

Supplementary material

Synthesis of Phosphine Oxide Based Amphiphilic Molecules via Ring-opening Wittig Olefination of A Macrocyclic Phosphoranylidene and Their Property Study as Non-ionic Surfactants

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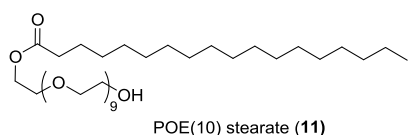
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1. Experimental section

1.1. General experimental method for chemistry and materials

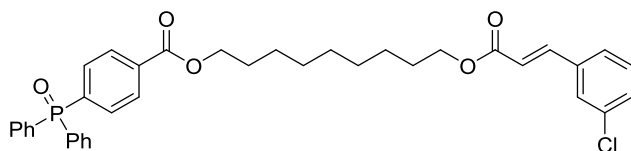
$^1\text{H}/^{13}\text{C}/^{31}\text{P}$ NMR spectra were recorded at 400/100/162 MHz respectively on a Bruker 400 UltraShield spectrometer and the chemical shifts are reported in units parts per million (ppm). All the proton and carbon spectra were referenced to the respective residual solvent peaks. High resolution mass spectra were obtained using the Agilent 6210 time-of-flight LC/MS. Flash silica gel column chromatography purification was carried out either by a Biotage SP1 purification system or manual glass column using Silica gel 60.

Bromoacetyl bromide (97%), tetraethylene glycol (99%), 1,4-diphenylphosphinobenzoic acid (97%), benzotriazol-1-yl-oxypyrrolidinophosphonium hexafluorophosphate (PyBop) (98%) and the aldehydes were purchased from Sigma-Aldrich. Cesium carbonate (99%) was from Alfa Aesar. Polyoxyethylene (10) monostearate (**11**, see structure below) was from Tee Hai (TCI P0719).



1.2. Syntheses of compounds

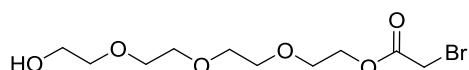
(*E*)-9-((3-(3-chlorophenyl)acryloyl)oxy)nonyl 4-(diphenylphosphoryl)benzoate (**5**)



To a solution of 9-bromononyl 2-bromoacetate (**1b**) (480 mg, 1.4 mmol) in anhydrous toluene (10 mL) was added 1,4-diphenylphosphinobenzoic acid (**2**) (427 mg, 1.4 mmol). The flask was fitted with a condenser and the mixture was stirred at 80 °C under argon for 18 hours. After being cooled down, toluene was removed by under reduced pressure. The crude product was purified by silica gel column chromatography using 0 – 10% methanol in dichloromethane to afford phosphonium salt **3b** (564 mg, 62%) as a white solid. To compound **3b** (210 mg, 0.32 mmol) in DMF (10 mL) was added *t*-BuOK (124 mg, 0.96 mmol) and the mixture was stirred at 80 °C in a sealed tube under argon for 18 hours, then cooled down, followed by addition of 3-chlorobenzaldehyde (77 mg, 0.48 mmol) via syringe, the mixture was further stirred at room temperature for 20 h. DMF was removed by under reduced pressure. The crude product was purified by silica gel column chromatography using 0 – 50% EtOAc in petroleum ether to afford pure product **5** (26 mg, 13% in 2 steps) as colorless gum.

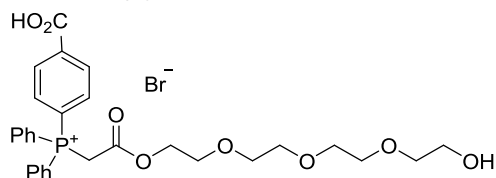
^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, $J = 8.3, 2.4$ Hz, 2H), 7.76 (dd, $J = 11.5, 8.5$ Hz, 2H), 7.70 – 7.61 (m, 4H), 7.60 – 7.53 (m, 2H), 7.53 – 7.44 (m, 5H), 7.41 – 7.28 (m, 4H), 6.43 (d, $J = 16.0$ Hz, 1H), 4.33 (t, $J = 6.7$ Hz, 2H), 4.20 (t, $J = 6.7$ Hz, 2H), 1.81 – 1.65 (m, 4H), 1.48 – 1.29 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 165.8, 142.9, 137.6 (d, $J = 100.9$ Hz), 136.3, 134.9, 133.6 (d, $J = 3.0$ Hz, 2C), 132.0 (d, $J = 105.4$ Hz, 2C), 132.5 - 132.0 (6C), 130.1 (d, $J = 4.3$ Hz, 2C), 129.3 (d, $J = 12.1$ Hz, 2C), 128.6 (d, $J = 12.2$ Hz, 4C), 127.8, 126.2, 119.8, 65.5, 64.8, 29.4, 29.2 (2C), 28.7 (2C), 26.0, 25.9. ^{31}P NMR (162 MHz, CDCl_3) δ 28.42. ESI-MS: m/z 630 $[\text{M}+\text{H}]^+$.

2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl 2-bromoacetate (**6**)



To a solution of tetraethylene glycol (1.94 g, 10 mmol) in dichloromethane (70 mL) was added anhydrous trimethylamine (1.55 mL, 11 mmol). The mixture was stirred at 0 °C for 20 minutes followed by slow addition of bromoacetyl bromide (870 μL , 10 mmol) over 1 hour *via* a syringe pump at 0 °C. The mixture was stirred for further 2 hours at room temperature. Dichloromethane was then removed under reduced pressure and the crude product was purified by silica gel column chromatography using 0 – 5% methanol in dichloromethane to afford compound **6** (1.53 g, 49%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.35 – 4.31 (m, 2H), 3.87 (s, 2H), 3.76 – 3.58 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 72.5, 70.6, 70.6, 70.5, 70.3, 68.8, 65.2, 61.7, 25.8. HRMS (ESI-TOF) m/z for $\text{C}_{10}\text{H}_{20}\text{BrO}_6$ $[\text{M}+\text{H}]^+$: 315.0438 (^{79}Br) and 317.0419 (^{81}Br), found 315.0429 and 317.0411 respectively.

4-Carboxyphenyl(14-hydroxy-2-oxo-3,6,9,12-tetraoxatetradecyl)diphenylphosphonium bromide (**7**)

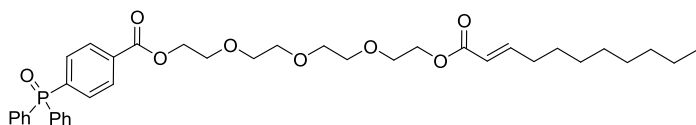


To a solution of **6** (3.78 g, 12 mmol) in anhydrous toluene (60 mL) was added 1,4-diphenylphosphinobenzoic acid (3.67 g, 12 mmol). The flask was fitted with a condenser and the mixture was stirred at 80 °C under argon for 8 hours. After being cooled down, toluene was removed by under reduced pressure. The crude product was purified by silica gel column chromatography using 0 – 15% methanol in dichloromethane to afford compound **7** (4.68 g, 49%) as a white amorphous solid after drying under vacuum. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (dd, $J = 8.4, 3.3$ Hz, 2H), 7.86 – 7.61 (m, 12H), 4.18 – 4.10 (m, 2H), 3.63 – 3.44 (m, 14H), 3.32 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 164.2, 164.1, 137.6, 137.6, 135.6, 135.5, 133.9, 133.8, 133.7, 131.0, 130.9, 130.5, 130.4, 122.3, 121.4, 117.5, 116.6, 72.4, 70.4, 70.2, 70.0, 68.1, 65.7, 61.1, 49.8. ^{31}P NMR (162 MHz, CDCl_3) δ 20.28. HRMS (ESI-TOF) m/z for $\text{C}_{29}\text{H}_{34}\text{O}_8\text{P}^+$ $[\text{M}]^+$: 541.1991, found 541.2002.

Synthesis of **9 (a-h)** *via* macrocyclization and Wittig olefination

The mixture of compound **7** (1.24 g, 2 mmol), PyBop (2.08 g, 4 mmol), Cs₂CO₃ (1.95 g, 6 mmol) in anhydrous dimethylformamide (150 mL) was degassed with argon and stirred at room temperature for 4 hours under an argon balloon, after which nonanal (569 mg, 4 mmol) was added. The mixture was stirred at 40 °C for 16 hours. The reaction was quenched by addition of saturated aqueous NH₄Cl solution, DMF and water was then removed under high vacuum. The crude mixture was re-dissolved in dichloromethane and water, extracted with dichloromethane (100 mL x 3), washed with brine, dried over anhydrous Na₂SO₄ and concentrated to give a crude product which was purified by silica gel column chromatography using 0 – 100% ethyl acetate in petroleum ether to afford compound **9a** (833 mg, 63%) as a colorless viscous gum.

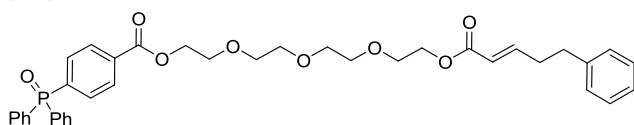
(*E*)-13-oxo-3,6,9,12-tetraoxatricos-14-en-1-yl 4-(diphenylphosphoryl)benzoate (**9a**)



¹H NMR (400 MHz, CDCl₃) δ 8.13 (dd, *J* = 8.3, 2.5 Hz, 2H), 7.76 (dd, *J* = 11.5, 8.3 Hz, 2H), 7.69 – 7.62 (m, 4H), 7.60 – 7.53 (m, 2H), 7.51 – 7.44 (m, 4H), 6.97 (dt, *J* = 16.2, 6.7 Hz, 1H), 5.83 (dt, *J* = 15.8, 1.4 Hz, 1H), 4.51 – 4.47 (m, 2H), 4.28 – 4.23 (m, 2H), 3.85 – 3.80 (m, 2H), 3.73 – 3.61 (m, 10H), 2.22 – 2.14 (m, 2H), 1.48 – 1.39 (m, 2H), 1.35 – 1.20 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 165.7, 150.1, 138.2, 137.2, 133.2, 133.2, 132.3, 132.3, 132.2, 132.2, 132.1, 132.0, 131.3, 129.6, 129.4, 128.7, 128.6, 120.9, 70.7, 70.7, 70.6, 70.6, 69.2, 69.1, 64.5, 63.3, 32.2, 31.8, 29.3, 29.1, 29.1, 28.0, 22.6, 14.0. ³¹P NMR (162 MHz, CDCl₃) δ 28.38. HRMS (ESI-TOF) *m/z* for C₃₈H₅₀O₈P [M+H]⁺: 665.3238, found 665.3267.

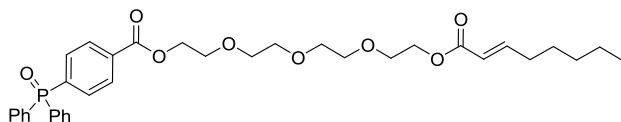
Other Wittig products **9 (b to g)** were prepared similarly from the corresponding aldehydes respectively using above procedure.

(*E*)-13-oxo-17-phenyl-3,6,9,12-tetraoxaheptadec-14-en-1-yl 4-(diphenylphosphoryl)benzoate (**9b**)



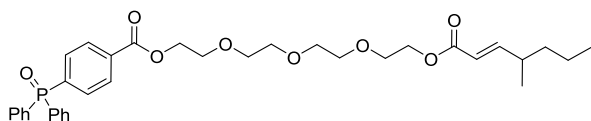
Colorless viscous gum (74% yield). ¹H NMR (400 MHz, MeOD) δ 8.18 (dd, *J* = 8.6, 2.7 Hz, 2H), 7.77 (dd, *J* = 11.7, 8.6 Hz, 2H), 7.61 (d, *J* = 1.7 Hz, 10H), 7.28 – 7.11 (m, 5H), 6.97 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.51 – 4.47 (m, 2H), 4.21 – 4.16 (m, 2H), 3.85 – 3.81 (m, 2H), 3.70 – 3.54 (m, 10H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.46 (m, 2H). ¹³C NMR (101 MHz, MeOD) δ 168.0, 166.9, 150.3, 142.1, 138.0 (d, *J* = 102.3 Hz), 135.1 (d, *J* = 2.7 Hz), 134.0 (d, *J* = 2.7 Hz, 2C), 133.3 (d, *J* = 10.3 Hz, 2C), 133.1 (d, *J* = 10.2 Hz, 4C), 132.1 (d, *J* = 106.1 Hz, 2C), 130.7 (d, *J* = 12.3 Hz, 2C), 130.1 (d, *J* = 12.4 Hz, 4C), 129.4 (4C), 127.1, 122.4, 71.7, 71.6 (3C), 70.1 (2C), 65.8, 64.6, 35.3, 34.9. ³¹P NMR (162 MHz, MeOD) δ 31.25. HRMS (ESI-TOF) *m/z* for C₃₈H₄₁NaO₈P [M+Na]⁺: 679.2431, found 679.2439.

(*E*)-13-oxo-3,6,9,12-tetraoxaicos-14-en-1-yl 4-(diphenylphosphoryl)benzoate (**9c**)



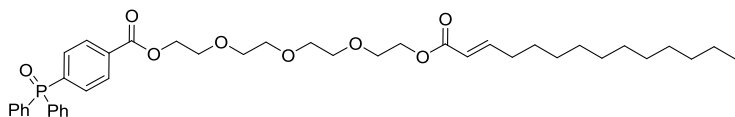
Colorless viscous gum (71% yield). ^1H NMR (400 MHz, Methanol- d_4) δ 8.19 (dd, $J = 8.5, 2.6$ Hz, 2H), 7.79 (dd, $J = 11.7, 8.5$ Hz, 2H), 7.71 – 7.54 (m, 10H), 6.96 (dt, $J = 15.6, 7.0$ Hz, 0H), 5.81 (dt, $J = 15.6, 1.5$ Hz, 1H), 4.51 – 4.47 (m, 2H), 4.20 (dd, $J = 5.5, 4.1$ Hz, 2H), 3.87 – 3.81 (m, 2H), 3.71 – 3.56 (m, 10H), 2.18 (qd, $J = 7.4, 1.5$ Hz, 1H), 1.44 (p, $J = 7.3$ Hz, 2H), 1.37 – 1.24 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, Methanol- D_4) δ 168.1, 166.9, 151.5, 138.0 (d, $J = 102.2$ Hz), 135.1 (d, $J = 2.8$ Hz), 134.0 (d, $J = 2.8$ Hz, 2C), 133.3 (d, $J = 10.4$ Hz, 2C), 133.1 (d, $J = 10.2$ Hz, 4C), 132.1 (d, $J = 106.1$ Hz, 2C), 130.7 (d, $J = 12.3$ Hz, 2C), 130.1 (d, $J = 12.4$ Hz, 4C), 121.9, 71.6, 71.5 (3C), 70.1, 70.1, 65.8, 64.5, 33.1, 32.4, 28.8, 23.4, 14.3. ^{31}P NMR (162 MHz, MeOD) δ 31.25. HRMS (ESI-TOF) m/z for $\text{C}_{35}\text{H}_{43}\text{NaO}_8\text{P}$ $[\text{M}+\text{Na}]^+$: 645.2588, found 645.2593.

(*E*)-16-methyl-13-oxo-3,6,9,12-tetraoxanonadec-14-en-1-yl 4-(diphenylphosphoryl)benzoate (**9d**)



Colorless viscous gum (48% yield). ^1H NMR (400 MHz, MeOD) δ 8.19 (dd, $J = 8.6, 2.7$ Hz, 2H), 7.79 (dd, $J = 11.7, 8.6$ Hz, 2H), 7.71 – 7.53 (m, 10H), 6.84 (dd, $J = 15.7, 8.1$ Hz, 1H), 5.78 (dd, $J = 15.7, 1.1$ Hz, 1H), 4.51 – 4.47 (m, 2H), 4.23 – 4.18 (m, 2H), 3.86 – 3.82 (m, 2H), 3.70 – 3.56 (m, 10H), 2.37 – 2.25 (m, 1H), 1.39 – 1.23 (m, 4H), 1.02 (d, $J = 6.7$ Hz, 3H), 0.88 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, MeOD) δ 168.3, 166.9, 156.6, 138.02 (d, $J = 102.3$ Hz), 135.08 (d, $J = 2.8$ Hz), 134.02 (d, $J = 2.9$ Hz, 2C), 133.29 (d, $J = 10.3$ Hz, 2C), 133.07 (d, $J = 10.2$ Hz, 4C), 132.12 (d, $J = 106.1$ Hz, 2C), 130.75 (d, $J = 12.3$ Hz, 2C), 130.12 (d, $J = 12.4$ Hz, 4C), 120.3, 71.7, 71.5, 70.2, 70.1, 65.8, 64.6, 39.3, 37.5, 21.4, 19.7, 14.3. ^{31}P NMR (162 MHz, MeOD) δ 31.25. HRMS (ESI-TOF) m/z for $\text{C}_{35}\text{H}_{43}\text{NaO}_8\text{P}$ $[\text{M}+\text{Na}]^+$: 645.2588, found 645.2601.

(*E*)-13-oxo-3,6,9,12-tetraoxahexacos-14-en-1-yl 4-(diphenylphosphoryl)benzoate (**9e**)

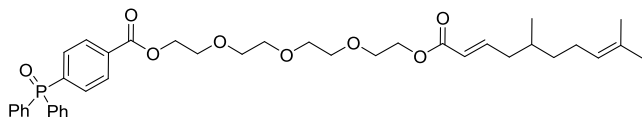


Colorless viscous gum (63% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, $J = 8.3, 2.4$ Hz, 2H), 7.77 (dd, $J = 11.5, 8.3$ Hz, 2H), 7.70 – 7.61 (m, 4H), 7.60 – 7.53 (m, 2H), 7.53 – 7.44 (m, 4H), 6.98 (dt, $J = 15.6, 6.9$ Hz, 1H), 5.83 (d, $J = 15.6$ Hz, 1H), 4.54 – 4.47 (m, 2H), 4.29 – 4.22 (m, 2H), 3.86 – 3.80 (m, 2H), 3.74 – 3.60 (m, 10H), 2.18 (ddd, $J = 14.8, 7.2, 1.6$ Hz, 1H), 1.48 – 1.38 (m, 2H), 1.33 – 1.21 (m, 18H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 13C NMR (101 MHz, CDCl_3) δ 166.6, 165.7, 150.1, 138.2, 137.2, 133.2 (2C), 132.4, 132.2 (2C), 132.1, 132.0, 131.3, 129.6, 129.4, 128.7, 128.6, 120.9, 70.7, 70.6, 69.3, 69.1, 64.5, 63.3, 32.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 28.0, 22.7, 14.1. ^{31}P NMR (162

MHz, CDCl₃) δ 28.33. HRMS (ESI-TOF) m/z for C₄₁H₅₆O₈P [M+H]⁺: 707.3707, found 707.3726.

(*E*)-17,21-dimethyl-13-oxo-3,6,9,12-tetraoxadocosa-14,20-dien-1-yl
(diphenylphosphoryl)benzoate (**9f**)

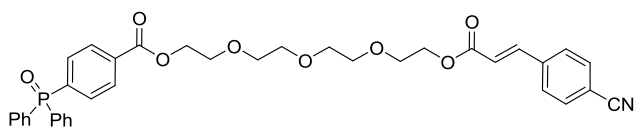
4-



Colorless viscous gum (61% yield). ¹H NMR (400 MHz, MeOD) δ 8.19 (dd, J = 8.5, 2.6 Hz, 1H), 7.79 (dd, J = 11.7, 8.5 Hz, 1H), 7.66 (ddd, J = 7.5, 6.0, 4.3 Hz, 6H), 7.58 (dd, J = 6.7, 2.8 Hz, 4H), 6.93 (dt, J = 15.3, 7.5 Hz, 1H), 5.82 (dt, J = 15.3, 1.4 Hz, 1H), 5.08 (br t, J = 7.3 Hz, 1H), 4.53 – 4.45 (m, 2H), 4.24 – 4.17 (m, 2H), 3.87 – 3.82 (m, 2H), 3.71 – 3.56 (m, 10H), 2.26 – 2.17 (m, 1H), 2.10 – 1.90 (m, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.39 – 1.11 (m, 3H), 0.89 (d, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, MeOD) δ 168.0, 166.8, 150.2, 138.5, 137.5, 135.1, 134.0, 134.0, 133.3, 133.2, 133.1, 133.0, 132.7, 132.3, 131.6, 130.8, 130.7, 130.2, 130.1, 125.5, 123.1, 71.7, 71.6, 71.6, 71.6, 70.2, 70.1, 65.8, 64.6, 40.5, 37.8, 33.3, 26.5, 25.9, 19.9, 17.7. ³¹P NMR (162 MHz, CDCl₃) δ 28.31. HRMS (ESI-TOF) m/z for C₃₉H₅₀O₈P [M+H]⁺: 677.3238, found 677.3252.

(*E*)-15-(4-cyanophenyl)-13-oxo-3,6,9,12-tetraoxapentadec-14-en-1-yl
(diphenylphosphoryl)benzoate
(**9g**)

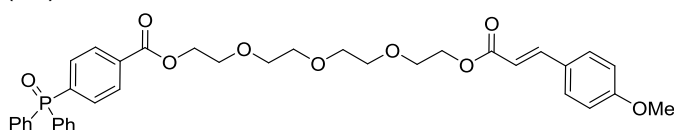
4-



Colorless viscous gum (64% yield). ¹H NMR (400 MHz, MeOD) δ 8.17 (dd, J = 8.3, 2.4 Hz, 2H), 7.82 – 7.53 (m, 17H), 6.65 (d, J = 16.1 Hz, 1H), 4.50 – 4.45 (m, 2H), 4.32 – 4.27 (m, 2H), 3.85 – 3.80 (m, 2H), 3.75 – 3.58 (m, 10H). ¹³C NMR (100 MHz, MeOD) δ 167.6, 166.9, 143.9, 140.2, 138.8 (d, J = 103.0 Hz), 135.1 (d, J = 2.7 Hz), 134.0 (d, J = 2.7 Hz, 2C), 133.8 (2C), 133.3 (d, J = 10.4 Hz, 2C), 133.1 (d, J = 10.2 Hz, 4C), 132.1 (d, J = 106.1 Hz, 2C), 130.7 (d, J = 12.2 Hz, 2C), 130.1 (d, J = 12.4 Hz, 4C), 129.9 (2C), 122.6, 119.3, 114.4, 71.6 (4C), 70.1 (2C), 65.8, 65.0. ³¹P NMR (162 MHz, MeOD) δ 31.23. HRMS (ESI-TOF) m/z for C₃₇H₃₆NaNO₈P [M+Na]⁺: 676.2071, found 676.2079.

(*E*)-15-(4-methoxyphenyl)-13-oxo-3,6,9,12-tetraoxapentadec-14-en-1-yl
(diphenylphosphoryl)benzoate
(**9h**)

4-



Colorless viscous gum (72% yield). ^1H NMR (400 MHz, MeOD) δ 8.17 (dd, $J = 8.5, 2.4$ Hz, 1H), 7.77 (dd, $J = 11.7, 8.5$ Hz, 2H), 7.70 – 7.48 (m, 13H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.49 – 4.45 (m, 2H), 4.29 – 4.25 (m, 2H), 3.84 – 3.78 (m, 2H), 3.80 (s, 3H), 3.73 – 3.58 (m, 10H). ^{13}C NMR (100 MHz, MeOD) δ 168.9, 166.9, 163.2, 146.3, 138.0 (d, $J = 102.3$ Hz), 135.1 (d, $J = 2.8$ Hz), 134.0 (d, $J = 2.8$ Hz, 2C), 133.2 (d, $J = 10.3$ Hz, 2C), 133.1 (d, $J = 10.2$ Hz, 4C), 132.1 (d, $J = 106.1$ Hz, 2C), 131.0 (2C), 130.7 (d, $J = 12.3$ Hz, 2C), 130.1 (d, $J = 12.4$ Hz, 4C), 128.2, 116.0, 115.4 (2C), 71.7, 71.6 (3C), 70.2, 70.1, 65.8, 64.6, 55.9. ^{31}P NMR (162 MHz, MeOD) δ 31.27. HRMS (ESI-TOF) m/z for $\text{C}_{37}\text{H}_{39}\text{NaO}_9\text{P}$ $[\text{M}+\text{Na}]^+$: 681.2224, found 681.2236.

1.3. Physicochemical characterizations

1.3.1. Determination of critical micelle concentration (CMC), surface tension at CMC (γ_{CMC}) and other physicochemical properties by surface tension

The surface tensions of surfactants were measured using DataphysicsTM contact angle system OCA by a pendant drop method. A drop of surfactant solution of known concentration was suspended by a needle and the image was captured by a camera, from where surface tension was calculated. The sample solution was prepared as a stock solution using DI water and then diluted to the desired concentration for each measurement. The CMC values were determined by plotting the curve of surface tension versus the logarithm of the concentration of the aqueous surfactant solution. The CMC value is defined as the concentration at the intersection point of the two derived trendlines where there is a sharp change of surface tension. The surface tension at concentration of CMC is denoted as γ_{CMC} .

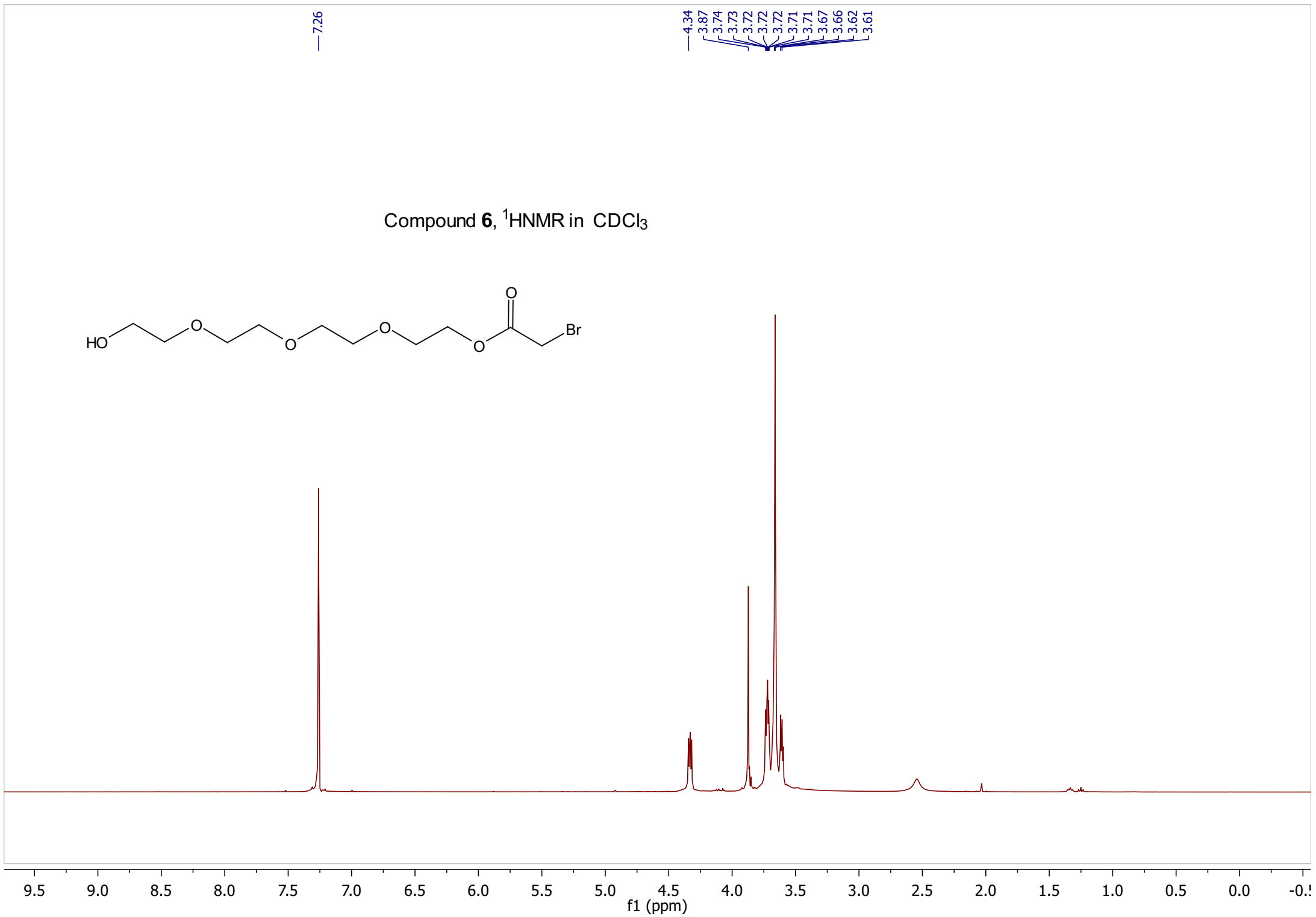
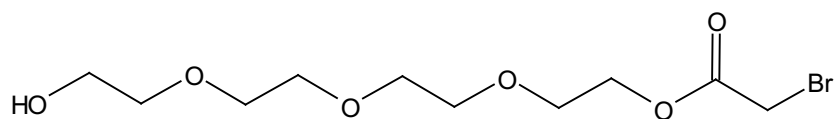
1.3.2. Interfacial tension

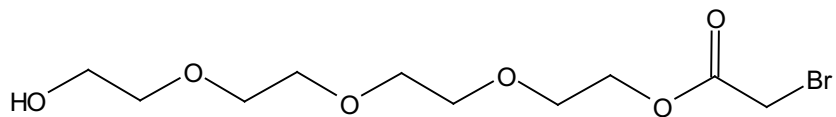
Interfacial tension (IFT) was measured by Spinning drop tensiometer SVT 20N from DataphysicsTM. Sample tube was filled with the denser fluid (aqueous surfactant solution or pure water in ca 10 mL). A small drop of less dense fluid (pure oil phase or oil dispersion of surfactant) was then injected into the sample tube. For the IFT of surfactant/water/*n*-decane system, the surfactant was dissolved in water whilst for that of surfactant/water/paraffin oil system, the surfactant was dissolved in paraffin oil. Sample tube was then rotated along an axis at required speed. IFT was determined by the shape of the oil drop which has been elongated by the spinning force applied on the sample tube.

1.3.3. Microscopic analysis of emulsion droplets

The emulsion samples for microscopic analysis were freshly prepared either using an MicrosonTM Ultrasonic homogenizer. The mixture of 0.1wt% of surfactant and rhodamine dye in water and *n*-decane (1:1) was sonicated for 5 minutes and the resulting emulsions prepared were visualized and analyzed with Trinocular biological microscope TM-Advance 5.0 MP. The images were recorded with ToupView X86 at 40x magnification.

Compound **6**, ^1H NMR in CDCl_3





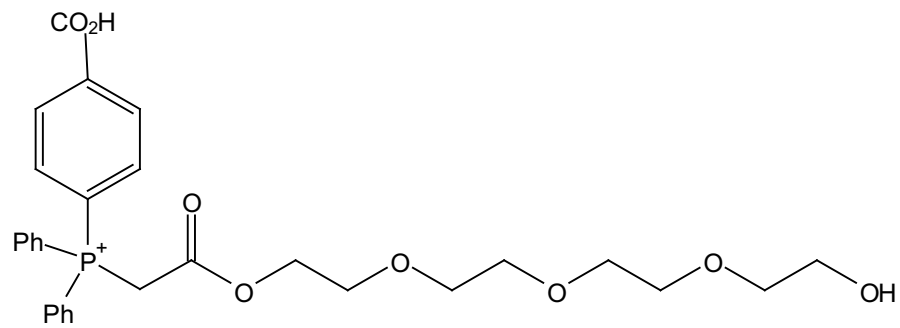
—167.23

77.33
77.01
76.69
72.53
70.65
70.63
70.52
70.33
68.77
65.23
61.74

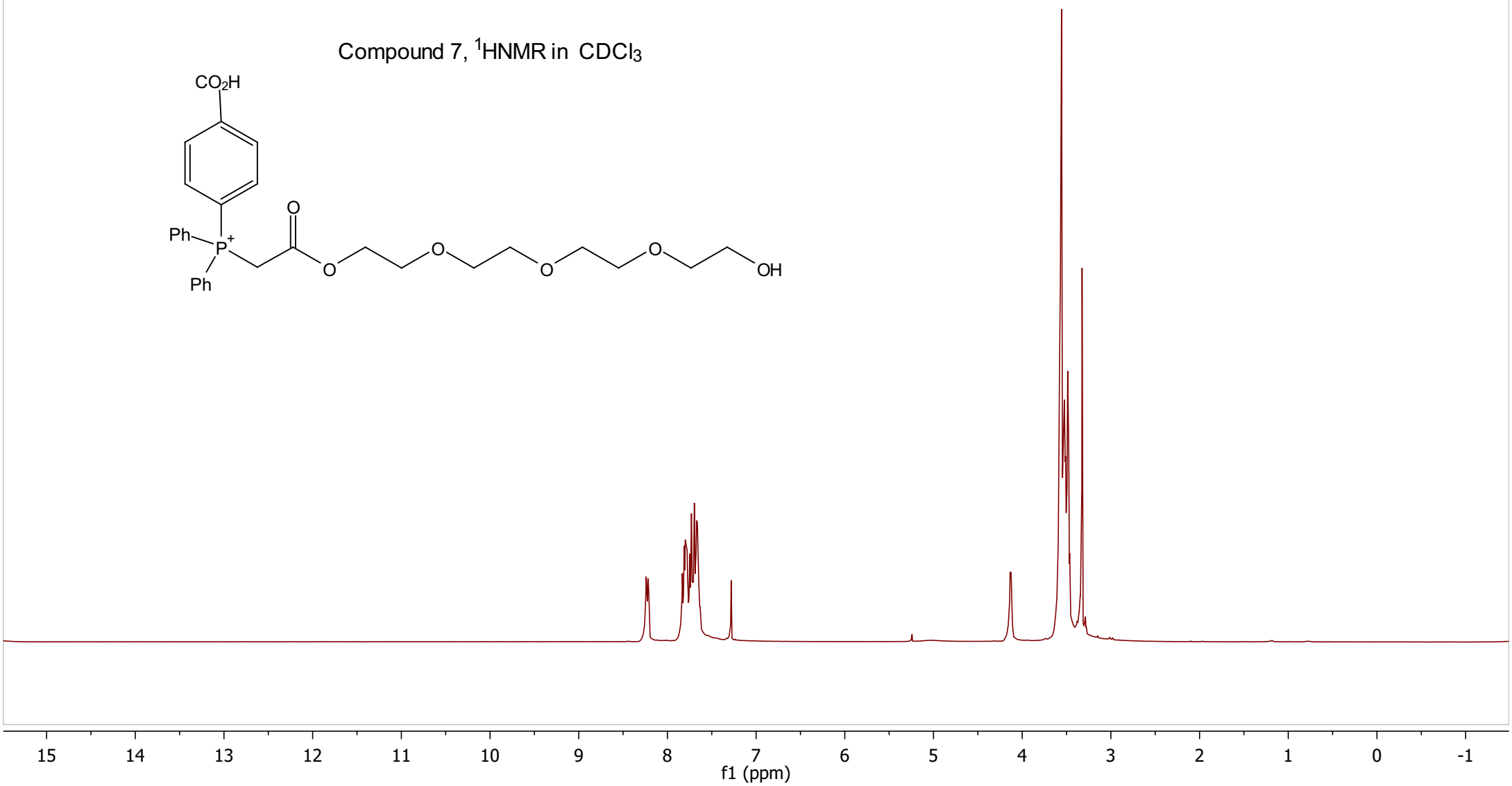
—25.77

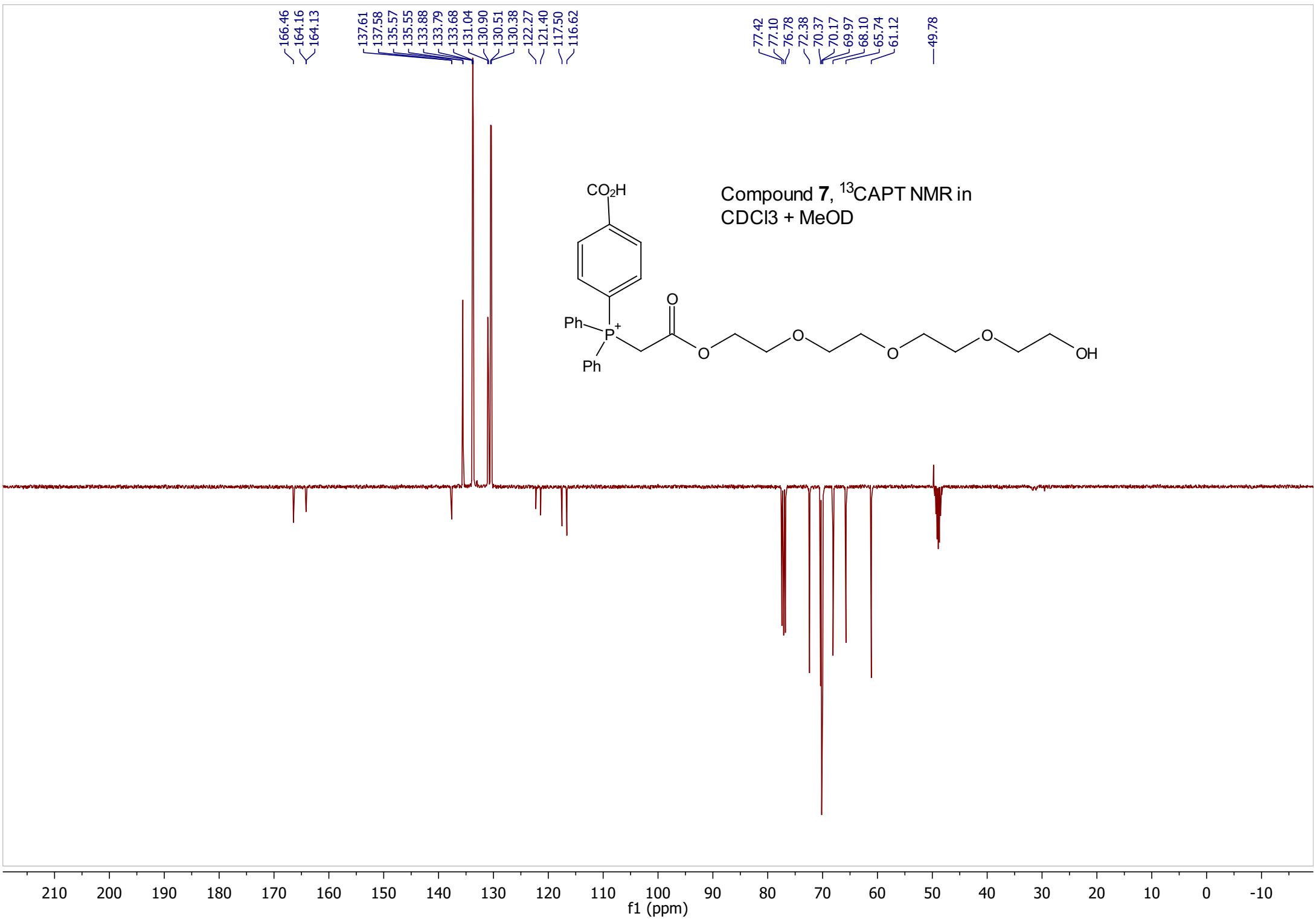
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



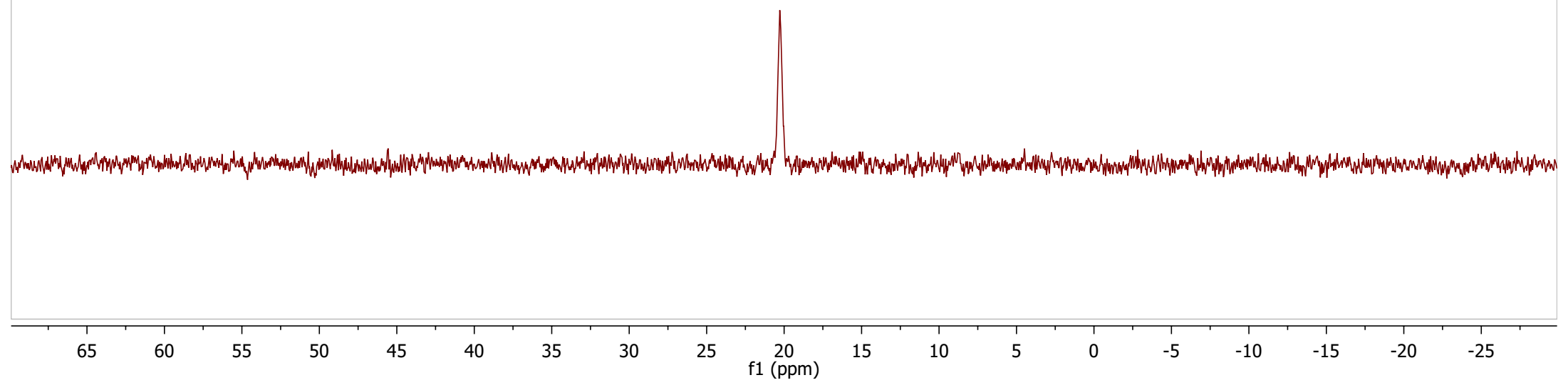
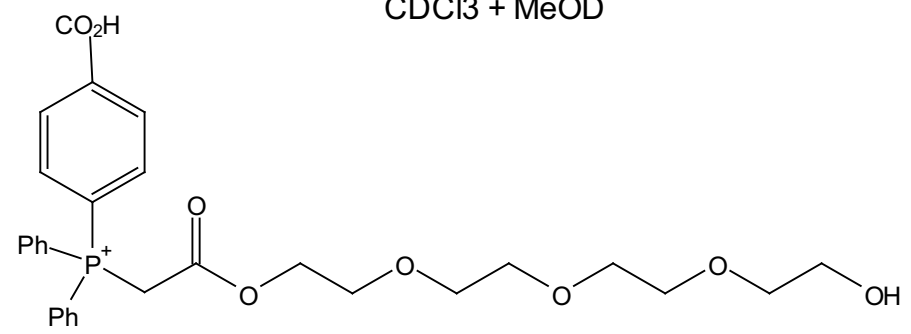
8.24
8.23
8.22
8.21
7.83
7.81
7.80
7.79
7.78
7.75
7.73
7.73
7.71
7.70
7.69
7.68
7.67
7.66
7.65
7.64
7.63
4.14
4.13
4.13
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3.51
3.50
3.49
3.48
3.47
3.46
3.32

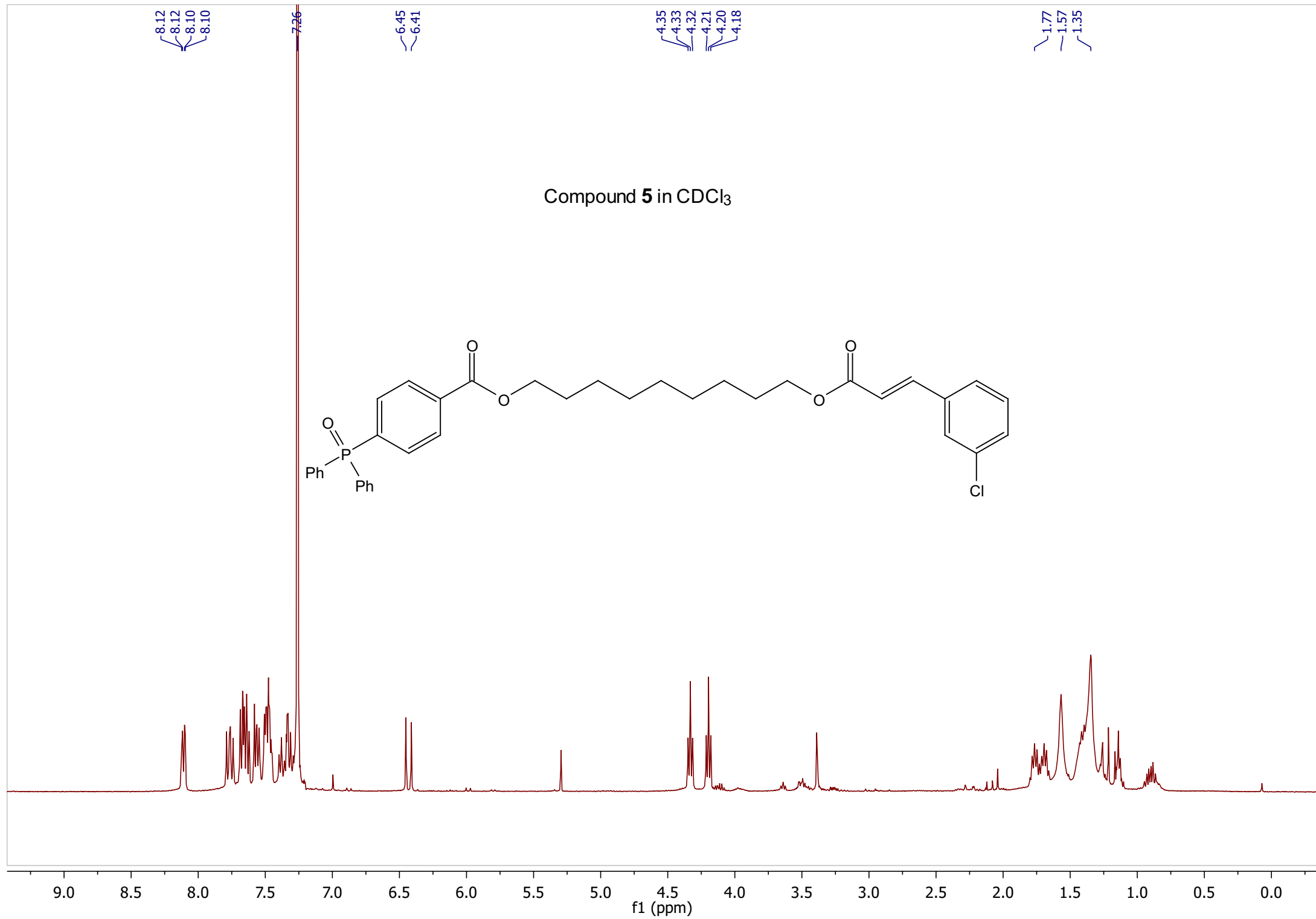


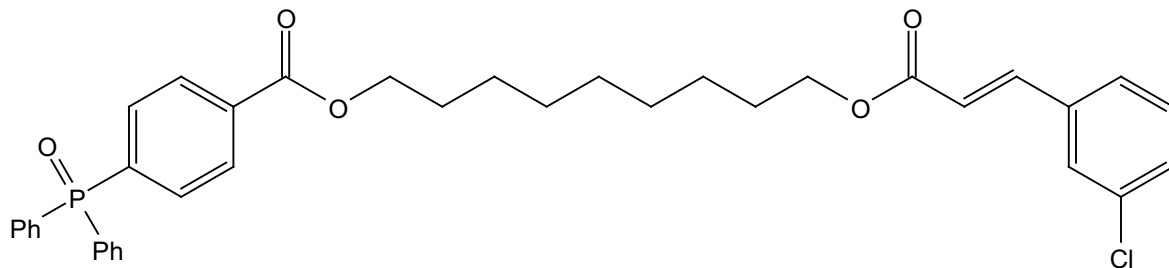


20.28

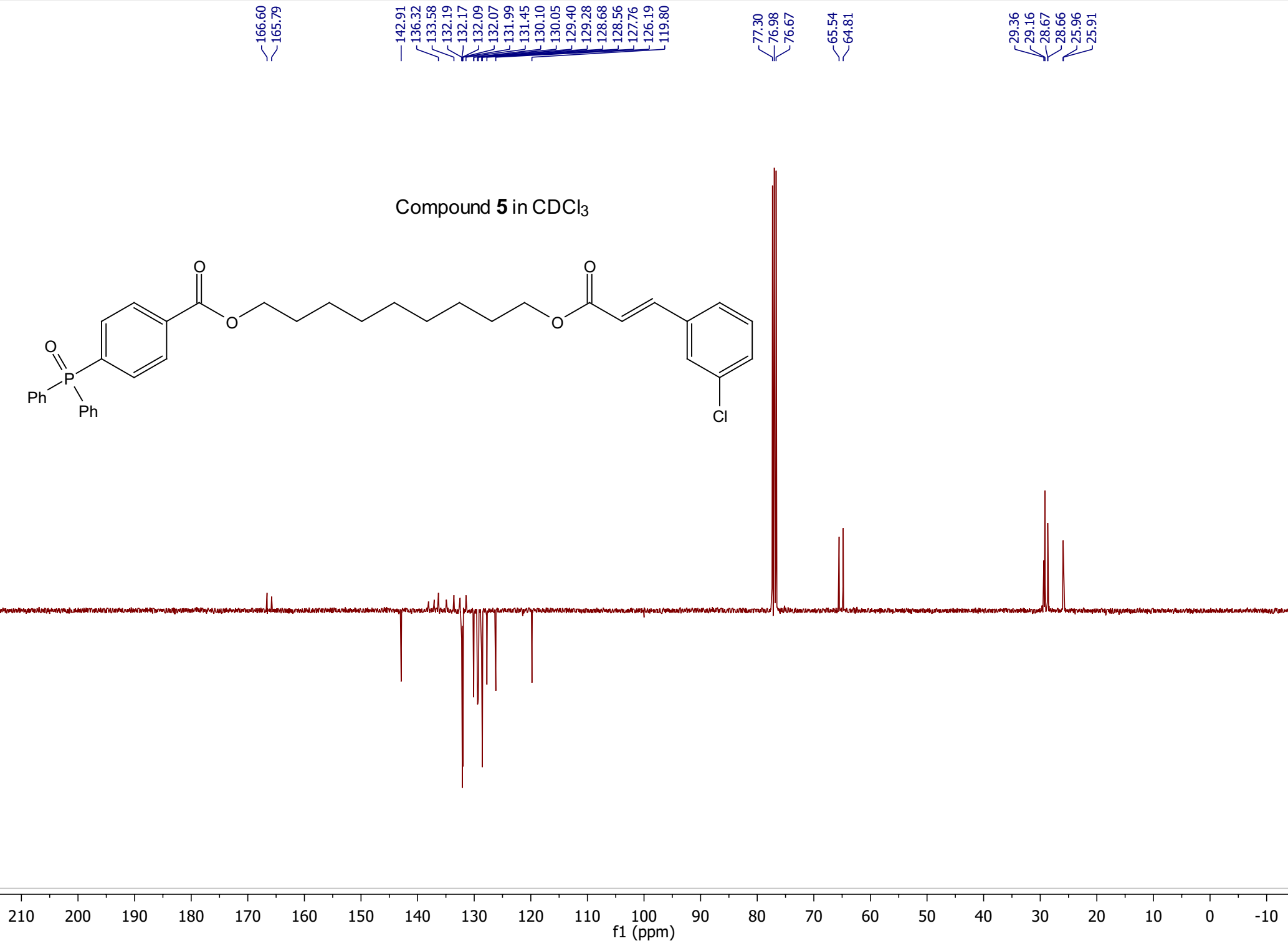
Compound 7, ³¹P NMR in
CDCl₃ + MeOD





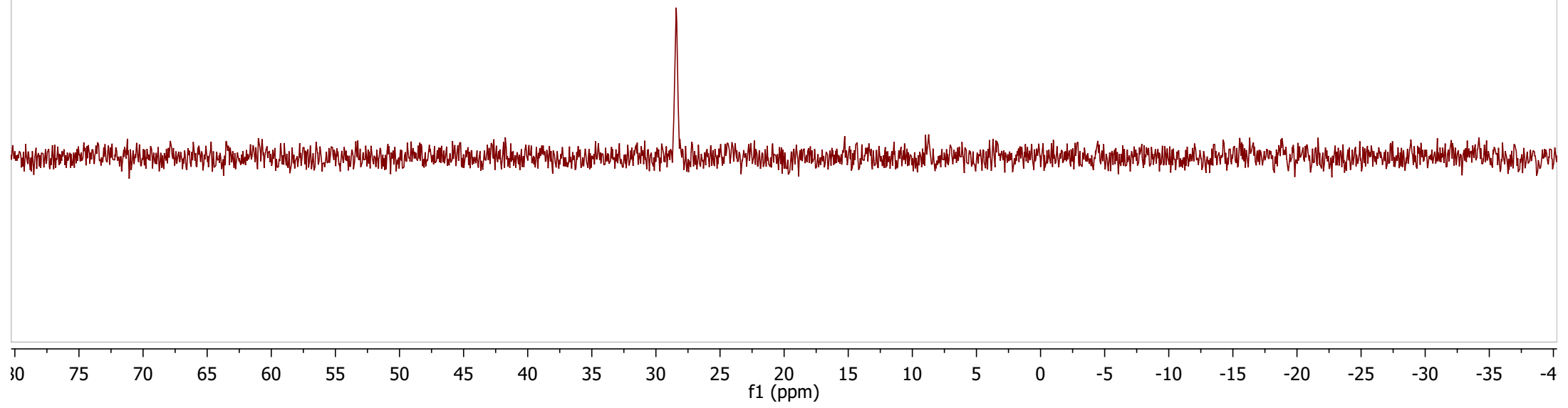
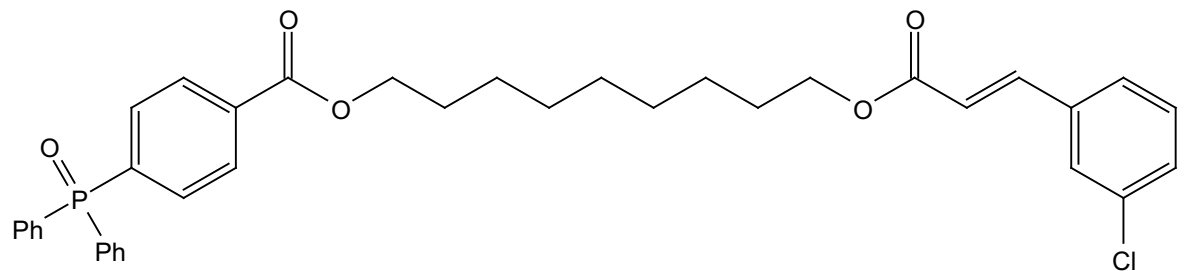


Compound 5 in CDCl₃



— 28.42

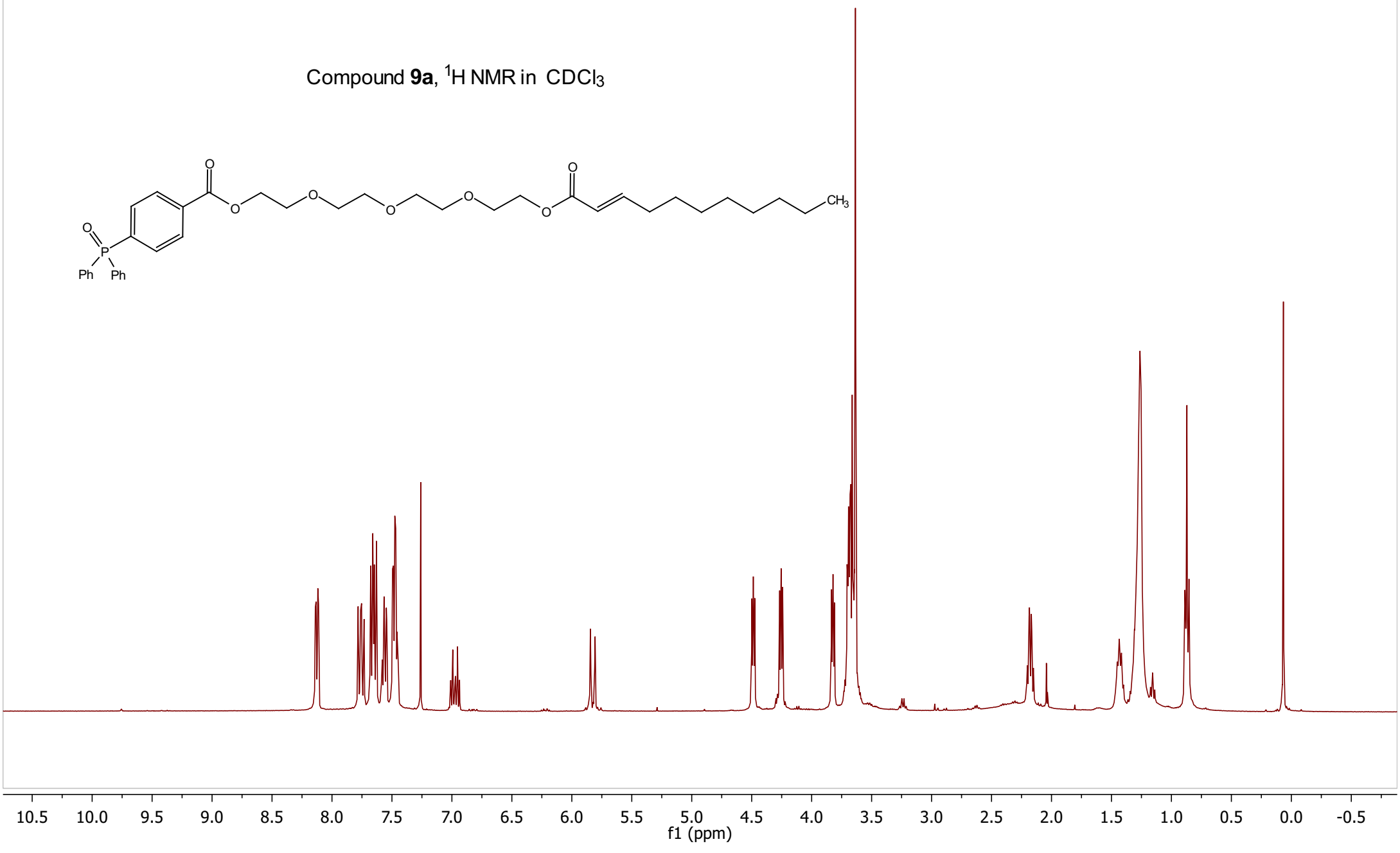
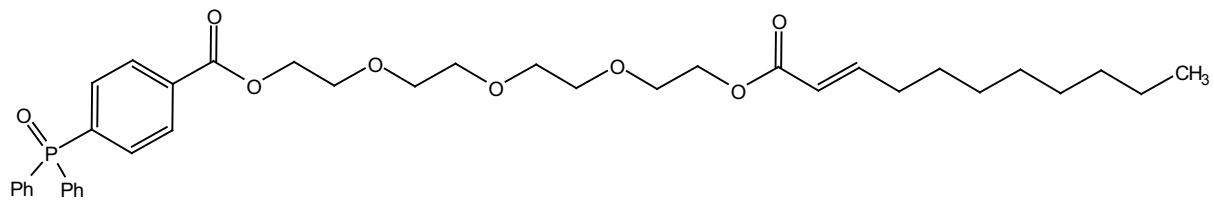
Compound **5** in CDCl₃

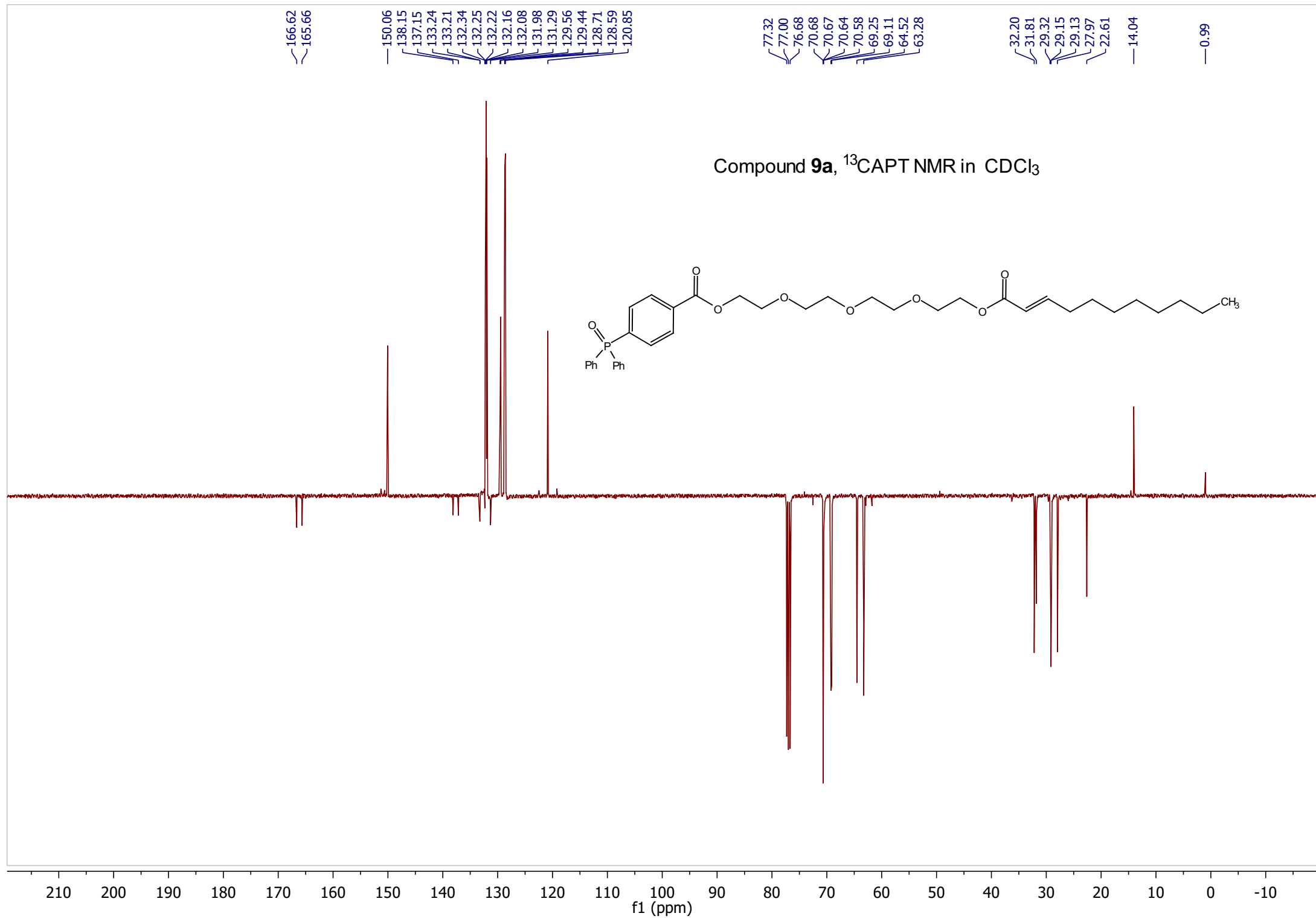


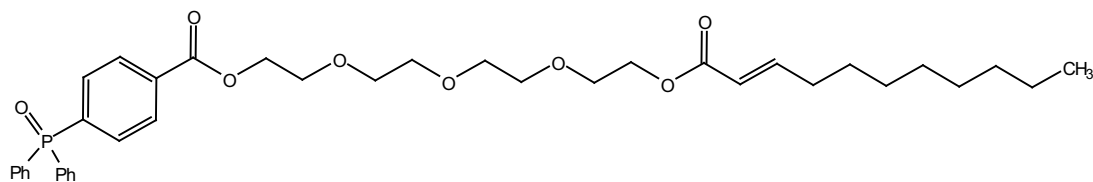
8.14
8.13
8.12
8.11
7.78
7.76
7.75
7.73
7.68
7.66
7.66
7.65
7.63
7.63
7.57
7.56
7.55
7.49
7.49
7.48
7.47
7.47
7.26
6.99
6.98
6.97
6.95
5.85
5.84
5.84
5.81
5.81
4.50
4.49
4.47
4.27
4.25
4.24
3.83
3.82
3.81
3.66
3.63
2.19
2.18
2.17
1.45
1.43
1.42
1.40
1.33
1.31
1.26
0.89
0.87
0.85

Nony

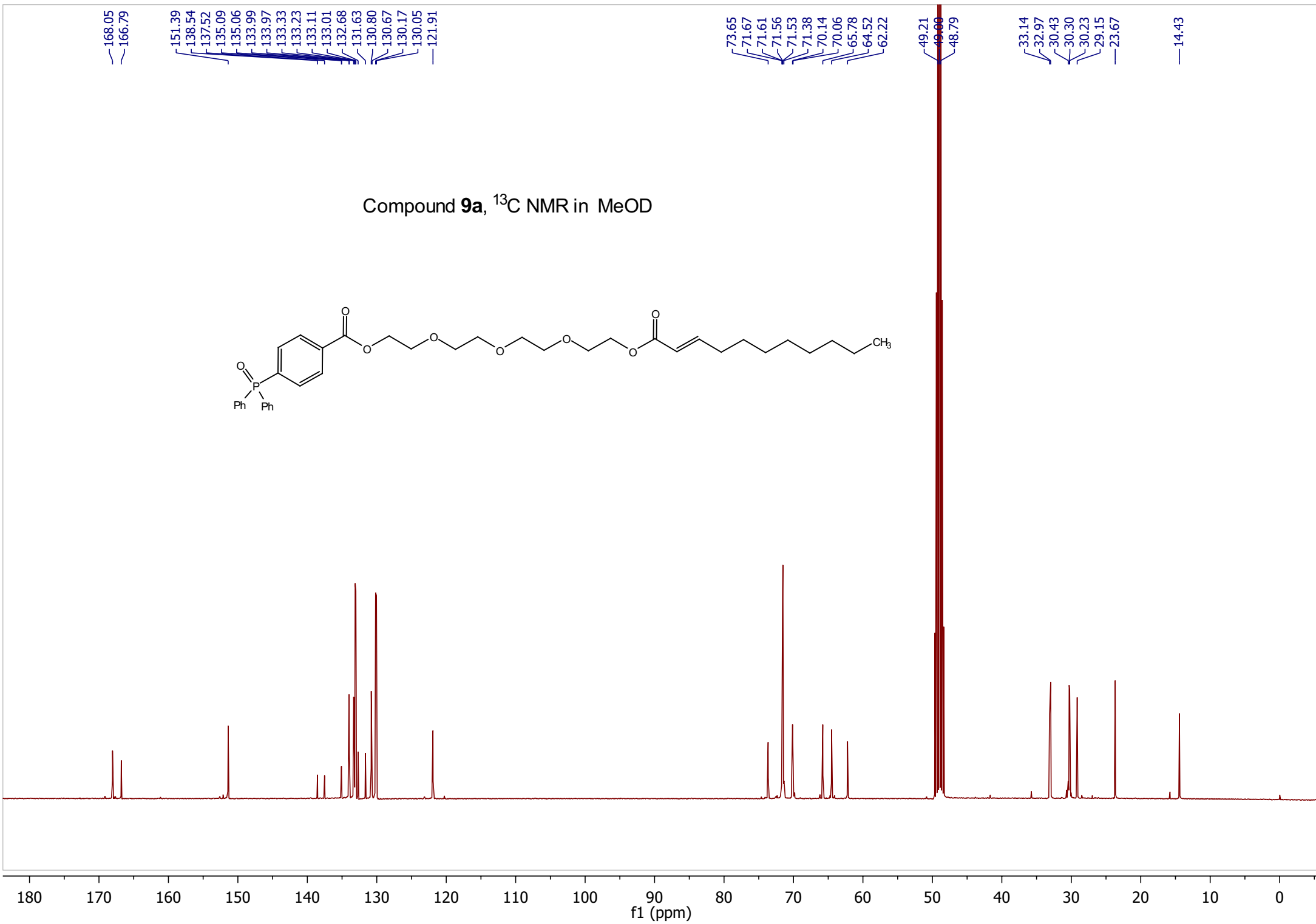
Compound **9a**, ¹H NMR in CDCl₃



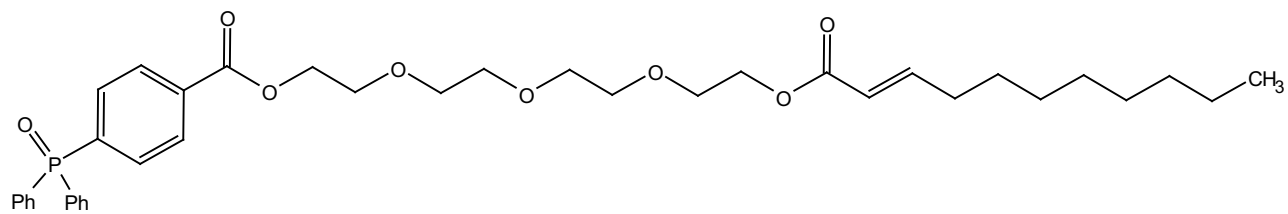




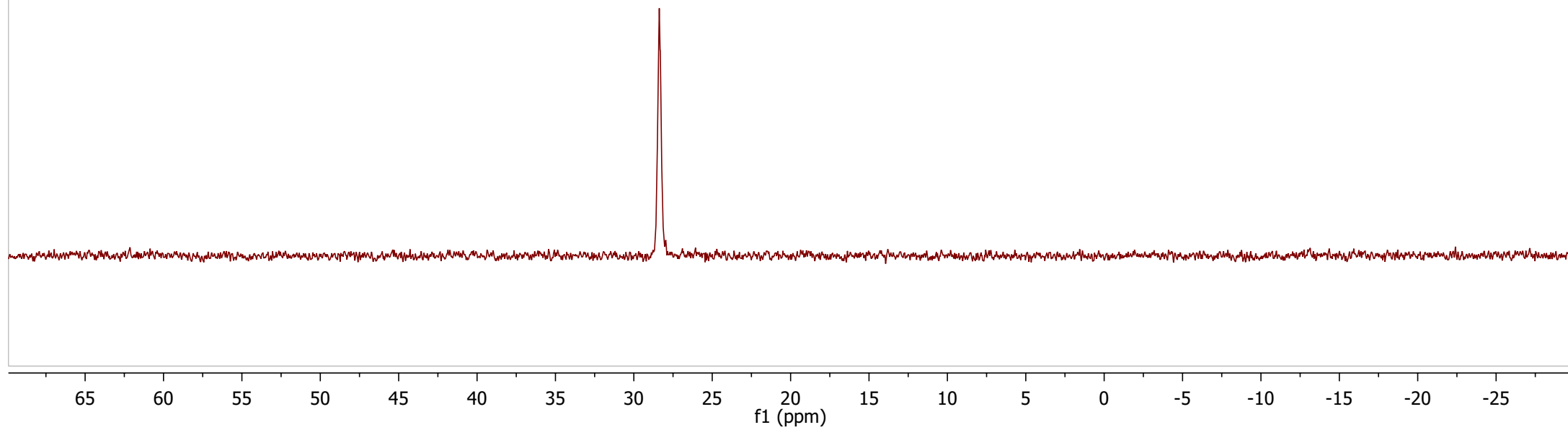
Compound 9a, ¹³C NMR in MeOD



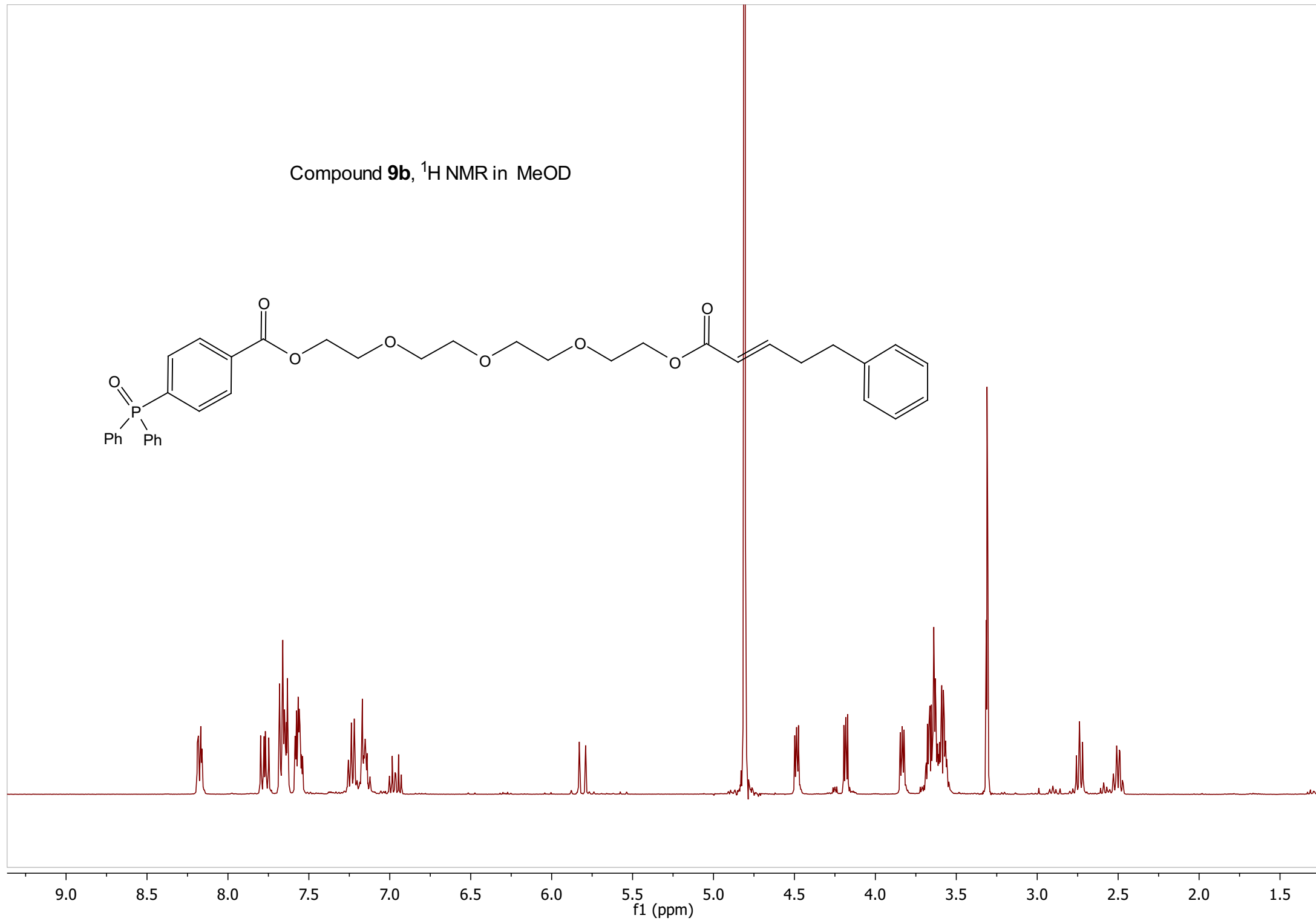
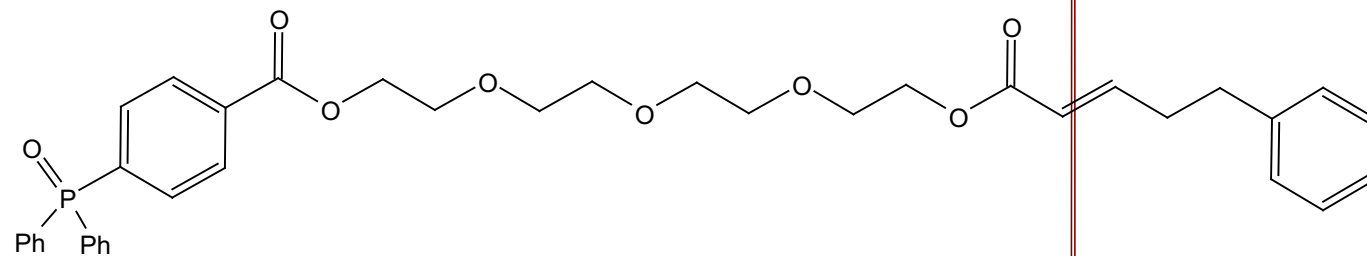
Compound **9a**, ^{31}P NMR in CDCl_3



— 28.38



Compound **9b**, ^1H NMR in MeOD

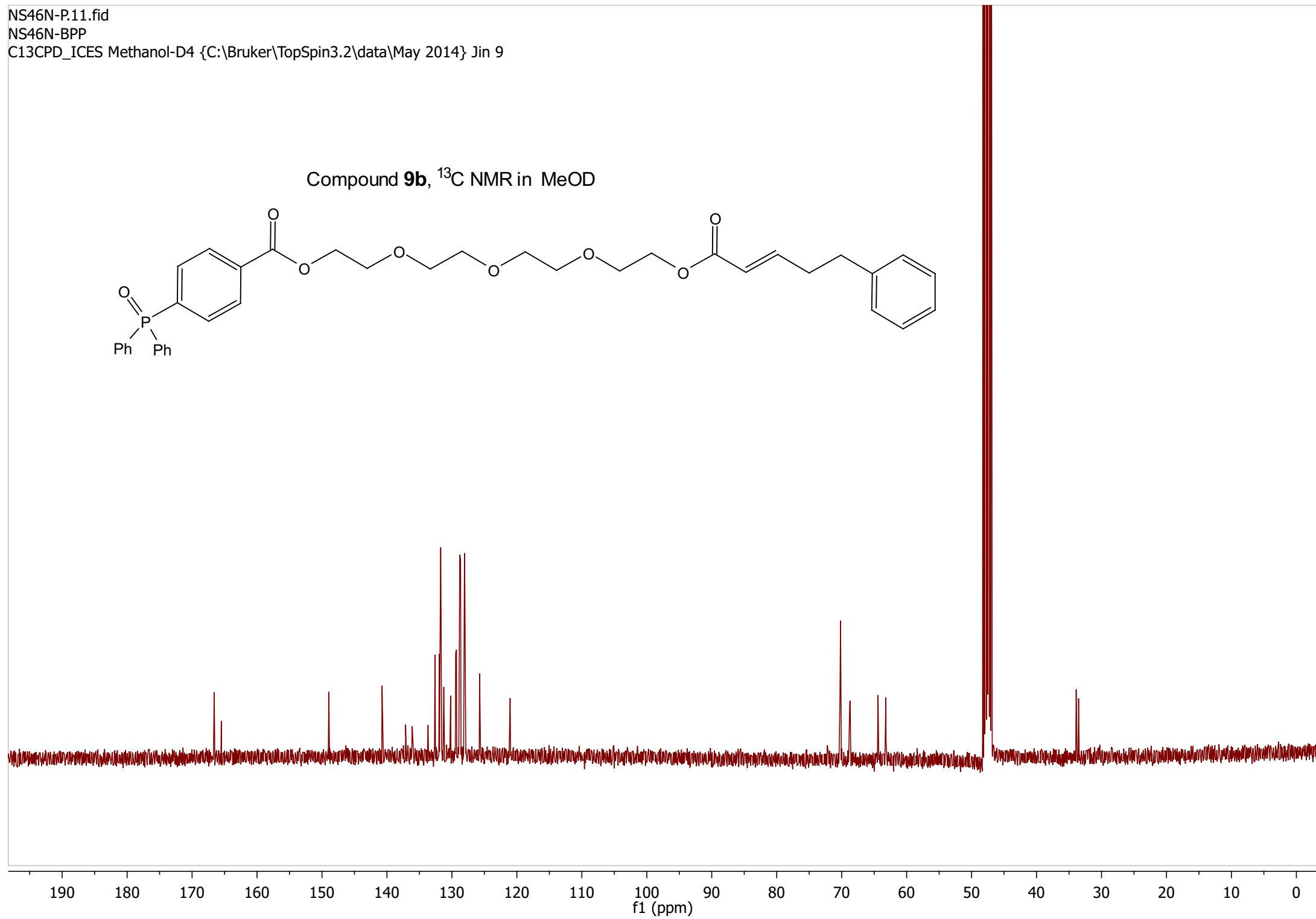
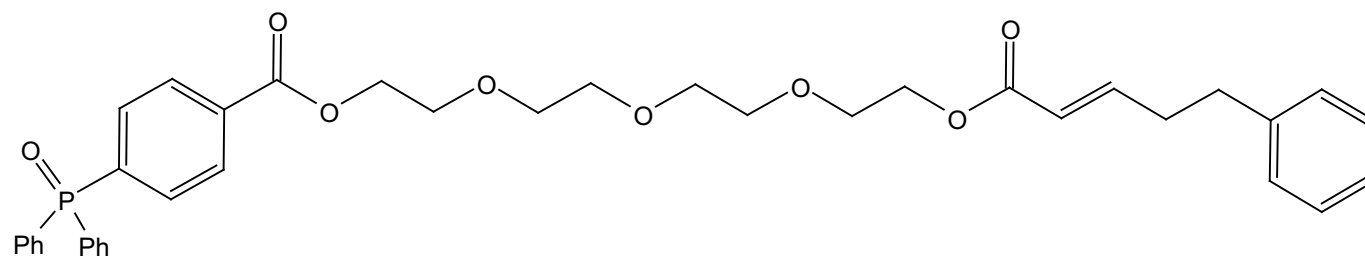


NS46N-P.11.fid

NS46N-BPP

C13CPD_ICES Methanol-D4 {C:\Bruker\TopSpin3.2\data\May 2014} Jin 9

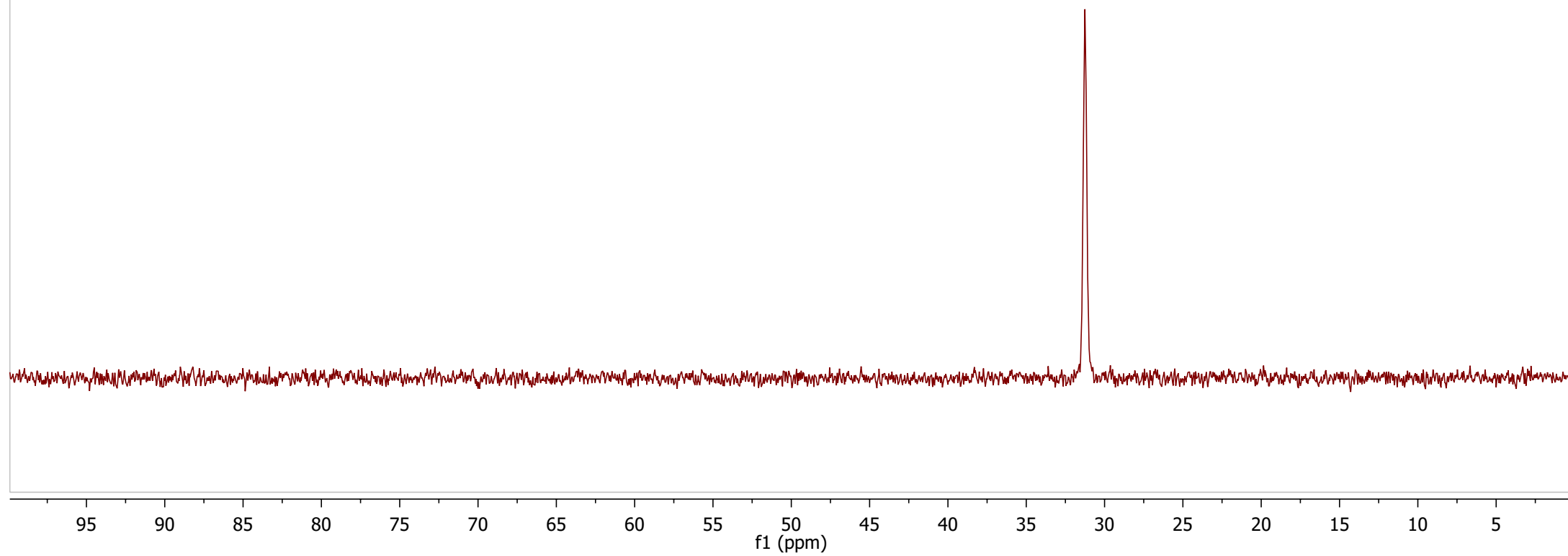
Compound **9b**, ^{13}C NMR in MeOD



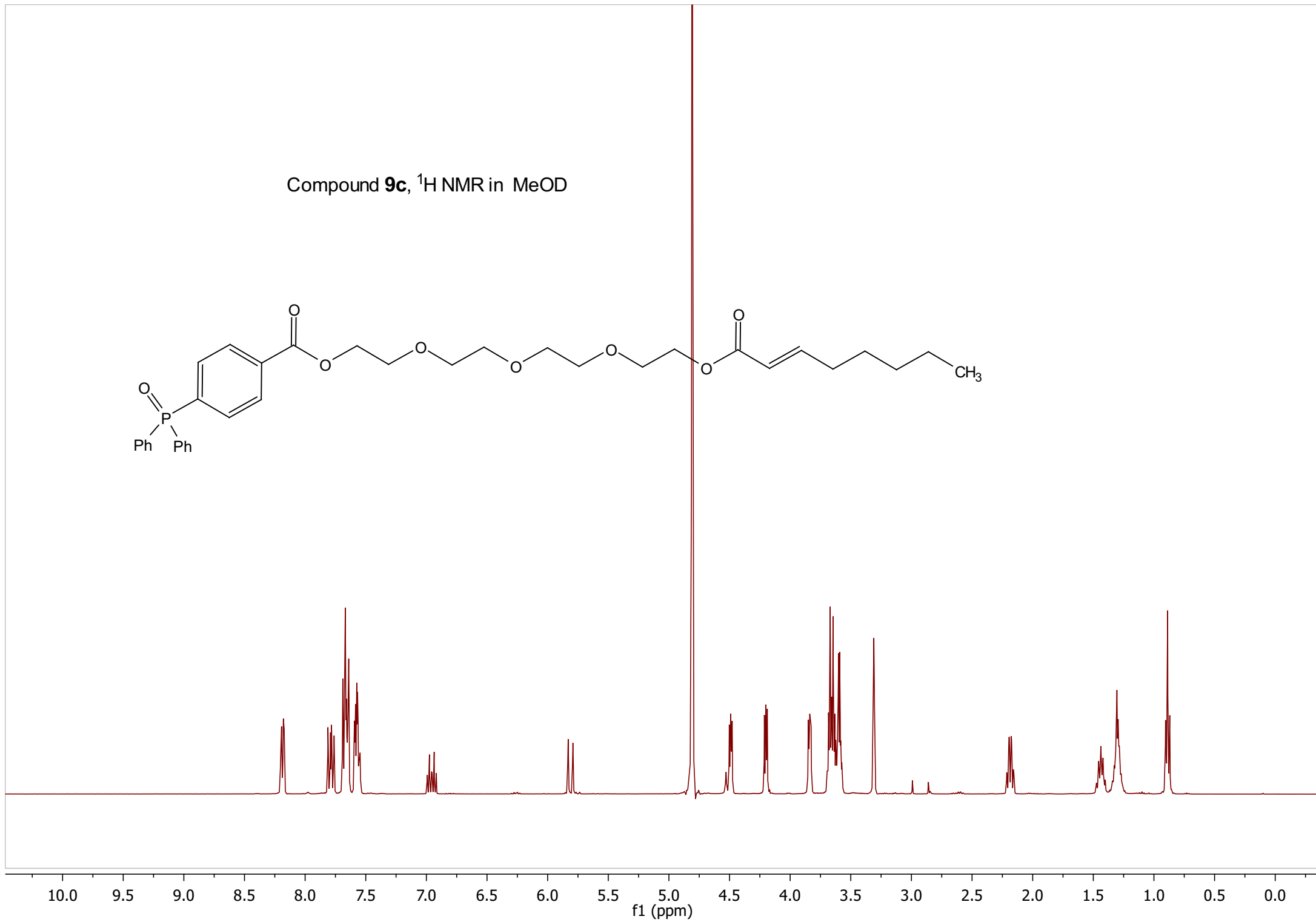
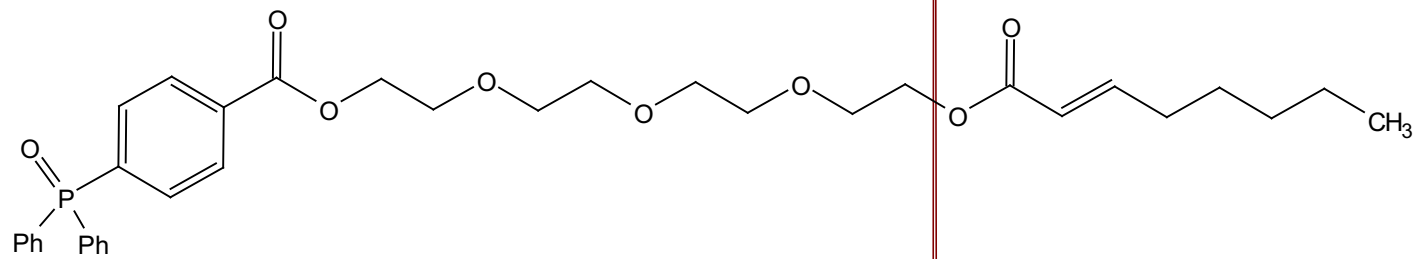
NS46N.2.fid
NS46N-BPP
bruker_31P_1D_1Hdecoupled MeOD {C:\Bruker\TOPSPIN\data\CSL\CSL} ICES 19

— 31.25

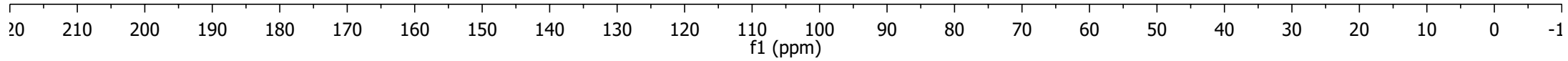
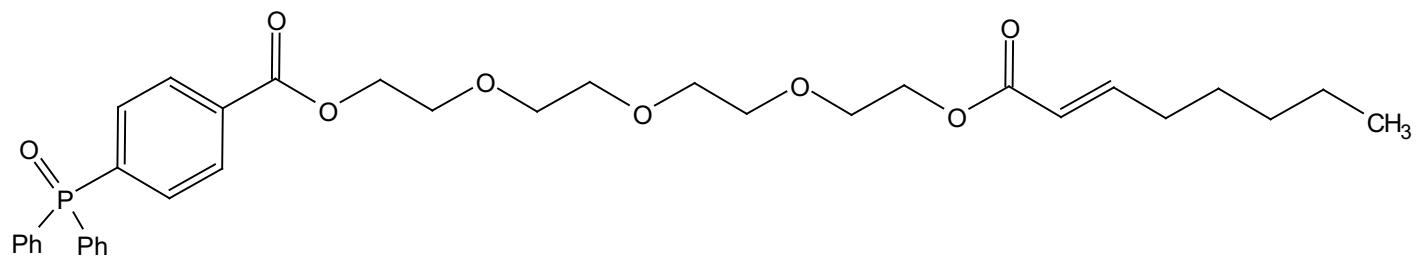
Compound **9b**, ^{31}P NMR in MeOD



Compound **9c**, ^1H NMR in MeOD



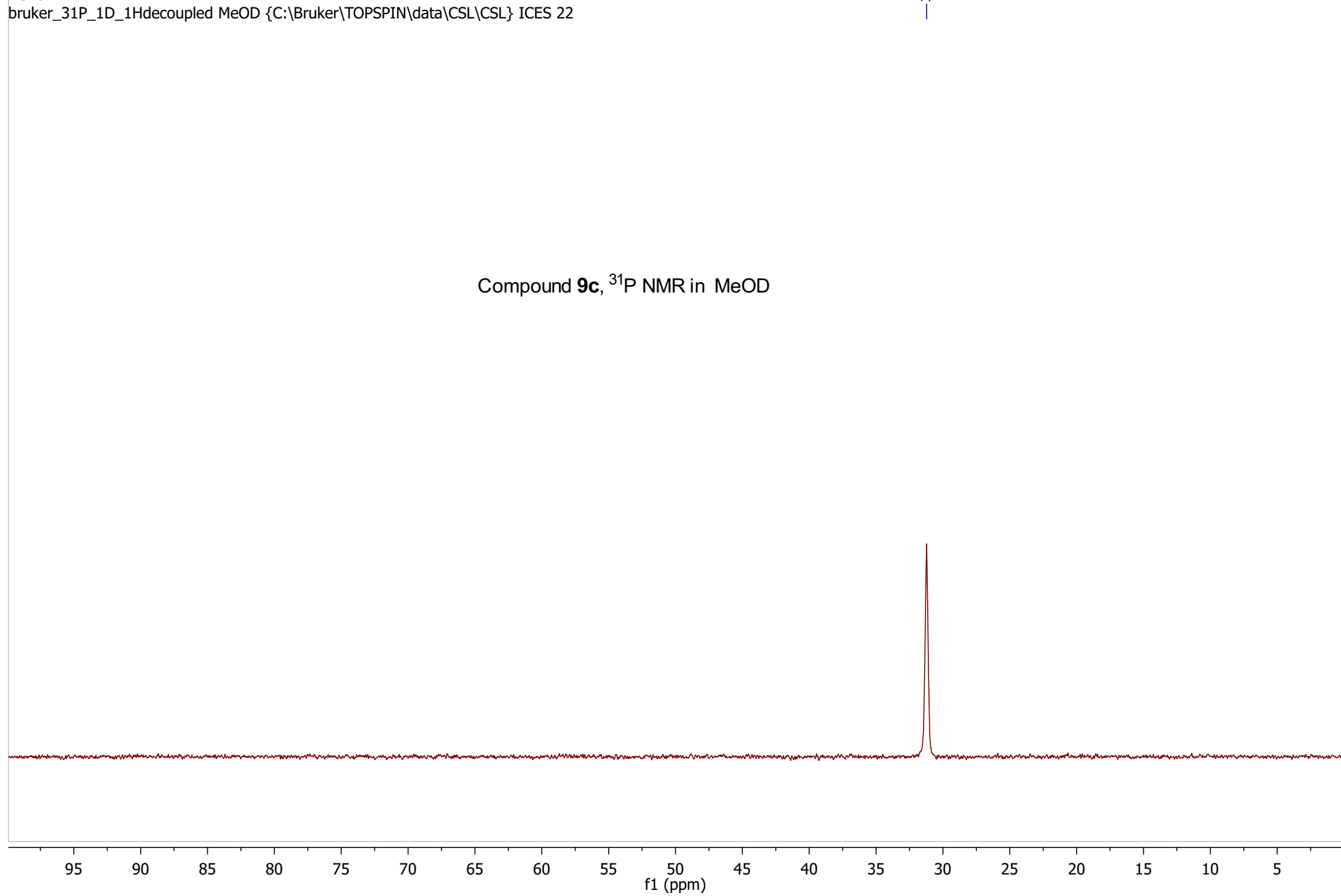
Compound **9c**, ^{13}C NMR in MeOD



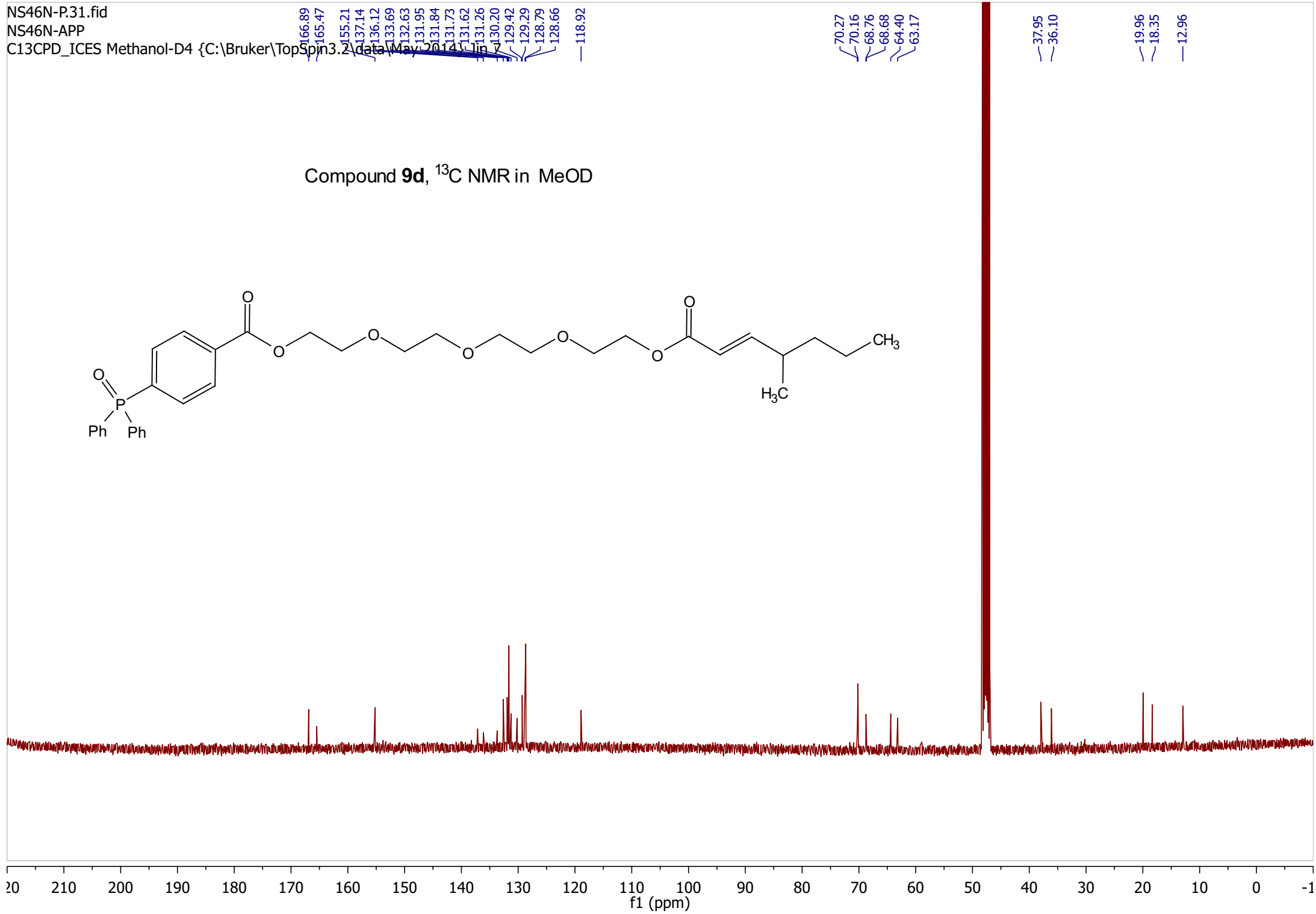
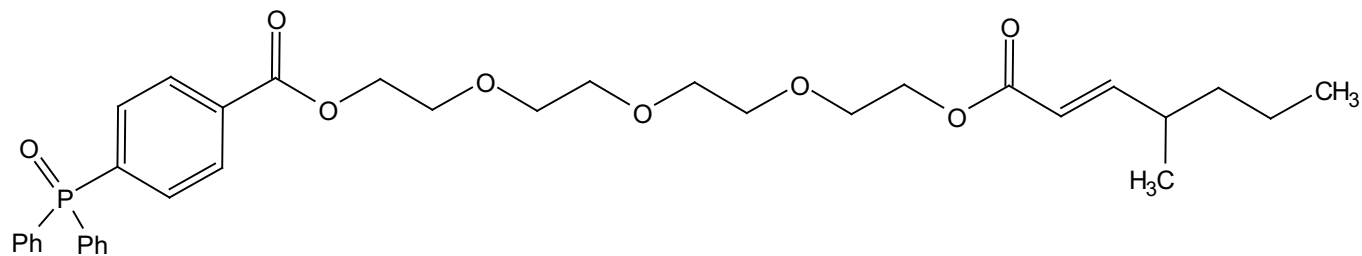
NS46N.5.fid
NS46N-EPP
bruker_31P_1D_1Hdecoupled MeOD {C:\Bruker\TOPSPIN\data\CSL\CSL} ICES 22

— 31.22

Compound **9c**, ^{31}P NMR in MeOD



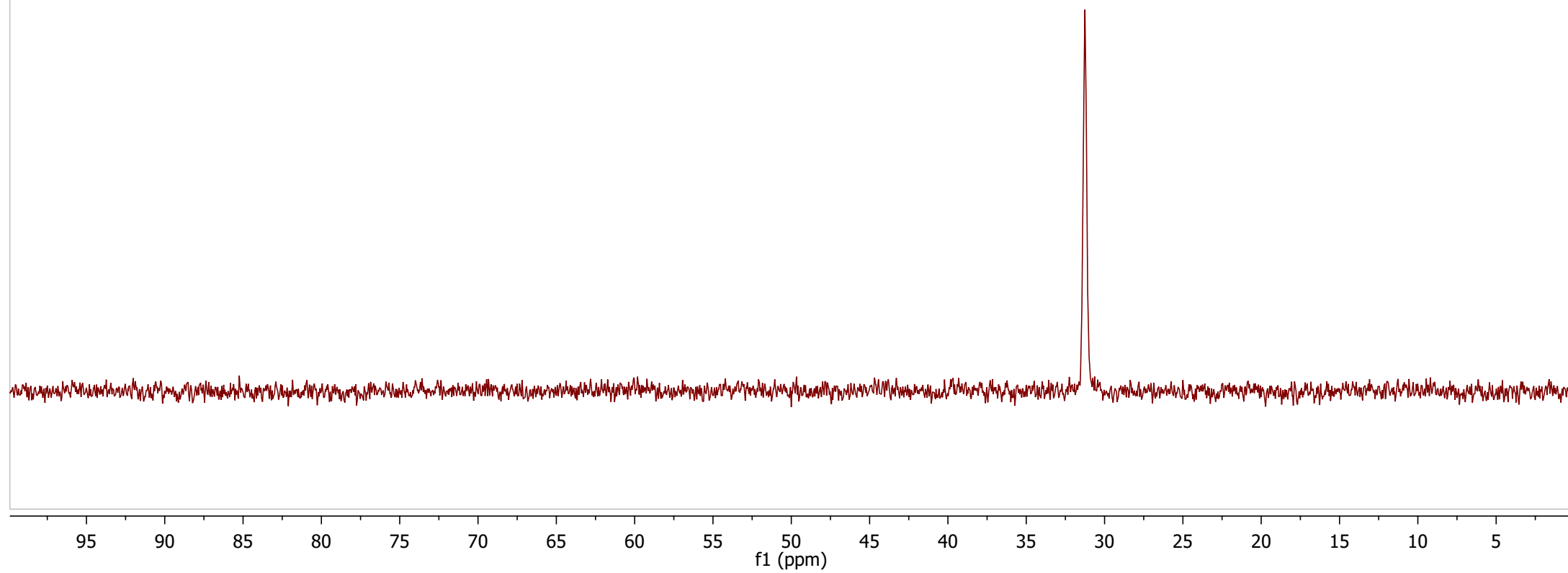
Compound **9d**, ¹³C NMR in MeOD

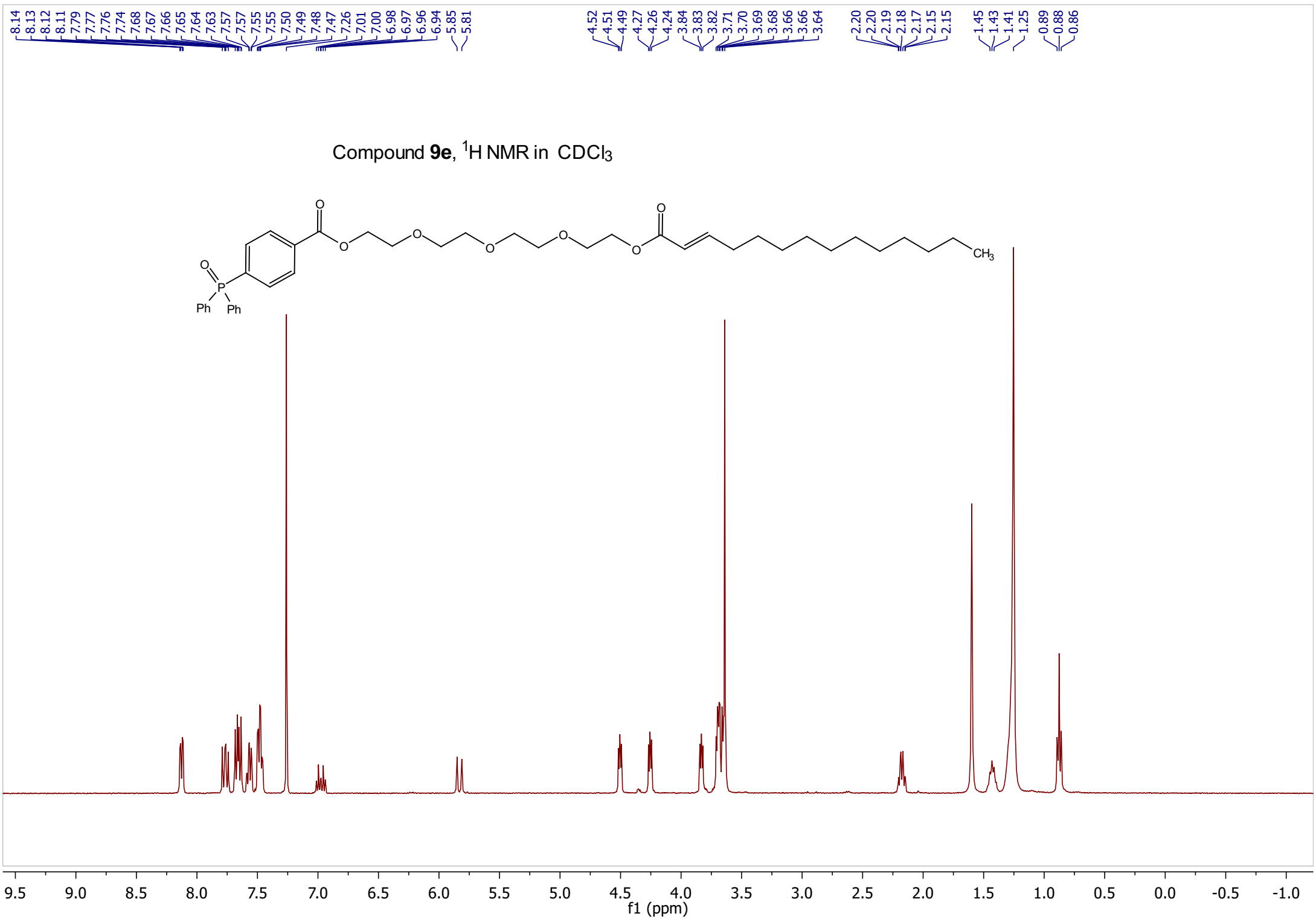


NS46N.1.fid
NS46N-APP
bruker_31P_1D_1Hdecoupled MeOD {C:\Bruker\TOPSPIN\data\CSL\CSL} ICES 18

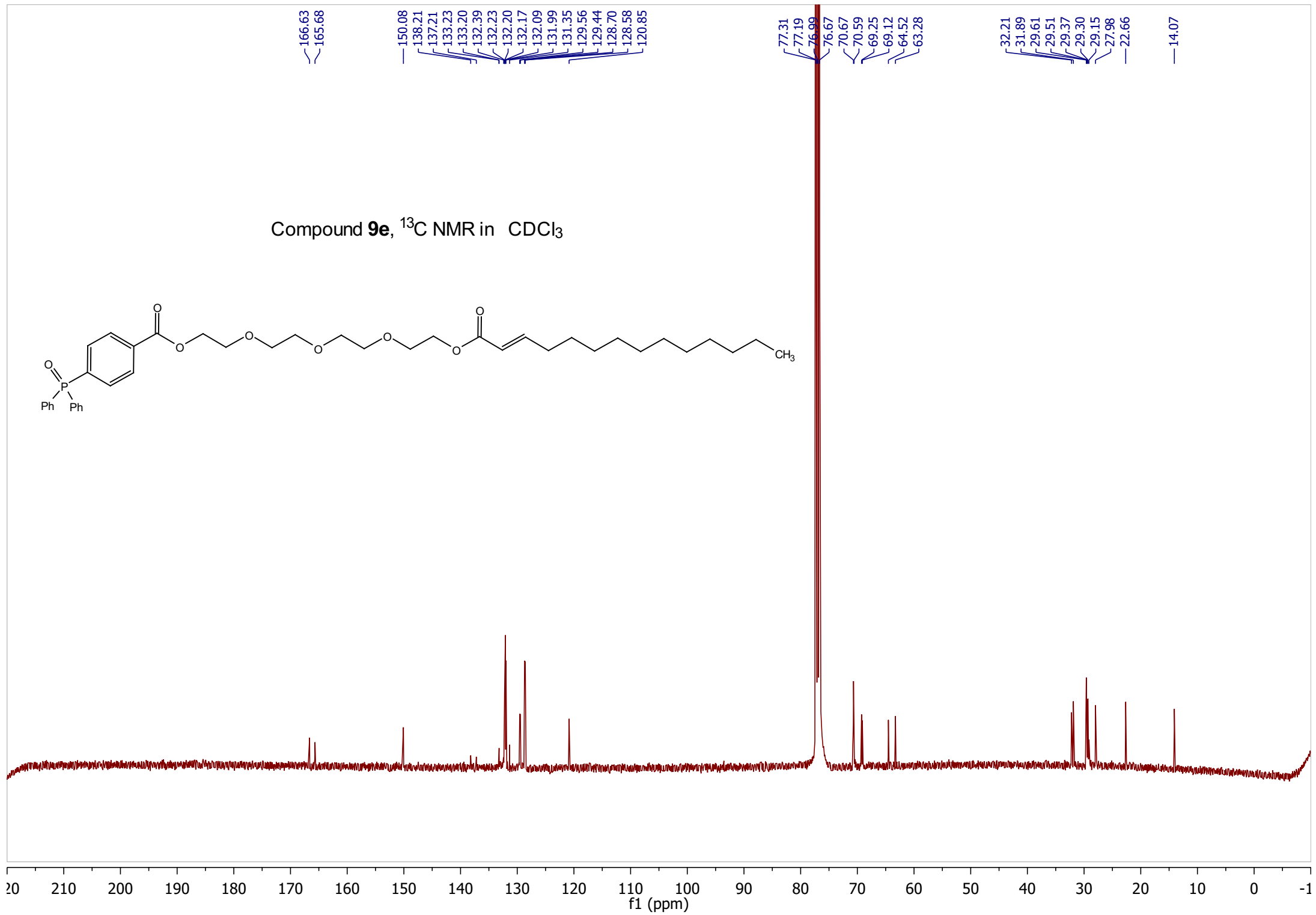
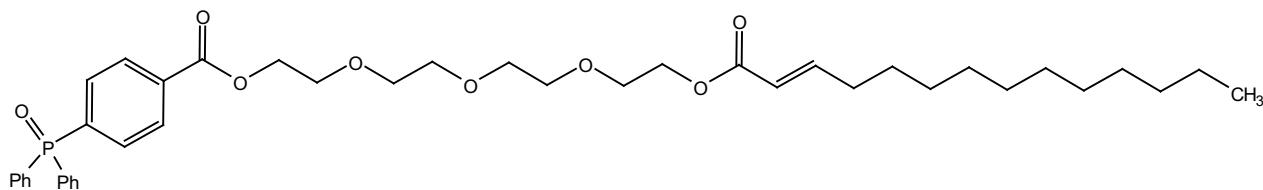
—31.25

Compound **9d**, ^{31}P NMR in MeOD





Compound **9e**, ^{13}C NMR in CDCl_3



168.08
166.81
151.42
138.53
137.52
135.10
135.08
134.00
133.98
133.33
133.23
133.12
133.02
132.68
131.62
130.80
130.68
130.17
130.05
121.91

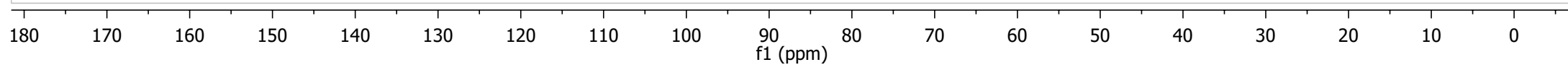
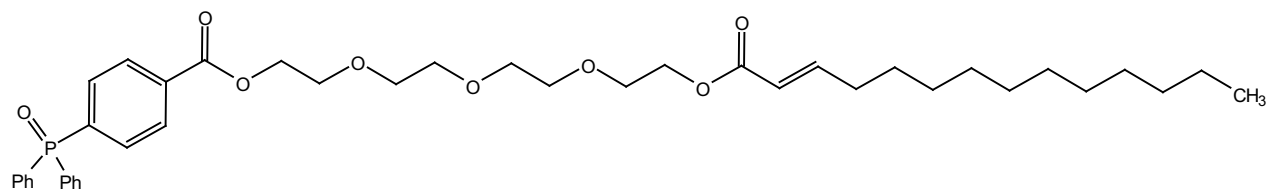
71.68
71.61
71.58
70.14
70.07
65.79
64.53

49.43
49.21
49.00
48.79
48.57

33.15
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30.71
30.63
30.46
30.44
30.23
29.15
23.71

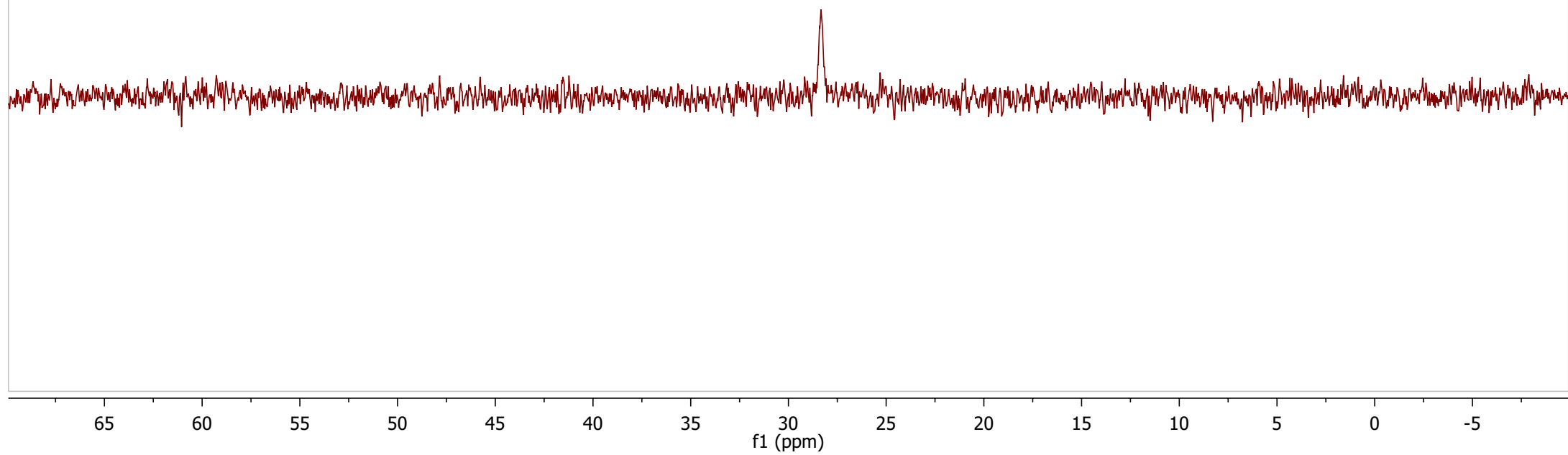
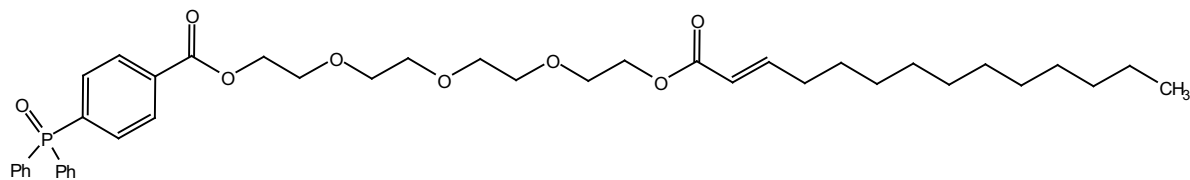
14.43

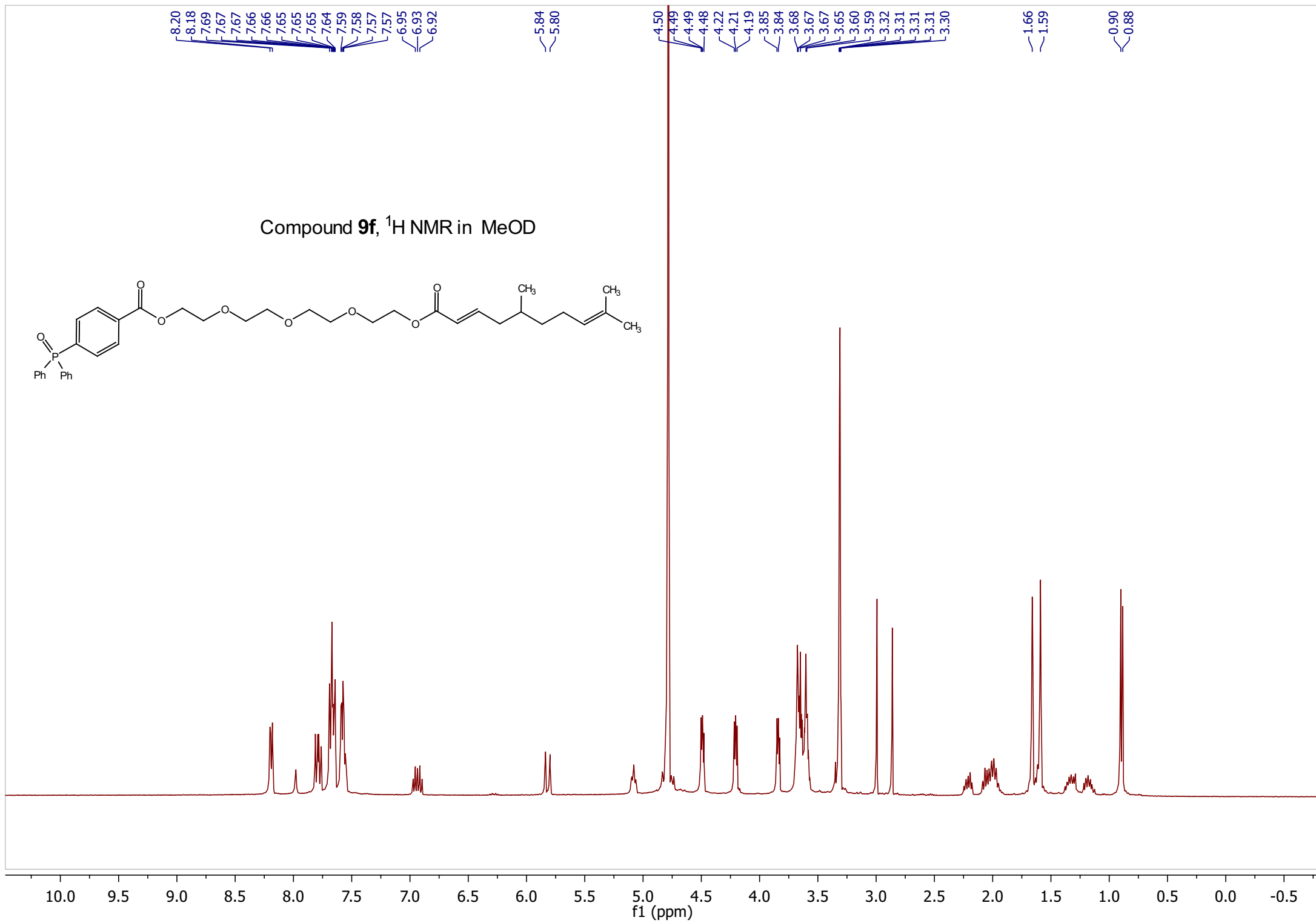
Compound **9e**, ^{13}C NMR in MeOD

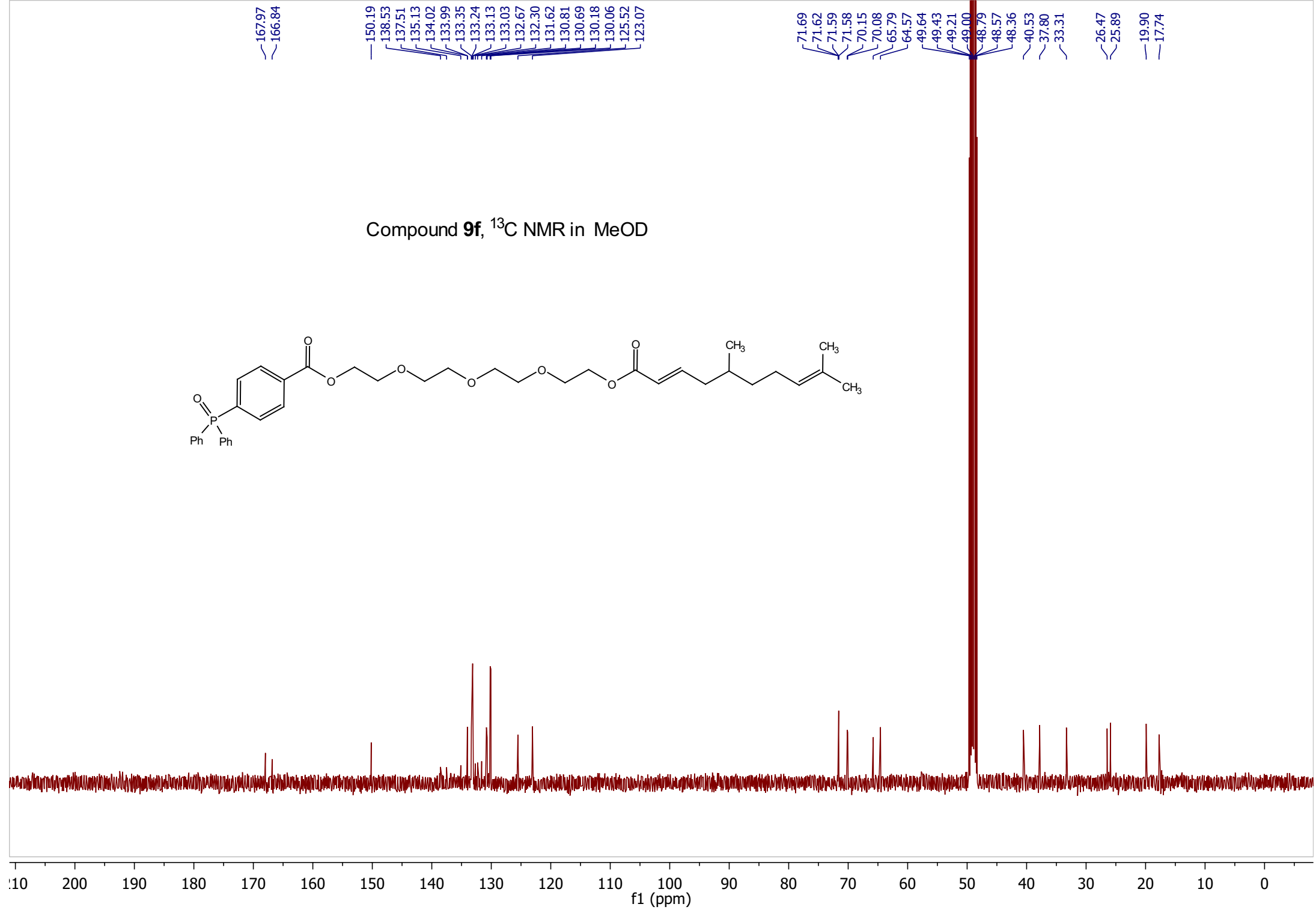
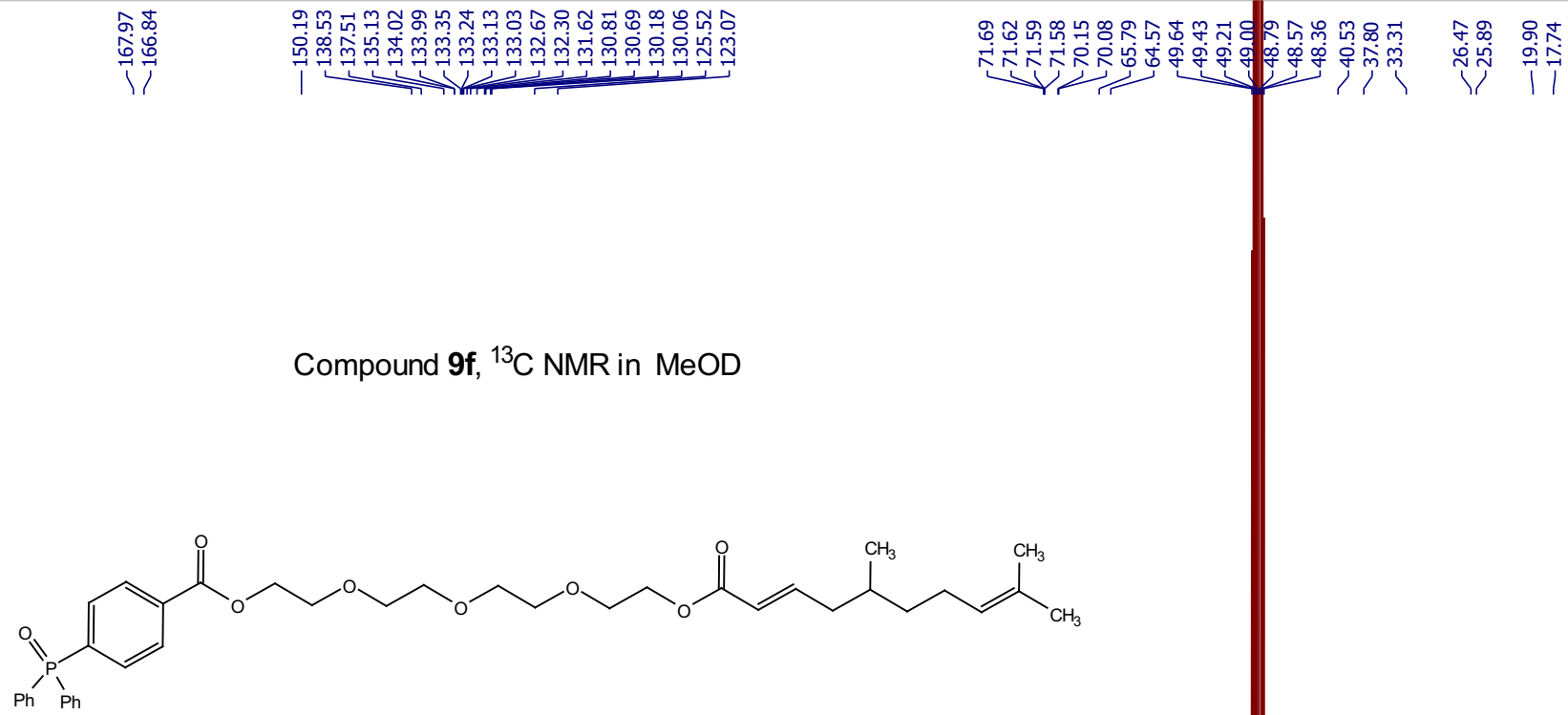


—28.33

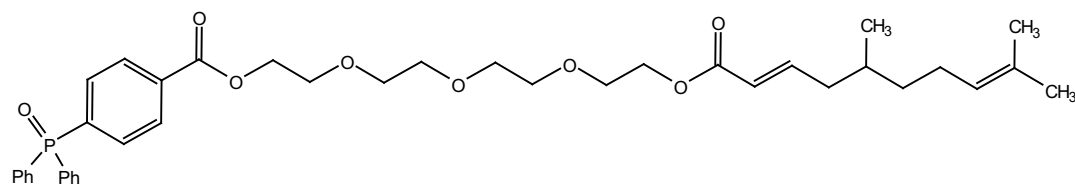
Compound **9e**, ^{31}P NMR in CDCl_3



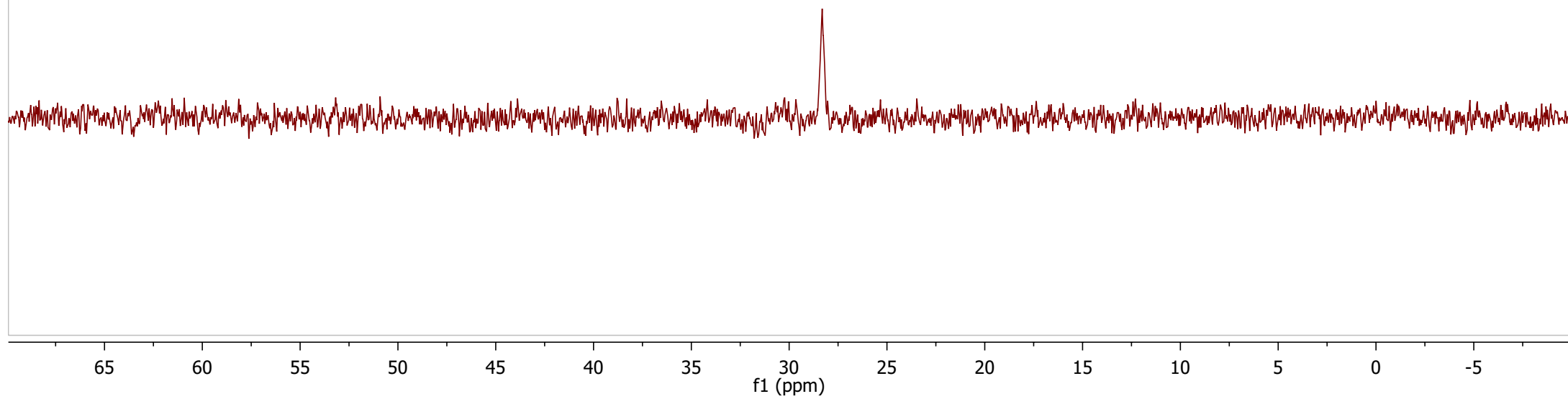




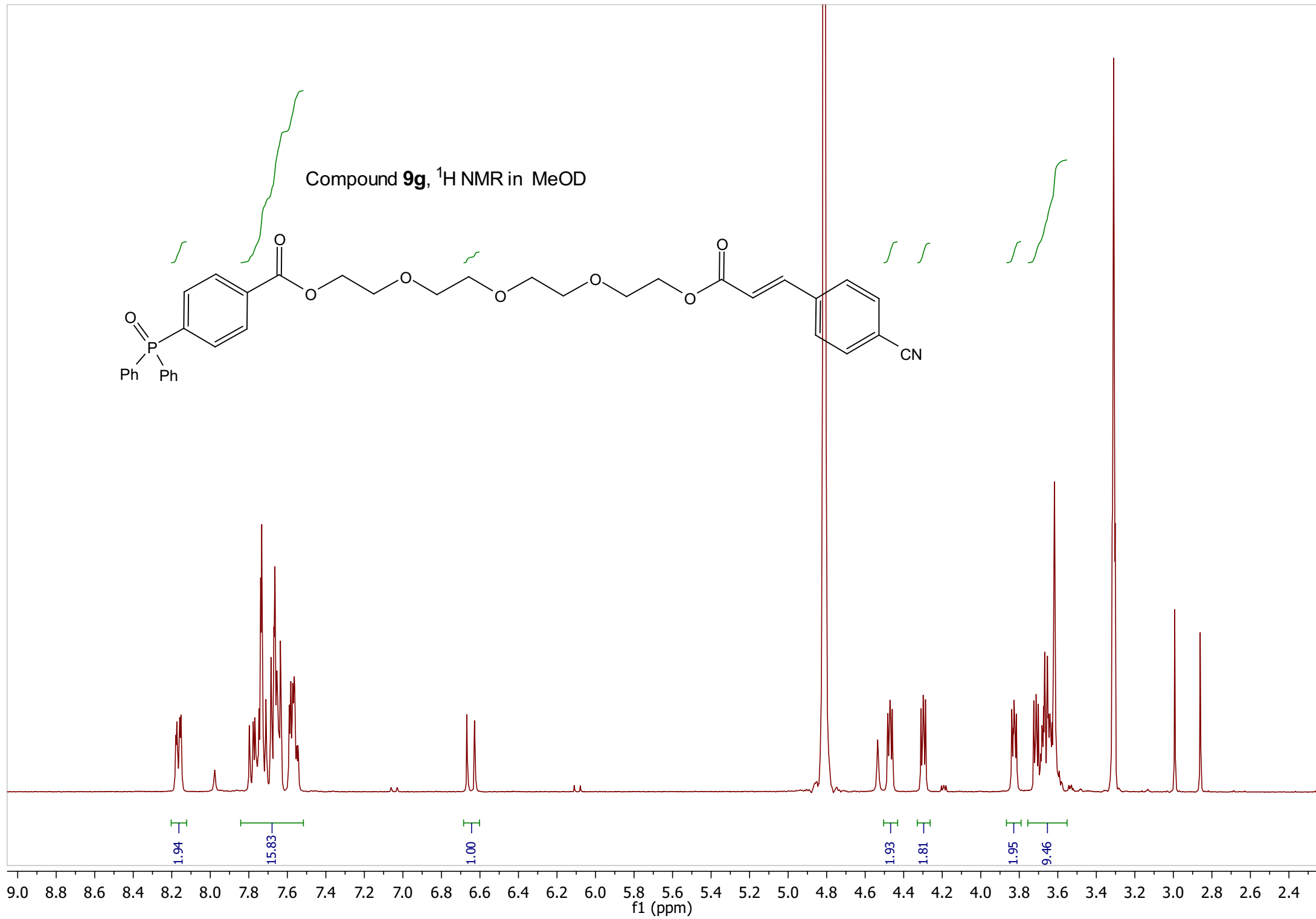
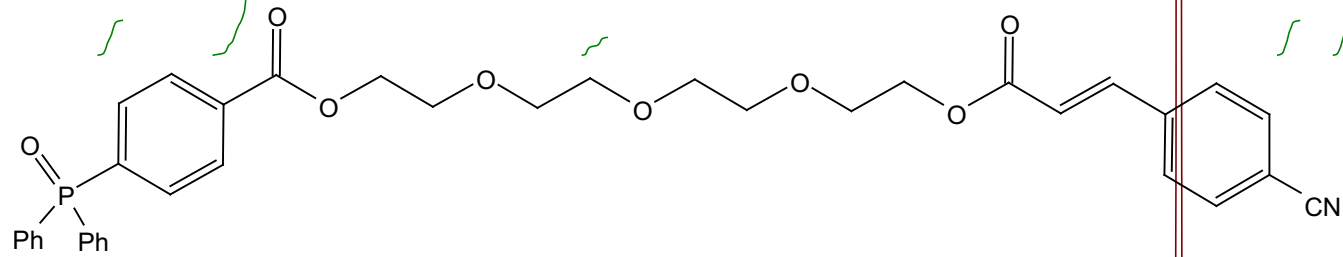
Compound **9f**, ^{31}P NMR in CDCl_3



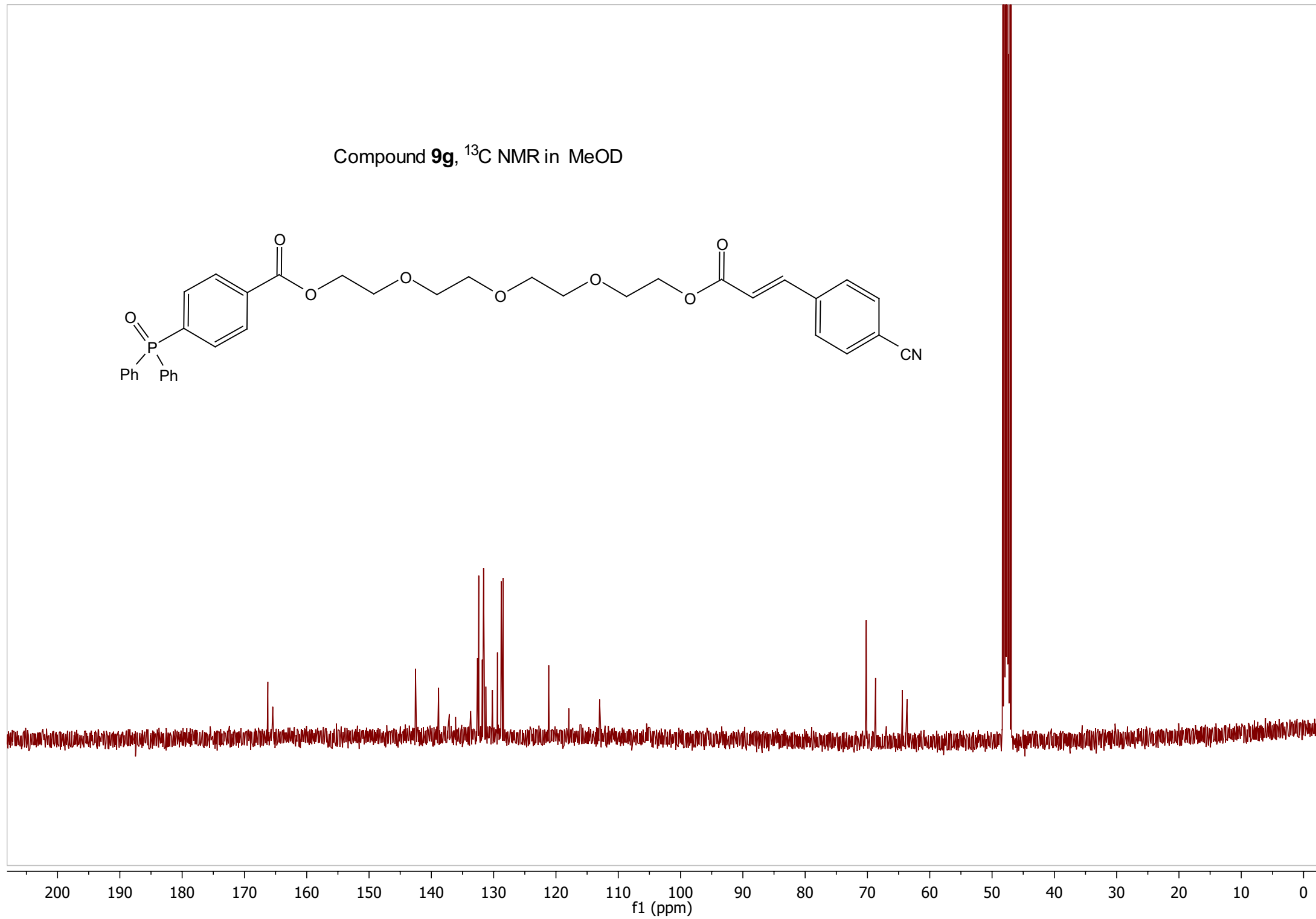
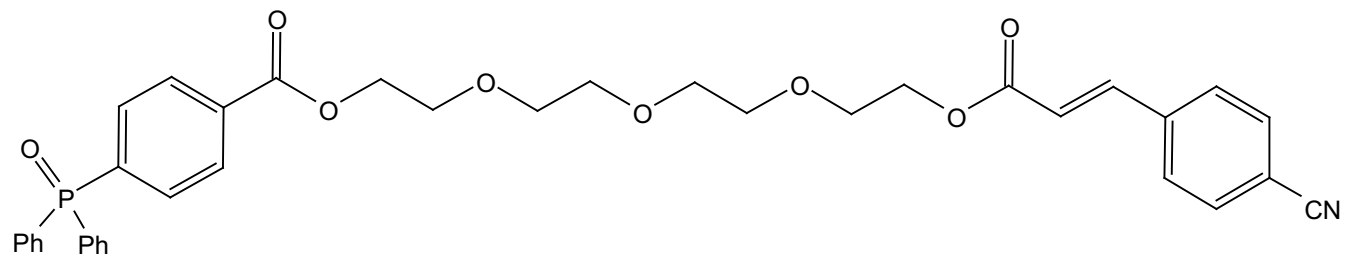
—28.31



Compound **9g**, ^1H NMR in MeOD

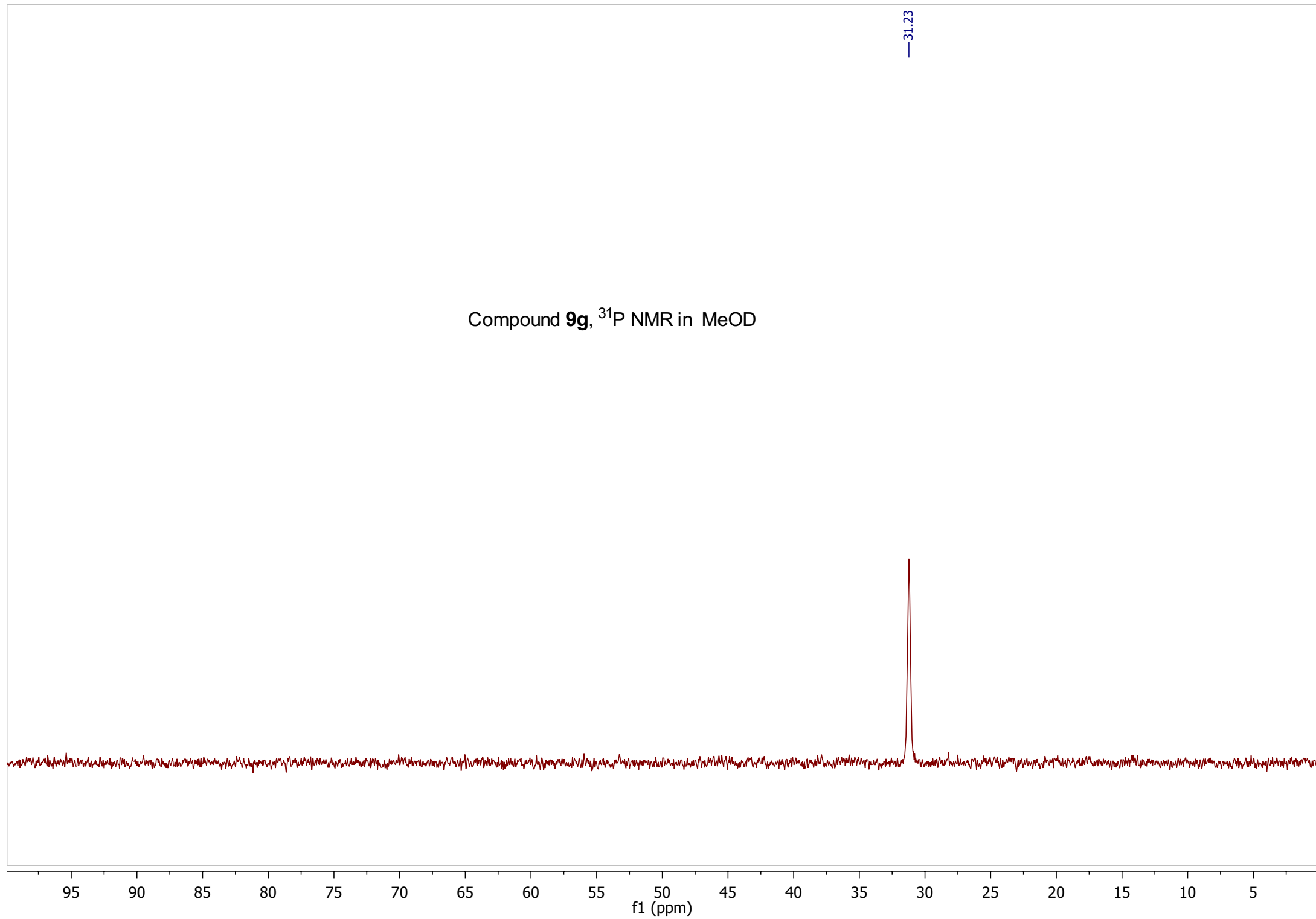


Compound **9g**, ^{13}C NMR in MeOD

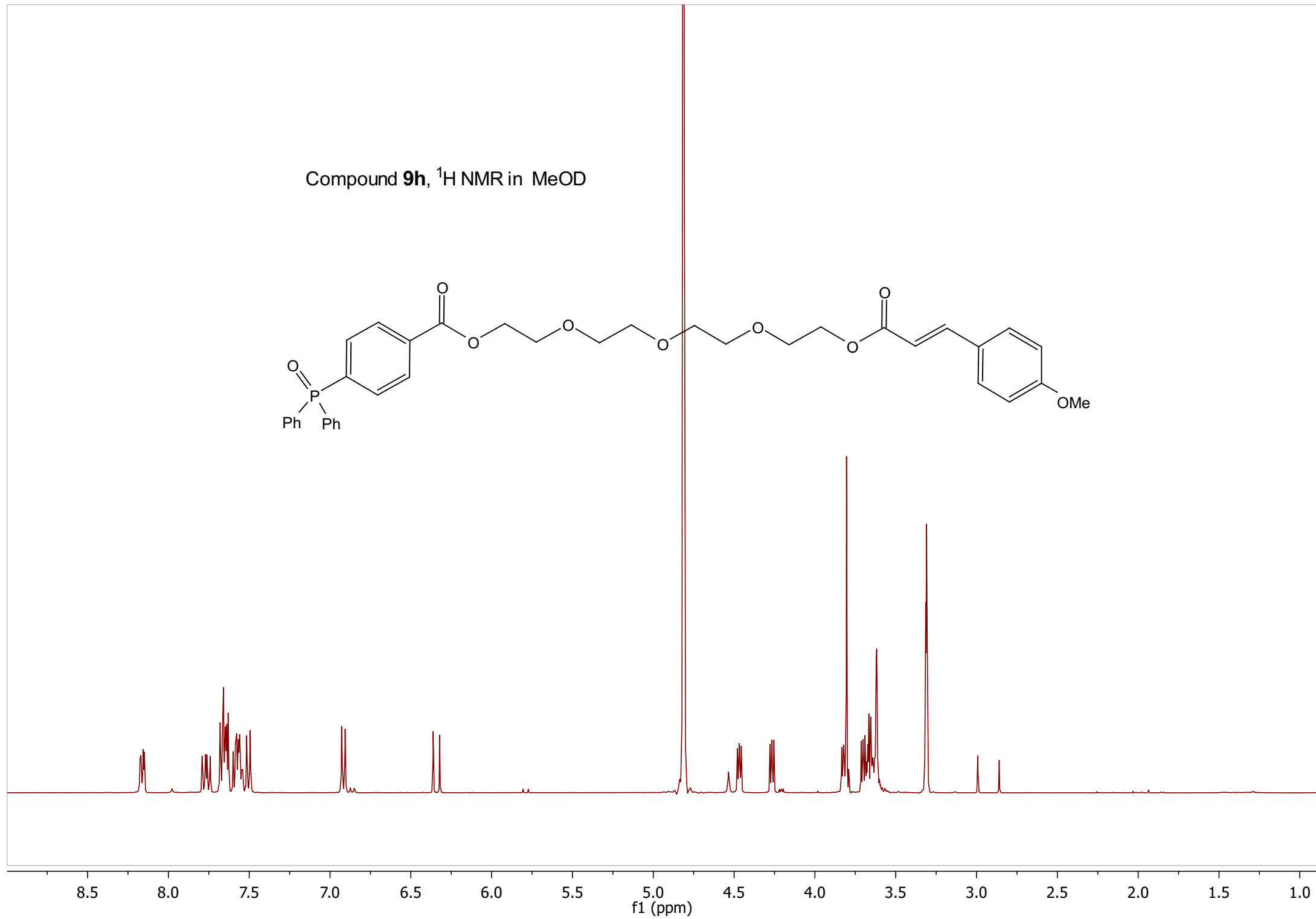
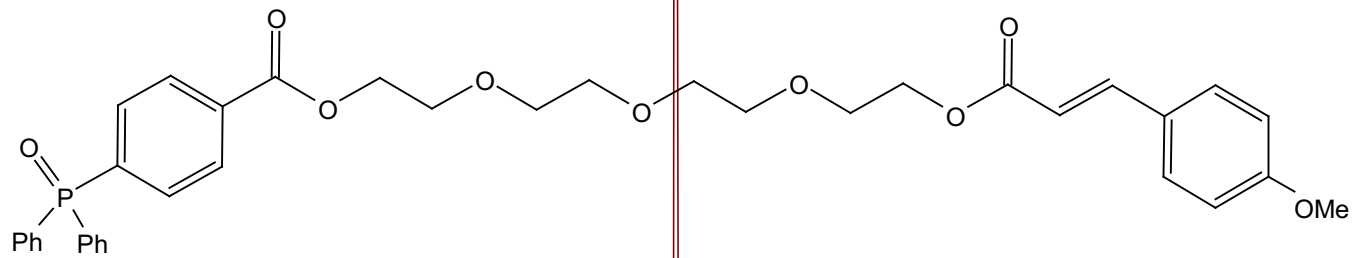


Compound **9g**, ^{31}P NMR in MeOD

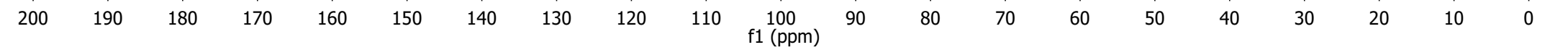
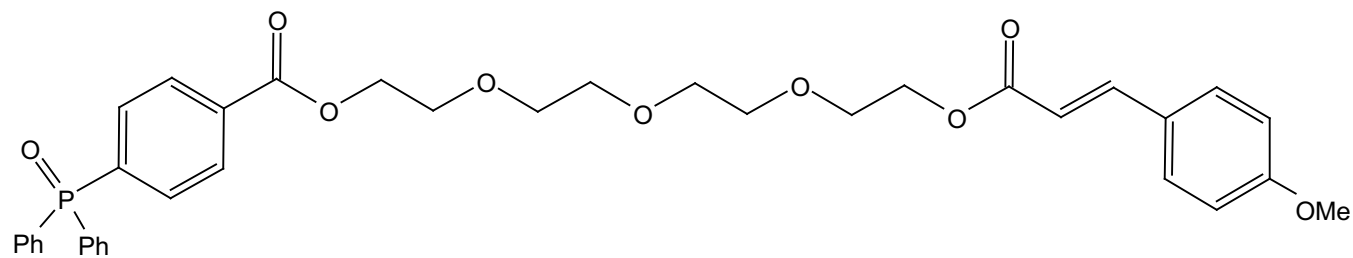
— 31.23



Compound **9h**, ^1H NMR in MeOD



Compound **9h**, ^{13}C NMR in MeOD



Compound **9h**, ^{31}P NMR in MeOD

—31.27

