## Supporting Information

**Two isomers of a bis(diphenylphosphino)phosphinine, and the synthesis and reactivity of Ru arene / Cp* phosphinophosphinine complexes**

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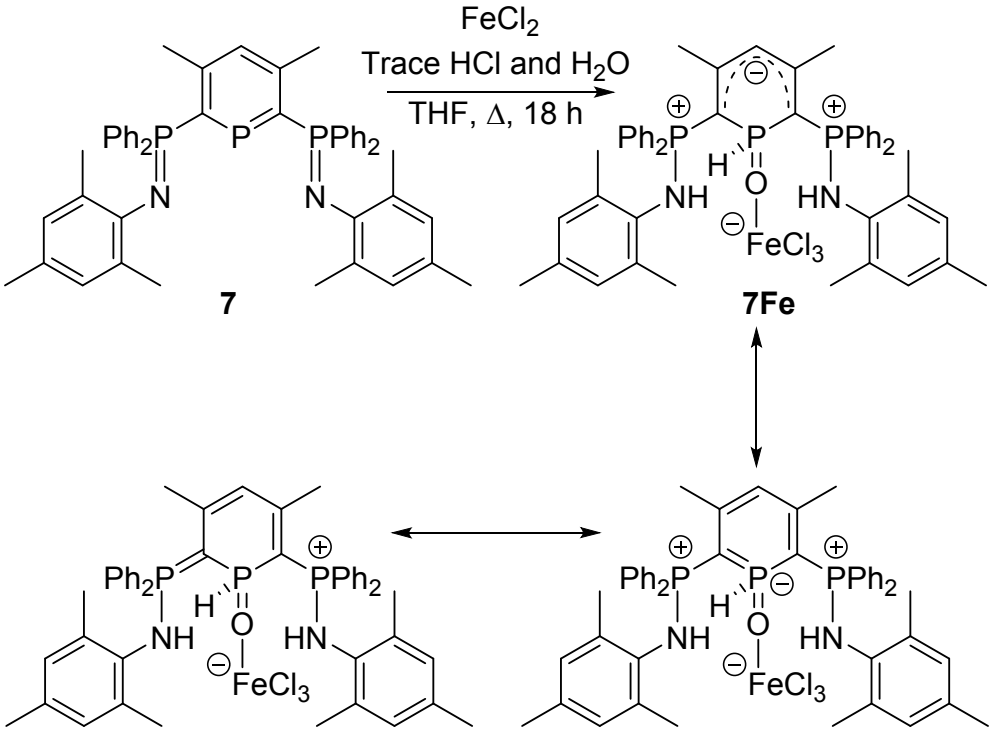
## Synthesis and crystal structure of 7Fe

An ampoule was charged with **7** (100 mg, 0.13 mmol, 1 equiv.), anhydrous $FeCl_2$ (17 mg, 0.13 mmol, 1 equiv.) and dry THF (10 $cm^3$), sealed with a Teflon tap and heated to 70°C for 18 hours. All volatiles were removed under high vacuum and the resulting residue dissolved in dry dichloromethane (1 $cm^3$). The solution was cannula filtered and layered with pet. ether (4 $cm^3$), with yellow needles of the product produced over one week, which X-ray diffraction revealed to be **7**.$H_2O$.$FeCl_2$.HCl

**$^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$):** δ = 18.4 (bs).



**Scheme S1**. Reaction of **7** with $FeCl_2$ and trace HCl / $H_2O$ (1 equivalent of each). Several potential resonance structures are given.

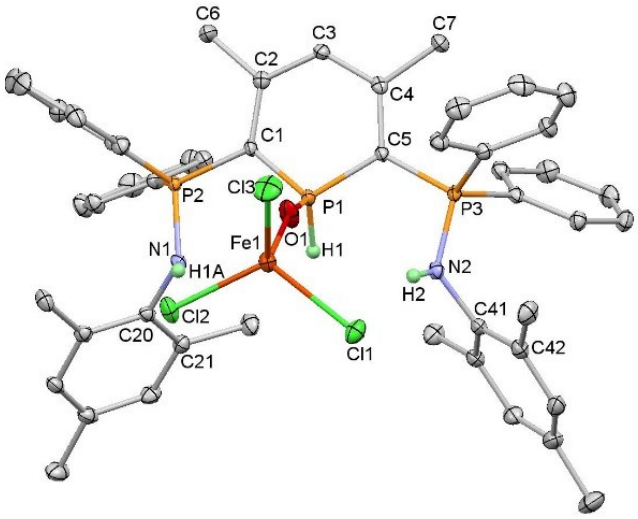



**Figure S1**. Molecular structure of **7Fe**; thermal ellipsoids at 50% probability. All H-atoms have been removed for clarity except for those attached to N or P atoms.

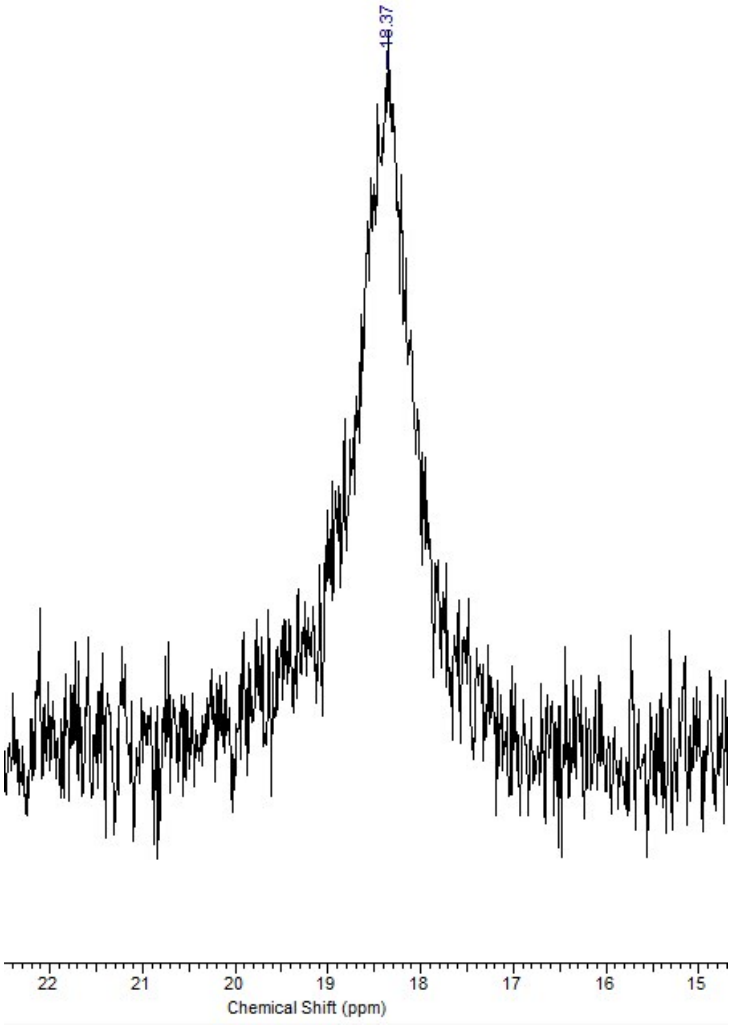



**Figure S2.** $^{31}P\{^{1}H\}$ NMR spectrum of **7Fe**

NMR/Mass Spectra/GC Traces

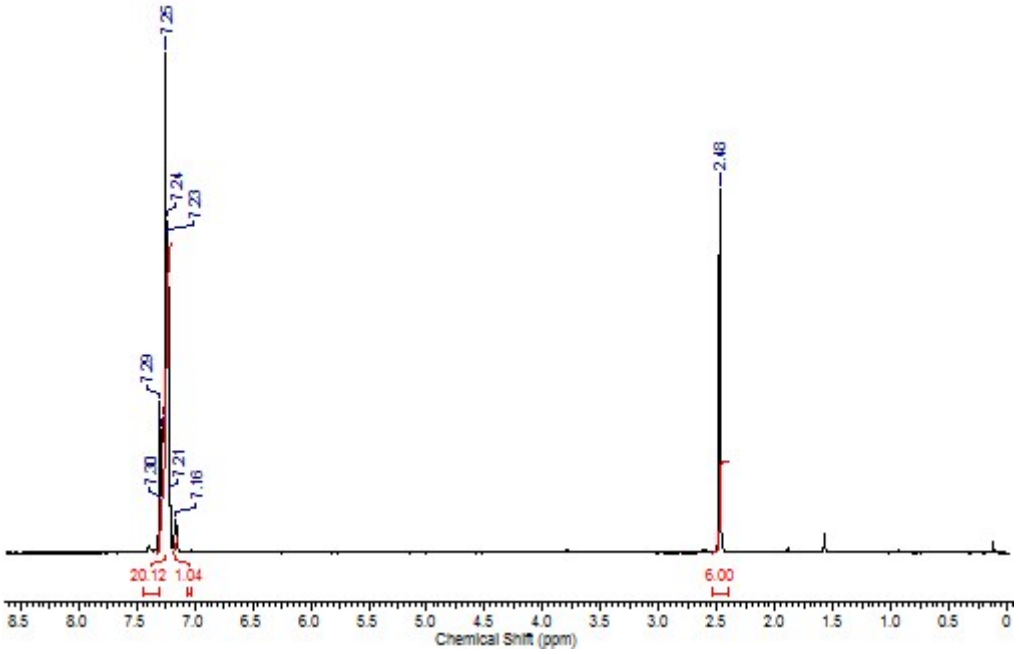



**Figure S3.** $^{1}H$ NMR spectrum of **5**

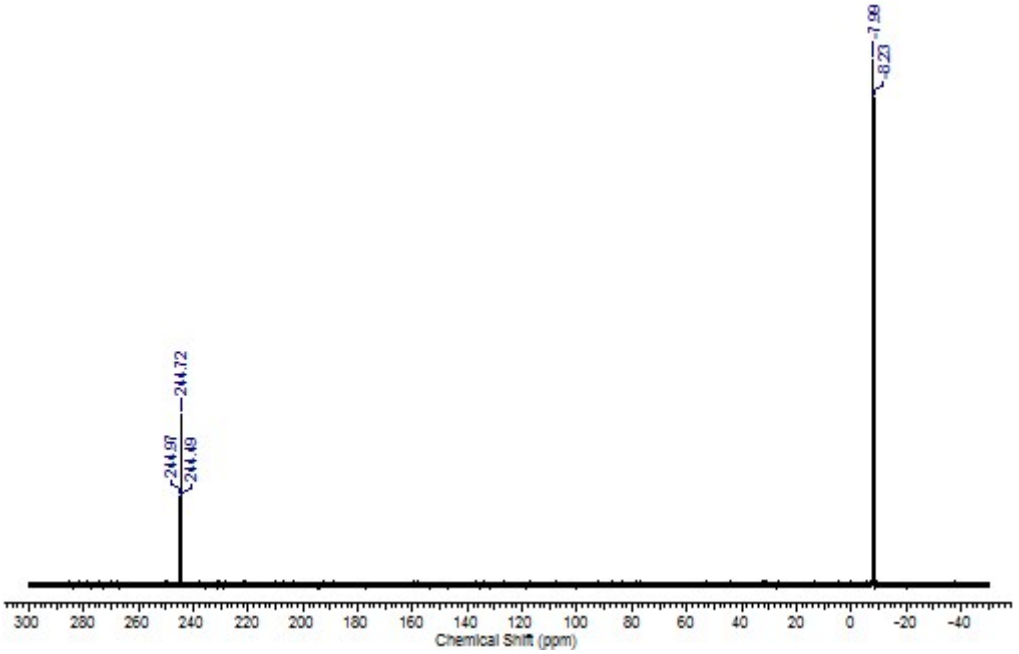



**Figure S4.** $^{31}P\{^{1}H\}$ NMR spectrum of **5**

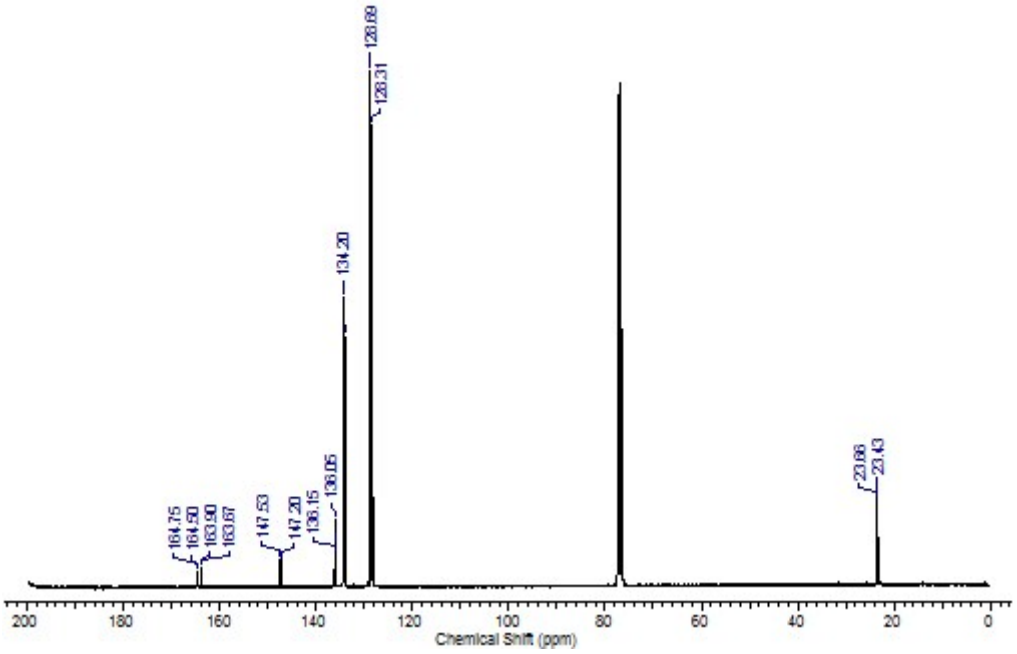



**Figure S5.** $^{13}C\{^{1}H\}$ NMR spectrum of **5**

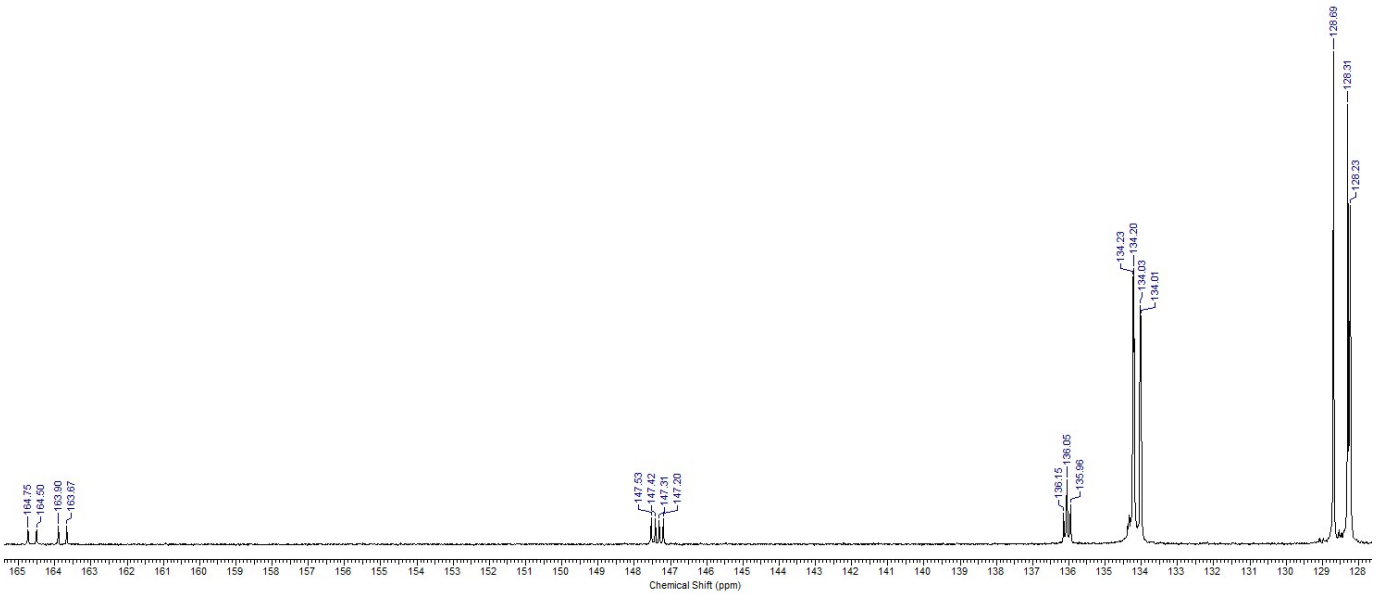



**Figure S6.** $^{13}C\{^{1}H\}$ NMR spectrum (aromatic region) of **5**

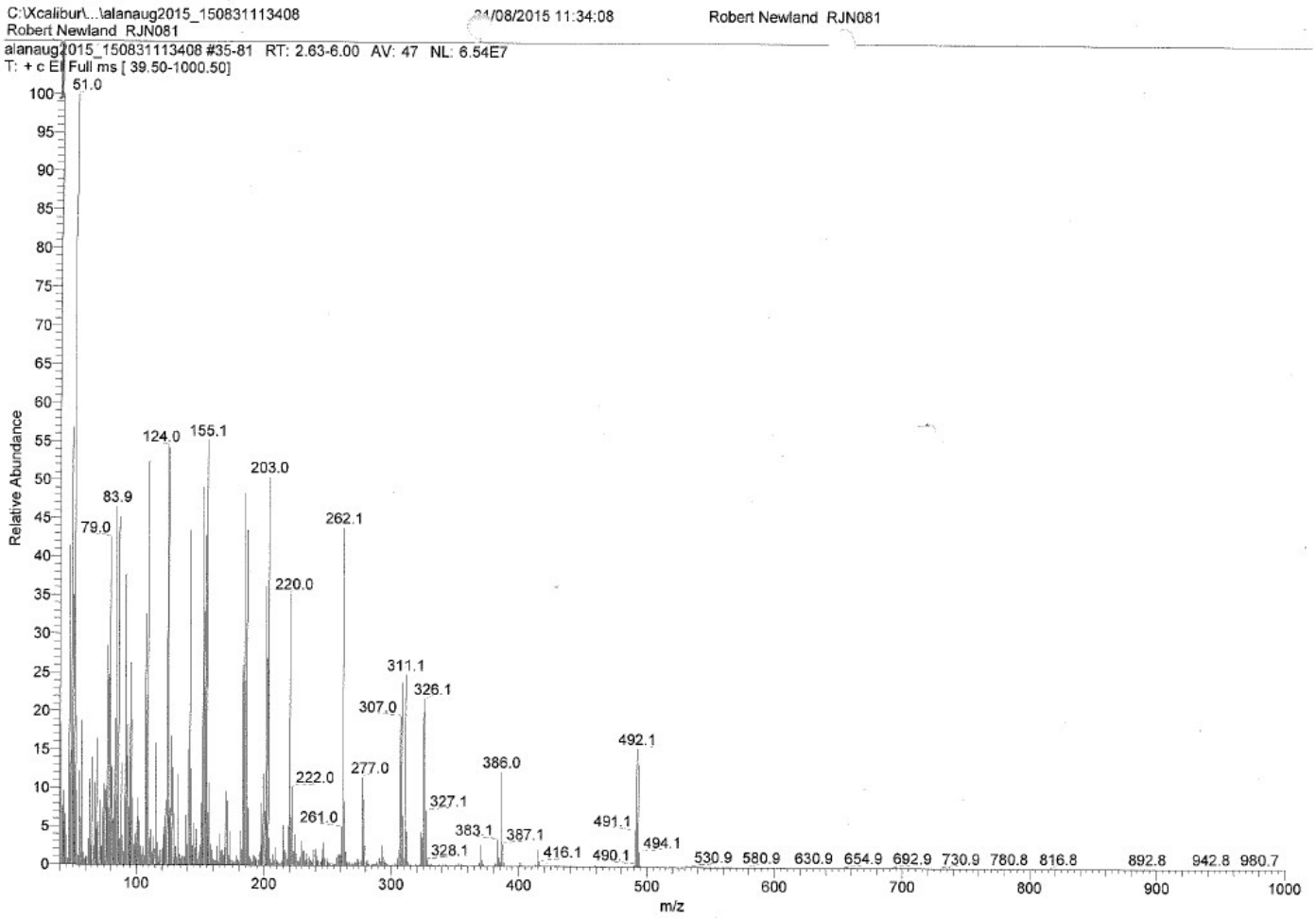



**Figure S7.** MS (EI) of **5**

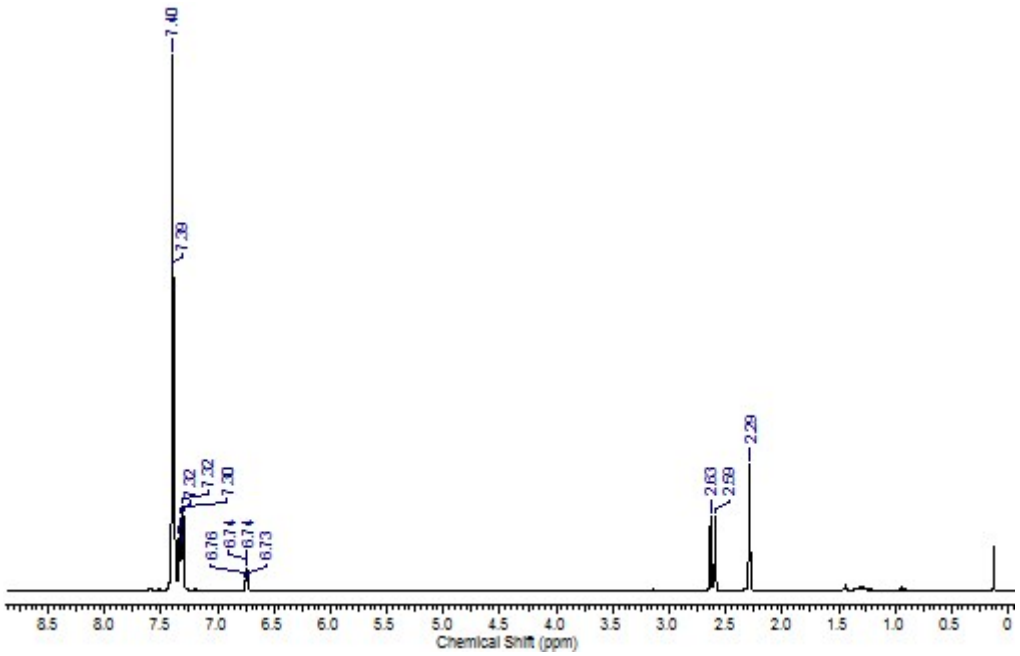



**Figure S8.** $^{1}$H NMR spectrum of **6**

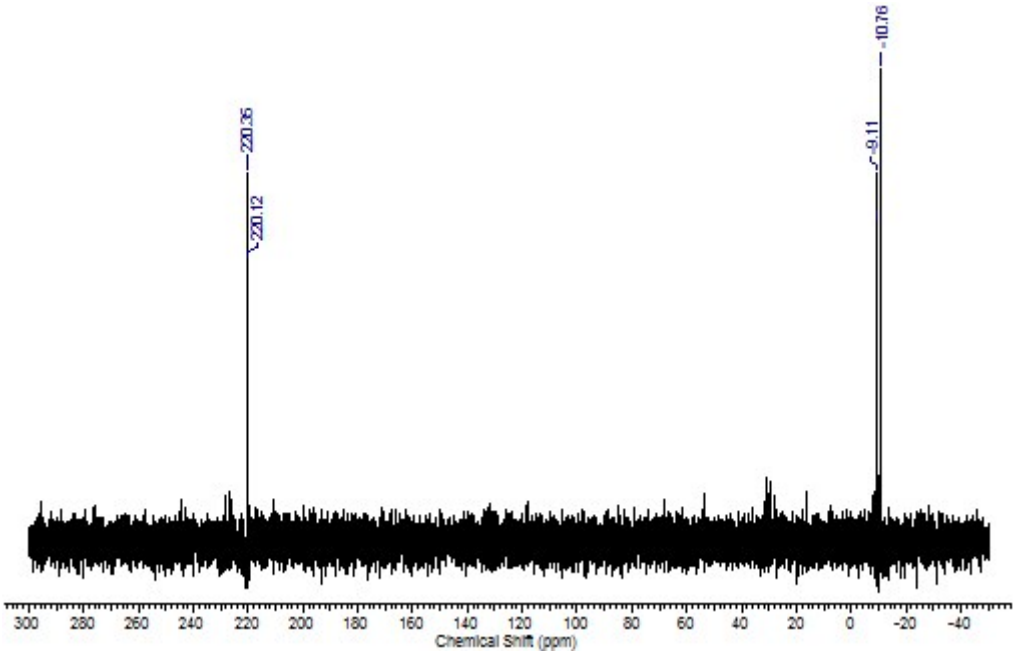



**Figure S9.** $^{31}P\{^{1}H\}$ NMR spectrum of **6**

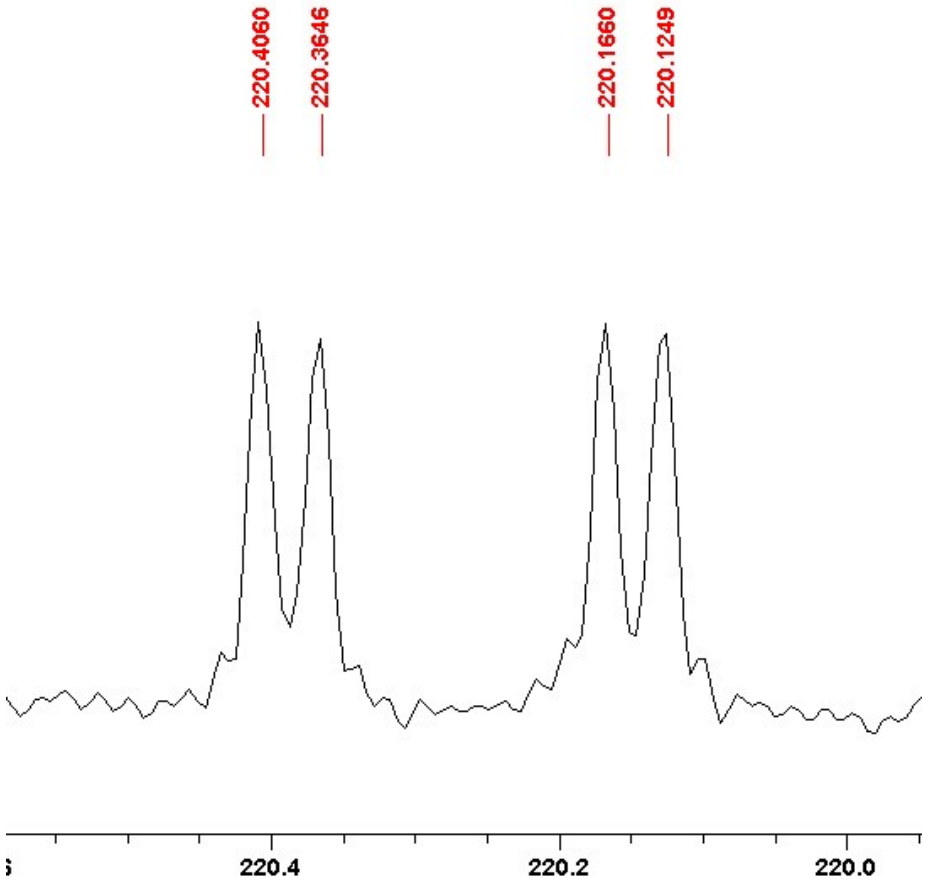



**Figure S10.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphinine region) of **6**

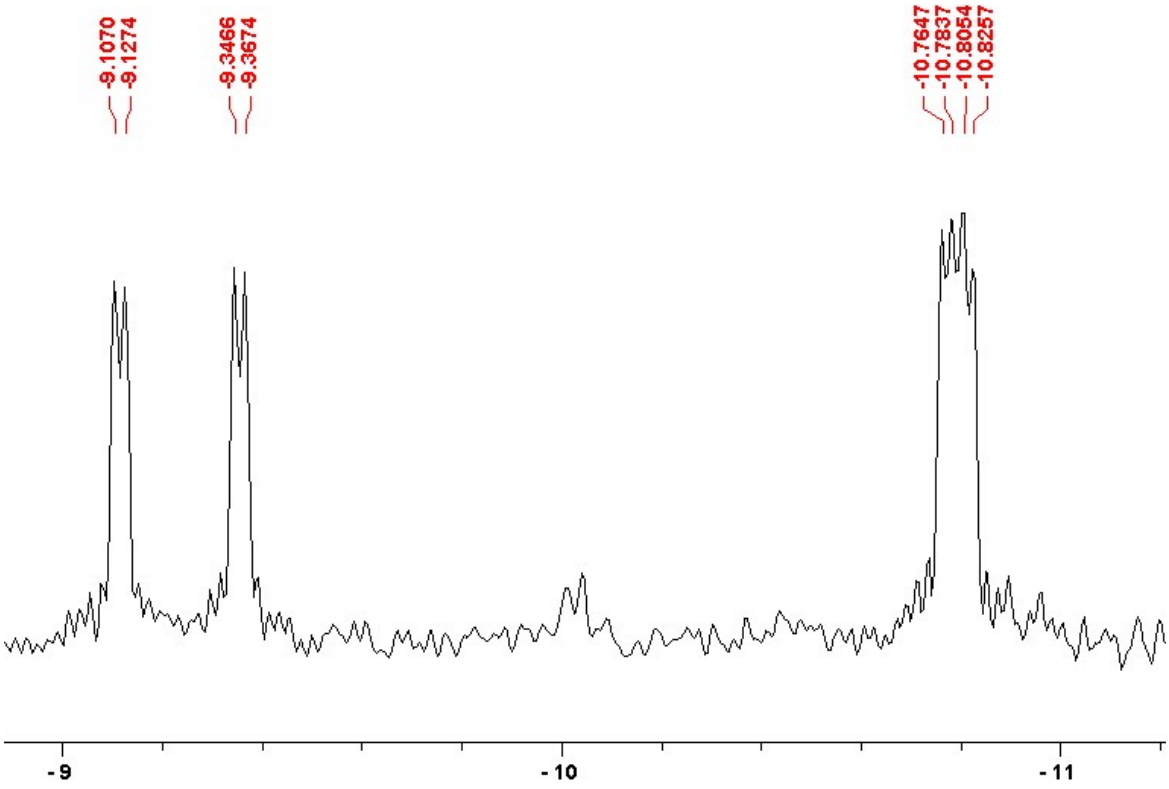



**Figure S11.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphine region) of **6**

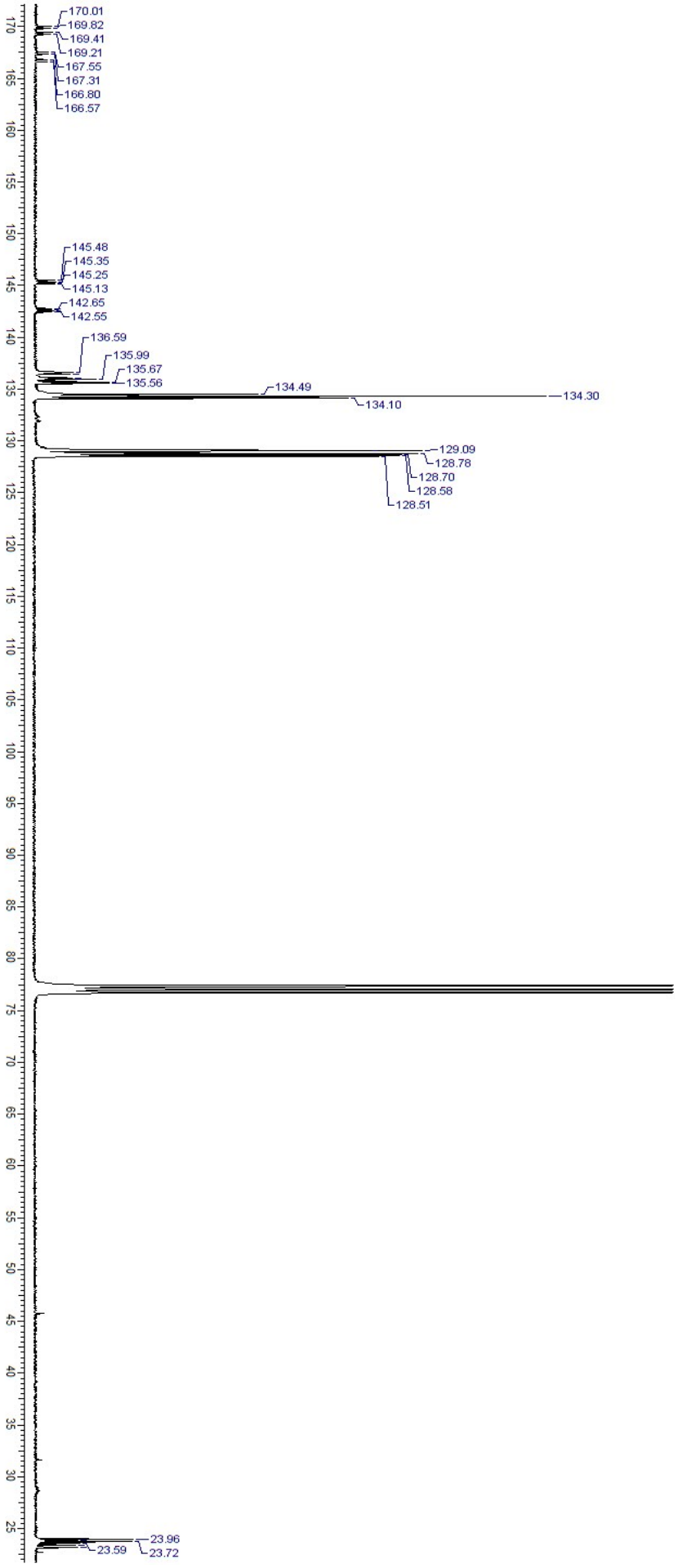



**Figure S12.** $^{13}C\{^{1}H\}$ NMR spectrum of **6**

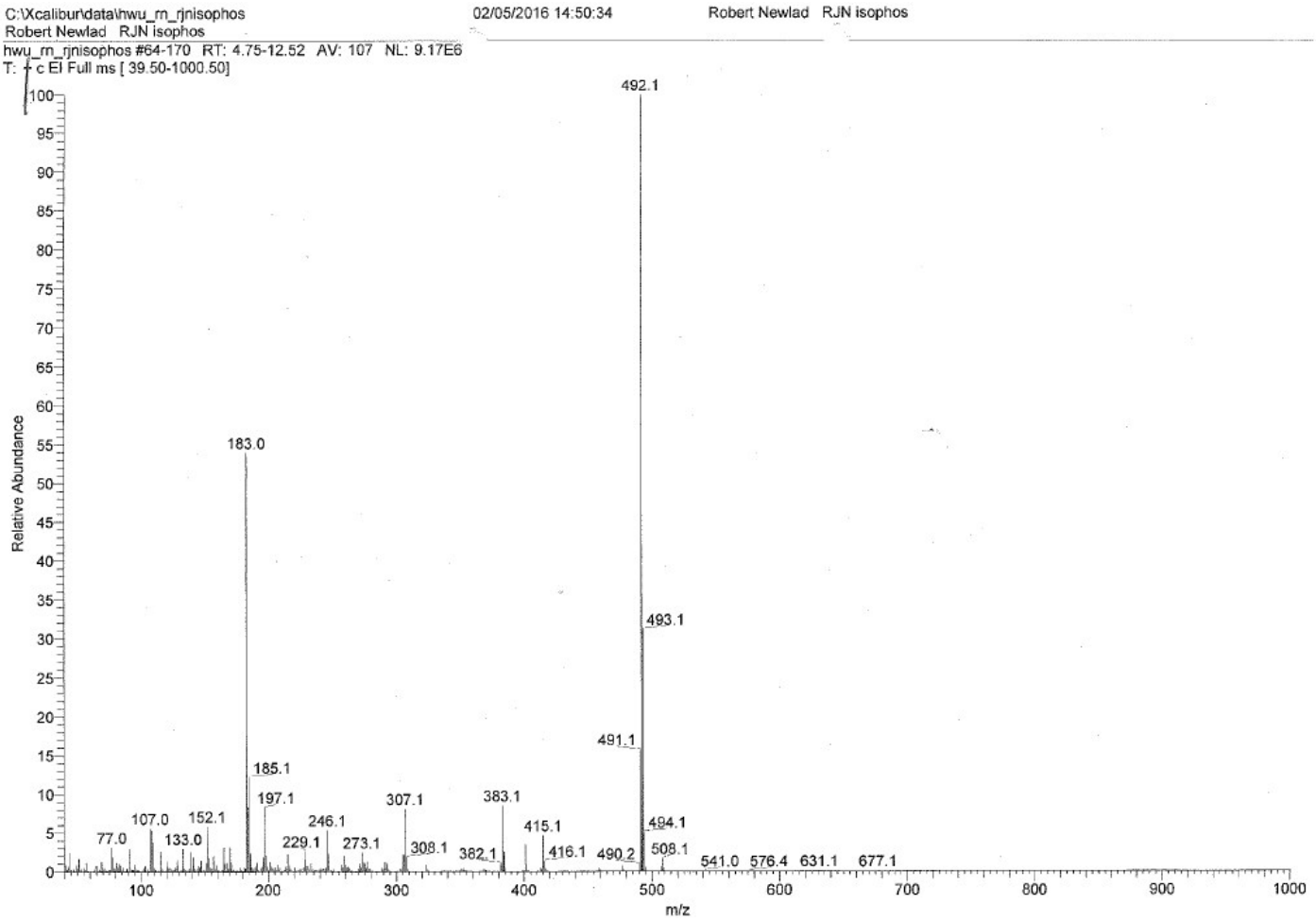



**Figure S13.** MS (EI) of **6**

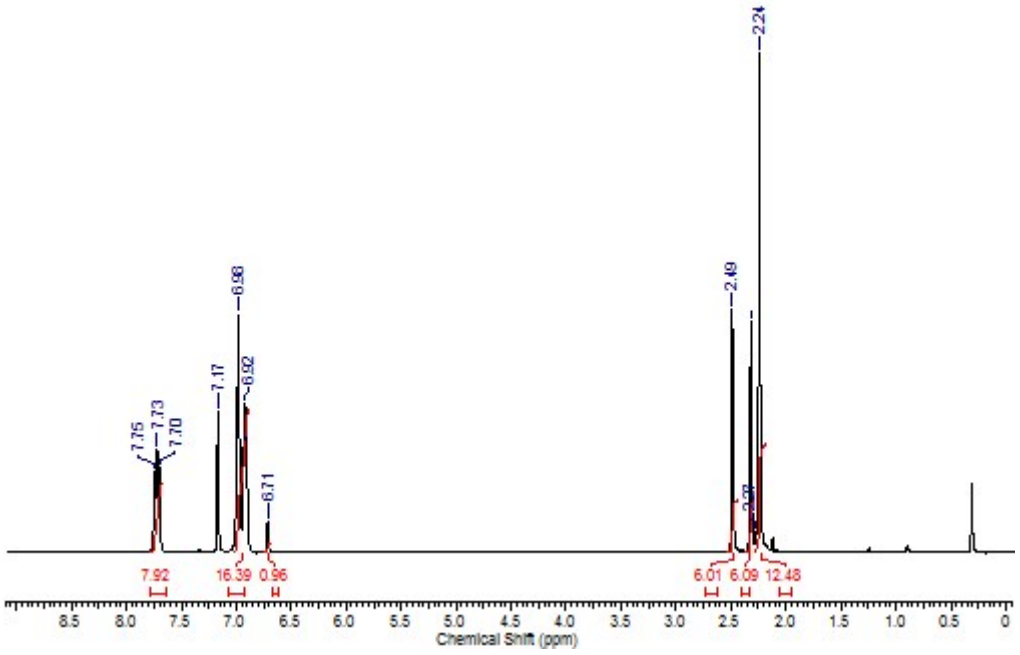



**Figure S14.** $^{1}$H NMR spectrum of **7**

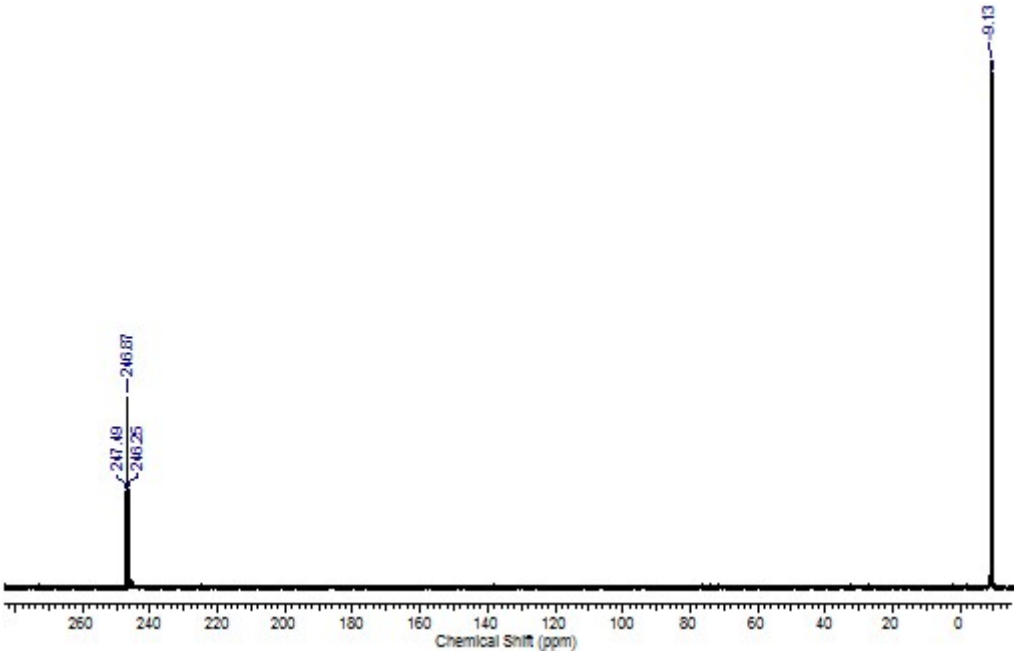



**Figure S15.** $^{31}P\{^{1}H\}$ NMR spectrum of **7**

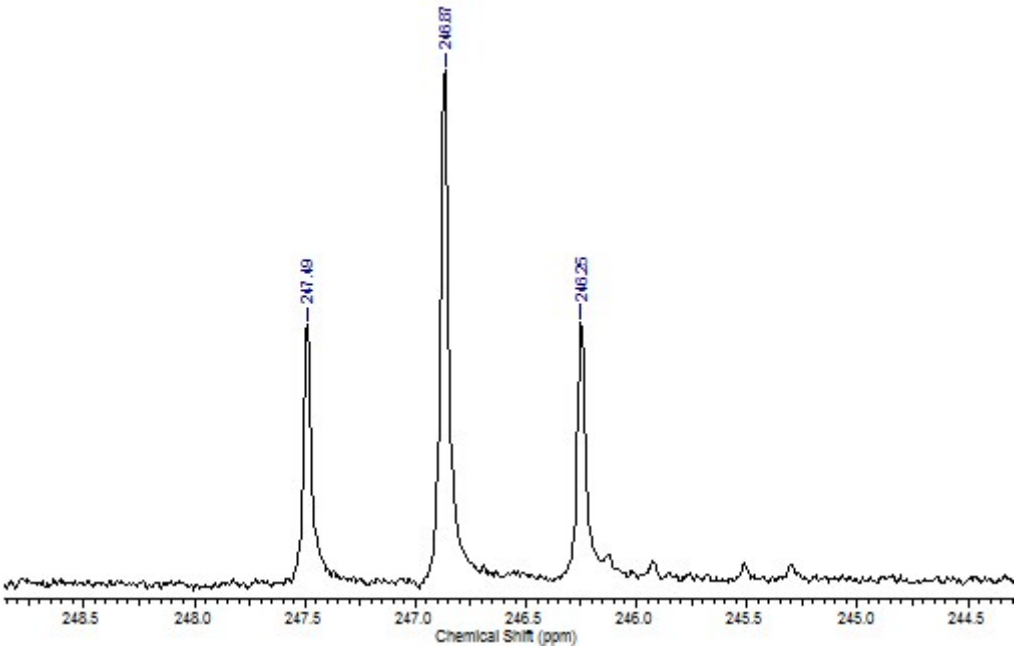



**Figure S16.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphinine region) of **7**

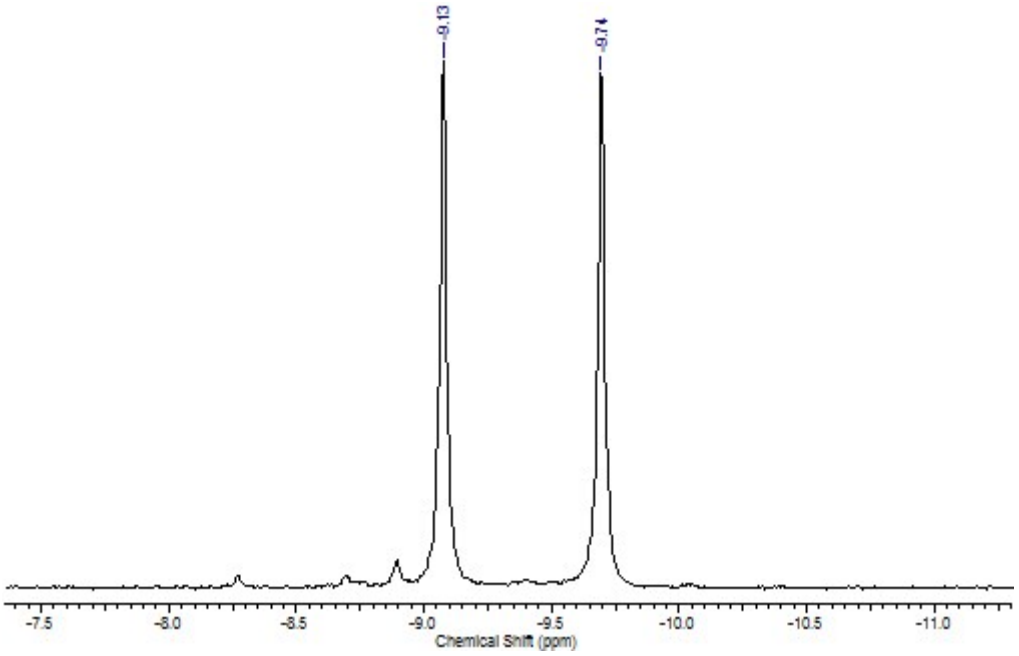



**Figure S17.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphine region) of **7**

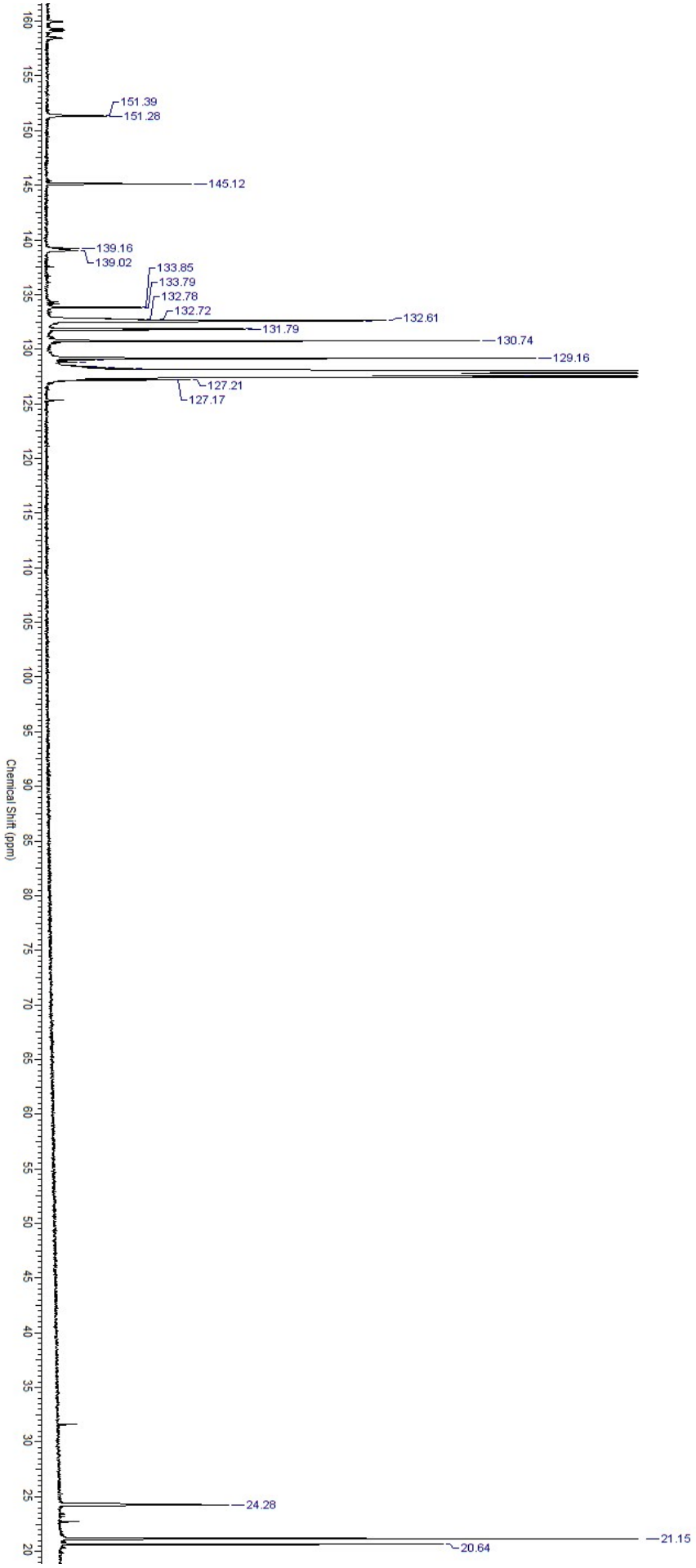



**Figure S18.** $^{13}C\{^{1}H\}$ NMR spectrum of **7**

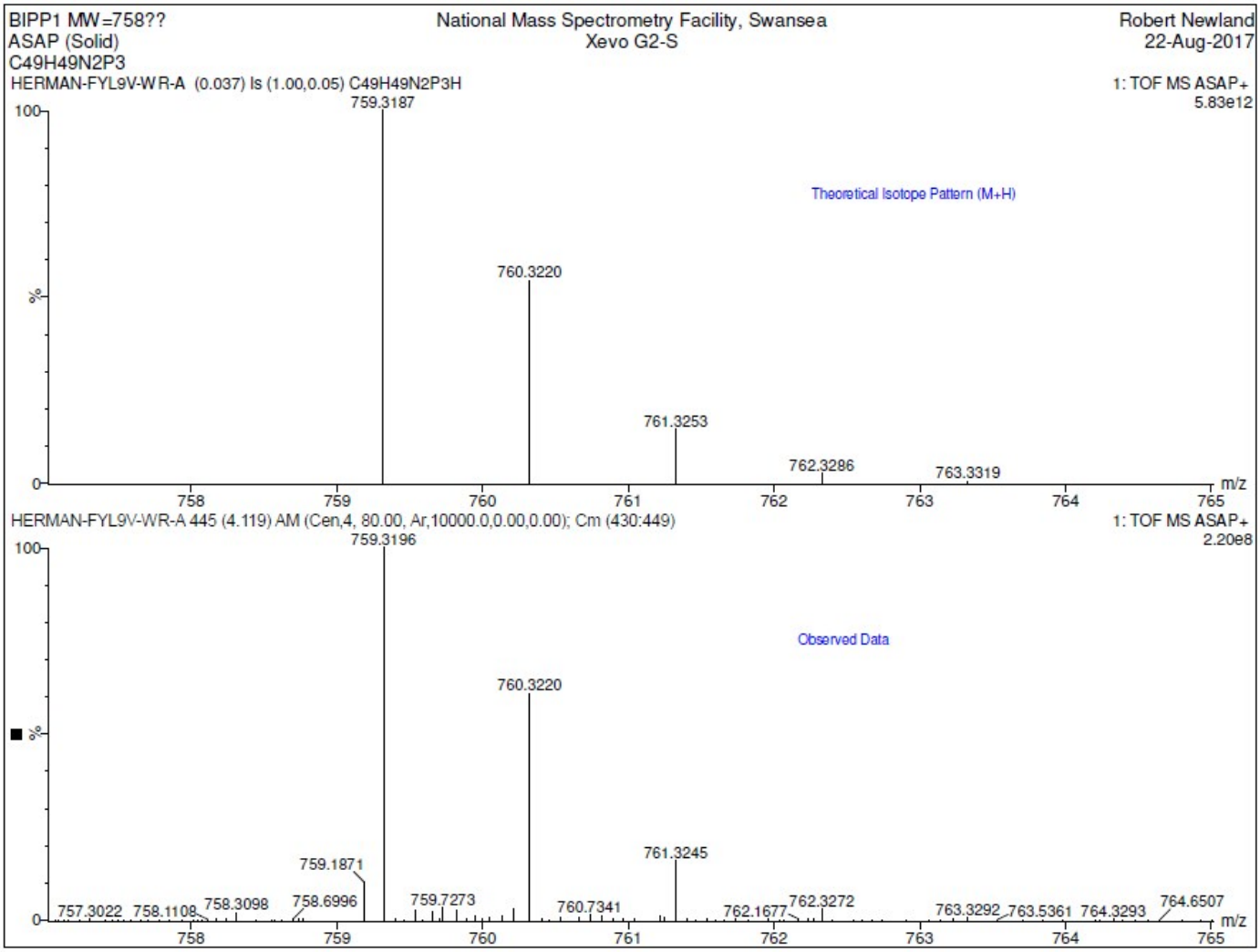



**Figure S19.** HRMS of **7**

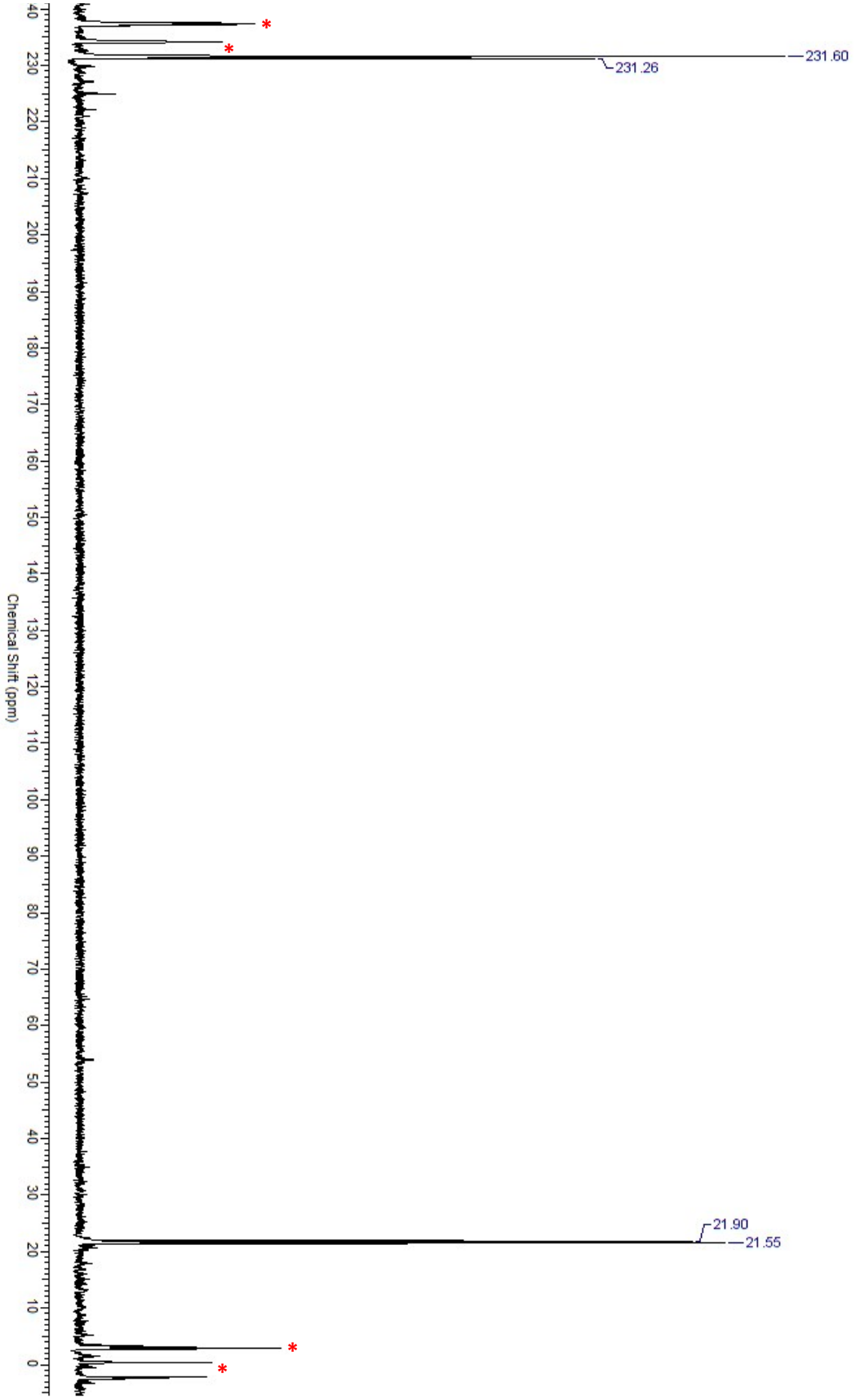



**Figure S20.** $^{31}P\{^{1}H\}$ NMR spectrum of mixture of **2** & **8** (* = **2**)

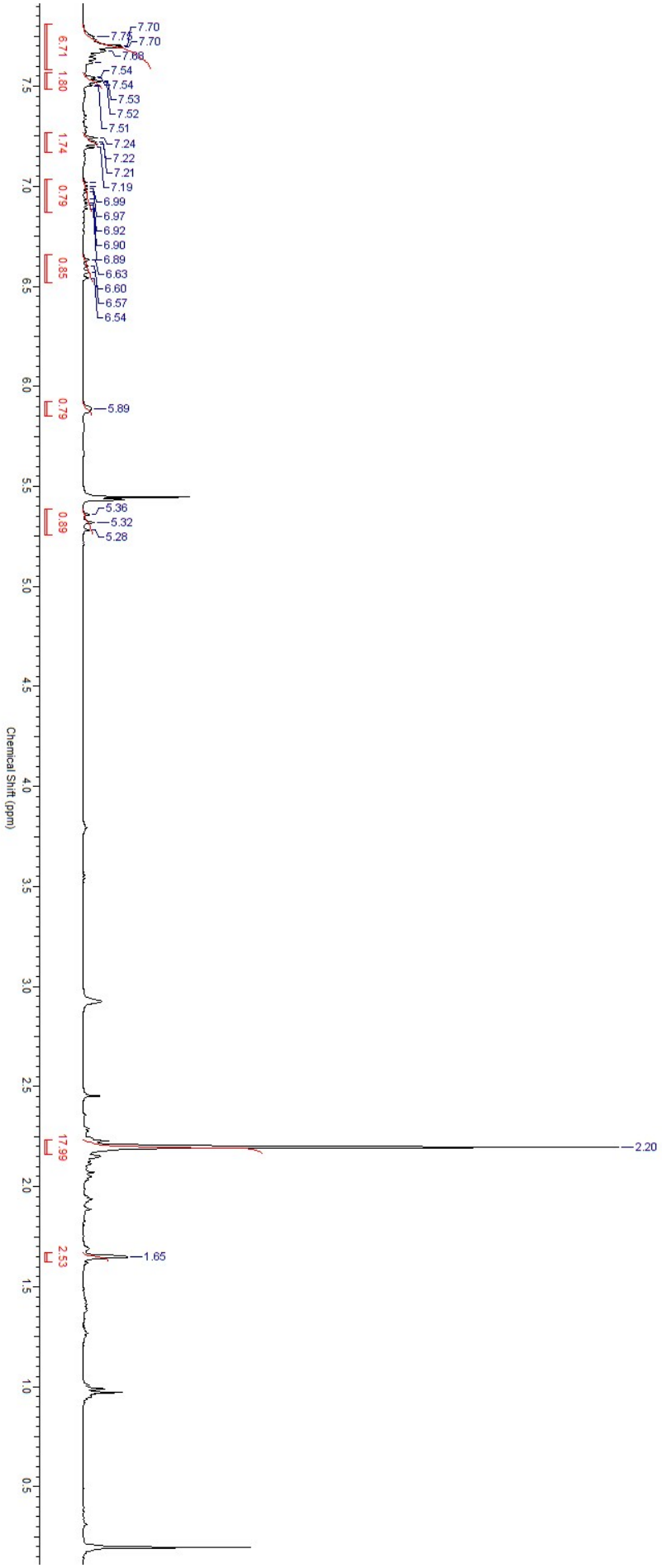



**Figure S21.** $^{1}$H NMR spectrum of **9**.

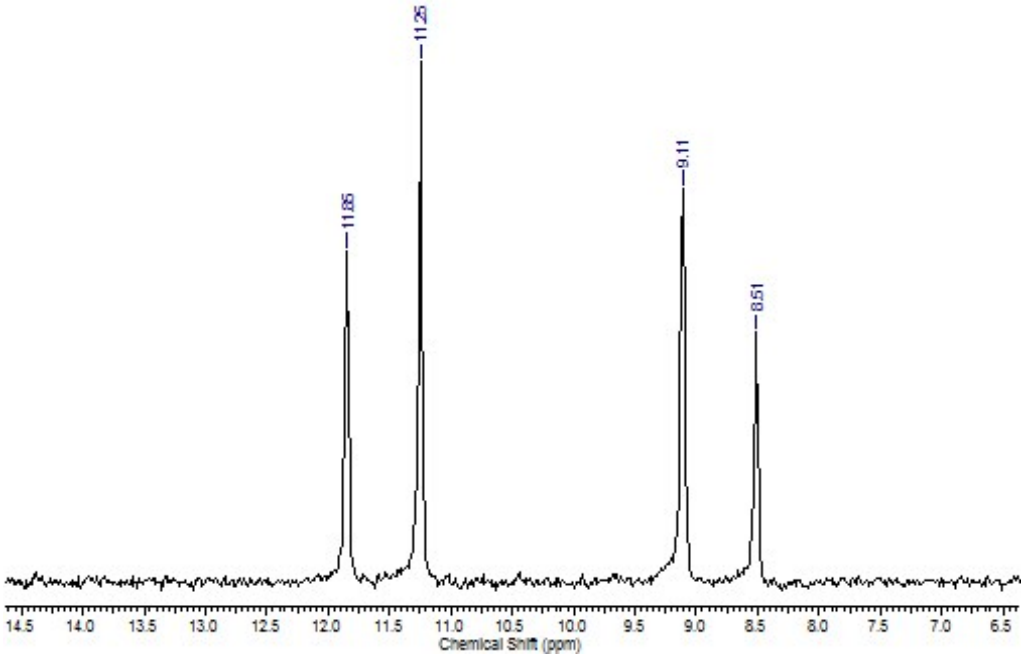



**Figure S22.** $^{31}P\{^{1}H\}$ NMR spectrum of **9**

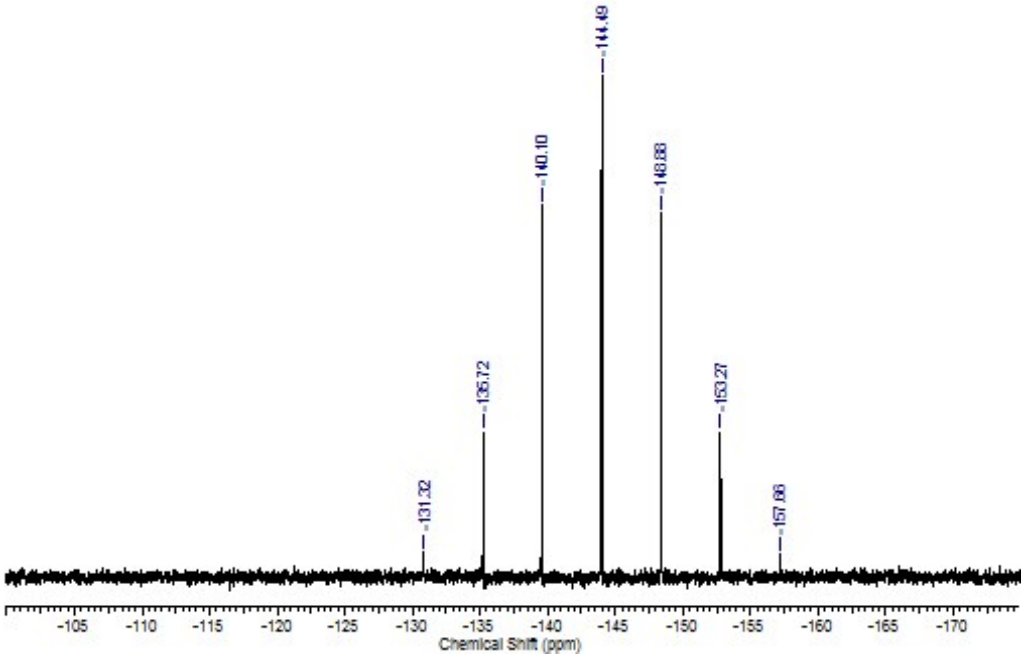



**Figure S23.** $^{31}P\{^{1}H\}$ NMR spectrum ($[PF_6]^-$ resonance) of **9**

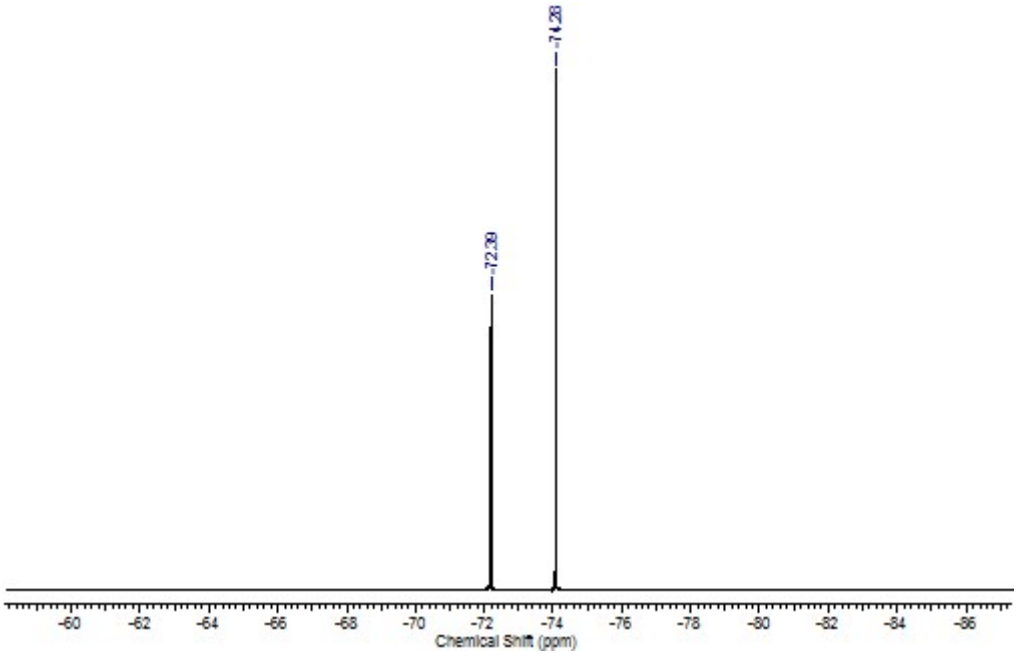



**Figure S24.** $^{19}F$ NMR spectrum ($[PF_6]^-$ resonance) of **9**

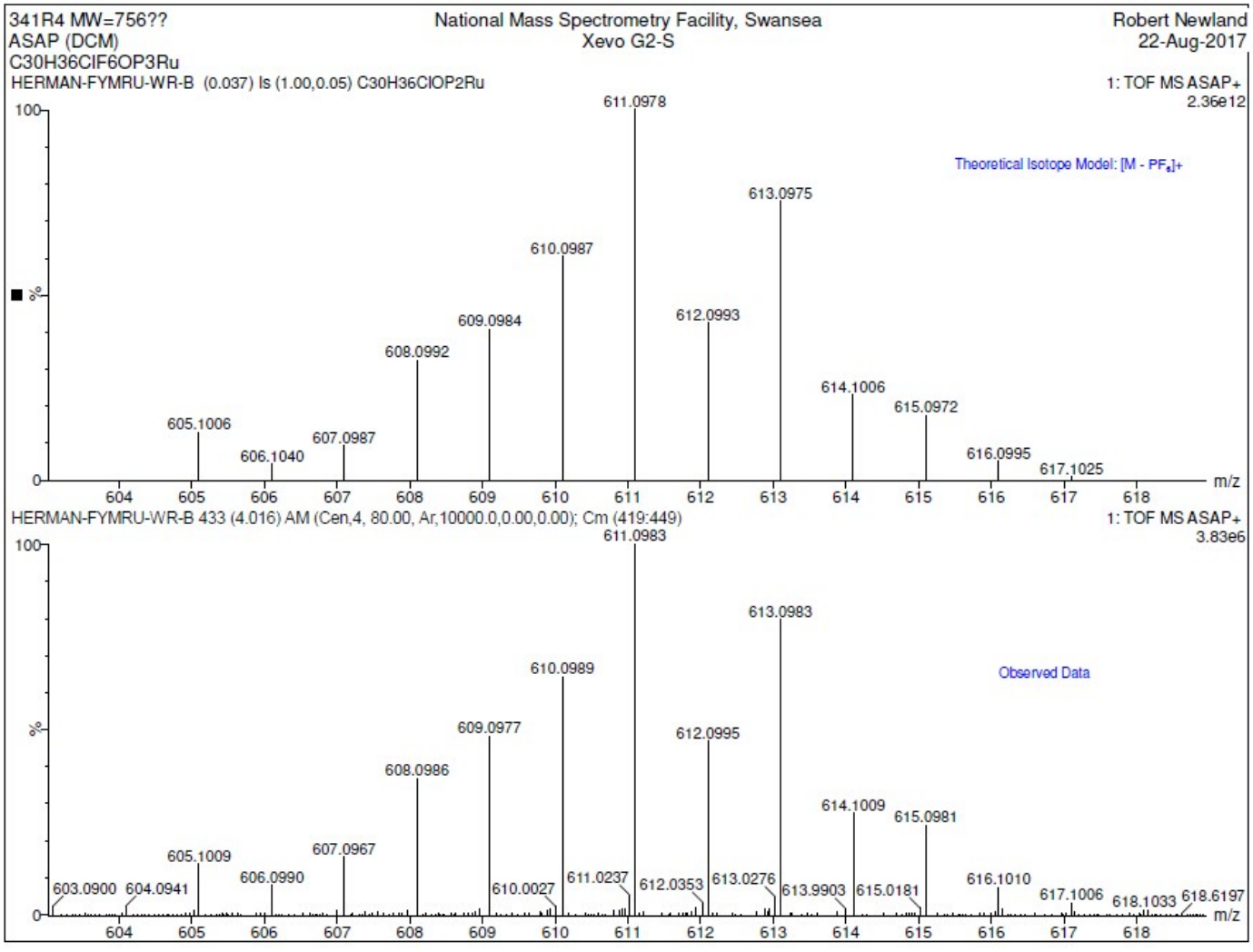



**Figure S25.** HRMS of **9**

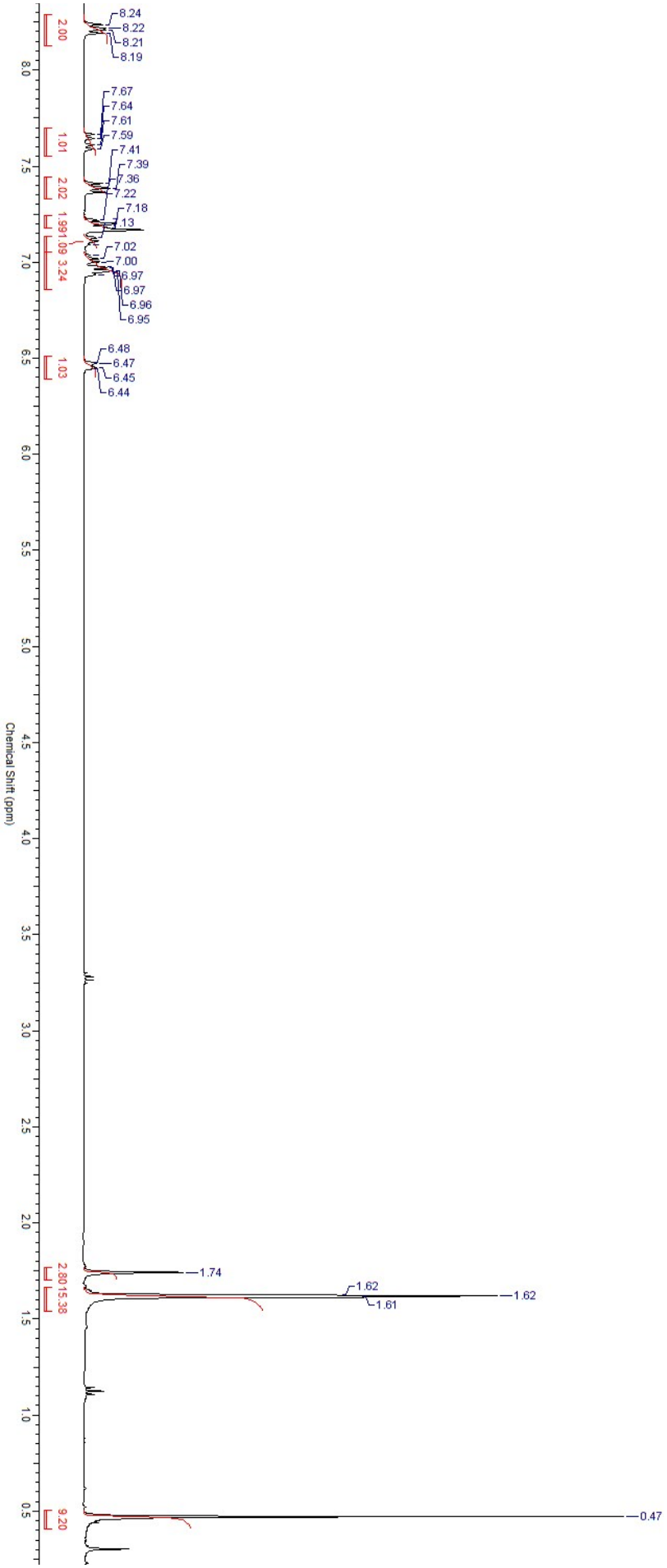



**Figure S26.** $^{1}$H NMR spectrum of **10**

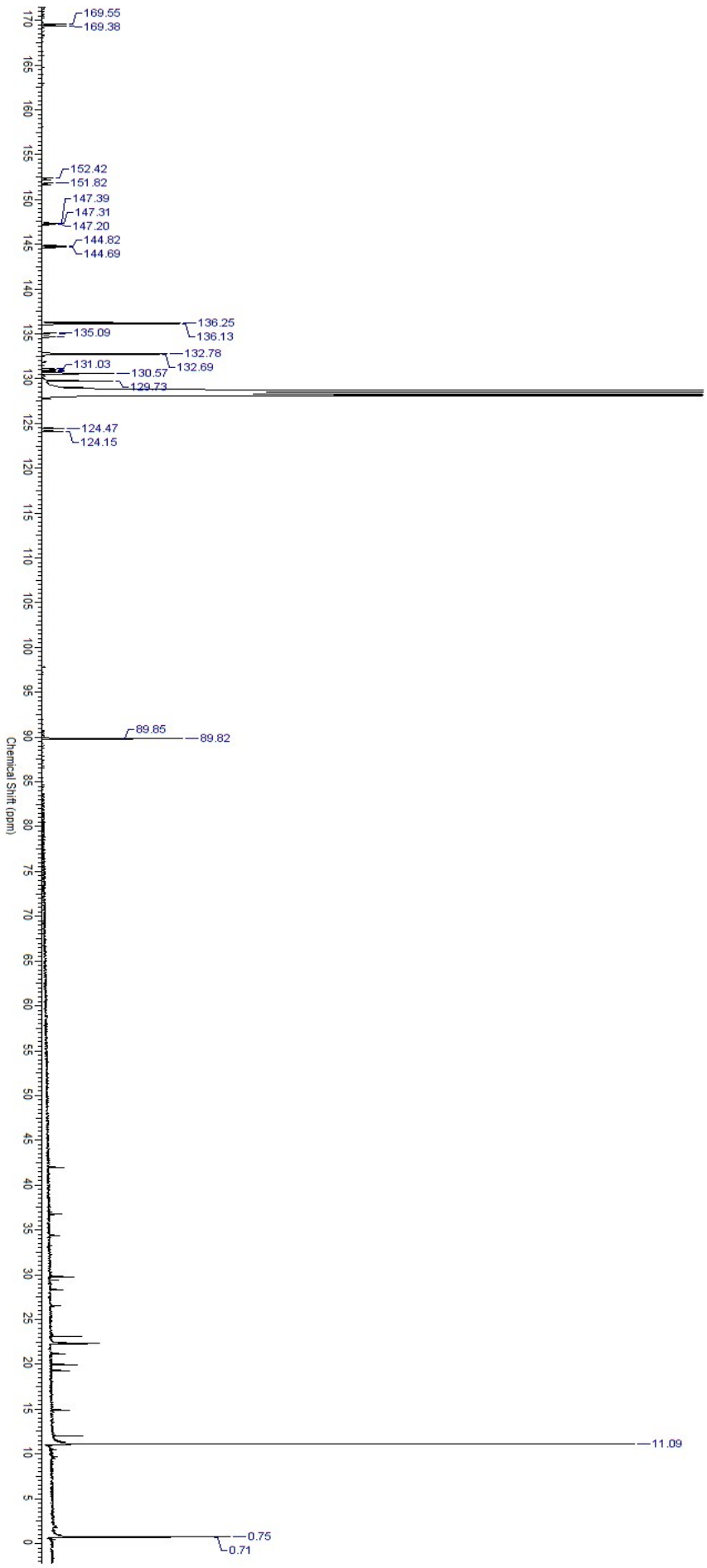



**Figure S27.** $^{13}C\{^{1}H\}$ NMR spectrum of **10**. Contains traces of petroleum ether.

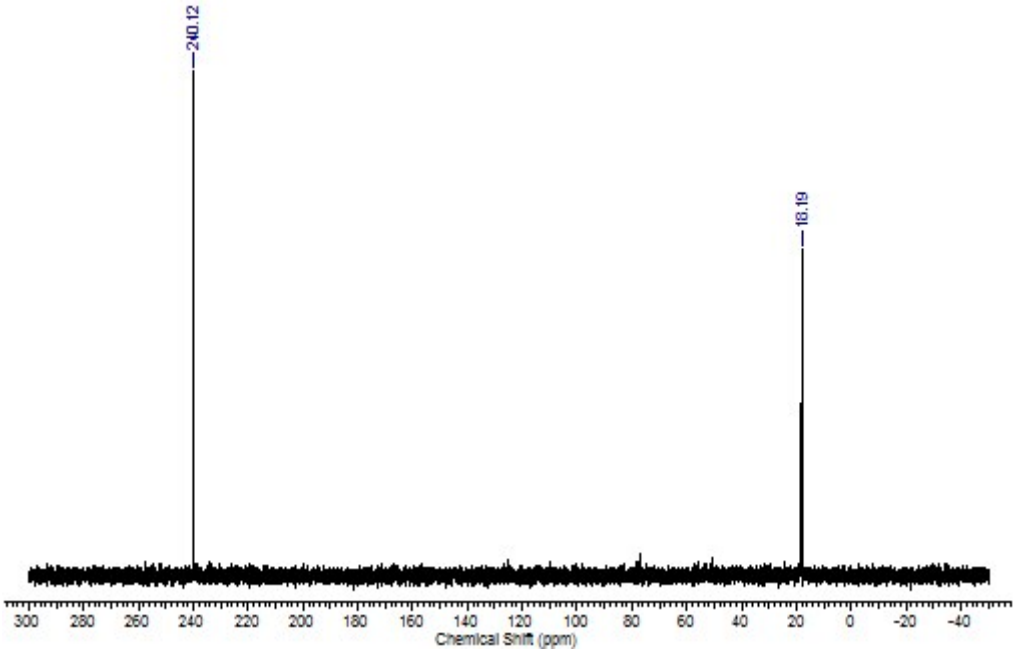



**Figure S28.** $^{31}P\{^{1}H\}$ NMR spectrum of **10**

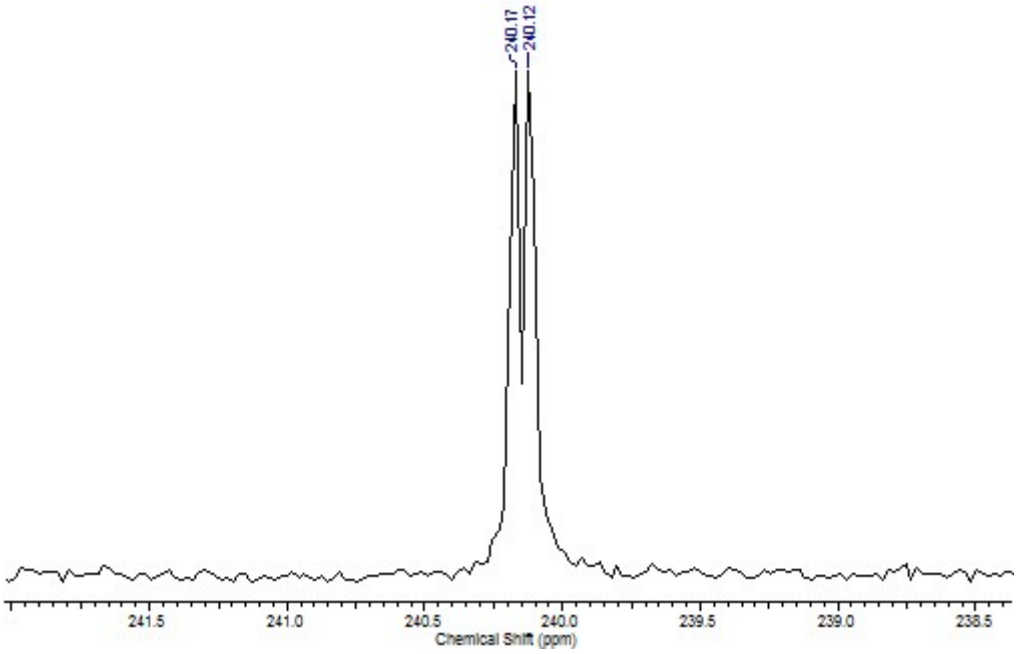



**Figure S29.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphinine region) of **10**

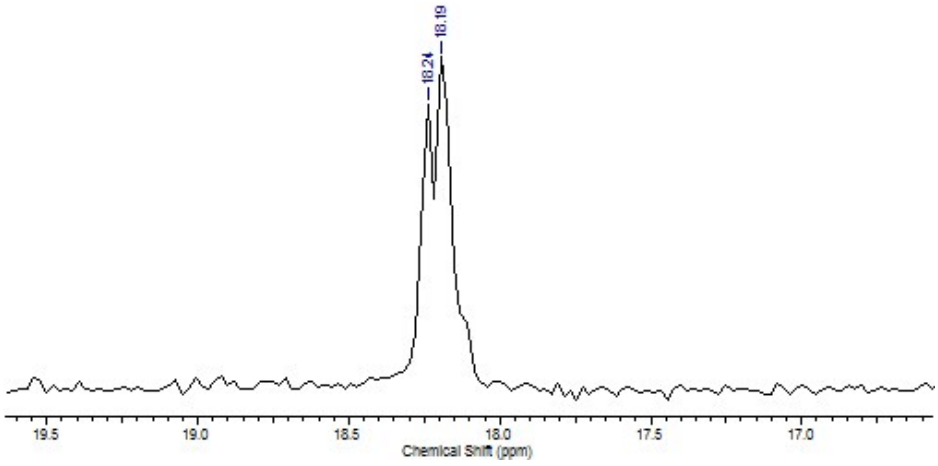



**Figure S30.** $^{31}P\{^{1}H\}$ NMR spectrum (phosphine region) of **10**

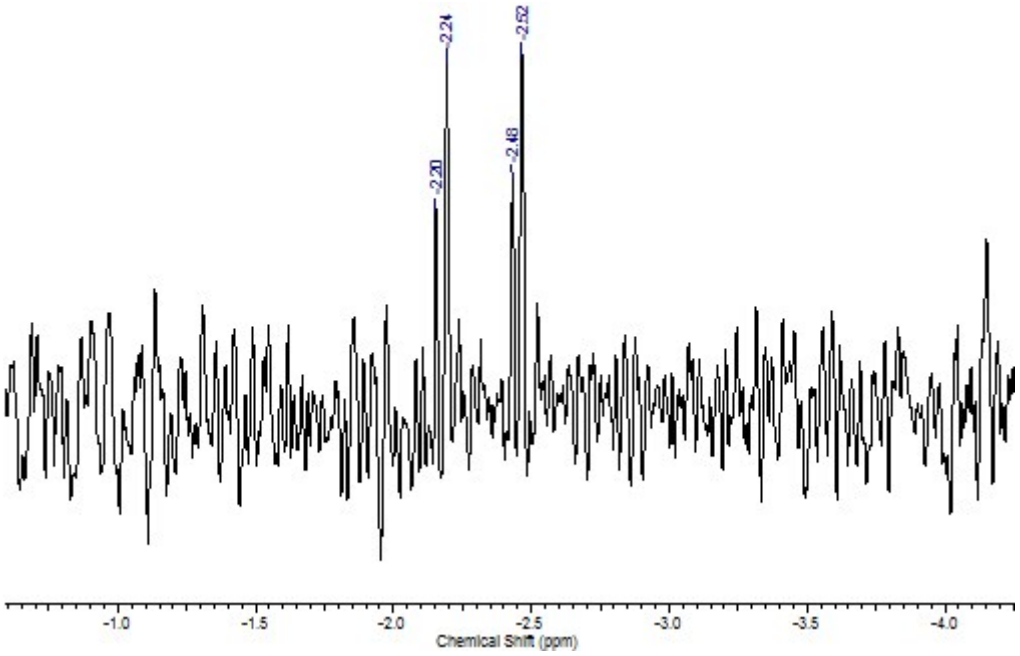



**Figure S31.** $^{29}Si\{^{1}H\}$ NMR spectrum of **10**

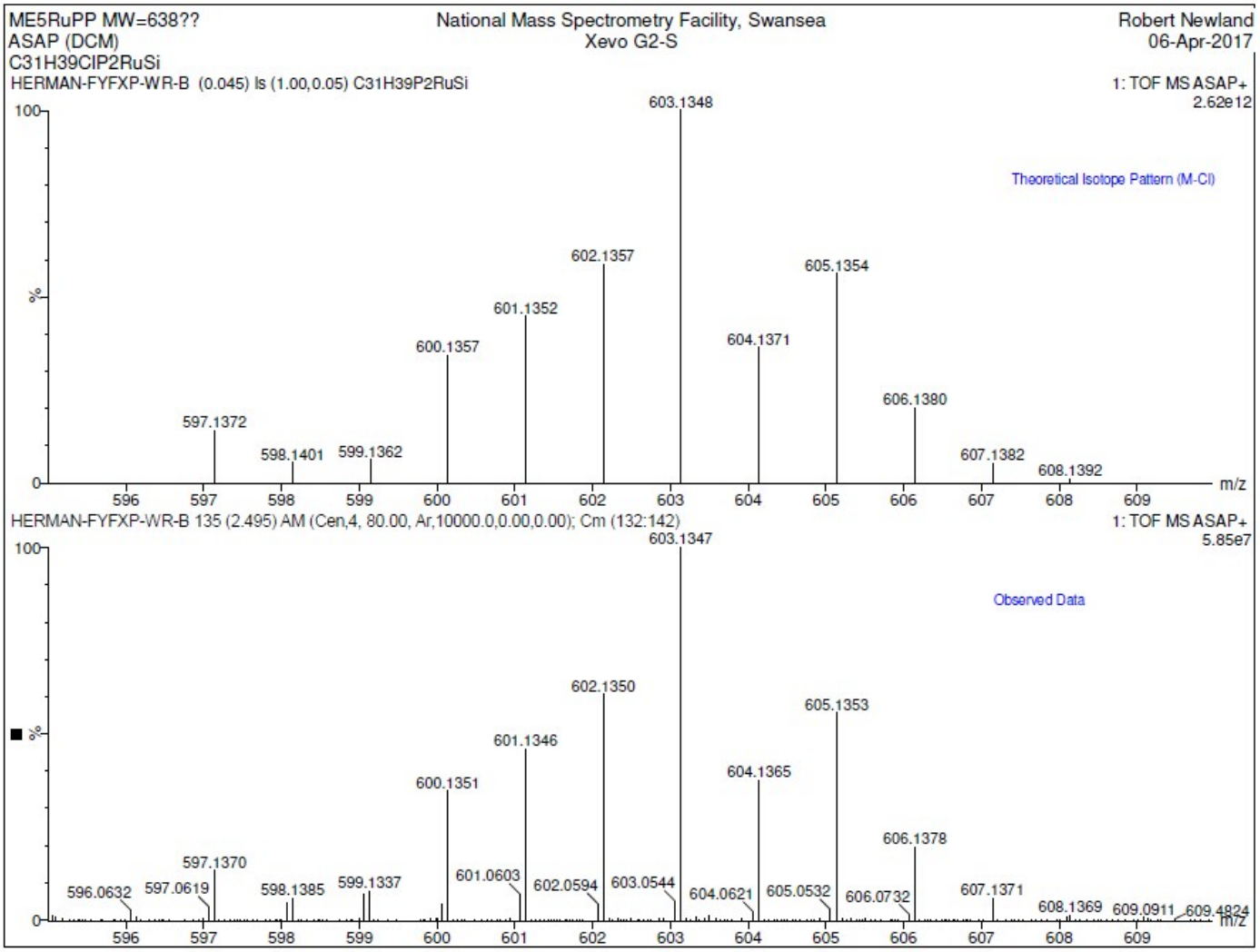



**Figure S32.** HRMS of **10**

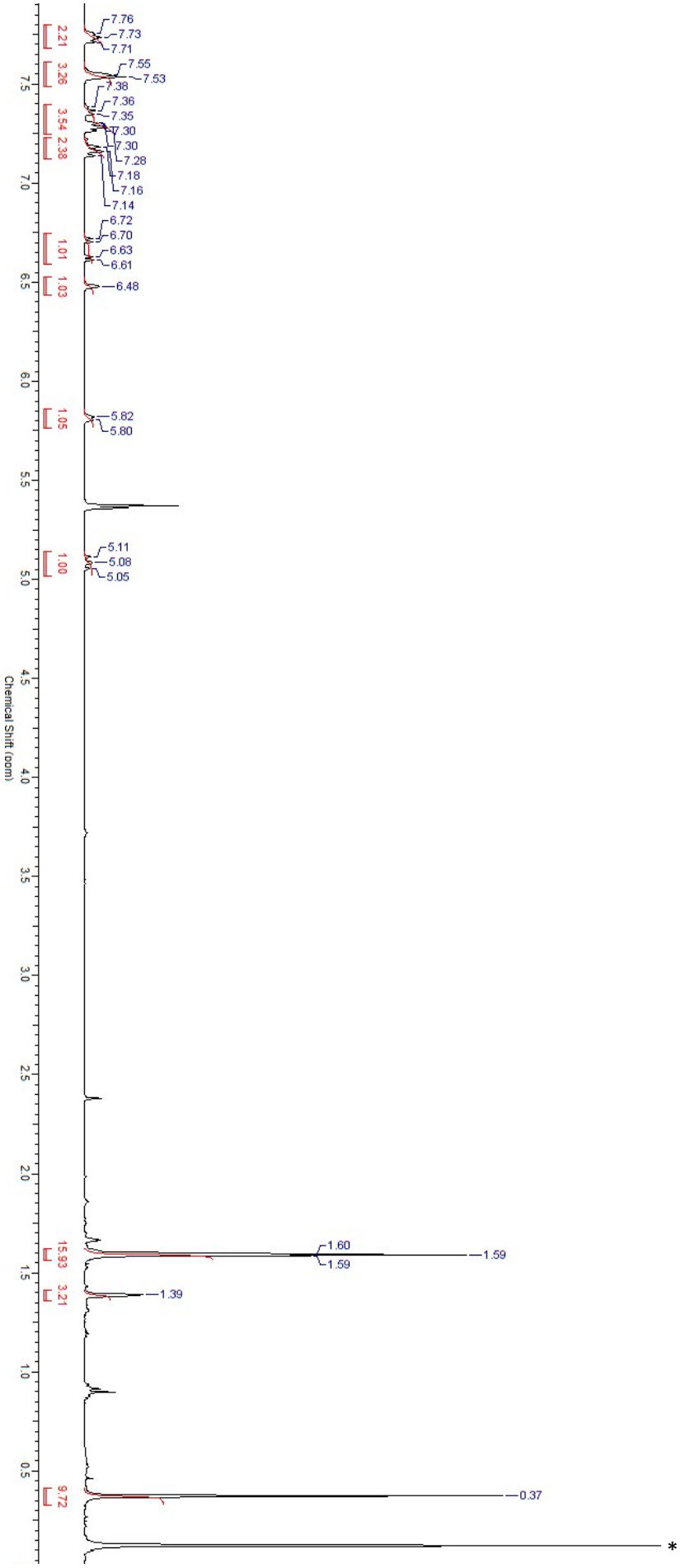



**Figure S33.** $^{1}$H NMR spectrum of **11**. * Contains silicone grease.

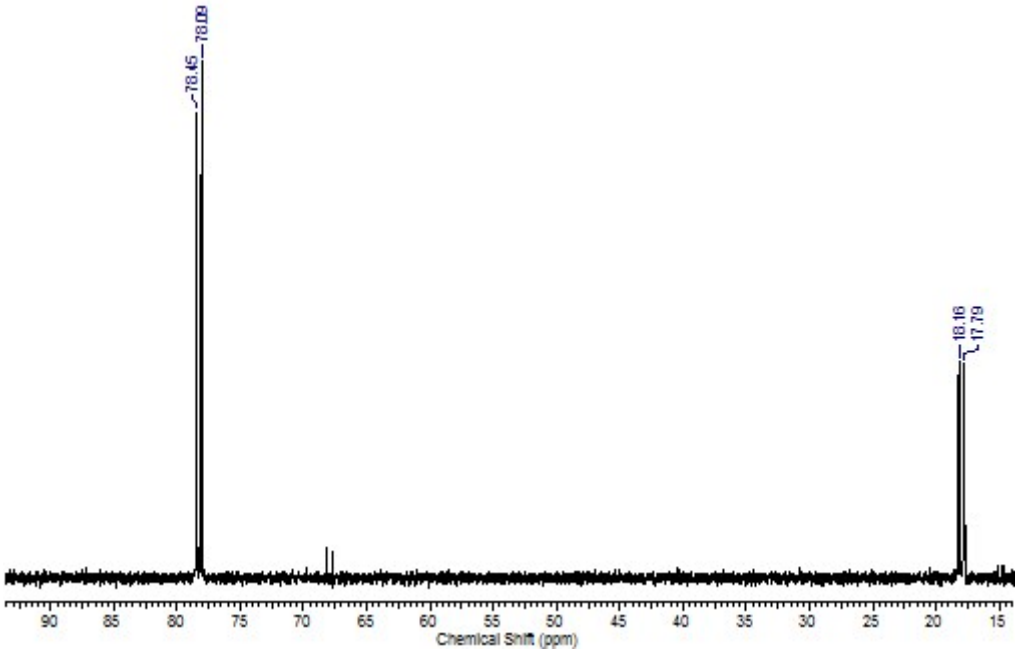



**Figure S34.** $^{31}P\{^{1}H\}$ NMR spectrum of **11**

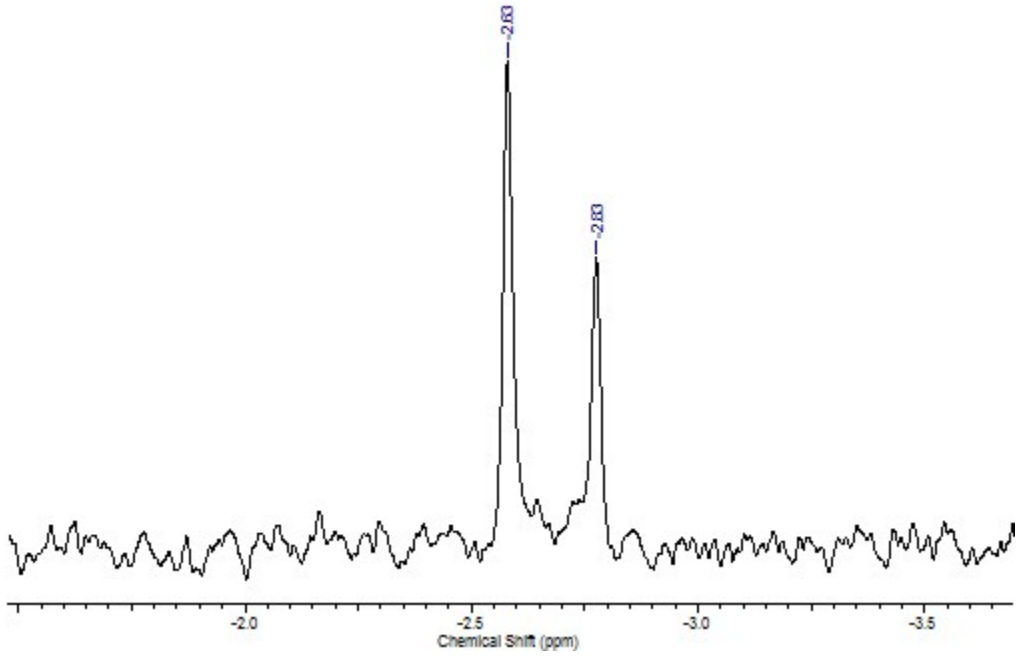



**Figure S35.** $^{29}Si\{^{1}H\}$ NMR spectrum of **11**

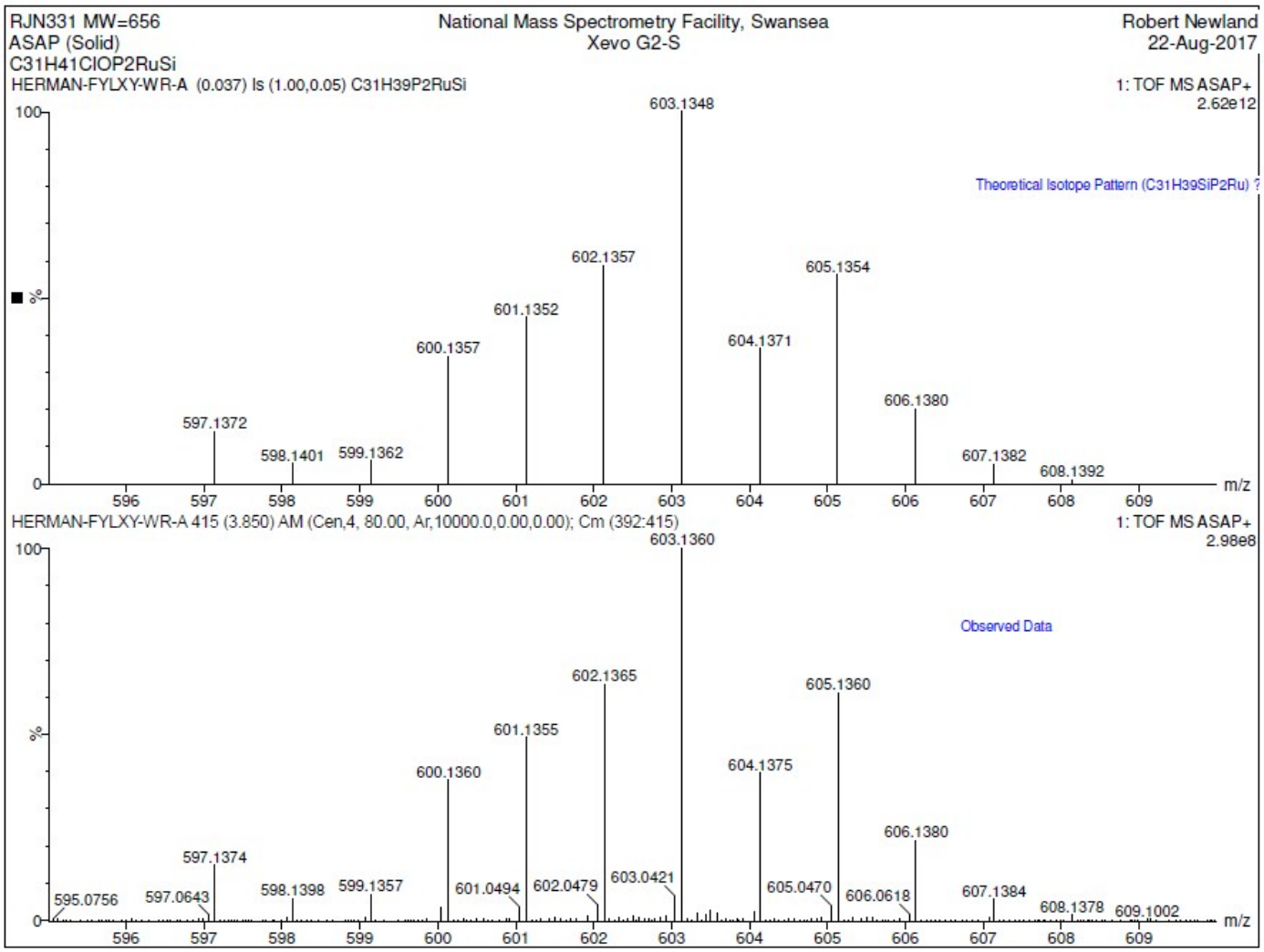



**Figure S36**. HRMS of **11**

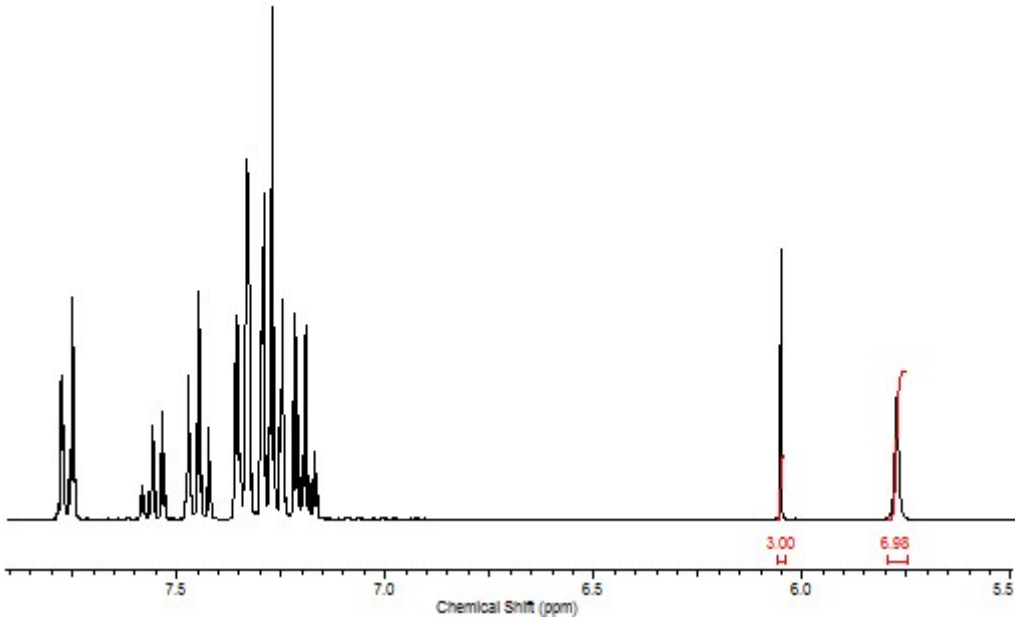



**Figure S37.** $^{1}$H NMR spectrum of the transfer hydrogenation of benzophenone (20°C, 0.1 mol% **2**, 24h: 70% yield)

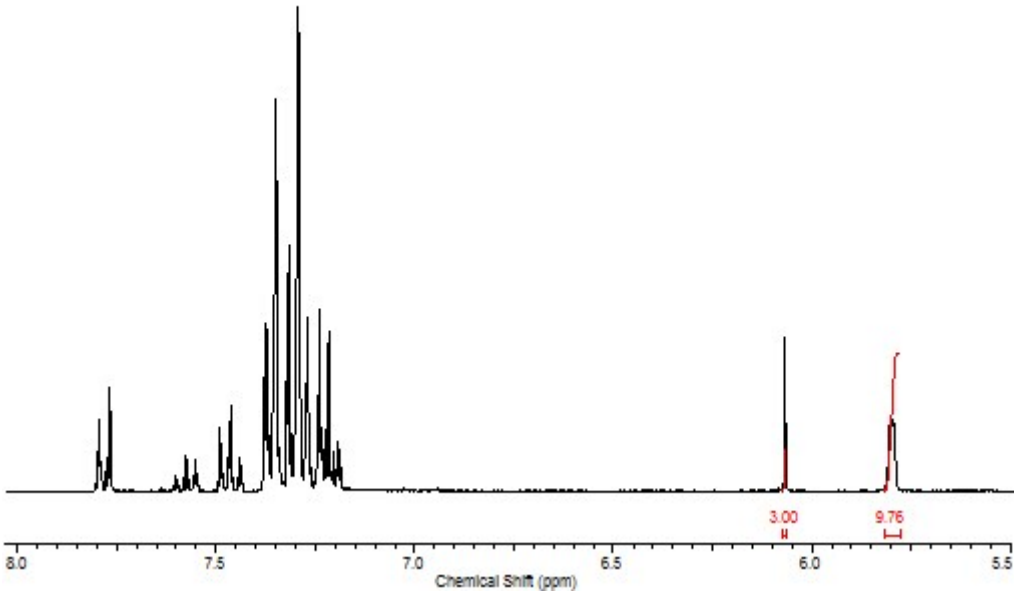



**Figure S38.** $^{1}$H NMR spectrum of the transfer hydrogenation of benzophenone (82°C, 0.1 mol% **2**, 4h: 95% yield)

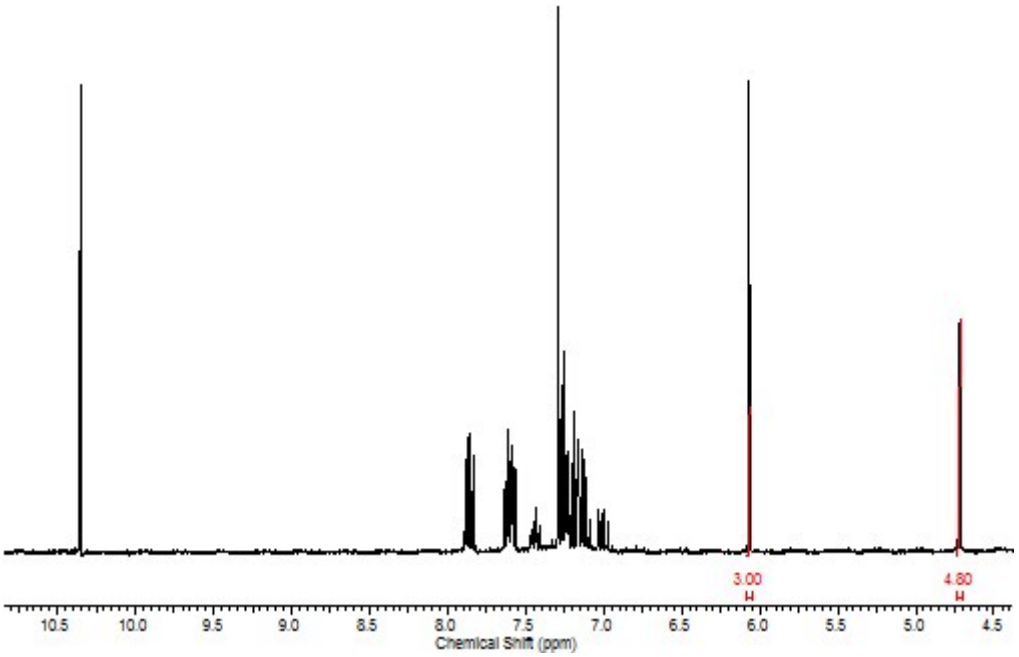



**Figure S39.** $^{1}$H NMR spectrum of the transfer hydrogenation of 2-fluorobenzaldehyde (82°C, 1 mol% **2**, 24h: 24% yield)

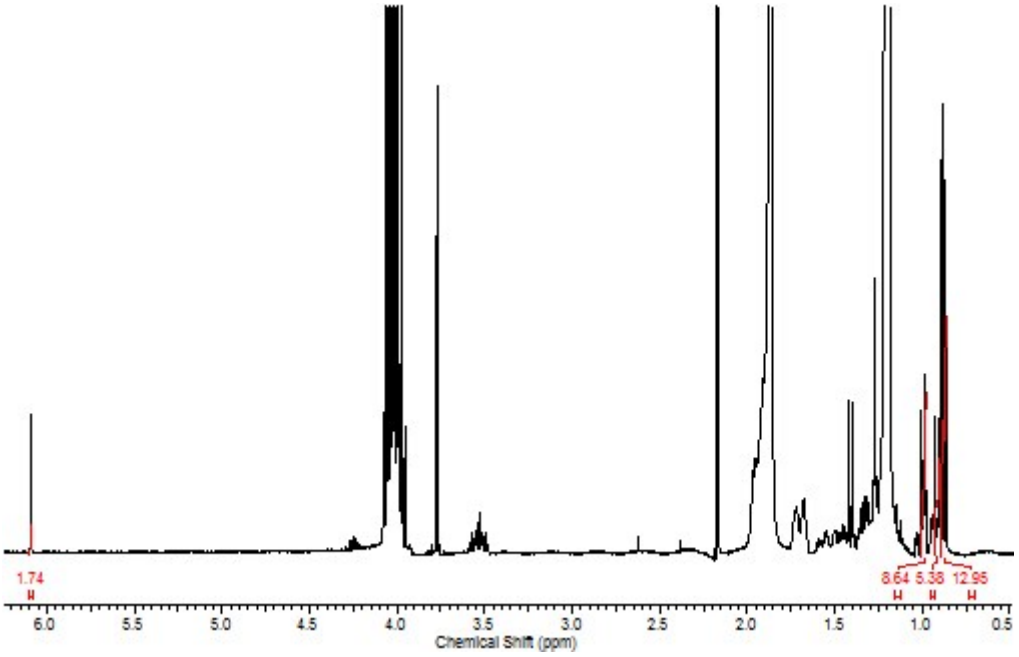



**Figure S40.** $^{1}$H NMR spectrum of the transfer hydrogenation of 4-methylcyclohexanone (82°C, 1 mol% **2**, 1h: 63% yield)

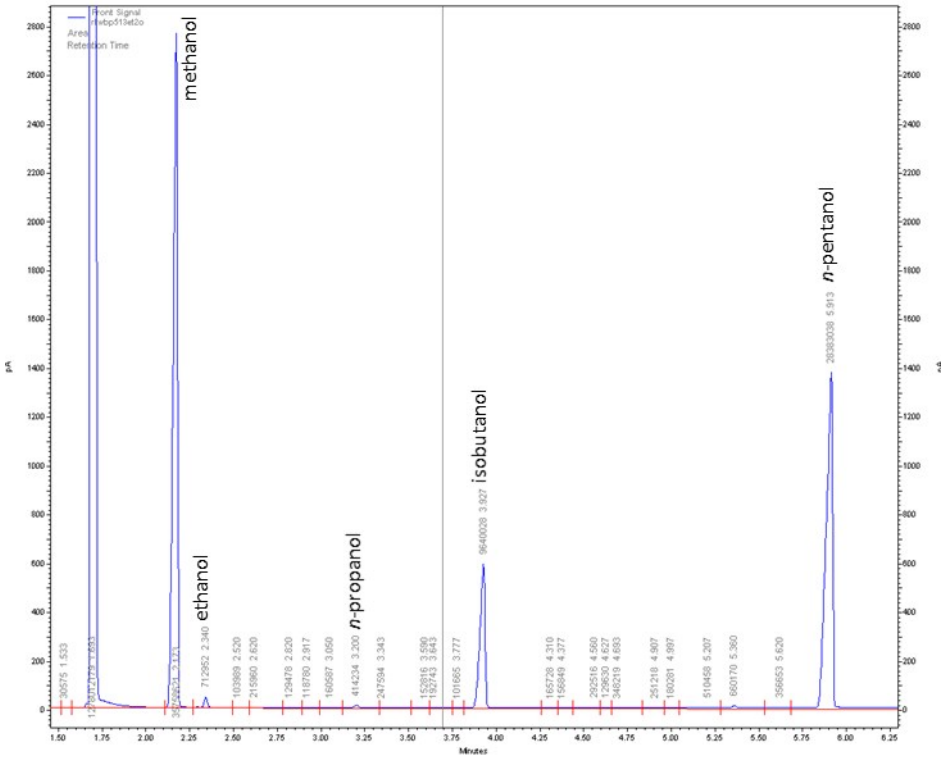



**Figure S41.** GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% *trans*-$[Ru(Cl)_2(dppm)_2]$, 2h: 64.6% yield). This catalytic sample was analysed using a different method to the other samples: Method: oven temperature starts at 35 °C for 3.5 minutes, heat to 200 °C at 20 °C min$^{-1}$ then to 250 °C at 50 °C min$^{-1}$ then hold at 250 °C for 5 minutes. Flow rate 1.8 cm$^3$ min$^{-1}$. *n*-Pentanol was used as a standard

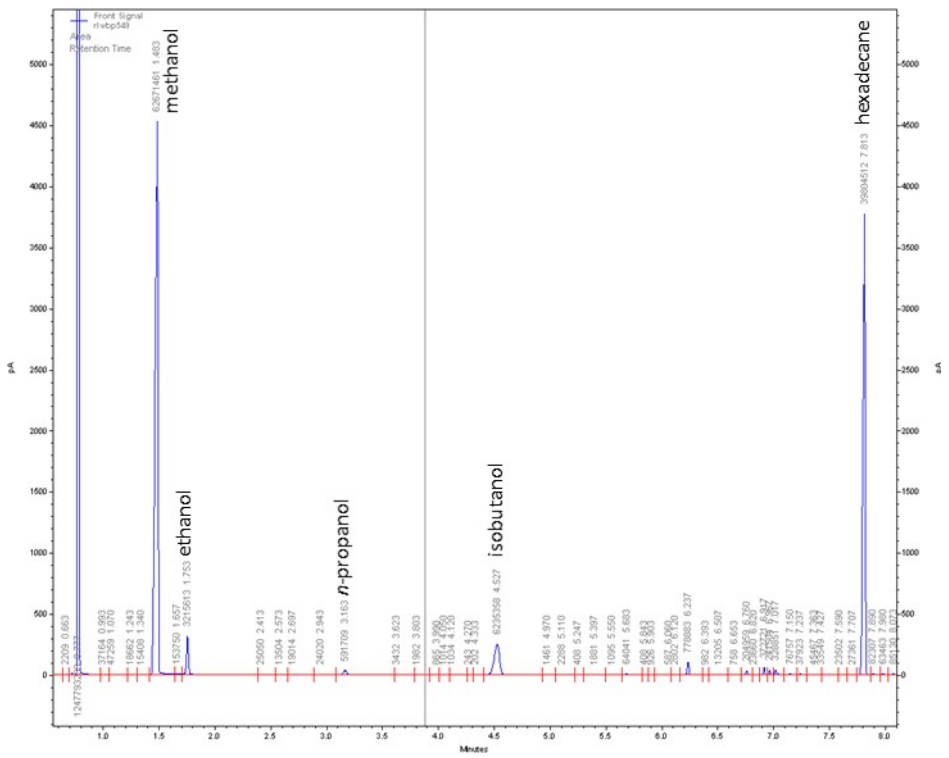



**Figure S42.** GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% **2**, 2h: 38.1% yield). Hexadecane was used as a standard.

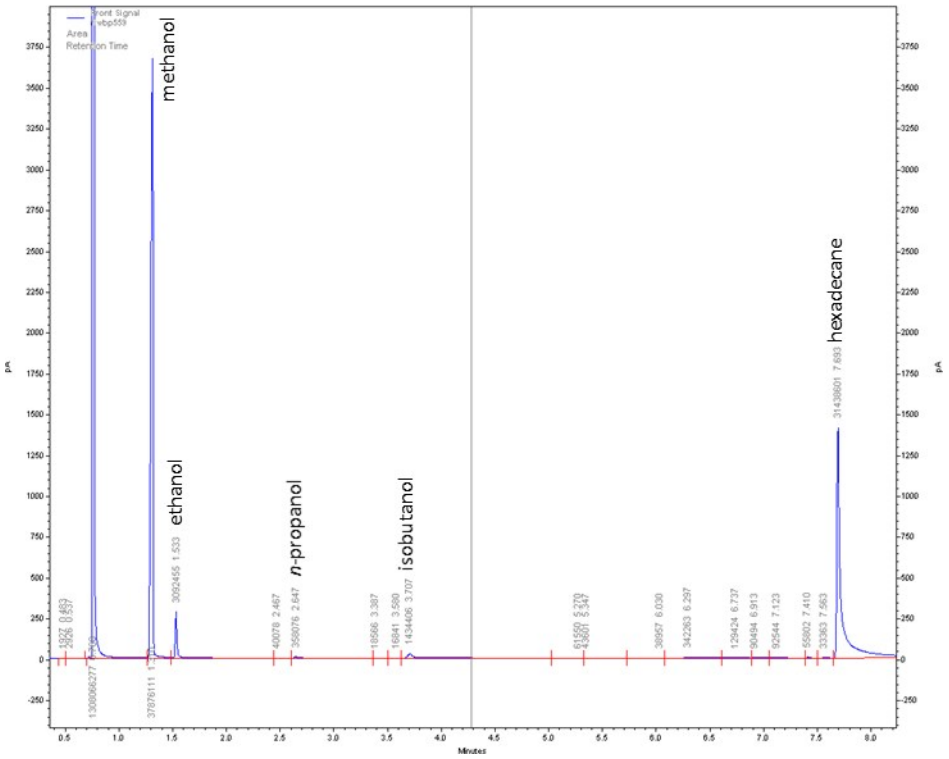



**Figure S43.** GC trace of the upgrading of ethanol and methanol to isobutanol (180°C, 0.1 mol% **9**, 2h: 11.1% yield). Hexadecane was used as a standard.

**Reaction of 1 with [{$RuCl_2(C_6Me_6)$}$_2$] and dried $NH_4PF_6$**

Under a nitrogen atmosphere, a Schlenk flask was charged with **1** (20 mg, 0.06 mmol, 1 equiv.), [{$RuCl_2(C_6Me_6)$}$_2$] (18 mg, 0.03 mmol, 0.5 equiv) and $NH_4PF_6$ (9 mg, 0.06 mmol, 1 equiv.). Dry dichloromethane (2 $cm^3$) was then added *via* syringe and the reaction stirred for two hours. All volatiles were then removed *in vacuo* before dry $CDCl_3$ (0.8 $cm^3$) was added. The crude reaction mixture was then analysed by $^{31}P\{^1H\}$ NMR spectroscopy.

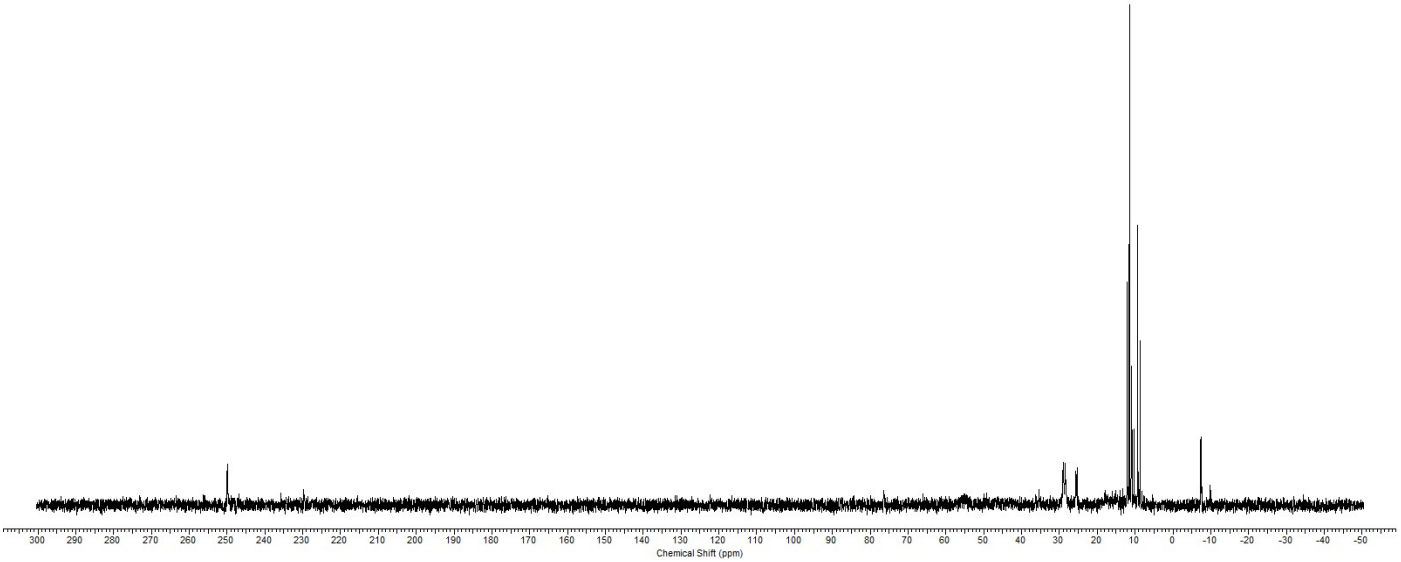



**Figure S44.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with [{$RuCl_2(C_6Me_6)$}$_2$] and dry $NH_4PF_6$

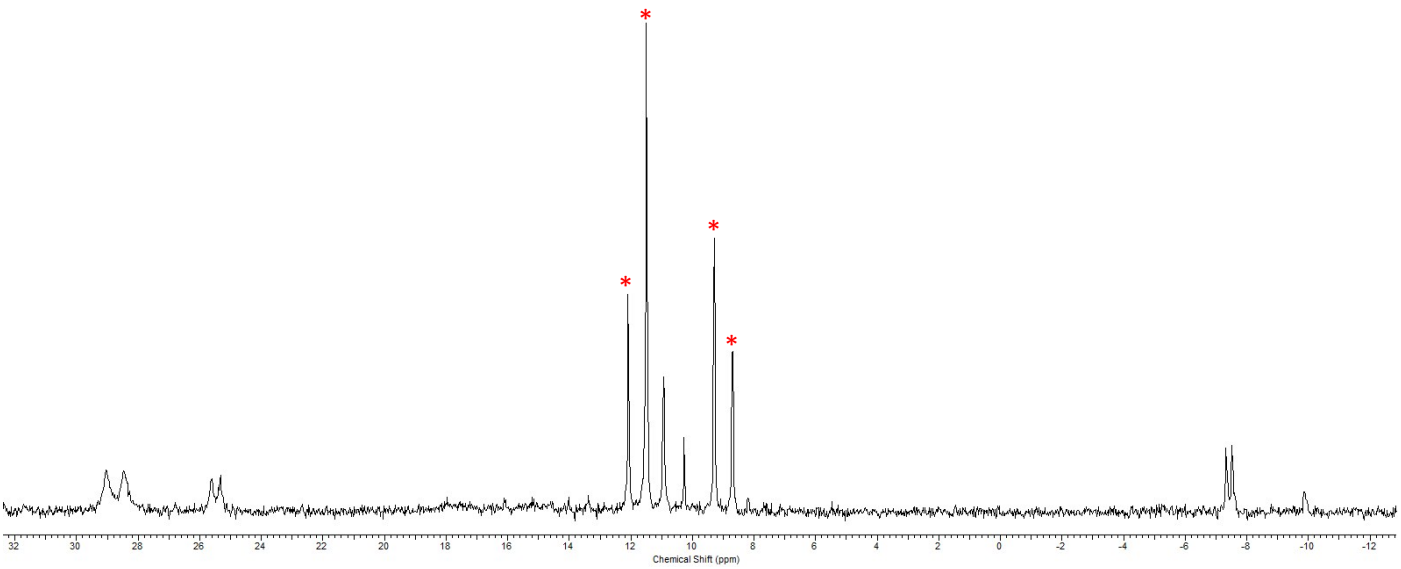



**Figure S45.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with [{$RuCl_2(C_6Me_6)$}$_2$] and dry $NH_4PF_6$ (magnification of low frequency area). * = **9**

**Reaction of 1 with [{$RuCl_2(C_6Me_6)$}$_2$] without any additional anions**

An NMR tube was charged with **1** (20 mg, 0.06 mmol) and [{$RuCl_2(C_6Me_6)$}$_2$] (18 mg, 0.03 mmol, 0.5 equiv), then an approx. 1:1 mixture of $C_6D_6$ : fluorobenzene (used to aid solubility of the Ru dimer) was added and the tube sealed with a J Young tap. The tube was heated to 90°C overnight and the contents analysed by $^{31}P\{^1H\}$ NMR spectroscopy, which revealed formation of **2** as the major product.

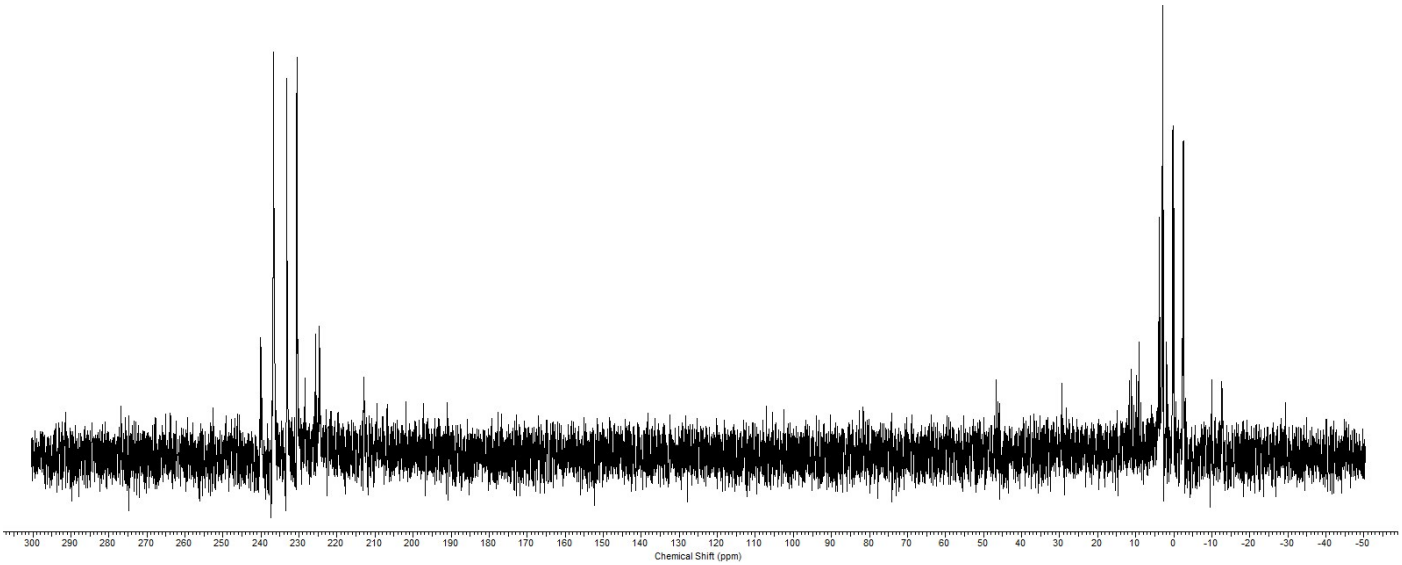



**Figure S46.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with [{$RuCl_2(C_6Me_6)$}$_2$]

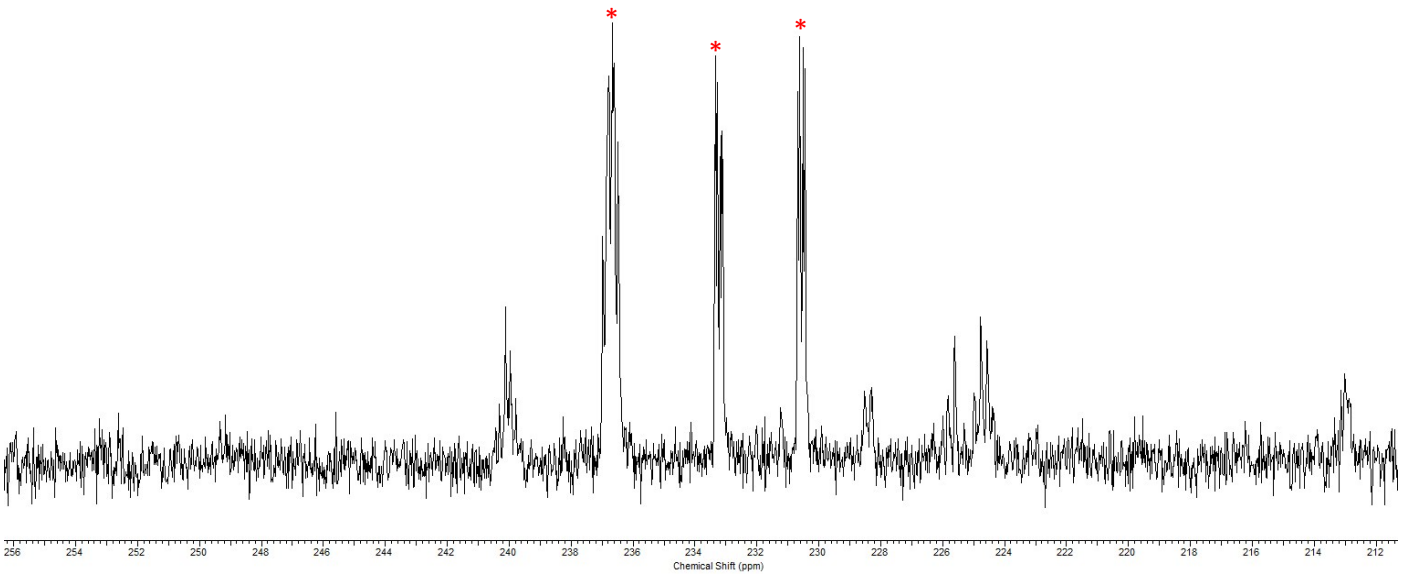



**Figure S47.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with [{$RuCl_2(C_6Me_6)$}$_2$] (magnification of high frequency area).
* = **2**

*

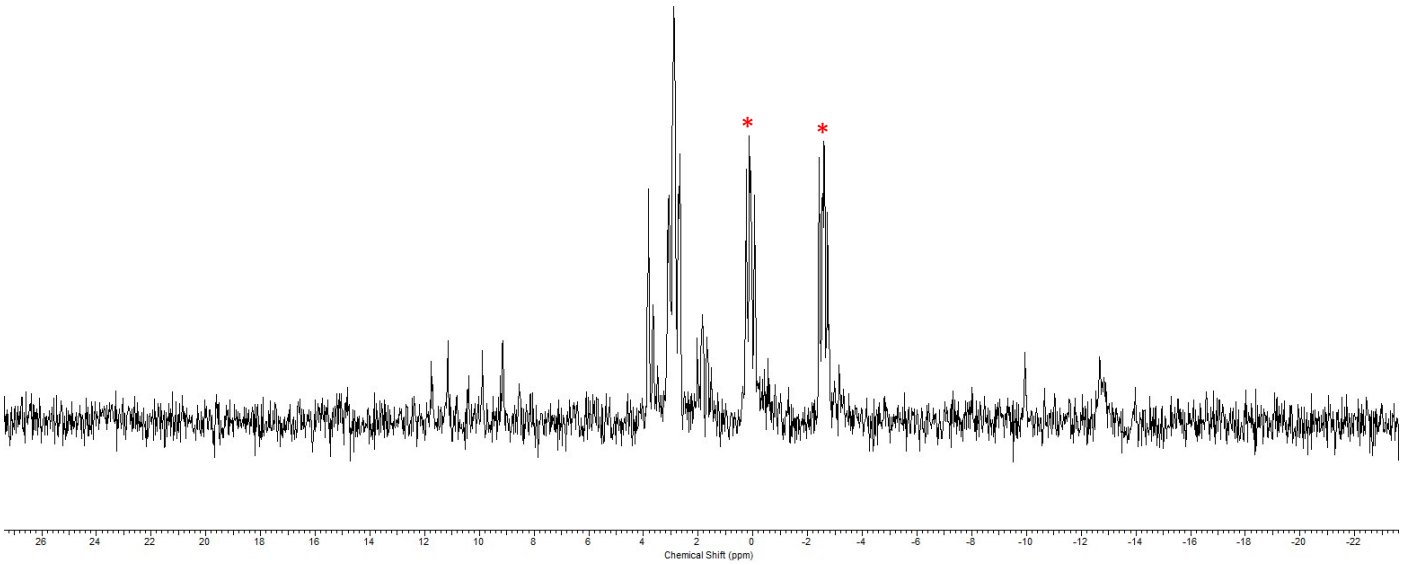



**Figure S48.** $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with $[\{RuCl_2(C_6Me_6)\}_2]$ (magnification of low frequency area). * = **2**

**Reaction of 10 with water**

An NMR tube was charged with a solution of **10** (20 mg, 0.03 mmol) in dry THF-$d_8$ (0.6 $cm^3$). Water (3 drops) was then added and the tube was then sealed with a J Young tap and thorough shaken. After an hour, the reaction was analysed by $^{31}P\{^1H\}$ NMR which revealed formation of mainly **11** as well as minor side products and unconsumed **10**.

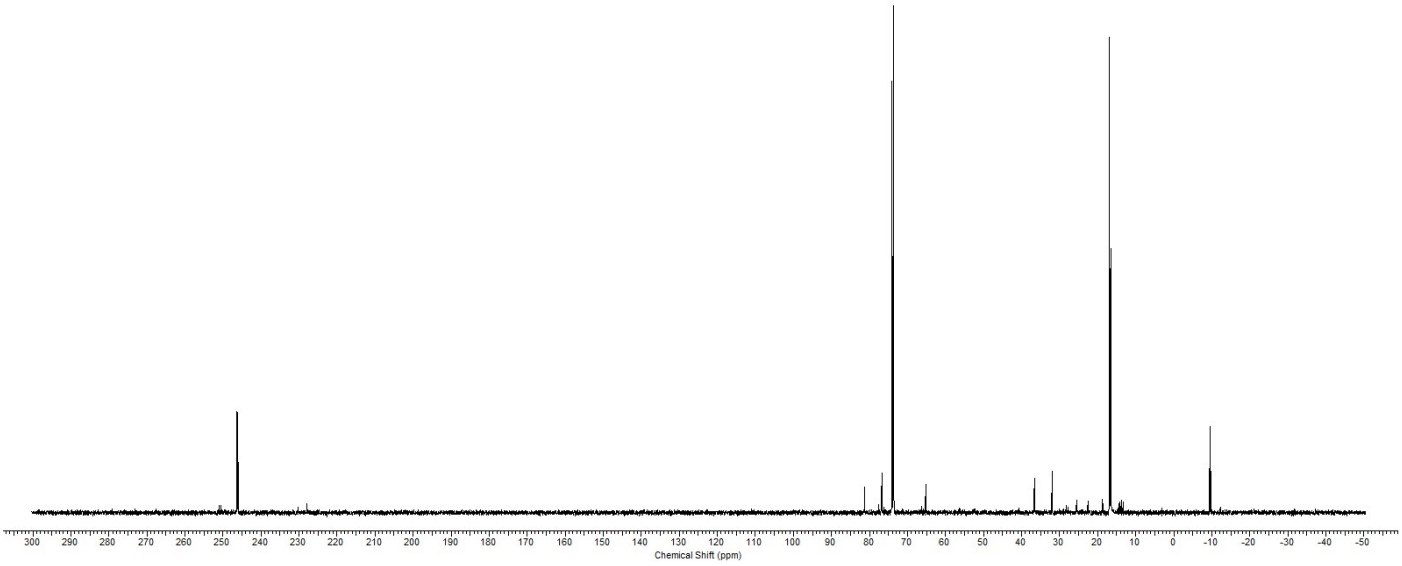



**Figure S49.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **10** with excess water

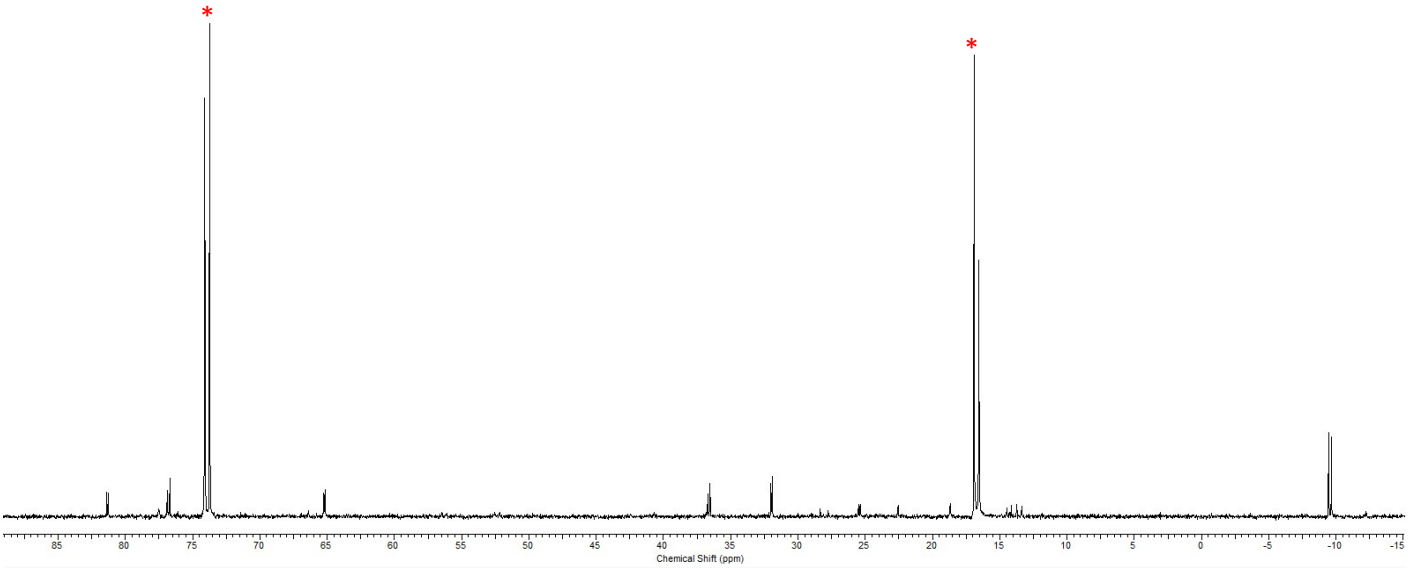



**Figure S50.** $^{31}P\{^1H\}$ NMR spectrum of the reaction of **10** with excess water (magnification of low frequency region). * = **11**