Supporting Information for:

Activation of group 15 based cage compounds by [$Cp^{BIG}Fe(CO)_2$] radicals

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1. Crystallographic details

The crystal structure analyses were performed on an Oxford Diffraction SuperNova diffractometer (**2a-d, 3**). Absorption corrections for **2a** and **2b** based on multi-scan, for **2c** based on nummerical gaussian integration over a multifaceted crystal model and for **2d** and **3** an analytical absorption correction was carried out.[1] The structures were solved by direct methods of the program SIR-92[2]and refined with least square method on F^2 employing SHELXL-97[3] with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model.

CCDC-997912 (**2a**), CCDC-997913 (**2b**), CCDC-997914 (**2c**), CCDC-997915 (**2d**) and CCDC-997916 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for compound [{$Cp^{BIG}Fe(CO)_2$}$_2$($\mu,\eta^{1:1}$-P_4)]*2(CH_2Cl_2) (**2a**): $C_{116}H_{134}Cl_4Fe_2O_4P_4$, M = 1969.61, space group $C2/c$ (no.15), a = 16.5044(2) Å, b = 23.0305(2) Å, c = 28.6494(3) Å, β = 104.041(1)°, V = 10564.4(2) Å^3, Z = 4, μ = 4.097 mm^{-1}, $F(000)$ = 4168, T = 123 K, 60294 reflections measured, 10951 unique (R_{int} = 0.0321), R_1 = 0.0400, wR_2 = 0.1090 for I > 2σ(I); CCDC-997912.

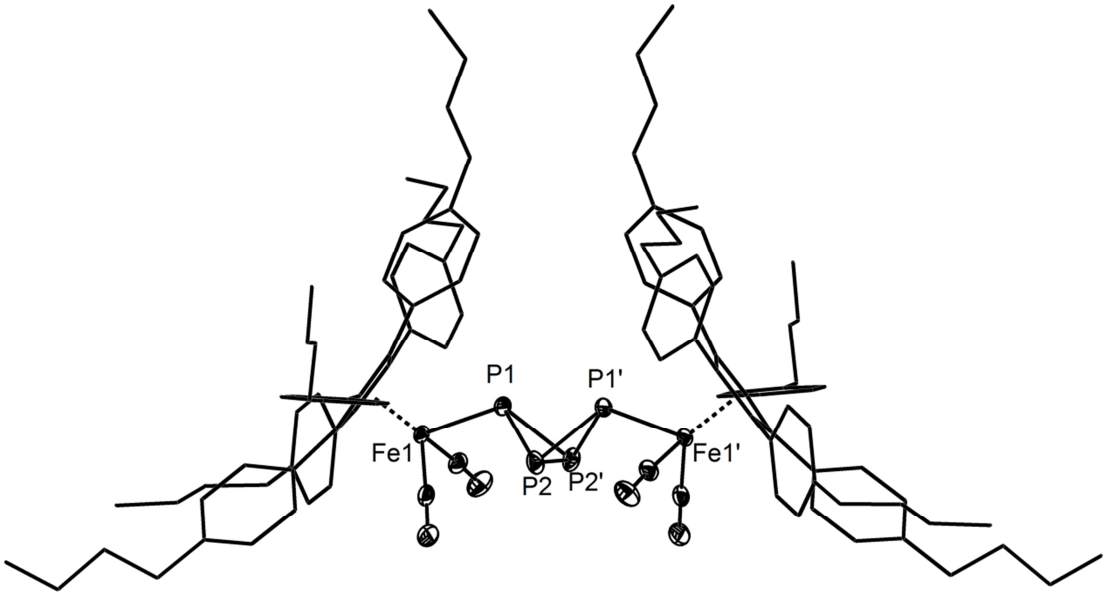

Fig. S1 Molecular structure of **2a** in the crystal. For clarity H atoms and solvent molecules are omitted, Cp^{BIG} ligands are drawn in 'wires or sticks' model and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level. Selected atom distances [Å] and angles [°] in **2a**: P1-P2 2.2343(5), P1-P2' 2.2094(6), P1···P1' 2.7749(4), P2-P2' 2.1717(7), Fe1-P1 2.3397(4), P1-P2-P1' 77.28(2), P1-P2-P2' 60.17(2), P2-P2'-P1 61.32(2), P2-P1-P2' 58.51(2).

Crystal data for compound [{$Cp^{BIG}Fe(CO)_2$}$_2$(μ,η$^{1:1}$-As_4)]*2(CH_2Cl_2) (**2b**): $C_{116}H_{134}Cl_4Fe_2O_4As_4$, M = 2145.41, space group $C2/c$ (no.15), a = 16.0862(4) Å, b = 23.1908(5) Å, c = 29.2063(6) Å, β = 103.712(2)°, V = 10584.9(4) Å^3, Z = 4, μ = 4.907 mm^{-1}, F(000) = 4456, T = 123 K, 18697 reflections measured, 10673 unique (R_{int} = 0.0404), R_1 = 0.0851, wR_2 = 0.1630 for I > 2σ(I); CCDC-997913.

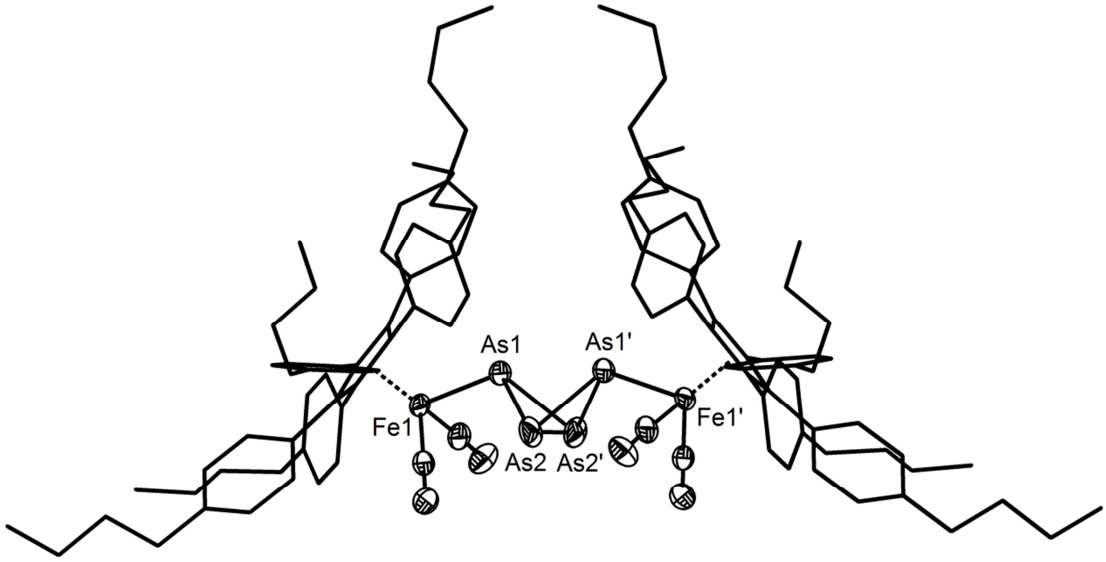

Fig. S2 Molecular structure of **2b** in the crystal. For clarity H atoms and solvent molecules are omitted, Cp^{BIG} ligands are drawn in 'wires or sticks' model and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level. Selected atom distances [Å] and angles [°] in **2b**: As1-As2 2.4639(6), As1-As2' 2.4357(7), As1···As1' 2.9958(4), As2-As2' 2.3976(9), Fe1-As1 2.4315(7), As1-As2-As1' 75.39(2), As1-As2-As2' 60.12(2), As2-As2'-As1 61.29(2), As2-As1-As2' 58.59(2).

Crystal data for compound [{$Cp^{BIG}Fe(CO)_2$}$_2$($\mu,\eta^{1:1}$-P_4S_3)]*(CH_2Cl_2)*0.5(CH_3CN) (**2c**): $C_{232}H_{267}Cl_4Fe_4NO_8P_8S_6$, M = 4002.86, space group $P\bar{1}$ (no.2), a = 18.6002(4) Å, b = 19.1311(2) Å, c = 30.2819(5) Å, α = 89.890(1)°, β = 88.546(2)°, γ = 84.899(1)°, V = 10729.5(3) Å^3, Z = 2, μ = 4.128 mm^{-1}, F(000) = 4236, T = 123 K, 84816 reflections measured, 41413 unique (R_{int} = 0.0329), R_1 = 0.0820, wR_2 = 0.1845 for I > 2σ(I); CCDC-997914.

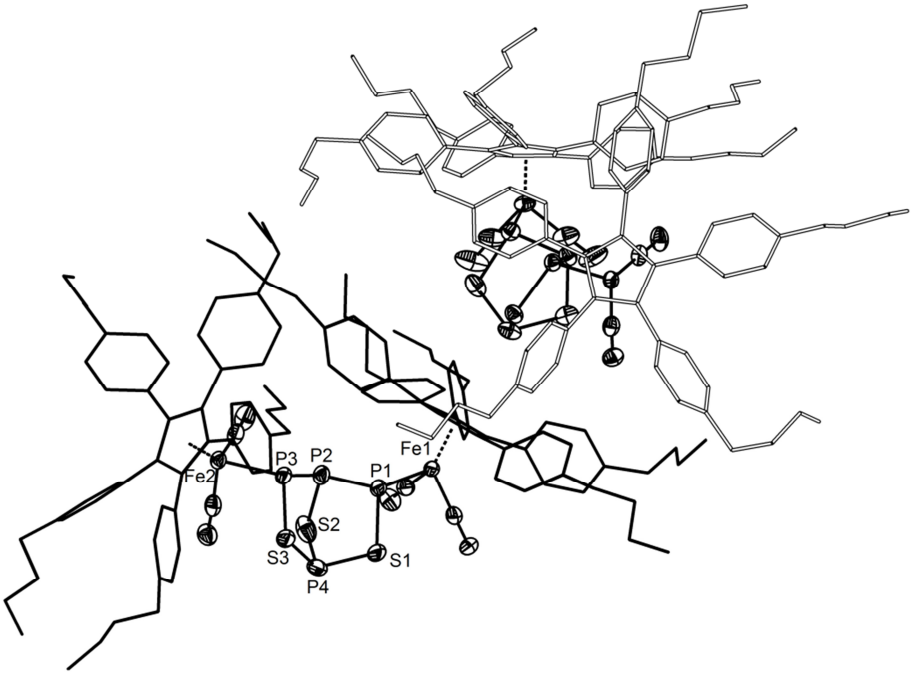

Fig. S3 Molecular structures of **2c** in the crystal. For clarity H atoms and solvent molecules are omitted, Cp^{BIG} ligands are drawn in 'wires or sticks' model and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.

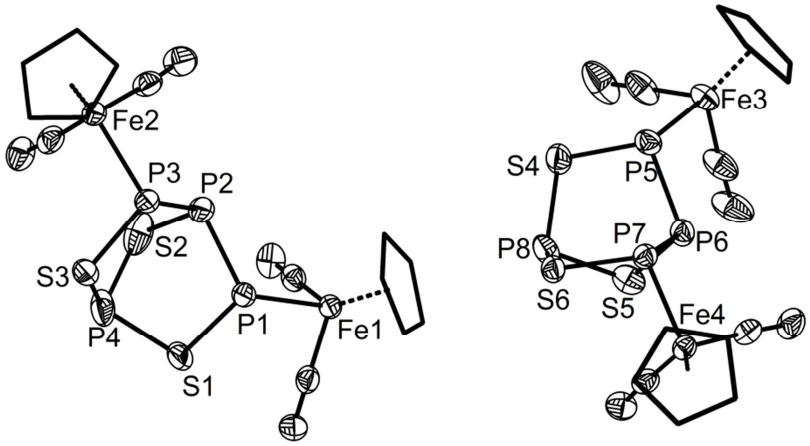

Fig. S4 Central structures of **2c** in the crystal. For clarity 4-nBuC_6H_4 groups of Cp^{BIG} lignads are omitted. Thermal ellipsoids are drawn with 50% probability level. Selected atom distances [Å] and angles [°] in **2c**, Molecule 1: P1-P2 2.227(2), P2-P3 2.185(1), P1···P3 3.268(1), P1-S1 2.156(1), P2-S2 2.108(2), P3-S3 2.157(1), P4-S1 2.074(2), P4-S2 2.107(2), P4-S3 2.097(2), Fe1-P1 2.314(1), Fe2-P3 2.309(1), P1-P2-P3 95.60(5), P1-S1-P4 105.34(6), P2-S2-P4 97.51(7), P3-S3-P4 108.02(6); Molecule 2: P5-P6 2.194(1), P6-P7 2.190(1), P5···P7 3.318(1), P5-S4 2.161(1), P6-S5 2.114(1), P7-S6 2.172(1), P8-S4 2.094(2), P8-S5 2.100(1), P8-S6 2.099(2), Fe3-P5 2.314(1), Fe4-P7 2.313(1), P5-P6-P7 98.38(5), P5-S4-P8 106.27(6), P6-S5-P8 97.46(5), P7-S6-P8 107.52(5).

Crystal data for compound [{$Cp^{BIG}Fe(CO)_2$}$_2$($\mu,\eta^{1:1}$-P_4Se_3)] (**2d**): $C_{114}H_{130}Fe_2O_4P_4Se_3$, M = 2036.65, space group $P\bar{1}$ (no.2), a = 13.6368(5) Å, b = 16.2697(5) Å, c = 23.7755(9) Å, α = 77.294(3)°, β = 86.087(3)°, γ = 85.081(3)°, V = 5120.9(3) Å^3, Z = 2, μ = 4.475 mm^{-1}, F(000) = 2120, T = 123 K, 27777 reflections measured, 15685 unique (R_{int} = 0.0893), R_1 = 0.1485, wR_2 = 0.1808 for I > 2σ(I); CCDC-997915.

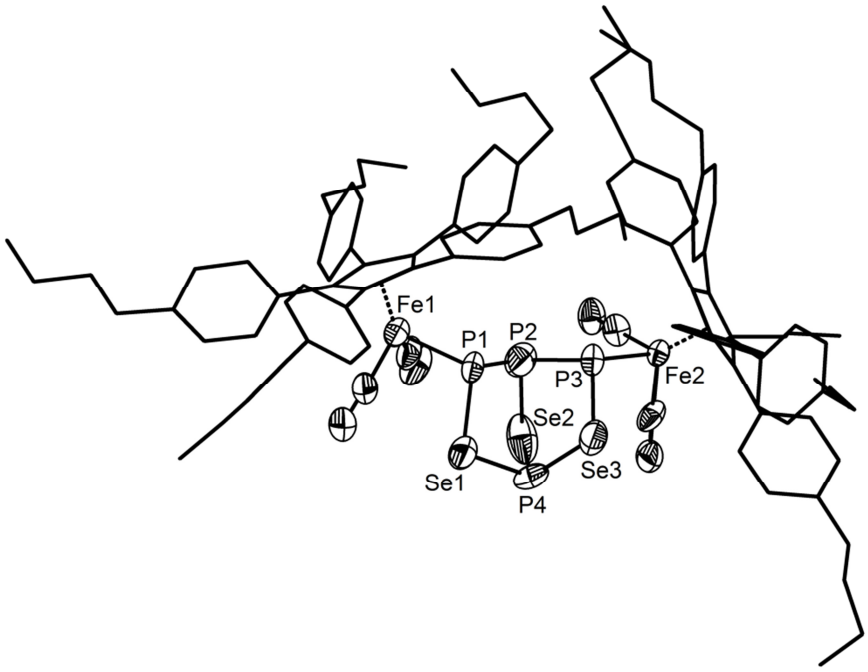

Fig. S5 Molecular structure of **2d** in the crystal. For clarity H atoms and solvent molecules are omitted, Cp^{BIG} ligands are drawn in 'wires or sticks' model and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.

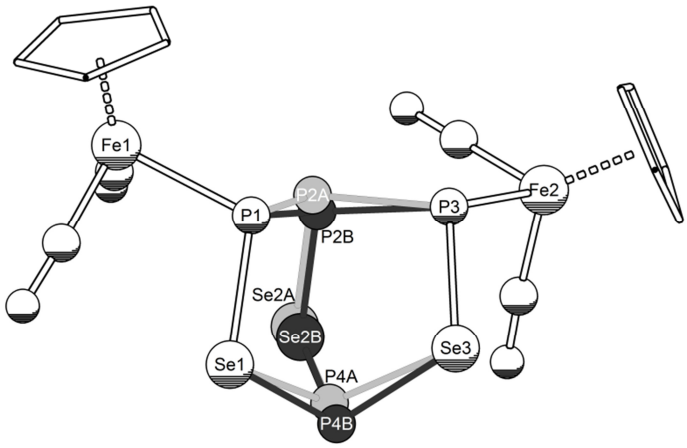

Fig. S6 Disordered central structure of **2d** in the crystal**.** Different parts are colored differently. The hatched globes belong to both parts. For clarity 4-nBuC$_6$H$_4$ groups of Cp^{BIG} lignads are omitted. Selected atom distances [Å] and angles [°] in **2d**: P1-P2A/P1-P2B 2.12(1)/2.247(8), P2A-P3/P2B-P3 2.18(1)/2.148(10), P1···P3 3.260(3), P1-Se1 2.299(2), P2A-Se2A/P2B-Se2B 2.32(2)/2.14(1), P3-Se3 2.304(2), P4A-Se1/P4B-Se1 2.25(2)/2.23(1), P4A-Se2A/P4B-Se2B 2.09(2)/2.36(2), P4A-Se3/P4B-Se3 2.30(1)/2.23(1), Fe1-P1 2.321(2), Fe2-P3 2.298(2), P1-P2A-P3/P1-P2B-P3 98.6(5)/95.7(3), P1-Se1-P4A/P1-Se1-P4B 96.1(3)/104.4(4), P2A-Se2A-P4A/P2B-Se2B-P4B 93.5(5)/97.1(5), P3-Se3-P4A/P3-Se3-P4B 98.9(3)/110.0(4).

Crystal data for compound [{$Cp^{BIG}Fe(CO)_2$}{$Cp^{BIG}FeCO$)(μ,$\eta^{1:2}$-CS_2)] (**3**): $C_{114}H_{130}Fe_2O_3S_2$, M = 1724.02, space group $P\bar{1}$ (no.2), a = 12.6885(2) Å, b = 13.6189(3) Å, c = 15.8914(3) Å, α = 103.957(2)°, β = 103.841(2)°, γ = 103.076(2)°, V = 2467.4(1) Å^3, Z = 1, μ = 3.128 mm^{-1}, F(000) = 922, T = 123 K, 22795 reflections measured, 9578 unique (R_{int} = 0.0184), R_1 = 0.0715, wR_2 = 0.1656 for I > 2σ(I); CCDC-997916.

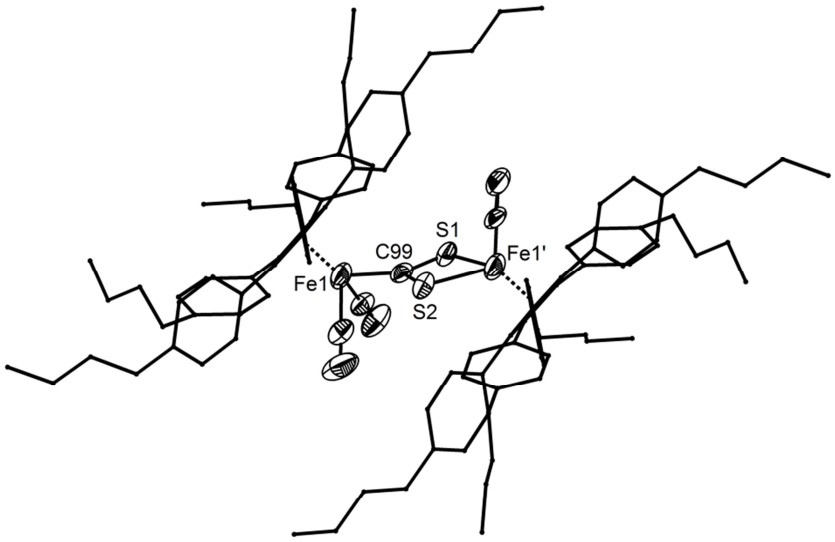

Fig. S 7 Molecular structures of **3** in the crystal with selected labels. Ellipsoids are drawn at 50% probability level. In case of disorder only the main part is shown. For clarity H atoms are omitted and Cp^{BIG} ligands are drawn in 'wires or sticks' model. Selected atom distances [Å] and angles [°] in **3**: Fe1-C99 1.893(5), C99-S1 1.762(6), C99-S2 1.660(6), S1-Fe1' 2.396(2), S2-Fe1' 2.302(2), S1-C99-S2 104.9(3), Fe1'-S1-C99 89.4(2), Fe1'-S2-C99 95.3(3), S1-Fe1'-S2 70.51(5).

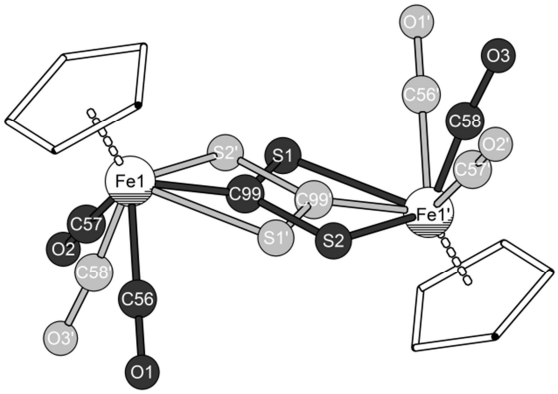

Fig. S8 Disordered central structure of **2d** in the crystal**.** Different parts are colored differently. The hatched globes belong to both parts. For clarity 4-nBuC_6H_4 groups of Cp^{BIG} ligands are omitted.

2. NMR spectra

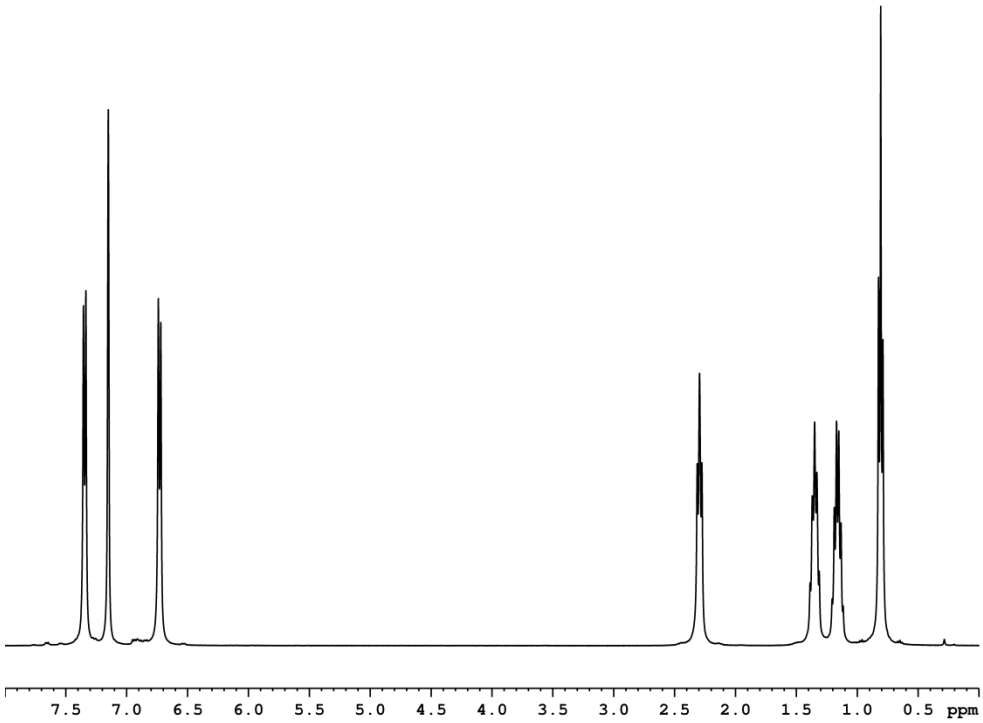

Fig. S9 ^{1}H NMR spectrum of **2a** in C_6D_6.

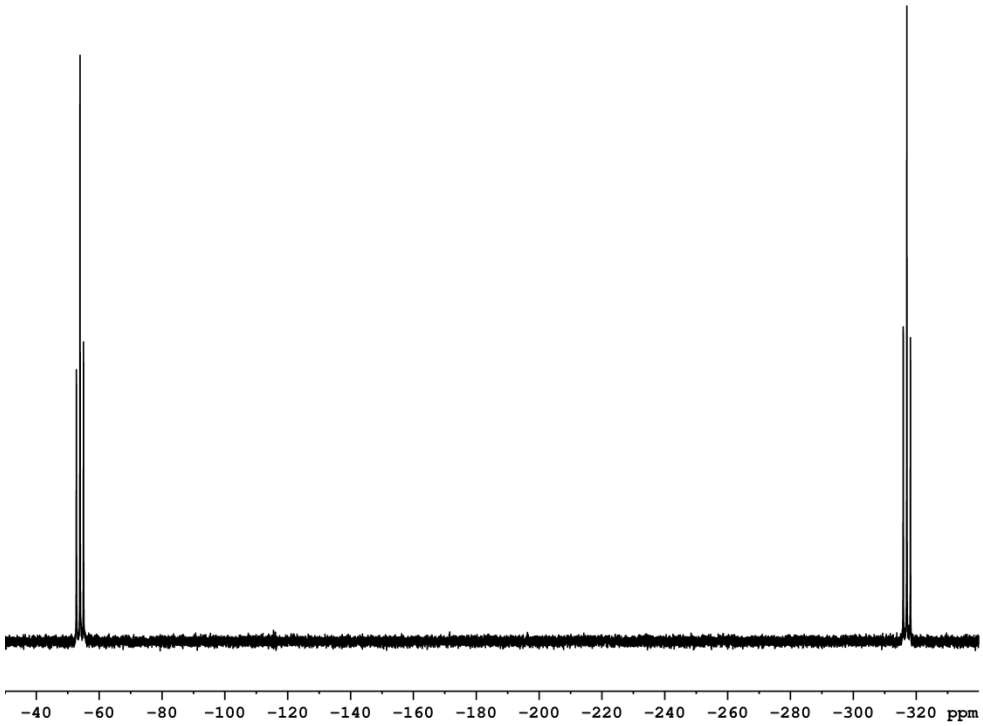

Fig. S10 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

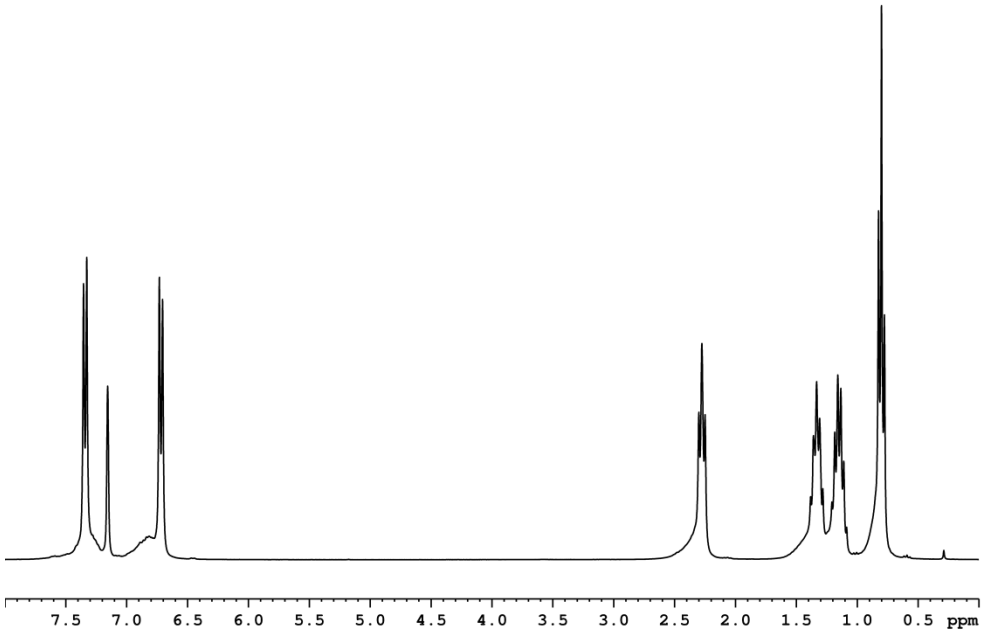

Fig. S11 ^{1}H NMR spectrum of **2b** in C_6D_6.

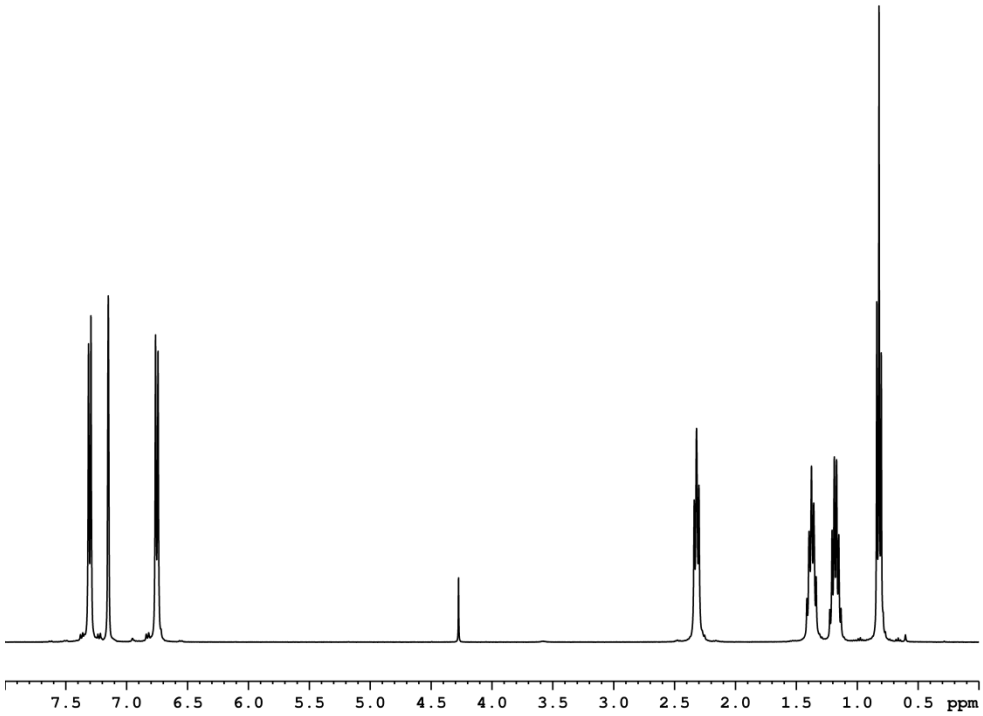

Fig. S12 ^{1}H NMR spectrum of **2c** in C_6D_6.

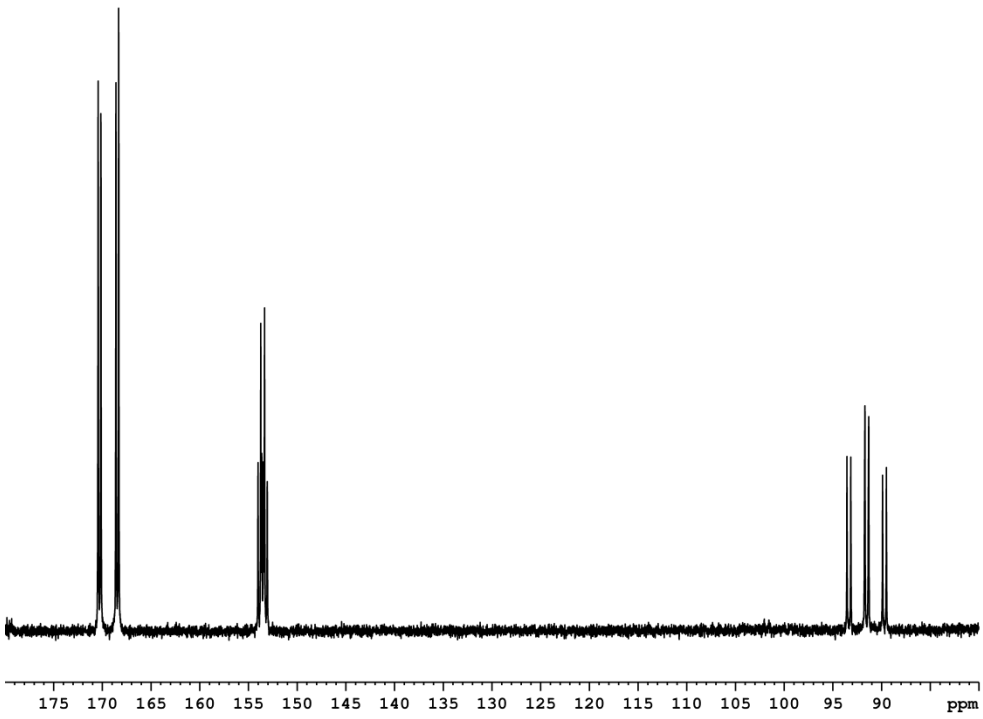

Fig. S13 $^{31}P\{^{1}H\}$ NMR spectrum of **2c** in C_6D_6.

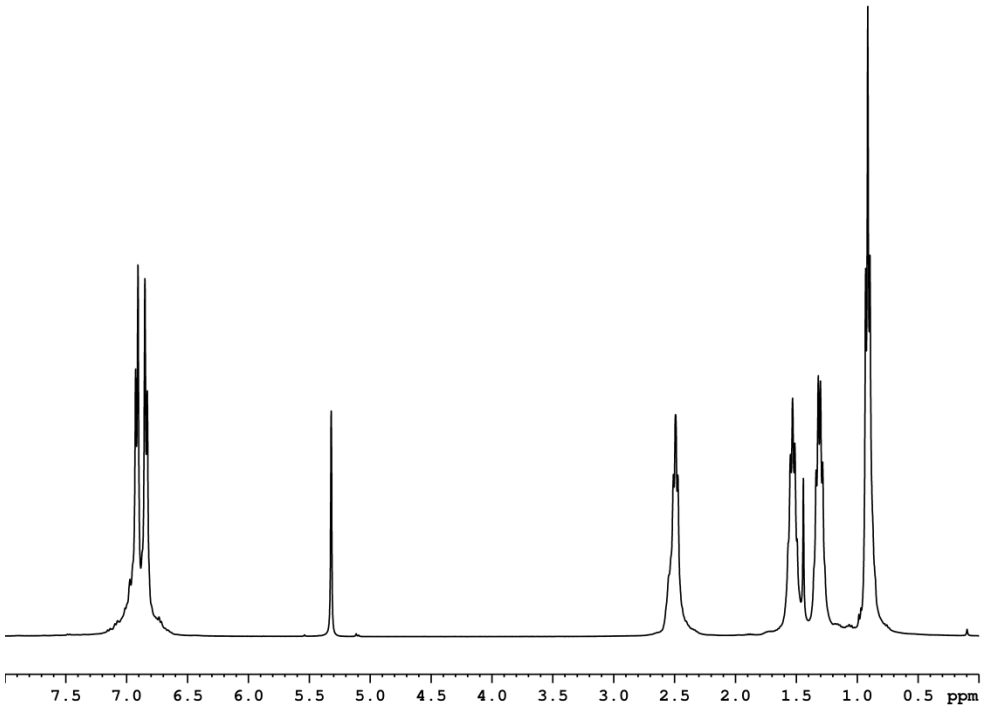

Fig. S14 ^{1}H NMR spectrum of **2d** in CD_2Cl_2.

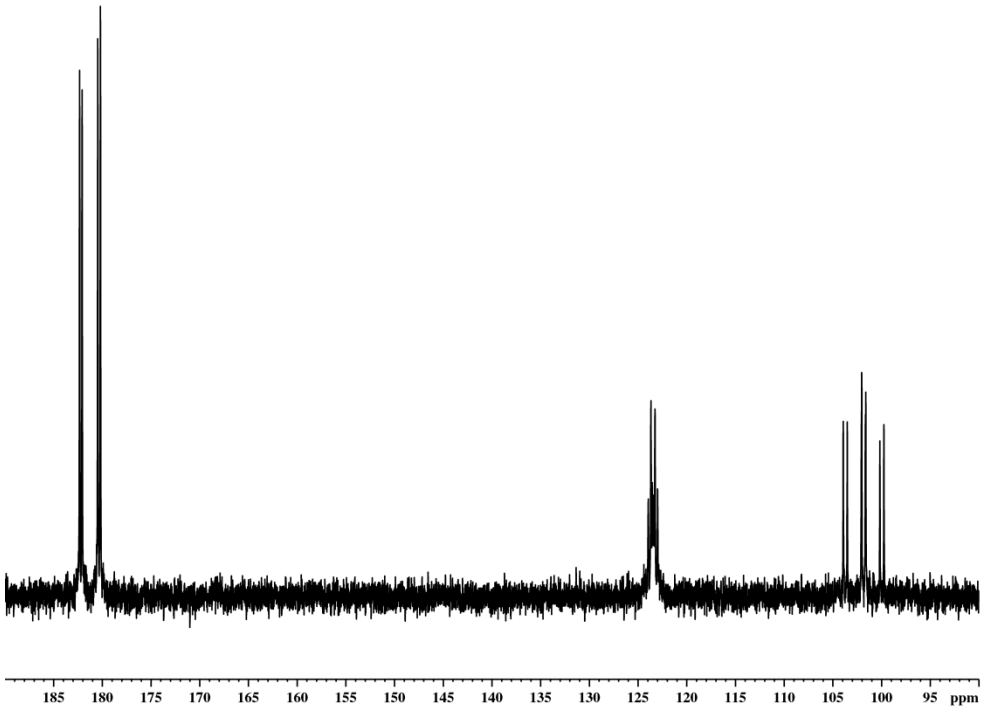

Fig. S15 $^{31}P\{^{1}H\}$ NMR spectrum of **2d** in CD_2Cl_2.

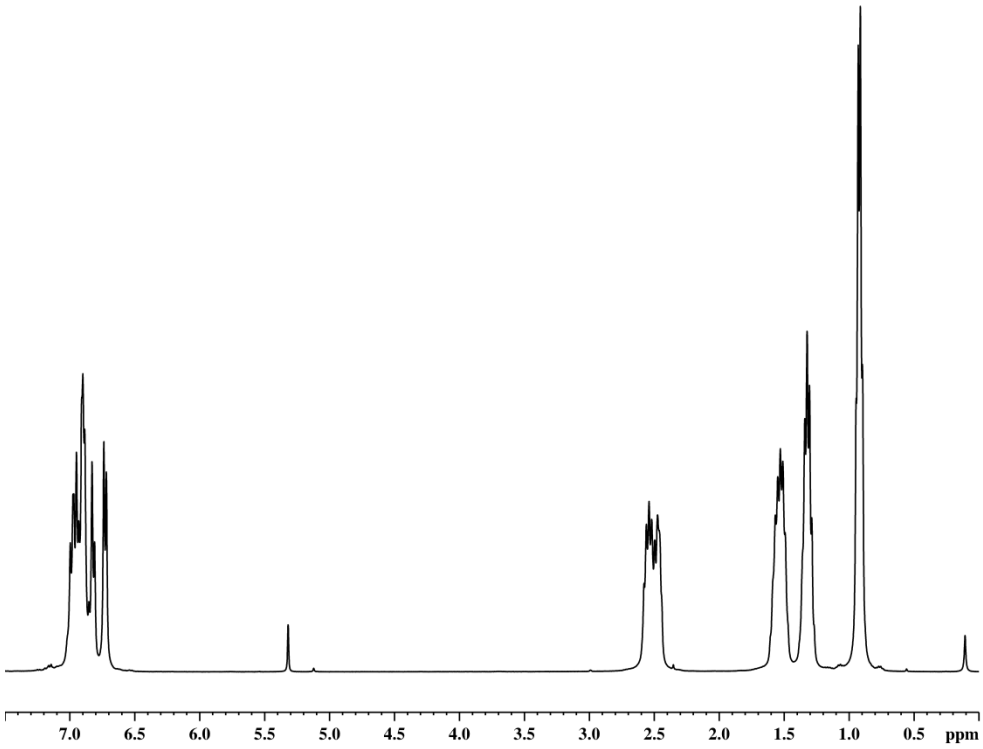

Fig. S16 ^{1}H NMR spectrum of **3** in CD_2Cl_2.

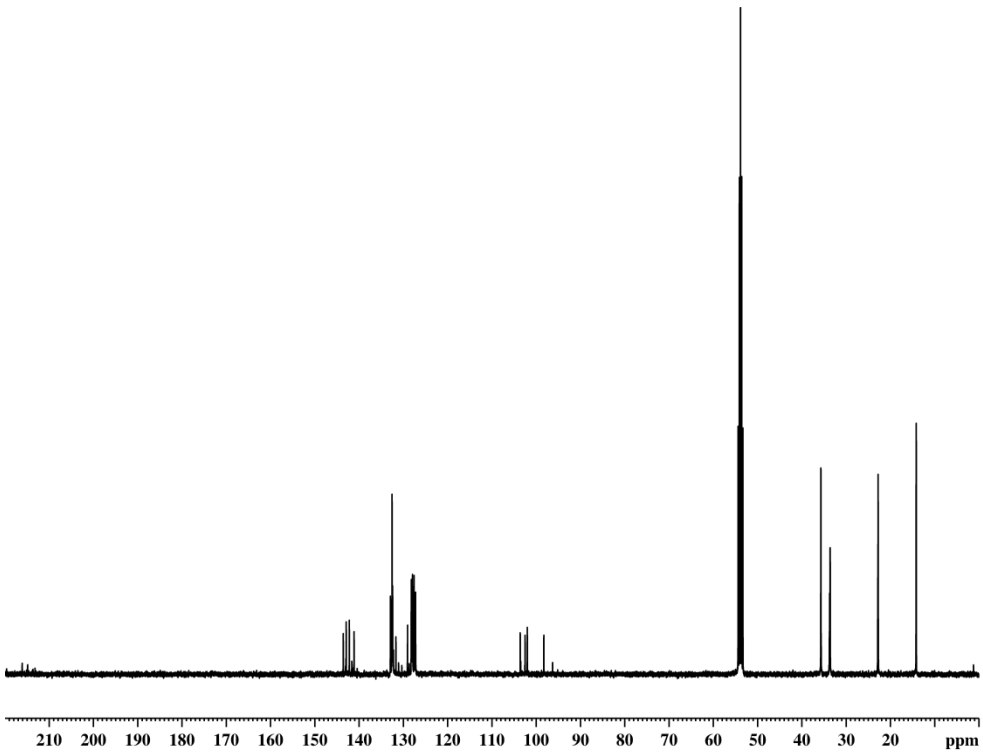

Fig. S17 $^{31}P\{^{1}H\}$ NMR spectrum of **2d** in CD_2Cl_2.

[1] R. C. Clark, J. S. Reid, *Acta Cryst.* **1995**, A51, 887-897.

[2] A. Altomare, M. C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, Polidori, G., Spagna, R. *J. Appl. Cryst.* **1999**, 32, 115-119

[3] G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122.