Supplementary information files for Dinuclear Palladium(II) and Platinum(II) Complexes of a Readily Accessible Bicyclic Diphosphane

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Supporting Information

Dinuclear Palladium(II) and Platinum(II) Complexes of a Readily Accessible Bicyclic Diphosphane

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Supporting Information

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Experimental for dichloropalladium(II) complexes 4a and 4b

Synthesis of **4a**: To [$PdCl_2(\eta^4\text{-}C_8H_{12})$] (0.027 g, 0.098 mmol) in CH_2Cl_2 (10 mL) was added $Ph_2PCH_2N\{C_6H_4(4\text{-}NMe_2)\}CH_2PPh_2$ (0.052 g, 0.098 mmol), preformed from 2 equiv. of Ph_2PCH_2OH and $H_2NC_6H_4(4\text{-}NMe_2)$, and the solution stirred for 1 h. The volume of CH_2Cl_2 was reduced in vacuo to approx. 1–2 mL. Addition of diethyl ether (20 mL) and hexanes (20 mL) afforded solid **4a** which was collected by suction filtration and dried. Yield 0.058 g, 83%. Selected data for **4a**: ^{1}H (500 MHz): δ 7.86–7.82 (8H, m, arom. *H*), 7.46 (4H, dd, J_{HH} 8.2, 6.7 Hz, arom. *H*), 7.37 (8H, dt, J_{HH} 7.6, 2.2 Hz, arom. *H*), 6.67 (4H, d, J_{HH} 8.2 Hz, arom. *H*), 3.84 (4H, t, $^2J_{PH}$ 3.1 Hz, C*H*$_2$), 2.88 (6H, s, C*H*$_3$).^{31}P{^{1}H} (202 MHz): δ 10.1 ppm. FT–IR (KBr): ν_{PdCl} 310, 293 cm^{-1}. Anal. Calcd for $C_{34}H_{34}Cl_2N_2P_2Pd{\cdot}CH_2Cl_2$ (%): C, 52.89; H, 4.57; N, 3.52. Found: C, 53.04; H, 4.55; N, 3.50.

Synthesis of **4b**: To [$PtCl_2(\eta^4\text{-}C_8H_{12})$] (0.035 g, 0.094 mmol) in CH_2Cl_2 (10 mL) was added $Ph_2PCH_2N\{C_6H_4(4\text{-}NMe_2)\}CH_2PPh_2$ (0.050 g, 0.094 mmol), preformed from 2 equiv. of Ph_2PCH_2OH and $H_2NC_6H_4(4\text{-}NMe_2)$, and the solution stirred for 1 h. The volume of CH_2Cl_2 was reduced in vacuo to approx. 1–2 mL. Addition of diethyl ether (20 mL) and hexanes (20 mL) afforded a yellow solid **4b** which was collected by suction filtration and dried. Yield 0.045 g, 65%. Selected data for **4b**: ^{1}H (500 MHz): δ 7.85–7.80 (8H, m, arom. *H*), 7.46 (4H, t, J_{HH} 7.0 Hz, arom. *H*), 7.38 (8H, t, J_{HH} 6.8 Hz, arom. *H*), 6.68–6.65 (2H, m, arom. *H*), 6.57 (2H, d, J_{HH} 9.1 Hz, arom. *H*), 3.88 (4H, dd, $^3J_{PtH}$ 50.0. $^2J_{PH}$ 5.0 Hz, C*H*$_2$), 2.87 (6H, s, C*H*$_3$). ^{31}P{^{1}H} (202 MHz): δ –6.1 ppm, $^1J_{PtP}$ 3400 Hz. FT–IR (KBr): ν_{PtCl} 317, 290 cm^{-1}. Anal. Calcd for $C_{34}H_{34}Cl_2N_2P_2Pd{\cdot}0.5CH_2Cl_2$ (%): C, 49.26; H, 4.20; N, 3.33. Found: C, 49.27; H, 4.32; N, 3.13.

NMR data

Figure S1 ^{1}H NMR spectrum of compound **P–P(NMe$_2$)** (recorded in $CDCl_3$).

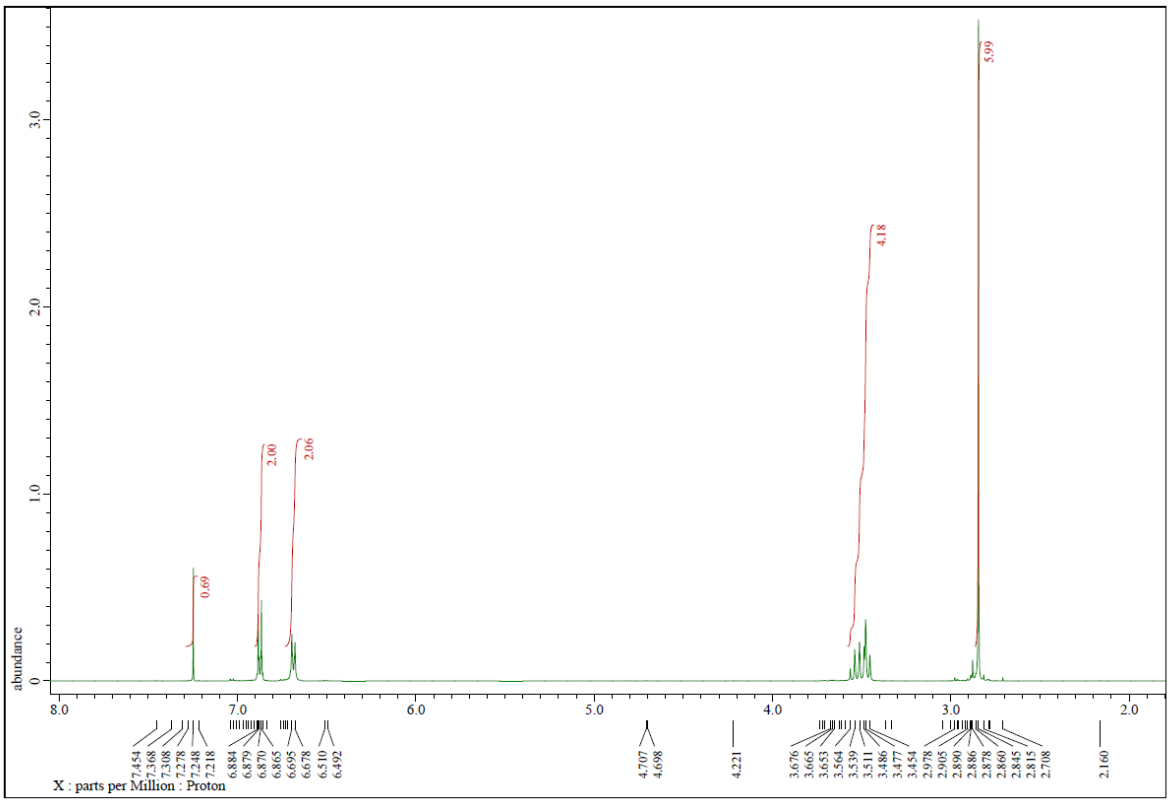


Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum of compound **P–P(NMe$_2$)** (recorded in $CDCl_3$).

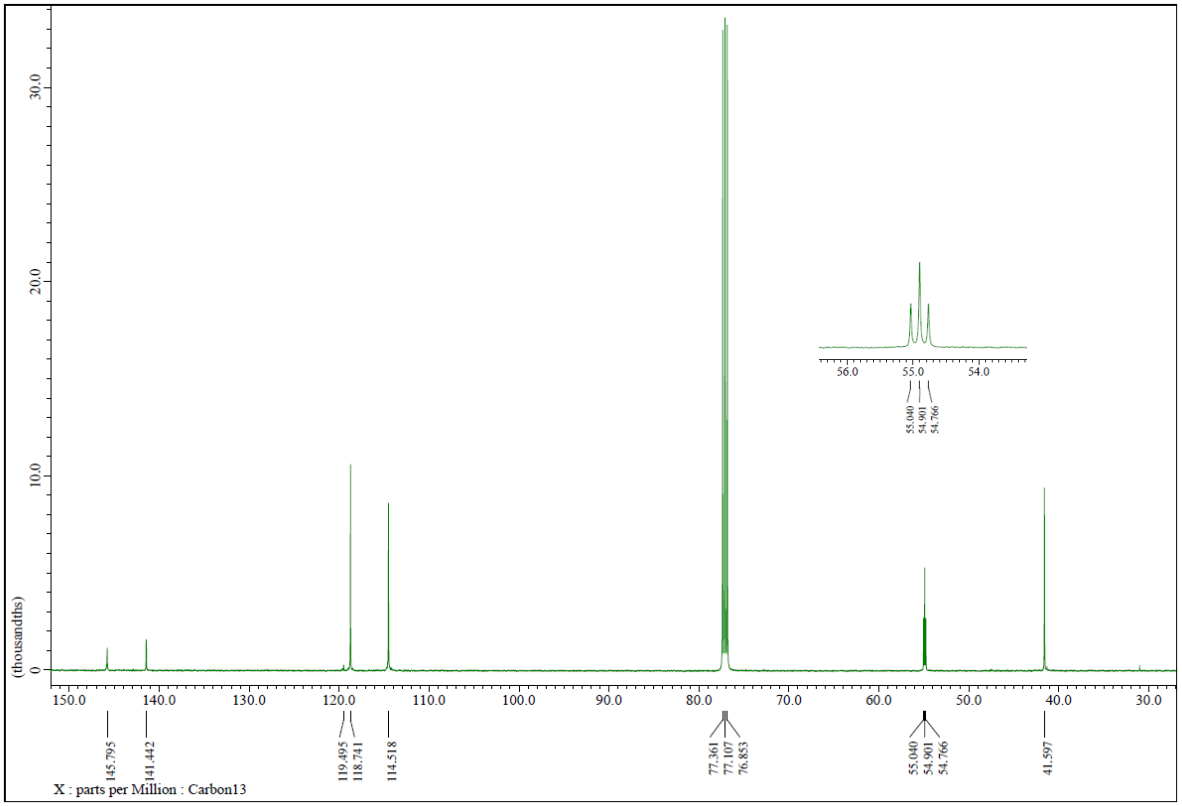


Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum of compound **P–P(NMe$_2$)** (recorded in $CDCl_3$).

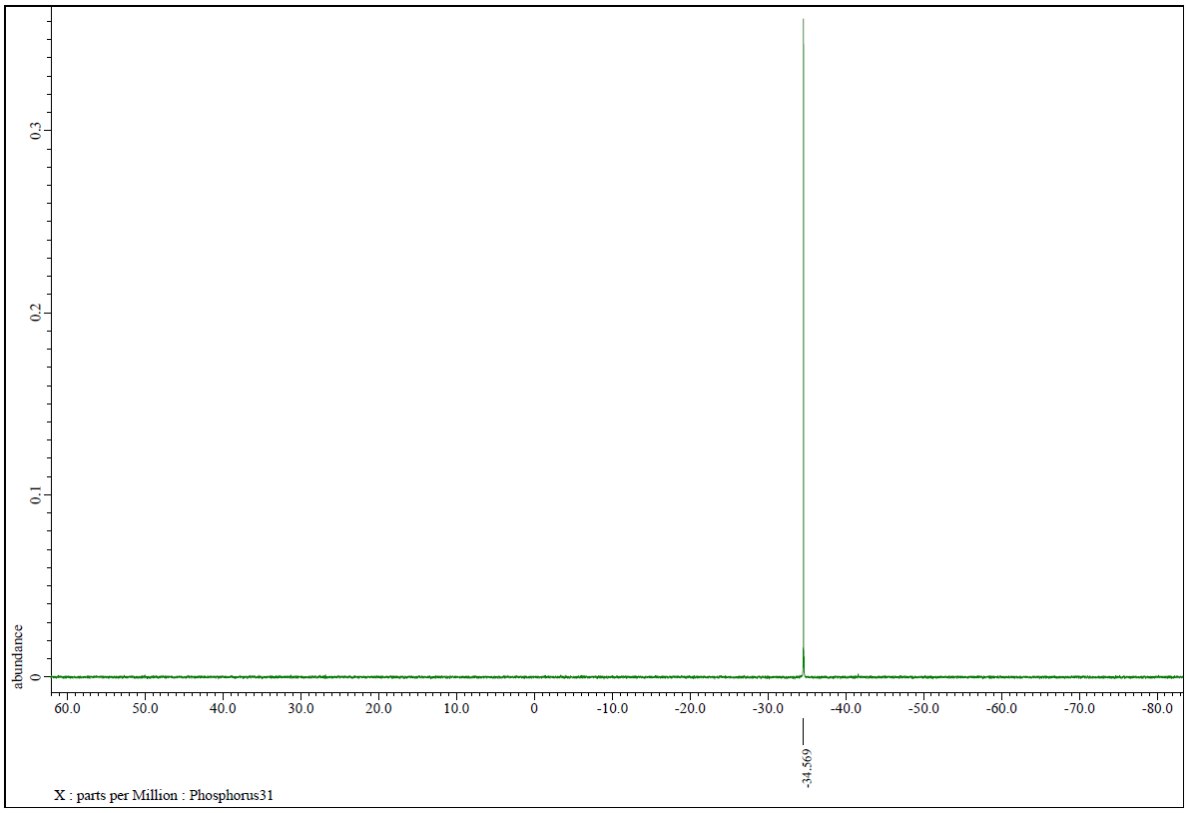


Figure S4 ^{1}H NMR spectrum of compound **1a** (recorded in $CDCl_3$).

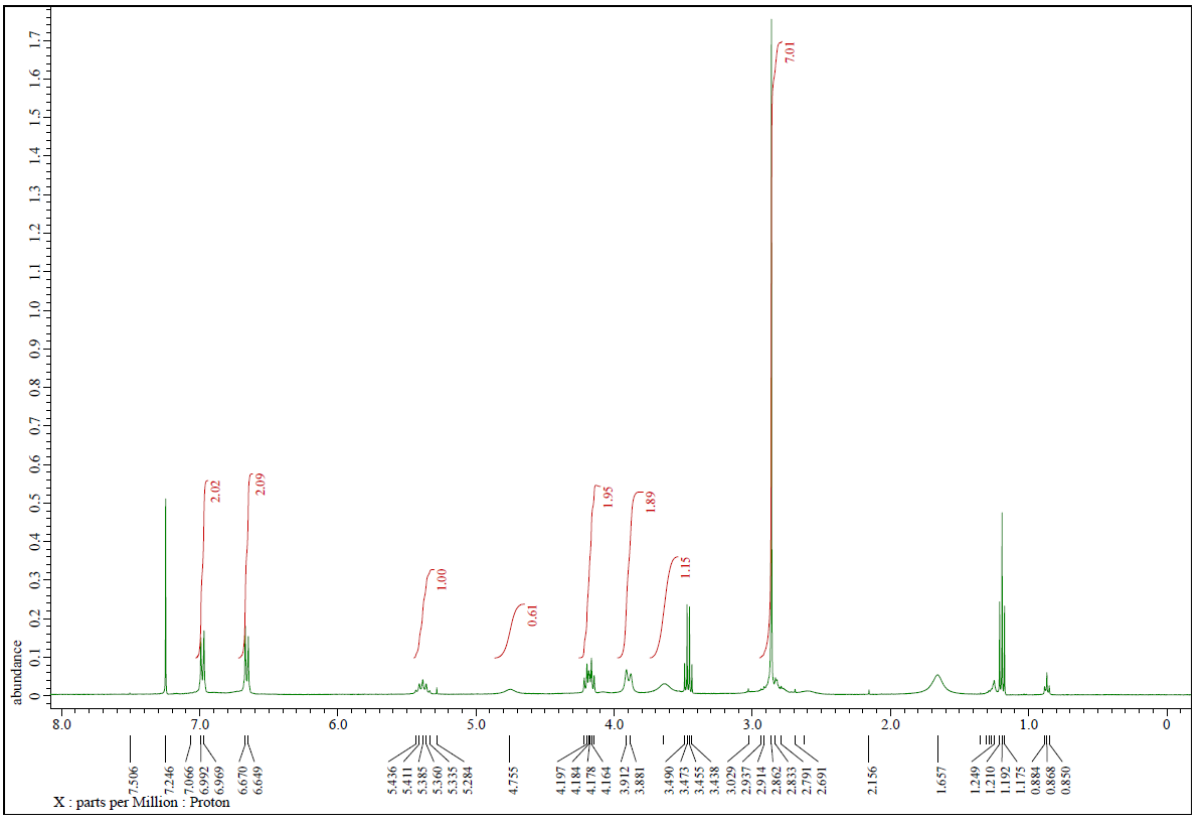


Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum of compound **1a** (recorded in $CDCl_3$).

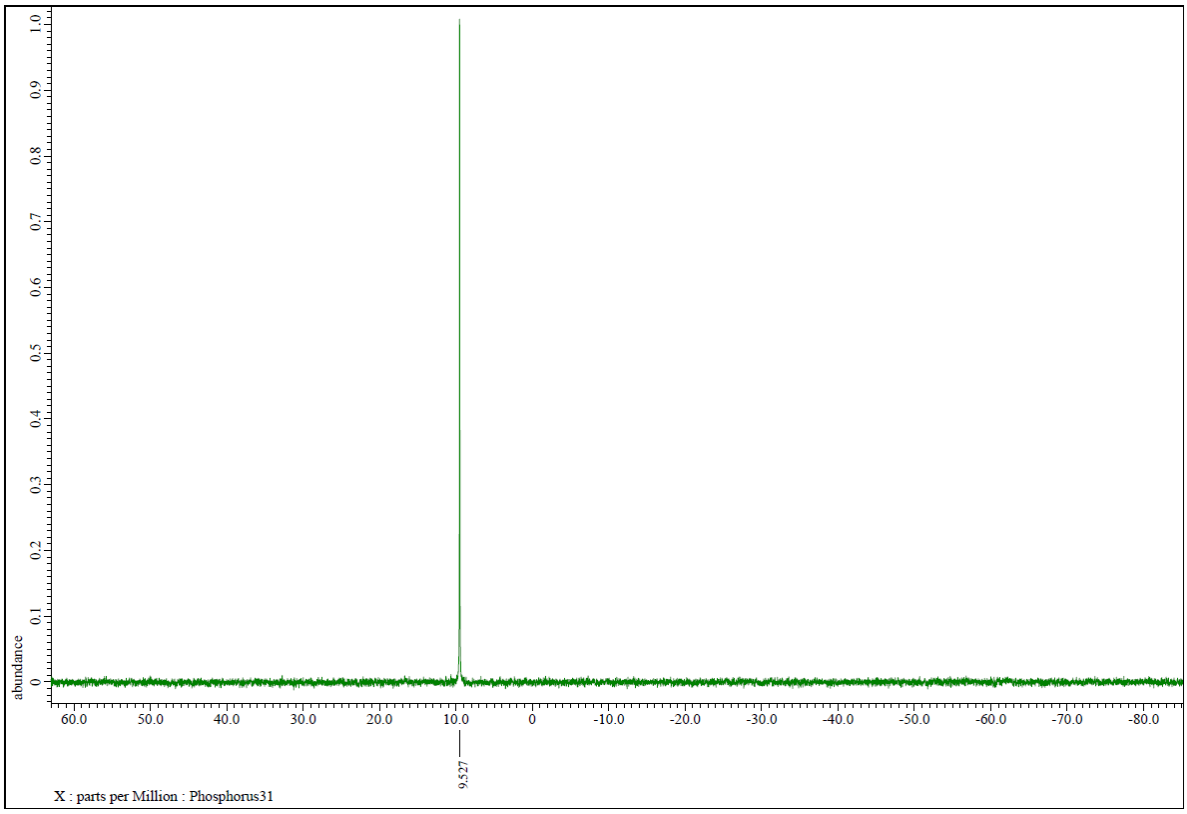


Figure S6 ^{1}H NMR spectrum of compound **1b** (recorded in $CDCl_3$).

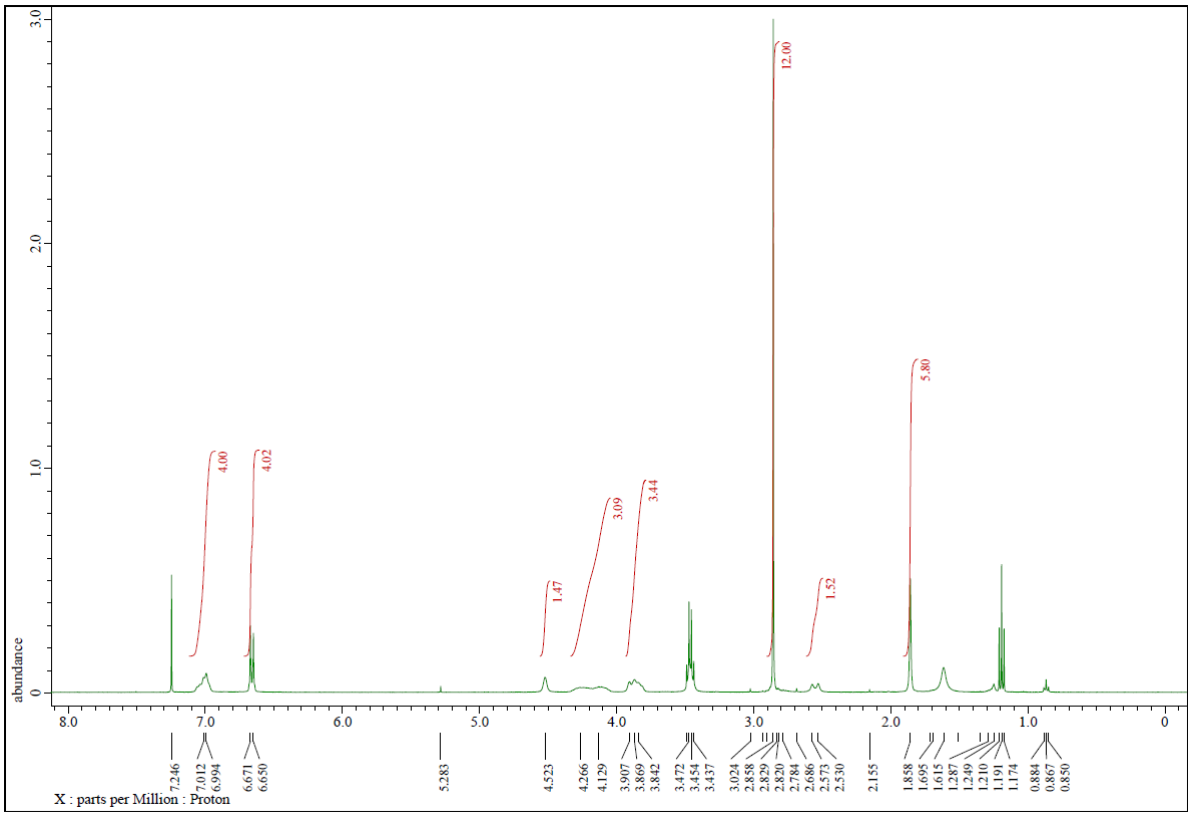


Figure S7 $^{31}P\{^{1}H\}$ NMR spectrum of compound **1b** (recorded in $CDCl_3$).

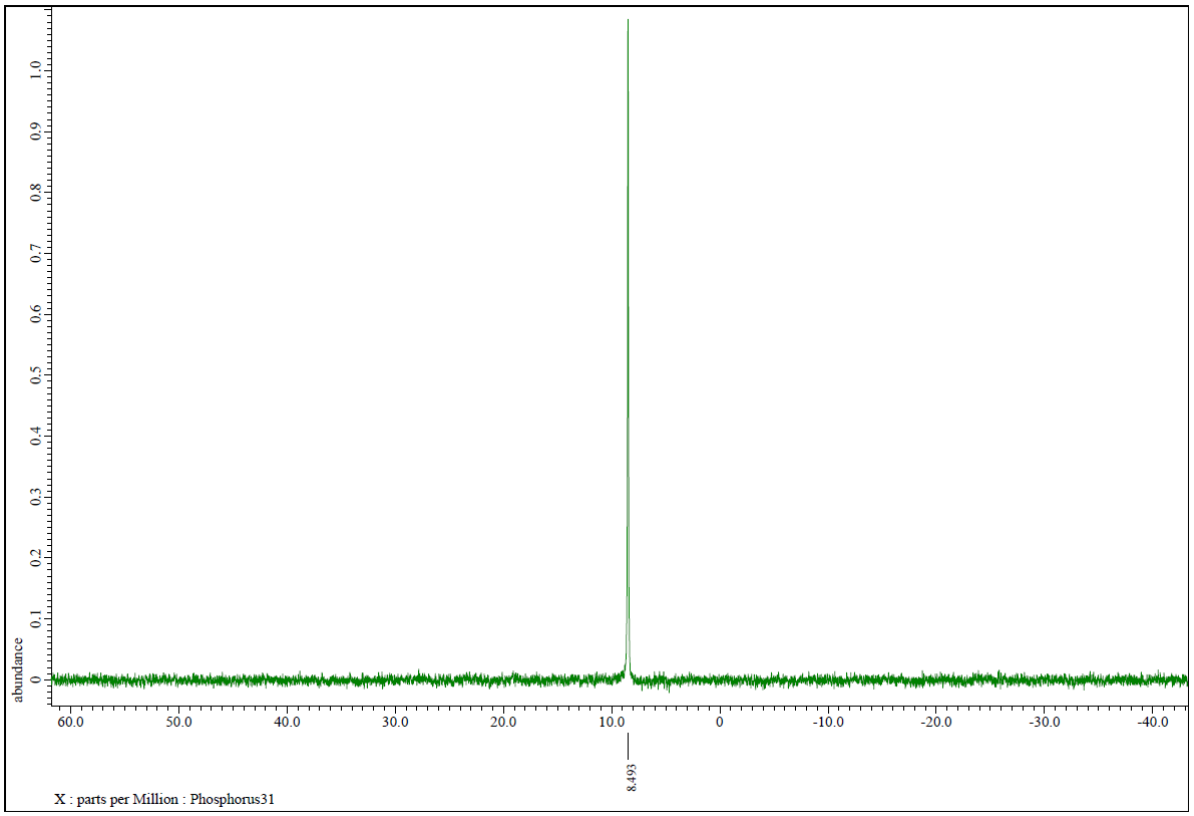


Figure S8 ^{1}H NMR spectrum of compound **1c** (recorded in $CDCl_3$).

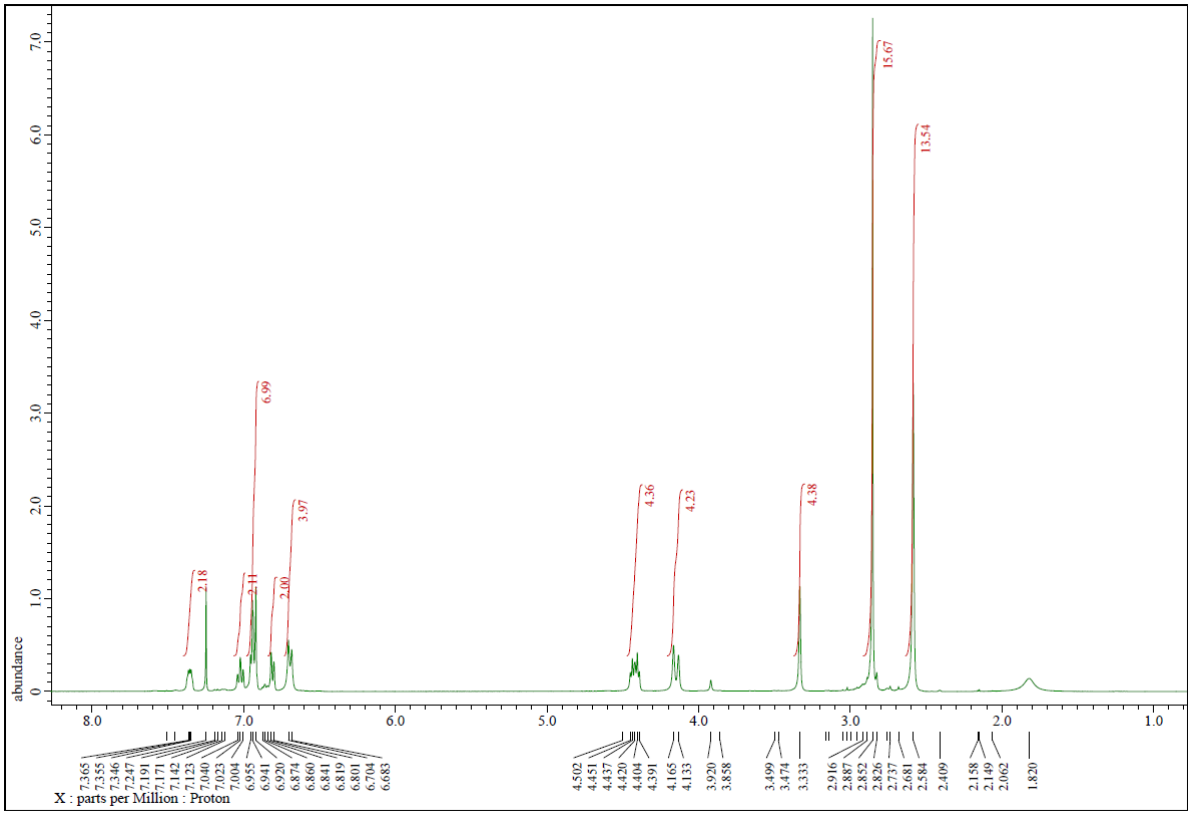


Figure S9 $^{31}P\{^{1}H\}$ NMR spectrum of compound **1c** (recorded in $CDCl_3$).

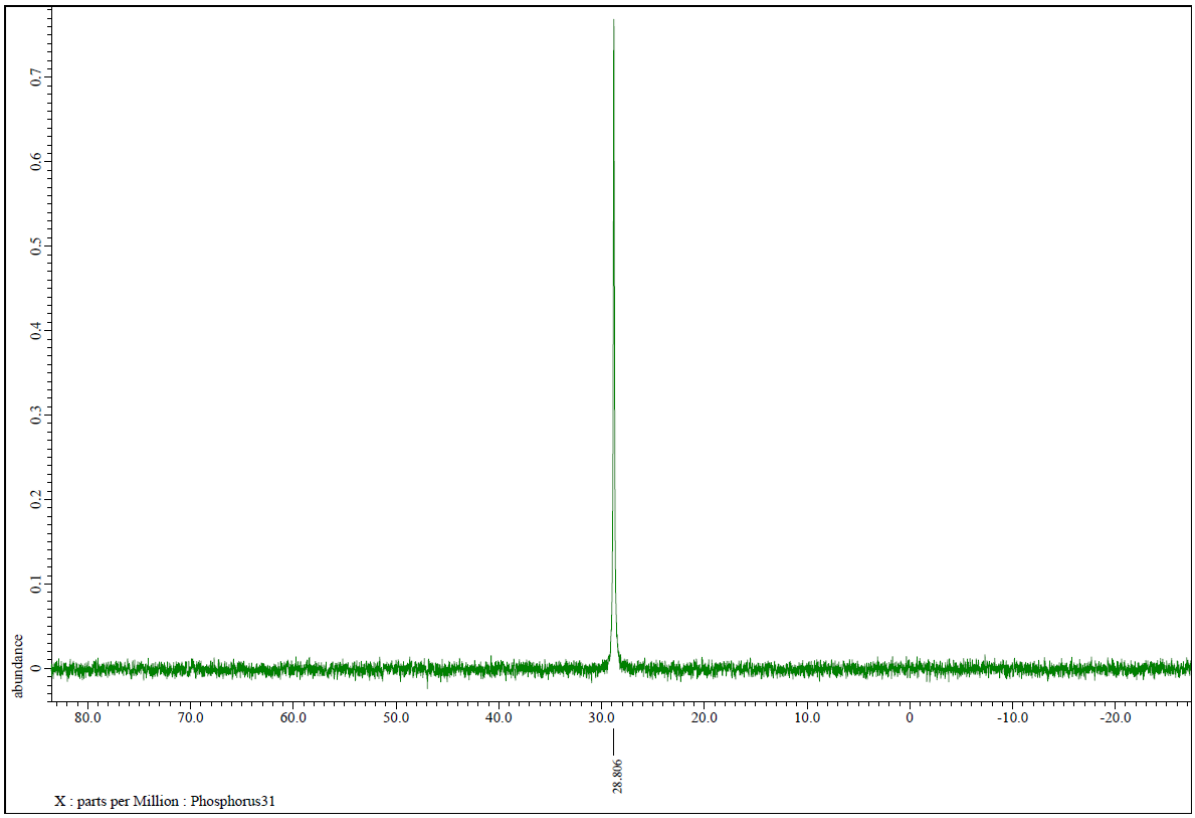


Figure S10 ^{1}H NMR spectrum of compound **2b** (recorded in $CDCl_3$).

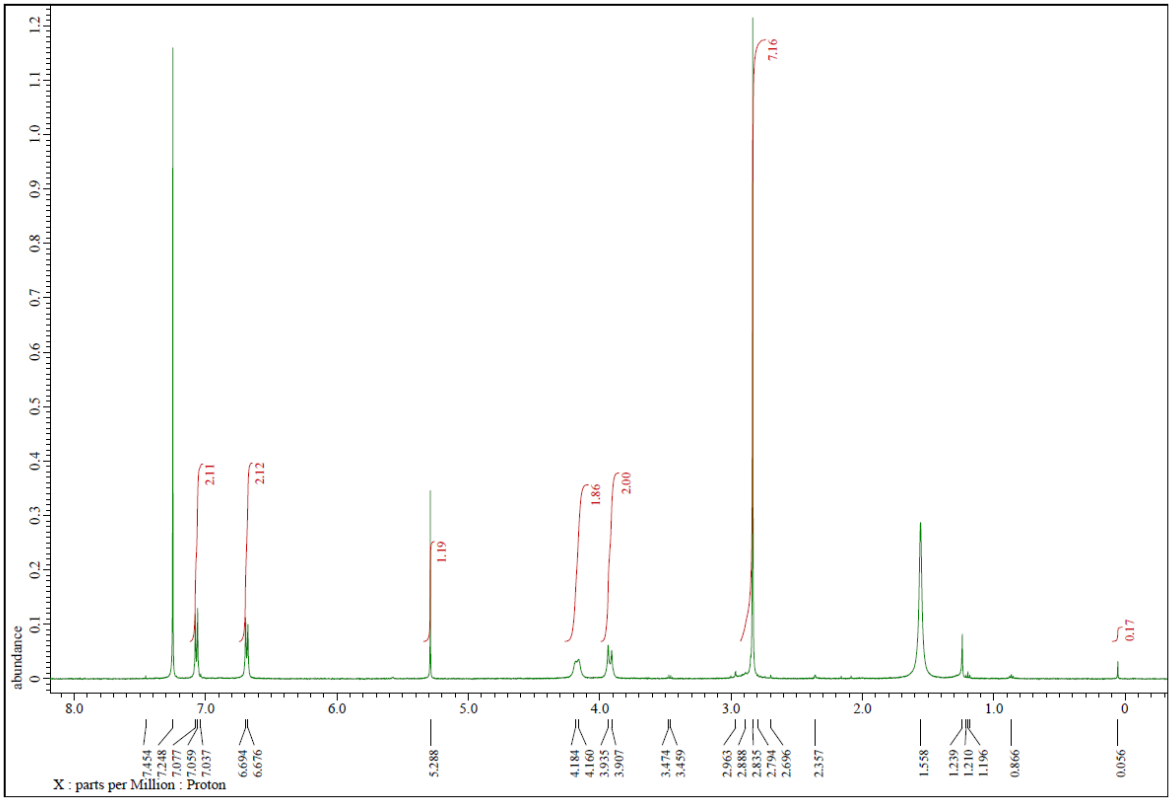


Figure S11 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2b** (recorded in $CDCl_3$).

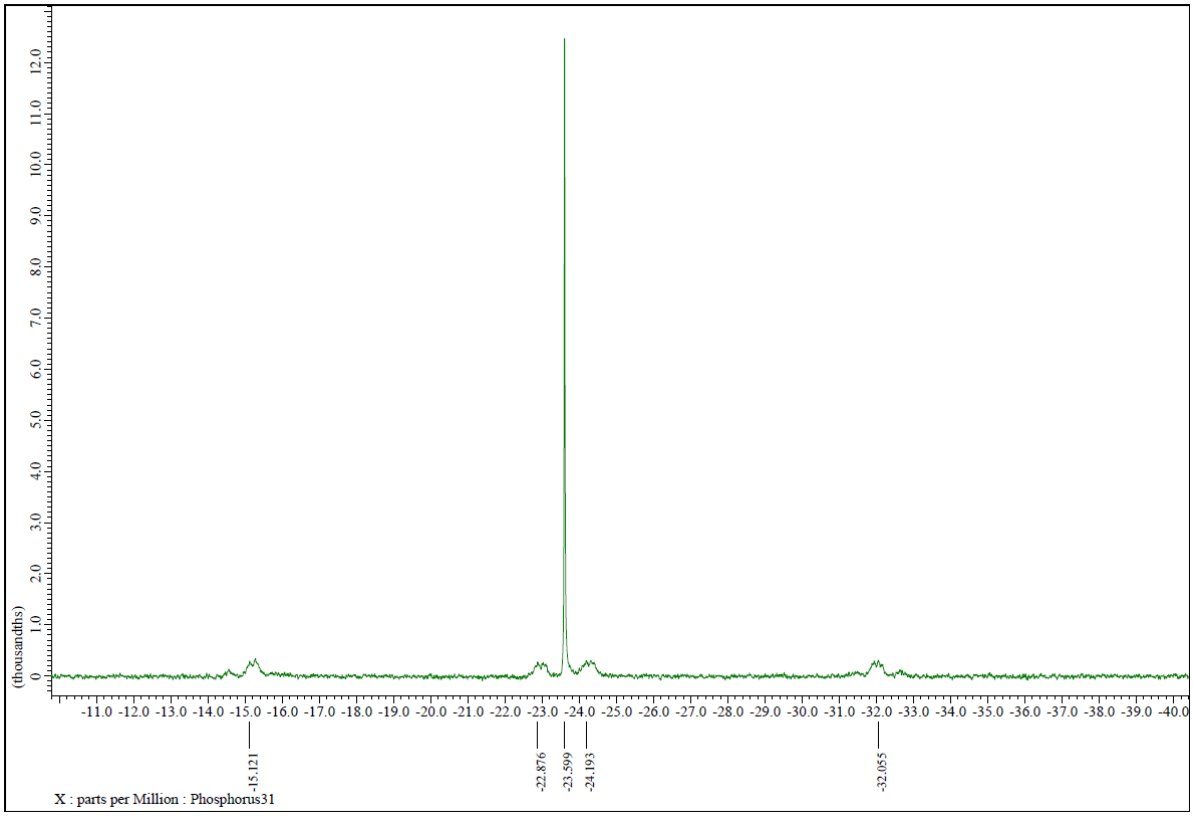


Figure S12 ^{1}H NMR spectrum of compound **2c** (recorded in $CDCl_3$).

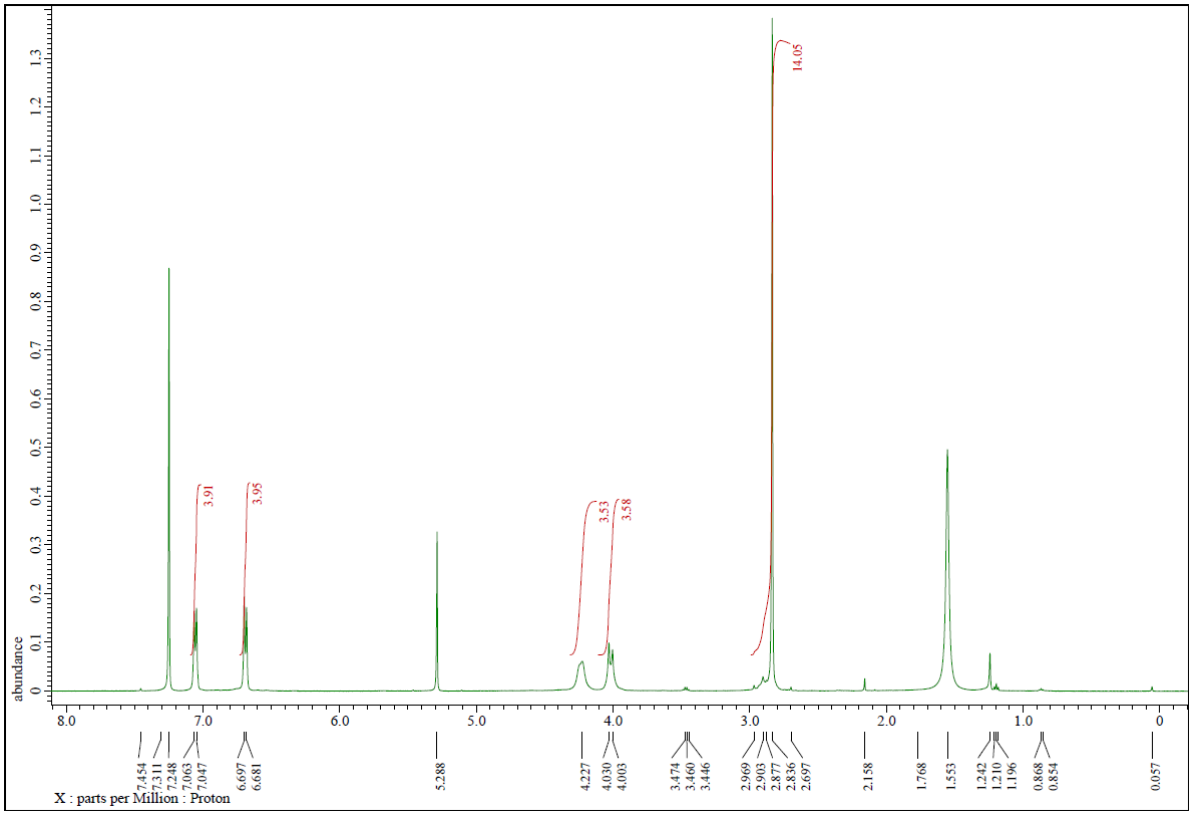


Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2c** (recorded in $CDCl_3$).

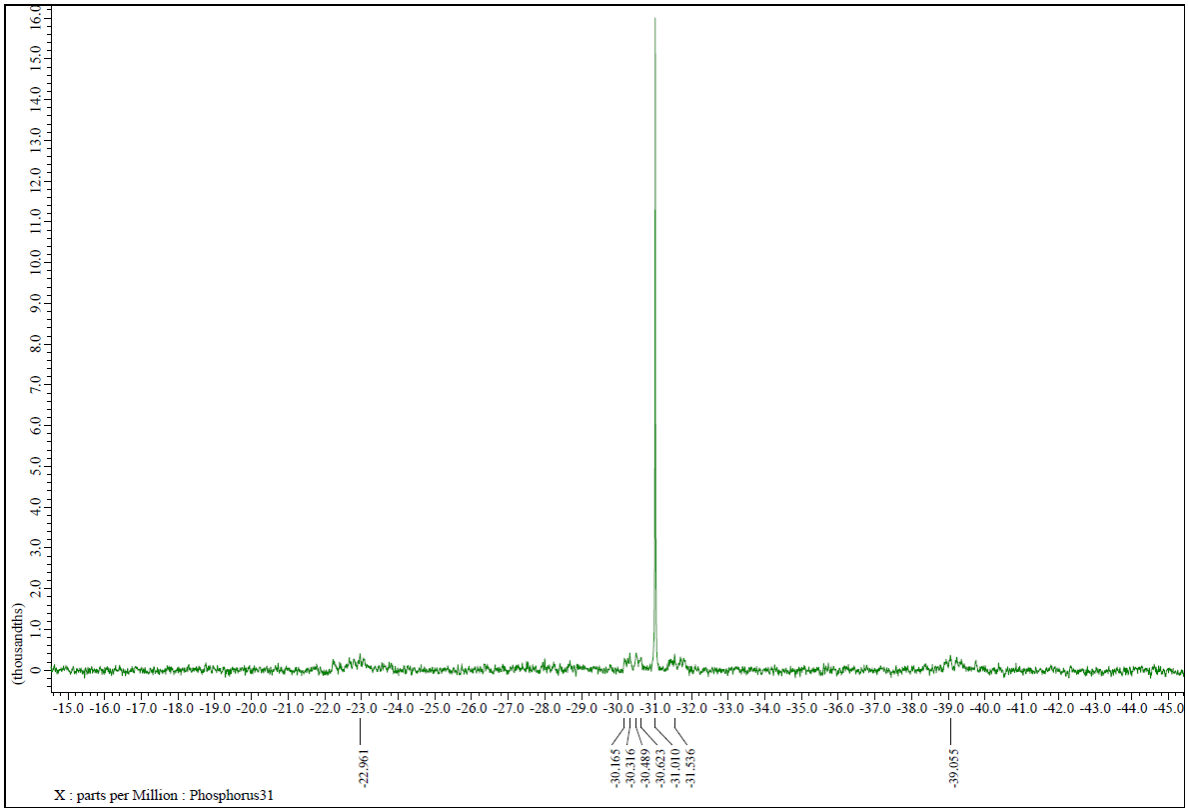


Figure S14 ^{1}H NMR spectrum of compound **2d** (recorded in $CDCl_3$).

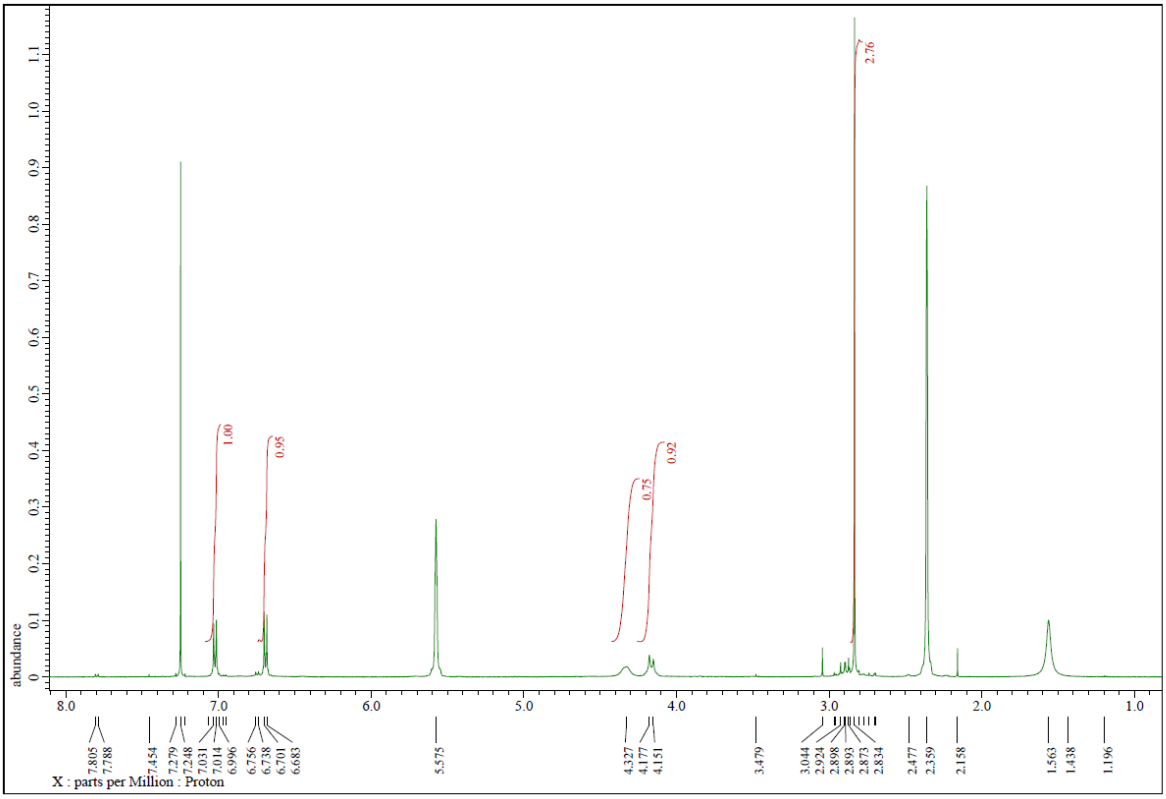


Figure S15 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2d** (recorded in $CDCl_3$).

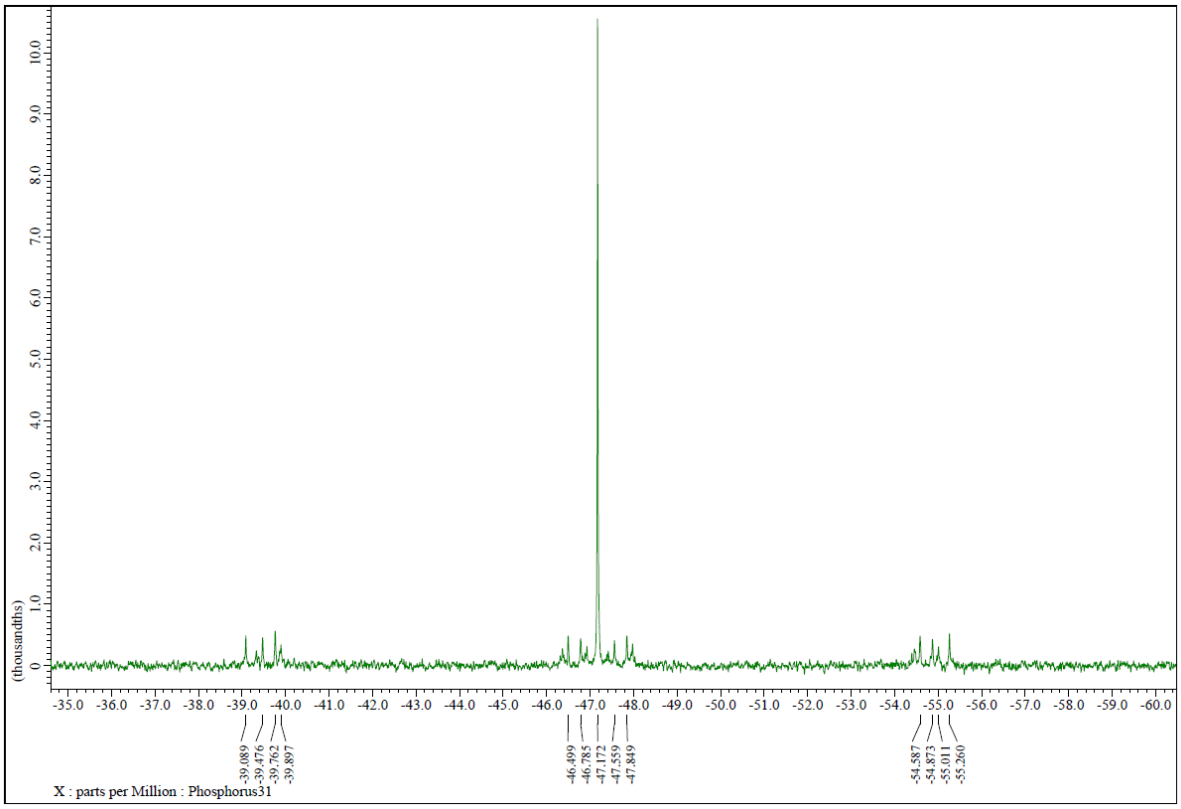


Figure S16 ^{1}H NMR spectrum of compound **2e** (recorded in $CDCl_3$).

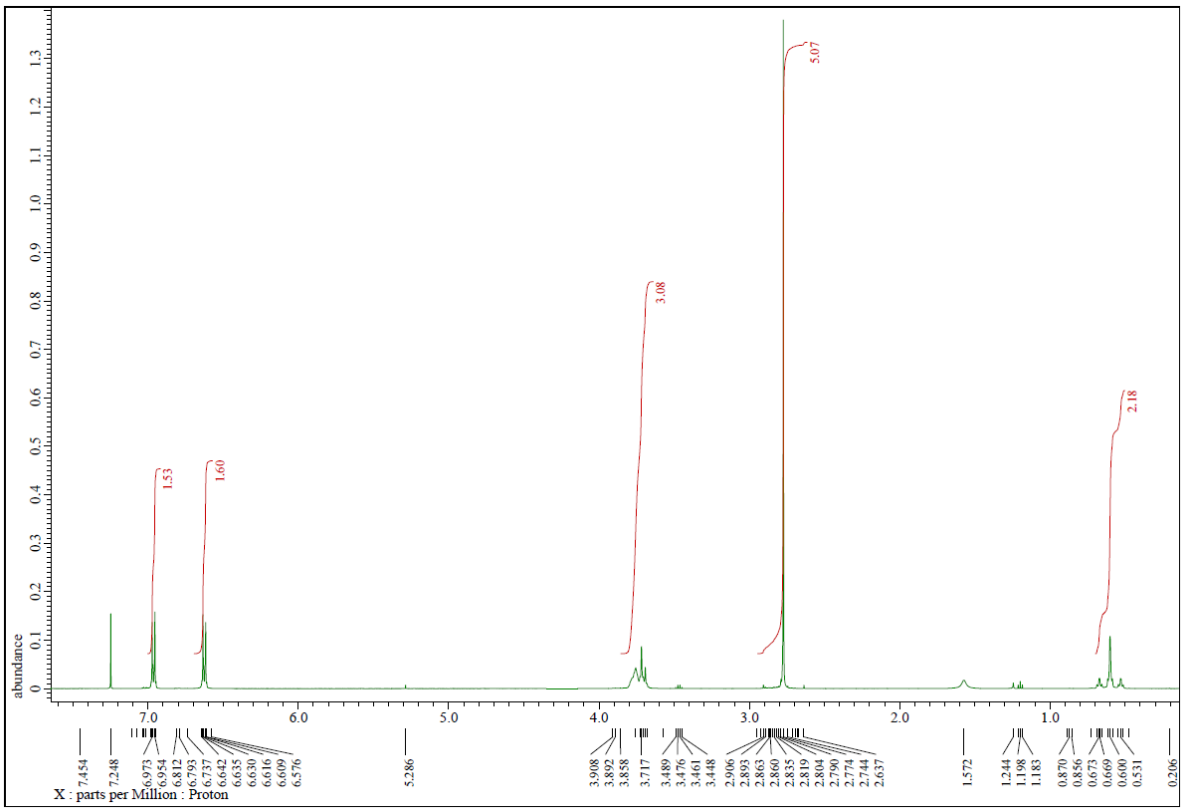


Figure S17 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2e** (recorded in $CDCl_3$).

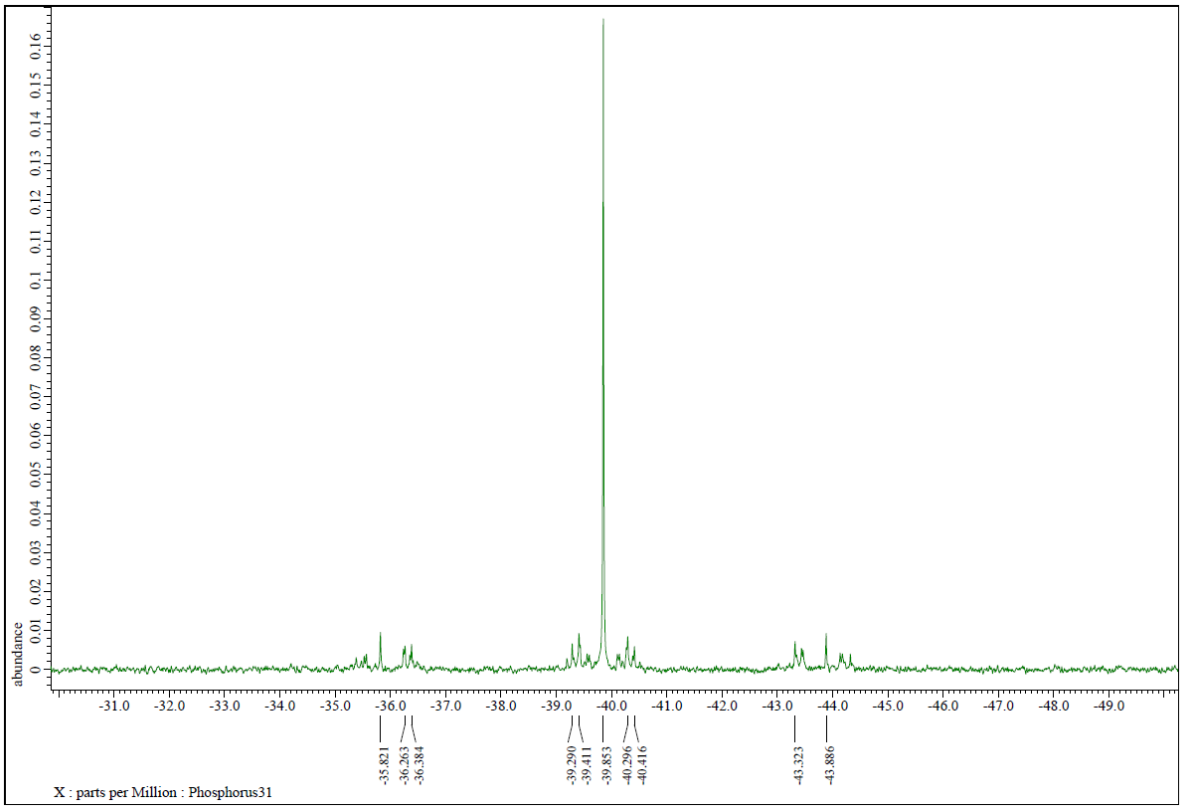


Figure S18 ^{1}H NMR spectrum of compound **3a** (recorded in CD_3CN).

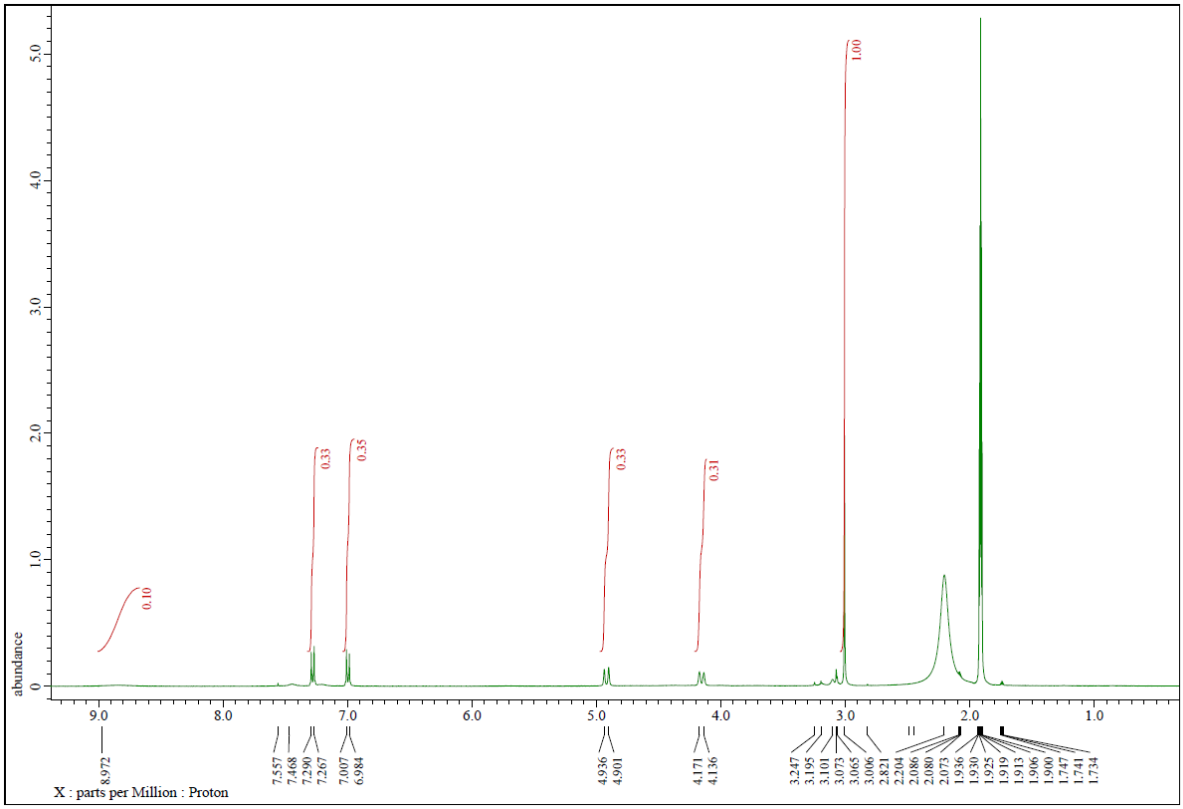


Figure S19 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3a** (recorded in CD_3CN).

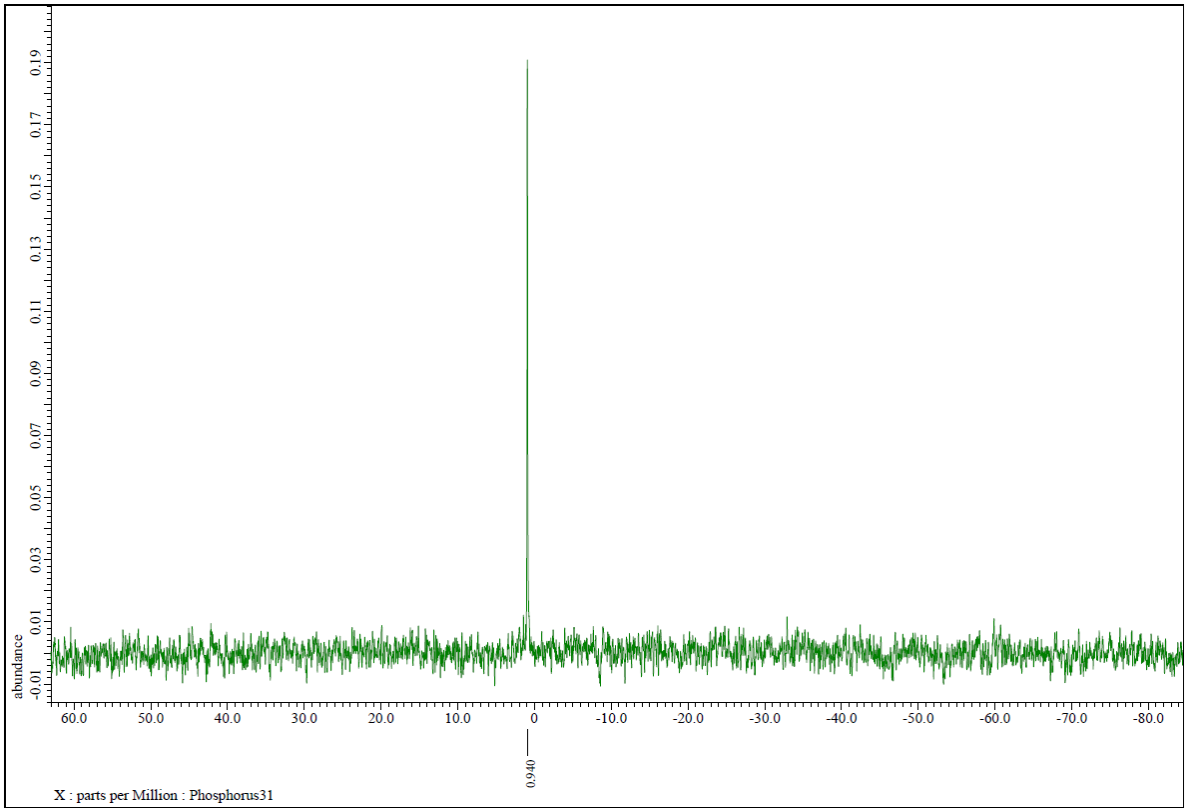

abundance
0.19
0.17
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
-0.01
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
0.940
X : parts per Million : Phosphorus31

Figure S20 ^{1}H NMR spectrum of compound **3b** (recorded in CD_3CN).

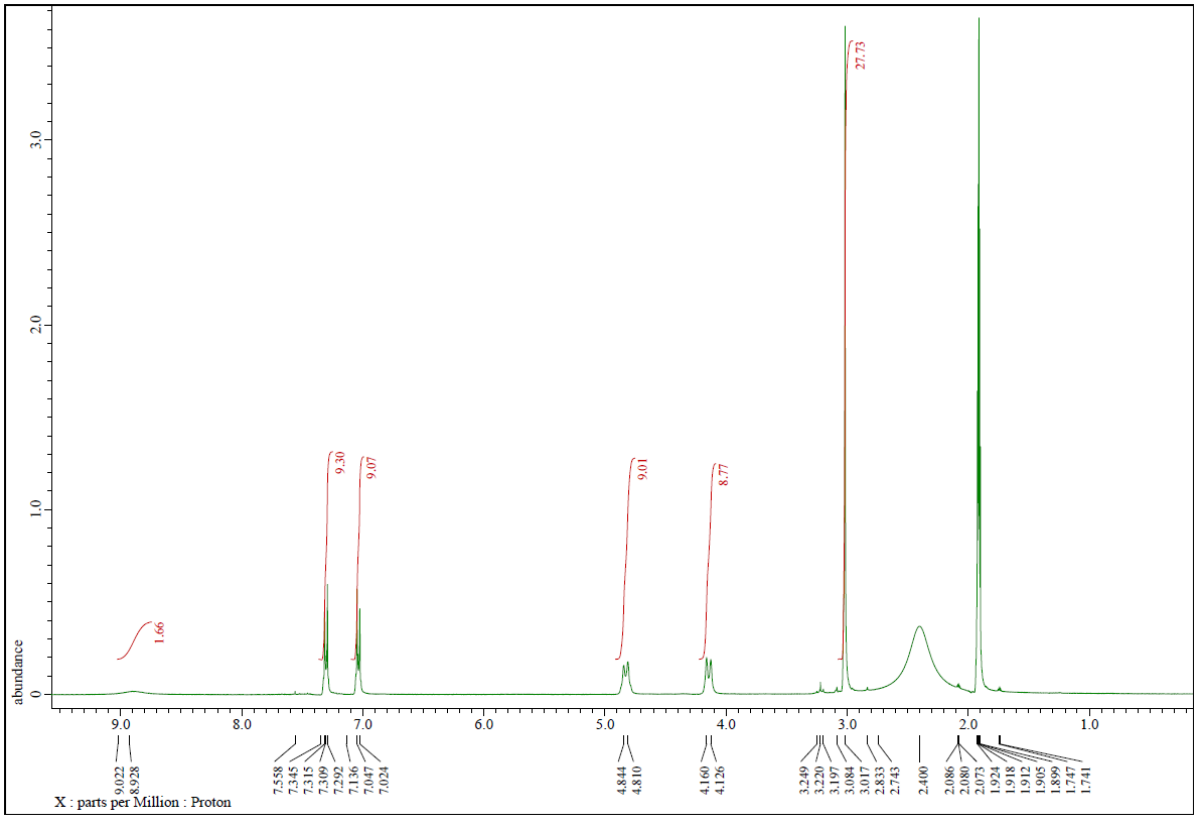


Figure S21 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3b** (recorded in CD_3CN).

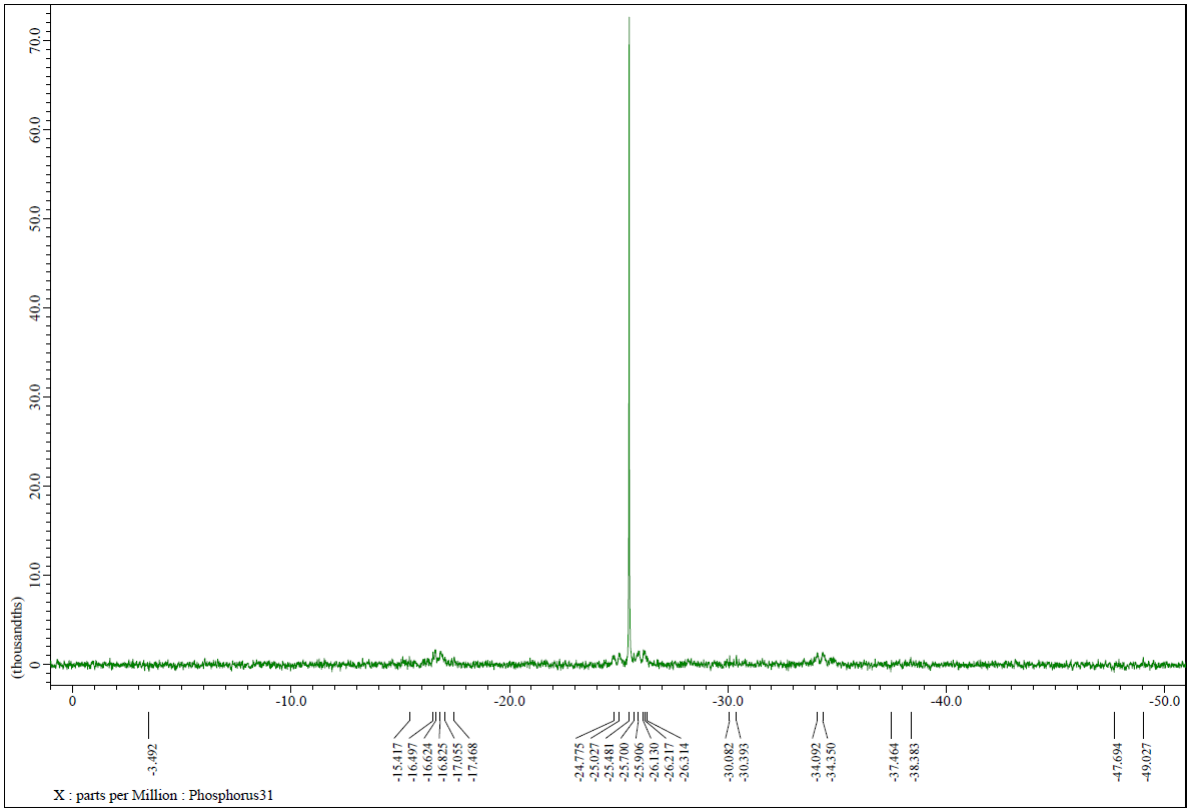


Figure S22 ^{1}H NMR spectrum of compound **3c** (recorded in CD_3CN).

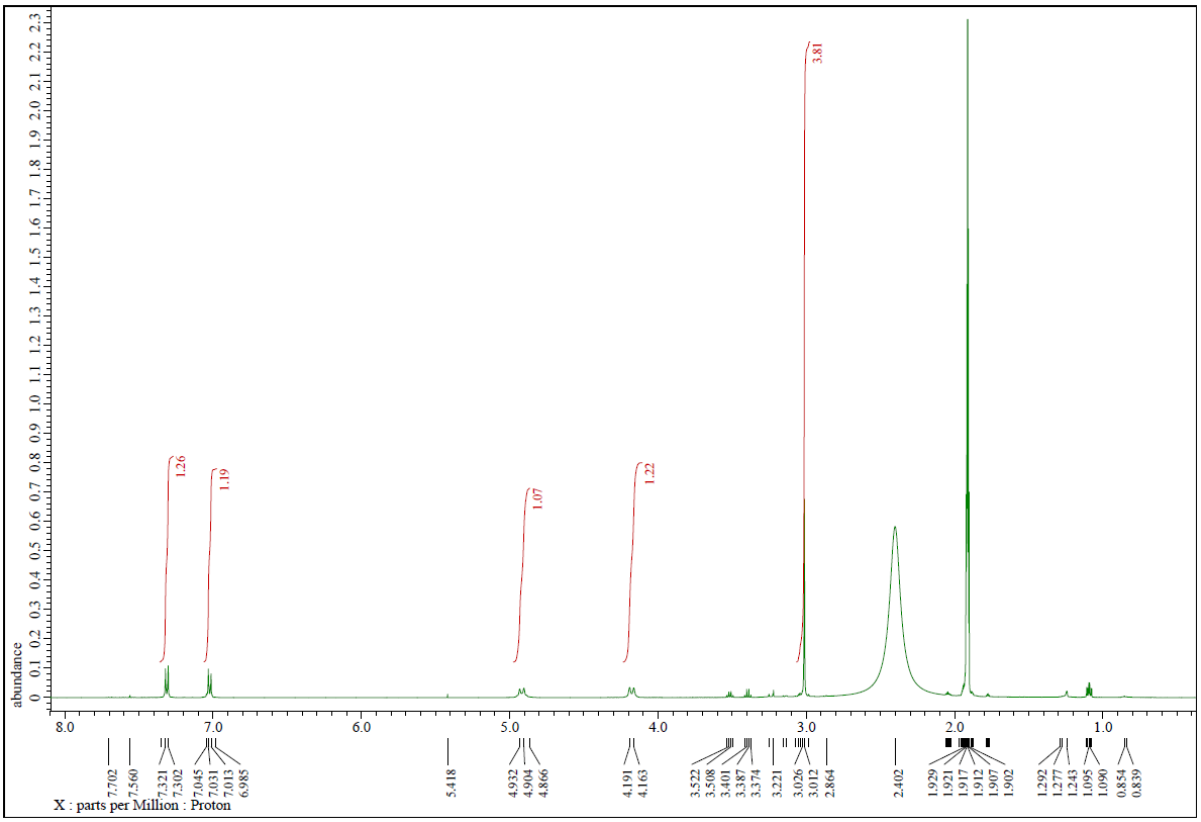


Figure S23 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3c** (recorded in CD_3CN).

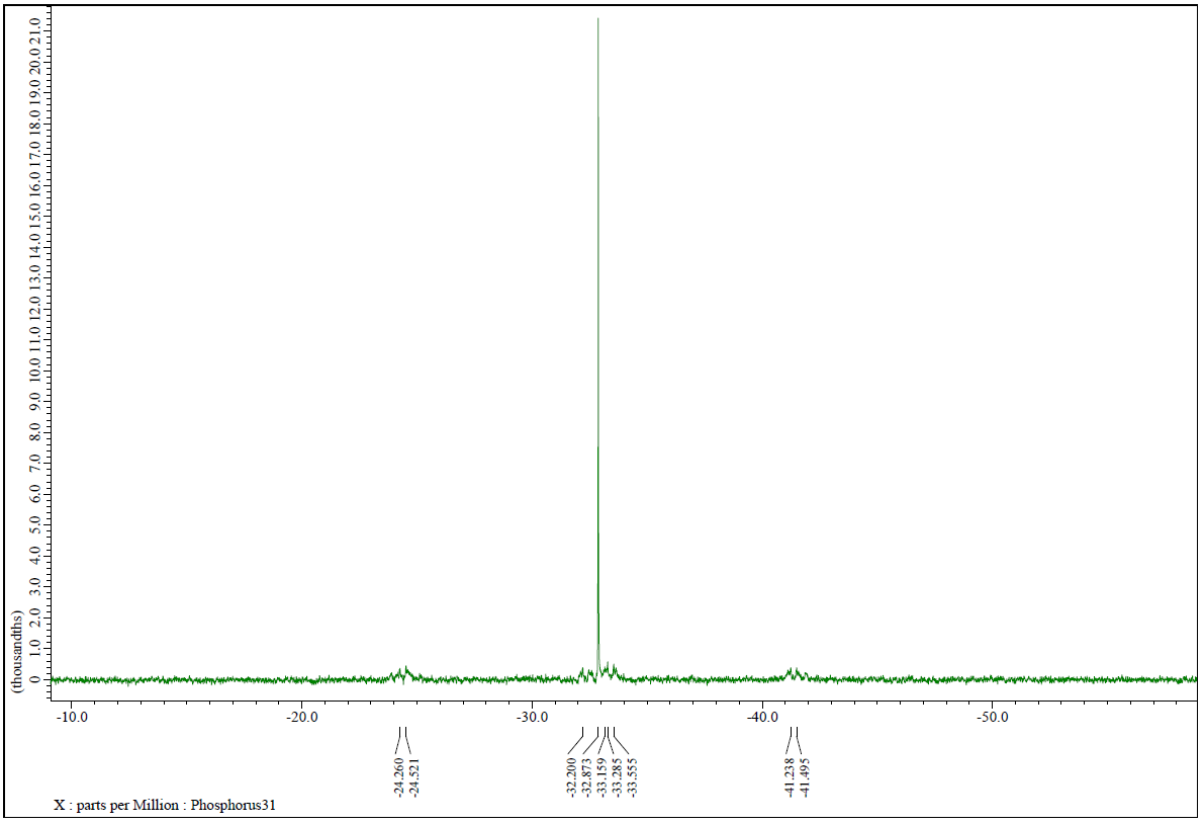


Figure S24 ^{1}H NMR spectrum of compound **3d** (recorded in CD_3CN).

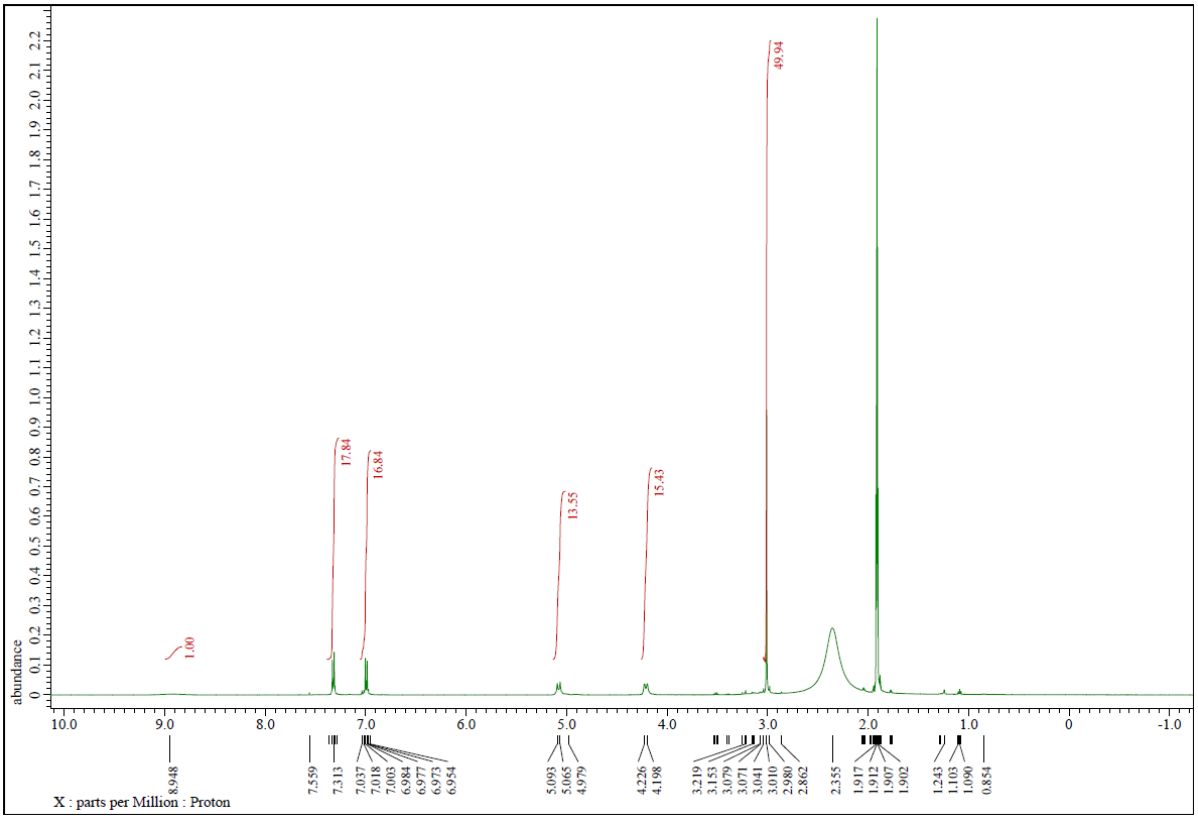


Figure S25 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3d** (recorded in CD_3CN).

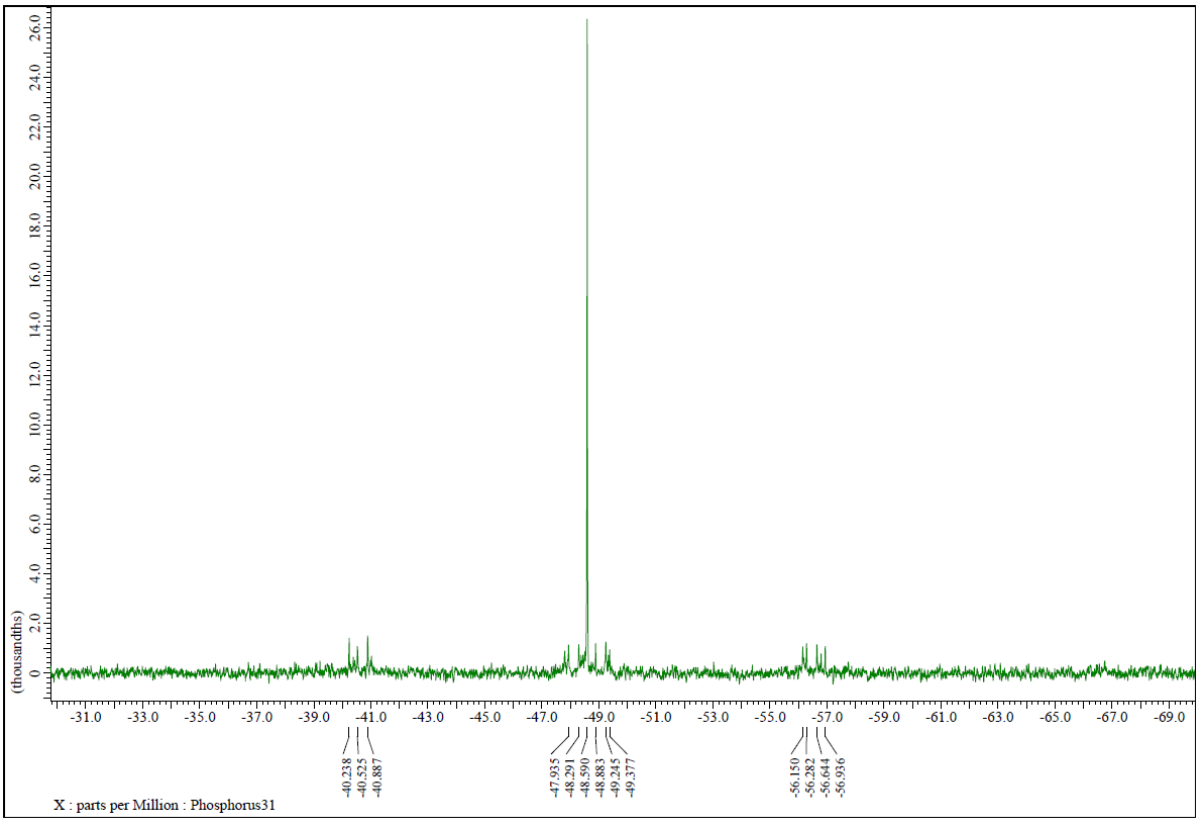


Figure S26 ^{1}H NMR spectrum of compound **4a** (recorded in $CDCl_3$).

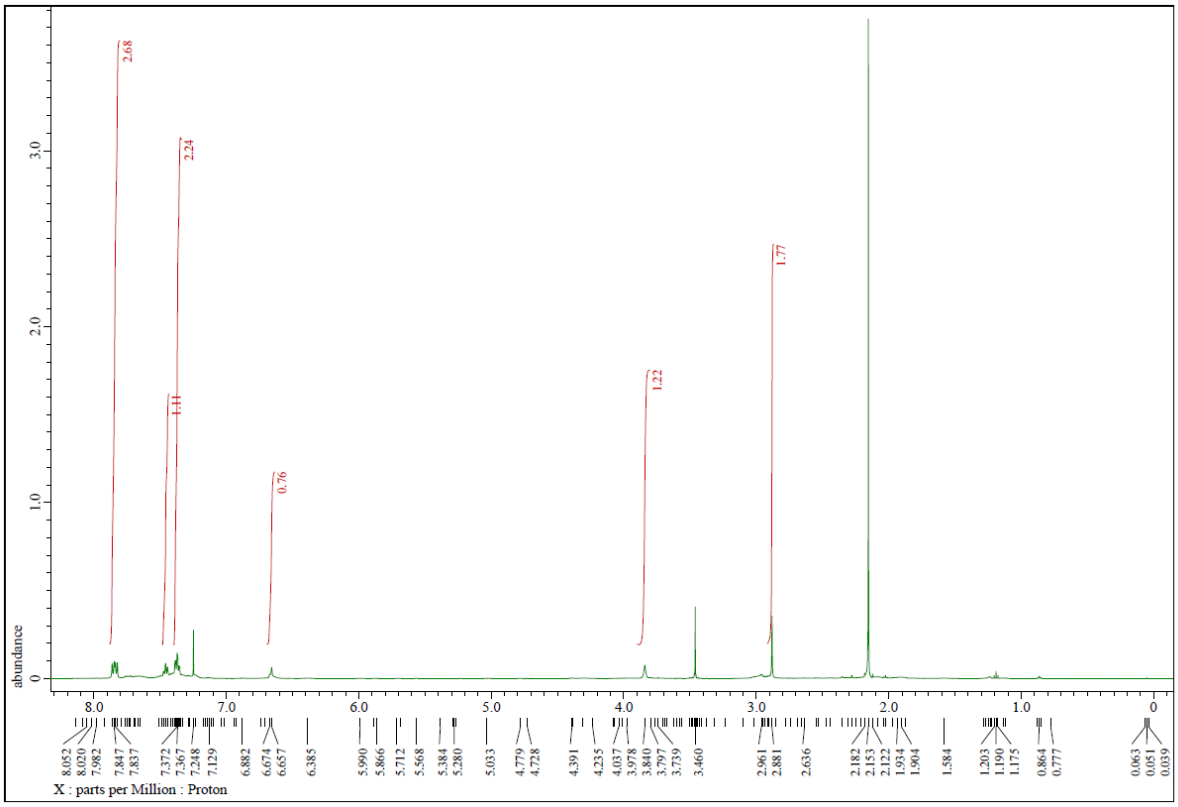


Figure S27 $^{31}P\{^{1}H\}$ NMR spectrum of compound **4a** (recorded in $CDCl_3$).

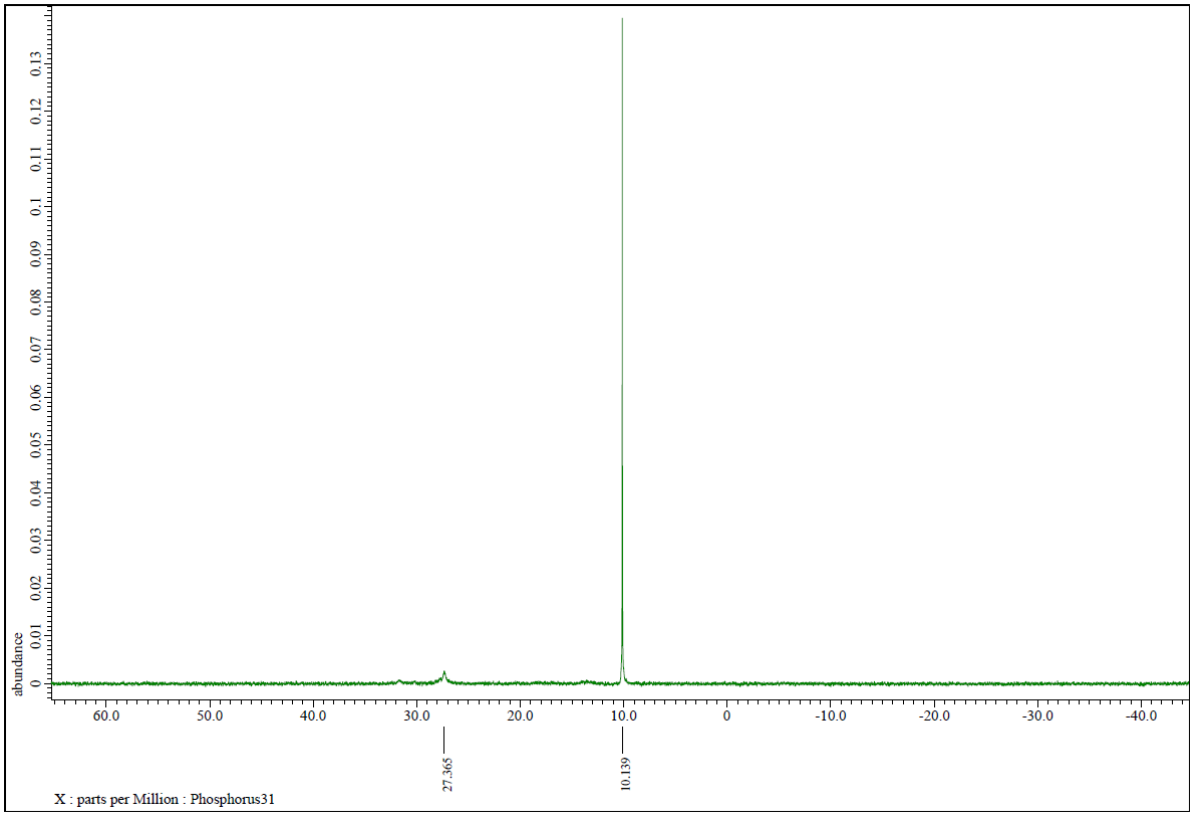


Figure S28 ^{1}H NMR spectrum of compound **4b** (recorded in $CDCl_3$).

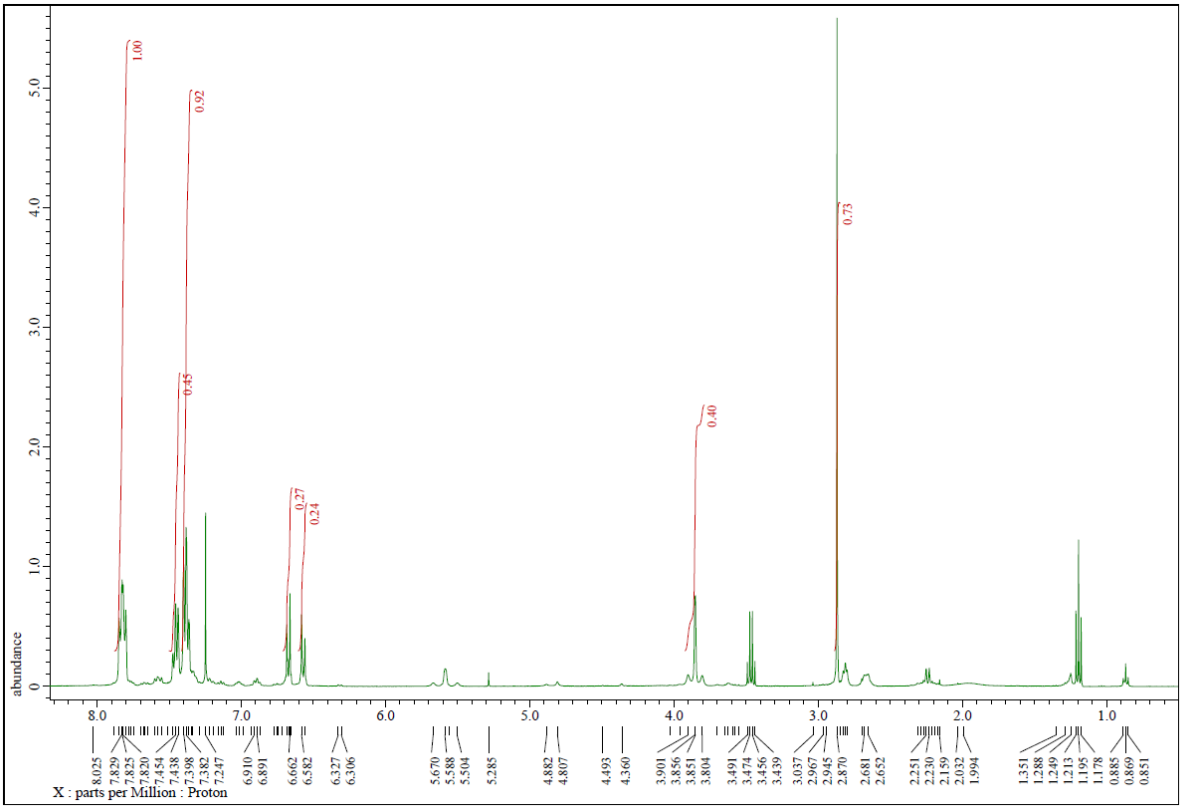
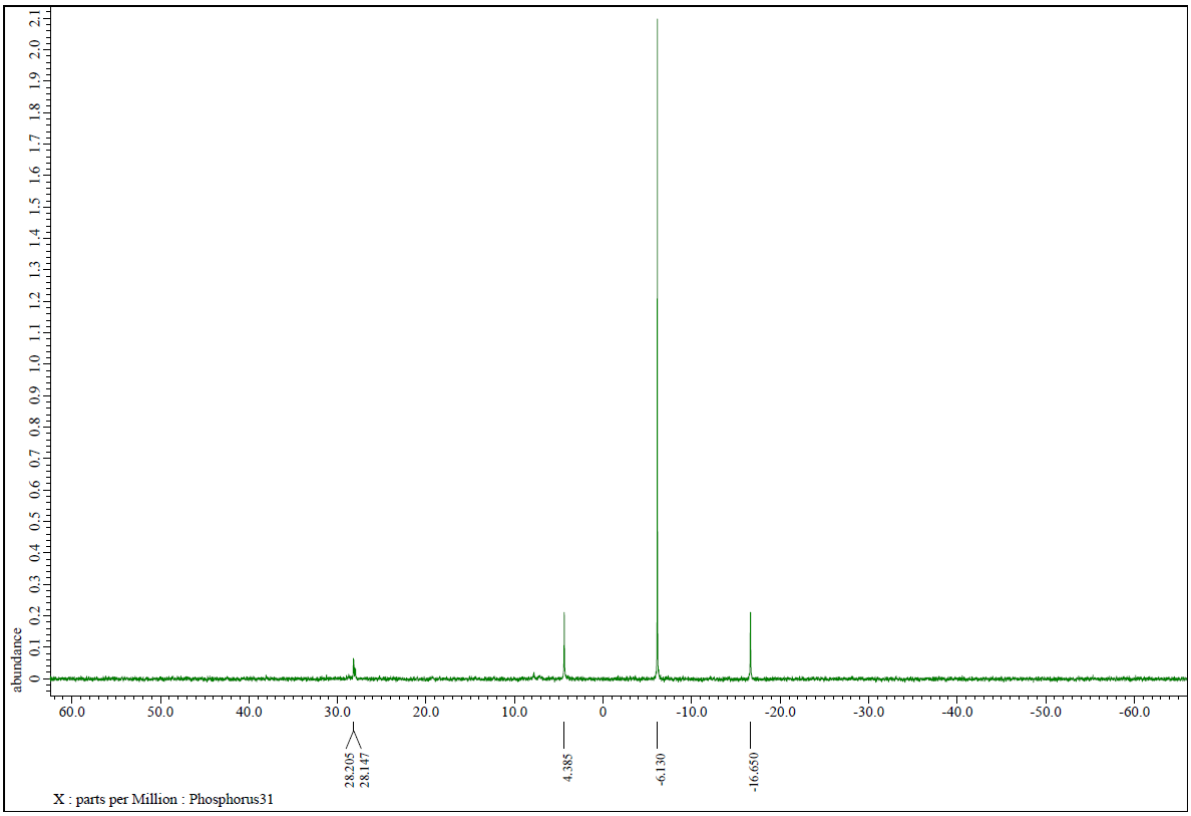


Figure S29 $^{31}P\{^{1}H\}$ NMR spectrum of compound **4b** (recorded in $CDCl_3$).



X-ray figures

Figure S30 Molecular structure of **3a**·12CD_3CN in the solid state. All hydrogen atoms and some solvents have been omitted for clarity. Selected bond lengths [Å] and angles [º]: Pd(1)–P(1) 2.2220(17), Pd(1)–P(2A) 2.2337(17), Pd(1)–Cl(1) 2.3410(18), Pd(1)–Cl(2) 2.3501(17), P(1)–P(2) 2.187(2); Cl(1)–Pd(1)–Cl(2) 94.72(7), P(1)–Pd(2)–P(2A) 98.56(6).

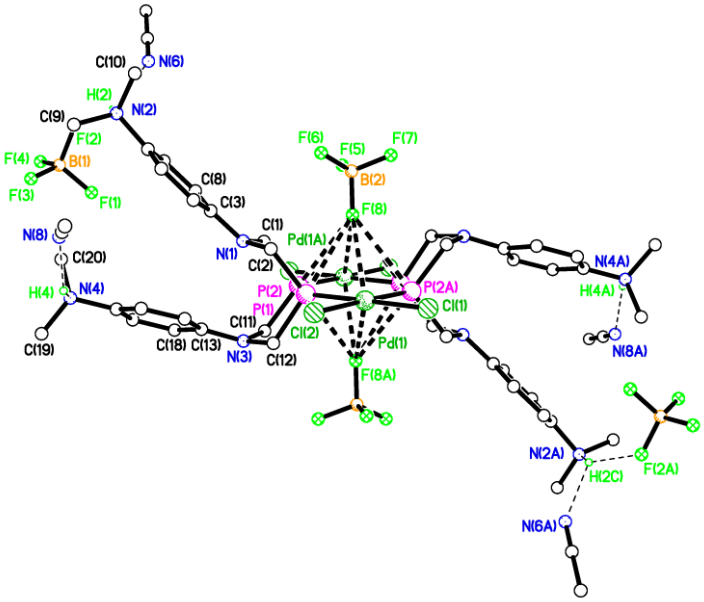
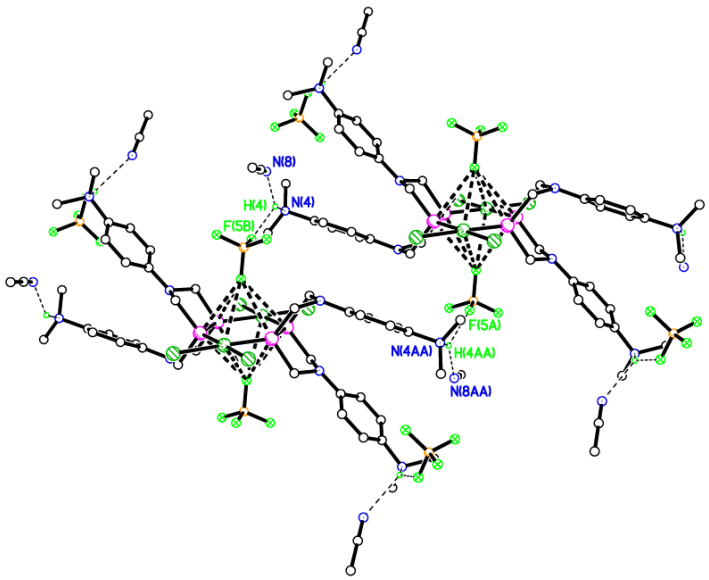


Figure S31 Packing plot of **3a**·12CD_3CN in the solid state showing packing arrangement.



Single crystal X-ray data for 4a·CH_2Cl_2

Suitable crystals of **4a**·CH_2Cl_2 were obtained by slow diffusion of hexanes onto a CH_2Cl_2 solution of **4a**. Crystal data for **4a**·CH_2Cl_2: $C_{34}H_{34}Cl_2N_2P_2Pd·CH_2Cl_2$: M_r = 794.80, yellow plate, 0.53 x 0.28 x 0.06 mm^3, monoclinic, space group $P2_1/c$, a = 9.852(2), b = 12.814(3), c = 27.315(6) Å, β = 98.547(4)°, V = 3410.0(13) $Å^3$, T = 150(2) K, Z = 4, λ = 0.71073 Å, μ(Mo-K_α) = 0.98 mm^{-1}, θ range for data collection = 1.8–25.0°, 5951 independent reflections measured, R_{int} = 0.042, d_{calc} = 1.548 g cm^{-3}, $R1$ = 0.099 (for 5114 data with $I > 2\sigma(I)$), $wR2$ = 0.246 (for all data), and 399 refined parameters, largest difference map features between 3.05 and –2.85 e/$Å^3$.

Figure S32 Molecular structure of **4a**·CH_2Cl_2 in the solid state. All hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–P(1) 2.254(3), Pd(1)–P(2) 2.239(3), Pd(1)–Cl(1) 2.365(3), Pd(1)–Cl(2) 2.342(3); P(1)–Pd(2)–P(2) 93.82(10), Cl(1)–Pd(1)–Cl(2) 90.88(10).