Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Cu-Catalyzed Hydrophosphorylative Ring Opening of Propargyl Epoxides: Highly Selective Access to 4-Phosphoryl 2,3-Allenols

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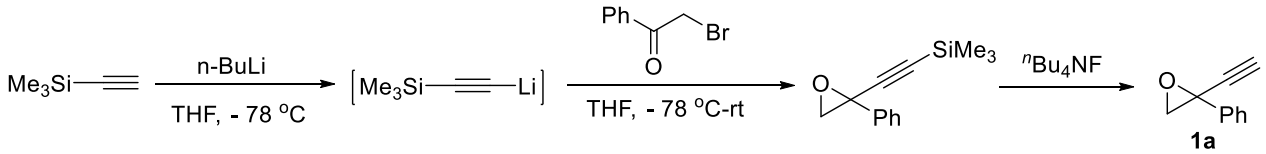
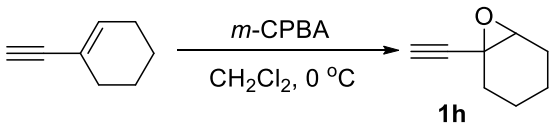
General Information. Unless otherwise specified, all reactions were performed under dry N_2 atmosphere. Anhydrous solvents were distilled prior to use: THF was distilled from sodium using benzophenone as the indicator; DCM and DMF were distilled from CaH_2; MeOH was commercially available and used after degass. Propargyl epoxides **1** were prepared following known procedures. [1] Typical procedure was given below. H-phosphonates **2a-2d** diphenylphosphine oxide **2e** were purchased from commercial sources and used as received. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruke-Advance 400 Ultra NMR spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. HRMS analysis of the products (EI-TOF) was performed at the Analytical Center of the Department of Chemistry of Zhejiang University, China.

Typical procedure for the preparation of the starting materials 1[1]



n-Butyl lithium (4 mL, 2.5 M in hexane) was added to a solution of ethynyltrimethylsilane (1.08 g, 11 mmol) in THF (15 mL) at –78 ^{o}C under N_2 atmophere. The reaction mixture was allowed to stir at this temperature for 30 min. 2-bromo-1-phenylethan-1-one (1.99 g, 10 mmol) in THF (10 mL) was then slowly added at –78 ^{o}C. The reaction mixture was naturally warmed to room temperature and kept stirring overnight. After quenched by aq. $NaHCO_3$ solution, extracted with EtOAc and concentrated to dryness, the residue was dissolved in THF and cooled to 0 ^{o}C. A solution of tetrabutylammonium fluoride (ca. 10 mmol, 85% purity containing water) in THF was dropwise added. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with water and extracted with EtOAc. The organic layers were dried with $MgSO_4$, and concentrated under vacumm. Pure 2-ethynyl-2-phenyloxirane **1a** (1.04 g, yield 72%) was obtained after column chromategraphy on silica gel (petroleum ether–ethyl acetate 60:1 v/v). Propargyl epoxides **1b-1g**, **1k** and **1l** were prepared from the corresponding alkynes and bromides with a similar procedure.

Synthetic procedure for the propargyl acetate 1q[2]



To a solution of 1-ethynylcyclohex-1-ene (2.120 g, 20 mmol) in CH_2Cl_2 (60 mL) at 0°C was

(1) J. Y. Kang, B. T. Connell, *J. Org. Chem.* **2011**, *76*, 2379; Gronnier, C.; Kramer, S.; Odabachian, Y. Gagosz, F. *J. Am. Chem. Soc.* **2012**, *134*, 828; Hattori, G.; Yoshida, A.; Miyake, Y.; Nishibayashi, Y. *J. Org. Chem.* **2009**, *74*, 7603.

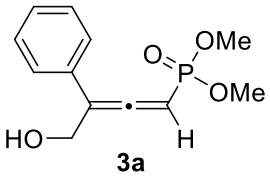
(2)Yoshida, M.; Hayashi, M.; Shishido, K. *Org. Lett.* **2007**, *9*, 1643.

added *m*-CPBA (85%, 22 mmol). The mixture was stirred at 0°C. The reaction was monitored by TLC until completion. The reaction mixture was filtered and the solution was washed with aq K_2CO_3 solution, brine, dried over Na_2SO_4 and concentrated. Pure product **1h** (976 mg, 40%) was obtained by distillation under a reduced pressure. Substrates **1i** and **1j** were prepared via the epoxidation of the corresponding olefins with a similar procedure.

General procedure for the Cu-catalyzed preparation of 4-phosphoryl 2,3-allenols via reactions of propargyl epoxides with P(O)H compounds

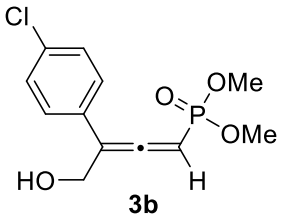
An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with CuI (2.9 mg, 5 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 1.0 mL of MeOH was injected, followed by the injection of $^{i}Pr_2NEt$ (5 uL) upon stirring. The mixture was cooled to 0 ^{o}C. Then **1** (0.36 mmol) and **2** (0.3 mmol) dissolved in 1.0 mL of MeOH was injected. The reaction was kept stirring at the same temperature. After the reaction was complete (monitored by TLC), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate) to afford the product **3.**

Characterization data of the products



3a

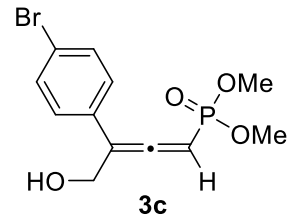
*dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3a**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 69.9 mg, 92%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.33 (m, 4H), 7.29−7.26 (m, 1H), 5.76 (s, 1H), 4.61 (s, 2H), 3.93 (br, 1H), 3.76 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.0, 131.9 (d, $J_{P\text{-}C}$ = 8.4 Hz), 128.8, 128.1 (d, $J_{P\text{-}C}$ = 1.6 Hz), 126.6 (d, $J_{P\text{-}C}$ = 2.7 Hz), 108.8 (d, $J_{P\text{-}C}$ = 16.5 Hz), 83.1 (d, $J_{P\text{-}C}$ = 195.9 Hz), 60.8 (d, $J_{P\text{-}C}$ = 6.5 Hz), 53.17 (d, $J_{P\text{-}C}$ = 6.8 Hz), 53.07 (d, $J_{P\text{-}C}$ = 5.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.5. HRMS (EI-TOF) (*m/z*): calcd for $C_{12}H_{15}O_4P$ [M^+] 254.0708 found 254.0710.



3b

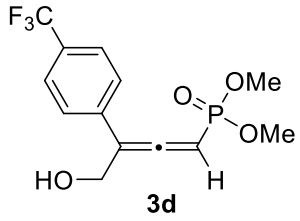
*dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3b**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 85.5 mg, 99%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.27 (m, 4H), 5.74 (s, 1H), 4.53 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 2H), 3.75 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8, 133.6 (d, $J_{P\text{-}C}$ = 1.3 Hz), 130.4 (d, $J_{P\text{-}C}$ = 8.0 Hz), 128.8, 127.7 (d, $J_{P\text{-}C}$ = 2.7 Hz), 107.6 (d, $J_{P\text{-}C}$ = 17.5 Hz), 82.9 (d, $J_{P\text{-}C}$ = 195.4 Hz), 60.5 (d, $J_{P\text{-}C}$ = 6.5 Hz), 53.06 (d, $J_{P\text{-}C}$ = 5.4 Hz), 52.95 (d,

$J_{P\text{-}C}$ = 6.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.3. HRMS (EI-TOF) (*m/z*): calcd for $C_{12}H_{14}ClO_4P$ [M^+] 288.0318 found 288.0320.



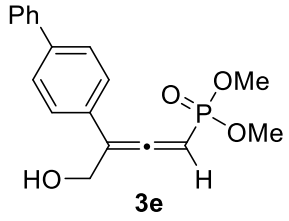
3c

*dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3c**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 93.2 mg, 94%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.74 (s, 1H), 4.54 (dd, J_1 = 5.2 Hz, J_1 = 2.0 Hz, 2H), 3.76 (dd, J_1 = 7.2 Hz, J_1 = 2.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.9, 131.8 (d, $J_{P\text{-}C}$ = 1.5 Hz), 130.9 (d, $J_{P\text{-}C}$ = 8.3 Hz), 128.1 (d, $J_{P\text{-}C}$ = 2.5 Hz), 121.9 (d, $J_{P\text{-}C}$ = 1.6 Hz), 107.8 (d, $J_{P\text{-}C}$ = 17.0 Hz), 83.2 (d, $J_{P\text{-}C}$ = 195.5 Hz), 60.7 (d, $J_{P\text{-}C}$ = 6.6 Hz), 53.1 (d, $J_{P\text{-}C}$ = 5.4 Hz), 53.0 (d, $J_{P\text{-}C}$ = 6.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.1. HRMS (EI-TOF) (*m/z*): calcd for $C_{12}H_{14}BrO_4P$ [M^+] 331.9813 found 331.9816.



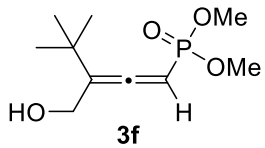
3d

*dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (**3d**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 80.7 mg, 84%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 5.79 (s, 1H), 4.59 (br, 2H), 3.77 (d, J = 7.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1, 135.9 (d, $J_{P\text{-}C}$ = 7.9 Hz), 129.8 (dd, J_1 = 64.9 Hz, J_2 = 31.5 Hz), 126.8 (d, $J_{P\text{-}C}$ = 2.1 Hz), 125.6 (d, $J_{P\text{-}C}$ = 2.9 Hz), 123.9 (q, $J_{F\text{-}C}$ = 270.1 Hz), 107.7 (d, $J_{P\text{-}C}$ = 16.9 Hz), 83.3 (d, $J_{P\text{-}C}$ = 195.7 Hz), 60.6 (d, $J_{P\text{-}C}$ = 5.9 Hz), 53.16 (d, $J_{P\text{-}C}$ = 6.7 Hz), 53.06 (d, $J_{P\text{-}C}$ = 5.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.9. HRMS (EI-TOF) (*m/z*): calcd for $C_{13}H_{14}F_3O_4P$ [M^+] 322.0582 found 322.0578.



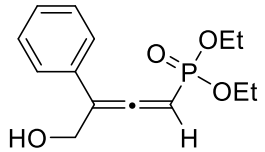
3e

*dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3e**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 90.0 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.55 (m, 4H), 7.47-7.40 (m, 4H), 7.36-7.32 (m, 1H), 5.79 (s, 1H), 4.63 (br, 2H), 3.77 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1, 140.7, 140.3, 130.7 (d, $J_{P\text{-}C}$ = 7.7 Hz), 128.8, 127.45, 127.37, 126.9 (d, $J_{P\text{-}C}$ = 2.0 Hz), 126.9, 108.4 (d, $J_{P\text{-}C}$ = 16.3 Hz), 83.1 (d, $J_{P\text{-}C}$ = 197.1 Hz), 60.7 (d, $J_{P\text{-}C}$ = 6.6 Hz), 53.1 (d, $J_{P\text{-}C}$ = 5.4 Hz), 53.0 (d, $J_{P\text{-}C}$ = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.3. HRMS (EI-TOF) (*m/z*): calcd for $C_{18}H_{19}O_4P$ [M^+] 330.1021 found 330.1021.



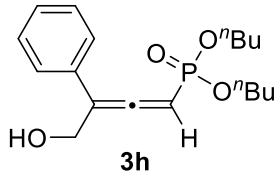
3f

*dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3f**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 66.9 mg, 95%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.35 (t, J = 2.8 Hz, 1H), 4.19-4.15 (m, 2H), 4.00 (br, 1H), 3.70 (d, J = 7.2 Hz, 6H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.8, 116.8 (d, $J_{P\text{-}C}$ = 16.8 Hz), 81.4 (d, $J_{P\text{-}C}$ = 197.8 Hz), 59.0 (d, $J_{P\text{-}C}$ = 6.6 Hz), 52.8 (d, $J_{P\text{-}C}$ = 5.9 Hz), 52.6 (d, $J_{P\text{-}C}$ = 6.0 Hz), 32.8 (d, $J_{P\text{-}C}$ = 4.5 Hz), 29.2 (d, $J_{P\text{-}C}$ = 2.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.8. HRMS (EI-TOF) (*m/z*): calcd for $C_{10}H_{19}O_4P$ [M^+] 234.1021 found 234.1025.



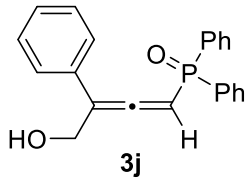
3g

*diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3g**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 75.2 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.32 (m, 4H), 7.28−7.25 (m, 1H), 5.78 (s, 1H), 4.59 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 2H), 4.16-4.08 (m, 4H), 3.69 (br, 1H), 1.33-1.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.4, 132.0 (d, $J_{P\text{-}C}$ = 7.5 Hz), 128.7 (d, $J_{P\text{-}C}$ = 1.6 Hz), 127.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 126.5 (d, $J_{P\text{-}C}$ = 2.7 Hz), 108.6 (d, $J_{P\text{-}C}$ = 16.6 Hz), 84.3 (d, $J_{P\text{-}C}$ = 195.2 Hz), 62.66 (d, $J_{P\text{-}C}$ = 5.6 Hz), 62.59 (d, $J_{P\text{-}C}$ = 5.7 Hz), 60.9 (d, $J_{P\text{-}C}$ = 6.6 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.6. HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{19}O_4P$ [M^+] 282.1021 found 282.1020.



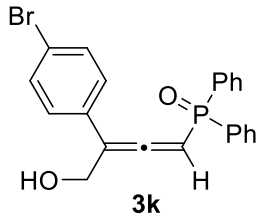
3h

*dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3h**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 67.0 mg, 66%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, $J_{P\text{-}C}$ = 8.0 Hz, 2H), 7.36−7.32 (m, 2H), 7.28−7.26 (m, 1H), 5.77 (s, 1H), 4.58 (dd, J_1 = 5.6 Hz, J_2 = 2.4 Hz, 2H), 4.07-4.02 (m, 4H), 3.63 (br, 1H), 1.67-1.58 (m, 4H), 1.40-1.33 (m, 4H), 0.89 (td, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.46 (d, $J_{P\text{-}C}$ = 1.5 Hz), 132.1 (d, $J_{P\text{-}C}$ = 7.4 Hz), 128.7 (d, $J_{P\text{-}C}$ = 1.5 Hz), 127.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 126.5 (d, $J_{P\text{-}C}$ = 1.8 Hz), 108.6 (d, $J_{P\text{-}C}$ = 16.7 Hz), 84.2 (d, $J_{P\text{-}C}$ = 195.1 Hz), 66.4 (d, $J_{P\text{-}C}$ = 5.4 Hz), 66.3 (d, $J_{P\text{-}C}$ = 7.1 Hz), 60.9 (d, $J_{P\text{-}C}$ = 5.5 Hz), 32.3 (d, $J_{P\text{-}C}$ = 6.2 Hz), 18.6, 13.5. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.7. HRMS (EI-TOF) (*m/z*): calcd for $C_{18}H_{27}O_4P$ [M^+] 338.1647 found 338.1650.



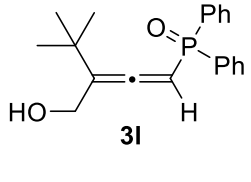
3j

*(4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**3j**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield (0.6 mmol scale): 184.8 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.72 (m, 4H), 7.52-7.47 (m, 2H), 7.43-7.39 (m, 4H), 7.28-7.20 (m, 5H), 6.26 (s, 1H), 4.41 (dd, J_1 = 4.8 Hz, J_2 = 2.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.1 (d, $J_{P\text{-}C}$ = 2.4 Hz), 132.36 (d, $J_{P\text{-}C}$ = 72.7 Hz), 132.11 (d, $J_{P\text{-}C}$ = 2.4 Hz), 132.08 (d, $J_{P\text{-}C}$ = 84.6 Hz), 128.60, 128.57 (d, $J_{P\text{-}C}$ = 2.1 Hz), 128.4 (d, J = 2.3 Hz), 127.8, 126.4 (d, J = 2.7 Hz), 109.6 (d, $J_{P\text{-}C}$ = 13.9 Hz), 89.7 (d, $J_{P\text{-}C}$ = 101.4 Hz), 60.9 (d, $J_{P\text{-}C}$ = 5.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.8. HRMS (EI-TOF) (*m/z*): calcd for $C_{22}H_{19}O_2P$ [M^+] 346.1123 found 346.1124.



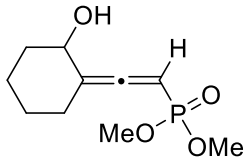
3k

*(3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (**3k**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield (0.6 mmol scale): 223.8 mg, 88%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76-7.68 (m, 4H), 7.54-7.48 (m, 2H), 7.44-7.34 (m, 6H), 7.06 (d, dd, J = 8.0 Hz, 2H), 6.23-6.21 (m, 1H), 4.37 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.33 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.8, 131.4 (d, $J_{P\text{-}C}$ = 7.1 Hz), 131.2 (d, $J_{P\text{-}C}$ = 6.5 Hz), 128.7 (d, $J_{P\text{-}C}$ = 2.2 Hz), 128.6 (d, J = 2.0 Hz), 128.1 (d, J = 0.8 Hz), 121.8, 109.6 (d, $J_{P\text{-}C}$ = 13.9 Hz), 89.8 (d, $J_{P\text{-}C}$ = 99.2 Hz), 60.8 (d, $J_{P\text{-}C}$ = 5.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.2. HRMS (EI-TOF) (*m/z*): calcd for $C_{22}H_{18}O_2PBr$ [M^+] 424.0228 found 424.0230.



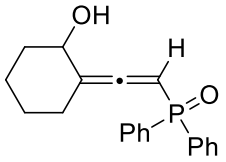
3l

*(3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**3l**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 66.5 mg, 68%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83-7.73 (m, 4H), 7.50-7.39 (m, 6H), 5.96-5.93 (m, 1H), 4.15-4.02 (m, 2H), 3.72 (br, 1H), 0.84 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.6, 133.0 (d, $J_{P\text{-}C}$ = 78.5 Hz), 132.6, 131.8 (d, $J_{P\text{-}C}$ = 1.8 Hz), 131.5, 131.44 (d, $J_{P\text{-}C}$ = 2.0 Hz), 131.36, 128.4 (d, J = 9.4 Hz), 128.3 (d, J = 9.4 Hz), 117.6 (d, $J_{P\text{-}C}$ = 13.7 Hz), 88.5 (d, $J_{P\text{-}C}$ = 104.6 Hz), 59.1 (d, $J_{P\text{-}C}$ = 6.4 Hz), 32.9 (d, $J_{P\text{-}C}$ = 4.6 Hz), 29.0 (d, $J_{P\text{-}C}$ = 2.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.3. HRMS (EI-TOF) (*m/z*): calcd for $C_{20}H_{23}O_2P$ [M^+] 326.1436 found 326.1438.



3m

*dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (**3m**). Obtained as a 56:44 diastereoisomer mixture. The dr value was determined from the ^{31}P NMR analysis.* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/3. Obtained amount and yield: 53.4 mg, 77%]:^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.36-5.29 (m, 1H), 4.17-4.13 (m, 1H), 4.03 (br, 1H), 3.74-3.70 (m, 6H), 2.47-2.41 (m, 1H), 2.08-1.39 (m, 7H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.4, 19.3. HRMS (EI-TOF) (*m/z*): calcd for $C_{10}H_{17}O_4P$ [M^+] 232.0864; found 232.0869.

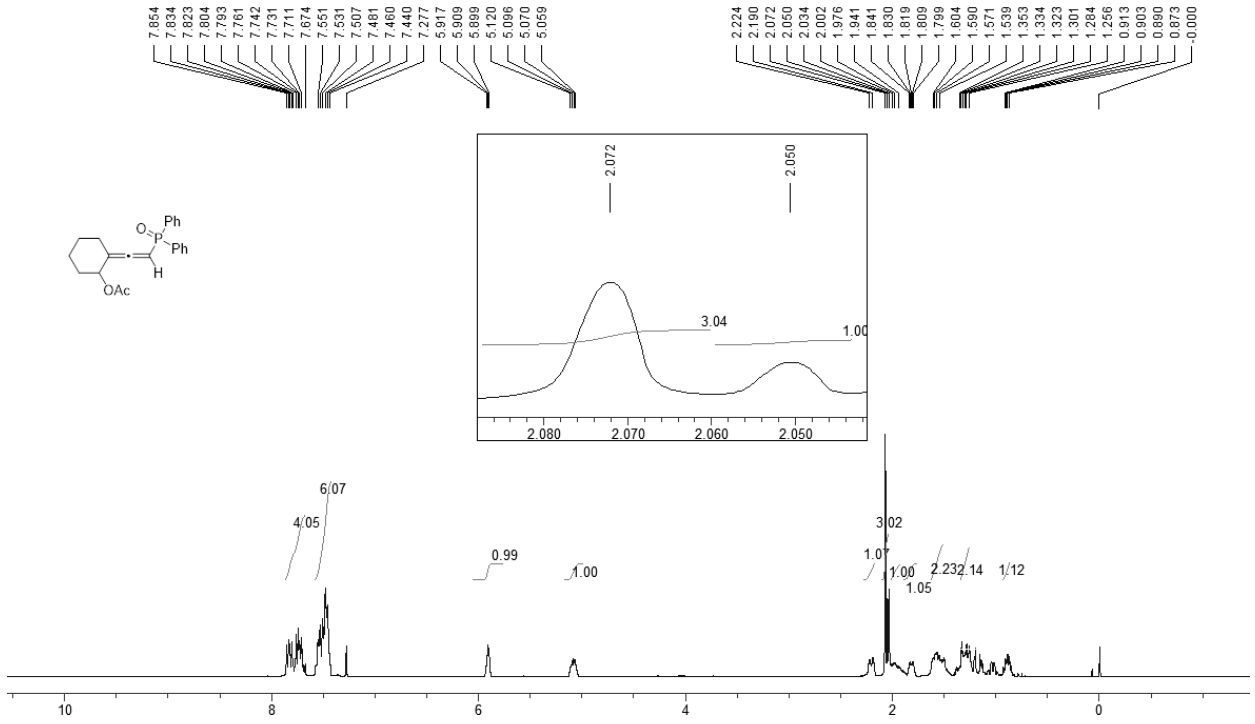


3n

*(2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (**3n**). The compound was obtained as a 75:25 diastereoisomer mixture.* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 70.2 mg, 72%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.78 (m, 2H), 7.62-7.67 (m, 2H), 7.49-7.38 (m, 6H), 5-85-5.83 (m, 1H), 4.02-3.98 (m, 1H), 4.00 (br, 1H), 2.26-2.16 (m, 1H), 1.90-1.78 (m, 2H), 1.58-1.55 (m, 1H), 1.45-1.39 (m, 1H), 1.30-1.06 (m, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.2. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.6, 206.1, 132.8, 132.7 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 128.3 (d, $J_{P\text{-}C}$ = 8.7 Hz), 128.2 (d, $J_{P\text{-}C}$ = 8.8 Hz), 109.5 (d, $J_{P\text{-}C}$ = 12.9 Hz), 109.3 (d, $J_{P\text{-}C}$ = 13.8 Hz), 87.0 (d, $J_{P\text{-}C}$ = 105.8 Hz), 86.2 (d, $J_{P\text{-}C}$ = 105.7 Hz), 68.3 (d, $J_{P\text{-}C}$ = 2.7 Hz), 68.0 (d, $J_{P\text{-}C}$ = 3.3 Hz), 34.8, 34.6, 28.2 (d, $J_{P\text{-}C}$ = 4.7 Hz), 27.5 (d, $J_{P\text{-}C}$ = 4.7 Hz), 25.8, 25.5, 22.9, 22.3. HRMS (EI-TOF) (*m/z*): calcd for $C_{20}H_{21}O_2P$ [M^+]324.1279; found 324.1282.

NOTE: The diastereomeric ratio of **3n** can not be directly determined from its ^{1}H and ^{31}P NMR spectra due to the overlap of the signals. Performing the esterification of **3n** with HOAc (1.2 equiv) in the presence of DMAP (0.1 equiv) and DCC (1.2 equiv) afforded the esterified derivative, namely 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (**3n-SI**). From the ^{1}H and ^{31}P NMR spectra (see below, Figure S1), we got the dr value of ca. 3/1.

^{1}H NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (**3n-SI**)



^{31}P NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (**3n-SI**)

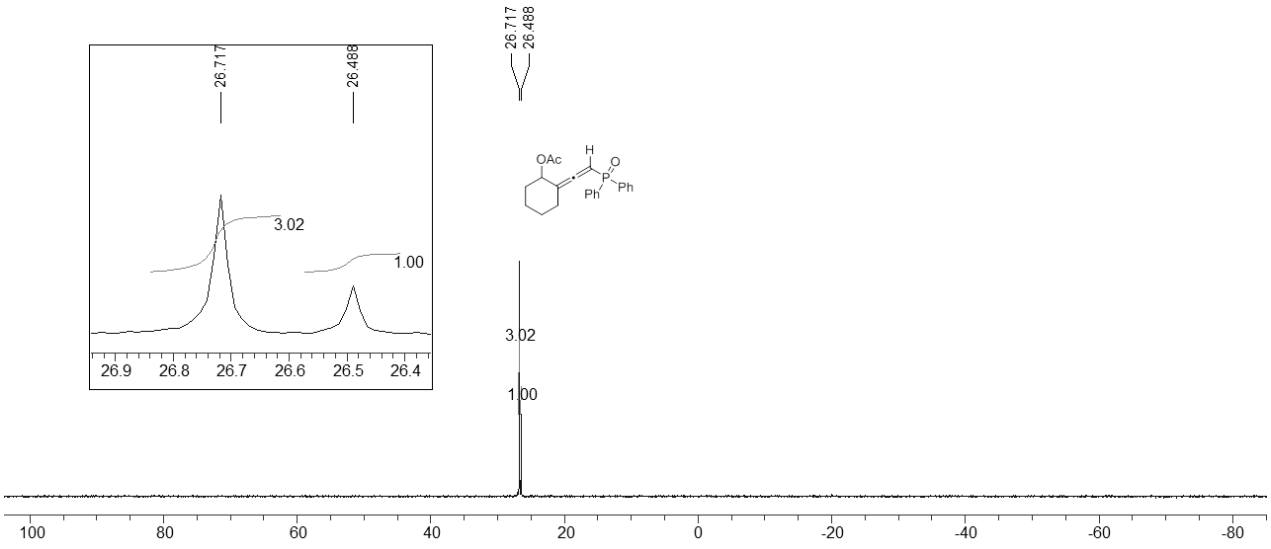
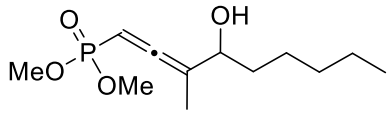


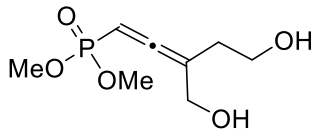
Figure S1. ^{1}H and ^{31}P NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (**3n-SI**)



3o

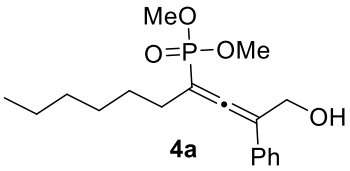
*dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (**3o**).*

The compound was obtained as a 55:45 diastereoisomer mixture. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 44.1 mg, 56%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.23−5.21 (m, 0.55H), 5.16−5.13 (m, 0.45H), 4.14−4.11 (m, 0.45), 4.05−4.00 (m, 0.55H), 3.70−3.67 (m, 7H), 1.76−1.71 (m, 3H), 1.57−1.49 (m, 2H), 1.40−1.20 (m, 6H), 0.85−0.82 (m, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.38, 19.27. HRMS (EI-TOF) (*m/z*): calcd for $C_{12}H_{23}O_4P$ [M^+] 262.1334 found 262.1337.



3p

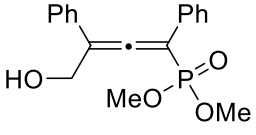
*dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (**3p**).* [Eluent for silica-gel column chromatography: EtOAc. Obtained amount and yield: 42.6 mg, 64%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.31 (s, 1H), 4.19−4.08 (m, 4H), 3.72 (d, J = 11.6 Hz, 6H), 3.71 (br 2H), 2.42-2.24 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.3, 104.7 (d, $J_{P\text{-}C}$ = 16.7 Hz), 79.5 (d, $J_{P\text{-}C}$ = 196.5 Hz), 62.1 (d, $J_{P\text{-}C}$ = 7.6 Hz), 60.2 (d, $J_{P\text{-}C}$ = 4.2 Hz), 52.95 (d, $J_{P\text{-}C}$ = 5.6 Hz), 52.89 (d, $J_{P\text{-}C}$ = 6.0 Hz), 32.1 (d, $J_{P\text{-}C}$ = 6.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.3. HRMS (EI-TOF) (*m/z*): calcd for $C_8H_{15}O_5P$ [M^+] 222.0657 found 222.0659.



4a

*dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (**4a**).*

[Eluent for silica-gel column chromatography: PE/EtOAc = 10/1 to 1/1. Obtained amount and yield: 79.7 mg, 79%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.34 (m, 4H), 7.29-7.25 (m, 1H), 4.65-4.56 (m, 2H), 3.76-3.72 (m, 6H), 2.65 (br, 1H), 2.32-2.26 (m, 2H), 1.56-1.49 (m, 2H), 1.35-1.25 (m, 6H), 0.85 (t, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.7 (d, $J_{P\text{-}C}$ = 4.5 Hz), 132.9 (d, $J_{P\text{-}C}$ = 7.4 Hz), 128.7 (d, $J_{P\text{-}C}$ = 1.4 Hz), 127.7 (d, $J_{P\text{-}C}$ = 1.4 Hz), 126.3 (d, $J_{P\text{-}C}$ = 3.4 Hz), 109.5 (d, $J_{P\text{-}C}$ = 16.7 Hz), 98.2 (d, $J_{P\text{-}C}$ = 183.8 Hz), 61.4 (d, $J_{P\text{-}C}$ = 6.6 Hz), 53.05 (d, $J_{P\text{-}C}$ = 3.4 Hz), 52.98 (d, $J_{P\text{-}C}$ = 3.5 Hz), 31.5, 29.0 (d, $J_{P\text{-}C}$ = 5.6 Hz), 28.8, 28.2 (d, $J_{P\text{-}C}$ = 6.6 Hz), 22.6, 14.0. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 20.2. HRMS (EI-TOF) (*m/z*): calcd for $C_{18}H_{27}O_4P$ [M^+] 338.1647; found 338.1645.

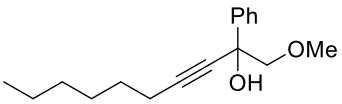


4b

*dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (**4b**).*

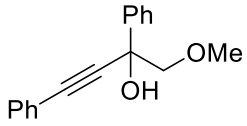
[Eluent for silica-gel column chromatography: PE/EtOAc = 10/1 to 1/1. Obtained amount and yield: 19.4 mg, 20%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H),

7.39-7.27 (m, 6H), 4.74 (d, J = 5.2 Hz, 2H), 3.79 (dd, J_1 = 20.4 Hz, J_2 = 7.6 Hz, 6H), 2.62 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.0, 132.1 (d, $J_{P\text{-}C}$ = 7.1 Hz), 131.2 (d, $J_{P\text{-}C}$ = 7.5 Hz), 129.0, 128.8, 128.2 (d, $J_{P\text{-}C}$ = 3.3 Hz), 127.6 (d, $J_{P\text{-}C}$ = 6.0 Hz), 126.5, 110.9 ($J_{P\text{-}C}$ = 15.1 Hz), 101.0 (d, $J_{P\text{-}C}$ = 187.3 Hz), 61.3 (d, $J_{P\text{-}C}$ = 5.8 Hz), 55.3 (t, $J_{P\text{-}C}$ = 5.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.8. HRMS (EI-TOF) (*m/z*): calcd for $C_{18}H_{19}O_4P$ [M^+] 330.1021; found 330.1025.



5a

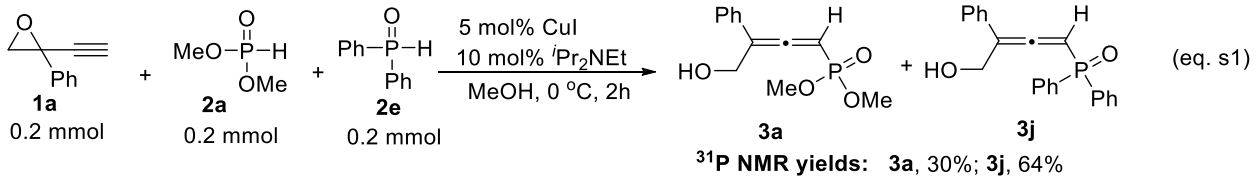
*1-methoxy-2-phenyldec-3-yn-2-ol (**5a**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 10/1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 7.6 Hz, 2H), 7.39-7.30 (m, 3H), 3.73-3.59 (m, 2H), 3.26 (s, 3H), 2.39 (br, 1H), 2.38 (t, J = 7.2 Hz, 2H), 1.65-1.58 (m, 2H), 1.49-1.44 (m, 2H), 1.33-1.30 (m, 4H), 0.90 (t, J = 6.8 Hz, sH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0, 132.0, 128.3, 128.2, 90.4, 81.1, 71.9, 52.4, 31.3, 28.7, 28.6, 22.6, 18.9, 14.1. HRMS (EI-TOF) (*m/z*): calcd for $C_{17}H_{24}O_2$ [M^+] 260.1776; found 260.1776.



5b

*1-methoxy-2,4-diphenylbut-3-yn-2-ol (**5b**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 10/1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, J = 8.0 Hz, 2H), 7.57-7.55 (m, 2H), 7.43-7.35 (m, 6H), 3.84-3.75 (m, 2H), 3.36 (s, 3H), 2.47 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4, 132.0, 128.8, 128.42, 128.38, 127.0, 122.2, 89.4, 86.1, 81.4, 71.8, 52.7. HRMS (EI-TOF) (*m/z*): calcd for $C_{17}H_{16}O_2$ [M^+] 252.1150; found 252.1150.

Competition experiment



^{31}P NMR yields: **3a**, 30%; **3j**, 64%

The reaction of **1a** (0.2 mmol), **2a** (0.2 mmol) and **2e** (0.2 mmol) was performed in CH_3OH (2 mL) for 2 h. Removal of the solvent under reduced pressure afforded a slurry liquid, a small amount of which was dissolved in $CDCl_3$. The ^{31}P NMR of the mixture was then recorded (Figure S2). Four peaks at 24.5, 21.7, 17.4 and 10.5 ppm were identified as the ^{31}P NMR signals of **3j**, **2e**, **3a**, and **2a**. Yields of **3a** and **3j** were calculated based on the integration of the peaks.

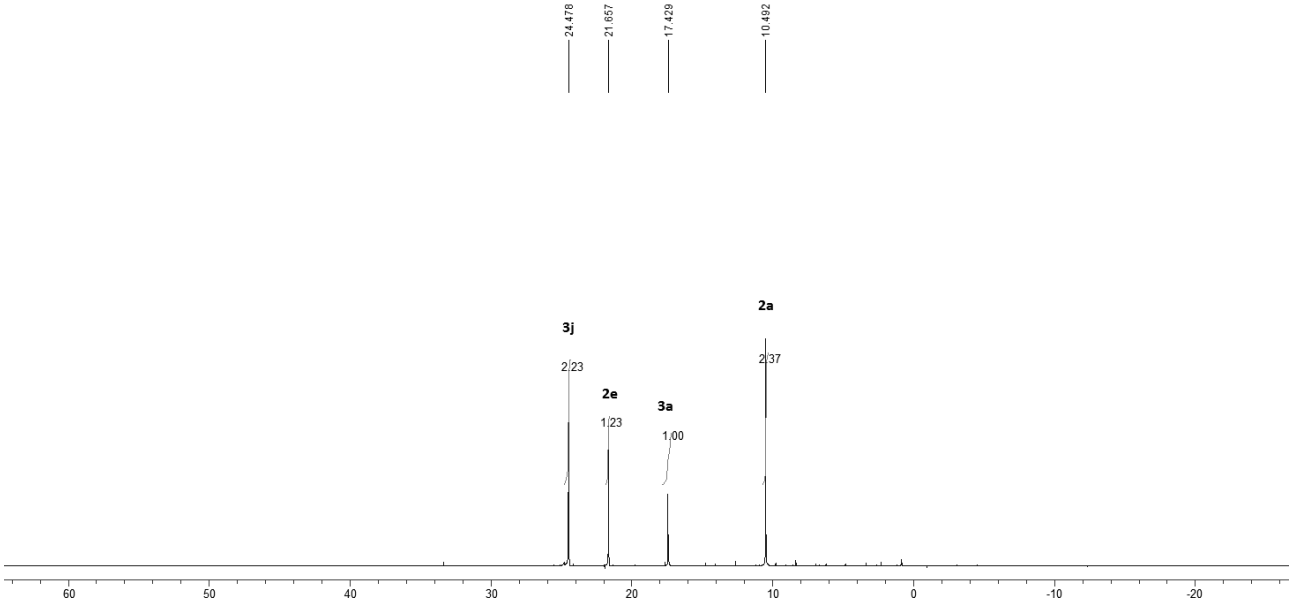
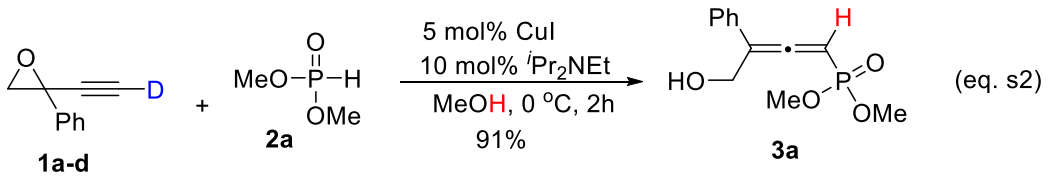
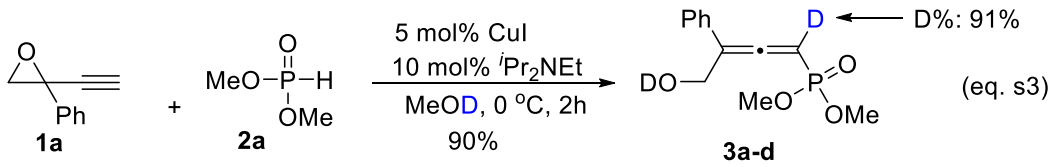


Figure S2

Deuterium labeling experiments

The reaction of **1a-d** (D% = ca. 93%, 0.24 mmol, 34.8 mg) and **2a** (0.2 mmol, 22.1 mg) in CH_3OH (2 mL) afforded **3a** (46.3 mg) in 91% yield (eq. s2).





On the other hand, the reaction of **1a** (0.24 mmol, 34.6 mg) and **2a** (0.2 mmol, 22.2 mg) in CH_3OD (D% > 99.5%, 2 mL) afforded the α-deuterated allenylphosphonate **3a-d** (46.2 mg) in 90% yield (eq. s3). D% = 91%, determined from the ^1H NMR analysis (Figure S3). *Dimethyl (4-hydroxy-3-phenyl buta-1,2-dien-1-yl-1-d) phosphonate (**3a**-d)*: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.42−7.34 (m, 4H), 7.30−7.26 (m, 1H), 5.76-5.75 (m, 0.09H), 4.66-4.57 (m, 2H), 3.77 (d, J =11.6 Hz, 6H).

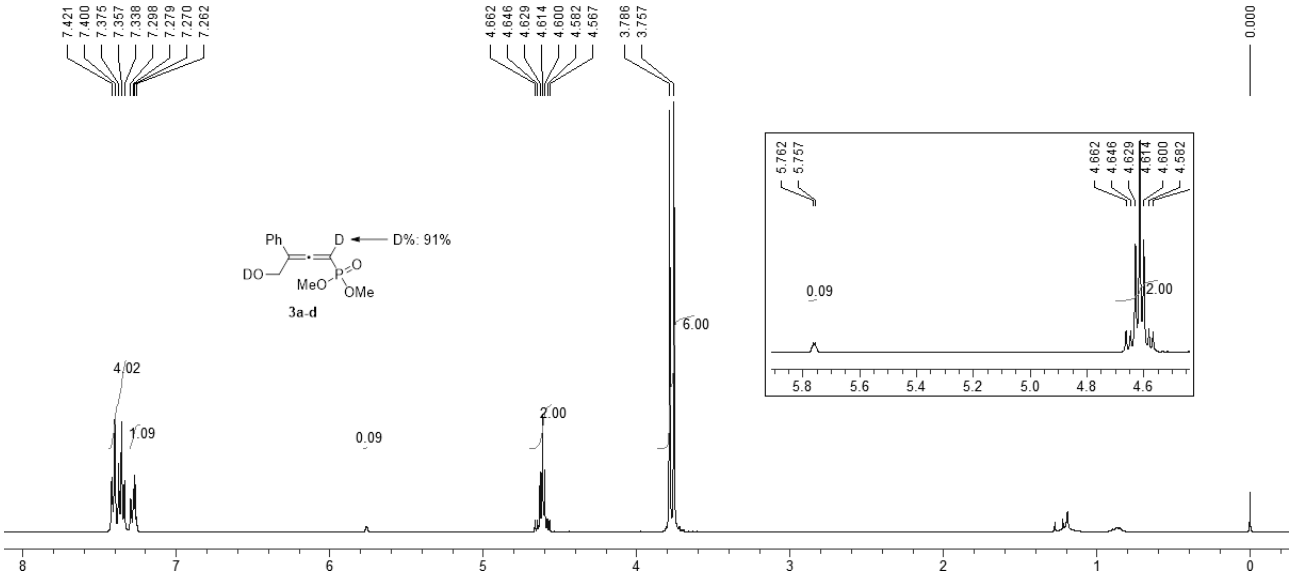
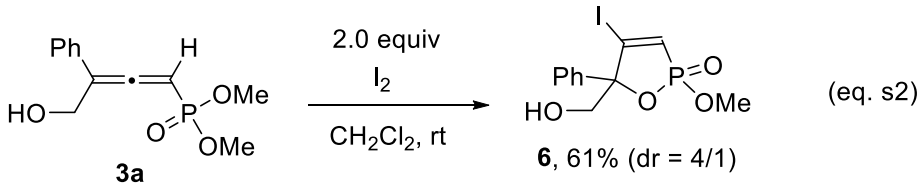


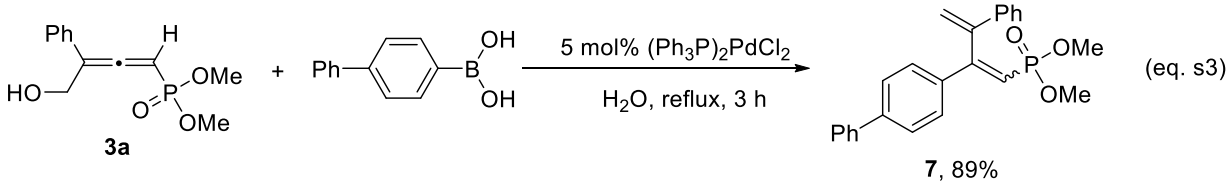
Figure S3

Synthetic transformations of 3a



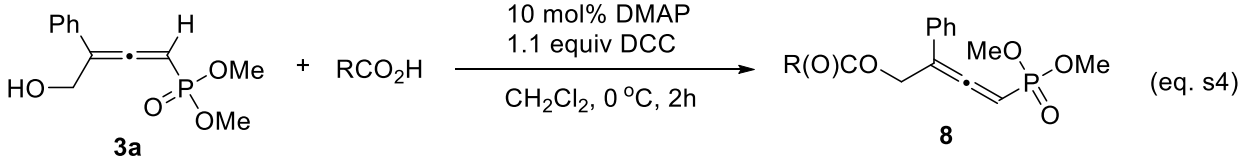
(eq. s2)

To a solution of **3a** (0.274 mmol, 69.5 mg) in CH_2Cl_2 (3 mL) at room temperature was added 2.0 equiv of I_2 (139.2 mg). The mixture was stirred overnight, then quenched with aq. $Na_2S_2O_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The product **6** (61.1 mg, 61%) was obtained by purification by flash chromatography on silica (petroleum ether/ethyl acetate)**.** The compound **6** was obtained as a diastereoisomers (dr: ca.4/1, determined from ^{31}P NMR analysis). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.39 (m, 5H), 6.76-6.65 (m, 1H), 4.37-4.20 (m, 3H), 3.96-3.90 (m, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 37.8, 37.2. HRMS (EI-TOF) (*m/z*): calcd for $C_{11}H_{22}O_4PI$ [M^+] 365.9518; found 365.9515.



(eq. s3)

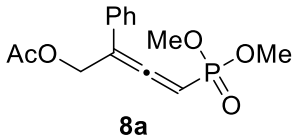
To a mixture of **3a** (0.257 mmol, 65.3 mg), [1,1'-biphenyl]-4-ylboronic acid (0.514 mmol, 101.8 mg) and water (2 mL) was added a catalytic amount of $(Ph_3P)_2PdCl_2$ (9 mg) under an atomosphere of N_2. After heated to reflux for 3 h, the reaction mixture was cooled down and extracted with EtOAc. The combined organic layers were washed with brine, dried with Na_2SO4 and concentrated under reduced pressure. The pure product **7** (89.1 mg, 89%) was obtained by purification by flash chromatography on silica (petroleum ether/ethyl acetate)**.** The exact configuration referring to the C-C double bonds in the product **7** has not been determined. We reason that this reaction proceeds with high stereoselectivity since the ^1H, ^{13}C and ^{31}P NMR data of **7** all indicate that only one of the stereoisomers is formed. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.0 Hz, 2H),7.46-7.43 (m, 2H), 7.37-7.32 (m, 6H), 5.80 (d, J = 16.8 Hz, 1H), 5.54 (s, 1H), 5.24 (s, 1H), 3.46 (d, J = 11.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.1 (d, J = 6.7 Hz), 151.3 (J = 23.6 Hz), 141.0, 140.3, 139.6, 136.8 (J = 7.9 Hz), 129.7 (d, J = 1.9 Hz), 128.8, 128.4 (d, J = 5.0 Hz), 127.9, 127.5, 127.0, 126.4, 122.0, 118.1, 116.2, 52.1 (d, J = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.5. HRMS (EI-TOF) (*m/z*): calcd for $C_{24}H_{23}O_3P$ [M^+] 390.1385; found 390.1389.



(eq. s4)

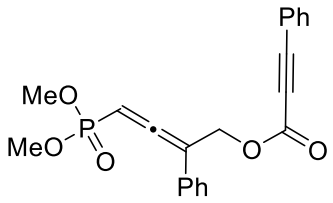
To a solution containing **3a** (0.348 mmol, 88.3 mg), 3-phenylpropiolic acid (0.383 mmol, 56.0 mg) and *N*, *N*-dimethylpyridin-4-amine (DMAP, 0.0348 mmol, 4.3 mg) in dry CH_2Cl_2 (3 mL) was added

a solution of dicyclohexylmethanediimine (DCC, 0.388 mmol, 80.1 mg) in CH_2Cl_2 (2 mL) at 0 °C. After the addition was complete, the reaction was naturally warmed to room temperature. Upon the consumption of **3a** (monitored by TLC), the reaction mixture was filtrated and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether – ethyl acetate 3:1 to 1:1) to afford **8b** (94.3 mg, 71%). **8a** was obtained following a similar procedure.



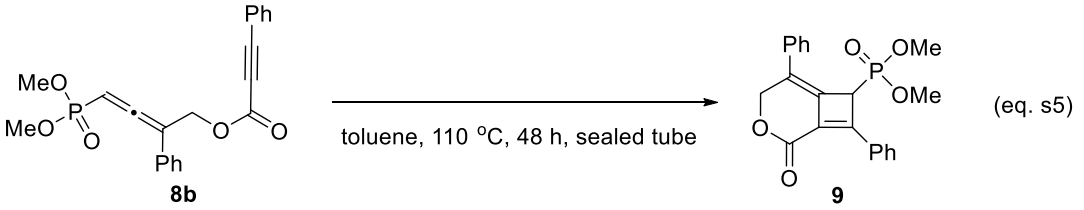
8a

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.37 (m, 4H), 7.32−7.28 (m, 1H), 5.85 (s, 1H), 5.08 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 2H), 3.78 (t, J = 12.0 Hz, 6H), 2.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.4 (d, $J_{P\text{-}C}$ = 1.3 Hz), 170.3, 131.2 (d, $J_{P\text{-}C}$ = 7.0 Hz), 128.8 (d, $J_{P\text{-}C}$ = 1.8 Hz), 128.1 (d, $J_{P\text{-}C}$ = 1.9 Hz), 126.1 (d, $J_{P\text{-}C}$ = 1.8 Hz), 104.0 (d, $J_{P\text{-}C}$ = 16.8 Hz), 83.7 (d, $J_{P\text{-}C}$ = 195.7 Hz), 61.3 (d, $J_{P\text{-}C}$ = 6.5 Hz), 53.0 (d, $J_{P\text{-}C}$ = 6.4 Hz), 20.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.7. HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{17}O_5P$ [M^+] 296.0814 found 296.0819.



8b

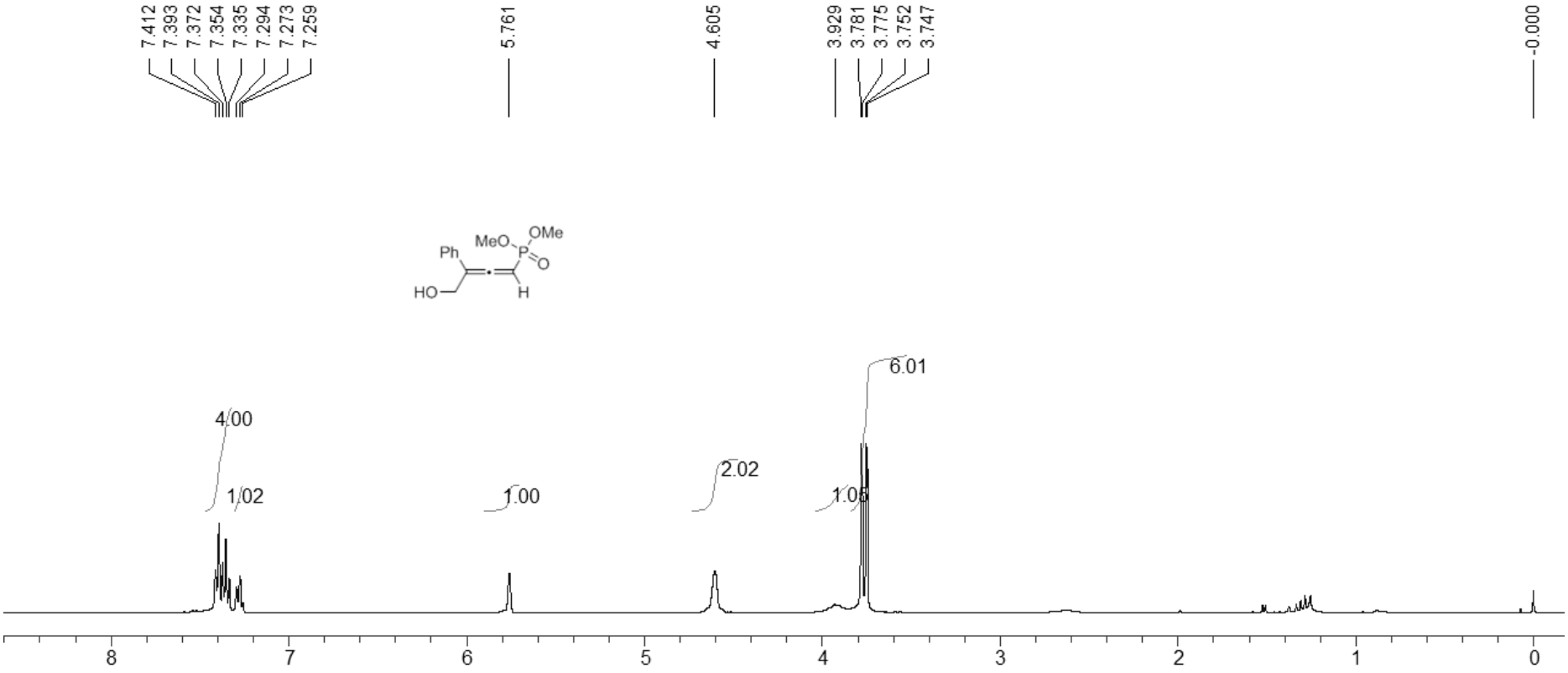
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 8.0 Hz, 2H), 7.48−7.32 (m, 8H), 5.90 (s, 1H), 5.29-5.18 (m, 2H), 3.80 (dd, J_1 = 11.6 Hz, J_2 = 7.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8 (d, $J_{P\text{-}C}$ = 1.3 Hz), 153.5, 133.0, 131.1 (d, $J_{P\text{-}C}$ = 8.1 Hz), 130.9, 129.0, 128.6, 128.4, 126.3 (d, $J_{P\text{-}C}$ = 2.3 Hz), 119.3, 103.4 (d, $J_{P\text{-}C}$ = 17.0 Hz), 87.4, 84.1 (d, $J_{P\text{-}C}$ = 194.3 Hz), 80.1, 62.9 (d, $J_{P\text{-}C}$ = 6.3 Hz), 53.2 (d, $J_{P\text{-}C}$ = 6.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 15.5. HRMS (EI-TOF) (*m/z*): calcd for $C_{21}H_{19}O_5P$ [M^+] 382.0970 found 382.0971.



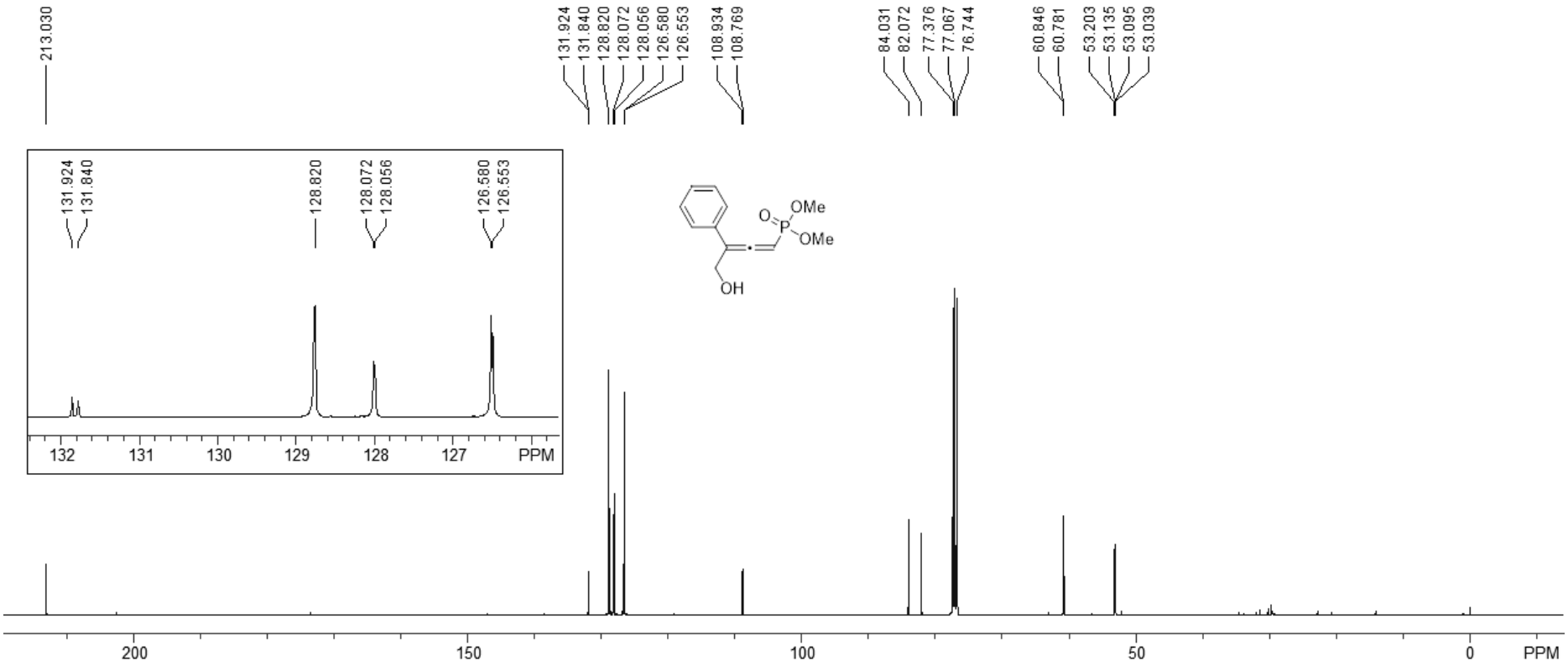
A solution of 50.0 mg of **8b** in toluene (3 mL) was heated to 110 °C for 48 h in a sealed tube. After removal of the solvent under a reduced pressure, the residue was passed through a short silica-gel column with PE-EtOAc as eluent. Pure product **9** was obtained by recrystallization from methol (20.3 mg, 41%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 7.6 Hz, 2H), 7.48−7.26 (m, 8H), 5.76 (d, J = 24.4 Hz, 1H), 5.38 (d, J = 16.4 Hz, 1H), 4.78 (d, J = 16.0 Hz, 1H), 3.46 (dd, J_1 = 11.6 Hz, J_2 = 11.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.1, 150.4 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.2.3, 131.4, 131.2, 129.6, 128.7, 128.6, 128.4, 126.9, 118.2, 74.5, 53.5 (d, $J_{P\text{-}C}$ = 7.4 Hz), 52.8 (d, $J_{P\text{-}C}$ = 7.7 Hz), 49.1 (d, $J_{P\text{-}C}$ = 146.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.4. HRMS (EI-TOF) (*m/z*): calcd for $C_{21}H_{19}O_5P$ [M^+] 382.0970 found 382.0971.

*^{1}H NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3a**)*

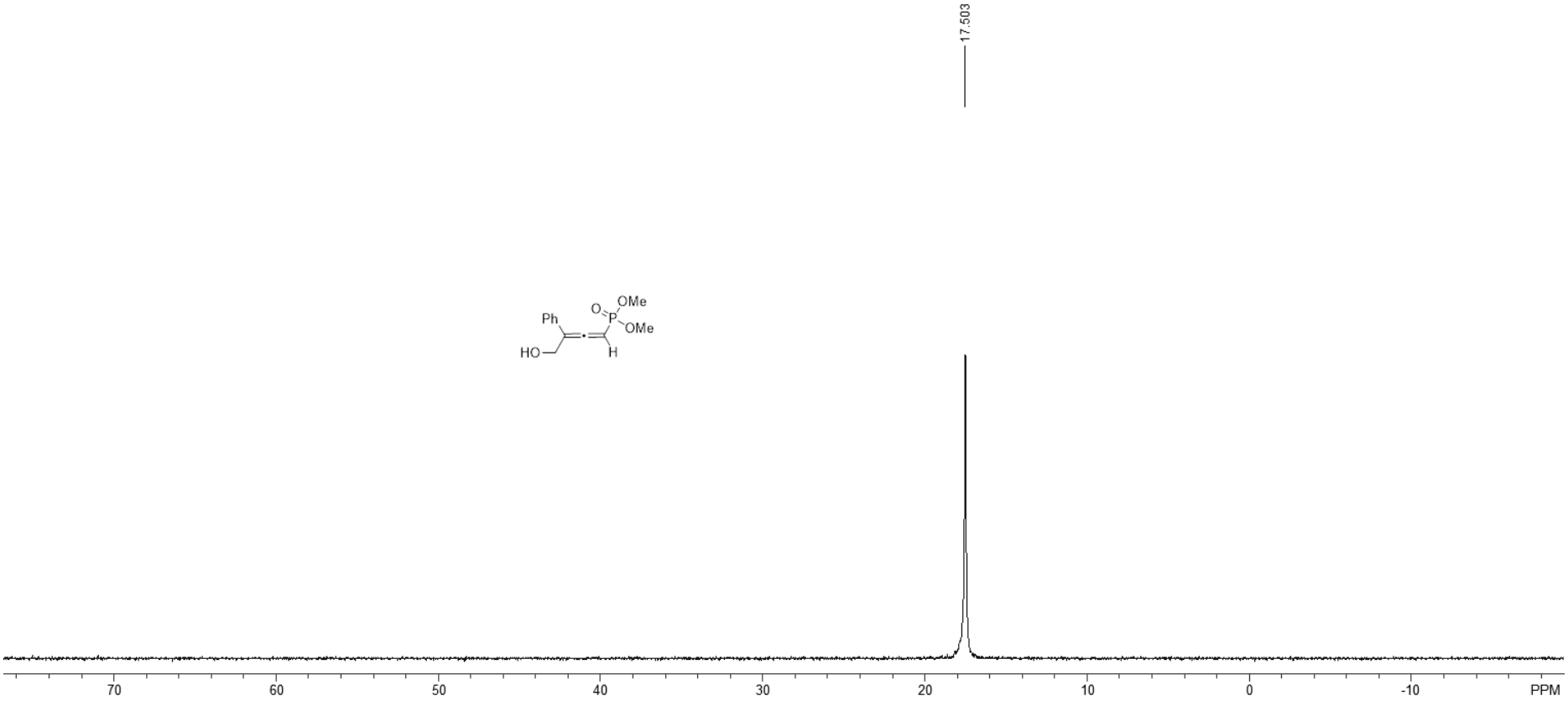
$CDCl_3$, 400 MHz



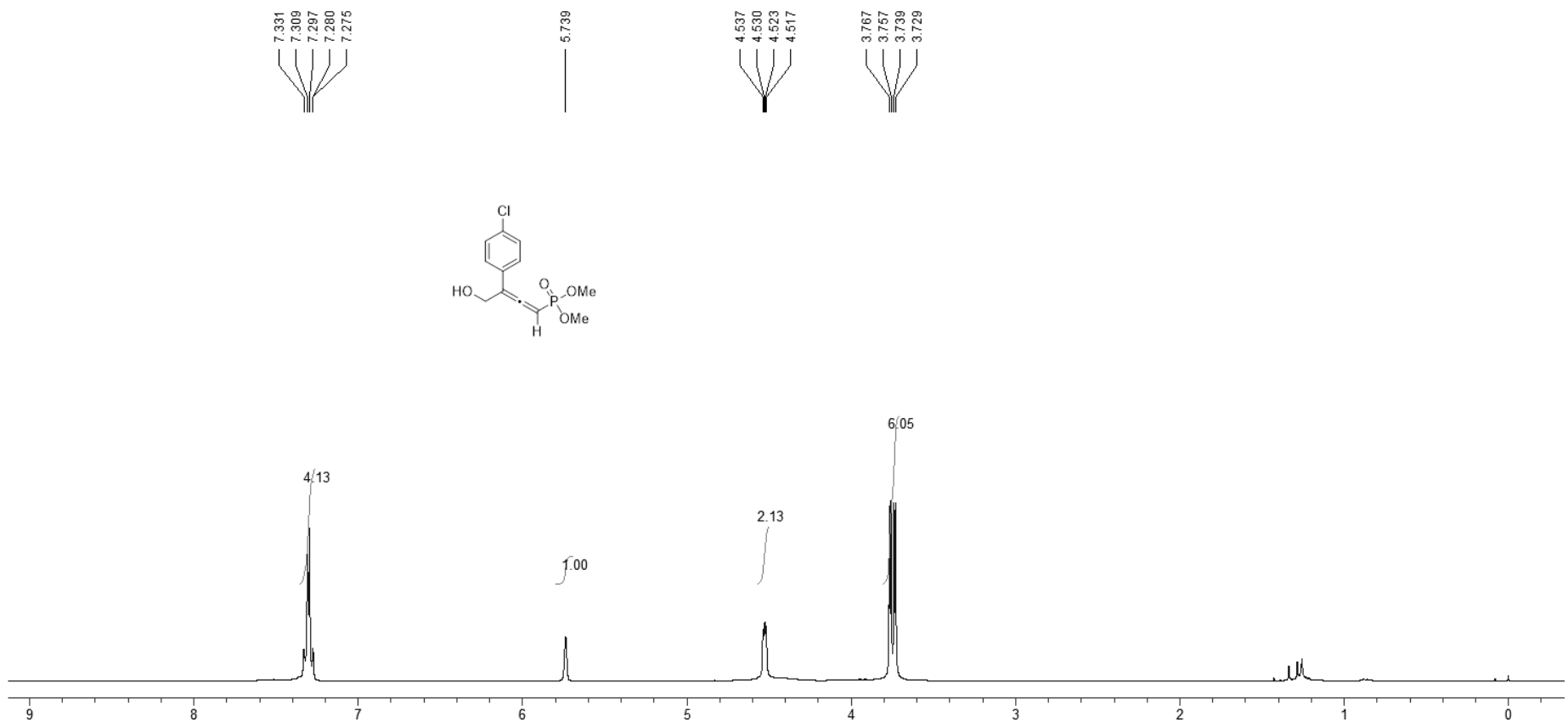
*^{13}C NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3a**)*
$CDCl_3$, 100 MHz



*^{31}P NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3a**)*
$CDCl_3$, 162 MHz

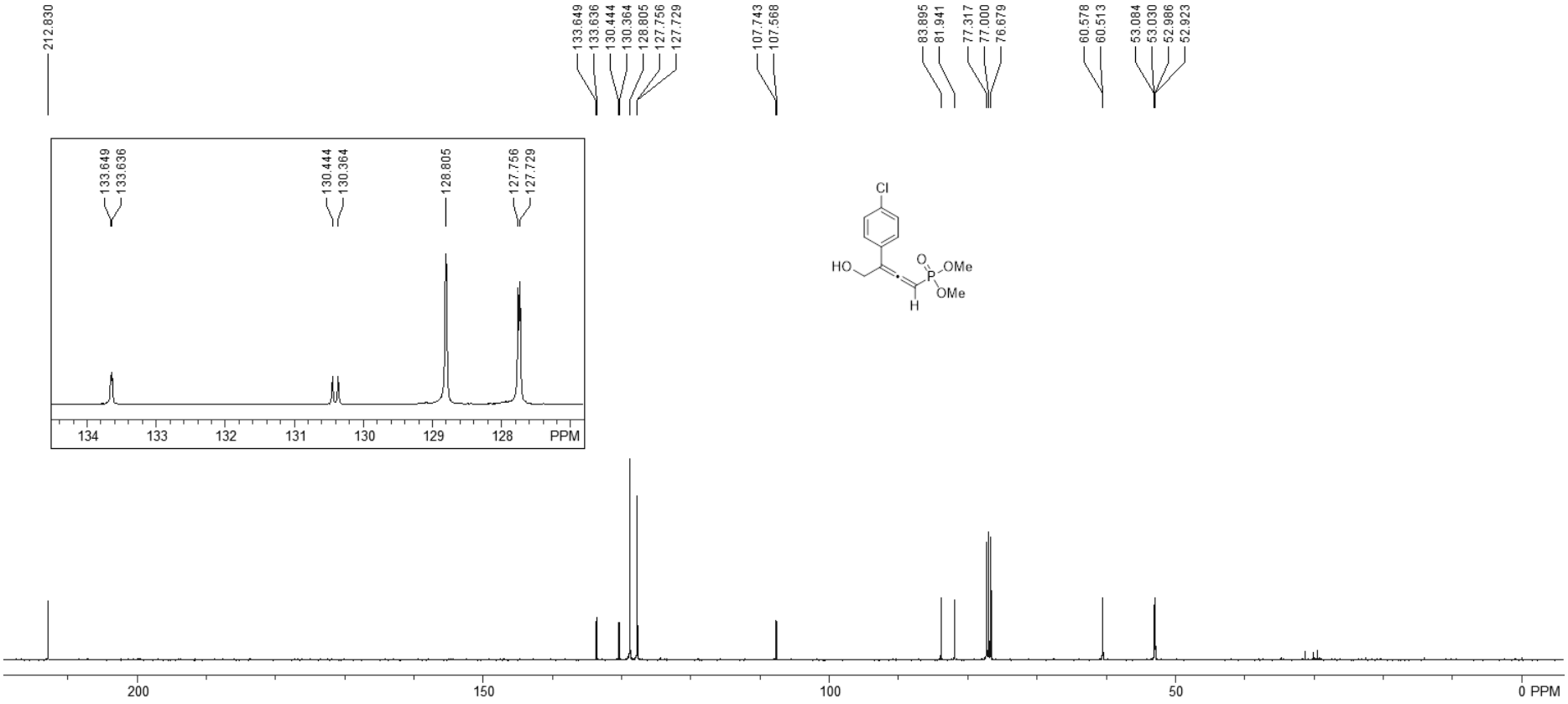


*^{1}H NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3b**)*
$CDCl_3$, 400 MHz



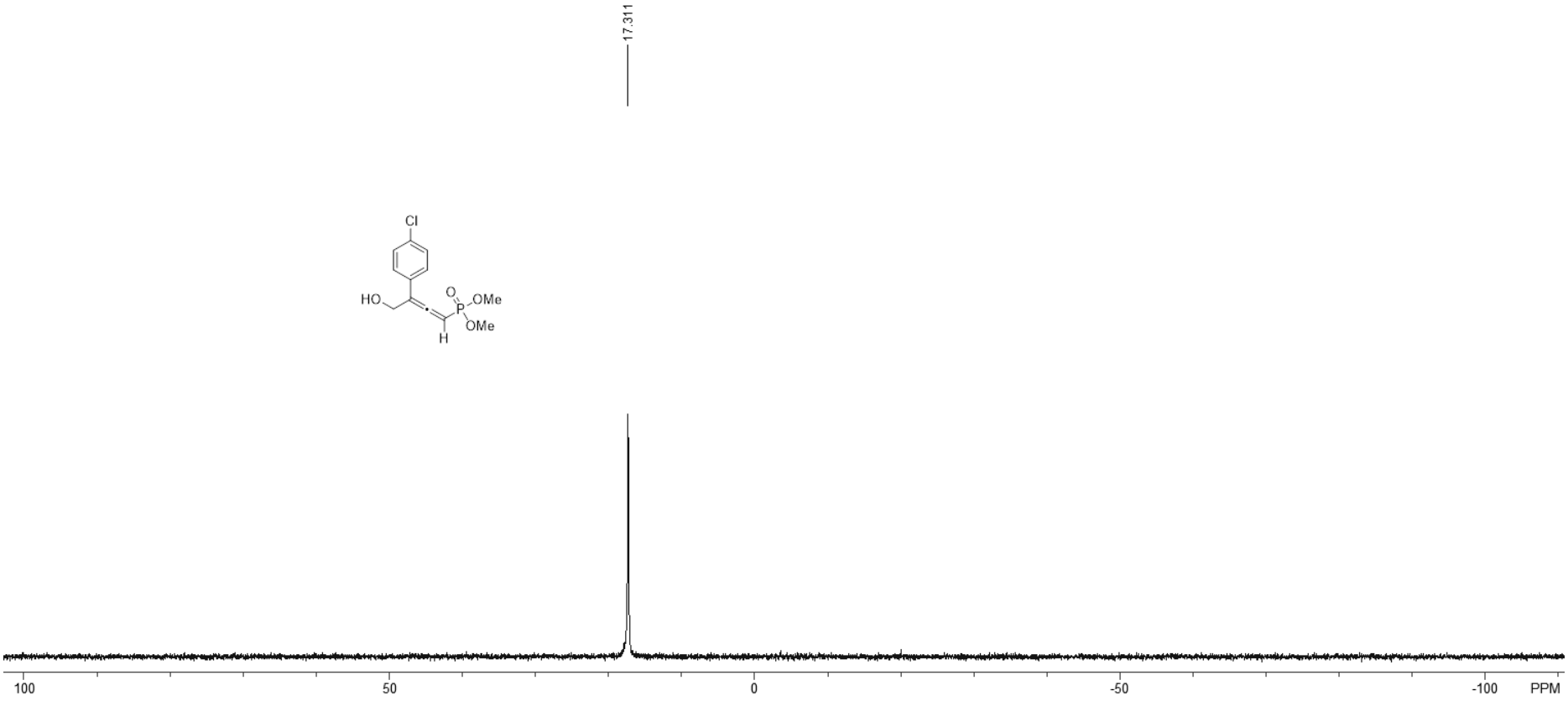
*^{13}C NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3b**)*

$CDCl_3$, 100 MHz



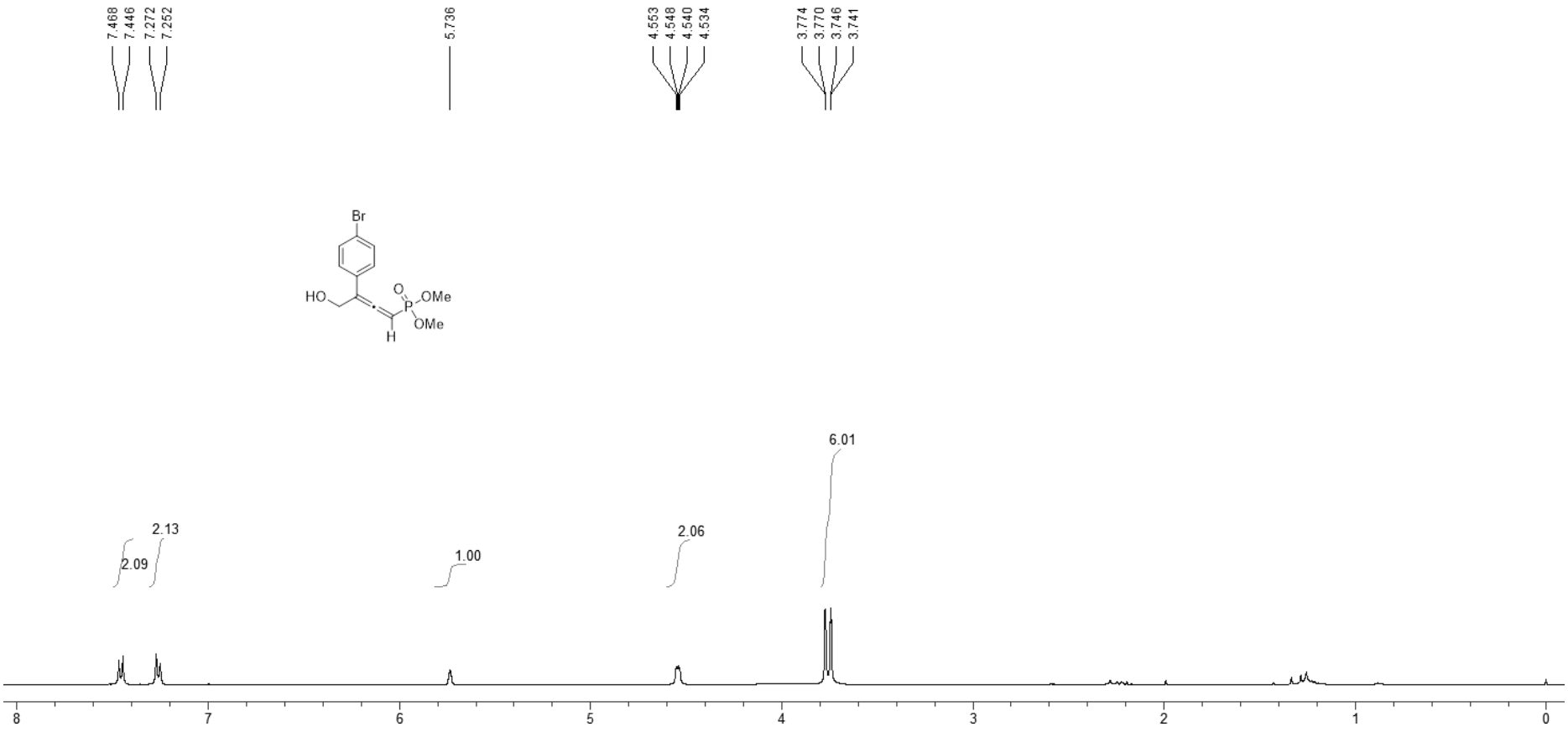
*^{31}P NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3b**)*

$CDCl_3$, 162 MHz



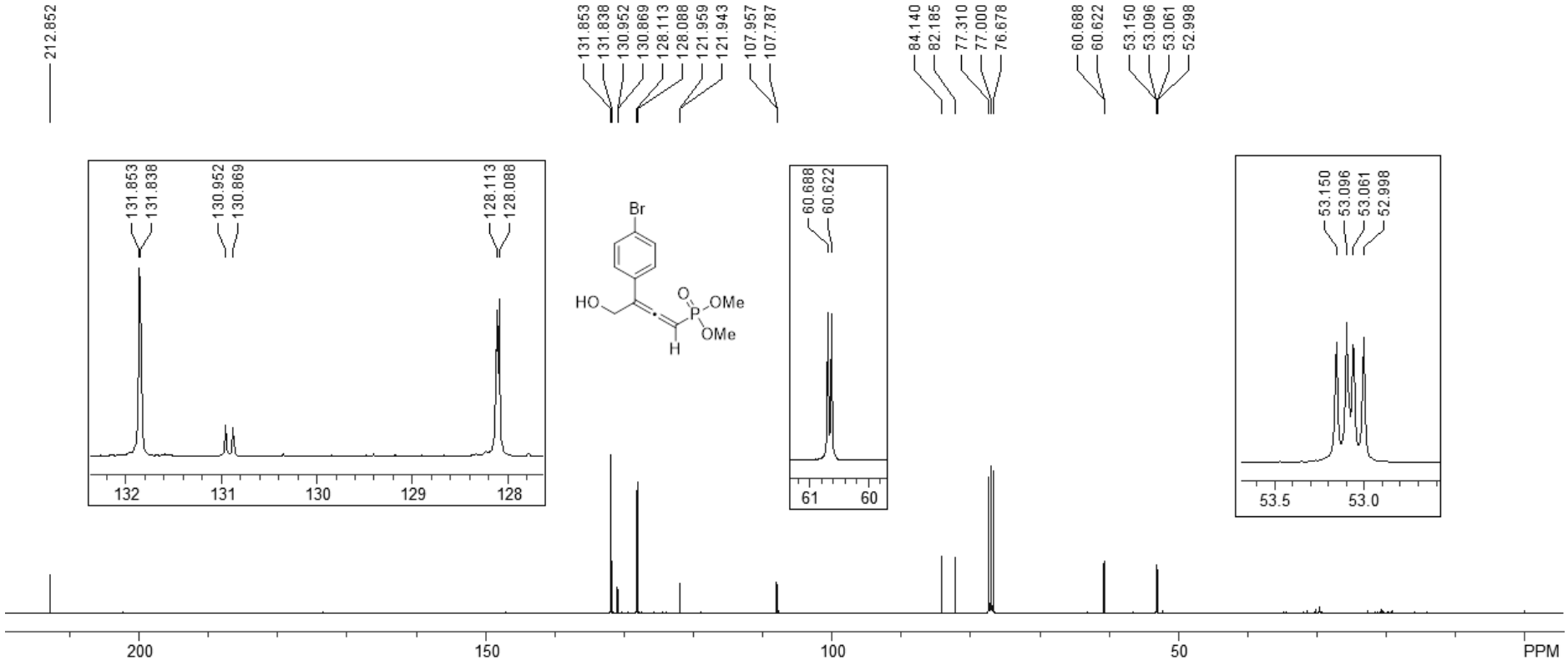
*^{1}H NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3c**)*

$CDCl_3$, 400 MHz

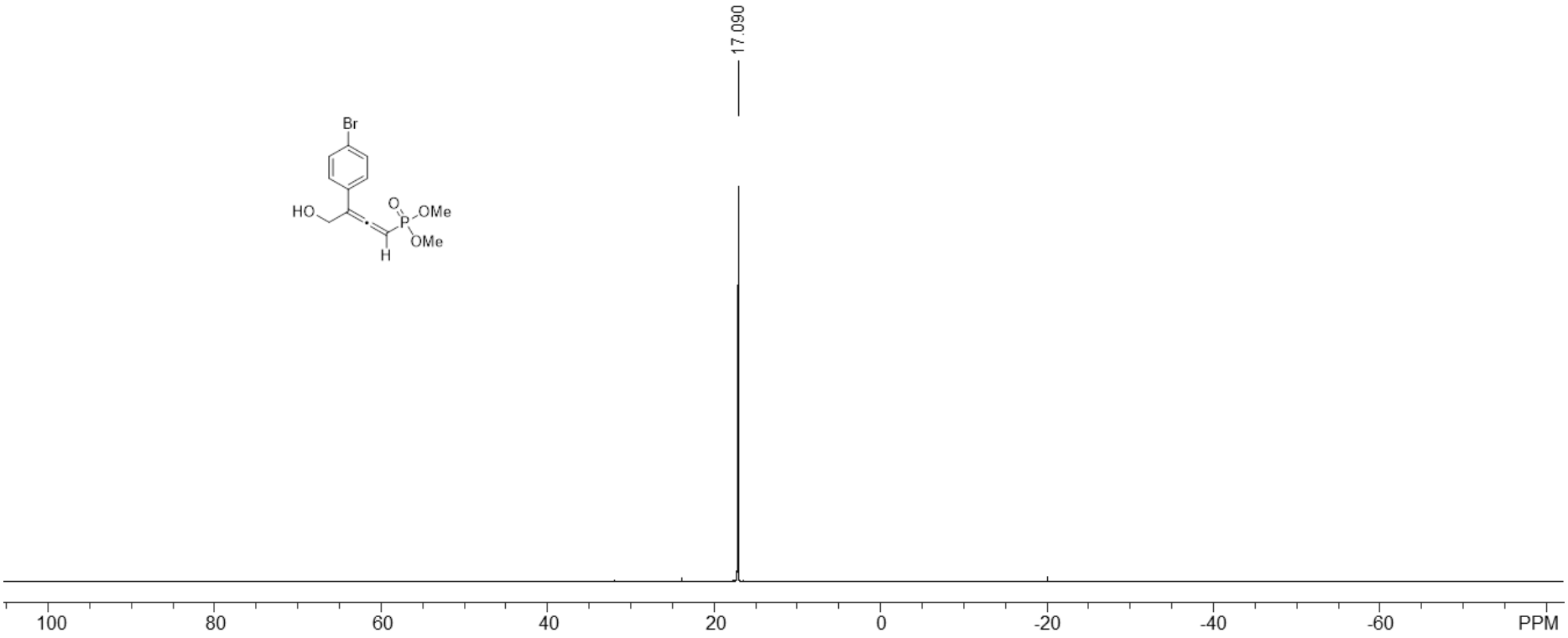


*^{13}C NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3c**)*

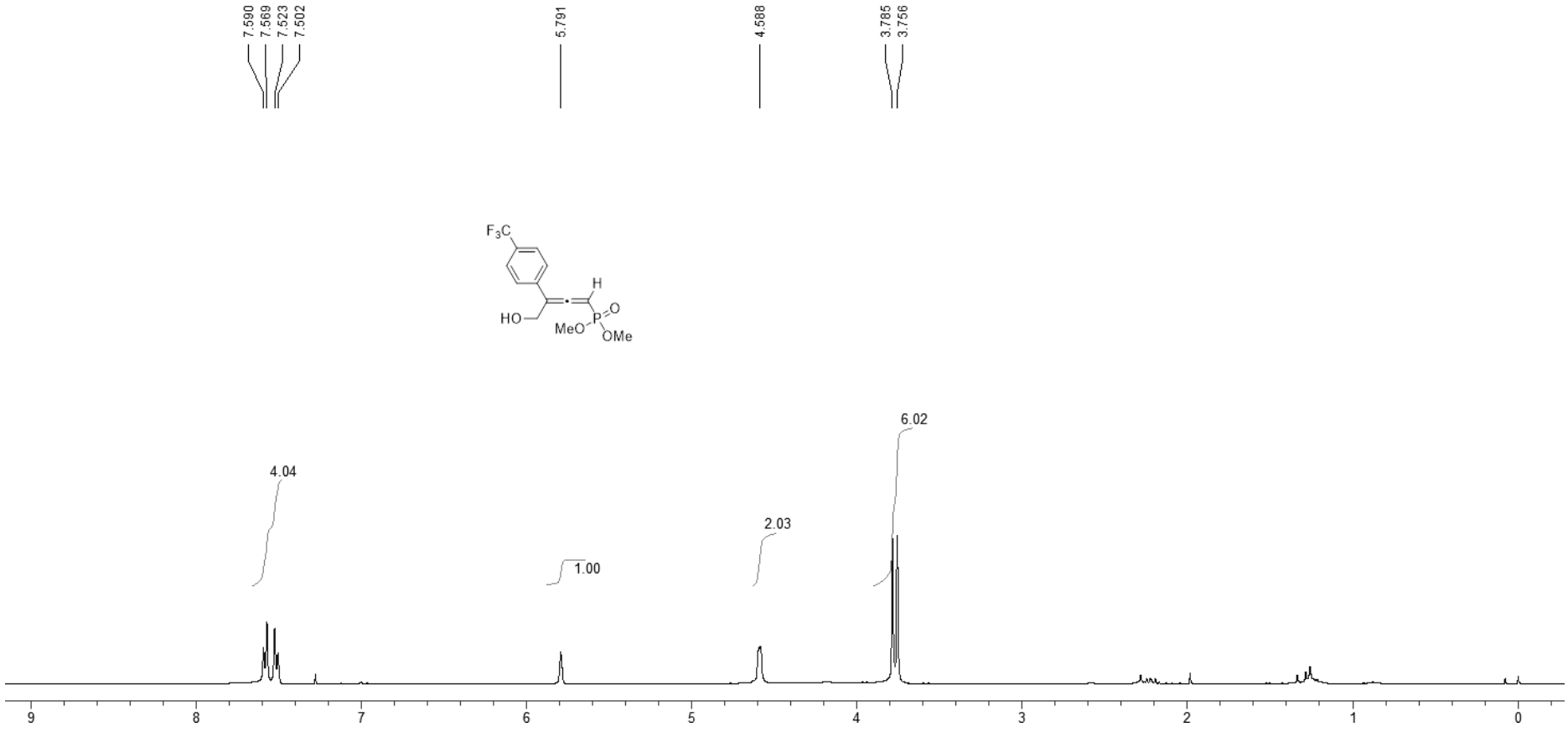
$CDCl_3$, 100 MHz



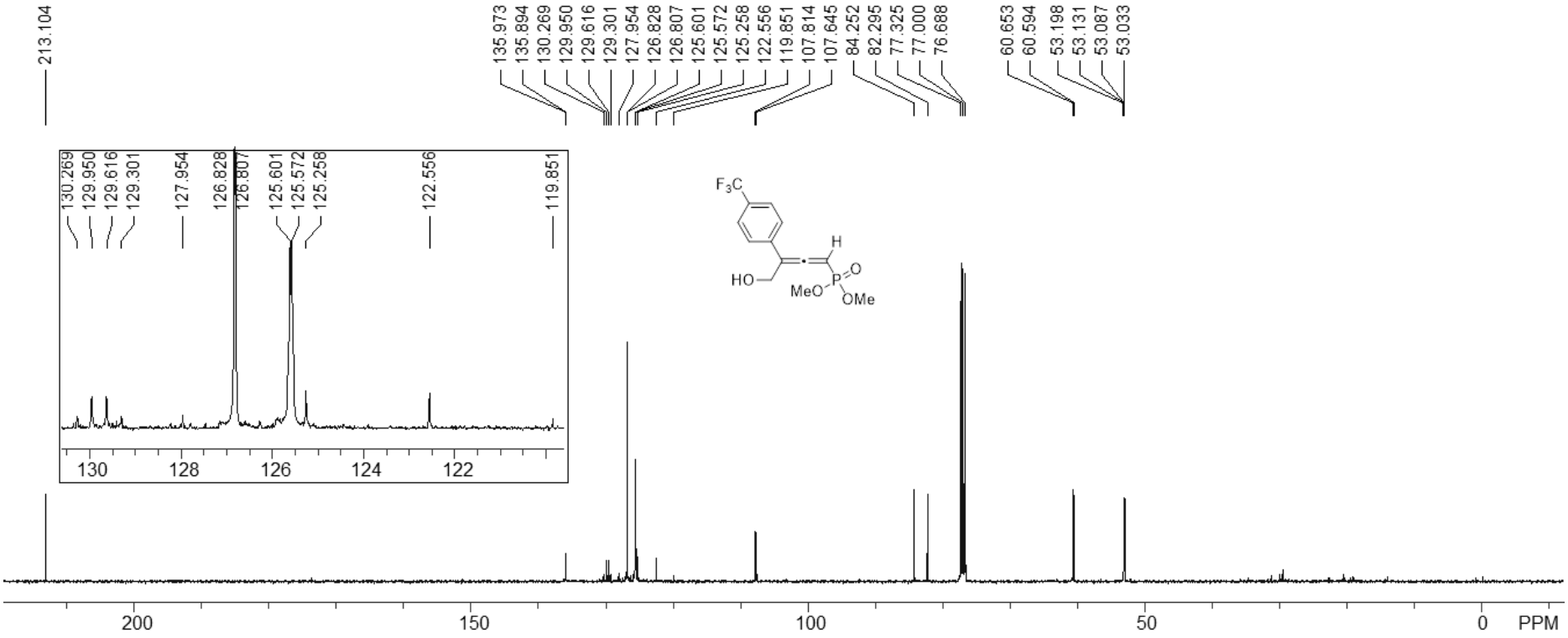
*^{31}P NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3c**)*
$CDCl_3$, 162 MHz



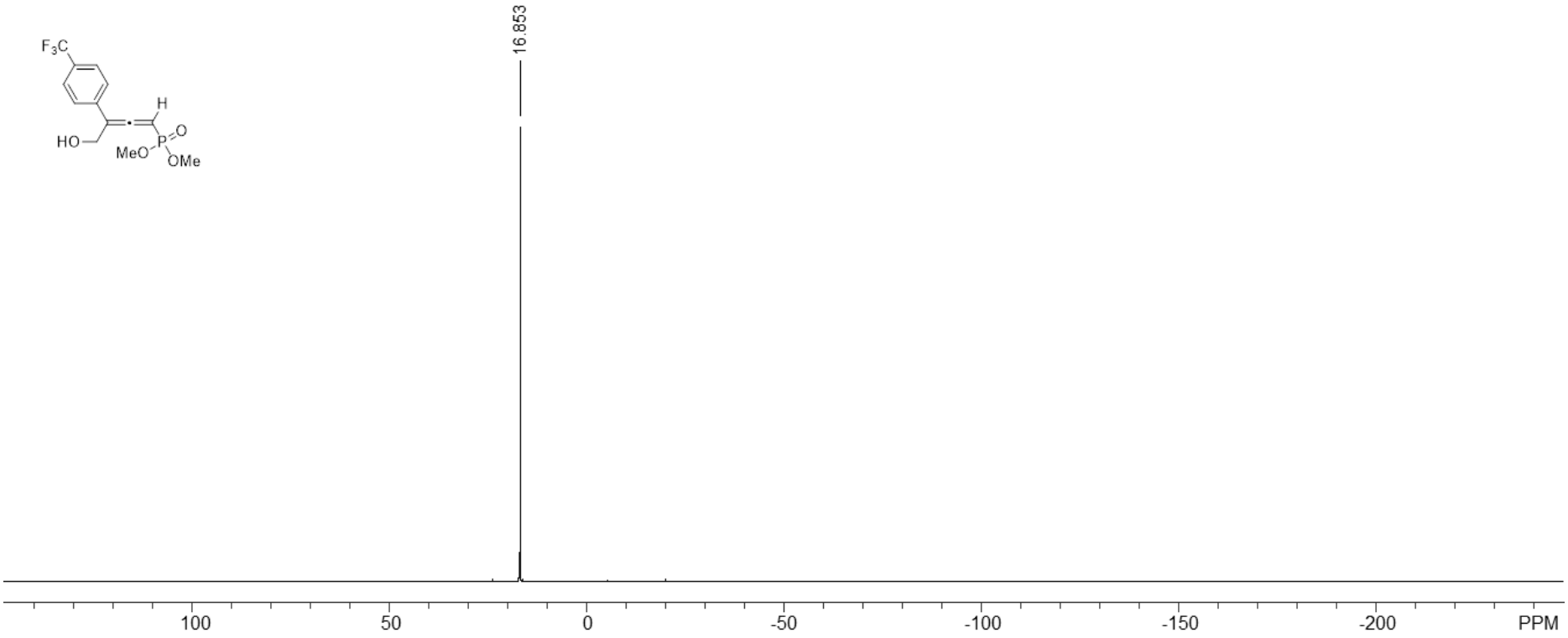
*^{1}H NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (**3d**)*
$CDCl_3$, 400 MHz



*^{13}C NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (**3d**)*
$CDCl_3$, 100 MHz

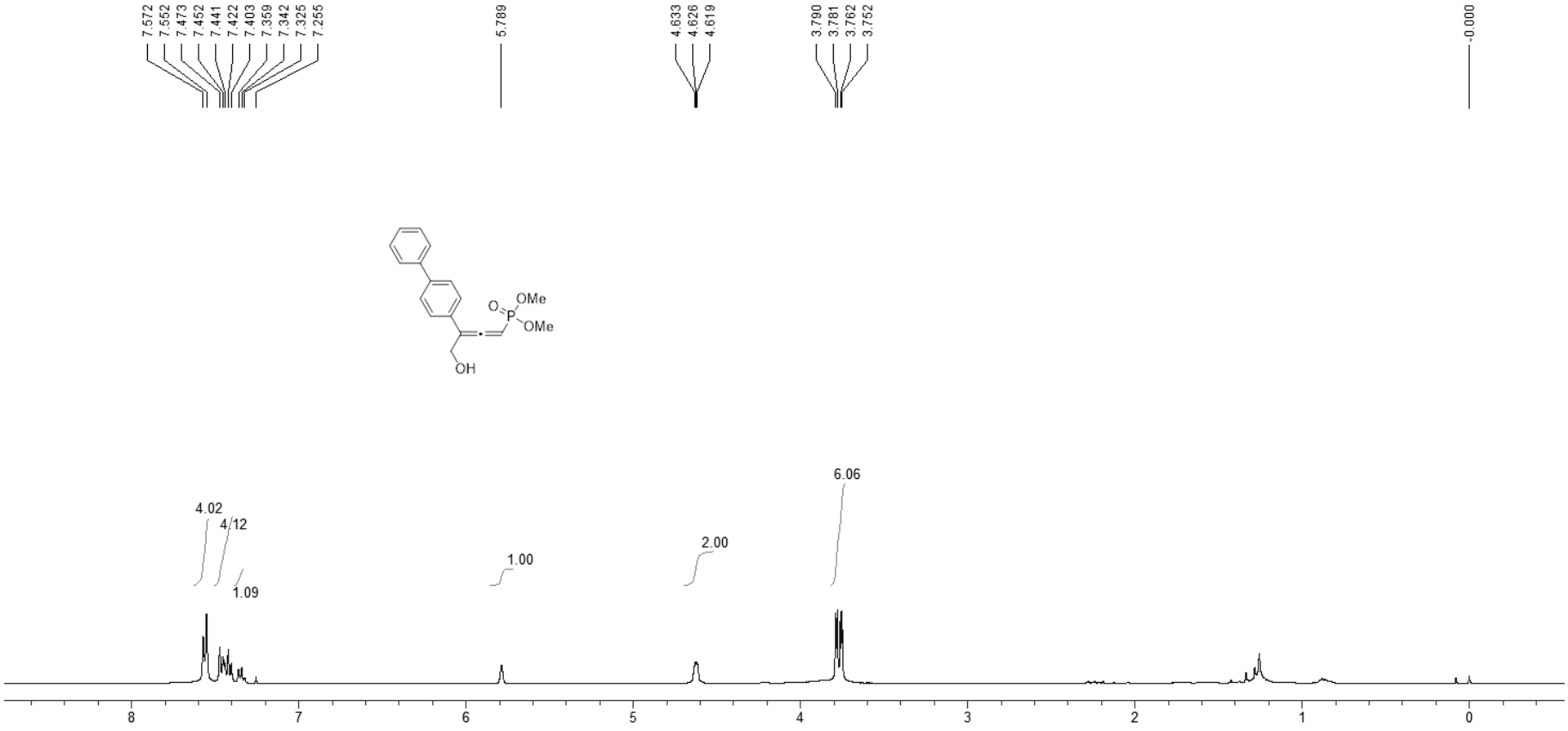


*^{31}P NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (**3d**)*
$CDCl_3$, 162 MHz



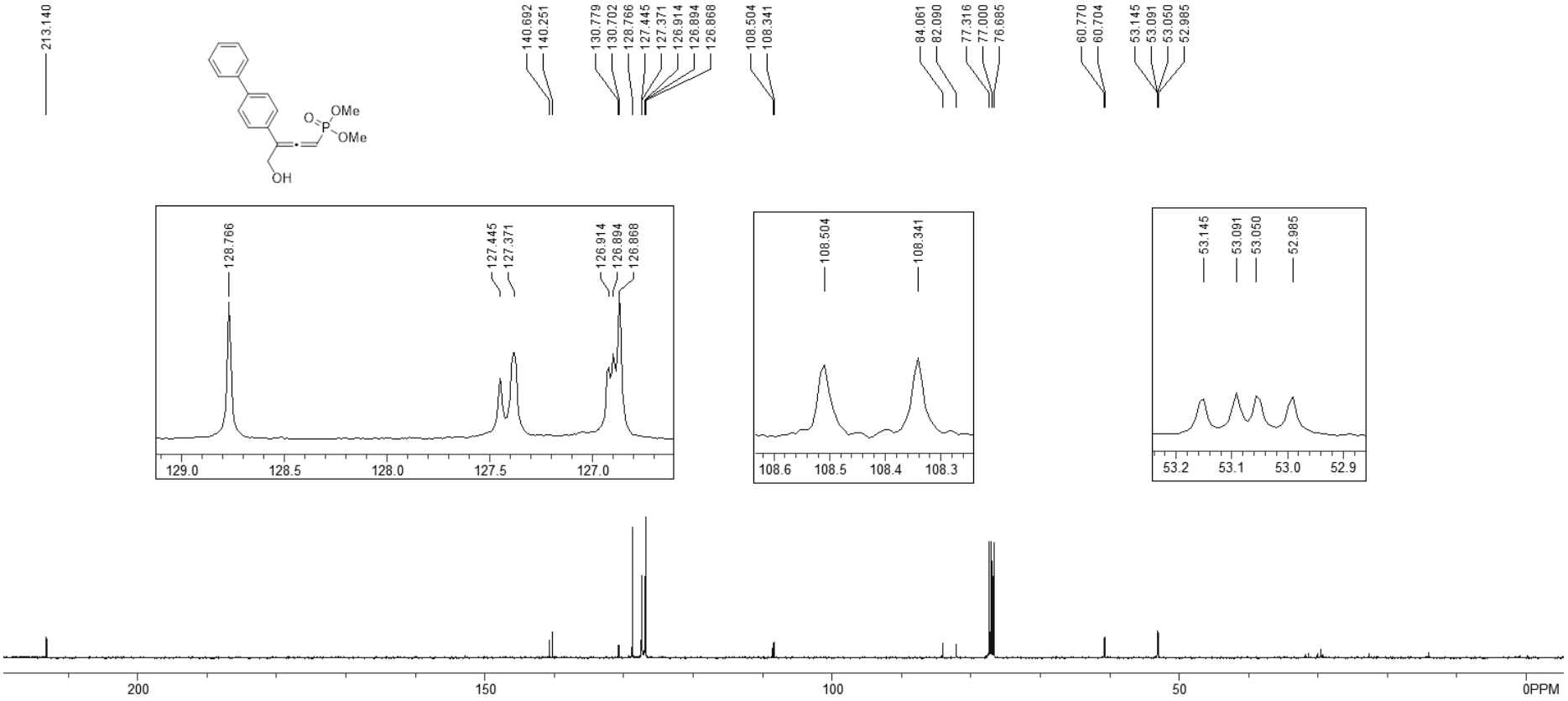
*^{1}H NMR spectrum of dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 400 MHz



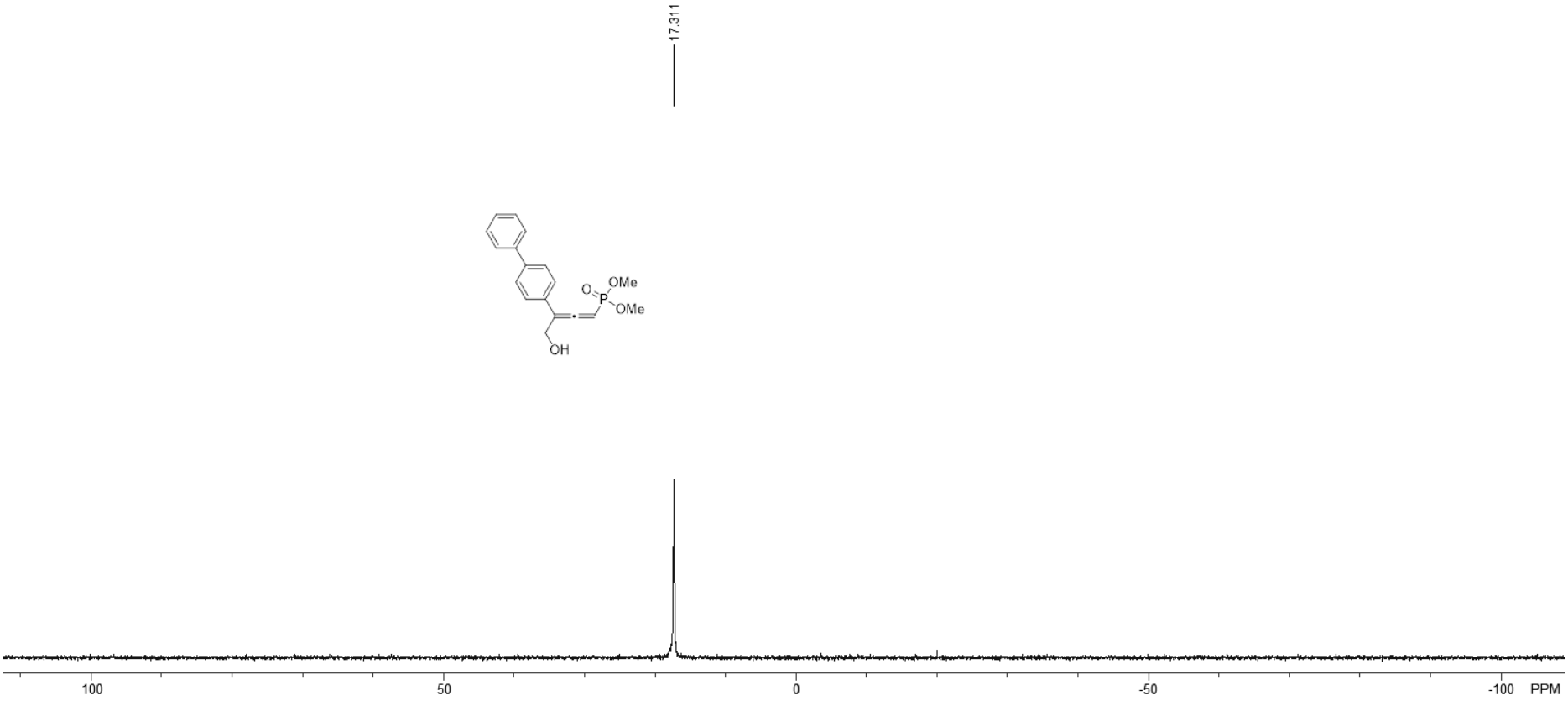
*^{13}C NMR spectrum of dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 100 MHz

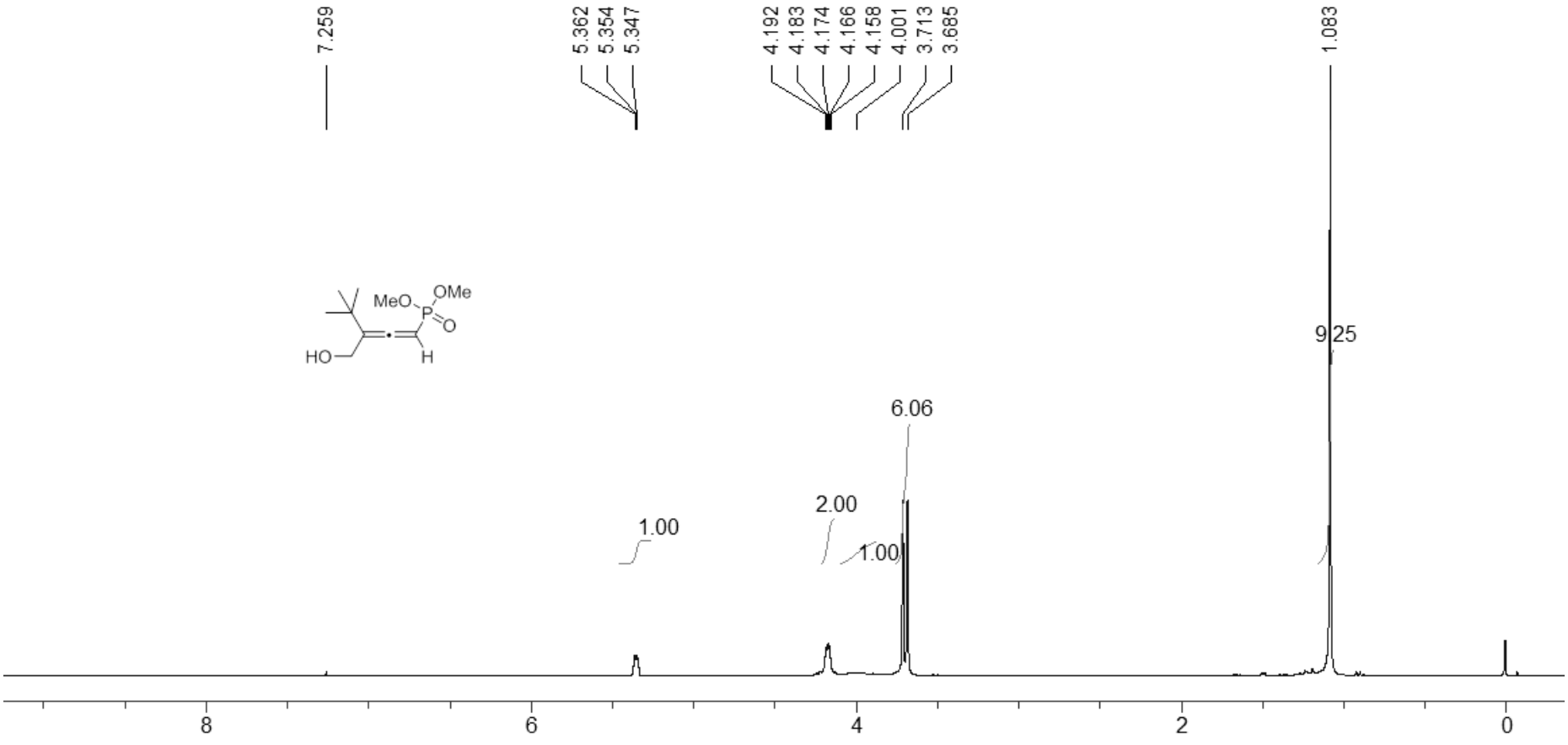


*^{31}P NMR spectrum of dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 162 MHz

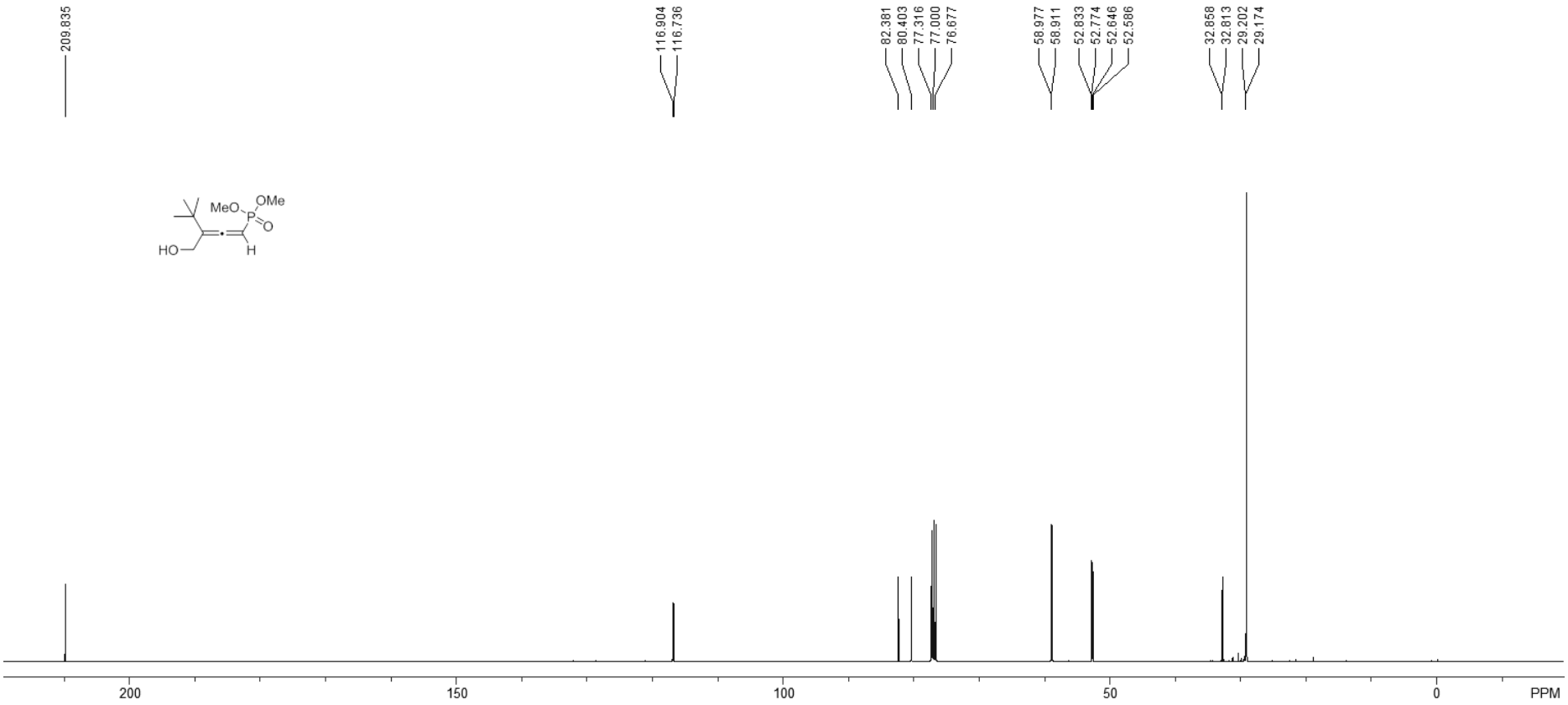


*^{1}H NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3f**)*
$CDCl_3$, 400 MHz

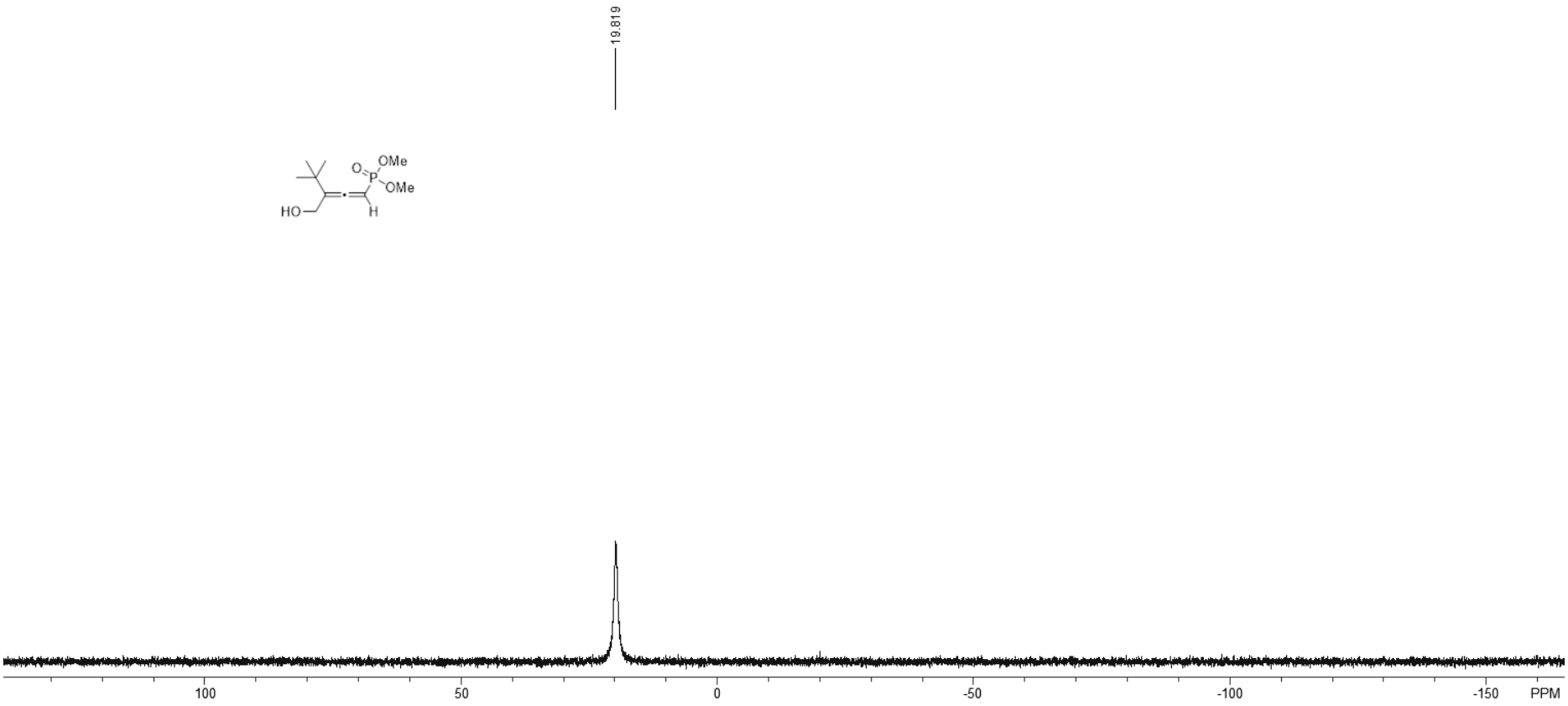


*^{13}C NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3f**)*

$CDCl_3$, 100 MHz

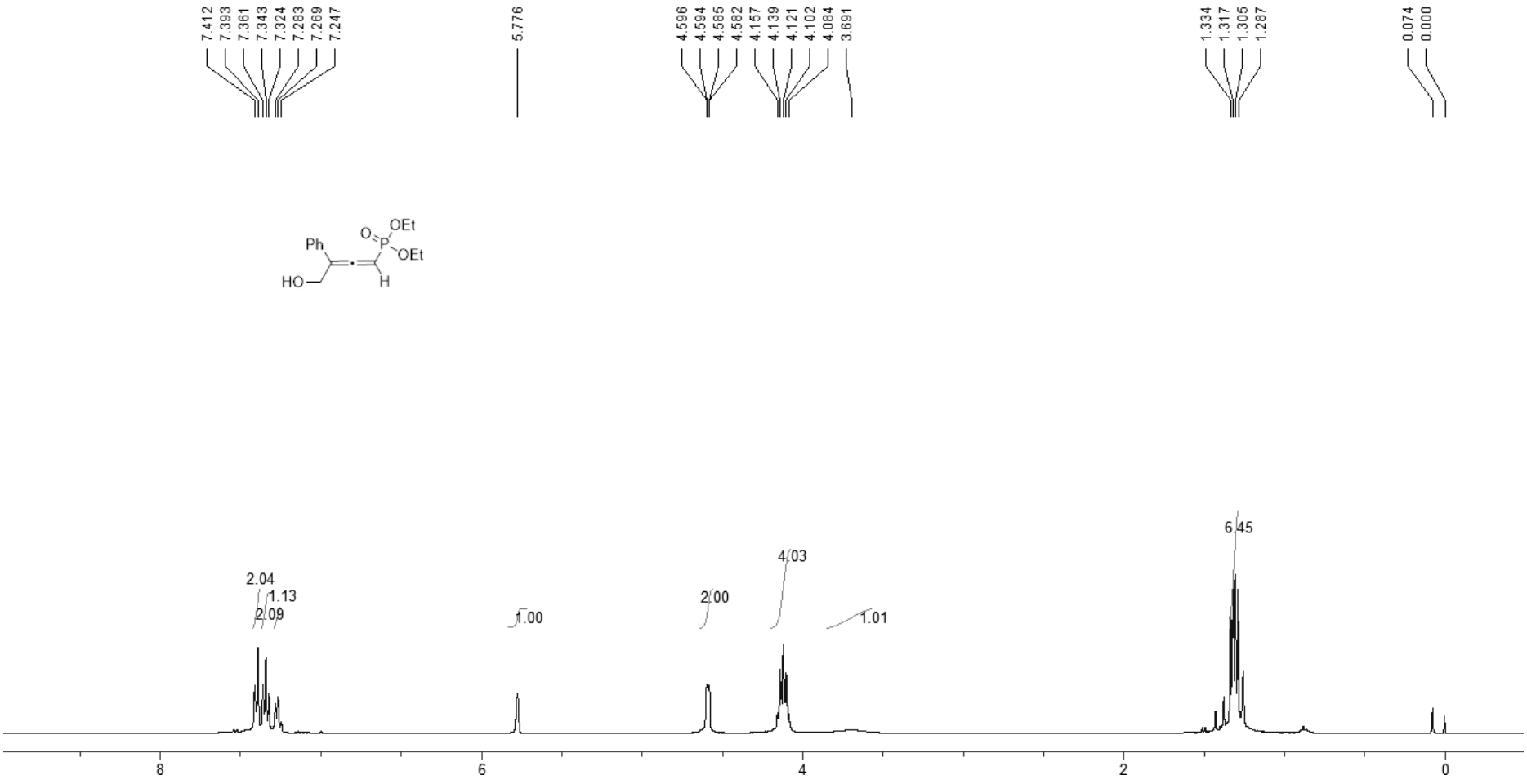


*^{31}P NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3f**)*
$CDCl_3$, 162 MHz



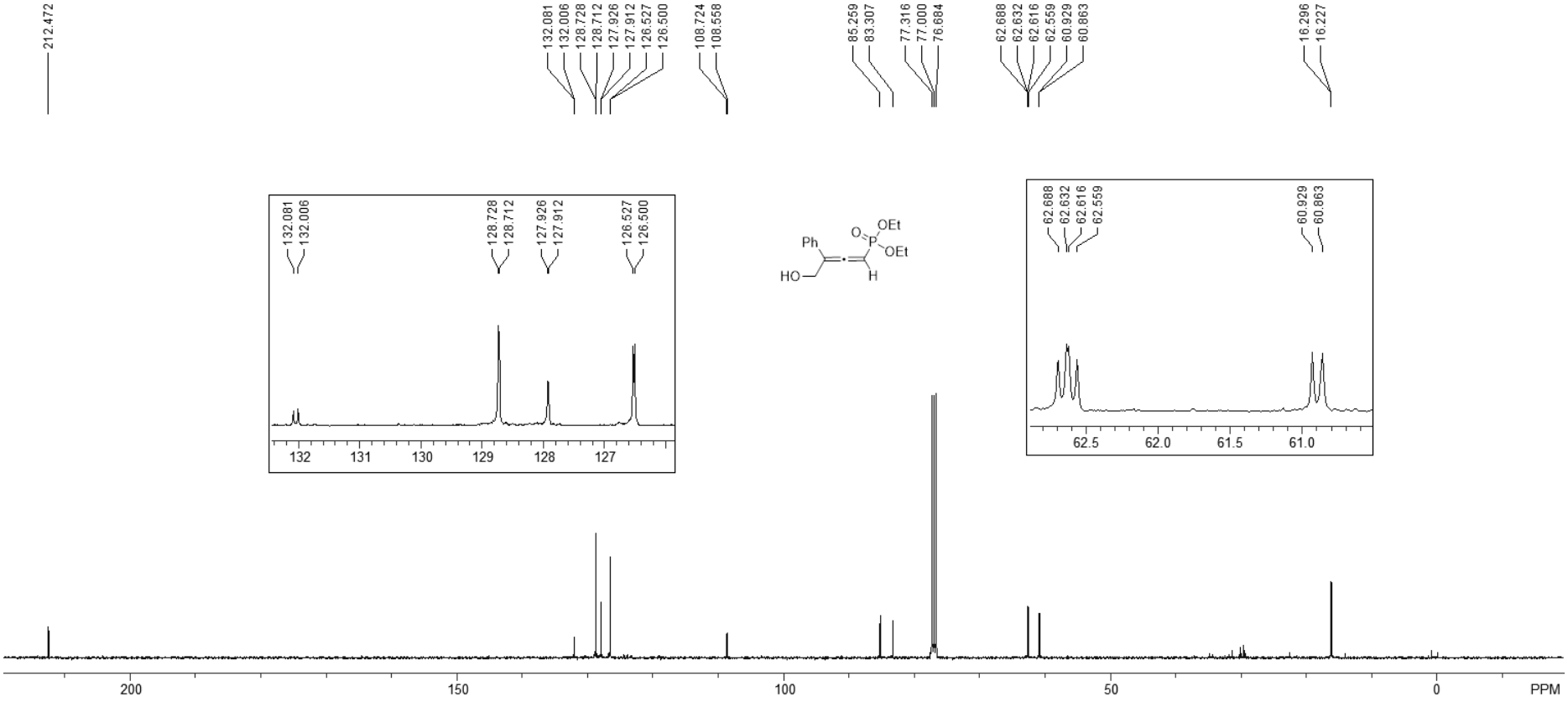
*^{1}H NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 400 MHz



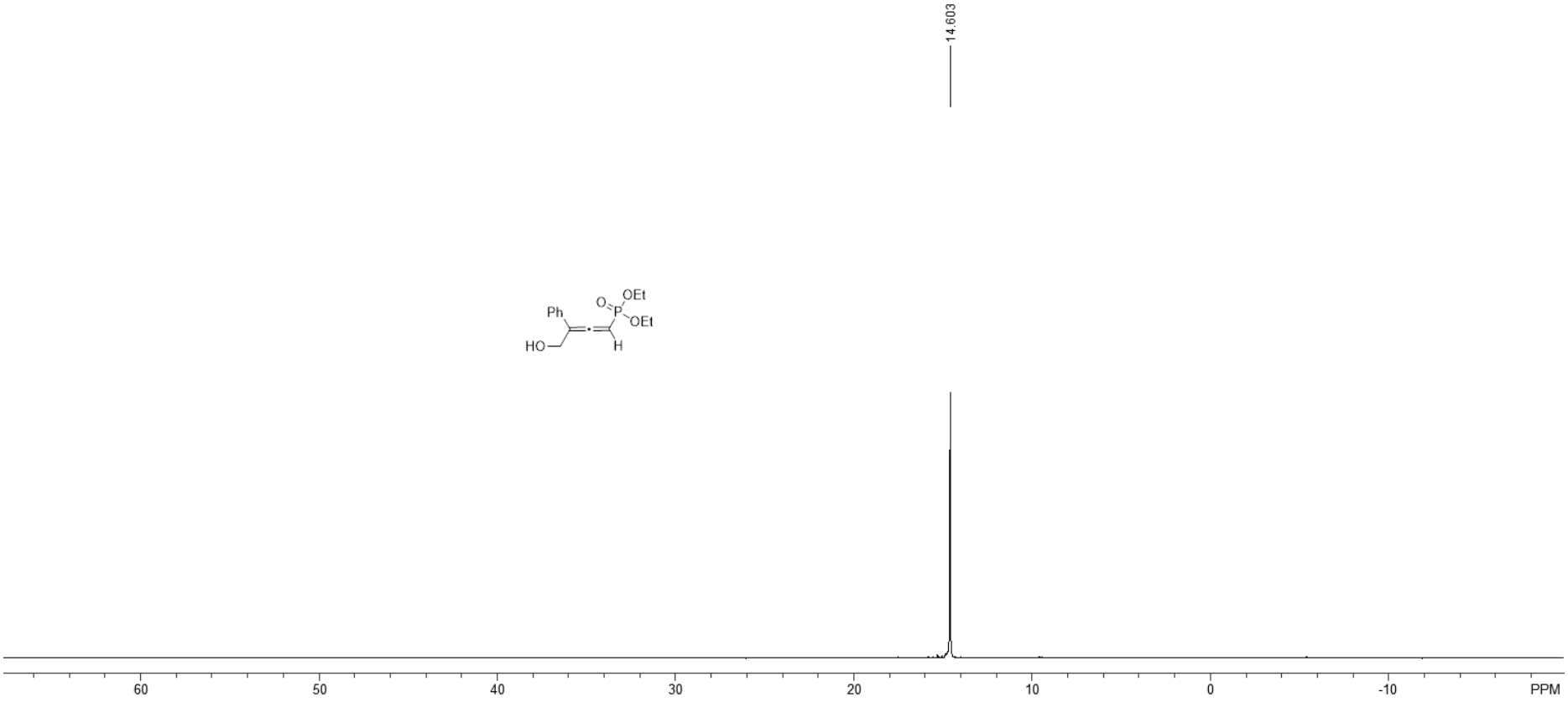
*^{13}C NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 100 MHz

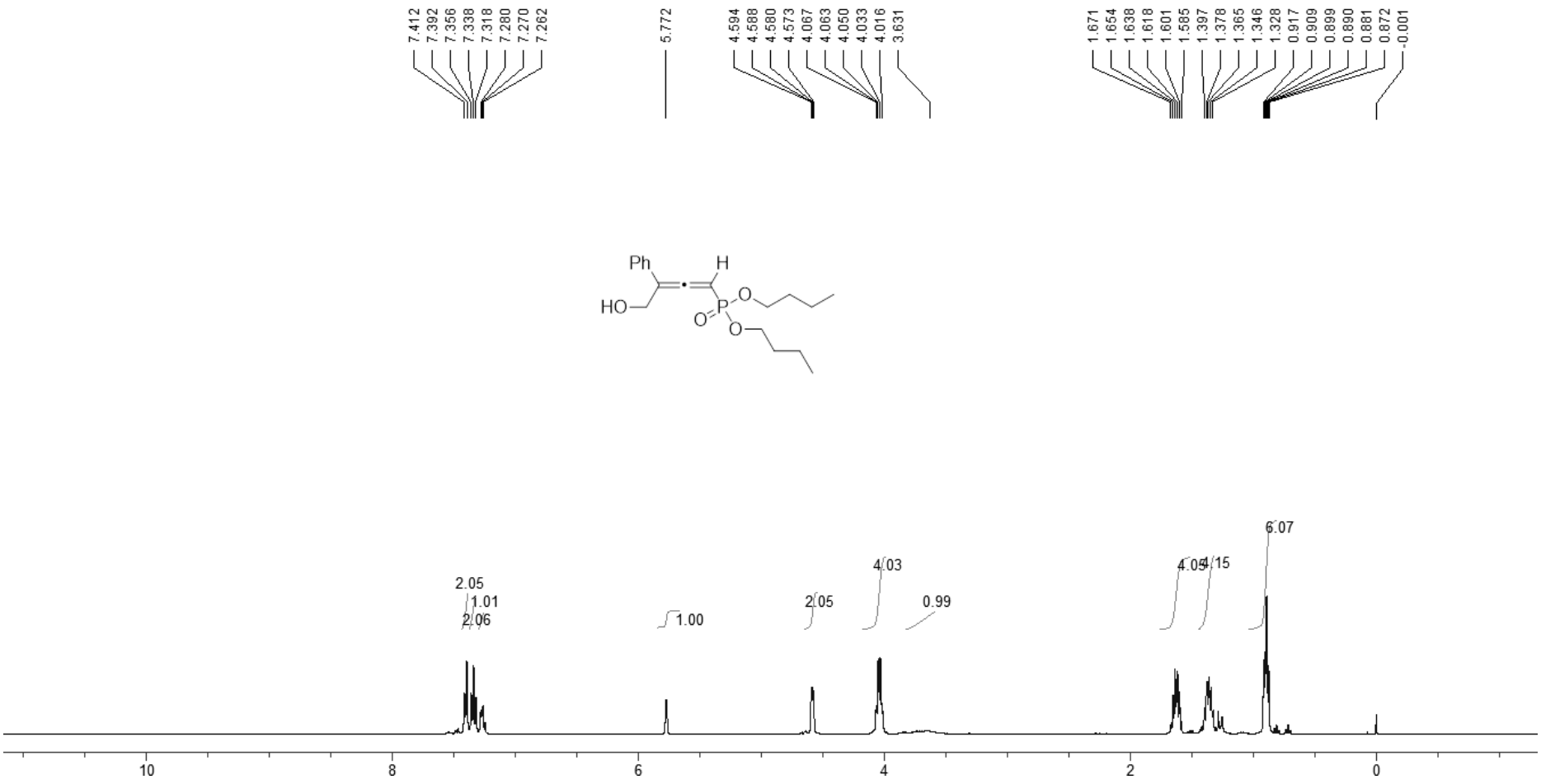


*^{31}P NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 162 MHz

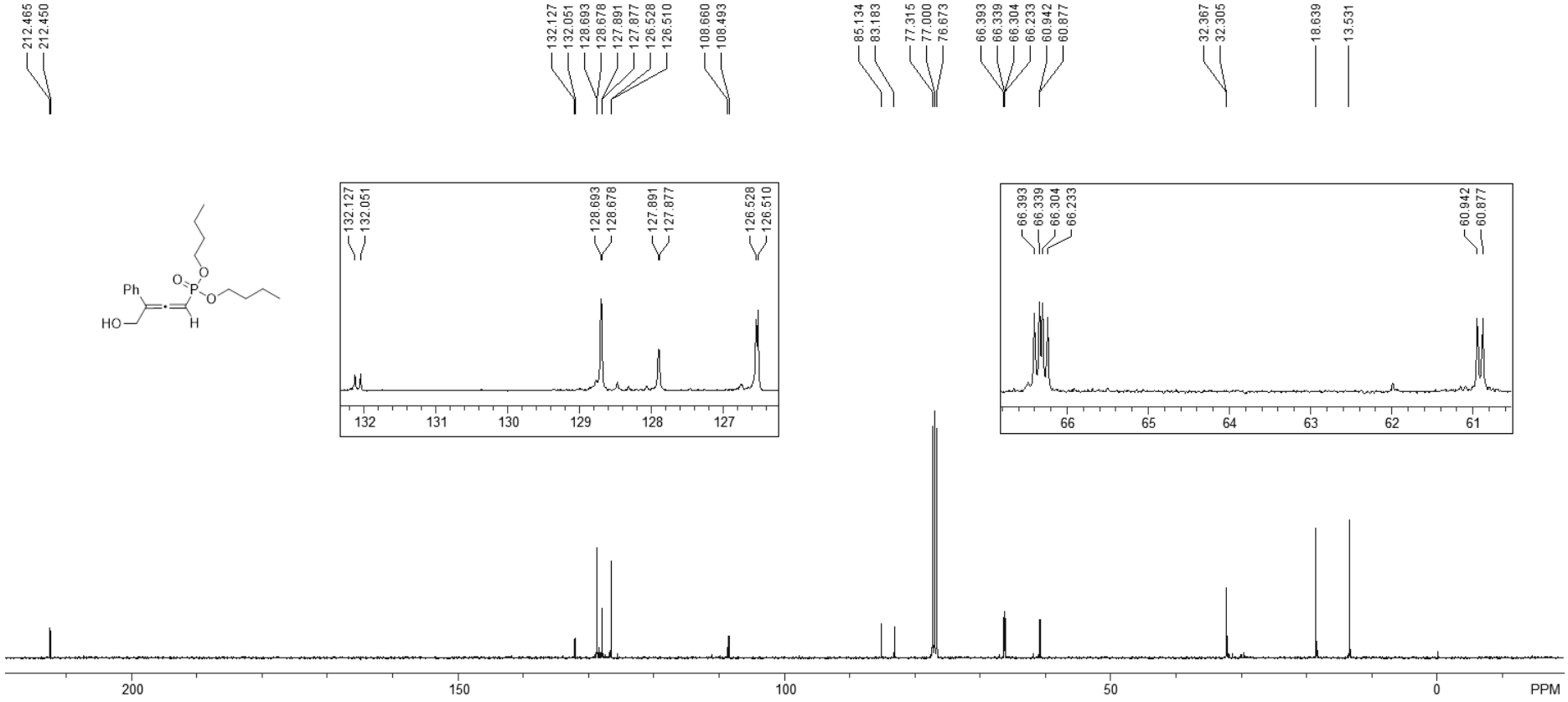


*^{1}H NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3h**)*
$CDCl_3$, 400 MHz



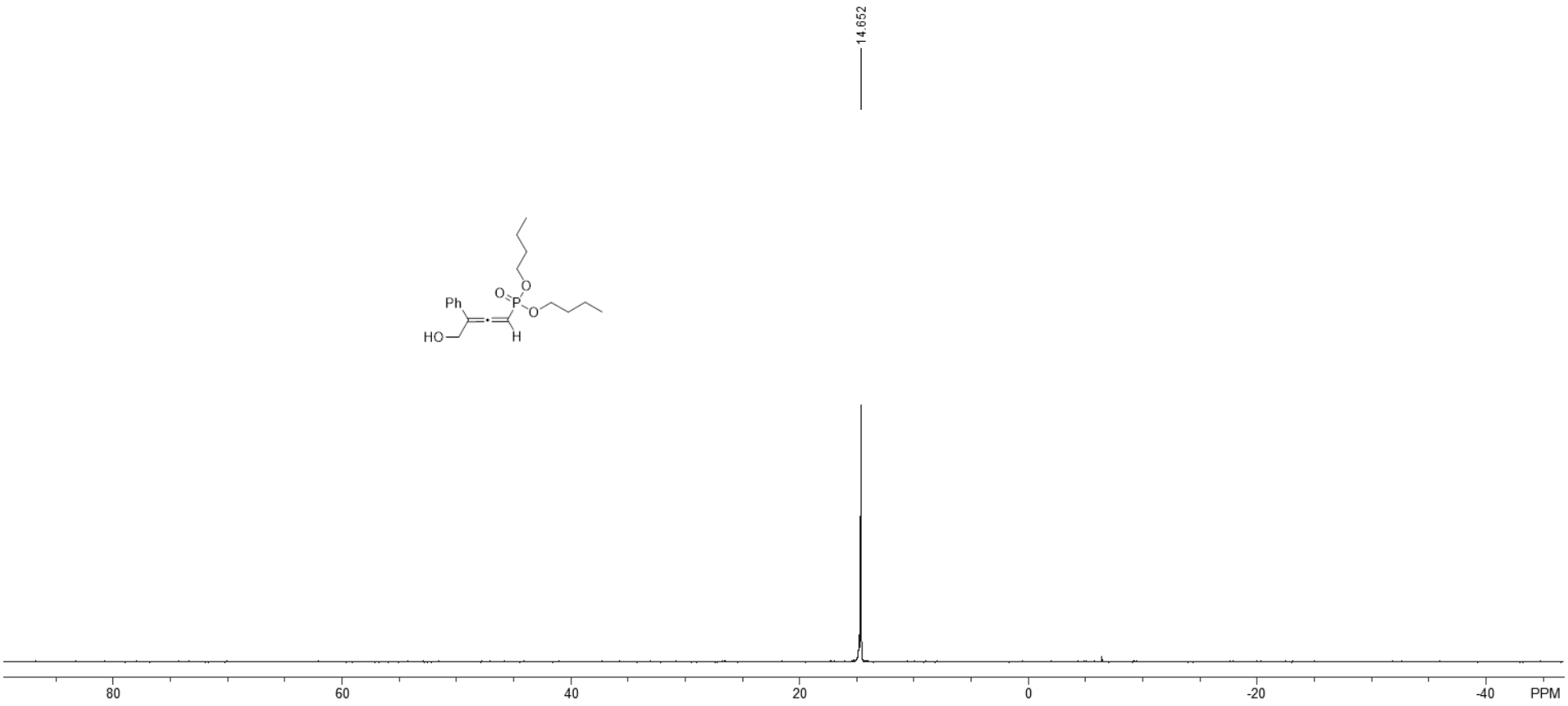
*^{13}C NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3h**)*

$CDCl_3$, 100 MHz

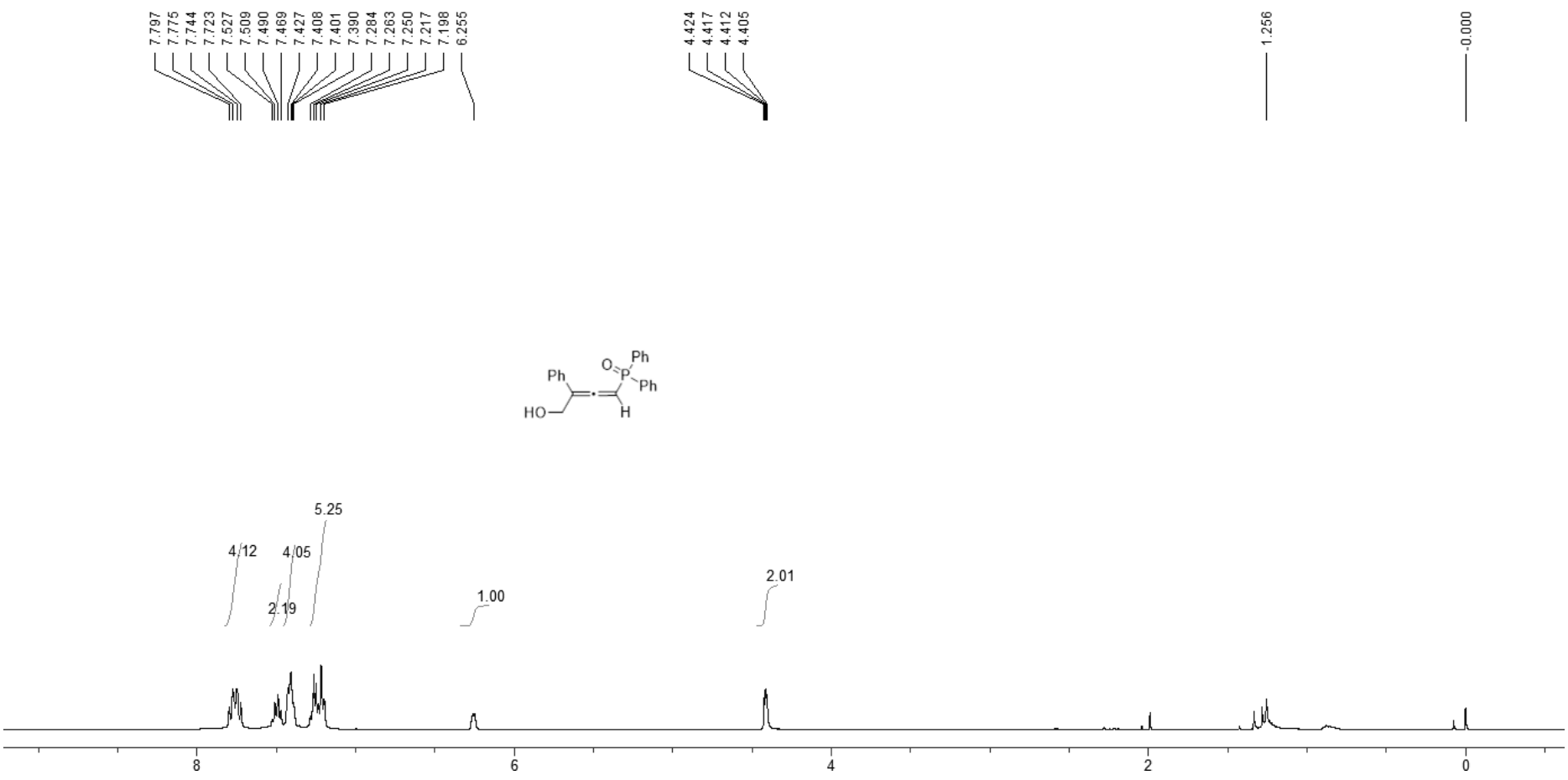


*^{31}P NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (**3h**)*

$CDCl_3$, 162 MHz

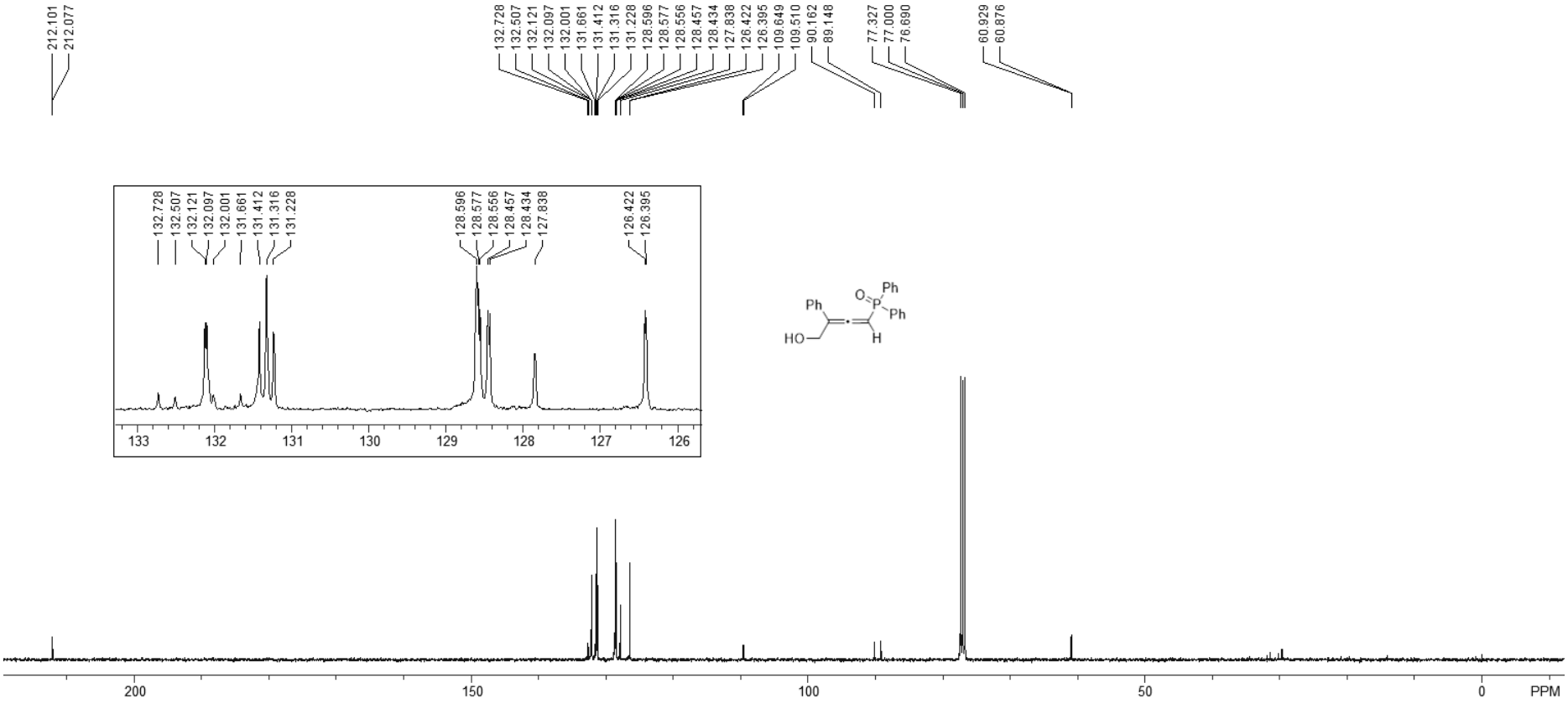


*[1]H NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**3j**)*
$CDCl_3$, 400 MHz



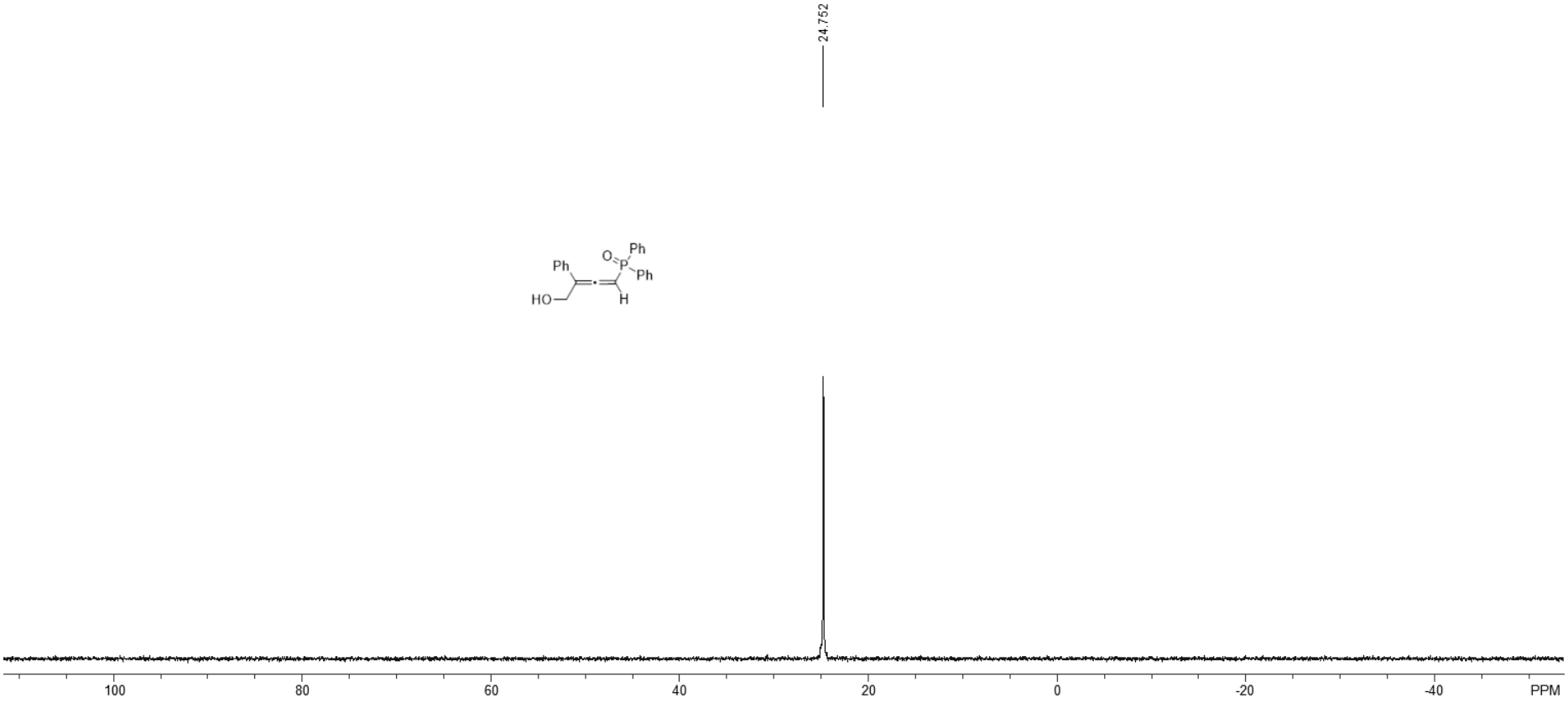
*^{13}C NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**3j**)*

$CDCl_3$, 100 MHz



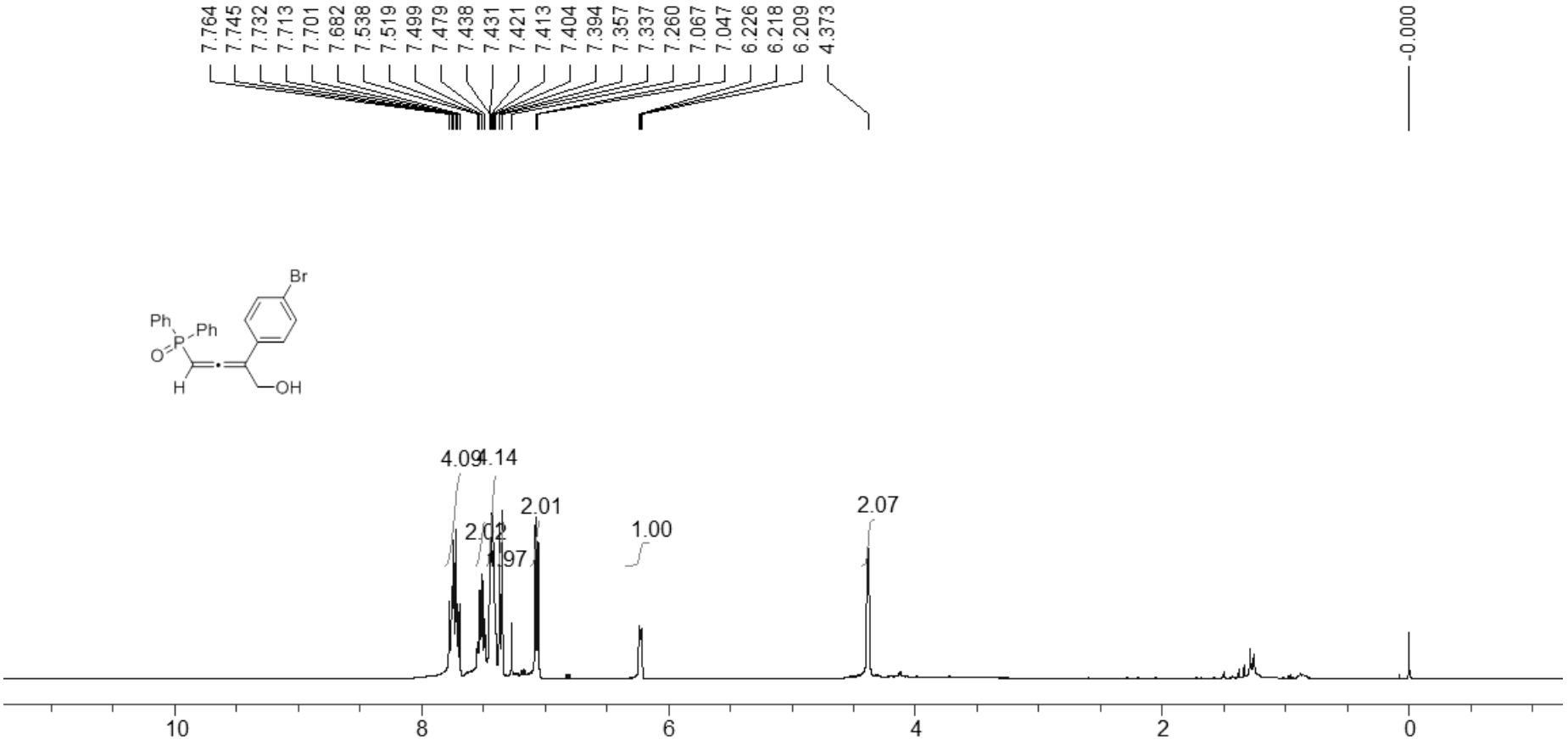
*^{31}P NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**3j**)*

$CDCl_3$, 162 MHz



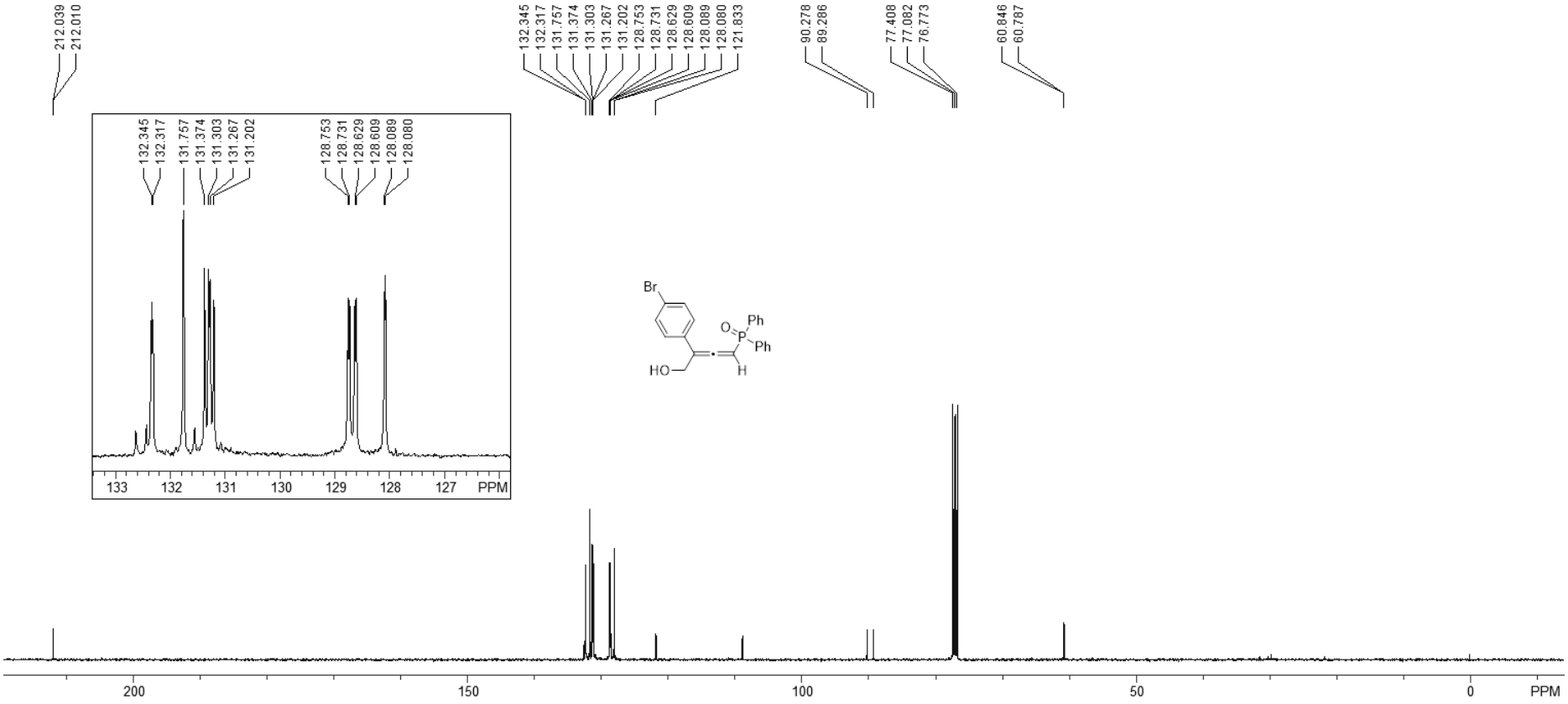
*^{1}H NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (**3k**)*

$CDCl_3$, 400 MHz



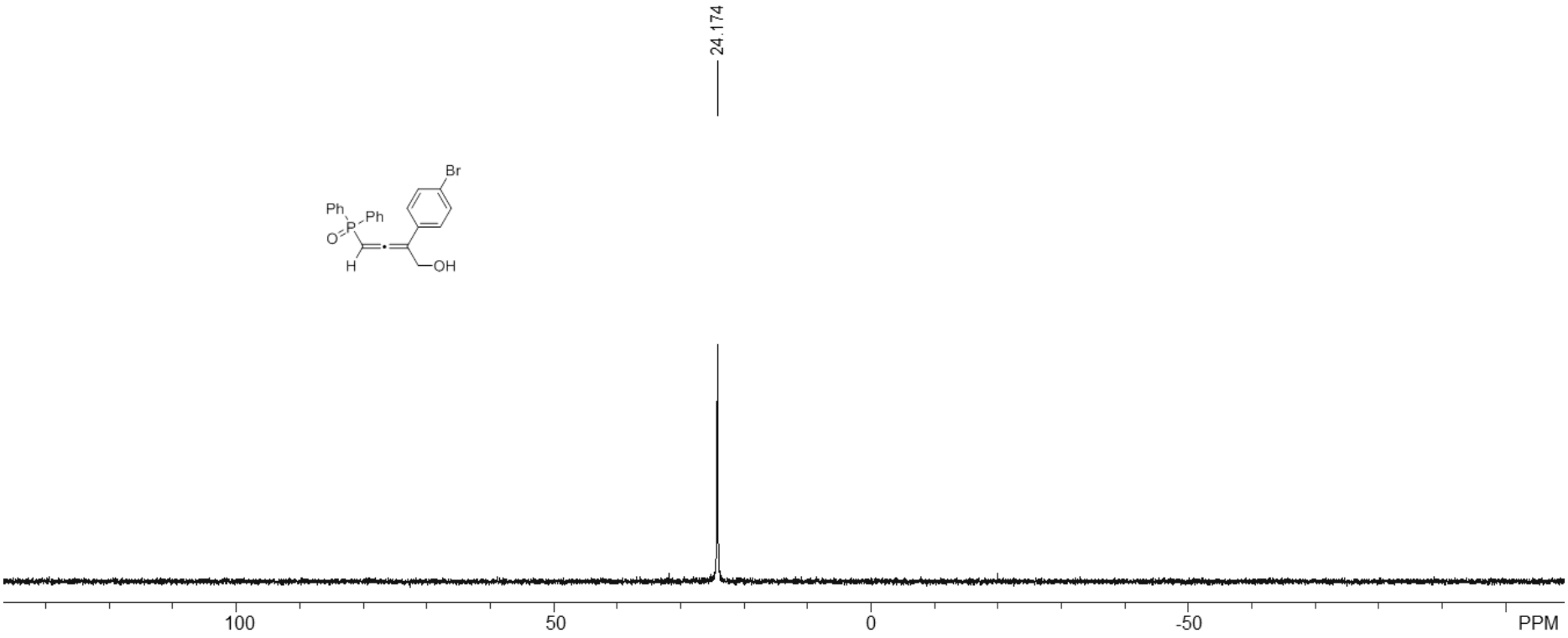
*^{13}C NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (**3k**)*

$CDCl_3$, 100 MHz

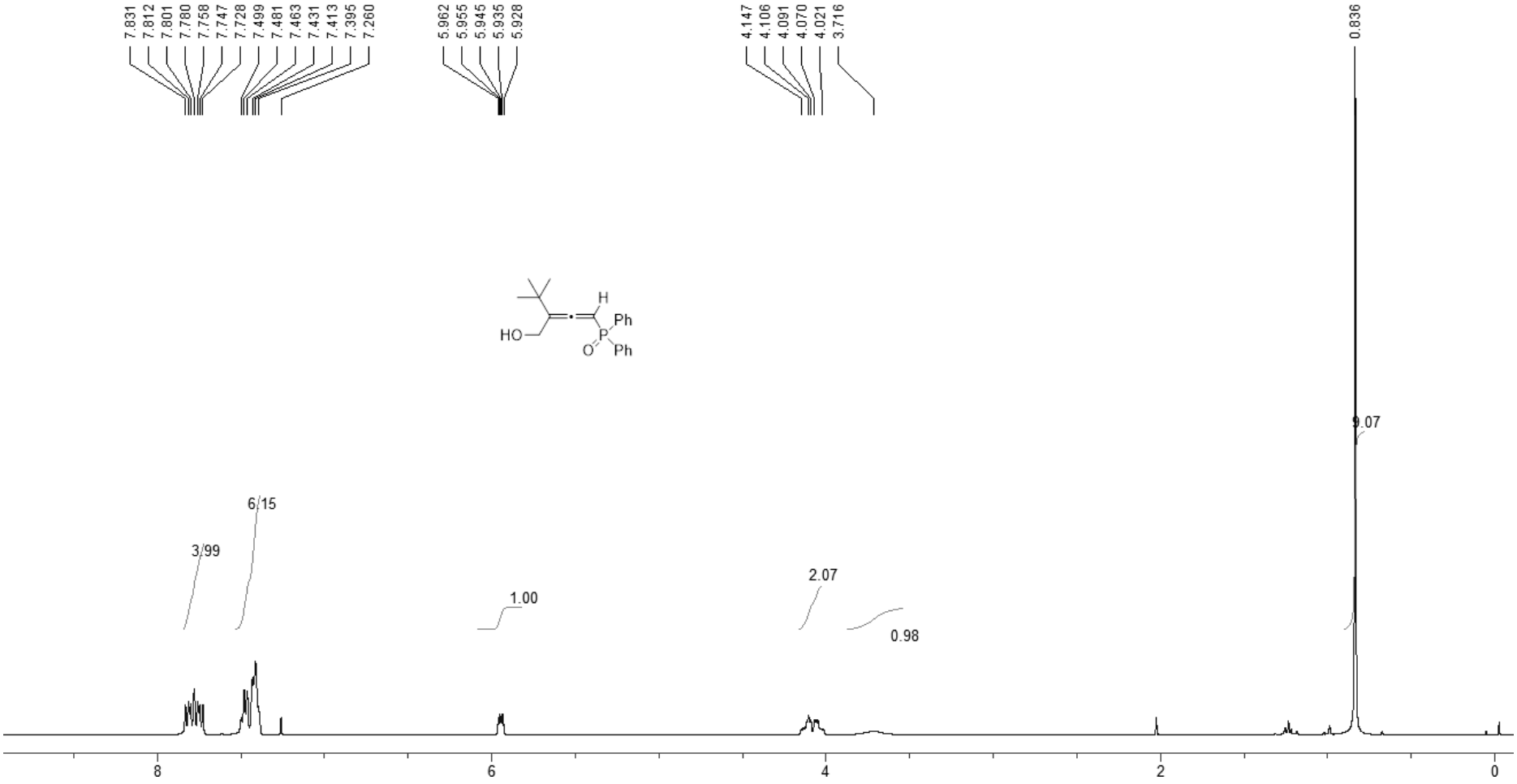


*^{31}P NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (**3k**)*

$CDCl_3$, 162 MHz

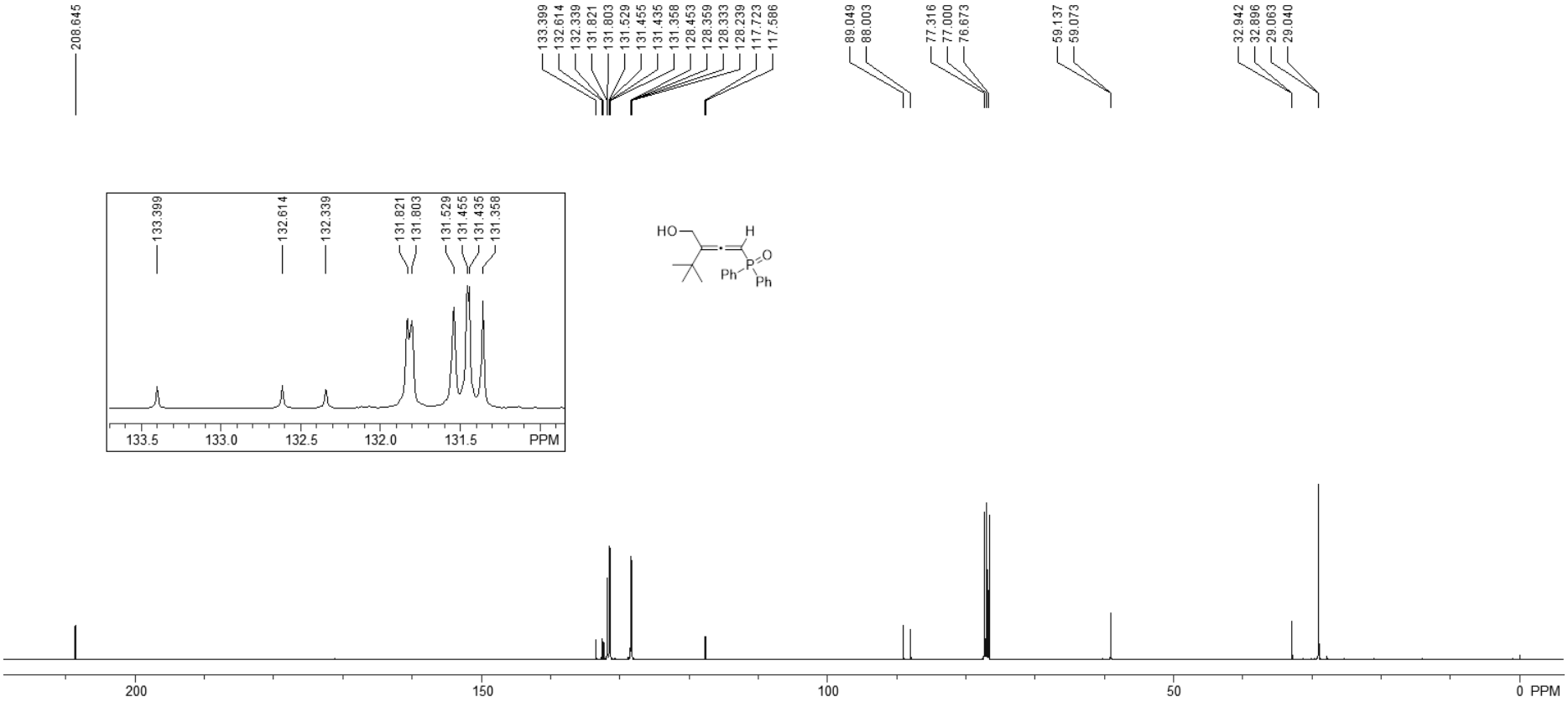


*^{1}H NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**3l**)*
$CDCl_3$, 400 MHz

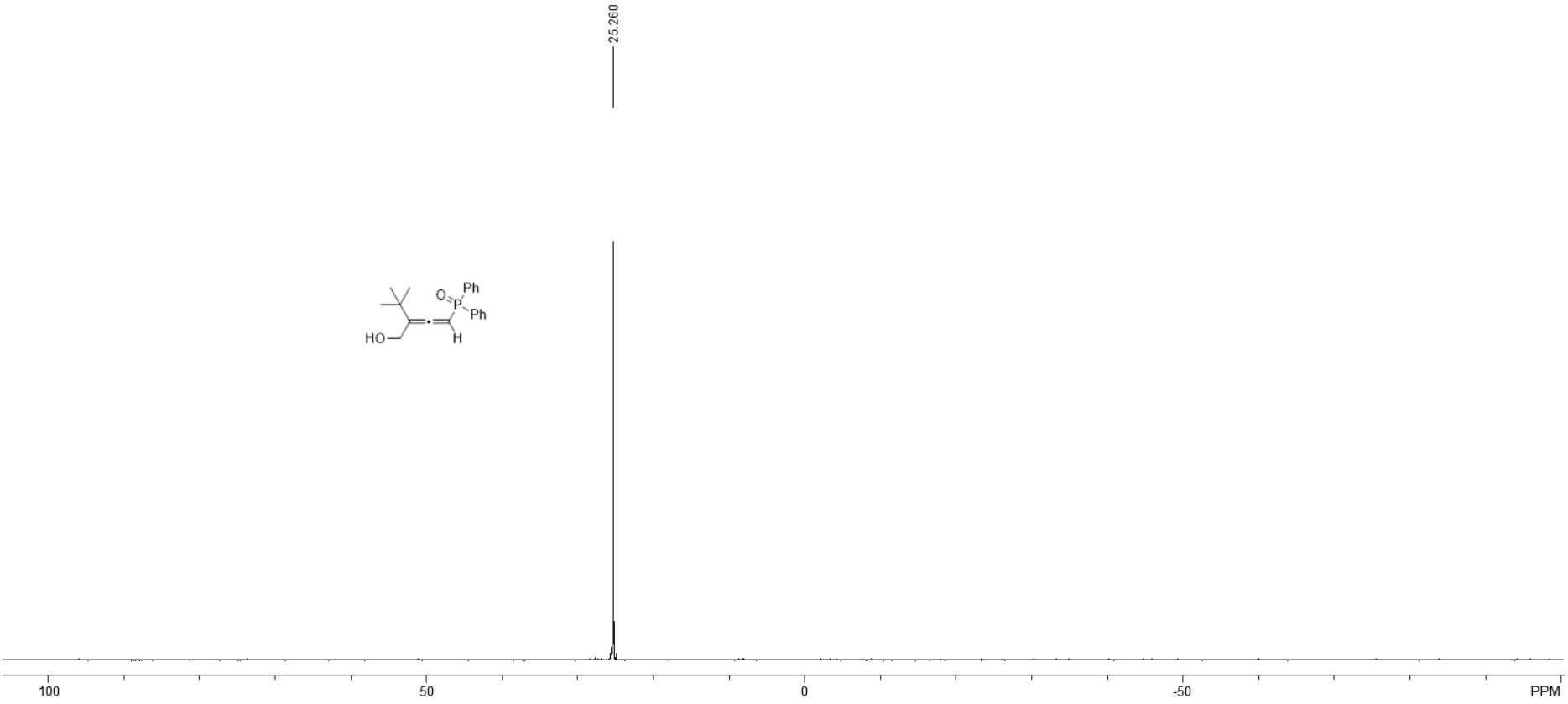


*^{13}C NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**3l**)*

$CDCl_3$, 100 MHz

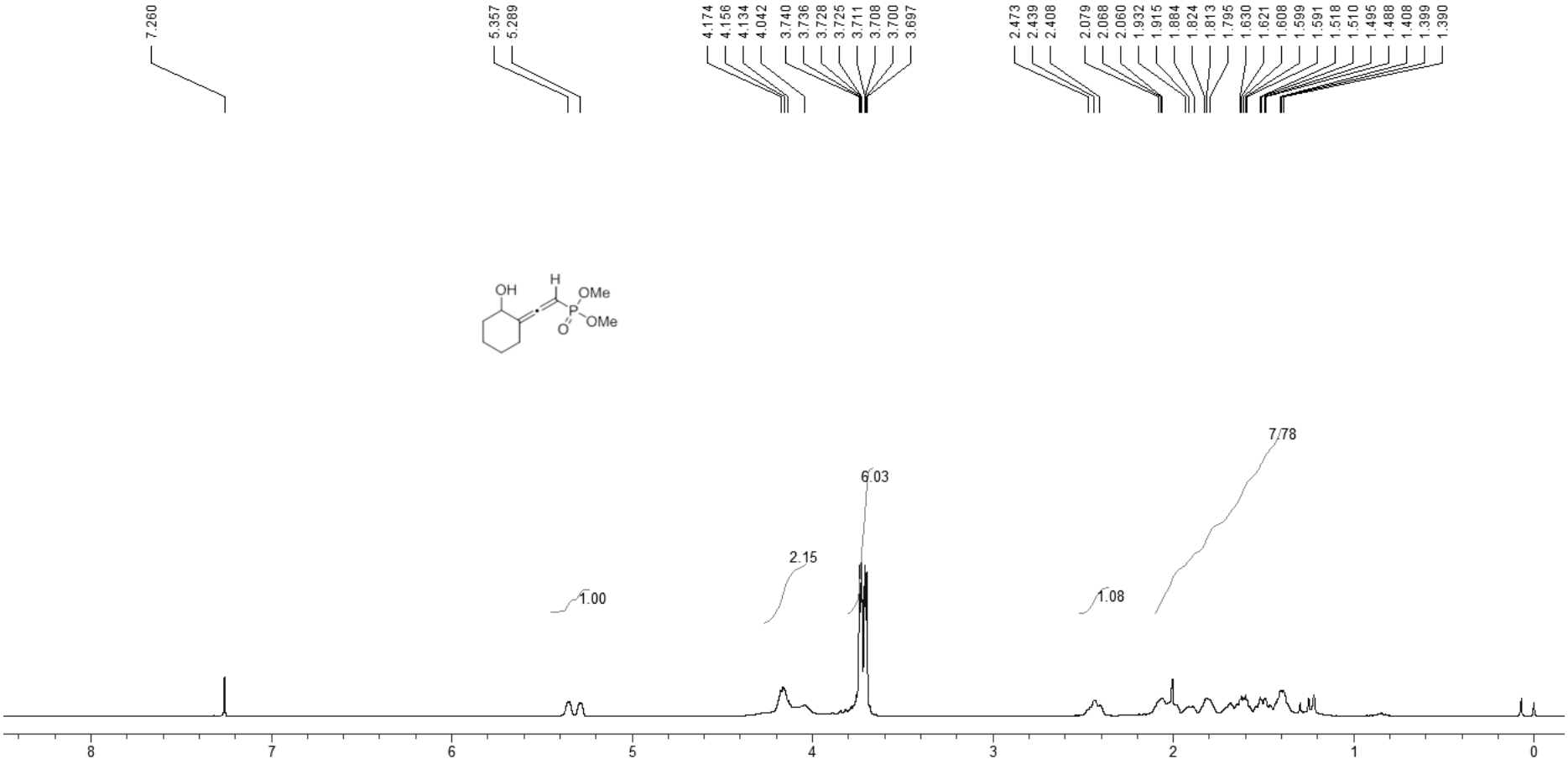


*^{31}P NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**3l**)*
$CDCl_3$, 162 MHz



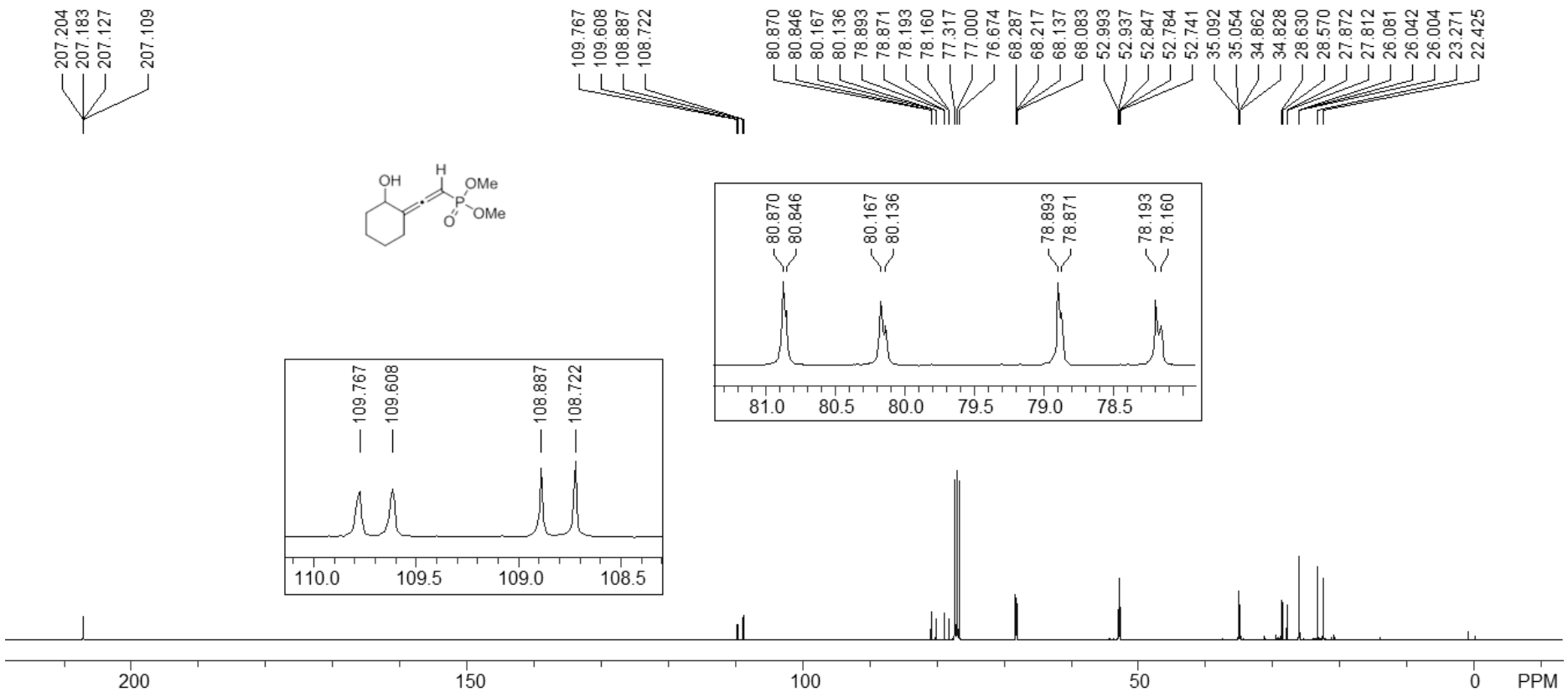
*^{1}H NMR spectrum of dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (**3m**). The compound was obtained as a diastereoisomer mixture.*

$CDCl_3$, 400 MHz



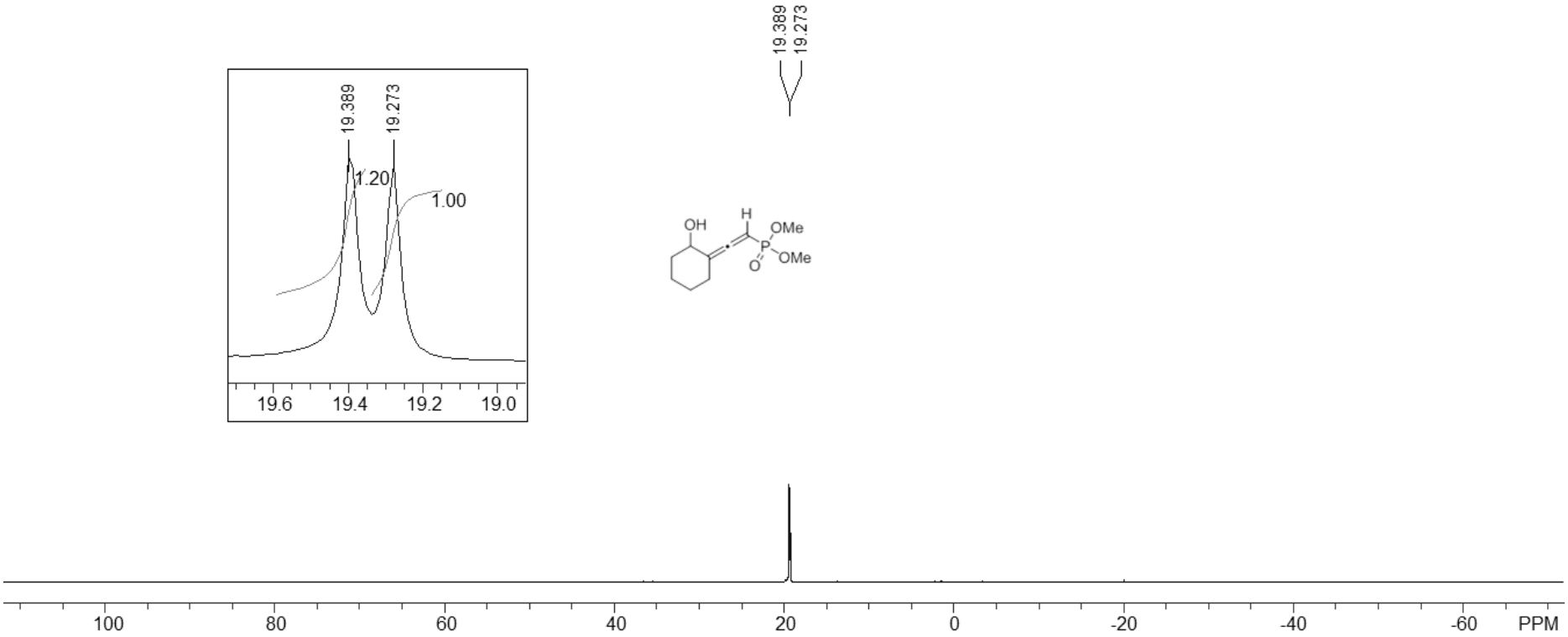
*^{13}C NMR spectrum of dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (**3m**). The compound was obtained as a diastereoisomer mixture.*

$CDCl_3$, 100 MHz



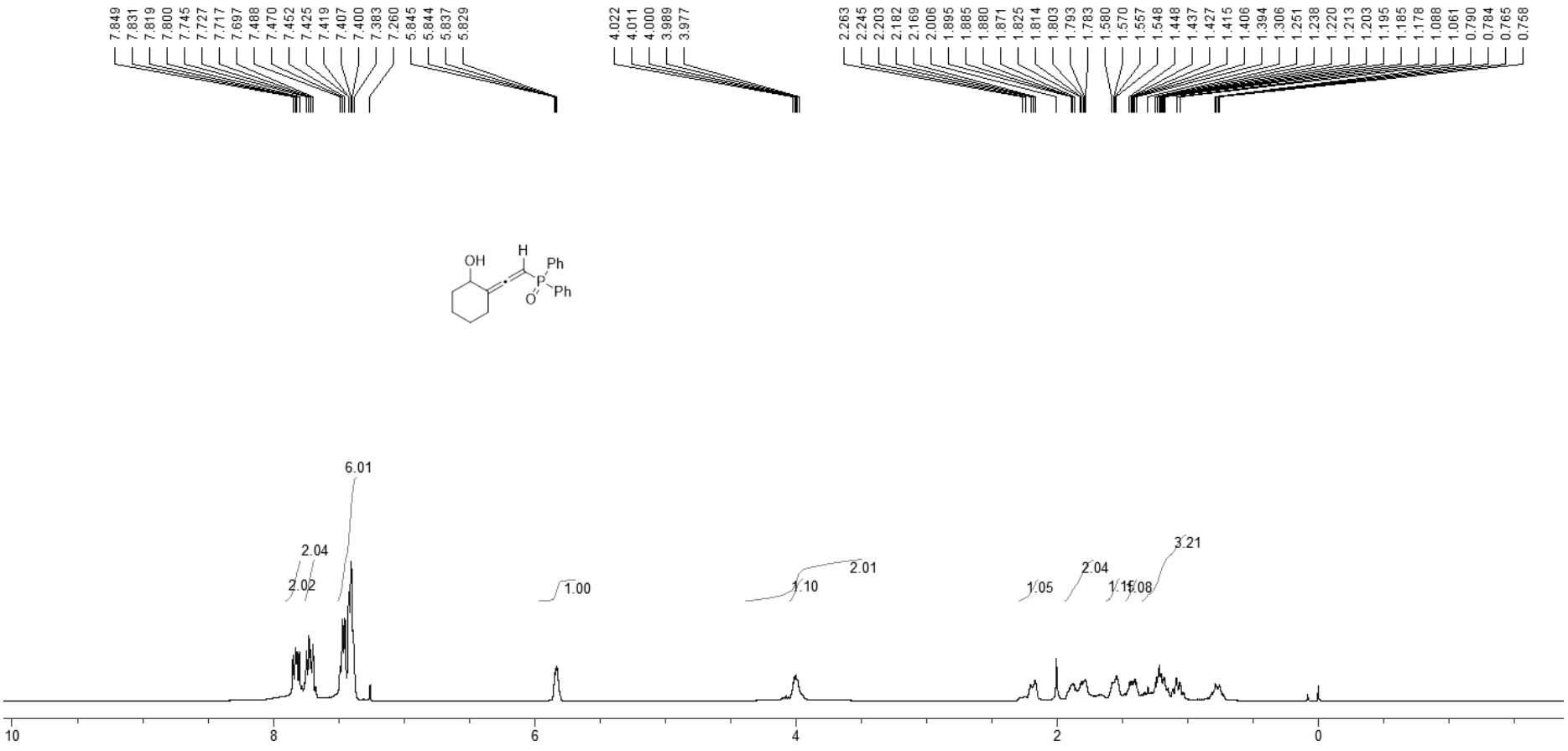
*^{31}P NMR spectrum of dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (**3m**). The compound was obtained as a diastereoisomer mixture.*

$CDCl_3$, 162 MHz



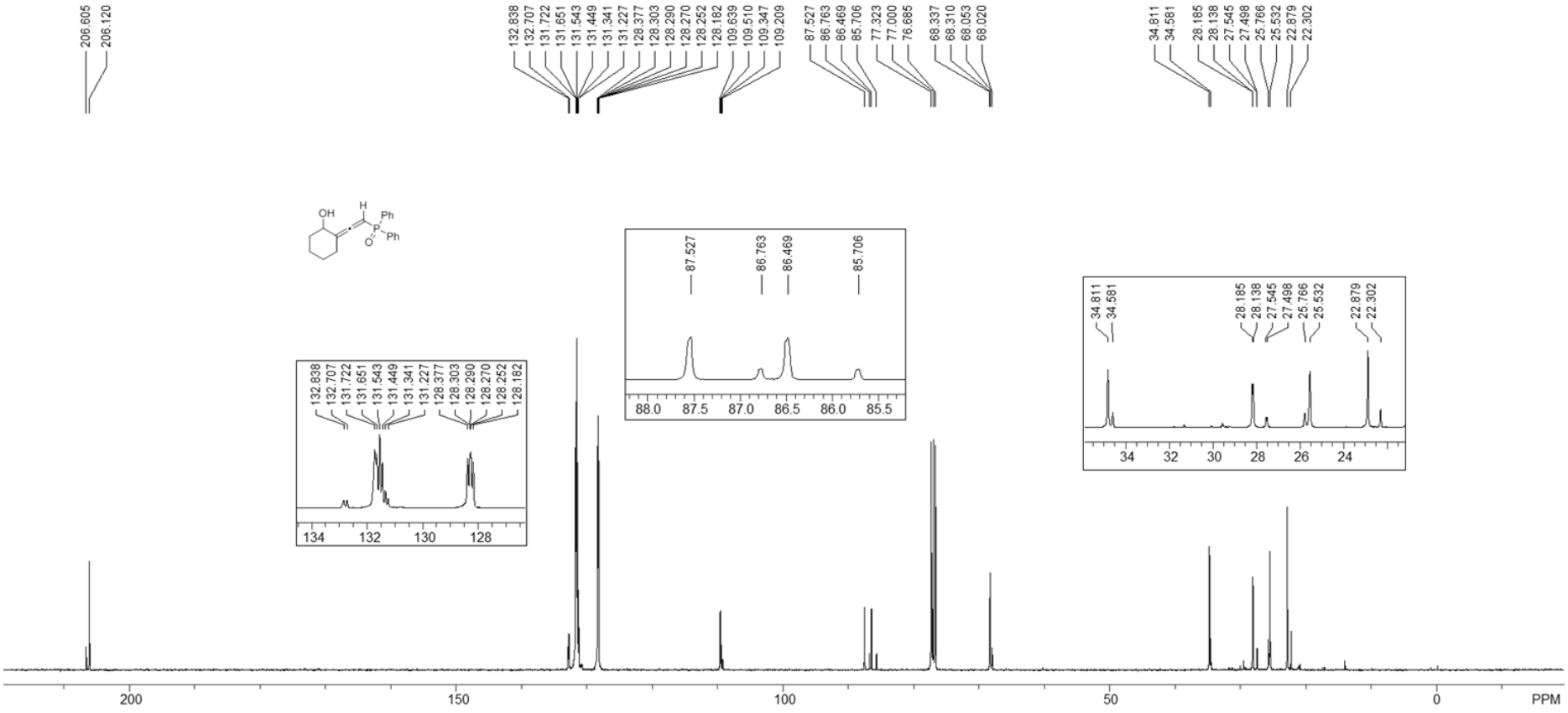
*^{1}H NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (**3n**)*

$CDCl_3$, 400 MHz



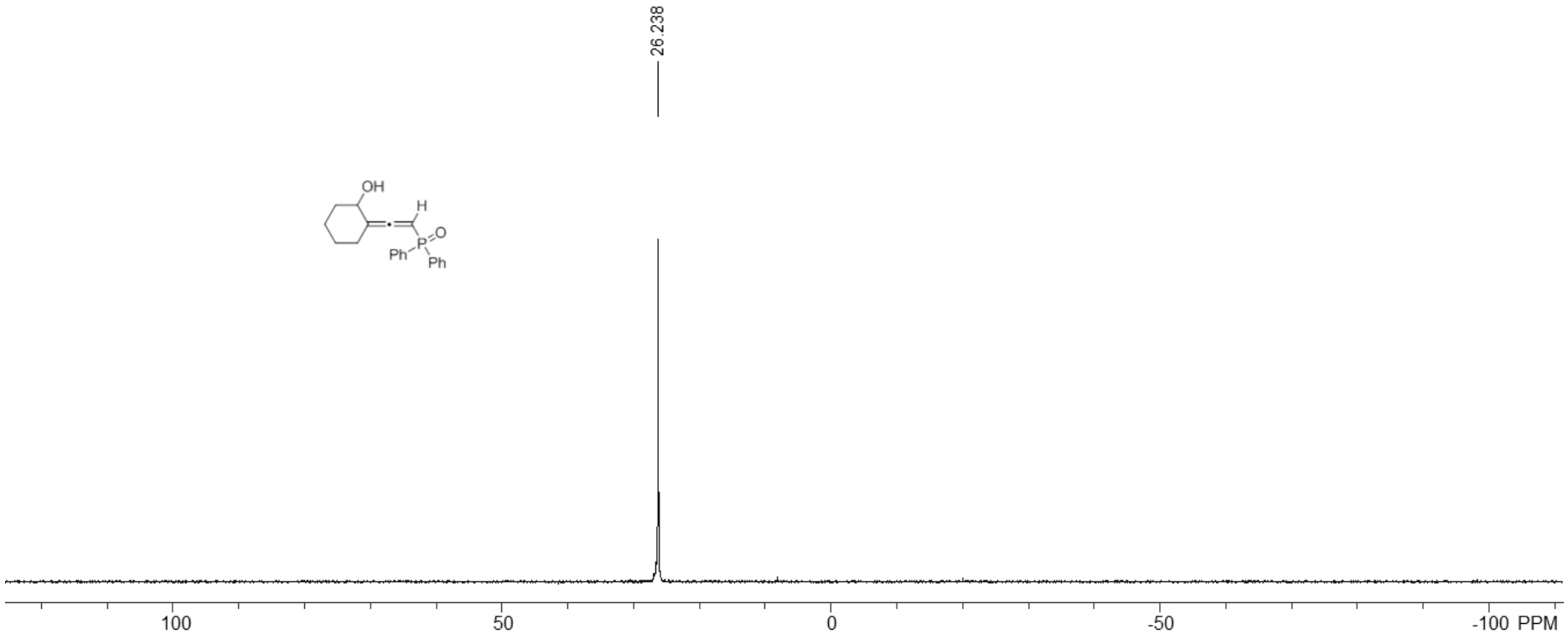
*^{13}C NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (**3n**)*

$CDCl_3$, 100 MHz

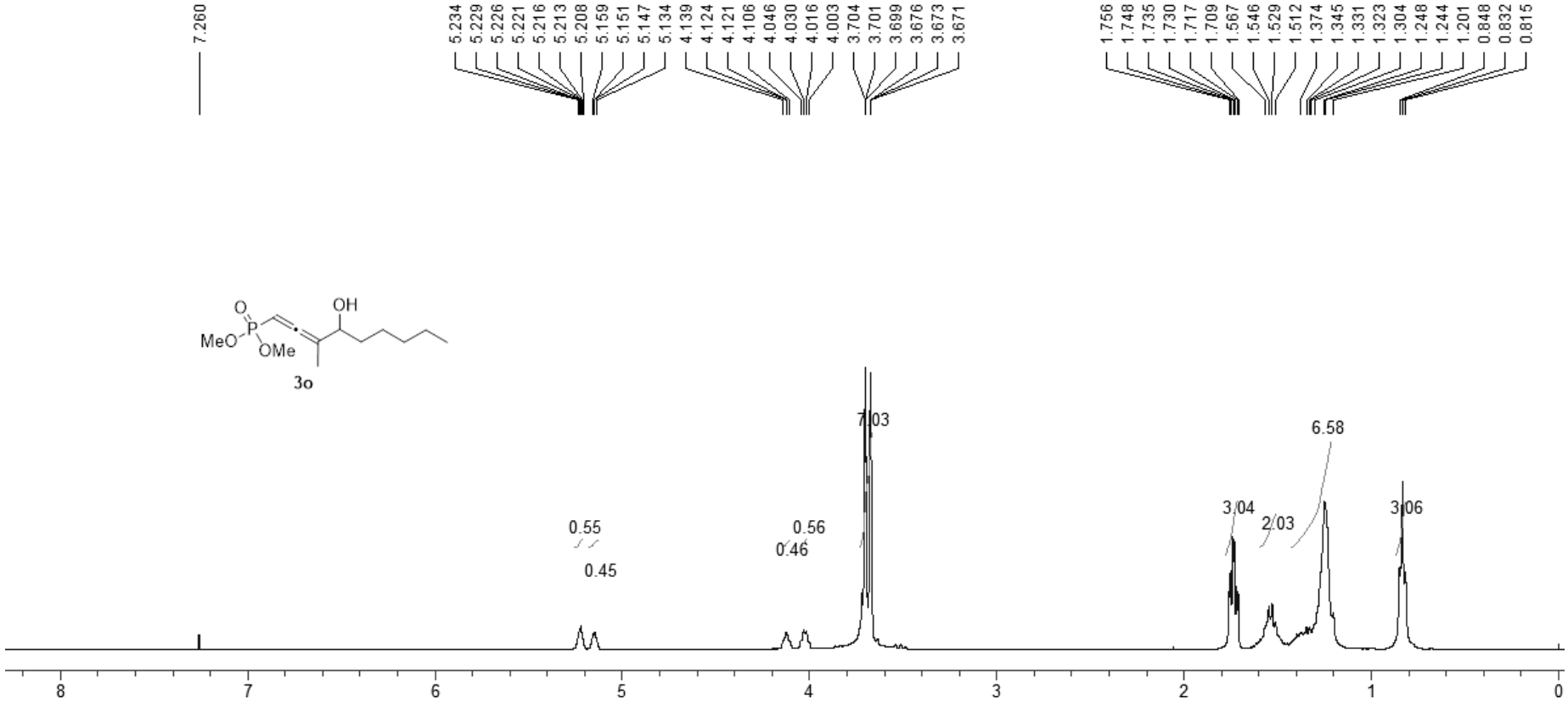


*^{31}P NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (**3n**)*

$CDCl_3$, 162 MHz

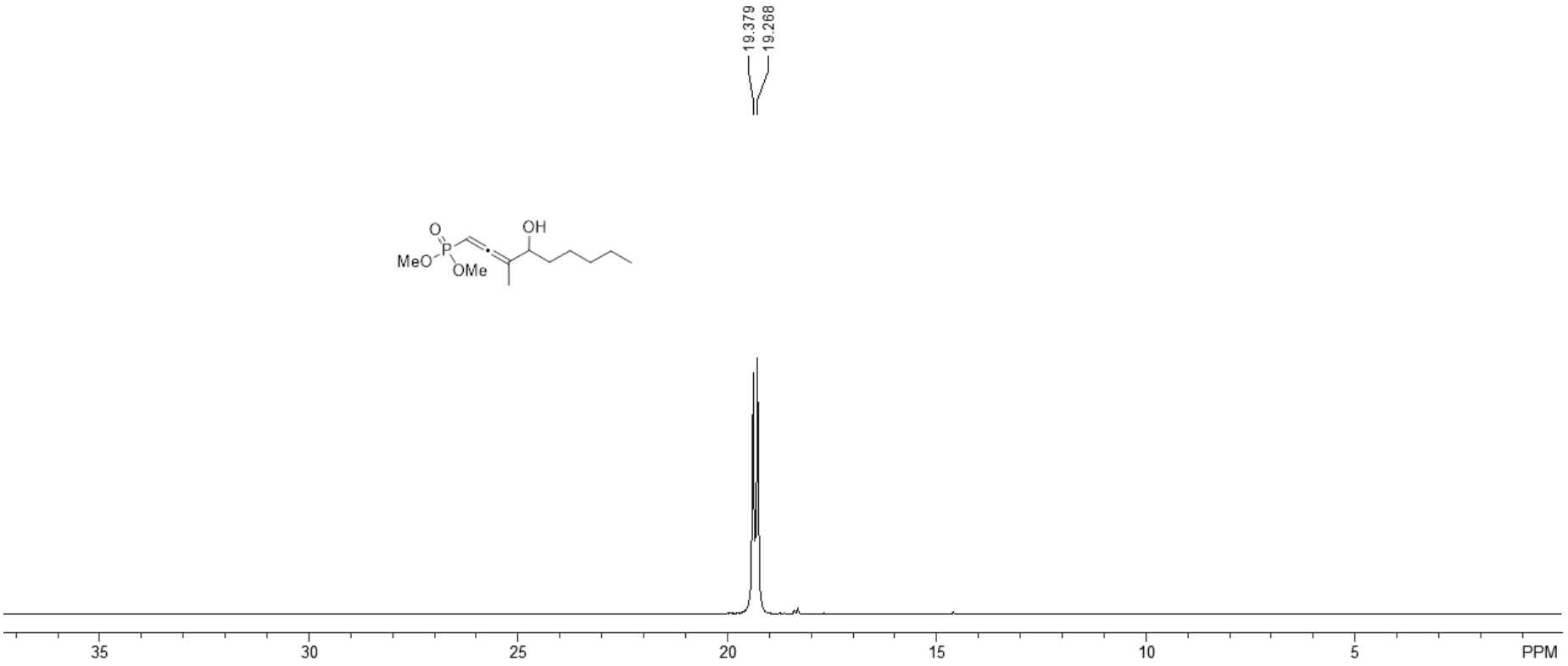


*^{1}H NMR spectrum of dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (**3o**)*
$CDCl_3$, 400 MHz



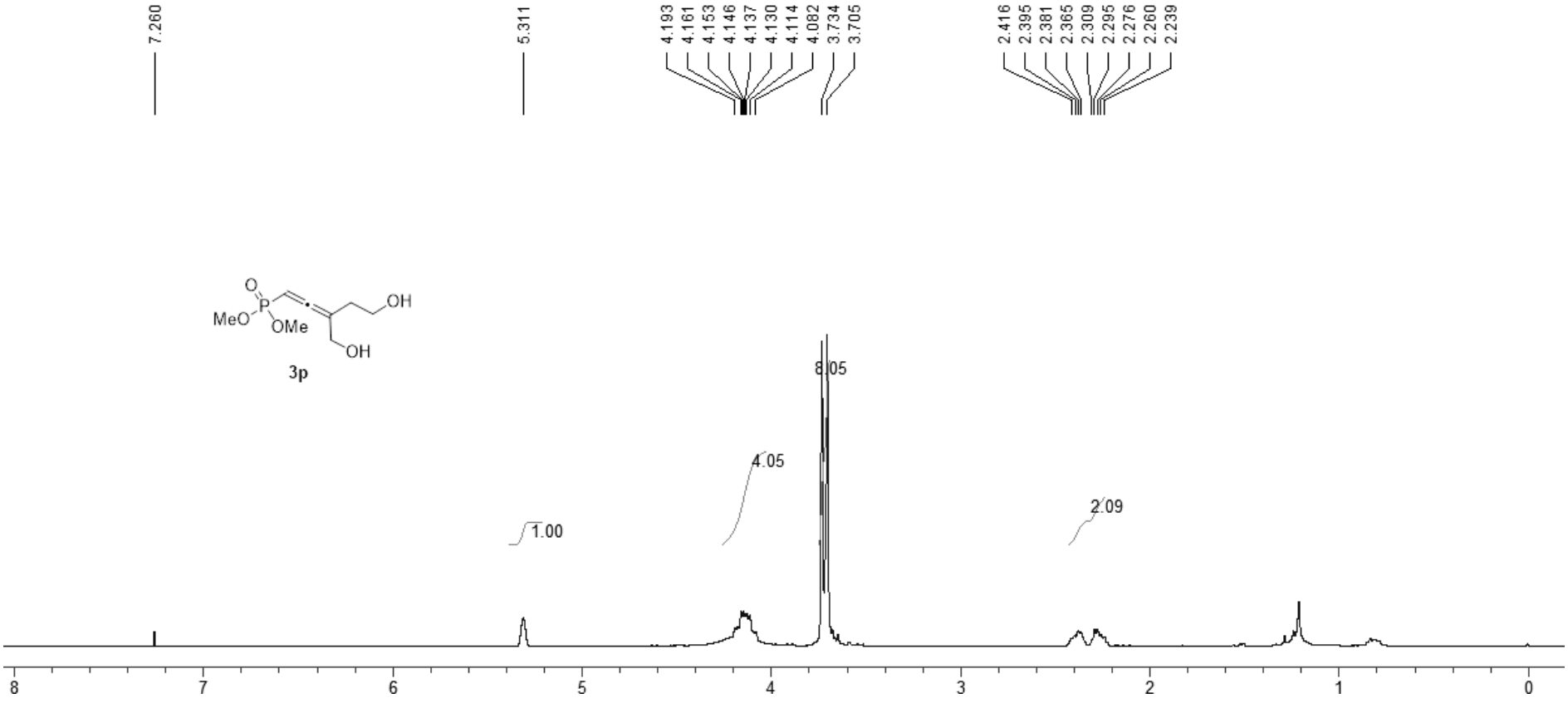
*^{31}P NMR spectrum of dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (**3o**)*

$CDCl_3$, 162 MHz



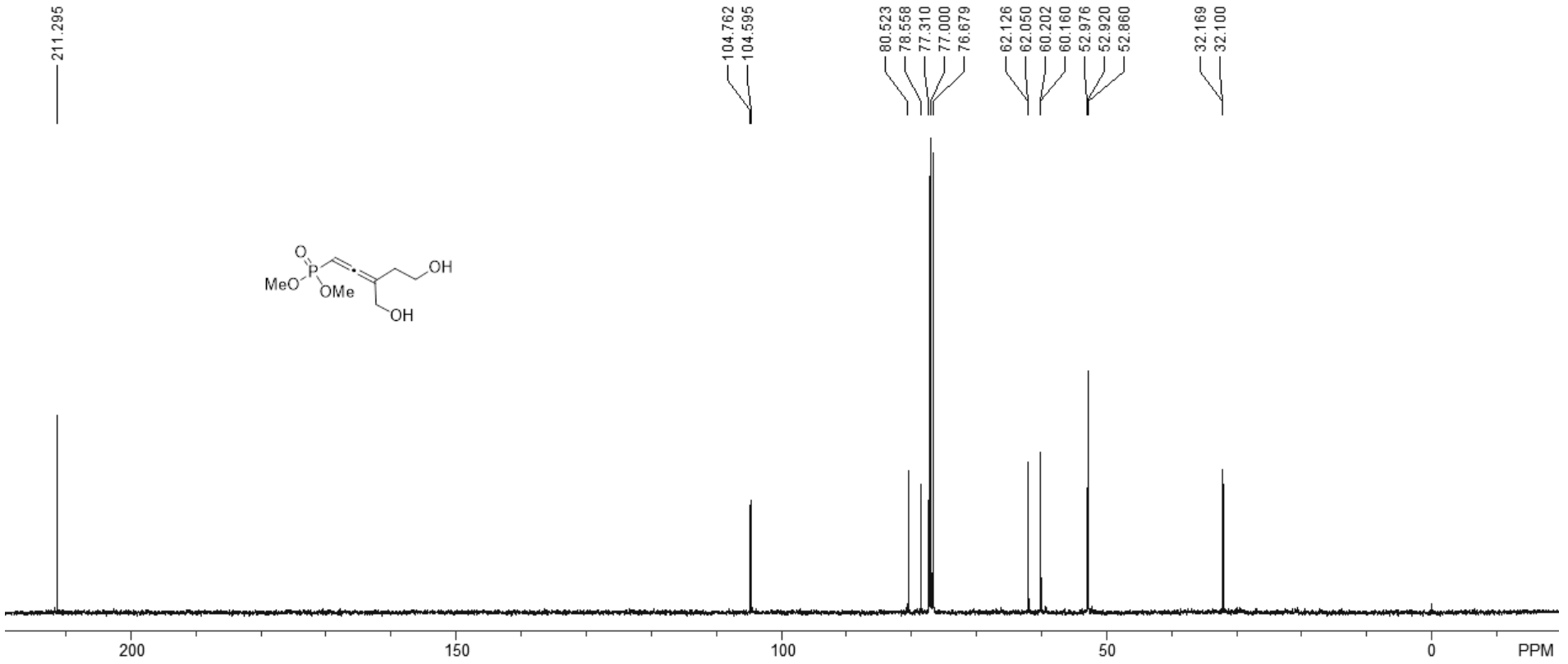
*^{1}H NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (**3p**)*

$CDCl_3$, 400 MHz

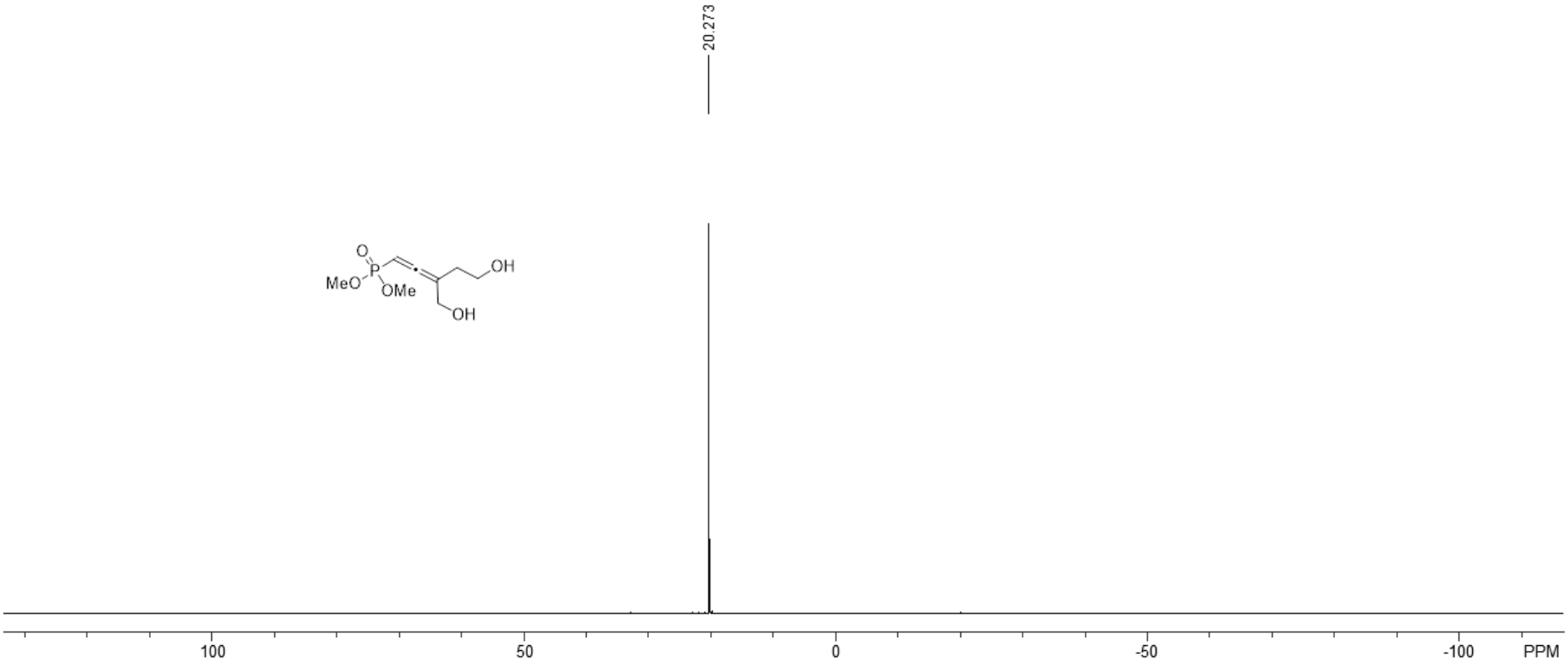


*^{13}C NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (**3p**)*

$CDCl_3$, 400 MHz

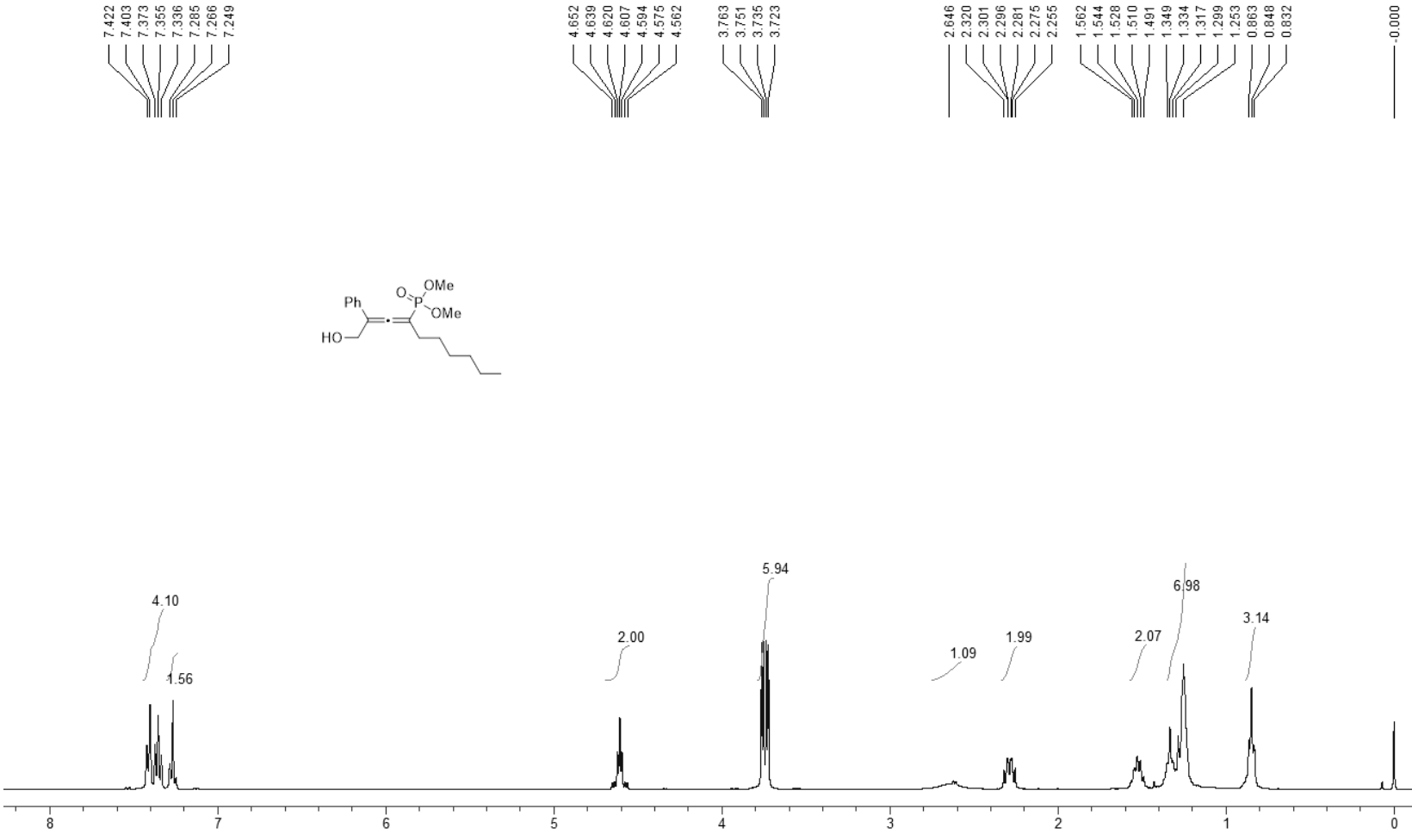


*^{31}P NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (**3p**)*
$CDCl_3$, 162 MHz



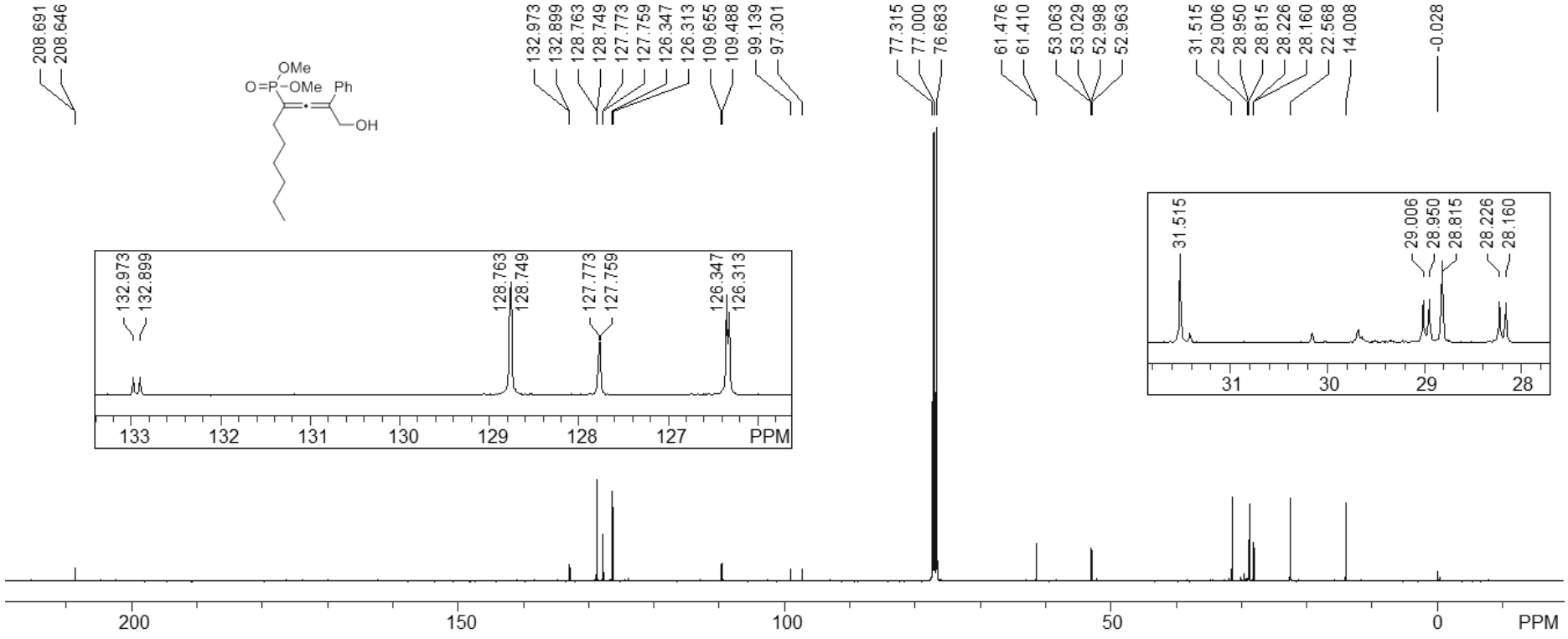
*^{1}H NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (**4a**)*

$CDCl_3$, 400 MHz



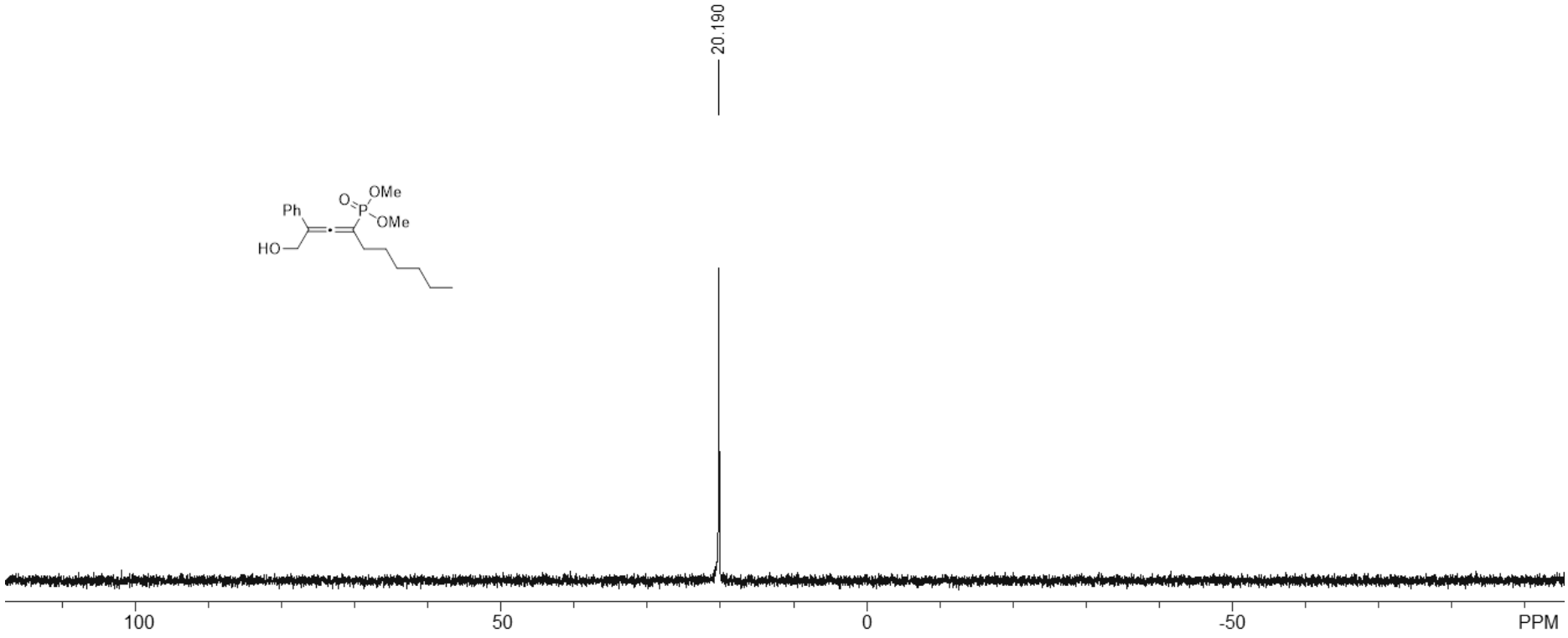
*^{13}C NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (**4a**)*

$CDCl_3$, 100 MHz



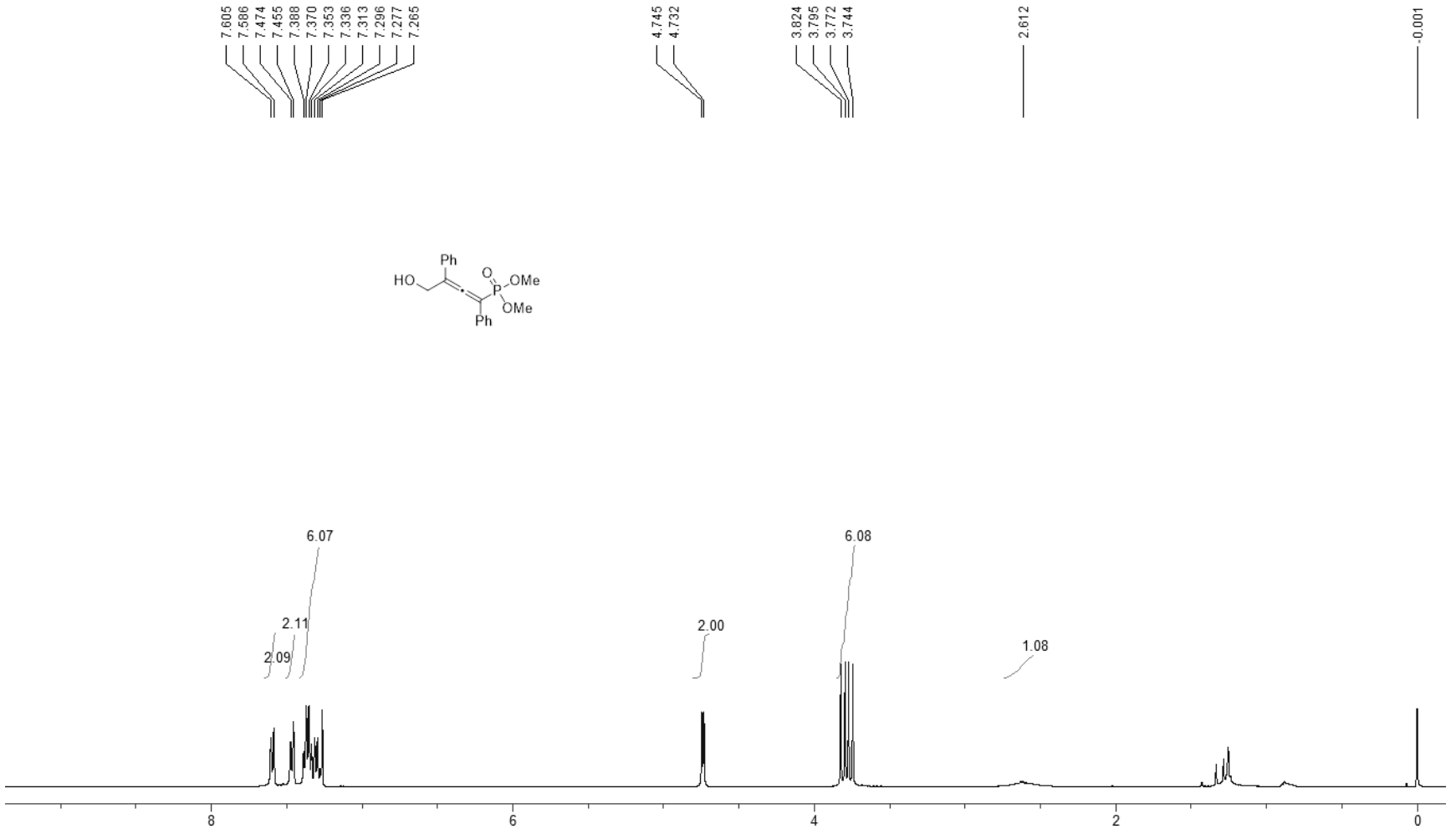
*^{31}P NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (**4a**)*

$CDCl_3$, 160 MHz



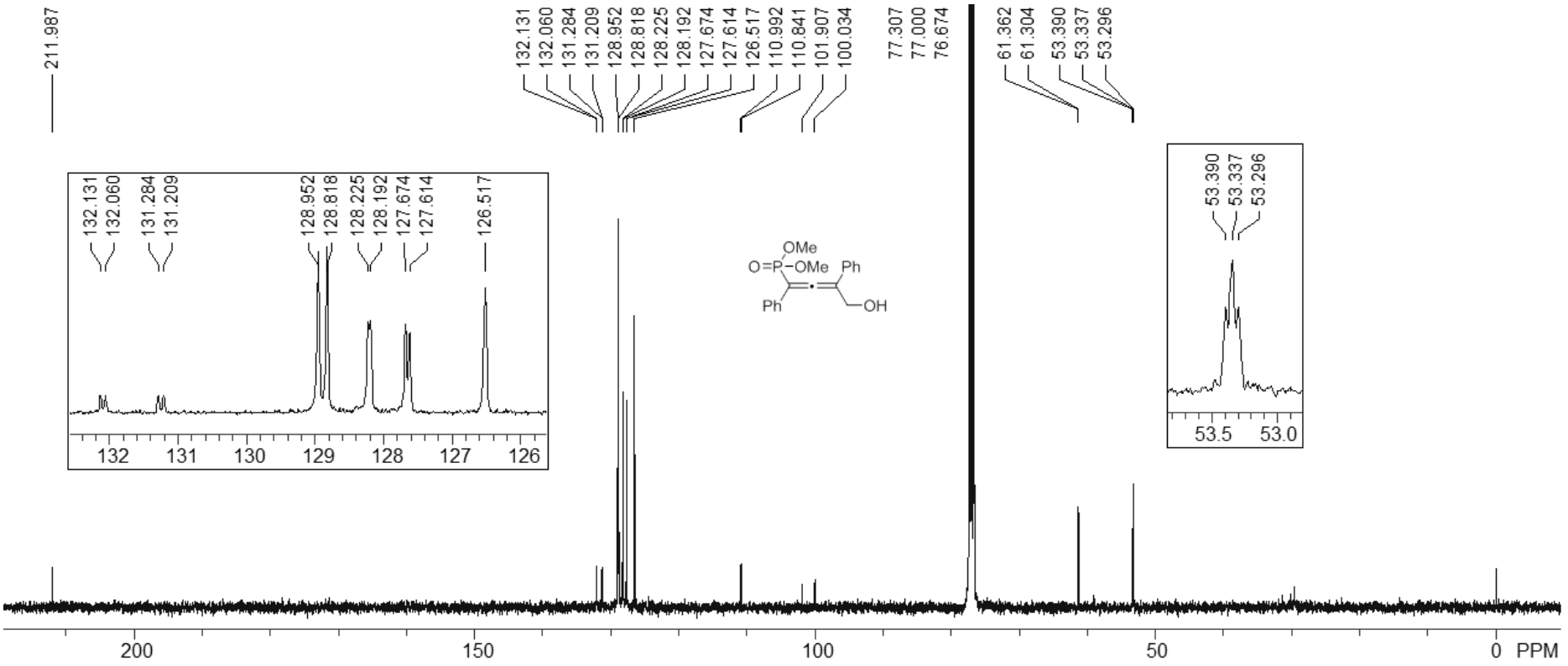
*^{1}H NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (**4b**)*

$CDCl_3$, 400 MHz



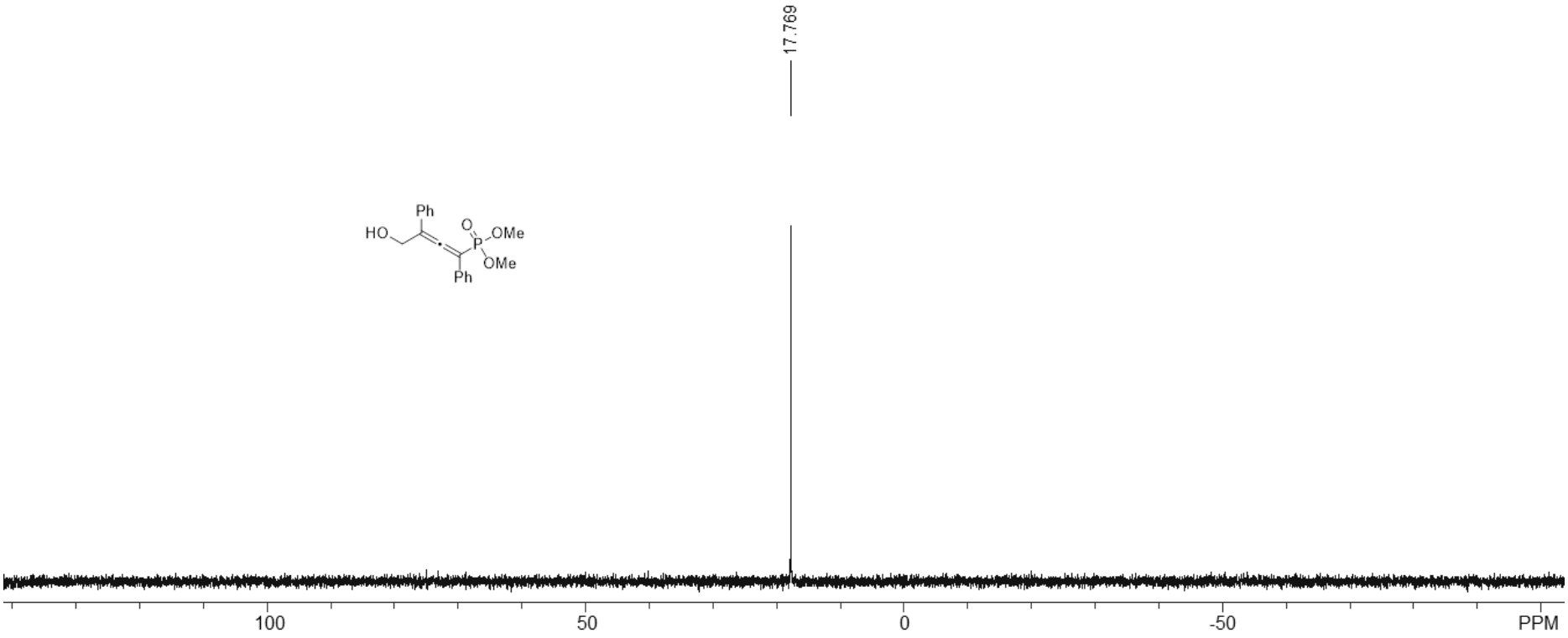
*^{13}C NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (**4b**)*

$CDCl_3$, 100 MHz



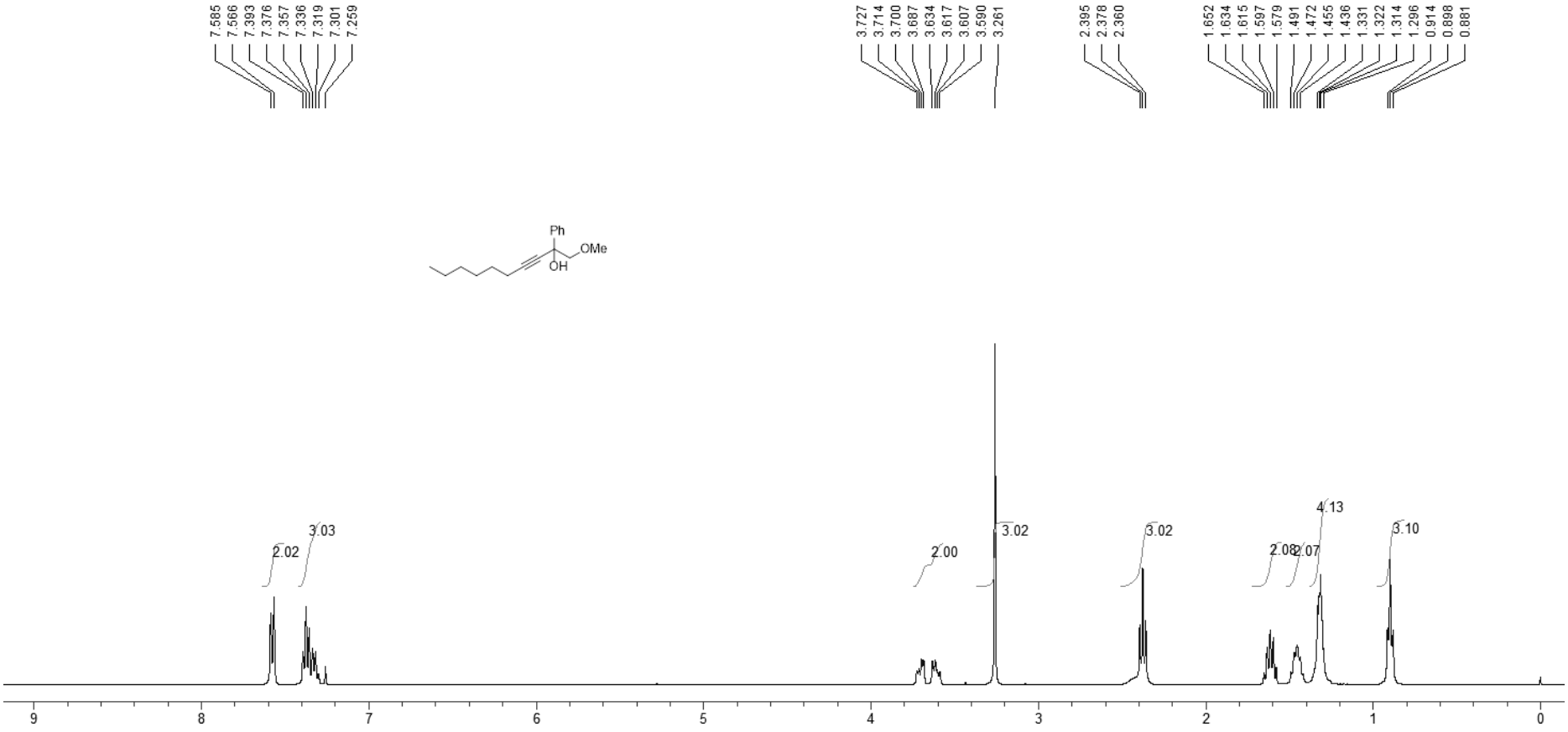
*^{31}P NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (**4b**)*

$CDCl_3$, 162 MHz



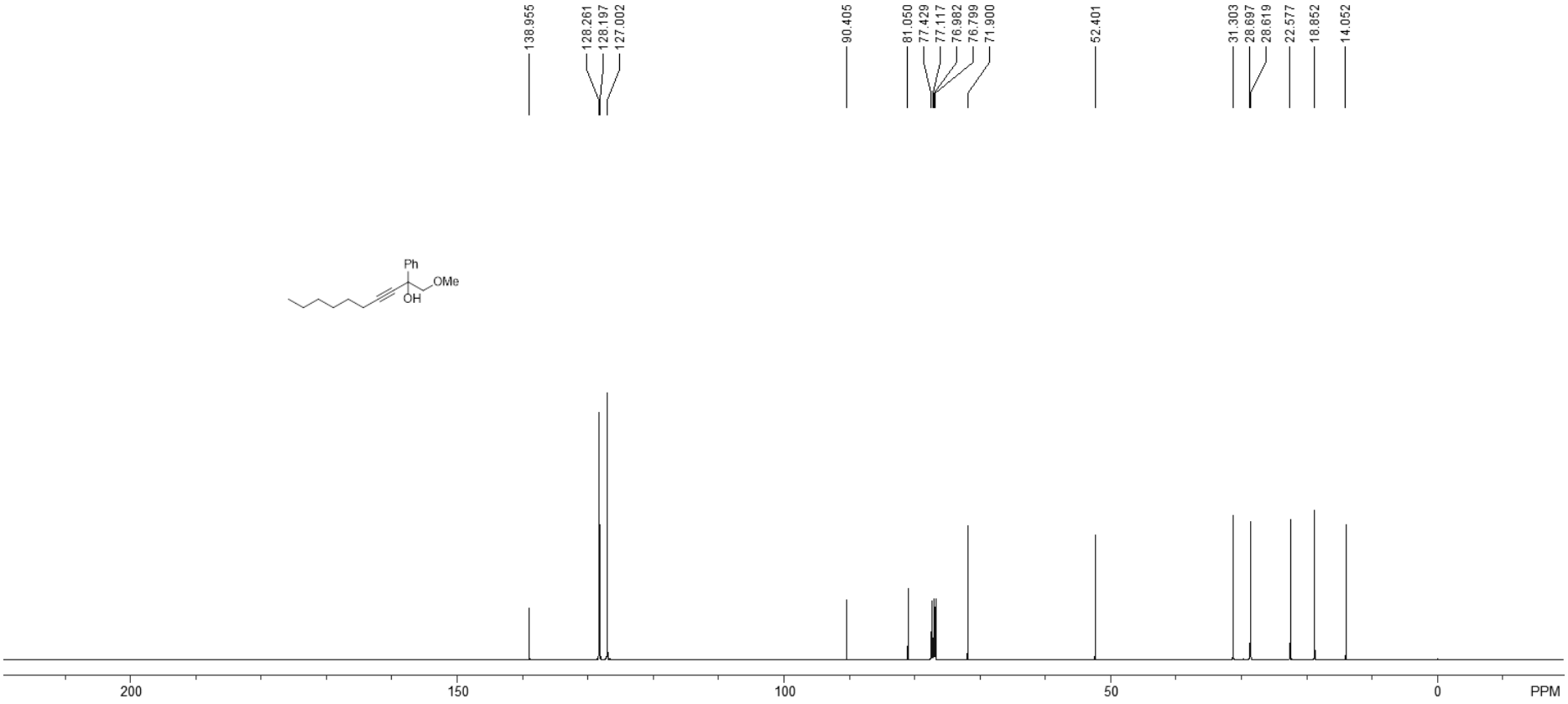
*^{1}H NMR spectrum of 1-methoxy-2-phenyldec-3-yn-2-ol (**5a**)*

$CDCl_3$, 400 MHz

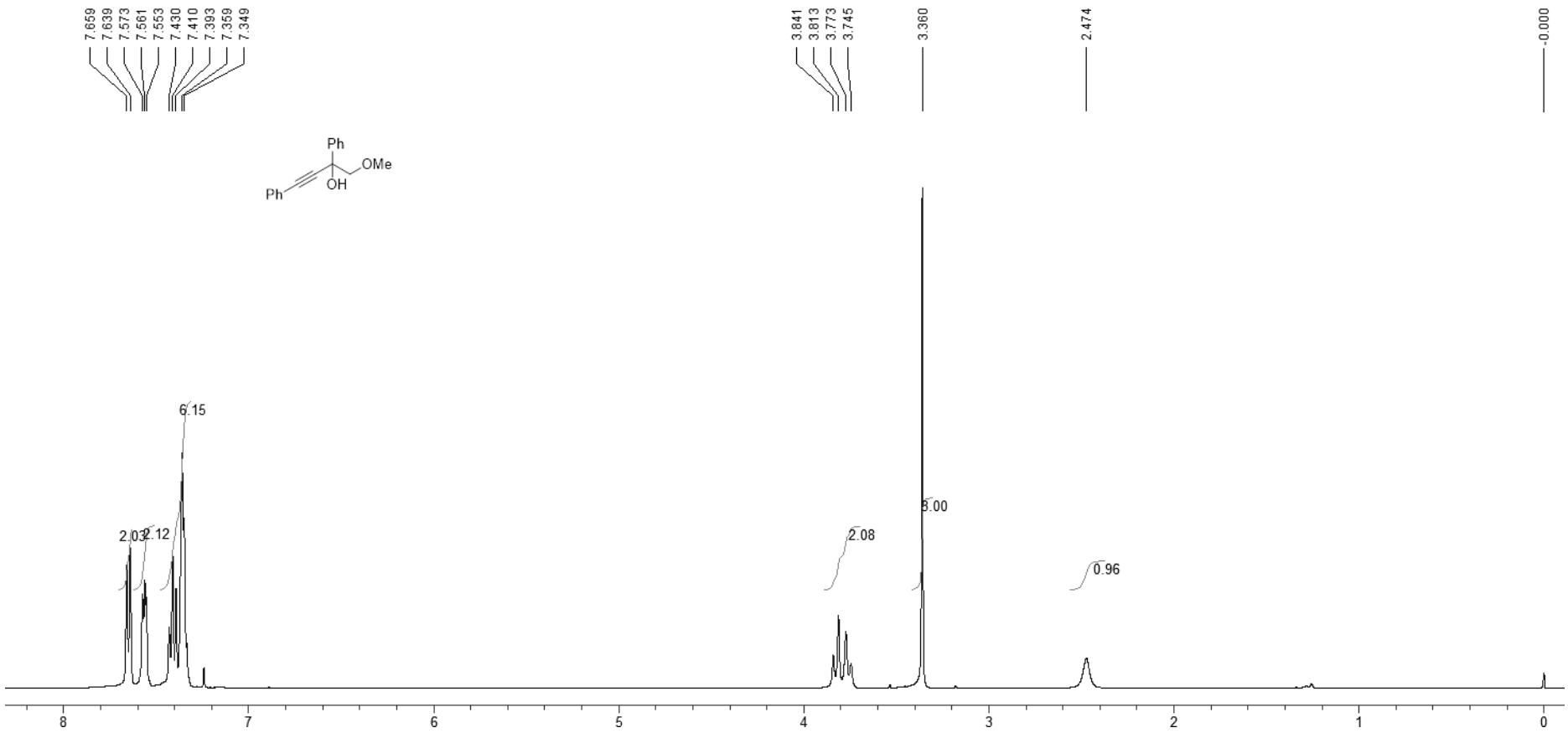


*^{13}C NMR spectrum of 1-methoxy-2-phenyldec-3-yn-2-ol (**5a**)*

$CDCl_3$, 100 MHz

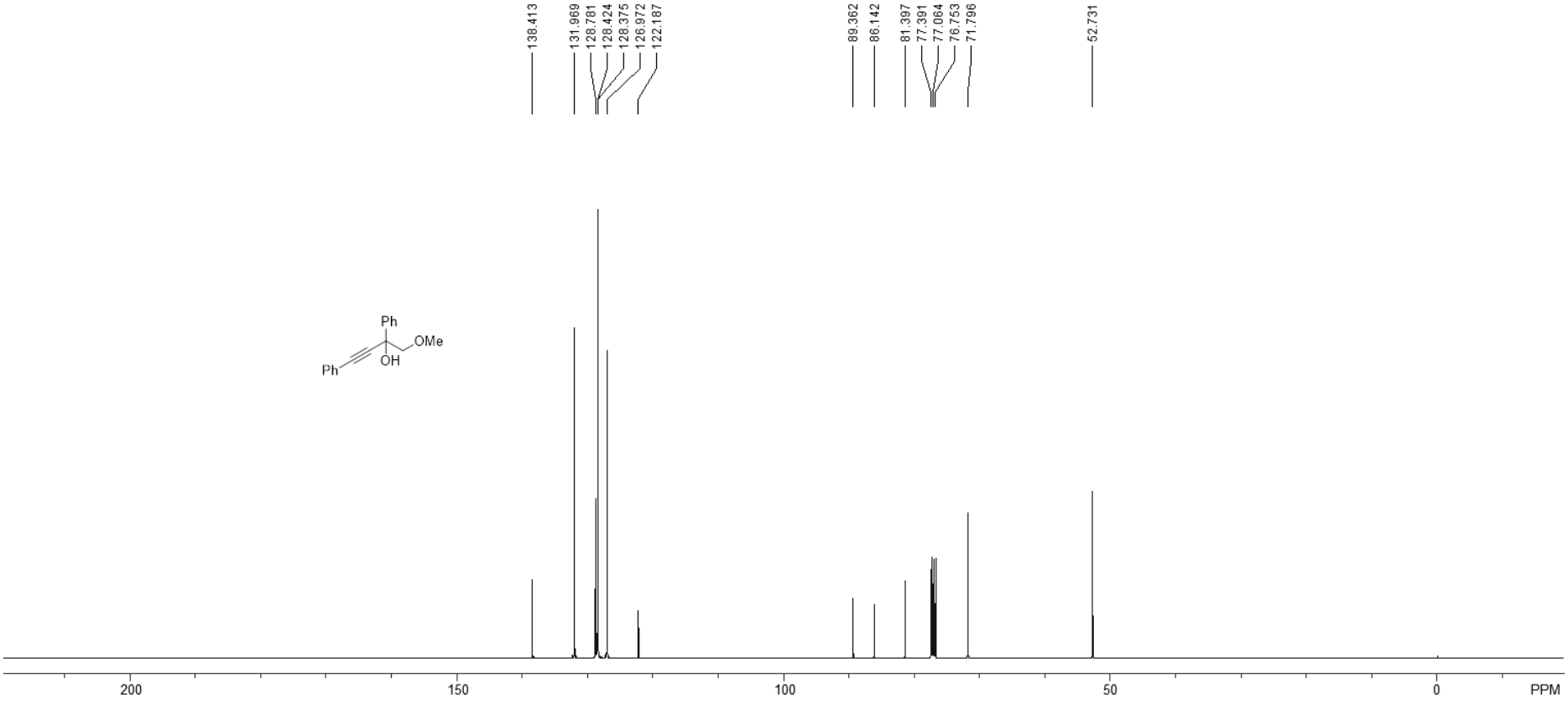


*^{1}H NMR spectrum of 1-methoxy-2,4-diphenylbut-3-yn-2-ol (**5b**)*
$CDCl_3$, 400 MHz



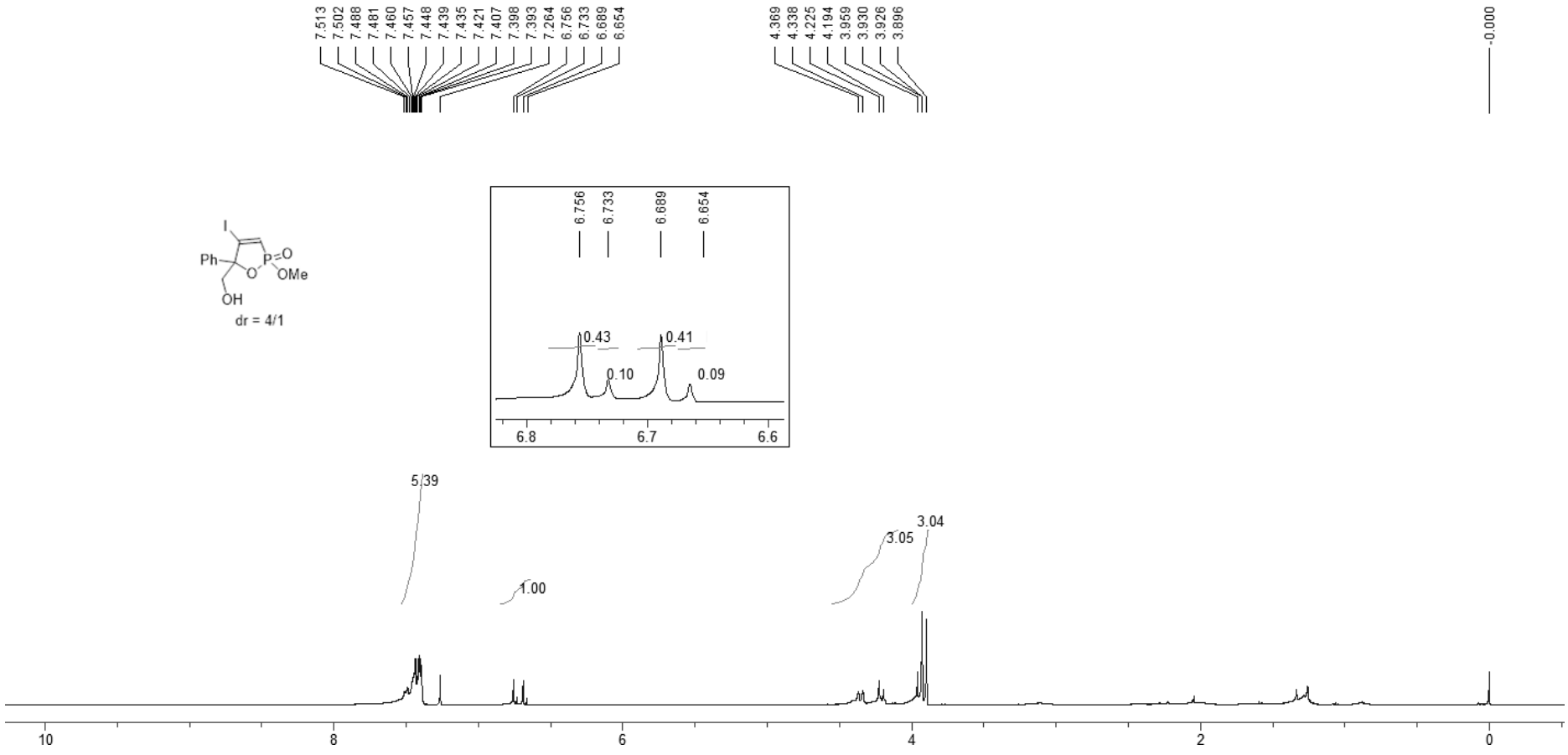
*^{13}C NMR spectrum of 1-methoxy-2,4-diphenylbut-3-yn-2-ol (**5b**)*

$CDCl_3$, 100 MHz



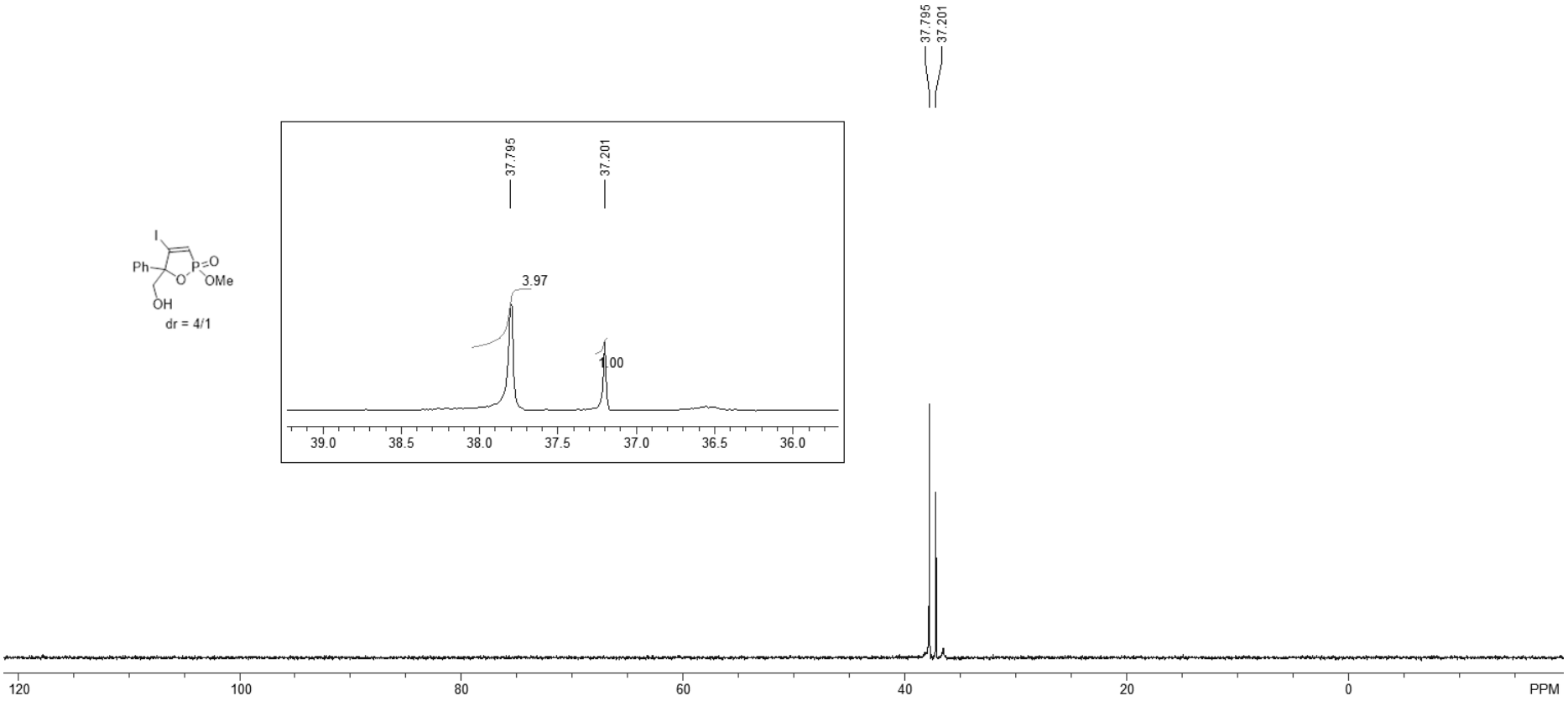
*^{1}H NMR spectrum of compound **6***

$CDCl_3$, 400 MHz



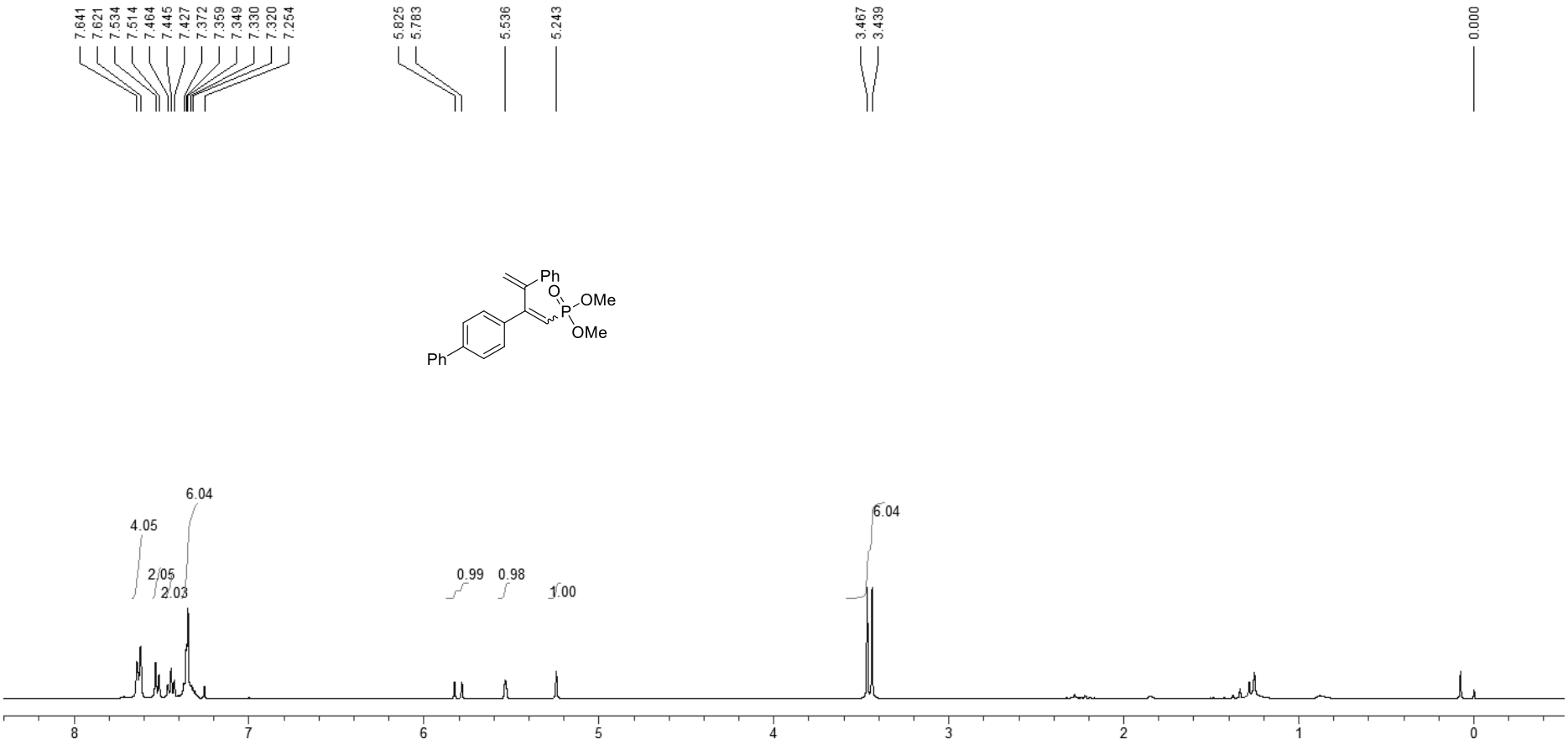
*^{31}P NMR spectrum of compound **6***

$CDCl_3$, 162 MHz



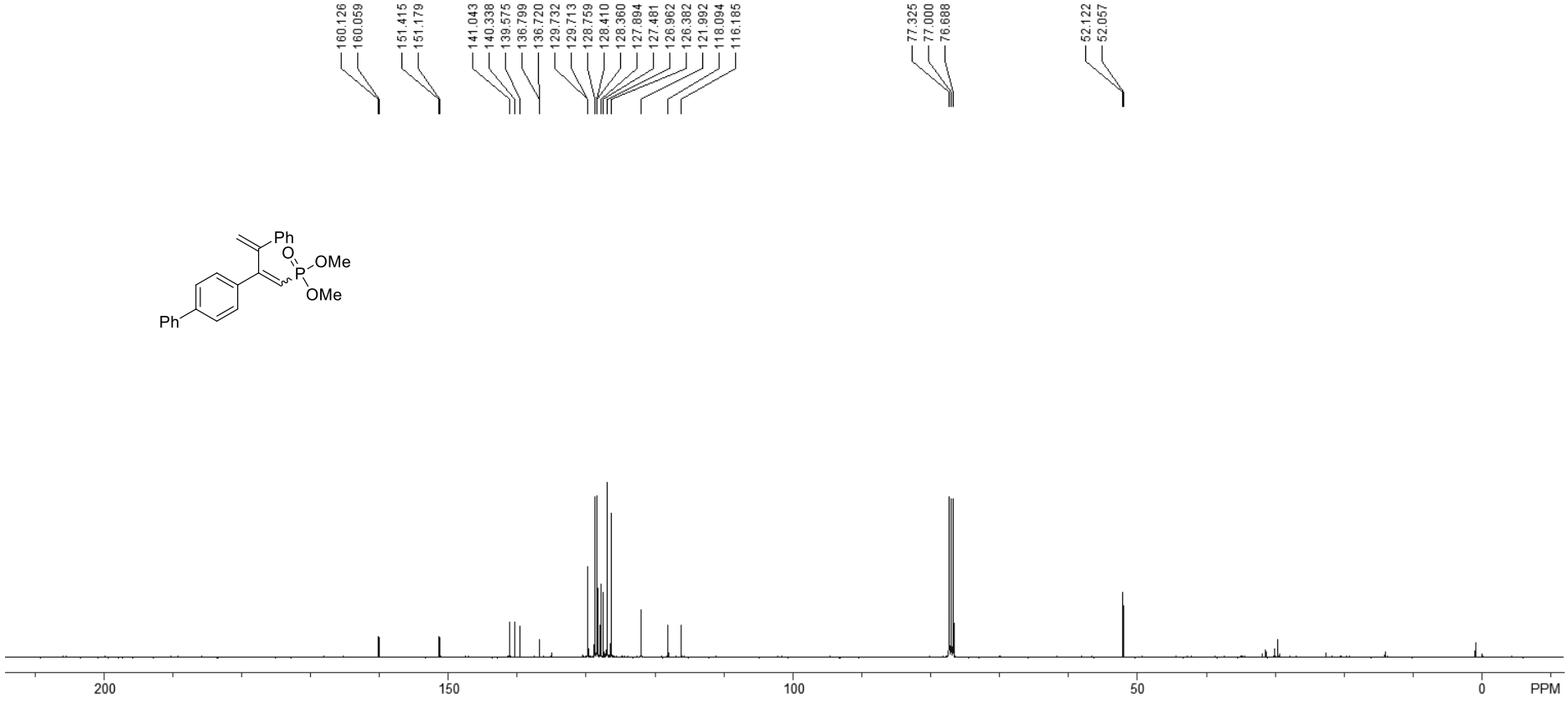
*^{1}H NMR spectrum of compound **7***

$CDCl_3$, 400 MHz



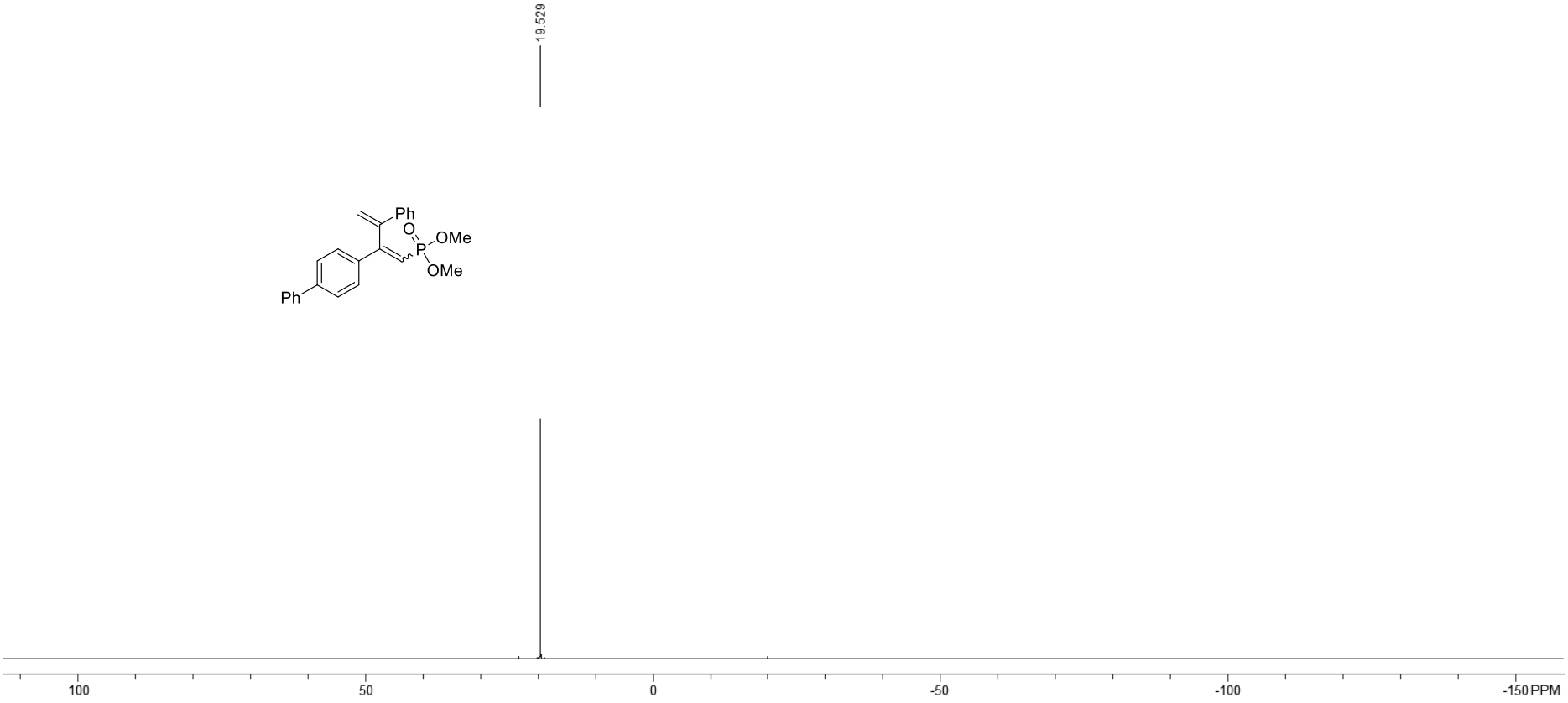
*^{13}C NMR spectrum of compound **7***

$CDCl_3$, 100 MHz



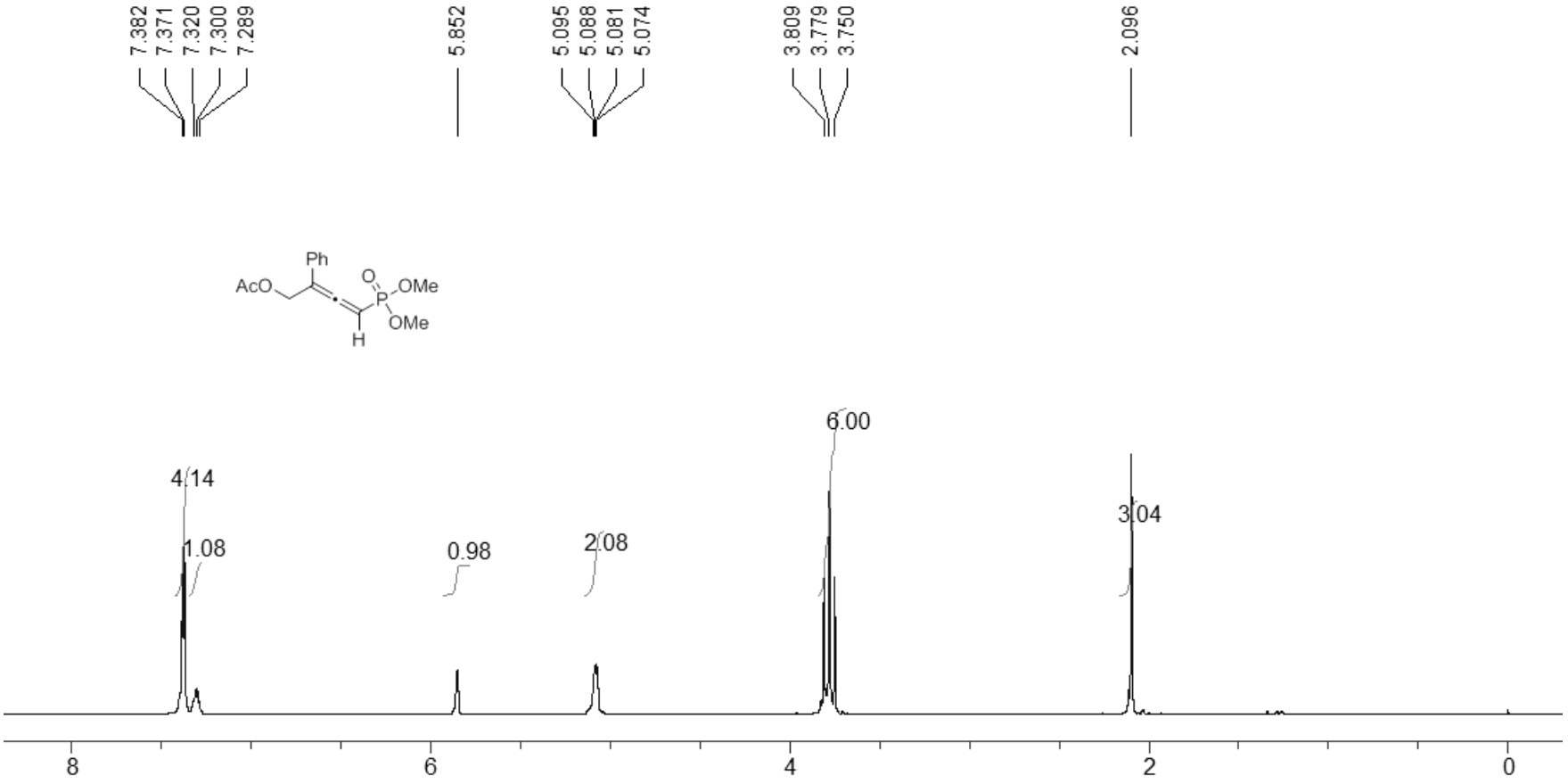
*^{31}P NMR spectrum of compound **7***

$CDCl_3$, 162 MHz



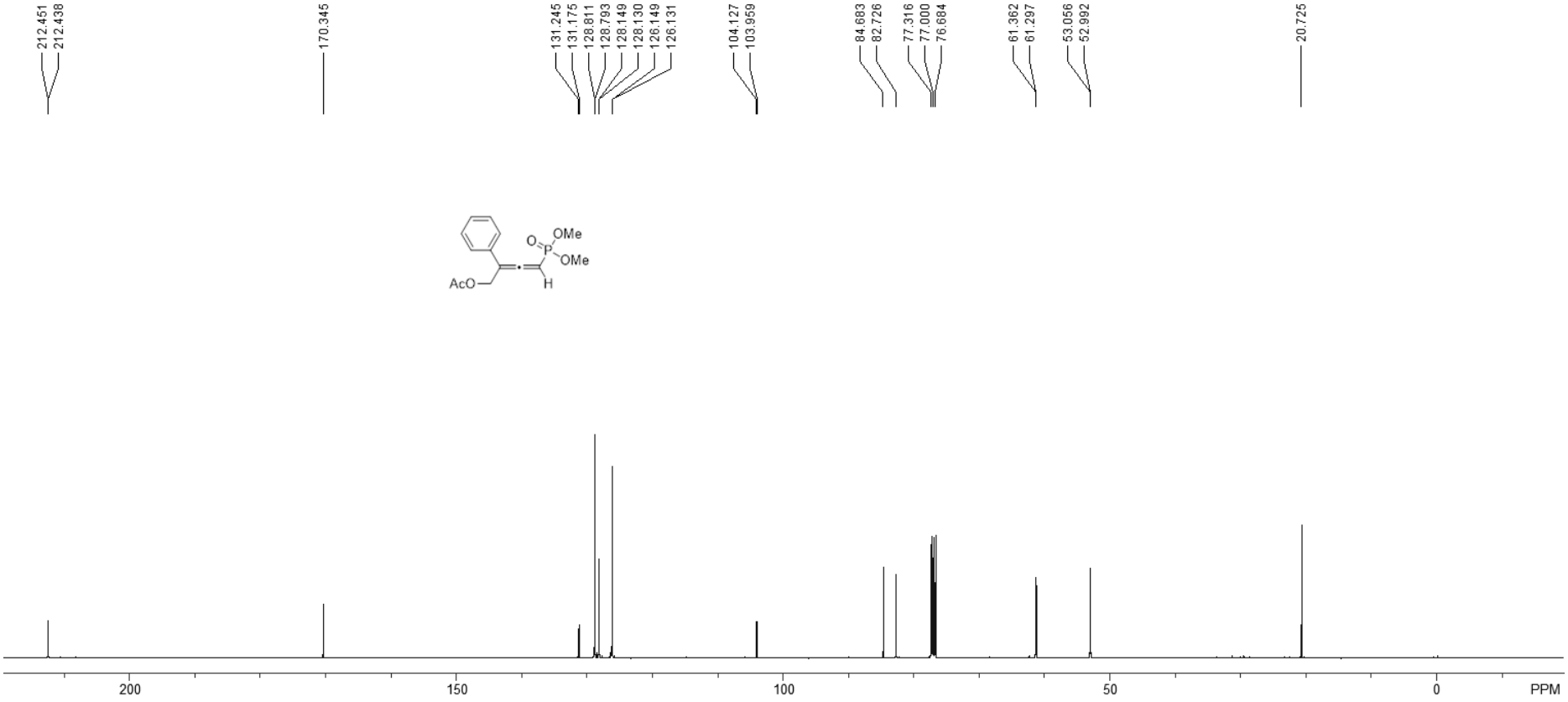
*^{1}H NMR spectrum of compound **8a***

$CDCl_3$, 400 MHz



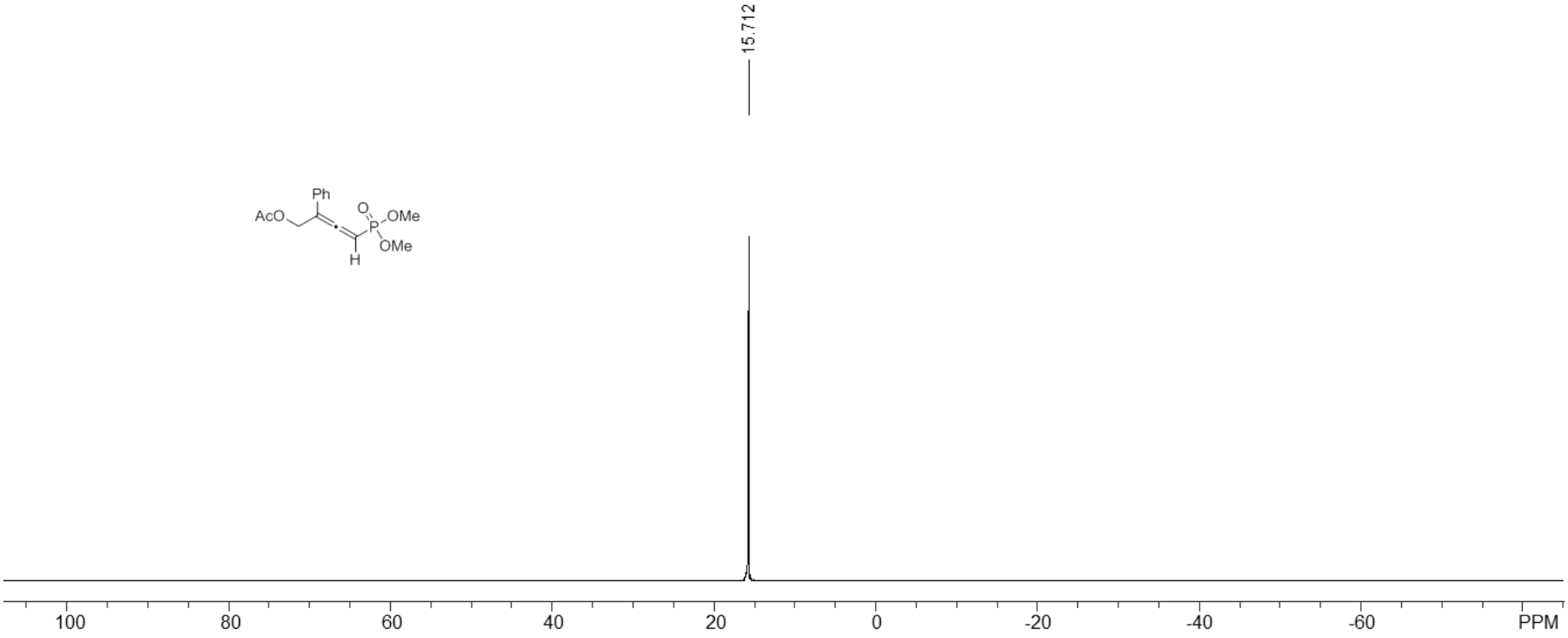
*^{13}C NMR spectrum of compound **8a***

$CDCl_3$, 100 MHz



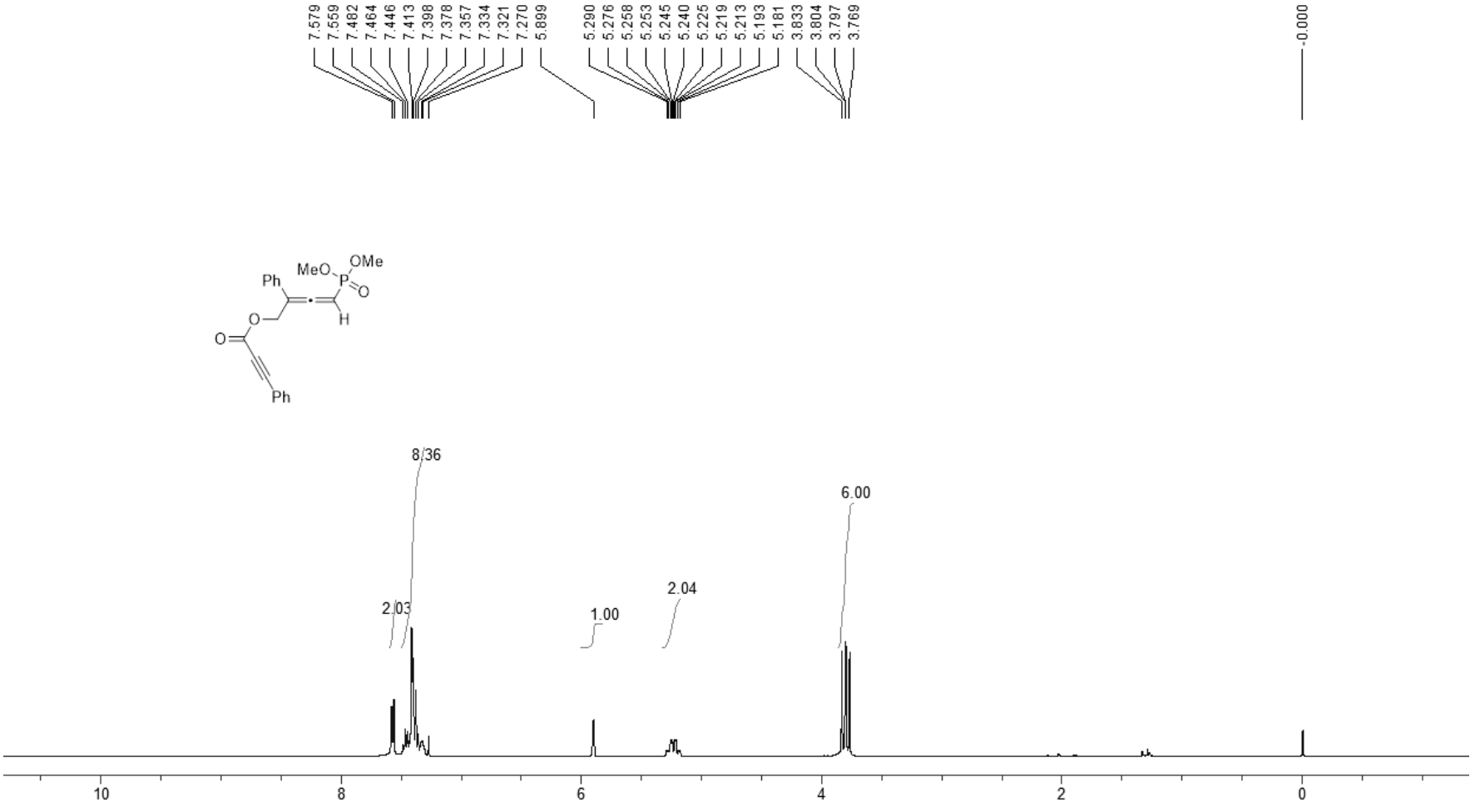
*^{31}P NMR spectrum of compound **8a***

$CDCl_3$, 162 MHz



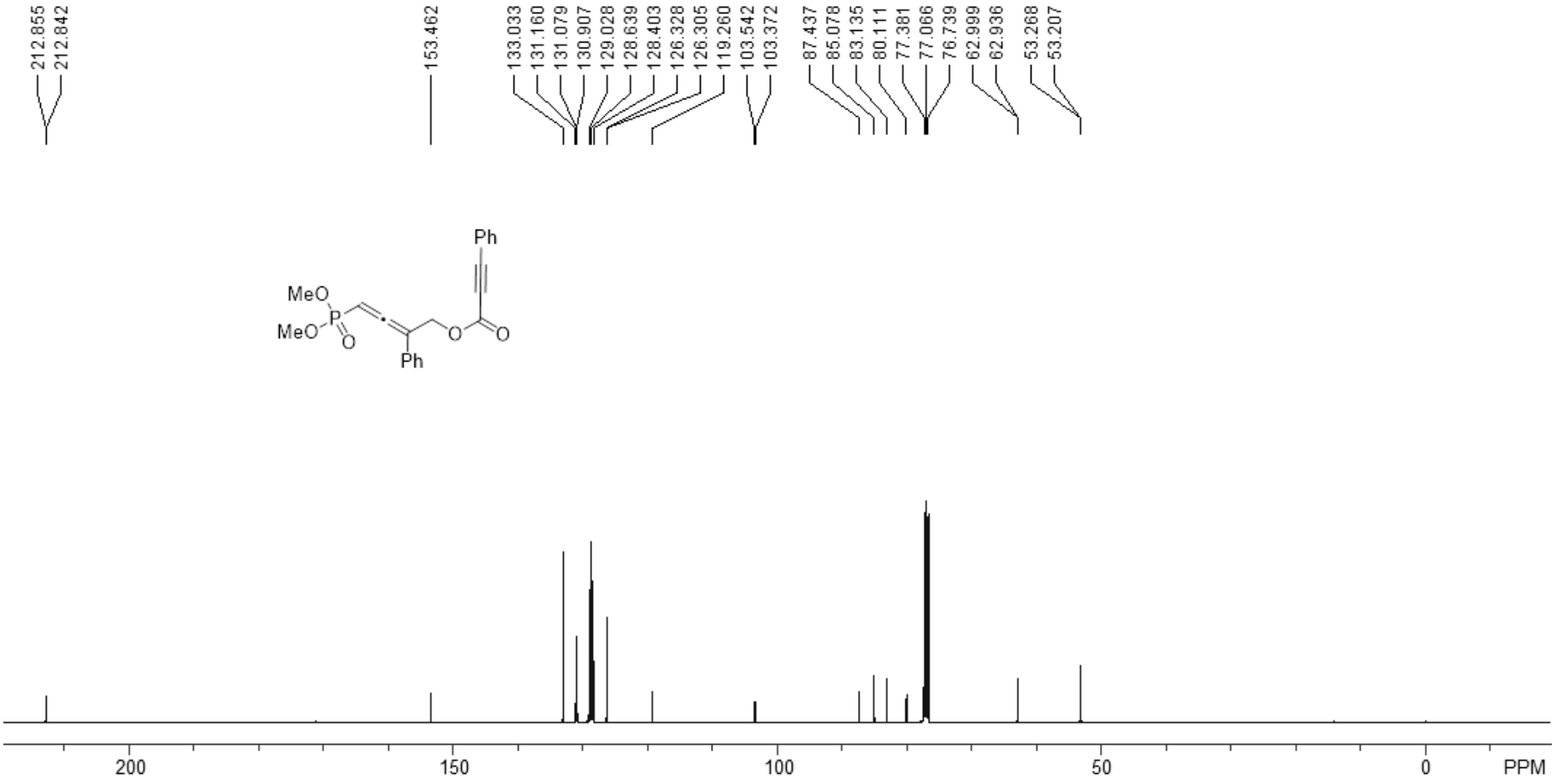
*^{1}H NMR spectrum of compound **8b***

$CDCl_3$, 400 MHz



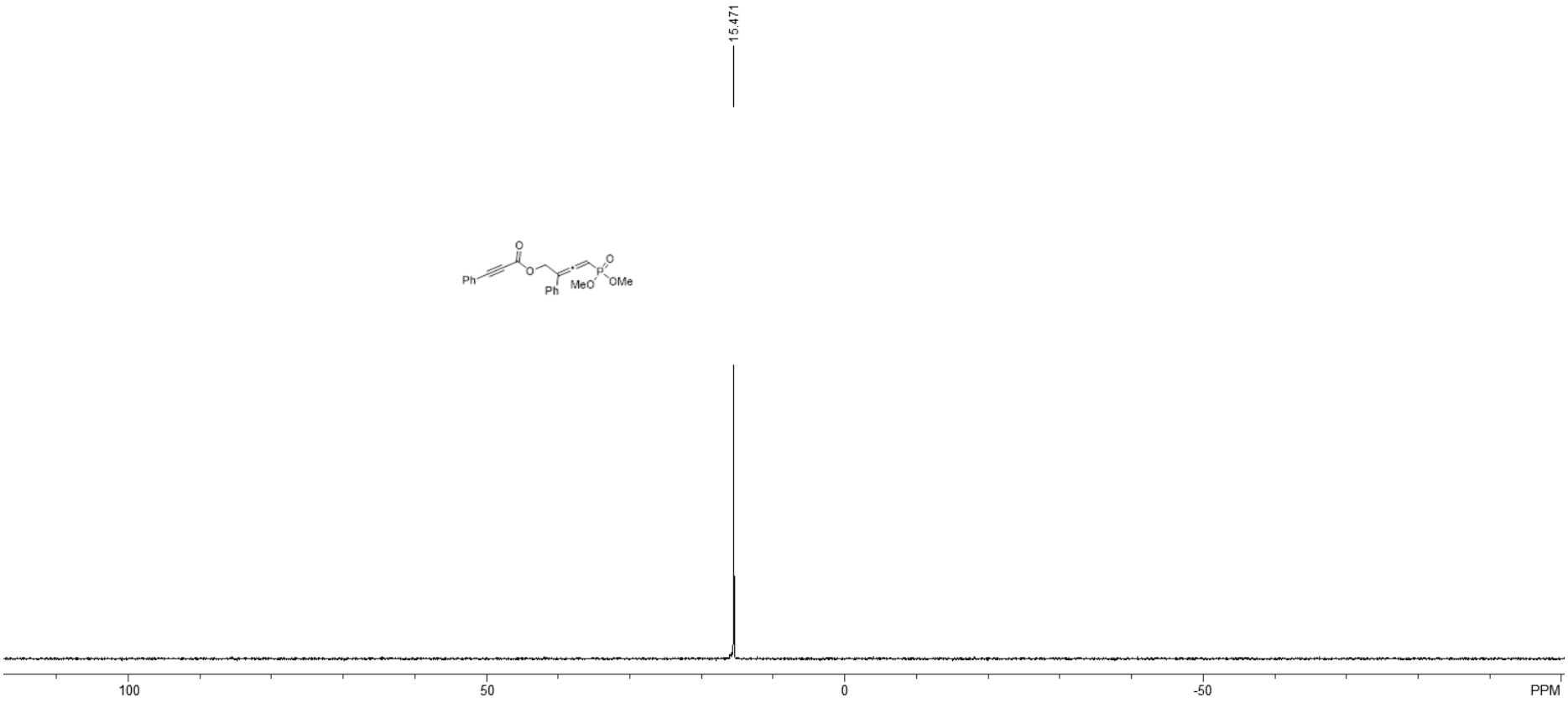
*^{13}C NMR spectrum of compound **8b***

$CDCl_3$, 100 MHz



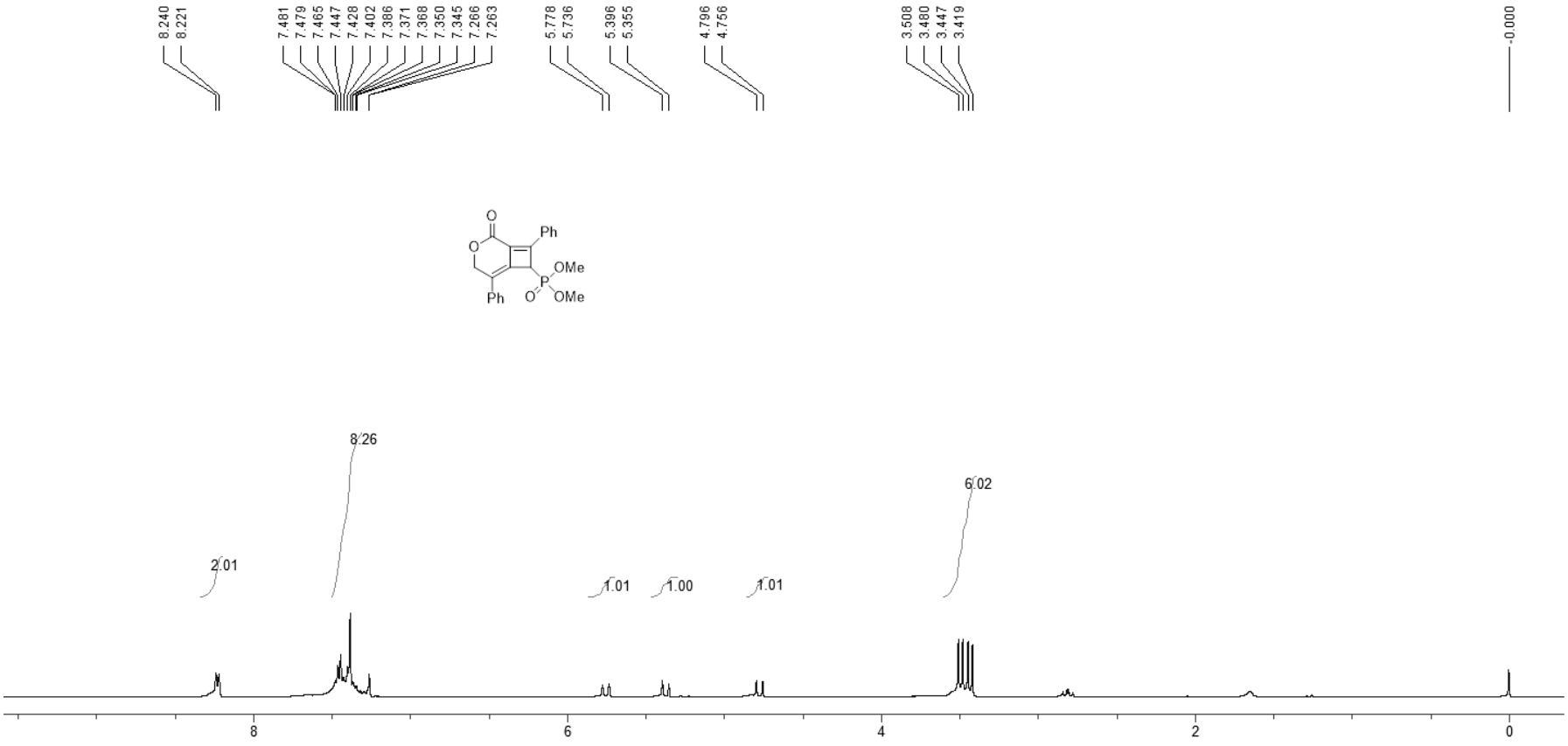
*^{31}P NMR spectrum of compound **8b***

$CDCl_3$, 162 MHz



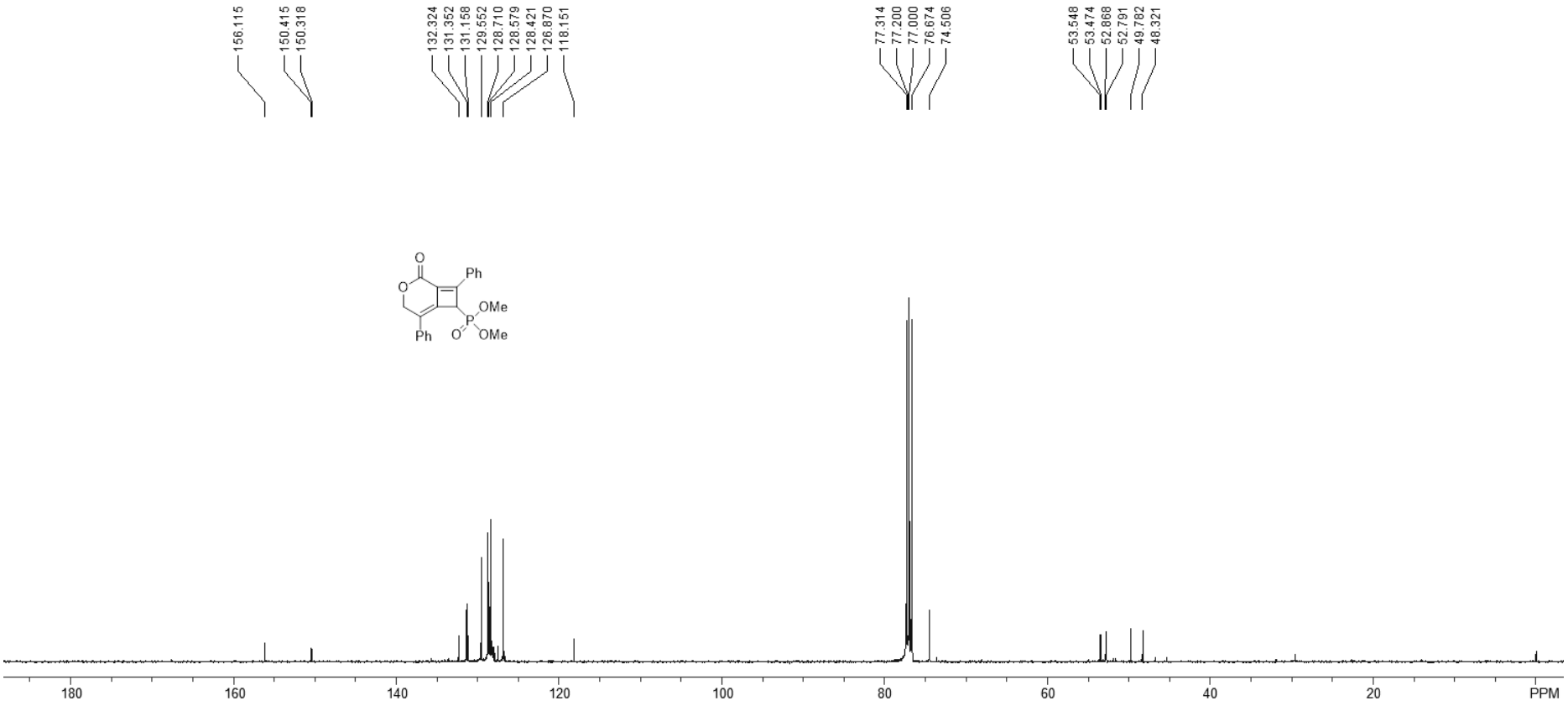
*^{1}H NMR spectrum of compound **9***

$CDCl_3$, 400 MHz



*^{13}C NMR spectrum of compound **9***

$CDCl_3$, 100 MHz



*^{31}P NMR spectrum of compound **9***

$CDCl_3$, 162 MHz