

**Synthesis and characterization of 1'-(diphenylphosphino)-1-isocyanoferrrocene,
an organometallic ligand combining two different soft donor moieties, and its
Group 11 metal complexes**

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Supporting Information

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Table S1. Summary of crystallographic data and structure refinement parameters.^a

Compound	1	2	4S
Formula	C ₂₃ H ₁₈ FeNP	C ₂₂ H ₂₀ FeNP	C ₂₂ H ₁₈ FeN ₃ PS
<i>M</i>	395.20	385.21	443.27
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> −1 (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> /Å	8.9430(2)	8.6644(4)	13.0004(3)
<i>b</i> /Å	16.7677(4)	10.1933(4)	8.9356(2)
<i>c</i> /Å	12.9894(3)	10.9689(5)	34.3940(8)
α /°	90	103.168(1)	90
β /°	108.1841(9)	102.967(2)	98.0205(8)
γ /°	90	101.417(1)	90
<i>V</i> /Å ³	1850.53(7)	887.01(7)	3956.3(2)
<i>Z</i>	4	2	8
μ (Mo K α)/mm ^{−1}	0.907	0.944	0.962
<i>F</i> (000)	816	400	1824
Diffns collected	28019	18965	67506
Independent diffns	4258	4078	9086
Observed ^b diffns	3581	3748	8528
<i>R</i> _{int} ^c /%	3.44	2.42	1.94
No. of parameters	235	226	505
<i>R</i> ^c obsd diffns/%	2.95	2.39	4.14
<i>R</i> , <i>wR</i> ^c all data/%	3.85, 7.63	2.77, 5.81	4.41, 10.25
$\Delta\rho$ /e Å ^{−3}	0.33, −0.26	0.27, −0.31	1.88, −0.95
CCDC entry	1558580	1558581	1558582

^a Common details: *T* = 150(2) K. ^b Diffractions with *I* > 2σ(*I*). ^c Definitions: $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum F_o^2$, where $F_o^2(\text{mean})$ is the average intensity of symmetry-equivalent diffractions. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = [\{\sum |w| F_o^2 - F_c^2|^2\} / \sum |w F_o^2|^2]^{1/2}$.

Table S1 continued

Compound	4B	5	6
Formula	C ₂₂ H ₂₁ BF ₃ N ₃ P	C ₂₃ H ₂₀ FeNOP	C ₂₃ H ₁₈ AgClFeP
<i>M</i>	425.05	413.22	538.52
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> -1 (no. 2)
<i>a</i> /Å	9.9966(2)	7.7210(3)	8.3719(2)
<i>b</i> /Å	15.9714(4)	26.8385(8)	9.6949(3)
<i>c</i> /Å	12.5443(3)	9.5519(3)	13.6401(4)
α /°	90	90	110.216(1)
β /°	92.8551(8)	99.412(1)	103.260(1)
γ /°	90	90	95.591(1)
<i>V</i> /Å ³	2000.33(8)	1952.7(1)	992.10(5)
<i>Z</i>	4	4	2
μ (Mo K α)/mm ⁻¹	0.846	0.866	1.942
<i>F</i> (000)	880	856	536
Diffns collected	13324	36002	10290
Independent diffns	4583	4458	4556
Observed ^c diffns	4147	4152	3960
<i>R</i> _{int} ^d /%	1.69	2.21	1.92
No. of parameters	253	244	257
<i>R</i> ^d obsd diffns/%	3.41	2.50	2.66
<i>R</i> , <i>wR</i> ^d all data/%	3.79, 9.96	2.75, 6.17	3.29, 6.94
$\Delta\rho$ /e Å ⁻³	0.70, -0.59	0.28, -0.30	0.66, -0.51
CCDC entry	1558583	1558584	1558585

Table S1 continued

Compound	7	8·3Me₂CO	9
Formula	C ₅₂ H ₄₈ Ag ₂ F ₁₂ Fe ₂ N ₂ O ₂ P ₂ Sb ₂	C ₁₀₁ H ₉₀ Ag ₂ F ₁₂ Fe ₄ N ₄ O ₃ P ₄ Sb ₂	C ₂₃ H ₁₈ AuClFeP
<i>M</i>	1593.80	2442.29	627.62
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	8.7552(3)	29.4021(5)	8.4598(1)
<i>b</i> /Å	14.2448(5)	21.8753(4)	18.9243(3)
<i>c</i> /Å	22.3852(7)	18.7554(3)	12.8116(2)
α /°	90	90	90
β /°	98.237(1)	127.1702(5)	94.3304(6)
γ /°	90	90	90
<i>V</i> /Å ³	2763.0(2)	9612.4(3)	2045.23(5)
<i>Z</i>	2	4	4
μ (Mo K α)/mm ⁻¹	2.310	1.680	8.092
<i>F</i> (000)	1552	4864	1200
Diffns collected	48377	38105	16559
Independent diffns	6354	11055	4692
Observed ^c diffns	5398	9073	4097
<i>R</i> _{int} ^d /%	3.59	2.41	2.80
No. of parameters	345	600	257
<i>R</i> ^d obsd diffns/%	3.77	3.07	1.93
<i>R</i> , <i>wR</i> ^d all data/%	4.59, 9.82	4.14, 7.83	2.58, 3.99
$\Delta\rho$ /e Å ⁻³	2.24, -2.43	1.79, -1.70	0.78, -0.41
CCDC entry	1558586	1558587	1558588

Table S1 continued

Compound	10	11a ·2Me ₂ CO
Formula	C ₂₃ H ₁₈ Au ₂ Cl ₂ FeNP	C ₅₂ H ₄₈ Au ₂ F ₁₂ Fe ₂ N ₂ O ₂ P ₂ Sb ₂
<i>M</i>	860.04	1772.00
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1 (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	7.7090(2)	8.8480(3)
<i>b</i> /Å	10.0529(3)	14.2781(9)
<i>c</i> /Å	15.6084(4)	22.257(1)
α /°	90.179(1)	90
β /°	100.158(1)	98.795(2)
γ /°	107.216(1)	90
<i>V</i> /Å ³	1135.34(5)	2778.7(2)
<i>Z</i>	2	2
μ (Mo K α)/mm ⁻¹	2.516	6.866
<i>F</i> (000)	792	1680
Diffns collected	15177	21495
Independent diffns	5212	6333
Observed ^c diffns	4531	5599
<i>R</i> _{int} ^d /%	2.47	2.82
No. of parameters	271	345
<i>R</i> ^d obsd diffns/%	2.14	2.58
<i>R</i> , <i>wR</i> ^d all data/%	2.79, 4.48	3.20, 5.39
$\Delta\rho$ /e Å ⁻³	1.03, -0.93	1.36, -1.34
CCDC entry	1558589	1558590

Additional structural diagrams

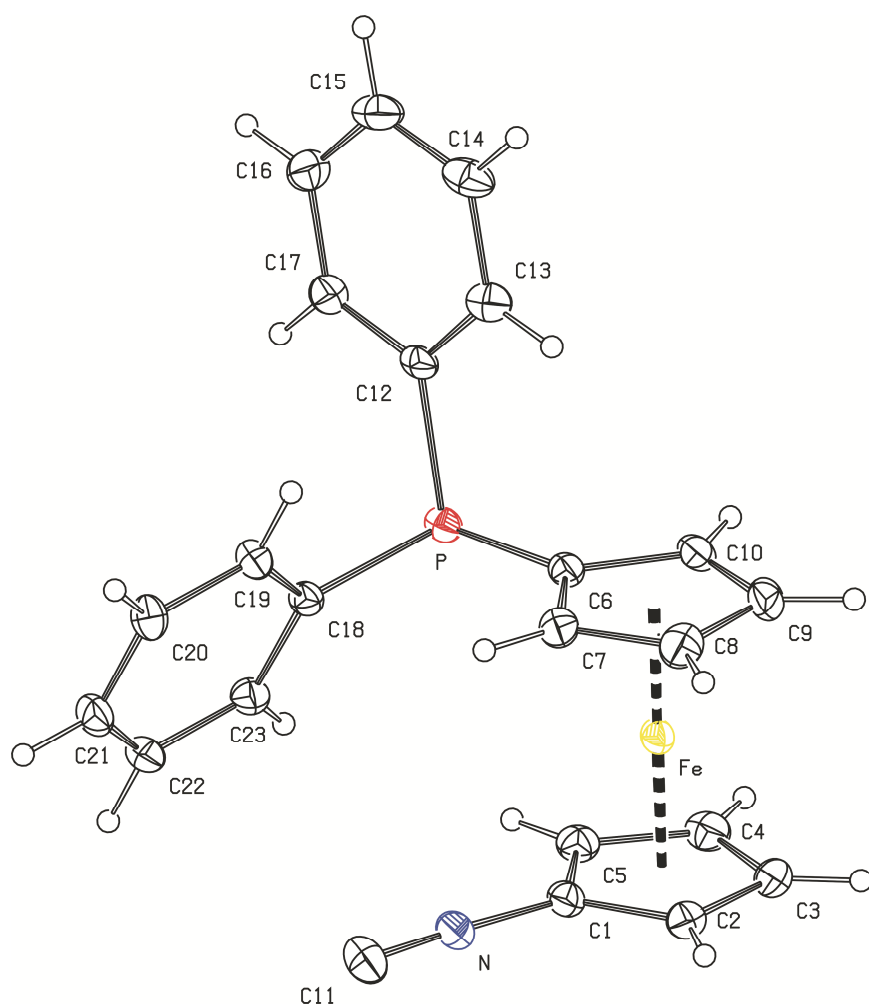


Figure S1. PLATON plot of the molecular structure of **1** showing displacement ellipsoids at the 30% probability level.

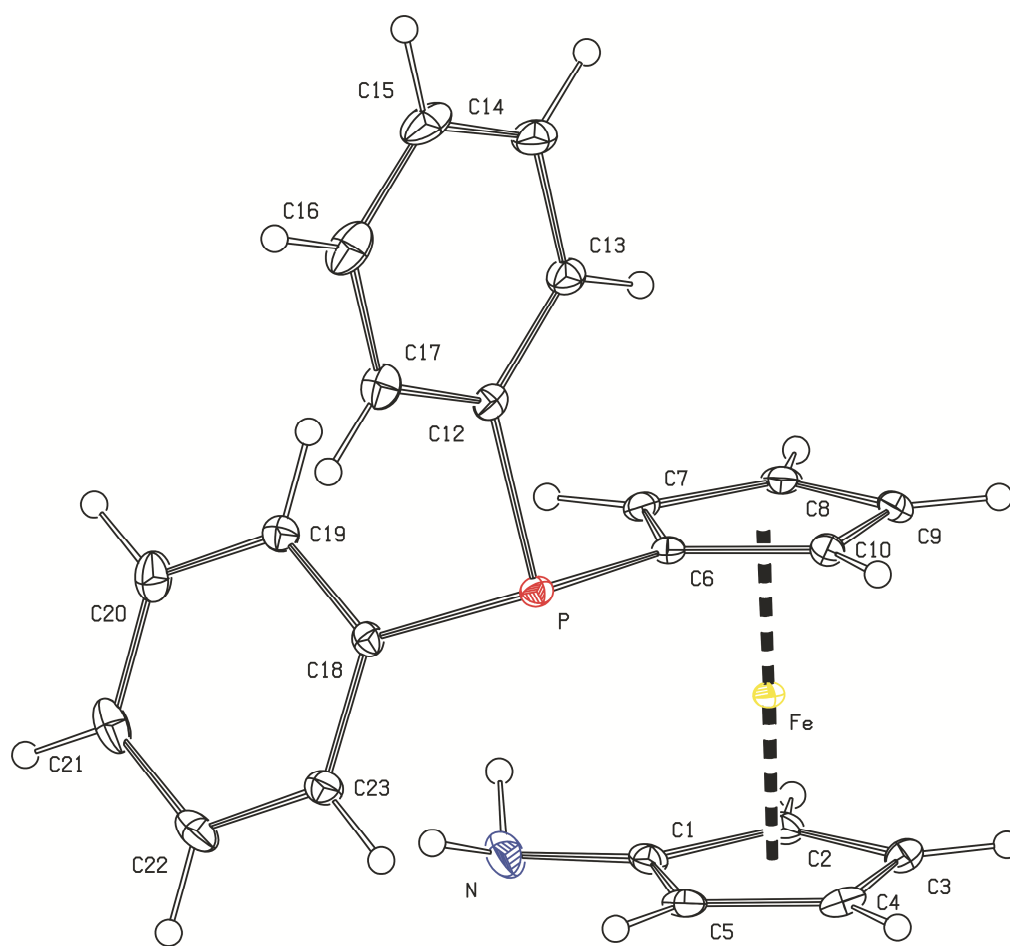


Figure S2. PLATON plot of the molecular structure of **2** showing displacement ellipsoids at the 30% probability level.

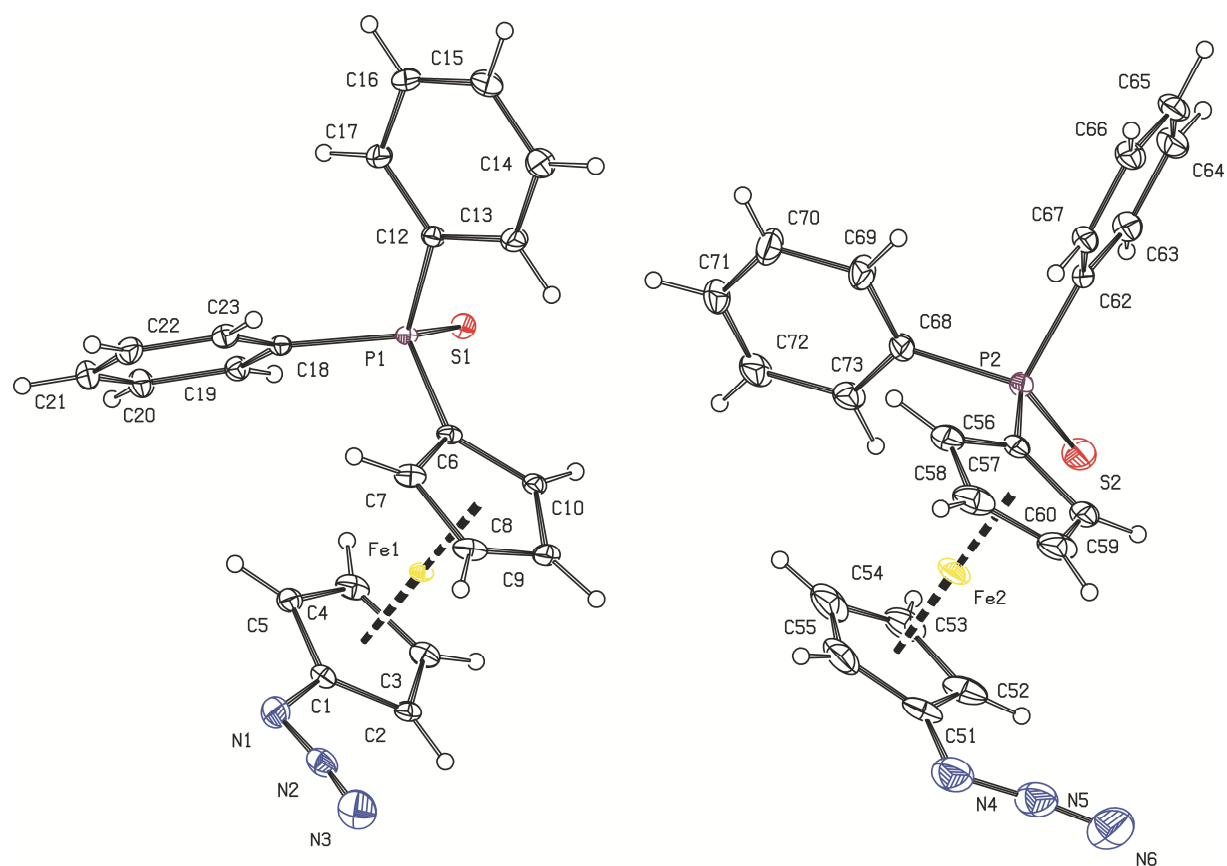


Figure S3. PLATON plot of the two crystallographically independent molecules of **4S** showing displacement ellipsoids at the 30% probability level.

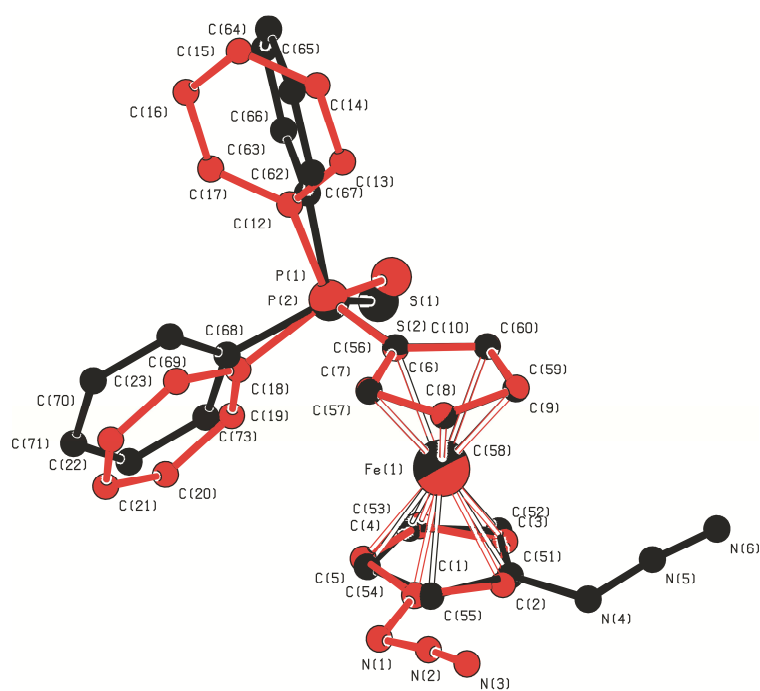


Figure S4. Overlap of the two crystallographically independent molecules of **4S**.

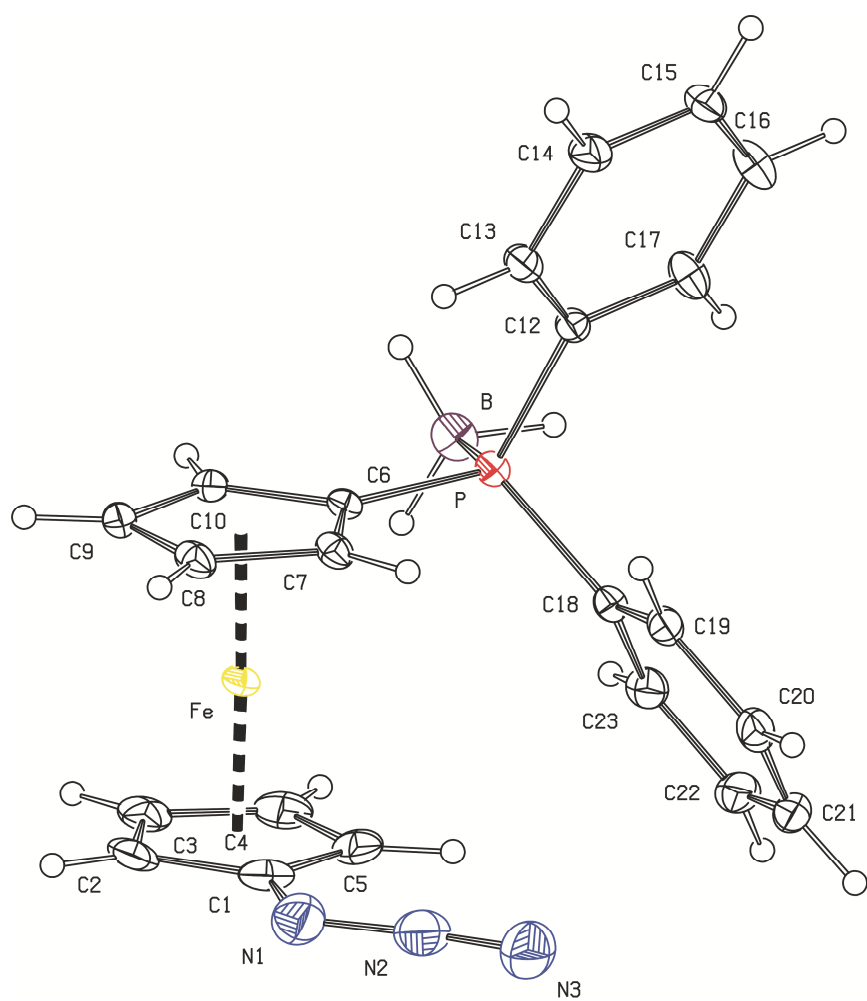


Figure S5. PLATON plot of the molecular structure of **4B** showing displacement ellipsoids at the 30% probability level.

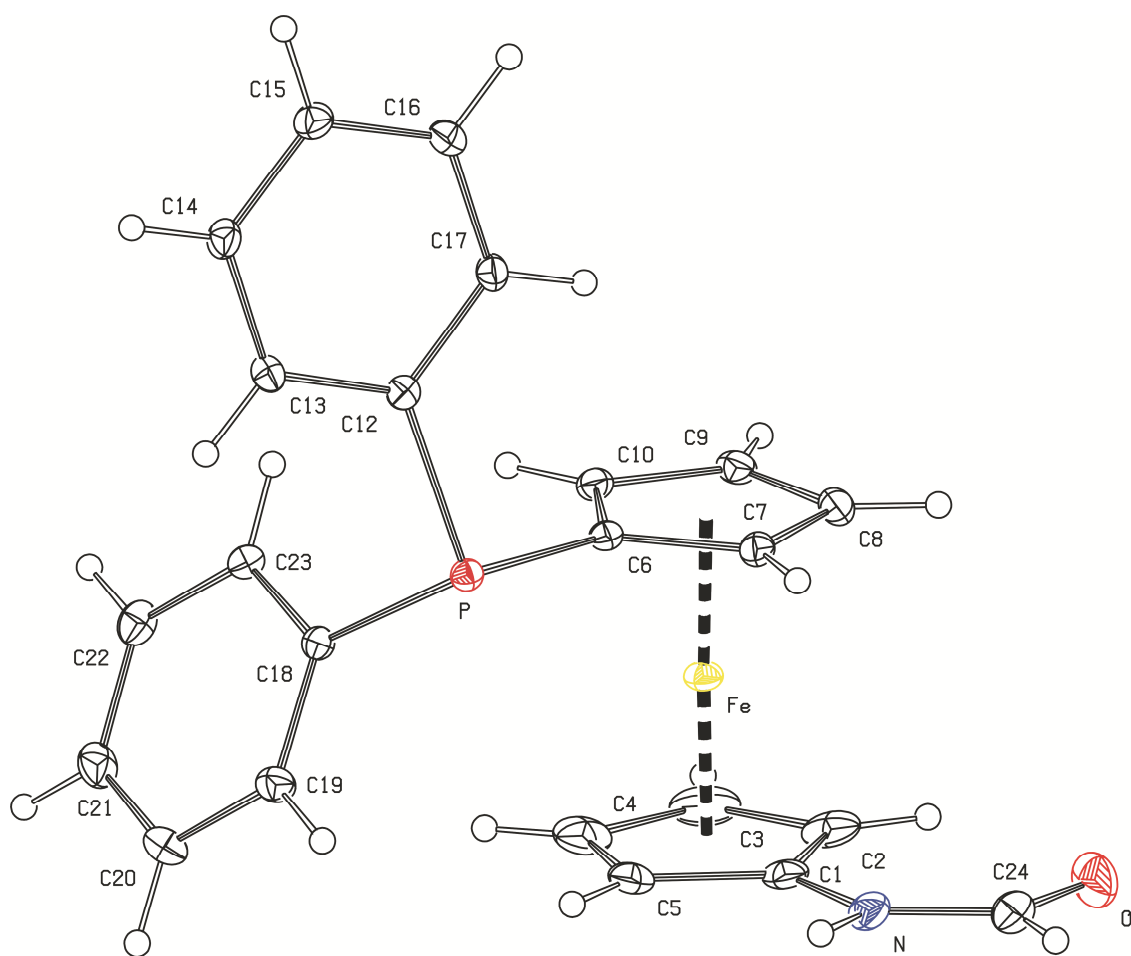


Figure S6. PLATON plot of the molecular structure of **5** showing displacement ellipsoids at the 30% probability level.

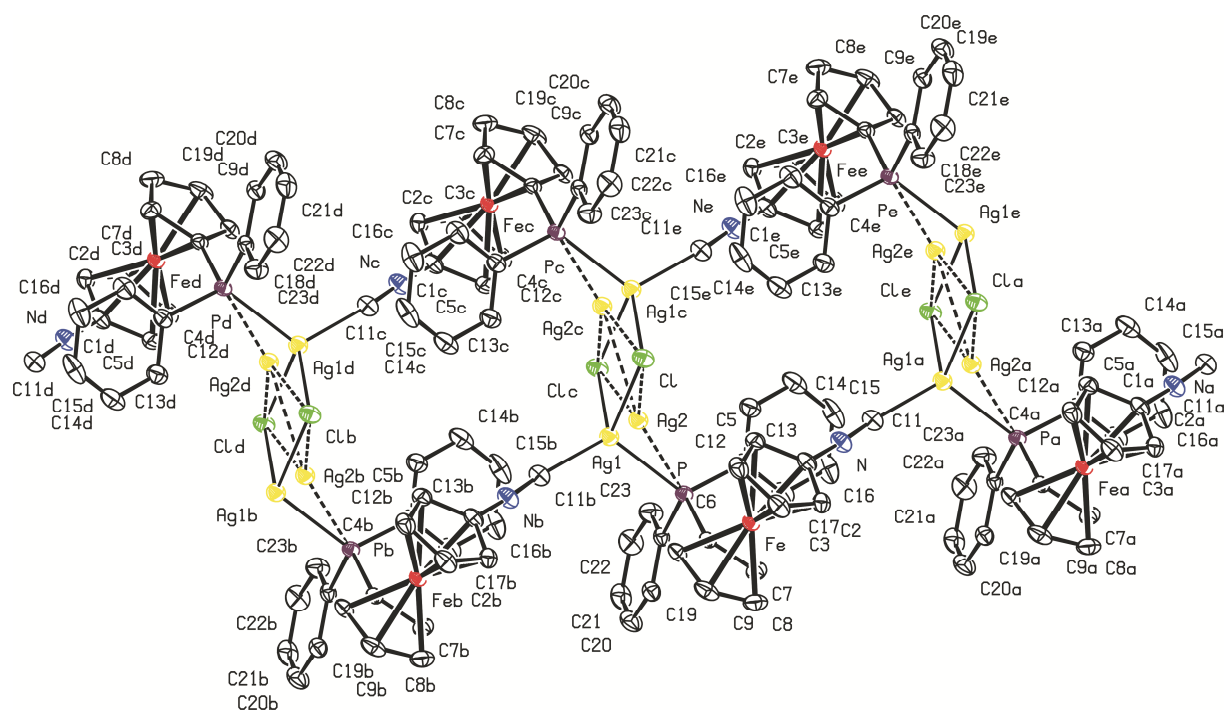


Figure S7. PLATON plot of the infinite assembly in the structure of **6** with displacement ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

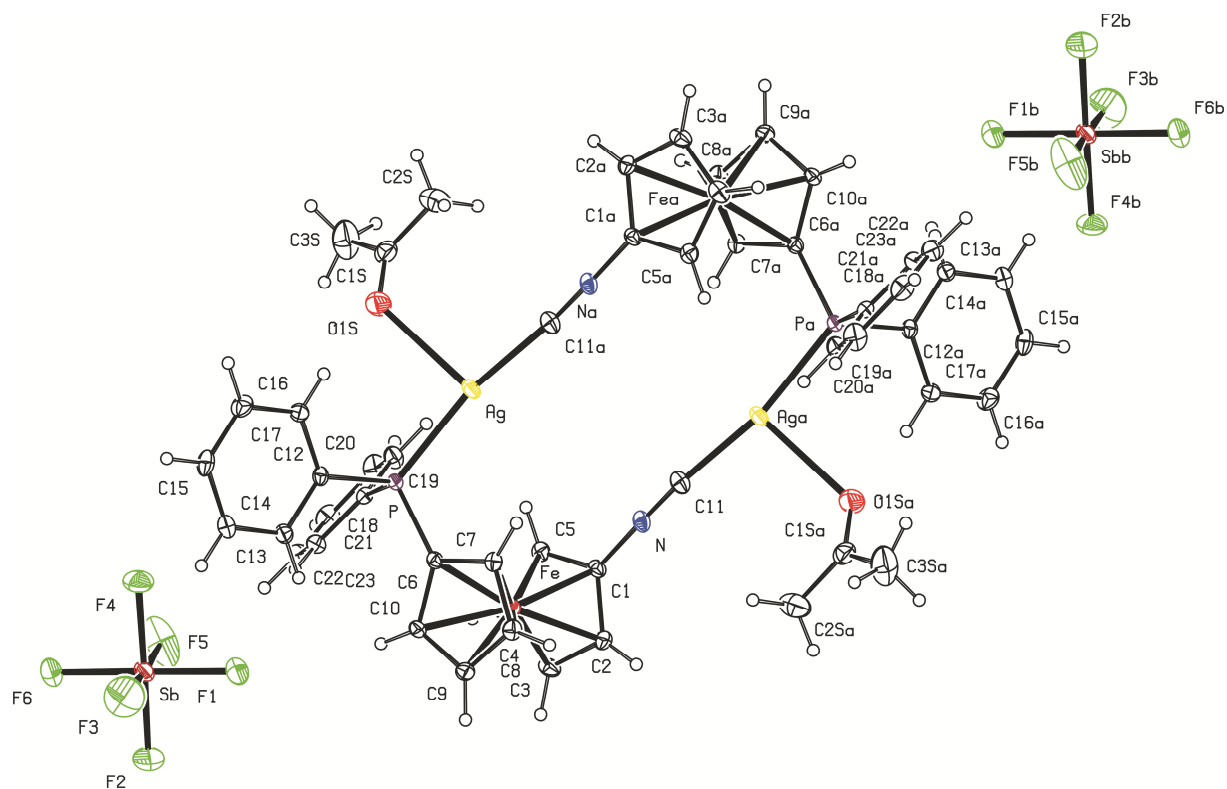


Figure S8. PLATON plot of the molecular structure of **7** showing displacement ellipsoids at the 30% probability level.

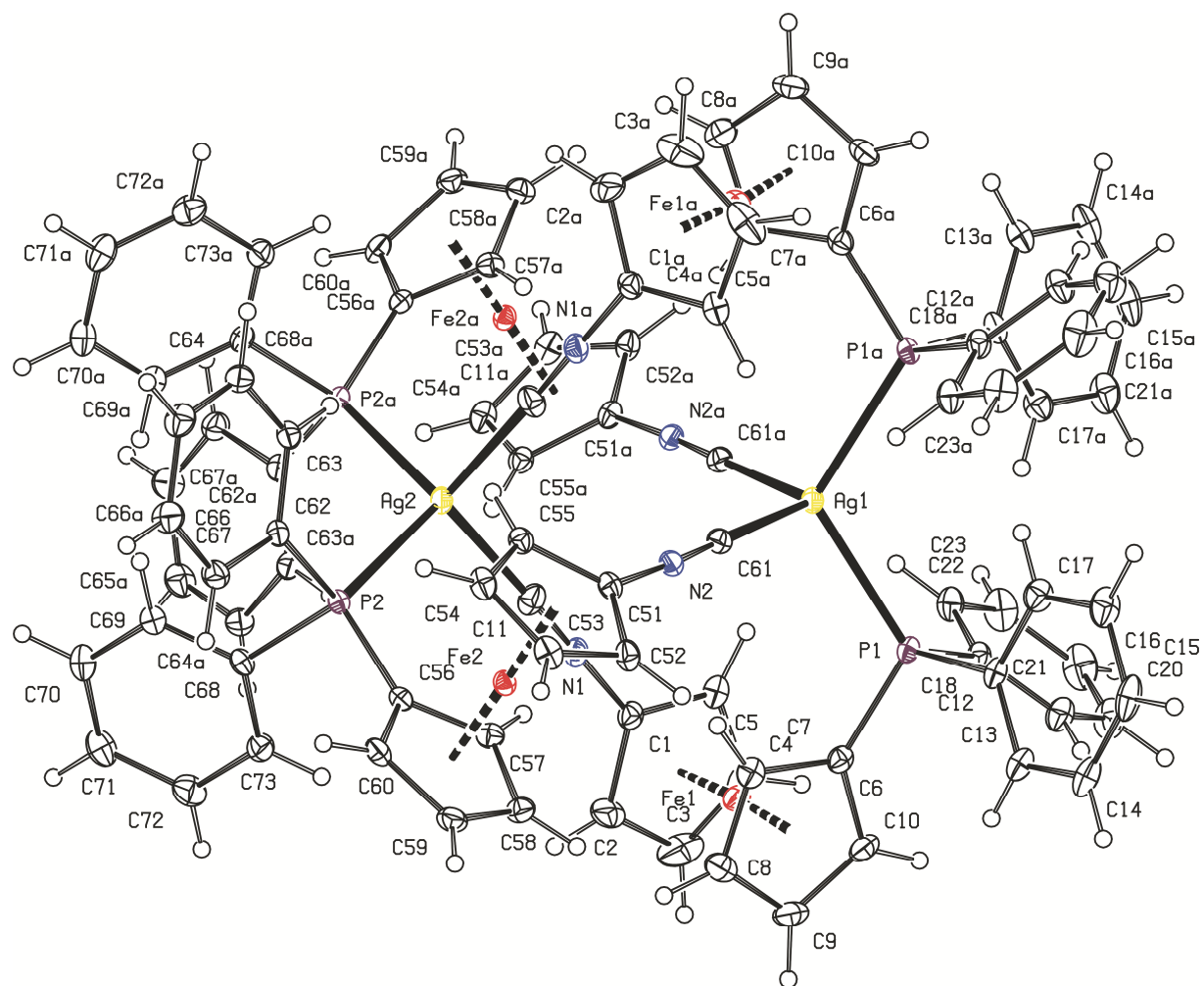


Figure S9. PLATON plot of the complex cation in the structure of **8**·3Me₂CO showing displacement ellipsoids at the 30% probability level.

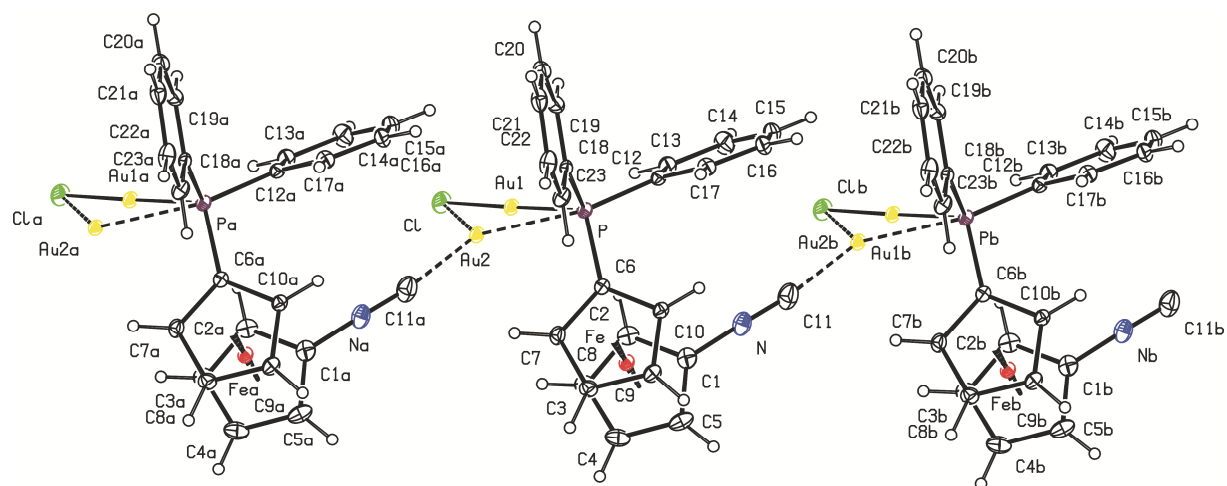


Figure S10. PLATON plot of the structure of **9** showing displacement ellipsoids at the 30% probability level.

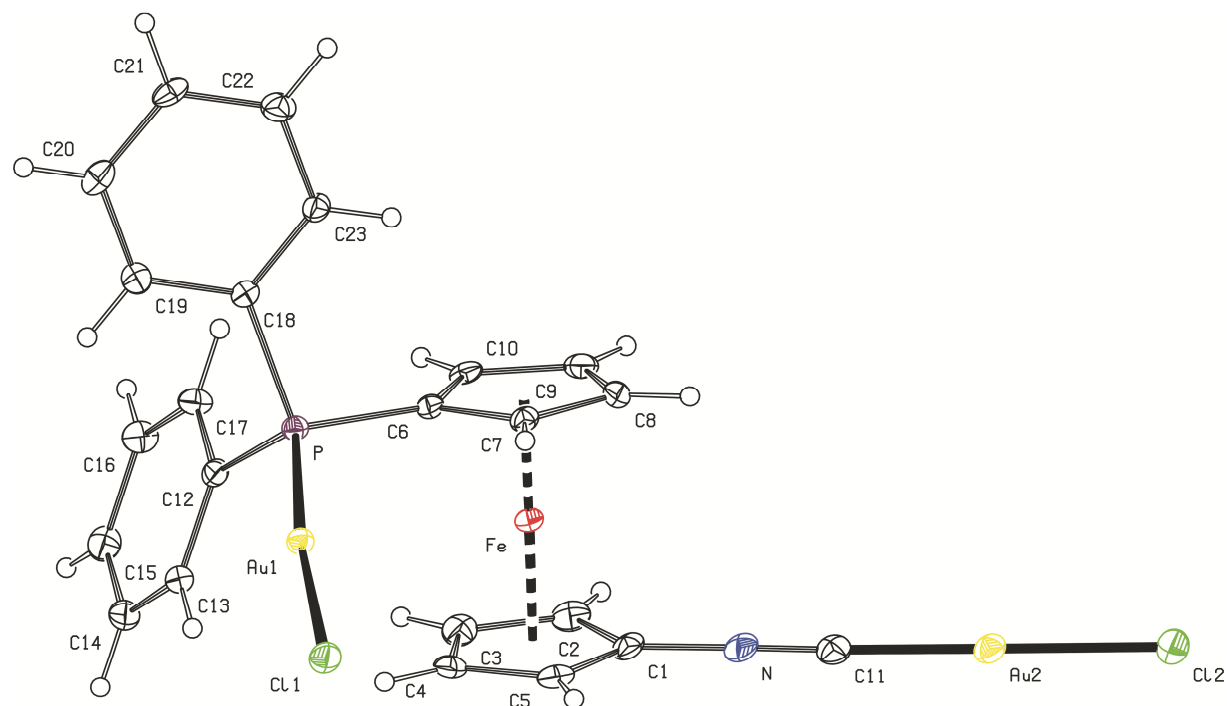


Figure S11. PLATON plot of the molecular structure of **10** showing displacement ellipsoids at the 30% probability level.

Table S2. Summary of computed energetic parameters^a

Compound	<i>E</i> (Hartree)	ZPE (Hartree)	<i>G</i> (kcal mol ⁻¹)
[Au ₂ (m(P,N)- D) ₂] ²⁺	-3083.470112	0.693103	-3082.867457
[Au D] ¹⁺	-1541.701959	0.345266	-1541.412095
[Au ₂ (m(P,C)- 11) ₂] ²⁺	-3083.435496	0.69292	-3082.830992
[Au(11)] ¹⁺	-1541.675001	0.345159	-1541.384068

^a Gaussian energetic parameters calculated at the PBE0/ccPVDZ:sdd(Fe,Au) level of theory.

Copies of the NMR spectra (newly prepared compounds only)

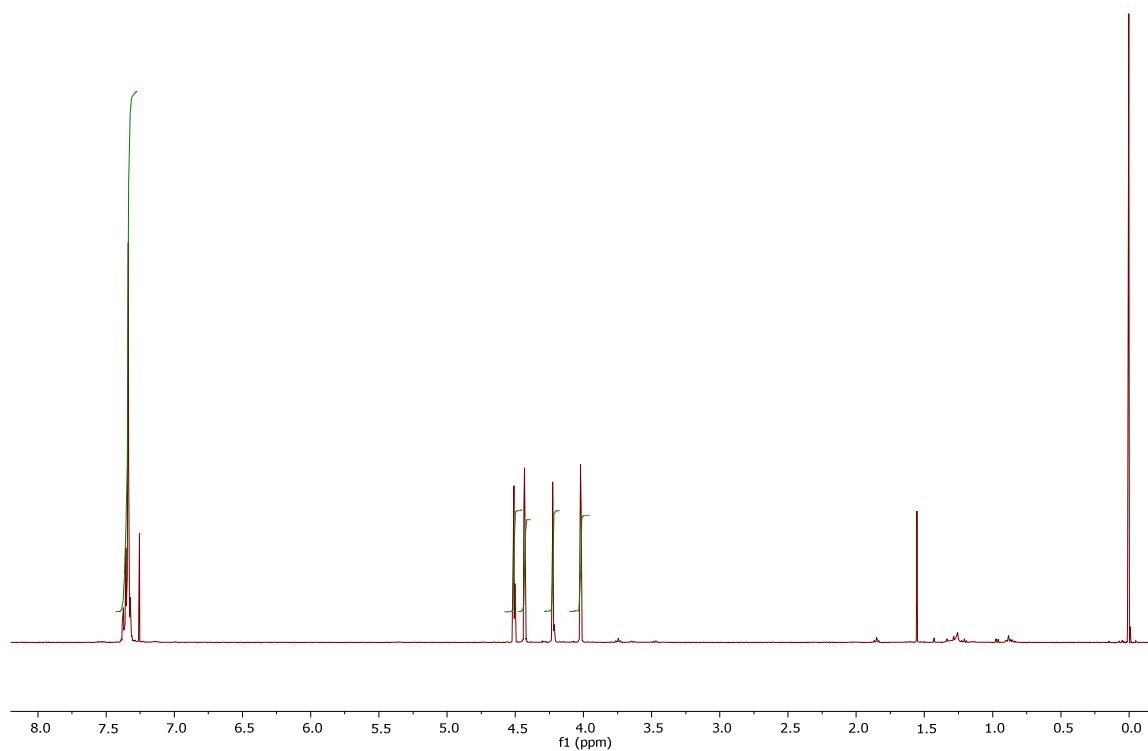


Figure S14. ^1H NMR spectrum of **1** (CDCl_3).

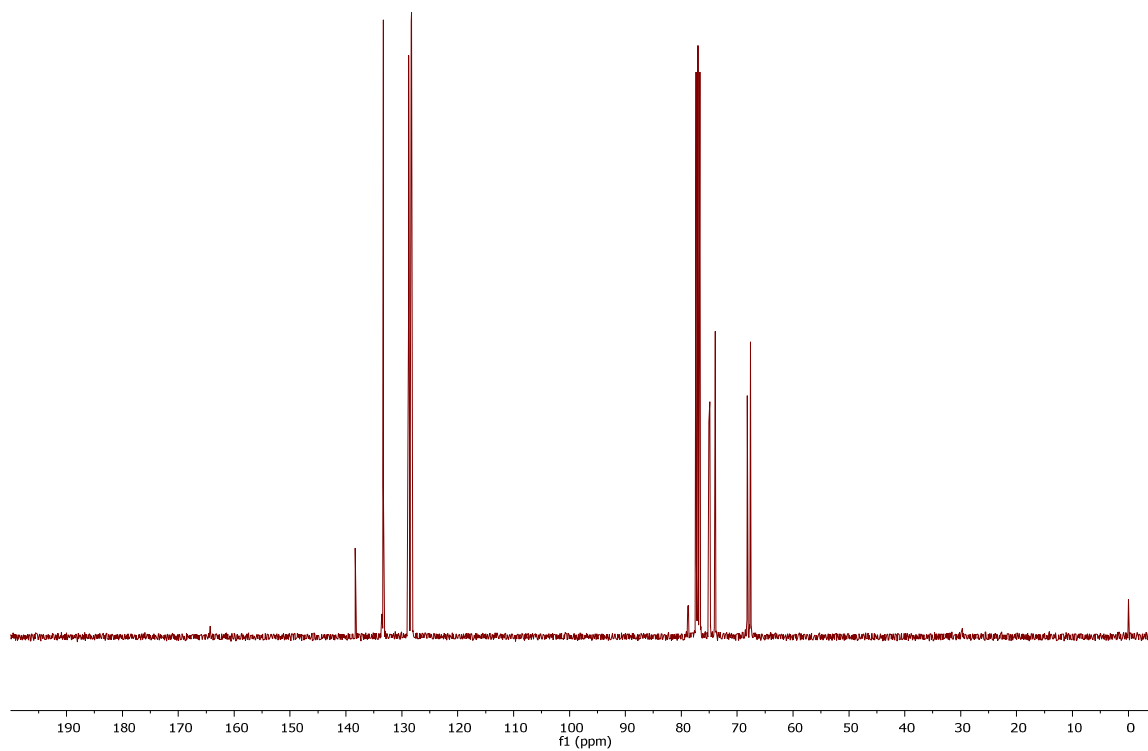


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (CDCl_3).

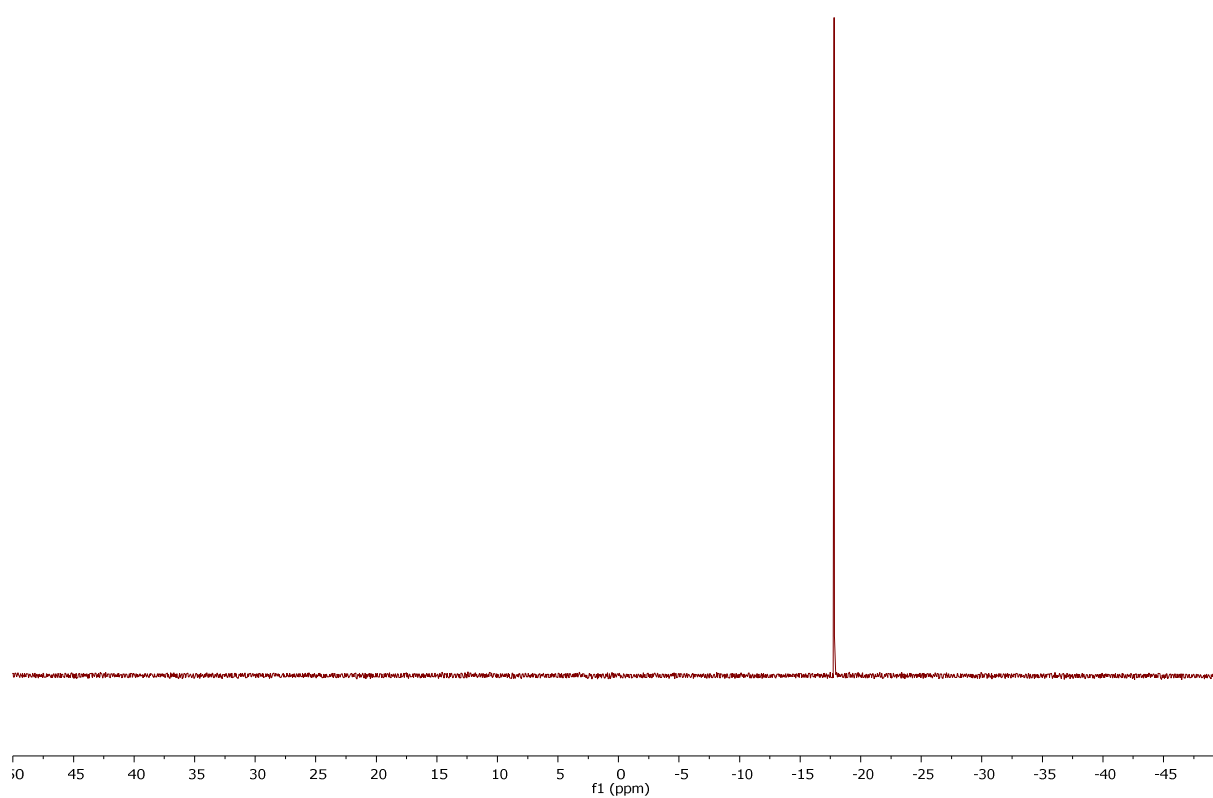


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** (CDCl_3).

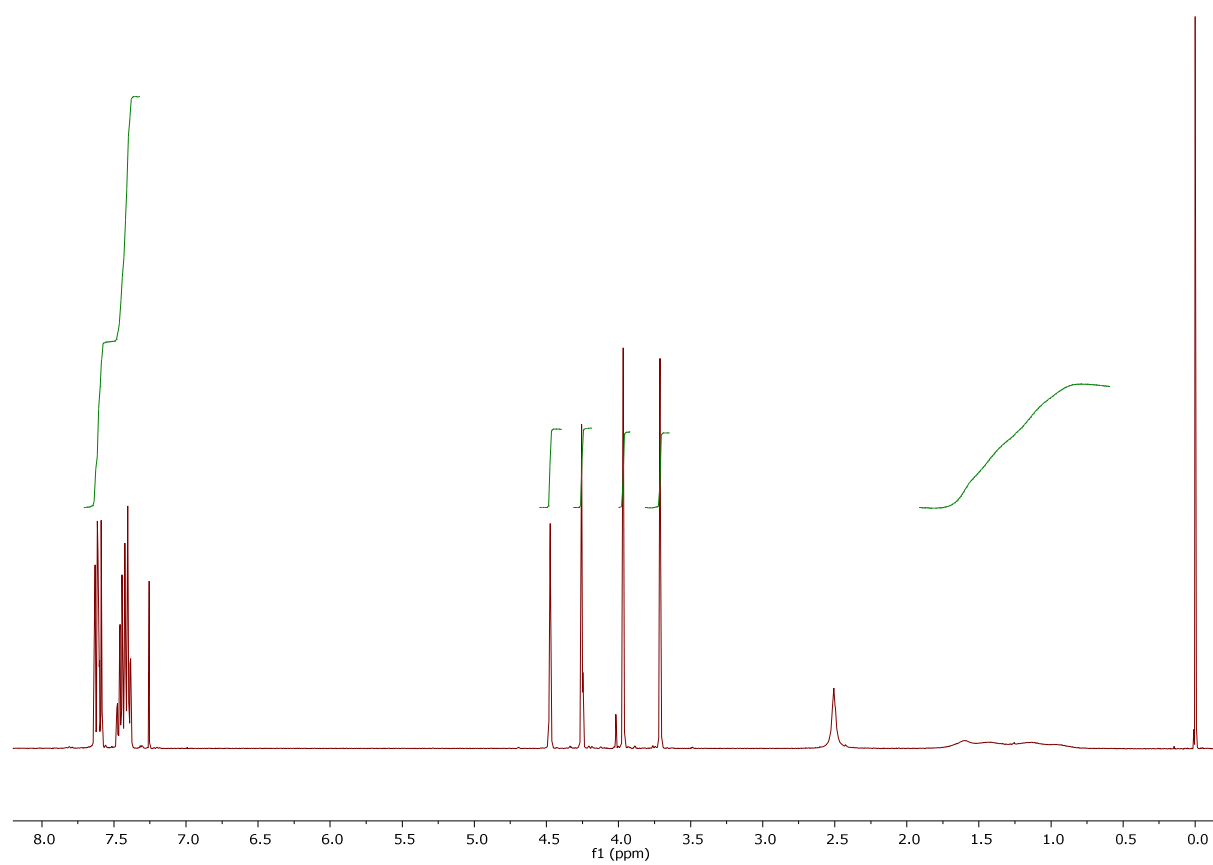


Figure S17. ^1H NMR spectrum of **2B** (CDCl_3).

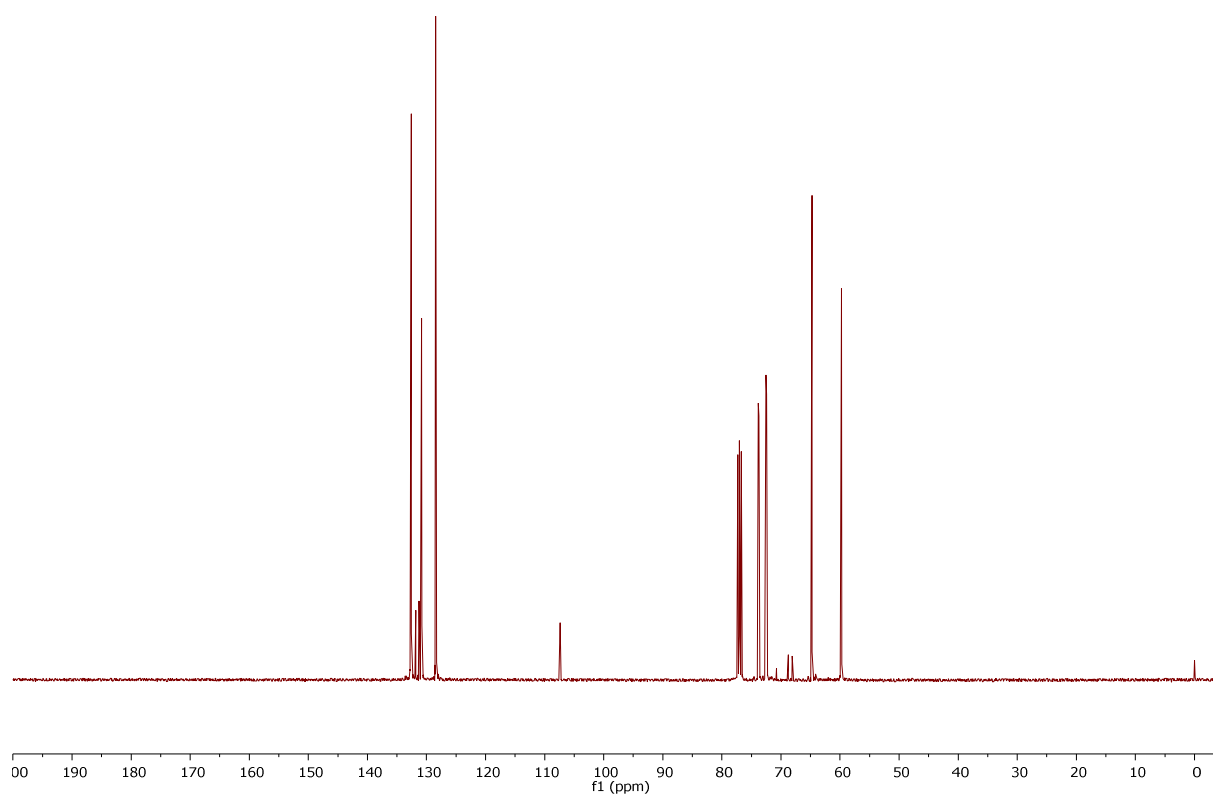


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B** (CDCl_3).

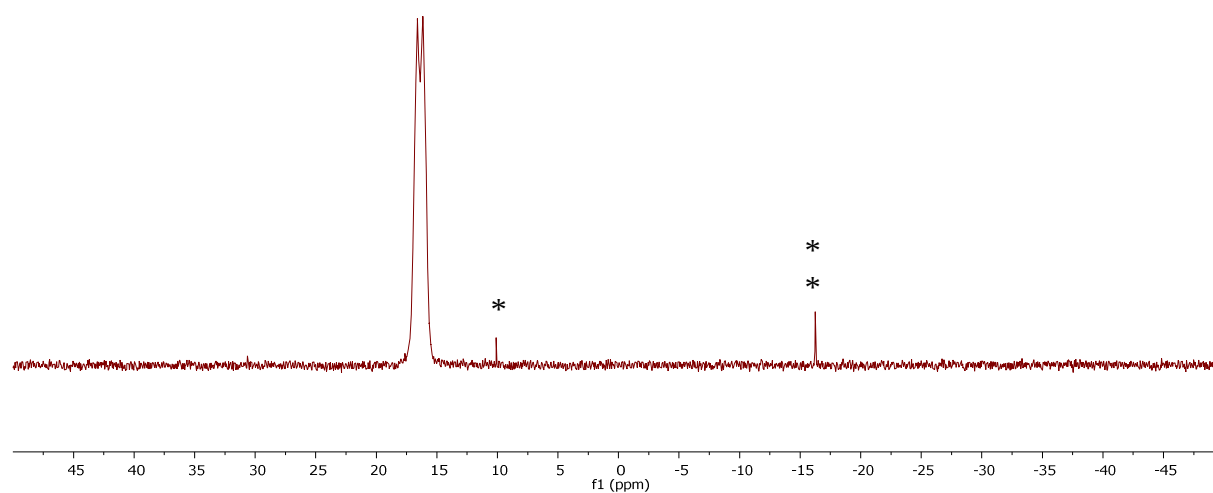


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2B** (CDCl_3 ; * = system peak; ** = 2).

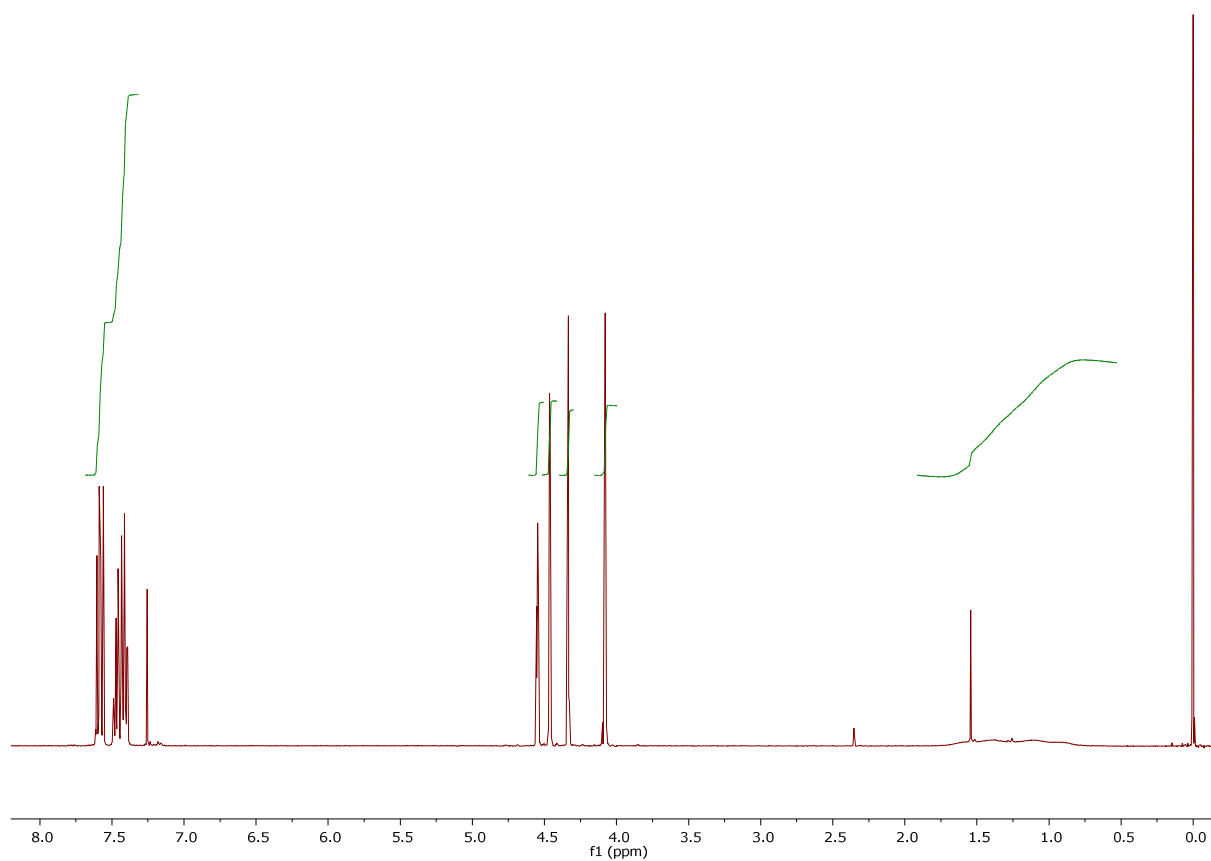


Figure S20. ^1H NMR spectrum of **3B** (CDCl_3).

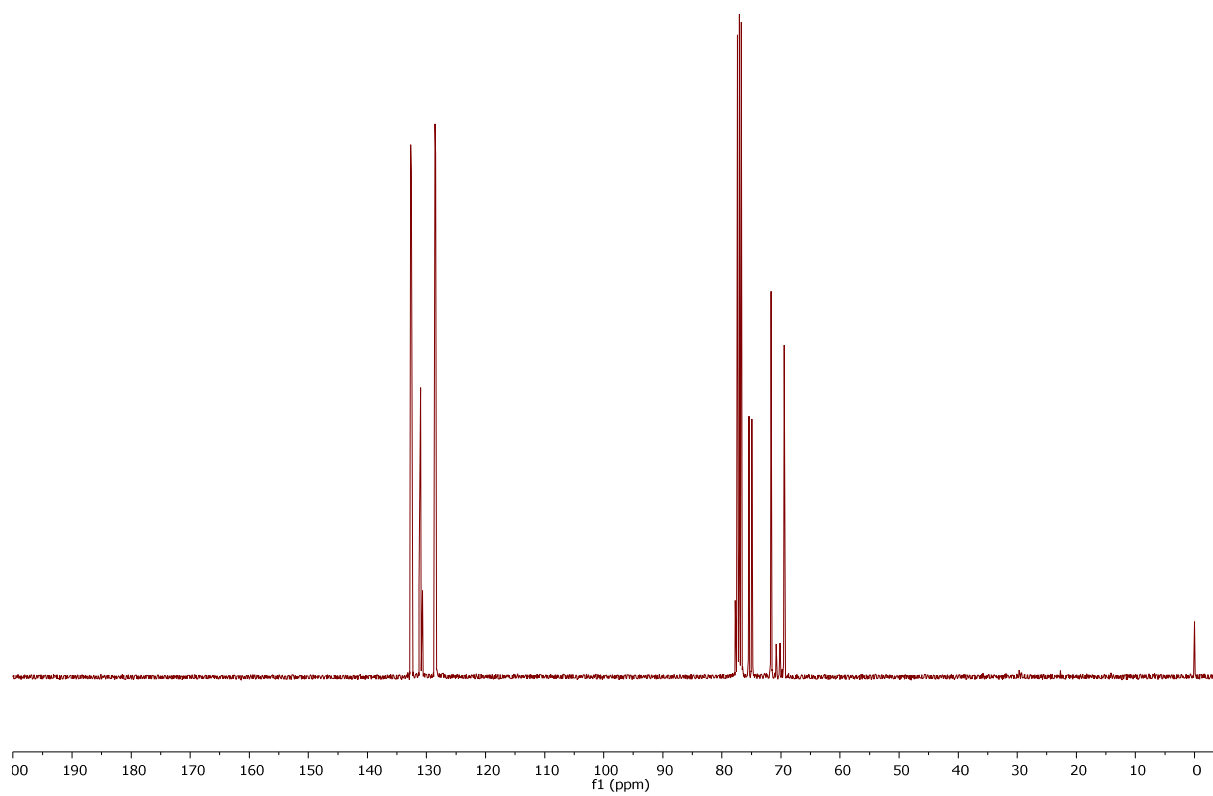


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3B** (CDCl_3).

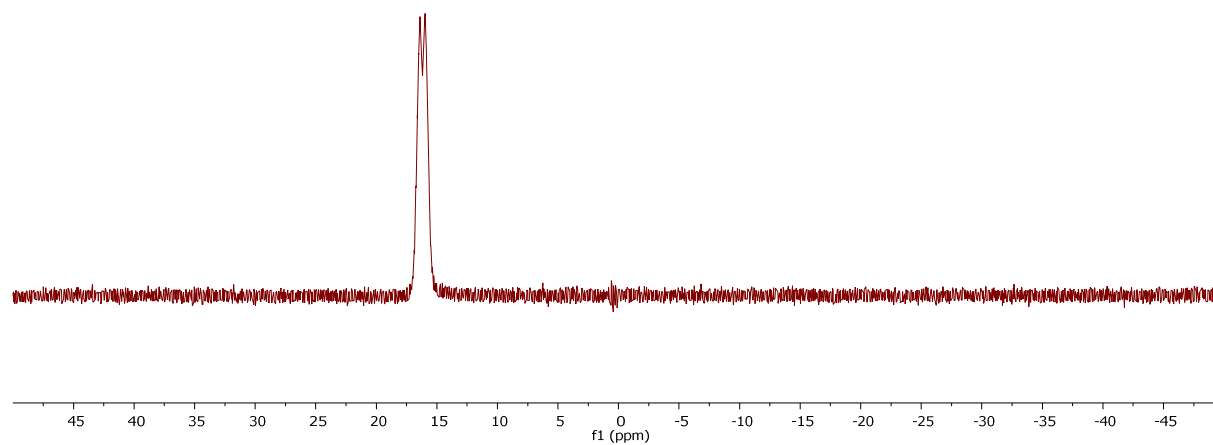


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3B** (CDCl_3).

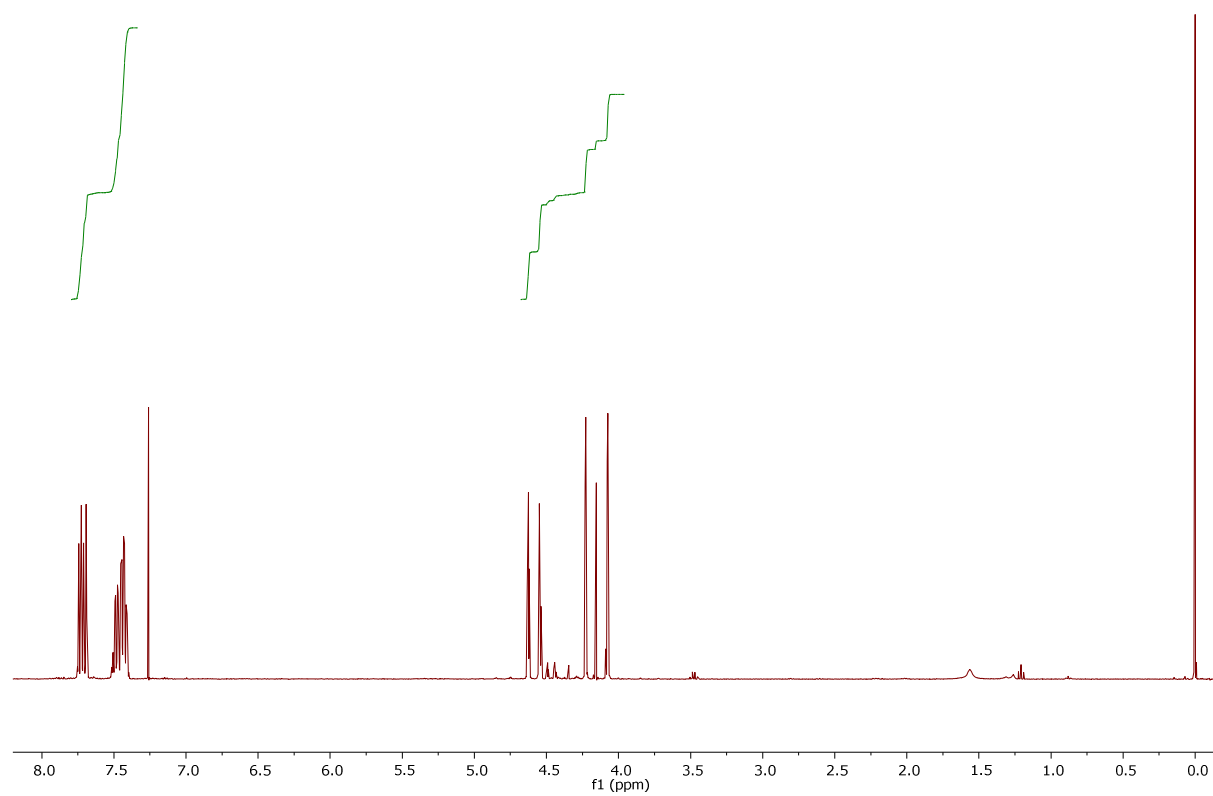


Figure S23. ^1H NMR spectrum of **4S** (CDCl_3).

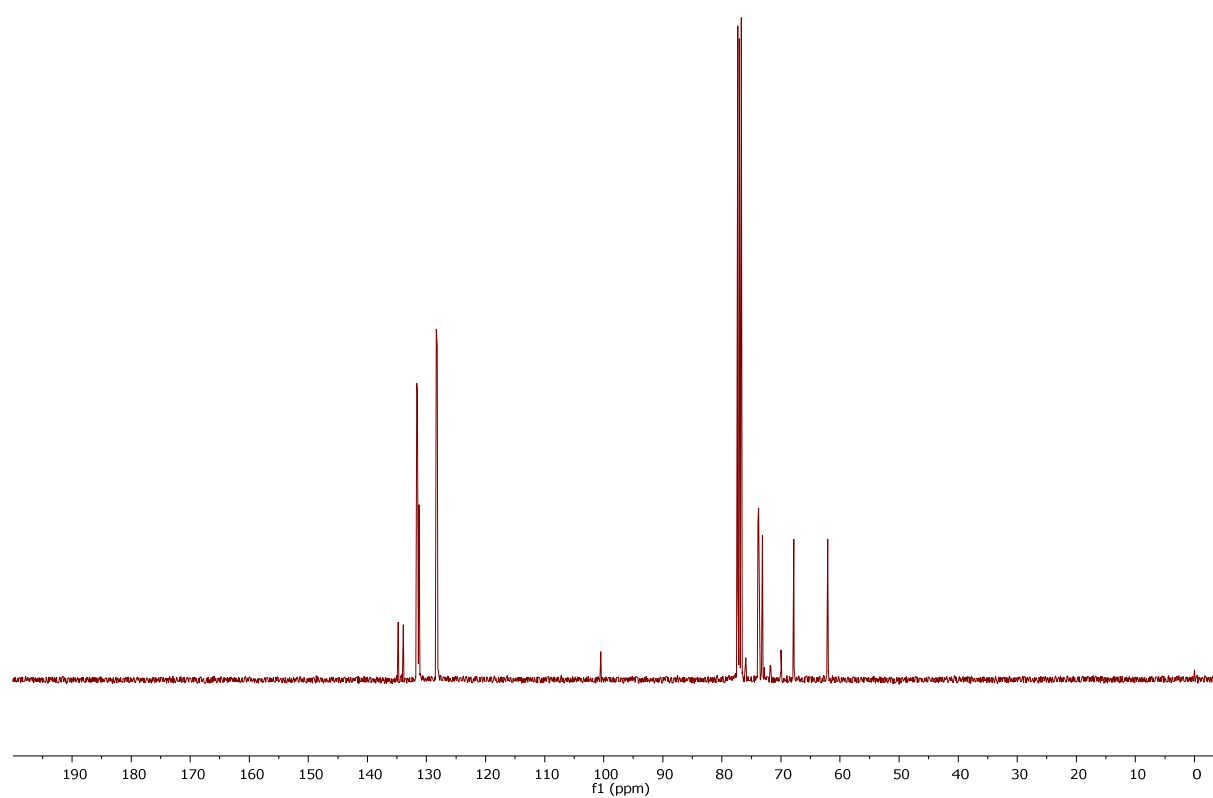


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4S** (CDCl_3).

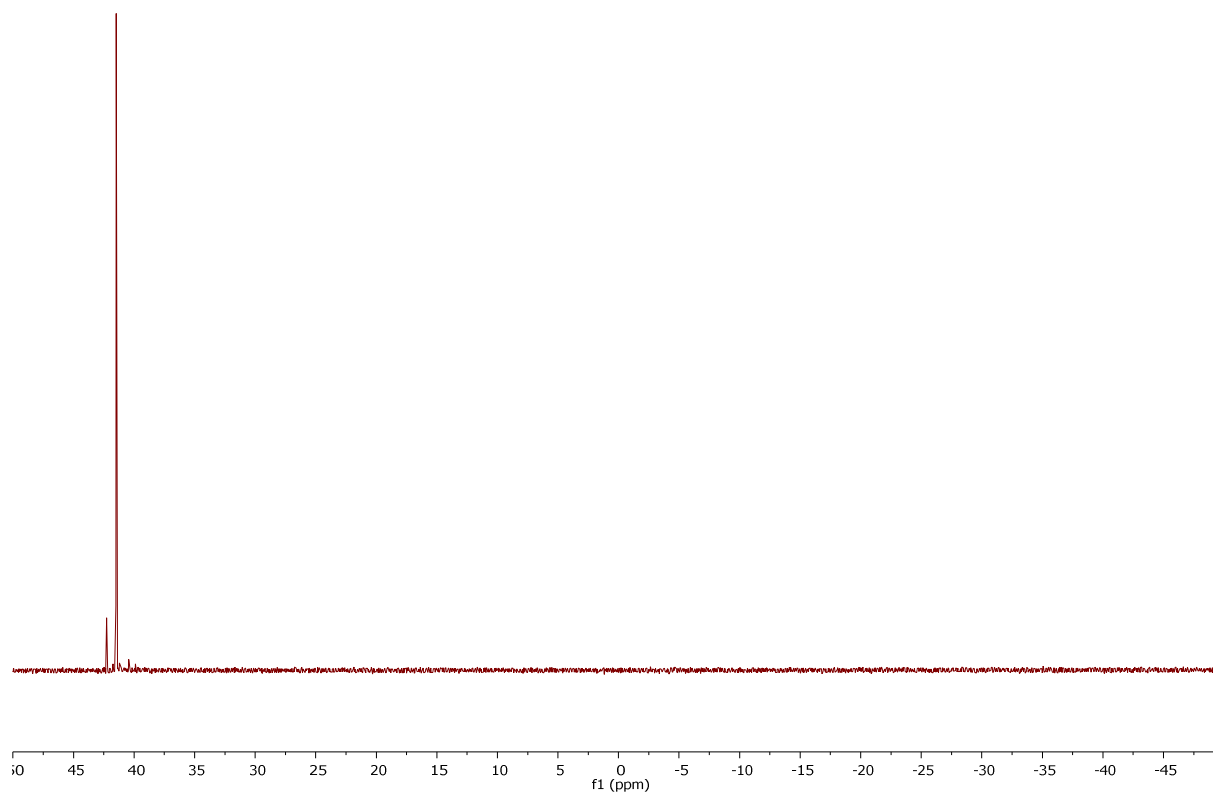


Figure S25. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4S** (CDCl_3).

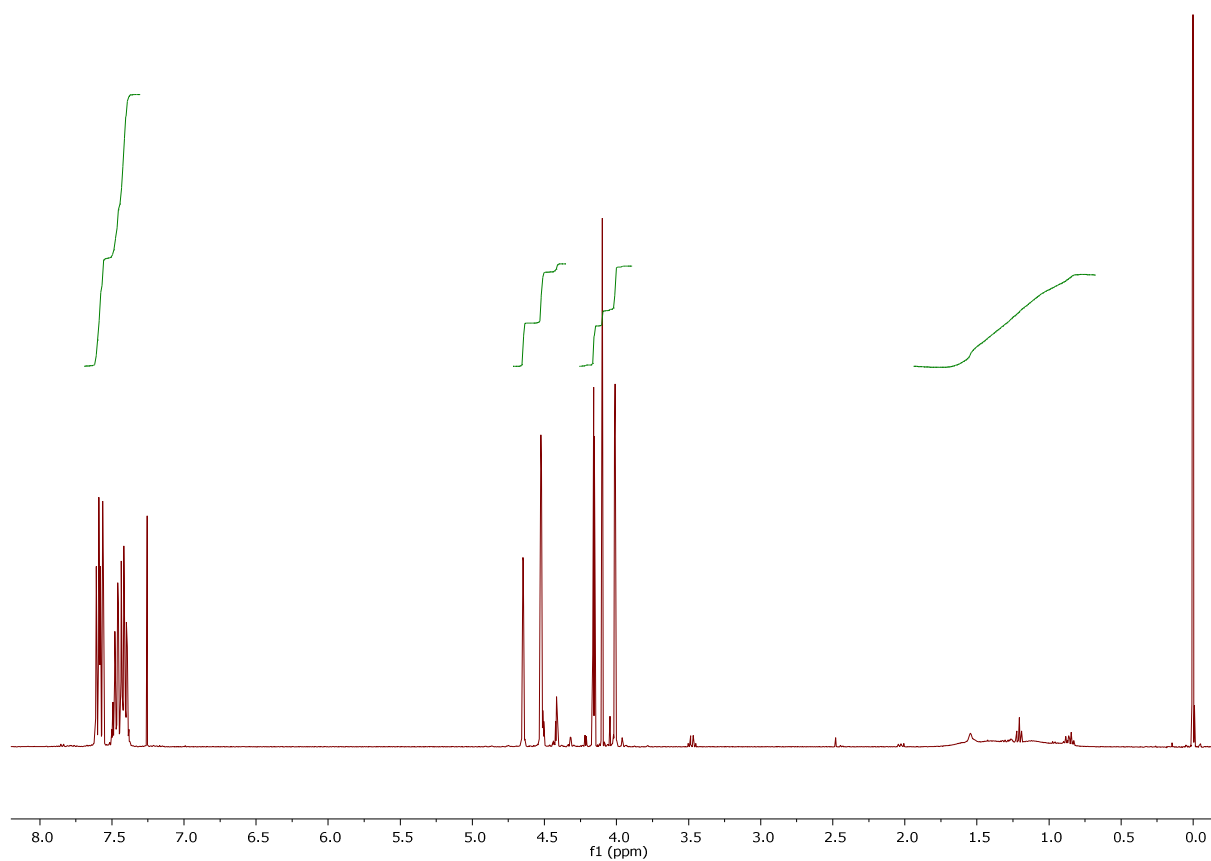


Figure S26. ^1H NMR spectrum of **4B** (CDCl_3).

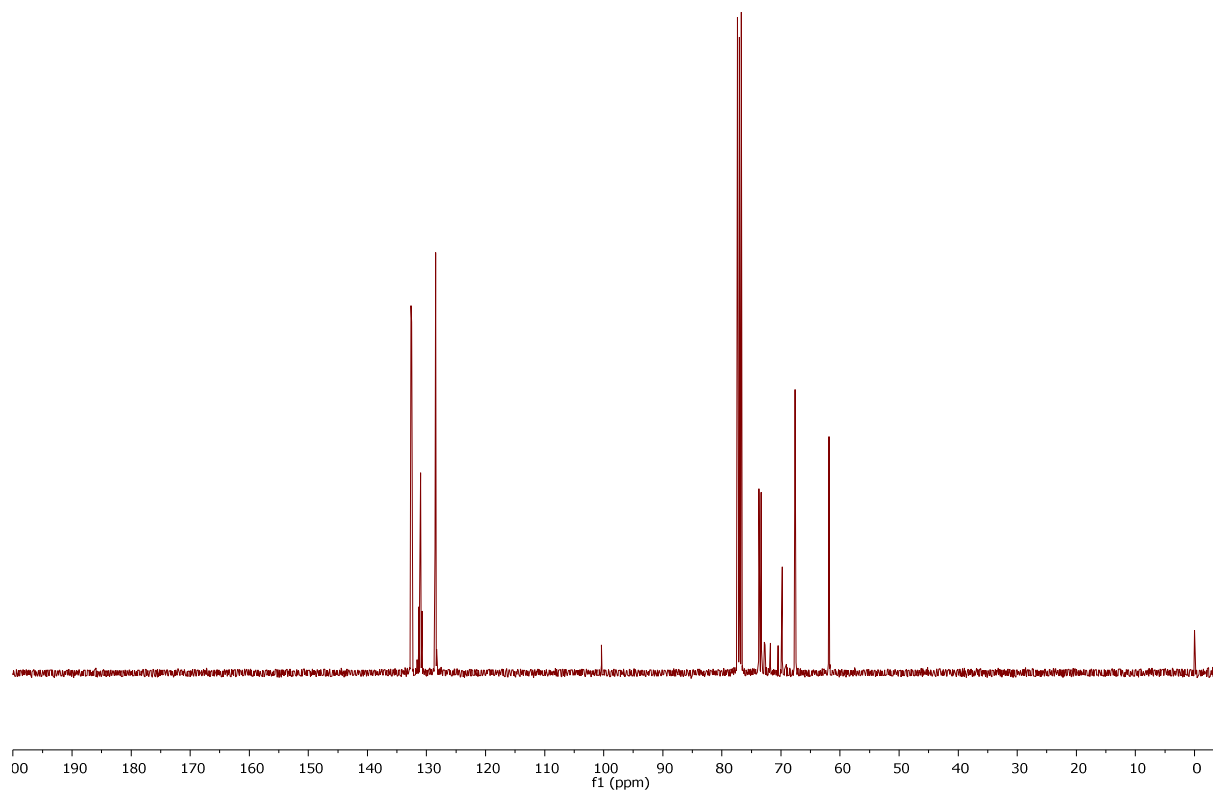


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4B** (CDCl_3).

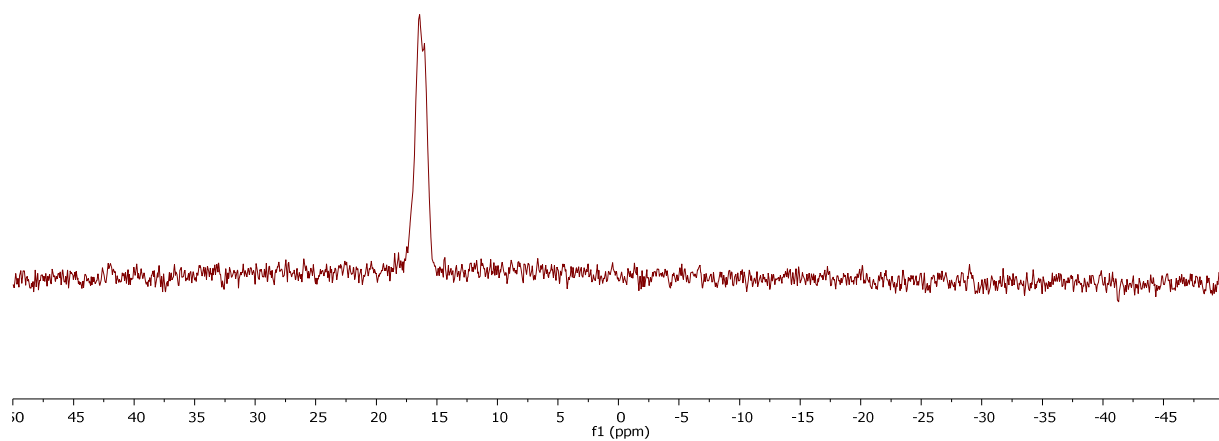


Figure S28. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4B** (CDCl_3).

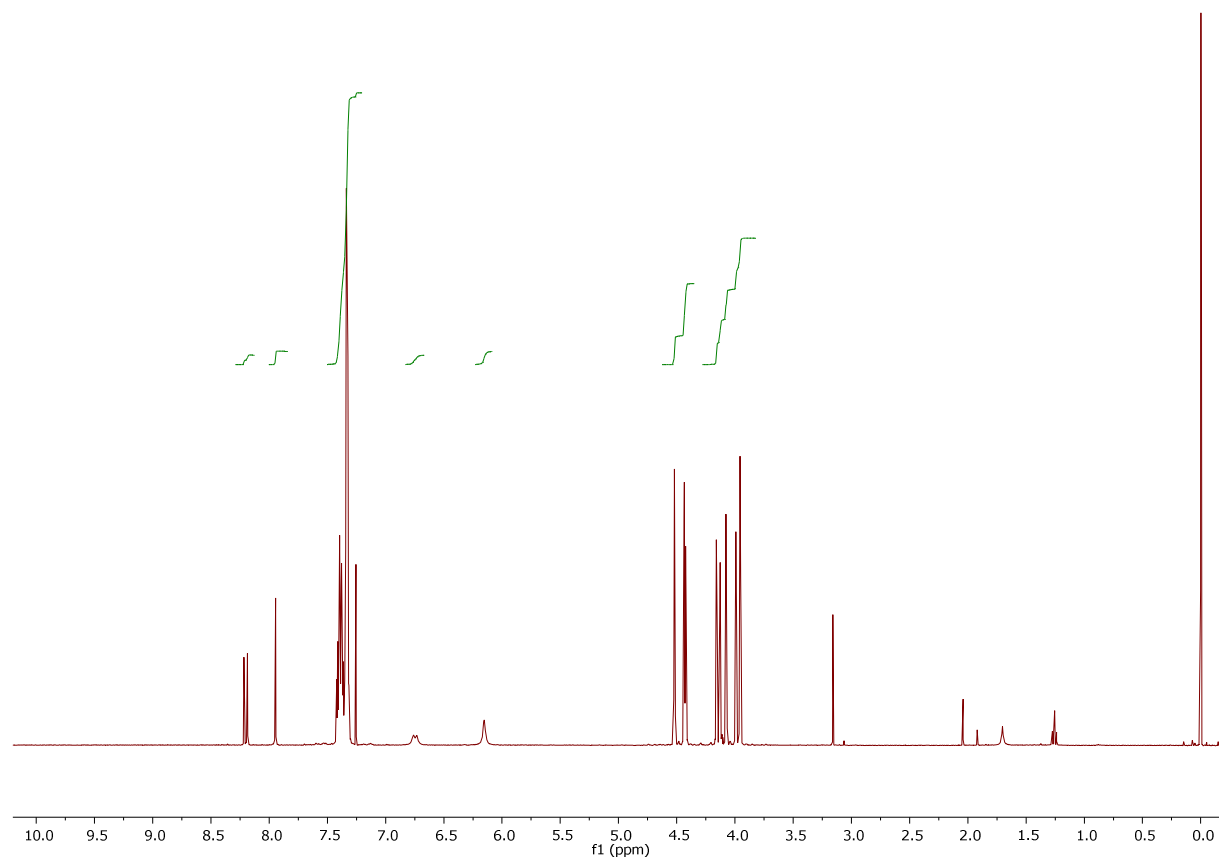


Figure S29. ^1H NMR spectrum of **5** (CDCl_3).

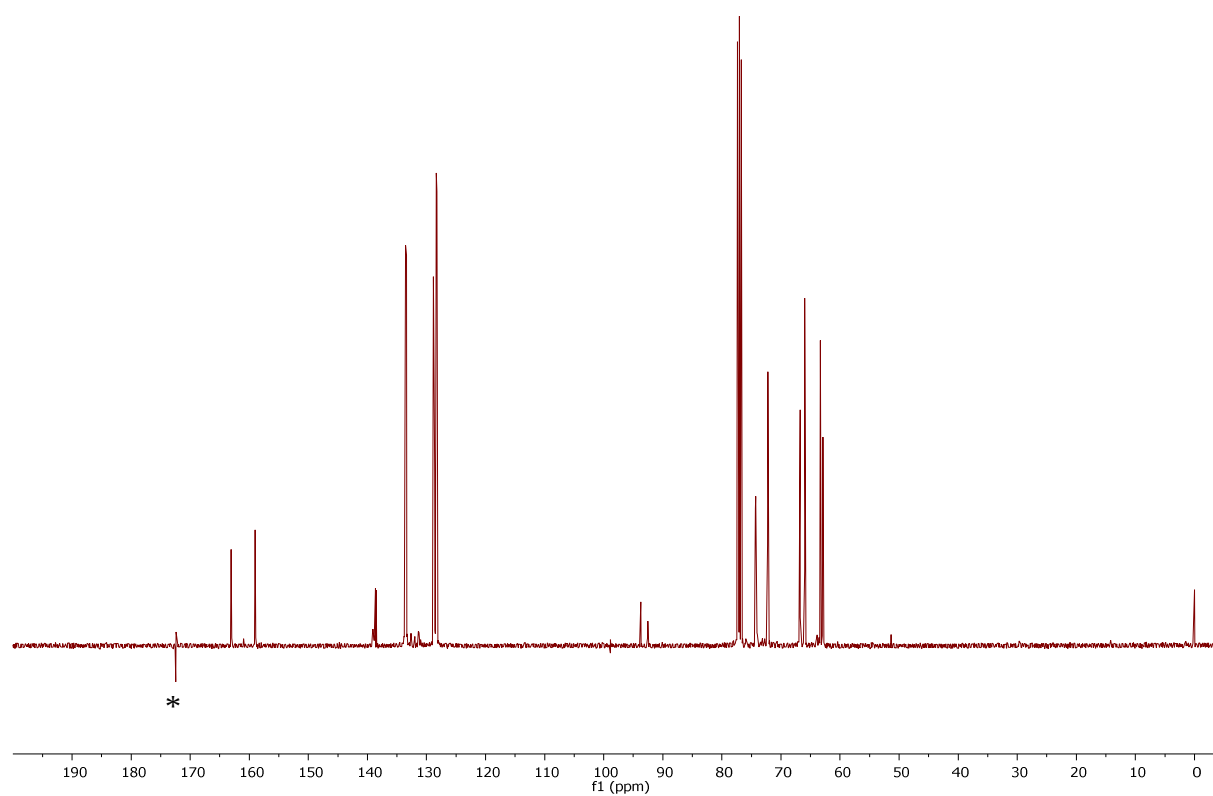


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (CDCl_3 ; * = system peak).

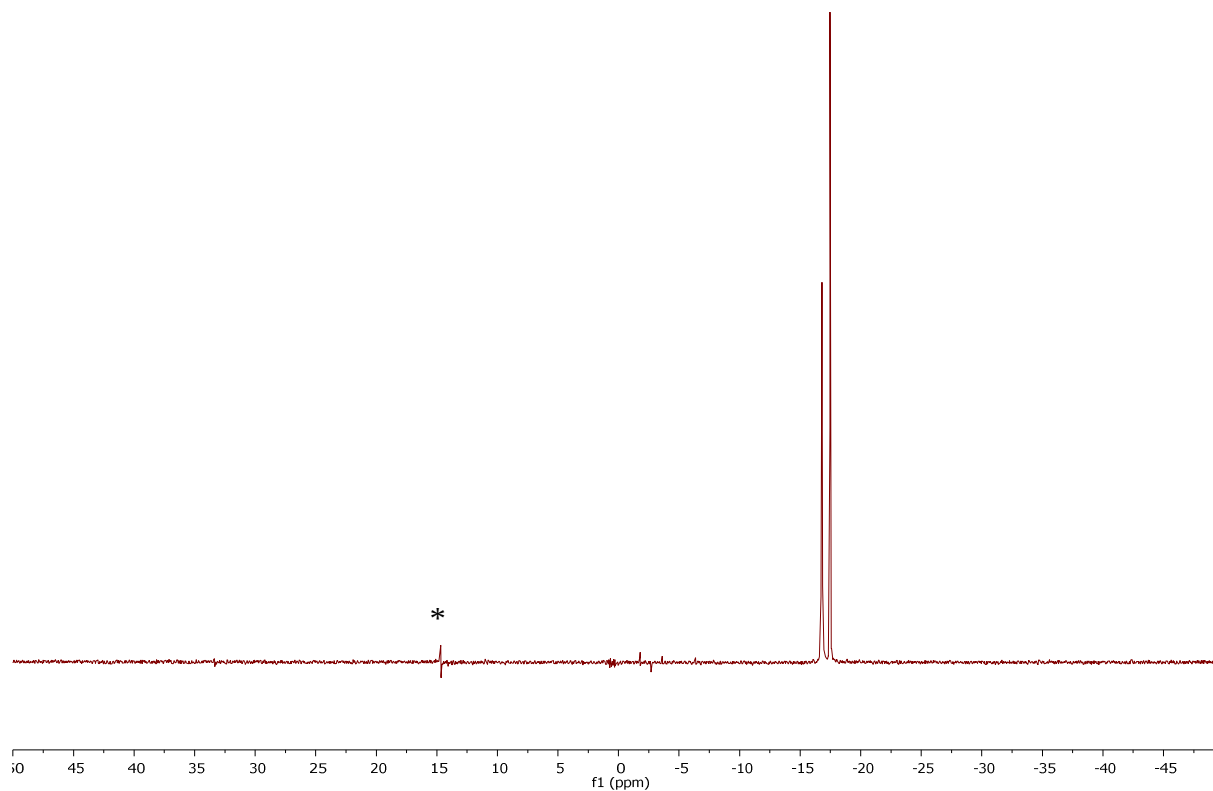


Figure S31. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** (CDCl_3 ; * = system peak).

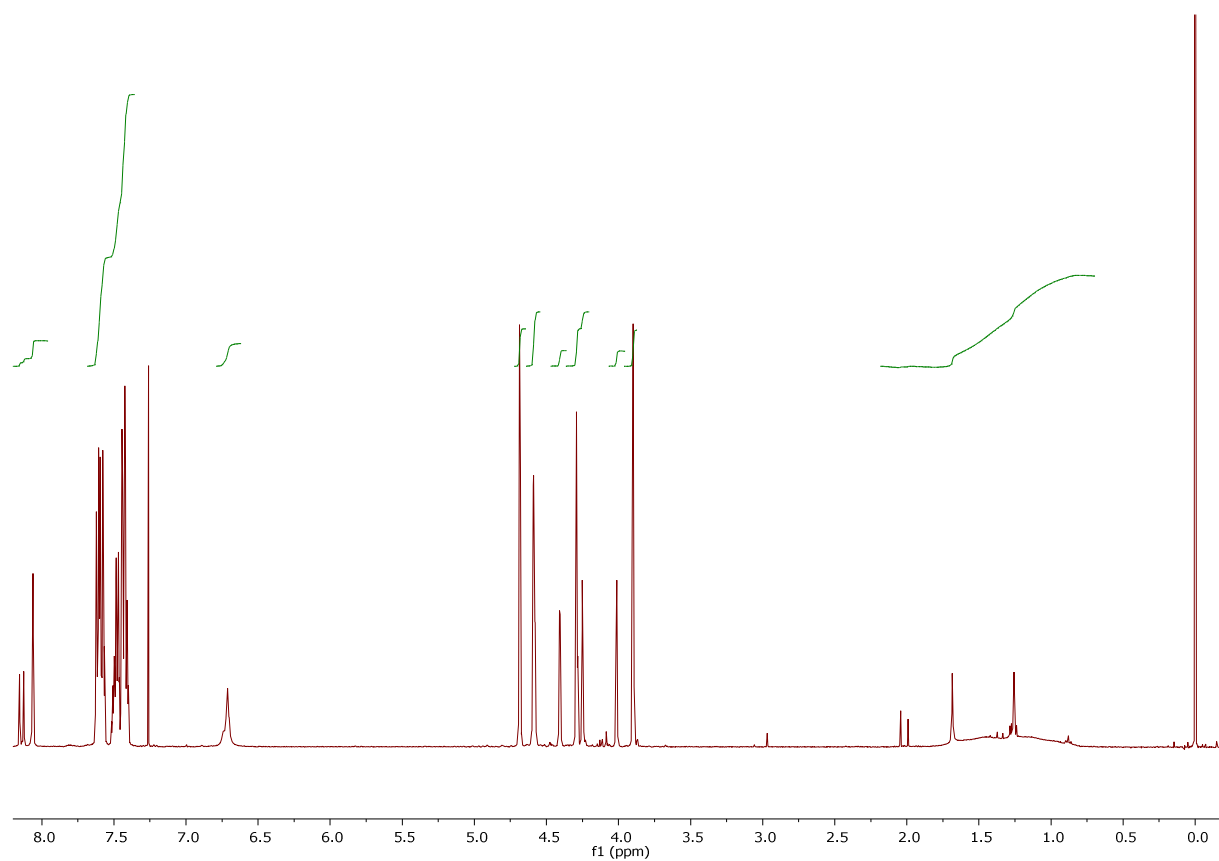


Figure S32. ^1H NMR spectrum of **5B** (CDCl_3).

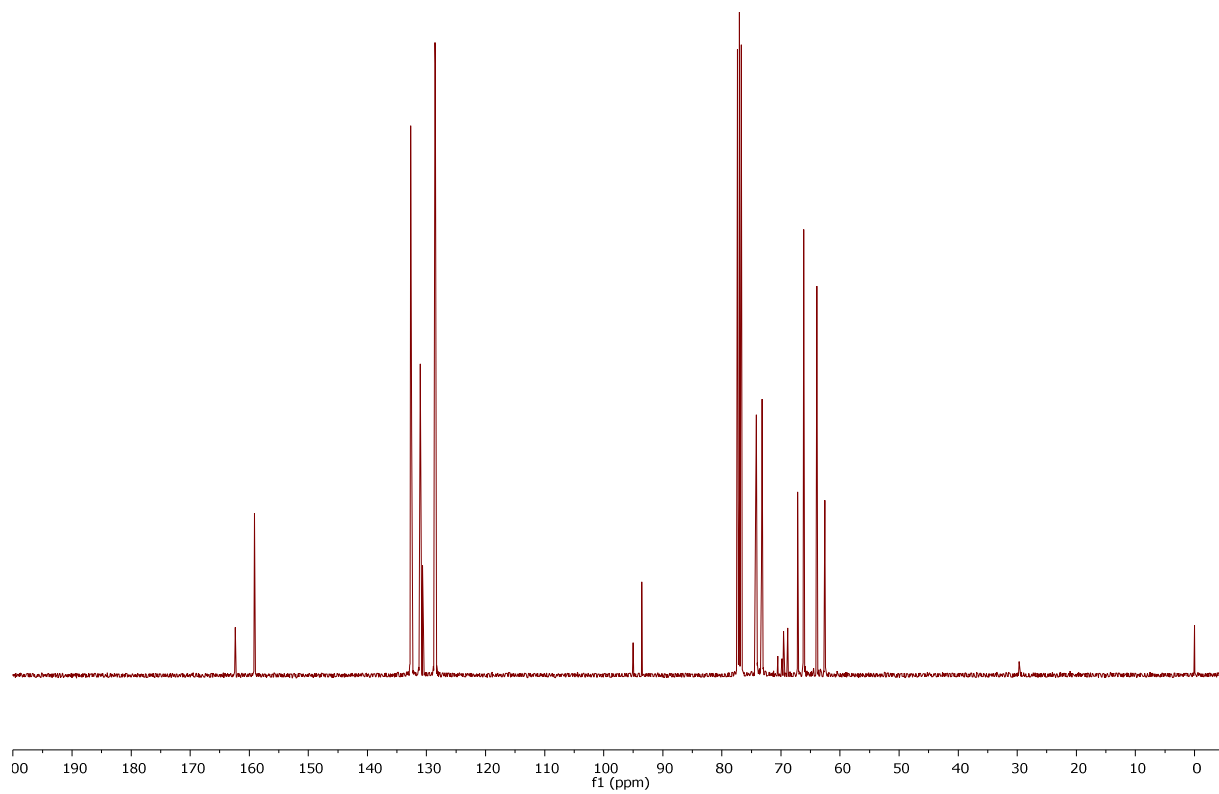


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5B** (CDCl_3).

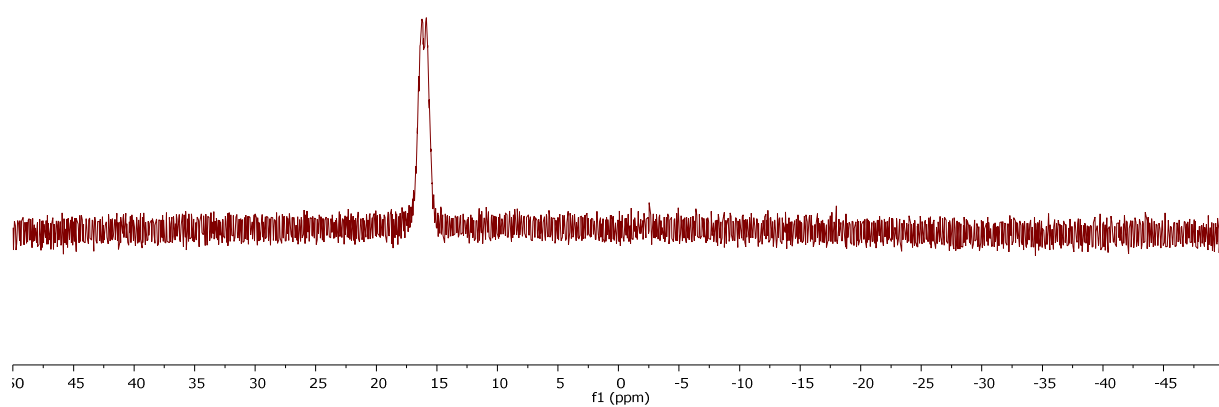


Figure S34. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5B** (CDCl_3).

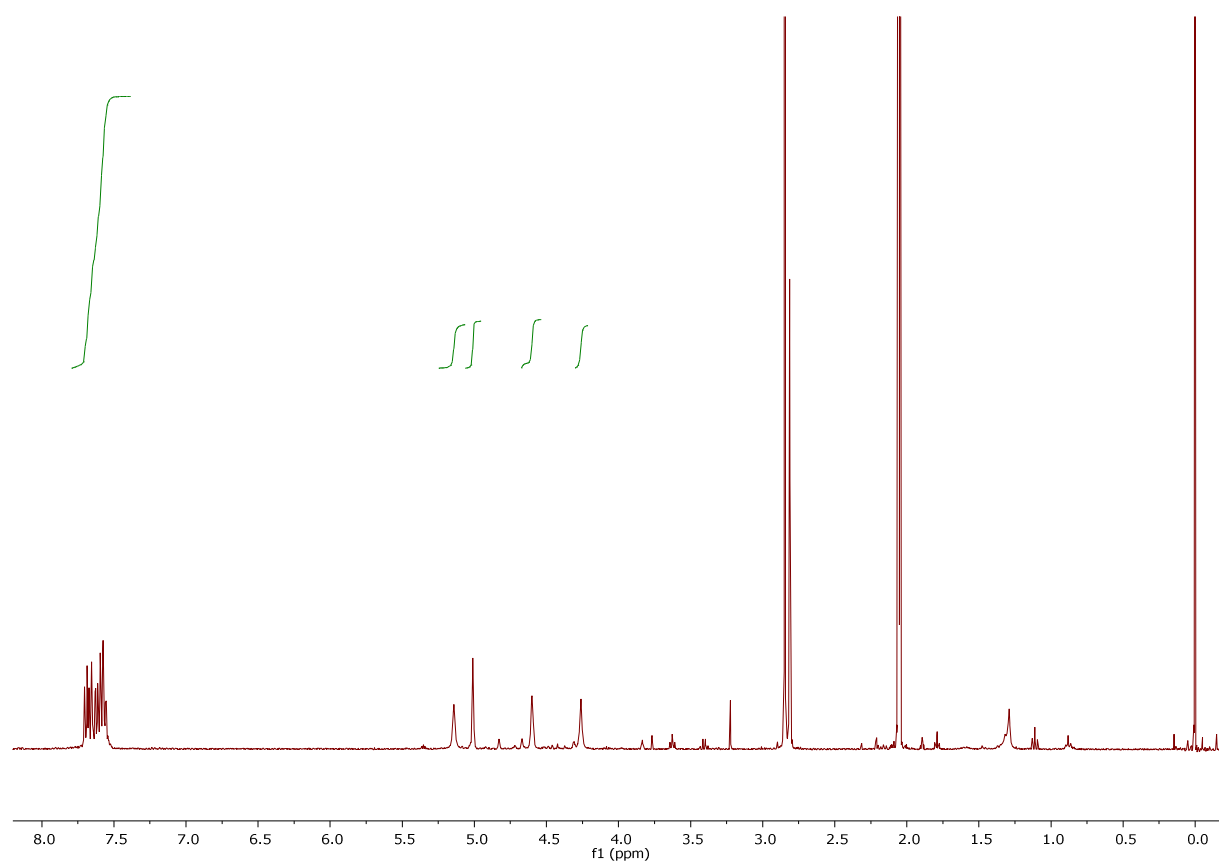


Figure S35. In situ ^1H NMR spectrum of **7** (acetone-d_6).

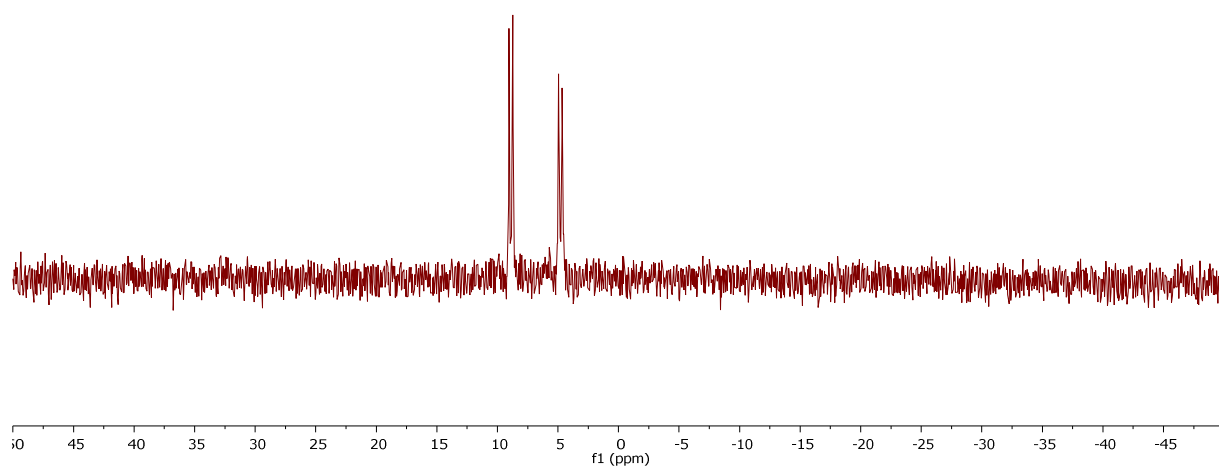


Figure S36. In situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** (acetone- d_6).

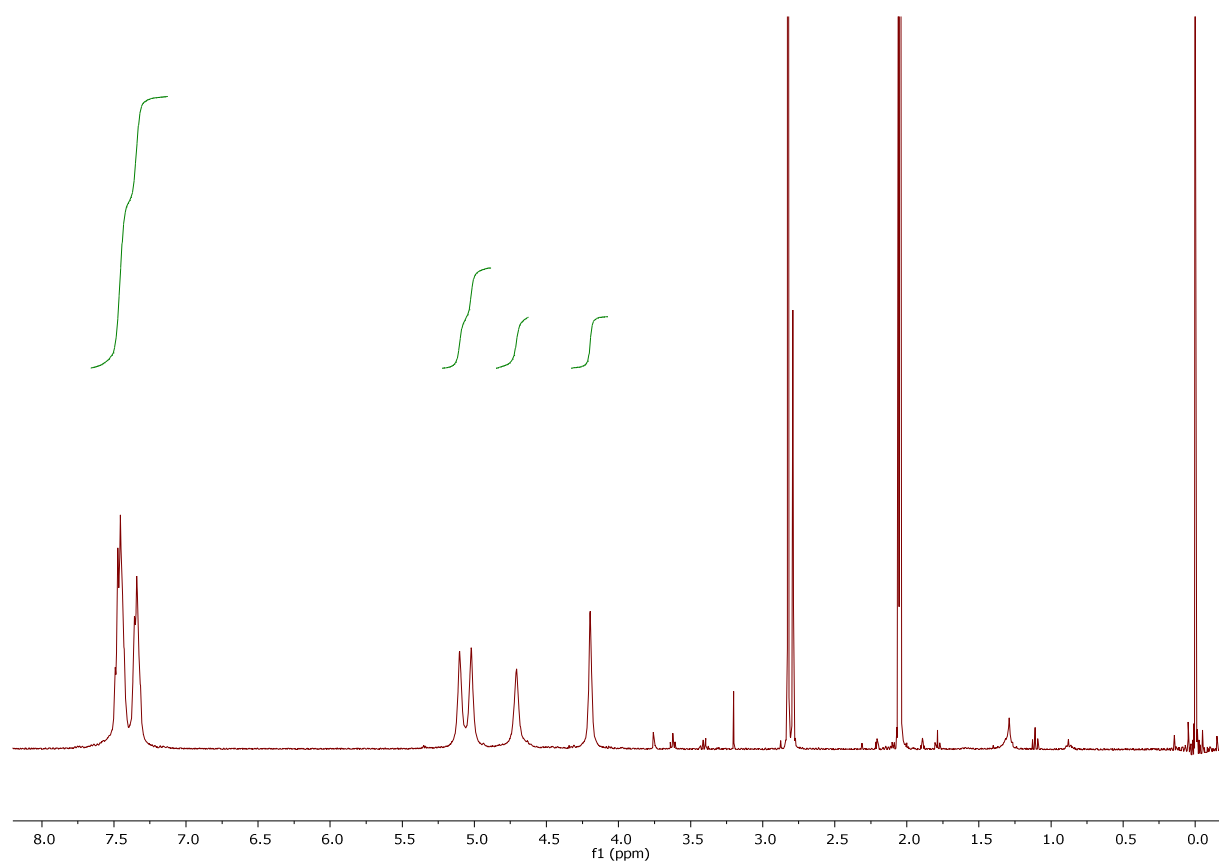


Figure S37. In situ ^1H NMR spectrum of **8** (acetone- d_6).

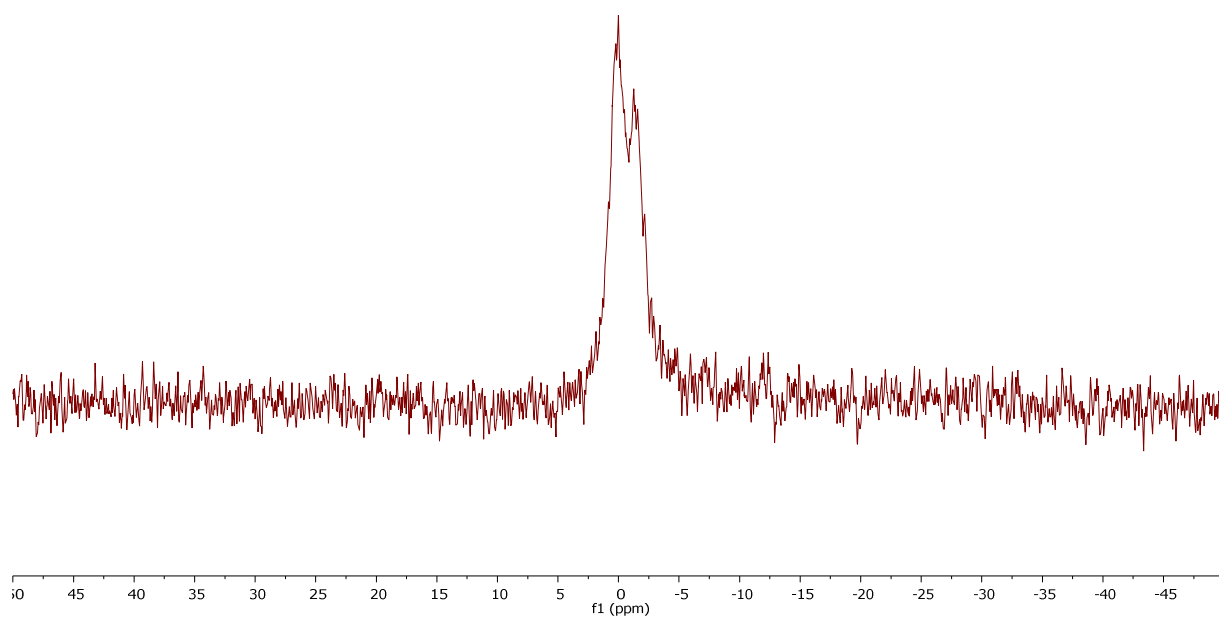


Figure S38. In situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** (acetone- d_6).

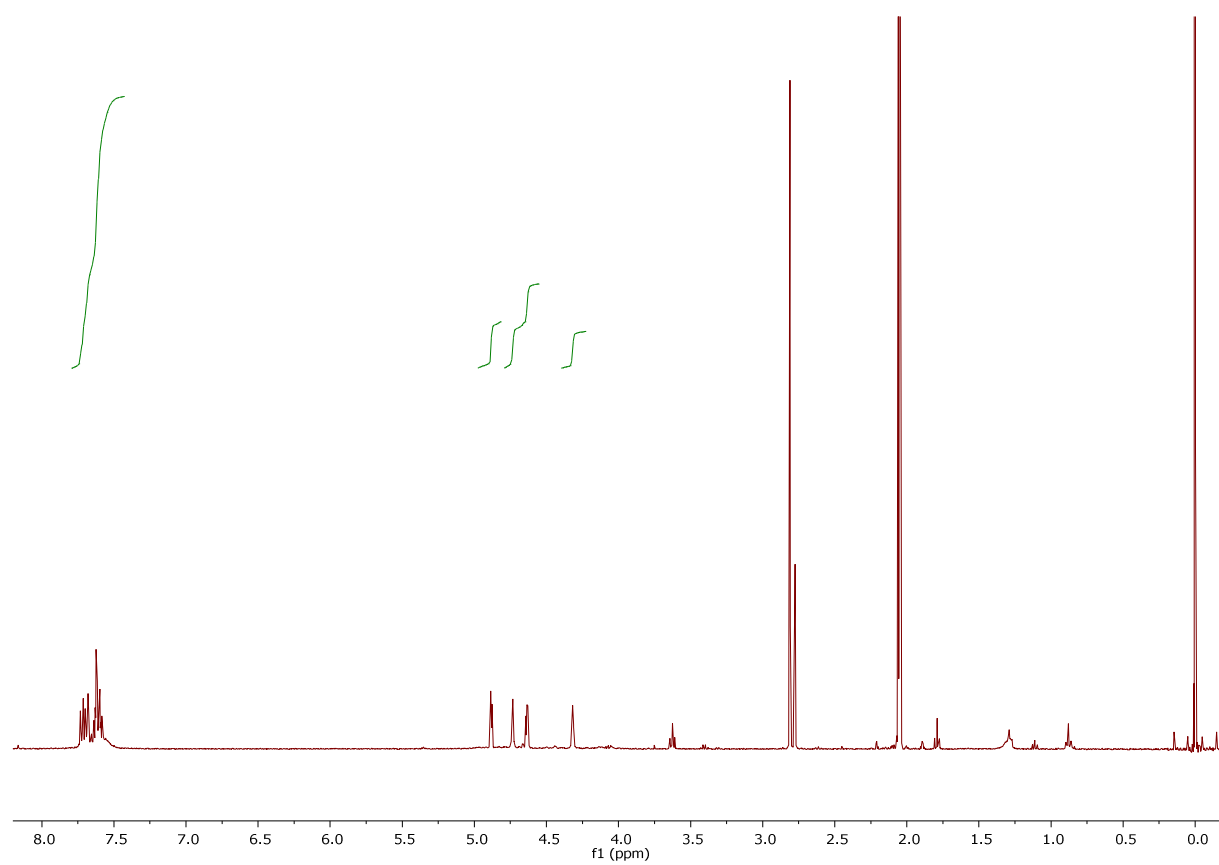


Figure S39. ^1H NMR spectrum of **9** (acetone- d_6).

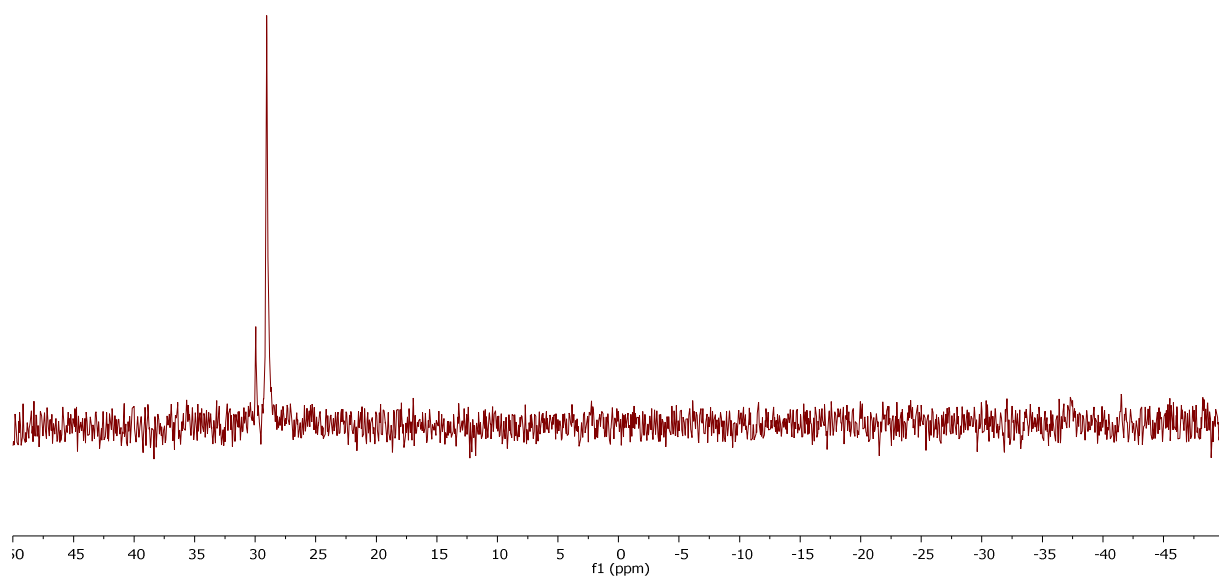


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (acetone- d_6).

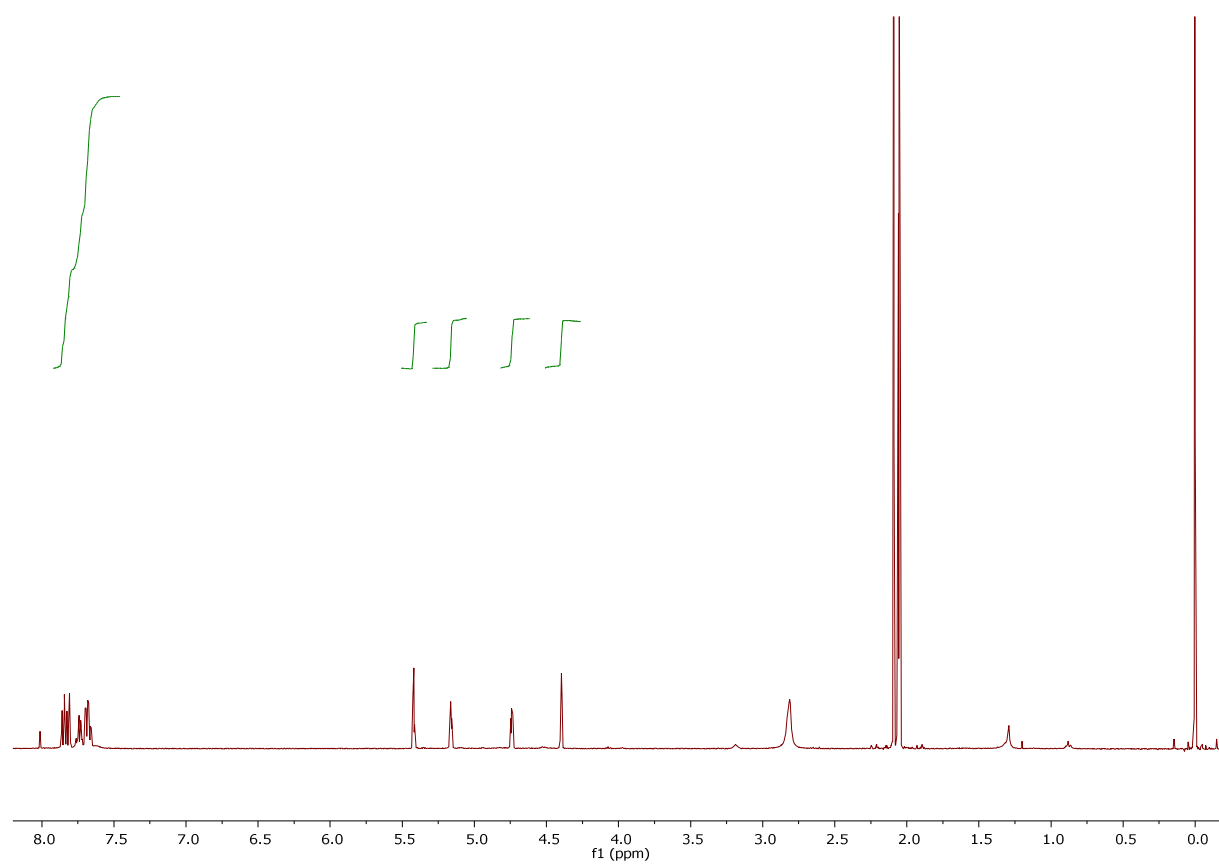


Figure S41. ^1H NMR spectrum of **11a** (acetone- d_6).

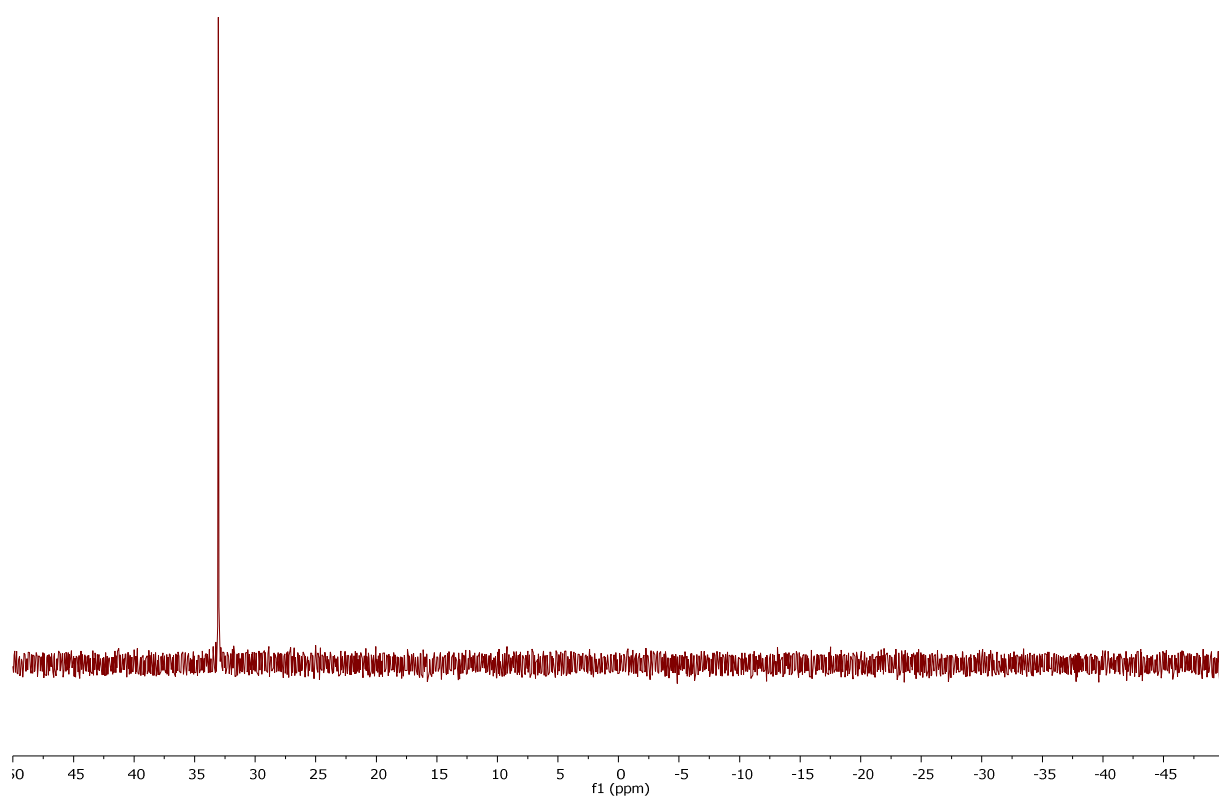


Figure S42. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11a** (acetone- d_6).

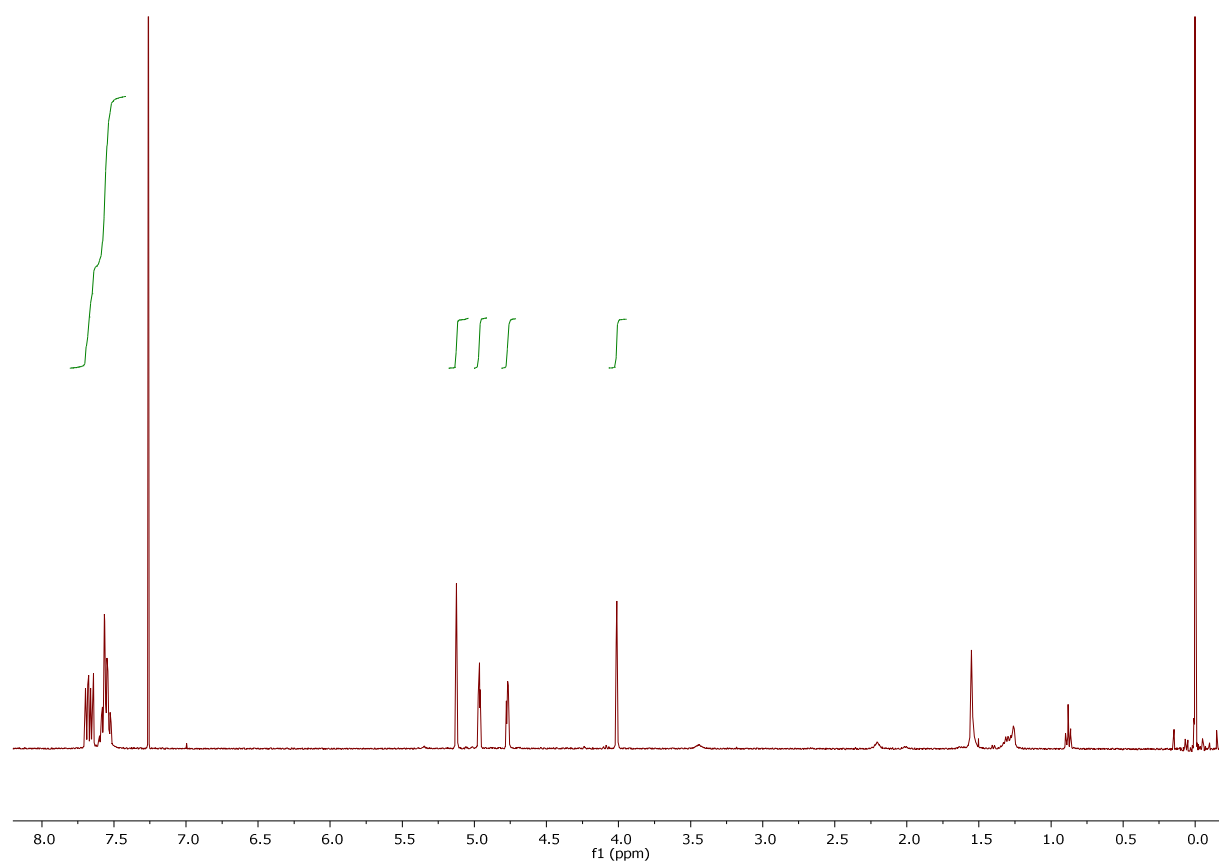


Figure S43. ^1H NMR spectrum of **11b** (CDCl_3).

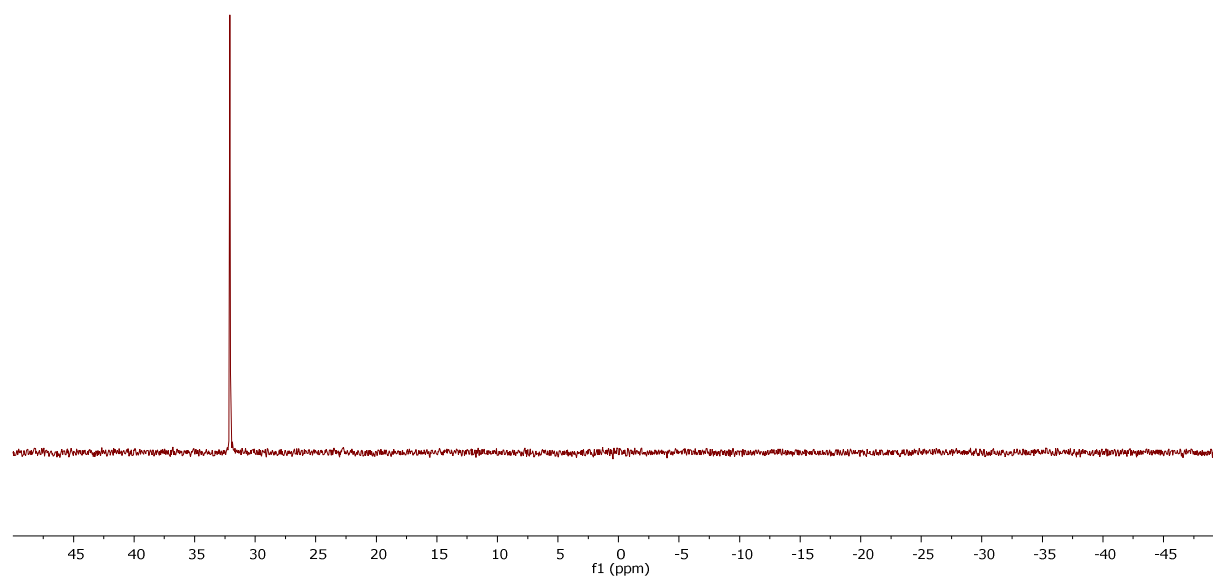


Figure S44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11b** (CDCl_3).

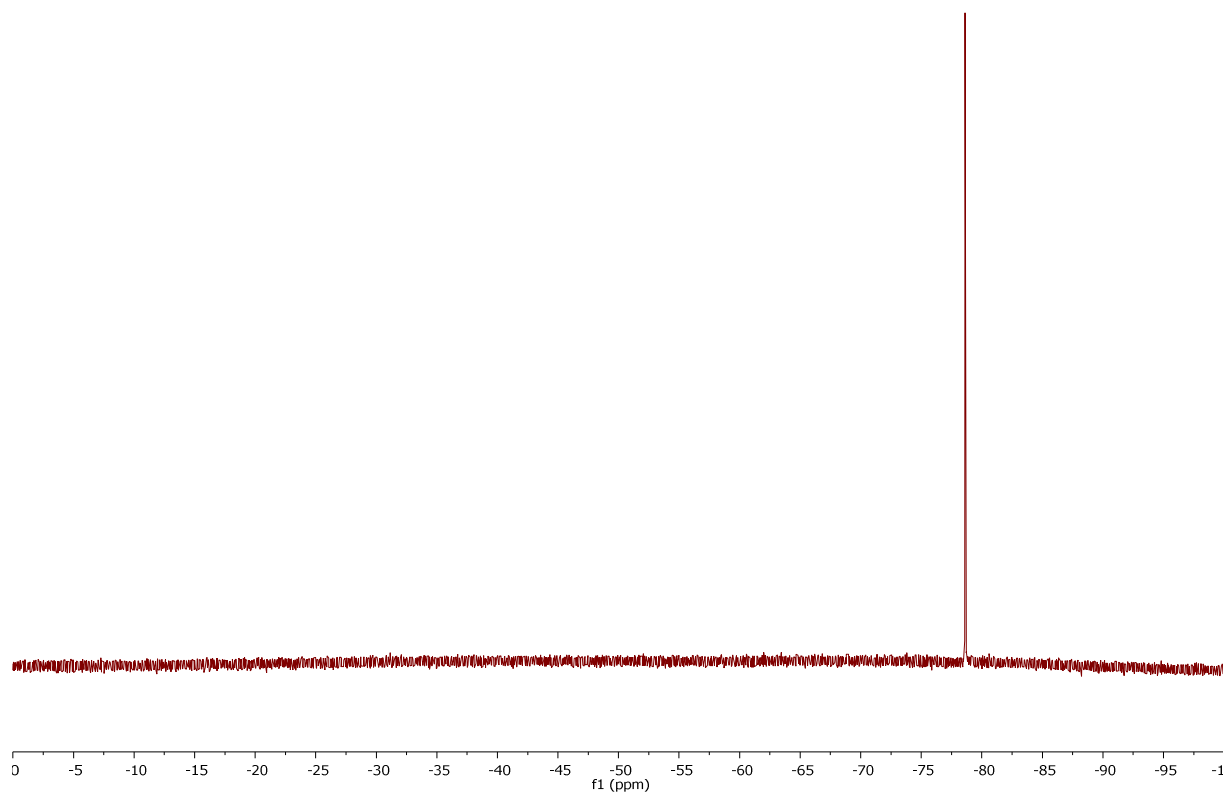


Figure S45. ^{19}F NMR spectrum of **11b** (CDCl_3).