Supporting Information
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Experimental details

Except when indicated otherwise, all reagents and solvents were purchased from commercial sources and used as received. All reactions and workup were conducted under air, except when noted otherwise. Flash column chromatography was performed using Merck Silica Gel 60 (0.040-0.063mm). TLC was performed on Macherey Nagel Polygram Sil G/UV254 plates and visualized by UV-light and KMnO₄-solution. Yields refer to pure isolated substances. NMR spectra were recorded on a Bruker AV500 MHz spectrometer. The chemical shifts are reported in ppm downfield of internal standard tetramethylsilane for ¹H NMR and ¹³C NMR. Chemical shifts are designated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a Finnigan MAT 8200 or a Finnigan SSQ 7000 instrument, high resolution mass determinations were performed on a Bruker APEX III FT-MS or a Finnigan MAT 95 instrument. Trace element analysis (ICP-OES) was performed by AlessaChemie, Frankfurt, Germany.

Synthesis of TRIP (2)

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\begin{align*}
\text{A. (R)-2,2'-dimethoxy-1,1'-binaphthyl (7). A 250-mL three-necked round-bottom flask} \\
\text{containing (R)-BINOL 6 (5.00 g, 17.29 mmol, 1.00 equiv.) is equipped with a magnetic stirrer} \\
\text{bar, an addition funnel, a reflux condenser with argon inlet and a glass stopper. The flask is}
\end{align*}
\]
evacuated and flushed with argon. Subsequently the vessel is charged with 160 mL dried acetone, upon complete solution of the prior compound, potassium carbonate (7.88 g, 57.10 mmol, 3.3 equiv.) is added followed by methyl iodide (4.35 ml, 9.91 g, 69.20 mmol, 4.0 equiv.). The resulting mixture is heated to reflux in an oil bath (oil temperature ~85°C) for 24 h. After that time the volatile compounds are removed under reduced pressure (40°C, 20 mbar). The resulting slurry is redissolved in 180 ml of water and stirred for 2 h. The resulting solid is collected on a funnel, washed with water and dried in vacuo (95°C, 3.0·10⁻² mbar) furnishing 5.23 g (96%) of the title compound 7 as a slight yellow solid.

Compound 7 exhibits the following physical and spectroscopic properties:
mp: 228-232°C;
IR (ATR-diamond) ν: 2837, 1590, 1460, 1248, 1063, 809 cm⁻¹;
¹H-NMR (500 MHz, CD₂Cl₂) δ: 3.73 (s, 6 H), 7.01 (d, 2 H, ³J = 8.5 Hz), 7.16 (m, 2 H), 7.28 (m, 2 H), 7.44 (d, 2 H, ³J = 9.1 Hz), 7.84 (d, 2 H, ³J = 8.2 Hz), 7.96 (d, 2 H, ³J = 9.1 Hz);
¹³C-NMR (125 MHz, CD₂Cl₂) δ: 56.93, 114.29, 119.62, 123.89, 125.33, 126.71, 128.34, 129.54, 129.77, 134.32, 155.34;
MS (EI) m/z: 314 (100 %), 268 (45 %), 239 (10 %), 134 (10 %), 120 (10 %);
HRMS (ESI+) m/z [M+Na]: calcd. 337.1197, found 337.1199.

B. (R)-3,3′-dibromo-2,2′-dimethoxy-1,1′-binaphthyl (3). A 500-mL three-necked round-bottom flask equipped with a magnetic stirrer bar, an addition funnel, an argon inlet and a glass stopper is evacuated and flushed with argon. Subsequently 250 mL dried diethyl ether are added, followed by tetramethylethylenediamine (5.21 ml, 4.07 g, 35.00 mmol, 2.2 equiv.). To the resulting solution n-butyllithium (2.5 M in hexanes, 22.27 ml, 55.70 mmol, 3.5 equiv.) is added slowly at r.t. via syringe, the mixture is allowed to stir for 1 h. Then compound 7 (5.00 g, 15.90 mmol, 1.0 equiv.) is added as a solid at r.t. and the resulting solution is stirred for 3.5 h. After this time the reaction is cooled to -78°C (dry ice/aceton bath) and bromine (12.71 g, 4.10 ml, 80.00 mmol, 5.0 equiv.) is added dropwise via addition funnel. After complete addition, the cooling is removed and the yellowish-brown reaction mixture is allowed to stir for 20 h at r.t. The reaction is quenched with 80 ml sat. Na₂SO₃-solution and stirred for 1 h. The mixture is extracted with Et₂O (3 x 50 ml), the organic phases are combined, washed with brine (100 ml) and dried over MgSO₄. After filtration the solvent is removed in vacuo (40°C, 20 mbar) and the crude mixture is subjected to column chromatography (hexanes/ethyl acetate 20:1) resulting in a yellowish solid material which was recrystallized from CH₂Cl₂/hexanes. The mother liquor was subjected to a second column chromatography (same conditions as above) and the resulting material was crystallized (same conditions as above). In total 4.02 g (54 %) of the title compound 3 were obtained as slight yellow crystals.

Compound 3 exhibits the following physical and spectroscopic properties:
mp: 178-182°C;
IR (ATR-diamond) ν: 2937, 1574, 1456, 1351, 1232, 1044, 750 cm⁻¹;
¹H-NMR (500 MHz, CD₂Cl₂) δ: 3.46 (s, 6 H), 7.03 (d, 2 H, ³J = 8.5 Hz), 7.24 (m, 2 H), 7.41 (m, 2 H), 7.82 (d, 2 H, ³J = 8.3 Hz), 8.27 (s, 2 H);
¹³C-NMR (125 MHz, CD₂Cl₂) δ: 61.75, 118.19, 126.46, 126.71, 127.35, 127.64, 127.96, 132.28, 133.80, 133.90, 153.28;
MS (EI) m/z: 474, 472, 470 (50 %, 100 %, 50 %), 428, 426, 424 (10 %, 20 %, 10 %), 361 (12 %), 239 (10 %), 156 (22 %), 141 (10 %), 119 (15 %);
HRMS (ESI+) m/z [M+Na]: calcd. 492.9407, found 492.9409.
C. (2,4,6-triisopropylphenyl)magnesium bromide (4). A dried 100-mL two necked flask with Ar-inlet, magnetic stirrer bar, reflux condenser and septum is charged with Mg (1.26 g, 52.00 mmol, 2.0 equiv., activated with a spatula tip of iodine). The Mg was covered with Et₂O (5 ml), subsequently 2-bromo-1,3,5-triisopropylbenzene (7.67 g, 26.00 mmol, 1.0 equiv.), the rest of the Et₂O (35 ml) and 0.1 ml 1,2-dibromoethane (as activator) are charged in different syringes and added in a manner of maintaining the exothermic Grignard-reaction active. After complete addition of the compounds, the resulting grey solution is placed in a pre-heated oil bath to be refluxed for 24 h. The resulting solution is filtered through a short pad of cotton and used in unmodified form in the next step.

D. (1R,3R)-2,2'-dimethoxy-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl (8). An oven dried 250-mL two-necked flask with Ar-inlet, magnetic stirrer and addition funnel is charged with compound 3 (2.00 g, 4.24 mmol, 1.0 equiv.) and Ni(PPh₃)₂Cl₂ (277 mg, 0.42 mmol, 0.1 equiv.) evacuated and set under Argon. Subsequently Et₂O (25 mL) is added and to the resulting suspension the Grignard-solution 4 is added dropwise at r.t. After complete addition the resulting mixture is refluxed for 6 h. The resulting brown solution is allowed to reach r.t. and then cooled to 0°C with an ice bath and quenched with 1 M HCl (30 mL). The resulting mixture is extracted with Et₂O (3 x 25 mL), the organic phase is dried over MgSO₄, filtered and the solvent is removed in vacuo (40°C, 20 mbar). The resulting slight yellow solid crude (3.05 g) was subjected to the next step without further purification.

E. (1R,3R)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diol (5). In a 500-mL three-necked flask with magnetic stirrer, Ar-inlet and addition funnel the crude material 8 is evacuated, set under Argon and dissolved in 105 mL dry dichloromethane. Subsequently the solution is cooled with an ice bath followed by slow addition of BBr₃ (1 M in hexanes, 29.70 ml, 29.70 mmol, 7.0 equiv.). After complete addition, the resulting clear solution is allowed to stir for 24 h at r.t. Subsequently water (40 mL) is added to quench the reaction. The aqueous layer is extracted with CH₂Cl₂ (3 x 25 mL), the combined organic layers are dried over MgSO₄, filtered and the solvent is reduced in vacuo (40°C, 20 mbar). Column chromatography (hexanes/ethyl acetate 99:1) gave a slight yellow material which was subsequently triturated with hexanes resulting in 1.32 g (45 % over two steps) of the title compound 5.

Compound 5 exhibits the following physical and spectroscopic properties:
IR (ATR-diamond) ν: 3505, 2958, 1605, 1424, 1233, 938, 875, 745 cm⁻¹;
¹H-NMR (500 MHz, CD₂Cl₂) δ: 1.01 (d, 6 H, 3J = 6.9 Hz), 1.07 (d, 6 H, 3J = 6.8 Hz), 1.09 (d, 6 H, 3J = 6.8 Hz), 1.16 (d, 6 H, 3J = 6.8 Hz), 1.29 (d, 12 H, 3J = 6.9 Hz), 2.67 (sept, 2 H, 3J = 6.9 Hz), 2.81 (sept, 2 H, 3J = 6.9 Hz), 2.94 (sept, 2 H, 3J = 6.9 Hz), 5.01 (s, 2H), 7.12-7.14 (m, 4 H), 7.21 (d, 2 H, 3J = 8.4 Hz), 7.27-7.38 (m, 4H), 7.74 (s, 2H), 7.87 (d, 2 H, 3J = 7.8 Hz);
¹³C-NMR (125 MHz, CD₂Cl₂) δ: 24.07, 24.19, 24.41, 24.58, 24.64, 31.49, 31.54, 35.02, 113.49, 121.76, 124.44, 124.79, 127.31, 128.91, 129.79, 129.81, 131.38, 131.56, 134.04, 148.45, 148.49, 149.91, 151.42;
MS (EI) m/z: 690 (100%), 563 (5%), 521 (5%), 287 (7%), 219 (5%);
HRMS (ESI+) m/z [M+Na]: calcd. 713.4333, found 713.4329.

F. TRIP-Phosphoric Acid (2). A 10-mL two-necked flask with reflux condenser, Ar-inlet and glass stopper is charged with 5 (500 mg, 0.724 mmol, 1 equiv.) and set under Argon. Subsequently pyridine (1.5 ml) is
added, followed by POCl$_3$ (198 μl, 333 mg, 2.172 mmol, 3 equiv.). The resulting mixture is refluxed for 14 h. After this time the reaction is allowed to reach r.t., followed by addition of water (1.5 ml). The resulting brownish slurry is heated to reflux and hydrolyzed for 3 h. After the reaction reached r.t. 5 ml CH$_2$Cl$_2$ are added. The resulting organic phase is thoroughly washed with 1 M HCl (3 x 5 ml). The resulting organic layer can be dried over MgSO$_4$ and recrystallized from MeCN. **Important:** the aqueous medium should be clearly acidic (pH = 1-2) throughout the last workup steps to maintain the product in its free acid form. 537 mg (99%) of analytically pure material were obtained following this route.

Compound 2 exhibits the following physical and spectroscopic properties:

IR (ATR-diamond) ν: 3561, 2959, 1608, 1408, 1280, 1198, 1019, 899, 752 cm$^{-1}$;

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$) δ: 0.69 (d, 6H, $^3J = 6.7$ Hz), 0.87 (d, 6H, $^3J = 6.8$ Hz), 0.94 (d, 6H, $^3J = 6.8$ Hz), 1.01 (d, 6H, $^3J = 6.8$ Hz), 1.19 (d, 6H, $^3J = 6.9$ Hz), 1.19 (d, 6H, $^3J = 6.9$ Hz), 2.49 (sept, 3H, $^3J = 6.8$ Hz), 2.56 (sept, 6H, $^3J = 6.8$ Hz), 2.81 (sept, 6H, $^3J = 6.9$ Hz), 5.90 (br s, 1H), 6.91 (d, 2H, $^4J = 1.5$ Hz), 6.94 (d, 2H, $^4J = 1.6$ Hz), 7.22-7.30 (m, 4H), 7.45-7.49 (m, 2H), 7.76 (s, 2H), 7.88 (d, 2H, $^3J = 8.2$ Hz).

$^{13}$C-NMR (125 MHz, CD$_2$Cl$_2$) δ: 22.76, 22.94, 23.77, 23.97, 24.70, 26.16, 30.79, 31.07, 34.27, 120.36, 121.18, 122.00, 125.75, 126.28, 127.20, 128.19, 131.12, 131.39, 132.01, 132.04, 132.37, 132.76, 145.75, 145.84, 147.49, 147.98, 148.61.

$^{31}$P-NMR (400 MHz, CD$_2$Cl$_2$) δ: 3.44.

MS (EI) m/z: 752 (88%), 709 (100%), 667 (40%), 625 (40%), 583 (30%), 541 (32%), 313 (15%).

HRMS (ESI+) m/z [M+Na]: calcd. 751.3921, found 751.3922.

RP-HPLC: column = Chiralpak QN-AX,
solvent system = MeOH/AcOH/NH$_4$Ac 98:2:0.5 (v/v/w),
solvent flow = 1 ml/min,
detection = UV/254nm,
temperature = 25°C,
t$R_1$ = 3.44 min (S),
t$R_2$ = 4.98 min (R).
$^1$H-NMR of 5 in CD$_2$Cl$_2$

$^{13}$C-NMR of 5 in CD$_2$Cl$_2$
$^1$H-NMR of 2 (TRIP) in CD$_2$Cl$_2$

$^{13}$C-NMR of 2 (TRIP) in CD$_2$Cl$_2$
NMR-comparison of batches A and B in different solvents (400 MHz)

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Crystal structure analysis 2·CH₃CN·½(H₂O)

The results of the crystal structure analysis of 2·CH₃CN·½(H₂O) are shown in Figure 1, which reveals that two phosphate molecules form a dimer with a single water molecule, which is completely enclosed by the two 3,3'-(2,4,6-triisopropylphenyl) substituents on the dinaphthylphosphate group. The water molecule is disordered over two positions, each with half occupancy. Hydrogen atoms on the disordered solute water molecule and disordered acids could not be located, but intermolecular distances in the dimeric unit and the disordered water molecule indicate that the hydrogen atoms on the acid are alternately carried by O₃ and O₄, since the P1-O₃ and P1-O₄ distances are approximately equal (1.486(3) Å cf. 1.481(3) Å). This is supported by the fact that the O₃···O₃* distance at 2.451(4) Å must be a hydrogen bond, but the symmetry equivalent O₃ atoms, O₃ and O₃*, cannot both carry a hydrogen atom. Since a shorter O₄...O₅ distance is expected when the hydrogen atom is carried by O₄, the hydrogen bonding sequence in the dimer is thus: P=O···H-O=P=O···H-O(H)···H-O-P, which is disordered with: P-O-H···O-P-O-H···O(-H)-H···O=P. The O₄···O₅ and O₅···O₄* distances are 2.473(4) Å and 2.817(4) Å, respectively, confirming this interpretation.
Figure S1. The crystal structure of the 2·CH₃CN·½(H₂O), showing a phosphate dimer with entrapped water molecule. The dotted lines show the hydrogen bonding interactions between two phosphate molecules and the entrapped water molecule (O5), which is disordered over two positions. Atomic displacement ellipsoids shown at the 20% level and ligand hydrogen atoms omitted for clarity.

Figure S2. Crystal structure of 2·CH₃CN·½(H₂O). Atomic displacement parameters shown at the 50% probability level. H atoms omitted for clarity.
Figure S3. Crystal structure of TRIP (2), projected along the approximate 2-fold axis of symmetry passing through P1 and the midpoint of the C1-C11 bond, showing the relationship of the two 2,4,6-triisopropylphenyl groups to one another. The angle between the mean planes of the two 2,4,6-triisopropylphenyl groups is 69(1)°. Atomic displacement parameters shown at the 20% probability level and H atoms omitted for clarity.

**X-ray crystal data for 2·CH₃CN·½(H₂O):** 2[C₅₀H₅₇O₄P]·2[C₂H₃N]·[H₂O], \(M_r = 1605.98\) g · mol⁻¹, colourless prism recrystallized from acetonitrile, crystal size 0.28 x 0.30 x 0.49 mm³, tetragonal, space group \(P4_12_12\) (no. 92), \(a = 16.4385(5)\) Å, \(c = 34.2068(13)\) Å, \(V = 9243.5(5)\) Å³, \(T = 100(2)\) K, \(Z = 4\), \(D_{calc} = 1.154\) g·cm⁻³, \(\lambda = 1.54178\) Å, \(\mu = 0.877\) mm⁻¹, SADABS multi-scan absorption correction (\(T_{min} = 0.8244, T_{max} = 1.0\)), Bruker-AXS X8 Proteum diffractometer, 2.98 < \(\theta\) < 71.62°, 215508 measured reflections, 8814 independent reflections (\(R_{int} = 0.2625\)), 5626 reflections with \(I > 2\sigma(I)\). Structure solved by direct methods and refined by full-matrix least-squares against \(F^2\) to \(R_f = 0.0699\) \([I > 2\sigma(I)]\), \(wR_2 = 0.1757\), 534 parameters (G. M. Sheldrick, *Acta Cryst.* 2008, *A64*, 112-122). \(R_{int}\) is relatively high because the crystal scattered weakly at high angles, presumably due to the slight disorder in the structure. In order to compensate for this, data were collected with a redundancy of over 41 to a resolution of 0.81 Å with a completeness of 99.9 % up to 0.84 Å. H atoms bonded to O could not be located on a difference Fourier synthesis due to hydrogen bond disorder, otherwise H atoms were calculated and refined using a riding model. In all, three crystals were investigated and all showed the same type of disorder. The absolute configuration of the
ligand (R) was confirmed (Flack parameter 0.00(3)). S = 0.967, residual electron density +0.59 / -0.51 e Å⁻³. CCDC 777645.