Supporting Information (SI) for:

Asymmetric 1,3-dipolar cycloaddition reaction of chiral 1-alkyl-1,2-diphosphole with diphenyldiazomethane

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Table S4. Basic crystallographic structure parameters for 5a.

Figure S31. Molecular structure of 5a.

Figure S32. Thermal ellipsoid plot (50% probability level) for the crystal structure of 5a.

References.
Calculation details
The quantum chemical calculations were performed with the Gaussian 03 software package.\textsuperscript{1} Full geometry optimizations have been carried out within the framework of DFT (PBE0) method using 6-31+G(d) basis sets. Chemical shifts were calculated at the PBE0/6-311G(2d,2p) level of theory. \textsuperscript{13}C chemical shifts were referred to TMS. \textsuperscript{31}P chemical shifts were referred to H\textsubscript{3}PO\textsubscript{4}, and a linear scaling procedure was applied.\textsuperscript{2}

References: see S37

Details of structure elucidation by NMR
The structures of compounds 3a, 3b and 5a were established by verity of 1D/2D NMR correlation methods. Namely, starting from the group with well known “finger prints” structure of whole compound can be established practically directly.

For example, for 3a we can start from the P2-CH\textsubscript{2}O protons with characteristic ABXY type spin system (at 3.95 and 3.62 ppm).

As to the menthyl fragment: There is \textsuperscript{1}H-\textsuperscript{13}C HMBC correlation from the P2-CH\textsubscript{2}O protons to C1' (80.52 ppm). Then from \textsuperscript{1}H-\textsuperscript{13}C HSQC experiment the H1' (3.01 ppm) proton can be established. Next there are \textsuperscript{1}H-\textsuperscript{13}C HMBC connectivity’s from the H1' proton to C2' (48.91 ppm), to C5' (31.56 ppm), to C7' (24.76 ppm) and to P2-CH\textsubscript{2}O (64.79 ppm) carbons. There are also NOE’s from the P2-CH\textsubscript{2}O protons to H1’, to H6eq’ and to H7’ protons. Then combination of \textsuperscript{1}H-COSY, \textsuperscript{1}H-\textsuperscript{13}C HSQC and \textsuperscript{1}H-\textsuperscript{13}C HMBC experiments allows to assign all signals in \textsuperscript{1}H and \textsuperscript{13}C spectra of the menthyl moiety. The most important connectivity’s are from H7’ to Me-8’ and Me-9’ (\textsuperscript{1}H-\textsuperscript{13}C COSY and \textsuperscript{1}H-\textsuperscript{13}C HMBC); and from H5’ to Me-10’ (\textsuperscript{1}H-COSY and \textsuperscript{1}H-\textsuperscript{13}C HMBC).

As to the bicyclic phosphirane fragment: There are \textsuperscript{1}H-\textsuperscript{31}P HMBC correlations from the P2-CH\textsubscript{2}O protons to P1 (-121.4 ppm) and to P2 (6.2 pm). There is also \textsuperscript{1}H-\textsuperscript{13}C HMBC connectivity from the P2-CH\textsubscript{2}O protons to C3 (144.52 ppm). \textsuperscript{13}C DEPT experiments help to distinguish protonated carbons from not protonated ones (CH versus C) in low field region. Then, four less intense signals of protonated carbons can be assigned to para-carbons of phenyl rings. Doublets in low field region of the \textsuperscript{1}H spectra are due to ortho-protons. Then there is correlation from the o-Ph3 (d, 6.3 ppm) protons to C3 (\textsuperscript{1}H-\textsuperscript{13}C HMBC), to P2 (\textsuperscript{1}H-\textsuperscript{31}P HMBC) and to the P2-CH\textsubscript{2}O protons (NOE). There are correlations from the o-Ph6 (d, 7.65 ppm) and the o-Ph6' (d, 6.9 ppm) protons to C6 (54.09 ppm, \textsuperscript{1}H-\textsuperscript{13}C HMBC) and P1 (\textsuperscript{1}H-\textsuperscript{31}P HMBC). The o-Ph6 versus o-Ph6’ protons can be distinguished upon NOE between the o-Ph6 and the o-Ph3 protons. There is also NOE between the o-Ph3 and the o-Ph4 protons. There is \textsuperscript{1}H-\textsuperscript{13}C HMBC correlation from the o-Ph4 protons to C4 (151.12 ppm). Unfortunately, there is no \textsuperscript{1}H-\textsuperscript{13}C HMBC connectivity’s to C5 (73.08 ppm) due to: 1) the o-Ph5 protons are broadened due to sterical hindrance; 2) there is no other protons in close proximity. But it’s characteristic chemical shift and \textsuperscript{1}H-\textsuperscript{1}JCP (37.8 Hz) allows assign the signal to C5. This is also in good agreement with results of calculations. Finally, starting from the ortho-protons all other signals in \textsuperscript{13}C and \textsuperscript{1}H spectra can be well assigned upon \textsuperscript{1}H-\textsuperscript{13}C HMBC, \textsuperscript{1}H-\textsuperscript{13}C HSQC and \textsuperscript{1}H-COSY connectivity’s.

In similar way structures of 3b and 5a were established.

In the case of compound 5b the bicyclic phosphirane fragment signals in \textsuperscript{1}H and \textsuperscript{13}C NMR spectra cannot be resolved (except C4-o-Ph and C3-o-Ph) due to intensive overlap with the main isomer (5a) signals therefore only the data for the neomenthyl fragment is given. In this case \textsuperscript{1}H-\textsuperscript{31}P HMBC, \textsuperscript{1}H-\textsuperscript{1}H COSY and \textsuperscript{1}H-\textsuperscript{13}C HSQC spectra are particularly helpful. The \textsuperscript{1}H-\textsuperscript{31}P HMBC spectra allows to reveal the protons coupled with minor phosphorus signals, while the \textsuperscript{1}H-\textsuperscript{1}H COSY and \textsuperscript{1}H-\textsuperscript{13}C HSQC spectra helps to resolve \textsuperscript{1}H and \textsuperscript{13}C signals of neomenthyl fragment. But no information about exact multiplet structure of the \textsuperscript{1}H and \textsuperscript{13}C spectra can be obtained in this way for some of the protons.
Table S1. Energies (PBE0/6-31+G(d)) of main forms due to rotation around P2-CH$_2$ bond in the model of compound 3 ($3'$, methyl instead of menthyl).

|        | -g$^*$          | trans          | +g            |
|--------|-----------------|----------------|---------------|
| hartree| -2145.8153312   | -2145.8190703  | -2145.8169151 |
| kcal/mol| 2.3             | 0              | 1.4           |

* orientation with respect to the lone pair of electrons at phosphorus, C-O with lone pair of electrons; “+” – clockwise;

Figure S1. The major form of the model compound $3'$ (methyl instead of menthyl): front and side views.

Table S2. Energies (PBE0/6-31+G(d)) and some key $^{13}$C and $^{31}$P NMR chemical shifts (GIAO PBE0/6-31+G(d)//PBE0/6-311G(2d,2p)) calculated for 3a and 3b.

|        | 3a            | 3b            |
|--------|---------------|---------------|
| Energy, hartree | -2498.0263604 | -2498.026385  |
| Energy, kcal/mol | 0.015         | 0             |
| P1     | -105.7        | -102.4        |
| P2     | 13.6          | 16.1          |
| C3     | 156.0         | 156.9         |
| C4     | 158.5         | 157.7         |
| C5     | 80.3          | 80.3          |
| C6     | 58.2          | 58.4          |
Figure S2. High field sections of the $^1$H NMR spectra of 3a (a, b) and 3b (c, d) in CDCl$_3$ at room and low temperatures.
Table S3. Energies (PBE0/6-31+G(d)) and some key $^{13}$C and $^{31}$P NMR chemical shifts (GIAO PBE0/6-31+G(d)//PBE0/6-311G(2d,2p)) calculated for 5a and 5b.

|       | 5a            | 5b            |
|-------|---------------|---------------|
| Energy, kcal/mol | -2383.6206784 | -2383.6181352 |
| Energy, kcal/mol  | 0              | 1.6           |
| P1     | -85.7         | -104.7        |
| P2     | 22.3          | 15.5          |
| C3     | 159.5         | 155.6         |
| C4     | 156.8         | 159.5         |
| C5     | 82.7          | 80.8          |
| C6     | 60.0          | 58.0          |

**Figure S3.** Structures of isomers 5a (a) and 5b (b) with indicative NMR effects.
Figure S4. 1D $^1$H and $^{31}$P{$^1$H} NMR spectra of 3a in CDCl$_3$ at $T = 303$ K.
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Figure S10. 2D $^1$H-$^{13}$C HMBC NMR spectrum of 3a in CDCl$_3$ at $T = 303$ K.
Figure S11. 1D $^1$H and $^1$H NOESY NMR spectra of 3a in CDCl$_3$ at T = 303 K.
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Figure S20. 1D $^1$H and $^1$H NOESY NMR spectra of 3b in CDCl$_3$ at T = 303 K.
Figure S21. 1D $^1$H and $^{31}$P{${}^1$H} NMR spectra of 5a and 5b in CDCl$_3$ at T = 303 K.
Figure S22. 2D $^1$H-$^{31}$P HMBC NMR spectrum of 5a and 5b in CDCl$_3$ at T = 303 K.
Figure S23. 1D $^1$H, $^{13}$C DEPT and $^{13}$C($^1$H) NMR spectra of 5a and 5b in CDCl$_3$ at T = 303 K.
Figure S24. 2D $^1$H-$^1$H COSY NMR spectrum of 5a and 5b in CDCl$_3$ at T = 303 K.
Figure S25. 2D $^1$H-$^{13}$C HSQC NMR spectrum of 5a and 5b in CDCl$_3$ at $T = 303$ K.
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Figure S27. 1D $^1$H and $^1$H NOESY NMR spectra of 5a and 5b in CDCl$_3$ at $T = 303$ K.
Figure S28. 1D $^1$H and $^1$H NOESY NMR spectra of 5a and 5b in CDCl$_3$ at $T = 303$ K.
Figure S29. 1D $^1$H and $^1$H NOESY NMR spectra of 5a and 5b in CDCl$_3$ at T = 303 K.
Figure S30. 1D $^1$H and $^1$H TOCSY NMR spectra of 5a and 5b in CDCl$_3$ at T = 303 K.
X-Ray Structure Determination

The data was collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation ($\lambda = 0.71073$ Å) and $\omega$-scan rotation. Data reduction was performed with CrysAlisPro \(^3\) including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by direct methods (SIR-92) \(^4\) and the refinement was performed with SHELXL-2018.\(^5\) Except disordered solvent THF molecules, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms for methyl substituents and disordered molecules were calculated on idealized positions using the riding model, whereas all other H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with DIAMOND-4.\(^6\) Both THF solvent molecules are disordered in the vicinity of a twofold axis. CCDC 198823 (5a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk ).

References: see S37

| Table S4. Basic crystallographic structure parameters for 5a. |
|-------------------------------------------------------------|
| **Molecular formula** | C$_{48}$H$_{48}$P$_2$·THF | **Crystal size** | 0.35 x 0.24 x 0.06 mm$^3$ |
| **Empirical formula** | C$_{48}$H$_{52}$OP$_2$ | **Theta range for data collection** | 2.311 to 30.508° |
| **Formula weight** | 706.83 | **Index ranges** | -24 $\leq$ h $\leq$ 24, -14 $\leq$ k $\leq$ 14, -32 $\leq$ l $\leq$ 32 |
| **Temperature** | 130(2) K | **Reflections collected** | 26465 |
| **Wavelength** | 0.71073 Å | **Independent reflections** | 12072 [R(int) = 0.0360] |
| **Crystal system** | Monoclinic | **Completeness to theta = 25.242°** | 99.9 % |
| **Space group** | C2 | **Absorption correction** | Semi-empirical from equivalents |
| **Unit cell dimensions** | a = 17.2172(4) Å | **Max. and min. transmission** | 1.00000 and 0.99370 |
| | b = 10.3390(3) Å | **Refinement method** | Full-matrix least-squares on F$^2$ |
| | c = 22.6719(5) Å | **Data / restraints / parameters** | 12072 / 39 / 590 |
| | $\beta$ = 101.889(2)$^\circ$ | **Goodness-of-fit on F$^2$** | 1.006 |
| **Volume** | 3949.2(2) Å$^3$ | **Final R indices [I>2sigma(I)]** | R1 = 0.0524, wR2 = 0.1224 |
| **Z** | 4 | **R indices (all data)** | R1 = 0.0745, wR2 = 0.1356 |
| **Density (calculated)** | 1.189 Mg/m$^3$ | **Absolute structure parameter** | -0.01(3) |
| **Absorption coefficient** | 0.146 mm$^{-1}$ | **Residual electron density** | 0.531 and -0.387 e·Å$^{-3}$ |
| **F(000)** | 1512 | | |
Figure S31. Molecular structure of 2-((+)-neomenthyl)-3,4,5,6,6-pentaphenyl-1,2-(P1\text{R}P2\text{R}C3\text{S})-diphosphabicyclo[3.1.0]hex-3-ene (5a). Hydrogen atoms are omitted for clarity. Configuration of chiral atoms in the five-membered ring: P1:(R), P2:(R), C3:(S). Selected bond lengths [Å] and angles [°]: P1-C1 1.818(3); P1-C5 1.888(3); P1-P2 2.194(1); P2-C4 1.877(3); P2-C3 1.879(3); C1-C2 1.354(4); C2-C3 1.513(4); C3-C4 1.554(4); C1-P1-C5 99.9(1); C1-P1-P2 93.4(1); C4-P2-C3 48.9(1); C4-P2-P1 100.8(1); C3-P2-P1 94.4(1).

A crystal structure analysis of 5a showed that only one diastereomer was obtained with the neomenthyl group in an *anti* orientation to the 3-membered P2-C3-C4(Ph2) fragment. Compound 5a crystallizes in the monoclinic space group C2 with a Flack parameter of -0.01(3). There are 6 chiral centers in 5a, each phosphorus atom has a typical pyramidal environment and the menthyl fragment has the configuration of (+)-neomenthol or (1S,2S,5R)-2-isopropyl-5-methylcyclohexanol.
Figure S32. Atom-labeling scheme of 5a. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.
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