Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Convenient Synthesis of Allenylphosphoryl Compounds via Cu-Catalysed Coupling of Propargyl Acetates with P(O)H Compounds

Ruwei Shen,*[a] Bing Luo,[a] Jianlin Yang,[a] Lixiong Zhang,[a] Li-Biao Han*[b]

[a]*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, China*

shenrw@njtech.edu.cn

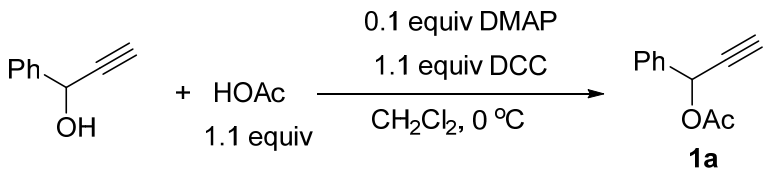
[b]*National Institute of Advanced Industrial Science & Technology (AIST), Tsukuba, Ibaraki, 305-8565 (Japan)*

libiao-han@aist.go.jp

Table of Content

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; DCE, DMF and MeCN were distilled from CaH_2; Absolute EtOH was commercially available and used without extra purification. Propargyl acetates **1** were prepared via Steglich esterification[1] excepert for the highly steric hindering substrate **1o**, synthetic procedure of which was given below. H-phosphonates were purchased from commercial sources and used as received. H-phosphonites were prepared via the Hewitt reaction.[2] Secondary phosphine oxides were prepared by the method of Hays.[3] 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 a 400 MHz 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



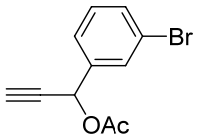
To a solution containing propargyl alcohol (10 mmol, 1.3206 g), acetic acid (11 mmol, 660.4 mg) and *N*, *N*-dimethylpyridin-4-amine (DMAP, 1 mmol, 122.0 mg) in CH_2Cl_2 (20 mL) was added a solution of dicyclohexylmethanediimine (DCC, 11 mmol, 2.2781 g) in CH_2Cl_2 (10 mL) at 0 ^{o}C. After the addition was complete, the reaction was naturally warmed to room temperature. Upon the consumption of the propargyl alcohol (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 20:1 v/v) to afford **1a** (1.6026 g, 92%). Known compound.[4a] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.53 (m, 2H), 7.42-7.38 (m, 3H), 6.46 (s, 1H), 2.65 (s, 1H), 2.12 (s, 3H). Other propargyl acetates except **1n** were prepared following a similar procedure from the corresponding alcohols and acetic acid. The characterization data of the new compounds are listed below.[4]

(1) B. Neises, W. Steglich, *Angew. Chem. Int. Ed.* **1978**, *17*, 522.

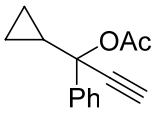
(2) K. Afarinkia, H.-W. Yu, *Tetrahedron Lett.* **2003**, 44, 781.

(3) (a) H.R. Hays, *J. Org. Chem.* **1968**, *33*, 3690. (b) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett*. **2005**, *7*, 4277.

(4) For characterization data of other propargyl acetates, see: a) N. Ghosh, S. Nayak, A. K. Sahoo, *J. Org. Chem.* **2011**, *76*, 500; b) N. Marion, P. Carlqvist, R. Gealageas, P. de Frémont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437; c) Y. Nakanishi, K. Miki, K. Ohe, *Tetrahedron* **2007**, *63*, 12138; d) R. J. Detz, M. M. E. Delville, H. Hiemstra, J. H. van Maarseveen, *Angew. Chem. Int. Ed.* **2008**, *47*, 3777; e) J. Abad, G. Villorbina, G. Fabriàs, F. Camps, *J. Org. Chem*. **2004**, *69*, 7108.

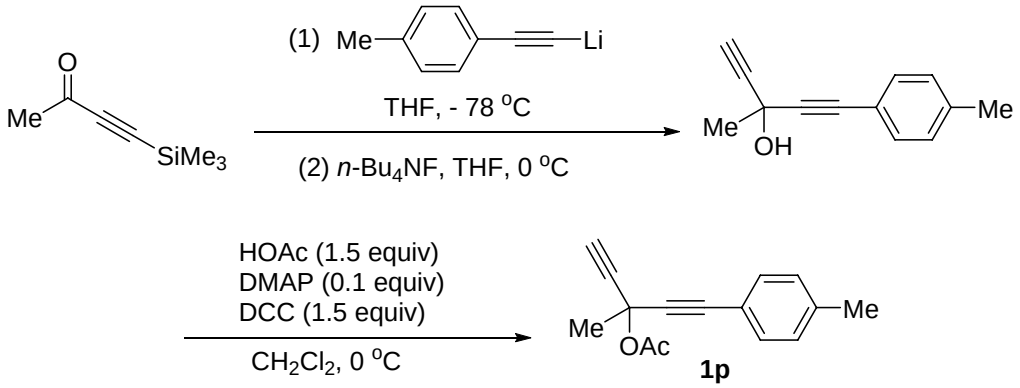


1-(3-bromophenyl)prop-2-yn-1-yl acetate (***1d***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.68 (m, 1H), 7.51-7.44 (m, 2H), 7.28-7.23 (m, 1H), 6.40 (d, J = 2.4 Hz, 1H), 2.68 (d, J = 2.4 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 138.5, 132.2, 130.7, 130.2, 126.3, 122.6, 79.6, 75.9, 64.4, 21.0. IR (KBr): 3278, 1737, 1431, 1226, 1022 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{11}H_9BrO_2$ [M^+] 251.9786 found 251.9783.



1-cyclopropyl-1-phenylprop-2-yn-1-yl acetate (***1m***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 7.6 Hz, 2H), 7.37-7.33 (m, 3H), 2.72 (s, 1H), 2.09 (s, 3H), 1.58-1.52 (m, 1H), 0.89-0.82 (m, 1H), 0.63-0.55 (m, 2H), 0.52-0.45 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 141.4, 128.2, 127.8, 125.0, 80.6, 79.5, 76.3, 22.0, 21.7, 3.4, 2.4. IR (KBr): 3289, 1745, 1441, 1236, 1052 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{14}O_2$ [M^+] 214.0994 found 214.0993.

Synthetic procedure for propargyl acetate 1p

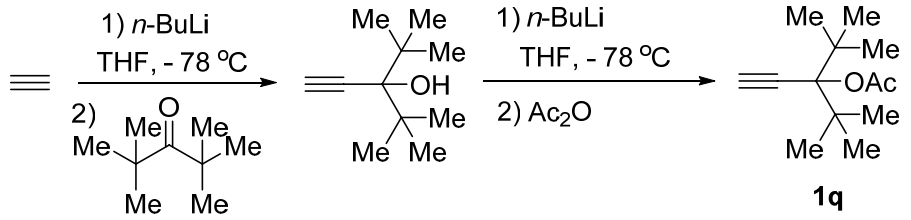


n-Butyl lithium (2.5 mL, 2.2 M in hexane) was added to a solution of 1-ethynyl-4-methylbenzene (638.0 mg, 5.5 mmol) in THF (15 mL) at –78 ^{o}C under N_2 atmophere. The reaction mixture was allowed to stir at this temperature for 30 min. 4-(Trimethylsilyl)but-3-yn-2-one (701.2 mg, 5 mmol) was then added and the reaction mixture was stirred at –78 ^{o}C for 30 min, naturally warmed to room temperature and kept stirring overnight. After quenched by saturated NH_4Cl solution, extracted with Et_2O and concentrated to dryness, the residue was dissolved in THF and cooled to 0 ^{o}C. A solution of tetrabutylammonium fluoride (ca. 5 mmol, 85% purity containing water) in THF was dropwise added. After stirred at 0 ^{o}C for 2 h, the reaction mixture was quenched with water and extracted with EtOAc. The organic layers were dried with $MgSO_4$, and concentrated under vacumm. Pure 3-methyl-1-(p-tolyl)penta-1,4-diyn-3-ol (754.5 mg, 82%) was obtained after column chromategraphy on silica gel (petroleum ether – ethyl acetate 8:1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.63 (br, 1H), 2.60 (s, 1H), 2.35 (s, 3H), 1.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0, 131.7, 129.1, 118.8, 88.9, 85.0, 83.0, 70.9, 60.3, 31.8, 21.5.

To a solution containing 3-methyl-1-(p-tolyl)penta-1,4-diyn-3-ol (2.0 mmol, 368.2 mg), acetic acid (3 mmol, 180.0 mg) and *N*, *N*-dimethylpyridin-4-amine (DMAP, 0.2 mmol, 24.4 mg) in CH_2Cl_2 (5 mL) was added a solution of dicyclohexylmethanediimine (DCC, 3 mmol, 618.0 mg) in CH_2Cl_2 at 0 ^{o}C. After the addition was complete, the reaction was stirred at 0 ^{o}C for 2 h. The reaction mixture was filtrated and concentrated. The obtained residue was purified by column

chromatography on silica gel (petroleum ether – ethyl acetate 20:1 v/v) to afford the propargyl acetate **1p** (407.3 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.67 (s, 1H), 2.34 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 139.0, 131.9, 128.9, 118.7, 85.7, 84.5, 81.6, 72.5, 64.1, 30.7, 21.5. IR (KBr): 3290, 1747, 1451, 1369, 1236, 1062 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{15}H_{14}O_2$ [M^+] 226.0994 found 226.0991.

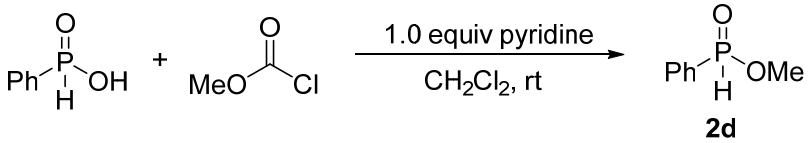
Synthetic procedure for the propargyl acetate 1q



Dry THF (60 mL) was bubbled with dry acetylene for 40 min at –40 °C. The solution was then cooled to –78 °C, and *n*-butyl lithium (5 mL, 2.2 M in hexane) was slowly added. The reaction mixture was allowed to stir at this temperature for 1 h, followed by the addition of 2,2,4,4-tetramethylpentan-3-one (1.4221 g, 10 mmol). The reaction mixture was stirred for 1 h at –78 °C, naturally warmed to room temperature, and kept stirring overnight. After quenched by saturated NH_4Cl solution at 0 °C, extracted with Et_2O, dried over $MgSO_4$ and concentrated to dryness, the residue was distilled under reduced pressure to afford 3-(tert-butyl)-4,4-dimethylpent-1-yn-3-ol (1.0390 g, 62%). Known compound. [5] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.43 (s, 1H), 1.92 (s, 1H), 1.18 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 87.0, 81.1, 73.4, 41.2, 28.6.

3-(Tert-butyl)-4,4-dimethylpent-1-yn-3-ol (924.0 mg, 5.5 mmol) was dissolved in dry THF (15 mL) under N_2 atmophere. The solution was cooled to –78 °C followed by the addition of a solution of *n*-butyl lithium (2.5 mL, 2.2 M in hexane). After stirred at this temperature for 30 min, acetic anhydride (1.0201 g, 10 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with water and extracted with Et_2O. The organic layers were washed with water and brine, dried with $MgSO_4$, and concentrated under vacumm. Pure 3-(tert-butyl)-4,4-dimethylpent-1-yn-3-yl acetate **1q** (693.1 mg, 60%) was obtained after column chromatography on silica gel (petroleum ether – ethyl acetate 80:1 v/v). Known compound.[5] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.74 (s, 1H), 2.06 (s, 3H), 1.19 (s, 18H).

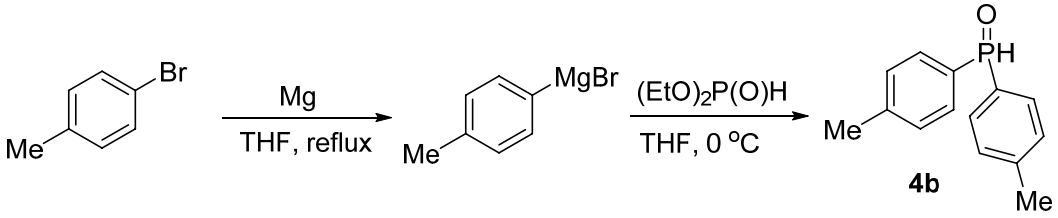
Typical procedure for the preparation of the starting materials 2



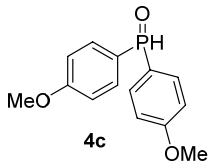
Pyridine (395.0 mg, 5 mmol) was carefully added to a vigorously stirred solution of methyl chloroformate (472.5 mg, 5 mmol) and phenylphosphinic acid (710.0 mg, 5 mmol) in DCM (20 ml)

(5) H. D. Hartzler, *J. Am. Chem. Soc.* **1971**, *93*, 4527.

at room temperature. Once effervescence had stopped, the solution was heated to reflux for 15 min, and then allowed to cool to room temperature. The solution was quenched with 5 mL of 0.1 M hydrochloric acid and the organic layer was separated. After washed with water and dried over Na_2SO_4, the solvent was removed in vacuo to give methyl phenylphosphinate **2d** (702.5 mg, 90%). The obtained product was pure enough for use. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.50 (m, 2H), 7.61-7.59 (m, 1H), 7.56 (d, J = 565.6 Hz, 1H), 7.54-7.49 (m, 2H), 3.79 (d, J = 12.0 Hz, 3H). Known compound.[2] Allyl phenylphosphinate **2e** was prepared via a similar procedure.[2]

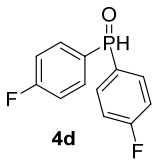


Typical procedure: A 100 mL round-bottom flask fitted with Teflon-coated stir bar, reflux condenser and addition funnel was evacuated and backfilled with N_2 (3 cycles), then charged with 0.792 g of Mg powder (33 mmol, 3.3 equiv). 20 mL of dry THF and a few crystals of I_2 were then added. To this was then added a few drops of a solution of 5.643 g of 4-methylphenyl bromide (33 mol, 3.3 equiv) in 20 mL of THF. Upon the initiation by heating the mixture, the remaining bromide solution was added dropwise so as to maintain reflux. When the addition was complete, the mixture was refluxed for 1 h. The reaction mixture was then cooled to 0 °C, and diethylphosphite (1.3811 g, 10 mmol, 1 equiv) in 10 mL of THF was added dropwise. The mixture was stirred overnight, then cooled to 0 °C and cautiously quenched with 40 mL of 1M HCl. The mixture was extracted with EtOAc, and the organic phase was dried over $MgSO_4$. Removal of the solvent under vacuum gave a white solid. Pure product (1.6110 g, 70%) was obtained by crystallization from hot Hexane/EtOAc. Known compound.[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 478.0 Hz, 1H), 7.58 (dd, J_1 = 13.6 Hz, J_2 = 8.0 Hz, 4H), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 5.6 Hz, 4H), 2.40 (s, 6H). ^{31}P NMR ($CDCl_3$, 162 MHz): 21.7. Compounds **4c**-**4e** were obtained following a similar procedure.[3]



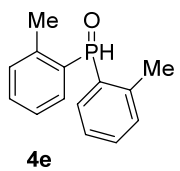
4c

4c, known compound.[3b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, J = 478.0 Hz, 1H), 7.60 (dd, J_1 = 12.8 Hz, J_2 = 8.8 Hz, 4H), 6.99 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 4H), 3.85 (s, 6H). ^{31}P NMR ($CDCl_3$, 162 MHz): 20.8.



4d

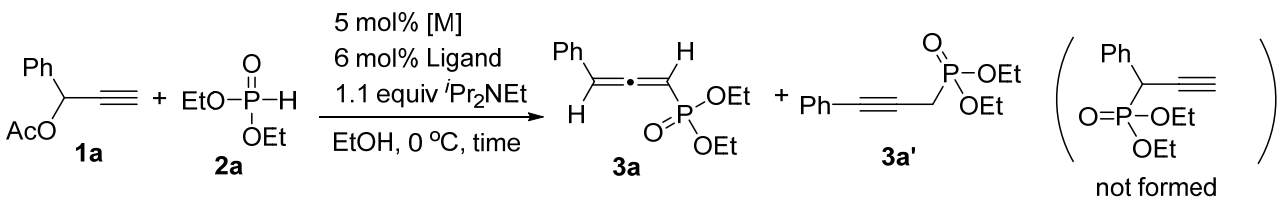
4d, known compound.[3b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, J = 485.6 Hz, 1H), 7.74-7.67 (m, 4H), 7.24-7.19 (m, 4H). ^{31}P NMR ($CDCl_3$, 162 MHz): 18.9.



4e

4e, known compound.[3b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.2 (d, J = 477.2 Hz, 1H), 7.74-7.69 (m, 2H), 7.48-7.45 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 2H), 2.37 (s, 6H). ^{31}P NMR ($CDCl_3$, 162 MHz): 17.7.

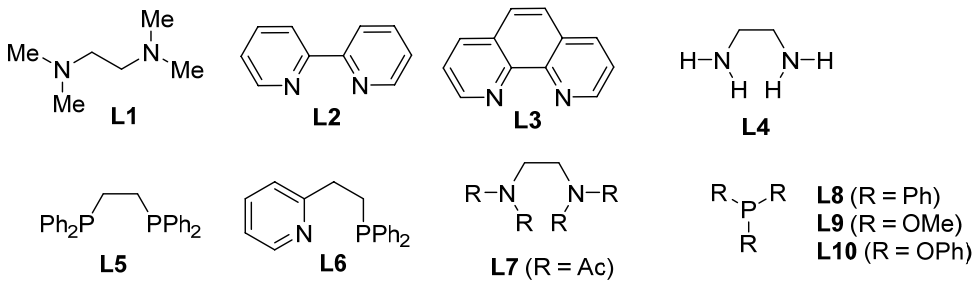
Table S1. Optimization of the reaction conditions[a]



Entry	Cat. [M]	Ligand	Solvent	Time (h)	Yield% (**3a**/**3a'**)[b]
1	CuI	L1	EtOH	5	95 (98/2)
2	CuI	L2	EtOH	5	16[c]
3	CuI	L2	EtOH	24	95 (84/16)[d]
4	CuI	L2	EtOH	4	89 (59/41)[e]
5	CuI	L3	EtOH	5	8[c]
6	CuI	L4	EtOH	5	0
7	CuI	L5	EtOH	5	trace[c]
8	CuI	L6	EtOH	5	5[c]
9	CuI	L7	EtOH	5	0
10	CuI	L8[f]	EtOH	5	0
11	CuI	L9[f]	EtOH	5	0
12	CuI	L10[f]	EtOH	5	0
13	CuBr	L1	EtOH	5	91 (97/3)
14	CuCl	L1	EtOH	5	91 (98/2)
15	$CuPF_6(MeCN)_4$	L1	EtOH	5	93 (96/4)
16	$Cu(OAc)_2$	L1	EtOH	5	84 (98/2)
17	$CuCl_2{\cdot}2H_2O$	L1	EtOH	5	86 (95/5)
18	CuI	L1	THF	5	14[c]
19	CuI	L1	DCE	5	14[c]
20	CuI	L1	DCE	12	25[c]
21	CuI	L1	DCE	8	96 (85/15)[e]
22	CuI	L1	DMF	5	36 (94/6)
23	CuI	L1	MeCN	5	7[c]
24	$Pd(OAc)_2$	L1	EtOH	8	0
25	$FeCl_3$	L1	EtOH	8	0
26	$RuCl_3$	L1	EtOH	8	0
27	$CoCl_2$	L1	EtOH	8	0

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), CuI (5 mol%), Ligand (6 mol%) and $^{i}Pr_2NEt$ (0.22 mmol) in EtOH (2 mL). [b] Yields and ratio were deduced from the ^{31}P NMR spectra. [c] Only **3a** was formed. [d] Reaction temperature: 0 °C-rt. [e] Reaction temperature: 60 °C. [f] 12 mol% of the ligand was used.

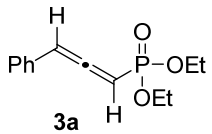
Ligands:



General procedure for the Cu-catalyzed preparation of phosphorylated allenes via reactions of propargyl acetates with >P(O)H compounds

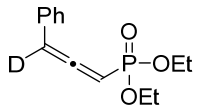
An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with CuI (1.9 mg, 5 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 1.0 mL of ethanol was injected, followed by the injection of TMEDA (2 uL) and $^{i}Pr_2NEt$ (38 uL) upon stirring. The mixture was stirred for 10 min and cooled to 0 °C. Then **1** (0.24 mmol) and **2** (or **4**) (0.2 mmol) dissolved in 1.0 mL of ethanol was injected. The reaction was kept stirring at the same temperature and monitored by TLC. After the reaction was complete, removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether – ethyl acetate 3:1 to 1:1 v/v) to afford the product **3** (or **5**)**.**

Spectroscopic data of the products



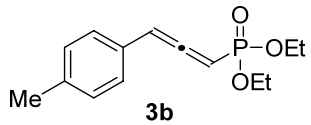
3a

*diethyl (3-phenylpropa-1,2-dien-1-yl)phosphonate (**3a**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 45.9 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.25 (m, 5H), 6.46 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 5.80 (d, J = 6.8 Hz, 1H), 4.19-4.11 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.9. Known compound: Cherbuliez, E.; Jaccard, S.;Prince, R.; Rabinowitz, J. *Helv. Chim. Acta* **1965**, *48*, 632.



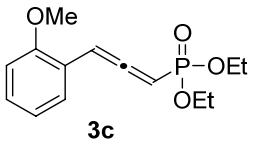
3a-*d*

*diethyl (3-phenylpropa-1,2-dien-1-yl-3-d)phosphonate (**3a**-d).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 45.5 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.25 (m, 5H), 5.81 (s, 1H), 4.19-4.11 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 131.2 (d, $J_{P\text{-}C}$ = 8.2 Hz), 128.8 (d, $J_{P\text{-}C}$ = 1.4 Hz), 127.8 (d, $J_{P\text{-}C}$ = 1.7 Hz), 127.1 (d, $J_{P\text{-}C}$ = 3.3 Hz), 84.4 (d, $J_{P\text{-}C}$ = 205.7 Hz), 62.56 (d, $J_{P\text{-}C}$ = 3.2 Hz), 62.50 (d, $J_{P\text{-}C}$ = 3.0 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.7. IR (KBr) 1937, 1260, 1027, 799 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{13}O_3PH_{16}D$ [M^+] 253.0978 found 253.0979.



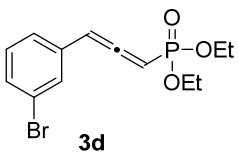
3b

*diethyl (3-(p-tolyl)propa-1,2-dien-1-yl)phosphonate (**3b**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 48.5 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17-7.11 (m, 4H), 6.42 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 5.77 (d, J = 6.8 Hz, 1H), 4.17-4.08 (m, 4H), 2.32 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2 (d, $J_{P\text{-}C}$ = 1.2 Hz), 137.7 (d, $J_{P\text{-}C}$ = 2.4 Hz), 129.5 (d, $J_{P\text{-}C}$ = 1.3 Hz), 128.2 (d, $J_{P\text{-}C}$ = 8.6 Hz), 127.0 (d, $J_{P\text{-}C}$ = 2.3 Hz), 95.5 (d, $J_{P\text{-}C}$ = 16.5 Hz), 84.2 (d, $J_{P\text{-}C}$ = 195.6 Hz), 62.55 (d, $J_{P\text{-}C}$ = 4.1 Hz), 62.49 (d, $J_{P\text{-}C}$ = 4.6 Hz), 21.2, 16.2 (d, $J_{P\text{-}C}$ = 5.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.9. IR (KBr) 1942, 1259, 1025, 820 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{19}O_3P$ [M^+] 266.1072 found 266.1074.



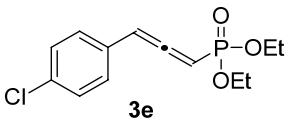
3c

*diethyl (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)phosphonate (**3c**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 50.7 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (d, J = 7.6 Hz, 1H), 7.22 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H), 6.91 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.81 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 5.72 (d, J = 6.8 Hz, 1H), 4.18-4.09 (m, 4H), 3.83 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.1 (d, $J_{P\text{-}C}$ = 1.4 Hz), 156.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 129.0 (d, $J_{P\text{-}C}$ = 1.7 Hz), 128.3 (d, $J_{P\text{-}C}$ = 3.4 Hz), 120.8 (d, $J_{P\text{-}C}$ = 1.3 Hz), 119.7 (d, $J_{P\text{-}C}$ = 8.3 Hz), 110.9 (d, $J_{P\text{-}C}$ = 1.5 Hz), 90.0 (d, $J_{P\text{-}C}$ = 16.0 Hz), 82.9 (d, $J_{P\text{-}C}$ = 196.2 Hz), 62.52 (d, $J_{P\text{-}C}$ = 1.4 Hz), 62.46 (d, $J_{P\text{-}C}$ = 1.4 Hz), 55.4, 16.28 (d, $J_{P\text{-}C}$ = 2.2 Hz), 16.22 (d, $J_{P\text{-}C}$ = 1.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.5. IR (KBr) 1943, 1597, 1495, 1252, 1051, 965 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{19}O_4P$ [M^+] 282.1021 found 282.1024.



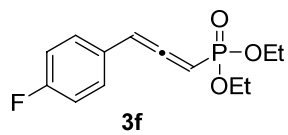
3d

*diethyl (3-(3-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3d**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 56.1 mg, 85%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (s, 1H), 7.37-7.35 (m, 1H), 7.19-7.17 (m, 2H), 6.38 (dd, J_1 = 13.2 Hz, J_2 = 6.8 Hz, 1H), 5.82 (d, J = 6.8 Hz, 1H), 4.18-4.10 (m, 4H), 1.33 (t, J = 6.8 Hz, 3H), 1.30 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.0 (d, $J_{P\text{-}C}$ = 1.5 Hz), 133.6 (d, $J_{P\text{-}C}$ = 9.1 Hz), 130.8 (d, $J_{P\text{-}C}$ = 1.9 Hz), 130.3 (d, $J_{P\text{-}C}$ = 1.7 Hz), 129.8 (d, $J_{P\text{-}C}$ = 2.5 Hz), 125.7 (d, $J_{P\text{-}C}$ = 2.8 Hz), 122.9 (d, $J_{P\text{-}C}$ = 0.9 Hz), 94.7 (d, $J_{P\text{-}C}$ = 16.3 Hz), 84.9 (d, $J_{P\text{-}C}$ = 194.5 Hz), 62.7 (d, $J_{P\text{-}C}$ = 6.4 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.3. IR (KBr) 1945, 1475, 1260, 1026, 798 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{13}H_{16}O_3PBr$ [M^+] 330.0020 found 330.0014.



3e

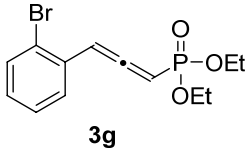
*diethyl (3-(4-chlorophenyl)propa-1,2-dien-1-yl)phosphonate (**3e**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 50.3 mg, 88%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.27 (m, 2 H), 7.21-7.19 (m, 2 H), 6.41 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 5.80 (d, J = 6.8 Hz, 1H), 4.18-4.09 (m, 4H), 1.33 (t, J = 6.4 Hz, 3H), 1.30 (t, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 133.5 (d, $J_{P\text{-}C}$ = 2.0 Hz), 129.9 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.0 (d, $J_{P\text{-}C}$ = 1.2 Hz), 128.3 (d, $J_{P\text{-}C}$ = 2.6 Hz), 94.9 (d, $J_{P\text{-}C}$ = 16.5 Hz), 84.8 (d, $J_{P\text{-}C}$ = 195.0 Hz), 62.70 (d, $J_{P\text{-}C}$ = 3.2 Hz), 62.63 (d, $J_{P\text{-}C}$ = 2.6 Hz), 16.2 (d, $J_{P\text{-}C}$ = 7.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.4. IR (KBr) 1944, 1491, 1257, 1025, 965 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{13}H_{16}O_3PCl$ [M^+] 286.0526 found 286.0529.



3f

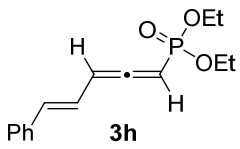
*diethyl (3-(4-fluorophenyl)propa-1,2-dien-1-yl)phosphonate (**3f**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 48.0 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.22 (m, 2 H), 7.03-6.98 (m, 2 H), 6.42 (dd, J_1 = 13.2 Hz, J_2 = 6.4 Hz, 1H), 5.78 (d, J = 6.4 Hz, 1H), 4.17-4.09 (m, 4H), 1.32 (t, J = 6.8 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.0 (dd, $J_{F\text{-}C}$ = 2.2 Hz, $J_{P\text{-}C}$ = 1.8 Hz), 162.3 (dd, $J_{F\text{-}C}$ = 246.5 Hz, $J_{P\text{-}C}$ = 2.4

Hz), 128.6 (dd, $J_{F\text{-}C}$ = 8.2 Hz, $J_{P\text{-}C}$ = 3.2 Hz), 127.2 (d, $J_{F\text{-}C}$ = 9.1 Hz, $J_{P\text{-}C}$ = 3.0 Hz), 115.9 (d, $J_{F\text{-}C}$ = 21.8 Hz, $J_{P\text{-}C}$ = 2.2 Hz), 94.8 (d, $J_{P\text{-}C}$ = 16.6 Hz), 84.6 (d, $J_{P\text{-}C}$ = 195.5 Hz), 62.62 (d, $J_{P\text{-}C}$ = 2.2 Hz), 62.56 (d, $J_{P\text{-}C}$ = 3.3 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.6 (d, $J_{F\text{-}P}$ = 4.0 Hz). IR (KBr) 1944, 1509, 1257, 1025, 966 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{13}H_{16}O_3PF$ [M^+] 270.0821 found 270.0819.



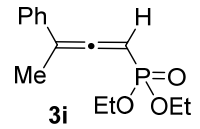
3g

*diethyl (3-(2-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3g**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 52.8 mg, 80%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.13-7.08 (m, 1H), 6.93 (dd, J_1 = 13.2 Hz, J_2 = 6.8 Hz, 1H), 5.83 (d, J = 6.8 Hz, 1H), 4.21-4.11 (m, 4H), 1.36 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.4 (d, $J_{P\text{-}C}$ = 1.6 Hz), 133.1 (d, $J_{P\text{-}C}$ = 1.4 Hz), 131.3 (d, $J_{P\text{-}C}$ = 8.3 Hz), 129.1 (d, $J_{P\text{-}C}$ = 1.6 Hz), 128.8 (d, $J_{P\text{-}C}$ = 2.6 Hz), 127.7, 122.6 (d, $J_{P\text{-}C}$ = 3.5 Hz), 94.8 (d, $J_{P\text{-}C}$ = 17.3 Hz), 84.6 (d, $J_{P\text{-}C}$ = 194.7 Hz), 62.71 (d, $J_{P\text{-}C}$ = 1.4 Hz), 62.65 (d, $J_{P\text{-}C}$ = 1.2 Hz), 16.32 (d, $J_{P\text{-}C}$ = 1.8 Hz), 16.25 (d, $J_{P\text{-}C}$ = 2.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.3. IR (KBr) 1945, 1475, 1258, 1023, 791 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{13}H_{16}O_3PBr$ [M^+] 330.0020 found 330.0014.



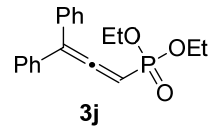
3h

*diethyl (E)-(5-phenylpenta-1,2,4-trien-1-yl)phosphonate (**3h**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 45.1 mg, 81%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, J = 7.2 Hz, 2H), 7.34-7.26 (m, 3H), 6.58-6.56 (m, 2H), 6.33-6.26 (m, 1H), 5.65 (d, J = 6.4 Hz, 1H), 4.18-4.11 (m, 4H), 1.36 (t, J = 4.0 Hz, 3H), 1.36 (t, J = 3.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.9 (d, $J_{P\text{-}C}$ = 2.1 Hz), 136.5 (d, $J_{P\text{-}C}$ = 1.9 Hz), 132.9 (d, $J_{P\text{-}C}$ = 6.6 Hz), 128.7, 128.0, 126.4 (d, $J_{P\text{-}C}$ = 1.5 Hz), 120.6 (d, $J_{P\text{-}C}$ = 10.9 Hz), 95.6 (d, $J_{P\text{-}C}$ = 16.9 Hz), 82.3 (d, $J_{P\text{-}C}$ = 196.1 Hz), 62.68 (d, $J_{P\text{-}C}$ = 5.6 Hz), 62.62 (d, $J_{P\text{-}C}$ = 6.61 Hz), 16.3 (d, $J_{P\text{-}C}$ = 6.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.7. IR (KBr) 1935, 1449, 1391, 1259, 1025 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{15}H_{19}O_3$ [M^+] 278.1072 found 278.1075.



3i

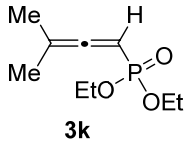
*diethyl (3-phenylbuta-1,2-dien-1-yl)phosphonate (**3i**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 52.7 mg, 99%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.33 (m, 4H), 7.27-7.24 (m, 1H), 5.70-5.66 (m, 1H), 4.17-4.09 (m, 4H), 2.17 (dd, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8 (d, $J_{P\text{-}C}$ = 2.4 Hz), 134.3 (d, $J_{P\text{-}C}$ = 8.1 Hz), 128.5 (d, $J_{P\text{-}C}$ = 1.5 Hz), 127.5 (d, $J_{P\text{-}C}$ = 1.3 Hz), 125.87 (d, $J_{P\text{-}C}$ = 2.7 Hz), 102.3 (d, $J_{P\text{-}C}$ = 16.9 Hz), 82.2 (d, $J_{P\text{-}C}$ = 195.9 Hz), 62.4 (d, $J_{P\text{-}C}$ = 2.0 Hz), 62.3 (d, $J_{P\text{-}C}$ = 2.0 Hz), 16.3 (dd, J_1 = 16.3 Hz, J_2 = 3.2 Hz), 15.9 (d, $J_{P\text{-}C}$ = 7.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.7. IR (KBr) 1943, 1259, 1027, 964, 798 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{19}O_3P$ [M^+] 266.1072 found 266.1070.



3j

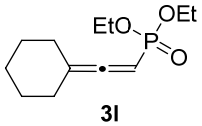
*diethyl (3,3-diphenylpropa-1,2-dien-1-yl)phosphonate (**3j**)*. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 64.2 mg, 98%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.31 (m, 10H), 5.89 (s, 1H), 4.14-4.04

(m, 4H), 1.27 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2 (d, $J_{P\text{-}C}$ = 2.5 Hz), 134.2 (d, $J_{P\text{-}C}$ = 7.3 Hz), 128.6, 128.56 (d, $J_{P\text{-}C}$ = 2.7 Hz), 128.1, 111.3 (d, $J_{P\text{-}C}$ = 17.3 Hz), 83.2 (d, $J_{P\text{-}C}$ = 194.6 Hz), 62.5 (d, $J_{P\text{-}C}$ = 5.6 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.0. IR (KBr) 1953, 1268, 1032, 974, 802 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{19}H_{21}O_3P$ [M^+] 328.1228 found 328.1226.



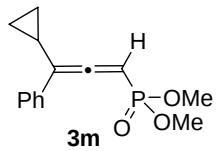
3k

*diethyl (3-methylbuta-1,2-dien-1-yl)phosphonate (**3k**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 32.6 mg, 80%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.16−5.11 (m, 1H), 4.09−4.02 (m, 4H), 1.74 (dd, J_1 = 7.6 Hz, J_2 = 3.2 Hz, 6H), 1.29 (t, J = 7.2 Hz, 6H). This is a known compound: Macomber, R. S.; Krudy, G. A.; Seff, K.; Rendon-Diazmiron, L. E. *J. Org. Chem.* **1983**, *48*, 1425.



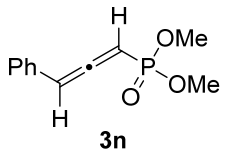
3l

*diethyl (2-cyclohexylidenevinyl)phosphonate (**3l**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 42.9 mg, 88%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.18−5.16 (m, 1H), 4.12−4.05 (m, 4H), 2.21-2.16 (m, 4H), 1.66-1.50 (m, 6H), 1.32 (t, J = 7.2 Hz, 6H). This is a known compound: Altenbach, H. J.; Korff, R. *Tetrahedron Lett.* **1981**, *22*, 5175.



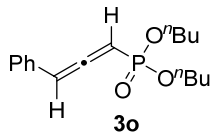
3m

*dimethyl (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)phosphonate (**3m**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 44.3 mg, 84%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 8.0 Hz, 2H), 7.38-7.34 (m, 2H), 7.29-7.25 (m, 1H), 5.72 (t, J = 2.8 Hz, 1H), 3.76 (d, J = 11.2 Hz, 3H), 3.73 (d, J = 11.2 Hz, 3H), 1.68-1.57 (m, 1H), 0.98-0.94 (m, 2H), 0.64-0.61 (m, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.8. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1 (d, $J_{P\text{-}C}$ = 2.1 Hz), 134.4 (d, $J_{P\text{-}C}$ = 8.1 Hz), 128.6 (d, $J_{P\text{-}C}$ = 1.7 Hz), 127.8 (d, $J_{P\text{-}C}$ = 1.7 Hz), 126.5 (d, $J_{P\text{-}C}$ = 2.5 Hz), 111.1 (d, $J_{P\text{-}C}$ = 16.7 Hz), 83.3(d, $J_{P\text{-}C}$ = 197.3 Hz), 52.9 (t, $J_{P\text{-}C}$ = 5.7 Hz), 10.2 (d, $J_{P\text{-}C}$ = 7.6 Hz), 7.1 (d, $J_{P\text{-}C}$ = 3.0 Hz), 7.0 (d, $J_{P\text{-}C}$ = 2.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.8. IR (KBr) 1945, 1251, 1021, 956, 801 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{14}H_{17}O_3P$ [M^+] 264.0915; found 264.0916.

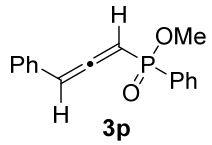


3n

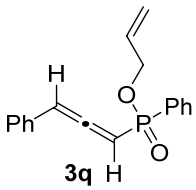
*dimethyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3n**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 39.8 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.24 (m, 5H), 6.47 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 5.78 (d, J = 6.8 Hz, 1H), 3.80 (d, J = 6.8 Hz, 3H), 3.77 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.6 (d, $J_{P\text{-}C}$ = 1.3 Hz), 131.1 (d, $J_{P\text{-}C}$ = 9.2 Hz), 128.9 (d, $J_{P\text{-}C}$ = 1.3 Hz), 128.0 (d, $J_{P\text{-}C}$ = 1.9 Hz), 127.2 (d, $J_{P\text{-}C}$ = 2.9 Hz), 95.8 (d, $J_{P\text{-}C}$ = 16.5 Hz), 83.1 (d, $J_{P\text{-}C}$ = 196.3 Hz), 53.14 (d, $J_{P\text{-}C}$ = 2.6 Hz), 53.08 (d, $J_{P\text{-}C}$ = 2.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.4. IR (KBr) 1942, 1457, 1256, 1026 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{11}H_{13}O_3P$ [M^+] 224.0602; found 224.0606.



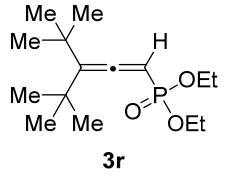
*dibutyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3o**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 49.3 mg, 80%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.25 (m, 5H), 6.45 (dd, J_1 = 13.2 Hz, J_2 = 6.8 Hz, 1H), 5.79 (d, J = 6.8 Hz, 1H), 4.10-4.02 (m, 4H), 1.70-1.59 (m, 4H), 1.42-1.32 (m, 4H), 0.91 (t, J = 7.6 Hz, 3H), 0.87 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1 (d, $J_{P\text{-}C}$ = 1.3 Hz), 131.4 (d, $J_{P\text{-}C}$ = 8.4 Hz), 128.8 (d, $J_{P\text{-}C}$ = 1.5 Hz), 127.8 (d, $J_{P\text{-}C}$ = 1.3 Hz), 127.2 (d, $J_{P\text{-}C}$ = 3.1 Hz), 95.7 (d, $J_{P\text{-}C}$ = 17.2 Hz), 84.3 (d, $J_{P\text{-}C}$ = 195.8 Hz), 66.3 (d, $J_{P\text{-}C}$ = 7.3 Hz), 32.4 (dd, $J_{P\text{-}C}$ = 6.6, 1.7 Hz), 18.7 (d, $J_{P\text{-}C}$ = 5.2 Hz), 13.6 (d, $J_{P\text{-}C}$ = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.7. IR (KBr) 1943, 1457, 1259, 1024 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{17}H_{25}O_3P$ [M^+] 308.1541; found 308.1537.



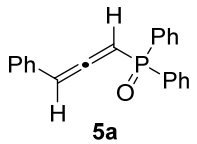
*methyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3p**). The compound was obtained as a 3.2:1 diastereoisomer mixture.* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 49.7 mg, 92%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.79 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.42 (m, 2H), 7.30-7.19 (m, 5H), 6.42-6.35 (m, 1H), 6.02-5.98 (m, 1H), 3.80-3.73 (m, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.7, 29.5. HRMS (EI-TOF) (*m/z*): calcd for $C_{16}H_{15}O_2P$ [M^+] 270.0810; found 270.0808.



*allyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3q**). The compound was obtained as a 2.9:1 diastereoisomer mixture.* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 53.2 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.81 (m, 2H), 7.54-7.50 (m, 1H), 7.46-7.41 (m, 2H), 7.31-7.15 (m, 5H), 6.40-6.35 (m, 1H), 6.04-6.02 (m, 1H), 5.95-5.87(m, 1H), 5.38-5.16 (m, 2H), 4.59-4.50 (m, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.8, 28.5. HRMS (EI-TOF) (*m/z*): calcd for $C_{18}H_{17}O_2P$ [M^+] 296.0966; found 296.0970.

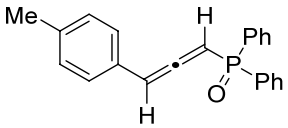


*diethyl (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3r**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 45.5 mg, 79%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.23 (d, J = 7.2 Hz, 1H), 4.11-4.04 (m, 4H), 1.30 (t, J = 7.2 Hz, 6H), 1.20 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.5, 122.8 (d, $J_{P\text{-}C}$ = 17.3 Hz), 80.9 (d, $J_{P\text{-}C}$ = 201.1 Hz), 61.7 (d, $J_{P\text{-}C}$ = 6.1 Hz), 34.6 (d, $J_{P\text{-}C}$ = 6.0 Hz), 31.7 (d, $J_{P\text{-}C}$ = 3.0 Hz), 16.3 (d, $J_{P\text{-}C}$ = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 17.0. IR (KBr) 1955, 1382, 1245, 1027 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{15}H_{29}O_3P$ [M^+] 288.1854; found 288.1852.



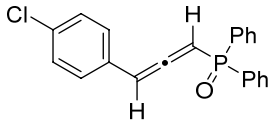
*diphenyl(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5a**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 60.0 mg, 95%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.74 (m, 4H), 7.53-7.39 (m, 6H), 7.29-7.20 (m, 3H), 7.14 (d, J = 7.6 Hz, 2H), 6.32-6.26 (m, 2H). ^{31}P NMR

($CDCl_3$, 162 MHz): δ 24.3. This is a known compound: Santelli-Rouvier, C.; Toupet, L.; Santelli, M. *J. Org. Chem.* **1997**, *62*, 9039.



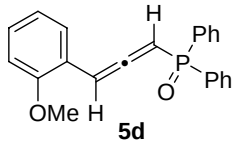
5b

*diphenyl(3-(p-tolyl)propa-1,2-dien-1-yl)phosphine oxide (**5b**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 60.7 mg, 92%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.74 (m, 4H), 7.51-7.39 (m, 6H), 7.07 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.29-6.23 (m, 2H), 2.31 (s, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.1. This is a known compound: He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035.



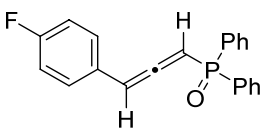
5c

*(3-(4-chlorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5c**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 63.1 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.72 (m, 4H), 7.54-7.39 (m, 6H), 7.23 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.33-6.22 (m, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.7. Known compound: He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035.



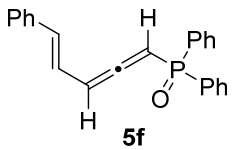
5d

*(3-(2-methoxyphenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5d**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 63.0 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.74 (m, 4H), 7.51-7.39 (m, 6H), 7.17 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.63 (dd, J_1 = 11.2 Hz, J_2 = 6.8 Hz, 1H), 6.22 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 156.0 (d, $J_{P\text{-}C}$ = 2.0 Hz), 132.5 (d, $J_{P\text{-}C}$ = 105.4 Hz), 132.3 (d, $J_{P\text{-}C}$ = 106.7 Hz), 131.81 (d, $J_{P\text{-}C}$ = 2.1 Hz), 131.79 (d, $J_{P\text{-}C}$ = 2.1 Hz), 131.3 (d, $J_{P\text{-}C}$ = 10.7 Hz), 131.2 (d, $J_{P\text{-}C}$ = 9.2 Hz), 128.9 (d, $J_{P\text{-}C}$ = 1.6 Hz), 128.28 (d, $J_{P\text{-}C}$ = 12.1 Hz), 128.27 (d, $J_{P\text{-}C}$ = 1.9 Hz), 120.7, 119.6 (d, $J_{P\text{-}C}$ = 6.9 Hz), 110.8, 90.7 (d, $J_{P\text{-}C}$ = 13.3 Hz), 88.0 (d, $J_{P\text{-}C}$ = 104.1 Hz), 55.3. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.9. IR (KBr) 1936, 1596, 1494, 1436, 1250, 1120, 745 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{22}H_{19}O_2P$ [M^+] 346.1123; found 346.1121.



5e

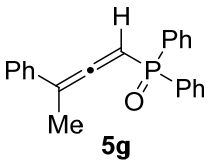
*(3-(4-fluorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5e**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 60.0 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.71 (m, 4H), 7.53-7.38 (m, 6H), 7.10-7.06 (m, 2H), 6.96-6.92 (m, 2H), 6.34-6.24 (m, 2H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.9. Known compound: He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035.



5f

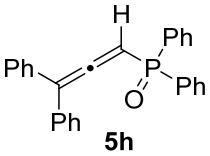
*(E)-diphenyl(5-phenylpenta-1,2,4-trien-1-yl)phosphine oxide (**5f**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 62.2 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.66 (m, 4 H), 7.45-7.36 (m, 6H), 7.27-7.15 (m, 5H), 6.38-6.36 (m, 2H), 6.10-6.01 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.7 (d, $J_{P\text{-}C}$ = 3.5 Hz), 136.6 (d, $J_{P\text{-}C}$ = 2.4 Hz), 132.8 (d, $J_{P\text{-}C}$ =

5.1 Hz), 132.4 (d, $J_{P\text{-}C}$ = 106.0 Hz), 132.1 (d, $J_{P\text{-}C}$ = 105.4 Hz), 132.02 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.99 (d, $J_{P\text{-}C}$ = 1.8 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 9.3 Hz), 128.6, 128.5, 128.4, 127.9, 126.4, 120.5 (d, $J_{P\text{-}C}$ = 9.1 Hz), 96.2 (d, $J_{P\text{-}C}$ = 14.1 Hz), 87.7 (d, $J_{P\text{-}C}$ = 102.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.4. IR (KBr) 1929, 1715, 1592, 1494, 1436, 1260, 1104, 906 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{23}H_{19}OP$ [M^+] 342.1174 found 342.1169.



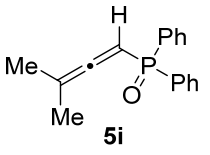
5g

*diphenyl(3-phenylbuta-1,2-dien-1-yl)phosphine oxide (**5g**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 62.7 mg, 95%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.71 (m, 4H), 7.51-7.37 (m, 6H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 3H), 6.16-6.14 (m, 1H), 1.93 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.5. Known compound: He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035.



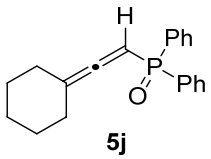
5h

*(3,3-diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5h**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 62.6 mg, 80%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.67 (m, 4H), 7.49-7.45 (m, 2H), 7.38-7.34 (m, 4H), 7.31-7.27 (m, 6H), 7.07-7.04 (m, 4H), 6.37 (d, J = 0.8 Hz, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.1. Known compound: Santelli-Rouvier, C.; Toupet, L.; Santelli, M. *J. Org. Chem.* **1997**, *62*, 9039.



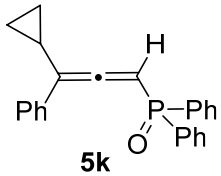
5i

*(3,3-dimethylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5i**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 47.2 mg, 88%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.69 (m, 4H), 7.52-7.41 (m, 6H), 5.69-5.64 (m, 1H), 1.52 (q, J = 0.8 Hz, 6H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.1. Known compound: Christov, V. C.; Ivanova, J. G. *Synth. Comm.* **2006***, 36,* 2231.



5j

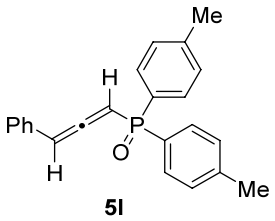
*(2-cyclohexylidenevinyl)diphenylphosphine oxide (**5j**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 54.8 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.71 (m, 4H), 7.51-7.41 (m, 6H), 5.67-5.65 (m, 1H), 1.99-1.93 (m, 4H), 1.49-1.43 (m, 2H), 1.34-1.26 (m, 2H), 1.06-0.99 (m, 2H). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 26.7. Known compound: Christov, V. C.; Ivanova, J. G. *Synth. Comm.* **2006***, 36,* 2231.



5k

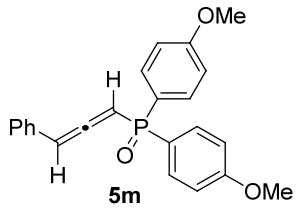
*(3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5k**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 64.1 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.68 (m, 4H), 7.51-7.45 (m, 2H), 7.41-7.35 (m, 6H), 7.34-7.23 (m, 3H), 6.26 (t, J = 2.8 Hz, 1H), 1.41-1.33 (m, 1H), 0.81-0.70 (m, 2H), 0.41-0.35 (m, 1H), (-0.11)-(-0.17) (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.3 (d, $J_{P\text{-}C}$ = 1.4 Hz), 134.6 (d, $J_{P\text{-}C}$ = 6.7 Hz), 132.6 (d, $J_{P\text{-}C}$ = 106.2 Hz), 131.9 (d, $J_{P\text{-}C}$ = 105.3 Hz), 131.8 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.2 (d, $J_{P\text{-}C}$ = 9.5 Hz), 128.4, 128.3 (d, $J_{P\text{-}C}$ = 8.5 Hz), 128.2 (d, $J_{P\text{-}C}$ = 8.2 Hz),

127.6 (d, $J_{P\text{-}C}$ = 1.4 Hz), 126.3 (d, $J_{P\text{-}C}$ = 1.8 Hz), 111.4 (d, $J_{P\text{-}C}$ = 13.7 Hz), 89.9 (d, $J_{P\text{-}C}$ = 102.7 Hz), 10.2 (d, $J_{P\text{-}C}$ = 5.4 Hz), 7.2 (d, $J_{P\text{-}C}$ = 3.3 Hz), 6.2 (br). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.9. IR (KBr) 1939, 1494, 1441, 1364, 1192,1117 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{24}H_{21}OP$ [M^+] 356.1330; found 356.1331.



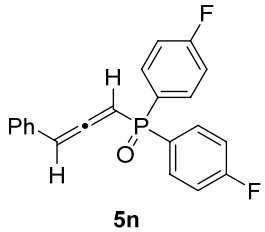
5l

*(3-phenylpropa-1,2-dien-1-yl)di-p-tolylphosphine oxide (**5l**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 60.5 mg, 88%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.62 (m, 4 H), 7.28-7.19 (m, 7H), 7.14 (d, J = 8.0 Hz, 2H), 6.29-6.24 (m, 2H), 2.35 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (d, J = 1.7 Hz), 142.4 (J = 2.6 Hz), 142.3 (J = 2.6 Hz), 131.5 (d, J = 7.7 Hz), 131.3 (d, J = 10.5 Hz), 131.2 (d, J = 9.8 Hz), 129.3 (d, J = 108.5 Hz), 129.1 (d, J = 108.2 Hz), 129.1 (d, J = 1.9 Hz), 129.0 (d, J = 1.4 Hz), 128.6 (d, J = 1.4 Hz), 127.6 (d, J = 1.4 Hz), 127.0 (d, J = 1.6 Hz), 96.1 (d, J = 13.4 Hz), 89.9 (d, J = 100.9 Hz), 21.5. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.2. IR (KBr) 1937, 1715, 1600, 1497, 1451, 1164, 808 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{23}H_{21}OP$ [M^+] 344.1330 found 344.1328.



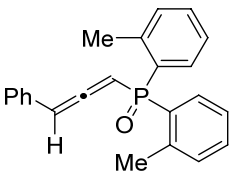
5m

*bis(4-methoxyphenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5m**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 61.0 mg, 81%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.64 (m, 4H), 7.30-7.21 (m, 3H), 7.16-7.14 (m, 2H), 6.94-6.89 (m, 4H), 6.27-6.24 (m, 2H), 3.82 (d, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.6 (br), 162.39 (d, $J_{P\text{-}C}$ = 1.5 Hz), 162.37 (d, $J_{P\text{-}C}$ = 1.5 Hz), 133.2 (d, $J_{P\text{-}C}$ = 12.5 Hz), 133.1 (d, $J_{P\text{-}C}$ = 14.0 Hz), 131.5 (d, $J_{P\text{-}C}$ = 6.7 Hz), 128.6 (d, $J_{P\text{-}C}$ = 1.5 Hz), 127.6 (d, $J_{P\text{-}C}$ = 1.5 Hz), 126.9 (d, $J_{P\text{-}C}$ = 2.0 Hz), 123.8 (d, $J_{P\text{-}C}$ = 114.2 Hz), 123.5 (d, $J_{P\text{-}C}$ = 114.3 Hz), 113.9 (d, $J_{P\text{-}C}$ = 12.5 Hz), 96.0 (d, $J_{P\text{-}C}$ = 13.5 Hz), 90.2 (d, $J_{P\text{-}C}$ = 101.8 Hz), 55.2. ^{31}P NMR ($CDCl_3$, 160 MHz): δ 24.1. IR (KBr) 1937, 1710, 1597, 1504, 1295, 1258, 1179, 1122, 1026, 830 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{23}H_{21}O_3P$ [M^+] 376.1228; found 376.1224.



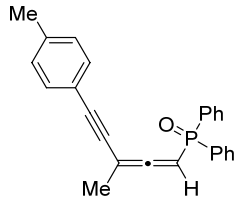
5n

*bis(4-fluorophenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5n**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 59.8 mg, 85%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.71 (m, 4H), 7.31-7.24 (m, 3H), 7.15-7.09 (m, 6H), 6.32-6.27 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2 (d, $J_{P\text{-}C}$ = 0.9 Hz), 163.6 (dt, $J_{F\text{-}C}$ = 252.5 Hz, $J_{P\text{-}C}$ = 3.2 Hz), 133.75 (dd, $J_{P\text{-}C}$ = 15.9 Hz, $J_{F\text{-}C}$ = 8.8 Hz), 133.74 (dd, $J_{P\text{-}C}$ = 9.3 Hz, $J_{F\text{-}C}$ = 2.5 Hz), 130.9 (d, $J_{P\text{-}C}$ = 6.7 Hz), 128.8, 128.1 (dd, $J_{P\text{-}C}$ = 110.1 Hz, $J_{F\text{-}C}$ = 3.5 Hz), 128.0 (d, J = 1.7 Hz), 127.8 (dd, $J_{P\text{-}C}$ = 110.5 Hz, $J_{F\text{-}C}$ = 3.3 Hz), 126.9 (d, $J_{P\text{-}C}$ = 2.1 Hz), 115.9 (dd, $J_{F\text{-}C}$ = 21.2 Hz, $J_{P\text{-}C}$ = 13.6 Hz), 96.5 (d, $J_{P\text{-}C}$ = 13.0 Hz), 89.5 (d, $J_{P\text{-}C}$ = 104.0 Hz). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 22.8 (br). IR (KBr) 1936, 1743, 1589, 1456, 1397, 1230, 1116, 828 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{21}H_{15}OPF_2$ [M^+] 352.0829; found 352.0826.



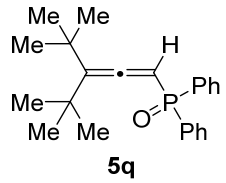
5o

*(3-phenylpropa-1,2-dien-1-yl)di-o-tolylphosphine oxide (**5o**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 50.2 mg, 73%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.67 (m, 2H), 7.43-7.36 (m, 2H), 7.25-7.16 (m, 7H), 7.11 (d, J = 7.6 Hz, 2H), 6.39 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H), 6.28 (dd, J_1 = 10.8 Hz, J_2 = 6.4 Hz, 1H), 2.41 (d, J = 3.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (d, $J_{P\text{-}C}$ = 1.1 Hz), 142.2 (d, $J_{P\text{-}C}$ = 8.7 Hz), 142.1 (d, $J_{P\text{-}C}$ = 8.5 Hz), 132.4 (d, $J_{P\text{-}C}$ = 2.3 Hz), 132.2 (d, $J_{P\text{-}C}$ = 1.3 Hz), 132.13 (d, $J_{P\text{-}C}$ = 3.0 Hz), 132.10 (d, $J_{P\text{-}C}$ = 3.2 Hz), 131.7, 131.6, 131.3 (d, $J_{P\text{-}C}$ = 7.7 Hz), 130.5 (d, $J_{P\text{-}C}$ = 104.4 Hz), 130.4 (d, $J_{P\text{-}C}$ = 104.3 Hz), 128.6, 127.7 (d, $J_{P\text{-}C}$ = 2.5 Hz), 127.1 (d, $J_{P\text{-}C}$ = 2.5 Hz), 125.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 125.5 (d, $J_{P\text{-}C}$ = 1.8 Hz), 96.3 (d, $J_{P\text{-}C}$ = 13.3 Hz), 89.2 (d, $J_{P\text{-}C}$ = 101.5 Hz), 21.50 (d, $J_{P\text{-}C}$ = 3.6 Hz), 21.47 (d, $J_{P\text{-}C}$ = 3.6 Hz). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 27.4. IR (KBr) 1939, 1717, 1605, 1497, 1452, 1165, 807 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{23}H_{21}OP$ [M^+] 344.1330; found 344.1328.



5p

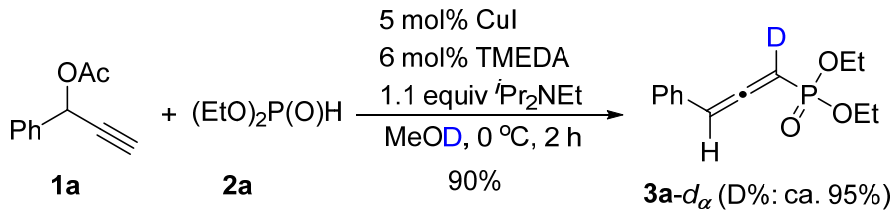
*(3-methyl-5-(p-tolyl)penta-1,2-dien-4-yn-1-yl)diphenylphosphine oxide (**5p**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 62.5 mg, 85%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.73 (m, 4H), 7.55-7.46 (m, 6H), 7.31 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.05-6.03 (m, 1H), 2.36 (s, 3H), 1.72 (dd, J_1 = 6.4 Hz, J_2 = 3.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 217.8 (d, $J_{P\text{-}C}$ = 3.4 Hz), 138.7, 132.3 (d, $J_{P\text{-}C}$ = 105.9 Hz), 132.5, 132.05 (d, $J_{P\text{-}C}$ = 3.2 Hz), 131.98 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.5 (d, $J_{P\text{-}C}$ = 6.2 Hz), 131.4 (d, $J_{P\text{-}C}$ = 5.8 Hz), 131.2 (d, $J_{P\text{-}C}$ = 1.5 Hz), 129.1, 128.5 (d, $J_{P\text{-}C}$ = 11.8 Hz), 128.3 (d, $J_{P\text{-}C}$ = 12.3 Hz), 119.8, 94.5 (d, $J_{P\text{-}C}$ = 4.7 Hz), 88.4 (d, $J_{P\text{-}C}$ = 13.3 Hz), 86.8 (d, $J_{P\text{-}C}$ = 101.0 Hz), 81.8 (d, $J_{P\text{-}C}$ = 10.6 Hz), 21.5, 18.4 (d, $J_{P\text{-}C}$ = 5.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.7. IR (KBr) 1928, 1717, 1590, 1442, 1260, 1101, 905 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{25}H_{21}OP$ [M^+] 368.1330; found 368.1332.



5q

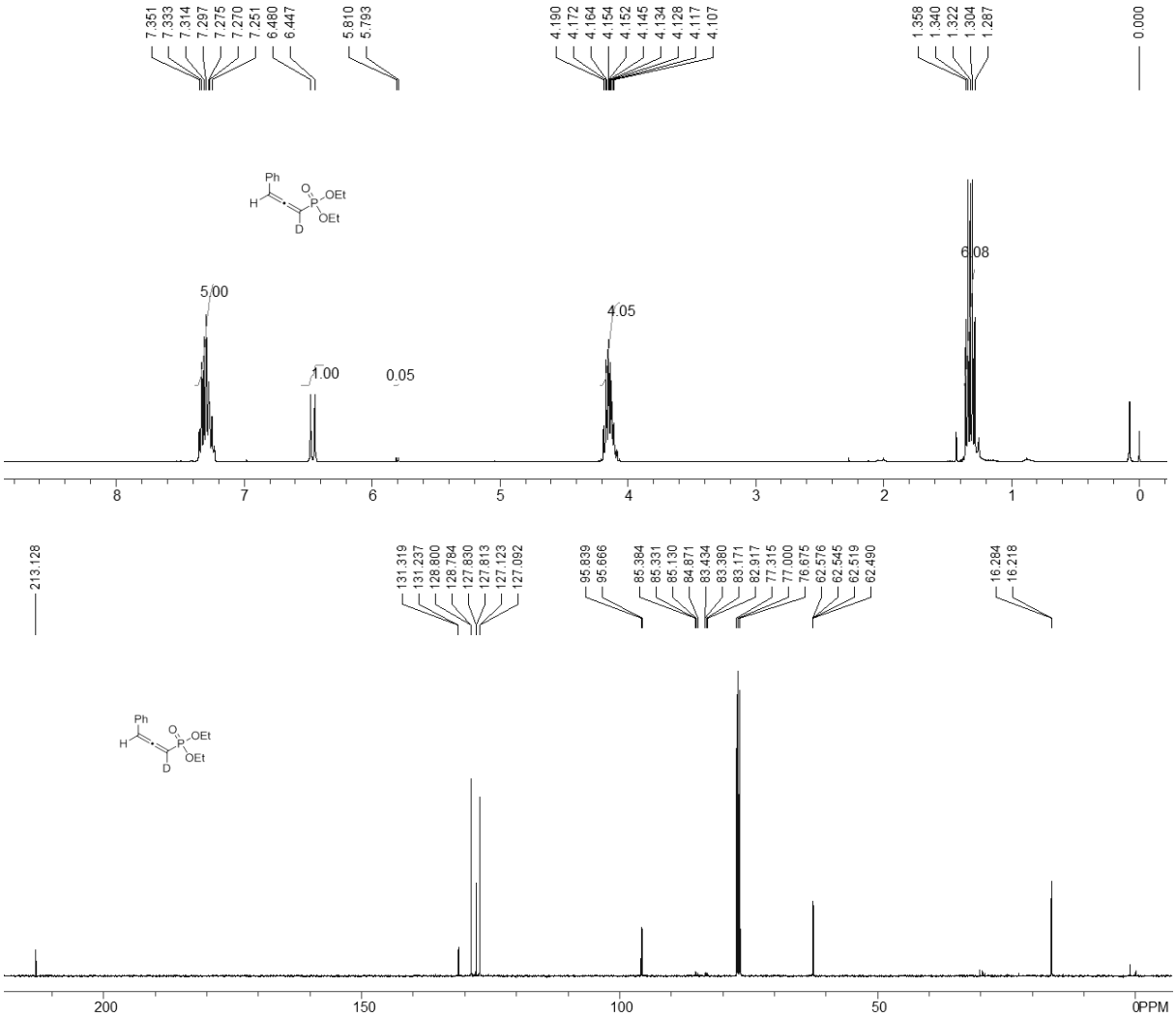
*(3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**5q**).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 62.2 mg, 89%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.72 (m, 4H), 7.51-7.41 (m, 6H), 5.84 (d, J = 5.6 Hz, 1H), 1.03 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.8, 133.1 (d, $J_{P\text{-}C}$ = 104.8 Hz), 131.62 (d, $J_{P\text{-}C}$ = 9.4 Hz), 131.64 (d, $J_{P\text{-}C}$ = 2.4 Hz), 128.2 (d, $J_{P\text{-}C}$ = 11.2 Hz), 123.2 (d, $J_{P\text{-}C}$ = 14.2 Hz), 86.3 (d, $J_{P\text{-}C}$ = 109.3 Hz), 34.7 (d, $J_{P\text{-}C}$ = 3.9 Hz), 31.8 (d, $J_{P\text{-}C}$ = 2.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.7. IR (KBr) 1956, 1434, 1192, 1165 cm^{-1}; HRMS (EI-TOF) (*m/z*): calcd for $C_{23}H_{29}OP$ [M^+] 352.1956; found 352.1959.

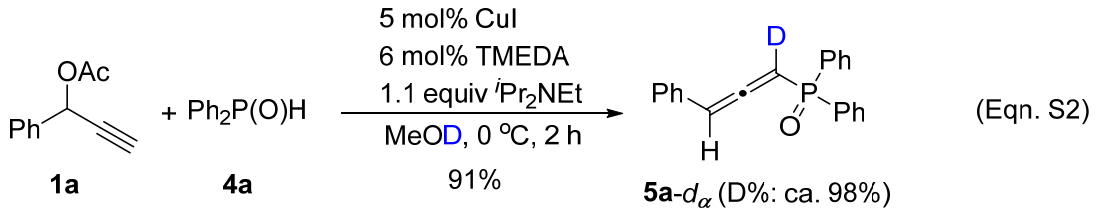
Experiments in deuterated methol



(Eqn. S1)

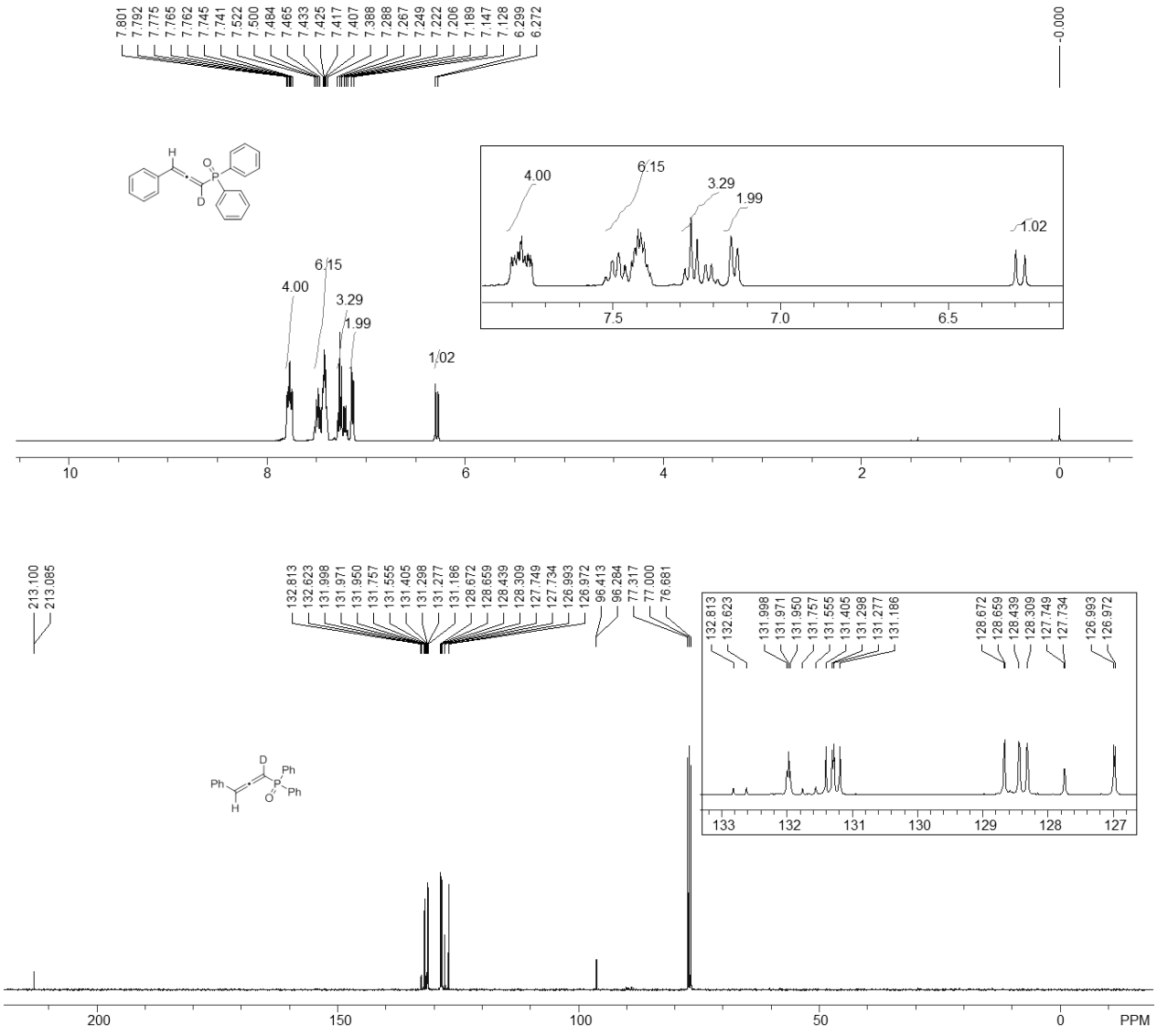
The reaction of **1a** (41.7 mg, 0.24 mmol) and **2a** (27.6 mg, 0.2 mmol) in CH_3OD (D% > 99.5%, 2 mL) afforded the α-deuterated allenylphosphonate **3a**-d_α (D%: ca. 95%) in 90% yield (Eqn. S1). *diethyl (3-phenylpropa-1,2-dien-1-yl-1-d)phosphonate (**3a**-d_α).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 45.5 mg, 90%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.25 (m, 5H), 6.46 (d, J = 13.2 Hz, 1H), 4.19-4.11 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1, 131.2 (d, $J_{P\text{-}C}$ = 8.2 Hz), 128.8 (d, $J_{P\text{-}C}$ = 1.6 Hz), 127.8 (d, $J_{P\text{-}C}$ = 1.7 Hz), 127.1 (d, $J_{P\text{-}C}$ = 3.1 Hz), 95.8 (d, $J_{P\text{-}C}$ = 17.3 Hz), 62.56 (d, $J_{P\text{-}C}$ = 3.1 Hz), 62.50 (d, $J_{P\text{-}C}$ = 2.9 Hz), 16.2 (d, $J_{P\text{-}C}$ = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.8. IR (neat) 1933, 1259, 1028, 798 cm^{-1}; HRMS (EI-TOF) (m/z): calcd for $C_{13}O_3PH_{16}D$ [M^+] 253.0978 found 253.0979.





(Eqn. S2)

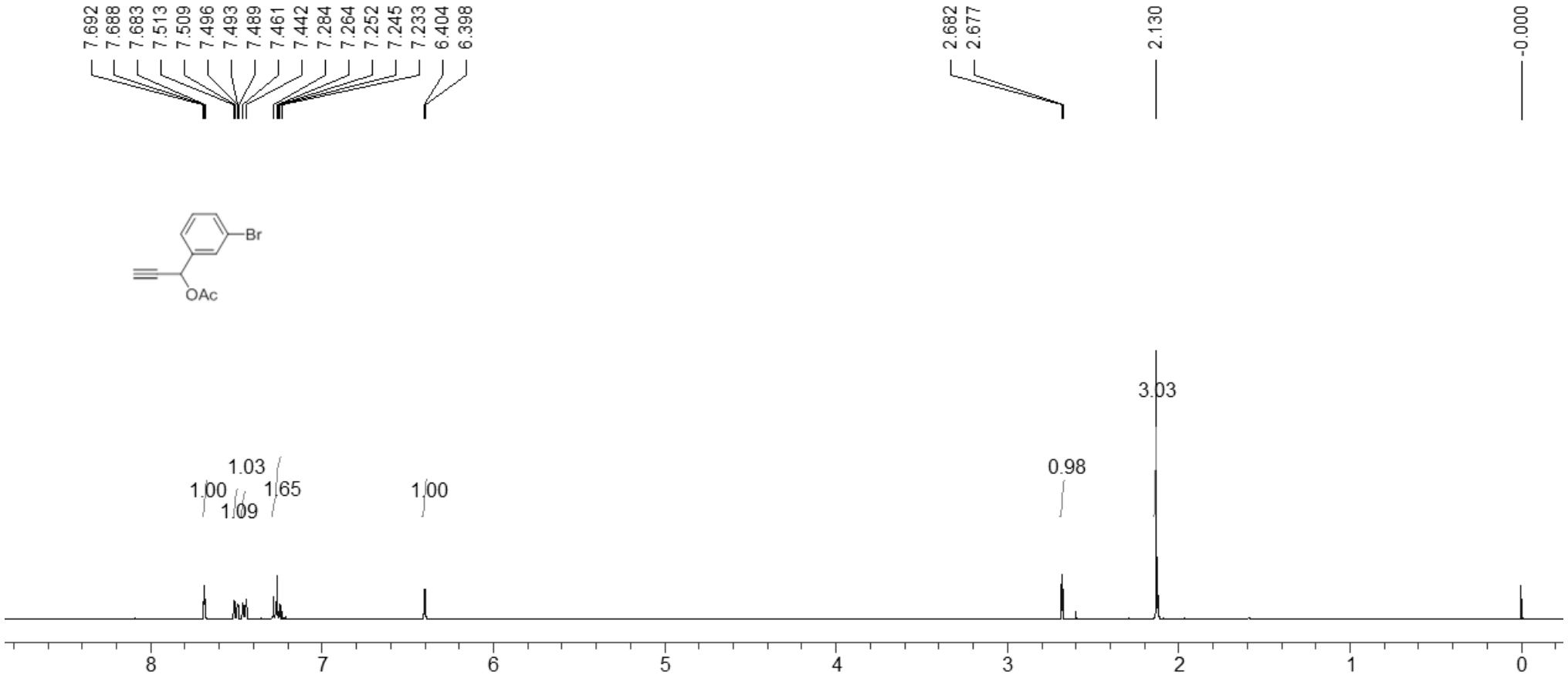
The reaction of **1a** (41.8 mg, 0.24 mmol) and **4a** (40.4 mg, 0.2 mmol) in CH_3OD (D% > 99.5%, 2 mL) was also performed, affording the α-deuterated allenylphosphine oxide **5a**-d_α (D%: ca. 98%) in 91% yield (Eqn. S2). *diphenyl(3-phenylpropa-1,2-dien-1-yl-1-d)phosphine oxide (**5a**-d_α).* [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 57.7 mg, 91%]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.74 (m, 4H), 7.52-7.39 (m, 6H), 7.29-7.19 (m, 3H), 7.14 (d, J = 7.6 Hz, 2H), 6.32-6.26 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.1 (d, J = 1.5 Hz), 132.4 (J = 105.6 Hz), 132.1 (J = 106.8 Hz), 131.98 (d, J = 2.7 Hz), 131.96 (d, J = 2.1 Hz), 131.4 (d, J = 15.0 Hz), 131.2 (d, J = 9.1 Hz), 128.7 (d, J = 11.3 Hz), 128.4, 128.3, 127.7 (d, J = 1.5 Hz), 127.0 (d, J = 2.1 Hz), 96.3 (d, J = 12.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.0. HRMS (EI-TOF) (*m/z*): calcd for $C_{21}OPH_{16}D$ [M^+] 317.1080; found 317.1084.



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

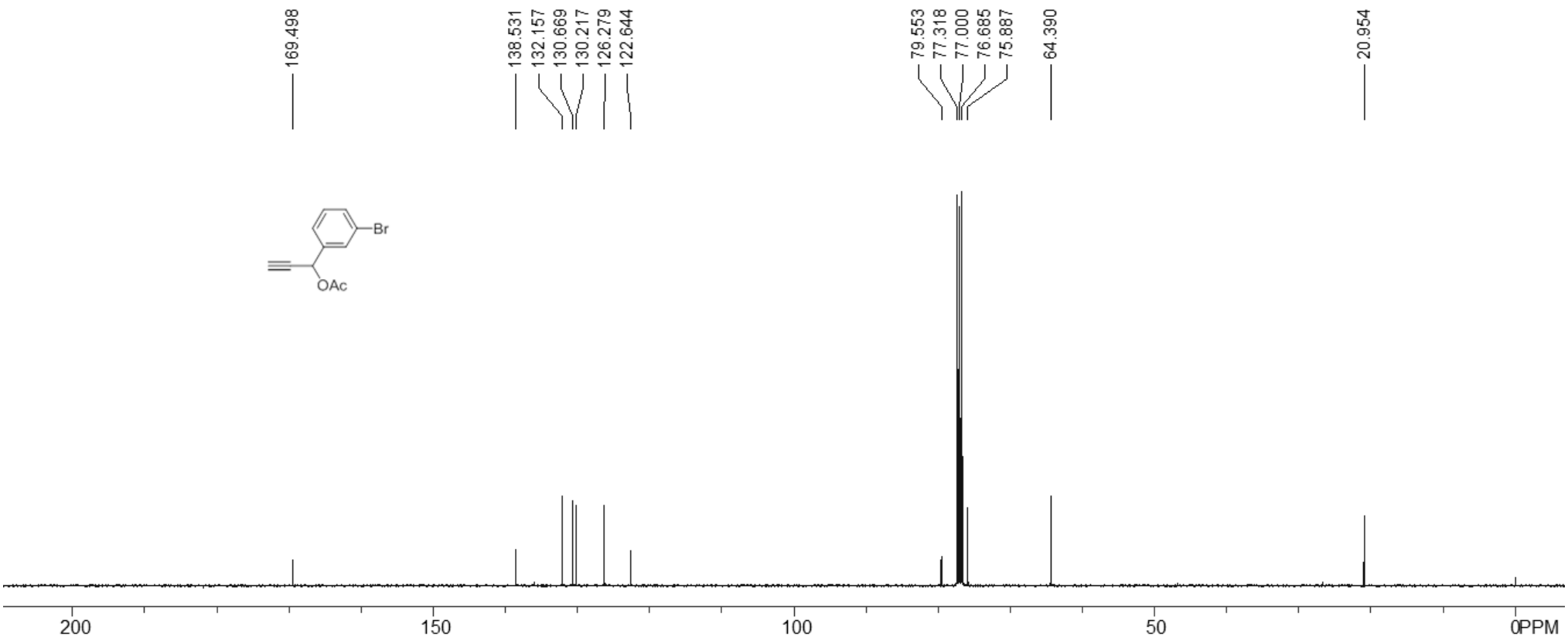
^{1}H NMR spectrum of 1-(3-bromophenyl)prop-2-yn-1-yl acetate (***1d***)

$CDCl_3$, 400MHz



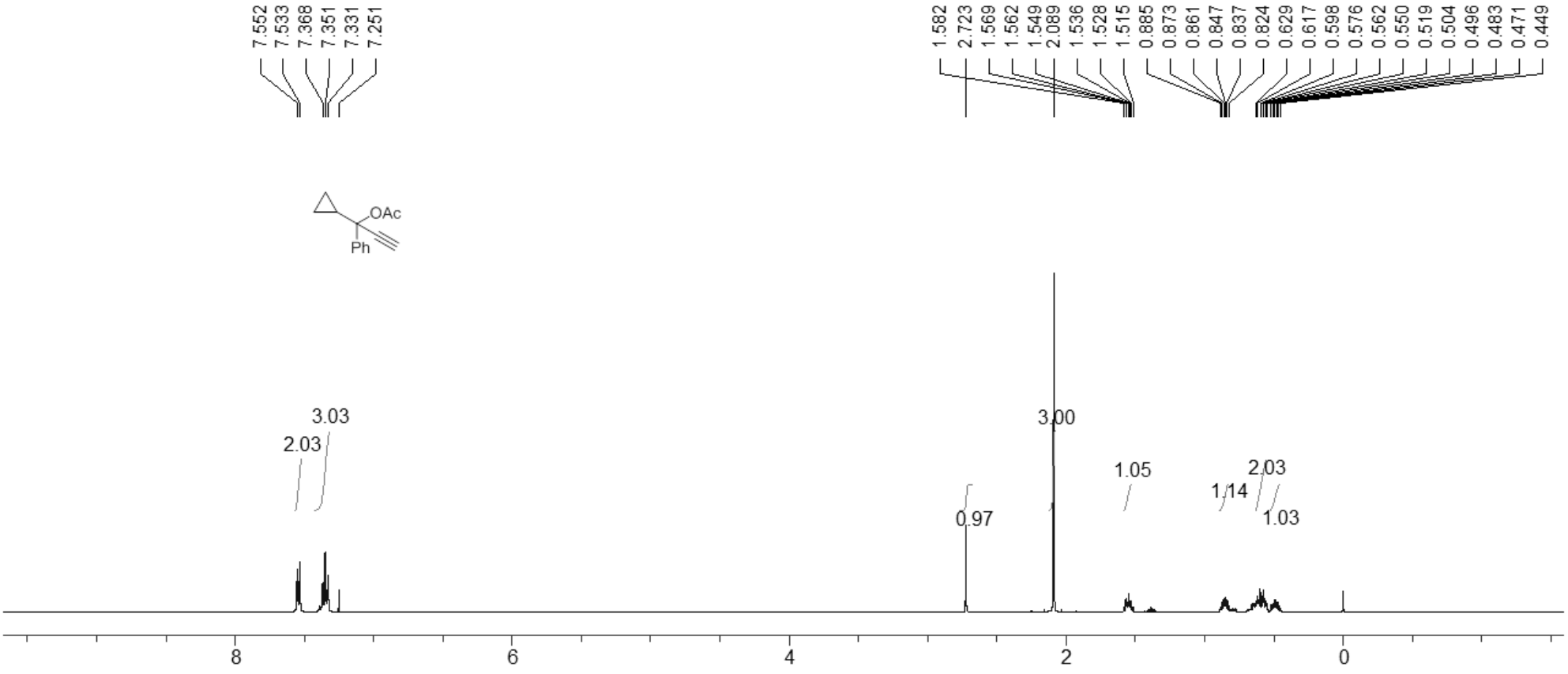
^{13}C NMR spectrum of 1-(3-bromophenyl)prop-2-yn-1-yl acetate (**1d**)

$CDCl_3$, 100MHz



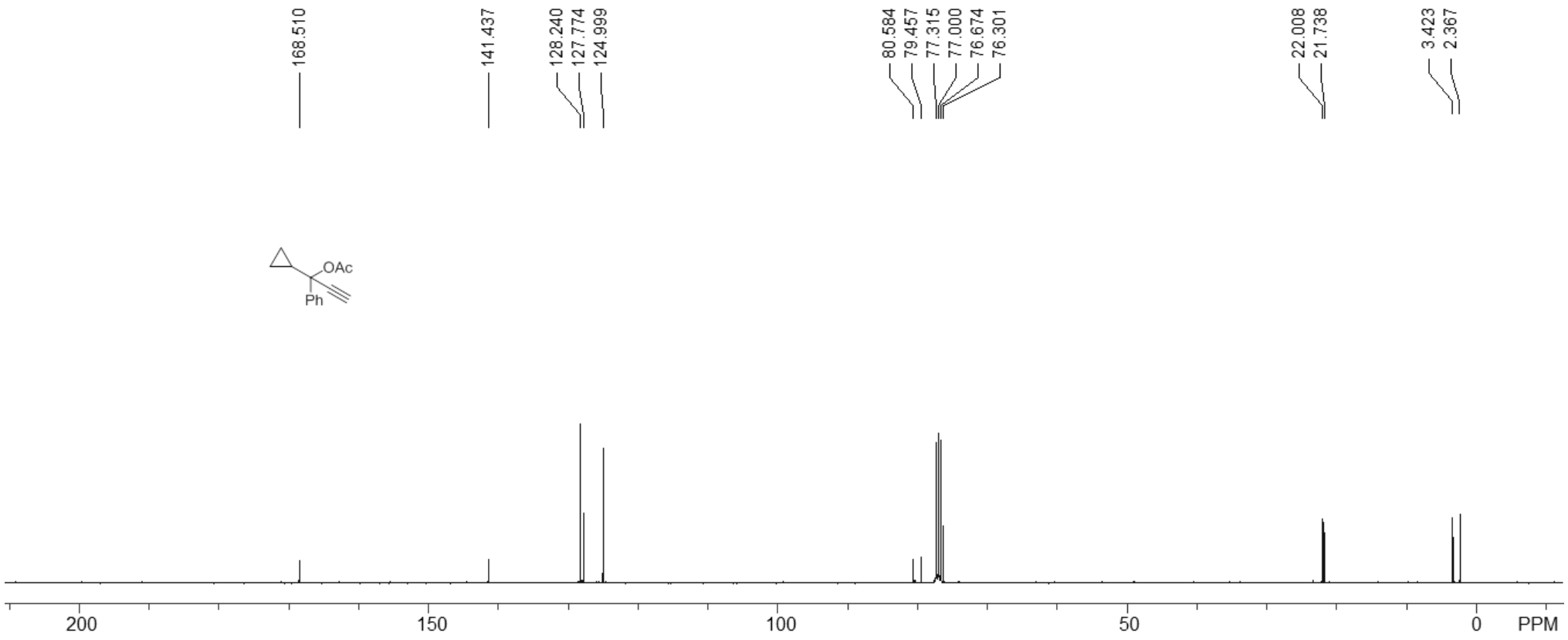
^{1}H NMR spectrum of 1-cyclopropyl-1-phenylprop-2-yn-1-yl acetate (**1m**)

$CDCl_3$, 400MHz



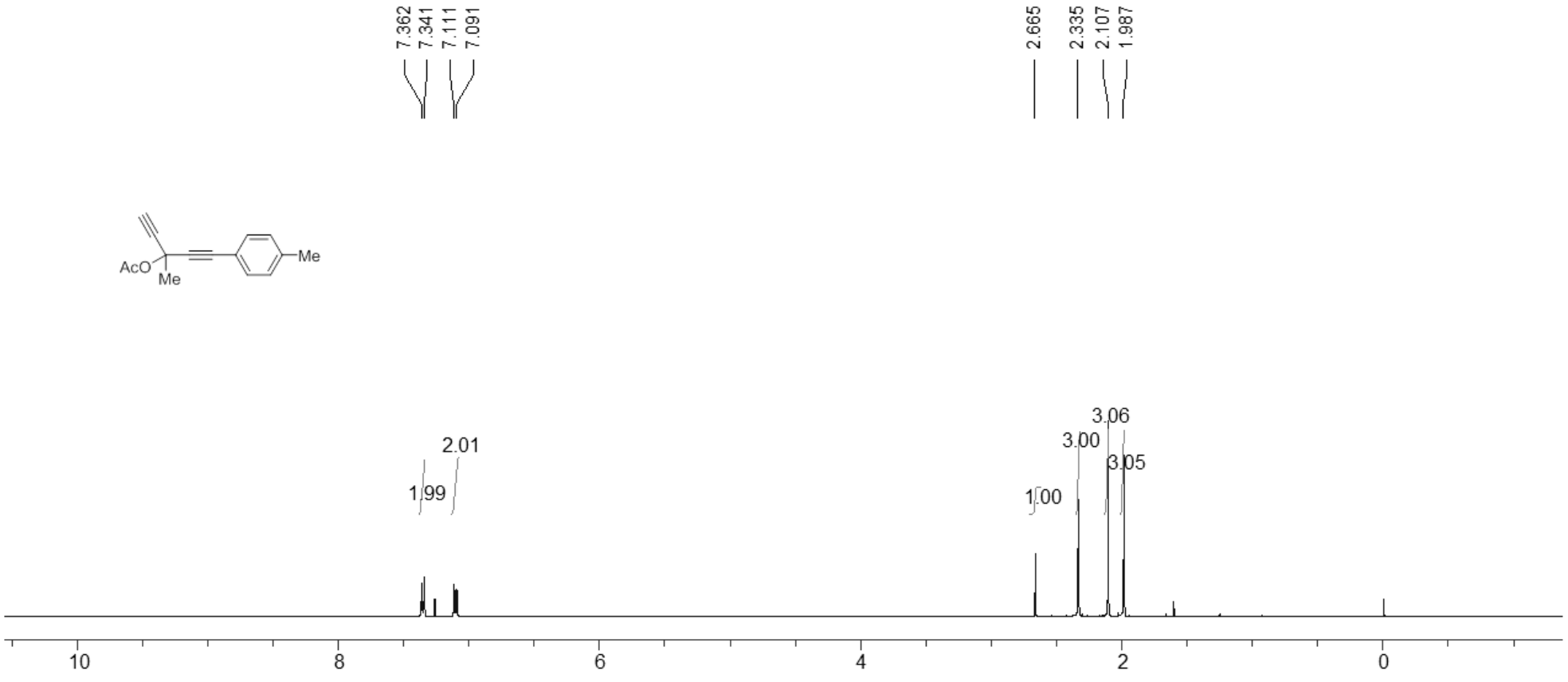
^{13}C NMR spectrum of 1-cyclopropyl-1-phenylprop-2-yn-1-yl acetate (**1m**)

$CDCl_3$, 100MHz



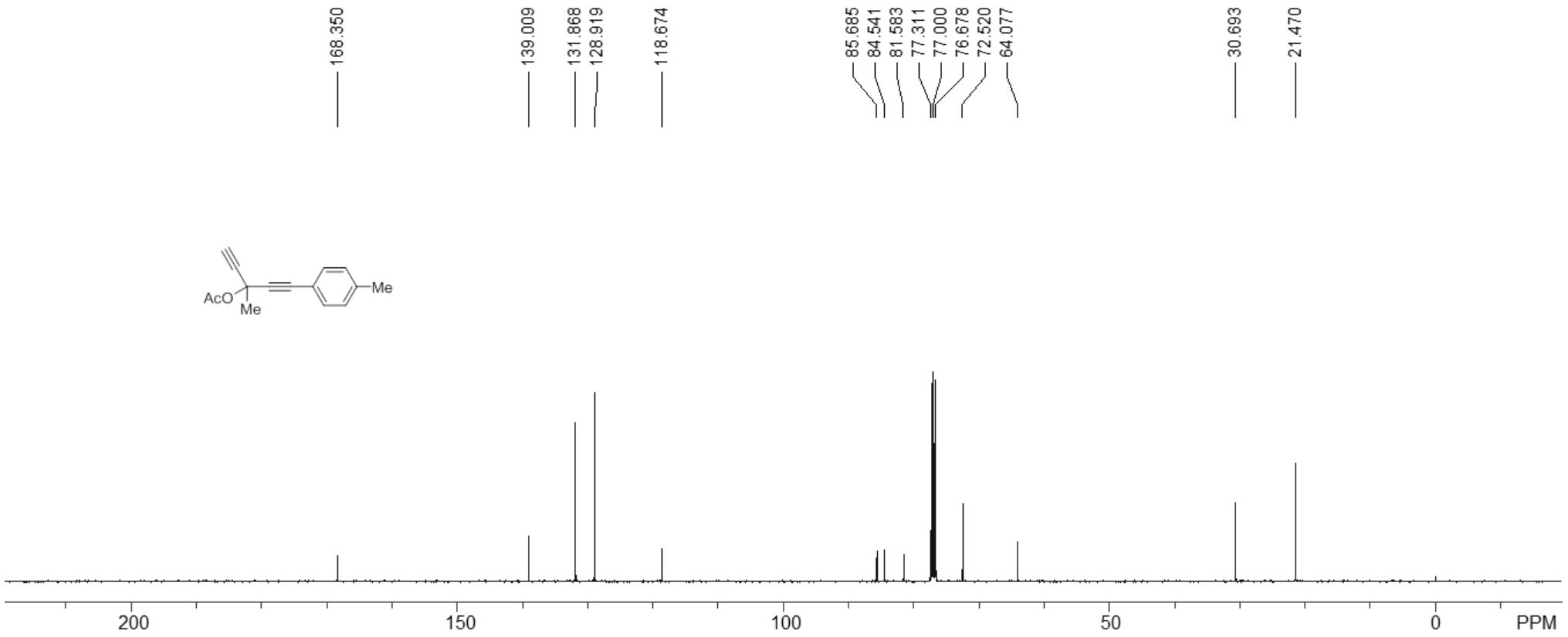
^{1}H NMR spectrum of 3-methyl-1-(p-tolyl)penta-1,4-diyn-3-yl acetate (***1p***)

$CDCl_3$, 400MHz



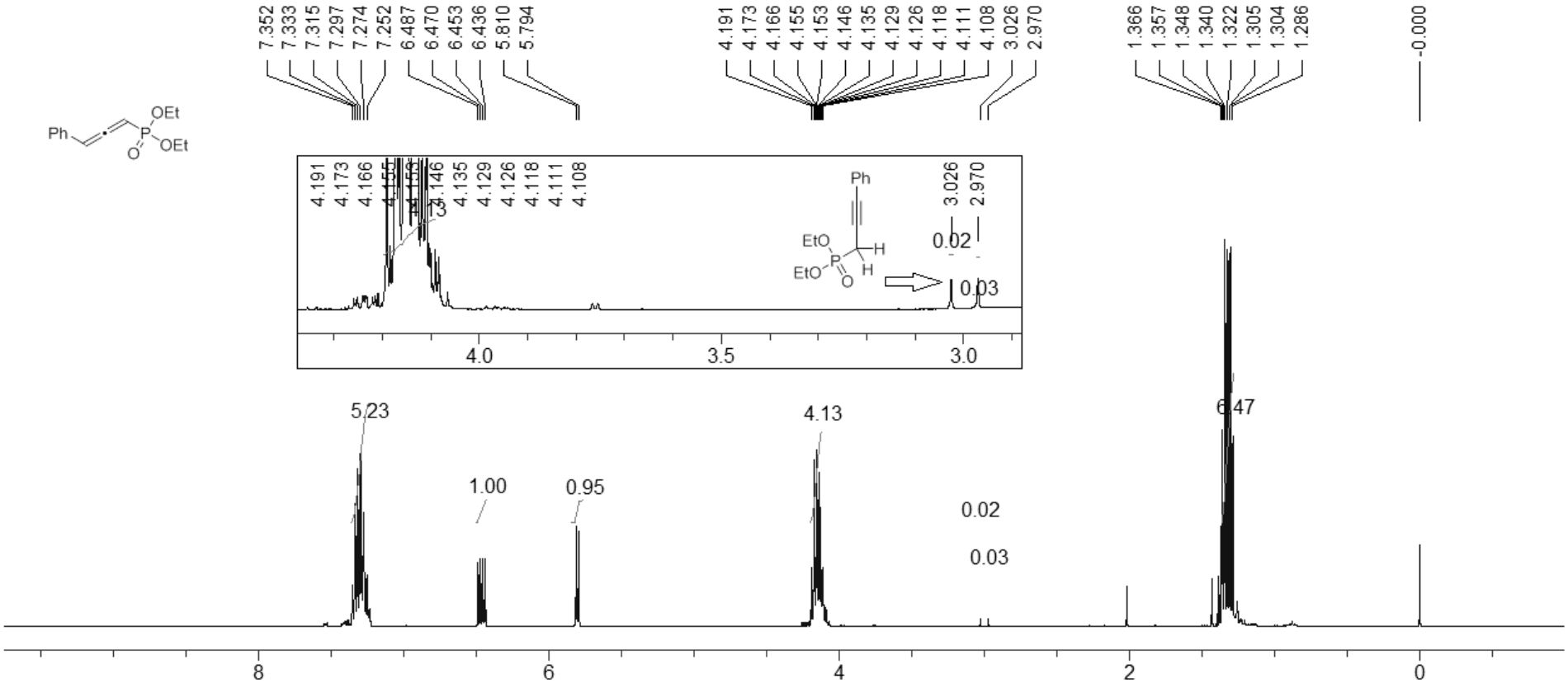
^{13}C NMR spectrum of 3-methyl-1-(p-tolyl)penta-1,4-diyn-3-yl acetate (**1p**)

$CDCl_3$, 100MHz



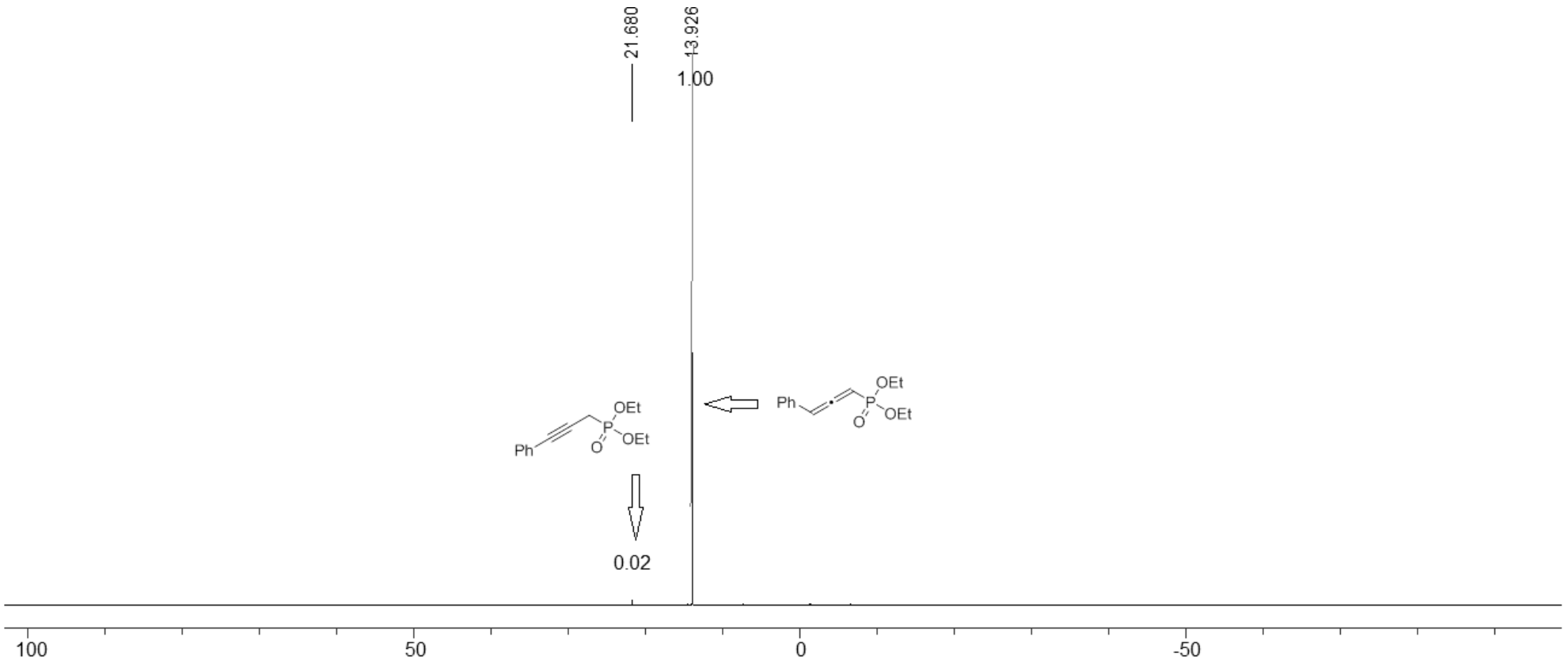
*[1]H NMR spectrum of diethyl (3-phenylpropa-1,2-dien-1-yl)phosphonate (**3a**)*

$CDCl_3$, 400MHz



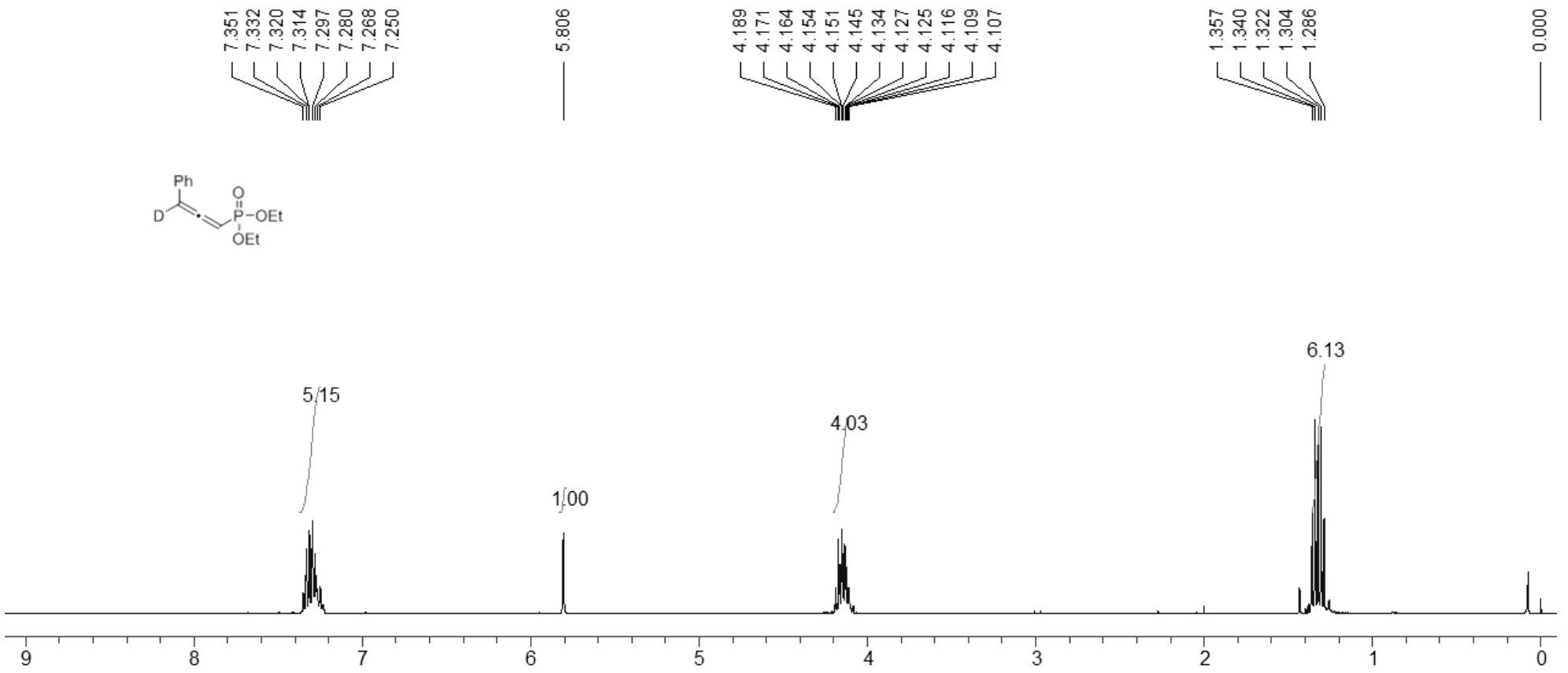
*^{31}P NMR spectrum of diethyl (3-phenylpropa-1,2-dien-1-yl)phosphonate (**3a**)*

$CDCl_3$, 162MHz



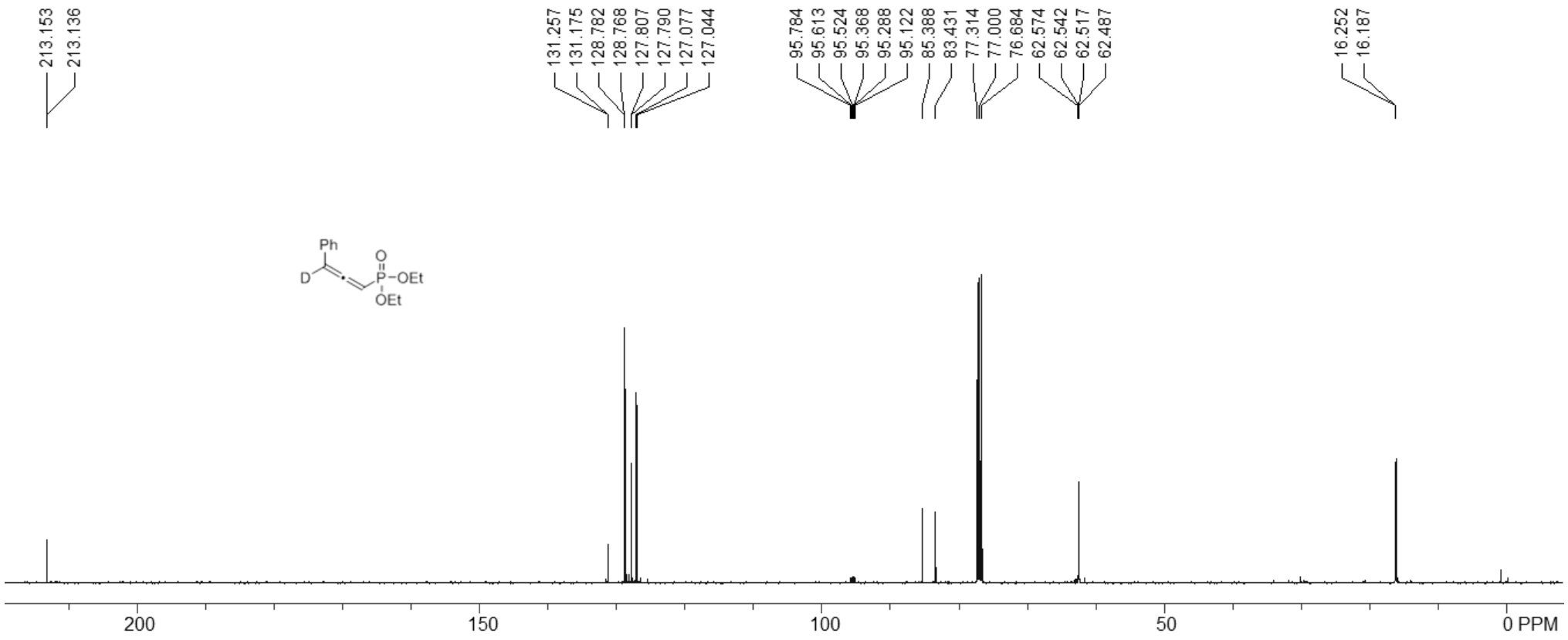
*^{1}H NMR spectrum of diethyl (3-phenylpropa-1,2-dien-1-yl-3-d)phosphonate (**3a**-d).*

$CDCl_3$, 400MHz



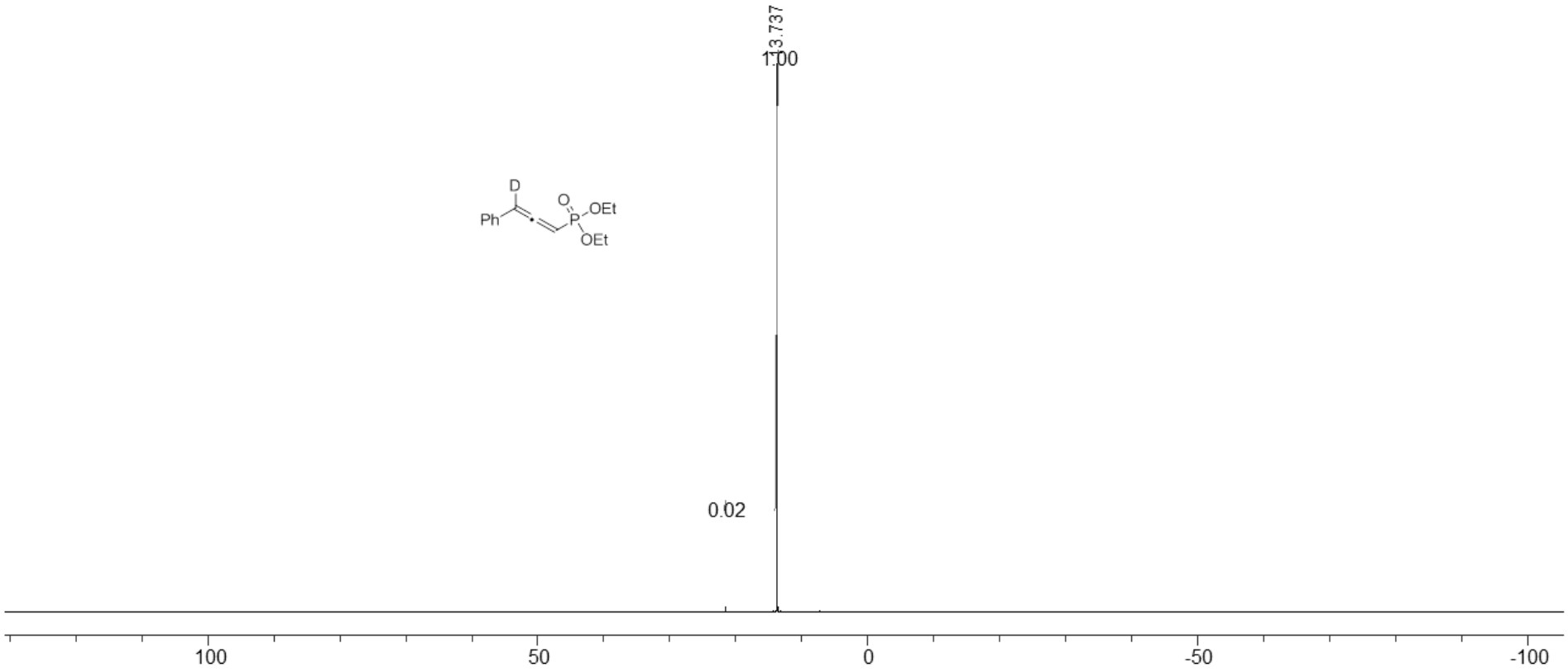
*^{13}C NMR spectrum of diethyl (3-phenylpropa-1,2-dien-1-yl-3-d)phosphonate (**3a**-d).*

$CDCl_3$, 100MHz



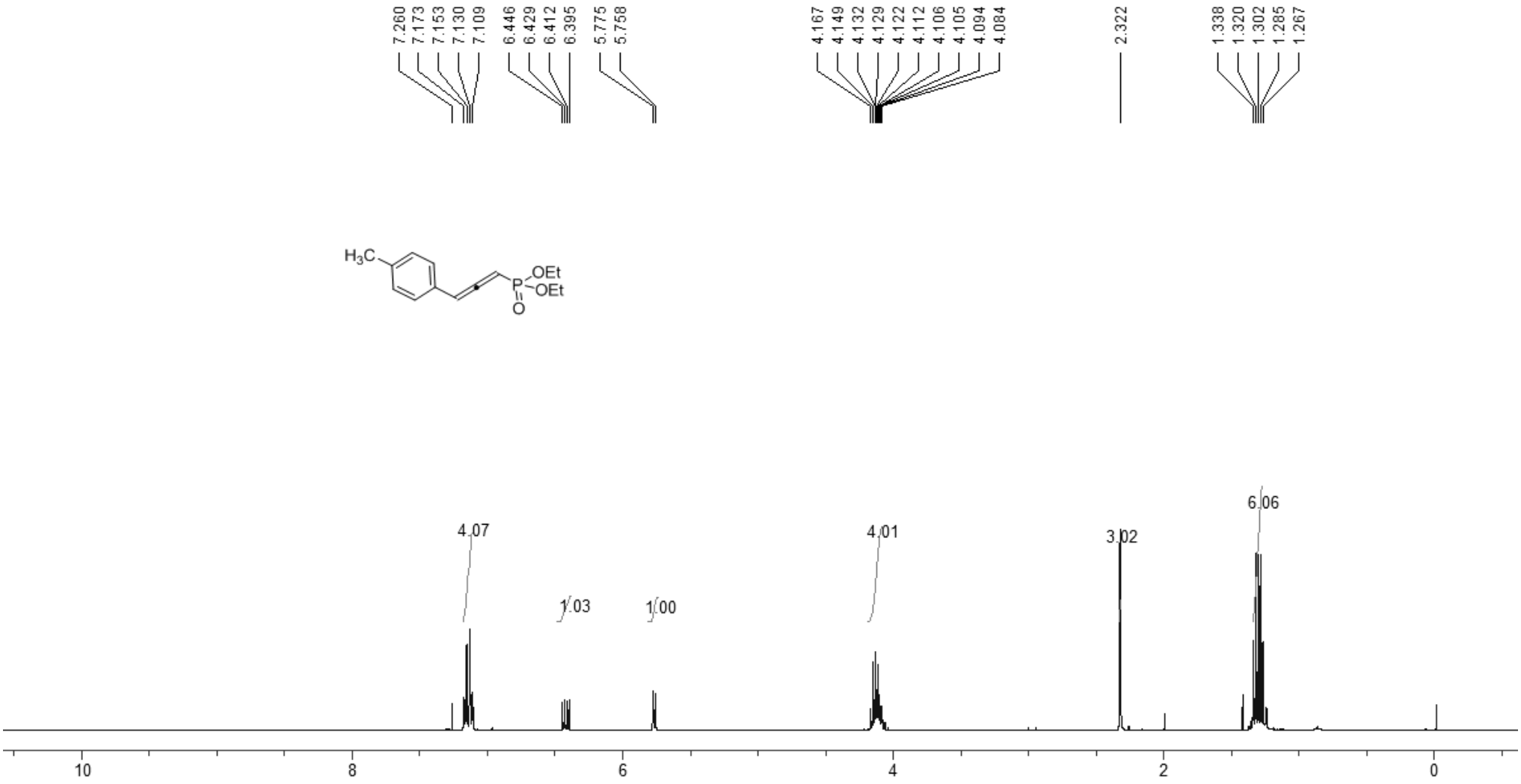
*^{31}P NMR spectrum of diethyl (3-phenylpropa-1,2-dien-1-yl-3-d)phosphonate (**3a**-d_y).*

$CDCl_3$, 162MHz



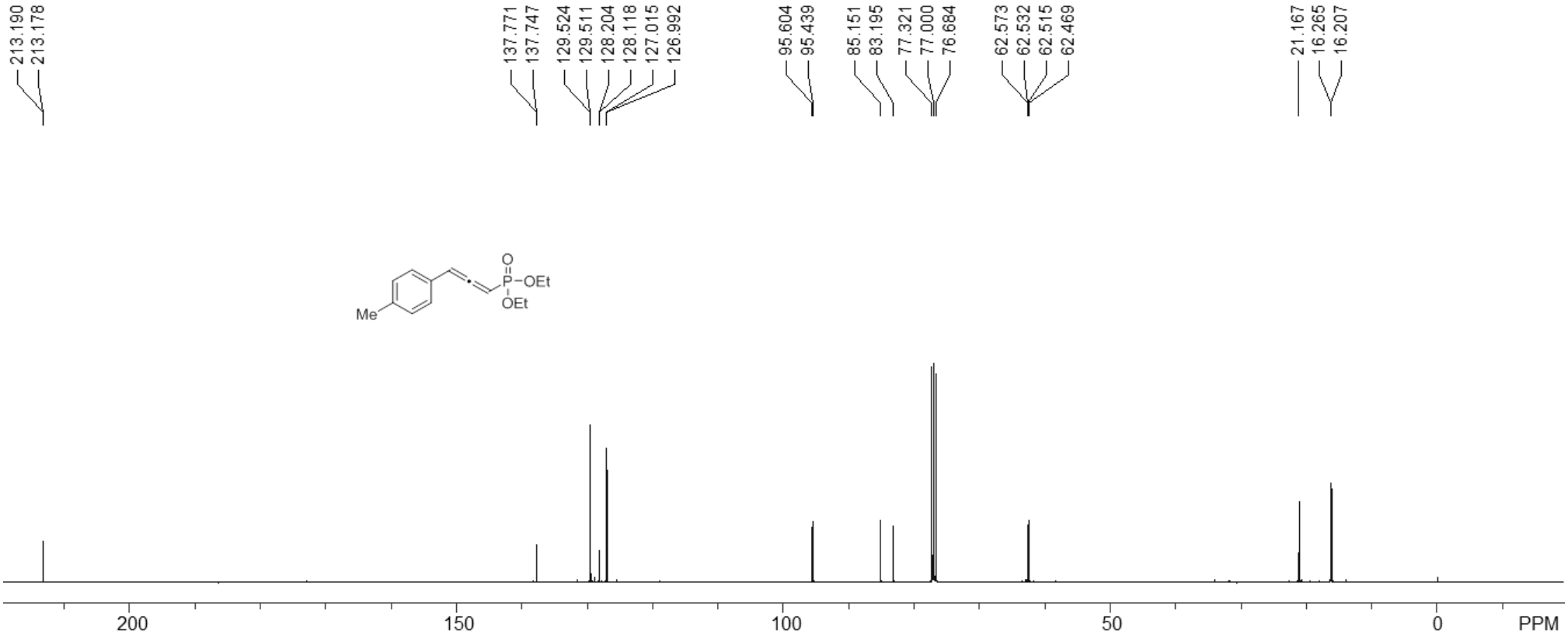
*^{1}H NMR spectrum of diethyl (3-(p-tolyl)propa-1,2-dien-1-yl)phosphonate (**3b**)*

$CDCl_3$, 400MHz



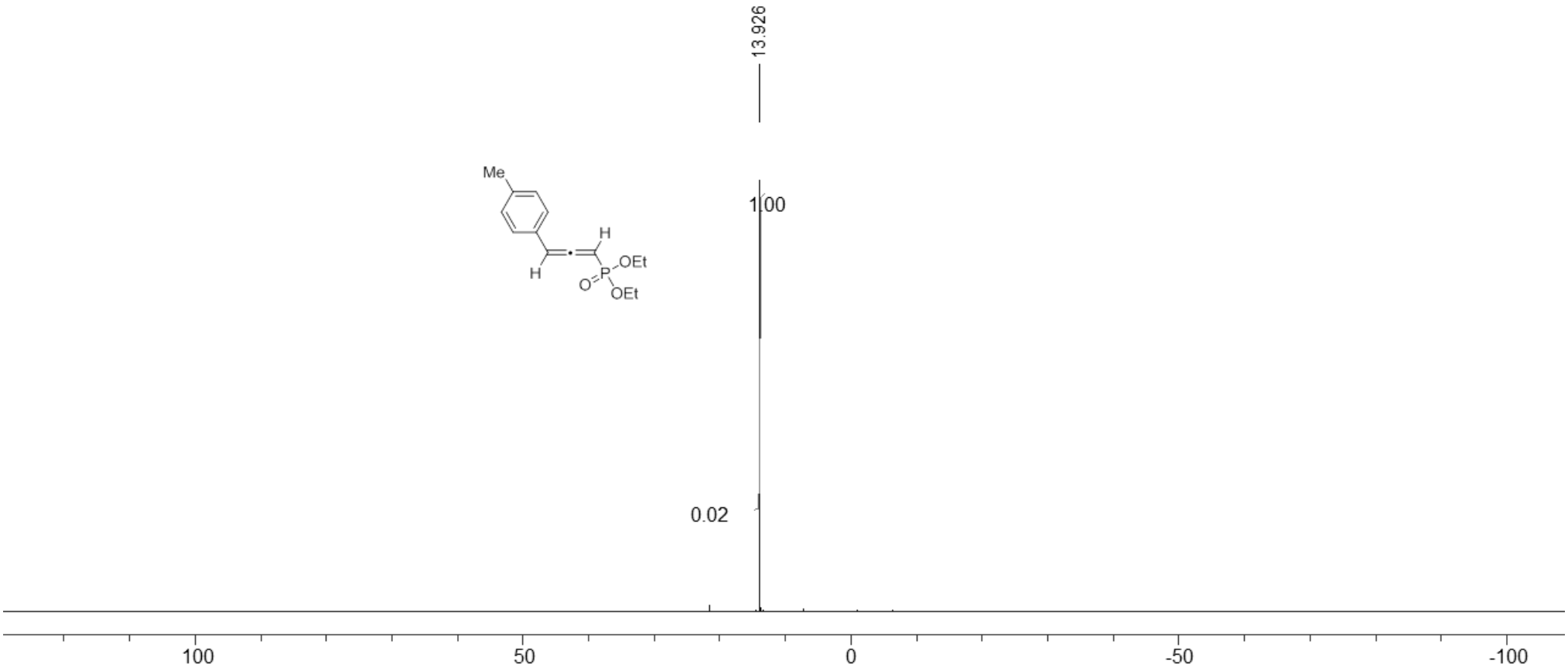
*^{13}C NMR spectrum of diethyl (3-(p-tolyl)propa-1,2-dien-1-yl)phosphonate (**3b**)*

$CDCl_3$, 100MHz



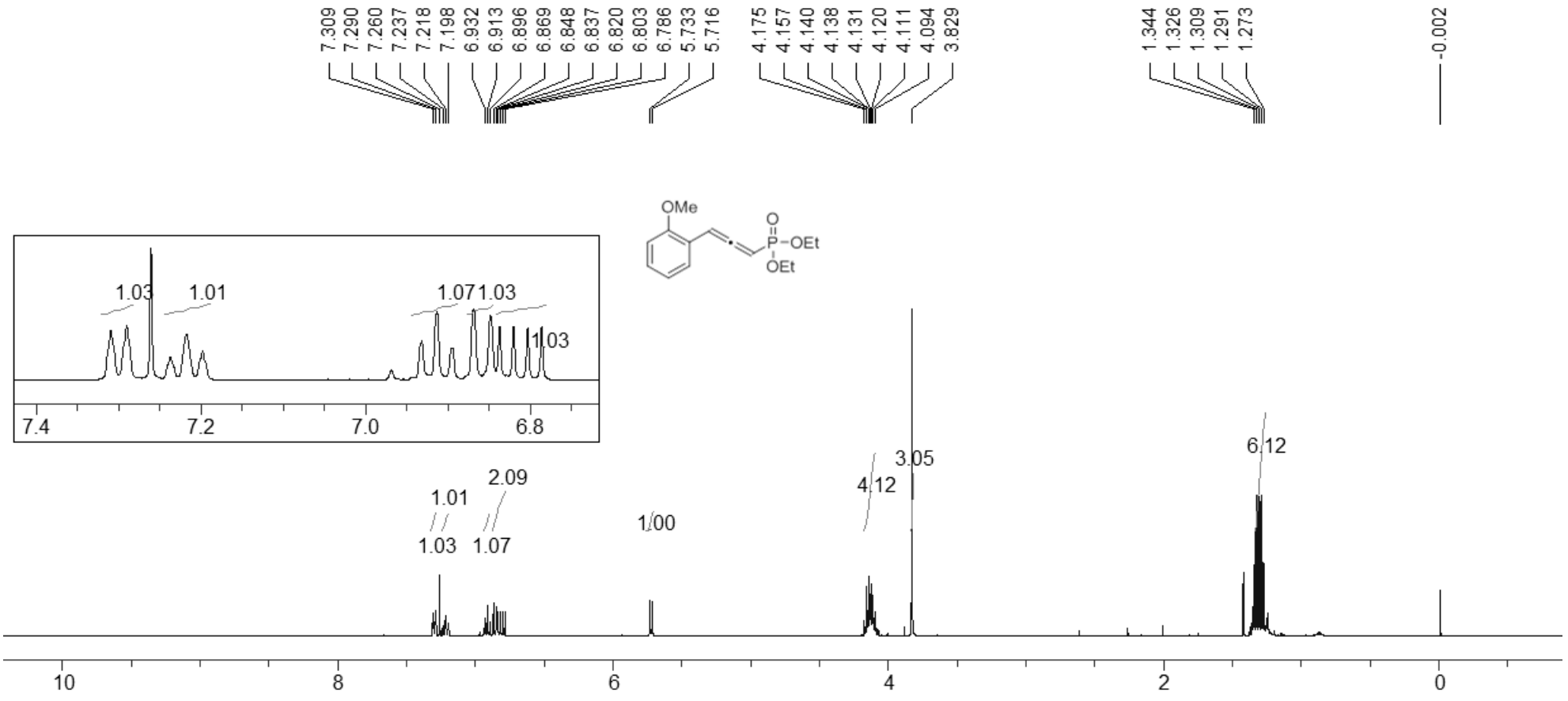
*^{31}P NMR spectrum of diethyl (3-(p-tolyl)propa-1,2-dien-1-yl)phosphonate (**3b**)*

$CDCl_3$, 162MHz



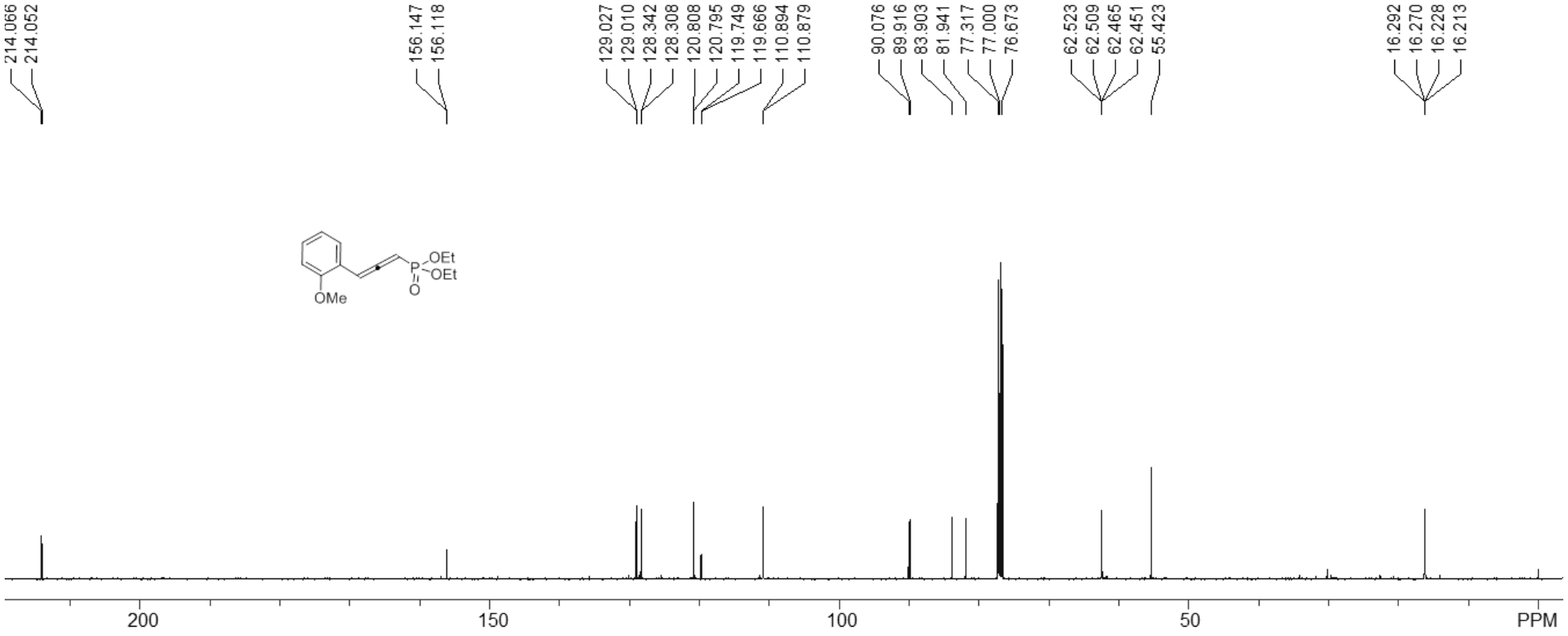
*[1]H NMR spectrum of diethyl (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)phosphonate (**3c**)*

$CDCl_3$, 400MHz



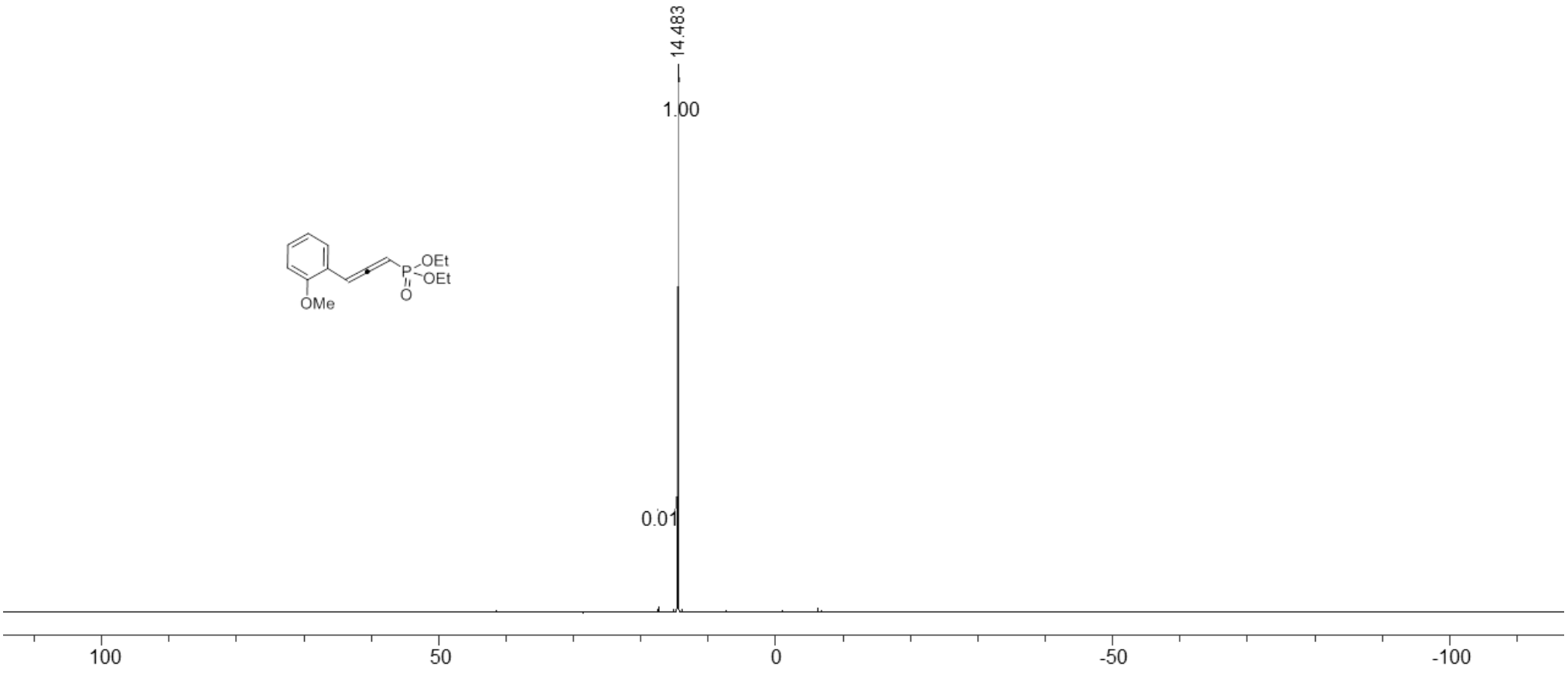
*^{13}C NMR spectrum of diethyl (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)phosphonate (**3c**)*

$CDCl_3$, 100MHz



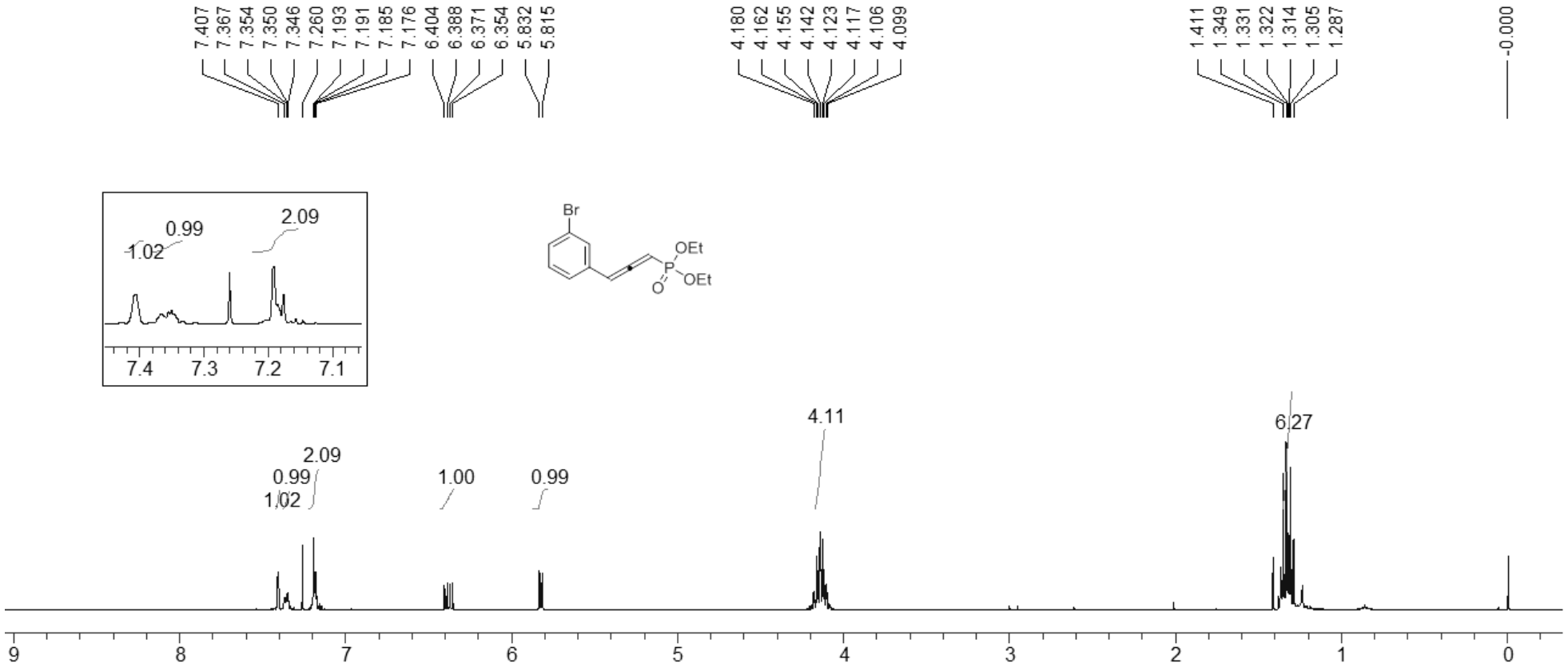
*^{31}P NMR spectrum of diethyl (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)phosphonate (**3c**)*

$CDCl_3$, 162MHz



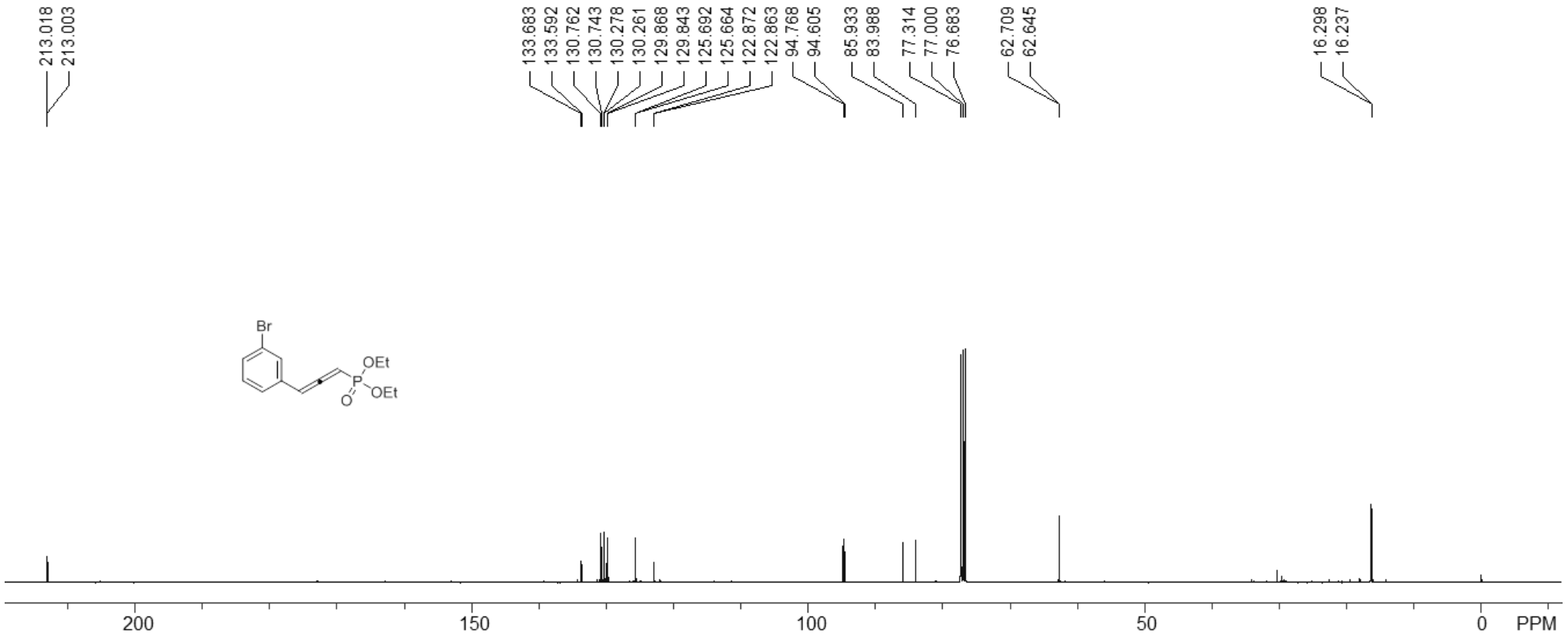
*[1]H NMR spectrum of diethyl (3-(3-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3d**)*

$CDCl_3$, 400MHz



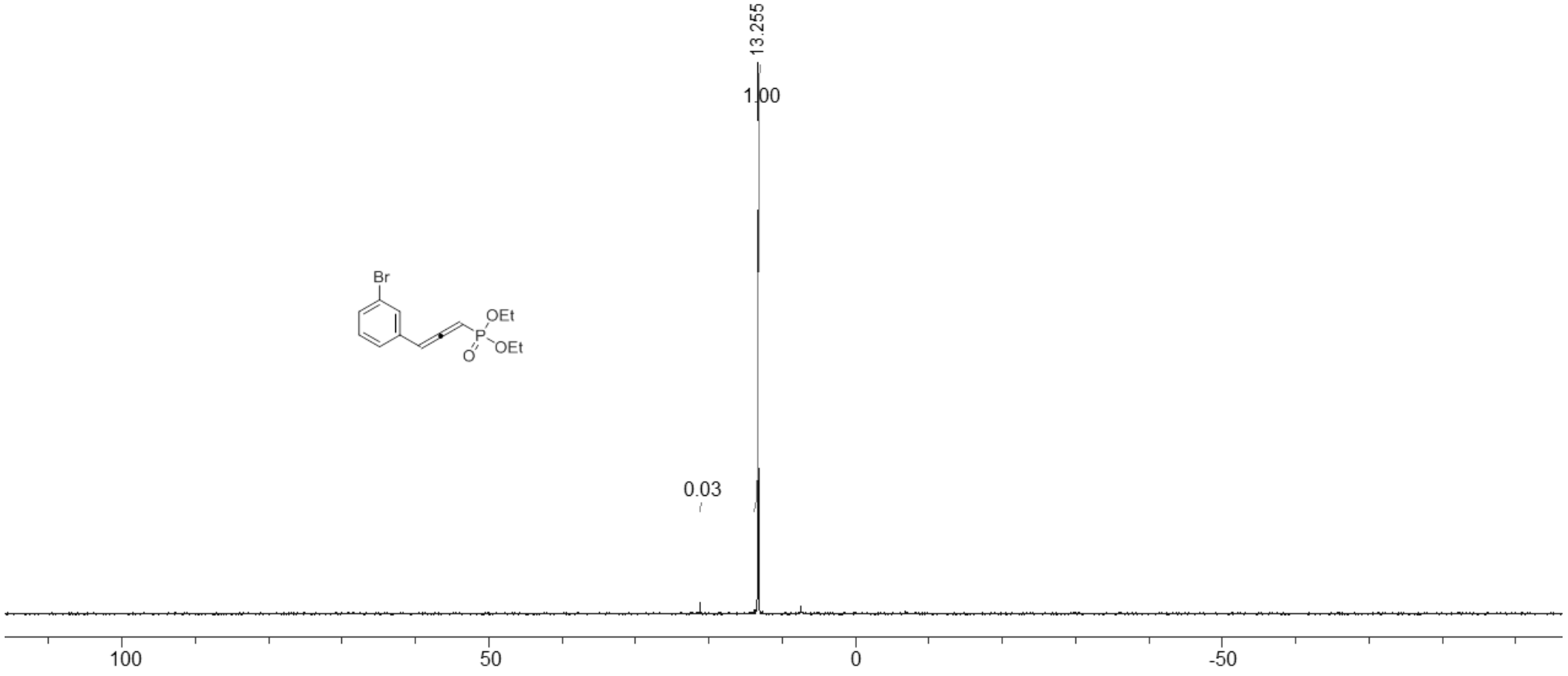
*^{13}C NMR spectrum of diethyl (3-(3-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3d**)*

$CDCl_3$, 100MHz



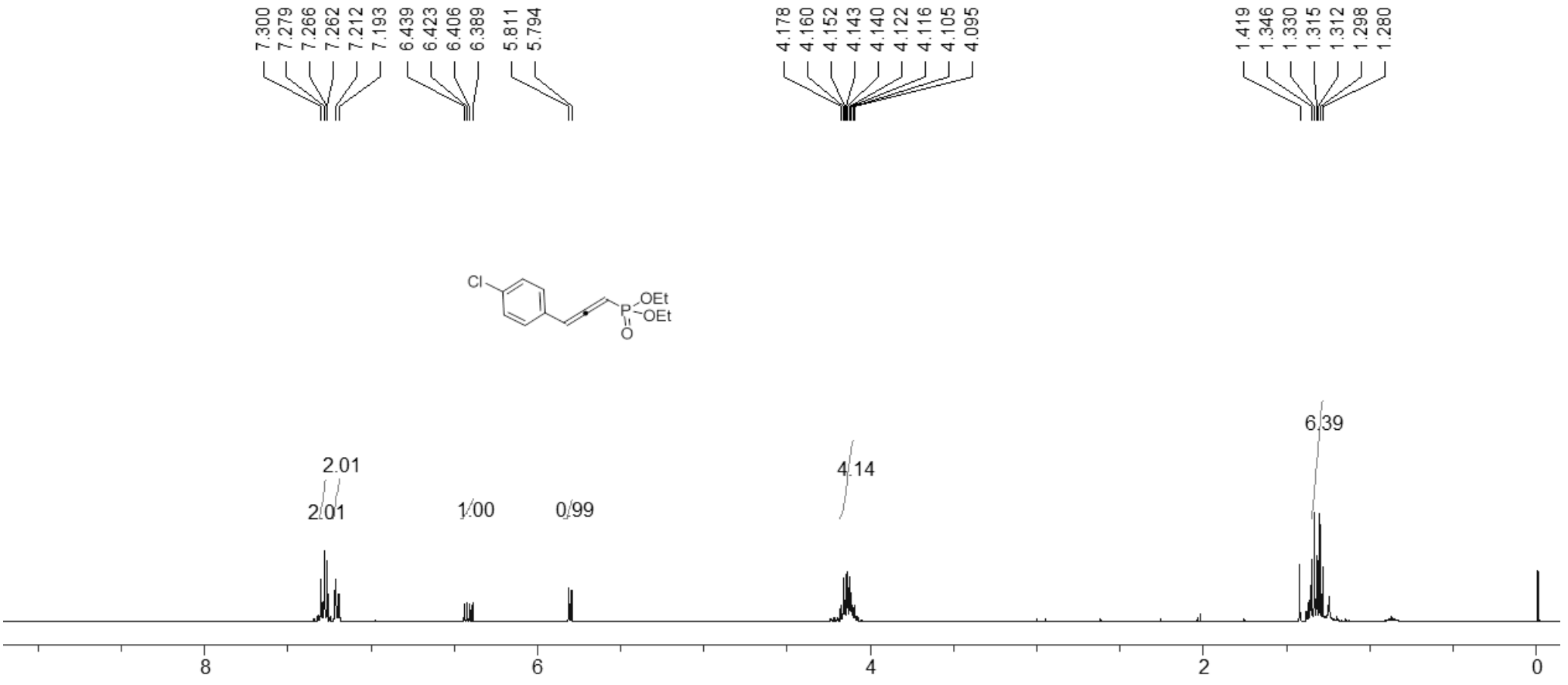
*^{31}P NMR spectrum of diethyl (3-(3-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3d**)*

$CDCl_3$, 162MHz



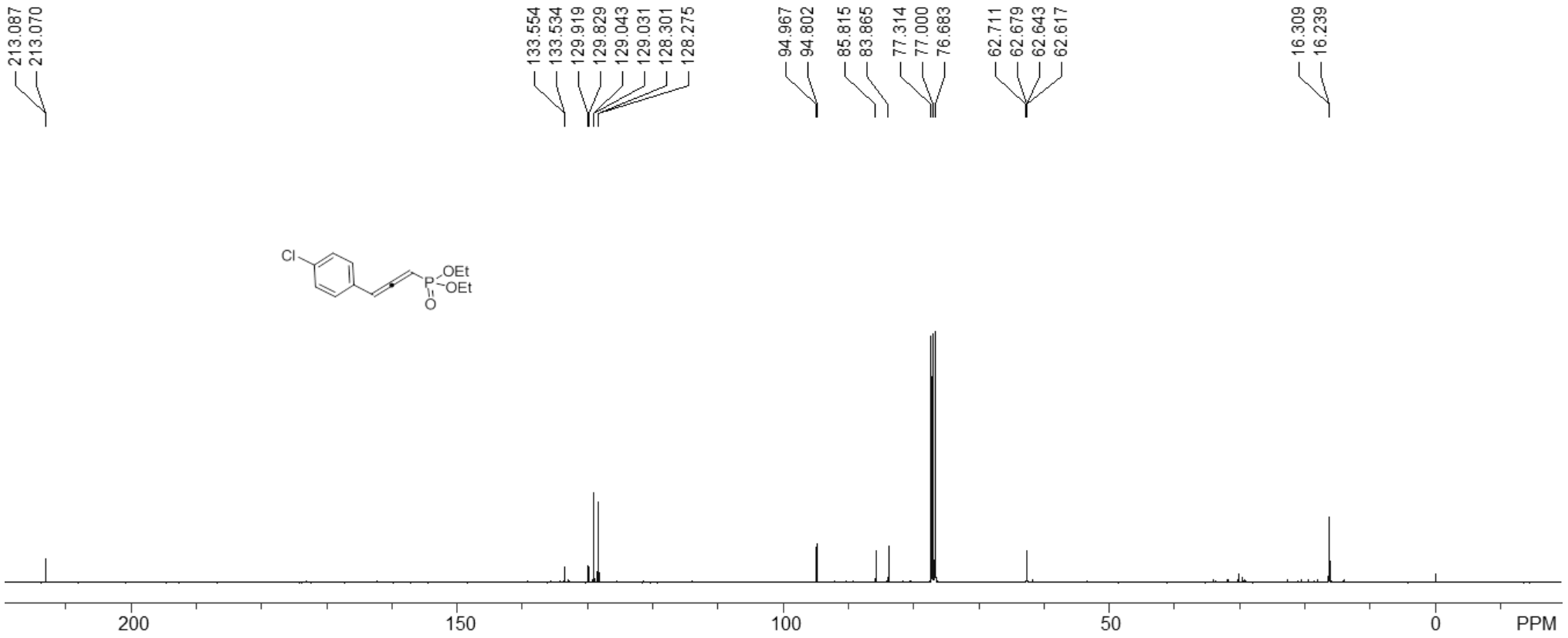
*^{1}H NMR spectrum of diethyl (3-(4-chlorophenyl)propa-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 400MHz



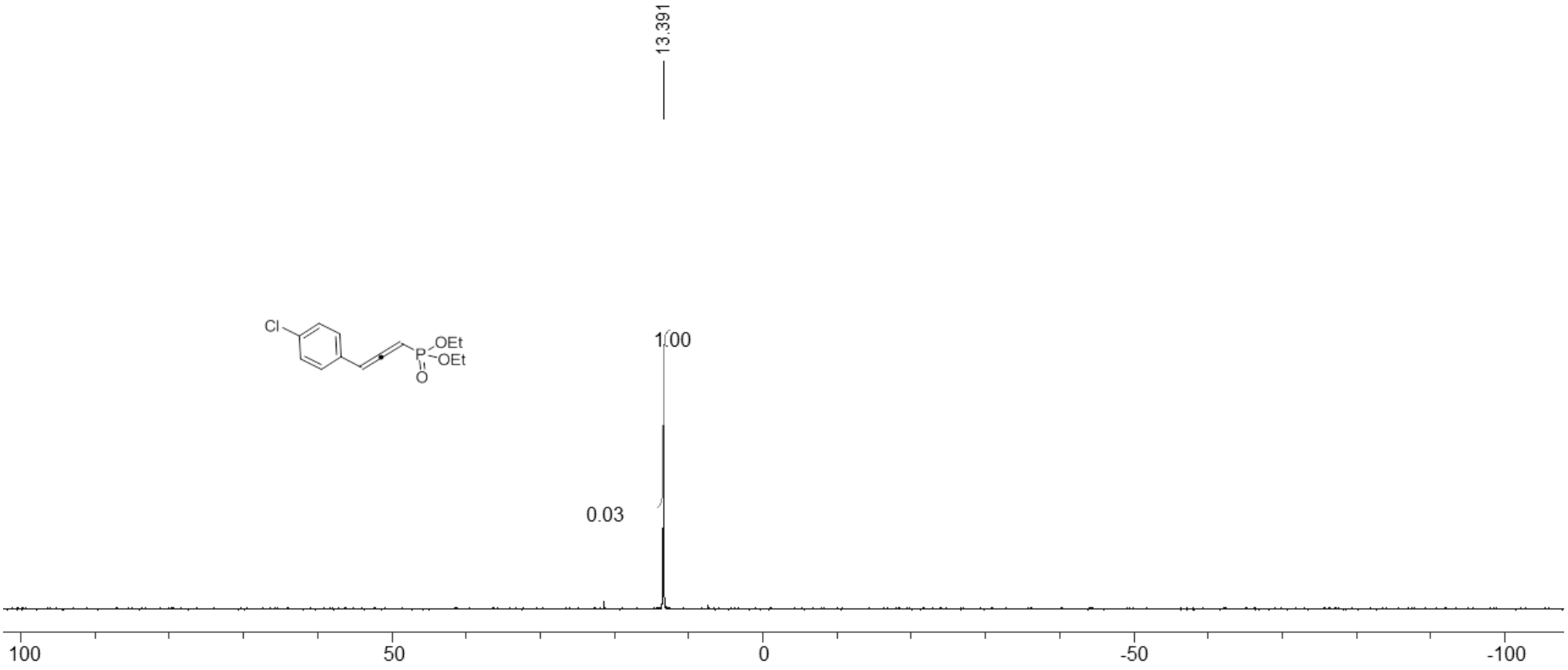
*^{13}C NMR spectrum of diethyl (3-(4-chlorophenyl)propa-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 100MHz



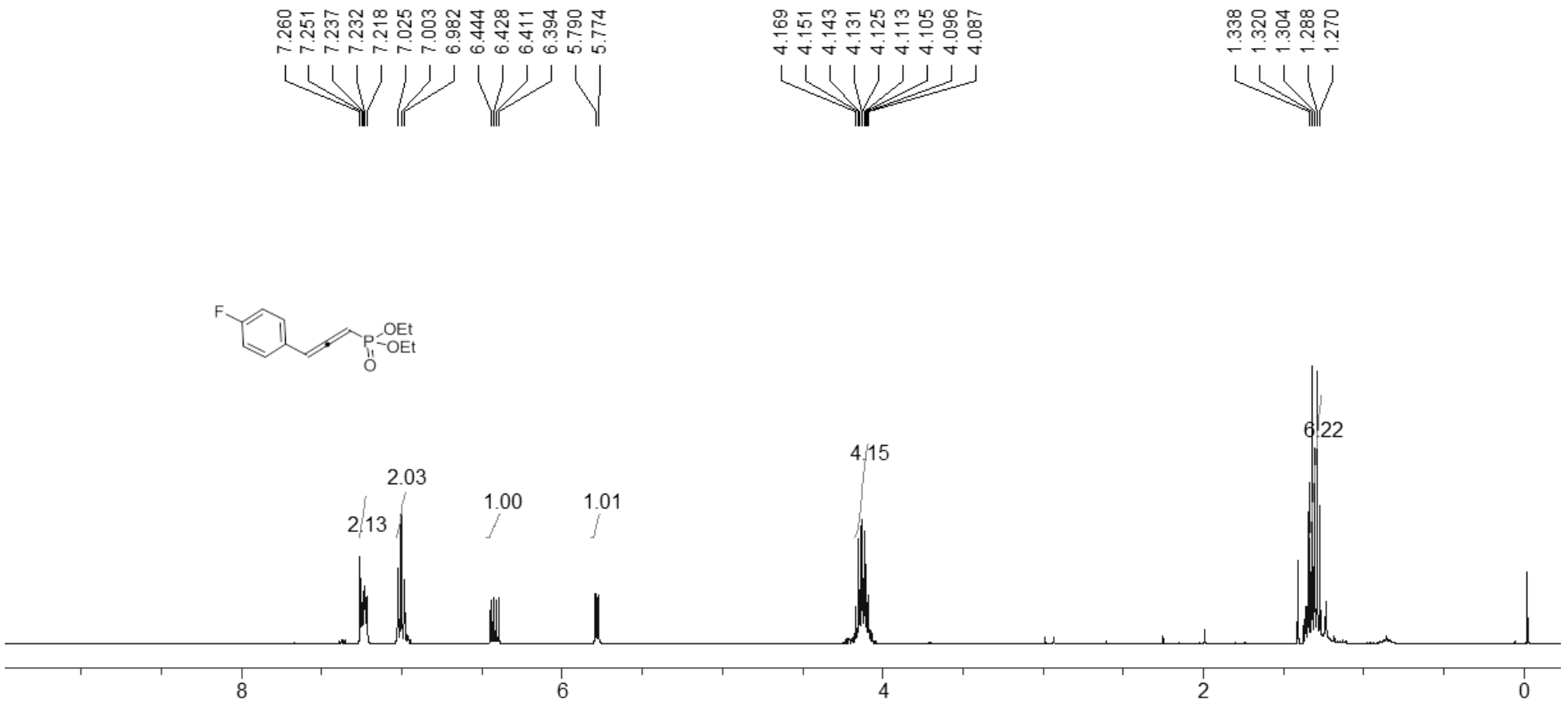
*^{31}P NMR spectrum of diethyl (3-(4-chlorophenyl)propa-1,2-dien-1-yl)phosphonate (**3e**)*

$CDCl_3$, 162MHz



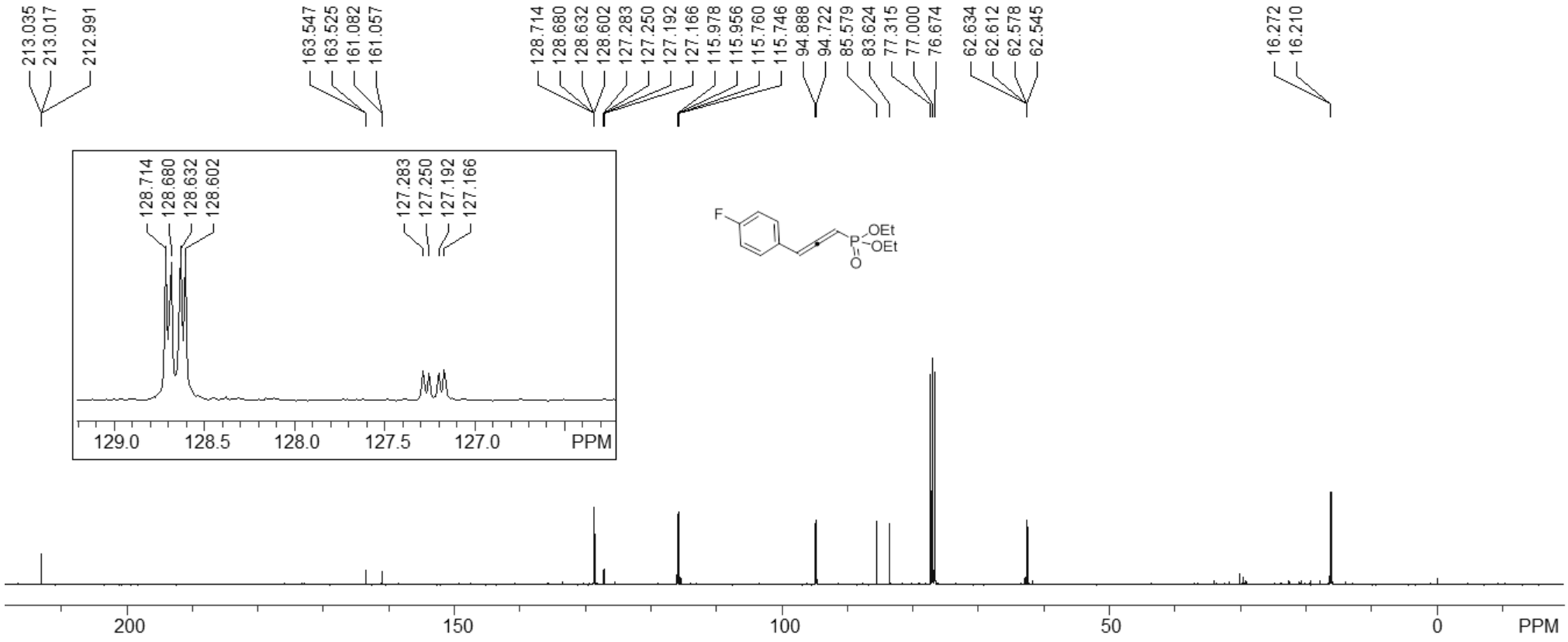
*^{1}H NMR spectrum of diethyl (3-(4-fluorophenyl)propa-1,2-dien-1-yl)phosphonate (**3f**)*

$CDCl_3$, 400MHz



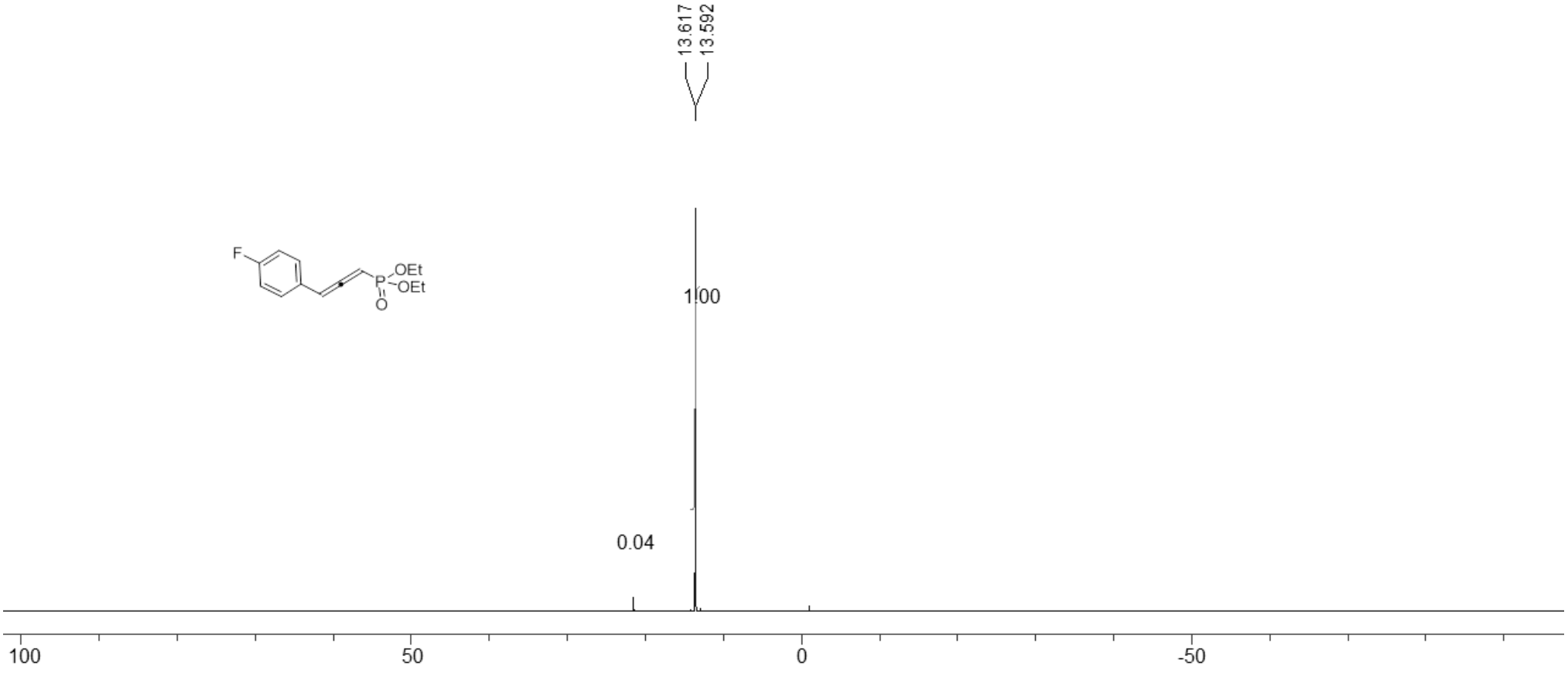
*^{13}C NMR spectrum of diethyl (3-(4-fluorophenyl)propa-1,2-dien-1-yl)phosphonate (**3f**)*

$CDCl_3$, 100MHz



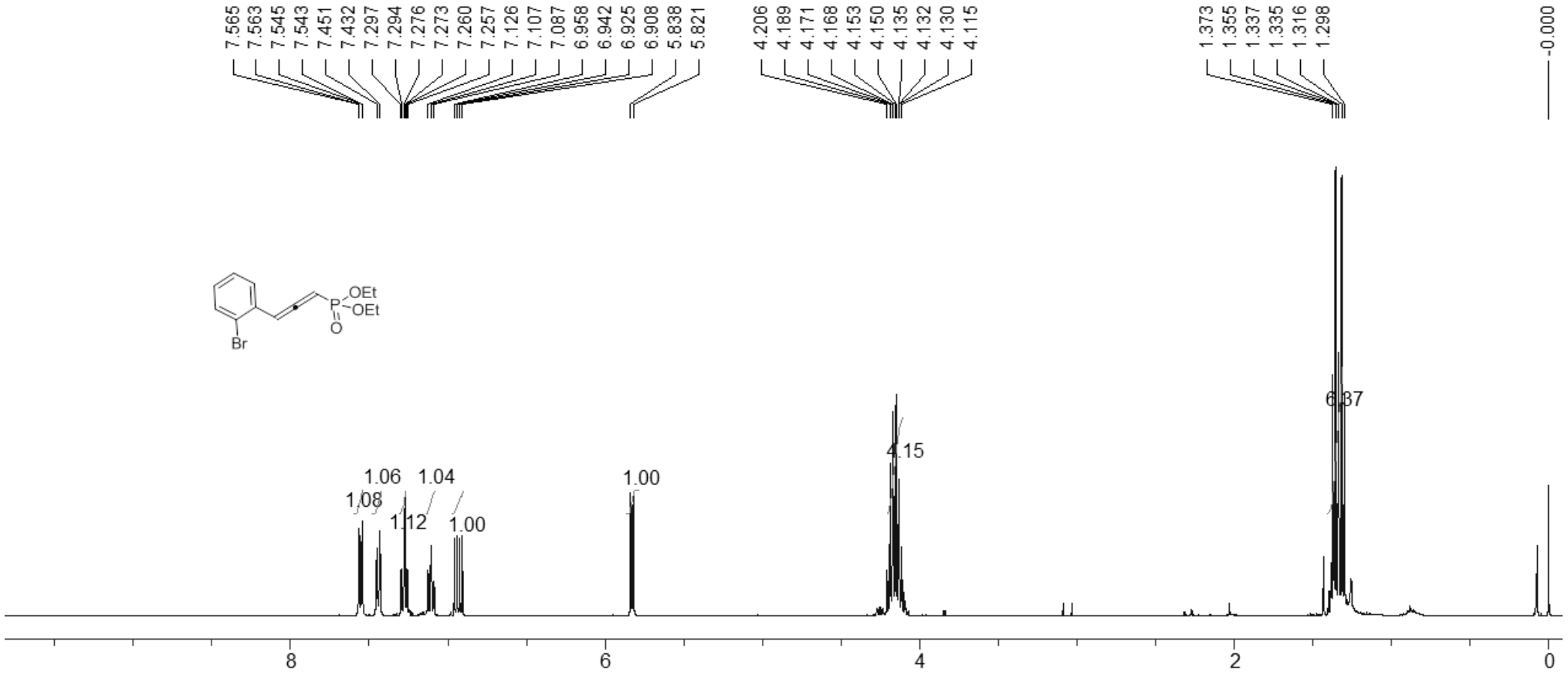
*^{31}P NMR spectrum of diethyl (3-(4-fluorophenyl)propa-1,2-dien-1-yl)phosphonate (**3f**)*

$CDCl_3$, 162MHz



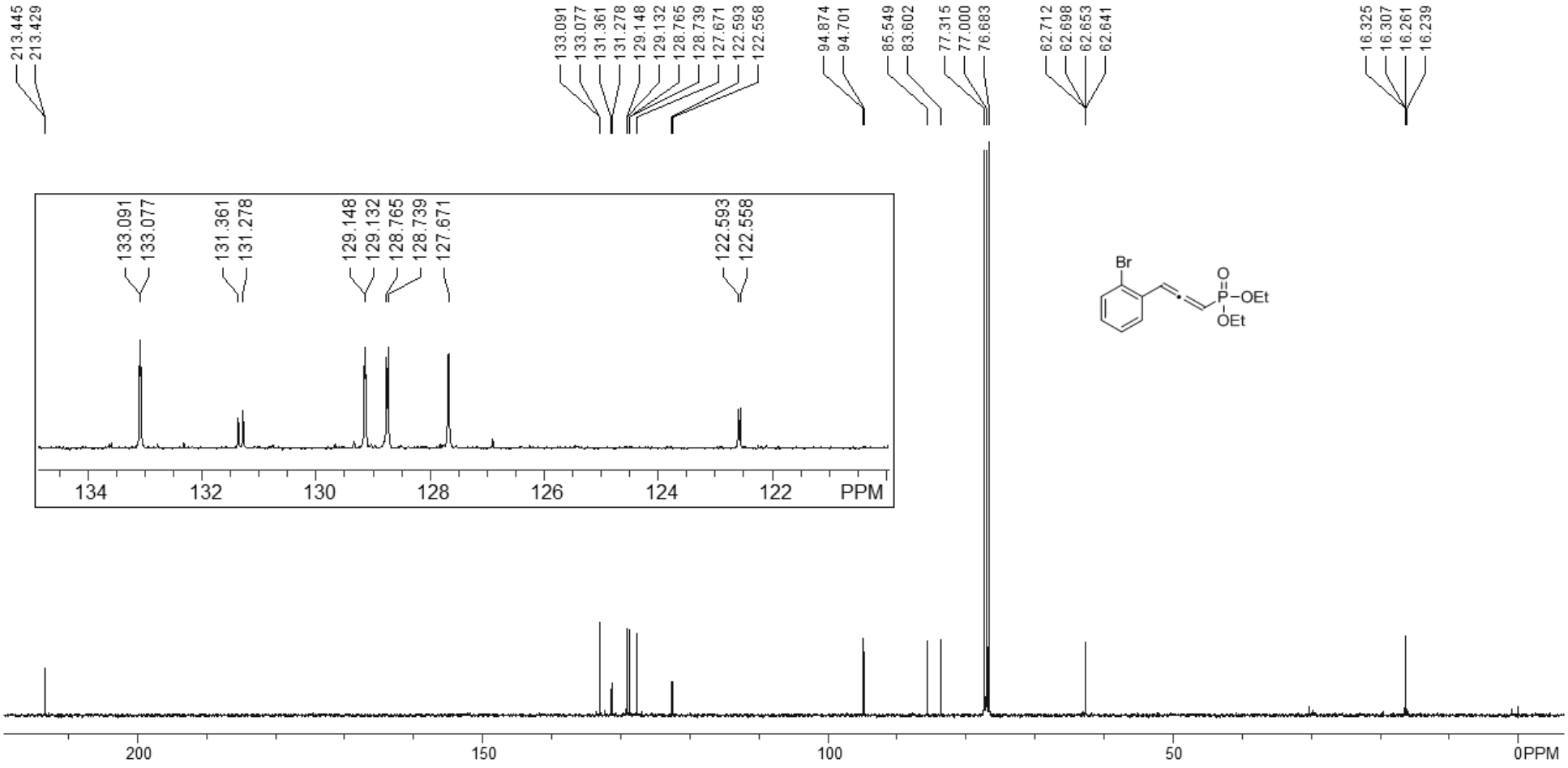
*[1]H NMR spectrum of diethyl (3-(2-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 400MHz



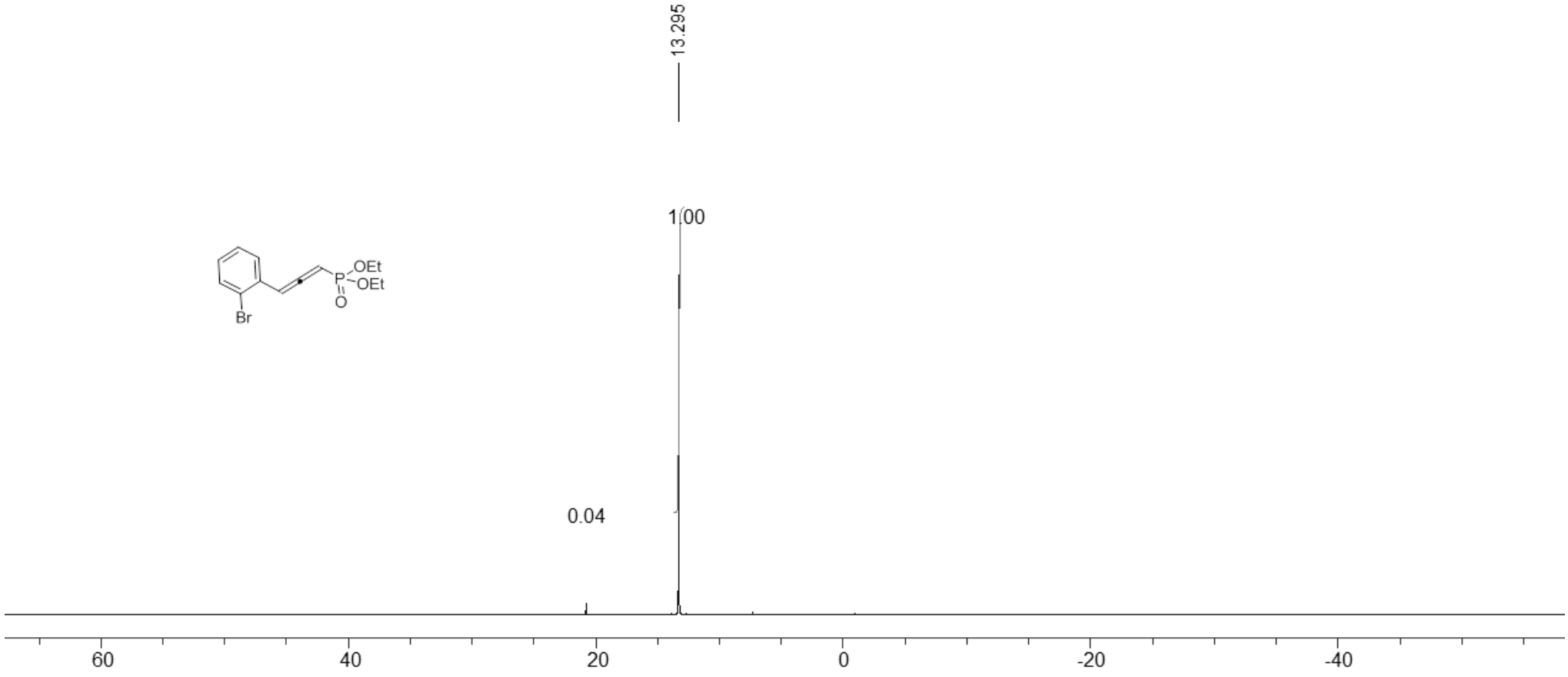
*^{13}C NMR spectrum of diethyl (3-(2-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 100MHz



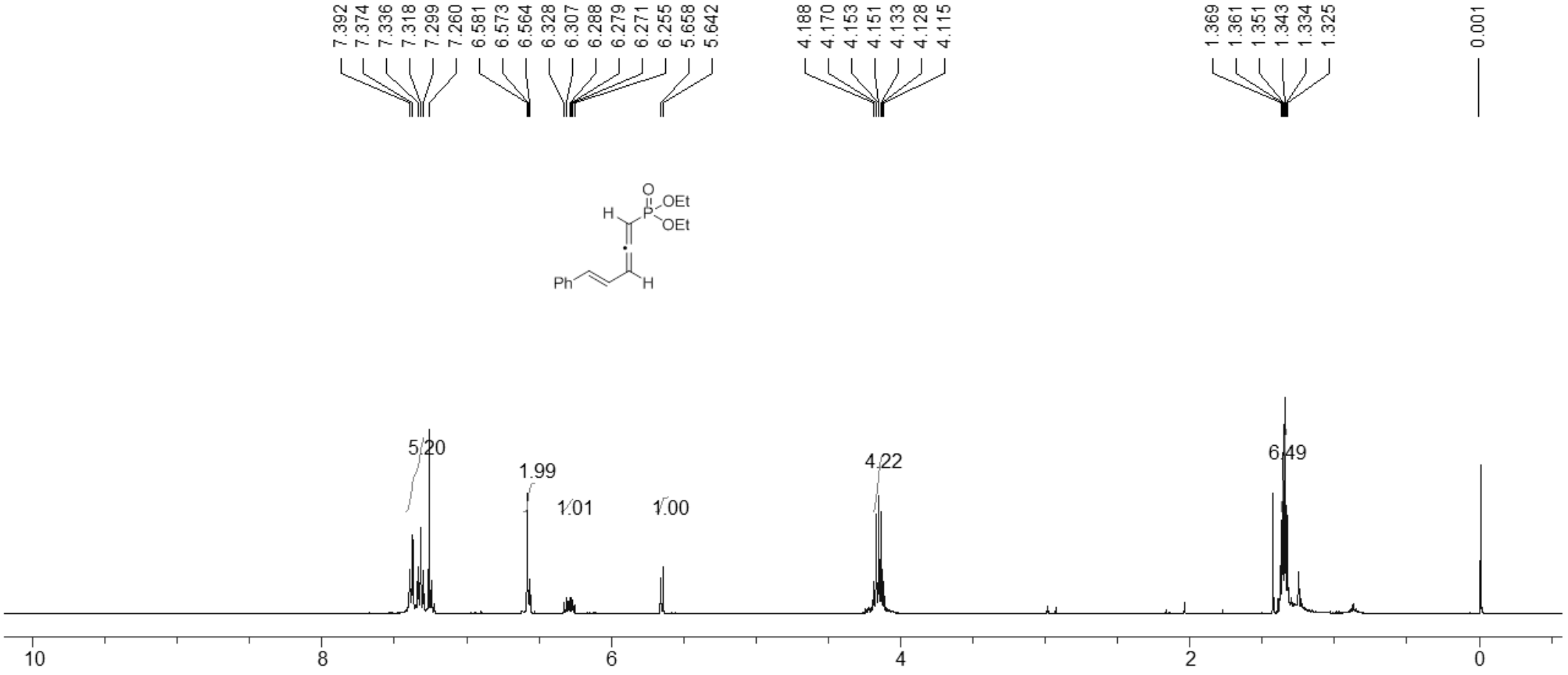
*^{31}P NMR spectrum of diethyl (3-(2-bromophenyl)propa-1,2-dien-1-yl)phosphonate (**3g**)*

$CDCl_3$, 162MHz



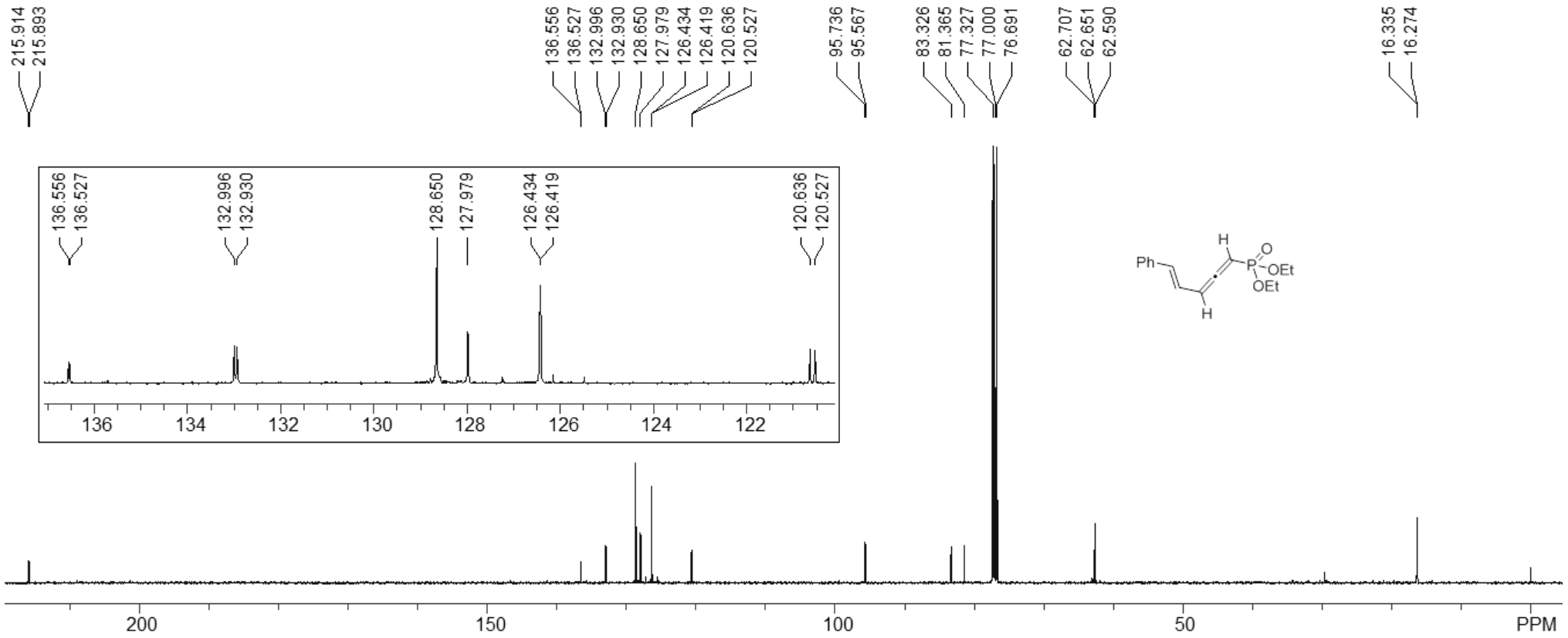
*^{1}H NMR spectrum of diethyl (E)-(5-phenylpenta-1,2,4-trien-1-yl)phosphonate (**3h**)*

$CDCl_3$, 400MHz



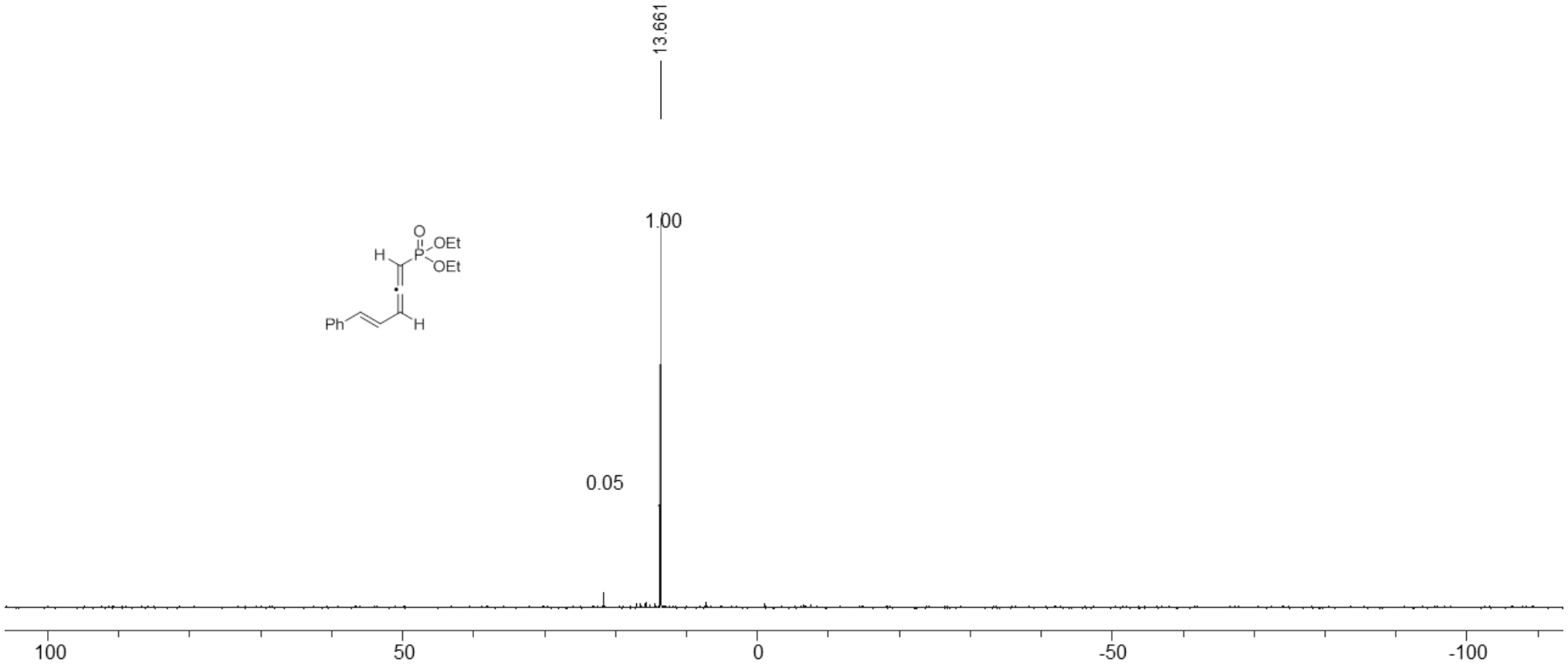
*^{31}C NMR spectrum of diethyl (E)-(5-phenylpenta-1,2,4-trien-1-yl)phosphonate (**3h**)*

$CDCl_3$, 100MHz



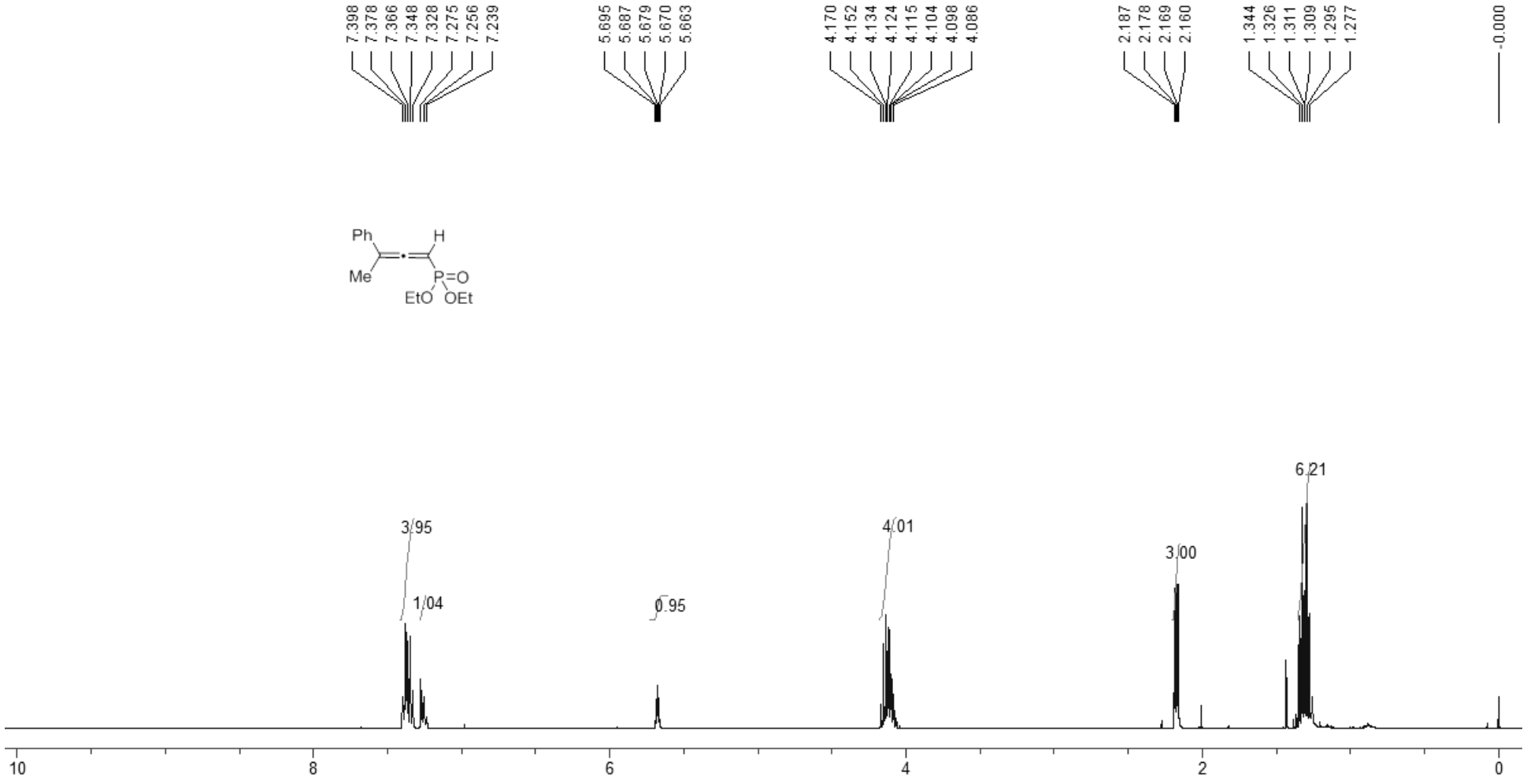
*^{31}P NMR spectrum of diethyl (E)-(5-phenylpenta-1,2,4-trien-1-yl)phosphonate (**3h**)*

$CDCl_3$, 162MHz



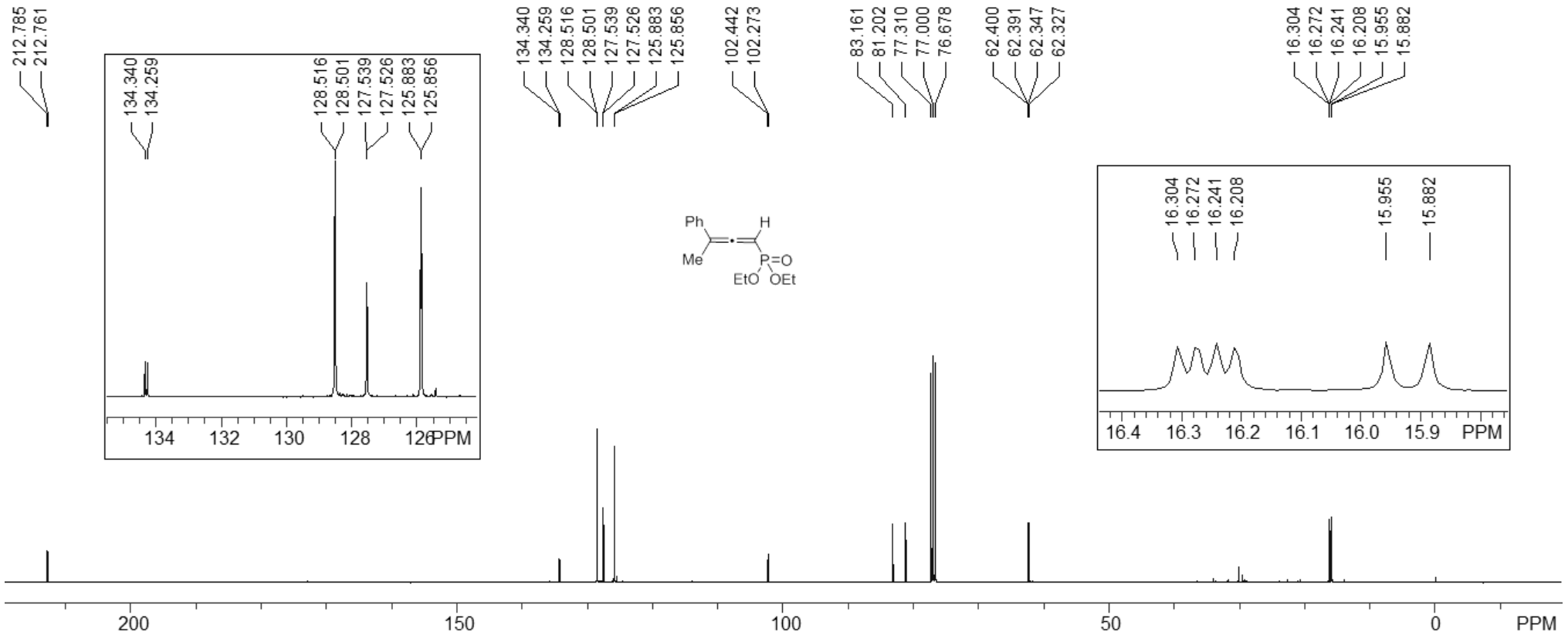
*[1]H NMR spectrum of diethyl (3-phenylbuta-1,2-dien-1-yl)phosphonate (**3i**)*

$CDCl_3$, 400MHz



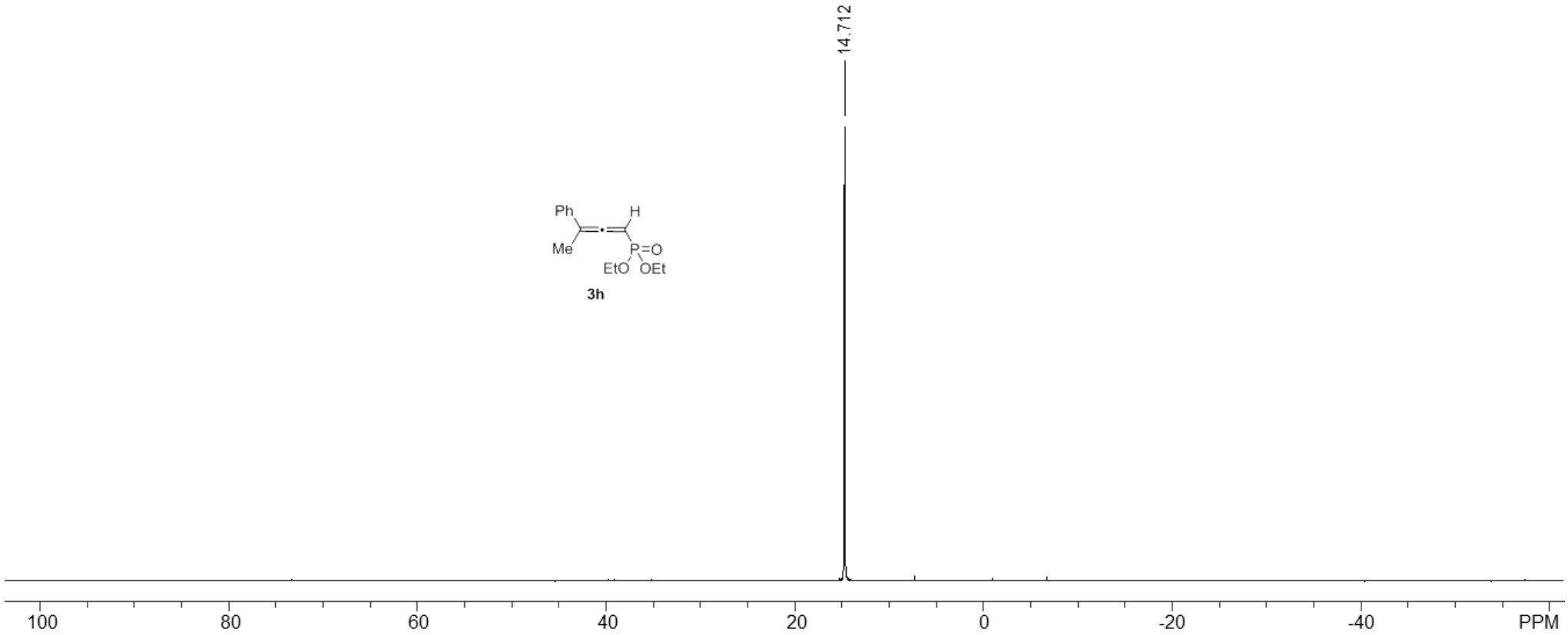
*^{13}C NMR spectrum of diethyl (3-phenylbuta-1,2-dien-1-yl)phosphonate (**3i**)*

$CDCl_3$, 100MHz



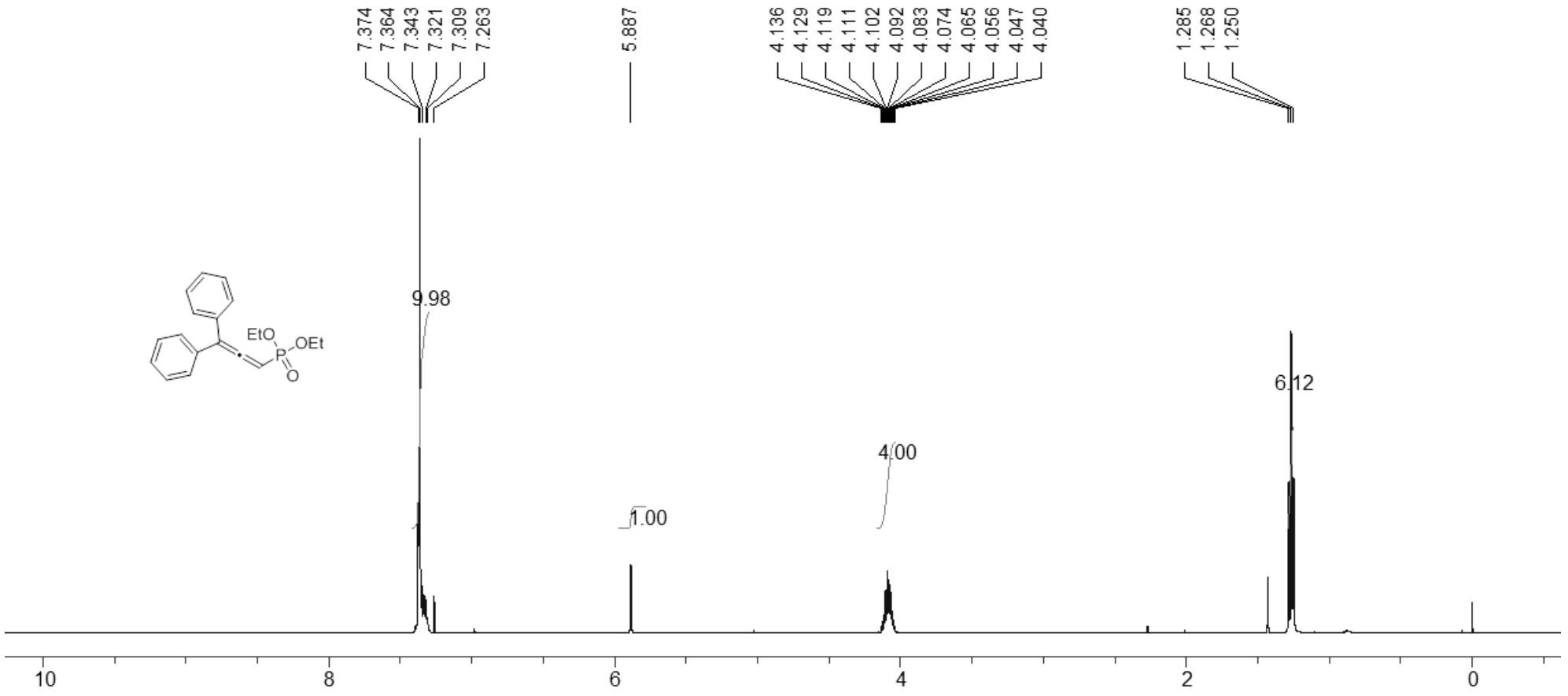
*^{31}P NMR spectrum of diethyl (3-phenylbuta-1,2-dien-1-yl)phosphonate (**3i**)*

$CDCl_3$, 162MHz



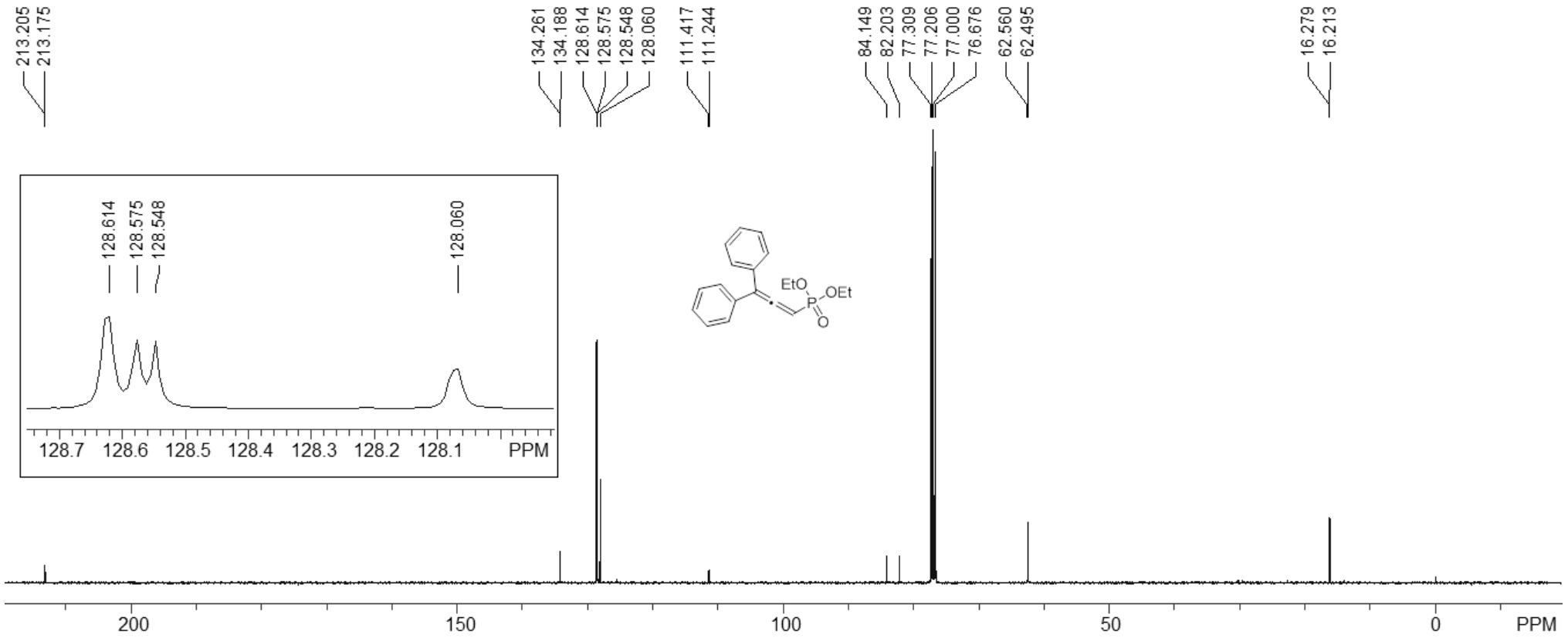
*^{1}H NMR spectrum of diethyl (3,3-diphenylpropa-1,2-dien-1-yl)phosphonate (**3j**)*

$CDCl_3$, 400MHz



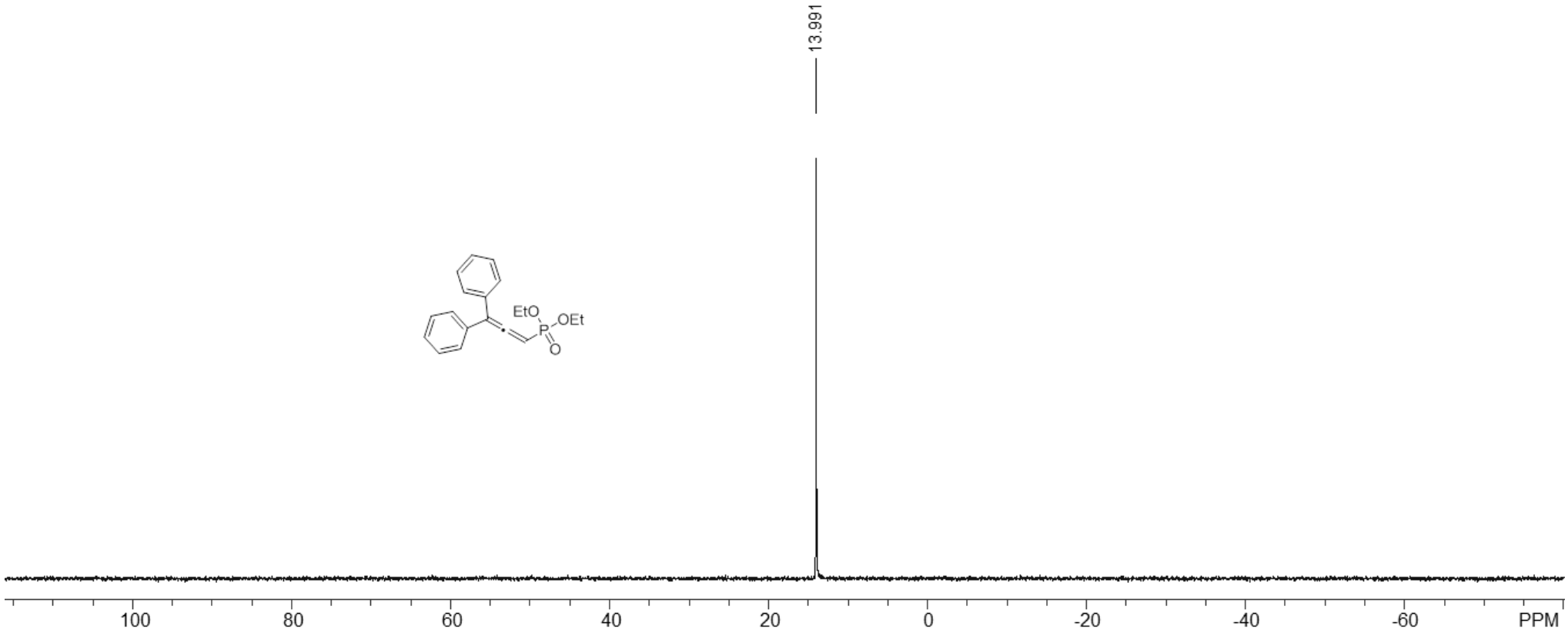
*^{13}C NMR spectrum of diethyl (3,3-diphenylpropa-1,2-dien-1-yl)phosphonate (**3j**)*

$CDCl_3$, 100MHz



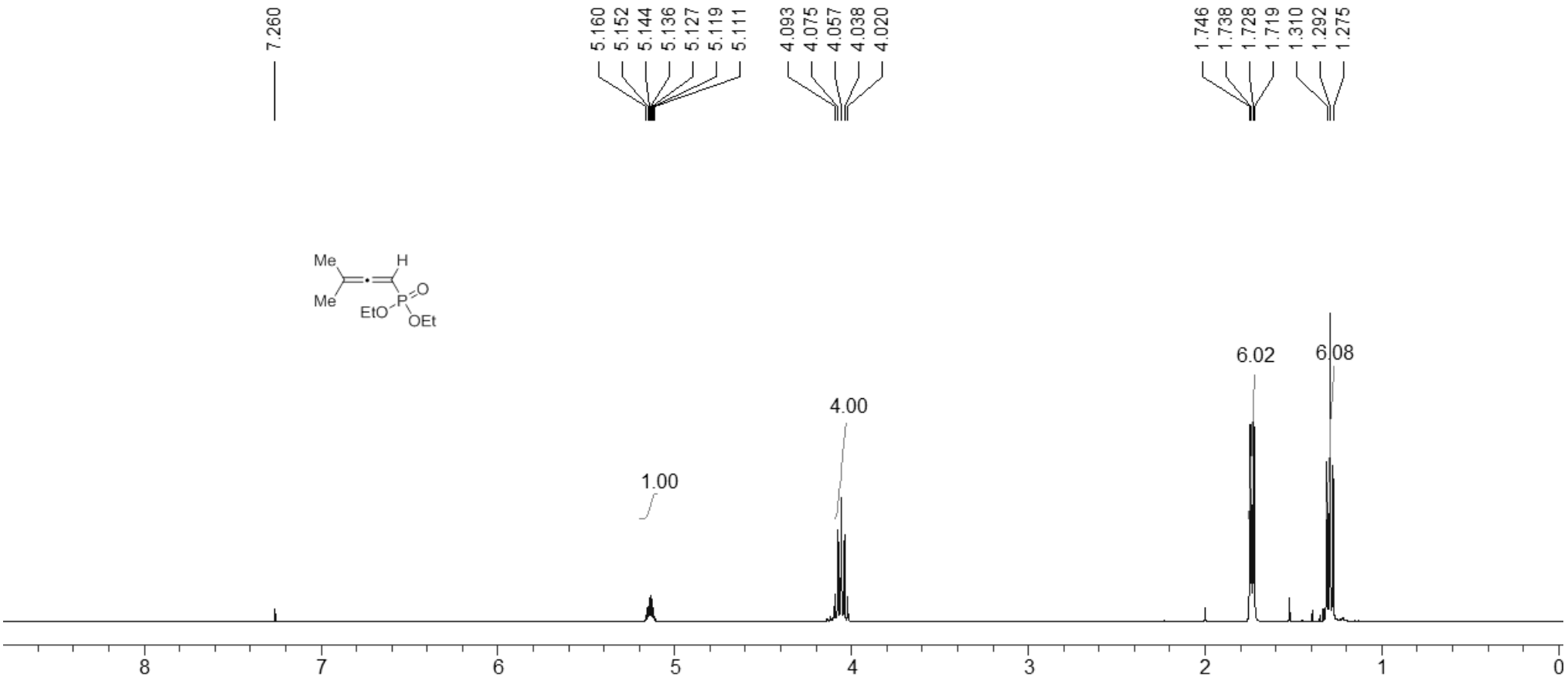
*^{31}P NMR spectrum of diethyl (3,3-diphenylpropa-1,2-dien-1-yl)phosphonate (**3j**)*

$CDCl_3$, 162MHz



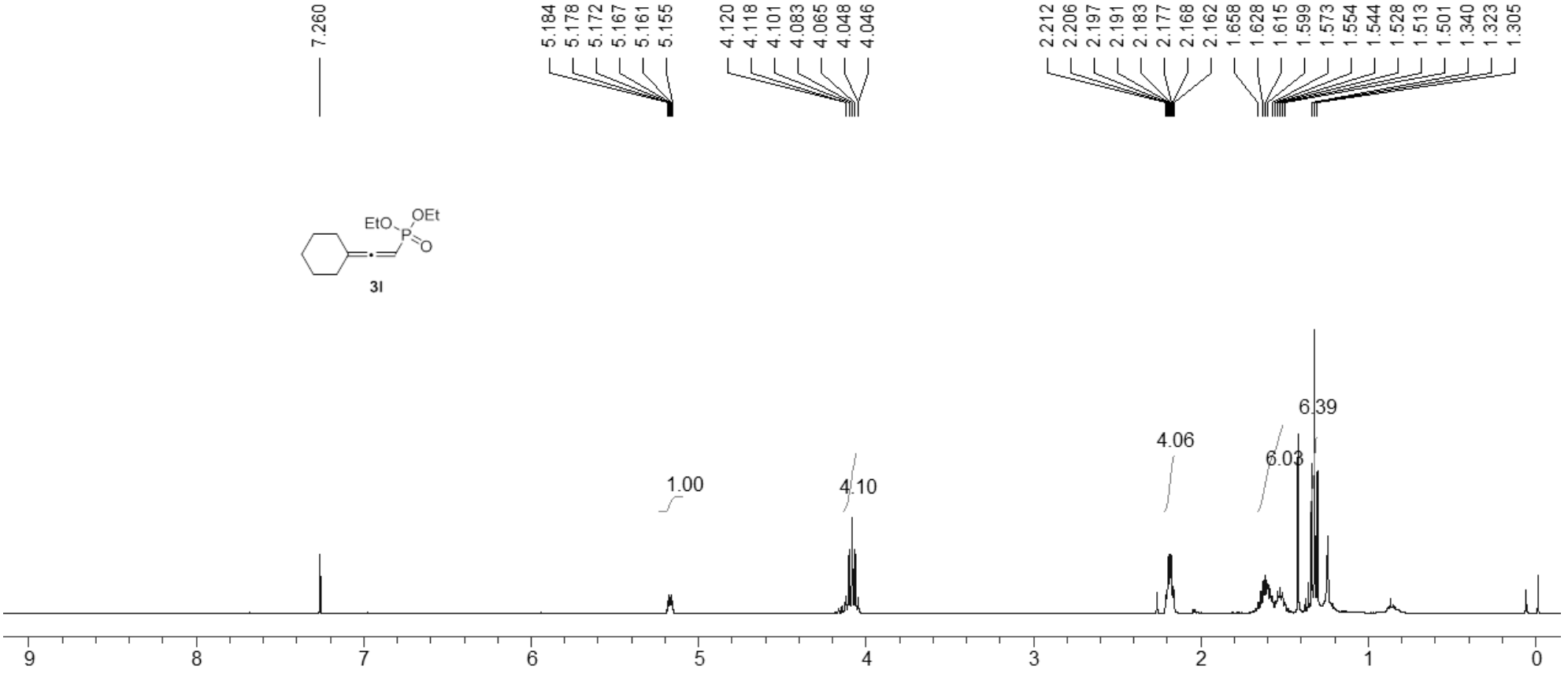
*^{1}H NMR spectrum of diethyl (3-methylbuta-1,2-dien-1-yl)phosphonate (**3k**)*

$CDCl_3$, 400MHz



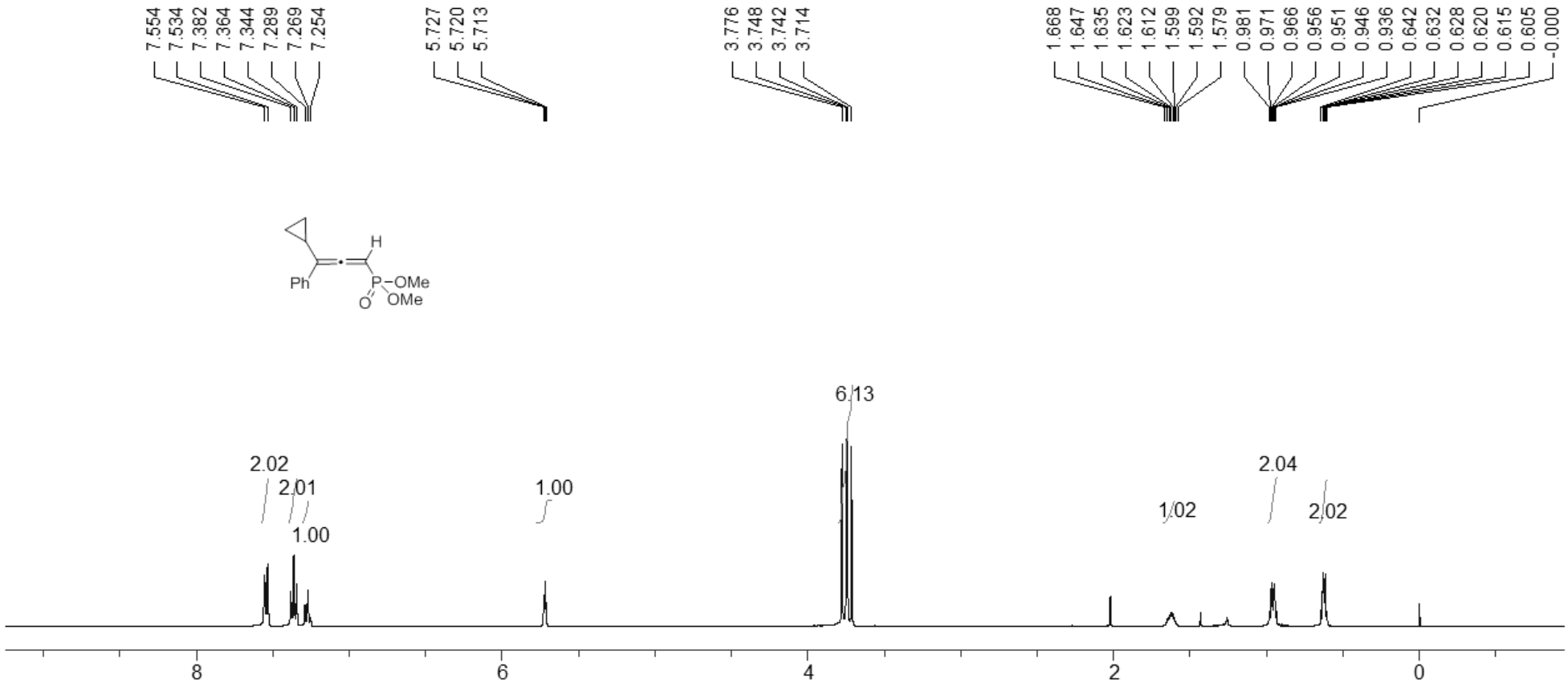
*^{1}H NMR spectrum of diethyl (2-cyclohexylidenevinyl)phosphonate (**3l**)*

$CDCl_3$, 400MHz



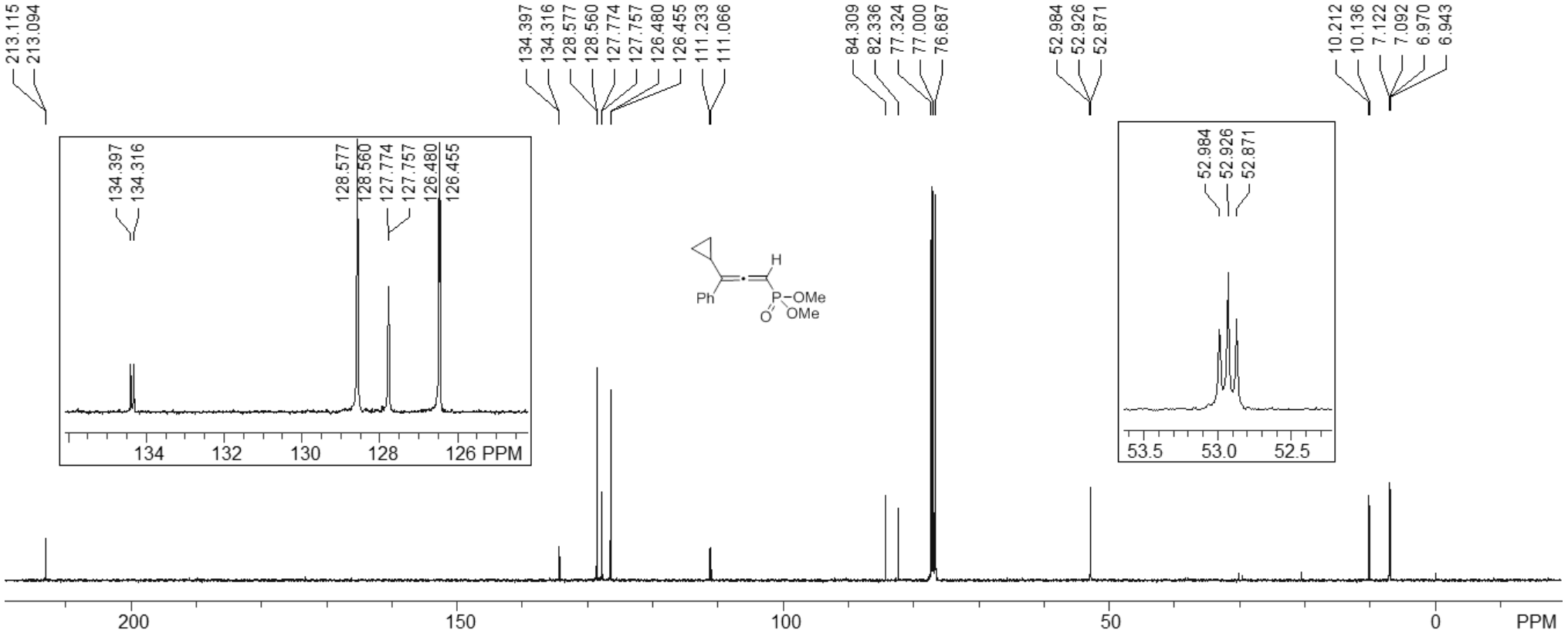
*^{1}H NMR spectrum of dimethyl (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)phosphonate (**3m**)*

$CDCl_3$, 400MHz



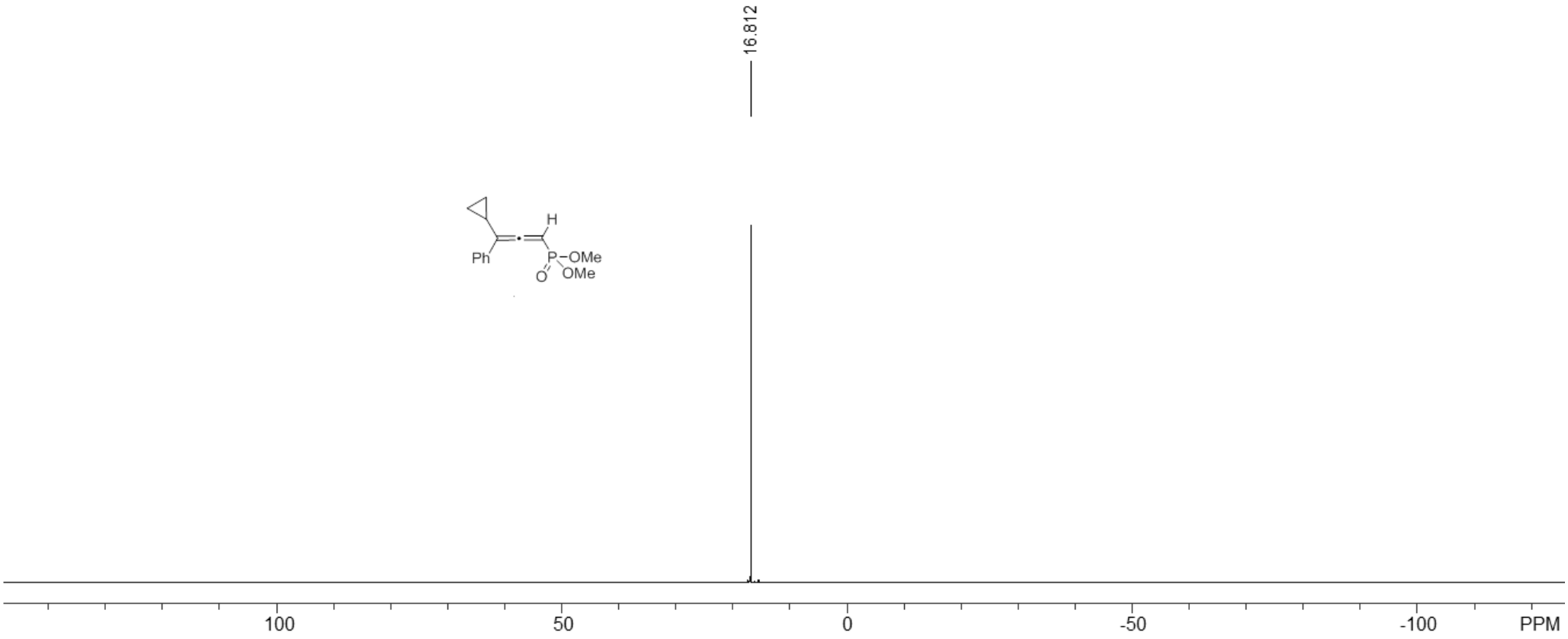
*^{31}C NMR spectrum of dimethyl (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)phosphonate (**3m**)*

$CDCl_3$, 100MHz



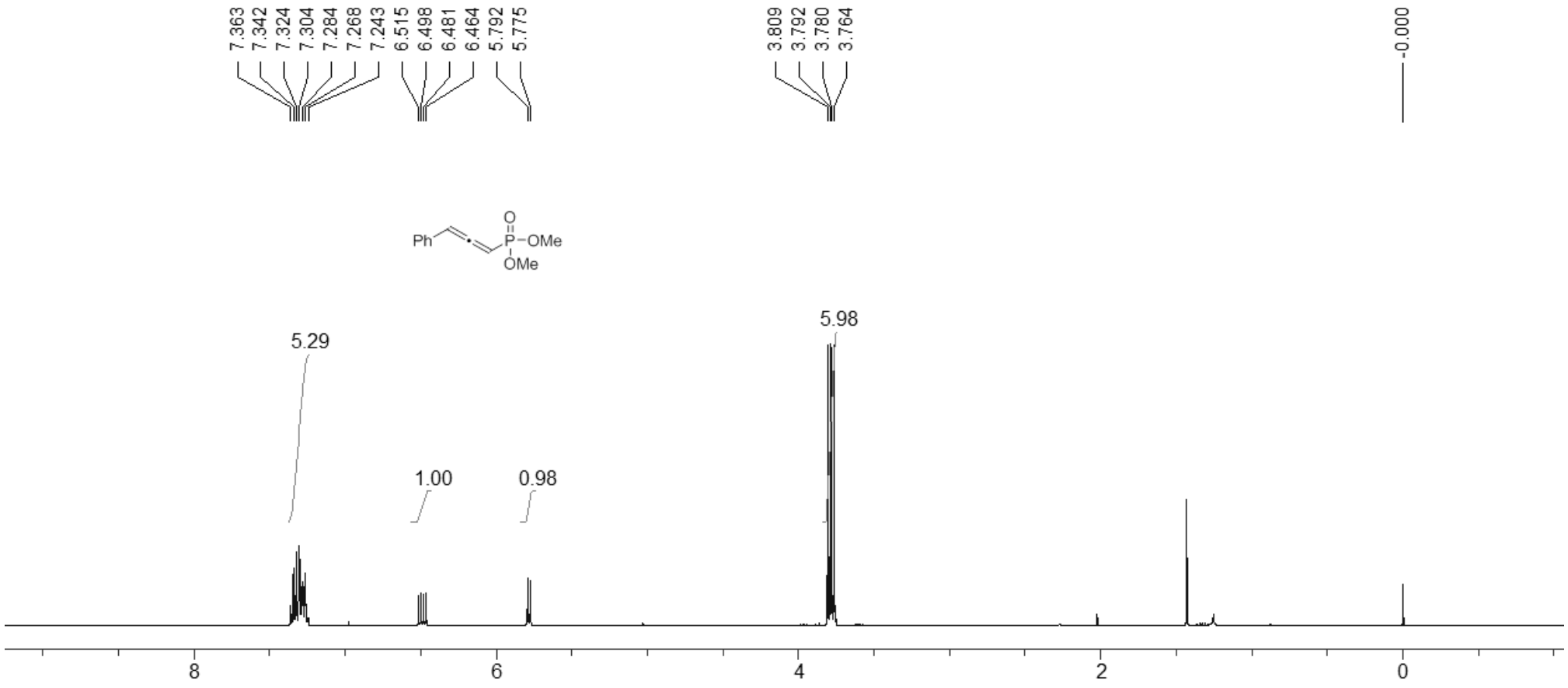
*^{31}P NMR spectrum of dimethyl (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)phosphonate (**3m**)*

$CDCl_3$, 162MHz



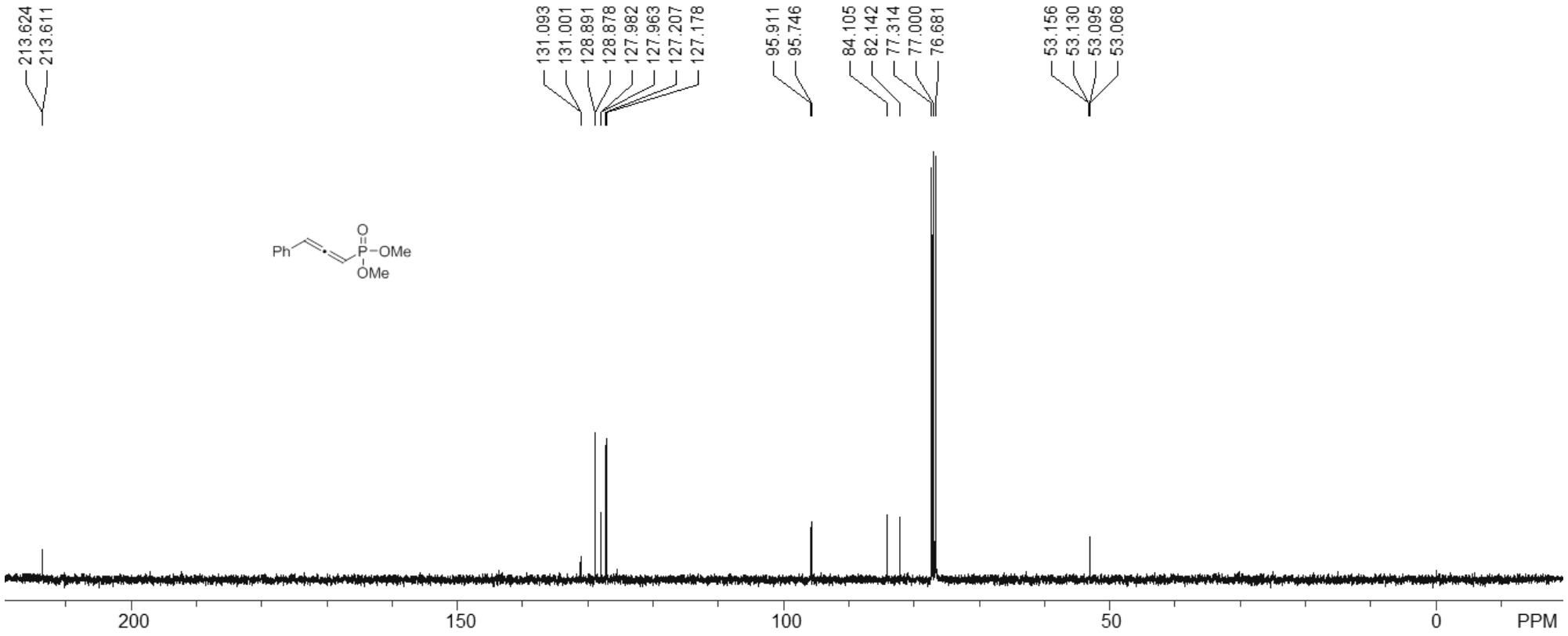
*^{1}H NMR spectrum of dimethyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3n**)*

$CDCl_3$, 400MHz



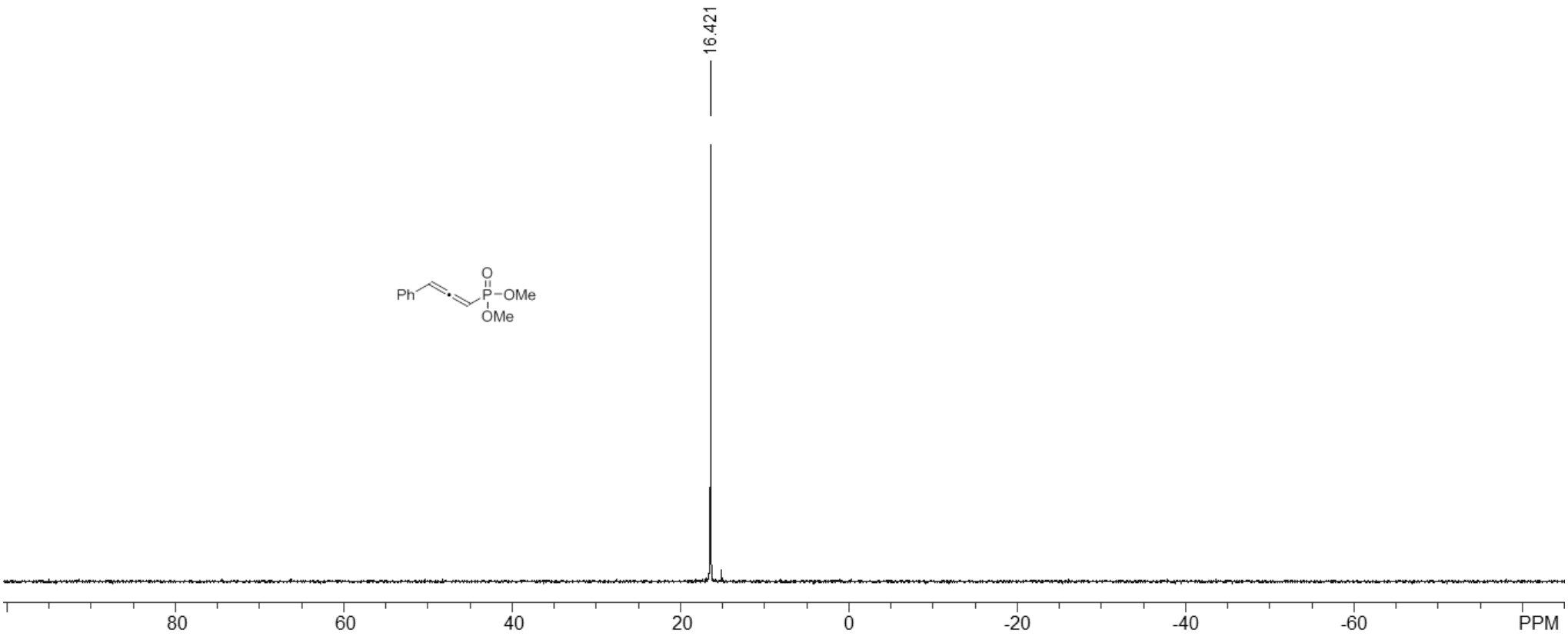
*^{31}C NMR spectrum of dimethyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3n**)*

$CDCl_3$, 100MHz



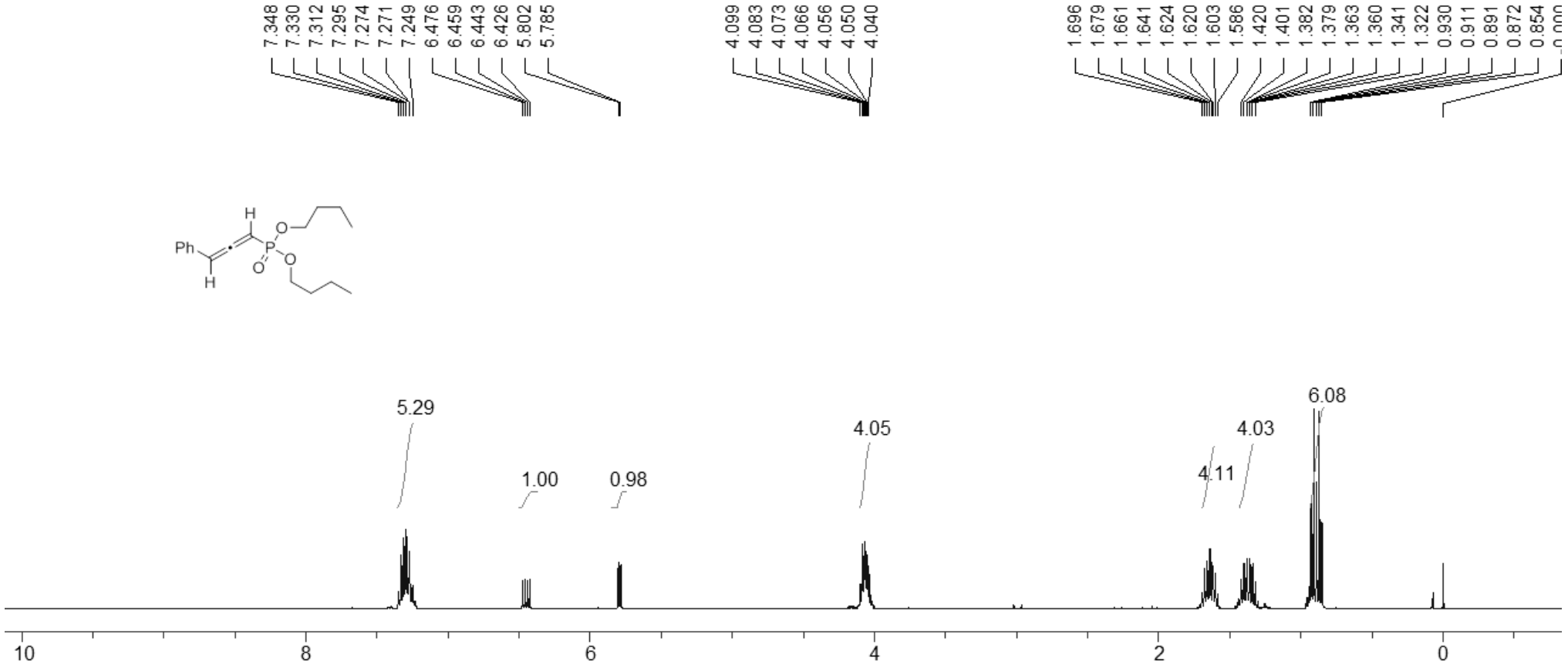
*^{31}P NMR spectrum of dimethyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3n**)*

$CDCl_3$, 162MHz



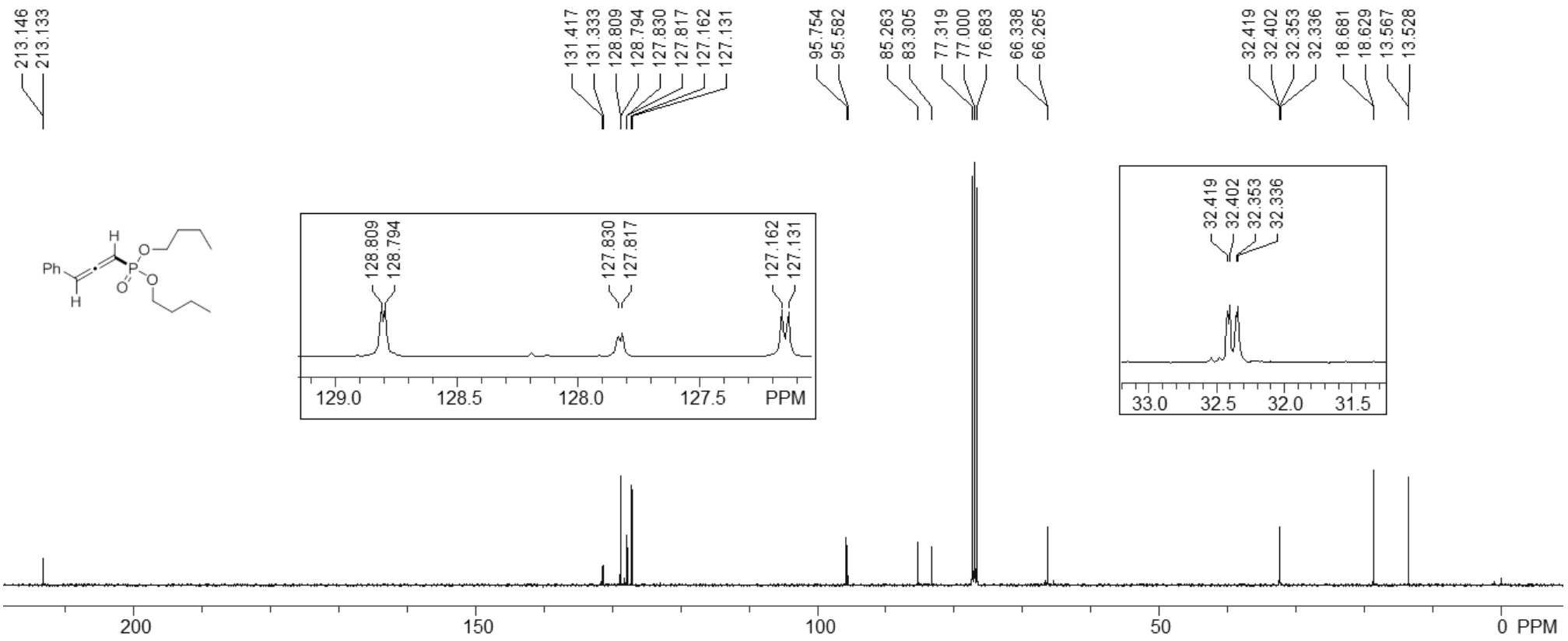
*^{1}H NMR spectrum of dibutyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3o**)*

$CDCl_3$, 400MHz



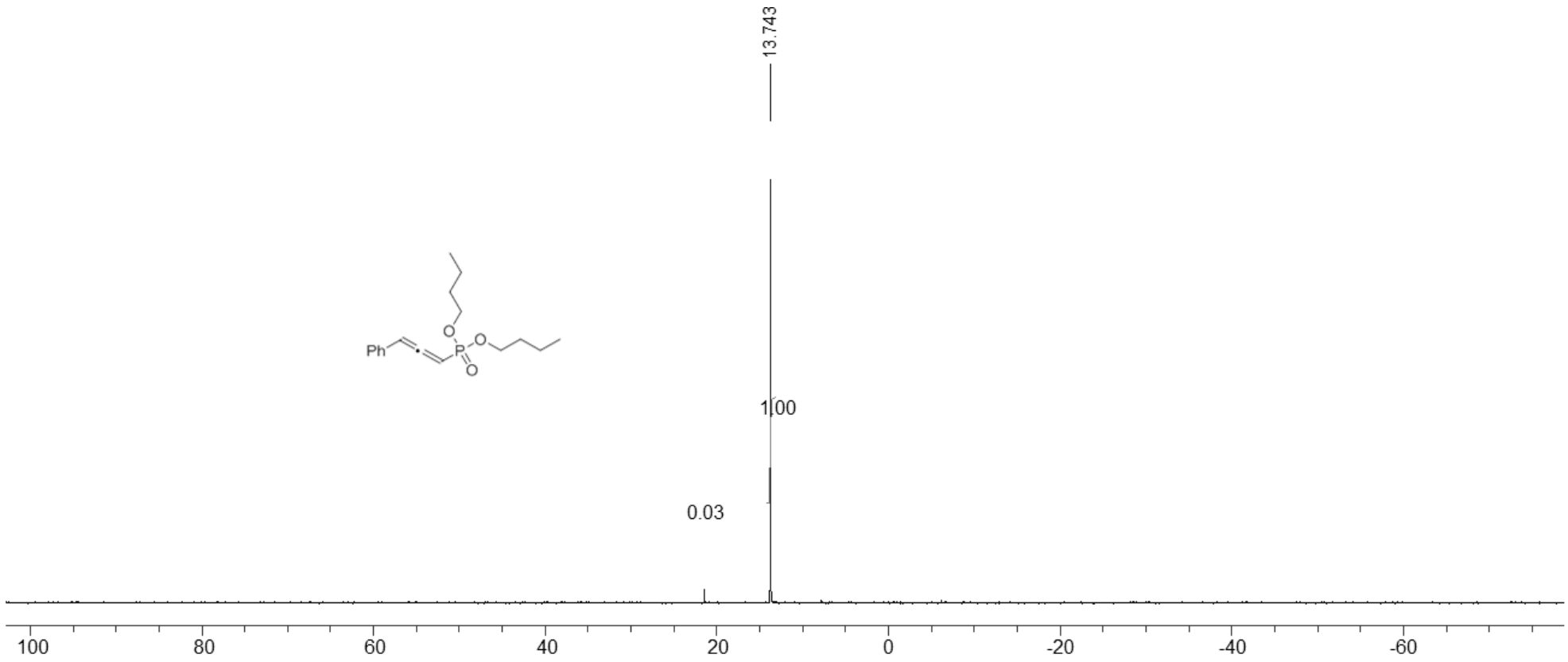
*^{13}C NMR spectrum of dibutyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3o**)*

$CDCl_3$, 100MHz



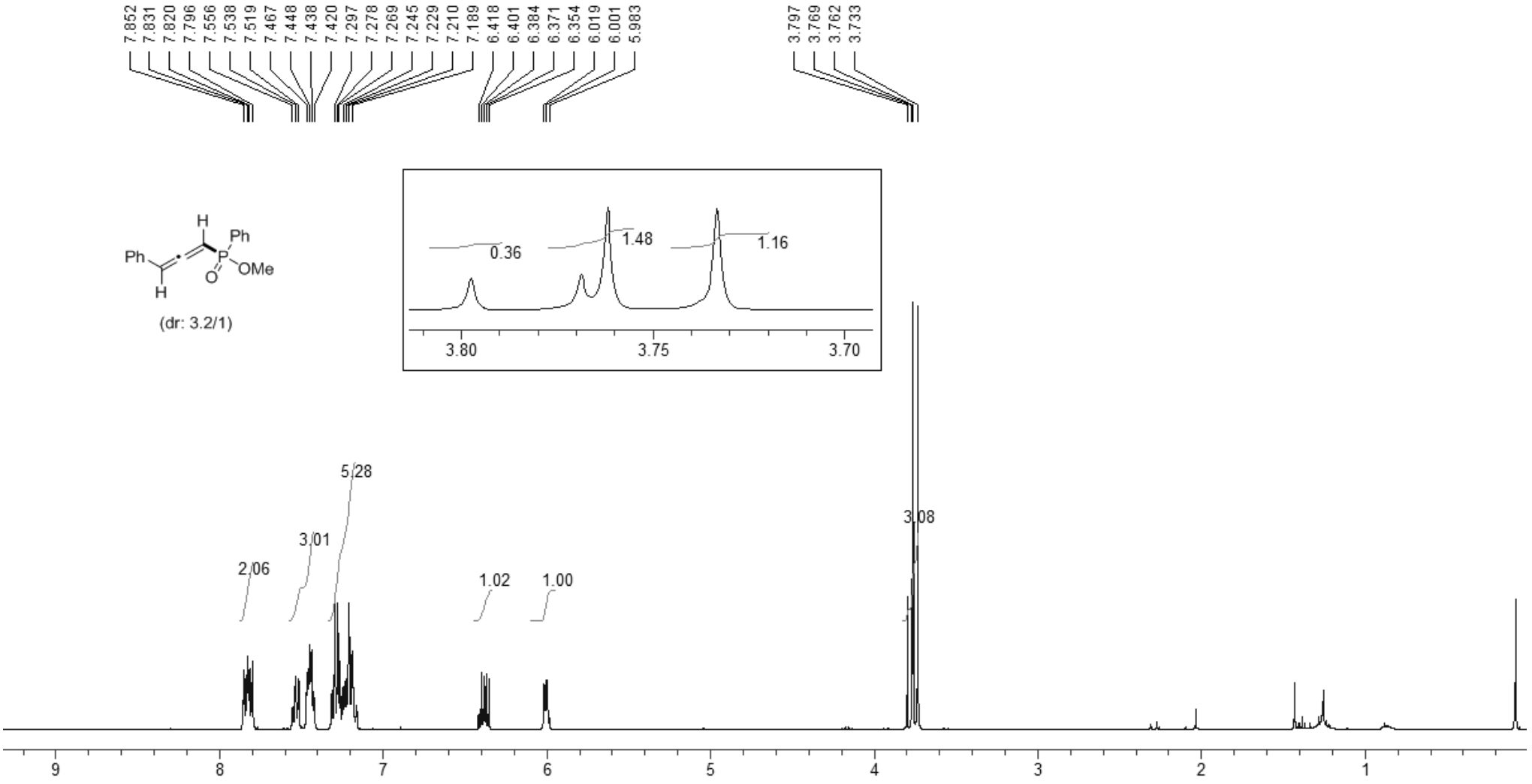
*^{31}P NMR spectrum of dibutyl (S)-(3-phenylpropa-1,2-dien-1-yl)phosphonate (**3o**)*

$CDCl_3$, 162MHz



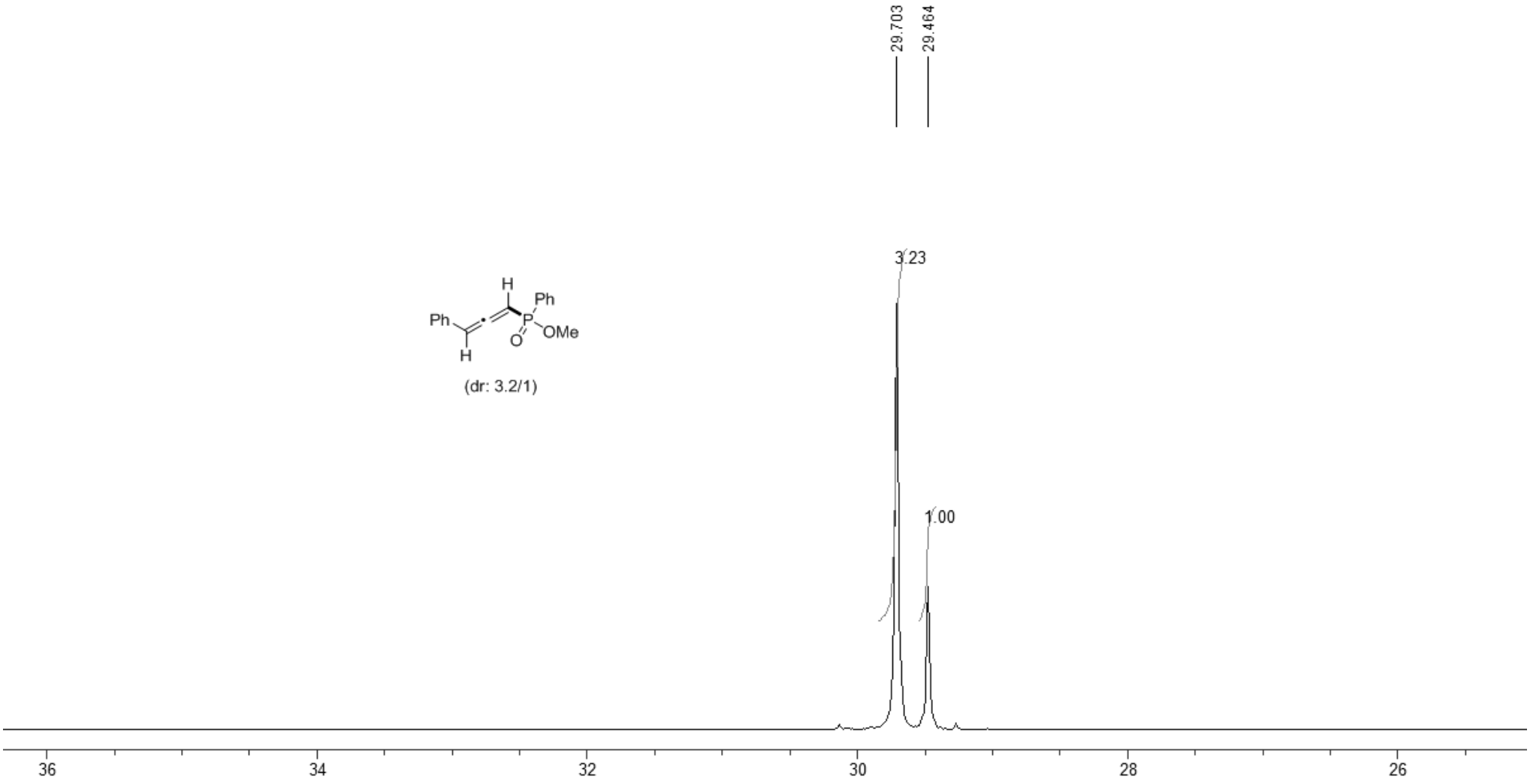
*[1]H NMR spectrum of methyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3p**)*

$CDCl_3$, 400MHz



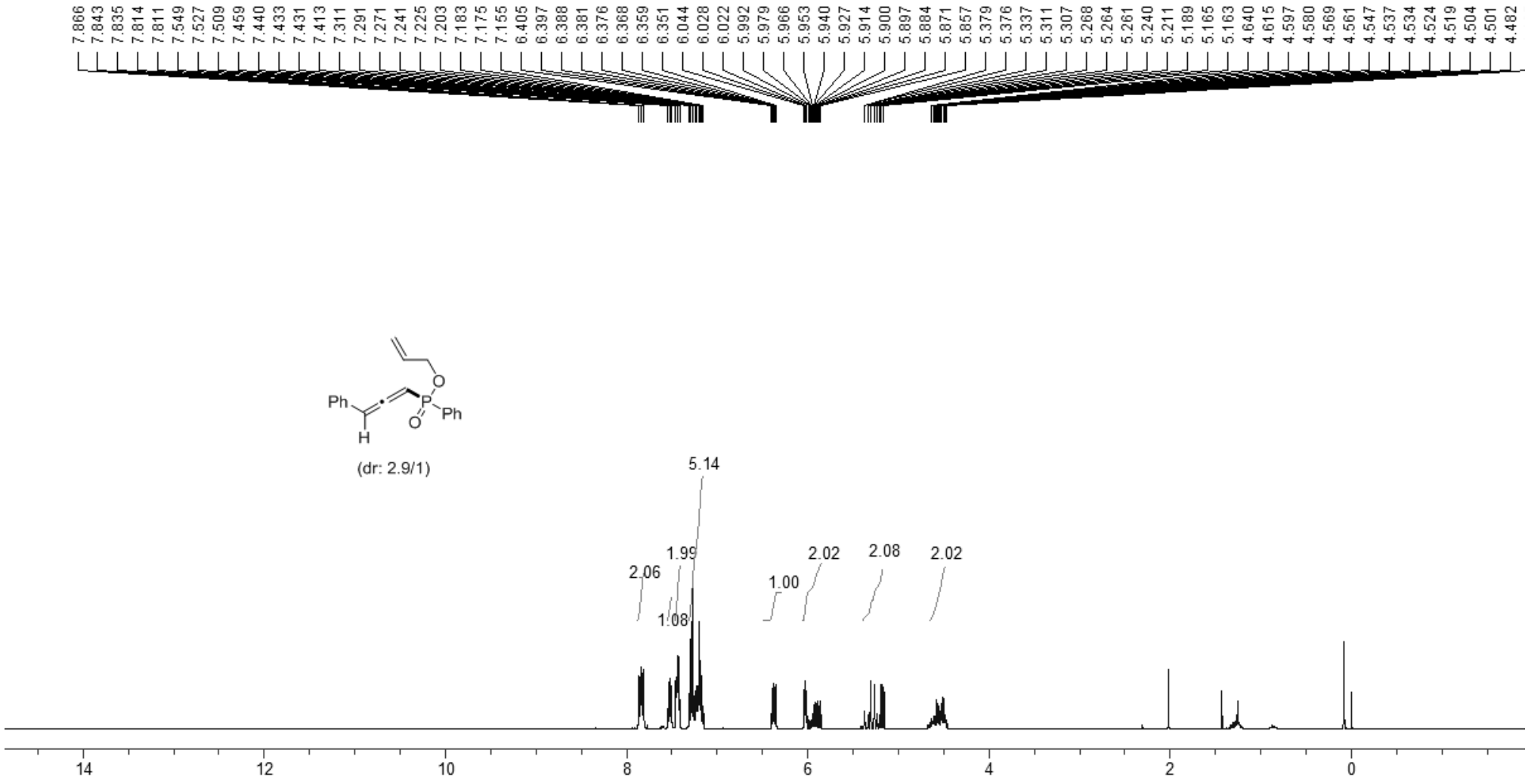
*^{31}P NMR spectrum of methyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3p**)*

$CDCl_3$, 162MHz



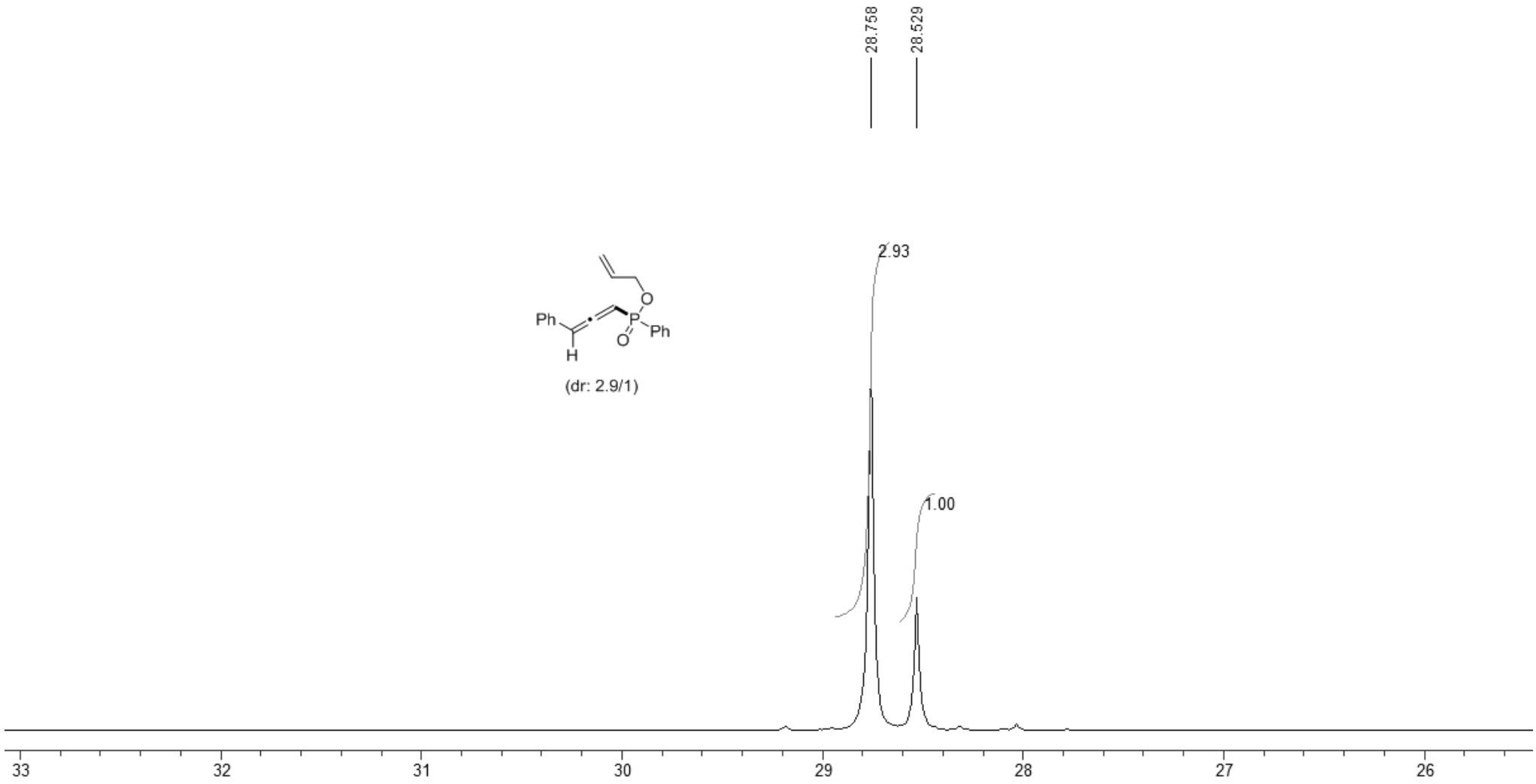
*^{1}H NMR spectrum of allyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3q**)*

$CDCl_3$, 400MHz



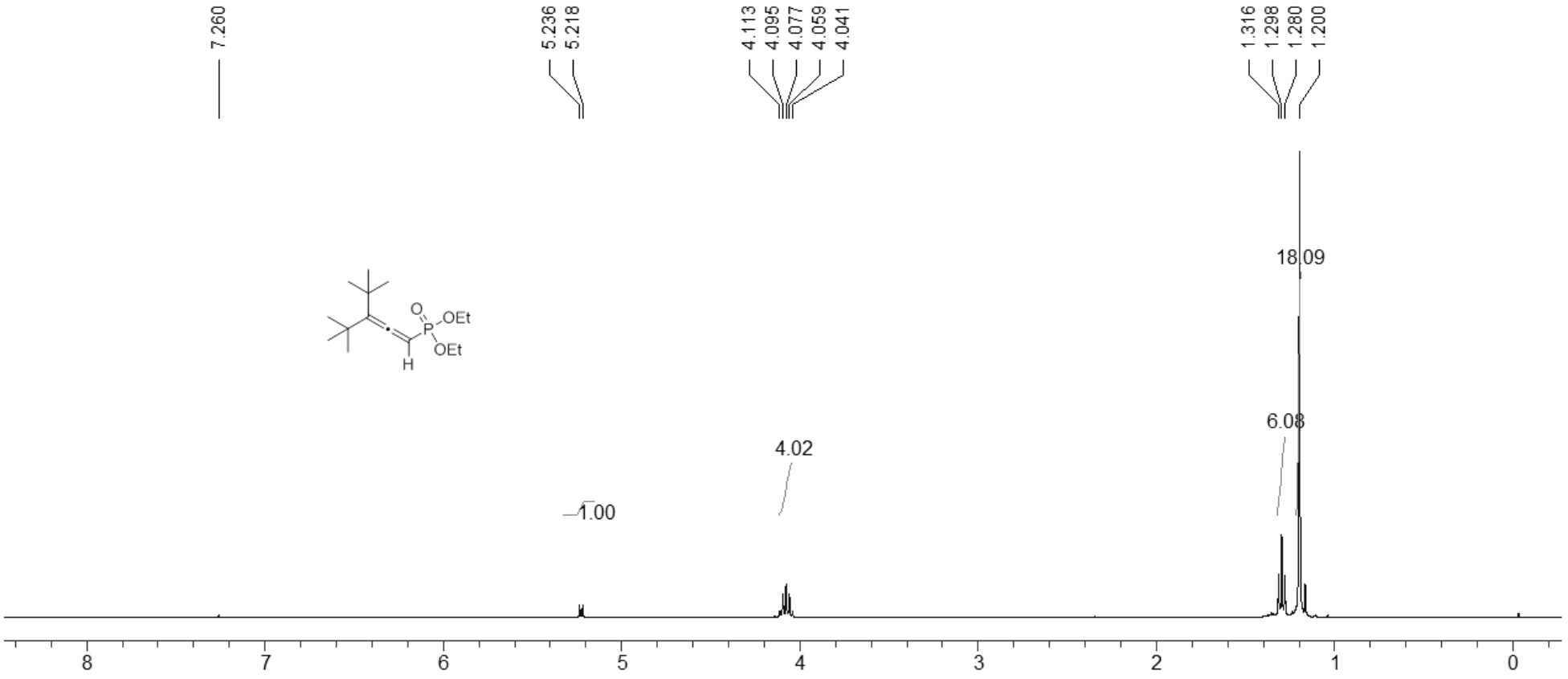
*^{31}P NMR spectrum of allyl phenyl(3-phenylpropa-1,2-dien-1-yl)phosphinate (**3q**)*

$CDCl_3$, 162MHz



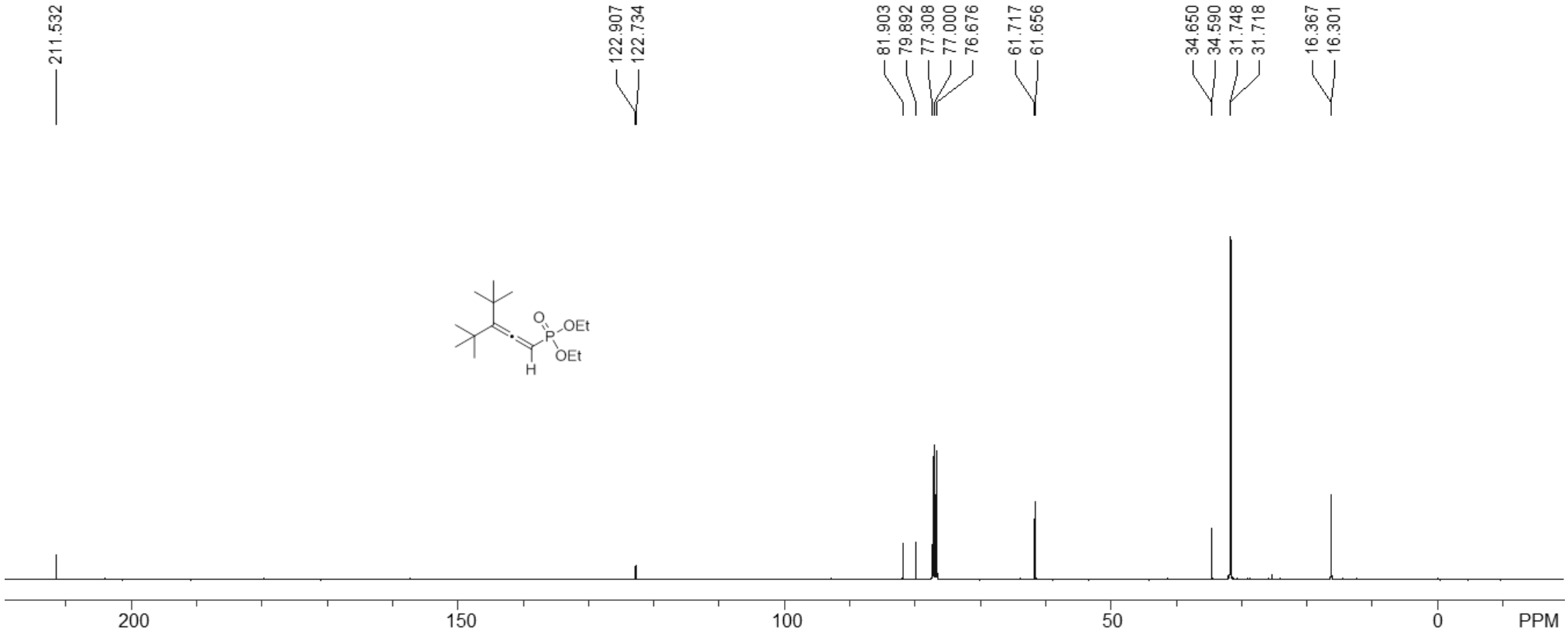
*^{1}H NMR spectrum of diethyl (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3r**)*

$CDCl_3$, 400MHz



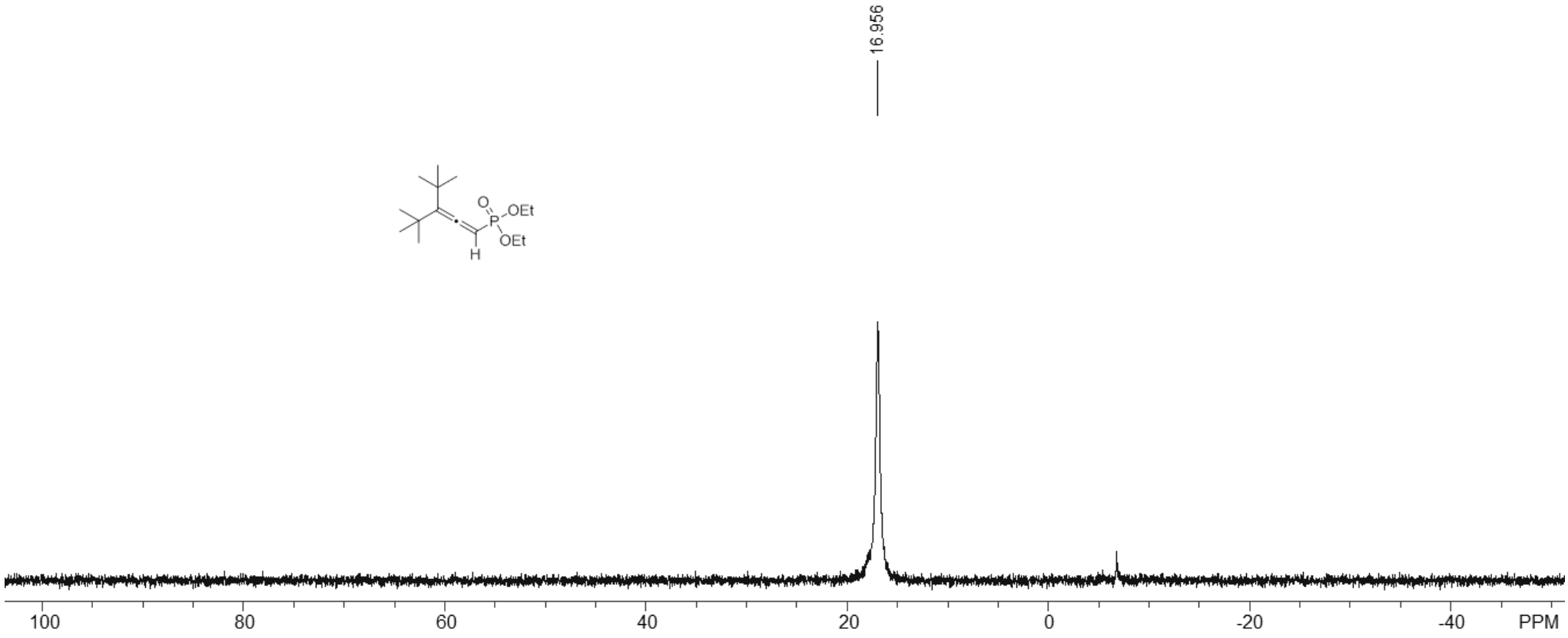
*^{13}C NMR spectrum of diethyl (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3r**)*

$CDCl_3$, 100MHz



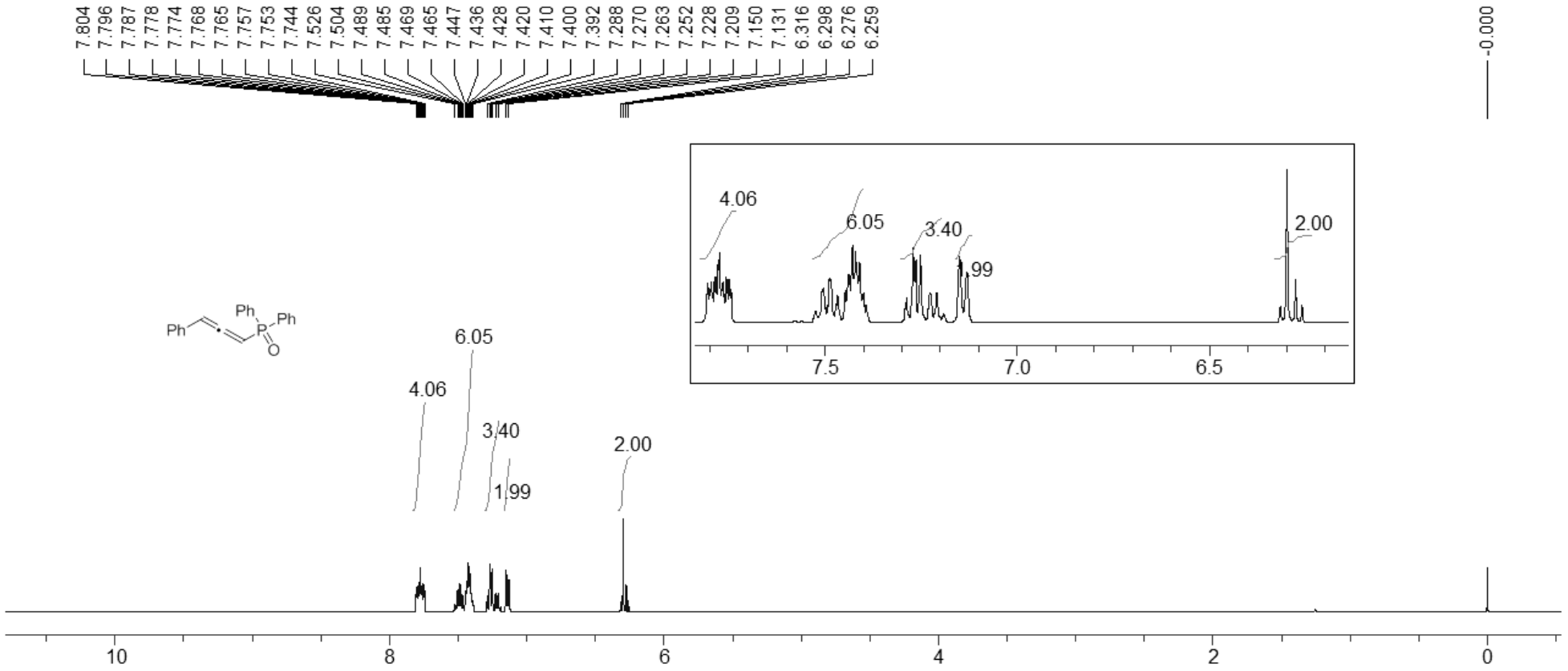
*^{31}P NMR spectrum of diethyl (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (**3r**)*

$CDCl_3$, 162MHz



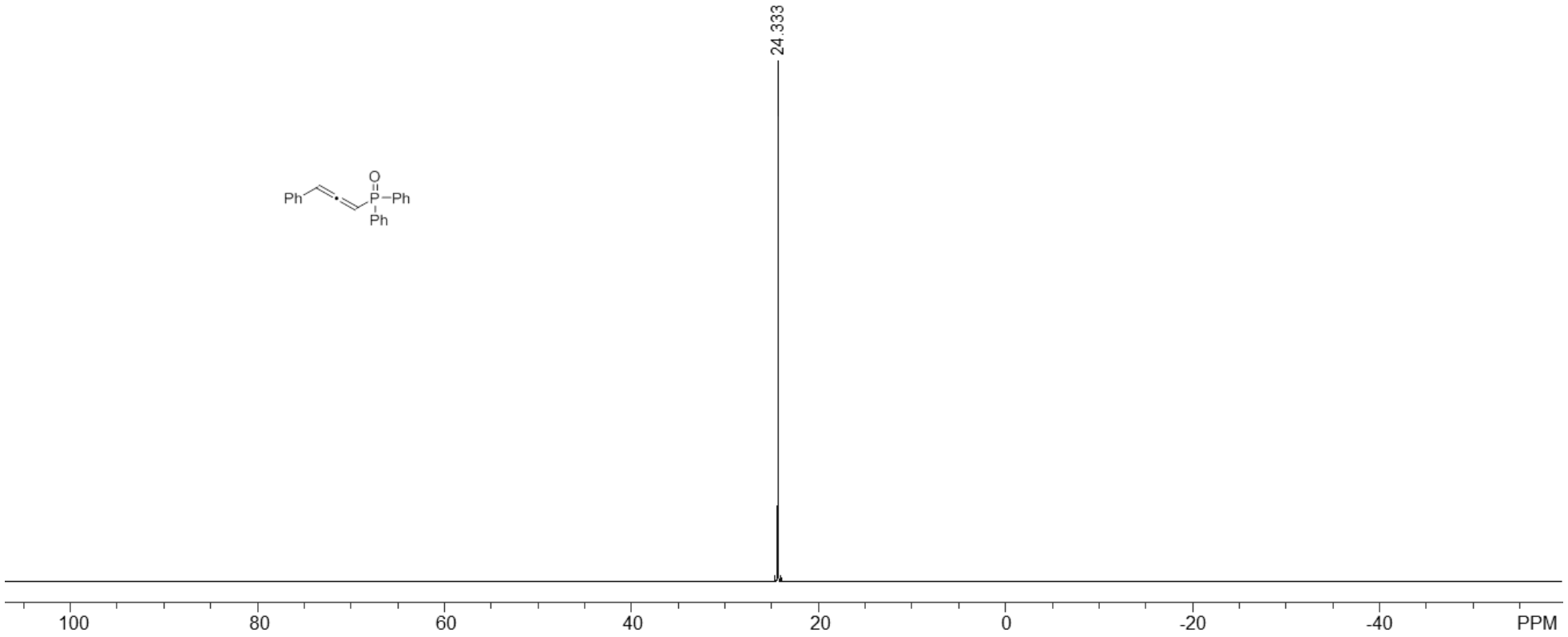
*[1]H NMR spectrum of diphenyl(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5a**)*

$CDCl_3$, 400MHz



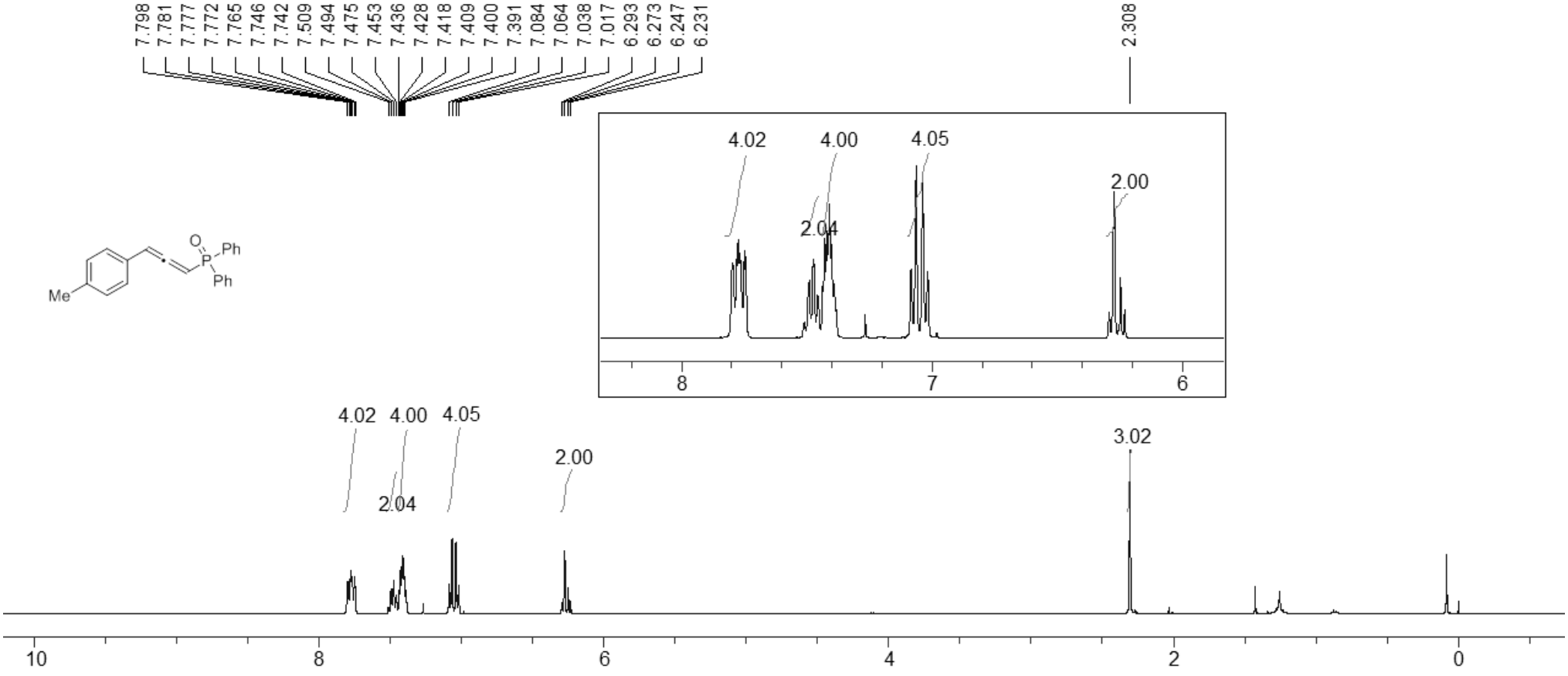
*^{31}P NMR spectrum of diphenyl(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5a**)*

$CDCl_3$, 162MHz



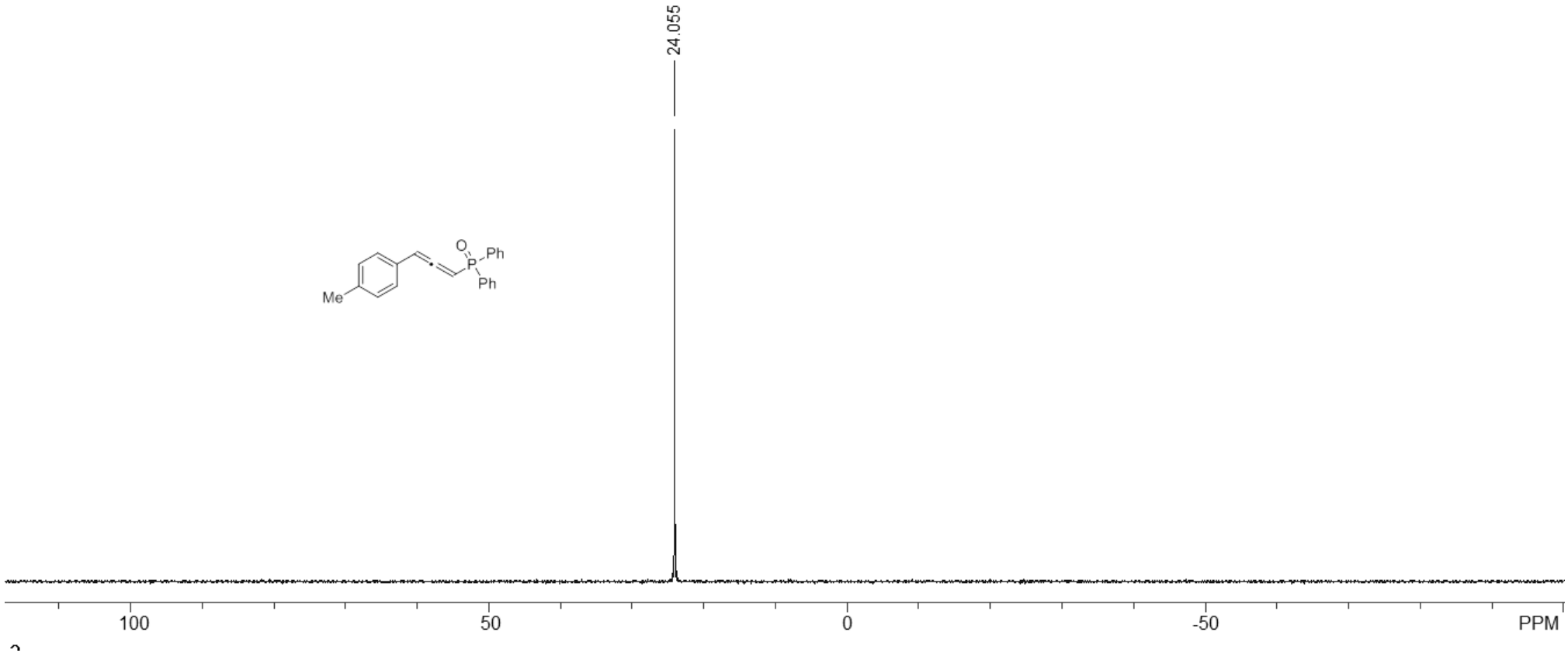
*[1]H NMR spectrum of diphenyl(3-(p-tolyl)propa-1,2-dien-1-yl)phosphine oxide (**5b**)*

$CDCl_3$, 400MHz



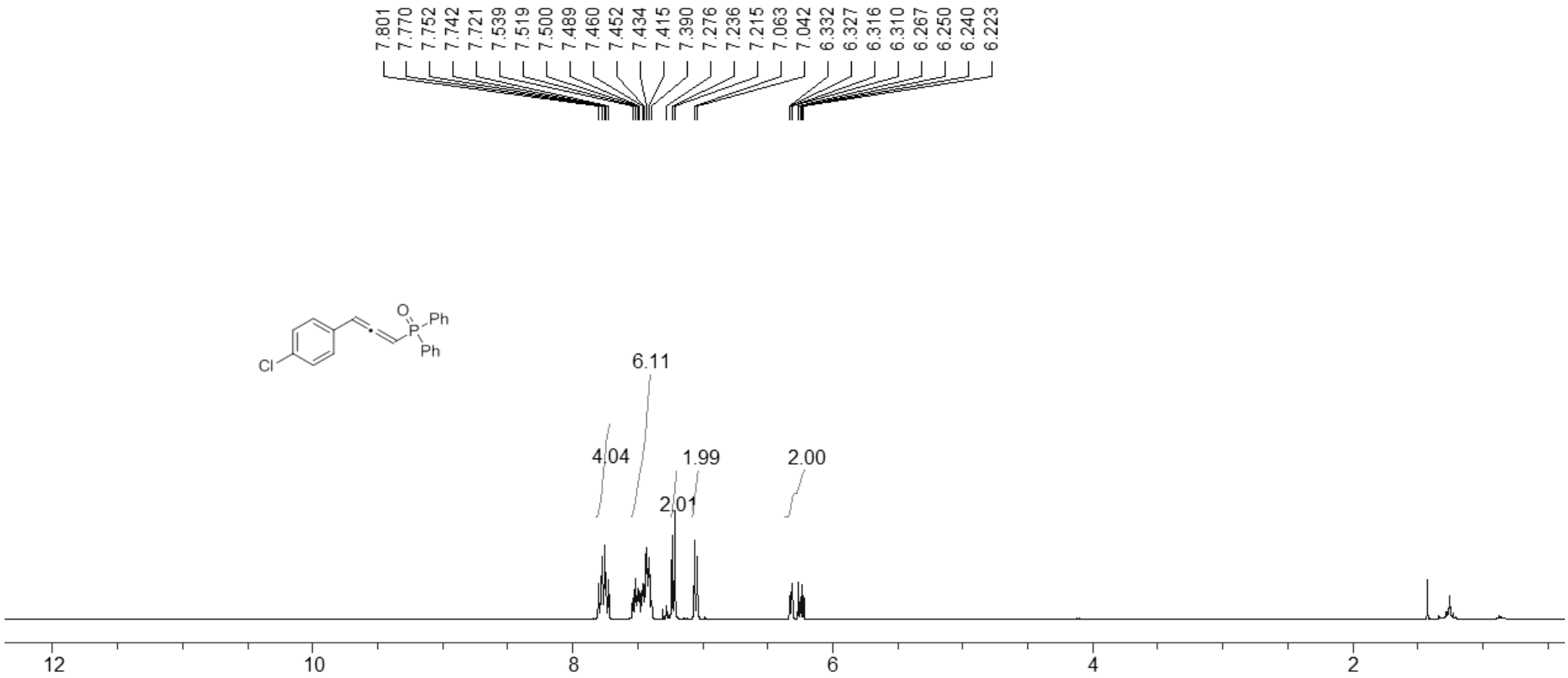
*^{31}P NMR spectrum of diphenyl(3-(p-tolyl)propa-1,2-dien-1-yl)phosphine oxide (**5b**)*

$CDCl_3$, 162MHz



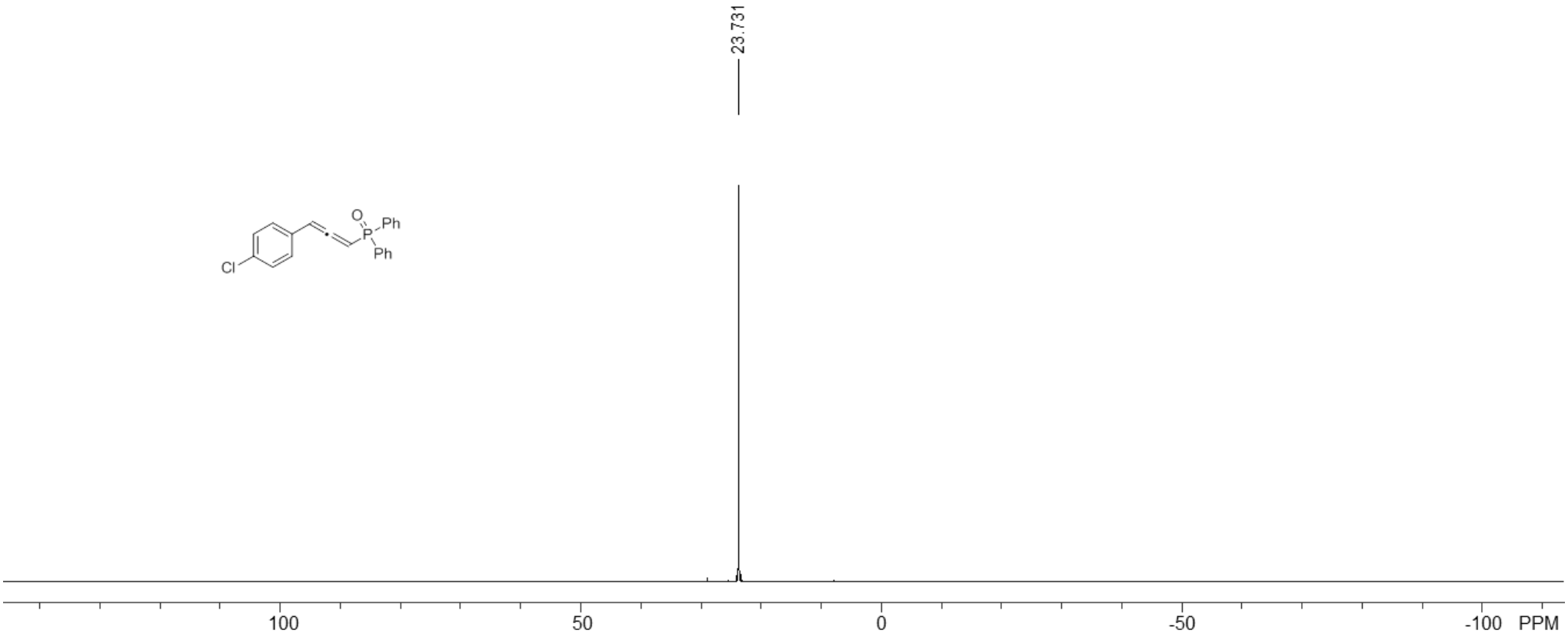
*^{1}H NMR spectrum of (3-(4-chlorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5c**)*

$CDCl_3$, 400MHz



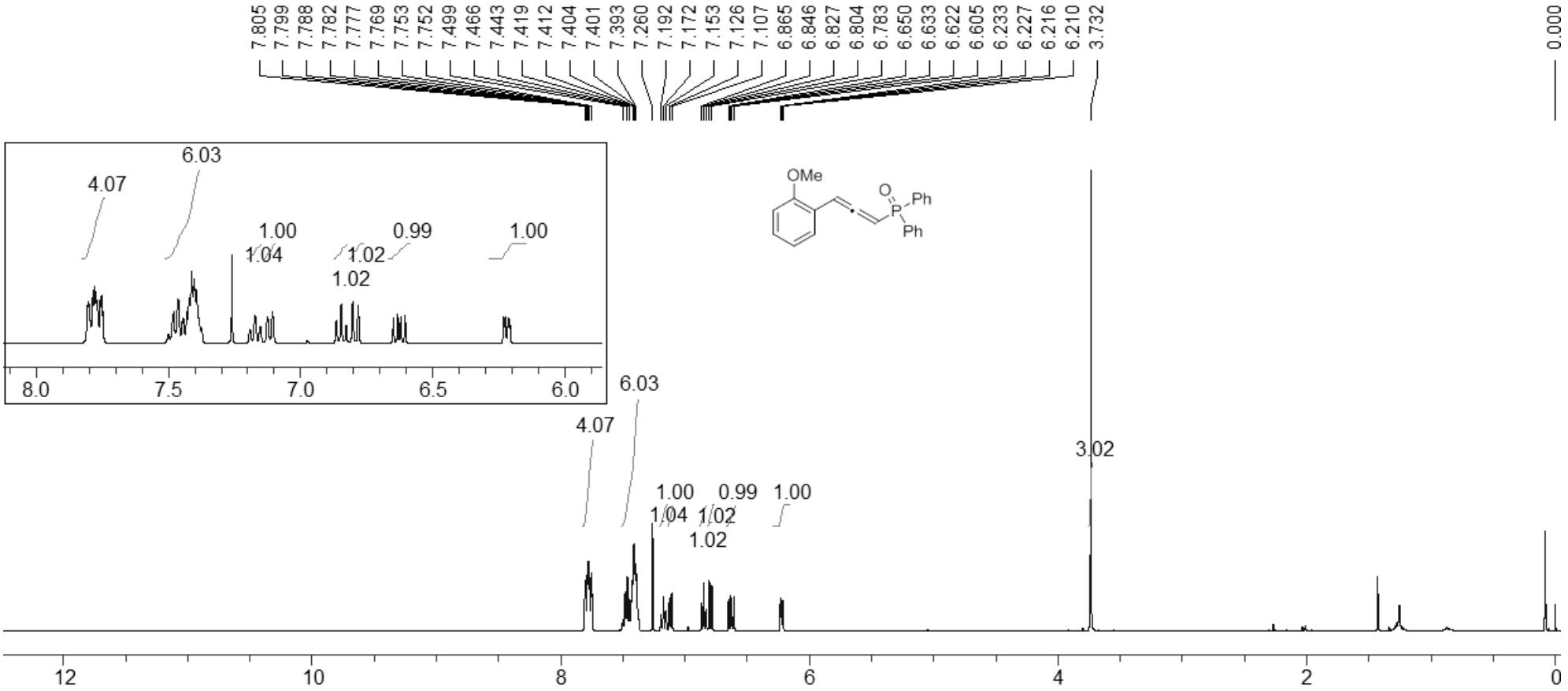
*^{31}P NMR spectrum of (3-(4-chlorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5c**)*

$CDCl_3$, 162MHz



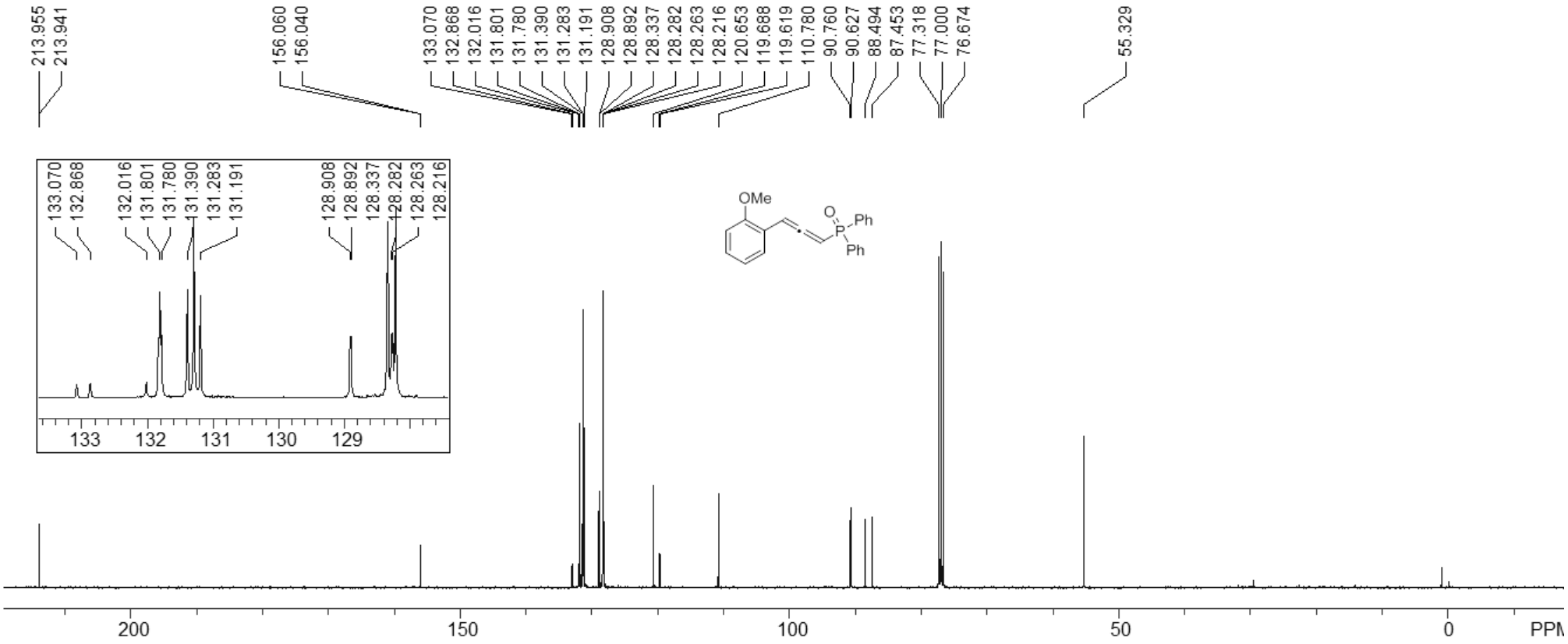
*^{1}H NMR spectrum of (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5d**)*

$CDCl_3$, 400MHz



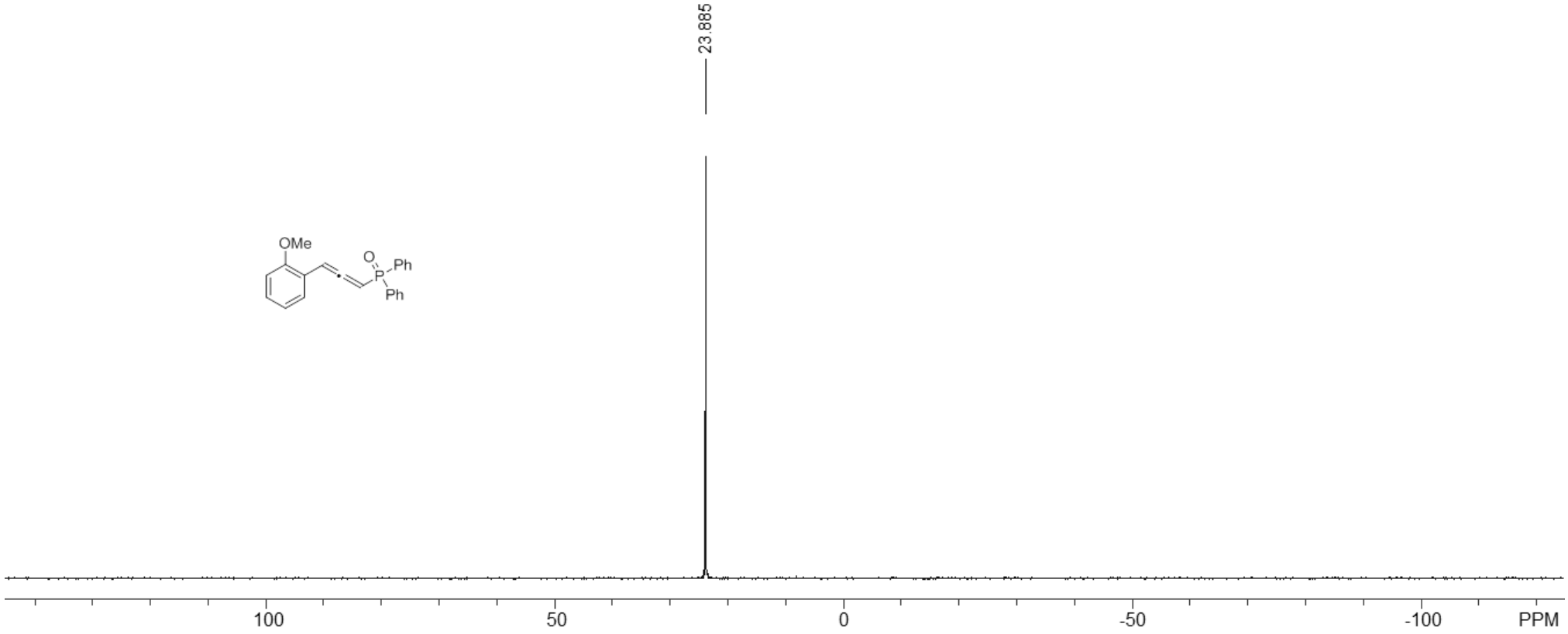
*^{13}C NMR spectrum of (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5d**)*

$CDCl_3$, 100MHz



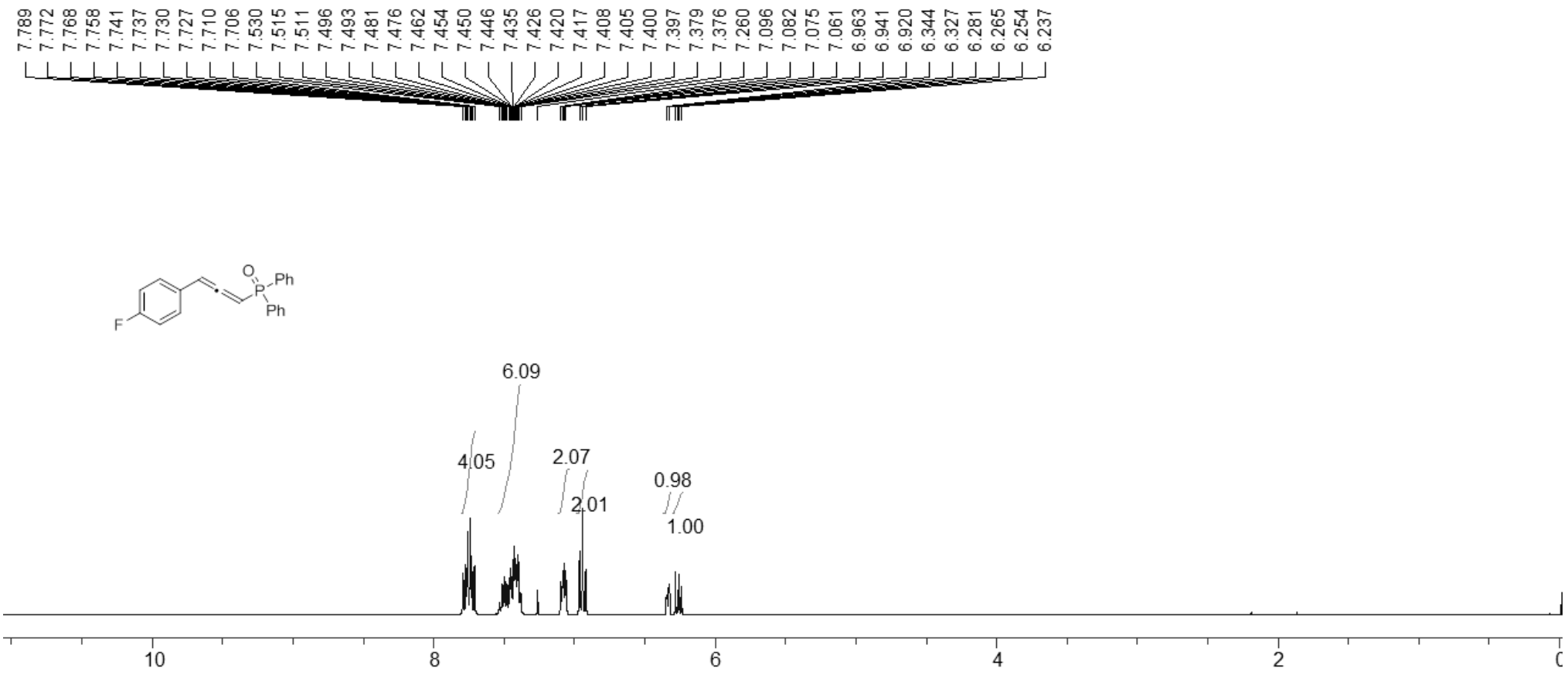
*^{31}P NMR spectrum of (3-(2-methoxyphenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5d**)*

$CDCl_3$, 162MHz



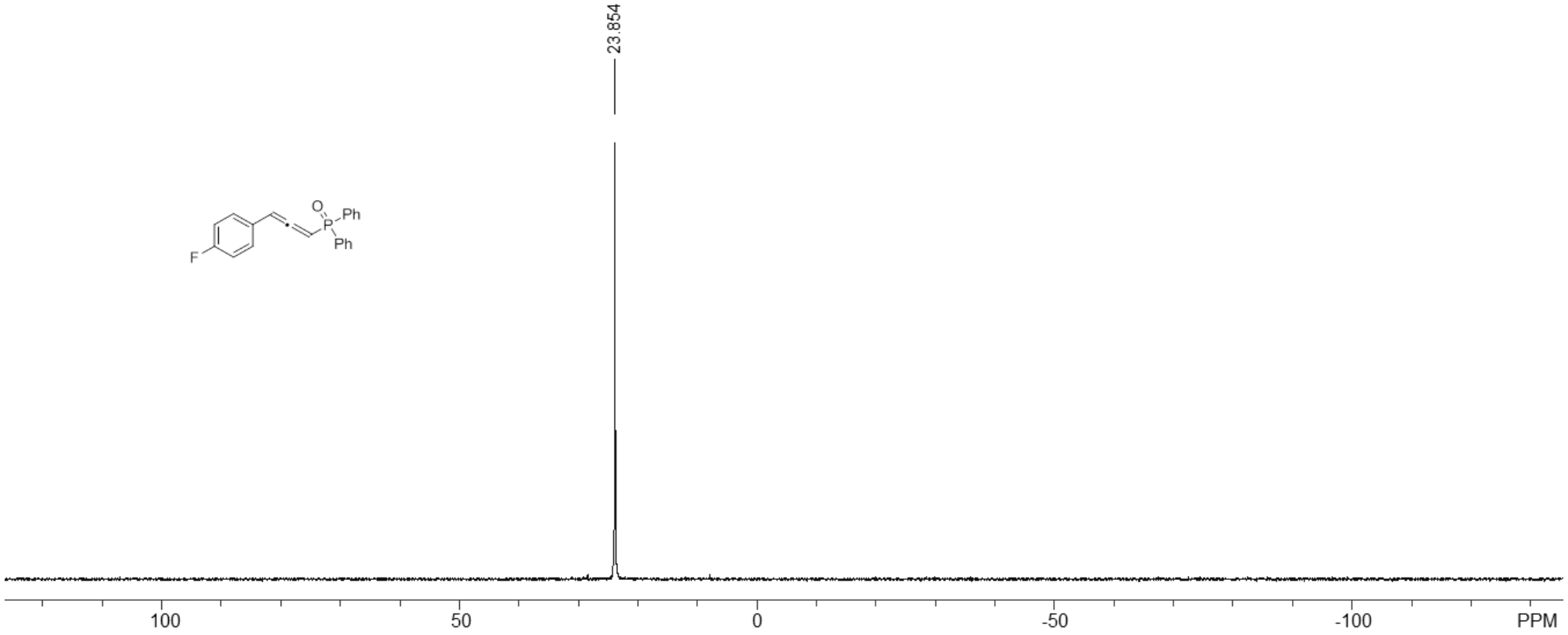
*[1]H NMR spectrum of (3-(4-fluorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5e**)*

$CDCl_3$, 400MHz



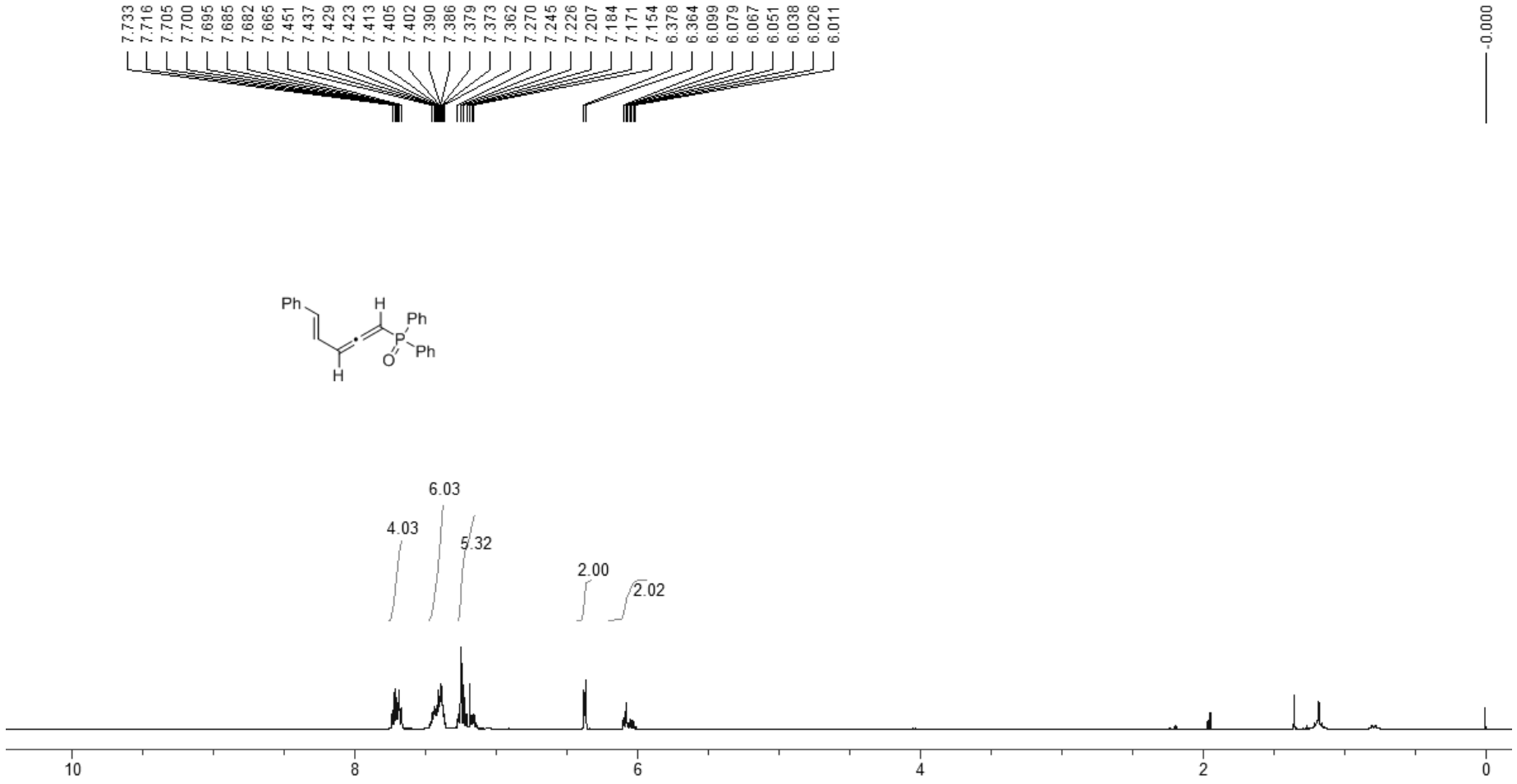
*^{31}P NMR spectrum of (3-(4-fluorophenyl)propa-1,2-dien-1-yl)diphenylphosphine oxide (**5e**)*

$CDCl_3$, 162MHz



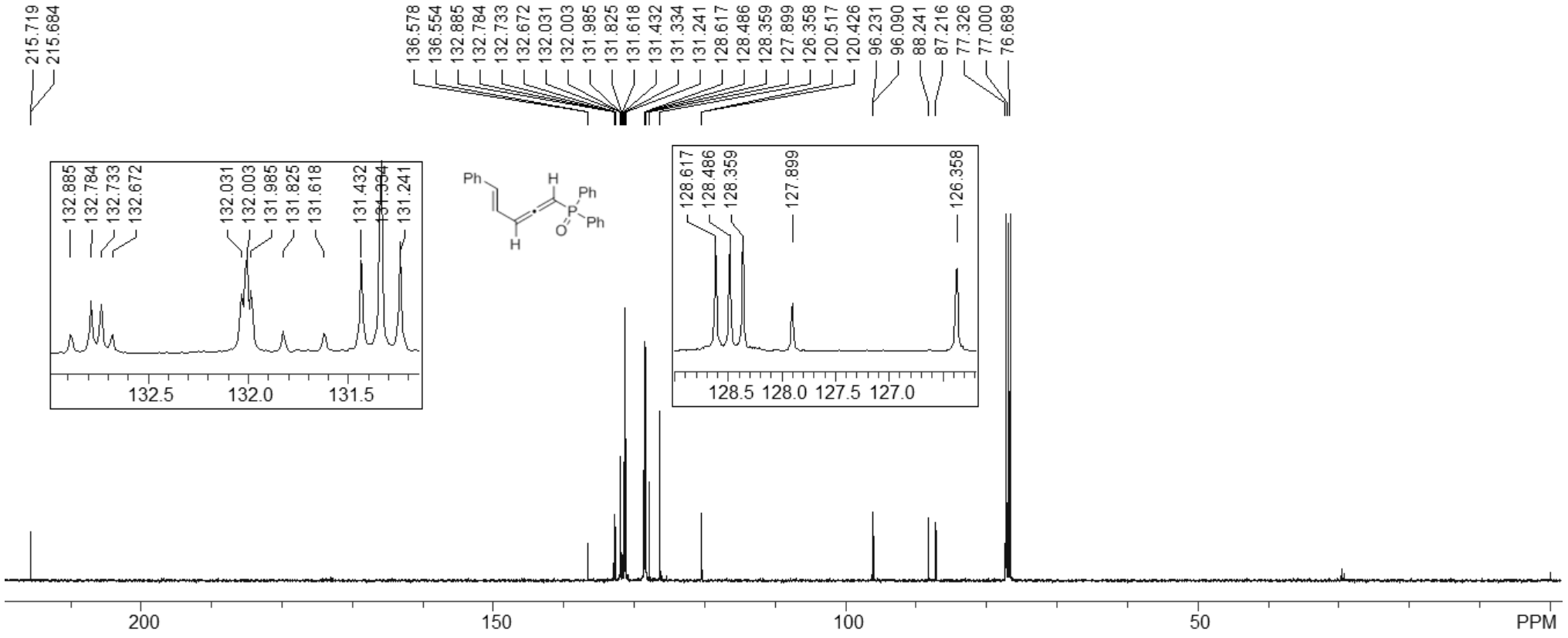
*^{1}H NMR spectrum of (E)-diphenyl(5-phenylpenta-1,2,4-trien-1-yl)phosphine oxide (**5f**)*

$CDCl_3$, 400MHz



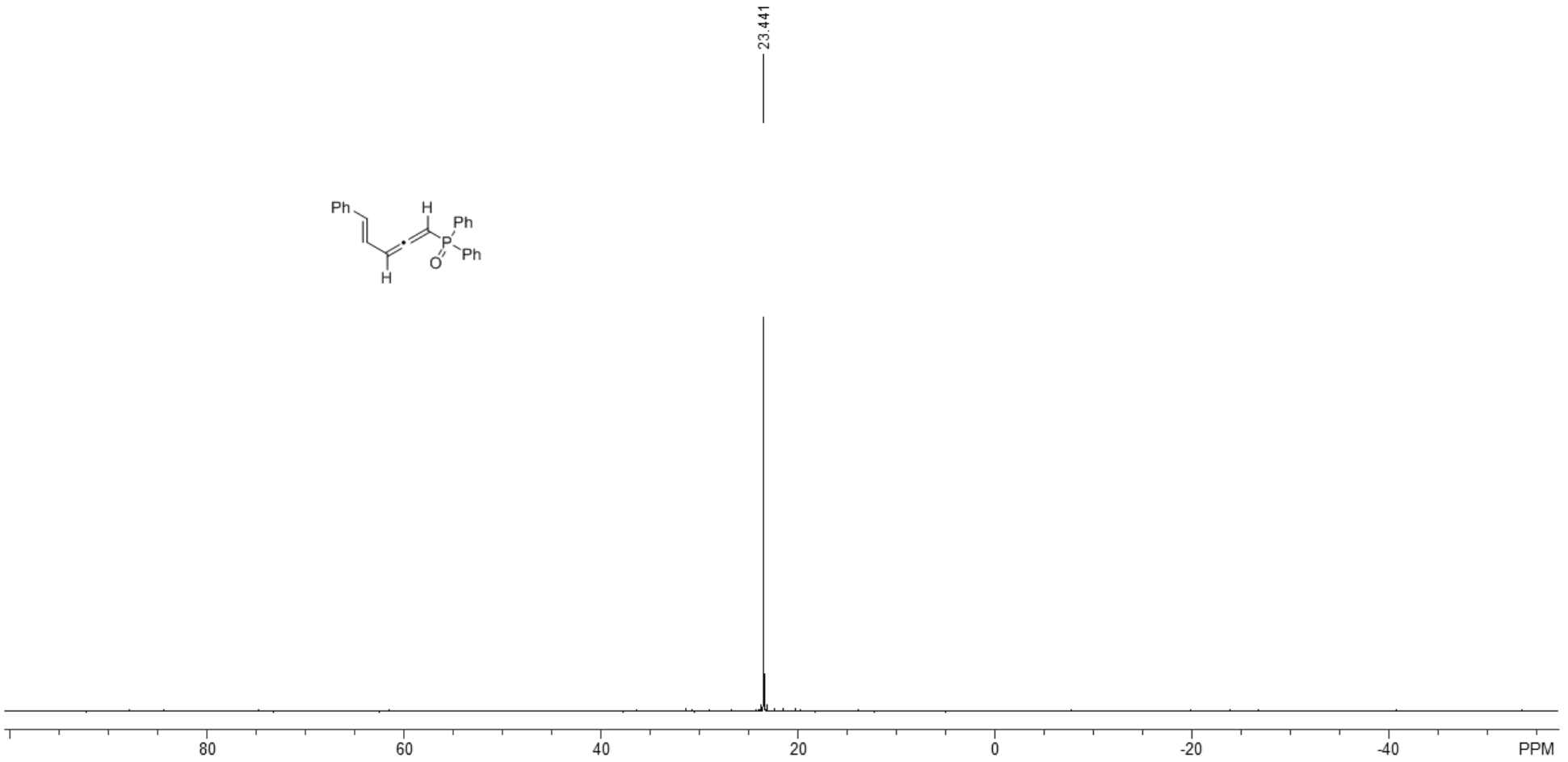
*^{13}C NMR spectrum of (E)-diphenyl(5-phenylpenta-1,2,4-trien-1-yl)phosphine oxide (**5f**)*

$CDCl_3$, 100MHz



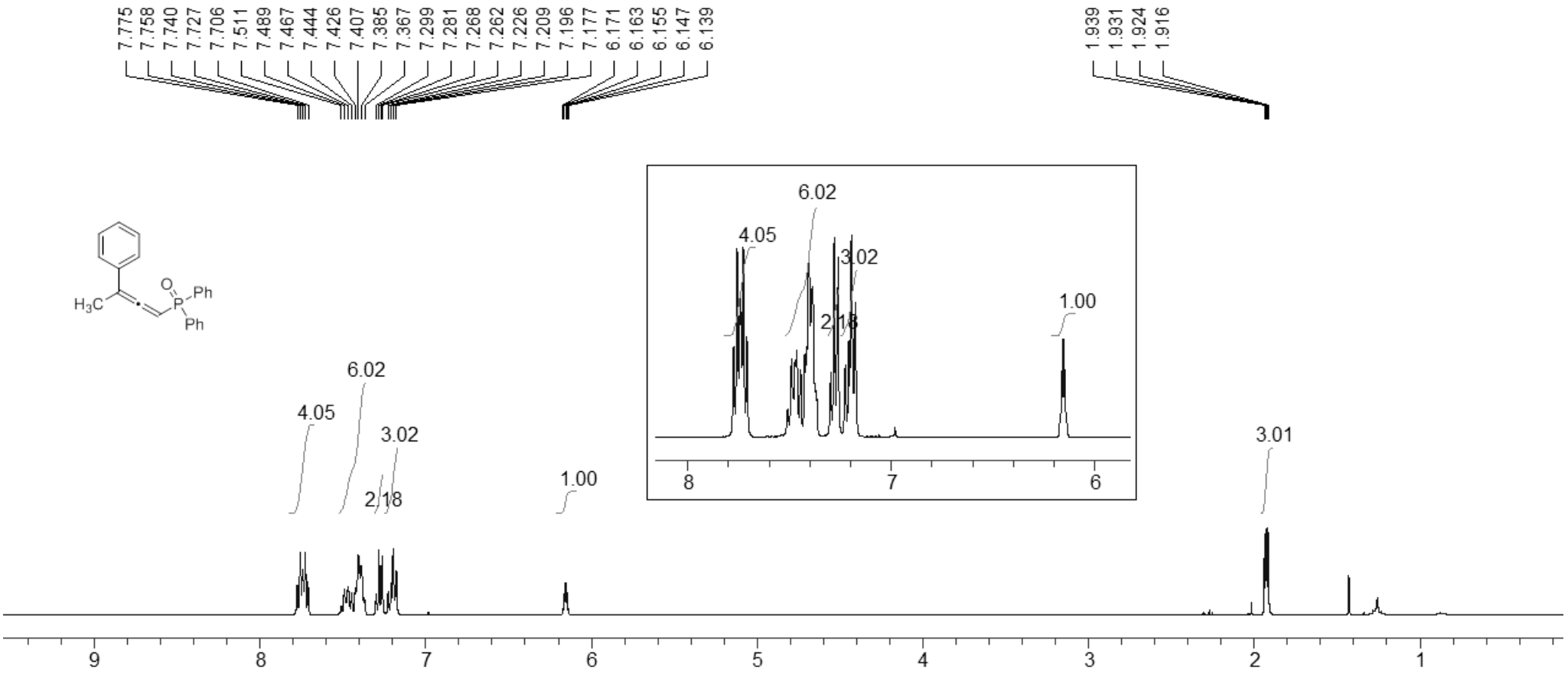
*^{31}P NMR spectrum of (E)-diphenyl(5-phenylpenta-1,2,4-trien-1-yl)phosphine oxide (**5f**)*

$CDCl_3$,162MHz



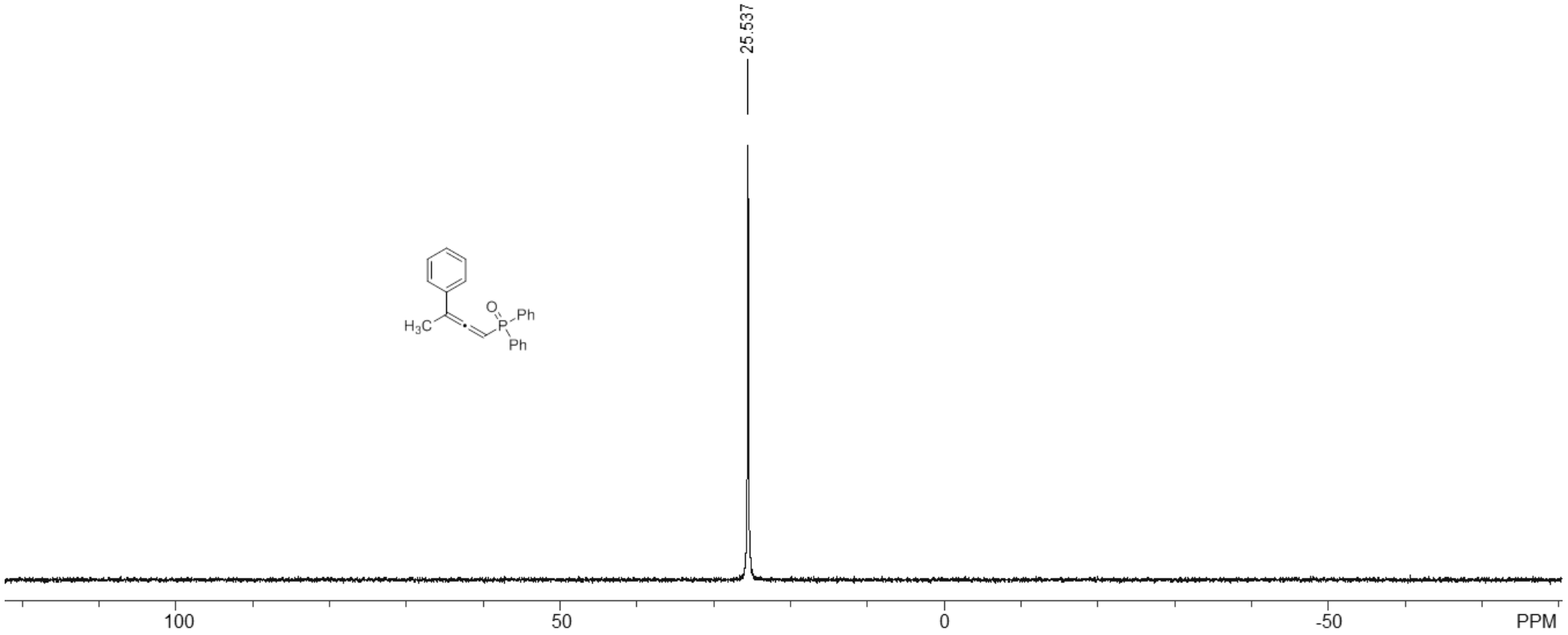
*^{1}H NMR spectrum of diphenyl(3-phenylbuta-1,2-dien-1-yl)phosphine oxide (**5g**)*

$CDCl_3$, 400MHz



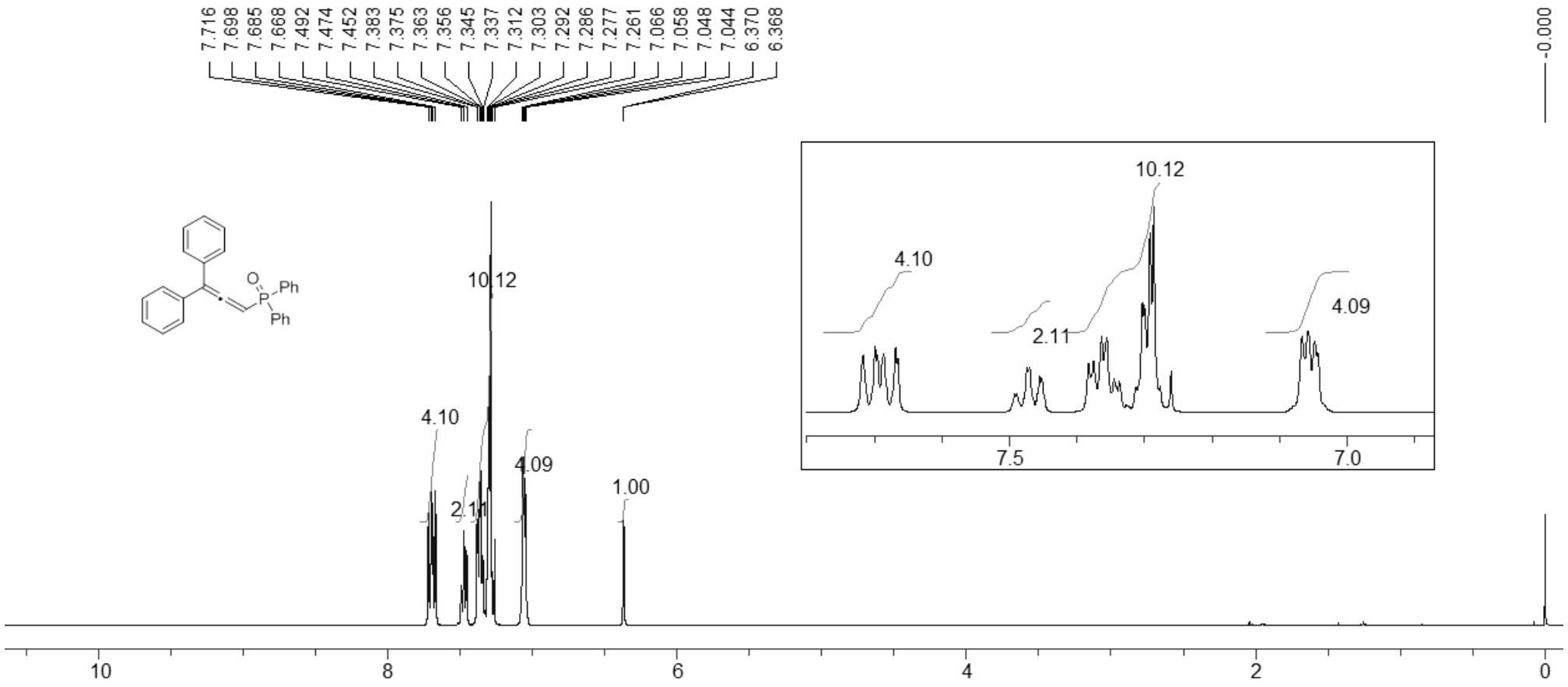
*^{31}P NMR spectrum of diphenyl(3-phenylbuta-1,2-dien-1-yl)phosphine oxide (**5g**)*

$CDCl_3$, 162MHz



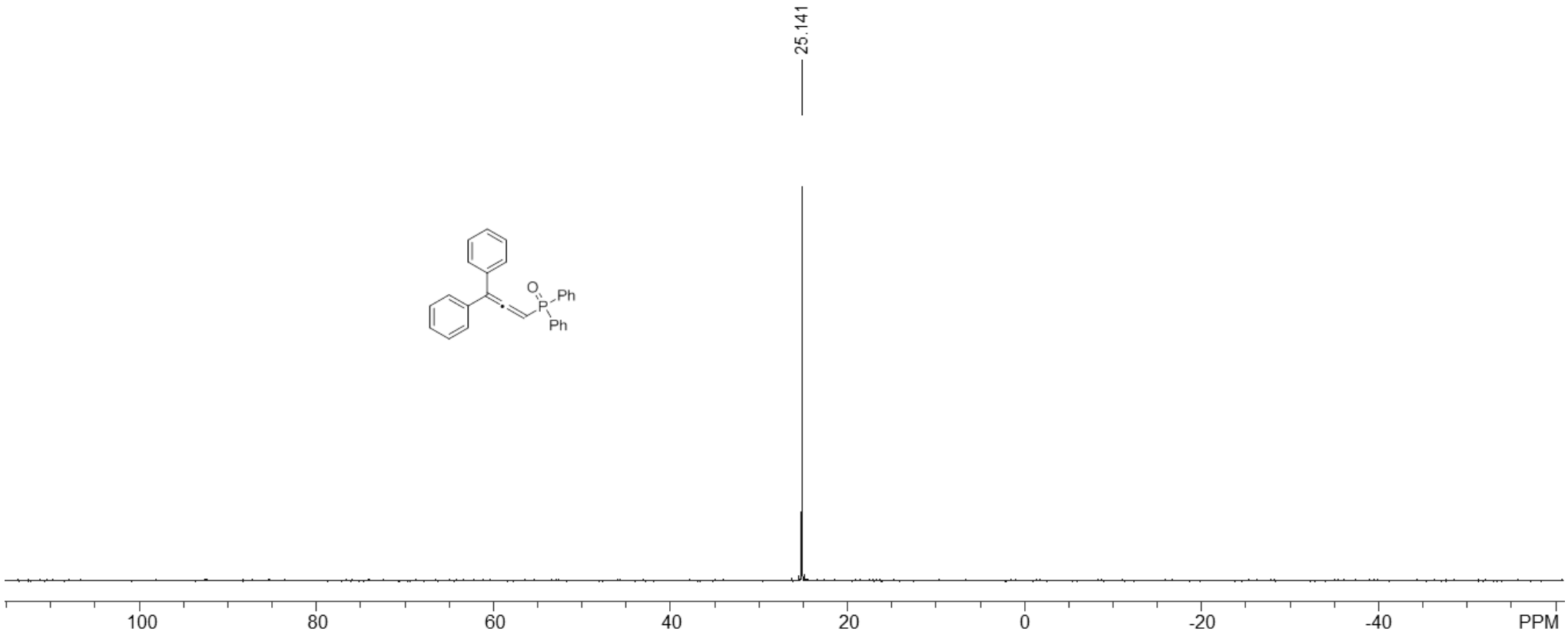
*[1]H NMR spectrum of (3,3-diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (***5h***)*

$CDCl_3$, 400MHz



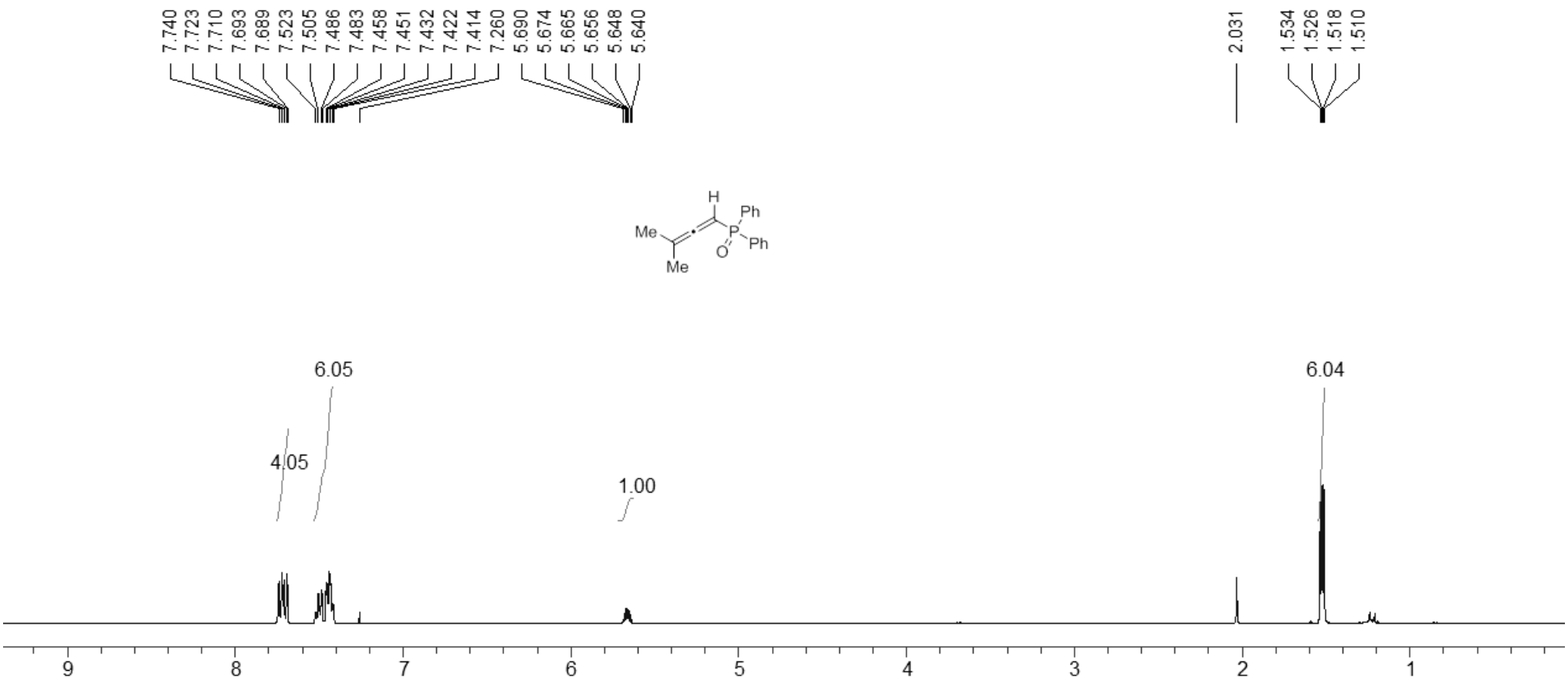
*^{31}P NMR spectrum of (3,3-diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5h**)*

$CDCl_3$, 162MHz



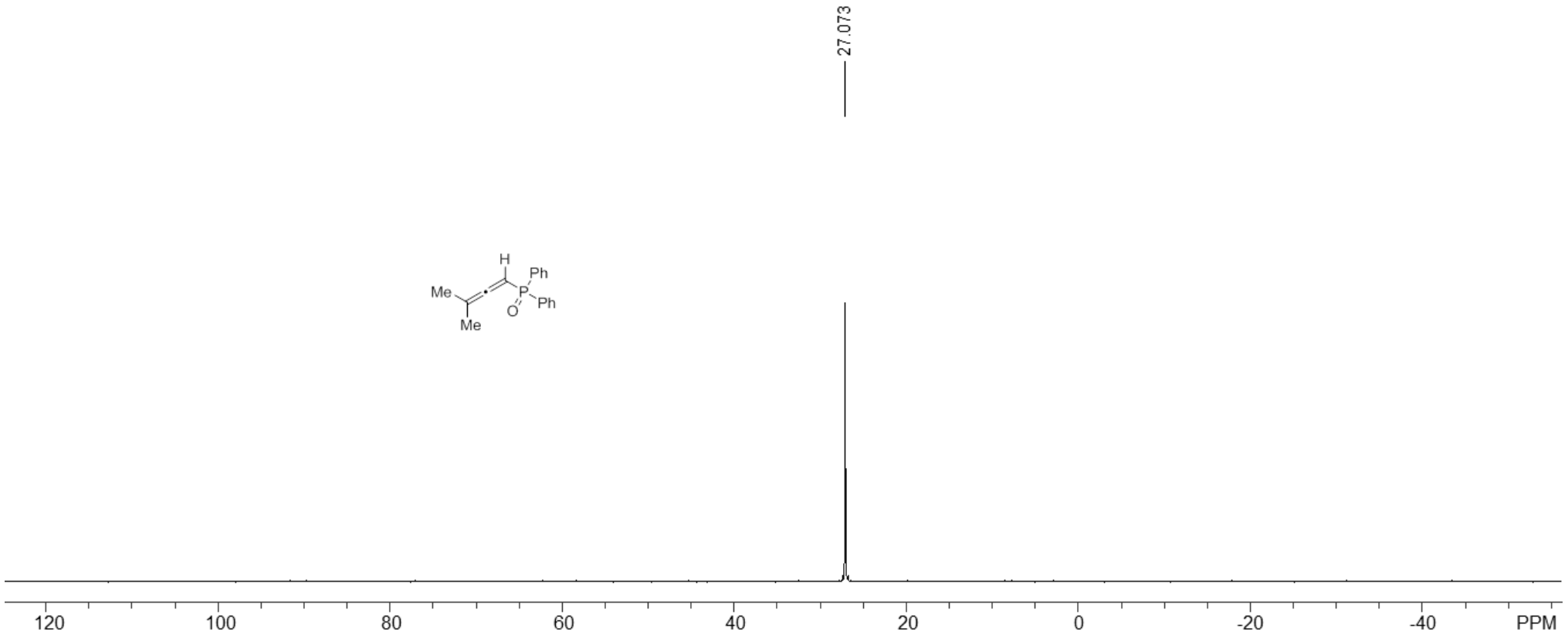
*[1]H NMR spectrum of (3-methylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**5i**)*

$CDCl_3$, 400MHz



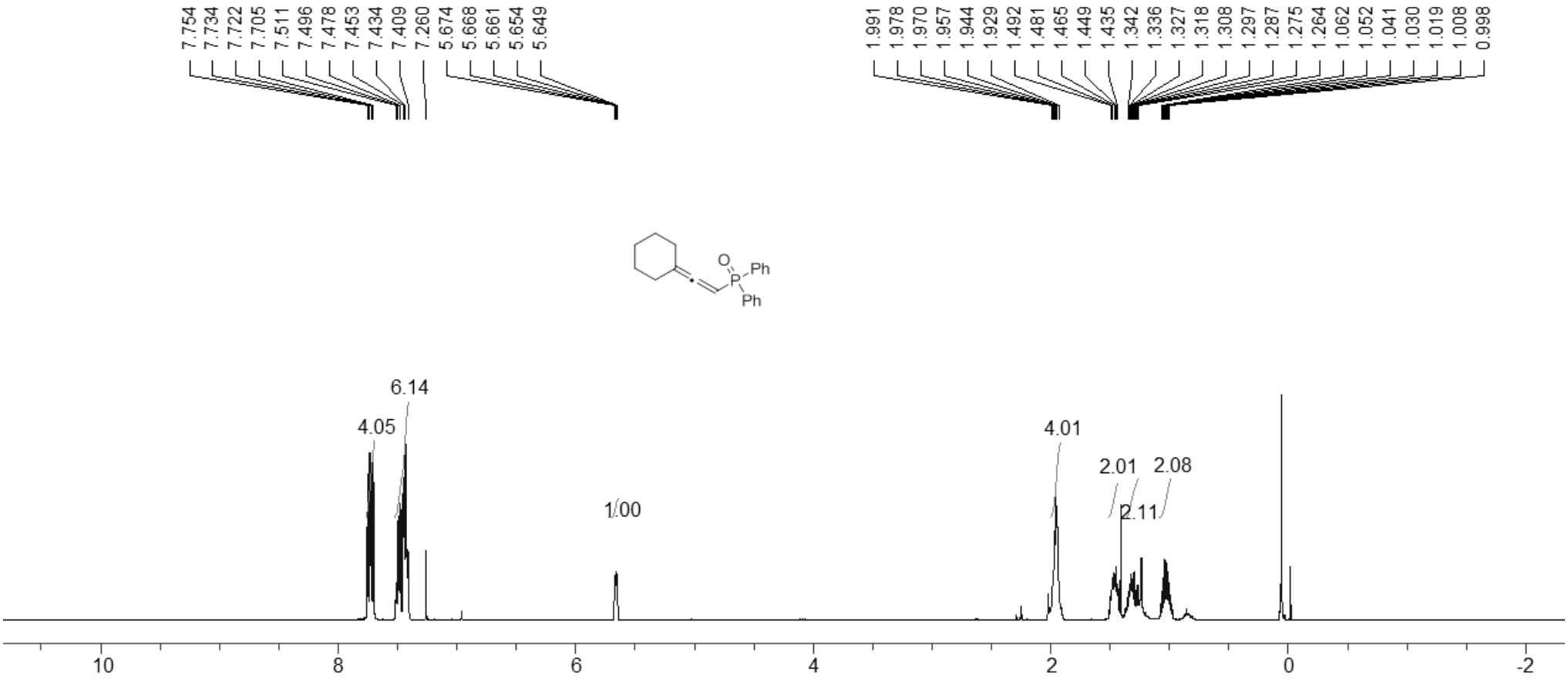
*^{31}P NMR spectrum of (3-methylbuta-1,2-dien-1-yl)diphenylphosphine oxide (**5i**)*

$CDCl_3$, 162MHz



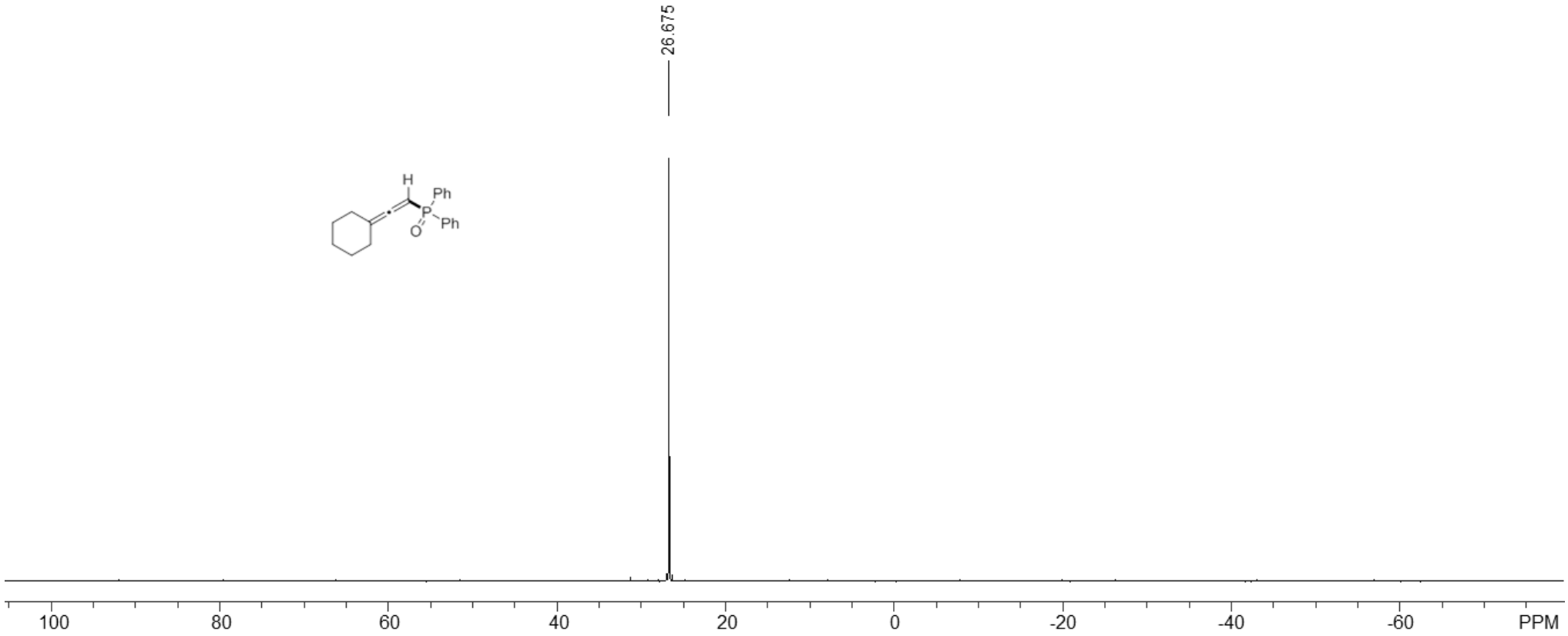
*[1]H NMR spectrum of (2-cyclohexylidenevinyl)diphenylphosphine oxide (**5j**)*

$CDCl_3$, 400MHz



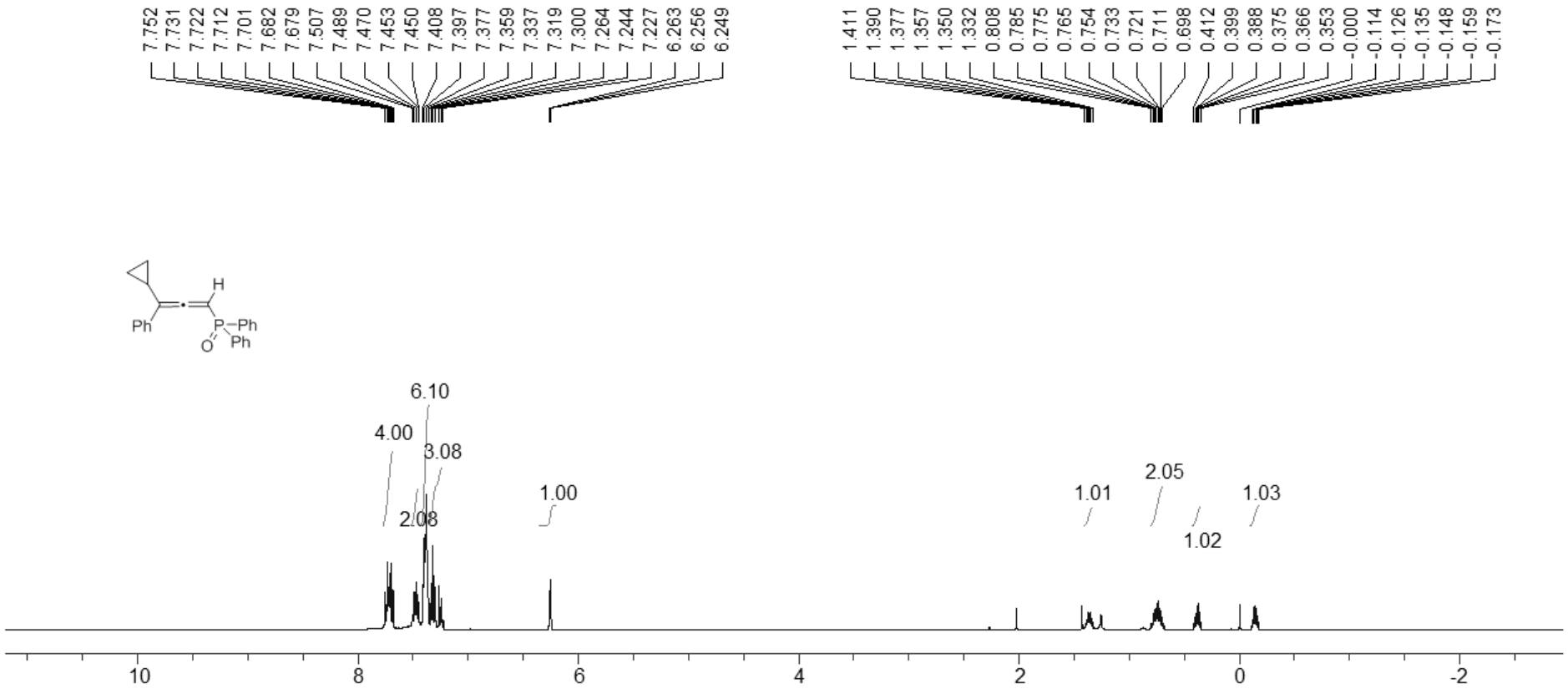
*^{31}P NMR spectrum of (2-cyclohexylidenevinyl)diphenylphosphine oxide (**5j**)*

$CDCl_3$, 162MHz



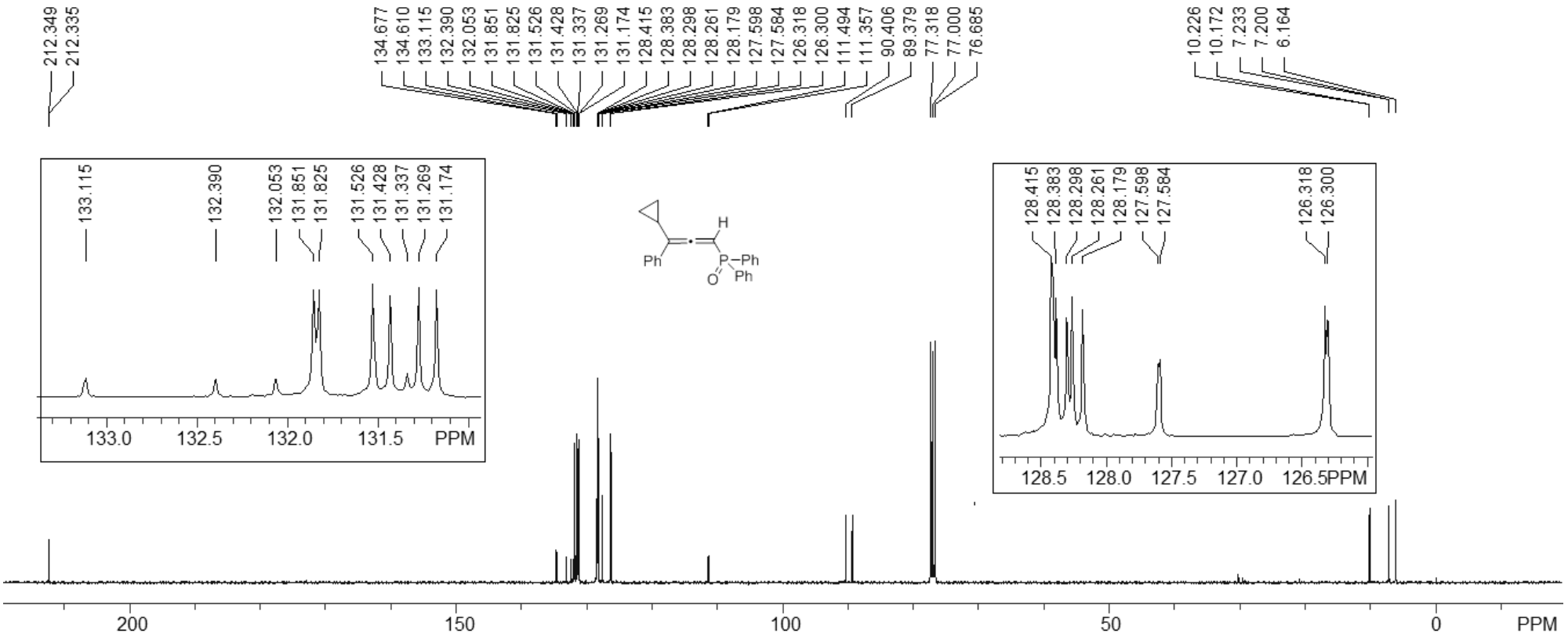
*[1]H NMR spectrum of (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (***5k***)*

$CDCl_3$, 400 MHz



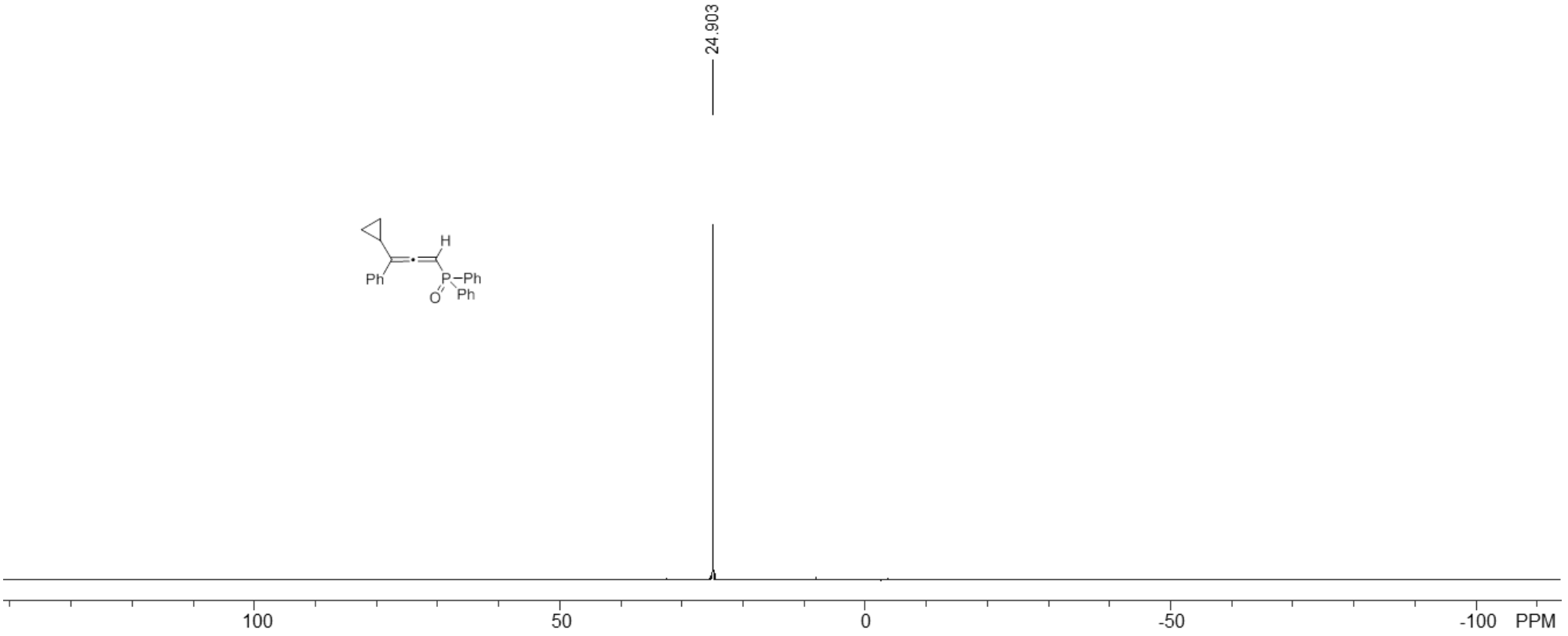
*^{13}C NMR spectrum of (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5k**)*

$CDCl_3$, 100 MHz



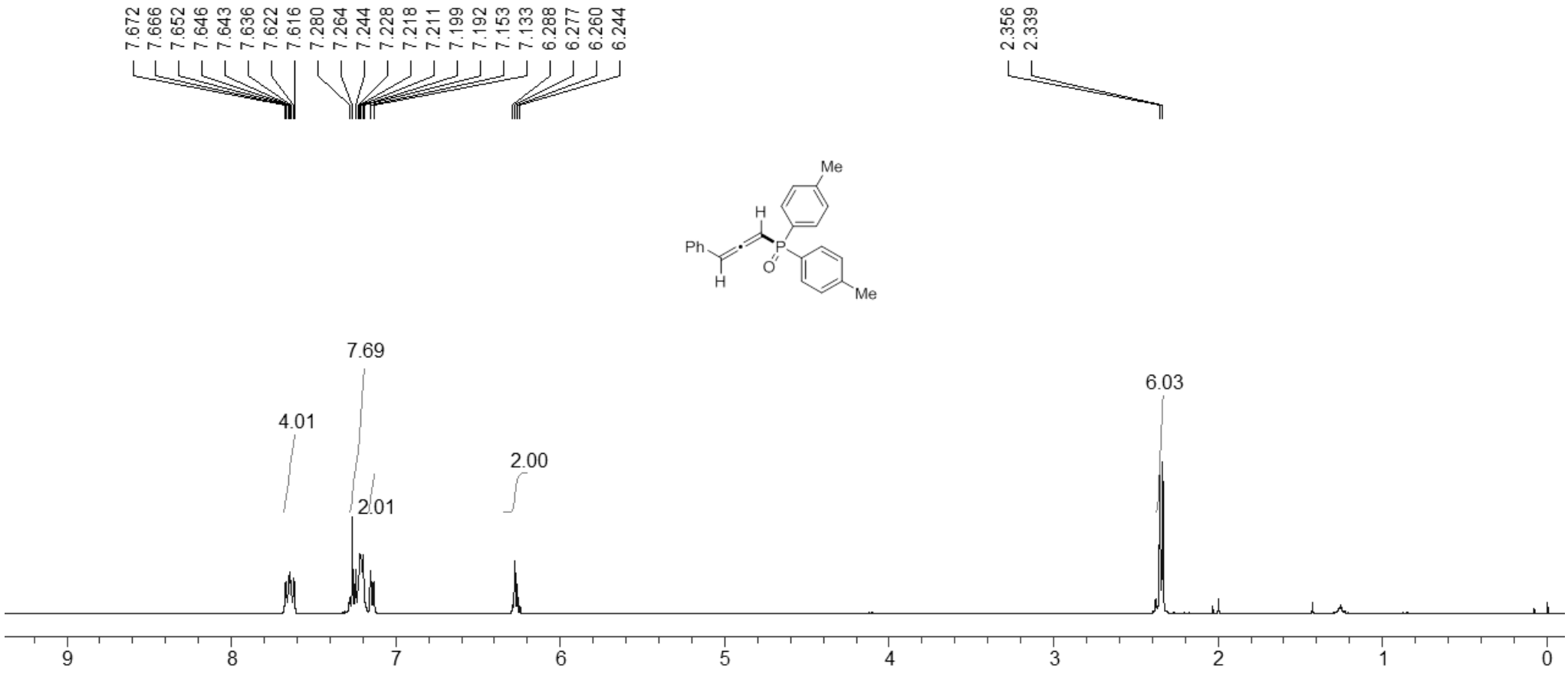
*^{31}P NMR spectrum of (3-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (**5k**)*

$CDCl_3$, 162MHz



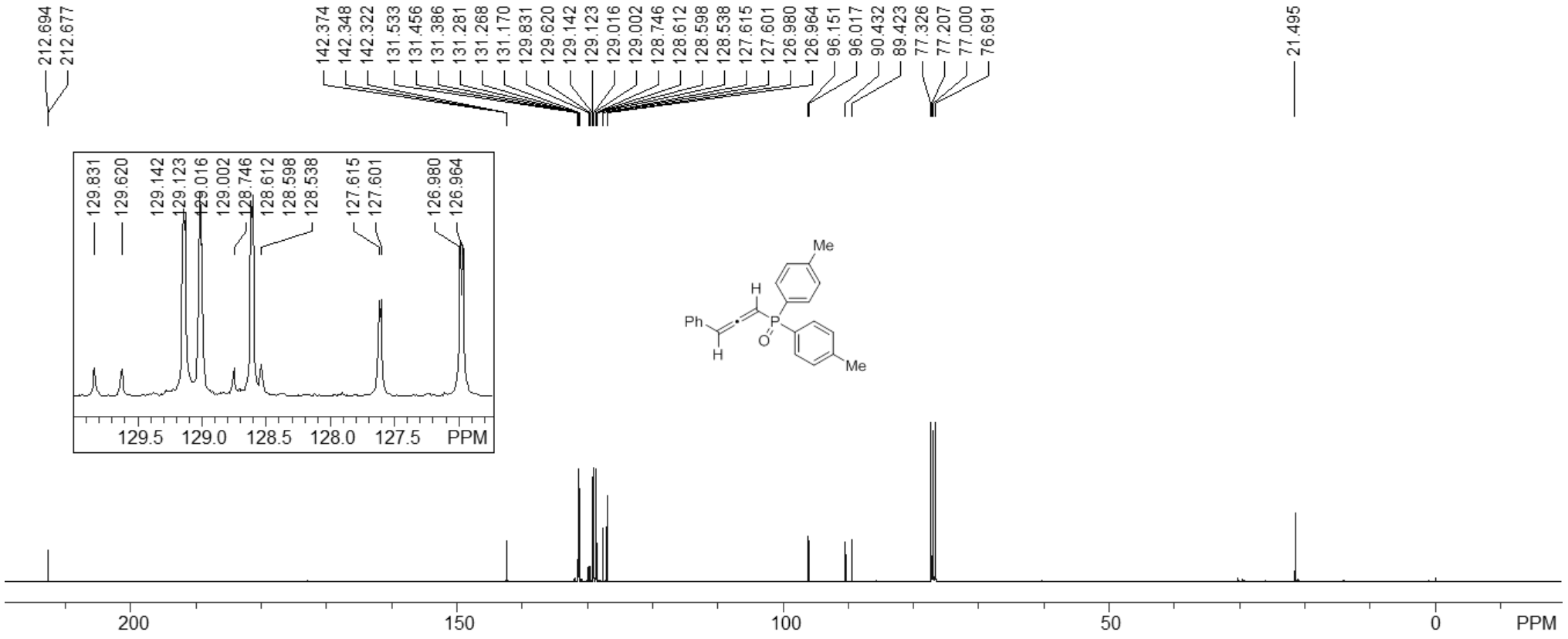
*^{1}H NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-p-tolylphosphine oxide (**5l**)*

$CDCl_3$, 400MHz



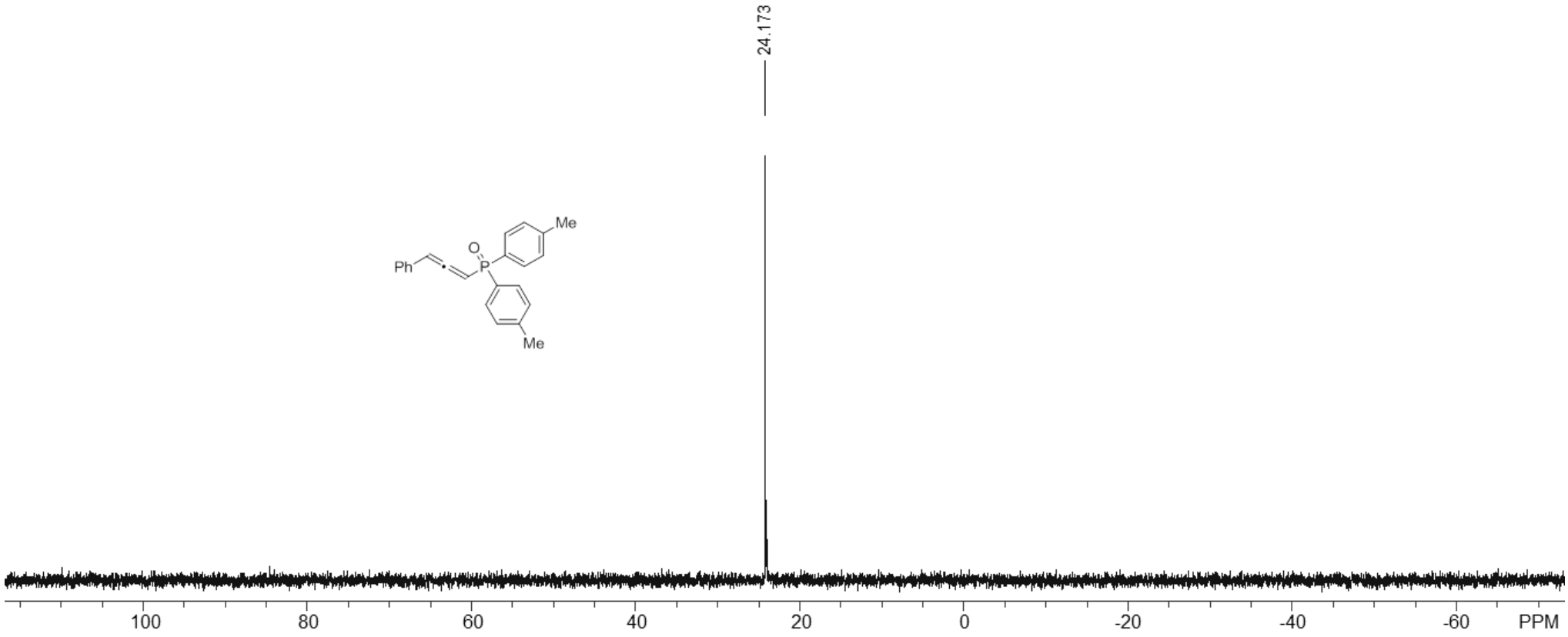
*^{13}C NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-p-tolylphosphine oxide (**5l**)*

$CDCl_3$, 100MHz



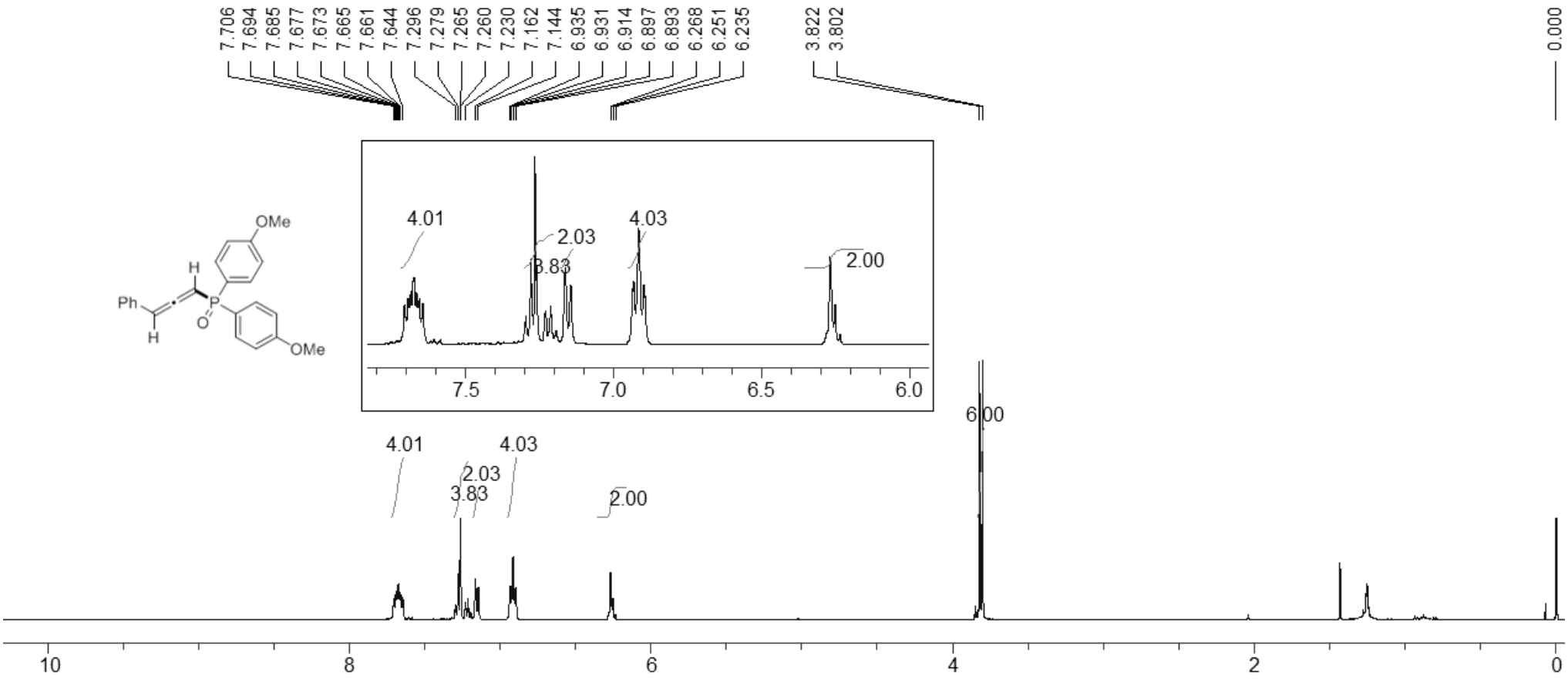
*^{31}P NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-p-tolylphosphine oxide (**5l**)*

$CDCl_3$, 162MHz



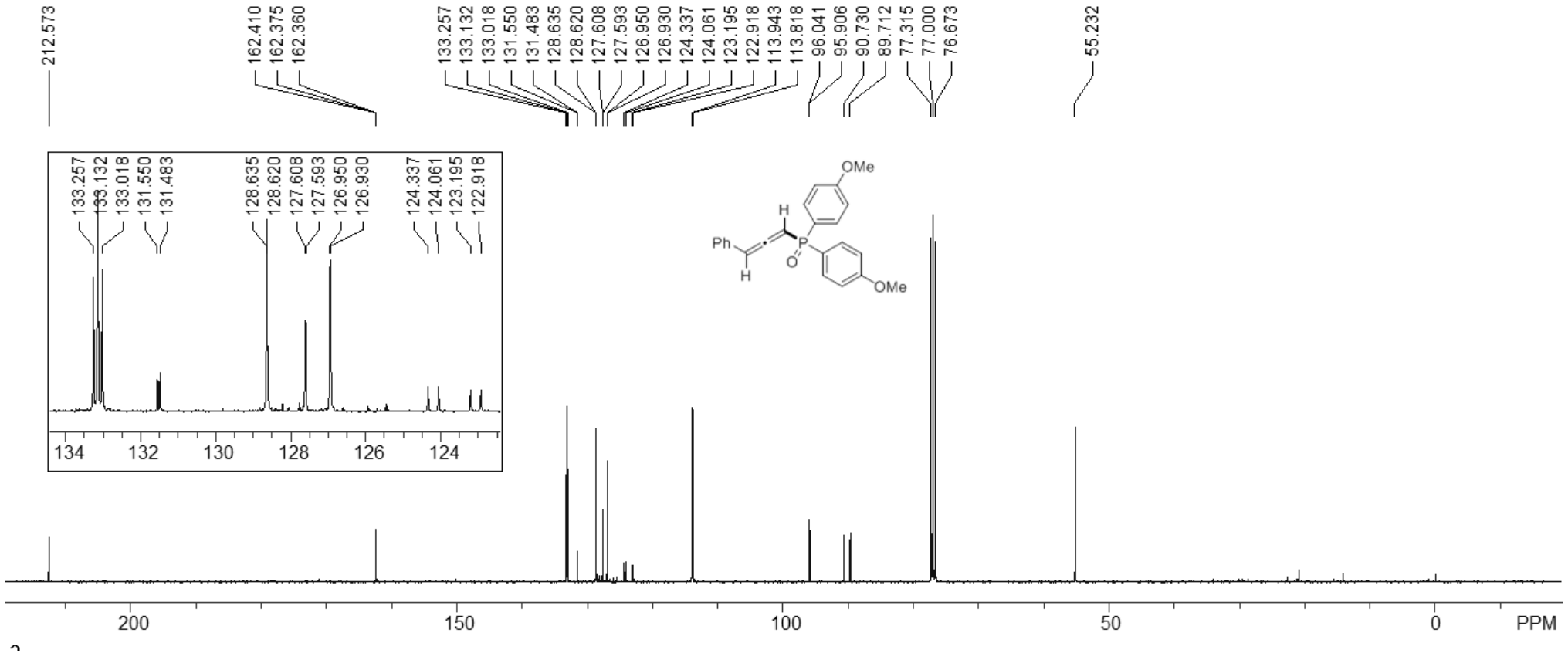
*^{1}H NMR spectrum of bis(4-methoxyphenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5m**)*

$CDCl_3$, 400MHz



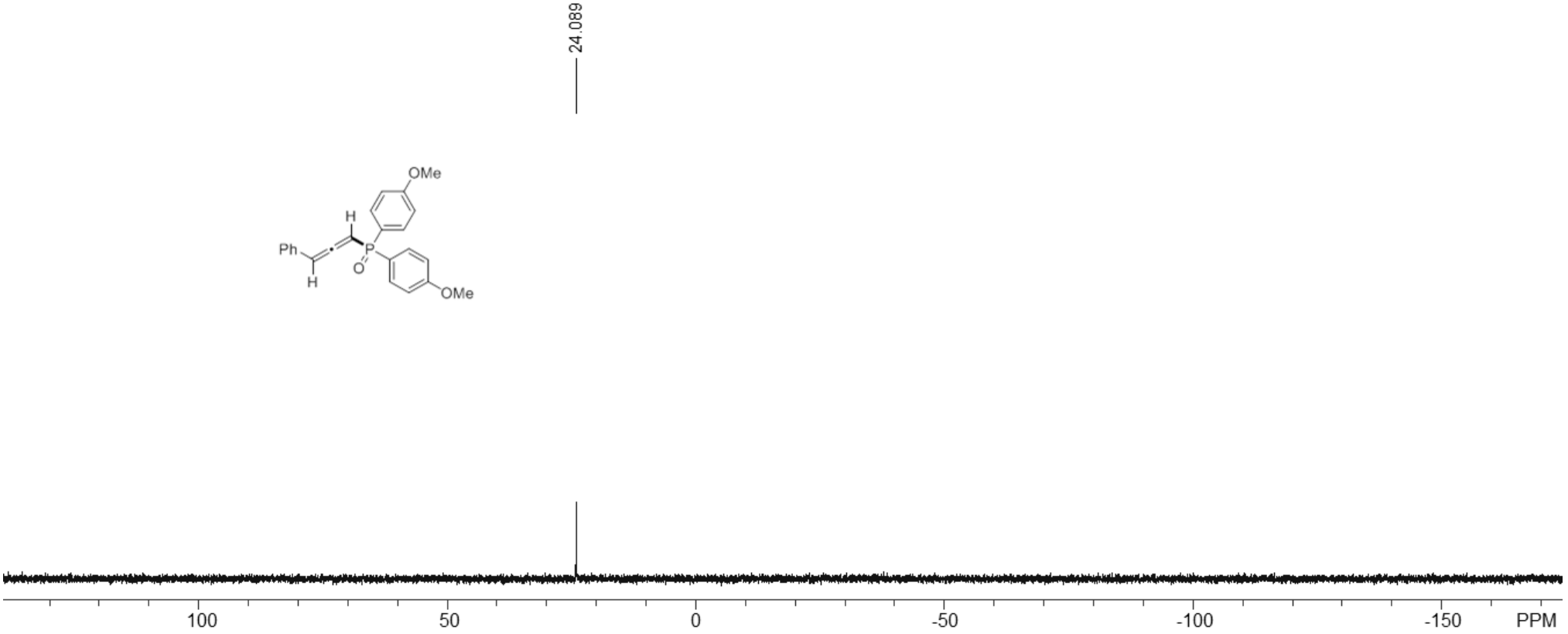
*^{13}C NMR spectrum of bis(4-methoxyphenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5m**)*

$CDCl_3$, 100MHz



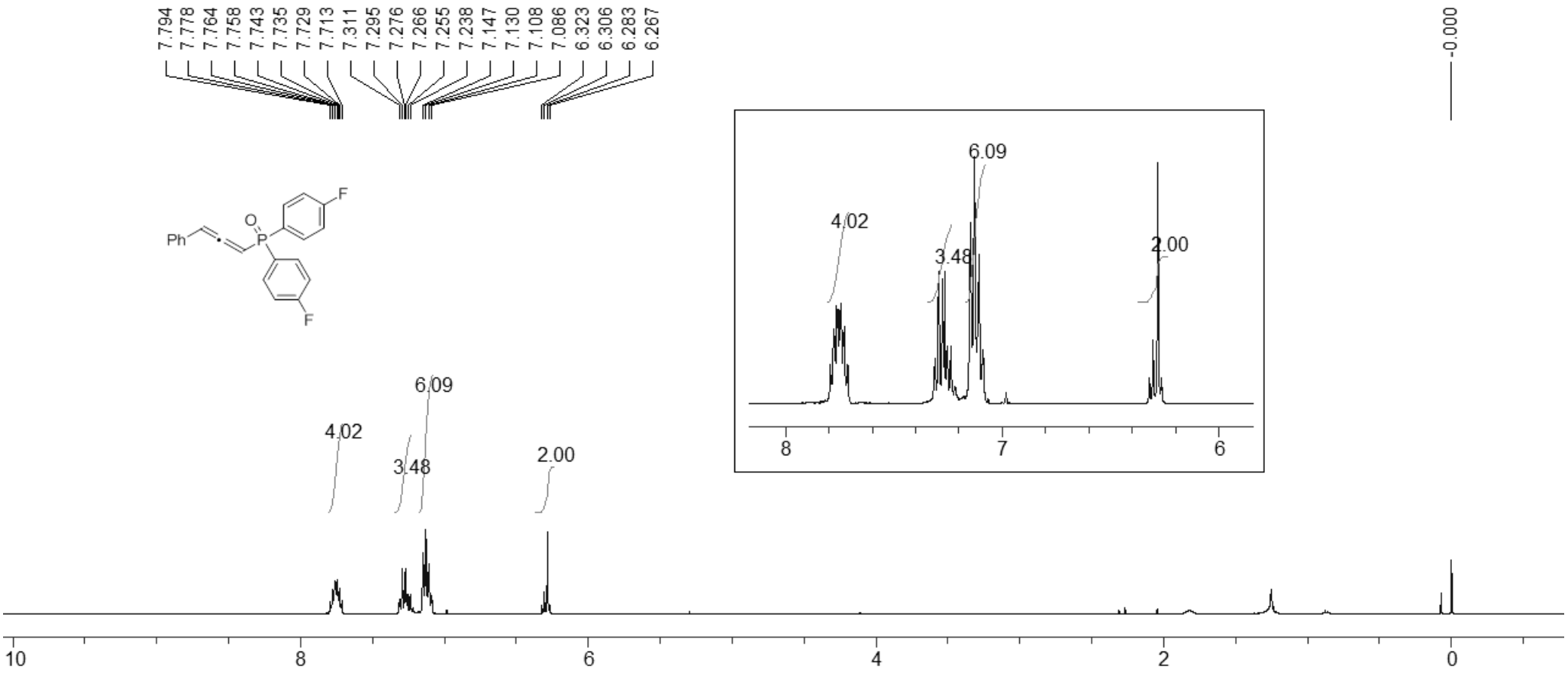
*^{31}P NMR spectrum of bis(4-methoxyphenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5m**)*

$CDCl_3$, 162MHz



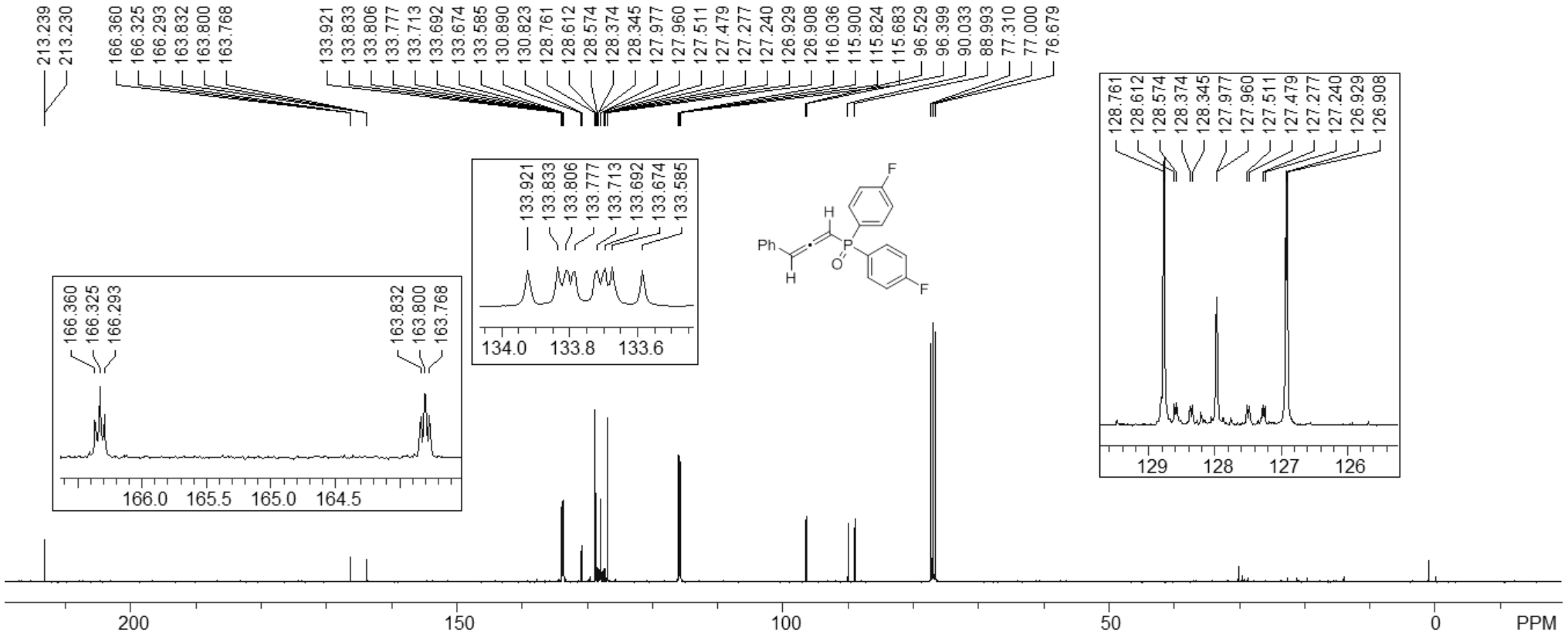
*[1]H NMR spectrum of bis(4-fluorophenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5n**)*

$CDCl_3$, 400MHz



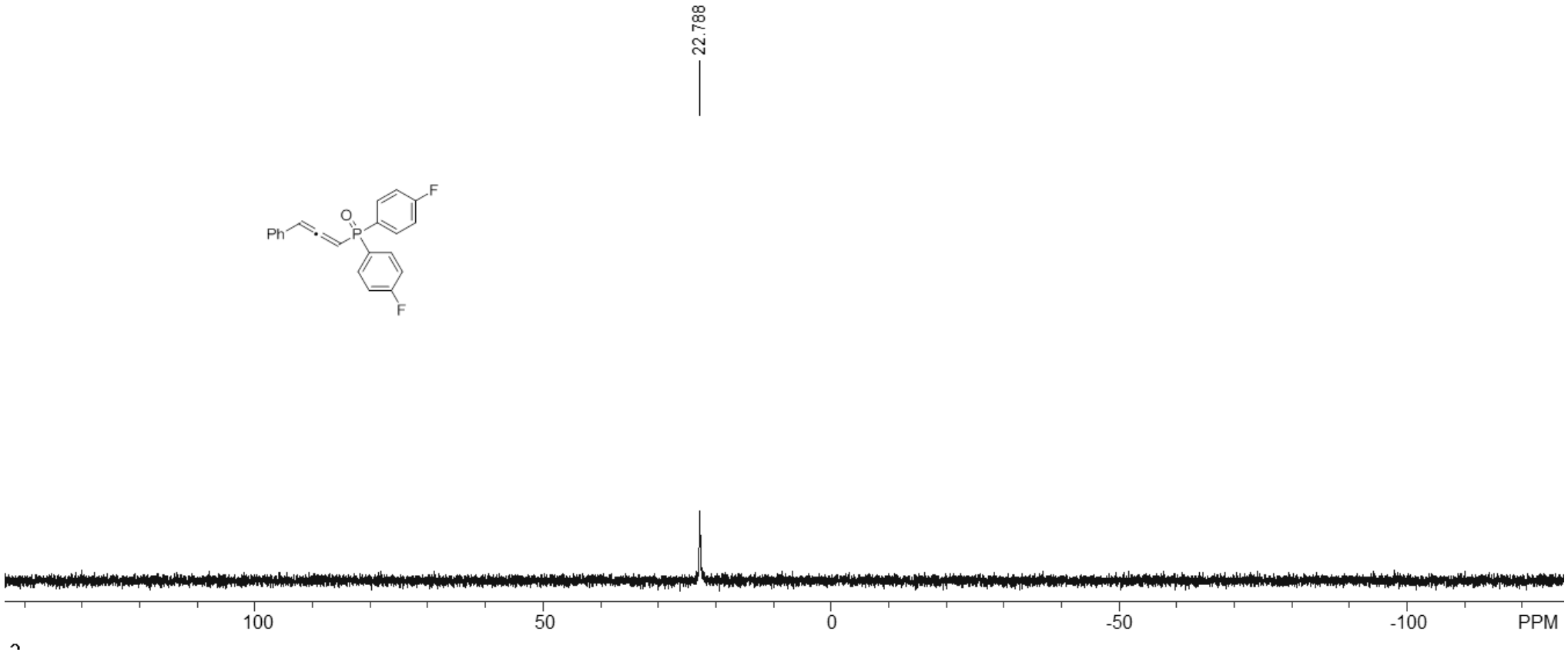
*^{13}C NMR spectrum of bis(4-fluorophenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5n**)*

$CDCl_3$, 100MHz



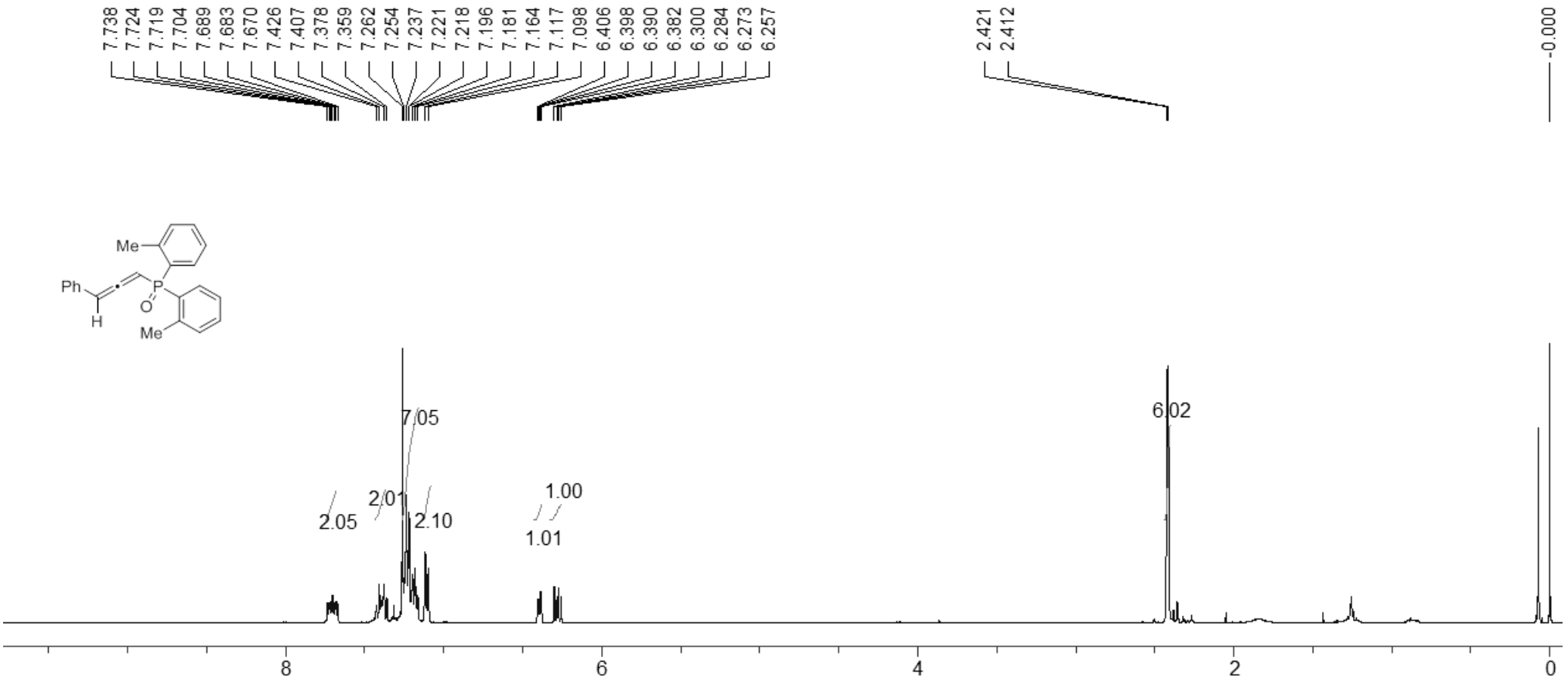
*^{31}P NMR spectrum of bis(4-fluorophenyl)(3-phenylpropa-1,2-dien-1-yl)phosphine oxide (**5n**)*

$CDCl_3$, 162MHz



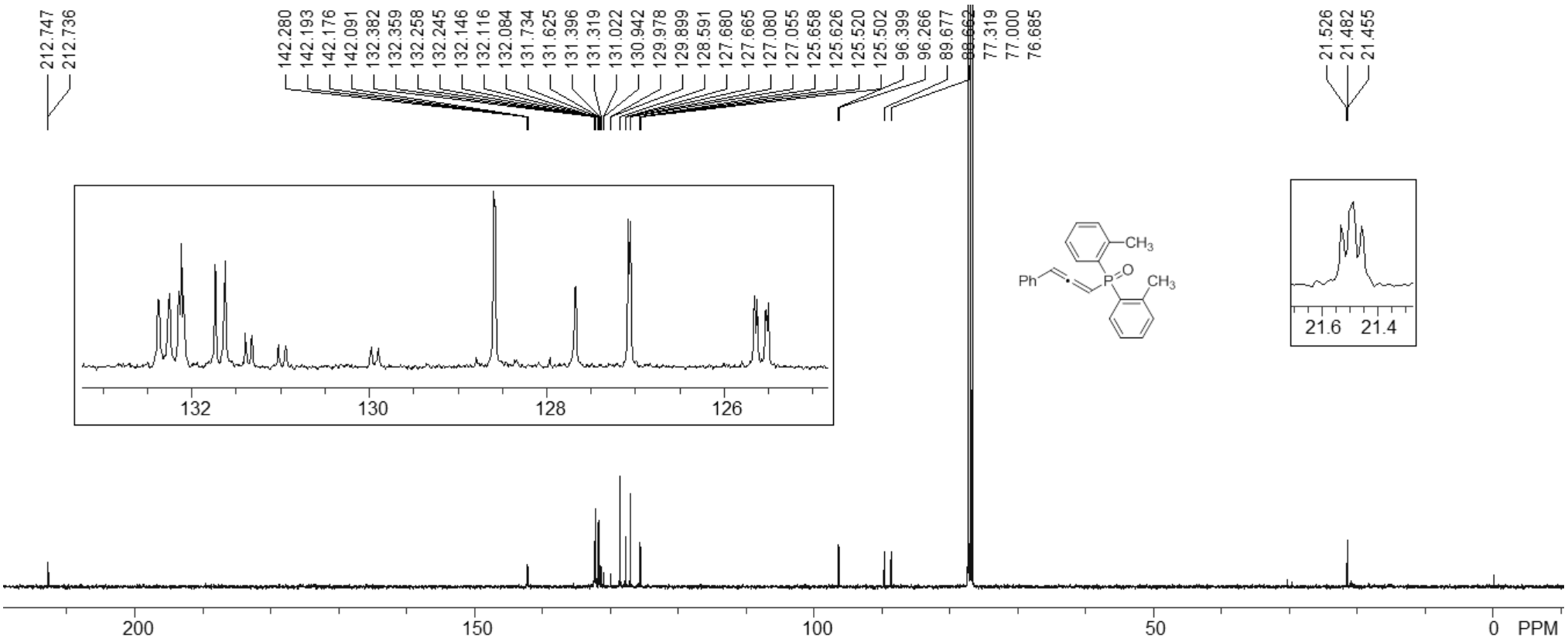
*^{1}H NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-o-tolylphosphine oxide (**5o**)*

$CDCl_3$, 400MHz



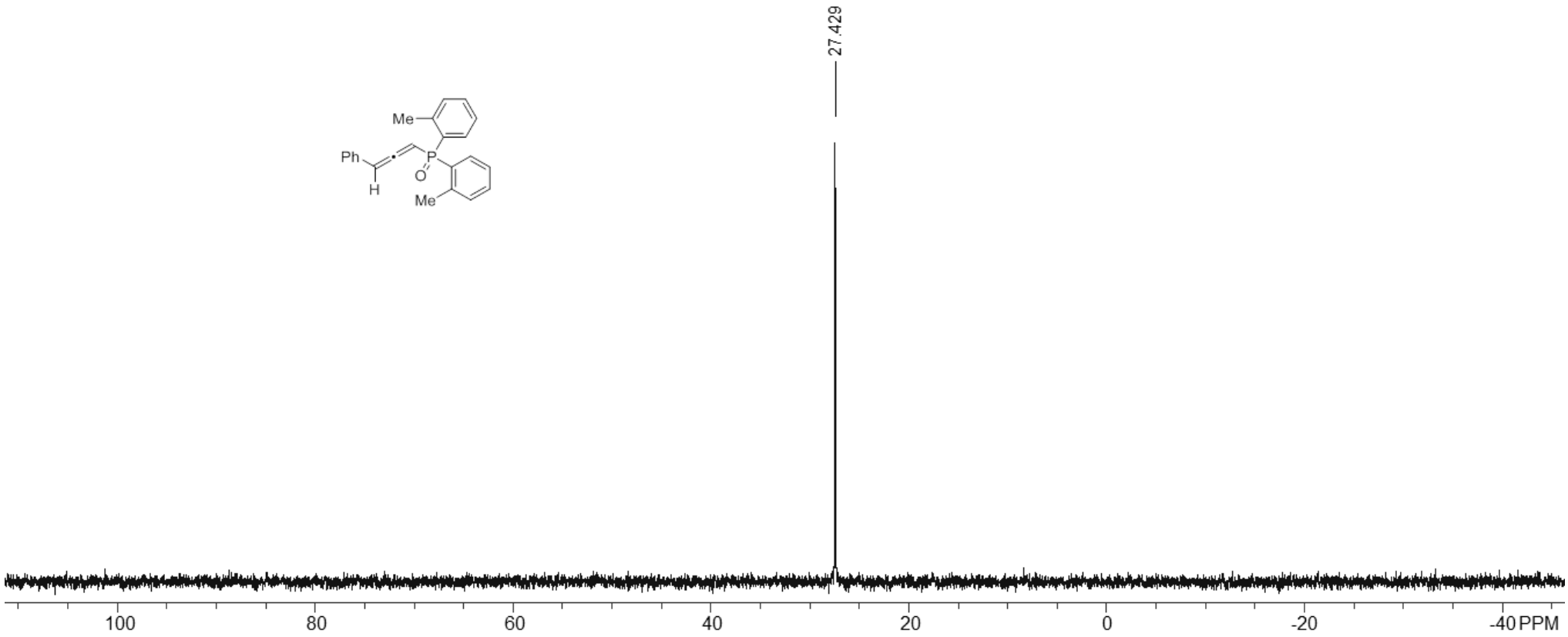
*^{13}C NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-o-tolylphosphine oxide (**5o**)*

$CDCl_3$, 100MHz



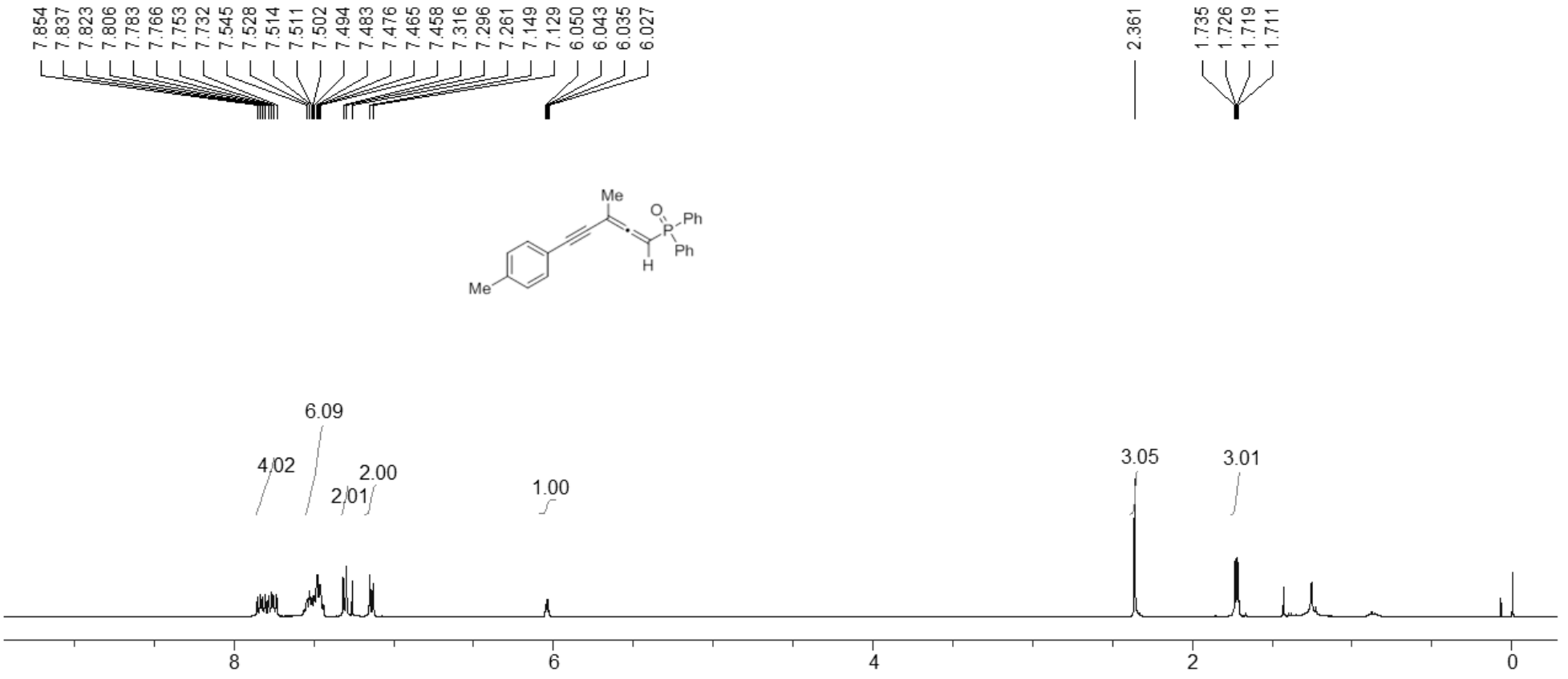
*^{31}P NMR spectrum of (3-phenylpropa-1,2-dien-1-yl)di-o-tolylphosphine oxide (**5o**)*

$CDCl_3$, 162MHz



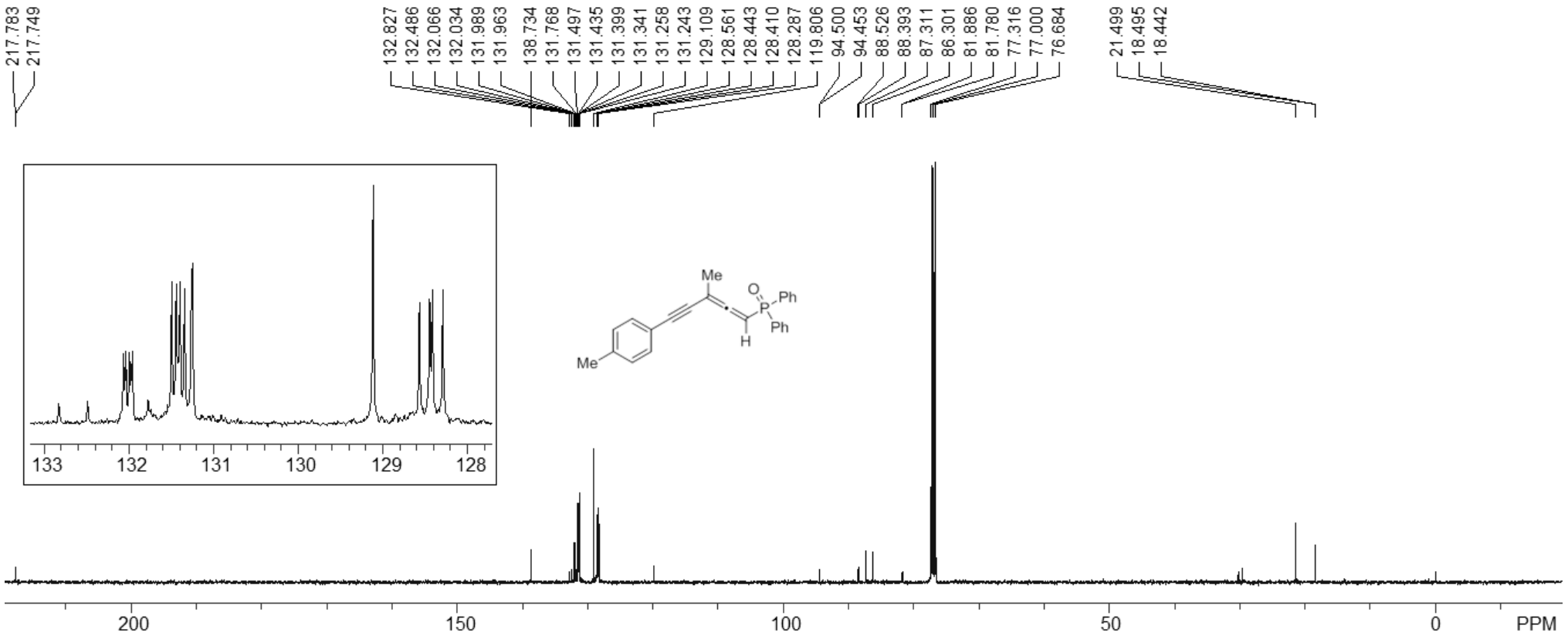
*[1]H NMR spectrum of (3-methyl-5-(p-tolyl)penta-1,2-dien-4-yn-1-yl)diphenylphosphine oxide (**5p**)*

$CDCl_3$, 400 MHz



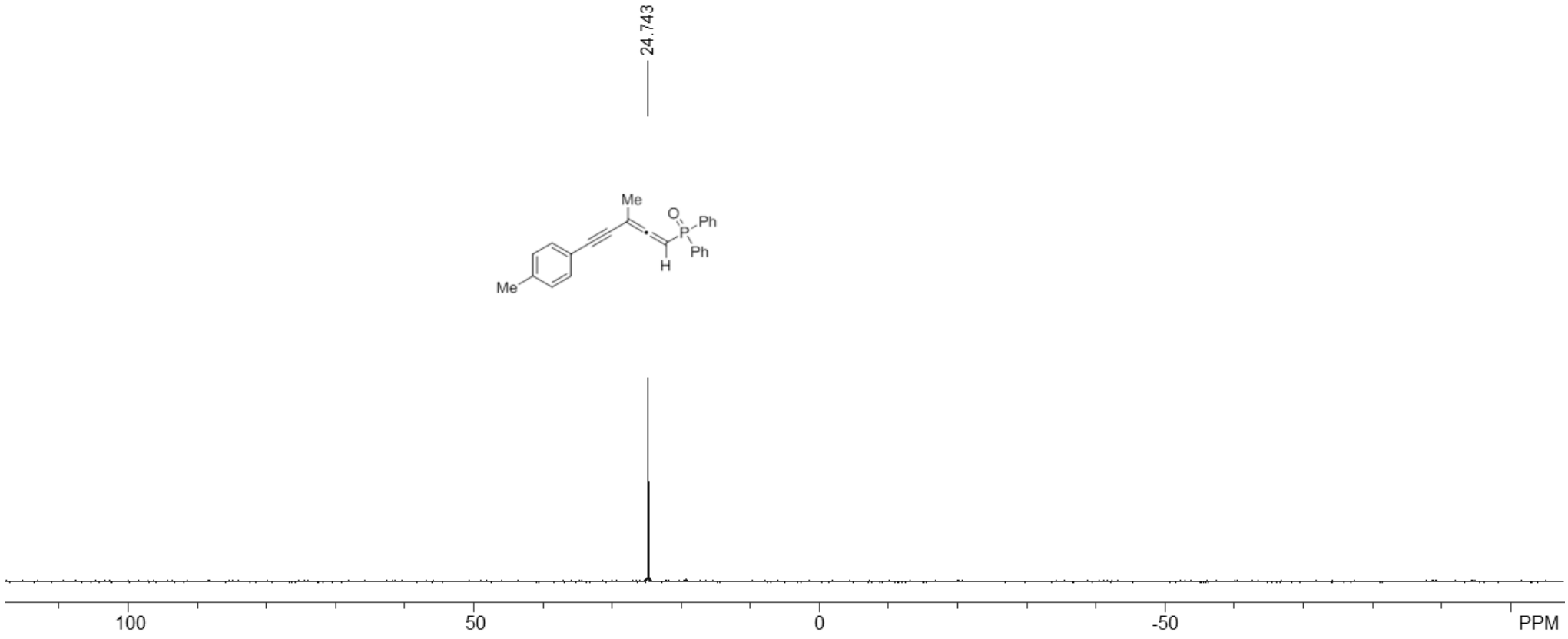
*^{13}C NMR spectrum of (3-methyl-5-(p-tolyl)penta-1,2-dien-4-yn-1-yl)diphenylphosphine oxide (**5p**)*

$CDCl_3$, 100 MHz



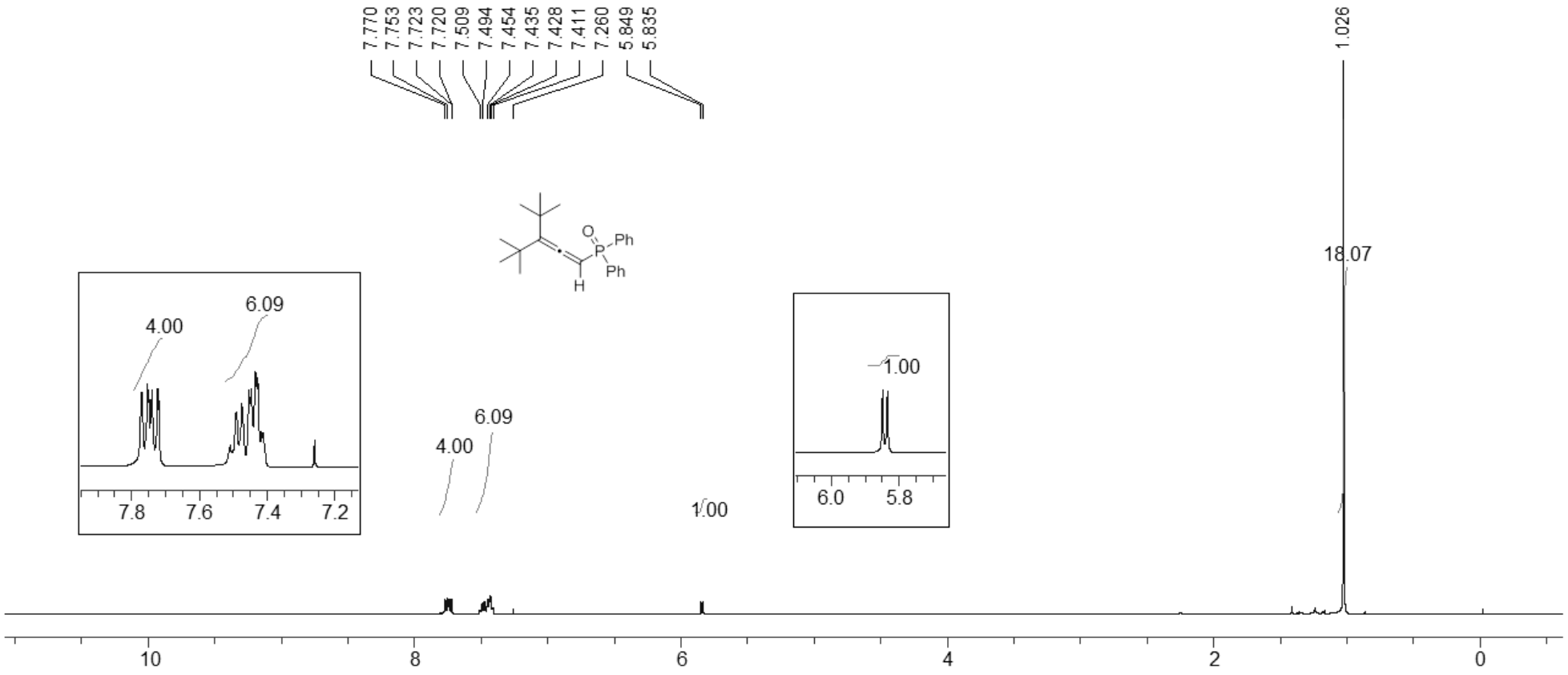
*^{31}P NMR spectrum of (3-methyl-5-(p-tolyl)penta-1,2-dien-4-yn-1-yl)diphenylphosphine oxide (**5p**)*

$CDCl_3$, 162MHz



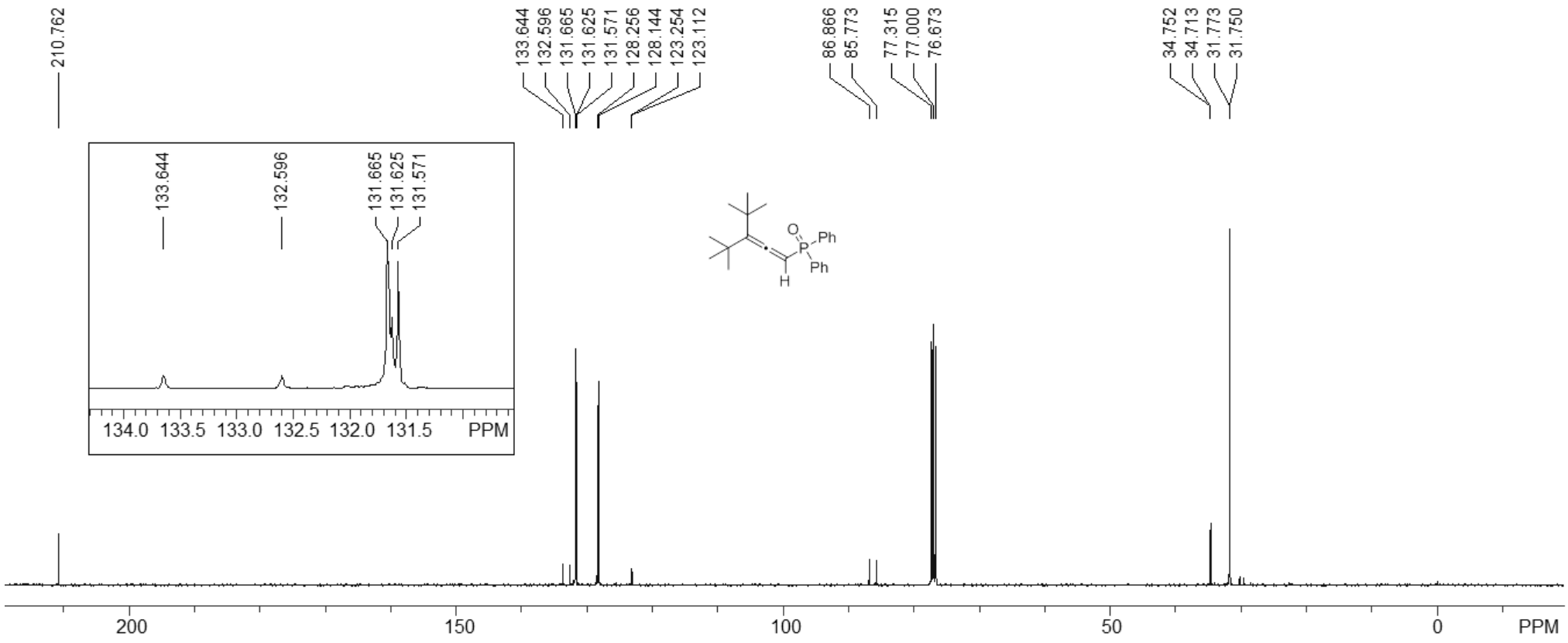
*^{1}H NMR spectrum of (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**5q**)*

$CDCl_3$, 400MHz



*[13] CNMR spectrum of (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**5q**)*

$CDCl_3$, 162MHz



*^{31}P NMR spectrum of (3-(tert-butyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (**5q**)*

$CDCl_3$, 162MHz