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Enantiomerically pure α-pinene derivatives from material of 65% enantiomeric purity. Part 2: C_2-symmetric *N*,*N*′-3-(2α-hydroxy)pinane diimines and diamines☆

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Abstract—The conversion of enantiomerically enriched (ee >99%) 2α-hydroxypinan-3-one and its oxime (obtained in previously described procedures* from α-pinene of 65% ee) into a range of derivatives with potential application in asymmetric synthesis was attempted. C_2-Symmetrical compounds, ligands for potential catalysts, were synthesized from 2α-hydroxypinan-3-one and either aliphatic or aromatic diamines. Reduction or etherification/reduction of selected diiminodiols afforded respective diaminodiols and diaminoethers, which were further transformed into azolium salts. Reactions of dipinanediaminoethers with dichlorophenylphosphine and subsequent in situ oxidation of the products afford the respective stable phosphinediamide oxides. Four selected compounds were crystallographically studied.

1. Introduction

The synthesis of enantiomerically pure ligands for potential catalysts of numerous reactions aimed at the generation of new chiral centers is one of the key challenges of today's organic chemistry. Extensive literature is currently available with regards to chiral ligands and catalysts, including numerous reviews (e.g., an issue of *Chemical Reviews* was devoted exclusively to this topic).[1]

Pinenes are a handy subset of the chiral pool and pinene derivatives are common building blocks for a broad range of asymmetric syntheses. In recent years, pinene derivatives have been used for the synthesis of enantiomeric amino acids containing cyclobutane rings,[2] pheromones[3] and catalysts ligands (Fig. 1).[4]

α-Pinenes belong to a very small group of compounds naturally occurring in both enantiomeric forms. However, the research applicability of these compounds is limited by the high cost of the material with sufficient enantiomeric excess. Therefore, of special importance are those derivatives of α-pinene, which can be enantiomerically enriched to obtain pure chemical entities.

In 2002, we published a convenient method for enantiomeric enrichment of 2α-hydroxypinan-3-one and its oxime obtained from α-pinene of 65% ee. We have also documented significant differences of crystalline networks of enantiomerically pure oxime and the racemic compound.[5] The synthesis of a C_2-symmetric ligand,

☆ Part 1: Markowicz, S. W.; Pokrzeptowicz, K.; Karolak-Wojciechowska, J.; Czylkowski, R.; Omelańczuk, J.; Sobczak, A. *Tetrahedron: Asymmetry* **2002**, *13*, 1981–1991. Preliminary communications; Figlus, M.; Markowicz, S. W. PTChem, Kraków, 2002, S16, p 1096 and Markowicz, S. W.; Figlus, M.; Lejkowski, M.; Karolak-Wojciechowska, J.; Verpoort, F. PTChem, Lublin, 2003, S1, p 91, Annals of the PTChem, Vol. 2, PI, pp 52–56.

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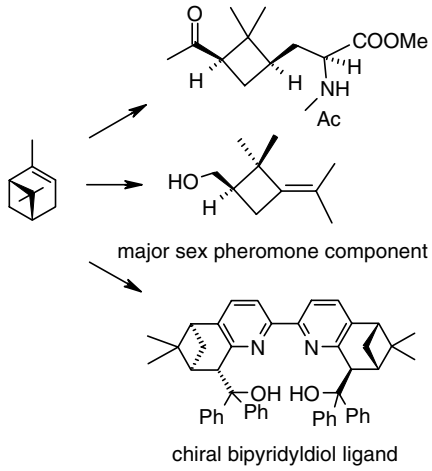


Figure 1.

di[3α-(2α-hydroxy)pinane]amine (Fig. 2), is described in the same paper.

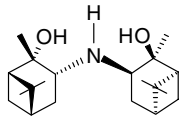


Figure 2.

In addition to the number of straightforward transformations of the oxime and the ketol, we wanted to present a series of hydroxypinanone-derived diiminodiols (Fig. 3a) and their derivatives (Fig. 3b), comprising a group of C_2-symmetric ligands for potential catalysts.

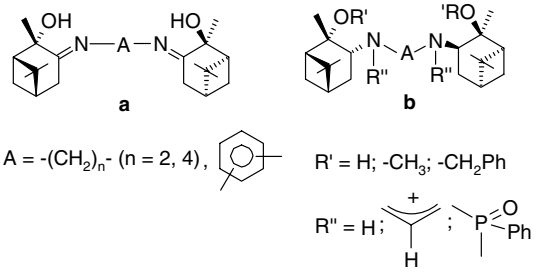


Figure 3.

The growing interest in pinenes as a source of chirality can be illustrated by the following examples: in 2001, Hiroi and Watanabe[6] obtained terpenic imine-phosphine ligands. One of them, based on 2α-hydroxypinan-3-one (Fig. 4a), allowed us to obtain a 44% enantiomeric excess of the product from palladium-catalyzed cycloaddition of acryloyl amide and cyclopentadiene. Recently, Basavaiah et al. have obtained a pinane-based compound with an N–P=O structural framework (Fig. 4b) and successfully used this compound in borane-mediated asymmetric reduction of prochiral ketones.[7]

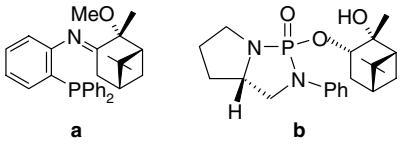
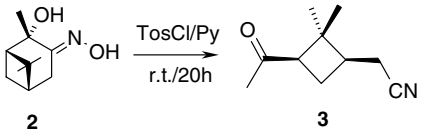


Figure 4.

2. Results and discussion

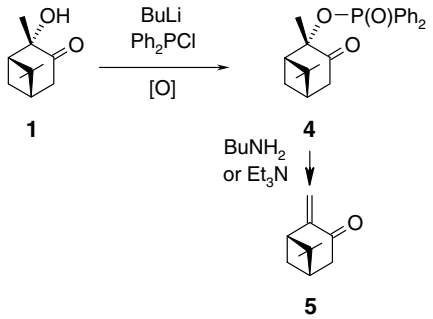
The fact that 2α-hydroxypinan-3-one, some of its imines and particularly its oxime, can be enantiomerically enriched to obtain practically pure enantiomers has influenced our attempt to use this compound in the synthesis of building blocks and ligands for potential catalysts. We observed that the oxime of 2α-hydroxypinan-3one **2**, when reacted with tosyl chloride in pyridine, forms ketonitrile **3** in close-to-quantitative yield (96.5% as calculated for the distilled, solidifying product) and with retention of cis-geometry of the substituents in the cyclobutane ring (Scheme 1).



Scheme 1.

The structure of ketonitrile **3** was determined by analyzing the ^{1}H NMR, IR, and MS spectra and comparing them to those described in the literature.[8]

Ketol **1** can be transformed into pinocarvone **5** via a phosphorous-containing intermediate in satisfactory yield (>60%) (Scheme 2); pinocarvone can successfully be used as a direct source of chirality in C_2-symmetric bipyridil Chen ligands.[4]



Scheme 2.

Diphenylpinanoxyphosphine, formed in the reaction of diphenylchlorophosphine and an alkoxide, can be easily oxidized although our attempts to obtain the pure compound failed. We present the complete characterization of the oxidized product—diphenylphosphinic acid (3-oxopinan-2α-yl) ester **4**.

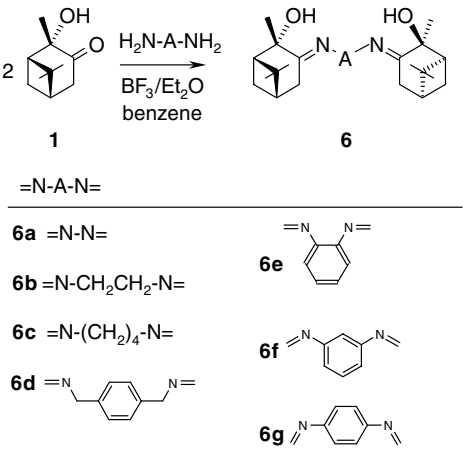
The ^{1}H NMR spectrum of the stable and non-moisture-sensitive compound **4** has a signal of $^{10}CH_3$ protons shifted by 0.19 ppm compared to the respective signal of the starting ketol **1**. The ^{13}C NMR signal of ^{3}C (205.9 ppm), as well as other signals, confirms the assumed structure. Other data: ^{31}P NMR $\delta = 29.15$ and MS (M+1 = 251) are as expected for the structure **4**.

2α-Diphenylphosphorylpinan-3-one **4** undergoes elimination in the presence of amines. For this reason, we have used butyllithium instead of triethylamine. In refluxing benzene and using an excess of *n*-butylamine, we transformed **4** into pinocarvone **5** with a satisfactory yield of 60%. This may not be the most effective method of pinocarvone synthesis described,[9] but by using this method, pinocarvone can be obtained in an enantiomeric excess equal to that of the substrate (>99%).

From amongst the side products of the latter reaction, we isolated, in addition to 2α-hydroxypinan-3-one, a compound, to which the structure of 2β-hydroxypinanon-3-one was ascribed, on the basis of MS and NMR spectra.

Diiminodiols obtained from ketol **1** and symmetrical aliphatic or aromatic diamines comprise a group of C_2-symmetric ligands, capable of undergoing transformations into respective diiminoethers. Reduction of the imine bond, leading to diaminodiols and diaminoethers, allows for further transformations of the compounds obtained by this method. Using the standard procedures, we obtained a series of diiminodiols with yields of 41–75%, as illustrated in Scheme 3 and Table 1. Optimization of the synthesis and isolation processes for the selected reactions with 1,2-diaminoethane and 1,2-phenyldiamine increased the yields from 72% to 90% and from 56% to 80%, respectively.

All crystalline diiminodiols obtained had MS molecular peaks as calculated. ^{13}C NMR data contain the signal for imine carbons at $\delta = 164.2$ ppm for the hydrazine derivative and 176.1–178.4 for other compounds. The 10 signals of terpenic moieties are as expected and confirm the proposed C_2-symmetrical structures (see Experimental for details). ^{1}H NMR spectra contain, in addition to signals from protons of fragment –A–, the signals of protons of the remaining seven carbons. In the sterically hindered structures of **6b** and **6e**, there is a significant difference in the shifts of two protons at



Scheme 3.

^{3}C and $^{3'}$C, as well as those at $^{1,1'}$C and $^{5,5'}$C, when compared to other compounds.

Due to similarity of the ^{1}H NMR spectra within both groups of diiminodiols, only the shifts of two representative compounds **6b** and **6e** are presented here: **6b**, ^{1}H NMR δ: 0.85 (s, 6H, $^{9,9'}CH_3$); 1.32 (s, 6H, $^{8,8'}CH_3$); 1.45 (s, 6H, $^{10,10'}CH_3$); 1.56 (d, 2H, $J_{7\alpha,7\beta} = 10.6$, $^{7\beta,7'\beta}$CH); 2.00–2.08 (m, 4H, $^{1,1'}$CH and $^{5,5'}$CH); 2.28–2.37 (m, 2H, $^{7\alpha,7'\alpha}$CH); 3.57–3.65 (m, 4H, –CH_2–CH_2–), **6e**, ^{1}H NMR δ: 0.90 (s, 6H, $^{9,9}CH_3$); 1.30 (s, 6H, $^{8,8'}CH_3$); 1.57 (s, 6H, $^{10,10'}CH_3$); 1.60 (d, 2H, $J_{7\beta,7\alpha} \approx 10.7$, $^{7\beta,7'\beta}$CH); 1.91 (hpt, 2H, $J_{5,1} \approx 5.75$, $J_{5,4\alpha} = J_{5,4\beta} \approx 2.75$, $J_{5,7\alpha} \approx 6$, $^{5,5'}$CH); 2.06 (dd, 2H, $J_{1,5} \approx 5.75$, $J_{1,7\alpha} \approx 6$, $^{1,1'}$CH), 2.26–2.31 (m, 2H, $^{7\alpha,7'\alpha}$CH), 2.32–2.44 (m, 2H, $^{4\alpha,4'\alpha}$CH), 2.58 (dd, 2H, $J_{4\beta,4\alpha} = 18.5$, $J_{4\beta,5} \approx 2.75$, $^{4\beta,4'\beta}$CH), 6.71 (dd, 2H, $J_{3,4\text{arom.}} \approx 6$, $J_{4,5\text{arom.}} \approx 4$, $J_{5,6\text{arom.}} \approx 6$, $^{4,5\text{arom.}}$CH), 7.02 (dd, 2H $J_{3,4\text{arom.}} \approx 6$, $J_{3,5\text{arom.}} \approx 3$, $^{3,6\text{arom.}}$CH). Other data from the diiminodiols obtained are presented in Table 1.

The progress of the reaction can be easily monitored by ^{1}H NMR, due to deshielding of $^{10,10'}CH_3$ protons and shielding of $^{9,9'}CH_3$ protons in the product, compared to the starting ketol **1**.

The C_2-symmetric diiminodiols obtained (and some of the derived diaminodiols and diaminoethers described

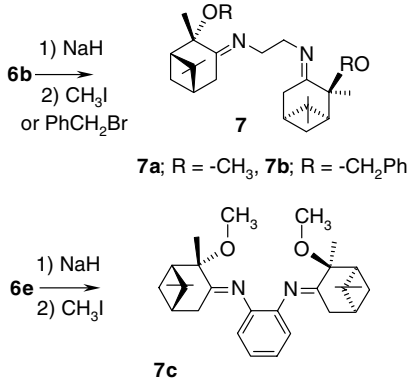
Table 1. Selected data for diiminodiols

	MS (M+H$^+$)	$[\alpha]_D^{20}$ ($CHCl_3$)	Mp (°C)	Isolated yield[a]	^{13}C NMR	^{1}H NMR			IR (>C=N–) (cm^{-1})
					$^{3,3'}$C (δ)	$^{9}CH_3$ (δ)	$^{8}CH_3$ (δ)	$^{10}CH_3$ (δ)	
1	169	−39.5, $c = 0.5$	37–38	—	214.1	0.89	1.38	1.39	—
6a	333	−24.5, $c = 1$	146–147	75 (84)	164.2	0.88	1.33	1.60	1648
6b	361	7.6, $c = 1$	126–127	72 (90)	176.1	0.85	1.32	1.45	1648
6c	389	5.9, $c = 1$	87–90	72	176.9	0.85	1.32	1.47	1648
6d	437	16.0, $c = 1$	148–151	75 (87)	176.3	0.87	1.38	1.53	1650
6e	409	−140.0, $c = 1$	173–174	56 (80)	177.2	0.90	1.30	1.57	1648
6f	409	14.8, $c = 0.5$	147–148	46	178.4	0.94	1.33	1.61	1654
6g	409	99.1, $c = 0.5$	107–108	41	177.9	0.95	1.34	1.61	1656

[a] Values in parentheses correspond to yields after optimization.

below) are able to coordinate one metal atom in a tetradentate system or two metal atoms in a double bidentate system. The distance between the terpene fragments in the molecule and their possible conformations can be the decisive factors here. In particular, we expected significant differences between the conformationally labile molecules of **6b**, **6c**, and **6d** (and their derivatives), in which the –A– spacer allows for a rotation around three bonds and the conformationally rigid molecules of **6e** and **6f**, featuring the aromatic ring.

Further research involved the protection of the hydroxyl groups of diimines. In three attempted reactions, protection with either methyl iodide or benzyl bromide led to the formation of the desired diiminoethers with high yields (76–95%) (for **6b** and **6e**, see Scheme 4). However, our attempts to introduce benzyl groups onto the hydroxyl groups of **6e** failed. Our working hypothesis to explain this failure involves the steric bulk of the benzyl group.



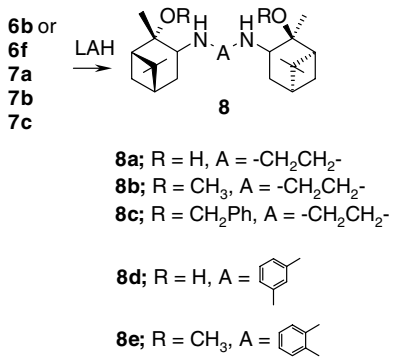
Scheme 4.

All MS, ^{1}H and ^{13}C NMR data confirmed the structures of **7a**, **7b**, and **7c** (see Experimental).

Stereoselective reduction of C_2-symmetrical diiminodiols and diiminoethers afforded the respective C_2-symmetrical diamine derivatives. On the basics of literature reports,[10] lithium aluminum hydride was chosen as a reducing agent for stereoselective reduction of the imine bond. The question, as to whether the methoxyl group would suffice to protect the reagent from approaching from the α side remains an open one.

The reactions presented in Scheme 5 proceeded with either very good (>80%), or good (>50%) yields. In some cases, the product required additional purification by column chromatography or via the amine hydrochlorides. ^{1}H NMR spectra of the products contained the expected double doublets of the $^{3,3'}$CH–N protons. The data, along with changes of chemical shifts of the methyl groups, are presented in Table 2.

The number and the integration of the ^{1}H NMR signals support the structures and C_2-class symmetries of the compounds obtained. The ^{13}C NMR and MS data are also supportive of this.



Scheme 5.

Having at our disposal the C_2-symmetrical diaminodiethers with nitrogen atoms separated by three bonds inbetween (**8b**, **8c**, and **8e**), we were able to attempt immobilization of the structures by incorporating the nitrogen atoms into a five-membered ring, including the formation of precursors of *N*-heterocyclic carbenes. The vicinal location of both nitrogens and the presence of large substituents might stabilize such structures. Literature reports regarding the efficacy of azolium salts as ruthenium catalyst ligands[11] and the possibility of their deprotonation to form the corresponding carbenes make this a very attractive step.

On the basis of literature analogies,[11] we heated the diaminodiether dihydrochlorides with ethyl orthoformate in the presence of catalytic amounts of formic acid. The reaction required high temperatures for tens of hours; the boiling point of ethyl orthoformate was sufficiently high only for **8c** (Scheme 6).

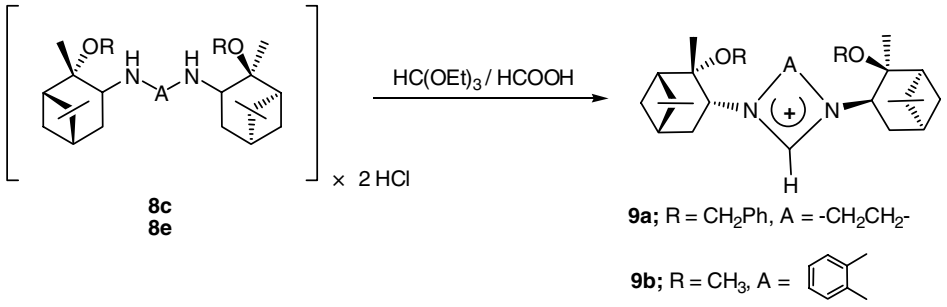
In the case of the more bulky dibenzyl derivative **8c**, the product was obtained in a satisfactory yield (37%) and the stable, crystalline product was fully characterized. The ^{1}H NMR signals of the terpene moieties δ: 1.11 (s, 6H, $^{9,9'}CH_3$); 1.34 (s, 6H, $^{8,8'}CH_3$); 1.51 (s, 6H, $^{10,10'}CH_3$); 1.82 (m, 4H); 1.99 (m, 2H); 2.18 (m, 4H); 2.27 (m, 4H); 3.45 (m, 2H, $^{aliph.}CH_2$); 3.90 (m, 2H, $^{aliph.}CH_2$); 4.03 (d, 2H, $J \approx 9.5$, $^{benzyl.}$CH); 4.28 (d, 2H, $J \approx 9.5$, $^{benzyl.}$CH); 4.66 (m, 2H, $^{3,3'}$CH); 7.12 (m, 10H, $^{arom.}$CH); 10.04 (s, 1H, $^{im.}$CH), distinct from those of the starting diaminodiether dihydrochloride **8b** confirms the C_2 symmetry, while the presence of the imidazolium system is confirmed by the signal of δ: 10.04 ppm. The analysis of the ^{13}C NMR spectrum (δ ^{13}C NMR: 23.78 ($^{9,9'}C$); 23.85 ($^{8,8'}C$); 28.01 ($^{7,7'}C$); 28.59 ($^{10,10'}C$); 30.68 ($^{4,4'}C$); 38.16 ($^{6,6'}C$); 39.86 ($^{5,4'}C$); 48.14 ($^{2aliph.}C$); 50.21 ($^{1,1'}C$); 57.84 ($^{3,3'}C$); 63.67 ($^{2benzyl.}C$); 80.11 ($^{2,2'}C$); 127.79 ($^{2arom.4}C$); 128.23 ($^{2arom.3,5}C$); 128.45 ($^{2arom.2,6}C$); 138.63 ($^{2arom.1}C$); 160.10 ($CH^{im.}$)) led to the same conclusions with regard to the structure of the product. The ultimate confirmation of the structure comes from X-ray crystallography.

Another benzimidazolium chloride was obtained in enamel form and all attempts to purify it have failed; however, the ^{1}H NMR spectrum (see Experimental) constitutes, in our opinion, a proof for the formation of this compound.

Table 2. Selected data of the reduced imines

	MS (M+H$^+$)	$[\alpha]_D^{20}$ ($CHCl_3$)	^{13}C NMR	^{1}H NMR[a]			
			3,3′ (δ)	3,3′ >CH–N	$^9CH_3$	$^{8,8'}CH_3$	$^{10,10'}CH_3$
8a	365	−46.5, $c = 2$	56.70	2.87	0.98 (0.88)	1.28 (1.33)	1.30 (1.60)
8b	393	−34.1, $c = 1$	59.05	3.40	1.00 (0.83)	1.26 (1.32)	1.28 (1.38)
8c	543	−19.8, $c = 0.2$	58.66	3.12	1.02 (0.85)	1.29 (1.31)	1.38 (1.48)
8d	413	−177.8, $c = 0.2$	53.95	3.80	1.08 (0.94)	1.30 (1.33)	1.36 (1.53)
8e	441	−93.5, $c = 1$	54.30	4.12[b]	1.09 (0.91)	1.14 (1.30)	1.31 (1.57)

[a] Values in parentheses are the chemical shifts of the corresponding imines.
[b] For dihydrochloride.



Scheme 6.

X-ray crystallography of a number of compounds obtained confirmed their structures.

Despite the fact that the molecules of **6b** contain, as well as other molecules described in this paper, two identical fragments, these fragments are not centrosymmetrical within the crystal. The asymmetric part of the **6b** unit cell contains three virtually identical molecules **a**, **b**, and **c**. Figure 5 presents molecule **a** as a model for atom numeration. According to this model, then labels of the right side of the molecule are marked with an additional character (′). The pinane backbones are located trans to the C11–C11′ bond (Table 3).

Molecules **a**, **b**, and **c** interlace, forming a supramolecule with more than 100 Å^3 of empty space inside (Fig. 6). The structure of the supramolecule is based on three eight-atom chains H–O1–C2–C3–N1–C11–C11′–N1′. The formation of the hydrogen bonds between these chains: O1a–H1a···N1′c, O1b–H1b···N1′a, and O1c–H1c···N1′b constitutes a 24-membered macrocycle (Fig. 7). Another three hydrogen bonds: O1′a–H1′a···N1b, O1′b–H1′b···N1c, and O1′c–H1′c···N1a provide for additional rigidity of the macrocycle by forming side buckles of N1′–C3′–C2′–O1′–H···N1 chains.

Modification of **6b** by protection of hydroxyl groups with –OCH_3 groups led to **7a**. The pinane groups in this molecule are located trans with respect to the C11–C11′ bond, as in **6b** (Fig. 8). However, conformations of linking chains (C11′–C11–N1–C3 and C11–C11′–N1′–C3′) vary from those in **6b** (Table 3). Due to lack of a proton donor in **7a**, H-bonds were not observed in the crystal.

Subsequently, the structure of the corresponding compounds with conformationally restricted central C11–C11′ bond was studied (Fig. 9). Opposite to **6b**, both pinanes in **6e** are cis with respect to C11–C11′ bond (Table 3). In the crystal, a dimer of two molecules connected by four hydrogen bonds of O–H···O type (Table 3) have been formed. There is no free space inside the structure.

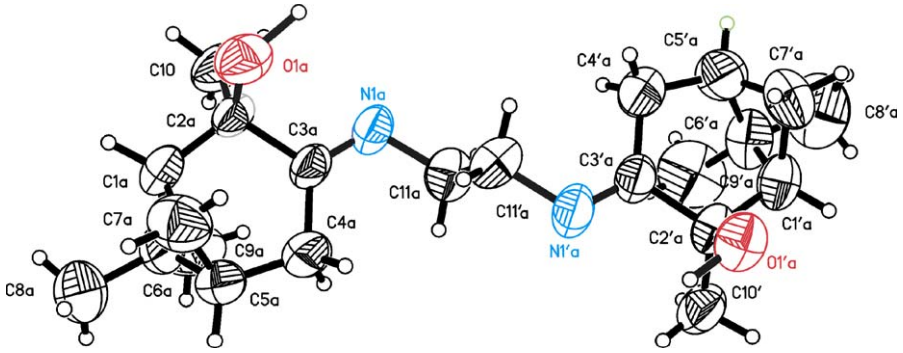


Figure 5. ORTEP drawing of one molecule from the structure of **6b**. Molecule **a** has been used as a model for atom numeration.

Table 3. Selected geometry details for crystallographically studied molecules

	Linking chain conformation					Conformation of the molecule	
	C11′–C11–N1–C3			C11–C11′–N1′–C3′			
(a) Molecule conformation with respect to C11–C11′ bond							
6a	+ac			−ac		trans	
6e	+sc			+sc		cis	
7a	−ap			+ap		trans	
9a	−ap			−ap		cis	
	N1–C3	N1–C11	C11–C11′	C11′–N1′	N1′–C3′	N1–C12	N1′–C12
(b) C3–N1–C11–C11′–N1′–C3′ spacer geometry (bond lengths in [Å])							
6a	1.276(5)	1.499(5)	1.503(7)	1.488(5)	1.231(5)		
	1.275(5)	1.490(6)	1.493(6)	1.470(6)	1.263(5)		
	1.266(6)	1.509(6)	1.482(6)	1.489(6)	1.248(6)		
6e	1.263(4)	1.425(3)	1.386(4)	1.418(3)	1.255(4)		
7a	1.256(3)	1.461(2)	1.495(3)	1.468(3)	1.272(3)		
9a	1.460(4)	1.465(7)[a]	1.529(8)[a]	1.447(7)[a]	1.453(4)	1.286(4)[a]	1.297(4)[a]
	X–H···Y	Sym. code		X–H	H···Y	X···Y	X–H···Y
(c) H-bonds geometry (bond lengths in [Å] and angles in [°])							
6a	O1a–H1a···N1′c			1.16	1.83	2.931(5)	157
	O1b–H1b···N1′a			1.04	2.07	3.030(5)	152
	O1c–H1c···N1′b			1.01	1.95	2.925(4)	162
	O1′a–H1′a···N1b			1.06	2.13	3.015(5)	139
	O1′b–H1′b···N1			1.11	1.98	3.029(5)	157
6e	O1–H1···O1′	$-x, y, 1-z$		0.96	1.84	2.767(2)	164
	O1′–H1′···O1			0.85	1.93	2.730(3)	157
7a	H-bonds were not observed						
9a	O1w–H1w···Cl	$x, y, 1+z$		0.98	2.19	3.139(7)	162
	O1w– H2w···Cl	$1-x+y, 1-x, 2/3+z$		1.10	2.19	3.132(8)	142

[a] Endocyclic bonds from five-membered ring adopted open envelope conformation with C11 in flap position (0.21 Å out of plane by N1, C12, C11, and N1′ atoms).

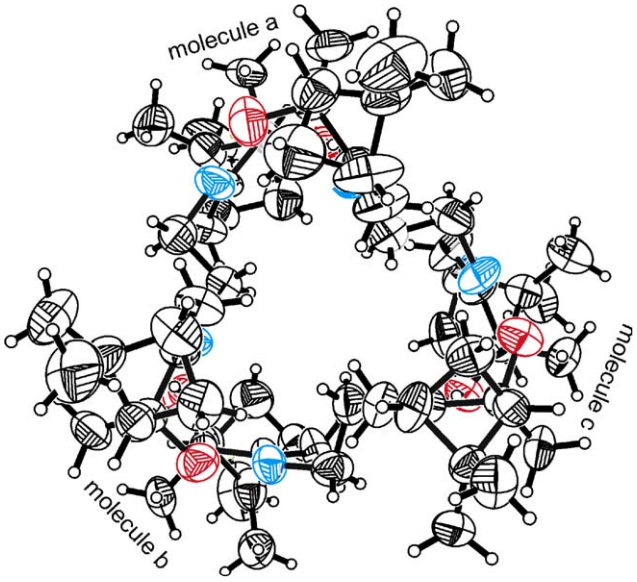


Figure 6. ORTEP drawing of the trimer of **6b**.

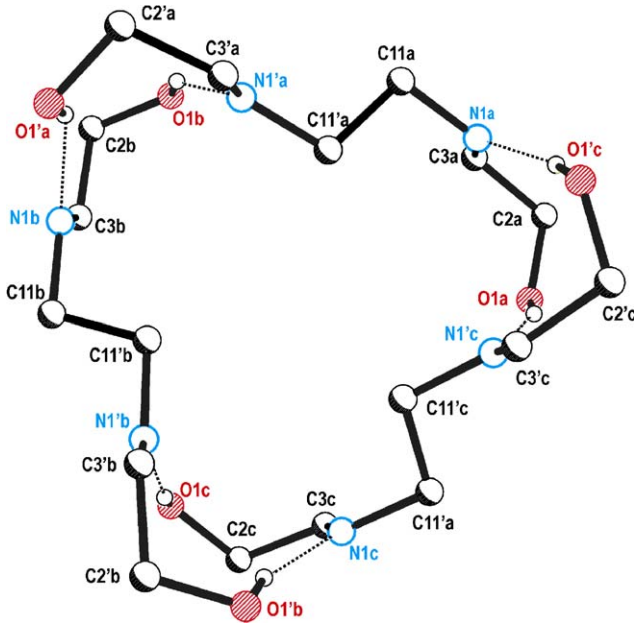


Figure 7. Details of macrocycle construction in the trimer of **6b**.

The structure of **9a** is significantly different from all other compounds. It is comprised of a positively charged molecule of **9a**, a chloride anion and two molecules of water (Figs. 10 and 11). Similar to **6e**, the C11–C11′ bond is immobilized as part of a ring (Figs. 12 and 13) while the pinene groups are located cis with respect to this bond. However, their placement is different in the case of **6e**. The positive charge of the molecule is not localized; it is 'spread' between the atoms of the five-membered ring. The ring is comprised of two nitrogen

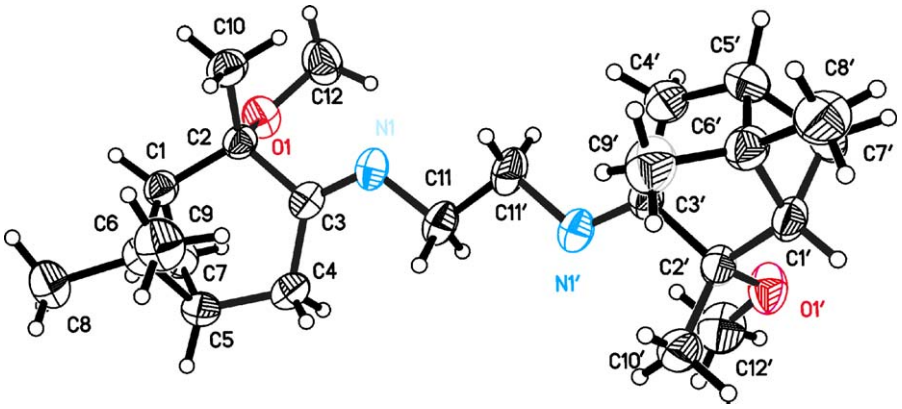


Figure 8. ORTEP drawing of **7a**.

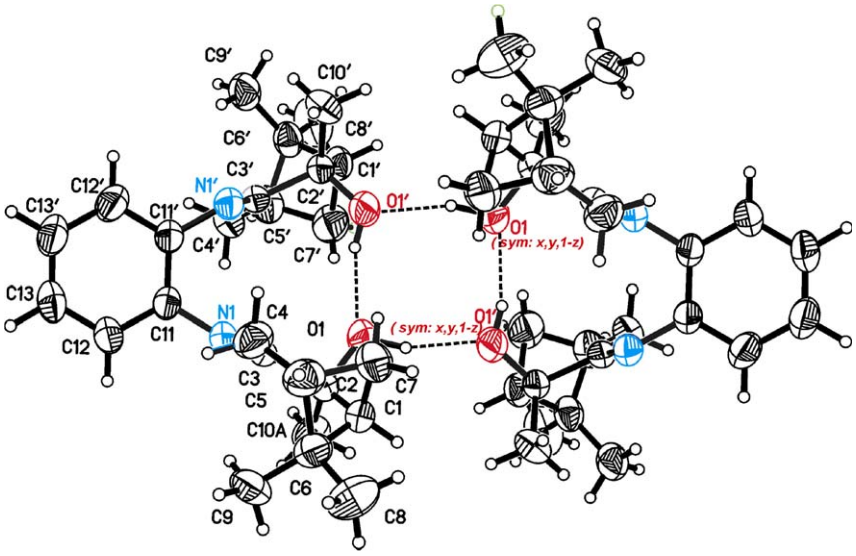


Figure 9. ORTEP drawing of the dimer from **6e**.

atoms (sp^2), two sp^3 carbon atoms, and one sp^2 carbon atom (Table 3) and attains an open envelope conformation with the C11 atom in a flap position.

No apparent contact with the anion or water molecules was observed. The shortest distance, Cl···H11D(C11), was 2.92 Å. At the same time, the Cl^- anion forms, together with one of the water molecules (O1w), a helical chain down the **c** direction of the crystal (Fig. 11). The other water molecule is labile (large ellipsoids of thermal vibrations, see Fig. 10); due to its lack of contact, for example, hydrogen bonds, it has a nature of adhesion water in the contact areas of **9a** molecules, repeated by a threefold rotation axis.

Diaminoethers **8** can be a handy starting material for the synthesis of yet another group of chiral ligands—phosphinediamides. The usefulness of these ligands in many asymmetric syntheses is extensively documented in the literature.[12] The products of the oxidation of phosphinediamides are also suitable ligands, successfully used, for example, in asymmetric reduction of prochiral ketones with borane. The phosphinamide catalysts exert a catalytic effect primarily through a Lewis base interaction of the phosphinamide oxygen atom with the borane reducing agent (a similar Lewis base effect was documented in phosphoramides by Denmark and Fu).[1a] The best results were obtained when catalysts with a proximal hydroxyl group were used; however, compounds of the type of **10**, presented below, also seem to be interesting in this aspect.

Treatment of diaminoether **8b** with dichlorophenylphosphine in the presence of triethylamine followed by in situ air oxidation of the initially formed phosphinediamide afforded the water-stable oxide **10** (Scheme 7).

Termination of the reaction at the stage of amide formation afforded the product of ca. 90% purity (estimated from ^1H and ^{31}P NMR spectra). Our attempts to purify further the product failed (due to decomposition and/or partial oxidation). Therefore, we decided to oxidize the product in situ and isolate the 1,3-di-3α-(2α-methoxypinane)-2-phenyl-[1,3,2]diazaphospholidine-2-oxide

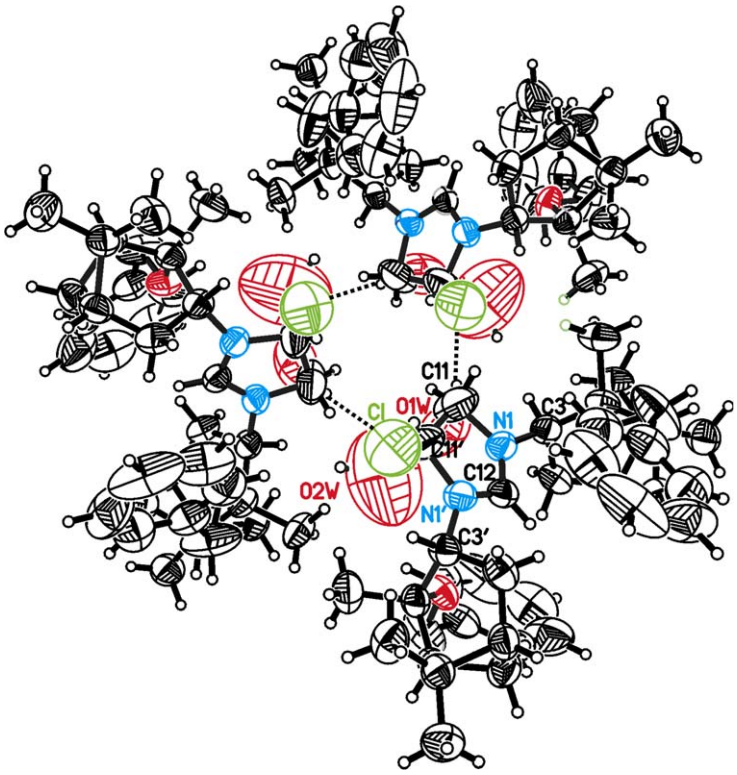


Figure 10. ORTEP drawing of the main motif in the crystal of **9a**.

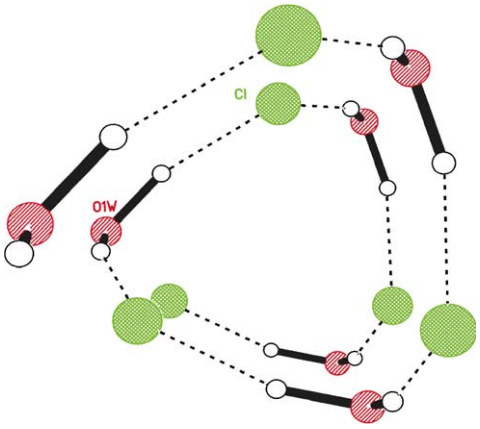


Figure 11. Helical H-bonds motif in the crystal of **9a**.

formed. The yield of the isolated product was only 63%, however, the process was not optimized and the neighboring fractions contained significant amounts of the target compound.

An analogous reaction of dibenzyl derivative **8c** required an increase of temperature; unfortunately, under such conditions the reaction was not under control and afforded an unidentifiable mixture of products.

3. Conclusion

The possibility of facile enantiomeric enrichment of 2α-hydroxypinan-3-one and its oxime, thus allowing us to obtain enantiomerically pure materials from inexpensive α-pinenes, makes it possible to use these materials for the synthesis of useful building blocks, such as *cis*-1-acetyl-3-cyanomethyl-2-2-dimethylcyclobutane or pinocarvone.

The formation of imines in the reactions of two molecules of ketol with aliphatic or aromatic amines led to a series of C_2-symmetric products, characterized by an adjustable distance between pinane fragments and the functional groups attached to them and serving as potential polydentate catalyst ligands.

Etherification of the hydroxyl groups and stereoselective reduction expand the ligand range by including the respective diaminodiols and diaminodiethers. In certain cases, whenever it is sterically possible, the diaminodiethers form stable phosphinediamides and azonium salts by 'coupling' the amine moieties into rings. The compounds presented illustrate only a part of potential uses of 2α-hydroxypinan-3-one.

4. Experimental

4.1. General

Boiling points are uncorrected. Melting points were determined with a Büchi apparatus in open capillaries and are uncorrected. Elemental analyses were performed at CBMiM PAN (Łódź). Optical rotation was measured with a Horiba SEPA-200 apparatus in a 10 cm cell. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 250 or 300,

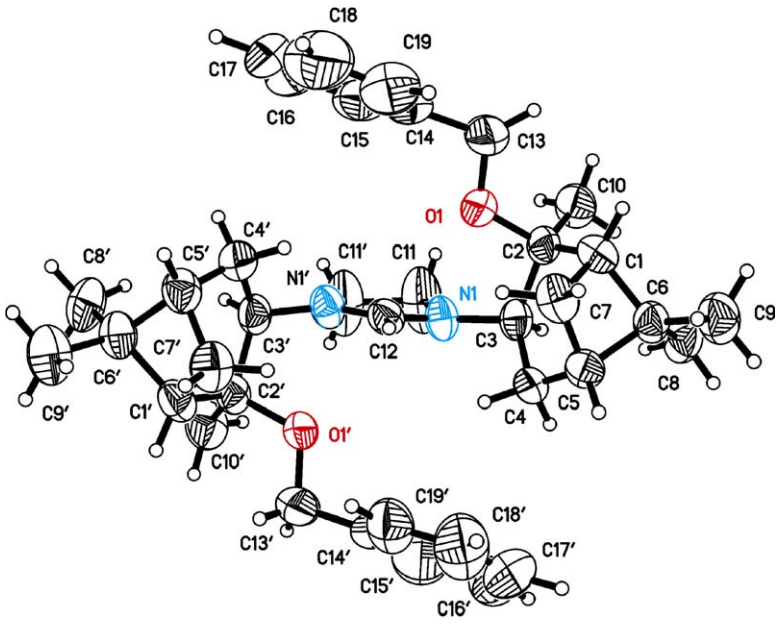


Figure 12. ORTEP drawing of the **9a** molecule.

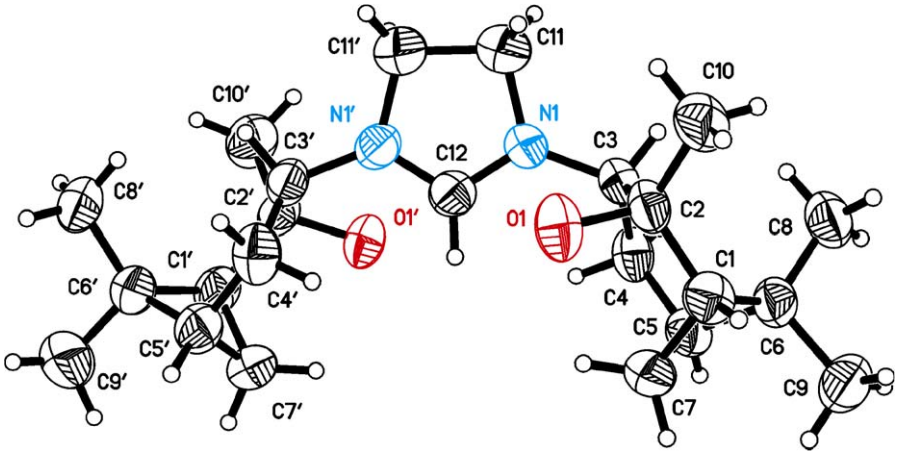
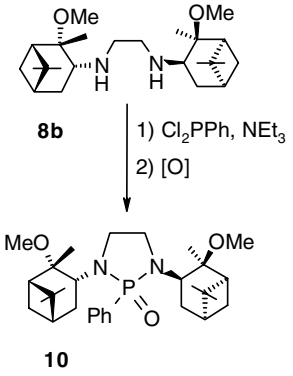


Figure 13. Molecule **9a** in the plane of a five-membered ring. Benzyl substituents were omitted for clearity.



Scheme 7.

62.6 MHz, respectively, on Bruker Avance DPX-250 or Varian-300 apparatus in $CDCl_3$ (TMS). The values of the coupling constants are reported in hertz. Mass spectra were determined with Fab MI 1201 E (P.O. Electron, Ukraine) (FAB) spectrometer. GC was performed with Shimadzu apparatus, using 25 m CP Chirasil Dex CB DF = 0.25 column. TLC was performed on silica gel $60F_{254}$ aluminum plates (0.2 mm). PLC was performed on silica gel $60F_{254}$ (2 mm) plates (Merck). Regular and flash column chromatography were carried out using Merck silica gel 60 (70–230 and 230–400 mesh, respectively). Diethyl ether and tetrahydrofurane were distilled from sodium and benzophenone prior to use. Dichloromethane was dried over calcium hydride and distilled before use. Other solvents were dried and purified using standard procedures.

Ketol **1** (2α-hydroxypinan-3-one) and its oxime **2** were obtained from (+)-α-pinene of 65% ee and enantiomerically enriched according to previously described proce-

dures.[5] All reactions were carried out using the ketol of $[\alpha]_D^{20} = -39.5$ (*c* 0.5, $CHCl_3$), ee >99% and the oxime of $[\alpha]_D^{20} = +19.1$ (*c* 3, $CHCl_3$), ee >99%. The remaining reagents were purchased from Sigma–Aldrich.

4.2. (+)-*cis*-Pinonic acid nitrile 3 (1*R*,3*R*)-(3-acetyl-2,2-dimethylcyclobutyl)acetonitrile

A three-necked 500-ml flask, moisture-proof, and equipped with a magnetic stirring bar, was charged with 36.0 g (0.196 mol) of 2α-hydroxypinan-3-one oxime **2** and 200 ml of pyridine. The mixture was cooled down to 0 °C and 39.3 g of tosyl chloride was added with vigorous stirring keeping temperature below 15 °C. The solution was left overnight and then poured into a mixture of 200 g of ice, 200 ml of water, and 200 ml of hydrochloric acid. The mixture was salted out and extracted with chloroform (3 × 100 ml). The combined extracts were washed with 3% sodium bicarbonate and water until neutral reaction, then dried over sodium sulfate. The solvent was removed and the residue distilled; bp 115–118 °C/2 mmHg. Light yellow oil (31.3 g), $n_D^{20} = 1.4630$; $R_f = 0.33$ (hexane–ethyl acetate 4:1), $[\alpha]_D^{20} = +124.7$ (*c* 2, $CHCl_3$), was obtained in 96.5% yield. IR_{film}, cm^{-1}; 2248 (CN); 1704 (C=O). ^1H NMR δ: 0.95 (s, 3H, $^{trans}CH_3$); 1.41 (s, 3H, $^{cis}CH_3$); 162–2.04 (m, 2H); 2.07 (s, 3H, $^{10}CH_3$); 2.27 (d, 2H); 2.29–2.35 (m, 1H); 2.92 (dd, 1H, $J = 9.25$, $J = 1$); ^{13}C NMR: 16.62; 17.20; 21.83; 29.75; 29.97; 37.80; 42.67; 53.44; 118.38; 206.38.

Part of the obtained ketonitrile **3** was crystallized from hexane after solidification of the oil; mp 44–46 °C, $[\alpha]_D^{20} = +124.9$ (*c* 2, $CHCl_3$). Anal. Calcd for $C_{10}H_{15}NO$: C = 72.60, H = 9.15, N = 8.47. Found: C = 72.41, H = 9.11, N = 8.38.

4.3. Diphenylphosphinic acid (3-oxopinan-2-yl) ester 4

A 250-ml three-necked flask equipped with a magnetic stirring bar, thermometer, septum, and argon supply was charged with a solution of 3.01 g (0.018 mol) of 2α-hydroxypinan-3-one **1** in 100 ml THF. The mixture was cooled down to 0 °C and 11.5 ml (0.018 mol) of BuLi solution added upon vigorous stirring. After 2 h, 3.4 ml (0.018 mol) of diphenylchlorophosphine was added in portions while maintaining the temperature at 0–5 °C and the mixture was stirred at this temperature for 10 h, after which air was purged through the reaction mixture for 4 h. The solvent was stripped, 150 ml of hexane was added, and the precipitating diphenylphosphoric acid was filtered out. The crystals of diphenylphosphoric acid were washed with hexane (2 × 25 ml). The combined hexane fractions were concentrated in vacuo, the residue dissolved in 100 ml of chloroform and washed with brine (3 × 50 ml). The solution was dried over sodium sulfate and the solvent was removed in vacuo, yielding 6.2 g of light yellow oil of >90% purity, as estimated from the ^1H NMR spectrum. Flash chromatography (hexane–ethyl acetate) yielded 5.15 g (78%) of oil with $[\alpha]_D^{20} = -0.9$ (*c* 1, $CHCl_3$); MS: M+1 = 369; ^1H NMR δ: 0.85 (s, 3H, $^9CH_3$); 1.35 (s, 3H, $^8CH_3$); 1.58 (s, 3H, $^{10}CH_3$); 1.75 (d, 1H, $J \approx 10$, $^{7\beta}CH$); 2.07–2.12 (m, 1H); 2.41–2.46 (m, 1H); 2.66–2.70 (m, 1H); 2.77–2.82 (m, 1H); 7.38–7.41 (m, $4H^{arom.}$); 7.63–7.75 (m, $4H^{arom.}$); 7.79–7.92 (m, $2H^{arom.}$); ^{13}C NMR δ: 22.44 (^9C); 23.48 (^8C); 26.87 (^{10}C); 37.70 (^5C); 38.46 (^7C); 38.73 (^6C); 42.86 (^4C); 50.78 (^1C); 87.79 (^2C); 205.90 (^3C); [128.12; 128.21; 128.33; 128.42; 130.83; 130.99; 131.34; 131.50; 131.67; 131.78 $^{arom.}C$]. ^{31}P, $\delta = 29.15$.

4.4. (−)-Pinocarvone 5 (1*R*)-6,6-dimethyl-2-methylene bicyclo[3.1.1]hept 3-one

(a) A 500-ml round-bottom flask equipped with an efficient reflux condenser was charged with a mixture of 5.08 g (0.014 mol) of 2α-diphenylphosphorylpinan-3-one and 3 ml of *n*-butylamine in 200 ml benzene. The mixture was refluxed for 6 h. After this time, the mixture was concentrated to ca. 30, 150 ml of methylene chloride then added and the solution washed with 2% hydrochloric acid (2 × 50 ml) and water (2 × 50 ml). The organic layer was dried over sodium sulfate, the solvent was removed in vacuo, and the residue (3.4 g) was distilled, affording 1.25 g of pinocarvone (GC 98%). Bp 89–90 °C/0.2 mmHg, $[\alpha]_D^{20} = -60.0$ (*c* 2, $CHCl_3$); MS: M+1 = 151; IR_{film}: 1706, 1625; ^1H NMR δ: 0.82 (s, 3H, $^8CH_3$); 1.30 (d, 1H, $J_{7\alpha,7\beta} \approx 10$, $^{7\beta}CH$); 1.37 (s, 3H $^8CH_3$); 2.21–2.24 (m, 1H); 2.48–2.51 (m, 1H); 2.60–2.71 (m, 3H); 5.02 (s, 1H, ^{10}CH); 5.98 (s, 1H, ^{10}CH), was consistent with the literature data.[13]

(b) Crude 2α-diphenylphosphorylpinan-3-one (71 g), obtained from 33.6 g (0.20 mol) of ketol **1**, was mixed with 35 ml of *n*-butylamine in 600 ml of benzene and refluxed for 10 h. A workup procedure analogous to the above afforded 19.7 g (60%) of pinocarvone (GC 97%), $[\alpha]_D^{20} = -64.1$ (neat). The following compounds were isolated (PLC, hexane–ethyl acetate 4:5) from the tail fraction (0.65 g): pinocarvone (0.080 g), the starting ketol (0.130 g) and 0.014 g of a compound of $[\alpha]_D^{20} = -12.4$ (*c* 0.7, $CHCl_3$); MS: M+1 = 169. ^1H NMR. δ: 0.91 (s, 3H, $^8CH_3$); 1.39 (s, 3H, $^9CH_3$); 1.77 (s, 3H, $^{10}CH_3$); 1.89 (d, 1H, $J_{7\alpha,7\beta} \approx 10.5$, $^{7\beta}CH$); 2.37–242 (m, 1H); 2.57–2.61 (m, 2H); 2.69–2.71 (m, 1H); 2.74–2.75 (m, 2H). On the basis of these data the identity of the compound 2β-hydroxypinan-3-one was determined.

4.5. General procedure for *N*,*N*′-[(2α-hydroxy)pinane-3-ene]diamines and modifications (optimizations) for 6b, 6d, and 6e

A 500-ml round-bottom flask equipped with a magnetic stirring bar and a Dean–Stark apparatus was charged with 0.02 mol of hydrazine, aliphatic diamine, or aromatic amine, 7.40 g (0.044 mol, 10% excess) of ketol **1**, 1 g of 4 Å molecular sieves, and 3–5 drops of $BF_3{\cdot}Et_2O$ in 250 ml of toluene (or, in case of **6a** and **6b**, benzene). After the air had been purged off the system by means of argon gas, the reaction mixture was refluxed until collection of water stopped and additionally for 2 h, after another 1–3 drops of $BF_3{\cdot}Et_2O$ were added. The reaction mixture was filtered through a 1-cm Celite pad, the solvent stripped, and the residue crystallized from hexane. Yields and selected physical properties are presented in Table 1.

Optimization of the synthesis of **6b** included using equimolar amounts of the reagents, replacing the molecular sieves with silica gel and extending the reaction time.

In case of the synthesis of **6d** and **6e**, a 20% excess of ketol **1** was applied. After the reaction, the excess ketol **1** was removed from the reaction mixture by flash chromatography before crystallization of the products.

Selected characteristics of dihydroxyimines obtained were as follows.

4.5.1. *N,N′*-[(2α-Hydroxy)pinane-3-ene]diazane 6a. Yield 84%; colorless prisms, mp 146–147 °C; $[\alpha]_D^{20} = -24.5$ (*c* 1, $CHCl_3$); MS, M+1 = 333; IR (KBr) 1648 cm^{-1} (>N–). ^1H NMR δ: 0.88 (s, 6H, $^{9,9'}CH_3$); 1.33 (s, 6H, $^{8,8'}CH_3$); 1.58 (d, 2H, $J_{7\alpha,7\beta} = 10.3$, $^{7\beta,7'\beta}CH$); 1.60 (s, 6H, $^{10,10'}CH_3$); 1.95–2.01 (m, 2H, $^{5,5'}CH$); 2.06 (dd, 2H, $J_{1,5} \approx 5.71$, $J_{1,7\alpha} \approx 5.76$, $^{1,1'}CH$), 2.29–2.36 (m, 2H, $^{7\alpha,7'\alpha}CH$); 2.37–2.43 (m, 2H, $^{4\alpha,4'\alpha}CH$); 2.53 (dd, 2H, $J_{4\beta,4'\alpha'} \approx 18.5$, $J_{4\beta,5} \approx 2.74$, $^{4\beta,4'\beta}CH$); ^{13}C NMR δ: 22.5 ($^{9,9'}C$), 27.2 ($^{8,8'}C$); 28.0 ($^{10,10'}C$, $^{7,7'}C$); 32.6 ($^{4,4'}C$); 38.0 ($^{5,5'}C$); 38.7 ($^{6,6'}C$); 50.8 ($^{1,1'}C$); 75.5 ($^{2,2'}C$); 164.2 ($^{3,3'}C$).

4.5.2. *N,N′*-[(2α-Hydroxy)pinane-3-ene]ethane 1,2-diamine (6b). Yield 72 (90 after optimization)%; colorless prisms, mp 126–127 °C; $[\alpha]_D^{20} = +7.6$ (*c* 1, $CHCl_3$); MS, M+1 = 361; IR (KBr) 1648 cm^{-1} (>C=N–); ^1H NMR δ: 0.85 (s, 6H, $^{9,9'}CH_3$); 1.32 (s, 6H, $^{8,8'}CH_3$); 1.45 (s, 6H, $^{10,10'}CH_3$); 1.56 (d, 2H, $J_{7\alpha,7\beta} = 10.6$, $^{7\beta,7'\beta}CH$); 2.00–2.08 (m, 4H, $^{1,1'}CH$ and $^{5,5'}CH$), 2.28–2.37 (m, 2H, $^{7\alpha,7'\alpha}CH$); 3.57–3.65 (m, 4H, –CH_2–CH_2–); ^{13}C NMR δ: 22.45 ($^{9,9'}C$); 26.94 ($^{8,8}C$); 27.71 ($^{7,7}C$); 27.93 ($^{10,10}C$); 33.50 ($^{4,4}C$); 37.91 ($^{5,5'}C$ and $^{6,6'}C$); 50.31 ($^{1,1'}C$); 50.62 ($^{-CH_2-CH_2-}C$); 75.72 ($^{2,2'}C$), 176.15 ($^{3,3'}C$).

4.5.3. *N,N′*-[(2α-Hydroxy)pinane-3-ene]butane 1,4-diamine 6c. Yield 72%; colorless prisms, mp 87–90 °C; $[\alpha]_D^{20} = +5.9$ (*c* 1, $CHCl_3$); MS, M+1 = 389; IR (KBr) 1648 cm^{-1} (>C=N–); ^1H NMR δ: 0.85 (s, 6H, $^{9,9}CH_3$); 1.32 (s, 6H, $^{8,8}CH_3$); 1.47 (s, 6H, $^{10,10}CH_3$); 1.54 (d, 2H, $J_{7\beta,7\alpha} = 10.5$, $^{7\beta,7\beta}CH$); 1.67–1.80 (m, 4H, –CH_2–CH_2–); 1.00–2.09 (m, 4H, $^{1,1}CH$ and $^{5,5}CH$); 2.28–2.38 (m, 2H, $^{7\alpha,7'\alpha}CH$); 2.52 (m, 4H, $^{4,4'\alpha}CH$ and $^{4,4'\beta}CH$); 3.33 (m, 4H, =N–CH_2–); ^{13}C NMR δ: 22.86 ($^{9,9}C$); 27.25 ($^{8,8}C$); 28.0 ($^{\text{aliph.2 and 3}}C$); 28.15 ($^{7,7'}C$); 28.36 ($^{10,10}C$); 33.50 ($^{4,4'}C$); 38.43 ($^{6,6'}C$); 39.23 ($^{5,5'}C$); 50.06 ($^{1,1'}C$); 50.55 ($^{\text{aliph.1 and 4}}C$); 76.21 ($^{2,2'}C$); 176.93 ($^{3,3'}C$).

4.5.4. *N,N′*-[(2α-Hydroxy)pinane-3-ene]α,α′-*p*-xylene diamine 6d. Yield 75 (87)%; colorless prisms, mp 148–151 °C; $[\alpha]_D^{20} = +16.0$ (*c* 1, $CHCl_3$); MS, M+1 = 437; IR (KBr) 1650 cm^{-1} (>C=N–); ^1H NMR δ: 0.87 (s, 6H, $^{9,9'}CH_3$); 1.34 (s, 6H, $^{8,8'}CH_3$); 1.53 (s, 6H, $^{10,10'}CH_3$); 1.58 (d, 2H, $J_{7\beta,7\alpha} = 10.5$, $^{7\beta,7'\beta}CH$); 2.04–2.13 (m, 4H, $^{1.1'\text{ and }5,5'}CH$); 2.34–2.39 (M, 2H, $^{7\alpha,7'\alpha}CH$); 2.61 (m, 4H, $^{4\alpha,4'\alpha\text{ and }4\beta,4'\beta}CH$); 4.53 (m, 4H, $^{\text{benzyl.}}CH_2$); 7.33 (s, 4H, $^{\text{arom.}}CH$); ^{13}C NMR δ: 22.60 ($^{9,9'}C$); 27.10 ($^{8,8'}C$); 27.89 ($^{7,7'}C$); 28.09 ($^{10,10'}C$); 33.38 ($^{4,4'}C$); 38.06 ($^{5,5'}C$); 38.15 ($^{6,6'}C$); 50.16 ($^{1,1'}C$); 53.55 ($^{\text{benzyl.}}C$); 76.16 ($^{2,2'}C$); 127.27 ($^{2,3,4\text{arom.}}C$); 137.95 ($^{1,4\text{arom.}}C$); 176.33 ($^{3,3'}C$).

4.5.5. *N,N′*-[(2α-Hydroxy)pinane-3-ene]benzene-1,2-diamine 6e. Yield 56 (80)%; colorless prisms, mp 173–174 °C; $[\alpha]_D^{20} = -140.0$ (*c* 1, $CHCl_3$); MS, M+1 = 409; IR (KBr) 1648 cm^{-1} (>C=N–); ^1H NMR δ: 0.90 (s, 6H, $^{9,9'}CH_3$); 1.30 (s, 6H, $^{8,8'}CH_3$); 1.57 (s, 6H, $^{10,10'}CH_3$); 1.60 (d, 2H, $J_{7\beta,7\alpha} \approx 10.7$, $^{7\beta,7'\beta}CH$); 1.91 (hpt, 2H, $J_{5,1} \approx 5.75$, $J_{5,4\alpha} = J_{5,4\beta} \approx 2.75$, $J_{5,7\alpha} \approx 6$, $^{5,5'}CH$); 2.06 (dd, 2H, $J_{1,5} \approx 5.75$, $J_{1,7\alpha} \approx 6$, $^{1,1'}CH$); 2.26–2.31 (m, 2H, $^{7\alpha,7'\alpha}CH$); 2.32–2.44 (m, 2H, $^{4\alpha,4'\alpha}CH$); 2.58 (dd, 2H, $J_{4\beta,4\alpha} = 18.5$, $J_{4\beta,5} \approx 2.75$, $^{4\beta,4'\beta}CH$); 6.71 (dd, 2H, $J_{3,4\text{arom.}} \approx 6$, $J_{4,5\text{arom.}} \approx 4$, $J_{5,6\ \text{arom.}} \approx 6$, $^{4,5\text{arom.}}CH$); 7.02 (dd, 2H $J_{3,4\text{arom.}} \approx 6$, $J_{3,5\text{arom.}} \approx 3$, $^{3,6\text{arom.}}CH$); ^{13}C NMR δ: 22.7 ($^{9,9'}C$); 27.11 ($^{8,8'}C$); 27.90 ($^{7,7'}C$); 35.13 ($^{4,4'}C$); 38.34 ($^{5,5'}C$); 38.46 ($^{6,6'}C$); 51.30 ($^{1,1'}C$); 76.22 ($^{2,2'}C$); 118.74 ($^{4,5\text{arom.}}C$), 123.81 ($^{3,6\text{arom.}}C$); 139.28 ($^{1,2\text{arom.}}C$); 177.18 ($^{3,3'}C$).

4.5.6. *N,N′*-[(2α-Hydroxy)pinane-3-ene]benzene-1,3-diamine 6f. Yield 46%; colorless prisms, mp 147–148 °C; $[\alpha]_D^{20} = +14.8$ (*c* 0.5, $CHCl_3$); MS, M+1 = 409; IR (KBr) 1654 cm^{-1} (>N–); ^1H NMR δ: 0.94 (s, 6H, $^{9,9'}CH_3$); 1.33 (s, 6H, $^{8,8'}CH_3$); 1.61 (s, 6H, $^{10,10'}CH_3$); 1.62 (d, 2H, $J_{7\beta,7\alpha} \approx 10.5$, $^{7\beta,7'\beta}CH$); 1.92–1.96 (m, 2H, $^{5,5'}CH$); 2.13 (dd, 2H, $J_{1,5} \approx 5.75$, $J_{1,7\alpha} \approx 6$, $^{1,1'}CH$); 2.34–2.39 (m, 2H, $^{7\alpha,7'\alpha}CH$); 2.45–2.47 (m, 4H. $^{4\alpha,4'\alpha,4\beta,4'\beta}CH$); 6.11 (t, 1H, $J_{4,5\text{arom.}} \approx 2 = J_{5,6\text{arom.}}$, $^{5\text{arom.}}CH$), 6.43 (dd, 2H, $J_{4,5\text{arom.}} \approx 2$, $J_{4,2\text{arom.}} \approx 7.75$, $J_{6,2\text{arom.}} \approx 7.75$ $^{4,6\text{arom.}}CH$); 7.26 (t, 1H, $J_{2,4\text{ and }2,6\text{arom.}} \approx 7.75$ $^{2\text{arom.}}CH$); ^{13}C NMR δ: 23.02 ($^{9,9'}C$); 27.29 ($^{8,8'}C$); 28.13 ($^{10,10'}C$); 28.19 ($^{7,7'}C$); 34.65 ($^{4,4'}C$); 38.44 ($^{5,5'}C$); 38.60 ($^{6,6'}C$); 50.54 ($^{1,1'}C$); 76.29 ($^{2,2'}C$); 108.02 ($^{5\text{arom.}}C$); 113.32 ($^{4,6\text{arom.}}C$); 129.93 ($^{2\text{arom.}}C$); 151.98 ($^{1,3\text{arom.}}C$); 178.41 ($^{3,3'}C$).

4.5.7. *N,N*-[(2α-Hydroxy)pinane-3-ene]benzene-1,4-diamine 6g. Yield 41%; light yellow prisms, mp 107–108 °C; $[\alpha]_D^{20} = +99.1$ (*c* 0.5, $CHCl_3$); MS, M+1 = 409; IR (KBr) 1656 cm^{-1} (>C=N–); ^1H NMR δ: 0.95 (s, 6H, $^{9,9'}CH_3$); 1.34 (s, 6H, $^{8,8'}CH_3$); 1.61 (s, 6H, $^{10,10'}CH_3$); 1.61 (d, 2H, $J_{7\beta,7\alpha} \approx 10.5$, $^{7\beta,7'\beta}CH$); 1.94 (hp, 2H, $J_{5,1} \approx 5.75$, $J_{5,4\alpha} \approx J_{5,4\beta} \approx 2.75$, $J_{5,7\alpha} \approx 6$, $^{5,5'}CH$); 2.06 (dd, 2H, $J_{1,5} \approx 5.75$, $J_{1,7\alpha} \approx 6$, $^{1,1'}CH$); 2.34–2.38 (m, 2H, $^{7\alpha,7'\alpha}CH$); 2.46–2.65 (m, 4H, $^{4\alpha,4'\alpha,4\beta,4'\beta}CH_2$); 6.73 (s, 4H, $^{\text{arom.}}CH$); ^{13}C NMR δ: 22.62 ($^{9,9'}C$); 27.00 ($^{8,8'}C$); 28.68 ($^{7,7',10,10'}C$); 34.36 ($^{4,4'}C$); 38.20 ($^{5,5',6,6'}C$); 50.33 ($^{1,1'}C$); 75.91 ($^{2,2'}C$); 118.91 ($^{2,3,5,6\text{arom.}}C$); 146.13 ($^{1,4'\text{arom.}}C$); 177.99 ($^{3,3'}C$).

4.6. *N,N′*-[(2α-Methoxy)pinane-3-ene]ethane 1,2-diamine 7a

A solution of 5.00 g (0.014 mol) of dihydroxydiimine **6b** in 75 ml of dry benzene was added under argon to a vigorously stirred suspension of 0.912 g (0.036 mol, 30% excess) of 95%, oil-free sodium hydride in 75 ml of dry benzene. The mixture was refluxed for 2 h and cooled down. A solution of 7.98 g (0.056 mol, 100% excess) of methyl iodide was added and the mixture refluxed again for 20 h. The reaction mixture was cooled down to room temperature, the undissolved salts were filtered out, and the solvent stripped, affording 5.32 g of reddish solid.

Crystallization from hexane yielded 4.85 g (90%) of the product. Mp 63–65 °C; $[\alpha]_D^{20} = +13.6$ (*c* 1, $CHCl_3$); ^1H NMR δ: 0.83 (s, 6H, $^{9,9'}CH_3$); 1.32 (s, 6H, $^{8,8'}CH_3$); 1.38 (s, 6H, $^{10,10'}CH_3$); 1.62 (d, 2H, $J_{7\alpha,7\beta} \approx 9.9$, $^{7,7'\beta}CH$); 2.02 (m, 2H, $^{5,5'}CH$); 2.14–2.17 (m, 2H, $^{1,1}CH$); 2.25–2.27 (m, 2H, $^{7,7'\alpha}CH$); 2.46–2.52 (m, 2H, $^{4,4'\alpha}CH$); 2.64–2.70 (m, 2H, $^{4,4'\beta}CH$); 3.18 (s, 6H, $2OCH_3$); 3.59–3.77 (m, 4H, $^{1,2aliph.}CH$); ^{13}C NMR δ: 21.30 ($^{9,9'}C$); 22.57 ($^{8,8'}C$); 27.35 ($^{7,7'}C$); 27.55 ($^{10,10'}C$); 33.96 ($^{4,4'}C$); 38.38 ($^{5,5' \text{ and } 6,6'}C$); 49.43 ($2OCH_3$); 49.48 ($^{1,1'}C$); 52.25 ($^{1,2aliph.}C$); 80.06 ($^{2,2'}C$); 171.64 ($^{3,3'}C$).

4.7. *N,N′*-[(2α-Benzoxy)pinane-3-ene]ethane 1,2-diamine 7b

A solution of 3.04 g (0.0083 mol) of dihydroxydiimine **6b** in 50 ml of dry benzene was added under argon to a vigorously stirred suspension of 0.51 g (0.02 mol, 20% excess) of 95%, oil-free sodium hydride in 50 ml of dry benzene. The mixture was refluxed for 1 h and cooled down. 3.21 g (0.018 mol, 10% excess) of benzyl bromide was added and the mixture refluxed again for 7 h. The reaction mixture was cooled down to room temperature, the undissolved salts filtered out, and the solvent stripped, affording 4.50 g of a light yellow oil. Solidification and subsequent crystallization from hexane yielded 3.28 g (73%) of the product in the form of colorless crystals. Mp 48–49 °C, $[\alpha]_D^{20} = +101.4$ (*c* 0.5, $CHCl_3$). ^1H NMR δ: 1.02 (s, 6H, $^{9,9'}CH_3$); 1.29 (s, 6H, $^{8,8'}CH_3$); 1.38 (s, 6H, $^{10,10'}CH_3$); 1.40 (d, 2H, $J \approx 10$, $^{7,7'\beta}CH$); 1.46–1.53 (m, 2H, $^{4,4'\beta}CH$); 1.91–1.96 (m, 2H, $^{5,5'}CH$); 2.07–2.13 (m, 2H, $^{1,1'}CH$); 2.19–2.21 (m, 2H, $^{4,4'\alpha}CH$); 2.31–2.38 (m, 2H, $^{7,7'\alpha}CH$); 2.74–2.95 (m, 4H, $^{1,2aliph.}CH_2$); 3.10–3.15 (m, 2H, $^{3,3'}CH$); 4.18 (d, 2H, $J_{\text{benzyl.-benzyl.}} \approx 11.4$, $^{\text{benzyl.}}CH$); 4.42 (d, 2H, $J_{\text{benzyl.-benzyl.}} \approx 11.4$, $^{\text{benzyl.}}CH$); 7.17–7.32 (m, 10H, $^{\text{arom.}}CH$); ^{13}C NMR δ: 23.66 ($^{9,9}C$); 25.04 ($^{8,8'}C$); 28.27 ($^{7,7'}C$); 28.78 ($^{10,10'}C$); 37.46 ($^{4,4'}C$); 38.12 ($^{6,6'}C$); 40.47 ($^{5,5'}C$); 49.10 ($^{\text{aliph.}}2C$); 51.71 ($^{1,1'}C$); 58.66 ($^{3,3'}C$); 62.86 ($^{\text{benzyl.}}2C$); 78.41 ($^{2,2'}C$); [126.87; 127.16; 128.13; 140.03 ($^{\text{arom.}}C$)].

4.8. *N,N′*-[(2α-Methoxy)pinane-3-ene]benzene 1,2-diamine (7c)

A solution of 2.01 g (0.0049 mol) of dihydroxydiimine **6e** in 30 ml of dry benzene was added under argon to a vigorously stirred suspension of 0.31 g (0.012 mol, 25% excess) of 95%, oil-free lithium hydride in 30 ml of dry benzene. The mixture was refluxed for 3 h and cooled down. A solution of 2.56 g (0.018 mol, 80% excess) of methyl iodide was added and the mixture was refluxed again for 20 h. The reaction mixture was cooled down to room temperature, the undissolved salts were filtered out, and the solvent stripped, affording 2.2 g of a light brown oil. Flash chromatography afforded 1.63 g (76%) of the oily product. $[\alpha]_D^{20} = -57.4$ (*c* 1, $CHCl_3$); MS, M+1 = 437; ^1H NMR δ: 0.96 (s, 6H, $^{9,9'}CH_3$); 1.30 (s, 6H, $^{8,8'}CH_3$); 1.44 (s, 6H, $^{10,10'}CH_3$); 1.67 (d, 2H, $J_{7\alpha,7\beta} \approx 10.2$, $^{7,7'\beta}CH$); 2.36–2.42 (m, 2H, $^{4,4'\alpha}CH$); 2.55–2.60 (m, 2H, $^{4,4'\beta}CH$); 3.29 (s, 6H, $2OCH_3$); 6.95–721 ($4H^{\text{arom.}}$).

4.9. *N,N′*-[3α-(2α-Hydroxypinane)]ethane-1,2-diamine 8a

A solution of 3.60 g (0.01 mol) of dihydroxydiimine **6b** in 40 ml of dry diethyl ether was added dropwise under argon to a vigorously stirred suspension of 2.0 g of 98% lithium aluminum hydride in 200 ml of dry diethyl ether. The mixture was refluxed for 20 h, cooled down to room temperature, and quenched by the dropwise addition of 100 ml of water. The organic layer was separated and the aqueous layer washed with diethyl ether. The combined organic extracts were dried over magnesium sulfate. Removal of the solvent afforded 3.95 g of a light brown oil, which was submitted to chromatographic purification ($R_f = 0.21$; hexane–ethyl acetate 3:2) to yield 3.25 g (90%) of the product as a colorless enamel. The interfraction product residues were not recovered. After crystallization from hexane–prisms: Mp 108–109 °C; $[\alpha]_D^{20} = -46.5$ (*c* 1, $CHCl_3$); MS, M+1 = 365; ^1H NMR δ: 0.97 (s, 6H, $^{9,9}CH_3$); 1.25 (2s, 12H, $^{9,9' \text{ and } 10,10}CH_3$); 1.25 (d, 2H, $J_{7\alpha,7\beta} \approx 15.5$, $^{7,7'\beta}CH$); 1.34 m, 2H, $^{4,4'\beta}CH$); 1.85 (m, 2H, $^{5,5'}CH$); 1.98 (dd, $J_{1,7\alpha} \approx J_{1,5} \approx 5.7$, $^{1,1'}CH$); 2.14 (m, 2H, $^{7,7'\alpha}CH$); 2.55 (m, 2H, $^{4,4'\alpha}CH$); 2.83 (m, 4H, $2^{\text{aliph.}}CH_2$); 2.87 (dd, 2H, $J_{3CH\beta,4CH\alpha} \approx 9.8$, $J_{3CH\beta,4CH\alpha} \approx 5.8$, $^{3,3'}CH$); ^{13}C NMR δ: 23.58 ($^{9,9'}C$); 27.52 ($^{8,8'}C$); 27.63 ($^{7,7'}C$); 30.87 ($^{10,10'}C$); 37.37 ($^{4,4'}C$); 37.79 9 ($^{6,6'}C$); 39.20 ($^{5,5'}C$); 48.87 ($^{\text{aliph.}}C$); 53.63 ($^{1,1'}C$); 56.70 ($^{3,3'}C$); 71.30 ($^{2,2'}C$).

4.10. *N,N*-[3α-(2α-Methoxypinane)]ethane-1,2-diamine 8b

A solution of 4.0 g (0.01 mol) of *O*-methyl protected dihydroxydiimine **7a** in 75 ml of dry diethyl ether was added dropwise to a solution of 1.04 g (0.027 mol) of 98% lithium aluminum hydride in 100 ml of dry diethyl ether. The mixture was stirred under argon for 6 h and refluxed for 25 h. After this time, the reaction mixture was cooled down to room temperature and quenched by the dropwise addition of 40 ml of water. The organic layer was separated and the aqueous layer washed with diethyl ether (3×50 ml). The combined organic fractions were dried over magnesium sulfate. Removal of the solvent afforded 3.62 g (90%) of a light yellow oil. $[\alpha]_D^{20} = -34.1$ (*c* 1, $CHCl_3$); ^1H NMR δ: 1.00 (s, 6H, $^{9,9'}CH_3$); 1.26 (s, 6H, $^{8,8'}CH_3$); 1.28 (s, 6H, $^{10,10'}CH_3$); 2.78–2.82 (m, 4H, $^{\text{aliph.}}CH_2$); 3.07 (s, 6H, $2OCH_3$); 3.30–3.50 (m, 2H, $^{3,3'}CH$). The crude product was used for the preparation of the chloride salt without purification.

Dihydrochloride: Dry hydrogen chloride was bubbled through a solution of 1.56 g (0.004 mol) of **8b** in 100 ml of dry diethyl ether in 0–5 °C until the precipitation was completed. The white precipitate was filtered off, washed with ether (2×10 ml) and dried in vacuum, affording 1.35 g (74%) of product. The liquor residue was not recovered. Temperature of decomposition: 198–205 °C; ^1H NMR δ: 0.95 (s, 6H, $^{9,9'}CH_3$); 1.30 (s, 6H, 8,8′CH_3); 1.51 (s, 6H, $^{10,10'}CH_3$); 1.68 (d, 2H, $J_{7\alpha,7\beta} \approx 9.3$, $^{7,7'\beta}CH$); 3.17 (s, 6H, $2OCH_3$); 3.58 (m, 2H, $^{3,3'}CH$); 3.77 (m, 4H, $^{\text{aliph.}}CH_2$); ^{13}C NMR δ: 23.99 ($^{9,9'}C$); 24.22 ($^{8,8'}C$); 27.01 ($^{7,7'}C$); 20.01 ($^{10,10'}C$);

30.95 ($^{4,4'}$C); 37.72 ($^{6,6'}$C); 39.69 ($^{5,5'}$C); 42.97 ($^{1,2aliph.}$C); 48.96 (OCH_3); 49.97 ($^{1,1'}$C); 59.05 ($^{3,3'}$C); 77.27 ($^{2,2'}$C).

4.11. Dihydrochloride of *N,N*-[3α-(2α-benzoxypinane)]-ethane-1,2-diamine 8c

A solution of 4.01 g (0.007 mol) of *O*-benzyl protected dihydroxydiimine **7b** in 50 ml of dry diethyl ether was added dropwise to a solution of 1.06 g (0.03 mol) of 98% lithium aluminum hydride in 100 ml of dry diethyl ether. The mixture was stirred under argon for 4 h and refluxed for 11 h. After this time, the reaction mixture was cooled down to room temperature and quenched by the dropwise addition of 60 ml of water. The organic layer was separated and the aqueous layer washed with diethyl ether (3×50 ml). The combined organic fractions were dried over magnesium sulfate. Removal of the solvent afforded 3.65 g of a light yellow oil, $[\alpha]_D^{20} = -19.8$ (*c* 0.2, $CHCl_3$). The crude product was used without purification to prepare the chloride salt.

Crude diamine (3.25 g) in 200 ml of dry diethyl ether was saturated by hydrogen chloride gas. The chloride salt precipitated out as a white solid. The solid was filtered out and dried in vacuum, affording 1.73 g (47%) of required product. Temperature of decomposition 185–190 °C; $[\alpha]_D^{20} = -17.4$ (*c* 0.5, MeOH); ^{1}H NMR δ: 0.94 (s, 6H, $^{9,9'}CH_3$); 1.30 (s, 6H, $^{8,8'}CH_3$); 1.60 (s, 6H, $^{10,10'}CH_3$); 1.72 (d, 2H, $J_{7\alpha,7\beta} \approx 9.6$, $^{7,7'\beta}$CH); 3.41–3.45 (m, 2H, $^{3,3'}$CH); 3.47–3.63 (m, 4H, $^{2aliph.}CH_2$); 4.27 (d, 2H, $J_{benzyl.} = 10.5$, $^{benzyl.}$CH); 4.43 (d, 2H, $J_{benzyl.} = 10.5$, $^{benzyl.}$CH); 7.23–7.48 (10H$^{arom.}$); ^{13}C NMR δ: 23.99 ($^{9,9'}$C); 25.24 ($^{8,8'}$C); 27.23 ($^{7,7'}$C); 28.00 ($^{10,10'}$C); 30.65 ($^{4,4'}$C); 37.89 ($^{6,6'}$C); 39.72 ($^{5,5'}$C); 43.02 ($^{2aliph.}$C); 50.60 ($^{1,1'}$C); 59.29 ($^{3,3'}$C); 64.10 ($^{2benzyl.}$C); 77.75 ($^{2,2'}$C); 127.67 ($^{arom.4}$C); 128.42 ($^{arom.3,5}$C); 128.52 ($^{arom.2,6}$C); 138.04 ($^{arom.1}$C).

The remaining product was not recovered from the diethyl ether solution.

4.12. *N,N'*-[3α-(2α-Hydroxypinane)]benzene-1,3-diamine 8d

A solution of 4.10 g (0.01 mol) of dihydroxydiimine **6f** in 40 ml of dry diethyl ether was added under argon to a vigorously stirred suspension of 2.0 g of 98% lithium aluminum hydride in 200 ml of dry diethyl ether. The mixture was refluxed for 18 h, cooled down to room temperature, and quenched by dropwise addition of 100 ml of water. The organic layer was separated and the aqueous layer washed with diethyl ether. The combined organic extracts were dried over magnesium sulfate. Removal of the solvent afforded 3.95 g of a light brown oil, which was submitted to chromatographic purification ($R_f = 0.21$; hexane–ethyl acetate 3:2) to yield 2.36 g (57%) of the product as a colorless enamel. The interfraction product residues were not recovered. MS, M+1 = 413; $[\alpha]_D^{20} = -177.8$ (*c* 0.2, $CHCl_3$); ^{1}H NMR δ: 1.08 (s, 6H, $^{9,9'}CH_3$); 1.30 (s, 6H, $^{8,8'}CH_3$); 1.36 (s, 6H, $^{10,10'}CH_3$); 1.40 (d, 2H, $J_{7\alpha,7\beta} \approx 10.25$, $^{7,7'\beta}$CH); 1.47–1.56 (m, 2H, $^{4,4'\beta}$CH); 1.93–1.99 (m, 2H, $^{5,5'}$CH); 2.04 (dd, 2H, $J_{1,5} \approx 5.5$, $J_{1,7\alpha} \approx 6.25$, $^{1,1'}$CH); 2.19–2.30 (m, 2H, $^{4,4'\alpha}$CH); 2.55–2.69 (m, 2H, $^{7,7'\alpha}$CH); 3.80 (dd, 2H, $J_{3,4\alpha} \approx 9.25$. $J_{3,4\beta} \approx 6.5$, $^{3,3'\beta}$CH); 6.01 (t, 1H, $J_{arom.5,4} = J_{5,6} \approx 2$, $^{arom.5}$CH); 6.08 (dd, 2H, $^{arom.4,6}$CH); 7.00 (t, 1H, $J_{arom.2,4} = J_{2,6} \approx 8$, $^{arom.2}$CH); ^{13}C NMR δ: 23.66 ($^{9,9'}$C); 27.88 ($^{8,8'}$C); 28.36 ($^{7,7'}$C); 30.37 ($^{10,10'}$C); 37.59 ($^{4,4'}$C); 38.41 ($^{6,6'}$C); 40.32 ($^{5,5'}$C); 52.68 ($^{1,1'}$C); 53.95 ($^{3,3'}$C); 74.11 ($^{2,2'}$C); 98.81 ($^{arom.5}$C); 103.53 ($^{arom.4,6}$C); 129.89 ($^{arom.2}$C); 148.93 ($^{arom.1,3}$C).

4.13. Dihydrochloride of *N,N'*-[3α-(2α-methoxy-pinane)]benzene-1,2-diamine 8e

A solution of 3.80 g (0.0087 mol) of **7c** in 40 ml of dry diethyl ether was added dropwise to a solution of 0.76 g (0.02 mol) of 98% lithium aluminum hydride in 50 ml of dry diethyl ether. The mixture was refluxed for 10 h, cooled down to room temperature, and quenched by the dropwise addition of 25 ml of water. The organic layer was separated from the aqueous solution, followed by extraction with three 50-ml portions of diethyl ether. The fractions were combined and dried over magnesium sulfate. After evaporation of the solvent 2.5 g (65%) of a yellow oil was obtained. Based on NMR spectra the purity of the product was >95%. $[\alpha]_D^{20} = -93.5$ (*c* 0.2, $CHCl_3$), ^{1}H NMR δ: 1.09 (s, 6H, $^{9'9'}CH_3$); 1.14 (s, 6H, $^{8,8'}CH_3$); 1.31 (s, 6H, $^{10,10'}CH_3$); 3.14 (s, 6H, $2OCH_3$). Crude product (1.70 g) from the previous reaction in 100 ml of dry diethyl ether was saturated by hydrogen chloride gas. The chloride salt precipitated out as a white solid. The white solid was filtered out and dried in vacuum, affording 0.970 g (~48%) of required product. ^{1}H NMR δ: 1.04 (s, 6H, $^{9,9'}CH_3$); 1.12 (s, 6H, $^{8,8'}CH_3$); 1.33 (s, 6H, $^{10,10'}CH_3$); 3.25 (s, 6H, $2OCH_3$); 4.12 (m, 2H, $^{3,3'}$CH); 6.95 (m, 2H, $^{arom.}$CH); 7.22 (m, 2H, $^{arom.}$CH). The rest of the impure product has not been recovered (0.93 g).

4.14. 1,3-Bis-[3α-(2α-benzoxypinane)]imidazolinium chloride 9a

A mixture of 0.97 g (0.0016 mol) of *N,N'*-bis-[3α-(2α-benzoxypinane)]ethane-1,2-diamine **8c** dihydrochloride, 15 ml of triethyl orthoformate, and one drop of 96% formic acid was refluxed for 80 h. The reaction mixture solidified after evaporation of the solvent. Crystallization from acetonitrile–diethyl ether yielded 0.36 g (37%) of light brown crystals. Mp 51–53 °C; $[\alpha]_D^{20} = -47.1$ (*c* 0.2, MeOH); ^{1}H NMR δ: 1.11 (s, 6H, $^{9,9'}CH_3$); 1.34 (s, 6H, $^{8,8'}CH_3$); 1.51 (s, 6H, $^{10,10'}CH_3$); 1.82 (m, 4H); 1.99 (m, 2H); 2.18 (m, 4H); 2.27 (m, 4H); 3.45 (m, 2H, $^{aliph.}CH_2$); 3.90 (m, 2H, $^{aliph.}CH_2$); 4.03 (d, 2H, $J \approx 9.5$, $^{benzyl.}$CH); 4.28 (d, 2H, $J \approx 9.5$, $^{benzyl.}$CH); 4.66 (m, 2H, $^{3,3'}$CH); 7.12 (m, 10H, $^{arom.}$CH); 10.04 (s, 1H, $^{im.}$CH); ^{13}C NMR δ: 23.78 ($^{9,9'}$C); 23.85 ($^{8,8'}$C); 28.01 ($^{7,7'}$C); 28.59 ($^{10,10'}$C); 30.68 ($^{4,4'}$C); 38.16 ($^{6,6'}$C); 39.86 ($^{5,4'}$C); 48.14 ($^{aliph.2}$C); 50.21 ($^{1,1'}$C); 57.84 ($^{3,3'}$C); 63.67 ($^{2benzyl.}$C); 80.11 ($^{2,2'}$C); 127.79 ($^{2arom.4}$C); 128.23 ($^{2arom.3,5}$C); 128.45 ($^{2arom.2,6}$C); 138.63 ($^{2arom.1}$C); 160.10 ($CH^{im.}$). Anal. Calcd for $C_{37}H_{51}N_2O_2Cl{\cdot}2H_2O$: C = 71.30, H = 8.25. Found: C = 71.46, H = 8.34.

4.15. 1,3-Bis-[3α-(2α-methoxypinane)]benzimidazolium chloride 9b

A mixture of 0.481 g (0.002 mol) of *N*,*N*′-bis-[3α-(2α-methoxypinane)]benzene-1,2-diamine **8e** dihydrochloride, 5 ml of triethyl orthoformate, and one drop of 96% formic acid was heated at 105 °C for 64 h. The reaction mixture was washed with ether and acetonitrile (2 × 5 ml). The vacuum-dried residue (0.210 g) was identified as the desired salt. Attempts to crystallize the product failed; the product was characterized as an enamel. ^{1}H NMR δ: 133 (s, 6H, $^{9,9'}CH_3$); 1.34 (s, 6H, $^{8,8'}CH_3$); 1.41 (s, 6H, $^{10,10'}CH_3$); 5.66 (m, 2H, $^{3,3'}CH$); 7.49–7.58 (4H$^{arom.}$); 11.11 (s, 1H, $^{im.}CH$); ^{13}C NMR δ: 147.77 ($^{im.}C$).

4.16. X-ray crystallographic studies[14]

4.16.1. Crystal data for 6b. $C_{22}H_{36}N_2O_2$, $M = 360.53$, monoclinic, space group $P2_1$ (No. 4), $a = 12.646(3)$ Å, $b = 12.554(3)$ Å, $c = 20.591(4)$ Å, $\beta = 98.8(3)°$, $V = 3230.4(13)$ Å^3, $Z = 6$, $D_x = 1.112$ g/cm^3, $T = 297$ K, $\mu = 0.071$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 1188$, colorless prisms (0.3 × 0.3 × 0.4 mm), data/parameters = 10,709/705; final $R_1 = 0.0657$, $wR_2 = 0.2018$ (all data).

4.16.2. Crystal data for 6e. $C_{26}H_{36}N_2O_2$, $M = 408.57$, monoclinic, space group $C2$ (No. 5), $a = 22.603(5)$ Å, $b = 8.080(2)$ Å, $c = 14.011(3)$ Å, $\gamma = 112.9(3)°$, $V = 2356.7(11)$ Å^3, $Z = 4$, $D_x = 1.511$ g/cm^3, $T = 297$ K, $\mu = 0.072$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 888$, colorless prisms (0.2 × 0.2 × 0.3 mm), data/parameters = 3773/275; final $R_1 = 0.0424$, $wR_2 = 0.0941$ (all data).

4.16.3. Crystal data for 7a. $C_{24}H_{40}N_2O_2$, $M = 388.58$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 7.646(2)$ Å, $b = 10.927(2)$ Å, $c = 27.051(5)$ Å, $V = 2260.1(8)$ Å^3, $Z = 4$, $D_x = 1.142$ g/cm^3, $T = 297$ K, $\mu = 0.072$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 856$, light yellow prisms (0.1 × 0.2 × 0.25 mm), data/parameters = 3960/254; final $R_1 = 0.0446$, $wR_2 = 0.1265$ (all data).

4.16.4. Crystal data for 9a. $[C_{37}H_{51}N_2O_2]^+ Cl^-{\cdot}2(H_2O)$, $M = 626.27$, trigonal, space group $P3_1$ (No. 144), $a = 15.873(2)$ Å, $b = 15.873(2)$ Å, $c = 11.706(2)$ Å, $\gamma = 120°$, $V = 2554.2(6)$ Å^3, $Z = 3$, $D_x = 1.222$ g/cm^3, $T = 297$ K, $\mu = 0.153$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 1017$, light brown prisms (0.3 × 0.3 × 0.35 mm), data/parameters = 5988/398; final $R_1 = 0.0595$, $wR_2 = 0.1577$ (all data).

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 291395 for **6b**, CCDC 291396 for **6e**, CCDC 291397 for **7a**, and CCDC 291398 for **9a**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: Int code +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

4.17. 1,3-Di-3α-(2α-methoxypinan)-2-phenyl-[1,3,2]diazaphospholidine 2-oxide 10

A 150-ml flask equipped with a thermometer, septum, a magnetic stirring bar, and continuously purged with argon was charged with 0.94 g (0.0024 mol) dimethoxydiamine **8b** and 0.70 ml (0.005 mol, 10% excess) of triethylamine in 70 ml THF. The mixture was cooled to 0 °C and 0.35 ml (0.0026 mol, 7% excess) of dichlorophenylphosphine was added in portions via syringe. The reaction continued at 0 °C for 8 h and at room temperature for the following 12 h. After this time, the mixture was oxidized by bubbling dry air through the solution over 3 h and the solvent removed in vacuo. Then 100 ml of hexane was added and the undissolved phenylphosphoric acid and triethylamine hydrochlorides were filtered out. Evaporation of hexane afforded 1.30 g of an oily residue. Flash chromatography yielded 0.765 g (63%) of oily product. $[\alpha]_D^{20} = +11.3$ (c 1, $CHCl_3$); MS: M+1 = 505; ^{1}H NMR δ: 0.93 (s, 6H, $^{9,9'}CH_3$), 1.29 (s, 6H, $^{8,8'}CH_3$), 1.53 (s, 6H, $^{10,10'}CH_3$), 1.75 (d, 2H, $J_{7\alpha,7\beta} = 10.5$, $^{7,7'\beta}CH$), 1.99–2.02 (m, 4H), 2.13 (m, 2H), 2.36–2.39 (m, 4H), 3.18 (s, 6H, OCH_3), 3.49–3.52 (m, 2H, $^{3,3'\beta}CH$); 3.73–3.76 (m, 4H, $2^{aliph.}CH_2$), 7.31–7.60 (m, 3H, $^{arom.}CH$), 7.88–7.92 (m, 2H, $^{arom.}CH$); ^{31}P NMR δ: 31.64.

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