Electronic Supplementary Information

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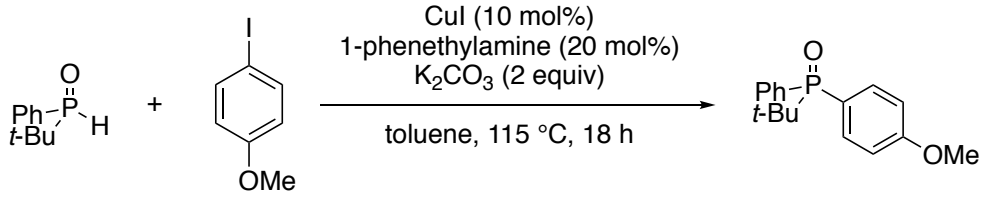
1. General

^{1}H NMR spectra (400 or 500 MHz) were recorded on a Bruker Avance 400 or 500 spectrometer in $CDCl_3$ [using TMS (for ^{1}H, $\delta = 0.00$) as internal standard]. ^{13}C NMR spectra (100 or 125 MHz) were recorded on a Bruker Avance 400 or 500 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as internal standard]. ^{19}F NMR spectra (376 MHz) were recorded on a Bruker AvanceIII 400 spectrometer in $CDCl_3$. ^{31}P NMR spectra (162 or 202 MHz) were recorded on a Bruker Avance 400 or 500 spectrometer in $CDCl_3$. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. High-resolution mass spectra were obtained with a Waters Q-Tof Premier mass spectrometer. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), acetonitrile (MeCN) and diethyl ether (Et_2O) were taken from a solvent purification system (PS-400-5, innovative technology Inc.). NaH (60% dispersion in mineral oil), NaI and LiI were purchased from Sigma-Aldrich, Inc. Due to moisture sensitivity of NaH, it was consistently handled under an Ar atmosphere in a glovebox or with Schlenk techniques under an inert (N_2 or Ar) atmosphere. NaI and LiI were dried over P_2O_5 under reduced pressure at 60 °C and 120 °C, respectively.[1] Other solvents and reagents, unless otherwise noted, were commercially available and used as received.

2. Synthesis and characterization of the starting materials

Triphenylphosphine oxide (**1a**) [CAS: 791-28-6] were purchased from Strem Chemicals, Inc. and used as received. Other phosphine oxides **1b**,[2] **1c**,[3] **1d**,[2] **1e**,[4] **1f**,[5] **1g**,[6] and **1h**[7] and **7**[8] were synthesized according to the literature procedures. Their spectra data were identical to those reported.

tert-butyl(4-methoxyphenyl)(phenyl)phosphine oxide **8**



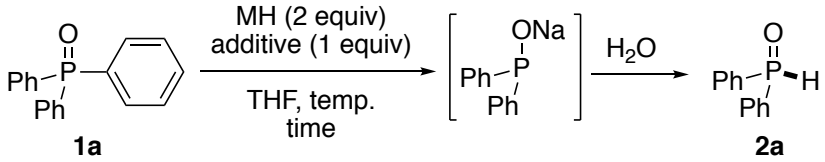
To a solution of *tert*-butyl(phenyl)phosphine oxide[9] (330.3 mg, 1.81 mmol) in toluene (2 mL) was added 4-iodoanisole (465.4 mg, 1.99 mmol), CuI (39.2 mg, 0.206 mmol), K_2CO_3 (540.5 mg, 3.91 mmol), and 1-phenethylamine (50 μL, 0.388 mmol) and the reaction mixture was

stirred at reflux temperature for 18 h. The reaction was then cooled to 23 °C and quenched with saturated aqueous NH_4Cl. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 45:55:2) to give 64% yield (332.9 mg, 1.15 mmol) of **8** as thick colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.86 (m, 4H), 7.51–7.44 (m, 3H), 6.99 (dd, J = 4.8, 2.0 Hz, 2H), 3.84 (s, 3H), 1.23 (d, J = 15.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J_{P-C} = 2.0 Hz), 133.9 (d, J_{P-C} = 9.0 Hz), 132.1 (d, J_{P-C} = 8.0 Hz), 131.6 (d, J_{P-C} = 91.0 Hz), 131.3 (d, J_{P-C} = 2.0 Hz), 128.1 (d, J_{P-C} = 11.0 Hz), 122.1 (d, J_{P-C} = 95.0 Hz), 113.8 (d, J_{P-C} = 12.0 Hz), 55.2, 33.9 (d, J_{P-C} = 71.0 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.7; ESIHRMS: Found *m/z* 289.1365; Calcd for $C_{17}H_{22}O_2P$ $[M + H]^+$ 289.1357.

3. Optimization of the reaction conditions with triphenylphosphine oxide (1a)

Table S1.[a]



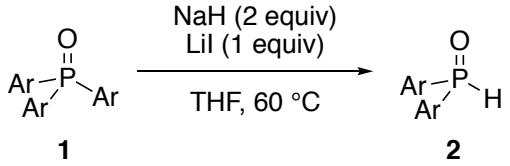
1a **2a**

Entry	MH (equiv)	Additive (equiv)	Temp (°C)	Time (h)	Yield of 2a (%)[b]
1	NaH (3)	NaI (2)	85 (sealed)	13	89
2	NaH (3)	LiI (2)	85 (sealed)	4	84
3	NaH (2)	LiI (2)	85 (sealed)	4	84
4	NaH (2)	LiI (1)	85 (sealed)	6	84
5	LiH (2)	-	85 (sealed)	12	0 (>95)[c]
6	LiH (2)	LiI (1)	85 (sealed)	12	0 (>95)[c]
7	NaH (2)	LiI (1)	60	13	98[d]
8	NaH (2)	NaI (1)	60	24	88[d]
9	NaH (2)	-	60	24	2 (>95)[c]
10	NaH (1.5)	LiI (0.75)	60	13	73 (27)[c]
10	NaH (2)	LiI (1)	40	24	68 (23)[c]

[a] The reactions were conducted at 0.5 mmol scale in 0.2 M of THF. [b] ^{1}H NMR yield with 1,1,2,2-tetrachloroethane as internal standard. [c] Recovery yield of **1a**. [d] Isolated yield of **2a**.

4. Hydrodearylation of triarylphosphine oxides 1

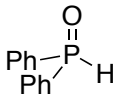
4.1. A general procedure for hydrodearylation of triarylphosphine oxides 1 (Scheme 2)



To a mixture of phosphine oxide **1** (0.5 mmol), NaH (40.0 mg, 1.0 mmol) and LiI (66.9 mg, 0.5 mmol) in 25 mL reaction vessel was added THF (2.5 mL) and the reaction mixture was stirred at 60 °C (the reaction time for each reaction was indicated below). Upon completion of the reaction based on TLC analysis, the reaction was quenched with saturated aqueous NH_4Cl at 0 °C. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to give the corresponding diaryl phosphine oxide **2**.

4.2. Characterization of the products

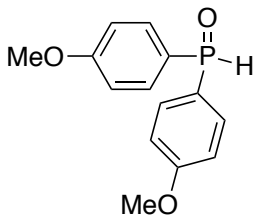
diphenylphosphine oxide (**2a**) [CAS: 4559-70-0]



Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) for 13 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 98% yield (99.2 mg, 0.4907 mmol) of **2a** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 481.1 Hz, 1H), 7.73–7.68 (m, 4H), 7.59–7.55 (m, 2H), 7.51–7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4 (d, J_{P-C} = 3.0 Hz), 131.2 (d, J_{P-C} = 101.0 Hz), 130.5 (d, J_{P-C} = 12.0 Hz), 128.8 (d, J_{P-C} = 13.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.5 (d, J = 481.1 Hz).

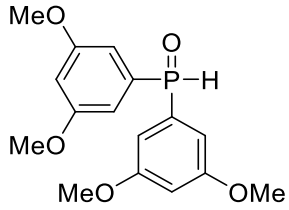
bis(4-methoxyphenyl)phosphine oxide (**2b**) [10]



Prepared from tris(4-methoxyphenyl)phosphine oxide (**1b**) (184.8 mg, 0.502 mmol) for 13 h. Purification by recrystallization (CH_2Cl_2:*n*-Hex, 10:90) to give 91% (120.1 mg, 0.458 mmol) of **2b** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 477.4 Hz, 1H), 7.61 (dd, J = 13.2, 8.8 Hz, 4H), 6.99 (dd, J = 8.8, 2.0 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{P-C} = 3.0 Hz), 132.6 (d, J_{P-C} = 13.0 Hz), 122.9 (d, J_{P-C} = 107.0 Hz), 114.4 (d, J_{P-C} = 14.0 Hz), 55.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.7 (d, J = 477.4 Hz).

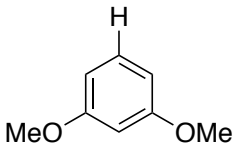
bis(3,5-dimethoxyphenyl)phosphine oxide (**2c**)



Prepared from tris(3,5-dimethoxyphenyl)phosphine oxide (**1c**) (229.6 mg, 0.501 mmol) with NaH (80.7 mg, 2.02 mmol) and LiI (133.0 mg, 0.994 mmol) for 16 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc, 90:10 for isolation of 1,3-dimethoxybenzene, followed by *n*-Hex:EtOAc:MeOH, 60:40:2 for isolation of **2c**) to give 76% yield (52.5 mg, 0.380 mmol) of 1,3-dimethoxybenzene as colorless oil and 60% yield (97.0 mg, 0.300 mmol) of **2c** as white solid.

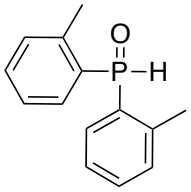
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94, (d, 475.4 Hz, 1H), 6.83 (dd, J = 15.1, 2.0 Hz, 4H), 6.62-6.61 (m, 2H), 3.81 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, J_{P-C} = 18.8 Hz), 133.0 (d, J_{P-C} = 101.0 Hz), 107.9 (d, J_{P-C} = 12.9 Hz), 104.7 (d, J_{P-C} = 2.0 Hz), 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.6 (d, J = 475.4 Hz); ESIHRMS: Found *m/z* 323.1049; Calcd for $C_{16}H_{20}O_5P$ $[M + H]^+$ 323.1048.

1,3-dimethoxybenzene [CAS: 151-10-0]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.0 Hz, 1H), 6.51 (dd, J = 8.0, 2.4 Hz, 2H), 6.47 (t, J = 2.4 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 129.8, 106.1, 100.4, 55.2.

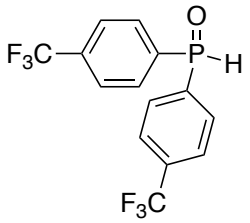
di-*o*-tolylphosphine oxide (**2d**) [10]



Prepared from tri-*o*-tolylphosphine oxide (**1d**) (160.6 mg, 0.501 mmol) for 27 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 61% yield (70.4 mg, 0.306 mmol) of **2d** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 476.8 Hz, 1H), 7.72 (dd, J = 15.2, 7.6 Hz, 2H), 7.46 (dd, J = 7.6, 7.6 Hz, 2H), 7.32 (d, J = 7.6, 7.6 Hz, 2H), 7.25 (dd, J = 13.6, 7.6 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (d, J_{P-C} = 10.0 Hz), 132.42 (d, J_{P-C} = 2.0 Hz), 132.37 (d, J_{P-C} = 16.0 Hz), 131.1 (d, J_{P-C} = 10.0 Hz), 129.2 (d, J_{P-C} = 99.0 Hz), 126.0 (d, J_{P-C} = 13.0 Hz), 20.1 (d, J_{P-C} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 (d, J = 476.8 Hz).

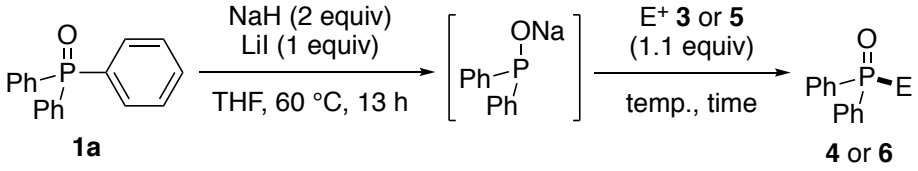
bis(4-(trifluoromethyl)phenyl)phosphine oxide (**2e)**



Prepared from tris(4-(trifluoromethyl)phenyl)phosphine oxide (**1e**) (241.8 mg, 0.501 mmol) with NaH (80.8 mg, 2.02 mmol) and LiI (133.3 mg, 0.947 mmol) at 85 °C for 11 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 60:40:2) to give 33% yield (55.9 mg, 0.165 mmol) of **2d** as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 492.0 Hz, 1H), 7.87 (dd, J = 9.6, 8.0 Hz, 4H), 7.80 (dd, J = 8.0, 2.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.81 (qd, J_{F-C} = 33.0 Hz, J_{P-C} = 3.0 Hz), 134.80 (d, J_{P-C} = 99.0 Hz), 131.2 (d, J_{P-C} = 12.0 Hz), 126.0 (dq, J_{P-C} = 13.0 Hz, J_{F-C} = 4.0 Hz), 123.3 (q, J_{F-C} = 271.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.9 (d, J = 492.0 Hz); ESIHRMS: Found *m/z* 339.0379; Calcd for $C_{14}H_{10}F_6OP$ $[M + H]^+$ 339.0373.

5. Dearylative functionalization of triphenylphosphine oxide (1a) (Schemes 3 and 4)

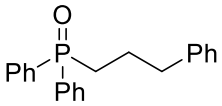
5.1. A general procedure



To a mixture of triphenylphosphine oxide (**1a**) (0.5 mmol), NaH (40.0 mg, 1.0 mmol) and LiI (66.9 mg, 0.5 mmol) in 25 mL reaction vessel was added THF (2.5 mL) and the reaction mixture was stirred at 60 °C for 13 h. The reaction was then cooled to 0 °C and the corresponding electrophile (E^+) **3** or **5** (1.1 equiv). Upon completion of the reaction based on TLC analysis (the reaction temperature and time were indicated below), the reaction was quenched with saturated aqueous NH_4Cl at 0 °C. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to give the trisubstituted phosphine oxide **4** or **6**.

5.2. Characterization of the products

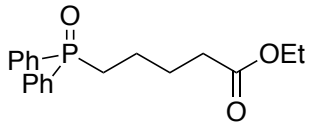
diphenyl(3-phenylpropyl)phosphine oxide (**4aa**) [11]



Prepared from triphenylphosphine oxide (**1a**) (139.6 mg, 0.502 mmol) with (3-bromopropyl)benzene (**3a**) (80 μL, 0.526 mmol) at 0 °C for 30 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 77% yield (123.8 mg, 0.386 mmol) of **4aa** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 4H), 7.51–7.40 (m, 6H), 7.27–7.23 (m, 2H), 7.19–7.15 (m, 1H), 7.12–7.10 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H) 2.28–2.21 (m, 2H), 2.03–1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 132.9 (d, J_{P-C} = 98.1 Hz), 131.6 (d, J_{P-C} = 2.8 Hz), 130.6 (d, J_{P-C} = 9.3 Hz), 128.5 (d, J_{P-C} = 11.5 Hz), 128.4, 128.3, 126.0, 36.5 (d, J_{P-C} = 14.7 Hz), 28.8 (d, J_{P-C} = 72.1 Hz), 22.9 (d, J_{P-C} = 3.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4.

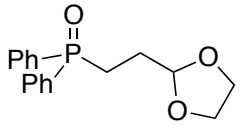
ethyl 5-(diphenylphosphoryl)pentanoate (**4ab**)



Prepared from triphenylphosphine oxide (**1a**) (139.8 mg, 0.502 mmol) with ethyl 5-bromovalerate (**3b**) (90 μL, 0.568 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 77% yield (128.0 mg, 0.387 mmol) of **4ab** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 4H), 7.53–7.44 (m, 6H), 4.08 (q, J = 7.2 Hz, 2H), 2.31–2.25 (m, 4H), 1.74–1.62 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 132.7 (d, J_{P-C} = 97.0 Hz), 131.6 (d, J_{P-C} = 3.0 Hz), 130.6 (d, J_{P-C} = 9.0 Hz), 128.6 (d, J_{P-C} = 11.0 Hz), 60.2, 33.6, 29.3 (d, J_{P-C} = 75.0 Hz), 26.0 (d, J_{P-C} = 15.0 Hz), 21.0 (d, J_{P-C} = 4.0 Hz), 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3; ESIHRMS: Found *m/z* 331.1473; Calcd for $C_{19}H_{24}O_3P$ $[M + H]^+$ 331.1463.

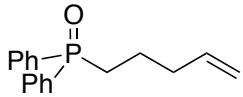
(2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide (**4ac**)



Prepared from triphenylphosphine oxide (**1a**) (139.4 mg, 0.501 mmol) with 2-(2-bromoethyl)-1,3-dioxolane (**3c**) (70 μL, 0.572 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 80:20:2) to give 67% yield (101.6 mg, 0.336 mmol) of **4ac** as pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 11.0, 6.5 Hz, 4H), 7.51 (dd, J = 6.5, 6.5 Hz, 2H), 7.46 (ddd, J = 6.5, 6.5, 1.5 Hz, 4H), 4.95 (t, J = 4.0 Hz, 1H), 3.94–3.92 (m, 2H), 3.85–3.83 (m, 2H), 2.42–2.36 (m, 2H), 2.00–1.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.7 (d, J_{P-C} = 98.8 Hz), 131.7 (d, J_{P-C} = 2.5 Hz), 130.7 (d, J_{P-C} = 8.8 Hz), 128.6 (d, J_{P-C} = 11.3 Hz), 103.4 (d, J_{P-C} = 15.0 Hz), 65.0, 25.8 (d, J_{P-C} = 2.5 Hz), 23.4 (d, J_{P-C} = 73.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.7; ESIHRMS: Found *m/z* 303.1153; Calcd for $C_{17}H_{20}O_3P$ $[M + H]^+$ 303.1150.

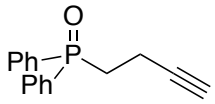
pent-4-en-1-yldiphenylphosphine oxide (**4ad**)



Prepared from triphenylphosphine oxide (**1a**) (139.5 mg, 0.501 mmol) with 5-bromo-1-pentene (70 μL, 0.592 mmol) (**3d**) at 0 °C for 30 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 71% yield (96.2 mg, 0.356 mmol) of **4ad** as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.71 (m, 4H), 7.52–7.49 (m, 2H), 7.47–7.44 (m, 4H), 5.71 (ddt, J = 13.6, 8.0, 5.6 Hz, 1H), 4.99 (d, J = 13.6 Hz, 2H), 4.98 (d, J = 8.0 Hz, 2H), 2.28–2.30 (m, 2H), 2.15 (dt, J = 5.6, 5.6 Hz, 2H), 1.77–1.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 133.0 (d, J_{P-C} = 97.5 Hz), 131.6 (d, J_{P-C} = 2.5 Hz), 130.6 (d, J_{P-C} = 8.8 Hz), 128.5 (d, J_{P-C} = 11.3 Hz), 115.7, 34.5 (d, J_{P-C} = 15.0 Hz), 28.9 (d, J_{P-C} = 71.3 Hz), 20.5 (d, J_{P-C} = 3.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.5; ESIHRMS: Found *m/z* 271.1273; Calcd for $C_{17}H_{20}OP$ $[M + H]^+$ 271.1252.

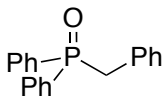
but-3-yn-1-yldiphenylphosphine oxide (**4ae**)



Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) with 4-bromo-1-butyne (**3e**) (50 μL, 0.533 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 85% yield (109.1 mg, 0.425 mmol) of **4ae** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 12.0, 7.6 Hz, 4H), 7.52 (ddd, J = 14.4, 7.6, 7.6 Hz, 2H), 7.48–7.46 (m, 4H), 2.58–2.49 (m, 4H), 1.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J_{P-C} = 99.0 Hz), 131.9 (d, J_{P-C} = 2.0 Hz), 130.7 (d, J_{P-C} = 9.0 Hz), 128.7 (d, J_{P-C} = 12.0 Hz), 82.7 (d, J_{P-C} = 19.0 Hz), 69.3, 29.2 (d, J_{P-C} = 70.0 Hz), 11.5 (d, J_{P-C} = 1.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; ESIHRMS: Found *m/z* 255.0940; Calcd for $C_{16}H_{16}OP$ $[M + H]^+$ 255.0939.

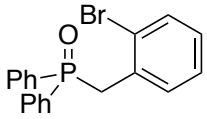
benzyldiphenylphosphine oxide (**4af**) [12]



Prepared from triphenylphosphine oxide (**1a**) (139.9 mg, 0.503 mmol) with benzyl bromide (**3f**) (65 μL, 0.547 mmol) at 0 °C for 10 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 79% yield (116.2 mg, 0.398 mmol) of **4af** as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 11.5, 7.0 Hz, 4H), 7.51 (dd, J = 7.5, 7.5 Hz, 2H), 7.43 (ddd, J = 7.5, 7.5, 2.5 Hz, 4H), 7.18–7.17 (m, 3H), 7.11–7.10 (m, 2H), 3.65 (d, J = 14.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.3 (d, J_{P-C} = 98.8 Hz), 131.7 (d, J_{P-C} = 2.5 Hz), 131.1 (d, J_{P-C} = 10.0 Hz), 130.1 (d, J_{P-C} = 5.0 Hz), 128.4, (d, J_{P-C} = 12.5 Hz), 128.32, 128.31 (d, J_{P-C} = 5.0 Hz), 126.7 (d, J_{P-C} = 5.0 Hz), 38.0 (d, J_{P-C} = 66.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.4.

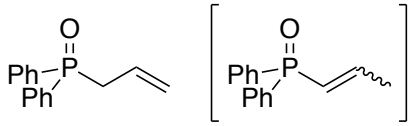
(2-bromobenzyl)diphenylphosphine oxide (**4ag**) [13]



Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) with 2-bromobenzyl bromide (**1g**) (137.0 mg, 0.548 mmol) at 0 °C for 15 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 89% yield (166.2 mg, 0.448 mmol) of **4ag** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 11.2, 7.2 Hz, 4H), 7.58 (dt, J = 7.6, 1.6 Hz, 1H), 7.51 (td, J = 7.2, 1.2 Hz, 2H), 7.45–7.40 (m, 5H), 7.21 (t, J = 7.2 Hz, 1H), 7.04 (td, J = 7.6, 1.6 Hz, 1H), 3.90 (d, J = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7 (d, J_{P-C} = 2.0 Hz), 132.0 (d, J_{P-C} = 95.0 Hz), 131.9 (d, J_{P-C} = 2.0 Hz), 131.8, 131.5 (d, J_{P-C} = 3.0 Hz), 131.1 (d, J_{P-C} = 9.0 Hz), 128.42 (d, J_{P-C} = 12.0 Hz), 128.43 (d, J_{P-C} = 2.0 Hz), 127.4 (d, J_{P-C} = 3.0 Hz), 125.3 (d, J_{P-C} = 7.0 Hz), 37.2 (d, J_{P-C} = 66.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5.

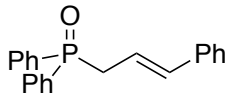
allyldiphenylphosphine oxide (**4ah**) [14]



Prepared from triphenylphosphine oxide (**1a**) (139.1 mg, 0.500 mmol) and allyl bromide (**3h**) (50 μL, 0.578 mmol) at 0 °C for 10 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 91% yield (110.3 mg, 0.455 mmol) of **4ah** as white solid including 4% of diphenyl(prop-1-en-1-yl)phosphine oxide (E/Z = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 4H), 7.55–7.51 (m, 2H), 7.49–7.45 (m, 4H), 5.86–5.76 (m, 1H), 5.13 (m, 2H), 3.15 (dd, J = 14.8, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4 (d, J_{P-C} = 98.0 Hz), 131.7 (d, J_{P-C} = 3.0 Hz), 130.9 (d, J_{P-C} = 9.0 Hz), 128.5 (d, J_{P-C} = 12.0 Hz), 127.0 (d, J_{P-C} = 9.0 Hz), 120.9 (d, J_{P-C} = 11.0 Hz), 36.1 (d, J_{P-C} = 68.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6.

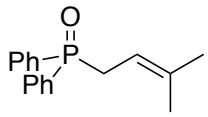
cinnamyldiphenylphosphine oxide (**4ai**) [15]



Prepared from triphenylphosphine oxide (**1a**) (139.4 mg, 0.501 mmol) and cinnamyl bromide (**3i**) (111.0 mg, 0.563 mmol) at 0 °C for 15 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 89% yield (141.6 mg, 0.445 mmol) of **4ai** as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 11.6, 6.8 Hz, 4H), 7.51 (td, J = 3.6, 1.6 Hz, 2H), 7.48–7.43 (m, 4H), 6.42 (dd, J = 16.0, 4.4 Hz, 1H), 6.17 (ddt, J = 16.0, 7.6, 7.6 Hz, 1H), 3.29 (dd, J = 14.8, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7 (d, J_{P-C} = 4.0 Hz), 135.5 (d, J_{P-C} = 12.0 Hz), 132.4 (d, J_{P-C} = 98.0 Hz), 131.8 (d, J_{P-C} = 2.0 Hz), 131.0 (d, J_{P-C} = 9.0 Hz), 128.6 (d, J_{P-C} = 11.0 Hz), 128.4, 127.5, 126.2, 118.4 (d, J_{P-C} = 10.0 Hz), 35.5 (d, J_{P-C} = 68.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0.

(3-methylbut-2-en-1-yl)diphenylphosphine oxide (**4aj**) [16]

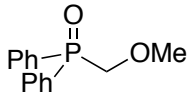


Prepared from triphenylphosphine oxide (**1a**) (139.4 mg, 0.501 mmol) with 3,3-dimethylallyl bromide (**3j**) (70 μL, 0.606 mmol) at 0 °C for 15 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 82% yield (111.7 mg, 0.413 mmol) of **4aj** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 11.0, 6.8 Hz, 4H), 7.51 (td, J = 7.2, 1.2 Hz, 2H), 7.48–7.43 (m, 4H), 5.24–5.19 (m, 1H), 3.08 (dd, J = 10.8, 8.0 Hz, 2H), 1.66 (d, J = 3.6 Hz, 3H), 1.45 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (d, J_{P-C} = 12.0 Hz), 132.9 (d, J_{P-C} = 98.0 Hz), 131.6 (d, J_{P-C} = 3.0 Hz), 131.0 (d, J_{P-C} = 10.0 Hz), 128.4 (d, J_{P-C} =

9.0 Hz), 112.2 (d, J_{P-C} = 9.0 Hz), 30.8 (d, J_{P-C} = 71.0 Hz), 25.7 (d, J_{P-C} = 3.0 Hz), 17.9 (d, J_{P-C} = 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.9.

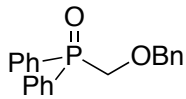
(methoxymethyl)diphenylphosphine oxide (**4ak**) [17]



Prepared from triphenylphosphine oxide (**1a**) (139.4 mg, 0.501 mmol) with methoxymethyl chloride (**3k**) (40 μL, 0.532 mmol) at 0 °C for 10 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 30:70:2) to give 86% yield (105.0 mg, 0.428 mmol) of **4ak** as pale yellow solid. The reaction in a larger scale using 1.394 g (5.01 mmol) of **1a** gave 80% yield (989.0 mg, 4.02 mmol) of **4ak**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.80 (m, 4H), 7.56 (ddd, J = 7.5, 7.5, 1.5 Hz, 2H), 7.48 (ddd, J = 7.5, 7.5, 3.0 Hz, 4H), 4.22 (d, J = 6.5 Hz, 2H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.0 (d, J_{P-C} = 2.5 Hz), 131.3 (d, J_{P-C} = 10.0 Hz), 131.1 (d, J_{P-C} = 98.8 Hz), 128.4 (d, J_{P-C} = 12.5 Hz), 71.0 (d, J_{P-C} = 87.5 Hz), 61.7 (d, J_{P-C} = 12.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.0.

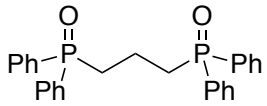
((benzyloxy)methyl)diphenylphosphine oxide (**4al**)



Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) with benzyloxymethyl chloride (**3l**) (80 μL, 0.575 mmol) at 0 °C for 10 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 40:60:2) to give 82% yield (131.9 mg, 0.410 mmol) of **4al** as pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.78 (m, 4H), 7.54 (ddd, J = 7.5, 7.5, 1.0 Hz, 2H), 7.46 (ddd, J = 7.5, 7.5, 2.5 Hz, 4H), 7.37–7.27 (m, 3H), 7.20–7.18 (m, 2H), 4.60 (s, 2H), 4.23 (d, J = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 132.0 (d, J_{P-C} = 2.5 Hz), 131.5, 131.4, 131.1 (d, J_{P-C} = 98.8 Hz), 128.44 (d, J_{P-C} = 12.5 Hz), 128.39, 128.0, 75.4 (d, J_{P-C} = 11.3 Hz), 67.9 (d, J_{P-C} = 87.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.7; ESIHRMS: Found *m/z* 323.1201; Calcd for $C_{20}H_{20}O_2P$ $[M + H]^+$ 323.1201.

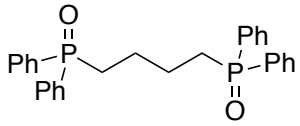
propane-1,3-diylbis(diphenylphosphine oxide) (**4am**) [18]



Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) with 1,3-dibromopropane (**3m**) (25 μL, 0.246 mmol) at 0 °C for 15 min. Purification by flash column chromatography (silica gel, EtOAc:MeOH, 94:6) to give 91% yield (100.1 mg, 0.225 mmol) of **4am** as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 10.4, 7.2 Hz, 8H), 7.50–7.47 (m, 4H), 7.44–7.40 (m, 8H), 2.50 (dt, J = 10.4, 7.6 Hz, 4H), 2.07–1.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.5 (d, J_{P-C} = 97.5 Hz), 131.7 (d, J_{P-C} = 2.5 Hz), 130.6 (d, J_{P-C} = 8.8 Hz), 128.6 (d, J_{P-C} = 11.2 Hz), 29.9 (dd, J_{P-C} = 57.0, 11.2 Hz), 18.8 (t, J_{P-C} = 3.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.1.

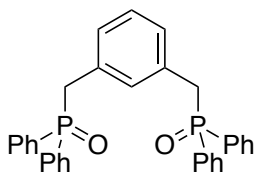
butane-1,4-diylbis(diphenylphosphine oxide) (**4an**) [18]



Prepared from triphenylphosphine oxide (**1a**) (139.0 mg, 0.500 mmol) and 1,4-dibromobutane (**3n**) (28.0 μL, 0.234 mmol) at 0 °C for 30 min. Purification by recrystallization ($CHCl_3$:*n*-Hex) to give 55% yield (59.5 mg, 0.130 mmol) of **4an** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 8H), 7.52–7.49 (m, 4H), 7.46–7.42 (m, 8H), 2.27–2.21 (m, 4H), 1.73–1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7 (d, J_{P-C} = 98.4 Hz), 131.7 (d, J_{P-C} = 2.6 Hz), 130.6 (d, J_{P-C} = 9.3 Hz), 128.6 (d, J_{P-C} = 11.6 Hz), 29.3 (d, J_{P-C} = 71.6 Hz), 22.8 (d, J_{P-C} = 19.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0.

(1,3-phenylenebis(methylene))bis(diphenylphosphine oxide) (**4ao**) [19]

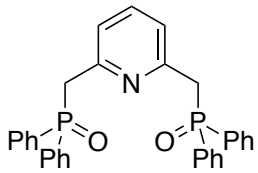


Prepared from triphenylphosphine oxide (**1a**) (139.5 mg, 0.501 mmol) with 1,3-bis(bromomethyl)benzene (**3o**) (65.4 mg, 0.248 mmol) at 0 °C for 10 min. Purification by

flash column chromatography (silica gel, EtOAc:MeOH, 90:10) to give 92% yield (115.1 mg, 0.227 mmol) of **4ao** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.62 (m, 8H), 7.51–7.47 (m, 4H), 7.43–7.39 (m, 8H), 7.02–6.91 (m, 4H), 3.65 (d, J = 13.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (d, J_{P-C} = 99.0 Hz), 132.0 (t, J_{P-C} = 5.4 Hz), 131.6, 131.2 (d, J_{P-C} = 10.2 Hz), 131.00, 131.00 (d, J_{P-C} = 9.4 Hz), 128.4 (d, J_{P-C} = 12.1 Hz), 128.3 (d, J_{P-C} = 11.3 Hz), 37.8 (d, J_{P-C} = 66.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5.

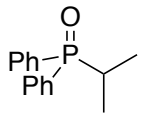
(pyridine-2,6-diylbis(methylene))bis(diphenylphosphine oxide) (**4ap**)



Prepared from triphenylphosphine oxide (**1a**) (139.5 mg, 0.501 mmol) and 2,6-bis(bromomethyl)pyridine (**3p**) (65.8 mg, 0.248 mmol) at 0 °C for 25 min. Purification by flash column chromatography (silica gel, EtOAc:MeOH, 90:10) to give 49% yield (62.0 mg, 0.123 mmol) of **4ap** as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 11.7, 7.0 Hz, 8H), 7.48 (td, J = 7.2, 1.2 Hz, 4H), 7.42–7.37 (m, 8H), 7.34 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 3.79 (d, J = 14.4 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 152.2 (d, J_{P-C} = 7.0 Hz), 136.8, 132.4 (d, J_{P-C} = 100.0 Hz), 131.8 (d, J_{P-C} = 2.0 Hz), 131.2 (d, J_{P-C} = 10.0 Hz), 128.4 (d, J_{P-C} = 12.0 Hz), 122.9, 40.5(d, J_{P-C} = 64.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; ESIHRMS: Found *m/z* 508.1598; Calcd for $C_{31}H_{28}NO_2P_2$ $[M + H]^+$ 508.1595.

isopropyldiphenylphosphine oxide (**4aq**) [20]

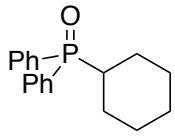


Prepared from triphenylphosphine oxide (**1a**) (139.7 mg, 0.502 mmol) with 2-bromopropane (**3q**) (50 μL, 0.532 mmol) at 60 °C for 14 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 61% yield (74.1 mg, 0.303 mmol) of **4aq** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (ddd, J = 10.5, 7.6, 1.6 Hz, 4H), 7.52–7.43 (m, 6H), 2.59–2.47 (m, 1H), 1.18 (dd, J = 16.4, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (d,

J_{P-C} = 94.0 Hz), 131.5 (d, J_{P-C} = 2.0 Hz), 131.0 (d, J_{P-C} = 8.0 Hz), 128.6 (d, J_{P-C} = 11.0 Hz), 27.1 (d, J_{P-C} = 73.0 Hz), 15.3 (d, J_{P-C} = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.9.

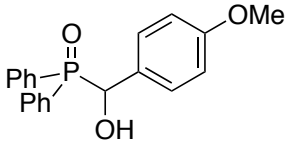
cyclohexyldiphenylphosphine oxide (**4ar**) [20]



Prepared from triphenylphosphine oxide (**1a**) (139.1 mg, 0.500 mmol) with iodocyclohexane (**3r**) (70 μL, 0.541 mmol) at 60 °C for 18 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2) to give 57% yield (80.9 mg, 0.284 mmol) of **4ar** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (ddd, J = 13.5, 8.0, 1.6 Hz, 4H), 7.52–7.43 (m, 6H), 2.28-2.19 (m, 1H), 1.81–1.71 (m, 5H), 1.55–1.51 (m, 2H), 1.32–1.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J_{P-C} = 94.0 Hz), 131.3 (d, J_{P-C} = 3.0 Hz), 131.0 (d, J_{P-C} = 8.0 Hz), 128.4 (d, J_{P-C} = 12.0 Hz), 37.1 (d, J_{P-C} = 73.0 Hz), 26.3 (d, J_{P-C} = 13.0 Hz), 25.7, 24.7 (d, J_{P-C} = 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6.

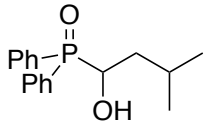
(hydroxy(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6aa**) [21]



Prepared from triphenylphosphine oxide (**1a**) (139.2 mg, 0.500 mmol) with anisaldehyde (**5a**) (70 μL, 0.575 mmol) at 0 °C for 18 h. Purification by recrystallization (*n*-Hex:CH_2Cl_2, 8:1) gave 65% yield (110.5 mg, 0.327 mmol) of **6aa** as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 11.0, 7.5, Hz, 2H), 7.64 (dd, J = 11.0, 7.5, Hz, 2H), 7.54 (dd, J = 7.5, 7.5 Hz, 1H), 7.48 (dd, J = 7.5, 7.5 Hz, 1H), 7.43 (ddd, J = 7.5, 7.5, 2.5 Hz, 2H), 7.36 (ddd, J = 7.5, 7.5, 2.5 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 4.51 (d, J = 4.0 Hz, 2H), 4.39 (brs, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4 (d, J_{P-C} = 2.5 Hz), 132.2 (d, J_{P-C} = 9.0 Hz), 132.0 (d, J_{P-C} = 2.5 Hz), 131.9 (d, J_{P-C} = 9.0 Hz), 131.8, 130.1 (d, J_{P-C} = 95.6 Hz), 129.4 (d, J_{P-C} = 94.6 Hz), 128.8 (d, J_{P-C} = 4.6 Hz), 128.20 (d, J_{P-C} = 1.8 Hz), 128.19 (d, J_{P-C} = 20.9 Hz), 128.10, 113.4 (d, J_{P-C} = 1.6 Hz), 73.5 (d, J_{P-C} = 81.9 Hz), 55.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.2.

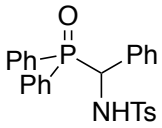
(1-hydroxy-3-methylbutyl)diphenylphosphine oxide (**6ab**)



Prepared from triphenylphosphine oxide (**1a**) (138.8 mg, 0.499 mmol) with isobutyraldehyde (**5b**) (60 μL, 0.559 mmol) at 0 °C for 30 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 65:35:2) to give 69% yield (99.6 mg, 0.345 mmol) of **6ab** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 10.8, 7.2 Hz, 2H), 7.79 (dd, J = 10.8, 7.2 Hz, 2H), 7.56–7.52 (m, 2H), 7.49–7.45 (m, 4H), 4.50 (dd, J = 11.6, 1.6 Hz, 1H), 1.97–1.88 (m, 2H), 1.72–1.62 (m, 1H), 1.48–1.41 (m, 1H), 0.89 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9 (d, J_{P-C} = 8.0 Hz), 131.74 (d, J_{P-C} = 2.0 Hz), 131.72 (d, J_{P-C} = 2.0 Hz), 131.4 (d, J_{P-C} = 9.0 Hz), 131.2 (d, J_{P-C} = 93.0 Hz), 130.5 (d, J_{P-C} = 94.0 Hz), 128.4 (d, J_{P-C} = 11.0 Hz), 128.3 (d, J_{P-C} = 11.0 Hz), 68.6 (d, J_{P-C} = 84.0 Hz), 38.9 (d, J_{P-C} = 3.0 Hz), 24.1 (d, J_{P-C} = 12.0 Hz), 23.5, 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3; ESIHRMS: Found *m/z* 289.1359; Calcd for $C_{17}H_{22}O_2P$ $[M + H]^+$ 289.1357.

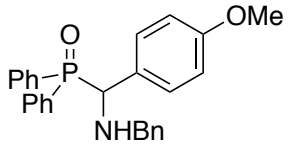
N-((diphenylphosphoryl)(phenyl)methyl)-4-methylbenzenesulfonamide (**6ac**)



Prepared from triphenylphosphine oxide (**1a**) (139.1 mg, 0.500 mmol) with *N*-benzylidene-4-methylbenzenesulfonamide[22] (**5c**) (142.6 mg, 0.550 mmol) at 0 °C for 30 min. Purification by recrystallization (*n*-Hex:CH_2Cl_2, 8:1) gave 68% yield (157.8 mg, 0.342 mmol) of **6ac** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 11.2, 7.6 Hz, 2H), 7.78 (br s, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.53–7.49 (m, 2H), 7.37 – 7.33 (m, 5H), 7.22 (td, J = 7.6, 3.2 Hz, 2H), 6.96– 6.95 (m, 3H), 6.83–6.80 (m, 4H), 5.35 (dd, J = 9.8, 9.8 Hz, 1H), 2.21(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.3 (d, J_{P-C} = 2.0 Hz), 132.4, 132.1 (d, J_{P-C} = 2.0 Hz), 131.9, 131.7, 131.3 (d, J_{P-C} = 9.0 Hz), 130.3 (d, J_{P-C} = 99.0 Hz), 129.6 (d, J_{P-C} = 100.0 Hz), 129.1 (d, J_{P-C} = 5.0 Hz), 128.8 (d, J_{P-C} = 12.0 Hz), 128.6, 128.1 (d, J_{P-C} = 12.0 Hz), 127.5 (d, J_{P-C} = 2.0 Hz), 127.1 (d, J_{P-C} = 3.0 Hz), 127.0, 57.4 (d, J_{P-C} = 2.0 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4; ESIHRMS: Found *m/z* 462.1298; Calcd for $C_{26}H_{25}NO_3PS$ $[M + H]^+$ 462.1293.

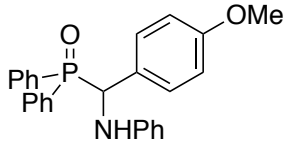
((benzylamino)(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6ad**)



Prepared from triphenylphosphine oxide (**1a**) (138.8 mg, 0.499 mmol) with *N*-benzyl-1-(4-methoxyphenyl)methanimine[23] (**5d**) (122.5 mg, 0.543 mmol) at 0 °C for 14 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 20:80:2) to give 78% yield (164.2 mg, 0.390 mmol) of **6ad** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (m, 2H), 7.54–7.42 (m, 1H) , 7.47–7.42 (m, 4H), 7.36–7.34 (m, 1H), 7.28–7.23 (m, 5H), 7.12–7.08 (m, 4H), 6.76 (d, J = 8.6 Hz, 2H), 4.31 (d, J = 10.2 Hz, 1H), 3.82 (d, J = 13.3 Hz, 1H), 3.76 (s, 3H), 3.49 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J_{P-C} = 2.2 Hz), 139.2, 132.0 (d, J_{P-C} = 9.1 Hz), 131.9, 131.8 (d, J_{P-C} = 3.2 Hz), 131.6 (d, J_{P-C} = 8.7 Hz), 131.5 (d, J_{P-C} = 9.5 Hz), 130.8 (d, J_{P-C} = 29.0 Hz), 130.3 (d, J_{P-C} = 5.3 Hz), 128.7, 128.30 (d, J_{P-C} = 11.5 Hz), 128.28, 128.0 (d, J_{P-C} = 11.4 Hz), 127.1, 126.9 (d, J_{P-C} = 2.4 Hz), 113.7 (d, J_{P-C} = 1.7 Hz), 60.5 (d, J_{P-C} = 81.4 Hz), 55.2, 50.8 (d, J_{P-C} = 14.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5; ESIHRMS: Found *m/z* 428.1779; Calcd for $C_{27}H_{27}NO_2P$ $[M + H]^+$ 428.1779.

((4-methoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**6ae**)

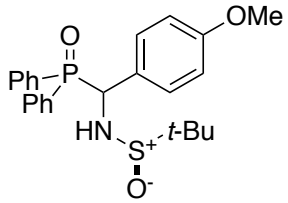


Prepared from triphenylphosphine oxide (**1a**) (142.5 mg, 0.512 mmol) with 1-(4-methoxyphenyl)-*N*-phenylmethanimine[23] (**5e**) (115.6 mg, 0.547 mmol) at 0 °C for 4 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2 - 40:60:2) to give 88% yield (181.5 mg, 0.439 mmol) of **6ae** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.83 (m, 2H), 7.55–7.39 (m, 6H), 7.30–7.26 (m, 2H), 7.10–7.06 (m, 4H), 6.68 (m, 1H), 6.62 (dd, J = 29.8, 8.0 Hz, 4H), 5.15–5.10 (m, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, J_{P-C} = 2.0 Hz), 146.2 (d, J_{P-C} = 12.0 Hz), 132.3 (d, J_{P-C} = 3.0 Hz), 131.9 (d, J_{P-C} = 3.0 Hz), 131.7, 131.6, 131.0 (d, J_{P-C} = 95.0 Hz), 130.4 (d, J_{P-C} = 100.0 Hz), 129.5 (d, J_{P-C} = 4.0 Hz), 129.2, 128.8 (d, J_{P-C} = 12.0 Hz), 128.2 (d, J_{P-C} = 12.0 Hz), 126.9, 118.4, 114.0, 113.7 (d, J_{P-C} = 2.0 Hz), 56.7 (d, J_{P-C} = 76.0 Hz),

55.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.0; ESIHRMS: Found *m/z* 436.1444; Calcd for $C_{26}H_{24}NO_2PNa$ $[M + Na]^+$ 436.1442.

(*R*)-*N*-((diphenylphosphoryl)(4-methoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (**6af**)

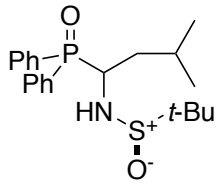


Prepared from triphenylphosphine oxide (**1a**) (141.6 mg, 0.509 mmol) with (*R*)-*N*-(4-methoxybenzylidene)-2-methylpropane-2-sulfinamide[24] (131.5 mg, 0.549 mmol) at 0 °C for 2 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2–40:60:2) to give 76% yield (170.5 mg, 0.386 mmol, dr = 72:28) of **6af** as white solid. The relative stereochemistry was not determined.

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.91 (m, 2H), 7.63–7.52 (m, 2H), 7.49–7.44 (m, 2H), 7.38–7.24 (m, 1H), 7.08 (dd, J = 8.6, 1.8 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 5.18 (dd, J = 5.8 Hz, 1.6 Hz, 1H), 4.21 (d, J = 4.3 Hz, 1H), 3.76 (s, 3H), 1.11 (s, 9H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J_{P-C} = 2.3 Hz), 132.7 (d, J_{P-C} = 2.7 Hz), 132.11 (d, J_{P-C} = 8.6 Hz), 131.8 (d, J_{P-C} = 8.8 Hz), 131.1 (d, J_{P-C} = 5.0 Hz), 130.0 (d, J_{P-C} = 5.2 Hz), 129.5 (d, J_{P-C} = 99.0 Hz), 129.1 (d, J_{P-C} = 94.6 Hz), 129.0 (d, J_{P-C} = 11.4 Hz), 128.3 (d, J_{P-C} = 12.0 Hz), 127.6, 113.6 (d, J_{P-C} = 1.9 Hz), 56.9 (d, J_{P-C} = 74.3 Hz), 55.8, 55.2, 22.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; ESIHRMS: Found *m/z* 464.1417; Calcd for $C_{24}H_{28}NO_3PSNa$ $[M + Na]^+$ 464.1425.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.91 (m, 2H), 7.63–7.52 (m, 2H), 7.49–7.44 (m, 2H), 7.38–7.24 (m, 3H), 6.75 (d, J = 8.4 Hz, 2H), 5.02 (dd, J = 10.0, 8.1 Hz, 1H), 4.28 (dd, J = 10.0, 3.8 Hz, 1H), 3.73 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, J_{P-C} = 2.4 Hz), 132.15 (d, J_{P-C} = 8.9 Hz), 131.9 (d, J_{P-C} = 2.8 Hz), 131.7 (d, J_{P-C} = 9.1 Hz), 131.2 (d, J_{P-C} = 8.9 Hz), 130.2, 129.5 (d, J_{P-C} = 99.0 Hz), 129.1 (d, J_{P-C} = 94.6 Hz), 128.6 (d, J_{P-C} = 11.6 Hz), 127.6, 124.7 (d, J_{P-C} = 5.8 Hz), 114.0 (d, J_{P-C} = 1.3 Hz), 59.1 (d, J_{P-C} = 79.0 Hz), 56.8, 55.2, 22.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5; ESIHRMS: Found *m/z* 464.1417; Calcd for $C_{24}H_{28}NO_3PSNa$ $[M + Na]^+$ 464.1425.

(*R*)-*N*-(1-(diphenylphosphoryl)-3-methylbutyl)-2-methylpropane-2-sulfinamide (**6ag**)

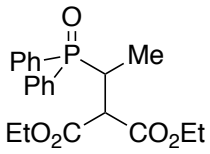


Prepared from triphenylphosphine oxide (**1a**) (139.2 mg, 0.500 mmol) with (*R*)-2-methyl-*N*-(3-methylbutylidene)propane-2-sulfinamide[25] (**5g**) (104.9 mg, 0.554 mmol) at 0 °C for 30 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 55:45:2–40:60:2) to give 63% yield (123.4 mg, 0.315 mmol, dr = 90:10) of **6ag** as white solid. The relative stereochemistry was not determined.

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 9.6, 8.0 Hz, 2H), 7.86–7.82 (m, 2H), 7.56–7.50 (m, 6H), 4.21–4.18 (m, 1H), 3.97 (dd, J = 7.2, 7.2 Hz, 1H), 1.86–1.82 (m, 1H), 1.80–1.74 (m, 1H), 1.49–1.44 (m, 1H), 1.11 (s, 9H), 0.88–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (d, J_{P-C} = 3.0 Hz), 132.1 (d, J_{P-C} = 3.0 Hz), 131.9 (d, J_{P-C} = 9.0 Hz), 131.1 (d, J_{P-C} = 9.0 Hz), 131.0 (d, J_{P-C} = 95.0 Hz), 129.7 (d, J_{P-C} = 97.0 Hz), 128.8 (d, J_{P-C} = 12.0 Hz), 128.6 (d, J_{P-C} = 12.0 Hz), 56.8, 51.3 (d, J_{P-C} = 74.0 Hz), 39.5, 24.5 (d, J_{P-C} = 10.0 Hz), 23.3, 22.5, 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.3; ESIHRMS: Found *m/z* 414.1633; Calcd for $C_{21}H_{30}NO_2PSNa$ $[M + Na]^+$ 414.1633.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 4H), 7.56–7.50 (m, 6H), 4.21–4.18 (m, 1H), 3.52 (d, J = 8.8 Hz, 1H), 1.80–1.74 (m, 2H), 1.49–1.44 (m, 1H), 0.88–0.86 (m, 15H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2; ESIHRMS: Found *m/z* 414.1633; Calcd for $C_{21}H_{30}NO_2PSNa$ $[M + Na]^+$ 414.1633.

diethyl 2-(1-(diphenylphosphoryl)ethyl)malonate (**6ah**)

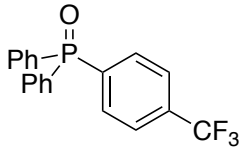


Prepared from triphenylphosphine oxide (**1a**) (139.4 mg, 0.501 mmol) with diethyl ethylidenemalonate (**5h**) (100 μL, 0.548 mmol) at -10 °C for 20 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 85% yield (165.8 mg, 0.427 mmol, dr = 90:10) of **6ah** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.79 (m, 4H), 7.56–7.42 (m, 6H), 4.16 (q, J = 7.1 Hz, 2H), 3.98–3.92 (m, 1H), 3.87–3.76 (m, 2H), 3.34–3.31 (m, 1H), 1.28 (dd, J = 14.8, 7.2 Hz,

3H), 1.25 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (d, J_{P-C} = 9.3 Hz), 167.6 (d, J_{P-C} = 8.9 Hz), 131.89 (d, J_{P-C} = 2.9 Hz), 131.87 (d, J_{P-C} = 2.5 Hz), 131.7 (d, J_{P-C} = 40.7 Hz), 131.4 (d, J_{P-C} = 9.4 Hz), 131.3 (d, J_{P-C} = 8.6 Hz), 130.8 (d, J_{P-C} = 42.9 Hz), 128.3 (d, J_{P-C} = 11.6 Hz), 128.5 (d, J_{P-C} = 11.3 Hz), 61.7 (d, J_{P-C} = 16.0 Hz), 50.6, 32.7 (d, J_{P-C} = 71.1 Hz), 13.9 (d, J_{P-C} = 17.0 Hz), 11.0, 10.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2.

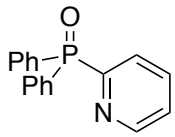
diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**6ai**)[26]



Prepared from triphenylphosphine oxide (**1a**) (139.2 mg, 0.500 mmol) with 4-fluorobenzotrifluoride (**5i**) (70 μL, 0.552 mmol) at 85 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 35:15:1) to give 66% yield (113.8 mg, 0.329 mmol) of **6ai** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 11.2, 8.0 Hz, 2H), 7.72 (dd, J = 8.0, 1.6 Hz, 2H), 7.66 (dd, J = 12.4, 7.6 Hz, 4H), 7.58 (td, J = 7.6, 1.6 Hz, 2H), 7.49 (td, J = 7.6, 2.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1 (d, J_{P-C} = 101.0 Hz), 133.7 (qd, J_{F-C} = 33.0 Hz, J_{P-C} = 2.0 Hz), 132.5 (d, J_{P-C} = 10.0 Hz), 132.3 (d, J_{P-C} = 3.0 Hz), 132.0 (d, J_{P-C} = 10.0 Hz), 131.6 (d, J_{P-C} = 105.0 Hz), 128.7 (d, J_{P-C} = 12.0 Hz), 123.6 (dq, J_{P-C} = 12.0 Hz, J_{F-C} = 4.0 Hz), 123.5 (q, J_{F-C} = 272.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0.

diphenyl(pyridin-2-yl)phosphine oxide (**6aj**) [26]



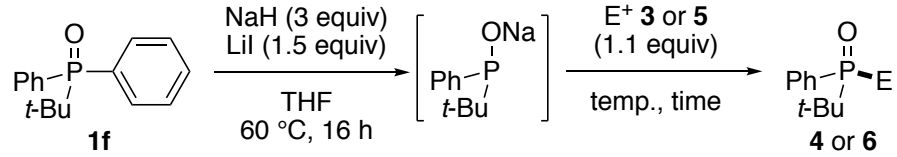
Prepared from triphenylphosphine oxide (**1a**) (139.0 mg, 0.500 mmol) with 2-chloropyridine (**5j**) (60 μL, 0.539 mmol) at 85 °C for 11 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 25:25:1) to give 71% yield (99.6 mg, 0.357 mmol) of **6aj** as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 4.4 Hz, 1H), 8.31 (dd, J = 6.8, 6.0 Hz, 1H), 7.91–7.83 (m, 5H), 7.42–7.50 (m, 2H), 7.47–7.42 (m, 4H), 7.40–7.37 (m, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 156.2 (d, J_{P-C} = 132.0 Hz), 150.0 (d, J_{P-C} = 19.0 Hz), 136.1 (d, J_{P-C} = 9.0 Hz), 132.00 (d, J_{P-C} = 103.0 Hz), 131.96 (d, J_{P-C} = 9.0 Hz), 131.8 (d, J_{P-C} = 3.0 Hz), 128.22 (d, J_{P-C} = 8.0 Hz), 128.20 (d, J_{P-C} = 19.0 Hz), 125.2 (d, J_{P-C} = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.0.

6. Dearylative-functionalization of diaryl(alkyl)phosphine oxides (Scheme 5)

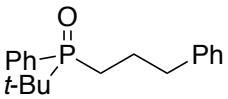
6.1. A general procedure for the reaction of *tert*-butyldiphenylphosphine oxide (1f)



To a mixture of *tert*-butyldiphenylphosphine oxide (**1f**) (0.5 mmol), NaH (60.0 mg, 1.5 mmol) and LiI (100.3 mg, 0.75 mmol) in 25 mL reaction vessel was added THF (2.5 mL) and the reaction was stirred at 60 °C for 16 h. The reaction was then cooled to 0 °C and the corresponding electrophile **3** or **5** (1.1 equiv) was added. Upon completion of the reaction based on TLC analysis (the reaction temperature and time were indicated below), the reaction was quenched with saturated aqueous NH_4Cl at 0 °C. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to give the corresponding unsymmetrical tertiary phosphine oxide **4** or **6**.

6.2. Characterization of the products

tert-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)

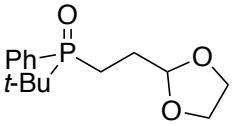


Prepared from *tert*-butyldiphenylphosphine oxide (**1f**) (129.5 mg, 0.501 mmol) with (3-bromopropyl)benzene (**3a**) (80 μL, 0.526 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 93% yield (140.2 mg, 0.467 mmol) of **4fa** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.52–7.48 (m, 1H), 7.46–7.41 (m, 2H), 7.27–7.24 (m, 2H), 7.19–7.16 (m, 1H) , 7.13–7.11 (m, 2H), 2.80–2.75 (m, 1H), 2.68–2.61 (m, 1H), 2.11–1.98 (m, 3H), 1.69–1.60 (m, 1H), 1.09 (d, J = 14.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 131.8 (d, J_{P-C} = 7.5 Hz), 131.3 (d, J_{P-C} = 2.5 Hz), 129.9 (d, J_{P-C} = 85.0 Hz),

128.4, 128.3, 128.1 (d, J_{P-C} = 11.2 Hz), 126.0, 36.8 (d, J_{P-C} = 1.2 Hz), 32.6 (d, J_{P-C} = 68.8 Hz), 23.0 (d, J_{P-C} = 3.8 Hz), 22.3, 21.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.8; ESIHRMS: Found *m/z* 301.1723; Calcd for $C_{19}H_{26}OP$ $[M + H]^+$ 301.1721.

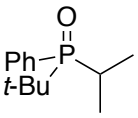
(2-(1,3-dioxolan-2-yl)ethyl)(*tert*-butyl)(phenyl)phosphine oxide (**4fc**)



Prepared from *tert*-butyldiphenylphosphine oxide (**1f**) (129.2 mg, 0.500 mmol) with 2-(2-bromoethyl)-1,3-dioxolane (**3c**) (70 μL, 0.572 mmol) at 0 °C for 20 min. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 10:90:2) to give 67% yield (95.1 mg, 0.337 mmol) of **4fc** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.0, 8.0 Hz, 2H), 7.52–7.47 (m, 3H), 4.93 (t, J = 4.0 Hz, 1H), 3.95–3.83 (m, 4H), 2.19–2.08 (m, 3H), 1.67–1.61 (m, 1H), 1.14 (d, J = 14.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8 (d, J_{P-C} = 8.0 Hz), 131.3 (d, J_{P-C} = 2.0 Hz), 129.6 (d, J_{P-C} = 87.0 Hz), 128.2 (d, J_{P-C} = 11.0 Hz), 103.7 (d, J_{P-C} = 14.0 Hz), 64.9 (d, J_{P-C} = 4.0 Hz), 32.6 (d, J_{P-C} = 69.0 Hz), 25.8 (d, J_{P-C} = 4.0 Hz), 24.4, 16.6 (d, J_{P-C} = 65.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.0; ESIHRMS: Found *m/z* 283.1463; Calcd for $C_{15}H_{24}O_3P$ $[M + H]^+$ 283.1463.

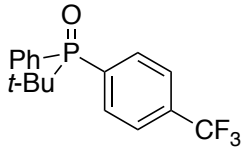
tert-butyl(isopropyl)(phenyl)phosphine oxide (**4fq**)



Prepared from *tert*-butyldiphenylphosphine oxide (**1f**) (129.6 mg, 0.502 mmol) with 2-bromopropane (**3q**) (50 μL, 0.533 mmol) at 60 °C for 16 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 62% yield (69.4 mg, 0.309 mmol) of **4fq** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.0, 8.0 Hz, 2H), 7.52–7.44 (m, 3H), 2.44–2.36 (m, 1H), 1.40 (dd, J = 14.4, 7.2 Hz, 3H), 1.16 (d, J = 14.4 Hz, 9H), 1.02 (dd, J = 14.4, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.42 (d, J_{P-C} = 83.0 Hz), 131.38 (d, J_{P-C} = 8.0 Hz), 130.9 (d, J_{P-C} = 3.0 Hz), 128.0 (d, J_{P-C} = 10.0 Hz), 33.3 (d, J_{P-C} = 65.0 Hz), 25.7, 24.8 (d, J_{P-C} = 63.0 Hz), 17.4 (d, J_{P-C} = 3.0 Hz), 16.5 (d, J_{P-C} = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.4; ESIHRMS: Found *m/z* 225.1412; Calcd for $C_{13}H_{22}OP$ $[M + H]^+$ 225.1408.

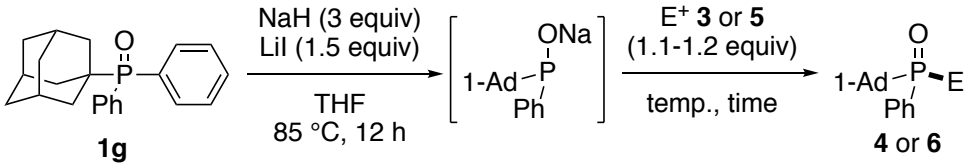
tert-butyl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6fi**)



Prepared from *tert*-butyldiphenylphosphine oxide (**1f**) (129.0 mg, 0.499 mmol) with 4-fluorobenzotrifluoride (**5i**) (70 μL, 0.552 mmol) at 85 °C for 22 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 75:25:2) to give 76% yield (123.4 mg, 0.378 mmol) of **6fi** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.8, 8.8 Hz, 2H), 7.96 (ddd, J = 8.8, 8.4, 1.6 Hz, 2H), 7.74 (dd, J = 8.8, 1.6 Hz, 2H), 7.56–7.48 (m, 3H), 1.27 (d, J = 15.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9 (d, J_{P-C} = 86.0 Hz), 133.2 (qd, J_{F-C} = 33.0 Hz, J_{P-C} = 3.0 Hz), 132.6 (d, J_{P-C} = 8.0 Hz), 132.0 (d, J_{P-C} = 8.0 Hz), 131.8 (d, J_{P-C} = 3.0 Hz), 130.3 (d, J_{P-C} = 90.0 Hz), 128.4 (d, J_{P-C} = 11.0 Hz), 125.0 (dq, J_{P-C} = 11.0 Hz, J_{F-C} = 4.0 Hz), 123.6 (q, J_{F-C} = 271.0 Hz), 34.0 (d, J_{P-C} = 70.0 Hz), 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.9; ESIHRMS: Found *m/z* 327.1135; Calcd for $C_{17}H_{19}F_3OP$ $[M + H]^+$ 327.1126.

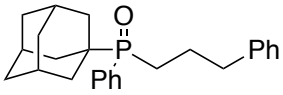
6.3. A general procedure for the reaction of (adamantan-1-yl)diphenylphosphine oxide (1g)



To a mixture of (adamantan-1-yl)diphenylphosphine oxide (**1g**) (0.5 mmol), NaH (60.0 mg, 1.5 mmol) and LiI (100.3 mg, 0.75 mmol) in 25 mL reaction vessel was added THF (2.5 mL) and the reaction was stirred at 85 °C for 12 h. The reaction was then cooled to 0 °C and the corresponding electrophile **3** or **5** (1.1 equiv) was added. Upon completion of the reaction based on TLC analysis (the reaction temperature and time were indicated below), the reaction was quenched with saturated aqueous NH_4Cl at 0 °C. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to give the corresponding unsymmetrical tertiary phosphine oxide **4** or **6**.

6.4. Characterization of the products

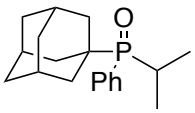
(adamantan-1-yl)(phenyl)(3-phenylpropyl)phosphine oxide (**4ga**)



Prepared from (adamantan-1-yl)diphenylphosphine oxide (**1g**) (166.0 mg, 0.493 mmol) with (3-bromopropyl)benzene (**3a**) (80 μL, 0.526 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 70:30:2) to give 80% yield (149.0 mg, 0.394 mmol) of **4ga** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 9.6, 8.0 Hz, 2H), 7.52–7.48 (m, 1H), 7.45–7.42 (m, 2H), 7.27–7.23 (m, 2H), 7.18 – 7.15 (m, 1H), 7.11 (d, J = 7.2 Hz, 2H), 2.79 – 2.72 (m, 2H), 2.66–2.59 (m, 1H), 2.01–1.90 (m, 6H), 1.82–1.80 (m, 3H), 1.71–1.60 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 131.8 (d, J_{P-C} = 8.0 Hz), 131.2 (d, J_{P-C} = 2.0 Hz), 129.0 (d, J_{P-C} = 86.0 Hz), 128.6, 128.3, 128.0 (d, J_{P-C} = 11.0 Hz), 125.9, 36.8 (d, J_{P-C} = 13.0 Hz), 36.3, 35.4 (d, J_{P-C} = 70.0 Hz), 34.9, 27.2 (d, J_{P-C} = 9.0 Hz), 22.7 (d, J_{P-C} = 4.0 Hz), 20.8 (d, J_{P-C} = 64.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.7; ESIHRMS: Found *m/z* 379.2197; Calcd for $C_{25}H_{32}OP$ $[M + H]^+$ 379.2191.

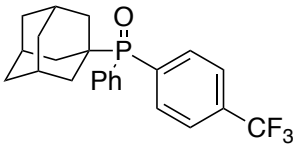
(adamantan-1-yl)(isopropyl)(phenyl)phosphine oxide (**4gq**)



Prepared from ((3*s*,5*s*,7*s*)-adamantan-1-yl)diphenylphosphine oxide (**1g**) (167.9 mg, 0.499 mmol) with 2-bromopropane (**3q**) (50 μL, 0.533 mmol) at 60 °C for 6 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 50:50:2) to give 64% yield (96.2 mg, 0.318 mmol) of **4gq** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.52–7.44 (m, 3H), 2.40–2.32 (m, 1H), 1.99–1.96 (m, 6H), 1.80–1.79 (m, 3H), 1.80–1.64 (m, 6H), 1.41 (dd, J = 14.4, 7.2 Hz, 3H), 0.99 (dd, J = 14.4, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5 (d, J_{P-C} = 7.3 Hz), 130.9 (d, J_{P-C} = 83.2 Hz), 130.8 (d, J_{P-C} = 2.5 Hz), 128.0 (d, J_{P-C} = 10.2 Hz), 36.6 (d, J_{P-C} = 66.4 Hz), 36.4, 36.0 (d, J_{P-C} = 1.5 Hz), 27.5 (d, J_{P-C} = 9.5 Hz), 24.3 (d, J_{P-C} = 63.7 Hz), 17.5 (d, J_{P-C} = 4.7 Hz), 17.0 (d, J_{P-C} = 3.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.8; ESIHRMS: Found *m/z* 303.1875; Calcd for $C_{19}H_{28}OP$ $[M + H]^+$ 303.1878.

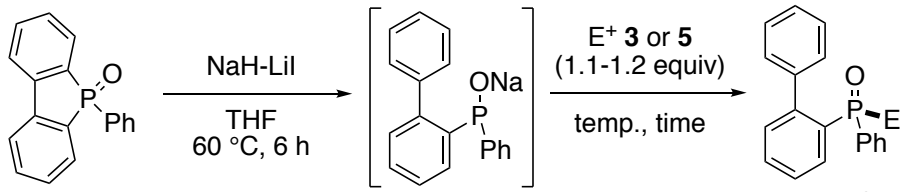
(adamantan-1-yl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6gi**)



Prepared from (adamantan-1-yl)diphenylphosphine oxide (**1g**) (168.7 mg, 0.502 mmol) with 4-fluorobenzotrifluoride (**5i**) (70 μL, 0.552 mmol) at 85 °C for 10 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 80:20:2) to give 77% yield (156.4 mg, 0.388 mmol) of **6gi** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.8, 8.8 Hz, 2H), 7.99–7.94 (m, 2H), 7.75 (d, J = 7.2 Hz, 2H), 7.55–7.49 (m, 3H), 1.96–1.91 (m, 9H), 1.73–1.64 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (d, J_{P-C} = 85.0 Hz), 133.2 (qd, J_{F-C} = 33.0 Hz, J_{P-C} = 3.0 Hz), 132.7 (d, J_{P-C} = 8.0 Hz), 132.1 (d, J_{P-C} = 8.0 Hz), 131.8 (d, J_{P-C} = 2.0 Hz), 129.8 (d, J_{P-C} = 90.0 Hz), 128.4 (d, J_{P-C} = 11.0 Hz), 125.0 (dq, J_{P-C} = 10.0 Hz, J_{F-C} = 3.0 Hz), 123.7 (q, J_{F-C} = 271.0 Hz), 37.1 (d, J_{P-C} = 72.0 Hz), 36.3, 35.3 (d, J_{P-C} = 1.0 Hz), 27.4 (d, J_{P-C} = 10.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.0; ESIHRMS: Found *m/z* 405.1607; Calcd for $C_{23}H_{25}F_3OP$ $[M + H]^+$ 405.1595.

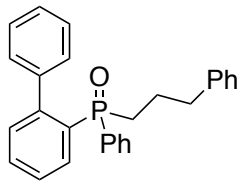
6.5 A general procedure for the reaction of 5-phenylbenzo[*b*]phosphindole 5-oxide (1h)



To a mixture of 5-phenylbenzo[*b*]phosphindole 5-oxide (**1h**) (0.5 mmol), NaH (40.0 mg, 1.0 mmol) and LiI (66.9 mg, 0.5 mmol) in 25 mL reaction vessel was added THF (2.5 mL) and the reaction was stirred at 60 °C for 6 h. The reaction was then cooled to 0 °C and then the corresponding electrophile **3** or **5** (1.1–1.2 equiv) was added. Upon completion of the reaction based on TLC analysis (the reaction temperature and time were noted below), the reaction was quenched with saturated aqueous NH_4Cl at 0 °C. The organic material was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography to give the trisubstituted phosphine oxide **4** or **6**.

6.6. Characterization of the products

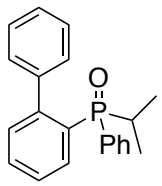
[1,1'-biphenyl]-2-yl(phenyl)(3-phenylpropyl)phosphine oxide (**4ha**)



Prepared from 5-phenylbenzo[*b*]phosphindole 5-oxide (**1h**) (137.1 mg, 0.496 mmol) with (3-bromopropyl)benzene (**3a**) (80 μL, 0.526 mmol) at 0 °C for 1.5 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 70:30:2) to give 94% yield (185.7 mg, 0.468 mmol) of **4ha** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.95 (m, 1H), 7.51–7.41 (m, 2H), 7.39–7.35 (m, 1H), 7.30–7.10 (m, 11H), 7.03–6.94 (m, 4H), 2.52 (t, J = 6.6 Hz, 2H), 1.93–1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, J_{P-C} = 9.3 Hz), 141.0, 140.6 (d, J_{P-C} = 3.4 Hz), 134.0 (d, J_{P-C} = 99.1 Hz), 133.0 (d, J_{P-C} = 8.9 Hz), 131.5 (d, J_{P-C} = 99.5 Hz), 131.4, 131.3, 131.1 (d, J_{P-C} = 2.7 Hz), 130.7 (d, J_{P-C} = 9.3 Hz), 129.6, 128.5, 128.4, 128.2 (d, J_{P-C} = 11.8 Hz), 127.61, 127.56, 127.1 (d, J_{P-C} = 11.0 Hz), 126.0, 36.7 (d, J_{P-C} = 15.5 Hz), 28.1 (d, J_{P-C} = 72.4 Hz), 23.2 (d, J_{P-C} = 3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.7; ESIHRMS: Found *m/z* 397.1724; Calcd for $C_{27}H_{26}OP$ $[M + H]^+$ 397.1721.

[1,1'-biphenyl]-2-yl(isopropyl)(phenyl)phosphine oxide (**4hq**)

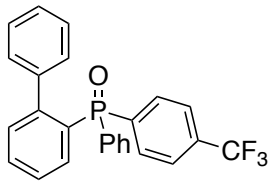


Prepared from 5-phenylbenzo[*b*]phosphindole 5-oxide (**1h**) (138.2 mg, 0.500 mmol) with 2-bromopropane (**3q**) (50 μL, 0.533 mmol) at 60 °C for 13 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 60:40:2) to give 84% yield (134.5 mg, 0.420 mmol) of **4hq** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (ddd, J = 12.0, 7.2, 1.6 Hz, 1H), 7.53–7.46 (m, 2H), 7.37 (td, J = 7.2, 1.2 Hz, 1H), 7.32–7.20 (m, 6H), 7.17 (t, J = 7.2 Hz, 2H), 7.01 (d, J = 7.2 Hz, 2H), 2.21–2.12 (m, 1H), 1.09 (dd, J = 7.6, 7.6 Hz, 3H), 1.05 (dd, J = 7.6, 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, J_{P-C} = 9.0 Hz), 140.7 (d, J_{P-C} = 3.0 Hz), 132.9 (d, J_{P-C} = 8.0 Hz), 132.1 (d, J_{P-C} = 94.0 Hz), 131.5 (d, J_{P-C} = 10.0 Hz), 131.2 (d, J_{P-C} = 9.0 Hz), 131.1 (d, J_{P-C} = 2.0 Hz), 130.8 (d, J_{P-C} = 3.0 Hz), 130.7 (d, J_{P-C} = 92.0 Hz), 129.5, 127.8 (d, J_{P-C} = 9.0

Hz), 127.41, 127.36, 126.9 (d, J_{P-C} = 9.0 Hz), 25.9 (d, J_{P-C} = 72.0 Hz), 16.1 (d, J_{P-C} = 2.0 Hz), 15.4 (d, J_{P-C} = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.4; ESIHRMS: Found *m/z* 321.1405; Calcd for $C_{21}H_{22}OP$ $[M + H]^+$ 321.1408.

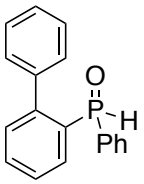
[1,1'-biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6hi**)



Prepared from 5-phenylbenzo[*b*]phosphindole 5-oxide (**1h**) (94.7 mg, 0.343 mmol) with 4-fluorobenzotrifluoride (**5i**) (70 μL, 0.552 mmol) at 85 °C for 24 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 75:25:2 for isolation of **6hi**, followed by *n*-Hex:EtOAc:MeOH, 70:30:2 for isolation of **2h**) to give 62% yield (90.1 mg, 0.213 mmol) of **6hi** as colorless oil and 20% yield (20.0 mg, 0.0725 mmol) of **2h** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.57 (m, 5H), 7.50–7.41 (m, 4H), 7.39–7.35 (m, 4H), 7.19 (d, *J* = 6.4 Hz, 2H), 7.09–7.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7 (d, J_{P-C} = 9.0 Hz), 140.0 (d, J_{P-C} = 4.0 Hz), 137.8 (d, J_{P-C} = 100.0 Hz), 133.9 (d, J_{P-C} = 12.0 Hz), 132.6 (qd, J_{F-C} = 32.0 Hz, J_{P-C} = 3.0 Hz), 132.14 (d, J_{P-C} = 2.0 Hz), 132.11 (d, J_{P-C} = 98.0 Hz), 132.0 (d, J_{P-C} = 10.0 Hz), 131.8 (d, J_{P-C} = 9.0 Hz), 131.6 (d, J_{P-C} = 10.0 Hz), 130.8 (d, J_{P-C} = 96.0 Hz), 130.1, 128.4 (d, J_{P-C} = 12.0 Hz), 127.33, 127.28, 126.7 (d, J_{P-C} = 13.0 Hz), 124.7 (dq, J_{P-C} = 12.0 Hz, J_{F-C} = 3.0 Hz), 123.6 (q, J_{F-C} = 271.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.4; ESIHRMS: Found *m/z* 423.1122; Calcd for $C_{25}H_{19}F_3OP$ $[M + H]^+$ 423.1126.

[1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**2h**) [27]

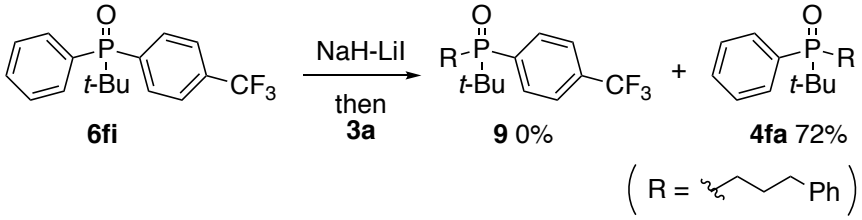


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 14.0, 7.6 Hz, 1H), 7.87 (d, *J* = 495.4 Hz, 1H), 7.59 (td, *J* = 7.4, 1.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.43–7.40 (m, 1H), 7.35–7.26 (m, 8H), 7.24–7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 (d, J_{P-C} = 10.0 Hz), 139.0 (d, J_{P-C} = 6.0 Hz), 132.5 (d, J_{P-C} = 9.0 Hz), 132.1 (d, J_{P-C} = 2.0 Hz), 131.7

(d, J_{P-C} = 2.0 Hz), 131.3 (d, J_{P-C} = 98.0 Hz), 130.5 (d, J_{P-C} = 10.0 Hz), 130.2 (d, J_{P-C} = 9.0 Hz), 130.0 (d, J_{P-C} = 99.0 Hz), 129.2, 128.2 (d, J_{P-C} = 13.0 Hz), 128.0, 127.8, 127.3 (d, J_{P-C} = 12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.4 (d, J = 495.4 Hz).

7. Competition studies (Scheme 6a)

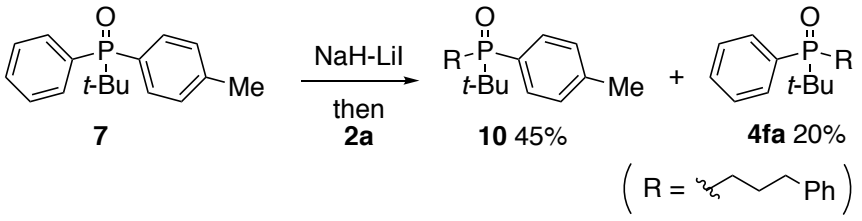
7.1 The reaction of 6fi



6fi

The reaction of **6fi** (98.5 mg, 0.302 mmol) was conducted by following the general procedure (Section 6.1) at 85 °C for 24 h for dearylation with subsequent treatment with (3-bromopropyl)benzene (**3a**) (50 μL, 0.329 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 65:35:2) to give 72% yield (65.9 mg, 0.219 mmol) of **4fa** as white solid.

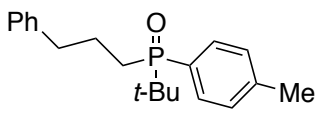
7.2 The reaction of 7



7

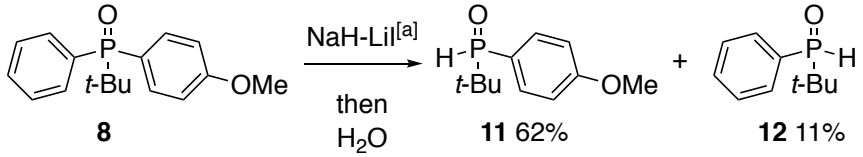
The reaction of **7** (104.7 mg, 0.384 mmol) was conducted by following the general procedure (Section 6.1) at 85 °C for 24 h for dearylation with subsequent treatment with (3-bromopropyl)benzene (**3a**) (65 μL, 0.427 mmol) at 0 °C for 1 h. Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc:MeOH, 70:30:2) to give inseparable mixture of **10** and **4fa** (77.4 mg) in 45% and 20% yields, respectively. The yields were calculated based on ^{31}P NMR analysis of the mixture.

tert-butyl(3-phenylpropyl)(*p*-tolyl)phosphine oxide (**10**)



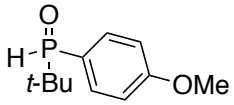
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 16.4, 8.0 Hz, 2H), 7.26–7.23 (m, 4H), 7.18–7.14 (m, 1H) , 7.12–7.10 (m, 2H), 2.80–2.75 (m, 1H), 2.68–2.61 (m, 1H), 2.38 (s, 3H), 2.08–1.96 (m, 3H), 1.69–1.61 (m, 1H), 1.08 (d, J = 14.4 Hz, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.1; ESIHRMS: Found *m/z* 315.1880; Calcd for $C_{20}H_{28}OP$ $[M + H]^+$ 315.1878.

7.3 The reaction of 8



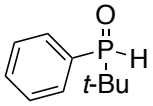
The reaction of **8** (142.3 mg, 0.494 mmol) was conducted by following the general procedure (Section 4) at 85 °C for 36 h for dearylation with quenching by water. Purification by flash column chromatography (silica gel, EtOAc:MeOH, 99:1) to give an inseparable mixture of **11** and **12** (77.4 mg) in 45% and 20% yields, respectively. The yields were calculated based on ^{1}H NMR analysis of the mixture.

tert-butyl(4-methoxyphenyl)phosphine oxide (**11**)[28]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 11.8, 8.8 Hz, 1H), 7.00 (dd, J = 8.8, 1.8 Hz, 1H), 6.99 (d, J = 450.4 Hz, 1H), 3.86 (s, 3H), 1.13 (d, J = 16.6 Hz, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.9 (d, J = 450.4 Hz).

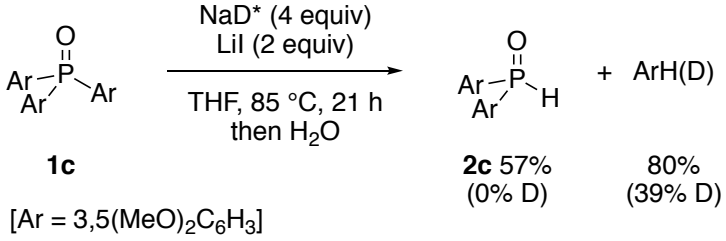
tert-butyl(phenyl)phosphine oxide (**12**)[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.60–7.56 (m, 1H), 7.52–7.48 (m, 2H), 7.04 (d, J = 453.2 Hz, 1H), 1.14 (d, J = 16.8 Hz, 9H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.5 (d, J = 453.2 Hz).

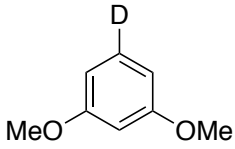
8. Deuterium labeling experiments

Employment of NaD[29] in place of NaH resulted in 39% of deuterium incorporation on 1,3-dimethoxybenzene (Scheme S2).



Scheme S2. The reactions were performed at 0.5 mmol scale according to general procedure for dearylation of triarylphosphine oxides **1** (Section 4). *NaD contains ca 9% of metallic Na.

1,3-dimethoxybenzene-5-*d*



Purification by flash column chromatography (silica gel, *n*-Hex:EtOAc, 90:10) to give 82% yield (56.9 mg, 0.412 mmol) of 1,3-dimethoxybenzene-5-*d* with 39% D-content as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.0 Hz, 0.61H), 6.52–6.50 (m, 2H), 6.47 (t, J = 2.4 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 129.8, 106.2, [106.4 as *ortho*-carbon with respect to deuterated carbon], 100.5, 55.2. GCMS (EI) *m/z* 138.08 [M] for 1,3-dimethoxybenzene, 139.10 [M] for 1,3-dimethoxybenzene-5-*d*.

9. DFT calculation

9.1 Computational details

All calculations were carried with the Gaussian 16[30] program package and the GRRM 11 (Version 11.03) program.[31] The molecular structures and harmonic vibrational frequencies were obtained using the long-range corrected hybrid density functional including a version of Grimme's D2 dispersion model developed by Chai and Head-Gordon (ωB97X-D).[32] We used 6–31+G* basis set.[33] All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the ωB97X-D/6-31+G* of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[34] The self-consistent reaction field (SCRF) method based on the Polarizable Continuum Model (PCM)[35] was employed to evaluate the solvent reaction field (THF; ε = 7.58).

9.2 Reaction pathway 1: nucleophilic attack of hydride on the P center-elimination of phenylsodium

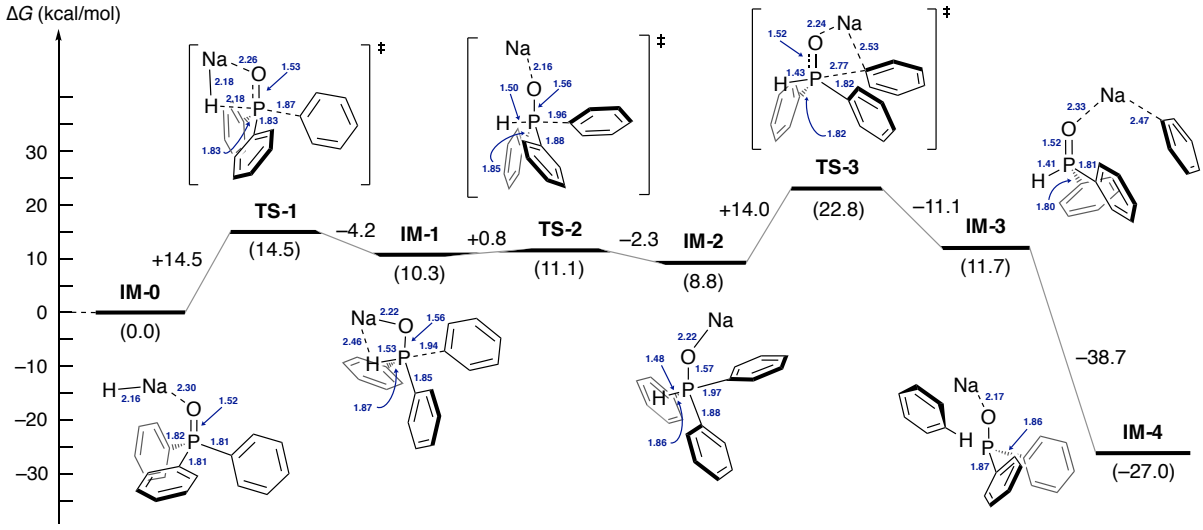


Figure S1. All calculations were performed at ωB97X-D/6-31+G* level of theory. The bulk solvent effect of THF was described with an implicit model (SCRF (solvent = THF, PCM)). The energies of intermediates (**IM**s) and transition states (**TS**s) were calculated with **IM-0** as a standard energy (ΔG (**IM-0**) = 0 kcal/mol).

9.3 Reaction pathway 1-2: the subsequent deprotonation step by phenylsodium in the pathway of nucleophilic attack of hydride on the P center-elimination

The following deprotonation of the P–H moiety of **IM-3** should lead to the sodium phosphinite; the competitive action of phenylsodium and NaH as a base was suggested by the deuterated label experiment (Scheme S2). In the former case (Figure S2.), through the smooth flipping of phenylsodium (Na–Ph) to the hydride side of P=O moiety (*i.e.* **IM-3**–**IM-3'**), the deprotonation was found to take place with a low activation barrier ($\Delta G^{\ddagger}$ = +3.6 kcal/mol). Given 39% deuterium incorporation in the deuterium labelling experiment described in the previous section, the deprotonation by co-existing NaH should proceed with a similar activation barrier.

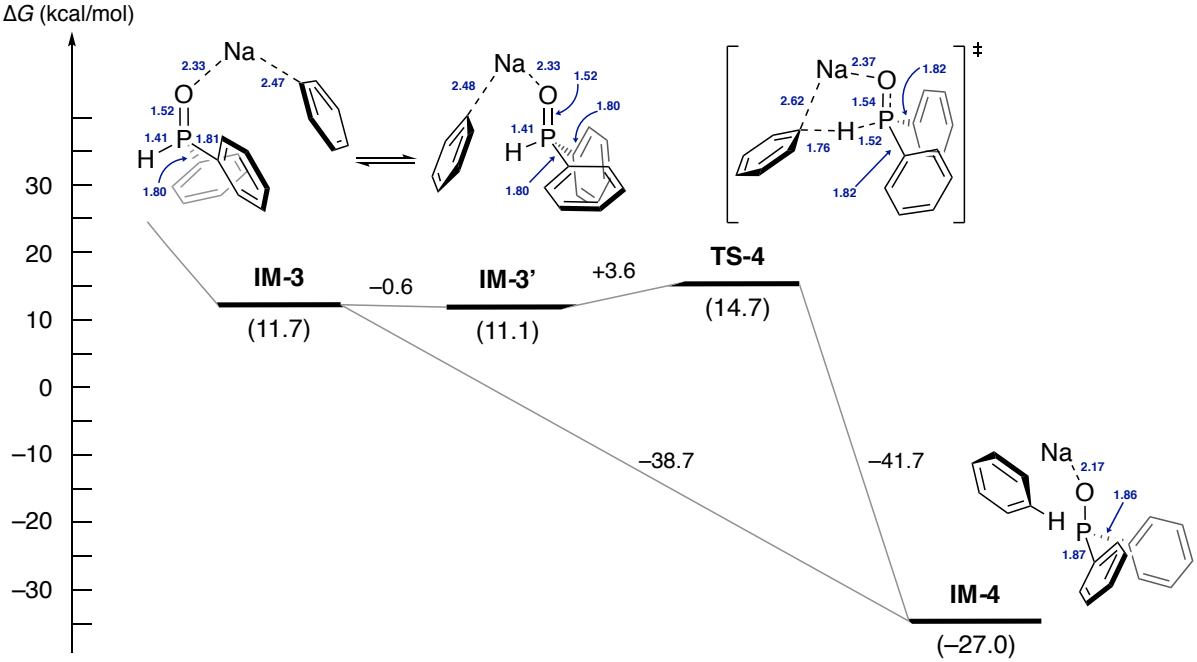


Figure S2.

9.4 Reaction pathway 2: nucleophilic aromatic substitution (S_NAr)

We also found the other reaction pathway, that is, nucleophilic aromatic substitution (S_NAr) mechanism (Figure S3). In this case, nucleophilic addition of hydride at the *ipso*-position of a phenyl ring of **1a** proceeded with a reasonable but slightly higher activation barrier ($\Delta G^{\ddagger}$ = +23.9 kcal/mol) than that of the above-mentioned pathway. Although this step afforded the transient Meisenheimer-type intermediate, **IM$_{SNAr}$-1**, the following elimination was an almost barrier-less step ($\Delta G^{\ddagger}$ = +1.1 kcal/mol). Finally, the corresponding sodium phosphinite product **IM$_{SNAr}$-2** was obtained with a large energy stabilization. At this moment, we consider this pathway less likely to take place, judged by the lower D-incorporation rate in the reaction of **1c** with NaD-LiI composite.

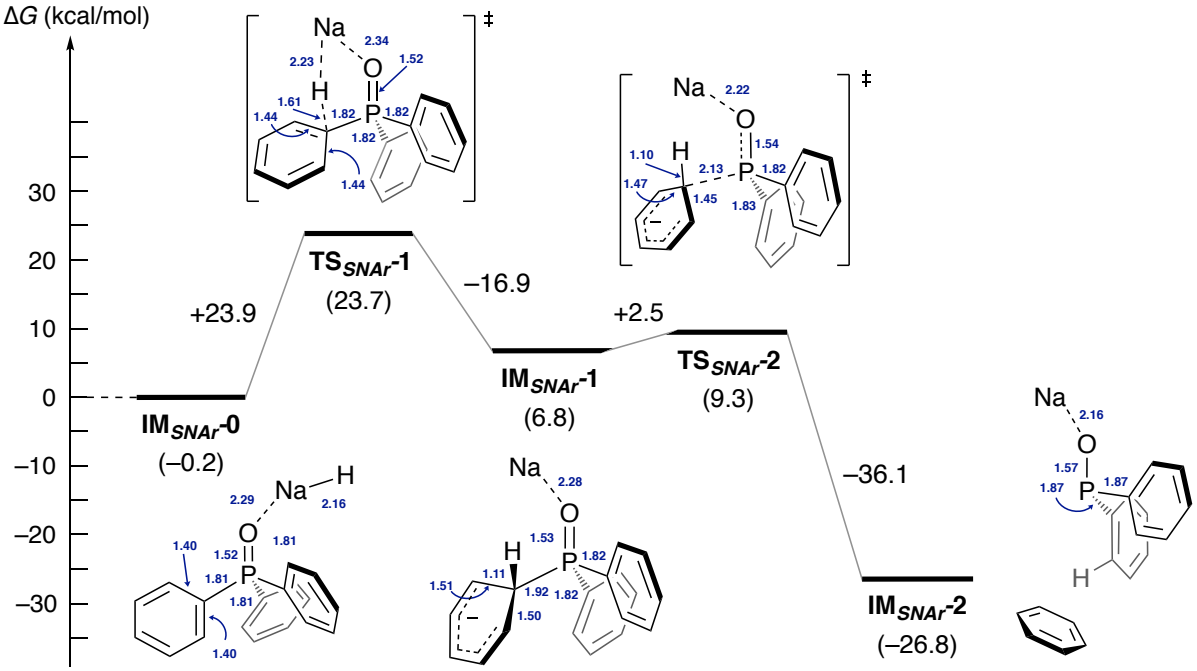
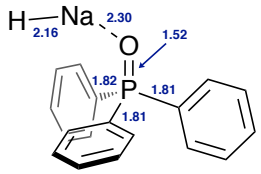


Figure S3.

9.5 Cartesian coordinates and energies

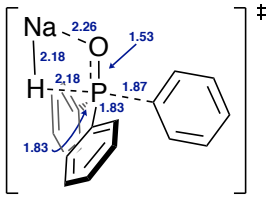
IM-0



Energy (RwB97XD): -1274.20473804 A.U.
Gibbs Free Energy: -1273.970192 A.U.

C	-1.041872	2.812155	-2.176483
C	-0.542776	1.655979	-1.586155
C	-0.591026	1.501668	-0.195682
C	-1.142461	2.511835	0.595714
C	-1.643347	3.669400	0.001224
C	-1.593033	3.819566	-1.382466
H	-1.005073	2.926417	-3.255612
H	-0.127067	0.873680	-2.215628
H	-2.074457	4.450044	0.620573
H	-1.984999	4.720310	-1.845584
P	0.057590	0.020058	0.629403
O	-0.198837	0.076086	2.122422
Na	-2.297542	-0.282437	2.997151
H	-1.178270	2.392504	1.674469
C	-0.728347	-1.405421	-0.171189
C	-0.087271	-2.650929	-0.169264
C	-2.028325	-1.298313	-0.679807
C	-0.735760	-3.771580	-0.679870
H	0.919754	-2.749323	0.227377
C	-2.675451	-2.422569	-1.186791
H	-2.540759	-0.340085	-0.682637
C	-2.029052	-3.657414	-1.189865
H	-0.231520	-4.733163	-0.680161
H	-3.683932	-2.332002	-1.578263
H	-2.533787	-4.532537	-1.588425
C	1.831241	-0.069028	0.262234
C	2.317618	-0.466969	-0.988335
C	2.725789	0.319821	1.263567
C	3.687435	-0.468228	-1.234783
H	1.635494	-0.793923	-1.768582
C	4.096710	0.316041	1.013923
H	2.346248	0.618660	2.236357
C	4.577115	-0.075149	-0.234544
H	4.060418	-0.781570	-2.205170
H	4.788221	0.616526	1.795318
H	5.645721	-0.079032	-0.428257
H	-4.419294	0.015563	2.736581

TS-1



Energy (RwB97XD): -1274.18465020 A.U.
Gibbs Free Energy: -1273.947159 A.U.

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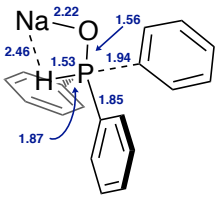
C	-1.442711	-0.866285	-0.223937
C	-2.565900	-1.312505	0.476748
C	-3.735885	-1.639886	-0.201492
C	-3.791865	-1.536822	-1.592554
H	-2.714774	-0.989227	-3.376743
H	-0.666429	-0.346851	-2.175042
H	-4.603601	-1.983504	0.354915
H	-4.700990	-1.803353	-2.123964
P	0.015307	-0.335688	0.739591
O	-0.074175	-0.371690	2.263324
Na	0.346027	-2.435969	3.078973
H	-2.514177	-1.415018	1.557363
C	1.618884	-0.646435	-0.082978
C	2.719122	0.073017	0.390412
C	1.784625	-1.519244	-1.160672
C	3.973958	-0.087037	-0.198295
H	2.599826	0.768680	1.217725
C	3.027789	-1.654146	-1.769795
H	0.944282	-2.115495	-1.503639
C	4.128720	-0.943233	-1.285666
H	4.825182	0.466623	0.187893
H	3.143368	-2.328531	-2.613673
H	5.102049	-1.061097	-1.753515
C	-0.128779	1.491455	0.372046
C	0.356084	2.071615	-0.806773
C	-0.823616	2.305220	1.273485
C	0.151366	3.423284	-1.078649

H	0.914102	1.472779	-1.522464
C	-1.031376	3.658387	1.006834
H	-1.197394	1.871485	2.196302
C	-0.545483	4.221472	-0.172123
H	0.540863	3.853470	-1.997483
H	-1.571489	4.273162	1.722064
H	-0.704422	5.275712	-0.381807
H	0.140827	-2.501487	0.908841

IM-1



Energy (RwB97XD): -1274.19449919 A.U.
Gibbs Free Energy: -1273.953749 A.U.

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C	-1.644746	-0.582282	-0.207270
C	-2.843572	-0.156896	0.372311
C	-4.052801	-0.291107	-0.309772
C	-4.076719	-0.850839	-1.586696
H	-2.893152	-1.714401	-3.167737
H	-0.758187	-1.492134	-1.952835
H	-4.975578	0.047788	0.154113
H	-5.016338	-0.952123	-2.122744
P	-0.100984	-0.450125	0.799156
O	-0.171590	-0.194052	2.338288
Na	-0.510127	-2.067778	3.481841
H	-2.829717	0.297633	1.360859
C	1.409366	-0.919376	-0.207167
C	1.773546	-0.281075	-1.399165
C	2.215358	-1.962113	0.256338
C	2.895130	-0.692937	-2.117290
H	1.175089	0.542976	-1.777125
C	3.364890	-2.350110	-0.431508
H	1.937032	-2.481737	1.171382
C	3.701602	-1.721280	-1.629219
H	3.146020	-0.201416	-3.053549
H	3.988635	-3.149490	-0.040165
H	4.586062	-2.030375	-2.179632
C	0.184059	1.436630	0.426619
C	-0.582317	2.225205	-0.438782
C	1.284392	2.059388	1.040404
C	-0.276262	3.570398	-0.677900
H	-1.439272	1.796217	-0.951745
C	1.604359	3.393650	0.807335
H	1.910298	1.480818	1.717077
C	0.819549	4.161591	-0.057615
H	-0.897939	4.151280	-1.355723
H	2.466151	3.839164	1.299406
H	1.062912	5.204708	-0.242969
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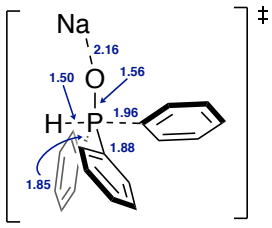
TS-2



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Gibbs Free Energy: -1273.952535 A.U.

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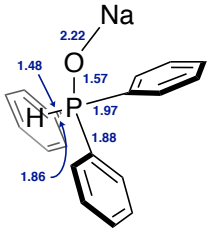
C	-1.533576	-0.901076	0.011507
C	-2.814465	-0.466518	0.366145
C	-3.947974	-1.008691	-0.238887
C	-3.814758	-1.999151	-1.211549
H	-2.426697	-3.213965	-2.326103
H	-0.425854	-2.256346	-1.253092
H	-4.935413	-0.654535	0.046356
H	-4.695362	-2.422241	-1.687073
P	-0.092684	-0.180236	0.921944
O	-0.315568	0.774562	2.139417
Na	-1.043464	1.386318	4.075070
H	-2.926031	0.314841	1.115353
C	1.520429	-0.905145	0.285333
C	1.951383	-0.803840	-1.043586
C	2.328967	-1.599920	1.188893
C	3.140738	-1.400489	-1.458914
H	1.351073	-0.258993	-1.766880
C	3.542792	-2.161773	0.792171
H	2.000272	-1.705798	2.221236
C	3.946866	-2.071442	-0.538724

H	3.443804	-1.332009	-2.500449
H	4.164595	-2.679823	1.517692
H	4.882714	-2.521963	-0.858398
C	0.087063	1.359933	-0.271200
C	-0.750682	1.667535	-1.348942
C	1.151835	2.246655	-0.030728
C	-0.546490	2.802332	-2.144695
H	-1.585569	1.015534	-1.593238
C	1.371289	3.374467	-0.815384
H	1.834210	2.041383	0.792705
C	0.515824	3.661377	-1.883741
H	-1.220993	3.006418	-2.973587
H	2.210159	4.032502	-0.598725
H	0.680891	4.540347	-2.501766
H	-0.146183	-1.369795	1.830147

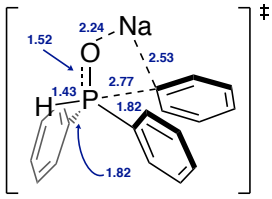
IM-2



Energy (RwB97XD): -1274.19796838 A.U.
Gibbs Free Energy: -1273.956100 A.U.

C	-2.313746	-2.506867	-1.619119
C	-1.265615	-1.749717	-1.095662
C	-2.439440	-1.568550	0.993140
C	-3.501014	-2.304412	0.468101
C	-3.438720	-2.779995	-0.841701
H	-2.253760	-2.877249	-2.639230
H	-0.408533	-1.529708	-1.725405
H	-4.372480	-2.513324	1.083240
H	-4.259247	-3.361999	-1.252419
P	0.041960	-0.303489	1.034649
O	-0.254202	0.668622	2.230185
Na	-0.888324	2.792088	2.141127
H	-2.484257	-1.218270	2.022804
C	1.705639	-0.774951	0.303366
C	2.061935	-0.598234	-1.039813
C	2.641596	-1.368421	1.156222
C	3.299292	-1.025506	-1.518628
H	1.372445	-0.115602	-1.726284
C	3.897274	-1.763527	0.695141
H	2.381068	-1.526217	2.201019
C	4.225677	-1.601791	-0.649685
H	3.543756	-0.897998	-2.569953
H	4.612557	-2.207307	1.382546
H	5.196166	-1.922093	-1.019027
C	-0.156765	1.239203	-0.179648
C	-1.360235	1.566934	-0.820244
C	0.871562	2.197641	-0.256141
C	-1.534598	2.778220	-1.499393
H	-2.192964	0.867844	-0.794683
C	0.713107	3.408188	-0.929310
H	1.827236	1.992652	0.224409
C	-0.498758	3.707181	-1.557334
H	-2.483993	2.991107	-1.985663
H	1.536034	4.118383	-0.967922
H	-0.628274	4.647251	-2.086992
C	-1.312526	-1.276183	0.218528
H	0.222048	-1.432339	1.973022

TS-3

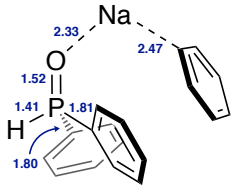


Energy (RwB97XD): -1274.17489933 A.U.
Gibbs Free Energy: -1273.933875 A.U.

C	-3.434992	-1.298981	-1.634108
C	-2.275442	-1.559590	-0.905730
C	-2.740791	0.329830	0.517622
C	-3.914826	0.573931	-0.189744
C	-4.258169	-0.233026	-1.274828
H	-3.700353	-1.936366	-2.472619
H	-1.657767	-2.414507	-1.172913
H	-4.556038	1.402246	0.098010
H	-5.167227	-0.034339	-1.835265
P	-0.442356	-1.159544	1.145610
O	-0.315723	-0.657744	2.579142
Na	-0.102996	1.561590	2.832380
H	-2.454324	0.980444	1.338063
C	1.057324	-1.408838	0.145435
C	1.119773	-1.184450	-1.232998

C	2.181913	-1.896488	0.814571
C	2.295663	-1.439615	-1.929173
H	0.263000	-0.772467	-1.757416
C	3.367454	-2.133883	0.117849
H	2.142134	-2.077410	1.886220
C	3.425816	-1.908170	-1.254979
H	2.337181	-1.255546	-2.999006
H	4.242085	-2.497623	0.649974
H	4.347063	-2.093935	-1.799916
C	0.339455	1.380920	0.348518
C	-0.248222	2.072205	-0.729343
C	1.708895	1.673434	0.534787
C	0.453888	2.949880	-1.565169
H	-1.305097	1.909349	-0.956472
C	2.438591	2.553721	-0.271061
H	2.261147	1.157657	1.328373
C	1.809149	3.195308	-1.339324
H	-0.053621	3.441045	-2.395182
H	3.496610	2.729374	-0.078675
H	2.364961	3.872401	-1.984397
C	-1.909617	-0.731491	0.159805
H	-0.760849	-2.540882	1.304970

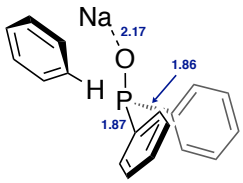
IM-3



Energy (RwB97XD): -1274.18981313 A.U.
Gibbs Free Energy: -1273.951618 A.U.

C	-3.671603	-2.021250	-0.714823
C	-2.461249	-2.382004	-0.125325
C	-1.804018	-0.048629	-0.049054
C	-3.014931	0.305235	-0.635528
C	-3.947211	-0.678537	-0.968630
H	-4.397083	-2.786984	-0.972376
H	-2.252426	-3.430467	0.073051
H	-3.222688	1.352268	-0.834465
H	-4.890654	-0.397682	-1.428007
P	0.037202	-1.864107	0.978889
O	0.281263	-1.323015	2.371998
Na	1.011696	0.808766	2.950431
H	-1.080300	0.723806	0.199753
C	1.370294	-1.423129	-0.164885
C	1.145738	-1.238384	-1.531792
C	2.659350	-1.265745	0.355999
C	2.202877	-0.891559	-2.369342
H	0.145910	-1.342053	-1.943796
C	3.713876	-0.919553	-0.483961
H	2.835082	-1.398307	1.420196
C	3.484921	-0.730481	-1.846768
H	2.021966	-0.735576	-3.428550
H	4.711407	-0.790509	-0.074876
H	4.305959	-0.451836	-2.500872
C	0.644350	2.422603	1.116269
C	-0.546775	3.189271	1.077772
C	1.162335	2.142262	-0.171809
C	-1.174761	3.614516	-0.100664
H	-1.036728	3.463800	2.016866
C	0.562423	2.550634	-1.369635
H	2.073241	1.545383	-0.264261
C	-0.621823	3.288358	-1.340054
H	-2.098882	4.190966	-0.054728
H	1.009854	2.279671	-2.325844
H	-1.104961	3.601430	-2.263526
C	-1.524789	-1.397379	0.206357
H	-0.030492	-3.271996	0.962615

IM-4

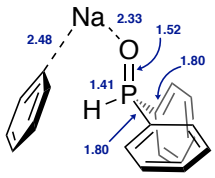


Energy (RwB97XD): -1274.25214511 A.U.
Gibbs Free Energy: -1274.013201 A.U.

C	-4.929355	0.272815	-0.712822
C	-3.578170	0.191402	-1.040949
C	-3.260535	-1.494408	0.644520
C	-4.615833	-1.420544	0.975009
C	-5.453998	-0.535517	0.299119
H	-5.576494	0.964439	-1.246599
H	-3.181509	0.825056	-1.833631
H	-5.017359	-2.055333	1.761482
H	-6.508919	-0.476689	0.553726

P	-0.924272	-0.827291	-0.827431
O	-0.318663	-1.813958	0.241427
Na	1.682538	-2.051222	1.039809
H	-2.600711	-2.182104	1.168369
C	-0.450025	0.878115	-0.223931
C	-0.362212	1.163465	1.144327
C	-0.127505	1.886625	-1.135204
C	0.032003	2.422412	1.590574
H	-0.606500	0.383623	1.863415
C	0.265997	3.153800	-0.696890
H	-0.172649	1.678416	-2.203259
C	0.348754	3.423437	0.667806
H	0.091502	2.629054	2.656428
H	0.517140	3.924791	-1.420829
H	0.660425	4.405624	1.012840
C	2.977841	-0.128734	-1.117974
C	3.108648	0.618750	0.054288
C	3.903368	-1.130600	-1.415469
C	4.164869	0.361494	0.930510
H	2.386132	1.397813	0.279994
C	4.959627	-1.386793	-0.539064
H	3.800580	-1.710291	-2.328400
C	5.089766	-0.641886	0.634181
H	4.268925	0.945784	1.840639
H	5.681526	-2.164826	-0.771132
H	5.913574	-0.839577	1.314394
C	-2.723315	-0.685515	-0.360015
H	2.150268	0.068771	-1.793368

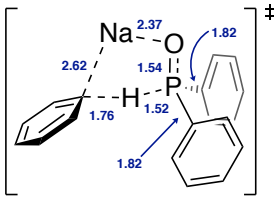
IM-3’



Energy (RwB97XD): -1274.18794882 A.U.
Gibbs Free Energy: -1273.952489 A.U.

C	-4.163974	0.345152	-1.750117
C	-2.836880	0.278801	-1.337187
C	-3.469182	-1.227402	0.450182
C	-4.799072	-1.155044	0.036556
C	-5.145218	-0.371400	-1.062360
H	-4.434204	0.957720	-2.604989
H	-2.077383	0.846982	-1.869654
H	-5.562619	-1.711016	0.572382
H	-6.180961	-0.316270	-1.384673
P	-0.760402	-0.628523	0.302125
O	-0.613908	-1.465553	1.555841
Na	1.460242	-2.302406	2.225964
H	-3.190708	-1.836794	1.305092
C	-0.146277	1.066019	0.407398
C	-0.834263	2.015039	1.175299
C	1.027691	1.423941	-0.261209
C	-0.347425	3.314002	1.272313
H	-1.752817	1.742672	1.689806
C	1.509282	2.728701	-0.163410
H	1.577096	0.689880	-0.844987
C	0.824628	3.670607	0.600836
H	-0.881436	4.049811	1.866112
H	2.424510	3.000992	-0.680547
H	1.202348	4.686324	0.676020
C	2.931954	-1.578736	0.370491
C	3.856352	-0.512157	0.488226
C	2.620260	-1.889215	-0.975832
C	4.399707	0.187342	-0.596874
H	4.169638	-0.184413	1.483992
C	3.140350	-1.211005	-2.086531
H	1.917732	-2.701739	-1.187758
C	4.036763	-0.156896	-1.900055
H	5.099039	1.006340	-0.428583
H	2.846459	-1.500042	-3.095599
H	4.445292	0.382407	-2.752237
C	-2.486845	-0.510189	-0.235362
H	-0.054449	-1.139476	-0.802758

TS-4



Energy (RwB97XD): -1274.17577629 A.U.
Gibbs Free Energy: -1273.946709 A.U.

C	-3.367780	-1.475812	-2.004269
C	-2.326575	-0.773242	-1.404303
C	-2.666808	-2.015610	0.640741

C	-3.711657	-2.716857	0.039033
C	-4.062039	-2.449049	-1.283127
H	-3.640814	-1.262196	-3.033729
H	-1.796187	-0.011357	-1.971279
H	-4.252441	-3.470802	0.604150
H	-4.875658	-2.995105	-1.752077
P	-0.562010	-0.188227	0.707586
O	-0.556023	-0.421201	2.226545
Na	1.655063	-1.146967	2.657120
H	-2.394193	-2.216319	1.673252
C	-0.779160	1.560770	0.251970
C	-1.776177	2.346233	0.842995
C	0.069779	2.126988	-0.703860
C	-1.925335	3.680281	0.475652
H	-2.435711	1.911857	1.590371
C	-0.083387	3.463403	-1.075205
H	0.857743	1.527469	-1.154119
C	-1.079676	4.238667	-0.485867
H	-2.700741	4.286118	0.935811
H	0.578583	3.897434	-1.818990
H	-1.197951	5.279931	-0.772094
C	2.557238	-0.886462	0.208830
C	3.279868	0.326524	0.181244
C	3.132573	-1.922944	-0.556686
C	4.474911	0.501254	-0.526835
H	2.891258	1.191795	0.727735
C	4.322691	-1.778342	-1.279886
H	2.633570	-2.894636	-0.603679
C	5.003086	-0.559154	-1.264978
H	4.991697	1.460130	-0.509296
H	4.720614	-2.612373	-1.856818
H	5.927987	-0.436323	-1.824117
C	-1.970769	-1.037584	-0.075603
H	0.820200	-0.620351	0.231343

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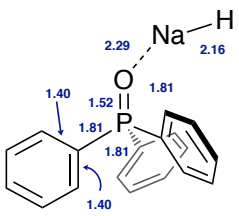
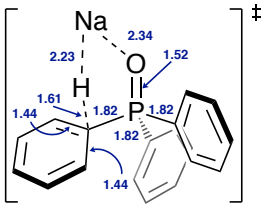


Energy (RwB97XD): -1274.20538668 A.U.
Gibbs Free Energy: -1273.970547 A.U.

C	2.375443	-1.586543	-2.303546
C	1.504962	-0.747128	-1.612093
C	1.129422	-1.056500	-0.300862
C	1.634059	-2.208064	0.313321
C	2.507573	-3.042214	-0.378619
C	2.877104	-2.731955	-1.687208
H	2.667559	-1.341072	-3.320079
H	1.126855	0.150761	-2.093789
H	2.903508	-3.930193	0.104633
H	3.561502	-3.381152	-2.225317
P	-0.024937	-0.026359	0.644788
O	0.277931	-0.060688	2.128947
Na	2.297929	0.056762	3.193196
H	1.350068	-2.445901	1.335000
C	0.099781	1.641342	-0.059505
C	-0.975271	2.269674	-0.693837
C	1.320484	2.318438	0.070269
C	-0.831470	3.563740	-1.193559
H	-1.926674	1.756742	-0.800661
C	1.460019	3.609062	-0.428144
H	2.167758	1.837548	0.553452
C	0.383116	4.232288	-1.061217
H	-1.670290	4.047210	-1.685130
H	2.408410	4.127425	-0.325267
H	0.493334	5.239916	-1.451151
C	-1.696539	-0.628585	0.286246
C	-2.027795	-1.198884	-0.947398
C	-2.678418	-0.481541	1.271318
C	-3.334419	-1.612128	-1.194640
H	-1.269998	-1.326694	-1.715730
C	-3.984140	-0.897344	1.020913
H	-2.418021	-0.048298	2.232768
C	-4.312262	-1.460487	-0.211760
H	-3.587225	-2.056842	-2.152407
H	-4.743554	-0.783968	1.788652
H	-5.330174	-1.785782	-0.405738
H	4.430434	0.297784	2.994149

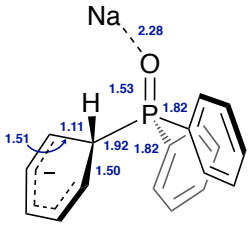
TS$_{SNAr}$-1



Energy (RwB97XD): -1274.16665566 A.U.
Gibbs Free Energy: -1273.932396 A.U.

C	-2.307175	-1.673718	-2.237061
C	-1.179099	-1.263083	-1.552710
C	-1.232269	-1.050506	-0.132424
C	-2.550693	-0.851181	0.406615
C	-3.667205	-1.264863	-0.298931
C	-3.563761	-1.742630	-1.612824
H	-2.218005	-1.924490	-3.292709
H	-0.220228	-1.234068	-2.064177
H	-4.646717	-1.185606	0.169989
H	-4.444471	-2.057908	-2.164227
P	0.077983	-0.131993	0.724446
O	0.074025	-0.363261	2.227466
Na	-0.857725	-2.395926	2.817473
H	-2.661682	-0.470730	1.420233
C	1.666731	-0.559279	-0.043208
C	2.106156	0.063751	-1.216479
C	2.459570	-1.545916	0.550471
C	3.316967	-0.307357	-1.796433
H	1.507336	0.842856	-1.680803
C	3.673999	-1.911698	-0.026487
H	2.125983	-2.019182	1.468600
C	4.101091	-1.295770	-1.202187
H	3.649575	0.178684	-2.708911
H	4.286028	-2.677392	0.441320
H	5.047191	-1.581956	-1.652822
C	-0.151125	1.642963	0.372423
C	-0.885714	2.103608	-0.725515
C	0.463873	2.568751	1.224299
C	-0.997817	3.472028	-0.969203
H	-1.376661	1.395260	-1.386442
C	0.350552	3.934617	0.979423
H	1.028451	2.218070	2.083955
C	-0.380077	4.387687	-0.119576
H	-1.572599	3.820972	-1.822259
H	0.830287	4.645274	1.646275
H	-0.470014	5.453373	-0.310475
H	-0.535472	-2.406400	0.572684

IM$_{SNAr}$-1



Energy (RwB97XD): -1274.20123524 A.U.
Gibbs Free Energy: -1273.959346 A.U.

C	-2.333686	-0.857424	-2.242794
C	-1.014393	-1.132240	-1.993410
C	-0.573685	-1.673979	-0.662466
C	-1.716389	-2.381225	0.020111
C	-3.025107	-2.070983	-0.288474
C	-3.378746	-1.204415	-1.344622
H	-2.592216	-0.397921	-3.197797
H	-0.257348	-0.934277	-2.749645
H	-3.819188	-2.578749	0.264347
H	-4.419197	-1.022495	-1.597142
P	0.242032	-0.394934	0.522477
O	0.029318	-0.791891	1.985394
Na	-2.135999	-1.242664	2.548625
H	-1.484987	-3.180478	0.722281
C	2.009235	-0.357972	0.100761
C	2.429193	0.048608	-1.172625
C	2.952235	-0.822781	1.020697
C	3.777002	-0.005684	-1.516206
H	1.705076	0.419150	-1.894328
C	4.302656	-0.875224	0.675666
H	2.624064	-1.140200	2.006579
C	4.715432	-0.467423	-0.591610
H	4.096112	0.314284	-2.503922
H	5.031579	-1.233665	1.396934
H	5.767111	-0.508188	-0.860591
C	-0.356208	1.304416	0.237720
C	-1.722111	1.520622	0.021704
C	0.500045	2.405890	0.353029
C	-2.220802	2.817215	-0.078138
H	-2.401142	0.677127	-0.102154
C	-0.000568	3.703072	0.252981

H	1.563392	2.257829	0.520926
C	-1.362129	3.910292	0.037494
H	-3.281193	2.972854	-0.257175
H	0.673811	4.549952	0.342885
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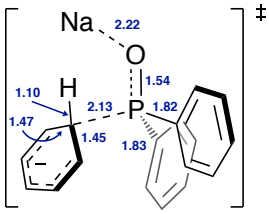
TS_{SNAr}-2



Energy (RwB97XD): -1274.19616257 A.U.
Gibbs Free Energy: -1273.955394 A.U.

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C	-0.376333	2.685727	-0.049354
C	0.360275	1.880852	0.931663
C	1.813866	2.063324	0.845127
C	2.398689	2.530924	-0.314993
C	1.634087	3.007478	-1.397653
H	-0.358033	3.645298	-1.948503
H	-1.446118	2.826995	0.085900
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P	-0.155164	-0.188092	0.828873
O	-0.176491	-0.808775	2.243160
Na	1.189316	-0.247410	3.897751
H	2.435916	1.725386	1.673366
C	-1.792592	-0.368479	0.053973
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H	-1.163680	0.303629	-1.903214
C	-4.171261	-0.774492	0.291092
H	-2.729577	-1.014342	1.878496
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H	-5.014606	-1.078347	0.905490
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C	0.961831	-1.159943	-0.242308
C	1.524566	-0.603792	-1.395460
C	1.292580	-2.471982	0.117078
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H	1.316386	0.430461	-1.663827
C	2.150909	-3.227153	-0.679170
H	0.868682	-2.900179	1.021981
C	2.694545	-2.672749	-1.839139
H	2.813012	-0.919967	-3.087920
H	2.394060	-4.248158	-0.397266
H	3.365991	-3.259609	-2.459984
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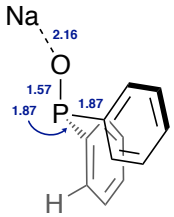
IM_{SNAr}-2



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Gibbs Free Energy: -1274.012845 A.U.

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C	3.111074	-0.018221	2.093334
C	3.923374	-0.800066	1.272129
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H	4.445290	1.421056	-1.250339
H	3.008225	2.815462	0.215496
H	4.172069	-1.816692	1.563546
H	5.031047	-0.894394	-0.573645
P	-1.174225	-0.372800	1.017382
O	-2.572896	-1.057921	1.245434
Na	-3.826592	-2.314816	2.469424
H	2.723784	-0.425879	3.022685
C	-1.566948	1.194319	0.080638
C	-0.558616	2.105515	-0.259885
C	-2.887809	1.511795	-0.247405
C	-0.858543	3.288837	-0.931552
H	0.475872	1.888334	-0.000592
C	-3.195403	2.698500	-0.916162
H	-3.674464	0.811803	0.024739
C	-2.181389	3.590569	-1.262562

H	-0.060762	3.979906	-1.193119
H	-4.228536	2.927093	-1.167515
H	-2.418173	4.515580	-1.781663
C	-0.431972	-1.270752	-0.441559
C	0.898418	-1.047799	-0.816845
C	-1.176620	-2.212821	-1.157438
C	1.461726	-1.726365	-1.895984
H	1.508687	-0.340963	-0.259424
C	-0.616770	-2.899229	-2.236272
H	-2.206563	-2.399232	-0.860566
C	0.704667	-2.655374	-2.611748
H	2.496385	-1.534852	-2.170381
H	-1.212072	-3.624675	-2.786026
H	1.143433	-3.189795	-3.450344
H	2.141940	1.888772	2.348977

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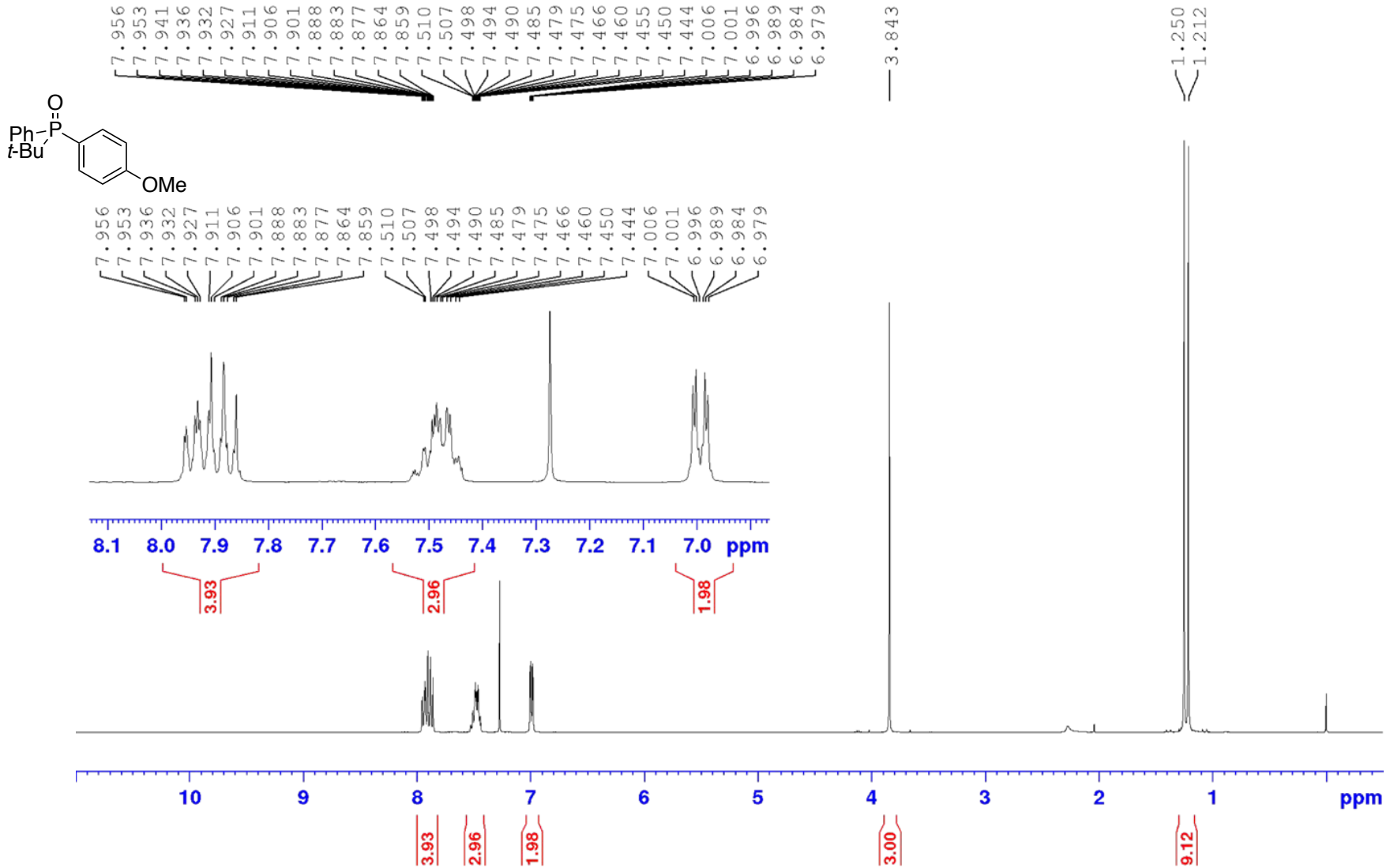
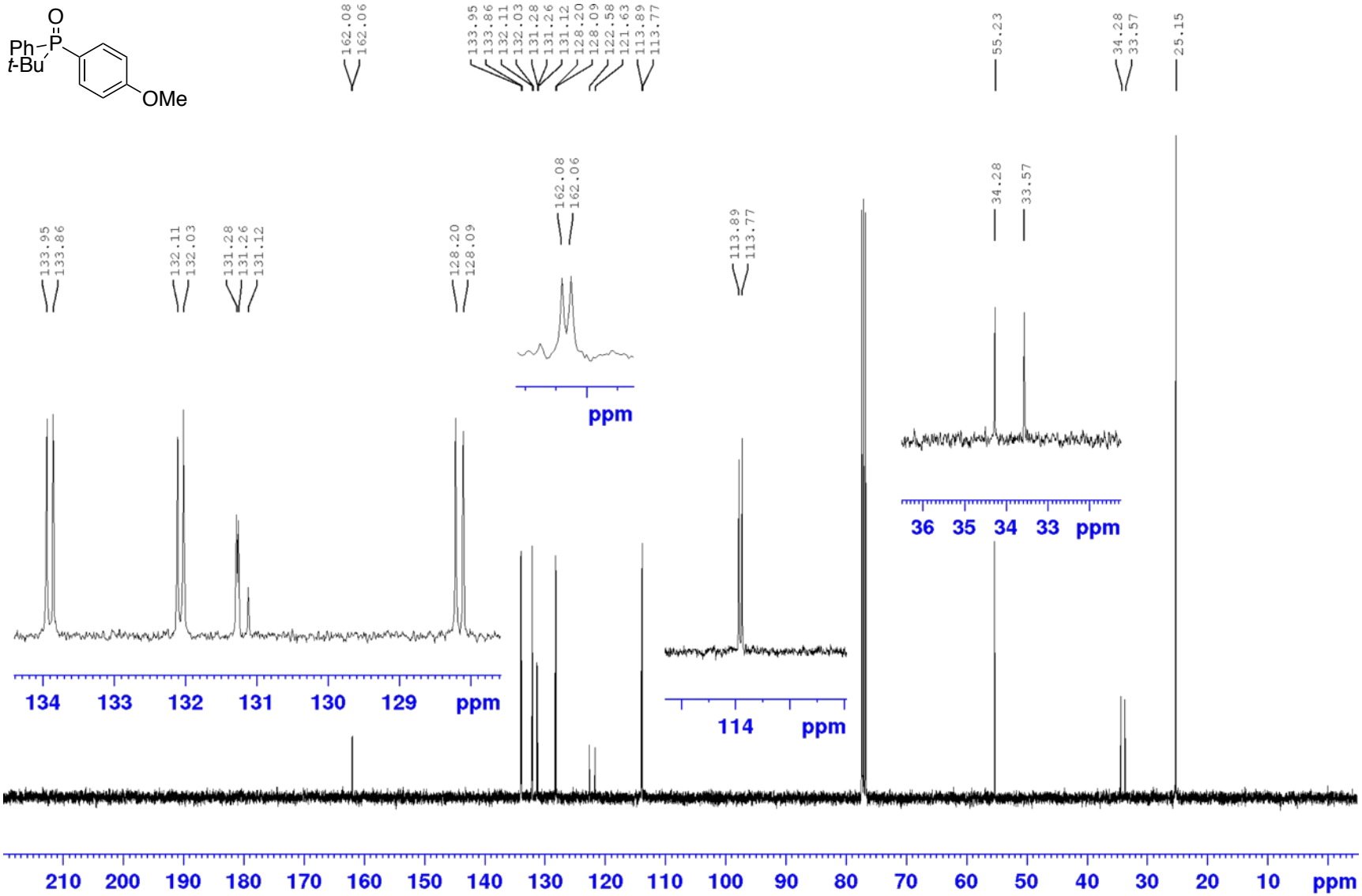
10. NMR spectra for new compounds

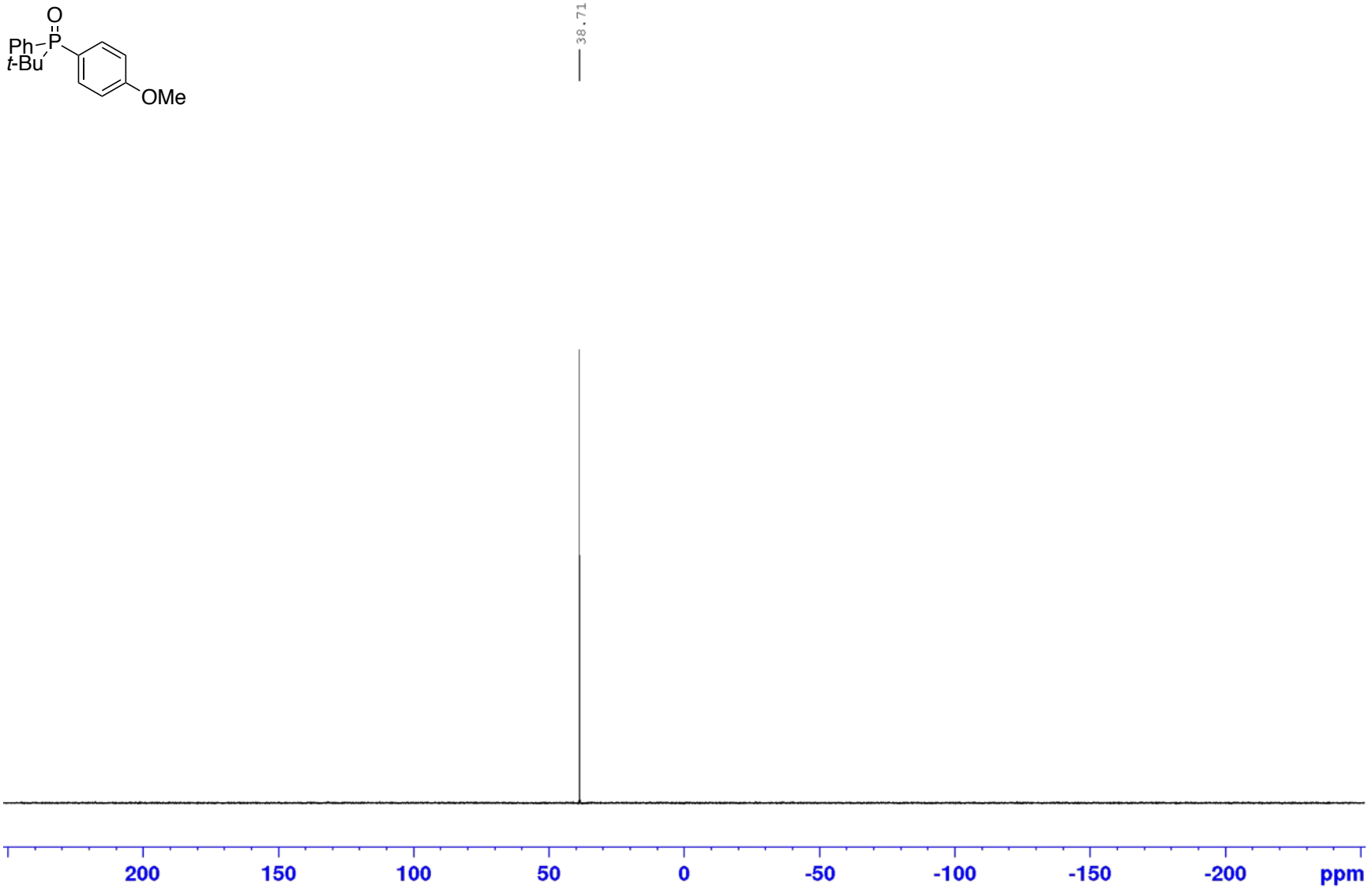
^{1}H NMR spectrum of *tert*-butyl(4-methoxyphenyl)(phenyl)phosphine oxide (**8**)



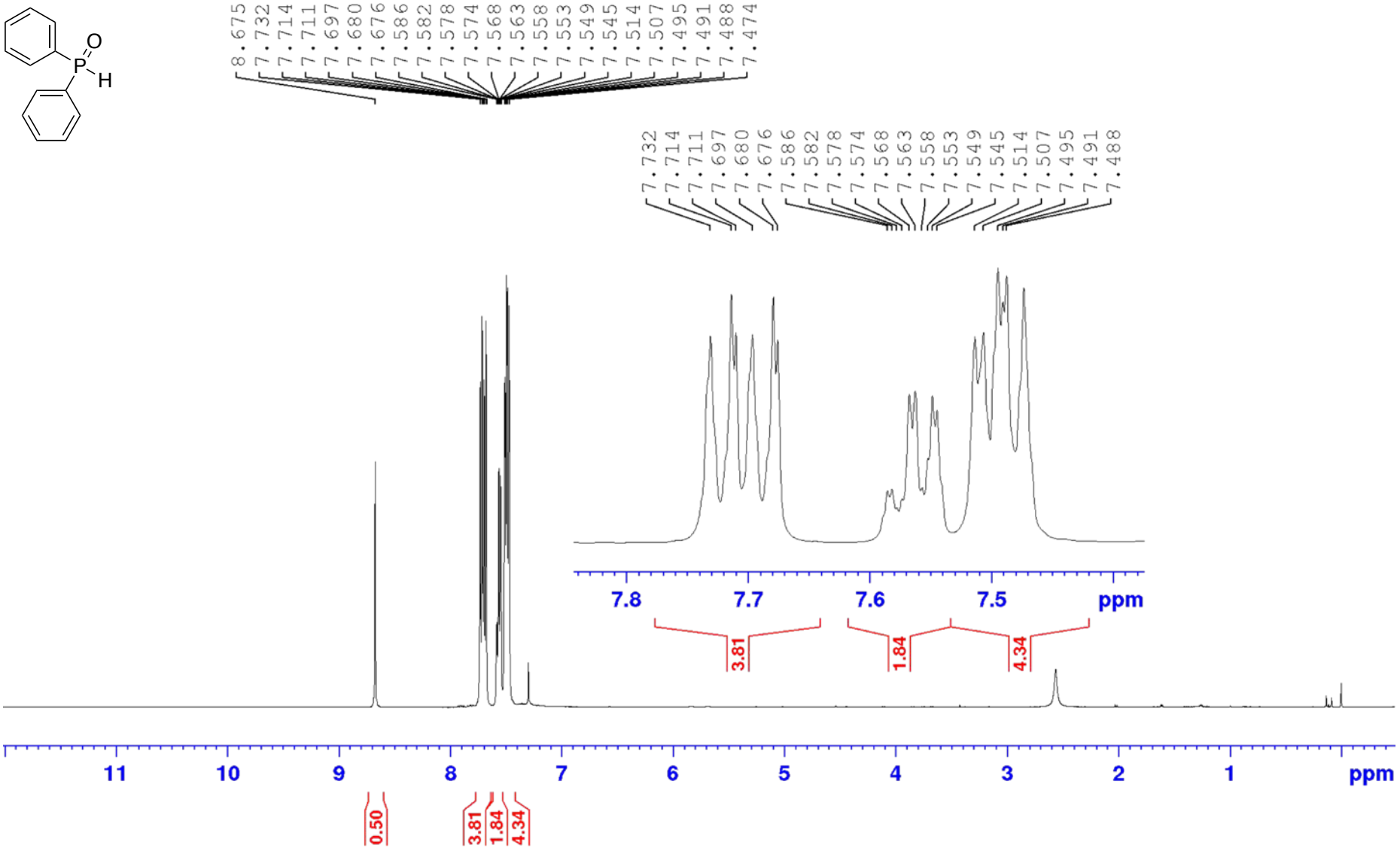
^{13}C NMR spectrum of *tert*-butyl(4-methoxyphenyl)(phenyl)phosphine oxide (**8**)



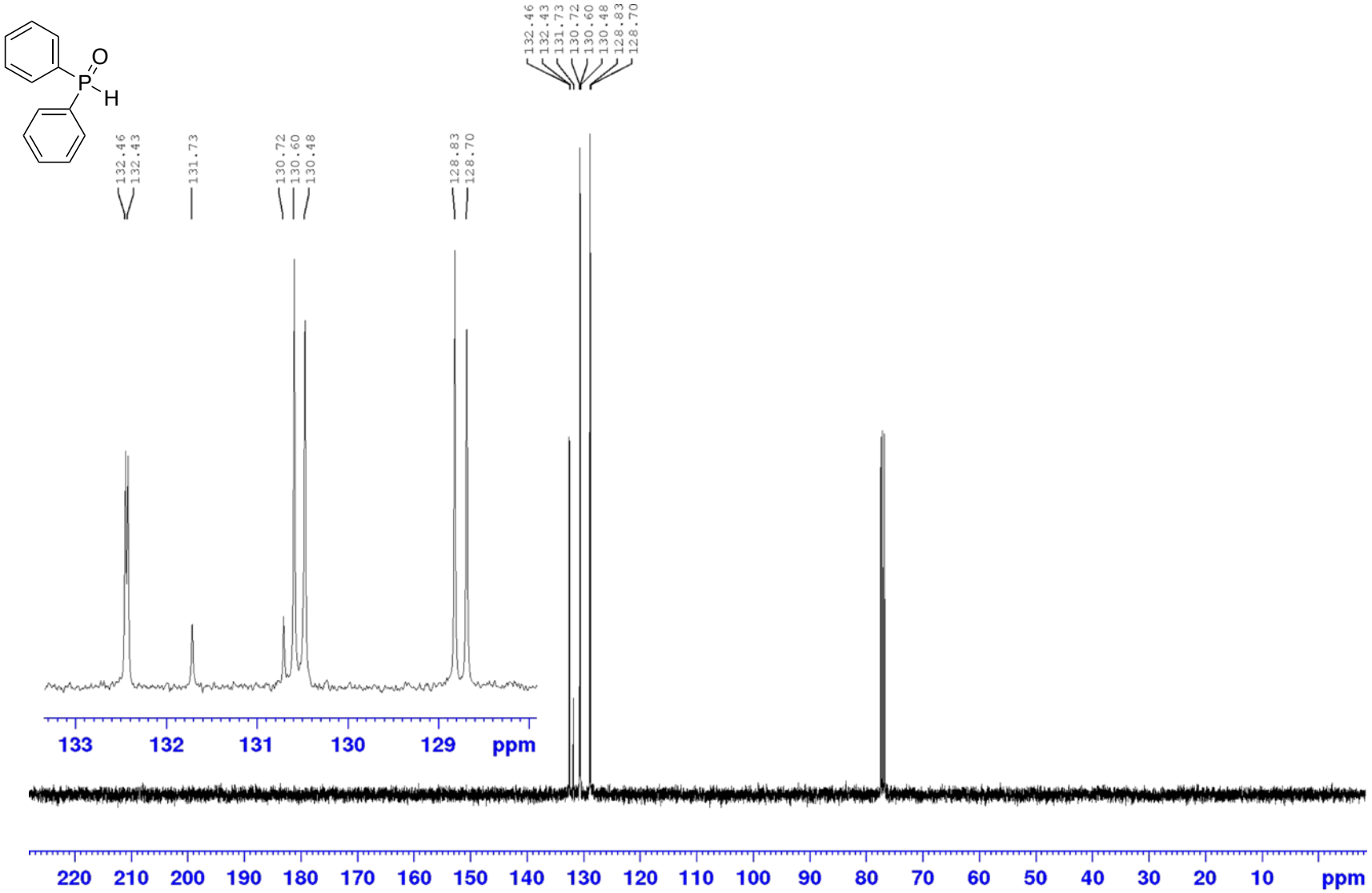
^{31}P NMR spectrum of *tert*-butyl(4-methoxyphenyl)(phenyl)phosphine oxide (**8**)



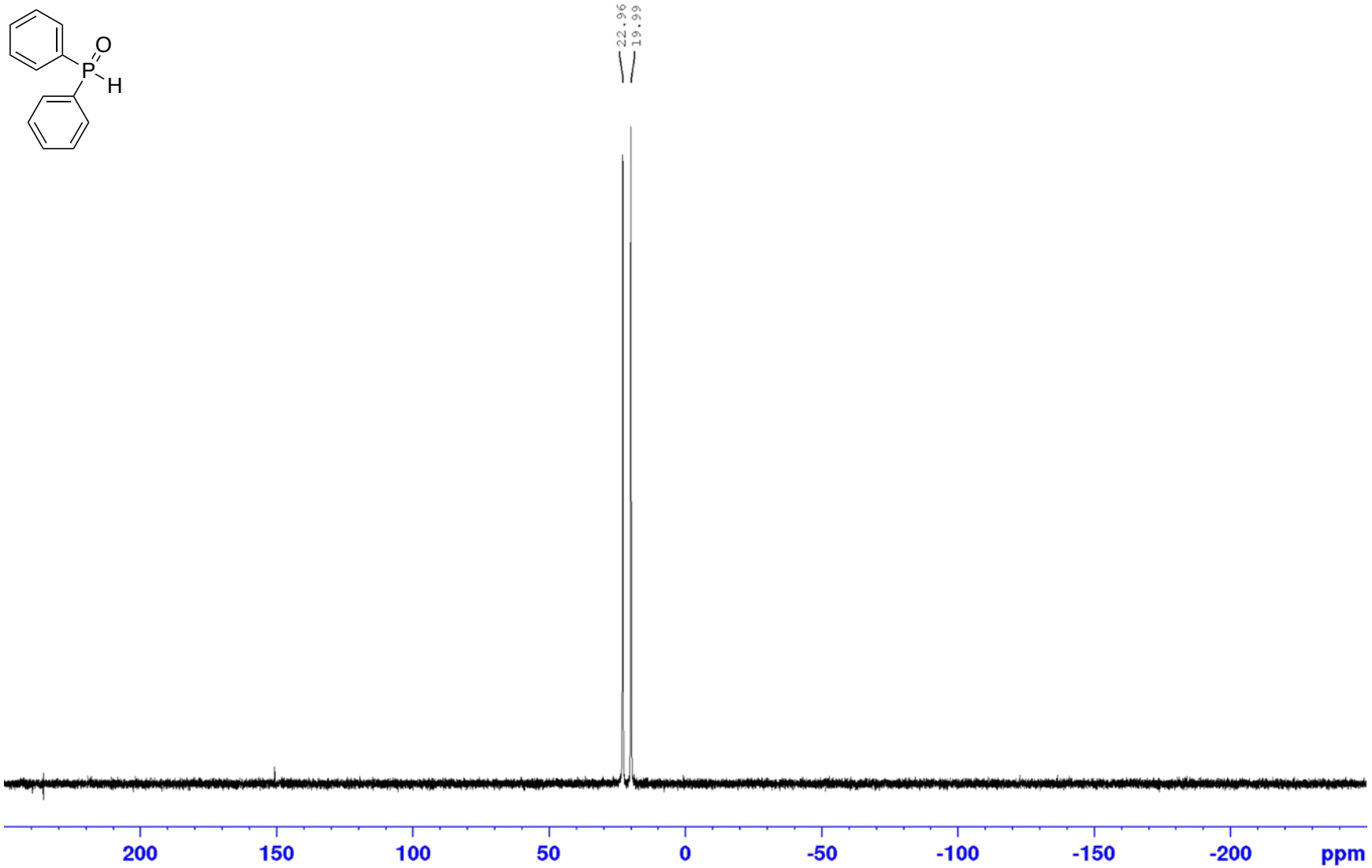
^{1}H NMR spectrum of diphenylphosphine oxide (**2a**)



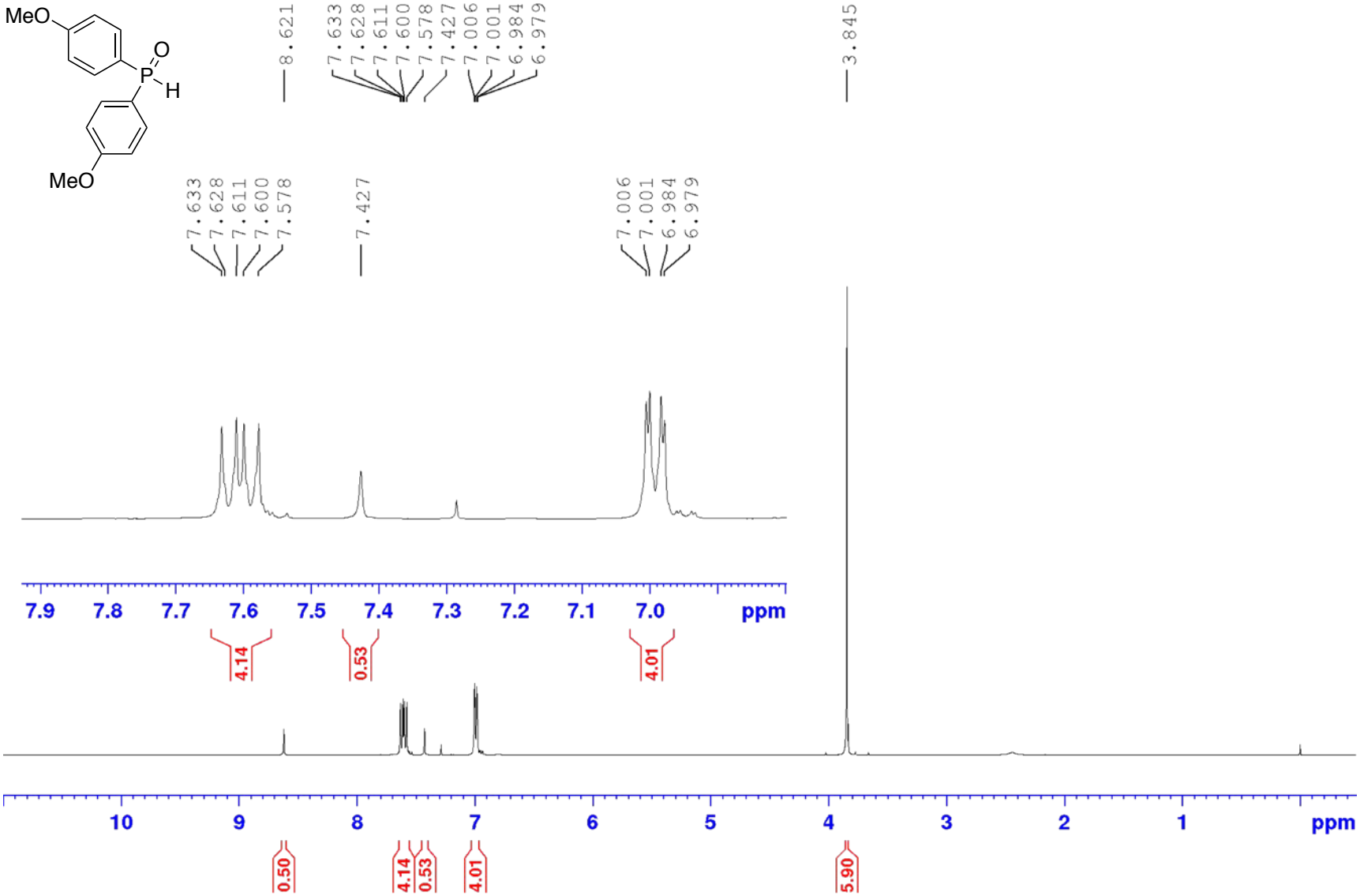
^{13}C NMR spectrum of diphenylphosphine oxide (**2a**)



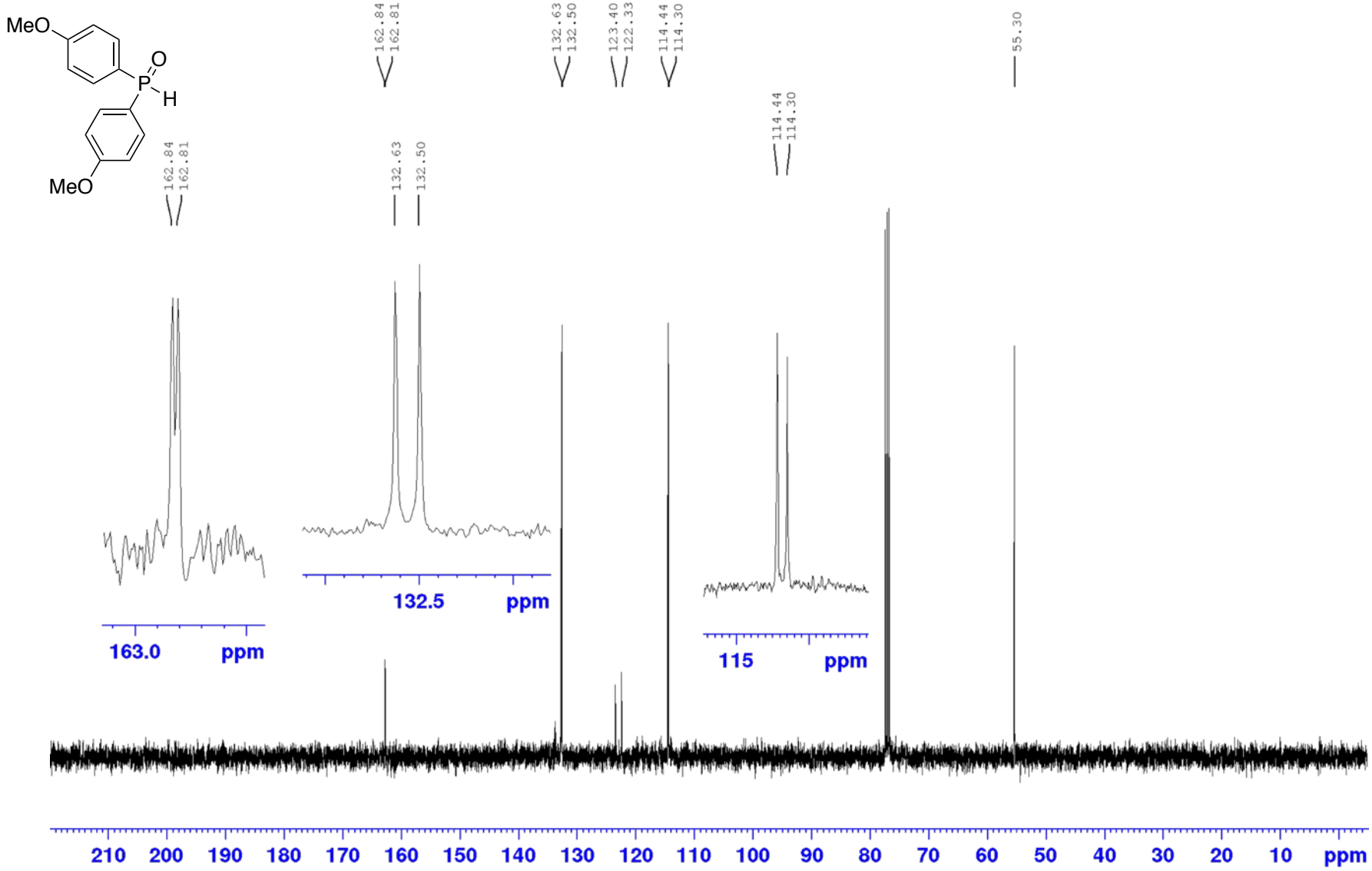
^{31}P NMR spectrum of diphenylphosphine oxide (**2a**)



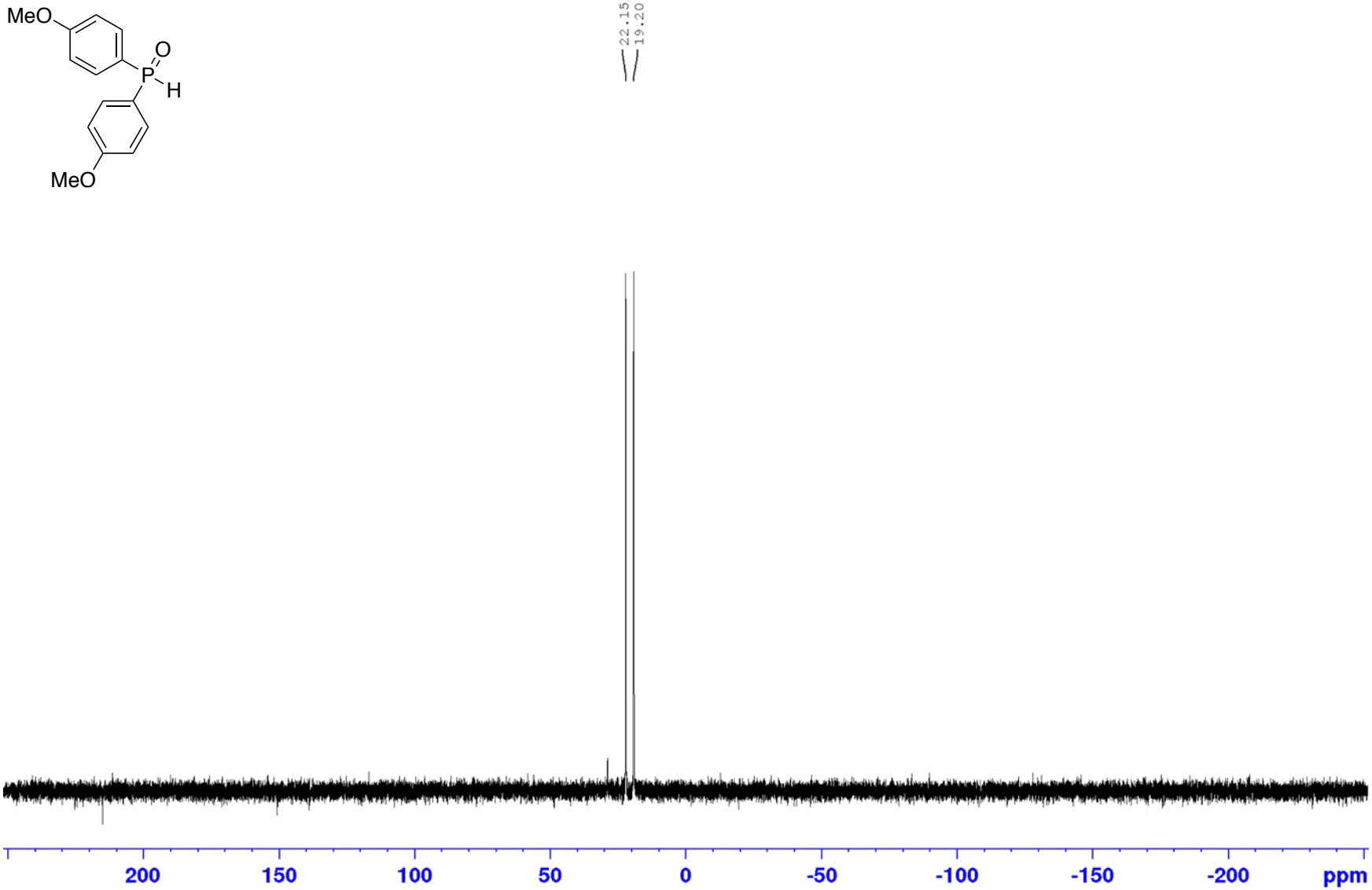
[1]H NMR spectrum of bis(4-methoxyphenyl)phosphine oxide (**2b**)



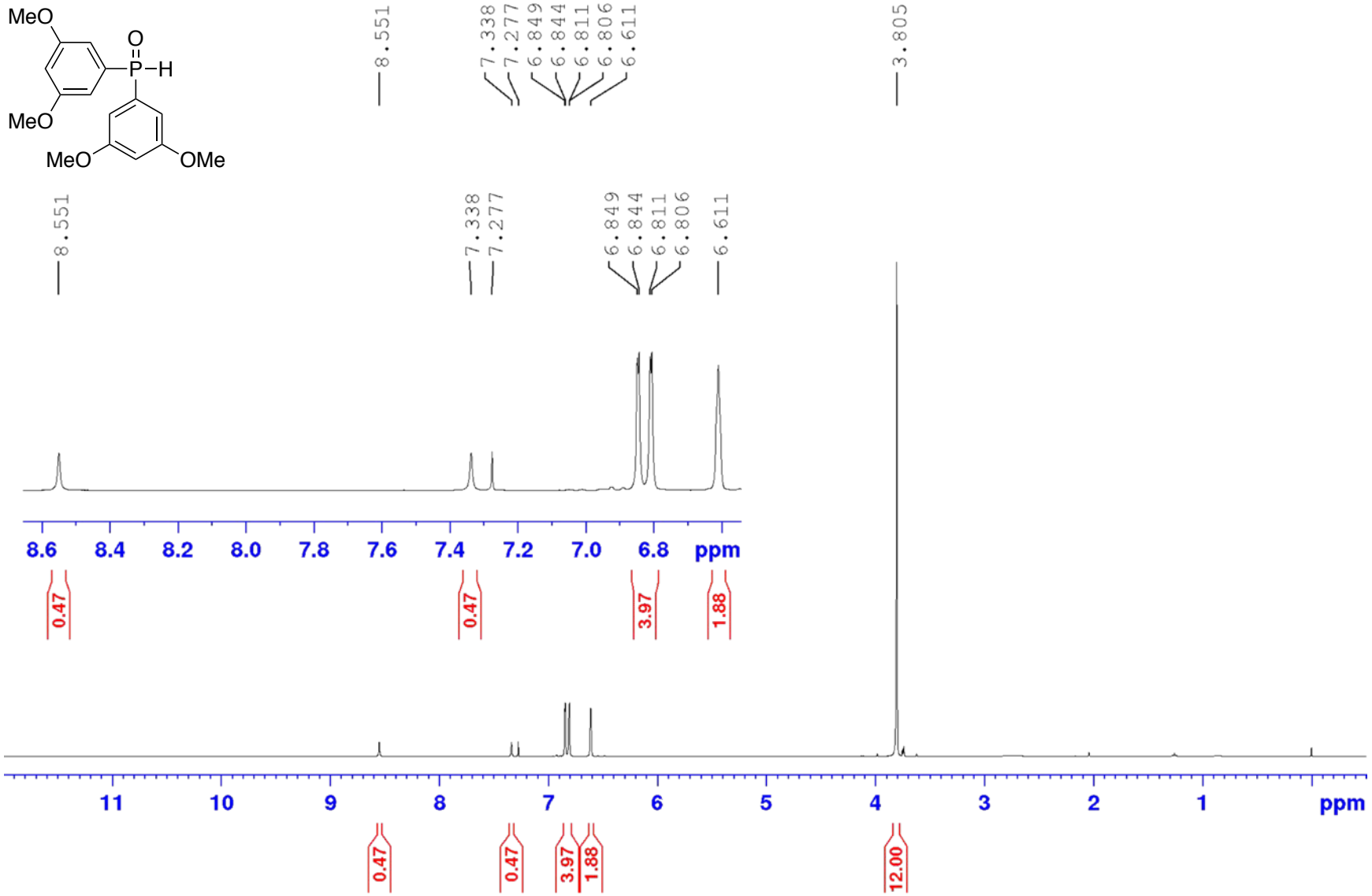
^{13}C NMR spectrum of bis(4-methoxyphenyl)phosphine oxide (**2b**)



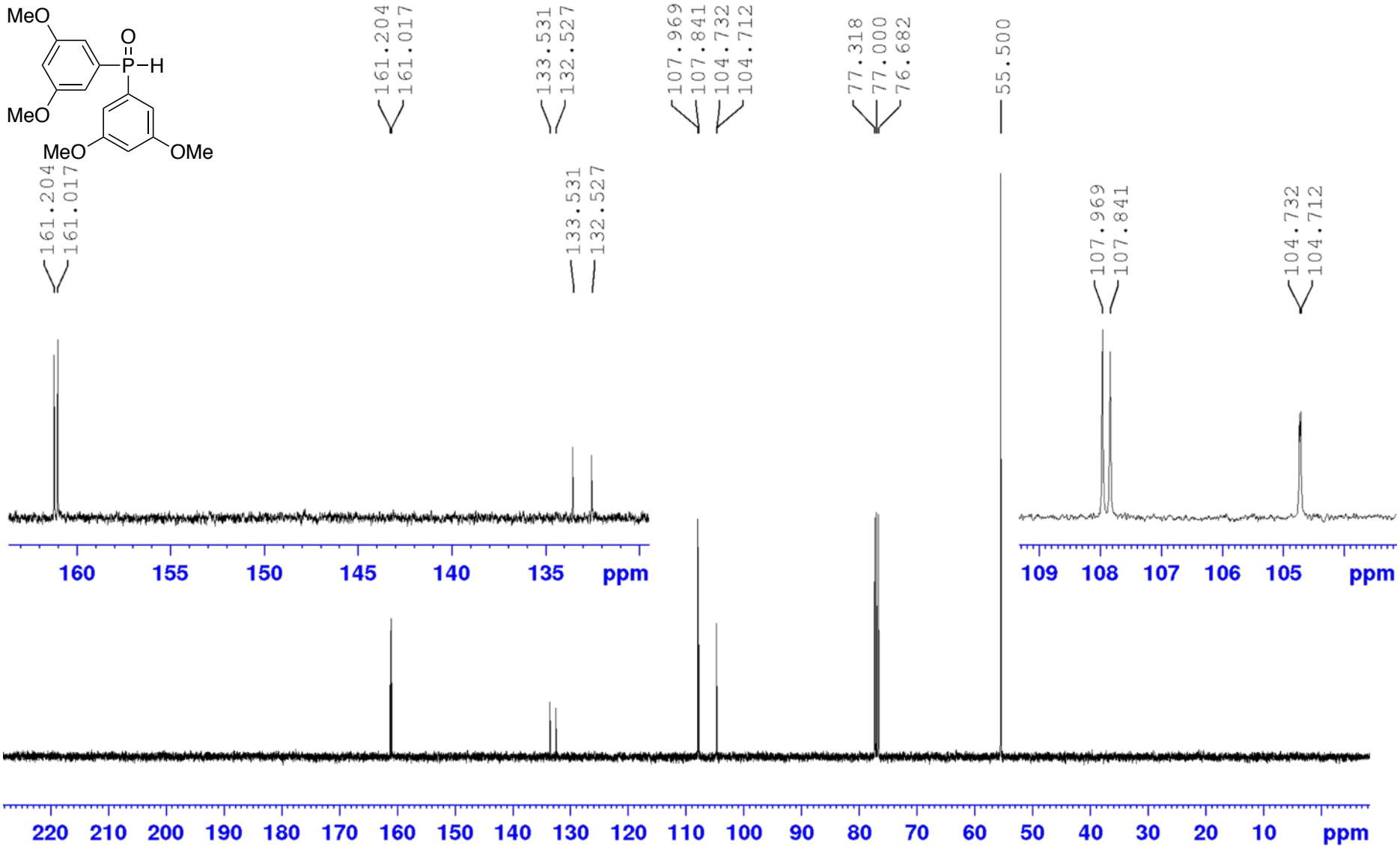
^{31}P NMR spectrum of bis(4-methoxyphenyl)phosphine oxide (**2b**)



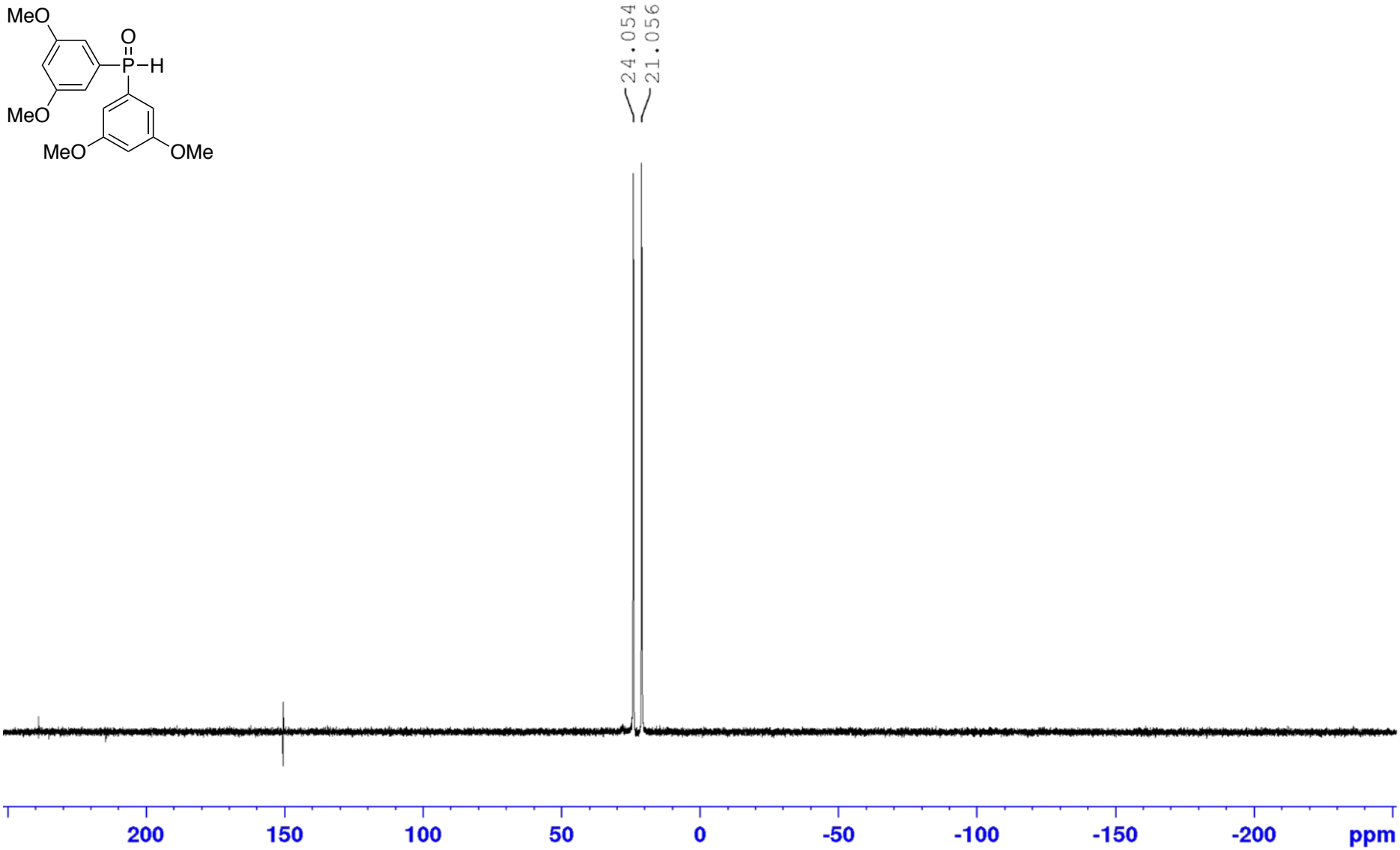
^{1}H NMR spectrum of bis(3,5-dimethoxyphenyl)phosphine oxide (**2c**)



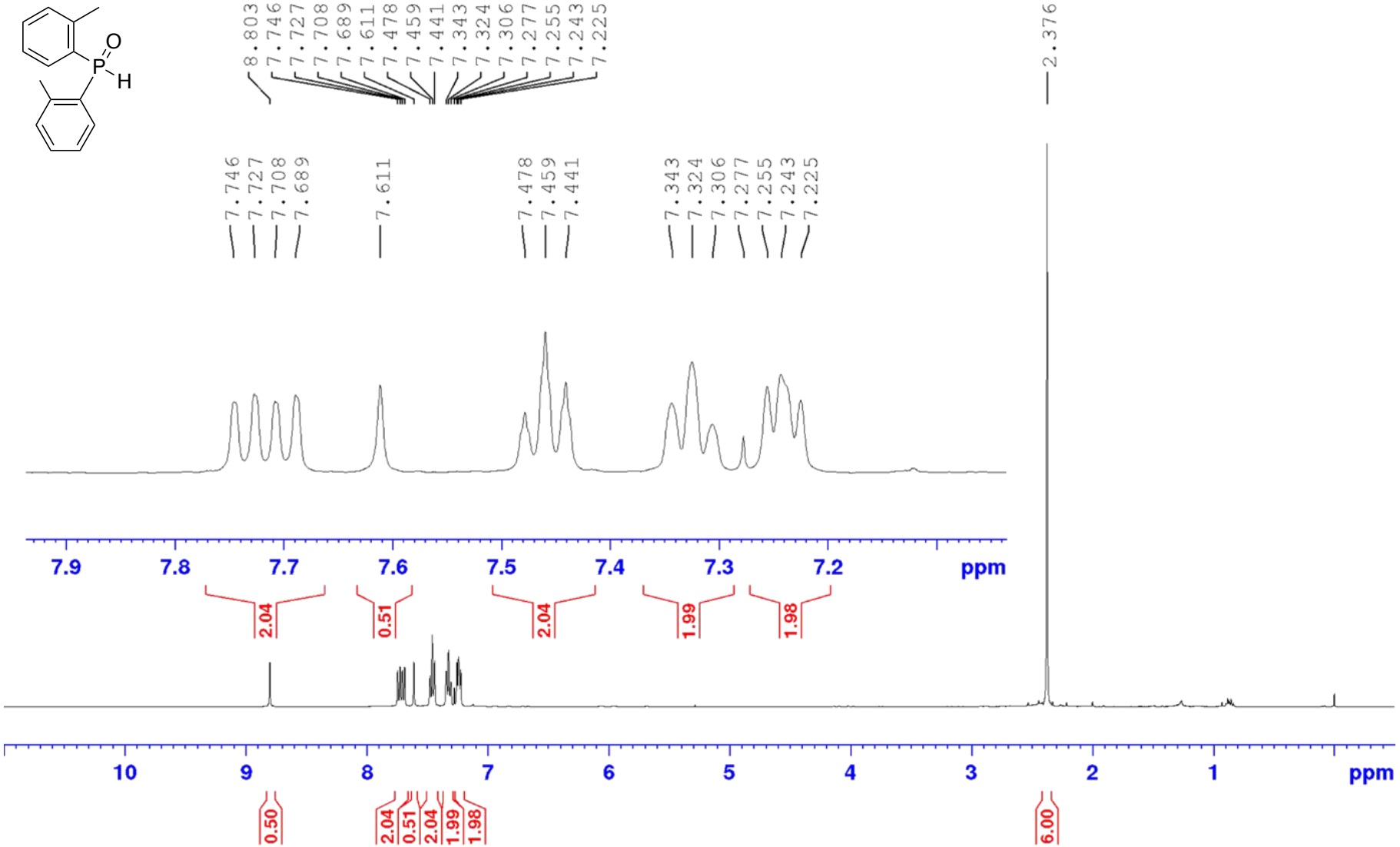
^{13}C NMR spectrum of bis(3,5-dimethoxyphenyl)phosphine oxide (**2c**)



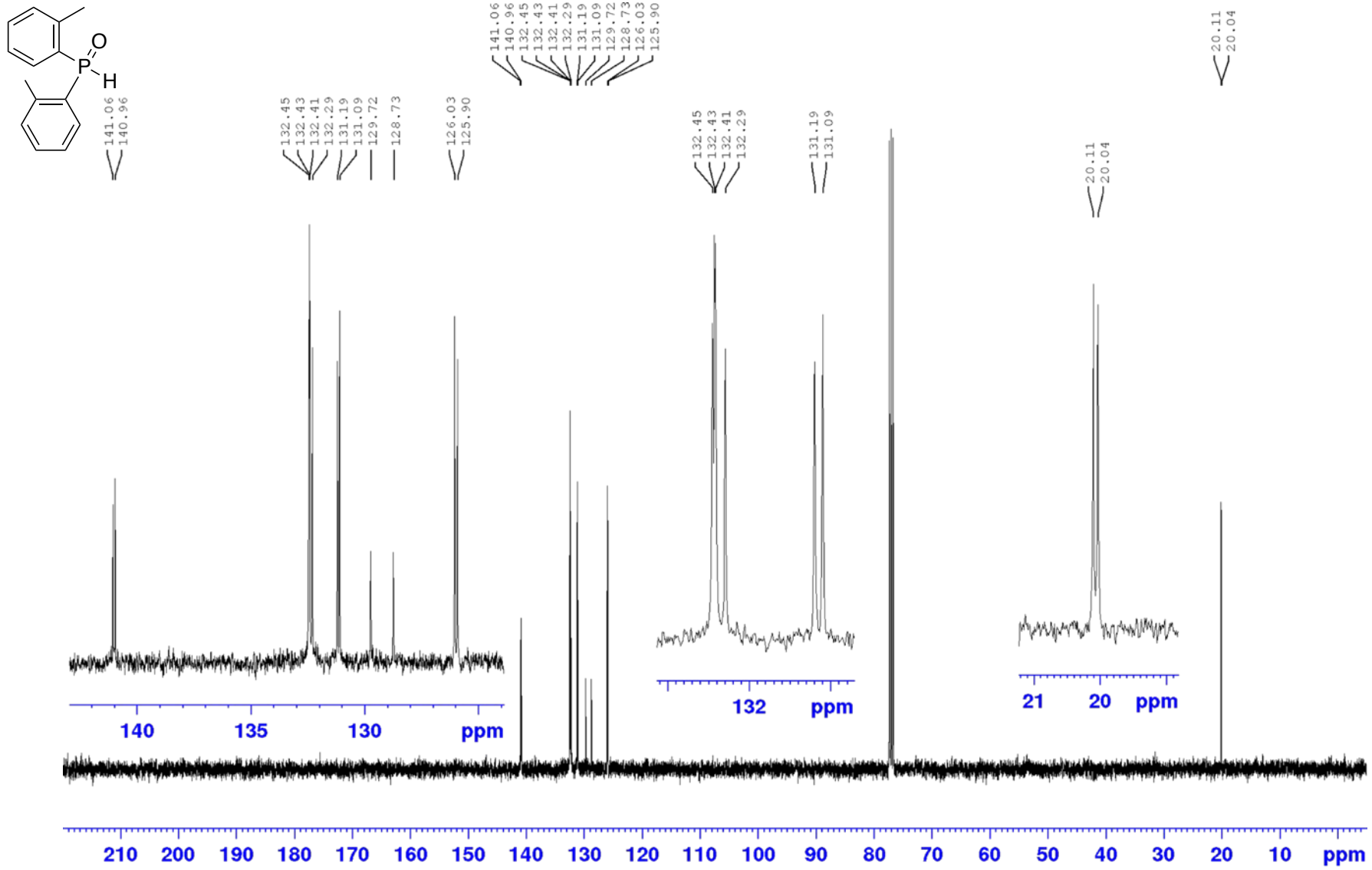
^{31}P NMR spectrum of bis(3,5-dimethoxyphenyl)phosphine oxide (**2c**)



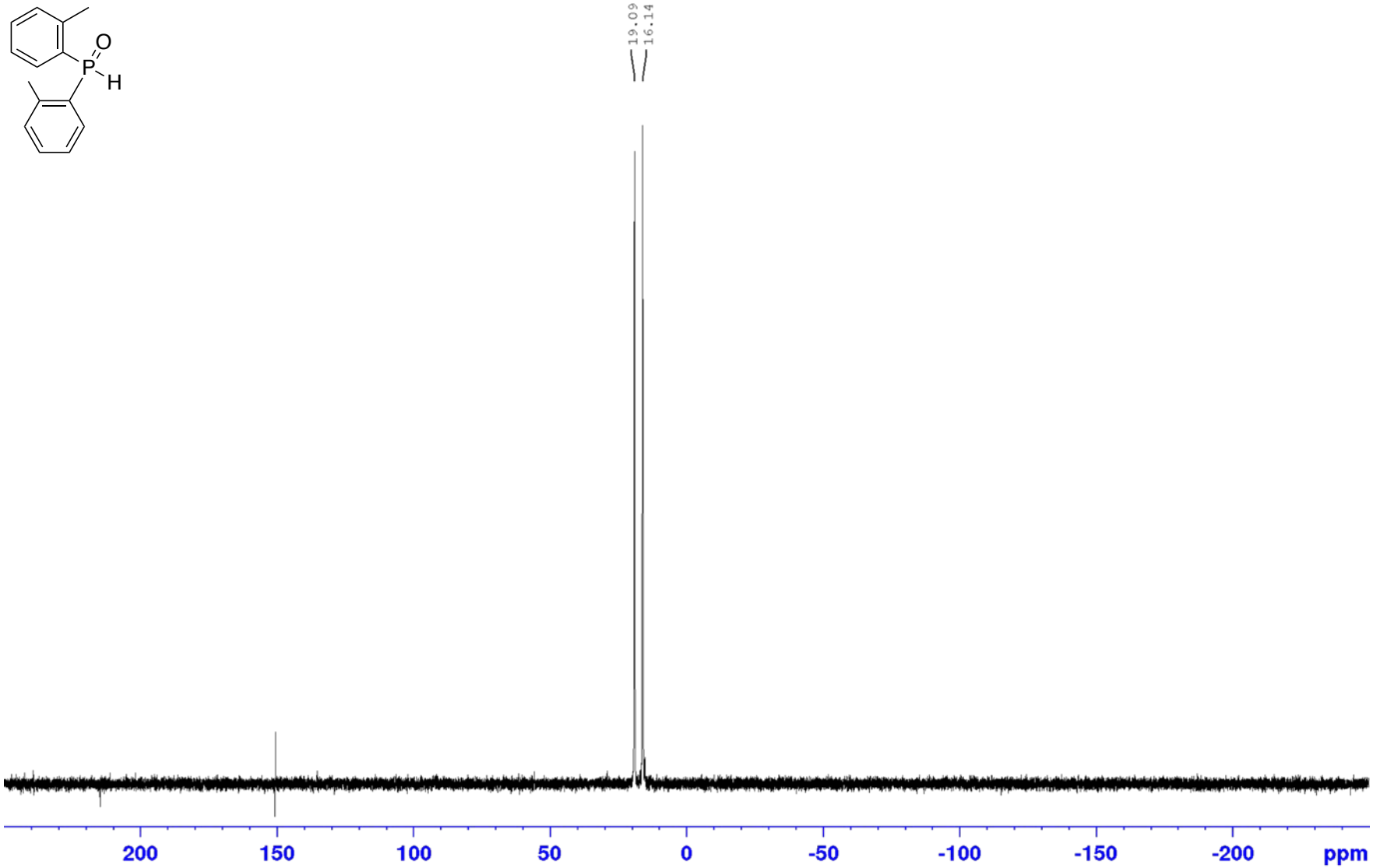
[1]H NMR spectrum of di-*o*-tolylphosphine oxide **2d**



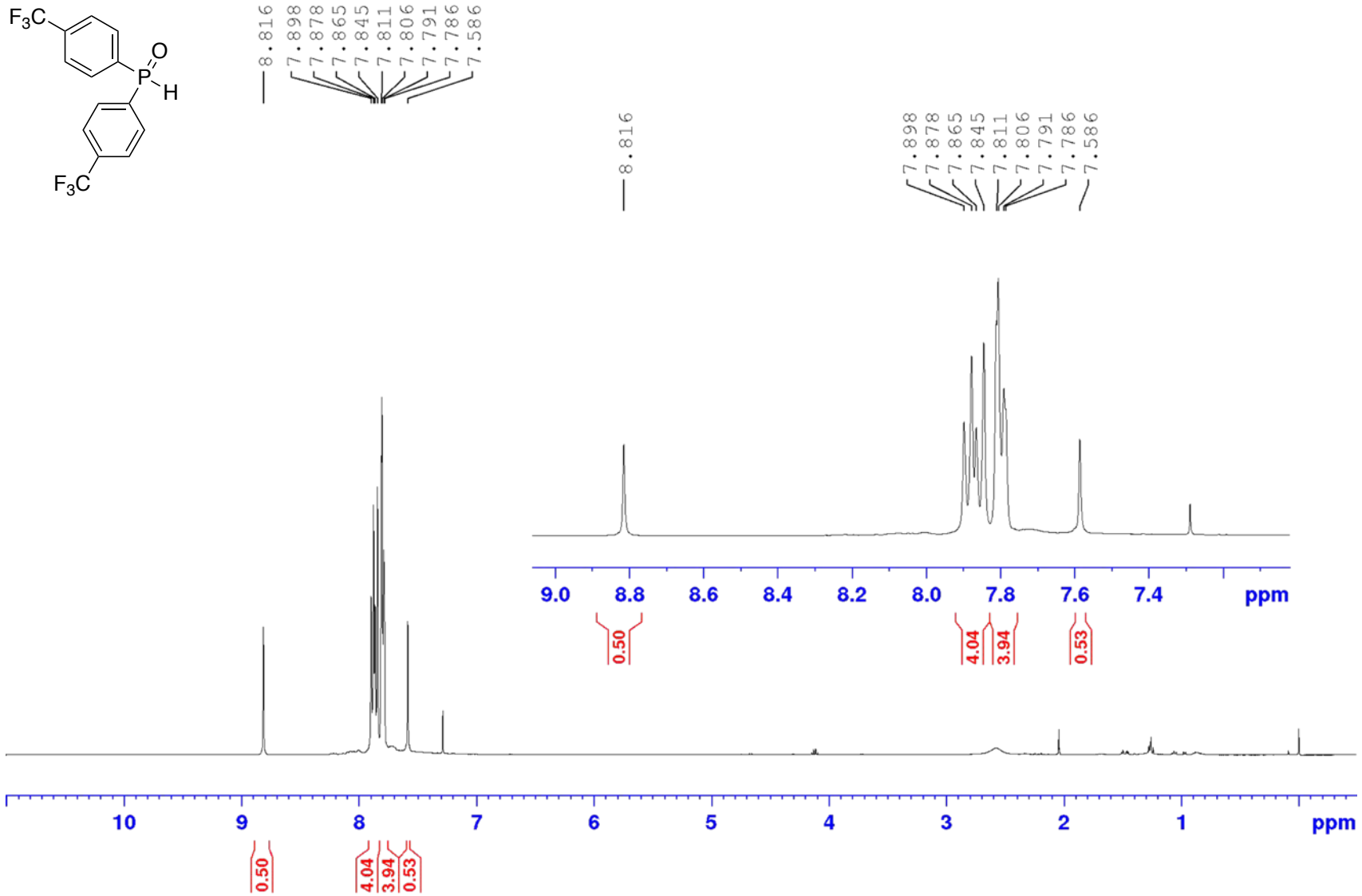
^{13}C NMR spectrum of di-*o*-tolylphosphine oxide (**2d**)



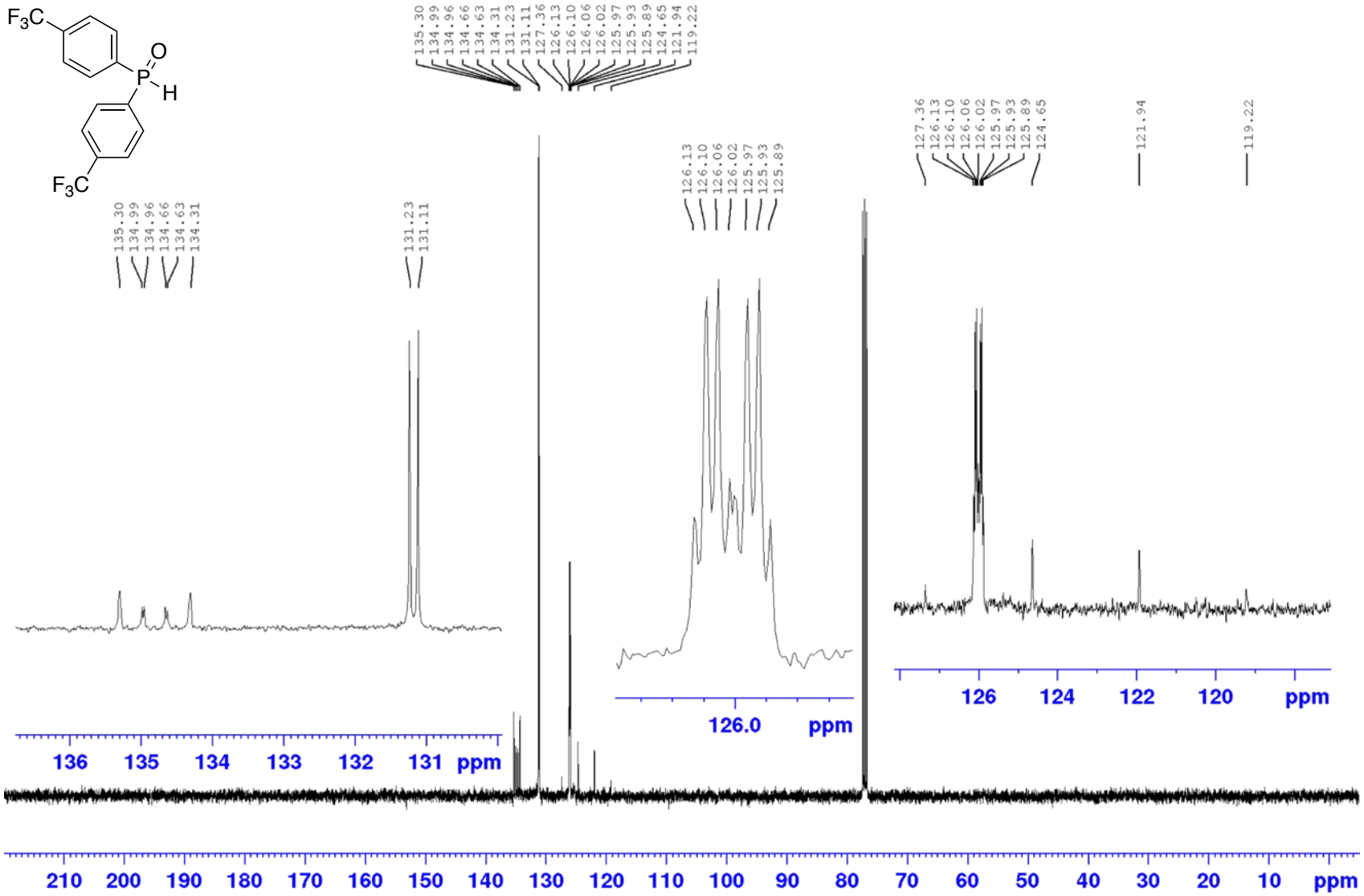
^{31}P NMR spectrum of di-*o*-tolylphosphine oxide (**2d**)



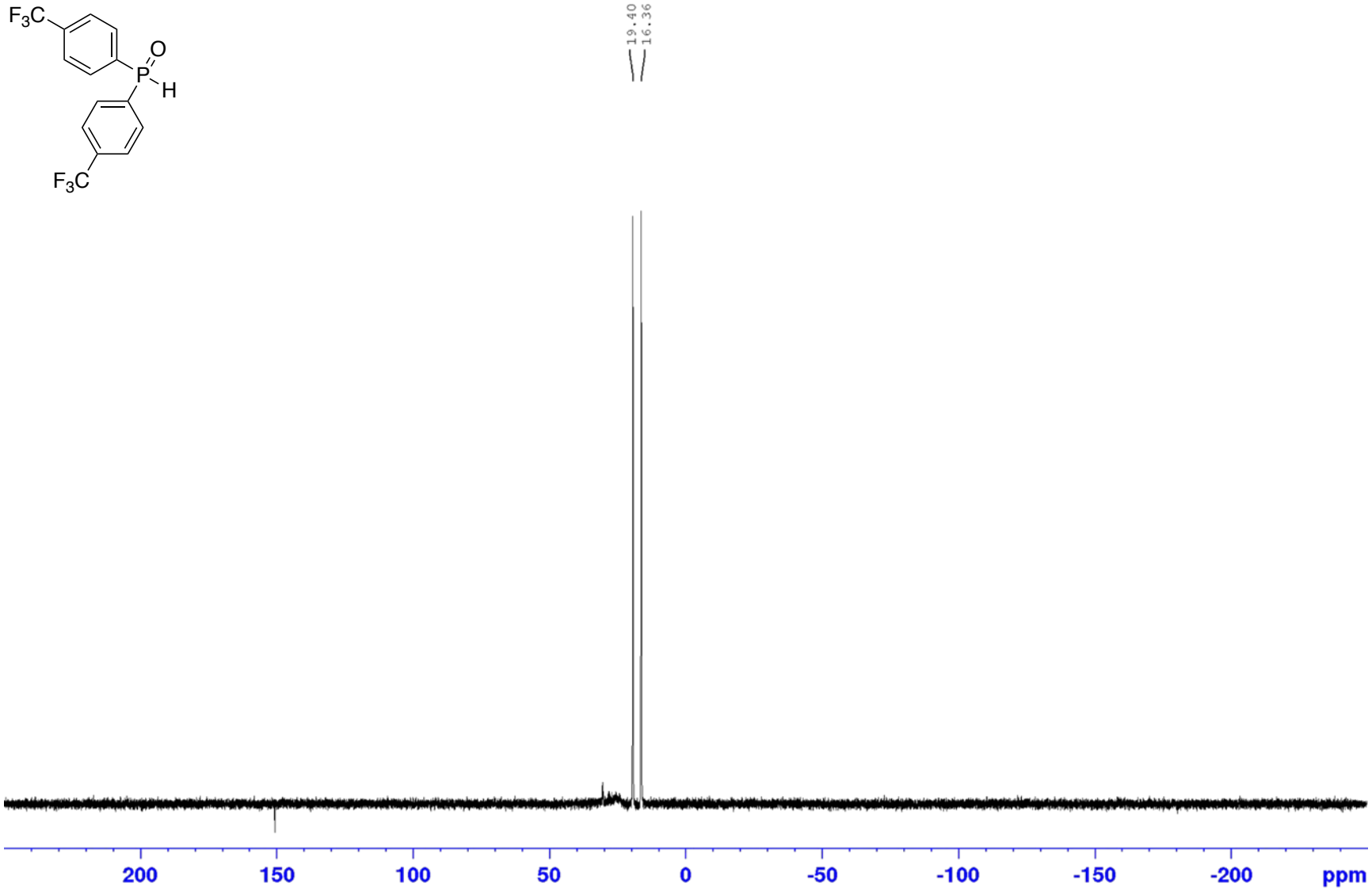
^{1}H NMR spectrum of bis(4-(trifluoromethyl)phenyl)phosphine oxide (**2e**)



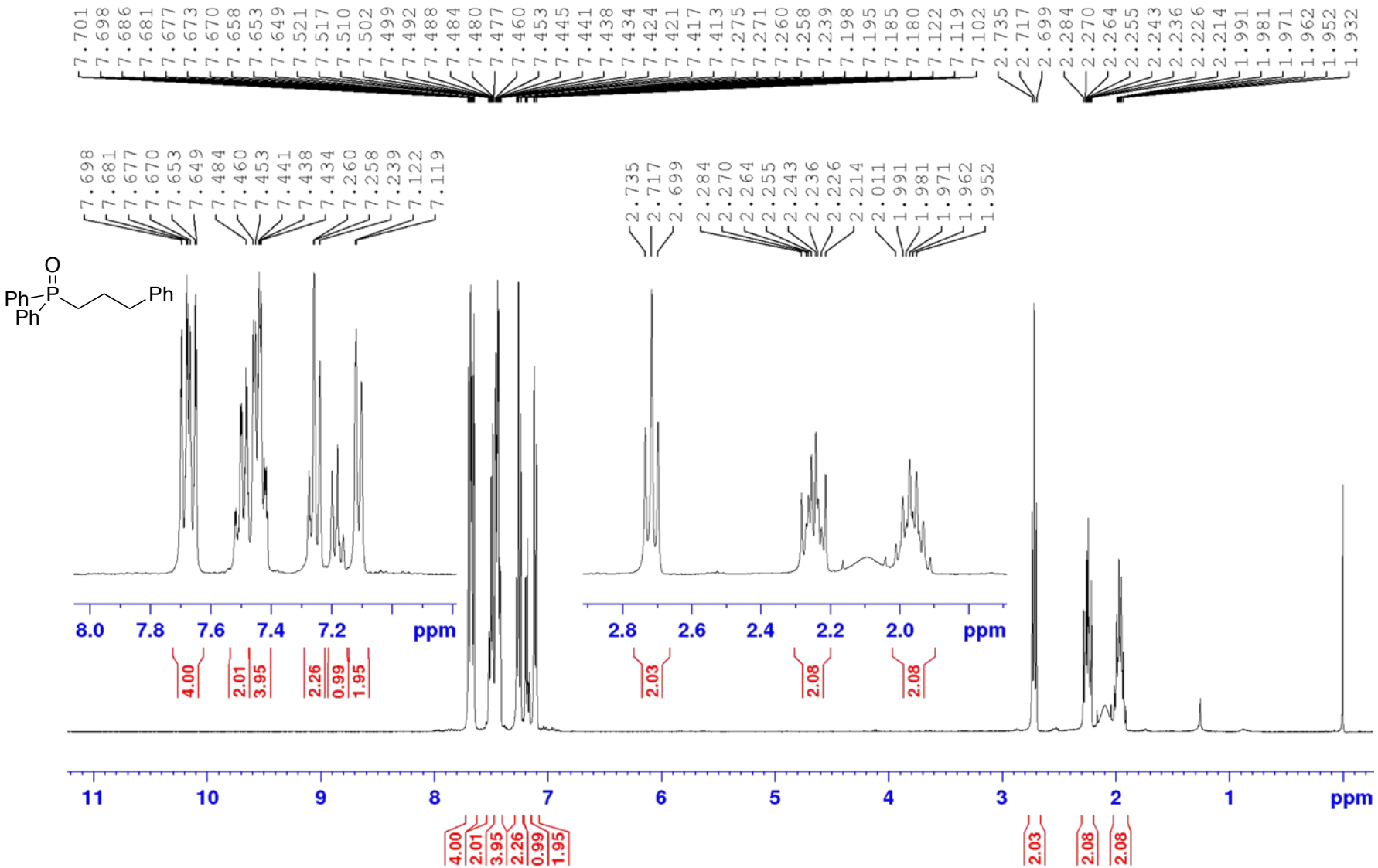
^{13}C NMR spectrum of bis(4-(trifluoromethyl)phenyl)phosphine oxide (**2e**)



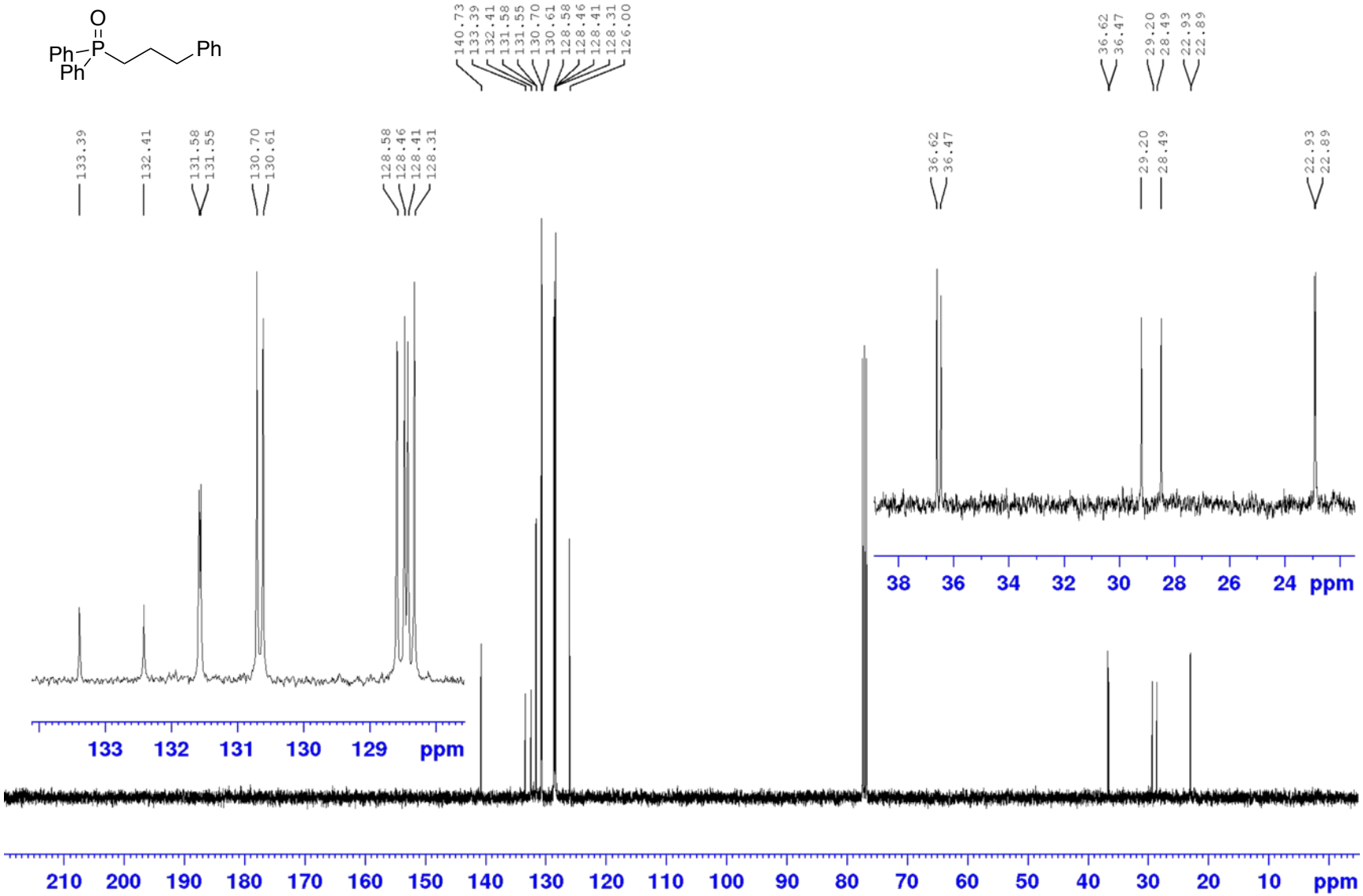
^{31}P NMR spectrum of bis(4-(trifluoromethyl)phenyl)phosphine oxide (**2e**)



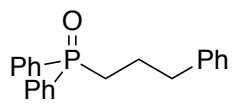
^{1}H NMR spectrum of diphenyl(3-phenylpropyl)phosphine oxide (**4aa**)



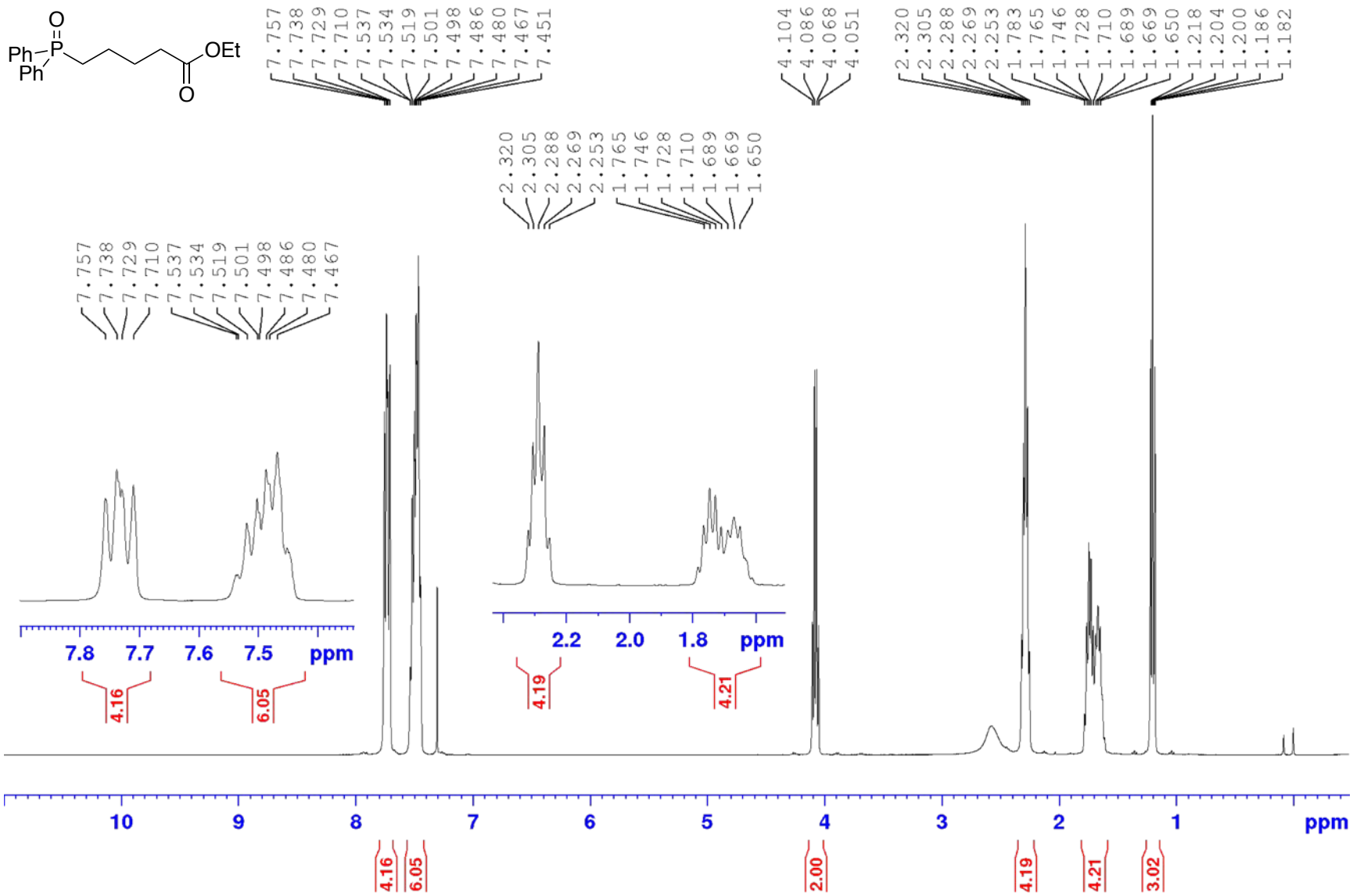
^{13}C NMR spectrum of diphenyl(3-phenylpropyl)phosphine oxide (**4aa**)



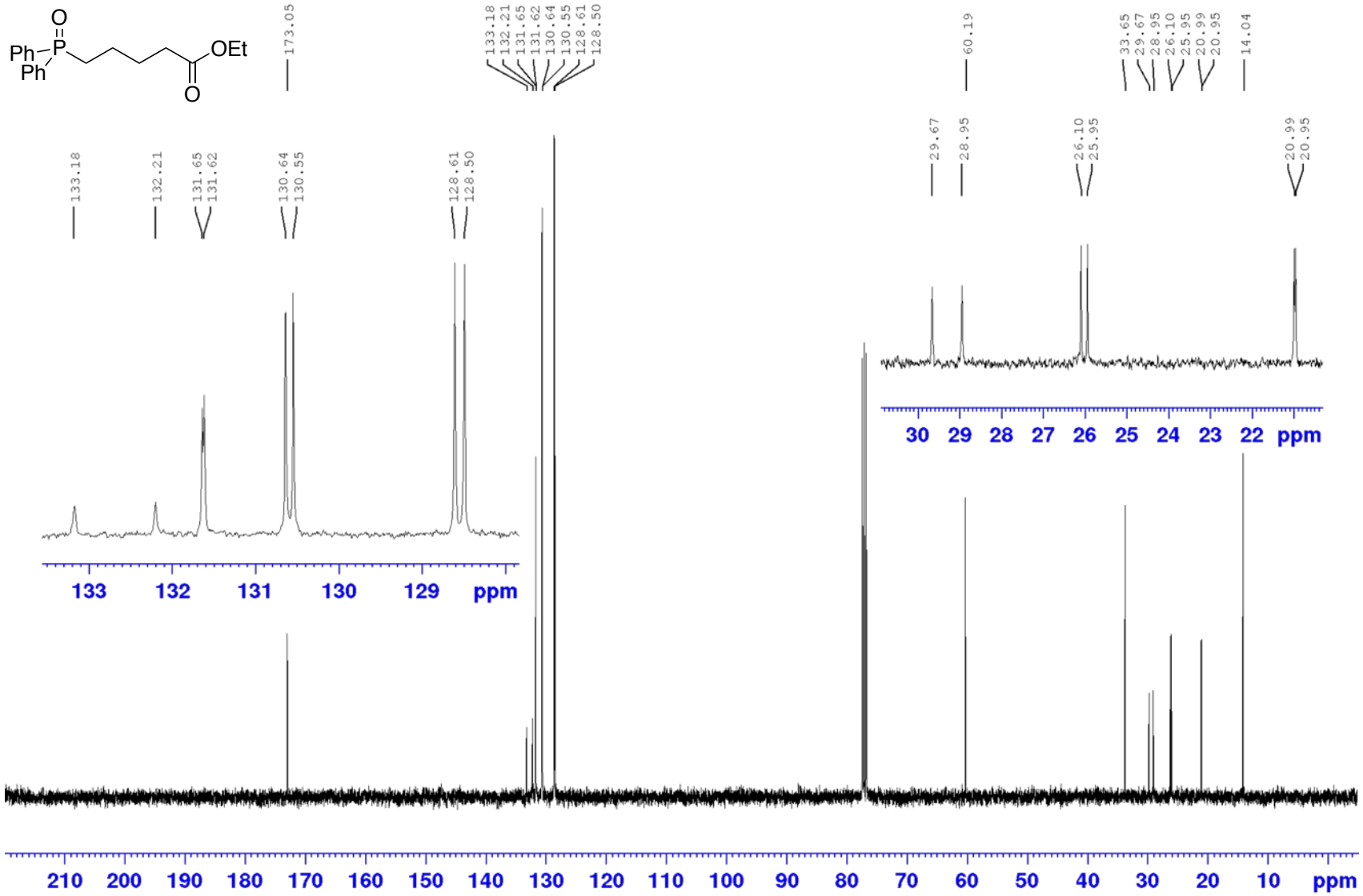
^{31}P NMR spectrum of diphenyl(3-phenylpropyl)phosphine oxide (**4aa**)



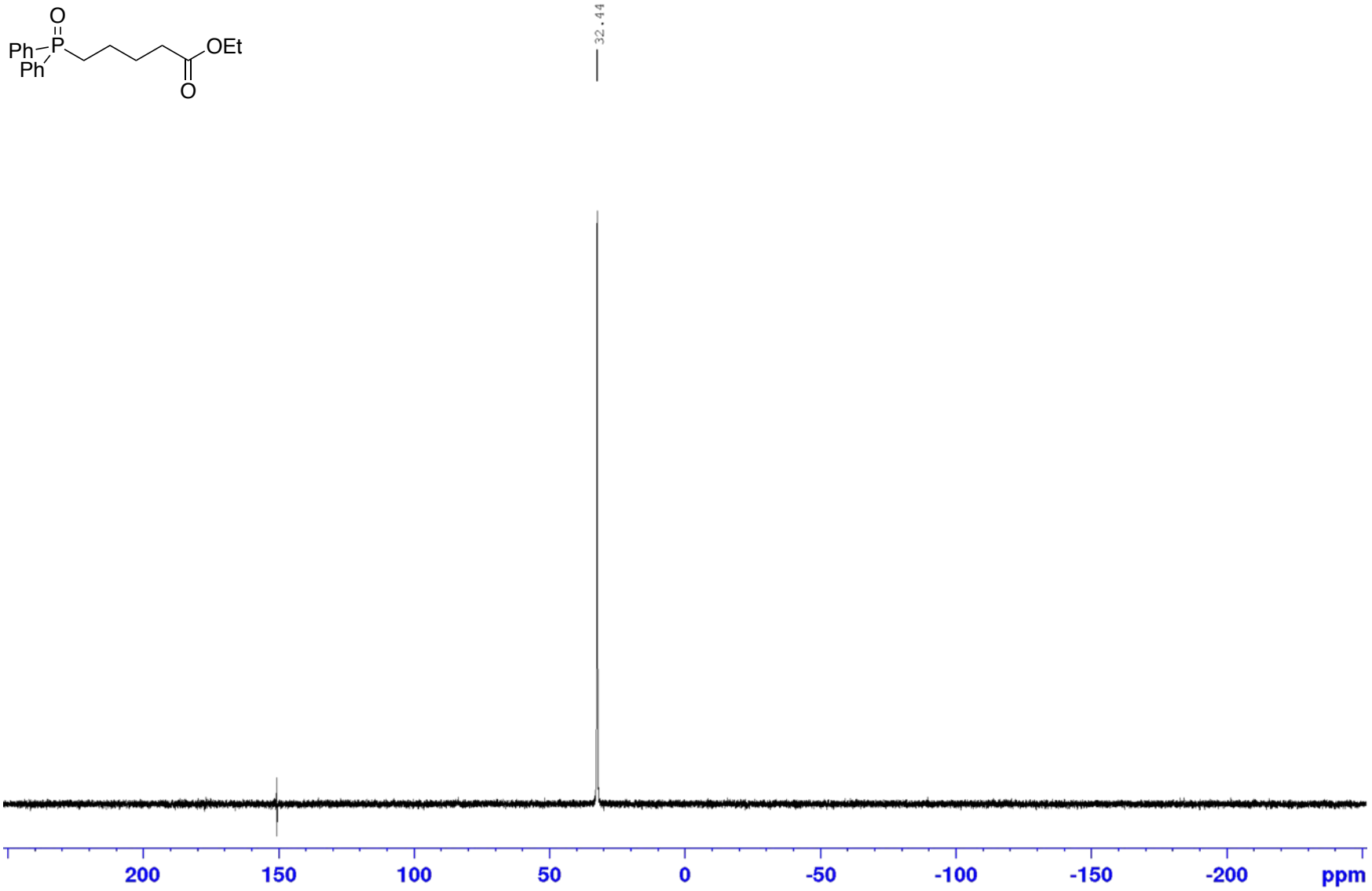
[1]H NMR spectrum of ethyl 5-(diphenylphosphoryl)pentanoate (**4ab**)



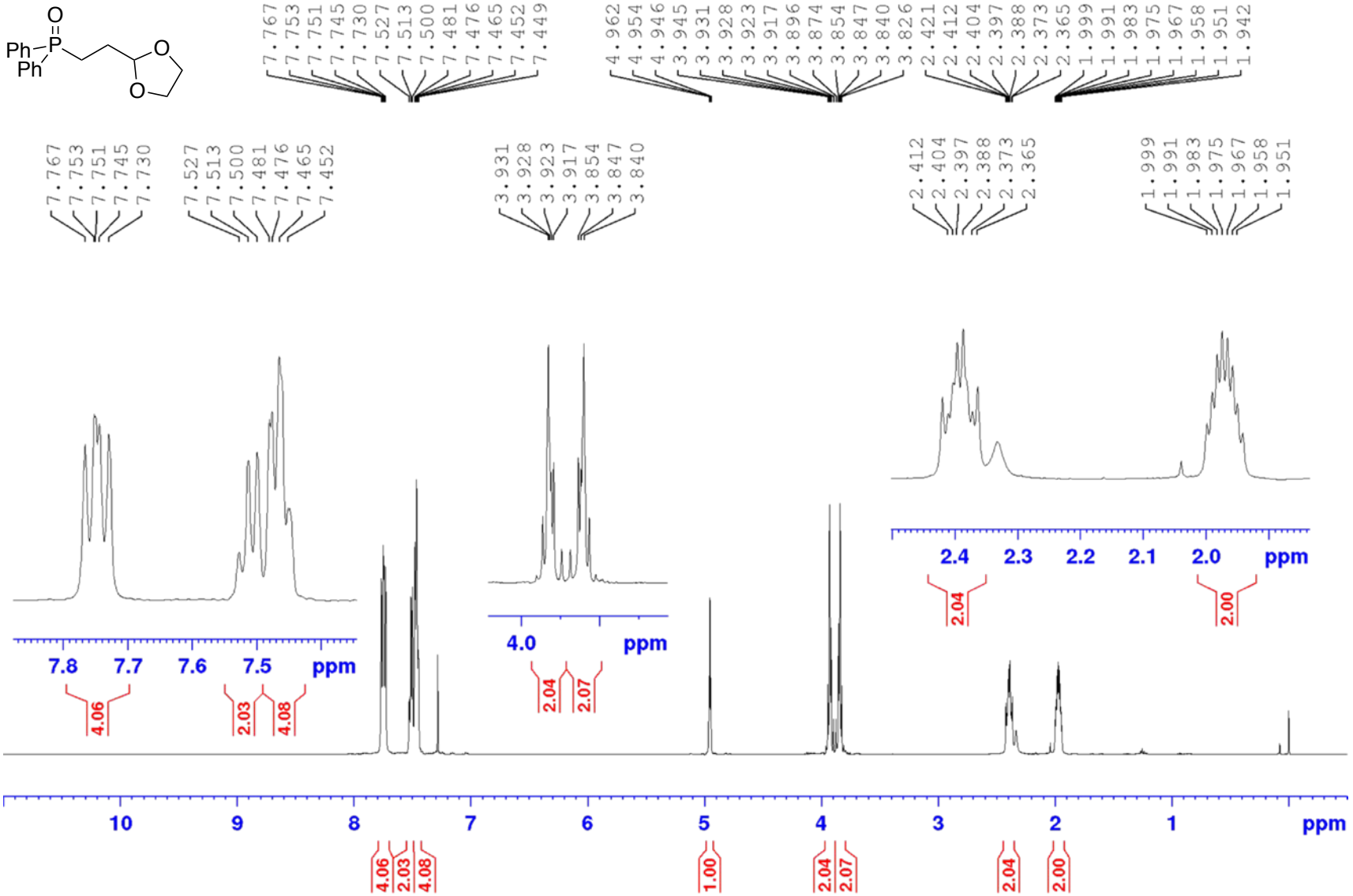
^{13}C NMR spectrum of ethyl 5-(diphenylphosphoryl)pentanoate (**4ab**)



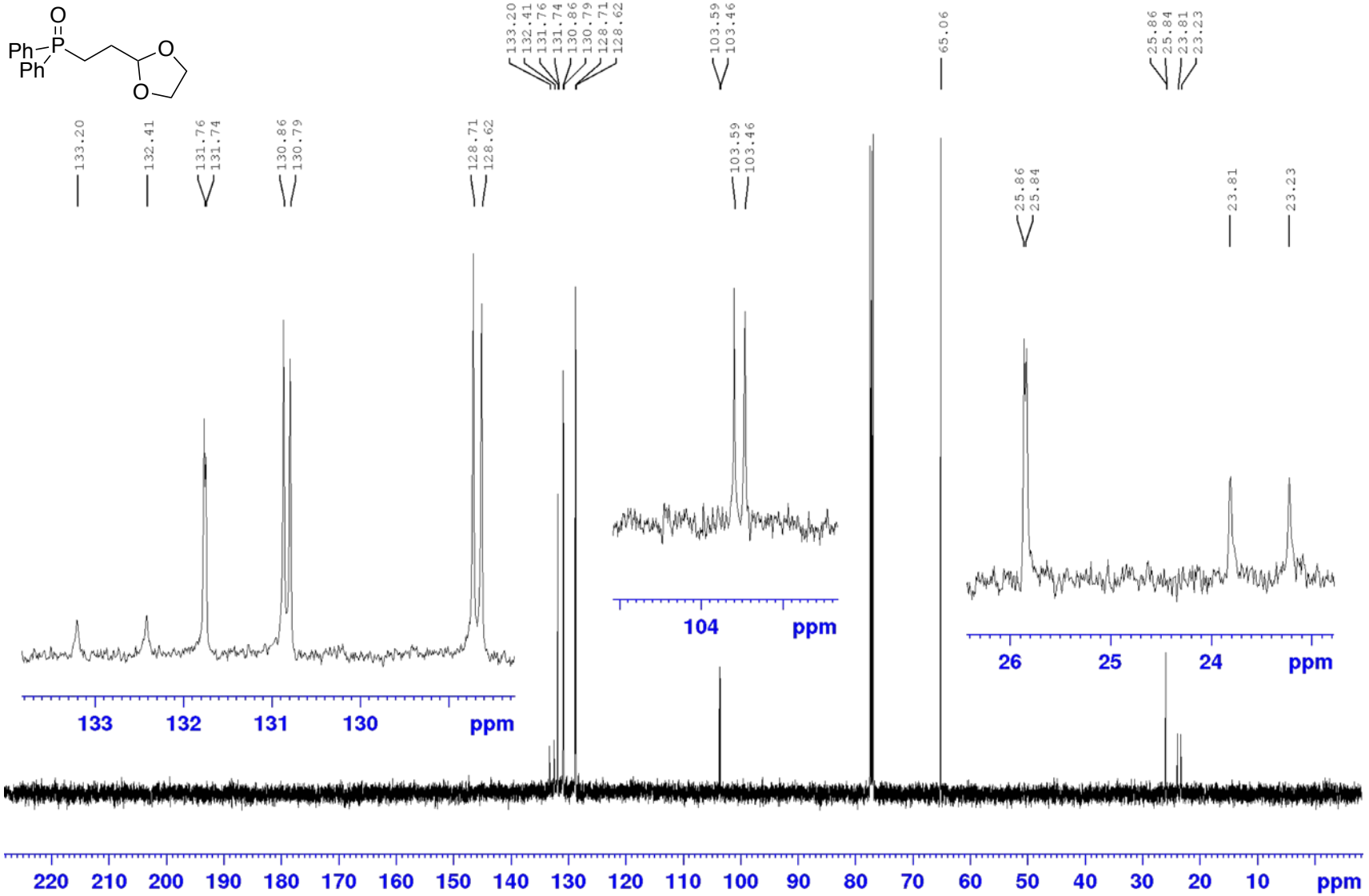
^{31}P NMR spectrum of ethyl 5-(diphenylphosphoryl)pentanoate (**4ab**)



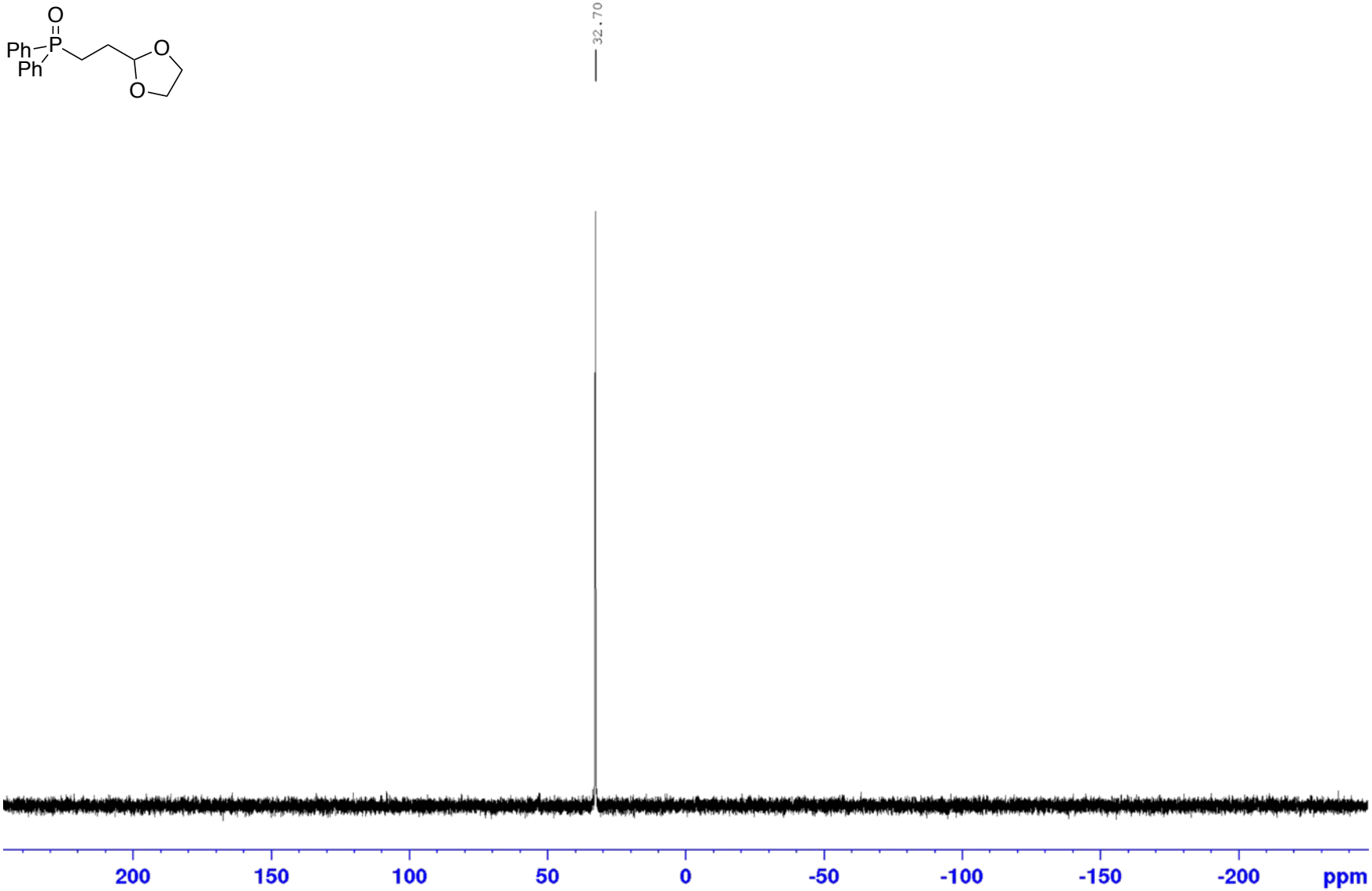
^{1}H NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide (**4ac**)



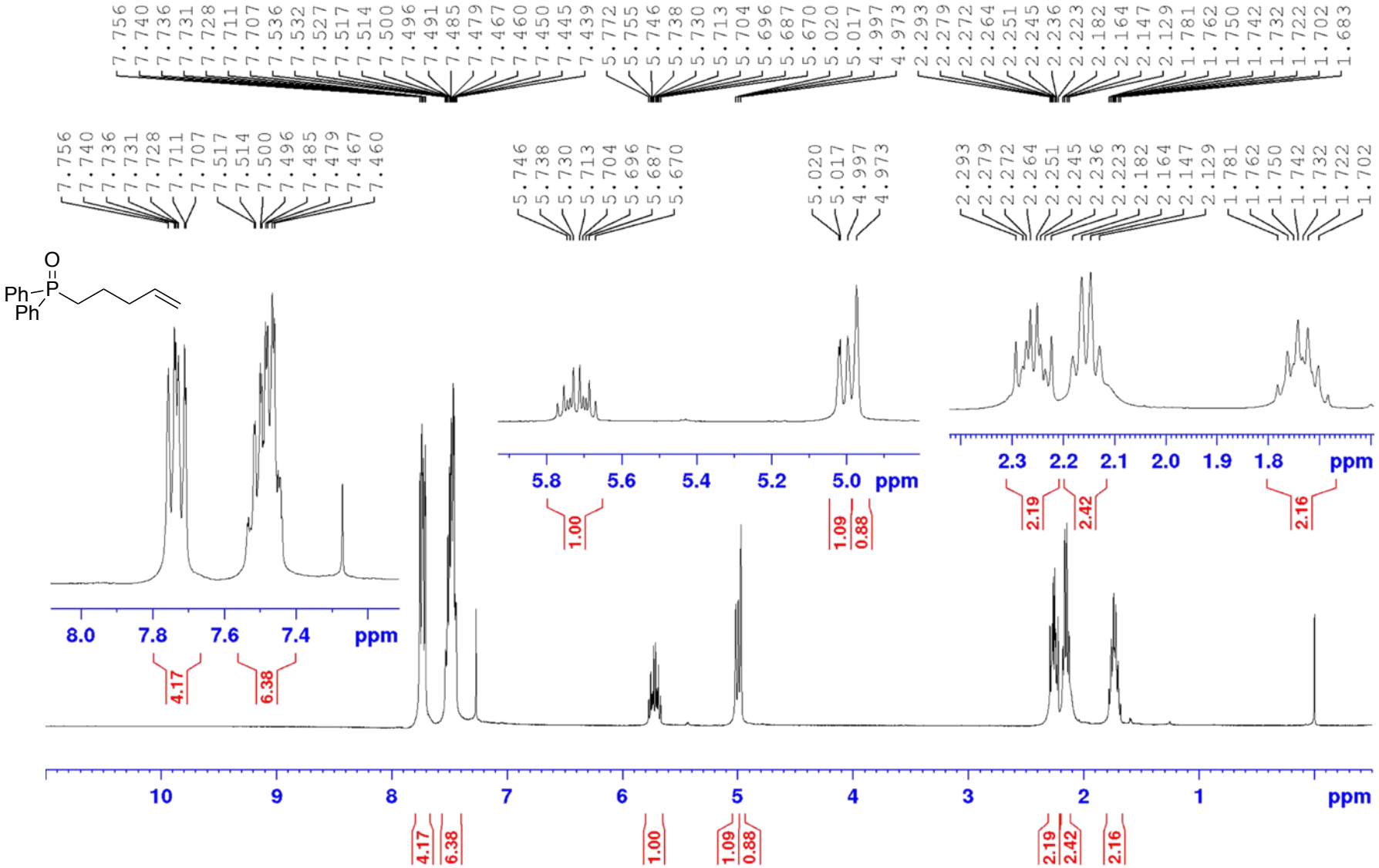
^{13}C NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide (**4ac**)



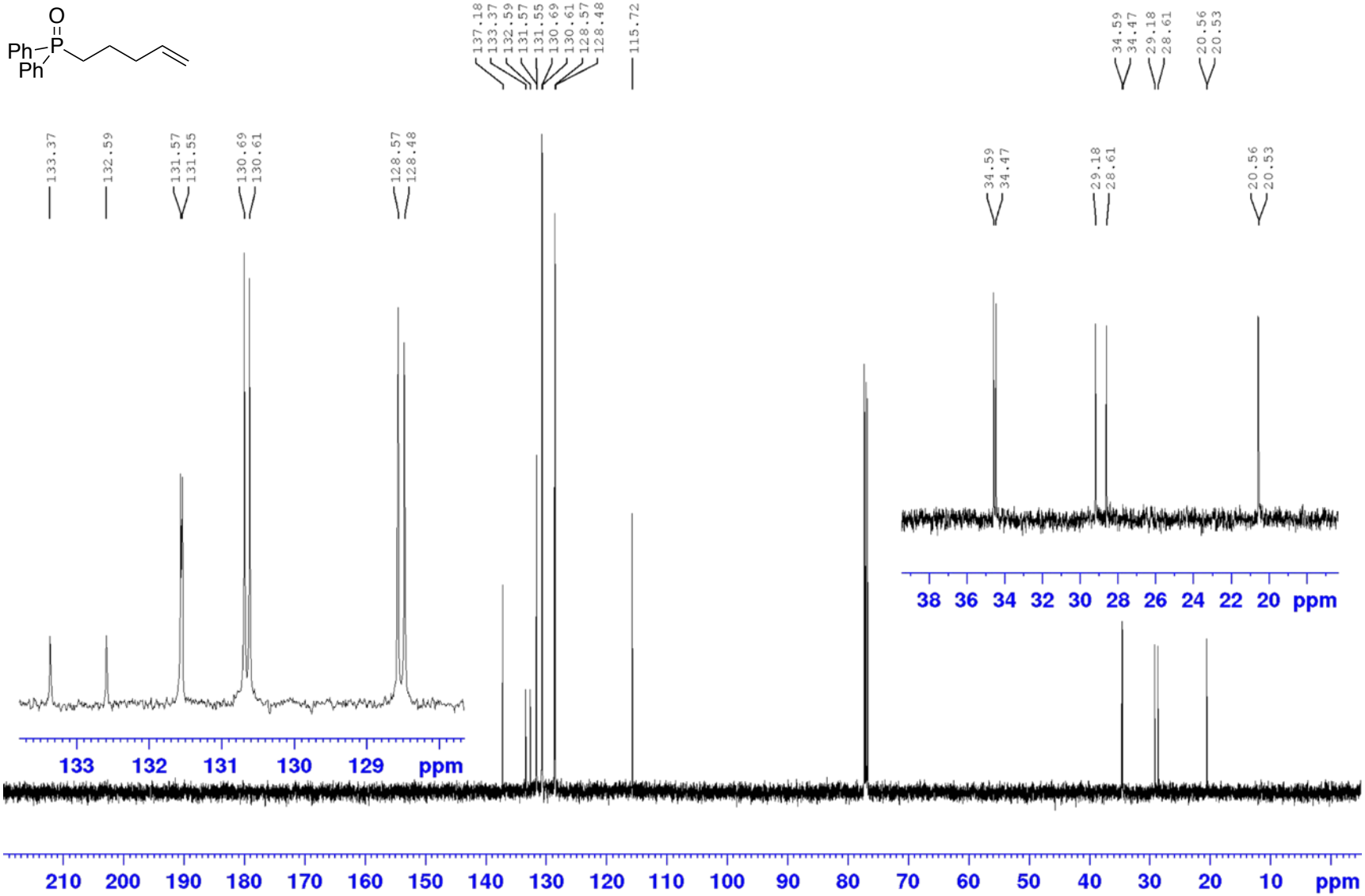
^{31}P NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide (**4ac**)



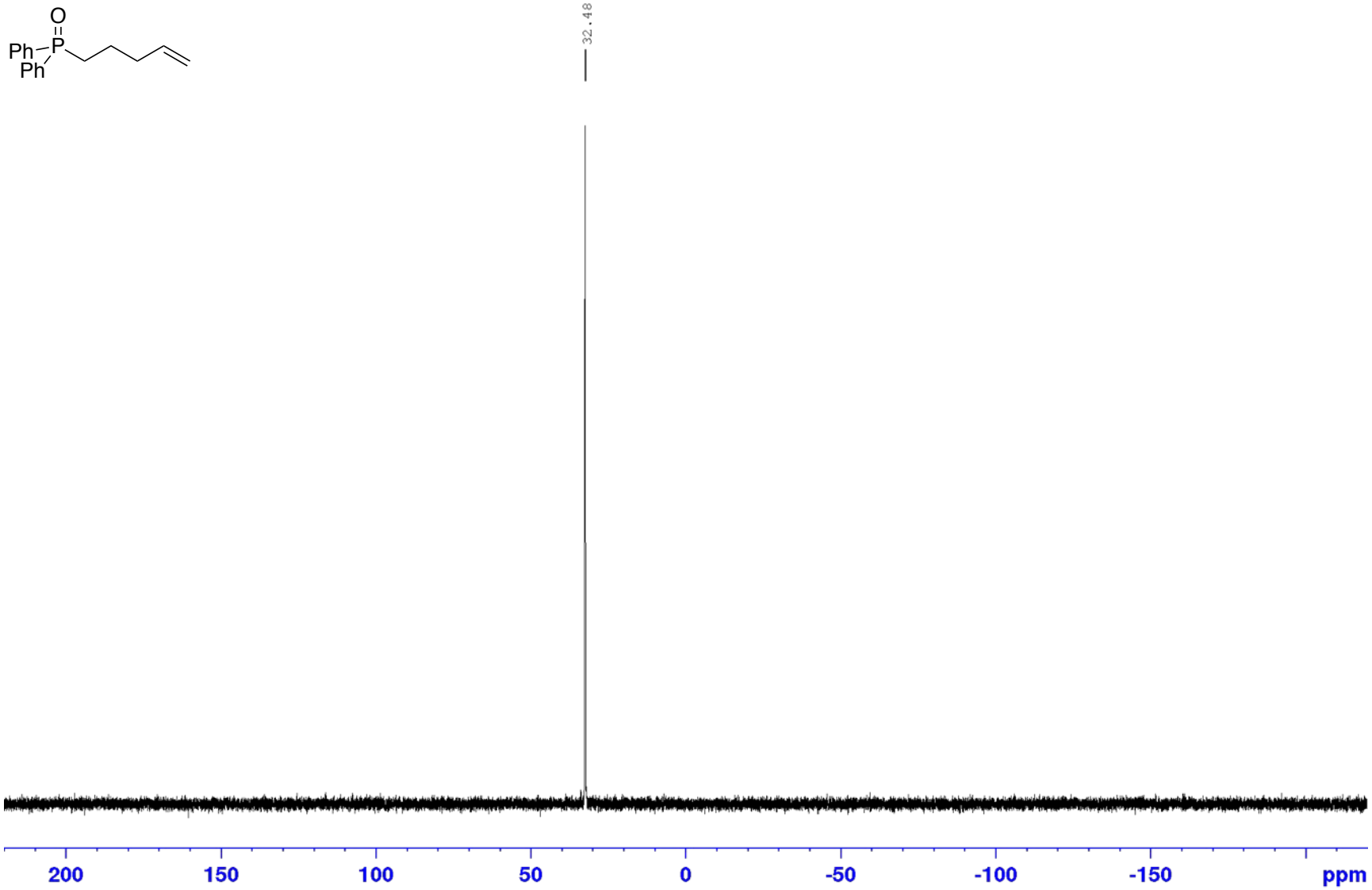
^{1}H NMR spectrum of pent-4-en-1-yldiphenylphosphine oxide (**4ad**)



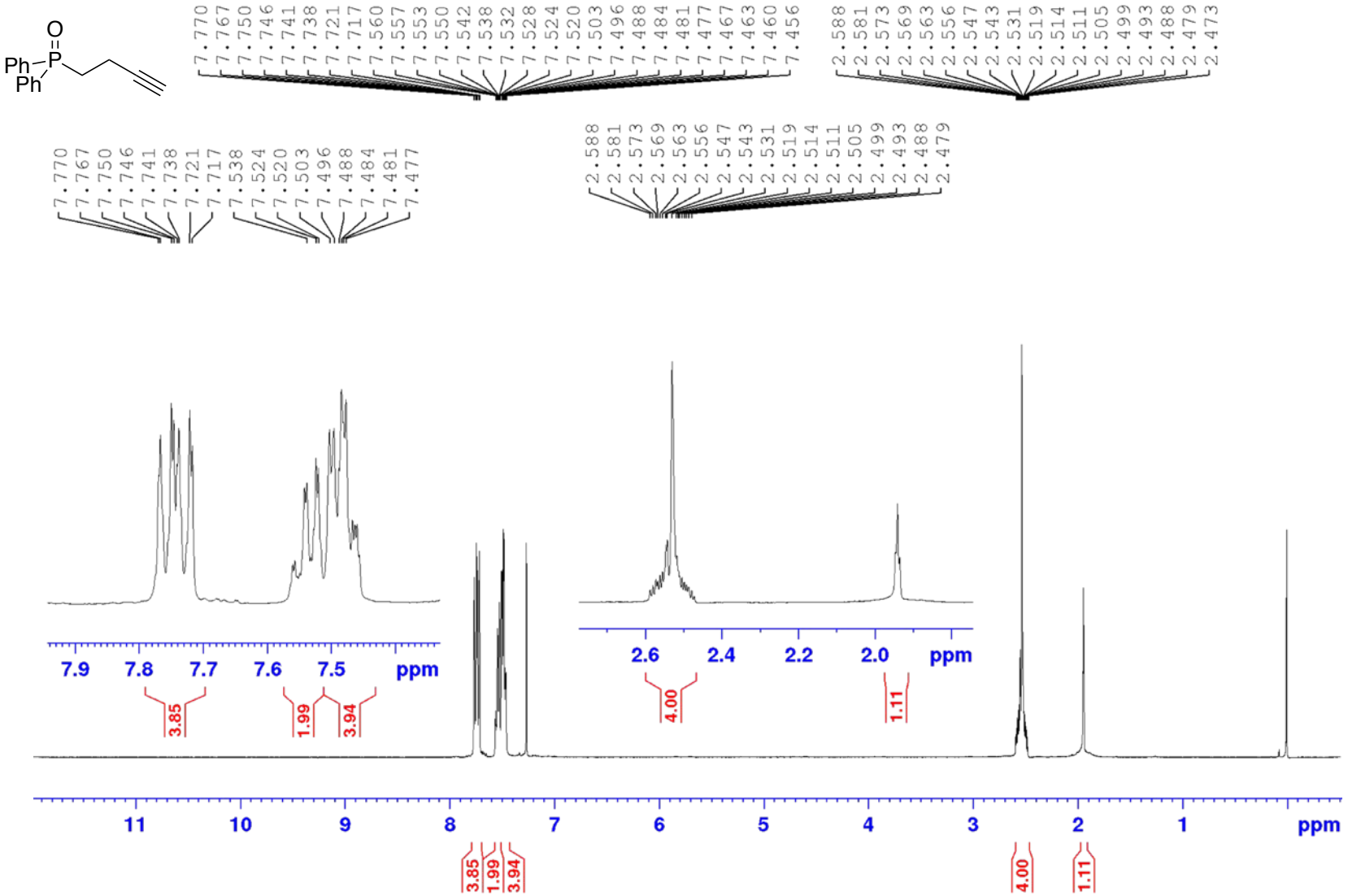
^{13}C NMR spectrum of pent-4-en-1-yldiphenylphosphine oxide (**4ad**)



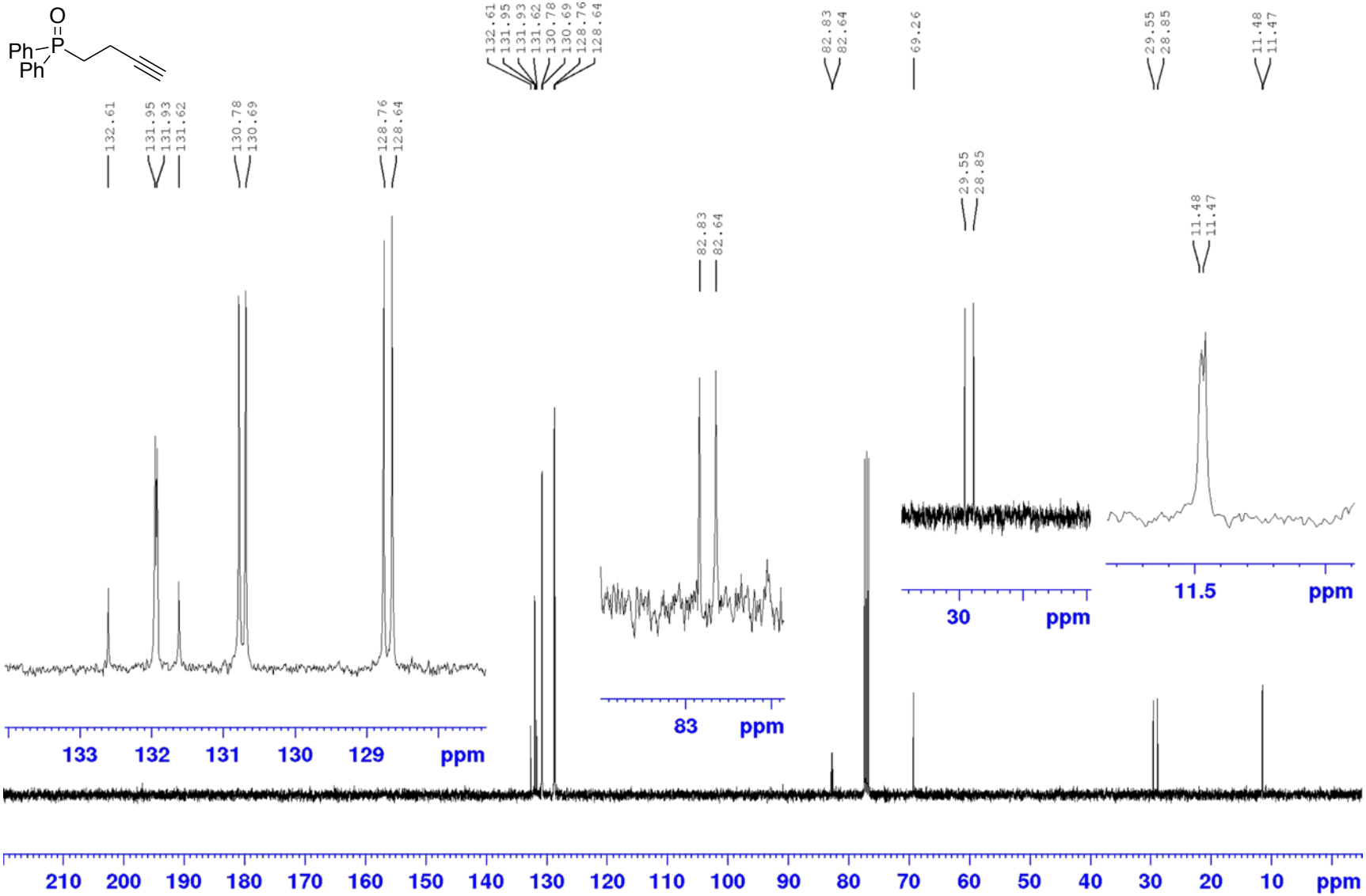
^{31}P NMR spectrum of pent-4-en-1-yldiphenylphosphine oxide (**4ad**)



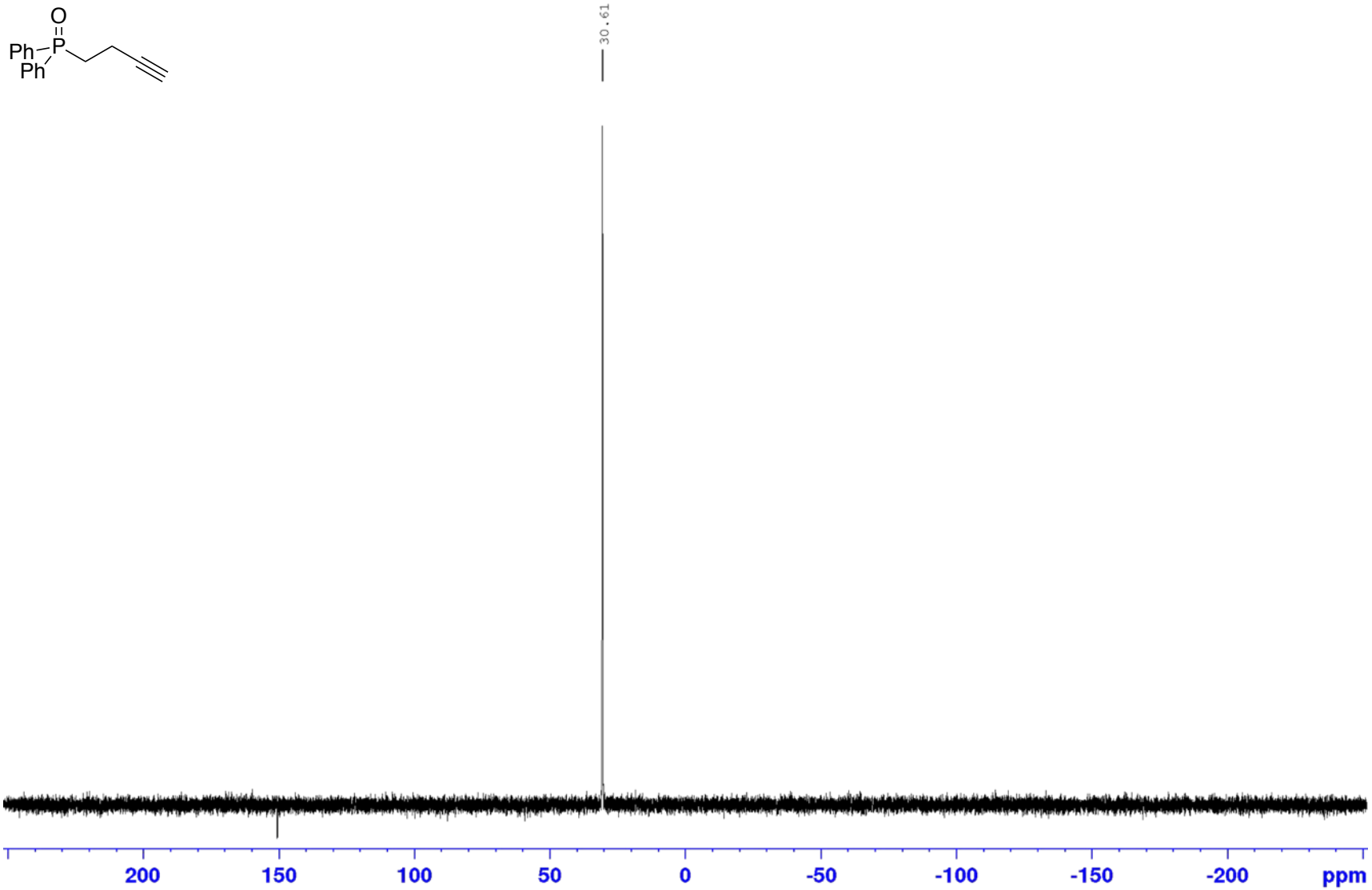
^{1}H NMR spectrum of but-3-yn-1-yldiphenylphosphine oxide (**4ae**)



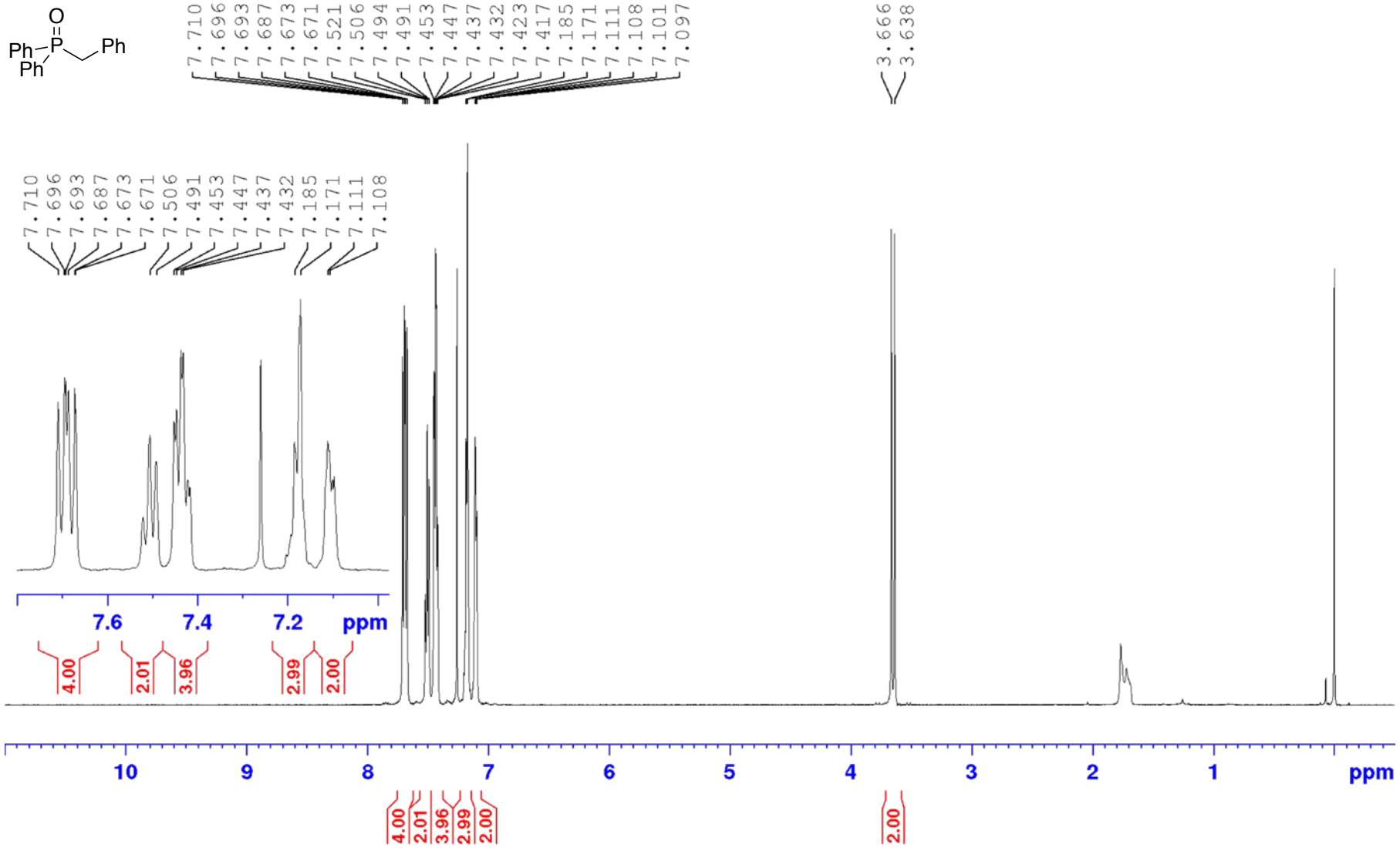
^{13}C NMR spectrum of but-3-yn-1-yldiphenylphosphine oxide (**4ae**)



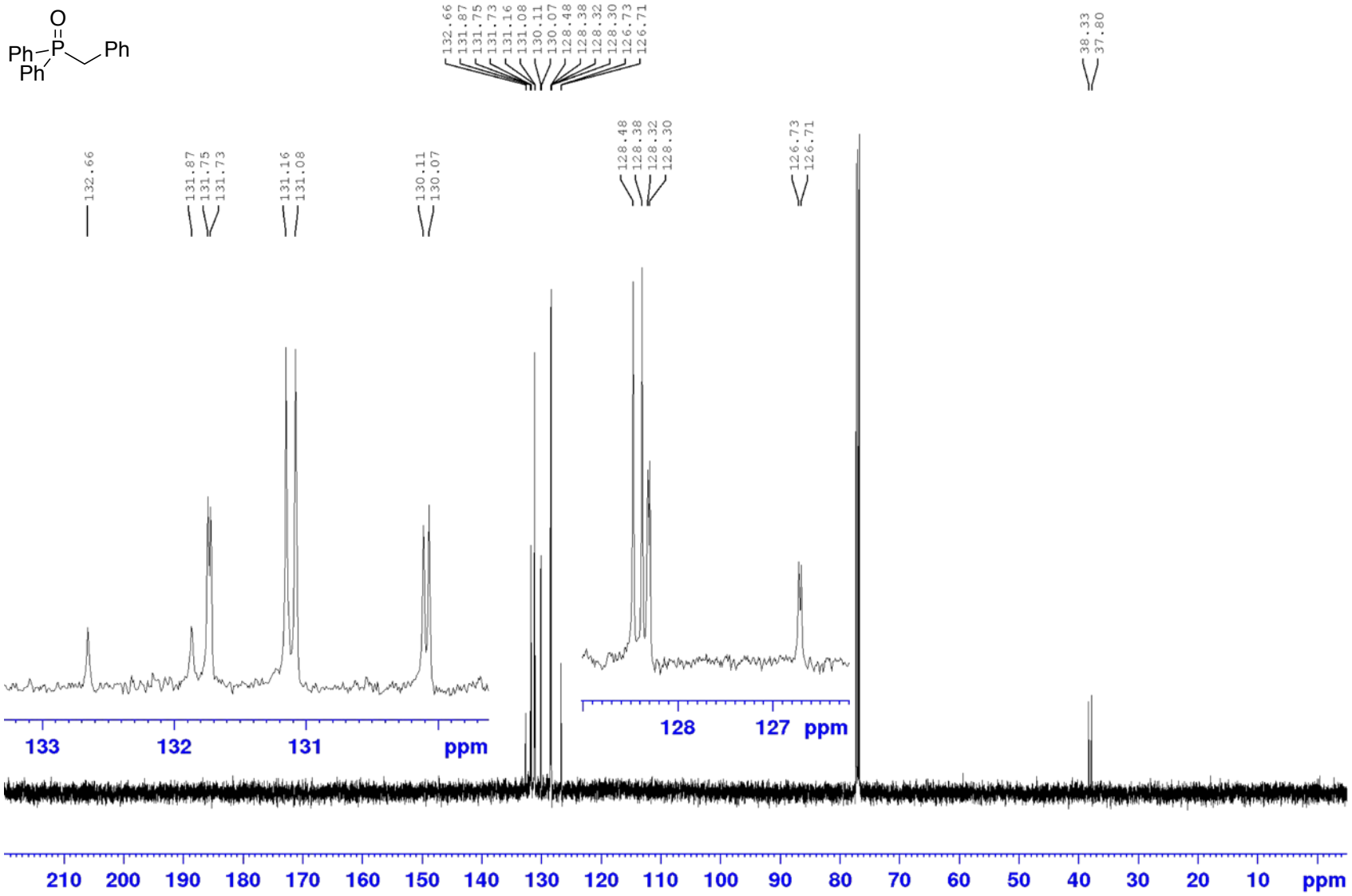
^{31}P NMR spectrum of but-3-yn-1-yldiphenylphosphine oxide (**4ae**)



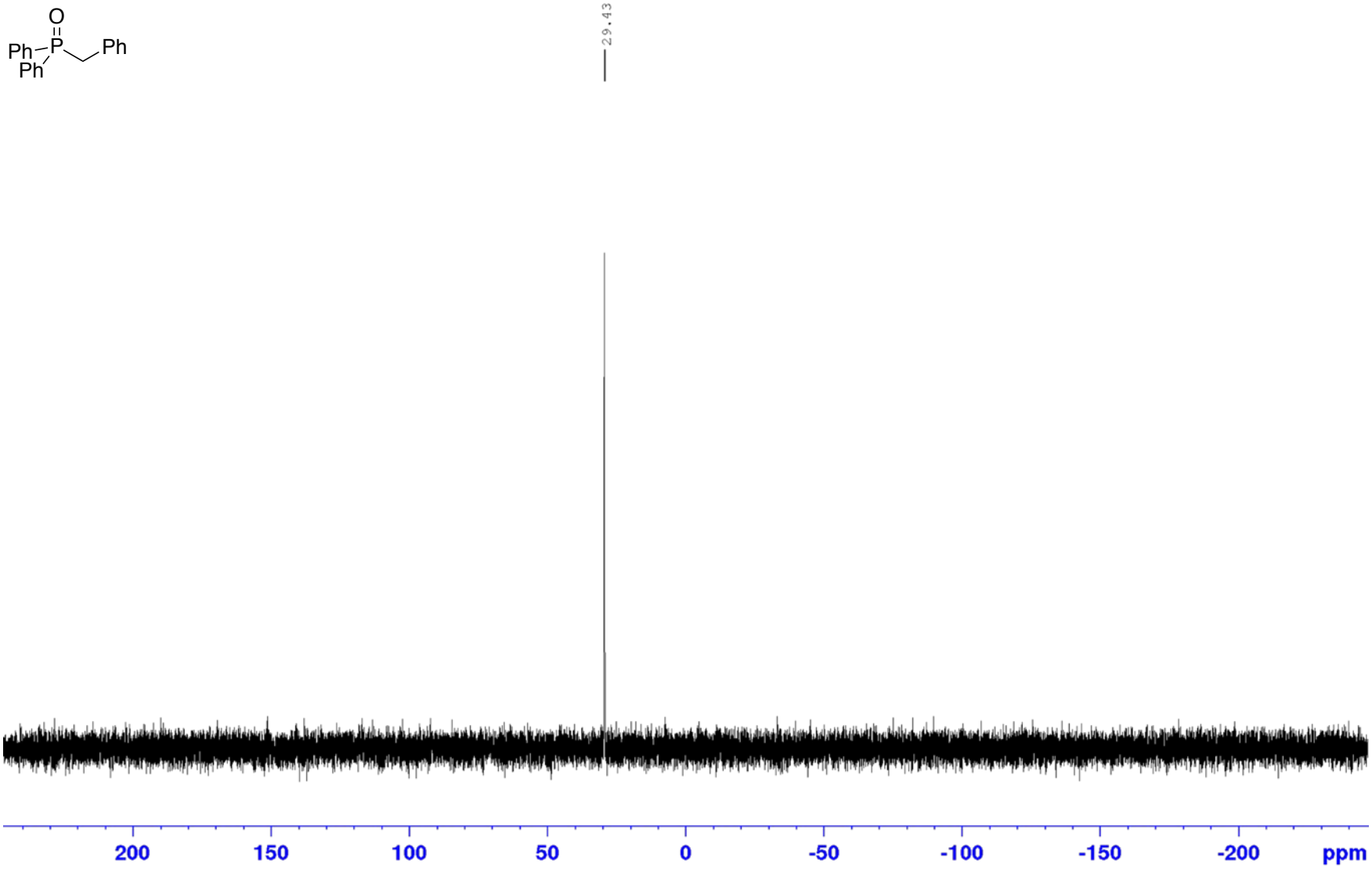
[1]H NMR spectrum of benzyldiphenylphosphine oxide (**4af**)



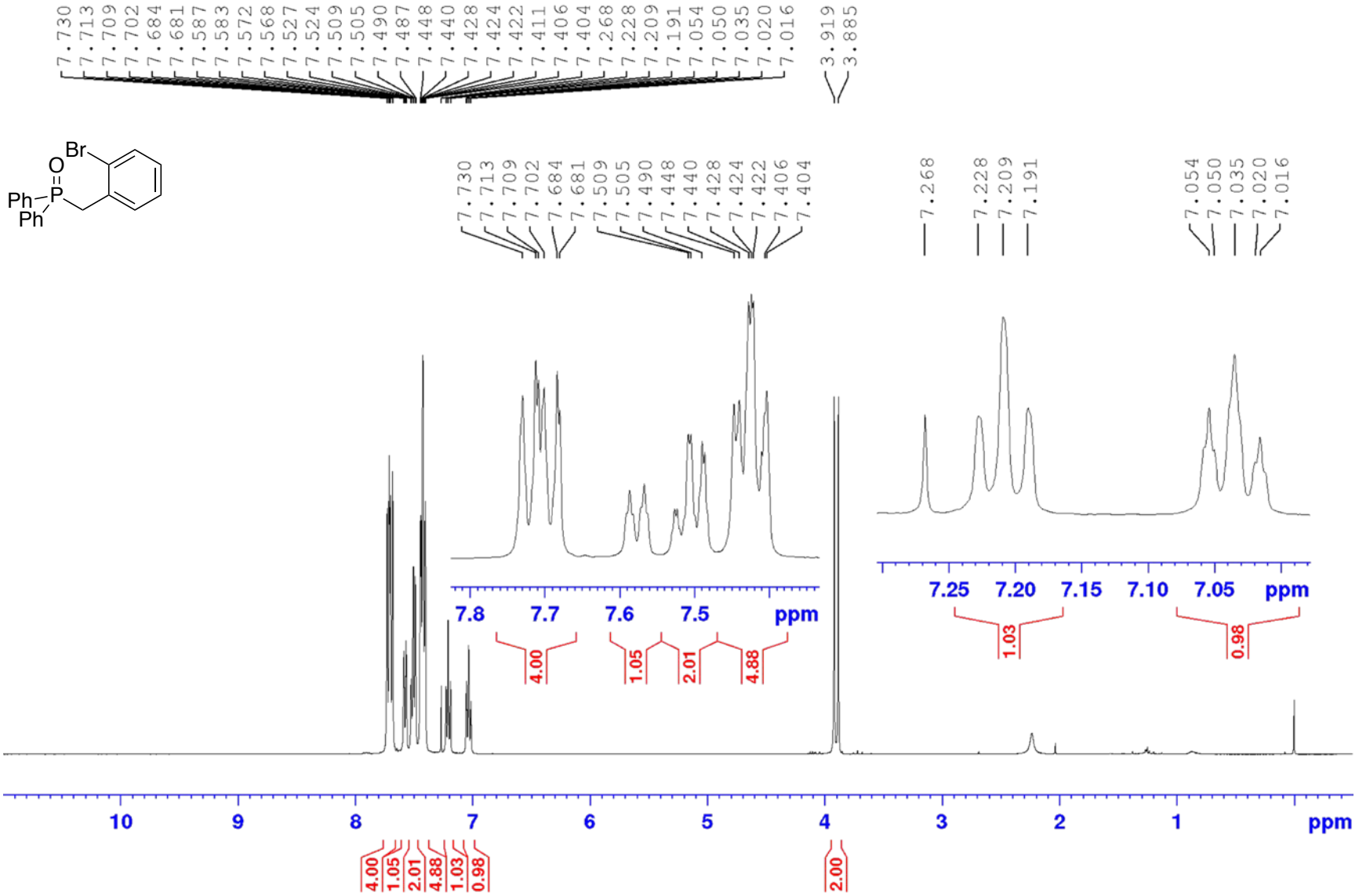
^{13}C NMR spectrum of benzyldiphenylphosphine oxide (**4af**)



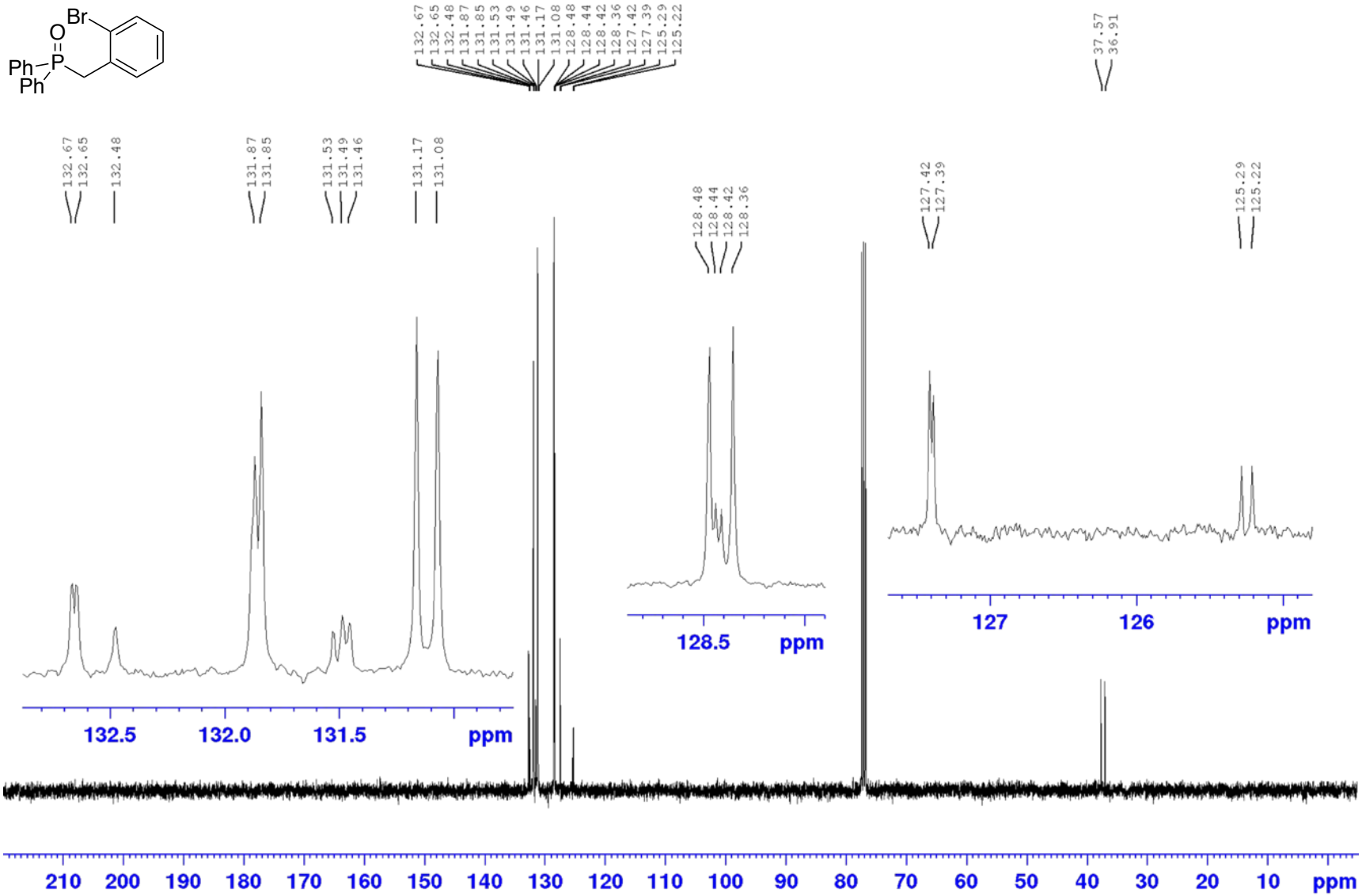
^{31}P NMR spectrum of benzyldiphenylphosphine oxide (**4af**)



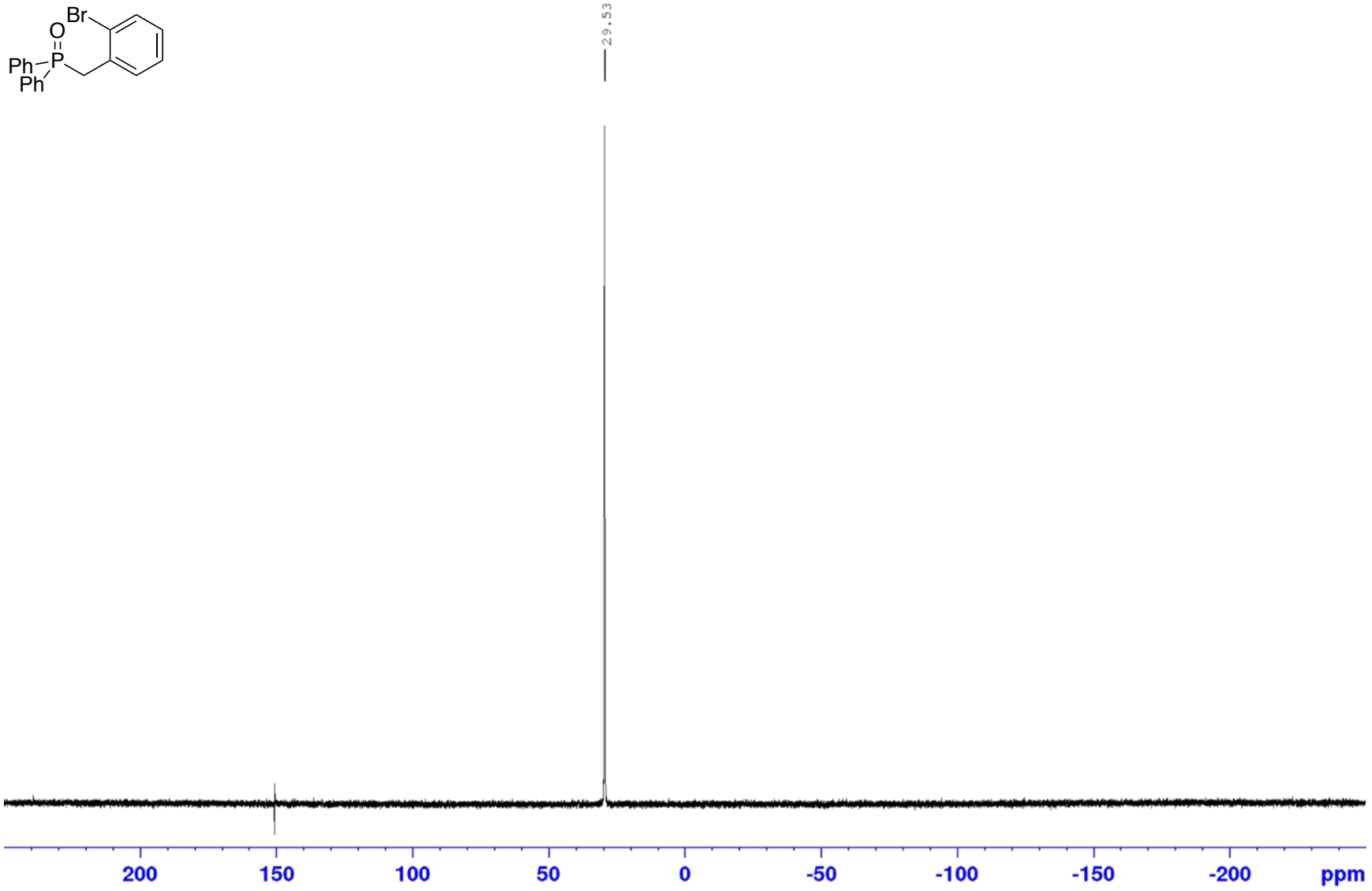
[1]H NMR spectrum of (2-bromobenzyl)diphenylphosphine oxide (**4ag**)



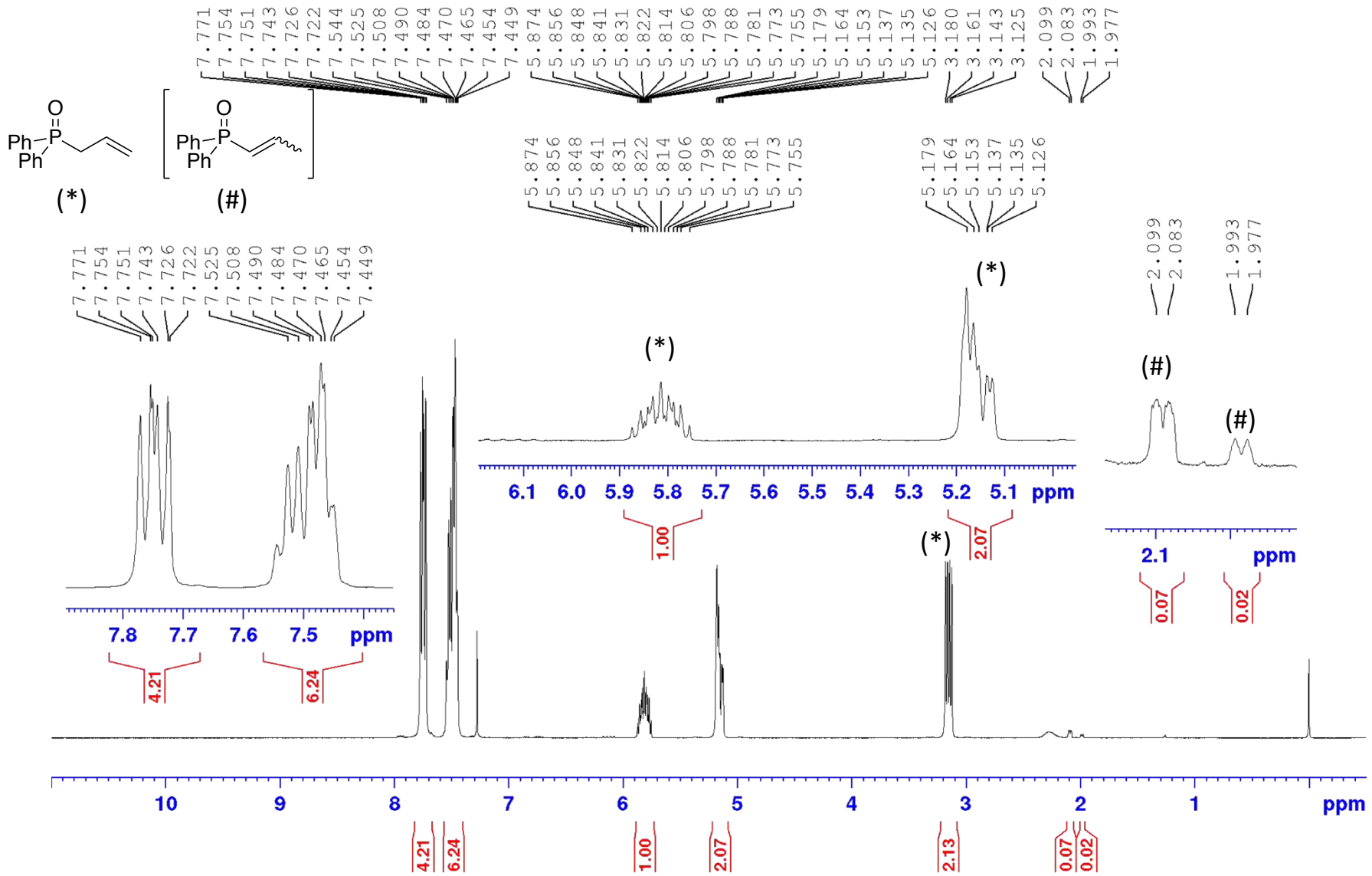
^{13}C NMR spectrum of (2-bromobenzyl)diphenylphosphine oxide (**4ag**)



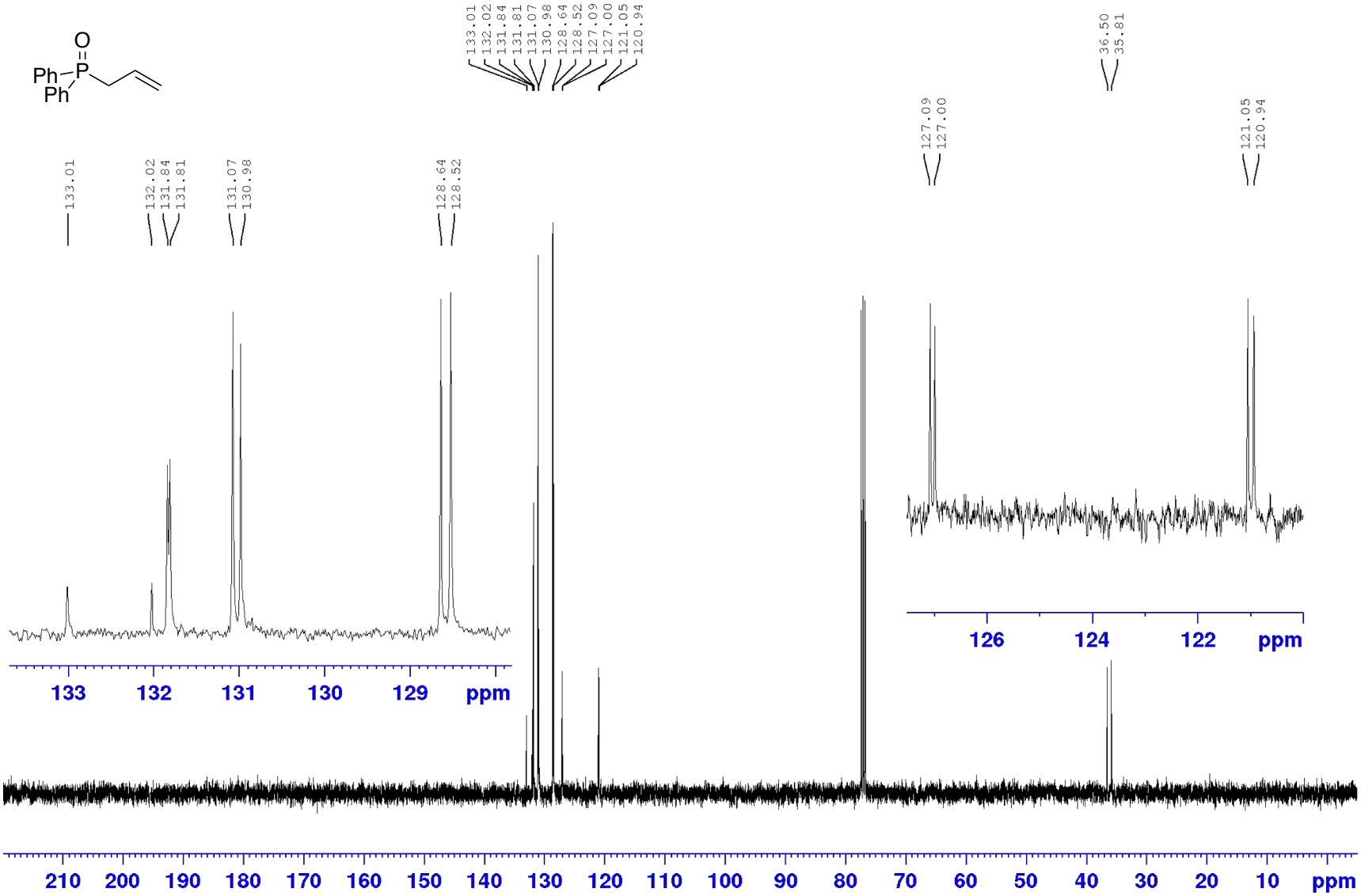
^{31}P NMR spectrum of (2-bromobenzyl)diphenylphosphine oxide (**4ag**)



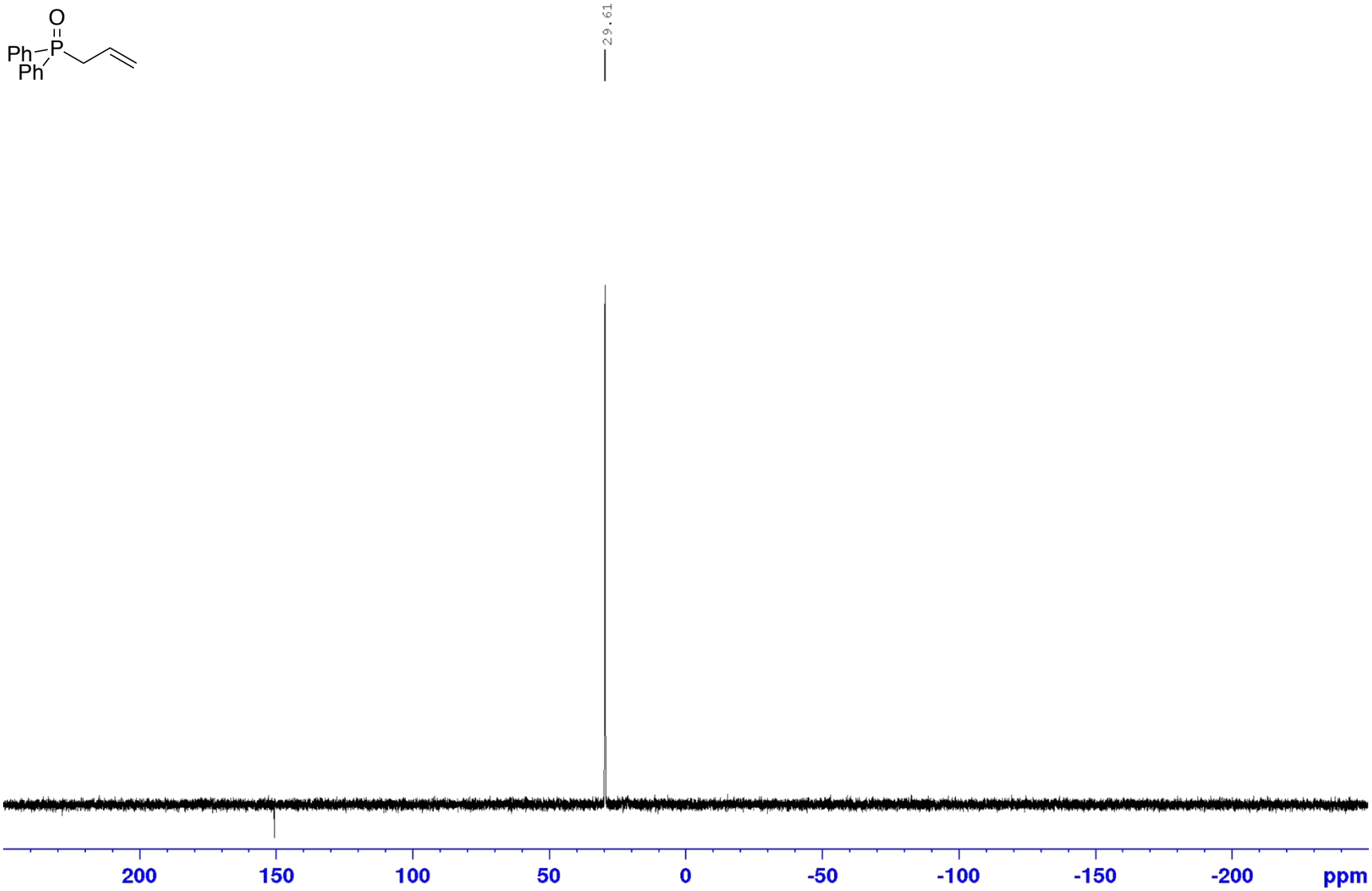
^{1}H NMR spectrum of allyldiphenylphosphine oxide (**4ah**)



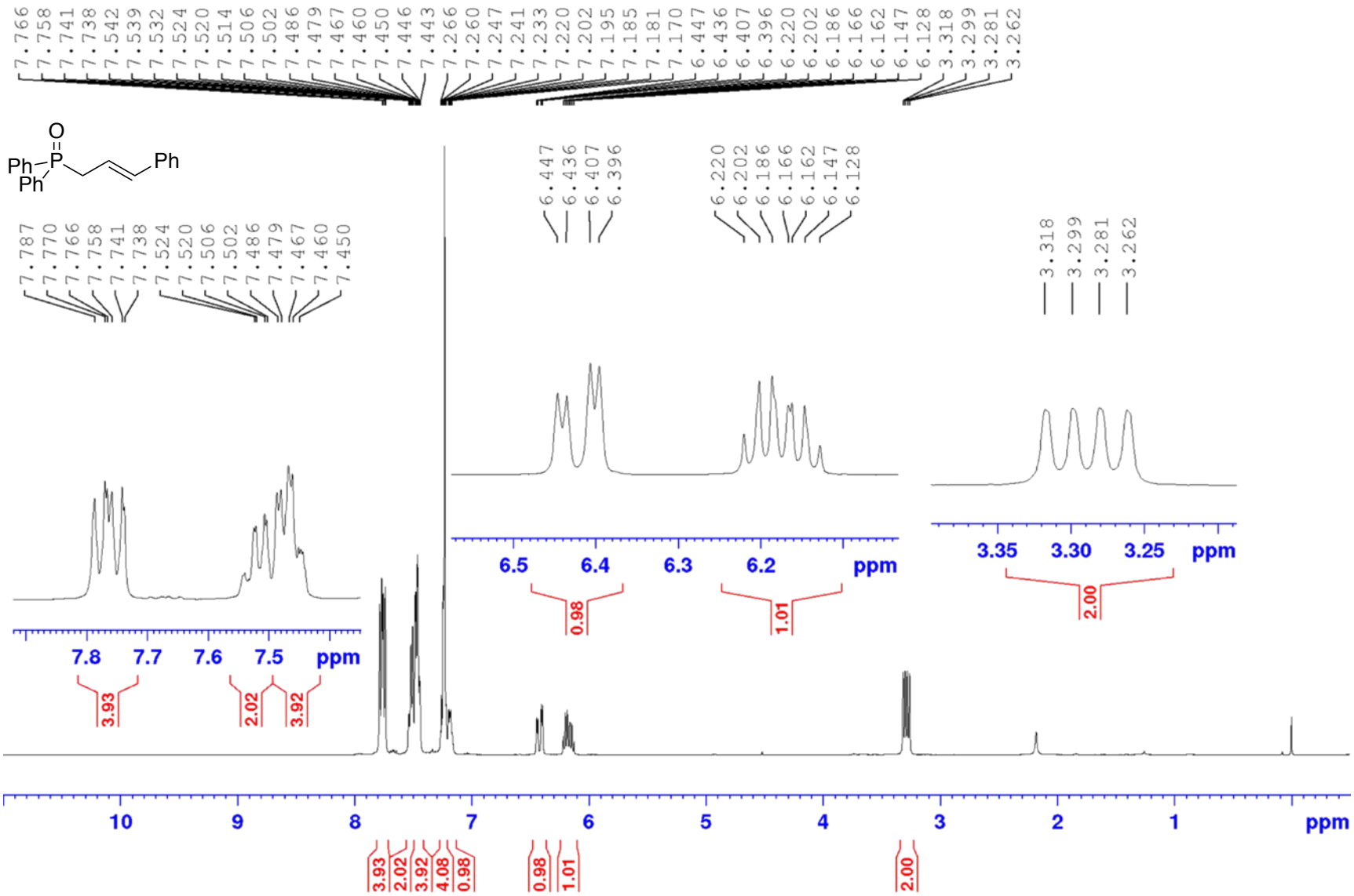
^{13}C NMR spectrum of allyldiphenylphosphine oxide **4ah**



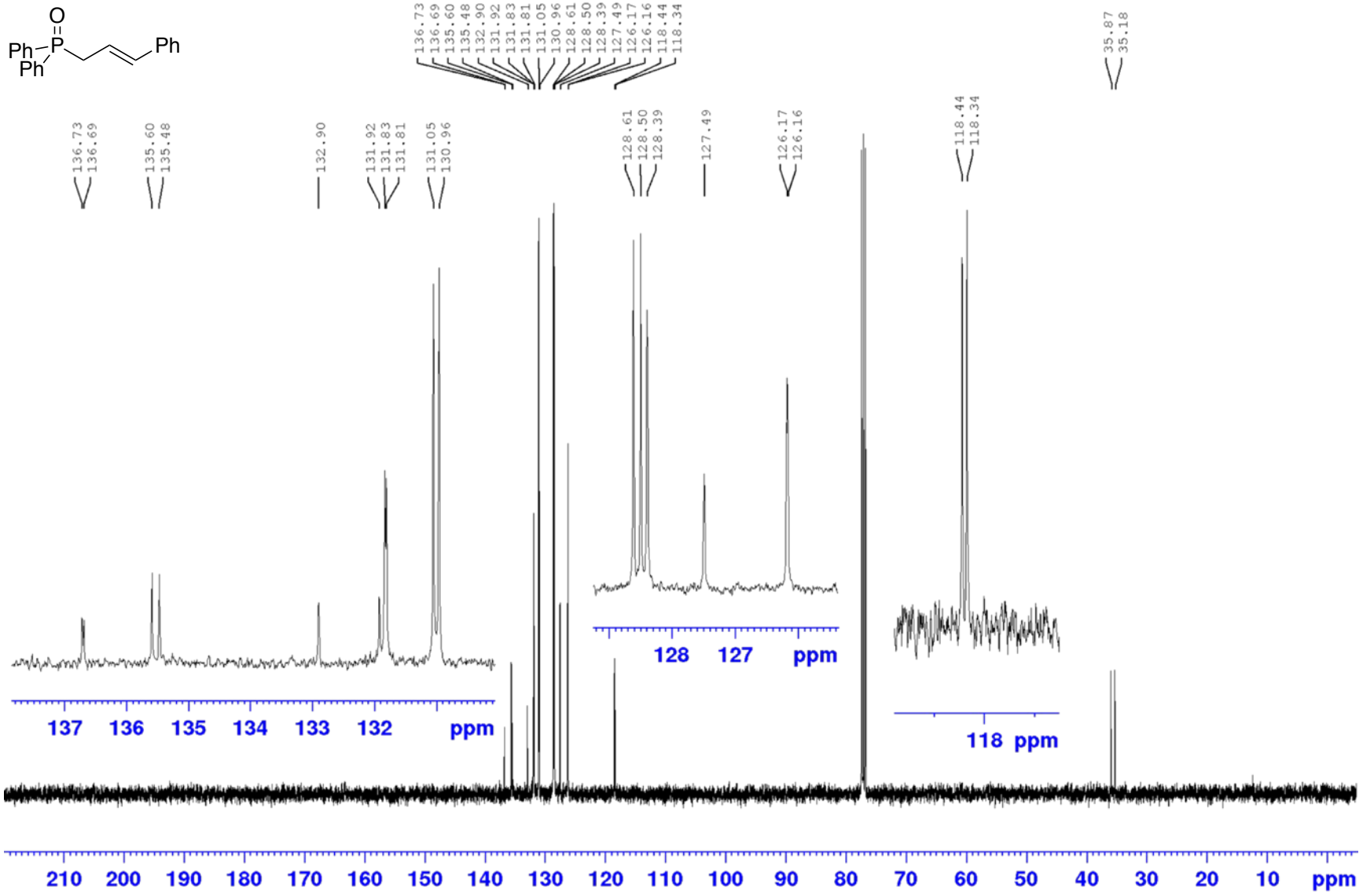
^{31}P NMR spectrum of allyldiphenylphosphine oxide **4ah**



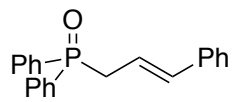
[1]H NMR spectrum of cinnamyldiphenylphosphine oxide (**4ai**)



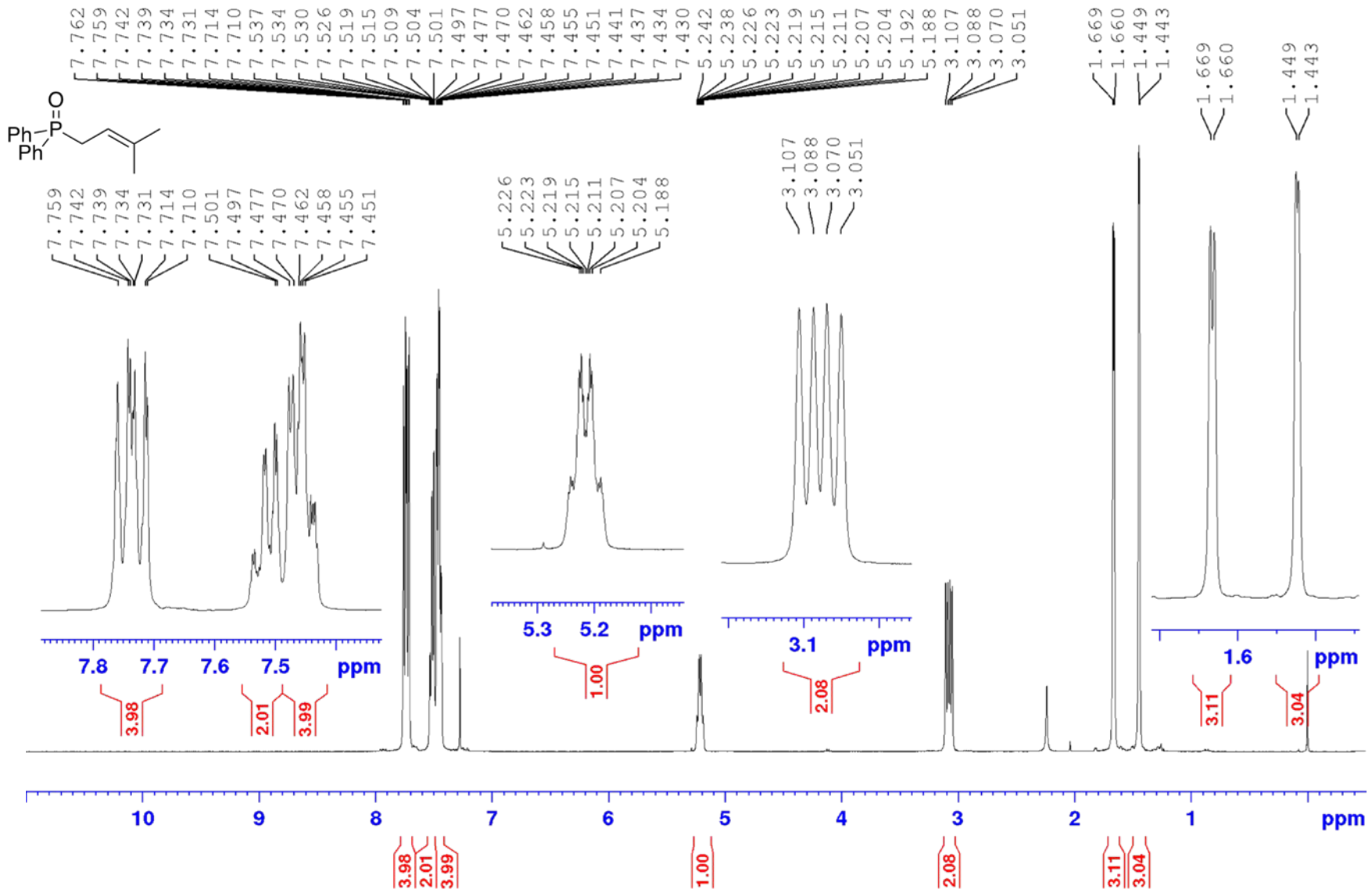
^{13}C NMR spectrum of cinnamyldiphenylphosphine oxide (**4ai**)



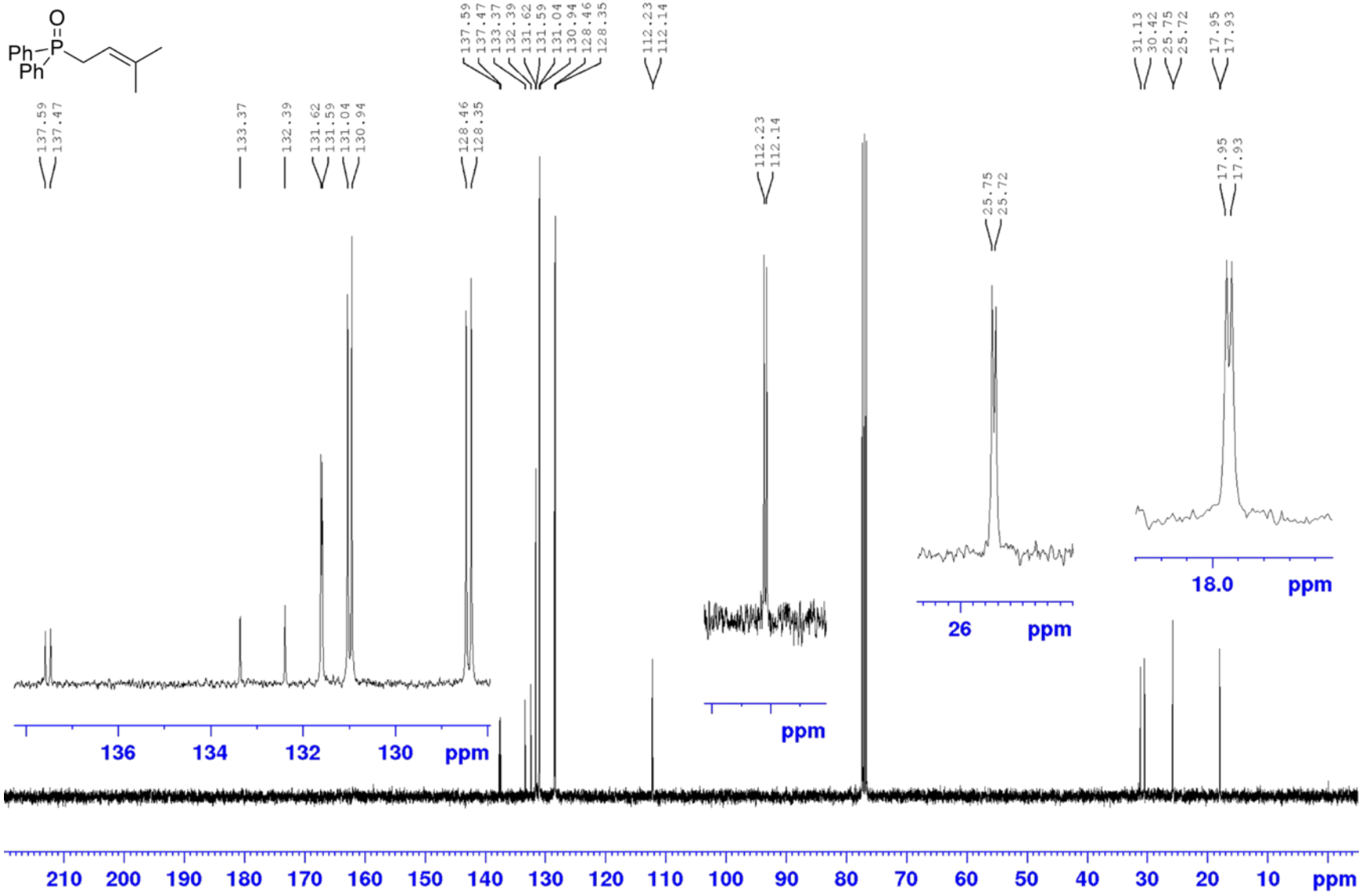
^{31}P NMR spectrum of cinnamyldiphenylphosphine oxide (**4ai**)



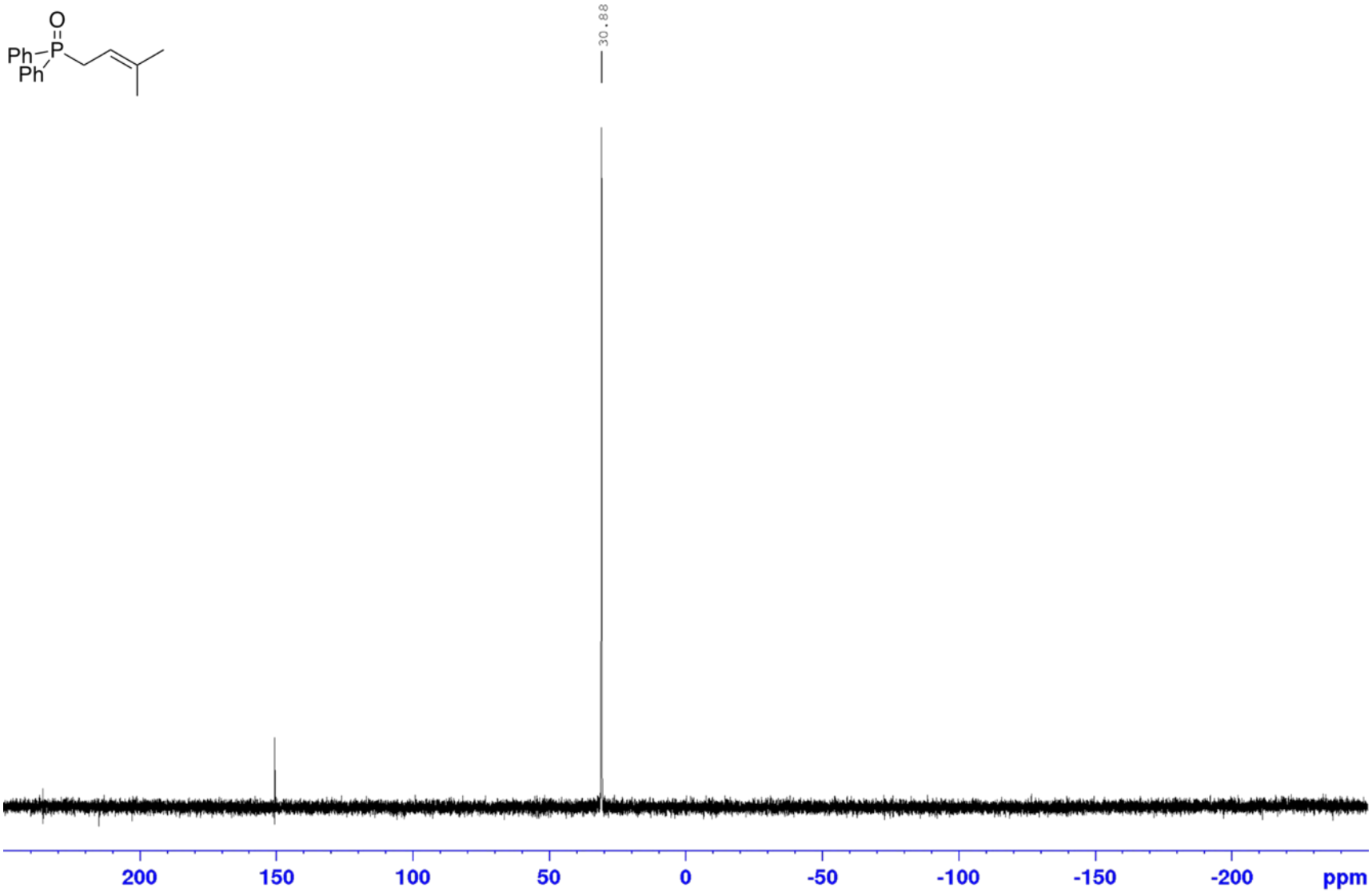
^{1}H NMR spectrum of (3-methylbut-2-en-1-yl)diphenylphosphine oxide (**4aj**)



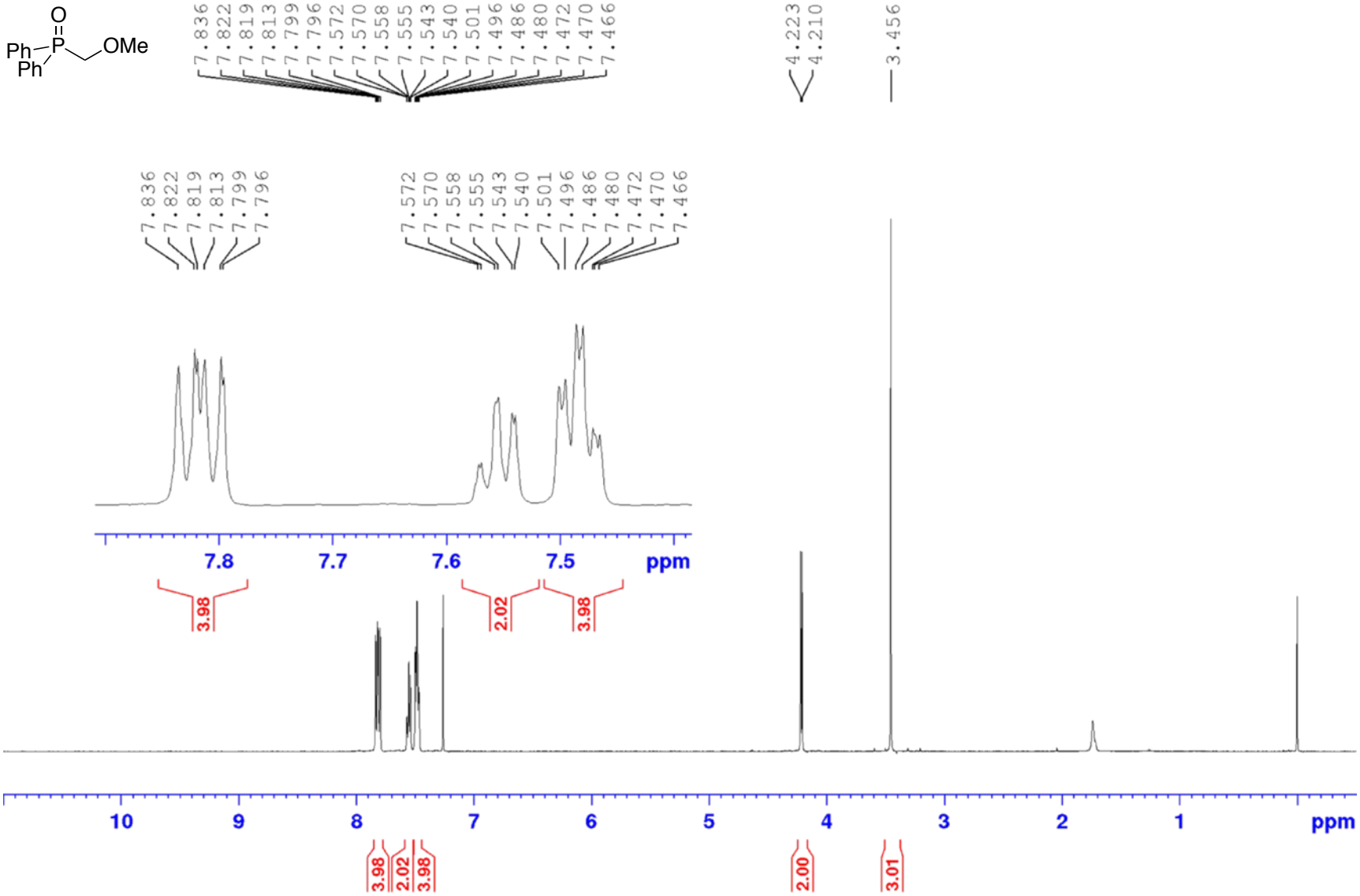
^{13}C NMR spectrum of (3-methylbut-2-en-1-yl)diphenylphosphine oxide (**4aj**)



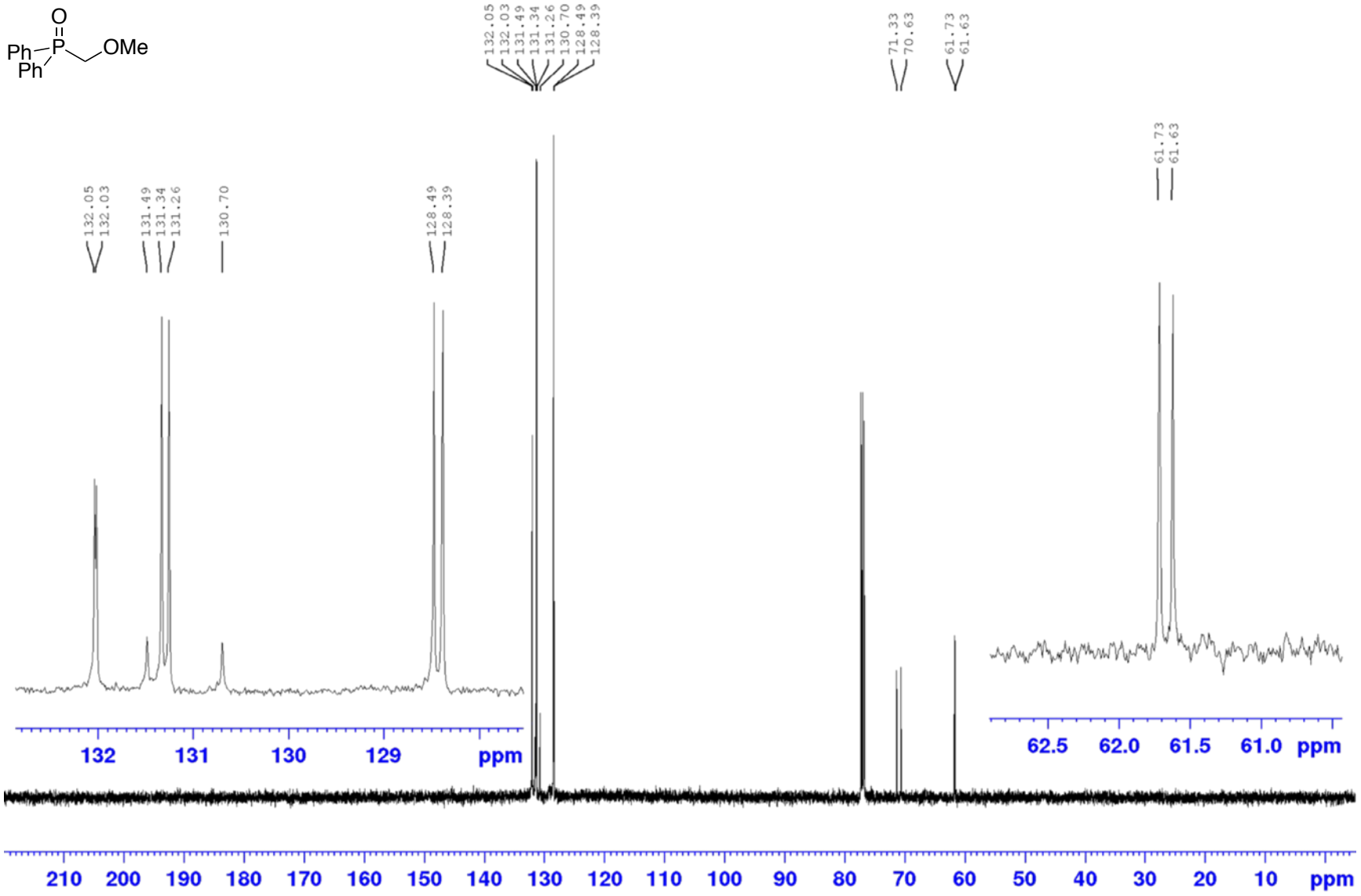
^{31}P NMR spectrum of (3-methylbut-2-en-1-yl)diphenylphosphine oxide (**4aj**)



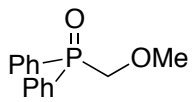
^{1}H NMR spectrum of (methoxymethyl)diphenylphosphine oxide (**4ak**)



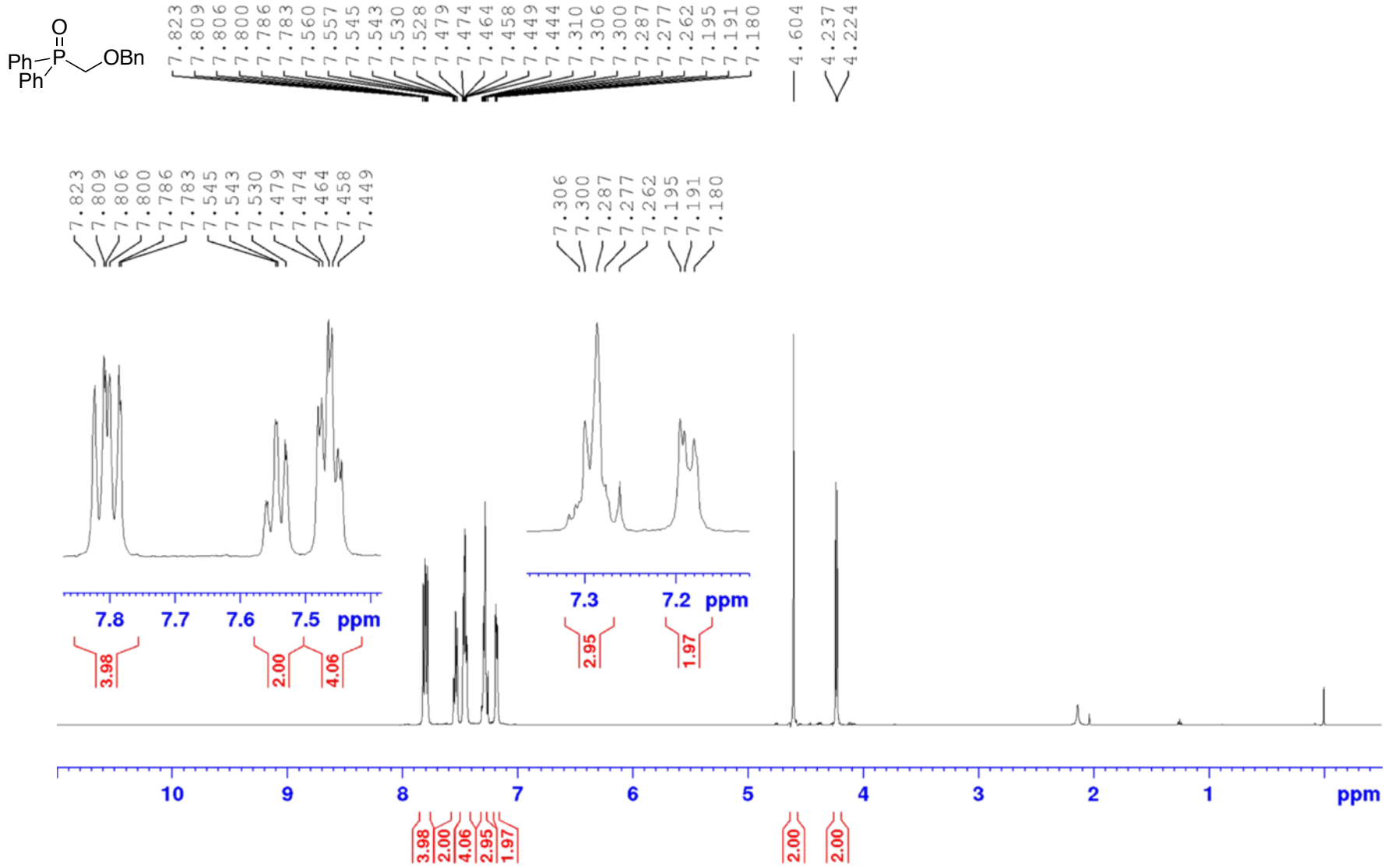
^{13}C NMR spectrum of (methoxymethyl)diphenylphosphine oxide (**4ak**)



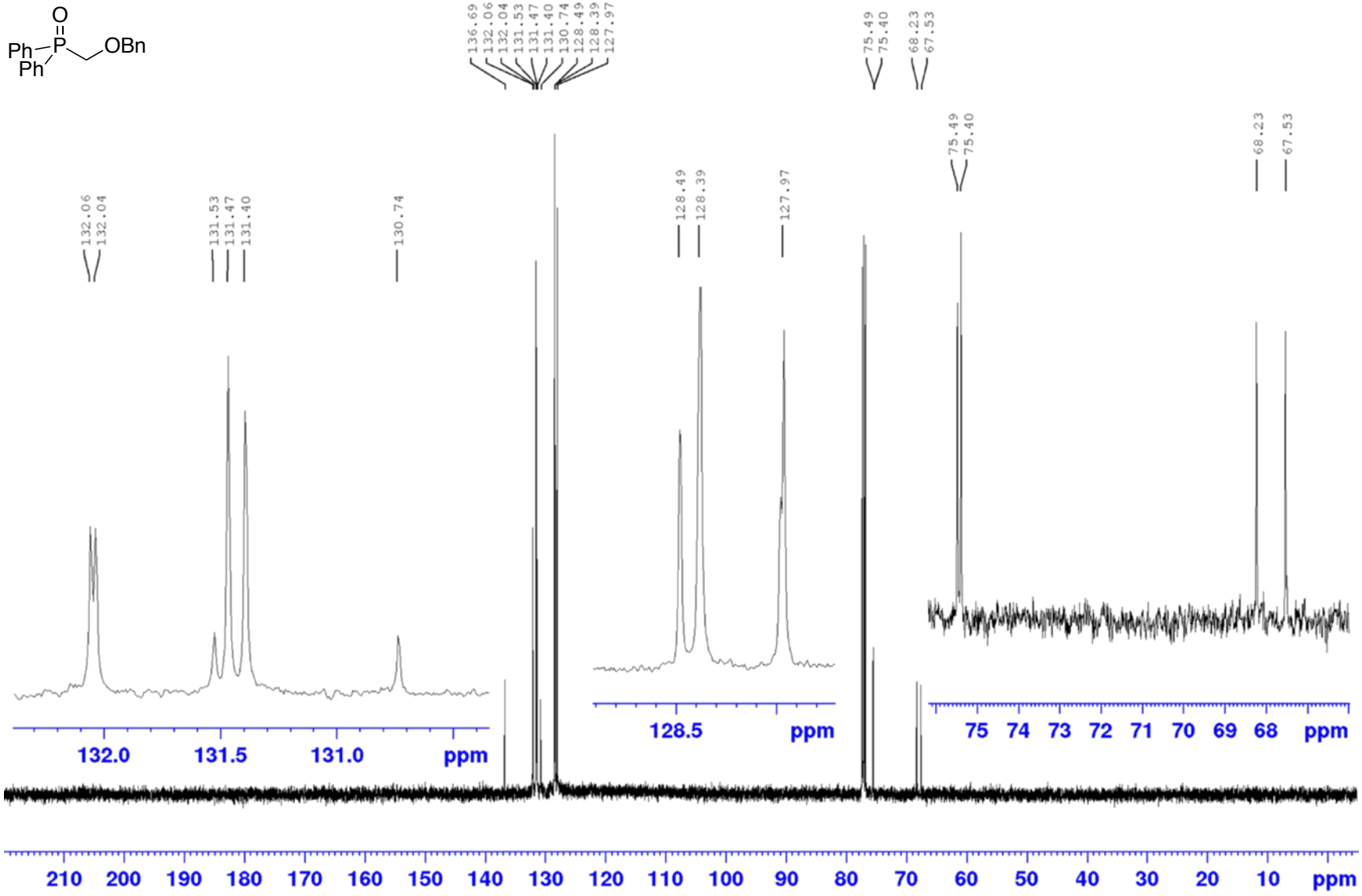
^{31}P NMR spectrum of (methoxymethyl)diphenylphosphine oxide (**4ak**)



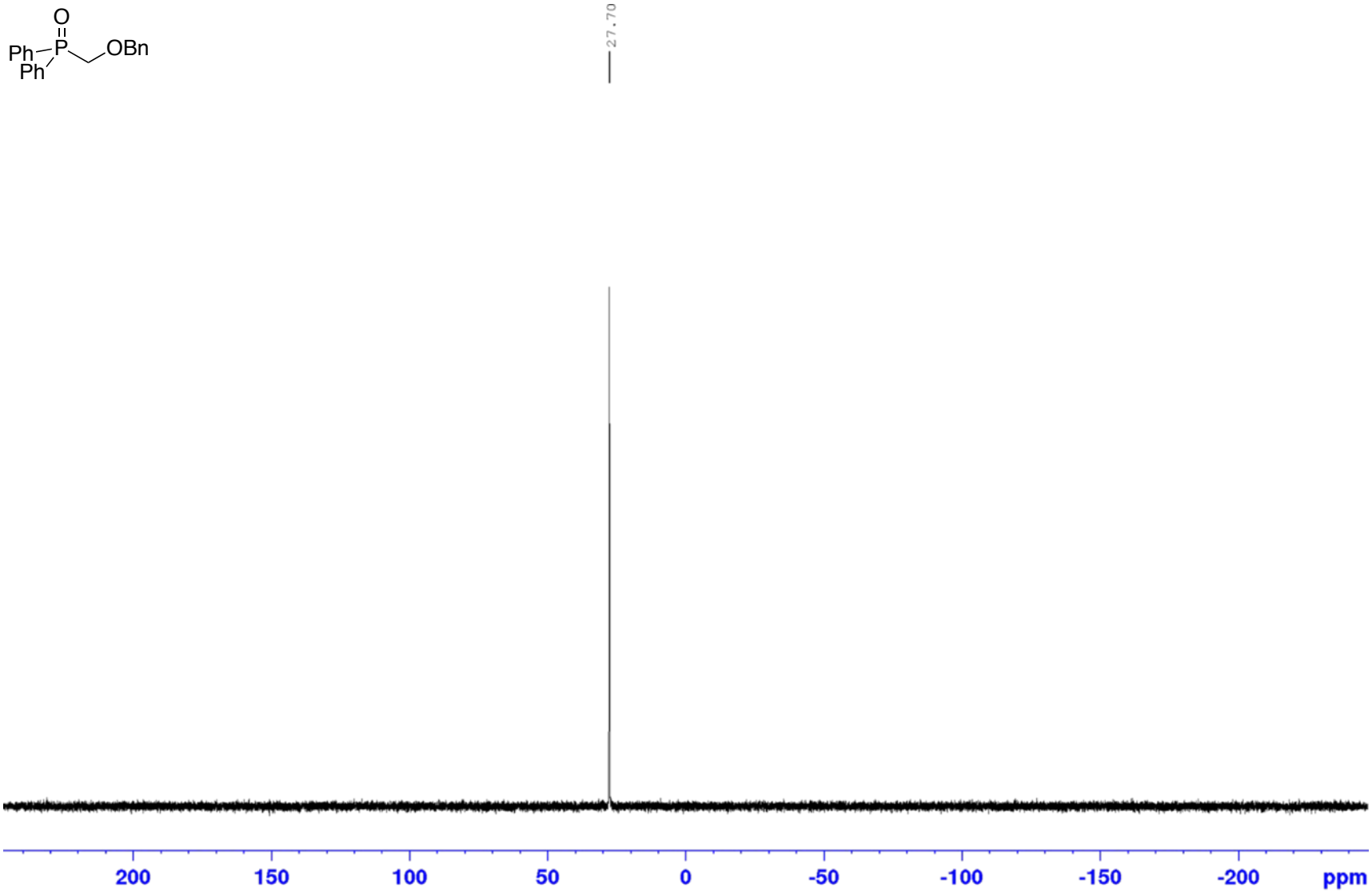
^{1}H NMR spectrum of ((benzyloxy)methyl)diphenylphosphine oxide (**4al**)



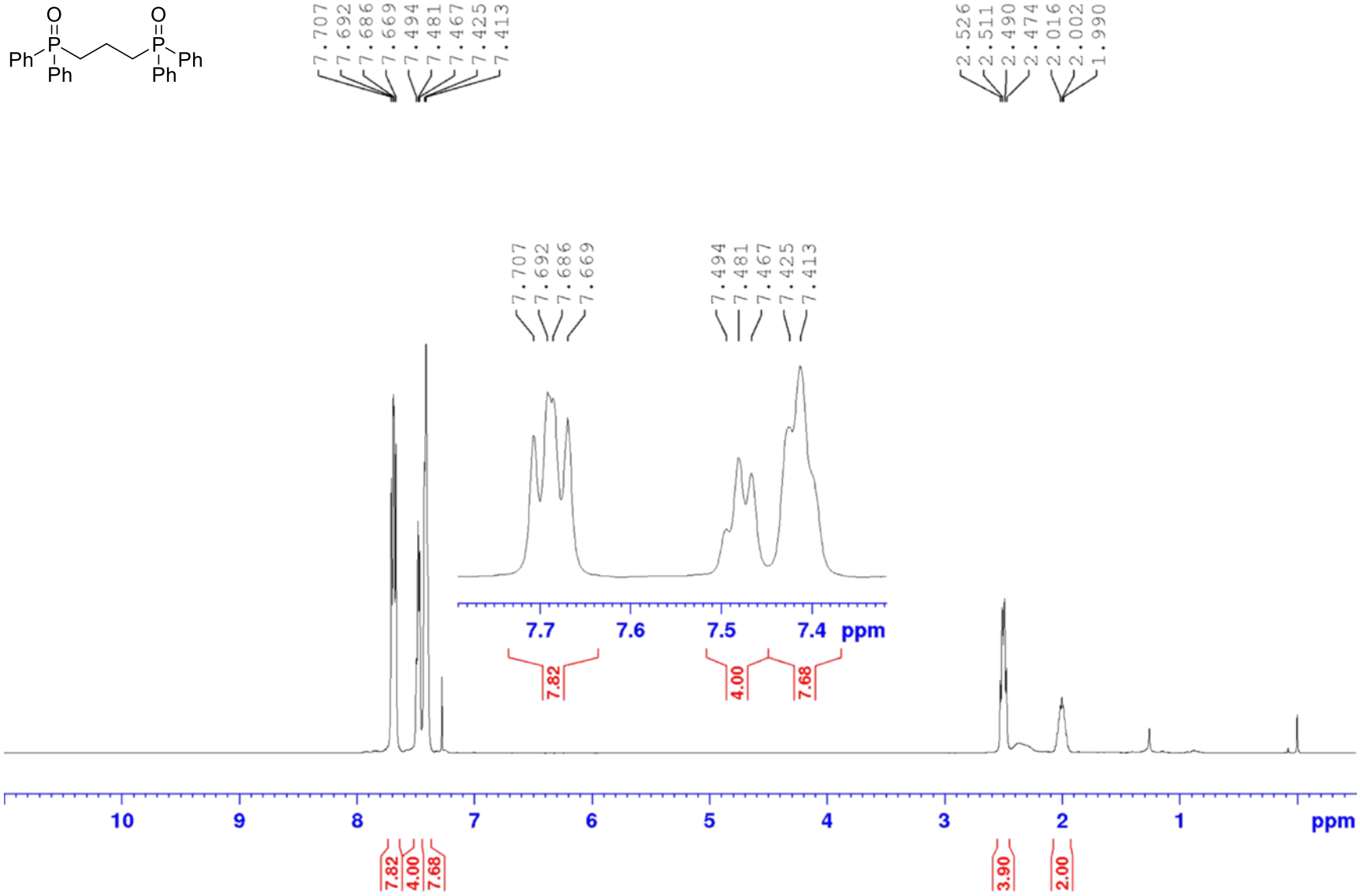
^{13}C NMR spectrum of ((benzyloxy)methyl)diphenylphosphine oxide (**4al**)



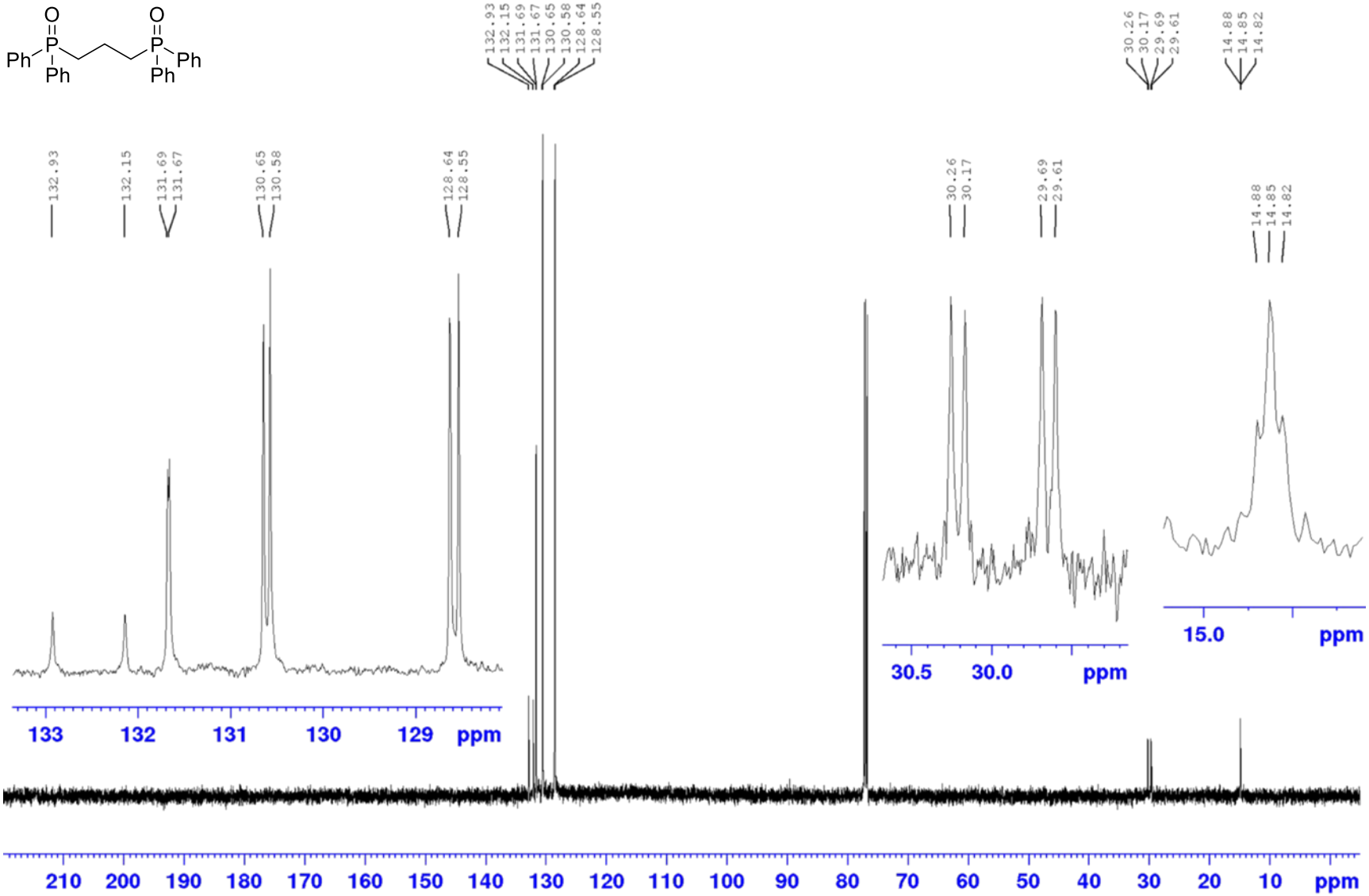
^{31}P NMR spectrum of ((benzyloxy)methyl)diphenylphosphine oxide (**4al**)



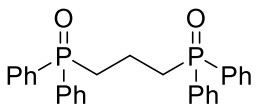
^{1}H NMR spectrum of propane-1,3-diylbis(diphenylphosphine oxide) (**4am**)



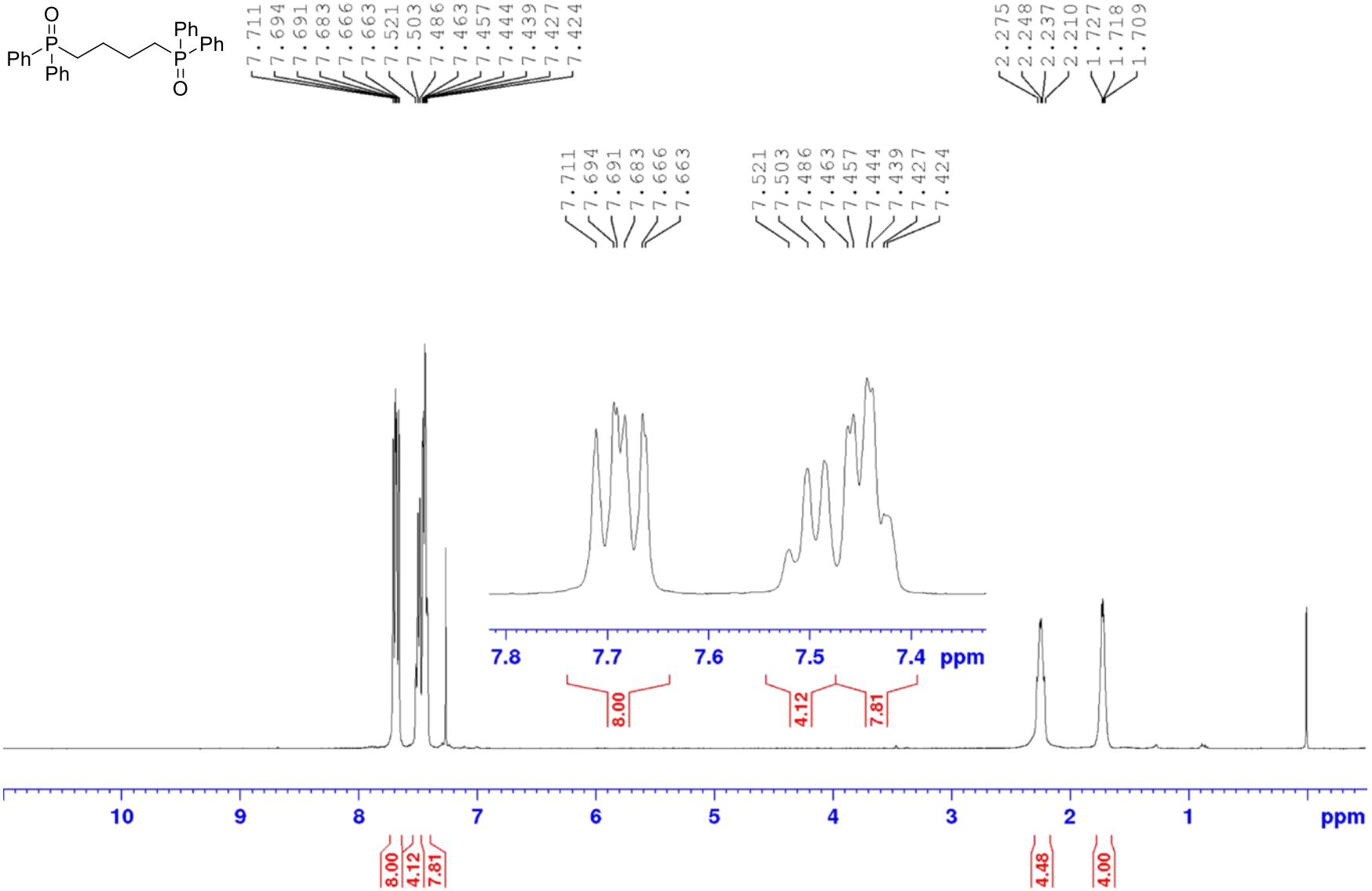
^{13}C NMR spectrum of propane-1,3-diylbis(diphenylphosphine oxide) (**4am**)



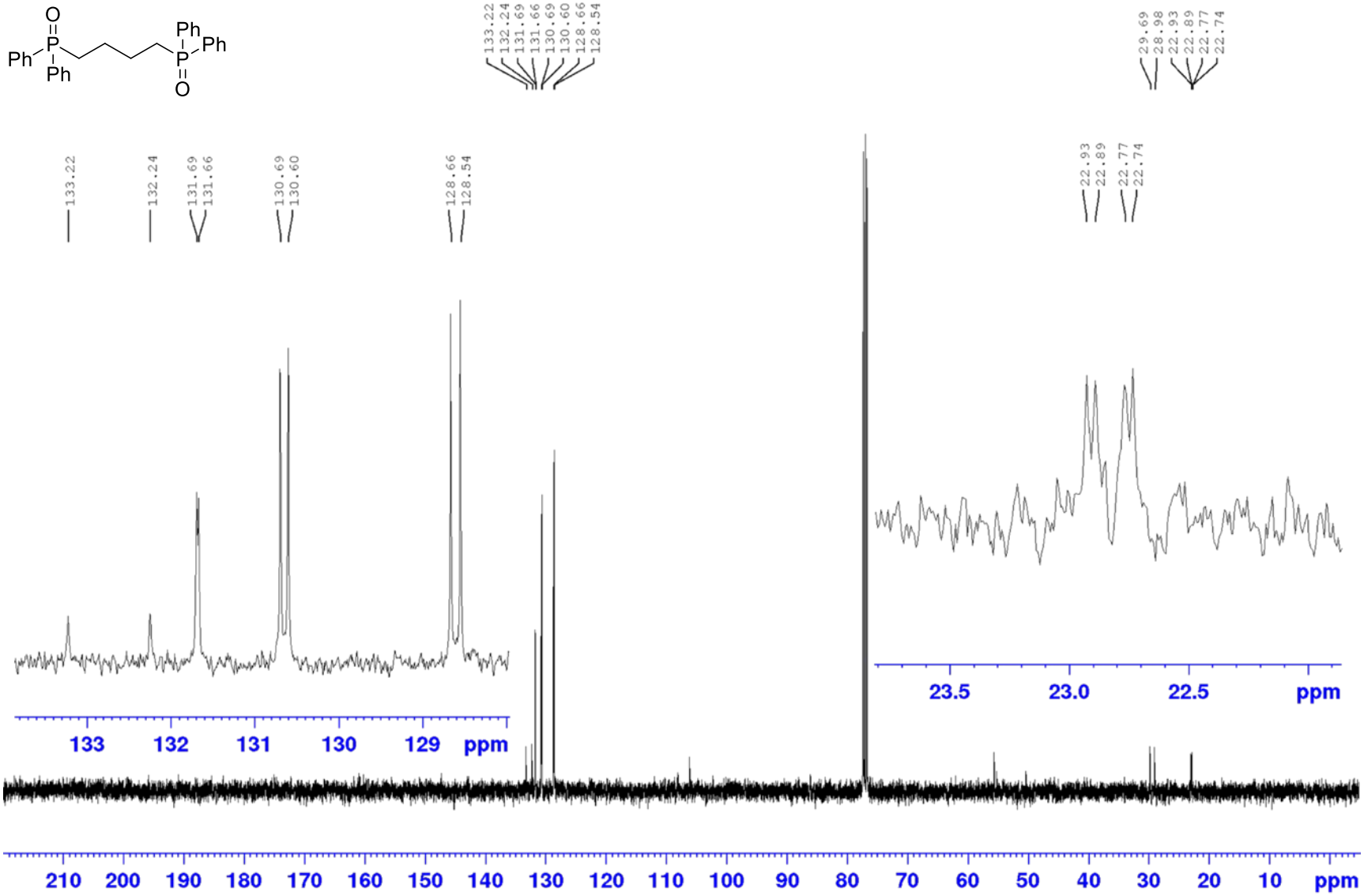
^{31}P NMR spectrum of propane-1,3-diylbis(diphenylphosphine oxide) (**4am**)



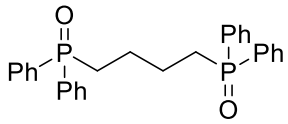
^{1}H NMR spectrum of butane-1,4-diylbis(diphenylphosphine oxide) (**4an**)



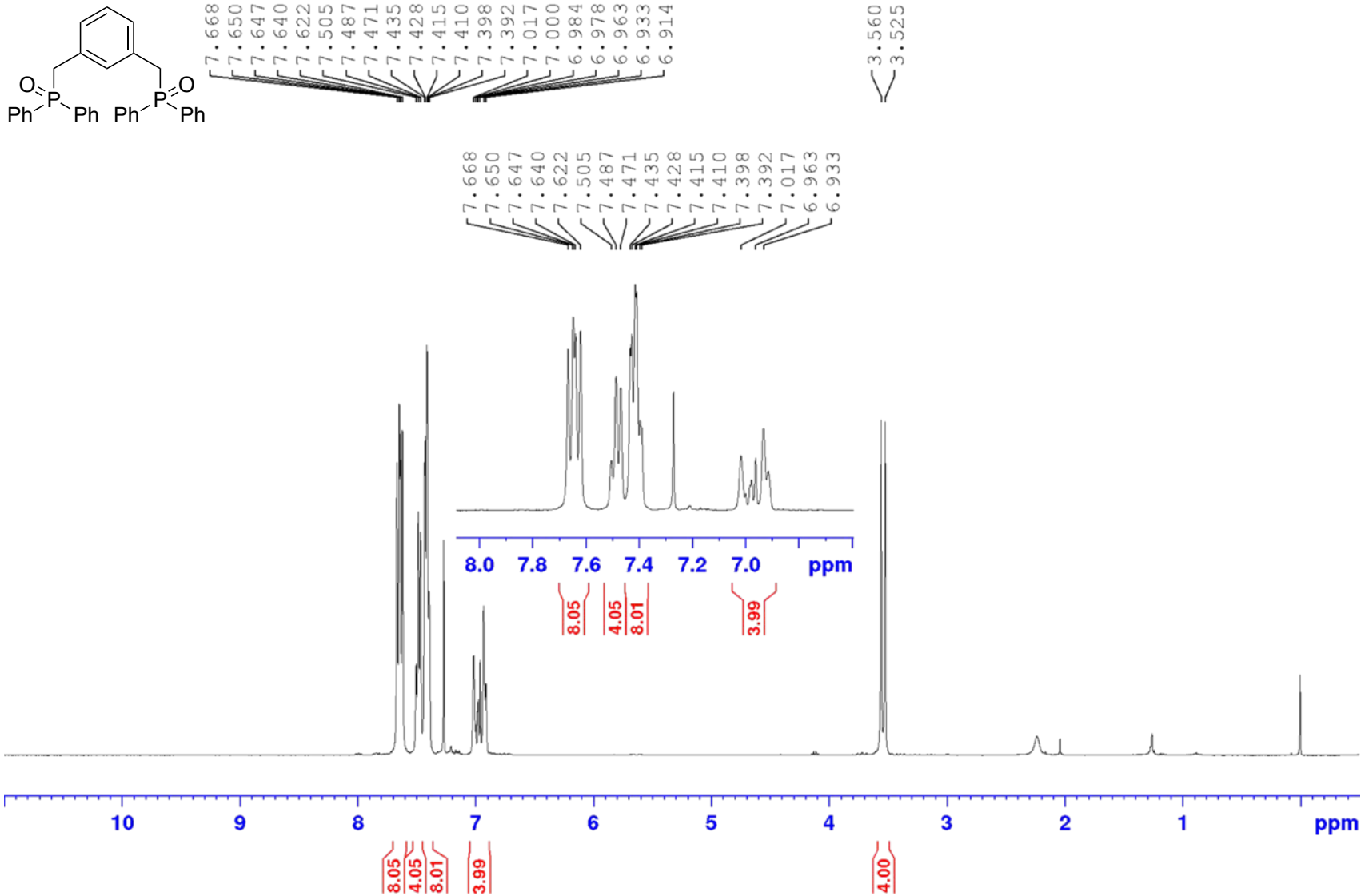
^{13}C NMR spectrum of of butane-1,4-diylbis(diphenylphosphine oxide) (**4an**)



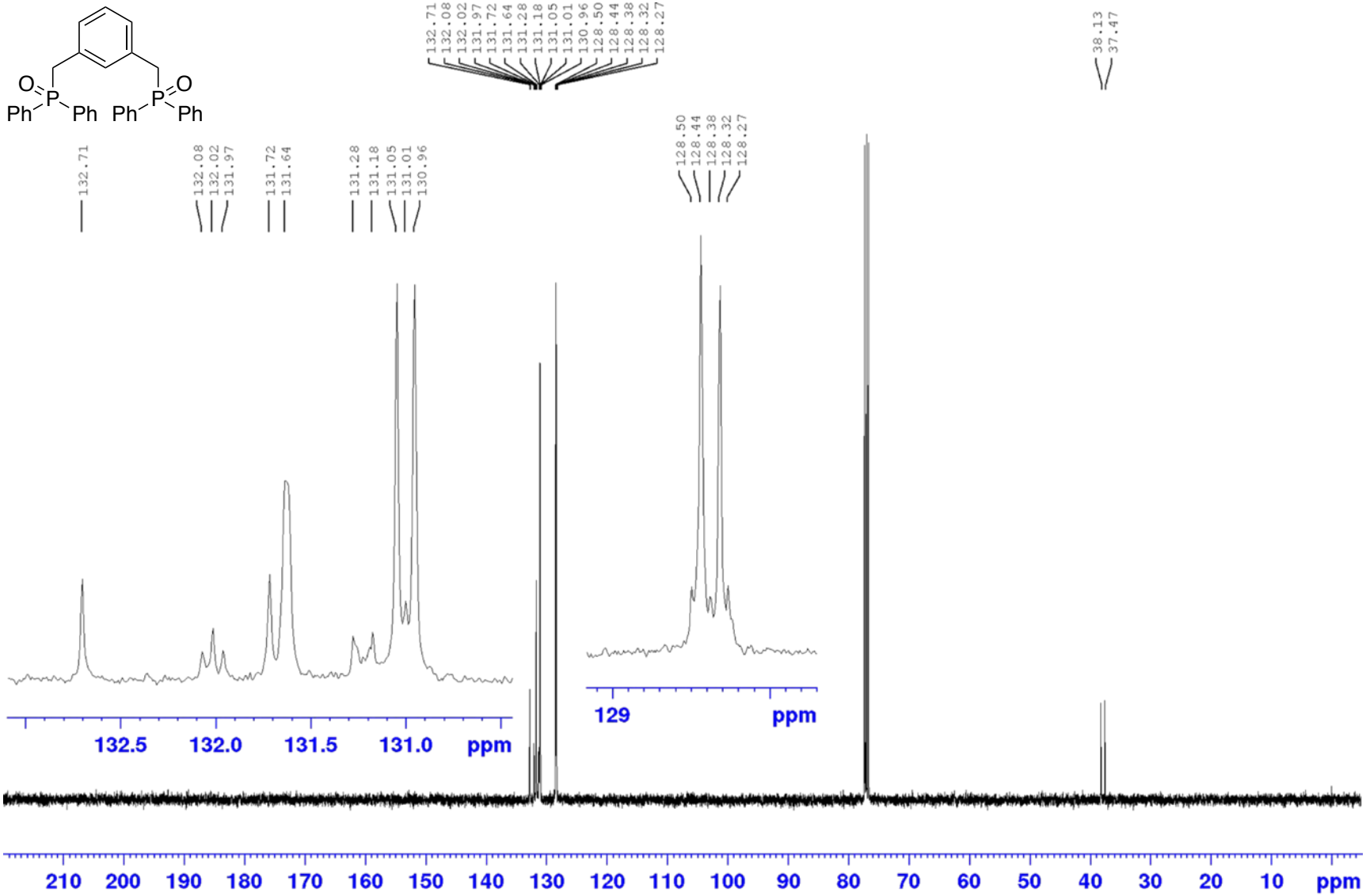
^{31}P of NMR spectrum of of butane-1,4-diylbis(diphenylphosphine oxide) (**4an**)



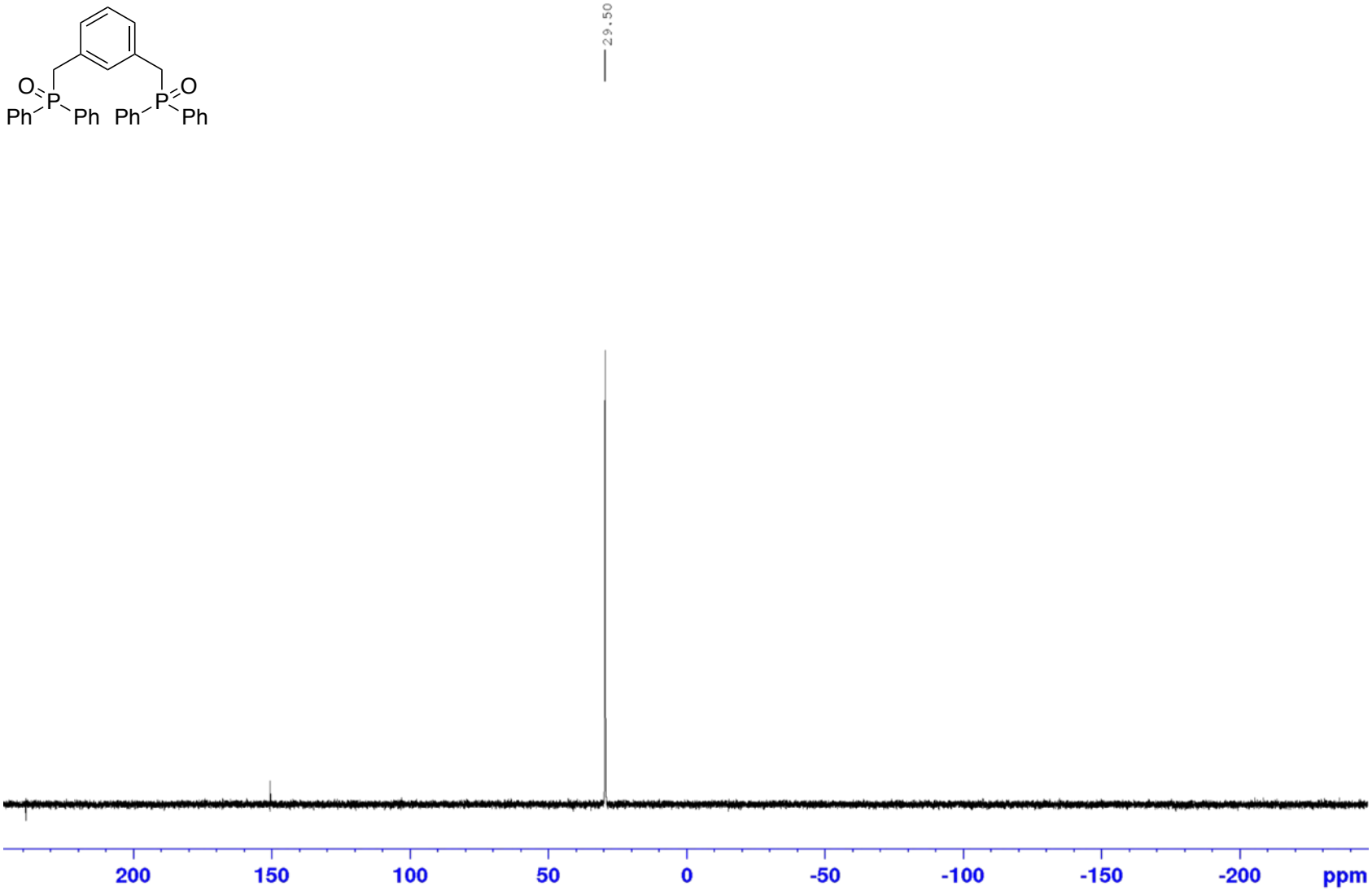
^{1}H NMR spectrum of (1,3-phenylenebis(methylene))bis(diphenylphosphine oxide) (**4ao**)



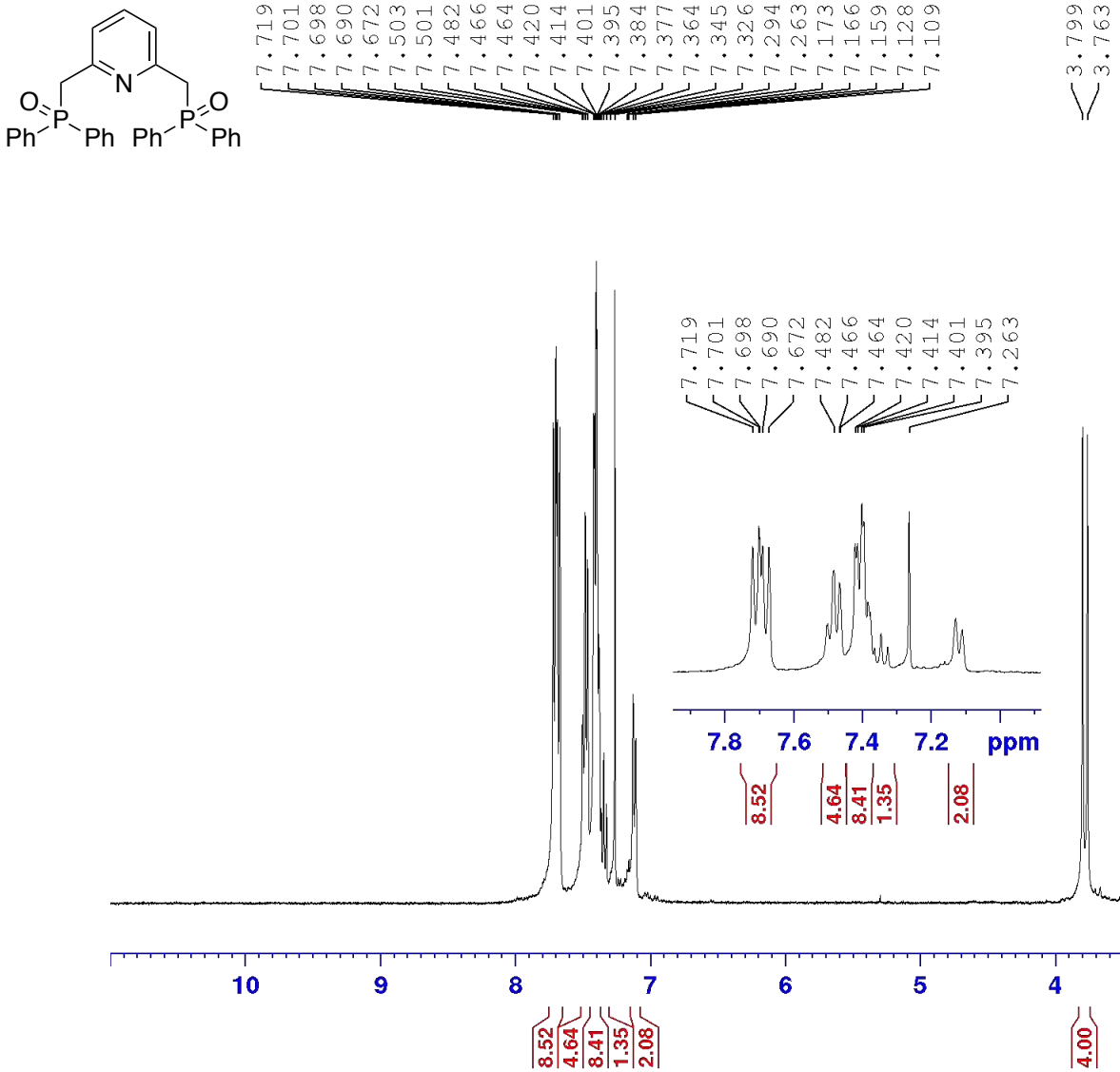
^{13}C NMR spectrum of (1,3-phenylenebis(methylene))bis(diphenylphosphine oxide) (**4ao**)



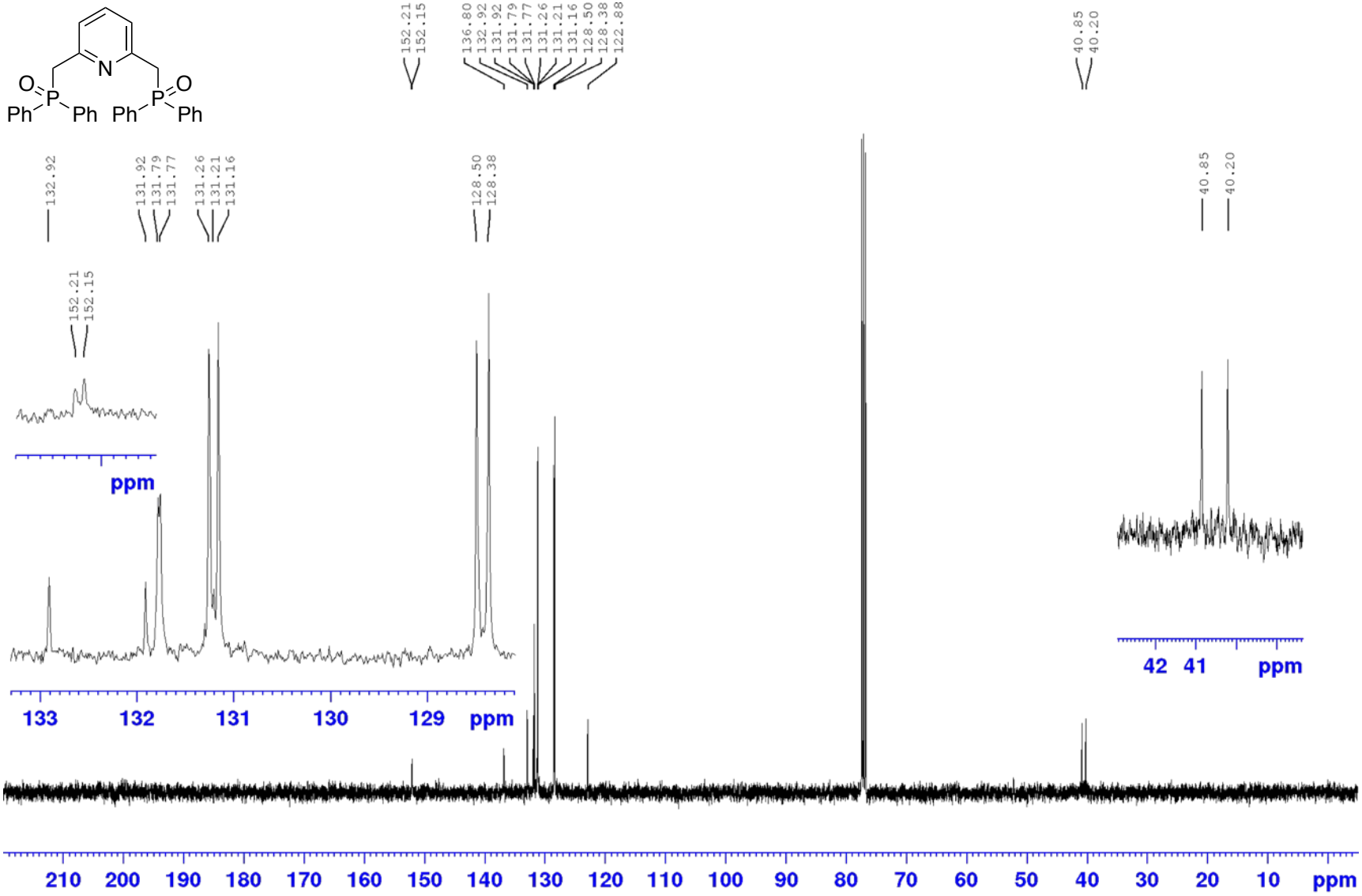
^{31}P NMR spectrum of (1,3-phenylenebis(methylene))bis(diphenylphosphine oxide) (**4ao**)



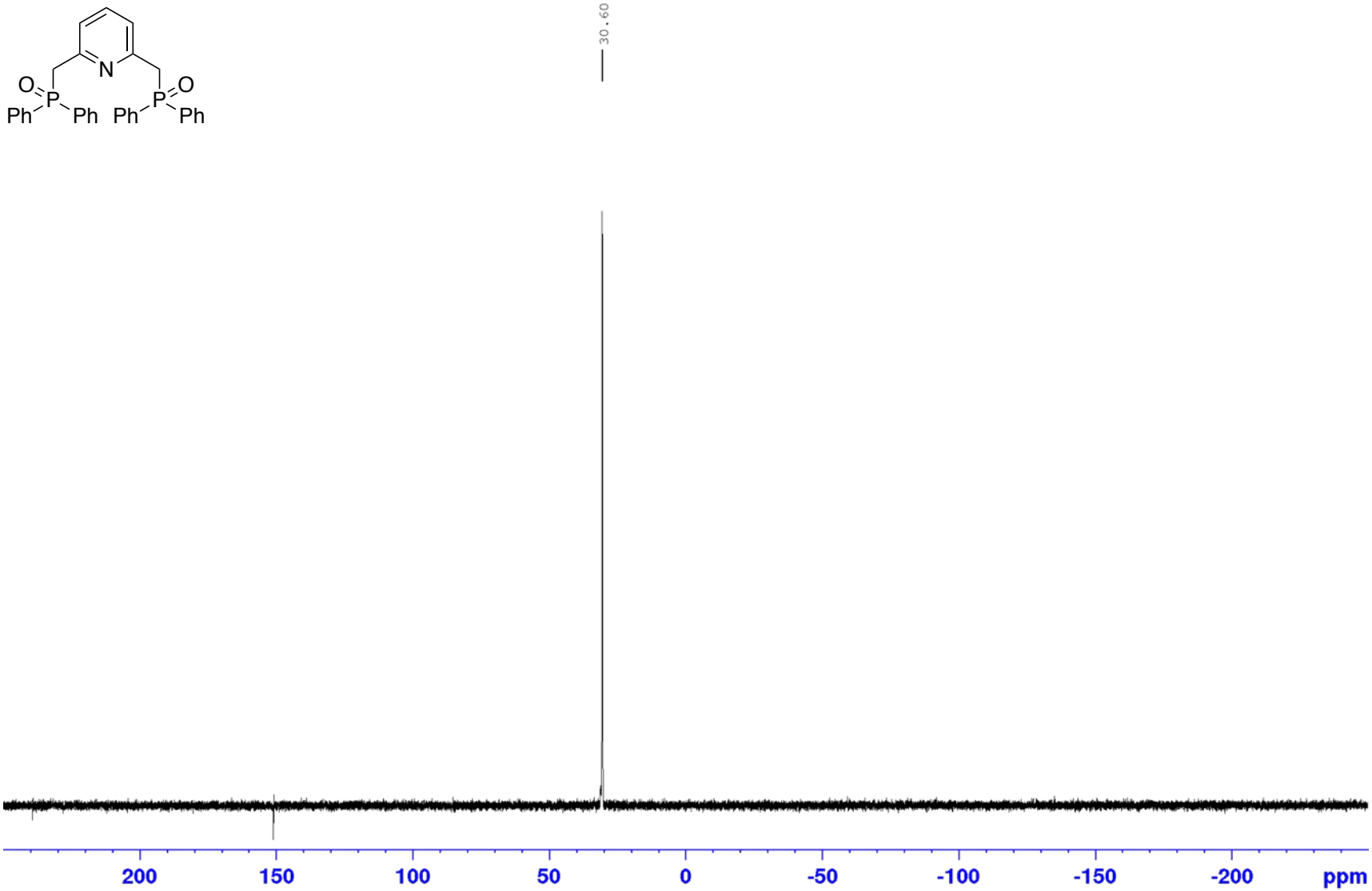
^{1}H NMR spectrum of (pyridine-2,6-diylbis(methylene))bis(diphenylphosphine oxide) (**4ap**)



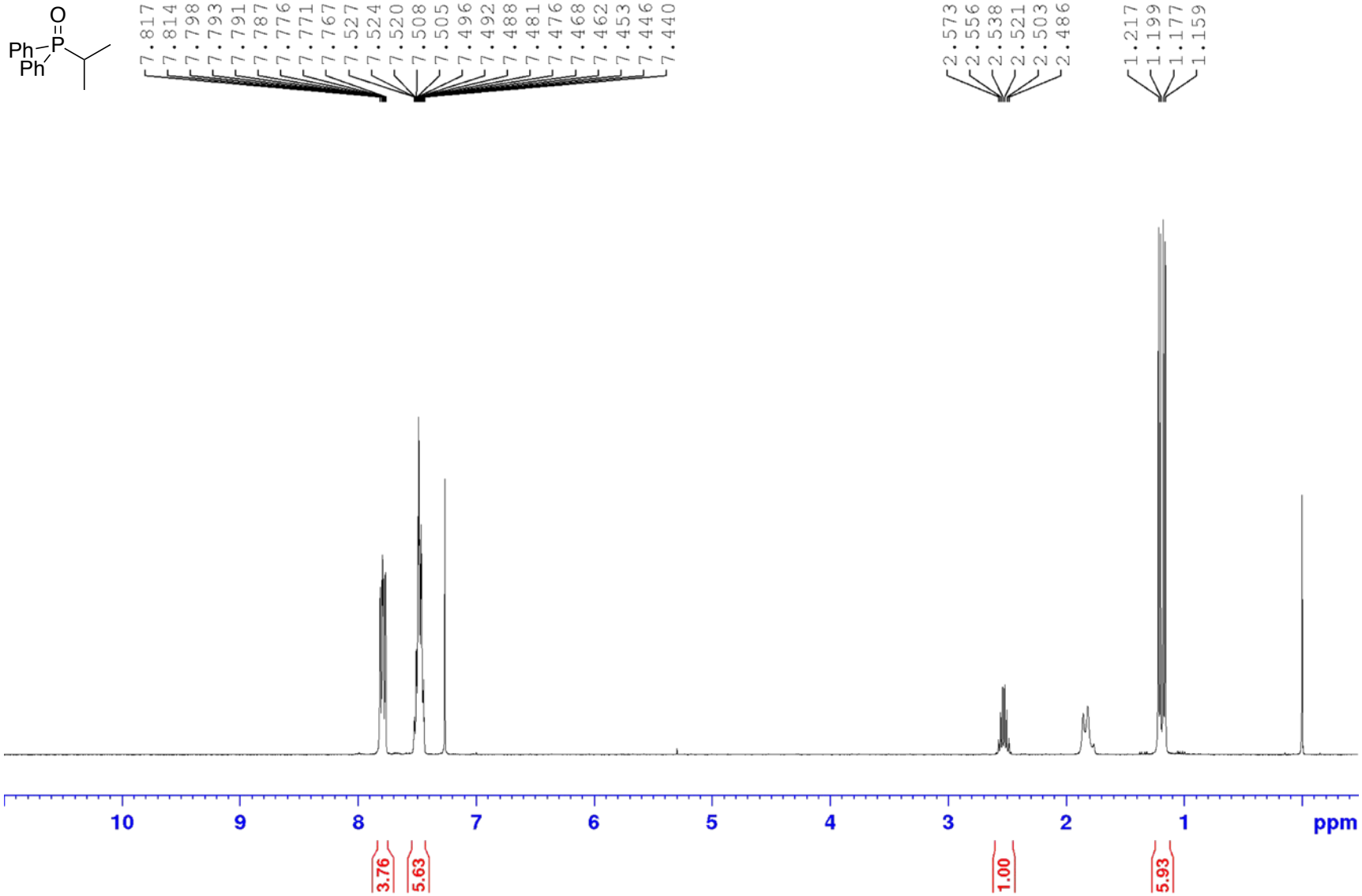
^{13}C NMR spectrum of (pyridine-2,6-diylbis(methylene))bis(diphenylphosphine oxide) (**4ap**)



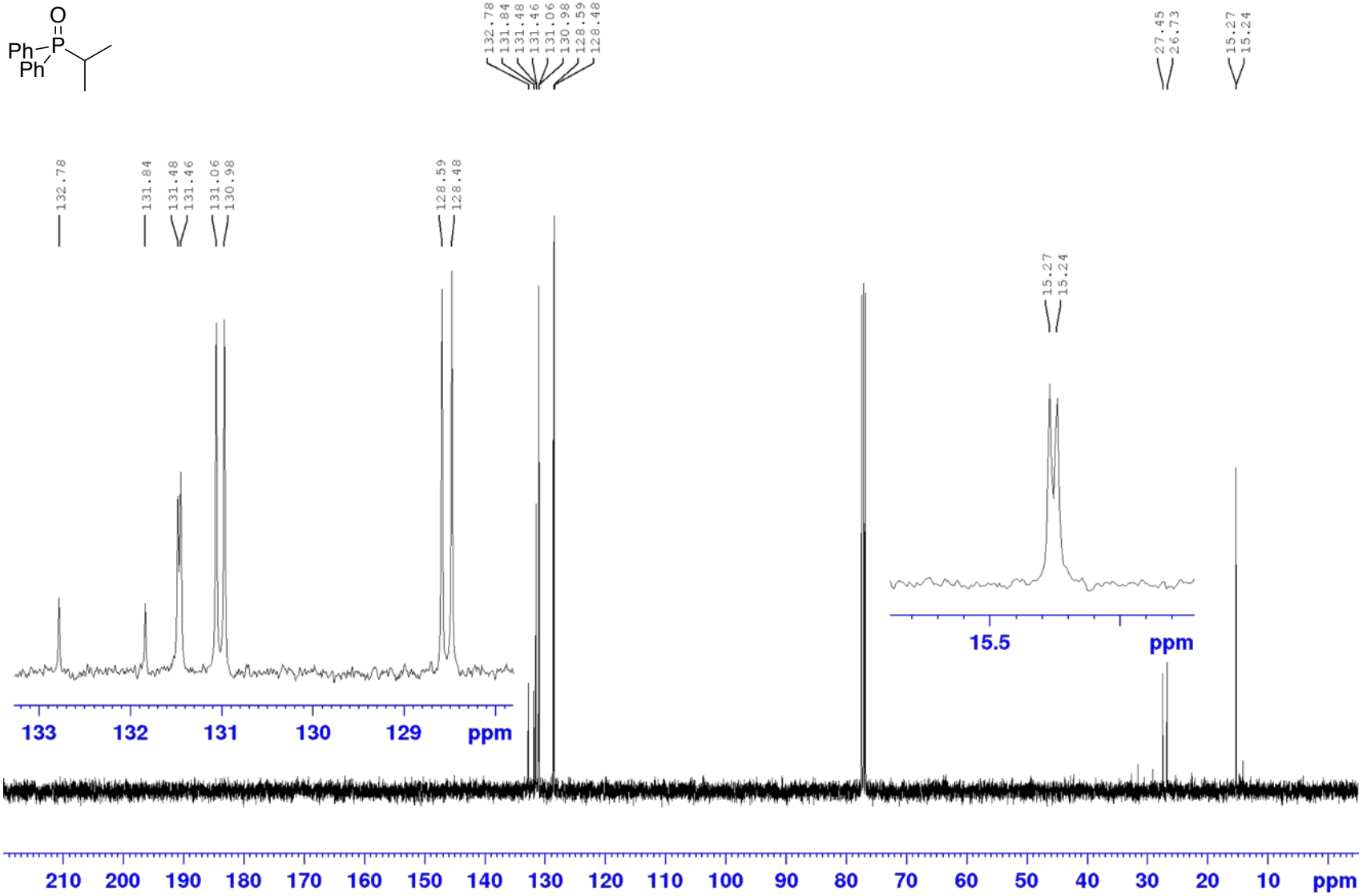
^{31}P NMR spectrum of (pyridine-2,6-diylbis(methylene))bis(diphenylphosphine oxide) (**4ap**)



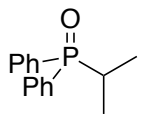
[1]H NMR spectrum of isopropyldiphenylphosphine oxide (**4aq**)



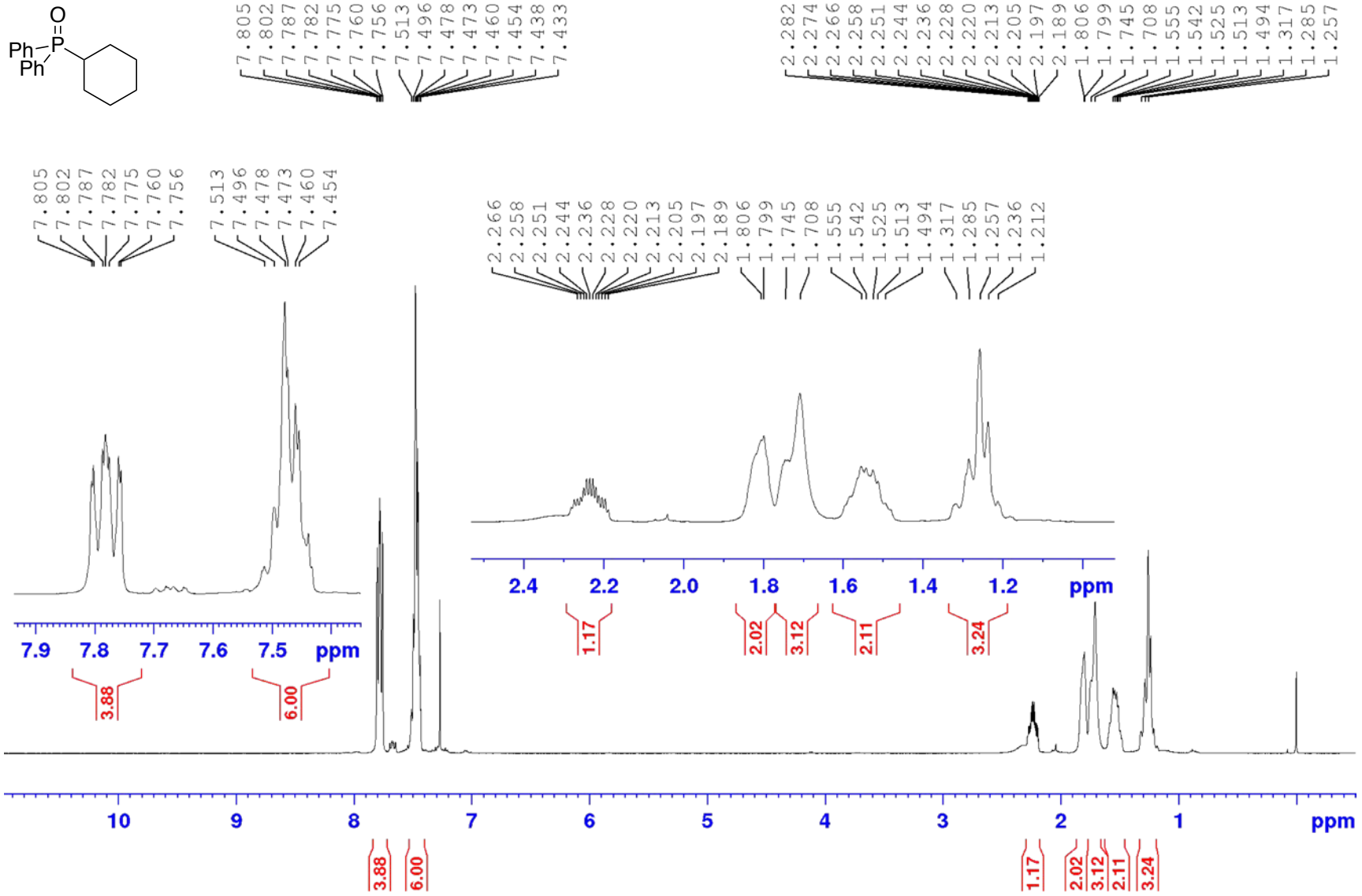
^{13}C NMR spectrum of isopropyldiphenylphosphine oxide (**4aq**)



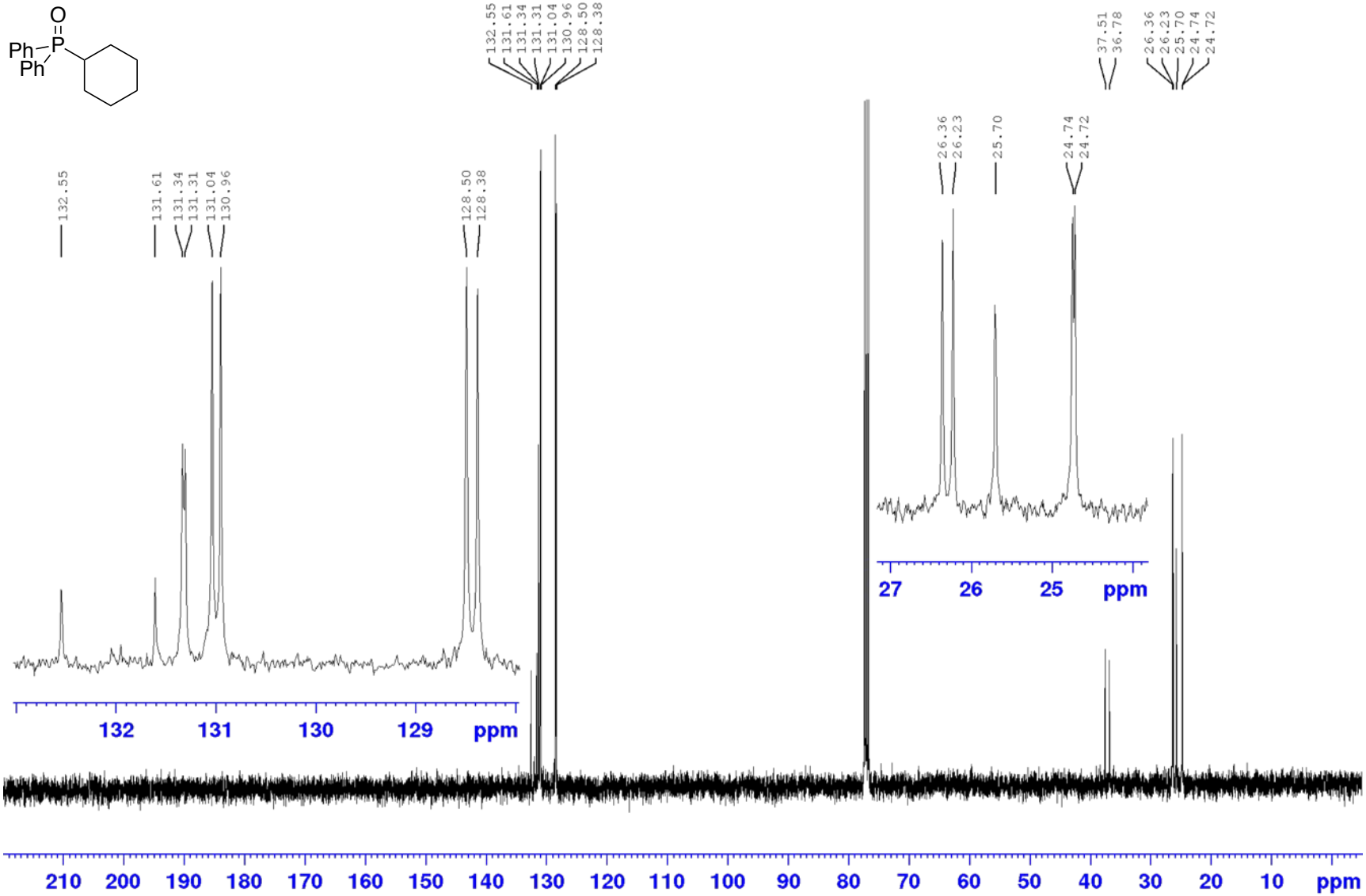
^{31}P NMR spectrum of isopropyldiphenylphosphine oxide (**4aq**)



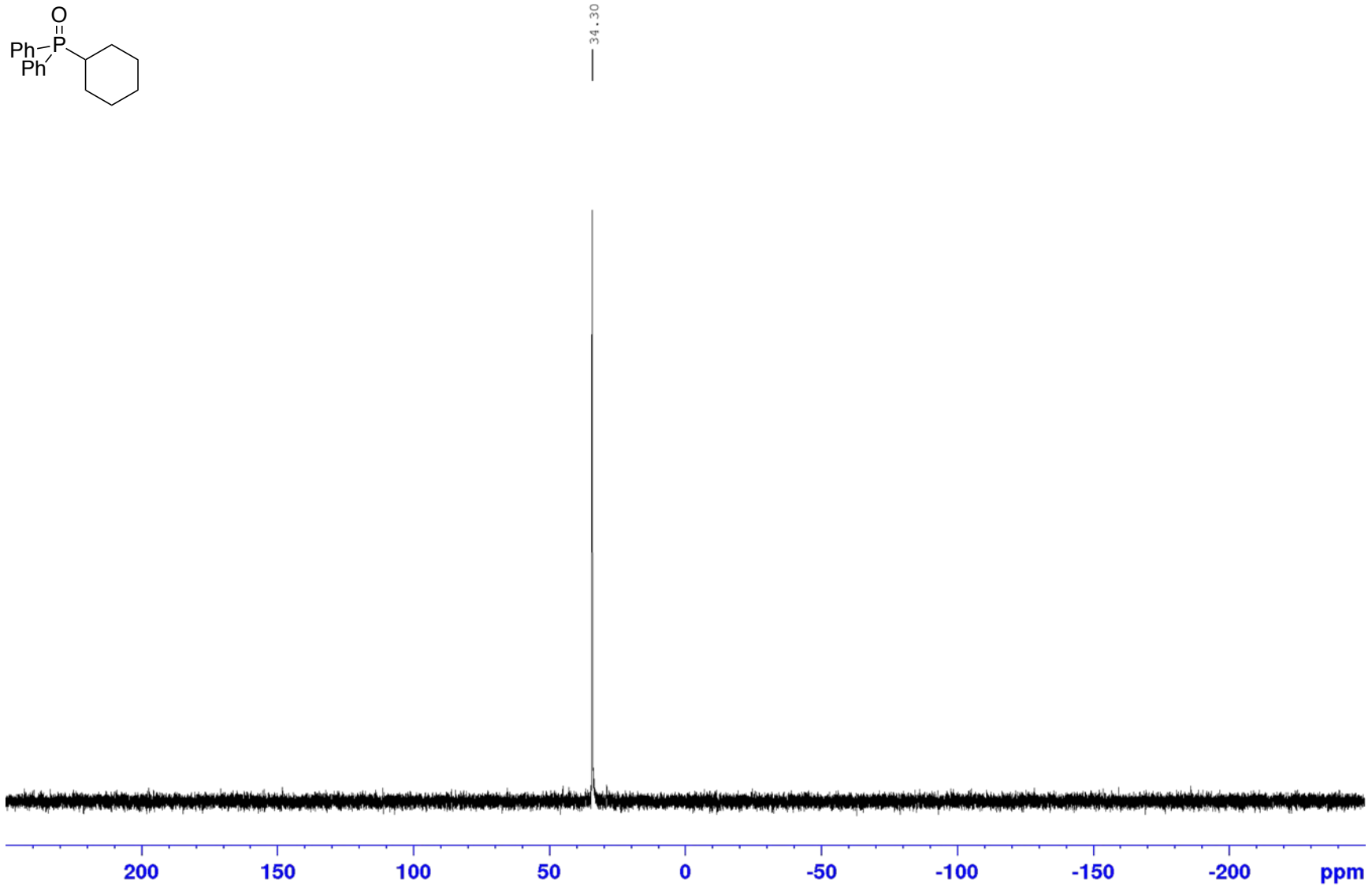
[1]H NMR spectrum of cyclohexyldiphenylphosphine oxide (**4ar**)



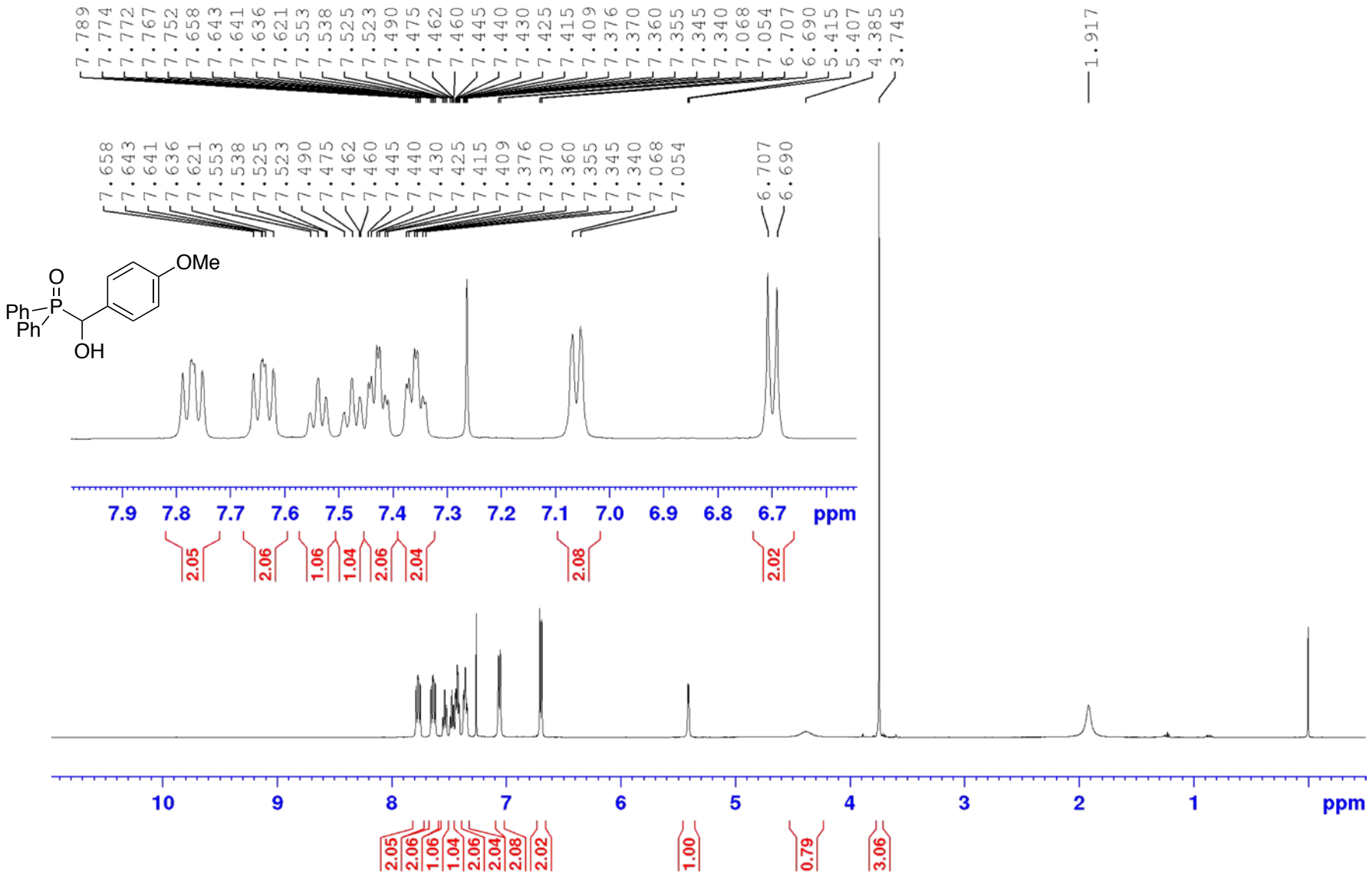
^{13}C NMR spectrum of cyclohexyldiphenylphosphine oxide (**4ar**)



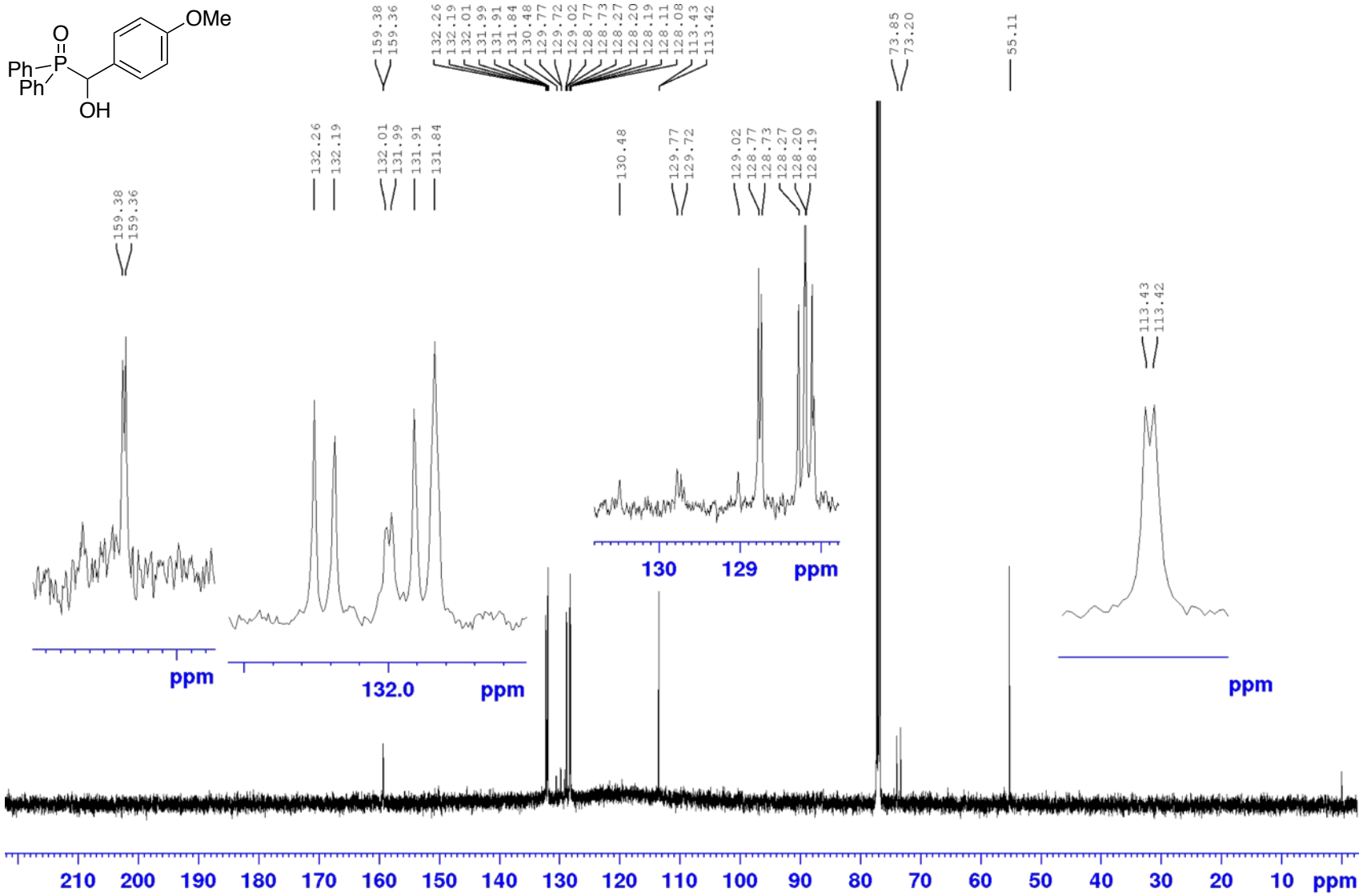
^{31}P NMR spectrum of cyclohexyldiphenylphosphine oxide (**4ar**)



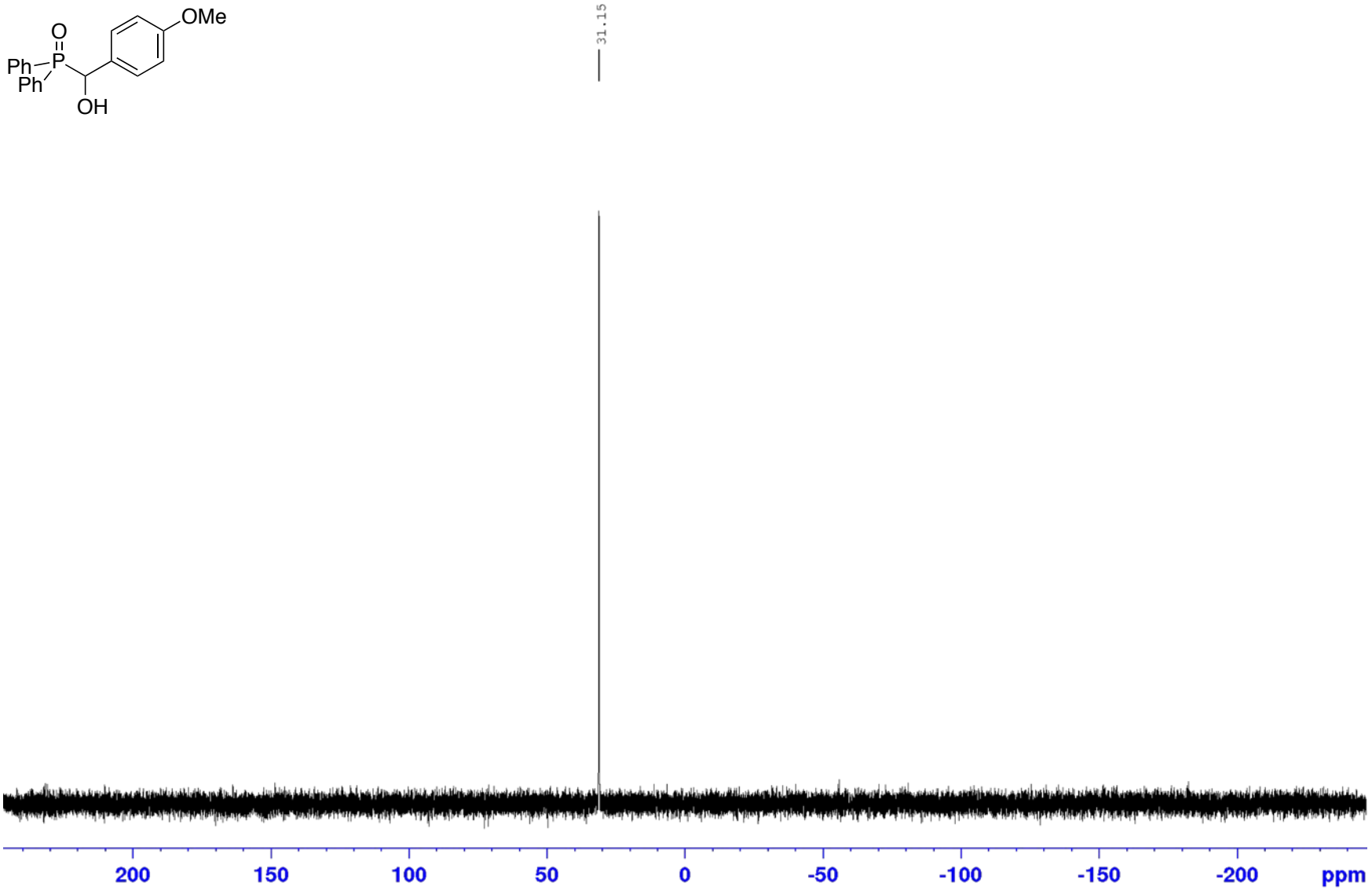
^{1}H NMR spectrum of (hydroxy(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6aa**)



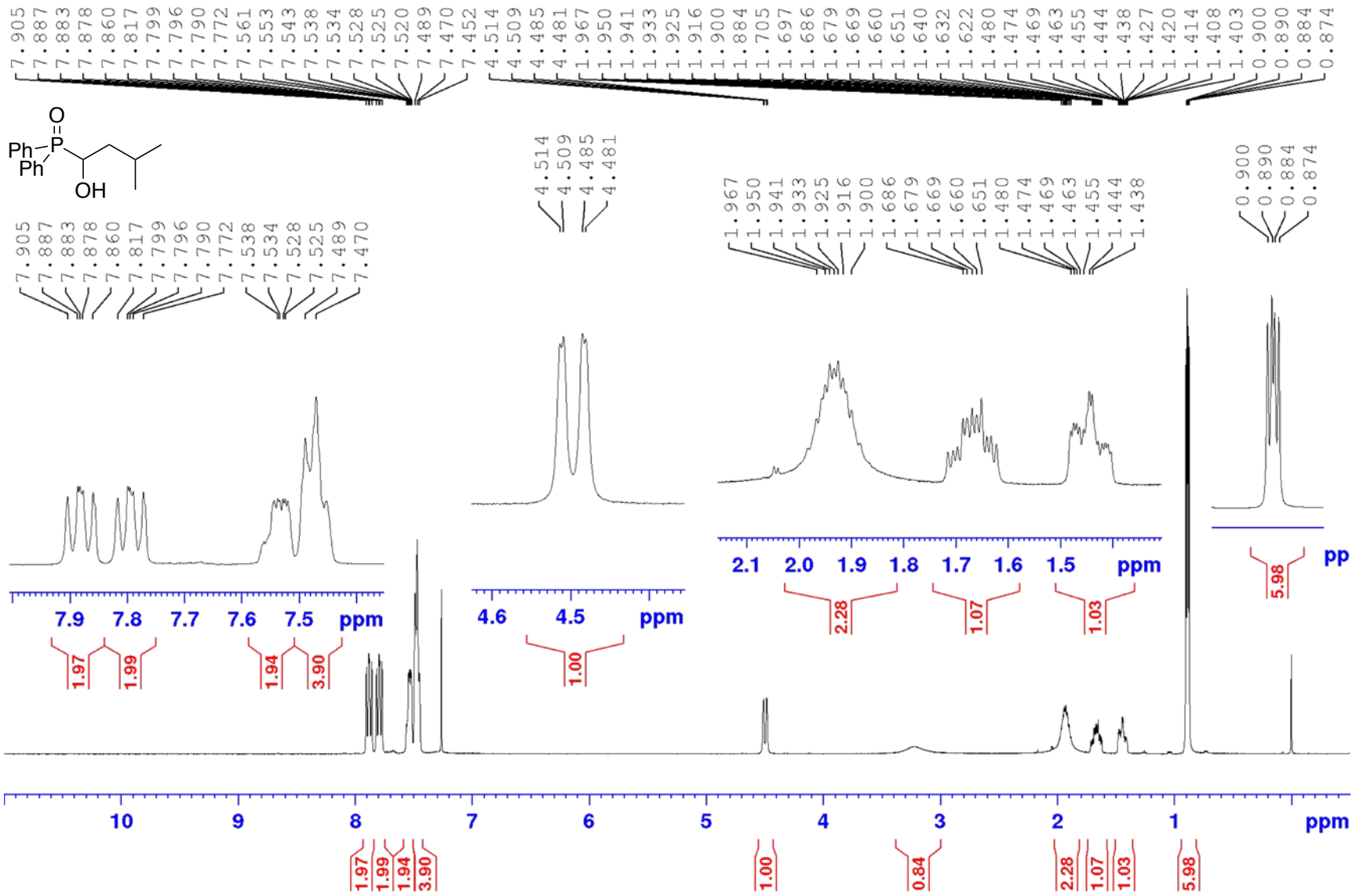
^{13}C NMR spectrum of (hydroxy(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6aa**)



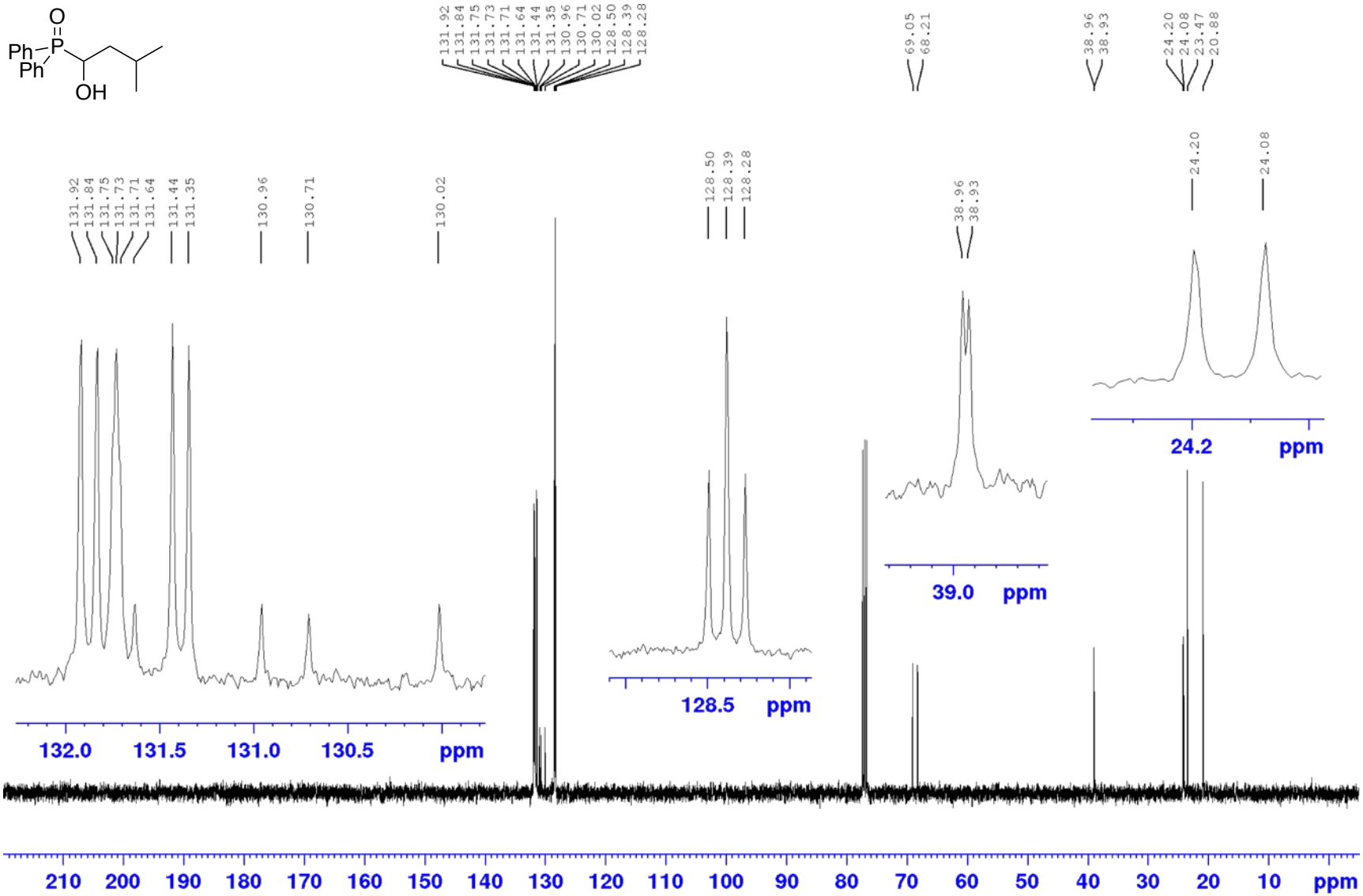
^{31}P NMR spectrum of (hydroxy(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6aa)**



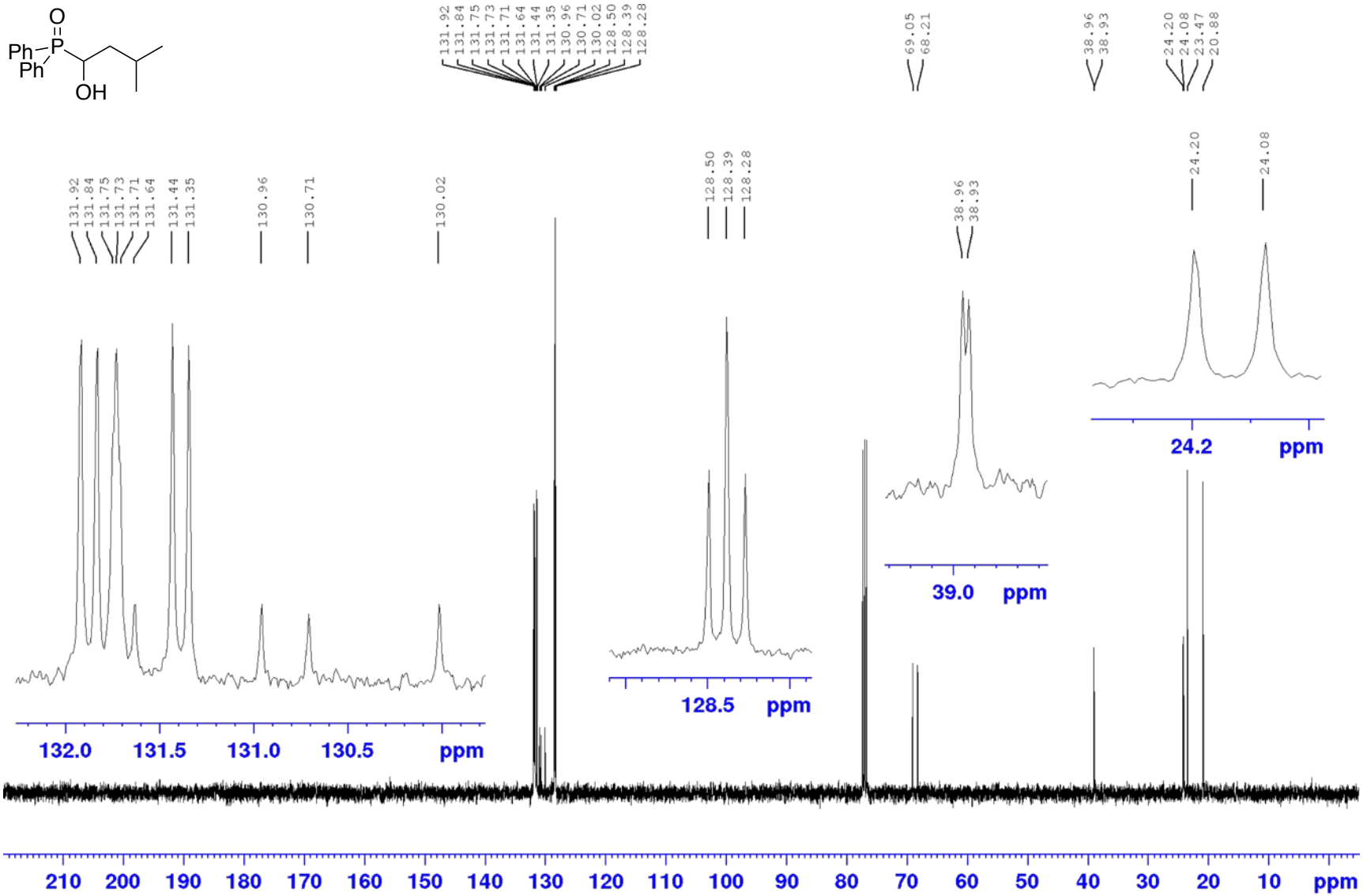
^{1}H NMR spectrum of (1-hydroxy-3-methylbutyl)diphenylphosphine oxide (**6ab**)



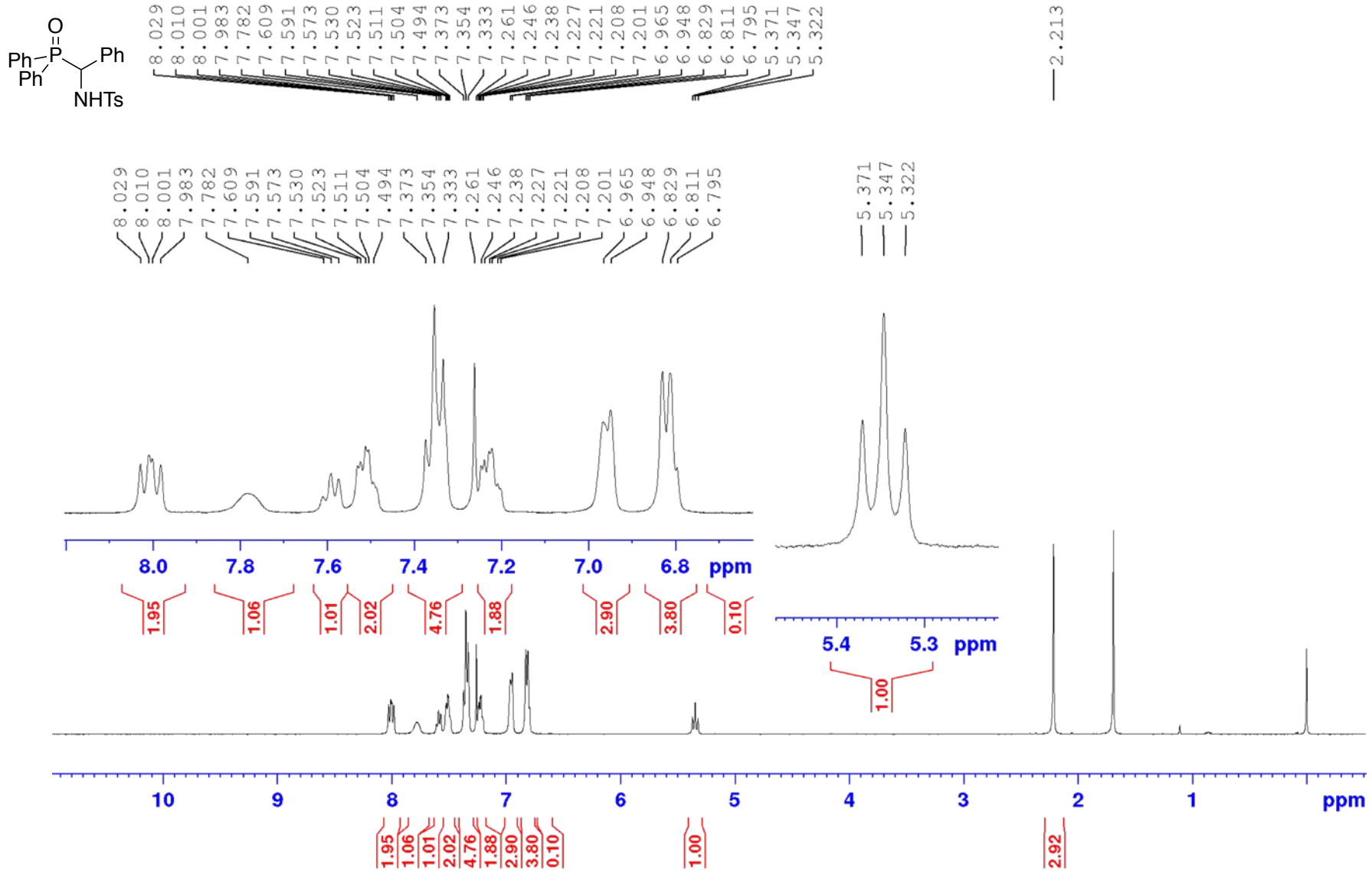
^{13}C NMR spectrum of (1-hydroxy-3-methylbutyl)diphenylphosphine oxide (**6ab**)



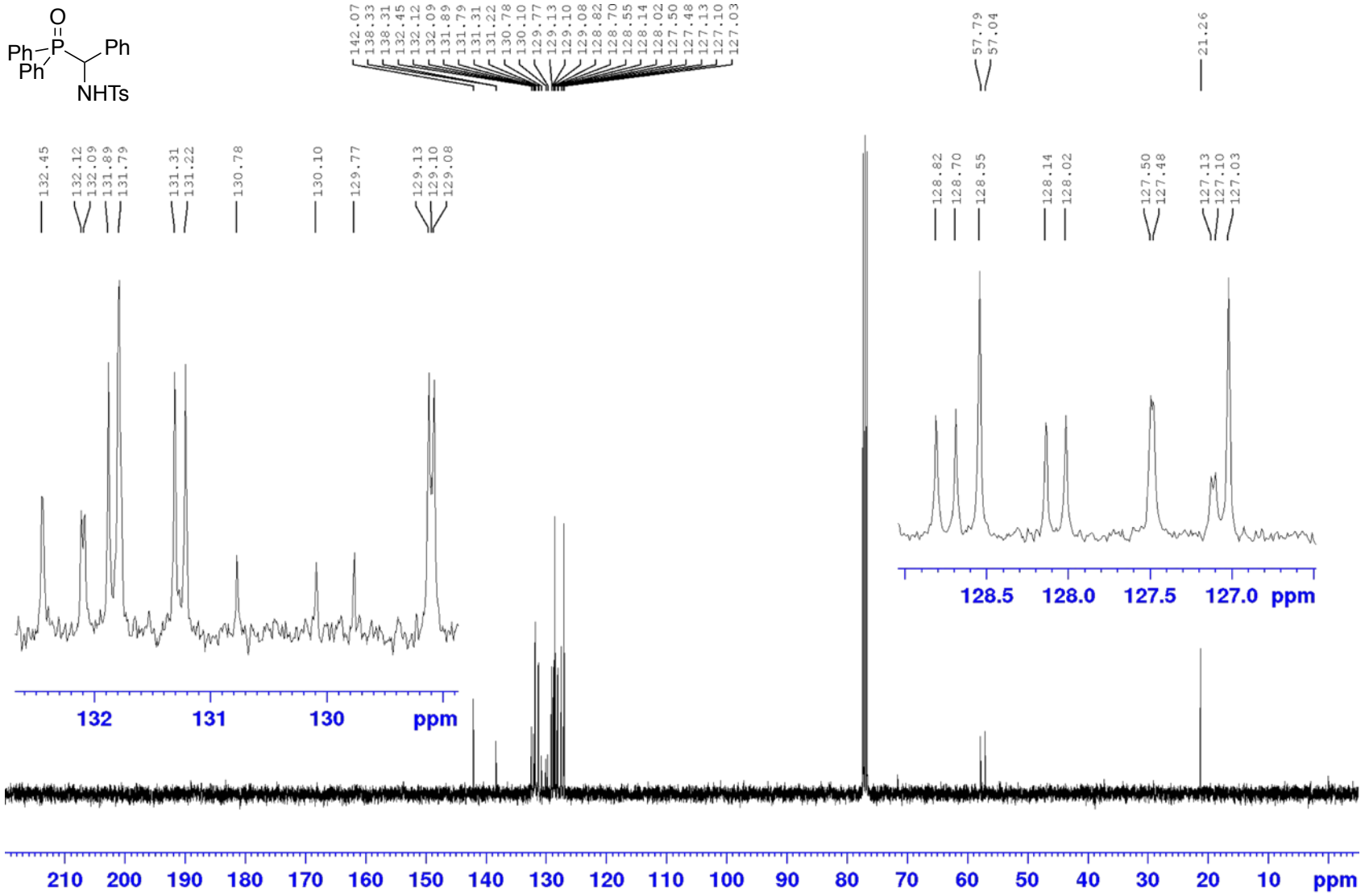
^{31}P NMR spectrum of (1-hydroxy-3-methylbutyl)diphenylphosphine oxide (**6ab**)



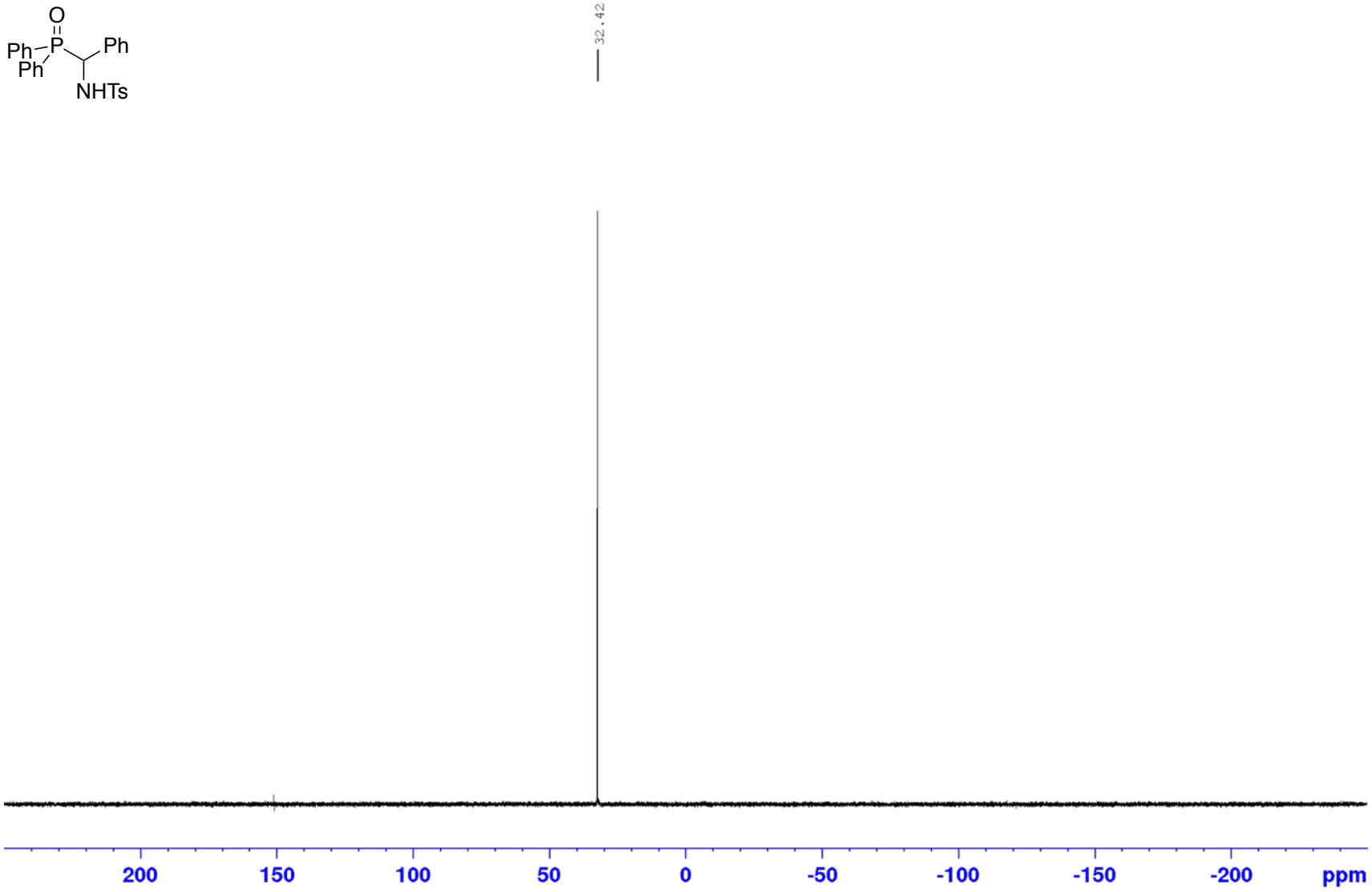
^{1}H NMR spectrum of *N*-((diphenylphosphoryl)(phenyl)methyl)-4-methylbenzenesulfonamide (**6ac**)



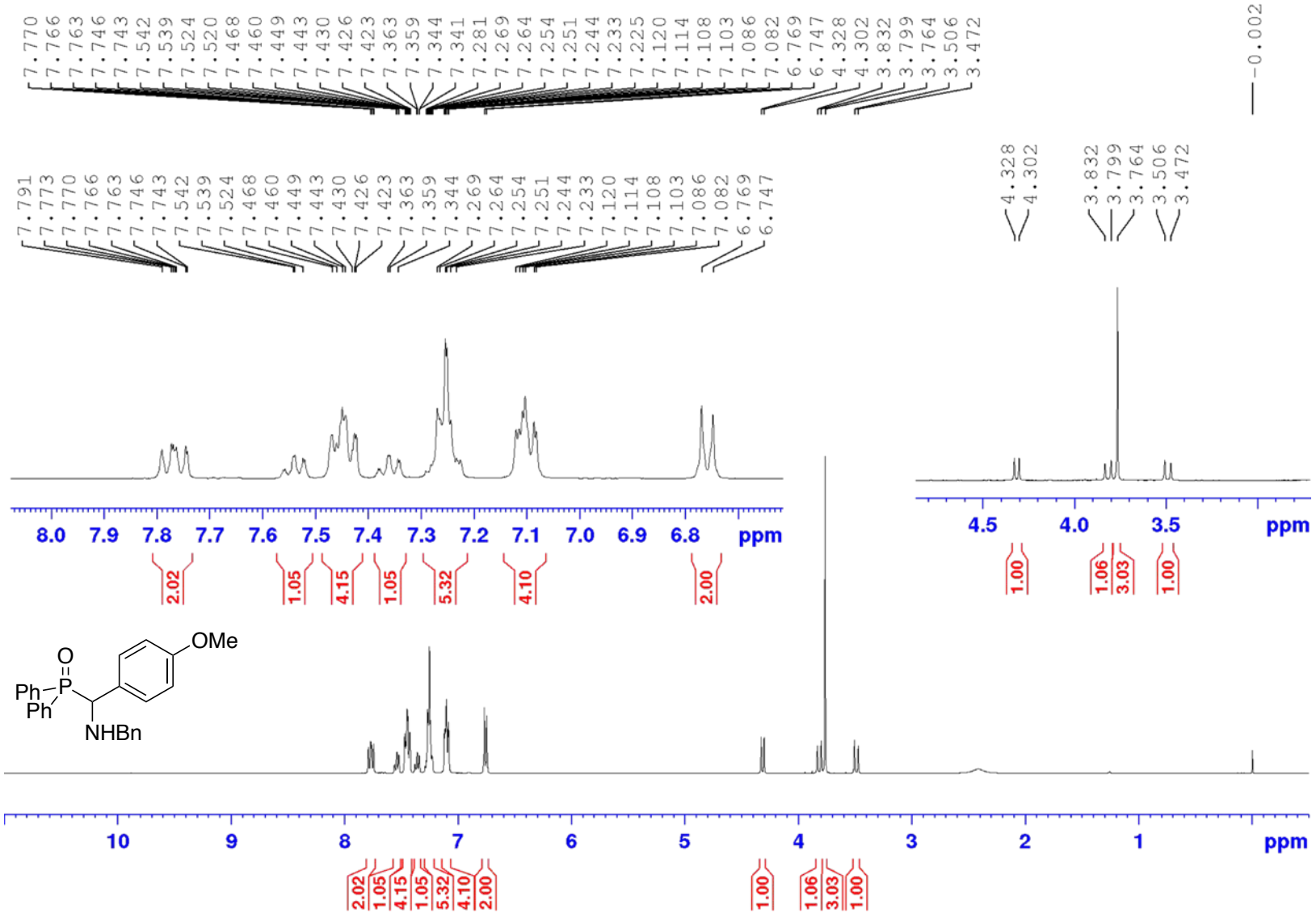
^{13}C NMR spectrum of *N*-((diphenylphosphoryl)(phenyl)methyl)-4-methylbenzenesulfonamide (**6ac**)



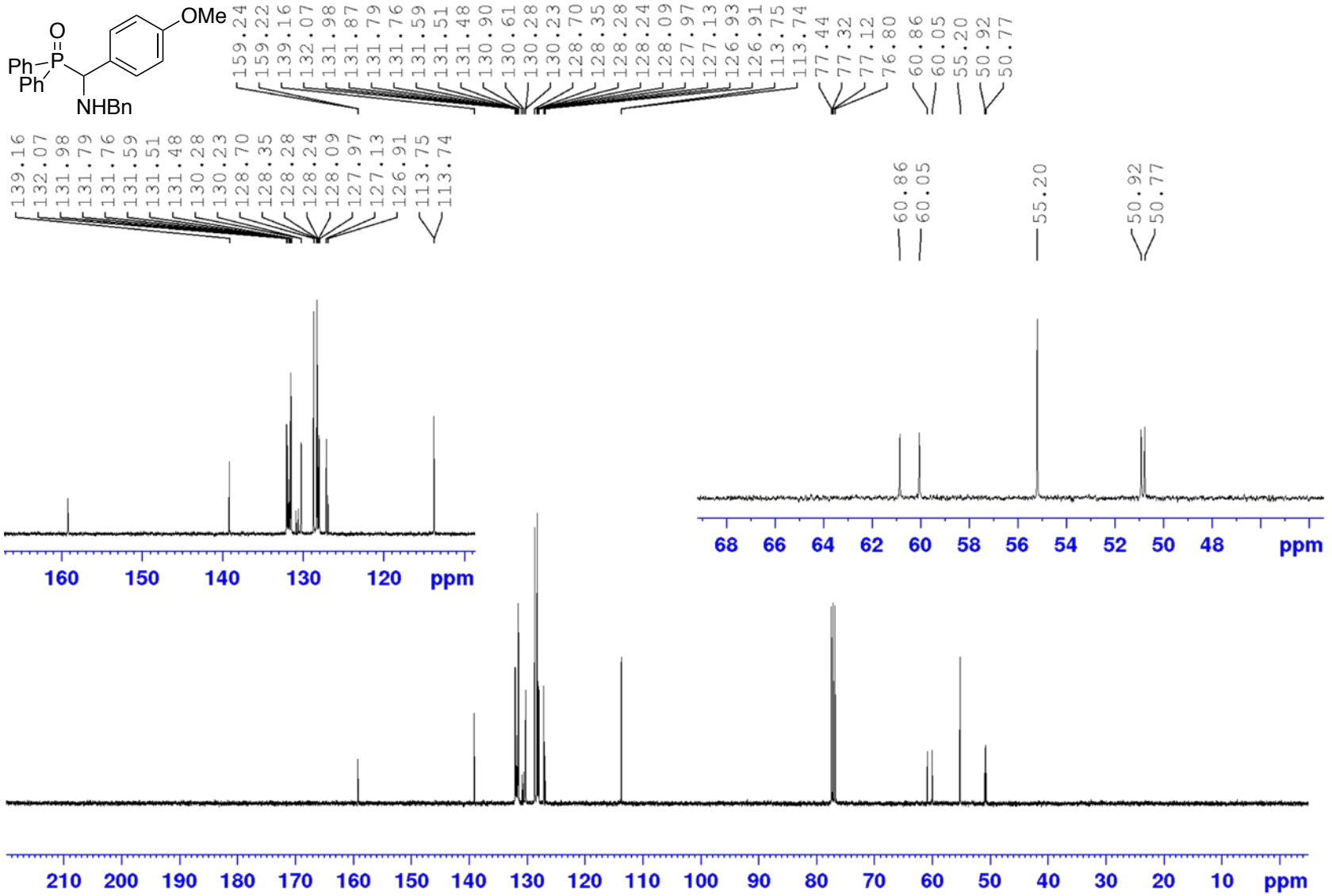
^{31}P NMR spectrum of *N*-((diphenylphosphoryl)(phenyl)methyl)-4-methylbenzenesulfonamide (**6ac**)



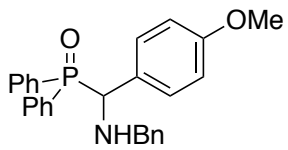
^{1}H NMR spectrum of ((benzylamino)(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6ad**)



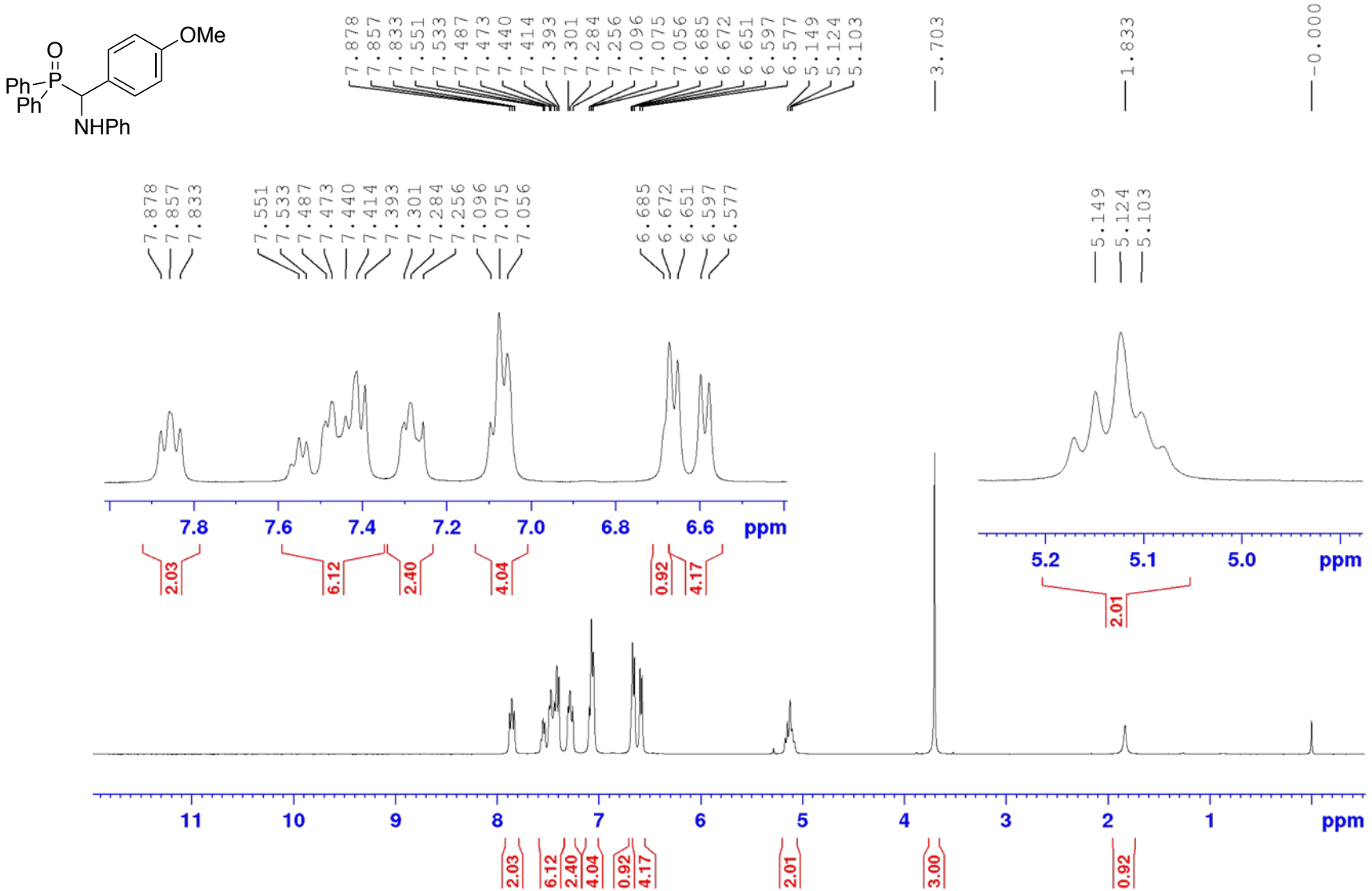
^{13}C NMR spectrum of ((benzylamino)(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6ad**)



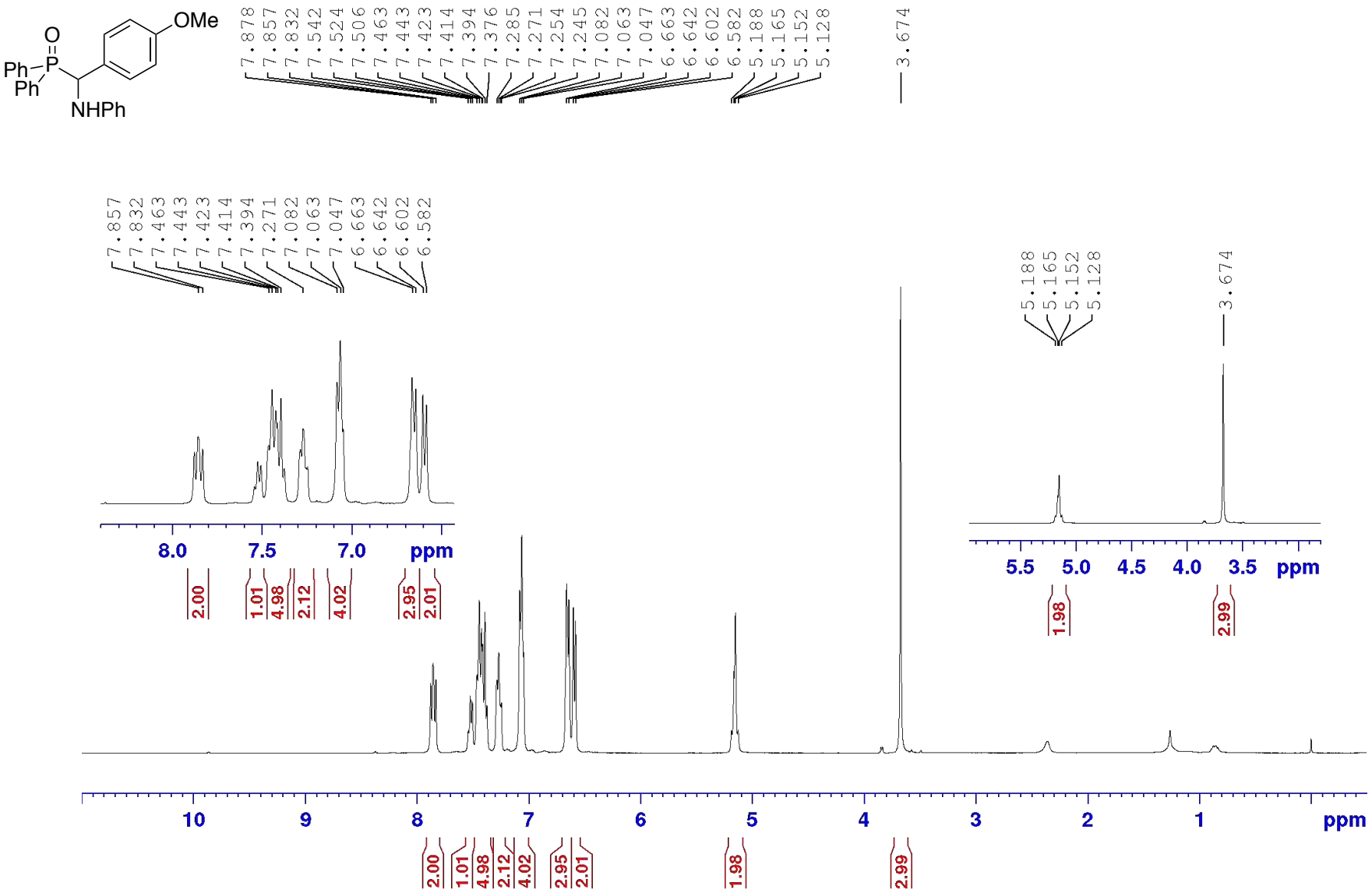
^{31}P NMR spectrum of ((benzylamino)(4-methoxyphenyl)methyl)diphenylphosphine oxide (**6ad**)



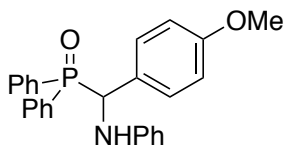
[1]H NMR spectrum of ((4-methoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**6ae**)



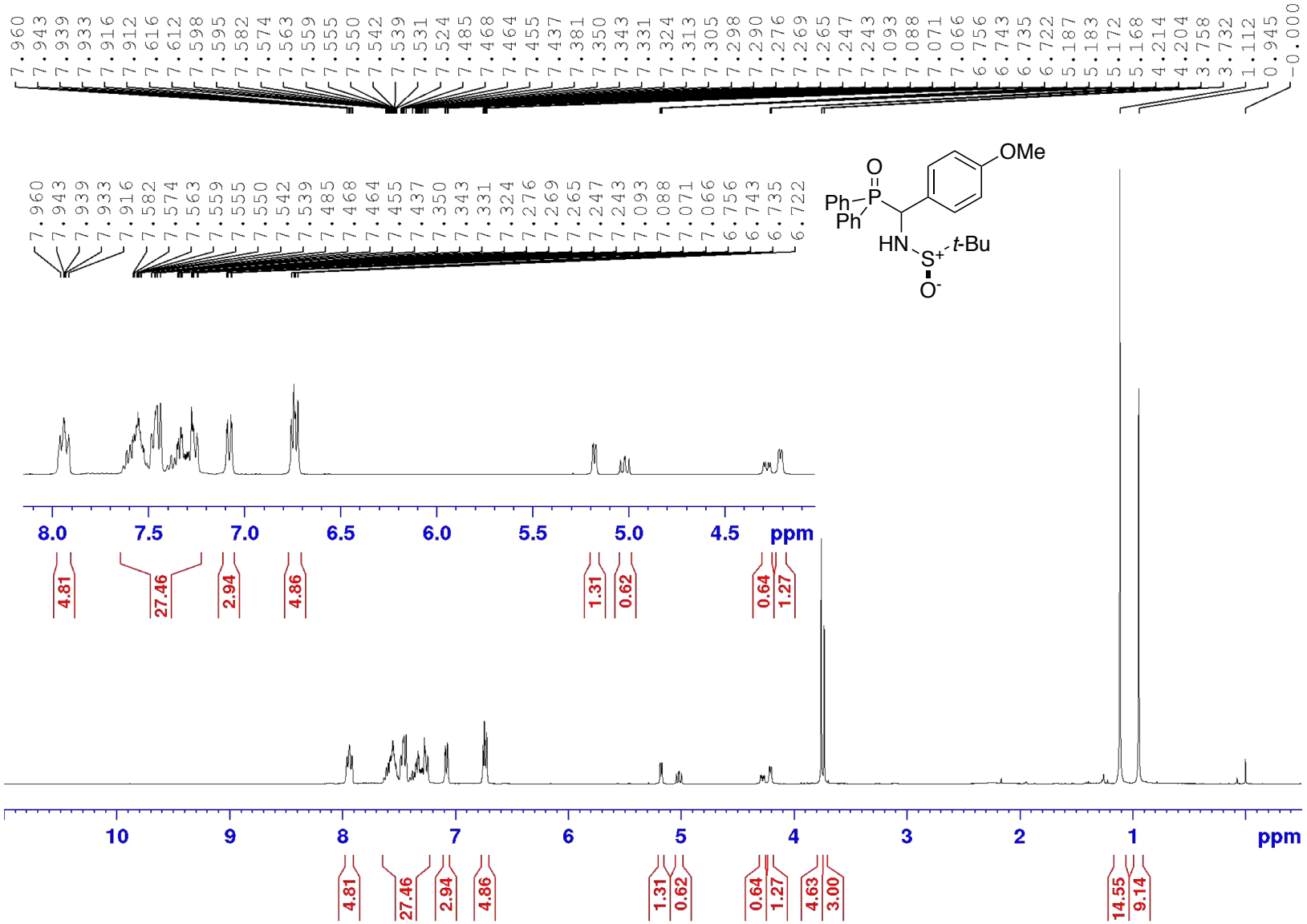
^{13}C NMR spectrum of ((4-methoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**6ae**)



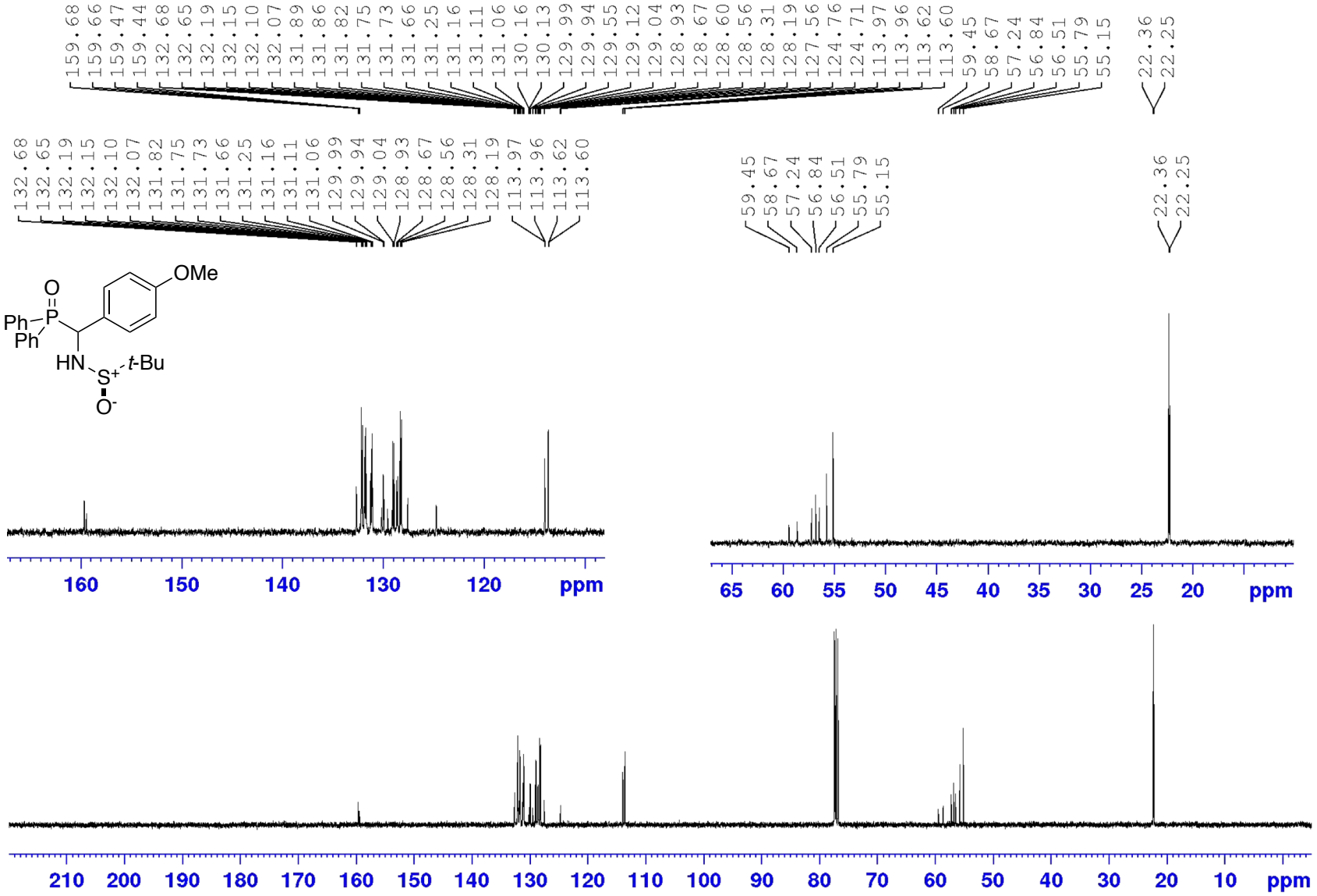
^{31}P NMR spectrum of ((4-methoxyphenyl)(phenylamino)methyl)diphenylphosphine oxide (**6ae**)



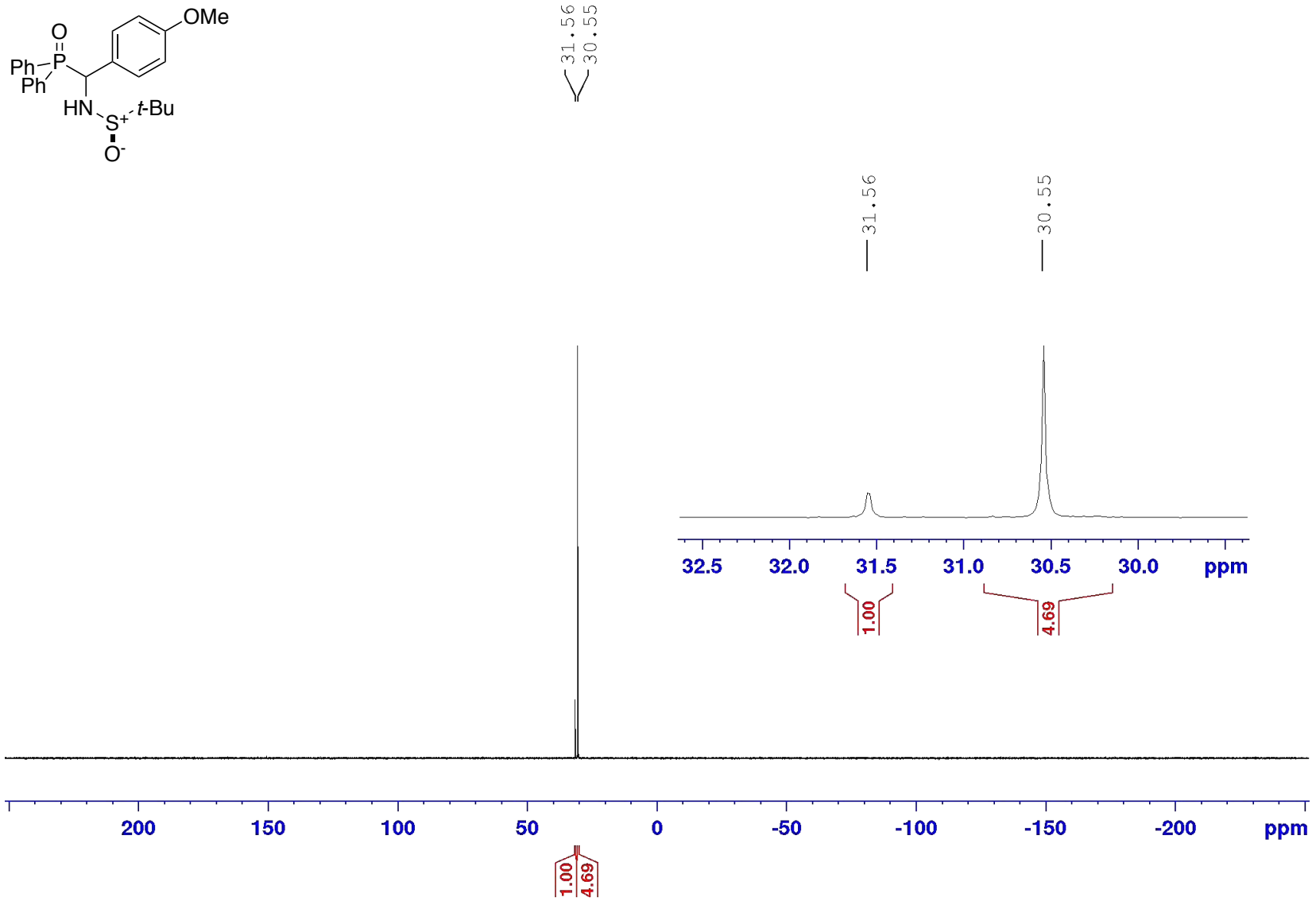
^{1}H NMR spectrum of (*R*)-*N*-((diphenylphosphoryl)(4-methoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (**6af**)



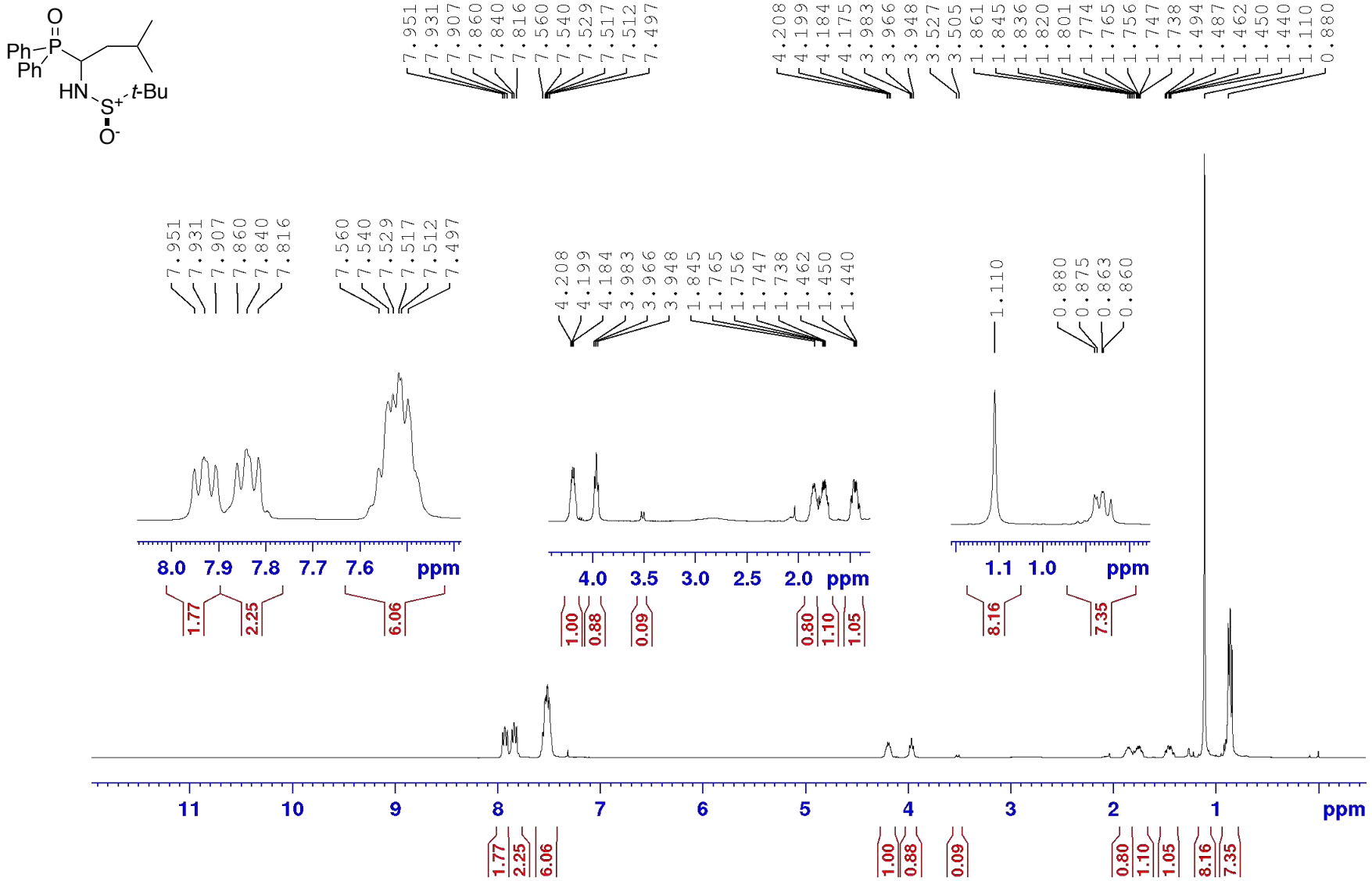
^{13}C NMR spectrum of (*R*)-*N*-((diphenylphosphoryl)(4-methoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (**6af**)



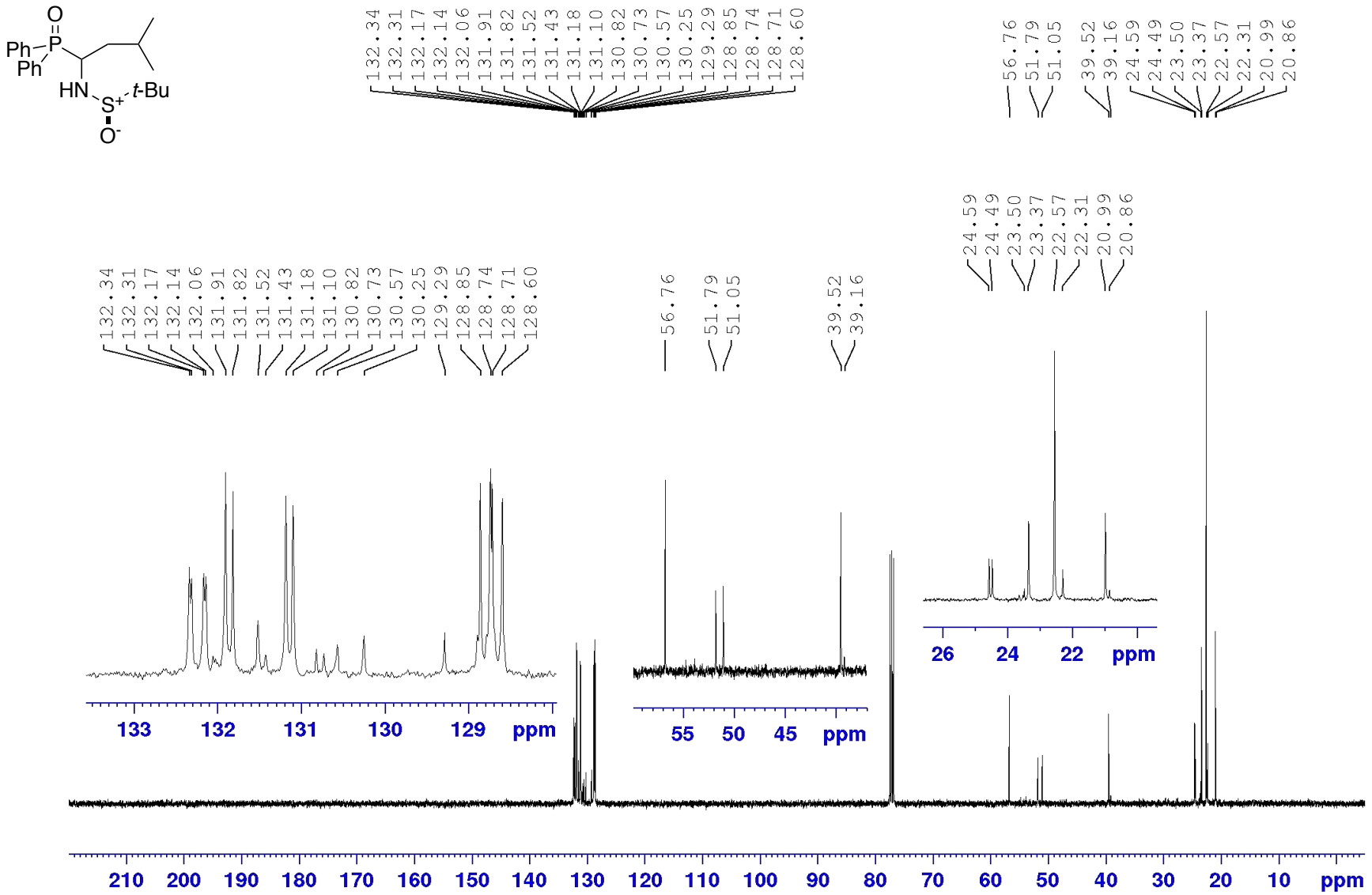
^{31}P NMR spectrum of (*R*)-*N*-((diphenylphosphoryl)(4-methoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (**6af**)



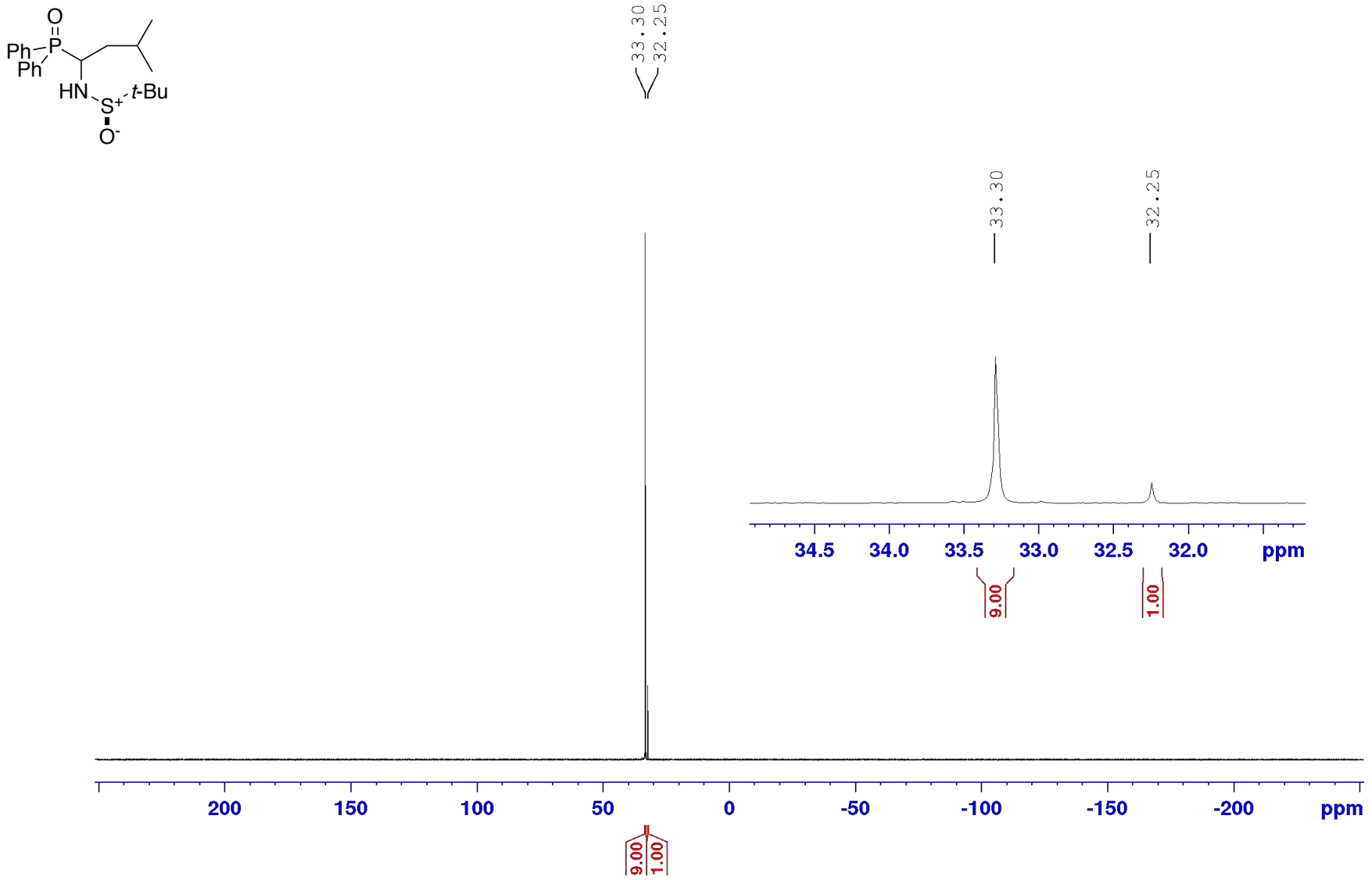
^{1}H NMR spectrum of (*R*)-*N*-(1-(diphenylphosphoryl)-3-methylbutyl)-2-methylpropane-2-sulfinamide (**6ag**)



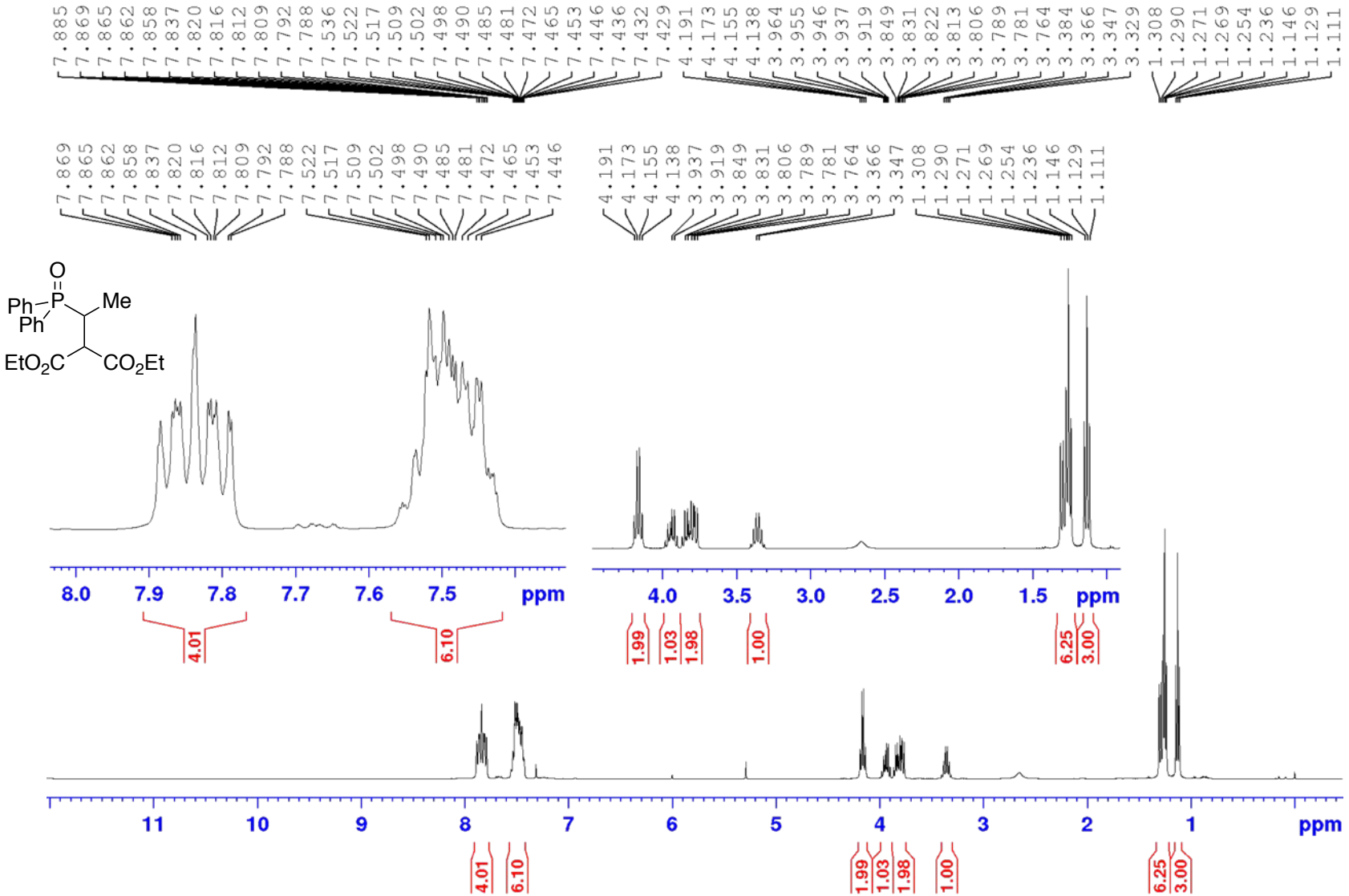
^{13}C NMR spectrum of (*R*)-*N*-(1-(diphenylphosphoryl)-3-methylbutyl)-2-methylpropane-2-sulfinamide (**6ag**)



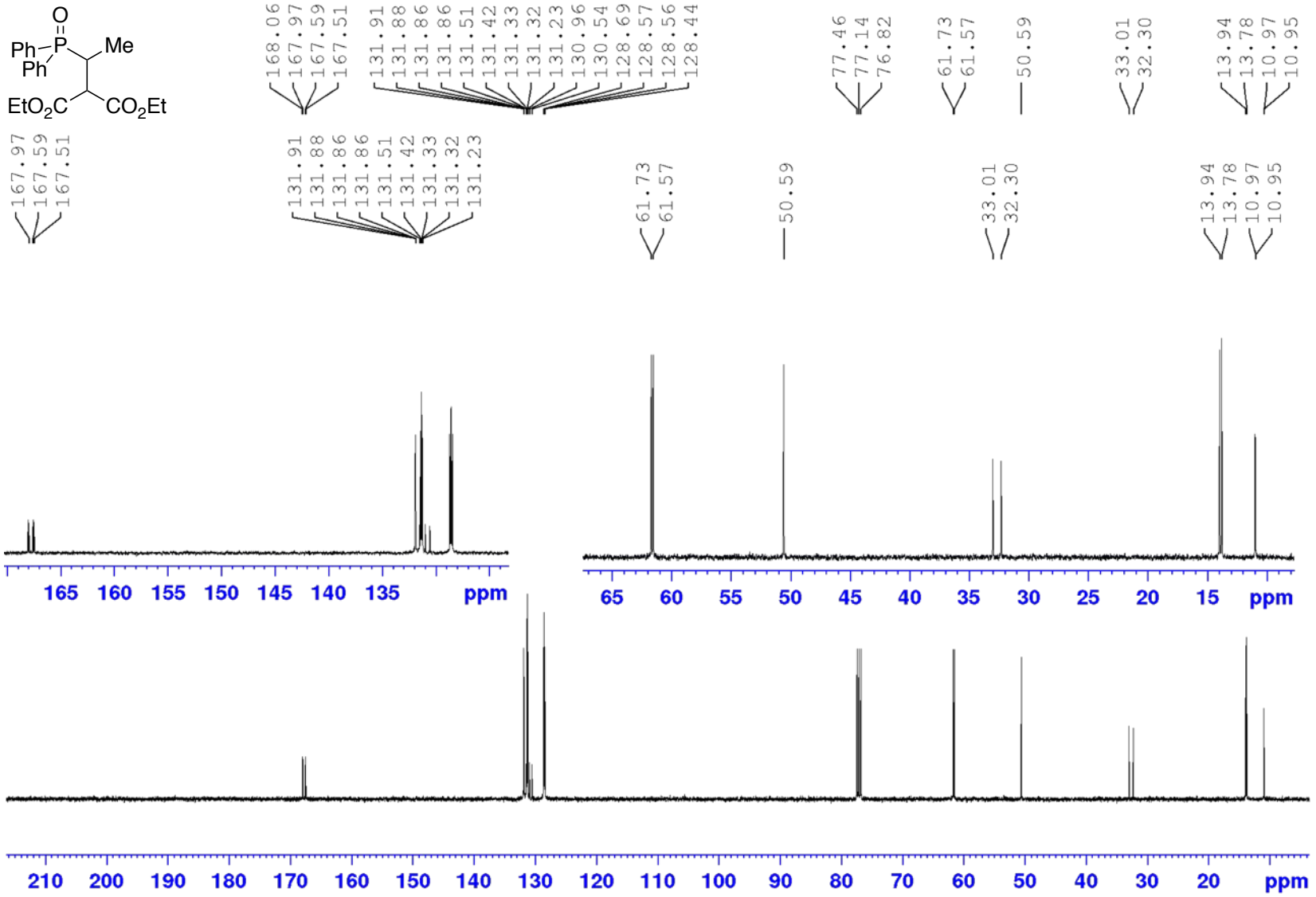
^{31}P NMR spectrum of (*R*)-*N*-(1-(diphenylphosphoryl)-3-methylbutyl)-2-methylpropane-2-sulfinamide (**6ag**)



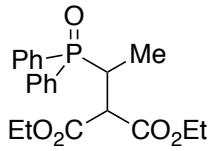
^{1}H NMR spectrum of diethyl 2-(1-(diphenylphosphoryl)ethyl)malonate (**6ah**)



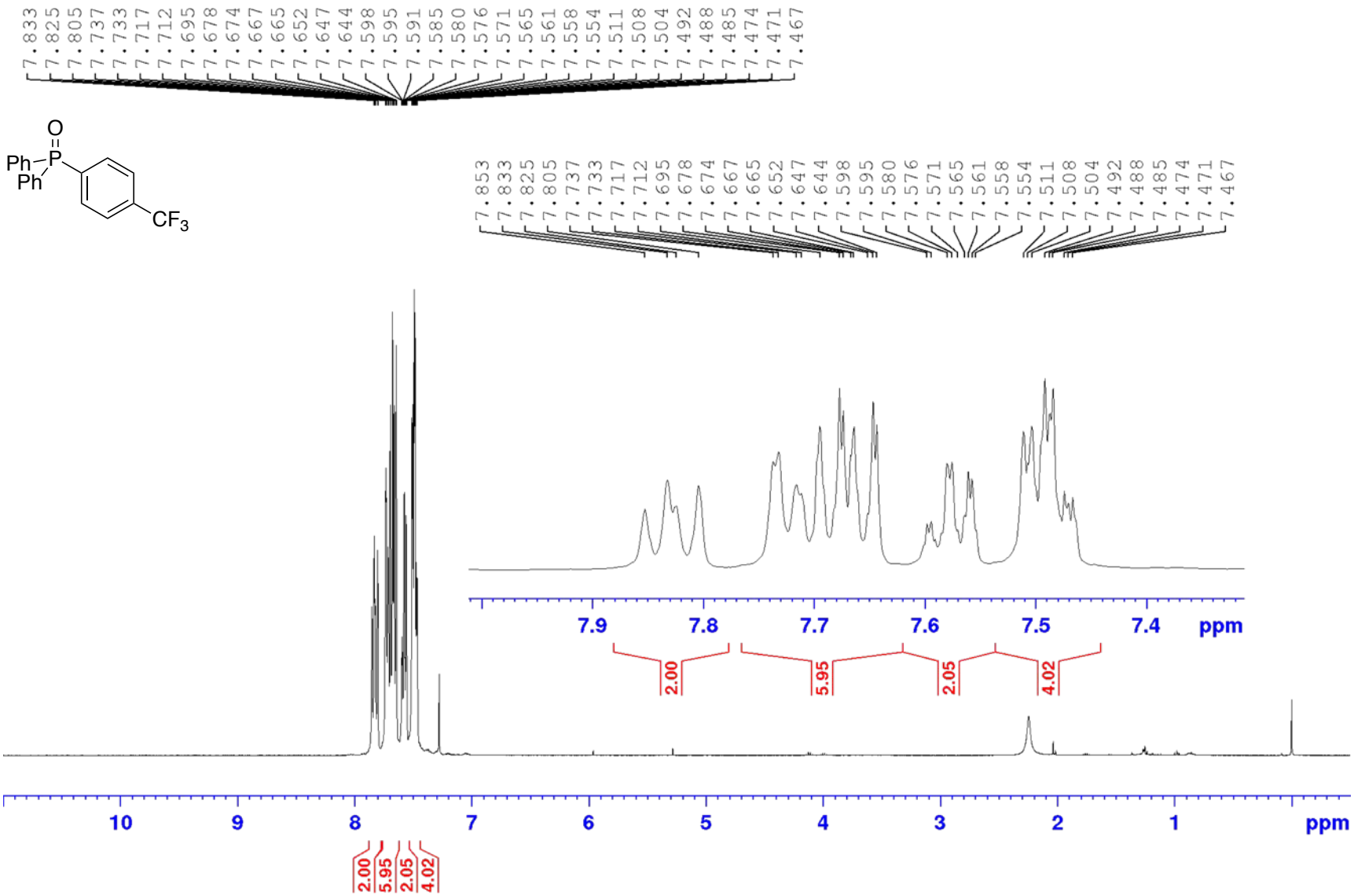
^{13}C NMR spectrum of diethyl 2-(1-(diphenylphosphoryl)ethyl)malonate (**6ah**)



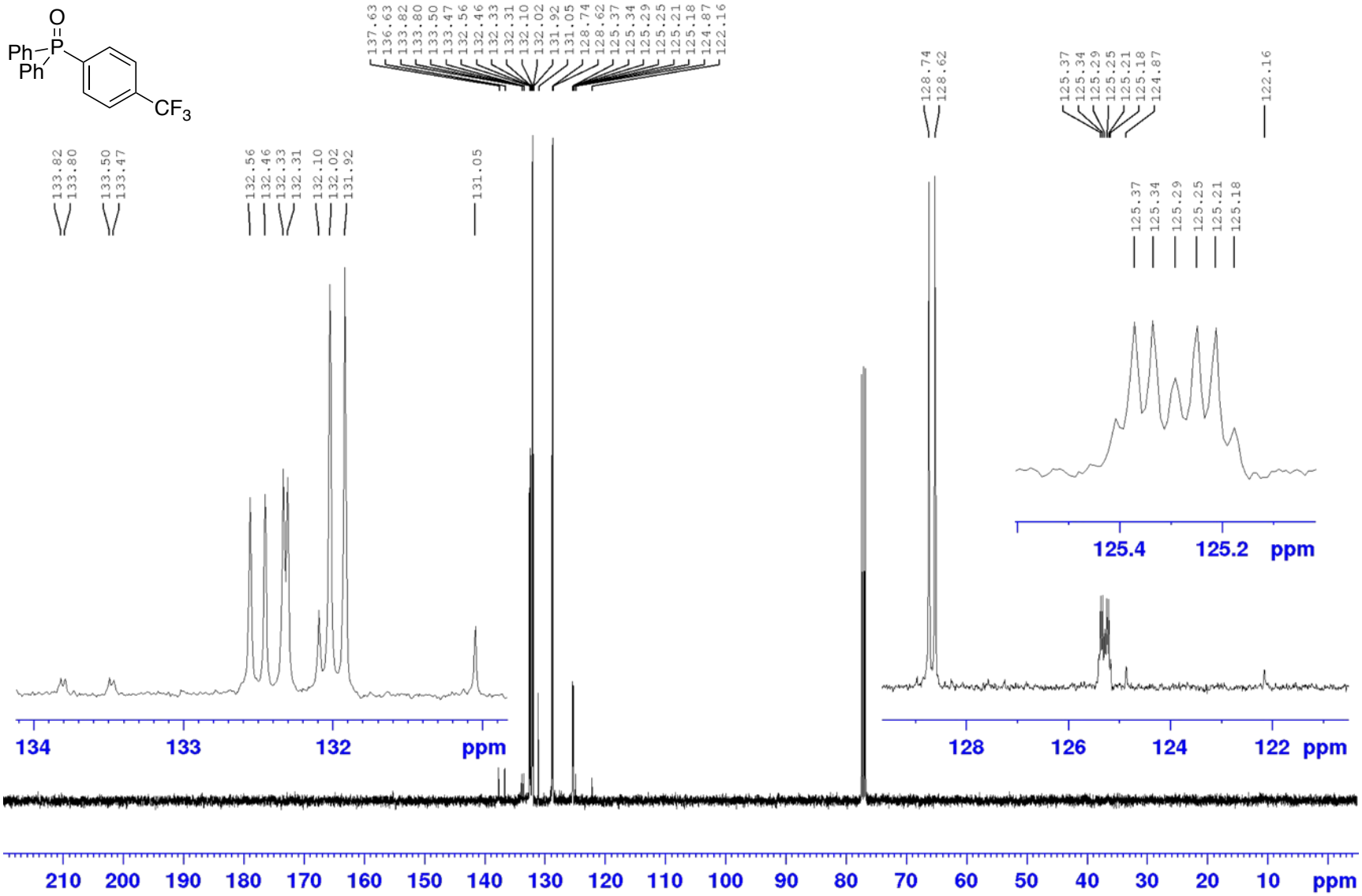
^{31}P NMR spectrum of diethyl 2-(1-(diphenylphosphoryl)ethyl)malonate (**6ah**)



^{1}H NMR spectrum of diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**6ai**)

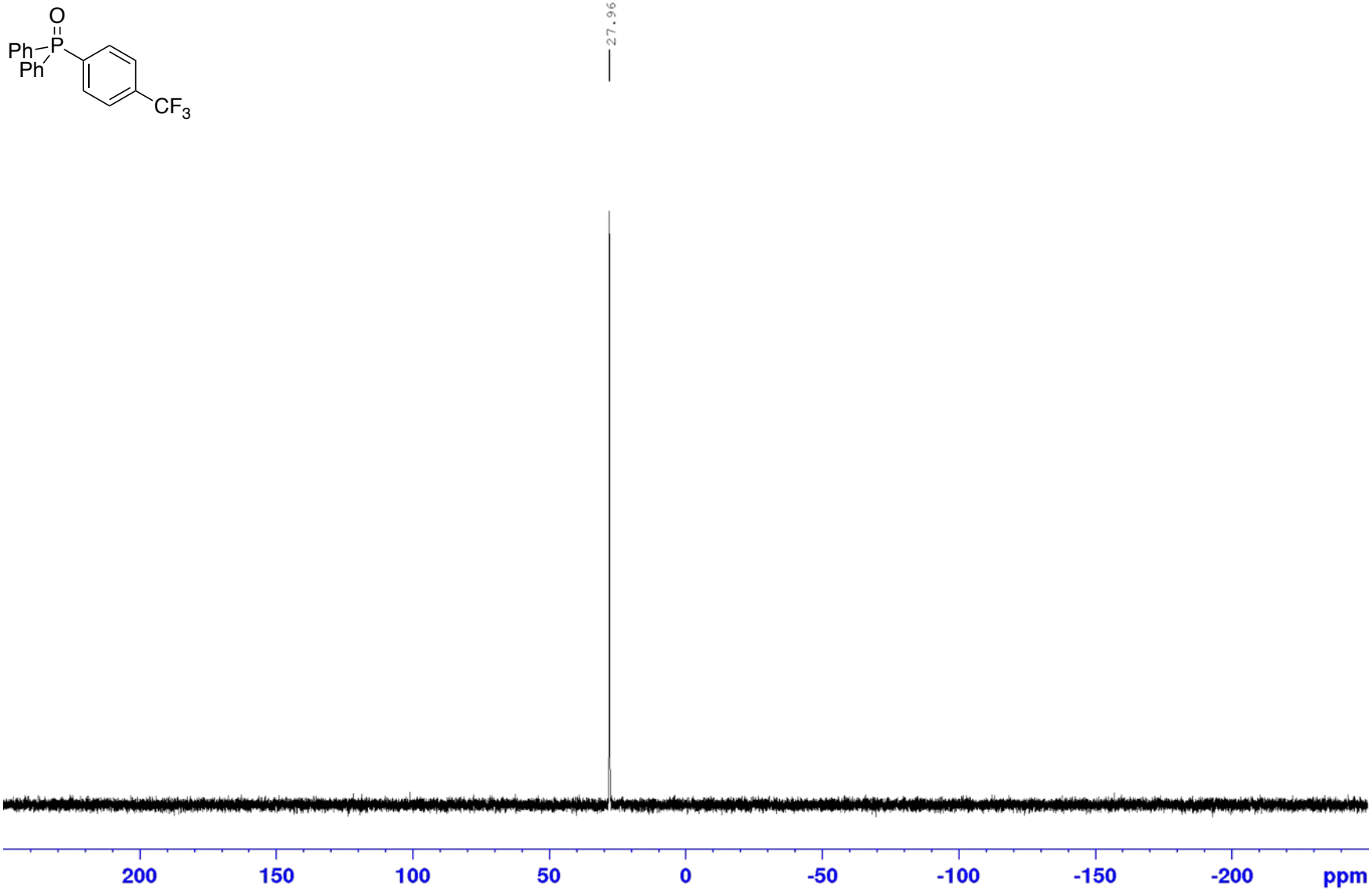


^{13}C NMR spectrum of diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**6ai**)

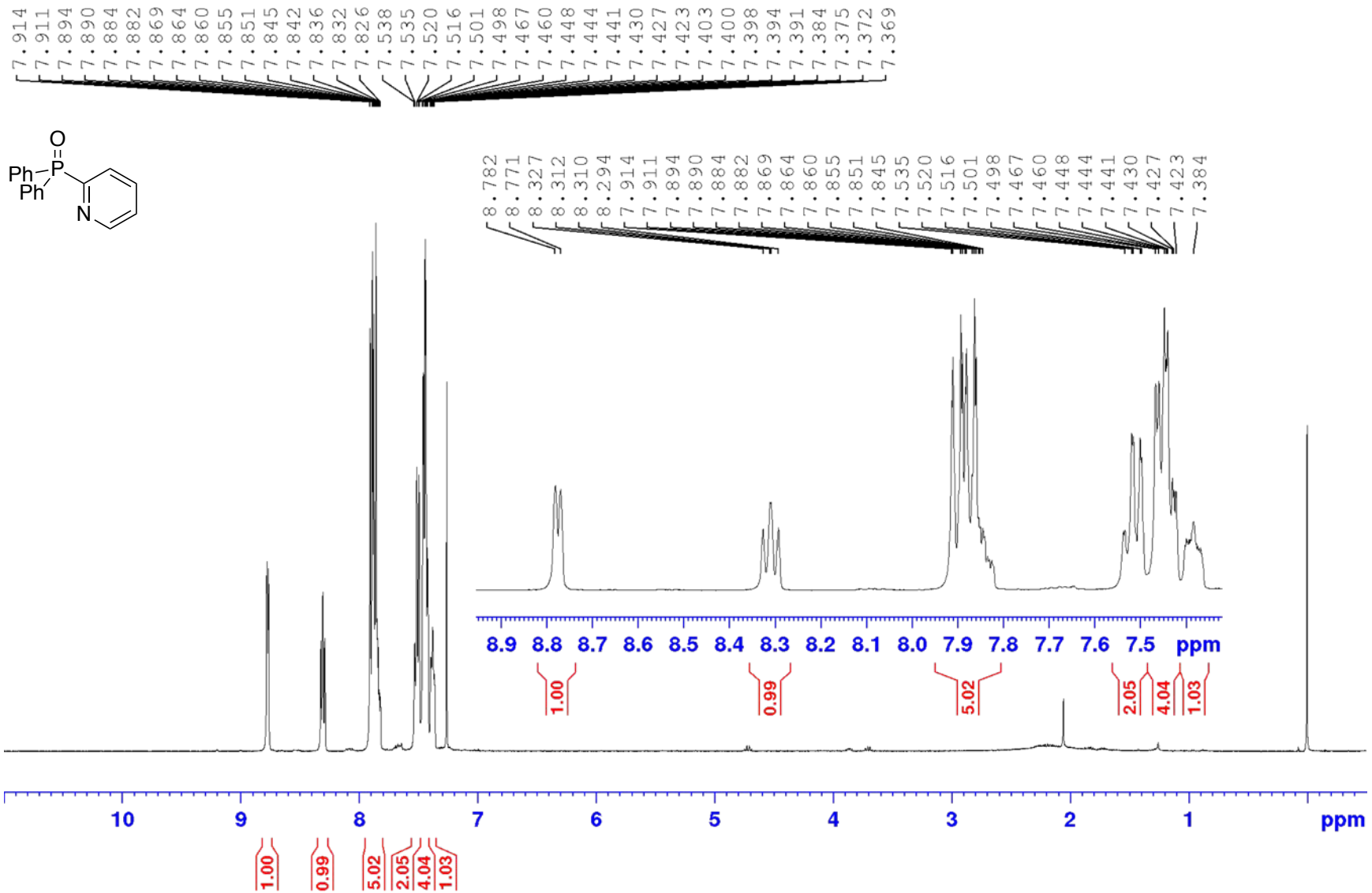


^{19}F NMR spectrum of diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**6ai**)

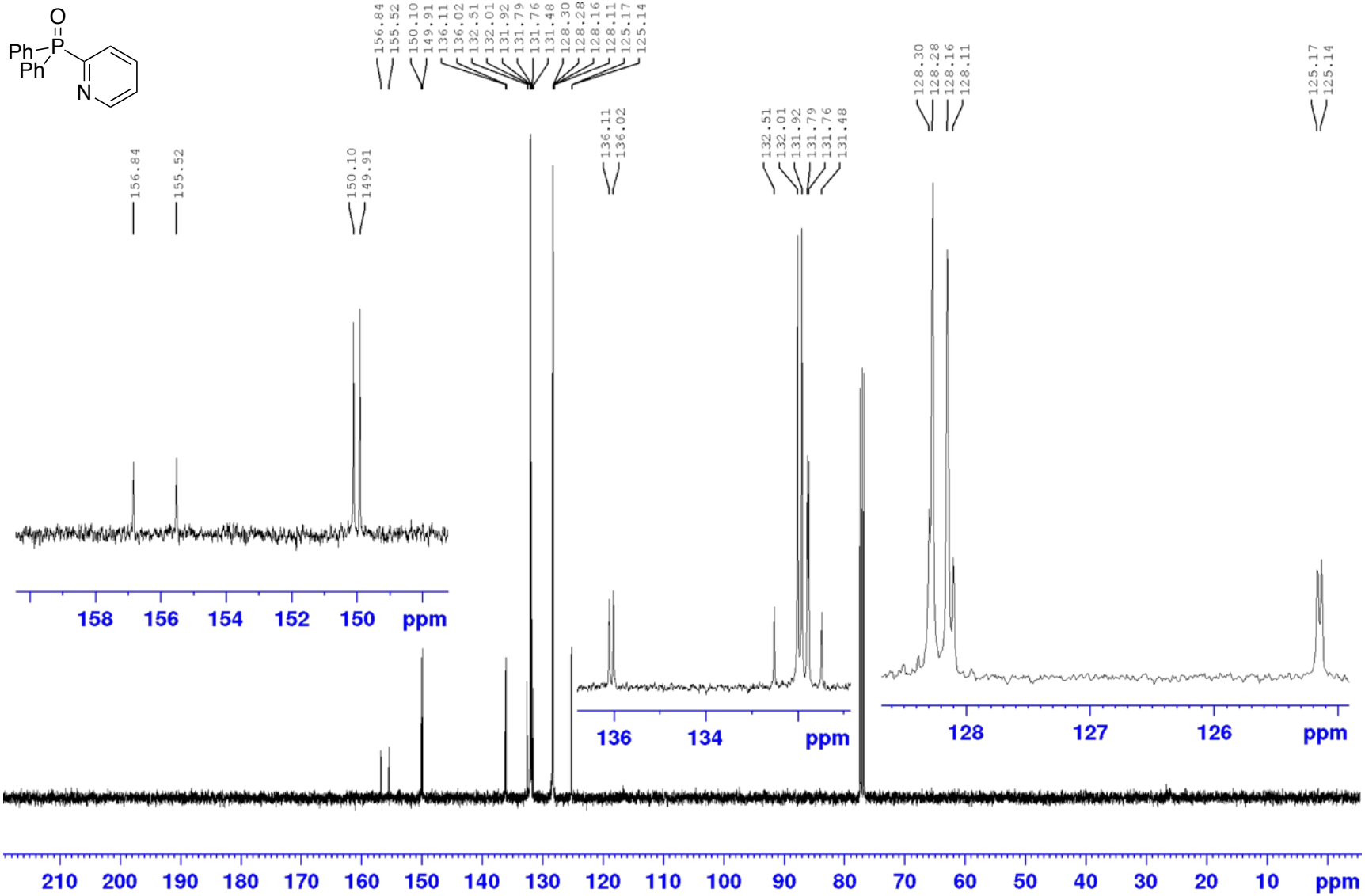
^{31}P NMR spectrum of diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**6ai**)



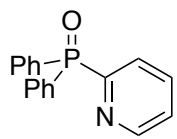
^{1}H NMR spectrum of diphenyl(pyridin-2-yl)phosphine oxide (**6aj**)



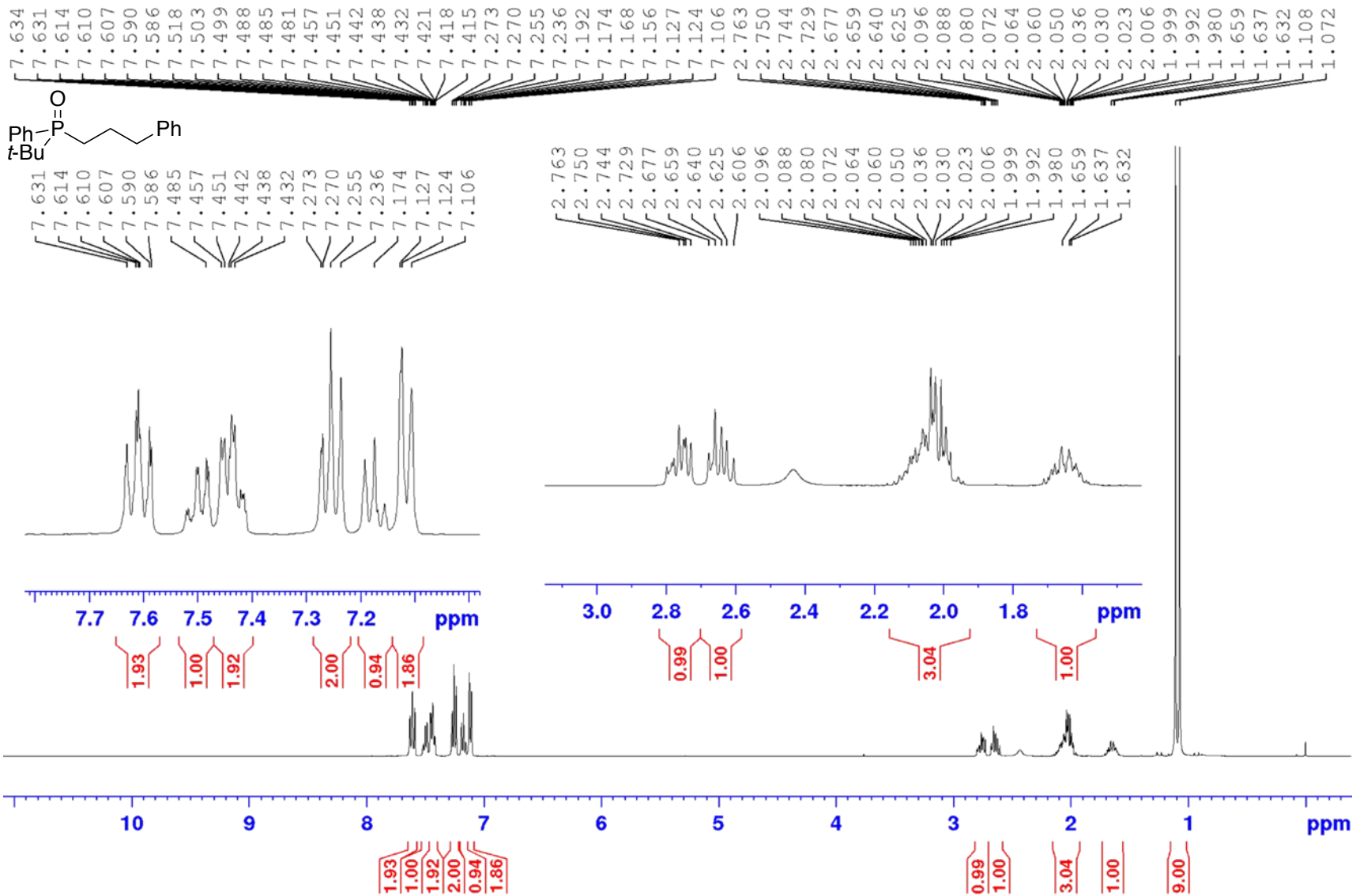
^{13}C NMR spectrum of diphenyl(pyridin-2-yl)phosphine oxide (**6aj**)



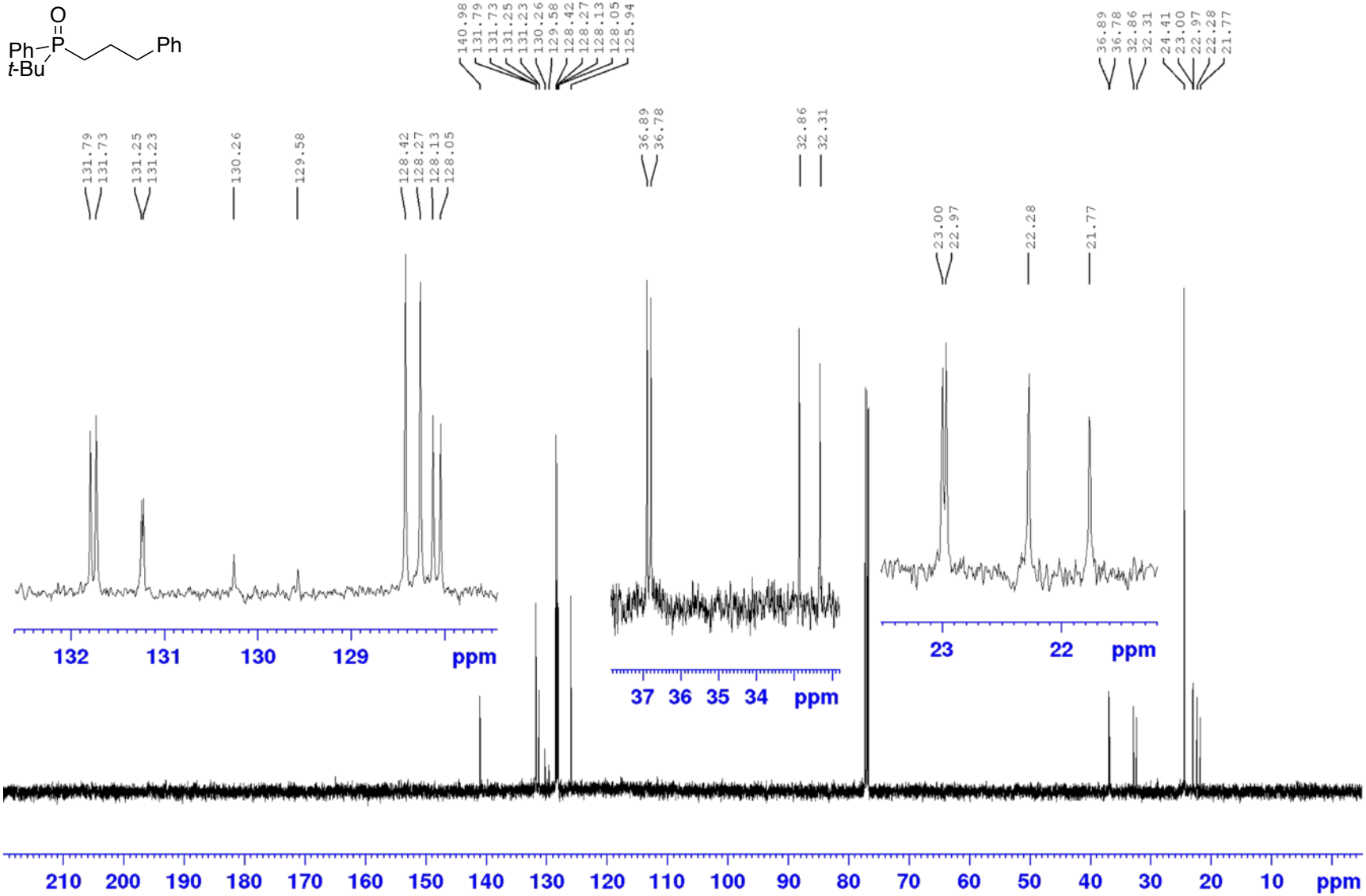
^{31}P NMR spectrum of diphenyl(pyridin-2-yl)phosphine oxide (**6aj**)



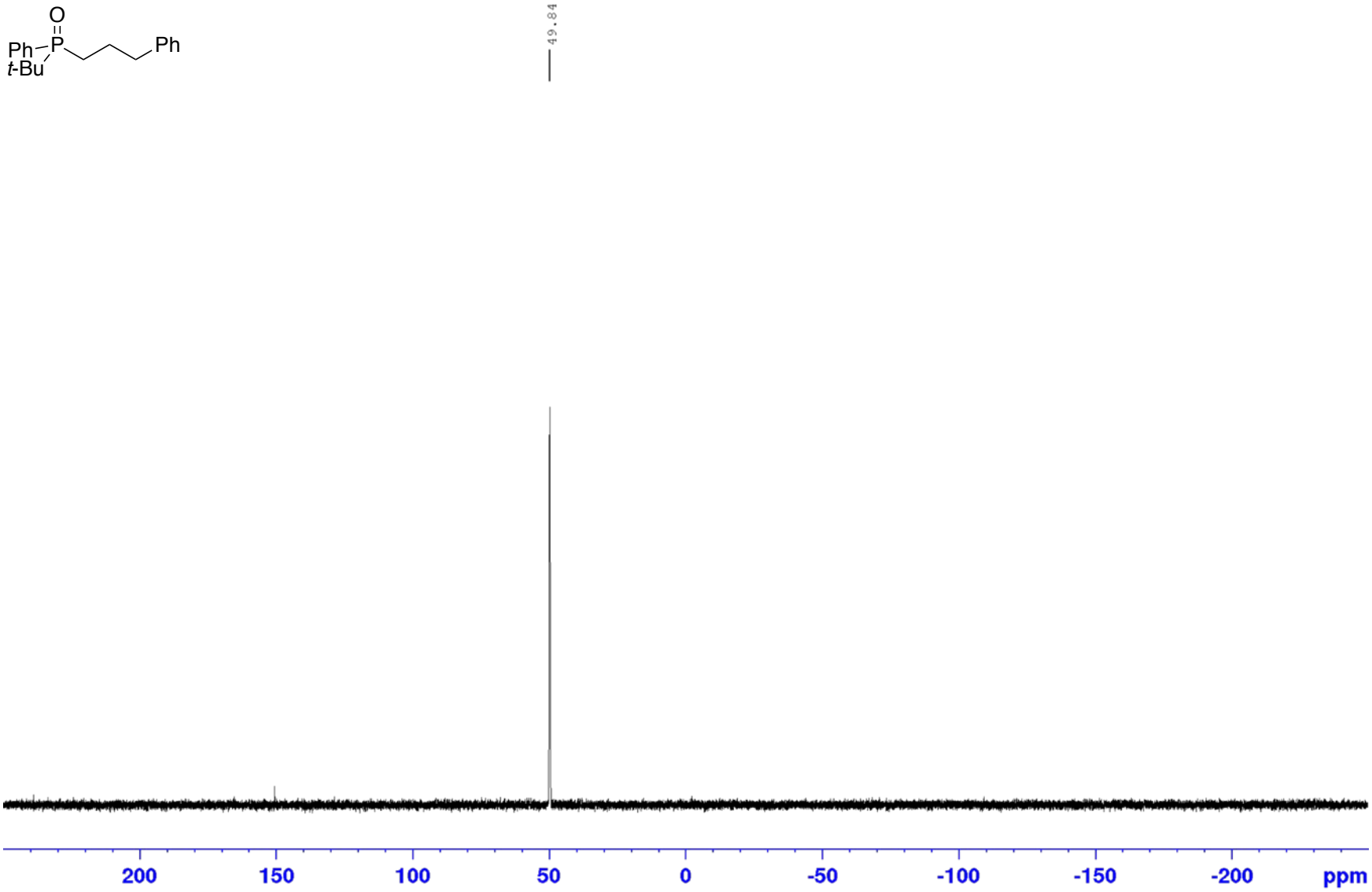
[1]H NMR spectrum of *tert*-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)



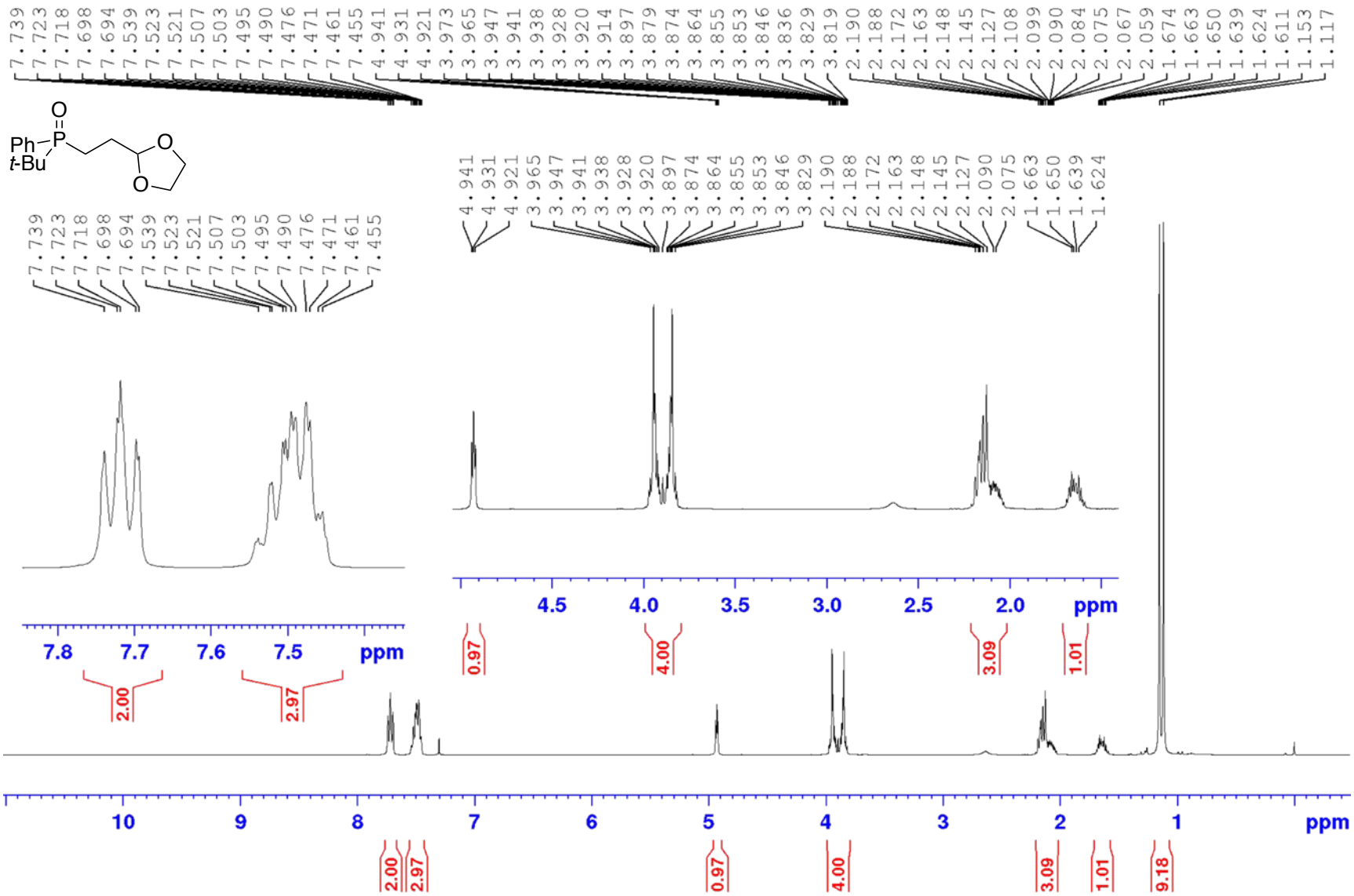
^{13}C NMR spectrum of *tert*-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)



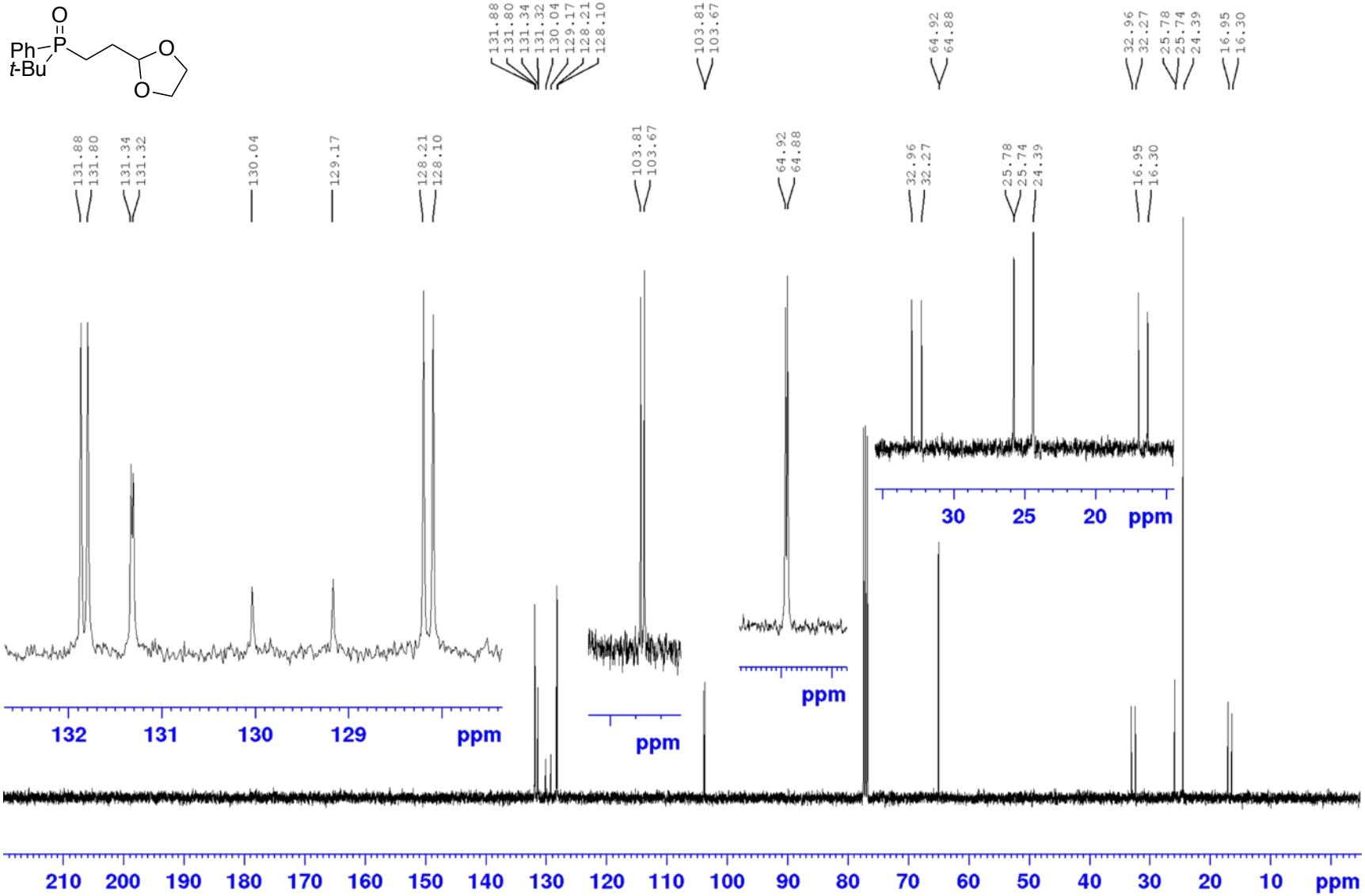
^{31}P NMR spectrum of of *tert*-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)



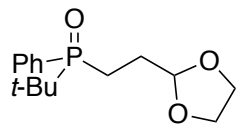
[1]H NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)(*tert*-butyl)(phenyl)phosphine oxide (**4fc**)



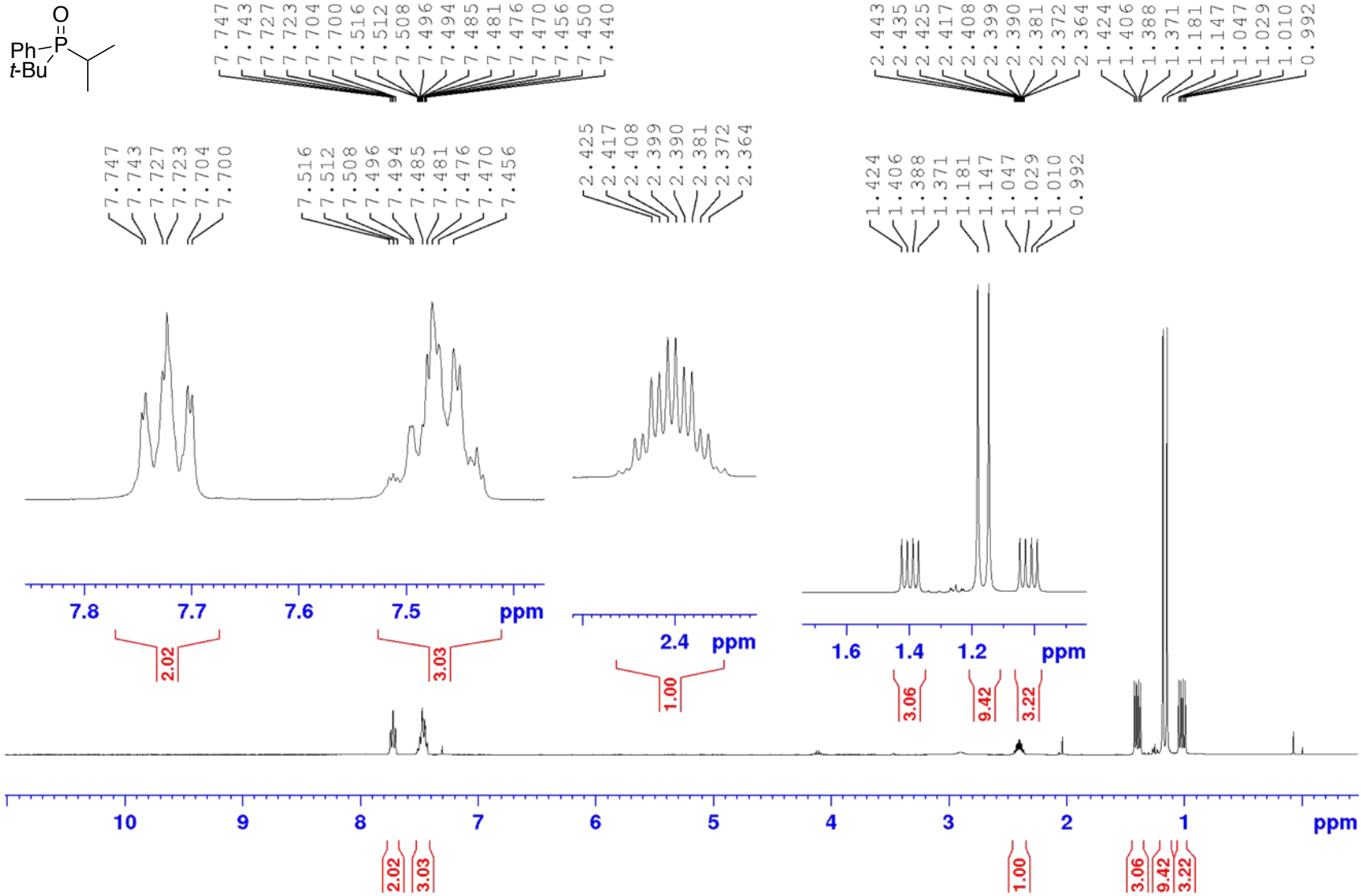
^{13}C NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)(*tert*-butyl)(phenyl)phosphine oxide (**4fc**)



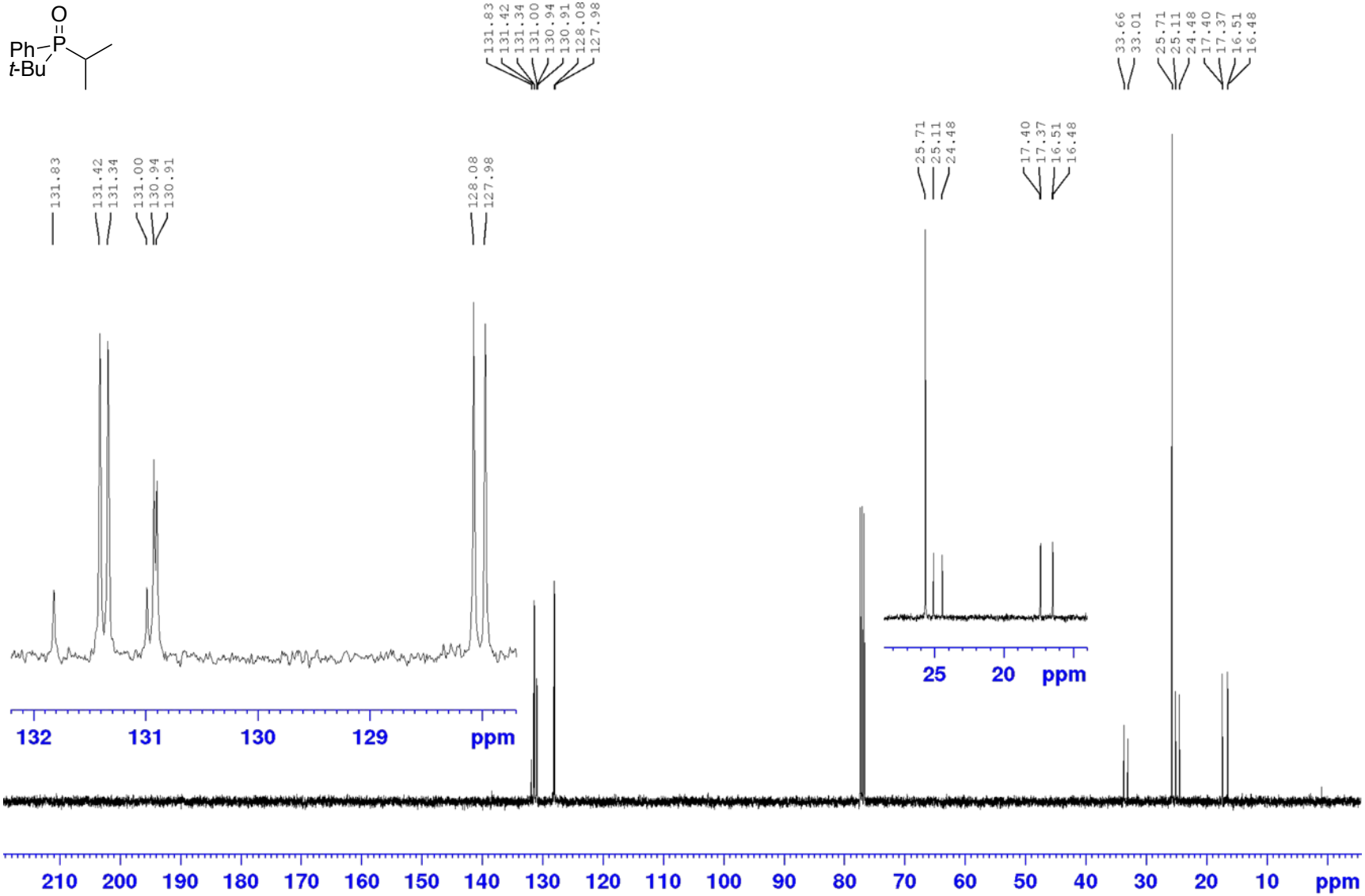
^{31}P NMR spectrum of (2-(1,3-dioxolan-2-yl)ethyl)(*tert*-butyl)(phenyl)phosphine oxide (**4fc**)



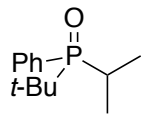
[1]H NMR spectrum of *tert*-butyl(isopropyl)(phenyl)phosphine oxide (**4fq**)



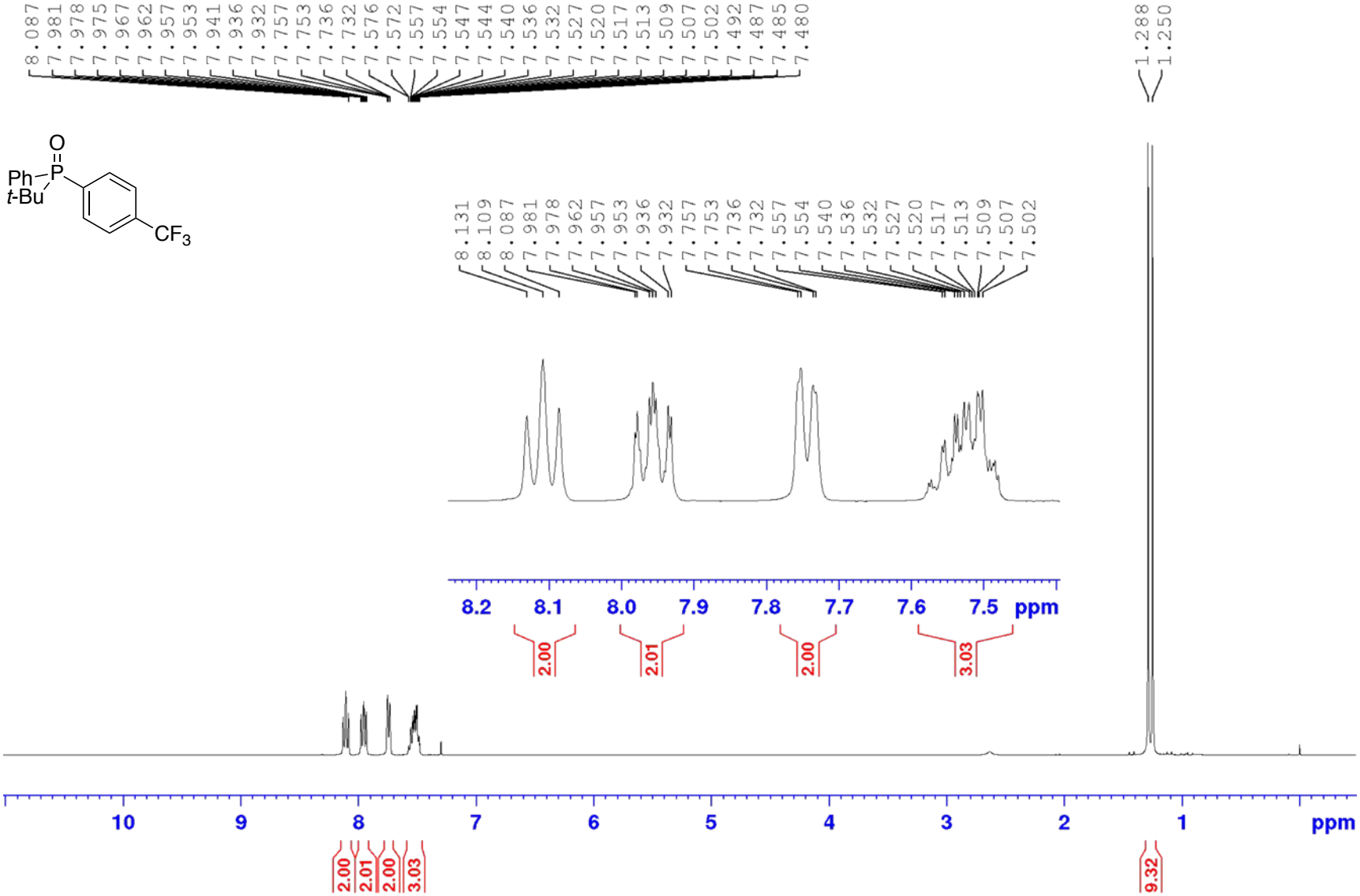
^{13}C NMR spectrum of *tert*-butyl(isopropyl)(phenyl)phosphine oxide (**4fq**)



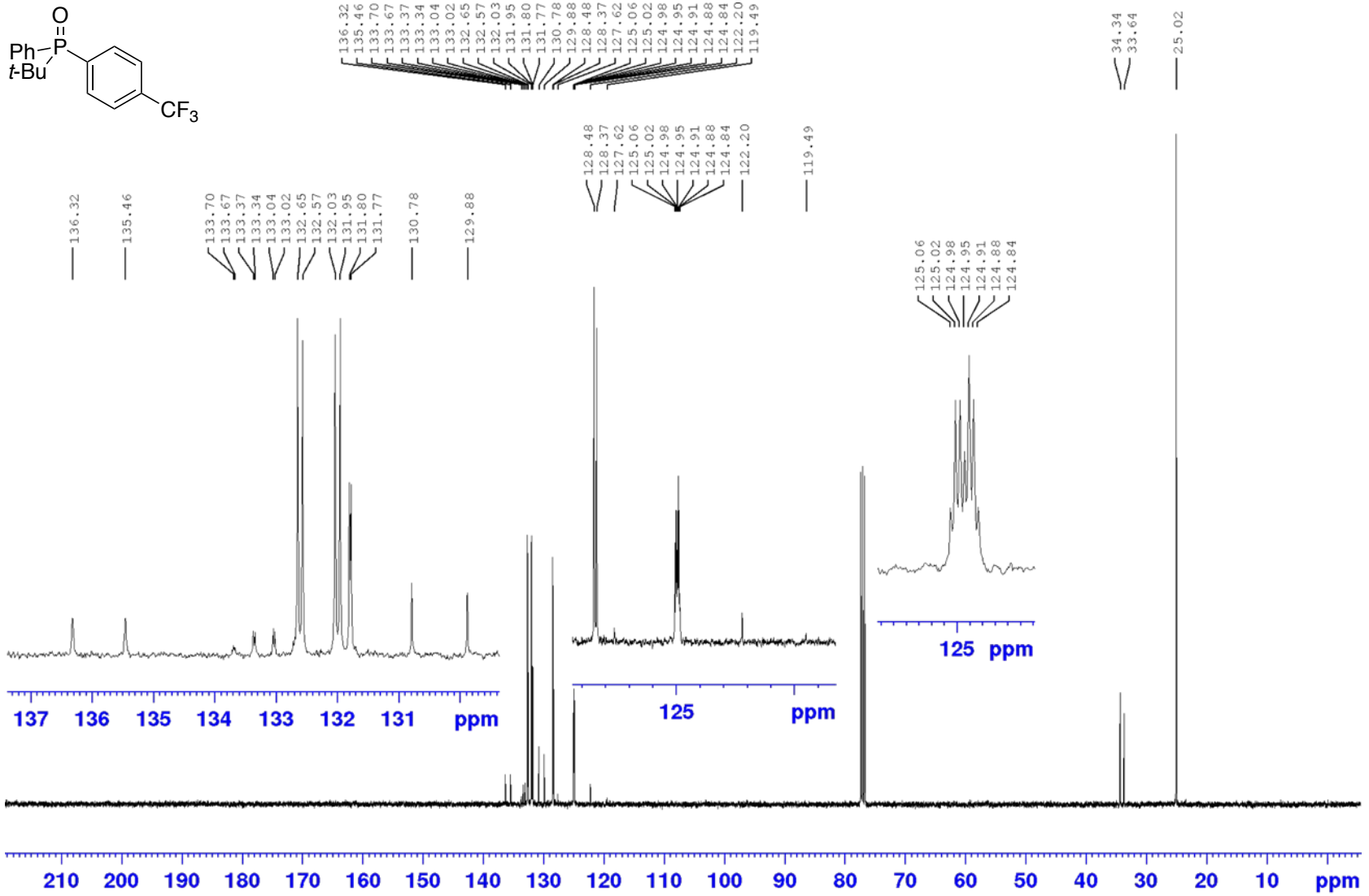
^{31}P NMR spectrum of *tert*-butyl(isopropyl)(phenyl)phosphine oxide (**4fq**)



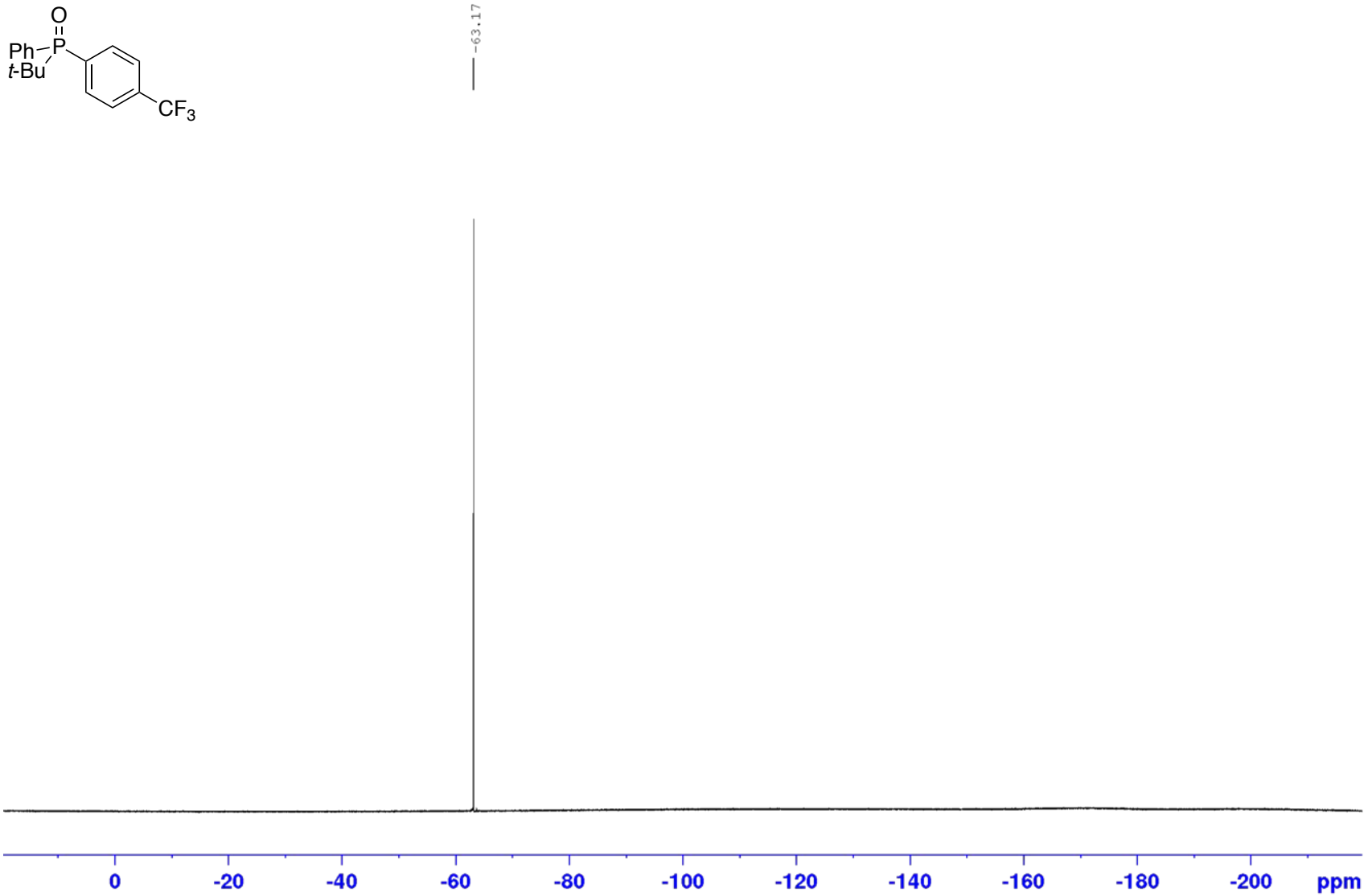
[1]H NMR spectrum of *tert*-butyl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6fi**)



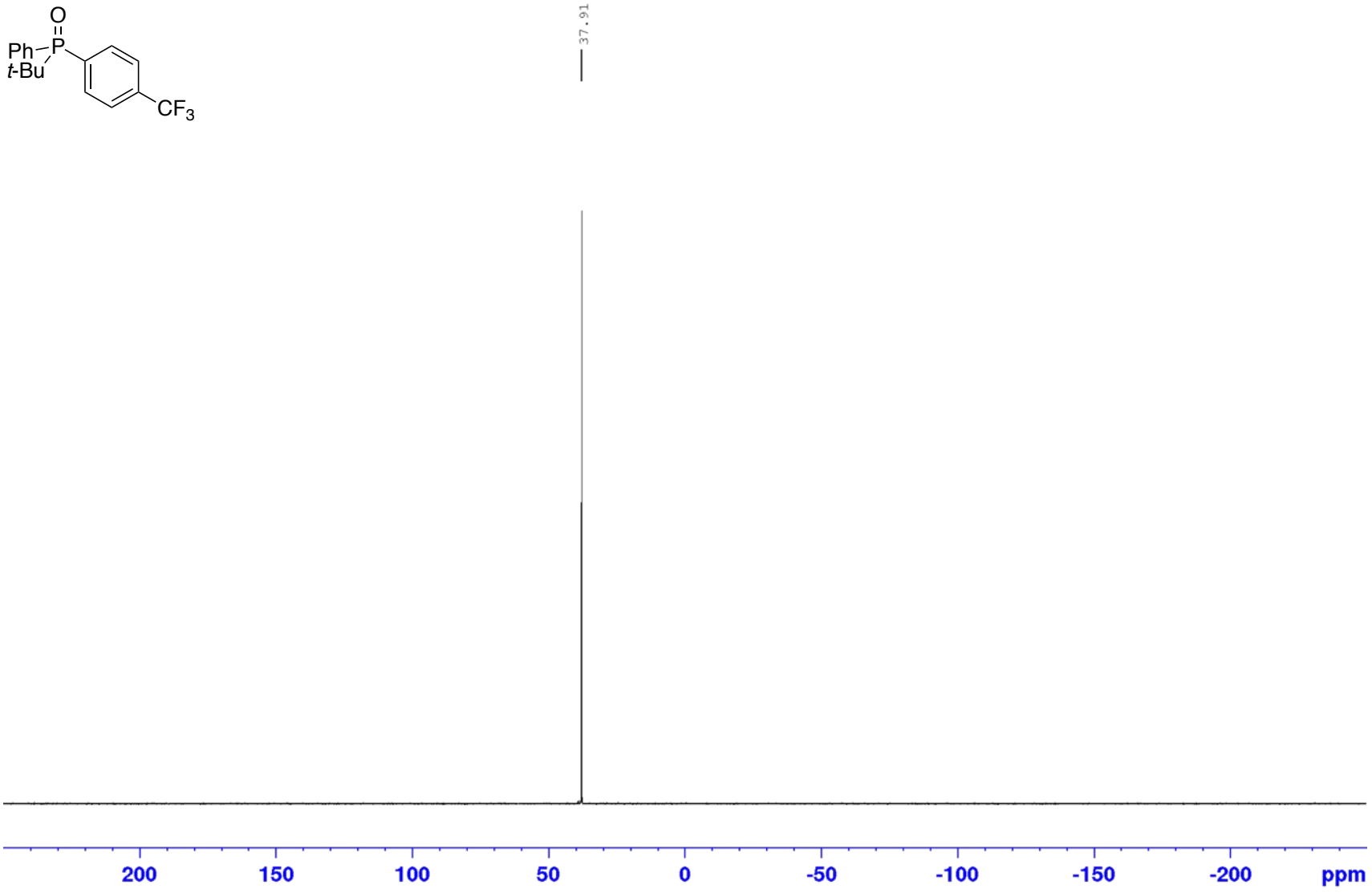
^{13}C NMR spectrum of *tert*-butyl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6fi**)



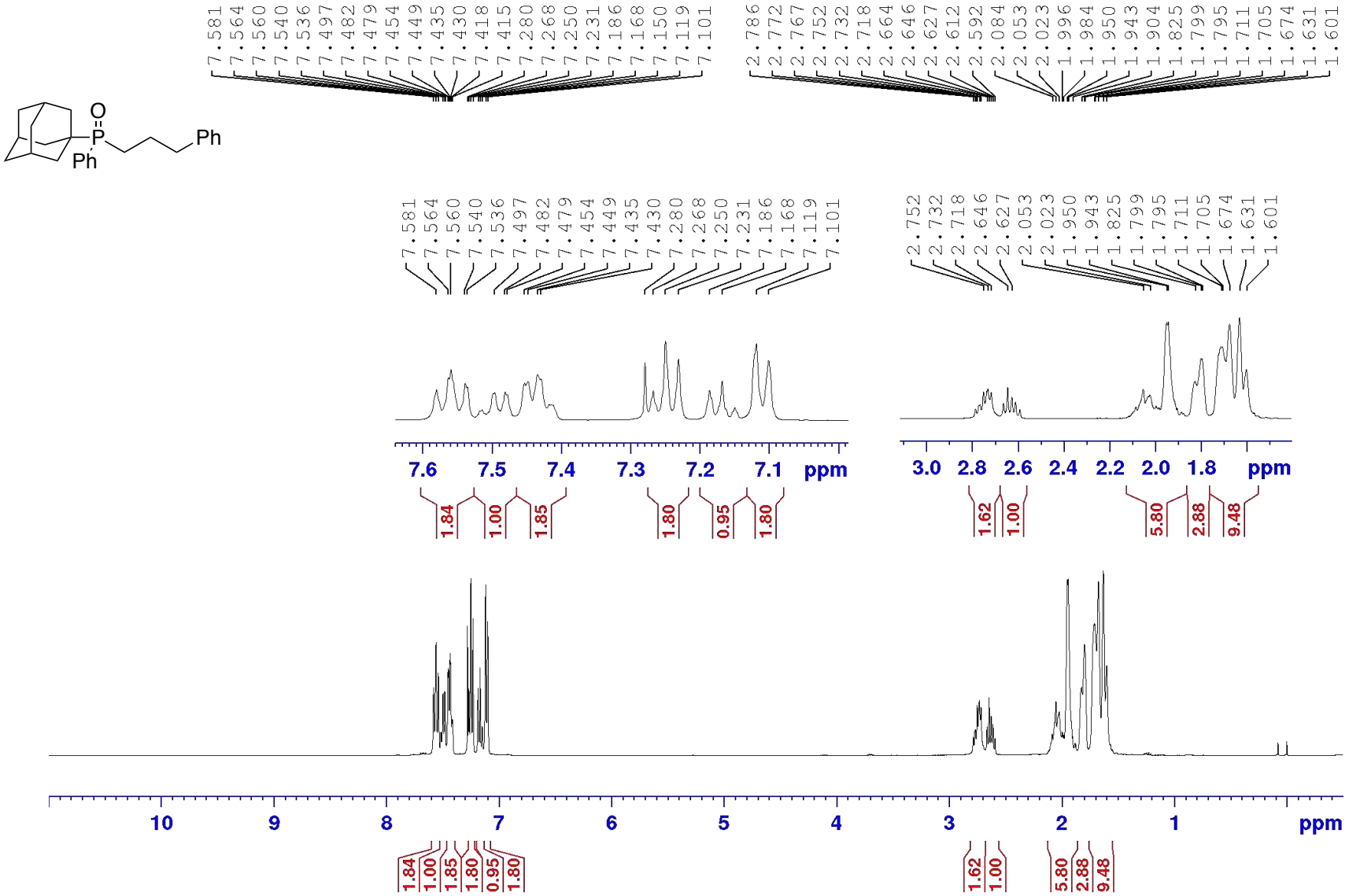
^{19}F NMR spectrum of *tert*-butyl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6fi**)



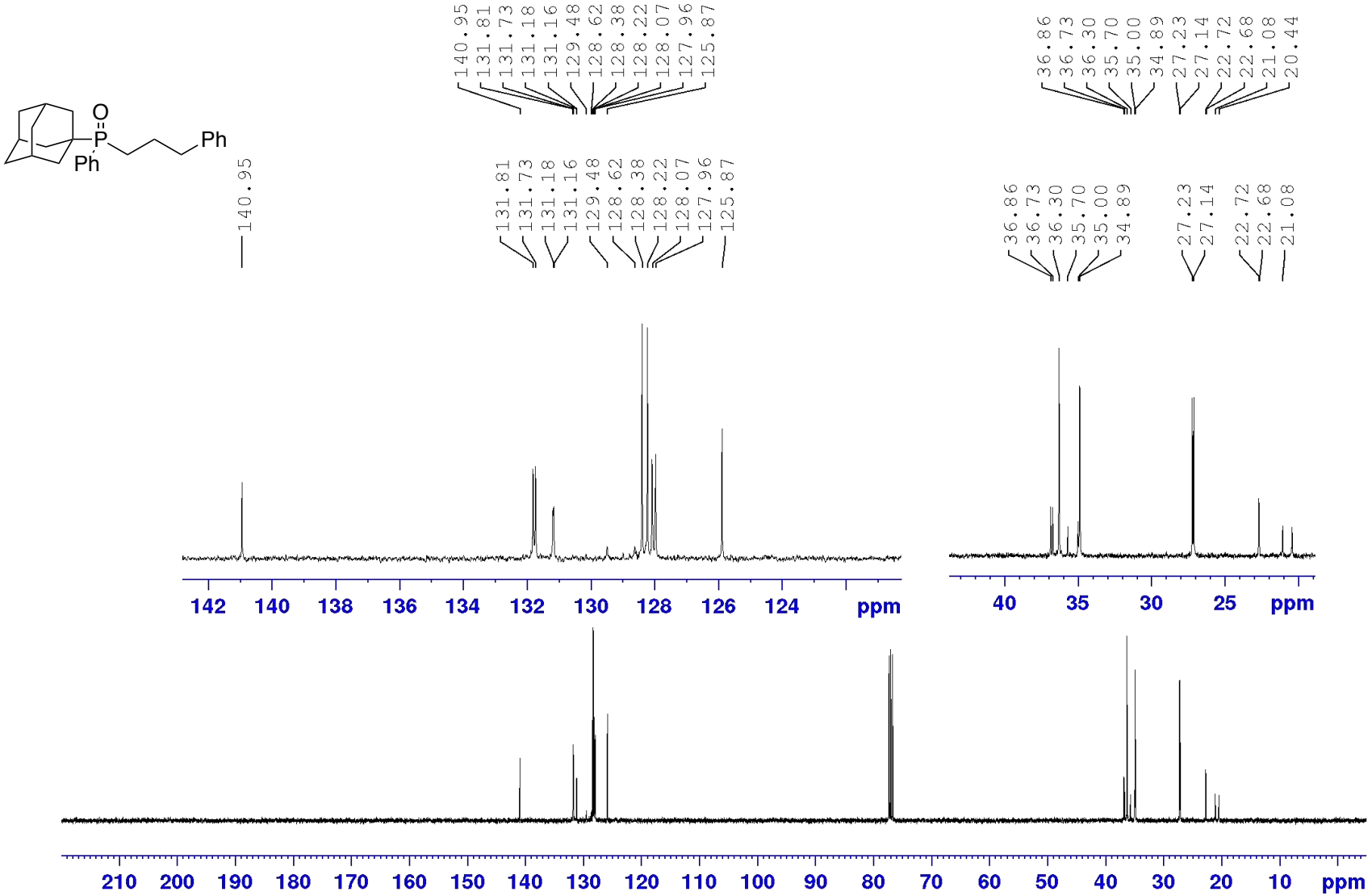
^{31}P NMR spectrum of *tert*-butyl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6fi**)



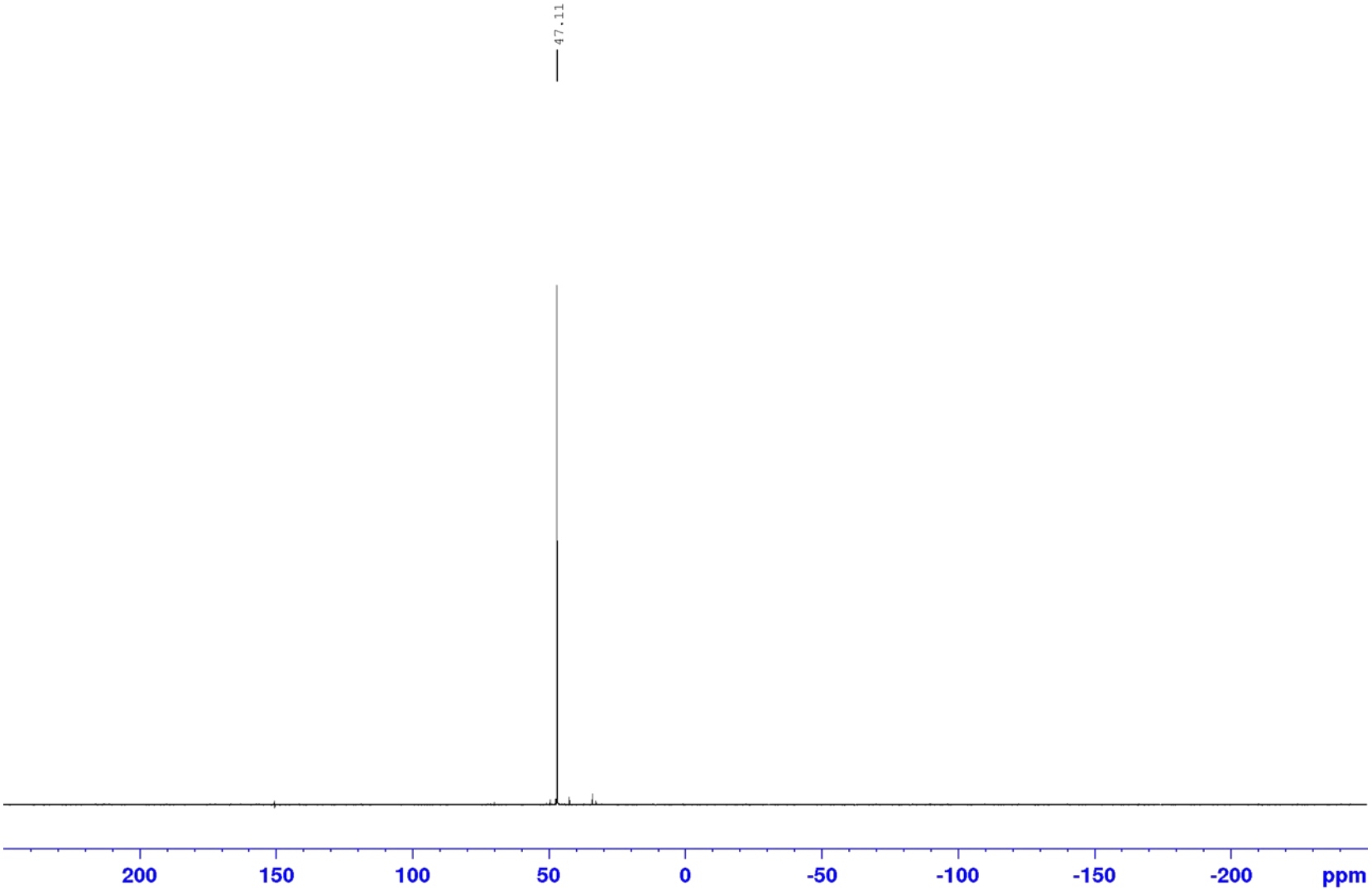
^{1}H NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(3-phenylpropyl)phosphine oxide (**4ga**)



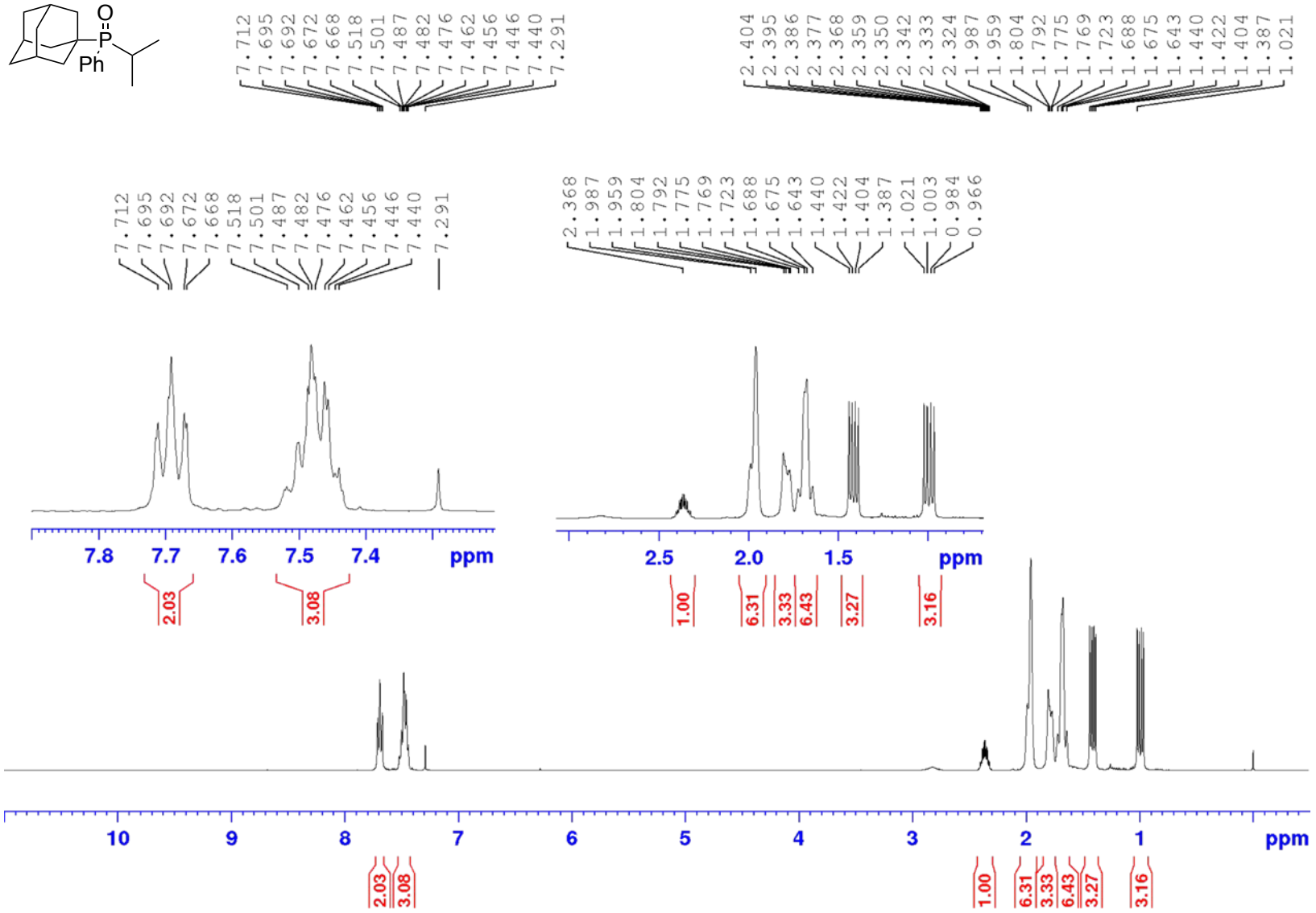
^{13}C NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(3-phenylpropyl)phosphine oxide (**4ga**)



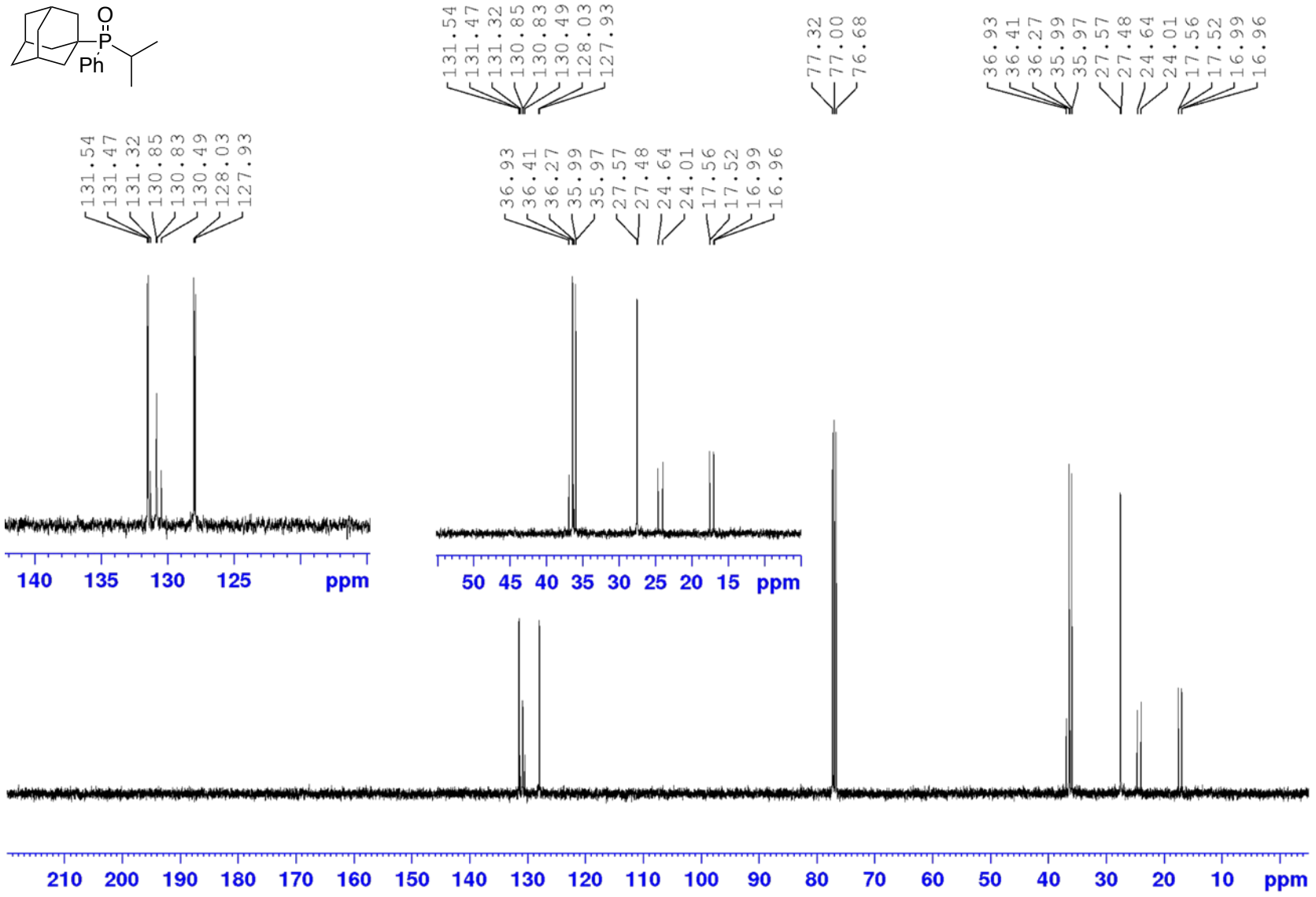
^{31}P NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(3-phenylpropyl)phosphine oxide (**4ga**)



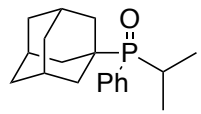
^{1}H NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(isopropyl)(phenyl)phosphine oxide (**4gq**)



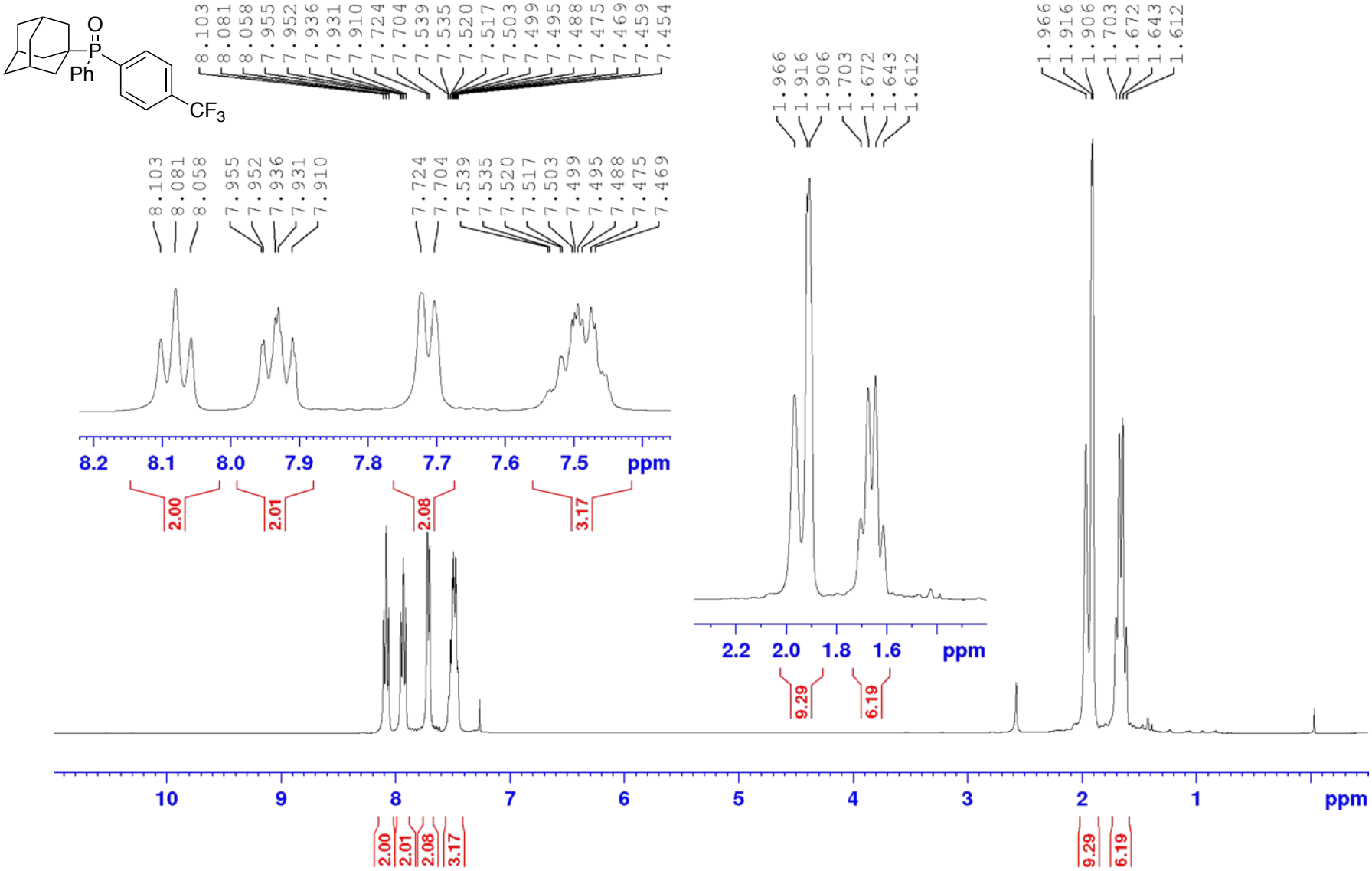
^{13}C NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(isopropyl)(phenyl)phosphine oxide (**4gq**)



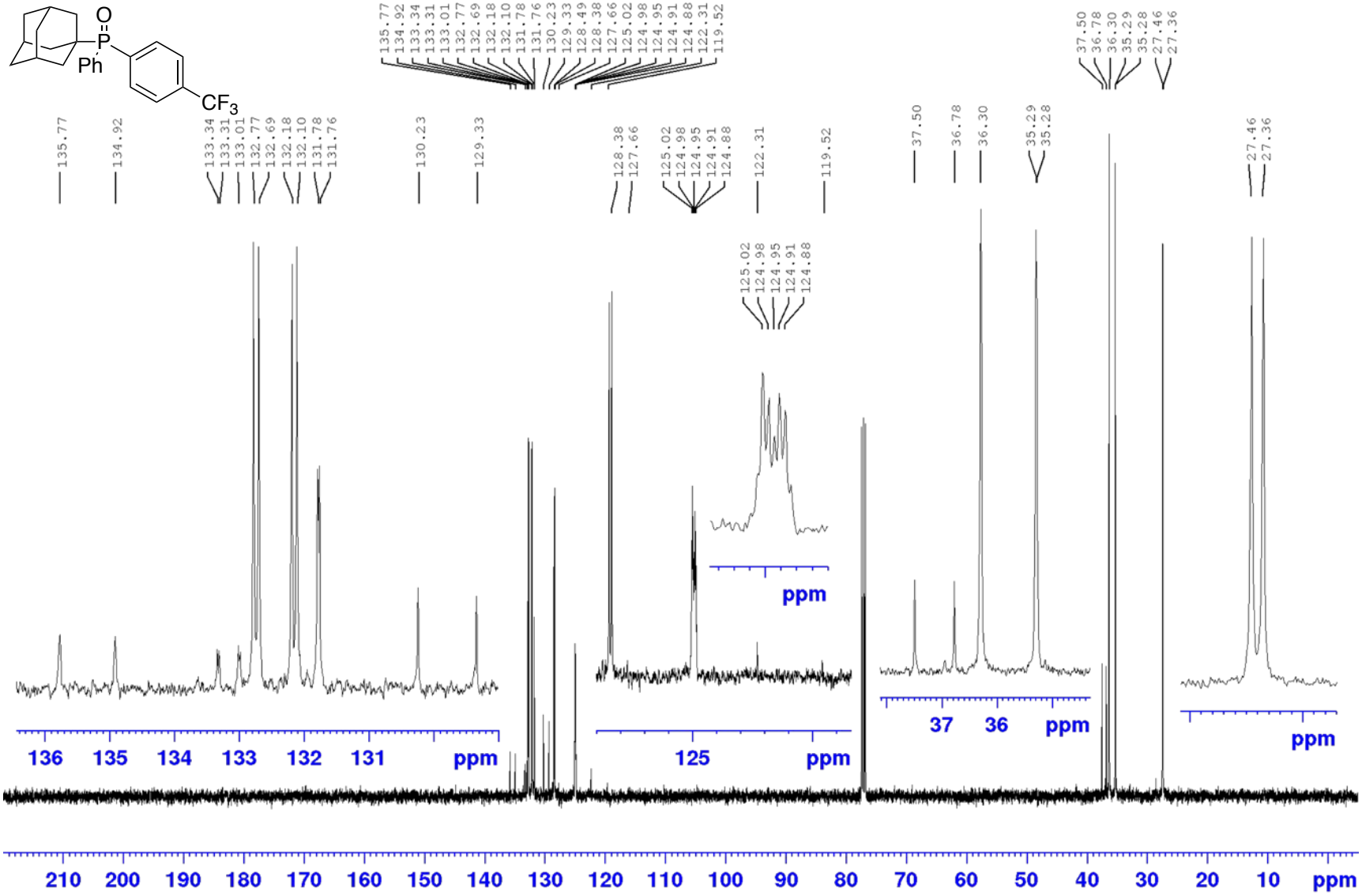
^{31}P NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(isopropyl)(phenyl)phosphine oxide (**4gq**)



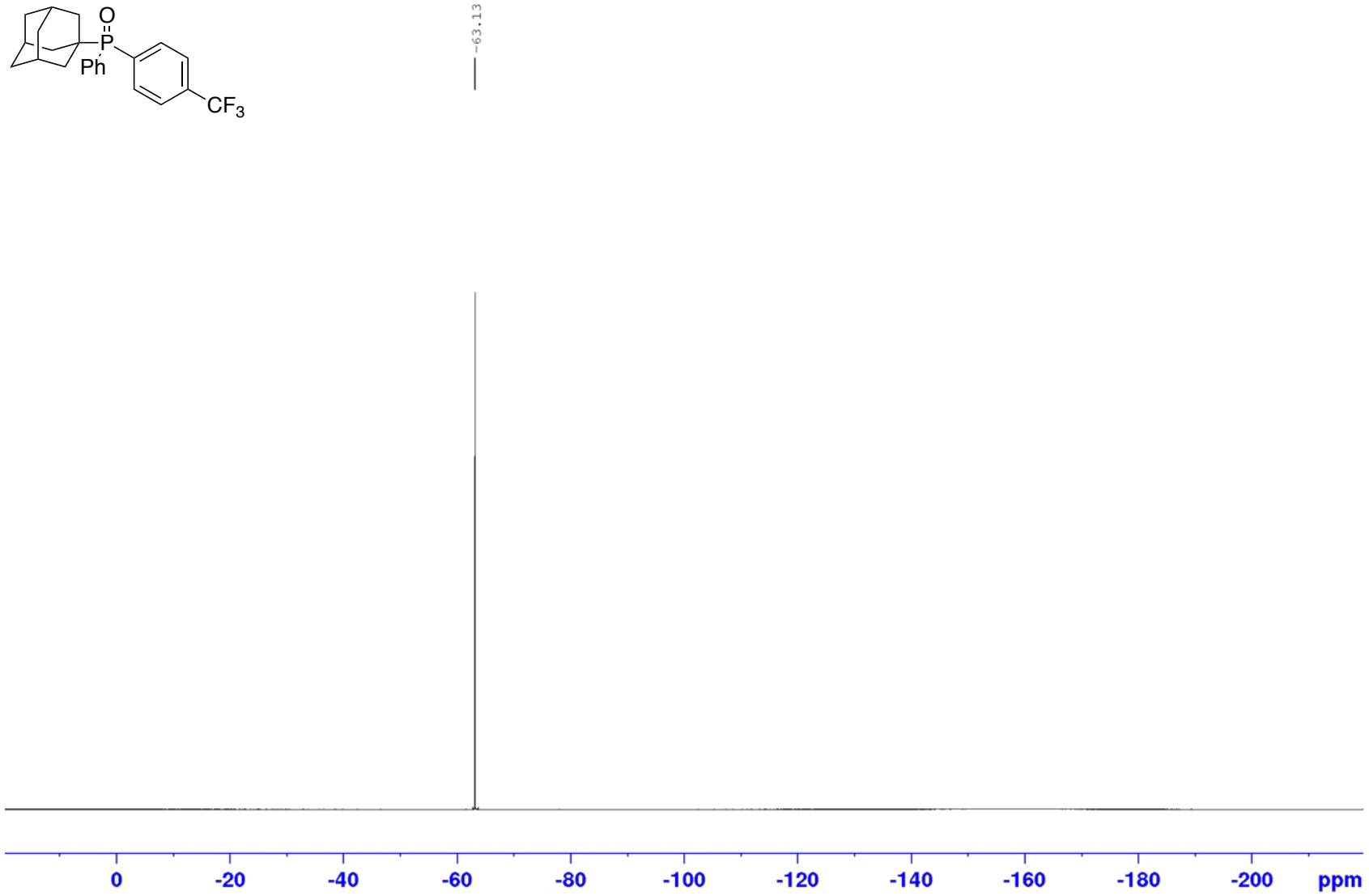
[1]H NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6gi**)



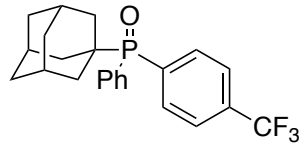
^{13}C NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6gi**)



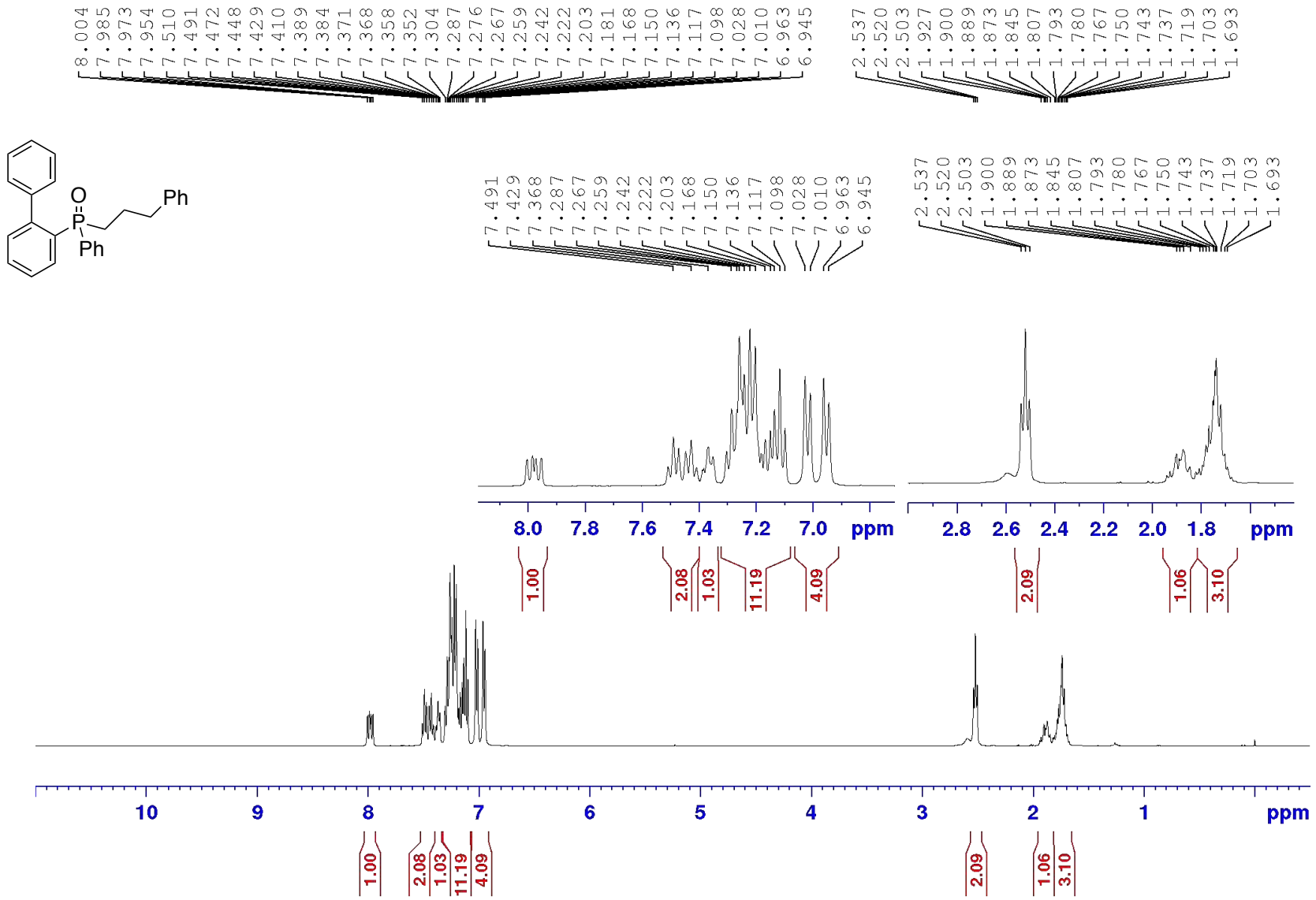
^{19}F NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6gi**)



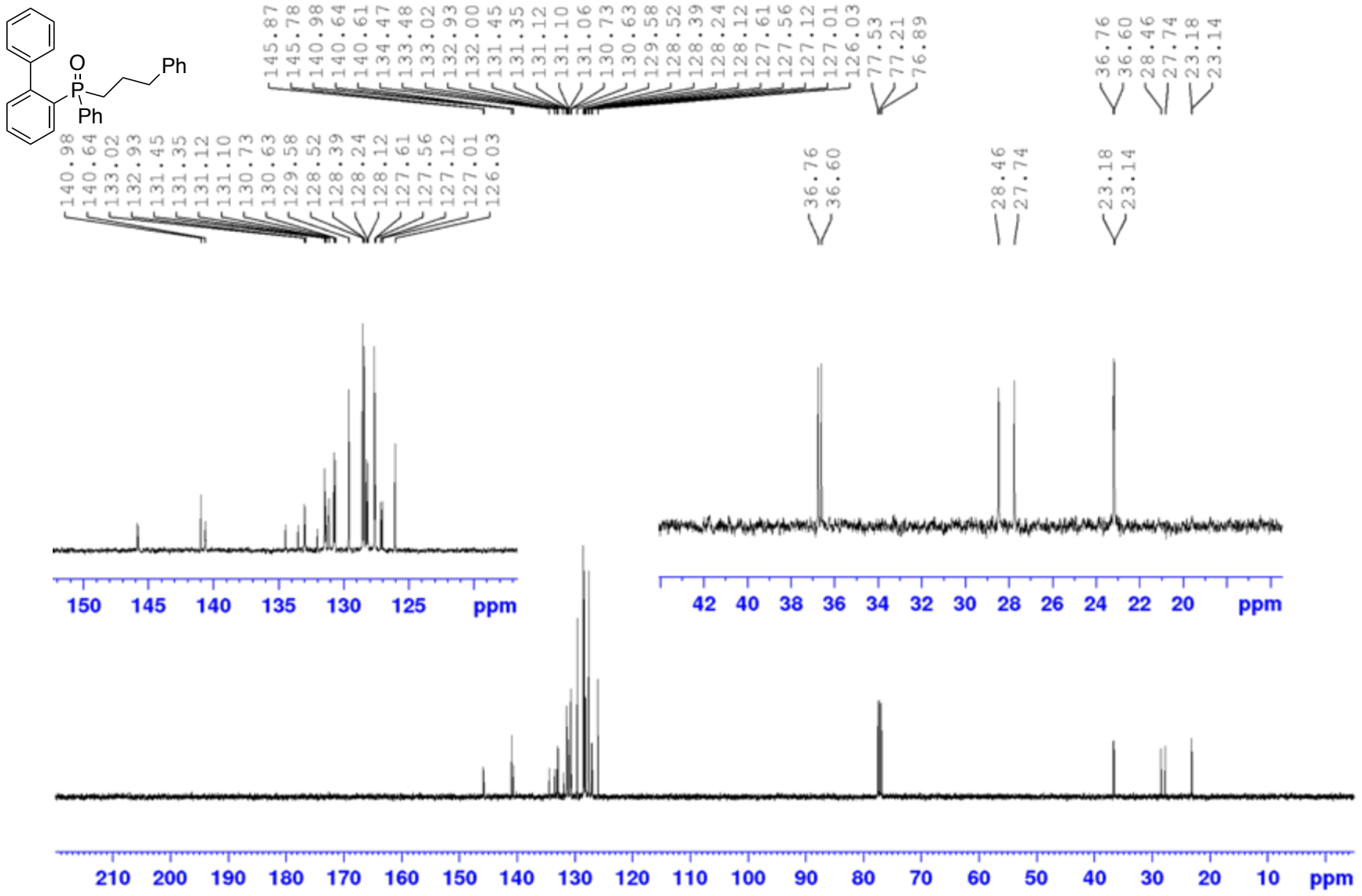
^{31}P NMR spectrum of ((3*s*,5*s*,7*s*)-adamantan-1-yl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6gi**)



^{1}H NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(3-phenylpropyl)phosphine oxide (**4ha**)

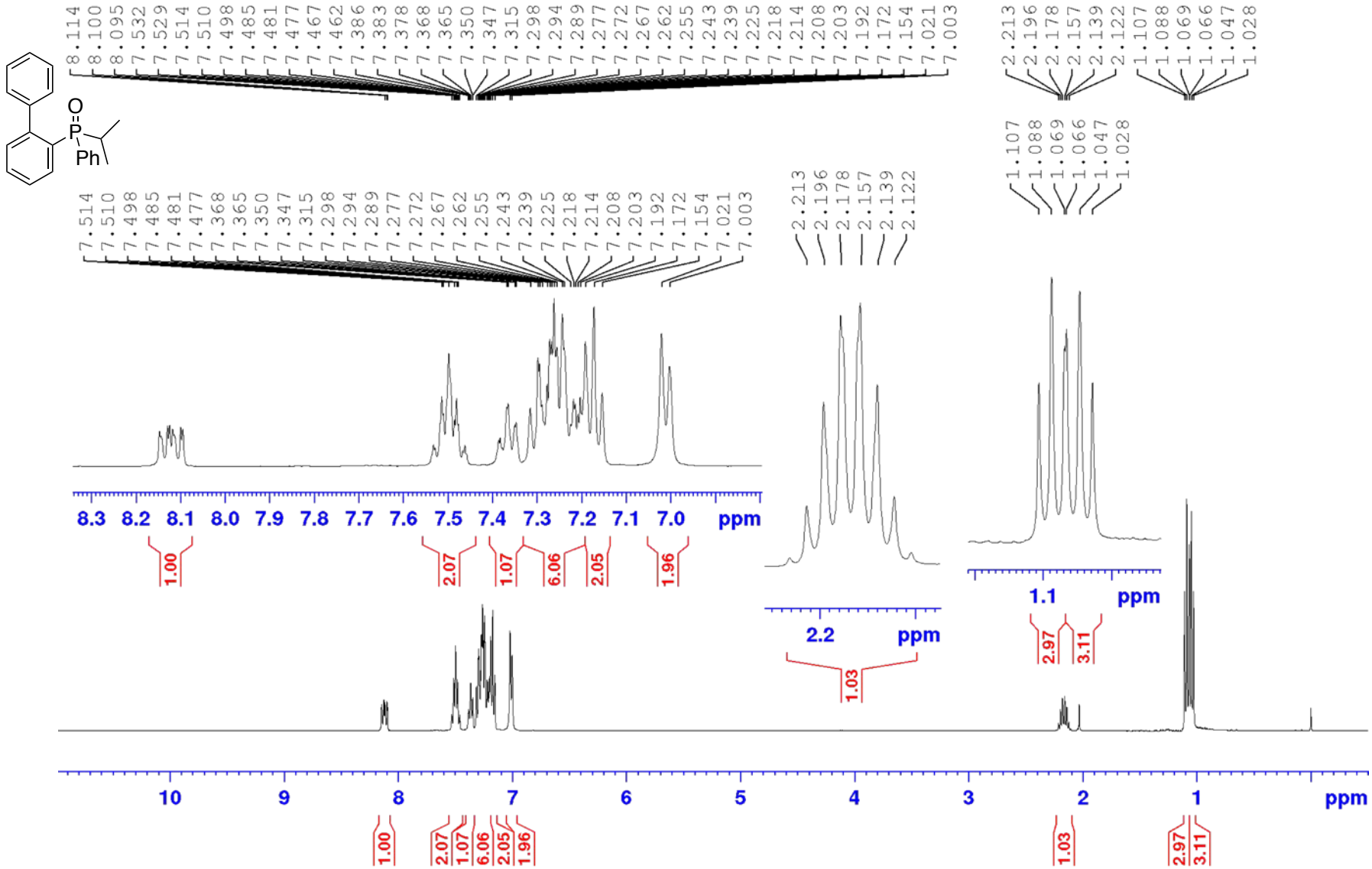


^{13}C NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(3-phenylpropyl)phosphine oxide (**4ha**)

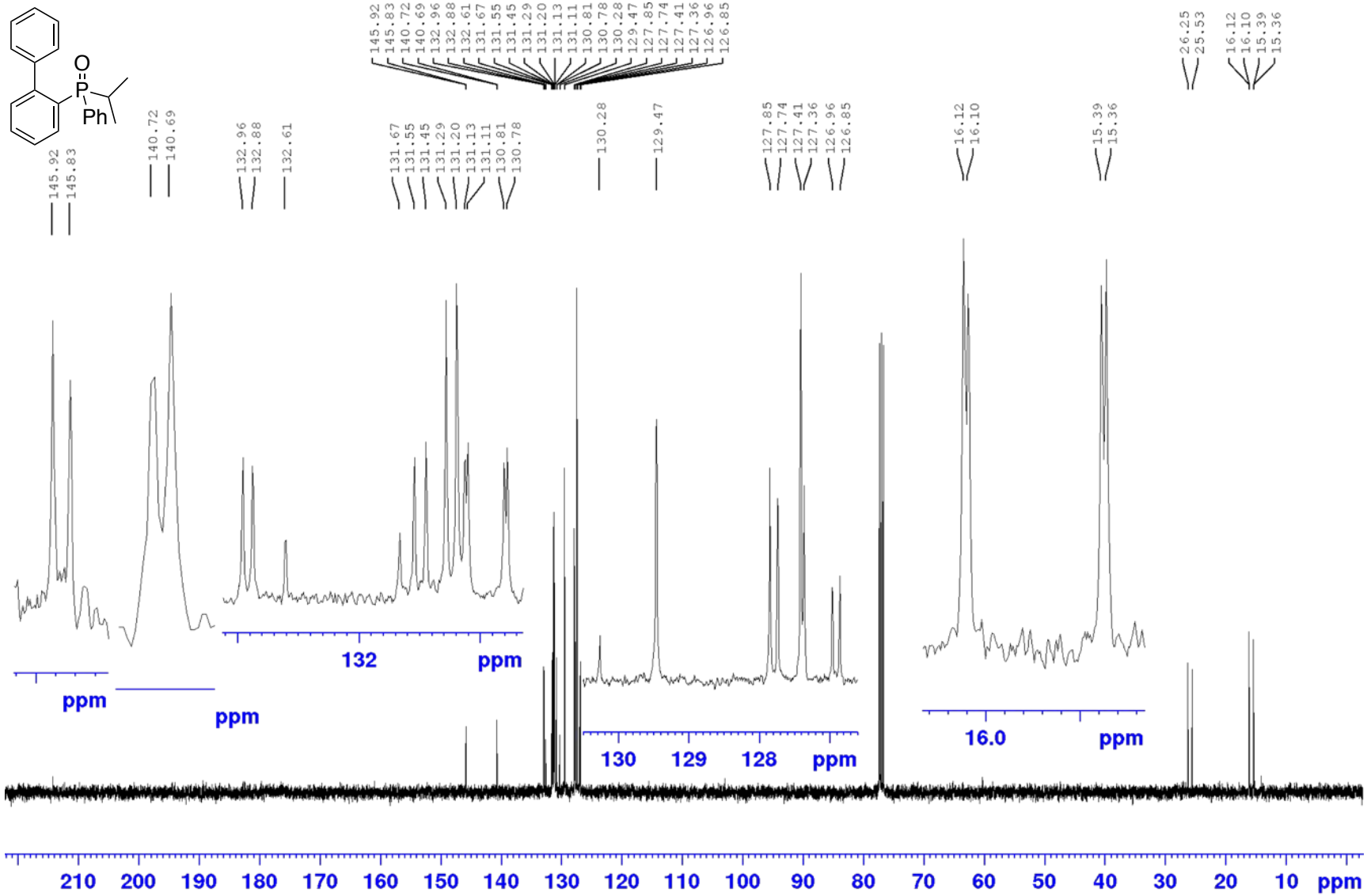


^{31}P NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(3-phenylpropyl)phosphine oxide (**4ha**)

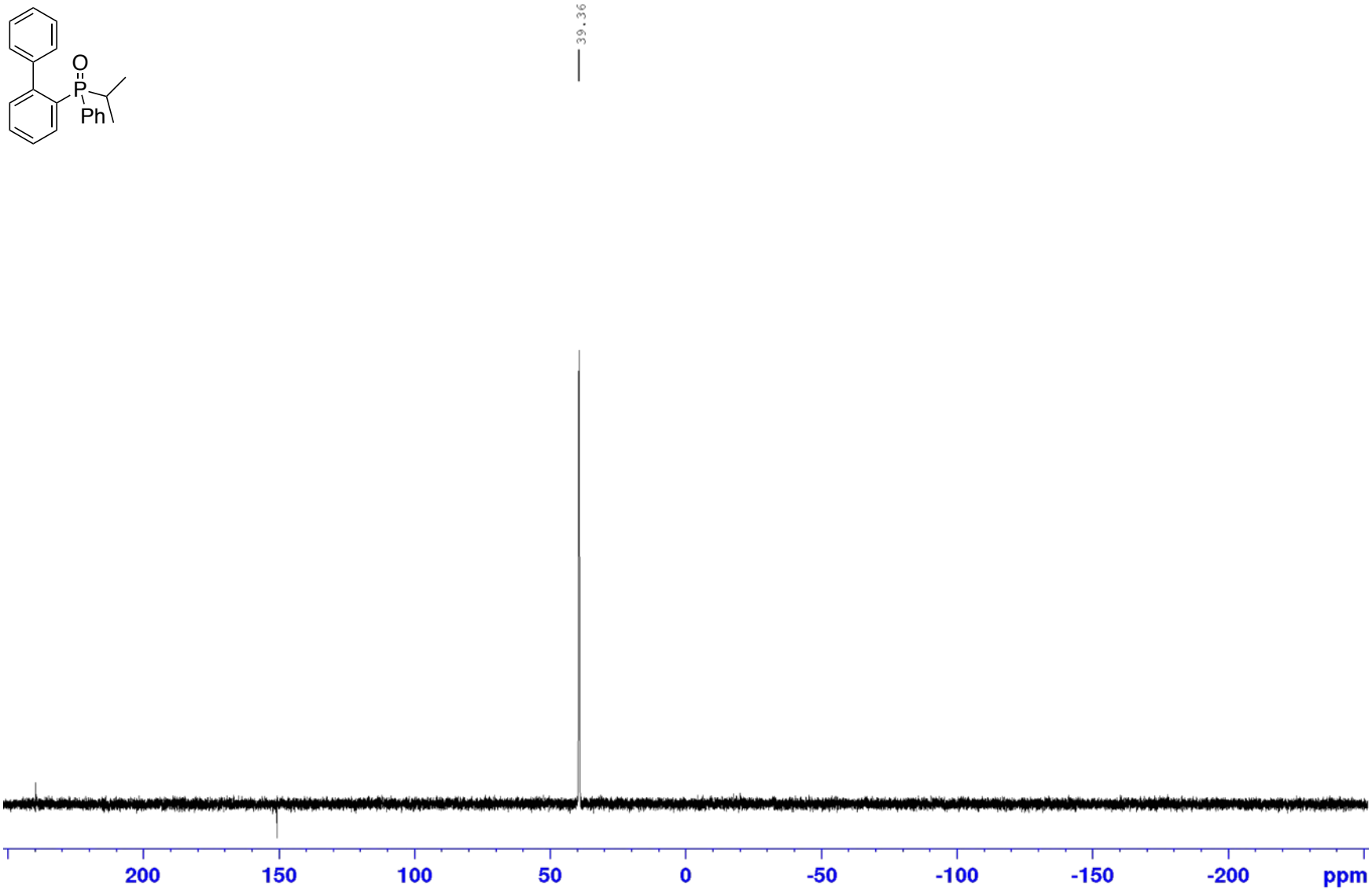
[1]H NMR spectrum of [1,1'-biphenyl]-2-yl(isopropyl)(phenyl)phosphine oxide (**4hq**)



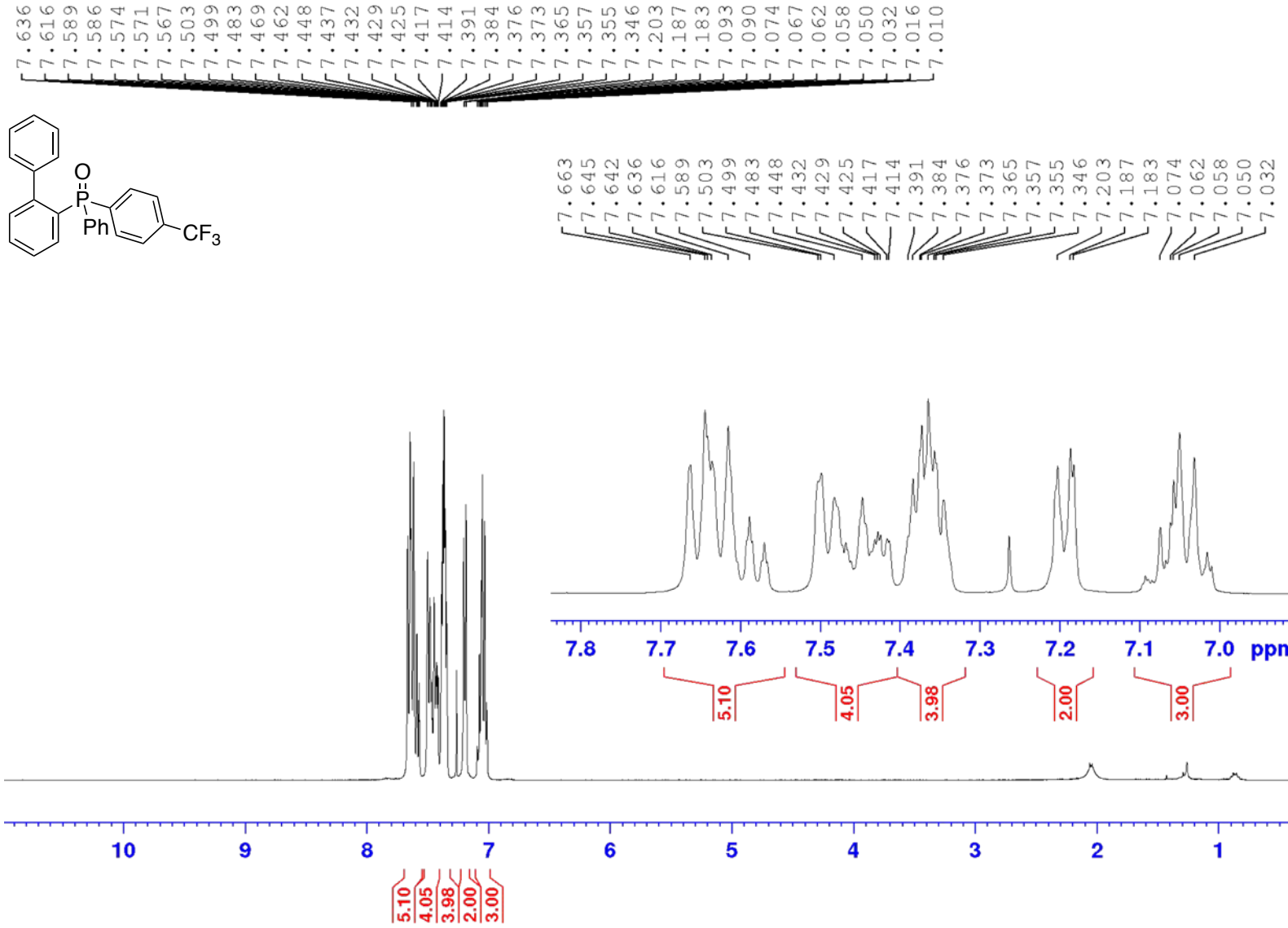
^{13}C NMR spectrum of [1,1'-biphenyl]-2-yl(isopropyl)(phenyl)phosphine oxide (**4hq**)



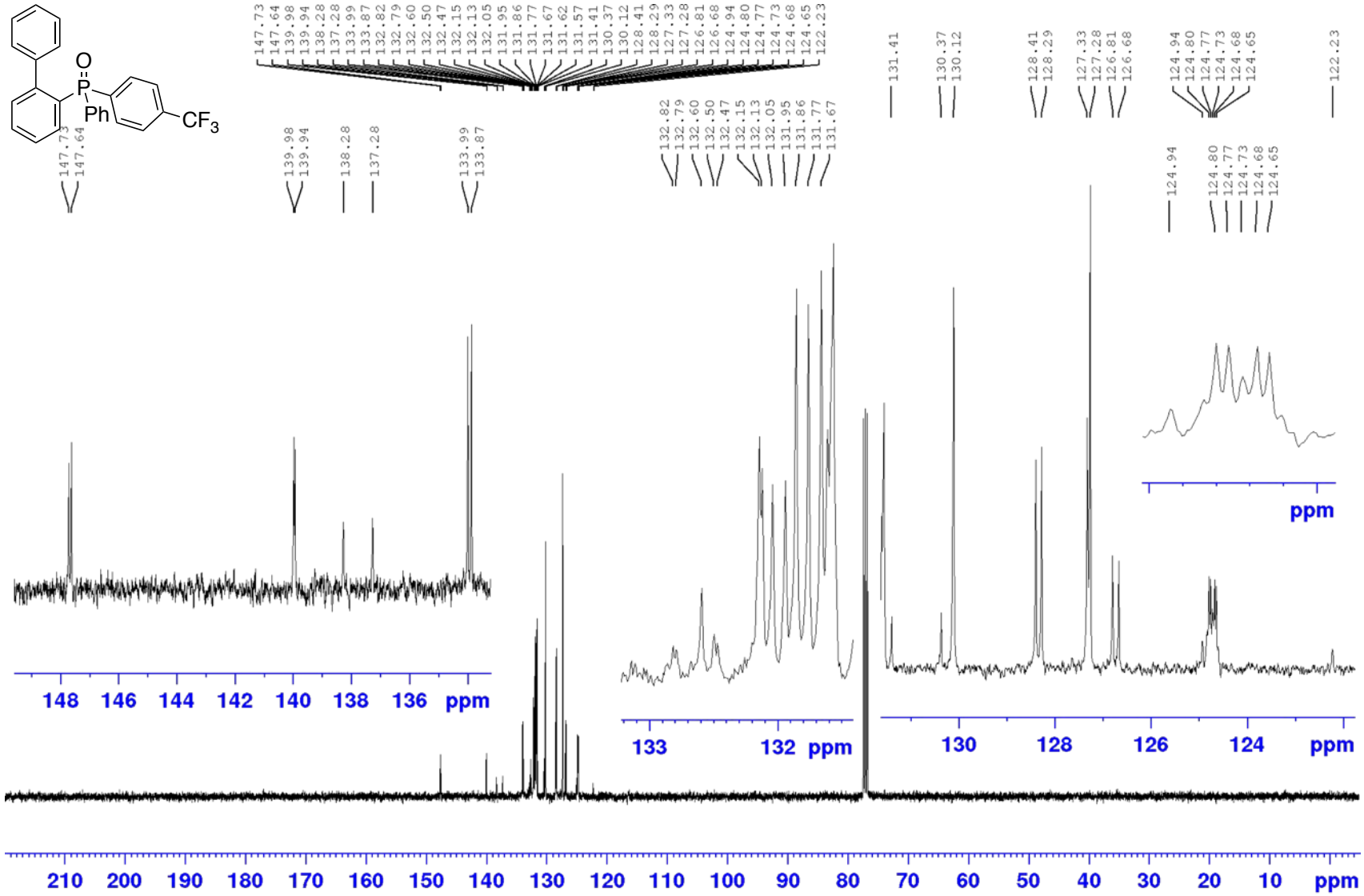
^{31}P NMR spectrum of [1,1'-biphenyl]-2-yl(isopropyl)(phenyl)phosphine oxide (**4hq**)



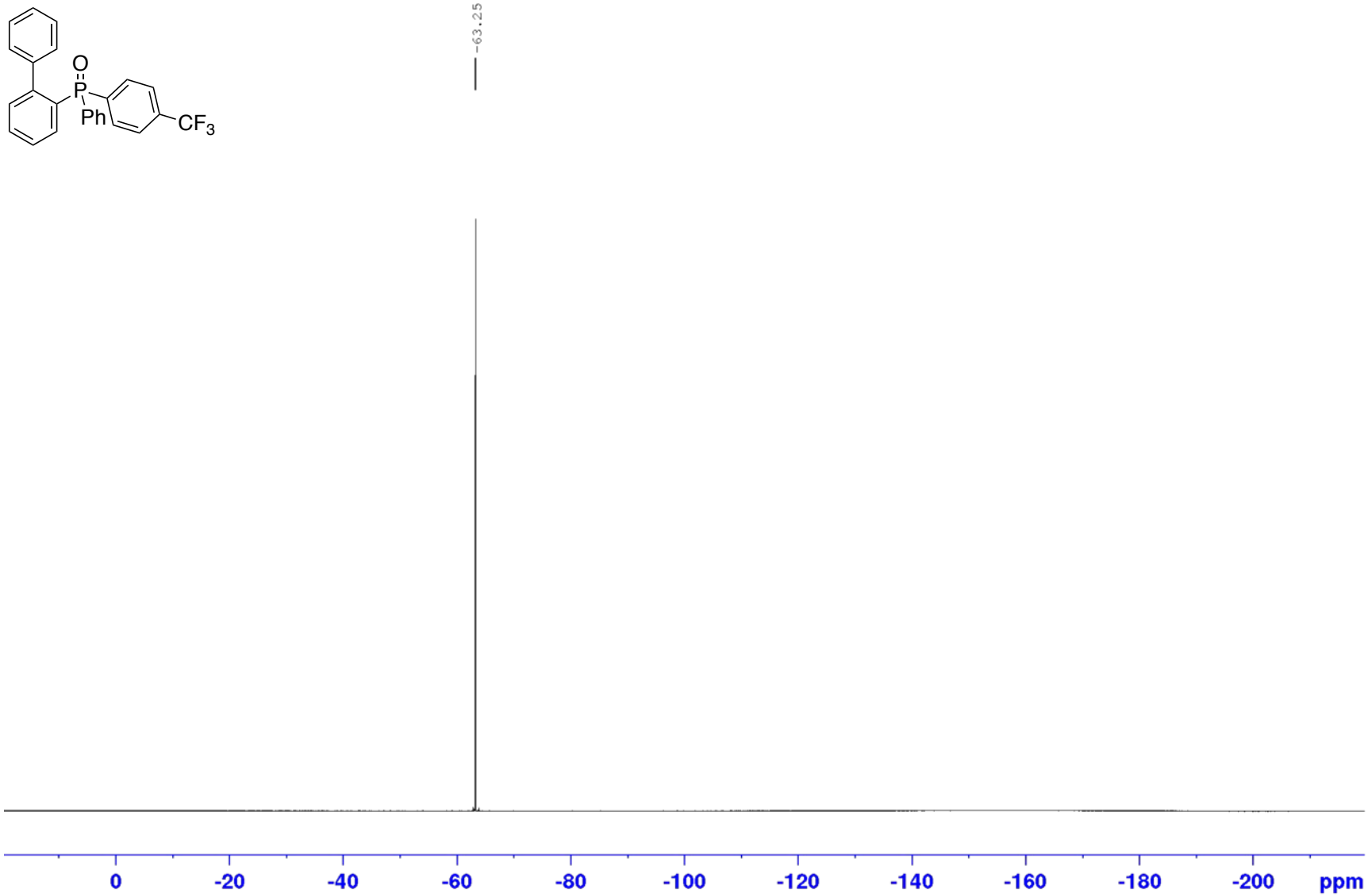
^{1}H NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6hi**)



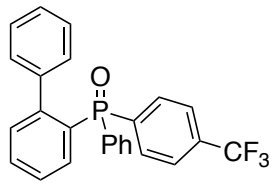
^{13}C NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6hi**)



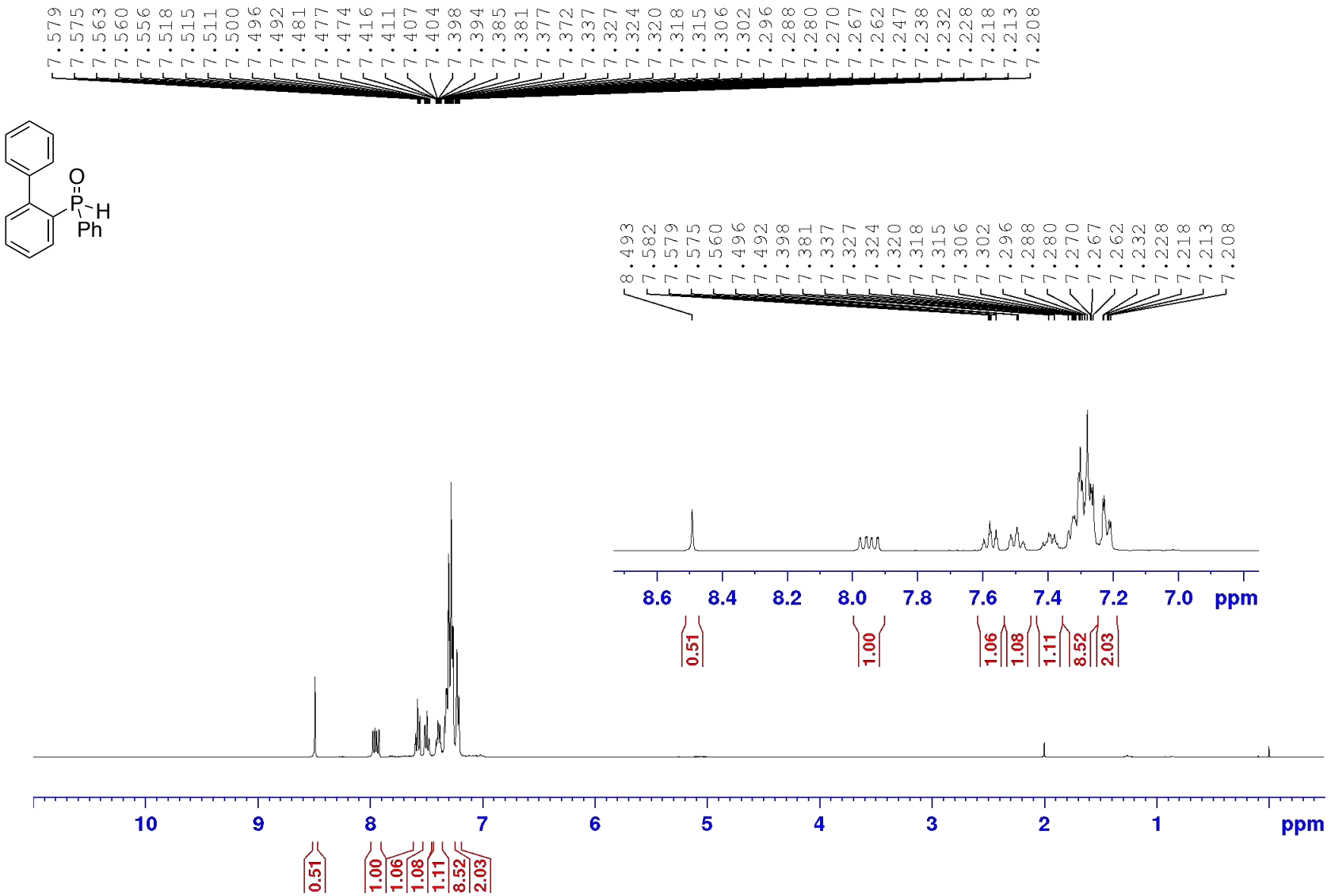
^{19}F NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6hi**)



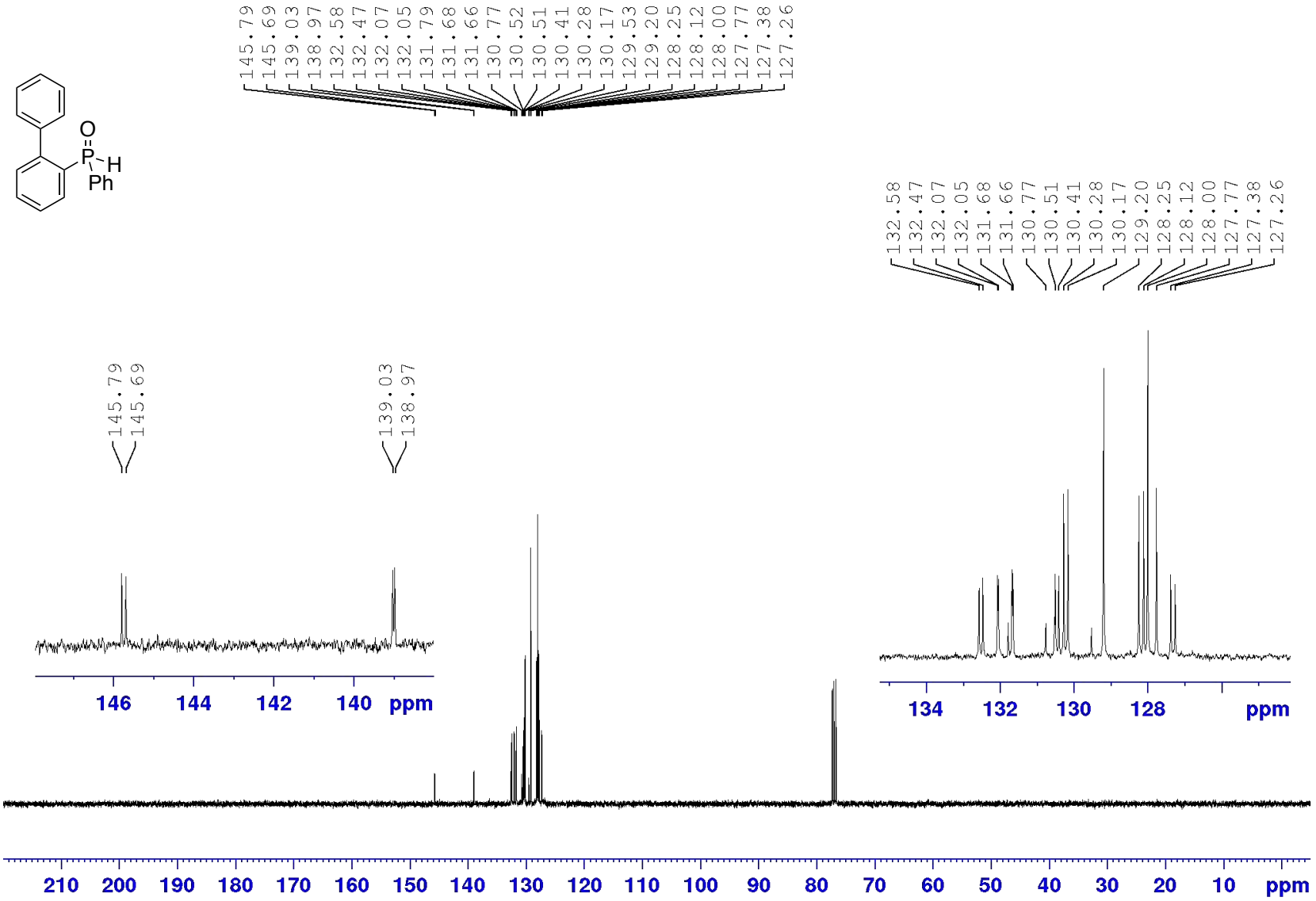
^{31}P NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (**6hi**)



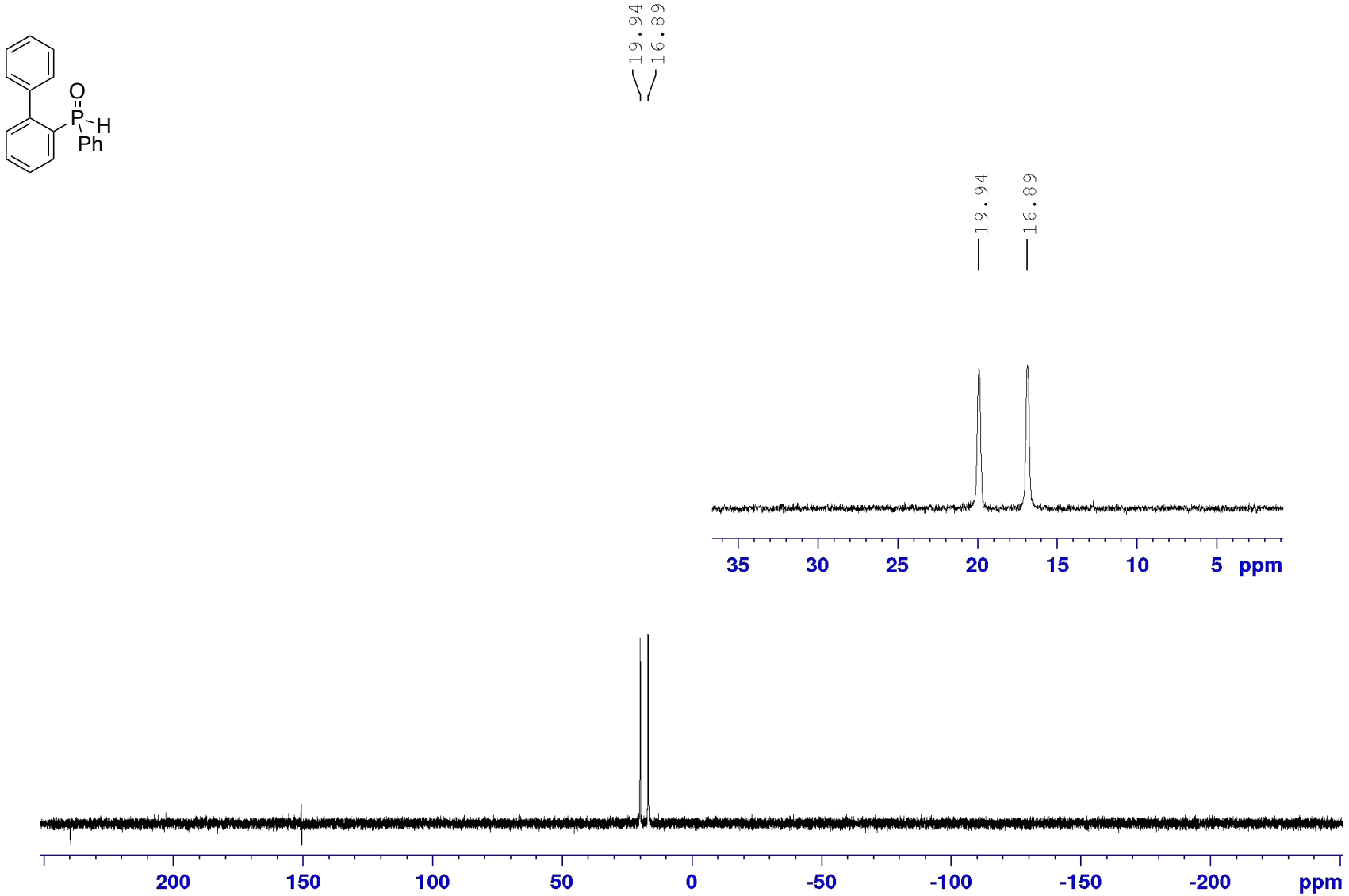
^{1}H NMR spectrum of [1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**2h**)



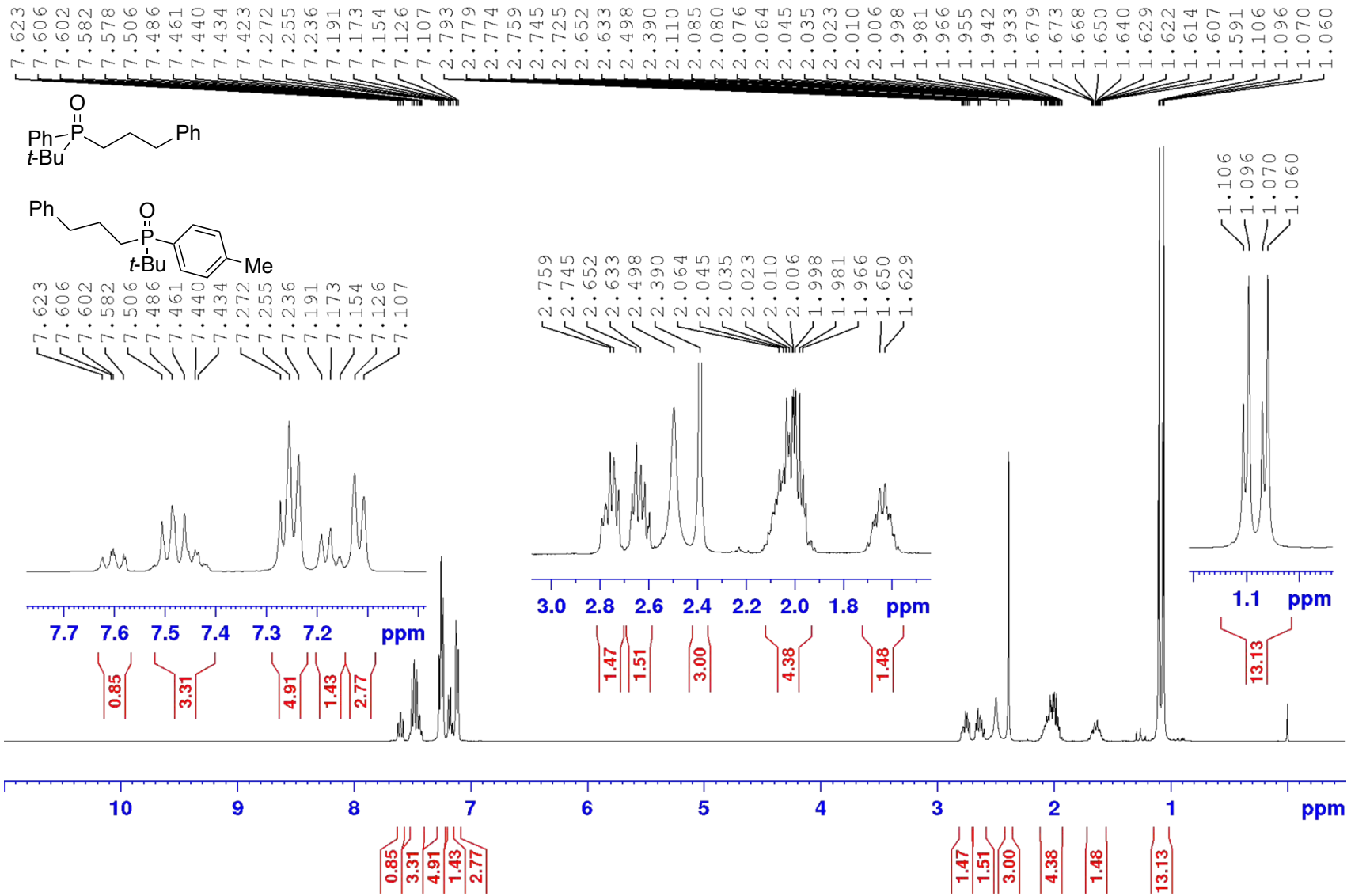
^{13}C NMR spectrum of 1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**2h**)



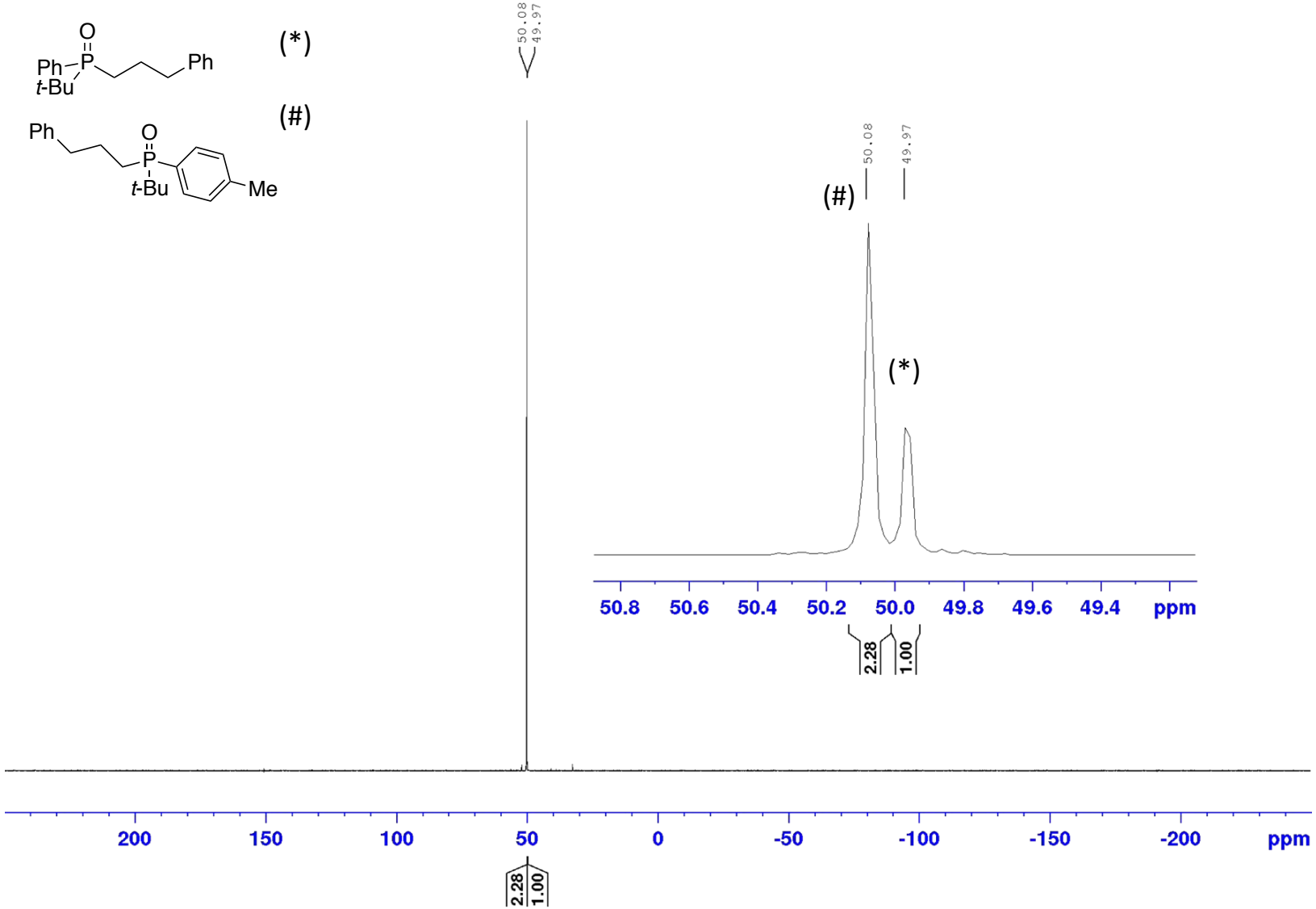
^{31}P NMR spectrum of 1,1'-biphenyl]-2-yl(phenyl)phosphine oxide (**2h**)



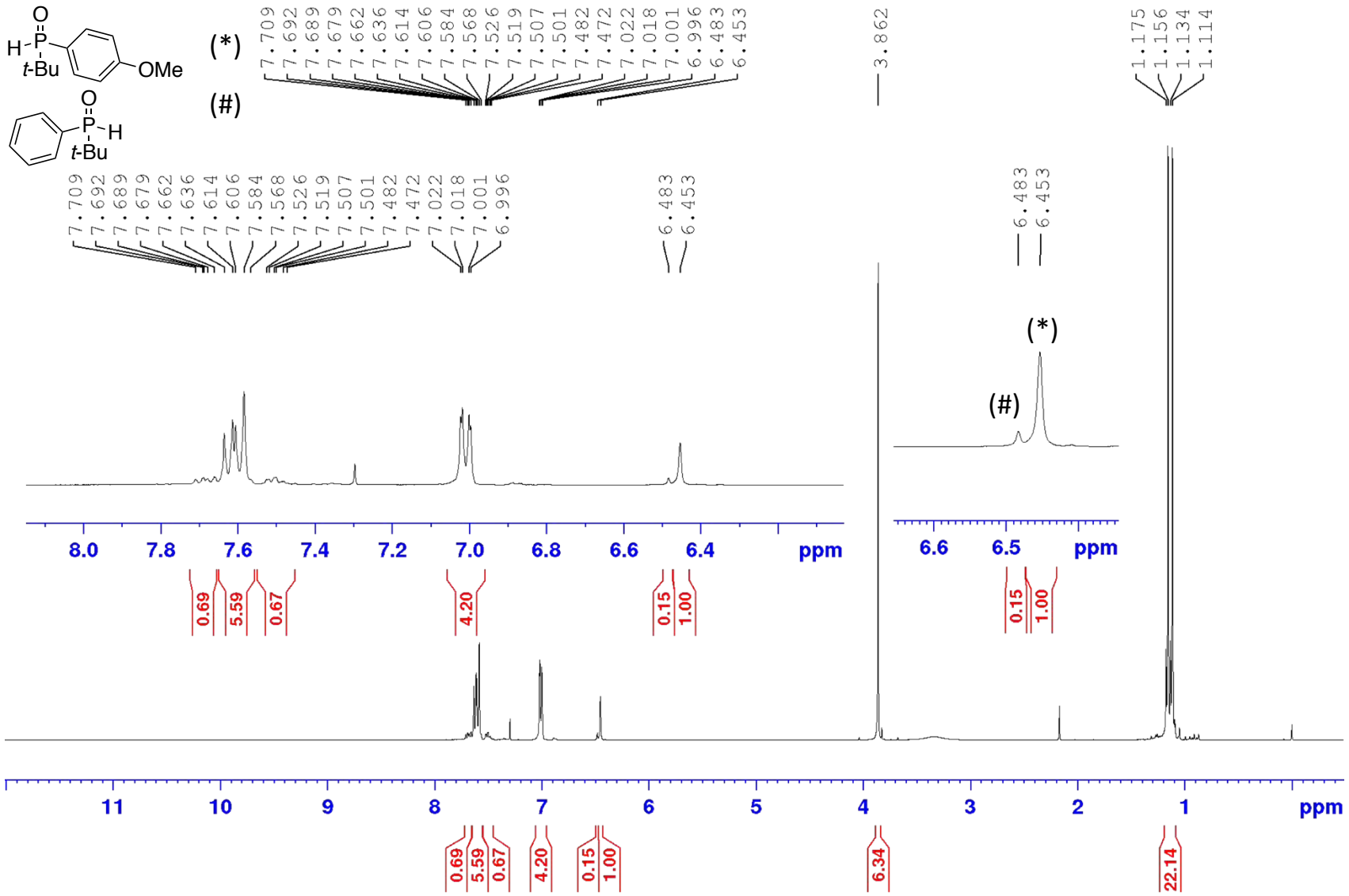
[1]H NMR spectrum of *tert*-butyl(3-phenylpropyl)(*p*-tolyl)phosphine oxide (**10**) and *tert*-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)



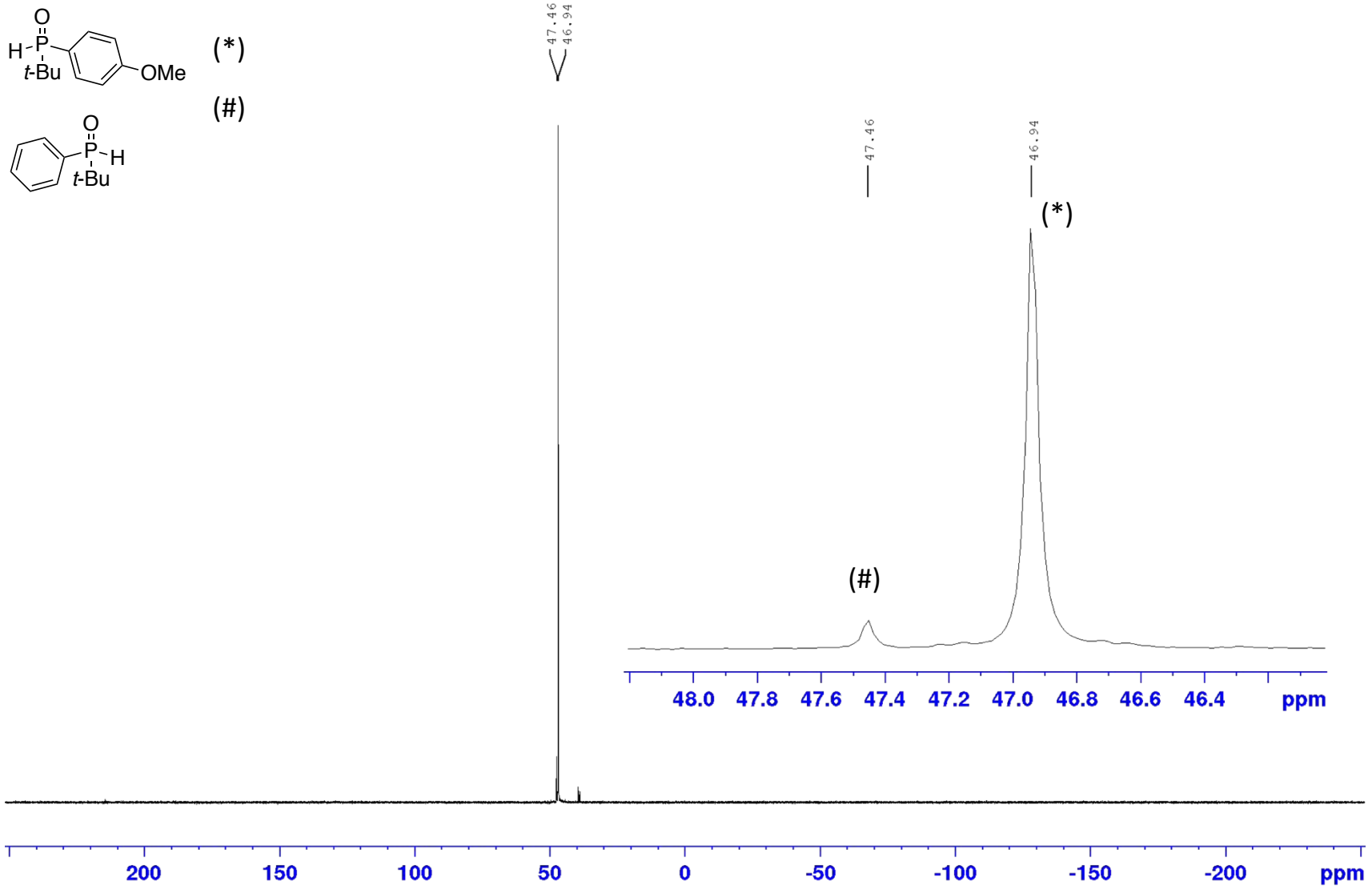
^{31}P NMR spectrum of *tert*-butyl(3-phenylpropyl)(*p*-tolyl)phosphine oxide (**10**) and *tert*-butyl(phenyl)(3-phenylpropyl)phosphine oxide (**4fa**)



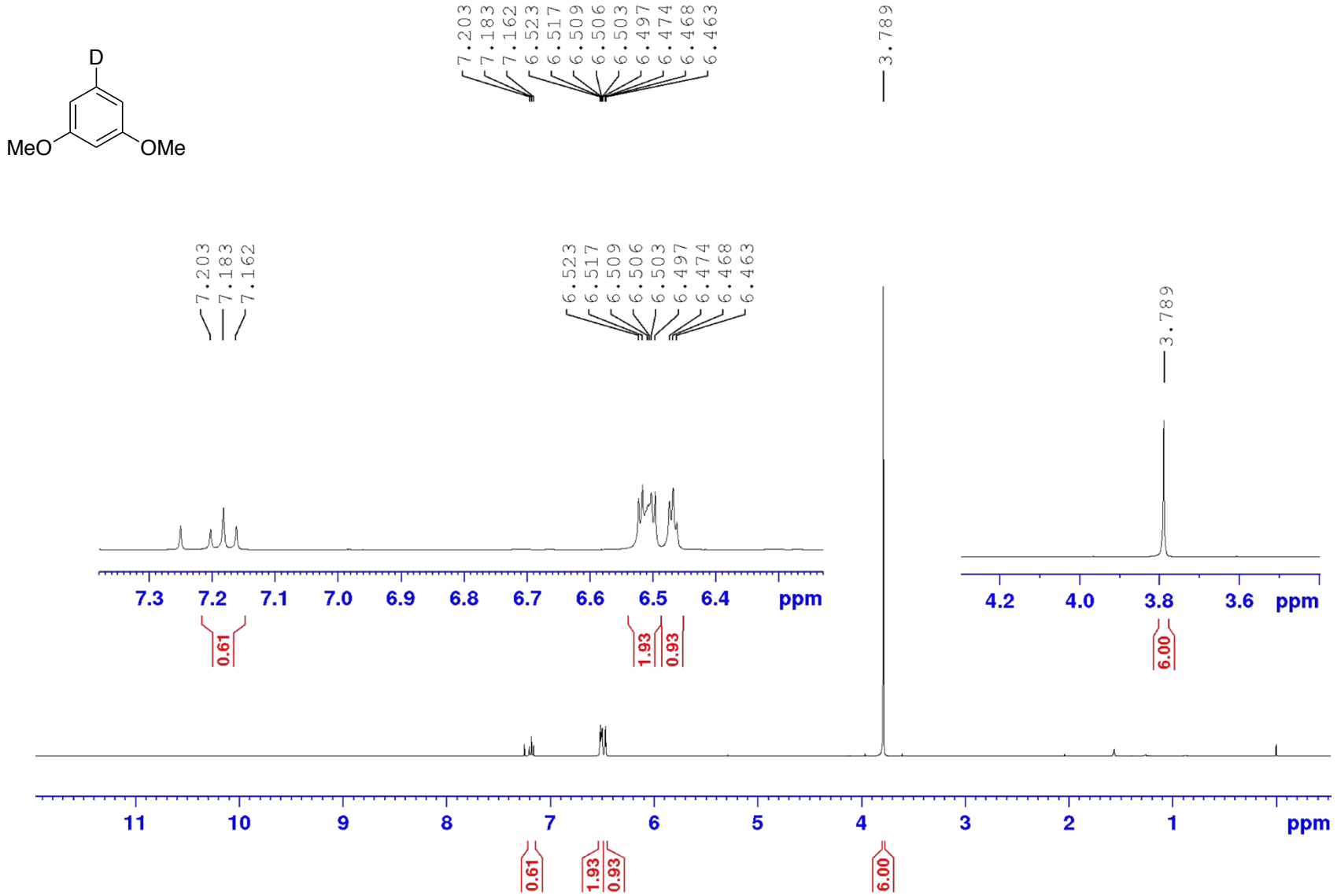
[1]H NMR spectrum of *tert*-butyl(4-methoxyphenyl)phosphine oxide **11** and *tert*-butyl(phenyl)phosphine oxide **12**



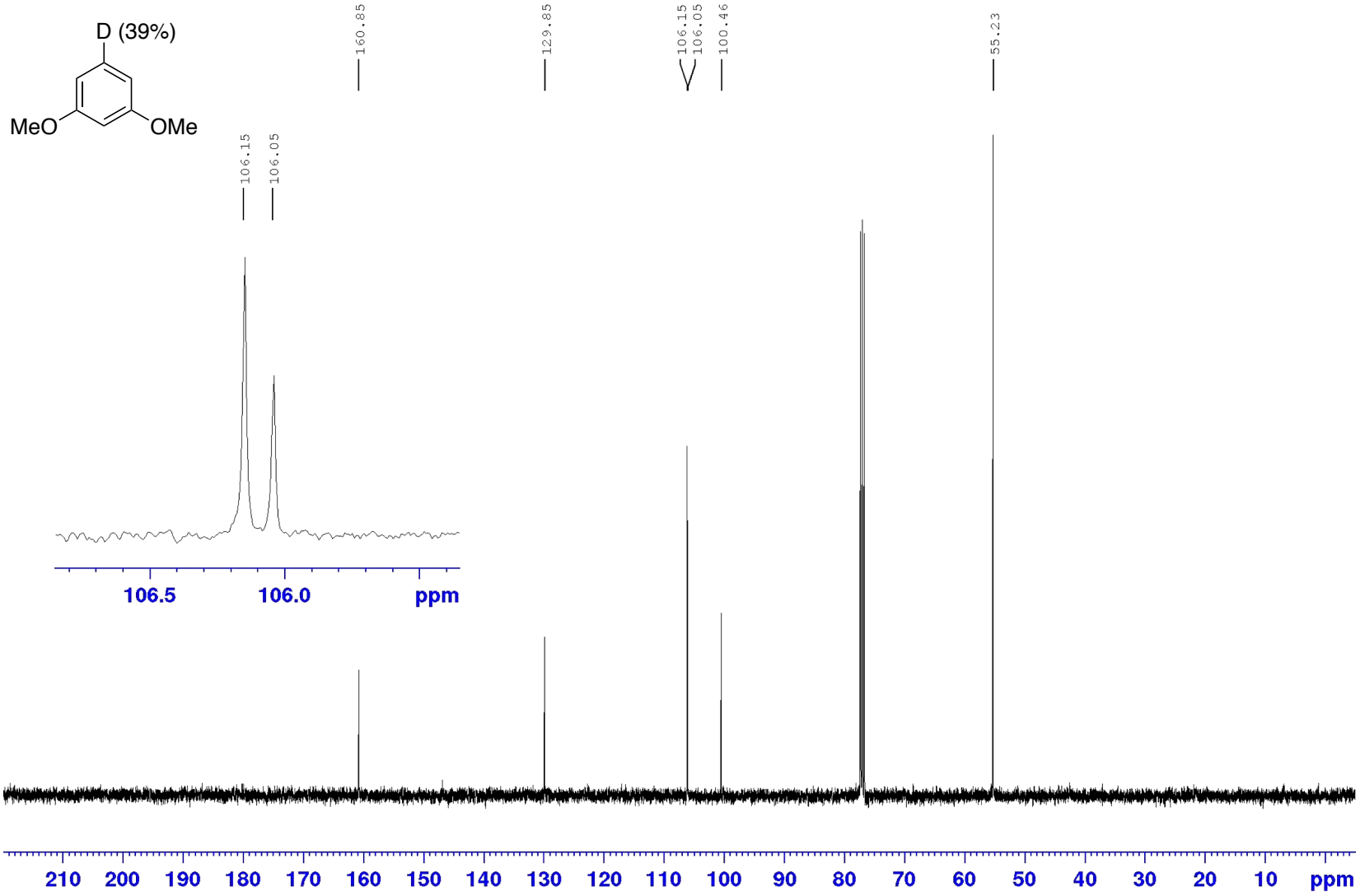
^{31}P NMR spectrum of *tert*-butyl(4-methoxyphenyl)phosphine oxide **11** and *tert*-butyl(phenyl)phosphine oxide **12**



[1]H NMR spectrum of 1,3-dimethoxybenzene-5-*d*



^{13}C NMR spectrum of 1,3-dimethoxybenzene-5-*d*



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