

Supporting Information

Synthesis, Crystal Structure and Magnetic Properties of a P-Stereogenic Ortho-(4-amino-tempo)Phosphinic Amide Radical and its Cu^{II} Complex

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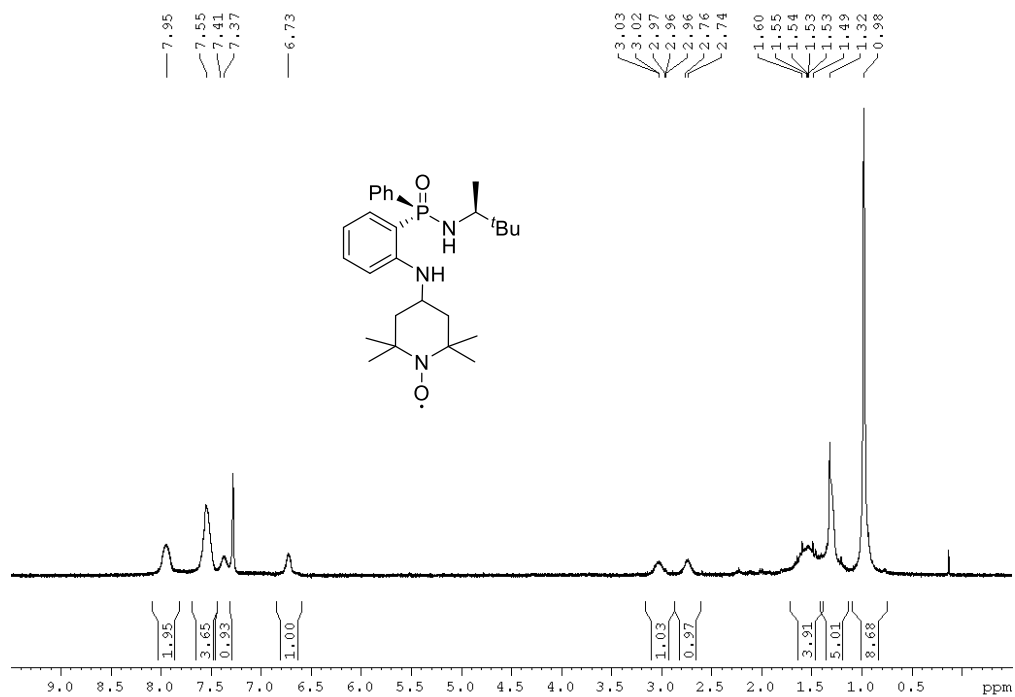


Figure S1. ¹H NMR spectrum (300.13 MHz) of compound 10.

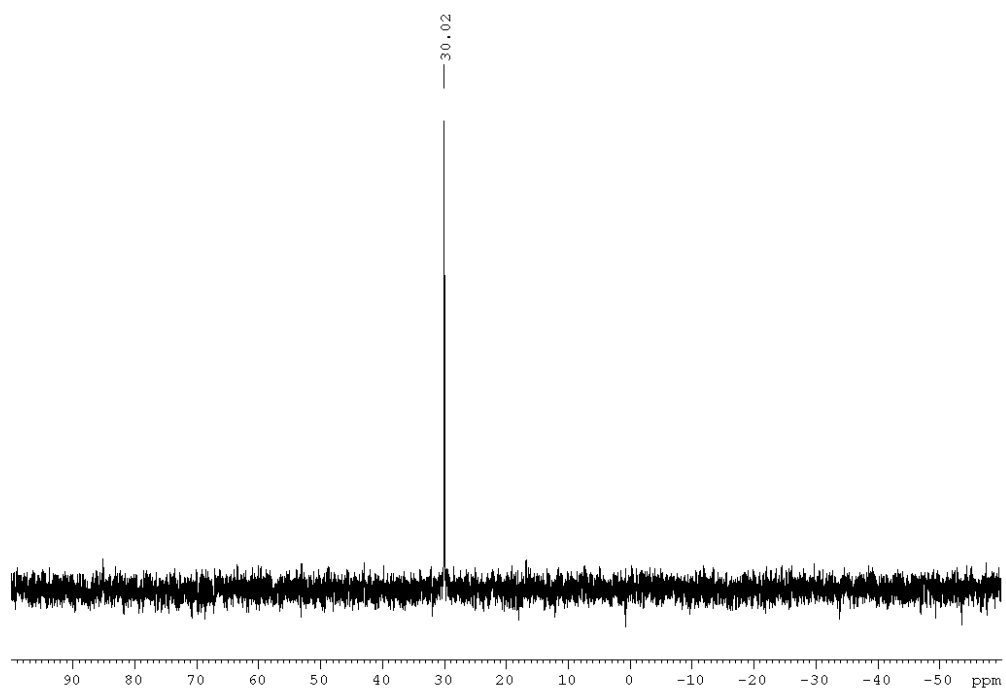


Figure S2. ³¹P{¹H} NMR spectrum (121.50 MHz) of compound 10.

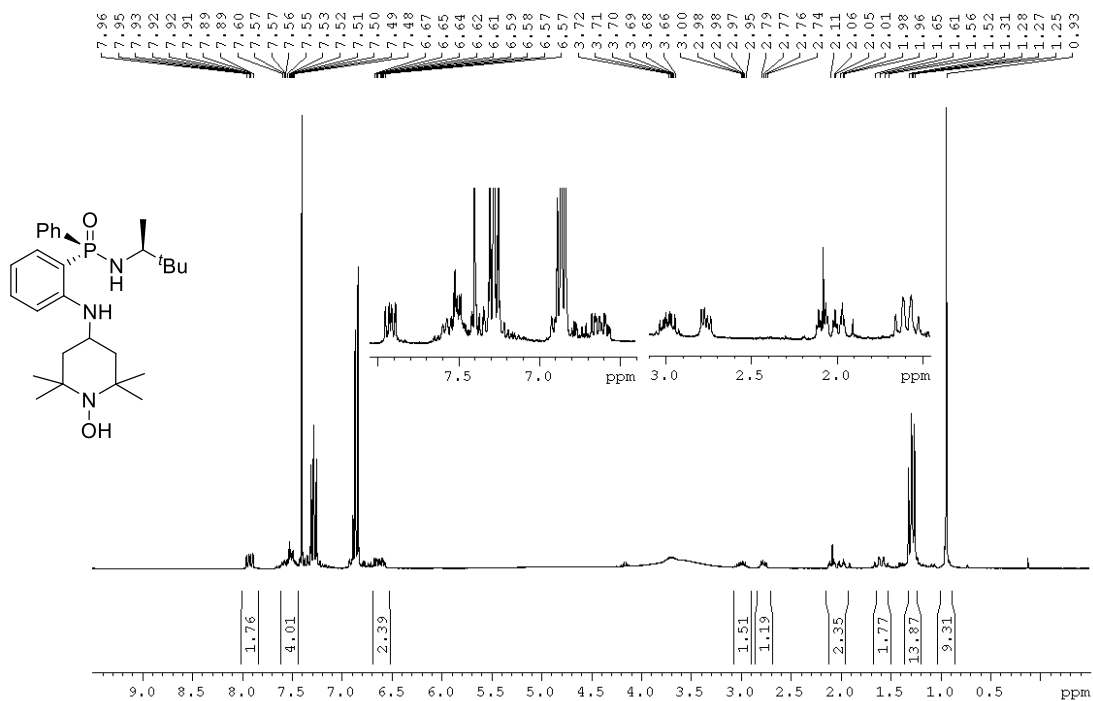


Figure S3. ¹H NMR spectrum (300.13 MHz) in the presence of PhNHNH₂ of compound 10.

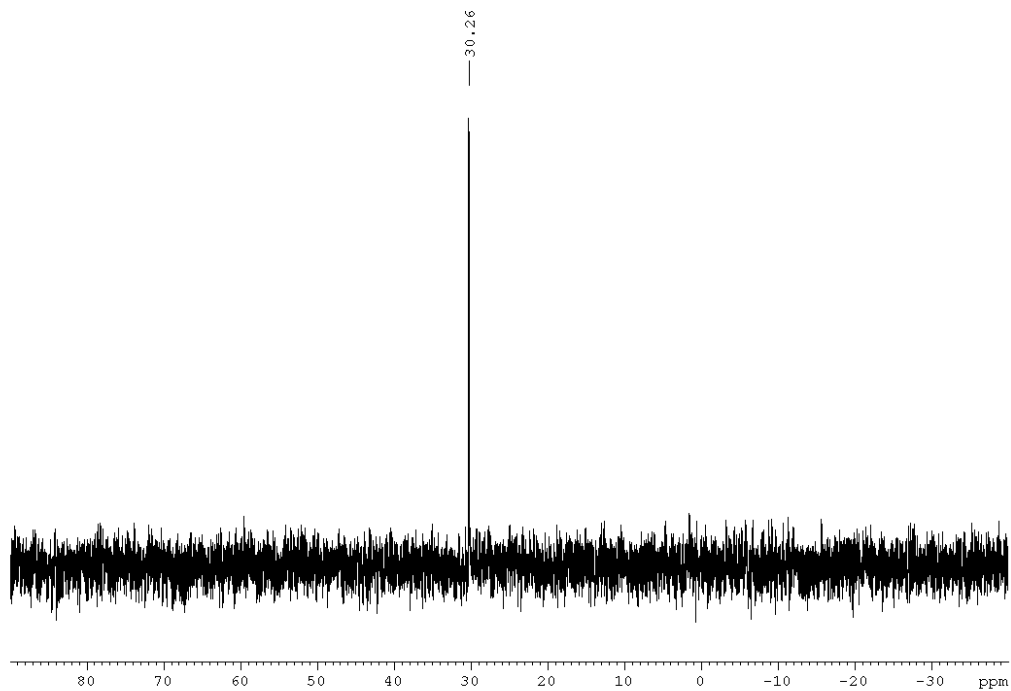
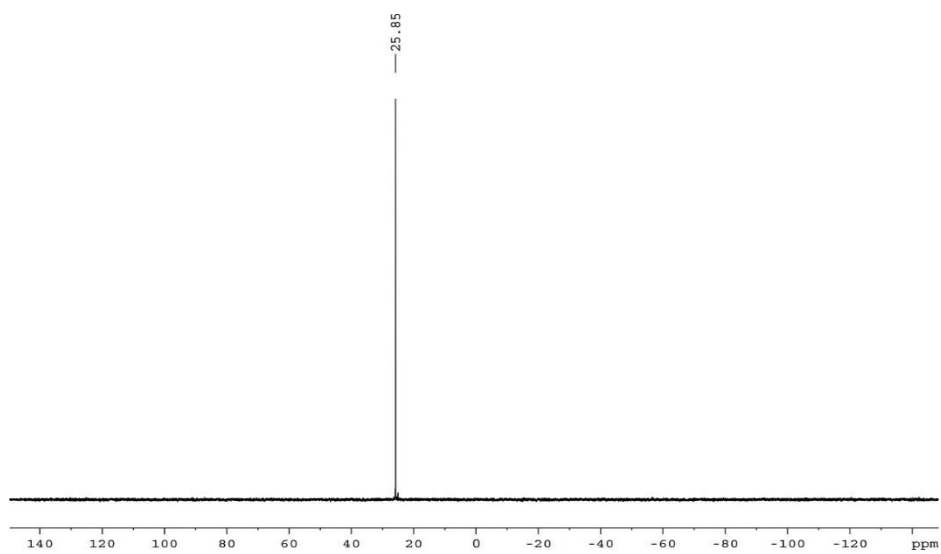
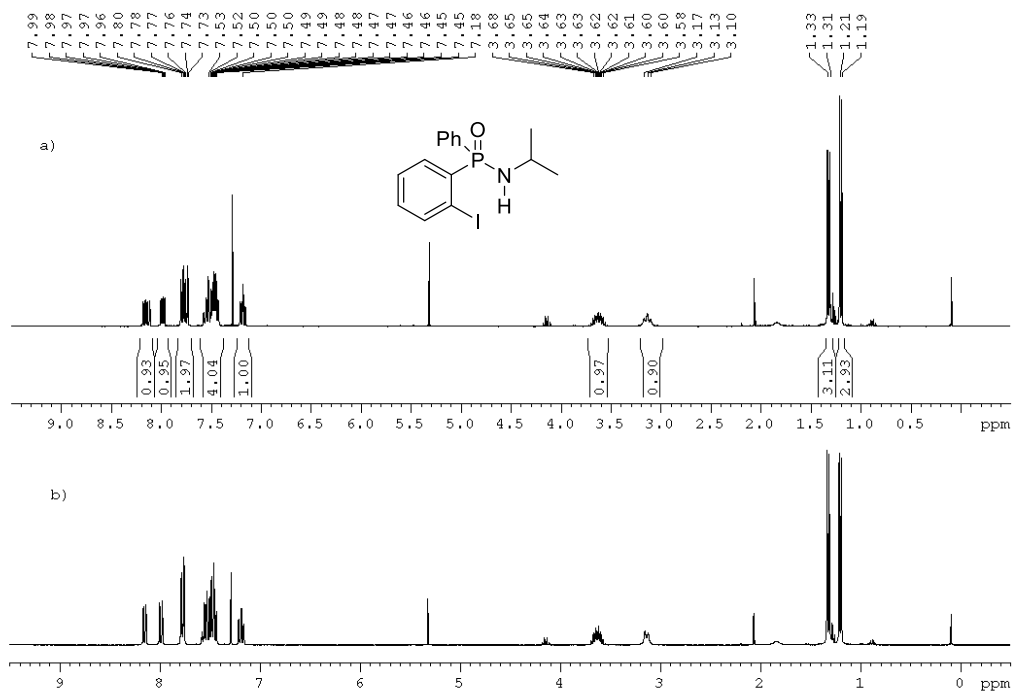


Figure S4. ³¹P{¹H} NMR spectrum (121.50 MHz) in the presence of PhNHNH₂ of compound 10.



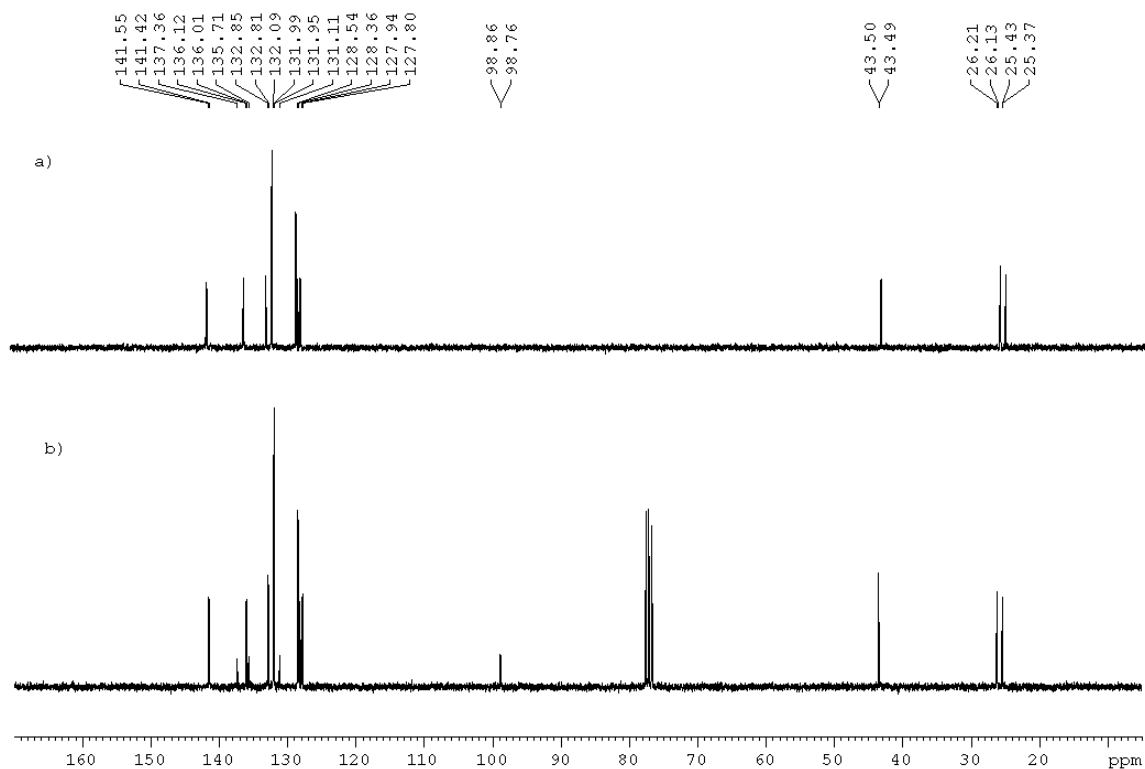


Figure S7. DEPT-135 (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR spectra (75.47 MHz) of compound **11**.

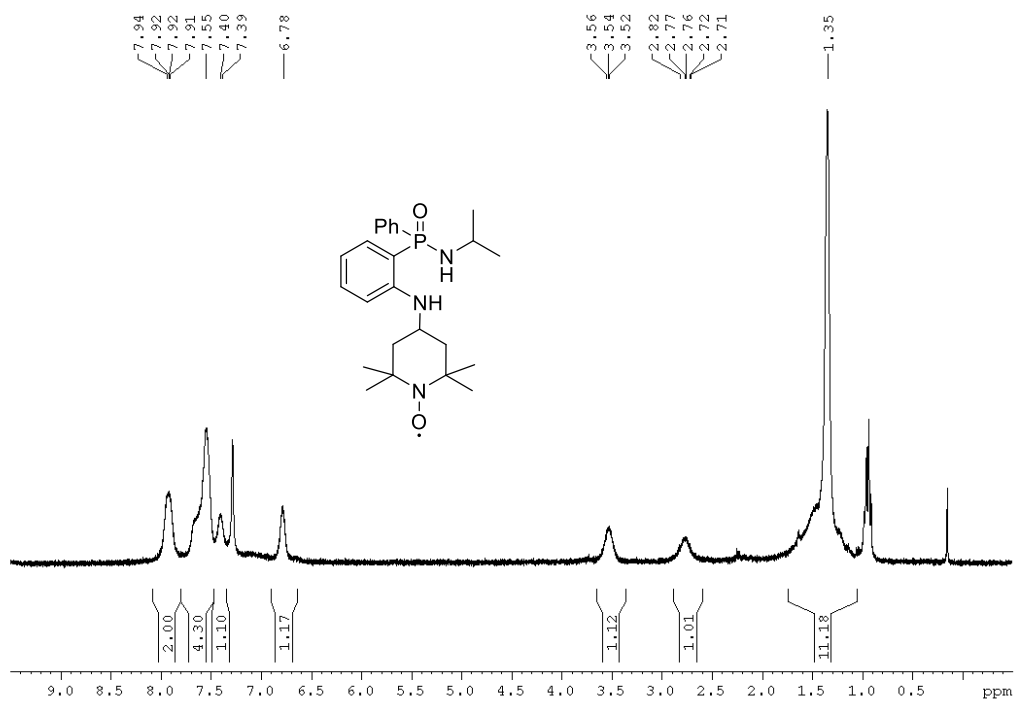


Figure S8. ^1H NMR spectrum (300.13 MHz) of compound **13**.

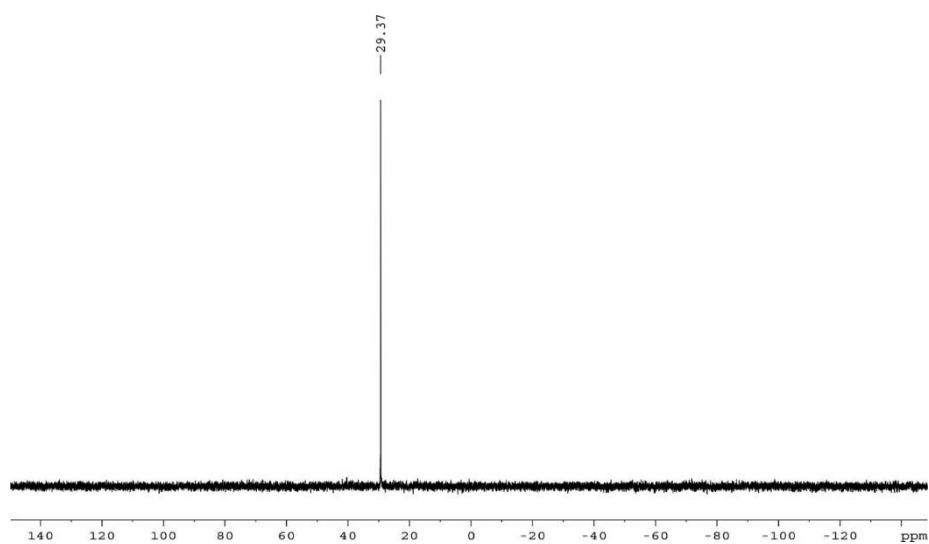


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) in the presence of PhNHNH₂ of compound **13**.

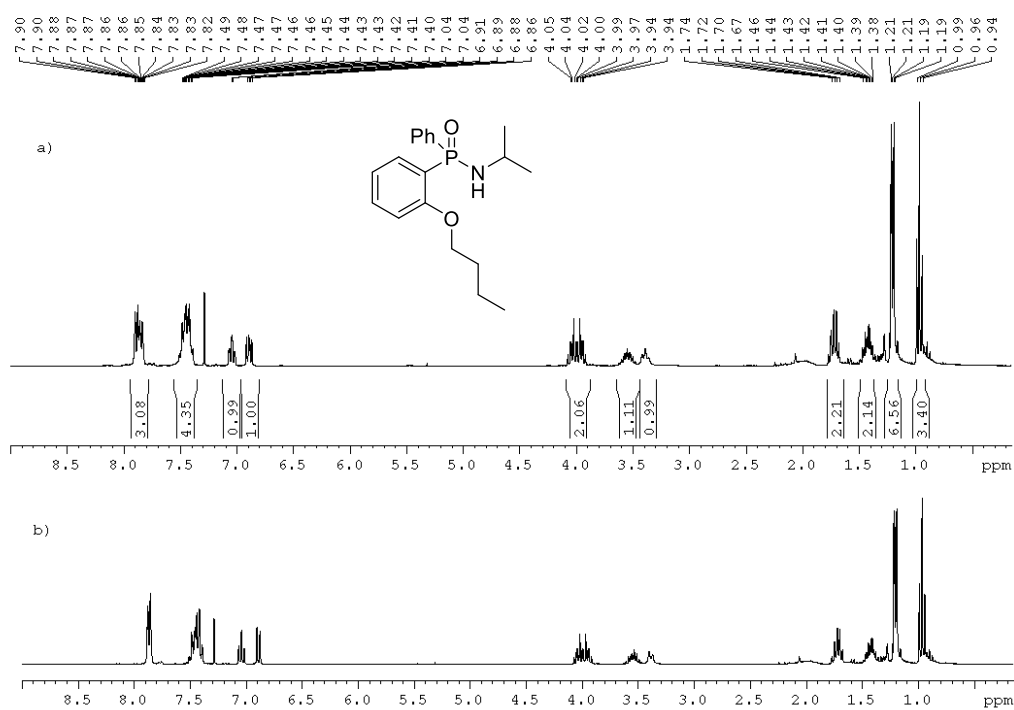


Figure S12. ^1H (a) and $^1\text{H}\{^{31}\text{P}\}$ (b) NMR spectra (300.13 MHz) of compound **14**.

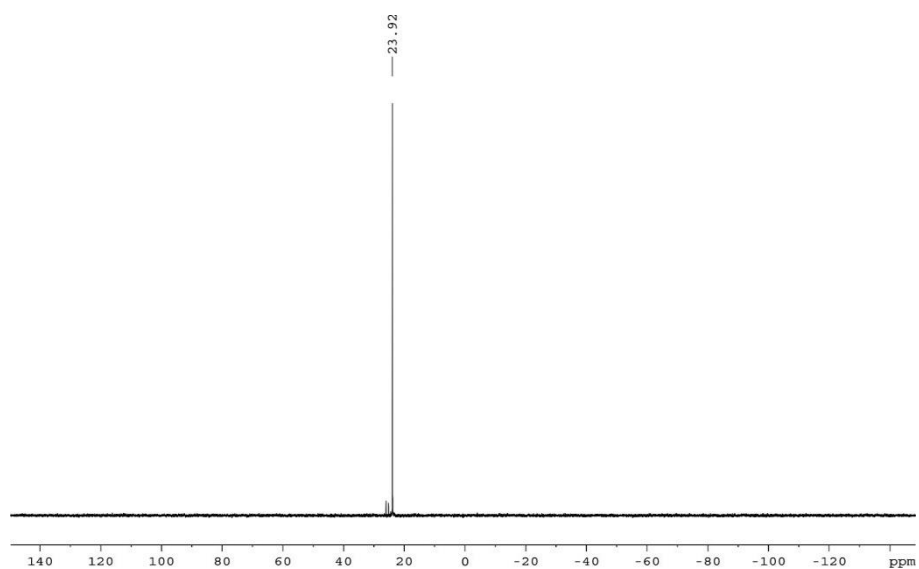


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) of compound **14**.

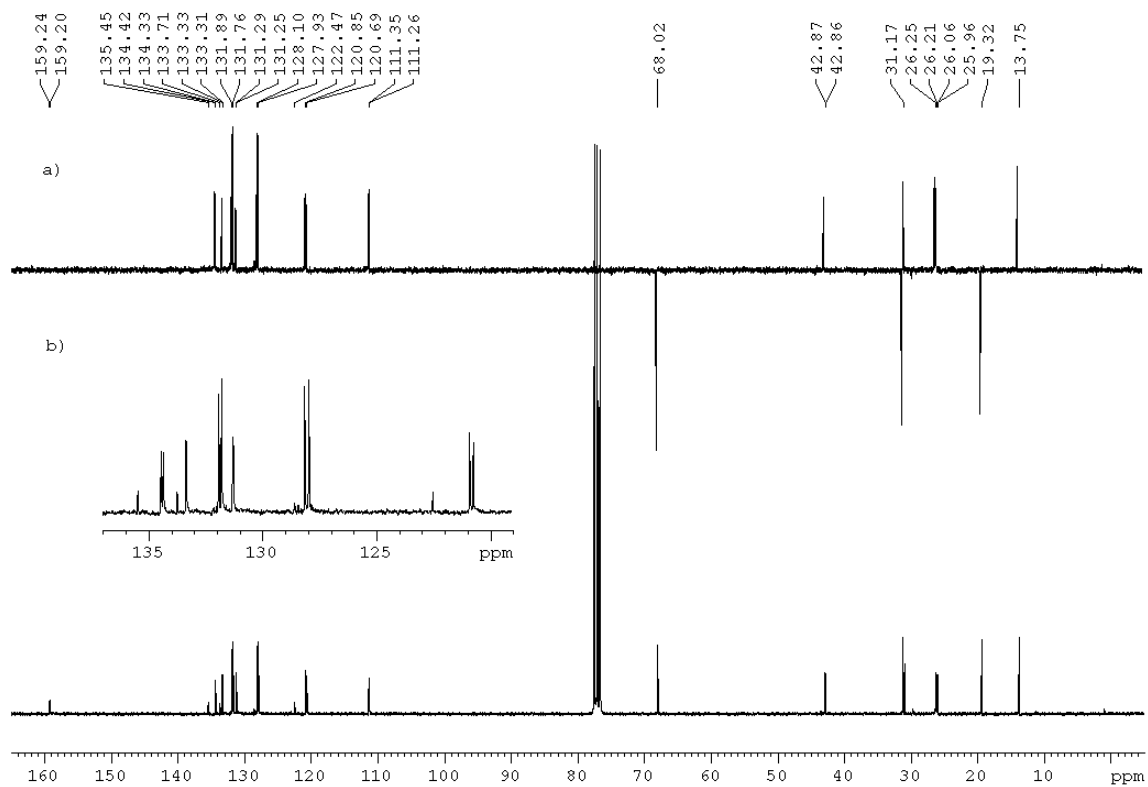


Figure S14. DEPT-135 (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR spectra (75.47 MHz) of compound **14**.

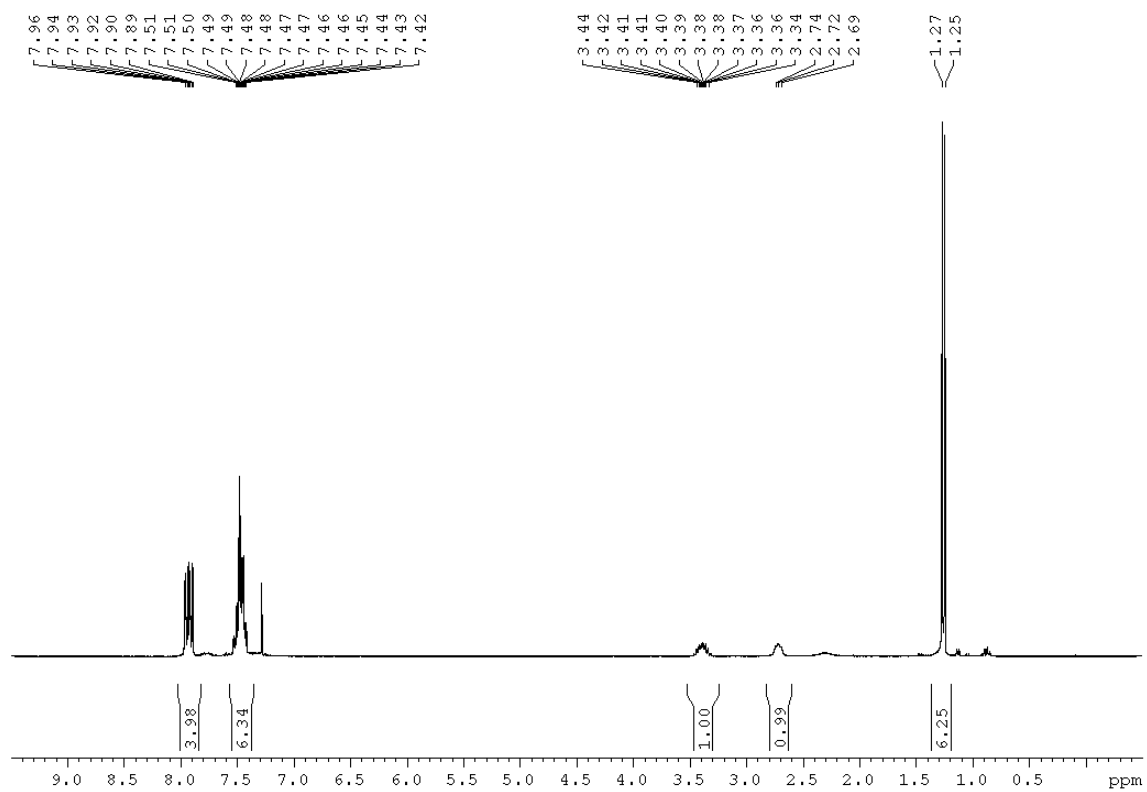


Figure S15. ^1H NMR spectrum (300.13 MHz) of compound **15**.

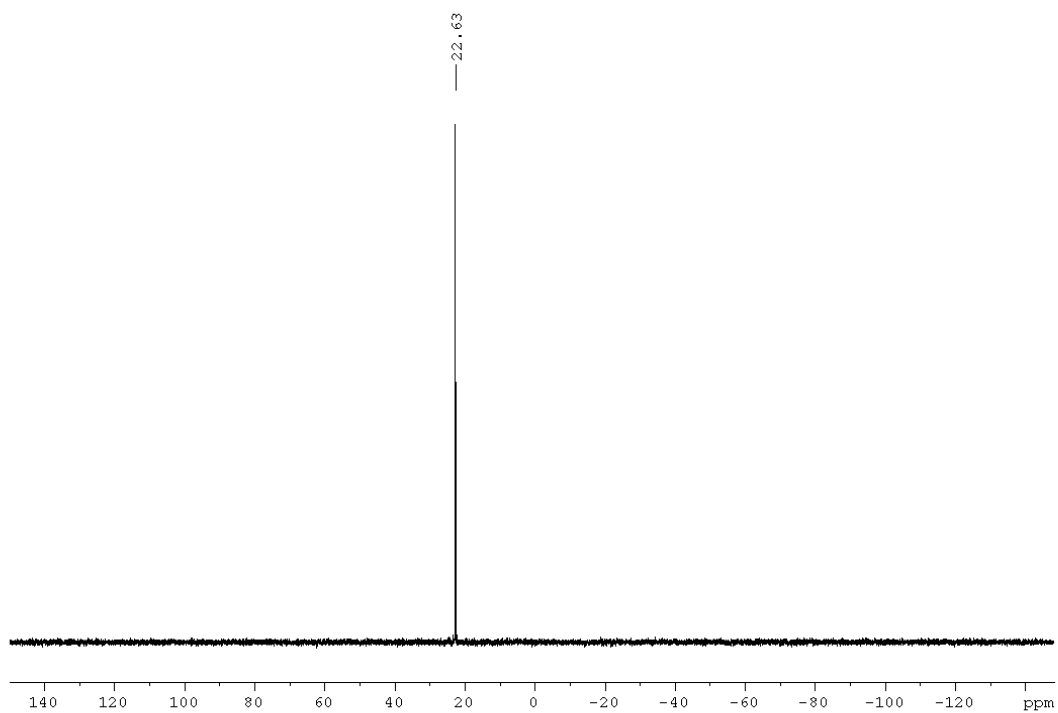


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) of compound **15**.

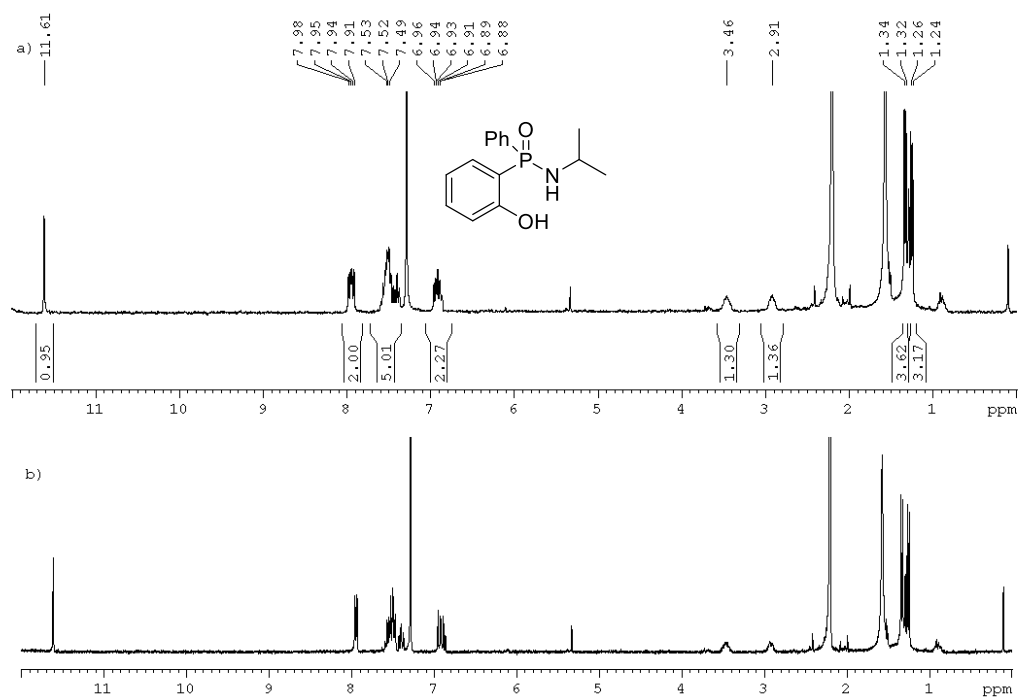


Figure S17. ^1H (a) and $^1\text{H}\{^{31}\text{P}\}$ (b) NMR spectra (300.13 MHz) of compound 16.

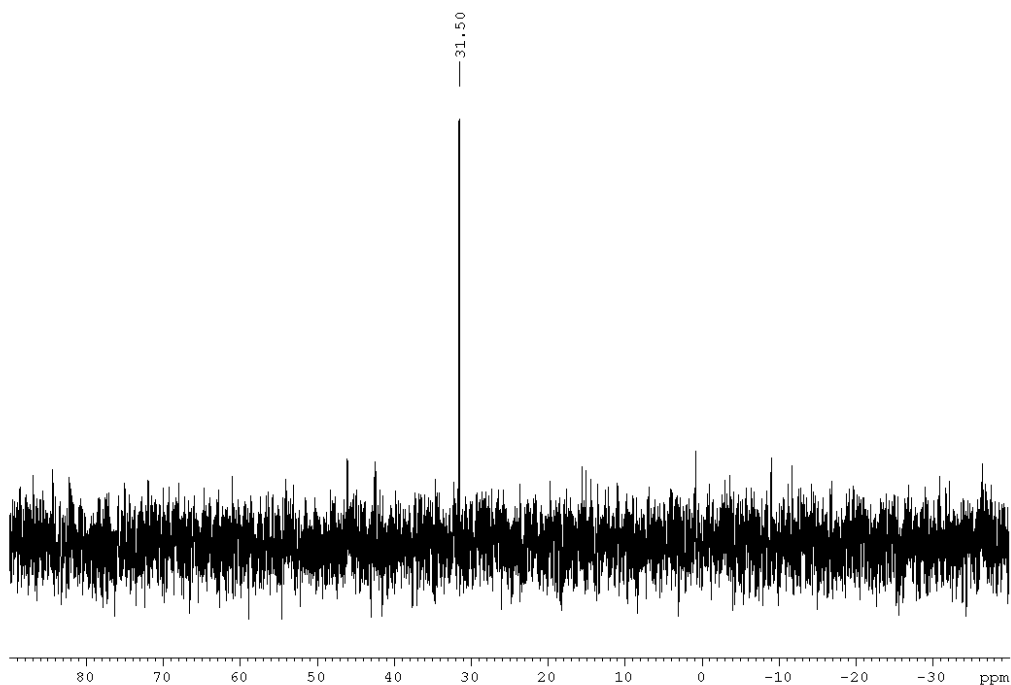


Figure S18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) of compound 16.

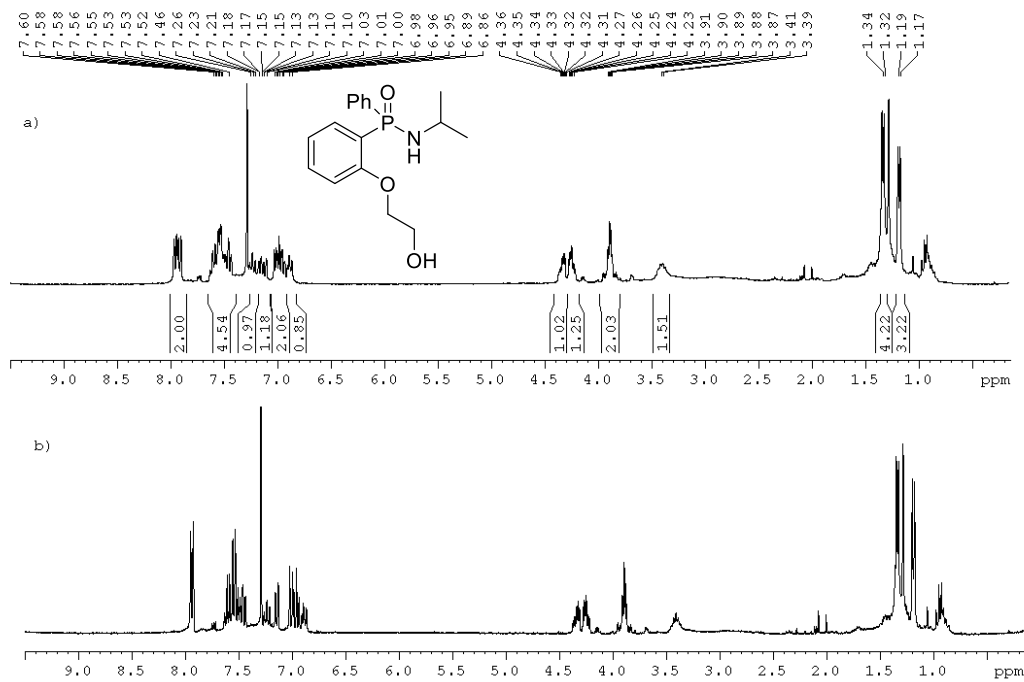


Figure S19. ^1H (a) and $^1\text{H}\{^{31}\text{P}\}$ (b) NMR spectra (300.13 MHz) of compound 17.

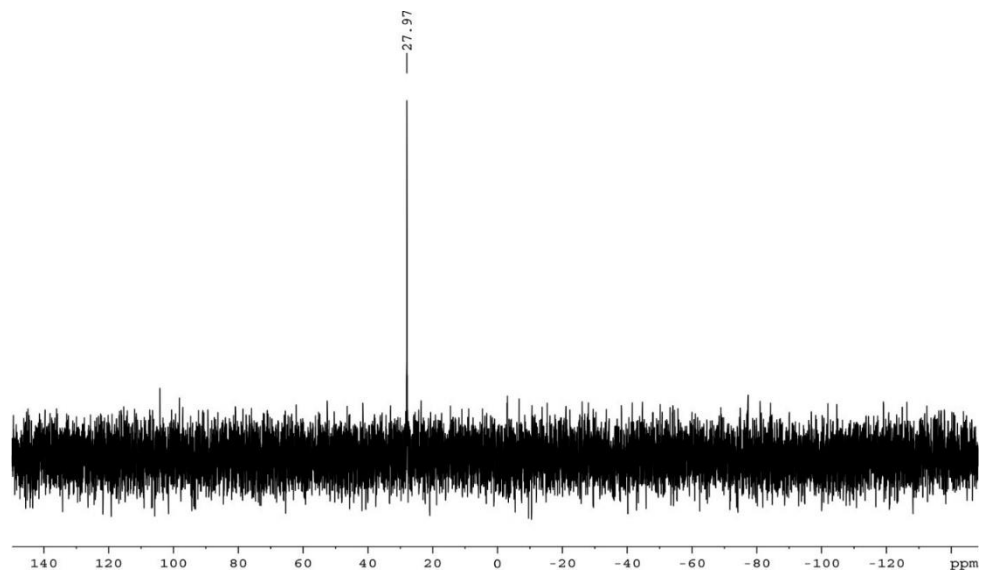


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) of compound 17.

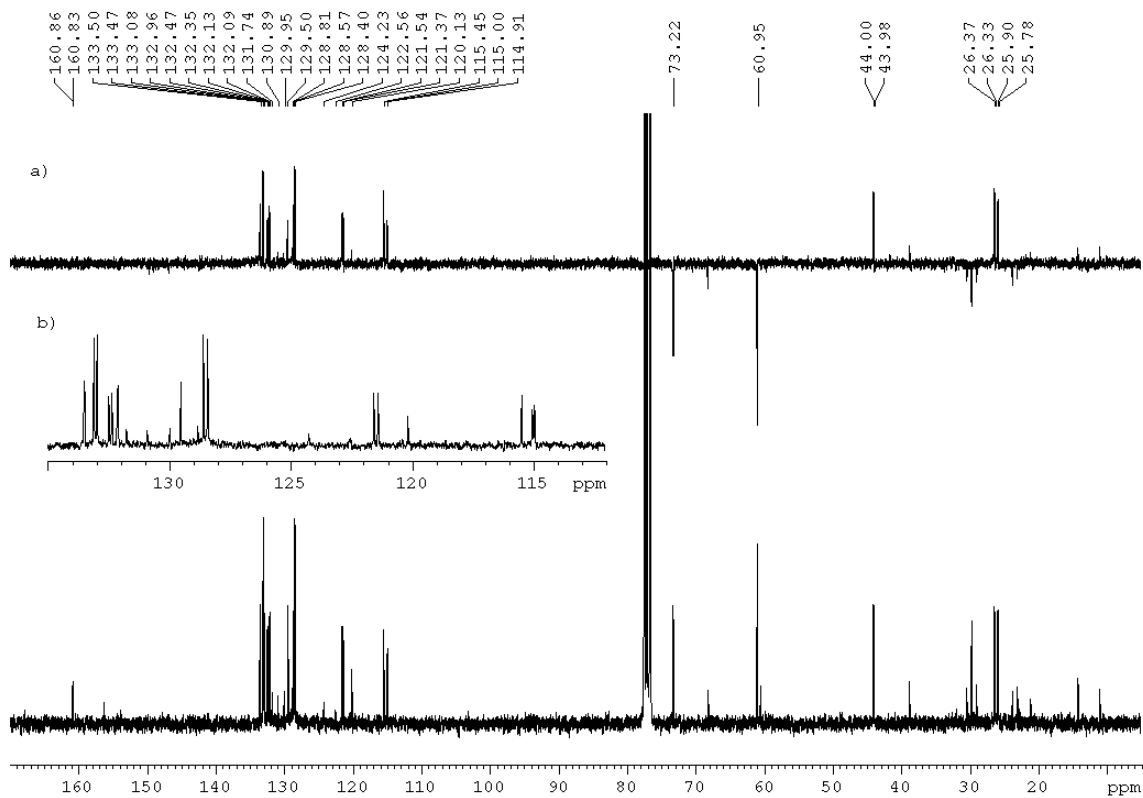


Figure S21. DEPT-135 (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR spectra (75.47 MHz) of compound **17**.

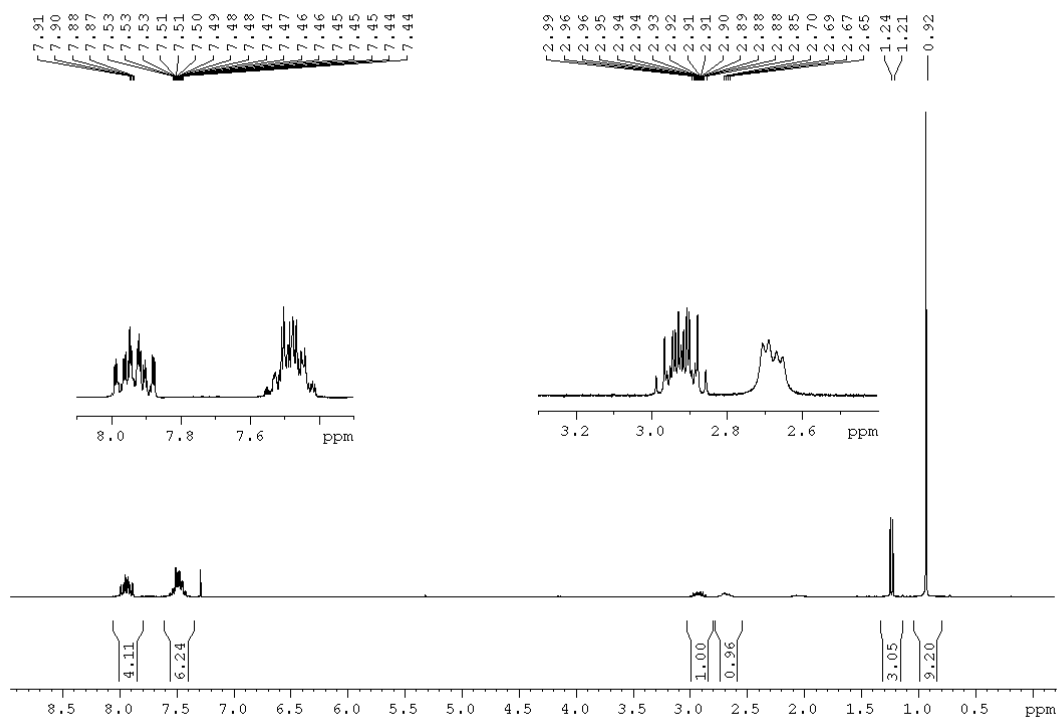


Figure S22. ^1H (a) NMR spectrum (300.13 MHz) of compound **18**.

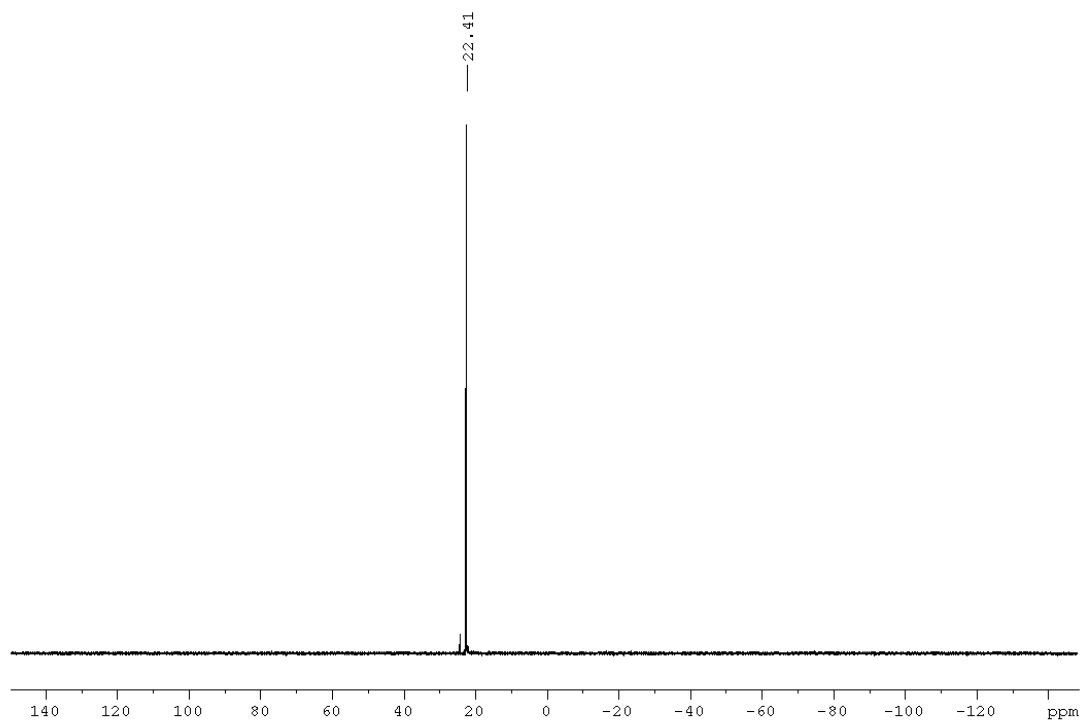


Figure S23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.50 MHz) of compound **18**.

Table S1: Summary of the crystal structure, data collection and refinement parameters for **10** and **19**.

| Compound reference | 10 | 19 |
|---|---|---|
| Chemical formula | C ₂₇ H ₄₁ N ₃ O ₂ P | C ₄₄ H ₅₁ CuF ₁₂ N ₃ O ₆ P |
| Formula Mass | 470.60 | 1040.40 |
| Crystal system | Orthorhombic | Orthorhombic |
| <i>a</i> /Å | 8.3792(2) Å | 14.6129(3) |
| <i>b</i> /Å | 17.0809(4) Å | 15.1415(4) |
| <i>c</i> /Å | 18.6707(4) Å | 21.6411(5) |
| α /° | 90 | 90 |
| β /° | 90 | 90 |
| γ /° | 90 | 90 |
| Unit cell volume/Å ³ | 2672.23(11) | 4788.34(19) |
| Temperature/K | 100(2) | 100(2) |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| No. of formula units per unit cell, <i>Z</i> | 4 | 4 |
| Radiation type | CuK α | CuK α |
| Absorption coefficient, μ /mm ⁻¹ | 1.12 | 1.81 |
| No. of reflections measured | 13459 | 25077 |
| No. of independent reflections | 5437 | 9753 |
| <i>R</i> _{int} | 0.037 | 0.033 |
| Final <i>R</i> _I values (<i>I</i> >2 σ (<i>I</i>)) | 0.030 | 0.034 |
| Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> >2 σ (<i>I</i>)) | 0.072 | 0.081 |
| Final <i>R</i> _I values (all data) | 0.035 | 0.040 |
| Final <i>wR</i> (<i>F</i> ²) values (all data) | 0.075 | 0.084 |
| Goodness of fit on <i>F</i> ² | 1.05 | 1.03 |
| $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$, eÅ ⁻³ | 0.21 and -0.32 | 0.46 and -0.30 |
| Flack parameter | 0.024(9) | -0.007(9) |
| CCDC Deposition | 2011812 | 2011813 |

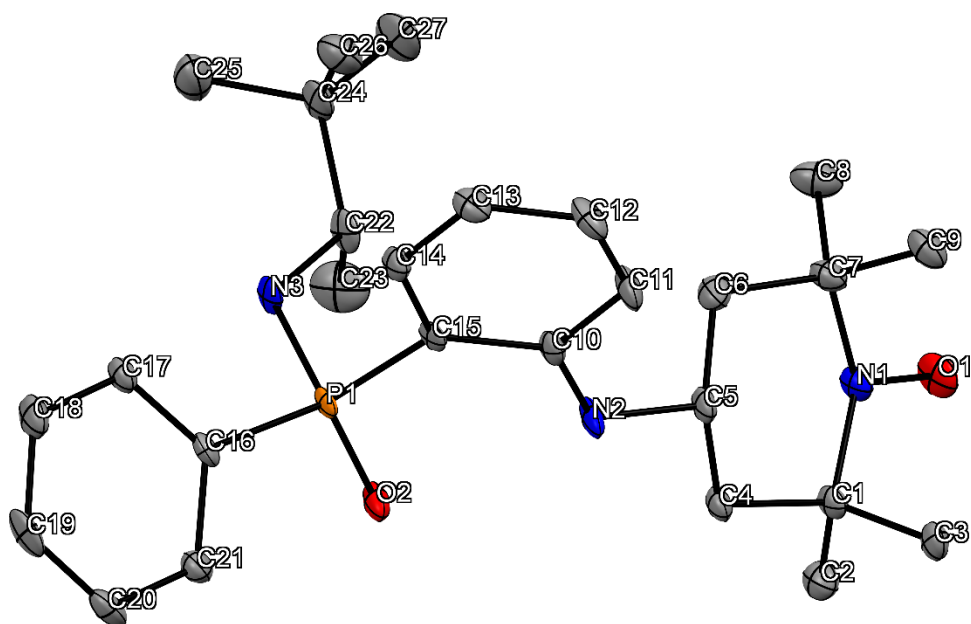


Figure S20: Thermal ellipsoids of the asymmetric unit of compound **10** drawn at 50% of probability level. Hydrogen atoms were omitted for clarity.

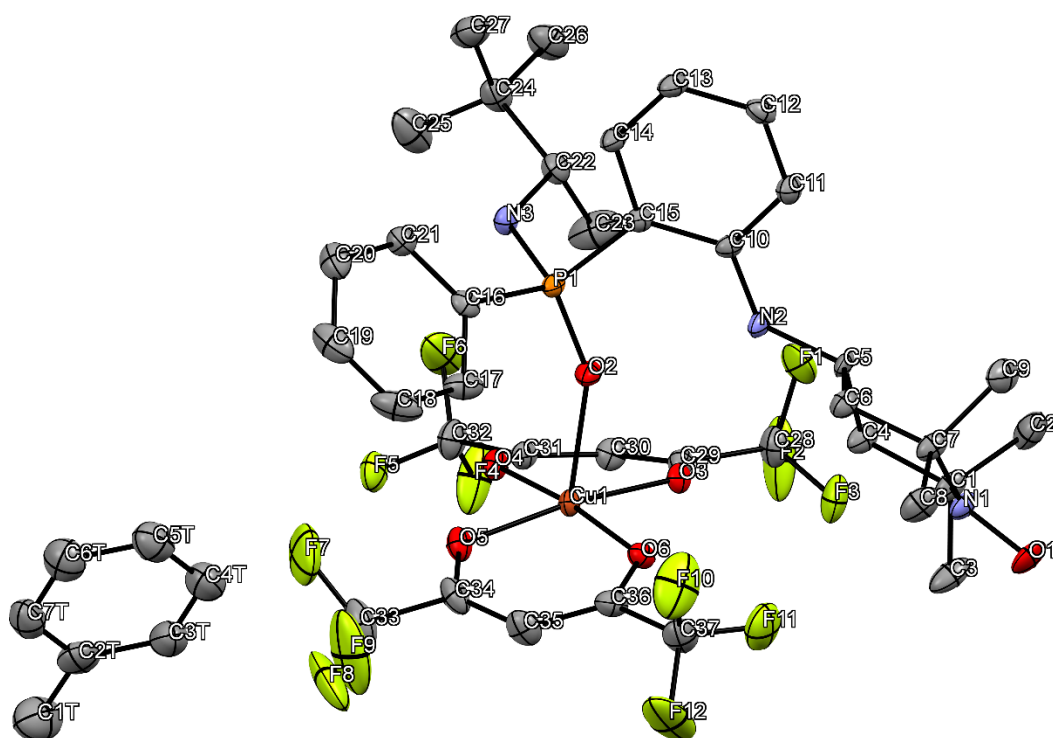


Figure S21: Thermal ellipsoids of the asymmetric unit of compound **19** drawn at 50% of probability level. Hydrogen atoms were omitted for clarity.