Electronic Supplementary Material (ESI) for Dalton Transactions.

- Supporting Information -

$GeCl_x[Co(CO)_3PR_3]_{4-x}$ (x = 0-3; R = ^{n}Pr, ^{n}Bu): From cobalt substituted germanes to novel binary cluster compounds.

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Content:

1. Experimental section

General Considerations

All manipulations were carried out under nitrogen or in vacuo in Schlenk-type glassware on a Schlenk line. Solvents were pre-dried over sodium benzophenone (thf, diethylether) or calcium hydride (pentane) and distilled. $GeCl_2$·dioxane was prepared according to Thorne et al..[1] $KCo(CO)_4$ was prepared from $Co_2(CO)_8$ using an excess of KOH.[2] $GeCl_3[Co(CO)_4)]$ was prepared from $GeCl_4$ and $KCo(CO)_4$ in a similar way to Patmore and Graham.[3] ^1H-, ^{13}C- and ^{31}P-NMR measurements were done at a Bruker Avance IIIHD-300 spectrometer. All values are given in ppm against the external standard $SiMe_4$. IR spectra were recorded at 298 K on a Bruker Vertex 70 spectrometer. All compounds were measured in a KBr-pellet under nitrogen atmosphere. The pellets were prepared under argon atmosphere.

2. Solid state structures of 4 and 10

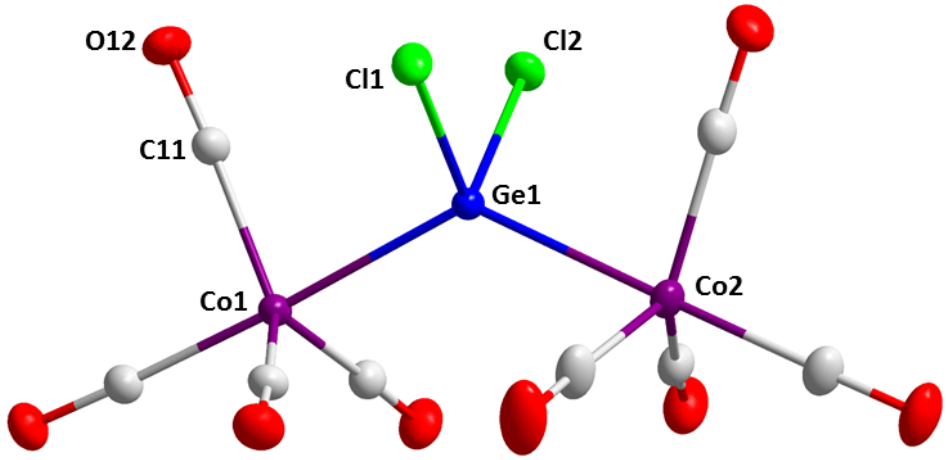

Figure S1. Molecular structure of $GeCl_2[Co(CO)_4]_2$ **4**. All atoms are shown with thermal ellipsoids set at 50% probability. Selected bond lengths /pm and angles /°: Ge1-Co1: 236.868(14), Ge1-Co2: 238.898(14), Ge1-Cl1: 219.69(2), Ge1-Cl2: 221.58(2), Co1-C11: 181.83(8), Co1-Ge1-Co2: 128.424(5), Cl1-Ge1-Cl2: 101.205(9), Cl1-Ge1-Co1: 107.082(7), C17-Co1-C11: 93.03, C17-Co1-Ge1: 177.33(3), C15-Co1-C11: 119.19(4).

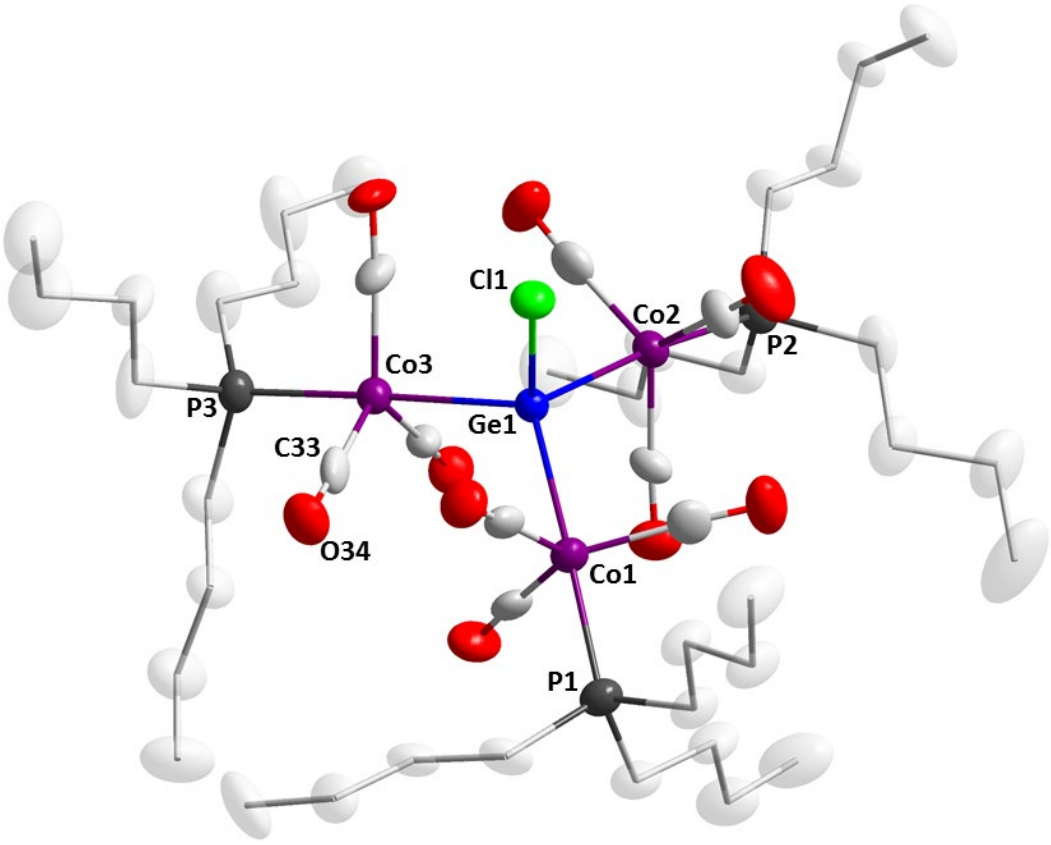

Figure S2. Molecular structure of $GeCl[Co(CO)_3P^nBu_3]_3$ **10** without hydrogen atoms. All atoms are shown with thermal ellipsoids set at 50% probability. The carbon atoms of the butyl groups are shown transparently (70%) for reasons of clarity. Selected bond lengths /pm and angles /°: Ge1-Cl1: 228.9(2), Ge1-Co1: 245.06(14), Ge1-Co2: 244.29(13), Ge1-Co3: 244.56(14), Co1-P1: 222.2(3), Co3-C33: 177.1(11), Co1-Ge1-Co2: 113.87(5), Cl1-Ge1-Co1: 104.72(7), P1-Co1-Ge1: 174.49(9), C33-Co3-Ge1: 89.4(3), C33-Co3-P3: 92.8(3), C33-Co3-C31: 121.4(4).

3. Spectroscopic investigations

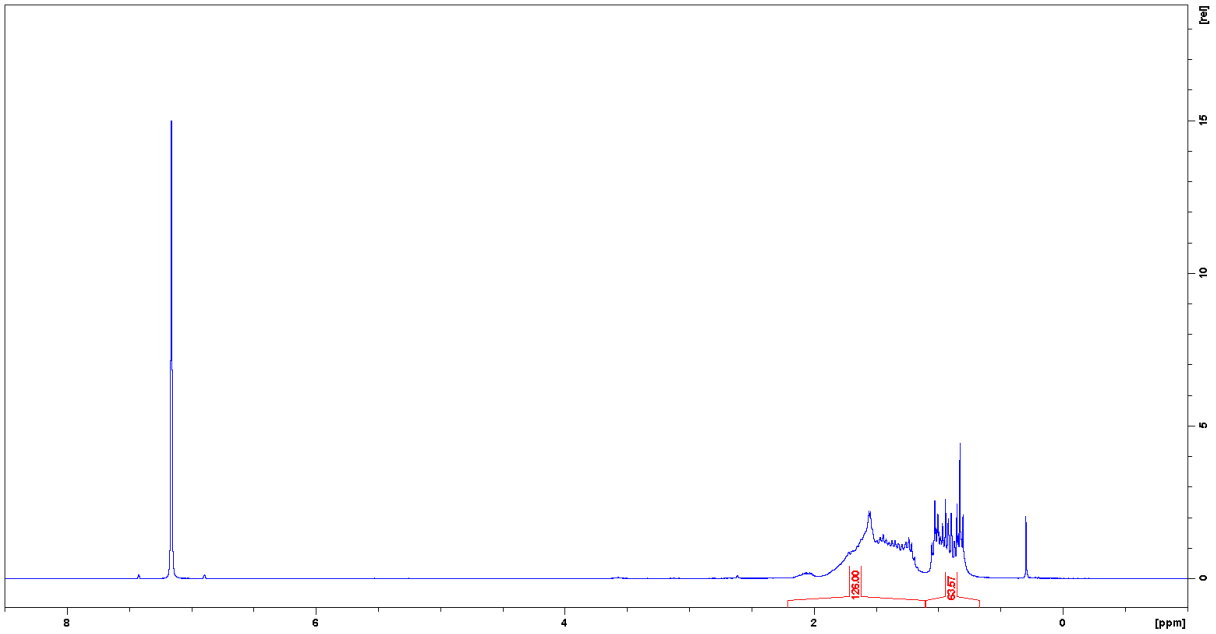

Figure S3. ^{1}H NMR spectrum of **2**.

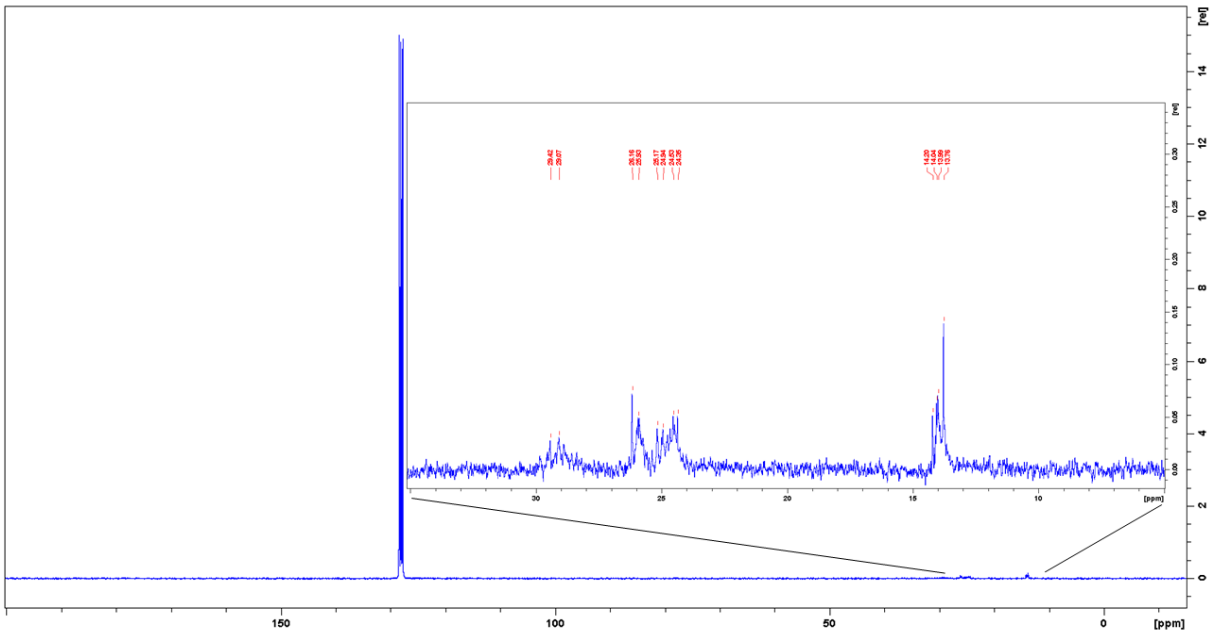

Figure S4. ^{13}C NMR spectrum of **2**.

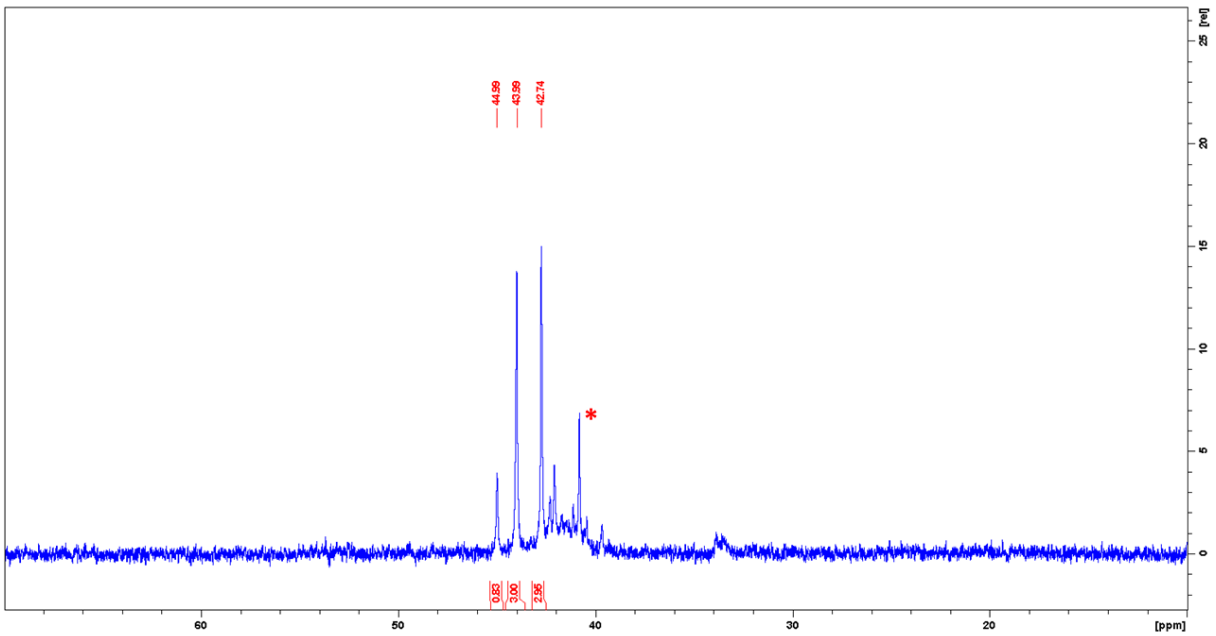

Figure S5. ^{31}P nmr spectrum of the pentane extract from which crystals of **2** were isolated. This spectrum shows some contamination with compound **13** (*, 40.8 ppm) and another minor contamination (42.1 ppm).

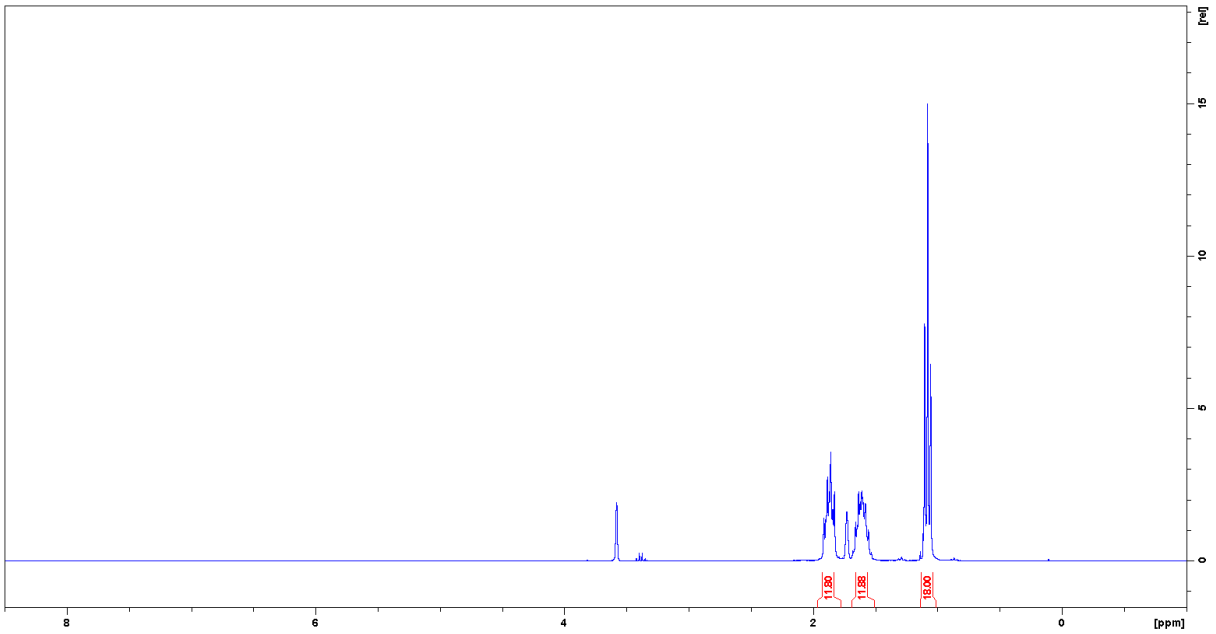

Figure S6. ^{1}H NMR spectrum of **3**.

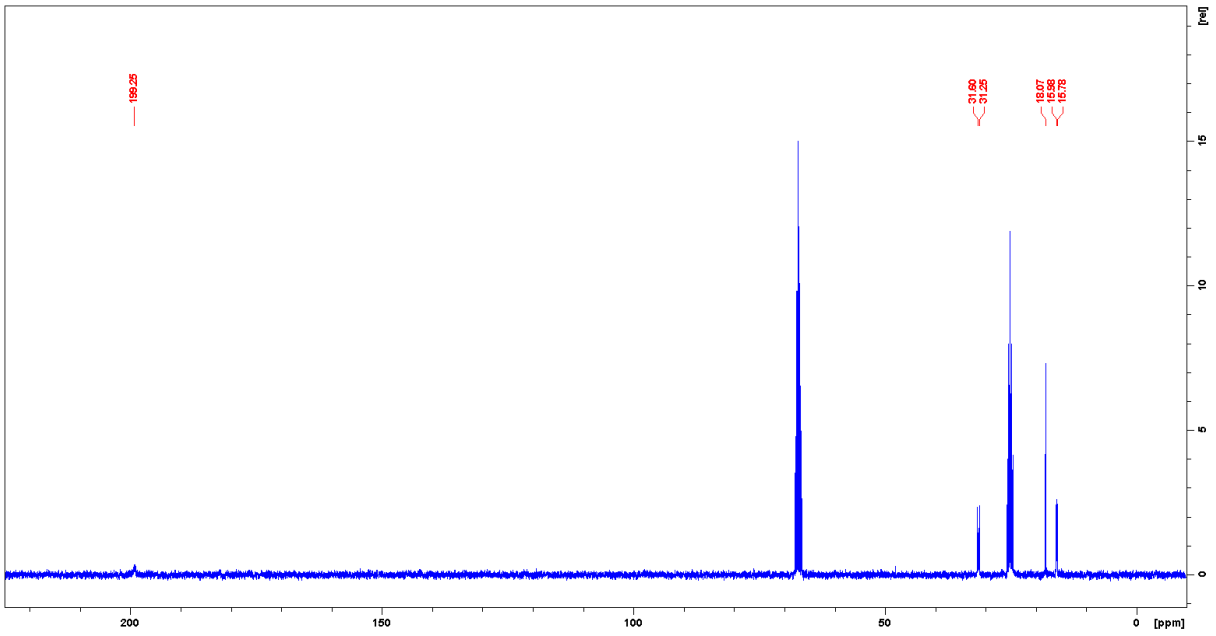

Figure S7. ^{13}C NMR spectrum of **3**.

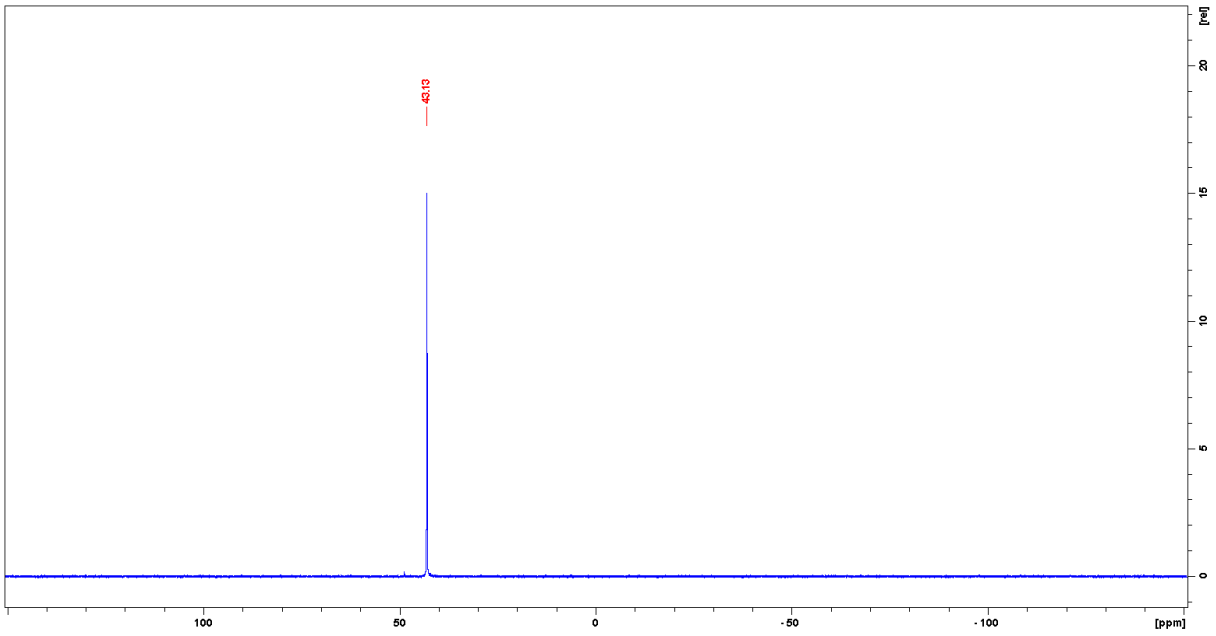

Figure S8. ^{31}P NMR spectrum of **3**.

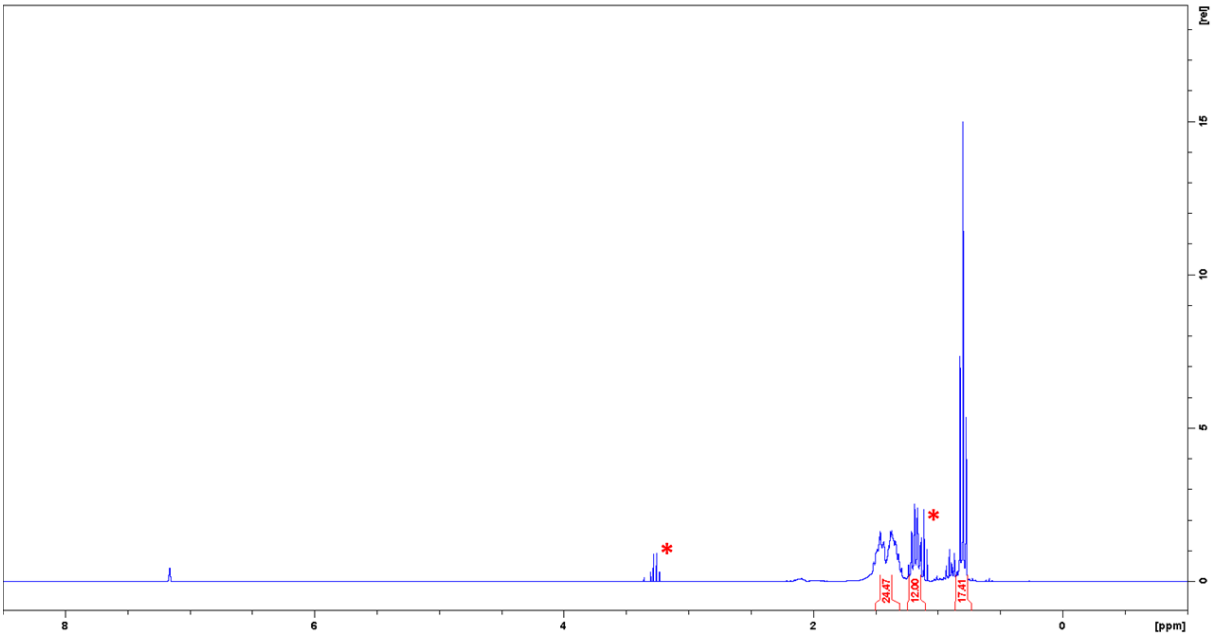

Figure S9. ^{1}H NMR spectrum of **5**. There is still some diethylether (*, triplet, 1.11 and quartet, 3.26) left in the sample, even after intense drying.

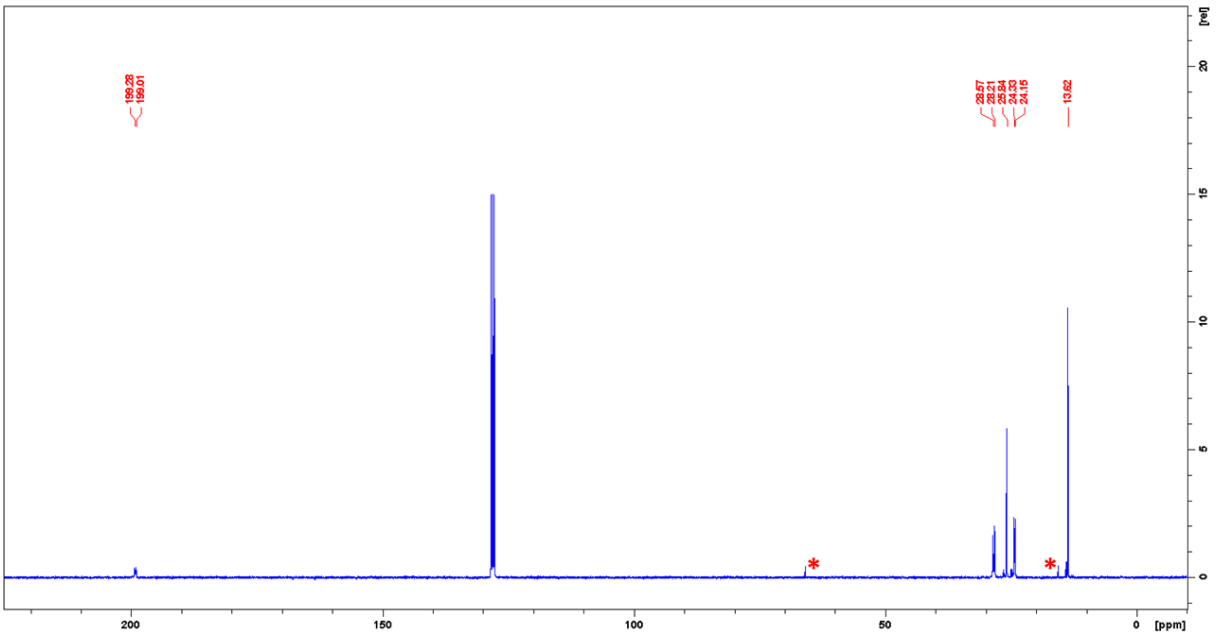

Figure S10. ^{13}C NMR spectrum of **5**. There is still some diethylether (*, singlets, 15.5, 65.9) left in the sample, even after intense drying.

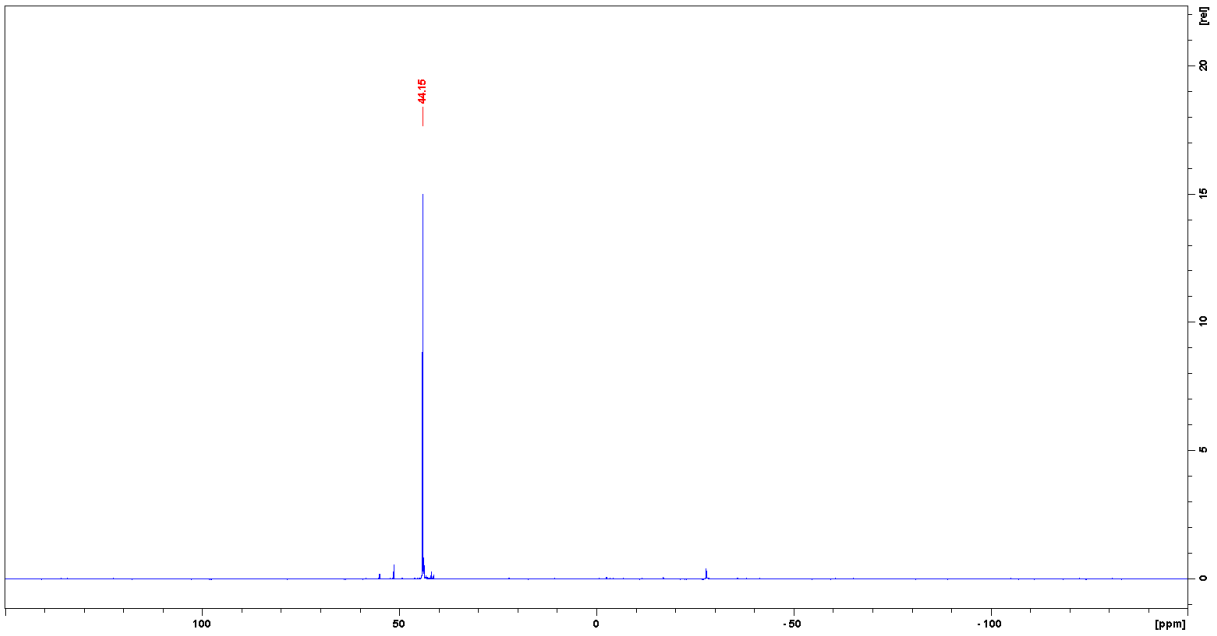

Figure S11. ^{31}P NMR spectrum of **5**.

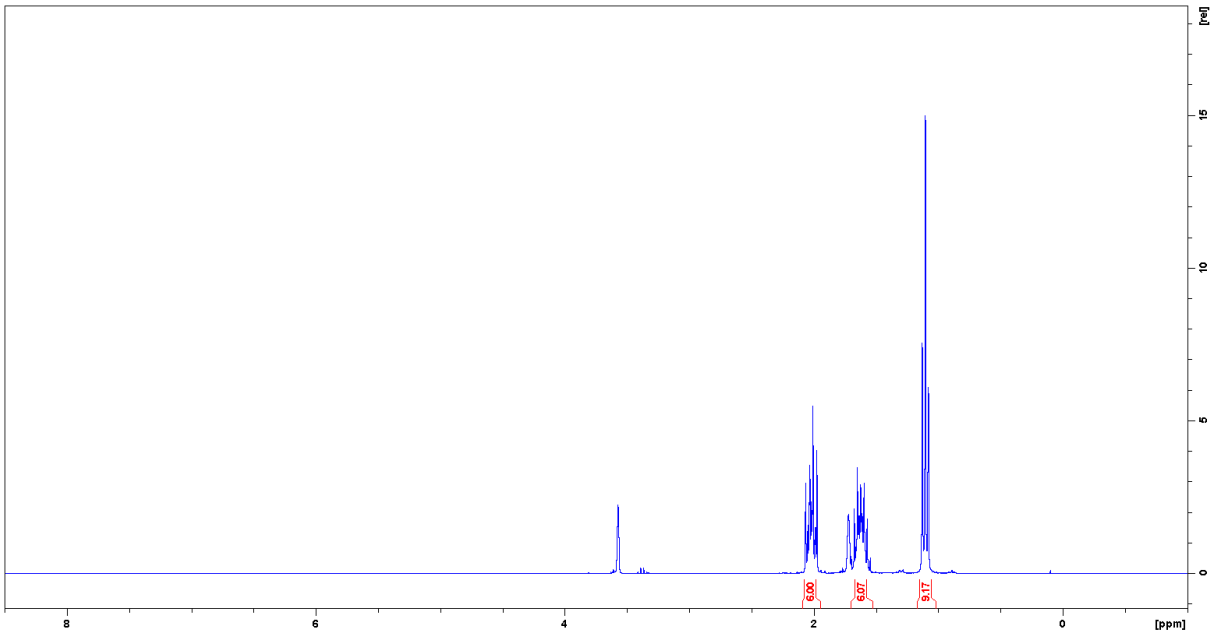

Figure S12. ^{1}H NMR spectrum of **6**.

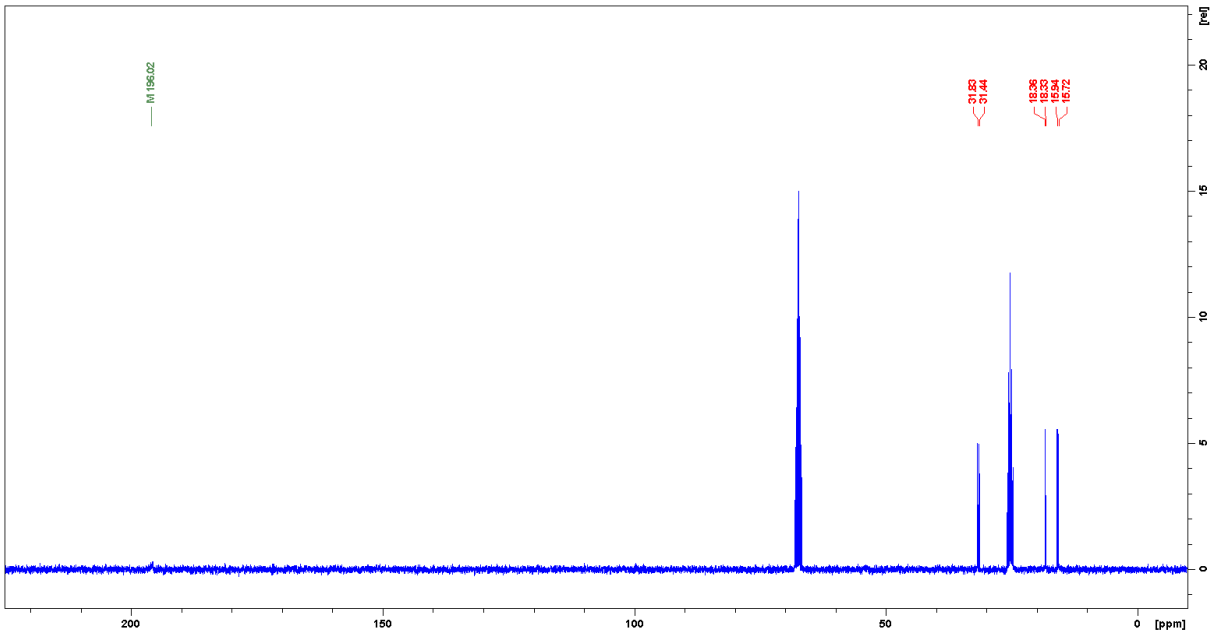

Figure S13. ^{13}C NMR spectrum of **6**.

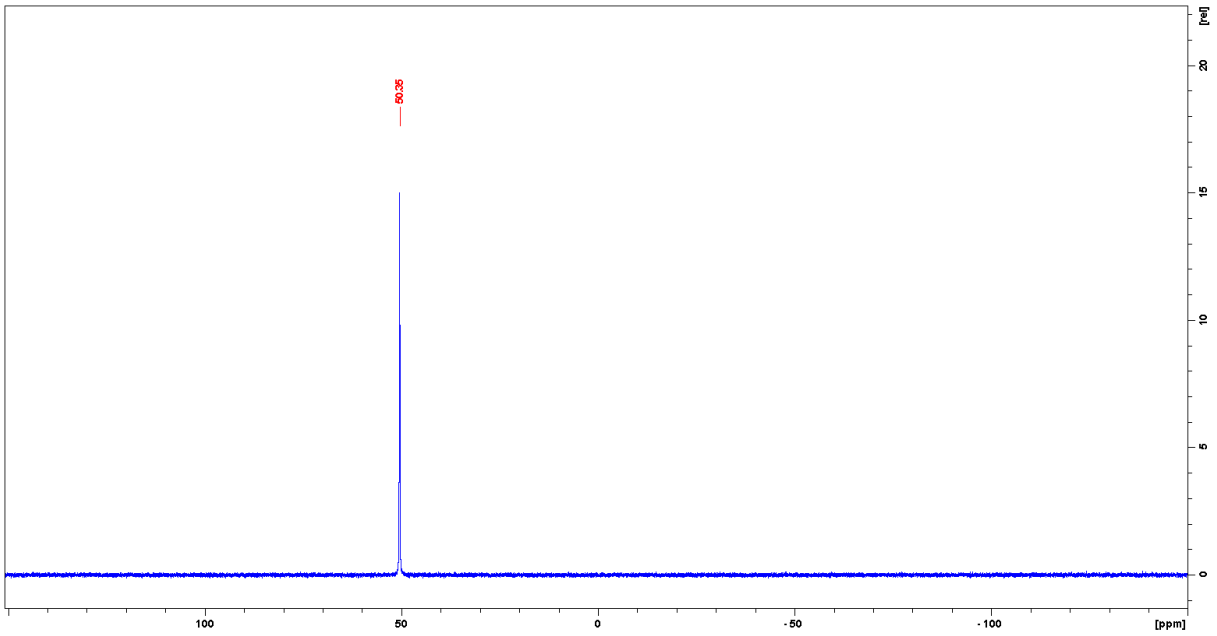

Figure S14. ^{31}P NMR spectrum of **6**.

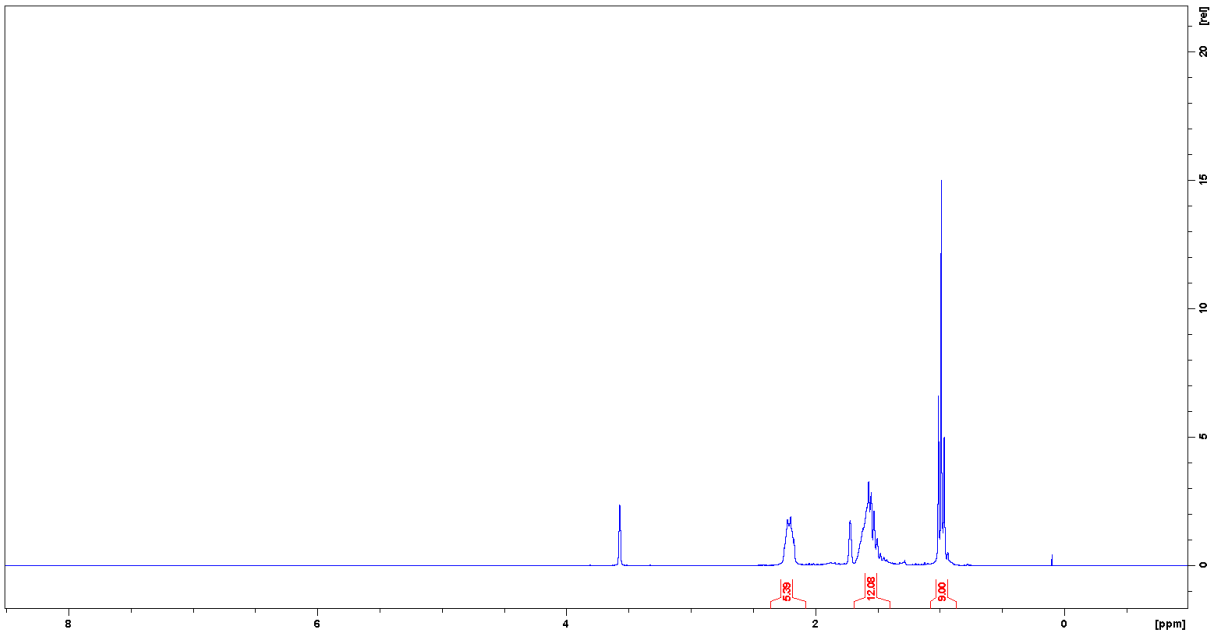

Figure S15. ^{1}H NMR spectrum of **8**.

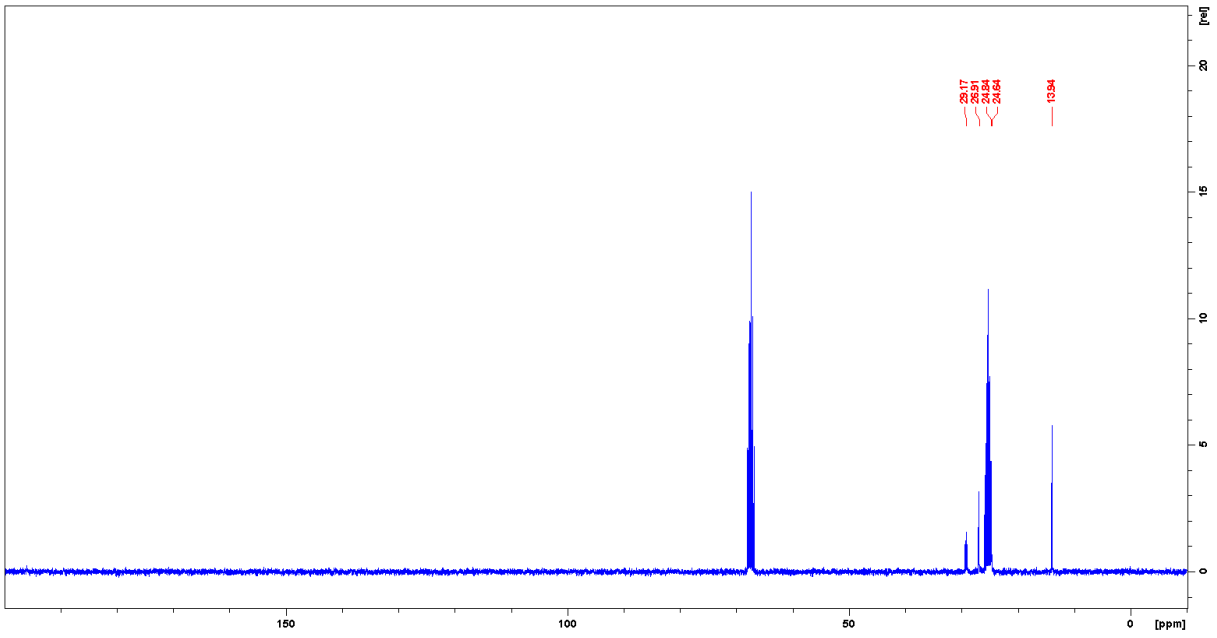

Figure S16. ^{13}C NMR spectrum of **8**.

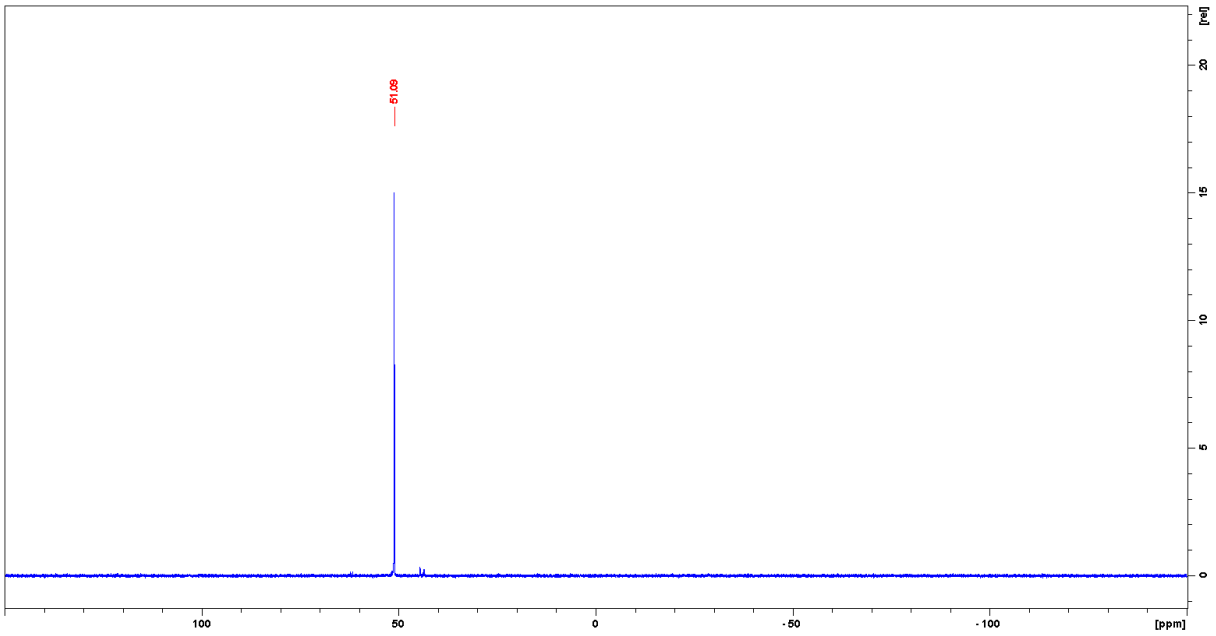

Figure S17. ^{31}P NMR spectrum of **8**.

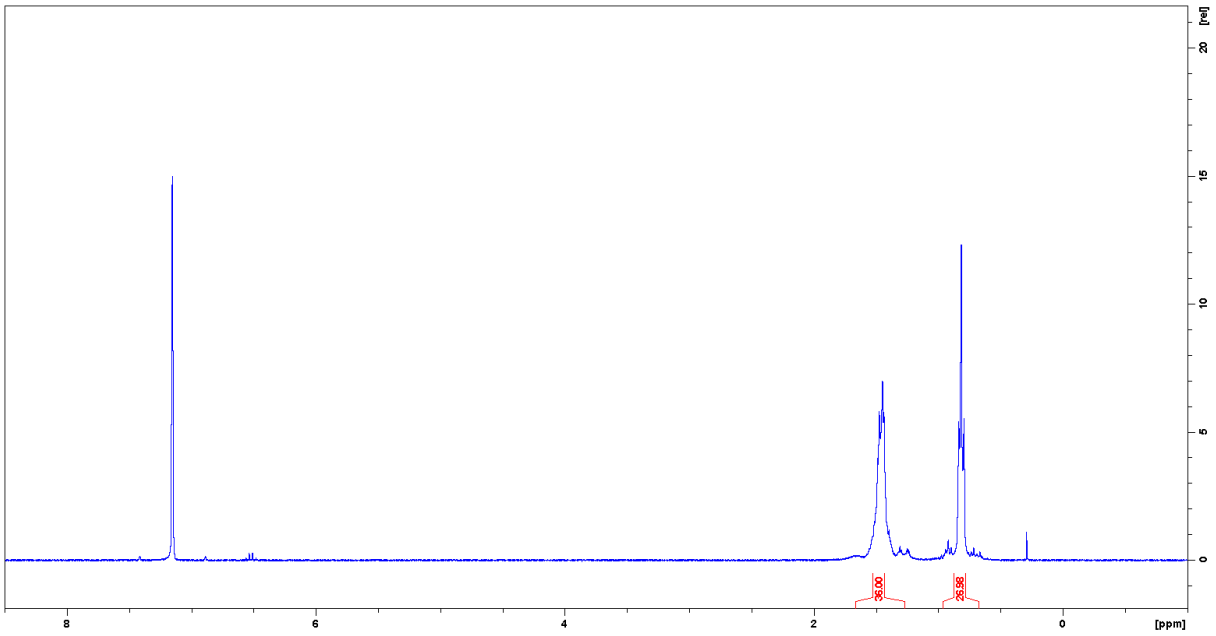

Figure S18. ^{1}H NMR spectrum of **9**.

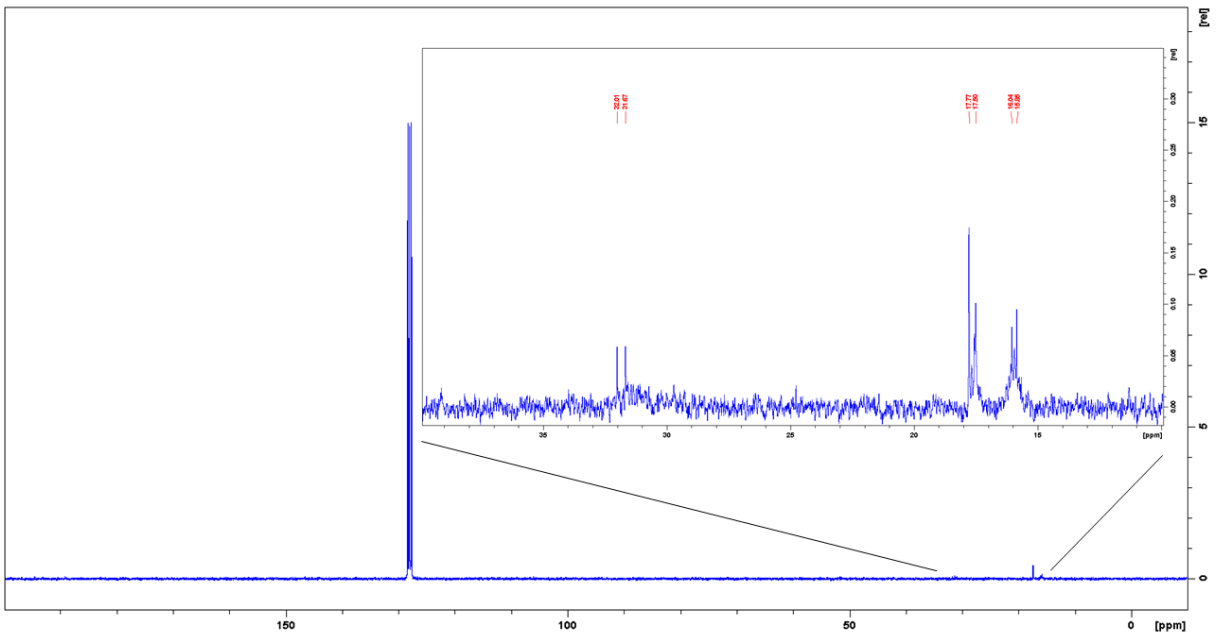

Figure S19. ^{13}C NMR spectrum of **9**.

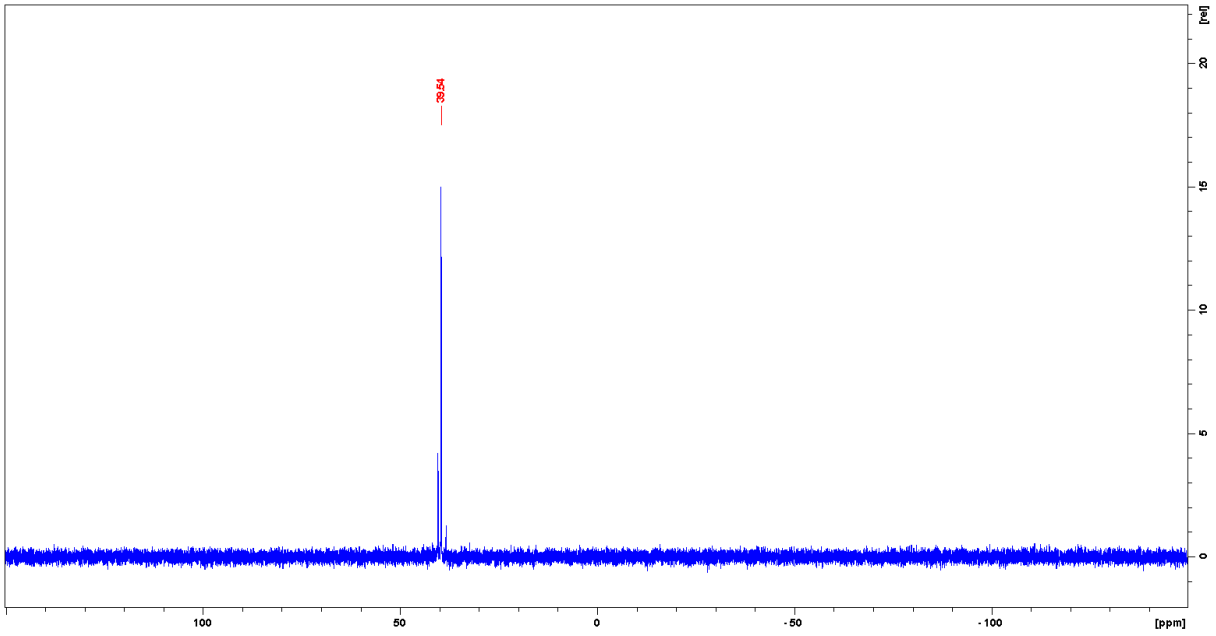

Figure S20. ^{31}P NMR spectrum of **9**.

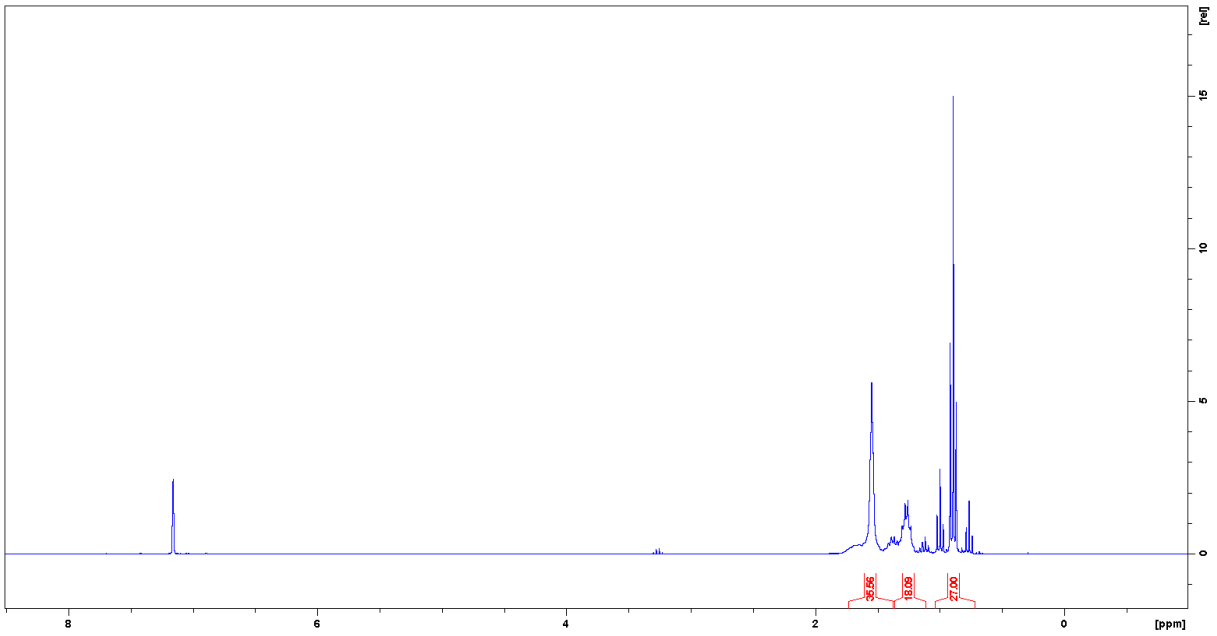

Figure S21. ^{1}H NMR spectrum of **10**.

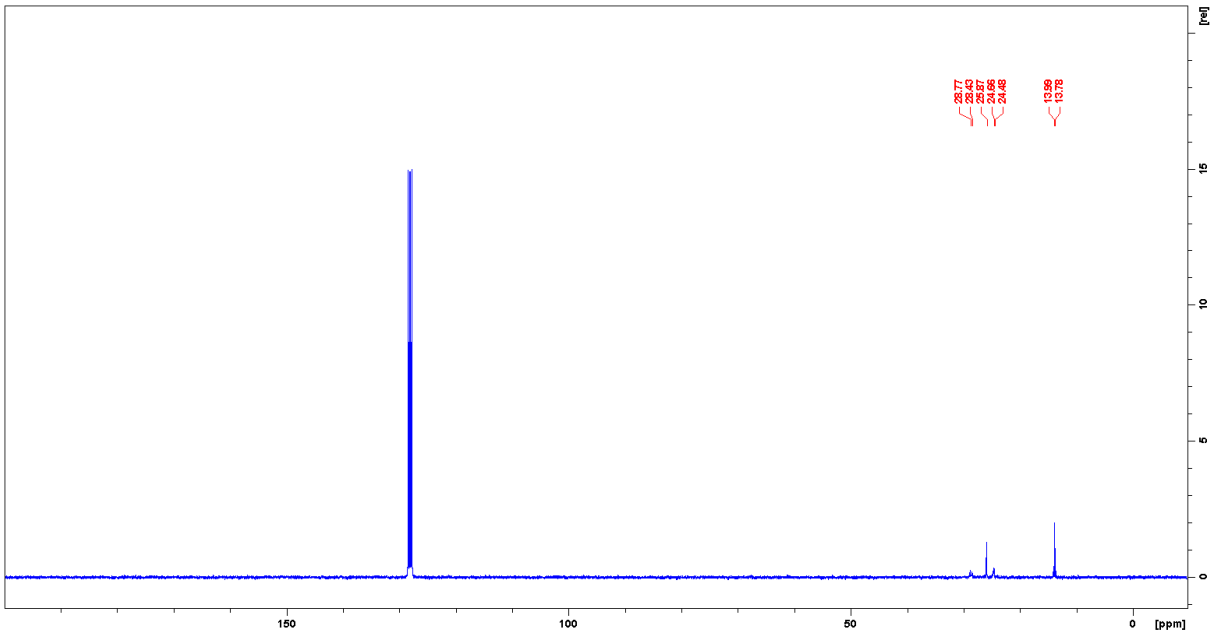

Figure S22. ^{13}C NMR spectrum of **10**.

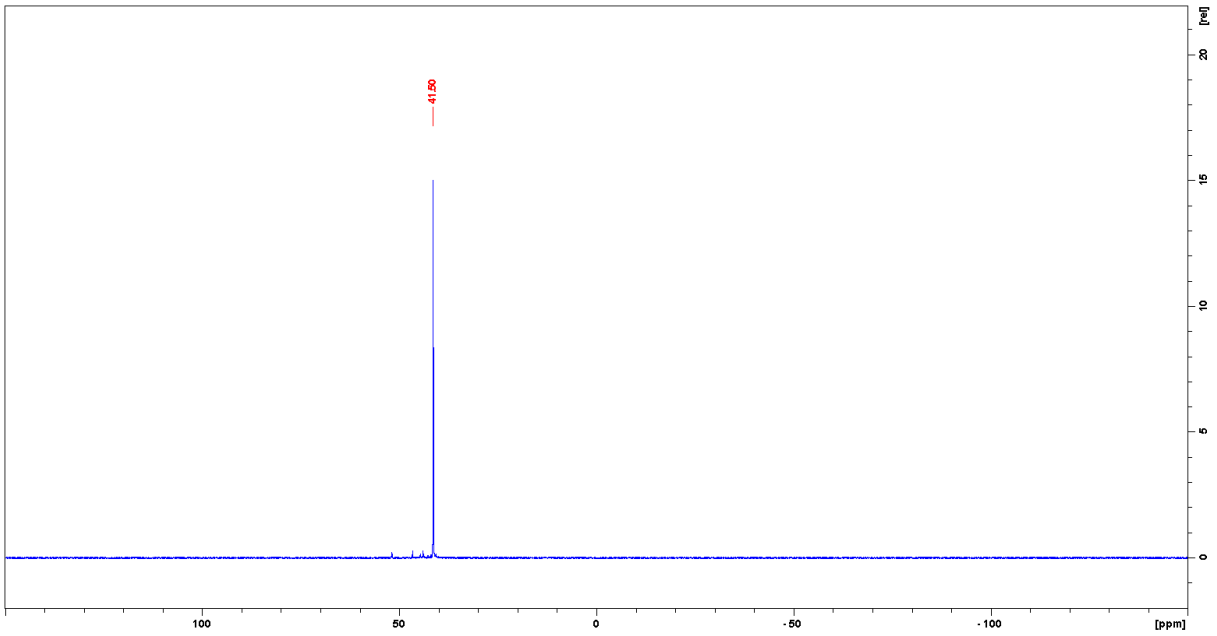

Figure S23. ^{31}P NMR spectrum of **10**.

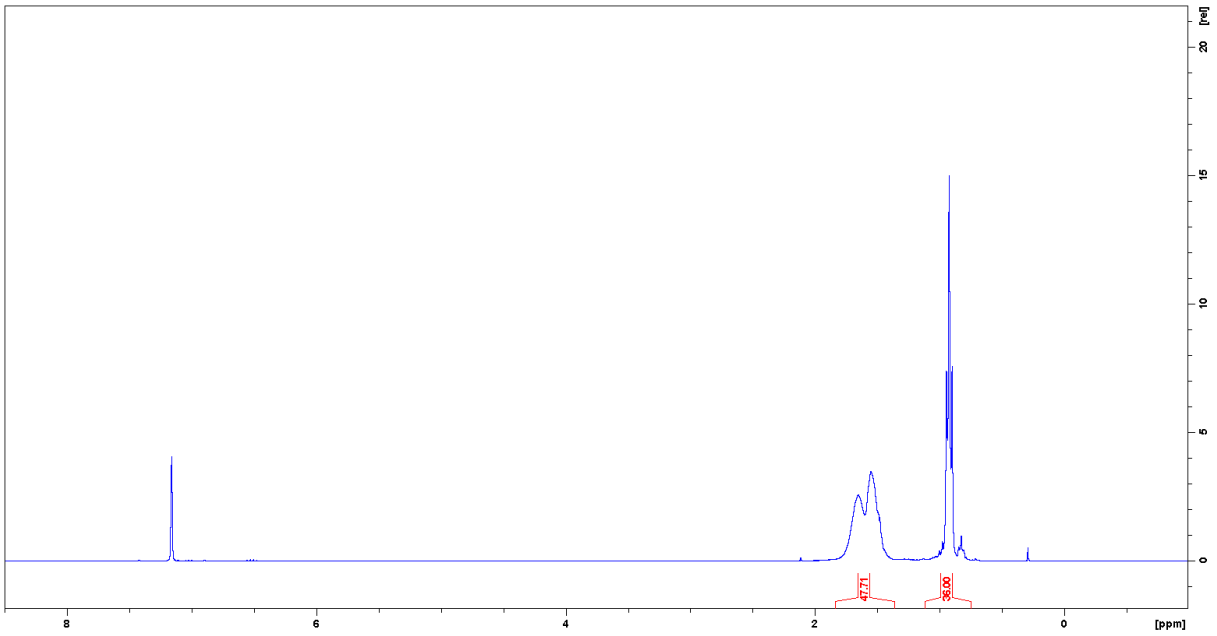

Figure S24. ^{1}H NMR spectrum of **12**.

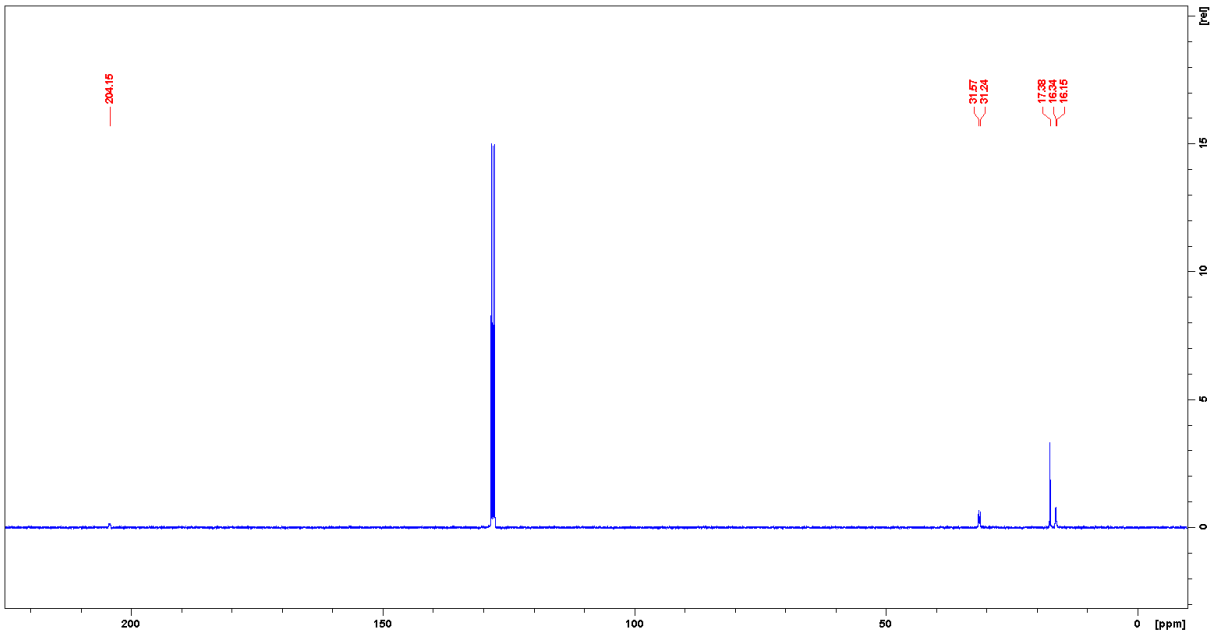

Figure S25. ^{13}C NMR spectrum of **12**.

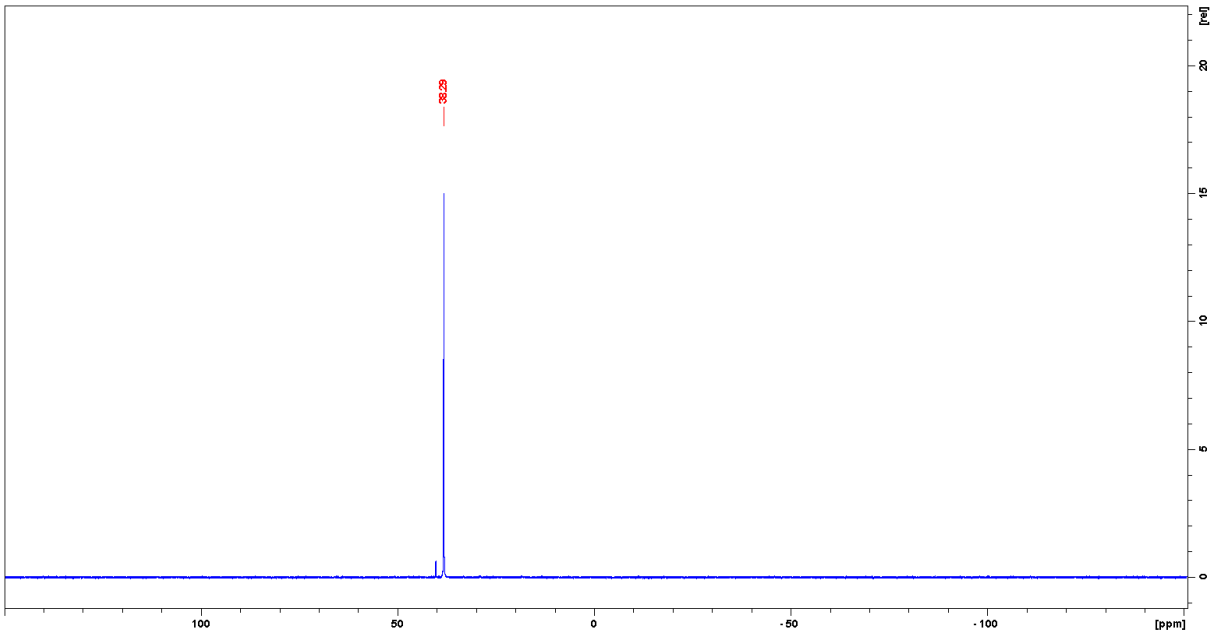

Figure S26. ^{31}P NMR spectrum of **12**.

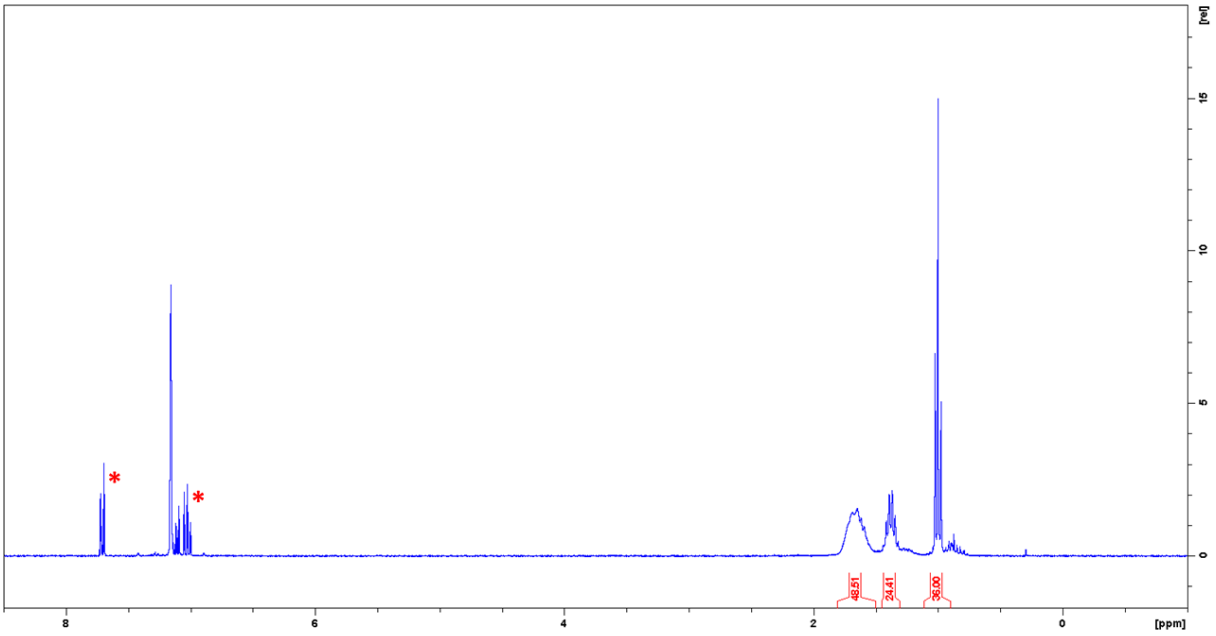

Figure S27. ^{1}H NMR spectrum of **13**. Co-crystallized benzophenone is also visible in the spectrum (*, multiplets, 6.99-7.15 and 7.67-7.74 ppm).

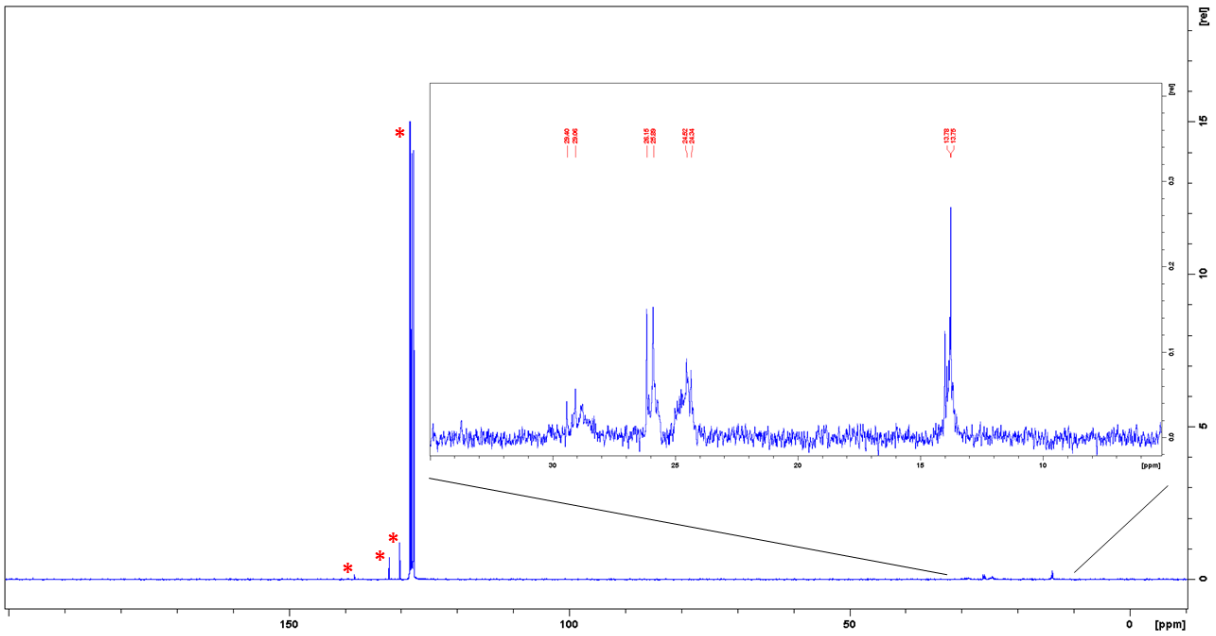

Figure S28. ^{13}C NMR spectrum of **13**. Co-crystallized benzophenone is also visible in the spectrum (*, singlets, 128.4, 130.2, 132.1 and 138.3 ppm).

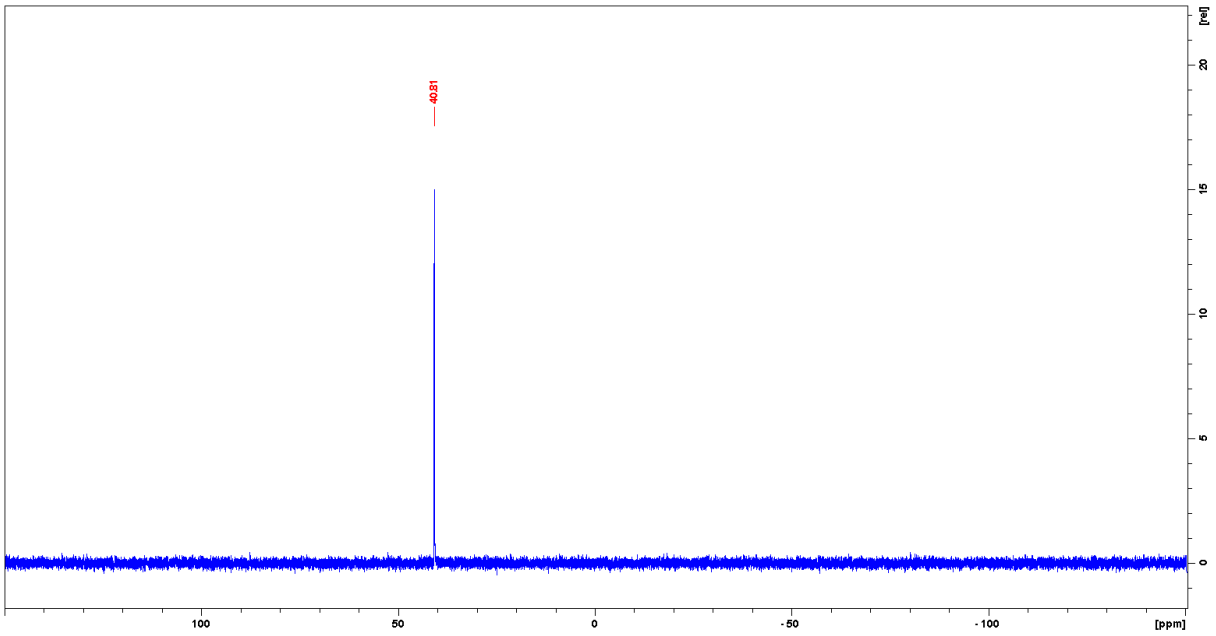

Figure S29. ^{31}P NMR spectrum of **13**.

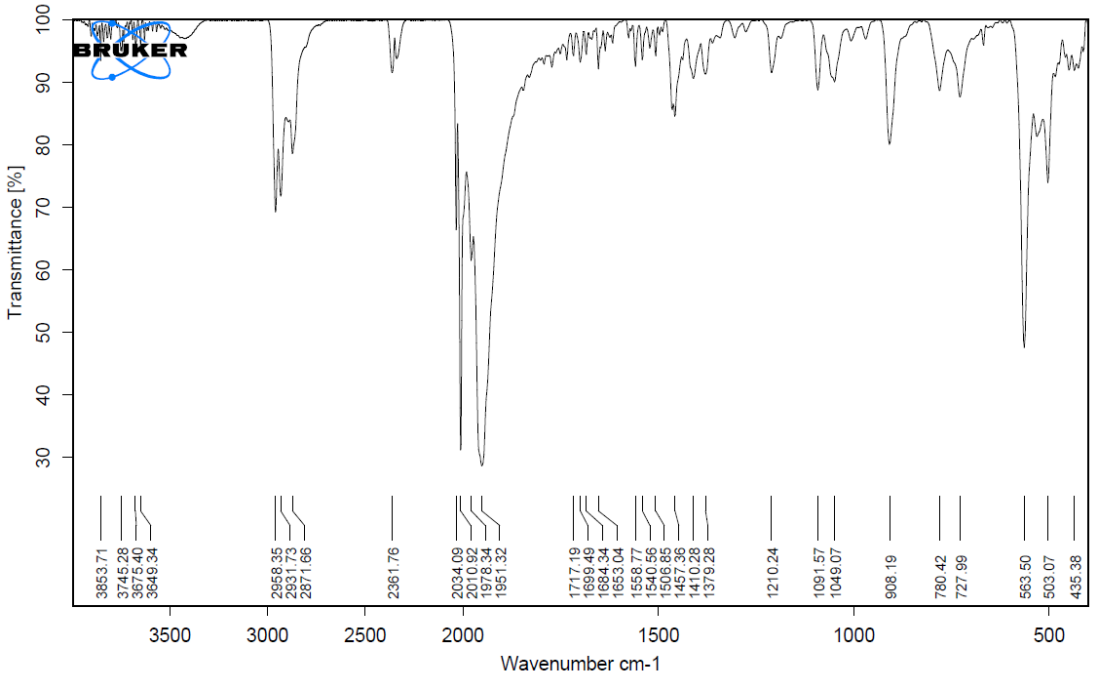

Figure S30. IR spectrum of **2**.

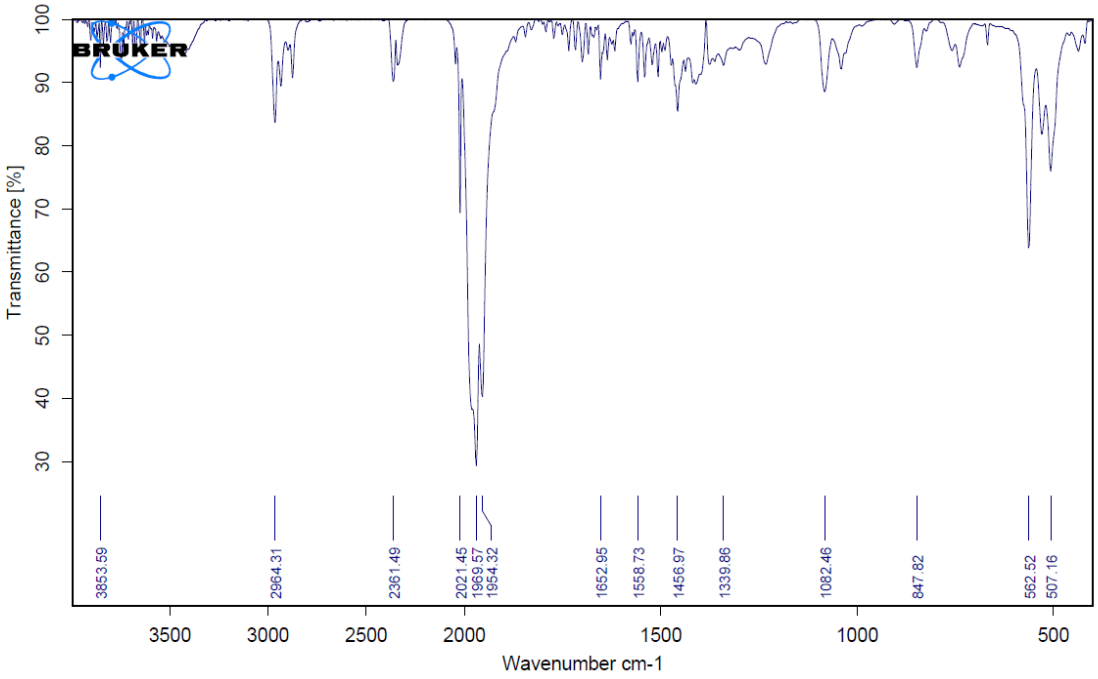

Figure S31. IR spectrum of **3**.

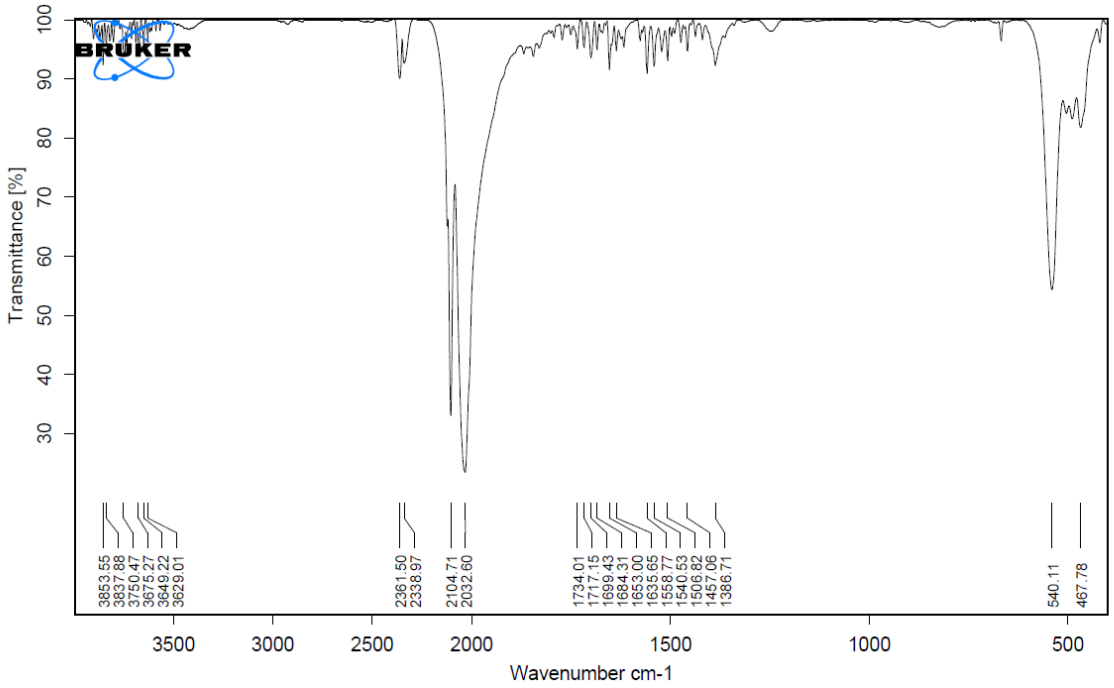

Figure S32. IR spectrum of **4**.

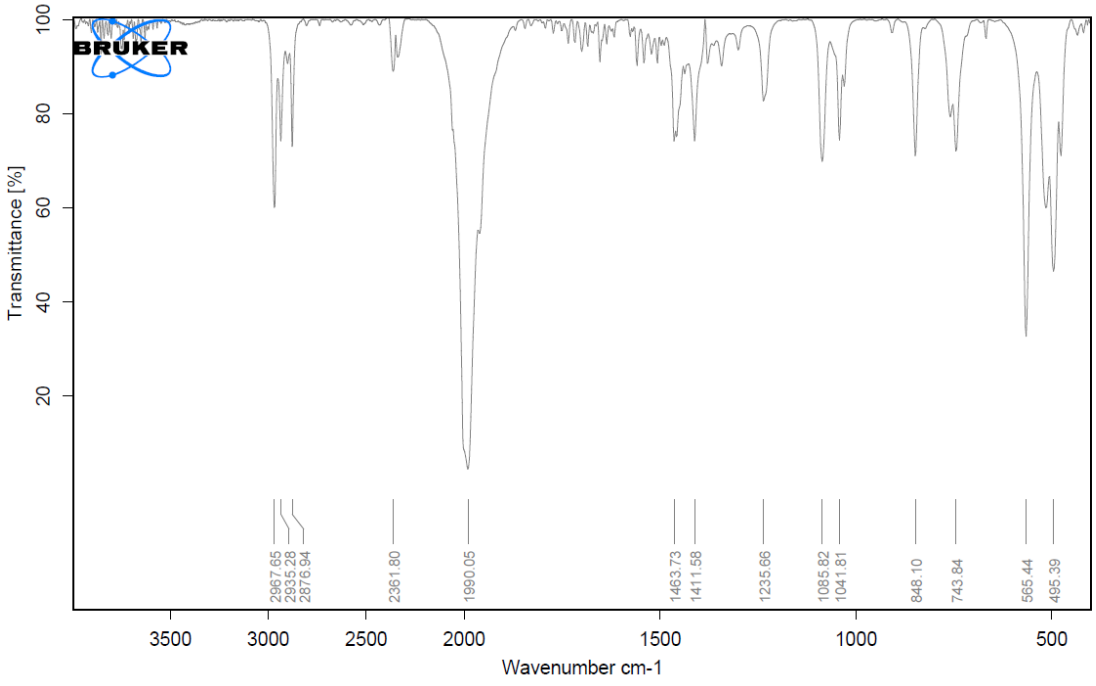

Figure S33. IR spectrum of **6**.

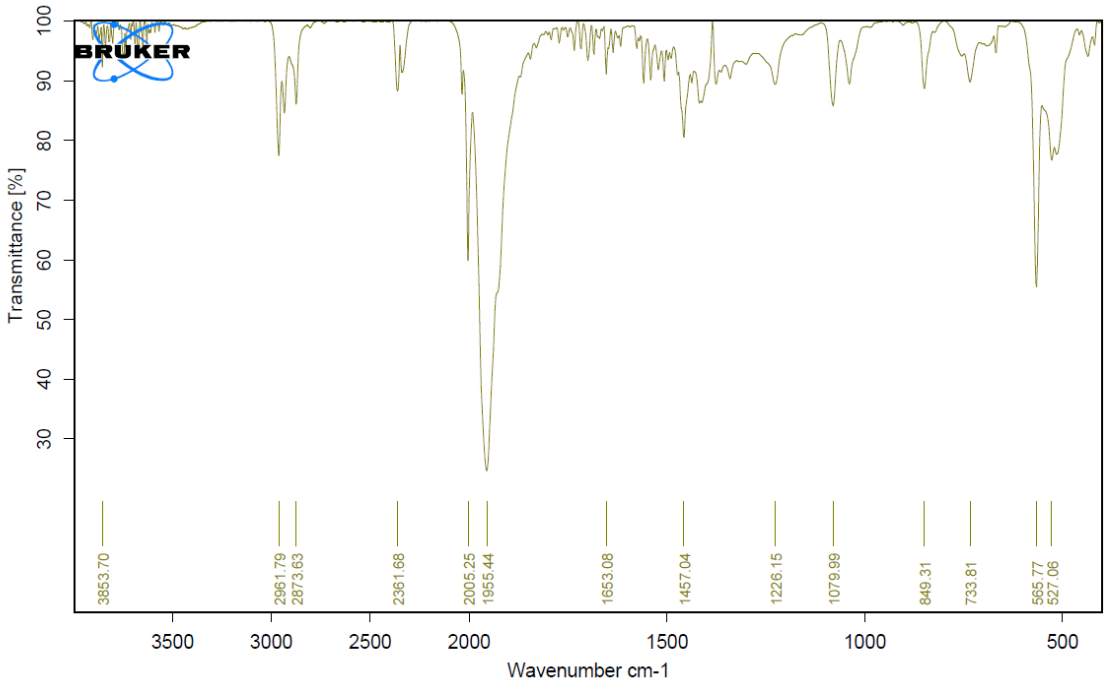

Figure S34. IR spectrum of **9**.

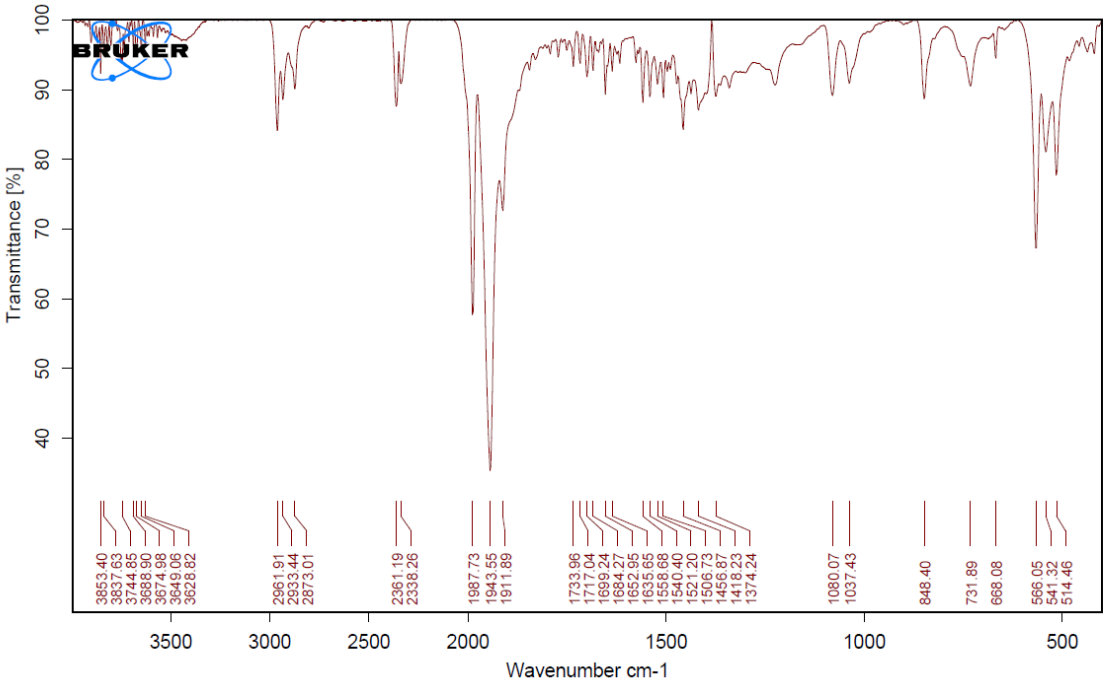

Figure S35. IR spectrum of **12**.

References

[1] T. Fjeldberg, A. Haaland, B. E. Schilling, M. F. Lappert, A. J. Thorne, *J. Chem. Soc. Dalton Trans.*, 1986, 1551-1556.

[2] S. Rajendiran, K. Park, K. Lee, S. Yoon, *Inorg. Chem.*, 2017, **56**, 7270-7277.

[3] D. J. Patmore, W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 981-988.