Supporting Information

for

Synthesis and coordination of hybrid phosphinoferrocene ligands with extended donor pendants

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Contents

Additional structure diagrams and crystallographic parameters

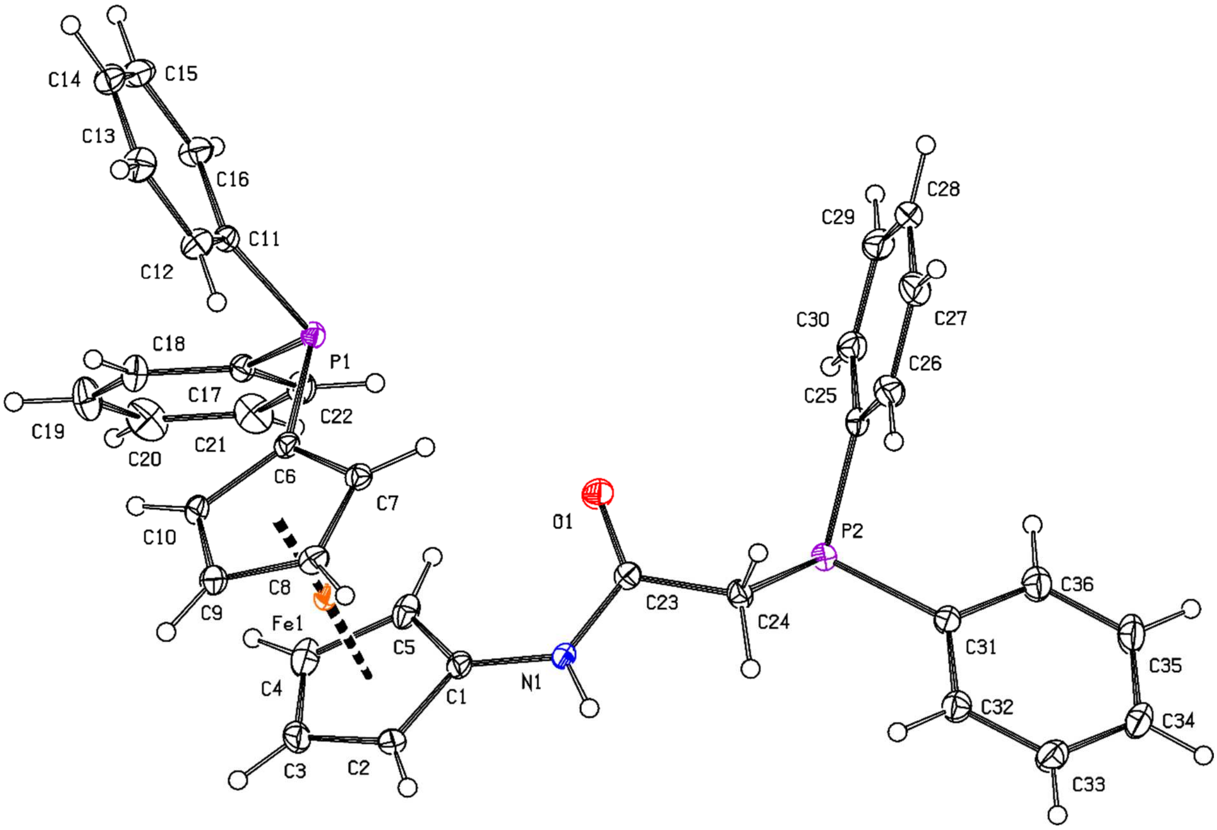


Figure S1 PLATON plot of the structure of **1** showing displacement ellipsoids at the 30% probability level

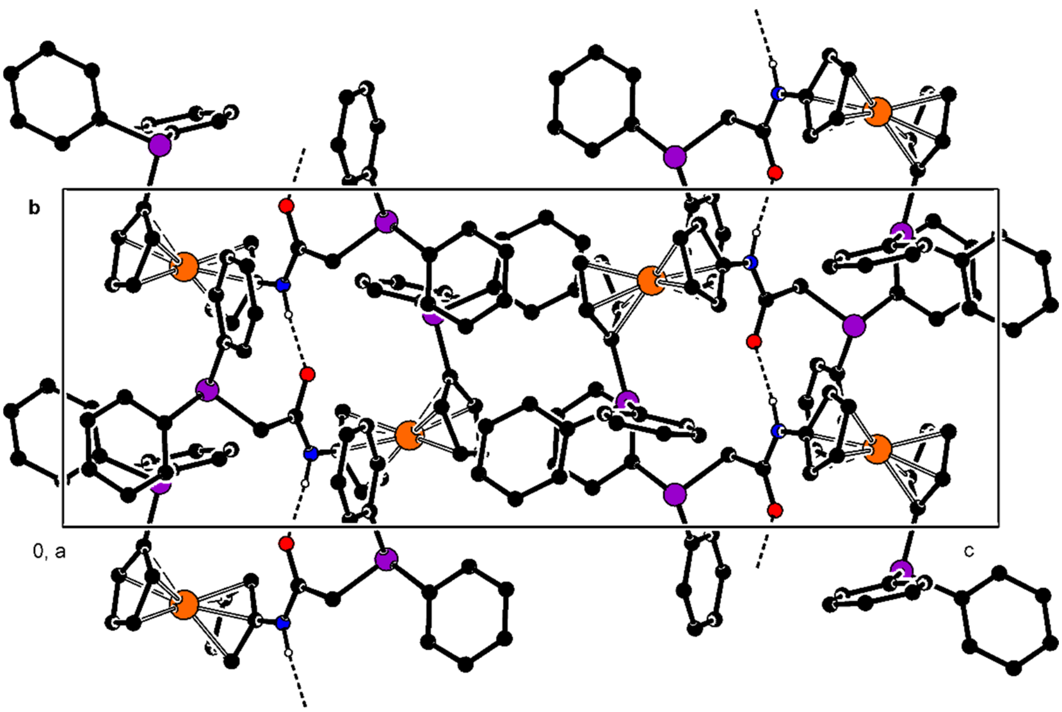


Figure S2 Packing diagram for **1** showing the NH···O=C hydrogen bonds (only NH hydrogens are shown for clarity)

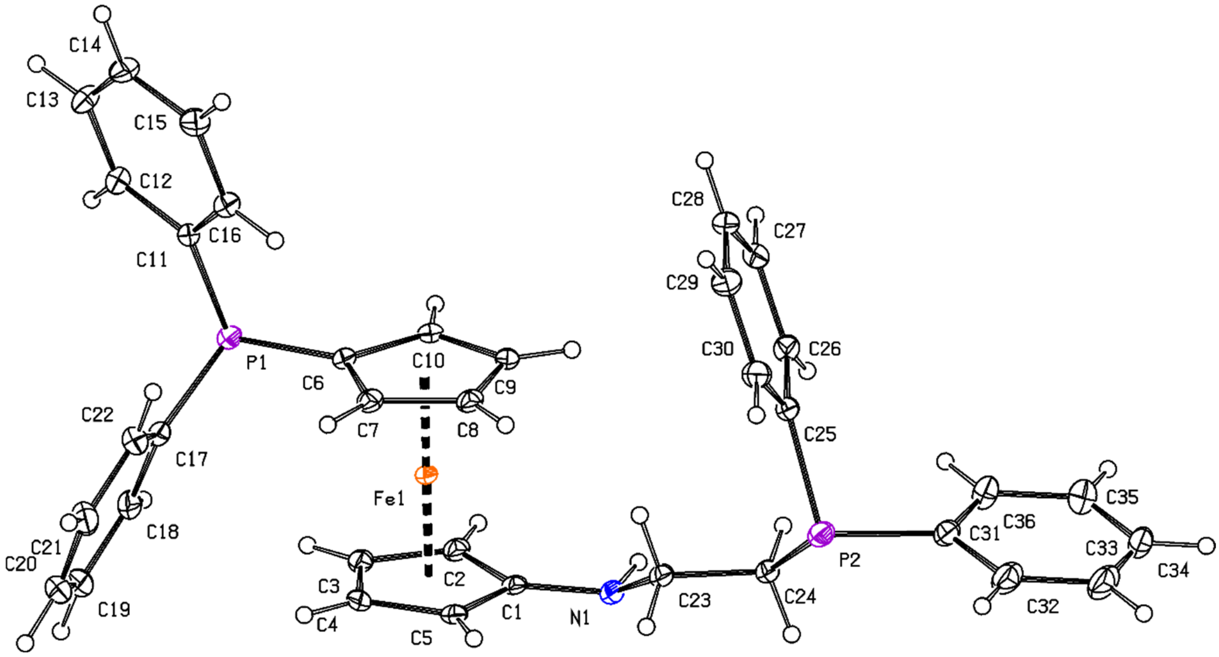


Figure S3 PLATON plot of the structure of **2** showing displacement ellipsoids at the 30% probability level

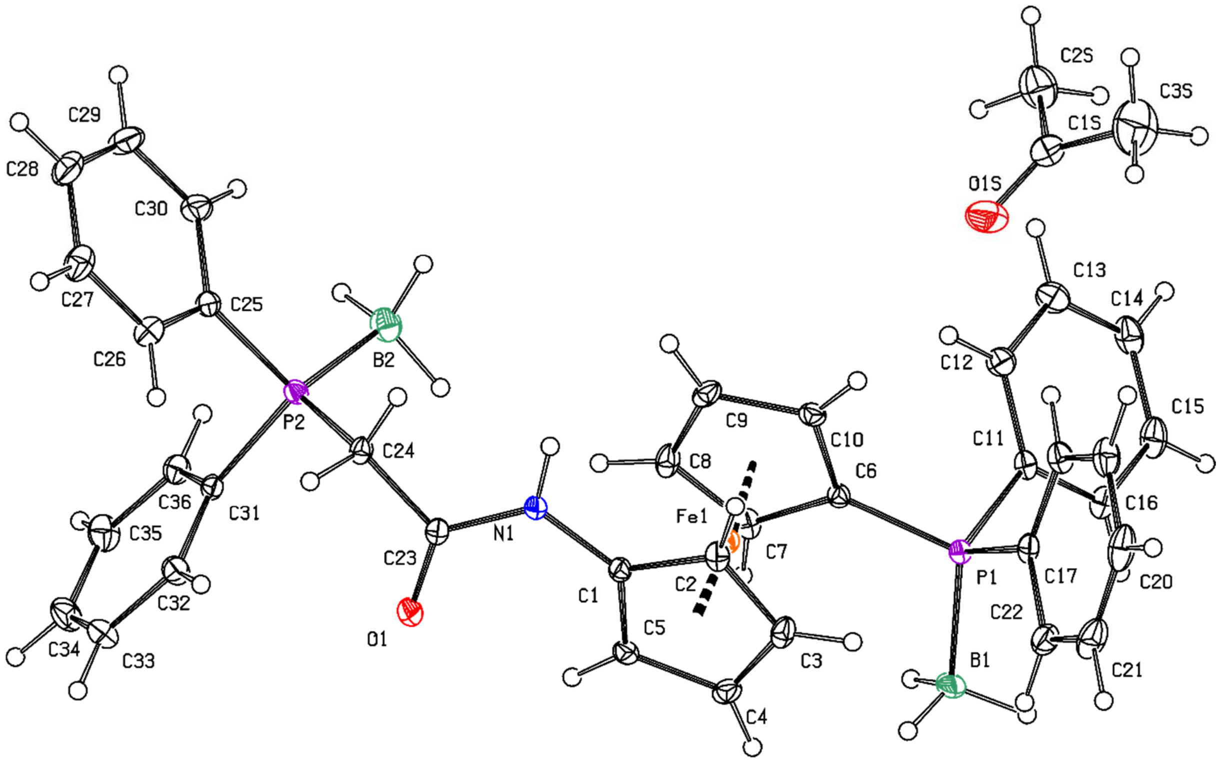


Figure S4 PLATON plot of the structure of **3**·Me_2CO showing displacement ellipsoids at the 30% probability level

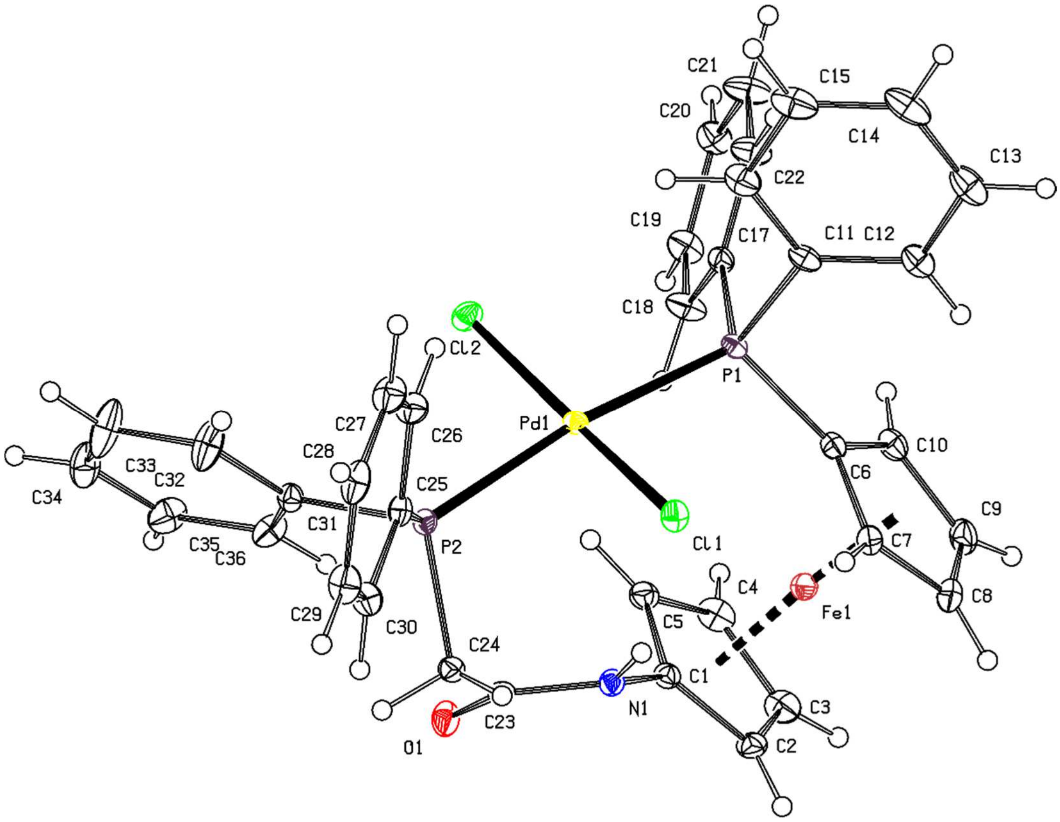


Figure S5 PLATON plot of the structure of *trans*-**5** showing displacement ellipsoids at the 30% probability level

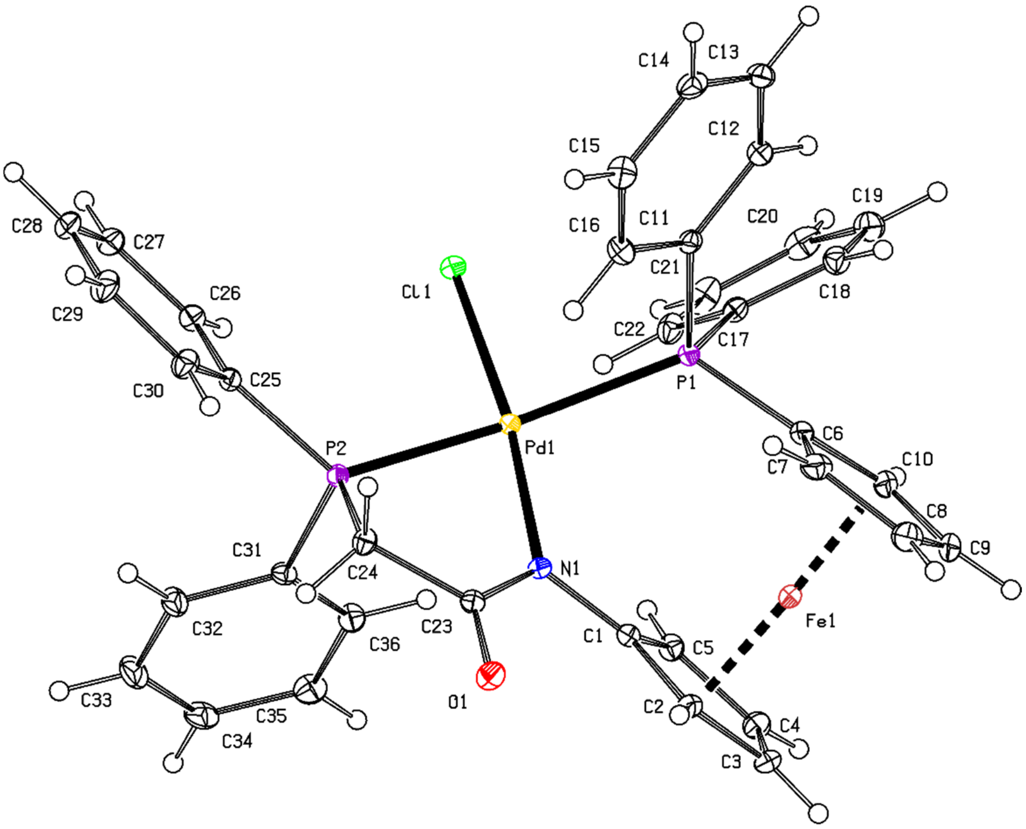


Figure S6 PLATON plot of the structure of **6** showing displacement ellipsoids at the 30% probability level

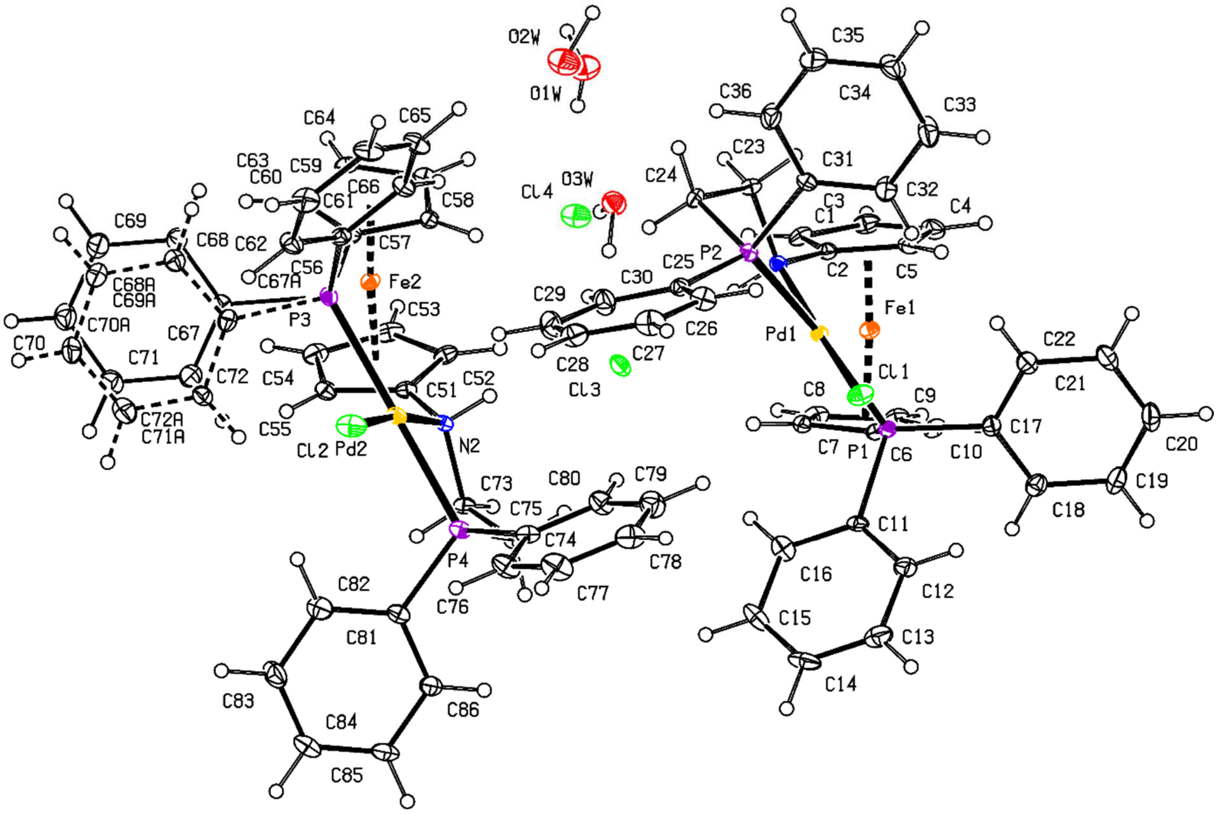


Figure S7 PLATON plot of **7**·$1.5H_2O$·$0.5C_2H_4Cl_2$ showing displacement ellipsoids at the 30% probability level (the solvating 1,2-dichloroethane was removed by using PLATON/SQUEEZE)

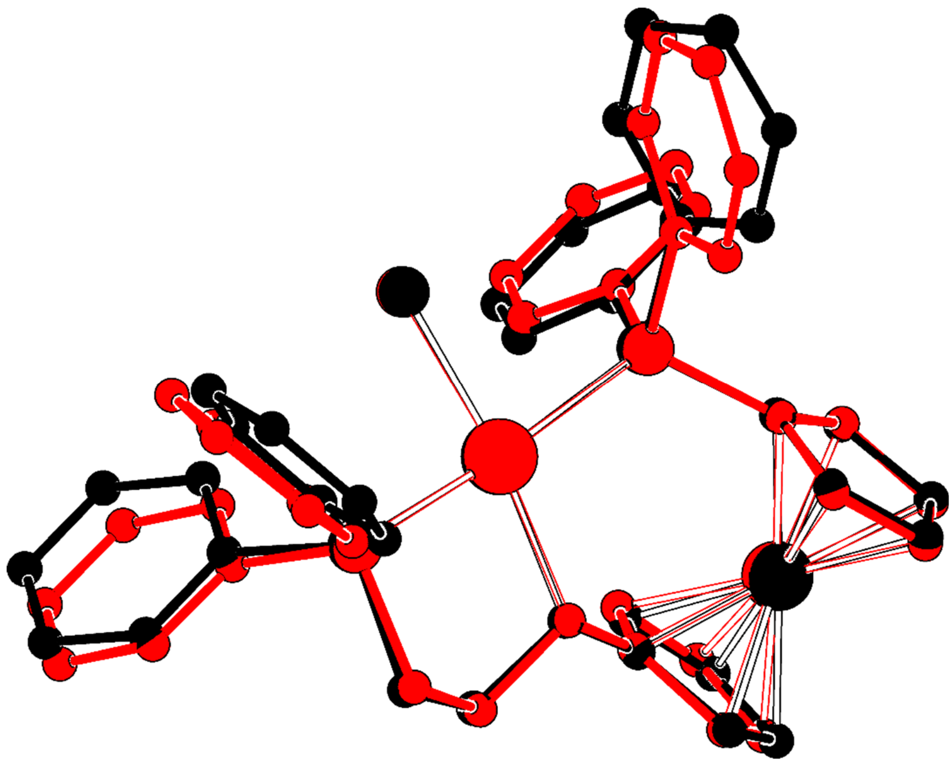


Figure S8 Overlap of the two structurally independent complex cations in the structure of **7**·$1.5H_2O$·$0.5C_2H_4Cl_2$ illustrating their minor structural differences

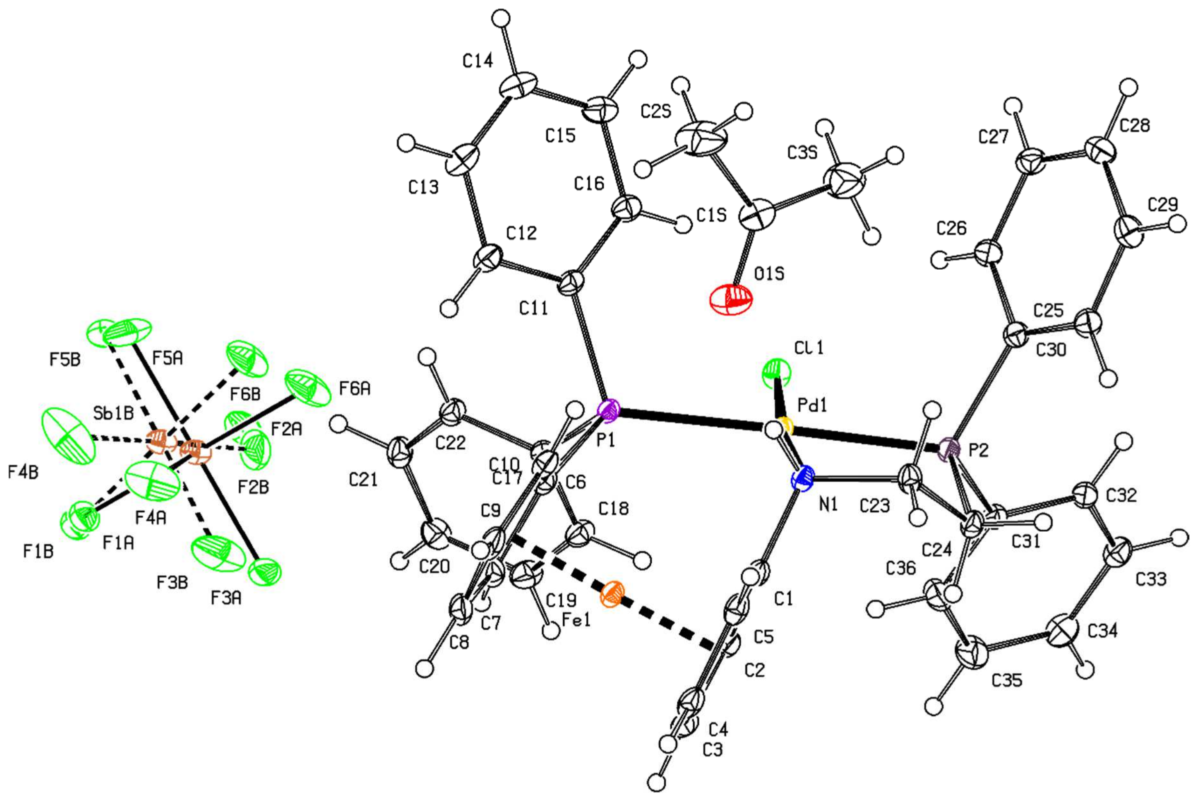


Figure S9 PLATON plot of the structure of **8**·Me_2CO showing displacement ellipsoids at the 30% probability level

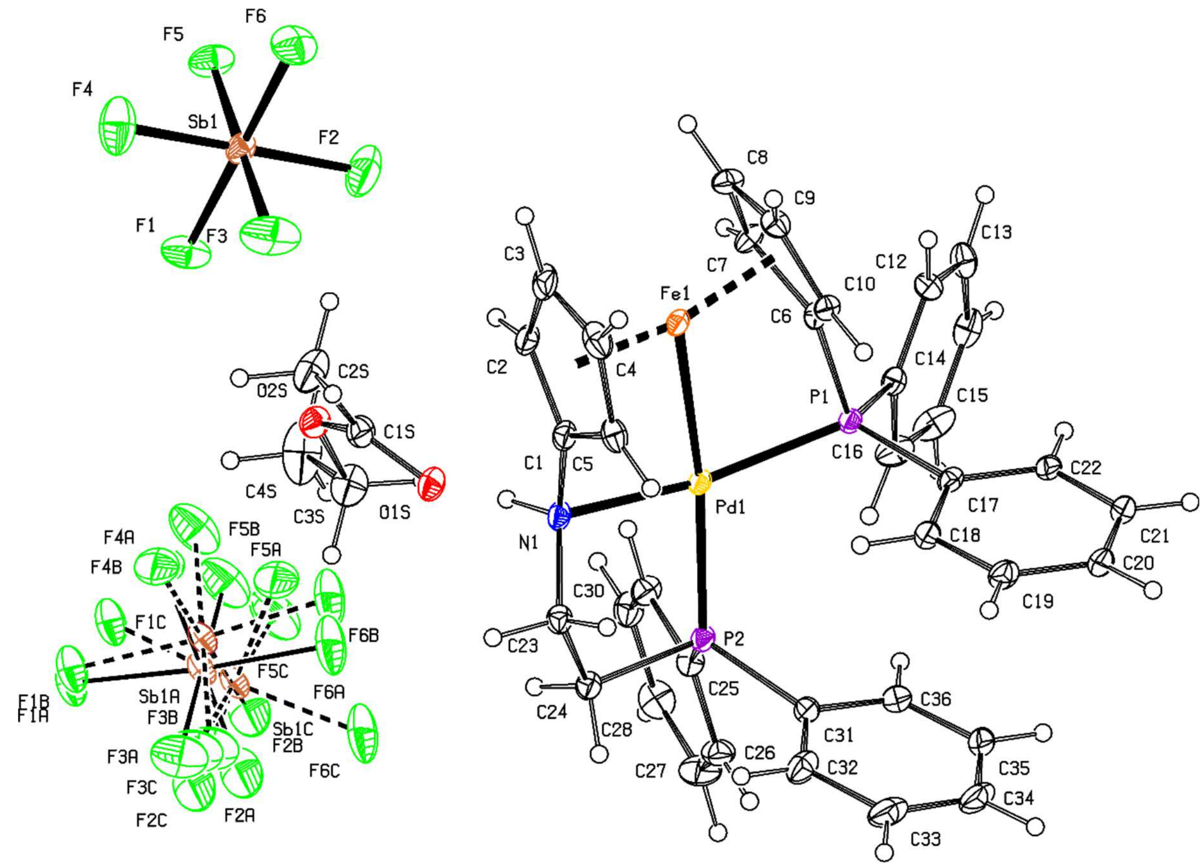


Figure S10 PLATON plot of the structure of **9**·AcOEt showing displacement ellipsoids at the 30% probability level

Table S1. Selected crystallographic data and structure refinement parameters.[a]

Compound	**1**	**2**	**3**·Me_2CO
Formula	$C_{36}H_{31}FeNOP_2$	$C_{36}H_{33}FeNP_2$	$C_{39}H_{43}B_2FeNO_2P_2$
M	611.41	597.42	697.15
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
T [K]	120(2)	120(2)	120(2)
a [Å]	12.0438(3)	16.6110(8)	8.7618(3)
b [Å]	25.9455(6)	6.0131(2)	13.7584(6)
c [Å]	9.4329(2)	29.413(1)	15.5032(6)
α [°]			74.449(1)
β [°]	96.276(1)	96.128(2)	80.315(1)
γ [°]			80.869(1)
V $[Å]^3$	2930.0(1)	2921.1(2)	1762.1(1)
Z	4	4	2
μ(Mo Kα) $[mm^{-1}]$	0.71073	0.71073	0.71073
Diffrns collected	34618	84577	36825
Independent diffrns	6711	6704	8068
Observed[a] diffrns	6068	6444	7737
R_{int}^b [%]	3.14	3.36	1.91
No. of parameters	370	361	426
R^b obsd diffrns [%]	3.52	4.47	3.04
R, wR^b all data [%]	4.03, 8.04	4.62, 10.70	3.17, 7.24
Δρ [e $Å^{-3}$]	0.43, –0.26	1.44, –0.61	0.60, –0.47

[a] Diffractions with $I > 2\sigma(I)$. [b] Definitions: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where $F_o^2(\text{mean})$ is the average intensity of symmetry-equivalent diffractions. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

Table S1 continued

Compound	**5**	**6**
Formula	$C_{36}H_{31}Cl_2FeNOP_2Pd$	$C_{36}H_{30}ClFeNOP_2Pd$
M	788.71	752.25
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T [K]	120(2)	120(2)
a [Å]	9.7041(3)	11.3016(6)
b [Å]	10.3958(3)	12.1891(7)
c [Å]	16.2586(5)	12.2831(6)
α [°]	91.820(1)	72.935(2)
β [°]	94.537(1)	88.173(2)
γ [°]	99.729(1)	72.517(2)
V [Å]^3	1609.84(8)	1540.1(1)
Z	2	2
μ(Mo Kα) [mm^{-1}]	0.71073	0.71073
Diffrns collected	29635	24893
Independent diffrns	7374	7002
Observed[a] diffrns	6866	6779
R_{int}[b] [%]	2.02	2.48
No. of parameters	397	388
R[b] obsd diffrns [%]	1.98	2.22
R, wR[b] all data [%]	2.24, 4.72	2.29, 5.80
Δρ [e Å^{-3}]	0.41, –0.46	0.86, –0.75

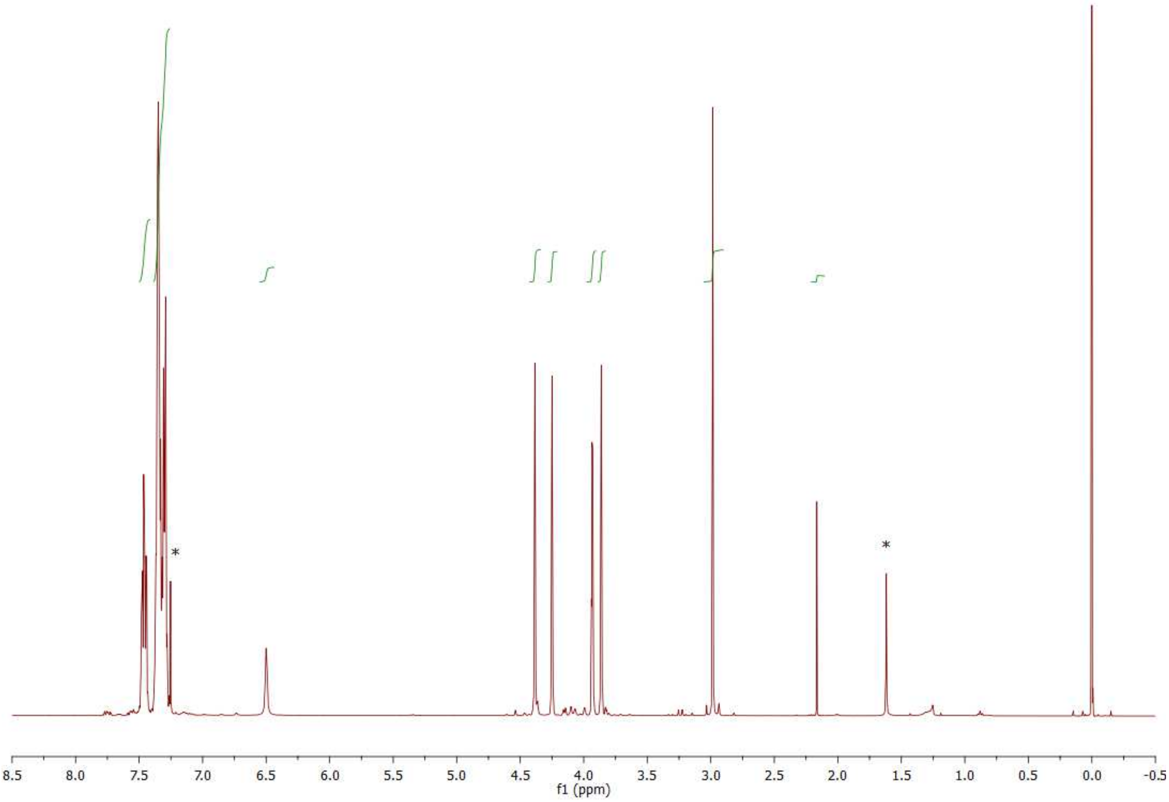
Table S1 continued

Compound	**7**· $^{3}/_{2}H_2O\cdot{}^{1}/_{2}$DCE	**8**·Me_2CO	**9**·AcOEt
Formula	$C_{37}H_{38}Cl_3FeNO_{1.5}P_2Pd$	$C_{39}H_{39}ClF_6FeNOP_2PdSb$	$C_{40}H_{41}F_{12}FeNO_2P_2PdSb_2$
M	851.22	1033.10	1263.43
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$P2_12_12_1$ (No. 19)[c]	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
T [K]	120(2)	120(2)	120(2)
a [Å]	14.6271(3)	10.6187(6)	10.8320(8)
b [Å]	19.8015(4)	15.764(1)	13.509(1)
c [Å]	25.4081(5)	23.902(2)	15.898(1)
α [°]			95.401(3)
β [°]		101.945(2)	107.996(3)
γ [°]			91.805(3)
V $[Å]^3$	7359.2(3)	3914.5(4)	2198.2(3)
Z	8	4	2
μ(Mo Kα) $[mm^{-1}]$	0.71073	0.71073	0.71073
Diffrns collected	75501	223757	89267
Independent diffrns	16834	9004	10139
Observed[a] diffrns	16087	8406	9435
R_{int}[b] [%]	3.55	3.44	3.59
No. of parameters	833	532	597
R[b] obsd diffrns [%]	2.43	2.54	5.54
R, *wR*[b] all data [%]	2.67, 4.66	2.79, 5.15	5.94, 13.42
Δρ $[e\ Å^{-3}]$	0.43, –0.32	0.76, –0.85	1.40, –1.55

[c] Flack's enantiomorph parameter: –0.006(5).

Copies of the NMR and MS spectra

(Note: solvent signals in the NMR spectra are denoted by an asterisk.)



Z

Figure S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**

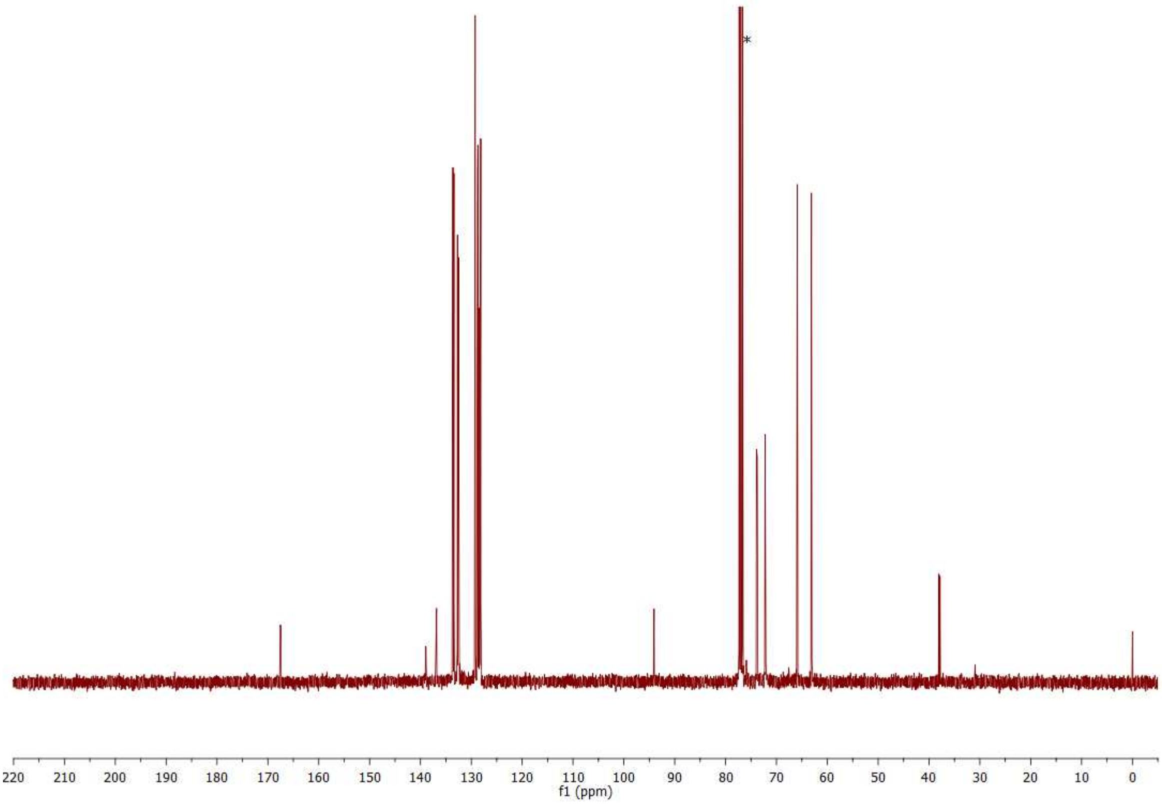


Figure S12 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1**

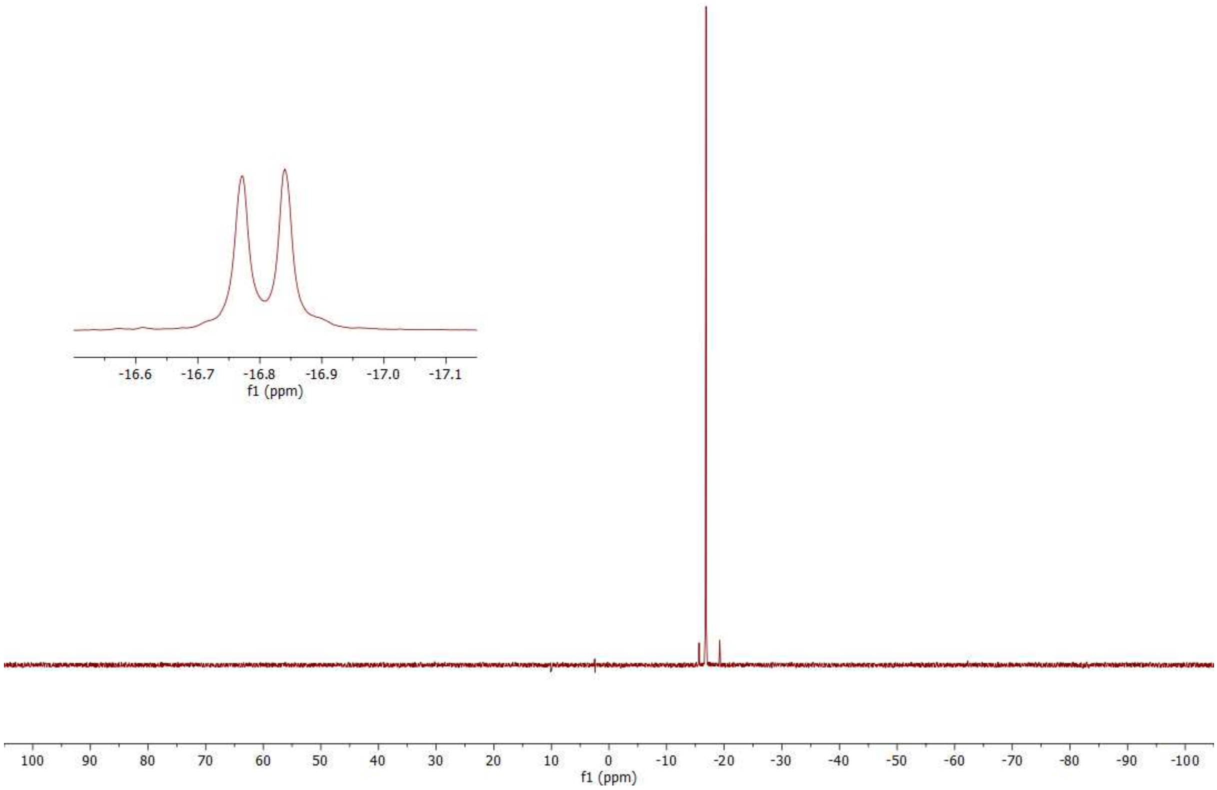


Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **1**

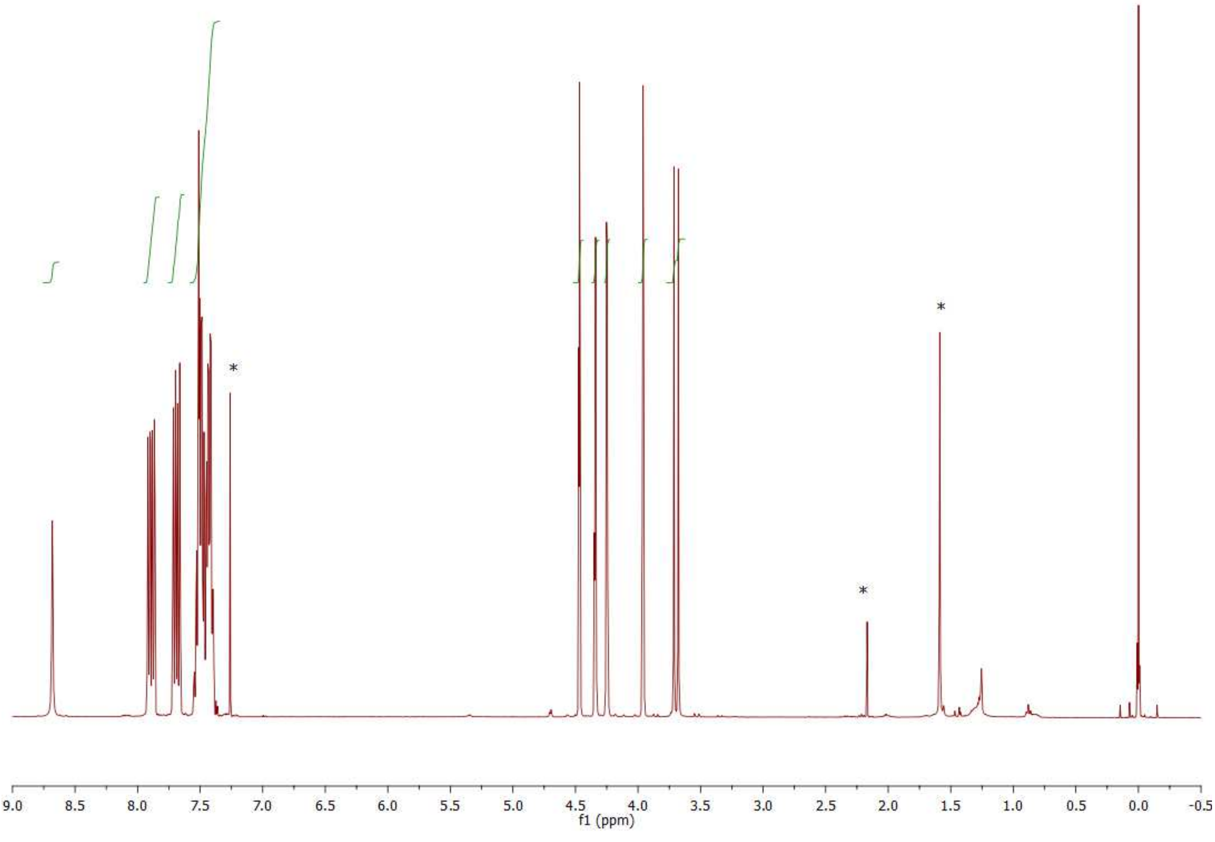


Figure S14 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1-Se**

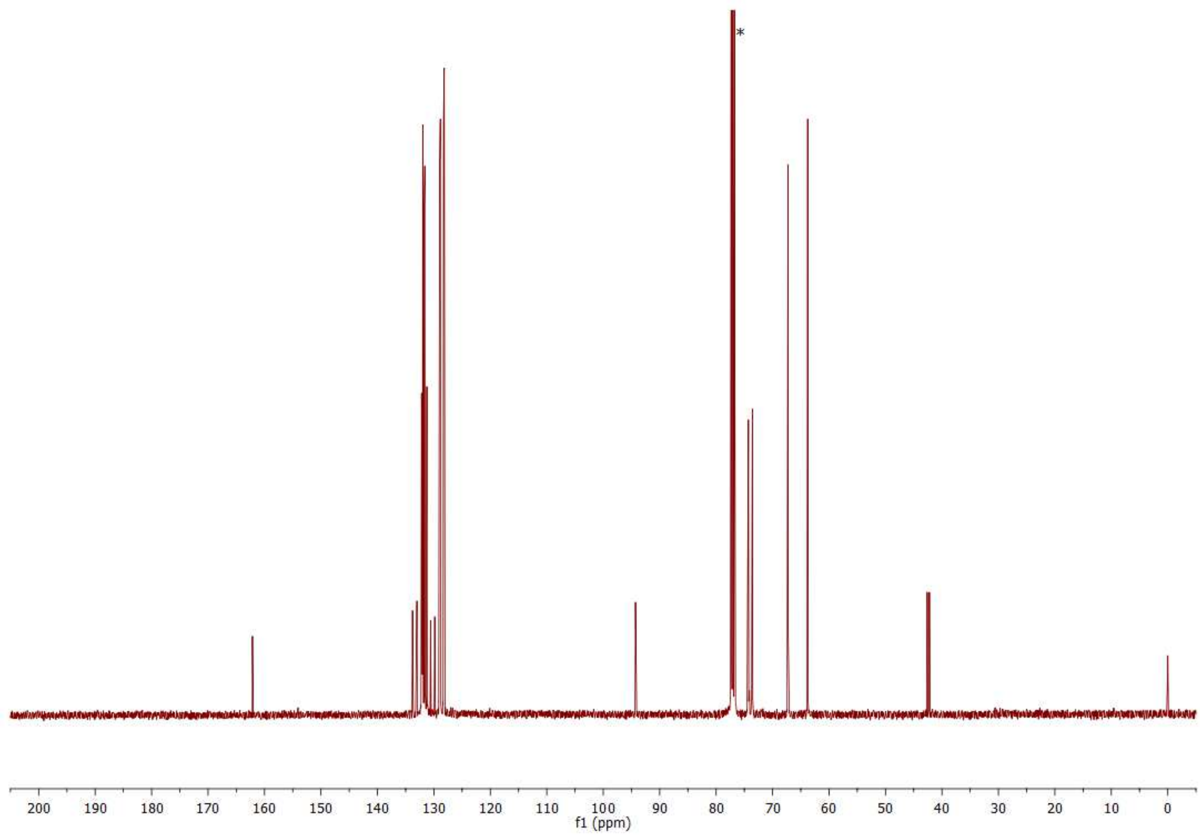


Figure S15 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1-Se**

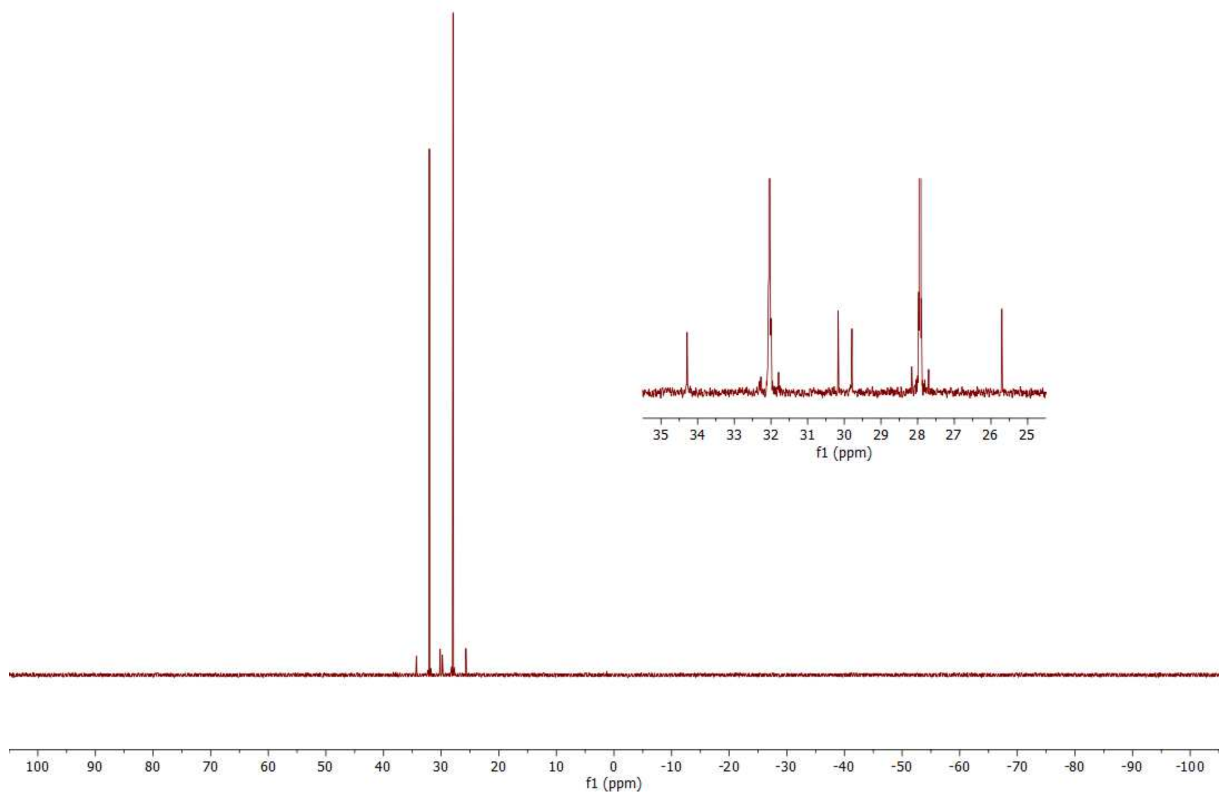


Figure S16 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **1-Se**

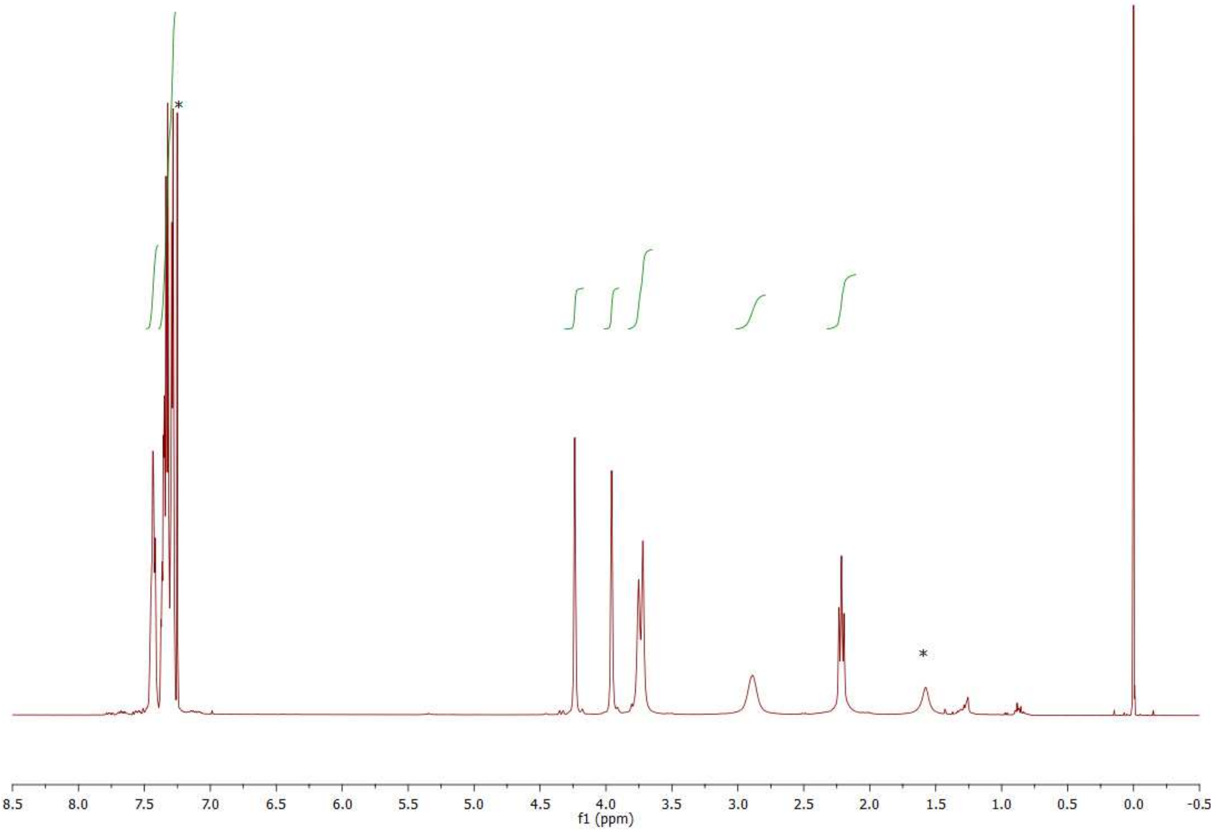


Figure S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**

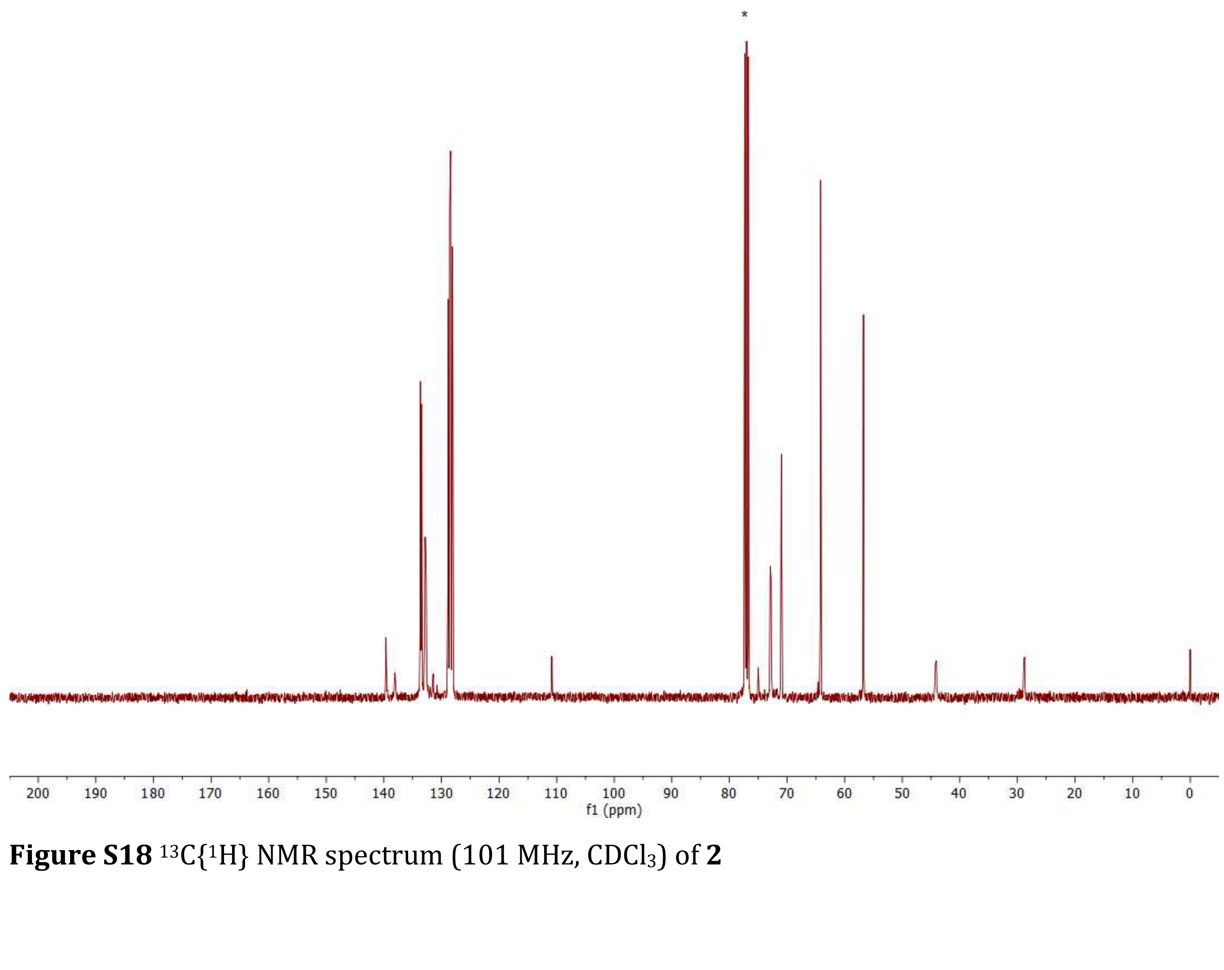


Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2**

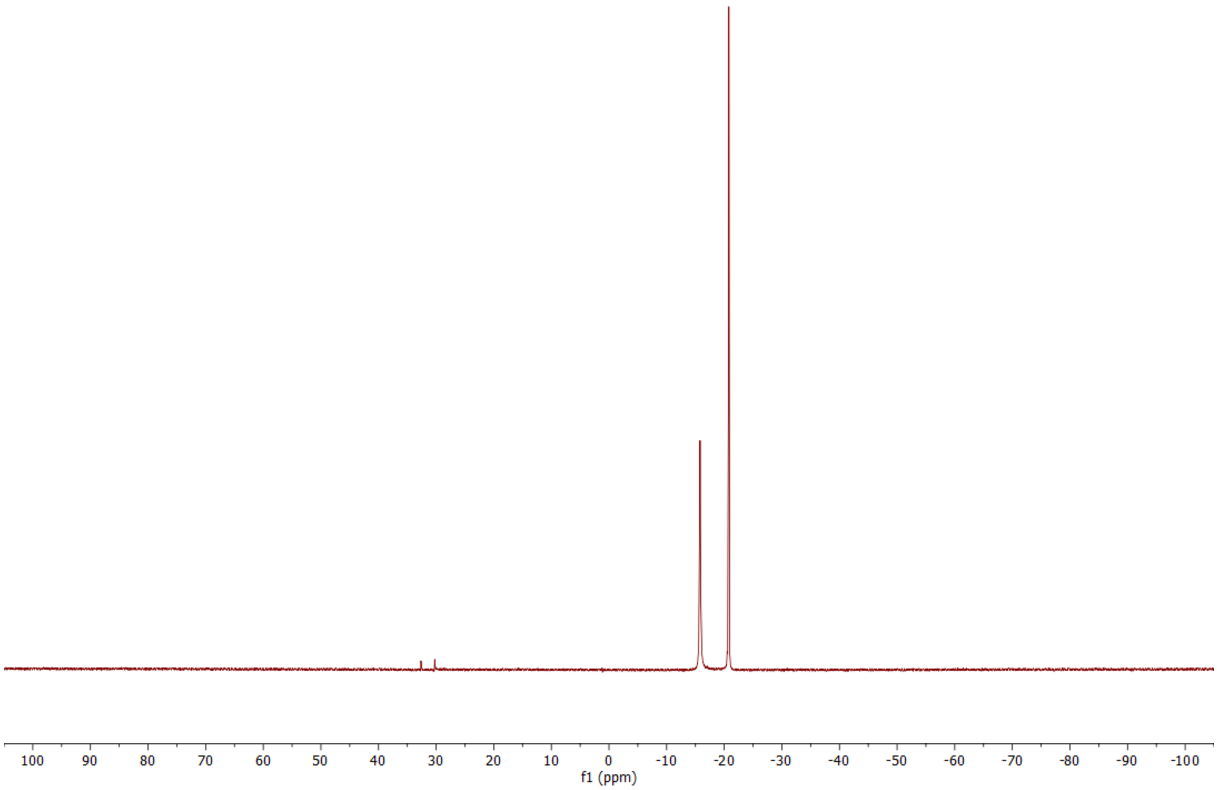


Figure S19 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **2**

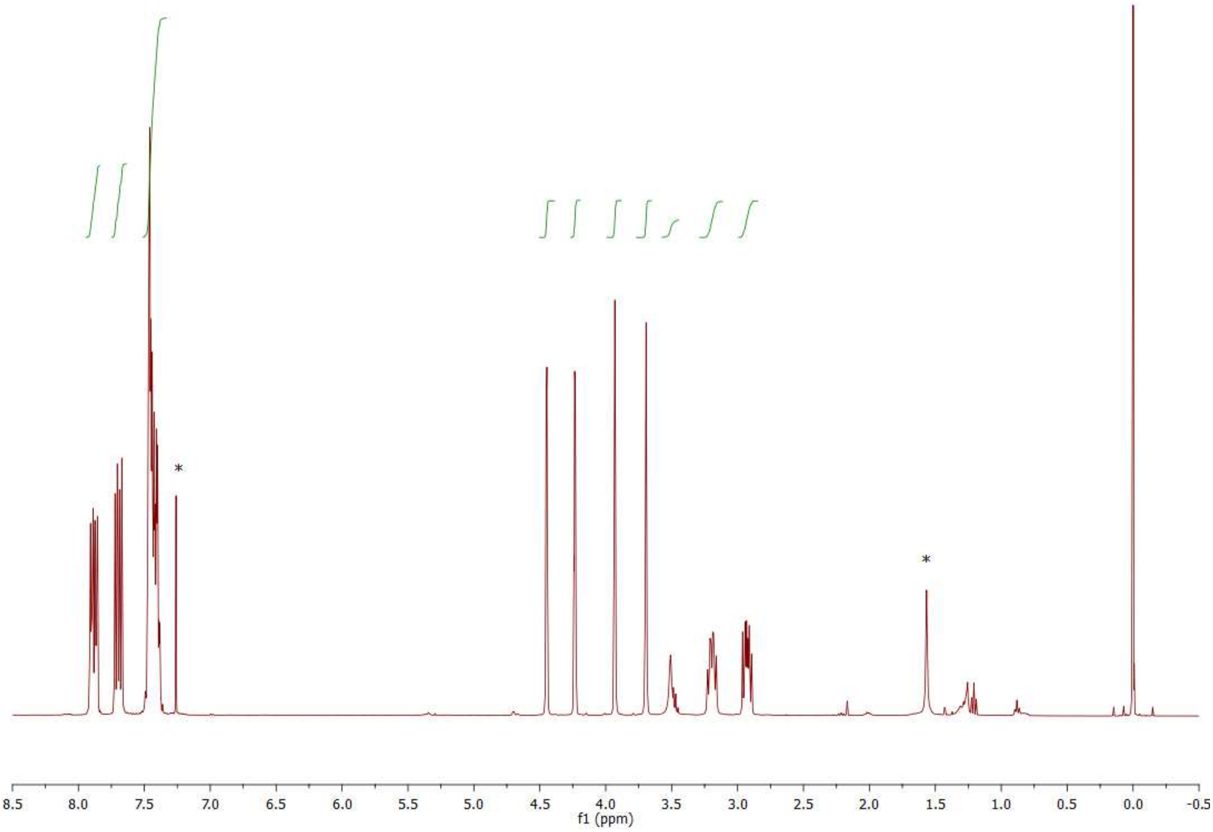


Figure S20 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2-Se**

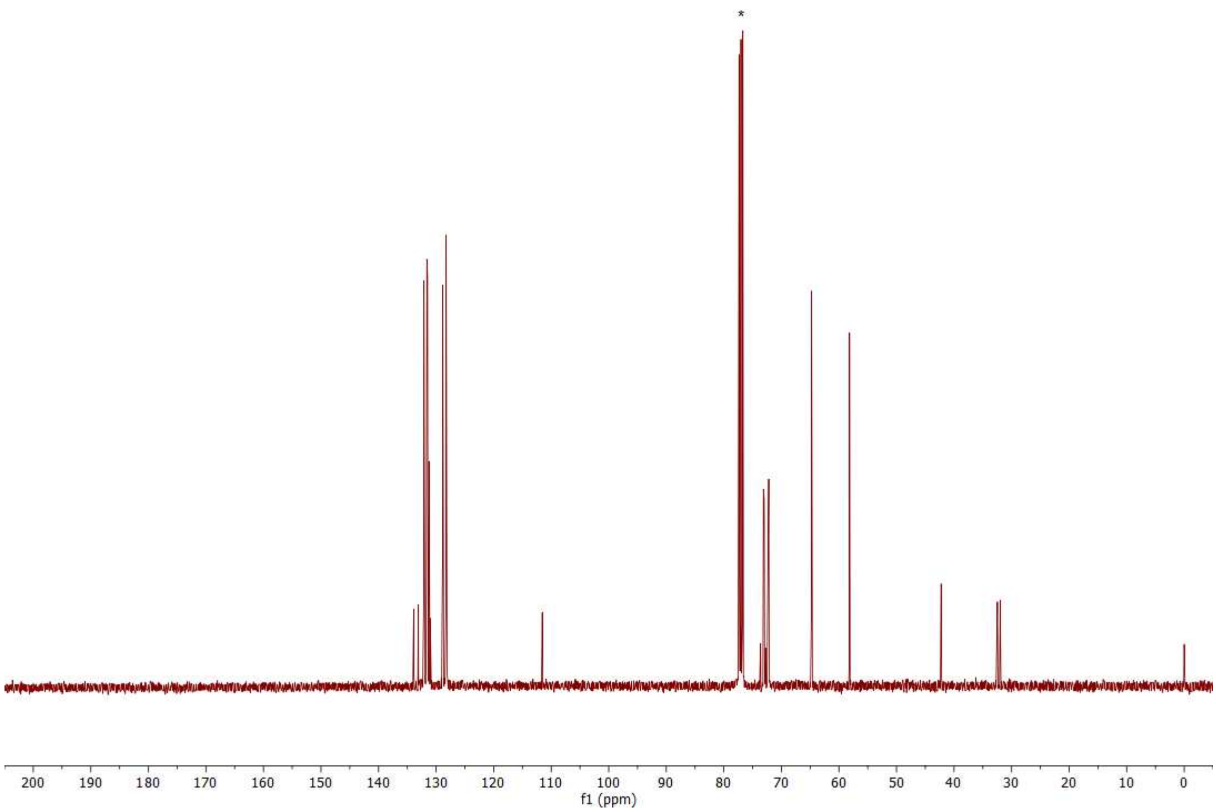


Figure S21 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2-Se**

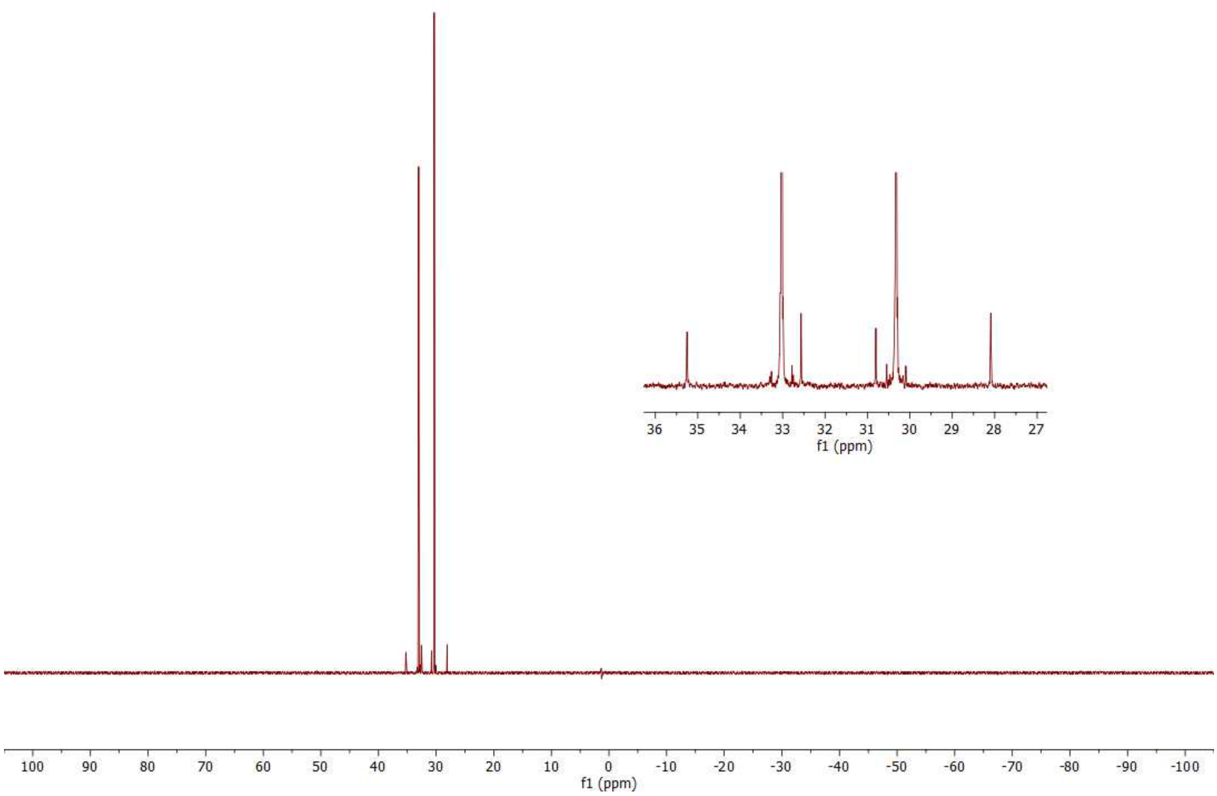


Figure S22 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **2-Se**

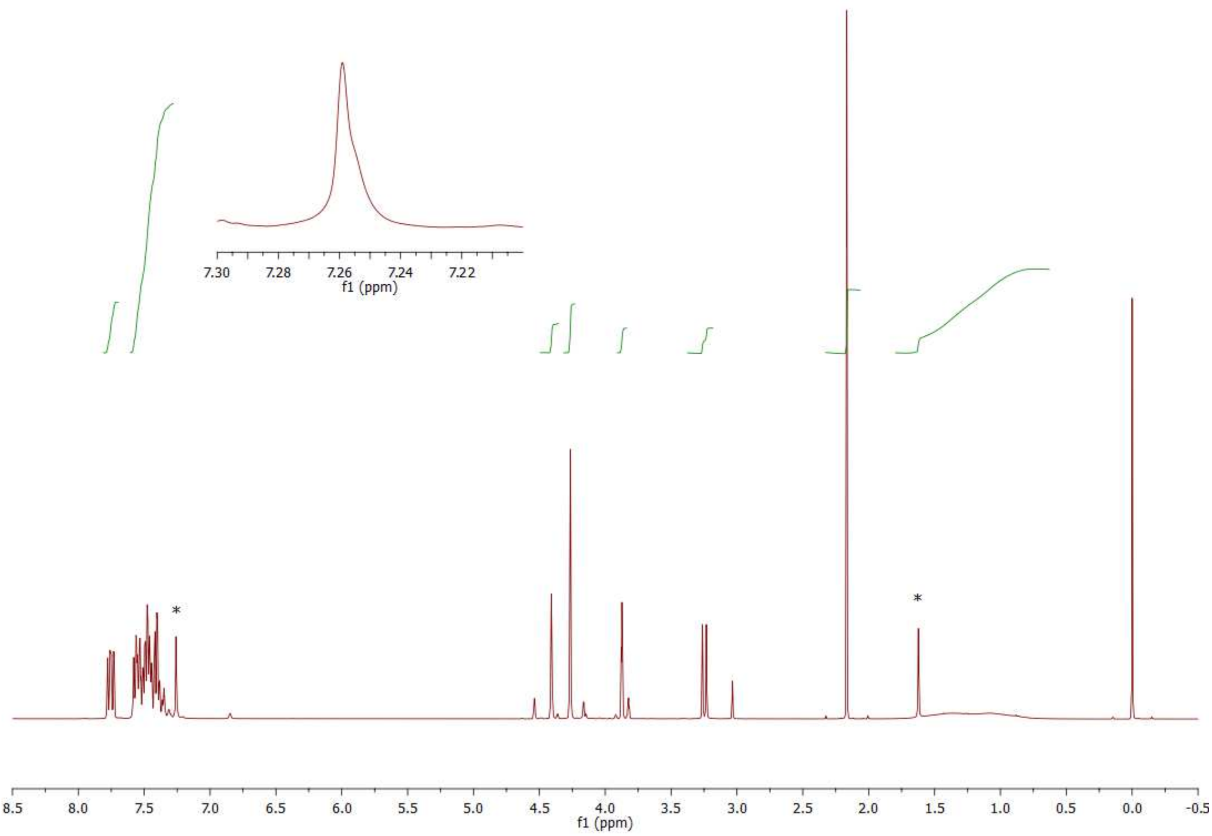


Figure S23 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**

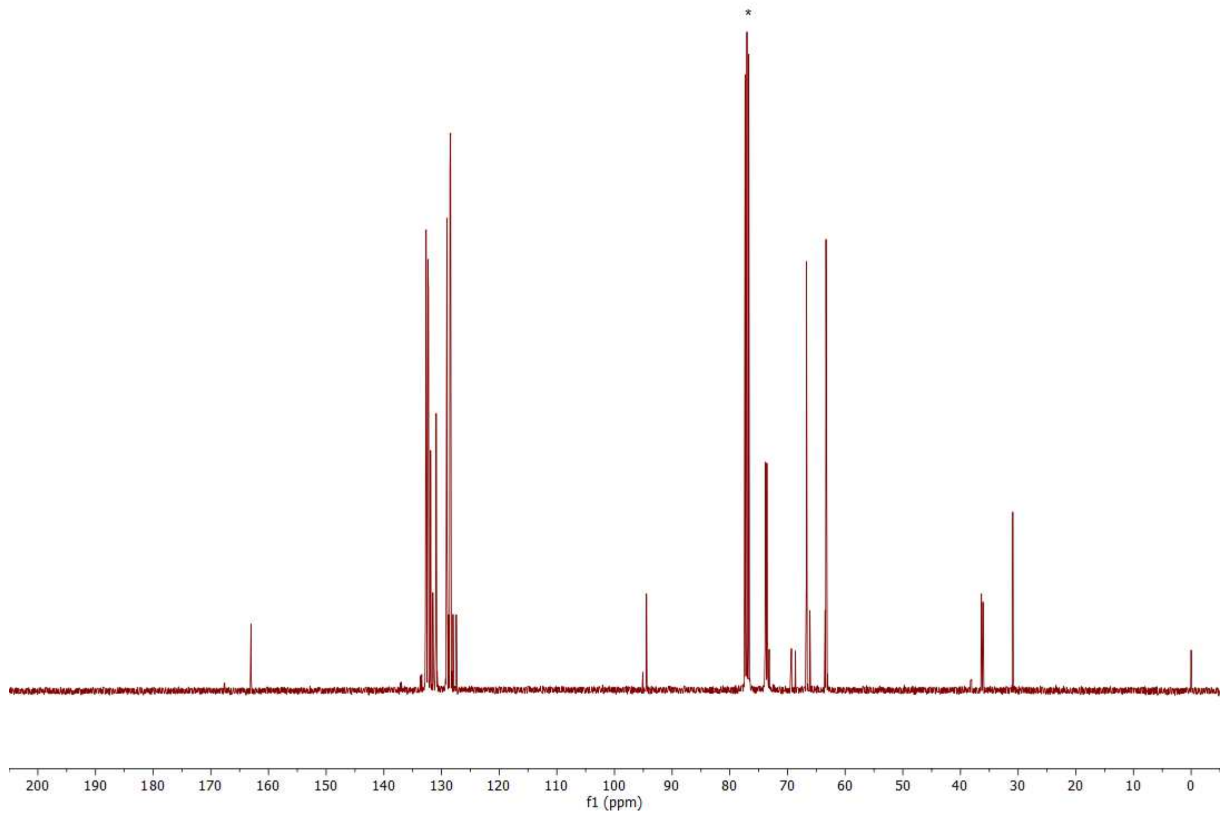


Figure S24 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**

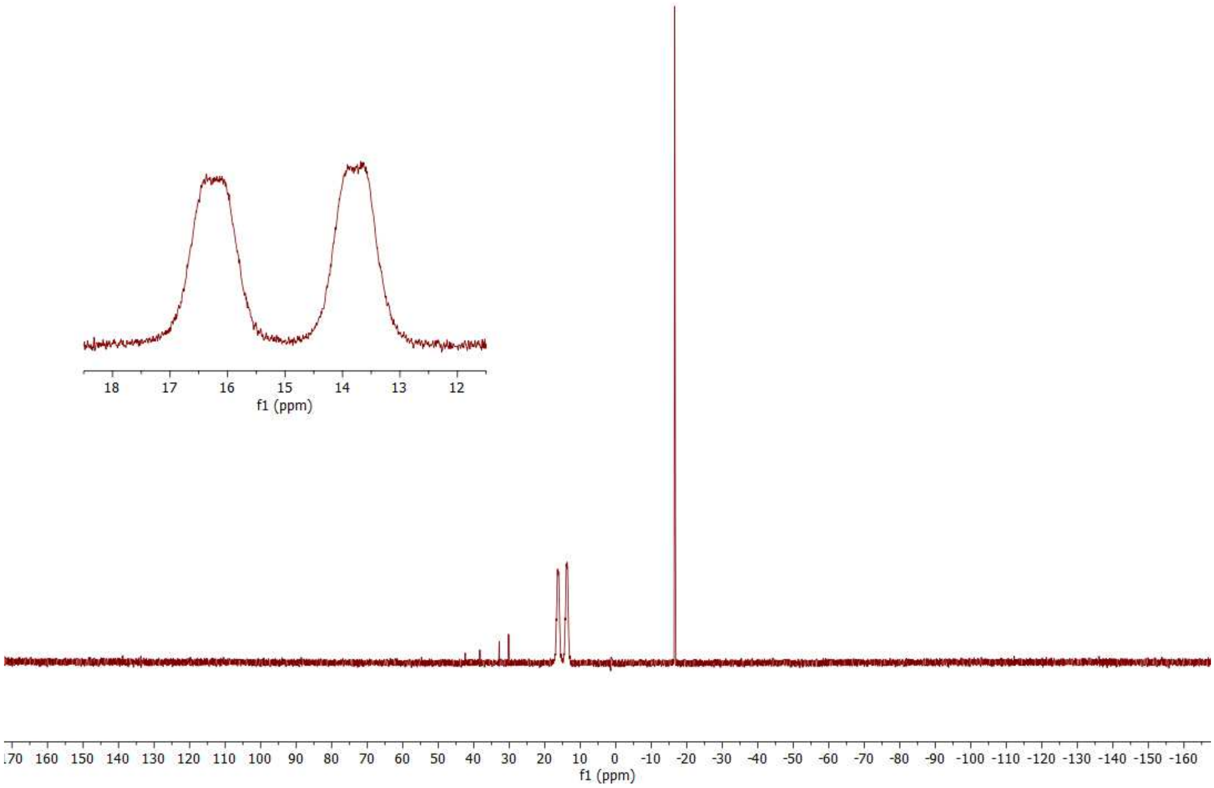


Figure S25 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3**

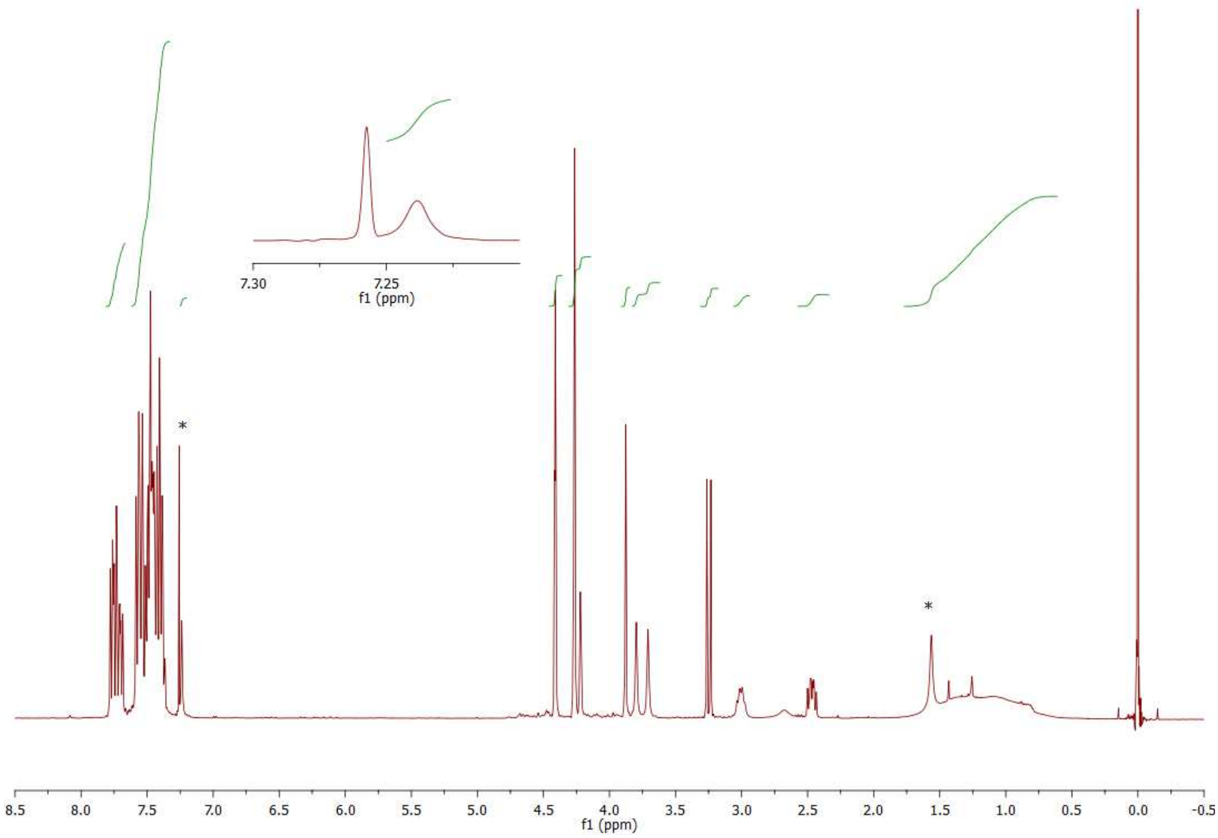


Figure S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**

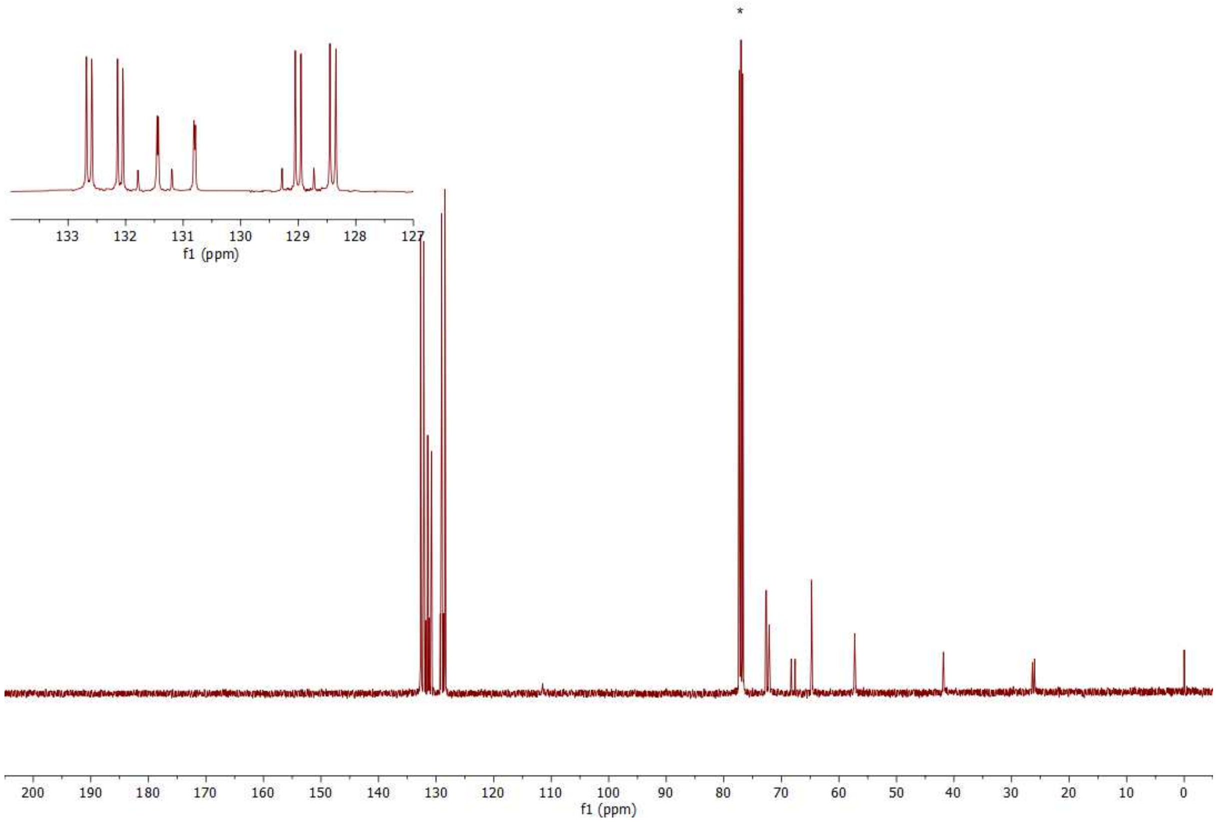


Figure S27 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4**

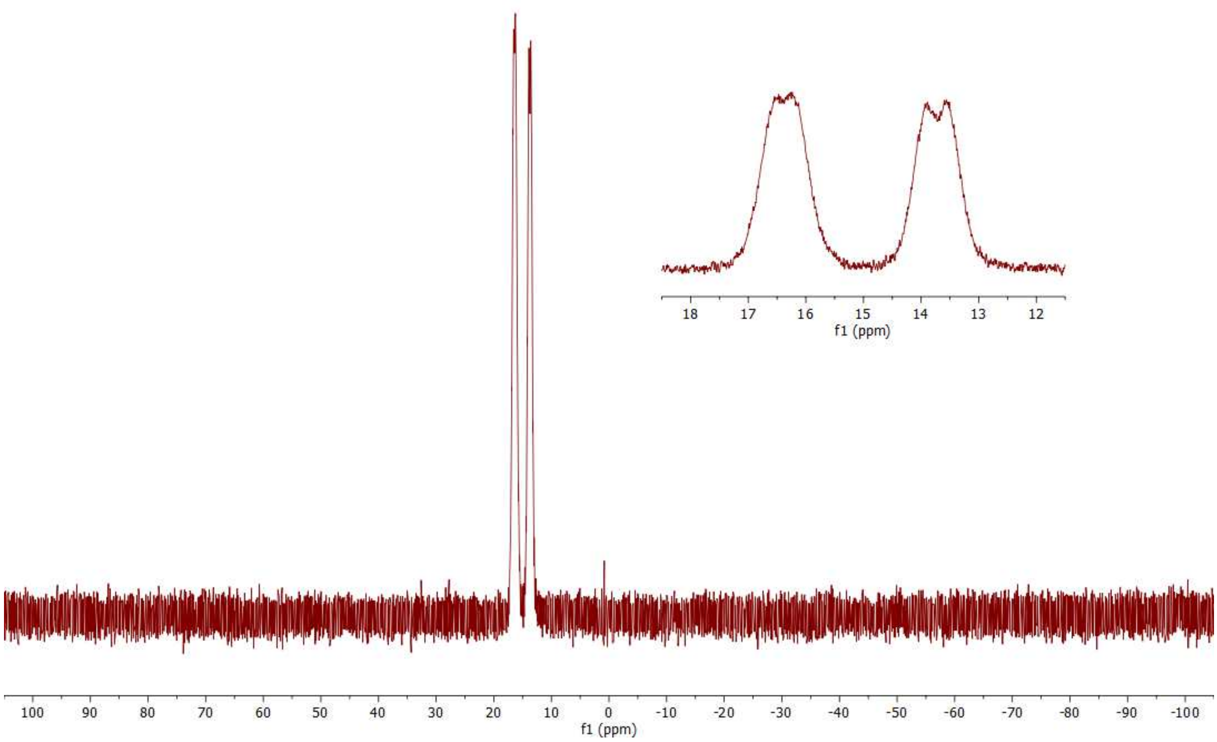


Figure S28 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4**

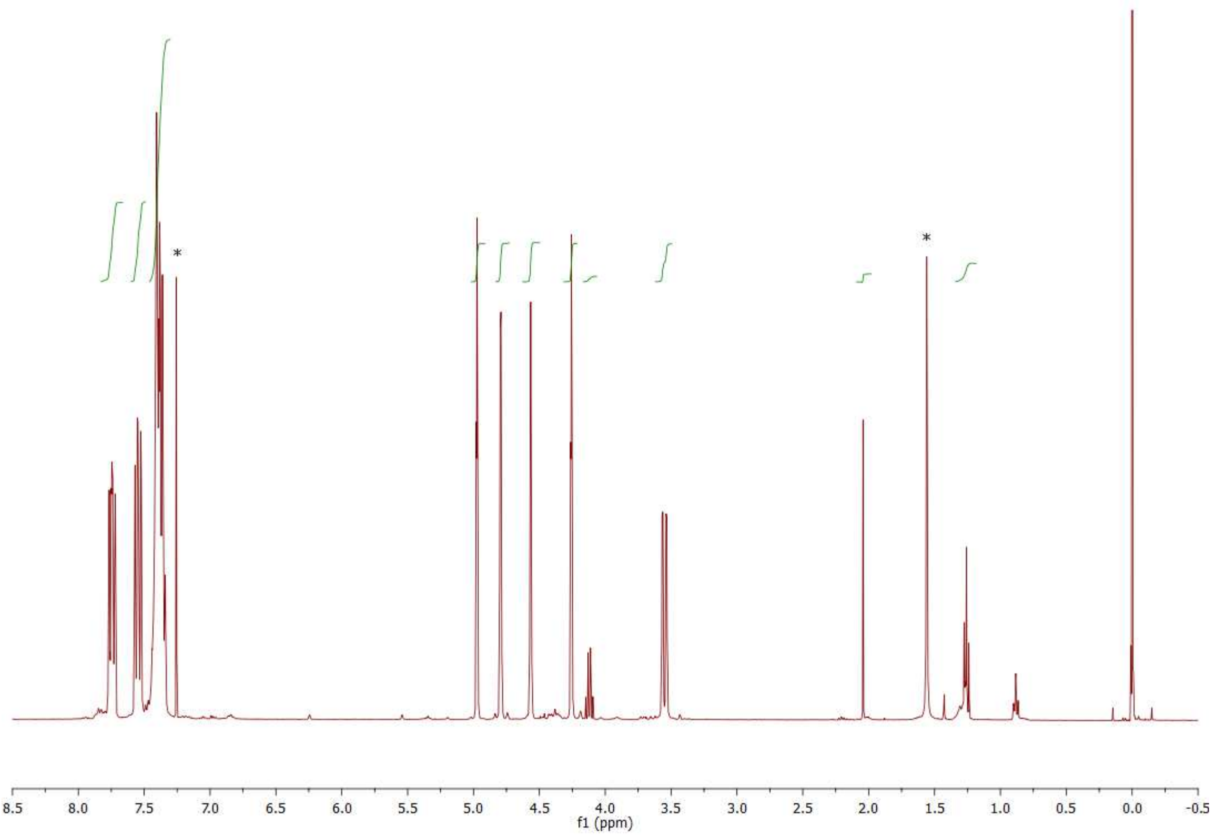


Figure S29 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5** (*trans*-isomer)

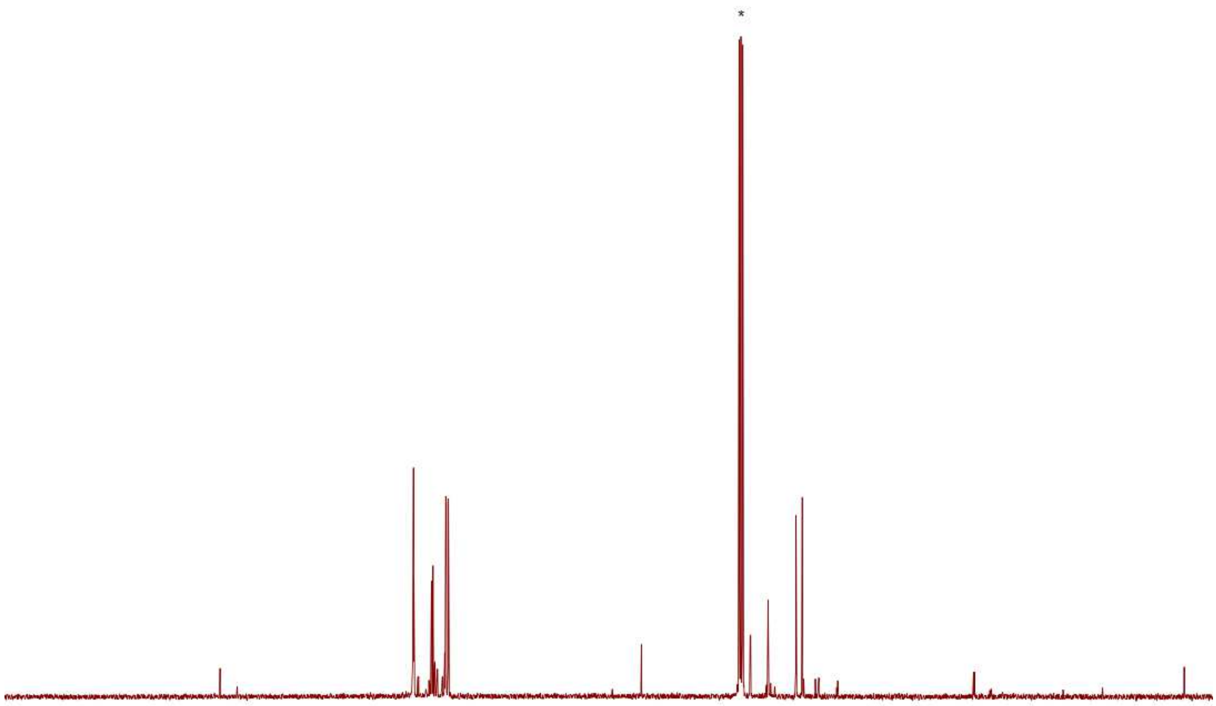


Figure S30 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5** (the dominating *trans* isomer partly isomerises to the *cis*/*trans* mixture during the data collection)

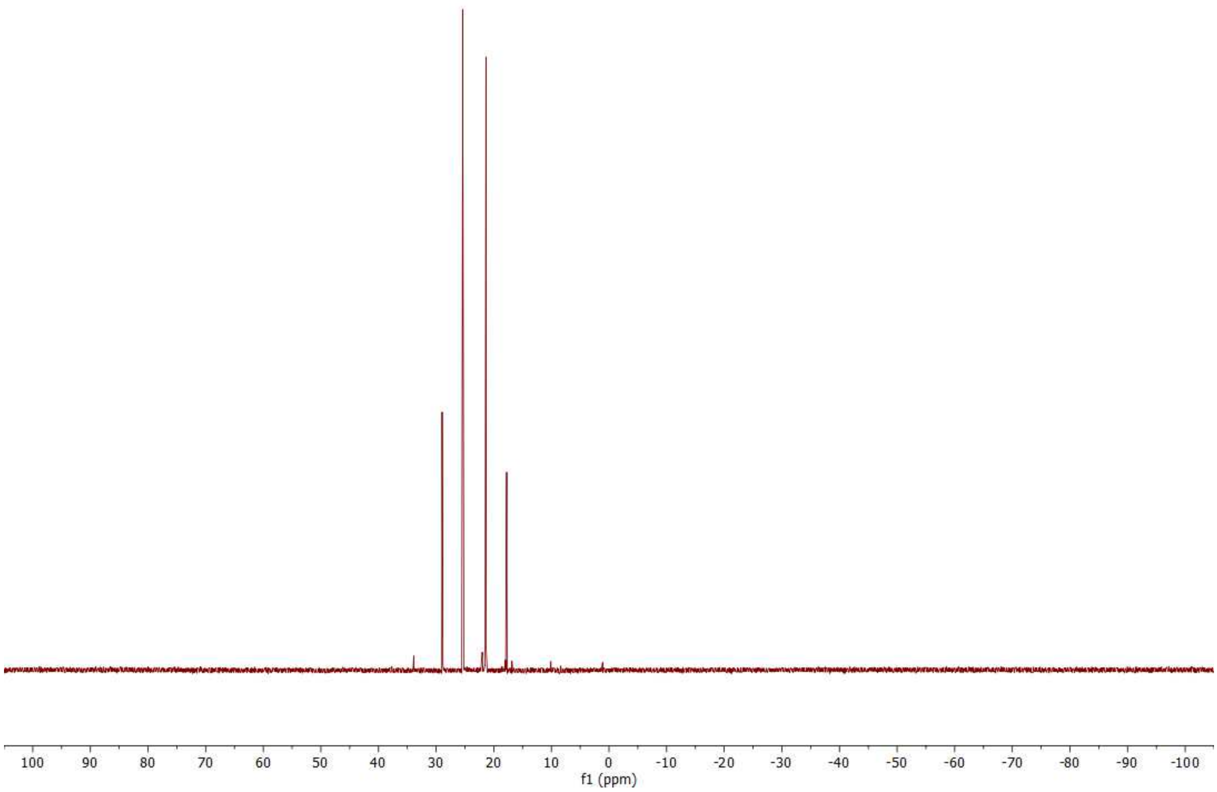


Figure S31 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5** (*trans*-isomer)

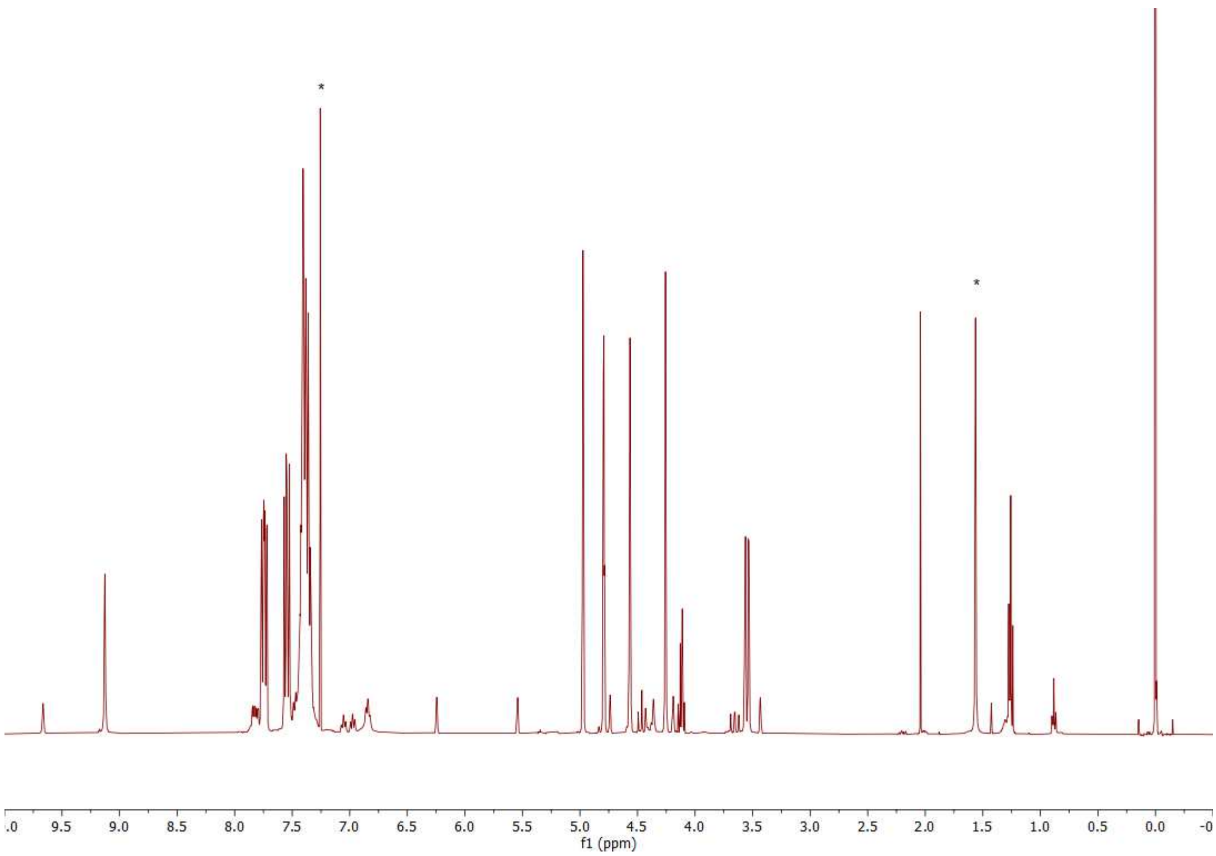


Figure S32 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5** (equilibrium mixture)

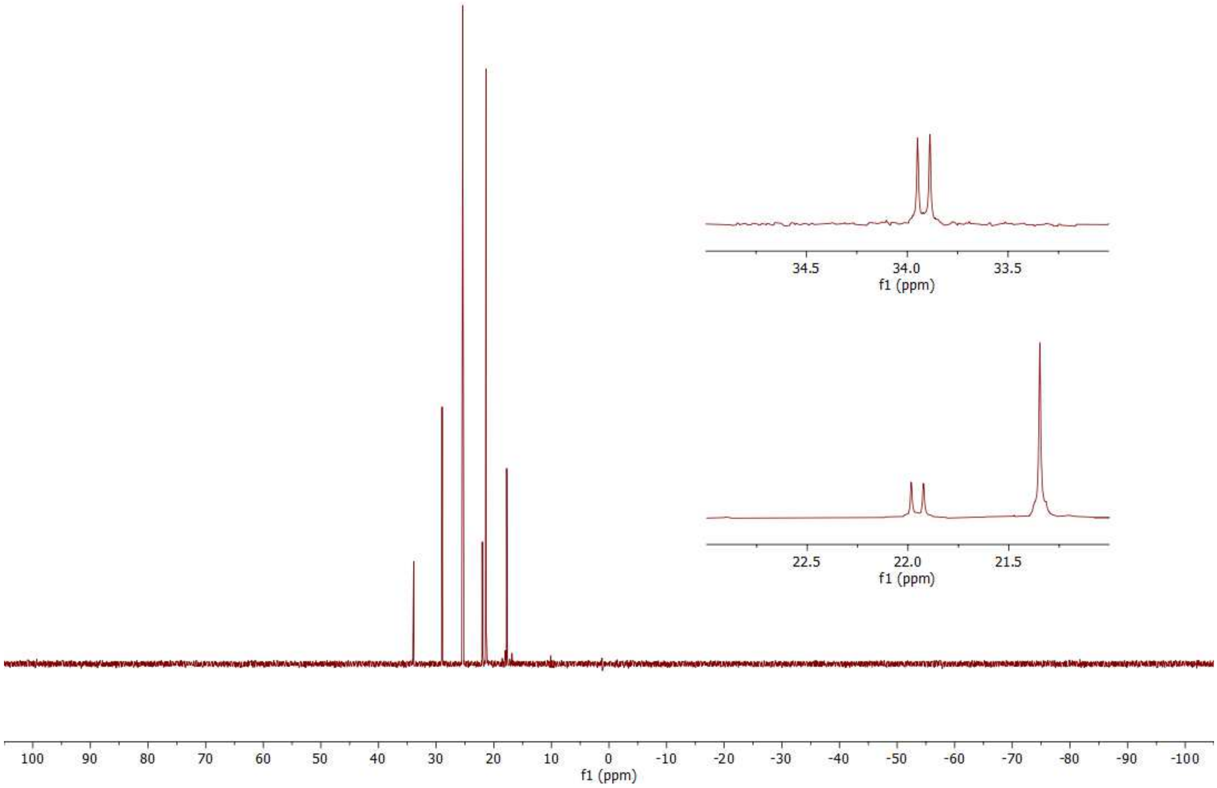


Figure S33 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5** (equilibrium mixture)

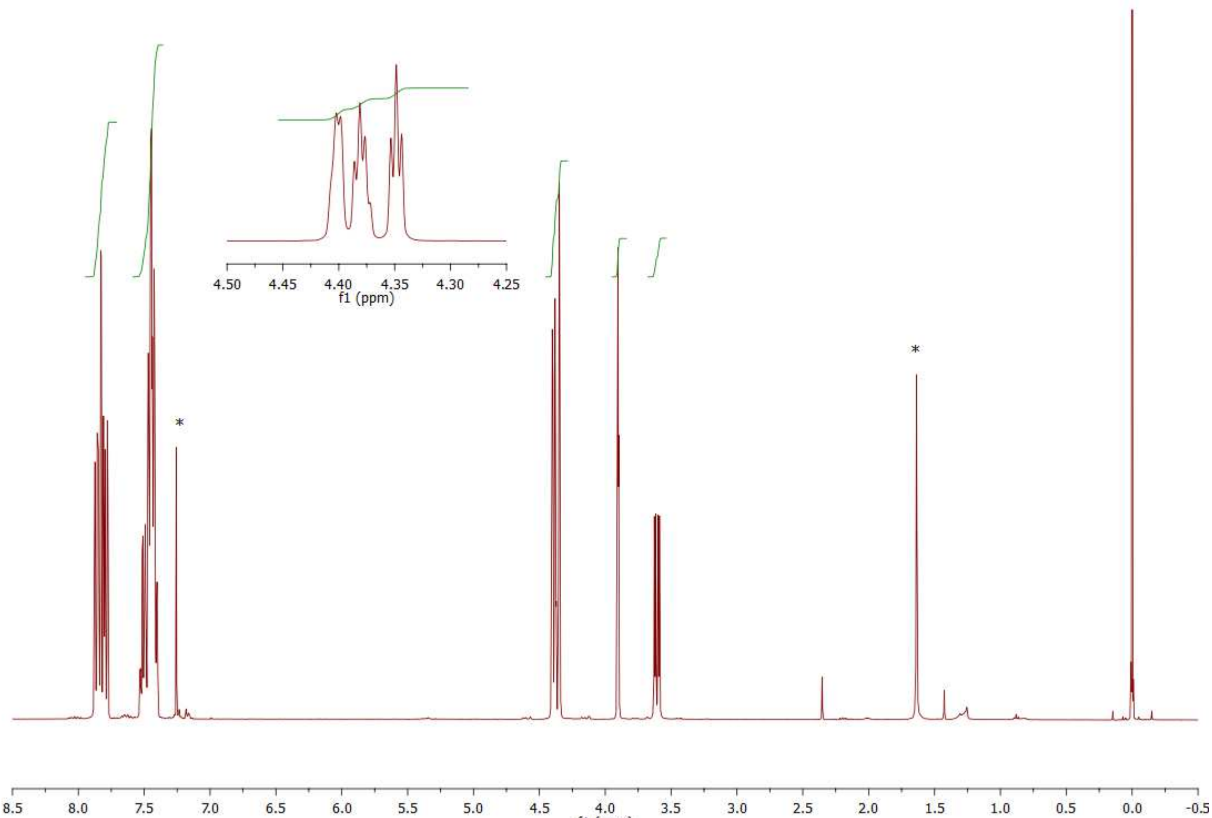


Figure S34 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**

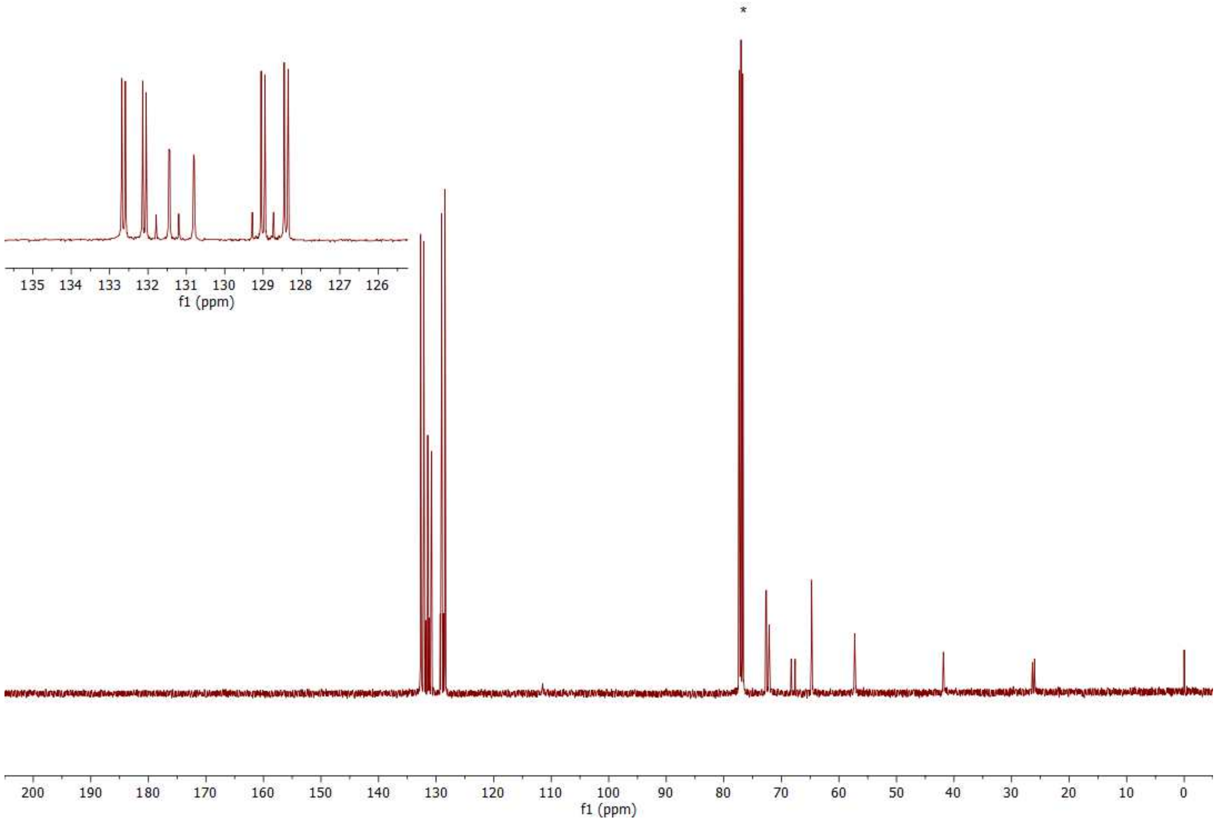


Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6**

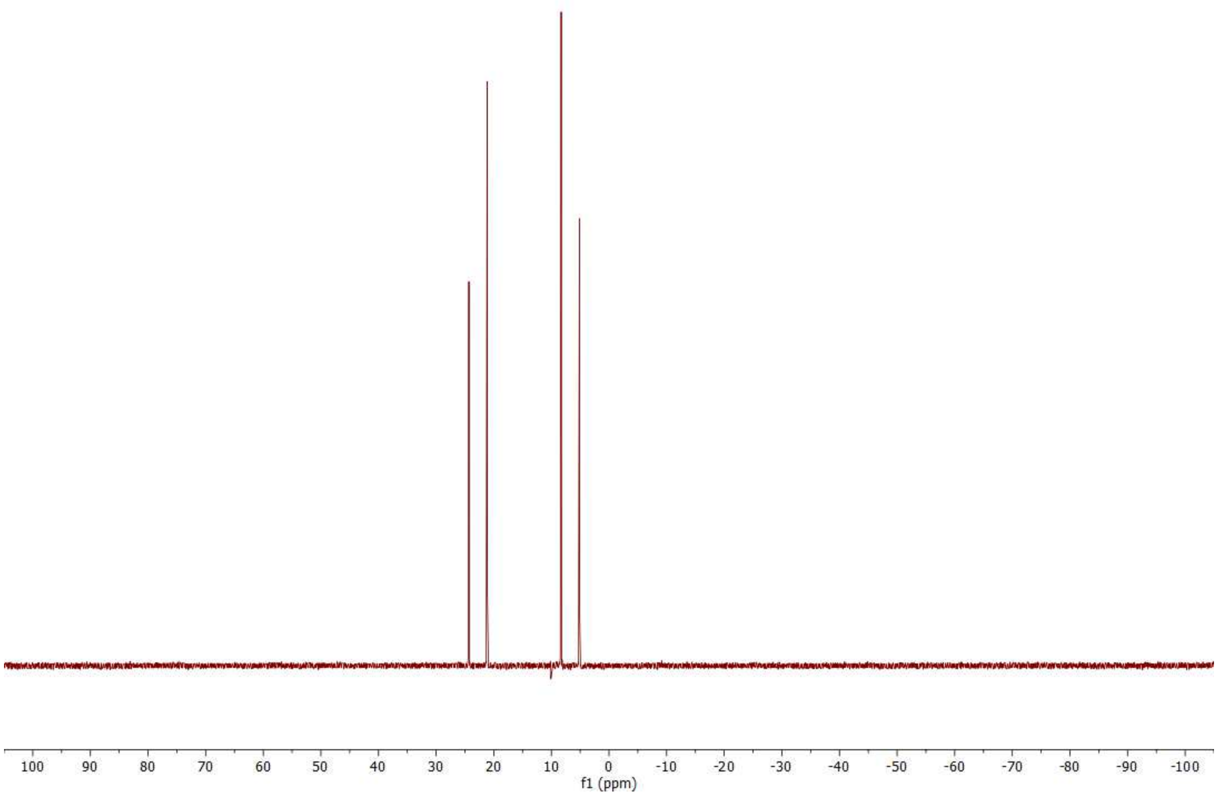


Figure S36 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6**

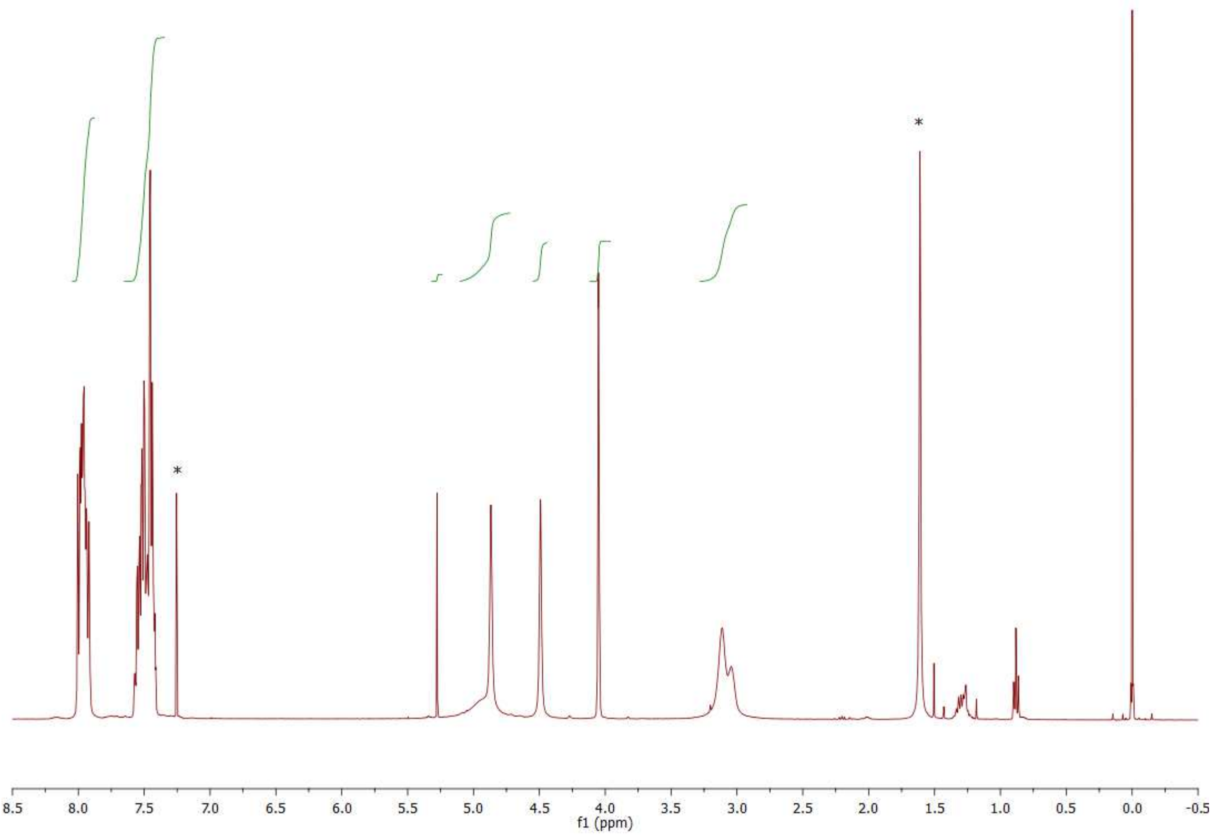


Figure S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 50°C) of **7**

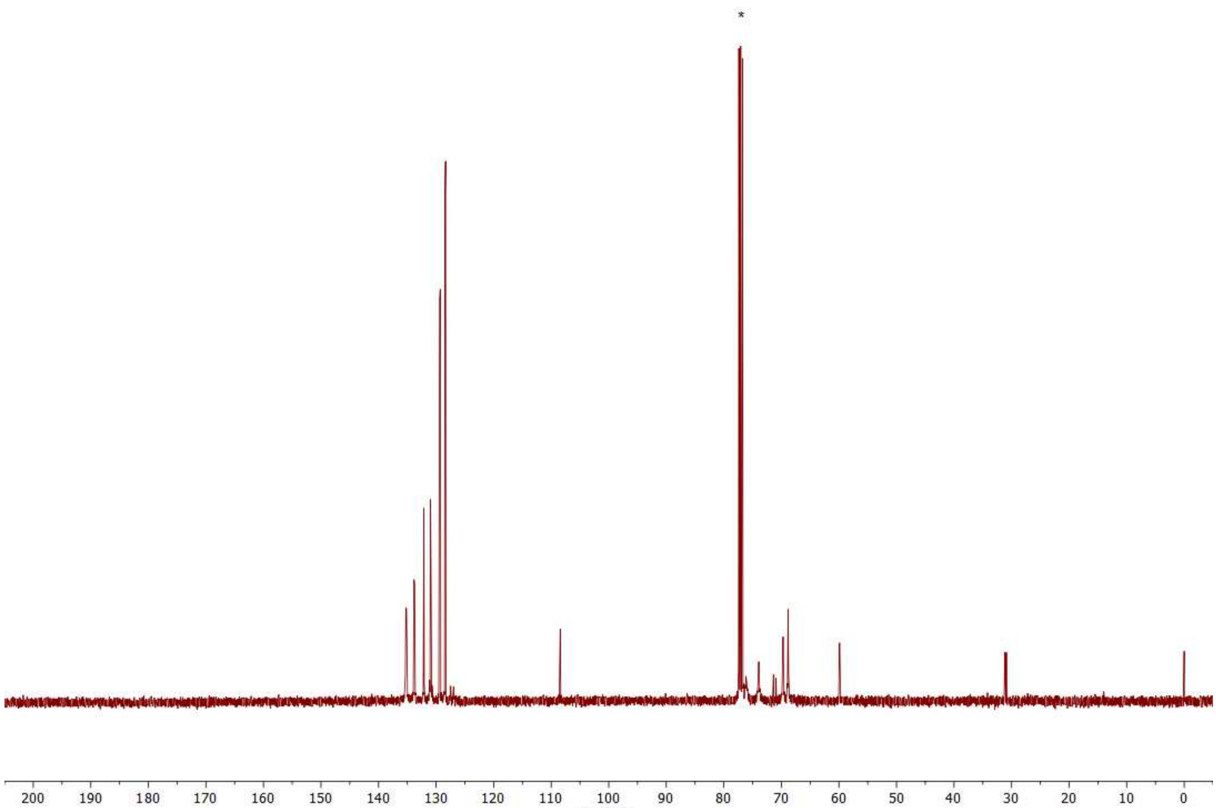


Figure S38 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 50°C) of **7**

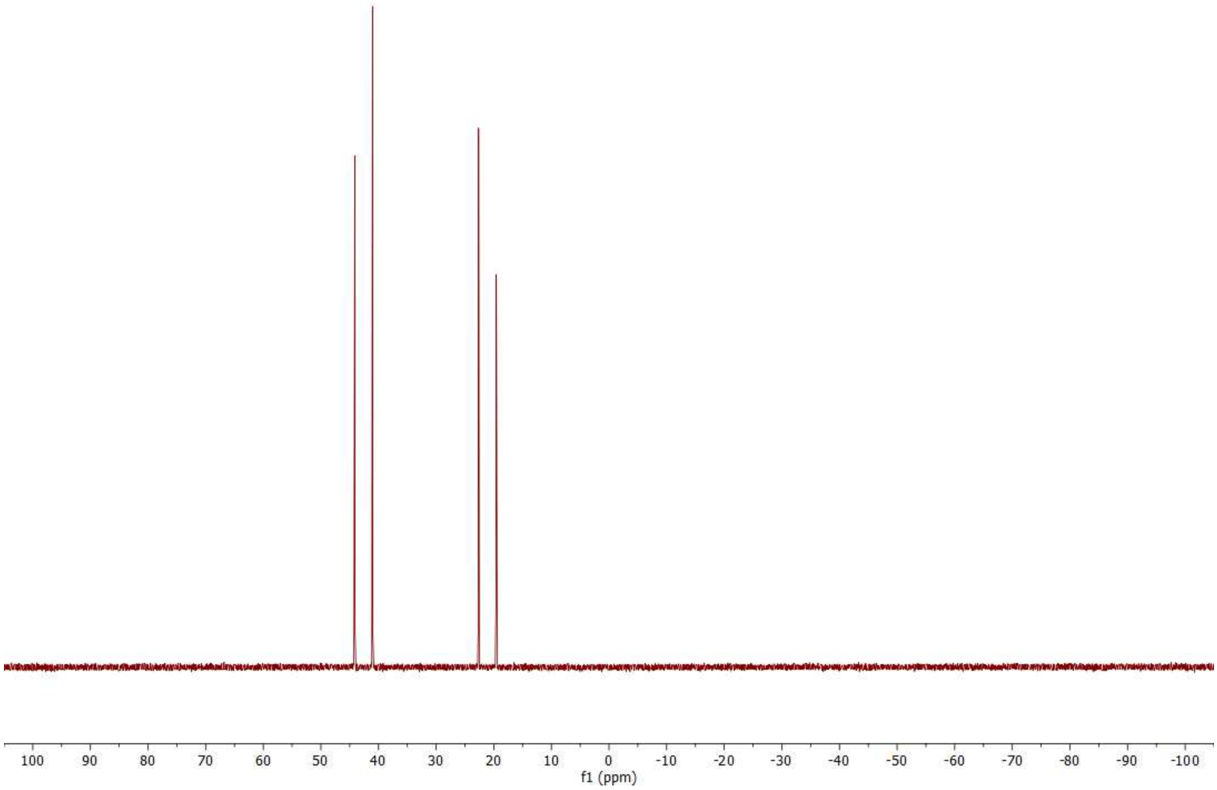


Figure S39 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7**

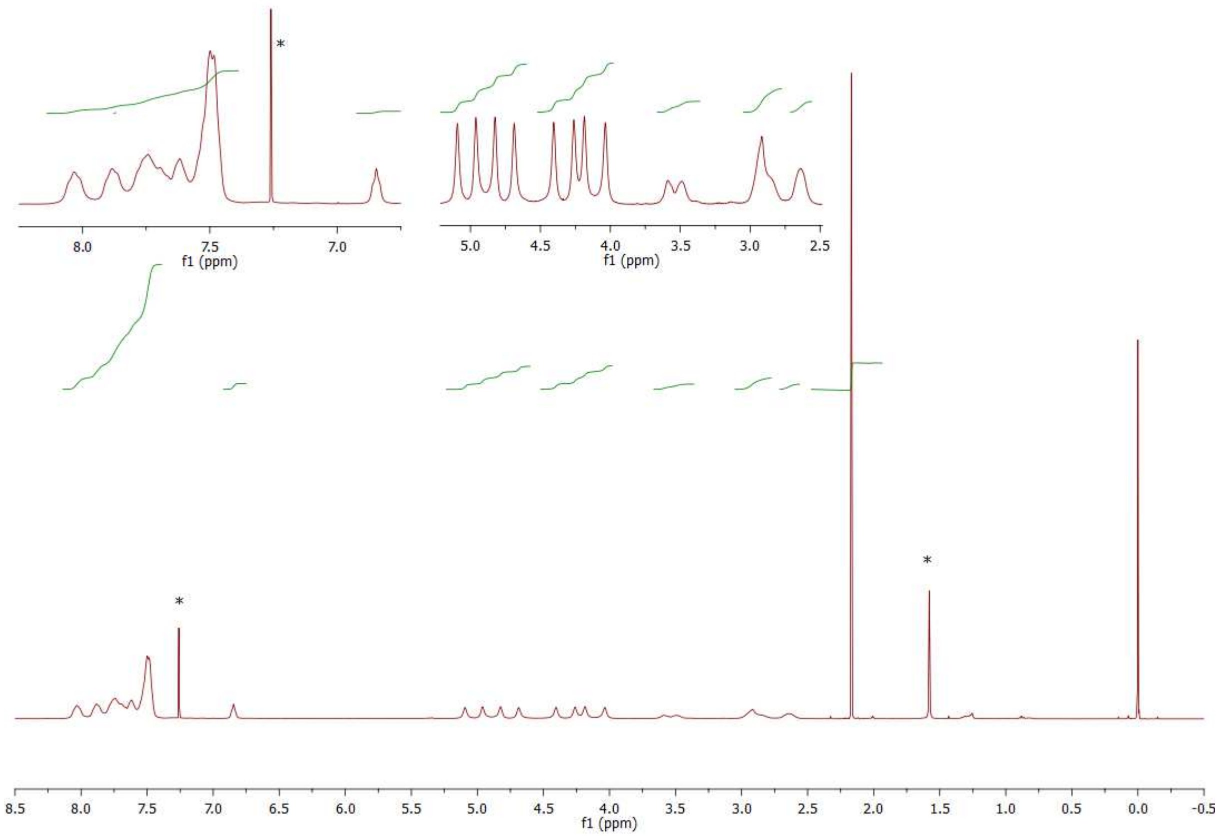


Figure S40 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**

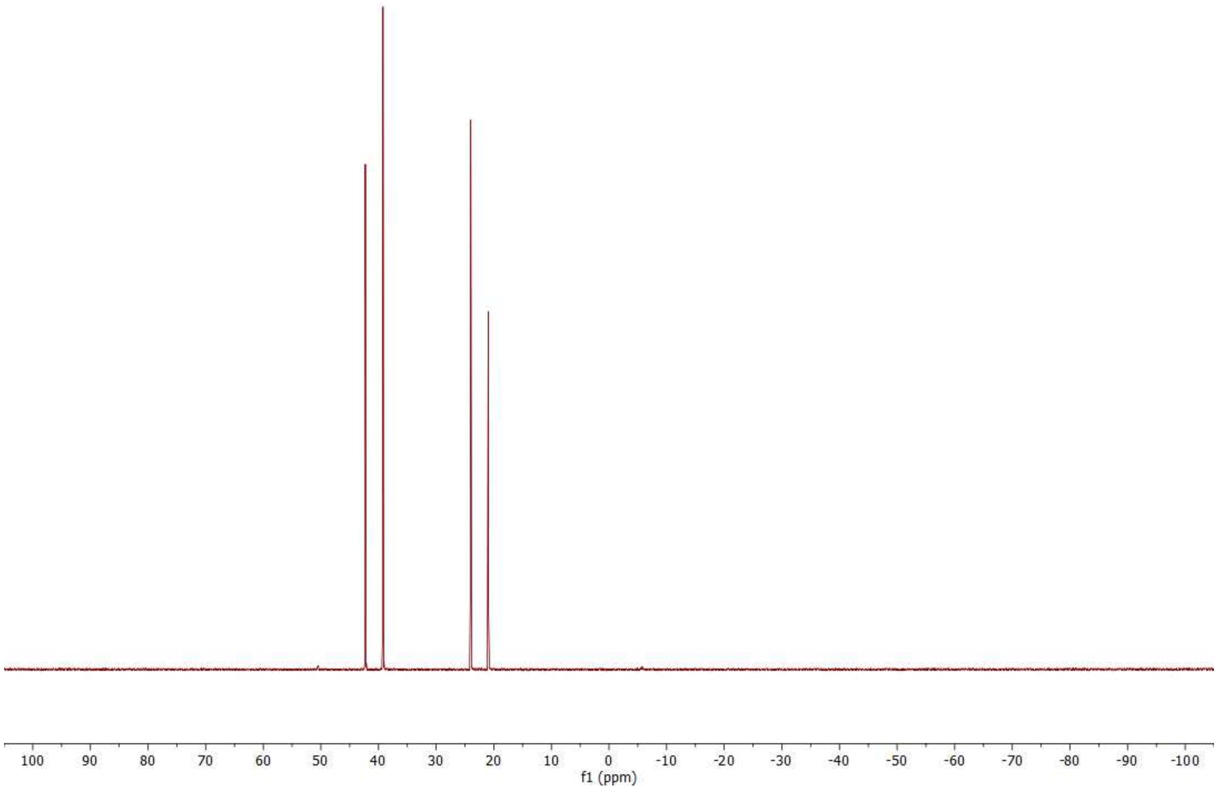


Figure S41. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8**.

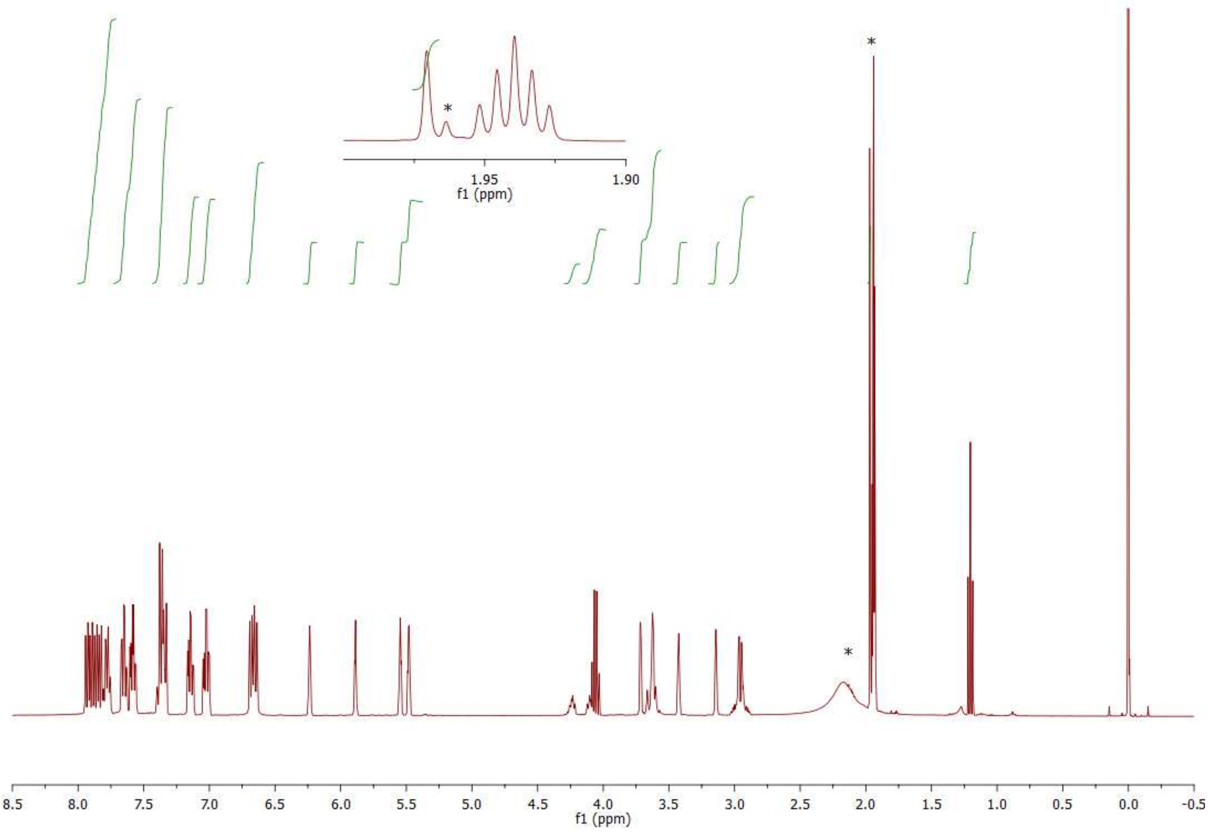


Figure S42 ^1H NMR spectrum (400 MHz, CD_3CN) of **9**

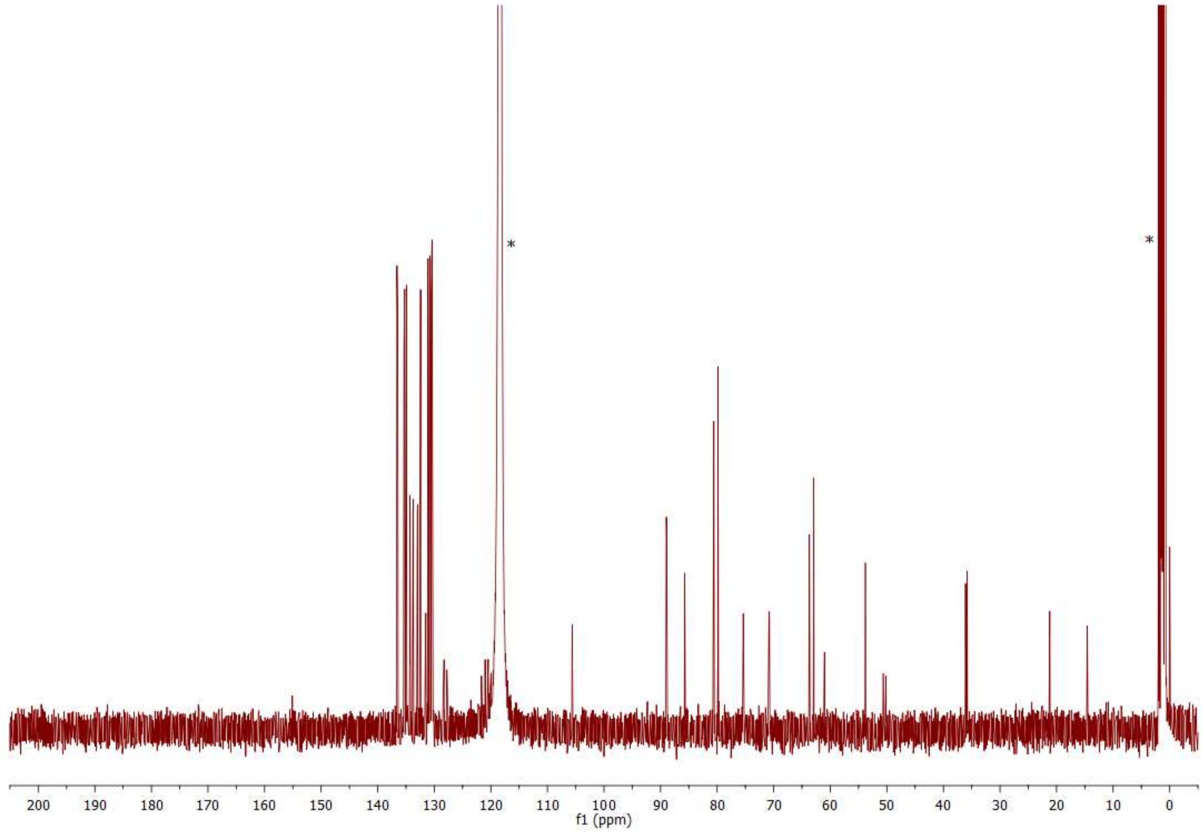


Figure S43 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_3CN) of **9**

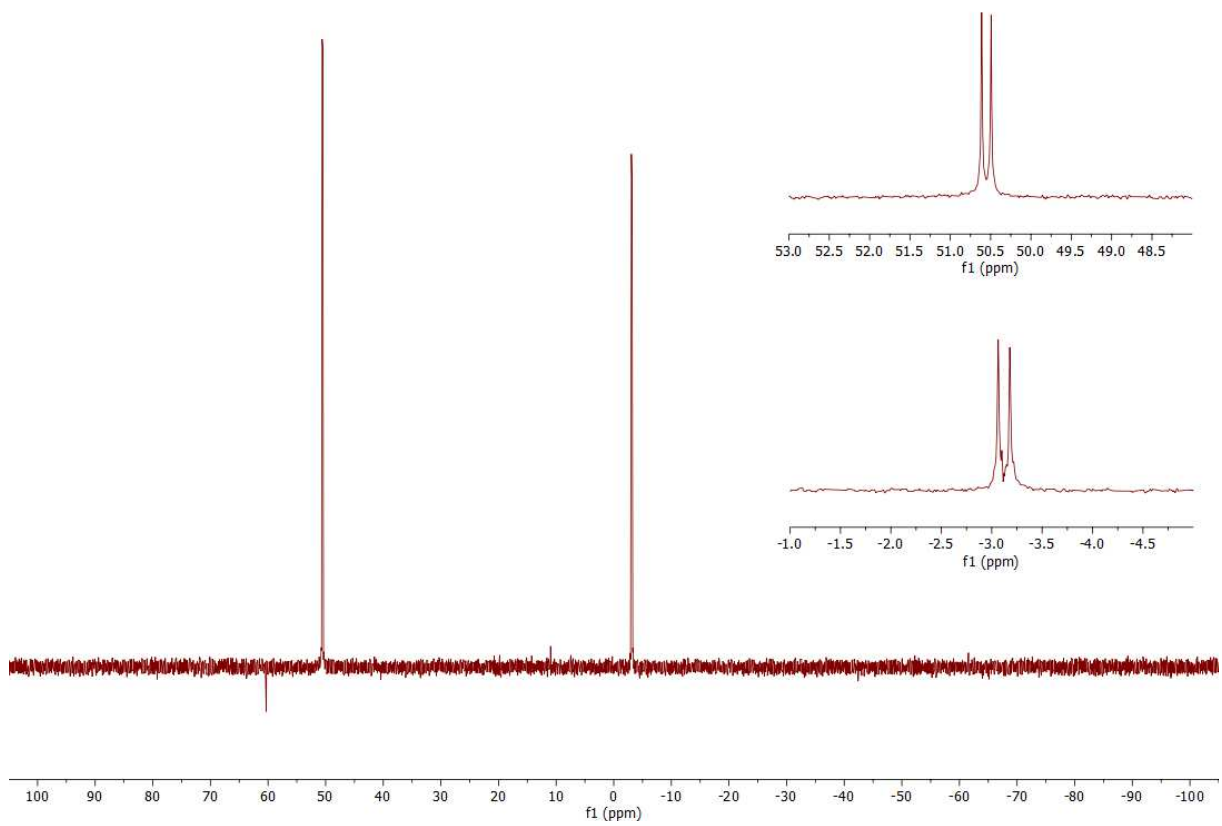


Figure S44 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_3CN) of **9**