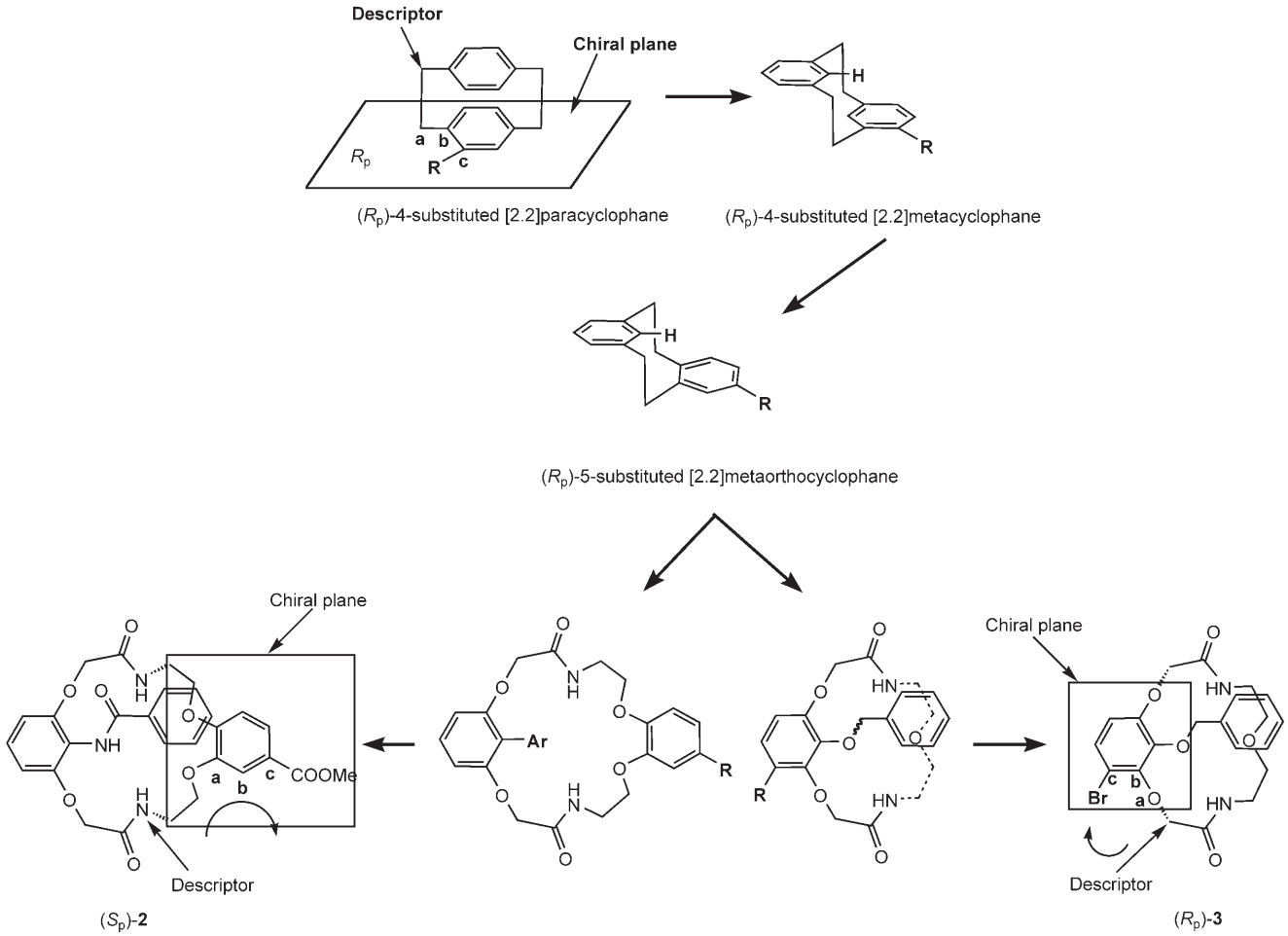


Figure 6. X-ray structure analysis of the diazacoronand *rac*-**23**.

Determination of absolute configurations: The assignment of R_p and S_p configurations to the title compounds was performed in the same way as for the cyclophane derivatives, as shown in Scheme 7, and is initiated by choosing a plane that contains as many atoms as possible. Thus, for the monosubstituted [2.2]paracyclophane depicted in Scheme 7 an appropriate chiral plane includes the bottom benzene ring. To determine the descriptor of a chiral plane, the closest atom out of the plane is chosen as a descriptor-determining atom. If there are several candidates, the one of highest priority according to CIP rules is chosen. Subsequently, three atoms adjacent to the descriptor-determining atom and belonging to the chiral plane are chosen and are labeled a, b, c, respectively. If, upon viewing from the descriptor-determining atom side of the chiral plane, these atoms are arranged



Scheme 7. Principle of the assignment of absolute configuration to diazacoronands with planar chirality.

clockwise, the configuration is R_p, conversely, it is S_p. The same procedure can be used for chiral [2.2]metacyclophane and [2.2]metaorthocyclophane derivatives and—after minor changes—for our macrocyclic system too.

The title compounds exhibit significantly higher conformational flexibility than [2.2]cyclophane derivatives; therefore, chiral plane and descriptor have to be established independently for each example of a chiral diazacoronand (Scheme 7). In the case of compound (R_p)-**3**, the chiral plane includes the 4-bromopyrogallol unit and the descriptor is the carbon atom located below it.

A slightly different procedure was applied for assigning the absolute configuration of compound **2** (Scheme 7). According to the X-ray structure analysis for racemic **2** (Figure 2), the chiral plane includes not only the 4-carboxycatechol unit, but also part of the macroring structure. The closest atom out of the chiral plane is the nitrogen atom, which is marked as the descriptor. The difference is that the descriptor is located further from the benzene ring than in the case of compound **3**, so the ethylenoxy unit should be labeled (a, b, and c) according to the original rule. Unfortunately, this unit is conformationally flexible and, because of free rotation about the σ bond, could give misleading stereochemistry results. In our approach, we decided to disregard the ethylenoxy unit and labeled only atoms in the aromatic ring. According to this modified procedure, the absolute configuration for compound **2** (Scheme 7) is defined as R_p. This operation allowed the use of a procedure analogous to that employed for compound **3**, with the atoms labeled a, b, and c adjacent to the descriptor. Only in the case of compound **3** was the absolute configuration established by X-ray studies.

Diazacoronands **1** and **2**, and **4** were also resolved into enantiomers, however, attempts to obtain single crystals were unsuccessful. Therefore, a different approach to establish their absolute configurations had to be employed. Among known methods, the most noteworthy and reliable ones are those based on chirooptical techniques. The time-dependent density functional theory (TD-DFT) method has recently become an important tool for electronic circular-dichroism spectra calculation and provides more reliable results than Hartree–Fock (HF) or characteristic isochromat spectroscopy (CIS) methods.[20,21] Unfortunately, the macrocycle **2** was too large to be subjected to the TD-DFT method with required accuracy. For large macrocycles, the semiempirical ZINDO/S method has been used successfully

for analysis of CD spectra.[22] Unfortunately, computation of the CD spectrum of compound **1** could not be performed, due to the lack of parameters for the bromine atom in the ZINDO/S method. This method was used instead for the calculation of the CD spectra of **2**, which was structurally very similar to bromine derivative **1**.

To this end, conformational analysis of **2** was carried out by using the structures generated by the Conflex/Cache[23] search routine, together with those generated from the X-ray data for **2** and **1**. These structures were optimized further by using semiempirical methods with molecular mechanics correction (PM3MM),[24] and their relative energies were calculated by using the DFT method (B3LYP/6–31g*). An S_p absolute configuration was arbitrarily assigned to a thus-obtained minimum-energy conformer, and the CD spectrum was calculated by using the ZINDO/S semiempirical method (Figure 7). The calculated rotatory strengths (shown as bars) of the transitions at 230 nm (negative) and 224 nm (positive) converge to a negative Cotton effect at 238 nm and a positive effect at 219 nm in the Gaussian CD curve. These match satisfactorily the Cotton effects attributable to the corresponding transitions in the experimentally measured CD curve of (+)-**2**: a negative one at 225 nm and a positive one at 207 nm. This allowed us to assign the S_p absolute configuration to the (+)-enantiomer of **2**. Note a red shift of the calculated transitions caused by underestimation of the electronic transition energies in the calculation and cancellation of the Cotton effects of opposite sign.

A similar analysis was performed for macrocycle **3**. The computed (TD-DFT B3LYP/6–31++g(d,p)) CD spectrum of the enantiomer (R_p)-**3** matched the experimentally measured CD spectrum of the (+) enantiomer of **3**, and this confirmed the absolute configuration of **3** that was determined by X-ray diffraction analysis (Figure 8).

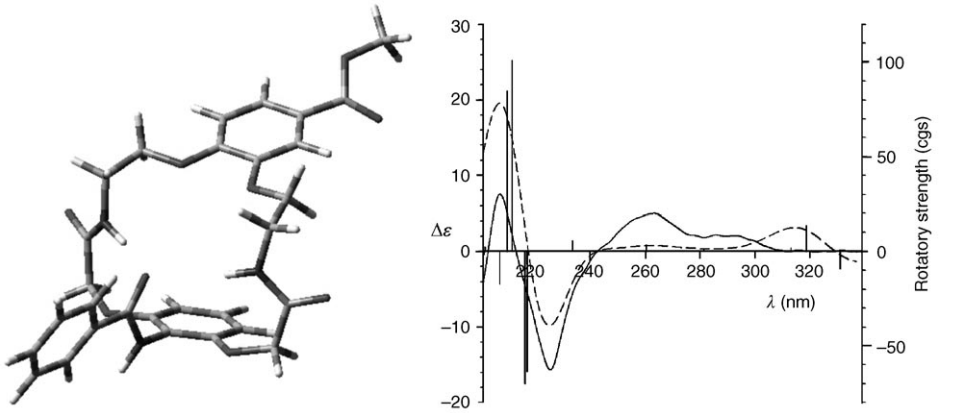


Figure 7. Left: calculated minimum-energy conformer of (S_p)-**2**. Right: comparison of the experimentally measured (solid line) and calculated (broken line) CD spectra of **2**. Bars represent calculated rotational strengths of the component electronic transitions. Calculated CDs were blue-shifted by 13 nm.

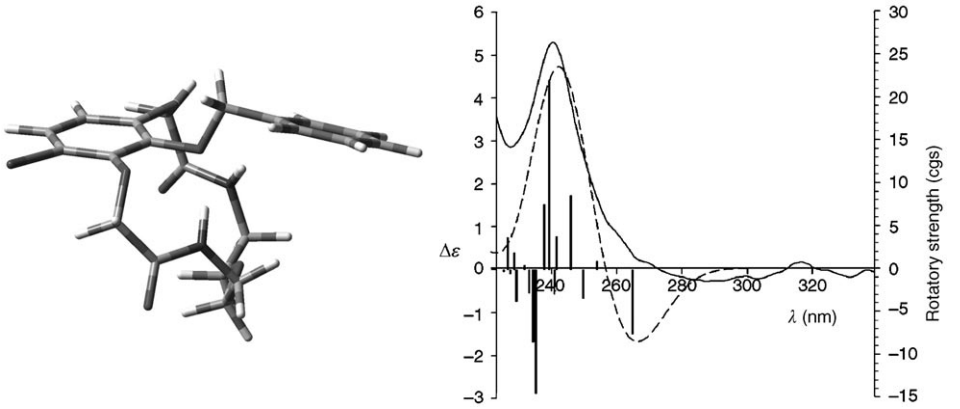


Figure 8. Left: calculated minimum-energy conformer of (R_p)-**3**. Right: comparison of the experimentally measured (solid line) and calculated (broken line) CD spectra of **3**. Bars represent calculated rotational strengths of the component electronic transitions.

Conclusion

We have developed a short and versatile route to diazacoronands with planar chirality, based on a system with two essential requirements. Our approach allowed us to obtain stable chiral receptors with larger macroring structures and including donor/acceptor functions. A range of macrocycles were readily synthesized, and their structures were examined by X-ray crystallography. Absolute configurations were established for two representative examples (**2** and **3**) from molecular modeling and experimental circular dichroism results. An applied theoretical approach was verified by results of independent crystallographic experiments performed for the diazacoronand (+)-(R_p)-**3**. The racemic compounds obtained should serve, after enantiomeric resolution, as a new type of chiral receptor for supramolecular purposes.

Experimental Section

All precursors for the syntheses were used as received from Aldrich or Fluka. THF was distilled from sodium/potassium alloy just before use. Methanol was distilled from magnesium and stored over anhydrous molecular sieves (4 Å). Acetonitrile was freshly distilled from calcium hydride. Thin-layer chromatography was performed by using Merck silica gel glass plates (60 F_{254}). Flash column chromatography was performed by using Merck silica gel (60, particle size 0.040–0.063 mm). Melting points were determined by using a Boëtius M HMK hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded by using Varian Gemini 200BB or Bruker AM 500 spectrometers. Chemical shifts are reported as δ values relative to the TMS peak defined at $\delta = 0.00$. The mass-spectral analysis was performed by using the ESI-TOF technique and a Mariner mass spectrometer from PerSeptive Biosystem, or by using high-resolution liquid secondary-ion mass spectrometry (HR-LSIMS) and an AMD-604 Intectra instrument.

Syntheses: Elemental analysis of the macrocycles under study gave unsatisfactory results, due to solvent molecules encapsulated in the crystals. This phenomenon is well known and, even after prolonged heating in high vacuum, the solvents can still be detected in the NMR spectra. The isotope patterns seen in the ESI-MS spectra are, however, consistent with those calculated on the basis of natural isotope abundances and, thus, confirm the elemental composition.

General method for the preparation of diamines 7 and 8: BMS (55 mL, 600 mmol, 4 equiv) was added to a solution of an appropriate dinitrile **5** or **6** (150 mmol) in anhydrous THF (700 mL), and the resulting mixture was stirred under reflux for 4 h. After cooling, the reaction mixture was cautiously quenched with a mixture of water and THF (50 mL:50 mL) and concentrated. An HCl_{conc}/H_2O solution (1:1, 150 mL) was added to the residue, and the mixture was stirred under reflux for 20 min. The mixture was then cooled, made alkaline with NaOH (20%), and extracted with CH_2Cl_2 (3×). The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated to give the crude product, which was distilled under vacuum.

2-[2-(2-Aminoethoxy)-4-methylphenoxy]ethanamine (7): Colorless oily wax, 83%. B.p. 106–108 °C (0.05 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.85$–6.65 (m, 3H), 4.02–3.94 (m, 4H), 3.11–2.99 (m, 4H), 2.27 (s, 3H; Me), 1.96 ppm (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.7$, 146.6, 131.3, 121.6, 115.6, 114.9, 71.9, 71.5, 41.6, 41.5, 20.8 ppm; ESI-HRMS (MeOH): m/z calcd for $C_{11}H_{19}N_2O_2$ $[M+H]^+$: 211.1441; found: 211.1451.

2-[2-(2-Aminoethoxy)-4-*tert*-butylphenoxy]ethanamine (8): Yellowish oily wax, 81%. B.p. 128–130 °C (0.05 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.01$–6.84 (m, 3H), 4.20–3.93 (m, 8H), 3.12 (br s, 4H), 1.27 ppm (s, 9H; *t*Bu); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 148.7, 147.2, 145.8, 119.2, 115.2, 113.9, 71.5, 71.1, 41.7, 41.6, 34.9 (CCH_3), 32.0 ppm (CH_3); ESI-HRMS (MeOH): m/z calcd for $C_{14}H_{25}N_2O_2$ $[M+H]^+$: 253.1911; found: 253.1922.

(3-Cyanomethoxy-2-oxo-2*H*-pyridin-1-yl)-acetonitrile (11): Anhydrous K_2CO_3 (91 g, 660 mmol) and chloroacetonitrile (71 mL, 1.1 mol) were added to a solution of 2,3-dihydroxypyridine (**9**, 25.0 g, 225 mmol) in anhydrous acetonitrile (500 mL). The resulting mixture was stirred under reflux for 48 h. After filtration through Celite, the filtrate was concentrated and the residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 9:1). The brown solid was decolorized with active charcoal to give a yellowish product (23.0 g, 54%). M.p. 121.9–123.4 °C; ^{1}H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.50$ (dd, $^3J_1$(H,H) = 6.9 Hz, $^3J_2$(H,H) = 1.6 Hz, 1H), 7.16 (dd, $^3J_1$(H,H) = 6.9 Hz, $^3J_2$(H,H) = 1.6 Hz, 1H), 6.31 (t, ^3J(H,H) = 6.9 Hz, 1H), 5.14 (s, 2H; CH_2CN), 5.04 ppm (s, 2H; CH_2CN); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 156.0$ (CO), 145.5, 131.6, 119.4, 115.9, 115.6, 104.7, 54.2 (CH_2CN), 36.8 ppm (CH_2CN); IR (KBr): $\tilde{\nu} = 2993$, 2971, 1662, 1605, 1229 cm^{-1}; ESI-HRMS (MeOH): m/z calcd for $C_9H_7N_3O_2Na$ $[M+Na]^+$: 212.0430; found: 212.0433.

3-(2-Amino-ethoxy)-1-(2-amino-ethyl)-1*H*-pyridin-2-one (12): BMS (55.0 mL, 600 mmol, 4 equiv) was added to a solution of dinitrile **11** (28.0 g, 150 mmol) in anhydrous THF (700 mL), and the resulting mixture was stirred under reflux for 3 h. After cooling, the reaction mixture was cautiously quenched with a mixture of water and THF (50 mL:50 mL), followed by HCl (5 M, 200 mL), and stirred under reflux for 20 min. The mixture was concentrated, made alkaline ($NaOH_{sat}$/MeOH solution), and, after cooling, filtered to remove the inorganic salt. The filtrate was concentrated and the residue was distilled under vacuum to give a yellow oil, 21.0 g (71%). B.p. 170–174 °C (0.01 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.01$ (d, ^3J(H,H) = 7.1 Hz, 1H), 6.68 (d, ^3J(H,H) = 7.1 Hz, 1H), 6.10 (t, ^3J(H,H) = 7.1 Hz, 1H), 4.06–3.90 (m, 4H), 3.17–3.01 (m, 4H), 1.79 ppm (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.6$ (CO), 149.6, 129.8, 114.6, 105.0, 71.4, 53.4, 41.7, 41.5 ppm; ESI-HRMS (MeOH): m/z calcd for $C_9H_{16}N_3O_2$ $[M+H]^+$: 198.1237; found: 198.1246.

General procedure for the synthesis of compounds 17–24: The appropriate diester **13** or **14** (10 mmol) was dissolved in dry MeOH (100 mL) and added to the solution of the diamine (10 mmol). Subsequently, a solution of MeONa (25 mmol in 100 mL MeOH) or DBU (3.8 g, 25 mmol, in the cases of **23** and **24**) was added. The mixture was left at ambient temperature over a period of 2–7 days (TLC monitoring). The solvent was then evaporated and the residue was purified by column chromatography (silica gel; AcOEt/MeOH 95:5 or 8:2 for **23** and **24**, respectively) to give the desired product.

Diazacoronand 17: Colorless solid, 16%. M.p. 72.7–75.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.12$–8.05 (m, 2H; CONH), 7.42–7.38 (m, 2H), 7.27–7.24 (m, 3H), 7.08 (t, ^3J(H,H) = 8.4 Hz, 1H), 6.69 (d, ^3J(H,H) = 8.4 Hz, 2H), 6.66 (s, 2H), 6.58 (s, 1H), 5.06 (s, 2H; CH_2Ph), 4.74–4.68 (m, 2H; CH_2CO), 4.51–4.46 (m, 2H; CH_2CO), 4.08–4.02 (m, 2H), 3.94–3.89 (m, 2H), 3.77–3.71 (m, 2H), 3.49–3.42 (m, 2H), 2.26 ppm (s, 3H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 168.8$ (CONH), 168.7 (CONH), 153.2, 153.1, 147.7, 145.8, 130.6, 128.6, 128.5, 128.4, 128.2, 127.5, 125.6, 121.0, 113.5, 112.2, 111.4, 111.3, 76.5 (CH_2Ph), 71.1, 71.0, 67.3, 67.2, 38.8, 38.8, 20.8 ppm; ESI-HRMS (MeOH): m/z calcd for $C_{28}H_{30}N_2O_7Na$ $[M+Na]^+$: 529.1945; found: 529.1962.

Diazacoronand 18: Colorless solid, 22%. M.p. 65.1–67.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.11$ (m, 2H; CONH), 7.45–7.39 (m, 3H), 7.28–7.24 (m, 3H), 7.08 (t, ^3J(H,H) = 8.4 Hz, 1H), 6.88 (dd, $^3J_1$(H,H) = 8.4 Hz, $^3J_2$(H,H) = 2.2 Hz, 1H), 6.82 (d, ^3J(H,H) = 2.2 Hz, 1H), 6.70 (d, ^3J(H,H) = 8.4 Hz, 2H), 5.08 (s, 2H; CH_2Ph), 4.75–4.70 (m, 2H; CH_2CO), 4.52–4.47 (m, 2H; CH_2CO), 4.14–4.03 (m, 2H), 3.97–3.90 (m, 2H), 3.82–3.72 (m, 2H), 3.46–3.38 (m, 2H), 1.28 ppm (s, 9H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 168.8$ (CONH), 168.7 (CONH), 153.2, 153.1, 147.4, 145.7, 144.2, 139.3, 136.3, 128.5, 128.2, 127.9, 125.6, 117.3, 111.6, 111.4, 111.3, 110.0, 76.4 (CH_2Ph), 71.1, 71.0, 67.3, 67.2, 38.8, 38.7, 34.3, 31.4 ppm; ESI-HRMS (MeOH): m/z calcd for $C_{31}H_{36}N_2O_7Na$ $[M+Na]^+$: 571.2415; found: 571.2430.

Diazacoronand 19: Crystallization in vapor diffusive system (MeOH/pentane) gave colorless crystals, 38%. M.p. 175.6–177.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.11$–8.04 (m, 2H; CONH), 7.43–7.40 (m, 2H), 7.30–7.27 (m, 3H), 7.09 (t, ^3J(H,H) = 8.5 Hz, 1H), 6.98 (dd, $^3J_1$(H,H) = 8.5 Hz, $^3J_2$(H,H) = 2.0 Hz, 1H), 6.82 (d, ^3J(H,H) = 2.0 Hz, 1H), 6.73–6.69 (m, 2H), 6.60 (d, ^3J(H,H) = 8.5 Hz, 1H), 5.06 (d_{AB}, ^3J(H,H) = 10.5 Hz, 1H; CH_2Ph), 5.03 (d_{AB}, ^3J(H,H) = 10.5 Hz, 1H; CH_2Ph), 4.77–4.72 (m, 2H; CH_2CO), 4.52 (d, ^3J(H,H) = 15.5 Hz, 2H; CH_2CO), 4.06–4.00 (m, 2H), 3.91–3.84 (m, 2H), 3.79–3.70 (m, 2H), 3.49–3.41 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 169.0$ (CONH), 168.9 (CONH), 153.2, 153.1, 148.6, 147.2, 139.4, 136.2, 129.0, 128.6, 128.5, 128.1, 125.7, 123.5, 115.5, 113.1, 112.8, 111.5, 111.3, 76.8 (CH_2Ph), 71.0, 70.1, 67.6, 67.4, 38.7, 38.6 ppm; HR-LSIMS: m/z calcd for $C_{27}H_{28}N_2O_7{}^{79}Br$ $[M+H]^+$: 571.1079; found: 571.1053.

Diazacoronand 20: Crystallization in vapor diffusive system [MeOH/$CHCl_3$ (1:1)/Et_2O] gave colorless crystals, 10%. M.p. 108.8–110.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.12$–8.06 (m, 2H; CONH), 7.62 (dd, $^3J_1$(H,H) = 8.4 Hz, $^3J_2$(H,H) = 1.9 Hz, 1H), 7.44–7.40 (m, 3H), 7.27–7.24 (m, 3H), 7.09 (t, ^3J(H,H) = 8.4 Hz, 1H), 6.75 (d, ^3J(H,H) = 8.4 Hz, 1H), 6.71 (d, ^3J(H,H) = 8.4 Hz, 2H), 5.07 (d_{AB}, ^3J(H,H) = 10.8 Hz, 1H; CH_2Ph), 5.04 (d_{AB}, ^3J(H,H) = 10.8 Hz, 1H; CH_2Ph), 4.75 (dd_{AB}, $^3J_1$(H,H) = 15.5 Hz, $^3J_2$(H,H) = 2.1 Hz, 2H; CH_2CO), 4.52 (dd_{AB}, $^3J_1$-

Table 1. Crystallographic data for the structures described.

Identification code	*rac*-**1**	*rac*-**2**	(R_p)-**3**
empirical formula	$C_{28}H_{25}BrN_3O_8$	$C_{21}H_{15}N_3O_{8.33}$	$C_{21}H_{23}BrN_2O_6$
M_r	611.42	428.68	479.32
T [K]	293(2)	120(2)	150(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic
space group	$P2(1)$	$P\bar{1}$	$P2(1)$
a [Å]	8.4590(17)	13.127(3)	10.567(2)
b [Å]	14.840(3)	15.887(3)	8.9840(18)
c [Å]	11.586(2)	16.134(3)	11.525(2)
α [°]	90	90.00(3)	90
β [°]	106.35(3)	89.70(3)	103.34(3)
γ [°]	90	77.90(3)	90
V [Å^3]	1395.6(5)	3289.9(11)	1064.6(4)
Z	2	6	2
ρ_{calcd} [g cm^{-3}]	1.455	1.298	1.495
μ [mm^{-1}]	1.527	0.102	1.971
$F(000)$	626	1330	492
crystal size [mm]	$0.37\times0.39\times0.26$	$0.43\times0.21\times0.07$	$0.3\times0.2\times0.1$
range of θ [°]	3.50–20.00	2.58–28.91	3.63–23.00
index ranges	$-8\le h\le7$, $-13\le k\le14$, $0\le l\le11$	$-17\le h\le17$, $-21\le k\le21$, $-21\le l\le21$	$-11\le h\le11$, $-9\le k\le9$, $-12\le l\le12$
rflns (collected/unique)	2174/2174	57349/16024	13573/2926
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restr./param.	2174/1/371	16024/36/879	2926/1/293
GoF	0.987	0.935	0.999
R indices [$I>2\sigma(I)$]	$R1=0.0597$, $wR2=0.1408$	$R1=0.1788$, $wR2=0.4116$	$R1=0.0261$, $wR2=0.0540$
R indices (all data)	$R1=0.0860$, $wR2=0.1661$	$R1=0.4251$, $wR2=0.5302$	$R1=0.0286$, $wR2=0.0549$
extinction coefficient	0.024(4)		0.0047(10)
$\Delta\rho_{max}/\rho_{min}$ [e Å^{-3}]	0.250/−0.196	0.573/−0.636	0.545/−0.159
Flack parameter			−0.016(7)

Identification code	*rac*-**19**	*rac*-**20**	*rac*-**23**
empirical formula	$C_{27}H_{27}BrN_2O_7$	$C_{29}H_{30}N_2O_9$	$C_{27}H_{31}N_3O_8$
M_r	571.42	582.59	525.55
T [K]	293(2)	120(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic
space group	$P2(1)/c$	$R\bar{3}$	$P2(1)/c$
a [Å]	10.106(2)	25.502(6)	7.6615(15)
b [Å]	17.225(3)	25.502(6)	19.539(4)
c [Å]	15.279(3)	25.502(6)	16.915(3)
α [°]	90	118.94(3)	90
β [°]	106.38(3)	118.94(3)	98.6
γ [°]	90	118.94(3)	90
V [Å^3]	2551.8(9)	4425.2(19)	2503.8(9)
Z	4	6	4
ρ_{calcd} [g cm^{-3}]	1.487	1.312	1.394
μ [mm^{-1}]	1.661	0.099	0.104
$F(000)$	1176	1848	1112
crystal size [mm]	$0.18\times0.44\times0.53$	$0.2\times0.1\times0.1$	$0.15\times0.15\times0.15$
range of θ [°]	3.65–22.00	3.21–22.49	2.65–28.76
index ranges	$-10\le h\le10$; $0\le k\le18$; $0\le l\le16$	$-27\le h\le27$, $-27\le k\le27$, $-27\le l\le27$	$-10\le h\le9$, $-26\le k\le25$, $-22\le l\le22$
rflns (collected/unique)	3082/3082	51674/3844	22273/6098
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restr./param.	3082/0/347	3844/0/418	6098/0/468
GoF	0.974	1.169	0.697
R indices [$I>2\sigma(I)$]	$R1=0.0601$, $wR2=0.1616$	$R1=0.0799$, $wR2=0.1765$	$R1=0.0424$, $wR2=0.0552$
R indices (all data)	$R1=0.0802$, $wR2=0.1835$	$R1=0.0983$, $wR2=0.1881$	$R1=0.1696$, $wR2=0.0746$
extinction coefficient	0.0	0.0016(7)	0.00085(15)
$\Delta\rho_{max}/\rho_{min}$ [e Å^{-3}]	1.019/−0.413	1.086/−0.296	0.209/−0.192

(H,H) = 15.5 Hz, $^3J_2$(H,H) = 2.1 Hz, 2H; CH_2CO), 4.15–4.10 (m, 2H), 4.00–3.94 (m, 2H), 3.88 (s, 3H; Me), 3.81–3.73 (m, 2H), 3.51–3.42 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 168.8 (CONH), 168.8 (CONH), 166.6 (COOMe), 153.2, 151.9, 147.6, 139.5, 136.3, 128.5, 128.4, 128.0, 125.6, 123.5, 122.7, 112.7, 111.4, 111.3, 111.0, 76.6 (CH_2Ph), 71.1, 71.0, 67.6, 67.5, 51.9, 38.7, 38.6 ppm; ESI-HRMS (MeOH): m/z calcd for $C_{29}H_{30}N_2O_9Na$ $[M+Na]^+$: 573.1844; found: 573.1872; elemental analysis calcd (%) for $C_{29}H_{30}N_2O_9$: C 63.27, H 5.45, N 5.09; found: C 63.48, H 5.66, N 4.85.

Diazacoronand 21: Crystallization in vapor diffusive system [MeOH/$CHCl_3$ (1:1)/pentane] gave colorless crystals, 13%. M.p. 244.8–245.8°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ = 8.22–8.15 (m, 2H; CONH), 7.98–7.95 (m, 2H), 7.83 (brs, 1H; NHCOPh), 7.64–7.59 (m, 1H), 7.54–7.50 (m, 2H), 6.66 (s, 2H), 6.64–6.60 (m, 2H), 6.32 (m, 2H), 4.66 (d_{AB}, ^3J(H,H) = 16.5 Hz, 2H; CH_2CO), 4.61 (d_{AB}, ^3J(H,H) = 16.5 Hz, 2H; CH_2CO), 4.30–4.23 (m, 2H), 3.94–3.87 (m, 2H), 3.75–3.69 (m, 2H), 3.38–3.29 (m, 2H), 2.28 ppm (s, 3H; Me); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ = 168.4 (CONH), 168.3 (CONH), 168.1 (COPh), 152.9, 147.3, 145.5, 133.1, 132.6, 130.3, 128.8, 128.5, 127.8, 120.7, 113.4, 112.7, 111.4, 104.8, 104.7, 66.7, 66.4, 66.3, 39.0, 20.9 ppm; ESI-HRMS (MeOH): *m*/*z* calcd for $C_{28}H_{29}N_3O_7Na$ $[M+Na]^+$: 542.1898; found: 542.1908.

Diazacoronand 22: Crystallization in vapor diffusive system (MeOH/petroleum ether) gave colorless crystals, 15%. M.p. 134.5–137.1°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ = 8.08 (m, 2H; CONH), 7,95–7.91 (m, 2H), 7.71 (s, 1H; NHCOPh), 7.62–7.58 (m, 1H), 7.52–7.48 (m, 2H), 6.86 (dd, $^3J_1$(H,H) = 8.4 Hz, $^3J_2$(H,H) = 2.2 Hz, 1H), 6.81 (d, ^3J(H,H) = 2.2 Hz, 1H), 6.72–6.65 (m, 2H), 6.37 (dd, $^3J_1$(H,H) = 8.4 Hz, $^3J_2$(H,H) = 4.5 Hz, 2H), 4.65 (s, 4H; CH_2CO), 4.28–4.20 (m, 2H), 3.95–3.85 (m, 2H), 3.80–3.72 (m, 2H), 3.40–3.32 (m, 2H), 1.30 ppm (s, 9H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ = 168.4 (CONH), 167.9 (COPh), 152.9, 152.8, 147.2, 145.5, 143.9, 133.2, 132.5, 128.8, 128.5, 127.7, 117.0, 113.5, 111.0, 109.4, 104.8, 104.7, 66.8, 66.7, 66.4, 66.3, 39.1, 39.0, 34.3, 31.5 ppm; ESI-HRMS (MeOH): *m*/*z* calcd for $C_{31}H_{35}N_3O_7Na$ $[M+Na]^+$: 584.2367; found: 584.2395.

Diazacoronand 23: Crystallization in vapor diffusive system [MeOH/$CHCl_3$ (1:1)/Et_2O] gave colorless crystals: 28% (DBU), 8% (MeONa). M.p. 104.5–107.2°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ = 7.85–7.80 (m, 1H; CONH), 7.72 (m, 1H; CONH), 7.54–7.52 (m, 2H), 7.38–7.30 (m, 3H), 6.79 (dd, $^3J_1$(H,H) = 6.8 Hz, $^3J_2$(H,H) = 1.5 Hz, 1H), 6.74 (t, ^3J(H,H) = 8.4 Hz, 1H), 6.47–6.44 (m, 1H), 6.37 (dd, $^3J_1$(H,H) = 6.8 Hz, $^3J_2$(H,H) = 1.5 Hz, 1H), 6.25 (d, ^3J(H,H) = 8.4 Hz, 1H), 6.00 (t, ^3J(H,H) = 7.1 Hz, 1H), 5.15 (s, 2H; CH_2Ph), 4.68 (d_{A1B1}, ^3J(H,H) = 15.8 Hz, 1H; CH_2CO), 4.57 (d_{A2B2}, ^3J(H,H) = 16.0 Hz, 1H; CH_2CO), 4.47 (d_{A1B1}, ^3J(H,H) = 15.8 Hz, 1H; CH_2CO), 4.29 (d_{A2B2}, ^3J(H,H) = 16.0 Hz, 1H; CH_2CO), 4.06–4.00 (m, 1H), 3.86–3.79 (m, 1H), 3.76–3.66 (m, 3H), 3.54–3.46 (m, 2H), 3.20–3.14 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ = 169.5 (CONH), 168.9 (CONH), 158.7, 152.5, 151.8, 148.8, 137.6, 137.5, 128.6, 128.2, 128.1, 127.8, 123.9, 113.0, 107.4, 107.2, 105.4, 75.8 (CH_2Ph), 68.8, 68.5, 67.0, 50.6, 46.9, 40.8, 38.2 ppm; ESI-HRMS (MeOH): *m*/*z* calcd for $C_{26}H_{27}N_3O_7Na$ $[M+Na]^+$: 516.1741; found: 516.1762; elemental analysis calcd (%) for $C_{26}H_{27}N_3O_7$: C 63.28, H 5.47, N 8.52; found: C 63.43, H 5.59, N 8.33.

Diazacoronand 24: Crystallization in vapor diffusive system ($CHCl_3$/THF) gave colorless crystals: 23% (DBU), 7% (MeONa). M.p. 119.2–122.4°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ = 10.05 (brs, 1H; NHCOPh), 8.66 (brs, 1H), 8.40 (brd, 2H), 8.09 (brd, 1H), 7.56–7.44 (m, 3H), 7.15 (t, ^3J(H,H) = 8.5 Hz, 1H), 6.97–6.92 (m, 1H), 6.74–6.70 (m, 1H), 6.65–6.61 (m, 1H), 6.53 (d, ^3J(H,H) = 8.5 Hz, 1H), 6.23 (t, ^3J(H,H) = 7.2 Hz, 1H), 4.75 (d_{A1B1}, ^3J(H,H) = 16.1 Hz, 1H; CH_2CO), 4.64 (d_{A1B1}, ^3J(H,H) = 16.1 Hz, 1H; CH_2CO), 4.57 (d_{A2B2}, ^3J(H,H) = 15.7 Hz, 1H; CH_2CO), 4.50 (d_{A2B2}, ^3J(H,H) = 15.7 Hz, 1H; CH_2CO), 4.26–4.18 (m, 1H), 3.91 (brd, 1H), 3.81–3.73 (m, 2H), 3.59–3.46 (m, 3H), 3.21–3.13 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C, TMS): δ = 169.0 (CONH), 168.7 (CONH), 167.1 (COPh), 159.6 (CO), 155.4, 153.2, 148.8, 133.6, 131.8, 129.9, 128.5, 128.3, 128.2, 128.1, 127.9, 116.8, 113.6, 108.7, 106.9, 105.0, 70.2, 67.4, 66.4, 49.2, 41.5, 37.6 ppm; ESI-HRMS (MeOH): *m*/*z* calcd for $C_{26}H_{26}N_4O_7Na$ $[M+Na]^+$: 529.1694; found: 529.1996.

X-ray crystallography: The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw. Crystal data and details of the crystal structure determinations are presented in Table 1. The intensity data were collected by using a Kuma KM4CCD diffractometer in the omega scan mode. Data were corrected for decay, Lorentz, and polarization effects. The structure was solved by direct methods[25] and refined by using SHELXL.[26] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were identified from a difference density map and refined without any constraints.

CCDC-288948 (*rac*-**1**), CCDC-288949 (*rac*-**2**), CCDC-288947 [(R_p)-**3**], CCDC-288950 (*rac*-**19**), CCDC-288951 (*rac*-**20**), and CCDC-288952 (*rac*-**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Molecular modeling: Conformational analysis of **2** and **3** was performed with structures generated by the Conflex/Cache[23] search routine as well as with structures generated from the X-ray data. These structures were further optimized by using PM3MM semiempirical methods with molecular mechanics correction,[24] and their relative energies were calculated additionally by the DFT method (B3LYP/6–31g*). CD spectra were calculated for the first 20 singlet transitions for each compound, by the ZINDO/S method for **2** and by TD-DFT (B3LYP/6–31++g(d,p)) for **3**.

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