A General Synthetic Approach to Functionalized Dihydrooxepines

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Supporting Information Available

I. Experimental Section

General Methods

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), diethyl ether (Et_2O), *N*,*N*′-dimethylformamide (DMF), and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, or an aqueous solution of potassium permanganate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040 – 0.063 mm) was used for flash column chromatography and deactivated by mixing with wet hexanes (containing 5% wt water) for 12 h prior to use. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker DRX-600 instruments and calibrated using residual undeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm and C_6D_6: δ_H = 7.16 ppm, δ_C = 128.1 ppm) as an internal reference. The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, sep = septet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Perkin–Elmer 100 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI-TOF (time of flight) mass spectrometer ESI (electrospray ionization). Electron ionization-mass spectra (EI-MS) were recorded on an Agilent 5973N GC/MS (gas chromatograph/mass spectrometer).

General procedure for the Baeyer–Villiger oxidation of enones to lactones. To a stirred slurry of flame-dried 4 Å MS (200 mg) and *trans*-1,2-diaminocyclohexane (60.1 µL, 0.50 mmol, 0.50 equiv) in CH_2Cl_2 (7.5 mL) was added $SnCl_4$ (500 µL, 1.0 M in CH_2Cl_2, 0.50 mmol, 0.50 equiv) at 25 °C. The resulting mixture was cooled to 0 °C and TMSOOTMS (646 µL, 3.0 mmol, 3.0 equiv) was added dropwise at this temperature. After stirring at 0 °C for 10 min, a solution of the enone substrate (1.0 mmol) in CH_2Cl_2 (2.0 mL) was added dropwise and the resulting mixture was warmed to 25 °C and stirred for 24 h. After the reaction was complete (as monitored by TLC), solid Na_2SO_3 (150 mg) was added to quench excess peroxide. After stirring at 25 °C for 1 h, the mixture was filtered through a short pad of Celite®, rinsed with ether and concentrated in vacuo. The residue was purified by flash column chromatography [deactivated silica gel (see general methods), ethyl acetate in hexanes] to give the pure lactone product.

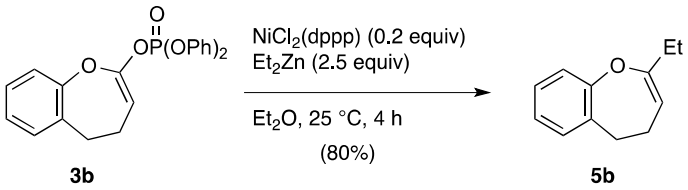
General procedure for the enol phosphate formation from lactones. To a stirred solution of the lactone substrate (0.50 mmol), $(PhO)_2P(O)Cl$ (207 µL, 1.0 mmol, 2.0 equiv) and HMPA (261 µL, 1.5 mmol, 3.0 equiv) in THF (5.0 mL) at −78 °C was added KHMDS (2.0 mL, 0.5 M in toluene, 1.0 mmol, 2.0 equiv) dropwise. After stirring at −78 °C for 30 min, the reaction was quenched at −78 °C with 2% aqueous solution of NH_4Cl. The resulting mixture was allowed to warm to 25 °C and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography [deactivated silica gel (see general methods), ethyl acetate in hexanes] to give the pure enol phosphate product.

General procedure for the enol phosphate reduction to dihydrooxepines (method A). To a stirred solution of the enol phosphate substrate (0.20 mmol) and $Pd(PPh_3)_4$ (46.2 mg, 0.040 mmol, 0.20 equiv) in anhydrous $ClCH_2CH_2Cl$ (4.0 mL) at 0 °C was added Et_3Al (500 µL, 1.0 M in hexanes, 0.50 mmol, 2.5 equiv) over 20 min. After stirring at 0 °C for 40 min, the mixture was allowed to warm to 25 °C and stirred for 1 h. After completion of the reaction (as monitored by TLC), 100 mg solid sodium potassium tartrate was added to the dark red solution and the mixture was stirred vigorously at 25 °C for 2 h. The resulting orange slurry was filtered through a short pad

of Celite® and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography [deactivated silica gel (see general methods), ethyl acetate in pentane] to give the pure dihydrooxepine product.

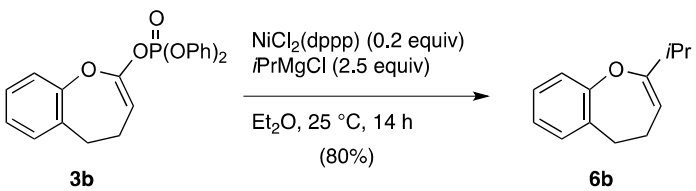
General procedure for the enol phosphate reduction to dihydrooxepines (method B). To a stirred solution of the enol phosphate substrate (0.20 mmol) and $Pd(PPh_3)_4$ (46.2 mg, 0.040 mmol, 0.20 equiv) in anhydrous THF (4.0 mL) at 0 °C was added $LiBH_4$ (1.0 mL, 2.0 M in THF, 2.0 mmol, 10 equiv) over 2 h. The mixture was stirred at 0 °C for an additional 1 h. After completion of the reaction (as monitored by TLC), 0.5 mL MeOH was added dropwise at 0 °C to quench excess $LiBH_4$. The resulting mixture was warmed to 25 °C and diluted with pentane (20 mL). The mixture was filtered through a short pad of Celite® and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography [deactivated silica gel (see general methods), ethyl acetate in pentane] to give the pure dihydrooxepine product.

Formation of compound 5b via Negishi coupling of enol phosphate 3b. To a stirred slurry of $NiCl_2$(dppp) (10.4 mg, 0.0191 mmol, 0.20 equiv) in anhydrous Et_2O (1.0 mL) at 25 °C was added



Et_2Zn (239 µL, 1.0 M in heptane, 0.239 mmol, 2.5 equiv). Then a solution of the enol phosphate **3b** (0.096 mmol) in anhydrous Et_2O (1.0 mL) was added dropwise to the above mixture. After stirring at 25 °C for 4 h, the reaction mixture was diluted with pentane (10 mL), and 50 mg solid sodium potassium tartrate was added. The resulting mixture was stirred vigorously for 30 min and filtered through a short pad of Celite® and the filtrate was concentrated in vacuo. The amount of the product **5b** was determined to be 13.4 mg (0.077 mmol, 80% yield) based on ^{1}H NMR spectroscopic analysis using CH_2Br_2 as internal standard. Pure product **5b** can be obtained by preparative thin layer chromatography.

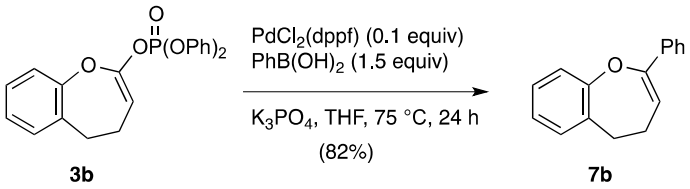
Formation of compound 6b via Kumada coupling of enol phosphate 3b. To a stirred slurry of



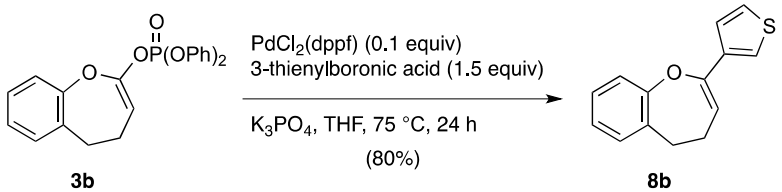
$NiCl_2$(dppp) (10.8 mg, 0.0200 mmol, 0.20 equiv) in anhydrous Et_2O (1.0 mL) at 25 °C was added *i*PrMgCl (125 µL, 2.0 M in THF,

0.250 mmol, 2.5 equiv). Then a solution of the enol phosphate **3b** (0.100 mmol) in anhydrous Et_2O (1.0 mL) was added dropwise to the above mixture. After stirring at 25 °C for 14 h, the reaction mixture was diluted with pentane (10 mL), and 50 mg solid sodium potassium tartrate was added. The resulting mixture was stirred vigorously for 30 min and filtered through a short pad of Celite® and the filtrate was concentrated in vacuo. The amount of the product **6b** was determined to be 15.0 mg (0.080 mmol, 80% yield) based on ^{1}H NMR spectroscopic analysis using CH_2Br_2 as internal standard. Pure product **6b** can be obtained by preparative thin layer chromatography.

Formation of compound 7b via Suzuki coupling of enol phosphate 3b. An oven-dried sealed tube was charged with a solution of the enol phosphate substrate **3b** (0.100 mmol) in degassed THF (1.0 mL). Then $PhB(OH)_2$ (18.3 mg, 0.150 mmol, 1.5 equiv), K_3PO_4 (63.7 mg, 0.300 mmol, 3.0 equiv) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (8.2 mg, 0.010 mmol, 0.10 equiv) were added at 25 °C. The tube was filled with argon and sealed immediately. The reaction mixture was submerged in an pre-heated oil bath at 75 °C and stirred for 24 h. After completion of the reaction (as monitored by TLC), the mixture was cooled to ambient temperature, diluted with Et_2O (5 mL), and filtered through a short pad of Celite®. The filtrate was concentrated in vacuo. The amount of the product **7b** was determined to be 18.3 mg (0.082 mmol, 82% yield) based on ^{1}H NMR spectroscopic analysis using CH_2Br_2 as internal standard. Pure product **7b** can be obtained by preparative thin layer chromatography.

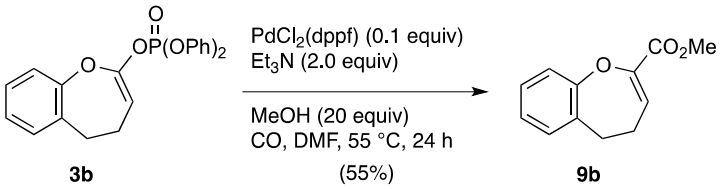


Formation of compound 8b via Suzuki coupling of enol phosphate 3b. An oven-dried sealed tube was charged with a solution of the enol phosphate substrate **3b** (0.100 mmol) in degassed THF (1.0 mL). Then 3-thienylboronic acid (19.2 mg, 0.150 mmol, 1.5 equiv), K_3PO_4 (63.7 mg, 0.300 mmol, 3.0 equiv) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (8.2 mg, 0.010 mmol, 0.10 equiv) were added at 25 °C. The tube was filled with argon and sealed immediately. The reaction mixture was submerged in an pre-heated oil bath at 75 °C and stirred for 24 h. After completion of the reaction (as monitored by TLC), the



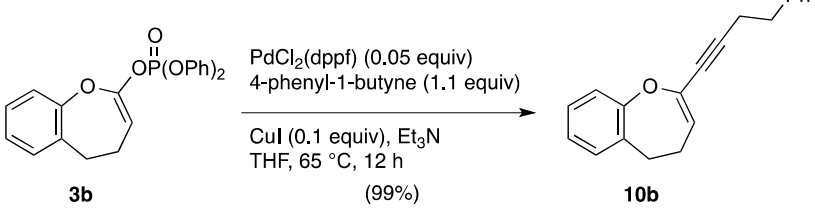
mixture was cooled to ambient temperature, diluted with Et_2O (5 mL), and filtered through a short pad of Celite®. The filtrate was concentrated in vacuo. The amount of the product **8b** was determined to be 18.3 mg (0.080 mmol, 80% yield) based on ^1H NMR spectroscopic analysis using CH_2Br_2 as internal standard. Pure product **8b** can be obtained by preparative thin layer chromatography.

Formation of compound 9b via carbonylation of enol phosphate 3b. To stirred solution of the enol phosphate substrate **3b** (0.100 mmol) in anhydrous DMF (1.0 mL) under argon was added



$PdCl_2(dppf)\cdot CH_2Cl_2$ (8.2 mg, 0.010 mmol, 0.10 equiv). After changing the atmosphere from argon to CO, Et_3N (28 µL, 0.200 mmol, 2.0 equiv) and MeOH (81 µL, 2.00 mmol, 20 equiv) were added sequentially at 25 °C. The reaction mixture was then stirred at 55 °C under a balloon pressure of CO for 24 h. After cooling to ambient temperature, the mixture was diluted with Et_2O (5 mL), and filtered through a short pad of Celite®. The filtrate was concentrated in vacuo. The amounts of the starting material **3b** and the product **9b** were determined to be 14.3 mg (0.036 mmol) and 10.7 mg (0.052 mmol, 52% yield), respectively, based on ^1H NMR spectroscopic analysis using CH_2Br_2 as internal standard. The product yield based on recovered starting material was calculated to be 81%. Pure product **9b** can be obtained by preparative thin layer chromatography.

Formation of compound 10b via Sonogashira coupling of enol phosphate 3b. To a stirred solution of the enol phosphate substrate **3b** (0.100 mmol) in anhydrous DMF (1.0 mL) at 25 °C was



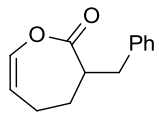
added $PdCl_2(dppf)\cdot CH_2Cl_2$ (4.1 mg, 0.0050 mmol, 0.050 equiv). After stirring at 25 °C for 15 min, 4-phenyl-1-butyne (15 µL, 0.11 mmol, 1.1 equiv), CuI (1.9 mg, 0.010 mmol, 0.10 equiv) and Et_3N (70 µL, 0.50 mmol, 5.0 equiv) were added sequentially. The resulting mixture was then stirred at 65 °C for 12 h. After completion of the reaction (as monitored by TLC), the mixture was cooled to ambient temperature and the

solvent was removed under reduced pressure. The residue was purified by flash column chromatography [deactivated silica gel (see general methods), 30:1 hexanes:ethyl acetate] to give the pure coupling product **10b** (27.2 mg, 0.099 mmol, 99% yield).

II. Physical Data for New Compounds

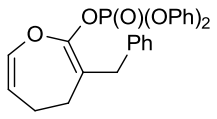
Compounds **1b**, **1e** and **1g** are commercially available from Sigma-Aldrich. Compounds **1a**,[1] **1c**,[2] **1f**,[3] **1h**[4] and **1i**[5] are known compounds and are prepared according to reported procedures. Compound **1d** is prepared according to a modified literature procedure[6] and its physical data are given below.

Enol lactone 2a. R_f = 0.53 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 3062, 3028, 2928, 2860, 1752, 1645, 1454, 1194, 1119, 1040, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.28 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.22 – 7.19 (m, 3 H), 6.36 (dd, *J* = 6.2, 2.4 Hz, 1 H), 5.42 (td, *J* = 7.3, 6.2 Hz, 1 H), 3.19 – 3.11 (m, 2 H), 2.69 (dd, *J* = 13.5, 7.0 Hz, 1 H), 2.45 – 2.38 (m, 1 H), 2.08 – 1.90 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 174.3, 140.4, 139.2, 129.2, 128.6, 126.6, 114.1, 44.3, 37.2, 33.7, 22.1 ppm; HRMS (ESI) calcd for $C_{13}H_{14}O_2H^+$ [M + H^+] 203.1067, found 203.1077.



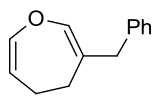
2a

Enol phosphate 3a. R_f = 0.45 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 3063, 2917, 2848, 1709, 1589, 1489, 1300, 1186, 1161, 1141, 946, 688 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 7.36 (dd, *J* = 8.7, 1.0 Hz, 4 H), 7.14 (d, *J* = 7.7 Hz, 2 H), 7.08 (t, *J* = 7.4 Hz, 2 H), 7.02 (t, *J* = 7.3 Hz, 1 H), 6.92 (t, *J* = 7.8 Hz, 4 H), 6.78 (td, *J* = 7.6, 0.8 Hz, 2 H), 6.15 (dt, *J* = 7.1, 1.9 Hz, 1 H), 4.51 (dt, *J* = 7.1, 4.6 Hz, 1 H), 3.25 (s, 2 H), 1.96 – 1.94 (m, 2 H), 1.66 – 1.63 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 151.3 (d, *J* = 7 Hz), 149.3 (d, *J* = 10 Hz), 141.9, 138.8, 129.9, 129.3, 128.7, 126.6, 125.6, 120.8 (d, *J* = 5 Hz), 111.0, 105.5 (d, *J* = 8 Hz), 37.3, 26.8, 25.2 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.3 ppm; HRMS (ESI) calcd for $C_{25}H_{23}O_5PH^+$ [M + H^+] 435.1356, found 435.1339.



3a

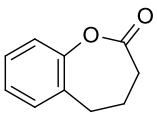
Dihydrooxepine 4a. R_f = 0.21 (silica gel, pentane); FT-IR (neat) ν_{max} = 3026, 2914, 2852, 1654, 1494, 1453, 1287, 1120, 699 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 7.13 (dd, *J* = 7.4, 7.4 Hz, 2 H),



4a

7.07 – 7.03 (m, 3 H), 6.27 (s, 1 H), 6.19 (dt, *J* = 7.4, 1.4 Hz, 1 H), 4.57 (dt, *J* = 7.4, 5.5 Hz, 1 H), 2.94 (s, 2 H), 2.08 – 2.06 (m, 2 H), 1.92 – 1.89 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 143.3, 141.2, 139.7, 129.1, 128.6, 126.6, 121.9, 108.3, 41.7, 30.4, 26.3 ppm; HRMS (ESI) calcd for $C_{13}H_{14}OH^+$ [M + H^+] 187.1117, found 187.1113.

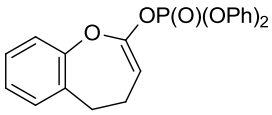
Enol lactone 2b. R_f = 0.53 (silica gel, ethyl acetate:hexanes, 1:3); FT-IR (neat) ν_{max} = 2951, 2869, 1763, 1486, 1456, 1213, 1127, 1094, 965, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.28 (ddd, *J* =



2b

7.6, 7.6, 1.6 Hz, 1 H), 7.20 (dd. *J* = 7.4, 1.4 Hz, 1 H), 7.16 (dd, *J* = 7.4, 7.4 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 2.83 (t, *J* = 7.3 Hz, 2 H), 2.48 (t, *J* = 7.3 Hz, 2 H), 2.19 (tt, *J* = 7.3, 7.3 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 171.7, 151.9, 130.1, 129.7, 128.4, 126.0, 119.4, 31.2, 28.3, 26.6 ppm; HRMS (ESI) calcd for $C_{10}H_{10}O_2H^+$ [M + H^+] 163.0754, found 163.0751.

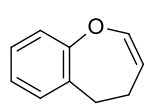
Enol phosphate 3b. R_f = 0.49 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2916, 2849, 1700, 1589, 1487, 1184, 1126, 946, 757, 688 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.38 (dd, *J*



3b

= 8.7, 0.9 Hz, 4 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 6.96 (t, *J* = 8.0 Hz, 4 H), 6.86 (t, *J* = 7.7 Hz, 1 H), 6.83 – 6.79 (m, 3 H), 6.73 (d, *J* = 7.3 Hz, 1 H), 4.58 – 4.57 (m, 1 H), 2.55 (t, *J* = 5.9 Hz, 2 H), 1.85 – 1.81 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 156.9, 151.3 (d, *J* = 7 Hz), 150.3 (d, *J* = 8 Hz), 133.9, 130.0, 129.6, 127.8, 125.6, 125.5, 121.0, 120.3 (d, *J* = 5 Hz), 99.7 (d, *J* = 7 Hz), 30.1, 25.7 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.7 ppm; HRMS (ESI) calcd for $C_{22}H_{19}O_5PH^+$ [M + H^+] 395.1043, found 395.1042.

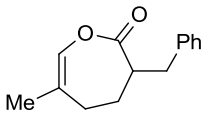
Dihydrooxepine 4b. R_f = 0.52 (silica gel, pentane); FT-IR (neat) ν_{max} = 2923, 2853, 1658, 1488, 1288, 1227, 1075, 749 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.06 (d, *J* = 7.9 Hz, 1 H), 6.95 – 6.92



4b

(m, 2 H), 6.85 – 6.82 (m, 1 H), 6.37 (dt, *J* = 7.4, 1.9 Hz, 1 H), 4.51 (dt, *J* = 7.4, 4.4 Hz, 1 H), 2.76 (t, *J* = 5.7 Hz, 2 H), 2.02 – 1.99 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 158.9, 143.6, 133.8, 130.2, 127.5, 124.1, 120.7, 108.3, 32.8, 27.6 ppm; EI-MS (*m/z*, relative intensity): 146 (M^+, 100), 145 (73), 131 (55), 117 (24), 115 (28).

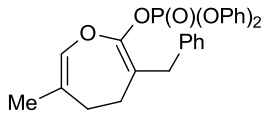
Enol lactone 2c. R_f = 0.51 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2943, 2861, 1744, 1152, 1104, 1079, 731, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.28 (dd, *J* = 7.4, 7.4 Hz,



2c

2 H), 7.22 – 7.19 (m, 3 H), 6.22 (s, 1 H), 3.17 – 3.07 (m, 2 H), 2.67 (dd, *J* = 13.6, 6.8 Hz, 1 H), 2.58 (tdd, *J* = 13.6, 7.4, 1.6 Hz, 1 H), 2.08 (tt, *J* = 13.4, 6.8 Hz, 1 H), 1.92 – 1.86 (m, 1 H), 1.82 (ddd, *J* = 14.3, 6.8, 2.3 Hz, 1 H), 1.73 (d, *J* = 1.5 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 174.7, 139.3, 134.7, 129.2, 128.6, 126.5, 124.5, 43.9, 37.2, 33.5, 27.6, 18.6 ppm; HRMS (ESI) calcd for $C_{14}H_{16}O_2H^+$ [M + H^+] 217.1223, found 217.1228.

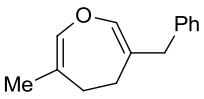
Enol phosphate 3c. R_f = 0.43 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2916, 1713, 1590, 1488, 1185, 946, 688 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.38 (d, *J* = 8.6 Hz, 4 H),



3c

7.10 (t, *J* = 7.5 Hz, 2 H), 7.03 (t, *J* = 7.3 Hz, 1 H), 6.92 (t, *J* = 7.7 Hz, 4 H), 6.78 (td, *J* = 7.4, 0.7 Hz, 2 H), 6.23 (q, *J* = 1.0 Hz, 1 H), 3.27 (s, 2 H), 1.98 – 1.95 (m, 2 H), 1.65 (t, *J* = 5.6 Hz, 2 H), 1.14 (d, *J* = 1.0 Hz, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 151.3 (d, *J* = 7 Hz), 149.2 (d, *J* = 10 Hz), 139.2, 138.1, 129.9, 129.3, 128.7, 126.5, 125.6, 120.9, 120.8 (d, *J* = 5 Hz), 104.7 (d, *J* = 8 Hz), 37.0, 30.0, 26.4, 19.8 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.3 ppm; HRMS (ESI) calcd for $C_{26}H_{25}O_5PH^+$ [M + H^+] 449.1512, found 449.1512.

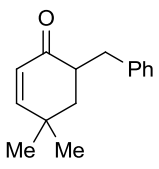
Dihydrooxepine 4c. R_f = 0.15 (silica gel, pentane); FT-IR (neat) ν_{max} = 2916, 1664, 1453, 1220, 1134, 700 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.14 (dd, *J* = 7.1, 7.1 Hz, 2 H), 7.08 – 7.05 (m, 3



4c

H), 6.34 (s, 1 H), 6.22 (q, *J* = 0.9 Hz, 1 H), 2.97 (s, 2 H), 2.05 – 2.03 (m, 2 H), 1.93 – 1.91 (m, 2 H), 1.32 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 141.6, 140.0, 139.5, 129.1, 128.6, 126.5, 121.8, 118.4, 41.5, 31.2, 28.8, 20.8 ppm; HRMS (ESI) calcd for $C_{14}H_{16}OH^+$ [M + H^+] 201.1274, found 201.1279.

Enone 1d. R_f = 0.64 (silica gel, ethyl acetate:hexanes, 1:5); FT-IR (neat) ν_{max} = 2959, 2926, 1676, 1453, 1236, 803, 744, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.29 (dd, *J* = 7.4, 7.4 Hz, 2 H),

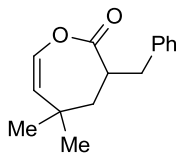


1d

7.21 (t, *J* = 7.4 Hz, 1 H), 7.17 (d, *J* = 7.4 Hz, 2 H), 6.59 (dd, *J* = 10.0, 2.0 Hz, 1 H), 5.86 (d, *J* = 10.0 Hz, 1 H), 3.46 (dd, *J* = 14.0, 3.9 Hz, 1 H), 2.71 (m, 1 H), 2.46 (dd, *J* = 14.0, 9.4 Hz, 1 H), 1.71 (ddd, *J* = 13.4, 4.6, 2.0 Hz, 1 H), 1.57 (t, *J* =13.6 Hz, 1 H), 1.08(5) (s, 3 H), 1.08(1) (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 200.6, 159.1,

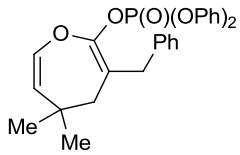
140.2, 129.3, 128.5, 126.7, 126.1, 44.5, 41.5, 35.4, 33.7, 30.6, 25.3 ppm; HRMS (ESI) calcd for $C_{15}H_{18}OH^+$ [M + H^+] 215.1436, found 215.1434.

Enol lactone 2d. R_f = 0.71 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2959, 2927, 1754, 1660, 1230, 1137, 1110, 1050, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.30 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.23 – 7.20 (m, 3 H), 6.07 (d, *J* = 7.7 Hz, 1 H), 4.79 (dd, *J* = 7.7, 1.6 Hz, 1 H), 3.25 (dd, *J* = 14.0, 5.4 Hz, 1 H), 2.85 (tdd, *J* = 9.8, 5.4, 1.9 Hz, 1 H), 2.61 (dd, *J* = 13.9, 9.3 Hz, 1 H), 1.81 (dd, *J* = 14.2, 10.4 Hz, 1 H), 1.65 (dt, *J* = 14.2, 1.7 Hz, 1 H), 1.04 (s, 3 H), 0.73 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 174.1, 139.0, 135.0, 129.6, 128.6, 126.6, 122.7, 42.2, 42.0, 37.3, 35.2, 29.5(1), 29.5(0) ppm; HRMS (ESI) calcd for $C_{15}H_{18}O_2H^+$ [M + H^+] 231.1379, found 231.1381.



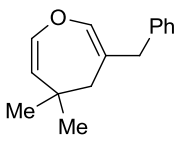
2d

Enol phosphate 3d. R_f = 0.56 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2957, 1711, 1656, 1590, 1489, 1301, 1186, 959, 946, 688 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 7.36 (d, *J* = 8.2 Hz, 4 H), 7.15 – 7.10 (m, 4 H), 7.04 (t, *J* = 7.1 Hz, 1 H), 6.92 (t, *J* = 7.8 Hz, 4 H), 6.78 (td, *J* = 7.3, 0.7 Hz, 2 H), 6.00 (d, *J* = 7.3 Hz, 1 H), 4.33 (d, *J* = 7.3 Hz, 1 H), 3.39 (s, 2 H), 1.96 (d, *J* = 1.5 Hz, 2 H), 0.79 (s, 6 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 151.2 (d, *J* = 7.0 Hz), 149.2 (d, *J* = 10 Hz), 139.3, 138.8, 130.0, 129.4, 128.7, 126.6, 125.6 (d, *J* = 1 Hz), 120.8 (d, *J* = 5 Hz), 120.7, 103.7 (d, *J* = 8 Hz), 40.1, 38.1, 34.6 (d, *J* = 2 Hz), 30.2 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.3 ppm; HRMS (ESI) calcd for $C_{27}H_{27}O_5PH^+$ [M + H^+] 463.1669, found 463.1656.



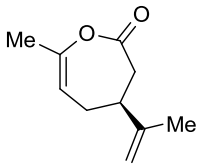
3d

Dihydrooxepine 4d. R_f = 0.31 (silica gel, pentane); FT-IR (neat) ν_{max} = 2956, 1670, 1651, 1454, 1281, 1239, 1096, 730, 699 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 7.14 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.07 – 7.05 (m, 3 H), 6.28 (s, 1 H), 6.03 (d, *J* = 7.7 Hz, 1 H), 4.37 (d, *J* = 7.7 Hz, 1 H), 3.02 (s, 2 H), 2.06 (s, 2 H), 0.90 (s, 6 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 141.1, 140.1(1), 140.0(5), 129.4, 128.6, 126.6, 120.1, 117.9, 43.9, 42.3, 35.3, 31.0 ppm; HRMS (ESI) calcd for $C_{15}H_{18}OH^+$ [M + H^+] 215.1430, found 215.1429.



4d

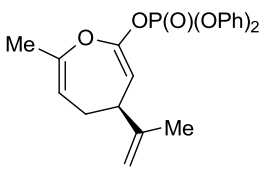
Enol lactone 2e. R_f = 0.61 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2923, 2856, 1754, 1446, 1229, 1161, 1130, 1023, 897, 801 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ = 5.28 (t, *J* =



2e

7.4 Hz, 1 H), 4.83 (s, 1 H), 4.78 (s, 1 H), 2.98 (tt, *J* = 6.9, 6.9 Hz, 1 H), 2.70 – 2.63 (m, 2 H), 2.33 (dt, *J* = 7.1, 7.1 Hz, 1 H), 2.13 (dt, *J* = 7.1, 7.1 Hz, 1 H), 1.91 (s, 3 H), 1.75 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 171.7, 150.2, 146.6, 110.8, 108.5, 47.0, 37.3, 27.1, 20.9, 19.5 ppm; HRMS (ESI) calcd for $C_{10}H_{14}O_2H^+$ [M + H^+] 167.1067, found 167.1064.

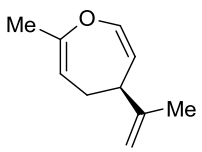
Enol phosphate 3e. R_f = 0.51 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2920, 1701, 1590, 1489, 1300, 1187, 1162, 1126, 947, 768, 755, 688 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ =



3e

7.35 (d, *J* = 7.6 Hz, 4 H), 6.94 (ddd, *J* = 7.6, 7.2, 3.5 Hz, 4 H), 6.80 (t, *J* = 7.2 Hz, 2 H), 4.82 (s, 1 H), 4.76 – 4.75 (m, 1 H), 4.71 (s, 1 H), 4.64 (t, *J* = 6.8 Hz, 1 H), 2.83 – 2.79 (m, 1 H), 2.19 – 2.14 (m, 1 H), 2.01 – 1.97 (m, 1 H), 1.69 (s, 3 H), 1.51 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 152.7, 151.3 (d, *J* = 3 Hz), 151.2 (d, *J* = 3 Hz), 150.0 (d, *J* = 8 Hz), 147.6, 130.0, 125.5, 120.6(9) (d, *J* = 5 Hz), 120.6(6) (d, *J* = 5 Hz), 111.7, 108.3, 94.6 (d, *J* = 7 Hz), 43.1, 28.8, 20.4, 20.2 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.4 ppm; HRMS (ESI) calcd for $C_{22}H_{23}O_5PH^+$ [M + H^+] 399.1356, found 399.1360.

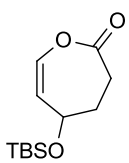
Dihydrooxepine 4e. R_f = 0.39 (silica gel, pentane); FT-IR (neat) ν_{max} = 2923, 1691, 1653, 1169 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 6.22 (d, *J* = 7.6 Hz, 1 H), 4.82 (s, 1 H), 4.78 (s, 1 H), 4.62 (t, *J*



4e

= 6.5 Hz, 1 H), 4.59 – 4.57 (m, 1 H), 2.98 (br, 1 H), 2.33 – 2.29 (m, 1 H), 2.19 – 2.15 (m, 1 H), 1.70 (s, 3 H), 1.60 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 152.7, 148.5, 142.1, 111.0, 110.8, 104.4, 45.5, 31.1, 21.5, 20.5 ppm; EI-MS (*m/z*, relative intensity): 150 (M^+, 1), 109 (88), 79 (100).

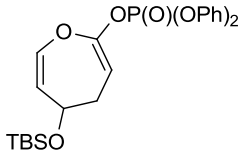
Enol lactone 2f. R_f = 0.55 (silica gel, ethyl acetate:hexanes, 1:5); FT-IR (neat) ν_{max} = 2955, 2930, 2857, 1764, 1251, 1124, 1106, 1057, 996, 867, 837, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ =



2f

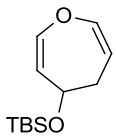
6.25 (dd, *J* = 7.0, 1.5 Hz, 1 H), 5.31 (dd, *J* = 7.0, 4.5 Hz, 1 H), 4.52 – 4.50 (m, 1 H), 2.81 (ddd, *J* = 13.5, 10.0, 5.5 Hz, 1 H), 2.57 (ddd, *J* = 13.5, 5.8, 4.8 Hz, 1 H), 2.25 – 2.21 (m, 1 H), 2.10 – 2.05 (m, 1 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 172.0, 138.0, 118.2, 66.4, 34.0, 29.7, 25.8, 18.2, −4.6, −4.7 ppm; HRMS (ESI) calcd for $C_{12}H_{22}O_3SiH^+$ [M + H^+] 243.1411, found 243.1417.

Enol phosphate 3f. R_f = 0.52 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2955, 2929, 2857, 1700, 1591, 1489, 1187, 1149, 1075, 964, 947, 775 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ 7.33 (dd, *J* = 7.8, 7.8 Hz, 4 H), 6.94 (td, *J* = 7.8, 4.8 Hz, 4 H), 6.04 (td, *J* = 7.8, 3.0 Hz, 2 H), 5.85 (dd, *J* = 7.8, 1.8 Hz, 1 H), 4.78 (dt, *J* = 7.8, 1.8 Hz, 1 H), 4.73 – 4.70 (m, 1 H), 4.19 – 4.16 (m, 1 H), 2.35 – 2.29 (m, 1 H), 2.09 – 2.05 (m, 1 H), 0.90 (s, 9 H), −0.06 (s, 3 H), −0.07 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 152.1 (d, *J* = 7 Hz), 151.2 (d, *J* = 6 Hz), 151.1 (d, *J* = 6 Hz), 137.7, 130.0 (d, *J* = 3 Hz), 125.6 (d, *J* = 2 Hz), 120.6(2) (d, *J* = 4 Hz), 120.5(9) (d, *J* = 4 Hz), 116.4, 86.7 (d, *J* = 6 Hz), 65.8 (d, *J* = 2 Hz), 32.3, 25.9, 18.2, −4.7, −4.8 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −17.2 ppm; HRMS (ESI) calcd for $C_{24}H_{31}O_6PSiH^+$ [M + H^+] 475.1702, found 475.1701.



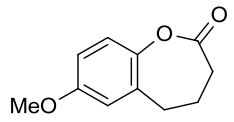
3f

Dihydrooxepine 4f. R_f = 0.07 (silica gel, pentane); FT-IR (neat) ν_{max} = 2954, 2929, 2857, 1665, 1651, 1297, 1252, 1137, 1076, 866, 835, 774, 746 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 6.13 (dd, *J* = 7.2, 2.4 Hz, 1 H), 6.03 (dd, *J* = 8.1, 2.1 Hz, 1 H), 4.85 (d, *J* = 8.1 Hz), 4.44 – 4.39 (m, 2 H), 2.58 – 2.54 (m, 1 H), 2.33 – 2.28 (m, 1 H), 0.95 (s, 9 H), 0.03 (s, 3 H), 0.01 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 144.0, 139.2, 114.5, 103.0, 67.3, 36.9, 26.0, 18.3, −4.6, −4.7 ppm; HRMS (ESI) calcd for $C_{12}H_{22}O_2SiH^+$ [M + H^+] 227.1462, found 227.1470.



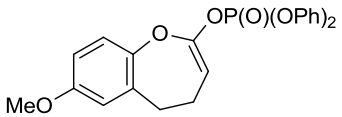
4f

Enol lactone 2g. R_f = 0.32 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2943, 1759, 1746, 1489, 1199, 1127, 1042, 1028, 964, 871 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.01 (d, *J* = 8.8 Hz, 1 H), 6.77 (dd, *J* = 8.8, 3.0 Hz, 1 H), 6.73 (d, *J* = 3.0 Hz, 1 H), 3.80 (s, 3 H), 2.79 (t, *J* = 7.2 Hz, 2 H), 2.47 (t, *J* = 7.2 Hz, 2 H), 2.18 (tt, *J* = 7.2, 7.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 172.3, 157.3, 145.6, 131.3, 120.2, 115.2, 112.6, 55.8, 31.1, 28.7, 26.4 ppm; HRMS (ESI) calcd for $C_{11}H_{12}O_3H^+$ [M + H^+] 193.0859, found 193.0861.



2g

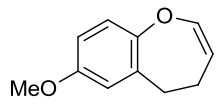
Enol phosphate 3g. R_f = 0.34 (silica gel, ethyl acetate:hexanes, 1:3); FT-IR (neat) ν_{max} = 2918, 1699, 1589, 1488, 1299, 1185, 1122, 944, 766, 754, 680 cm^{-1}; ^1H NMR (C_6D_6, 600 MHz): δ = 7.40 (d, *J* = 8.0 Hz, 4 H), 7.18 (d, *J* = 8.8 Hz, 1 H), 6.96 (dd, *J* = 8.0, 8.0 Hz, 4 H), 6.82 (dd, *J* = 8.0 Hz, 2 H), 6.47 (d, *J* = 3.0 Hz, 1 H), 6.38 (dd, *J* = 8.8, 3.0 Hz, 1 H), 4.57 (td, *J* = 4.0, 2.2 Hz, 1 H), 3.23 (s, 3



3g

H), 2.53 (t, *J* = 6.0 Hz, 2 H), 1.87 – 1.84 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 157.3, 151.3 (d, *J* = 7 Hz), 150.9(3), 150.8(6) (d, *J* = 8 Hz), 134.9, 130.0, 125.6, 121.7, 120.7 (d, *J* = 5 Hz), 115.1, 111.8, 90.4 (d, *J* = 7 Hz), 55.0, 30.2, 25.8 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −16.6 ppm; HRMS (ESI) calcd for $C_{23}H_{21}O_6PH^+$ [M + H^+] 425.1148, found 425.1145.

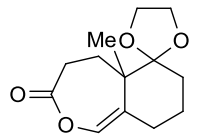
Dihydrooxepine 4g. R_f = 0.84 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2916, 1656, 1495, 1253, 1226, 1199, 1074, 1043, 794, 694 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 6.99 (d, *J*



4g

= 9.0 Hz, 1 H), 6.56 (d, *J* = 3.0 Hz, 1 H), 6.50 (dd, *J* = 9.0, 3.0 Hz, 1 H), 6.42 (dt, *J* = 7.2, 1.8 Hz, 1 H), 4.52 (d, *J* = 7.2, 4.5 Hz, 1 H), 3.30 (s, 3 H), 2.74 (t, *J* = 5.7 Hz, 2 H), 2.04 – 2.02 (m, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 156.4, 152.9, 144.1, 134.9, 121.3, 115.4, 111.9, 108.0, 55.1, 32.8, 27.7 ppm; HRMS (ESI) calcd for $C_{11}H_{12}O_2H^+$ [M + H^+] 177.0910, found 177.0909.

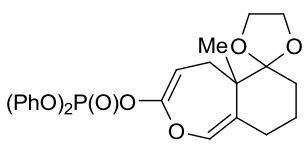
Enol lactone 2h. R_f = 0.46 (silica gel, ethyl acetate:hexanes, 1:2); FT-IR (neat) ν_{max} = 2944, 2888, 1753, 1649, 1283, 1156, 1106, 1055, 955, 913 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 6.12 (s, 1 H),



2h

4.00 – 3.90 (m, 4 H), 2.95 (dd, *J* = 14.7, 9.9 Hz, 1 H), 2.52 (dd, *J* = 14.7, 10.5 Hz, 1 H), 2.29 – 2.23 (m, 2 H), 1.98 – 1.96 (m, 1 H), 1.80 – 1.73 (m, 2 H), 1.68 – 1.60 (m, 2 H), 1.58 – 1.49 (m, 1 H), 1.24 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 173.3, 132.3, 127.0, 112.8, 65.2, 65.1, 46.7, 30.7, 30.5, 28.9, 27.7, 23.6, 23.2 ppm; HRMS (ESI) calcd for $C_{13}H_{18}O_4H^+$ [M + H^+] 239.1278, found 239.1284.

Enol phosphate 3h. R_f = 0.46 (silica gel, ethyl acetate:hexanes, 1:2); FT-IR (neat) ν_{max} = 2928, 1705, 1589, 1488, 1301, 1186, 1145, 1103, 944, 754, 686 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.36

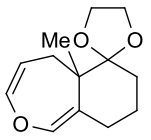


3h

– 7.34 (m, 4 H), 6.94 (ddd, *J* = 8.0, 8.0, 3.0 Hz, 4 H), 6.80 (ddd, *J* = 8.0, 8.0, 2.4 Hz, 2 H), 6.18 (d, *J* = 2.4 Hz, 1 H), 5.11 (ddd, *J* = 9.0, 6.0, 2.5 Hz, 1 H), 3.40 – 3.28 (m, 4 H), 2.87 (ddd, *J* = 13.8, 6.0, 3.0 Hz, 1 H), 1.91 – 1.86 (m, 1 H), 1.81 (dd, *J* = 13.8, 9.0 Hz, 1 H), 1.62 – 1.54 (m, 2 H), 1.49 – 1.47 (m, 1 H), 1.41 – 1.39 (m, 1 H), 1.31 – 1.29 (m, 1 H), 1.27 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 153.4 (d, *J* = 8 Hz), 151.3 (d, *J* = 7 Hz), 136.1, 130.0 (d, *J* = 3 Hz), 126.3, 125.5, 120.7 (d, *J* = 8 Hz), 120.6 (d, *J*

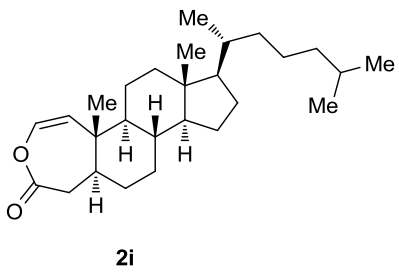
= 8 Hz), 112.1, 92.3 (d, J = 6 Hz), 65.1, 64.9, 46.3, 31.0, 28.8, 26.4, 23.5, 23.3 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −17.3 ppm; HRMS (ESI) calcd for $C_{25}H_{27}O_7PH^+$ [M + H^+] 471.1567, found 471.1574.

Dihydrooxepine 4h. R_f = 0.78 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2936, 2880, 1665, 1640, 1282, 1163, 1115, 1073, 1036, 919, 761, 657 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 6.38 (dd, J = 6.0, 2.4 Hz, 1 H), 6.28 (d, J = 1.8 Hz, 1 H), 5.02 (dt, J = 9.0, 5.7 Hz, 1 H), 3.45 – 3.37 (m, 4 H), 3.11 – 3.07 (m, 1 H), 2.06 – 2.01 (m, 1 H), 1.94 (dd, J = 8.8, 6.0 Hz, 1 H), 1.75 – 1.66 (m, 3 H), 1.51 – 1.48 (m, 1 H), 1.42 – 1.40 (m, 1 H), 1.39 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 147.0, 138.2, 123.4, 112.3, 111.6, 65.1, 64.9, 47.3, 31.0, 29.5, 28.8, 23.9, 23.7 ppm; HRMS (ESI) calcd for $C_{13}H_{18}O_3H^+$ [M + H^+] 223.1329, found 223.1327.



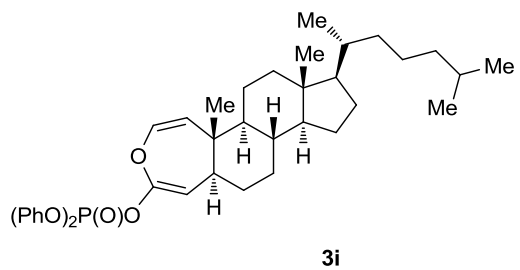
4h

Enol lactone 2i. R_f = 0.73 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2930, 2867, 1753, 1738, 1651, 1248, 1239, 1172, 1044, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 6.02 (d, J = 8.4 Hz, 1 H), 4.97 (d, J = 8.4 Hz, 1 H), 2.72 (dd, J = 14.7, 9.9 Hz, 1 H), 2.31 (d, J = 15.0 Hz, 1 H), 1.99 (d, J = 12.6 Hz, 1 H), 1.90 (t, J = 11.1 Hz, 1 H), 1.83 – 1.79 (m, 1 H), 1.70 (d, J = 13.2 Hz, 1 H), 1.63 (d, J = 13.2 Hz, 1 H), 1.56 – 1.53 (m, 2 H), 1.52 – 1.47 (m, 2 H), 1.45 – 1.40 (m, 1 H), 1.38 – 1.32 (m, 4 H), 1.27 – 1.21 (m, 1 H), 1.17 – 1.05 (m, 6 H), 1.04 – 0.99 (m, 4 H), 0.95 (s, 3 H), 0.90 (d, J = 6.0 Hz, 3 H), 0.86 – 0.85 (m, 6 H), 0.66 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 172.2, 134.4, 120.7, 56.3, 56.2, 52.6, 42.7, 42.3, 41.9, 39.8, 39.6, 38.1, 36.2, 35.9, 34.7, 31.9, 29.0, 28.3, 28.1, 24.3, 24.0, 23.0, 22.7, 22.3, 18.8, 15.3, 12.2 ppm; HRMS (ESI) calcd for $C_{27}H_{44}O_2H^+$ [M + H^+] 401.3414, found 401.3413.



2i

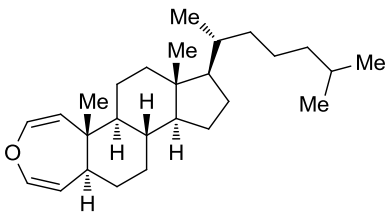
Enol phosphate 3i. R_f = 0.65 (silica gel, ethyl acetate:hexanes, 1:4); FT-IR (neat) ν_{max} = 2932, 2867, 1701, 1591, 1489, 1313, 1302, 1187, 1162, 952, 753, 687 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.39 (d, J = 7.8 Hz, 4 H), 6.96 (dd, J = 7.8, 7.8 Hz, 4 H), 6.81 (dd, J = 7.8 Hz, 2 H), 5.95 (d, J = 7.5 Hz, 1 H), 4.81 (d, J = 7.5 Hz, 1 H), 4.64 (s, 1 H), 2.32 (d, J = 12.6 Hz, 1 H), 1.92 (d, J = 12.0 Hz, 1 H), 1.85 – 1.79 (m, 1 H), 1.56



3i

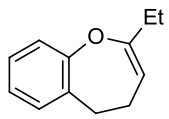
(sep, J = 6.6 Hz, 1 H), 1.49 – 1.39 (m, 6 H), 1.33 (d, J = 13.2 Hz, 1 H), 1.26 – 1.21 (m, 5 H), 1.13 – 0.99 (m, 12 H), 0.94 (d, J = 6.6 Hz, 6 H), 0.83 – 0.78 (m, 1 H), 0.69 – 0.64 (m, 2 H), 0.59 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 151.3 (d, J = 5 Hz), 148.8 (d, J = 8 Hz), 137.8, 130.0, 125.6, 120.6 (d, J = 5 Hz), 120.0, 96.5 (d, J = 6 Hz), 56.6, 56.4, 52.1, 42.9, 42.7, 40.8, 40.4, 39.9, 36.6, 36.2, 34.7, 31.3, 29.0, 28.7, 28.4, 24.4, 24.3, 23.1, 22.8, 22.1, 19.0, 17.0, 12.4 ppm; ^{31}P NMR (C_6D_6, 161 MHz): δ = −17.0 ppm; HRMS (ESI) calcd for $C_{39}H_{53}O_5PH^+$ [M + H^+] 633.3703, found 633.3713.

Dihydrooxepine 4i. R_f = 0.49 (silica gel, pentane); FT-IR (neat) ν_{max} = 2932, 2868, 1663, 1642, 1466, 1442, 1382, 1374, 1325, 1157, 852, 733 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 6.15 (d, J = 7.2 Hz, 1 H), 6.12 (d, J = 7.8 Hz, 1 H), 4.86 (d, J = 7.8 Hz, 1 H), 4.31 (d, J = 7.2 Hz, 1 H), 2.44 (d, J = 13.2 Hz, 1 H), 1.98 (d, J = 12.0 Hz, 1 H), 1.88 – 1.82 (m, 1 H), 1.61 – 1.52 (m, 4 H), 1.48 – 1.35 (m, 6 H), 1.29 – 1.17 (m, 5 H), 1.14 – 1.08 (m, 7 H), 1.02 (d, J = 6.6 Hz, 3 H), 0.94 (d, J = 6.0 Hz, 6 H), 0.90 – 0.85 (m, 1 H), 0.80 – 0.76 (m, 2 H), 0.66 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 140.5 (2 C), 118.5, 112.6, 56.7, 56.6, 52.6, 46.1, 43.0, 42.1, 40.6, 40.0, 36.7, 36.3, 34.8, 31.6, 29.8, 28.8, 28.4, 24.4(1), 24.3(8), 23.1, 22.9, 22.8, 19.0, 17.3, 12.5 ppm; HRMS (ESI) calcd for $C_{27}H_{44}OH^+$ [M + H^+] 385.3465, found 385.3473.



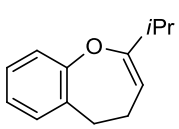
4i

Dihydrooxepine 5b. R_f = 0.30 (silica gel, pentane); FT-IR (neat) ν_{max} = 2968, 2915, 1683, 1488, 1455, 1237, 1189, 756 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.06 (d, J = 8.4 Hz, 1 H), 6.97 (td, J = 7.8, 1.8 Hz, 1 H), 6.90 – 6.86 (m, 2 H), 4.50 (t, J = 4.5 Hz, 1 H), 2.81 (t, J = 6.0 Hz, 2 H), 2.16 (q, J = 7.2 Hz, 2 H), 2.09 – 2.06 (m, 2 H), 1.10 (t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 159.0, 156.4, 134.8, 129.7, 127.4, 124.1, 120.6, 103.0, 31.6, 30.4, 27.6, 12.4 ppm; HRMS (ESI) calcd for $C_{12}H_{14}OH^+$ [M + H^+] 175.1117, found 175.1124.



5b

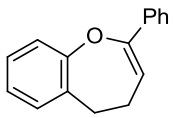
Dihydrooxepine 6b. R_f = 0.32 (silica gel, pentane); FT-IR (neat) ν_{max} = 2964, 2916, 1679, 1489, 1457, 1238, 1048, 758 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.06 (d, J = 8.4 Hz, 1 H), 6.97 (td, J = 7.6, 2.1 Hz, 1 H), 6.90 – 6.86 (m, 2 H), 4.54 (t, J = 4.8 Hz, 1 H), 2.80 (t, J = 6.0 Hz, 2 H), 2.36 (sep, J = 6.6 Hz, 1 H), 2.08 (dt, J = 6.0, 4.8 Hz, 2 H),



6b

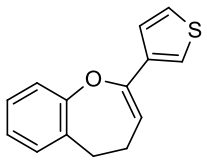
1.17 (d, J = 6.6 Hz, 6 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 159.7, 159.4, 135.0, 129.6, 127.4, 124.1, 120.5, 101.9, 35.8, 31.5, 27.5, 20.9 ppm; HRMS (ESI) calcd for $C_{13}H_{16}OH^+$ [M + H^+] 189.1274, found 189.1277.

Dihydrooxepine 7b. R_f = 0.12 (silica gel, pentane); FT-IR (neat) ν_{max} = 2921, 1655, 1488, 1231, 1072, 1033, 1012, 752, 690 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.76 (d, J = 7.8 Hz, 2 H), 7.22 (t, J = 7.5 Hz, 2 H), 7.14 (t, J = 7.8 Hz, 2 H), 6.97 (td, J = 7.2, 3.0 Hz, 1 H), 6.92 – 6.89 (m, 2 H), 5.26 (t, J = 4.8 Hz, 1 H), 2.82 (t, J = 6.6 Hz, 2 H), 2.15 (dt, J = 6.6, 4.8 Hz, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 159.1, 152.9, 138.1, 135.2, 129.6, 128.5, 128.1, 127.6, 125.7, 124.6, 120.8, 106.7, 30.8, 28.1 ppm; HRMS (ESI) calcd for $C_{16}H_{14}OH^+$ [M + H^+] 223.1117, found 223.1119.



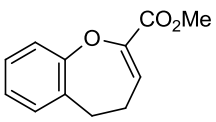
7b

Dihydrooxepine 8b. R_f = 0.12 (silica gel, pentane); FT-IR (neat) ν_{max} = 3036, 2917, 1659, 1488, 1248, 1236, 1186, 860, 785, 767, 751 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.47 (d, J = 2.4 Hz, 1 H), 7.06 – 7.04 (m, 2 H), 6.98 (td, J = 6.9, 3.0 Hz, 1 H), 6.91 – 6.89 (m, 2 H), 6.86 (dd, J = 5.4, 3.0 Hz, 1 H), 5.14 (t, J = 4.8 Hz, 1 H), 2.81 (t, J = 6.0 Hz, 2 H), 2.12 (dt, J = 6.0, 5.1 Hz, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 158.9, 149.8, 140.3, 135.0, 129.6, 127.5, 125.9, 125.2, 124.6, 121.1, 120.8, 105.9, 30.8, 27.8 ppm; HRMS (ESI) calcd for $C_{14}H_{12}OSH^+$ [M + H^+] 229.0682, found 229.0686.



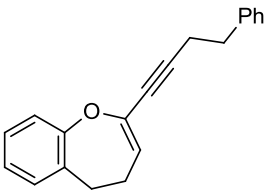
8b

Dihydrooxepine 9b. R_f = 0.59 (silica gel, ethyl acetate:hexanes, 1:5); FT-IR (neat) ν_{max} = 2951, 2919, 1726, 1654, 1488, 1268, 1231, 1217, 1185, 1092, 1060, 753 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.30 (d, J = 7.8 Hz, 1 H), 6.91 (dd, J = 7.8, 7.8 Hz, 1 H), 6.83 (dd, J = 7.8, 7.8 Hz, 1 H), 6.78 (d, J = 7.8 Hz, 1 H), 6.23 (t, J = 4.8 Hz, 1 H), 3.44 (s, 3 H), 2.60 (t, J = 6.0 Hz, 2 H), 1.92 (td, J = 6.0, 4.8 Hz, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 164.1, 159.2, 145.1, 134.3, 129.6, 127.8, 124.9, 121.2, 119.8, 51.8, 30.0, 27.8 ppm; HRMS (ESI) calcd for $C_{12}H_{12}O_3H^+$ [M + H^+] 205.0859, found 205.0867.



9b

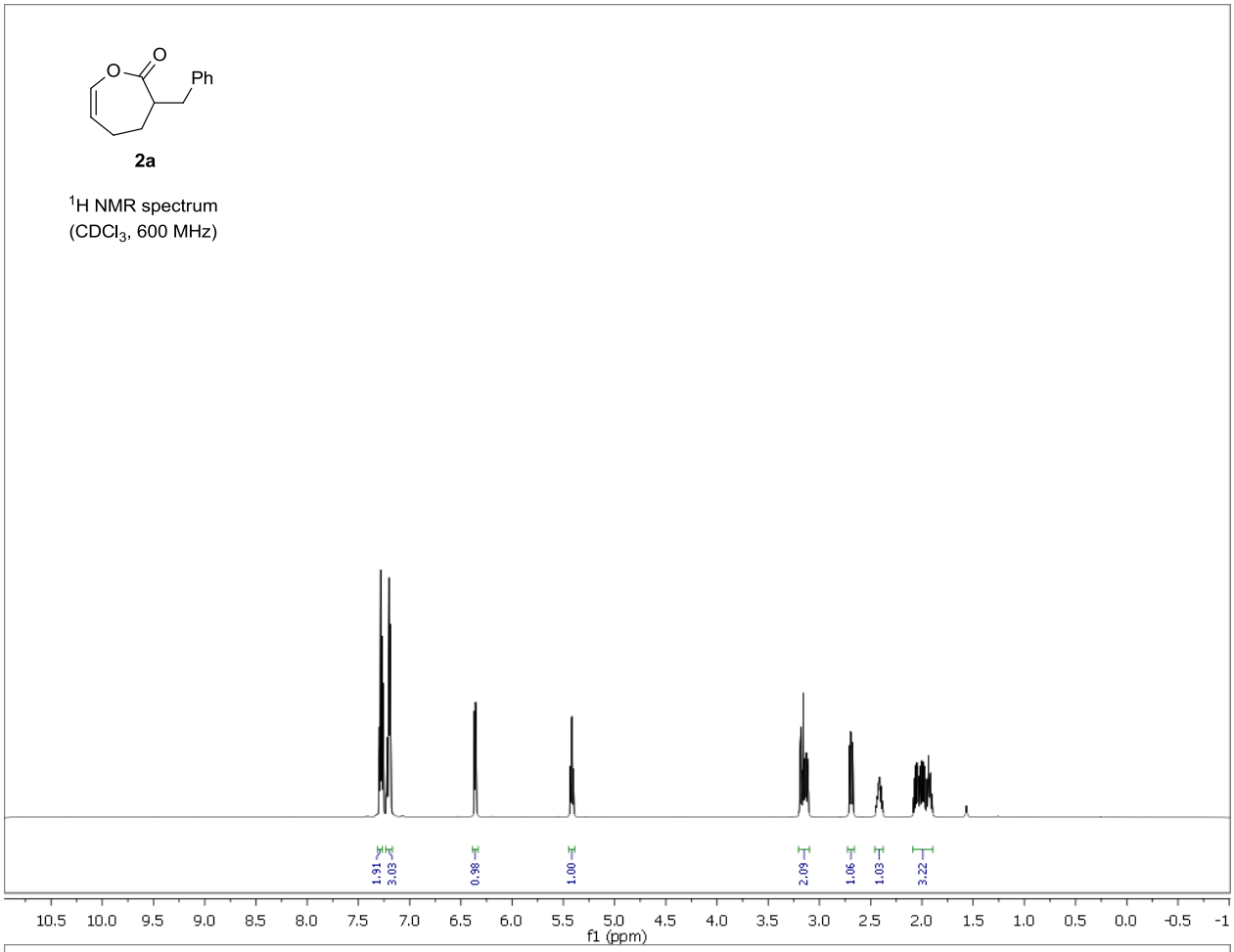
Dihydrooxepine 10b. R_f = 0.84 (silica gel, ethyl acetate:hexanes, 1:5); FT-IR (neat) ν_{max} = 3028, 2919, 2229, 1644, 1488, 1454, 1311, 1240, 1229, 1185, 1070, 757, 697 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz): δ = 7.21 (d, J = 7.8 Hz, 1 H), 7.13 (t, J = 7.5 Hz, 2 H), 7.05 (t, J = 7.2 Hz, 1 H), 7.02 (d, J =



10b

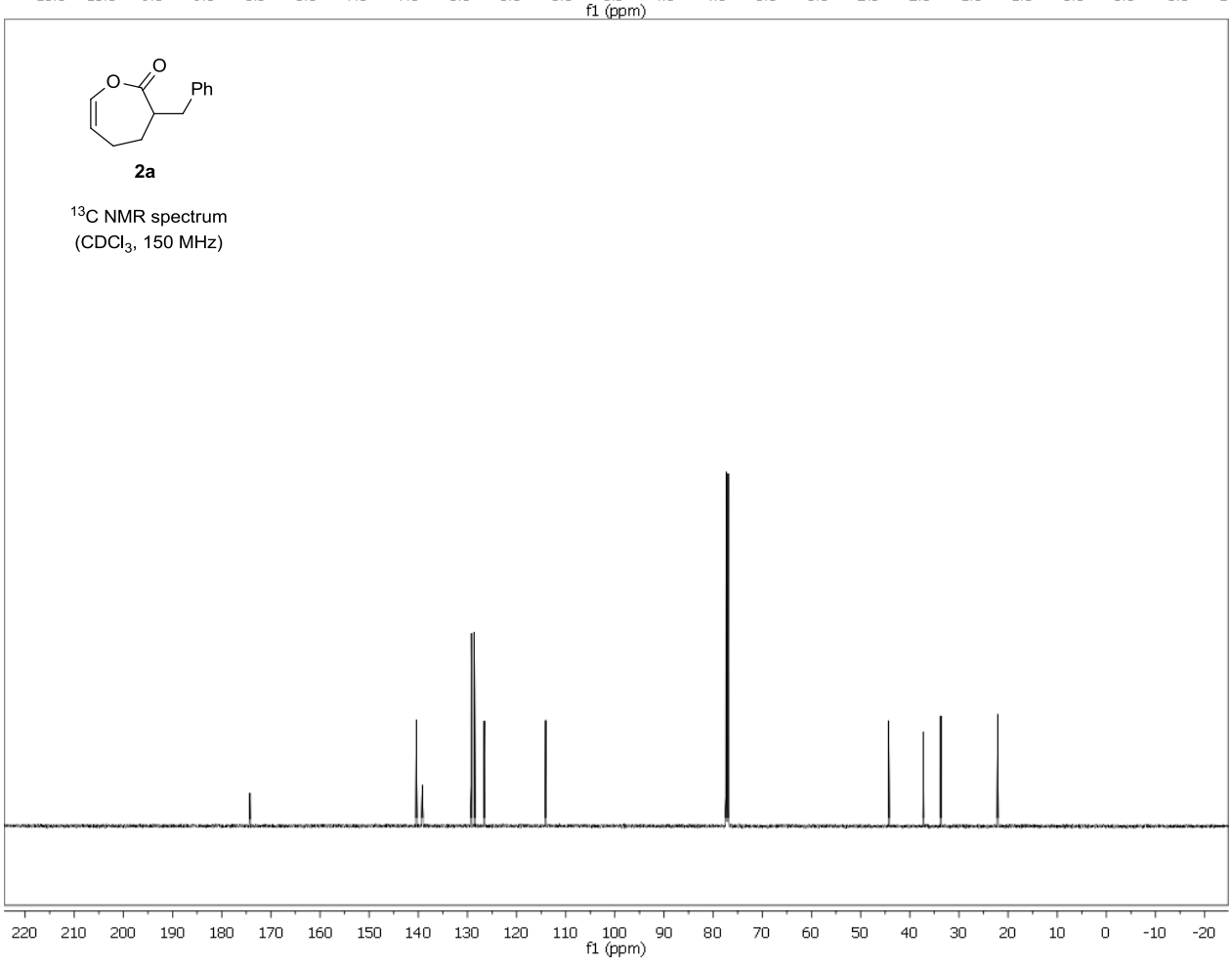
7.2 Hz, 2 H), 6.90 (td, *J* = 7.5, 1.8 Hz, 1 H), 6.83 (t, *J* = 7.2 Hz, 1 H), 6.81 (dd, *J* = 7.2, 1.8 Hz, 1 H), 5.24 (t, *J* = 4.8 Hz, 1 H), 2.68 (t, *J* = 6.3 Hz, 2 H), 2.63 (t, *J* = 7.5 Hz, 2 H), 2.37 (t, *J* = 7.5 Hz, 2 H), 1.96 (dt, *J* = 6.3, 4.8 Hz, 2 H) ppm; ^{13}C NMR (C_6D_6, 150 MHz): δ = 159.1, 140.8, 138.8, 134.6, 129.6, 128.8, 128.6, 127.6, 126.6, 124.7, 121.1, 115.6, 87.1, 79.7, 35.2, 30.7, 28.3, 21.7 ppm; HRMS (ESI) calcd for $C_{20}H_{18}OH^+$ [M + H^+] 275.1430, found 275.1440.

III. ^{1}H, ^{13}C and ^{31}P NMR Spectra of New Compounds



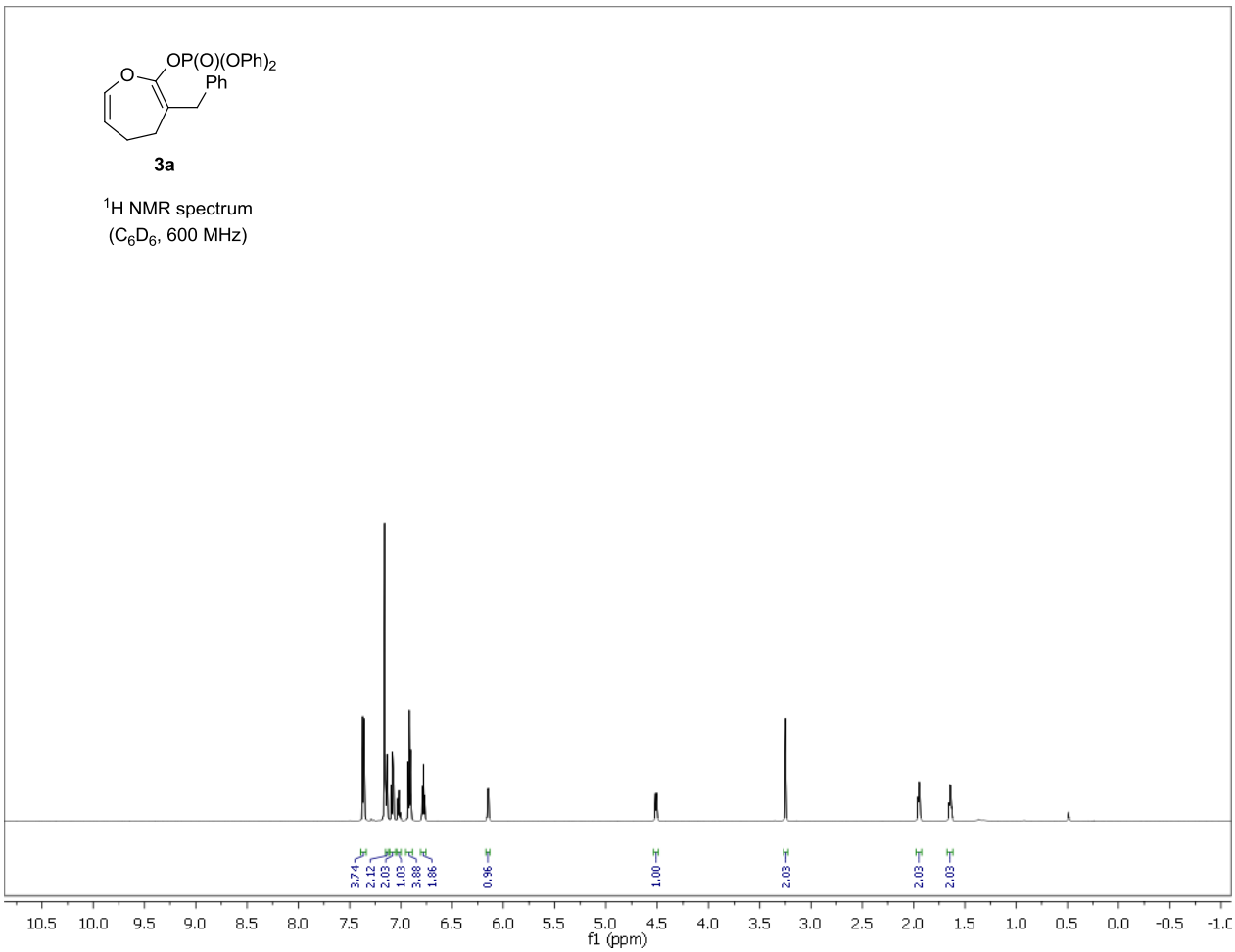
2a

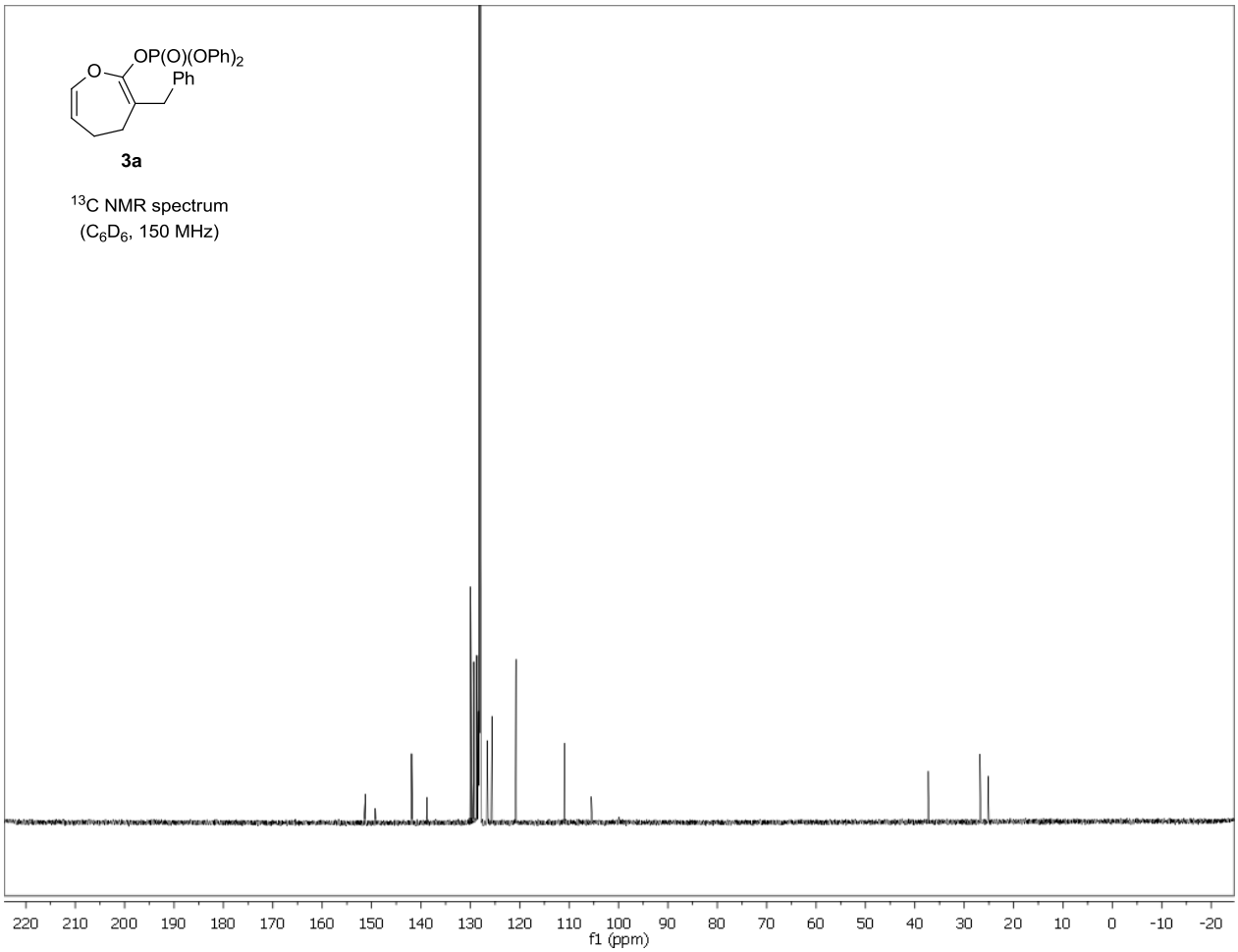
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

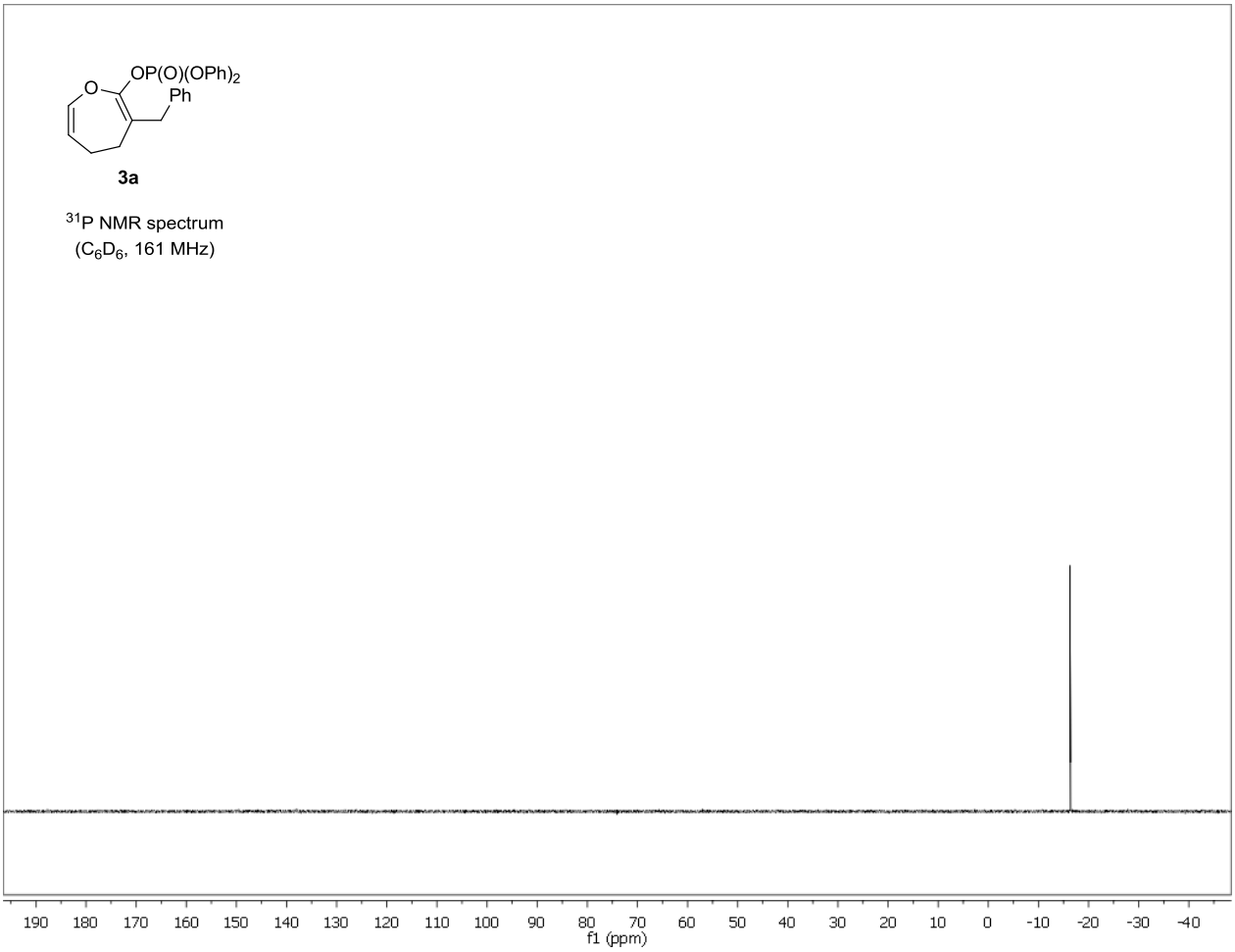


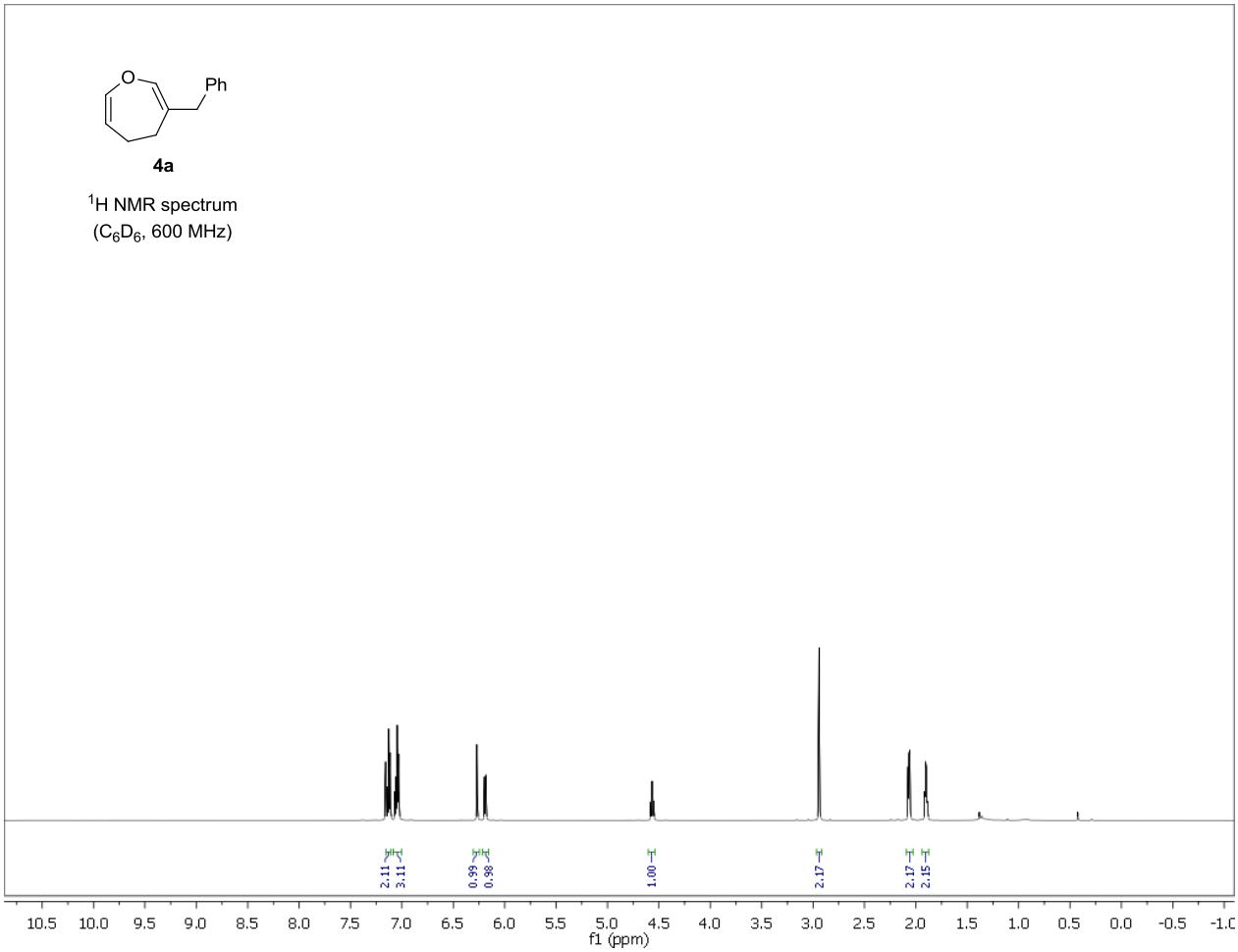
2a

^{13}C NMR spectrum
($CDCl_3$, 150 MHz)


OP(O)(OPh)2
O
Ph
3a
1H NMR spectrum
(C6D6, 600 MHz)
3.74
2.12
2.03
1.03
3.88
1.86
0.96
1.00
2.03
2.03
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

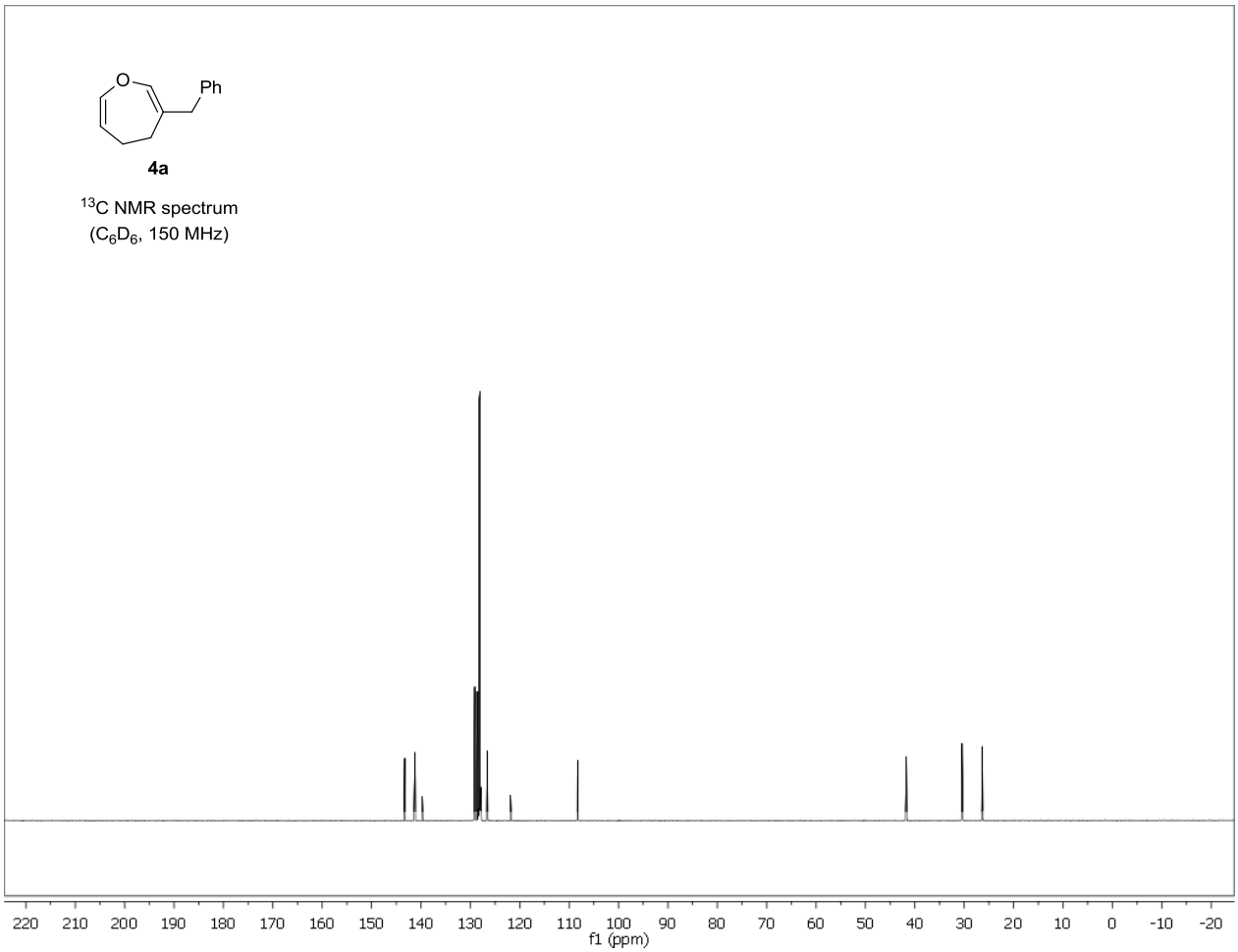

OP(O)(OPh)2
O
Ph
3a
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OP(O)(OPh)2
O
Ph
3a
31P NMR spectrum
(C6D6, 161 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)



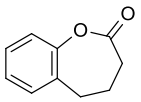
4a

^{1}H NMR spectrum
(C_6D_6, 600 MHz)



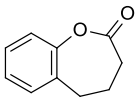
4a

^{13}C NMR spectrum
(C_6D_6, 150 MHz)



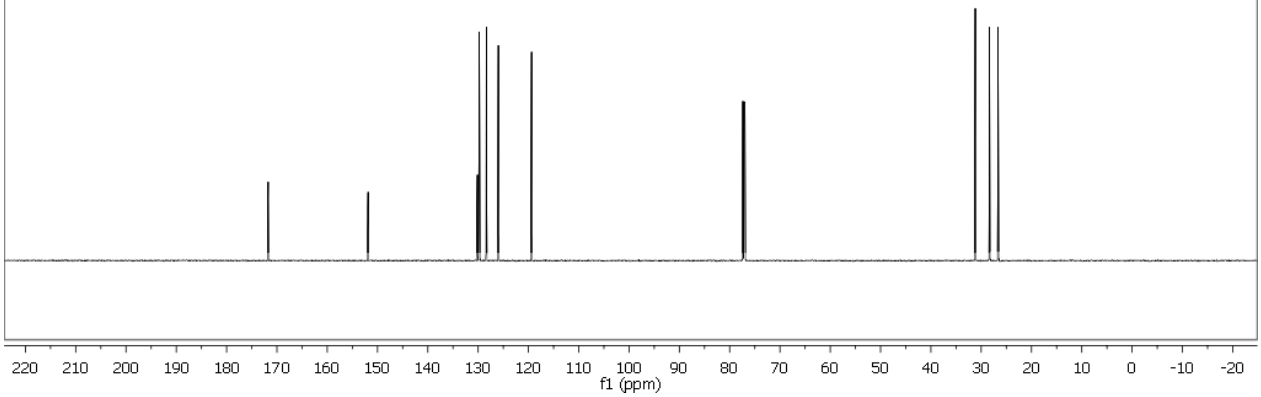
2b

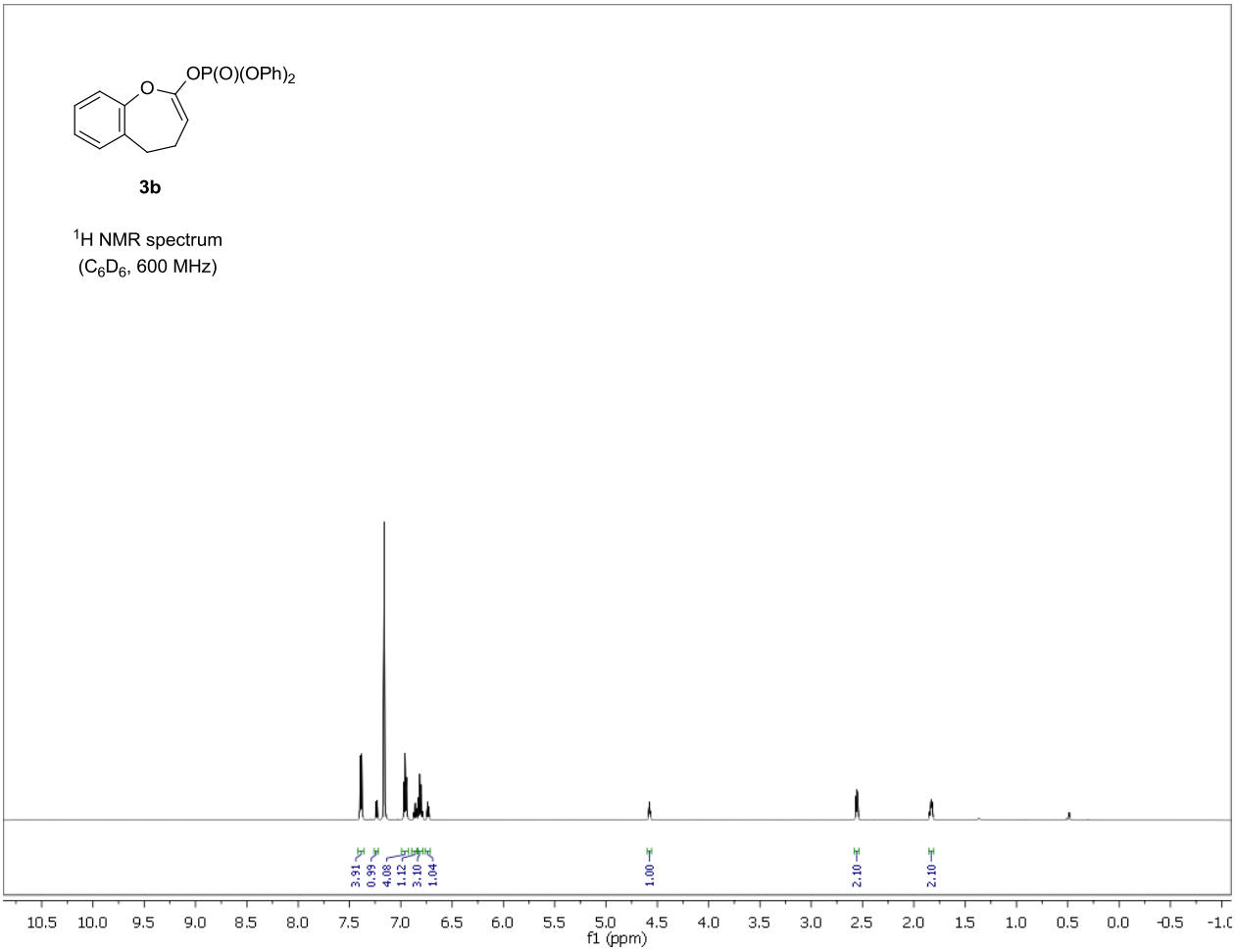
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

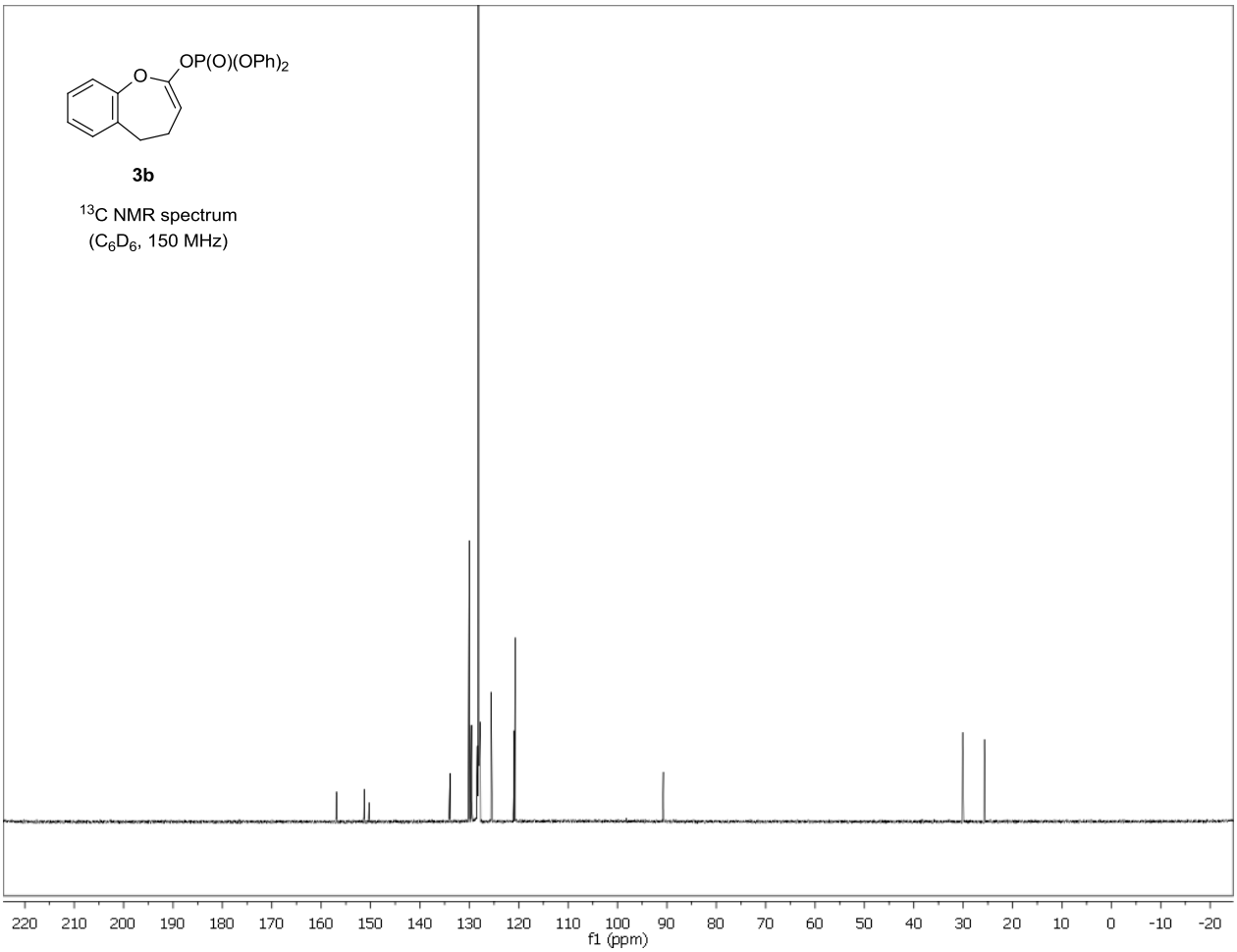


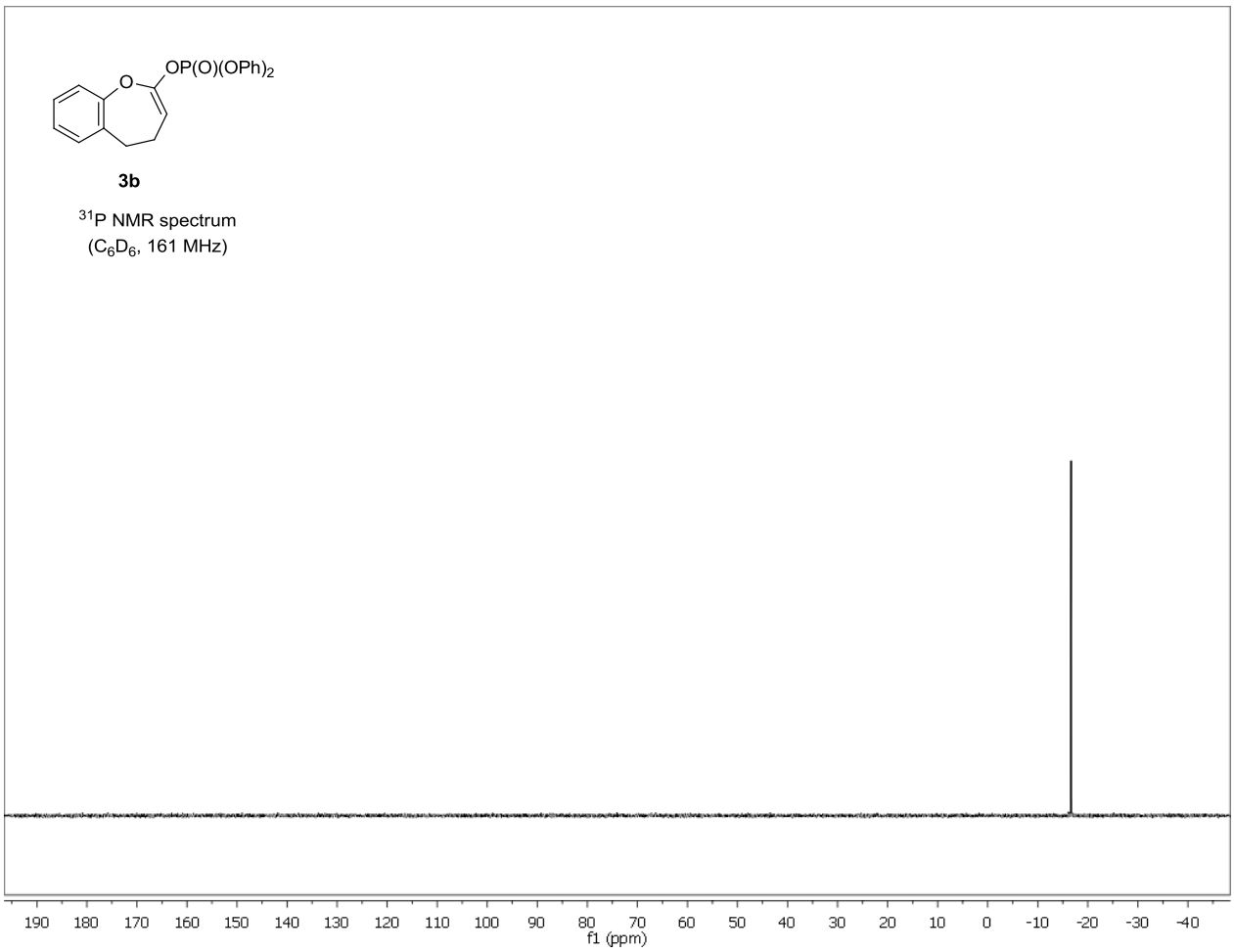
2b

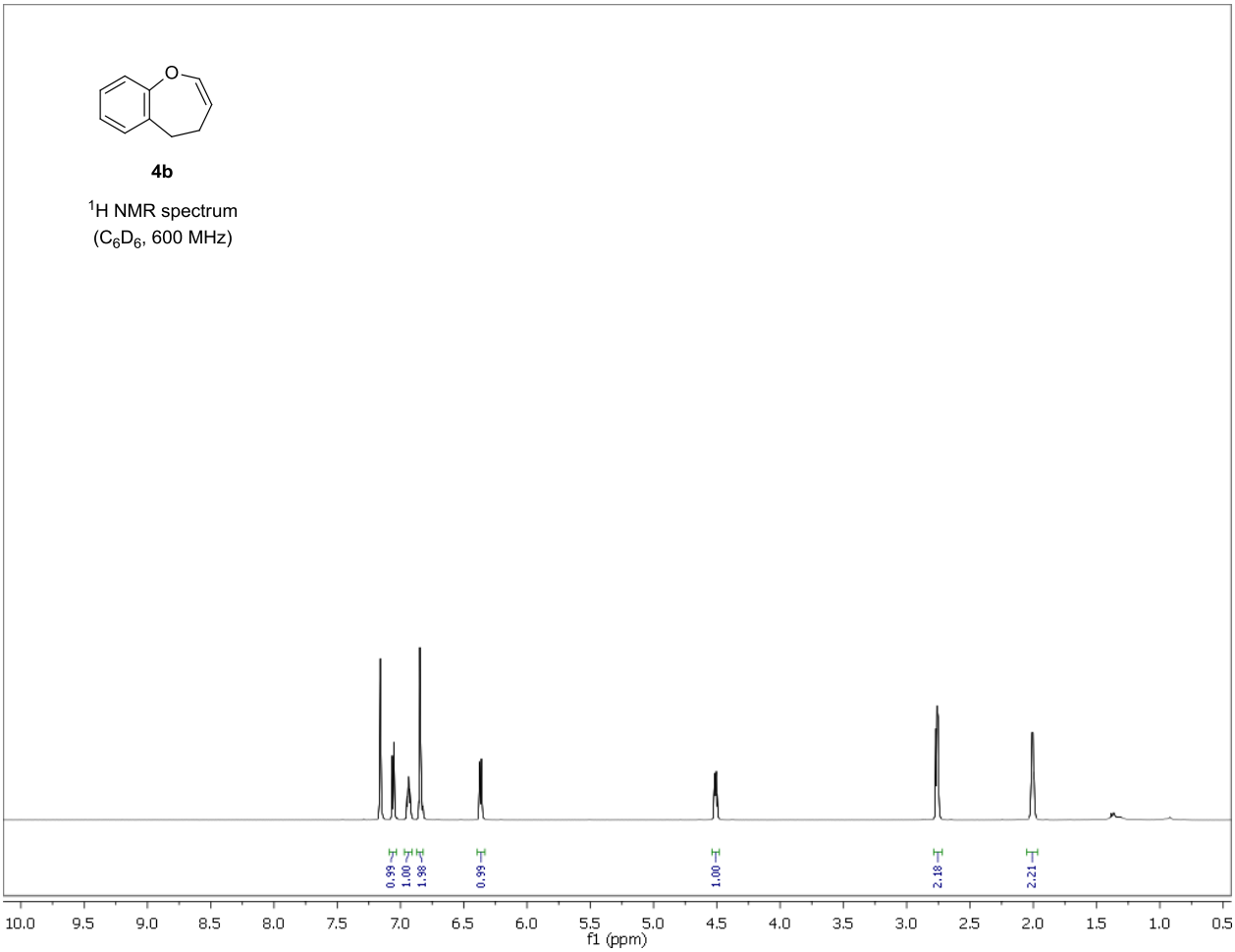
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)

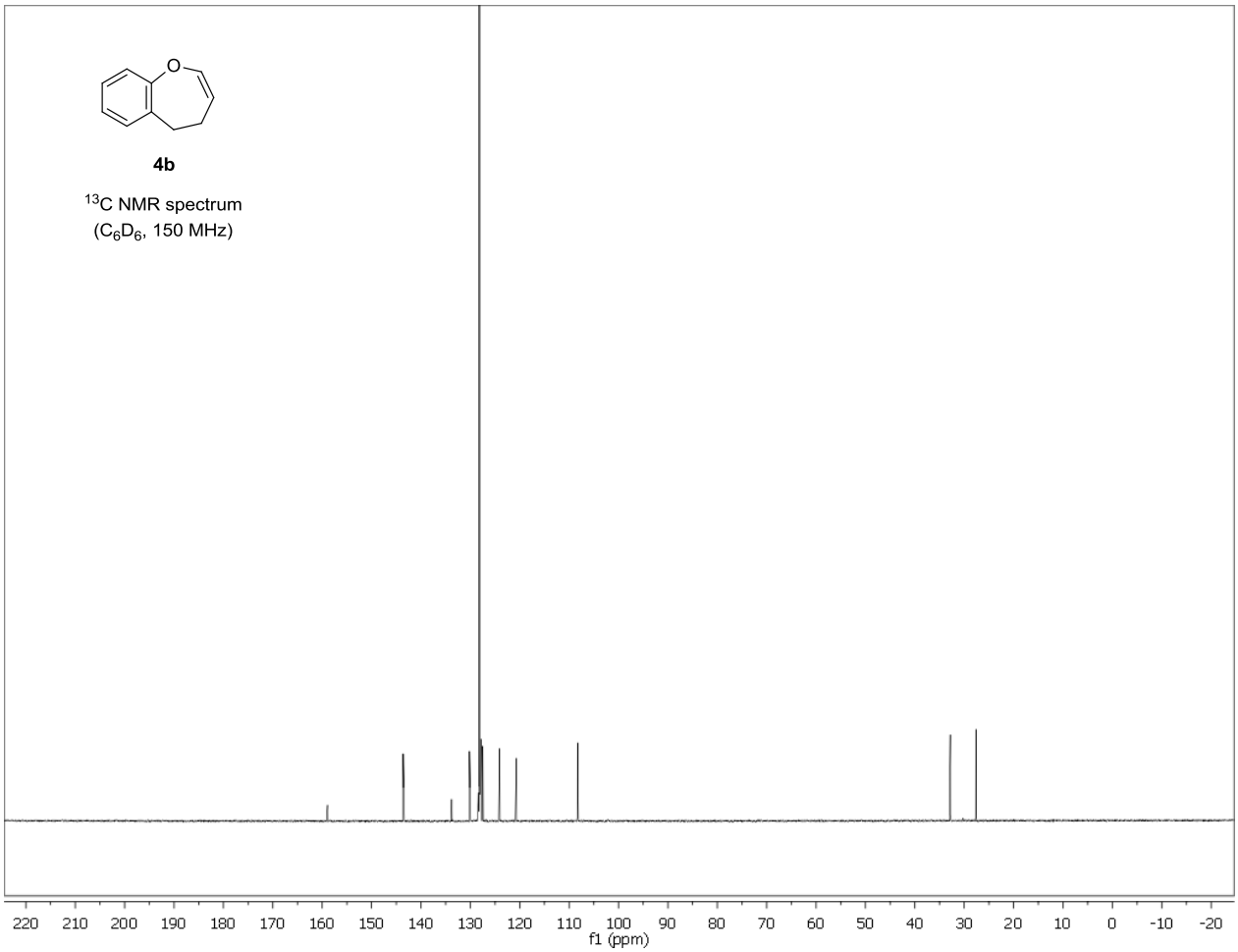


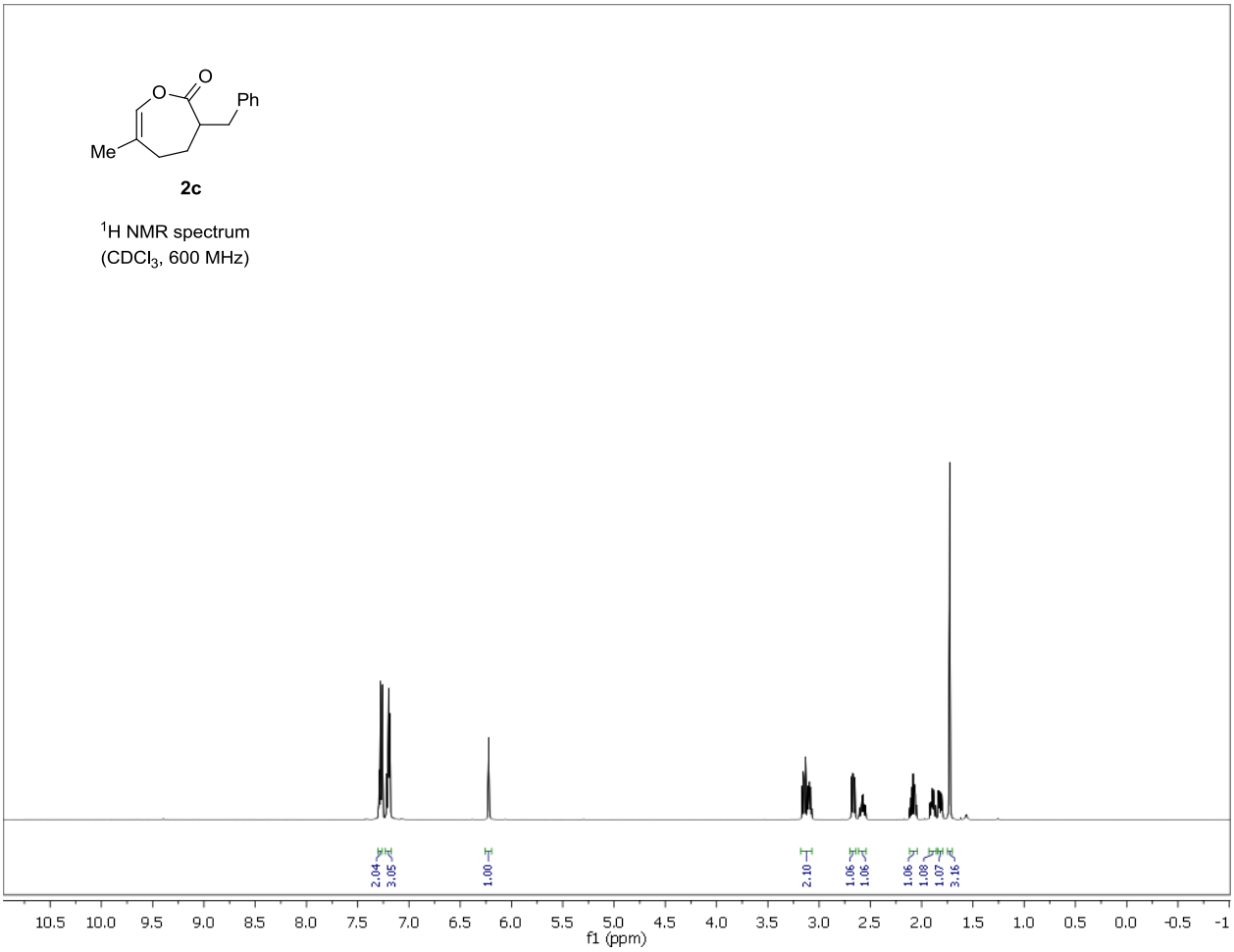

OP(O)(OPh)2
O
3b
1H NMR spectrum
(C6D6, 600 MHz)
3.91
0.99
4.08
1.12
3.10
1.04
1.00
2.10
2.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


OP(O)(OPh)2
O
3b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OP(O)(OPh)2
O
3b
31P NMR spectrum
(C6D6, 161 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

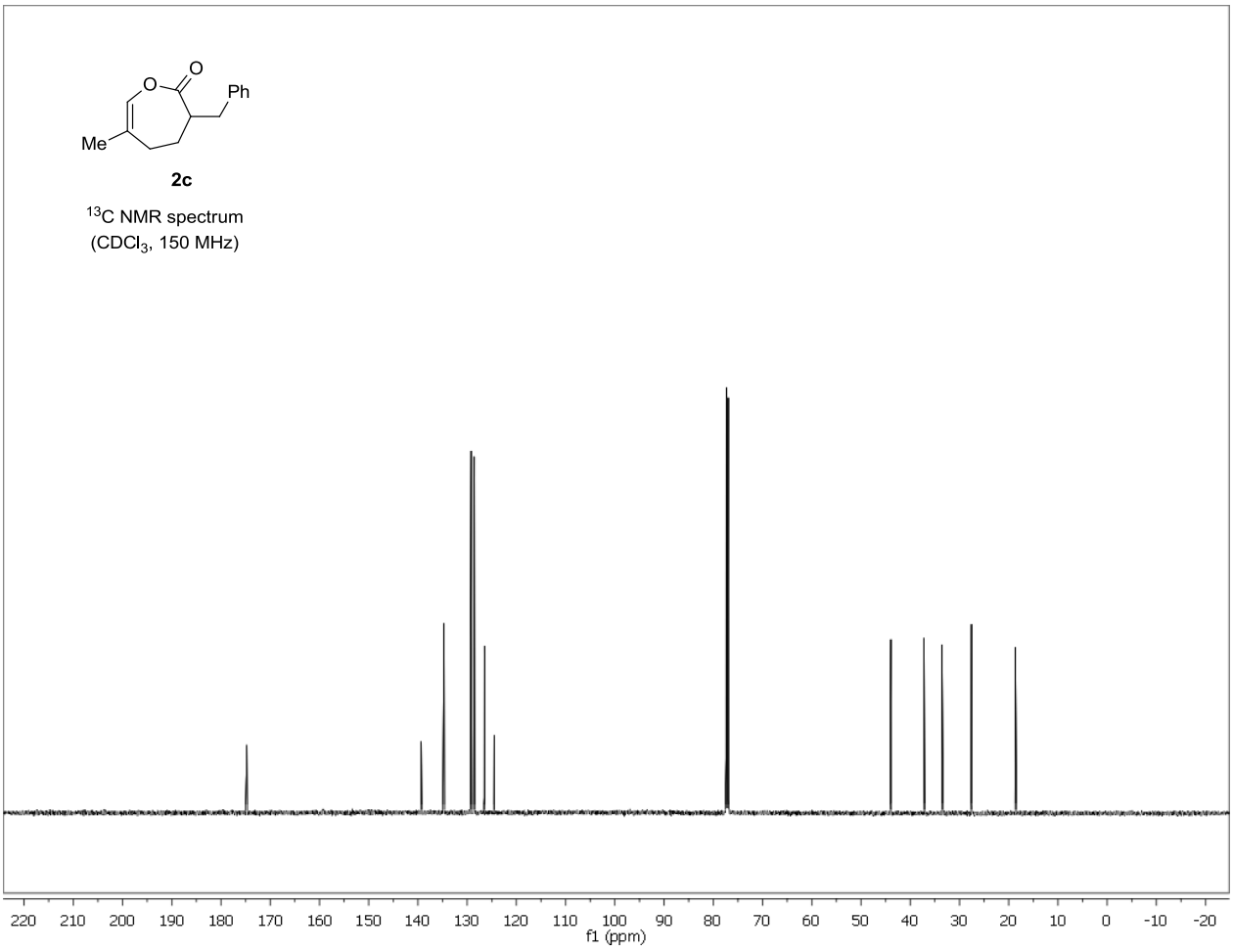

O
4b
1H NMR spectrum
(C6D6, 600 MHz)
0.99
1.00
1.98
0.99
1.00
2.18
2.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


O
4b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



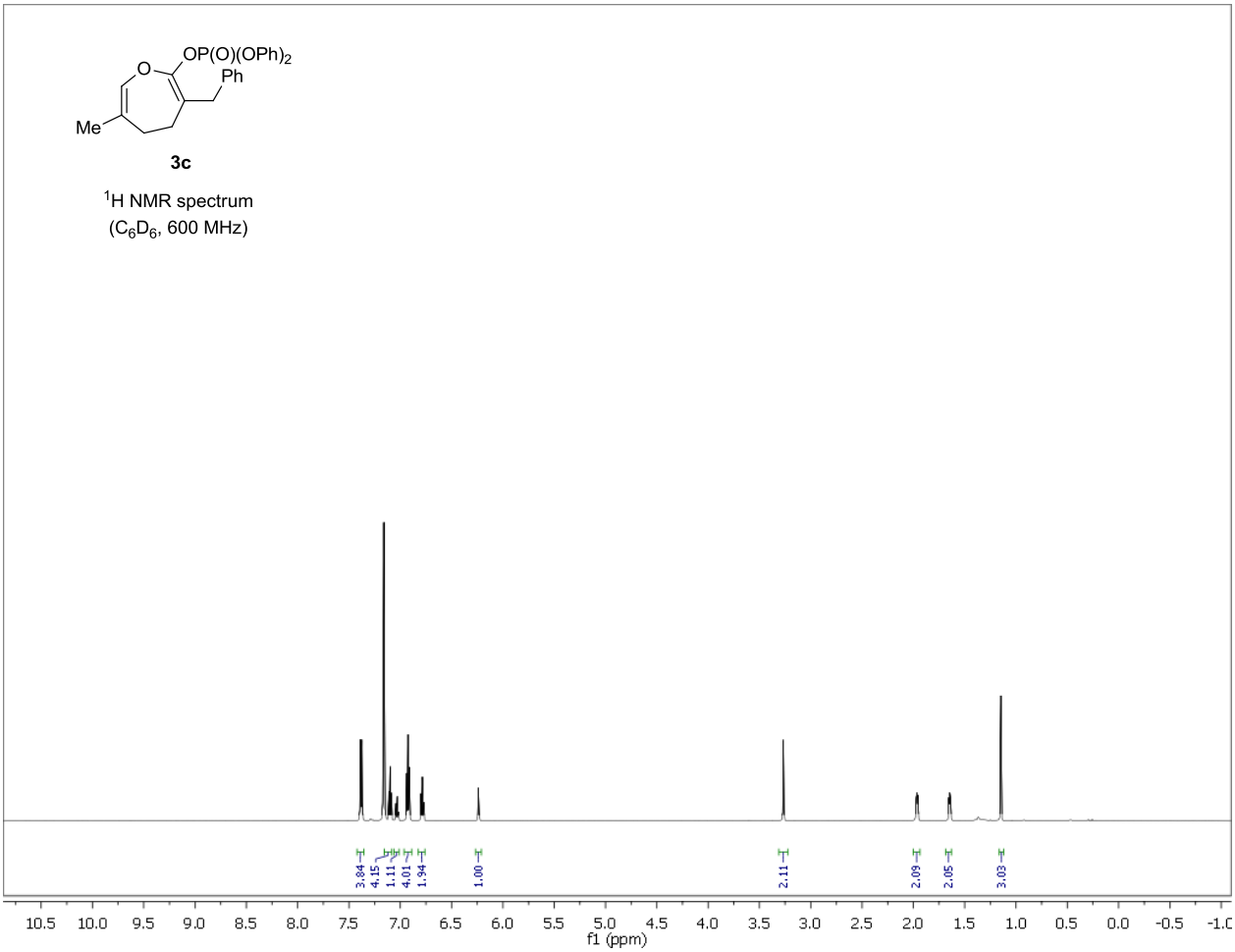
2c

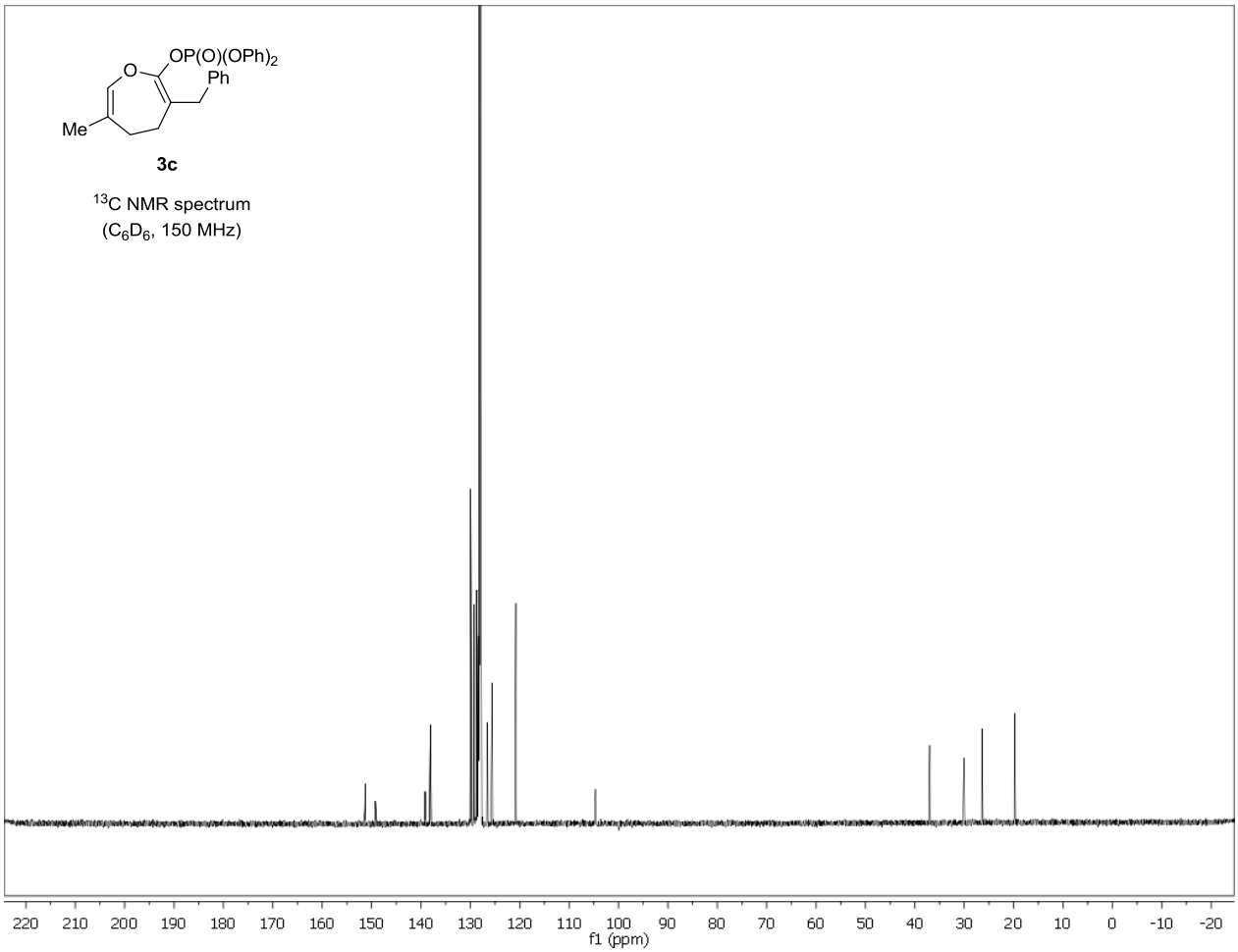
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

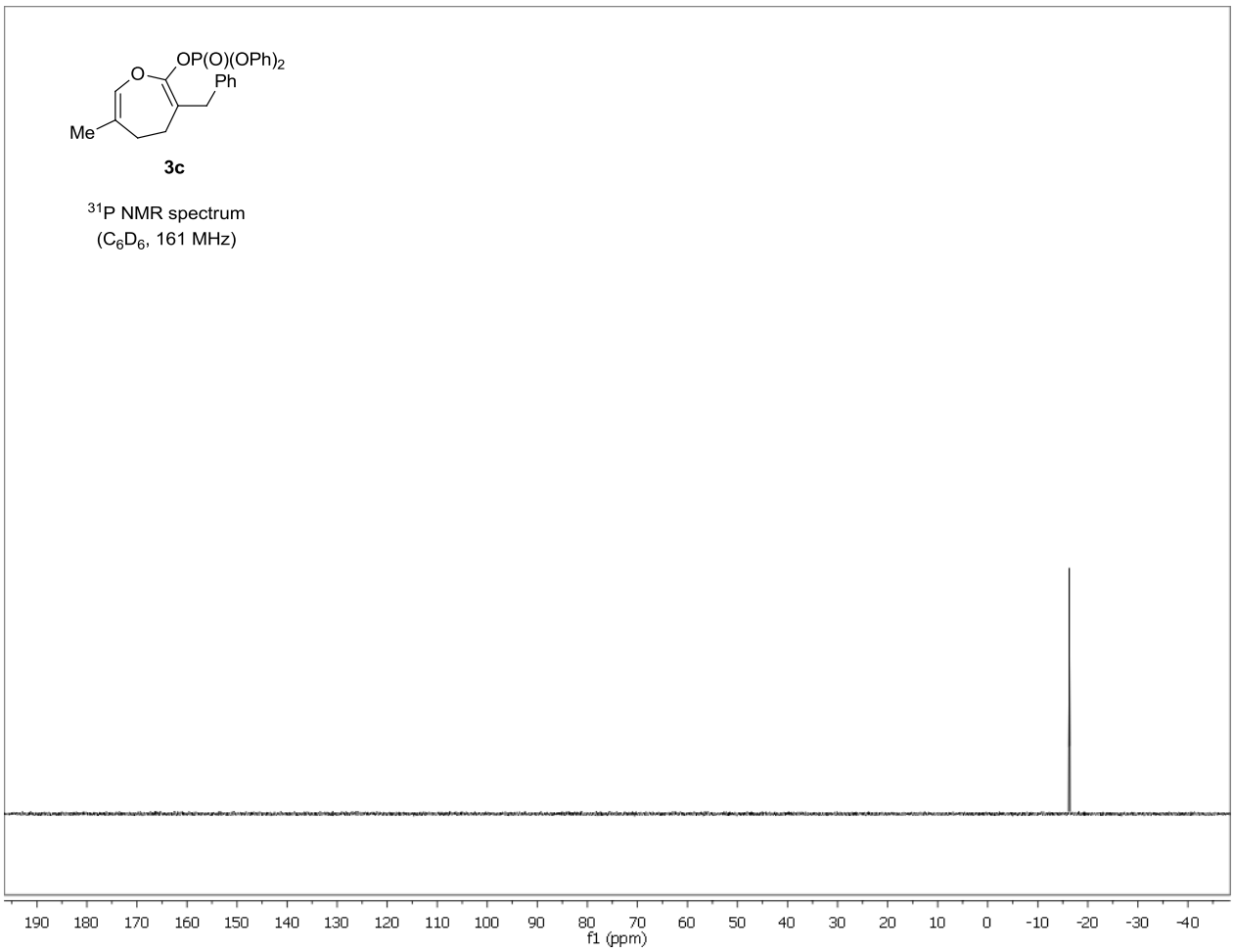


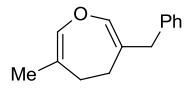
2c

^{13}C NMR spectrum
($CDCl_3$, 150 MHz)


OP(O)(OPh)2
Ph
O
Me
3c
1H NMR spectrum
(C6D6, 600 MHz)
3.84
4.15
1.11
4.01
1.94
1.00
2.11
2.09
2.05
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

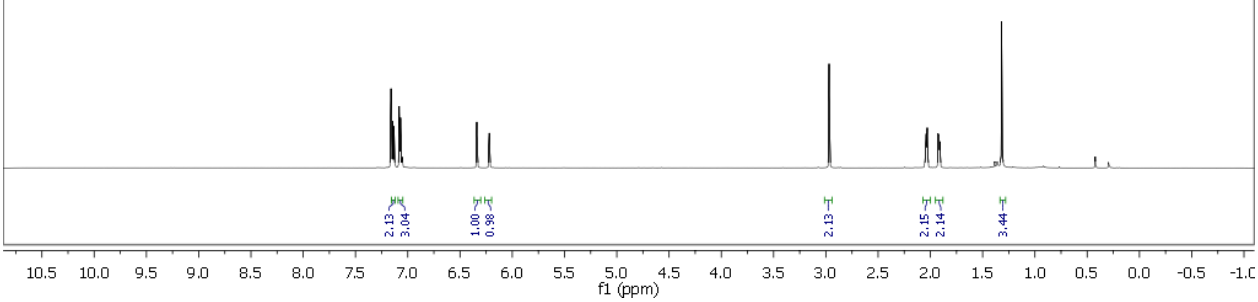

OP(O)(OPh)2
Ph
O
Me
3c
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OP(O)(OPh)2
O
Ph
Me
3c
31P NMR spectrum
(C6D6, 161 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)



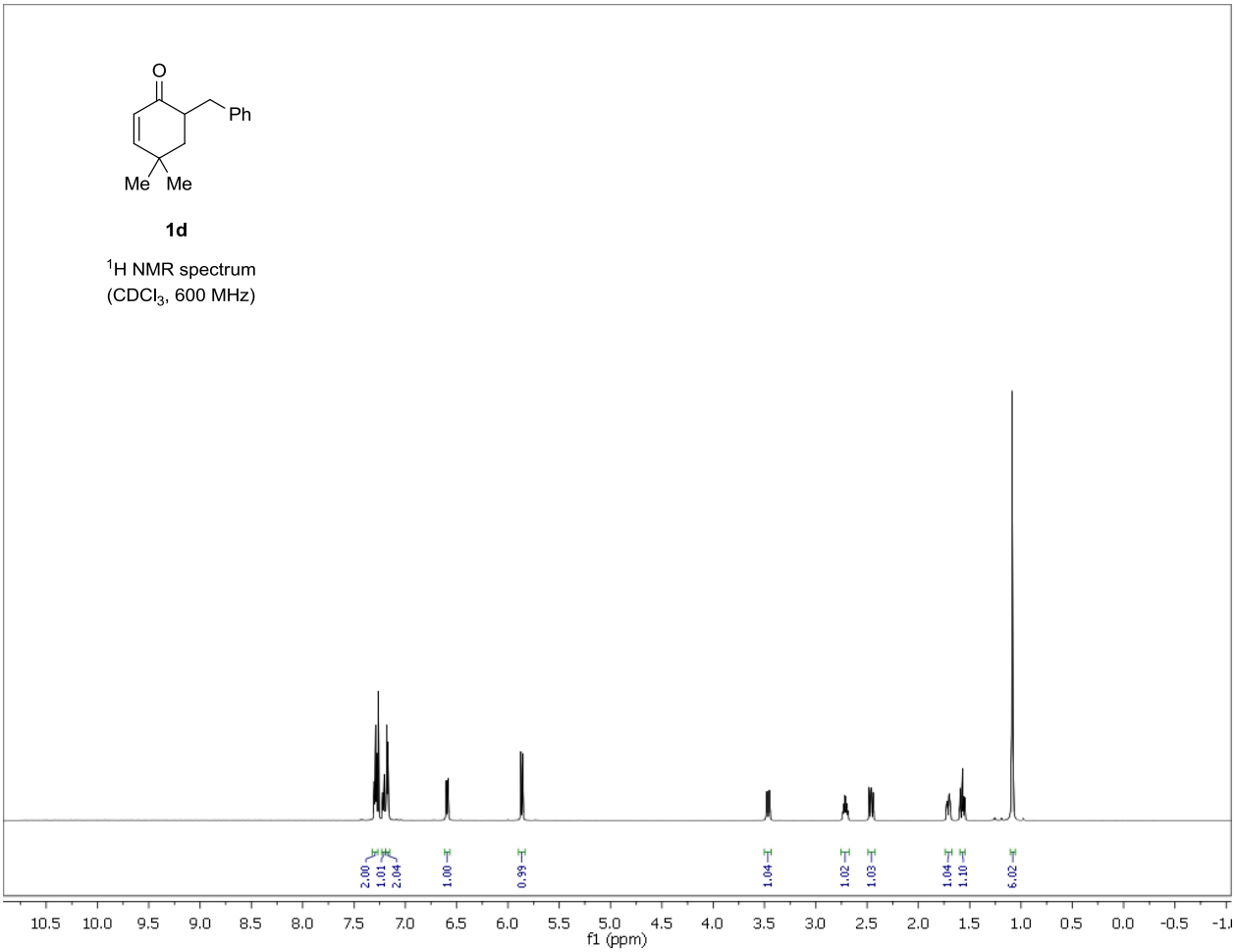
4c

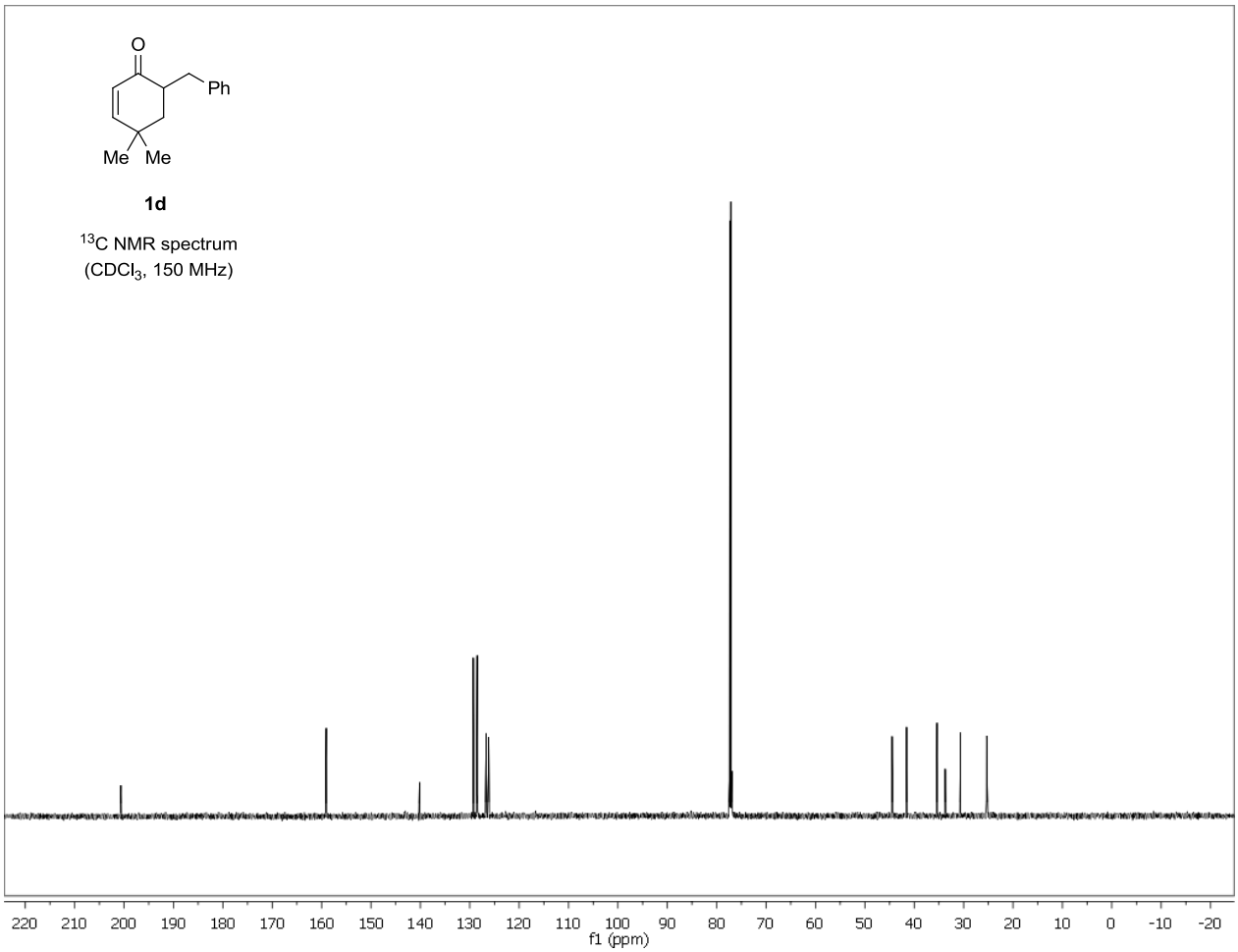
^{1}H NMR spectrum
(C_6D_6, 600 MHz)

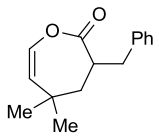


4c

^{13}C NMR spectrum
(C_6D_6, 150 MHz)

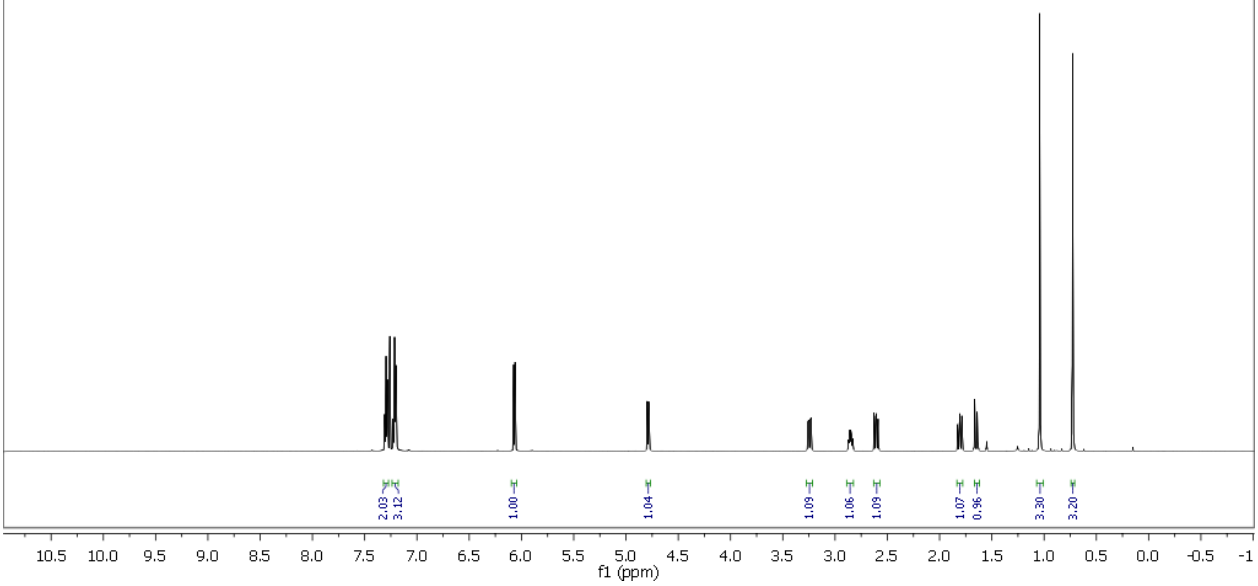

O
Ph
Me Me
1d
1H NMR spectrum
(CDCl3, 600 MHz)
2.00
1.01
2.04
1.00
0.99
1.04
1.02
1.03
1.04
1.10
6.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

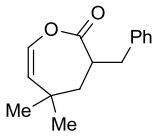

O
Ph
Me Me
1d
13C NMR spectrum
(CDCl3, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



2d

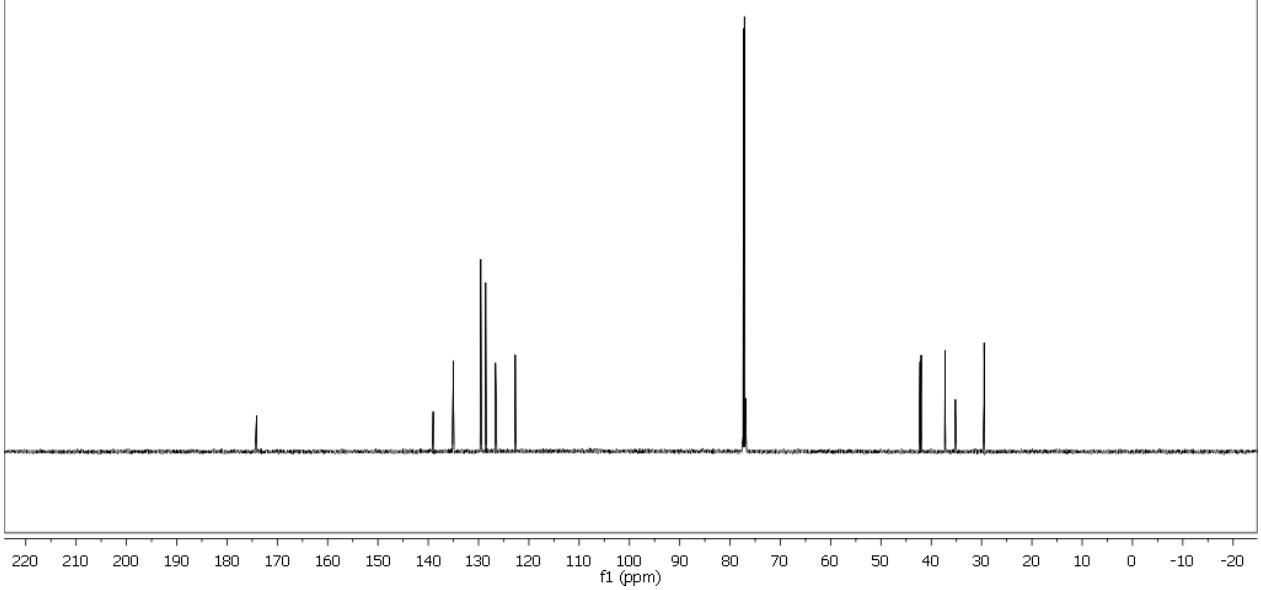
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

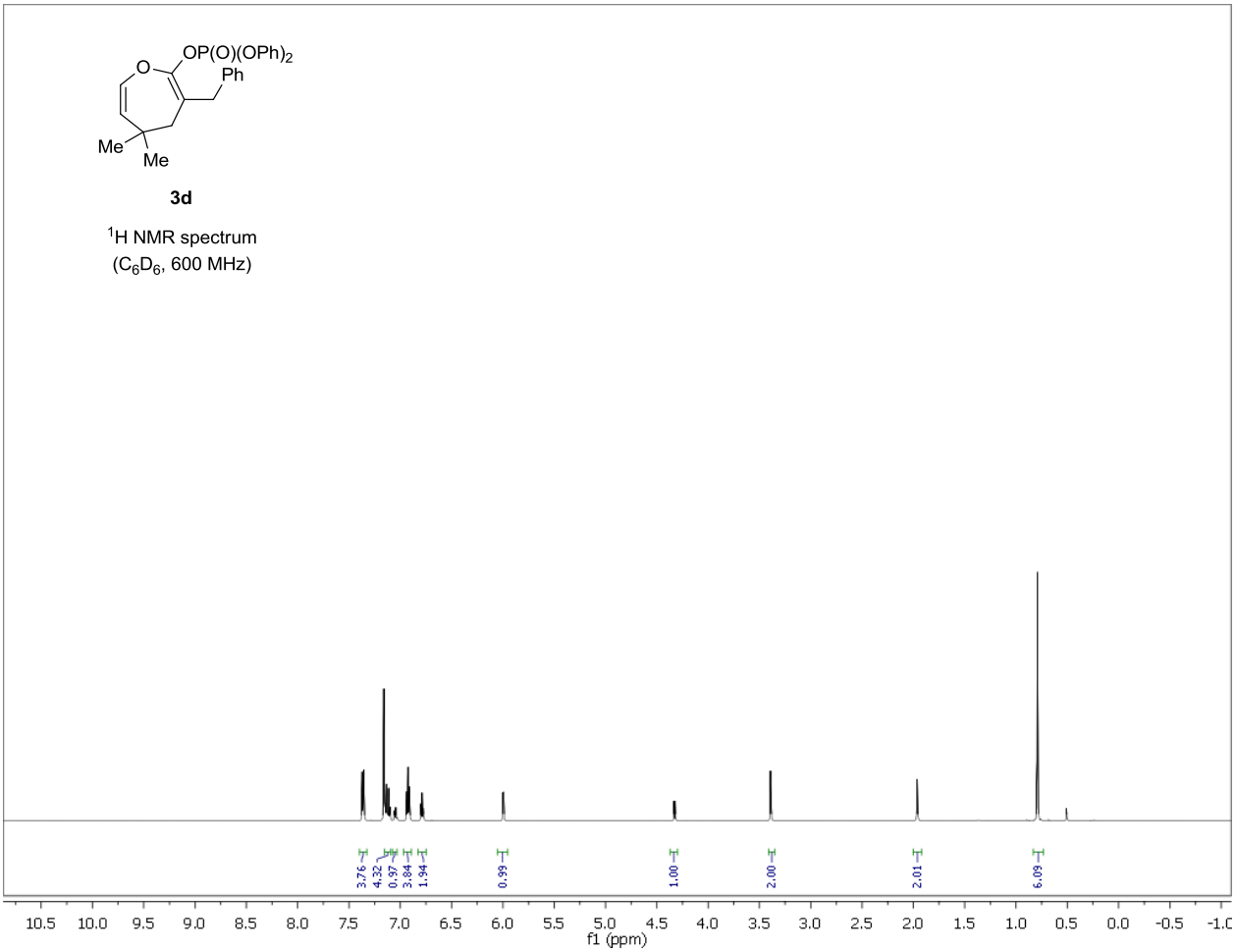


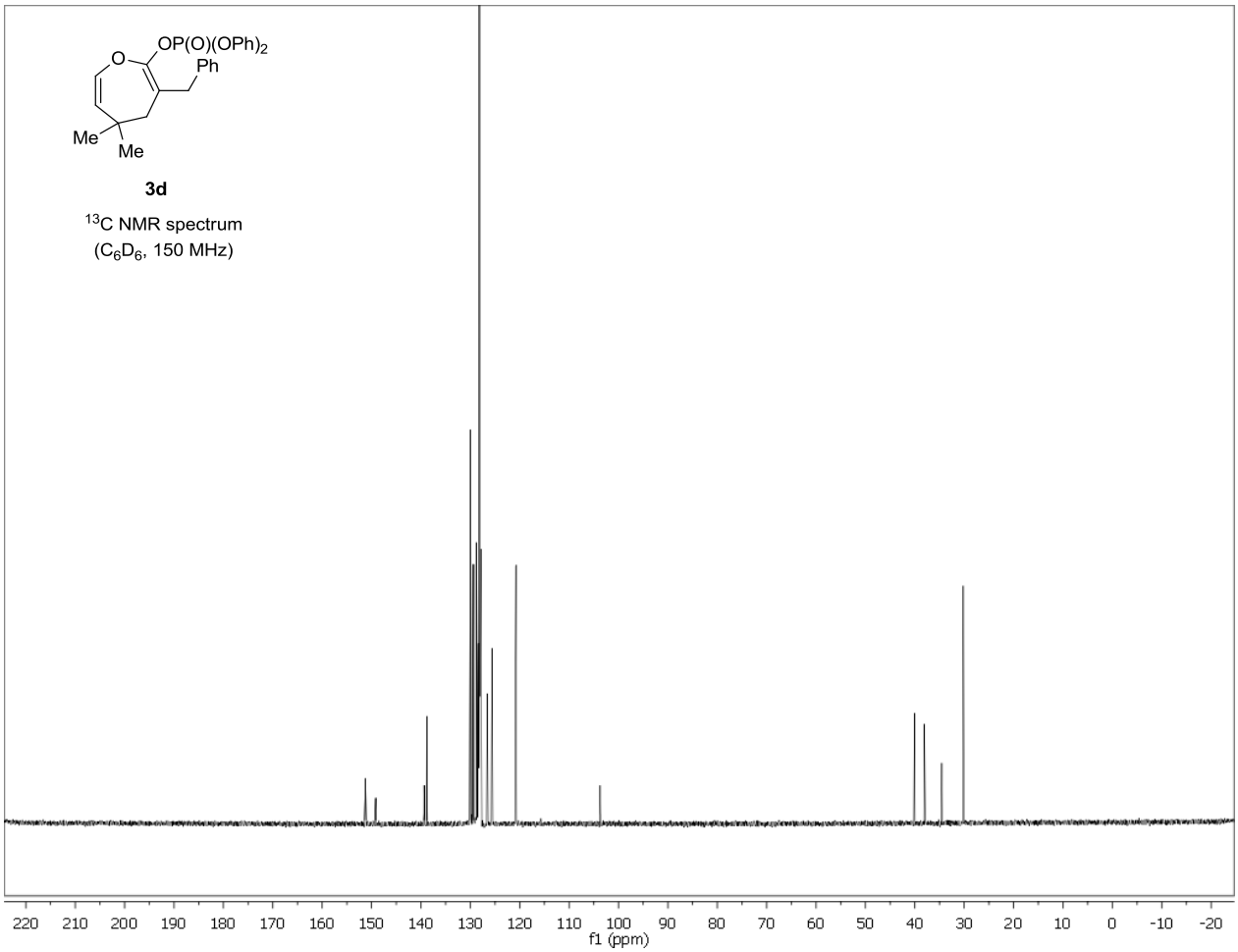


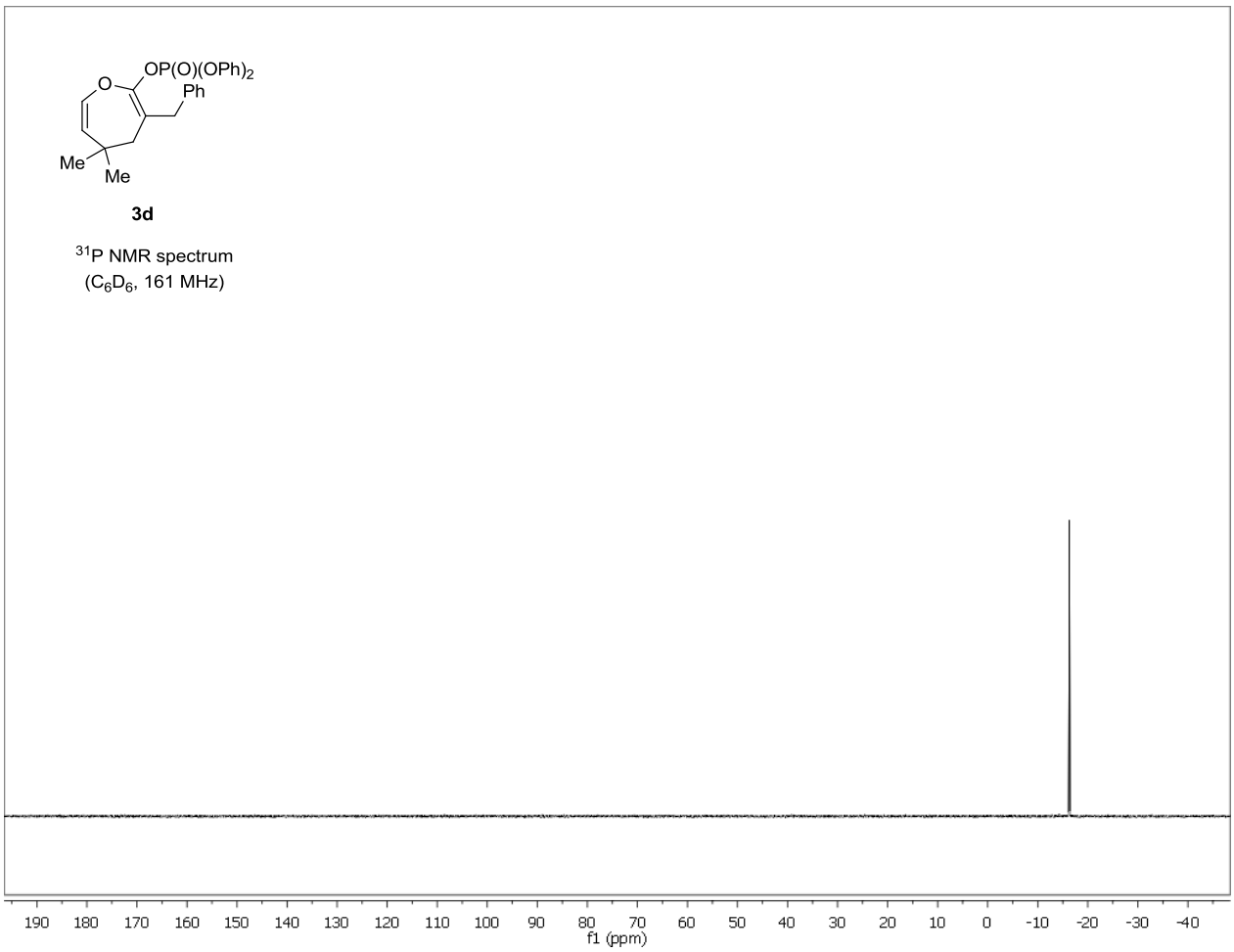
2d

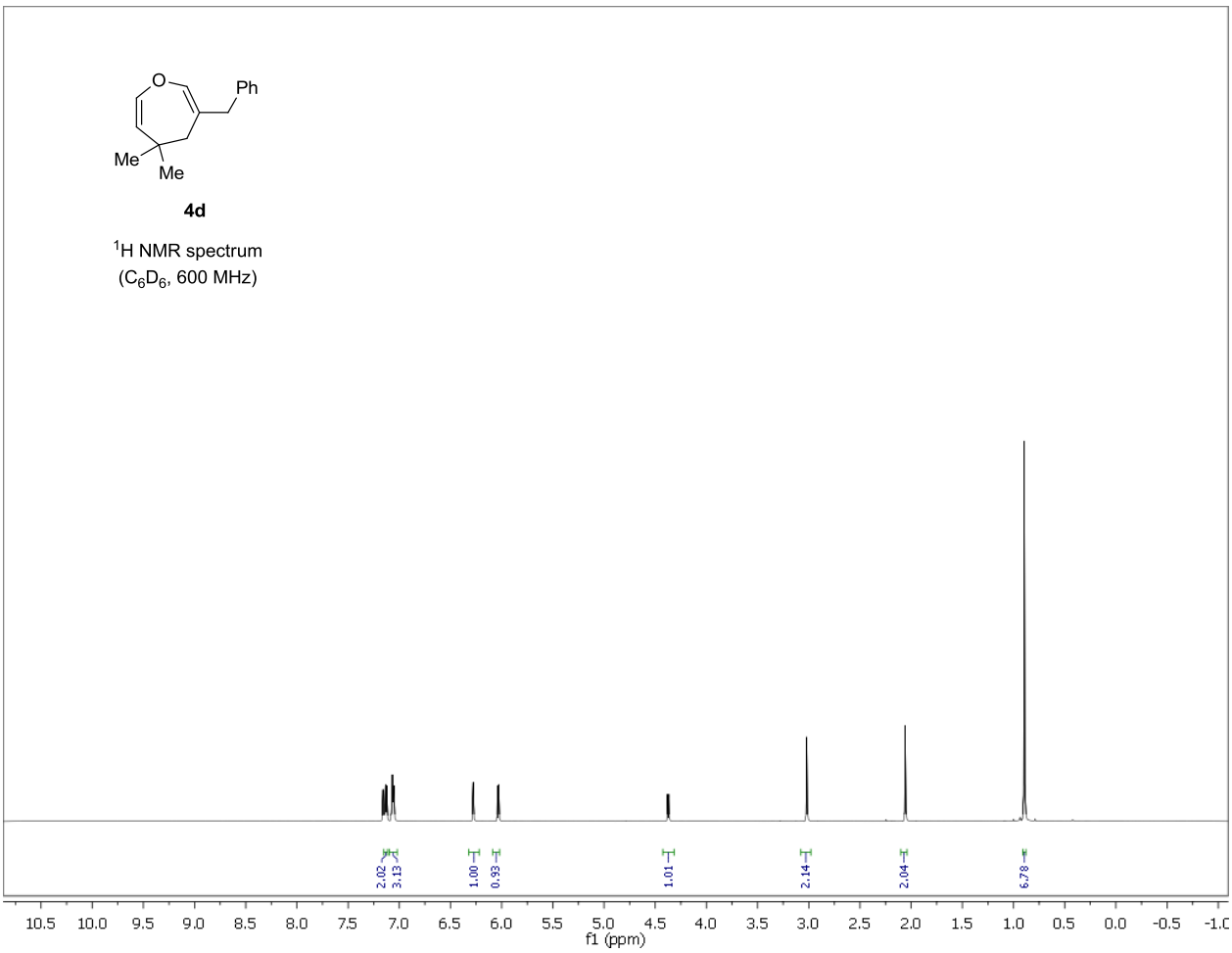
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)




OP(O)(OPh)2
Ph
O
Me
Me
3d
1H NMR spectrum
(C6D6, 600 MHz)
3.76
4.32
0.97
3.84
1.94
0.99
1.00
2.00
2.01
6.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

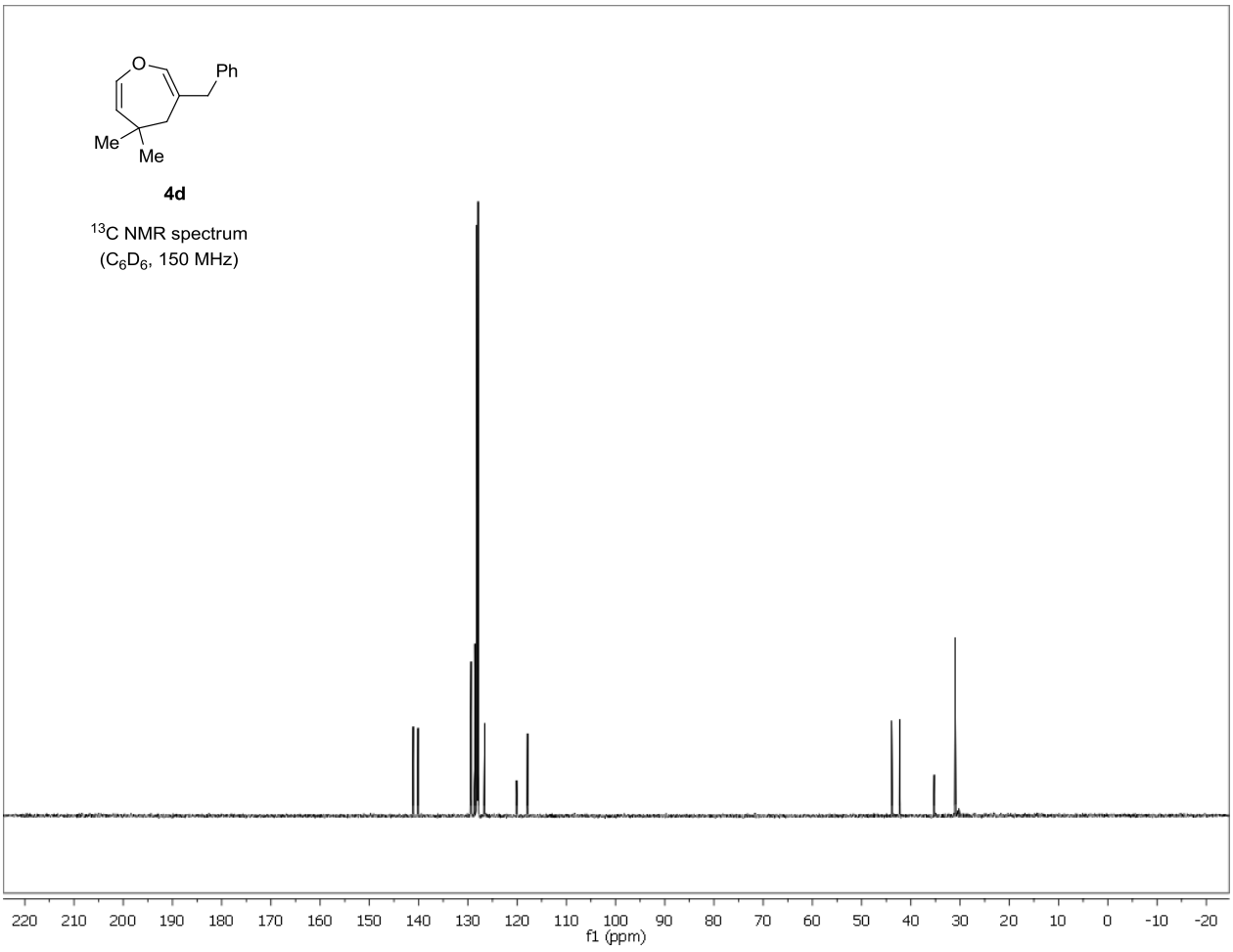

OP(O)(OPh)2
Ph
O
Me
Me
3d
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OP(O)(OPh)2
O
Ph
Me
Me
3d
31P NMR spectrum
(C6D6, 161 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)



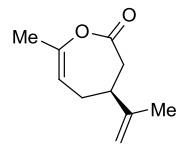
4d

^{1}H NMR spectrum
(C_6D_6, 600 MHz)



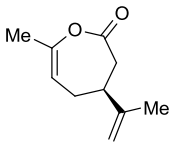
4d

^{13}C NMR spectrum
(C_6D_6, 150 MHz)



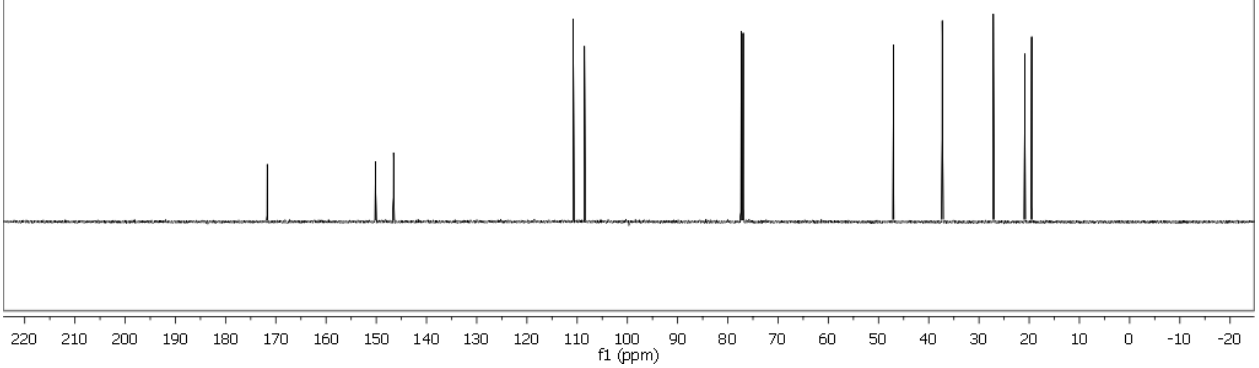
2e

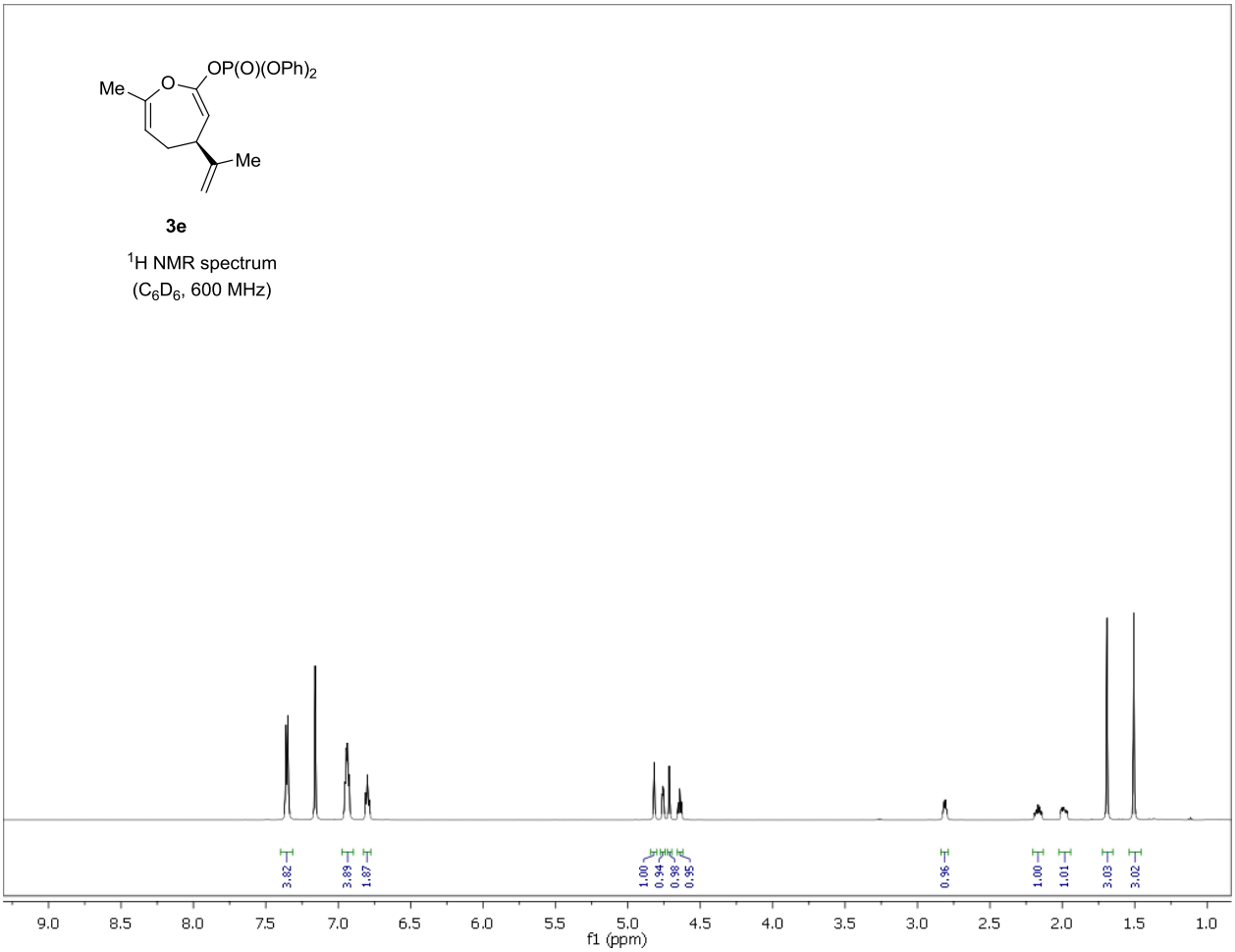
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)



2e

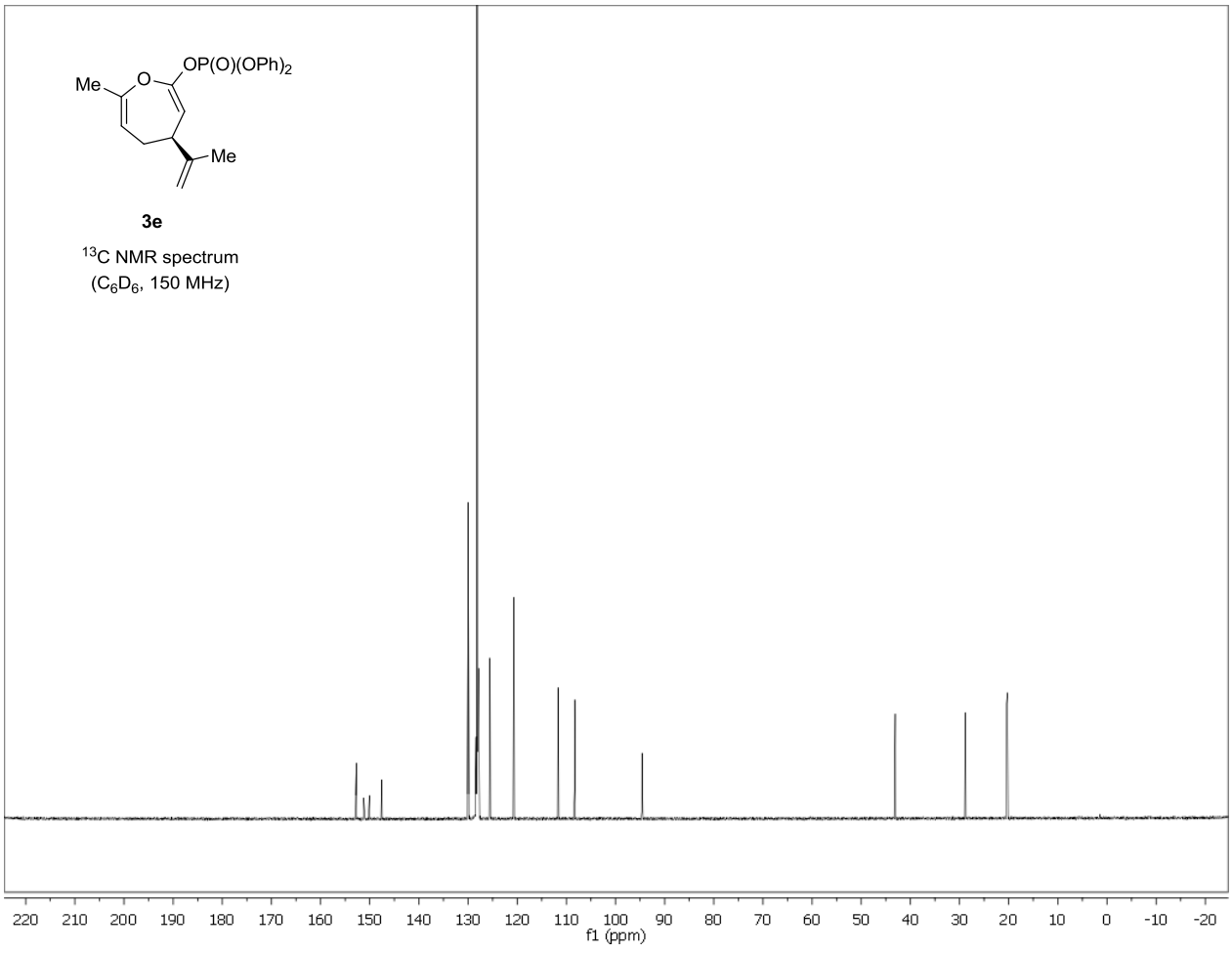
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)





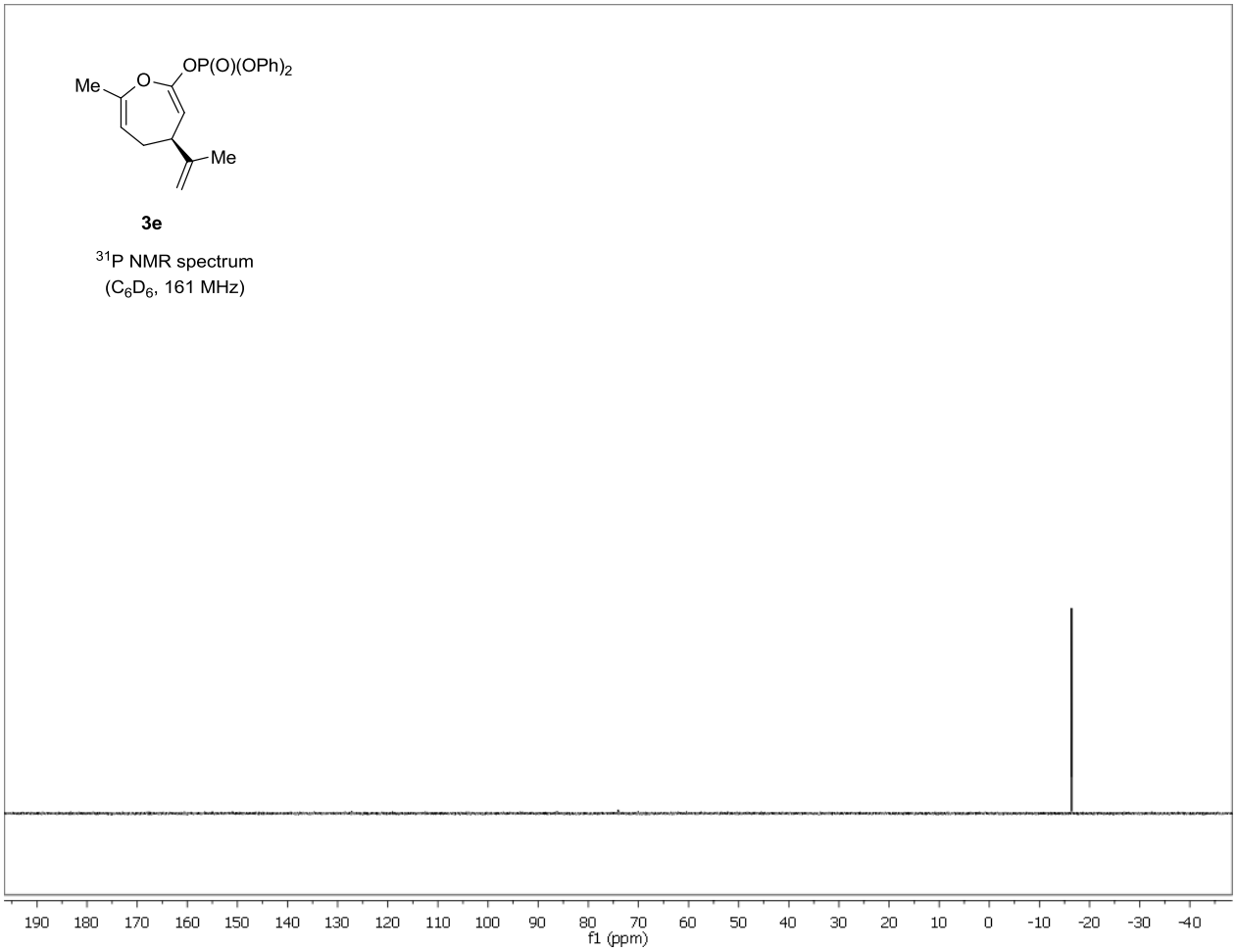
3e

^{1}H NMR spectrum
(C_6D_6, 600 MHz)



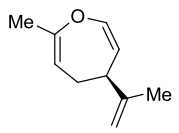
3e

^{13}C NMR spectrum
(C_6D_6, 150 MHz)



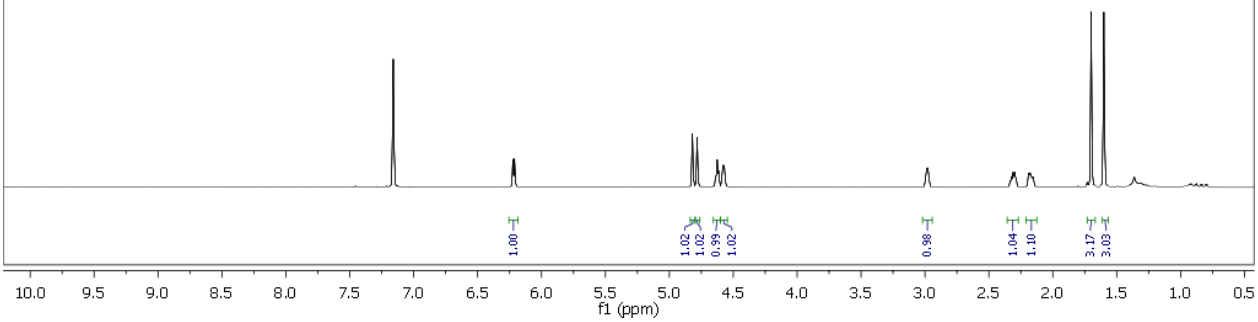
3e

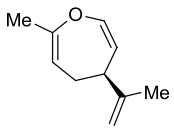
^{31}P NMR spectrum
(C_6D_6, 161 MHz)



4e

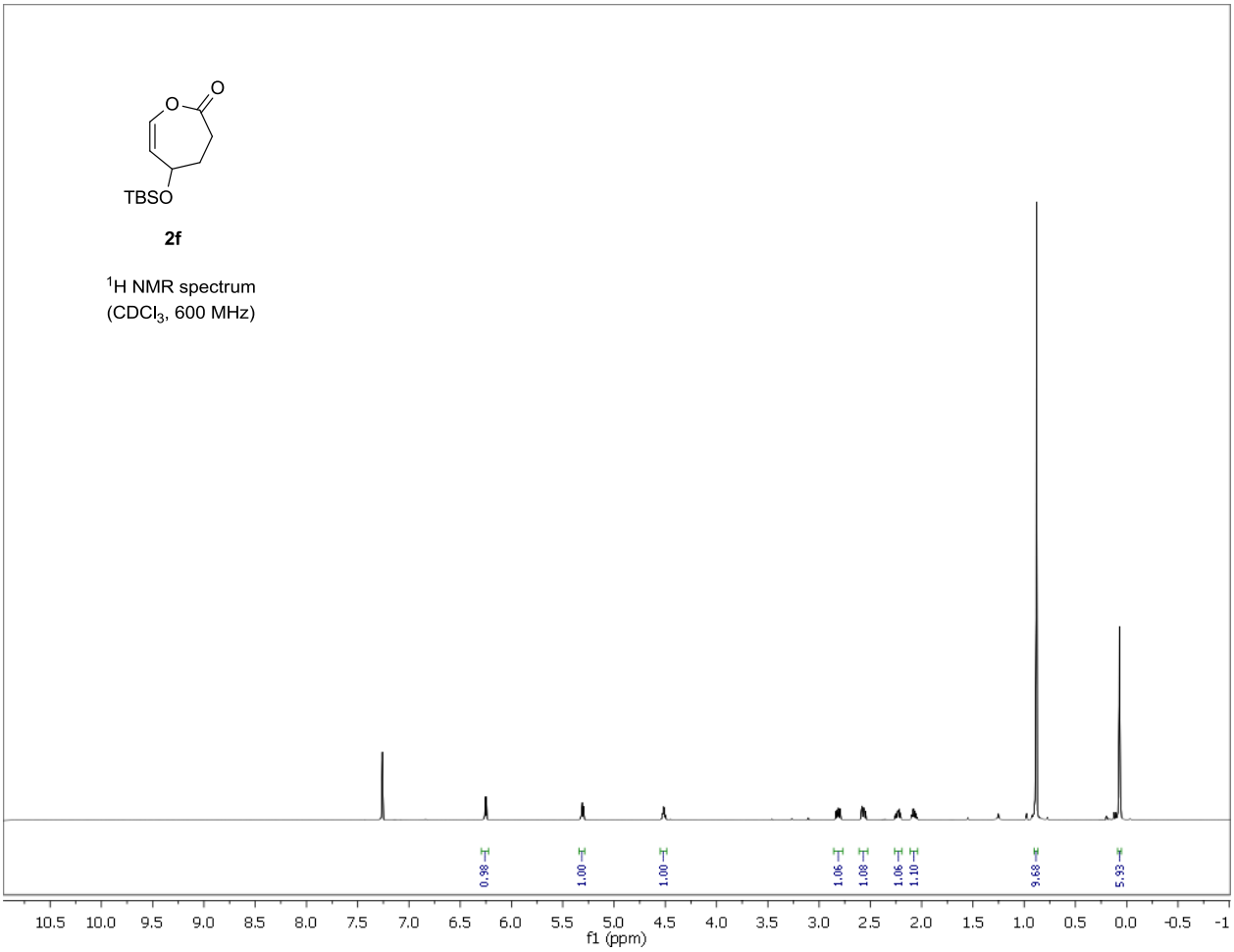
^{1}H NMR spectrum
(C_6D_6, 600 MHz)





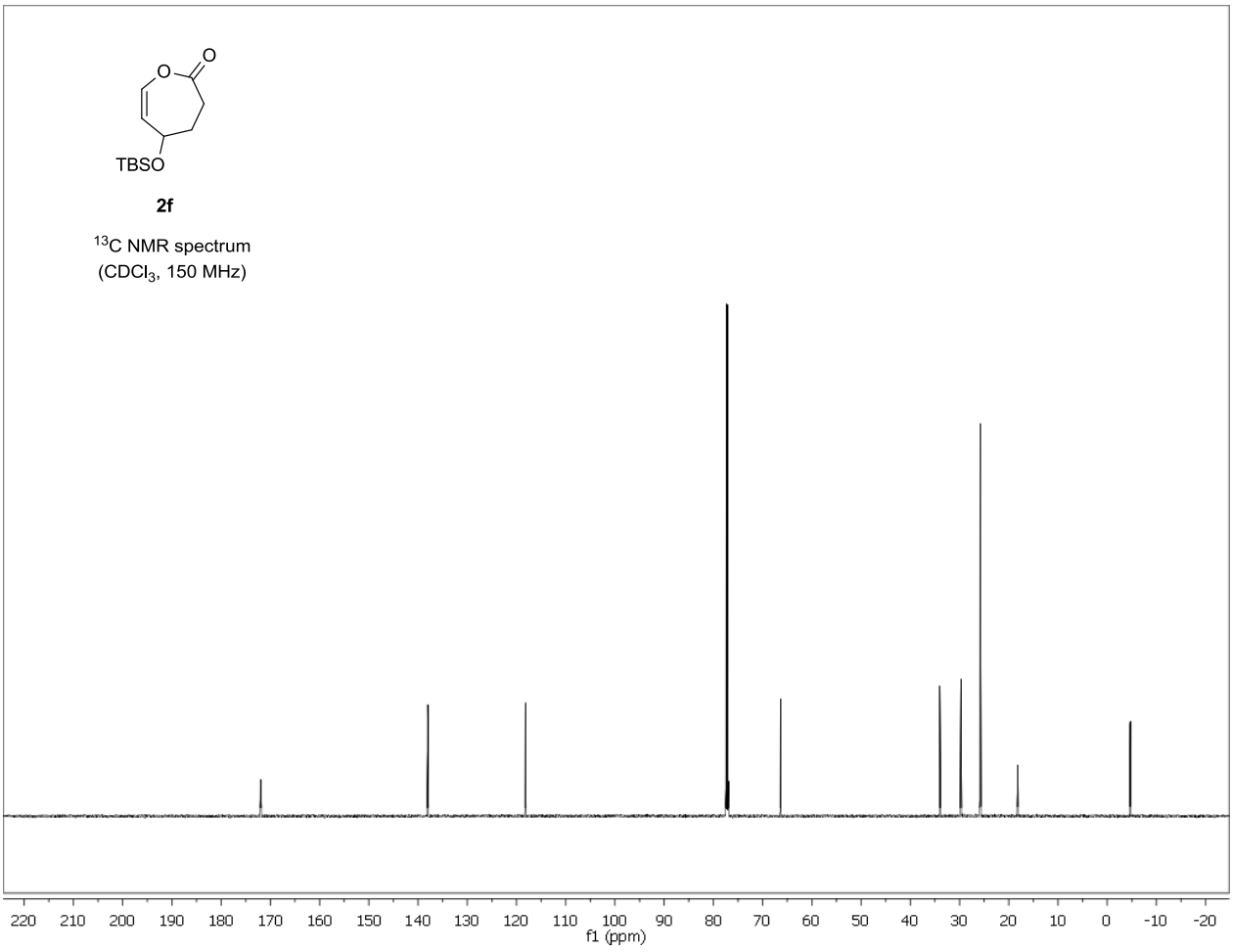
4e

^{13}C NMR spectrum
(C_6D_6, 150 MHz)



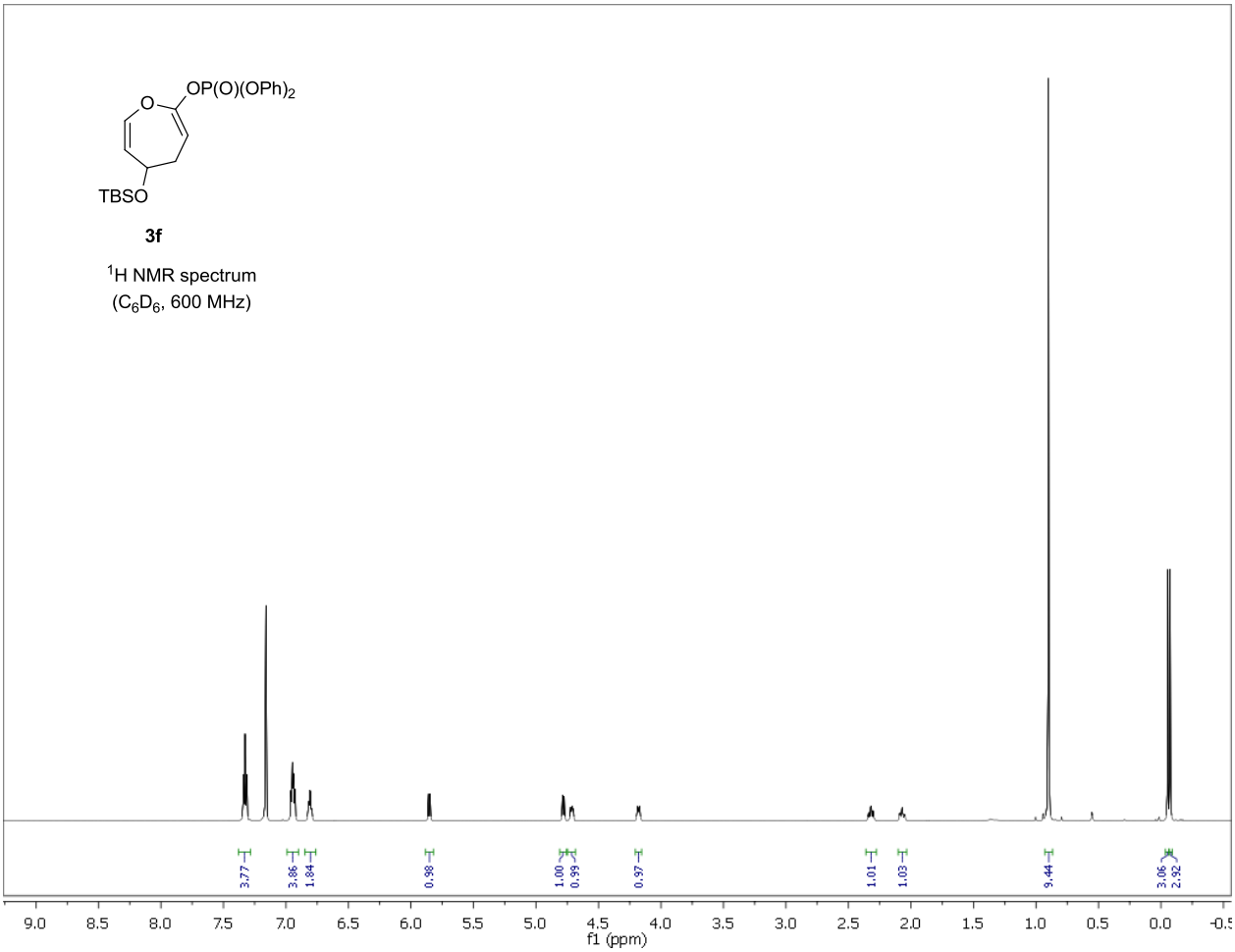
2f

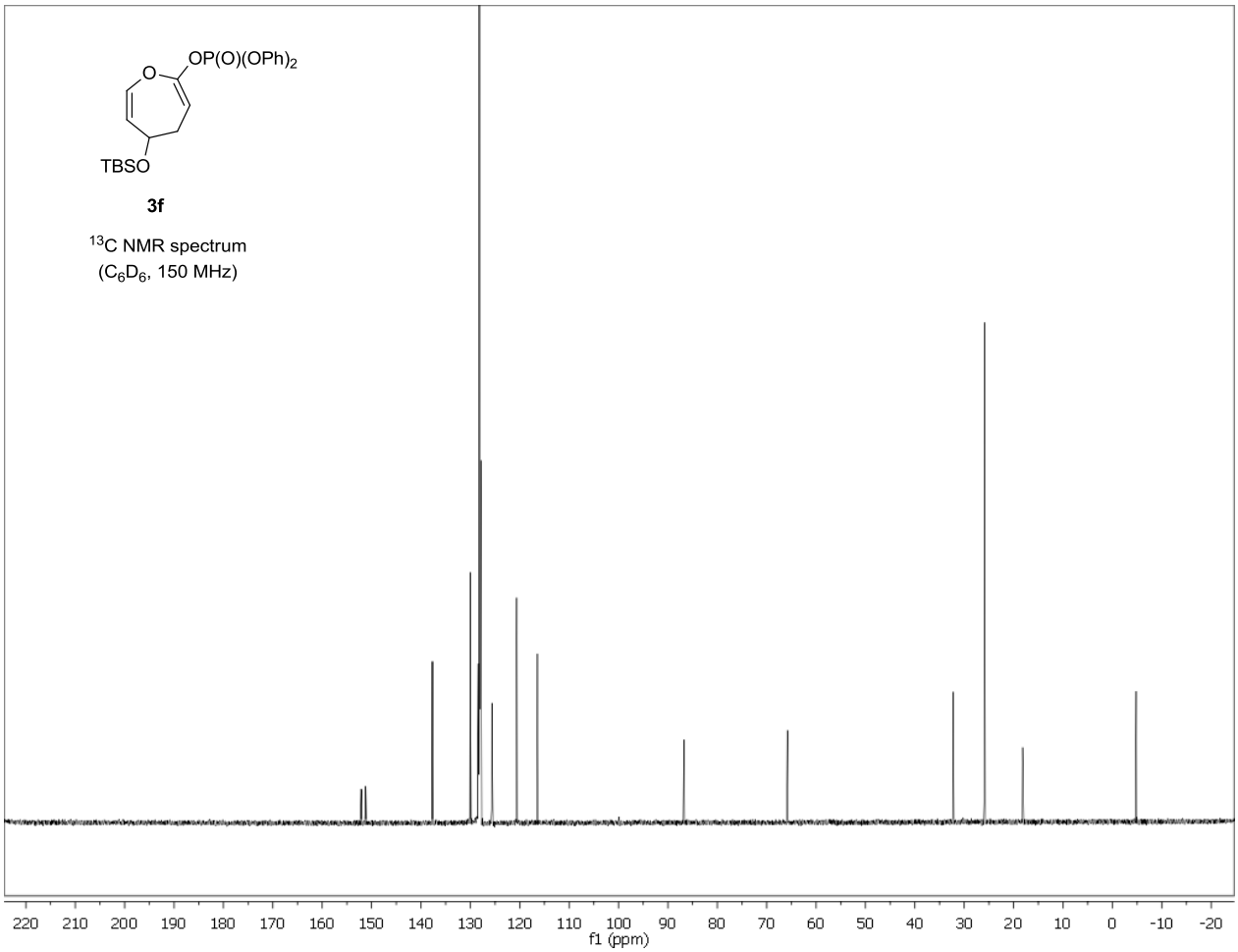
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

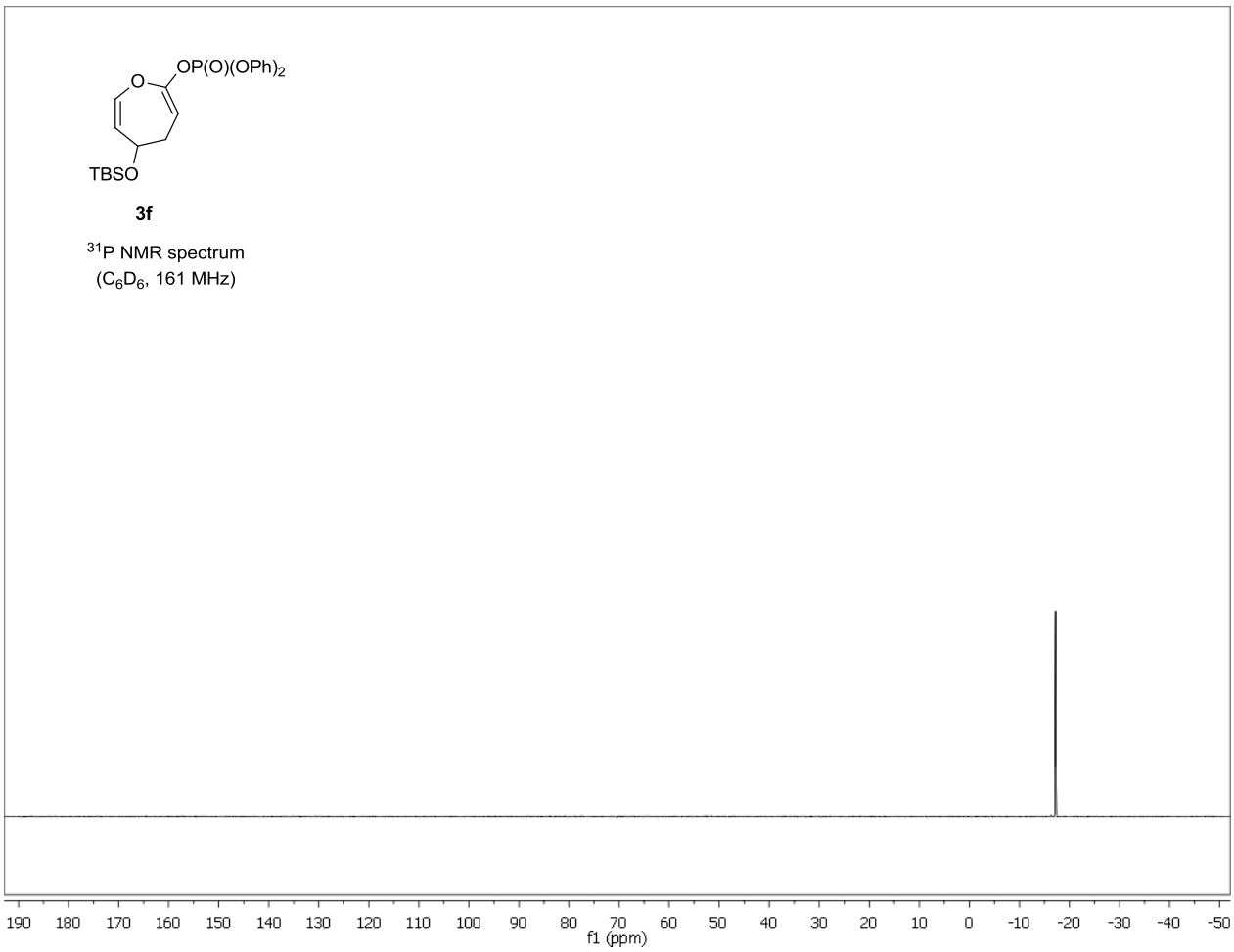


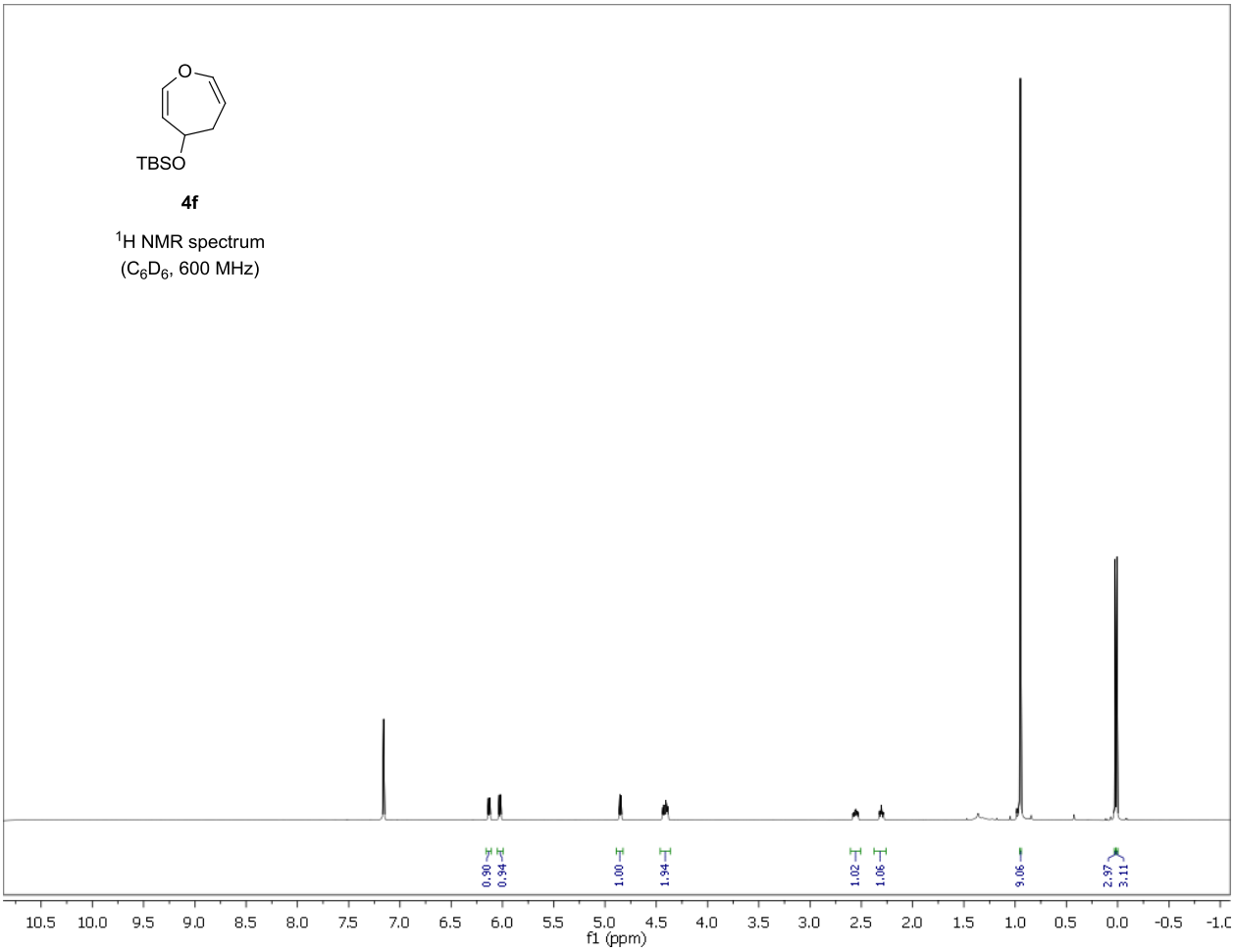
2f

^{13}C NMR spectrum
($CDCl_3$, 150 MHz)


OP(O)(OPh)2
O
TBSO
3f
1H NMR spectrum
(C6D6, 600 MHz)
3.77
3.86
1.84
0.98
1.00
0.99
0.97
1.01
1.03
9.44
3.06
2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

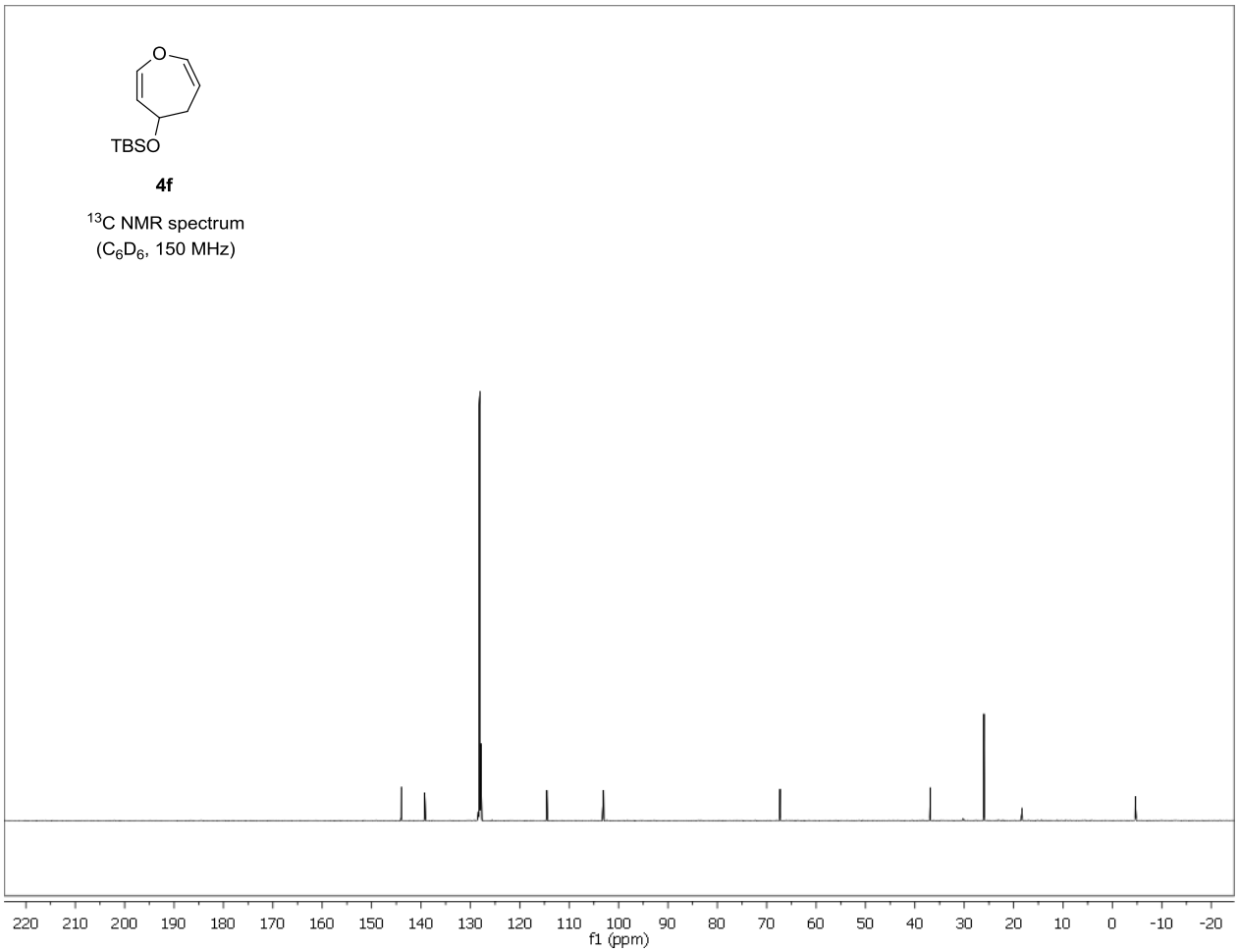

OP(O)(OPh)2
O
TBSO
3f
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OP(O)(OPh)2
O
TBSO
3f
31P NMR spectrum
(C6D6, 161 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)



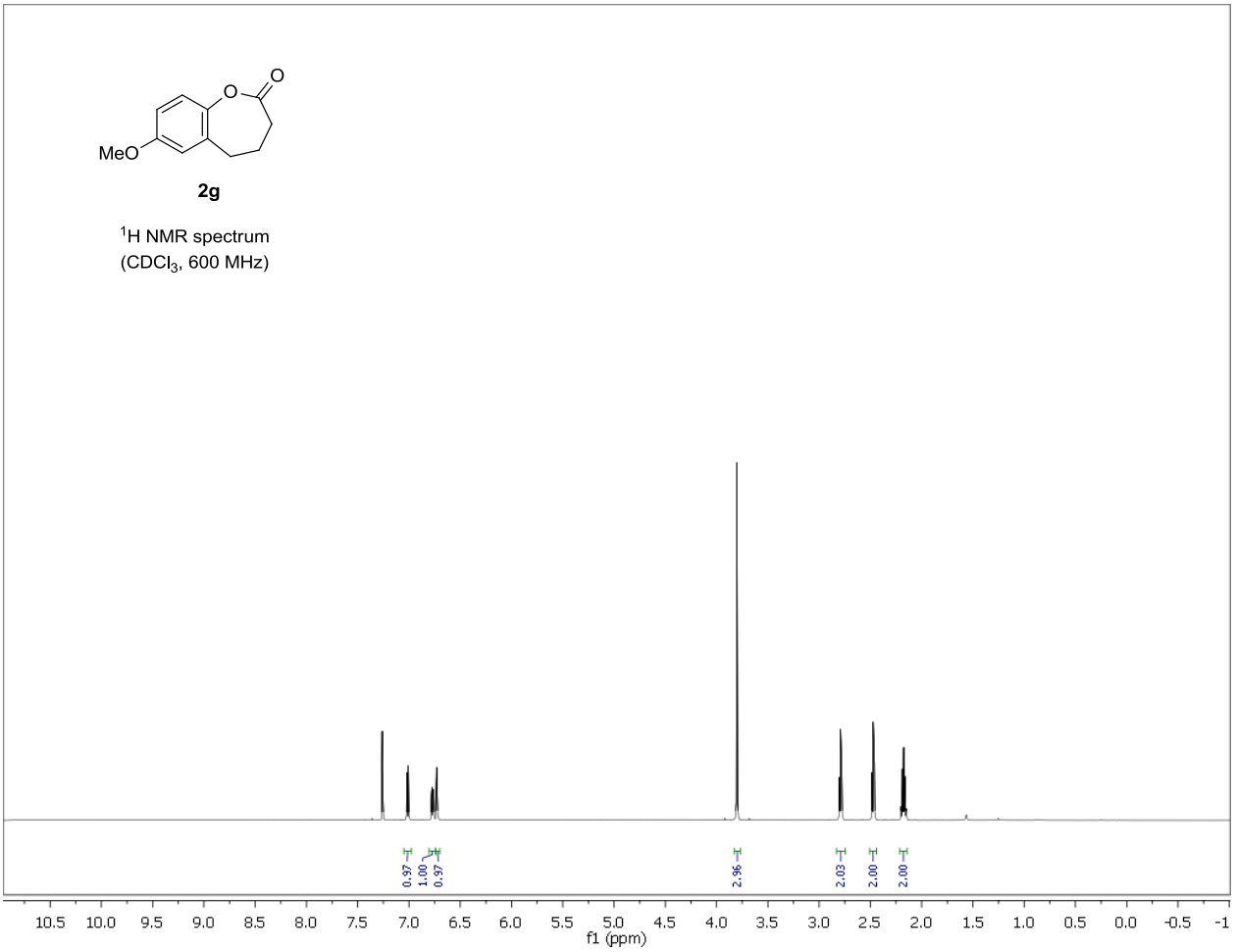
4f

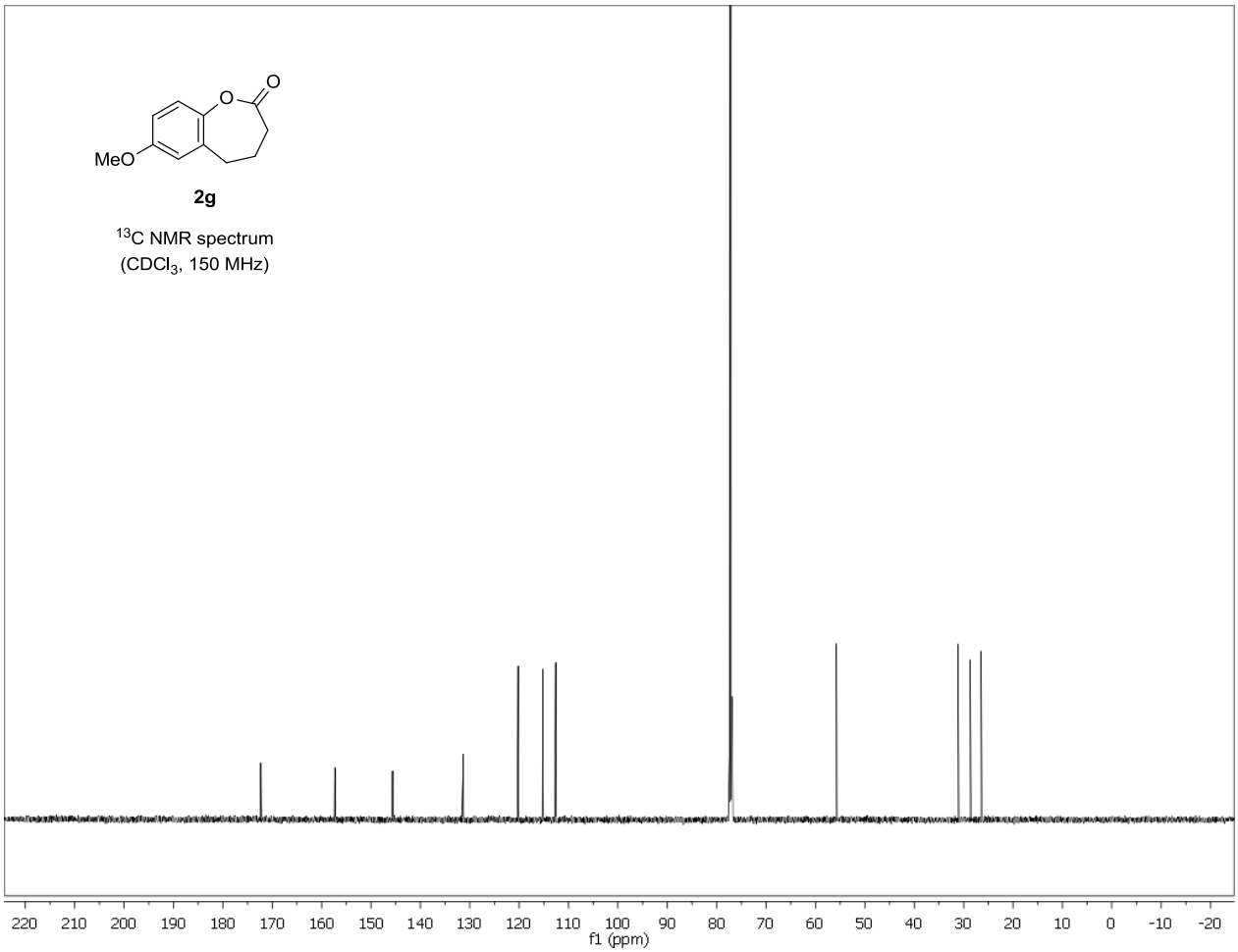
^{1}H NMR spectrum
(C_6D_6, 600 MHz)

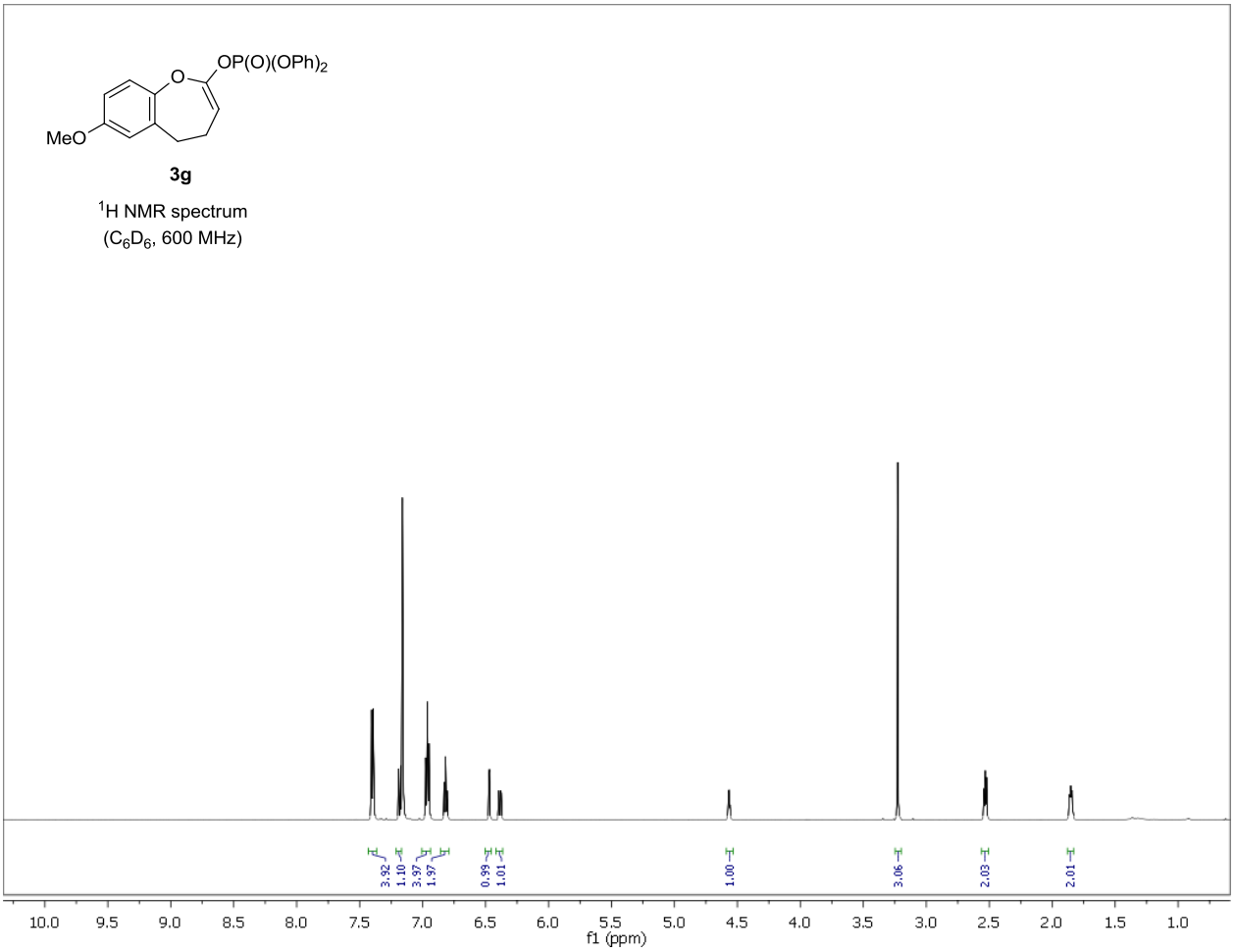


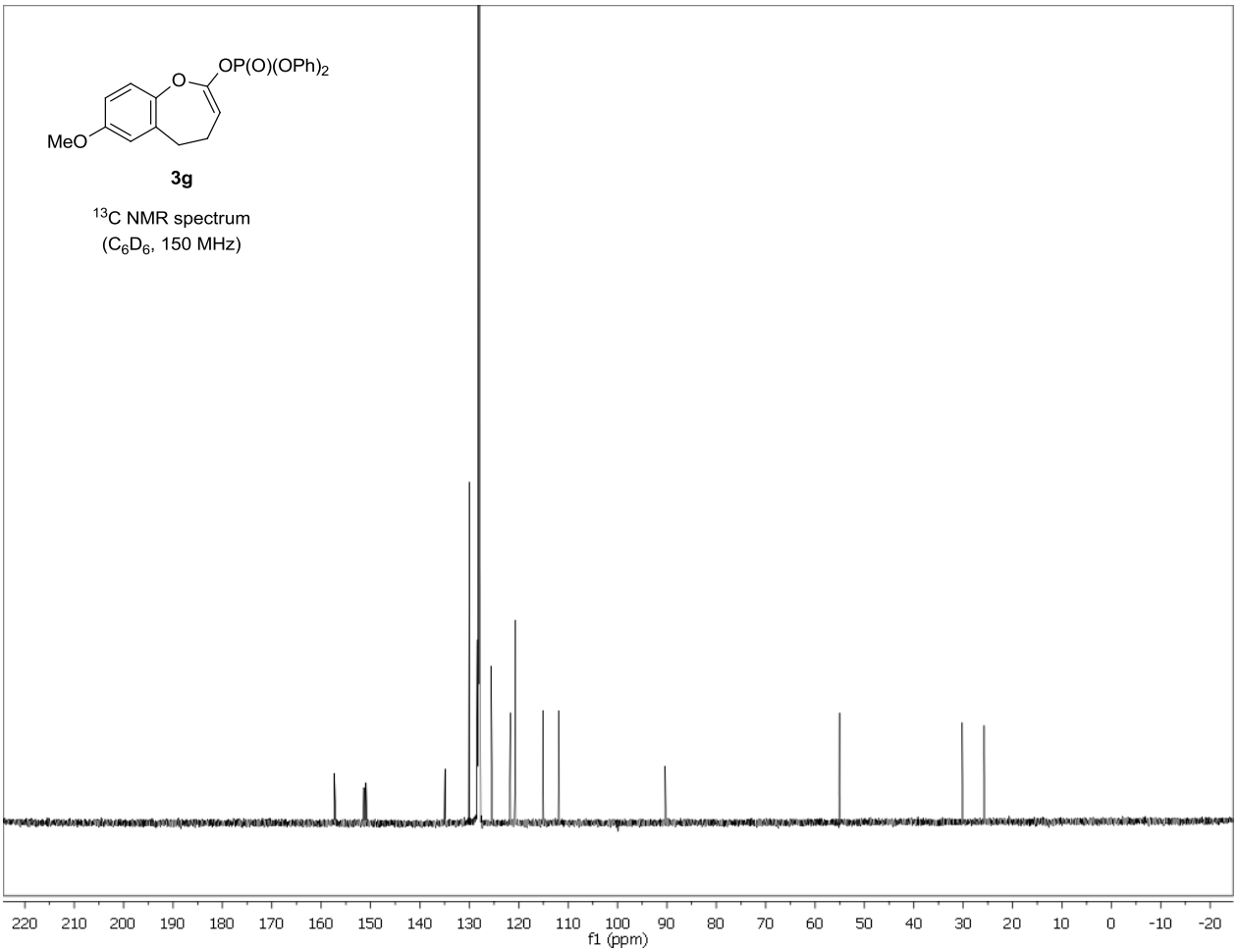
4f

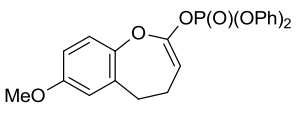
^{13}C NMR spectrum
(C_6D_6, 150 MHz)


MeO
O
O
2g
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)
0.97
1.00
0.97
2.96
2.03
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


MeO
O
O
2g
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

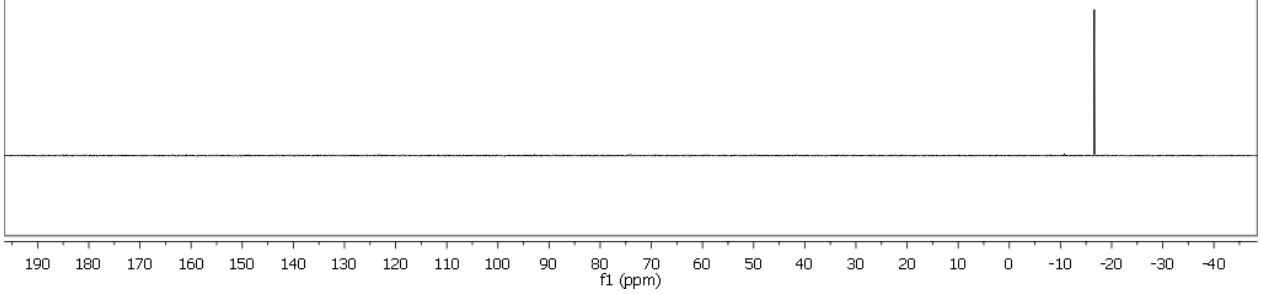

OP(O)(OPh)2
O
MeO
3g
1H NMR spectrum
(C6D6, 600 MHz)
3.92
1.10
3.97
1.97
0.99
1.01
1.00
3.06
2.03
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

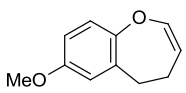

OP(O)(OPh)2
O
MeO
3g
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



3g

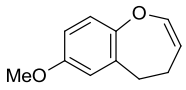
^{31}P NMR spectrum
(C_6D_6, 161 MHz)





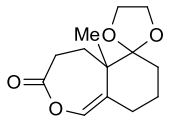
4g

^{1}H NMR spectrum
(C_6D_6, 600 MHz)



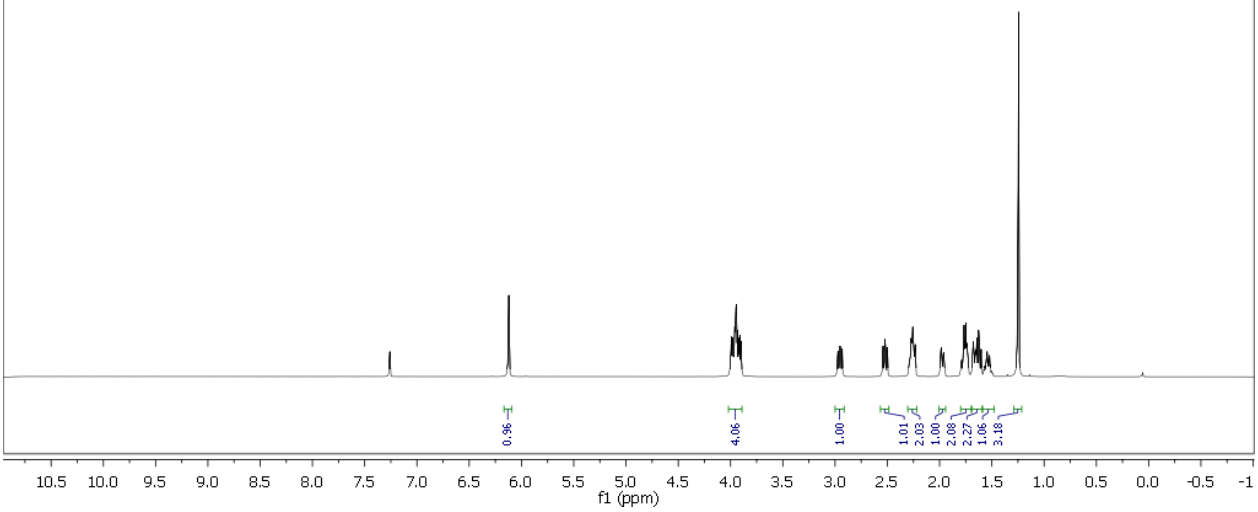
4g

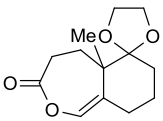
^{13}C NMR spectrum
(C_6D_6, 150 MHz)



2h

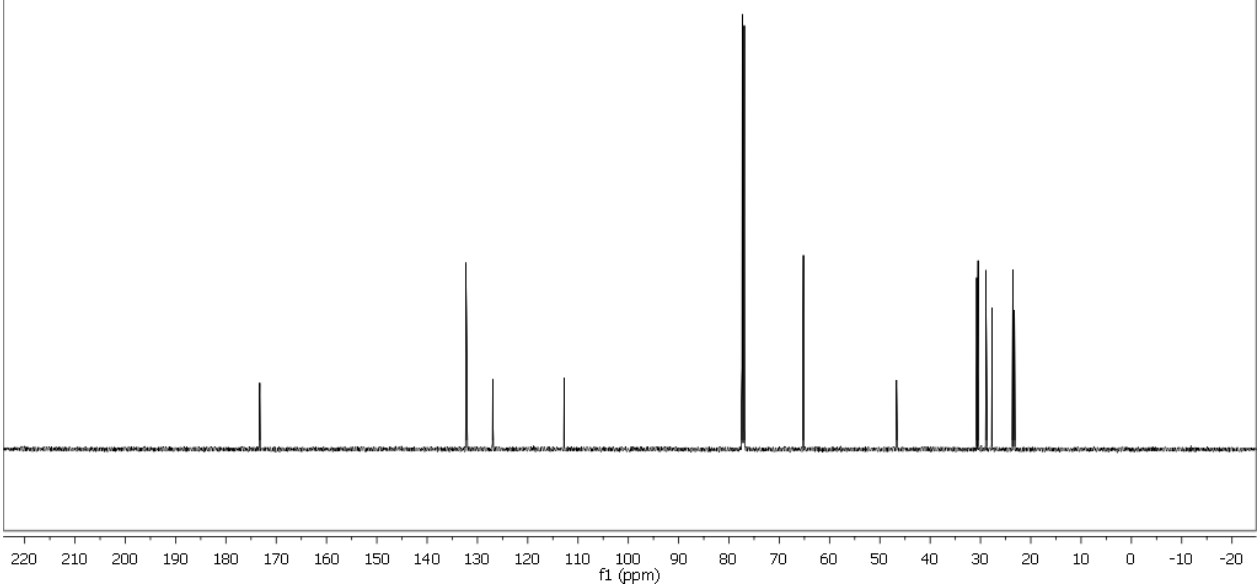
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

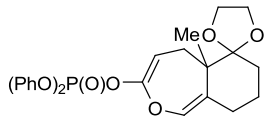




2h

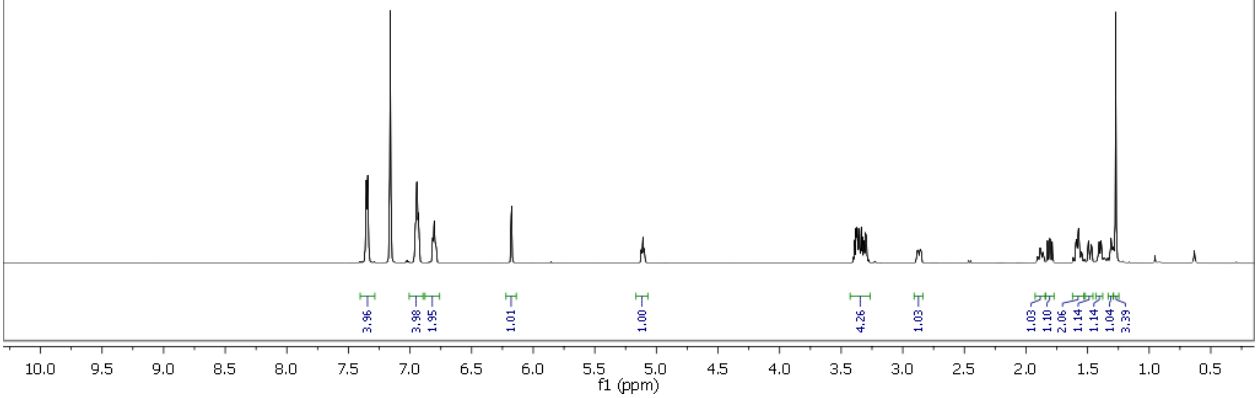
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)

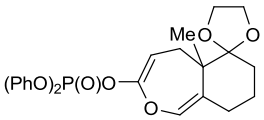




3h

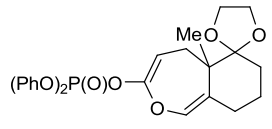
^{1}H NMR spectrum
(C_6D_6, 600 MHz)





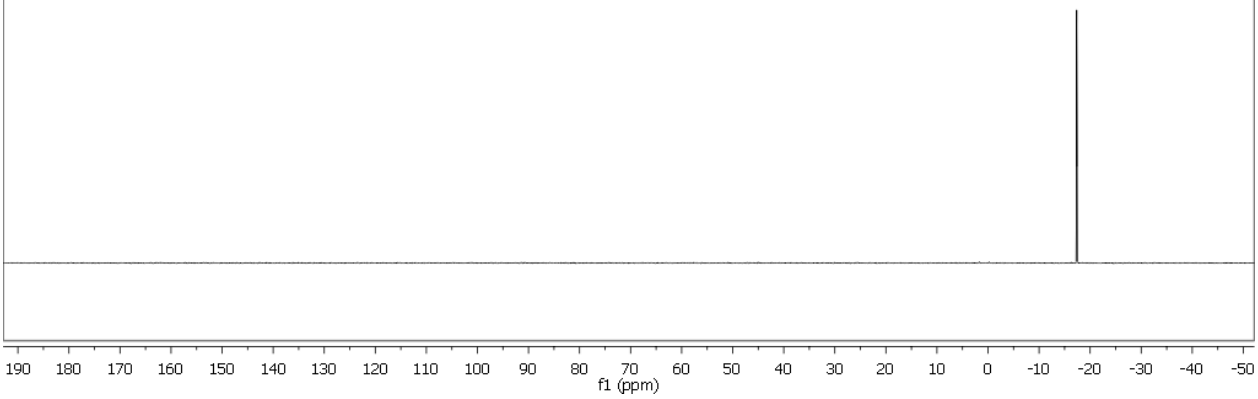
3h

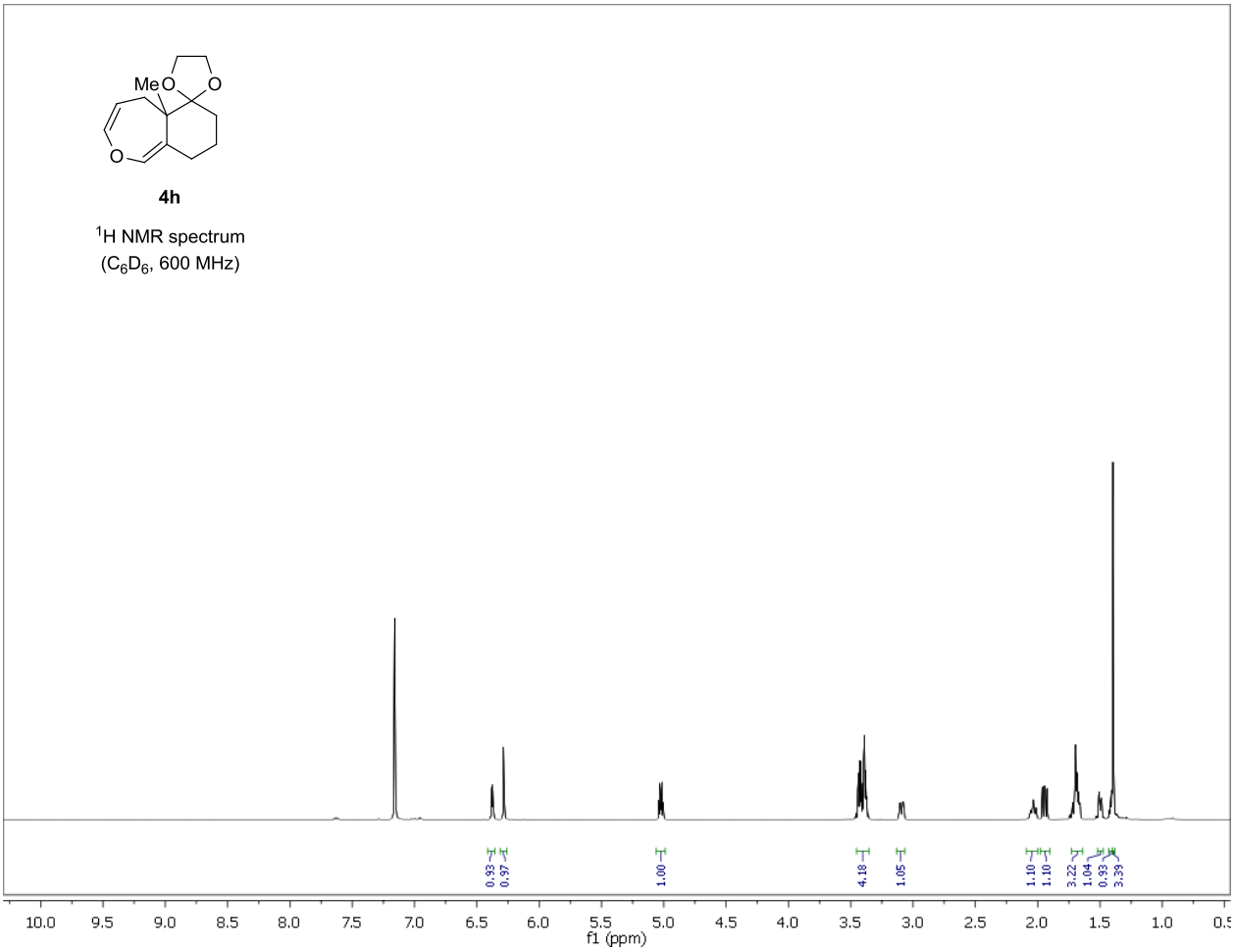
^{13}C NMR spectrum
(C_6D_6, 150 MHz)

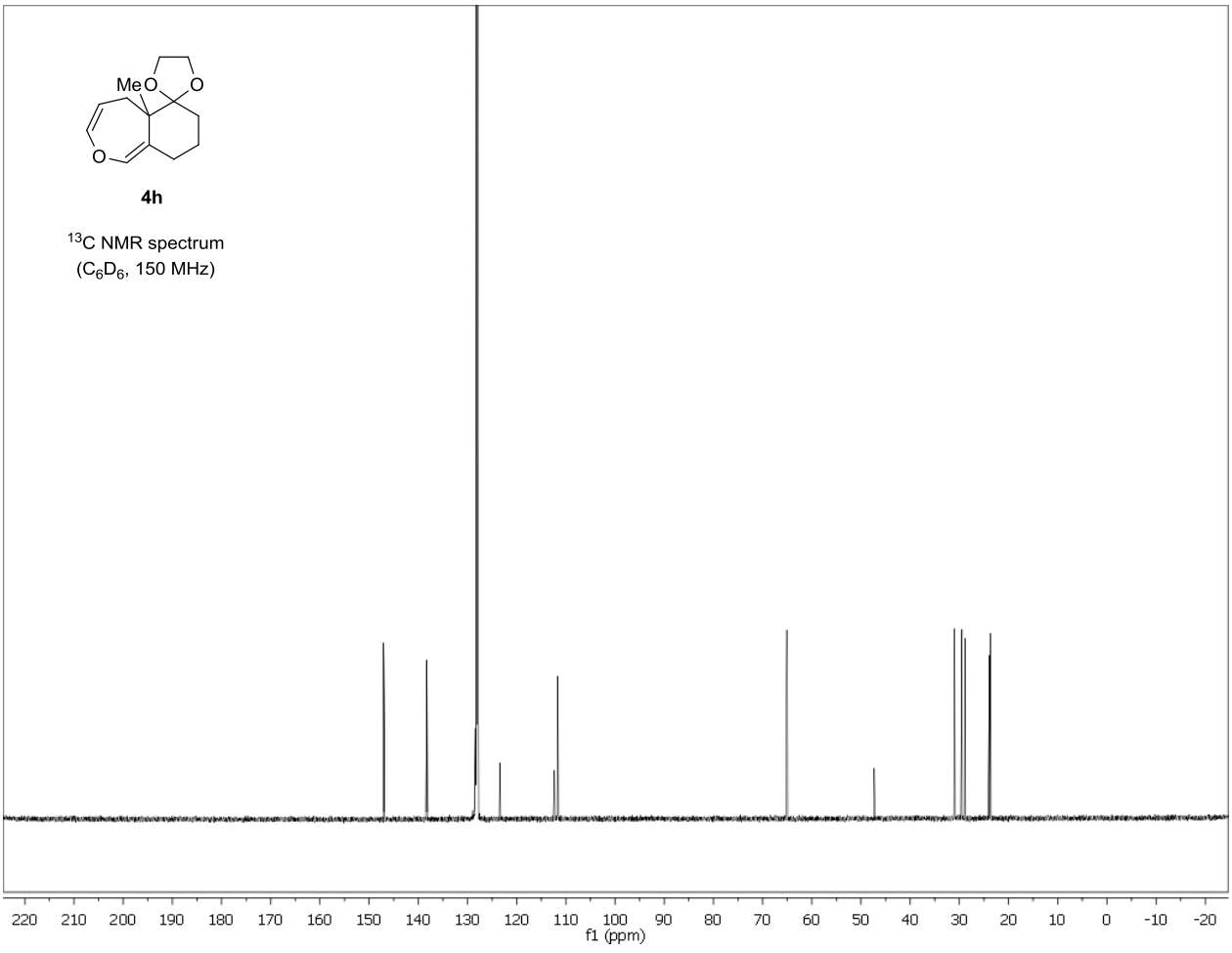


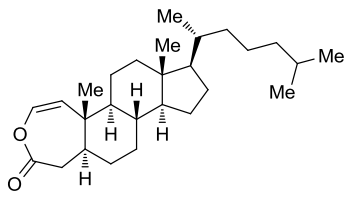
3h

^{31}P NMR spectrum
(C_6D_6, 161 MHz)



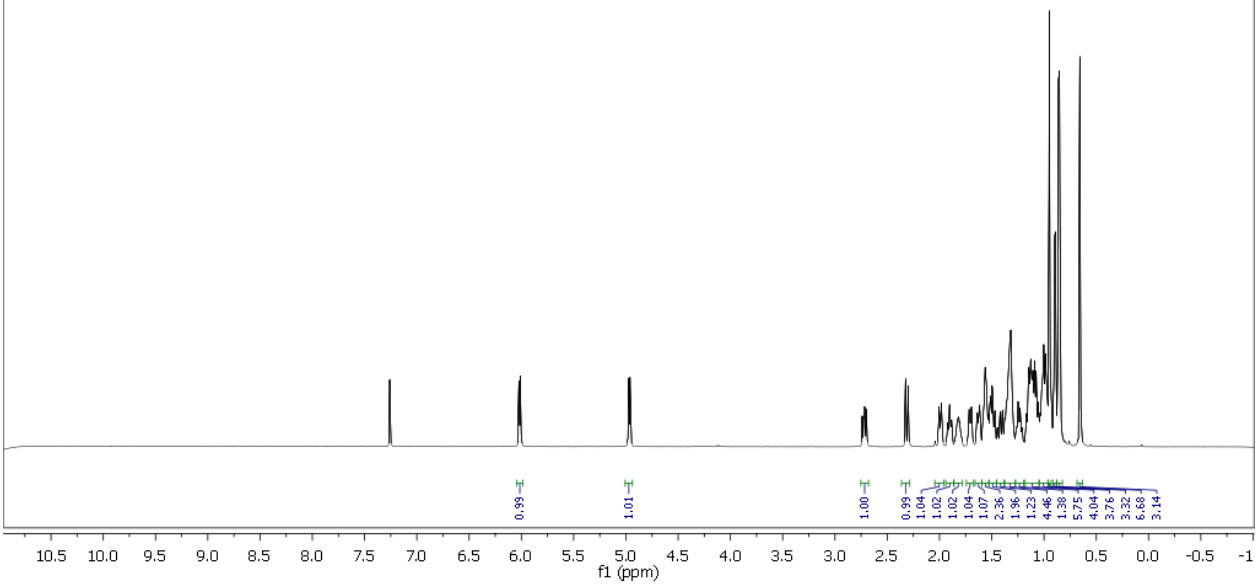

MeO
O
O
4h
1H NMR spectrum
(C6D6, 600 MHz)
0.93
0.97
1.00
4.18
1.05
1.10
1.10
3.22
1.04
0.93
3.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

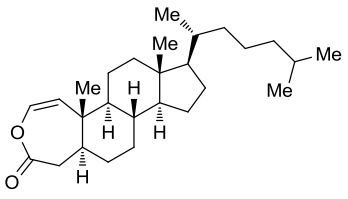

MeO
O
O
4h
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



2i

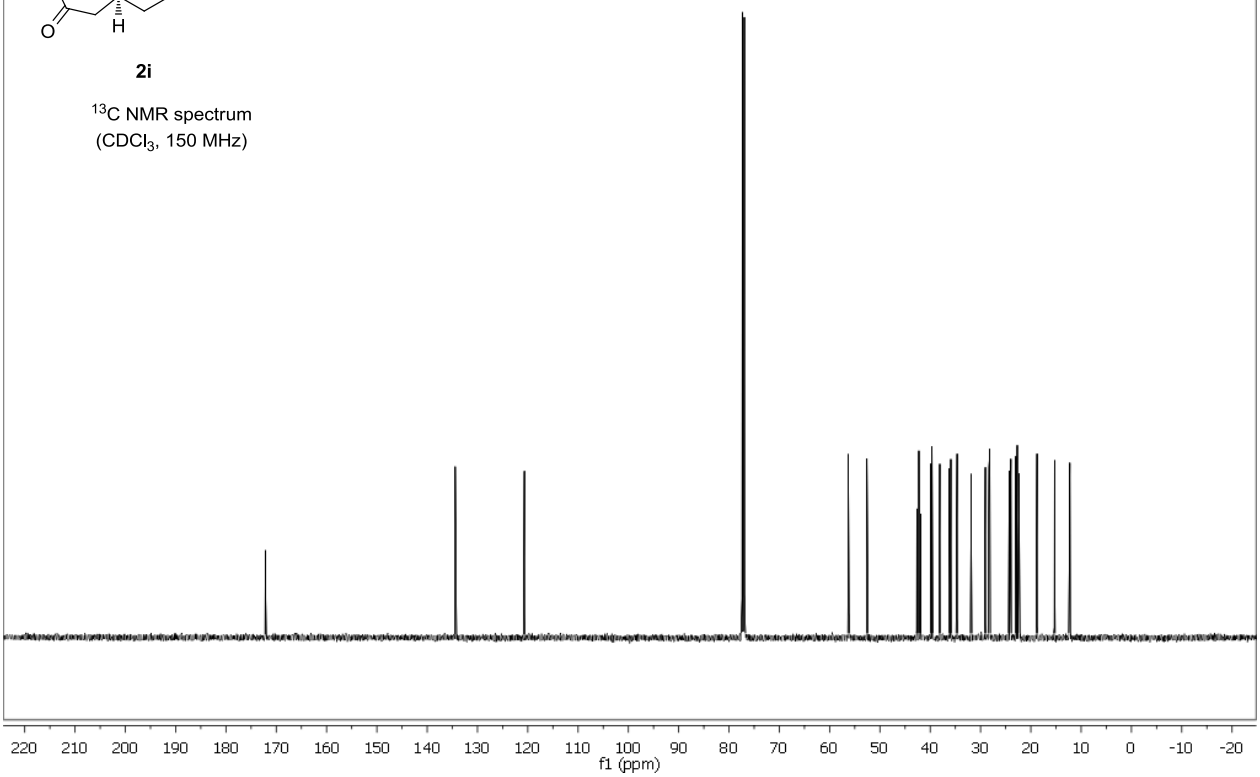
^{1}H NMR spectrum
($CDCl_3$, 600 MHz)

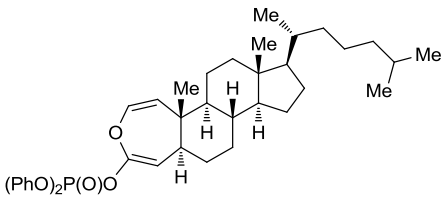




2i

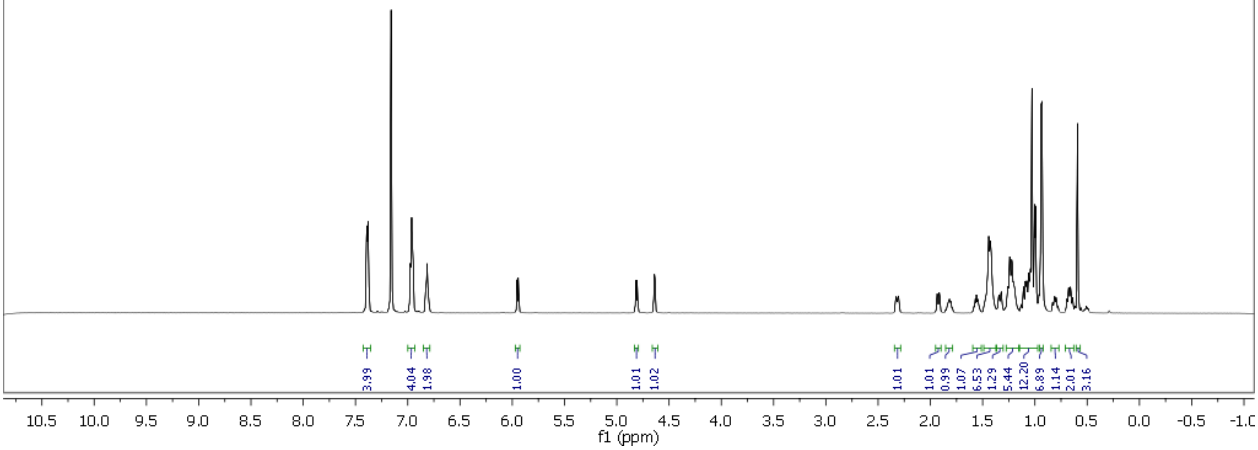
^{13}C NMR spectrum
($CDCl_3$, 150 MHz)

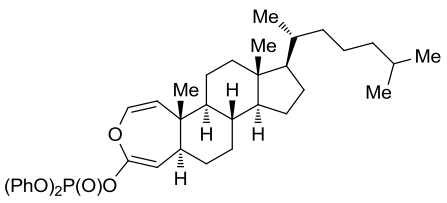




3i

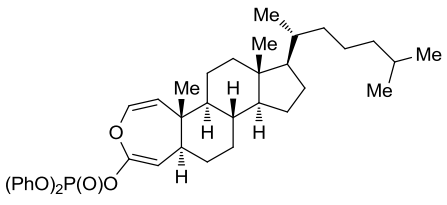
^{1}H NMR spectrum
(C_6D_6, 600 MHz)





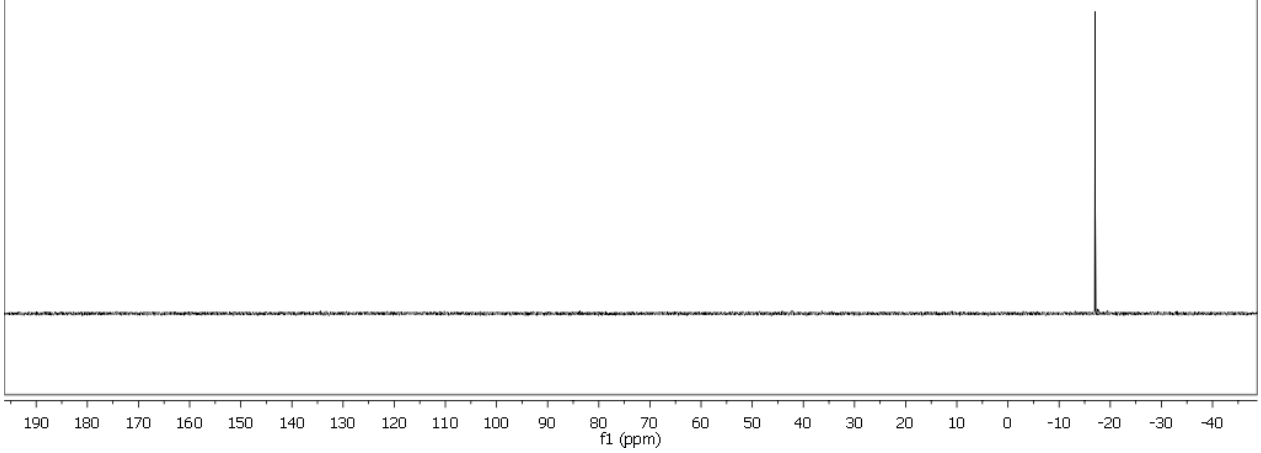
3i

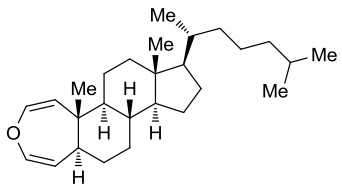
^{13}C NMR spectrum
(C_6D_6, 150 MHz)



3i

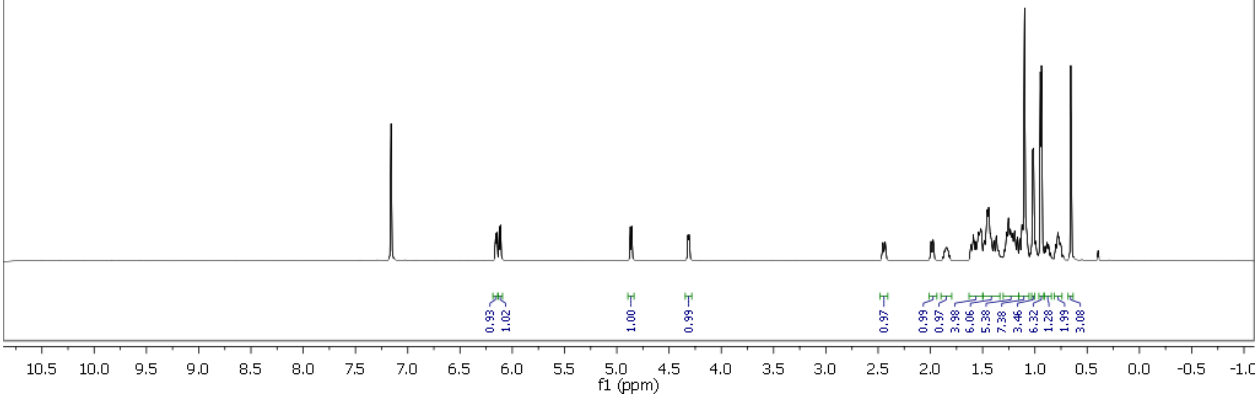
^{31}P NMR spectrum
(C_6D_6, 161 MHz)

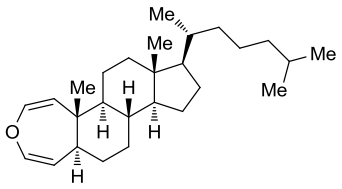




4i

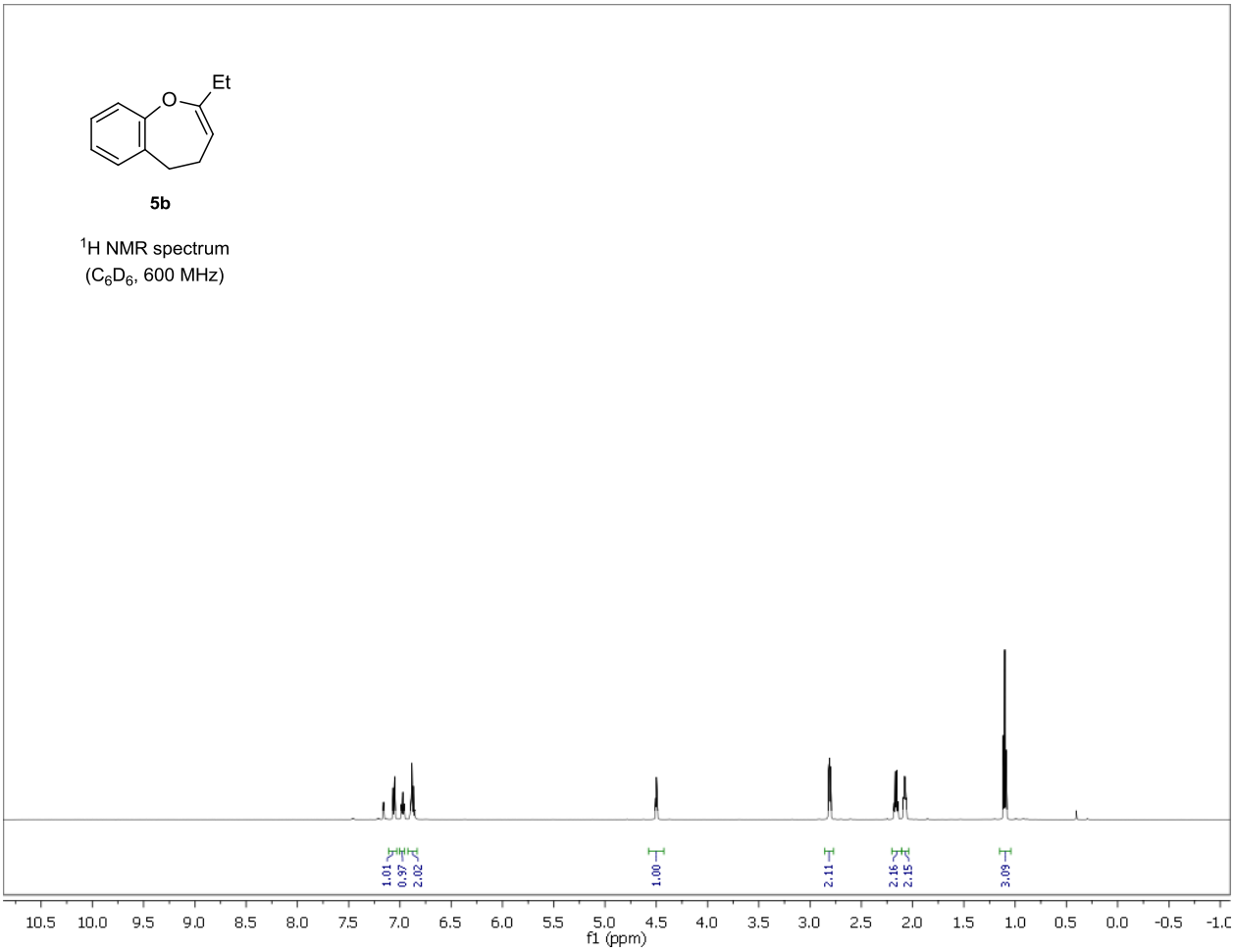
^{1}H NMR spectrum
(C_6D_6, 600 MHz)

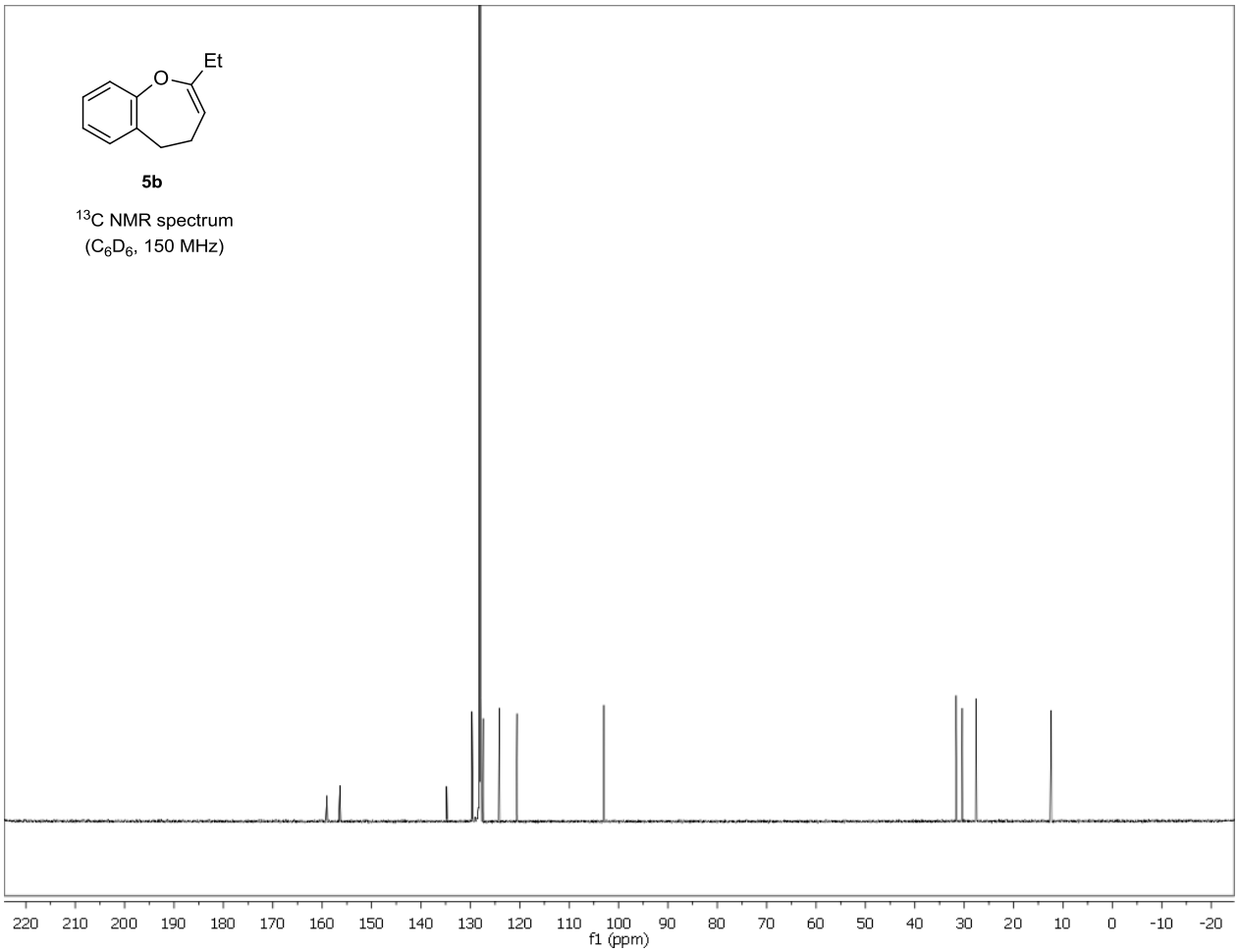


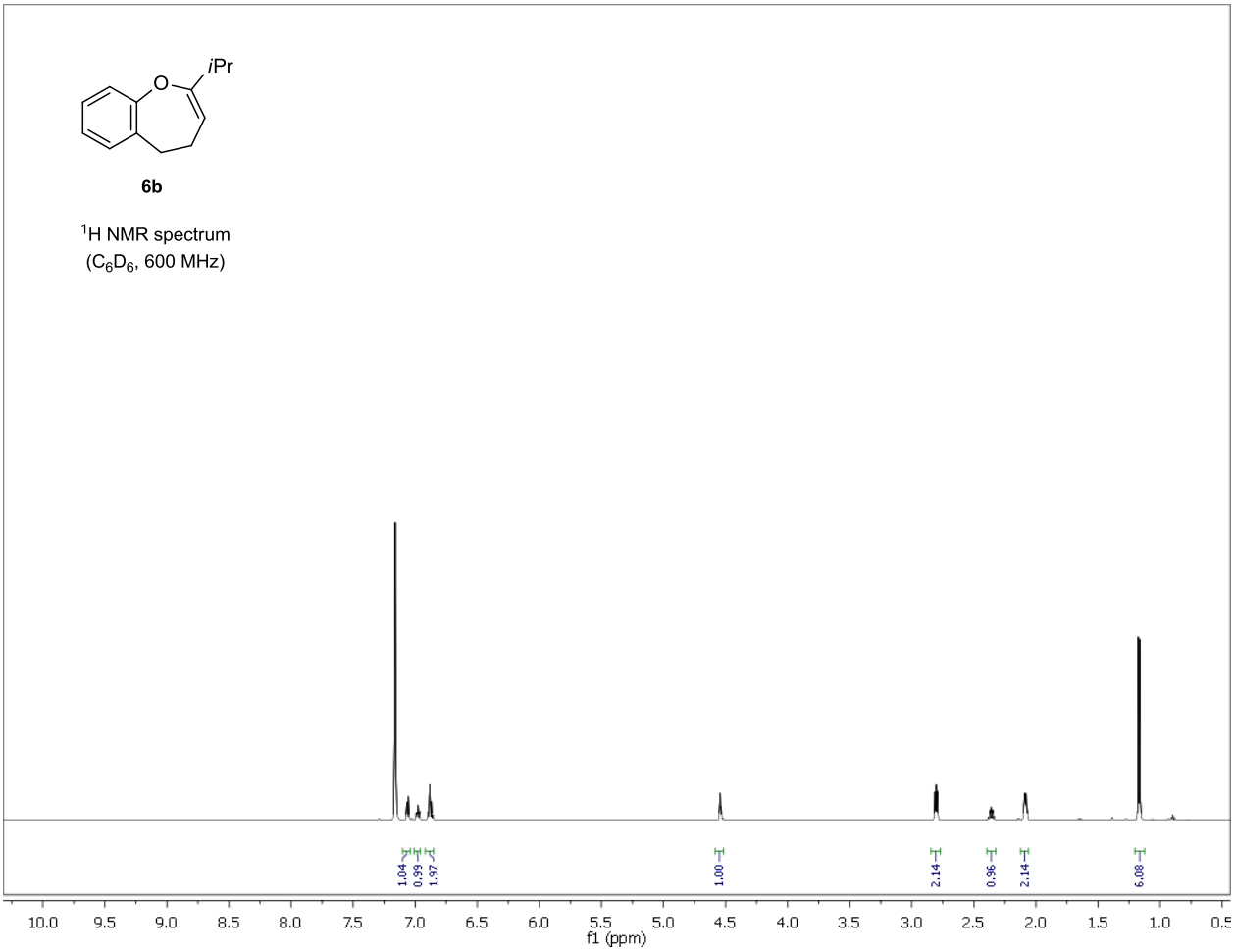


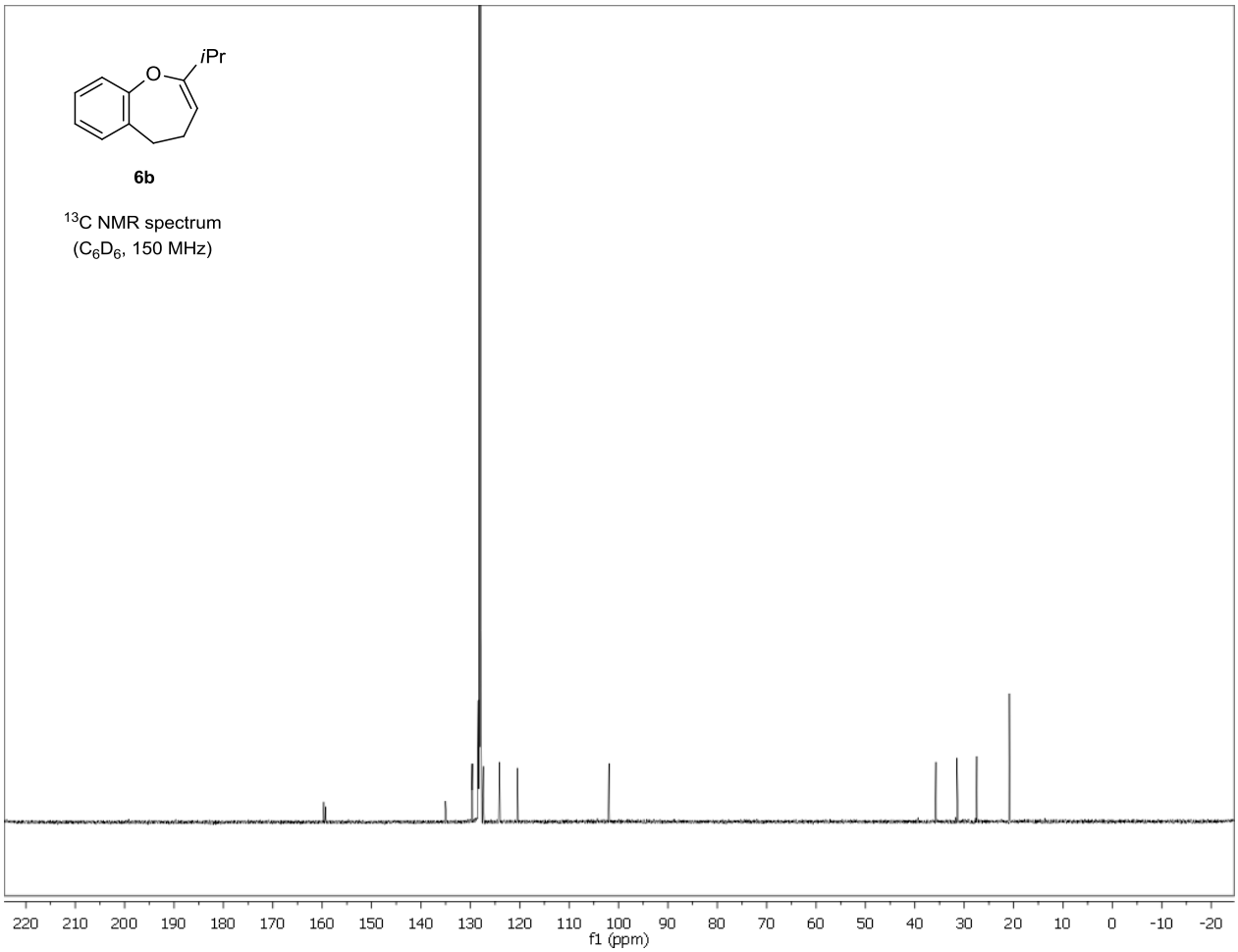
4i

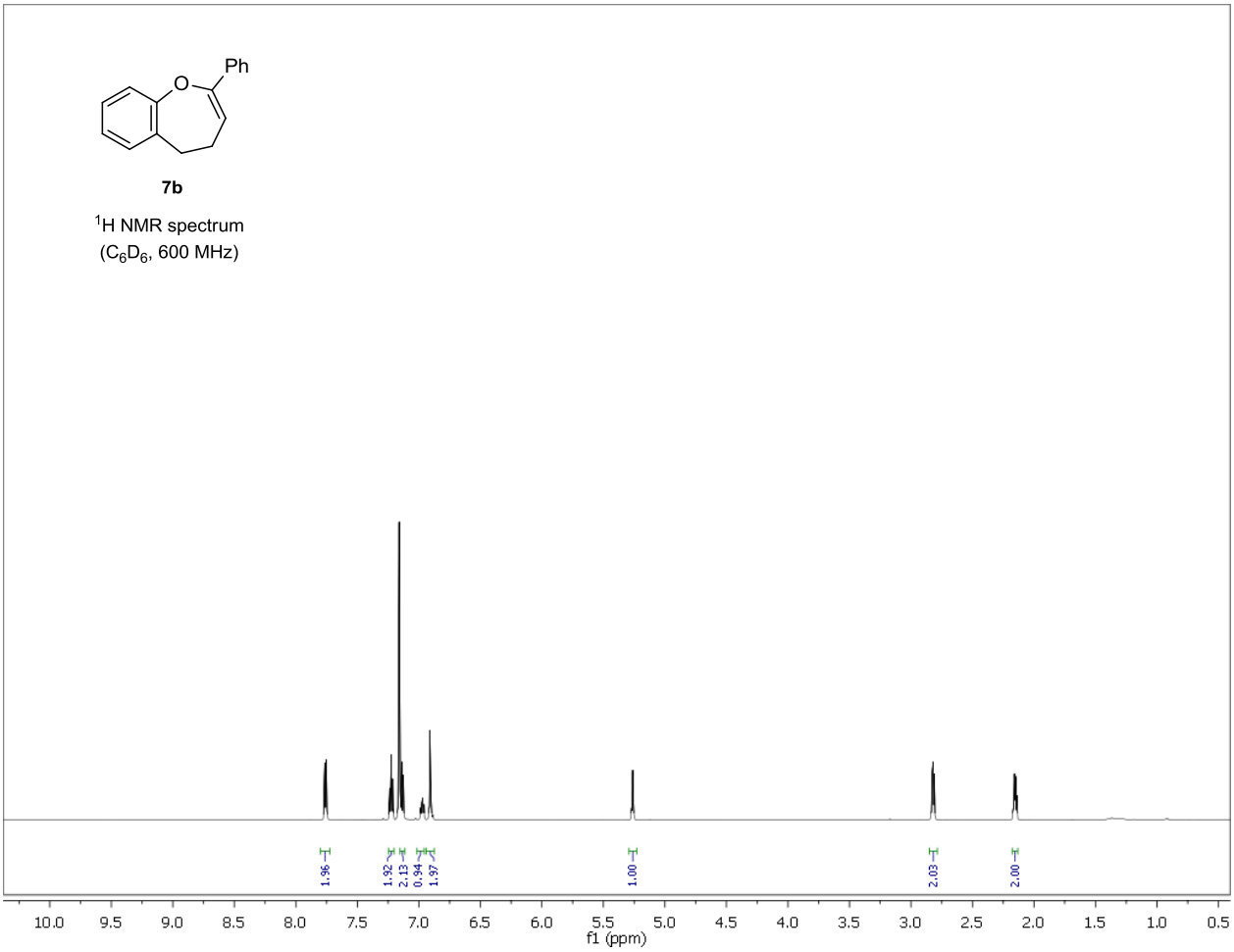
^{13}C NMR spectrum
(C_6D_6, 150 MHz)

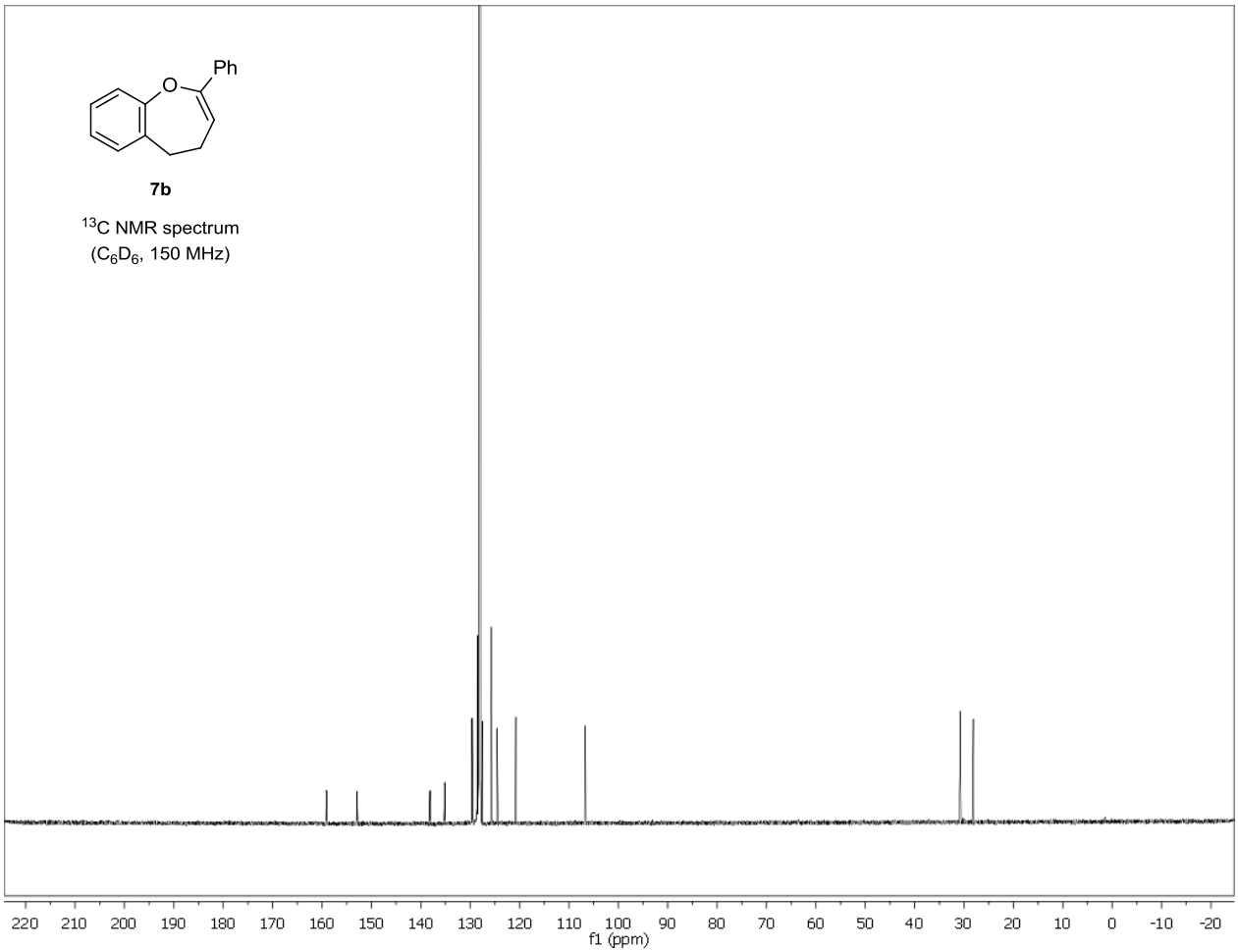

Et
O
5b
1H NMR spectrum
(C6D6, 600 MHz)
1.01
0.97
2.02
1.00
2.11
2.16
2.15
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

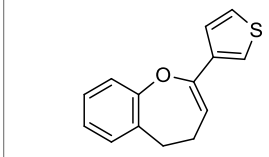

Et
O
5b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


iPr
O
6b
1H NMR spectrum
(C6D6, 600 MHz)
1.04
0.99
1.97
1.00
2.14
0.96
2.14
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


iPr
O
6b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

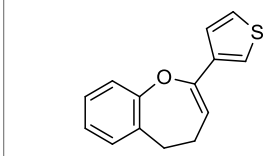

Ph
O
7b
1H NMR spectrum
(C6D6, 600 MHz)
1.96
1.92
2.13
0.94
1.97
1.00
2.03
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
O
7b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



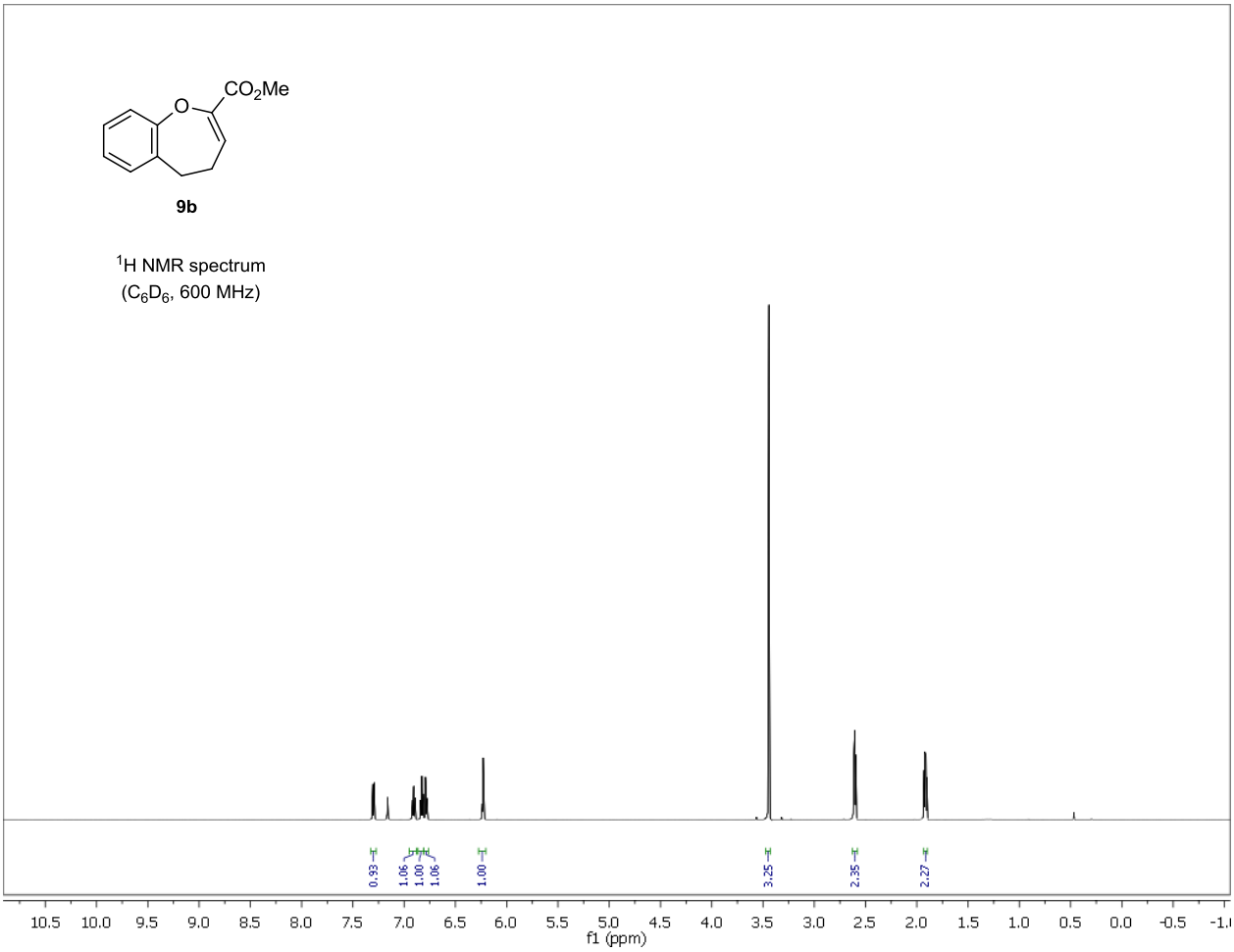
8b

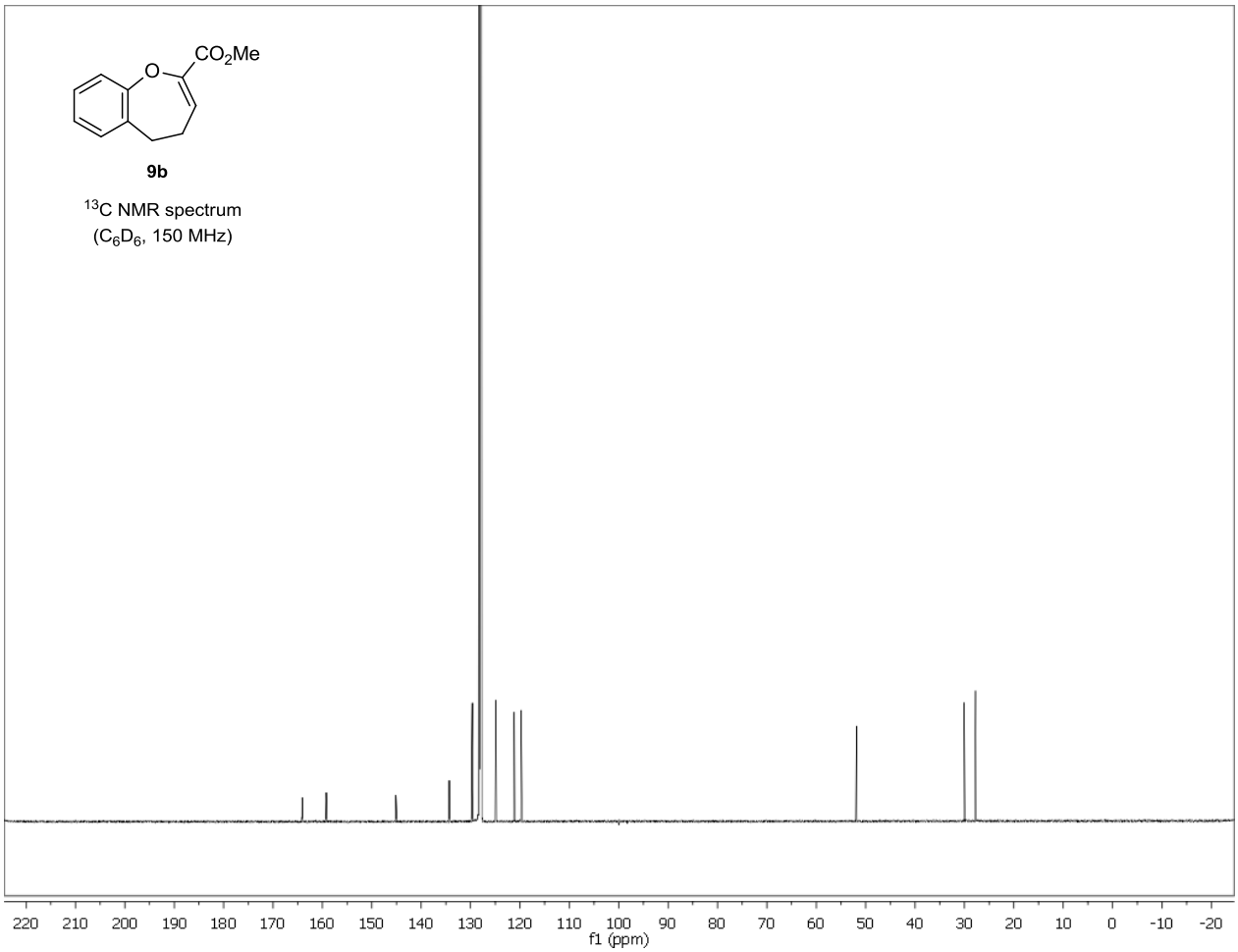
^{1}H NMR spectrum
(C_6D_6, 600 MHz)

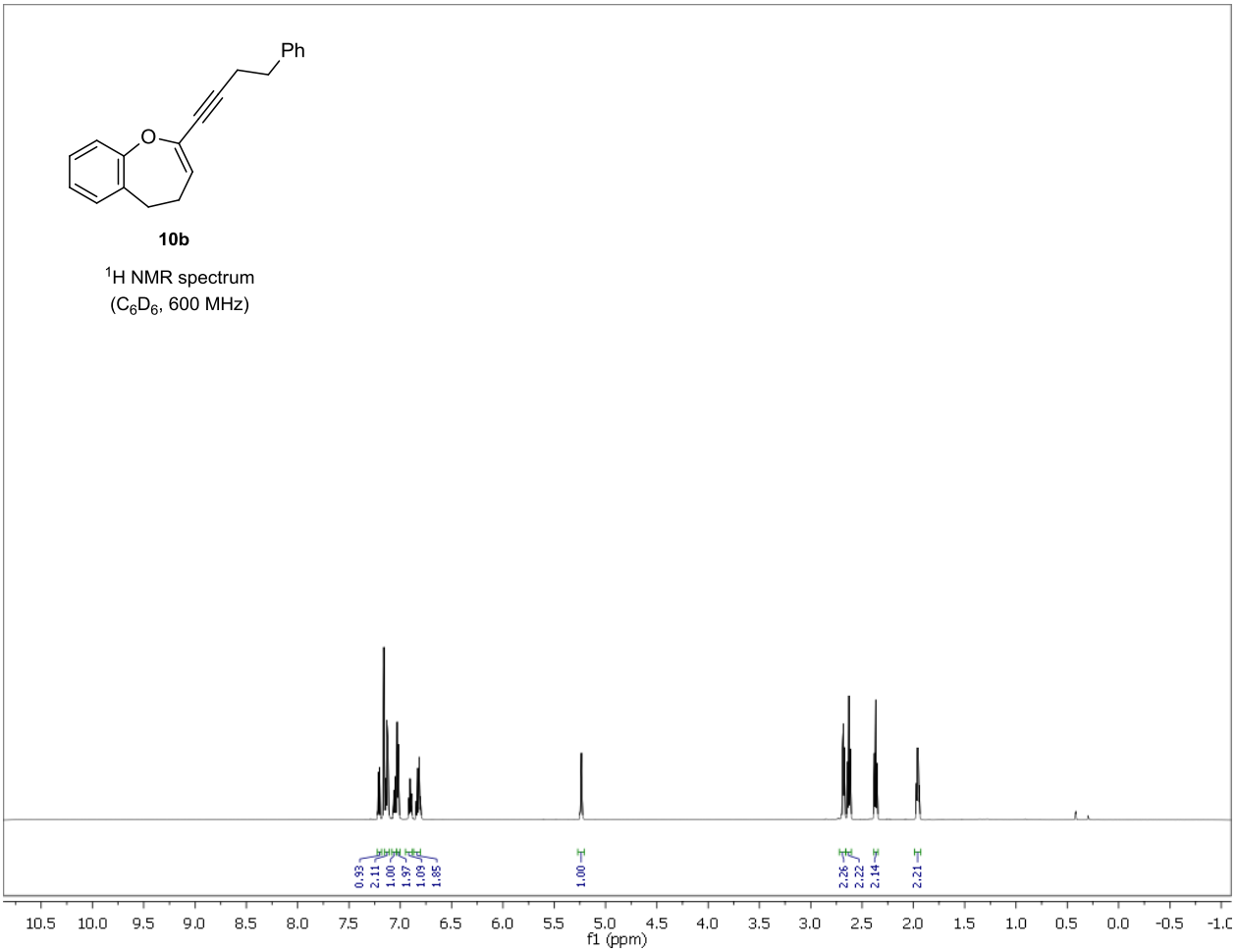


8b

^{13}C NMR spectrum
(C_6D_6, 150 MHz)

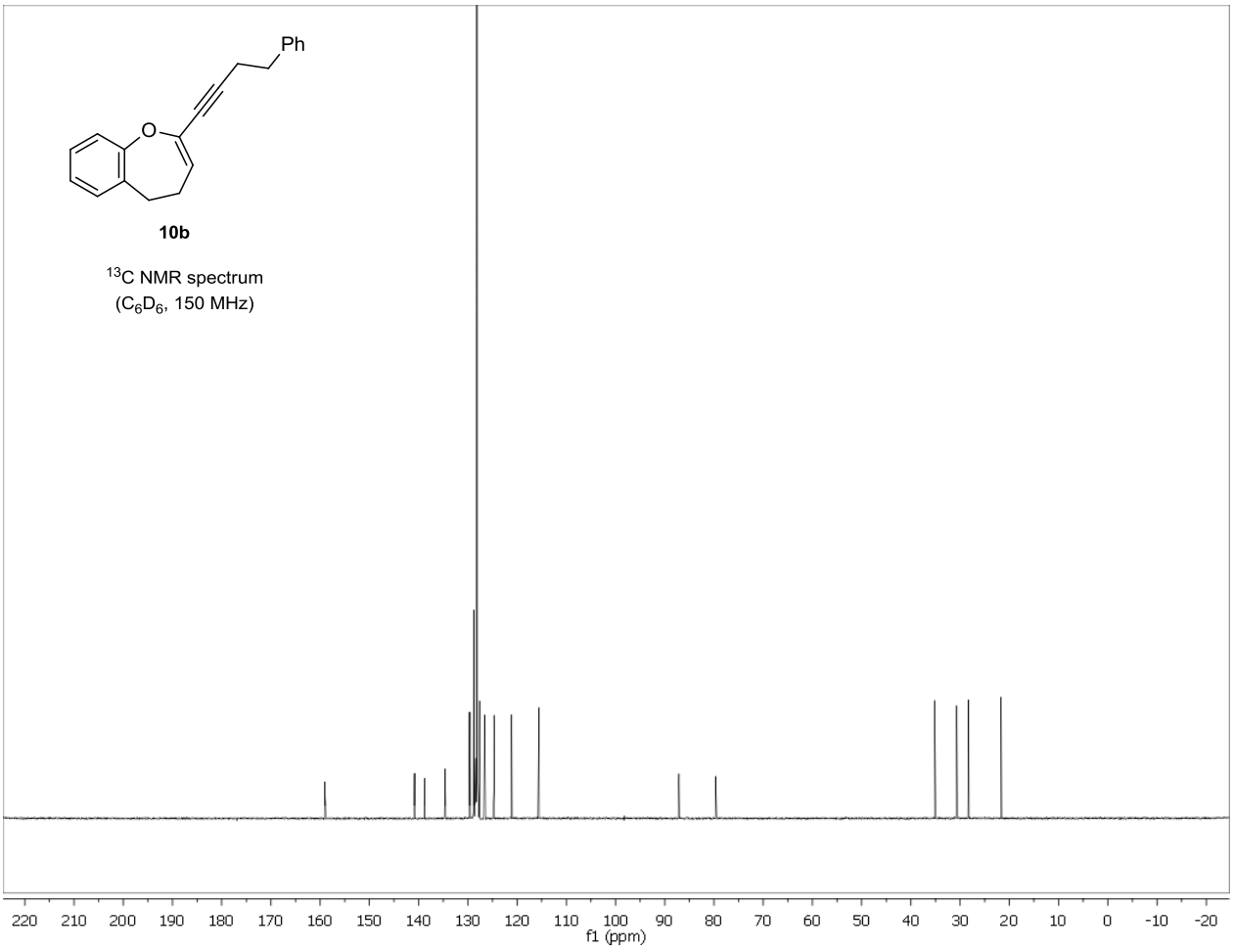

CO2Me
O
9b
1H NMR spectrum
(C6D6, 600 MHz)
0.93
1.06
1.00
1.06
1.00
3.25
2.35
2.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


CO2Me
O
9b
13C NMR spectrum
(C6D6, 150 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



10b

^{1}H NMR spectrum
(C_6D_6, 600 MHz)



10b

^{13}C NMR spectrum
(C_6D_6, 150 MHz)

IV. References

(1) Magnus, P.; Lacour, J.; Evans, P. A.; Rigollier, P.; Tobler, H. *J. Am. Chem. Soc.* **1998**, *120*, 12486.

(2) Nagano, H.; Yamada, K.; Hazeki, N.; Mori, Y.; Hirano, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2421.

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