Electronic Supplementary Material (ESI) for RSC Advances.

Direct synthesis of β-ketophosphonates and vinylphosphonates from alkenes or alkynes catalyzed by CuNPs/ZnO

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Supporting Information

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1. General experimental details

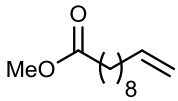
All moisture sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents were treated prior to use by standard methods.[1] All starting materials were of the best available grade (Aldrich, Fluka, Merck) and were used without further purification. Commercially available copper(II) chloride dihydrate was dehydrated upon heating in oven (150 ºC, 45 min) prior to use for the preparation of CuNPs. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm, 240–400 mesh). Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in ethanol.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (TMS) using the residual solvent resonance ($CDCl_3$: 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; brs = broad signal). Coupling constants (*J*) were reported in Hz.

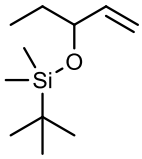
Mass spectra (EI) were obtained at 70 eV on a Agilent Technologies GC-7890B GC/MS instrument equipped with a MSD-5977A selective mass detector. Infrared (FT-IR) spectra were obtained on a Nicolet-Nexus spectrophotometer. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-14B instrument equipped with a flame-ionisation detector and a 30 m column (HP-5MS, 0.25mm, 0.25μm), using nitrogen as carrier gas. High resolution mass spectra were recorded on Thermo Fisher LTQ Orbitrap XL, (for EI) and a Finnigen MAT 95 (for ESI).

The freshly prepared catalyst was characterized by Transmission Electron Microscopy (TEM) in a JEOL JEM-2100F-UHR instrument, operated at an acceleration voltage of 200 kV. For their observation, the samples were mounted on holey-carbon coated 300 mesh gold- or copper grids. Near one hundred metal particles were measured to perform the particle size distribution. X-EDS analyses were carried out with an Oxford Inca Energy TEM100 attachment. Copper content in the supported catalyst was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), in a Spectro Arcos instrument. The XRD diagrams were collected in the θ–θ mode using a Bruker D8 Advance X-ray diffractometer: Cu Kα1 irradiation, λ = 1.5406 Å; room temperature (25 ºC); 2θ = 4–80.

2. Synthesis of starting alkenes 3f and 3g



Methyl undec-10-enoate (3f)[1] was synthesized starting from a 10-undecenoic acid solution (921.4 mg, 5.0 mmol) in 2% H_2SO_4/CH_3OH (10 mL) under reflux for 4 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The obtained residue was purified by column chromatography (100% hexane) affording pure methyl undec-10-enoate (911.5 mg, 92%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.84 (m, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.03 (q, *J* = 6.7 Hz, 2H), 1.67 – 1.56 (m, 2H), 1.39 – 1.25 (m, 10H).



***tert*-Butyldimethyl(pent-1-en-3-yloxy)silane (3g)[2]** was synthesized using a procedure described by Corey et al. To a stirred solution of pent-1-en-3-ol (520 µL, 5.0 mmol) and imidazole (850 mg, 12.5 mmol) in dry DMF (10 mL) was added slowly dropwise, at 0 °C, *tert*-butyldimethylsilyl chloride (825 mg, 5.5 mmol) in DMF (5 mL). The reaction was stirred at 0 °C for 1 hour before being allowed to warm to room temperature and stirred for 16 hours. The resulting solution was diluted with EtOAc (50 mL) and washed with saturated aq. $Na_2S_2O_3$ (2 x15 mL), brine (15 mL) and water (2 x15 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. Purification of the residue by column chromatography (100% hexane) gave the product (880 mg, 88%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (ddd, *J* = 17.0, 10.4, 6.0 Hz, 1H), 5.00–5.17 (m, 2H), 4.05–3.99 (m, 1H), 1.55–1.45 (m, 2H), 0.90 (s, 9H), 0.87 (t, overlap, 3H), 0.05 (s, 3H), 0.03 (s, 3H).

3. Synthesis of β-ketophosphonates and vinylphosphonates. General procedure. The alkyne or alkene (1.0 mmol) and diethylphosphite (170 µL, 1.3 mmol) were added to a suspension of the CuNPs/ZnO catalyst (40 mg, 1.7 mol% Cu) in MeCN (2 mL) under air atmosphere. The reaction mixture was warmed to 70 ºC and monitored by TLC and/or GLC

until total conversion of the starting material. Water (20 mL) was added to the reaction mixture followed by extraction with EtOAc (3 × 10 mL). The collected organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo to give the corresponding β-ketophosphonate or vinylphosphonate, which was purified by flash column chromatography (hexane-EtOAc).

4. Preparation and characterization of the catalyst

Anhydrous copper(II) chloride (135 mg, 1 mmol) was added to a suspension of lithium (14 mg, 2 mmol) and 4,4'-di-tert-butylbiphenyl (DTBB, 27 mg, 0.1 mmol) in THF (2 mL) at room temperature under a nitrogen atmosphere. The reaction mixture, which was initially dark blue, rapidly changed to black, indicating that the suspension of copper nanoparticles was formed. This suspension was diluted with THF (18 mL) followed by the addition of the zinc oxide (800 mg). The resulting mixture was stirred for 1 h at room temperature, filtered, and the solid successively washed with THF (20 mL) and diethyl ether (20 mL), and then dried under vacuum.

The catalyst was characterized by means of transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, powder X-ray diffraction (XRD), and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Analysis by TEM showed the presence of well dispersed spherical nanoparticles on the support, with an average particle size of 6.0 ± 0.5 nm (Figures 1 and 2).

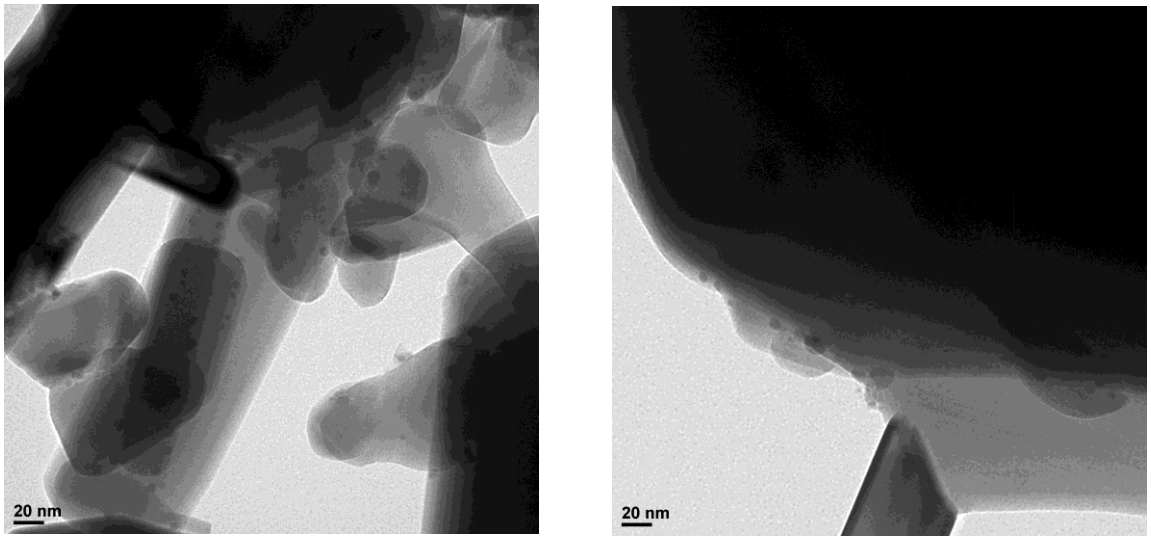


Figure 1. Representative TEM micrographs of the CuNPs/ZnO catalyst.

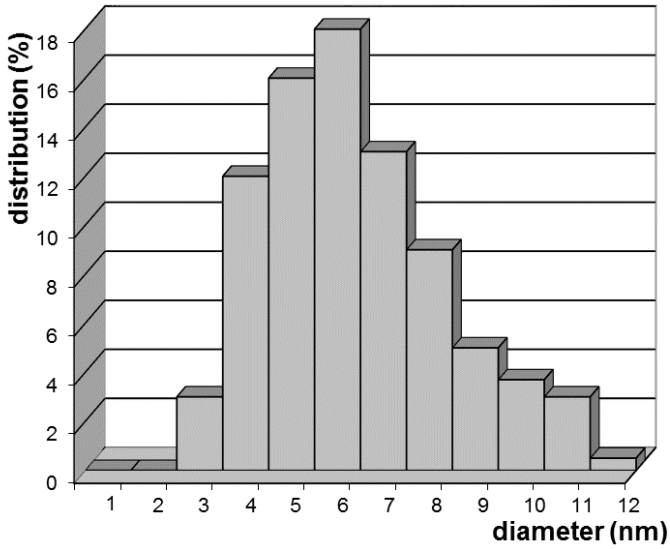


Figure 2. Size distribution graphic of CuNPs. The sizes were determined for 100 nanoparticles selected at random.

Energy dispersive X-ray analysis on various regions confirmed the presence of copper, with energy bands of 8.04, 8.90 (K lines) and 0.92 keV (L line).

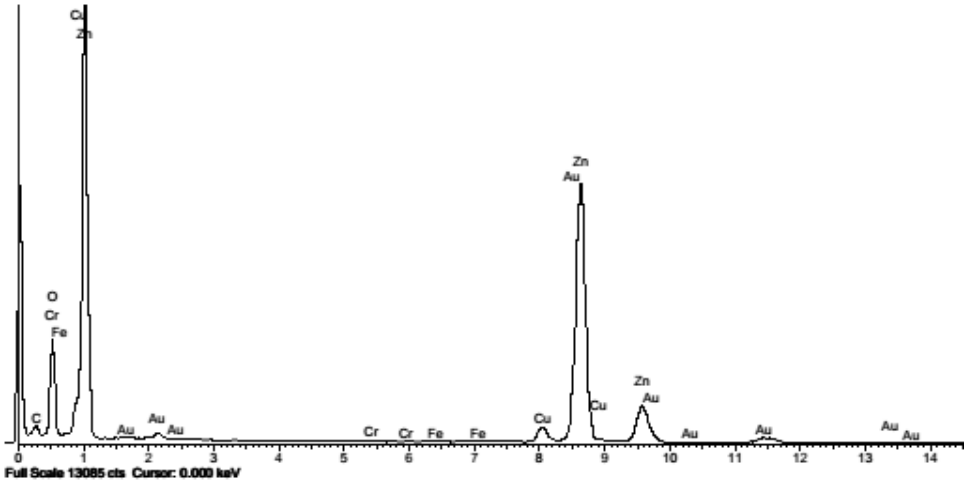


Figure 3. EDX spectra of the CuNPs/ZnO catalyst.

The XRD diffractogram showed the support (ZnO) diffraction pattern, but no diffraction peaks owing to copper species were detected, this could be attributed to the amorphous character of the CuNPs deposited on the support and/or to the existence of crystal domains below 10 nm in size.

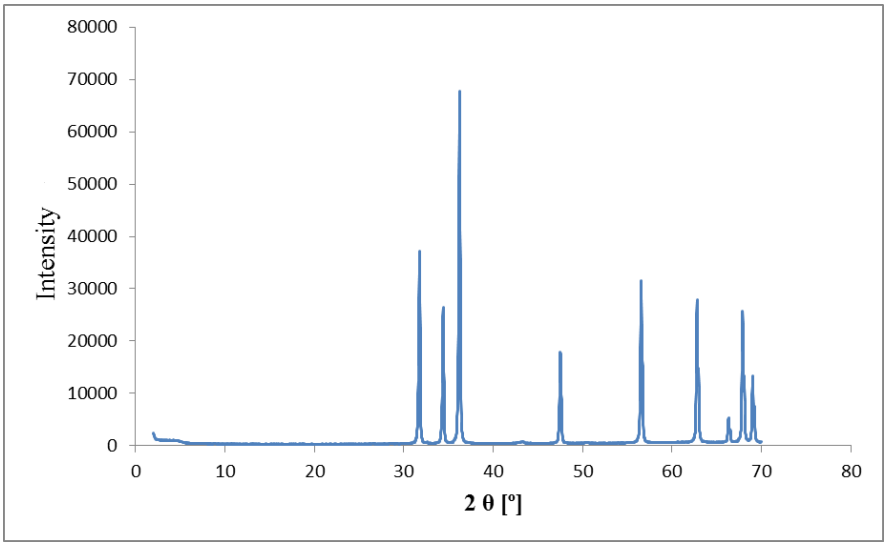
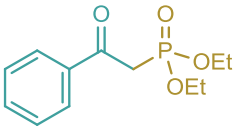


Figure 4. XRD difractogram of the CuNPs/ZnO catalyst.

The ICP-AES analysis of the catalyst gave 2.81 mg of copper per 100 mg of catalyst. *Experimental procedure*: the digestion of the sample was done by using a microwave digestor (MARS-5, CEM Corporation, USA), utilizing nitric acid pro-analysis (Merck), according to standard SRM 1577a. Nitric acid was ultrapurified by distillation prior to use (Berghof Distillacid BSB-939-IR, GmbH, Germany). Quantification of the metal content of the samples was carried out by external calibration using certified standards (Chem-Lab, Zedelgem B-8210, Belgium). The sample was analyzed using Induced Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), with a Shimadzu ICP 9000 of High Resolution according to standard EPA 200.7.

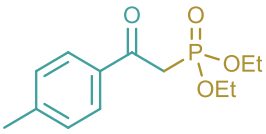
5. Compound characterization data

All known compounds were characterized by comparison of their physical and spectroscopic data with those described in the literature. For new compounds, copies of ^{1}H-, ^{13}C- and ^{31}P-NMR graphical spectra are also provided.

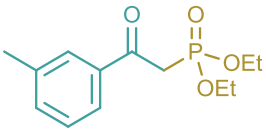


Diethyl 2-oxo-2-phenylethylphosphonate (2a, 4a)[3]: Yellow oil. 220.0 mg, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (d, *J* =

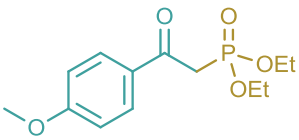
7.6 Hz, 2H), 4.15 – 4.05 (m, 4H), 3.60 (d, *J* = 22.7 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9 (d, *J* = 6.6 Hz), 136.6 (d, *J* = 2.1 Hz), 133.7, 129.1, 128.6, 62.8 (d, *J* = 6.5 Hz), 38.5 (d, *J* = 130.2 Hz), 16.3 (d, *J* = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.0.



Diethyl (2-oxo-2-(p-tolyl)ethyl)phosphonate (2b)[3]: Yellow oil. 261.9 mg, 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.18 – 4.03 (m, 4H), 3.58 (d, *J* = 22.7 Hz, 2H), 2.38 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4 (d, *J* = 6.6 Hz), 144.5, 134.0, 129.2, 129.1, 62.5 (d, *J* = 6.5 Hz), 38.3 (d, *J* = 130.1 Hz), 21.6, 16.1 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.1.

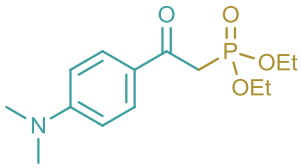


Diethyl (2-oxo-2-(*m*-tolyl)ethyl)phosphonate (2c)[3]: Yellow oil. 253.8 mg, 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.40 – 7.32 (m, 2H), 4.17 – 4.08 (m, 4H), 3.61 (d, *J* = 22.7 Hz, 2H), 2.40 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1 (d, *J* = 6.7 Hz), 138.4, 136.6 (d, *J* = 1.9 Hz), 134.4, 129.4, 128.4, 126.3, 62.6 (d, *J* = 6.5 Hz), 38.4 (d, *J* = 130.2 Hz), 21.3, 16.2 (d, *J* = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.0.

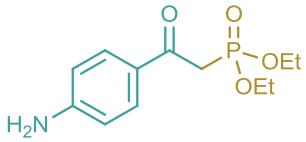


Diethyl (2-(4-methoxyphenyl)-2-oxoethyl)phosphonate (2d)[3]: Orange oil. 240.2 mg, 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.16 – 3.98 (m, 4H), 3.79 (s, 3H), 3.52 (d, *J* = 22.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3 (d, *J* = 6.5 Hz), 164.1, 131.6, 129.7 (d, *J* = 2.0 Hz),

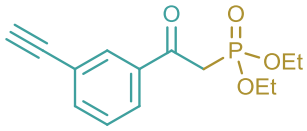
113.9, 62.8 (d, J = 6.5 Hz), 55.6, 38.1 (d, J = 130.1 Hz), 16.3 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.6.



Diethyl (2-(4-(dimethylamino)phenyl)-2-oxoethyl)phosphonate (2e)[4]: Orange oil. 179.4 mg, 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 2H), 6.64 (t, J = 9.0 Hz, 2H), 4.17 – 4.07 (m, 4H), 3.53 (d, J = 22.6 Hz, 2H), 3.06 (s, 6H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3 (d, J = 6.4 Hz), 153.7, 131.4, 124.5 (d, J = 2.2 Hz), 110.5, 62.5 (d, J = 6.5 Hz), 39.9, 37.8 (d, J = 129.8 Hz), 16.3 (d, J = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.4.

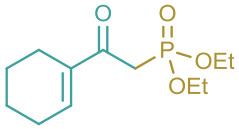


Diethyl (2-(4-aminophenyl)-2-oxoethyl)phosphonate (2f): Orange solid. 216.8 mg, 80% yield. IR (KBr): 3416, 3342, 2986, 1642, 1589, 1229, 1045, 1020, 813 cm^{-1}; mp 112.3 – 114.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.7 Hz, 2H), 4.35 (brs, 2H), 4.19 – 4.01 (m, 4H), 3.50 (d, J = 22.6 Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5 (d, J = 6.2 Hz), 152.0, 131.7, 126.8 (d, J = 2.0 Hz), 113.6, 62.6 (d, J = 6.5 Hz), 37.8 (d, J = 130.0 Hz), 16.3 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.1. MS: m/z = 271 (M^+, 18%), 207 (26), 135 (10), 120 (100), 92 (10). HRMS (EI) calcd for $C_{12}H_{18}NO_4P$ 271.0973, found 271.0981

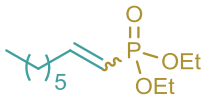


Diethyl (2-(3-ethynylphenyl)-2-oxoethyl)phosphonate (2g): Yellow oil. 218.4 mg, 78% yield. IR (neat): 3284, 2987, 2933, 2908, 2103, 1679, 1594, 1575, 1252, 1059, 1021, 799

cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 4.17 – 4.07 (m, 4H), 3.60 (d, *J* = 22.8 Hz, 2H), 3.13 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1 (d, *J* = 6.8 Hz), 136.7, 136.6 (d, *J* = 1.7 Hz), 132.7, 129.1, 128.7, 122.8, 82.3, 78.4, 62.7 (d, *J* = 6.5 Hz), 38.5 (d, *J* = 129.7 Hz), 16.2 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.4. MS: *m/z* = 280 (M^+, 6%), 144 (18), 130 (10), 129 (100), 123 (9), 101 (31), 75 (10). HRMS (EI) calcd for $C_{14}H_{17}O_4P$ 280.0864, found 280.0859.

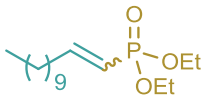


Diethyl (2-(cyclohex-1-en-1-yl)-2-oxoethyl)phosphonate (2h)[3]: Colorless oil. 213.2 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 1H), 4.22 – 4.00 (m, 4H), 3.31 (d, *J* = 22.5 Hz, 2H), 2.28 – 2.24 (m, 4H), 1.62 – 1.58 (m, 4 H), 1.30 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5 (d, *J* = 6.2 Hz), 143.6, 139.3 (d, *J* = 1.8 Hz), 62.4 (d, *J* = 6.5 Hz), 37.0 (d, *J* = 130.8 Hz), 26.3, 23.1, 21.8, 21.3, 16.3 (d, *J* = 6.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.0.

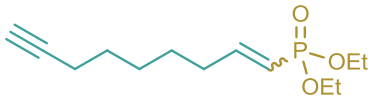


Diethyl oct-1-en-1-ylphosphonate (2i)[5]: Pale yellow oil. 203.4 mg, 82% yield. After column chromatography an analytical sample of the mixture of ***E*-2i** and ***Z*-2i** (1:2) was characterized by NMR spectroscopy. The peaks could be easily distinguished by comparison to literature spectral data. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (ddt, *J* = 22.1, 17.1, 6.6 Hz, 1H, ***E*-2i**), 6.47 (ddt, *J* = 53.2, 13.0, 7.7 Hz, 2H, ***Z*-2i**), 5.69 – 5.50 (m, 3H, ***E*-2i** and ***Z*-2i**), 4.12 – 4.01 (m, 12H, ***E*-2i** and ***Z*-2i**), 2.55 – 2.46 (m, 4H, ***Z*-2i**), 2.35 – 2.16 (m, 2H, ***E*-2i**), 1.34 – 1.24 (overlap, 42H, ***E*-2i** and ***Z*-2i**), 0.89 – 0.85 (m, 9H, ***E*-2i** and ***Z*-2i**). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (d, *J* = 4.7 Hz, ***Z*-2i**), 154.2 (d, *J* = 4.3 Hz, ***E*-2i**), 116.5 (d, *J* = 188.1 Hz, ***E*-2i**), 116.2 (d, *J* = 184.2 Hz, ***Z*-2i**), 61.6 (d, *J* = 5.5 Hz, ***E*-2i**), 61.4 (d, *J* = 5.6 Hz, ***Z*-2i**), 34.2 (d, *J* = 22.1 Hz, ***E*-2i**), 31.6 (***Z*-2i**), 31.5 (***E*-2i**), 30.8 (d, *J* = 8.2

Hz, ***Z*-2i**), 29.7 (***Z*-2i**), 28.9 (***E*-2i** and ***Z*-2i**), 27.7 (d, *J* = 0.9 Hz, ***E*-2i**), 22.5 (***E*-2i** and ***Z*-2i**), 16.3 (d, *J* = 6.4 Hz, ***E*-2i** and ***Z*-2i**), 14.0 (***E*-2i** and ***Z*-2i**). ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.03 (***E*-2i**), 17.40 (***Z*-2i**).



Diethyl dodec-1-en-1-ylphosphonate (2j): Pale yellow oil. 216.4 mg, 86% yield. After column chromatography an analytical sample of the mixture of ***E*-2j** and ***Z*-2j** (1:1) was characterized by NMR spectroscopy. The peaks could be easily distinguished by comparison to literature spectral data of ***E*-2j**.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (ddt, *J* = 23.7, 17.3, 6.7 Hz, 1H, ***E*-2j**), 6.63 – 6.32 (m, 1H, *Z*-**2j**), 5.70 – 5.50 (m, 2H, ***E*-2j** and ***Z*-2j**), 4.15 – 4.00 (m, 8H, ***E*-2j** and ***Z*-2j**), 2.74 – 2.58 (m, 1H), 2.55 – 2.28 (m, 7H), 2.21 (m, 2H), 1.63 – 1.51 (m, 4H), 1.44 – 1.25 (overlap, 34H, ***E*-2j** and ***Z*-2j**), 0.87 (t, *J* = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (d, *J* = 4.6 Hz, ***E*-2j**), 154.3 (d, *J* = 4.4 Hz, ***Z*-2j**), 116.4 (d, *J* = 188.2 Hz, ***E*-2j**), 116.1 (d, *J* = 184.4 Hz, ***Z*-2j**), 61.7 (d, *J* = 5.5 Hz, ***E*-2j**), 61.4 (d, *J* = 5.6 Hz, ***Z*-2j**), 34.2 (d, *J* = 22.0 Hz, ***E*-2j**), 31.9, 30.8 (d, *J* = 8.1 Hz, ***Z*-2j**), 29.5 x 2, 29.4, 29.3 x 3, 29.2, 29.1, 28.9 (d, *J* = 2.0 Hz, ***Z*-2j**), 27.7 (d, *J* = 0.9 Hz, ***E*-2j**), 22.6, 16.3 (d, *J* = 6.5 Hz (***E*-2j** and ***Z*-2j**), 14.1(***E*-2j** and ***Z*-2j**). ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.1 (***E*-2j**), 17.4 (***Z*-2j**).

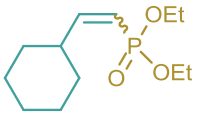


Diethyl non-1-en-8-yn-1-ylphosphonate (2k): Pale yellow oil. 193.5 mg, 75% yield. After column chromatography an analytical sample of ***E*-2k** and ***Z*-2k** were characterized by their spectroscopic properties.

(*E*)-Diethyl non-1-en-8-yn-1-ylphosphonate (*E*-2k): IR (neat): 3294, 2980, 2927, 2860, 2116, 1634, 1246, 1027, 799 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (ddt, *J* = 23.6, 17.1, 6.6 Hz, 1H), 5.58 (dd, *J* = 21.4, 16.9 Hz, 1H), 4.05 – 3.96 (m, 4H), 2.18 – 2.09 (m, 4H), 1.87 (t, *J* = 2.5 Hz, 1H), 1.49 – 1.38 (m, 4H), 1.32 – 1.23 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6 (d, *J* = 4.5 Hz), 116.8 (d, *J* = 188.2 Hz), 84.3, 68.3, 61.6 (d, *J* = 5.5 Hz), 33.9 (d, *J* = 22.1 Hz), 28.1, 28.0, 27.2 (d, *J* = 0.9 Hz), 18.2, 16.2 (d, *J* = 6.1 Hz). ^{31}P NMR

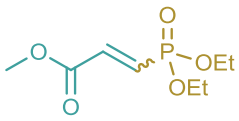
(121 MHz, $CDCl_3$) δ 18.8. MS: *m/z* = 258 (M^+, 1%), 229 (16), 215 (12), 202 (16), 201 (27), 191 (17), 187 (12), 173 (12), 163 (28), 159 (20), 150 (12), 149 (22), 138 (15), 137 (11), 136 (10), 135 (66), 133 (11), 125 (15), 123 (12), 122 (43), 121 (45), 120 (100), 119 (48), 117 (13), 111 (24), 109 (34), 106 (11), 105 (39), 104 (12), 103 (11), 97 (13), 96 (10), 93 (36), 92 (42), 91 (53), 83 (14), 82 (22), 81 (50), 80 (14), 79 (50), 78 (11), 77 (16), 67 (20), 65 (32), 57 (10), 55 (18), 53 (18). HRMS (EI) calcd for $C_{13}H_{23}O_3P$ 258,1385, found 258.1377.

(*Z*)-Diethyl non-1-en-8-yn-1-ylphosphonate (*Z*-2k): IR (neat): 3300, 2984, 2930, 2857, 2116, 1622, 1255, 1030, 799 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.45 (ddt, *J* = 53.0, 13.1, 7.7 Hz, 1H), 5.56 (dd, *J* = 19.8, 13.0 Hz, 1H), 4.13 – 3.99 (m, 4H), 2.58 – 2.46 (m, 2H), 2.16 (td, *J* = 6.7, 2.5 Hz, 2H), 1.91 (t, *J* = 2.6 Hz, 1H), 1.55 – 1.44 (m, 6H), 1.30 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9 (d, *J* = 4.7 Hz), 116.5 (d, *J* = 184.2 Hz), 84.4, 68.2, 61.4 (d, *J* = 5.6 Hz), 30.5 (d, *J* = 8.1 Hz), 28.3 (d, *J* = 2.1 Hz), 28.2, 28.1, 18.2, 16.1 (d, *J* = 6.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.2. MS: *m/z* = 258 (M^+, 1%), 215 (16), 201 (13), 191 (38), 178 (20), 163 (35), 159 (10), 138 (10), 135 (100), 125 (11), 122 (26), 121 (23), 120 (85), 119 (35), 117 (18), 111 (16), 109 (12), 105 (18), 93 (13), 92 (35), 91 (43), 83 (10), 82 (13), 81 (28), 79 (28), 77 (10), 67 (12), 65 (17), 53 (12). HRMS (EI) calcd for $C_{13}H_{23}O_3P$ 258,1385, found 258,1380.



Diethyl (2-cyclohexylvinyl)phosphonate (2l)[7]: Pale yellow oil. 186.9 mg, 76% yield. After column chromatography an analytical sample of the mixture of ***E*-2l** and ***Z*-2l** (1:1) was characterized by NMR spectroscopy. The peaks could be easily distinguished by comparison to literature data. ^1H NMR (300 MHz, $CDCl_3$) δ 6.74 (ddd, *J* = 22.7, 17.3, 6.3 Hz, 1H, ***E*-2l**), 6.27 (ddd, *J* = 53.1, 13.0, 10.4 Hz, 1H, ***Z*-2l**), 5.58 (ddd, *J* = 20.4, 17.0, 1.2 Hz, 1H, ***E*-2l**), 5.46 (ddd, *J* = 19.9, 13.1, 0.7 Hz, 1H, ***Z*-2l**), 4.17 – 4.01 (m, 8H), 3.02 – 2.89 (m, 1H, ***Z*-2l**), 2.18 – 2.06 (m, 1H, ***E*-2l**), 1.80 – 1.64 (m, 12H, ***E*-2l** and ***Z*-2l**), 1.45 – 1.03 (m overlap, 8H, ***E*-2l** and ***Z*-2l**), 1.32 (t overlap, *J* = 7.1 Hz, 6H), 1.31 (t overlap, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1 (d, *J* = 5.2 Hz, ***Z*-2l**), 158.8 (d, *J* = 4.0 Hz, ***E*-2l**), 114.1 (d, *J* = 184.6 Hz, ***Z*-2l**), 113.9 (d, *J* = 188.0 Hz, ***E*-2l**), 61.6 (d, *J* = 5.5 Hz, ***E*-2l**), 61.4

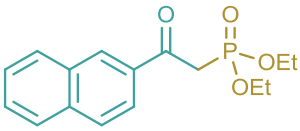
(d, *J* = 5.5 Hz, ***Z*-2l**), 41.9 (d, *J* = 20.4 Hz, ***E*-2l**), 39.4 (d, *J* = 7.8 Hz, ***Z*-2l**), 32.2 (d, *J* = 2.2 Hz, ***Z*-2l)**, 31.4 (d, *J* = 0.8 Hz, ***E*-2l)**, 25.9 (***E*-2l)**, 25.8 (***Z*-2l)**, 25.7 (***E*-2l)**, 25.3 (***Z*-2l)**, 16.3 (d, *J* = 6.4 Hz, ***E*-2l**), 16.2 (d, *J* = 6.3 Hz, ***Z*-2l**). ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.80 (***E*-2l**), 17.45 (***Z*-2l**).



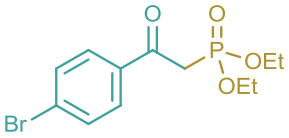
Methyl 3-(diethoxyphosphoryl)acrylate (2m): Pale yellow oil. 113.2 mg, 51% yield. After column chromatography an analytical sample of ***E*-2m** and ***Z*-2m** were characterized by their spectroscopic properties.

(*E*)-Methyl 3-(diethoxyphosphoryl)acrylate (*E*-2m): IR (neat): 2983, 2921, 1728, 1638, 1242, 1033, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 – 6.65 (m, 2H), 4.20 – 4.09 (m, 4H), 3.81 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 137.1 (d, *J* = 7.1 Hz), 132.3 (d, *J* = 184.8 Hz), 62.8 (d, *J* = 5.8 Hz), 52.5, 16.5 (d, *J* = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.3. MS: *m/z* = 222 (M^+, 1%), 191 (14), 167 (24), 163 (72), 149 (40), 135 (100), 113 (16), 109 (10), 107 (15), 82 (10), 81 (28), 65 (12). HRMS (EI) calcd for $C_{18}H_{15}O_5P$ 222.0657, found 222.0666.

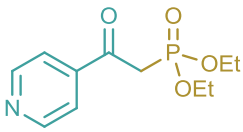
(*Z*)-Methyl 3-(diethoxyphosphoryl)acrylate (*Z*-2m): IR (neat): 2980, 2918, 1730, 1660, 1234, 1029, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 47.3, 13.8 Hz, 1H), 6.21 (t, *J* = 14.4 Hz, 1H), 4.18 (m, 4H), 3.81 (s, 3H), 1.30 (t, *J* = 6.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (d, *J* = 11.0 Hz), 137.0, 129.5 (d, *J* = 186.6 Hz), 62.7 (d, *J* = 5.9 Hz), 52.3, 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 12.2. MS: *m/z* = 222 (M^+, 1%), 177 (10), 163 (54), 149 (38), 135 (100), 113 (11), 95 (12), 81 (18). HRMS (EI) calcd for $C_{18}H_{15}O_5P$ 222.0657, found 222.0661.



Diethyl (2-(naphthalen-2-yl)-2-oxoethyl)phosphonate (4b): Yellow oil. 266.2 mg, 87% yield. IR (neat): 3056, 2978, 2929, 2905, 1674, 1626, 1597, 1245, 1058, 1017, 817 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.95 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.54 – 7.39 (m, 2H), 4.11 – 3.97 (m, 4H), 3.65 (d, *J* = 22.7 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7 (d, *J* = 6.6 Hz), 135.7, 133.8 (d, *J* = 2.0 Hz), 132.3, 131.4, 129.7, 128.8, 128.4, 127.7, 126.8, 124.1, 62.6 (d, *J* = 6.5 Hz), 38.5 (d, *J* = 130.1 Hz), 16.2 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.1. MS: *m/z* = 306 (M^+, 92%), 307 (M^{+1}, 16), 278 (21), 197 (10), 196 (46), 181 (14), 170 (60), 156 (65), 155 (100), 153 (13), 152 (17), 141 (35), 139 (12), 128 (45), 127 (199), 126 (35), 123 (16), 115 (22), 101 (11), 81 (14), 77 (16). HRMS (EI) calcd for $C_{16}H_{19}O_4P$ 306.1021, found 306.1019

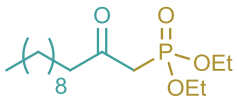


Diethyl (2-(4-bromophenyl)-2-oxoethyl)phosphonate (4c)[3]: Yellow oil. 303.9 mg, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.9 Hz, 2H), 7.52 (d, *J* = 6.7 Hz, 2H), 4.15 – 3.91 (m, 4H), 3.53 (d, *J* = 22.8 Hz, 2H), 1.19 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7 (d, *J* = 6.7 Hz), 135.6 (d, *J* = 1.9 Hz), 131.7, 130.4, 128.9, 62.7 (d, *J* = 6.5 Hz), 38.3 (d, *J* = 129.9 Hz), 16.1 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 19.6.

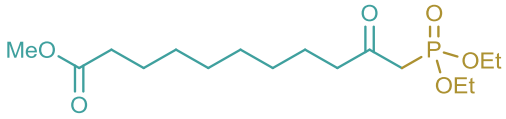


Diethyl (2-oxo-2-(pyridin-4-yl)ethyl)phosphonate (4d): Yellow oil. 133.6 mg, 52% yield. IR (neat): 2982, 2925, 1691, 1597, 1548, 1246, 1054, 1021, 796 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (brs, 2H), 7.82 – 7.80 (d, *J* = 4.2 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.63 (d, *J* =

23.0 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7 (d, *J* = 6.9 Hz), 151.0, 143.3 (d, *J* = 2.1 Hz), 121.8 (d, *J* = 2.6 Hz), 63.0 (d, *J* = 6.5 Hz), 38.9 (d, *J* = 129.0 Hz), 16.3 (d, *J* = 6.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 18.4. MS: *m/z* = 257 (M^+, 11%), 230 (17), 212 (14), 202 (27), 201 (12), 184 (17), 179 (10), 151 (21), 148 (34), 147 (21), 123 (77), 122 (15), 121 (58), 109 (18), 107 (16), 106 (100), 105 (19), 104 (23), 93 (19), 81 (25), 79 (36), 78 (62), 65 (18), 51 (32). HRMS (EI) calcd for $C_{11}H_{16}NO_4P$ 257.0817, found 257.0809.

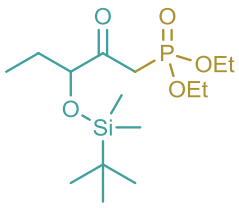


Diethyl (2-oxododecyl)phosphonate (4e)[3]: Yellow oil. 294.4 mg, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 – 4.06 (m, 4H), 3.06 (d, *J* = 22.8 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 1.29 – 1.21 (m, 16H), 0.86 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1 (d, *J* = 6.2 Hz), 62.5 (d, *J* = 6.3 Hz), 44.0, 42.1 (d, *J* = 127.9 Hz), 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 23.4, 22.6, 16.2 (d, *J* = 6.0 Hz), 14.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.2.



Methyl 11-(diethoxyphosphoryl)-10-oxoundecanoate (4f): Colorless oil. 227.5 mg, 65% yield. IR (neat): 2982, 2933, 2856, 1736, 1245, 1160, 1033, 800 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 – 4.04 (m, 4H), 3.60 (s, 3H), 3.02 (d, *J* = 22.8 Hz, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.57 – 1.51 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H), 1.30 – 1.19 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1 (d, *J* = 6.2 Hz), 174.3 (d, *J* = 2.5 Hz), 62.7 (d, *J* = 6.5 Hz), 51.4, 44.1 (d, *J* = 0.7 Hz), 42.3 (d, *J* = 127.6 Hz), 34.1, 29.2, 29.1, 29.0, 28.9, 24.9 (d, *J* = 1.7 Hz), 23.4, 16.3 (d, *J* = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.2. MS: *m/z* = 350 (M^+, 2%), 319 (24), 272 (32), 221 (11), 208 (13), 207 (80), 195 (21), 194 (99), 179 (100), 167 (35), 166 (12), 153 (11), 152 (78), 151 (80), 150 (10), 139 (18), 137 (17), 133 (11), 125 (95), 124 (18), 123 (89), 121 (13), 109 (44), 108 (22), 105 (13), 97 (42), 96 (16),

95 (10), 91 (11), 81 (34), 80 (11), 79 (13), 74 (15), 69 (16), 59 (16), 55 (44). HRMS (EI) calcd for $C_{16}H_{31}O_6P$ 350.1858, found 350.1863



Diethyl (3-(tert-butyldimethylsilyloxy)-2-oxopentyl)phosphonate (4g): Yellow oil. 200.6 mg, 57% yield. IR (neat): 2954, 2925, 2856, 1724, 1250, 1053, 1029, 841, 776 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.16 – 4.08 (m, 4H), 4.04 (t, *J* = 6.0 Hz, 1H), 3.32 (dd, *J* = 20.5, 15.2 Hz, 1H), 3.08 (dd, *J* = 22.0, 15.2 Hz, 1H), 1.72 – 1.62 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H), 0.89 (s, 9H), 0.87 (t, *J* = 6.0 Hz, 3H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8 (d, *J* = 6.7 Hz), 79.9 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.4 Hz), 36.0 (d, *J* = 135.6 Hz), 27.4, 25.8, 18.2, 16.4 (d, *J* = 6.3 Hz), 9.3, -4.8. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.1. MS: *m/z* = 352 (M^+, 2%), 296 (17), 295 (100), 267 (21), 239 (10), 221 (41), 210 (35), 203 (17), 179 (33), 173 (46), 157 (33), 155 (15), 153 (13), 152 (39), 129 (10), 125 (18), 123 (17), 117 (17), 115 (20), 75 (27), 73 (76), 59 (11). HRMS (EI) calcd for $C_{15}H_{33}O_5PSi$ 352,1835, found 352.1842

6. References

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7. NMR Spectra

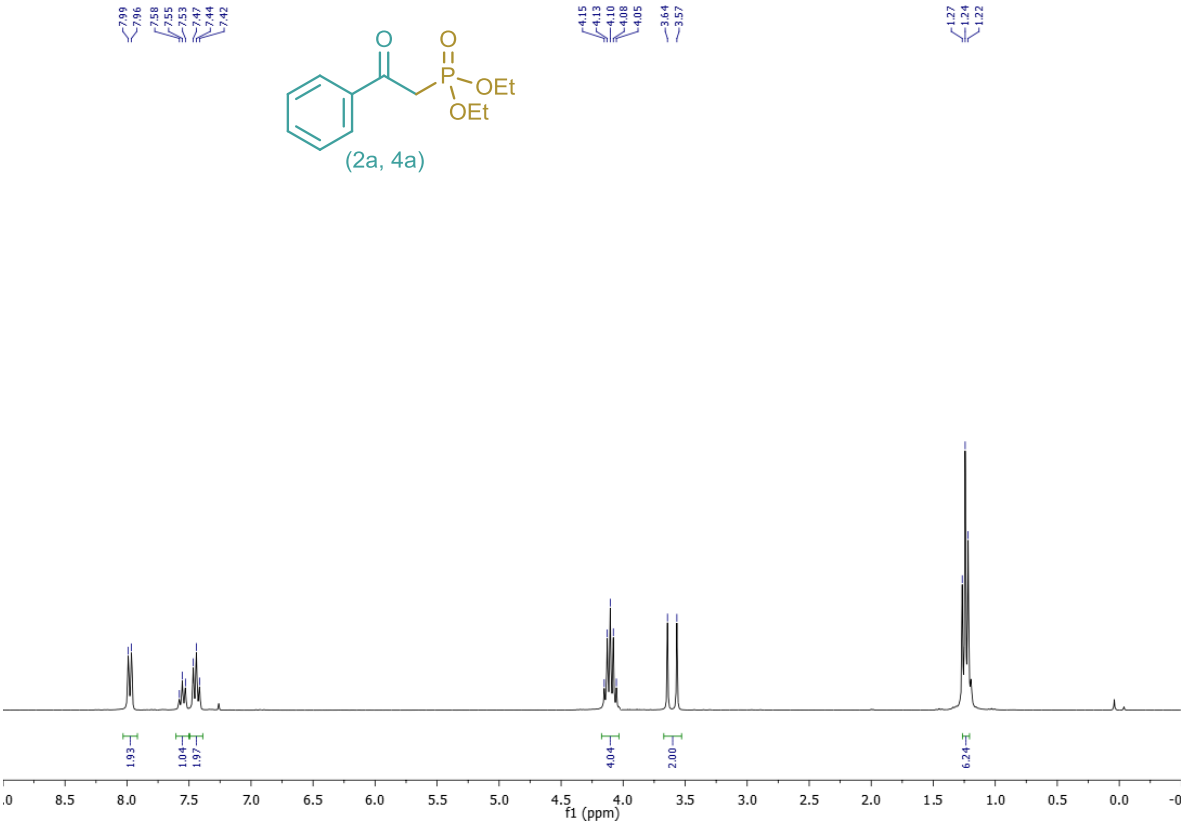

Figure 5. ^{1}H spectrum of **2a** (300 MHz, $CDCl_3$).

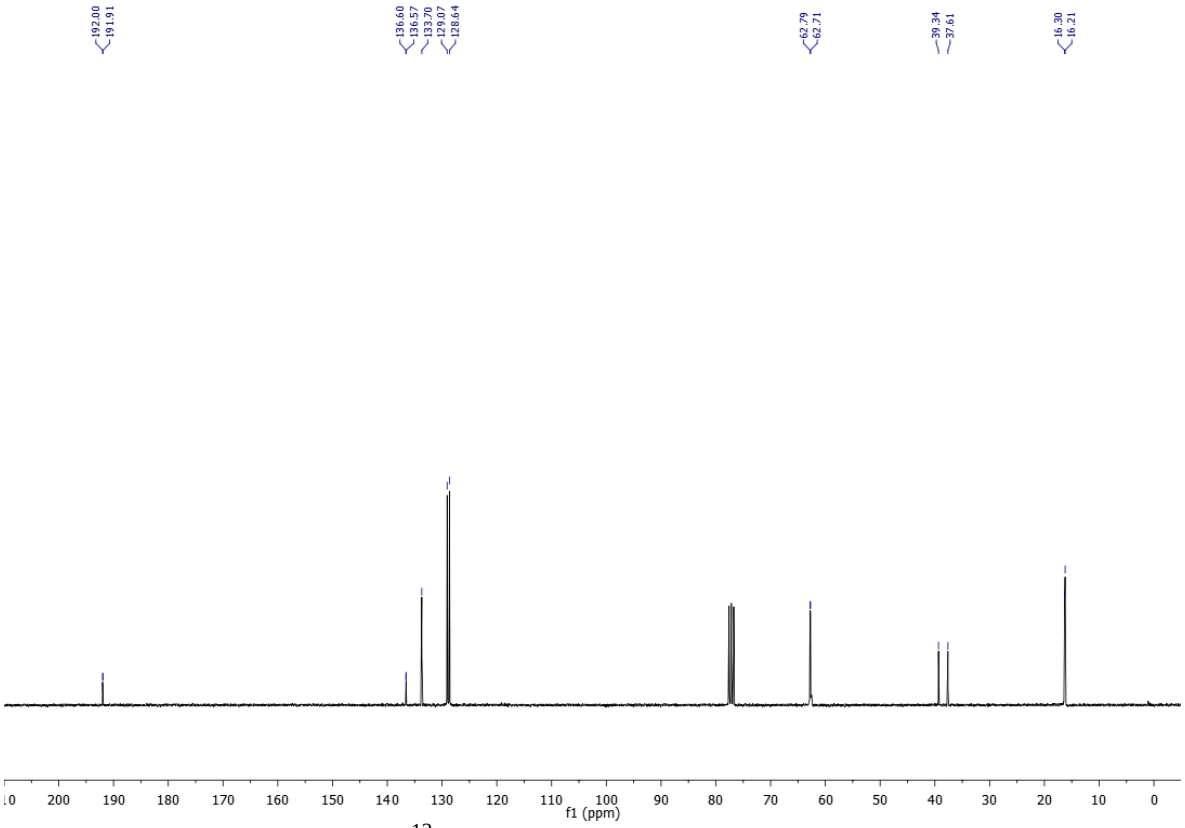

Figure 6. ^{13}C spectrum of **2a** (75 MHz, $CDCl_3$).

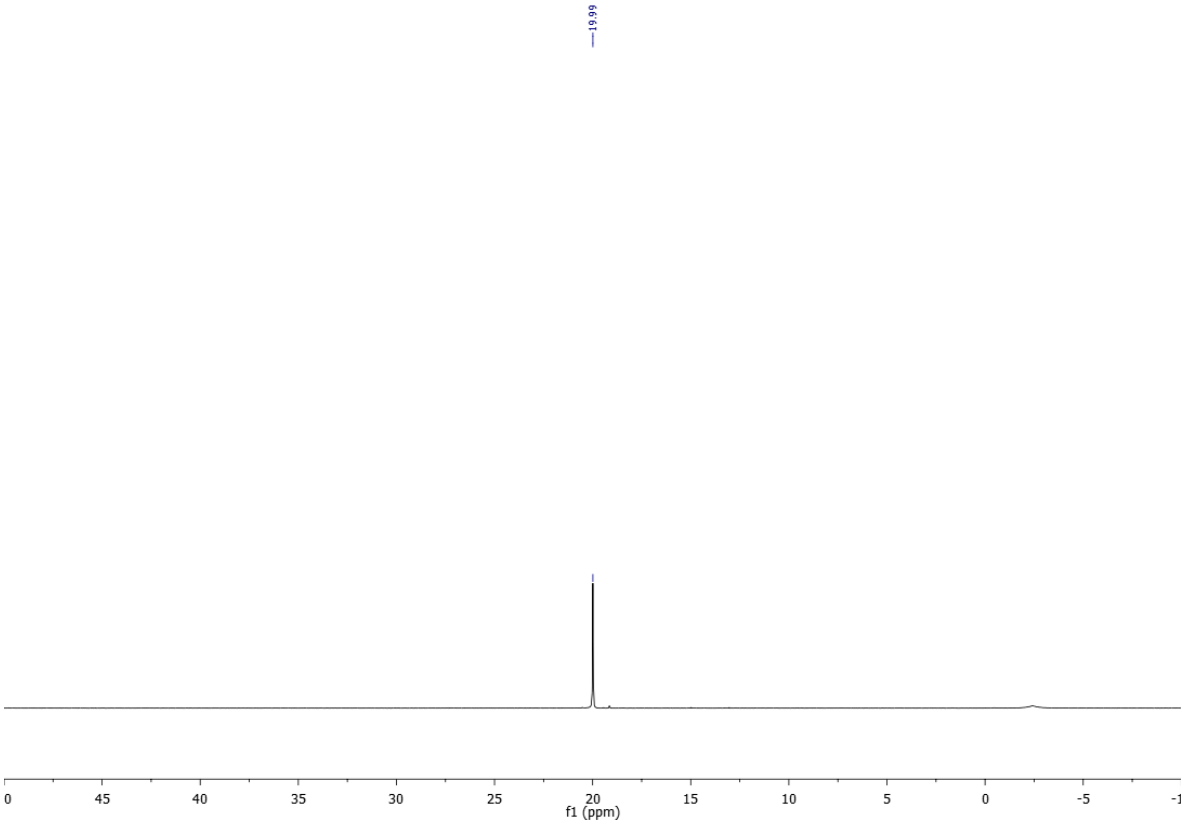

Figure 7. ^{31}P spectrum of **2a** (121 MHz, $CDCl_3$).

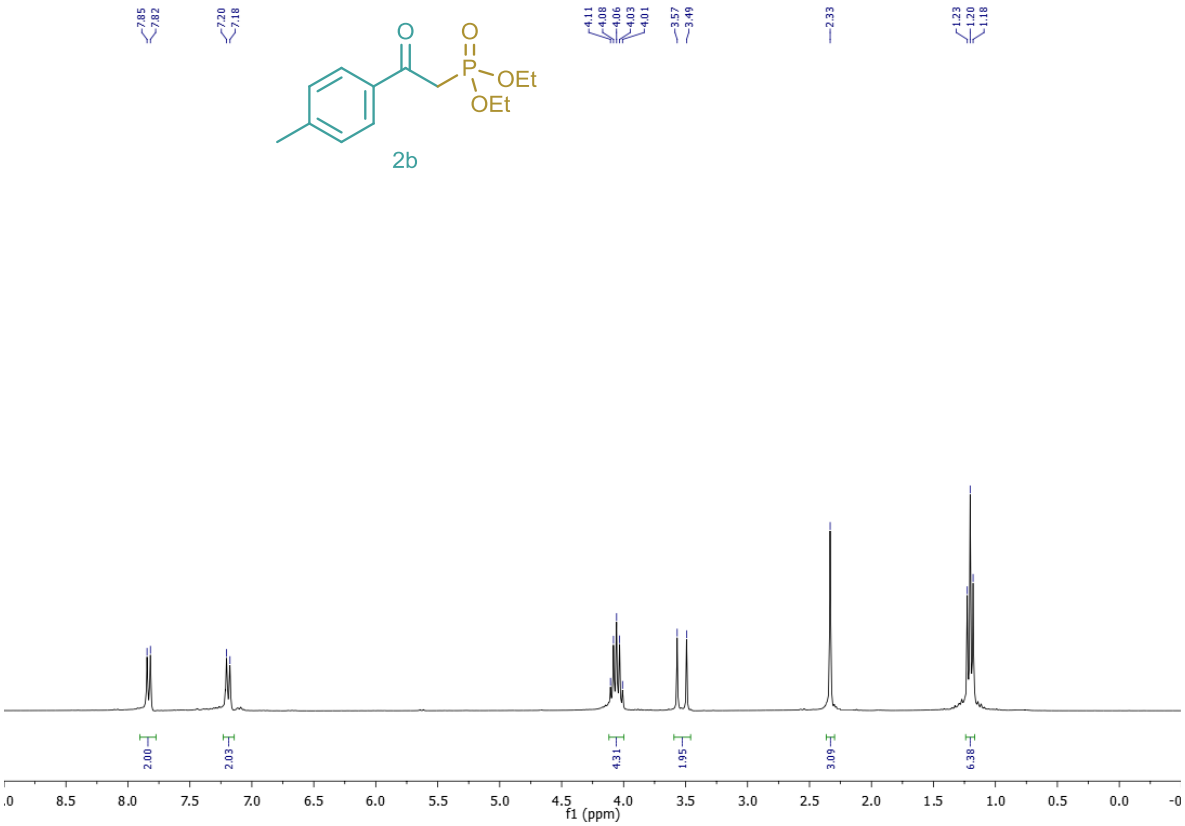

Figure 8. ^{1}H spectrum of **2b** (300 MHz, $CDCl_3$).

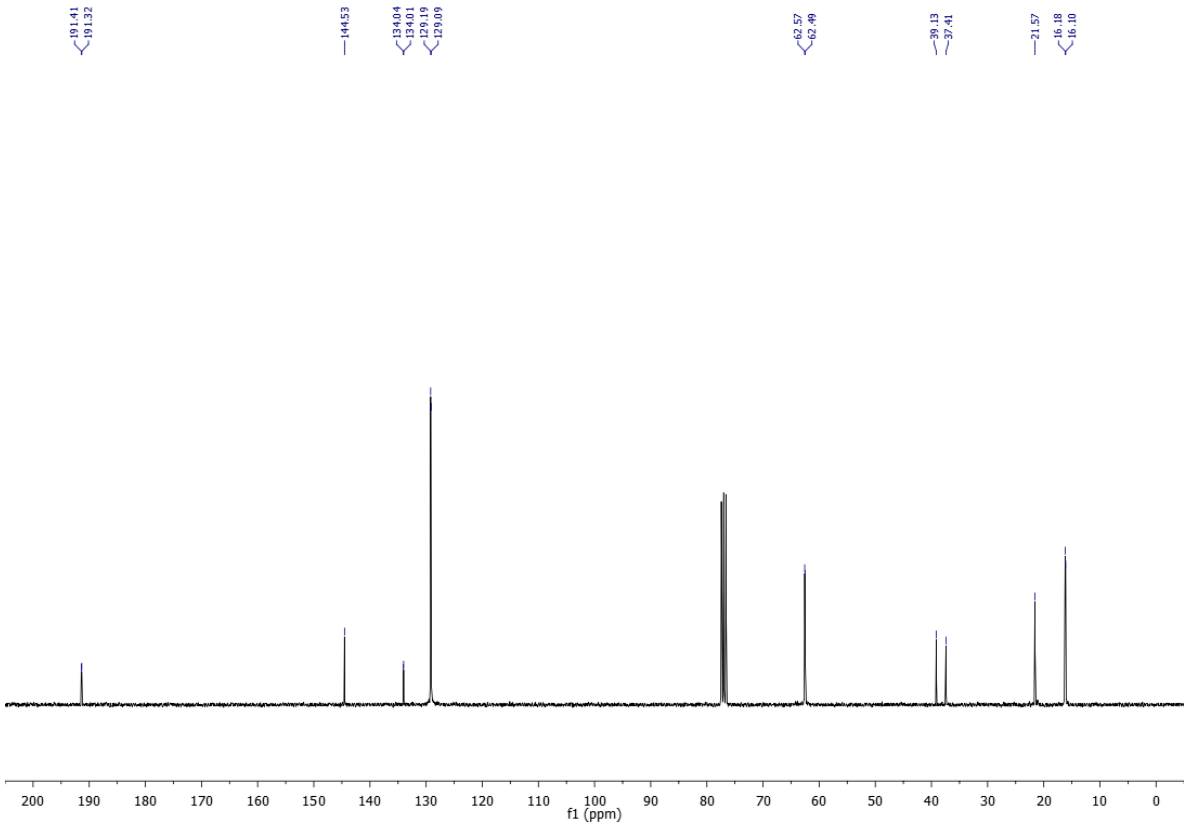

Figure 9. ^{13}C spectrum of **2b** (75 MHz, $CDCl_3$).

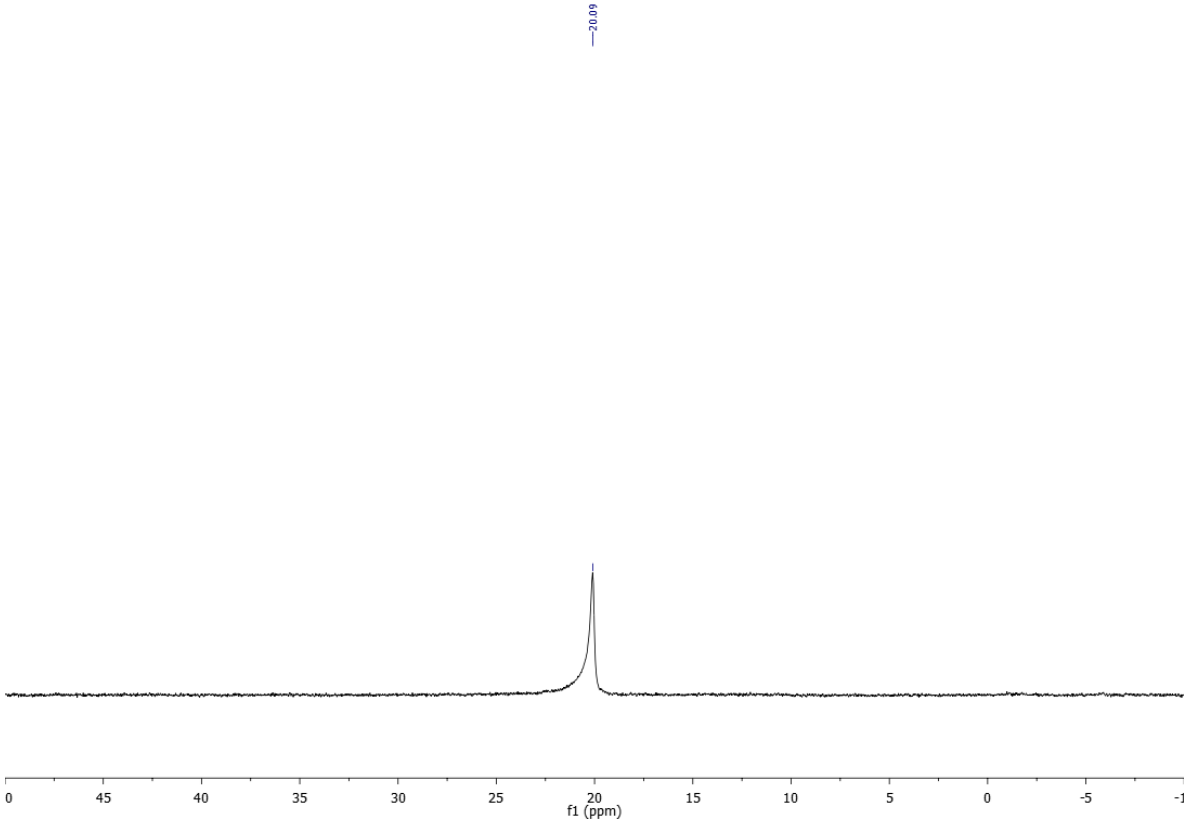

Figure 10. ^{31}P spectrum of **2b** (121 MHz, $CDCl_3$).

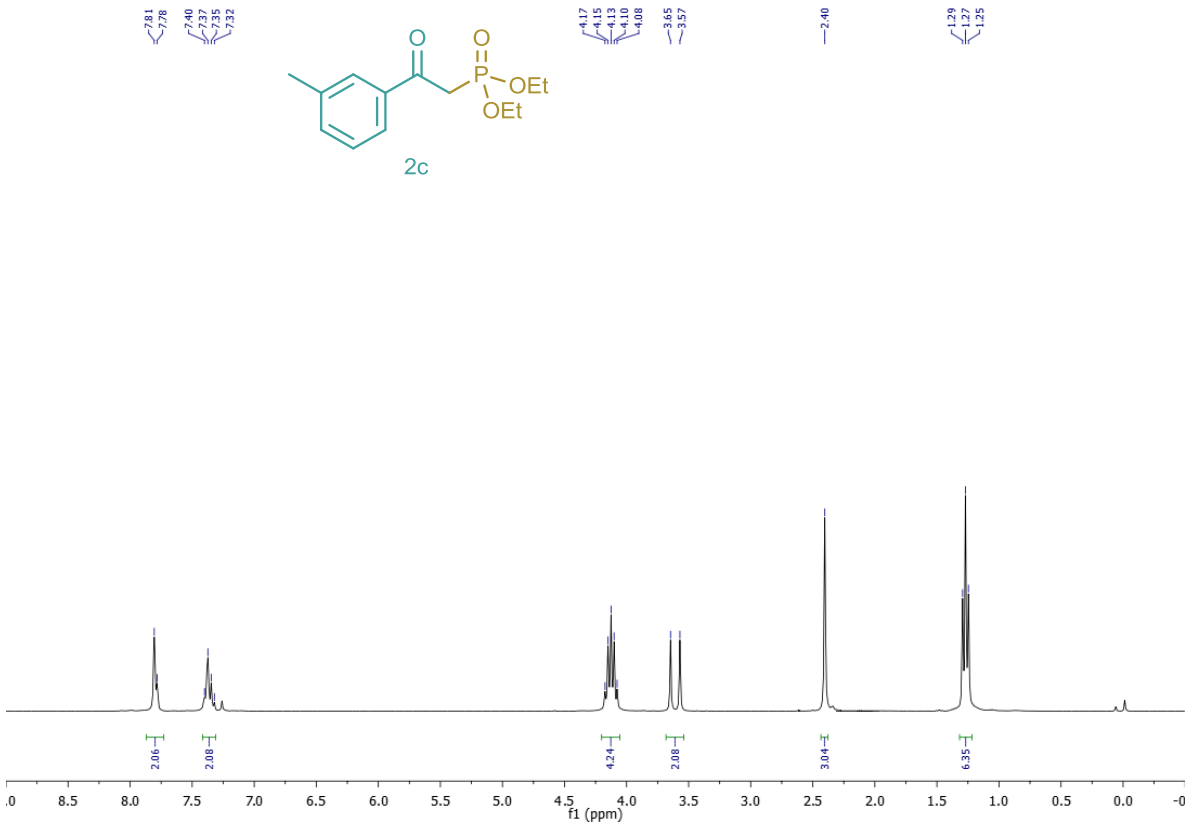

Figure 11. ^{1}H spectrum of **2c** (300 MHz, $CDCl_3$).

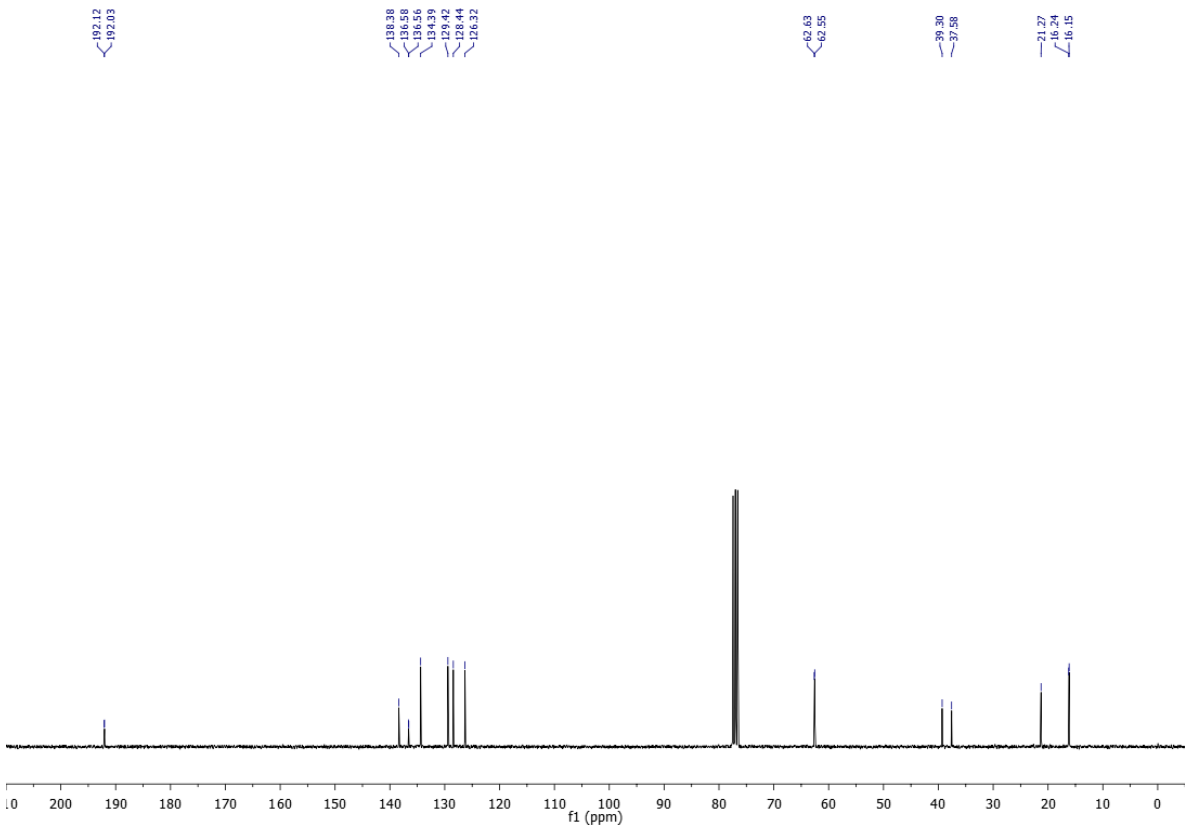

Figure 12. ^{13}C spectrum of **2c** (75 MHz, $CDCl_3$).

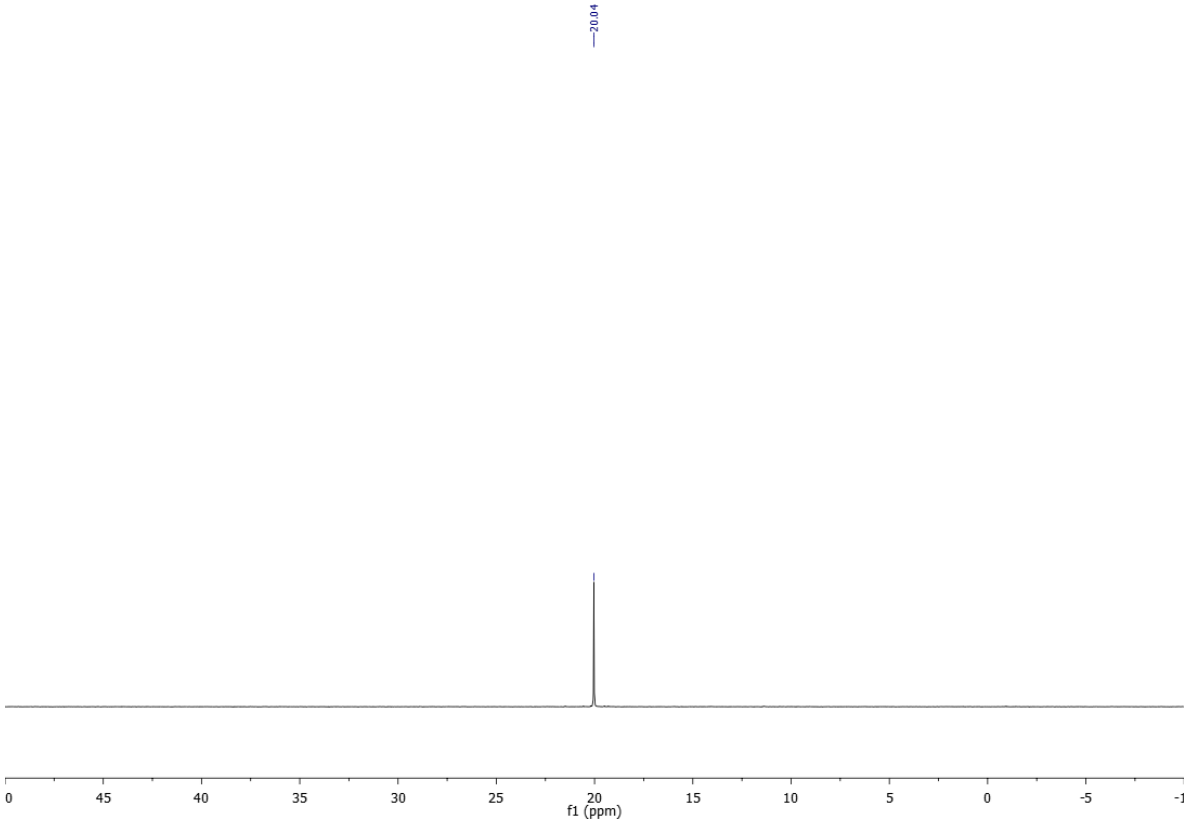

Figure 13. ^{31}P spectrum of **2c** (121 MHz, $CDCl_3$).

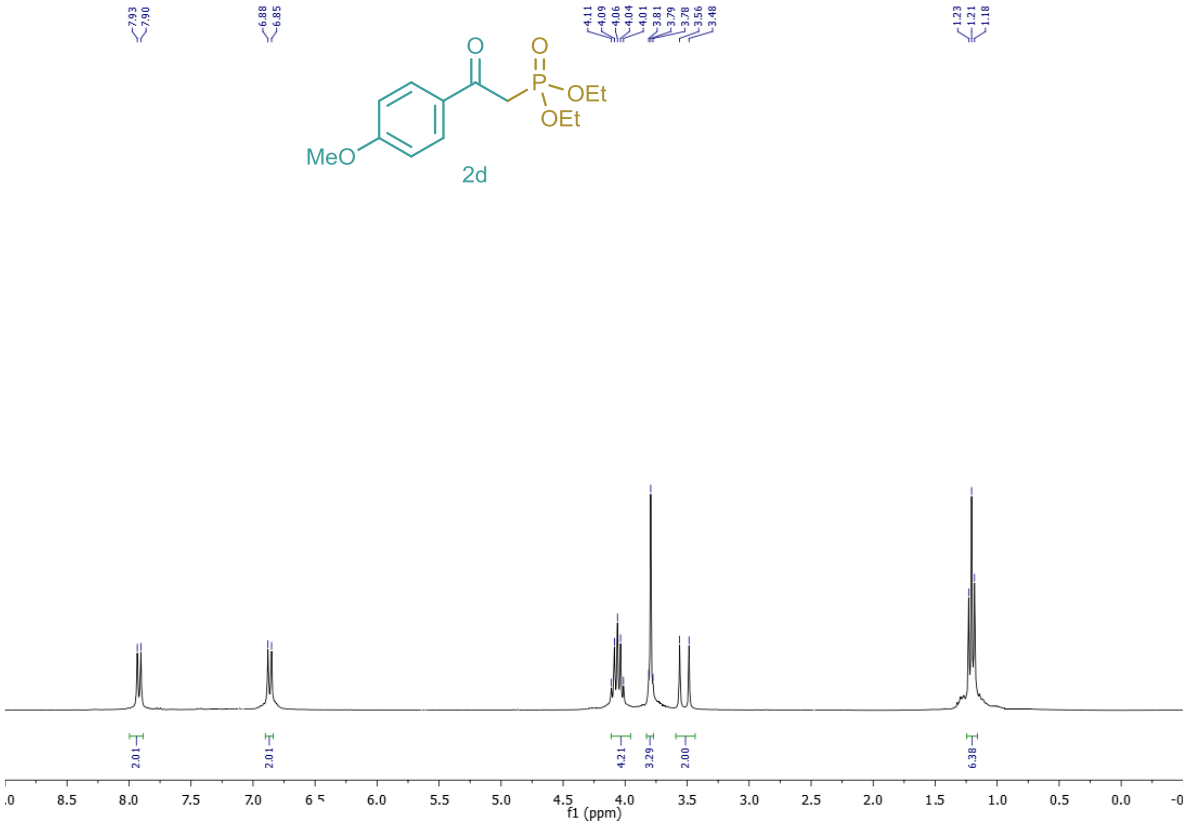

Figure 14. ^{1}H spectrum of **2d** (300 MHz, $CDCl_3$).

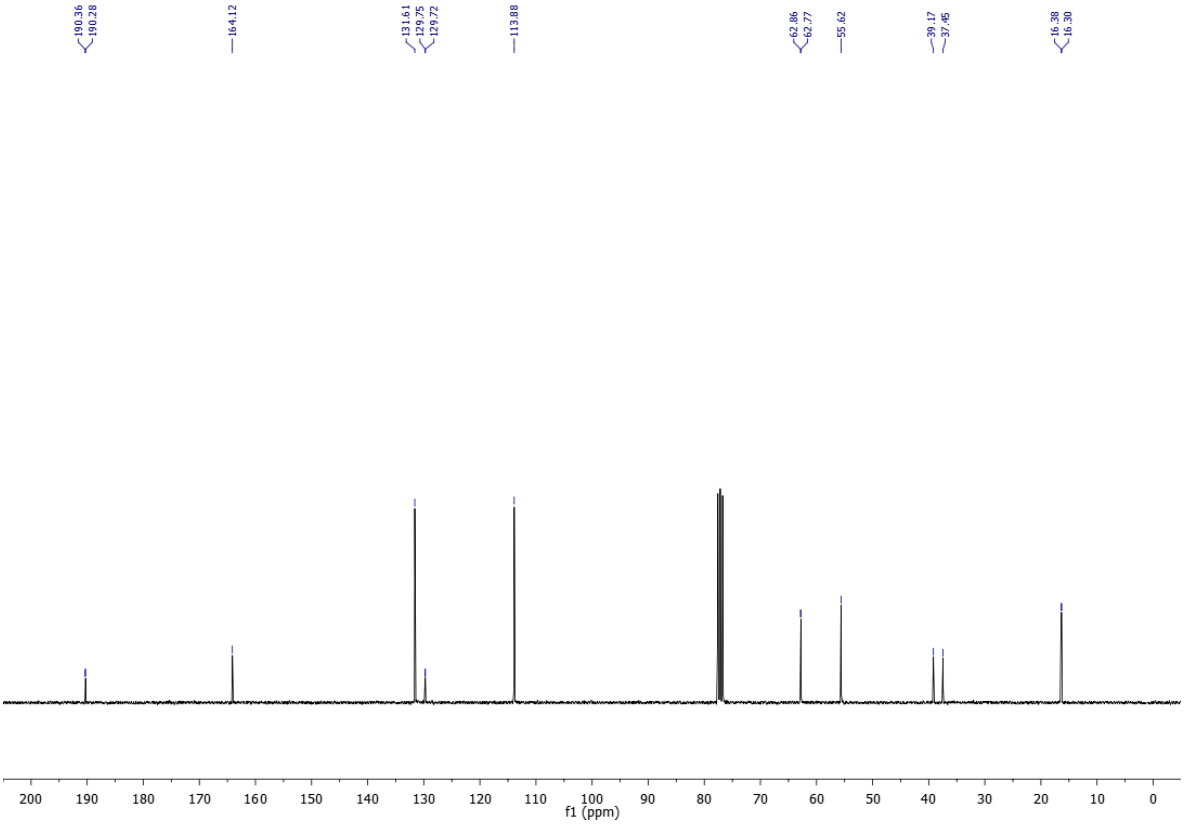

Figure 15. ^{13}C spectrum of **2d** (75 MHz, $CDCl_3$).

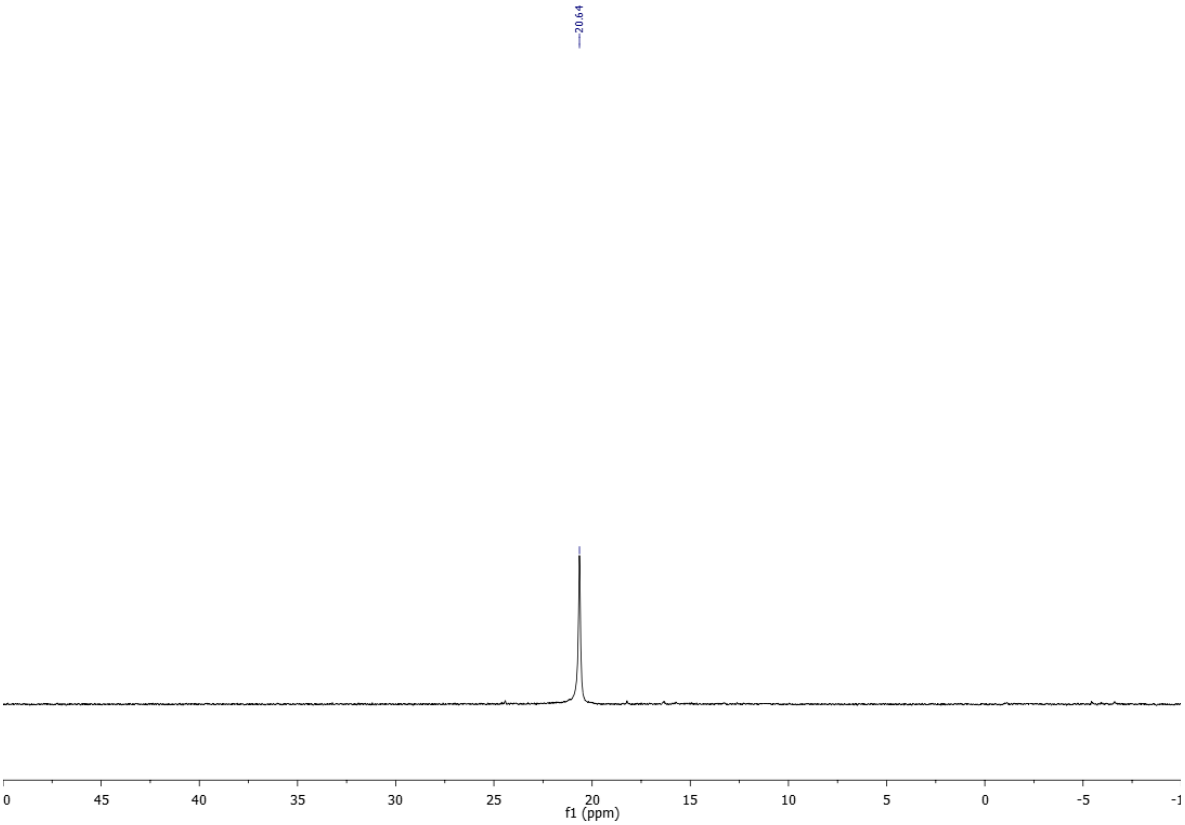

Figure 16. ^{31}P spectrum of **2d** (121 MHz, $CDCl_3$).

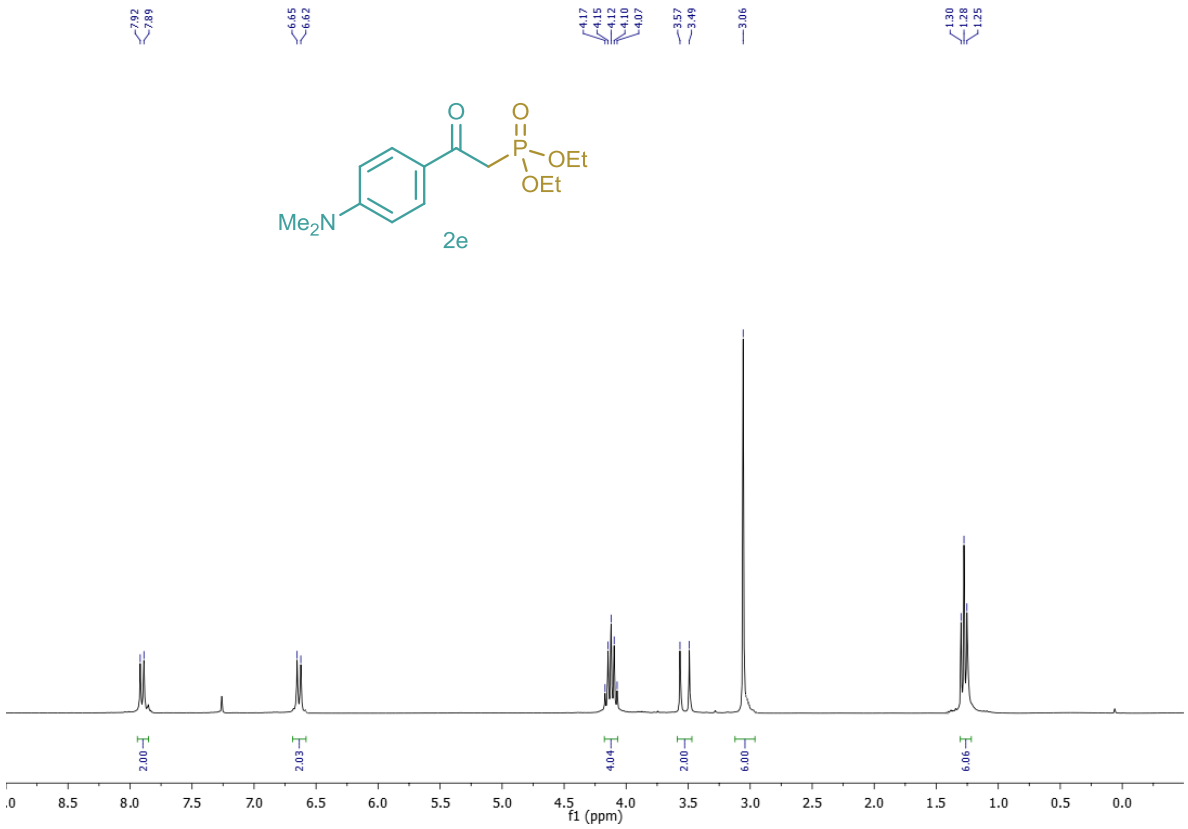

Figure 17. ^{1}H spectrum of **2e** (300 MHz, $CDCl_3$).

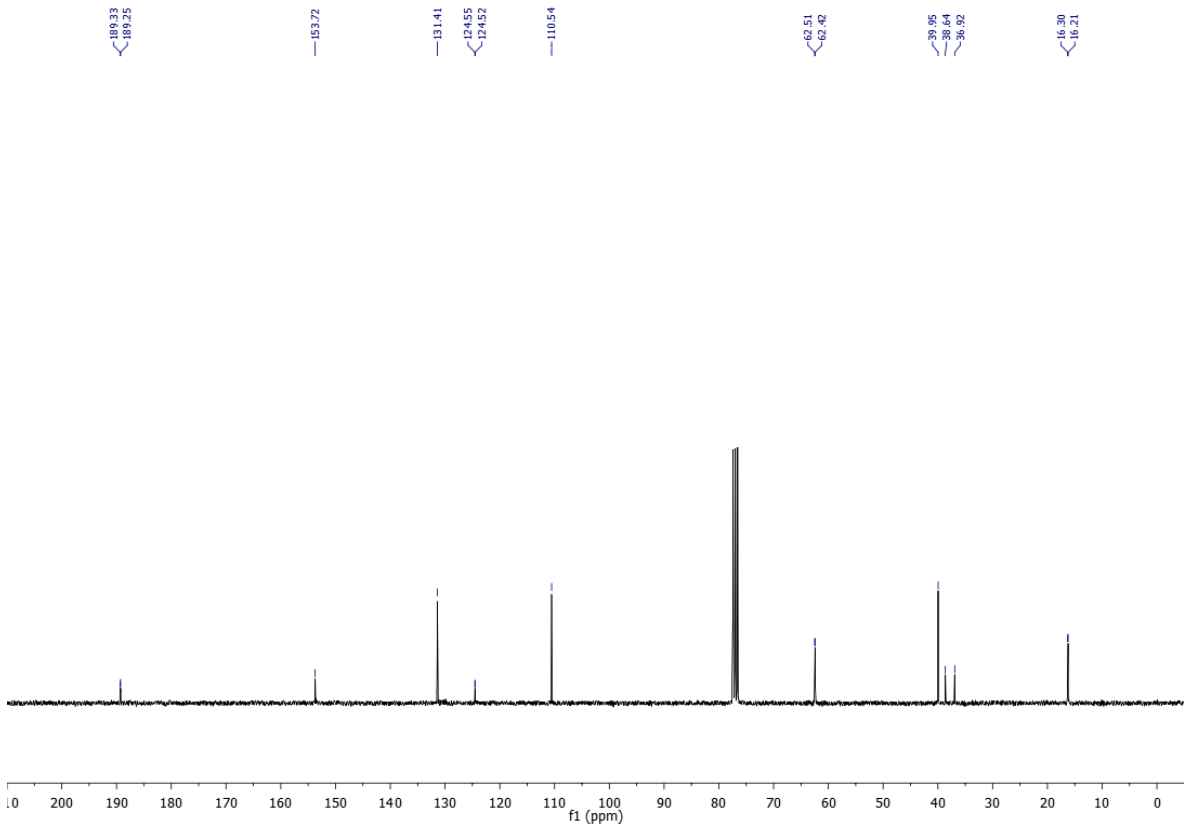

Figure 18. ^{13}C spectrum of **2e** (75 MHz, $CDCl_3$).

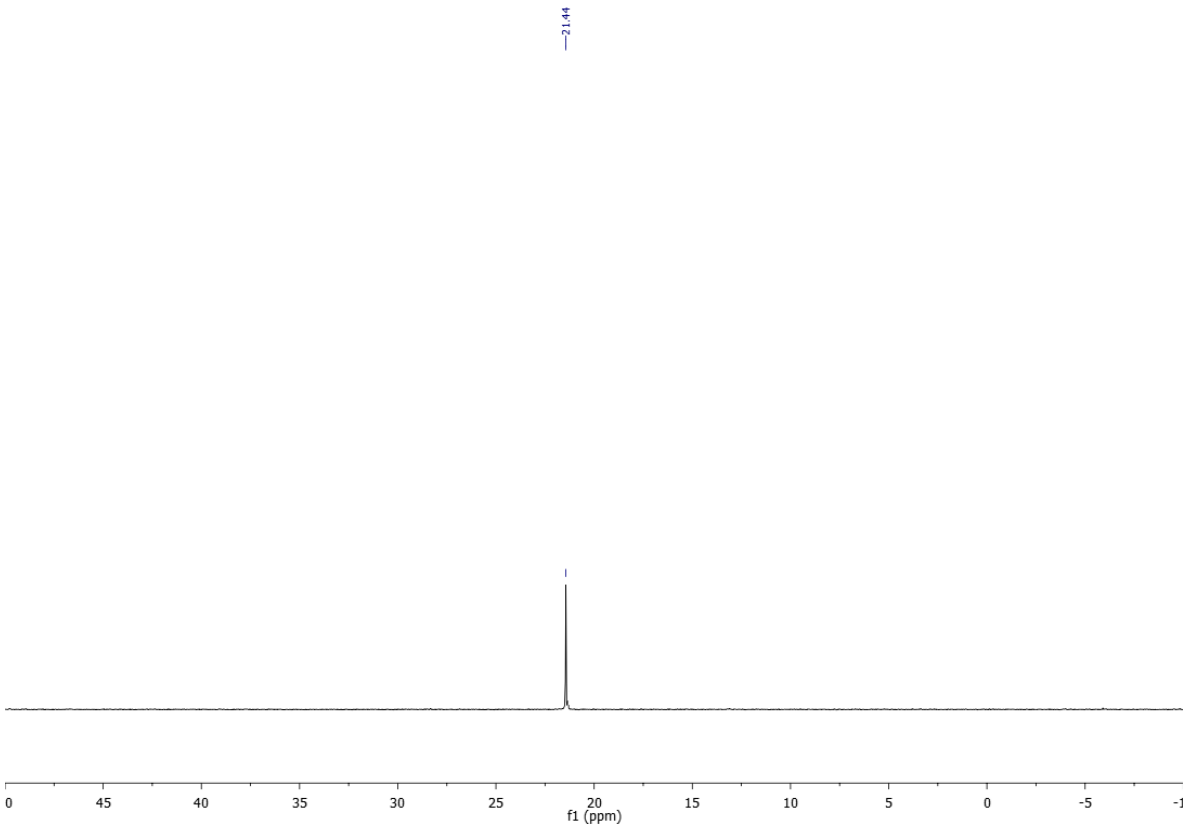

Figure 19. ^{31}P spectrum of **2e** (121 MHz, $CDCl_3$).

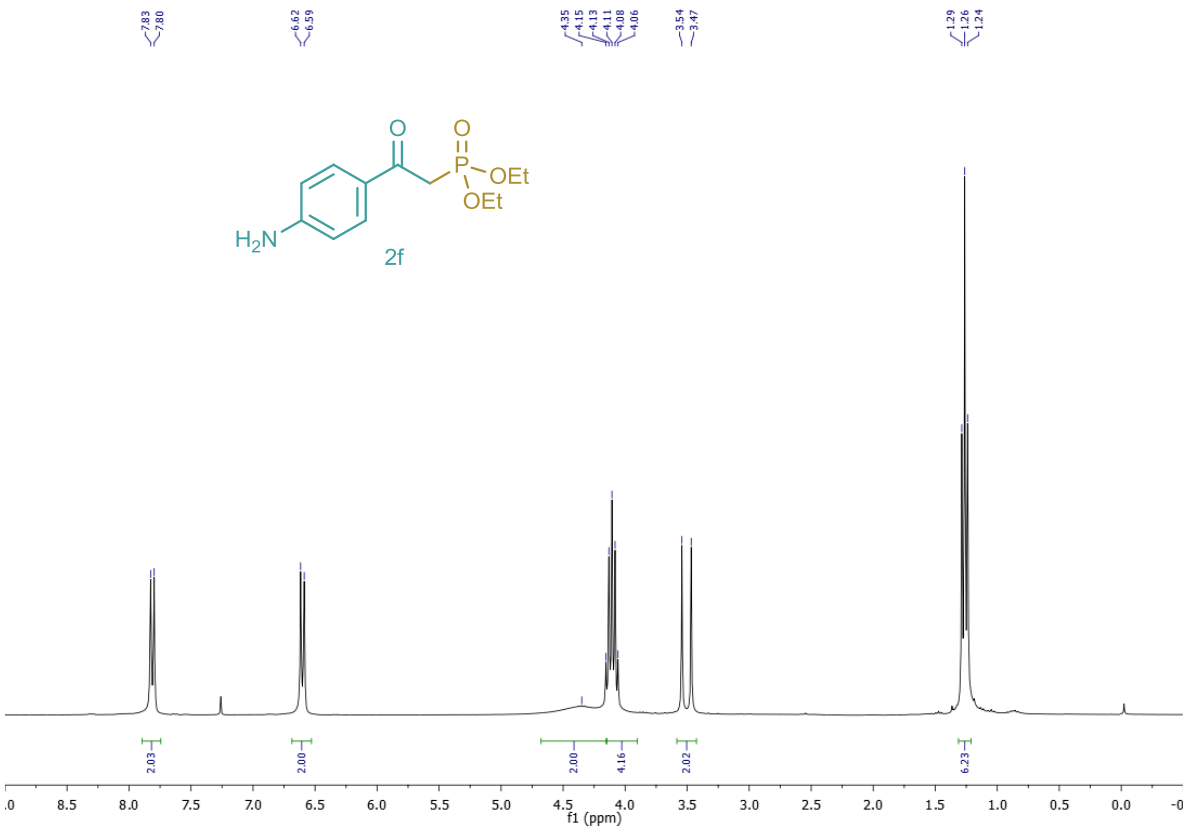

Figure 20. ^{1}H spectrum of **2f** (300 MHz, $CDCl_3$).

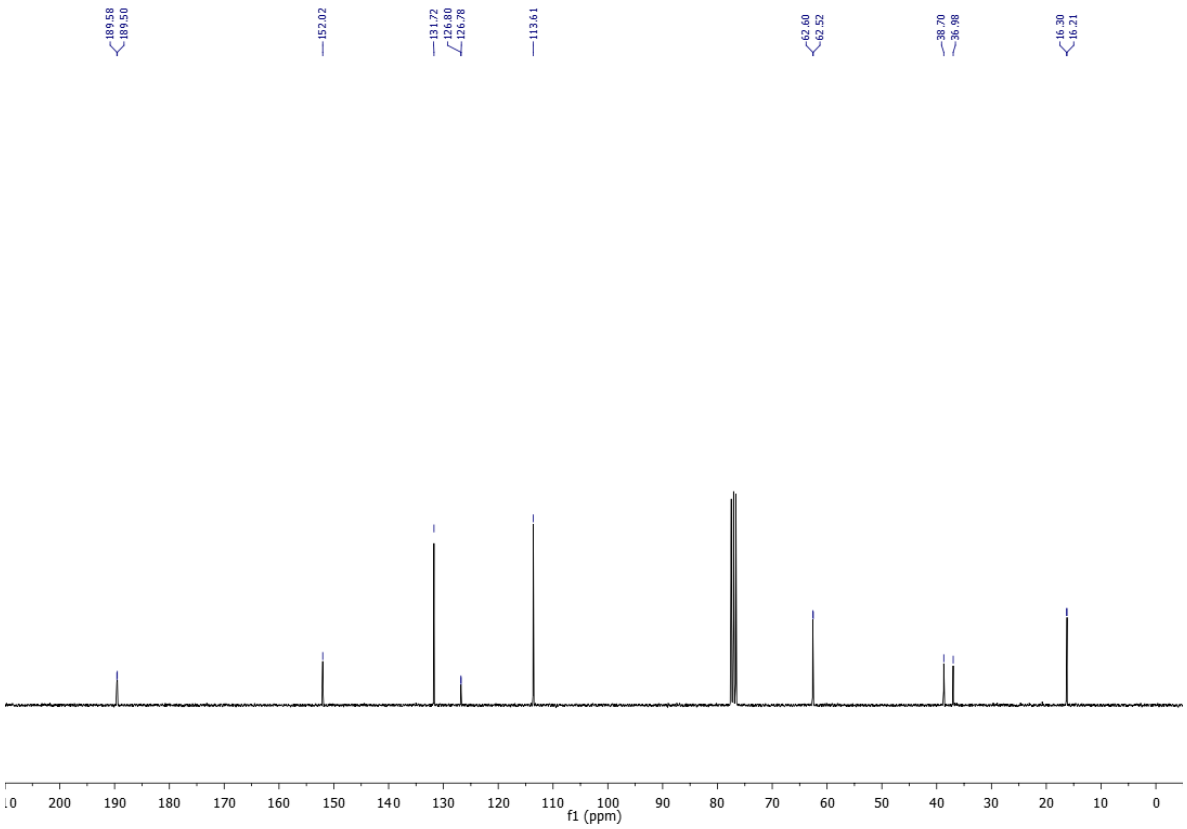

Figure 21. ^{13}C spectrum of **2f** (75 MHz, $CDCl_3$).

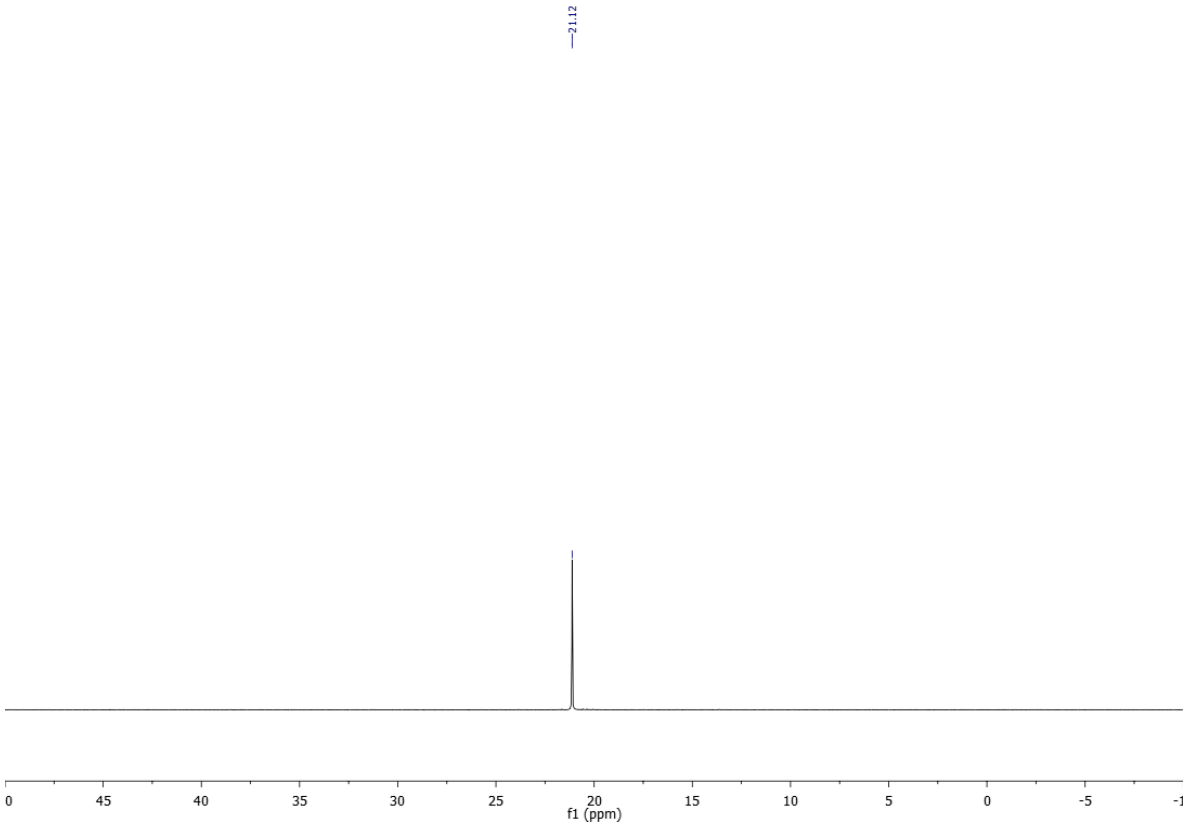

Figure 22. ^{31}P spectrum of **2f** (121 MHz, $CDCl_3$).

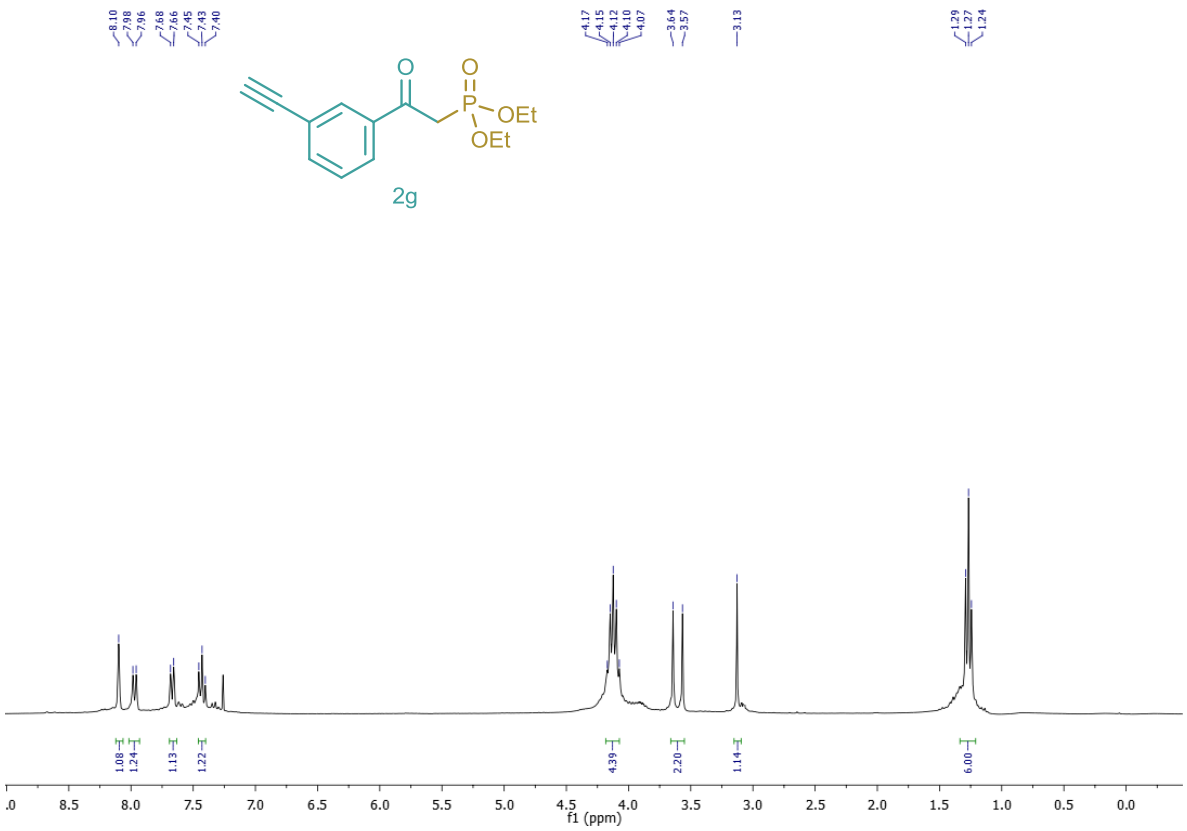

Figure 23. ^{1}H spectrum of **2g** (300 MHz, $CDCl_3$).

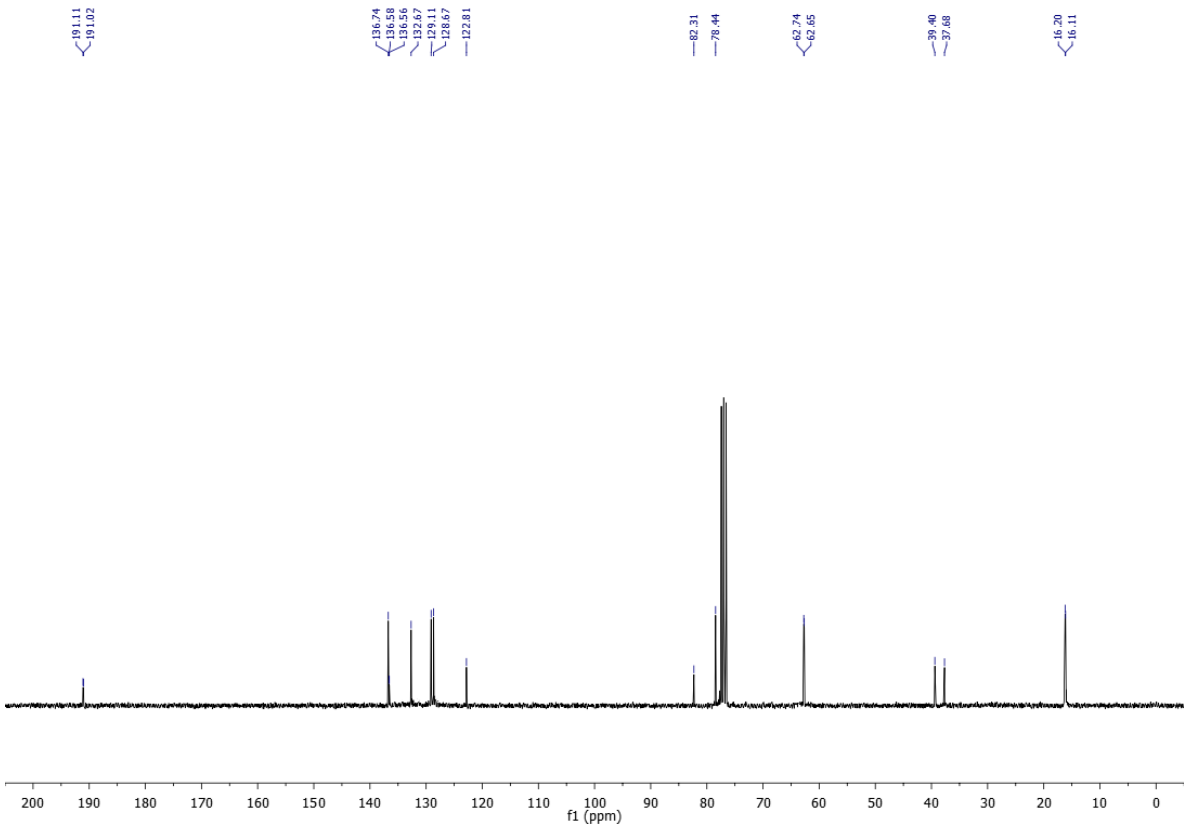

Figure 24. ^{13}C spectrum of **2g** (75 MHz, $CDCl_3$).

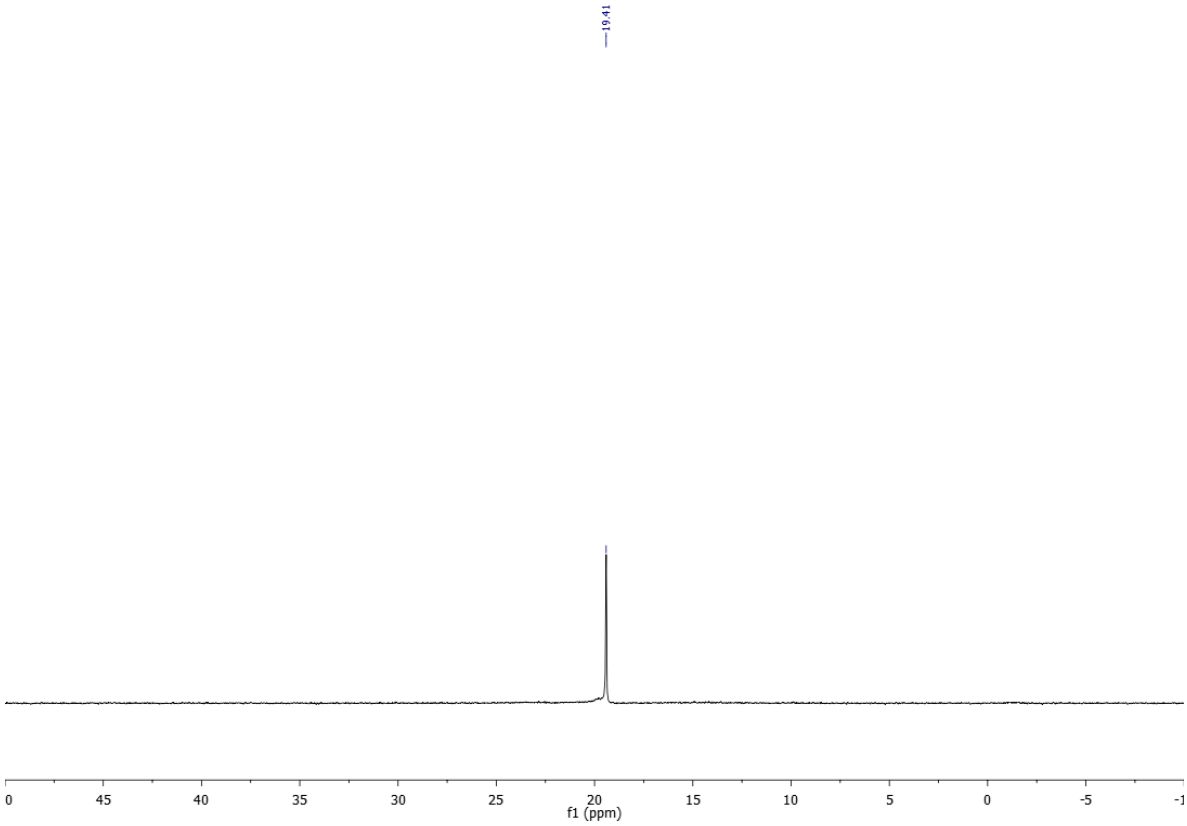

Figure 25. ^{31}P spectrum of **2g** (121 MHz, $CDCl_3$).

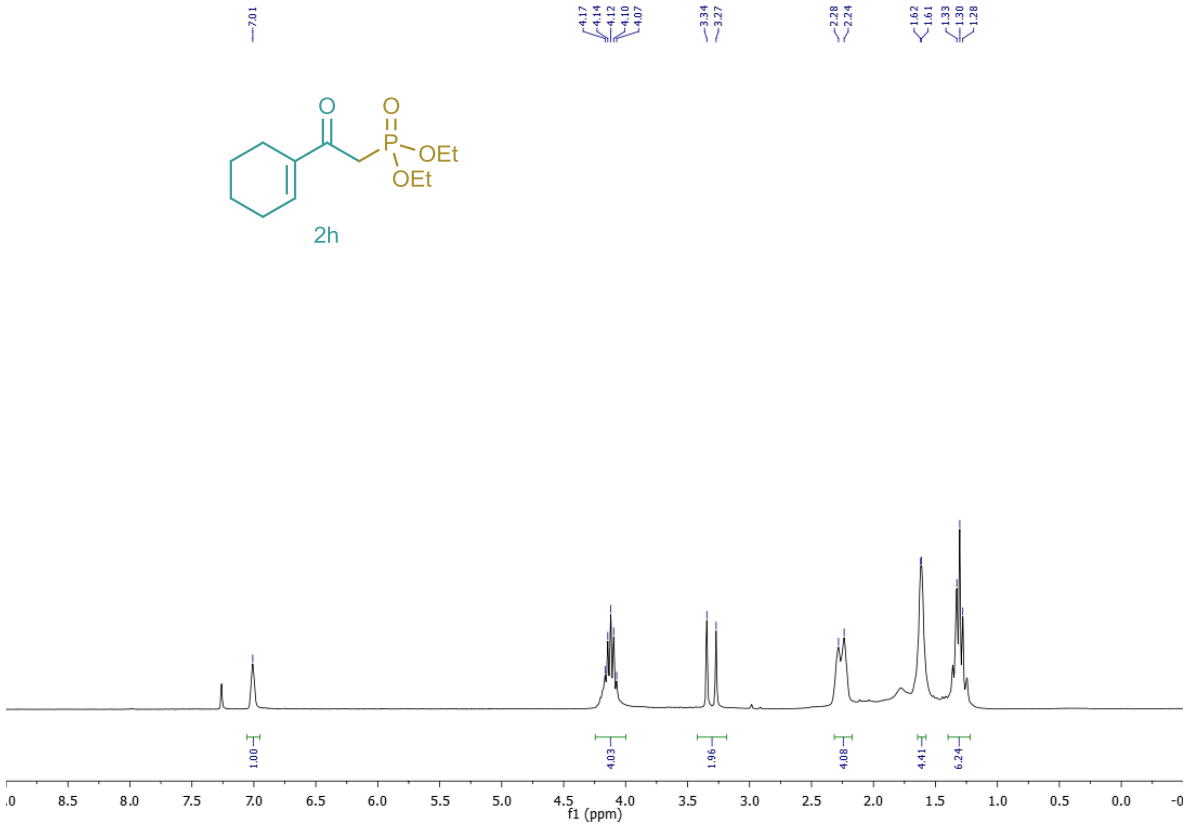

Figure 26. ^{1}H spectrum of **2h** (300 MHz, $CDCl_3$).

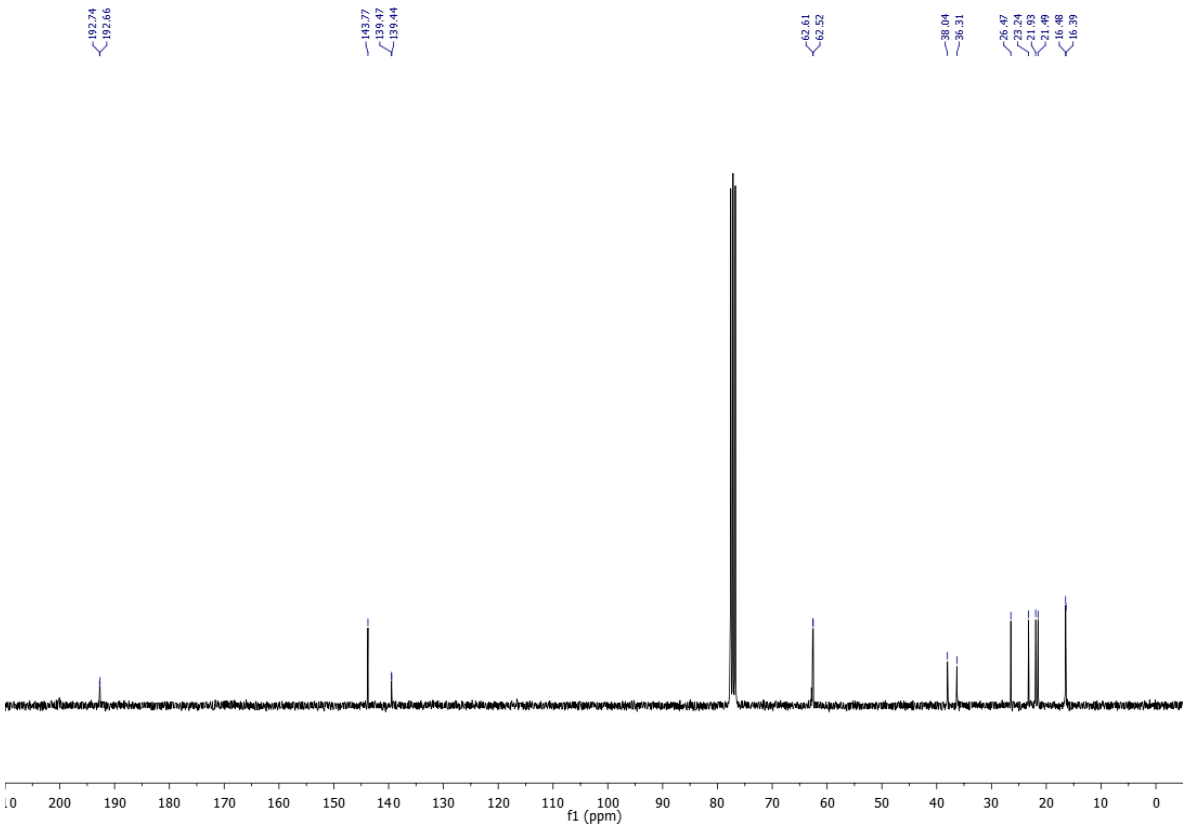

Figure 27. ^{13}C spectrum of **2h** (75 MHz, $CDCl_3$).

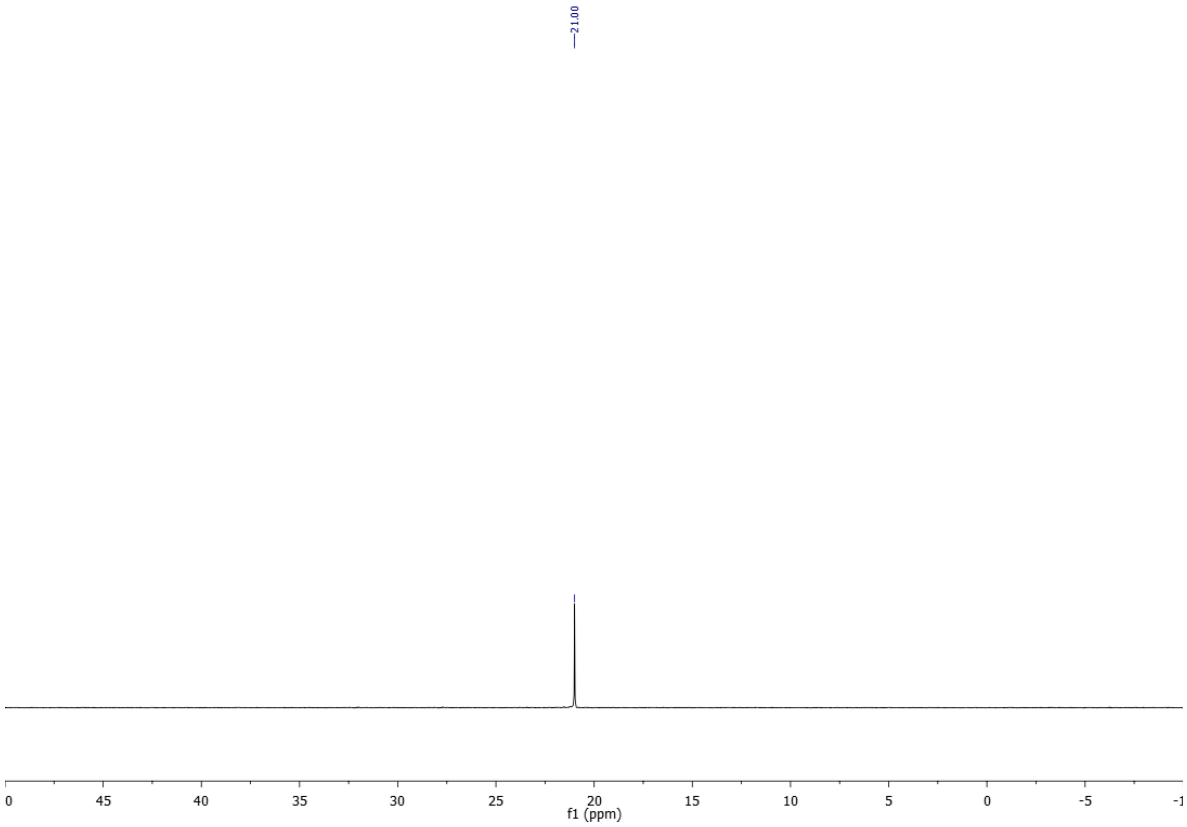

Figure 28. ^{31}P spectrum of **2h** (121 MHz, $CDCl_3$).

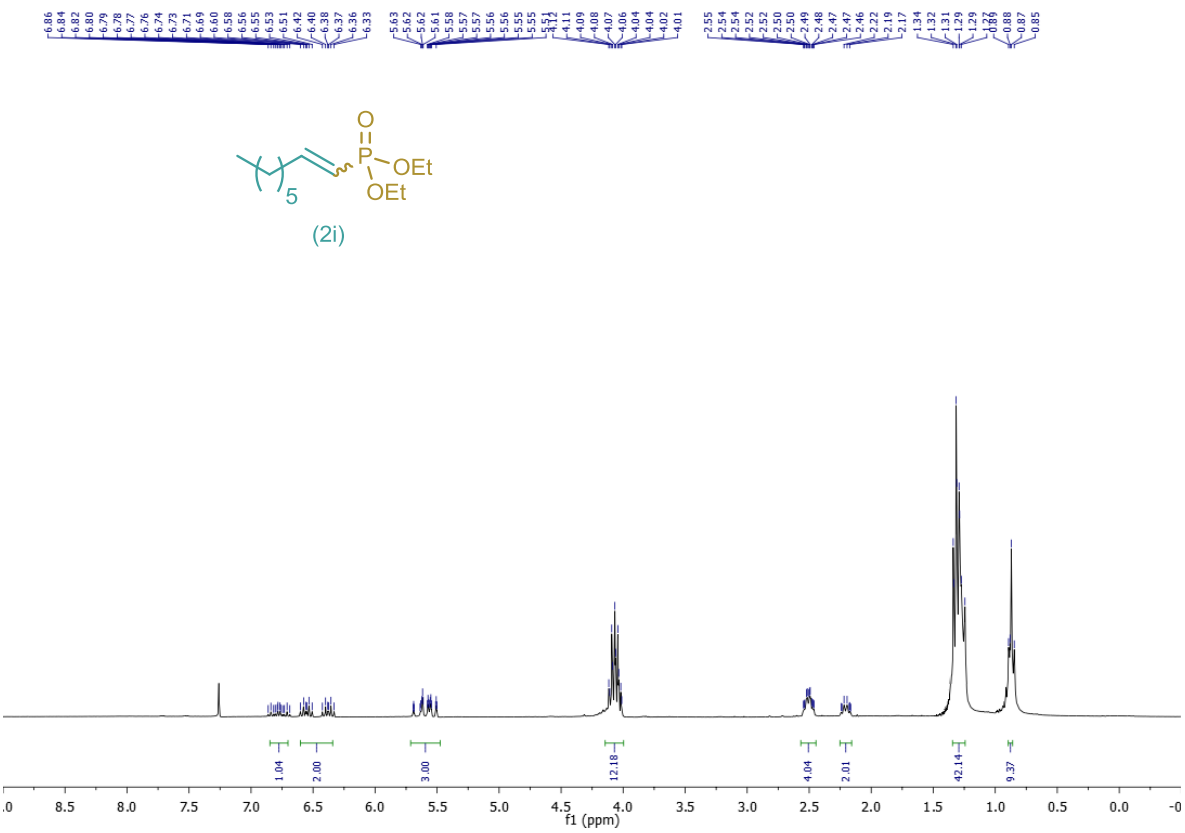

Figure 29. ^{1}H spectrum of **2i** (300 MHz, $CDCl_3$).

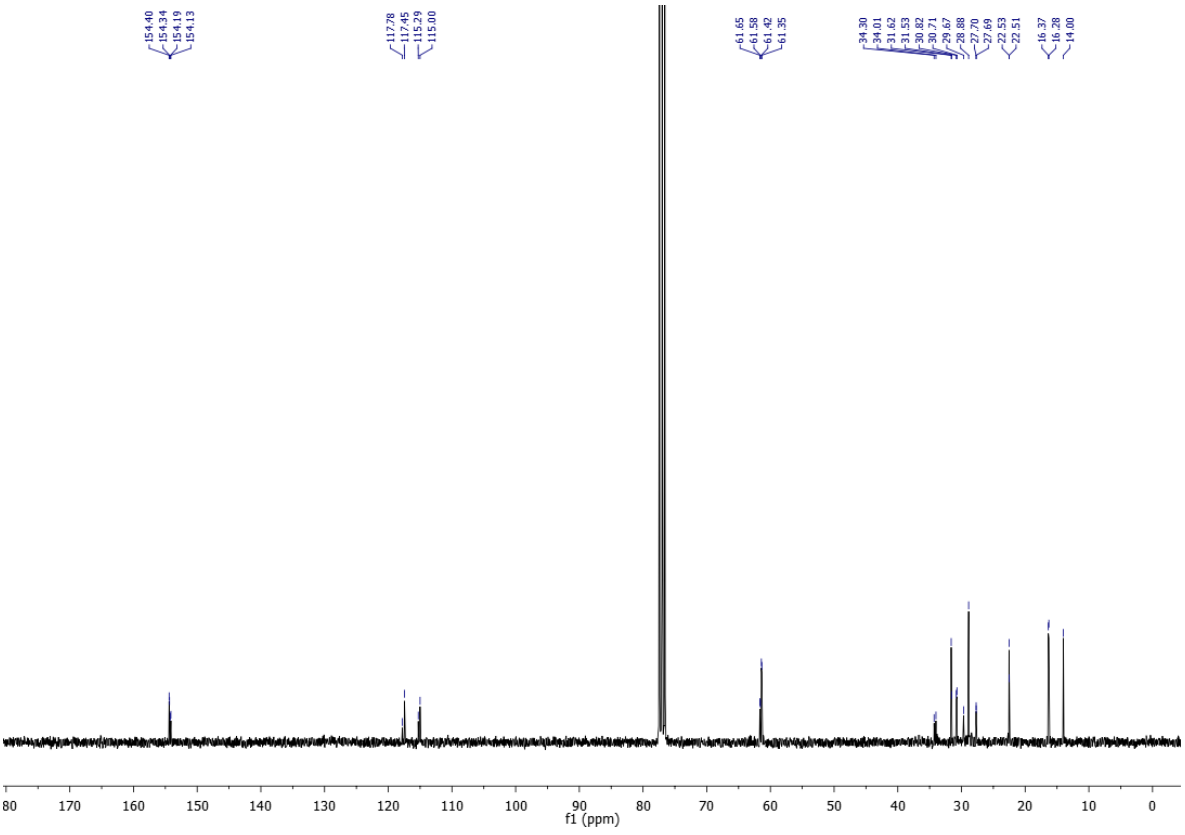

Figure 30. ^{13}C spectrum of **2i** (75 MHz, $CDCl_3$).

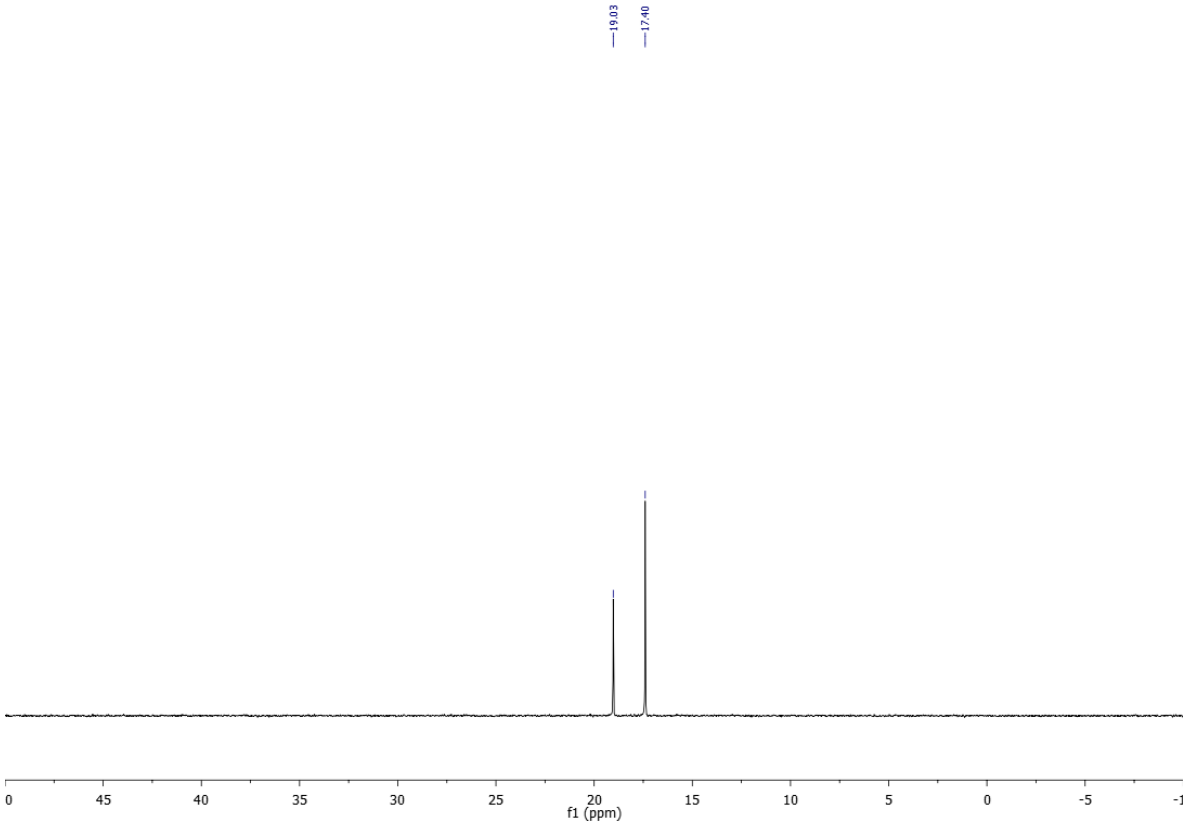

Figure 31. ^{31}P spectrum of **2i** (121 MHz, $CDCl_3$).

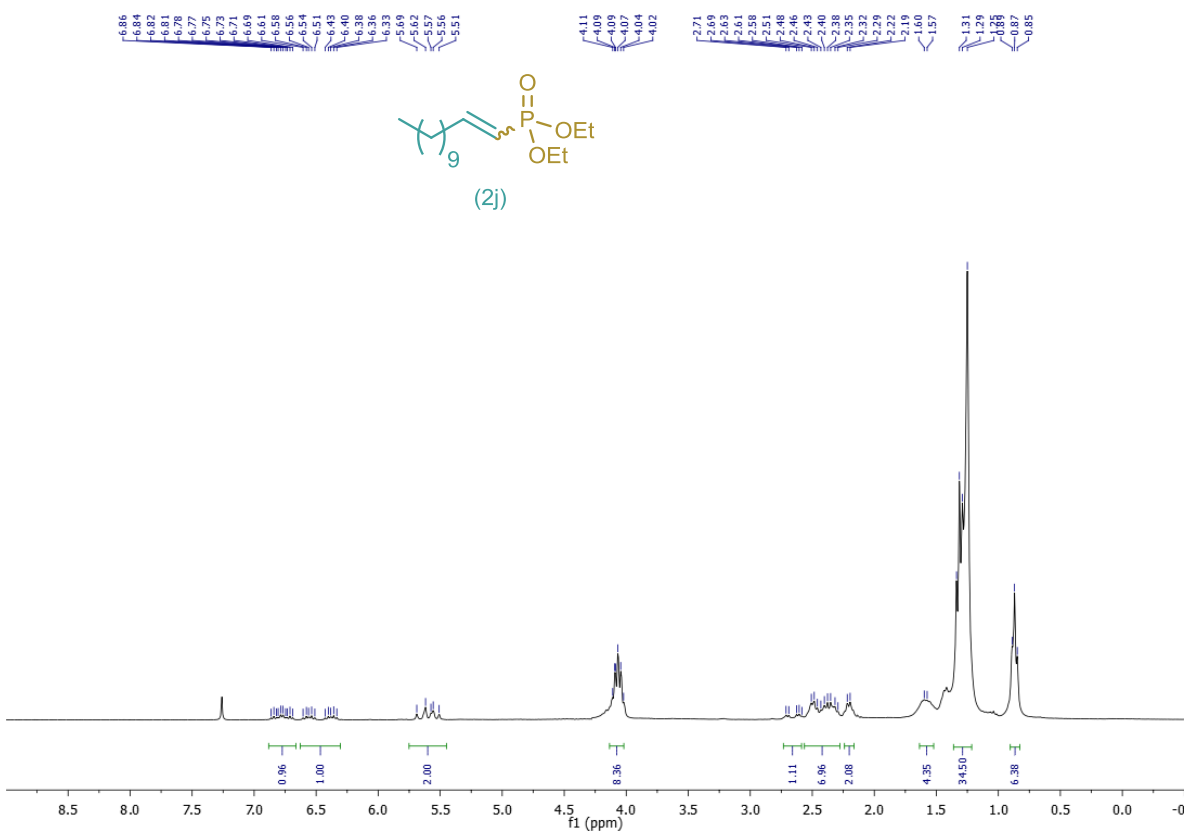

Figure 32. ^{1}H spectrum of **2j** (300 MHz, $CDCl_3$).

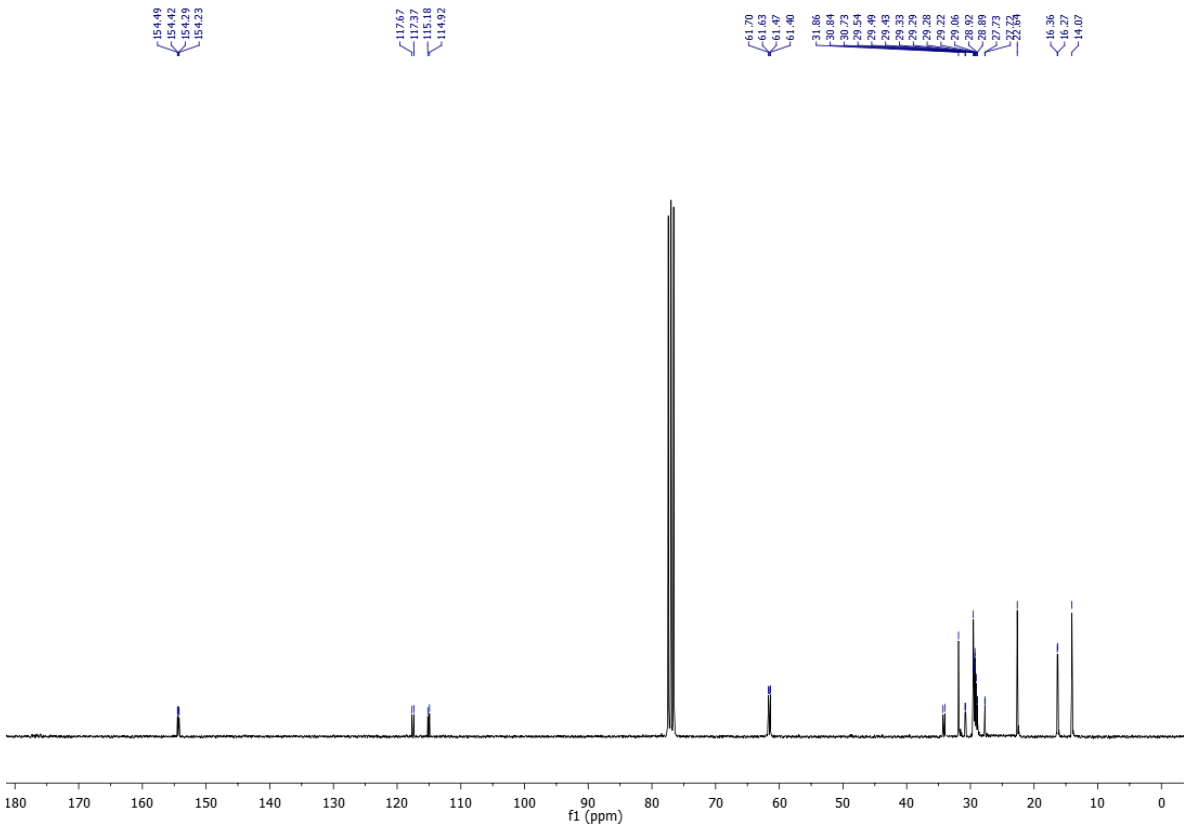

Figure 33. ^{13}C spectrum of **2j** (75 MHz, $CDCl_3$).

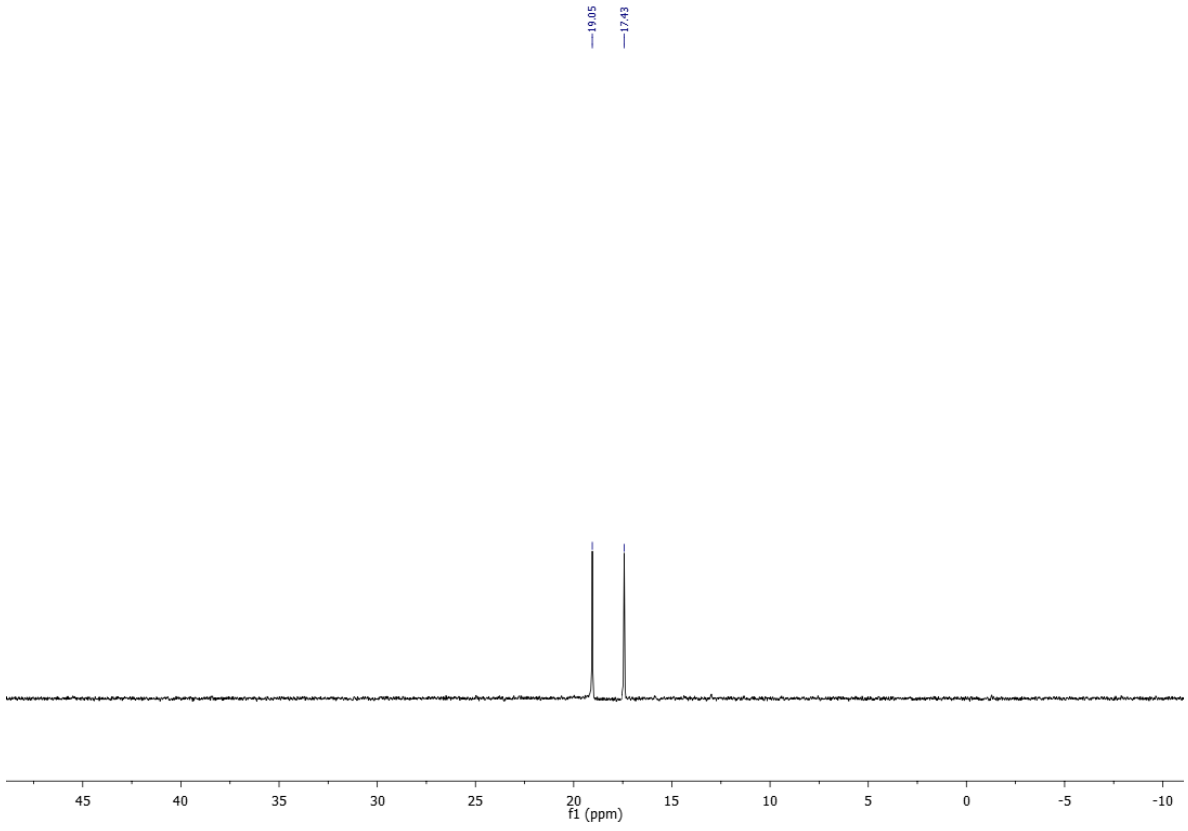

Figure 34. ^{31}P spectrum of **2j** (121 MHz, $CDCl_3$).

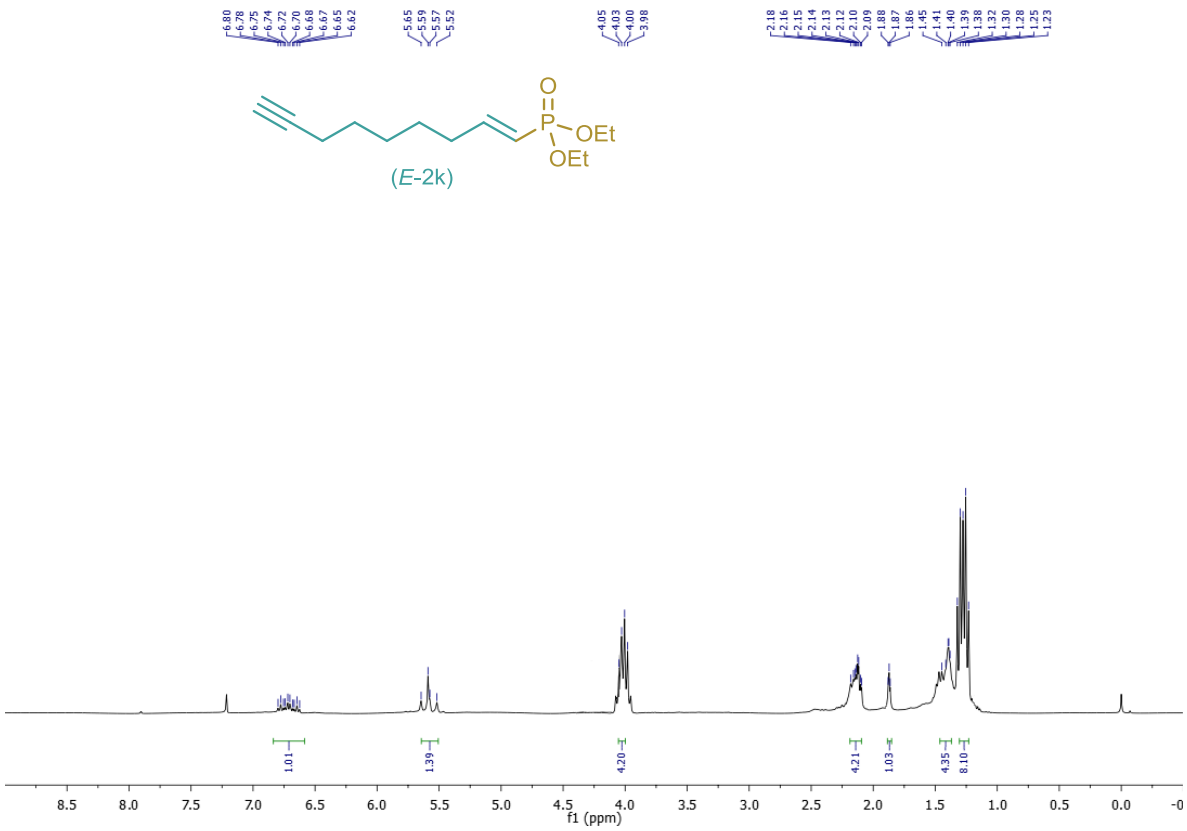

Figure 35. ^{1}H spectrum of ***E*-2k** (300 MHz, $CDCl_3$).

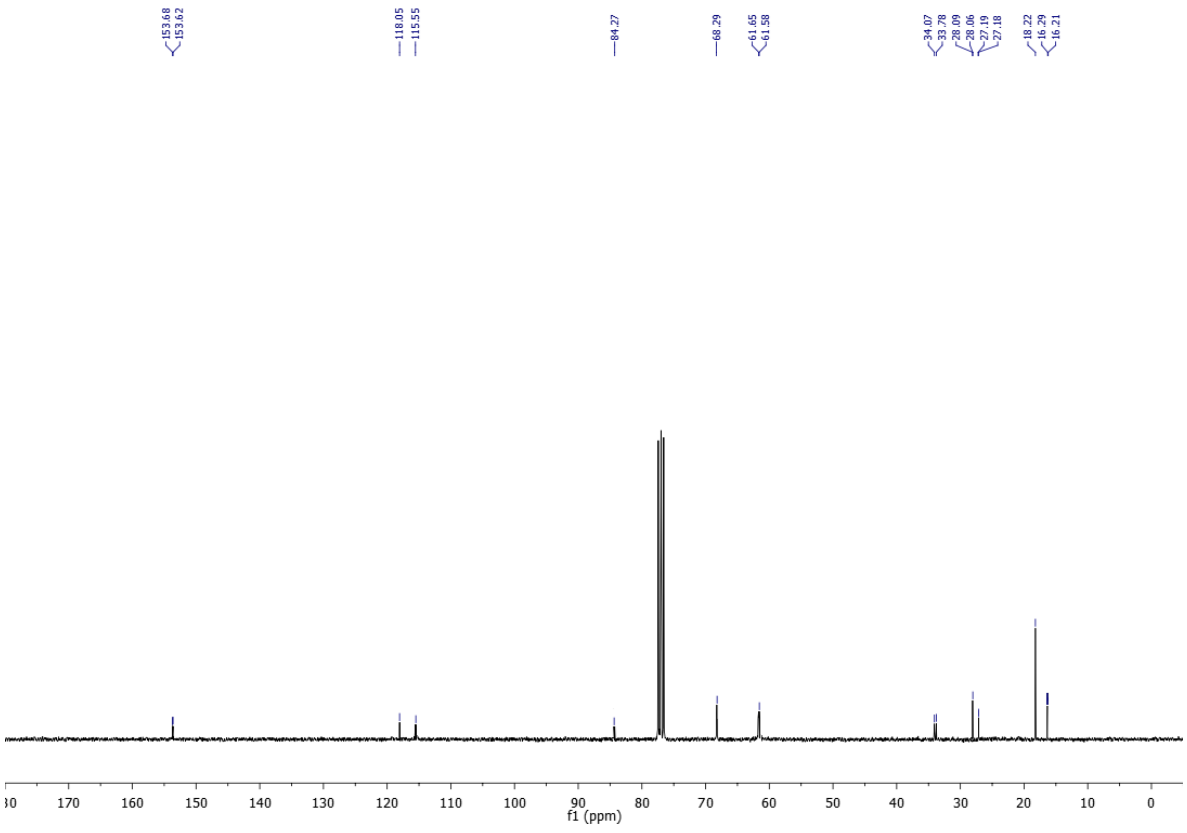

Figure 36. ^{13}C spectrum of ***E*-2k** (75 MHz, $CDCl_3$).

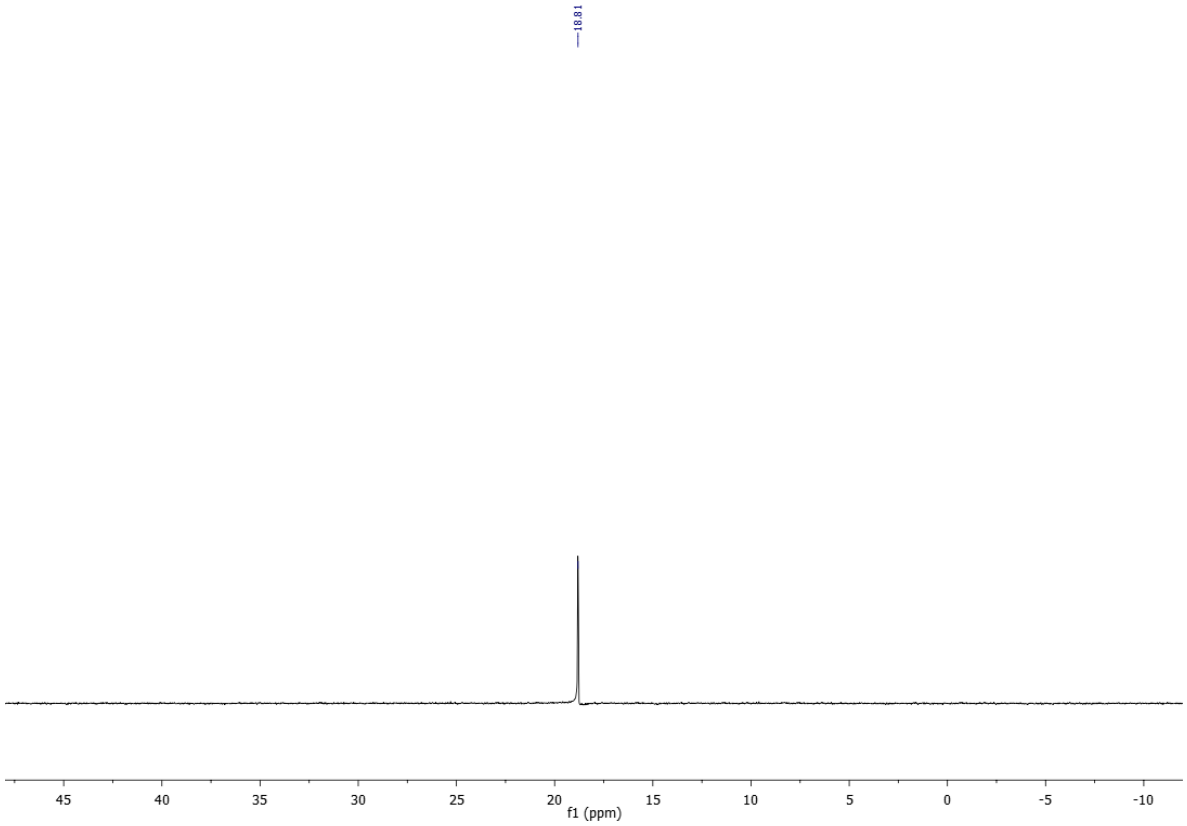

Figure 37. ^{31}P spectrum of ***E*-2k** (121 MHz, $CDCl_3$).

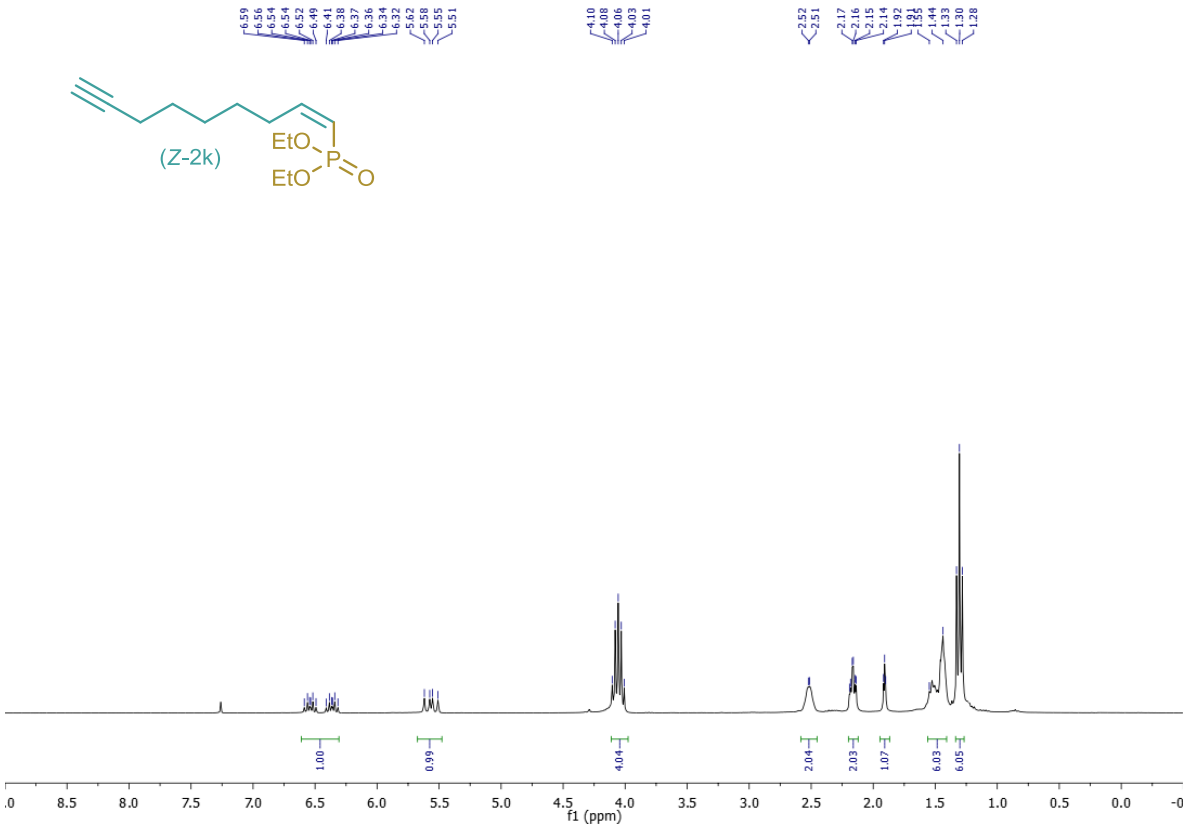

Figure 38. ^{1}H spectrum of ***Z*-2k** (300 MHz, $CDCl_3$).

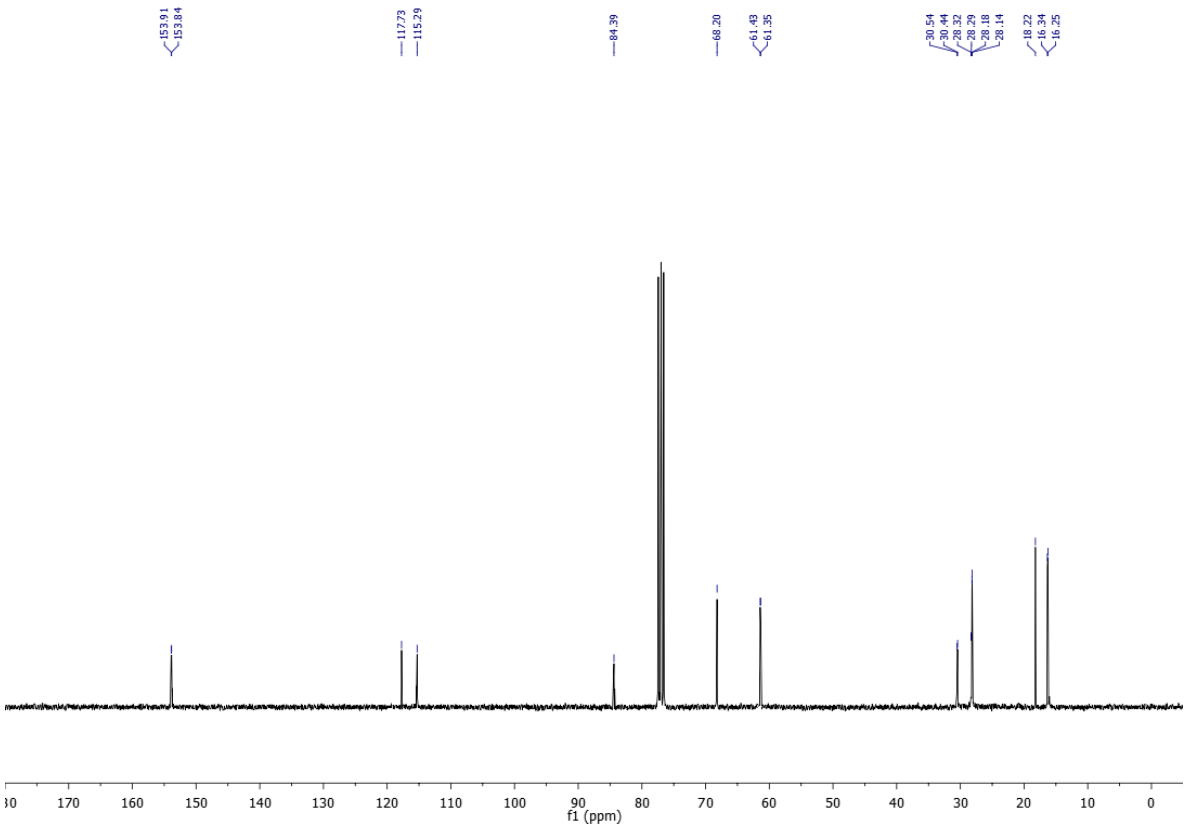

Figure 39. ^{13}C spectrum of ***Z*-2k** (75 MHz, $CDCl_3$).

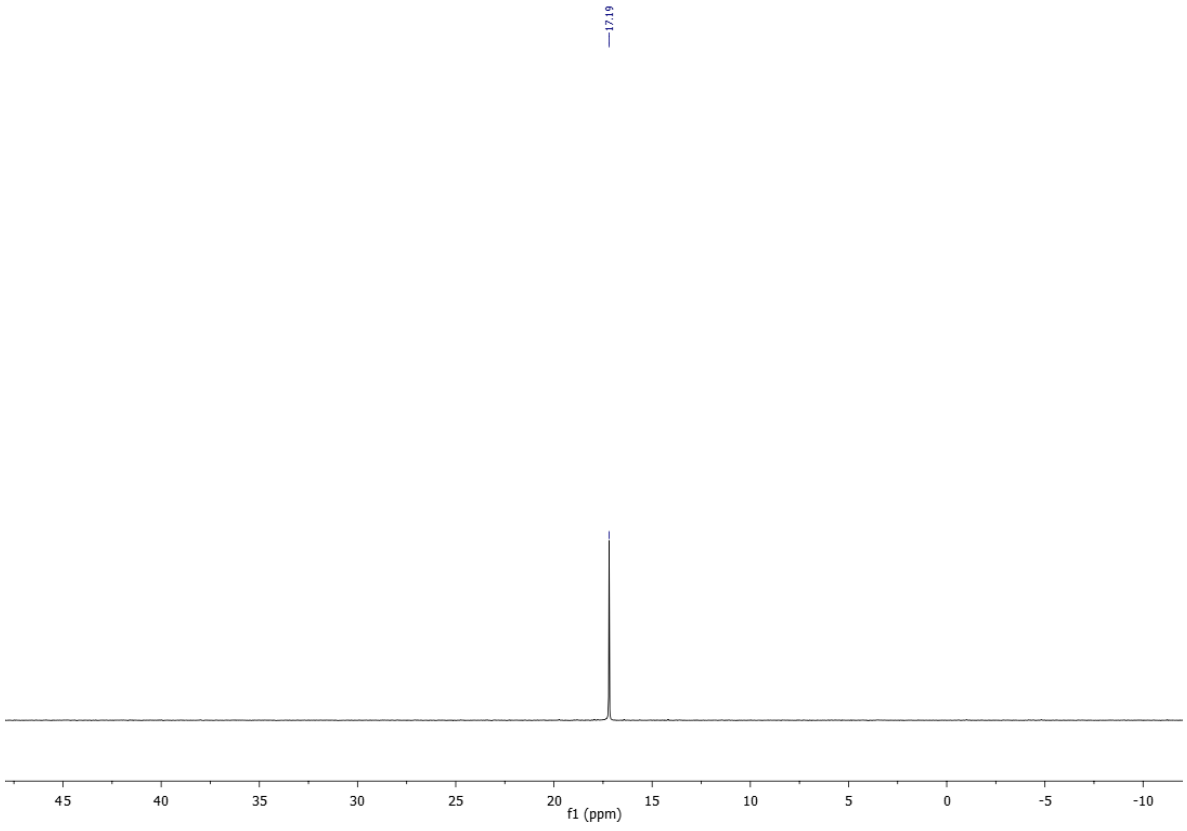

Figure 40. ^{31}P spectrum of ***Z*-2k** (121 MHz, $CDCl_3$).

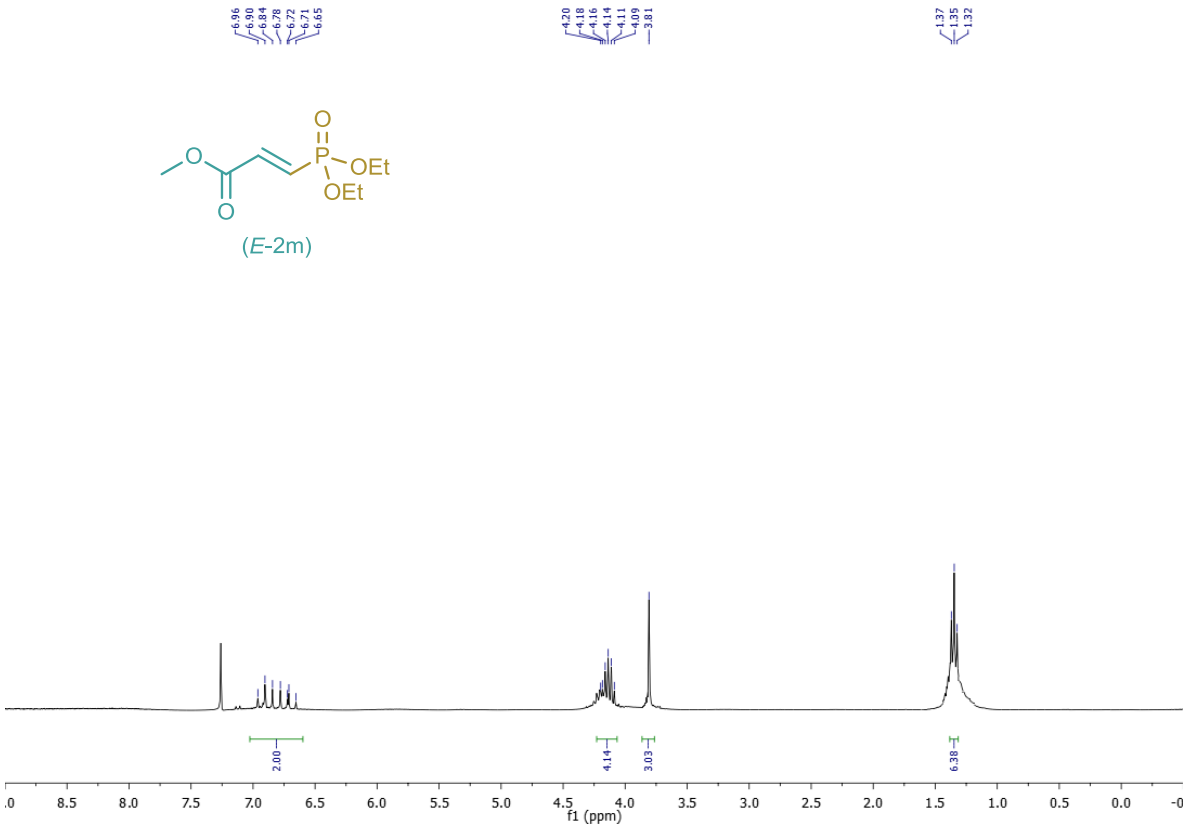

Figure 41. ^{1}H spectrum of ***E*-2m** (300 MHz, $CDCl_3$).

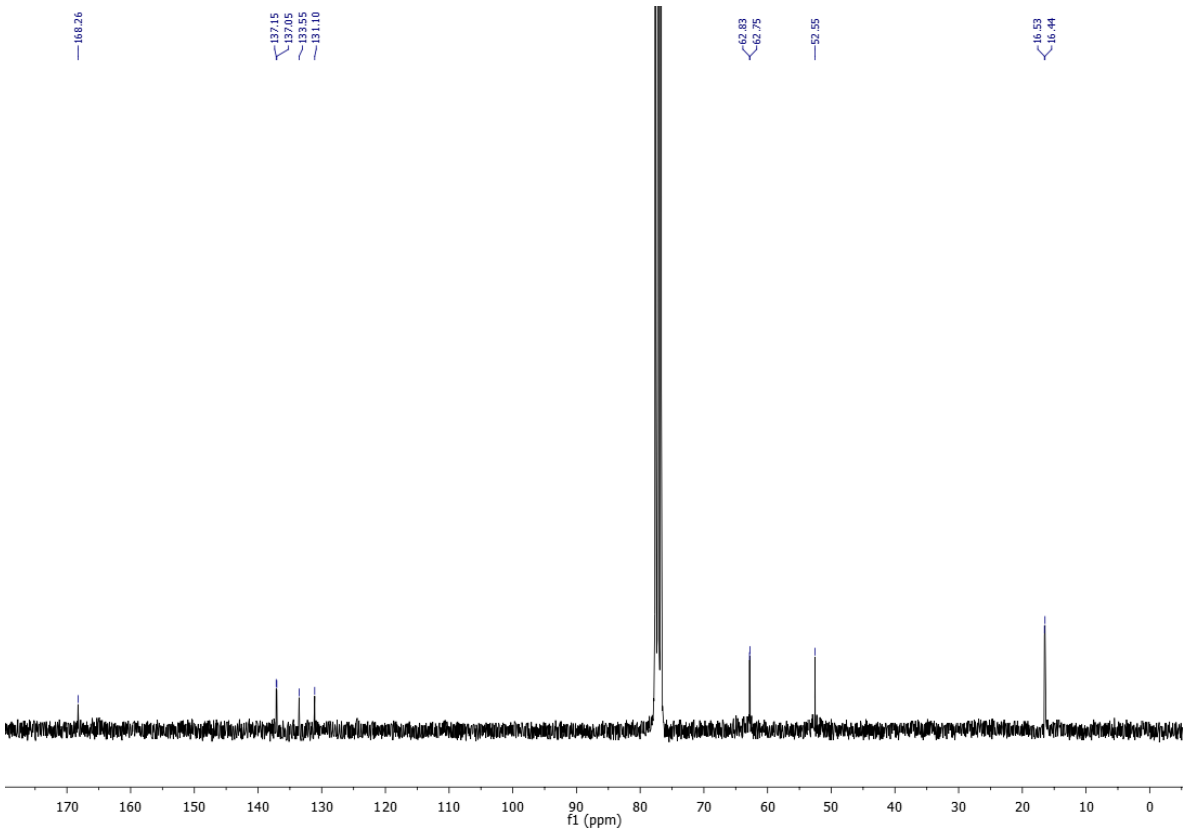

Figure 42. ^{13}C spectrum of ***E*-2m** (75 MHz, $CDCl_3$).

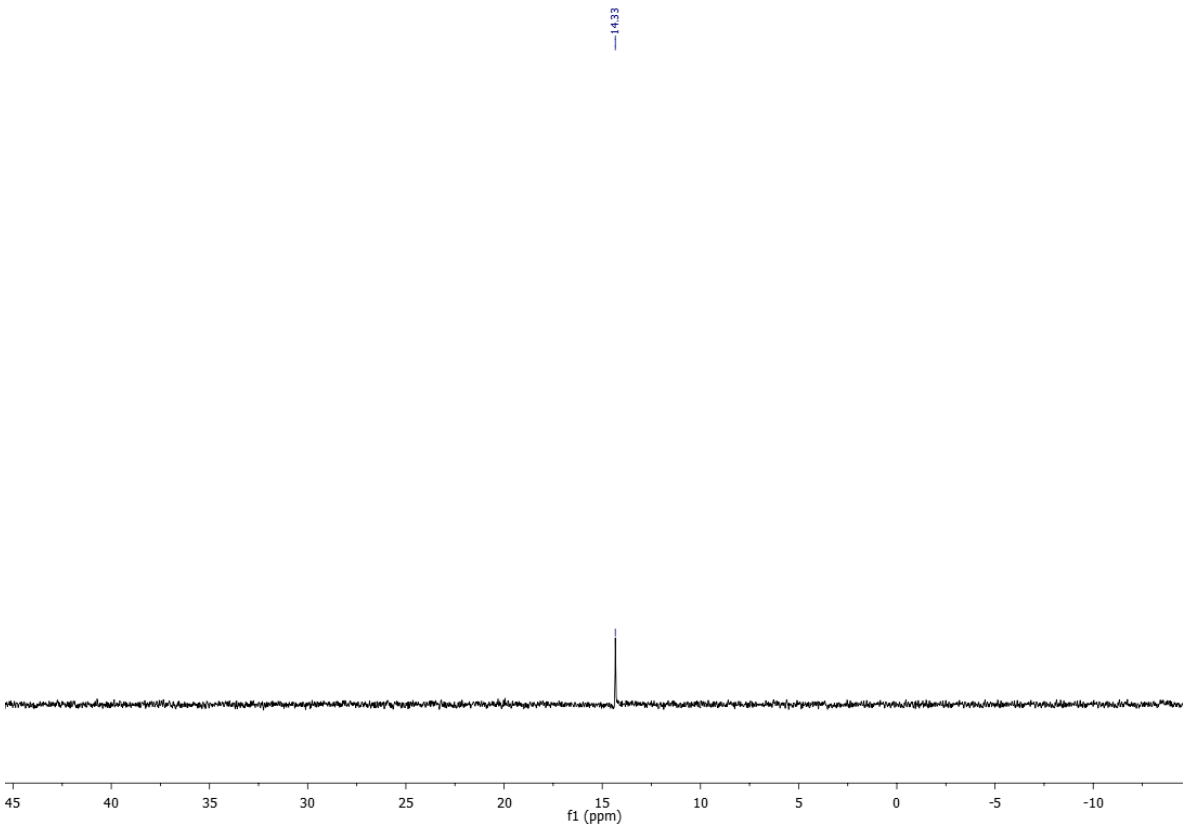

Figure 43. ^{31}P spectrum of ***E*-2m** (121 MHz, $CDCl_3$).

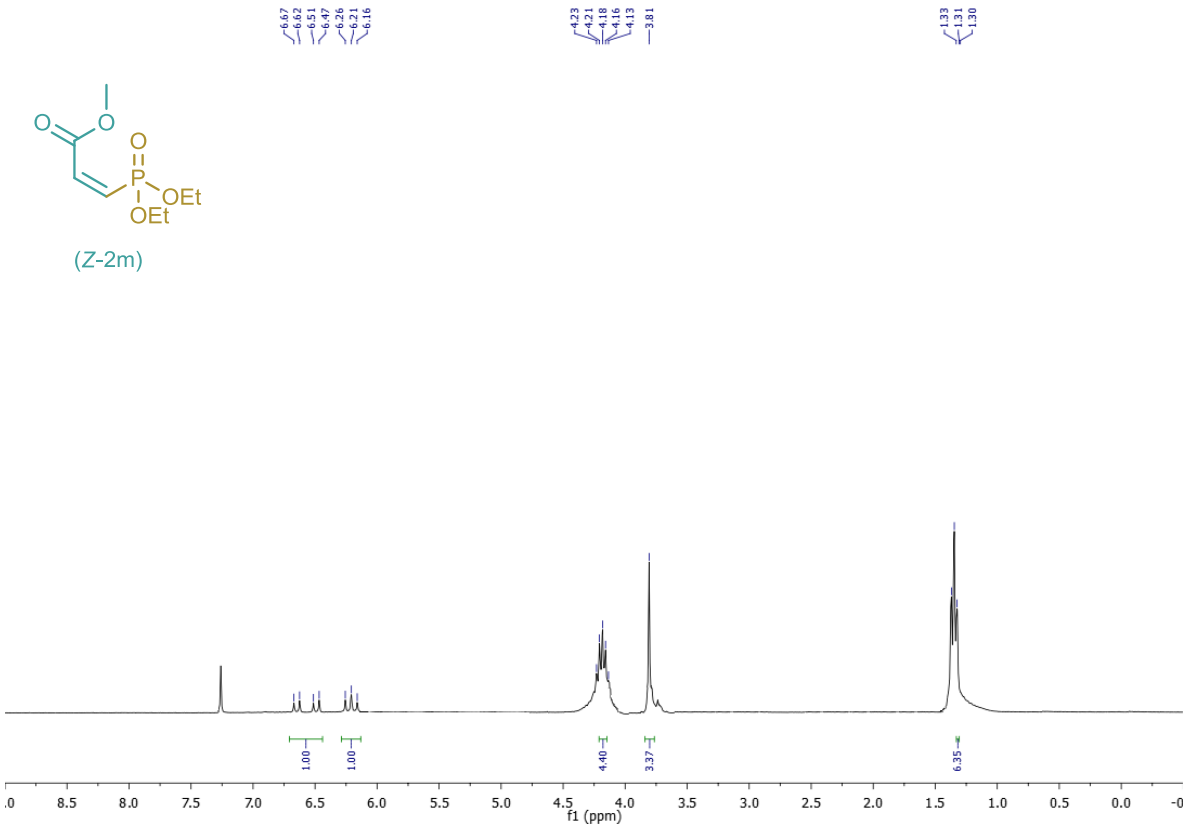

Figure 44. ^{1}H spectrum of ***Z*-2m** (300 MHz, $CDCl_3$).

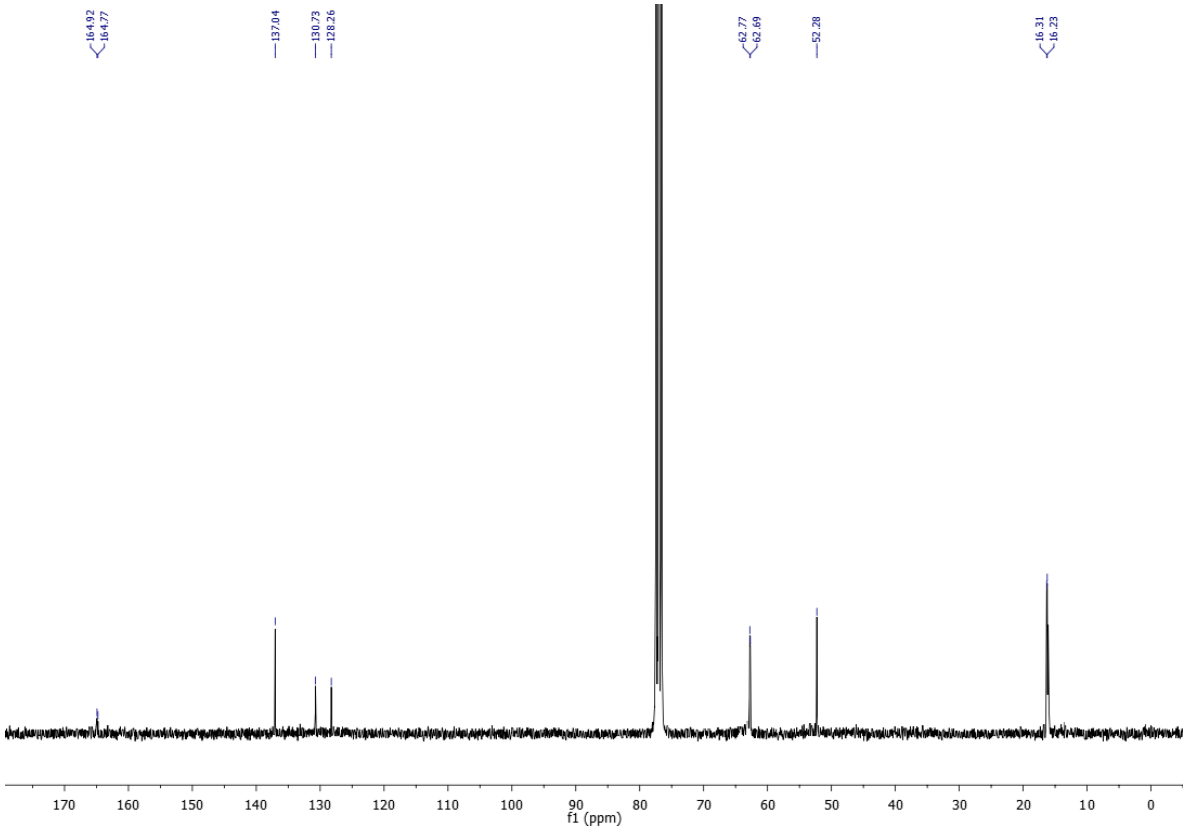

Figure 45. ^{13}C spectrum of ***Z*-2m** (75 MHz, $CDCl_3$).

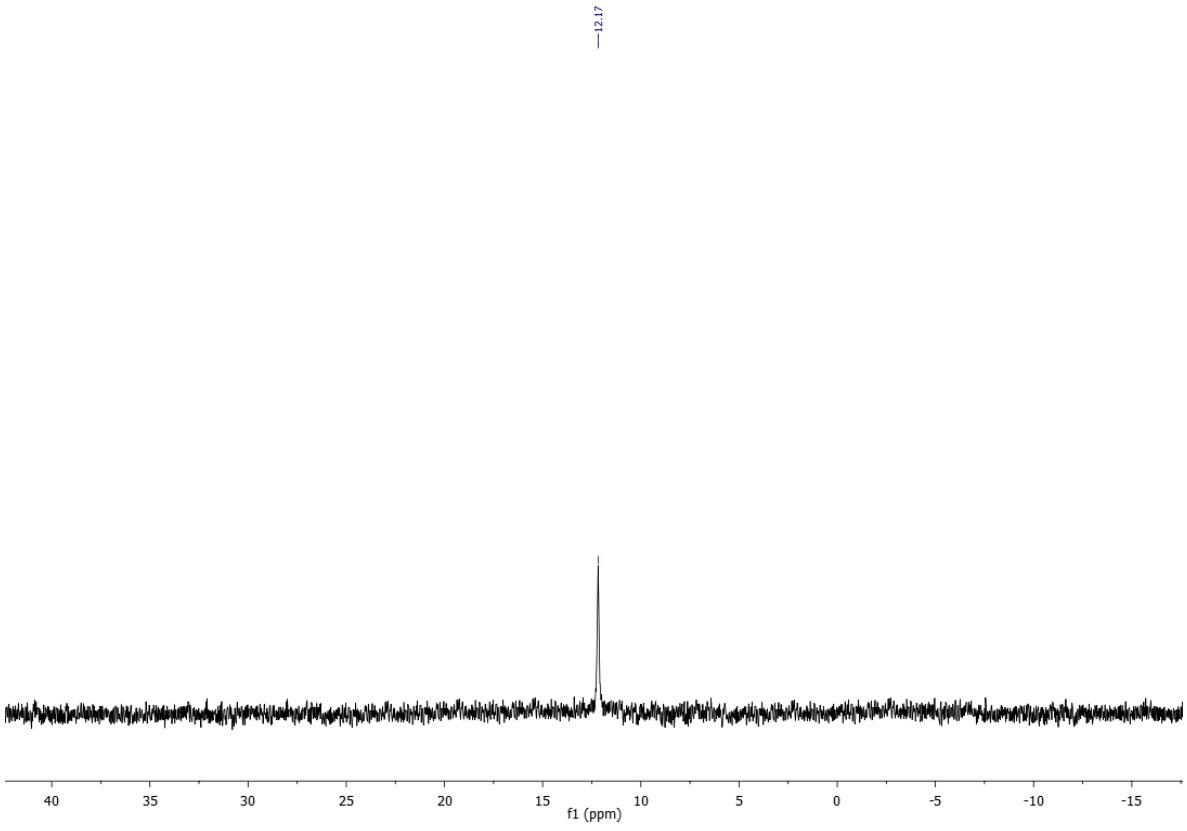

Figure 46. ^{31}P spectrum of ***Z*-2m** (121 MHz, $CDCl_3$).

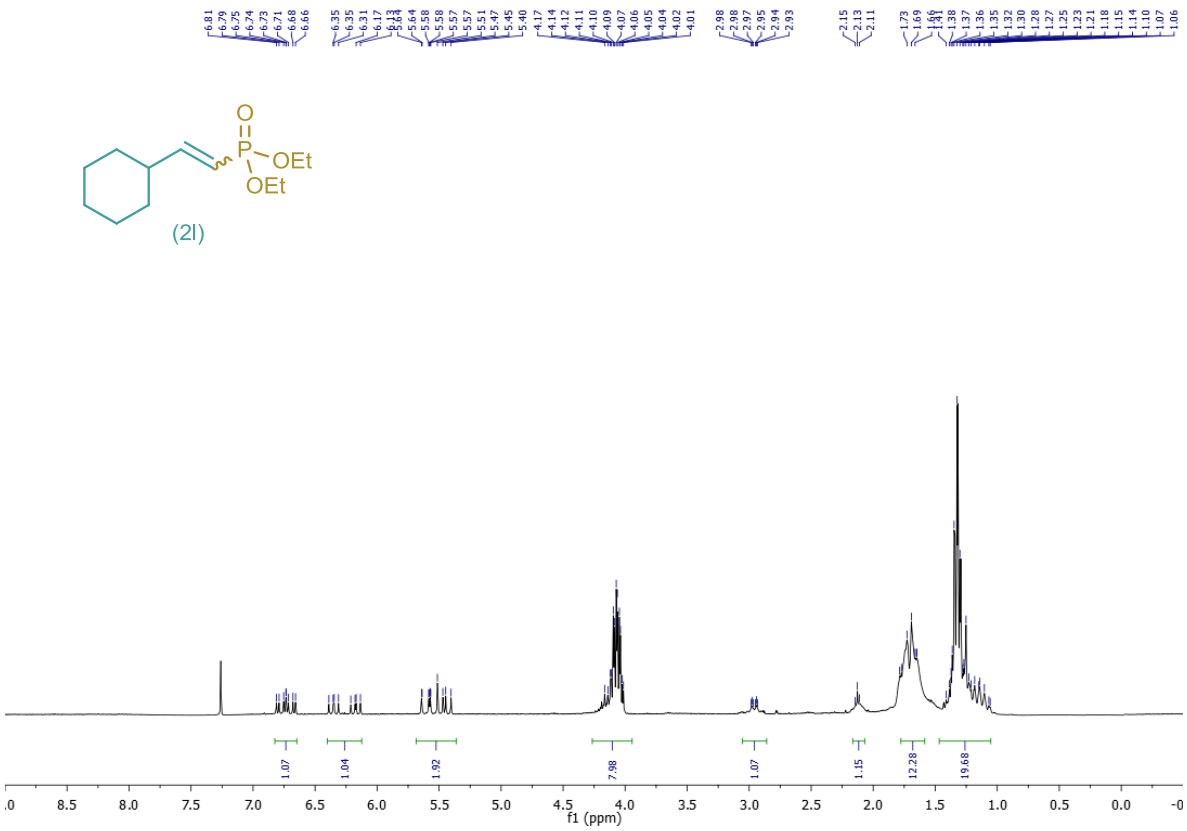

Figure 47. ^{1}H spectrum of **2l** (300 MHz, $CDCl_3$).

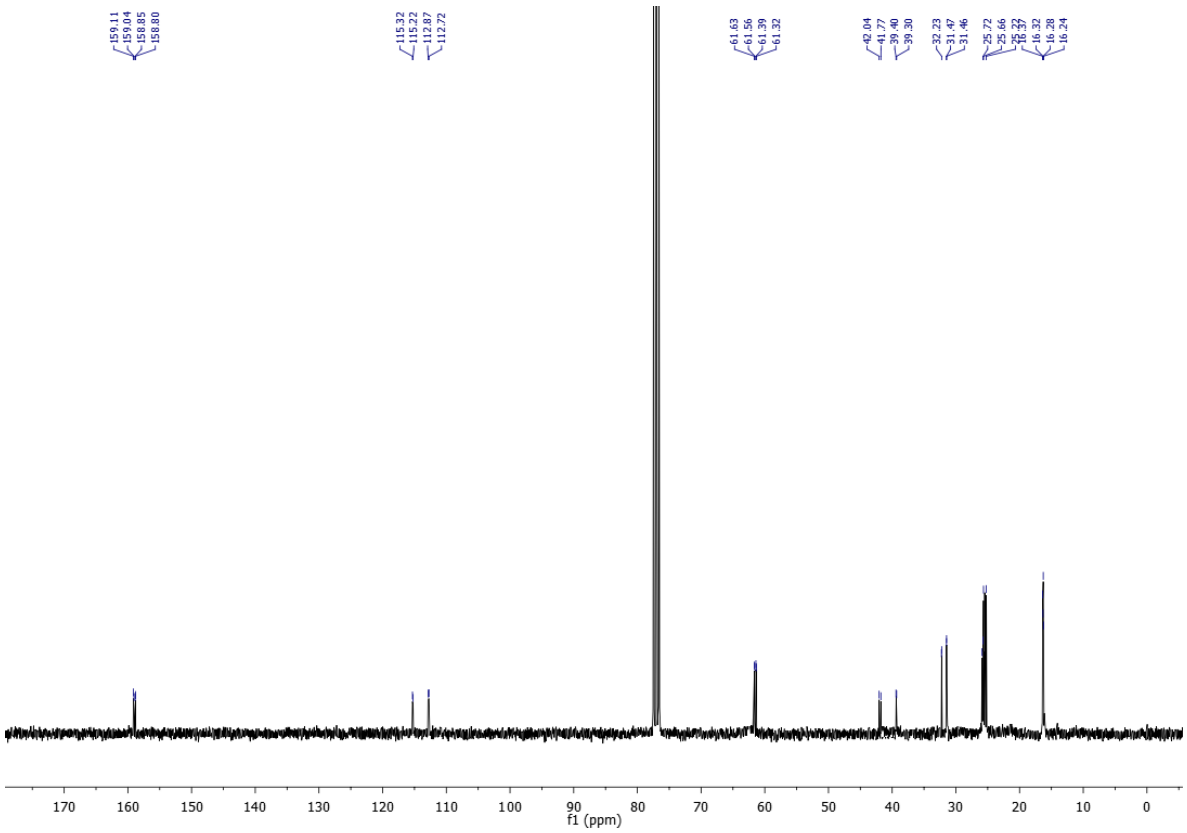

Figure 48. ^{13}C spectrum of **2l** (75 MHz, $CDCl_3$).

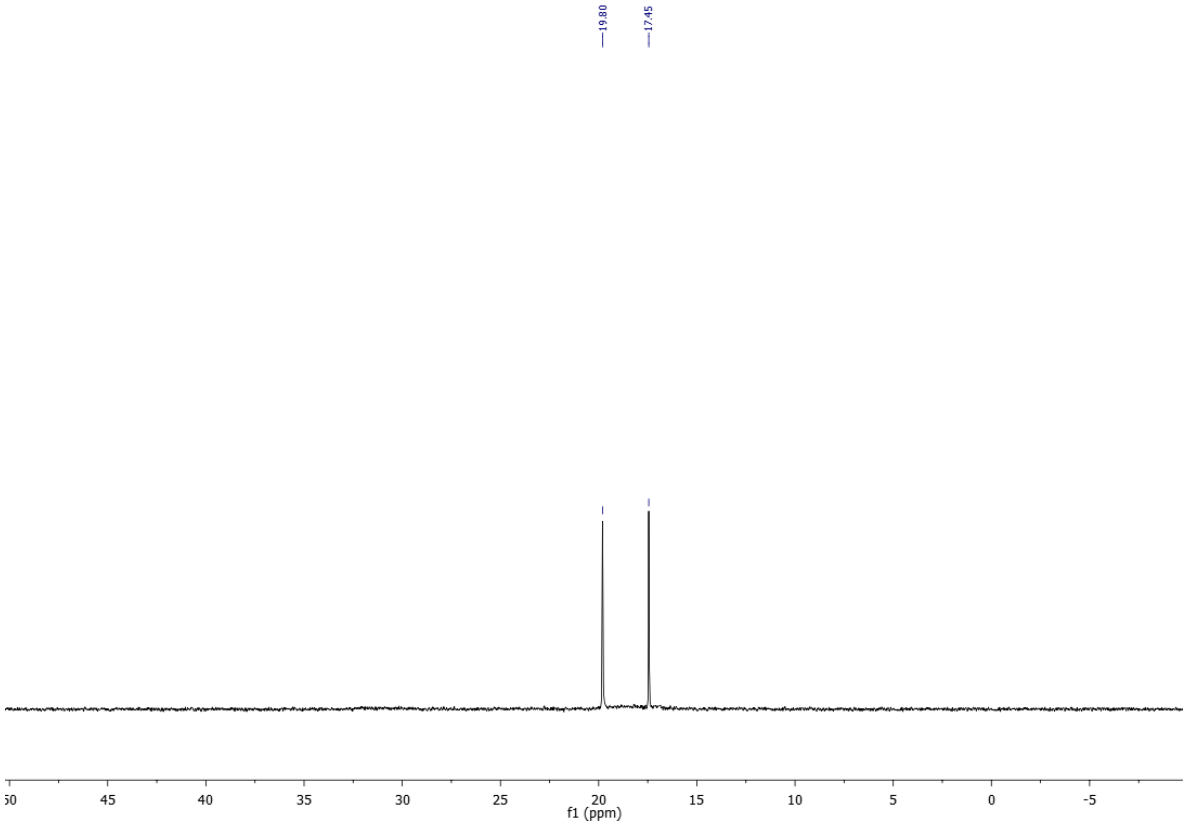

Figure 49. ^{31}P spectrum of **2l** (121 MHz, $CDCl_3$).

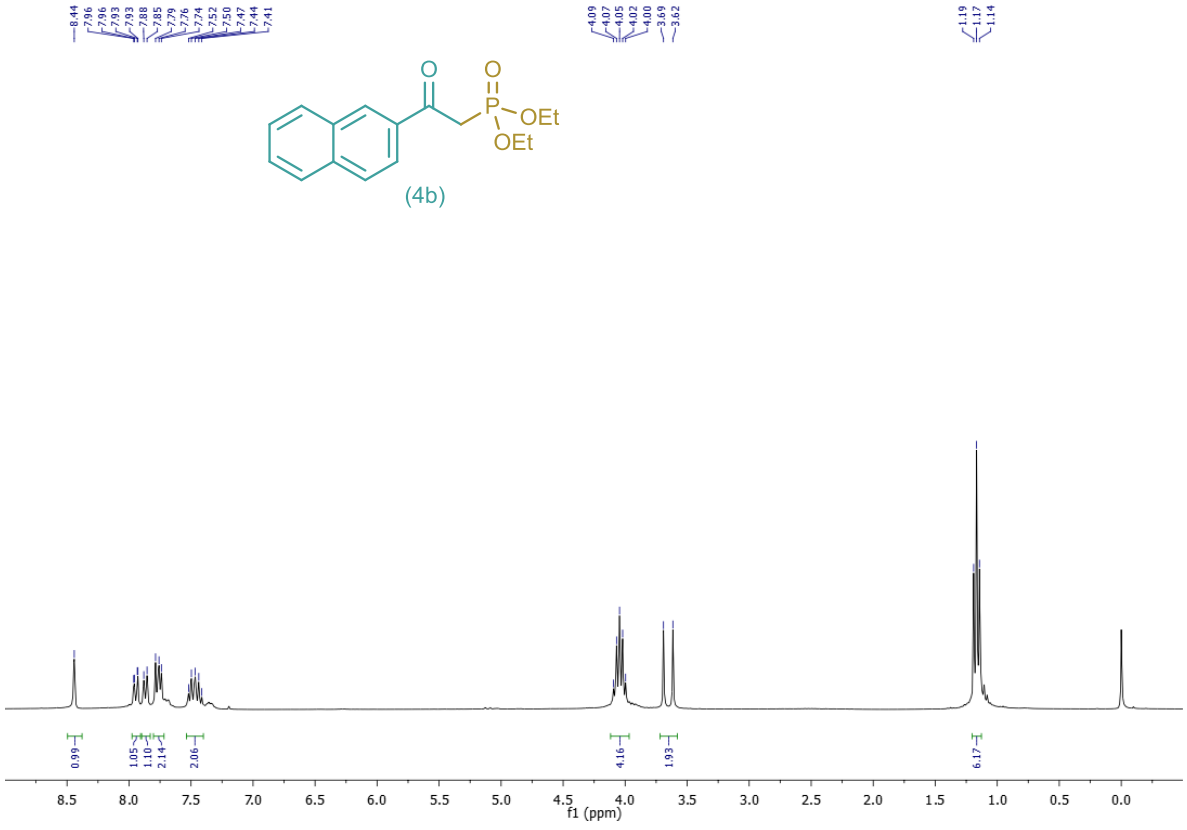

Figure 50. ^{1}H spectrum of **4b** (300 MHz, $CDCl_3$).

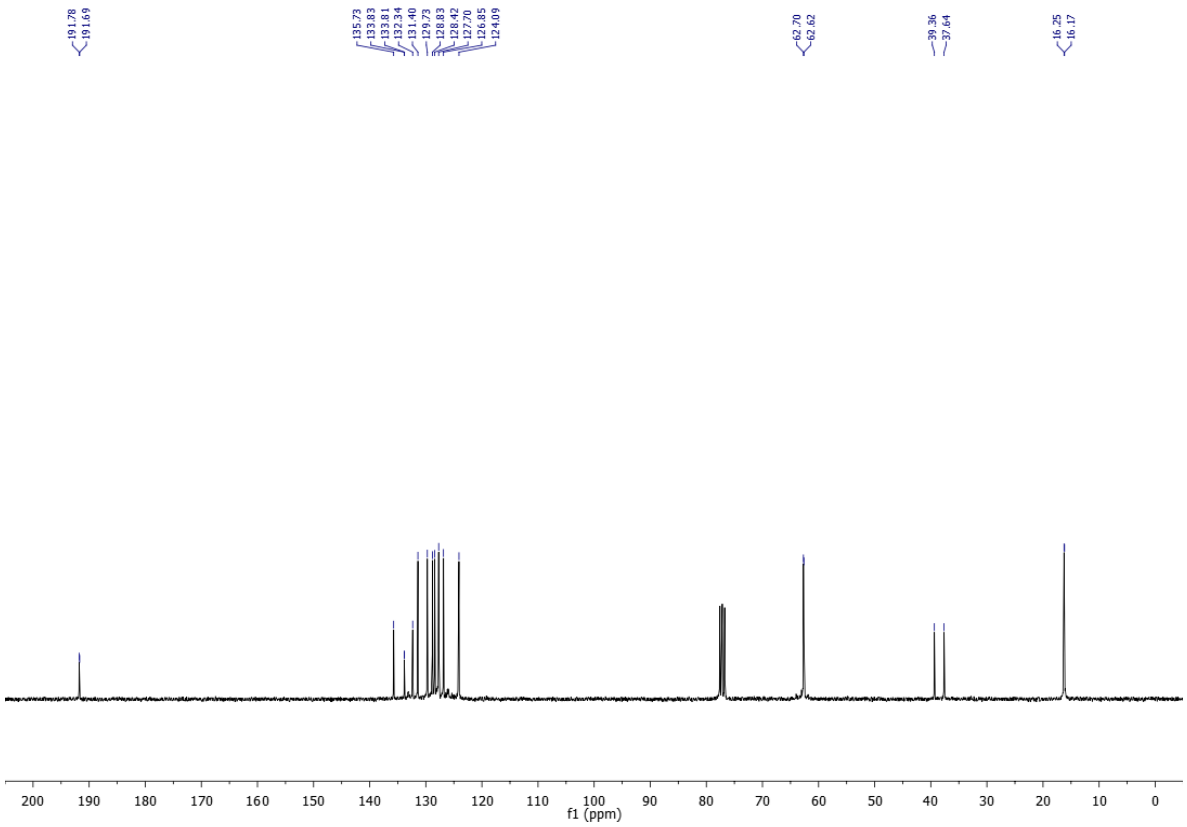

Figure 51. ^{13}C spectrum of **4b** (75 MHz, $CDCl_3$).

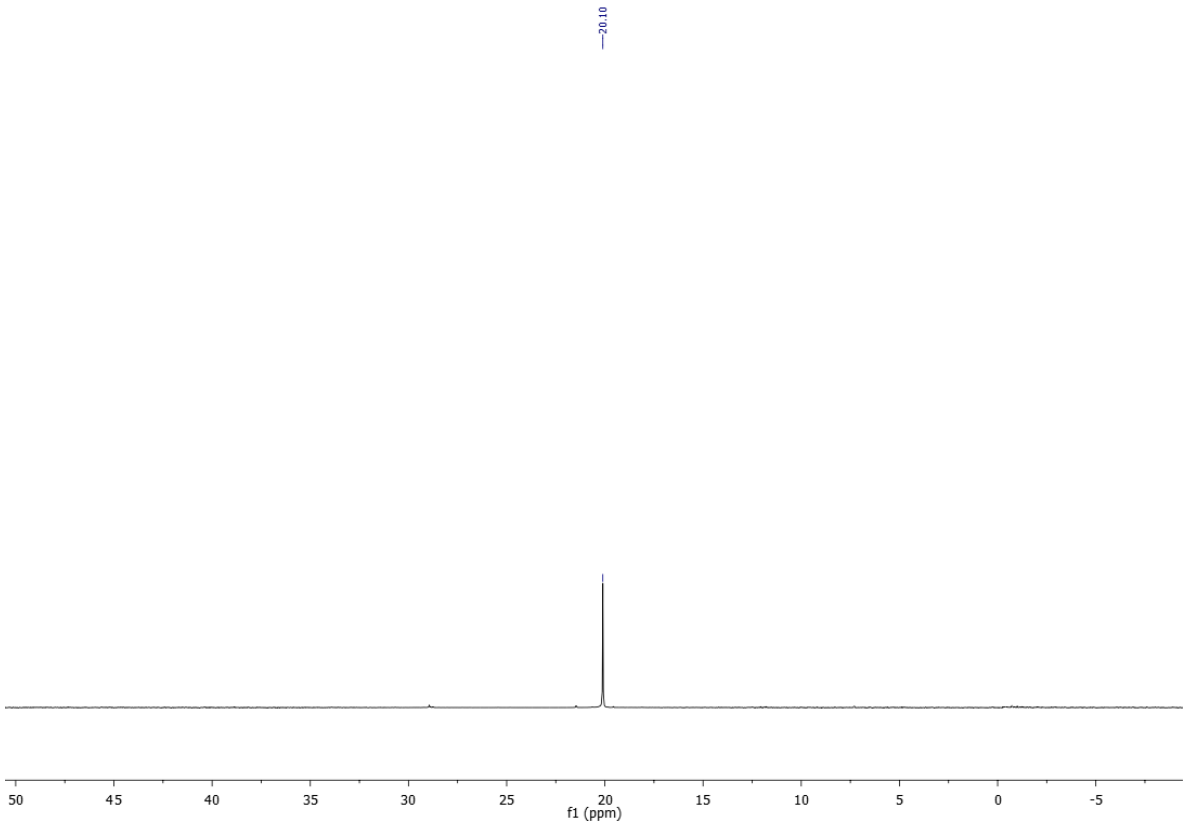

Figure 52. ^{31}P spectrum of **4b** (121 MHz, $CDCl_3$).

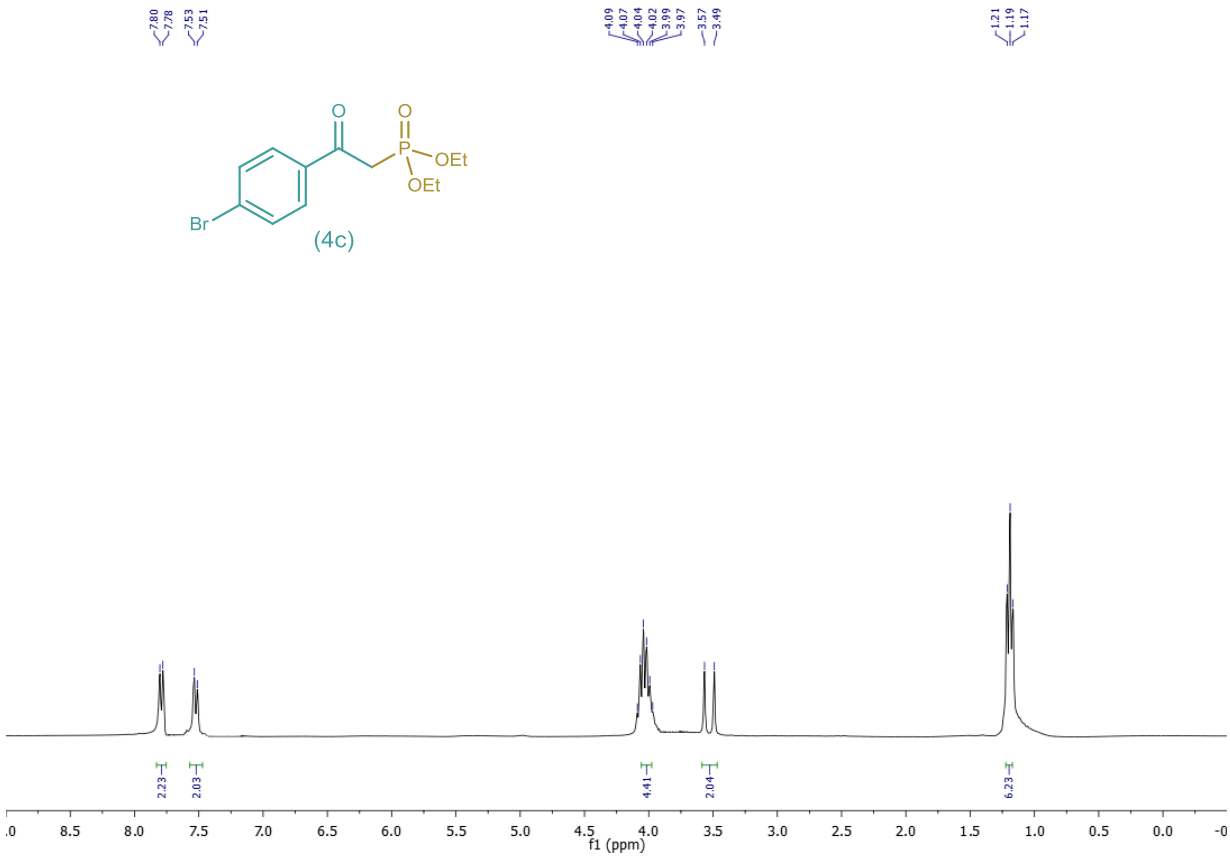

Figure 53. ^{1}H spectrum of **4c** (300 MHz, $CDCl_3$).

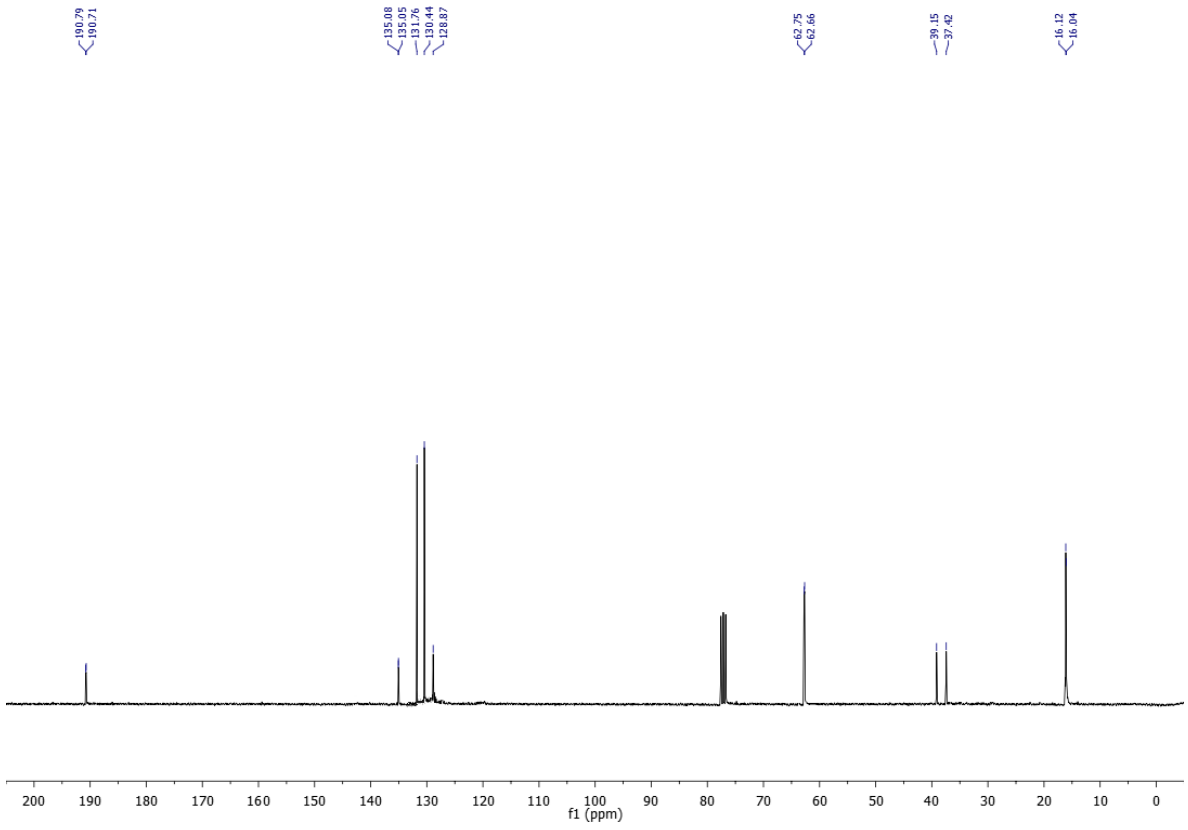

Figure 54. ^{13}C spectrum of **4c** (75 MHz, $CDCl_3$).

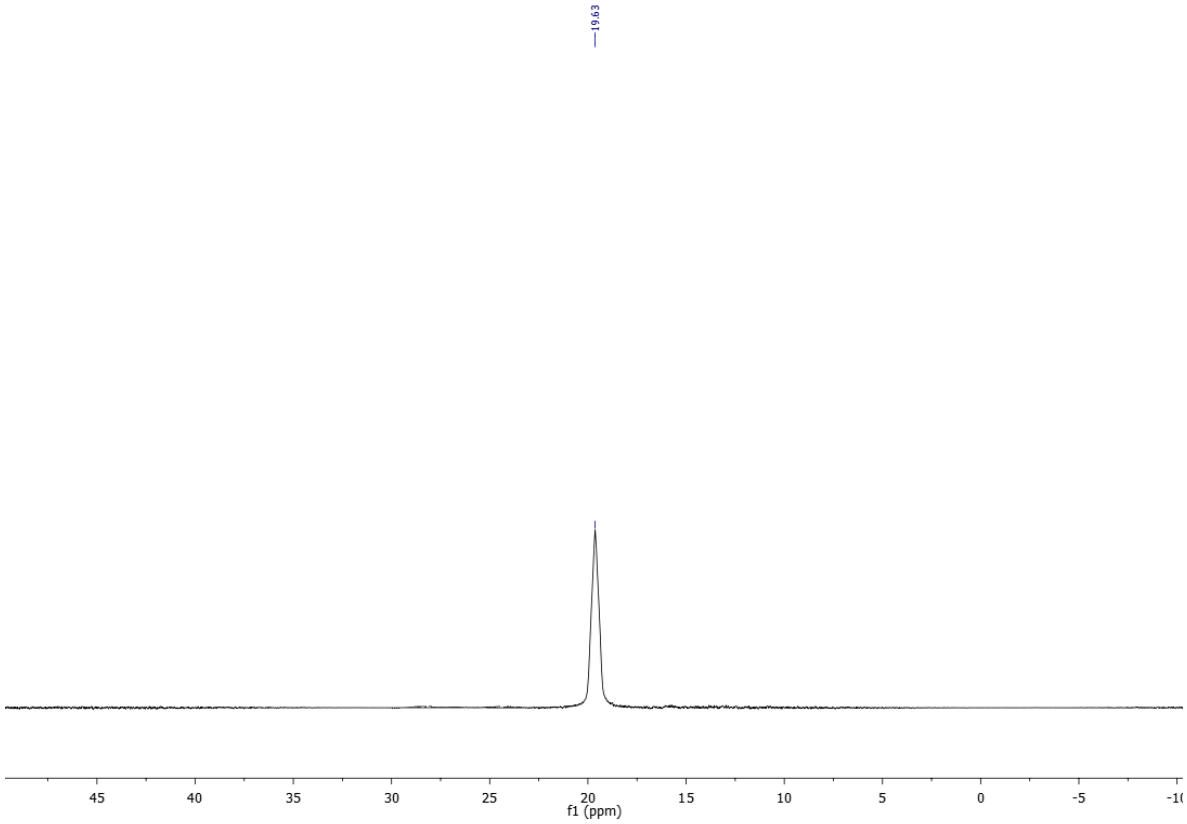

Figure 55. ^{31}P spectrum of **4c** (121 MHz, $CDCl_3$).

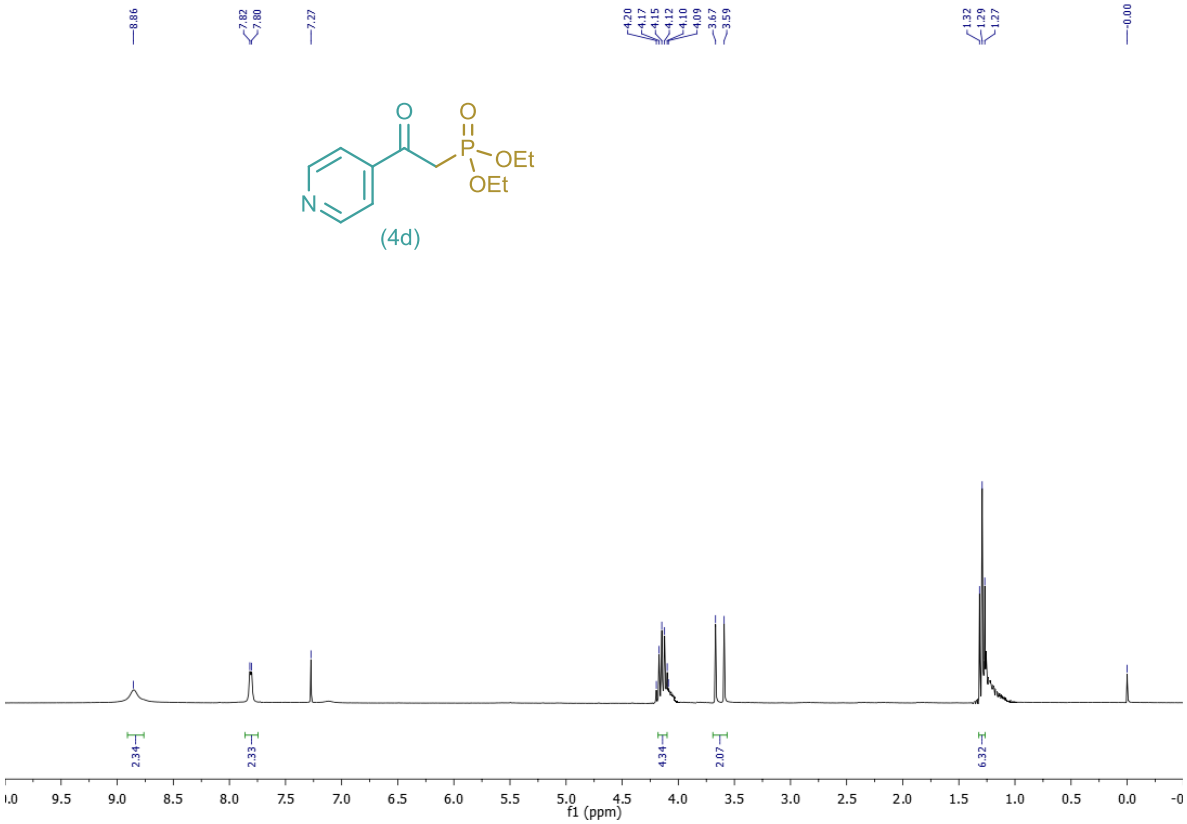

Figure 56. ^{1}H spectrum of **4d** (300 MHz, $CDCl_3$).

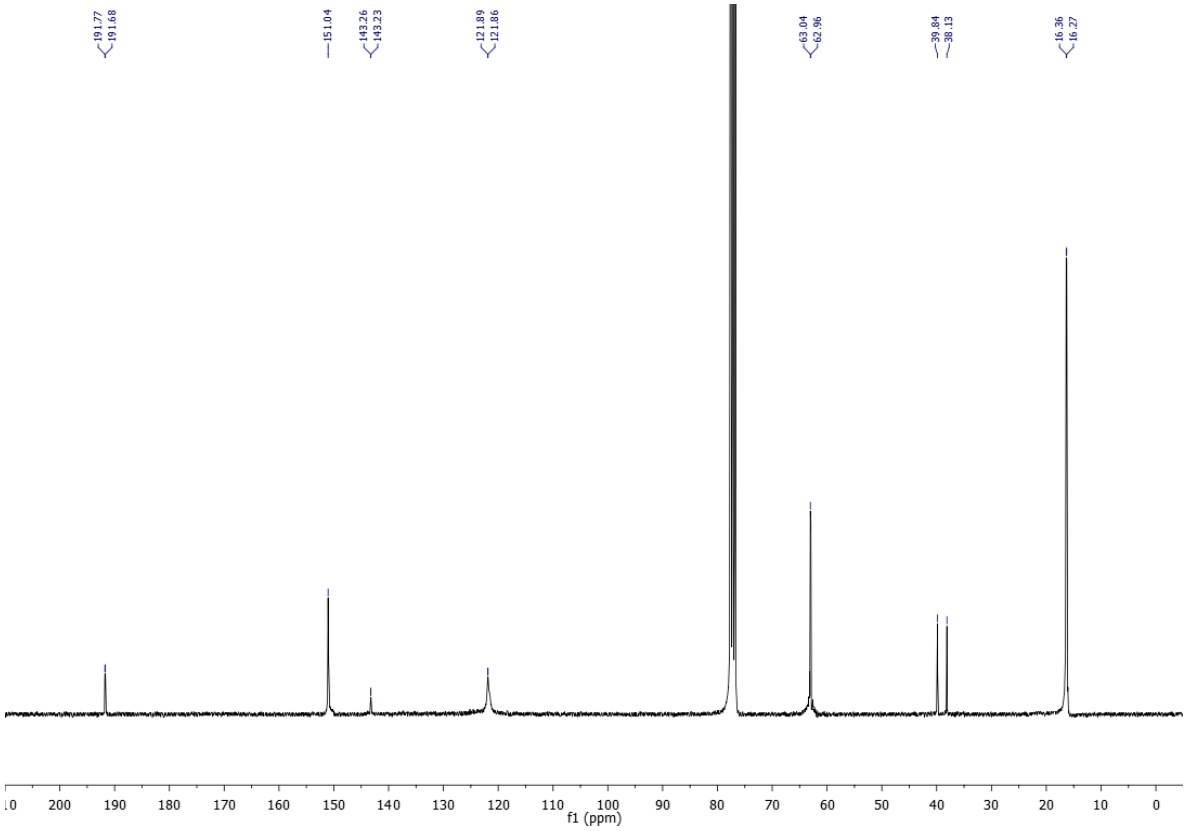

Figure 57. ^{13}C spectrum of **4d** (75 MHz, $CDCl_3$).

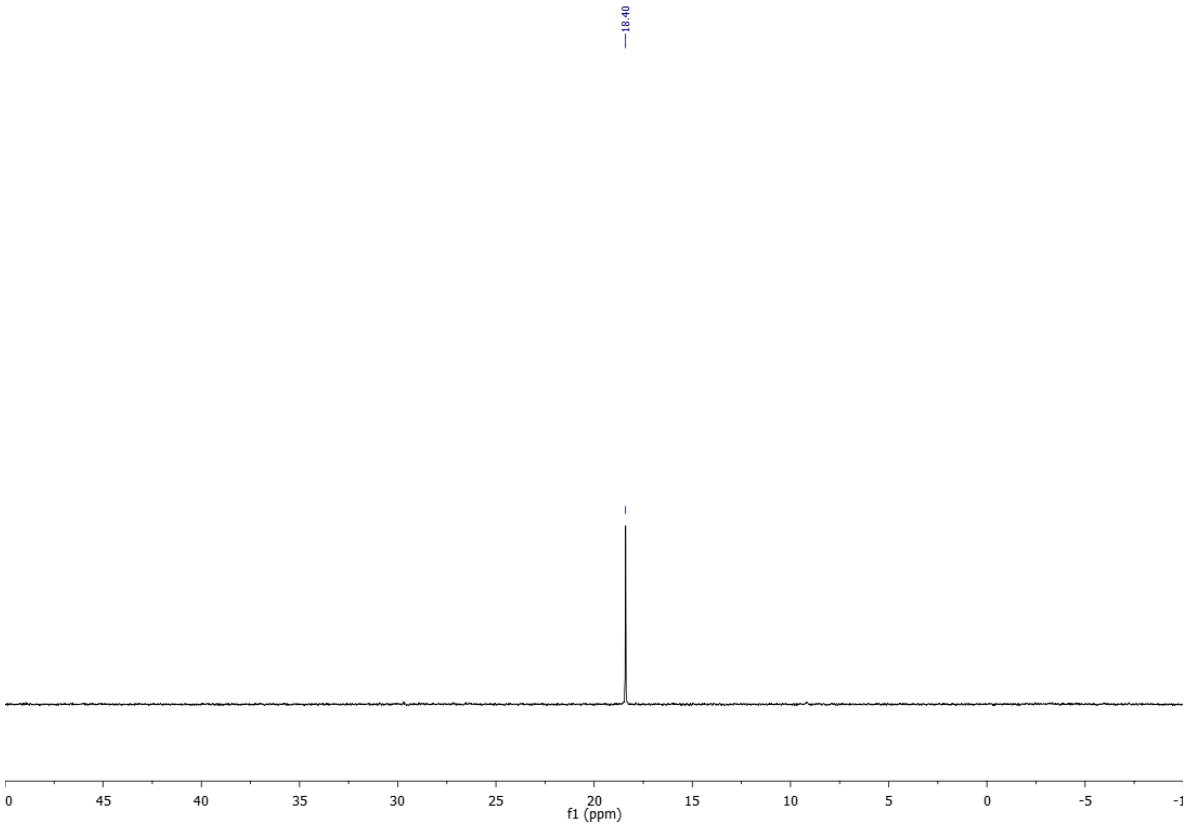

Figure 58. ^{31}P spectrum of **4d** (121 MHz, $CDCl_3$).

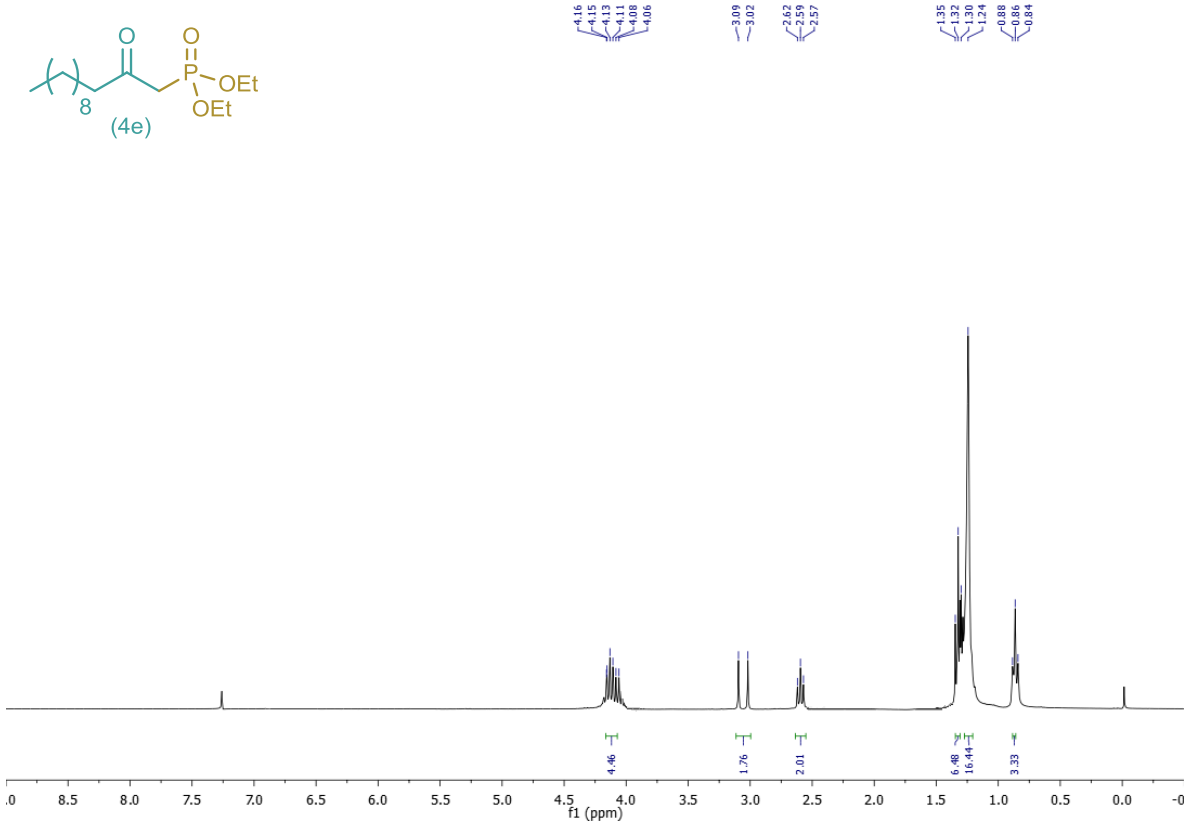

Figure 59. ^{1}H spectrum of **4e** (300 MHz, $CDCl_3$).

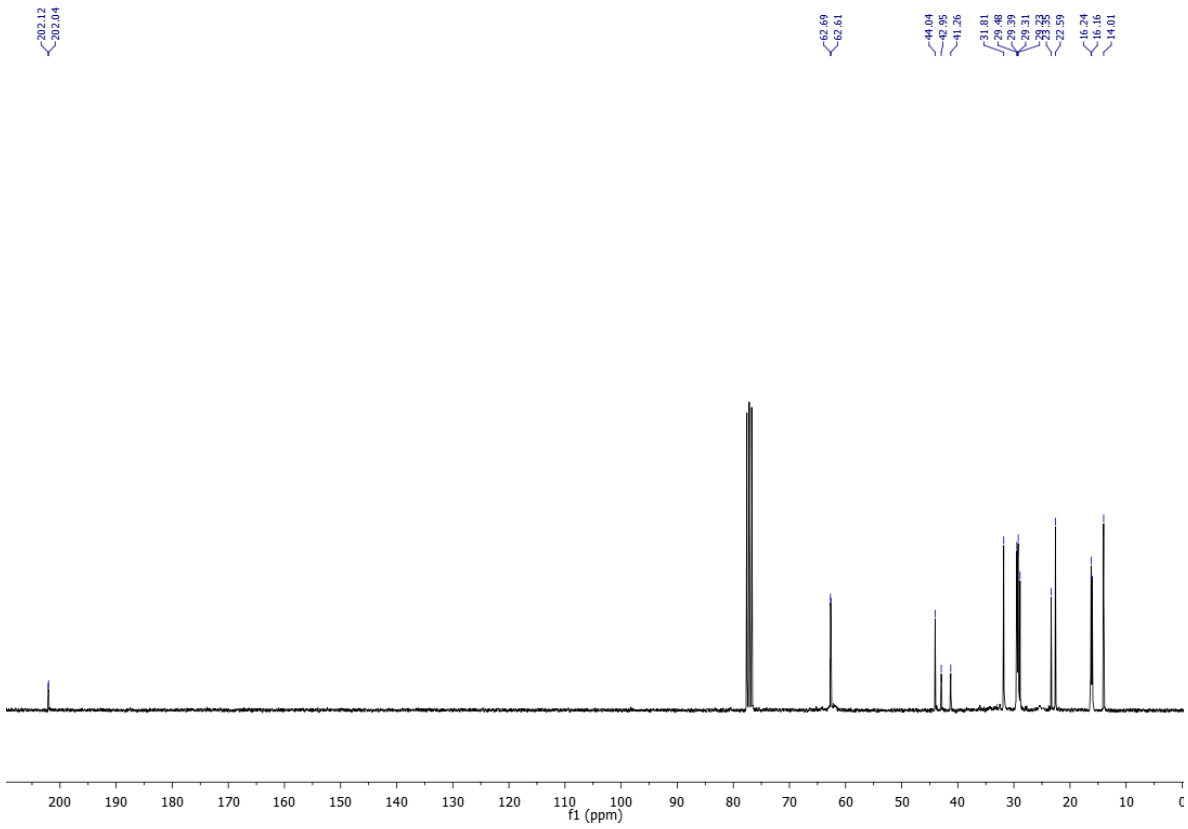

Figure 60. ^{13}C spectrum of **4e** (75 MHz, $CDCl_3$).

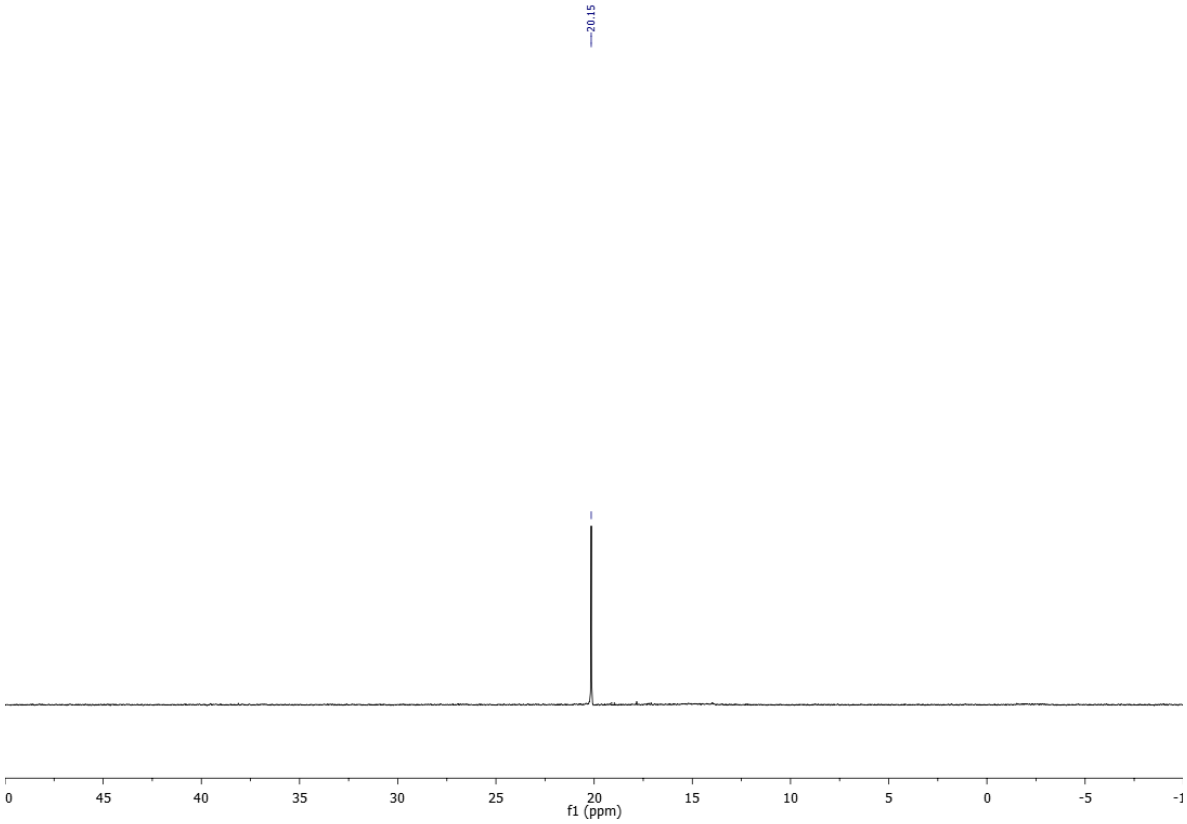

Figure 61. ^{31}P spectrum of **4e** (121 MHz, $CDCl_3$).

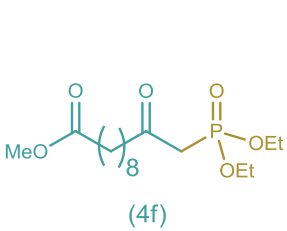

Figure 62. ^{1}H spectrum of **4f** (300 MHz, $CDCl_3$).

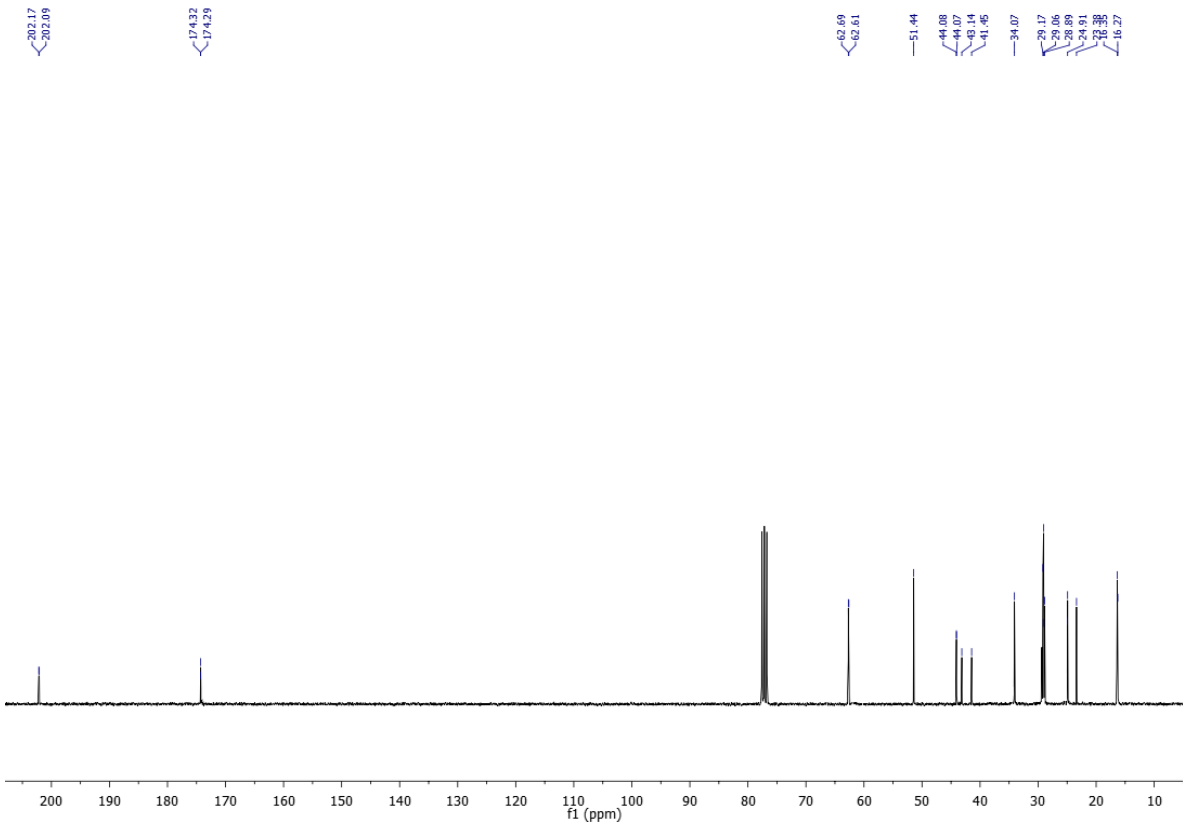

Figure 63. ^{13}C spectrum of **4f** (75 MHz, $CDCl_3$).

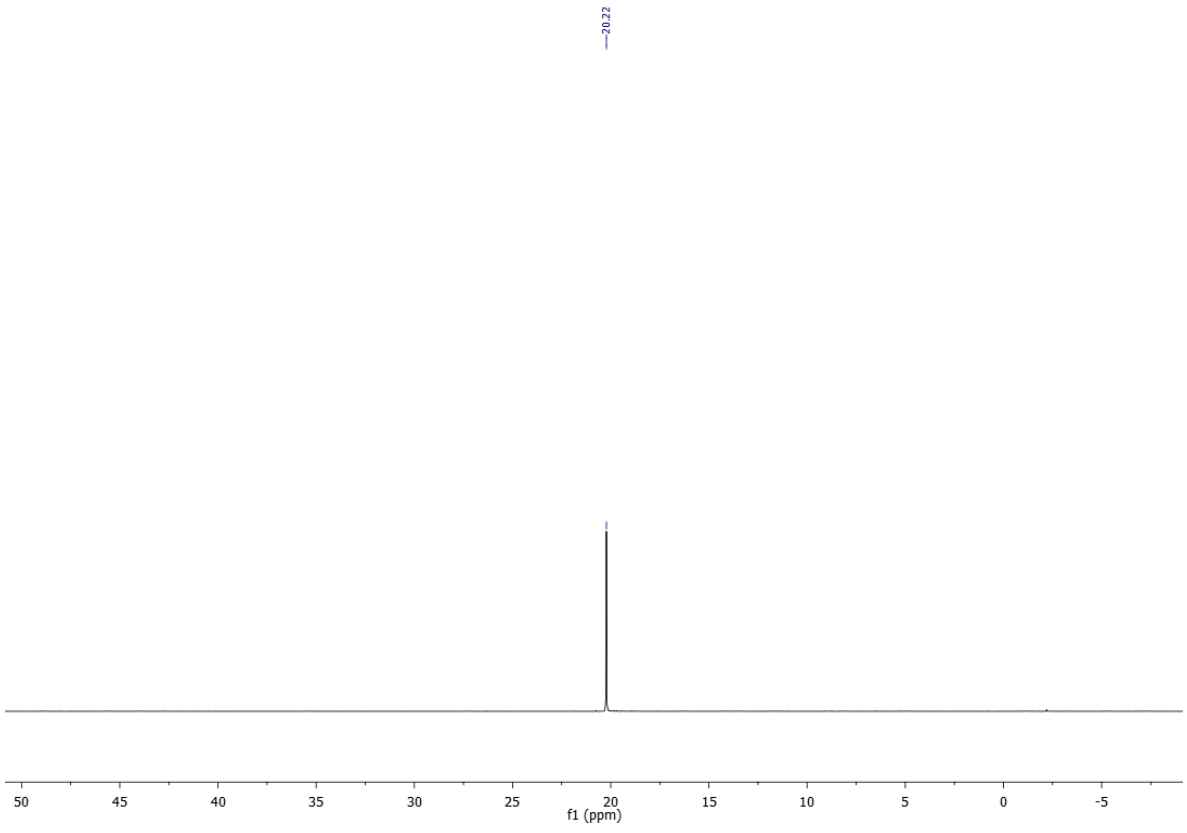

Figure 64. ^{31}P spectrum of **4f** (121 MHz, $CDCl_3$).

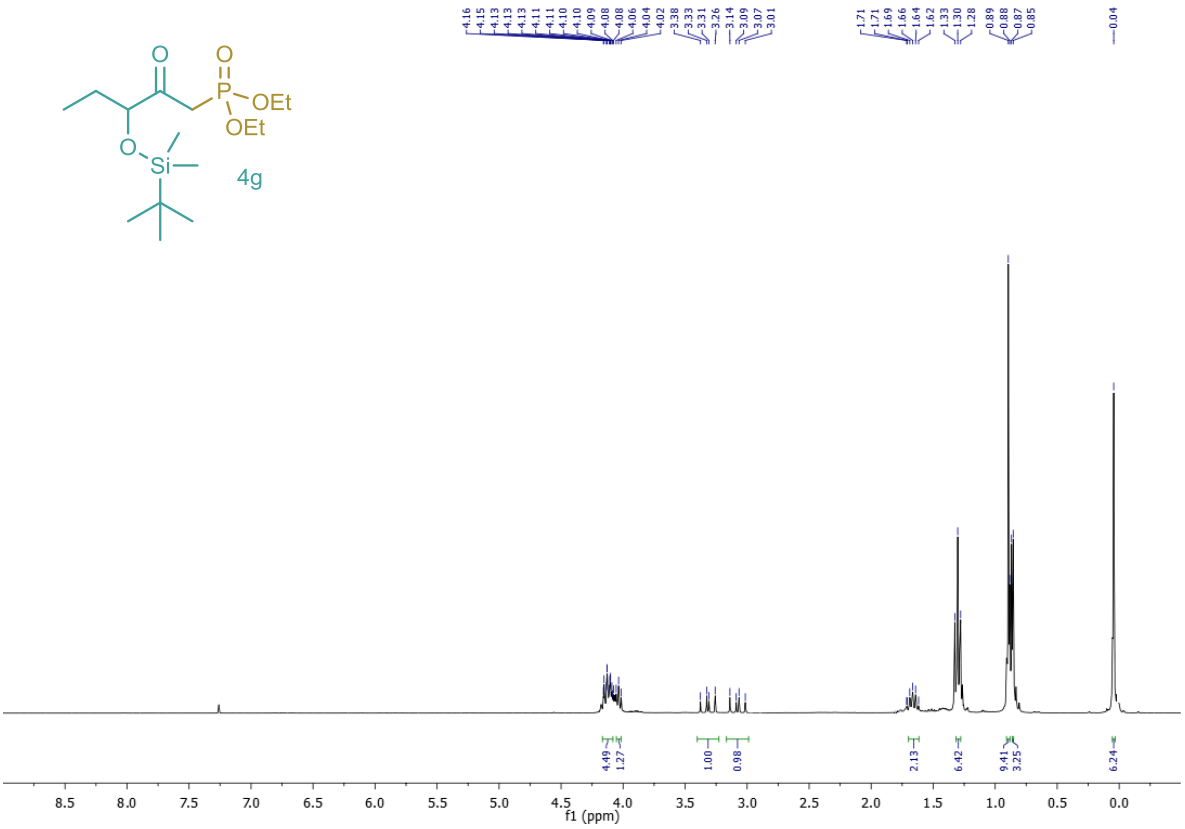

Figure 65. ^{1}H spectrum of **4g** (300 MHz, $CDCl_3$).

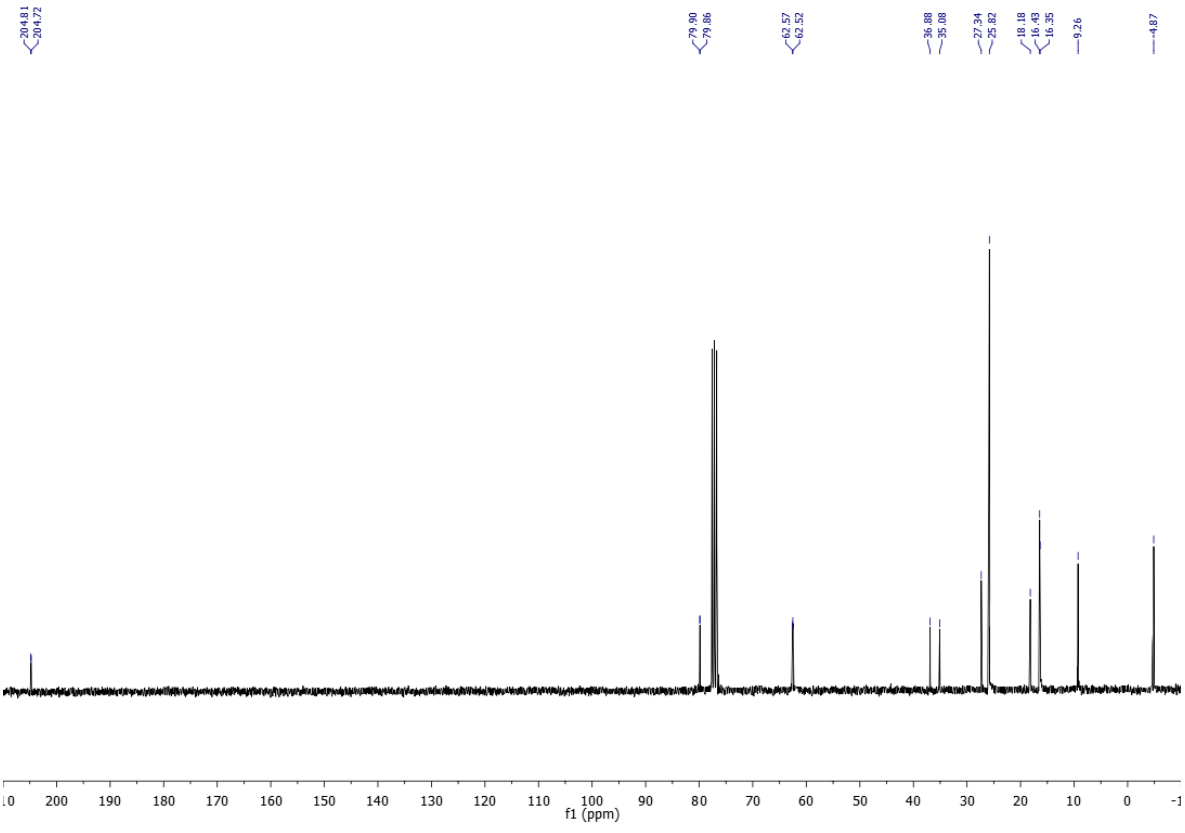

Figure 66. ^{13}C spectrum of **4g** (75 MHz, $CDCl_3$).

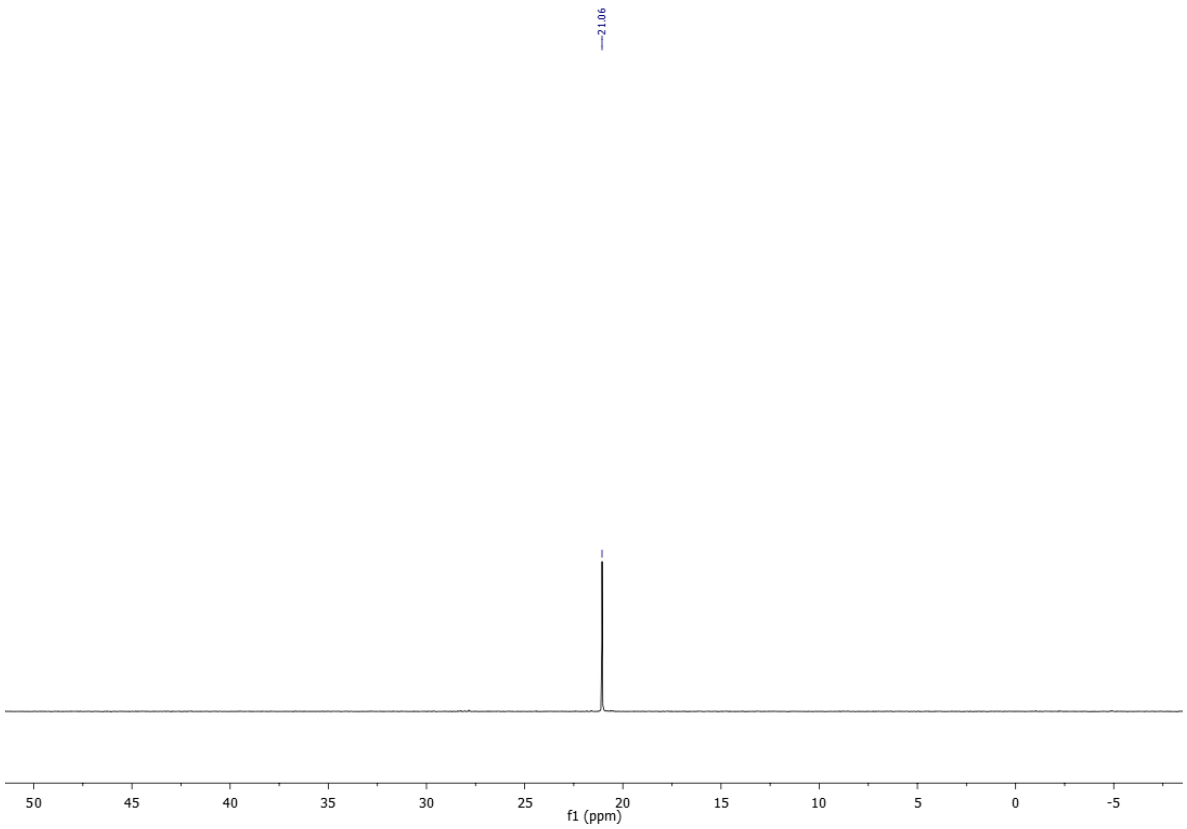

Figure 67. ^{31}P spectrum of **4g** (121 MHz, $CDCl_3$).