Supplementary Material for Chemical Communications

Supplementary data

Non-stoichiometry induced by differential oxygen/ lone pair occupation in chiral bicyclic 1,1'-binaphthoxy cyclodiphosphazanes

Manab Chakravarty, Praveen Kommana and K. C. Kumara Swamy*

Supplementary information

Title: Nonstoichiometry induced by differential oxygen/ lone pair occupation in chiral bicyclic 1,1'-binaphthoxy cyclodiphosphazanes

Authors: Manab Chakravarty, Praveen Kommana and K. C. Kumara Swamy*

Experimental details and crystal data for 5-9

NMR spectra were recorded using either a Bruker 200 or a Bruker 400 MHz spectrometer.

Compounds 5 and 9: To **1a** (1.05 g, 3.82 mmol) in toluene (5 mL) was added a mixture of 1,1'-bi-2-naphthol (racemic or *S*(-)) (1.09 g, 3.82 mmol) and Et_3N (0.77 g, 7.63 mmol) in toluene (10 mL) drop-wise and the mixture was refluxed overnight. Filtration, followed by concentration of the solution (*ca* 5 mL) resulted in the crystallization of **5** or **9**. Data for compound **5** is given here. Yield: 1.51 g (81%). Mp: 172-174 °C [Found: C, 68.79; H, 6.16; N, 5.76. Calc. for $C_{28}H_{30}N_2O_2P_2$: C, 68.84; H, 6.19; N, 5.73]. IR (KBr): $\bar{\nu}$ = 2959, 1593, 1504, 1323, 1204, 1144, 1010, 951 cm^{-1}**.** ^1H NMR ($CDCl_3$): δ 0.94 (s, 18 H, *t*-Bu-*H*), 6.65 (d, 2 H), 6.69 (t, 2H) and 7.40 (t, 2H), 7.62 (d, 2H), 7.88 (d, 2H) and 8.06 (d, 2H) (all Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 30.6 (br, $C(CH_3)_3$), 52.3 (br, t, *J* ~ 10.3 Hz,

C(CH_3)$_3$), 124.4, 125.0, 126.0, 126.4, 127.4, 128.7, 130.4, 134.6, 151.4. ^{31}P NMR: δ 171.4. $[\alpha]^{27}_D$ = (+) 155 (c = 0.23, $CHCl_3$). The racemic compound **9** (mp 168-170^{o}C) initially was pure but partial oxidation had occurred in the process of crystallization. Although the original sample was pure [CHN analysis; ^{31}P NMR], for the crystals there were additional low intensity *t*-Bu-*H* signals at δ 1.01, 1.04, 1.06 and 1.15.

Compound 6: To a solution of **2** (0.50 g, 1.02 mmol) in dry tetrahydrofuran (5 mL), diisopropyl azodicarboxylate (DIAD) (0.207 g, 1.02 mmol) was added. The yellow solution was stirred overnight at 25°C upon which it became colourless. Removal of the solvent followed by column chromatography (ethyl acetate/ hexane) afforded a solid that was crystallized from dichloromethane-hexane mixture (5:2, 7 mL). Yield: 0.35 g (68 %). Mp: 240 – 242 °C. IR (KBr): $\bar{\nu}$ = 2963, 1287 (s), 1211, 1057, 963 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.00 and 1.04 (2 s, 18 H, *t*-Bu-*H*), 6.50 -8.10 (m, 12 H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 30.9 (C(*C*H_3)$_3$), 54.5 (*C*(CH_3)$_3$), 120.7, 123.5, 124.4, 125.0, 125.4, 125.9, 126.9, 127.6, 127.7, 129.6, 130.7, 131.0, 134.4, 134.8, 150.2. ^{31}P NMR: δ 98.3 and 4.2 (d, ^2J(P-P) = 12.8 Hz). $[\alpha]^{27}_D$ = (+) 174 (c = 0.46, $CHCl_3$). A small peak (ca 5%) for bis-oxidized product [δ –7.8] also was observed [Fig. 2].

Compound 7: To a solution of *m*-CPBA (0.11 g, 0.64 mmol) in dichloromethane (5 mL) was added a solution of **2** (0.13 g, 0.26 mmol) in dichloromethane (5 mL). The solution was stirred overnight at 25°C and was quenched by water. The reaction mixture was washed with $NaHCO_3$ solution (10 mL) for three times to remove the remaining acid, extracted by dichloromethane and finally purified by column chromatography (ethyl acetate/ hexane) and crystallized from dichloromethane-hexane (1:1). Yield: 0.10 g (72 %). Mp: 260°C (charring). IR: $\bar{\nu}$ = 2973, 1289 (s), 1208, 1074, 976 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.03 (s, 18 H, *t*-Bu-*H*), 6.55 (d, 2 H), 7.10 (t, 2H) and 7.40 (t, 2H), 7.60 (d, 2H), 7.90 (d, 2H) and 8.05 (d, 2H) (all Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 30.4 (C(*C*H_3)$_3$,), 57.7 (*C*(CH_3)$_3$), 123.1, 124.0, 125.9, 126.0, 127.5, 128.0, 130.6, 131.3, 134.8, 149.6. The triplet at δ 57.7 is not resolved. ^{31}P NMR: δ –7.8. $[\alpha]^{27}_D$ = (+) 176 (*c* = 0.23, $CHCl_3$).

Mixed crystal 8: This was obtained by first dissolving a 1:1 mixture (total 0.45 g) of **2** and **3** in toluene (5 mL); for complete dissolution CH_2Cl_2 (1 mL) was added and subsequently removed. Mp: > 300 °C, but at 240 °C, colour changed to yellow. The ^{1}H

NMR spectrum showed a mixture of **5** and **7**, and was complex as expected. ^{31}P NMR: δ 171.5 and –7.8 (2 s, 2:5) [Fig. 2].

The CD spectra of **5-7** were essentially identical (this is to be expected since all of these are derived from the same chiral binaphthol).

Crystal data:

5: $C_{28}H_{30}N_2O_2P_2$, M = 488.48, orthorhombic, space group $P2_12_12_1$, a = 9.661(3), b = 15.095(2), c = 17.904(4), V = 2610.8(10) Å^3, Z = 4, μ = 0.194 mm^{-1}, data/restraints/parameters: 2604/0/313. Flack parameter: -0.19(19). R indices ($I > 2\sigma(I)$): R1 = 0.0444, *wR*2 (all data) = 0.1149.

6: $C_{28}H_{30}N_2O_{3.1}P_2$, M = 506.08, orthorhombic, space group $P2_12_12_1$, a = 9.7123(6), b = 15.1885(9), c = 17.8209(10), V = 2628.9(3) Å^3, Z = 4, μ = 0.197 mm^{-1}, data/restraints/parameters: 4635/0/ 331. Flack parameter: -0.04(6). R indices ($I > 2\sigma(I)$): R1 = 0.0309, *wR*2 (all data) = 0.0841.

7: $C_{28}H_{30}N_2O_4P_2$, M = 520.48, orthorhombic, space group $P2_12_12_1$, a = 9.7305(14), b = 15.256(2), c = 17.737(3), V = 2633.0(7) Å^3, Z = 4, μ = 0.202 mm^{-1}, data/restraints/parameters: 4638/0/ 331. Flack parameter: -0.05(7). R indices ($I > 2\sigma(I)$): R1 = 0.0329, *wR*2 (all data) = 0.0913 [The molecular structure is shown in the main text as Figure 1. Selected bond parameters: P(1) – N(1) 1.6623(16), P(1) – N(2) 1.6796(17), P(1) – O(1) 1.6055(13), P(1) – O(3) 1.4526(14), P(2) – N(1) 1.6804(16), P(2) – N(2) 1.6714(17), P(2) – O(2) 1.5943(14), P(2) – O(4) 1.4560(15) Å. N(1) – P(1) – N(2) 86.48(8), N(1) – P(2) – N(2) 86.17(8), P(1) – N(1) – P(2) 93.67(8), P(1) – N(2) – P(2) 93.37(8)^o].

8: $C_{28}H_{30}N_2O_{3.4}P_2$, M = 510.88, orthorhombic, space group $P2_12_12_1$, a = 9.7160(8), b = 15.1905(12), c = 17.8076(14), V = 2628.2(4) Å^3, Z = 4, μ = 0.200 mm^{-1}, data/restraints/parameters: 4512/0/ 331. Flack parameter: 0.05(10). R indices ($I > 2\sigma(I)$): R1 = 0.0471, *wR*2 (all data) = 0.1034.

9: $C_{56}H_{60}N_4O_{4.34}P_4$, M = 982.40, monoclinic, space group $P2_1/c$, a = 22.838(3), b = 9.590(3), c = 23.901(5), β = 106.344(14), V = 5023(2) Å^3, Z = 4, μ = 0.202 mm^{-1}, data/restraints/parameters: 9828/0/ 644. R indices ($I > 2\sigma(I)$): R1 = 0.0518, *wR*2 (all data) = 0.1831.

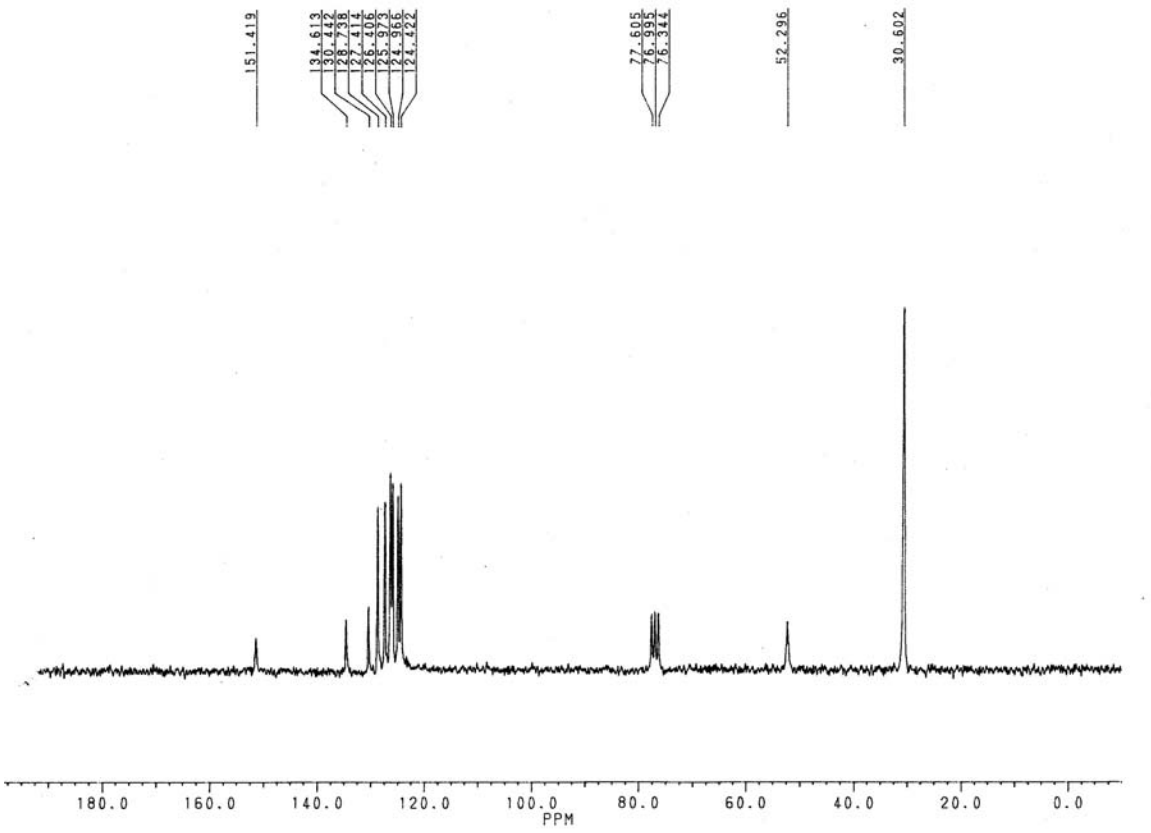

Fig. S1. The ^{13}C NMR spectrum of compound **5**.

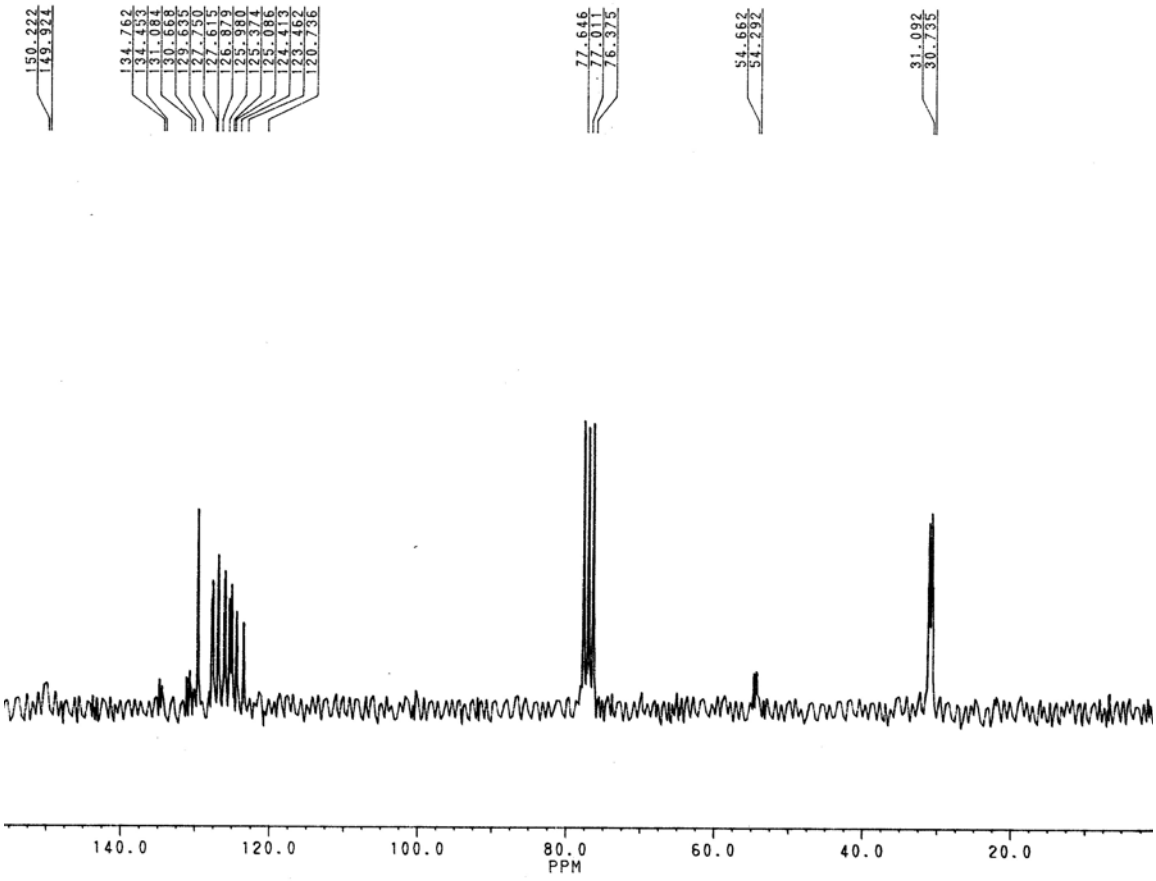

Fig. S2. The ^{13}C NMR spectrum of compound **6**; the multiplet patterns at δ ~ 150, ~54 and ~30 are not well-resolved; other expected peaks are merged with the major peaks.

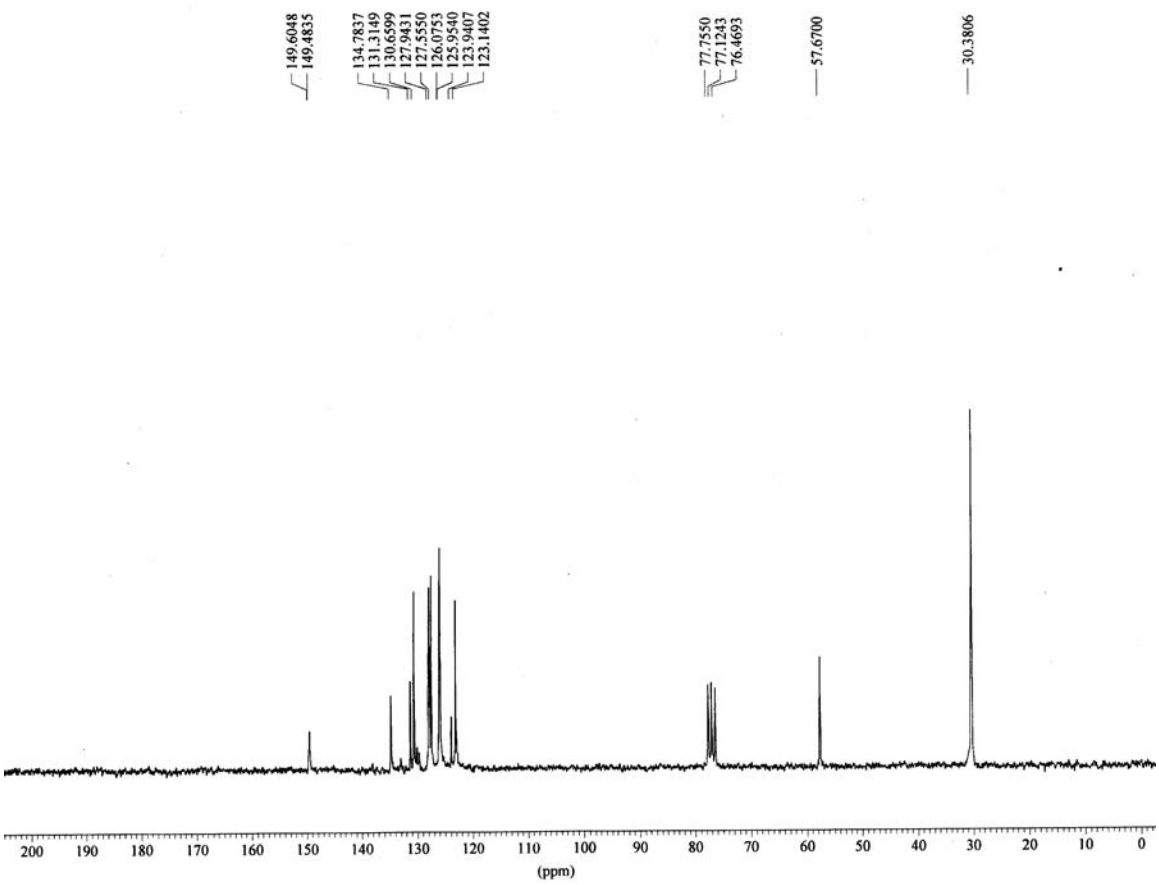

Fig. S3 The ^{13}C NMR spectrum of compound **7**.

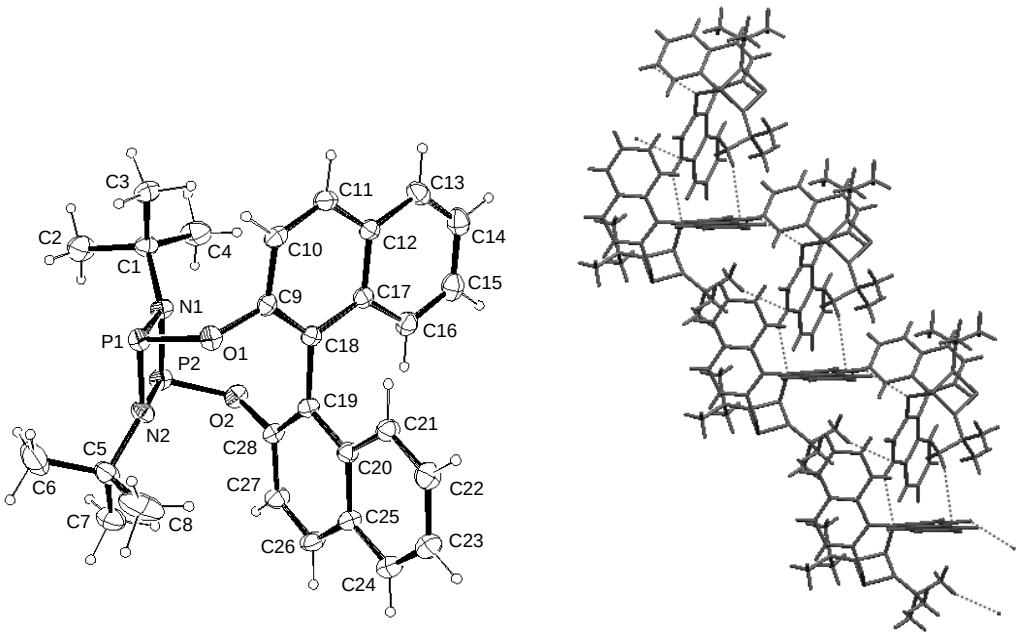

Fig. S4 Molecular structure of **5**; only non-hydrogen atoms are labeled. On the right hand side is shown the packing diagram. Selected bond parameters: P(1) – N(1) 1.687(4), P(1) – N(2) 1.707(4), P(1) – O(1) 1.670(3), P(2) – N(1) 1.715(4), P(2) – N(2) 1.697(4), P(2) – O(2) 1.657(3) Å. N(1) – P(1) – N(2) 82.54(19), N(1) – P(2) – N(2) 81.99(18), P(1) – N(1) – P(2) 97.72(19), P(1) – N(2) – P(2) 97.6(2)^{o}.

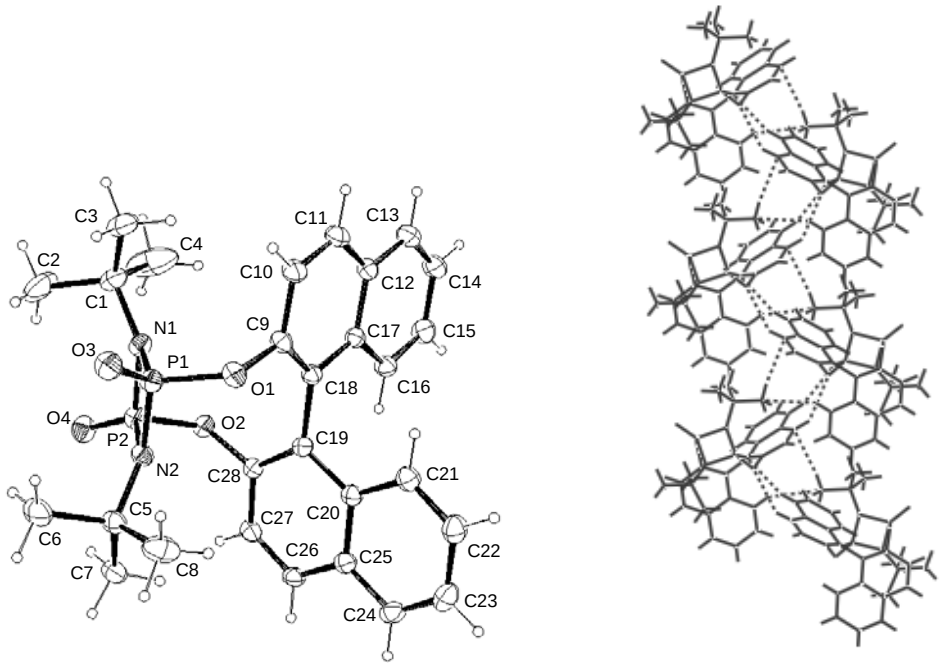

Fig. S5. Molecular structure of **6**; only non-hydrogen atoms are labeled. On the right hand side is shown the packing diagram. Selected bond parameters: P(1) – N(1) 1.6770(14), P(1) – N(2) 1.6908(15), P(1) – O(1) 1.6327(12), P(1) – O(3) 1.388(2), P(2) – N(1) 1.6989(14), P(2) – N(2) 1.6891(15), P(2) – O(2) 1.6281(13), P(2) – O(4) 1.397(3)Å. N(1) – P(1) – N(2) 85.05(7), N(1) – P(2) – N(2) 84.42(7), P(1) – N(1) – P(2) 95.29(7), P(1) – N(2) – P(2) 95.14(8)^{o}.

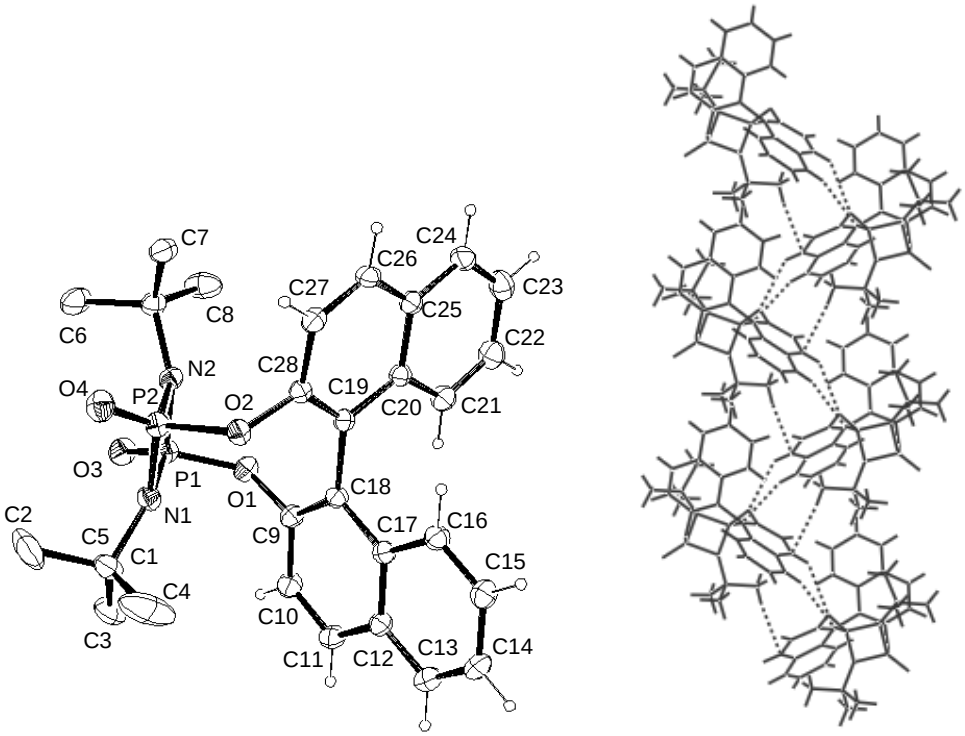

Fig. S6. Molecular structure of **8**; only non-hydrogen atoms are labeled. On the right hand side is shown the packing diagram. Selected bond parameters: P(1) – N(1) 1.675(2), P(1) – N(2) 1.683(3), P(1) – O(1) 1.622(2), P(1) – O(3) 1.426(3), P(2) - N(1) 1.686(3), P(2) – N(2) 1.680(3), P(2) - O(2) 1.617(2), P(2) – O(4) 1.413(3) Å. N(1) – P(1) – N(2) 85.19(13), N(1) – P(2) – N(2) 84.93(12), P(1) – N(1) – P(2) 94.94(13), P(1) – N(2) – P(2) 94.86(14)^{o}.

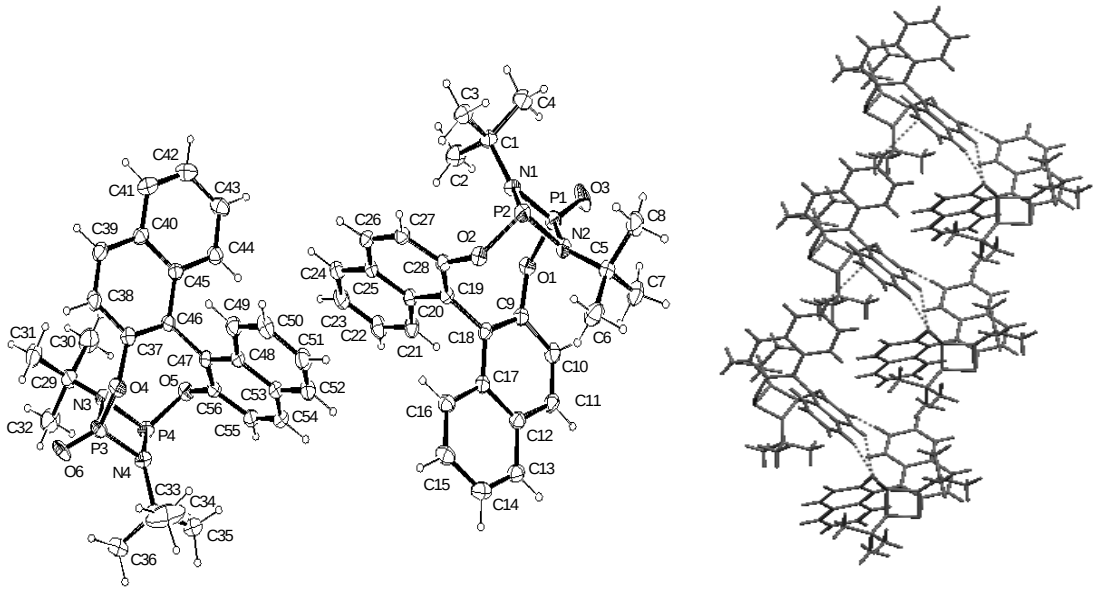

Fig. S7. Molecular structure of **9**. Two molecules are there in the asymmetric unit; only non-hydrogen atoms are labeled. On the right hand side is shown the packing diagram. Selected bond parameters: P(1) – N(1) 1.675(3), P(1) – N(2) 1.676(3), P(1) – O(1) 1.640(3), P(1) - O(3) 1.327(13), P(2) – N(1) 1.678(3), P(2) – N(2) 1.698(3), P(2) – O(2) 1.641(3), P(3) – O(6) 1.328(14), P(3) – N(3) 1.672(3), P(3) – N(4) 1.683(3), P(3) – O(4) 1.636(3), P(4) – N(3) 1.696(3), P(4) – N(4) 1.681(3), P(4) – O(5) 1.635(3) Å. N(1) – P(1) N(2) 82.73(13), N(1) – P(2) – N(2) 81.99(13), N(3) – P(3) – N(4) 83.49(14), N(3) – P(4) N(4) 82.82(14), P(1) – N(1) – P(2) 98.01(14), P(1) – N(2) – P(2) 97.22(14), P(3) – N(3) – P(4) 96.73(14), P(3) – N(4) –P(4) 96.91(15)^{o}.