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A new efficient synthesis of Pyrphos ligand

Yuriy N. Kononevich, Alexander D. Volodin, Alexander A. Korlyukov, Valery K. Brel and Aziz M. Muzafarov

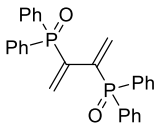
Table of Contents

1. General Methods and Materials

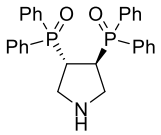
All solvents were purified before use. Toluene and tetrahydrofuran were distilled over CaH_2. Pyridine and methanol were distilled. But-2-yne-1,4-diol and chloro(diphenyl)phosphine were purchased from ABCR. Phenylsilane was purchased from Acros Organics. Column chromatography was carried out using Merck 60 (230–400 mesh) silica gel. Thin-layer chromatography (TLC) was performed using Fluka silica gel (60 F 254) plates (0.25 mm). Visualization was made with UV light. IR spectra were recorded on an IR spectrometer with a Fourier transform Shimadzu IRTracer-100 (Japan). The samples were prepared by pressing KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 400 (400 MHz; Germany) spectrometer. Chemical shifts are reported relative to chloroform (δ=7.25 ppm) for ^{1}H NMR and chloroform (δ=77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI) (Germany). Single crystals of **9** were grown from dichloromethane. A suitable crystal was selected and collected on a Bruker D8 QUEST diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,[S1] the structure was solved with the XT[S2] structure solution program using Intrinsic Phasing and refined with the XL[S3] refinement package using Least Squares minimization. Crystallographic data for the **9** was shown in the Table S1 and have been deposited in the Cambridge Crystallographic Data Centre as CCDC 2255112.

2. Synthesis

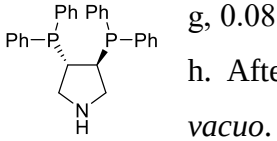
2,3-Bis(diphenylphosphoryl)buta-1,3-diene ***(3)*** was synthesized by the method described earlier.[S4]



rac-(3R,4R*)-3,4-Bis(diphenylphosphoryl)pyrrolidine* ***(4)****.* A solution of 2,3-bis(diphenylphosphoryl)buta-1,3-diene **3** (0.5 g, 1.1 mmol) in methanol (5 mL) was placed in a stainless steel autoclave (20 mL). The solution was cooled down to -50 °C followed by ammonia (2 g) which was condensed into the autoclave. The vessel was sealed, and the reaction mixture was stirred at 60 °C for 12 h. After the reaction was complete ammonia excess was ventilated at room temperature. The solvent was removed by rotor evaporator and the residue was purified by column chromatography on silica using a mixture dichloromethane-methanol (3:1) as an eluent. The product was obtained as a white solid. **Yield**: 91%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.45 (br s, 1H, NH), 3.15-3.39 (m, 6H, CH_2,CH), 7.12 (t, 4H, J = 6.9 Hz, Ar), 7.30 (t, 2H, J = 7.3 Hz, Ar), 7.38-7.48 (m, 10H, Ar), 7.69-7.73 (m, 4H, Ar). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 37.68, 37.80, 38.14, 38.48, 38.60, 51.03, 128.55, 128.61, 128.67, 128.73, 128.79, 130.32, 130.36, 130.41, 130.61, 130.66, 130.70, 130.99, 131.08, 131.38, 131.79, 131.85, 132.04, 132.12, 132.82, 132.90. **^{31}P NMR** (121 MHz, $CDCl_3$): δ 35.33. **IR** (KBr, cm^{-1}): 3051, 3025, 2965, 2916, 2877, 1592, 1487, 1438, 1344, 1190, 1182, 1118, 1103, 1071, 1029, 1015, 997, 919, 898, 877, 823, 763, 754, 722, 701, 691, 674, 568, 558, 539, 532, 517, 435. **HRMS** (ESI) m/z calcd. for $C_{28}H_{28}NO_2P_2$ $[(M+H)^+]$: 472.1590, found 472.1594.



rac-(3R,4R*)-3,4-Bis(diphenylphosphino)pyrrolidine (rac-****1****).* A mixture of compound **4** (0.04 g, 0.085 mmol) and phenylsilane (0.176 g, 1.6 mmol) was heated at 120 °C for 24 h. After the reaction was complete, the volatile components were removed *in vacuo*. The product was obtained as viscous oil. **Yield**: 73% (conversion by NMR). **^{31}P NMR** (162 MHz, $CDCl_3$): δ -7.05 (s). **HRMS** (ESI) m/z calcd. for $C_{28}H_{28}NP_2$ $[(M+H)^+]$: 440.1691, found 440.1687.



[4-(Hexylamino)but-1-ene-2,3-diyl]bis(diphenylphosphine oxide) ***(6)****.* A solution of 2,3-bis(diphenylphosphoryl)buta-1,3-diene **4** (0.1 g, 0.22 mmol) and hexylamine (0.033 g, 0.33 mmol) in THF (2 mL) was stirred at room temperature for 24 h. After the reaction was complete, the solvent and excess of hexylamine were removed *in vacuo*. The product was obtained

as a viscous colorless oil. **Yield**: 95%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.81-1.28 (m, 11H, CH_2, CH_3), 2.12-2.25 (m, 2H, CH_2), 2.64 (br s, 1H, NH), 2.94-3.02 (m, 2H, CH_2), 4.27-4.35 (m, 1H, CH), 5.55 (dd, 1H, J_1 = 20.8 Hz, J_2 = 3.5 Hz, CH_2), 5.85 (dd, 1H, J_1 = 44.2 Hz, J_2 = 3.1 Hz, CH_2), 7.15-7.19 (m, 2H, Ar), 7.35-7.55 (m, 10H, Ar), 7.35-7.45 (m, 6H, Ar), 7.73-7.78 (m, 2H, Ar), 7.91-7.98 (m, 4H, Ar). **^{31}P NMR** (121 MHz, $CDCl_3$): δ 31.00 (1P, J = 19.8 Hz), 32.04 (1P, J = 19.8 Hz). **HRMS** (ESI) m/z calcd. for $C_{34}H_{40}NO_2P_2$ $[(M+H)^+]$: 556.2529, found 556.2529.

(rac-(3S,4S*)-1-Hexylpyrrolidine-3,4-diyl)bis(diphenylphosphine oxide) (**5**).* A solution of 2,3-bis(diphenylphosphoryl)buta-1,3-diene **4** (0.1 g, 0.22 mmol) and hexylamine (0.033 g, 0.33 mmol) in MeOH (2 mL) was stirred at room temperature for 48 h. After the reaction was complete, the solvent and excess of hexylamine were removed *in vacuo*, and the residue was purified by column chromatography on silica using a mixture dichloromethane-methanol (20:1) as an eluent. The product was obtained as a viscous colorless oil. **Yield**: 89%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.82 (t, 3H, J = 7.1 Hz, CH_3), 1.11-1.23 (m, 8H, CH_2), 2.14-2.17 (m, 1H, CH), 2.27-2.32 (m, 1H, CH), 2.62-2.68 (m, 2H, CH_2), 2.81-2.88 (m, 2H, CH_2), 3.65-3.70 (m, 2H, CH), 7.14 (t, 4H, J = 6.8 Hz, Ar), 7.24 (t, 2H, J = 7.3 Hz, Ar), 7.35-7.45 (m, 6H, Ar), 7.57 (t, 4H, J = 8.2 Hz, Ar), 7.70 (t, 4H, J = 8.3 Hz, Ar). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 14.0, 22.5, 27.0, 28.3, 31.3, 36.0, 36.1, 36.8, 36.9, 54.8, 55.0, 128.26, 128.32, 128.4, 130.82, 130.86, 130.90, 130.98, 131.02, 131.1, 131.4, 131.5. **^{31}P NMR** (162 MHz, $CDCl_3$): δ 33.91 (s). **HRMS** (ESI) m/z calcd. for $C_{34}H_{40}NO_2P_2$ $[(M+H)^+]$: 556.2529, found 556.2523.

3. Spectral Data

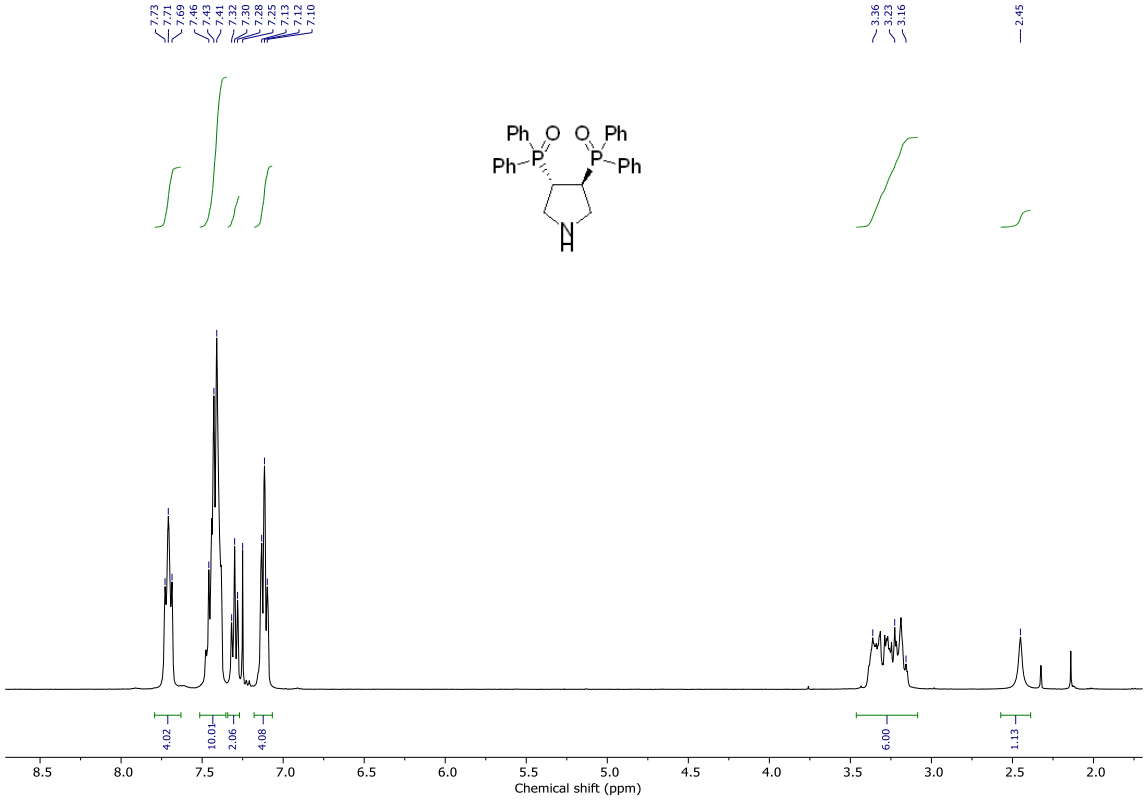


Figure S1. ^{1}H NMR spectrum of **4** in $CDCl_3$.

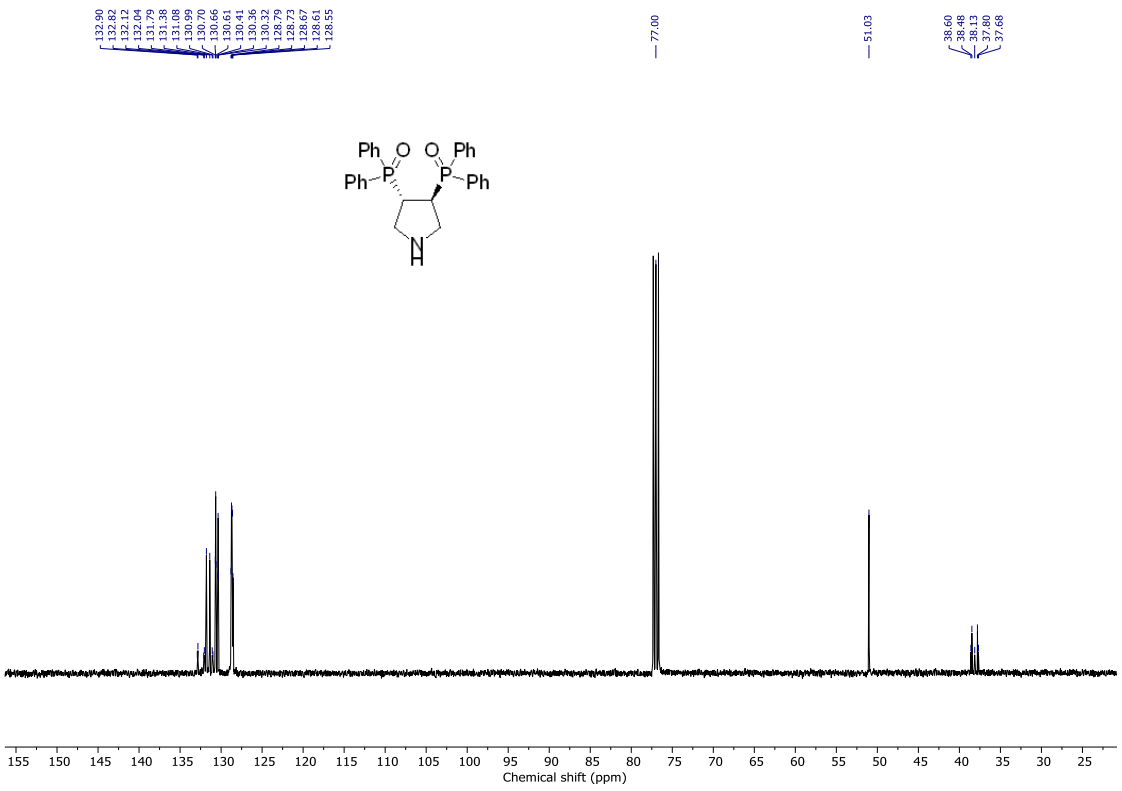


Figure S2. ^{13}C NMR spectrum of **4** in $CDCl_3$.

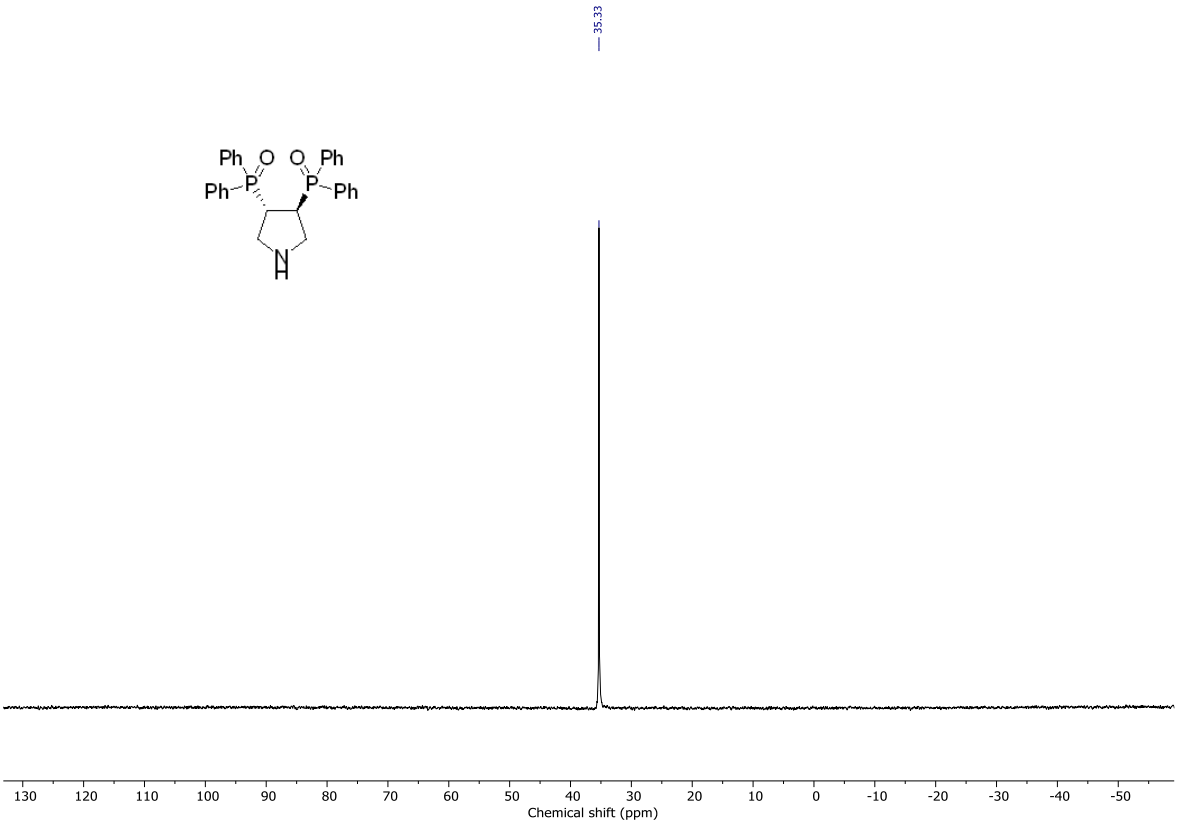


Figure S3. ^{31}P NMR spectrum of **4** in $CDCl_3$.

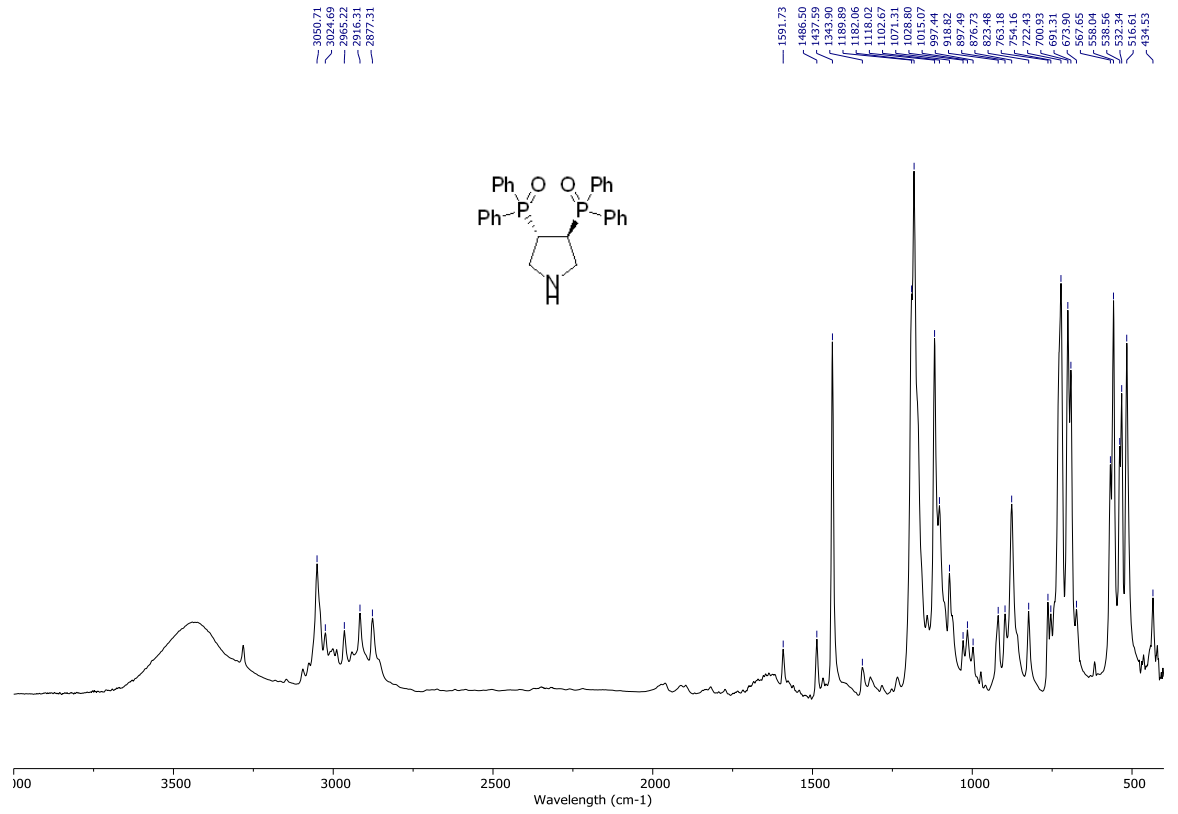
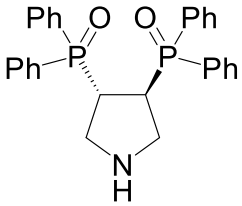


Figure S4. IR spectrum of **4**.



m/z calcd. for $C_{28}H_{28}NO_2P_2$ [$(M+H)^+$]: 472.1590

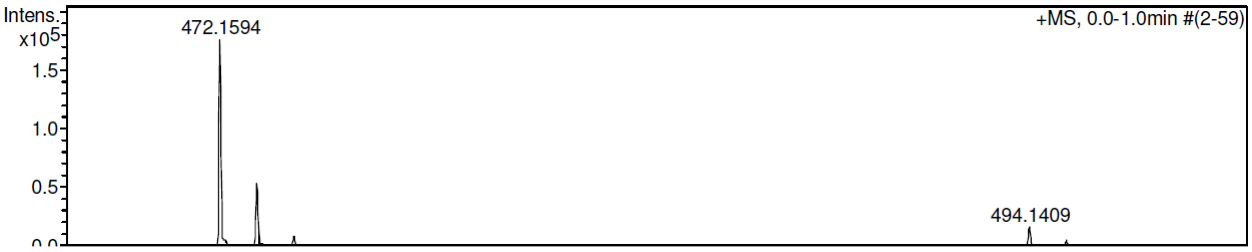


Figure S5. MS spectrum of **4**.

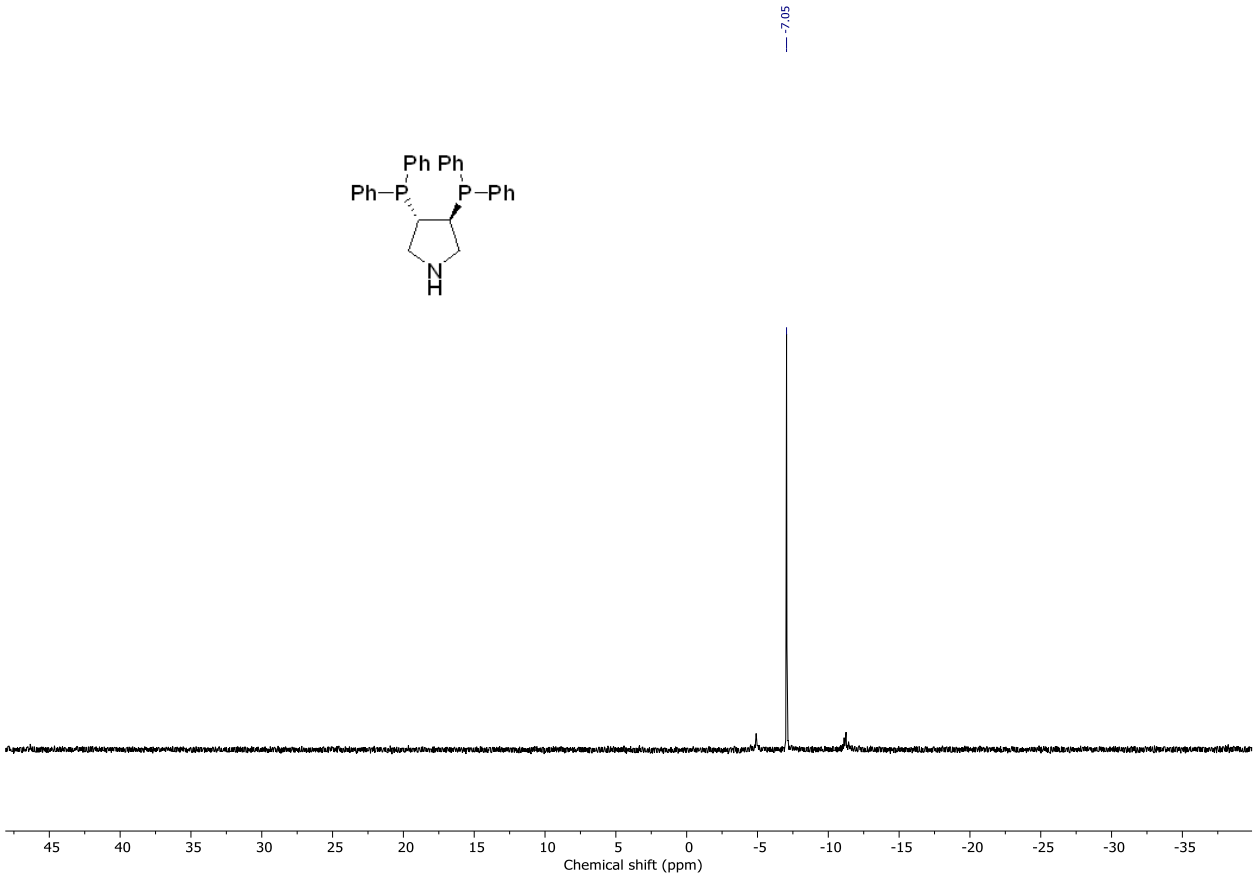
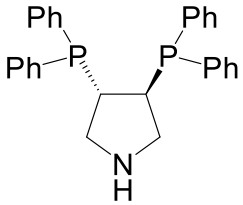


Figure S6. ^{31}P NMR spectrum of **1** in $CDCl_3$.



m/z calcd. for $C_{28}H_{28}NP_2$ [$(M+H)^+$]: 440.1691

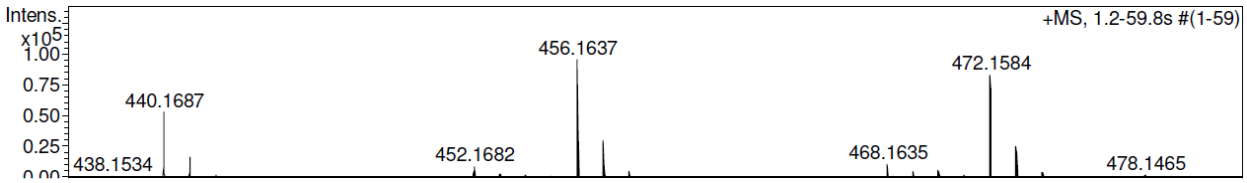


Figure S7. MS spectrum of **1**.

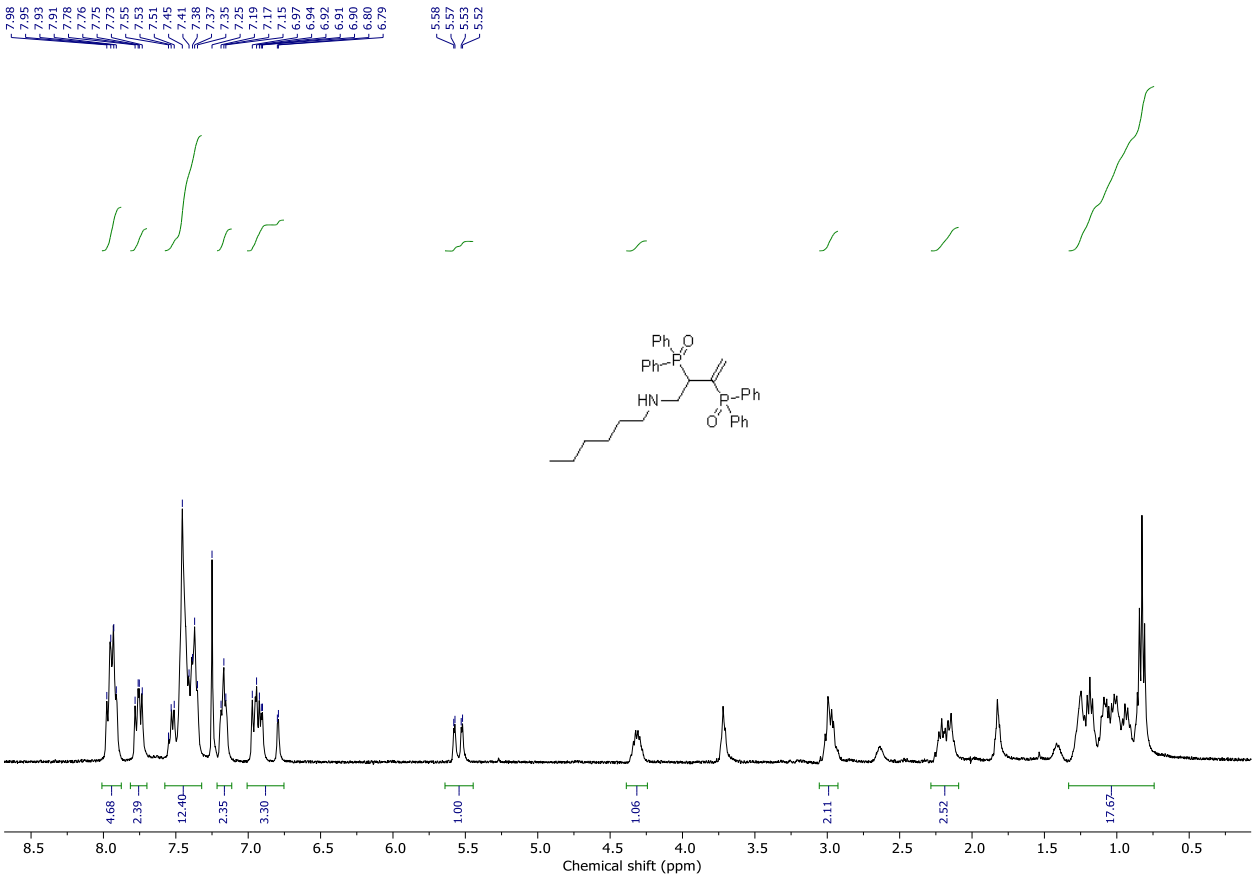


Figure S8. ^{1}H NMR spectrum of **6** in $CDCl_3$.

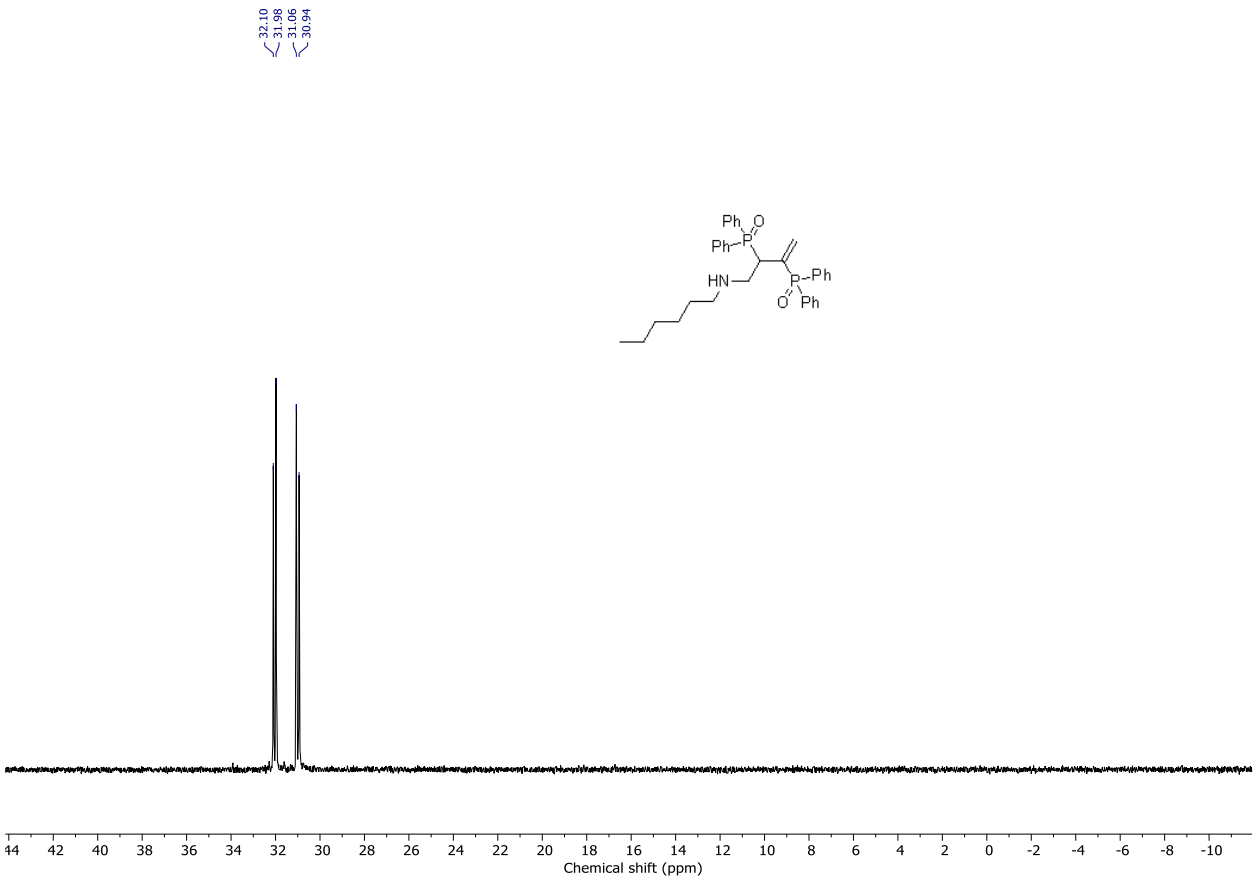
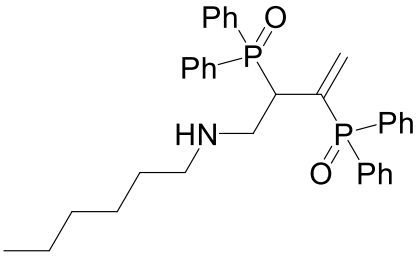


Figure S9. ^{31}P NMR spectrum of **6** in $CDCl_3$.



m/z calcd. for $C_{34}H_{40}NO_2P_2$ $[(M+H)^+]$: 556.2529

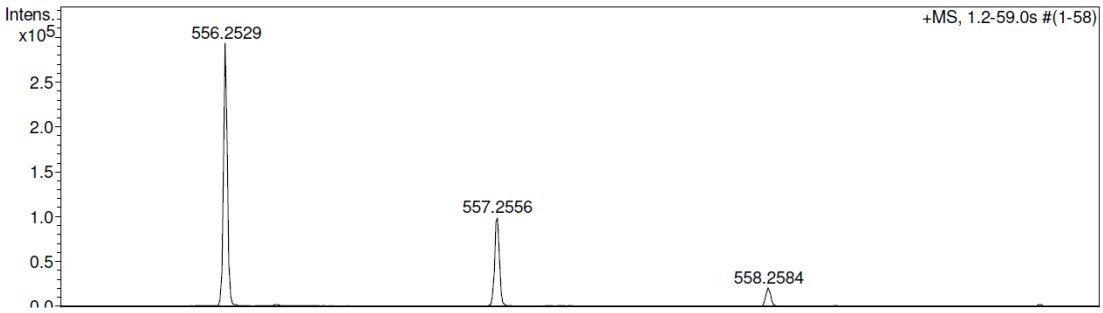


Figure S10. MS spectrum of **6**.

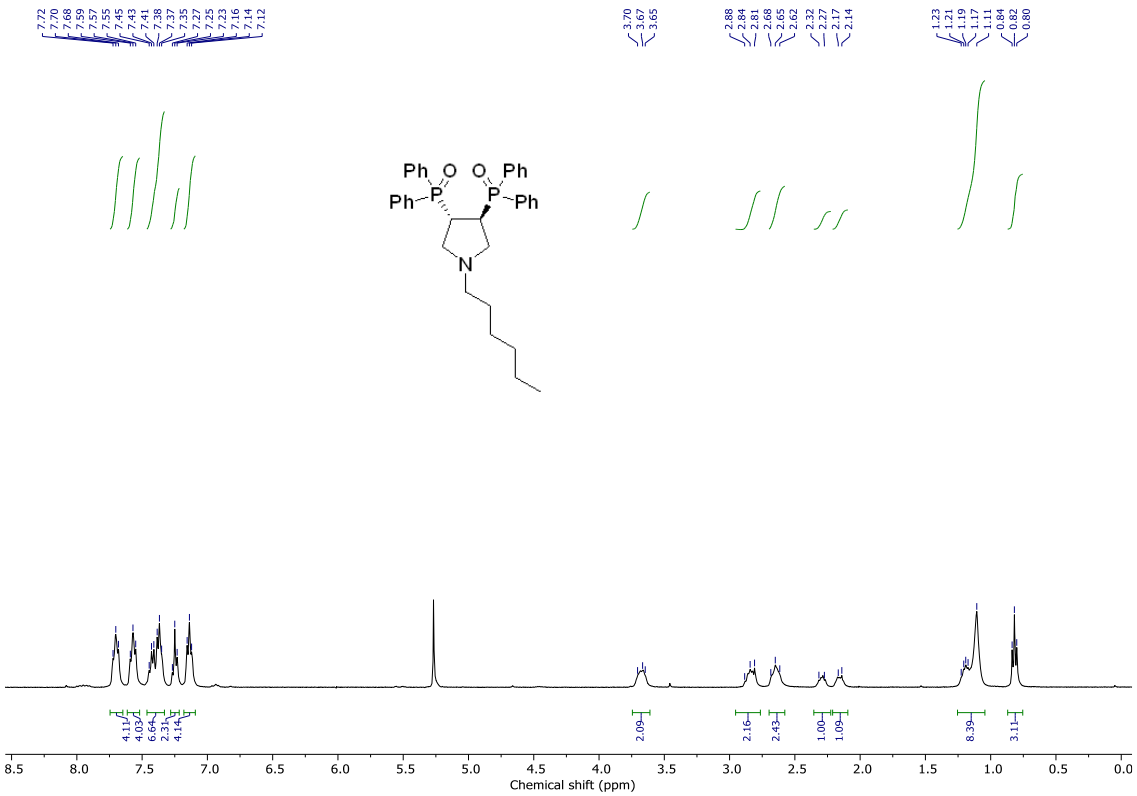


Figure S11. ^{1}H NMR spectrum of **5** in $CDCl_3$.

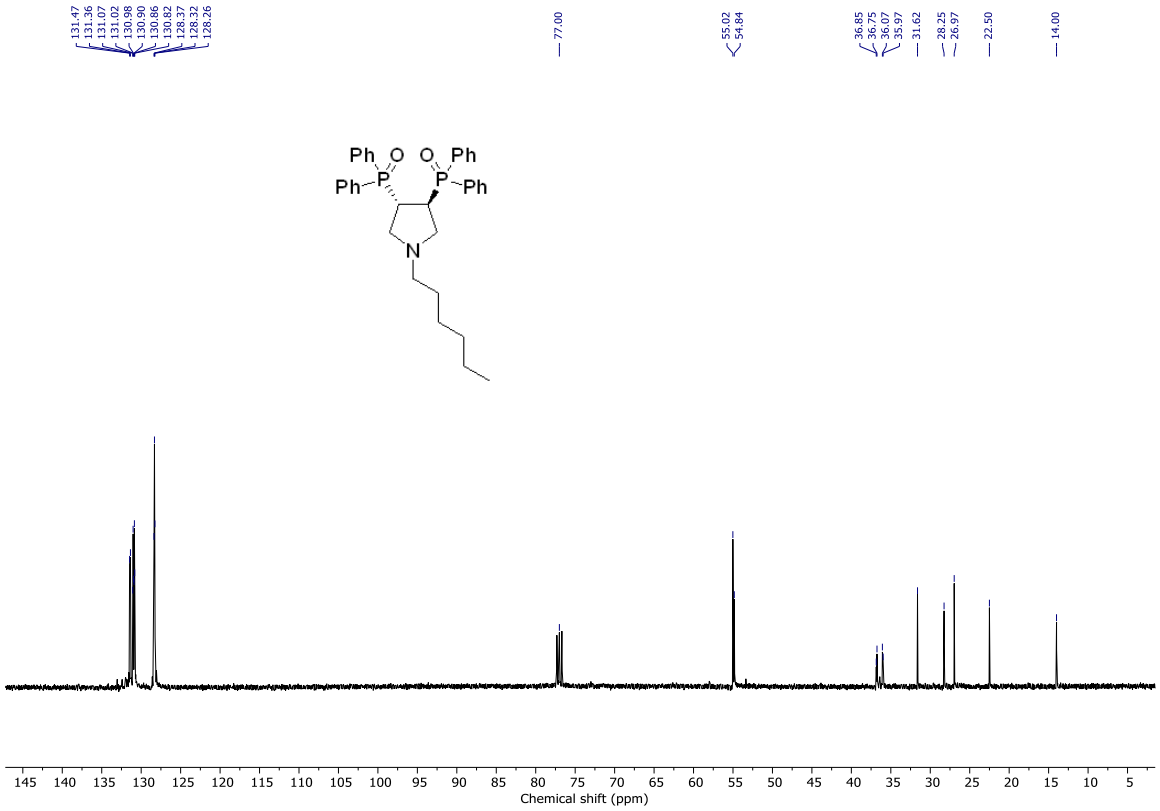


Figure S12. ^{13}C NMR spectrum of **5** in $CDCl_3$.

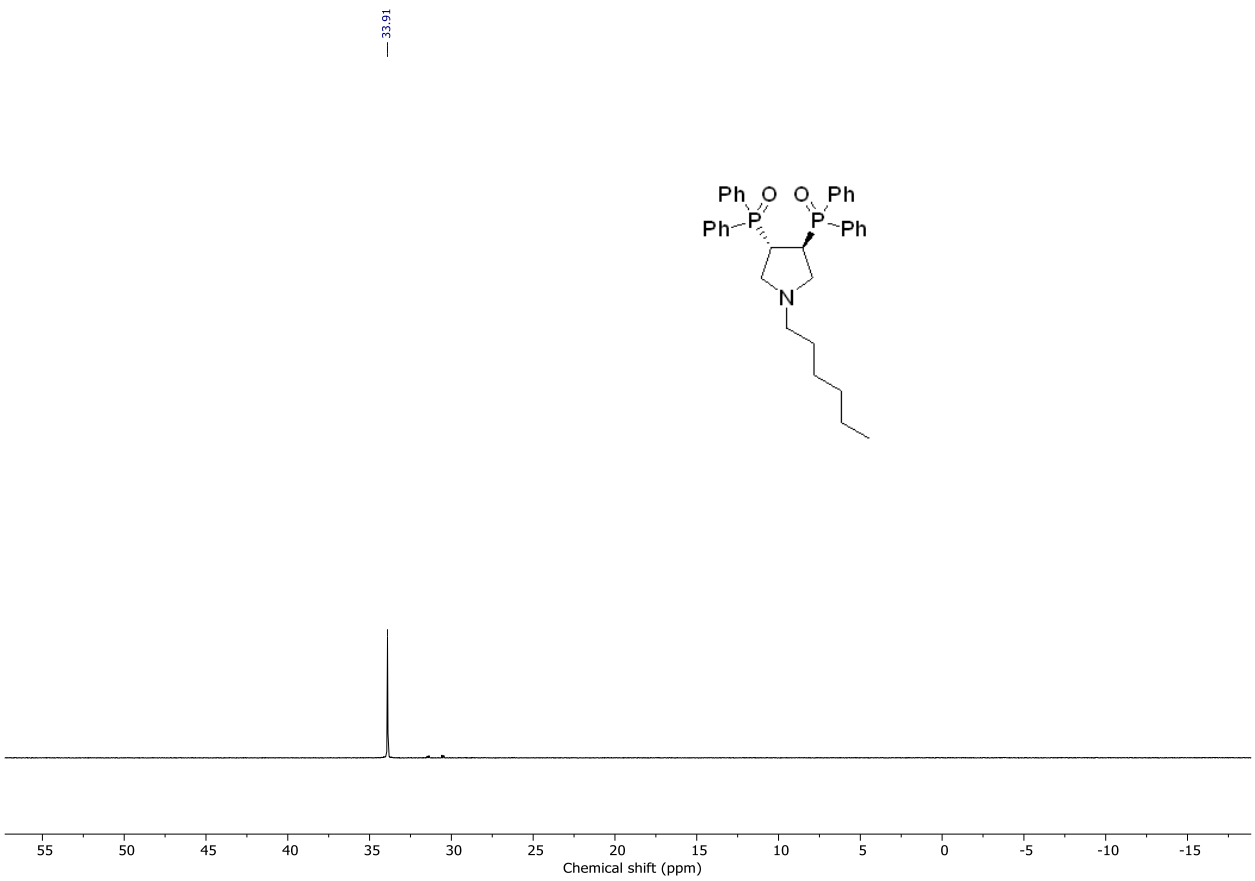
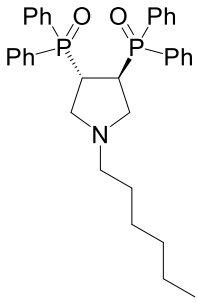


Figure S13. ^{31}P NMR spectrum of **5** in $CDCl_3$.



m/z calcd. for $C_{34}H_{40}NO_2P_2$ [$(M+H)^+$]: 556.2529

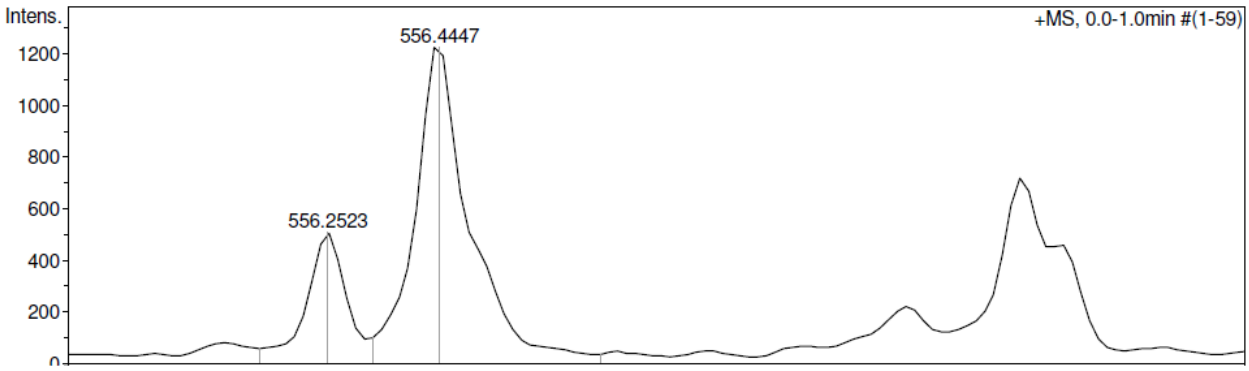


Figure S14. MS spectrum of **5**.

4. X-ray Analysis Data

Table S1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{28}H_{27}NO_2P_2$
Formula weight	471.44
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	10.750(3)
b/Å	11.328(3)
c/Å	11.464(3)
α/°	68.292(9)
β/°	81.297(9)
γ/°	69.240(9)
Volume/Å^3	1212.5(5)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.205
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.824 to 61.326
Reflections collected	7386
Independent reflections	7386
R_{int}	0.1389
Goodness-of-fit on F^2	1.066
Final R_1 indexes [I>=2σ (I)]	0.0862
Final wR_2 indexes [all data]	0.2173
Largest diff. peak/hole / e Å^{-3}	1.04/–0.68

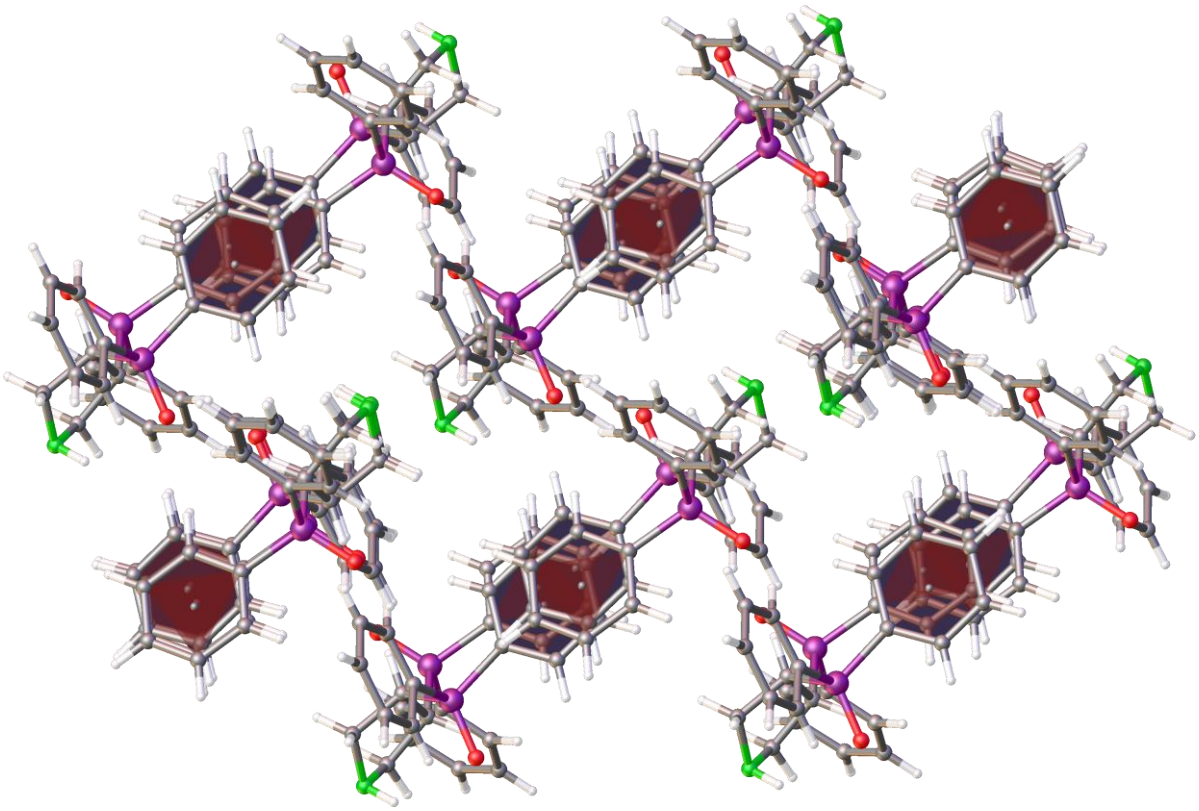


Figure S15. Crystal packing of compound **4** presented as ADP ellipsoids at 50% probability. C (grey), O (red), N (green), P (violet), H (white).

5. References

S1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

S2 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **71**, 3.

S3 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **64**, 112.

S4 T. Pollok and H. Schmidbaur, *Tetrahedron Lett.*, 1987, **28**, 1085.