# Supporting Information

# Developing bulky P-alkene ligands: Stabilization of copper complexes with 14 valence electrons

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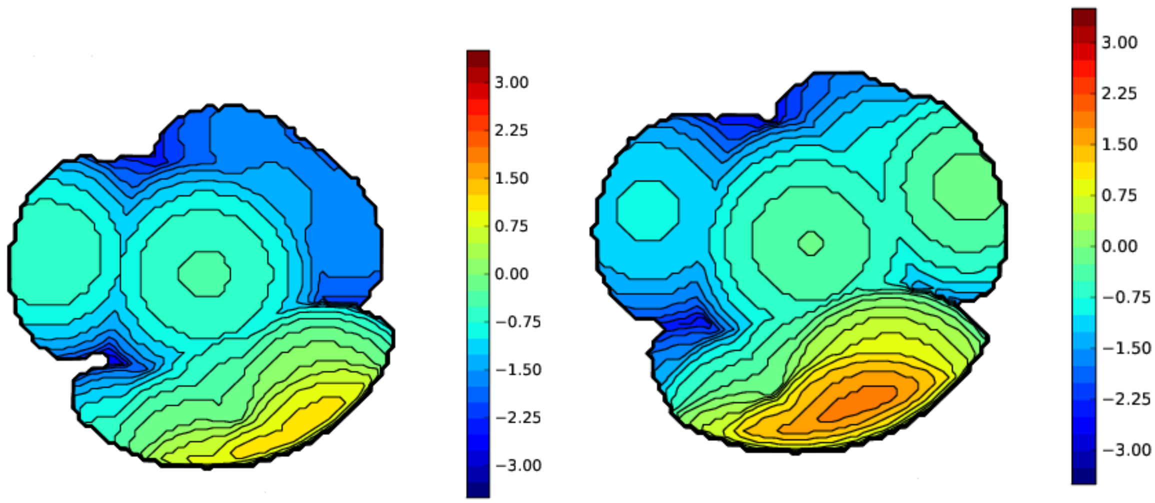
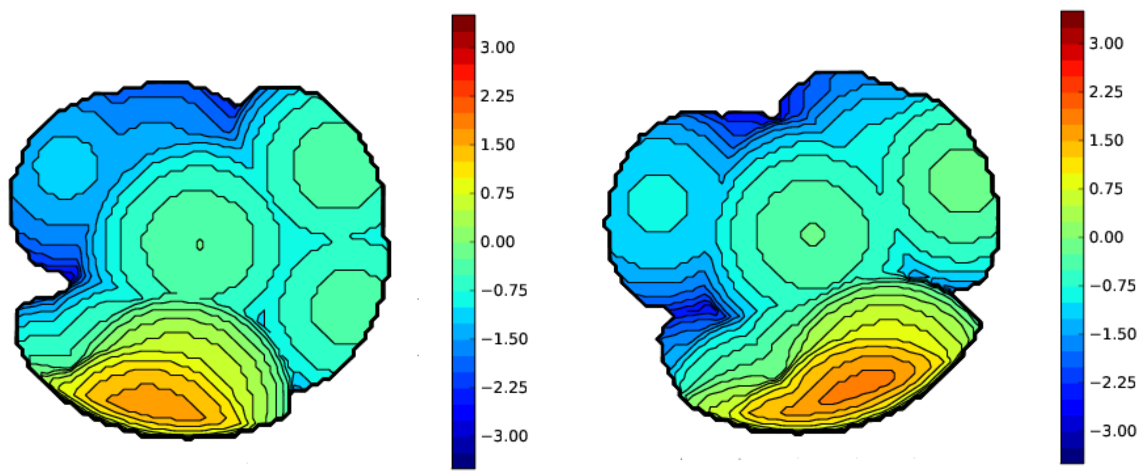
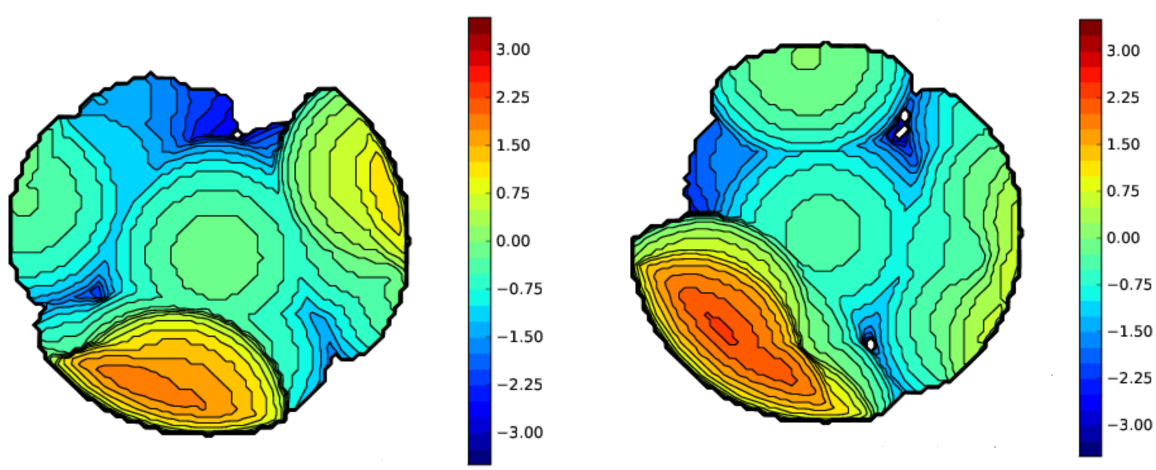



Topographic map of **7** coordinated in complex **10 (left)** and complex **14 (right)**.




Topographic map of **7** coordinated in complex **16 (left**) and of **8** in complex **12 (right).**




Topographic map of **9** coordinated in complex **18** (**left**) and of **20** in complex **22 (right)**.

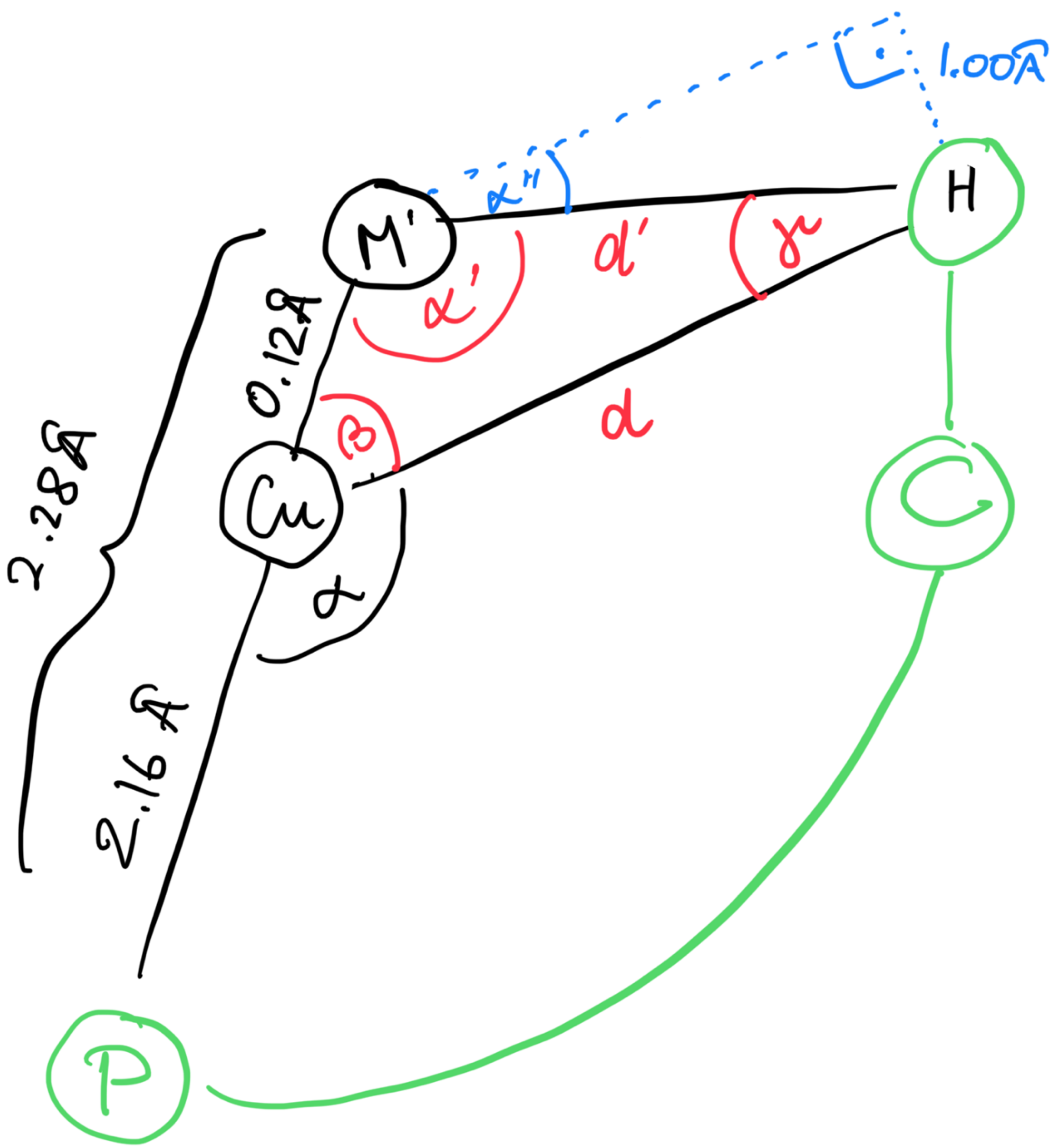
The steric maps were generated with SambVca 2.1 and are based on the crystal structures. Sphere radius is 3.5 Å, and Bondi radii are scaled at 1.17. For all complexes the Cu atom was defined as the centre of the sphere and the z axis was placed along the Cu-P bond. In the dimeric complexes **12** and **22**, the Cu, Cl, and H atoms were not included in the calculations. In addition, for the monomeric complexes **10**, **12**, **14**, **16**, and **18** one of the two ligand was excluded.

| ligand | complex | $V\%_{bur}$ |
|---|---|---|
| | **10** | 33.9 |
| **7** | **14** | 36.6 |
| | **16** | 38.2 |
| **8** | **12** | 37,7 |
| **9** | **18** | 43.5 |
| **20** | **22** | 46.6 |
| **21** | **23** | 60.6 |

**Table S1**: Values of the buried volumes of the ligands in complexes.

Crystallographic Tolman angle in complex **23**

Müller, T. E.; Mingos, D. M. P. Determination of the Tolman cone angle from parameters and a statistical analysis using the Crystallographic Data Base *Transition Met. Chem*. **1995**, *20*, 533-539.



Law of cosines:

$$a^2 = b^2 + c^2 - 2b.c.cosA$$

$$d'^2 = d^2 + 12^2 - 2.d.12.\cos\beta$$

$$\boldsymbol{d' = \pm\sqrt{(d^2 + 12^2 - 2.d.12.\cos\beta)}}$$

Law of sines:

$$\frac{a}{sinA} = \frac{b}{sinB} = \frac{c}{sinC}$$

$$\frac{12}{\sin\alpha'} = \frac{d'}{\sin\beta}$$

$$\sin\alpha' = \frac{12.\sin\beta}{d'}$$

$$\alpha' = \sin^{-1}\frac{12.\sin\beta}{d'}$$

In order to make sure that the principal value of $\sin^{-1}$ is correct it is preferrable to use:

$$\boldsymbol{\gamma = \sin^{-1}\frac{12.\sin\beta}{d'}}$$

Law of angles in triangle:

$$\alpha' + \beta + \gamma = 180$$

$$\boldsymbol{\alpha' = 180 - \gamma - \beta}$$

**N1 – H7** $\theta_1 = 110.7°$

$d = 307.6 \quad \alpha = 93.98° \quad \beta = 86.02°$

$d' = 307.0 \Rightarrow \alpha' = 91.7° \quad ; \quad \frac{r_H}{d'} = 0.3257$

$\gamma = 2.23°$

$\alpha'' = 19.0°$

**N2 – H25** $\theta_2 = 113.3°$

$d = 508.3 \quad \alpha = 103.21° \quad \beta = 76.79°$

$d' = 505.7$

$\gamma = 1.32° \Rightarrow \alpha' = 101.9° \quad ; \quad \frac{r_H}{d'} = 0.1977$

$\alpha'' = 11.4°$

**N3 – H39** $\theta_3 = 119.6°$

$d = 494.9 \quad \alpha = 109.25° \quad \beta = 70.75°$

$d' = 491.1 \quad ; \quad \frac{r_H}{d'} = 0.2036$

$\gamma = 1.32° \Rightarrow \alpha' = 107.9° \quad \alpha'' = 11.7°$

$\sum \theta_i = 343.7°$

$\Theta = 229°$

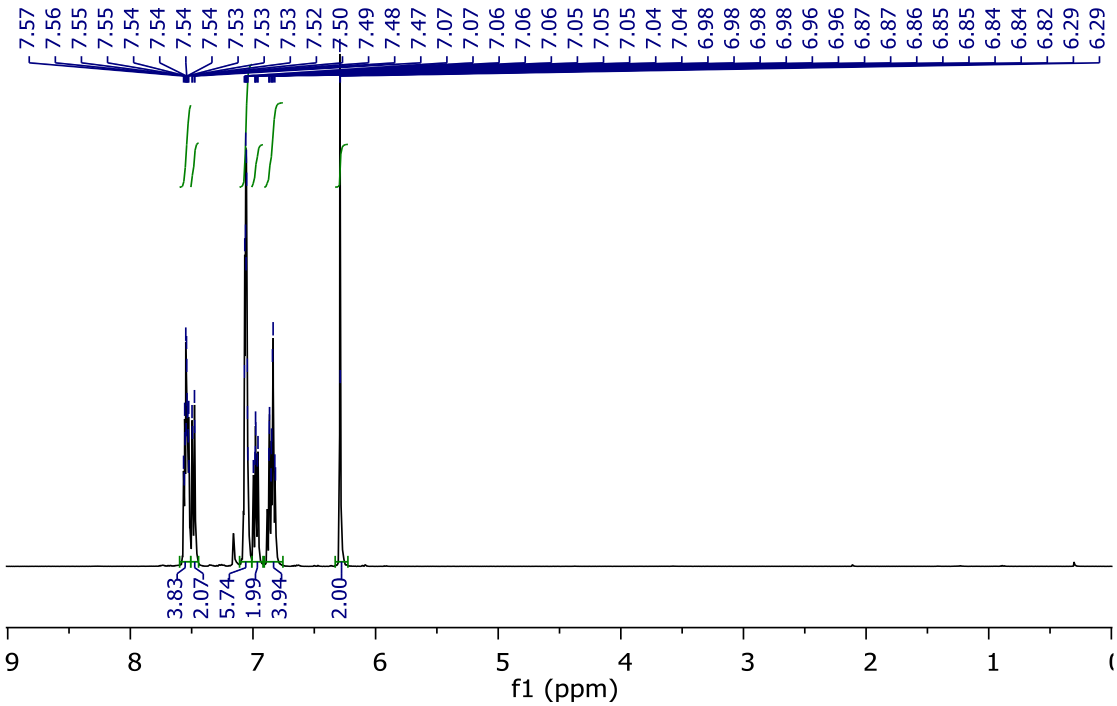



**Figure S1**: $^{1}$H NMR of **7** in $C_6D_6$.

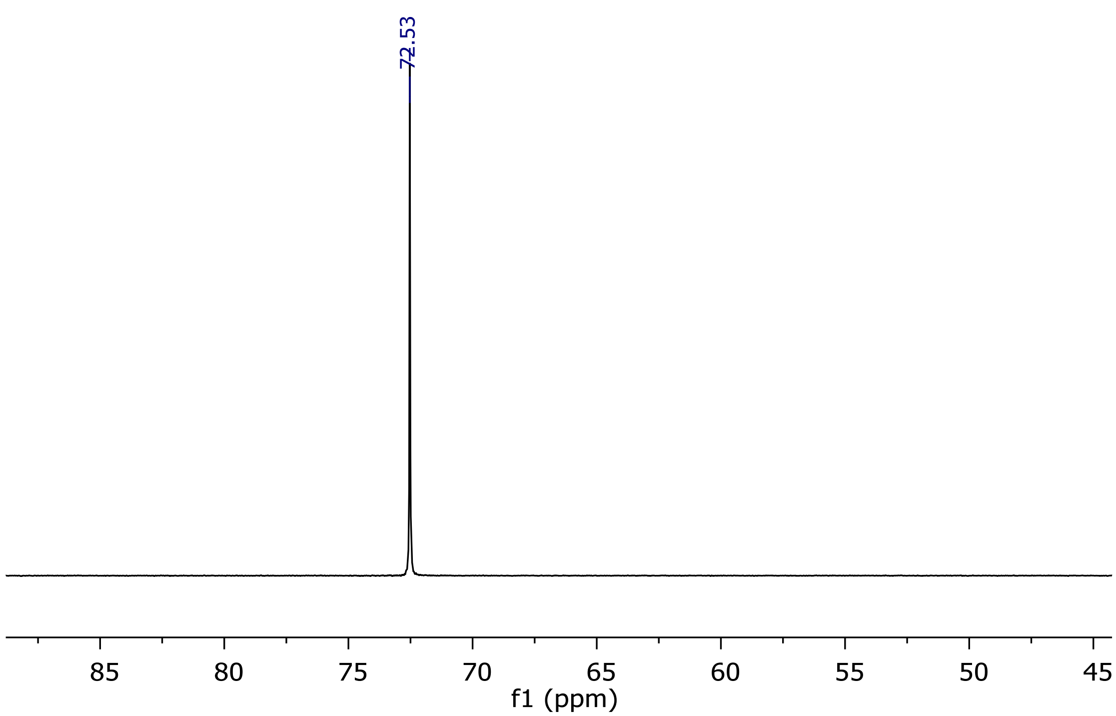



**Figure S2**: $^{31}$P NMR of **7** in $C_6D_6$.

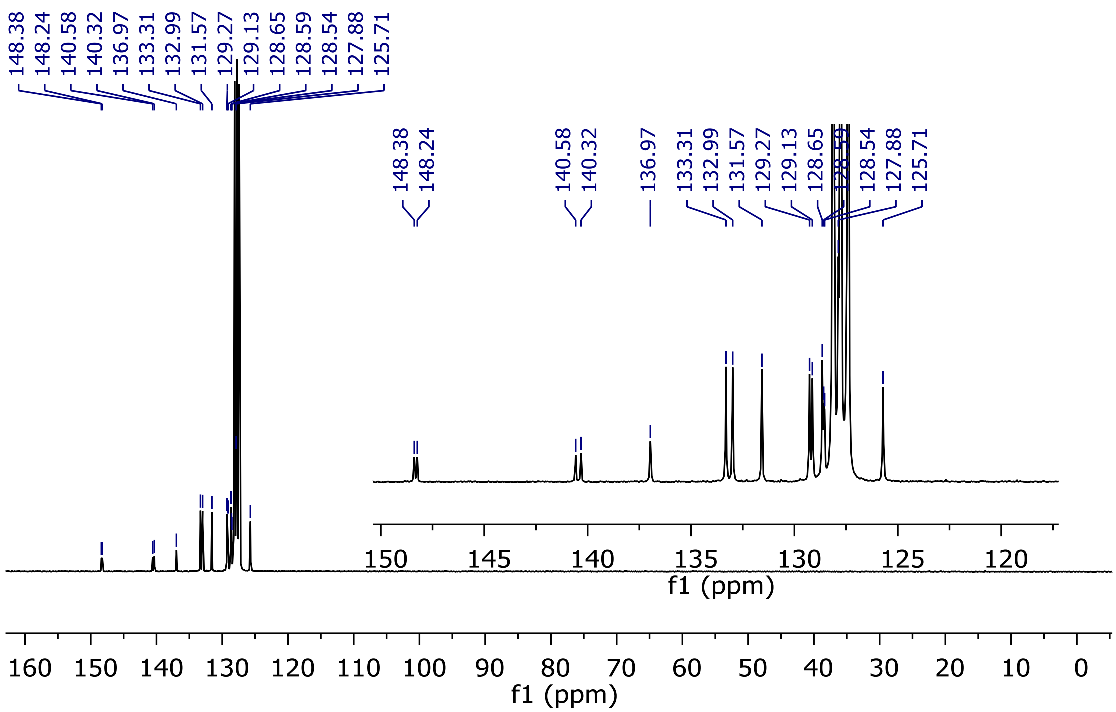



**Figure S3**: $^{13}C$ NMR of **7** in $C_6D_6$.

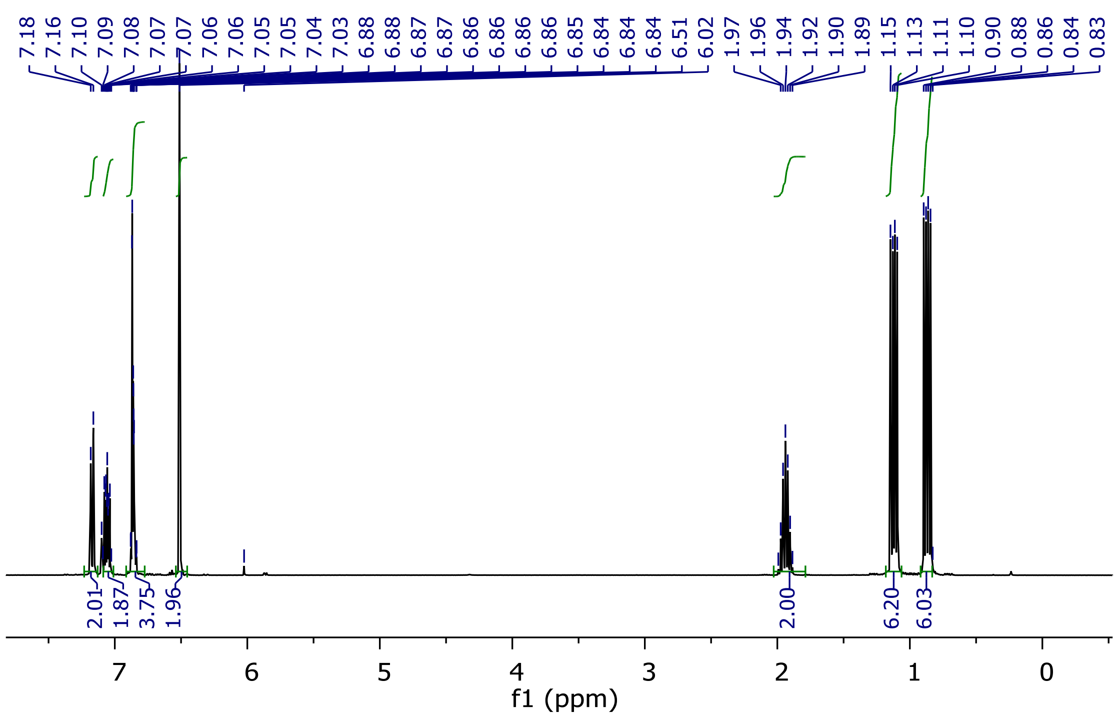



**Figure S4**: $^{1}H$ NMR of **8** in $C_6D_6$.

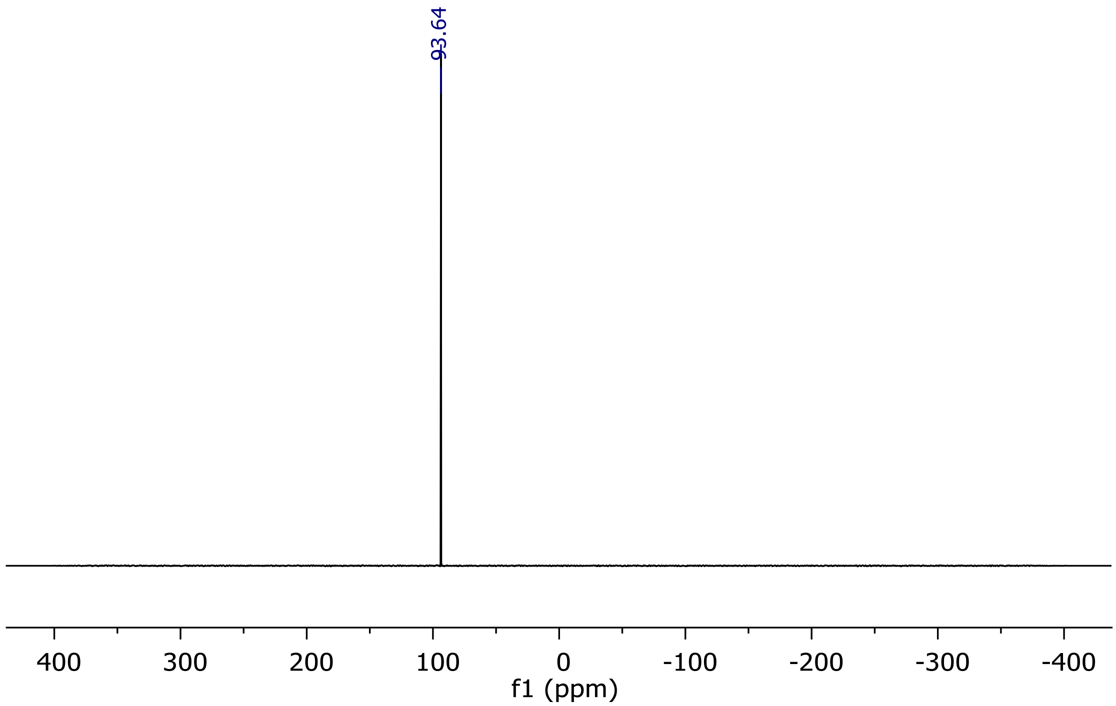



**Figure S5**: $^{31}P$ NMR of **8** in $C_6D_6$.

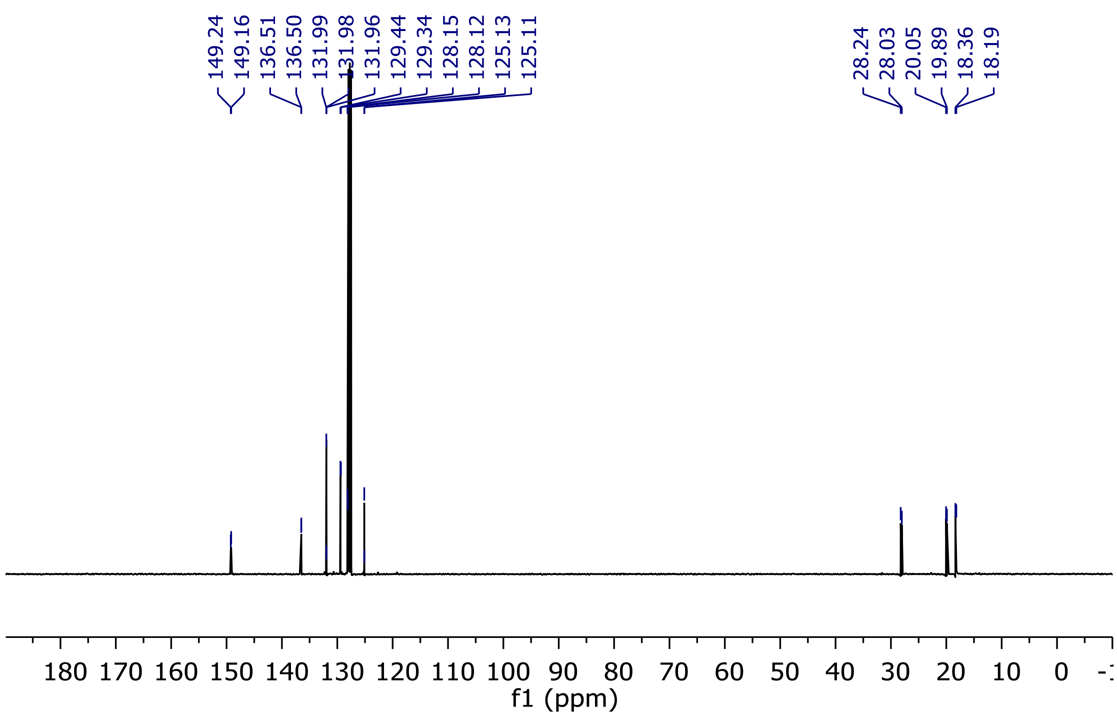



**Figure S6:** $^{13}C$ NMR of **8** in $C_6D_6$.

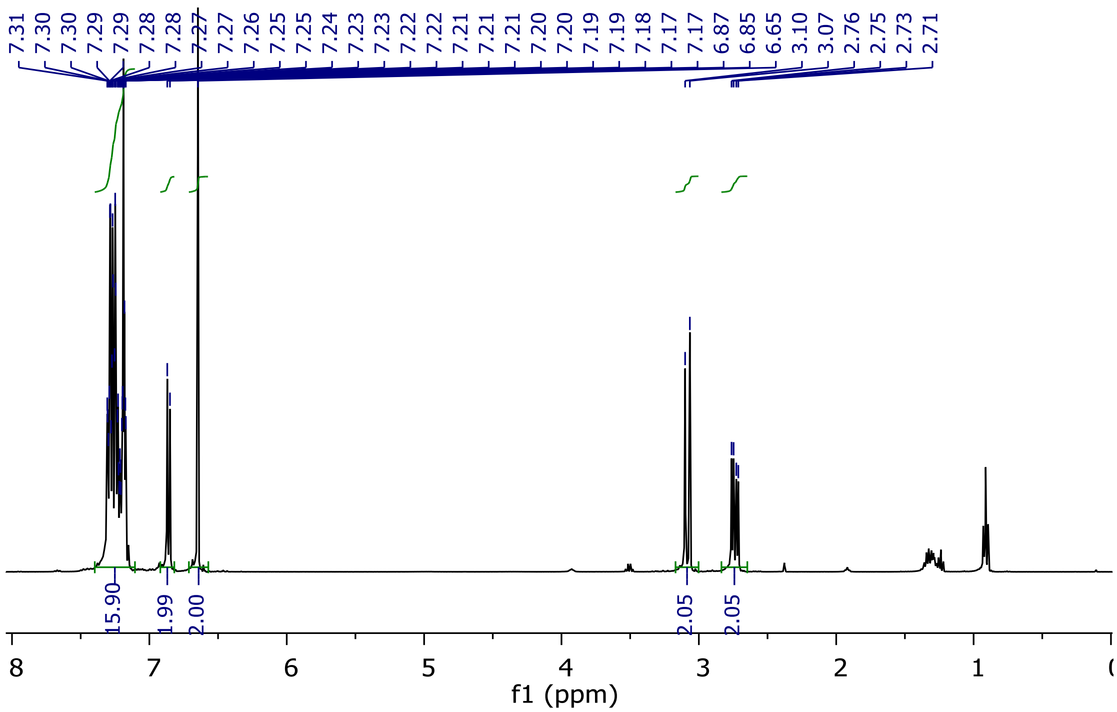



**Figure S7**: $^{1}H$ NMR of **9** in $CDCl_3$.

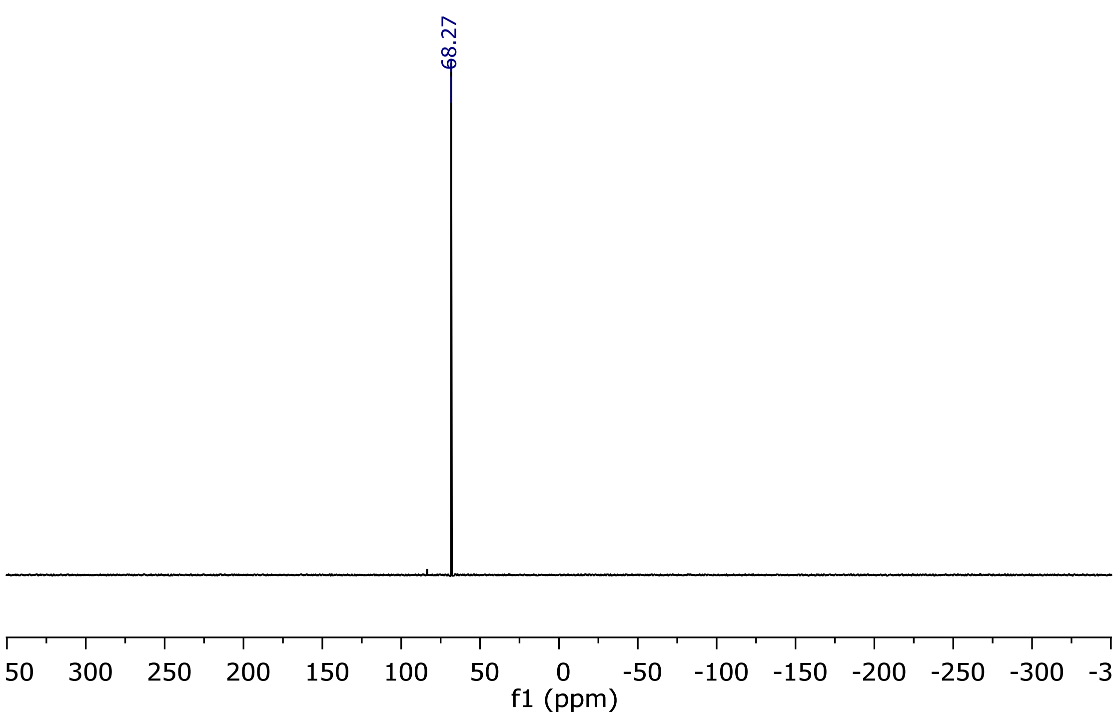



**Figure S8**: $^{31}P$ NMR of **9** in $CDCl_3$.

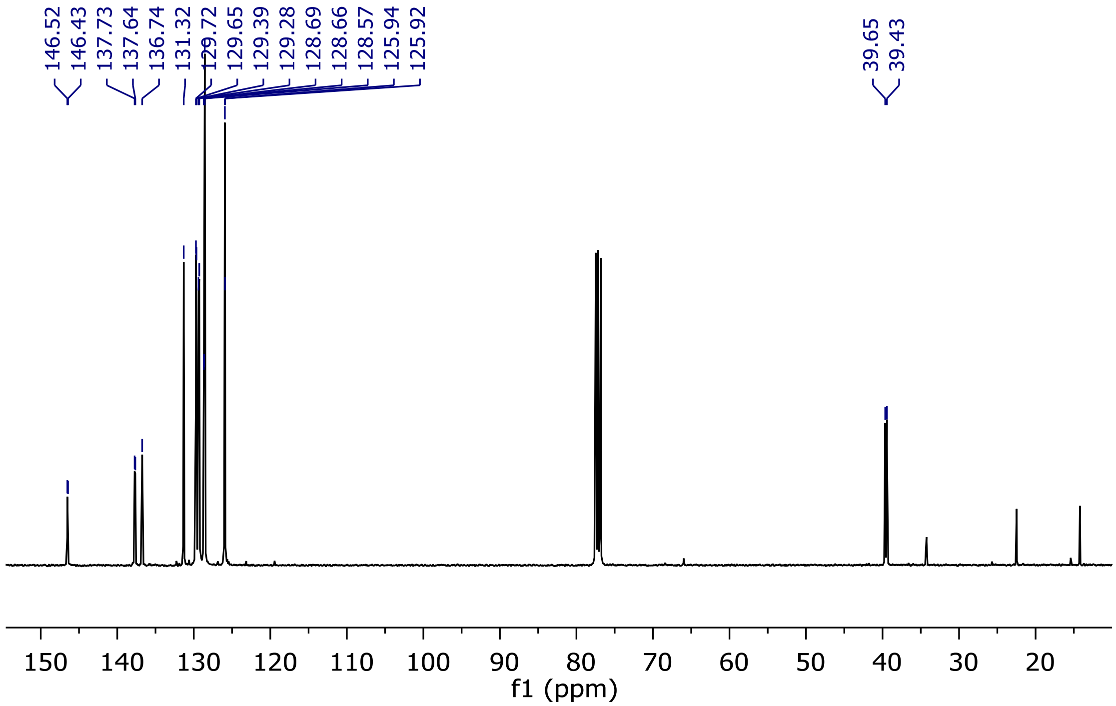



**Figure S9**: $^{13}C$ NMR of **9** in $CDCl_3$.

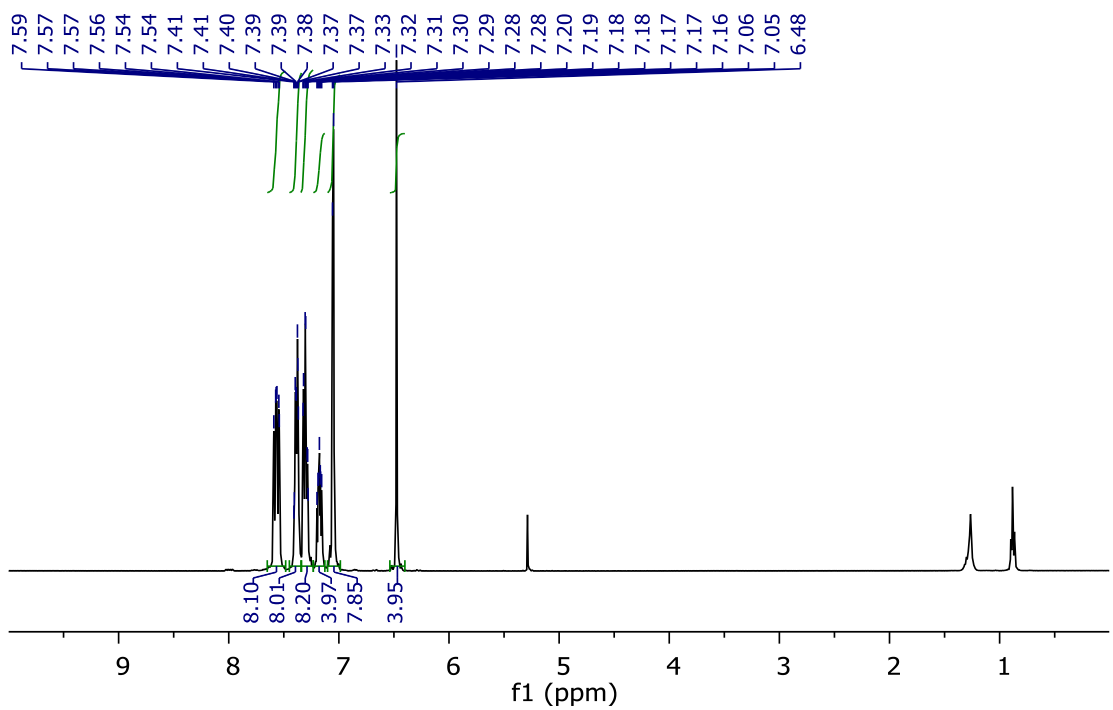



**Figure S10**: $^{1}H$ NMR of **10** in $CDCl_3$.

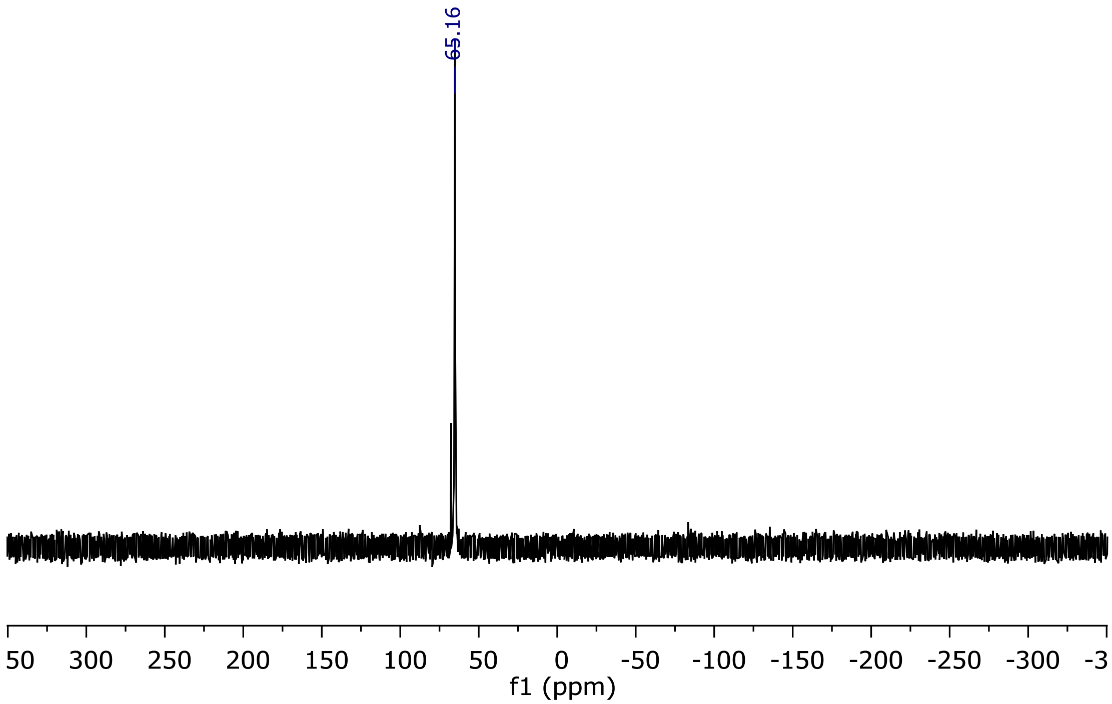



**Figure S11**: $^{31}$P NMR of **10** in $CDCl_3$ (the small peak is an artifact)

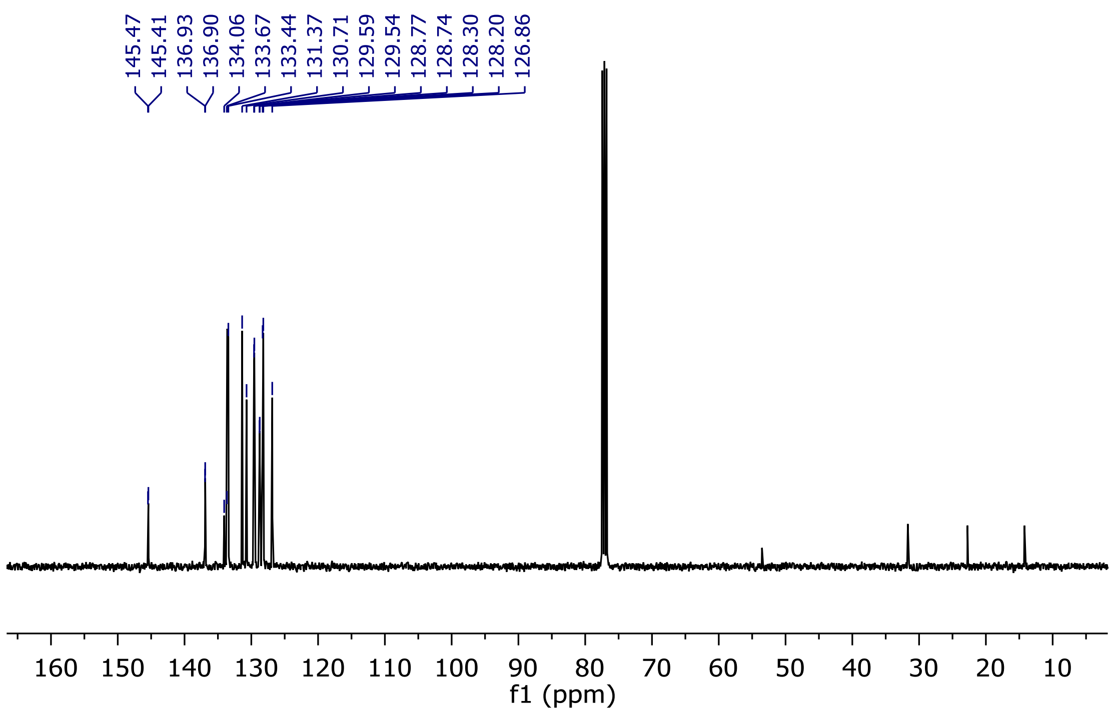



**Figure S12**: $^{13}$C NMR of **10** in $CDCl_3$.

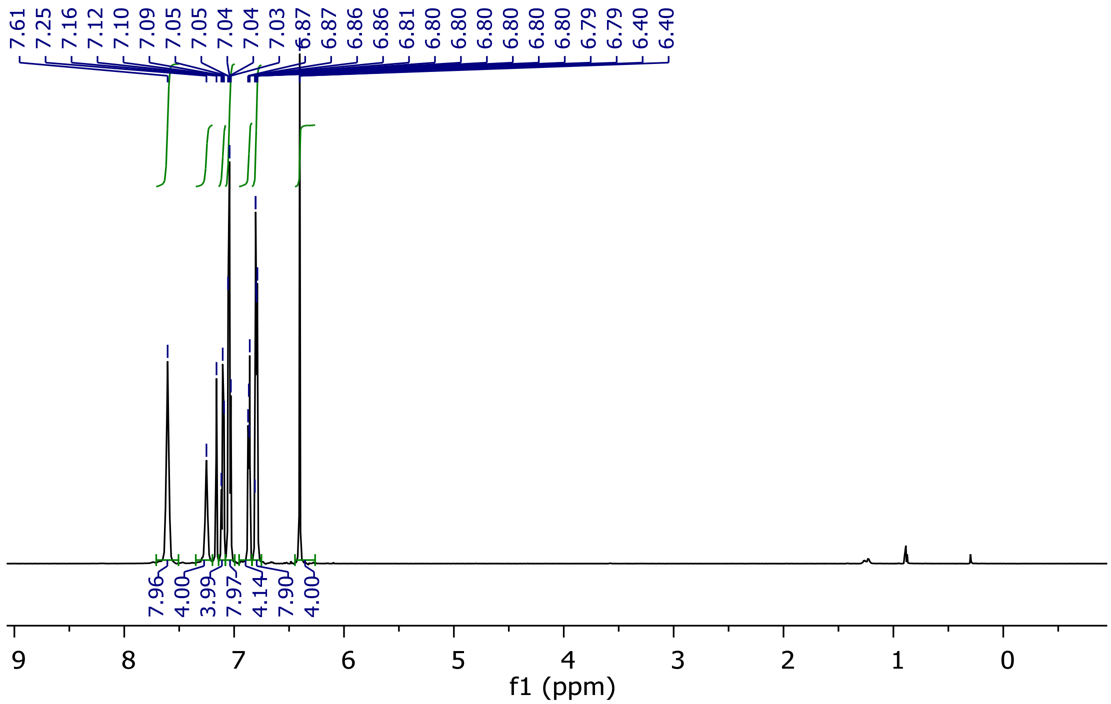



**Figure S13**: $^{1}$H NMR of **11** in $C_6D_6$.

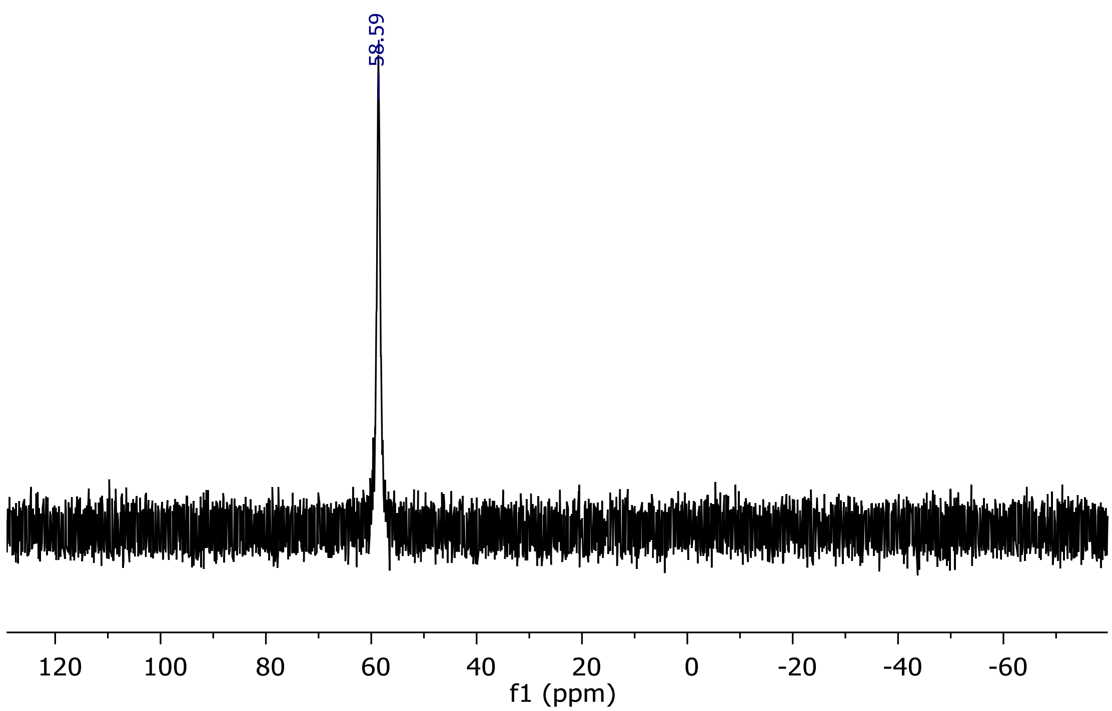



**Figure S14**: $^{31}$P NMR of **11** in $C_6D_6$.

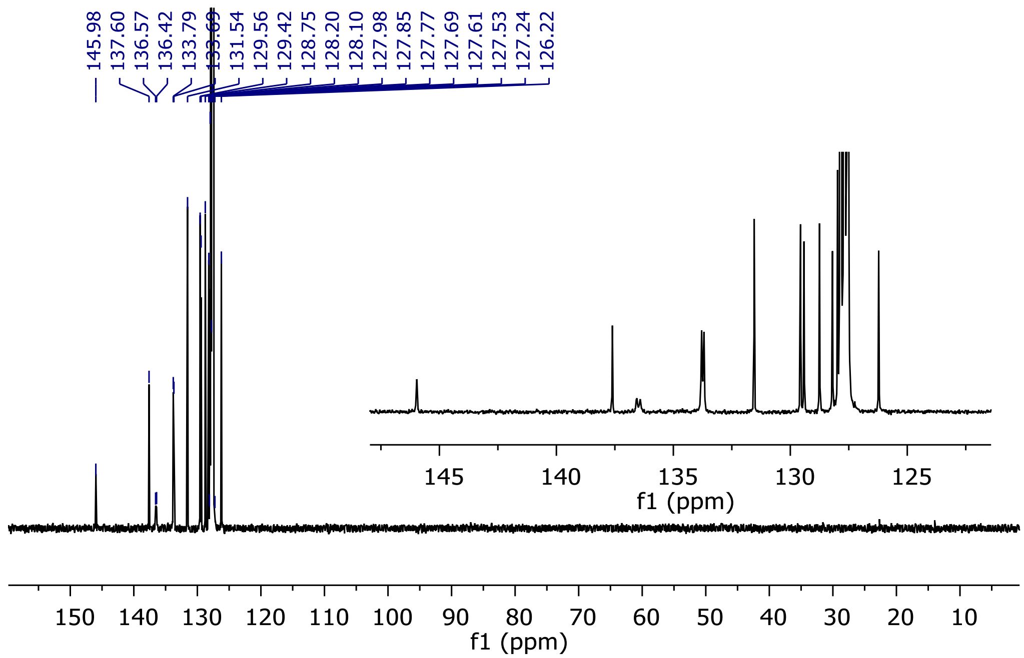



**Figure S15**: $^{13}$C NMR of **11** in $C_6D_6$.

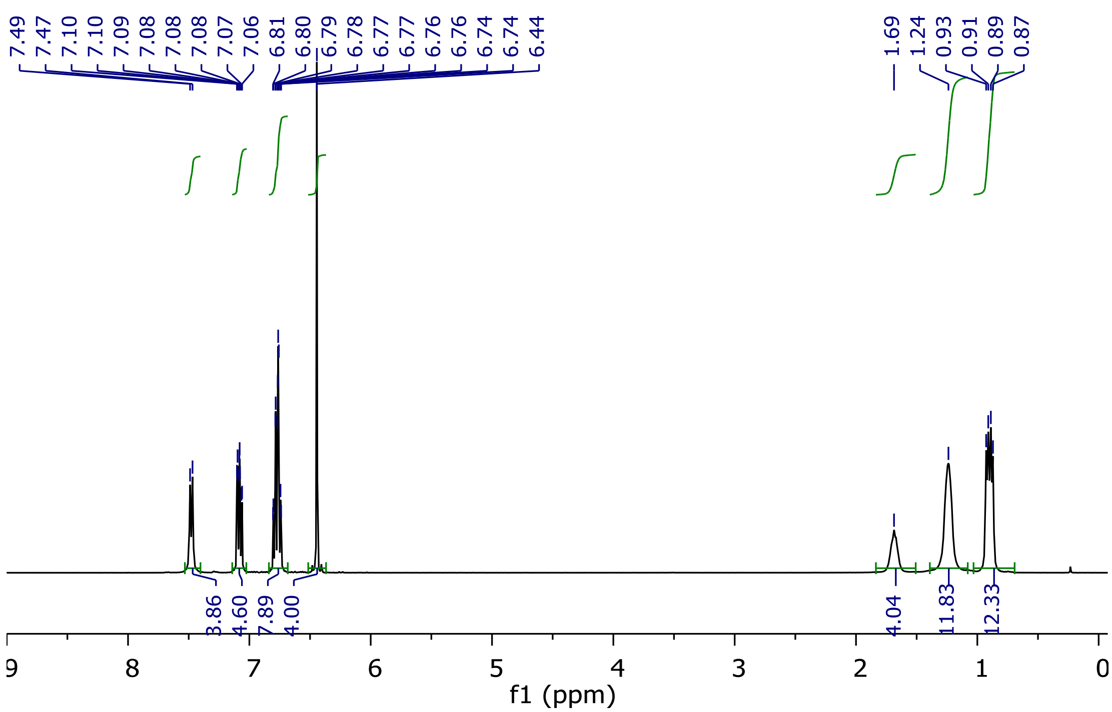



**Figure S16**: $^{1}$H NMR of **12** in $C_6D_6$.

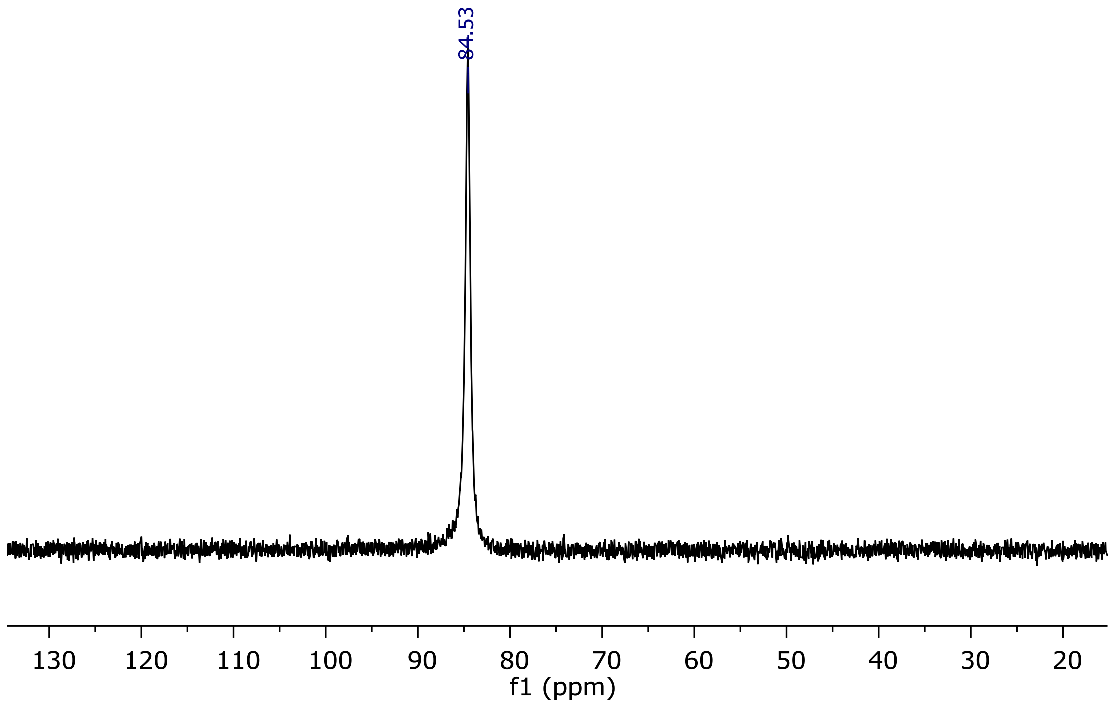



**Figure S17**: $^{31}$P NMR of **12** in $C_6D_6$.

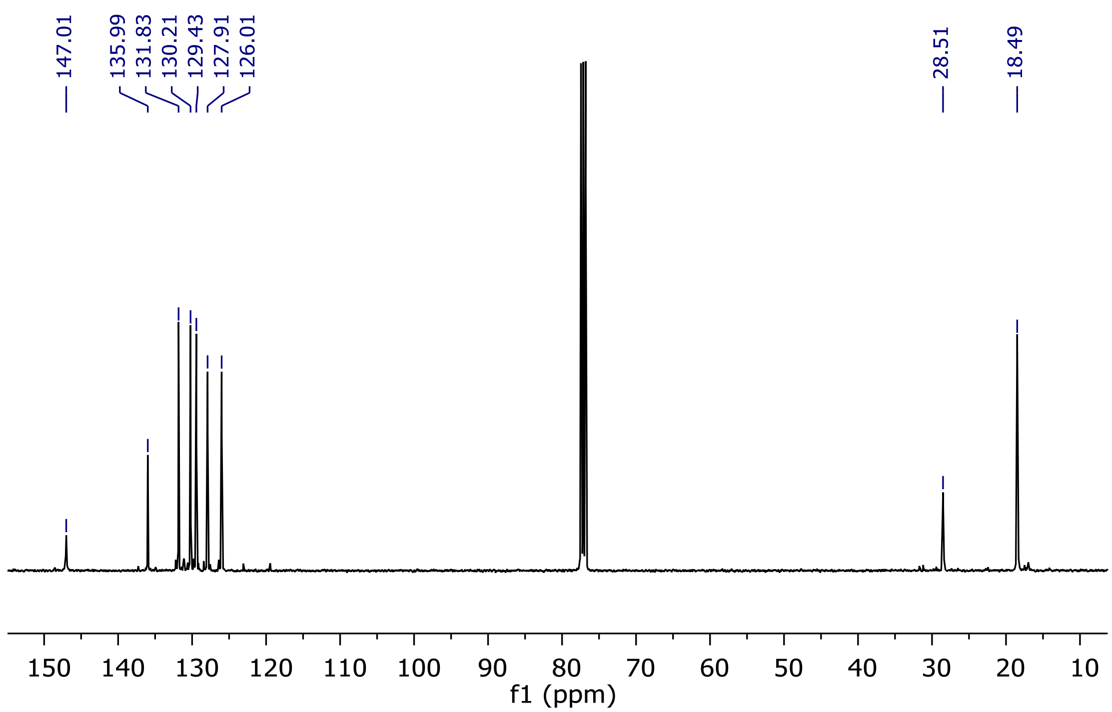



**Figure S18**: $^{13}$C NMR of **12** in $CDCl_3$.

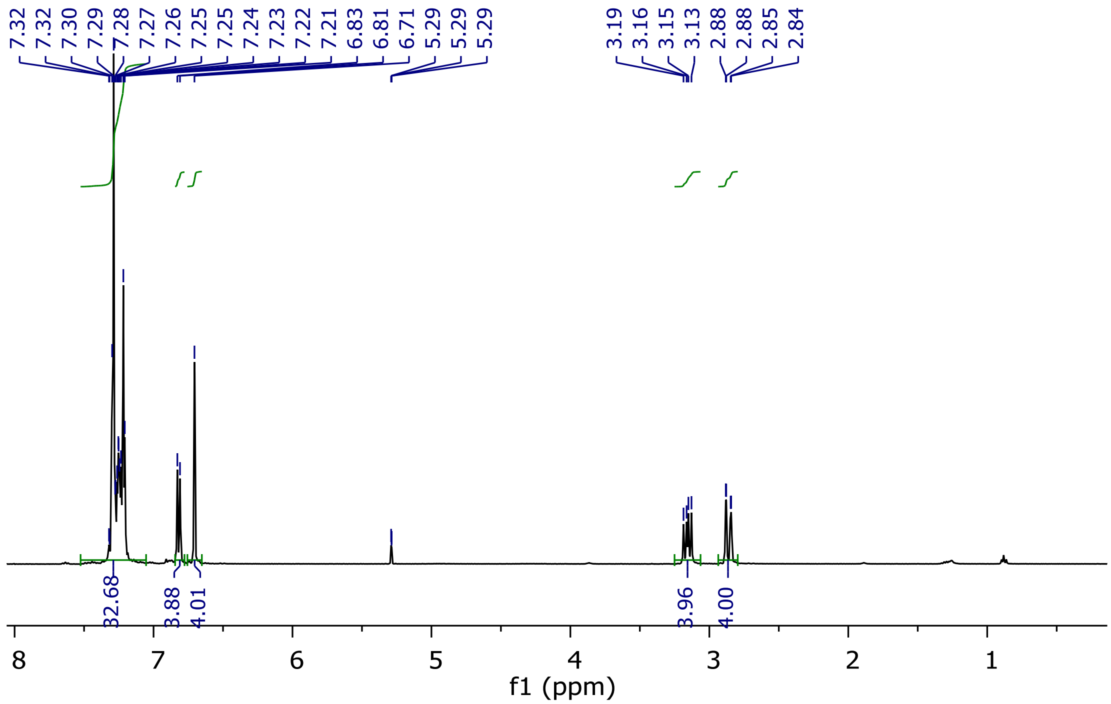



**Figure S19**: $^{1}$H NMR of **13** in $CDCl_3$.

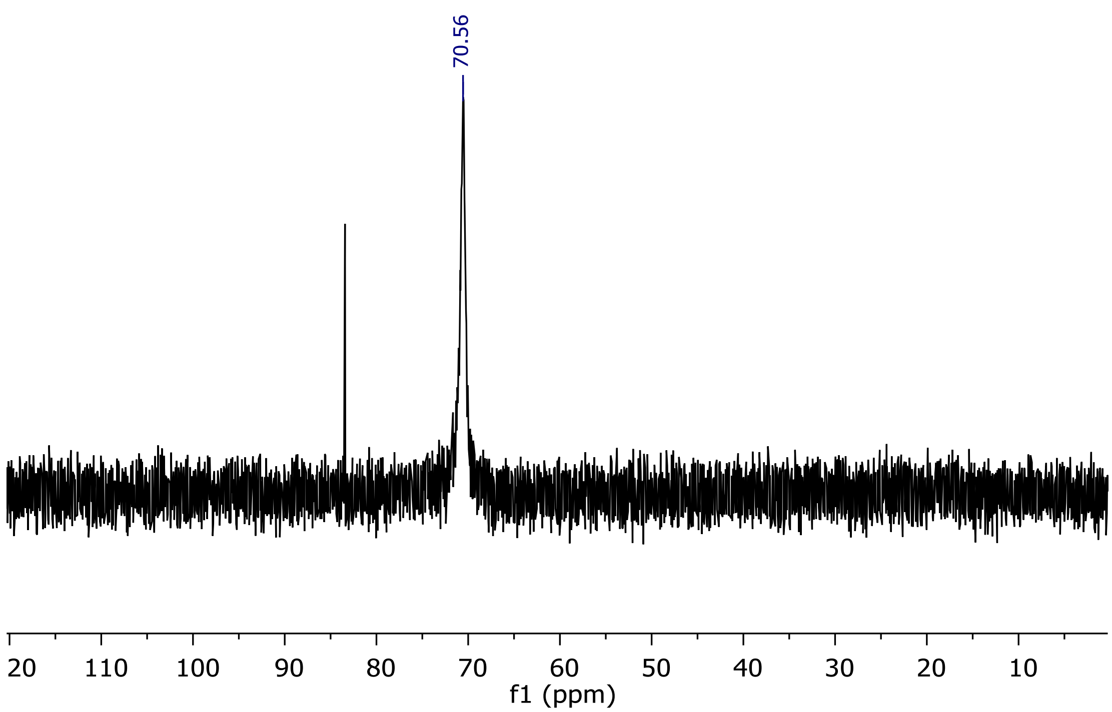



**Figure S20**: $^{31}$P NMR of **13** in $CDCl_3$ (the small peak is an artefact)

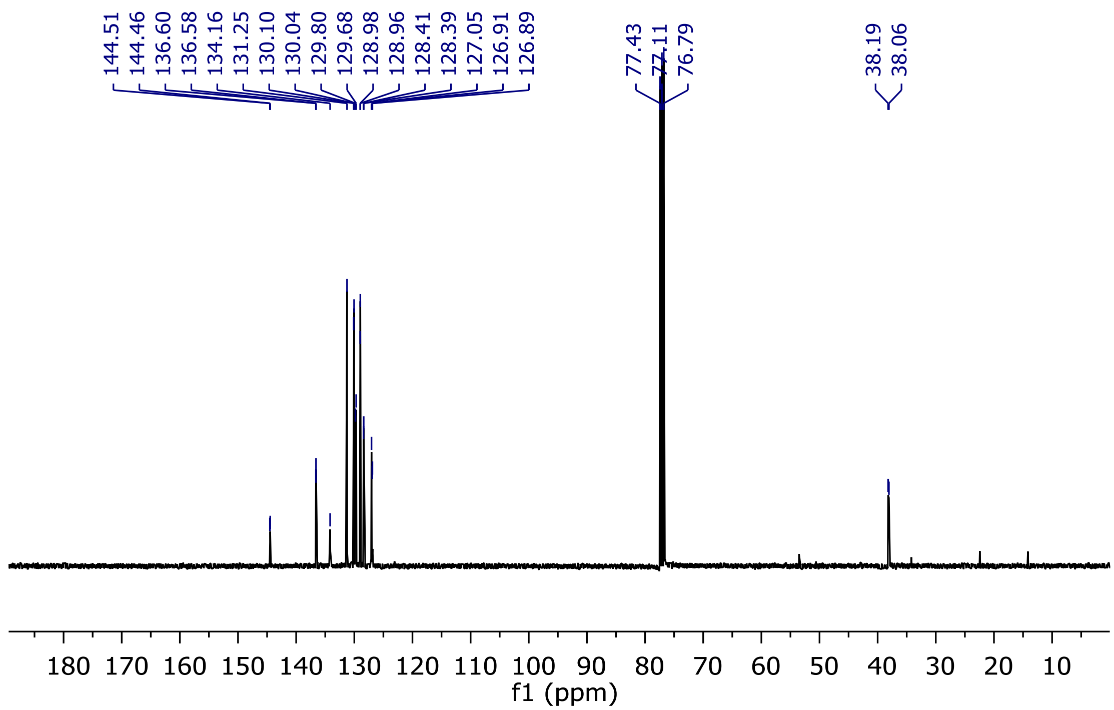



**Figure S21**: $^{13}$C NMR of **13** in $CDCl_3$.

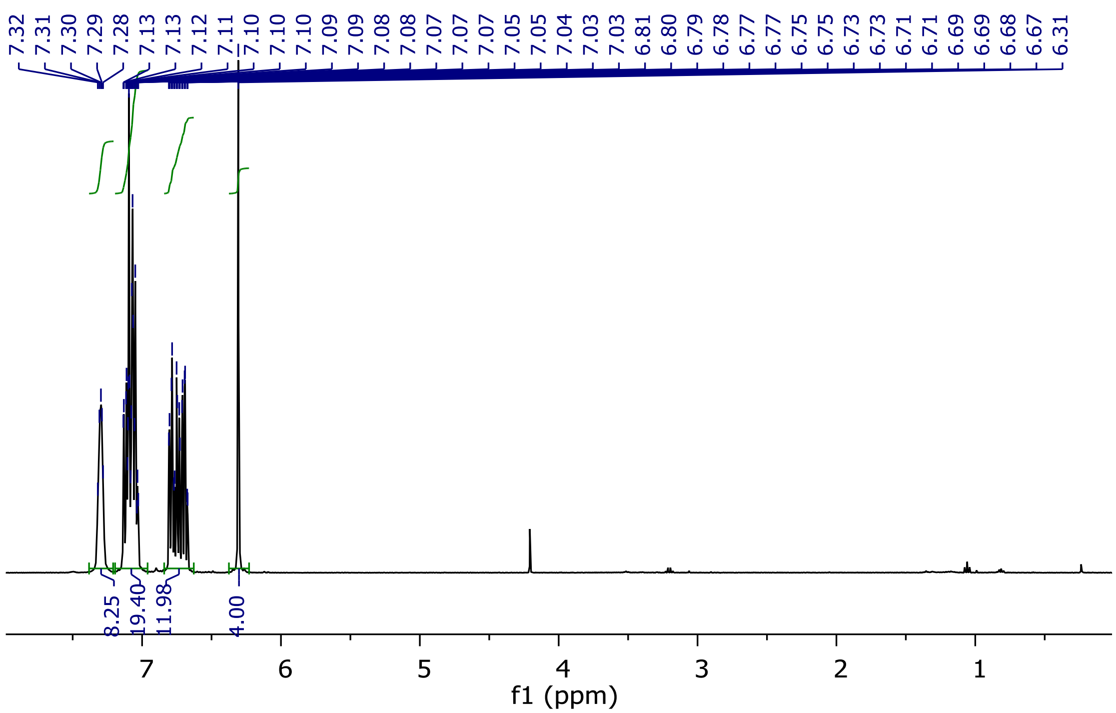



**Figure S22**: $^{1}$H NMR of **14** in $C_6D_6$.

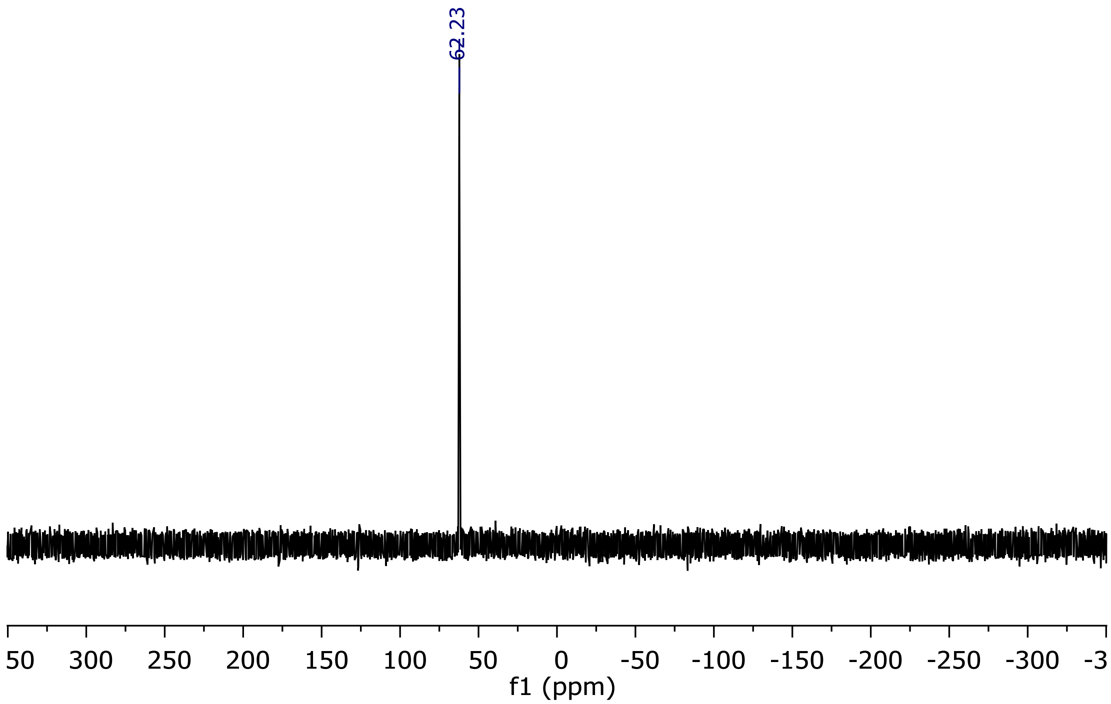



**Figure S23**: $^{31}$P NMR of **14** in $C_6D_6$.

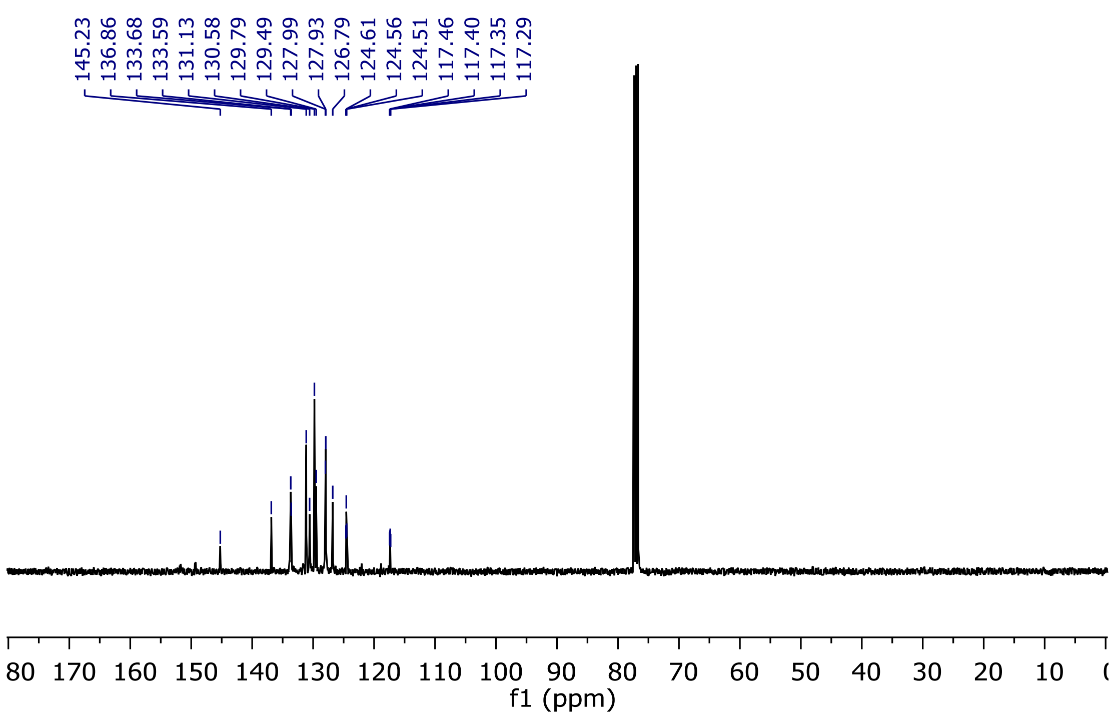



**Figure S24**: $^{13}$C NMR of **12** in $CDCl_3$.

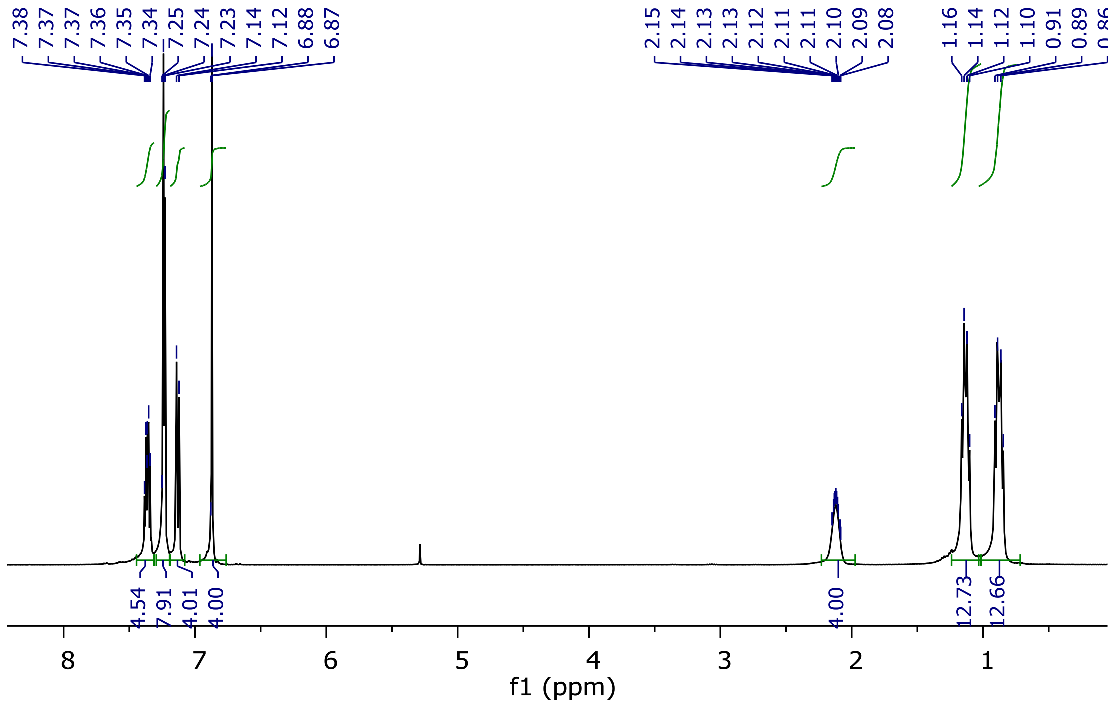



**Figure S25**: ${}^{1}H$ NMR of **13** in $CDCl_3$.

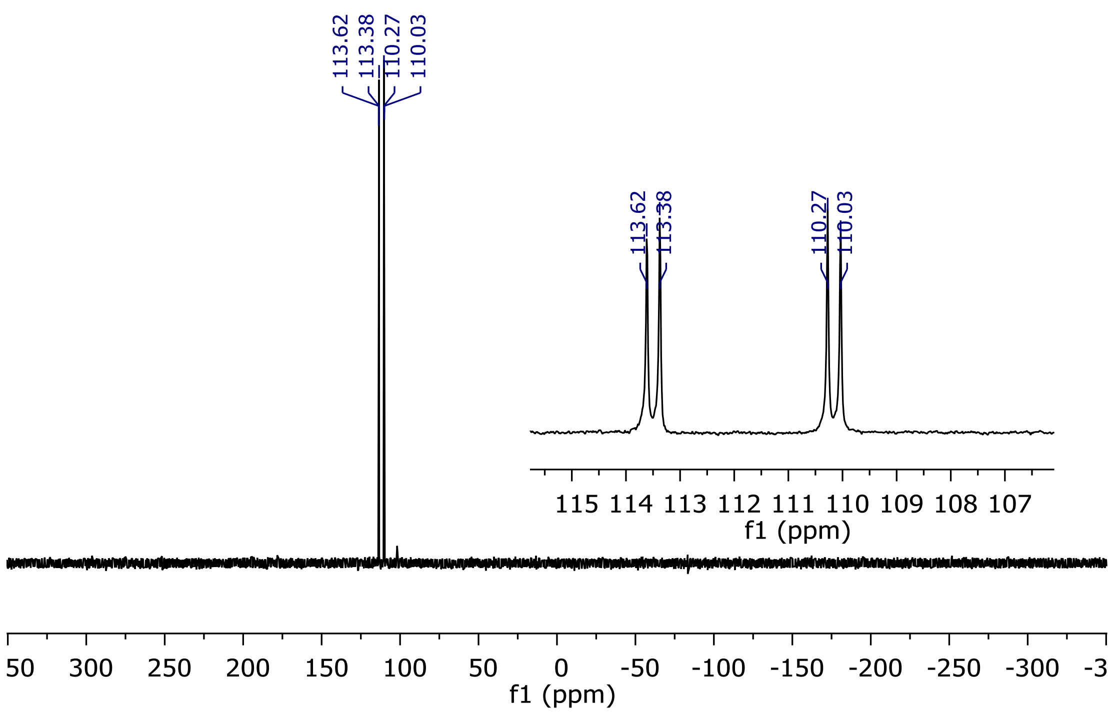



**Figure S26**: ${}^{31}P$ NMR of **13** in $CDCl_3$.

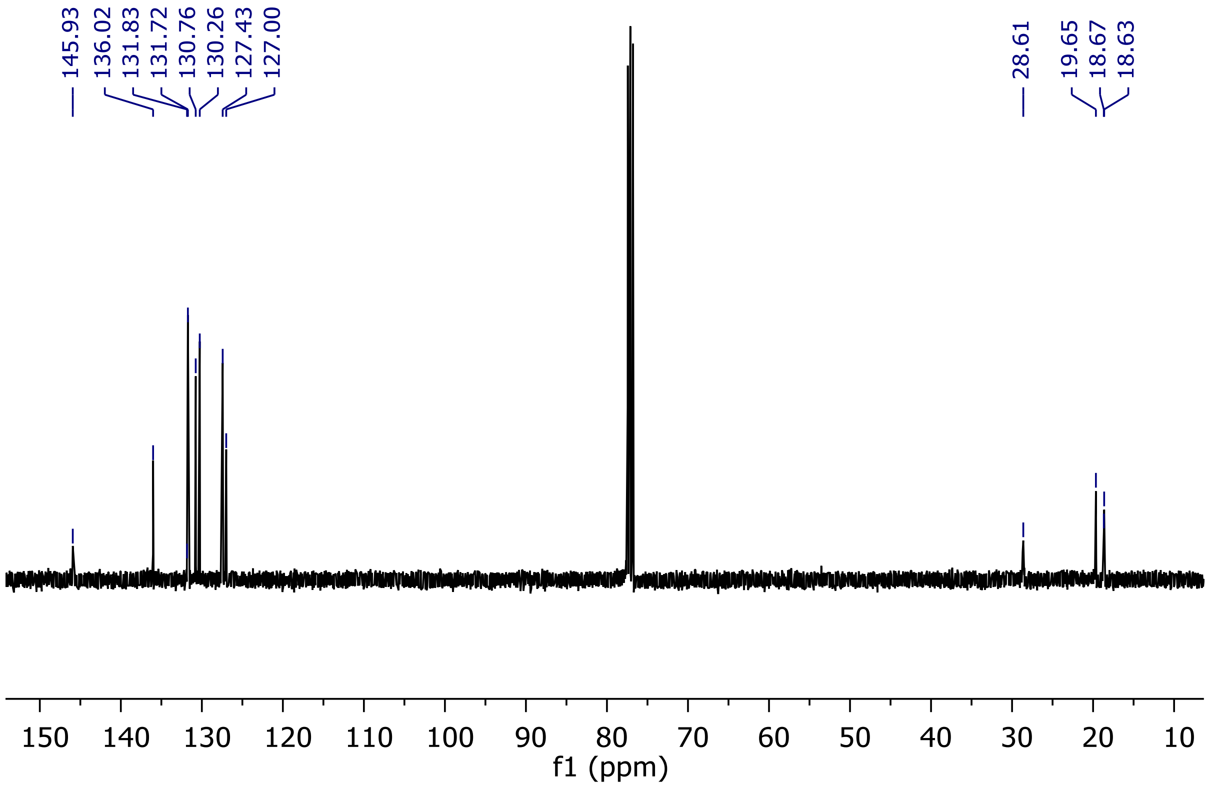



**Figure S27**: $^{13}C$ NMR of **13** in $CDCl_3$.

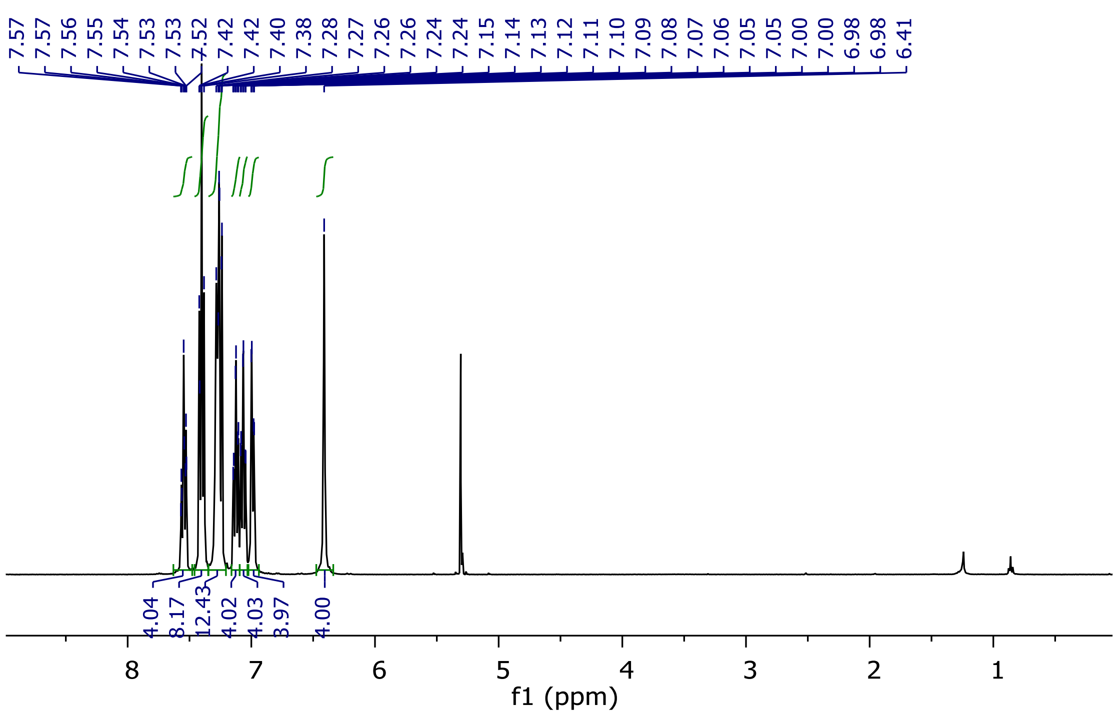



**Figure S28**: $^{1}H$ NMR of **14** in $CD_2Cl_2$.

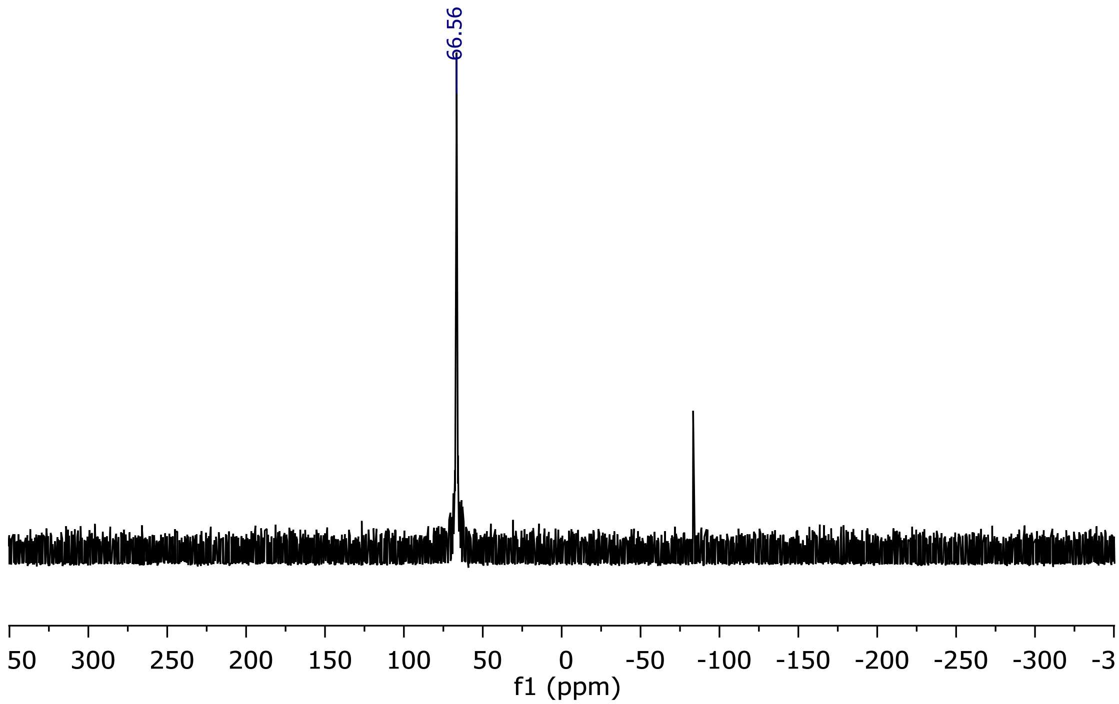



**Figure S29**: $^{31}$P NMR of **14** in $CD_2Cl_2$.

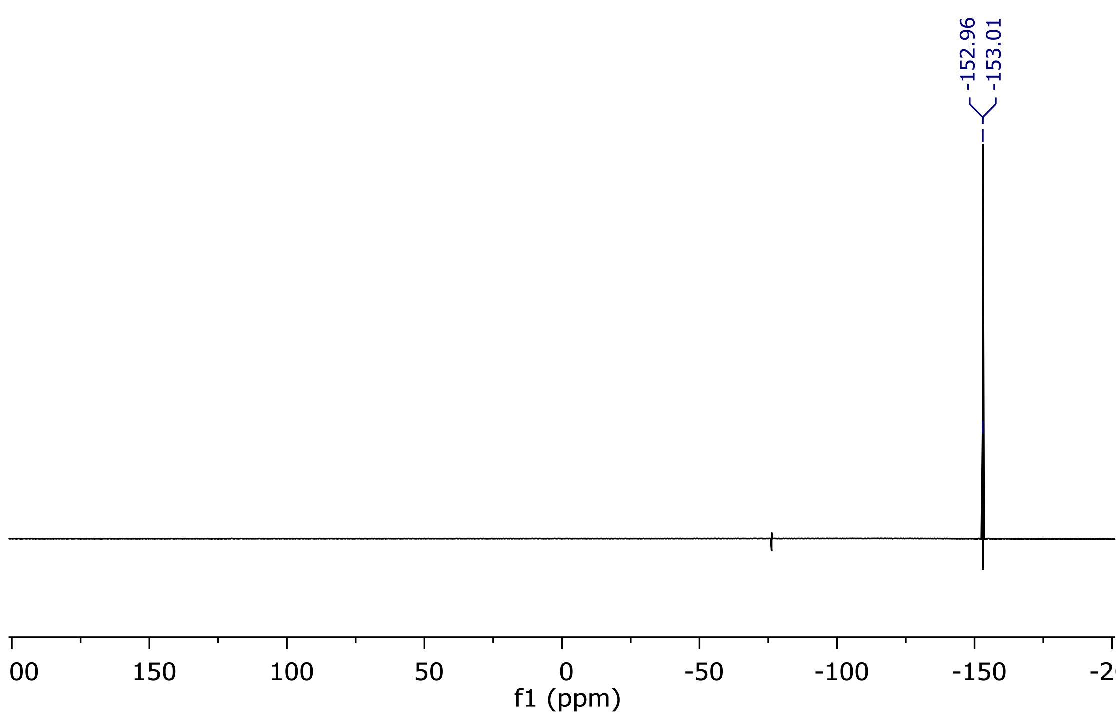



**Figure S30**: $^{19}$F NMR of **14** in $CD_2Cl_2$.

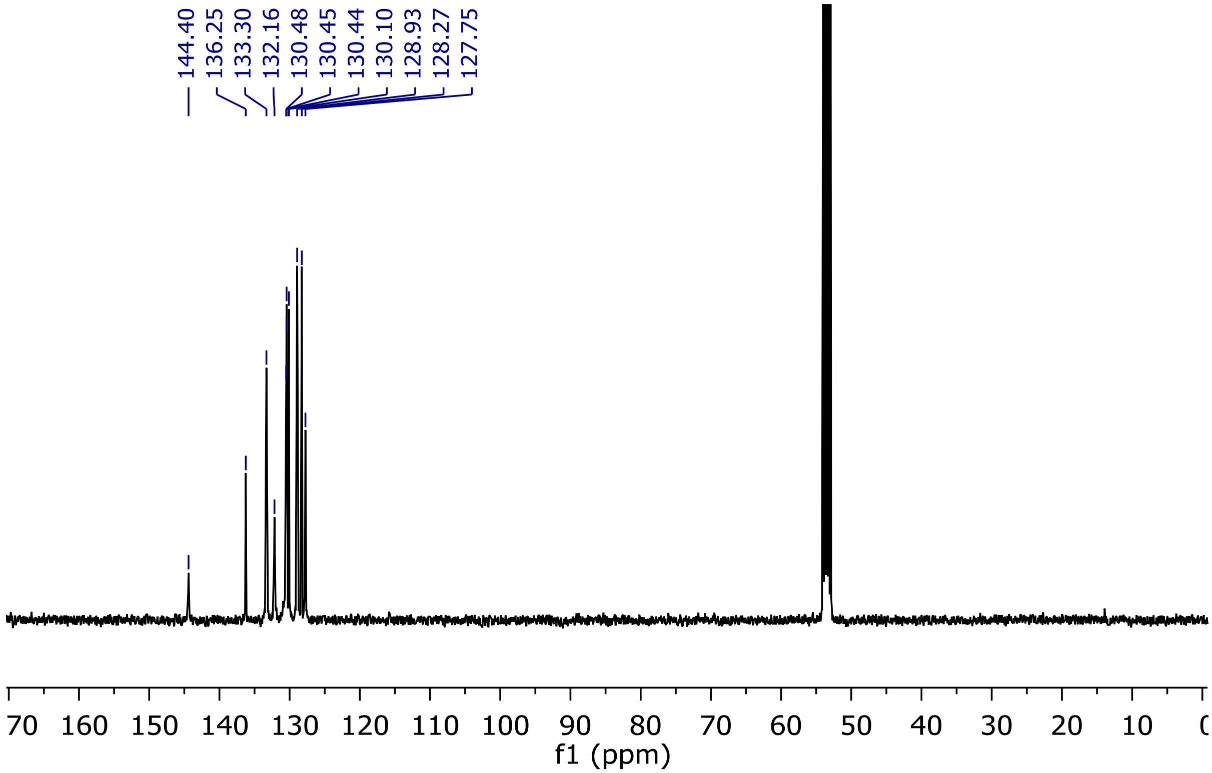



**Figure S 31**: $^{13}C$ NMR of **14** in $CD_2Cl_2$.

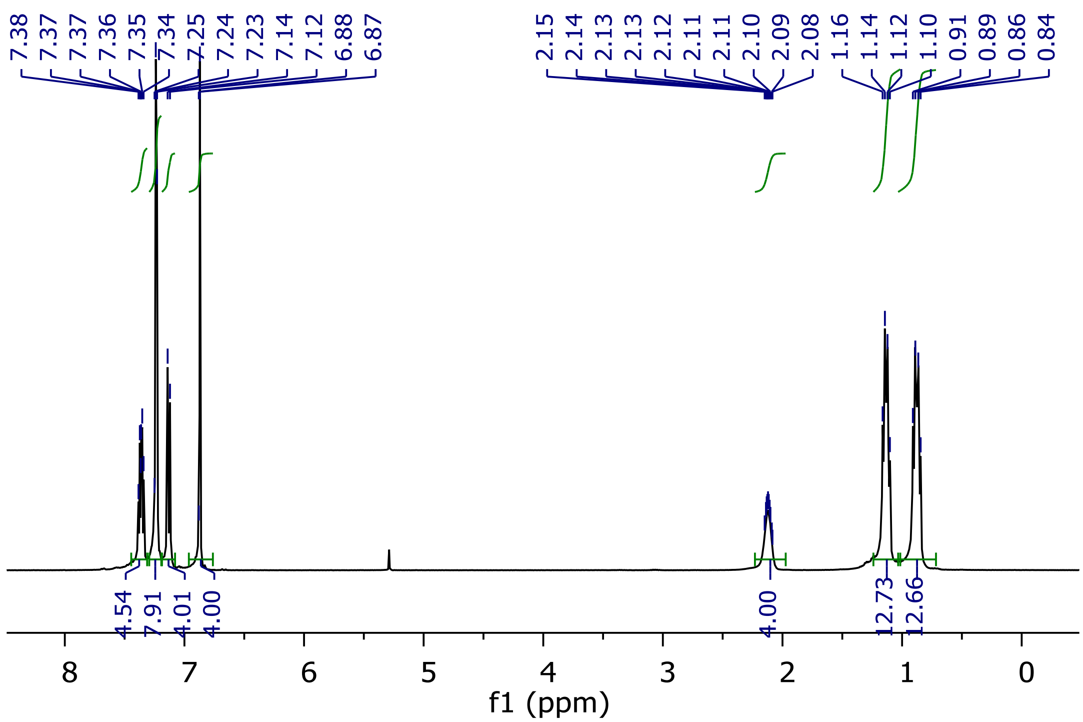



**Figure S32**: $^{1}H$ NMR of **15** in $CDCl_3$.

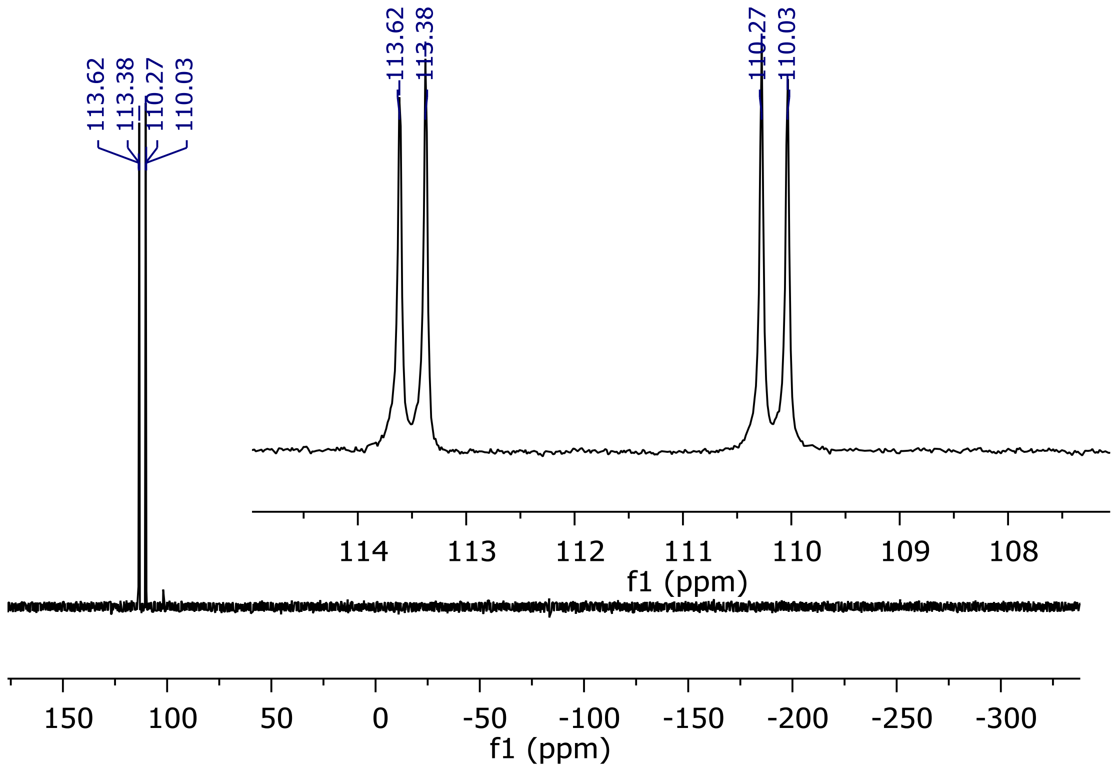



**Figure S33**: $^{31}P$ NMR of **15** in $CDCl_3$.

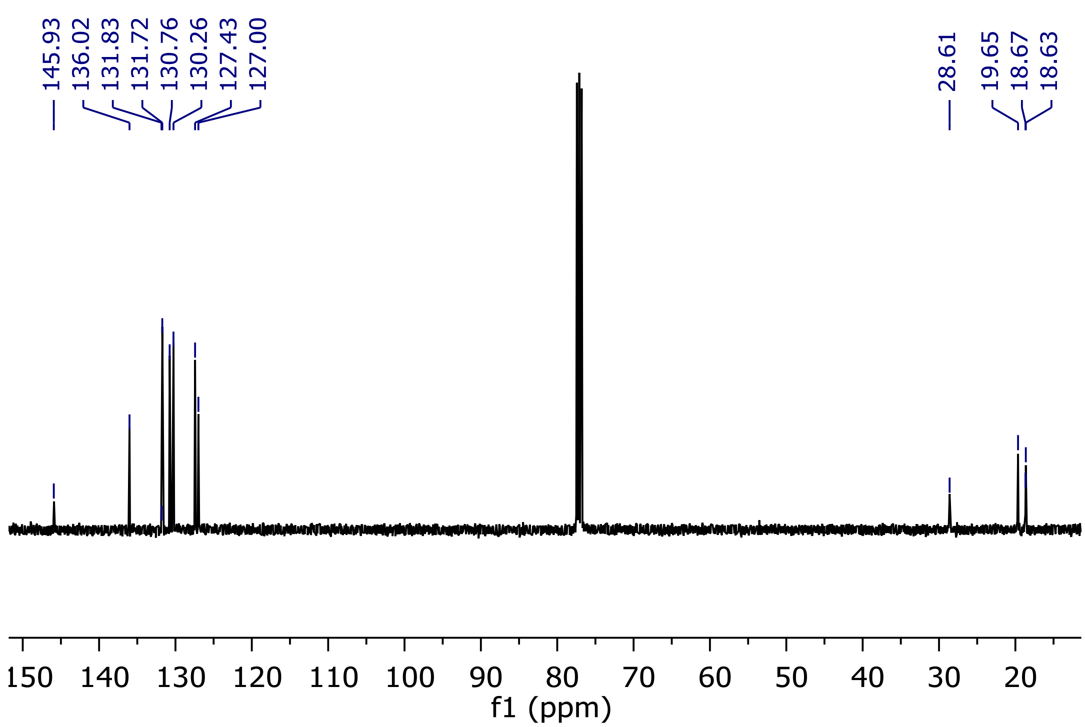



**Figure S34**: $^{13}C$ NMR of **15** in $CDCl_3$.

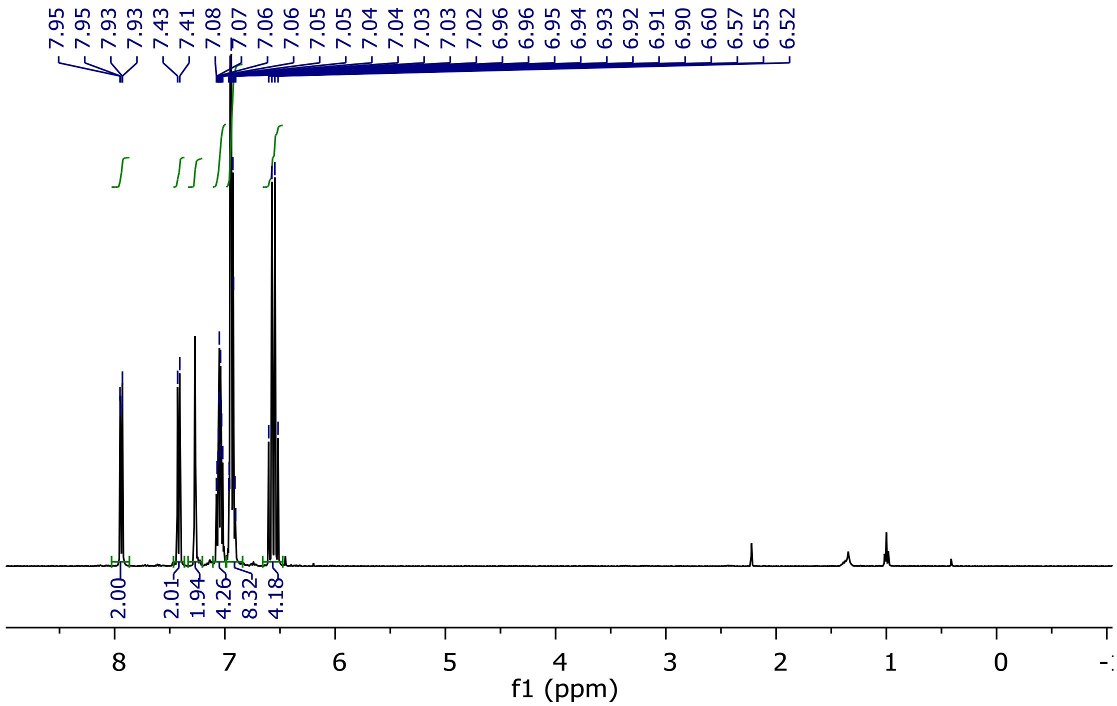



**Figure S35**: $^{1}$H NMR of **16** in $C_6D_6$.

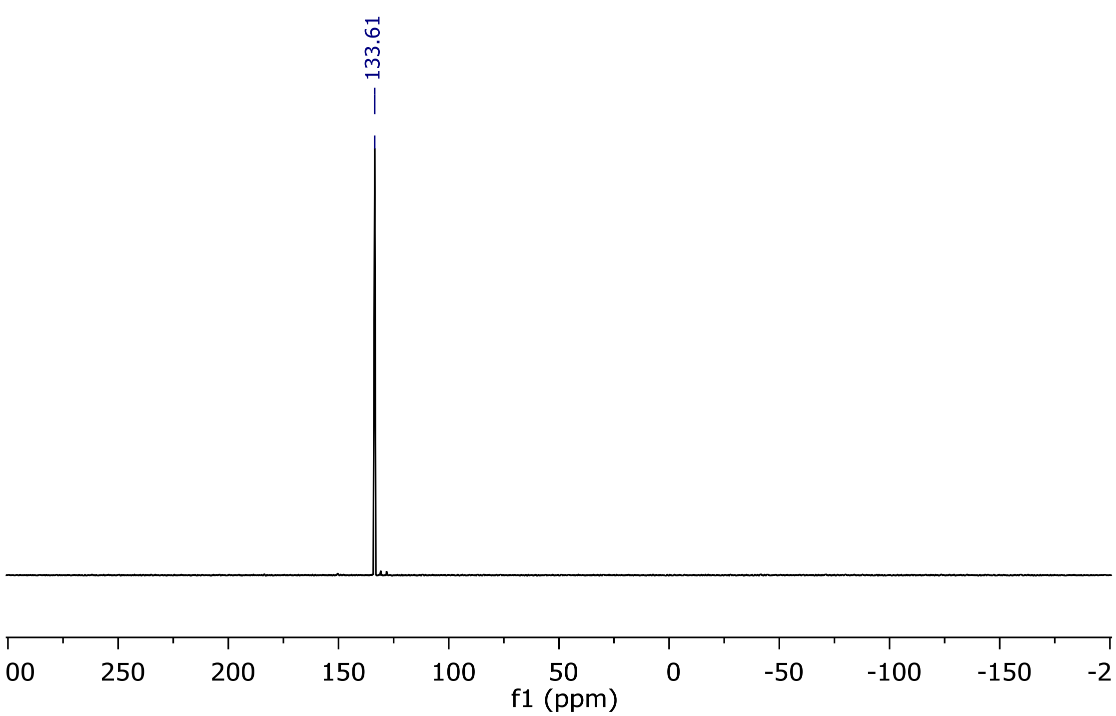



**Figure S36**: $^{31}$P NMR of **16** in $C_6D_6$.

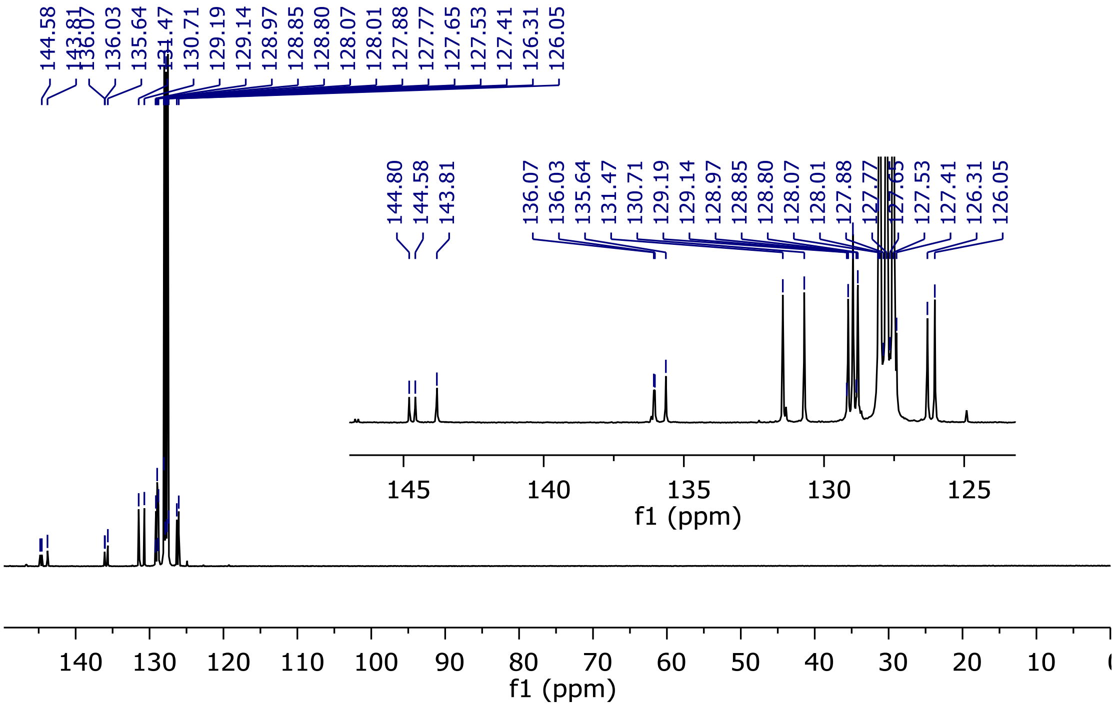



**Figure S37**: $^{13}$C NMR of **16** in $C_6D_6$.

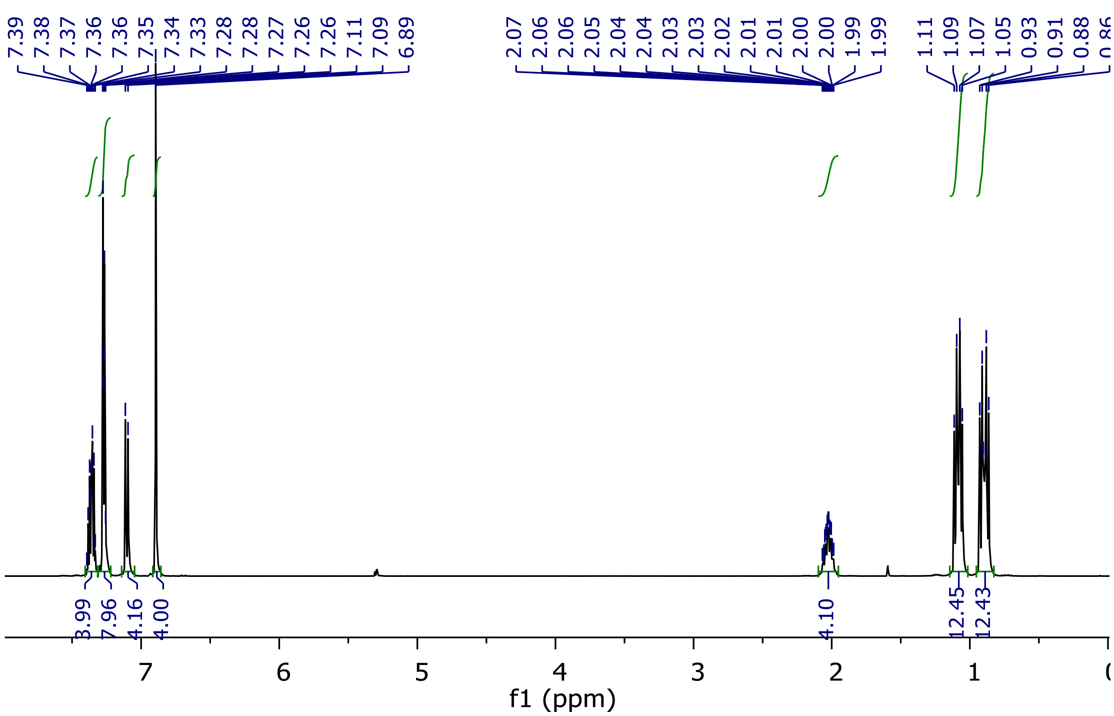



**Figure S38**: $^{1}$H NMR of **17** in $CD_2Cl_2$.

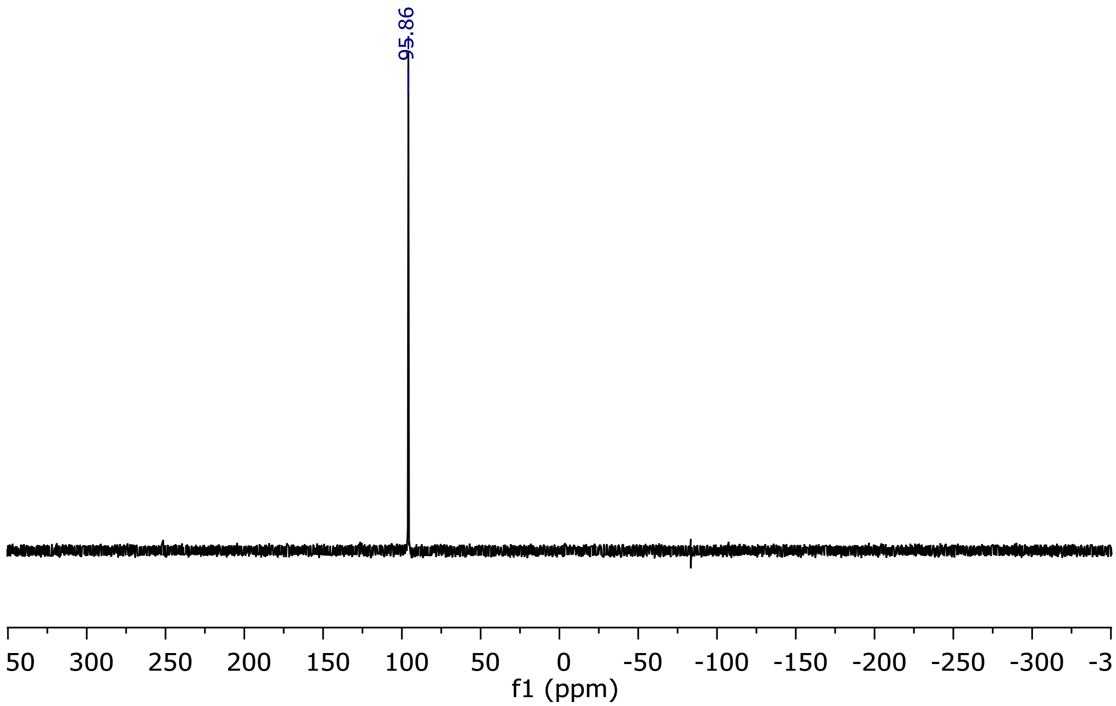



**Figure S39**: $^{31}$P NMR of **17** in $CD_2Cl_2$.

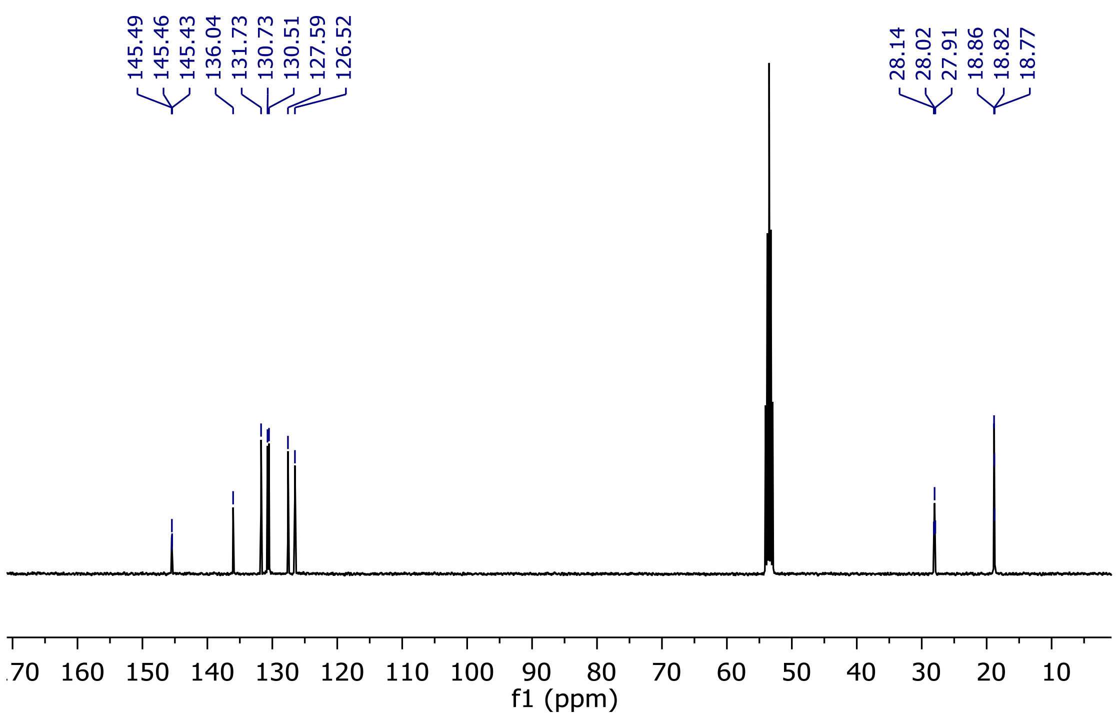



**Figure S40**: $^{13}$C NMR of **17** in $CD_2Cl_2$.

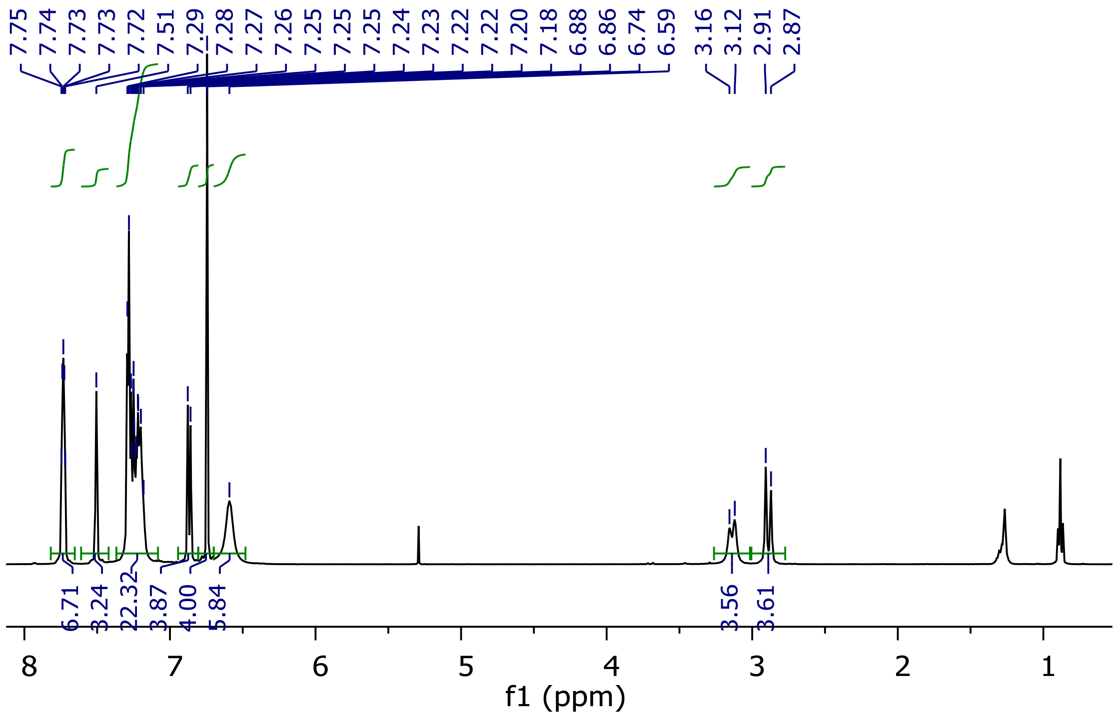



**Figure S41**: $^{1}H$ NMR of **18** in $CDCl_3$.

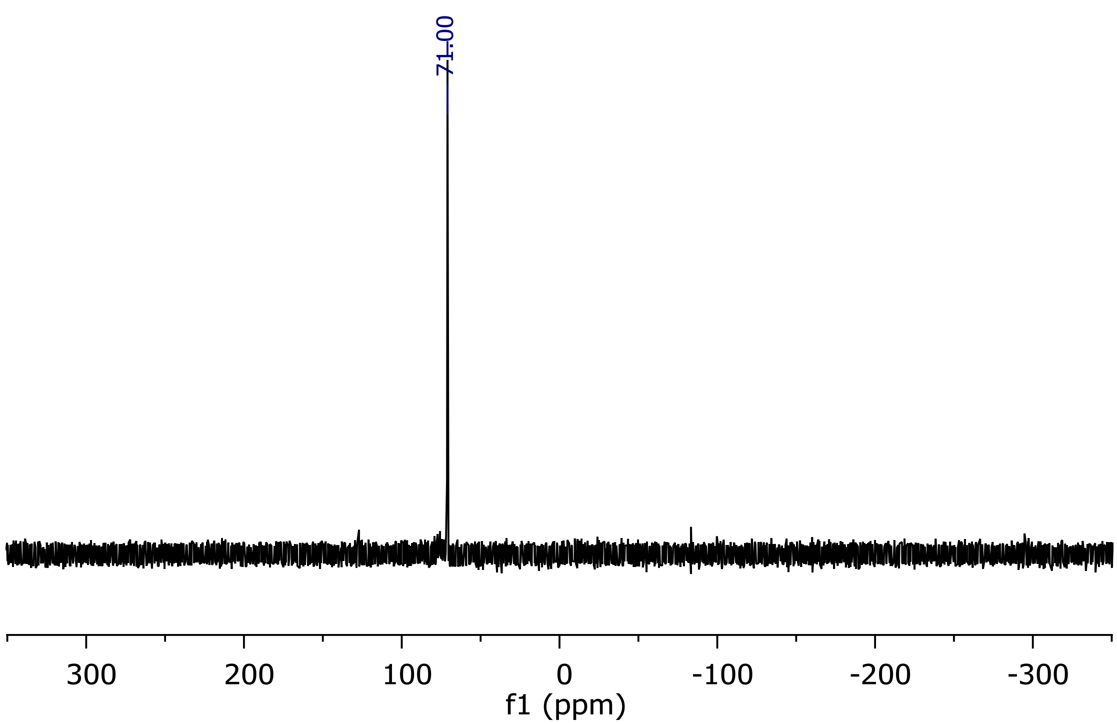



**Figure S42**: $^{31}P$ NMR of **18** in $CDCl_3$.

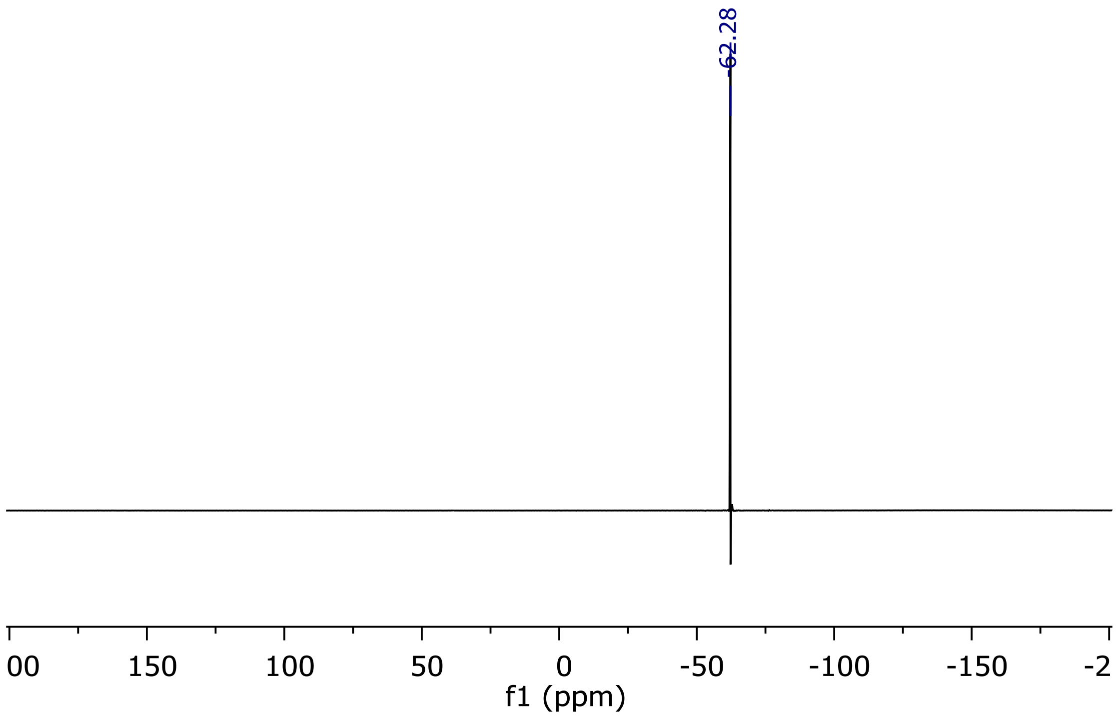



**Figure S43**: $^{19}$F NMR of **18** in $CDCl_3$.

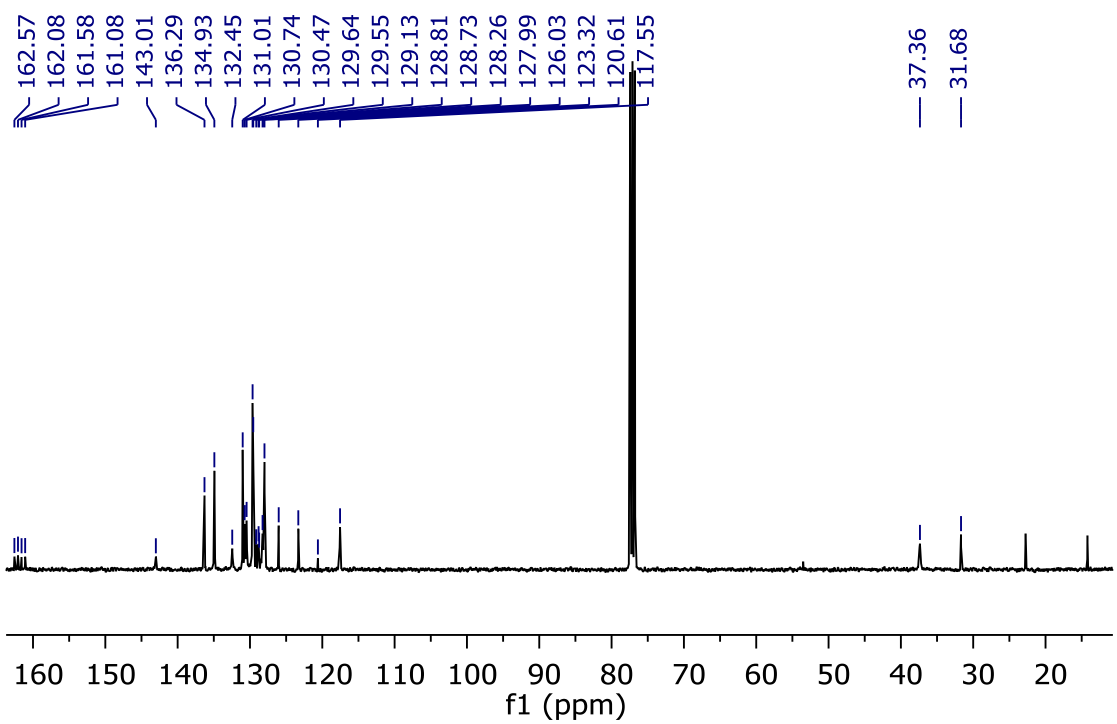



**Figure S44**: $^{13}$C NMR of **18** in $CDCl_3$.

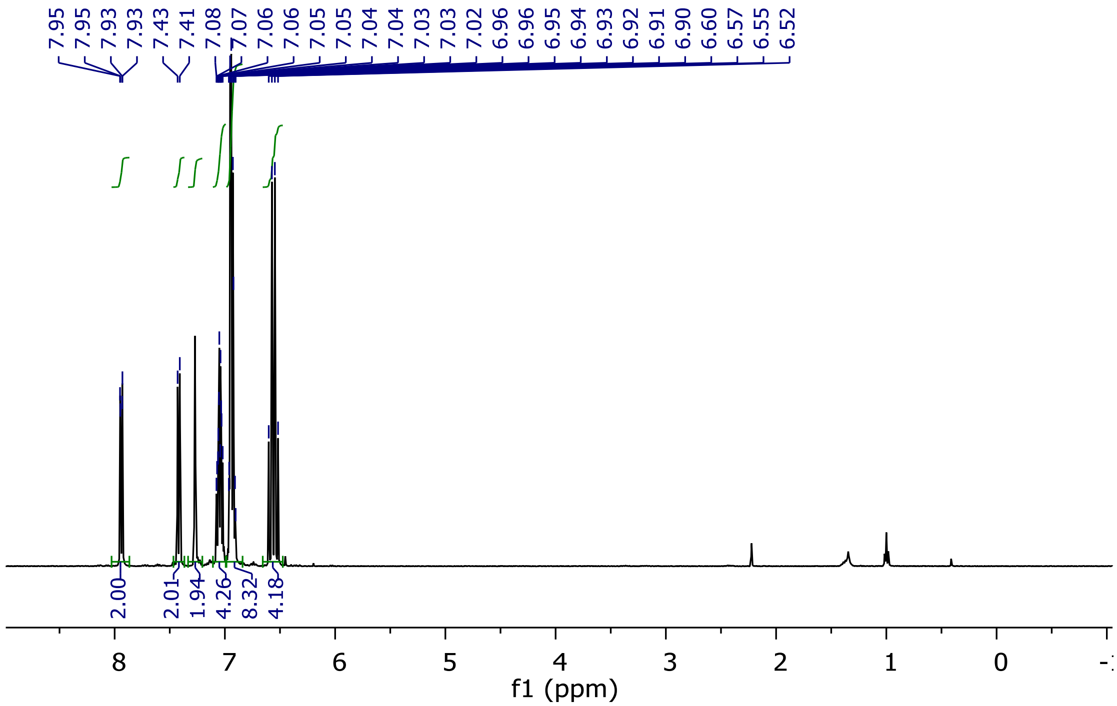


**Figure S45**: $^{1}$H NMR of **19** in $C_6D_6$.

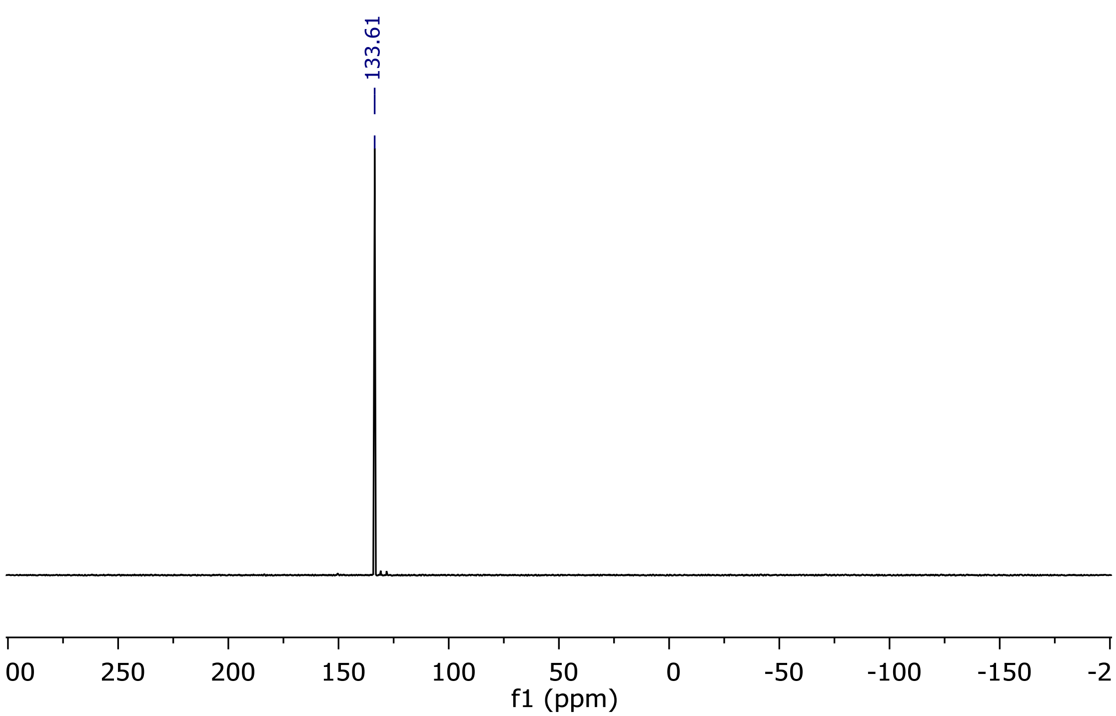


**Figure S46**: $^{31}$P NMR of **19** in $C_6D_6$.

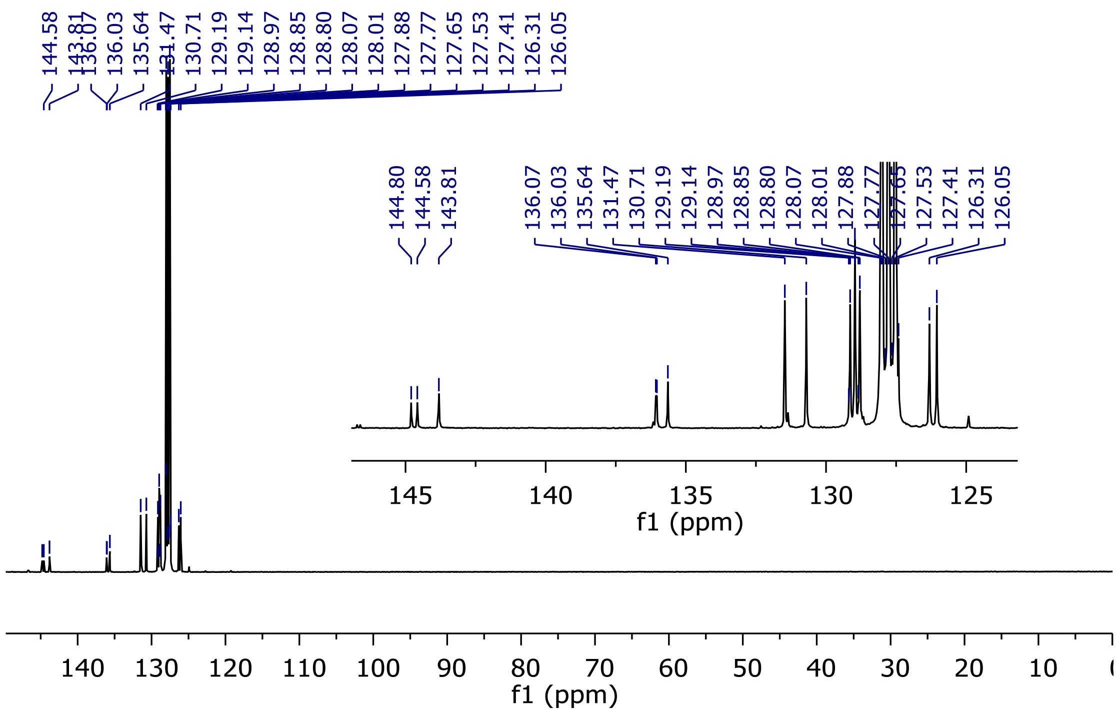


**Figure S47**: $^{13}C$ NMR of **19** in $C_6D_6$.

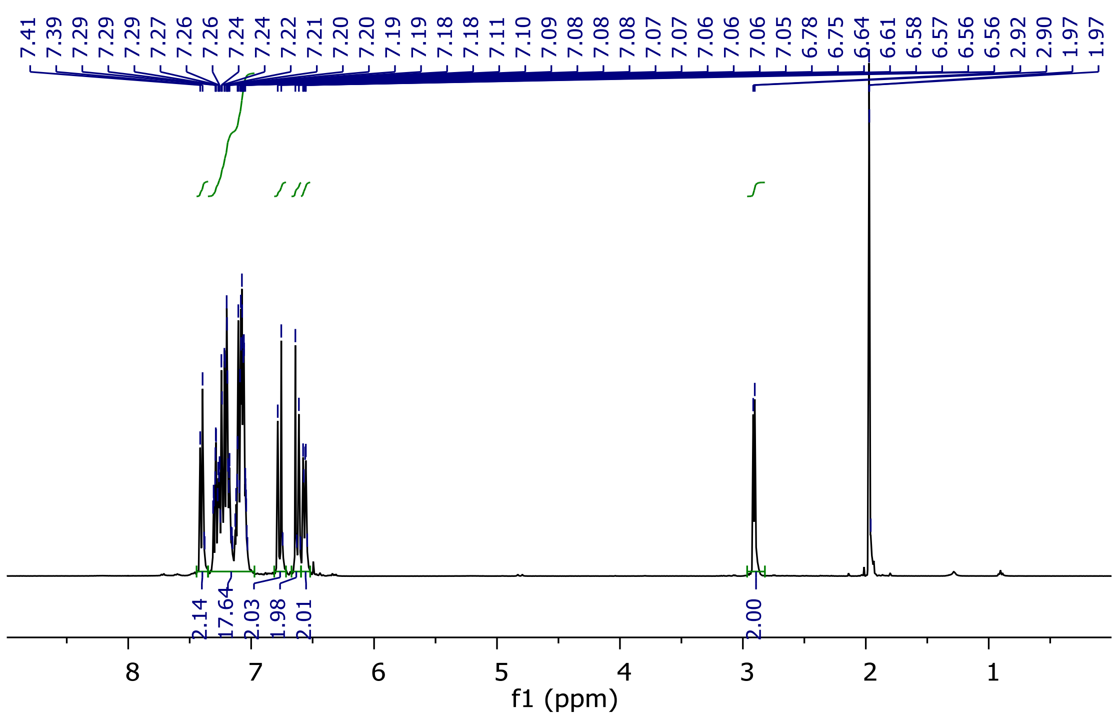


**Figure S48**: $^{1}H$ NMR of **20** in $CDCl_3$

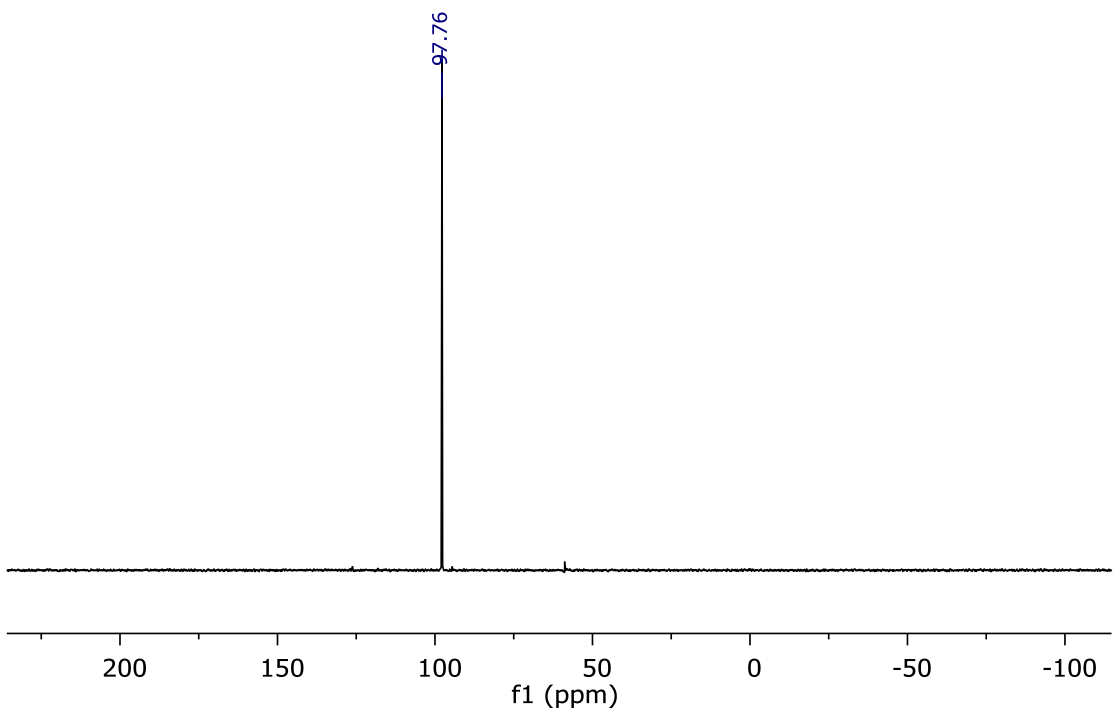



**Figure S49**: $^{31}$P NMR of **20** in $CDCl_3$.

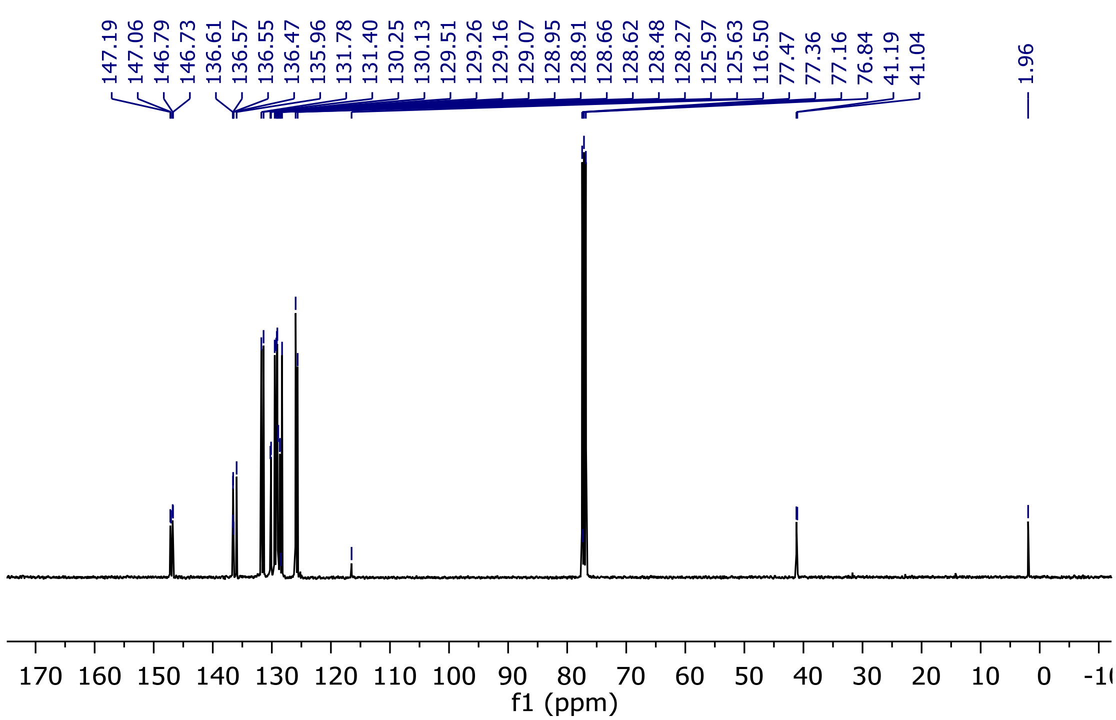



**Figure S50**: $^{13}$C NMR of **20** in $CDCl_3$.

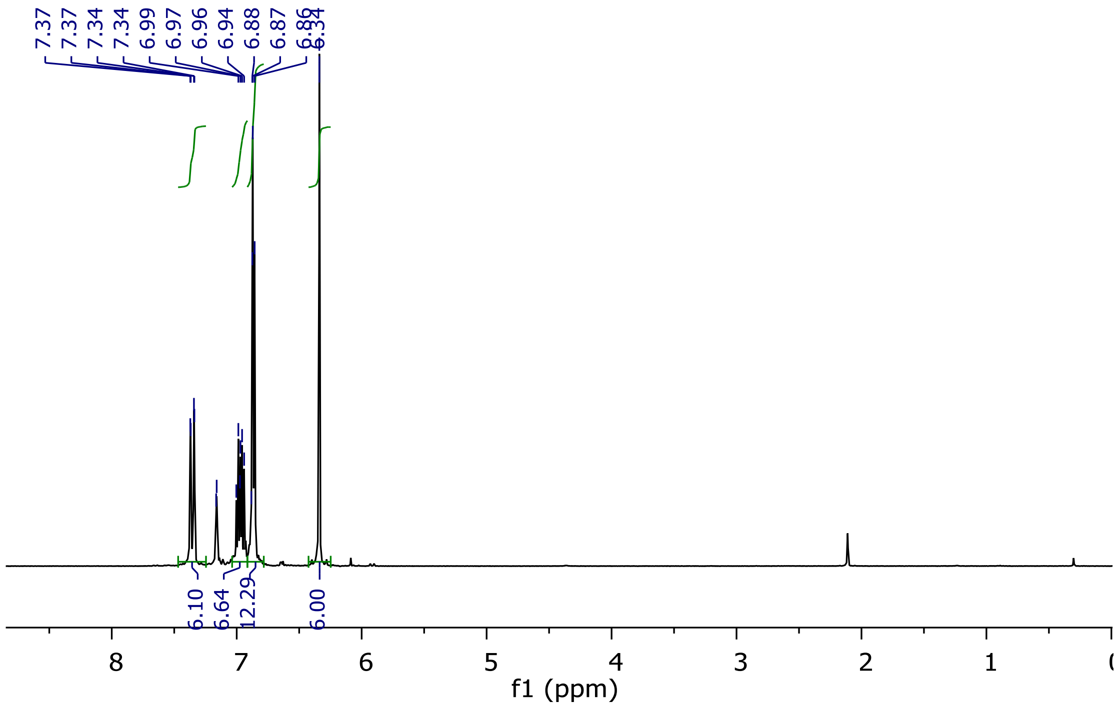



**Figure S51**: $^{1}H$ NMR of **21** in $C_6D_6$.

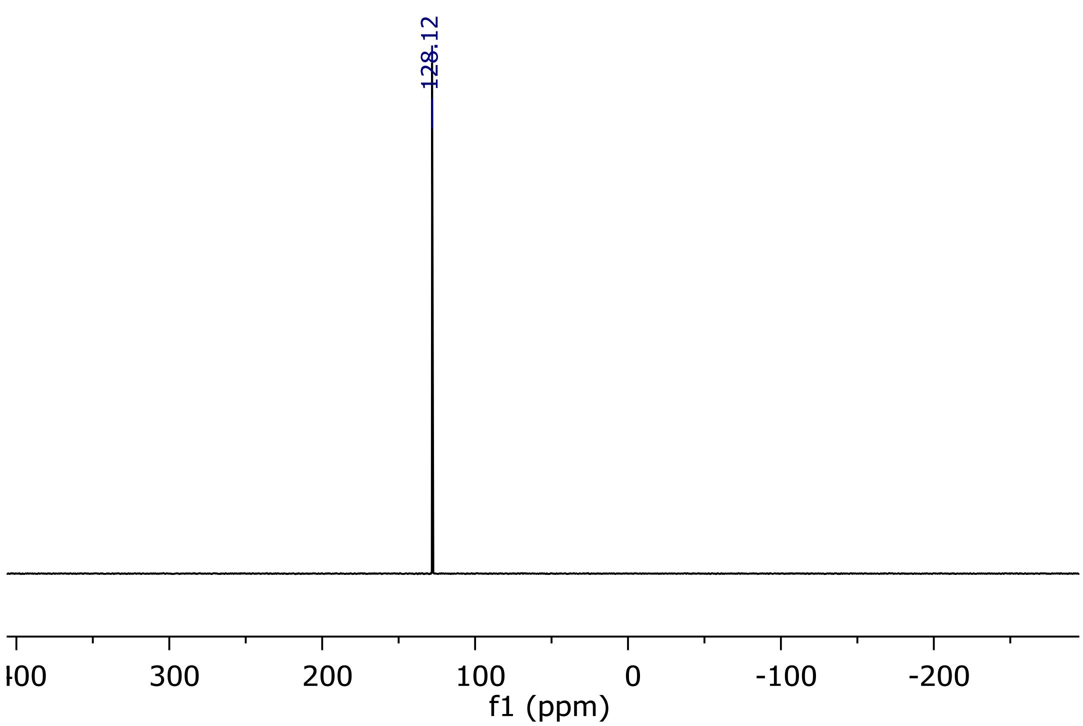



**Figure S52**: $^{31}P$ NMR of **21** in $C_6D_6$.

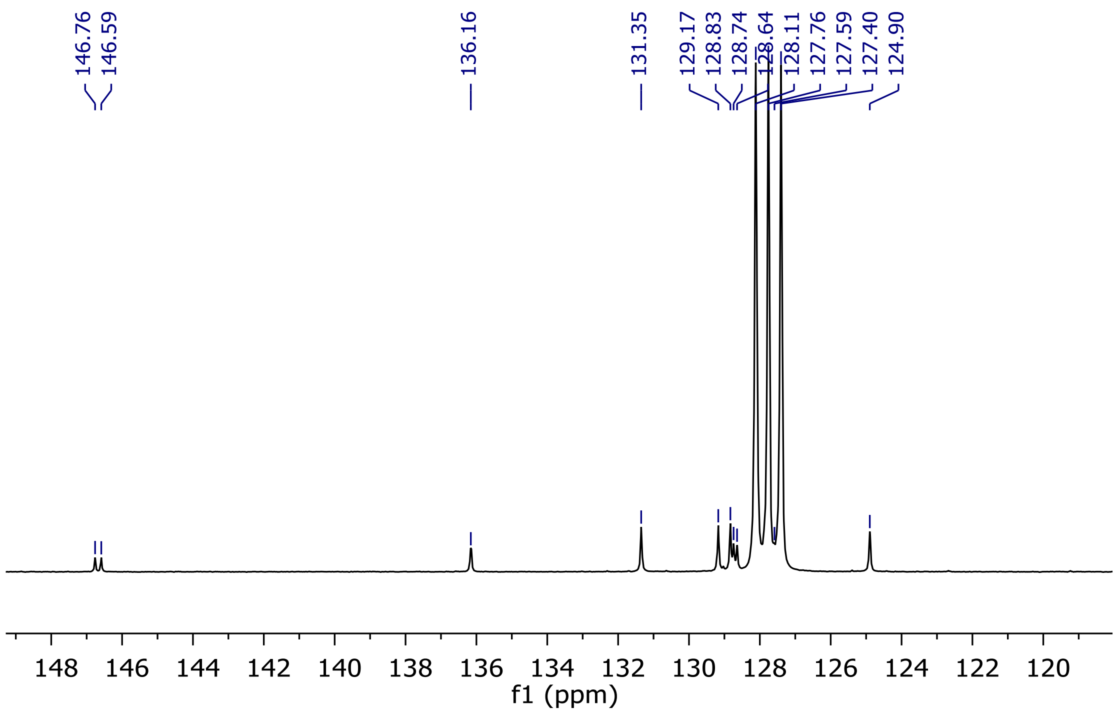



**Figure S53**: $^{13}$C NMR of **21** in $C_6D_6$.

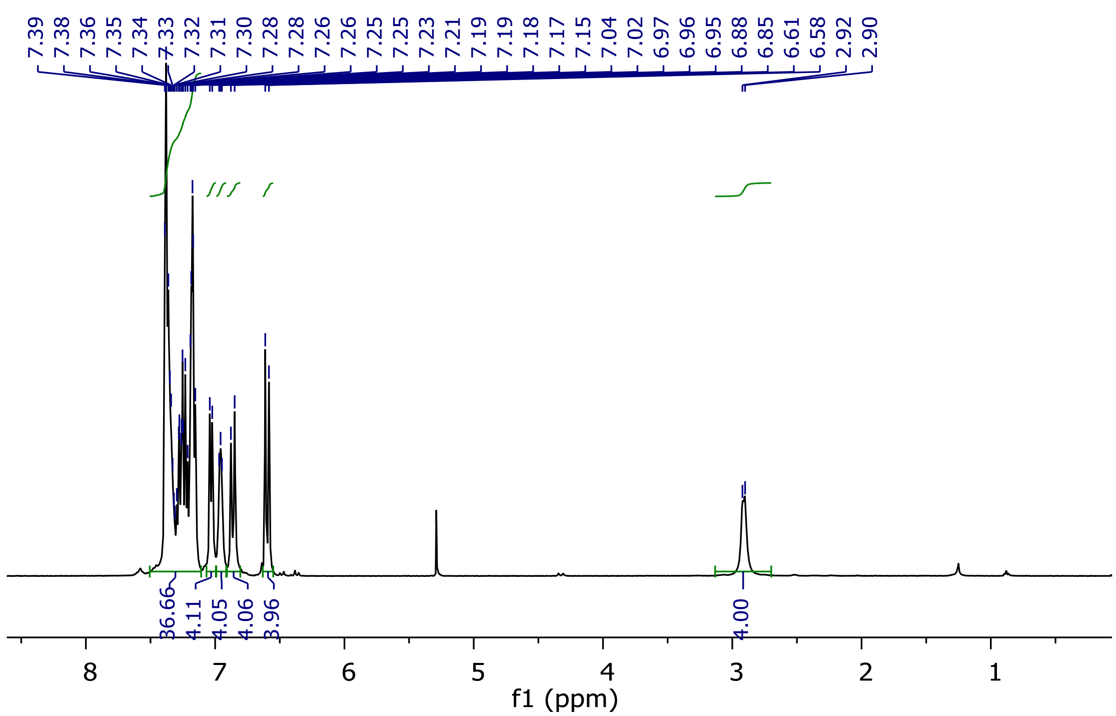



**Figure S54**: $^1$H NMR of **22** in $CDCl_3$

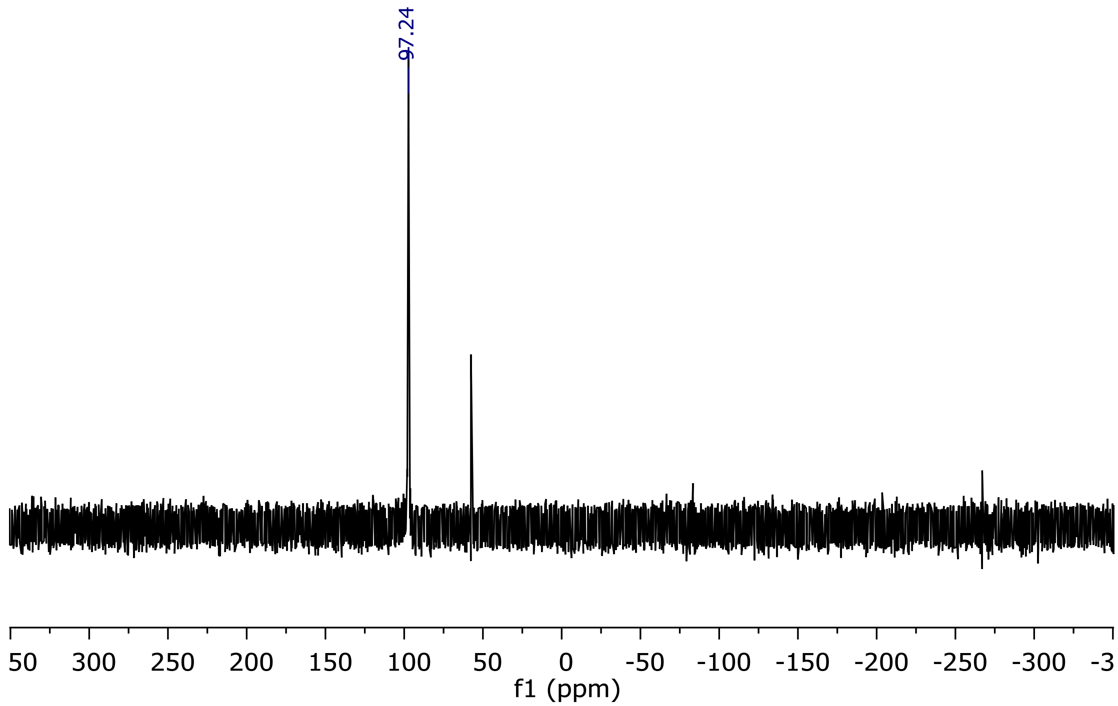



**Figure S55**: $^{31}$P NMR of **22** in $CDCl_3$.

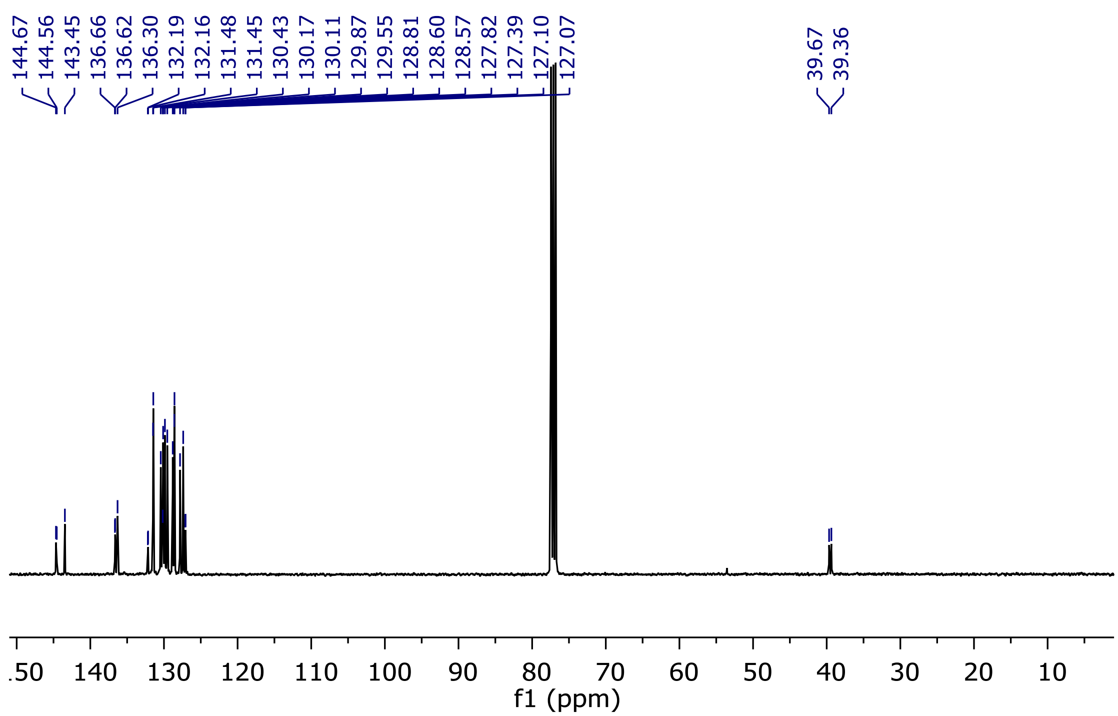



**Figure S56**: $^{13}$C NMR of **22** in $CDCl_3$.

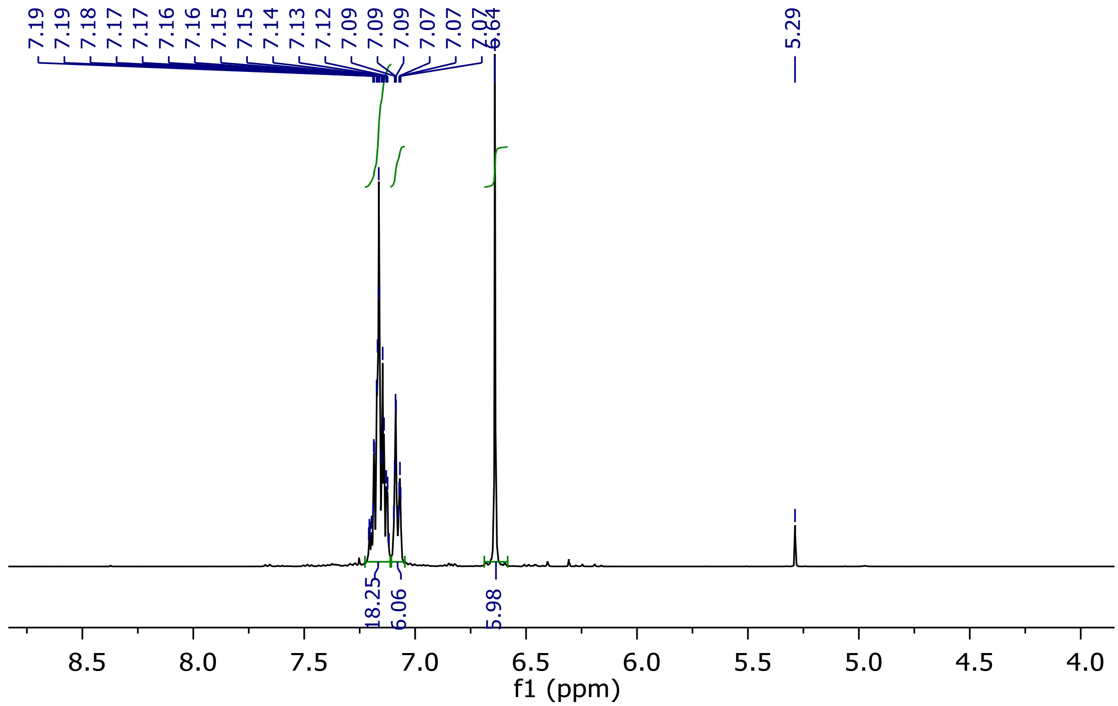



**Figure S57**: [1]H NMR of **23** in $CDCl_3$.

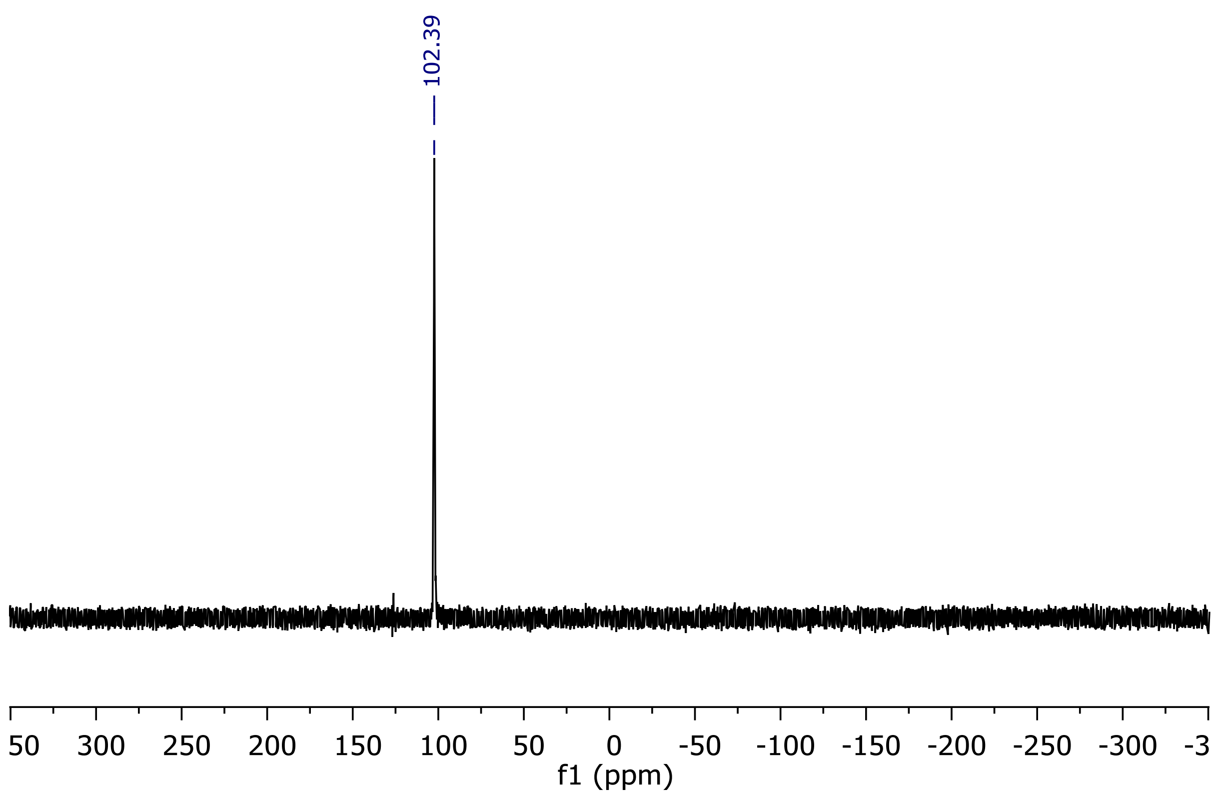



**Figure 58**: [31]P NMR of **23** in $CDCl_3$.

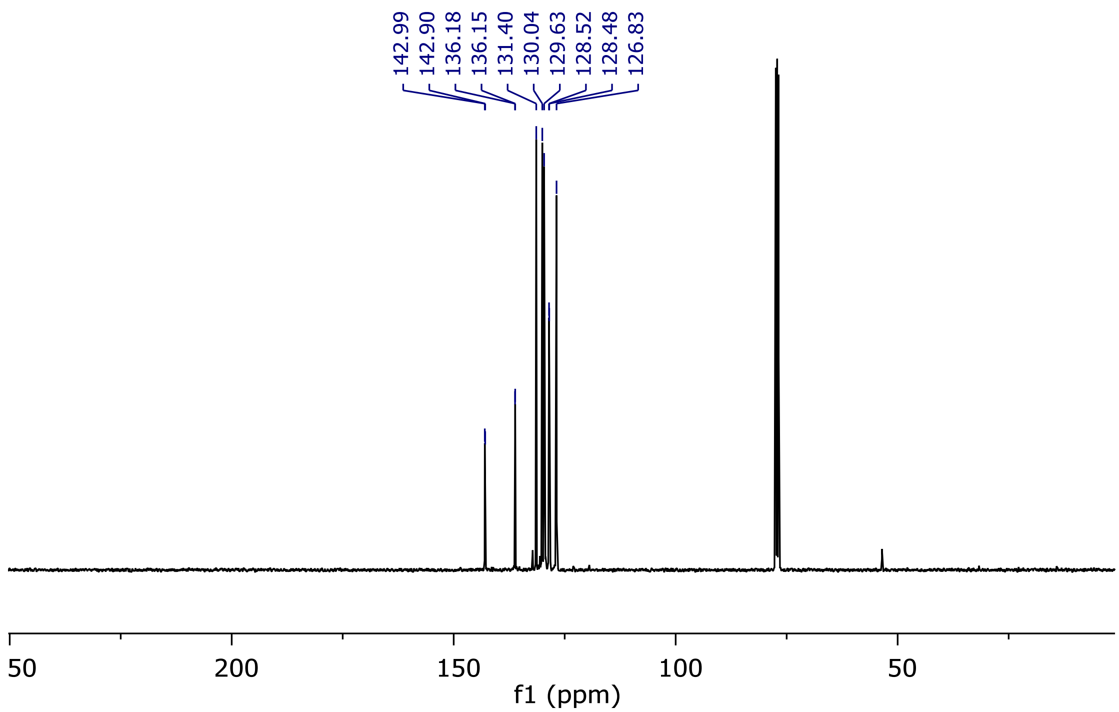



**Figure S59**: $^{13}C$ NMR of **23** in $CDCl_3$.

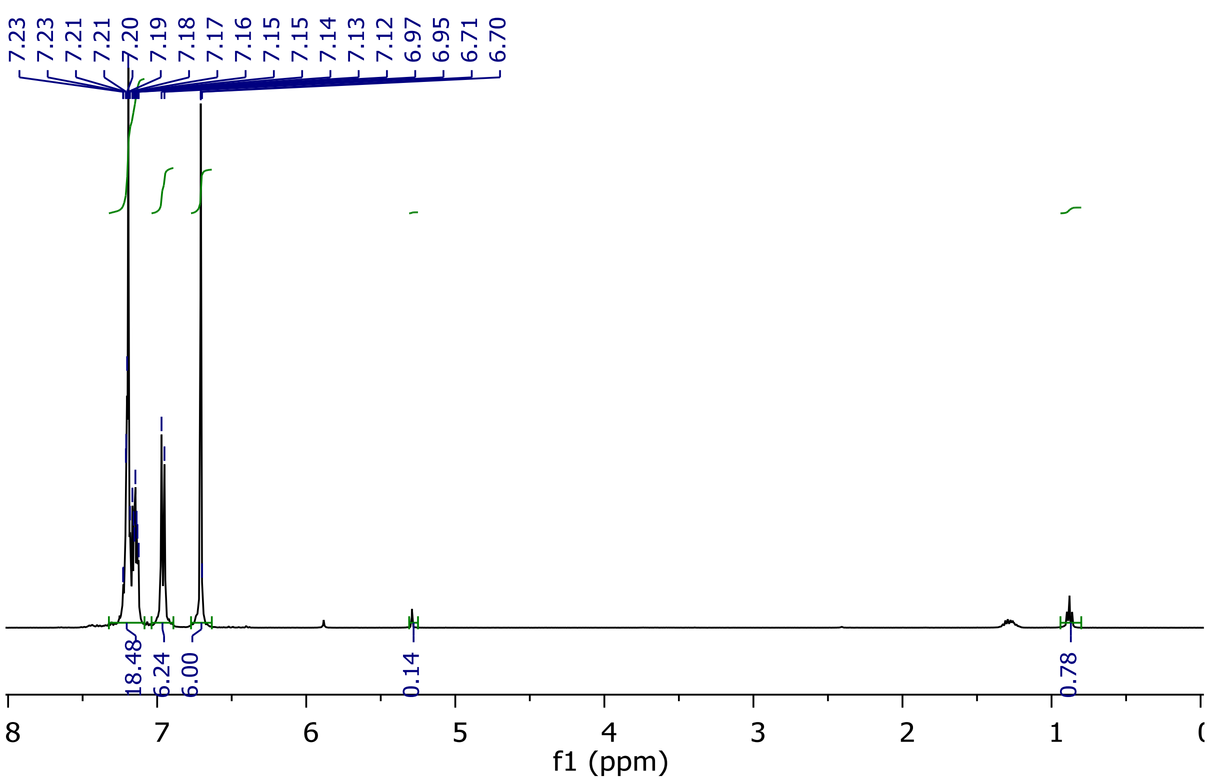



**Figure S60**: $^{1}H$ NMR of **24** in $CDCl_3$.

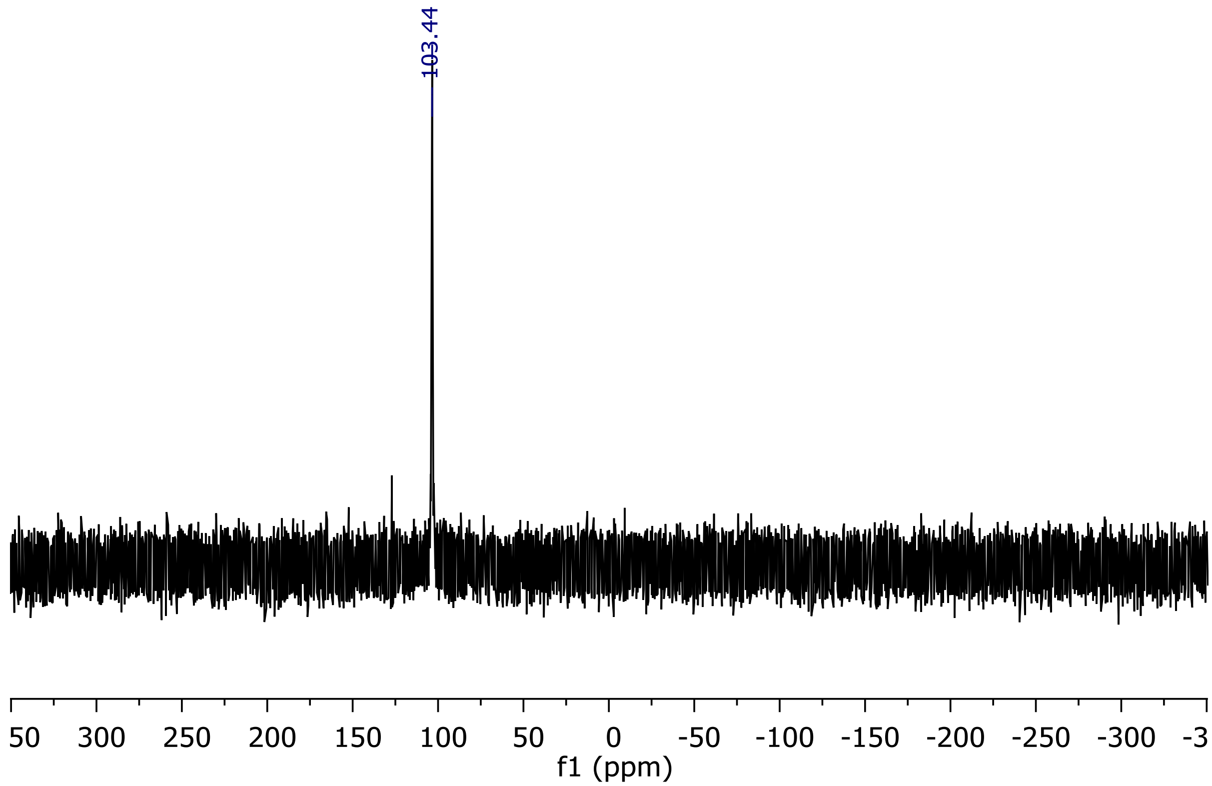



**Figure S61:** $^{31}P$ NMR of **24** in $CDCl_3$.

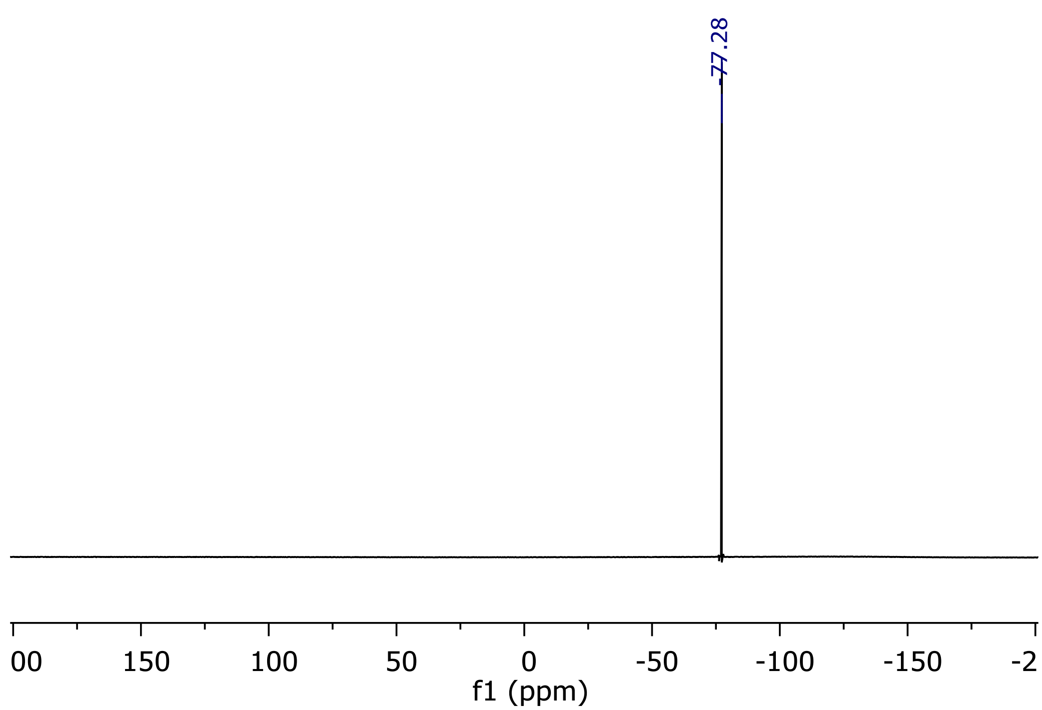



**Figure S62**: $^{19}F$ NMR of **24** in $CDCl_3$.

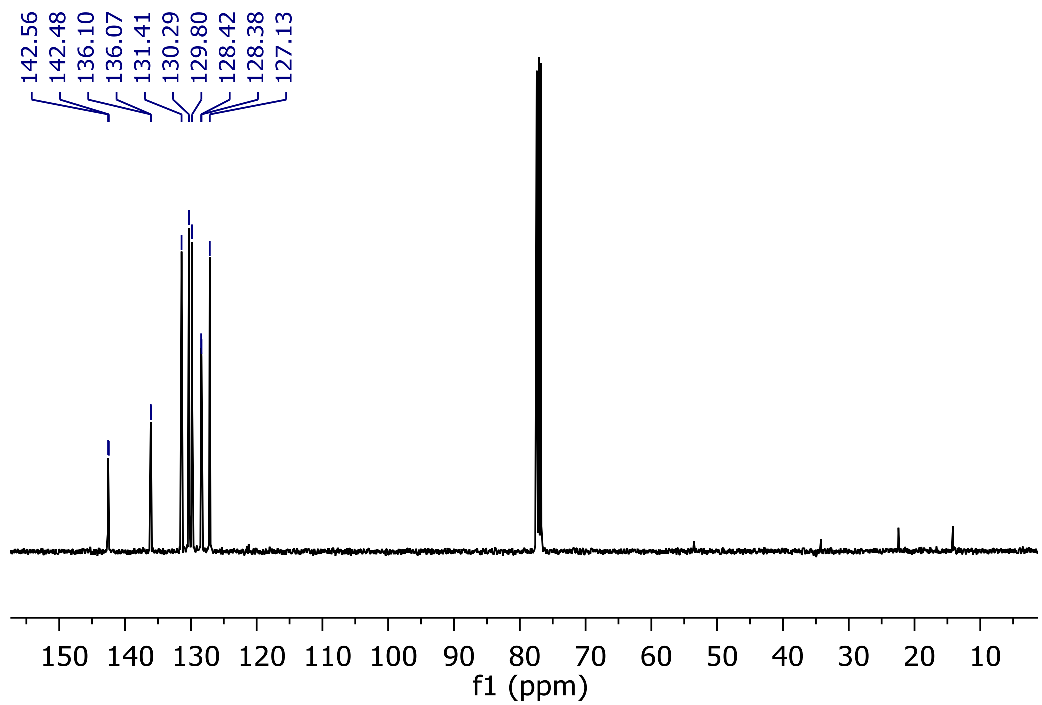



**Figure S63**: $^{13}C$ NMR of **24** in $CDCl_3$.

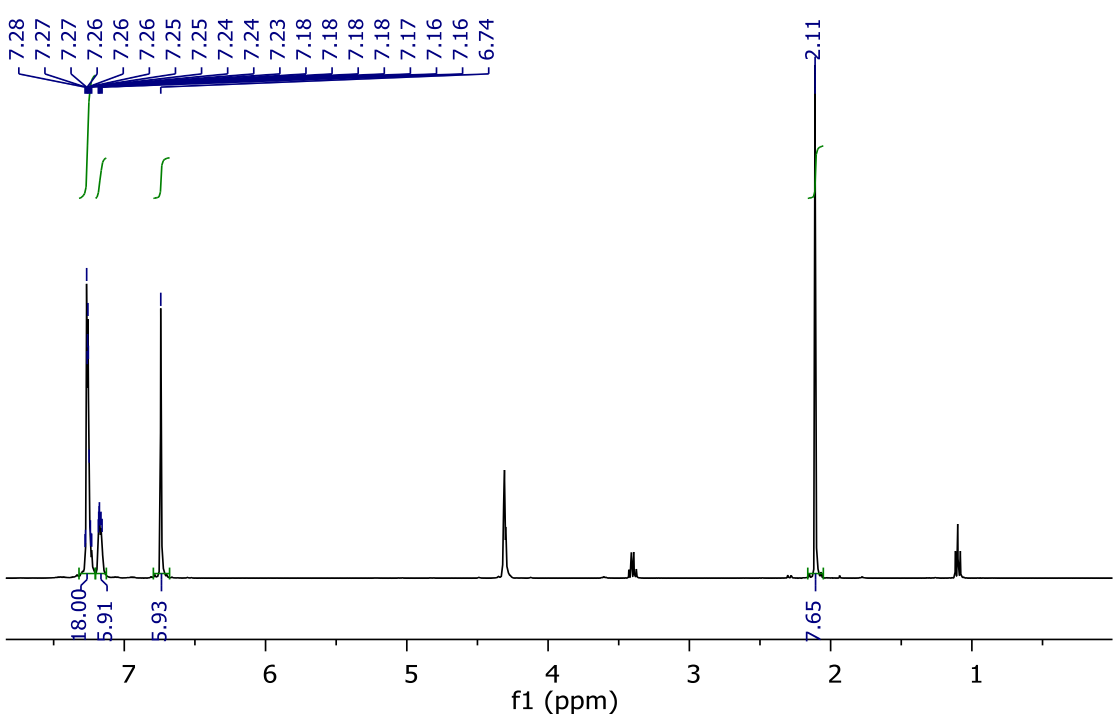



**Figure S64**: $^{1}H$ NMR of **25** in $CD_3NO_2$.

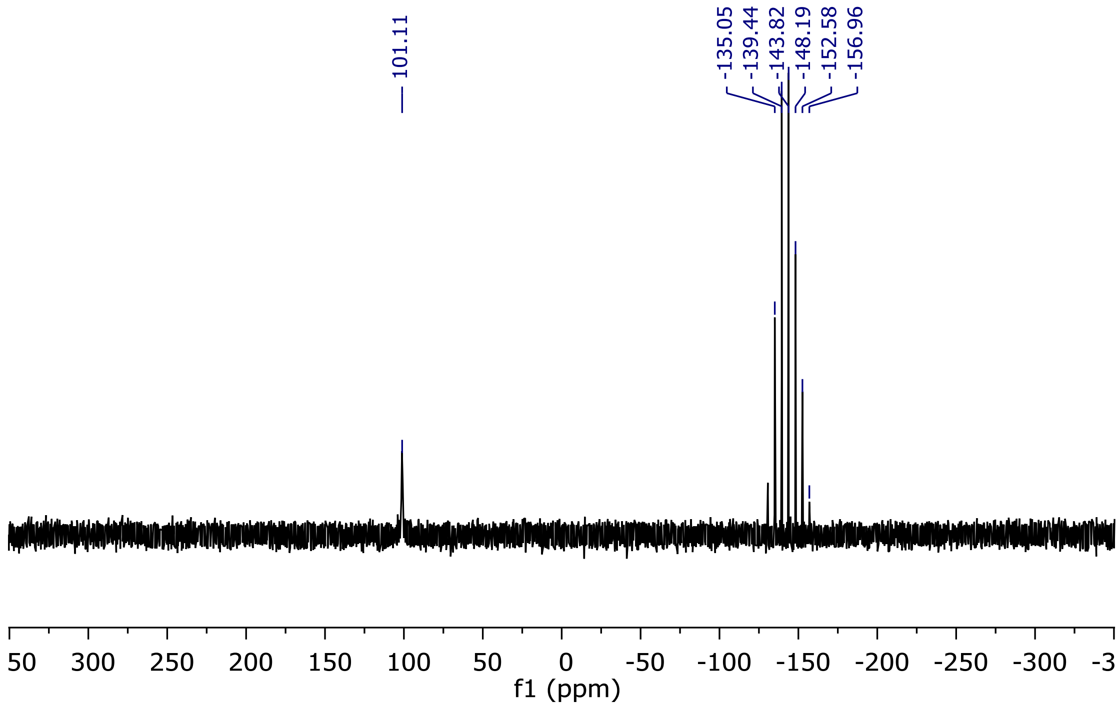



**Figure S65**: $^{31}$P NMR of **25** in $CD_3NO_2$.

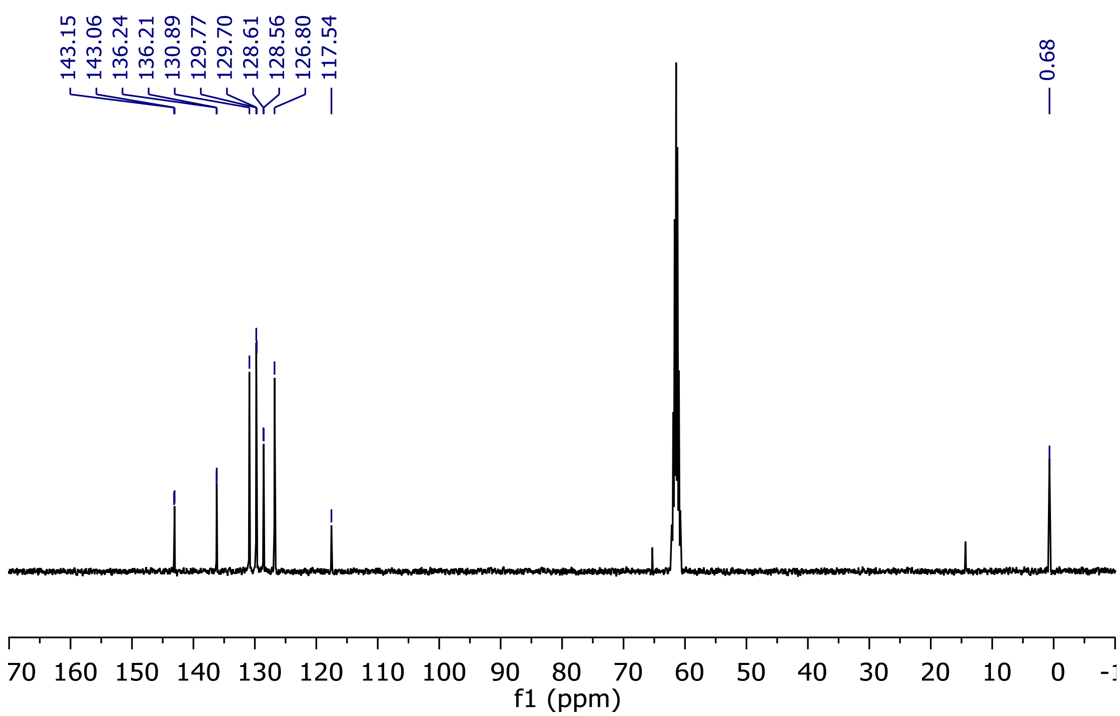



**Figure S66**: $^{13}$C NMR of **25** in $CD_3NO_2$.

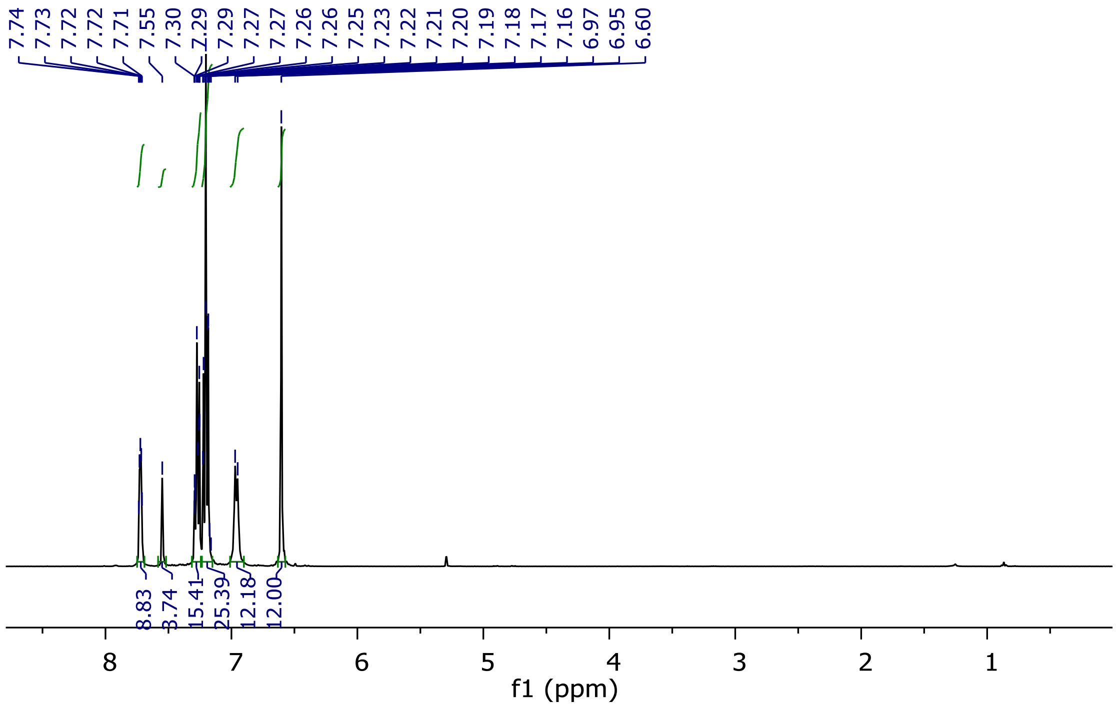



**Figure S67**: $^{1}H$ NMR of **26** in $CD_2Cl_2$.

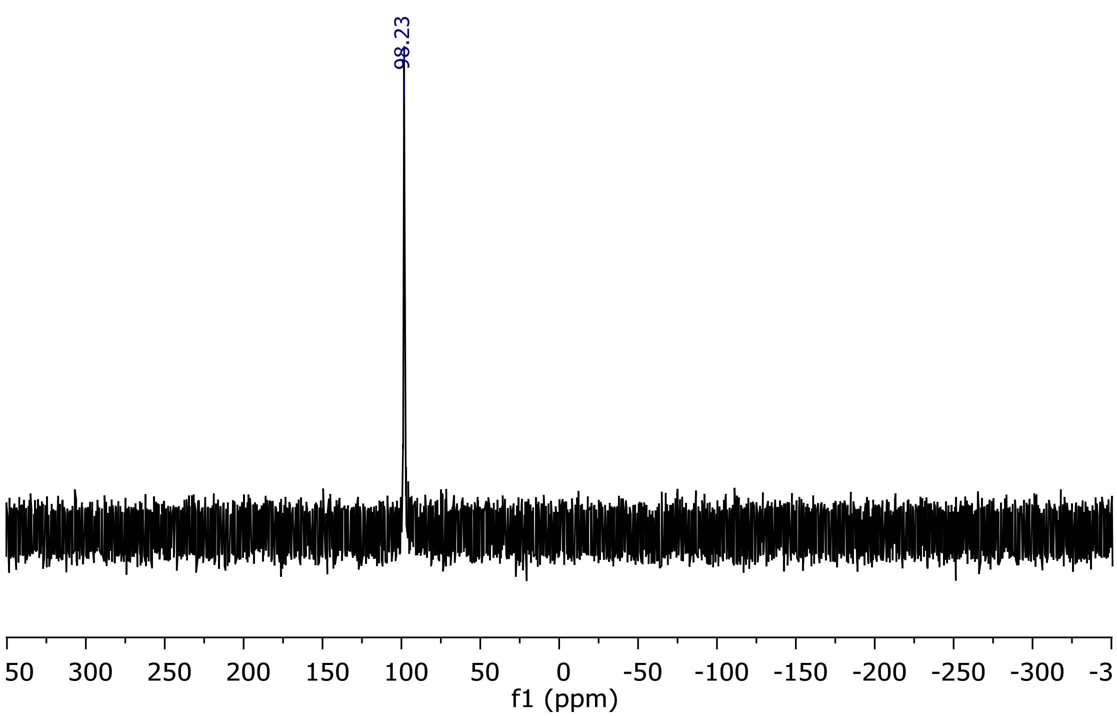



**Figure S68**: $^{31}P$ NMR of **26** in $CD_2Cl_2$.

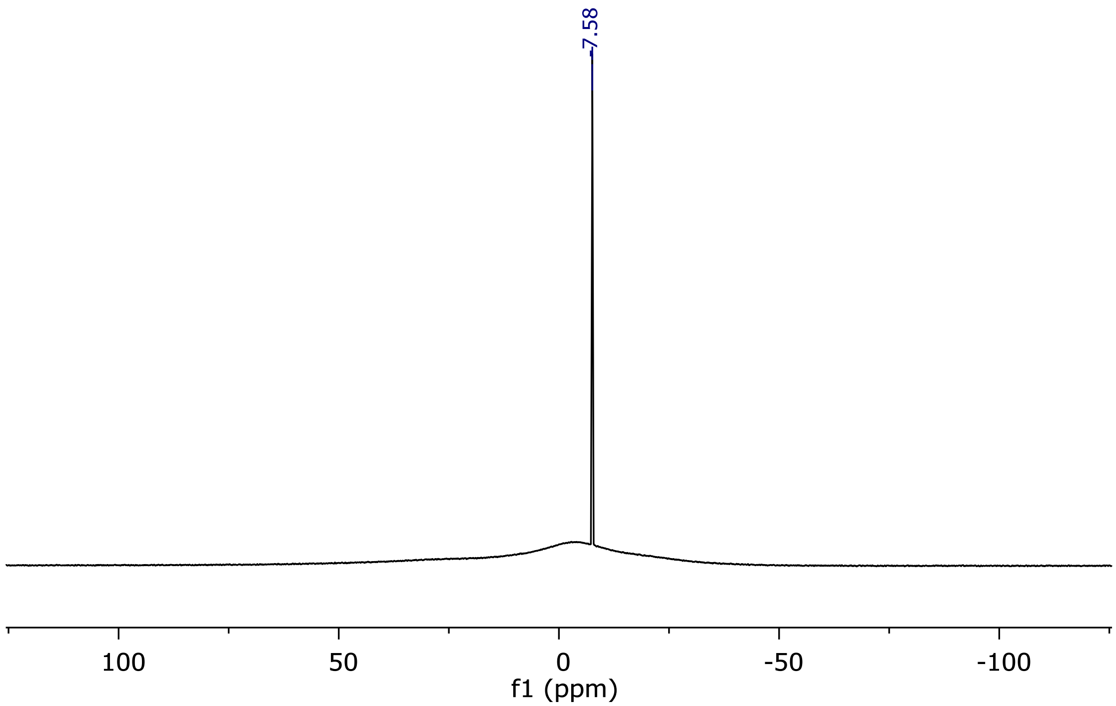



**Figure S69**: $^{11}$B NMR of **26** in $CD_2Cl_2$.

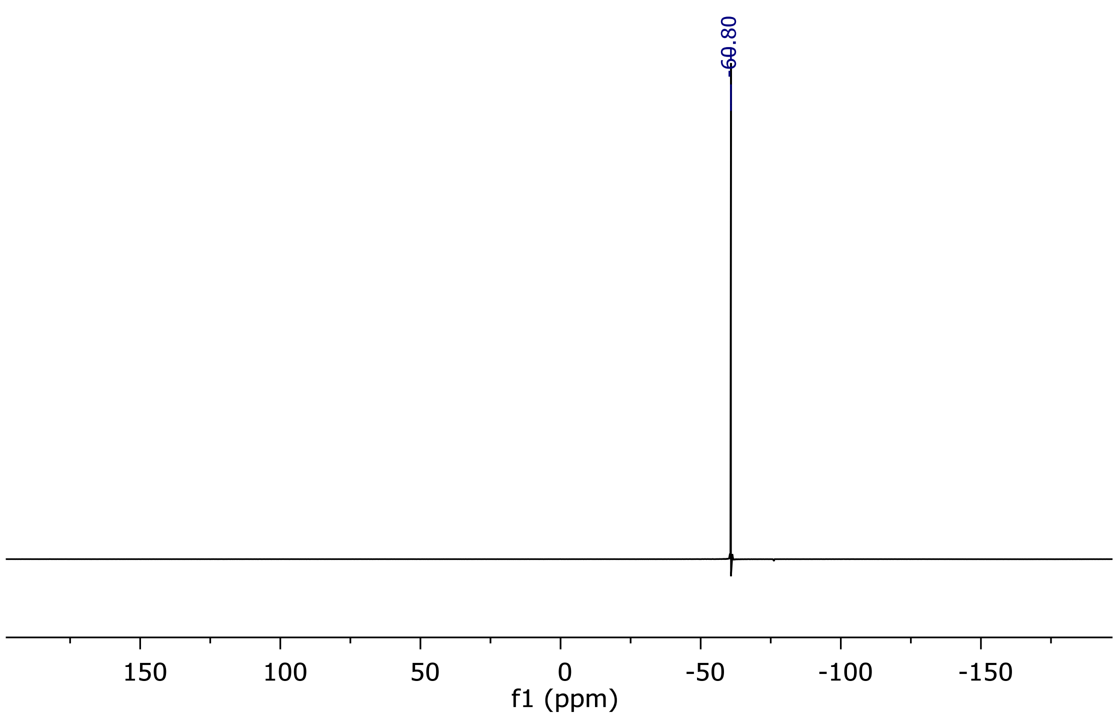



**Figure S70**: $^{19}$F NMR of **26** in $CD_2Cl_2$.

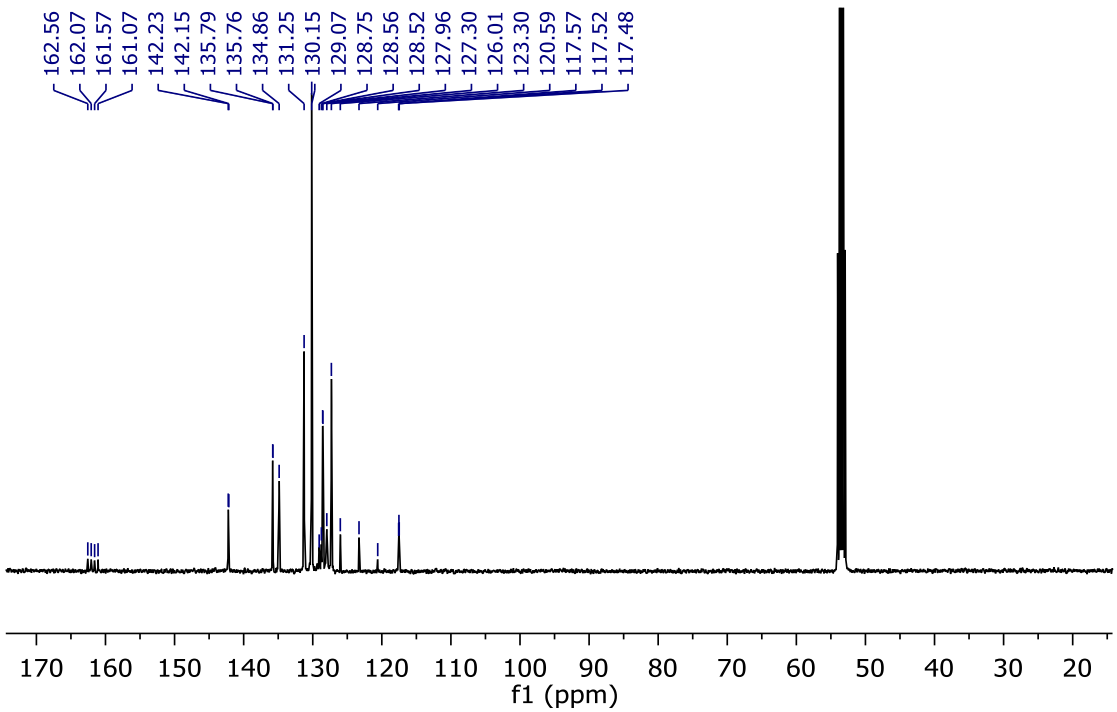



**Figure S71**: $^{13}C$ NMR of **26** in $CD_2Cl_2$