Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 697–699

Stereoselective synthesis of the $R_PS_PS_PR_P$ isomer of 22-membered P_4N_2 macrocycles

Elvira I. Musina, Tatiana I. Wittmann, Alena S. Shpagina, Andrey A. Karasik, Peter Lönnecke and Evamarie Hey-Hawkins

General Methods. All the reactions and manipulations with phosphines **3a-c** were carried out under a dry argon atmosphere using standard vacuum-line techniques. Solvents were purified, dried, deoxygenated, and distilled before use. ^{1}H NMR spectra were recorded on a Bruker Avance-DRX 400 spectrometer (400 MHz). Chemical shifts are reported in parts per million relative to tetramethylsilane, with the solvents resonances as an internal standards. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (in Hertz), integration, and assignment. ^{31}P NMR spectra were recorded on a Bruker Avance-DRX 400 (162 MHz) and a Bruker Avance-600 (242 MHz) spectrometer, and chemical shifts are reported relative to 85% H_3PO_4. MALDI-TOF mass spectrometry was performed using an Ultraflex III TOF/TOF (Bruker Daltonics, Germany) spectrometer. The FlexAnalysis 3.0 (Bruker Daltonics) program was used to process the mass spectrometry data. ESI mass spectrometry (positive mode) was performed using an AmazonX (Bruker Daltonic GmbH, Bremen, Germany) spectrometer at a capillary voltage of 3500 V. The DataAnalysis 4.0 (Bruker Daltonic GmbH, Bremen, Germany) program was used to process the mass spectrometry data. The mass spectra are reported as m/z values. Determination of the CHN content was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). Determination of the phosphorus content was provided by combustion in an oxygen stream.

Synthesis of 1,6-Bis(phenylphosphino)hexane 1. A solution of 1,6-bis(diphenylphosphino)hexane (22.7 g, 0.05 mol) in dry degassed THF (100 ml) was added dropwise to lithium chips (1.8 g, 0.25 mol) in dry degassed THF (100 ml) at 0 °C over 4 h. The mixture was stirred under reflux for 2 h. The hot reaction mixture was filtered to remove unreacted lithium, and the filtrate was cooled to 0 °C. A THF-water mixture (4:1) (15 ml) was added dropwise to this deep-red filtrate. Discoloration and the formation of a white precipitate were observed. THF was removed *in vacuo* and the residual aqueous solution was extracted with diethyl ether (3×50 ml). The combined organic fractions were dried with $MgSO_4$ overnight, and diethyl ether was removed by distillation under atmospheric pressure. The residue was heated to 150 °C at 0.01 Torr for 30 min to remove all volatiles. The

residual viscous oil was 1,6-bis(phenylphosphino)hexane **1** (20.4 g, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.41 – 7.49 (m, 4H, Ph), 7.25 – 7.29 (m, 6H, Ph), 4.08 (ddd, 2H, $^{1}J_{PH}$ = 210.0, $^{2}J_{PH}$ = 7.0, $^{2}J_{PH}$ = 6.8, PH), 1.74 – 1.83 (m, 2H, PCH_2), 1.64 – 1.71 (m, 2H, PCH_2), 1.38 – 1.41 (m, 4H, PCH_2CH_2), 1.28 – 1.31 (m, 4H, $PCH_2CH_2CH_2$). ^{31}P NMR ($CDCl_3$): δ_P = -52.02 ($^{1}J_{PH}$ = 210.0), -52.04 ($^{1}J_{PH}$ = 210.0).

Synthesis of 1,12-diaza-3,10,14,21-tetraphosphacyclododocosanes 3a-c (general procedure). A neat mixture of 1,6-bis(phenylphosphino)hexane **1** (3 mmol) and paraformaldehyde (6 mmol) was heated at 100–110 °C until homogenization to produce *in situ* 1,6-bis[(hydroxymethyl)-phenylphosphino]hexane **2** (3 mmol). *N*,*N*-Dimethylformamide (10 ml) and the corresponding primary amine (3 mmol) were added, and this was stirred at 80 °C for 24 h. The reaction mixture was then cooled and concentrated *in vacuo* up to 1/4 to 1/6 of the initial volume. The residue was crystallized from a 4:1:4 acetone/benzene/ethanol mixture (for compound **3a**), 10:1 diethyl ether/benzene mixture (for compound **3b**), and compound **3c** was crystallized from diethyl ether which was employed for the extraction of the residue. The crystalline precipitate was filtered off, washed with ethanol or diethyl ether and dried for 4–5 h at 0.01 Torr.

(3R,10S*,14S*,21R*)-1,12-Dibenzyl-3,10,14,21-tetraphenyl-1,12-diaza-3,10,14,21-tetraphosphacyclododocosane (**3a**).*Yield: 0.42 g (32 %); white solid, mp 145–148 °C. ^{1}H NMR (400 MHz, C_6D_6): δ_H = 7.51 (ddd, 8H, $^{3}J_{HH}$ = 7.2, $^{3}J_{HH}$ = 7.0, $^{4}J_{HH}$ = 1.7, *m*-H in Ph), 7.33 (d, 4H, $^{3}J_{HH}$ = 7.3, *o*-H in Bn), 7.24 (dd, 4H, $^{3}J_{HH}$ = 7.3, $^{3}J_{HH}$ = 7.6, *m*-H in Bn), 7.08 – 7.16 (m, 12H, *o*,*p*-H in Ph + 2H *p*-H in Bn), 4.60 (d, 2H, $^{2}J_{HH}$ = 13.1, CH_2Ph), 3.76 (br.d, 4H, $^{2}J_{HH}$ = 12.2, PCH_2N), 3.17 (d, 2H, $^{2}J_{HH}$ = 13.1, CH_2Ph), 2.64 (dd, 4H, $^{2}J_{HH}$ = 12.2, $^{2}J_{PH}$ = 11.2, PCH_2N), 1.97 – 2.05 (m, 4H, PCH_2), 1.74 – 1.80 (m, 4H, PCH_2), 1.64 – 1.71 (m, 4H, PCH_2CH_2), 1.55 – 1.62 (m, 4H, PCH_2CH_2), 1.44 – 1.49 (m, 8H, $PCH_2CH_2CH_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, ppm): δ_P = -36.7. ESI MS, *m*/*z* (I_{rel}, %): 931 (100.0) $[M+4O]^+$. Anal. calc. for $C_{54}H_{66}N_2P_4$ [866]: C, 74.81; H, 7.67; N, 3.23; P, 14.29 %, found: C, 74.91; H, 7.91; N, 3.42; P, 14.13 %.

(3R,10S*,14S*,21R*)-1,12-Bis(4-methylbenzyl)-3,10,14,21-tetraphenyl-1,12-diaza-3,10,14,21-tetraphosphacyclododocosane (**3b**).* Yield: 0.44 g (33 %); white solid, mp 168–169 °C. ^{1}H NMR (400 MHz, C_6D_6): δ_H = 7.57 (ddd, 8H, $^{3}J_{HH}$ = 7.5, $^{3}J_{HH}$ = 7.3, $^{4}J_{HH}$ = 1.6, *m*-H in Ph), 7.33 (d, 4H, $^{3}J_{HH}$ = 7.8, C_6H_4), 7.15 – 7.21 (m, 12H, *o*,*m*-H in Ph), 7.13 (d, 4H, $^{3}J_{HH}$ = 7.8, C_6H_4), 4.68 (d, 2H, $^{2}J_{HH}$ = 13.0, CH_2(*p*-Tol)), 3.83 (br.d, 4H, $^{2}J_{HH}$ = 12.2, PCH_2N), 3.24 (d, 2H, $^{2}J_{HH}$ = 13.0, CH_2(*p*-Tol)), 2.69 (dd, $^{2}J_{HH}$ = 12.2, $^{2}J_{PH}$ = 11.8, 4H, PCH_2N), 2.21 (s, 6H, CH_3), 2.05 – 2.13 (m, 4H, PCH_2), 1.81 – 1.89 (m, 4H, PCH_2), 1.71 – 1.79 (m, 4H, PCH_2CH_2), 1.62 – 1.68 (m, 4H, PCH_2CH_2), 1.49 –

1.56 (m, 8H, $PCH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, ppm): δ_P = -36.5. ESI MS, *m*/*z* (I_{rel}, %): 958 (100.0) $[M+4O]^+$. Anal. calc. for $C_{56}H_{70}N_2P_4$ [894]: C, 75.15; H, 7.88; N, 3.13; P, 13.84 %, found: C, 75.23; H, 7.92; N, 3.16; P, 13.88 %.

(3R,10S*,14S*,21R*)-1,12-Dicyclohexyl-3,10,14,21-tetraphenyl-1,12-diaza-3,10,14,21-tetraphosphacyclodocosane (**3c**).* Yield: 0.45 g (35 %); white solid, mp 154–157 °C. ^1H NMR (400 MHz, C_6D_6): δ_H = 7.61 (ddm, 8H, $^3J_{HH}$ = 6.7, $^3J_{HH}$ = 6.7, *m*-H in Ph), 7.11 – 7.20 (m, 12H, *o*,*p*-H in Ph), 3.57 (dd, 4H, $^2J_{HH}$ = 12.6, $^2J_{HH}$ = 4.7, PCH_2N), 3.37 (m, 2H, NCH), 2.80 (dd, 4H, $^2J_{HH}$ = 12.6, $^2J_{PH}$ = 15.0, PCH_2N), 2.10 – 2.17 (m, 4H, PCH_2), 1.88 – 1.95 (m, 4H, PCH_2), 1.83 – 1.88 (m, 2H, Cy), 1.58 – 1.78 (m, 8H, PCH_2CH_2 + 6H, Cy), 1.47 – 1.55 (m, 8H, $PCH_2CH_2CH_2$), 1.26 – 1.38 (m, 2H, Cy), 1.04 – 1.13 (m, 2H, Cy), 0.88 – 0.99 (m, 4H, Cy), 0.75 – 0.85 (m, 4H, Cy). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, ppm): δ_P = -35.8. ESI MS, *m*/*z* (I_{rel}, %): 851 (30.0) $[M]^+$, 915 (100.0) $[M+4O]^+$. Anal. calc. for $C_{52}H_{74}N_2P_4$ [850]: C, 73.39; H, 8.76; N, 3.29; P, 14.56 %, found: C, 73.45; H, 8.91; N, 3.36; P, 14.71 %.

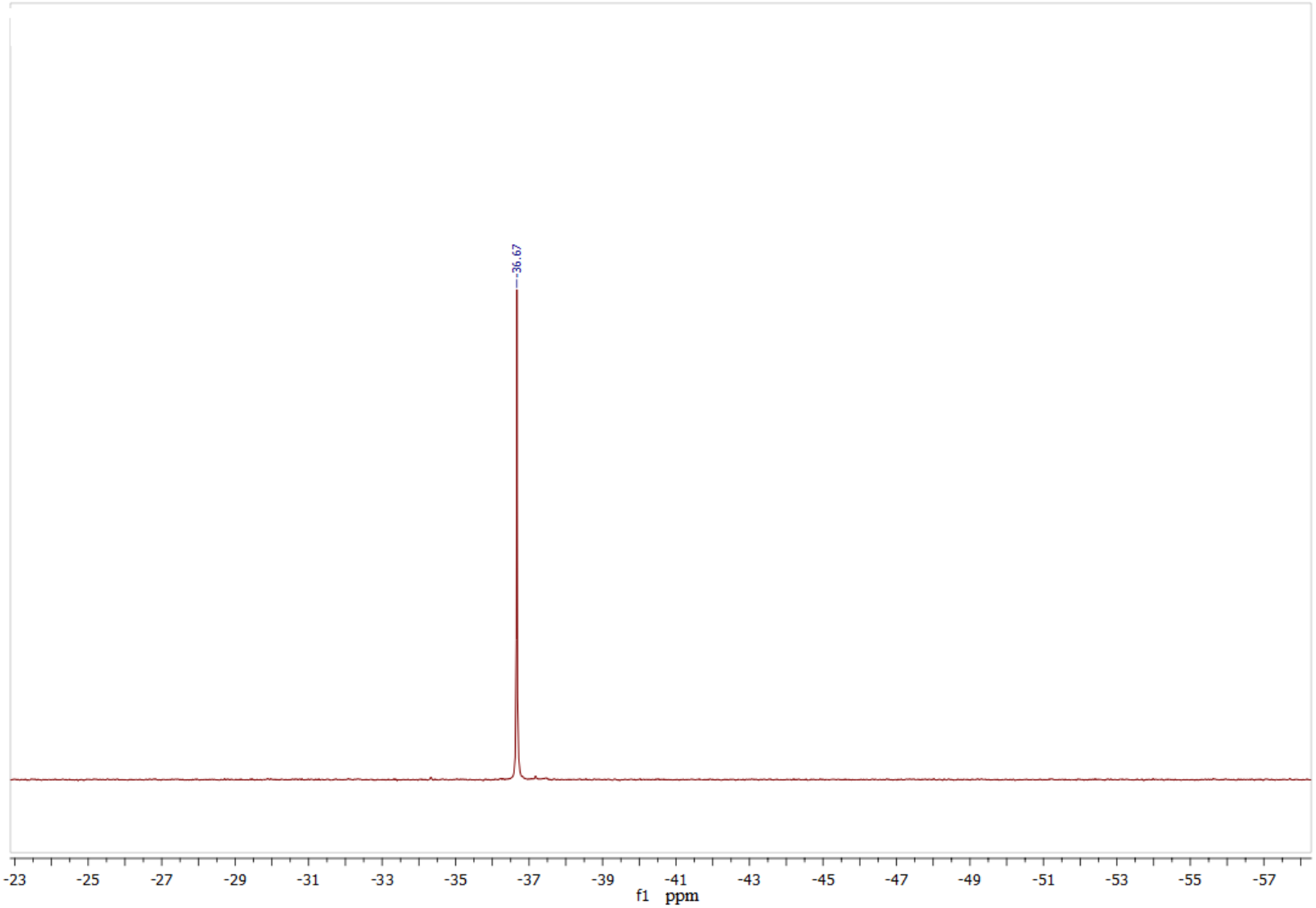

Fig. S1. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** (162 MHz, C_6D_6)

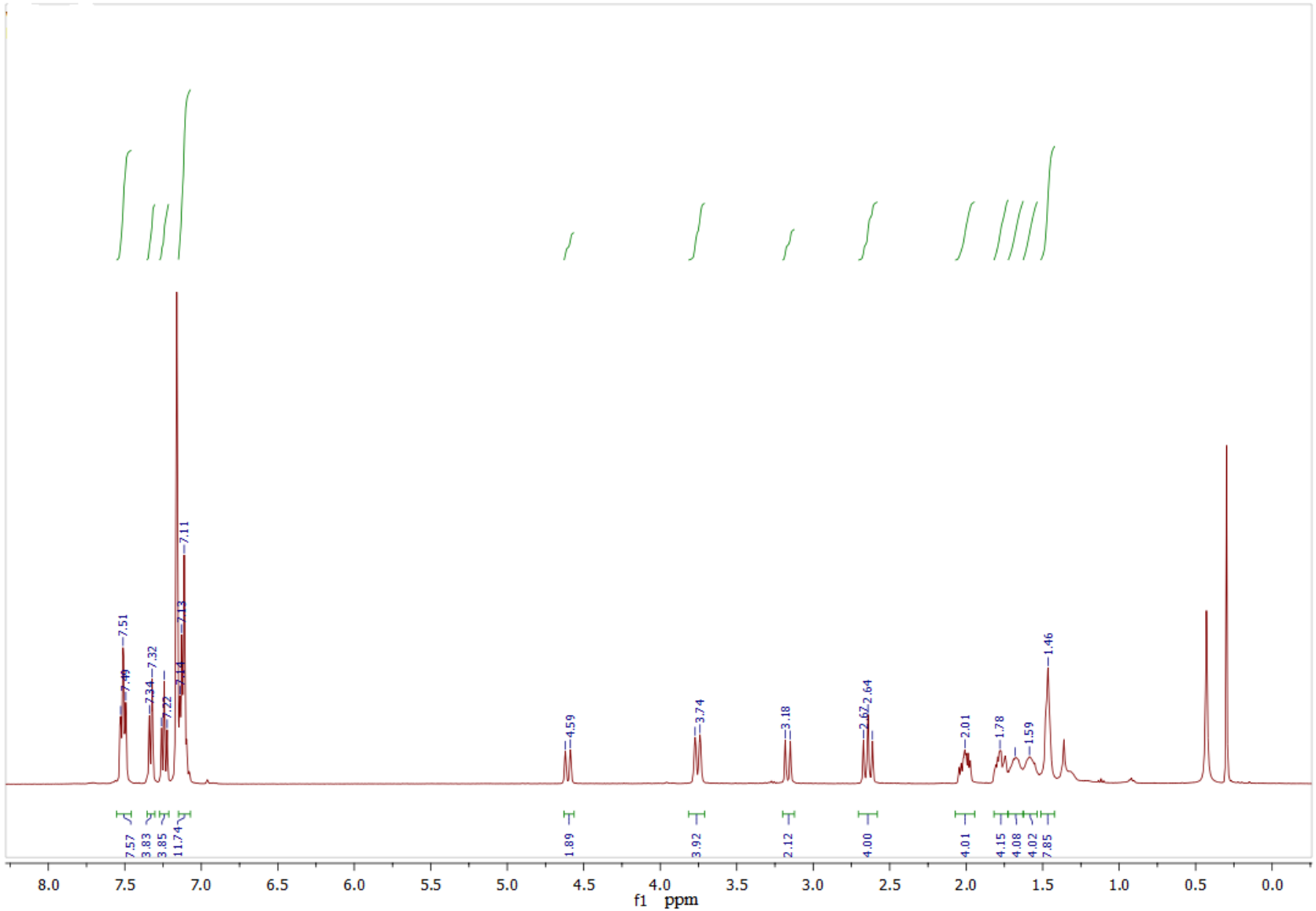

Fig. S2. ^{1}H NMR spectrum of **3a** (400 MHz, C_6D_6)

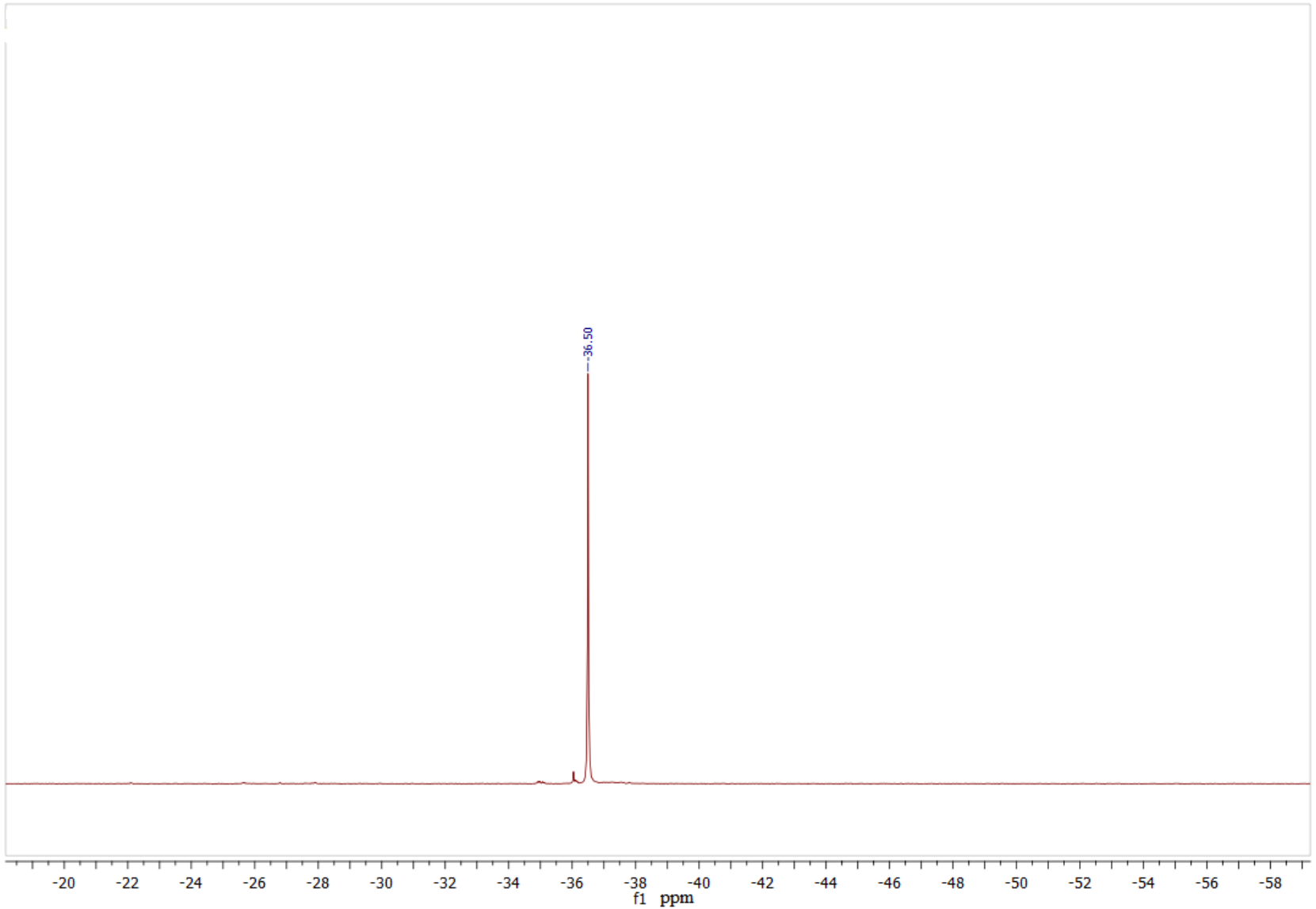

Fig. S3. $^{31}P\{^{1}H\}$ NMR spectrum of **3b** (162 MHz, C_6D_6)

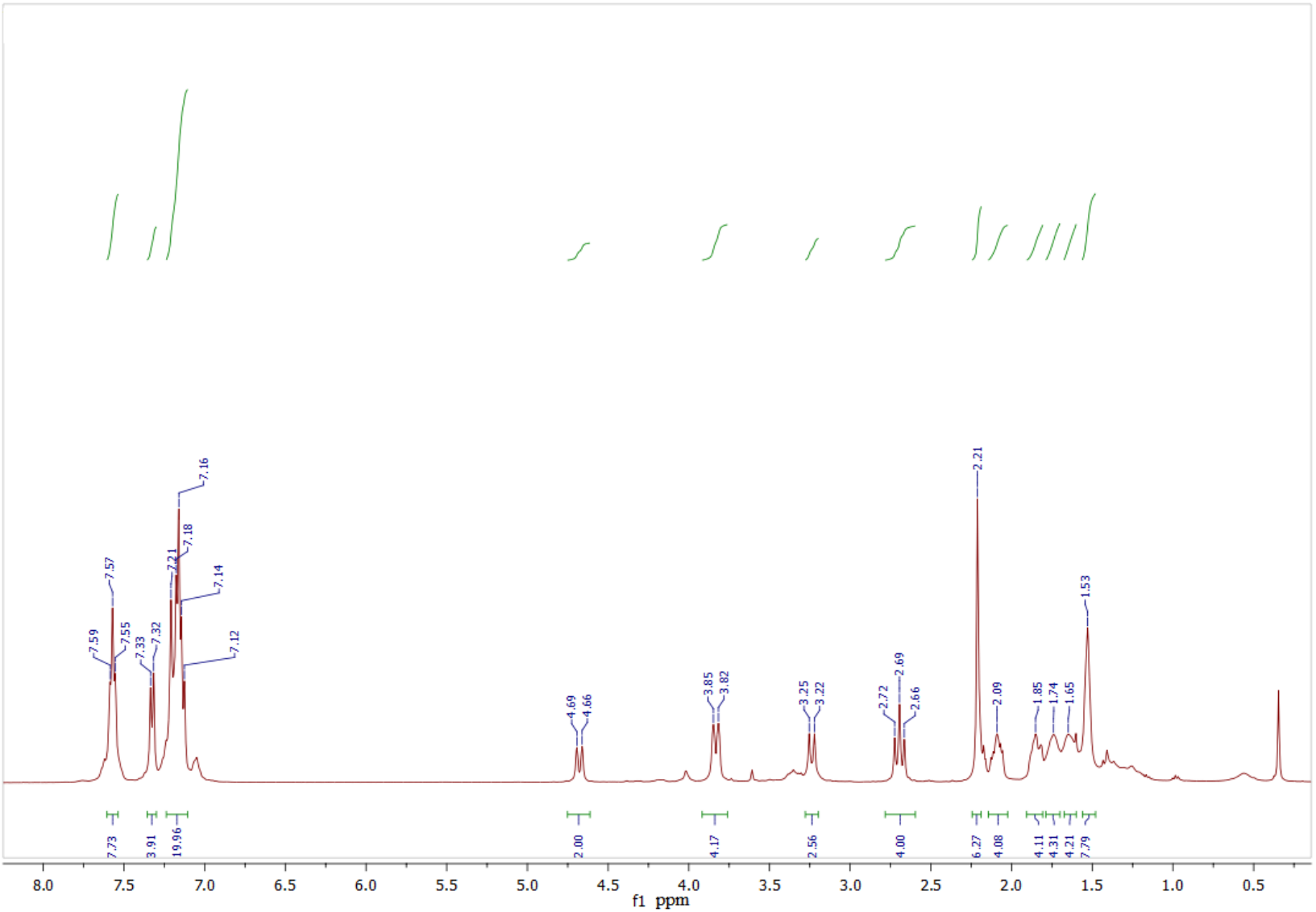

Fig. S4. ^{1}H NMR spectrum of **3b** (400 MHz, C_6D_6)

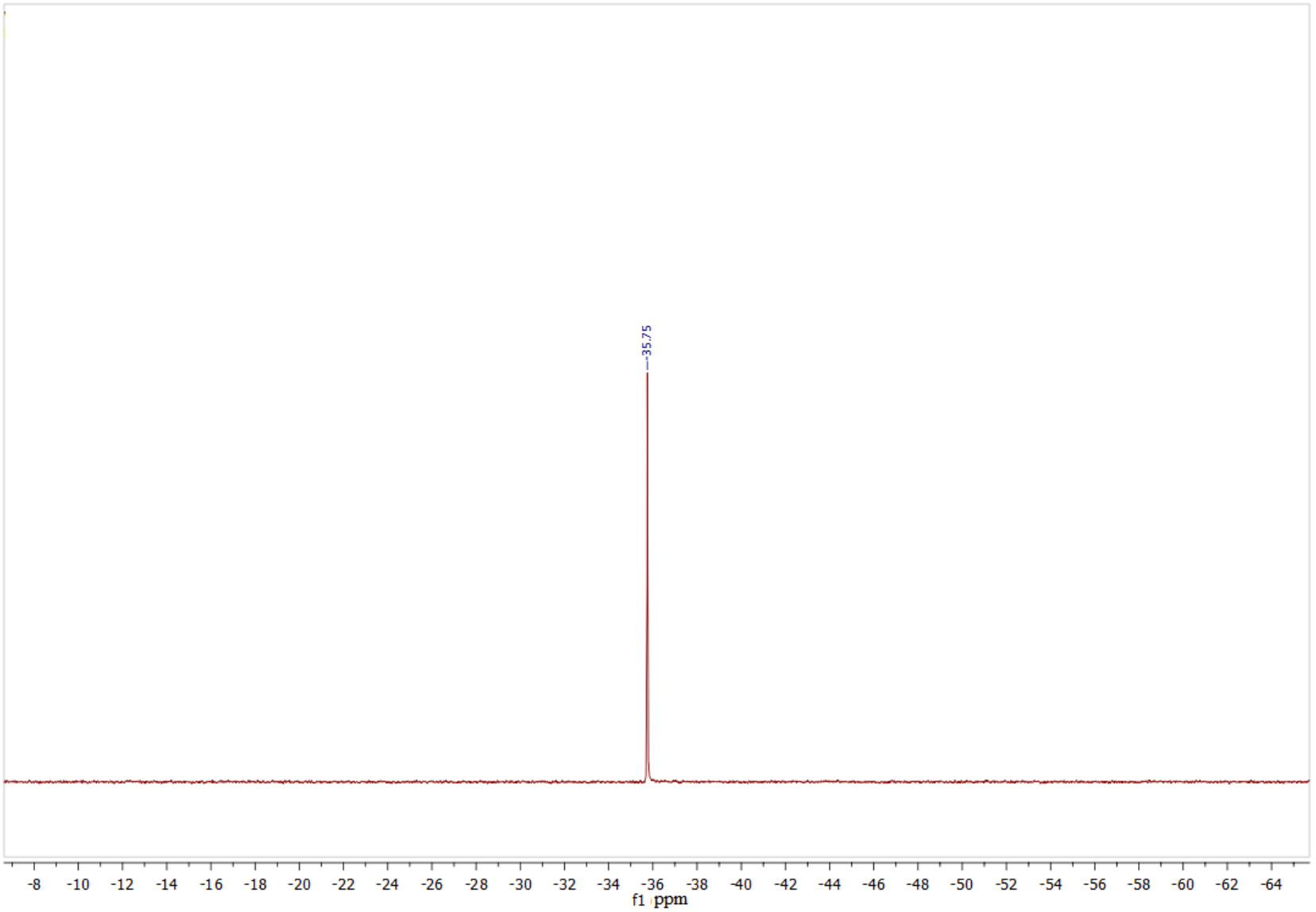

Fig. S5. $^{31}P\{^{1}H\}$ NMR spectrum of **3c** (162 MHz, C_6D_6)

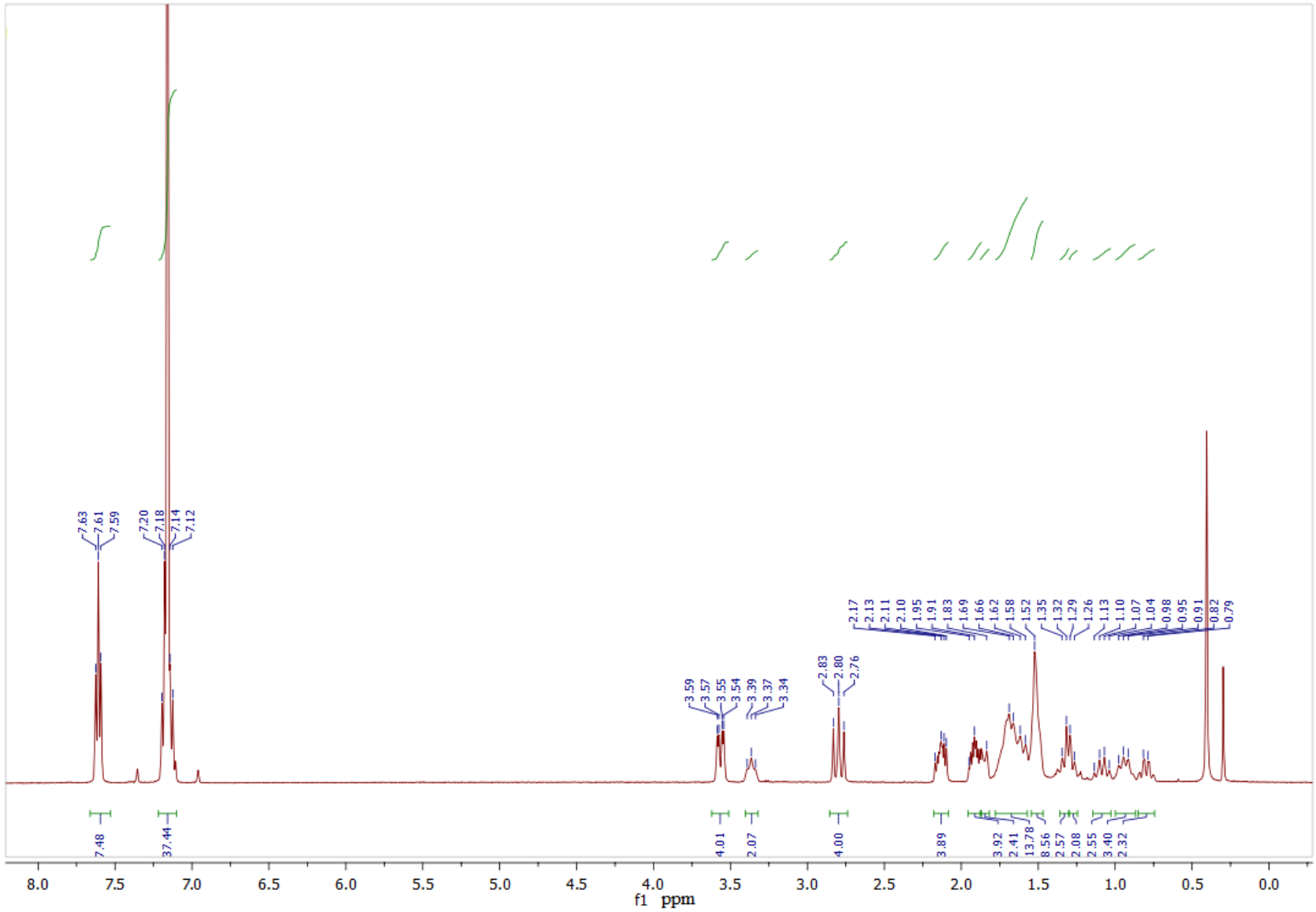

Fig. S6. ^{1}H NMR spectrum of **3c** (400 MHz, C_6D_6)

X-ray crystallography data. The data were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation (λ = 0.71073 Å) and ω-scan rotation. Data reduction was performed with CrysAlisPro including the program SCALE3 ABSPACK for empirical absorption correction. The structures were solved by dual space methods with SHELXT-2014 and the refinement was performed with SHELXL-2018. Hydrogen atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with DIAMOND-4. Fundamental structure parameters are given in Table S1. CCDC 2016579 (for **3a**) 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).

Table S1. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{58}H_{76}N_2OP_4$	
Formula weight	941.08	
Temperature	130(2) K	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 5.5934(3) Å	α = 90.037(5)°
	b = 12.5104(9) Å	β = 97.683(4)°
	c = 19.4871(10) Å	γ = 100.199(5)°
Volume	1329.61(14) $Å^3$	
Z	1	
Density (calculated)	1.175 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	506	
Crystal size	0.40 x 0.04 x 0.01 mm^3	
Theta range for data collection	1.940 to 29.053°.	
Index ranges	$-7 \leq h \leq 6$; $-16 \leq k \leq 5$; $-25 \leq l \leq 26$	
Reflections collected	13834	
Independent reflections	6126 [R(int) = 0.0549]	
Completeness to theta = 26.375°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.87949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6126 / 0 / 403	
Goodness-of-fit on F2	1.022	
Final R indices [I>2sigma(I)]	$R_1 = 0.0554$, $wR_2 = 0.1129$	
R indices (all data)	$R_1 = 0.1019$, $wR_2 = 0.1326$	
Residual electron density	0.296 and -0.332 e · $Å^{-3}$	

The crystal was crystallized from diethylether. Even after several attempts we were unable to localize the solvent molecule with a reasonable accuracy. The electron density of this solvent ether molecule had been removed with the SQUEEZE routine implemented in PLATON. The squeezed electron density of 41 electrons for the unit cell is closely related to one poorly defined

and diffuse oriented Et_2O molecule (42 electrons). A volume of 209 $Å^3$ for one diethylether molecule (Approximately 42 $Å^3$ for each non-hydrogen atom) is acceptable for loosely packed solvent molecules. The given formulae had been corrected for this solvent contribution.

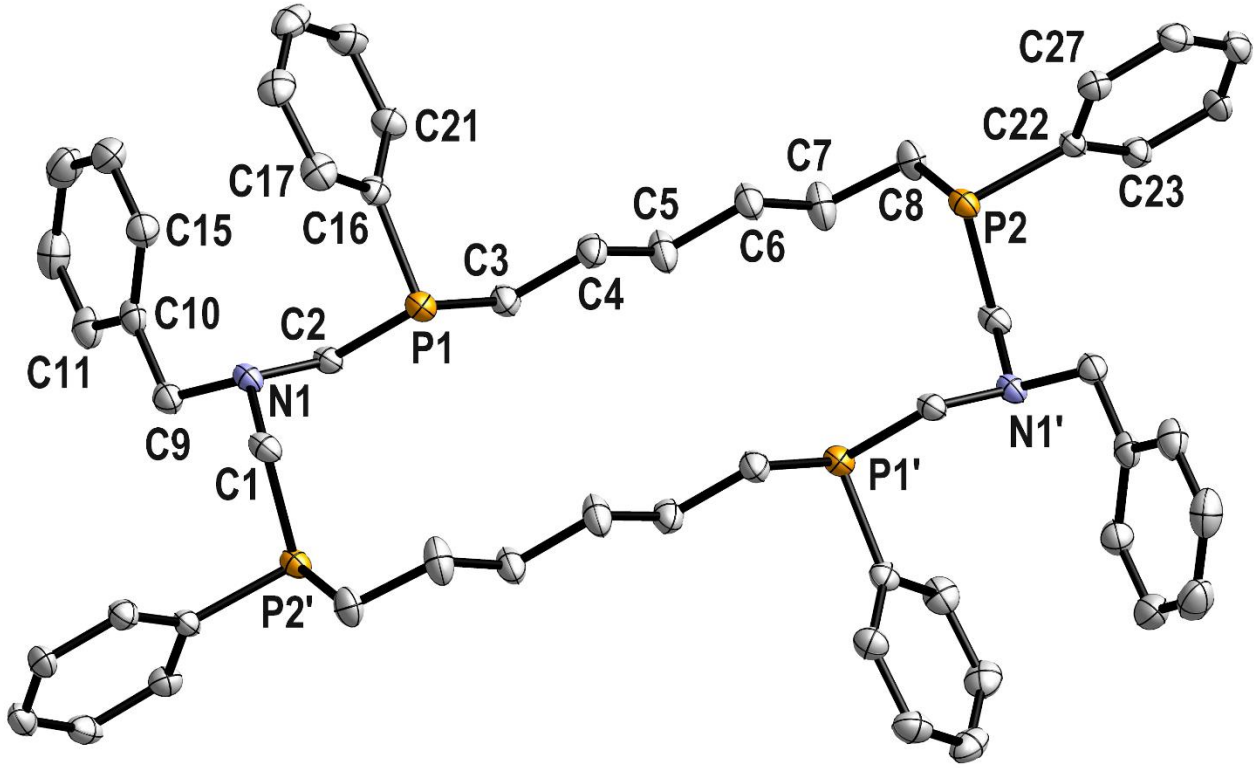

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	6894(1)	5810(1)	6628(1)	23(1)
P(2)	3044(1)	7336(1)	2579(1)	22(1)
N(1)	7180(3)	4838(2)	7904(1)	21(1)
C(1)	8641(4)	4059(2)	7705(2)	23(1)
C(2)	5391(4)	5070(2)	7329(1)	20(1)
C(3)	4093(5)	5876(2)	6028(1)	26(1)
C(4)	4557(5)	6539(2)	5387(1)	28(1)
C(5)	2237(5)	6530(3)	4877(2)	34(1)
C(6)	2667(5)	7196(2)	4241(1)	30(1)
C(7)	340(5)	7141(3)	3720(1)	36(1)
C(8)	689(5)	7759(2)	3052(1)	28(1)
C(9)	6061(5)	4518(2)	8527(1)	25(1)
C(10)	5177(4)	5436(2)	8862(1)	24(1)
C(11)	3205(4)	5232(2)	9234(1)	30(1)
C(12)	2419(5)	6067(3)	9555(1)	37(1)
C(13)	3609(5)	7128(3)	9511(2)	40(1)
C(14)	5599(5)	7347(3)	9150(2)	37(1)
C(15)	6396(5)	6510(2)	8825(1)	29(1)
C(16)	7716(4)	7167(2)	7044(1)	22(1)
C(17)	10008(4)	7406(2)	7453(1)	27(1)
C(18)	10722(5)	8386(2)	7821(1)	31(1)
C(19)	9181(5)	9144(2)	7780(2)	32(1)
C(20)	6932(5)	8924(2)	7369(2)	31(1)
C(21)	6204(5)	7940(2)	7006(1)	26(1)
C(22)	2621(4)	8112(2)	1790(1)	20(1)
C(23)	441(4)	8009(2)	1328(1)	23(1)
C(24)	266(5)	8621(2)	740(1)	26(1)
C(25)	2263(5)	9366(2)	595(1)	29(1)
C(26)	4442(5)	9491(2)	1043(1)	28(1)
C(27)	4630(4)	8865(2)	1631(1)	24(1)

Table S3. Bond lengths [Å] and angles [°].

P(1)-C(16)	1.836(2)
P(1)-C(3)	1.841(3)
P(1)-C(2)	1.862(2)
P(2)-C(22)	1.832(2)
P(2)-C(8)	1.854(3)
P(2)-C(1)#1	1.875(3)
N(1)-C(1)	1.461(3)
N(1)-C(9)	1.462(3)
N(1)-C(2)	1.464(3)
C(1)-H(1A)	0.94(3)
C(1)-H(1B)	0.96(2)
C(2)-H(2A)	0.97(2)
C(2)-H(2B)	1.00(2)
C(3)-C(4)	1.524(4)
C(3)-H(3A)	1.00(3)
C(3)-H(3B)	0.98(3)
C(4)-C(5)	1.524(4)
C(4)-H(4A)	1.00(2)
C(4)-H(4B)	0.93(2)
C(5)-C(6)	1.516(4)
C(5)-H(5A)	1.01(3)
C(5)-H(5B)	0.93(3)
C(6)-C(7)	1.531(4)
C(6)-H(6A)	1.03(2)
C(6)-H(6B)	0.98(3)
C(7)-C(8)	1.532(4)
C(7)-H(7A)	1.11(3)
C(7)-H(7B)	0.99(3)
C(8)-H(8A)	0.96(3)
C(8)-H(8B)	1.03(2)
C(9)-C(10)	1.510(3)
C(9)-H(9A)	1.01(2)
C(9)-H(9B)	0.96(2)
C(10)-C(11)	1.385(3)
C(10)-C(15)	1.401(4)
C(11)-C(12)	1.383(4)
C(11)-H(11)	0.98(2)
C(12)-C(13)	1.385(4)

C(12)-H(12)	0.98(2)
C(13)-C(14)	1.383(4)
C(13)-H(13)	0.95(3)
C(14)-C(15)	1.391(4)
C(14)-H(14)	0.89(3)
C(15)-H(15)	0.98(2)
C(16)-C(21)	1.388(3)
C(16)-C(17)	1.400(3)
C(17)-C(18)	1.388(4)
C(17)-H(17)	1.02(3)
C(18)-C(19)	1.386(4)
C(18)-H(18)	1.05(3)
C(19)-C(20)	1.381(4)
C(19)-H(19)	0.94(3)
C(20)-C(21)	1.389(4)
C(20)-H(20)	0.94(3)
C(21)-H(21)	0.97(3)
C(22)-C(23)	1.401(3)
C(22)-C(27)	1.401(3)
C(23)-C(24)	1.381(3)
C(23)-H(23)	0.97(2)
C(24)-C(25)	1.383(4)
C(24)-H(24)	0.91(2)
C(25)-C(26)	1.386(4)
C(25)-H(25)	0.95(3)
C(26)-C(27)	1.390(4)
C(26)-H(26)	0.94(3)
C(27)-H(27)	1.01(2)

C(16)-P(1)-C(3)	104.07(12)
C(16)-P(1)-C(2)	98.70(11)
C(3)-P(1)-C(2)	97.53(11)
C(22)-P(2)-C(8)	99.91(11)
C(22)-P(2)-C(1)#1	102.51(12)
C(8)-P(2)-C(1)#1	98.14(12)
C(1)-N(1)-C(9)	112.2(2)
C(1)-N(1)-C(2)	112.24(19)
C(9)-N(1)-C(2)	112.51(18)
N(1)-C(1)-P(2)#1	117.06(16)
N(1)-C(1)-H(1A)	107.1(15)

P(2)#1-C(1)-H(1A)	105.6(14)
N(1)-C(1)-H(1B)	104.0(13)
P(2)#1-C(1)-H(1B)	111.5(14)
H(1A)-C(1)-H(1B)	111.6(19)
N(1)-C(2)-P(1)	112.04(15)
N(1)-C(2)-H(2A)	112.7(15)
P(1)-C(2)-H(2A)	106.8(14)
N(1)-C(2)-H(2B)	109.7(12)
P(1)-C(2)-H(2B)	109.6(13)
H(2A)-C(2)-H(2B)	105.8(18)
C(4)-C(3)-P(1)	113.72(18)
C(4)-C(3)-H(3A)	108.5(16)
P(1)-C(3)-H(3A)	101.2(15)
C(4)-C(3)-H(3B)	111.6(17)
P(1)-C(3)-H(3B)	112.0(15)
H(3A)-C(3)-H(3B)	109(2)
C(5)-C(4)-C(3)	112.9(2)
C(5)-C(4)-H(4A)	110.4(13)
C(3)-C(4)-H(4A)	107.9(15)
C(5)-C(4)-H(4B)	109.1(15)
C(3)-C(4)-H(4B)	111.2(15)
H(4A)-C(4)-H(4B)	105.1(19)
C(6)-C(5)-C(4)	113.5(2)
C(6)-C(5)-H(5A)	110.5(17)
C(4)-C(5)-H(5A)	108.2(16)
C(6)-C(5)-H(5B)	113.7(19)
C(4)-C(5)-H(5B)	106.1(17)
H(5A)-C(5)-H(5B)	104(2)
C(5)-C(6)-C(7)	112.8(2)
C(5)-C(6)-H(6A)	107.7(15)
C(7)-C(6)-H(6A)	109.6(14)
C(5)-C(6)-H(6B)	113.4(16)
C(7)-C(6)-H(6B)	107.3(16)
H(6A)-C(6)-H(6B)	106(2)
C(6)-C(7)-C(8)	115.1(2)
C(6)-C(7)-H(7A)	107.5(16)
C(8)-C(7)-H(7A)	110.2(16)
C(6)-C(7)-H(7B)	108.4(16)
C(8)-C(7)-H(7B)	103.2(18)
H(7A)-C(7)-H(7B)	113(2)

C(7)-C(8)-P(2)	113.6(2)
C(7)-C(8)-H(8A)	111.3(16)
P(2)-C(8)-H(8A)	109.0(15)
C(7)-C(8)-H(8B)	108.5(14)
P(2)-C(8)-H(8B)	106.4(13)
H(8A)-C(8)-H(8B)	108(2)
N(1)-C(9)-C(10)	113.2(2)
N(1)-C(9)-H(9A)	113.3(13)
C(10)-C(9)-H(9A)	109.5(13)
N(1)-C(9)-H(9B)	107.1(14)
C(10)-C(9)-H(9B)	109.9(14)
H(9A)-C(9)-H(9B)	103(2)
C(11)-C(10)-C(15)	118.7(3)
C(11)-C(10)-C(9)	120.8(2)
C(15)-C(10)-C(9)	120.5(2)
C(12)-C(11)-C(10)	121.2(3)
C(12)-C(11)-H(11)	121.8(13)
C(10)-C(11)-H(11)	117.0(13)
C(11)-C(12)-C(13)	120.1(3)
C(11)-C(12)-H(12)	117.5(16)
C(13)-C(12)-H(12)	122.4(16)
C(14)-C(13)-C(12)	119.6(3)
C(14)-C(13)-H(13)	115.9(19)
C(12)-C(13)-H(13)	124.5(19)
C(13)-C(14)-C(15)	120.5(3)
C(13)-C(14)-H(14)	121.5(18)
C(15)-C(14)-H(14)	118.0(19)
C(14)-C(15)-C(10)	120.0(3)
C(14)-C(15)-H(15)	119.1(14)
C(10)-C(15)-H(15)	120.9(14)
C(21)-C(16)-C(17)	118.5(2)
C(21)-C(16)-P(1)	125.02(19)
C(17)-C(16)-P(1)	116.45(19)
C(18)-C(17)-C(16)	120.5(3)
C(18)-C(17)-H(17)	118.0(14)
C(16)-C(17)-H(17)	121.5(14)
C(19)-C(18)-C(17)	120.2(2)
C(19)-C(18)-H(18)	121.5(15)
C(17)-C(18)-H(18)	118.3(15)
C(20)-C(19)-C(18)	119.8(3)

C(20)-C(19)-H(19)	120.3(17)
C(18)-C(19)-H(19)	119.9(17)
C(19)-C(20)-C(21)	120.1(3)
C(19)-C(20)-H(20)	119.4(16)
C(21)-C(20)-H(20)	120.6(16)
C(16)-C(21)-C(20)	121.0(2)
C(16)-C(21)-H(21)	124.6(16)
C(20)-C(21)-H(21)	114.4(16)
C(23)-C(22)-C(27)	117.2(2)
C(23)-C(22)-P(2)	125.02(18)
C(27)-C(22)-P(2)	117.73(18)
C(24)-C(23)-C(22)	121.7(2)
C(24)-C(23)-H(23)	120.0(15)
C(22)-C(23)-H(23)	118.3(14)
C(23)-C(24)-C(25)	120.2(2)
C(23)-C(24)-H(24)	122.1(17)
C(25)-C(24)-H(24)	117.6(17)
C(24)-C(25)-C(26)	119.5(3)
C(24)-C(25)-H(25)	121.4(14)
C(26)-C(25)-H(25)	119.1(14)
C(25)-C(26)-C(27)	120.3(2)
C(25)-C(26)-H(26)	120.5(17)
C(27)-C(26)-H(26)	119.1(17)
C(26)-C(27)-C(22)	121.0(2)
C(26)-C(27)-H(27)	118.7(14)
C(22)-C(27)-H(27)	120.2(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	25(1)	20(1)	23(1)	3(1)	3(1)	5(1)
P(2)	21(1)	21(1)	23(1)	5(1)	1(1)	4(1)
N(1)	20(1)	20(1)	22(1)	6(1)	1(1)	4(1)
C(1)	21(1)	21(1)	27(2)	8(1)	1(1)	3(1)
C(2)	21(1)	17(1)	23(1)	4(1)	1(1)	3(1)
C(3)	30(1)	24(2)	22(1)	4(1)	2(1)	0(1)
C(4)	29(1)	28(2)	22(1)	2(1)	0(1)	-1(1)
C(5)	33(2)	42(2)	22(2)	10(1)	-1(1)	-4(1)
C(6)	33(2)	31(2)	23(2)	8(1)	-2(1)	-2(1)
C(7)	32(2)	52(2)	22(2)	11(1)	2(1)	6(1)
C(8)	26(1)	35(2)	23(2)	6(1)	-1(1)	9(1)
C(9)	26(1)	24(1)	22(1)	4(1)	-1(1)	2(1)
C(10)	24(1)	30(2)	18(1)	3(1)	-2(1)	5(1)
C(11)	26(1)	38(2)	24(2)	3(1)	0(1)	2(1)
C(12)	31(2)	56(2)	24(2)	1(1)	4(1)	11(1)
C(13)	50(2)	43(2)	31(2)	-6(2)	2(1)	21(2)
C(14)	48(2)	29(2)	30(2)	-2(1)	-3(1)	6(1)
C(15)	31(1)	30(2)	25(2)	2(1)	2(1)	4(1)
C(16)	21(1)	21(1)	22(1)	3(1)	6(1)	1(1)
C(17)	18(1)	32(2)	31(2)	4(1)	3(1)	2(1)
C(18)	24(1)	33(2)	33(2)	-1(1)	0(1)	-4(1)
C(19)	32(2)	29(2)	33(2)	-8(1)	9(1)	-6(1)
C(20)	33(2)	25(2)	37(2)	1(1)	8(1)	9(1)
C(21)	24(1)	26(2)	29(2)	2(1)	3(1)	7(1)
C(22)	24(1)	17(1)	19(1)	4(1)	5(1)	5(1)
C(23)	23(1)	22(1)	23(1)	2(1)	3(1)	3(1)
C(24)	33(2)	25(1)	20(1)	3(1)	-2(1)	10(1)
C(25)	43(2)	26(2)	21(2)	7(1)	11(1)	12(1)
C(26)	34(2)	19(1)	32(2)	4(1)	11(1)	4(1)
C(27)	24(1)	22(1)	25(1)	-1(1)	4(1)	4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(1A)	9380(40)	4340(20)	7322(13)	24(7)
H(1B)	9830(40)	4035(19)	8104(12)	19(6)
H(2A)	4350(40)	4410(20)	7116(13)	29(7)
H(2B)	4250(40)	5508(18)	7505(11)	16(6)
H(3A)	3550(40)	5100(20)	5882(14)	40(8)
H(3B)	2830(50)	6120(20)	6263(14)	42(8)
H(4A)	5810(40)	6240(20)	5159(12)	26(7)
H(4B)	5280(40)	7260(20)	5508(12)	23(7)
H(5A)	1510(50)	5750(20)	4739(14)	48(9)
H(5B)	1110(50)	6760(20)	5130(15)	44(9)
H(6A)	3980(40)	6900(20)	4010(13)	33(7)
H(6B)	3330(40)	7970(20)	4349(13)	39(8)
H(7A)	-410(50)	6270(30)	3598(16)	63(10)
H(7B)	-820(50)	7520(20)	3930(15)	51(9)
H(8A)	-830(50)	7690(20)	2744(14)	34(7)
H(8B)	1280(40)	8570(20)	3179(12)	28(7)
H(9A)	4680(40)	3870(20)	8446(11)	21(6)
H(9B)	7270(40)	4257(19)	8844(12)	20(6)
H(11)	2420(40)	4470(20)	9263(11)	17(6)
H(12)	980(40)	5880(20)	9798(13)	35(7)
H(13)	3160(50)	7740(30)	9718(16)	62(10)
H(14)	6370(50)	8020(20)	9103(14)	44(9)
H(15)	7800(40)	6683(19)	8571(12)	24(7)
H(17)	11190(40)	6870(20)	7496(13)	40(8)
H(18)	12460(50)	8530(20)	8127(14)	45(8)
H(19)	9660(40)	9800(20)	8039(14)	44(8)
H(20)	5910(40)	9450(20)	7337(13)	36(8)
H(21)	4620(50)	7860(20)	6722(14)	40(8)
H(23)	-980(40)	7510(20)	1439(12)	24(7)
H(24)	-1140(40)	8560(20)	441(13)	32(7)
H(25)	2190(40)	9780(20)	184(13)	32(7)
H(26)	5790(40)	10020(20)	966(14)	40(8)
H(27)	6220(40)	8983(19)	1953(12)	23(6)