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Title: P-chiral 1-phosphanorbornenes: from asymmetric phospha-Diels–Alder reactions towards ligand design and functionalization

A diastereoselective route to P-chiral 1-phosphanorbornenes was established from 2H-phosphole and (5R)-(–)-menthoxyl-2(5H)-furanone as chiral auxiliary, reduction of which followed by stereospecific intramolecular Michael addition gave the chiral 1-phosphanorbornane alcohol as the key to divergent ligand synthesis. Thus, electrophilic substitution at the OH group gave phosphinites, and bromination the bromide, which reacts with nucleophiles to give precursors for chelating chiral bis-phosphanes with great potential as ligands in asymmetric transition metal catalysis.
P-chiral 1-phosphanorbornenes: from asymmetric phospha-Diels–Alder reactions towards ligand design and functionalisation†‡

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The principle of stereotopic face differentiation was successfully applied to 2H-phospholes which undergo a very efficient and highly stereoselective Diels–Alder reaction giving phosphorus-chiral 1-phosphanorbornenes with up to 87% yield. The observed reaction pathway has been supported by theoretical calculations showing that the cycloaddition reaction between 2H-phosphole 3a and the dienophile (5R)-(-)-menthoyloxy-2(5H)-furanone (8) is of normal electron demand. Optically pure phospholes were obtained by separation of the single diastereomers and subsequent desulfurisation of the sulfur-protected phosphorus atom. Finally, divergent ligand synthesis is feasible by reduction of the chiral auxiliary, subsequent stereoselective intramolecular Michael addition, and various functionalisations of the obtained key compound 13a. Furthermore, the unique structural properties of phosphanorbornenes are presented and compared to those of phosphanorbornanes.

Introduction

In the beginning of enantioselective catalysis, ligands in which a chiral coordinating phosphorus atom bears the optical information were used.¹ Today, the most widely applied ligands in asymmetric transition metal catalysis carry their optical information in the chiral backbone of the ligand.² Because of the easy access to this type of molecule, C-chiral ligands have dominated the field of enantioselective catalysis until today. Nevertheless, tremendous efforts in recent years have furnished novel synthetic pathways towards P-chiral phosphanes and triggered a comeback of this class of ligands.³ Most of these synthetic pathways are based on resolution of racemates or diastereomers, kinetic and dynamic–kinetic resolution, and desymmetrisation.⁴ These methods have one common feature: they start from a phosphorus atom with tetrahedral or trigonal-pyramidal coordination. This is in contrast to the main method applied in the generation of C chirality – the principle of stereotopic face differentiation – which starts from a carbon atom with trigonal-planar coordination. Differences in the applied methods are due to different stabilities and accessibility of the starting materials. Compounds with carbon or phosphorus in a tetrahedral or trigonal-pyramidal environment are stable and readily available, as are trigonal-planar carbon compounds (alkenes, ketones, singlet carbenes), whereas the corresponding phosphorus compounds (phospha-alkenes, singlet phosphinidenes) are often not stable or difficult to synthesise.⁵ Therefore, kinetic (sterically demanding groups) or thermodynamic stabilisation (delocalisation or coordination to a metal atom) is necessary to obtain such low-coordinate phosphorus species. The resulting compounds are often expensive and not readily available. Furthermore, their substitution pattern is less suitable for stereoselective synthesis. As a result, there have been only two examples in which the principle of stereotopic face differentiation has been applied. In both cases a chiral substituent at the trigonal-planar phosphorus atom was necessary to obtain optical induction.⁶ Recently, we contributed to this hardly explored field by applying a diastereoselective Diels–Alder reaction to 2H-phospholes.⁷ Even though these compounds with a planar-coordinated phosphorus atom in a five-membered ring are generated in situ, they are readily accessible and their chemistry is well understood.⁸ Herein, we present our detailed investigations on the diastereoselective Diels–Alder reaction of 2H-phospholes and further functionalisation of the obtained 1-phosphanorbornenes for divergent ligand design.
Results and discussion

The asymmetric Diels–Alder reaction of 2H-phospholes

In a first attempt to facilitate a Diels–Alder reaction of a 2H-phosphole, phospholide 1 was protonated in situ and the 2H-phosphole 3a trapped with the chiral dienophile 4 at low temperature to ensure good stereoselectivity (Scheme 1). Usually a dienophile like crotonic acid amide is applied together with a Lewis acid to activate the dienophile and connect it with the chiral auxiliary.6

As a Lewis acid would also interact with the phosphorus atom, deactivating the diene for cycloaddition reactions, the Diels–Alder reaction was performed without adding a Lewis acid. When acetic acid, sulfuric acid, or water were used as protonating reagent, an inseparable product mixture was obtained; using propan-2-ol gave the diastereomerically pure compound 5 (absolute configuration was not determined). Other products or isomers could not be isolated; hence, the de of the crude product could not be determined. Obviously, a Michael addition occurred, probably base-catalysed by the generated lithium isopropanolate. Thus, the synthetic route via protonation of 1 did not seem to furnish the targeted 1-phosphanorbornene 6.

We, therefore, switched to SiMe3, as this group is known to migrate in a [1,5]-sigmatropic shift at low temperatures as well.7a,9 31P{1H} NMR spectroscopic investigations in which the temperature was varied over time revealed that an equilibrium between monomeric 1H-phosphole (~51.5 ppm, s) 2b and only one dimer 7 exists at low temperature (Fig. 1). Monomeric 1H-phosphole 2b rearranges by a [1,5]-sigmatropic shift to 2H-phosphole 3b, which cannot be observed in NMR experiments due to its fast dimerisation to give 7. Only one isomer of the dimer (~49.6 ppm, ~26.2 ppm, d, 1JPP = 202.6 Hz) is formed, and the coupling constant suggests a P–P bond.7b,d Increasing the temperature shifts the equilibrium towards 2b. At room temperature a different isomer of the dimer is formed, and this suggests a kinetically favoured isomer at low temperatures. This system seemed to be suitable for stereoselective Diels–Alder reactions for two reasons: the fast equilibrium between 2b and 7 provides the intermediate 2H-phosphole 3b, which is then available for an additional cycloaddition reaction. Furthermore, 3b seems to react in a highly stereoselective manner in cycloaddition reactions, since only one of its dimers is formed at low temperatures. However, treating 2b/3b with 4 at ~30 °C (addition of SiMe3Cl to a solution of 1 in THF at ~30 °C, 30 min equilibration, addition of 4, 16 h at ~30 °C) and subsequent filtration over silica gave 5 (characterised by 31P{1H} NMR spectroscopy). Therefore, direct trapping of a 2H-phosphole, generated from the corresponding protonated or silylated 1H-phosphole, with 4 did not yield the desired 1-phosphanorbornene.

Generating 2H-phosphole 3a in situ from its corresponding dimer required a chiral dienophile that offers good stereoselectivity at the high temperatures needed for the cycloreversion of the dimer of 3a. These requirements are met by (5R)-(-)-menthyl-2(5H)-furanone (8). Owing to its rigid cyclic structure and fixed chiral centre, which is close to the C=C bond, it has shown high selectivities in cycloaddition reactions.10

As shown previously, this approach resulted in the desired products 9 and 10.6 The yields and selectivities were good to high and the absolute configuration of the obtained isomers was completely determined by NOE NMR spectroscopy and X-ray crystallography (Table 1). The sulphurisation of the phos-
The phosphorus atom made the separation of the single isomers feasible. The molecular structure of \textit{endo}-9d is shown in Fig. 2. However, the synthesis of \textit{C}_2-symmetric bis-phosphanes starting from bis-phospholes\textsuperscript{11} was not successful.\textsuperscript{6}

Furthermore, a detailed explanation of the observed selectivities was given which was supported by DFT calculations. The observed cycloaddition reaction is a Diels–Alder reaction with normal electron demand.\textsuperscript{6} A closer look at the energetic profile of the reaction (Fig. 3) gave further insight into the course of the reaction. Under both conditions (THF at 60 °C and xylenes at 140 °C), \textit{endo}-11a is slightly more thermodynamically stable than \textit{exo}-11a, and the activation enthalpy is smaller for the \textit{endo} transition state, which is in agreement with the observed selectivities. Since the activation enthalpies are very similar under both conditions, a cycloreversion is more likely at higher temperatures.

Deprotection of P-chiral 1-phosphanorbornenes 9a,c,d

After an efficient method to create P-chiral 1-phosphanorbornenes in a stereoselective manner had been established, we focused on their functionalisation. In this context the application in transition metal catalysis is an important aspect. Consequently, desulphurisation of the diastereomerically pure compounds 9a,c,d to yield their trivalent derivatives 11a,c,d was performed with Raney nickel or electron-rich phosphanes like triethylphosphane, which – unlike hyridic reagents such as LiAlH\textsubscript{4} or BH\textsubscript{3}(THF) – tolerate a number of functional groups and selectively reduce the P\textsubscript{v}S bond (Scheme 2). The \textsuperscript{31}P\textsubscript{1}H NMR spectra of the reaction mixture of triethylphosphane and diastereomerically pure 1-phosphanorbornenes 9a,c,d revealed a mixture of products containing \textit{endo} and \textit{exo} diastereomers of 11a,c,d. This suggests that a cycloreversion reaction takes place, in agreement with the computational results. In this regard, heating only diastereomerically pure 9a,c,d in xylenes at 130 °C for 16 h did not result in

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<th>Regioisomers 9 : 10</th>
<th>endo : exo (9, S\textsubscript{C}C\textsubscript{v}C)</th>
<th>Diastereomers: S\textsubscript{C}C\textsubscript{v}C : R\textsubscript{e}C\textsubscript{v}C</th>
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<td>c</td>
<td>140 °C</td>
<td>Xylenes</td>
<td>97 : 3</td>
<td>70 : 30</td>
<td>92 : 8</td>
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<td>d</td>
<td>140 °C</td>
<td>Cylenes</td>
<td>97 : 3</td>
<td>73 : 27</td>
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\textsuperscript{a} Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{b} Sum of yields of separated diastereomers.
transformation into the other diastereomer. Thus, cycloreversion only takes place for the trivalent derivatives 11a,c,d and not for pentavalent 9a,c,d. In the case of endo-11d, only traces of the exo diastereomer were observed in the reaction mixture, and pure endo-11d was isolated in high yield. For endo-9a, endo-9c, exo-9c, and exo-9d, Raney nickel is the reagent of choice and gives the corresponding trivalent compounds 11a, c,d in moderate to good yields. However, it is important to perform the desulfurisation with Raney nickel at room temperature to avoid transformation into the other diastereomer. A transition metal complex, namely, [W(CO)₅(endo-11a)], has been obtained previously.²

Functionalisation of 1-phosphanorbornenes

Functionalisation of the 1-phosphanorbornenes should facilitate an efficient ligand design. As an improved synthesis compared to the reported one⁶ afforded endo-9a on a multigram scale, this derivative was studied first. In general, the different functional groups in endo-9a allow various modifications. However, when introduction of a second donor group is considered, functionalisation of the C=C bond employing hydroboration or epoxidation followed by ring opening would result in regioisomers with uncontrollable regioselectivity. Furthermore, introducing another donor group at the α position of the carbonyl group via the enolate would result in an anti position to the phosphorus atom and thus the resulting compound could not act as a chelating ligand. We, therefore, focused on functionalisation of the menthloyx-furanone ring. Reductive cleavage of the chiral auxiliary gave diol 12a (Scheme 3). For further modifications, sulfur protection was necessary due to a higher tolerance of the P=S group towards various reagents (see further discussion). A selective chemical transformation of only one of the two OH groups in diol 12a seems challenging. However, treatment of 12a with a strong base resulted in a Michael addition of the OH group in the 4-position relative to the phosphorus atom. The overall yield of 13a over a two-step process is good. The intramolecular Michael addition is regio- and stereospecific, since only the OH group in 4-position to the phosphorus atom can attack the C=C bond; the attack proceeds anti to the bridge of the 1-phosphanorbornene. Consequently this transformation is restricted to the endo isomers. This simple and facile derivatisation of endo-9a prompted us to expand this synthetic strategy to endo-9c and endo-9d. The additional challenge in these two cases is the generation of a second stereogenic centre in α position to the phosphorus atom, which does not proceed in a stereospecific manner (Scheme 4). Reduction of endo-9c gives diol 12c in moderate yield due to low solubility of 12c in common organic solvents (see Exp. Section). The subsequent intramolecular Michael addition is an equilibrium reaction. Full conversion of 12c could not be observed. Furthermore, when the pure isomer (S)-13c (obtained by fractional crystallisation) was treated with KOt(Bu) in THF, the formation of 12c and (R)-13c was observed by 31P(1H) NMR spectroscopy; after 20 h at room temperature an equilibrium was reached showing the ratio 12c : (R)-13c : (S)-13c = 2 : 33 : 66.

M06-2X/MG3S calculations showed that the difference in energy between the two diastereomers is very small (3.5 kJ mol⁻¹), and thus thermodynamic control of the reaction is impossible, in agreement with the observed selectivities. Varying the base or temperature gave neither full conversion of 12c nor improved stereoselectivity, so that kinetic control of the reaction is impossible as well. Therefore, functionalisation by reductive cleavage and subsequent Michael addition is only applicable to endo-9a.

Crystals of both diols (12a and 12c) and all three alcohols (13a, (R)-13c and (S)-13c) suitable for crystal structure analysis were obtained, and thus the absolute configurations of (R)-13c and (S)-13c could be deduced (Fig. 4 and 5). Comparing the molecular structures of 12a and 13a reveals the unique structural features of a 1-phosphanorbornene in contrast to a 1-phosphanorbornane (Fig. 4). The biggest difference between the two structures is observed for the σ bonds in the six-
Fig. 4 Molecular structures of 12a (left) and 13a (right); ellipsoid level at 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths (in pm): 12a: S(1)–P(1) 194.47(4), P(1)–C(1) 184.5(1), P(1)–C(5) 179.3(1), P(1)–C(6) 180.4(1), C(1)–C(2) 156.6(1), C(2)–C(5) 158.2(1), C(3)–C(4) 153.1(1), C(3)–C(6) 154.3(2), C(4)–C(5) 133.4(1), C(2)–C(7) 151.8(1); 13a: S(1)–P(1) 195.1(1), P(1)–C(1) 183.0(1), P(1)–C(5) 181.4(1), P(1)–C(6) 180.9(9), C(1)–C(2) 156.1(2), C(2)–C(3) 156.2(2), C(3)–C(4) 156.6(1), C(3)–C(6) 153.6(1), C(4)–C(5) 155.5(2), C(2)–C(7) 151.4(2).

Fig. 5 Molecular structures of 12c (top), (R)-13c (centre), (S)-13c (bottom); ellipsoid level at 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths (in pm) and angles (in °): 12c: S(1)–P(1) 193.8(1), P(1)–C(1) 184.5(1), P(1)–C(5) 181.3(2), P(1)–C(6) 180.0(2), C(1)–C(2) 156.7(2), C(2)–C(3) 158.1(2), C(3)–C(4) 153.5(2), C(4)–C(5) 135.1(2), O(2)–C(8) 142.7(2), C(4)–C(3)–C(2) 109.4(1), C(5)–P(1)–C(1) 101.6(6), (R)-13c: S(1)–P(1) 195.0(8), P(1)–C(1) 181.4(2), P(1)–C(5) 182.6(2), P(1)–C(6) 181.0(2), C(1)–C(2) 155.4(2), C(2)–C(3) 155.7(2), C(3)–C(4) 157.0(2), C(4)–C(5) 157.8(2), O(2)–C(18) 142.9(2), C(4)–C(3)–C(2) 99.3(1), C(5)–P(1)–C(1) 105.9(7), (S)-13c: S(1)–P(1) 194.2(9), P(1)–C(1) 182.6(1), P(1)–C(5) 183.9(2), P(1)–C(6) 182.1(1), C(1)–C(2) 155.5(2), C(2)–C(3) 156.0(2), C(3)–C(4) 156.2(2), C(4)–C(5) 158.9(2), O(2)–C(8) 142.3(2); C(4)–C(3)–C(2) 99.6(8), C(5)–P(1)–C(1) 102.1(4).

Scheme 5 Synthesis of phosphinites 14.
structurally characterised (Fig. 6). Unfortunately, a subsequent sulfur deprotection of 14a,b was not successful with the methods described in Scheme 2. 31P{1H} NMR spectroscopic studies showed that only the endocyclic phosphorus atom and not the exocyclic one is desulfurised.

Since preparation of the phosphane–phosphinite ligands (deprotected 14a,b) was not successful, another approach was pursued to obtain bis-phosphanes having only P–C bonds (Scheme 6). Bromination of 13a with Br2PPh3 gave bromide 15 in excellent yield. However, the following nucleophilic substitution turned out to be challenging. Treating 15 with LiPPh2 resulted in elimination of HBr giving 16; apparently, the exocyclic proton in α position is rather acidic. Nevertheless, applying the less basic lithium phospholide 1 followed by sulfur protection afforded the desired product 17 in excellent yield. The thio phospholide group of 17 can now be employed in other asymmetric Diels–Alder reactions. The basicity of lithium phosphanides like LiPPh2 can be reduced by coordination to borane. Accordingly, LiP(BH3)Ph2 gave access to 18 in good yield. Compound 18 was fully characterised, also by X-ray crystallography (Fig. 7). Since no reducible groups, such as the P–O bond in 14a,b are present, sulfur deprotection was performed under very mild conditions with LiAlH4. The corresponding bis-phosphane was isolated as bis-borane adduct 19 in good yield. 31P{1H} NMR studies showed that its trivalent species 20 can be generated quantitatively in situ with morpholine; however, 20 was not isolated.

Conclusions
A diastereoselective synthetic route towards P-chiral 1-phospha-norbornenes has been established by using the principle of

Fig. 6 Molecular structures of 14a (left) and 14b (right); ellipsoid level at 50%. Hydrogen atoms are omitted for clarity. Selected bonds lengths (in pm): 14a: S(1)–P(1) 194.71(6), S(2)–P(2) 193.50(6), C(1)–C(8) 150.1(3), O(2)–C(8) 145.7(2); 14b: S(1)–P(1) 194.60(7), S(2)–P(2) 193.68(7), C(1)–C(8) 151.3(2), O(2)–C(8) 144.9(2).

Scheme 6 Bromination of 13a and subsequent nucleophilic substitution at 15.
stereotopic face differentiation. The observed reaction pathway was supported by theoretical calculations showing that the cycloaddition reaction between 2H-phosphate 3a and dienophile 8 is of normal electron demand. The phosphorus atom in the obtained Diels–Alder products 9a,c,d was easily desulphurised to give the corresponding trivalent species 11a,c,d. Further functionalisation yielded alcohol 13a as a key compound for divergent ligand synthesis. A subsequent electrophilic substitution at the OH group gave phosphinites which are sensitive towards hydrolysis. This problem was overcome by phosphorus and the desired nucleophilic substitution products (17 and 18) were obtained. The phosphines presented in this work are expected to be very useful as ligands in asymmetric transition metal catalysis.

**Experimental**

**General methods**

All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and distilled from potassium. The argon. THF was degassed and distilled from potassium. All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and distilled from potassium. The elemental lithium were carried out under dry high purity nitrogen using standard Schlenk techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and distilled from potassium.

**Synthesis of 5.** Isopropanol was added at −30 °C to a 0.11 M stock solution of 1-lithium-3,4-dimethyl phosphole (see synthesis of 9a) in THF (5.0 ml, 0.55 mmol). The solution was stirred at this temperature for one hour; then crotonic acid amide 4 (0.13 g, 0.54 mmol) was added. After 72 hours at −30 °C, the solution was warmed to room temperature, sulfur (0.018 g, 0.56 mmol) and three drops of triethylamine were added and the solution was stirred for 16 hours at room temperature. Chromatographic workup (hexanes/diethyl ether = 1 : 2, v/v) of the crude product gave 5 as a white solid. Yield: 0.18 g, 87%. Rf (hexanes/diethyl ether = 1 : 3, v/v) = 0.22 – UV light, iodine. m.p.: 58–60 °C. [α]D 25 = +37.9° (c = 2.35 in toluene).

**In situ generation of 2b and 7.** A 0.11 M stock solution of 1-lithium-3,4-dimethyl phosphole (see synthesis of 9a) in THF (0.6 ml, 0.07 mmol) in an NMR tube was frozen in liquid nitrogen. Afterwards SiMe2Cl (2–3 fold excess) was added and the sample was equilibrated in the NMR machine at the given temperature. 31P{1H} NMR (162 MHz, no deuterated solvent): δ = 61.5 ppm. IR (KBr): v = 3453 (s), 2963 (m, νC–H), 2345 (w), 1179 (s), 1699 (s), 1631 (m), 1543 (w), 1456 (m), 1387 (m), 1262 (m), 1217 (m), 1102 (m), 1121 (w), 802 (m), 763 (w), 603 (2H, d, δJHP = 30.4 Hz), 7.18–7.25 (2H, m), 7.26–7.40 (3H, m) ppm. 13C{1H} NMR (76 MHz): δ = 18.7 ppm. MS (ESI, DCM/MeOH): m/z: calculated for C20H24NO3PS [M + Na]+: 412.1; found: 412.2. C20H24NO3PS (389.45): calculated: C 61.68%, H 6.21%; found: C 61.63%, H 6.19%.

**Synthesis of endo-9a: endo-9a was synthesised by a modified method reported before.** A mixture of 3,4-dimethyl-1-phenylphosphole (2b) (7.05 g, 37.55 mmol) and Pieces of lithium (excess) in 200 ml THF was stirred at room temperature for 3–4 hours (conversion was monitored by TLC, with phosphomolybdic acid). The deep brown solution was filtered, cooled to −80 °C and oxygen-free water (4.05 ml, 225 mmol) was added dropwise. After complete addition, the solution was kept at −80 °C for 5 minutes and then warmed to room temperature over 30 minutes. Afterwards, the solution was dried over MgSO4, filtered and added to a flask containing (5R)- (1-methoxy)-2-(5H)-furanone (8) (7.44 g, 31.2 mmol). The pale yellow solution was heated at 63 °C for 24 hours. Sulfur (1.25 g, 39.2 mmol) and two drops of triethylamine were added and the solution was kept at 40 °C for 18 hours. After cooling to rt, the solvent was removed in vacuum and the crude product was purified by recrystallisation (isopropanol/hexanes = 3 : 5, v/v) to give the main diastereomer endo-9a as a...
white solid. Compound 10 could not be isolated. Yield: 9.66 g, 81%. Rf (hexanes/diethyl ether = 1:1, v/v) = 0.33 – para-ani-


1H NMR (400 MHz): δ = 0.75 (3H, d, JHH = 6.9 Hz), 0.81–0.91 (1H, m), 0.84 (3H, d, JHH = 7.1 Hz), 0.91–1.04 (2H, m), 0.93 (3H, d, JHH = 6.5 Hz), 1.19–1.29 (1H, m), 1.30–1.40 (1H, m), 1.63 (3H, s), 1.61–1.65 (2H, m), 1.94 (3H, s), 1.91–1.97 (1H, m), 2.02–2.08 (2H, m), 2.11–2.18 (1H, m), 3.13–3.20 (1H, m), 3.25–3.31 (1H, m), 3.50 (1H, ddd, JHH = 10.7 Hz, JHH = 10.7 Hz, JHH = 2.4 Hz), 5.49 (1H, d, JHH = 13.0 Hz), 5.90 (1H, d, JHH = 26.3 Hz). ppm. 13C{1H} NMR (101 MHz): δ = 15.7 (s), 18.6 (d, JCP = 14.2 Hz), 19.3 (d, JCP = 16.2 Hz), 20.9 (s), 22.2 (s), 23.1 (s), 25.4 (s), 31.5 (s), 34.2 (s), 40.0 (s), 47.5 (s), 48.6 (d, JCP = 46.6 Hz), 50.9 (d, JCP = 21.7 Hz), 53.5 (s), 56.5 (d, JCP = 57.6 Hz), 78.7 (s), 99.5 (d, JCP = 5.9 Hz), 121.1 (d, JCP = 69.3 Hz), 165.5 (d, JCP = 7.2 Hz), 173.6 (d, JCP = 3.0 Hz). ppm. 31P{1H} NMR (162 MHz): δ = 48.7 ppm. IR (KBr): ν = 1355 (m), 2935 (s, νC–H), 2925 (s, νC–H), 2870 (m, νC–H). 1766 (s), 1603 (s), 1533 (m, 1565 (m), 1456 (m), 1436 (m), 1414 (m), 1385 (m), 1371 (m), 1346 (m), 1303 (w), 1244 (m), 1231 (m), 1203 (w), 1178 (s), 1166 (s), 1119 (s), 1074 (m), 1038 (m), 1010 (m), 989 (s), 975 (s), 942 (s), 902 (m), 890 (m), 858 (w), 848 (w), 833 (m), 819 (m), 776 (m), 740 (s), 723 (s), 708 (m), 678 (s), 631 (w), 420 (s). cm−1. HRMS (ESI, MeOH): m/z: calculated for C29H22O13PS [M + Na]+: 531.1605; found: 531.1584. C29H22O13PS (382.50): calculated: C 62.8%, H 8.17%; found: C 63.4%, H 8.23%.

General procedure for the activation of Raney nickel

In a Schlenk flask under nitrogen atmosphere solid NaOH was added to a vigorously stirred suspension of an aluminum-nickel alloy (Raney type) in 20 ml of water portionwise in such a manner that the gas evolution was kept under control (caution: initiation time required, solution warms up!). In this process, the greyish metal alloy turned into a dark black solid.

After the gas evolution had ceased, the reaction mixture was stirred at 80 °C for one hour. The clear solution was decanted and the black metal was washed with 15 ml portions of water under vigorous stirring until a pH of 8–9 was accomplished (usually 6–8 washing steps). Afterward, the Raney nickel was washed three times with 15 ml of ethanol and twice with 15 ml of THF. After desulphurisation was completed, the nickel waste was destroyed by addition of diluted HCl and subsequently concentrated HCl.

Synthesis of endo-11a. A suspension of freshly prepared Raney nickel (2.02 g, excess) and endo-9c (0.310 g, 0.676 mmol) in 15 ml of THF was stirred for 30 hours at room temperature. The solution was filtered and the black solid was washed with three times with 15 ml of THF. Chromatographic workup (toluene) gave endo-11c as a white solid. Yield: 0.213 g, 75%. Rf (toluene) = 0.40 – UV light, para-ani-

salddehyde. m.p.: 128–130 °C. [α]D 25 = +260° (c = 1.27 in toluene). 1H NMR (300 MHz): δ = 0.74 (3H, d, JHH = 6.9 Hz), 0.64–1.03 (9H, m), 1.06–1.20 (1H, m), 1.20–1.32 (1H, m), 1.35–1.49 (1H, m), 1.50–1.74 (3H, m), 1.70–1.84 (1H, m), 1.94 (3H, s), 1.99–2.13 (1H, m), 3.00–3.24 (2H, m), 3.36 (1H, ddd, JHH = 10.4 Hz, JHH = 10.4 Hz, JHH = 4.1 Hz), 5.06 (1H, d, JHH = 7.1 Hz), 7.20–7.41 (5H, m). ppm. 13C{1H} NMR (76 MHz): δ = 15.0 (s), 15.7 (s), 20.2 (s), 20.8 (s), 22.1 (s), 23.1 (s), 25.4 (s), 31.3 (s), 34.2 (s), 39.8 (s), 46.8 (d, JCP = 21.3 Hz), 47.6 (s), 51.0–51.2 (m), 64.5 (d, JCP = 6.3 Hz), 77.1 (s), 101.0 (d, JCP = 10.6 Hz), 127.0 (s), 128.4 (s), 129.0 (d, JCP = 6.8 Hz), 136.8–139.3 (m), 153.9 (s), 175.6 (s). ppm. 31P{1H} NMR (162 MHz): δ = −14.5 ppm. IR (KBr): ν = 3445 (s), 2963 (s, νC–H), 2922 (s, νC–H), 2868 (m, νC–H), 1754 (s, νO–C=O), 1631 (w), 1558 (w), 1506 (w), 1489 (w), 1456 (m), 1442 (w), 1386 (m), 1379 (m), 1351 (s), 1331 (m), 1298 (w), 1262 (w), 1246 (w), 1200 (m), 1168 (s), 1129 (m), 1106 (s), 1074 (m), 1038 (w), 1007 (w), 987 (m), 973 (w), 938 (s), 879 (w), 847 (w), 813 (w), 790 (w), 754 (w), 703 (m), 671 (w), 633 (w), 611 (w), 541 (w), 514 (w), 492 (w), 475 (w), 448 (w), 439 (w), 417 (w), 408 (w) cm−1. MS (ESI, MeOH): m/z: calculated for C29H22O13P [M + Na]+: 449.2; found: 449.3. C29H22O13PS (426.53): calculated: C 73.2%, H 8.27%; found: C 73.3%, H 8.14%.

Synthesis of exo-11c. A suspension of freshly prepared Raney nickel (2.01 g, excess) and exo-9c (0.329 g, 0.717 mmol) in 15 ml of THF was stirred for 30 hours at room temperature. The solution was filtered and the black solid was washed three times with 15 ml of THF. Chromatographic workup (toluene) gave exo-11c as a white solid. Yield: 0.267 g, 87%. Rf (toluene) = 0.42 – UV light, para-ani-
salddehyde. m.p.: 55–57 °C. [α]D 25 = −188° (c = 3.60 in toluene). 1H NMR (300 MHz): δ = 0.80 (3H, d, JHH = 6.9 Hz), 0.87 (3H, d, JHH = 7.0 Hz), 0.71–1.08 (3H, m), 0.94 (3H, d, JHH = 6.5 Hz), 1.14–1.42 (3H, m), 1.51
Synthesis of endo-11d. A solution of endo-9d (0.35 g, 0.75 mmol) and PET (0.25 ml, 1.7 mmol) in 5 ml of xylene was heated at 130 °C for 5 hours. Chromatographic workup (hexanes/diethyl ether = 5:1 to 3:1, v/v) gave endo-11d as a white solid. Yield: 0.30 g, 93%. R₅ (hexanes/diethyl ether = 2:1, v/v) = 0.35 – UV light, para-anisaldehyde. m.p.: 129-131 °C. [α]D²⁵ = -27.2° (c = 1.62 in toluene). ¹H NMR (300 MHz): δ = 0.67 (3H, d, J_H,H = 6.9 Hz), 0.80 (3H, d, J_H,H = 7.0 Hz), 0.59-0.99 (3H, m), 0.88 (3H, d, J_H,H = 6.5 Hz), 1.10-1.30 (2H, m), 1.32-1.44 (1H, m), 1.50-1.62 (3H, m), 1.65 (3H, s), 1.95 (3H, s), 2.00-2.09 (1H, m), 2.09-2.18 (1H, m), 2.95-3.18 (2H, m), 3.31 (1H, d, J_H,H = 10.6 Hz, J_H,H = 10.6 Hz, J_H,H = 7.7 Hz), 5.58 (1H, d, J_H,H = 8.3 Hz), 7.06-7.12 (1H, m), 7.16-7.27 (1H, m), 7.44-7.75 (1H, m), 8.43-8.60 (1H, m) ppm. ¹³C¹H NMR (76 MHz): δ = 15.0 (s), 15.8 (s), 20.1 (s), 20.9 (s), 22.4 (s), 23.2 (s), 25.5 (s), 31.5 (s), 34.4 (s), 40.1 (s), 46.3 (d, J_C,P = 21.8 Hz), 47.6 (s), 50.9 (d, J_C,P = 5.6 Hz), 52.2 (s), 65.1 (d, J_C,P = 6.7 Hz), 77.5 (s), 102.7 (d, J_C,P = 10.0 Hz), 121.3 (s), 123.1 (d, J_C,P = 4.1 Hz), 135.8 (s), 140.6 (d, J_C,P = 18.1 Hz), 149.4 (s), 155.8 (s), 157.2 (d, J_C,P = 17.3 Hz), 175.5 (s) ppm. ³¹P¹H NMR (162 MHz): δ = -13.6 ppm. IR (KBr): ν = 3424 (s), 2949 (s, ν-C-H), 2864 (m, ν-C-H), 1739 s ( ν-O-C=O), 1603 (m), 1584 (s), 1563 (w), 1460 (s), 1433 (m), 1411 (w), 1386 (m), 1357 (m), 1281 (w), 1262 (w), 1245 (w), 1205 (m), 1180 (s), 1156 (m), 1128 (s), 1114 (s), 1040 (w), 1011 (m), 987 (m), 970 (w), 944 (s), 916 (m), 879 (w), 843 (w), 798 (w), 777 (m), 751 (w), 719 (w), 704 (w), 681 (m), 645 (w), 612 (w), 541 (w), 492 (w), 469 (w), 448 (w), 440 (w), 423 (w) cm⁻¹. MS (ESI, MeOH): m/z: calculated for C₂₃H₃₄NO₃P [M+Na]⁺: 450.2; found: 450.3. C₂₃H₃₄NO₃P (427.52): calculated: C 70.2%, H 8.02%; found: C 70.1%, H 8.08%. Synthesis of exo-11d. A suspension of freshly prepared Raney nickel (2.08 g, excess) and exo-9d (0.320 g, 0.696 mmol) in 15 ml of THF was stirred for 43 hours at room temperature. The solution was filtered and the black solid was washed three times with 10 ml of THF. Chromatographic workup (hexanes/diethyl ether = 2:1, v/v) gave exo-11d as a white solid. Yield: 0.211 g, 71%. R₅ (hexanes/diethyl ether = 2:1, v/v) = 0.25 – UV light, para-anisaldehyde. m.p.: 58-60 °C, [α]D²⁵ = -170° (c = 2.27 in toluene). ¹H NMR (300 MHz): δ = 0.70 (3H, d, J_H,H = 6.9 Hz), 0.77 (3H, d, J_H,H = 7.0 Hz), 0.57-0.59 (3H, m), 0.86 (3H, d, J_H,H = 6.4 Hz), 1.01-1.32 (3H, m), 1.33-1.47 (1H, m), 1.48-1.64 (2H, m), 1.57 (3H, s), 1.93 (3H, s), 1.96-2.03 (1H, m), 2.03-2.11 (1H, m), 2.51-2.59 (1H, m), 2.61-2.73 (1H, m), 3.46 (1H, d, J_H,H = 10.6 Hz, J_H,H = 10.6 Hz, J_H,H = 4.1 Hz), 5.48 (1H, d, J_H,H = 9.0 Hz), 7.04 (1H, dd, J_H,H = 7.7 Hz, J_H,H = 4.8 Hz), 7.19 (1H, dd, J_H,H = 7.7 Hz), 7.57 (1H, dd, J_H,H = 7.7 Hz, J_H,H = 7.7 Hz), 8.51 (1H, d, J_H,H = 4.8 Hz) ppm. ¹³C¹H NMR (76 MHz): δ = 13.4 (s), 15.7 (s), 17.7 (s), 20.8 (s), 22.2 (s), 23.2 (s), 25.4 (s), 31.3 (s), 34.3 (s), 39.7 (s), 41.7 (d, J_C,P = 7.2 Hz), 47.7 (s), 48.8 (s), 49.3 (d, J_C,P = 19.2 Hz), 64.3 (d, J_C,P = 6.6 Hz), 76.4 (s), 101.1 (d, J_C,P = 29.9 Hz), 121.3 (s), 122.8 (d, J_C,P = 6.7 Hz), 135.9 (s), 142.8 (d, J_C,P = 14.8 Hz), 149.4 (s), 156.5 (d, J_C,P = 19.8 Hz), 157.8 (s), 174.7 (s) ppm. ³¹P¹H NMR (162 MHz): δ = -12.1 ppm. IR (KBr): ν = 3440 (s), 2961 (s, ν-C-H), 2925 (s, ν-C-H) 2868 (m, ν-C-H), 1767 (s, ν-O-C=O), 1717 (w), 1608 (m), 1584 (m), 1564 (w), 1527 (w), 1506 (w), 1464 (m), 1432 (w), 1386 (w), 1348 (w), 1261 (m), 1160 (m), 1097 (s), 1050 (m), 978 (w), 943 (m), 921 (w), 868 (w), 802 (w), 747 (w), 681 (w), 647 (w), 542 (w), 521 (w), 469 (w), 440 (w), 429 (w), 409 (w) cm⁻¹. MS (ESI, MeOH): m/z: calculated for C₂₃H₃₄NO₃P [M+Na]⁺: 450.2; found: 450.3. C₂₃H₃₄NO₃P (427.52): calculated: C 70.0%, H 8.02%; found: C 70.1%, H 8.13%.
Synthesis of 13a. A solution of endo-9a (12.91 g, 33.8 mmol) in 150 ml THF was added at 0 °C over 5 minutes to a mixture of LiAlH₄ (2.56 g, 67.5 mmol) in 50 ml THF. The cooling bath was removed and the solution was left to stir for 20 hours. The reaction was quenched by slowly adding a solution of KOH (3.1 g in 10 ml degassed water) at 0 °C. The slurry was heated to 60 °C for one hour and then cooled to room temperature. The mixture was filtered and the residue was washed with 200 ml of THF. The combined filtrates were treated with sulfur (1.20 g, 37.4 mmol) and 0.50 ml of triethylamine, and the solution was stirred at 55 °C for 16 hours. The solvent was removed under vacuum, the residue transferred to a pad of silica and washed with a mixture of hexanes/diethyl ether (1:1, v/v). Crude 12a was eluted by washing the silica pad with a mixture of DCM/methanol (1:1, v/v). The solvent was removed and the residue was dissolved in a solution of NaOEt (232.28) in 170 ml of ethanol (prepared by dissolving sodium (1.60 g, 60.2 mmol) in 200 ml of THF. The combined filtrates were treated with sulfur (0.050 g, 1.6 mmol) and three drops of triethylamine were added and the solution was stirred at 110 °C for one hour. After chromatographic workup (DCM/Methanol = 60:1 to 10:1, v/v) 12c was obtained as a white solid. Crystals suitable for X-ray diffraction measurements were obtained from DCM.

Yield: 0.072 g, 45%. Rf (DCM/methanol = 40:1, v/v) = 0.96 - iodine. m.p.: 198–200 °C (c = 0.795 in DMSO).

1H NMR (400 MHz): δ = 1.54 (3H, s), 1.94 (3H, d, J_HH = 2.7 Hz), 2.00–2.10 (2H, m), 2.61–2.72 (1H, m), 2.85–2.98 (1H, m), 3.54–3.63 (1H, m), 3.73–3.82 (1H, m), 3.83–3.91 (1H, m), 4.20–4.31 (1H, m), 7.26–7.30 (2H, m), 7.34 (1H, t, J_HH = 7.4 Hz), 7.42 (2H, t, J_HH = 7.4 Hz) ppm. 13Cl[4](H) NMR (101 MHz): δ = 16.0 (d, J_C,P = 11.6 Hz), 20.3 (d, J_C,P = 16.9 Hz), 45.1 (d, J_C,P = 41.6 Hz), 48.4 (d, J_C,P = 22.8 Hz), 52.6 (s), 53.6 (d, J_C,P = 56.8 Hz), 59.5 (d, J_C,P = 6.2 Hz), 59.8 (d, J_C,P = 3.7 Hz), 127.8 (d, J_C,P = 1.6 Hz), 128.3 (s), 129.5 (d, J_C,P = 5.1 Hz), 132.1 (d, J_C,P = 9.5 Hz), 132.8 (d, J_C,P = 64.3 Hz), 154.6 (d, J_C,P = 13.7 Hz) ppm. 13P(1)H NMR (162 MHz): δ = 56.1 ppm. IR (KBr): δ = 3424 s (2H, s, C-H), 2927 s (s, C-H), 1631 (m), 1606 (s), 1458 (m), 1456 (m), 1440 (s), 1385 (w), 1372 (w), 1344 (w), 1319 (w), 1261 (m), 1223 (w), 1151 (w), 1135 (m), 1106 (m), 1176 (m), 1037 (s), 938 (w), 902 (w), 883 (w), 802 (m), 793 (m), 785 (m), 763 (m), 734 (w), 708 (s), 638 (m), 563 (w), 502 (w), 495 (w), 449 (w) cm⁻¹.

Synthesis of (R)-13c and (S)-13c. A solution of endo-9c (1.2 g, 2.6 mmol) in 5 ml THF was added to a suspension of LiAlH₄ (0.19 g, 5.0 mmol) in 10 ml THF at 0 °C. The cooling bath was removed and the solution was left to stir for 5 h. The reaction was quenched by the addition of 4 ml of an aqueous sodium hydroxide solution (32%). 15 ml of THF and MgSO₄ were added, the suspension was transferred onto a frit and the white solid was continuously extracted with THF for 12 h. Sulfur (0.09 g, 2.8 mmol) and three drops of triethylamine were added and the solution was left to stir for 11 days. After chromatographic workup (DCM/Methanol = 50:1) a mixture of (R)-13c and (S)-13c was obtained as a white solid. Analytical amounts of the separated diastereomers as well as crystals suitable for X-ray diffraction measurements were obtained by recrystallisation from DCM/hexanes. Yield: 0.37 g, 45%.

(S)-13c: Rf (DCM/methanol = 40:1, v/v) = 0.14 - iodine, m.p.: 167–169 °C (c = 1035 in CHCl₃). 1H NMR (300 MHz): δ = 0.85 (3H, s), 1.21 (3H, s), 2.26 (1H, ddd, J_HH = 13.4 Hz), J_HP = 9.9 Hz, J_HP = 2.2 Hz), 2.37 (1H, dd, J_HH = 13.4 Hz, J_HP = 6.5 Hz), 2.52–2.67 (2H, m), 2.67–2.84 (1H, m), 3.55 (1H, dd, J_HP = 13.9 Hz, J_HP = 2.2 Hz), 3.99–4.19 (3H, m), 4.21–4.37 (1H, m), 7.17–7.42 (5H, m) ppm. 13Cl[4](H) NMR (76 MHz): δ = 15.8 (d, J_C,P = 15.1 Hz), 20.9 (d, J_C,P = 2.6 Hz), 40.7 (d, J_C,P = 47.7 Hz), 45.1 (d, J_C,P = 49.7 Hz), 46.9 (d, J_C,P =
Synthesis of 14b. Chlorodimesitylphosphene (0.81 g, 2.61 mmol) was added to a solution of 13a (0.41 g, 1.8 mmol) and triethylamine (0.74 ml, 5.3 mmol) in 20 ml DCM at 0 °C. After 15 min the cooling bath was removed and the solution was stirred for another 30 min at room temperature. Subsequently, sulfur (excess) was added and the solution stirred for 16 h after which the reaction was quenched with 100 μl of isopropanol. Chromatographic workup (hexanes/diethyl ether = 2:1 to 1:1, v/v) gave 14b as a white solid. Crystals suitable for X-ray diffraction measurements were obtained from DCM/hexanes at 4 °C. Yield: 0.28 g, 30%. Rf (hexanes/diethyl ether = 1:3, v/v) = 0.16 – 0.17 (iodoxy). m.p.: 188–190 °C. Due to the small amount of pure (R)-13b, only NMR and MS data were obtained. 1H NMR (300 MHz): δ = 1.34 (3H, s), 1.42 (3H, d, JCH = 1.8 Hz), 1.94 (1H, dd, JCH = 6.9 Hz, JHH = 13.0 Hz), 2.14 (1H, dd, JCH = 8.2 Hz, JHH = 13.0 Hz), 2.14 (1H, s [br]), 2.57–2.68 (1H, m), 2.71–2.86 (1H, m), 3.17 (1H, d, JCH = 19.8 Hz), 3.79–3.95 (2H, m), 3.99–4.13 (3H, m), 7.27–7.38 (3H, m), 7.63–7.74 (2H, m) ppm. 31P{1H} NMR (76 MHz): δ = 19.2 (d, JPC = 14.5 Hz), 24.2 (d, JPC = 8.8 Hz), 39.5 (d, JPC = 54.3 Hz), 46.3 (d, JPC = 43.0 Hz), 47.5 (d, JPC = 2.1 Hz), 51.8 (d, JPC = 17.9 Hz), 56.0 (d, JPC = 42.0 Hz), 58.3 (d, JPC = 3.4 Hz), 65.8 (s), 86.7 (d, JPC = 3.2 Hz), 127.3 (d, JPC = 2.2 Hz), 128.2 (s), 130.3 (d, JPC = 6.7 Hz), 132.2 (d, JPC = 4.3 Hz) ppm. 31P{1H} NMR (162 MHz): δ = 51.0 ppm. MS (ESI, DCM/MeOH): m/z: calculated for C16H18O2PS [M + Na]+: 331.1; found: 333.1.

Synthesis of 14a. Chlorodiphosphoxydiphenilphosphane (0.067 g, 0.30 mmol) was added to a solution of 13a (0.048 g, 0.21 mmol) and triethylamine (0.10 ml, 0.72 mmol) in 6 ml DCM at 0 °C. After 15 min the cooling bath was removed and the solution was stirred for another 30 min at room temperature. Subsequently, sulfur (0.022 g, 0.67 mmol) was added and the solution stirred for 16 h. Then the reaction was quenched with 20 μl of isopropanol. Chromatographic workup (hexanes/diethyl ether = 1:1 to 1:1, v/v) gave 14a as a white solid. Crystals suitable for X-ray diffraction measurements were obtained from DCM/hexanes at 4 °C. Yield: 0.086 g, 93%. Rf (hexanes/diethyl ether = 1:3, v/v) = 0.32 – UV light, iodine. m.p.: 184–186 °C. [α]D20 = −9.6° (c = 1.77 in chloroform). 1H NMR (400 MHz): δ = 1.19 (3H, s), 1.24 (3H, s), 1.82–1.98 (2H, m), 2.00–2.12 (1H, m), 2.18–2.32 (1H, m), 2.45–2.58 (1H, m), 2.77–2.93 (1H, m), 3.93 (1H, dd, JHH = 10.2 Hz, JCH = 5.8 Hz), 4.19 (1H, d, JCH = 10.2 Hz), 4.27–4.40 (1H, m), 4.40–4.50 (1H, m), 7.38–7.58 (6H, m), 7.81–7.97 (4H, m) ppm. 31P{1H} NMR (101 MHz): δ = 18.2 (d, JPC = 15.7 Hz), 23.9 (d, JPC = 7.3 Hz), 40.3 (d, JPC = 52.2 Hz), 41.6 (d, JPC = 44.8 Hz), 43.1 (dd, JPC = 46.5 Hz, JPC = 9.1 Hz), 47.3 (d, JPC = 2.0 Hz), 51.5 (d, JPC = 18.7 Hz), 60.3 (dd, JPC = 5.3 Hz, JPC = 5.3 Hz), 66.2 (s), 86.3 (d, JPC = 1.4 Hz), 128.6 (dd, JPC = 13.5 Hz, JPC = 2.5 Hz), 131.3 (dd, JPC = 11.6 Hz, JPC = 5.7 Hz), 132.1 (d, JPC = 2.4 Hz), 133.6 (dd, JPC = 109.8 Hz, JPC = 6.2 Hz) ppm. 31P{1H} NMR (162 MHz): δ = 44.2 (s), 83.0 (s) ppm. IR (KBr): " = 3429 (s), 2956 (m, s), 2877 (m, s), 2346 (w), 1611 (w) ppm. 1H NMR (300 MHz): δ = 1.24. 

Synthesis of 15. Compound 13a (2.65 g, 11.4 mmol), dissolved in 40 ml DCM, was added to a solution of Br2PPh3 (7.37 g, 17.5 mmol) in 40 ml of DCM at 0 °C. The solution was allowed to warm up to room temperature overnight. The reaction was quenched by addition of 35 ml water and the phases were separated. The aqueous layer was extracted twice with 20 ml DCM, the combined organic layers were washed with brine and dried over MgSO4. After chromatographic workup (hexanes/diethyl ether = 1:1 to 1:2, v/v) 15 was obtained as a white solid. Yield: 3.27 g, 97%. Rf (hexanes/diethyl ether = 1:2, v/v) = 0.44 – iodine. m.p.: 159–160 °C. [α]D20 = +50.0° (c = 2.50 in toluene). 1H NMR (300 MHz): δ = 1.24.
The deep brown solution was filtered, the mixture was stirred for another 10 min at room temp-
0.56 mmol) in 20 ml THF was added at 0 °C over five minutes and the reaction mixture was stirred for 10 min at room temperature. Afterward, a solution of (0.16 ml, 1.5 mmol) was added and the solution was stirred at 65 °C for one hour. Afterwards, a solution of 18 (0.435 g, 1.47 mmol) in 5 ml diethyl ether at 0 °C. The mixture was stirred for 18 h. Chromatographic workup of the crude product (hexanes/diethyl ether = 1:1, v/v) yielded 18 as a white solid. Yield: 0.520 g, 85%. Rf (hexanes/diethyl ether = 1:1, v/v) = 0.43 – iodine. m.p.: 216–220 °C. [α]D = –11.3° (c = 1.16 in toluene). 1H NMR (400 MHz): δ = 1.19 (3H, s), 1.23 (3H, s), 0.30–1.50 (3H, m, B–H, –B–H), 1.79–2.01 (3H, m), 2.06–2.42 (3H, m), 2.56–2.68 (1H, m), 3.11–3.26 (1H, m), 3.94 (1H, dd, JH,H = 10.8 Hz, JH,H = 5.4 Hz), 4.10 (1H, d, JH,H = 10.8 Hz), 7.37–7.58 (6H, m), 7.60–7.72 (2H, m), 7.86–7.98 (2H, m) ppm. 13C{1H} NMR (76 MHz): δ = 18.6 (d, JCP = 18.9 Hz), 19.0 (d, JCP = 35.3 Hz), 23.9 (d, JCP = 7.5 Hz), 37.2 (d, JCP = 46.9 Hz), 38.8 (d, JCP = 51.0 Hz), 41.0 (d, JCP = 44.2 Hz), 47.8 (d, JCP = 2.4 Hz), 51.5 (d, JCP = 19.9 Hz), 67.0 (s), 86.2 (d, JCP = 2.0 Hz), 126.5 (d, JCP = 55.5 Hz), 128.6–129.7 (m), 130.3 (d, JCP = 55.6 Hz), 131.3–132.3 (m), 133.0 (d, J = 9.2 Hz) ppm. 31P{1H} NMR (162 MHz): δ = 15.1–16.8 (m) (br), 51.8 (d, JCP = 47.3 Hz) ppm. IR (KBr): υ = 3348 (3H, m, C–H), 2873 (3H, m, C–H–H), 2345 (2H, m, 1806 (w), 1631 (s), 1539 (w), 1450 (m), 1402 (w), 1386 (w), 1262 (m), 1137 (m), 1085 (s), 1048 (s), 865 (w), 801 (s), 741 (m), 674 (m), 643 (m), 587 (w), 502 (w), 482 (w), 473 (w), 456 (w), 444 (w), 430 (w), 417 (w), 405 (w) cm–1. MS (ESI, DCM/MeOH): m/z: calculated for C16H16OP2S2 [M + Na]+: 381.1; found: 381.1. C16H16OP2S2 (326.37): calculated: C 53.6%, H 6.75%; found: C 53.5%, H 6.67%.

Synthesis of 18. A 1.64 M solution of n-butyl lithium in n-hexane (0.990 ml, 1.62 mmol) was added to a solution of (PH3)HPh2 (0.382 g, 1.92 mmol) in 8 ml of diethyl ether at 0 °C. After 5 min at this temperature, the solution was added to a suspension of 15 (0.435 g, 1.47 mmol) in 5 ml diethyl ether at 0 °C. The mixture was stirred for 18 h. Chromatographic workup of the crude product (hexanes/diethyl ether = 1:1, v/v) yielded 18 as a white solid. Yield: 0.520 g, 85%. Rf (hexanes/diethyl ether = 1:1, v/v) = 0.43 – iodine. m.p.: 216–220 °C. [α]D = –11.3° (c = 1.16 in toluene). 1H NMR (400 MHz): δ = 1.19 (3H, s), 1.23 (3H, s), 0.30–1.50 (3H, m, B–H, –B–H), 1.79–2.01 (3H, m), 2.06–2.42 (3H, m), 2.56–2.68 (1H, m), 3.11–3.26 (1H, m), 3.94 (1H, dd, JH,H = 10.8 Hz, JH,H = 5.4 Hz), 4.10 (1H, d, JH,H = 10.8 Hz), 7.37–7.58 (6H, m), 7.60–7.72 (2H, m), 7.86–7.98 (2H, m) ppm. 13C{1H} NMR (76 MHz): δ = 18.6 (d, JCP = 18.9 Hz), 19.0 (d, JCP = 35.3 Hz), 23.9 (d, JCP = 7.5 Hz), 37.2 (d, JCP = 46.9 Hz), 38.8 (d, JCP = 51.0 Hz), 41.0 (d, JCP = 44.2 Hz), 47.8 (d, JCP = 2.4 Hz), 51.5 (d, JCP = 19.9 Hz), 67.0 (s), 86.2 (d, JCP = 2.0 Hz), 126.5 (d, JCP = 55.5 Hz), 128.6–129.7 (m), 130.3 (d, JCP = 55.6 Hz), 131.3–132.3 (m), 133.0 (d, J = 9.2 Hz) ppm. 31P{1H} NMR (162 MHz): δ = 15.1–16.8 (m) (br), 51.8 (d, JCP = 47.3 Hz) ppm. IR (KBr): υ = 3348 (3H, m, C–H), 2873 (3H, m, C–H–H), 2345 (2H, m, 1806 (w), 1631 (s), 1539 (w), 1450 (m), 1402 (w), 1386 (w), 1262 (m), 1137 (m), 1085 (s), 1048 (s), 865 (w), 801 (s), 741 (m), 674 (m), 643 (m), 587 (w), 502 (w), 482 (w), 473 (w), 456 (w), 444 (w), 430 (w), 417 (w), 405 (w) cm–1. MS (ESI, DCM/MeOH): m/z: calculated for C16H16OP2S2 [M + Na]+: 381.1; found: 381.1. C16H16OP2S2 (326.37): calculated: C 53.6%, H 6.75%; found: C 53.5%, H 6.67%.

Synthesis of 19. LiH2C8H18 (0.040 g, 1.1 mmol) was added to a solution of 18 (0.655 g, 0.13 mmol) in 3 ml of THF and the suspension was stirred for 20 h at 60 °C. The reaction was cooled to 0 °C and quenched by addition of 0.3 ml of an aqueous KOH solution (20%). The mixture was diluted with 3 ml of diethyl ether, dried over MgSO4, filtered and the residue was washed three times with 3 ml diethyl ether. From the combined organic layers the solvent was removed in vacuum and the residue was dissolved in 2 ml THF. A 1 M solution of borane in THF (0.65 ml, 0.65 mmol) was added and the solution was stirred for 18 h. Chromatographic workup of the crude product (hexanes/diethyl ether = 3:2 v/v) yielded 19 as a white solid. Yield: 0.041 g, 78%. Rf (hexanes/diethyl ether = 3:2, v/v) = 0.46 – iodine. m.p.: 159–164 °C. [α]D = –16.9° (c = 0.2 in toluene). 1H NMR (300 MHz): δ = 1.19 (3H, s), 1.24 (3H, s), 0.00–2.10 (6H, m, B–H), 1.55–1.79 (3H, m), 1.83–1.97
(1H, m), 2.10–2.42 (2H, m), 2.48–2.62 (1H, m), 2.80–3.00 (1H, m), 3.89 (1H, dd, $\delta_J_{CH-H} = 10.8$ Hz, $\delta_J_{HH-H} = 5.0$ Hz), 4.01 (1H, d, $\delta_J_{CH-P} = 8.9$ Hz), 5.43–5.62 (8H, m), 7.37–7.68 (8H, m), 7.81–7.91 (2H, m) ppm. $^{31}$P [$^1$H] NMR (76 MHz): $\delta = 18.6$ (d, $\delta_J_{CP,P} = 10.0$ Hz), 20.3 (d, $\delta_J_{CP,P} = 35.4$ Hz), 24.3 (d, $\delta_J_{CP,P} = 4.3$ Hz), 32.7 (d, $\delta_J_{CP,P} = 28.8$ Hz), 34.1 (d, $\delta_J_{CP,P} = 33.2$ Hz), 35.4 (d, $\delta_J_{CP,P} = 27.2$ Hz), 47.9 (d, $\delta_J_{CP,P} = 3.6$ Hz), 56.9 (d, $\delta_J_{CP,P} = 4.5$ Hz), 66.1 (s), 86.6 (d, $\delta_J_{CP,P} = 4.2$ Hz), 126.5 (d, $\delta_J_{CP,P} = 56.6$ Hz), 129.0–129.5 (m), 130.2 (d, $\delta_J_{CP,P} = 55.3$ Hz), 131.7 (d, $\delta_J = 9.4$ Hz), 133.0 (d, $\delta_J = 9.3$ Hz) ppm. $^{31}$P [$^1$H] NMR (162 MHz): $\delta = 15.7–17.8$ (m, br), 28.8–30.0 (m, br) ppm. IR (KBr): $\tilde{v} = 3422$ (m), 3060 (w), 2967 (w), 1637 (w), 1587 (w), 1507 (w), 1489 (w), 1437 (m), 1317 (s), 1295 (m), 1225 (m), 1185 (m), 1106 (m), 1062 (s), 1046 (s), 984 (w), 928 (w), 868 (w), 794 (m), 751 (m), 737 (m), 704 (m), 660 (w), 635 (w), 593 (w), 499 (w), 469 (w), 456 (w), 430 (w), 419 (w), 410 (w) cm$^{-1}$. MS (ESI, DCM/MeCN): 660 (w), 635 (w), 593 (w), 499 (w), 469 (w), 456 (w), 430 (w), 398 (w), 369 (w), 340 (w), 328 (w), 317 (w), 306 (w), 296 (w), 198 (w), 186 (w), 174 (w), 162 (w), 151 (w), 140 (w), 128 (w), 117 (w), 106 (w), 95 (w), 84 (w), 73 (w)."}

Notes and references


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