Supporting Information

General methods

All solvents were distilled using standard methods. CPD was freshly bi-distilled prior to use. All starting materials from commercial suppliers (Aldrich, Fluka, TCI America) were used without further purification. Compounds **1/2** have purity higher than 98 %, as attested by G.C. analysis.

Analytical methods

The quantitative analyses were performed by either ^{1}H-NMR (compounds **5/6**) or ^{31}P-NMR (compounds **3/4** and **7/8**).

In the case of analyses on phosphorylation reactions, the procedure was as follows: a quantitatively known mixture of **1/2** was left to react with $PClPh_2$ as described in the experimental section. At the end of the reaction, the mixture was evaporated under reduced pressure at room temperature and the residue was filtered through a funnel with cotton using ethyl acetate in order to remove triethylammonium chloride and other insoluble residues. A known amount of diethylphosphoramidate was added to the mixture as a standard for ^{31}P-NMR quantifications. After removal of the solvent, NMR analyses were performed (figures 21 and 22).

Similar results were obtained by weighing the compounds after isolation through column chromatography.

Figure 23 represents the ^{31}P-NMR spectrum obtained from the reaction in which 2.0 eq. of **2**, 1.0 eq. of $PClPh_2$ and 1.0 eq. of Et_3N were used.

Mass spectra

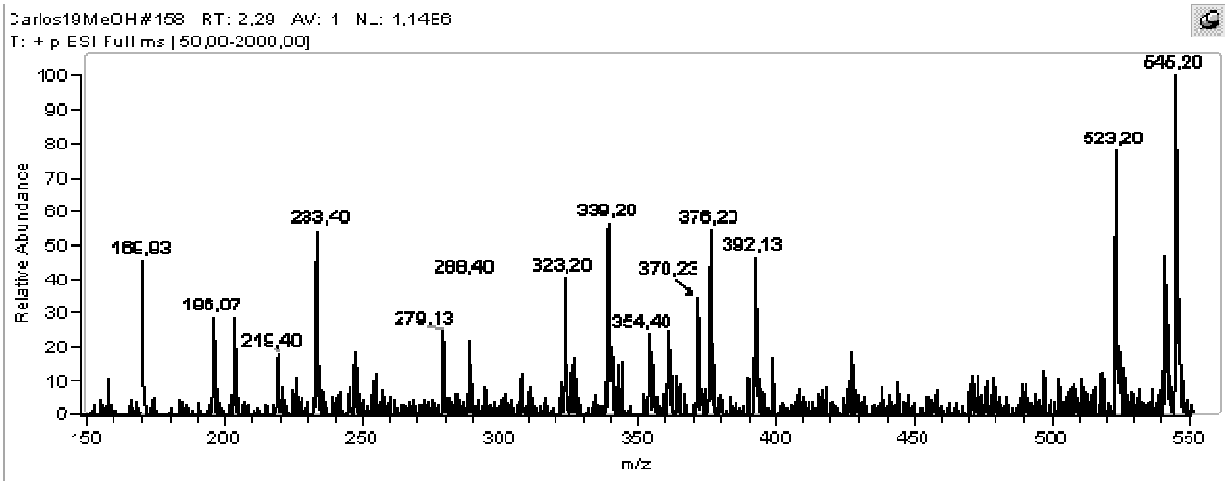

Figure 1. Phosphorylation of adduct **1** with $PClPh_2$: Mass spectrum of an ESI analysis of a fraction from column chromatography. Most significant peaks (M+1/M+23): 219.40 – diphenylphosphinic acid; 233.40 - methoxydiphenylphosphine oxide; 354.40/376.20 – adduct **7**; 370.23/392.13 – adduct **3**; 523.20/545.20 – intermediate **11**-*endo*.

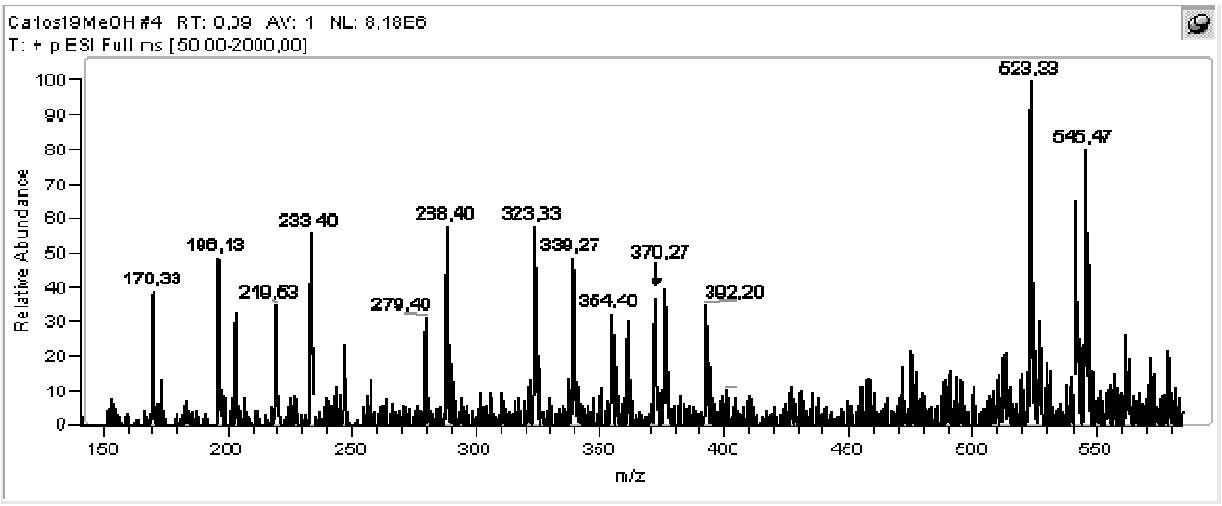

Figure 2. Phosphorylation of adduct **2** with $PClPh_2$: Mass spectrum of an ESI analysis of a fraction from a column chromatography. Most significant peaks (M+1/M+23): 219.53 – diphenylphosphinic acid; 233.40 - methoxydiphenylphosphine oxide; 354.40/376.23 – adduct **8**; 370.27/392.20 – adduct **4**; 523.33/545.47 – intermediate **11**-*exo*.

^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra

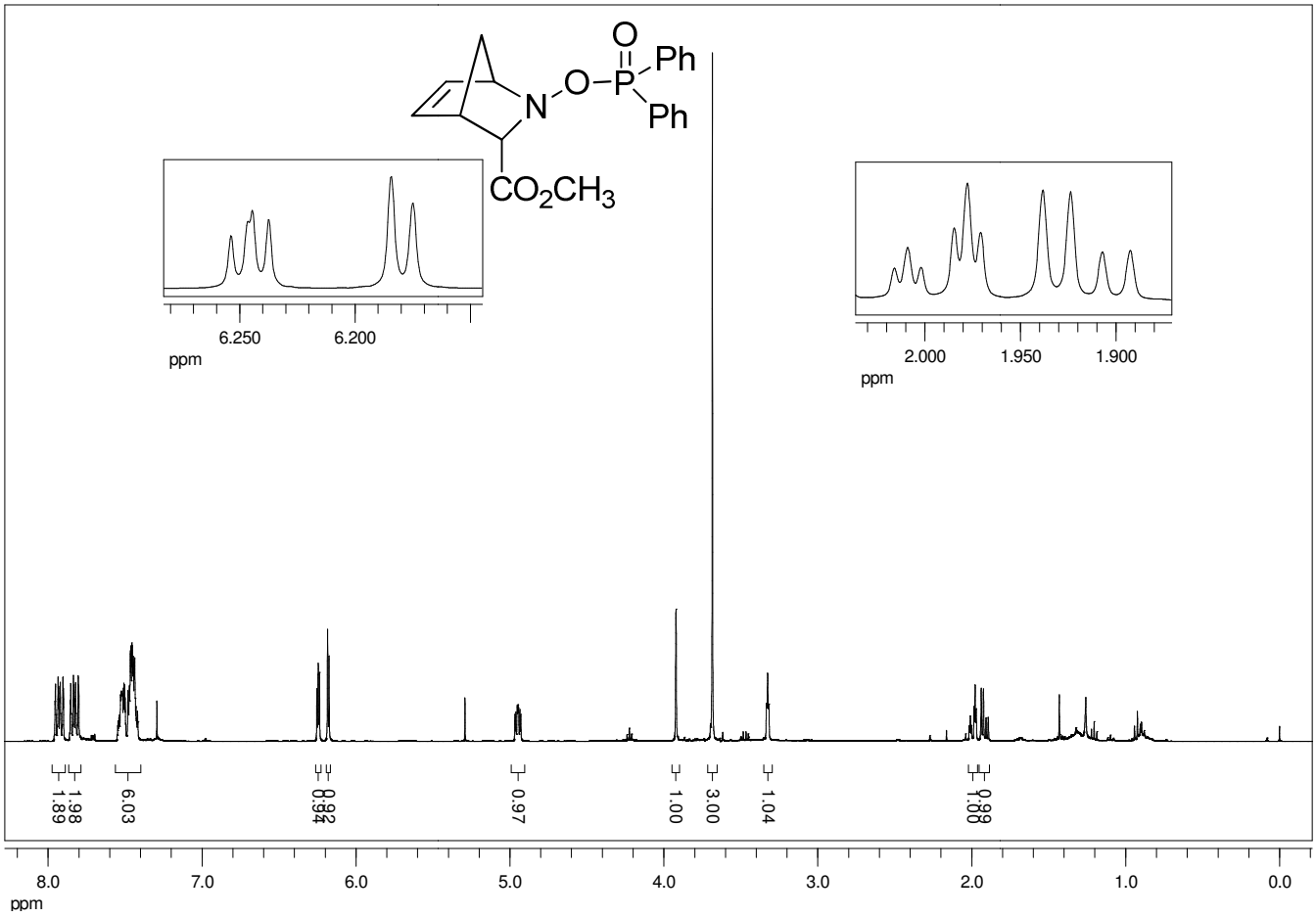

Figure 3. ^{1}H-NMR spectrum of compound **3**.

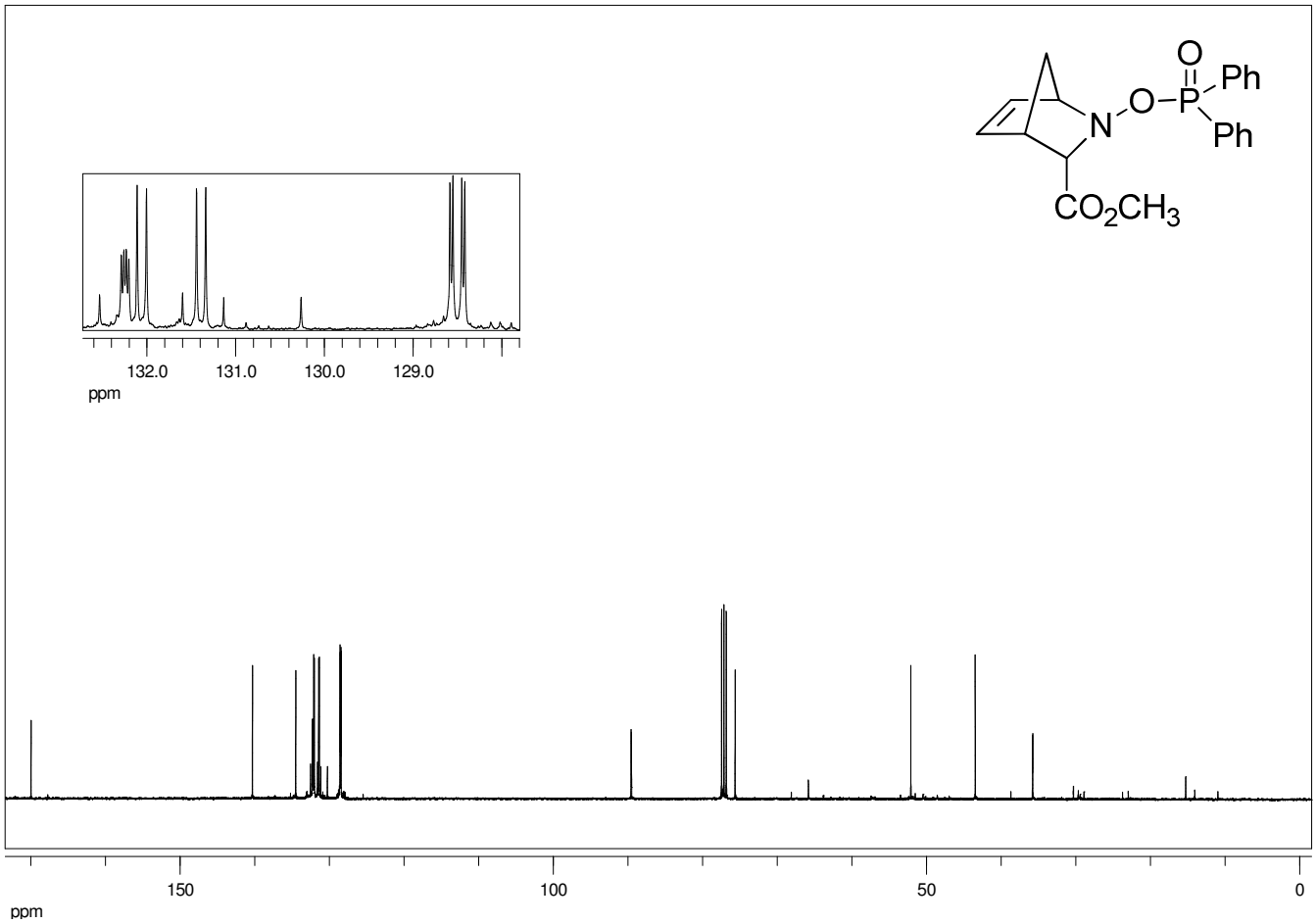

Figure 4. ^{13}C-NMR spectrum of compound **3**.

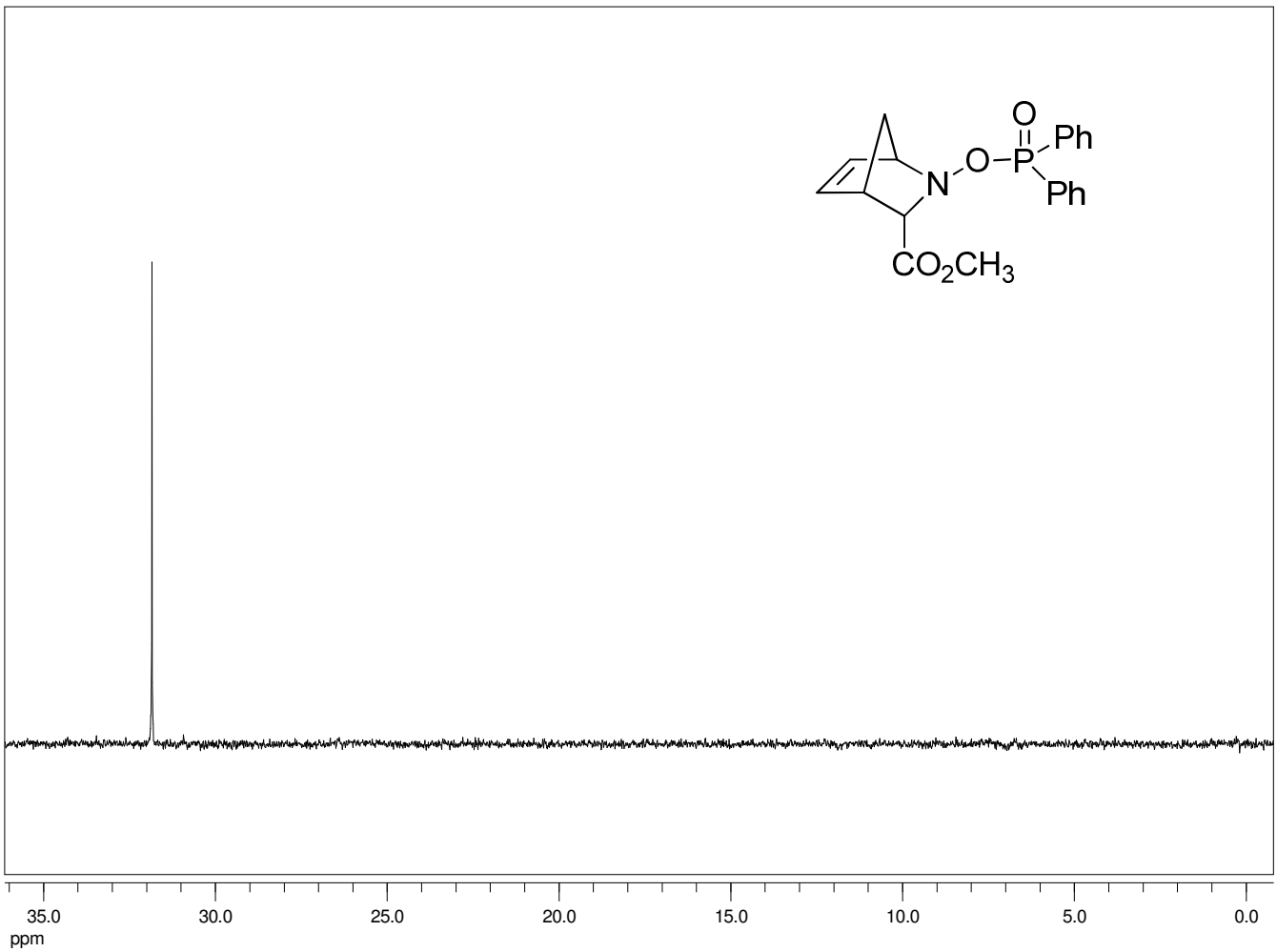

Figure 5. ^{31}P-NMR spectrum of compound **3**.

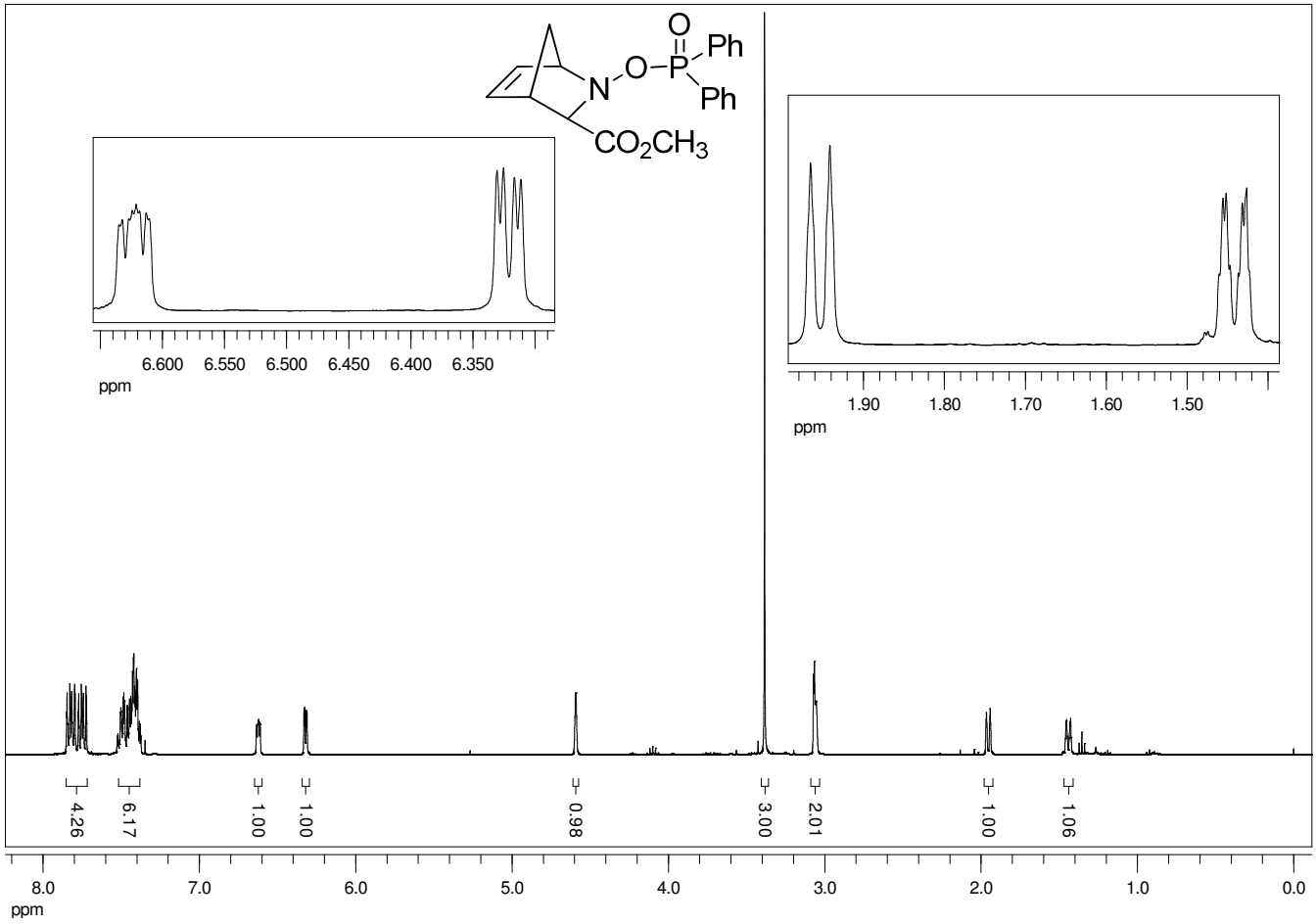

Figure 6. ^{1}H-NMR spectrum of compound **4**.

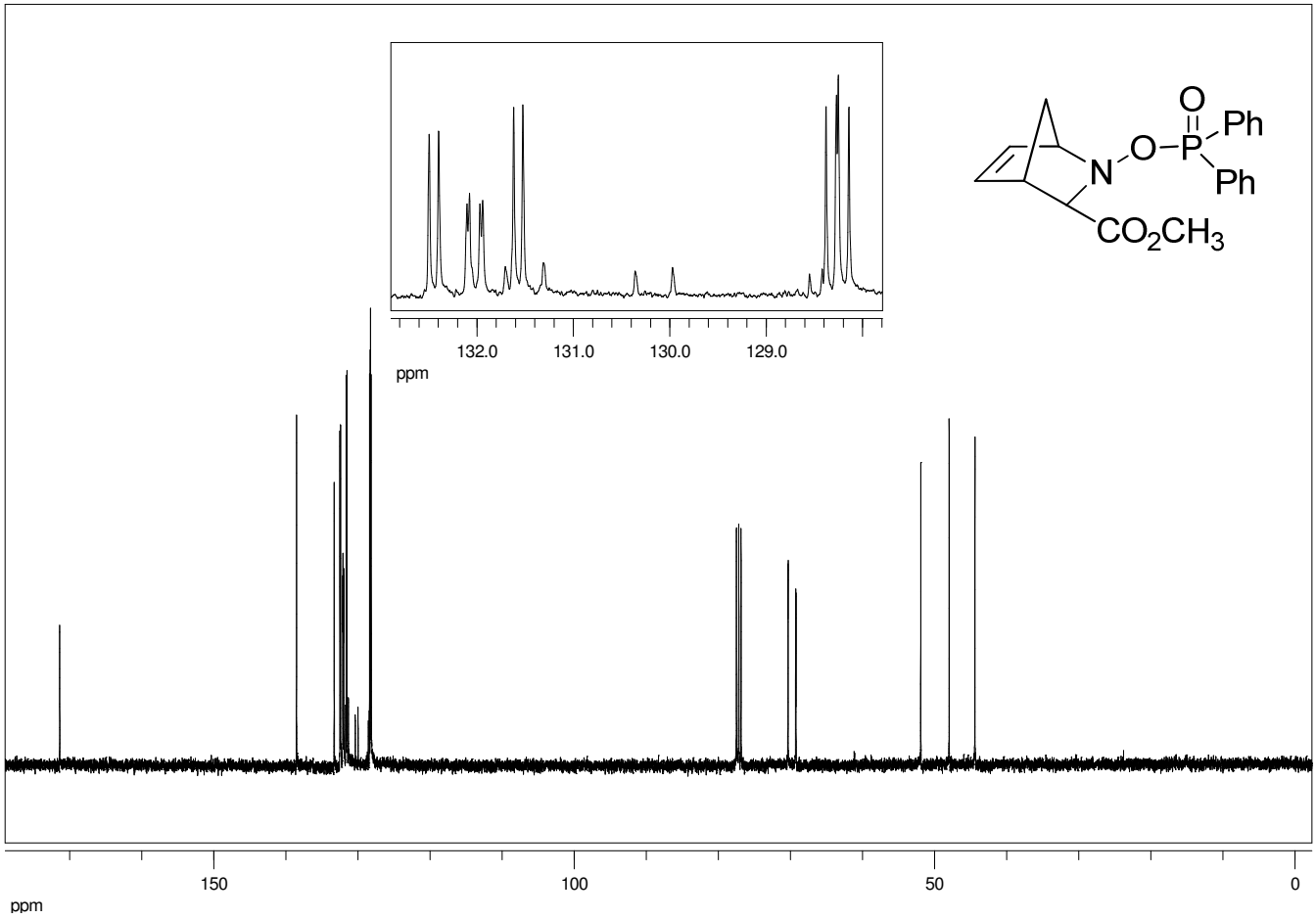

Figure 7. ^{13}C-NMR spectrum of compound **4**.

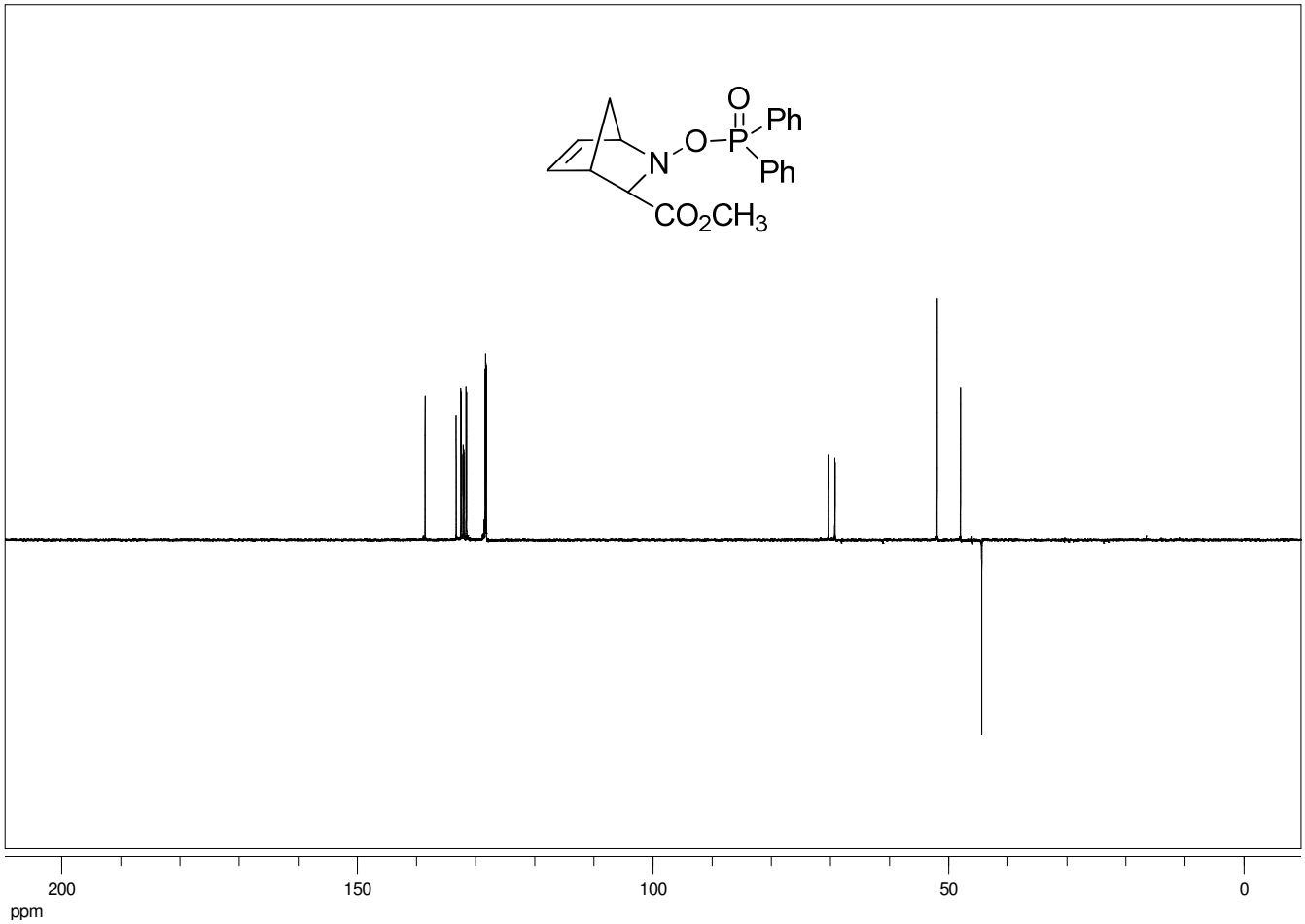

Figure 8. DEPT spectrum of compound **4**.

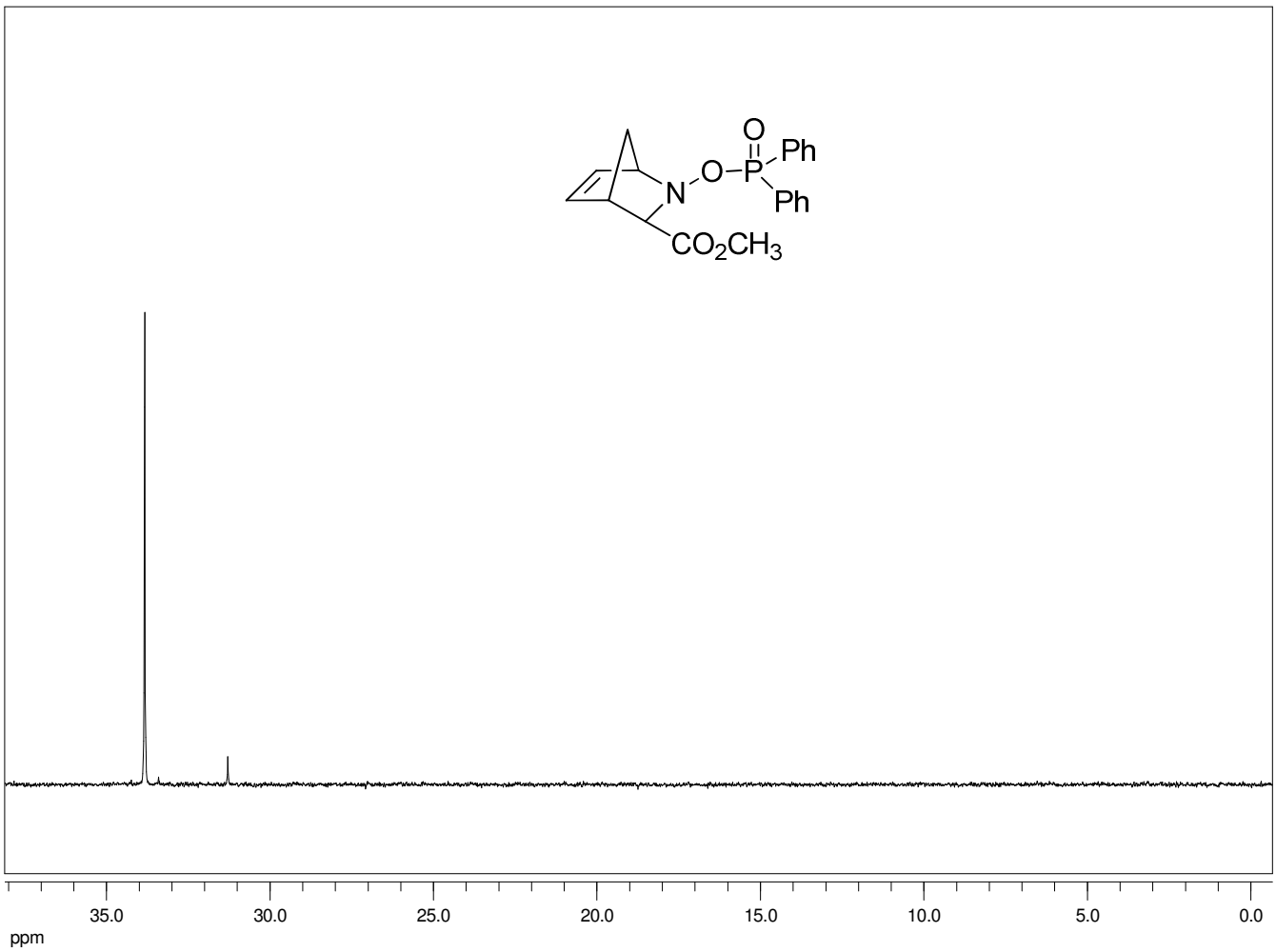

Figure 9. ^{31}P-NMR spectrum of compound **4**.

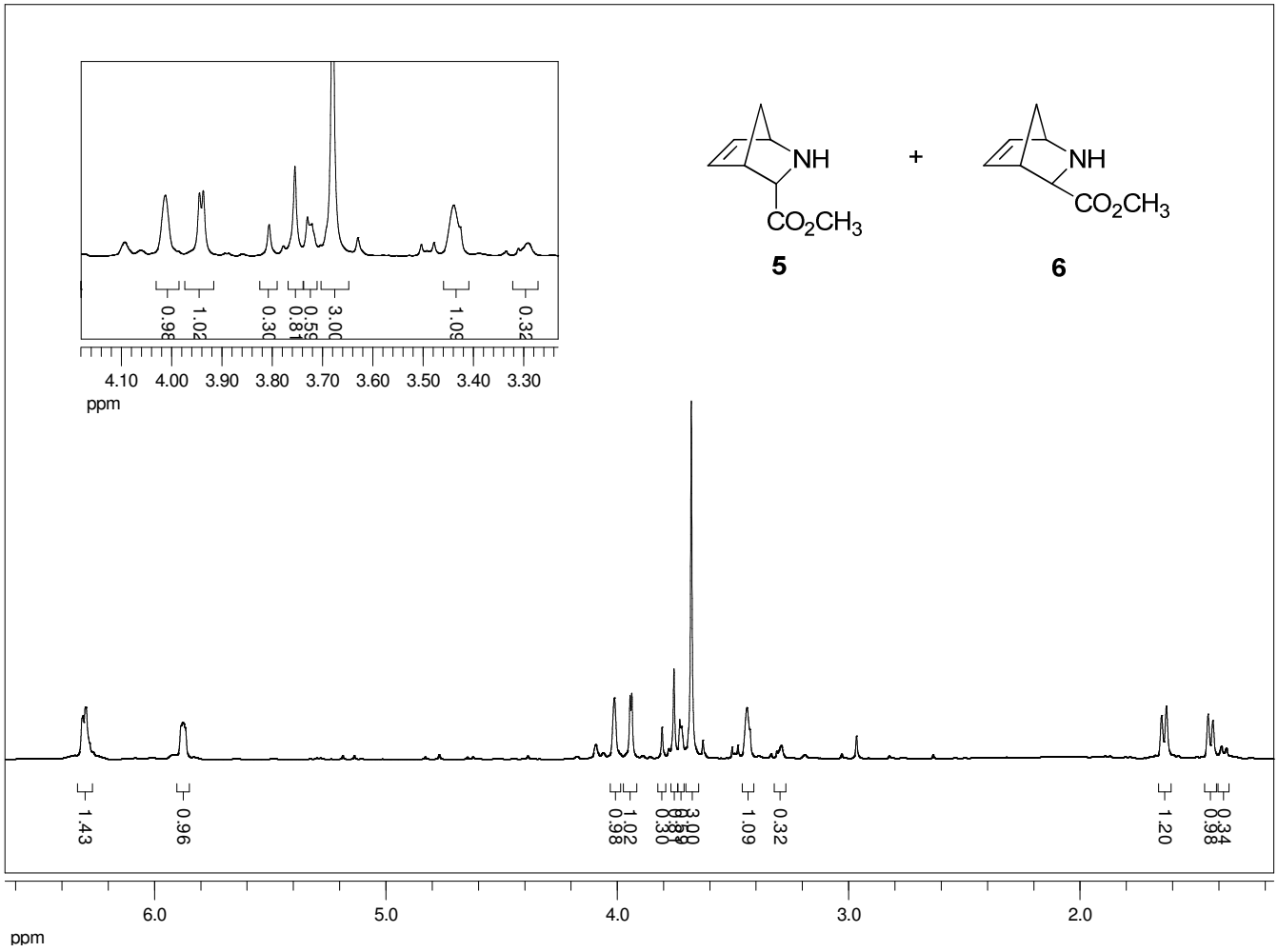

Figure 10. ^{1}H-NMR spectrum of the mixture of compounds **5** and **6**.

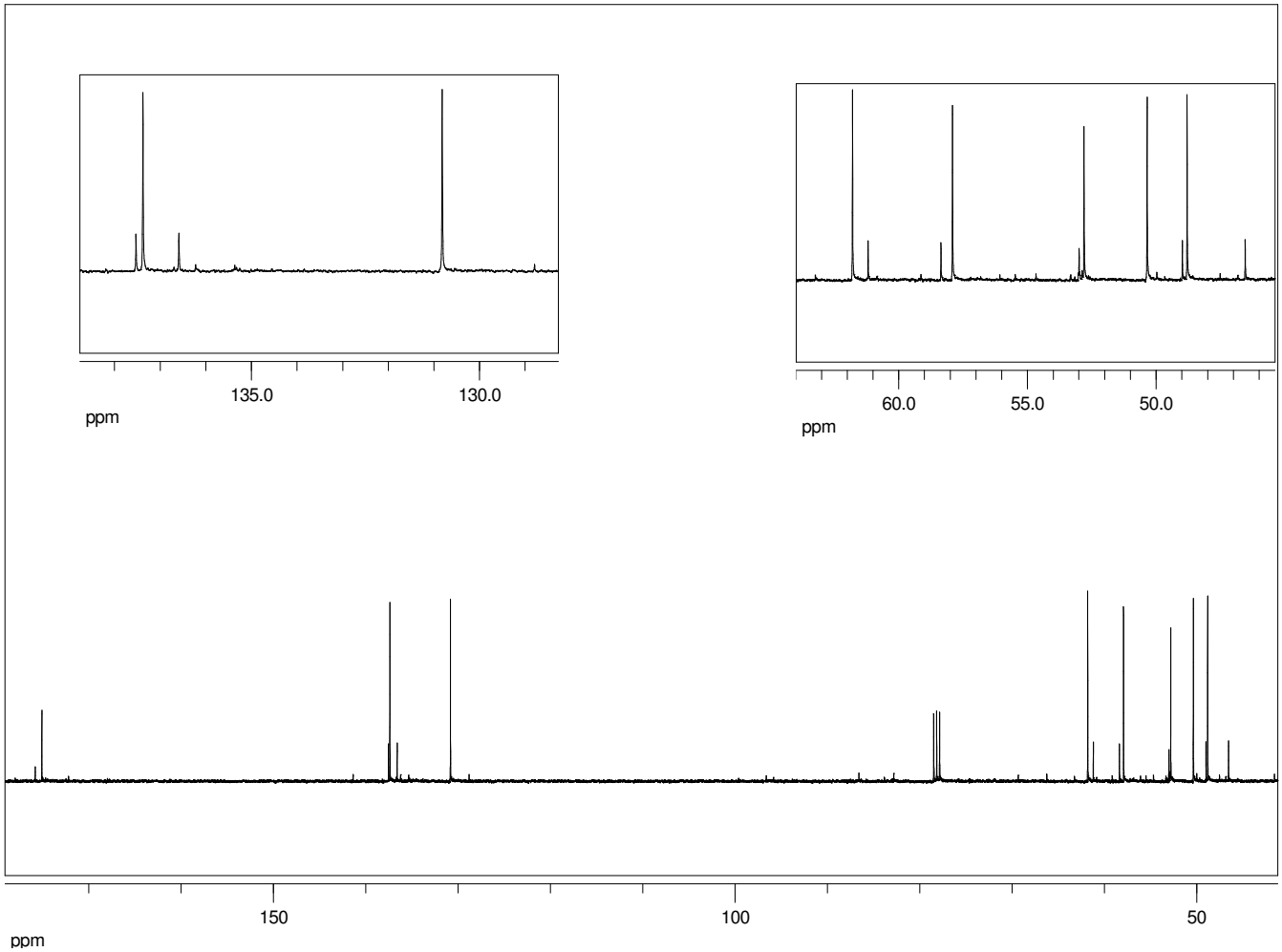

Figure 11. ^{13}C-NMR spectrum of the mixture of compounds **5** and **6**.

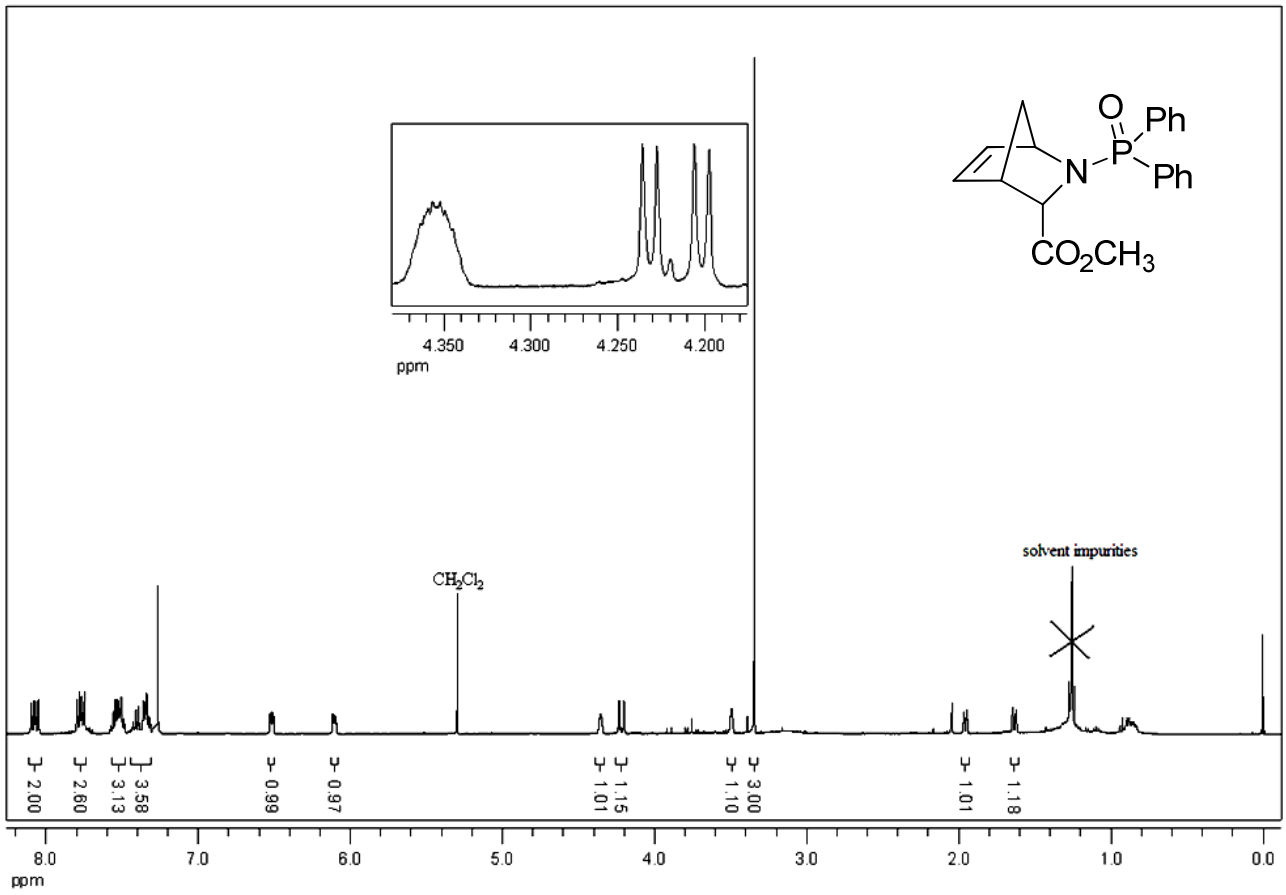

Figure 12. ^{1}H-NMR spectrum of compound **7**.

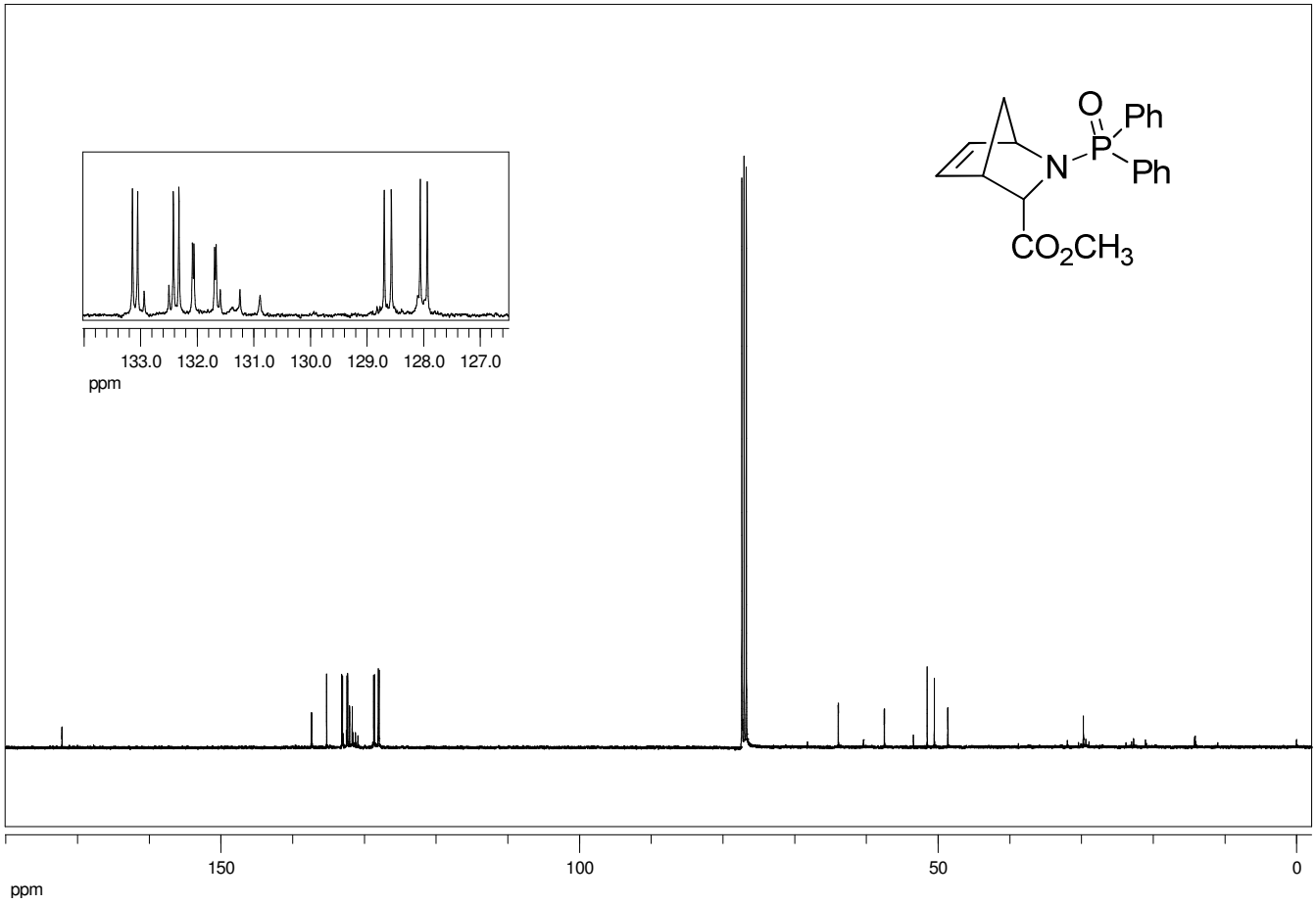

Figure 13. ^{13}C-NMR spectrum of compound **7**.

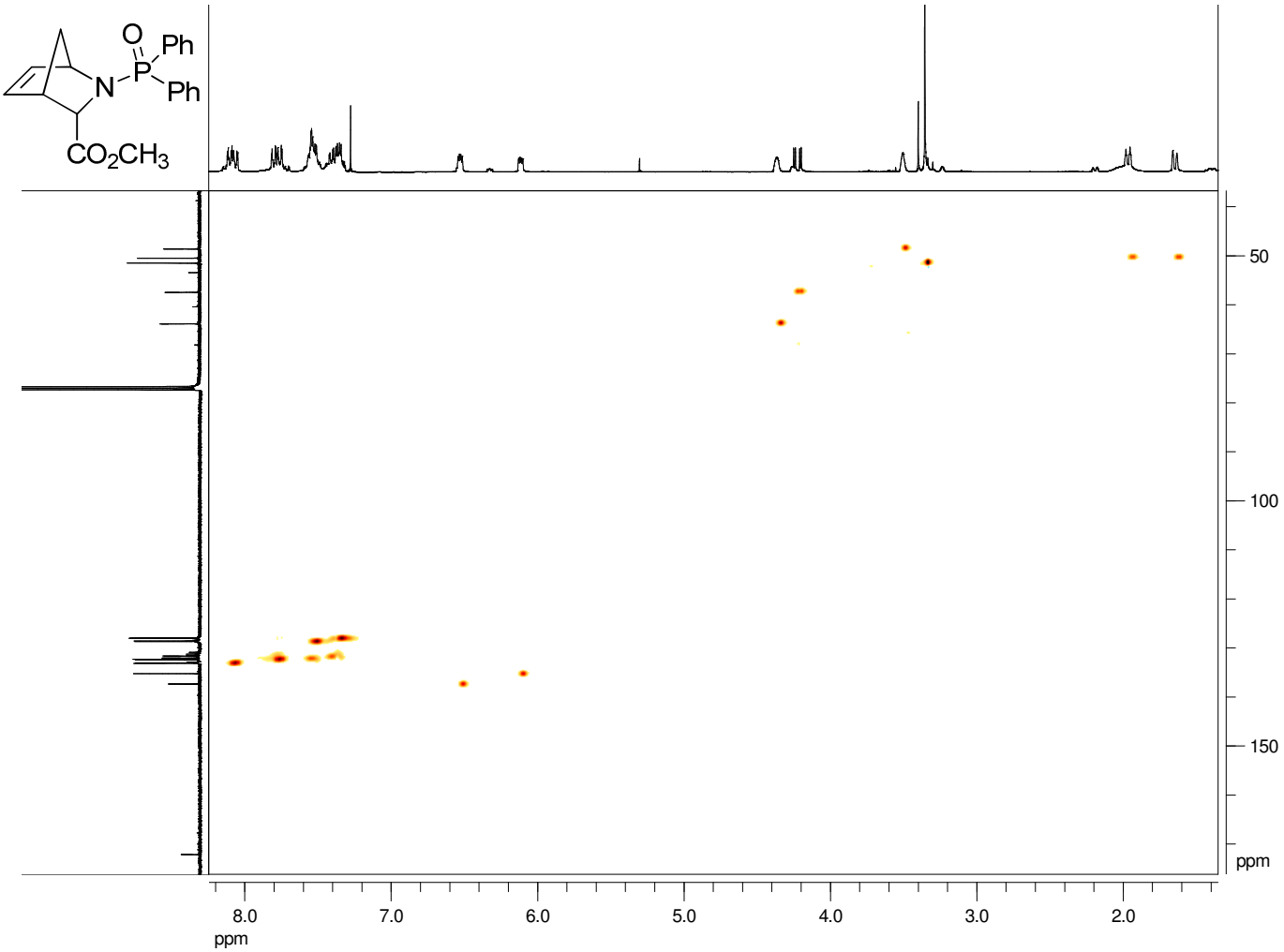

Figure 14. HSQC spectrum of compound **7**.

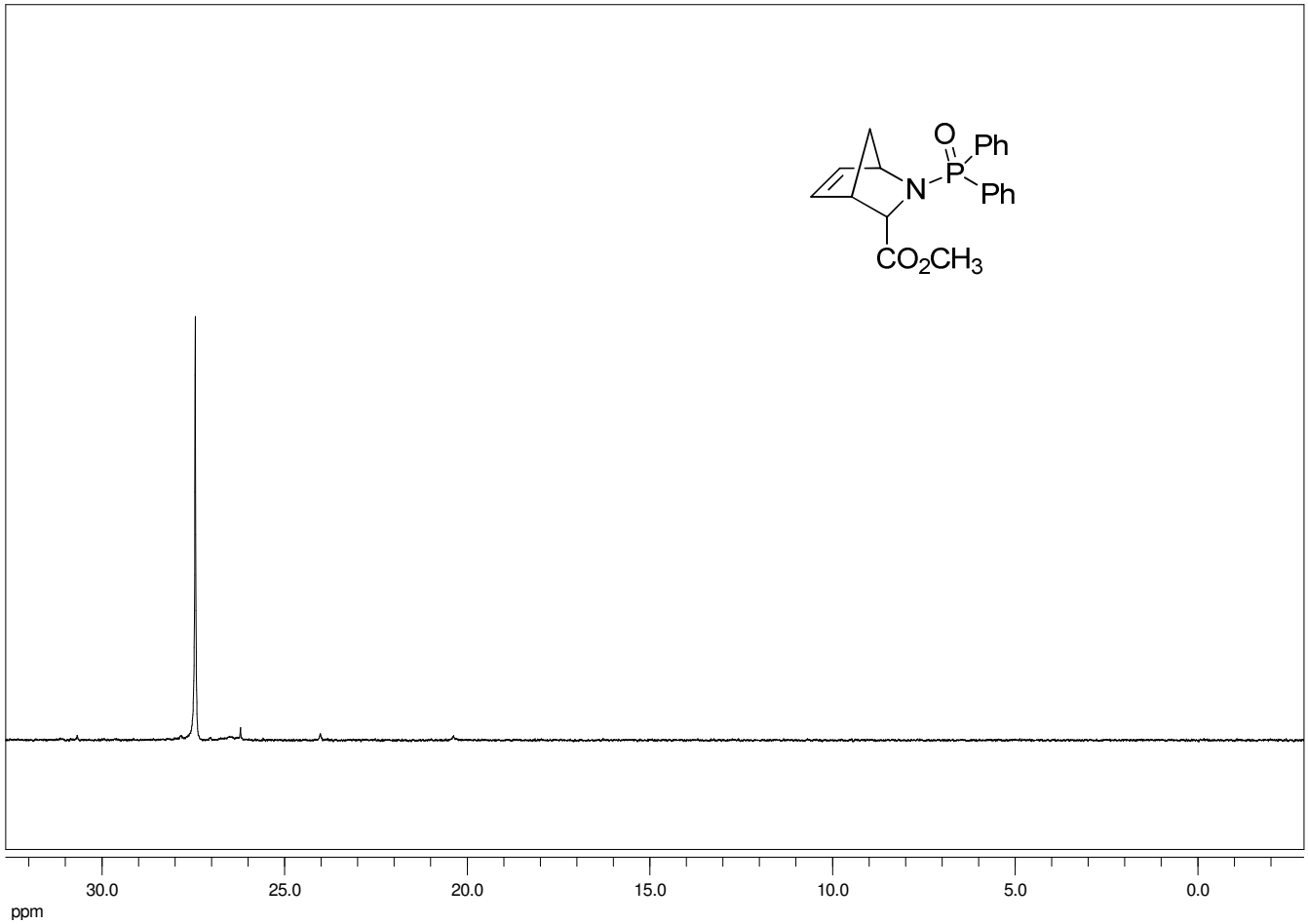

Figure 15. ^{31}P-NMR spectrum of compound **7**.

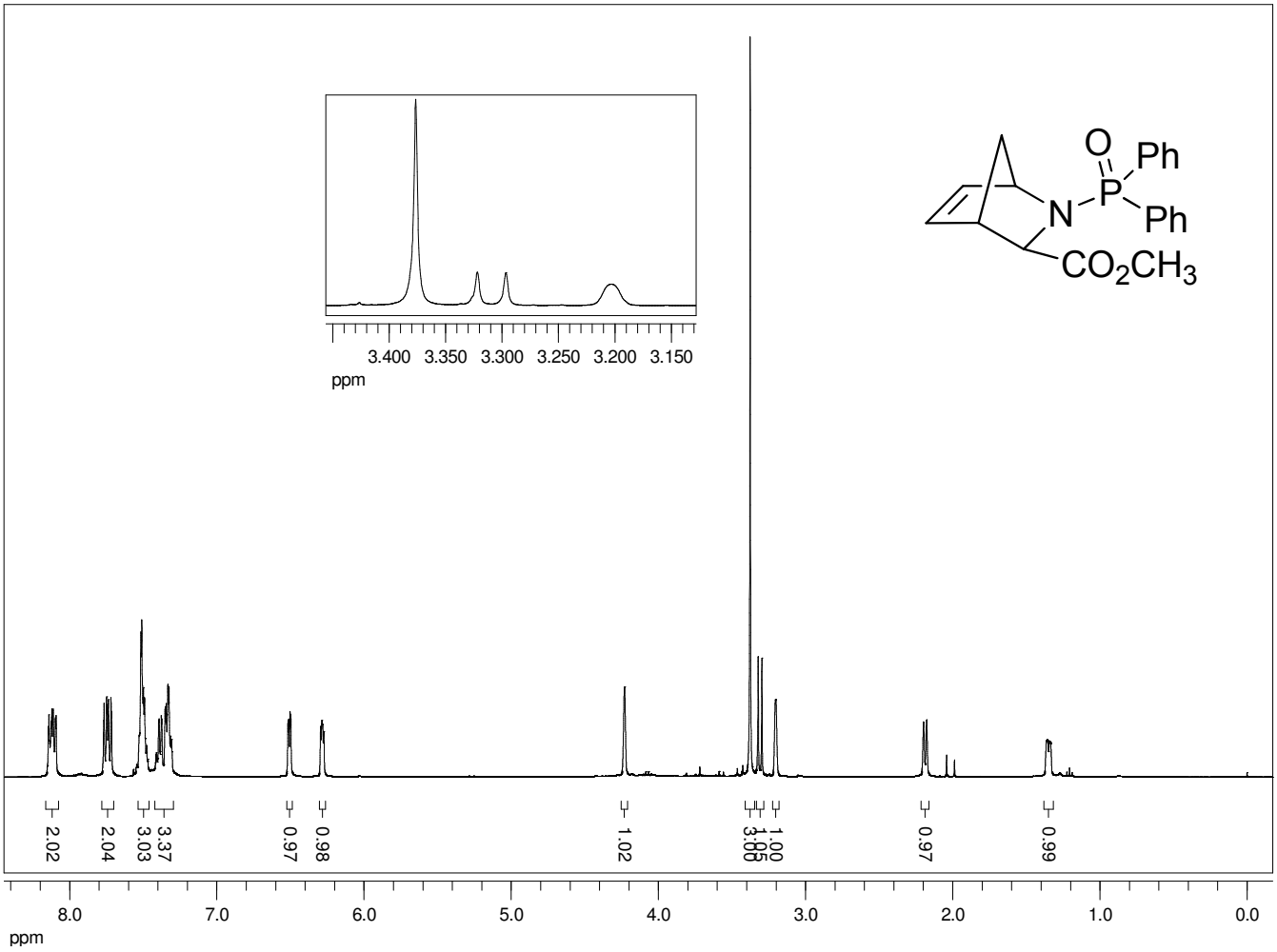

Figure 16. ^{1}H-NMR spectrum of compound **8**.

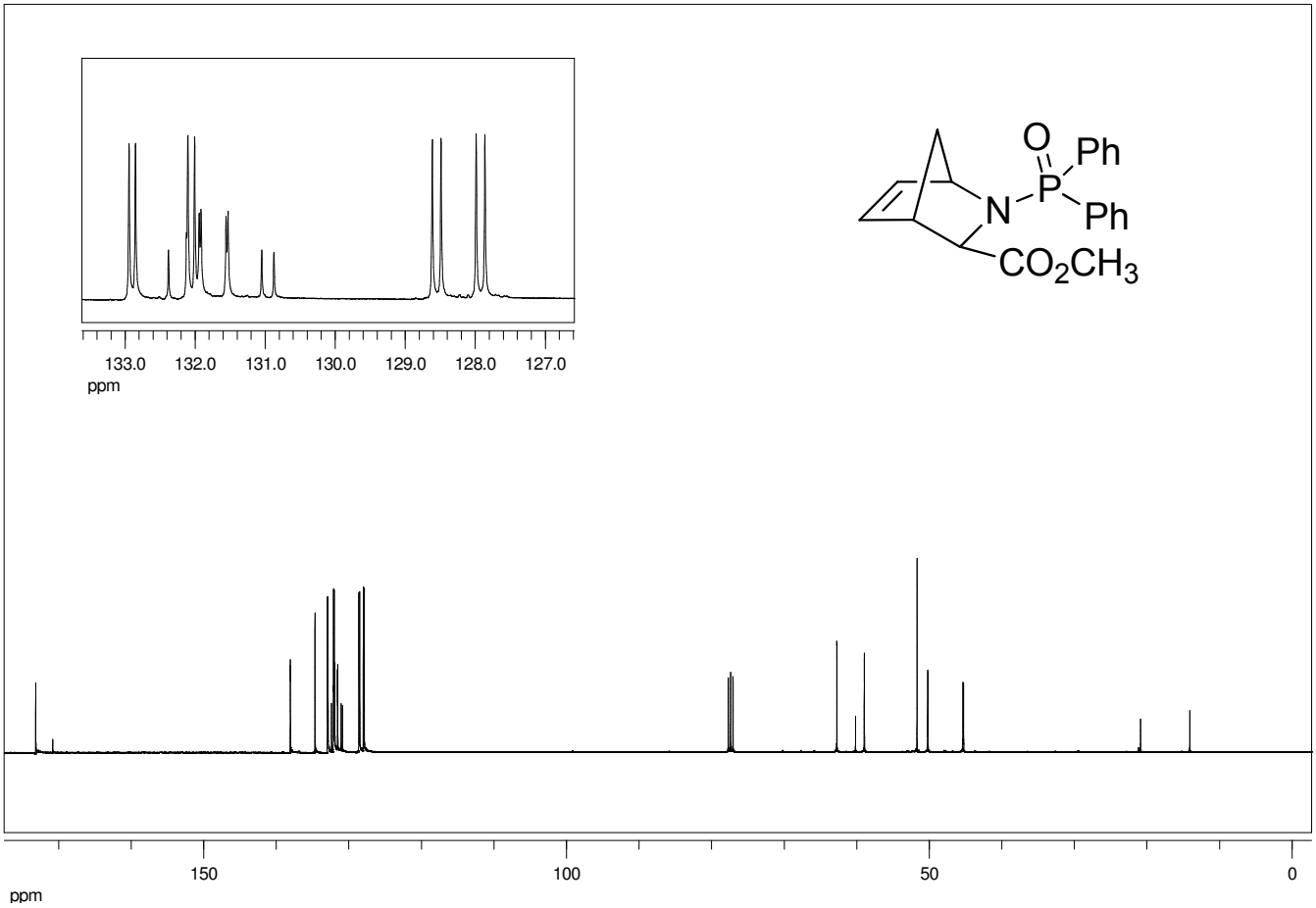

Figure 17. ^{13}C-NMR spectrum of compound **8**.

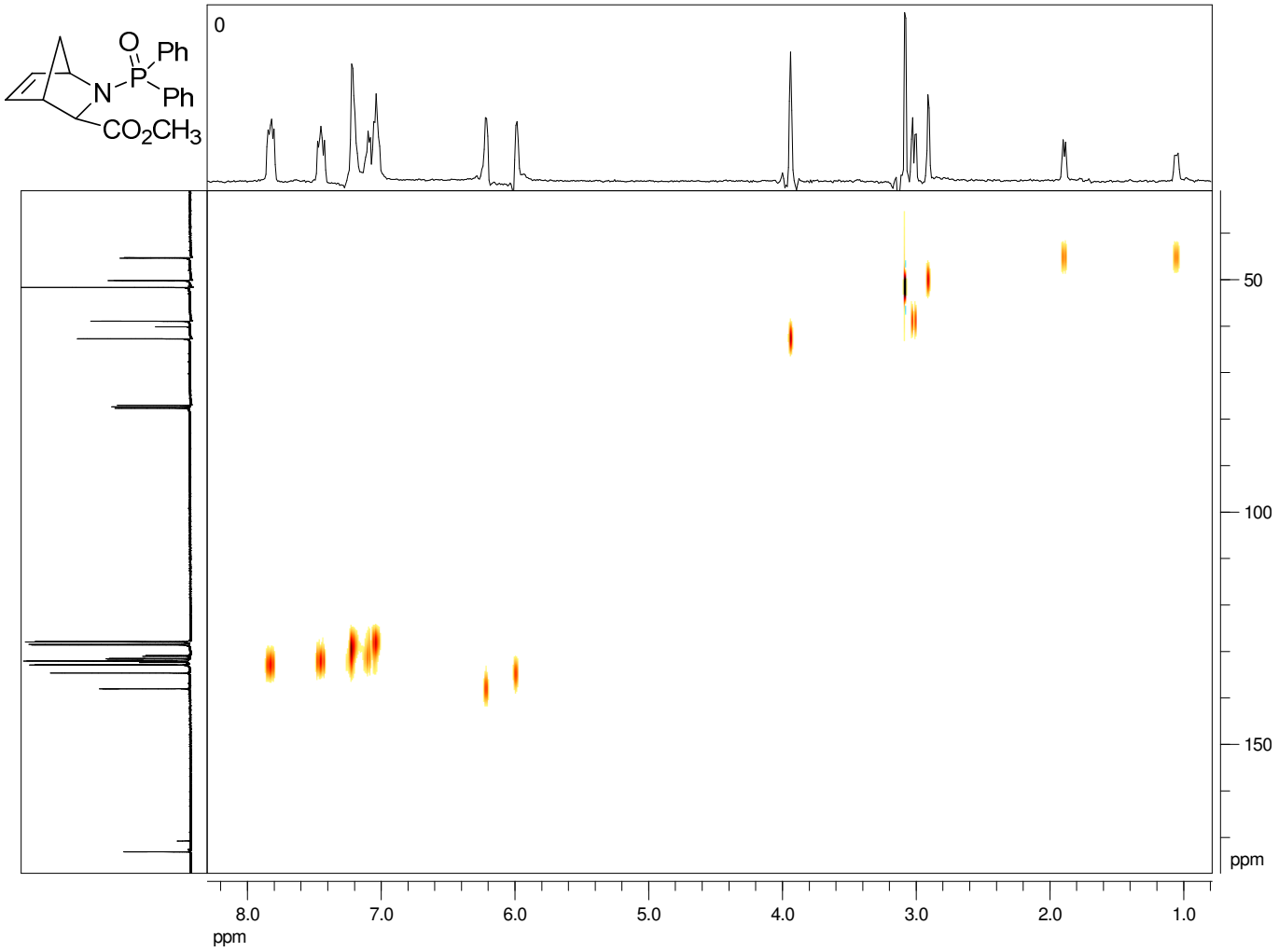

Figure 18. HSQC spectrum of compound **8**.

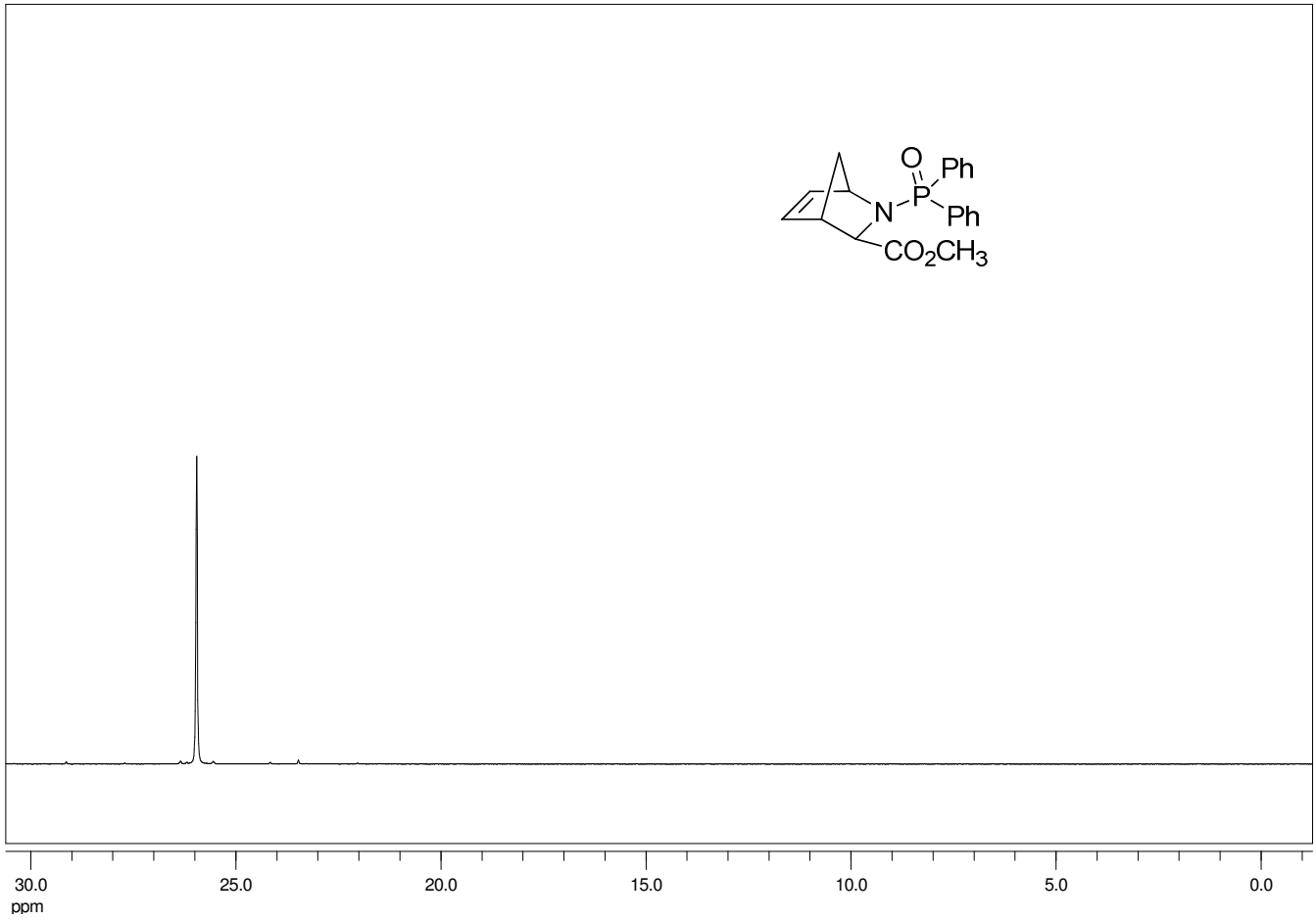

Figure 19. ^{31}P-NMR spectrum of compound **8**.

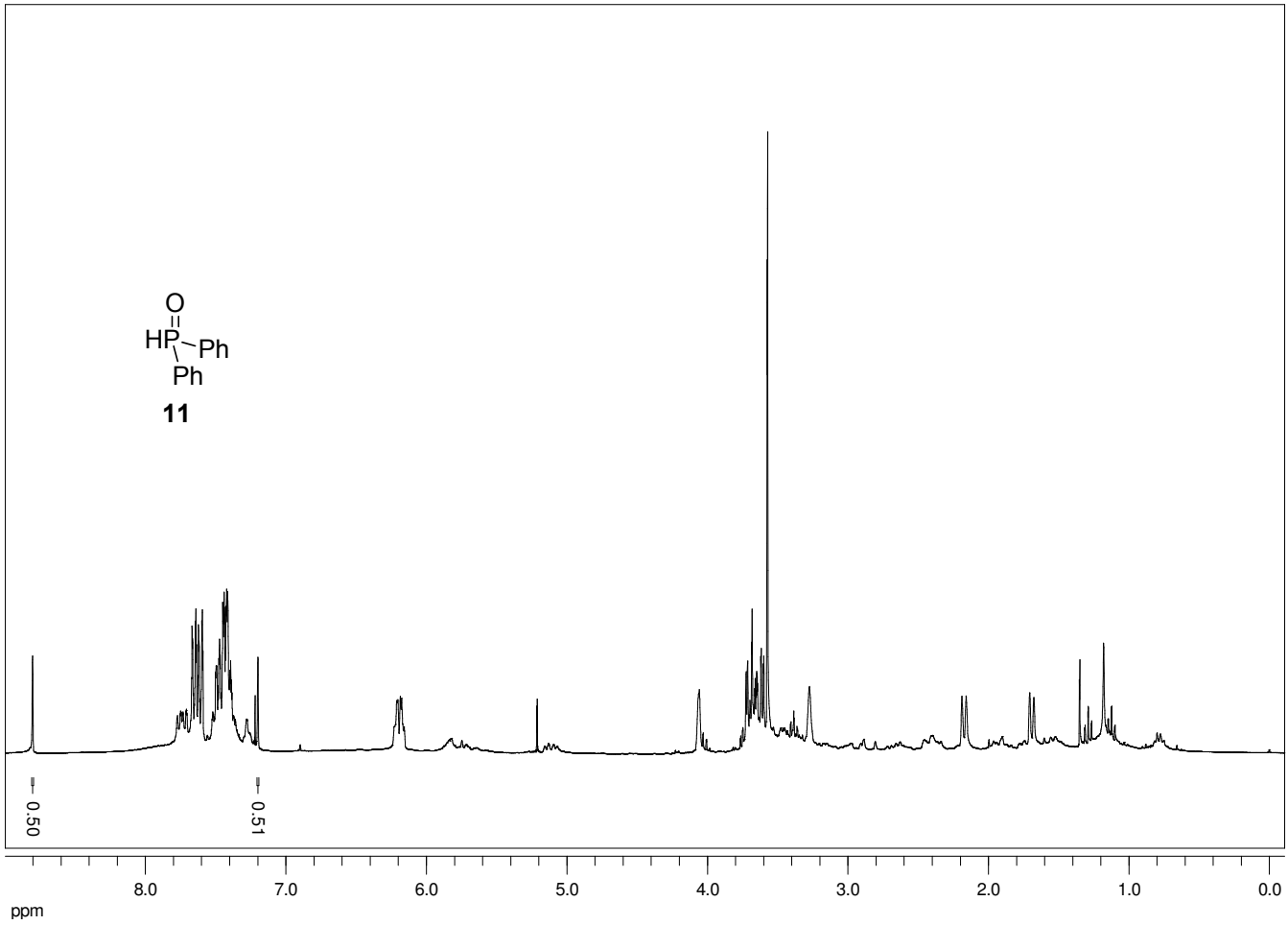

Figure 20. ^{1}H-NMR spectrum of compound **11** plus an unidentified bicycle. The integrated signal is a doublet corresponding to the hydrogen atom bonded to phosphorus (J = 481 Hz) in compound **11**.

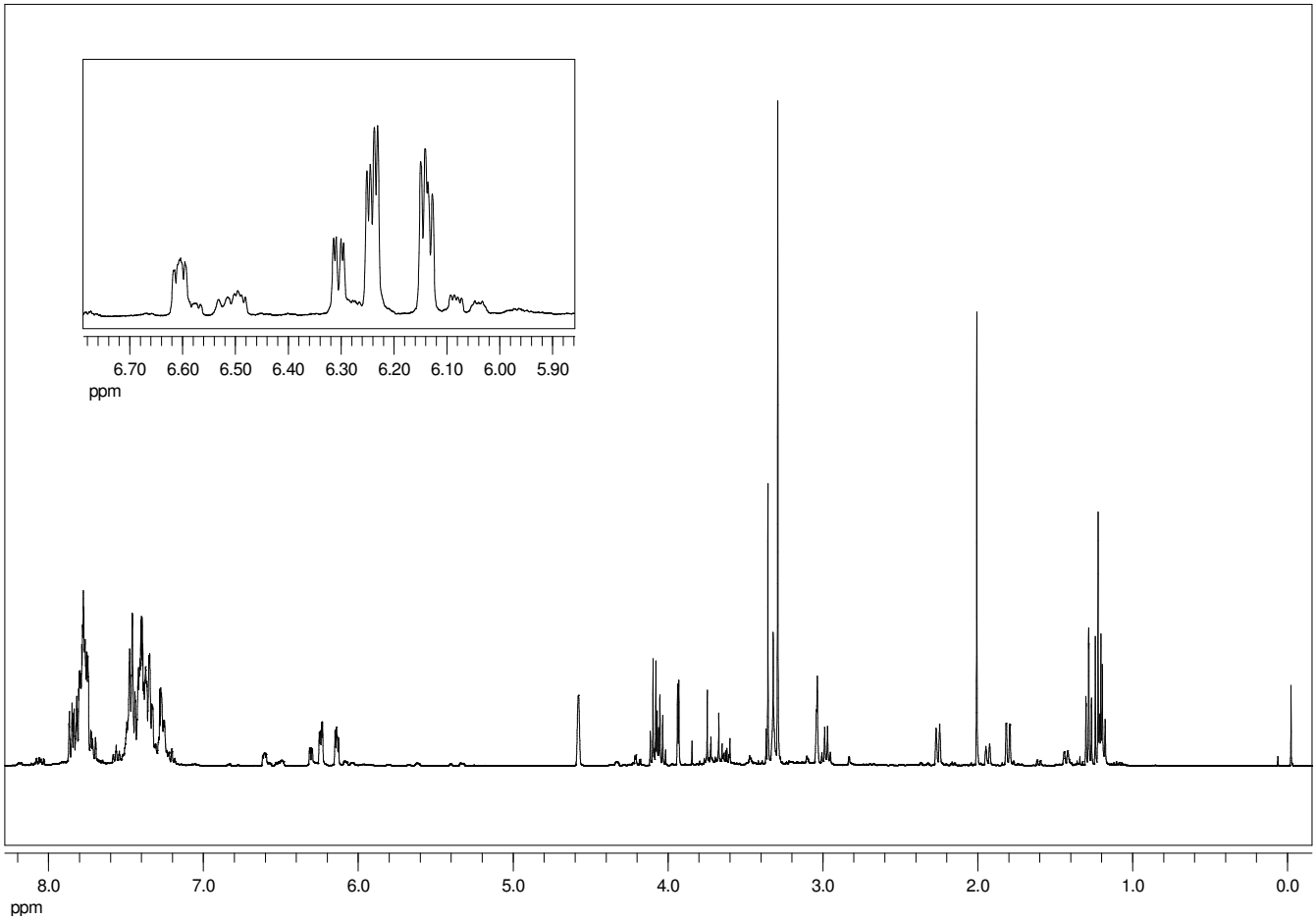

Figure 21. ^{1}H-NMR spectrum of the residue (**3/7** and **4/8**) obtained from reaction between **1/2** and $PClPh_2$.

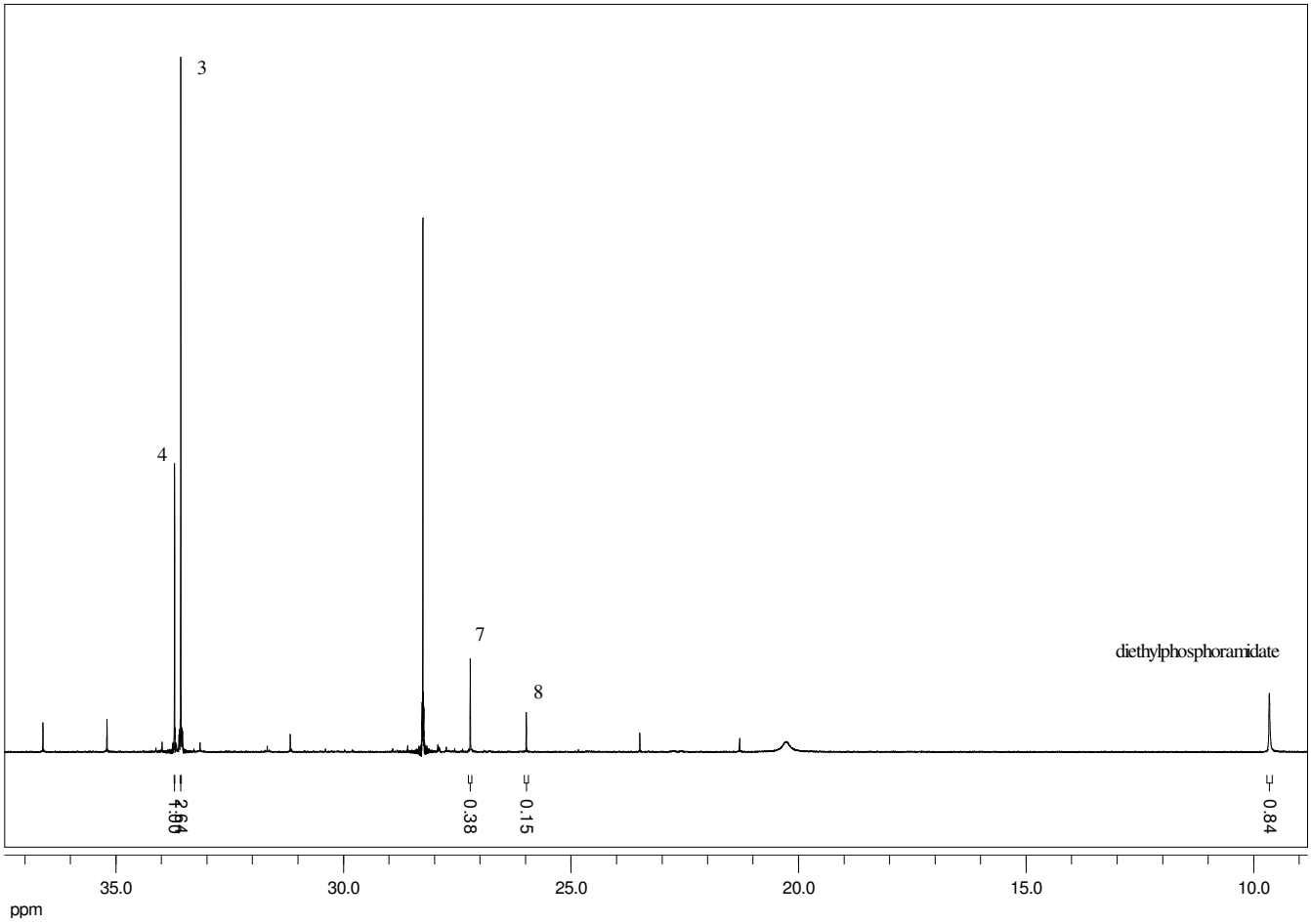

Figure 22. ^{31}P-NMR spectrum of the residue (**3/7** and **4/8**) obtained from reaction between **1/2** and $PClPh_2$.

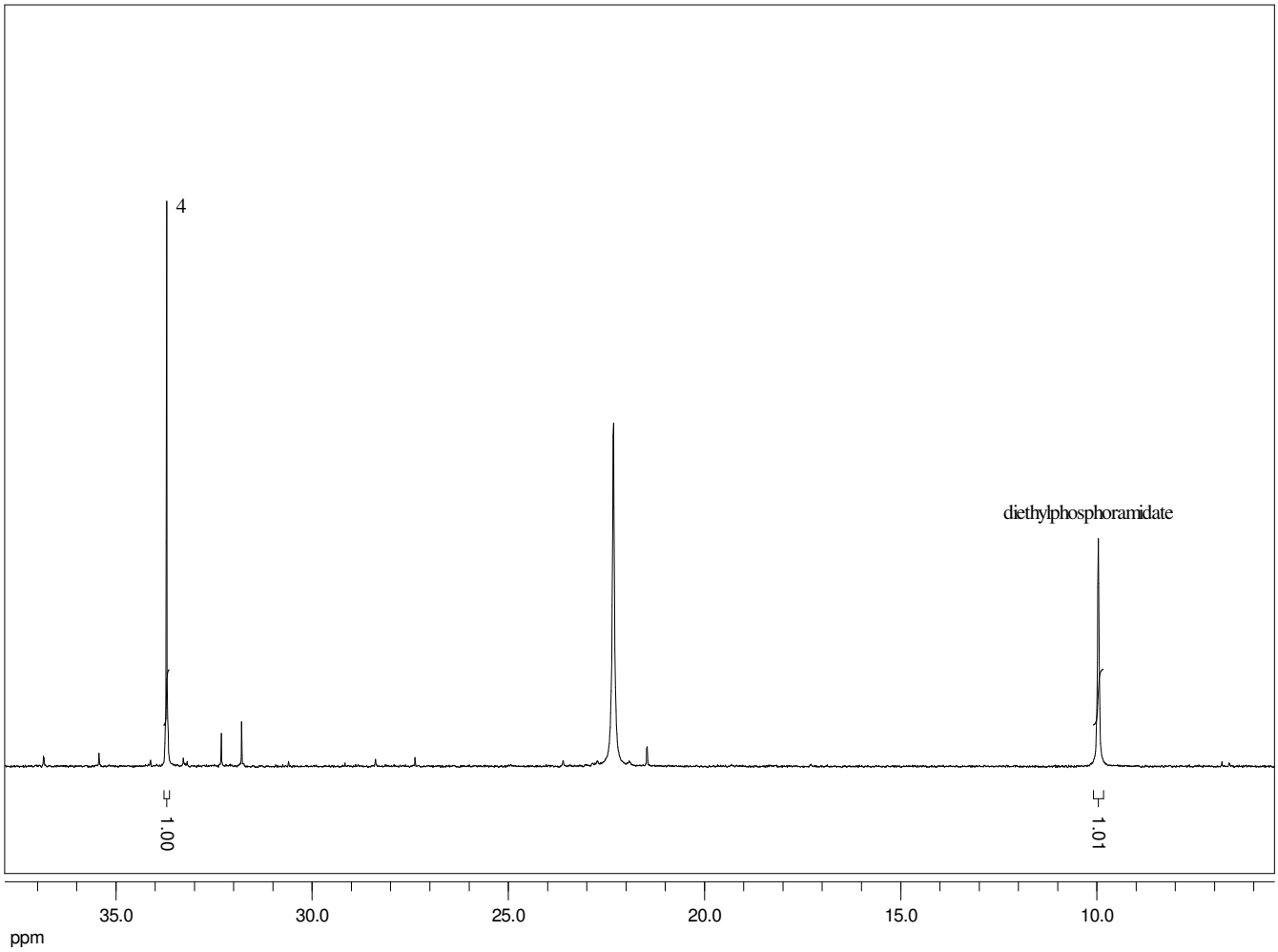

Figure 23. ^{31}P-NMR spectrum obtained from reaction between **2** and $PClPh_2$, originating only compound **4**.

HPLC-MS analyses

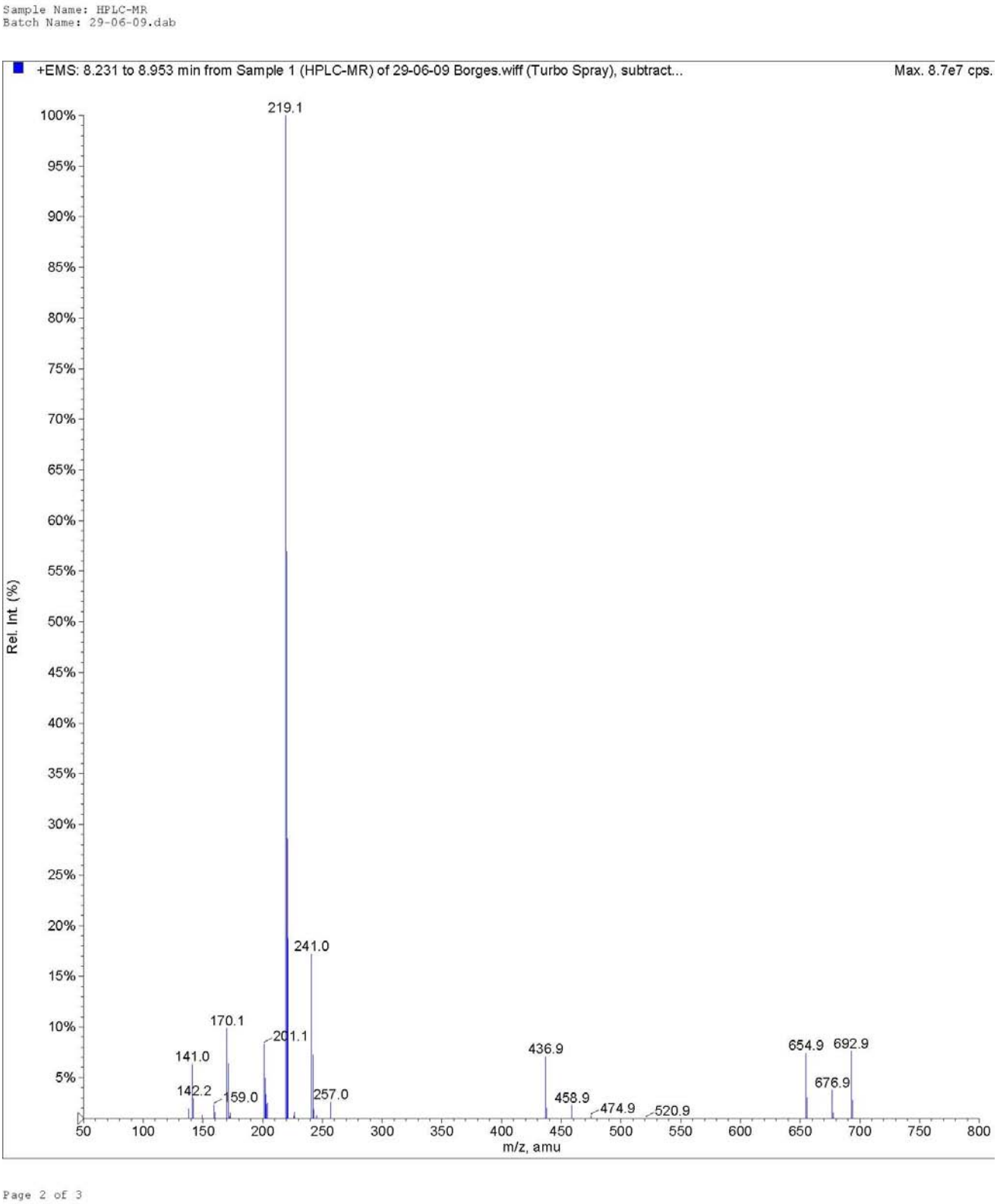

Figure 24. HPLC-MS spectrum showing a mass peak corresponding to diphenylphosphinic acid.

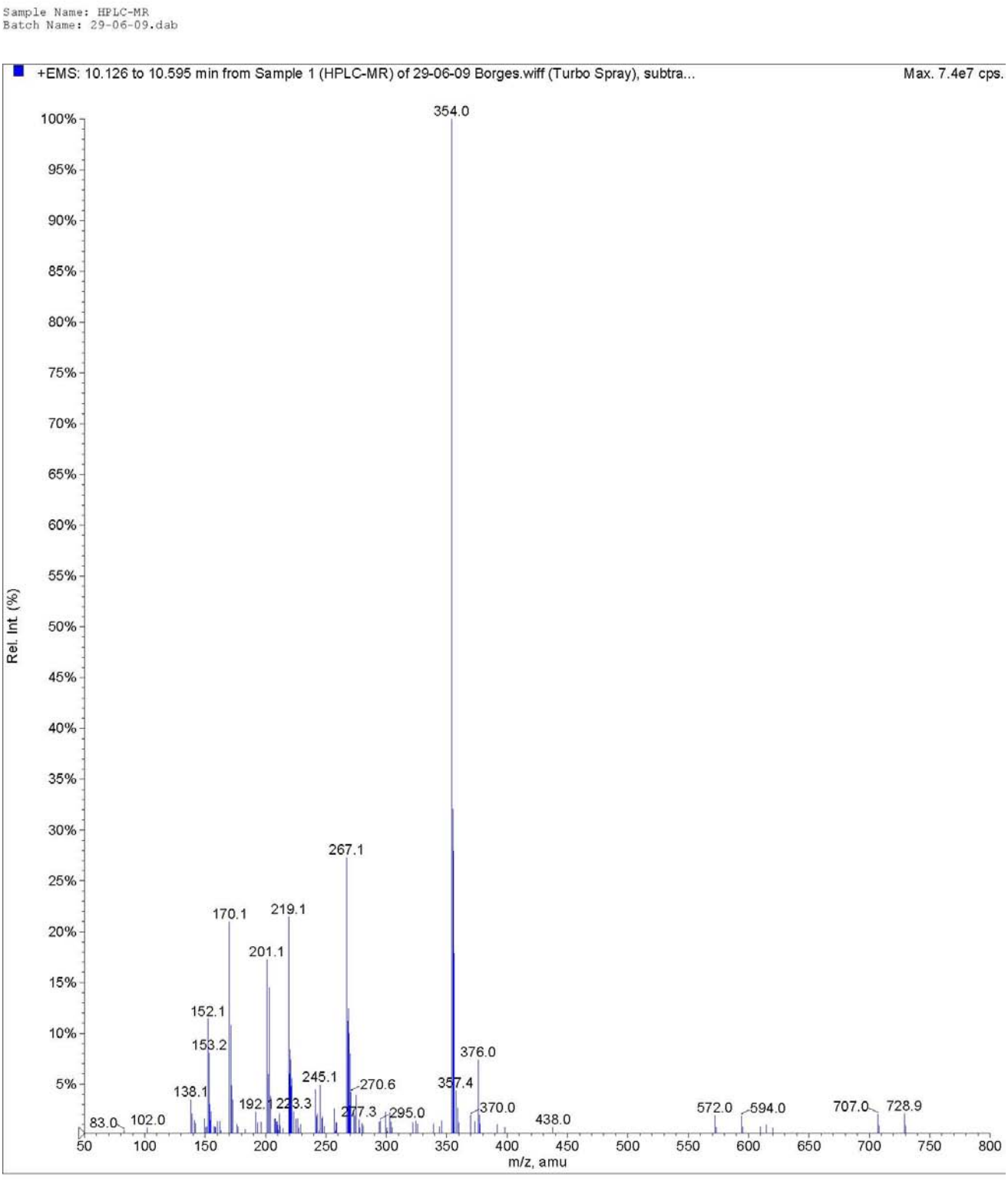

Figure 25. HPLC-MS spectrum showing a mass peak corresponding to adduct **7/8**.

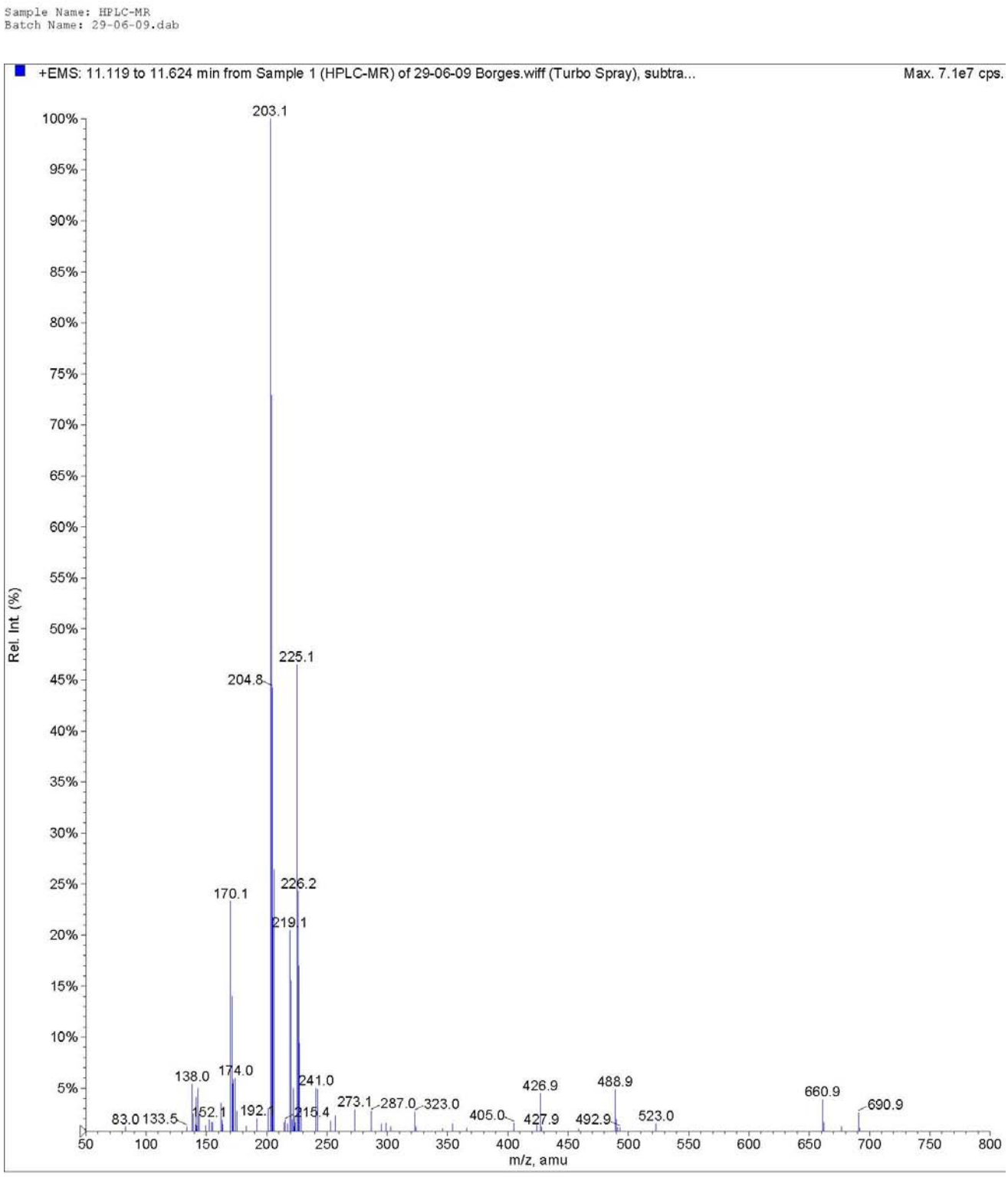

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Figure 26. HPLC-MS spectrum showing a mass peak corresponding to diphenylphosphinic oxide (**11**).

Sample Name: HPLC-MR
Batch Name: 29-06-09.dab

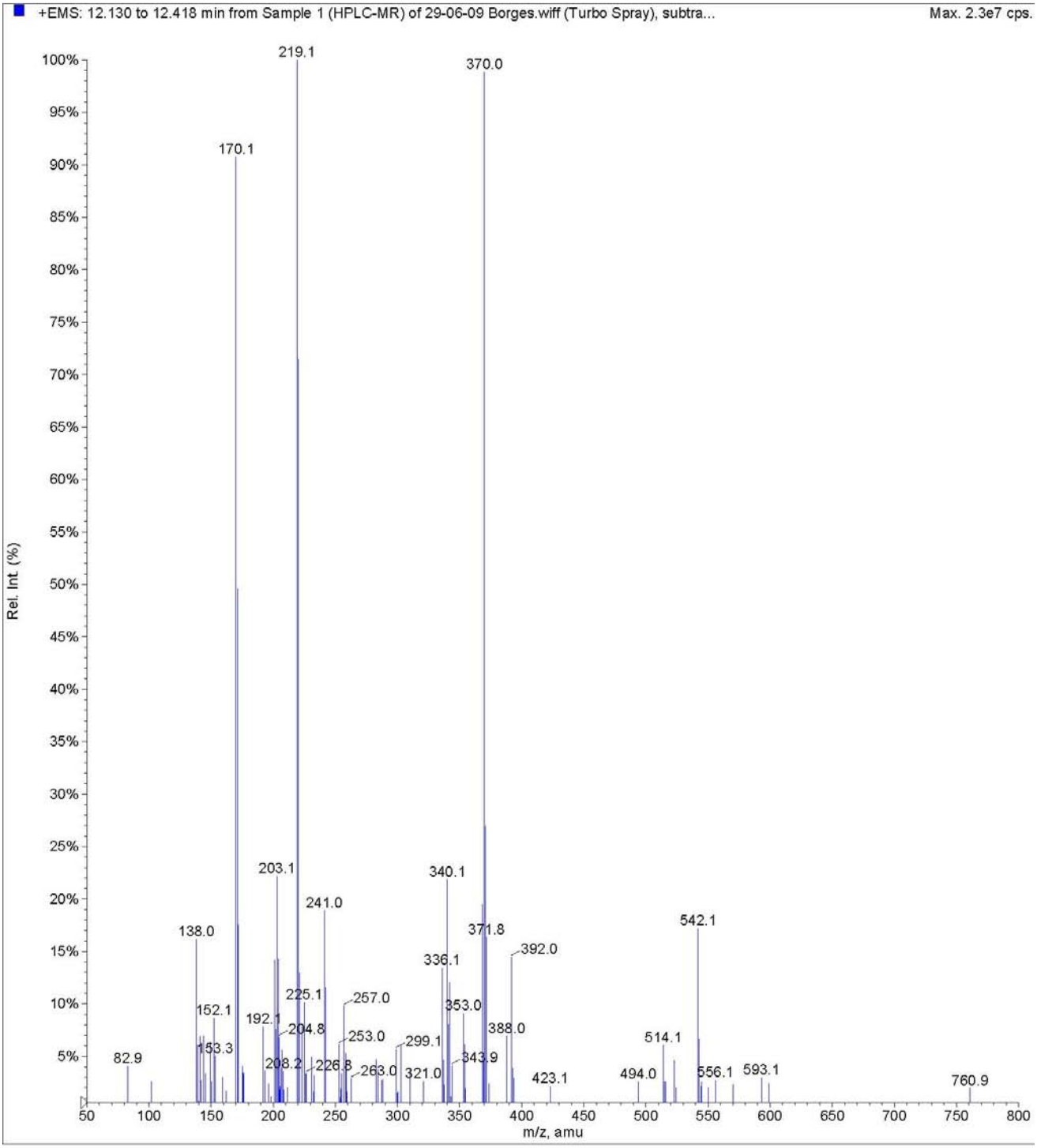

Figure 27. HPLC-MS spectrum showing mass peaks corresponding to starting material (**1/2**), diphenylphosphinic acid and adduct **3/4**, respectively.

Sample Name: HPLC-MR
Batch Name: 29-06-09.dab

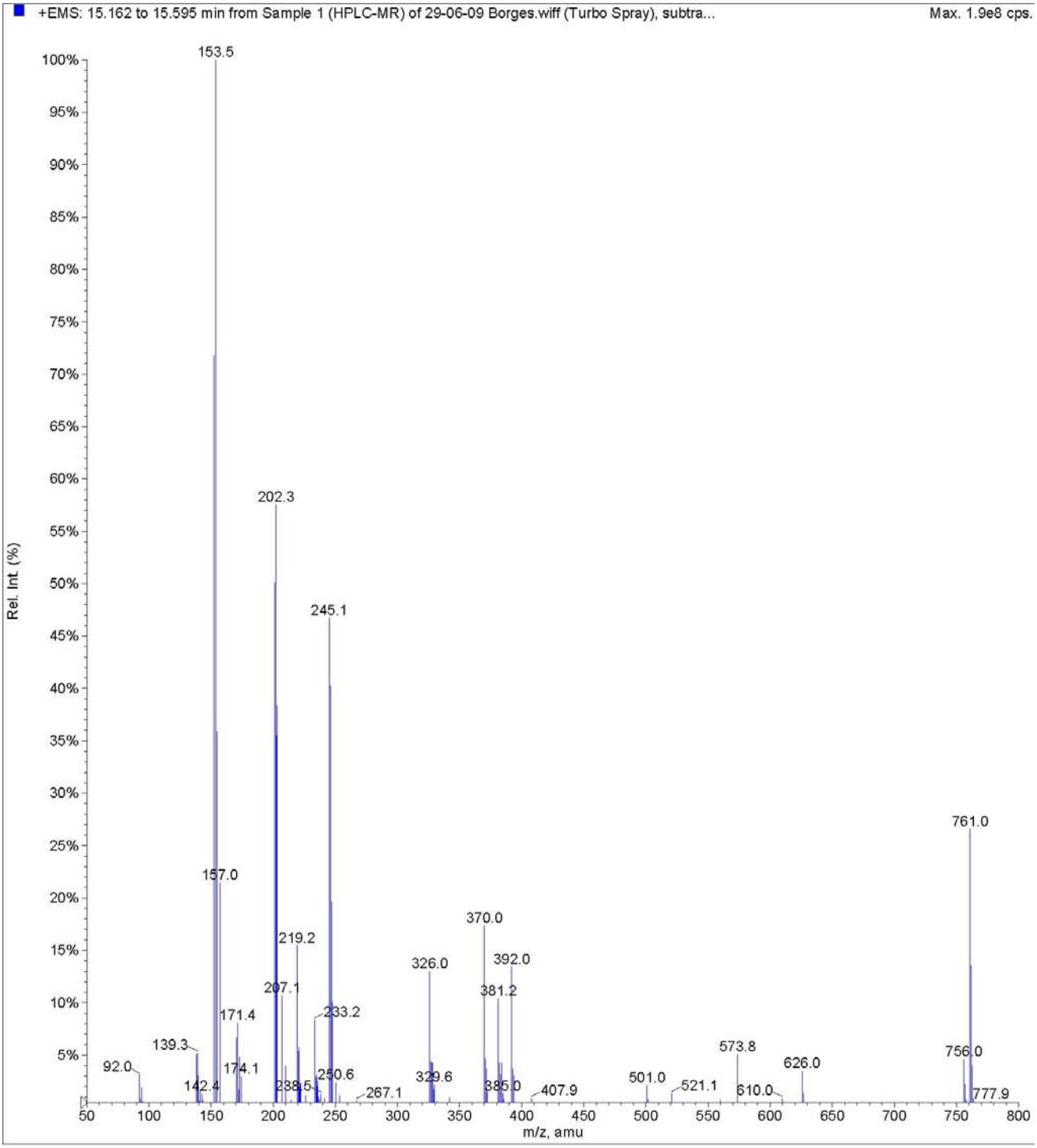

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Figure 28. HPLC-MS spectrum showing a mass peak corresponding to **5/6**.