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New conformational flexible phosphane and phosphane oxide macrobicycles

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ABSTRACT

The synthesis of two large diastereomeric phosphane oxide macrobicycles **3** and **4** succeeded in comparatively good yield by a tripod-coupling strategy using the tripodal components **1** and **2** as building blocks. ^{1}H, ^{13}C and ^{31}P NMR spectra of the two cage compounds are in accordance with a time-averaged D_{3h} symmetry each, which in the case of **3** can be attributed to a fast interconversion of two degenerate *in*,*out*-structures. Kinetic measurements of the reduction of both diastereomeric macrobicycles, and the results of an inversion experiment also support the assumption that the phosphane and phosphane oxide cage molecules described herein are conformational flexible and undergo fast homeomorphic isomerisation. The bisiminophosphorane derivative **8** was prepared and assigned as an *out*,*out*-isomer. An alternative tripod-capping reaction between bisphenol **10** and capping reagent **2** did not result in the formation of macrobicyclic products. Instead, three complex structures **11**, **12** and **13** with macrocyclic sub-units could be isolated.

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1. Introduction

Phosphorus-containing macrocycles offer potential applications in supramolecular and synthetic organic chemistry.[1] Of special interest are *in*-functionalised macrobicycles bearing phosphorus atoms at the bridgehead positions and providing large cavities inside the bicyclic structure. In the case of a phosphane oxide moiety as bridgehead segment, with the oxygen directing inside this cavity, such structures might be interesting as ionophores.[2] The corresponding phosphane compounds can potentially be employed as organocatalysts[3] or as ligands for metal catalysed reactions.[4] The exceptional location of the lone pair as active centre inside the cavity should lead to an increase of regio- and stereospecifity.

Goto and Kawashima, for example, synthesised monocyclic, bowl-shaped phosphorus ligands with a 'quasi'-*in* phosphorus lone pair.[5] They used them for the stabilisation of highly reactive species inside the bowl-shaped ligand. Some of them were used by Tsuji et al. for the rhodium-catalysed hydrosilylation of ketones[6] and Suzuki–Miyaura coupling reactions.[4] They pointed out that such large bowl-shaped phosphane ligands were highly effective and increased reaction rates significantly. The depth of the bowl affected the catalytic activity considerably; in general the deeper bowl ligands were more effective than the shallower ones.[4] Noncyclic chiral phosphane ligands with a pronounced cavity have also been described for asymmetric metal catalysed allylic alkylations.[7]

Extending the idea of bowl-shaped molecules leads to macrobicyclic structures bearing *in*-functionalities. Only a few examples of bicyclic structures with *in*-groups have been described. For example, Whitlock et al. prepared phosphane oxide cage compounds with *in*-P=O moieties.[8,9] Pascal was able to isolate *in*-Si–F,[10] *in*-P–lp,[11] *in*-Si–H[11] and *in*-C–CH_3[12] cyclophanes.[13]

We synthesised and characterised *in*/*out*-isomeric phosphorus bridgehead cage compounds in form of phosphites and phosphates.[14–19] Recently, we obtained a new phosphane oxide macrobicycle possessing only one phosphorus bridgehead atom and studied its isomeric peculiarities.[20] In this case it was not possible to isolate a stable *in*-conformer. This was in contrast to our earlier reported syntheses of phosphite and phosphate cryptands, which led to different, isolable homeomorphic isomers.

In the present paper we present a tripod-coupling approach to phosphane oxide macrobicycles of related design with two phosphorus bridgeheads.

2. Results and discussion

For the assembly of phosphorus macrobicycles two strategies are of special interest, namely tripod-coupling and tripod-capping (Fig. 1).[21] In the case of the tripod-capping method six bonds have to be formed in one step, in comparison to only three for the tripod-coupling approach. Taking this into consideration it is apparent that the latter strategy should afford macrobicyclic structures in higher yields. Nevertheless, both procedures have been tested in the present work.

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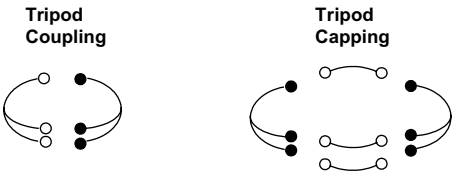
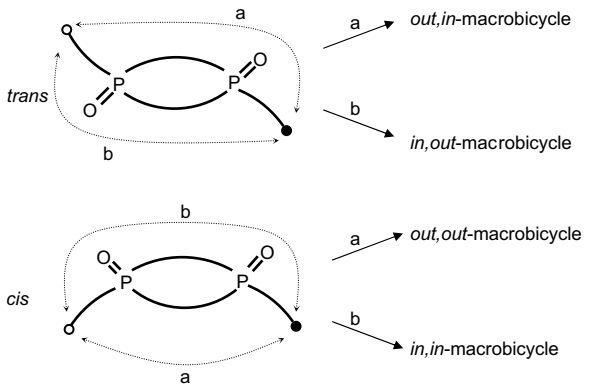


Figure 1. Two selected strategies for the synthesis of macrobicycles.

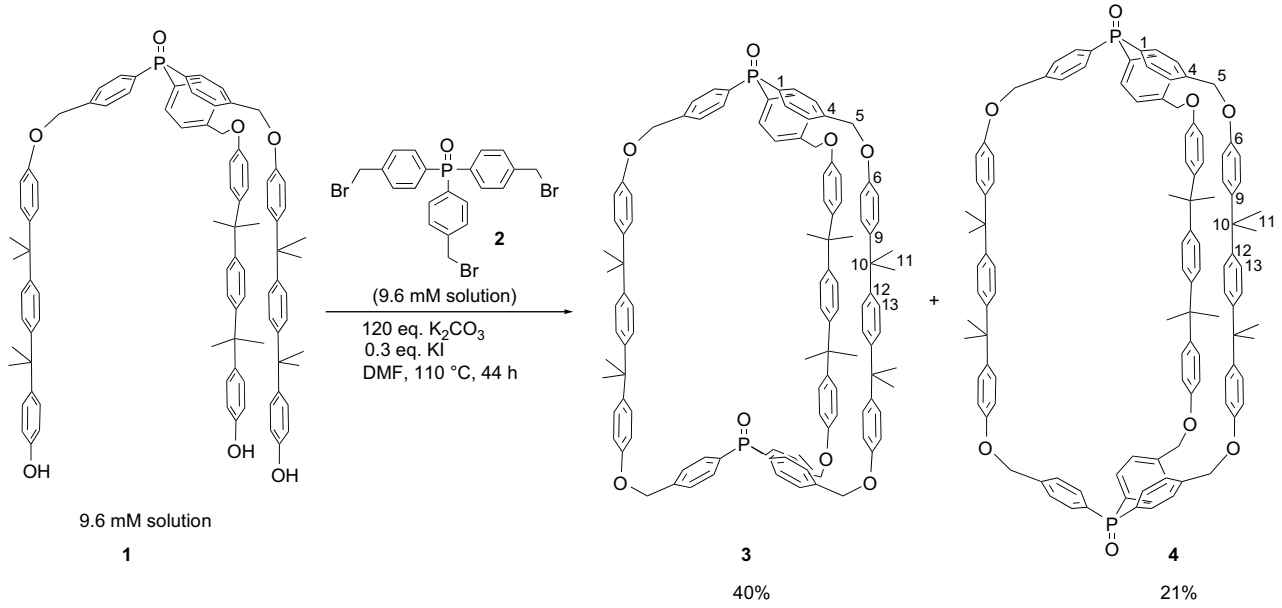
For the tripod-coupling strategy two coupling reagents were required (**1** and **2**). We synthesised the elongated tripod **1** via Williamson ether synthesis of bromide **2** and a mono-*O*-acylated bisphenol followed by cleavage of the ester moieties.[20] The diastereomeric macrobicycles **3** and **4** could be constructed via a second Williamson ether synthesis of tripods **1** and **2** under highly diluted conditions in comparatively high yield of 40% and 21%, respectively (Scheme 1). The tentative isomeric assignment of **3** and **4** was done according to structural investigations described below.

It is interesting to point out that the configuration of the resulting macrobicycle (*in*,*out*/*out*,*in* vs *out*,*out*/*in*,*in*) is already fixed by the first ring closure to give *cis*- or *trans*-monocycles, respectively (Scheme 2). A second ring closure converts the cis-compound to the *out*,*out*- or *in*,*in*-bicycle and the trans-compound to the *in*,*out*- or *out*,*in*-bicycle. Interestingly, both diastereomeric compounds **3** and **4** showed only one ^{31}P NMR signal at 28.9 ppm and 29.5 ppm, respectively. This is in contrast to the expected two different ^{31}P NMR signals for an *in*,*out*-isomer. Moreover, the ^{1}H and ^{13}C NMR spectra also reflected time-averaged D_{3h} symmetry as expected for an *out*,*out*- or *in*,*in*-isomer (e.g., **4**). For the C_{3v}-symmetric macrobicycle *in*,*out*/*out*,*in*-**3**, missing a C_2-axis and a symmetry plane between the upper and the lower half of the molecule, more complicated ^{1}H and ^{13}C NMR spectra were anticipated. A possible explanation would have been the assignment of the two isomers to an *out*,*out*- and an *in*,*in*-structure. However, the fact that no corresponding *in*,*out*-macrobicycle had formed is implausible for statistical reasons. Moreover, in our related syntheses of phosphite and phosphate cryptands we mostly obtained the *in*,*out*-isomer as the main product. Hence, we do not attribute the D_{3h} symmetry to the presence of stable *out*,*out*- and *in*,*in*-isomers but to a rapid homeomorphic isomerisation[22] of the two possible diastereomers (*out*,*out*/*in*,*in* and *in*,*out*/*out*,*in*) at room temperature. Apparently, in these phosphane oxide systems the number of pivots and the length of the 'arms' are sufficient to allow an intramolecular

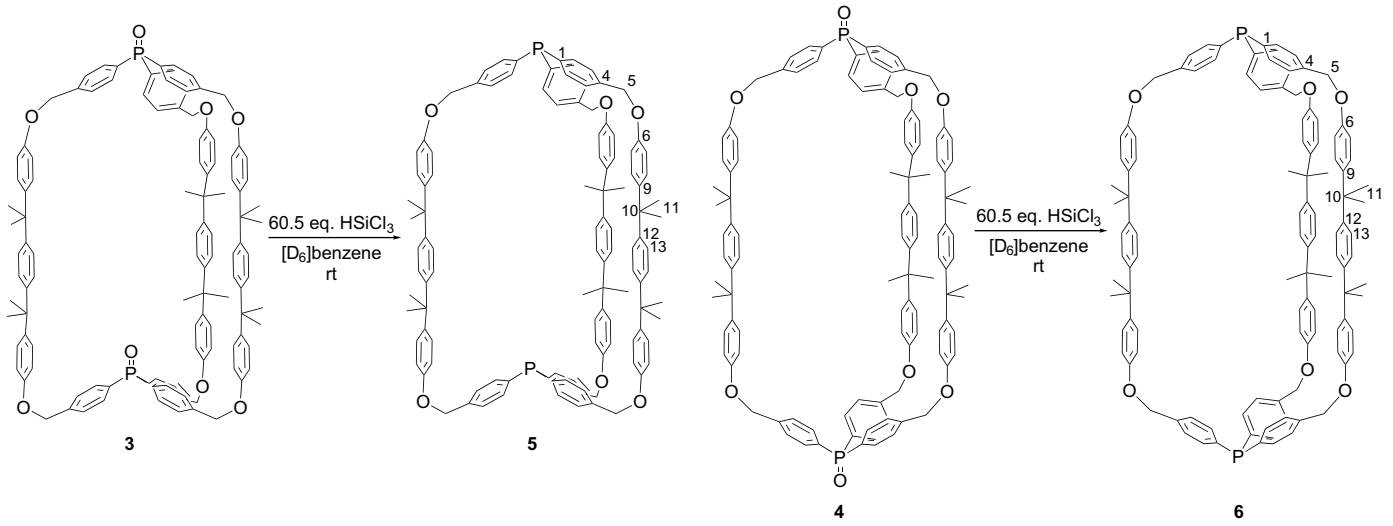


Scheme 2. Formation of isomeric *in*/*out*-macrobicycles from the intermediate *cis*- and *trans*-monocycles.

movement leading to conversion of the *out*,*out*-conformer to the *in*,*in*-conformer and vice versa, via an *intertwined* state. Such conformational flexibility was also observed for a macrobicyclic system of related design reported earlier.[20] This interpretation was further supported by kinetic measurements we performed during reduction of the phosphane oxide macrobicycles **3** and **4** with an excess of trichlorosilane proceeding under retention of the configuration at the phosphorus (Scheme 3).[23–25] We monitored the progress of the reaction at room temperature in benzene-d_6 by ^{31}P NMR and determined rate constants for the two different diastereomers, namely k_1 of 1.1×10^{-3} s^{-1} (**3**) versus 2.0×10^{-3} s^{-1} (**4**) for the reduction of the first P═O moiety and k_2 of 0.5×10^{-3} s^{-1} (**3**) versus 2.0×10^{-3} s^{-1} (**4**) for the reduction of the second P═O moiety. Complete conversion was achieved after about 24 h. The differences in the rate constants are not as pronounced as observed earlier for the oxidation of distinct *in*,*out*-isomers.[16,19] In those systems the fixed *in*-positions were less accessible by the reagent leading to lower reaction rates compared to *out*-positions. In the present situation, however, no permanent *in*-moieties exist. Instead, a fast conformational change (homeomorphic isomerisation) leads to conversion of *in*- to *out*-positions. The latter are easier accessible and, thus, react faster. The two phosphanes **5** and **6** obtained were characterised directly from the reaction mixture of the kinetic experiment due to their high tendency to oxidation during workup and purification.



Scheme 1. Tripod-coupling of **1** and **2** leading to *in*,*out*/*out*,*in*-**3** and *out*,*out*/*in*,*in*-**4**.

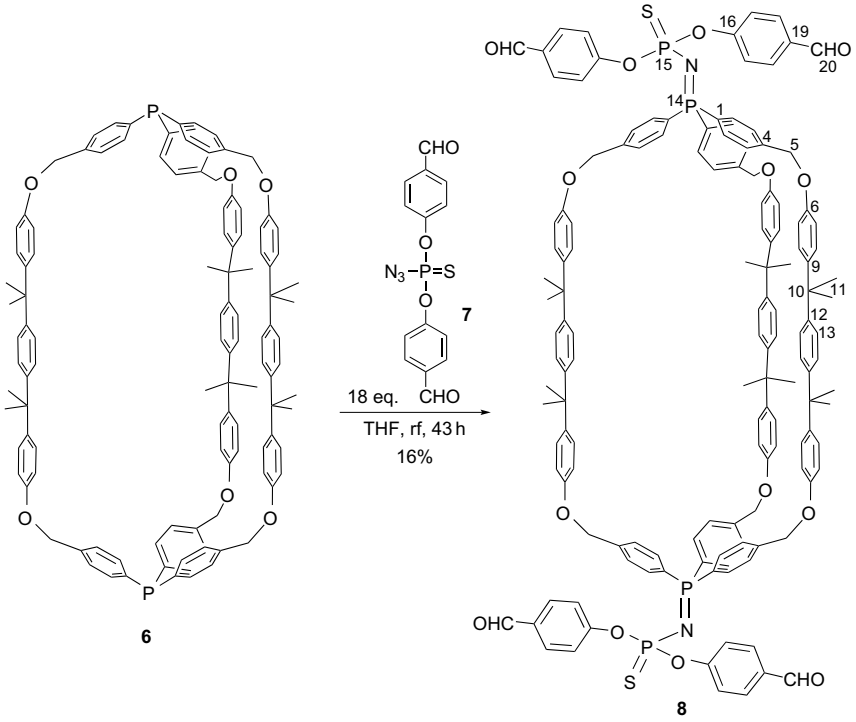


Scheme 3. Kinetic measurements during reduction of phosphane oxide cage compounds **3** and **4**.

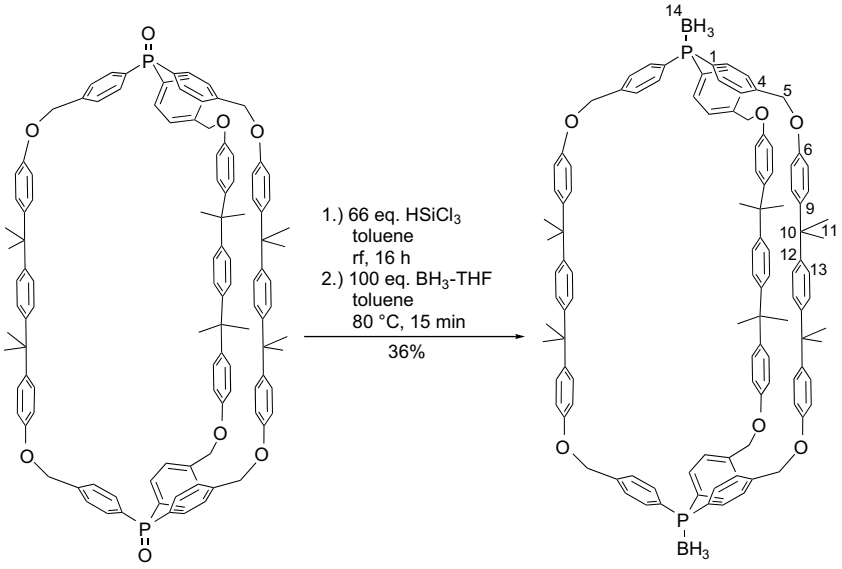
Both isomeric phosphanes showed only one ^{31}P NMR signal at 6.5 ppm (**5**) and 6.6 ppm (**6**), respectively. In analogy to the parent phosphane oxides **3** and **4** the ^{1}H and ^{13}C NMR spectra of **5** and **6** reflect a time-averaged D_{3h} symmetry for both molecules. In order to assign the compounds to the two possible isomers we treated one of it with thiophosphorylazide **7** (Scheme 4). In the case of an *in*-position of the introduced bulky group we expected NOE interactions of their protons with those of the macrobicyclic skeleton as observed for a similar system in our previous work.[18] The obtained bisiminophosphorane **8** showed no such NOE interactions. Thus, we tentatively assign this product, the corresponding phosphane **6**, phosphane oxide **4** and phosphane–borane-complex **9** to the *out*,*out*/*in*,*in*-isomer. Consequently, the *in*,*out*/*out*,*in*-structure results for the second isomer.

In-moieties are of special interest for a number of applications. A promising approach is the conversion of *out*- into *in*-functions as usually the former are predominantly formed during macrobicycle synthesis. This strategy could be realised by inversion reactions at the bridgehead atoms, such as, for example, S_N2 reactions at carbon centres. For the present phosphane oxide cage compounds a reduction method using $HSiCl_3/Et_3N$, which has been described to proceed under inversion at the phosphorus atom,[23–25] was envisaged.

Thus, a stable *out*,*out*-phosphane oxide should be transformed to the corresponding *in*,*in*-phosphane. This procedure was applied to compound **4**, followed by reoxidation of the intermediate phosphane with H_2O_2 under retention.[23,26–28] We expected the resulting *in*,*in*-phosphane oxide to be identical with the starting material **4** due to homeomorphic isomerisation.[22] In fact, we obtained a mixture of both diastereomers *in*,*out*/*out*,*in*-**3** and *out*,*out*/*in*,*in*-**4** during this reaction sequence. This indicates that the reductive step is not fully stereospecific. Again no stable *in*,*in*-isomer was formed.



Scheme 4. Staudinger reaction of *out*,*out*/*in*,*in*-phosphane **6** with thiophosphorylazide **7**.



4 9

Scheme 5. Synthesis of *out*,*out*/*in*,*in*-bisphosphane–borane complex **9**.

Additionally, phosphane–borane complex **9** was synthesised from *out*,*out*/*in*,*in*-phosphane oxide **4** via reduction with trichlorosilane under retention[23–25] and subsequent quenching with borane–tetrahydrofurane complex supporting the structural assignment of **4** (Scheme 5).[25]

As an alternative approach to the present phosphane oxide macrobicycles we applied a tripod-capping strategy (Fig. 1) using benzyl bromide **2** as the capping reagent and bisphenol **10**. We reacted 2 equiv of benzyl bromide **2** and 3 equiv of bisphenol **10** in dry DMF under highly diluted conditions (Scheme 6). The obtained product mixture revealed the bisphenolic moieties being flexible enough to perform a direct intramolecular ring closure leading to macromonocyclic structures **11** (8%), **12** (1%) and **13** (58%). Bicyclic structures could not be observed.

3. Conclusion

In conclusion we synthesised a new phosphane oxide macrobicycle with two phosphorus bridgehead atoms in comparatively high yield by a tripod-coupling procedure. We isolated two isomers, which we tentatively assign to *in*,*out*/*out*,*in*-**3** and *out*,*out*/*in*,*in*-**4** undergoing homeomorphic isomerisation in solution. Thus, NMR spectra of both isomers are in accordance with time-averaged D_{3h}-symmetric structures. We carried out kinetic measurements during the reduction of both isomers in the state of phosphane oxides. No pronounced differences between the respective reaction rate constants were found. The *out*,*out*/*in*,*in*-phosphane was converted by a Staudinger reaction with the bulky azide **7** to afford the corresponding bisiminophosphorane **8**. An alternative tripod-capping strategy for the synthesis of phosphorus cryptands **3** and **4** did not give macrobicyclic products but interesting large macromonocyclic structures (**11**, **12**, **13**).

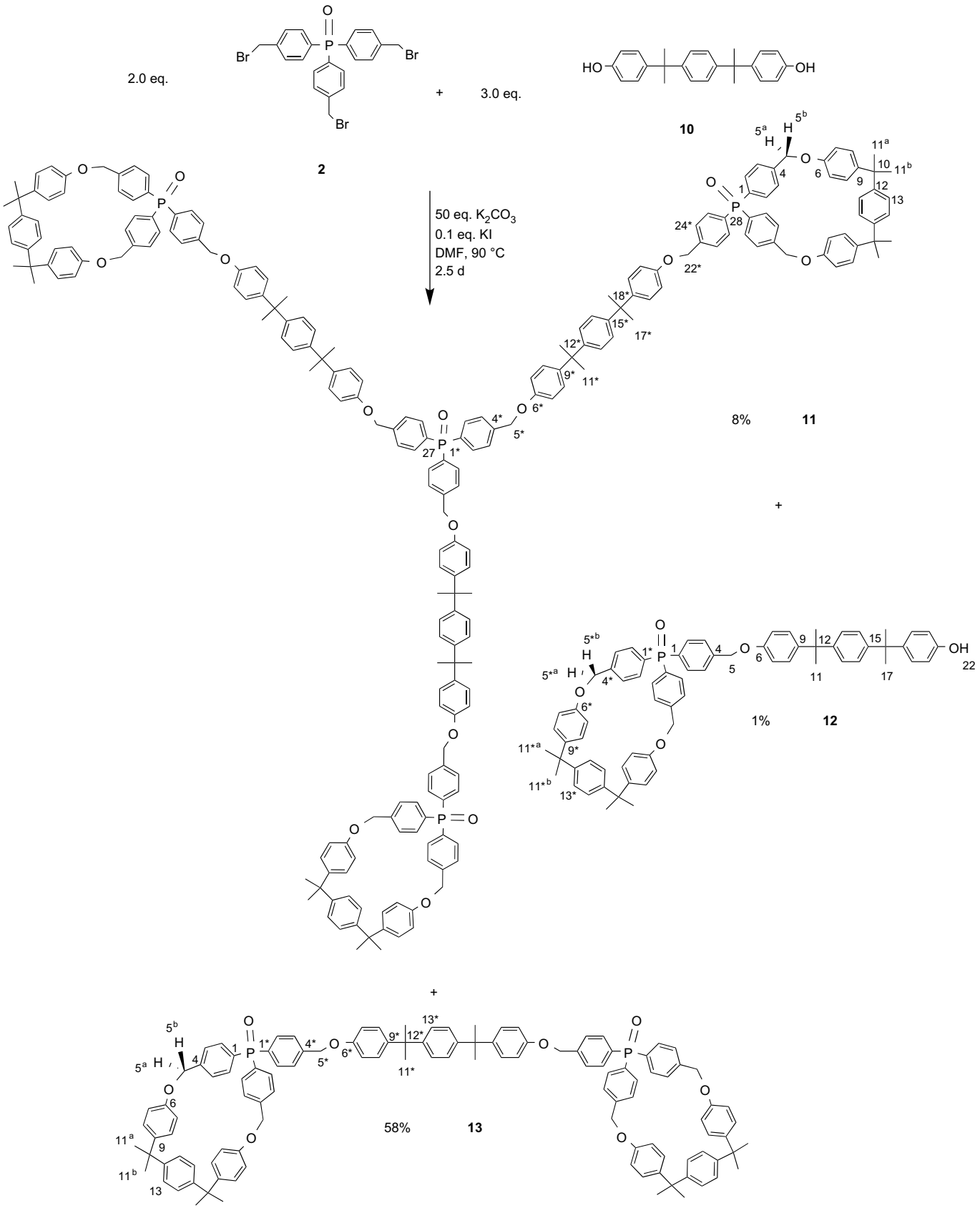
4. Experimental section

4.1. General

The melting points were determined on a Boëtius melting point apparatus. ^{1}H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) were recorded on a Bruker DRX-500 and an AC300-P spectrometer, respectively, at the frequencies indicated. Exact assignment of ^{1}H and ^{13}C NMR spectra for a number of substances was carried out by 2D NMR techniques (**3**: NOESY, ^{1}H/^{13}C HMBC; **4**: NOESY; **8**: ^{1}H/^{31}P HMBC, NOESY; **11**: COSY, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, ^{1}H/^{31}P HMBC, NOESY; **12**: COSY, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, ^{1}H/^{31}P HMBC, NOESY; **13**: COSY, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, ^{1}H/^{31}P HMBC, NOESY, ROESY). The signals of **5**, **6** and **9** were assigned in analogy to the compounds above. ESI-MS spectra were determined with a Bruker Esquire mass spectrometer with ion trap detector. High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL mass spectrometer. Analytical HPLC measurements were performed on an Agilent 1100 HPLC instrument. Conditions are provided in supplementary data. Elemental analysis was carried out with a Hekatech EA 3000 Euro Vector device. IR spectra were recorded on a Thermo Nicolet Avatar 260 FT-IR device using ATR technique. Thin layer chromatography (TLC) was carried out on aluminium sheets coated with silica gel obtained from Merck. Plates were developed by UV irradiation. Column chromatography was performed using silica gel (Merck, 0.040–0.063 mm). All reactions were carried out in dry solvents under an argon atmosphere. The solvents were dried using a solvent purification system (MBraun-SPS). Chemicals (e.g., **10**) were used as received from commercial sources. Capping reagents **1** and **2**[20] and thiophosphorylazide **7**[29] were synthesised according to literature procedures.

4.2. Bisphosphane oxide macrobicycles 3 and 4

A suspension of dry K_2CO_3 (7.96 g, 57.620 mmol), KI (0.024 g, 0.144 mmol) in dry DMF (650 mL) was provided under an argon atmosphere. After heating to 110 °C a solution of tripodal alcohol **1**[20] (0.65 g, 0.480 mmol) in dry DMF (50 mL) and simultaneously a solution of bromide **2**[20] (0.268 g, 0.480 mmol) in dry DMF (50 mL) were added dropwise with two syringe pumps over about 2 h with equal drop speeds. During stirring at 110 °C for 42 h the solution colour changed from pink to grey. Finally the reaction was quenched with a saturated solution of $NaHCO_3$, stirred for additional 10 min at 110 °C and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was dissolved in THF. The organic phase was washed with NH_4Cl and NaCl and subsequently dried over $MgSO_4$. After evaporation of



Scheme 6. Tripod-capping synthesis resulting in the formation of products containing macrocyclic sub-units.

the solvent and column chromatography on silica gel with CH_2Cl_2/EtOH=100:5 *in,out/out,in*-**3** was obtained in 40% yield (0.322 g, 0.193 mmol) and *out,out/in,in*-**4** in 21% yield (0.169 g, 0.101 mmol) both as yellow powders.

*4.2.1. Phosphane oxide in,out/out,in-**3***

Decomposition >315 °C; ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=28.47 ppm (s); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.65 (s, 36H, 11-H), 5.02 (s, 12H, 5-H), 6.86 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 7.11 (s, 12H, 13-H), 7.15 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.53 (dd, ^4J(P,H)=1.8 Hz, ^3J(H,H)=8.1 Hz, 12H, 3-H), 7.69 ppm (dd, ^3J(P,H)=11.7 Hz, ^3J(H,H)=8.1 Hz, 12H, 2-H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, TMS): δ=30.76 (C-11), 41.84 (C-10), 69.28 (C-5), 113.90 (C-7), 126.22 (C-13), 127.40 (d, ^3J(P,C)=12.3 Hz, C-3), 127.82 (C-8), 131.83 (d, ^1J(P,C)=105.1 Hz, C-1), 132.36 (d, ^2J(P,C)=10.0 Hz, C-2), 141.32 (C-4), 143.65 (C-9), 147.72 (C-12), 156.32 ppm (C-6); IR (ATR): ν=2963, 2925, 2854, 1606, 1509 (st, P–C_{phenyl}), 1461, 1403, 1297, 1245 (st, P=O), 1181 (st), 1116, 1018, 829 (st, *p*-disubst. aromatics), 731, 679 cm^{-1}; ESI-MS (50 V): *m/z* (%)=1667.8 (100) $[M+H]^+$; HRMS calcd for $C_{114}H_{109}O_8P_2$ (1×^{13}C) 1668.7626 $[M+H]^+$, found 1668.7634.

*4.2.2. Phosphane oxide out,out/in,in-**4***

Mp 172 °C; ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=28.62 ppm (s); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.57 (s, 36H, 11-H), 4.98 (s, 12H, 5-H), 6.72 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 6.99 (s, 12H, 13-H), 7.04 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.41 (dd, ^4J(P,H)=2.2 Hz, ^3J(H,H)=8.1 Hz, 12H, 3-H), 7.59 ppm (dd, ^3J(P,H)=11.7 Hz, ^3J(H,H)=8.1 Hz, 12H, 2-H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, TMS): δ=30.71 (C-11), 41.83 (C-10), 69.33 (C-5), 114.14 (C-7), 126.17 (C-13), 127.16 (d, ^3J(P,C)=12.3 Hz, C-3), 127.83 (C-8), 131.68 (d, ^1J(P,C)=104.8 Hz, C-1), 132.34 (d, ^2J(P,C)=10.0 Hz, C-2), 141.68 (C-4), 143.46 (C-9), 147.83 (C-12), 156.26 ppm (C-6); IR (ATR): ν=2963, 2925, 2855, 1606, 1508 (st, P–C_{phenyl}), 1461, 1403, 1298, 1245 (P=O), 1227, 1181 (st), 1116, 1018, 829 (*p*-disubst. aromatics), 731, 679 cm^{-1}; ESI-MS (50 V): *m/z* (%)=1667.8 (100) $[M+H]^+$; HRMS calcd for $C_{114}H_{109}O_8P_2$ (1×^{13}C) 1668.7626 $[M+H]^+$, found 1668.7623.

4.3. Kinetic experiment: reduction of bisphosphane oxide macrobicycles 3 and 4

Phosphane oxide macrobicycles **3** and **4** (20.2 mg each, 0.012 mmol), respectively, were provided in NMR tubes in benzene-d_6 (0.8 mL each). $HSiCl_3$ (0.07 mL, 98.4 mg, 0.727 mol) was added. The progress of the reaction at room temperature was monitored by ^{31}P NMR after periodic shaking. After complete conversion (~24 h) the corresponding phosphanes **5** and **6** were characterised directly from the reaction mixture. Rate constants for the consecutive reduction steps were determined according to the literature.[30]

*4.3.1. Phosphane in,out/out,in-**5***

^{31}P NMR (121.5 MHz, C_6D_6, 25 °C, H_3PO_4): δ=6.51 ppm (s); ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C, TMS): δ=1.45 (s, 36H, 11-H), 4.46 (s, 12H, 5-H), 5.31 (s, $HSiCl_3$), 6.61 (d, ^3J(H,H)=8.7 Hz, 12H, 7-H), 6.95 (d, ^3J(H,H)=8.7 Hz, 12H, 8-H), 6.98–7.04* (m, benzene/3-H/13-H), 7.20 ppm (t, *J*=7.6 Hz, 12H, 2-H); * denotes signals of 3-H and 13-H superposed by the benzene signal; ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C, TMS): δ=31.07 (C-11), 42.10 (C-10), 69.69 (C-5), 114.48 (C-7), 126.72 (C-13), 127.67 (d, ^3J(P,C)=7.2 Hz, C-3), 128.15 (C-8), 134.25 (d, ^2J(P,C)=19.7 Hz, C-2), 137.26 (d, ^1J(P,C)=12.1 Hz, C-1), 138.39 (C-4), 143.46 (C-9), 148.46 (C-12), 157.28 ppm (C-6).

*4.3.2. Phosphane out,out/in,in-**6***

^{31}P NMR (121.5 MHz, C_6D_6, 25 °C, H_3PO_4): δ=6.62 ppm (s); ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C, TMS): δ=1.66 (s, 36H, 11-H), 4.76 (s, 12H, 5-H), 5.54 (s, $HSiCl_3$), 6.82 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 7.14 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.17 (s, 12H, 13-H), 7.21* (d, *J*=7.4 Hz, 12H, 3-H), 7.37 ppm (t, *J*=7.8 Hz, 12H, 2-H); * denotes signal partially overlapped by the benzene signal; ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C, TMS): δ=31.51 (C-11), 42.56 (C-10), 70.14 (C-5), 115.21 (C-7), 127.16 (C-13), 128.17 (d, ^3J(P,C)=7.2 Hz, C-3), 128.65 (C-8), 134.74 (d, ^2J(P,C)=19.9 Hz, C-2), 137.75 (d, ^1J(P,C)=12.2 Hz, C-1), 139.13 (C-4), 143.83 (C-9), 148.95 (C-12), 157.67 ppm (C-6).

4.4. Bisiminophosphorane *out,out*-8

Phosphane macrobicycle *out,out/in,in*-**6** was obtained from the reaction mixture of the kinetic experiment. The solution was diluted with CH_2Cl_2 and quenched with water. After addition of 1 M NaOH to dissolve the solid residue, the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with NaCl and dried over $MgSO_4$. Finally, the solvent was evaporated under reduced pressure and impurities were removed by column chromatography on alumina with diethylether (product: R_f=1). The phosphane **6** obtained as a yellow solid (15 mg, 0.009 mmol) was dissolved in dry THF (6 mL) under an argon atmosphere and thiophosphorylazide **7**[29] (55.6 mg, 0.160 mmol) was added. After stirring under reflux for 43 h the crude product was purified via column chromatography on silica gel with CH_2Cl_2. Compound **8** was obtained in 16% yield as a colourless solid (3.3 mg, 1.451 μmol). ^{31}P NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=13.74 (d, ^2J(P,P)=29.3 Hz, 2P, 14-P), 49.67 (d, ^2J(P,P)=29.3 Hz, 2P, 15-P); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.63 (s, 36H, 11-H), 5.01 (s, 12H, 5-H), 6.76 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 7.04 (s, 12H, 13-H), 7.08 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.17 (d, ^3J(H,H)=7.3 Hz, 8H, 17-H), 7.41 (dd, ^4J(P,H)=2.8 Hz, ^3J(H,H)=8.2 Hz, 12H, 3-H), 7.50 (dd, ^3J(P,H)=12.9 Hz, ^3J(H,H)=8.2 Hz, 12H, 2-H), 7.58 (d, ^3J(H,H)=8.8 Hz, 8H, 18-H), 9.72 ppm (s, 4H, 20-H); ^{13}C NMR spectra could not be measured due to low concentration; IR (ATR): ν=2960, 2923, 2853, 1702 (C=O), 1598, 1508 (st), 1264 (st, P=N–PR_2), 1211 (st, P=N–PR_2), 1155, 892, 831 (*p*-disubst. aromatics), 731 (st, P=S), 705 cm^{-1} (st); ESI-MS* (50 V): *m/z* (%)=1175.4 (2) $[M+2K]^{2+}$, 1159.4 (19) $[M+2Na]^{2+}$, 1148.4 (31) $[M+Na+H]^{2+}$, 1137.4 (78) $[M+2H]^{2+}$; ESI-MS** (24 V): *m/z* (%)=2311.8 (3) $[M+K]^+$, 2297.4 (100, br, single isotopic peaks not resolved), 2273.8 (2) $[M+H]^+$; * denotes recorded mass range: 700–2200; ** denotes recorded mass range: 1500–2500; HRMS calcd for $C_{142}H_{130}N_2O_{14}P_4S_2$ 1137.3951 $[M+2H]^{2+}$, found 1137.3972.

4.5. Phosphane–borane complex 9

The following reaction procedure is based on a method described by Odinets et al. for the reduction of phosphane oxides with trichlorosilane.[25] Under an argon atmosphere phosphane oxide macrobicycle *out,out/in,in*-**4** (31.7 mg, 0.019 mmol) was dissolved in dry toluene (12 mL) and rapidly $HSiCl_3$ (171.6 mg, 1.254 mmol) was added. After stirring for 16 h at reflux the reaction mixture was quenched with a 1 M solution of BH_3–THF in THF (1.90 mL, 163.3 mg, 1.901 mmol) and was additionally stirred for 5 min at 80 °C. After quenching with water and separation of the phases the aqueous layer was extracted with EtOAc and the combined organic layers were washed with a saturated solution of NaCl. After drying over $MgSO_4$ and evaporation of the solvent under reduced pressure the crude product could be purified by column chromatography on silica gel with pentane/diethylether=2:1. Compound **9** could be obtained in 36% yield (11.3 mg, 0.007 mmol) as a yellow solid. Decomposition >245 °C; ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=19.73 ppm (br s); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.57 (s, 36H, 11-H), 4.97 (s, 12H, 5-H), 6.72 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 7.00 (s, 12H, 13-H), 7.04 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.37 (dd, ^4J(P,H)=1.9 Hz, ^3J(H,H)=8.3 Hz, 12H, 3-H), 7.48 ppm (dd,

^3J(P,H)=10.6 Hz, ^3J(H,H)=8.3 Hz, 12H, 2-H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ=29.36 (C-11), 41.84 (C-10), 70.62 (C-5), 114.18 (C-7), 126.18 (C-13), 127.39 (d, ^3J(P,C)=10.5 Hz, C-3), 127.82 (C-8), 133.40 (d, ^2J(P,C)=9.9 Hz, C-2), 141.04 (C-4), 143.46 (C-9), 147.82 (C-12), 156.29 ppm (C-6), C-1 signal missing due to low concentration; IR (ATR): ν=2924 (st), 2854 (st), 1729, 1509 (P–C_{phenyl}), 1463, 1248 (P═O), 1109, 830 cm^{-1} (*p*-disubst. aromatics); ESI-MS (50 V): *m*/*z* (%)=1701.9 (15) $[M+K]^+$, 1685.9 (38) $[M+Na]^+$, 1683.0 (44) $[M(2\cdot{}^{11}B/2\cdot{}^{13}C)+NH_4]^+$, 1682.0 (85) $[M(2\cdot{}^{11}B/1\cdot{}^{13}C)+NH_4]^+$ and $[M(1\cdot{}^{10}B/1\cdot{}^{11}B/2\cdot{}^{13}C)+NH_4]^+$, 1681.0 (100) $[M(2\cdot{}^{11}B/{}^{12}C)+NH_4]^+$, $[M(1\cdot{}^{10}B/1\cdot{}^{11}B\ /1\cdot{}^{13}C)+NH_4]^+$ and $[M(2\cdot{}^{10}B/2\cdot{}^{13}C)+NH_4]^+$, 1680.0 (43) $[M(1\cdot{}^{10}B/1\cdot{}^{11}B/{}^{12}C)+NH_4]^+$ and $[M(2\cdot{}^{10}B/1\cdot{}^{13}C)+NH_4]^+$, 1679.0 (18) $[M(2\cdot{}^{10}B/{}^{12}C)+NH_4]^+$, 1667.0 (14) $[M-BH_3+NH_4]^+$. The exact assignment of the isotopic pattern is only given for the $[M+NH_4]^+$-ions. The corresponding $[M+K]^+$- and $[M+Na]^+$-ions show the same pattern.

4.6. Macromonocyclic products 11, 12 and 13

A suspension of dry K_2CO_3 (29.25 g, 89.758 mmol) and KI (29.8 mg, 0.180 mmol) in dry DMF (750 mL) was provided under an argon atmosphere and heated to 90 °C. Subsequently a solution of capping reagent **2** (2.00 g, 3.590 mmol) in dry DMF (150 mL) and a solution of commercially available bisphenol **10** (1.87 g, 5.385 mmol) in dry DMF (150 mL) were added with equal drop speeds. After stirring for 60 h at 90 °C the reaction mixture was quenched by addition of water (150 mL) and the solvents were evaporated under reduced pressure. The residue was dissolved in THF/water. Solid NaCl was added until phase separation and saturation of the aqueous layer. After extraction of the aqueous layer with THF the combined organic layers were washed with $NaHCO_3$, NH_4Cl and NaCl and subsequently dried over $MgSO_4$. After solvent evaporation in vacuum the product mixture was separated and purified by column chromatography on silica gel with toluene/Et_2O=100:2. Three macromonocyclic products were obtained as yellow solids: **11** in 8% yield (235.7 mg, 0.071 mmol), **12** in 1% yield (28.1 mg, 0.028 mmol) and **13** in 58% yield (1.75 g, 1.050 mmol).

4.6.1. Compound *11*

Mp 219 °C; ^{31}P NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=26.68 (s, 3P, 28-P), 28.42 ppm (s, 1P, 27-P); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.60 (s, 36H, 11a/11b-H), 1.61 (s, 18H, 11*-H or 17*-H), 1.62 (s, 18H, 11*-H or 17*-H), 5.05 (s, 6H, 22*-H), 5.06 (s, 6H, 5*-H), 5.17 (d, ^2J(H,H)=15.6 Hz, 6H, 5a-H or 5b-H), 5.25 (d, ^2J(H,H)=15.6 Hz, 6H, 5a-H or 5b-H), 6.69 (d, ^3J(H,H)=8.8 Hz, 12H, 7-H), 6.82 (d, ^3J(H,H)=8.9 Hz, 6H, 20*-H), 6.84 (d, ^3J(H,H)=9.0 Hz, 6H, 7*-H), 6.98 (s, 12H, 13-H), 7.05 (d, ^3J(H,H)=8.8 Hz, 12H, 8-H), 7.08 (s, 12H, 13*/14*-H), 7.13 (d, ^3J(H,H)=8.7 Hz, 6H, 19*-H), 7.15 (d, ^3J(H,H)=8.7 Hz, 6H, 8*-H), 7.39 (dd, ^4J(P,H)=1.9 Hz, ^3J(H,H)=7.9 Hz, 12H, 3-H), 7.47 (dd, ^4J(P,H)=1.9 Hz, ^3J(H,H)=8.2 Hz, 6H, 24*-H), 7.51 (dd, ^4J(P,H)=2.2 Hz, ^3J(H,H)=8.2 Hz, 6H, 3*-H), 7.56 (dd, ^3J(P,H)=11.9 Hz, ^3J(H,H)=8.2 Hz, 6H, 25*-H), 7.68 (dd, ^3J(P,H)=11.6 Hz, ^3J(H,H)=8.1 Hz, 6H, 2*-H), 7.69 ppm (dd, ^3J(P,H)=11.5 Hz, ^3J(H,H)=8.1 Hz, 12H, 2-H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, TMS): δ=30.50 (C-11a or C-11b), 30.66 (C-11a or C-11b), 30.87 (C-11*/17*), 41.56 (C-10), 41.87 (C-10*/16*), 68.87 (C-5), 69.20 (C-5* or C-22*), 69.24 (C-5* or C-22*), 114.05 (C-7*/20*), 114.31 (C-7), 125.92 (C-13), 126.10 (d, ^3J(P,C)=12.4 Hz, C-3), 126.20 (C-13*/14*), 127.21 (d, ^3J(P,C)=12.6 Hz, C-3*/24*), 127.78 (C-8), 127.87 (C-8*/19*), 131.09 (d, ^1J(P,C)=105.4 Hz, C-1), 131.40 (C-4), 132.19 (d, ^2J(P,C)=10.0 Hz, C-2/2*), 132.34 (d, ^2J(P,C)=9.8 Hz, C-25*), 141.59 (C-4*/23*), 142.45 (C-4), 143.03 (C-9), 143.57 (C-9*/18*), 147.71 (C-12 or C-12*/15*), 147.75 (C-12 or C-12*/15*), 155.90 (C-6), 156.22 (C-6* or C-21*), 156.28 ppm (C-6* or C-21*), C-1*/C-26* signals missing due to low concentration; IR (ATR): ν=3404 (we, br), 3038 (we, br), 2963, 2927, 2869, 1709, 1604, 1506 (st, P–C_{Phenyl}), 1460, 1401, 1361, 1296, 1222 (st, P═O), 1179 (st), 1113 (st), 1091, 1039, 1015, 827, 674 cm^{-1}; MALDI-TOF-MS (32% laser intensity, matrix: 1,8-dihydroxy-10*H*-anthracen-9-one): *m*/*z* (%)=found 3336.1 (100) $[M+H]^+$, calcd 3334.5 $[M+H]^+$; HRMS calcd for $C_{228}H_{218}O_{16}P_4$ 1667.7592 $[M+2H]^{2+}$, found 1667.7622; elemental analysis (%): $C_{228}H_{216}O_{16}P_4$ (3336.04): calcd C 82.09, H 6.53; found C 81.25, H 6.76.

4.6.2. Compound *12*

Decomposition >340 °C; ^{31}P NMR (202.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=27.32 ppm (s); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.60 (s, 12H, 11*a/11*b-H), 1.61 (s, 6H, 17-H), 1.64 (s, 6H, 11-H), 5.09 (s, 2H, 5-H), 5.17 (d, ^2J(H,H)=15.5 Hz, 2H, 5*a-H or 5*b-H), 5.25 (d, ^2J(H,H)=15.6 Hz, 2H, 5*a-H or 5*b-H), 6.68 (d, ^3J(H,H)=8.7 Hz, 4H, 7*-H), 6.72 (d, ^3J(H,H)=8.6 Hz, 2H, 20-H), 6.76 (d, ^3J(H,H)=8.7 Hz, 2H, 7-H), 6.96 (d, ^3J(H,H)=9.1 Hz, 2H, 19-H), 6.98 (s, 4H, 13*-H), 7.05 (d, ^3J(H,H)=8.7 Hz, 4H, 8*-H), 7.09 (s, 4H, 13/14-H), 7.09 (d, ^3J(H,H)=8.3 Hz, 2H, 8-H), 7.39 (dd, ^4J(P,H)=2.4 Hz, ^3J(H,H)=8.0 Hz, 4H, 3*-H), 7.43 (dd, ^4J(P,H)=2.5 Hz, ^3J(H,H)=8.1 Hz, 2H, 3-H), 7.53 (dd, ^3J(P,H)=11.9 Hz, ^3J(H,H)=8.1 Hz, 2H, 2-H), 7.69 ppm (dd, ^3J(P,H)=11.7 Hz, ^3J(H,H)=8.1 Hz, 4H, 2*-H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, TMS): δ=30.44 (C-11 or C-17), 30.51 (C-11*a or C-11*b), 30.65 (C-11*a or C-11*b), 30.79 (C-11 or C-17), 41.56 (C-10*), 41.73 (C-10 or C-16), 68.86 (C-5*), 69.09 (C-5), 114.11 (C-7), 114.31 (C-7*), 114.69 (C-20), 125.93 (C-13*), 126.04 (C-13 or C-14), 126.15 (d, ^3J(P,C)=11.8 Hz, C-3*), 126.30 (C-13 or C-14), 126.99 (d, ^3J(P,C)=11.6 Hz, C-3), 127.72 (C-8), 127.79 (C-8*/19), 130.60 (d, ^1J(P,C)=105.4 Hz, C-1*), 131.91 (d, ^1J(P,C)=106.2 Hz, C-1), 132.20 (d, ^2J(P,C)=10.0 Hz, C-2*), 132.35 (d, br, ^2J(P,C)=10.7 Hz, C-2), 142.06 (C-4), 142.29 (C-18), 142.61 (C-4*), 143.07 (C-9*), 143.70 (C-9), 147.55 (C-12), 147.71 (C-12*), 147.99 (C-15), 154.32 (C-21), 155.88 (C-6*), 155.93 ppm (C-6); IR (ATR): ν=3046 (br, we, –O–H), 2962, 2924, 2853, 1605, 1507 (st), 1462, 1402, 1296, 1224 (st), 1180 (st), 1115 (st), 1091, 1040, 1016 (st), 908, 828 (st, *p*-disubst. aromatics), 727 (st), 677 cm^{-1} (st); ESI-MS (50 V): *m*/*z* (%)=1007.6 (91) $[M+H]^+$, 1029.5 (13) $[M+Na]^+$, 1045.5 (3) $[M+K]^+$, 2014.0 (100) $[2M+H]^+$, 2036 (28) $[2M+Na]^+$; HRMS calcd for $C_{69}H_{68}O_5P$ 1007.4799 $[M+H]^+$, found 1007.4732.

4.6.3. Compound *13*

Mp 321 °C; ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ=26.54 ppm (s); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C, TMS): δ=1.53 (s, 24H, 11a/11b-H), 1.56 (s, 12H, 11*-H), 4.99 (s, 4H, 5*-H), 5.11 (d, ^2J(H,H)=15.7 Hz, 4H, 5a-H or 5b-H), 5.19 (d, ^2J(H,H)=15.6 Hz, 4H, 5a-H or 5b-H), 6.63 (d, ^3J(H,H)=8.9 Hz, 8H, 7-H), 6.77 (d, ^3J(H,H)=8.8 Hz, 4H, 7*-H), 6.91 (s, 8H, 13-H), 6.99 (d, ^3J(H,H)=8.9 Hz, 8H, 8-H), 7.02 (s, 4H, 13*-H), 7.07 (d, ^3J(H,H)=8.9 Hz, 4H, 8*-H), 7.33 (dd, ^4J(P,H)=2.5 Hz, ^3J(H,H)=8.1 Hz, 8H, 3-H), 7.41 (dd, ^4J(P,H)=2.6 Hz, ^3J(H,H)=8.2 Hz, 4H, 3*-H), 7.51 (dd, ^3J(P,H)=11.8 Hz, ^3J(H,H)=8.2 Hz, 4H, 2*-H), 7.64 ppm (dd, ^3J(P,H)=11.5 Hz, ^3J(H,H)=8.1 Hz, 8H, 2-H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): δ=30.51 (C-11a or C-11b), 30.67 (C-11a or C-11b), 30.88 (C-11), 41.58 (C-10), 41.89 (C-10*), 68.90 (C-5), 69.24 (C-5*), 114.08 (C-7*), 114.34 (C-7), 125.94 (C-13), 126.13 (d, ^3J(P,C)=12.1 Hz, C-3), 126.21 (C-13*), 127.21 (d, ^3J(P,C)=12.4 Hz, C-3*), 127.79 (C-8), 127.88 (C-8*), 131.15 (d, ^1J(P,C)=105.1 Hz, C-1), 132.21 (d, ^2J(P,C)=9.9 Hz, C-2), 132.35 (d, ^2J(P,C)=11.0 Hz, C-2*), 141.59 (C-4*), 142.47 (d, ^4J(P,C)=2.8 Hz, C-4), 143.06 (C-9), 143.60 (C-9*), 147.74 (C-12 or C-12*), 147.76 (C-12 or C-12*), 155.92 (C-6), 156.26 ppm (C-6*); IR (ATR): ν=3037 (we, br), 2963, 2929, 2865, 1605, 1507 (st, P–C_{Phenyl}), 1459, 1402, 1360, 1296, 1225 (st, P═O), 1179 (st), 1113, 1091, 1037, 1016, 825, 729, 676 cm^{-1}; ESI-MS (100 V): *m*/*z* (%)=1667.8 (100) $[M+H]^+$; HRMS calcd for $C_{114}H_{109}O_8P_2$ 1667.7592 $[M+H]^+$, found 1667.7604.

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Supplementary data

Supplementary data for compounds **3**–**6**, **8**, **9**, and **11**–**13** can be found in the online version, at doi:10.1016/j.tet.2009.01.102.

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