# *Supporting Information for*

## $Ph_3P$-Mediated Highly Selective C(α)–P Couplings of Quinone Monoacetals with $R_2P(O)H$: Convenient and Practical Synthesis of *ortho*-Phosphinyl Phenols

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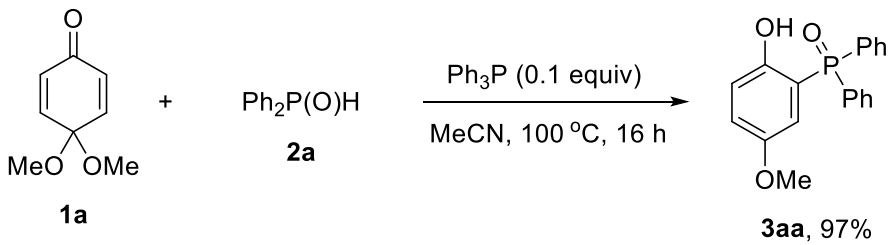
## 1. General Information

Unless otherwise specified, all reactions were performed under dry $N_2$ atmosphere, and the reaction temperatures are referred to the oil bath used. All solvents were distilled prior to use using the appropriate drying agents. Quinone monoacetals **1** were prepared following the known procedures.[1] Secondary phosphine oxides **2** were prepared via a procedure as reported in a previous report.[2] Thin layer chromatography was performed on precoated glass-backed plates and visualized with UV light at 254 nm. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker Ascend™ 400 spectrometer or a a JEOL LA-400 spectrometer at 400 MHz. Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Bruker Ascend™ 400 spectrometer or a JEOL LA-400 spectrometer at 100 MHz. Phosphorus nuclear magnetic resonance ($^{31}$P NMR) spectra were recorded on a Bruker Ascend™ 400 spectrometer or a JEOL LA-400 spectrometer at 160 MHz. Spectra were obtained in $CDCl_3$ or DMSO-$d_6$. Chemical shifts are expressed in ppm and *J* values are given in Hz. Proton chemical shifts are reported relative to internal tetramethylsilane (TMS, δ 0.0 ppm), or with the solvent reference relative to TMS employed as an internal standard ($CDCl_3$, δ 7.26 ppm; DMSO-$d_6$, δ 2.50 ppm). Carbon chemical shifts were reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm; DMSO-$d_6$, δ 39.5 ppm). Phosphorus chemical shifts were recorded using 85% phosphoric acid as the external standard. HRMS analysis was performed at the analytical center of State Key Laboratory of Materials-Oriented Chemical Engineering at NanJingTech (Nanjing, China) and the analytical center of National Institute of Advanced Industrial Science and Technology (AIST, Tsukuba, Japan).

## 2. General synthetic procedure for compounds 3

To a flame-dried Schlenk tube were added $Ph_3P$ (5.2 mg, 0.02 mmol), QMA **1** (0.2 mmol), SPO **2** (1.2–3.0 equiv) and MeCN (2 mL) under a dry nitrogen atmosphere. The tube was sealed and the resulting mixture was stirred at 100 °C. When the reaction was complete (monitored by TLC), the volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc) to afford the pure product **3**. Note: SPOs **2** were flashly prepared, or were pretreated with aq. $Na_2CO_3$ and dried to remove any acidic impurity.

## 3. Experimental details and the characterization data of the products

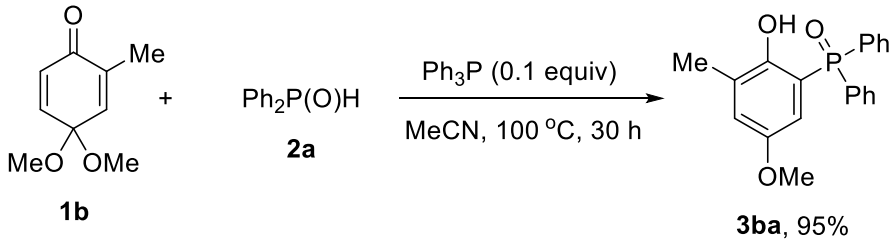



**(2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3aa):** the reaction of **1a** (31.0 mg,

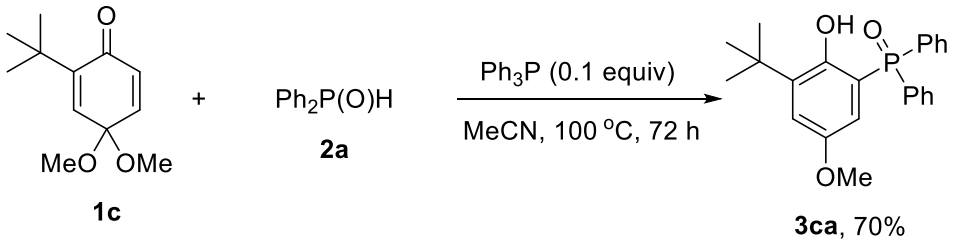
[1] (a) R. M. Moriarty and O. Prakash, *Org. React.*, 2001, **57**, 327; (b) Y. Tamura, T. Yakura, J. Haruta and Y. Kita, *J. Org. Chem.*, 1987, **52**, 3927; (c) A. E. Fleck, J. A. Hobart and G. W. Morrow, *Synth. Commun.*, 1992, **22**, 179.

[2] R. Shen, J. Yang, H. Zhao, Y. Fu, L. Zhang and L.-B. Han, *Chem. Comm.* 2016, **52**, 11959.

0.2 mmol), **2a** (48.6 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 16 h afforded **3aa** (yield: 63.2 mg, 97%), which was purified by column chromatography (PE/EtOAc = 4/1). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.67 (br, 1H), 7.73–7.67 (m, 4H), 7.62–7.57 (m, 2H), 7.52–7.48 (m, 4H), 7.02 (dd, $J_1$ = 8.8 Hz, $J_2$ =2.8Hz, 1H), 6.94 (dd, $J_1$ = 9.2 Hz, $J_2$ =5.2Hz, 1H), 6.47 (dd, $J_1$ = 14.0 Hz, $J_2$ =2.8Hz, 1H), 3.66 (s, 3H). $^{31}P$ NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.0. This is a known compound.[3]



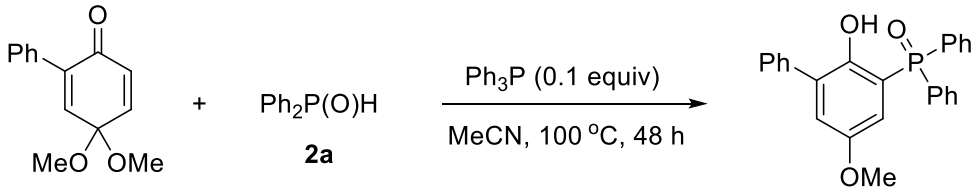

**(2-hydroxy-5-methoxy-3-methylphenyl)diphenylphosphine oxide (3ba):** the reaction of **1b** (33.6 mg, 0.2 mmol), **2a** (48.9 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 30 h afforded **3ba** (yield: 64.3 mg, 95%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 110.3–111.4 $^oC$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.81 (br, 1H), 7.72–7.67 (m, 4H), 7.60–7.56 (m, 2H), 7.51–7.46 (m, 4H), 6.90 (d, $J$ = 2.8 Hz, 1H), 6.30 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.63 (s, 3H) , 2.26 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 156.2 (d, $J_{P\text{-}C}$ = 2.5 Hz), 151.3 (d, $J_{P\text{-}C}$ = 17.0 Hz), 132.5 (d, $J_{P\text{-}C}$ = 2.5 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.4 Hz), 131.7 (d, $J_{P\text{-}C}$ =104.1 Hz), 129.0 (d, $J_{P\text{-}C}$ = 8.3 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.3 Hz), 121.6 (d, $J_{P\text{-}C}$ = 2.1 Hz), 113.3 (d, $J_{P\text{-}C}$ = 11.1 Hz), 110.0 (d, $J_{P\text{-}C}$ = 103.3 Hz), 55.7, 16.3 (d, $J_{P\text{-}C}$ = 2.4 Hz). $^{31}P$ NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.5; HRMS (ESI-TOF): *m/z* = 339.1147, calcd for $C_{20}H_{20}O_3P$ [$MH^+$] 339.1150.



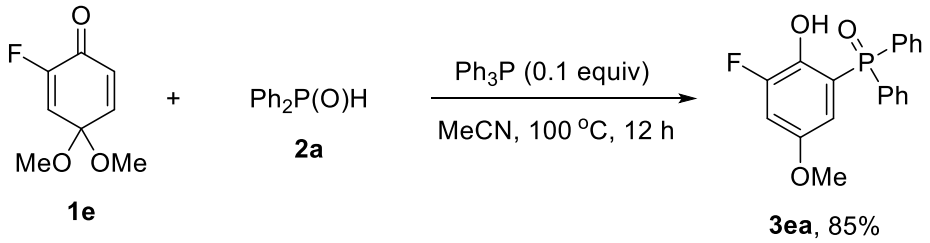

**(3-(tert-butyl)-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ca):** the reaction of **1c** (41.5 mg, 0.2 mmol), **2a** (48.5 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 72 h afforded **3ca** (yield: 52.6 mg, 70%), which was obtained by filtration of the reaction sulution and washing with ether. *Note: this compound is rather insoluable in many solvents including $CDCl_3$ or DMSO-$d_6$.* White solid, mp. 328.8–329.4 $^oC$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.11 (br, 1H), 8.17 (d, $J$ = 13.6 Hz, 1H), 7.80–7.74 (m, 4H), 7.50–7.46 (m, 2H), 7.42–7.38(m, 4H), 6.79 (d, $J$ = 6.8 Hz, 1H), 3.35 (s, 3H), 1.39 (s, 9H). $^{13}C$ NMR (DMSO-$d_6$, 100 MHz): $\delta$ = 152.5 (d, $J_{P\text{-}C}$ = 2.7 Hz), 149.8 (d, $J_{P\text{-}C}$ = 12.9 Hz), 141.5 (d, $J_{P\text{-}C}$ = 1.8 Hz), 133.7 (d, $J_{P\text{-}C}$ = 101.7 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.0 Hz), 131.1 (d, $J_{P\text{-}C}$ = 10.1 Hz), 128.2 (d, $J_{P\text{-}C}$ = 12.0 Hz), 120.3 (d, $J_{P\text{-}C}$ = 7.5 Hz), 117.7 (d, $J_{P\text{-}C}$ = 102.3 Hz), 111.4 (d, $J_{P\text{-}C}$ =

[3] S. Wu, M. He and X. Zhang, *Tetrahedron: Asymmetry*, 2004, **15**, 2177.

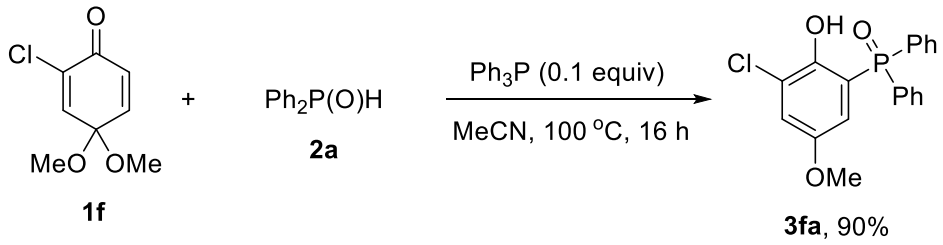
7.9 Hz), 55.6, 34.9, 28.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 29.1; HRMS (ESI-TOF): *m/z* = 381.1622, calcd for $C_{23}H_{26}O_3P$ [$MH^+$] 381.1620.



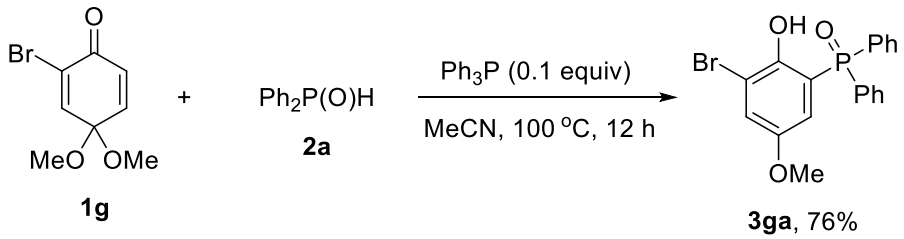

**(2-hydroxy-5-methoxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3da):** the reaction of **1d** (46.1 mg, 0.2 mmol), **2a** (48.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 48h afforded **3da** (yield: 53.8 mg, 67%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 170.6–171.5 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.01 (br, 1H), 7.77–7.72 (m, 4H), 7.62–7.58 (m, 4H), 7.53–7.49 (m, 4H), 7.45–7.41 (m, 2H), 7.36–7.32 (m, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.50 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.9 (d, $J_{P\text{-}C}$ = 3.1 Hz), 151.6 (d, $J_{P\text{-}C}$ = 16.5 Hz), 137.3 (d, $J_{P\text{-}C}$ = 1.7 Hz), 132.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 132.07 (d, $J_{P\text{-}C}$ = 9.8 Hz), 132.05, 131.9 (d, $J_{P\text{-}C}$ = 103.8 Hz), 129.4, 128.8 (d, $J_{P\text{-}C}$ = 12.4 Hz), 128.1, 127.5, 121.1 (d, $J_{P\text{-}C}$ = 2.1 Hz), 115.8 (d, $J_{P\text{-}C}$ = 12.2 Hz), 111.8 (d, $J_{P\text{-}C}$ = 102.5 Hz), 56.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.6. HRMS (ESI-TOF): *m/z* = 401.1311, calcd for $C_{25}H_{22}O_3P$ [$MH^+$] 401.1307.



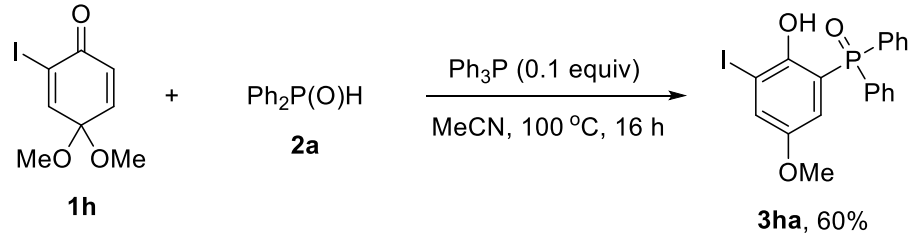

**(3-fluoro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ea):** the reaction of **1e** (34.5 mg, 0.2 mmol), **2a** (49.0 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3ea** (yield: 58.5 mg, 85%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 168.2–169.4 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.85 (br, 1H), 7.72–7.67 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.49 (m, 4H), 6.87 (dd, $J_1$ = 12.0 Hz, $J_2$= 2.8 Hz, 1H), 6.29 (dq, $J_1$ = 13.6 Hz, $J_2$= 1.2 Hz , 1H), 3.65 (s, 3H). *Due to the F-C and P-C couplings, the $^{13}$C NMR spectrum is not easy to be interpreted. A full list of the signals is given.* $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.40, 153.25, 151.66, 151.58, 151.48, 151.40, 150.92, 150.77, 146.27, 146.24, 146.15, 146.12, 132.86, 132.84, 132.04, 131.93, 131.48, 130.42, 128.90, 128.77, 114.04, 114.01, 111.11, 111.08, 111.00, 110.96, 107.70, 107.69, 107.49, 107.47, 55.93. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.4 (d, $J_{F\text{-}P}$ = 10.2); HRMS (ESI-TOF): *m/z* = 343.0897, calcd for $C_{19}H_{17}O_3PF$ [$MH^+$] 343.0899.




**(3-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3fa):** the reaction of **1f** (38.1 mg, 0.2 mmol), **2a** (48.9 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 16 h afforded **3fa** (yield: 65.2 mg, 90%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 170.6–172.5 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.28 (br, 1H), 7.72–7.67 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.48 (m, 4H), 7.12 (d, $J$ = 2.8 Hz, 1H), 6.46 (dd, $J_1$ = 14.0 Hz, $J_2$ = 2.8 Hz, 1H), 3.66 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.1 (d, $J_{P\text{-}C}$ = 3.6 Hz), 151.5 (d, $J_{P\text{-}C}$ = 17.7 Hz), 132.8 (d, $J_{P\text{-}C}$ = 3.3 Hz), 131.9 (d, $J_{P\text{-}C}$ = 10.2 Hz), 130.7 (d, $J_{P\text{-}C}$ = 105.3 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.6 Hz), 123.3 (d, $J_{P\text{-}C}$ = 13.0 Hz), 120.2 (d, $J_{P\text{-}C}$ = 2.6 Hz), 115.5 (d, $J_{P\text{-}C}$ = 11.1 Hz), 112.9 (d, $J_{P\text{-}C}$ = 100.7 Hz), 55.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.4; HRMS (ESI-TOF): *m/z* = 359.0606, calcd for $C_{19}H_{17}O_3PCl$ [$MH^+$] 359.0604.

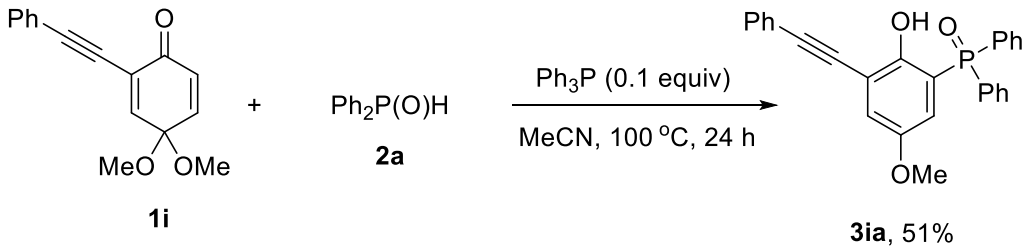



**(3-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ga):** the reaction of **1g** (46.6 mg, 0.2 mmol), **2a** (48.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3ga** (yield: 61.2 mg, 76%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 147.7–148.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.39 (br, 1H), 7.72–7.66 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.48 (m, 4H), 7.28 (d, $J$ = 2.8 Hz, 1H), 6.50 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.66 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.0 (d, $J_{P\text{-}C}$ = 2.6 Hz), 151.8 (d, $J_{P\text{-}C}$ = 16.0 Hz), 132.9 (d, $J_{P\text{-}C}$ = 2.5 Hz), 132.1 (d, $J_{P\text{-}C}$ = 9.78 Hz), 130.8 (d, $J_{P\text{-}C}$ = 105.4 Hz), 128.9 (d, $J_{P\text{-}C}$ = 12.6 Hz), 123.2 (d, $J_{P\text{-}C}$ = 1.8 Hz), 116.5 (d, $J_{P\text{-}C}$ = 11.8 Hz), 112.8 (d, $J_{P\text{-}C}$ = 99.5 Hz), 112.75 (d, $J_{P\text{-}C}$ = 12.4 Hz), 56.1. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.3; HRMS (ESI-TOF): *m/z* = 403.0103, calcd for $C_{19}H_{17}O_3PBr$ [$MH^+$] 403.0099.

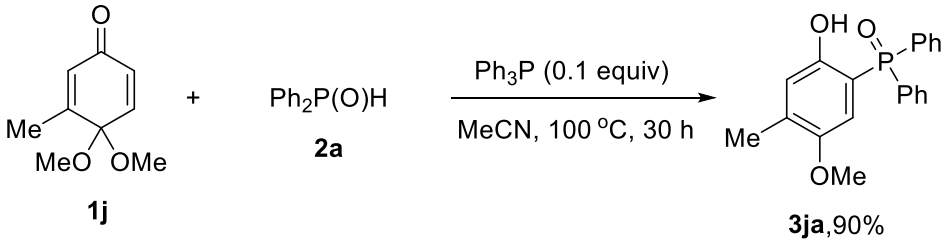



**(2-hydroxy-3-iodo-5-methoxyphenyl)diphenylphosphine oxide (3ha):** the reaction of **1h** (56.0 mg, 0.2 mmol), **2a** (48.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2

mL) at 100 °C for 16 h afforded **3ha** (yield: 54.0 mg, 60%), which was purified by column chromatography (PE/EtOAc = 10/1). White solid, mp. 115.6–116.3 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.61 (br, 1H), 7.71–7.66 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.48 (m, 5H), 6.53 (dd, $J_1$ = 14.0 Hz, $J_2$= 2.8 Hz, 1H), 3.66 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 156.2 (d, $J_{P\text{-}C}$ = 2.7 Hz), 152.1 (d, $J_{P\text{-}C}$ = 16.1 Hz), 132.9 (d, $J_{P\text{-}C}$ = 12.7 Hz), 132.1 (d, $J_{P\text{-}C}$ = 11.0 Hz), 130.7 (d, $J_{P\text{-}C}$ = 104.5 Hz), 129.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 128.9 (d, $J_{P\text{-}C}$ = 12.1 Hz), 117.6 (d, $J_{P\text{-}C}$ = 11.6 Hz), 111.5 (d, $J_{P\text{-}C}$ = 99.8 Hz), 87.2 (d, $J_{P\text{-}C}$ = 8.2 Hz), 56.1. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.0; HRMS (ESI-TOF): *m/z* = 450. 9965, calcd for $C_{19}H_{17}O_3PI$ [$MH^+$] 450.9960.

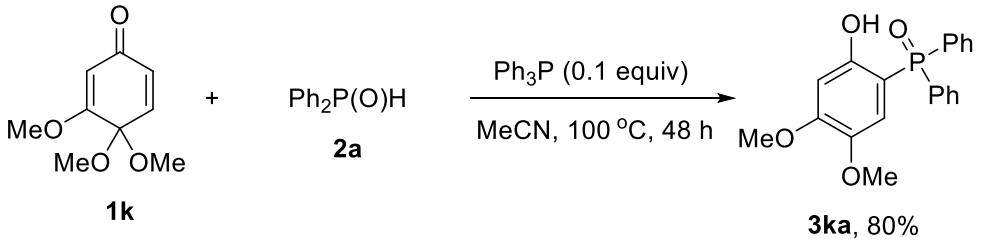



**(2-hydroxy-5-methoxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (3ia):** the reaction of **1i** (50.9 mg, 0.2 mmol), **2a** (48.3 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24h afforded **3ia** (yield: 43.7 mg, 51%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 182.2–184.2 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.13 (br, 1H), 7.73–7.68 (m, 4H), 7.61–7.57 (m, 4H), 7.52–7.47 (m, 4H), 7.35–7.32 (m, 3H), 7.20 (d, $J$ = 2.8 Hz, 1H), 6.55 (dd, $J_1$ = 14.0 Hz, $J_2$= 3.2 Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 151.2 (d, $J_{P\text{-}C}$ = 15.8 Hz), 132.7 (d, $J_{P\text{-}C}$ = 2.2 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.8 Hz), 131.7, 131.0 (d, $J_{P\text{-}C}$ = 105.4 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.6 Hz), 128.4, 128.2, 122.9, 122.0 (d, $J_{P\text{-}C}$ = 2.1 Hz), 118.1 (d, $J_{P\text{-}C}$ = 10.6 Hz), 113.9 (d, $J_{P\text{-}C}$ = 11.1 Hz), 111.4 (d, $J_{P\text{-}C}$ = 102.2 Hz), 94.7, 84.5 (d, $J_{P\text{-}C}$ = 3.3 Hz), 55.8. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.7; HRMS (ESI-TOF): *m/z* = 425.1309, calcd for $C_{27}H_{22}O_3P$ [$MH^+$] 425.1307.

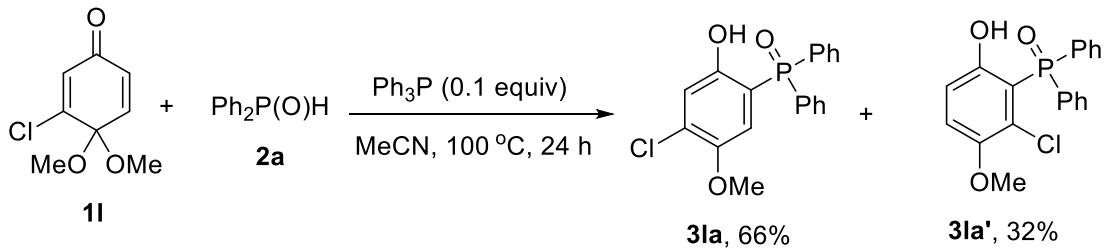



**(2-hydroxy-5-methoxy-4-methylphenyl)diphenylphosphine oxide (3ja):** the reaction of **1j** (33.6 mg, 0.2 mmol), **2a** (49.0 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 30 h afforded **3ja** (yield: 60.9 mg, 90%), which was purified by column chromatography (PE/EtOAc = 10/1). White solid, mp. 204.1–205.0 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.60 (br, 1H), 7.73–7.68 (m, 4H), 7.60–7.57 (m, 2H), 7.51–7.48 (m, 4H), 6.81 (d, $J$ = 5.2 Hz, 1H), 6.30 (d, $J$ = 14.0 Hz, 1H), 3.57 (s, 3H) , 2.20 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 150.6 (d, $J_{P\text{-}C}$ = 14.8 Hz), 135.0 (d, $J_{P\text{-}C}$ = 2.5 Hz), 132.4 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.90 (d, $J_{P\text{-}C}$ = 11.2 Hz), 131.87 (d, $J_{P\text{-}C}$ = 104.7 Hz), 128.6 (d, $J_{P\text{-}C}$ = 12.2

Hz), 120.8 (d, $J_{P\text{-}C}$ = 9.8 Hz), 111.5 (d, $J_{P\text{-}C}$ = 11.7 Hz), 106.9 (d, $J_{P\text{-}C}$ = 106.9 Hz), 55.8, 16.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.2. HRMS (ESI-TOF): *m/z* = 339.1151, calcd for $C_{20}H_{20}O_3P$ [$MH^+$] 339.1150. The structure of this compound was further confirmed by an X-ray crystallographic analysis.



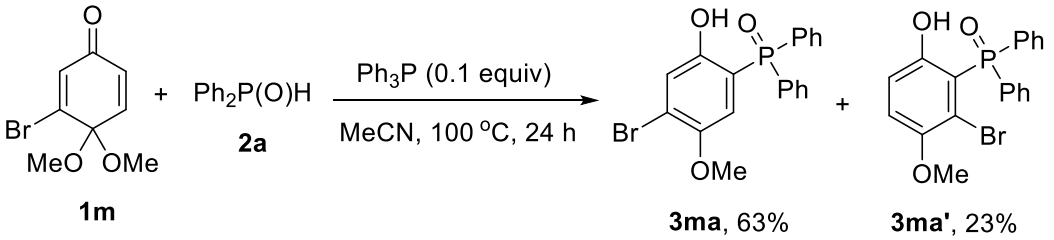

**(2-hydroxy-4,5-dimethoxyphenyl)diphenylphosphine oxide (3ka):** the reaction of **1k** (37.2 mg, 0.2 mmol), **2a** (80.8 mg, 0.4 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^o$C for 48 h afforded **3ka** (yield: 56.7 mg, 80%), which was purified by column chromatography (PE/EtOAc = 3/1). White solid, mp. 232.6–233.4 $^o$C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.98 (br, 1H), 7.72–7.69 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.48 (m, 4H), 6.53 (d, *J* = 4.4 Hz, 1H), 6.35 (d, *J* = 13.2 Hz, 1H), 3.89 (s, 3H) , 3.64 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 160.1 (d, $J_{P\text{-}C}$ = 3.0 Hz), 154.6 (d, $J_{P\text{-}C}$ = 1.5 Hz), 142.3 (d, $J_{P\text{-}C}$ = 15.0 Hz), 132.5 (d, $J_{P\text{-}C}$ = 12.5 Hz), 132.1 (d, $J_{P\text{-}C}$ = 105.3 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.3 Hz), 113.4 (d, $J_{P\text{-}C}$ = 12.6 Hz), 102.0 (d, $J_{P\text{-}C}$ = 9.6 Hz), 99.6 (d, $J_{P\text{-}C}$ = 110.3 Hz), 55.7, 56.0. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.4; HRMS (ESI-TOF): *m/z* = 355.1097, calcd for $C_{20}H_{20}O_4P$ [$MH^+$] 355.1099.




The reaction of **1l** (37.8 mg, 0.2 mmol), **2a** (49.1 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^o$C for 24 h afforded **3la** (yield: 47.3 mg, 66%) and **3la'** (yield: 23.0 mg, 32%). The **3la** and **3la'** was seperated by column chromatography (PE/EtOAc = 10/1-4/1). **(4-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3la):** white solid, mp. 239.3–240.5 $^o$C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.86 (br, 1H), 7.72–7.67 (m, 4H), 7.64–7.60 (m, 2H), 7.54–7.50 (m, 4H), 7.06 (d, *J* = 4.8 Hz, 1H), 6.44 (d, *J* = 13.6 Hz, 1H), 3.64 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.3 (d, $J_{P\text{-}C}$ = 3.1 Hz), 148.1 (d, $J_{P\text{-}C}$ = 5.9 Hz), 132.8 (d, $J_{P\text{-}C}$ = 2.4 Hz), 132.0 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.2 (d, $J_{P\text{-}C}$ = 105.3 Hz), 129.8 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.9 (d, $J_{P\text{-}C}$ = 12.3 Hz), 120.6 (d, $J_{P\text{-}C}$ = 9.1 Hz), 114.4 (d, $J_{P\text{-}C}$ = 12.0 Hz), 109.3 (d, $J_{P\text{-}C}$ = 104.2 Hz), 57.0. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.9; HRMS (ESI-TOF): *m/z* = 359.0608, calcd for $C_{19}H_{17}O_3PCl$ [$MH^+$] 359.0604.

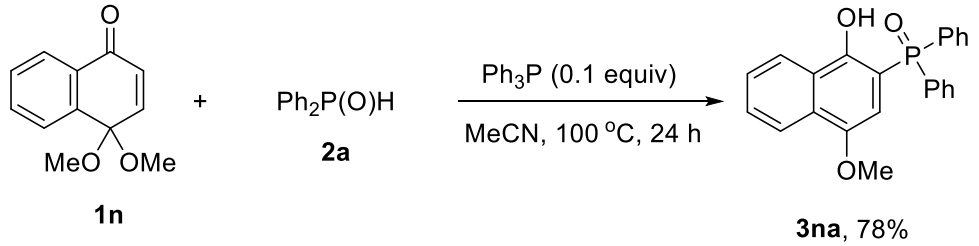
**(2-chloro-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3la'):** white solid, mp. 107.9–108.8 $^o$C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 12.42 (br, 1H), 7.86–7.80 (m, 4H), 7.62–7.58 (m, 2H), 7.53–7.48 (m, 4H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.96 (dd, $J_1$ = 9.2 Hz, $J_2$= 4.8 Hz,

1H), 3.81 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 160.2 (d, $J_{P\text{-}C}$ = 11.9 Hz), 148.1 (d, $J_{P\text{-}C}$ = 10.6 Hz), 132.5 (d, $J_{P\text{-}C}$ = 3.2 Hz), 132.3 (d, $J_{P\text{-}C}$ = 10.1 Hz), 130.8 (d, $J_{P\text{-}C}$ = 108.8 Hz), 128.5 (d, $J_{P\text{-}C}$ = 12.9 Hz), 123.3 (d, $J_{P\text{-}C}$ = 4.0 Hz), 119.3 (d, $J_{P\text{-}C}$ = 2.7 Hz), 118.1 (d, $J_{P\text{-}C}$ = 8.9 Hz), 109.6 (d, $J_{P\text{-}C}$ = 102.8 Hz), 56.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 43.1; HRMS (ESI-TOF): *m/z* = 359.0608, calcd for $C_{19}H_{17}O_3PCl$ [$MH^+$] 359.0604.



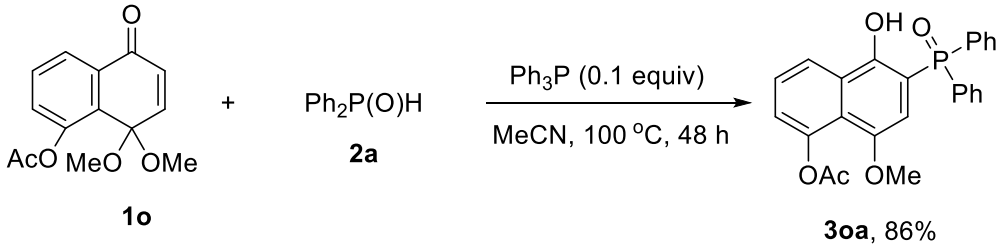

The reaction of **1m** (47.3 mg, 0.2 mmol), **2a** (48.3 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24 h afforded **3ma** (yield: 51.0 mg, 63%) and **3ma'** (yield: 19.0 mg, 23%). **3ma** and **3ma'** were seperated by column chromatography (PE/EtOAc = 10/1-4/1). **(4-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ma):** white solid, mp. 227.9–229.0 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.81 (br, 1H), 7.72–7.67 (m, 4H), 7.63–7.60 (m, 2H), 7.53–7.50 (m, 4H), 7.25 (d, *J* = 4.4 Hz, 1H), 6.41 (d, *J* = 13.6 Hz, 1H), 3.63 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.2 (d, $J_{P\text{-}C}$ = 1.7 Hz), 148.9 (d, $J_{P\text{-}C}$ = 14.1 Hz), 132.8, 131.9 (d, $J_{P\text{-}C}$ = 10.3 Hz), 131.1 (d, $J_{P\text{-}C}$ = 105.3 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.2 Hz), 123.7 (d, $J_{P\text{-}C}$ = 9.4 Hz), 119.2, 113.9 (d, $J_{P\text{-}C}$ = 11.5 Hz), 110.0 (d, $J_{P\text{-}C}$ = 101.7 Hz), 56.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.9; HRMS (ESI-TOF): *m/z* = 403. 0101, calcd for $C_{19}H_{17}O_3PBr$ [$MH^+$] 403.0099. The structure of this compound was further confirmed by an X-ray crystallographic analysis.

**(2-bromo-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3ma'):** white solid, mp. 141.3–142.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 12.58 (br, 1H), 7.89–7.84 (m, 4H), 7.62–7.58 (m, 2H), 7.53–7.48 (m, 4H), 7.12 (d, *J* = 9.2 Hz, 1H), 7.02 (dd, $J_1$ = 9.2 Hz, $J_2$= 4.8 Hz, 1H), 3.81 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.1 (d, $J_{P\text{-}C}$ = 2.7 Hz), 149.0 (d, $J_{P\text{-}C}$ = 10.0 Hz), 132.6 (d, $J_{P\text{-}C}$ = 10.8 Hz), 132.5 (d, $J_{P\text{-}C}$ = 3.0 Hz), 130.8 (d, $J_{P\text{-}C}$ = 8.1 Hz), 128.5 (d, $J_{P\text{-}C}$ = 12.4 Hz), 119.1 (d, $J_{P\text{-}C}$ = 8.6 Hz), 119.0, 114.0 (d, $J_{P\text{-}C}$ = 5.9 Hz), 111.0 (d, $J_{P\text{-}C}$ = 104.1 Hz), 57.2. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 45.2; HRMS (ESI-TOF): *m/z* = 403. 0103, calcd for $C_{19}H_{17}O_3PBr$ [$MH^+$] 403.0099. The structure of this compound was further confirmed by an X-ray crystallographic analysis.

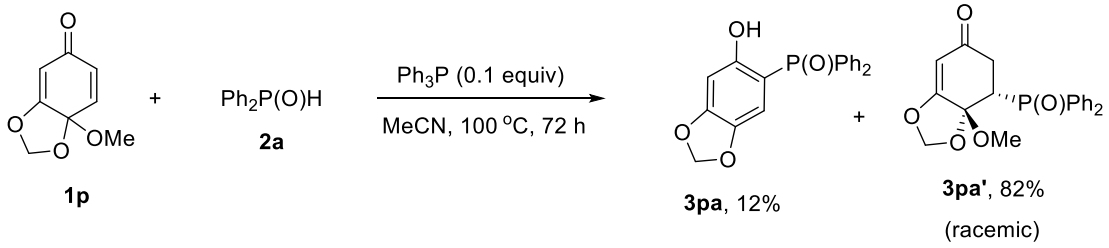



**(1-hydroxy-4-methoxynaphthalen-2-yl)diphenylphosphine oxide (3na):** the reaction of **1n** (40.8 mg, 0.2 mmol), **2a** (48.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24 h afforded **3na** (yield: 58.4 mg, 78%), which was purified by column

chromatography (PE/EtOAc = 6/1). White solid, mp. 161.0–161.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.86 (br, 1H), 8.38 (d, $J$ = 7.6 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.76 (dd, $J_1$ = 12.0 Hz, $J_2$= 6.8 Hz, 4H), 7.63–7.55 (m, 4H), 7.52–7.47 (m, 4H), 6.19 (d, $J$ = 12.4 Hz, 1H), 3.73 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 156.8 (d, $J_{P\text{-}C}$ = 1.5 Hz), 147.7 (d, $J_{P\text{-}C}$ = 15.4 Hz), 132.5 (d, $J_{P\text{-}C}$ = 1.8 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.6 Hz), 131.9 (d, $J_{P\text{-}C}$ = 104.2 Hz), 128.8 (d, $J_{P\text{-}C}$ = 2.6 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.2 Hz), 128.5, 126.6, 126.5, 123.1, 121.7, 102.6 (d, $J_{P\text{-}C}$ = 12.4 Hz), 100.3 (d, $J_{P\text{-}C}$ = 106.6 Hz), 55.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 40.6; HRMS (ESI-TOF): $m/z$ = 375.1154, calcd for $C_{23}H_{20}O_3P$ [$MH^+$] 375.1150.



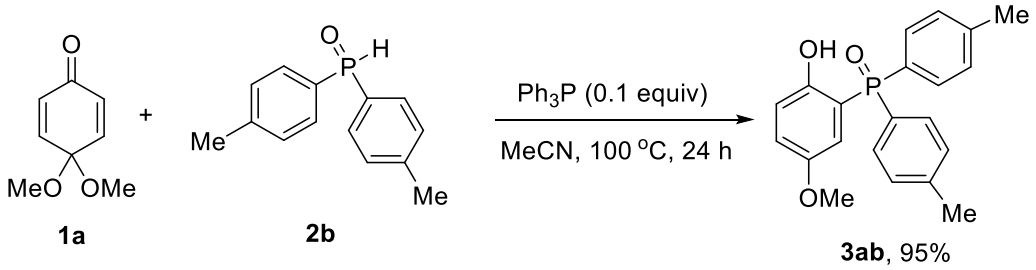

**6-(diphenylphosphoryl)-5-hydroxy-8-methoxynaphthalen-1-yl acetate (3oa):** the reaction of **1oa** (53.2 mg, 0.2 mmol), **2a** (49.0 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 48 h afforded **3oa** (yield: 75.4 mg, 86%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 239.0–240.0 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.92 (br, 1H), 8.34 (dd, $J_1$ = 8.4 Hz, $J_2$= 1.2 Hz, 1H), 7.77–7.71 (m, 4H), 7.62–7.58 (m, 2H), 7.55–7.48 (m, 5H), 7.22 (dd, $J_1$ = 7.2 Hz, $J_2$= 0.8 Hz, 1H), 6.25 (d, $J$ = 12.8 Hz, 1H) 3.65 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 170.3, 156.7 (d, $J_{P\text{-}C}$ = 1.8 Hz), 147.2 (d, $J_{P\text{-}C}$ = 13.9 Hz), 146.1, 132.7 (d, $J_{P\text{-}C}$ = 3.4 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.7 Hz), 131.5 (d, $J_{P\text{-}C}$ = 104.5 Hz), 128.83 (d, $J_{P\text{-}C}$ = 9.9 Hz), 128.80 (d, $J_{P\text{-}C}$ = 12.4 Hz), 126.5, 122.9, 122.2 (d, $J_{P\text{-}C}$ = 2.7 Hz), 121.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 105.6 (d, $J_{P\text{-}C}$ = 11.9 Hz), 101.5 (d, $J_{P\text{-}C}$ = 105.4 Hz), 56.6, 20.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 40.1; HRMS (ESI-TOF): $m/z$ = 433.1207, calcd for $C_{25}H_{22}O_5P$ [$MH^+$] 433.1205.



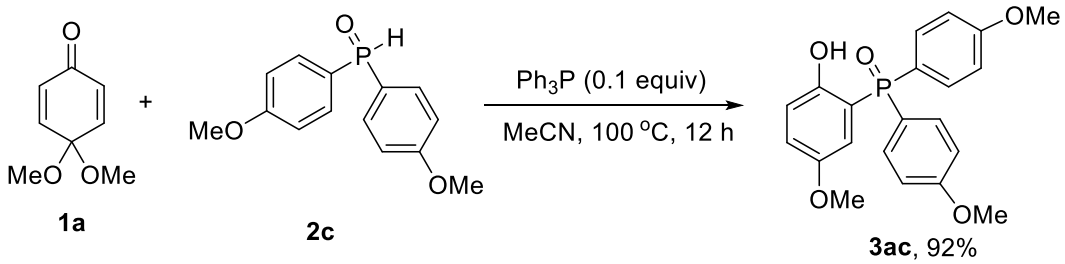

The reaction of **1p** (67.6 mg, 0.4 mmol), **2a** (96.6 mg, 0.48 mmol) and $Ph_3P$ (10.5 mg, 0.04 mmol) in MeCN (4 mL) at 100 °C for 72 h afforded **3pa** (yield: 16.5 mg, 12%) and **3pa'** (yield: 118.4 mg, 80%), which were purified after column chromatography (PE/EtOAc = 3/1-1/1). **(6-hydroxybenzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (3pa):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.15 (br, 1H), 7.71–7.66 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.47 (m, 4H), 6.50 (d, $J$ = 4.0 Hz, 1H), 6.32 (t, $J$ = 12.4 Hz, 1H), 5.92 (s, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.3 (d, $J_{P\text{-}C}$ = 4.2 Hz), 152.7 (d, $J_{P\text{-}C}$ = 2.3 Hz), 140.8 (d, $J_{P\text{-}C}$ = 18.2 Hz), 132.5 (d, $J_{P\text{-}C}$ = 2.0 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.5 Hz), 131.9 (d, $J_{P\text{-}C}$ = 104.9 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.3

Hz), 108.7 (d, $J_{P\text{-}C}$ = 12.7 Hz), 101.6, 100.5 (d, $J_{P\text{-}C}$ = 108.9 Hz), 100.2 (d, $J_{P\text{-}C}$ = 9.0 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.9. HRMS (ESI-TOF): *m/z* = 339.0787, calcd for $C_{19}H_{16}O_4P$ [$MH^+$] 339.0786.

**7-(diphenylphosphoryl)-7a-methoxy-7,7a-dihydrobenzo[d][1,3]dioxol-5(6H)-one (3pa'):** White solid, mp. 207.7–209.4 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.84–7.78 (m, 2H), 7.74–7.69 (m, 2H), 7.54–7.47 (m, 6H), 5.57 (s, 1H), 5.49 (s, 1H), 5.40 (s, 1H), 3.71 (t, $J$ = 6.6 Hz, 1H), 3.40 (s, 3H), 2.91–2.77 (m, 1H), 2.52 (dd, $J_1$ = 18.0 Hz, $J_2$= 10.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 194.7, 168.6, 133.0 (d, $J_{P\text{-}C}$ = 101.4 Hz), 132.1 (d, $J_{P\text{-}C}$ = 1.5 Hz), 131.7 (d, $J_{P\text{-}C}$ = 3.3 Hz), 130.9 (d, $J_{P\text{-}C}$ = 10.0 Hz), 130.8, 130.6 (d, $J_{P\text{-}C}$ = 8.6 Hz), 128.9 (d, $J_{P\text{-}C}$ = 11.6 Hz), 128.5 (d, $J_{P\text{-}C}$ = 11.5 Hz), 102.6, 101.6, 99.5, 50.4, 38.6 (d, $J_{P\text{-}C}$ = 70.3 Hz), 34.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 28.4. HRMS (ESI-TOF): *m/z* = 371.1050, calcd for $C_{20}H_{20}O_5P$ [$MH^+$] 371.1048. The structure of this compound was further confirmed by an X-ray crystallographic analysis.

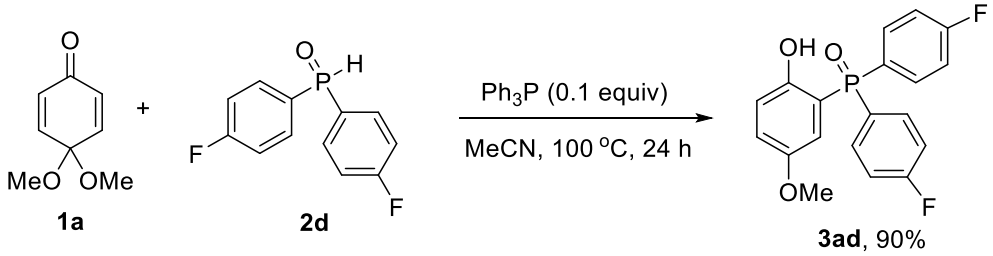



**(2-hydroxy-5-methoxyphenyl)di-p-tolylphosphine oxide (3ab):** the reaction of **1a** (30.8 mg, 0.2 mmol), **2b** (55.2 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24 h afforded **3ab** (yield: 66.9 mg, 95%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 170.5–172.3 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.74 (br, 1H), 7.60–7.55 (m, 4H), 7.30–7.27 (m, 4H), 6.99 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.91 (dd, $J_1$ = 8.8 Hz, $J_2$= 5.2 Hz, 1H), 6.47 (dd, $J_1$ = 14.0 Hz, $J_2$= 3.2 Hz, 1H), 3.64 (s, 3H) , 2.41 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.8 (d, $J_{P\text{-}C}$ = 1.8 Hz), 151.8 (d, $J_{P\text{-}C}$ = 14.3 Hz), 143.2 (d, $J_{P\text{-}C}$ = 3.2 Hz), 132.1 (d, $J_{P\text{-}C}$ = 10.3 Hz), 129.5 (d, $J_{P\text{-}C}$ = 12.7 Hz), 128.4 (d, $J_{P\text{-}C}$ = 107.4 Hz), 120.3 (d, $J_{P\text{-}C}$ = 2.0 Hz), 119.3 (d, $J_{P\text{-}C}$ = 8.5 Hz), 116.2 (d, $J_{P\text{-}C}$ = 10.8 Hz), 111.9 (d, $J_{P\text{-}C}$ = 103.8 Hz), 55.8, 21.7. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.2. HRMS (ESI-TOF): *m/z* = 353.1305, calcd for $C_{21}H_{22}O_3P$ [$MH^+$] 353.1307.

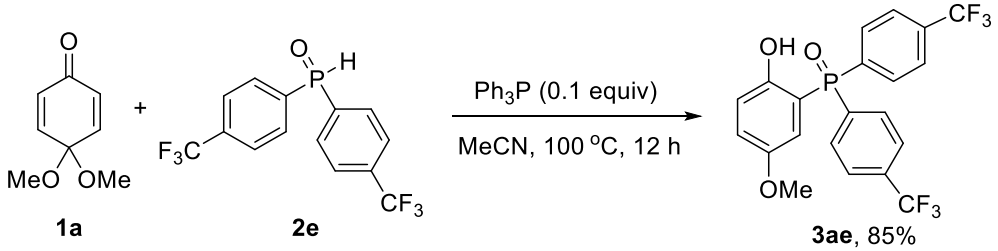



**(2-hydroxy-5-methoxyphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac):** the reaction of **1a** (31.7 mg, 0.21 mmol), **2c** (100.0 mg, 0.38 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12h afforded **3ac** (yield: 73.1 mg, 92%), which was purified by column chromatography (PE/EtOAc = 2/1). White solid, mp. 167.1–168.0 °C. $^1$H NMR ($CDCl_3$, 400

MHz): $\delta$ = 10.77 (br, 1H), 7.64–7.58 (m, 4H), 7.00–6.97 (m, 5H), 6.91 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.6, 1H), 6.46 (dd, $J_1$ = 14.0 Hz, $J_2$= 2.8, 1H), 3.84 (s, 6H) , 3.65 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 162.8 (d, $J_{P\text{-}C}$ = 3.3 Hz), 157.5 (d, $J_{P\text{-}C}$ = 1.6 Hz), 151.7 (d, $J_{P\text{-}C}$ = 15.4 Hz), 133.9 (d, $J_{P\text{-}C}$ = 11.5 Hz), 122.8 (d, $J_{P\text{-}C}$ = 111.3 Hz), 120.1 (d, $J_{P\text{-}C}$ = 2.1 Hz), 119.2 (d, $J_{P\text{-}C}$ = 8.2 Hz), 116.2 (d, $J_{P\text{-}C}$ = 10.8 Hz), 114.2 (d, $J_{P\text{-}C}$ = 13.6 Hz), 112.2 (d, $J_{P\text{-}C}$ = 103.9 Hz), 55.7, 55.3. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.7. HRMS (ESI-TOF): *m/z* = 385.1208, calcd for $C_{21}H_{22}O_5P$ [$MH^+$] 385.1205.

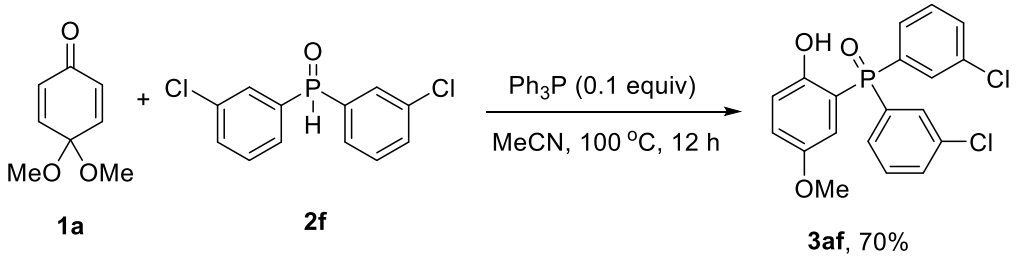



**bis(4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3ad):** the reaction of **1a** (30.7 mg, 0.2 mmol), **2d** (57.2 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24 h afforded **3ad** (yield: 64.8 mg, 90%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 182.7–184.0 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.44 (br, 1H), 7.72–7.66 (m, 4H), 7.21–7.17 (m, 4H), 7.03 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.94 (dd, $J_1$ = 8.8 Hz, $J_2$= 5.6 Hz, 1H), 6.46 (d, $J$ = 14.4 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.4 (dd, $J_{F\text{-}C}$ = 252.9 Hz, $J_{P\text{-}C}$ = 3.1 Hz), 157.4 (d, $J_{P\text{-}C}$ = 2.4 Hz), 152.0 (d, $J_{P\text{-}C}$ = 15.3 Hz), 134.5 (dd, $J_{F\text{-}C}$ = 11.6 Hz, $J_{P\text{-}C}$ = 8.7Hz), 127.2 (dd, $J_{P\text{-}C}$ = 108.2 Hz, $J_{F\text{-}C}$ = 3.5 Hz), 120.7 (d, $J_{P\text{-}C}$ = 2.3 Hz), 119.6 (d, $J_{P\text{-}C}$ = 9.8 Hz), 116.2 (dd, $J_{F\text{-}C}$ = 21.2 Hz, $J_{P\text{-}C}$ = 13.8 Hz), 115.9 (d, $J_{P\text{-}C}$ = 11.3 Hz), 111.0 (d, $J_{P\text{-}C}$ = 105.0 Hz), 55.7. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 37.1; HRMS (ESI-TOF): *m/z* = 361.0807, calcd for $C_{19}H_{16}O_3PF_2$ [$MH^+$] 361.0805.

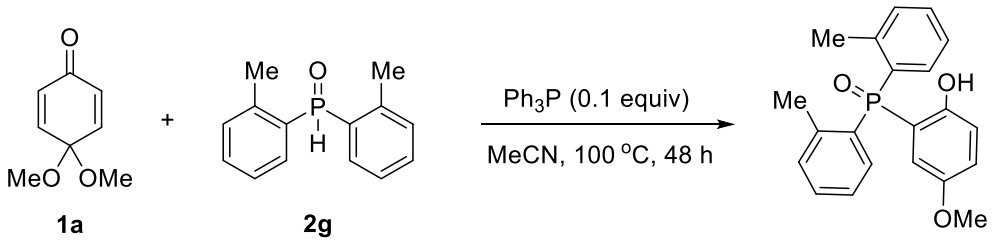



**(2-hydroxy-5-methoxyphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae):** the reaction of **1a** (30.6 mg, 0.2 mmol), **2e** (81.2 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12h afforded **3ae** (yield: 77.6 mg, 85%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 154.8–155.9 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.12 (br, 1H), 7.85–7.74 (m, 8H), 7.06 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.97 (dd, $J_1$ = 9.2 Hz, $J_2$= 6.0 Hz, 1H), 6.57–6.53 (m, 1H), 3.68 (s, 3H). *Due to the F-C and P-C couplings, the $^{13}$C NMR spectrum is not easy to be interpreted. A full list of the signals is given.* $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.02, 157.00, 152.40, 152.25, 135.72, 134.98, 134.96, 134.68, 134.66, 134.63, 134.33, 134.30, 134.00, 133.98, 132.44, 132.33,

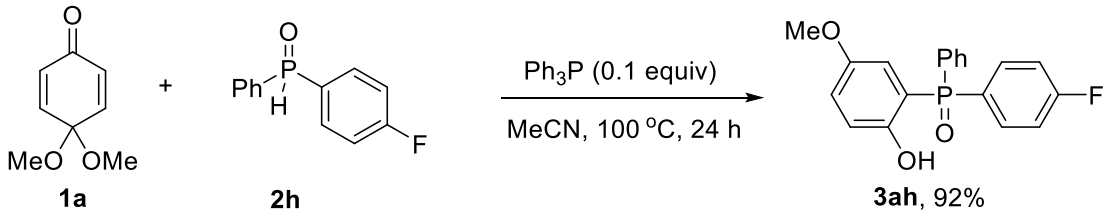
127.34, 125.77, 125.73, 125.70, 125.66, 125.60, 125.57, 125.52, 124.62, 121.91, 121.29, 121.27, 119.74, 119.64, 119.20, 115.91, 115.80, 110.66, 109.60, 55.77. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 35.5; HRMS (ESI-TOF): *m/z* = 461.0746, calcd for $C_{21}H_{16}O_3PF_6$ [$MH^+$] 461.0741.




**bis(3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3af):** the reaction of **1a** (31.3 mg, 0.2 mmol), **2f** (65.1 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 12h afforded **3af** (yield: 55.7 mg, 70%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 191.5–192.7 $^oC$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.29 (br, 1H), 7.67 (d, *J* = 12.8 Hz, 2H), 7.59–7.52 (m, 4H), 7.48–7.43 (m, 2H), 7.05 (dd, $J_1$ = 9.2 Hz, $J_2$= 2.8 Hz, 1H), 6.96 (dd, $J_1$ = 8.8 Hz, $J_2$= 5.2 Hz, 1H), 6.46 (dd, $J_1$ = 14.4 Hz, $J_2$= 2.8 Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.6 (d, $J_{P\text{-}C}$ = 2.0 Hz), 152.1 (d, $J_{P\text{-}C}$ = 15.7 Hz), 135.4 (d, $J_{P\text{-}C}$ = 15.7 Hz), 133.3 (d, $J_{P\text{-}C}$ = 102.5 Hz), 133.0 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.7 (d, $J_{P\text{-}C}$ = 11.6 Hz), 130.3 (d, $J_{P\text{-}C}$ = 12.5 Hz), 129.9 (d, $J_{P\text{-}C}$ = 9.9 Hz), 121.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 119.8 (d, $J_{P\text{-}C}$ = 9.5 Hz), 115.8 (d, $J_{P\text{-}C}$ = 11.3 Hz), 109.9 (d, $J_{P\text{-}C}$ = 104.8 Hz), 55.8. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 36.5; HRMS (ESI-TOF): *m/z* = 393.0215, calcd for $C_{19}H_{16}O_3P\ Cl_2$ [$MH^+$] 393.0214.

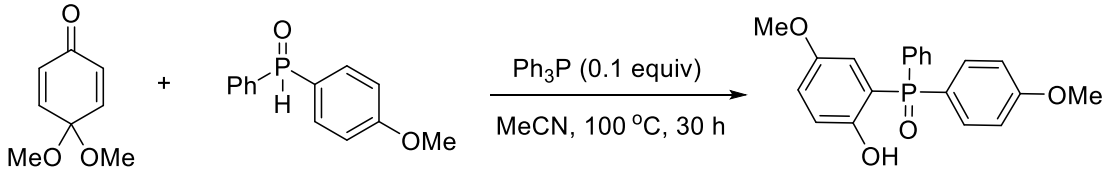



**(2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ag):** the reaction of **1a** (30.8 mg, 0.2 mmol), **2g** (138.1 mg, 0.6 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 48 h afforded **3ag** (yield: 61.3 mg, 87%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 177.7–178.6 $^oC$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.80 (br, 1H), 7.49–7.45 (m, 2H), 7.36–7.33 (m, 2H), 7.21–7.16 (m, 2H), 7.14–7.08 (m, 2H), 7.06–7.03 (m, 1H), 6.99–6.95 (m, 1H), 6.16 (dd, $J_1$ = 17.2 Hz, $J_2$= 2.8 Hz, 1H), 3.60 (s, 3H) , 2.58 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.3 (d, $J_{P\text{-}C}$ = 1.7 Hz), 151.8 (d, $J_{P\text{-}C}$ = 15.6 Hz), 143.4 (d, $J_{P\text{-}C}$ = 8.3 Hz), 132.6 (d, $J_{P\text{-}C}$ = 2.0 Hz), 132.5 (d, $J_{P\text{-}C}$ = 13.3 Hz), 132.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.3 (d, $J_{P\text{-}C}$ = 10.8 Hz), 129.5 (d, $J_{P\text{-}C}$ = 103.8 Hz), 125.6 (d, $J_{P\text{-}C}$ = 13.0 Hz), 120.5 (d, $J_{P\text{-}C}$ = 2.2 Hz), 119.5 (d, $J_{P\text{-}C}$ = 9.3 Hz), 116.2 (d, $J_{P\text{-}C}$ = 10.5 Hz), 111.1 (d, $J_{P\text{-}C}$ = 101.9 Hz), 55.7, 21.6 (d, $J_{P\text{-}C}$ = 5.4 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 46.2; HRMS (ESI-TOF): *m/z* = 353.1310, calcd for $C_{21}H_{22}O_3P$ [$MH^+$] 353.1307.



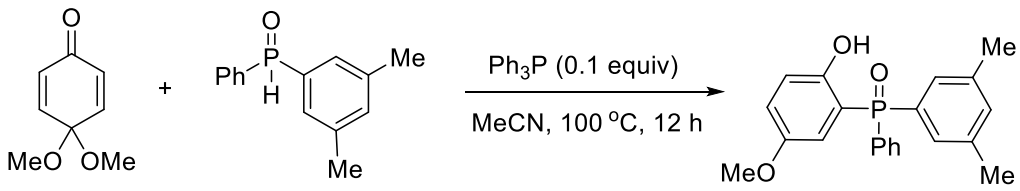

**1a** **2h** **3ah**, 92%

**(4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ah):** the reaction of **1a** (30.8 mg, 0.2 mmol), **2h** (52.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24 h afforded **3ah** (yield: 62.7 mg, 92%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 185.9–186.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.56 (br, 1H), 7.73–7.66 (m, 4H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.53–7.48 (m, 2H), 7.21–7.16 (m , 2H), 7.02 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.94 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.6 Hz, 1H), 6.46 (dd, $J_1$ = 14.4 Hz, $J_2$= 2.8 Hz, 1H),3.58 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.3 (dd, $J_{F\text{-}C}$ = 253.7 Hz, $J_{P\text{-}C}$ = 3.6 Hz), 157.6 (d, $J_{P\text{-}C}$ = 1.8 Hz), 151.9 (d, $J_{P\text{-}C}$ = 15.2 Hz), 134.5 (dd, $J_{F\text{-}C}$ = 12.2 Hz, $J_{P\text{-}C}$ = 9.3 Hz), 132.7 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.9 (d, $J_{P\text{-}C}$ = 11.0 Hz), 132.2 (d, $J_{P\text{-}C}$ = 105.3 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.3 Hz), 127.5 (dd, $J_{P\text{-}C}$ = 107.1 Hz, $J_{F\text{-}C}$ =3.4 Hz), 120.6 (d, $J_{P\text{-}C}$ = 1.9 Hz), 119.5 (d, $J_{P\text{-}C}$ = 8.7 Hz), 116.1 (dd, $J_{F\text{-}C}$ = 21.0 Hz, $J_{P\text{-}C}$ = 13.4 Hz), 116.0 (d, $J_{P\text{-}C}$ = 10.6 Hz), 111.0 (d, $J_{P\text{-}C}$ = 104.4 Hz), 55.7. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.1; HRMS (ESI-TOF): $m/z$ = 343.0901, calcd for $C_{19}H_{17}O_3PF$ [$MH^+$] 343.0899.



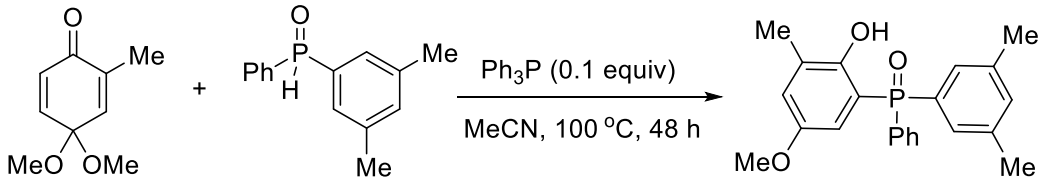

**1a** **2i** **3ai**, 98%

**(2-hydroxy-5-methoxyphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3ai):** the reaction of **1a** (30.9 mg, 0.2 mmol), **2i** (56.1 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 30 h afforded **3ai** (yield: 69.6 mg, 98%), which was purified by column chromatography (PE/EtOAc = 2/1). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.73 (br, 1H), 7.73–7.67 (m, 2H), 7.63–7.56 (m, 3H), 7.51–7.46 (m, 2H), 7.02–6.98 (m, 3H), 6.93 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.6 Hz, 1H), 6.47 (dd, $J_1$ = 14.0 Hz, $J_2$= 2.8 Hz, 1H), 3.85 (s, 3H), 3.65 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.0 (d, $J_{P\text{-}C}$ = 2.6 Hz), 157.7 (d, $J_{P\text{-}C}$ = 3.1 Hz), 151.8 (d, $J_{P\text{-}C}$ = 15.7 Hz), 134.0 (d, $J_{P\text{-}C}$ = 11.9 Hz), 132.4 (d, $J_{P\text{-}C}$ = 2.5 Hz), 132.0 (d, $J_{P\text{-}C}$ = 10.5 Hz), 131.8 (d, $J_{P\text{-}C}$ = 104.7 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.3 Hz), 122.5 (d, $J_{P\text{-}C}$ = 110.5 Hz), 120.3 (d, $J_{P\text{-}C}$ = 3.1 Hz), 119.4 (d, $J_{P\text{-}C}$ = 8.6 Hz), 116.2 (d, $J_{P\text{-}C}$ = 10.5 Hz), 114.3 (d, $J_{P\text{-}C}$ = 13.1 Hz), 111.7 (d, $J_{P\text{-}C}$ = 103.5 Hz), 55.8, 55.4. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 38.9; HRMS (ESI-TOF): $m/z$ = 355.1097, calcd for $C_{20}H_{20}O_4P$ [$MH^+$] 355.1099.



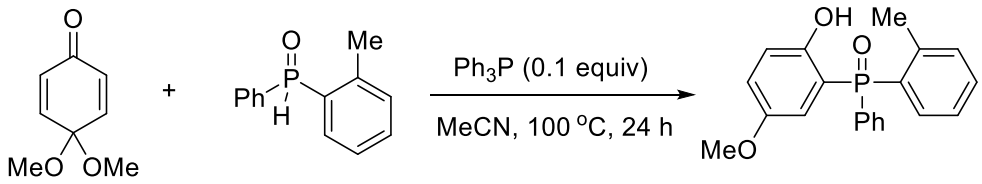

**1a** **2j** **3aj**, 97%

**(3,5-dimethylphenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3aj):** the reaction of **1a** (31.0 mg, 0.2 mmol), **2j** (55.3 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3aj** (yield: 68.6 mg, 97%), which was purified by column chromatography (PE/EtOAc = 4/1). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.72–7.66 (m, 2H), 7.59–7.56 (m, 1H), 7.51–7.46 (m, 2H), 7.29 (d, $J$ = 13.2 Hz, 2H), 7.20 (s, 1H), 7.01 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.93 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.2 Hz, 1H), 6.49 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.66 (s, 3H), 2.32 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.7 (d, $J_{P\text{-}C}$ = 12.5 Hz), 151.7 (d, $J_{P\text{-}C}$ = 15.5 Hz), 138.5 (d, $J_{P\text{-}C}$ = 7.0 Hz), 134.3 (d, $J_{P\text{-}C}$ = 3.2 Hz), 132.4 (d, $J_{P\text{-}C}$ = 3.4 Hz), 131.9 (d, $J_{P\text{-}C}$ = 10.5 Hz), 131.6 (d, $J_{P\text{-}C}$ = 104.5 Hz), 130.9 (d, $J_{P\text{-}C}$ = 104.1 Hz), 129.4 (d, $J_{P\text{-}C}$ = 9.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 12.3 Hz), 120.2 (d, $J_{P\text{-}C}$ = 2.4 Hz), 119.3 (d, $J_{P\text{-}C}$ = 8.4 Hz), 116.3 (d, $J_{P\text{-}C}$ = 11.4 Hz), 110.5 (d, $J_{P\text{-}C}$ = 103.1 Hz), 55.7, 21.3. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.4. HRMS (ESI-TOF): $m/z$ = 353.1304, calcd for $C_{21}H_{22}O_3P$ [$MH^+$] 353.1307. The structure of this compound was further confirmed by an X-ray crystallographic analysis.




**1b** **2j** **3bj**, 93%

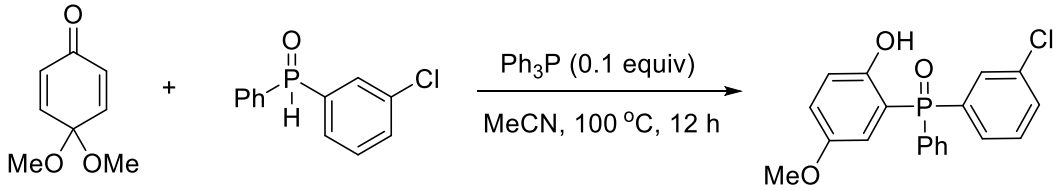
**(3,5-dimethylphenyl)(2-hydroxy-5-methoxy-3-methylphenyl)(phenyl)phosphine oxide (3bj):** the reaction of **1b** (34.0 mg, 0.2 mmol), **2j** (56.0 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 48 h afforded **3bj** (yield: 68.8 mg, 93%), which was purified by column chromatography (PE/EtOAc = 15/1). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.87 (br, 1H), 7.72–7.66 (m, 2H), 7.59–7.55 (m, 1H), 7.50–7.45 (m, 2H), 7.29 (d, $J$ = 12.8 Hz, 2H), 7.19 (s, 1H), 6.89 (d, $J$ = 2.8 Hz, 1H), 6.32 (dd, $J_1$ = 13.6 Hz, $J_2$= 2.8 Hz, 1H), 3.64 (s, 3H), 2.32 (s, 6H), 2.26 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 156.2 (d, $J_{P\text{-}C}$ = 2.9 Hz), 151.2 (d, $J_{P\text{-}C}$ = 15.6 Hz), 138.5 (d, $J_{P\text{-}C}$ = 13.0 Hz), 134.3 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.4 (d, $J_{P\text{-}C}$ = 3.3 Hz), 132.02 (d, $J_{P\text{-}C}$ = 9.9 Hz), 131.97 (d, $J_{P\text{-}C}$ = 103.9 Hz), 131.3 (d, $J_{P\text{-}C}$ = 104.5 Hz), 129.5 (d, $J_{P\text{-}C}$ = 10.4 Hz), 128.9 (d, $J_{P\text{-}C}$ = 8.2 Hz), 128.7 (d, $J_{P\text{-}C}$ = 12.5 Hz), 121.5 (d, $J_{P\text{-}C}$ = 2.3 Hz), 113.5 (d, $J_{P\text{-}C}$ = 12.2 Hz), 110.4 (d, $J_{P\text{-}C}$ = 103.3 Hz), 55.8, 21.4, 16.4 (d, $J_{P\text{-}C}$ = 2.7 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 39.8; HRMS (ESI-TOF): $m/z$ = 367.1465, calcd for $C_{22}H_{24}O_3P$ [$MH^+$] 367.1463.




**1a** **2k** **3ak**, 84%

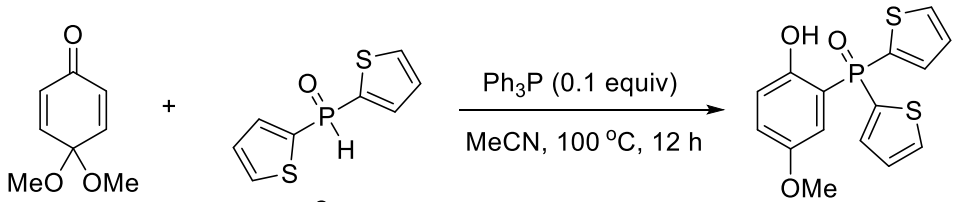
**(2-hydroxy-5-methoxyphenyl)(phenyl)(o-tolyl)phosphine oxide (3ak):** the reaction of **1a** (30.3 mg, 0.2 mmol), **2k** (51.9 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 24h afforded **3ak** (yield: 55.9 mg, 84%), which was purified by column

chromatography (PE/EtOAc = 4/1). White solid, mp. 188.4–190.1 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.68 (br, 1H), 7.74–7.69 (m, 2H), 7.61–7.57 (m, 1H), 7.53–7.44 (m, 3H), 7.32–7.29 (m, 1H), 7.20–7.10 (m, 2H), 7.02 (dd, $J_1$ = 8.8 Hz, $J_2$= 3.2 Hz, 1H), 6.95 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.6 Hz, 1H), 6.35 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.63 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.6 (d, $J_{P\text{-}C}$ = 3.1 Hz), 151.8 (d, $J_{P\text{-}C}$ = 15.1 Hz), 143.3 (d, $J_{P\text{-}C}$ = 7.7 Hz), 133.2 (d, $J_{P\text{-}C}$ = 13.4 Hz), 132.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 132.3 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.1 (d, $J_{P\text{-}C}$ = 11.3 Hz), 131.54 (d, $J_{P\text{-}C}$ = 103.9 Hz), 131.48 (d, $J_{P\text{-}C}$ = 10.6 Hz), 129.4 (d, $J_{P\text{-}C}$ = 105.5 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.3 Hz), 125.4 (d, $J_{P\text{-}C}$ = 13.3 Hz), 120.2 (d, $J_{P\text{-}C}$ = 2.34 Hz), 119.4 (d, $J_{P\text{-}C}$ = 8.4 Hz), 116.0 (d, $J_{P\text{-}C}$ = 11.3 Hz), 111.5 (d, $J_{P\text{-}C}$ = 102.5 Hz), 55.7, 21.2 (d, $J_{P\text{-}C}$ = 5.2 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 41.4; HRMS (ESI-TOF): *m/z* = 339.1157, calcd for $C_{20}H_{20}O_3P$ [$MH^+$] 339.1150.




**1a** **2l** **3al**, 77%

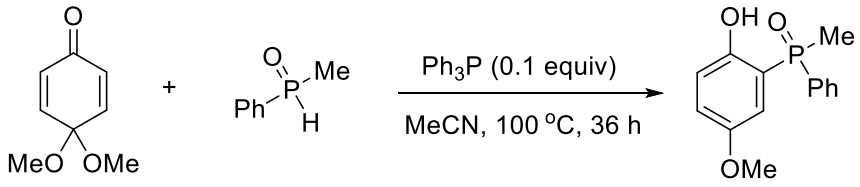
**(3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3al):** the reaction of **1a** (30.9 mg, 0.2 mmol), **2l** (56.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3al** (yield: 55.3 mg, 77%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 171.0–171.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.47 (br, 1H), 7.71–7.66 (m, 3H), 7.63–7.50 (m, 5H), 7.43 (td, $J_1$ = 7.6 Hz, $J_2$= 3.2 Hz, 1H), 7.03 (dd, $J_1$ = 8.8 Hz, $J_2$= 5.4 Hz, 1H), 6.95 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.6 Hz, 1H), 6.47(dd, $J_1$ = 14.0 Hz, $J_2$= 2.8 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.7 (d, $J_{P\text{-}C}$ = 2.0 Hz), 151.9 (d, $J_{P\text{-}C}$ = 15.1 Hz), 135.2 (d, $J_{P\text{-}C}$ = 16.1 Hz), 134.9 (d, $J_{P\text{-}C}$ = 102.2 Hz), 132.8 (d, $J_{P\text{-}C}$ = 2.5 Hz), 132.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.9 (d, $J_{P\text{-}C}$ = 10.6 Hz), 131.7 (d, $J_{P\text{-}C}$ = 10.5 Hz), 130.7 (d, $J_{P\text{-}C}$ = 105.5 Hz), 130.1 (d, $J_{P\text{-}C}$ = 13.9 Hz), 130.0 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.5 Hz), 120.8 (d, $J_{P\text{-}C}$ = 2.2 Hz), 119.6 (d, $J_{P\text{-}C}$ = 10.1 Hz), 115.9 (d, $J_{P\text{-}C}$ = 11.1 Hz), 110.5 (d, $J_{P\text{-}C}$ = 104.5 Hz), 55.8. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 37.8; HRMS (ESI-TOF): *m/z* = 359.0605, calcd for $C_{19}H_{17}O_3PCl$ [$MH^+$] 359.0604.




**1a** **2m** **3am**, 80%

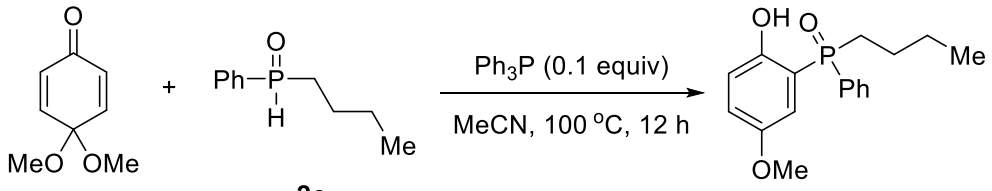
**(2-hydroxy-5-methoxyphenyl)di(thiophen-2-yl)phosphine oxide (3am):** the reaction of **1a** (30.5 mg, 0.2 mmol), **2m** (51.8 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3am** (yield: 53.3 mg, 80%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 190.8–191.7 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.51 (br, 1H), 7.81 (td, $J_1$ = 4.4 Hz, $J_2$= 0.8 Hz, 2H), 7.64–7.61 (m, 2H), 7.25–

7.22 (m, 2H), 7.04 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.94 (dd, $J_1$ = 9.2 Hz, $J_2$= 6.4 Hz, 1H), 6.64 (dd, $J_1$ = 16.2 Hz, $J_2$= 6.2 Hz, 1H), 3.68 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.3 (d, $J_{P\text{-}C}$ = 3.8 Hz), 152.0 (d, $J_{P\text{-}C}$ = 16.4 Hz), 137.6 (d, $J_{P\text{-}C}$ = 12.1 Hz), 135.0 (d, $J_{P\text{-}C}$ = 6.0 Hz), 133.2 (d, $J_{P\text{-}C}$ = 121.5 Hz), 128.5 (d, $J_{P\text{-}C}$ = 14.6 Hz), 121.6 (d, $J_{P\text{-}C}$ = 2.2 Hz), 119.6 (d, $J_{P\text{-}C}$ = 10.3 Hz), 115.3 (d, $J_{P\text{-}C}$ = 11.9 Hz), 111.9 (d, $J_{P\text{-}C}$ = 115.2 Hz), 55.9. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 23.2; HRMS (ESI-TOF): *m/z* = 337.0125, calcd for $C_{15}H_{14}O_3PS_2$ [$MH^+$] 337.0122.




**1a** **2n** **3an**, 91%

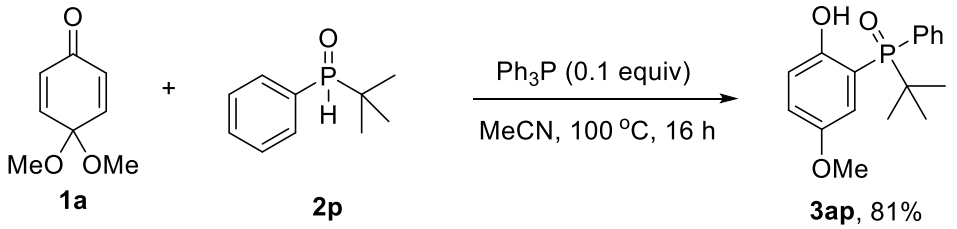
**(2-hydroxy-5-methoxyphenyl)(methyl)(phenyl)phosphine oxide (3an):** the reaction of **1a** (31.0 mg, 0.2 mmol), **2n** (33.6 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 36h afforded **3an** (yield: 48.0 mg, 91%), which was purified by column chromatography (PE/EtOAc = 2/1). White solid, mp. 188.1–188.9 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.63 (br, 1H), 7.80–7.74 (m, 2H), 7.59–7.48 (m, 3H), 7.00 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.90 (dd, $J_1$ = 8.8 Hz, $J_2$= 5.2 Hz, 1H), 6.54 (dd, $J_1$ = 14.4 Hz, $J_2$= 3.2 Hz, 1H), 3.71 (s, 3H), 2.10 (d, $J$ = 13.6 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.1 (d, $J_{P\text{-}C}$ = 2.3 Hz), 152.2 (d, $J_{P\text{-}C}$ = 15.6 Hz), 133.4 (d, $J_{P\text{-}C}$ = 101.1 Hz), 132.4 (d, $J_{P\text{-}C}$ = 2.5 Hz), 130.2 (d, $J_{P\text{-}C}$ = 10.1 Hz), 128.9 (d, $J_{P\text{-}C}$ = 11.5 Hz), 120.4 (d, $J_{P\text{-}C}$ = 2.4 Hz), 119.3 (d, $J_{P\text{-}C}$ = 8.5 Hz), 114.6 (d, $J_{P\text{-}C}$ = 11.8 Hz), 112.8 (d, $J_{P\text{-}C}$ = 100.9 Hz), 55.9, 16.9 (d, $J_{P\text{-}C}$ = 72.5 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 41.9; HRMS (ESI-TOF): *m/z* = 263.0838, calcd for $C_{14}H_{16}O_3P$ [$MH^+$] 263.0837.



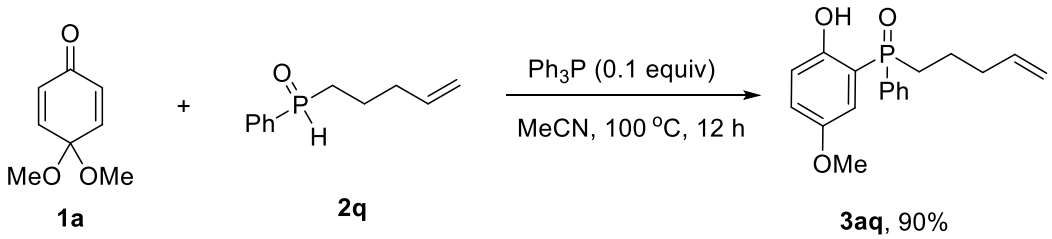

**1a** **2o** **3ao**, 92%

**butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ao):** the reaction of **1a** (31.2 mg, 0.2 mmol), **2o** (54.7 mg, 0.3 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12h afforded **3ao** (yield: 56.7 mg, 92%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 129.3–131.0 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.74 (br, 1H), 7.81–7.76 (m, 2H), 7.56–7.46 (m, 3H), 6.97 (dd, $J_1$ = 9.2 Hz, $J_2$= 2.8 Hz, 1H), 6.88 (dd, $J_1$ = 8.8 Hz, $J_2$= 4.8 Hz, 1H), 6.34 (dd, $J_1$ = 13.6 Hz, $J_2$= 2.8 Hz, 1H), 3.71 (s, 3H), 2.34–2.27 (m, 2H), 1.76–1.55 (m, 2H), 1.47–1.41 (m, 2H), 0.90 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.2 (d, $J_{P\text{-}C}$ = 2.4 Hz), 152.2 (d, $J_{P\text{-}C}$ = 14.8 Hz), 132.6 (d, $J_{P\text{-}C}$ = 97.7 Hz), 132.2 (d, $J_{P\text{-}C}$ = 1.9 Hz), 130.4 (d, $J_{P\text{-}C}$ = 10.0 Hz), 128.9 (d, $J_{P\text{-}C}$ = 11.7 Hz), 120.1 (d, $J_{P\text{-}C}$ = 2.2 Hz), 119.1 (d, $J_{P\text{-}C}$ = 8.6 Hz), 114.7 (d, $J_{P\text{-}C}$ = 11.0 Hz), 112.1 (d, $J_{P\text{-}C}$ = 97.1 Hz), 55.9, 29.5 (d, $J_{P\text{-}C}$ = 71.7 Hz), 23.9 (d, $J_{P\text{-}C}$ = 15.7 Hz), 23.1 (d, $J_{P\text{-}C}$ = 4.6 Hz),

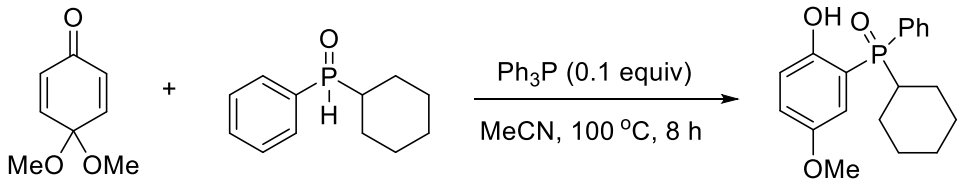
13.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 44.2; HRMS (ESI-TOF): *m/z* = 305.1312, calcd for $C_{17}H_{22}O_3P$ [$MH^+$] 305.1307.




**tert-butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ap):** the reaction of **1a** (15.4 mg, 0.1 mmol), **2p** (54.6 mg, 0.3 mmol) and $Ph_3P$ (2.6 mg, 0.01 mmol) in MeCN (1 mL) at 100 °C for 16 h afforded **3ap** (yield: 25.0 mg, 81%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 174.5–175.8 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.39 (br, 1H), 7.97–7.92 (m, 2H), 7.55–7.49 (m, 3H), 7.00–6.97 (m, 1H), 6.92–6.85 (m, 2H), 3.74 (s, 3H), 1.29 (d, *J* = 1.6 Hz, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.7, 151.5 (d, $J_{P\text{-}C}$ = 14.0 Hz), 132.1 (d, $J_{P\text{-}C}$ = 2.0 Hz), 131.8 (d, $J_{P\text{-}C}$ = 9.0 Hz), 130.4 (d, $J_{P\text{-}C}$ = 90.0 Hz), 128.7 (d, $J_{P\text{-}C}$ = 11.0 Hz), 119.9 (d, $J_{P\text{-}C}$ = 1.0 Hz), 119.5 (d, $J_{P\text{-}C}$ = 8.0 Hz), 116.1 (d, $J_{P\text{-}C}$ = 10.0 Hz), 110.0 (d, $J_{P\text{-}C}$ = 89.0 Hz), 56.0, 35.3 (d, $J_{P\text{-}C}$ = 69.0 Hz), 24.8. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 50.9; HRMS (ESI-TOF): *m/z* = 305.1309, calcd for $C_{17}H_{22}O_3P$ [$MH^+$] 305.1307.

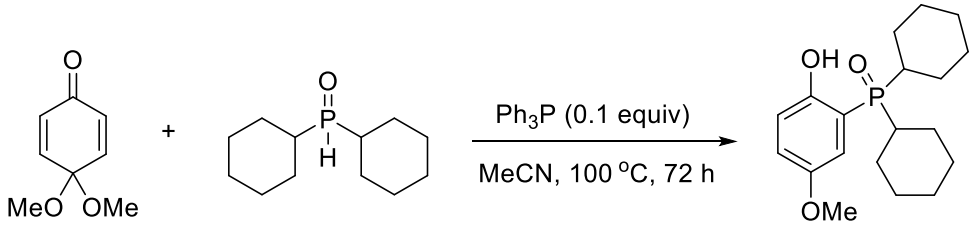



**(2-hydroxy-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (3aq):** the reaction of **1a** (31.3 mg, 0.2 mmol), **2q** (47.3 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3aq** (yield: 58.0 mg, 90%), which was purified by column chromatography (PE/EtOAc = 3/1). White solid, mp. 129.7–132.1 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.76 (br, 1H), 7.81–7.75 (m, 2H), 7.58–7.48 (m, 3H), 6.98 (dd, $J_1$ = 9.2 Hz, $J_2$= 2.8 Hz, 1H), 6.88 (dd, $J_1$ = 9.2 Hz, $J_2$= 5.2 Hz, 1H), 6.56 (dd, $J_1$ = 13.6 Hz, $J_2$= 3.2 Hz, 1H), 5.78–5.68 (m, 2H), 5.04–5.00 (m, 1H), 3.71 (s, 3H), 2.33–2.16 (m, 4H), 1.89–1.71 (m, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.6, 152.2 (d, $J_{P\text{-}C}$ = 14.3 Hz), 137.1, 132.5 (d, $J_{P\text{-}C}$ = 98.2 Hz), 132.3 (d, $J_{P\text{-}C}$ = 2.4 Hz), 130.4 (d, $J_{P\text{-}C}$ = 9.3 Hz), 128.9 (d, $J_{P\text{-}C}$ = 11.5 Hz), 120.1 (d, $J_{P\text{-}C}$ = 2.1 Hz), 119.3 (d, $J_{P\text{-}C}$ = 8.9 Hz), 116.2, 114.6 (d, $J_{P\text{-}C}$ = 10.4 Hz), 111.7 (d, $J_{P\text{-}C}$ = 96.9 Hz), 55.9, 34.4 (d, $J_{P\text{-}C}$ = 16.0 Hz), 29.1 (d, $J_{P\text{-}C}$ = 71.5 Hz), 20.3 (d, $J_{P\text{-}C}$ = 3.4 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 44.6; HRMS (ESI-TOF): *m/z* = 317.1311, calcd for $C_{18}H_{22}O_3P$ [$MH^+$] 317.1307.



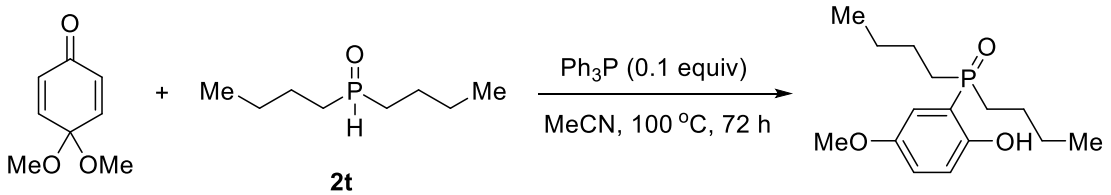

**1a** **2r** **3ar**, 96%

**cyclohexyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ar):** the reaction of **1a** (30.8 mg, 0.2 mmol), **2r** (124.8 mg, 0.6 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 8 h afforded **3ar** (yield: 63.4 mg, 96%), which was purified by column chromatography (PE/EtOAc = 3/1). White solid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.92 (br, 1H), 7.85–7.80 (m, 2H), 7.55–7.49 (m, 3H), 6.96 (dd, $J_1$ = 9.2 Hz, $J_2$= 2.8 Hz, 1H), 6.86 (dd, $J_1$ = 9.2 Hz, $J_2$= 4.8 Hz, 1H), 6.63 (dd, $J_1$ = 12.8 Hz, $J_2$= 3.2 Hz, 1H), 3.73 (s, 3H), 2.28–2.20 (m, 1H), 1.84–1.51 (m, 6H), 1.33–1.26 (m, 4H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.1 (d, $J_{P\text{-}C}$ = 2.2 Hz), 152.0 (d, $J_{P\text{-}C}$ = 14.6 Hz), 132.1 (d, $J_{P\text{-}C}$ = 1.8 Hz), 130.9 (d, $J_{P\text{-}C}$ = 94.8 Hz), 130.7 (d, $J_{P\text{-}C}$ = 8.9 Hz), 128.9 (d, $J_{P\text{-}C}$ = 10.4 Hz), 119.5 (d, $J_{P\text{-}C}$ = 2.1 Hz), 119.2 (d, $J_{P\text{-}C}$ = 8.3 Hz), 114.7 (d, $J_{P\text{-}C}$ =10.7 Hz), 111.1 (d, $J_{P\text{-}C}$ = 92.9 Hz), 55.9, 37.4 (d, $J_{P\text{-}C}$ = 72.6 Hz), 26.2 (d, $J_{P\text{-}C}$ = 8.0 Hz), 26.1 (d, $J_{P\text{-}C}$ = 8.0 Hz), 25.7 (d, $J_{P\text{-}C}$ = 1.6 Hz), 24.4 (d, $J_{P\text{-}C}$ = 2.1 Hz), 23.8 (d, $J_{P\text{-}C}$ = 2.6 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 46.7; HRMS (ESI-TOF): *m/z* = 331.1467, calcd for $C_{19}H_{24}O_3P$ [$MH^+$] 331.1463.

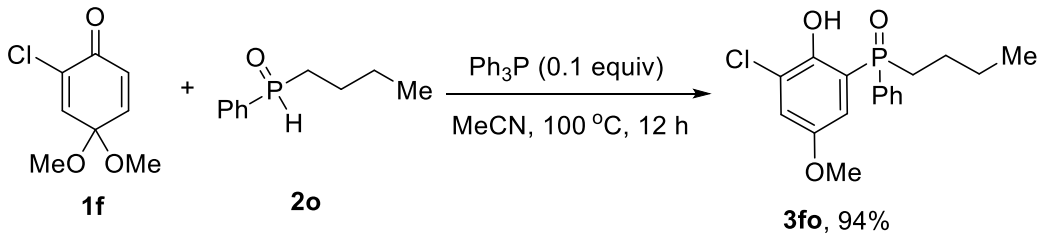



**1a** **2s** **3as**, 92%

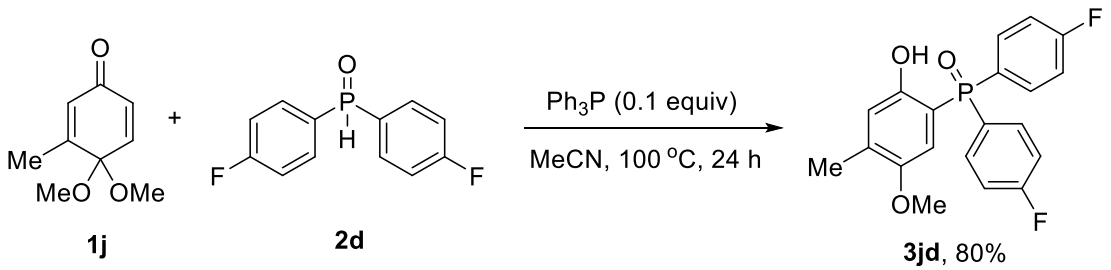
**dicyclohexyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3as):** the reaction of **1a** (31.3 mg, 0.2 mmol), **2s** (128.6 mg, 0.6 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 72h afforded **3as** (yield: 62.9 mg, 92%), which was purified by column chromatography (PE/EtOAc = 3/1). White solid, mp. 204.8–205.5 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.08 (br, 1H), 6.99 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.4 Hz, 1H), 6.86 (dd, $J_1$ = 9.2 Hz, $J_2$= 4.8 Hz, 1H), 6.50 (dd, $J_1$ = 11.6 Hz, $J_2$= 3.2 Hz, 1H), 3.78 (s, 3H), 2.05–1.97 (m, 4H), 1.87–1.69 (m, 8H), 1.44–1.17 (m, 10H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 159.2, 151.6 (d, $J_{P\text{-}C}$ = 13.2 Hz), 119.2 (d, $J_{P\text{-}C}$ = 2.1 Hz), 119.0 (d, $J_{P\text{-}C}$ = 7.5 Hz), 108.6 (d, $J_{P\text{-}C}$ = 84.3 Hz), 55.9, 35.7 (d, $J_{P\text{-}C}$ = 65.7 Hz), 26.4, 26.2 (d, $J_{P\text{-}C}$ = 1.8 Hz), 25.7, 25.2 (d, $J_{P\text{-}C}$ = 2.4 Hz), 24.1 (d, $J_{P\text{-}C}$ = 2.5 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 60.2; HRMS (ESI-TOF): *m/z* = 337.1937, calcd for $C_{19}H_{30}O_3P$ [$MH^+$] 337.1933.




**dibutyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3at):** the reaction of **1a** (30.9 mg, 0.2 mmol), **2t** (97.4 mg, 0.6 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 72 h afforded **3at** (yield: 53.0 mg, 93%), which was purified by column chromatography (PE/EtOAc = 3/1). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.69 (br, 1H), 6.99 (dd, $J_1$ = 8.8 Hz, $J_2$= 2.8 Hz, 1H), 6.88 (dd, $J_1$ = 8.8 Hz, $J_2$= 4.8 Hz, 1H), 6.57 (dd, $J_1$ = 13.2 Hz, $J_2$= 3.2 Hz, 1H), 3.77 (s, 3H), 2.03–1.85 (m, 4H), 1.74–1.61 (m, 4H), 1.42–1.37 (m, 4H), 0.89 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.4, 152.1 (d, $J_{P\text{-}C}$ = 15.1 Hz), 119.9 (d, $J_{P\text{-}C}$ = 1.8 Hz), 118.8 (d, $J_{P\text{-}C}$ = 8.4 Hz), 113.8 (d, $J_{P\text{-}C}$ = 11.3 Hz), 111.4 (d, $J_{P\text{-}C}$ = 92.0 Hz), 55.8, 29.9 (d, $J_{P\text{-}C}$ = 67.7 Hz), 23.8 (d, $J_{P\text{-}C}$ = 14.8 Hz), 23.1 (d, $J_{P\text{-}C}$ = 4.4 Hz), 13.5. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 55.2. HRMS (ESI-TOF): $m/z$ = 285.1625, calcd for $C_{15}H_{26}O_3P$ [$MH^+$] 285.1620.

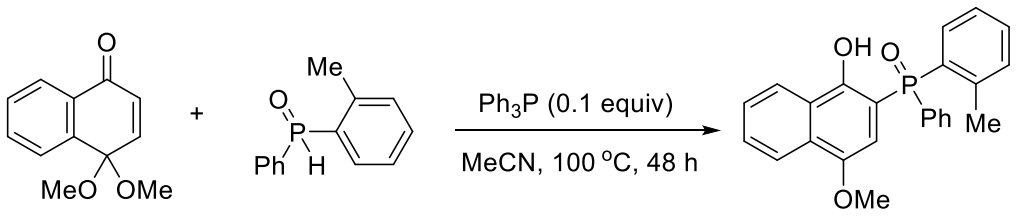



**butyl(3-chloro-2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3fo):** the reaction of **1f** (38.0 mg, 0.2 mmol), **2o** (56.0 mg, 0.3 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 °C for 12 h afforded **3fo** (yield: 64.4 mg, 94%), which was purified by column chromatography (PE/EtOAc = 10/1). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.23 (br, 1H), 7.81–7.76 (m, 2H), 7.59–7.49 (m, 3H), 7.08 (d, $J$ = 2.0 Hz, 1H), 6.56 (dd, $J_1$ = 13.2 Hz, $J_2$ = 2.0 Hz, 1H), 3.72 (s, 3H), 2.35–2.29 (m, 2H), 1.77–1.55 (m, 2H) , 1.50–1.41 (m, 2H) , 0.91 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 152.8 (d, $J_{P\text{-}C}$ = 3.4 Hz), 151.9 (d, $J_{P\text{-}C}$ = 15.4 Hz), 132.6 (d, $J_{P\text{-}C}$ = 3.5 Hz), 132.0 (d, $J_{P\text{-}C}$ = 97.9 Hz), 130.4 (d, $J_{P\text{-}C}$ = 9.7 Hz), 129.0 (d, $J_{P\text{-}C}$ = 11.9 Hz), 123.1 (d, $J_{P\text{-}C}$ = 12.4 Hz), 119.9 (d, $J_{P\text{-}C}$ = 2.5 Hz), 114.1 (d, $J_{P\text{-}C}$ = 10.7 Hz), 113.8 (d, $J_{P\text{-}C}$ = 94.3 Hz), 56.1, 29.4 (d, $J_{P\text{-}C}$ = 70.7 Hz), 23.9 (d, $J_{P\text{-}C}$ = 15.5 Hz), 13.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 45.1; HRMS (ESI-TOF): $m/z$ = 339.0915, calcd for $C_{17}H_{21}O_3PCl$ [$MH^+$] 339.0917.




**bis(4-fluorophenyl)(2-hydroxy-5-methoxy-4-methylphenyl)phosphine oxide (3jd):** the

reaction of **1j** (34.0 mg, 0.2 mmol), **2d** (58.0 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 24h afforded **3jd** (yield: 60.5 mg, 80%), which was purified by column chromatography (PE/EtOAc = 4/1). White solid, mp. 196.3–196.7 $^oC$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 10.43 (br, 1H), 7.73–7.66(m, 4H), 7.22–7.17 (m, 4H), 6.81 (d, $J$ = 5.6 Hz, 1H), 6.24 (d, $J$ = 13.6 Hz, 1H), 3.58 (s, 3H), 2.21 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.4 (dd, $J_{F\text{-}C}$ = 253.7 Hz, $J_{P\text{-}C}$ = 3.3 Hz), 157.8 (d, $J_{P\text{-}C}$ = 2.8 Hz), 150.8 (d, $J_{P\text{-}C}$ = 15.1 Hz), 135.5 (d, $J_{P\text{-}C}$ = 2.5 Hz), 134.5 (dd, $J_{F\text{-}C}$ = 12.2 Hz, $J_{P\text{-}C}$ = 9.1 Hz), 127.8 (dd, $J_{F\text{-}C}$ = 107.7 Hz, $J_{P\text{-}C}$ = 3.6 Hz), 121.1 (d, $J_{P\text{-}C}$ = 9.5 Hz), 134.5 (dd, $J_{F\text{-}C}$ = 21.1 Hz, $J_{P\text{-}C}$ = 13.9 Hz), 111.0 (d, $J_{P\text{-}C}$ = 11.6 Hz), 106.4 (d, $J_{P\text{-}C}$ = 108.3 Hz), 55.8, 16.6. $^{31}P$ NMR ($CDCl_3$, 160 MHz): $\delta$ = 37.4; HRMS (ESI-TOF): $m/z$ = 375.0967, calcd for $C_{20}H_{18}O_3PF_2$ [$MH^+$] 375.0962.




**1n** **2k** **3nk**, 56%

**(1-hydroxy-4-methoxynaphthalen-2-yl)(phenyl)(o-tolyl)phosphine oxide (3nk):** the reaction of **1n** (41.0 mg, 0.2 mmol), **2k** (52.1 mg, 0.24 mmol) and $Ph_3P$ (5.2 mg, 0.02 mmol) in MeCN (2 mL) at 100 $^oC$ for 48h afforded **3nk** (yield: 43.5 mg, 56%), which was purified by column chromatography (PE/EtOAc = 4/1). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 11.81 (br, 1H), 8.38 (d, $J$ = 9.2 Hz, 1H), 8.19 (d, $J$ = 9.2 Hz, 1H), 7.80–7.75 (m, 2H), 7.64–7.56 (m, 3H), 7.53–7.45 (m, 3H), 7.35–7.30 (m, 1H), 7.24–7.16 (m, 2H), 6.07 (d, $J$ = 12.4 Hz, 1H), 3.69 (s, 3H) , 2.50 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 156.6 (d, $J_{P\text{-}C}$ = 2.2 Hz), 147.7 (d, $J_{P\text{-}C}$ = 15.3 Hz), 143.4 (d, $J_{P\text{-}C}$ = 4.6 Hz), 133.4 (d, $J_{P\text{-}C}$ = 13.7 Hz), 132.7 (d, $J_{P\text{-}C}$ = 2.7 Hz), 132.4 (d, $J_{P\text{-}C}$ = 104.1 Hz), 132.2 (d, $J_{P\text{-}C}$ = 2.9 Hz), 132.1 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.4 (d, $J_{P\text{-}C}$ = 10.5 Hz), 129.7 (d, $J_{P\text{-}C}$ = 103.9 Hz), 128.82, 128.79 (d, $J_{P\text{-}C}$ = 12.3 Hz), 128.4, 126.6 (d, $J_{P\text{-}C}$ = 9.9 Hz), 126.5, 125.4 (d, $J_{P\text{-}C}$ = 13.1 Hz), 123.2 (d, $J_{P\text{-}C}$ = 1.5 Hz), 121.7, 102.8 (d, $J_{P\text{-}C}$ = 12.6 Hz), 101.0 (d, $J_{P\text{-}C}$ = 106.3 Hz), 55.6, 21.4 (d, $J_{P\text{-}C}$ = 5.2 Hz). $^{31}P$ NMR ($CDCl_3$, 160 MHz): $\delta$ = 42.8; HRMS (ESI-TOF): $m/z$ = 389.1310, calcd for $C_{24}H_{22}O_3P$ [$MH^+$] 389.1307.

## 4. Crystal structure determination

The well-shaped single crystals were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo $K_\alpha$ ($\lambda$ = 0.71073 Å) radiation. The structure was solved by direct methods and refined on $F^2$ by full-matrix least squares procedures using SHELXTL software. All non-hydrogen atoms were refined anisotropically. All H atoms were located from a difference map and refined isotropically. ORTEP representation (30% probability level) of the molecular structures and CCDC numbers for compounds **3ja**, **3ma**, **3ma'**, **3pa'** and **3aj** are presented in Table S1. Crystallographic data for **3ja**, **3ma**, **3ma'**, **3pa'** and **3aj** are listed in Table S2. These data can be obtained free of charge from the Cambridge Crystallographic Date Center via www.ccdc.cam.ac.uk.

**Table S1** Molecular structures of **3ja**, **3ma**, **3ma'**, **3pa'** and **3aj**

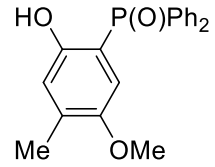
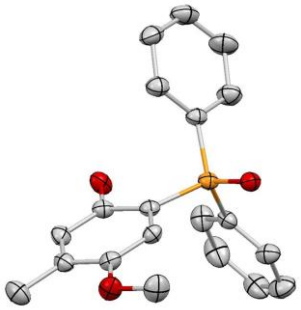
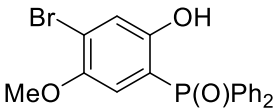
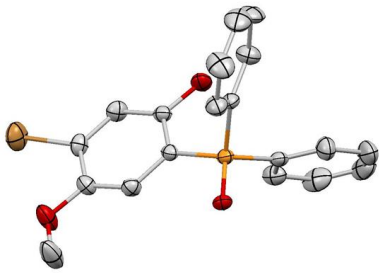
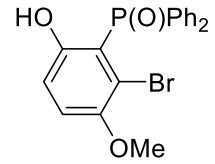
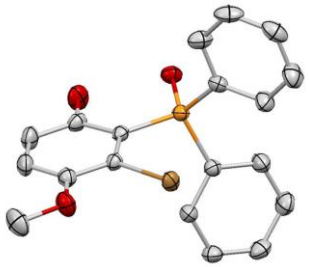
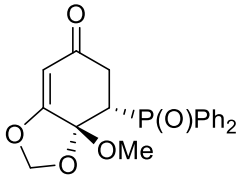
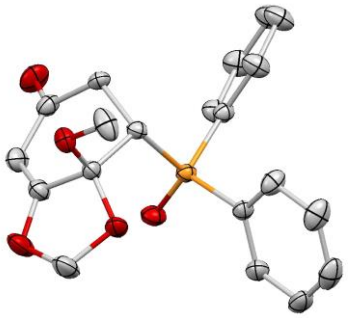
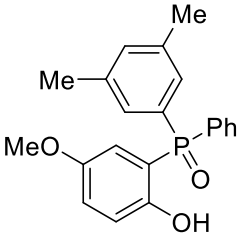
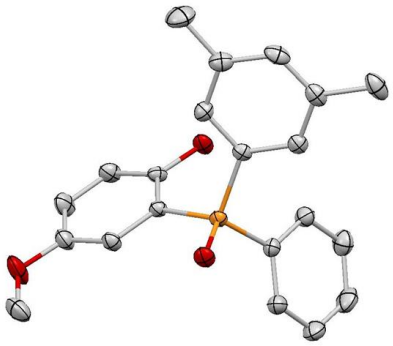
| Compound | X-Ray structure | CCDC Number |
|---|---|---|
|  **3ja** |  | 1840621 |
|  **3ma** |  | 1840623 |
|  **3ma'** |  | 1840620 |
|  **3pa'** (racemic) |  | 1854975 |
|  **3aj** |  | 1840622 |

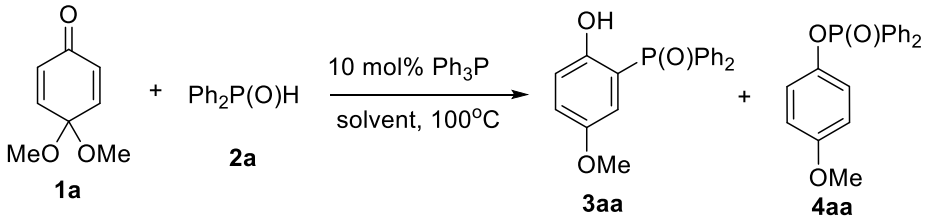
**Table S2** Crystal data and structure refinements for the products

| Compound | **3ja** | **3ma** | **3ma'** | **3pa'** | **3aj** |
|---|---|---|---|---|---|
| Empirical formula | $C_{20}H_{19}O_3P$ | $C_{19}H_{16}Br\ O_3P$ | $C_{19}H_{16}Br\ O_3P$ | $C_{20}H_{19}O_5P$ | $C_{17}H_{17}NO$ |
| Formula weight | 338.32 | 403.20 | 403.20 | 370.32 | 251.31 |
| Crystal system | monoclinic | orthorhombic | monoclinic | orthorhombic | orthorhombic |
| Space group | *C2/c* | *Pbca* | $P2_1/c$ | $Pna2_1$ | *Aba2* |
| *a* / Å | 18.086(10) | 11.472(9) | 14.870(3) | 12.4510(7) | 32.26(3) |
| *b* / Å | 11.245(6) | 17.116(13) | 8.1150(18) | 8.5872(10) | 16.224(15) |
| *c* / Å | 17.491(10) | 18.240(14) | 15.295(4) | 7.9138(5) | 7.120(7) |
| $\beta$ / (°) | 98.109(7) | 90 | 106.026(3) | 90 | 90 |
| *V* / Å$^3$ | 3522(3) | 3582(5) | 1773.8(7) | 1831.48(18) | 3726(6) |
| *Z* | 8 | 8 | 4 | 4 | 4 |
| $D_c$ / (g.cm$^{-3}$) | 1.276 | 1.495 | 1.510 | 1.343 | 1.256 |
| $\mu$ / mm$^{-1}$ | 0.170 | 2.398 | 2.421 | 0.178 | 0.164 |
| *F*(000) | 1424.0 | 1632.0 | 816.0 | 776.0 | 1488.0 |
| Crystal size / mm$^3$ | 0.13×0.12×0.10 | 0.20×0.18×0.15 | 0.13×0.12×0.10 | 0.49×0.46×0.40 | 0.20×0.18×0.15 |
| $\theta$ range / (°) | 2.14~25.004 | 2.233~25.004 | 1.425~25.001 | 3.241~25.341 | 1.262~25.242 |
| Reflections collected | 12250 | 23501 | 12190 | 25295 | 13479 |
| Independent reflections | 3108 ($R_{int}$ = 0.0498 ) | 3164 ($R_{int}$ = 0.1182) | 3127 ($R_{int}$ = 0.0292) | 3352 ($R_{int}$ = 0.0435) | 3537 ($R_{int}$ = 0.0260) |
| Reflections observed ($I$>2σ($I$)) | 2121 | 1934 | 2561 | 3013 | 3302 |
| Data/restraints/parameters | 3108/0/217 | 3164/0/217 | 3127/0/217 | 3352/1/236 | 3537/1/226 |
| Goodness-of-fit on $F^2$ | 1.053 | 1.064 | 1.033 | 1.041 | 1.049 |
| $R_1/wR_2$ ($I$>2σ($I$)) | 0.0478/ 0.1161 | 0.0705/0.1681 | 0.0291/0.0756 | 0.0362/0.0867 | 0.0325/0.0835 |
| $R_1/wR_2$ (all data) | 0.0805/ 0.1287 | 0.1216/0.1873 | 0.0396/0.0791 | 0.0429/0.0919 | 0.0355/0.0851 |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·Å$^{-3}$) | 0.235, -0.265 | 0.850, -0.807 | 0.228, -0.309 | 0.189, -0.215 | 0.217, -0.199 |

## 5. Additional Results

### 5.1 The solvent effect

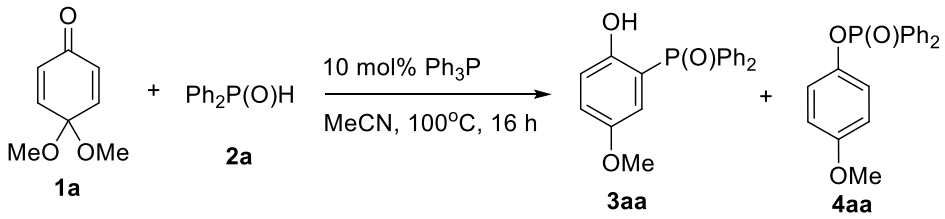
**Table S3.** The solvent effect on the reaction of **1a** and **2a**[a]




| entry | solvent | yield (%)[b]/selectivity (**3aa**/**4aa**)[c] | prod. precip.[d] |
|---|---|---|---|
| 1 | MeCN | 97 (>100/1) | yes[e] |
| 2 | Toluene | 92 (>100/1) | yes[e] |
| 3 | dioxane | 95 (>100/1) | no |
| 4 | DCE | 92 (>100/1) | no |
| 5 | DMF | 69 (25/1)[f] | no |
| 6 | DMSO | 86 (88/1) | no |
| 7 | EtOH | 85 (>100/1) | no |
| 8 | $^{i}$PrOH | 84 (>100/1) | no |

[a]Conditions: to a 10 mL screw-capped Schlenk tube, a mixture of **1a** (0.2 mmol), **2a** (0.24 mmol) and additives (0.1 mmol) in 2 mL solvent was charged and heated at 100 °C for 16 h under $N_2$. [b]Combined yields. [c]Deduced from $^{31}$P NMR spectra of the crude products. [d]prod. precip.: the product precipitated at room temperature (ca. 20-25 °C) or not. [e]Solubility of **3aa** in MeCN at 22 °C: ca. 3.4 g/L; in toluene: ca. 10.6 g/L. [f]other unidentified byproducts were observed.

**Table S4.** The temperature effect on the reaction of **1a** and **2a**[a]




| entry | temperature (°C) | yield (%)[b]/selectivity (**3aa**/**4aa**)[c] |
|---|---|---|
| 1 | 100 | 97 (>100/1) |
| 2 | 80 | 76 (>100/1) |
| 3 | 60 | 61 (> 100/1) |

[a]Conditions: to a 10 mL screw-capped Schlenk tube, a mixture of **1a** (0.2 mmol), **2a** (0.24 mmol) and $Ph_3P$ (0.1 mmol) in 2 mL MeCN was charged and heated to the specific temperature for 16 h under $N_2$. [b]Combined yields. [c]Deduced from $^{31}$P NMR spectra of the crude products.

**5.2 Time course of the control reactions**

The control reactions of **1a** and **2a** in the presence of 10 mol% TPP, 10 mol% TPP and 10 mol% $PhCO_2H$, and 10 mol% TPP with addition of 20 mol% **3na** (90 min) were performed. As shown in Figure S1, the reaction in the presence of 10 mol% (TPP and $PhCO_2H$) proceeded faster initially and become slow with the consumption of the starting materials. The addition of **3na** (90 min later) could significantly accelerate the reaction of **1a** and **2a** with 10 mol% TPP. An induction time (ca. 210 min) for the reaction of **1a** and **2a** with 10 mol% TPP was observed.

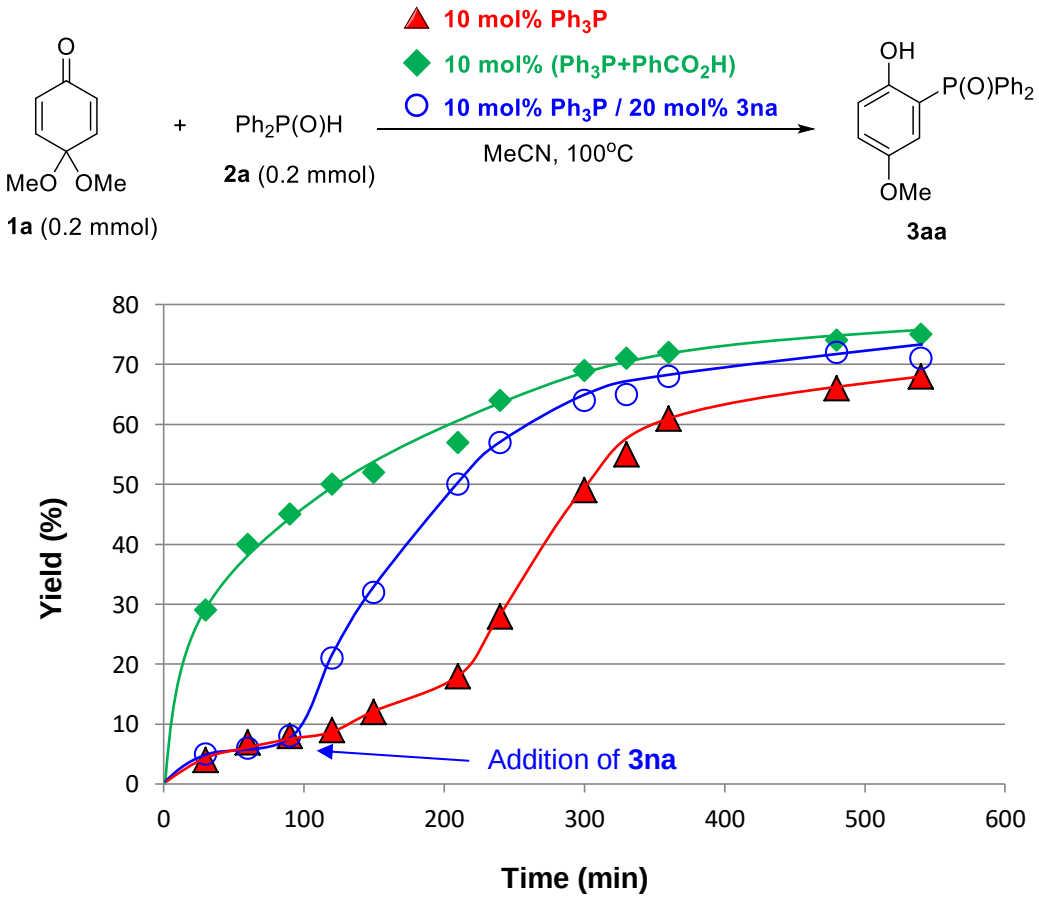
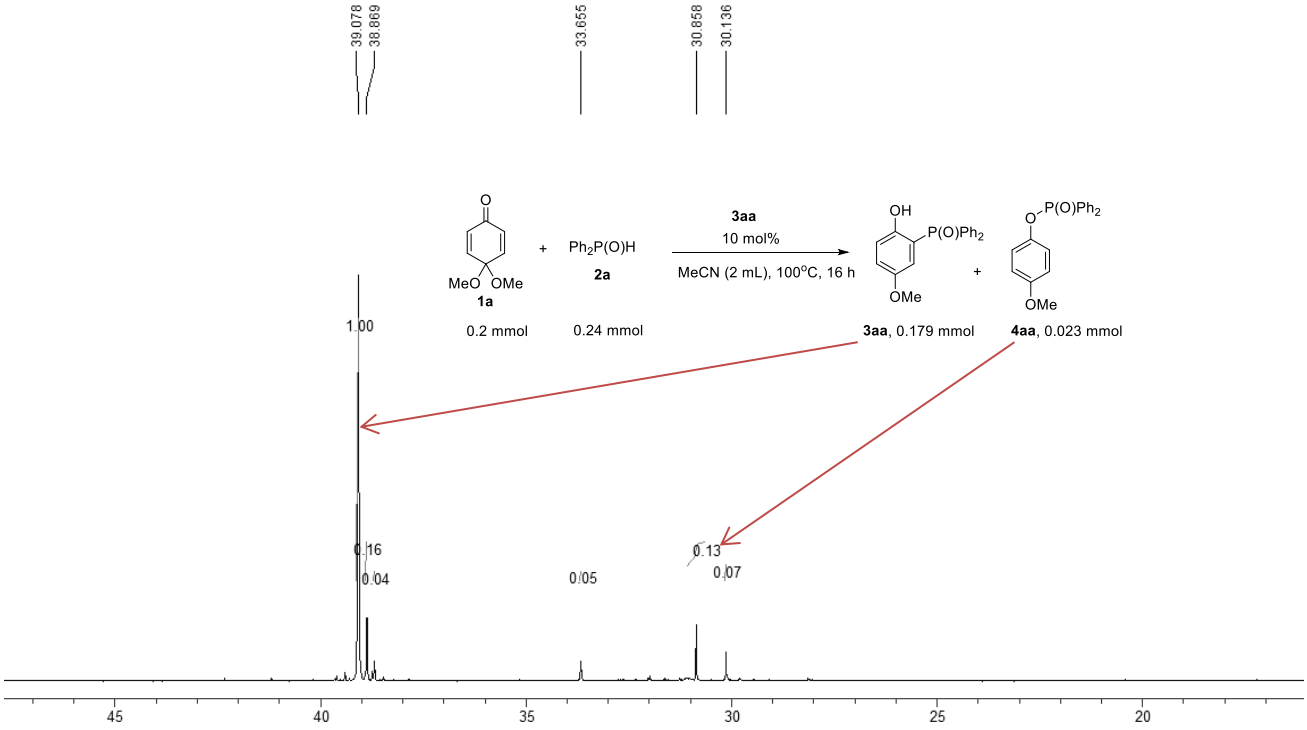



**Figure S1**. Time-course of the C–P coupling reaction of **1a** and **2a** in the presence of 10 mol% $Ph_3P$ ( ▲ ) or 10 mol% ($Ph_3P$ and $PhCO_2H$) ( ◆ ) or 10 mol% $Ph_3P$ with the addition of 20 mol% **3na** ( ○ )

**5.2 Reactions of 1a and 2a in the presence of 10 mol% of 3aa, or a combination of 10 mol% 3aa and 10 mol% TPP**

The reaction of **1a** and **2a** with 10 mol% **3aa** was performed and the reaction mixture after removal of volatiles in vacuo was analyzed by $^{31}P$ NMR. The reaction produced a mixture of **3aa**, **4aa** and other impurities (Figure S2A). In contrast, the reaction of **1a** and **2a** in the presence of 10 mol% $Ph_3P$ and 10 mol% **3aa** took place with high selectivity and afforded the product in high yield. The $^{31}P$ NMR of the reaction mixture was shown in Figure S2B.

**(A)**




**(B)**

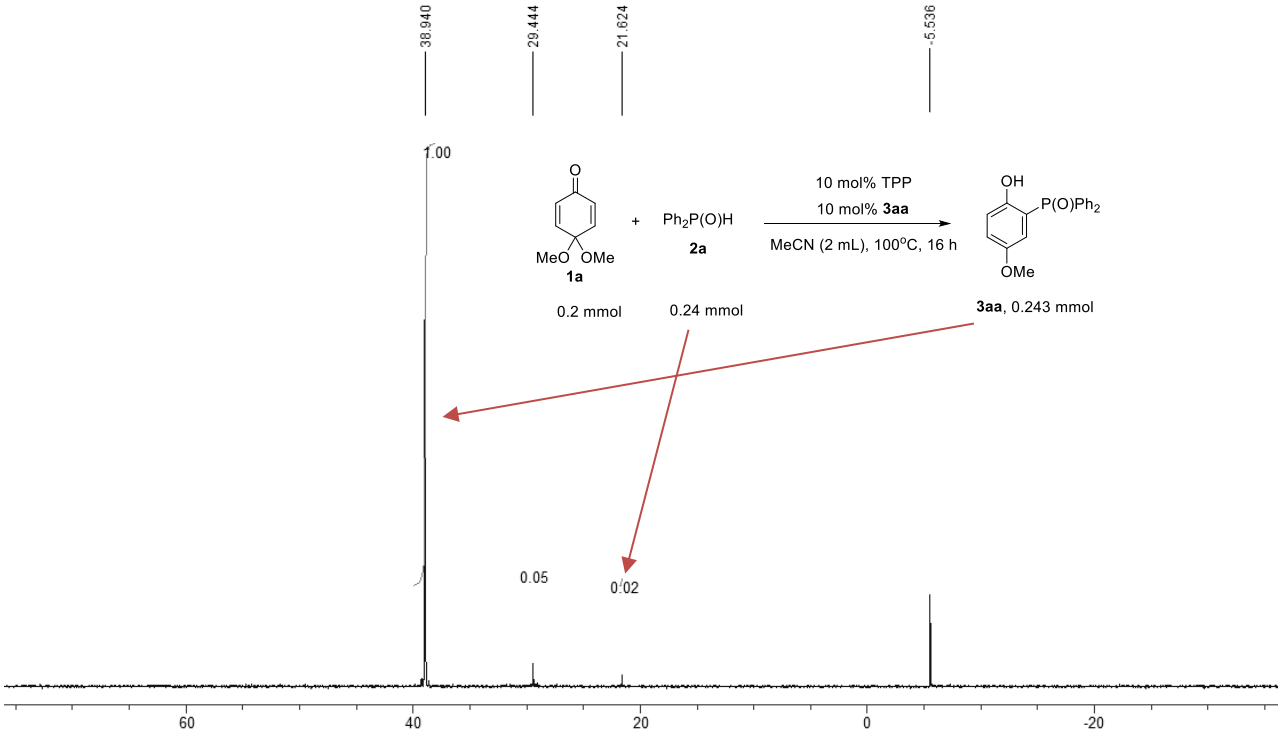
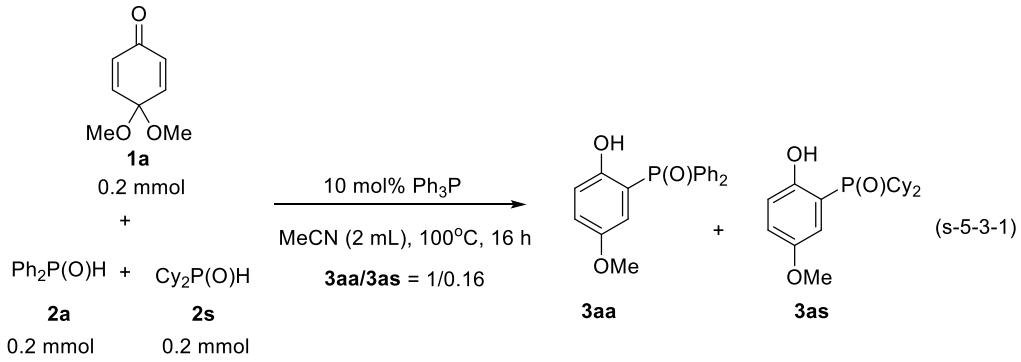



**Figure S2**. The $^{31}P$ NMR of the C-P coupling reaction of **1a** and **2a** in the presence of **(A)** 10 mol% of **3aa** only, and **(B)** 10 mol% of **3aa** and 10 mol% $Ph_3P$

### 5.3 Competition experiments

**A comparison on the reactivity between diarylphosphine oxide and dialkylphosphine oxide:** a mixture of **1a** (0.2 mmol), **2a** (0.2 mmol) and **2s** (0.2 mmol) with TPP (0.02 mmol) in MeCN (2 mL) was heated at 100 °C for 16 h (eq. s-5-3-1). After removal of volatiles in vacuo, the reaction mixture was analyzed by $^{31}$P NMR (Figure S3). The ratio of the products **3aa** and **3as** was ca. 1/0.16. This result indicates that diarylphosphine oxide shows higher reactivity.



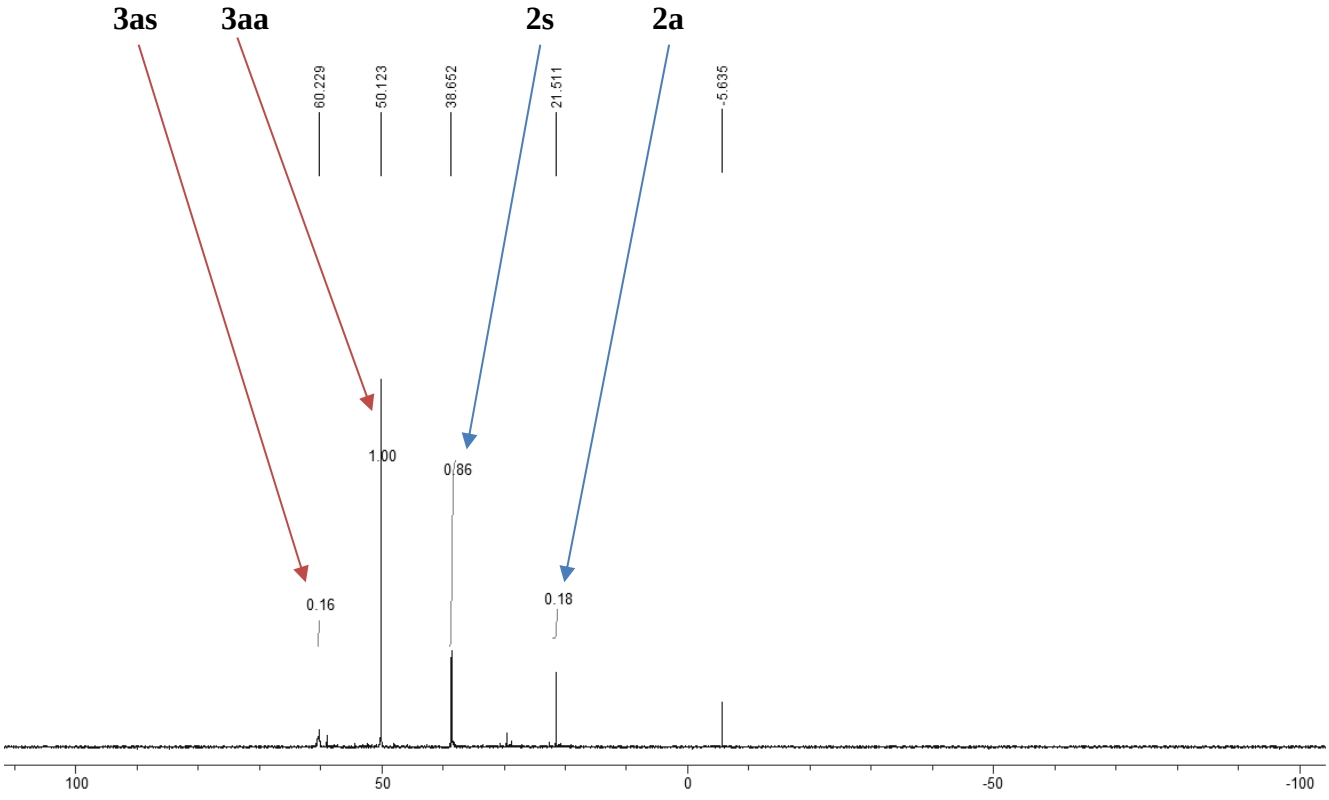
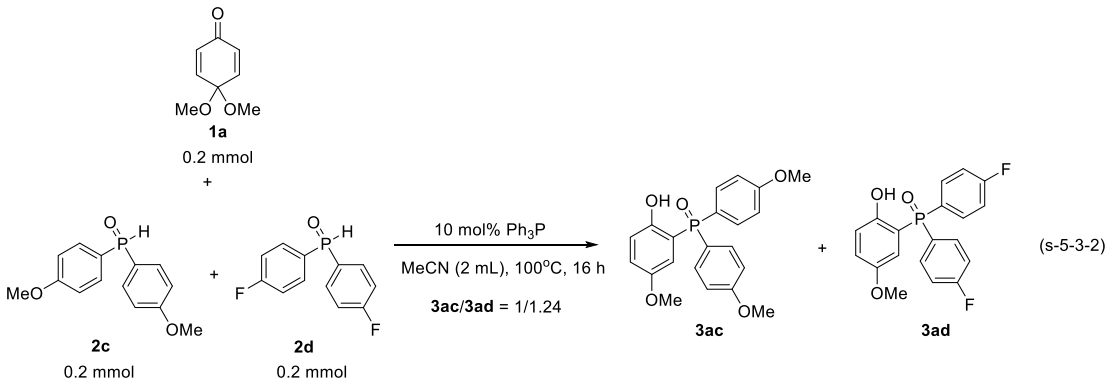




**Figure S3**. The $^{31}$P NMR spectra of the reaction mixture for the reaction **s-5-3-1**

**A comparison on the reactivity of electronically different diarylphosphine oxides:** a mixture of **1a** (0.2 mmol), **2c** (0.2 mmol) and **2d** (0.2 mmol) with TPP (0.02 mmol) in MeCN (2 mL) was heated at 100 °C for 16 h. After removal of volatiles in vacuo, the reaction

mixture was analyzed by $^{31}$P NMR (Figure S4). The ratio of the products **3ac** and **3ad** was ca. 1/1.24. This result indicates that This result may suggest that $Ar_2P(O)H$ **2** bearing electron-withdrawing groups reacts slightly fast to form the product.



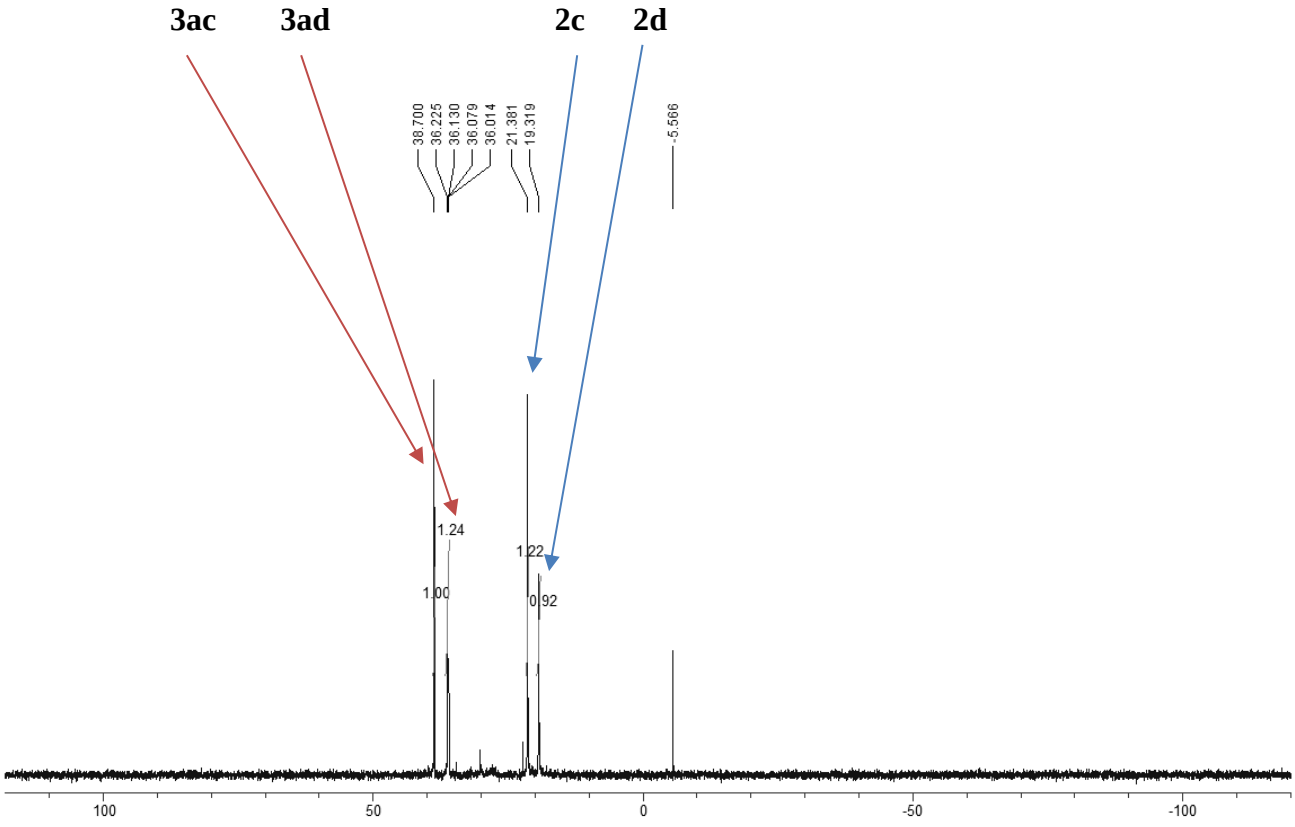
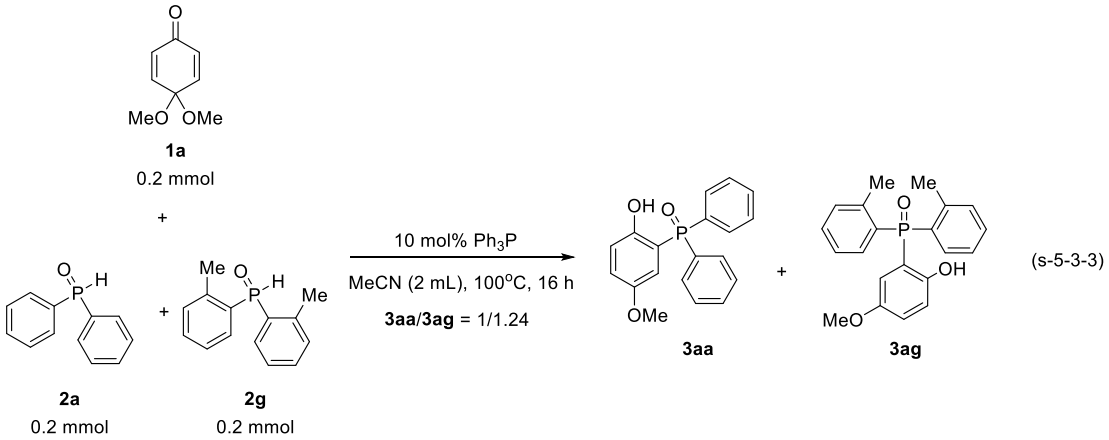




**Figure S4**. The $^{31}$P NMR spectra of the reaction mixture for the reaction **s-5-3-2**

**A comparison on the reactivity of sterically different diarylphosphine oxides:** a mixture of **1a** (0.2 mmol), **2a** (0.2 mmol) and **2g** (0.2 mmol) with TPP (0.02 mmol) in MeCN (2 mL) was heated at 100 °C for 16 h. After removal of volatiles in vacuo, the reaction mixture was analyzed by $^{31}$P NMR (Figure S5). The ratio of the products **3aa** and **3ag** was ca. 1/0.16. This result indicates that sterically demanding $Ar_2P(O)H$ **2** reacts much more slowly to form the product.



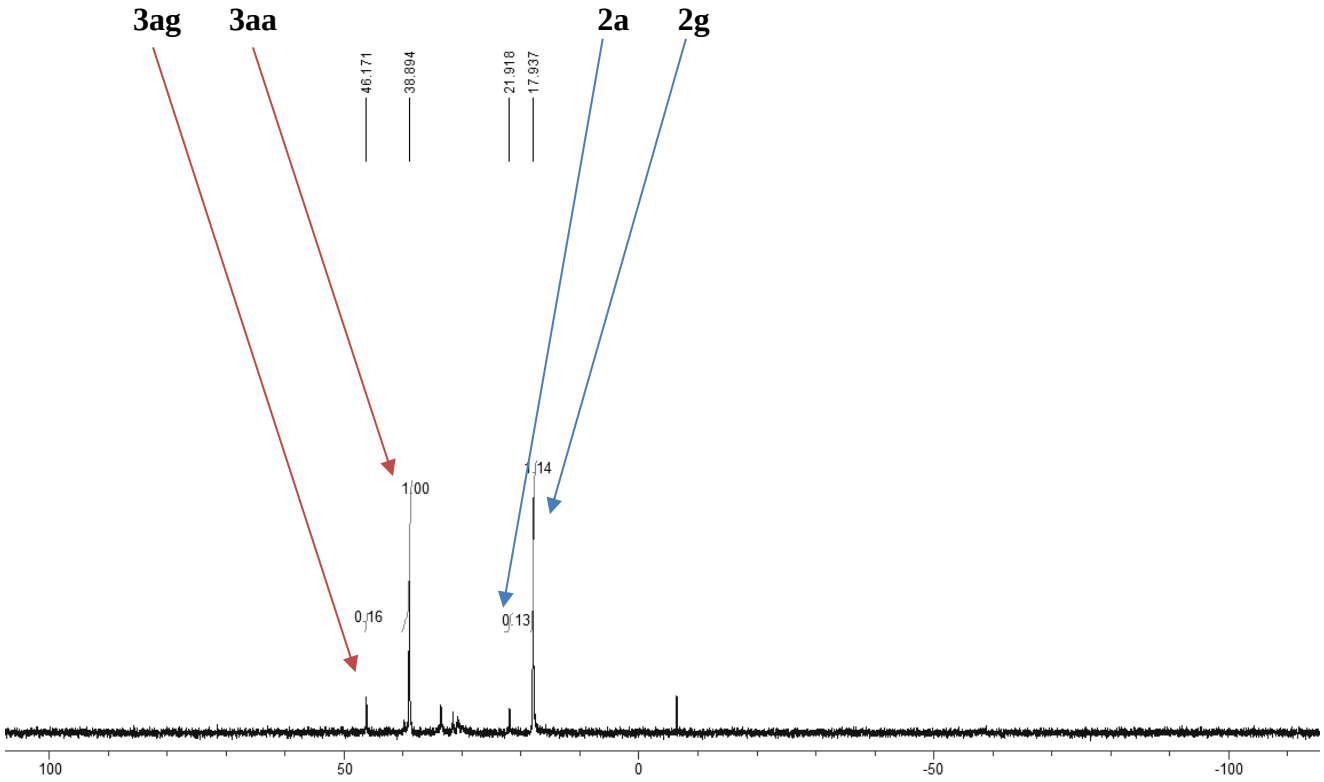
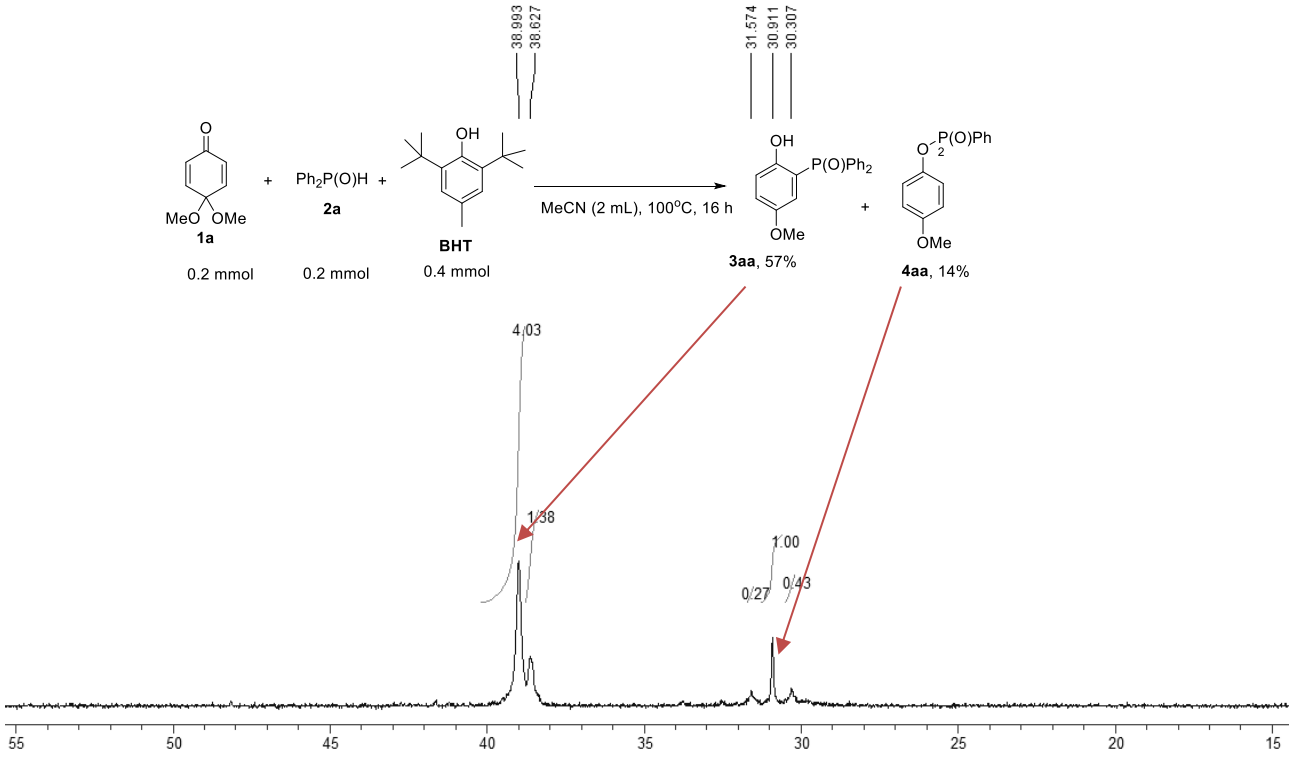




**Figure S5**. The $^{31}$P NMR spectra of the reaction mixture for the reaction **s-5-3-3**

### 5.4 The influence of the radical scavenger (BHT) on the reaction

The reaction of **1a** and **2a** in the presence of 2.0 equiv of butylated hydroxytoluene (BHT) gave a mixture of products: **3aa** 57%; **4aa** 14%; and other byproducts 29% (Figure S6A). Miscellaneous processes may take place in this reaction. In contrast, the reaction of **1a** and **2a** in the presence of 2.0 equiv of BHT and 10 mol% of TPP gave the product **3aa** selectively in 90% yield with <5% impurity, and <5% of **2a** unconsumed (Figure S6B).

**(A)**




**(B)**

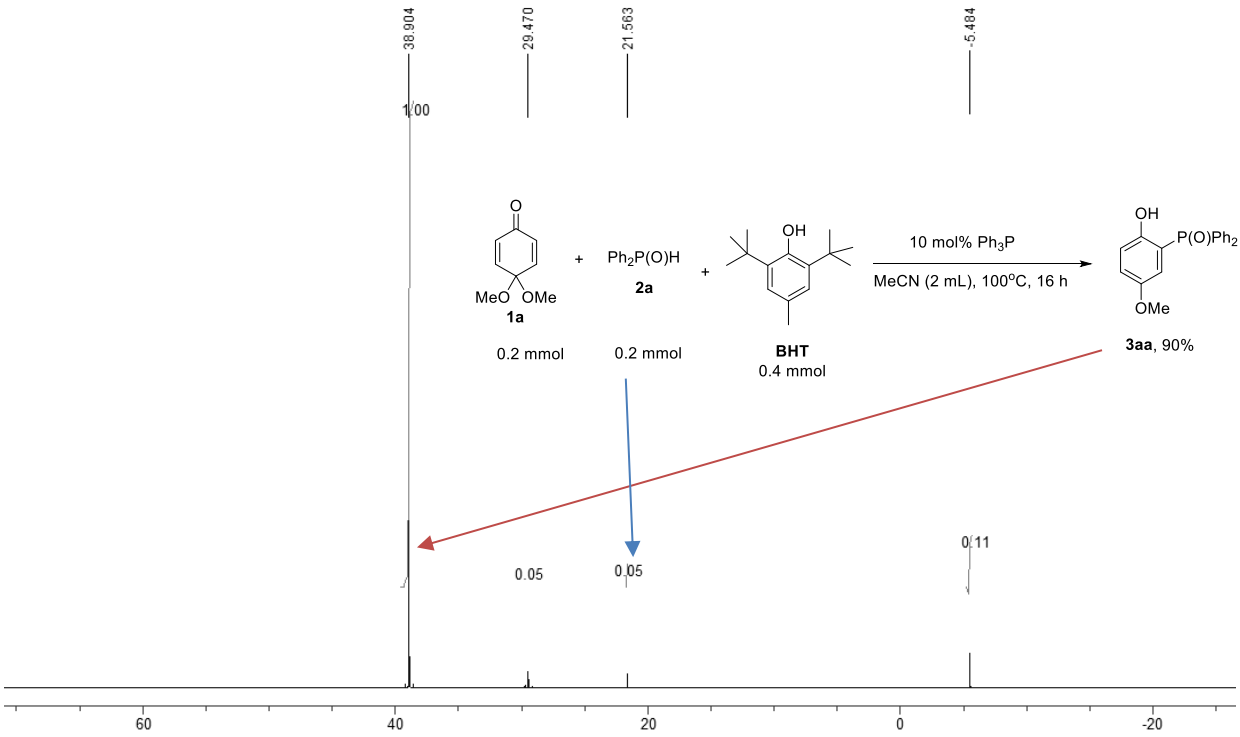
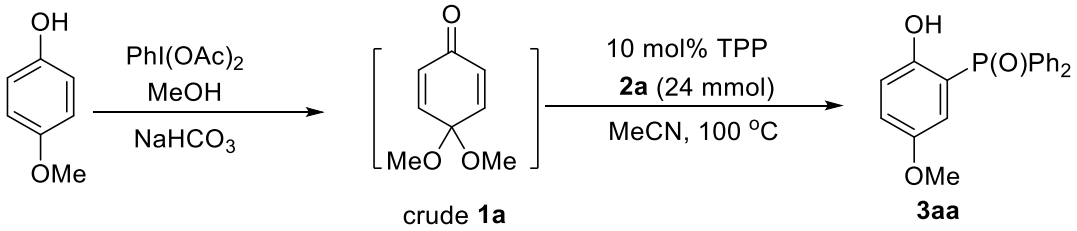



**Figure S6**. The $^{31}$P NMR of the C-P coupling reaction of **1a** and **2a** in the presence of **(A)** 2 equiv of BHT, and **(B)** 2.0 equiv of BHT and 10 mol% $Ph_3P$

## 6. Scaled-up experiments




To a solution of 4-methoxyphenol (2.48 g, 20 mmol) in MeOH (20 mL) was added dropwise a solution of $PhI(OAc)_2$ (7.08 g, 22 mmol) in MeOH (40 mL) at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was concentrated to ca. 20 mL under a reduced pressure. The mixture was quenched with aq. $NaHCO_3$ and extracted with ether (20 mL×3). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent to dryness led to a yellow liquid (crude **1a**) which was used without further purification.

To a 100 mL oven-dried Schlenk tube with a Teflon-coated stir bar was added triphenylphosphine (524 mg, 2 mmol), the crude **1a**, diphenylphosphine oxide **2a** (4.85 g, 24 mmol) and 20 mL of MeCN under an atmoshphere of dry $N_2$ (Figure S7, pic a). The Schlenk tube was sealed and heated in an oil bath at 100 °C. After the reaction mxiture was stirred for 16 h (Figure S7, pic b), the reaction was cooled to room temperature with a mild stirring. The product started to precipitate during this process (Figure S7, pic c). After filtrating on a glass Buchner funnel (Figure S7, pic d), washing with a small amount of ether and drying under vacuum, the major portion of the product **3aa** (5.10 g) was obtained (Figure S7, pic e). The combined filtrate was concentrated to dryness on a rotary evaporator, redisolved in 10 mL MeCN, and stored in a refrigerator for one night. The precipitate was collected and washed with a few drops of ether to afford the second portion of the product (0.50 g). Total yield 86%. Note: the obtained product is a litte yellowish but pure enough for synthetic use.

The synthesis of **3fa**, **3na**, **3ad** and **3aj** on 5-10 mmol scale was followed a similar procedure.

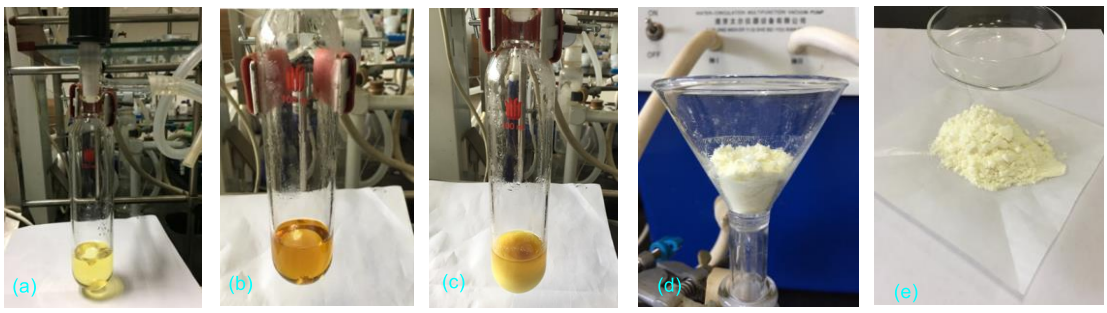
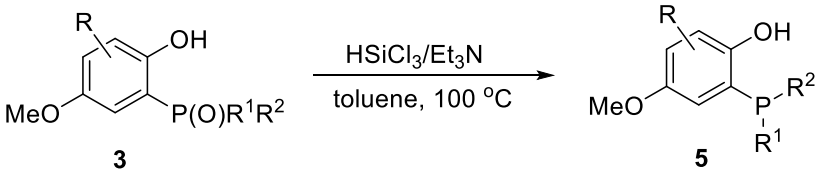



**Figure S7.** (a) before heating; (b) after heating for 16 h; (c) cooling down; (d) filtrating; (e) the product **3aa**

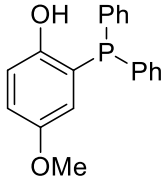
## 7. Synthetic transformation of products 3

### 7.1 General procedure for the P(O) redcution of 3 to afford phenol-phosphines 5

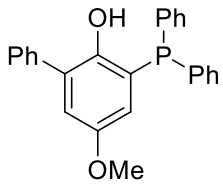



**3** **5**

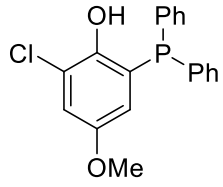
To a flame-dried Schlenk tube was charged with **3** (0.1 mmol) and a magnetic stir bar under $N_2$ atmosphere. Then, toluene (3.0 mL) and $Et_3N$ (1.5 mmol) were added by a syringe. The reaction mixture was cooled with an ice-water bath. $HSiCl_3$ (1 mmol) was carefully added by a syringe. The ice-water bath was removed, and the reaction mixture was heated at 100 ℃ in an oil bath for 48 h. After cooling, ca.1.0 mL of 5% aq. NaOH was added and stirred for 10 min. The resulting mixture was diluted with water and extracted with ethylacetate (20.0 mL×3). The combined organic layers were dried over $MgSO_4$ and solvent were removed in vacuo. Purification of the residue by column chromatography on silica gel using hexane/ethyl acetate (50:1, v/v) gave product **5**.




**2-(diphenylphosphanyl)-4-methoxyphenol (5a):** yield: 24.6 mg, 80%. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.36–7.30 (m, 10H), 6.88–6.83 (m, 2H), 6.49–6.47 (m, 1H), 5.72 (d, $J$ = 2.4 Hz, 1H), 3.61 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.5 (d, $J_{P\text{-}C}$ = 2.2 Hz), 153.0 (d, $J_{P\text{-}C}$ = 18.4 Hz), 134.8 (d, $J_{P\text{-}C}$ = 5.8 Hz), 133.4 (d, $J_{P\text{-}C}$ = 18.6 Hz), 129.0, 128.7 (d, $J_{P\text{-}C}$ = 7.5 Hz), 122.0 (d, $J_{P\text{-}C}$ = 7.7 Hz), 119.1 (d, $J_{P\text{-}C}$ = 4.5 Hz), 117.0, 116.3 (d, $J_{P\text{-}C}$ = 2.0 Hz), 55.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -26.2; HRMS (ESI-TOF): $m/z$ = 309.1047, calcd for $C_{19}H_{18}O_2P$ [$MH^+$] 309.1044.

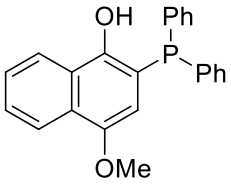



**3-(diphenylphosphanyl)-5-methoxy-[1,1'-biphenyl]-2-ol (5b):** yield: 30.0 mg, 78%. White solid, mp. 113.2–113.7 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.53–7.50 (m, 2H), 7.47–7.43 (m, 2H), 7.40–7.35 (m, 11H), 6.87 (d, $J$= 3.2 Hz, 1H), 6.39 (dd, $J_1$ = 4.8 Hz, $J_2$= 3.2 Hz, 1H), 3.63 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.3 (d, $J_{P\text{-}C}$ = 2.2 Hz), 149.0 (d, $J_{P\text{-}C}$ = 16.5 Hz), 137.2 (d, $J_{P\text{-}C}$ = 0.9 Hz), 133.7 (d, $J_{P\text{-}C}$ = 19.5 Hz), 129.1 (d, $J_{P\text{-}C}$ = 18.1 Hz), 128.8, 128.7, 128.6 (d, $J_{P\text{-}C}$ = 7.1 Hz), 127.8, 123.9 (d, $J_{P\text{-}C}$ = 10.3 Hz), 118.7 (d, $J_{P\text{-}C}$ = 2.9 Hz), 116.9, 55.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -21.9; HRMS (ESI-TOF): $m/z$ = 385.1359, calcd for $C_{25}H_{22}O_2P$ [$MH^+$] 385.1357.

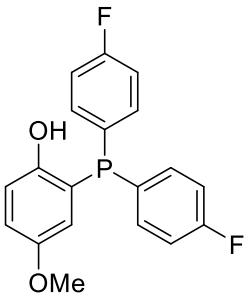



**2-chloro-6-(diphenylphosphanyl)-4-methoxyphenol (5c):** yield: 26.7 mg, 78%. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.37–7.30 (m, 11H), 6.89 (dd, $J_1$ = 2.8 Hz, $J_2$= 0.4 Hz, 1H), 6.23 (dd, $J_1$ = 4.4 Hz, $J_2$= 2.8 Hz, 1H),

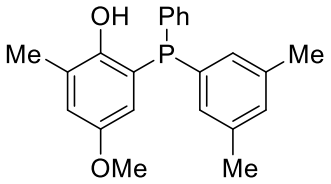
3.59 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.2 (d, $J_{P\text{-}C}$ = 1.2 Hz), 147.2 (d, $J_{P\text{-}C}$ = 6.6 Hz), 135.1 (d, $J_{P\text{-}C}$ = 8.9 Hz), 133.8 (d, $J_{P\text{-}C}$ = 20.3 Hz), 129.1, 128.6 (d, $J_{P\text{-}C}$ = 7.4 Hz), 125.5 (d, $J_{P\text{-}C}$ = 17.2 Hz), 120.0 (d, $J_{P\text{-}C}$ = 3.7 Hz), 118.6 (d, $J_{P\text{-}C}$ = 2.9 Hz), 115.0, 55.7. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -17.4; HRMS (ESI-TOF): *m/z* = 343.0657, calcd for $C_{19}H_{17}O_2PCl$ [$MH^+$] 343.0655.




**2-(diphenylphosphanyl)-4-methoxynaphthalen-1-ol (5d):** yield: 25.8 mg, 72%. White solid, mp. 84.4–84.9 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.27–8.23 (m, 1H), 8.19–8.15 (m, 1H), 7.57–7.51 (m, 2H), 7.42–7.33 (m, 10H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.37 (d, *J* = 4.8 Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 151.2 (d, $J_{P\text{-}C}$ = 19.6 Hz), 149.2 (d, $J_{P\text{-}C}$ = 2.6 Hz), 135.3 (d, $J_{P\text{-}C}$ = 3.7 Hz), 133.1 (d, $J_{P\text{-}C}$ = 18.4 Hz), 128.9, 128.7 (d, $J_{P\text{-}C}$ = 7.8 Hz), 127.7, 127.2, 126.2, 124.8 (d, $J_{P\text{-}C}$ = 3.3 Hz), 122.8 (d, $J_{P\text{-}C}$ = 3.2 Hz), 121.8, 110.9 (d, $J_{P\text{-}C}$ = 3.5 Hz), 106.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 55.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -30.9; HRMS (ESI-TOF): *m/z* = 359.1206, calcd for $C_{23}H_{20}O_2P$ [$MH^+$] 359.1201.

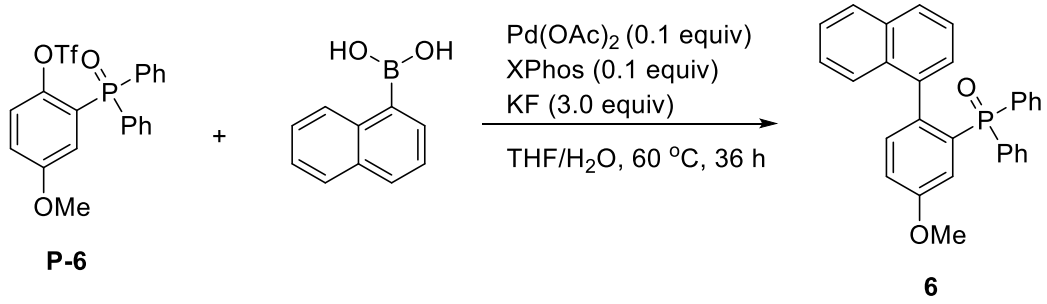



**2-(bis(4-fluorophenyl)phosphanyl)-4-methoxyphenol (5e):** yield: 27.5 mg, 80%. White solid, mp. 116.2–117.3 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.32–7.26 (m, 4H), 7.09–7.04 (m, 4H), 6.87–6.82 (m, 2H), 6.38–6.36 (m, 1H), 5.58 (s, 1H), 3.63 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.6 (d, $J_{F\text{-}C}$ = 249.0 Hz), 153.8 (d, $J_{P\text{-}C}$ = 2.2 Hz), 152.6 (d, $J_{P\text{-}C}$ = 19.2 Hz), 135.4 (q, $J_{F\text{-}C}$ = 21.2 Hz, $J_{P\text{-}C}$ = 8.0 Hz), 130.3 (m), 122.3 (d, $J_{P\text{-}C}$ = 7.8 Hz), 118.8 (d, $J_{P\text{-}C}$ = 2.8 Hz), 116.8, 116.4 (d, $J_{P\text{-}C}$ = 1.4 Hz), 116.0 (dd, $J_{F\text{-}C}$ = 21.7 Hz, $J_{P\text{-}C}$ = 8.0 Hz), 55.6. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -27.3; HRMS (ESI-TOF): *m/z* =345.0857, calcd for $C_{19}H_{16}O_2PF_2$ [$MH^+$] 345.0856.




**2-((3,5-dimethylphenyl)(phenyl)phosphanyl)-4-methoxy-6-methylphenol (5f):** yield: 21.6 mg, 62%. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.35–7.30 (m, 5H), 6.98 (s, 1H), 6.95 (d, *J*= 8.8 Hz, 2H), 6.75 (d, *J*= 7.2 Hz, 1H), 6.38 (dd, $J_1$ = 5.6 Hz, $J_2$= 3.2 Hz, 1H), 5.93 (d, *J*= 7.6 Hz, 1H), 3.61 (s, 3H) , 2.26 (s, 6H), 2.25 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.0 (d, $J_{P\text{-}C}$ = 3.2 Hz), 151.6 (d, $J_{P\text{-}C}$ = 17.4 Hz), 138.2 (d, $J_{P\text{-}C}$ = 7.2 Hz), 135.2 (d, $J_{P\text{-}C}$ = 5.2 Hz), 134.4 (d, $J_{P\text{-}C}$ = 4.3 Hz), 133.4 (d, $J_{P\text{-}C}$ = 18.8 Hz), 131.1 (d, $J_{P\text{-}C}$ = 15.8 Hz), 131.0, 128.8 (d, $J_{P\text{-}C}$ = 20.6 Hz), 128.6, 125.6 (d, $J_{P\text{-}C}$ = 2.1 Hz), 121.1 (d, $J_{P\text{-}C}$ = 5.6 Hz), 118.7, 116.5 (d, $J_{P\text{-}C}$ = 5.7 Hz), 55.6, 21.4, 16.6 (d, $J_{P\text{-}C}$ = 1.7 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = -27.4; HRMS (ESI-TOF): *m/z* = 351.1517, calcd for $C_{22}H_{24}O_2P$ [$MH^+$] 351.1514.

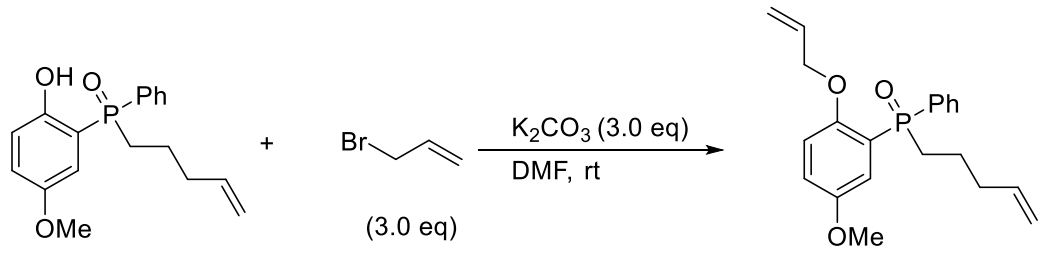
## 7.2 Synthesis of 6 via the Suzuki-Miyaura coupling reaction




**P-6** **6**

**(5-methoxy-2-(naphthalen-1-yl)phenyl)diphenylphosphine oxide (6):** to a solution of the triflate **P-6** [4] (180.0 mg, 0.395 mmol) and naphthalen-1-ylboronic acid (191.5 mg, 1.1 mmol) in THF/$H_2O$ (v/v 8/1, 3 mL), were added KF (69.6 mg, 1.2 mmol), $Pd(OAc)_2$ (8.8 mg, 0.04 mmol) and XPhos (19.2 mg, 0.04 mmol) at 60℃. The reaction was stirred under nitrogen at 60℃ for 36 h. The mixture was diluted with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (PE/EtOAc 3/1) to afford compound **6** (150.3 mg, 88%). White solid, mp. 201.7–203.1 ℃. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.57–7.5 (m, 4H), 7.46 (dd, $J_1$ = 9.6 Hz, $J_2$= 1.2 Hz, 1H), 7.33–7.23 (m, 8H), 7.21–7.12 (m, 4H), 7.00–6.96 (m, 1H), 6.91–6.86 (m, 2H), 3.80 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.3 (d, $J_{P\text{-}C}$ = 14.6 Hz), 136.7 (d, $J_{P\text{-}C}$ = 3.7 Hz), 136.6 (d, $J_{P\text{-}C}$ = 8.9 Hz), 134.2 (d, $J_{P\text{-}C}$ = 100.6 Hz), 134.0 (d, $J_{P\text{-}C}$ = 10.9 Hz), 133.1 (d, $J_{P\text{-}C}$ = 103.1 Hz),133.0, 132.0, 131.9 (d, $J_{P\text{-}C}$ = 104.5 Hz), 131.8 (d, $J_{P\text{-}C}$ = 9.0 Hz), 131.0 (d, $J_{P\text{-}C}$ = 2.8 Hz), 130.6 (d, $J_{P\text{-}C}$ = 9.7 Hz), 130.2 (d, $J_{P\text{-}C}$ = 3.3 Hz), 129.6, 127.9 (d, $J_{P\text{-}C}$ = 11.2 Hz), 127.7 (d, $J_{P\text{-}C}$ = 5.8 Hz), 127.3 (d, $J_{P\text{-}C}$ = 12.0 Hz), 126.1, 125.2 (d, $J_{P\text{-}C}$ = 13.3 Hz), 124.3, 119.4 (d, $J_{P\text{-}C}$ = 12.5 Hz), 117.0 (d, $J_{P\text{-}C}$ = 3.0 Hz), 55.4. $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 27.3; HRMS (ESI-TOF): *m/z* = 435.1515, calcd for $C_{29}H_{24}O_2P$ [$MH^+$] 435.1514.

## 7.3 Synthesis of the phosphomacracycle 7 via RCM reaction

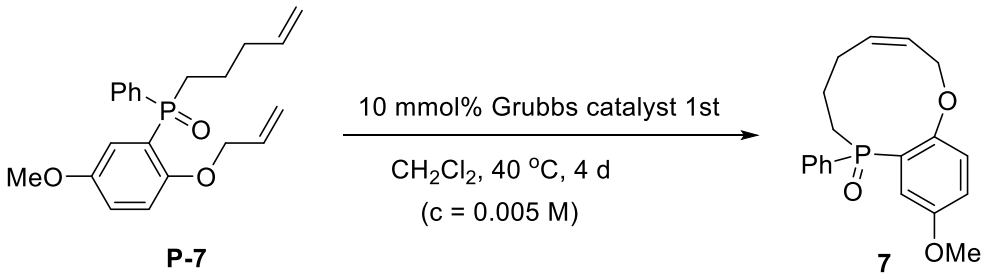



**3aq** **P-7**

**(2-(allyloxy)-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (P-7):** to a solution of compound **3aq** (142.7 mg, 0.45 mmol, 1.0 equiv) and ally bromide (162.1 mg, 1.35 mmol, 3.0 equiv) in DMF (2 mL), were added $K_2CO_3$ (187.0 mg, 1.35 mmol, 3.0 equiv) at rt. The reaction was stirred under nitrogen for 4 h. The mixture was diluted with $H_2O$ and

[4] The triflate **P-6** (92%) was prepared from **3aa** on a 1 mmol scale via a known procedure: S. Wu, M. He and X. Zhang, *Tetrahedron: Asymmetry*, 2004, **15**, 2177.

extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (PE/EtOAc 2/1) to afford compound **P-7** (160.6 mg, 100%). $^1$H NMR ($CDCl_3$, 400 MHz): 7.80–7.75 (m, 2H), 7.62 (dd, $J_1$ = 3.2 Hz, $J_2$= 13.6 Hz, 1H), 7.48–7.38 (m, 3H), 7.01 (dd, $J_1$ = 9.2 Hz, $J_2$= 3.2 Hz, 1H), 6.81 (dd, $J_1$ = 8.8 Hz, $J_2$= 6.0 Hz, 1H), 5.87–5.68 (m, 2H), 5.23–5.18 (m, 2H), 5.02–4.95 (m, 2H), 4.45 (dd, $J_1$ = 12.4 Hz, $J_2$= 5.6 Hz, 1H), 4.37 (dd, $J_1$ = 12.4 Hz, $J_2$= 5.2 Hz, 1H), 3.83 (s, 3H), 2.54–2.36 (m, 2H), 2.15 (q, $J$ = 6.8 Hz, 2H), 1.86–1.58 (m, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.0 (d, $J_{P\text{-}C}$ = 2.6 Hz), 152.6 (d, $J_{P\text{-}C}$ = 4.2 Hz), 137.6, 133.7 (d, $J_{P\text{-}C}$ = 100.6 Hz), 132.4, 131.4 (d, $J_{P\text{-}C}$ = 2.8 Hz), 130.7 (d, $J_{P\text{-}C}$ = 10.9 Hz), 128.2 (d, $J_{P\text{-}C}$ = 10.7 Hz), 120.7 (d, $J_{P\text{-}C}$ = 95.0 Hz), 120.1 (d, $J_{P\text{-}C}$ = 2.2 Hz), 118.5, 118.2 (d, $J_{P\text{-}C}$ = 5.9 Hz), 115.6, 113.2 (d, $J_{P\text{-}C}$ = 7.9 Hz), 69.6, 56.0, 34.7 (d, $J_{P\text{-}C}$ = 15.9 Hz), 28.1 (d, $J_{P\text{-}C}$ = 73.2 Hz), 20.8 (d, $J_{P\text{-}C}$ = 3.5 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 33.5. HRMS (ESI-TOF): *m/z* =357.1629, calcd for $C_{21}H_{26}O_3P$ [$MH^+$] 357.1620.

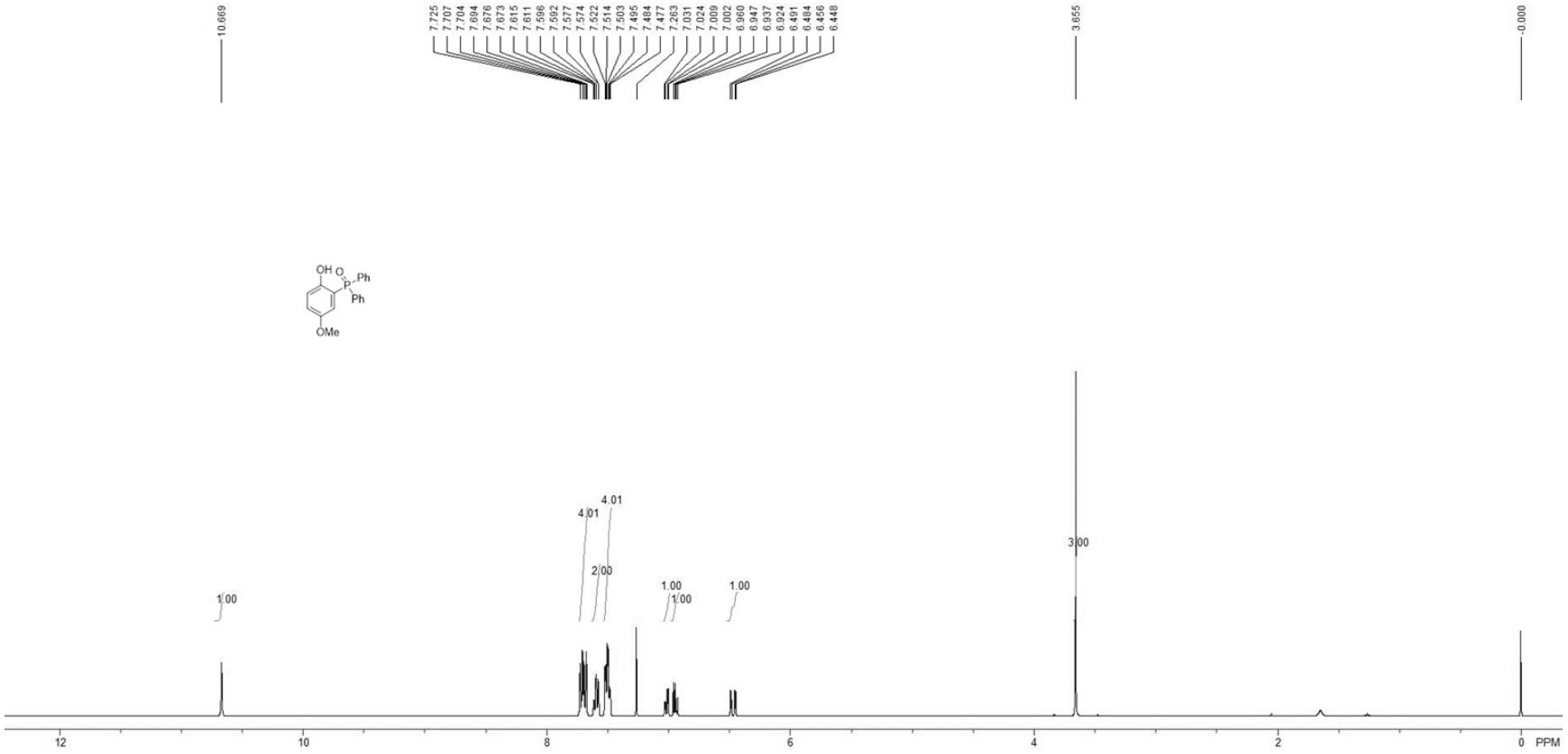



**P-7** **7**

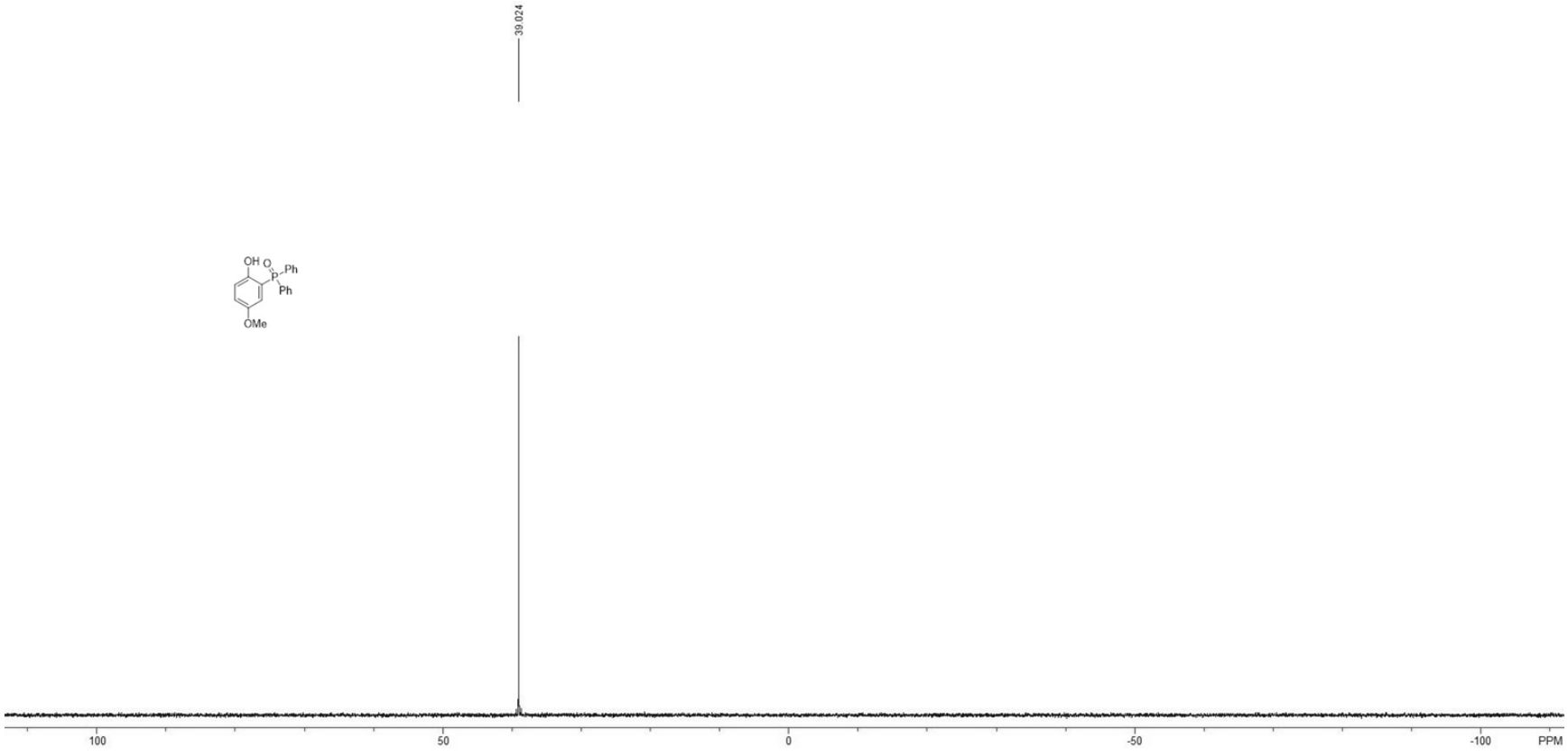
**(*Z*)-10-methoxy-8-phenyl-2,5,6,7-tetrahydrobenzo[b][1,4]oxaphosphecine 8-oxide (7):** to a solution of the compound **P-7** (140.0 mg, 0.39 mmol) in $CH_2Cl_2$ (80 mL), were added the Grubbs catalyst 1st (32.9 mg, 0.1 equiv) under an atmosphere of dry nitrogen. The reaction was stirred at 40 $^o$C for 4 d. The mixture was concentrated and purified with silica gel column chromatography (PE/EtOAc 1/1) to afford compound **7** (60.7 mg, 46%), and the recovered P-7 (60.9 mg). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.77–7.72 (m, 2H), 7.55 (dd, $J_1$ = 13.2 Hz, $J_2$= 7.2 Hz, 1H), 7.44–7.36 (m, 3H), 7.04 (dd, $J_1$ = 8.8 Hz, $J_2$ = 3.2 Hz, 1H), 6.91 (dd, $J_1$ = 8.8 Hz, $J_2$ = 6.0 Hz, 1H), 5.98 (dt, $J_1$ = 10.4 Hz, $J_2$ = 4.2 Hz, 1H), 5.77–5.70 (m, 1H), 4.76 (dd, $J_1$ = 11.6 Hz, $J_2$ = 6.4 Hz, 1H), 4.57 (dd, $J_1$ = 11.6 Hz, $J_2$= 4.4 Hz, 1H), 3.79 (s, 3H), 2.92–2.84 (m, 1H), 2.41–2.29 (m, 1H), 2.21–2.10 (m, 1H), 2.06–1.99 (m, 2H), 1.85–1.72 (m, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.7 (d, $J_{P\text{-}C}$ = 5.1 Hz), 154.3 (d, $J_{P\text{-}C}$ = 12.3 Hz), 137.6, 135.0 (d, $J_{P\text{-}C}$ = 100.5 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.6 Hz), 129.8 (d, $J_{P\text{-}C}$ = 10.2 Hz), 128.4 (d, $J_{P\text{-}C}$ = 12.2 Hz), 125.5, 122.4 (d, $J_{P\text{-}C}$ = 93.3 Hz), 120.9 (d, $J_{P\text{-}C}$ = 2.0 Hz), 117.0 (d, $J_{P\text{-}C}$ = 5.7 Hz), 116.4 (d, $J_{P\text{-}C}$ = 8.3 Hz), 68.1, 55.8, 28.5 (d, $J_{P\text{-}C}$ = 72.7 Hz), 28.0, 18.5 (d, $J_{P\text{-}C}$ = 5.2 Hz). $^{31}$P NMR ($CDCl_3$, 160 MHz): $\delta$ = 33.3. HRMS (ESI-TOF): *m/z* =329.1312, calcd for $C_{19}H_{22}O_3P$ [$MH^+$] 329.1307.

## 8. Copies of $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra

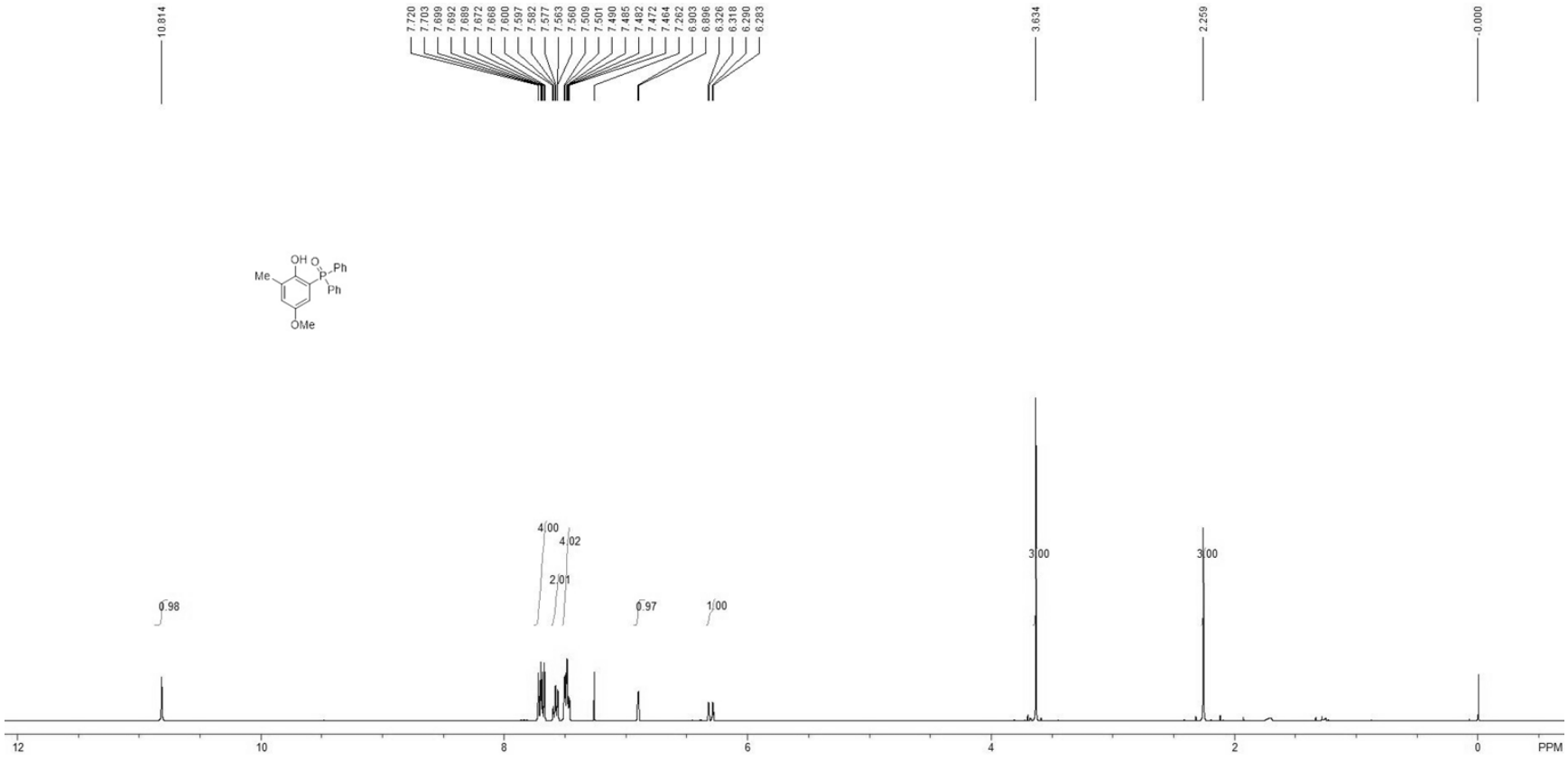
### $^{1}H$ NMR of (2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3aa)



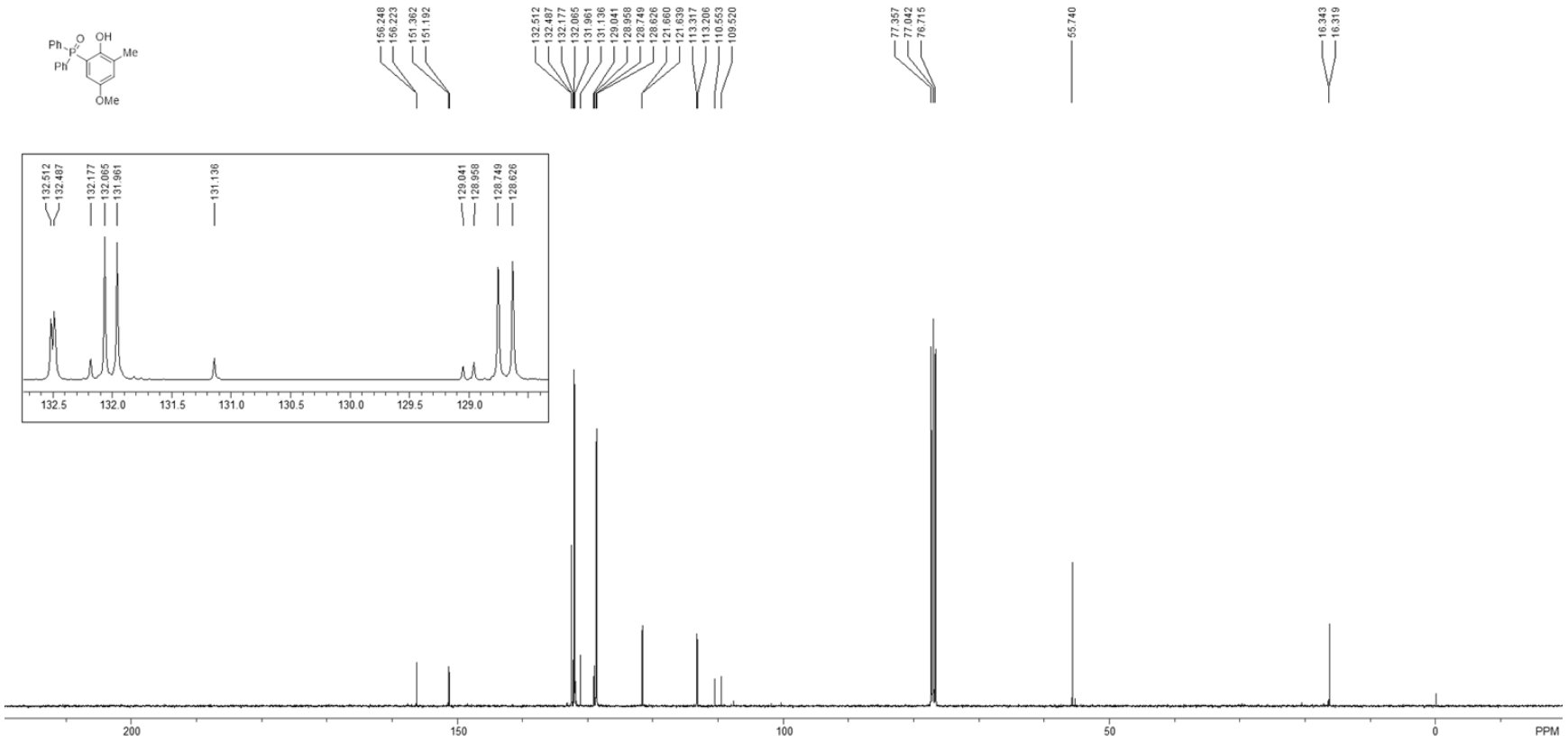
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3aa)**



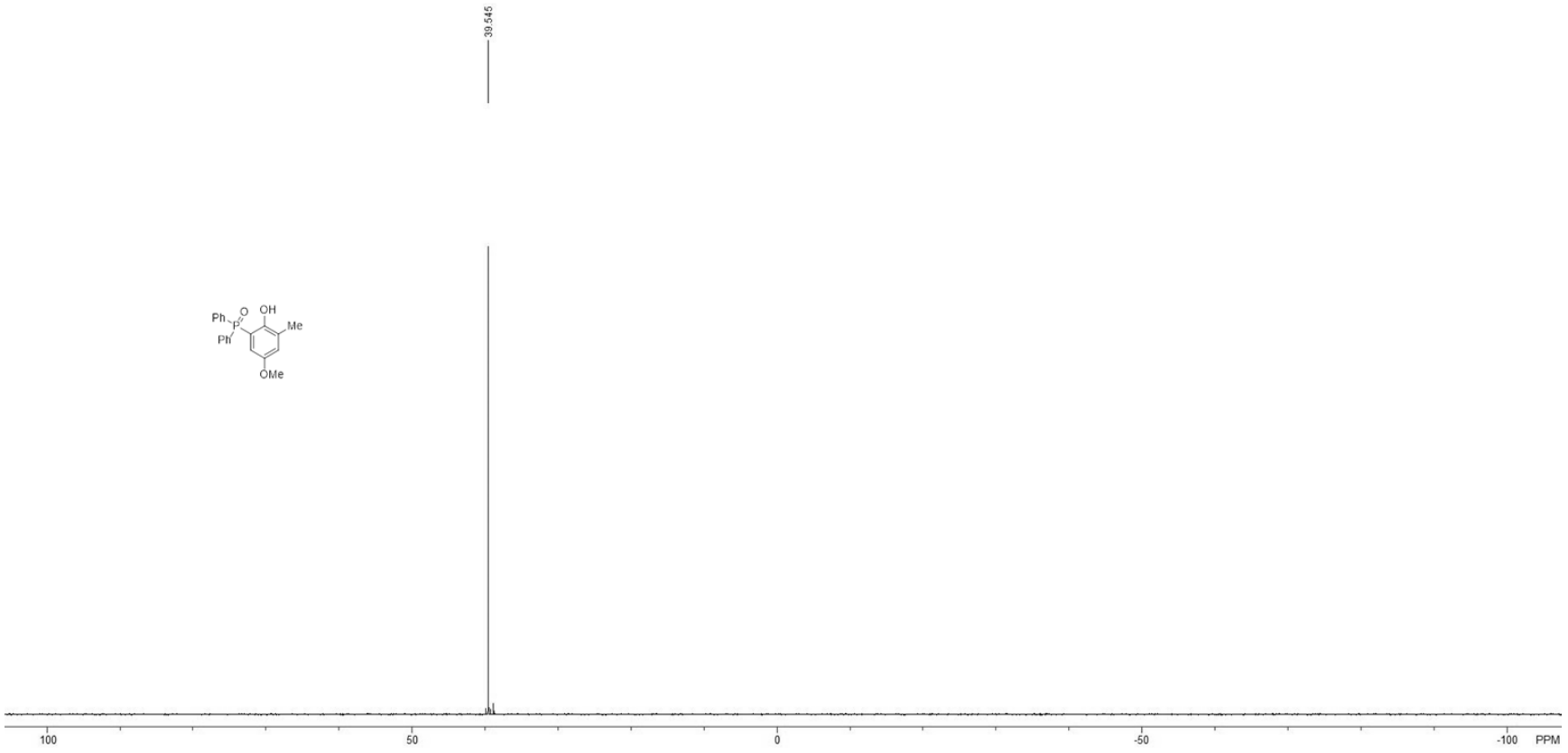
**$^{1}$H NMR of (2-hydroxy-5-methoxy-3-methylphenyl)diphenylphosphine oxide (3ba)**



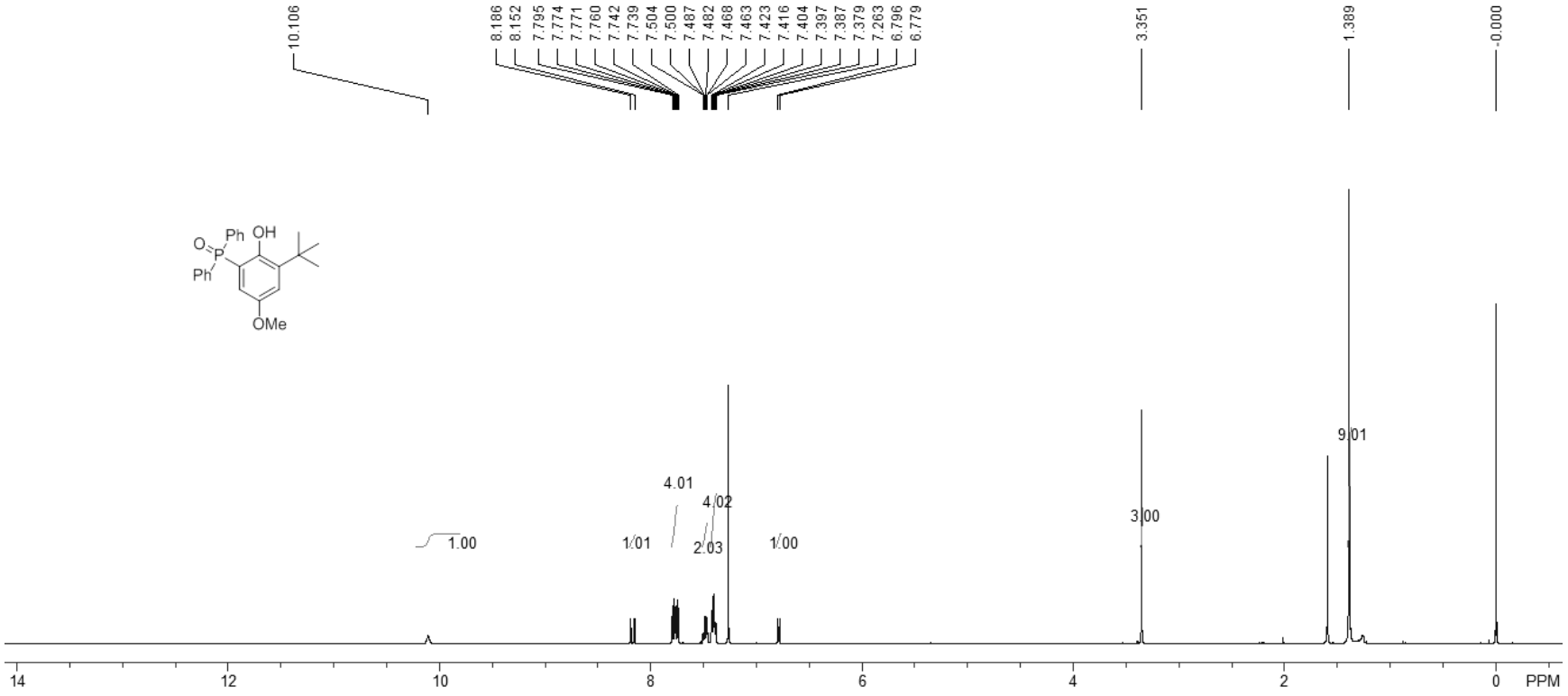
**$^{13}$C NMR of (2-hydroxy-5-methoxy-3-methylphenyl)diphenylphosphine oxide (3ba)**



**$^{31}$P NMR of (2-hydroxy-5-methoxy-3-methylphenyl)diphenylphosphine oxide (3ba)**

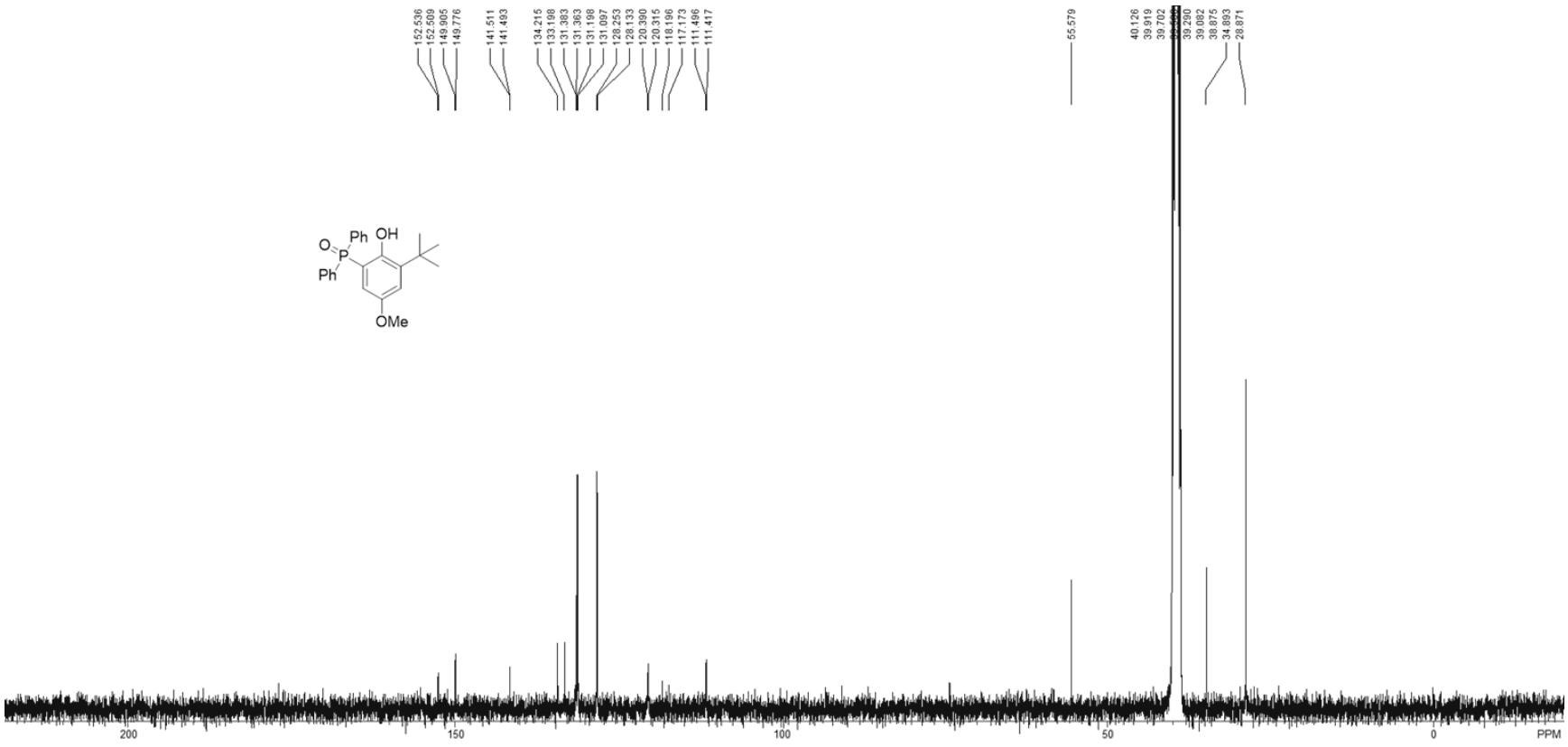


**[1]H NMR of (3-(tert-butyl)-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ca)**

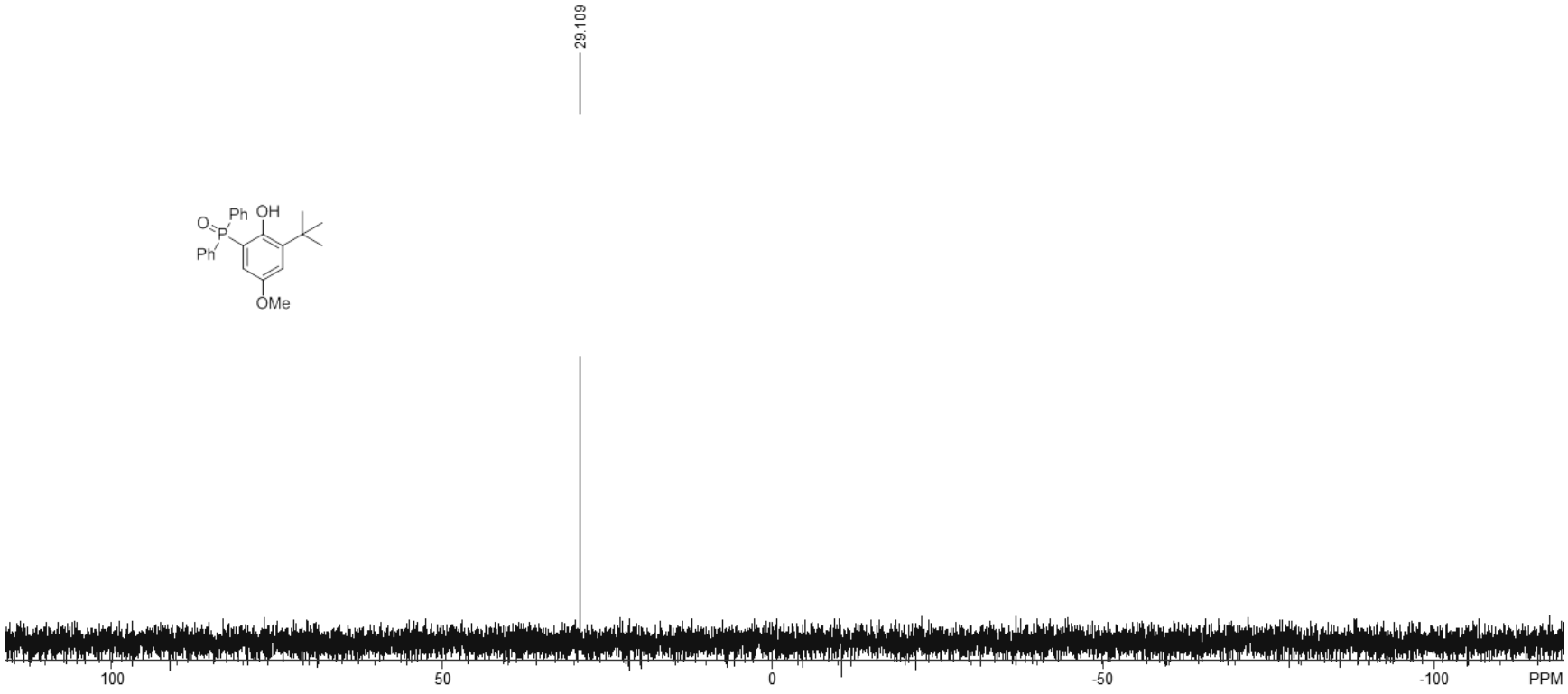


**$^{13}$C NMR of (3-(tert-butyl)-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ca)**

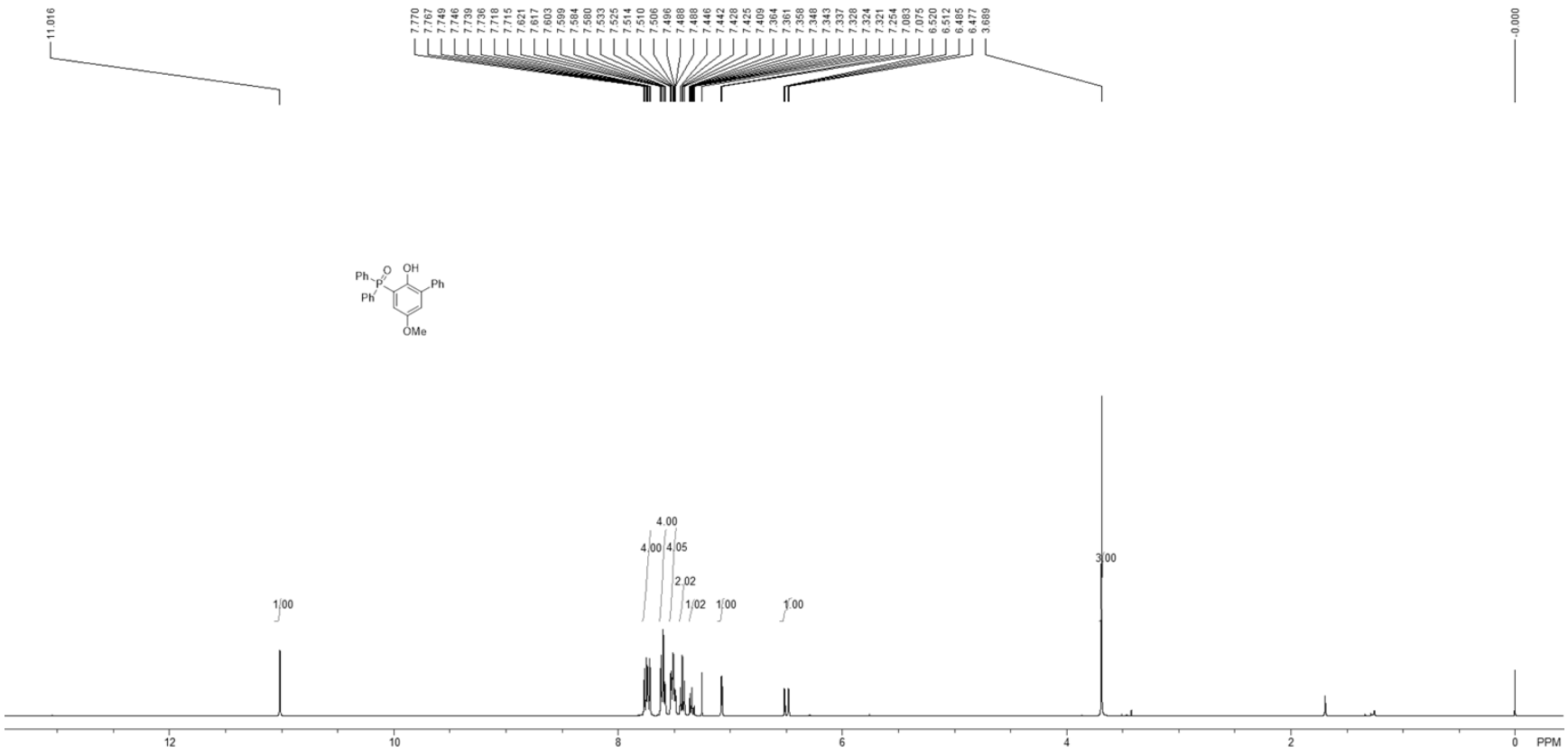
***Solvent: DMSO-$d_6$***



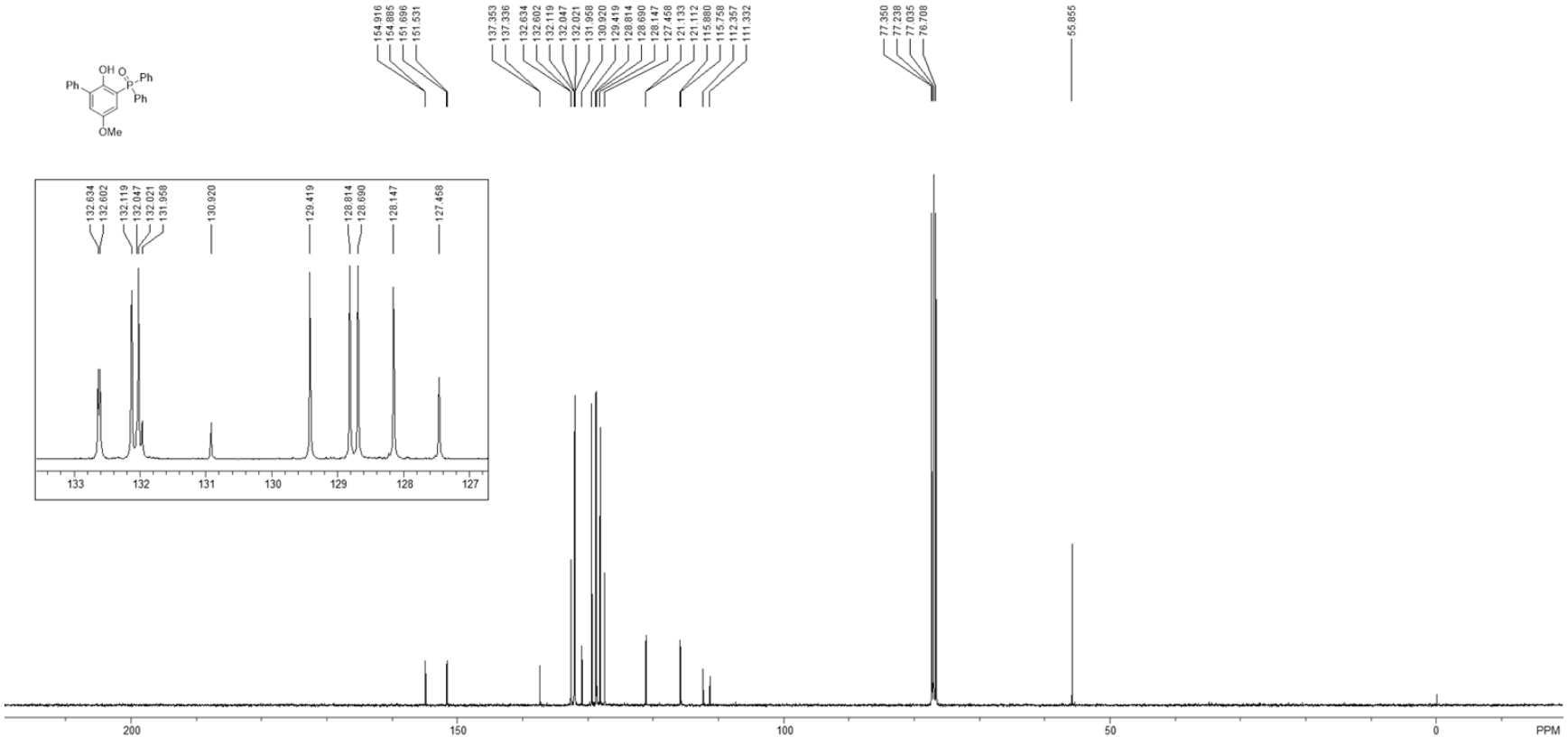
**$^{31}$P NMR of (3-(tert-butyl)-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ca)**



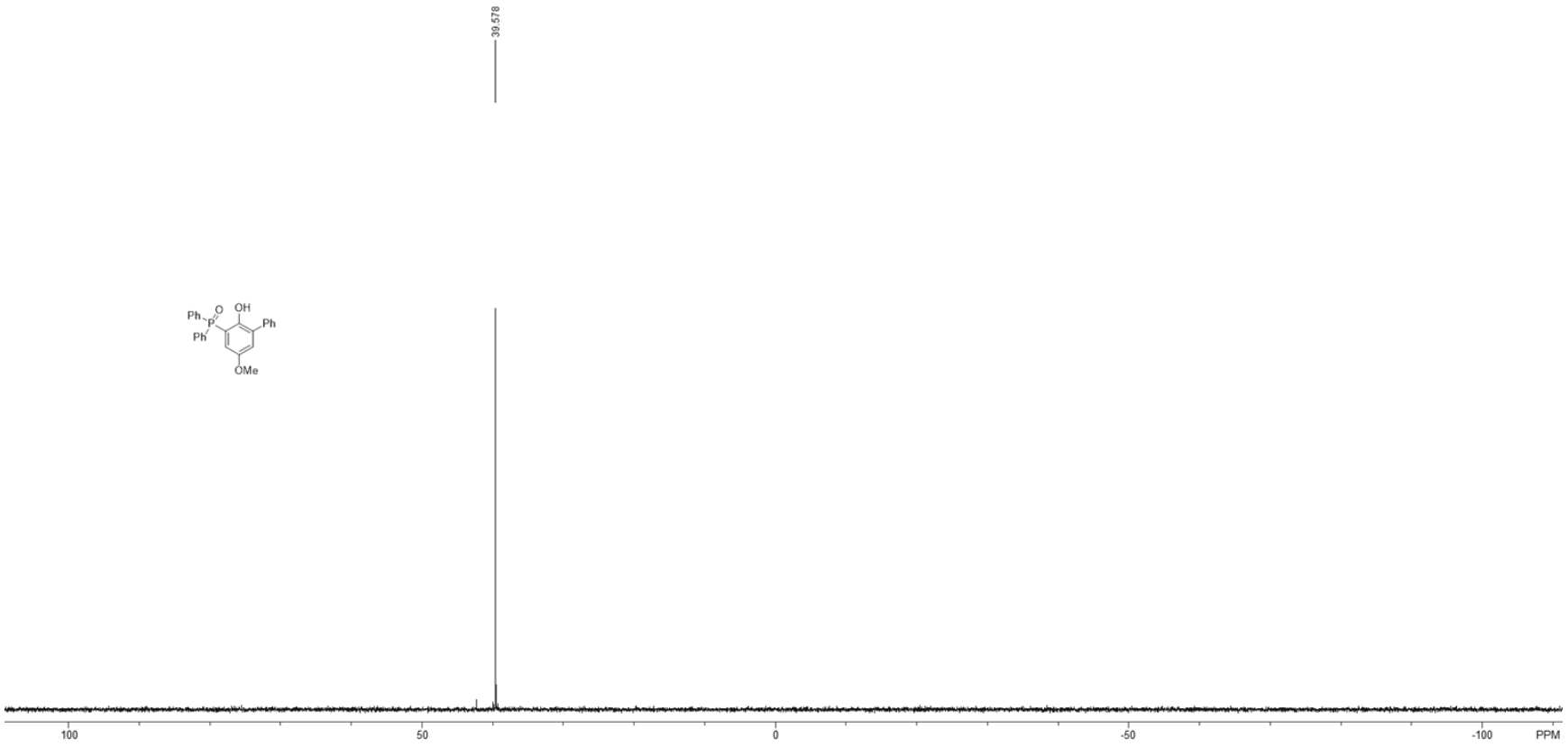
**$^{1}$H NMR of (2-hydroxy-5-methoxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3da)**



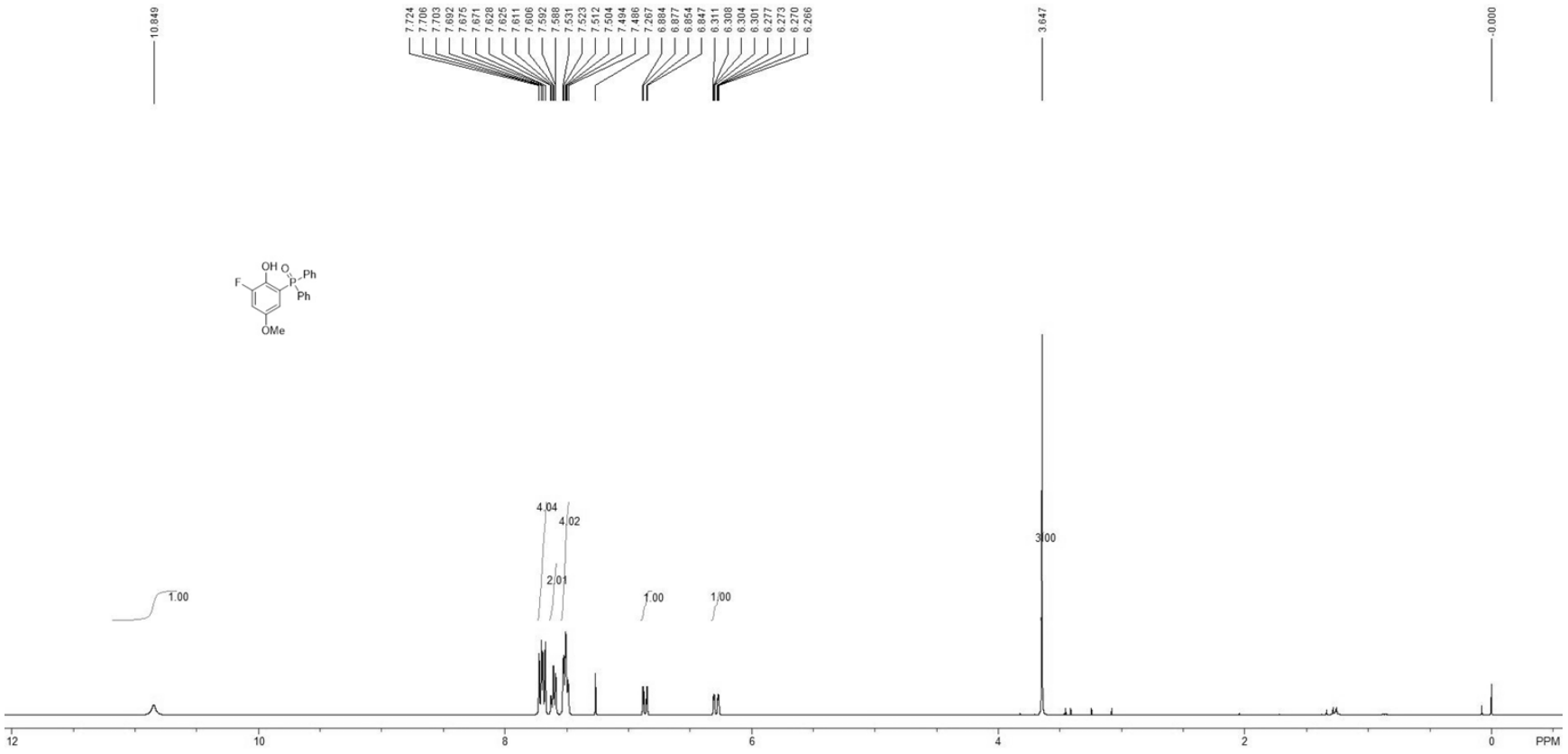
**$^{13}$C NMR of (2-hydroxy-5-methoxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3da)**



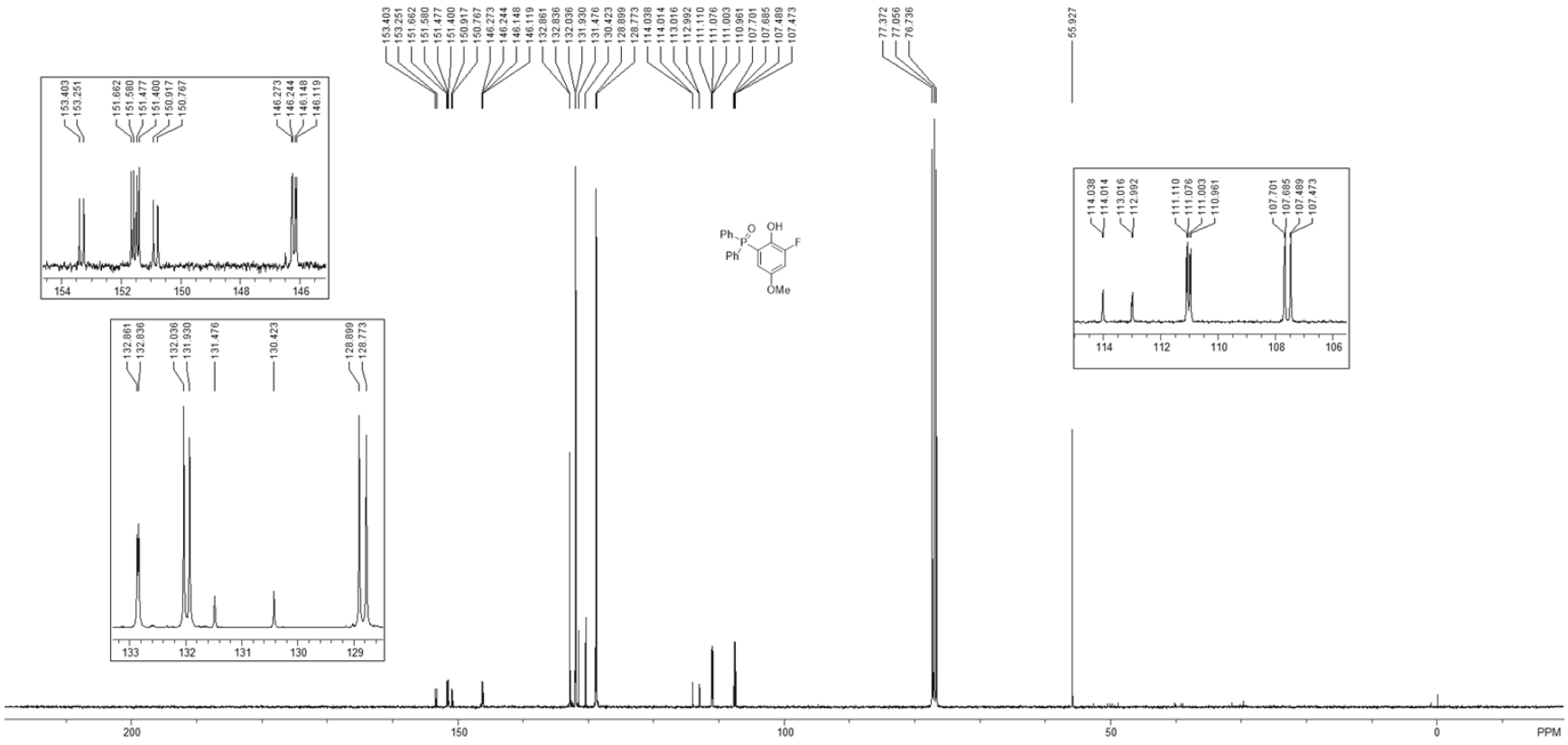
**$^{31}$P NMR of (2-hydroxy-5-methoxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3da)**



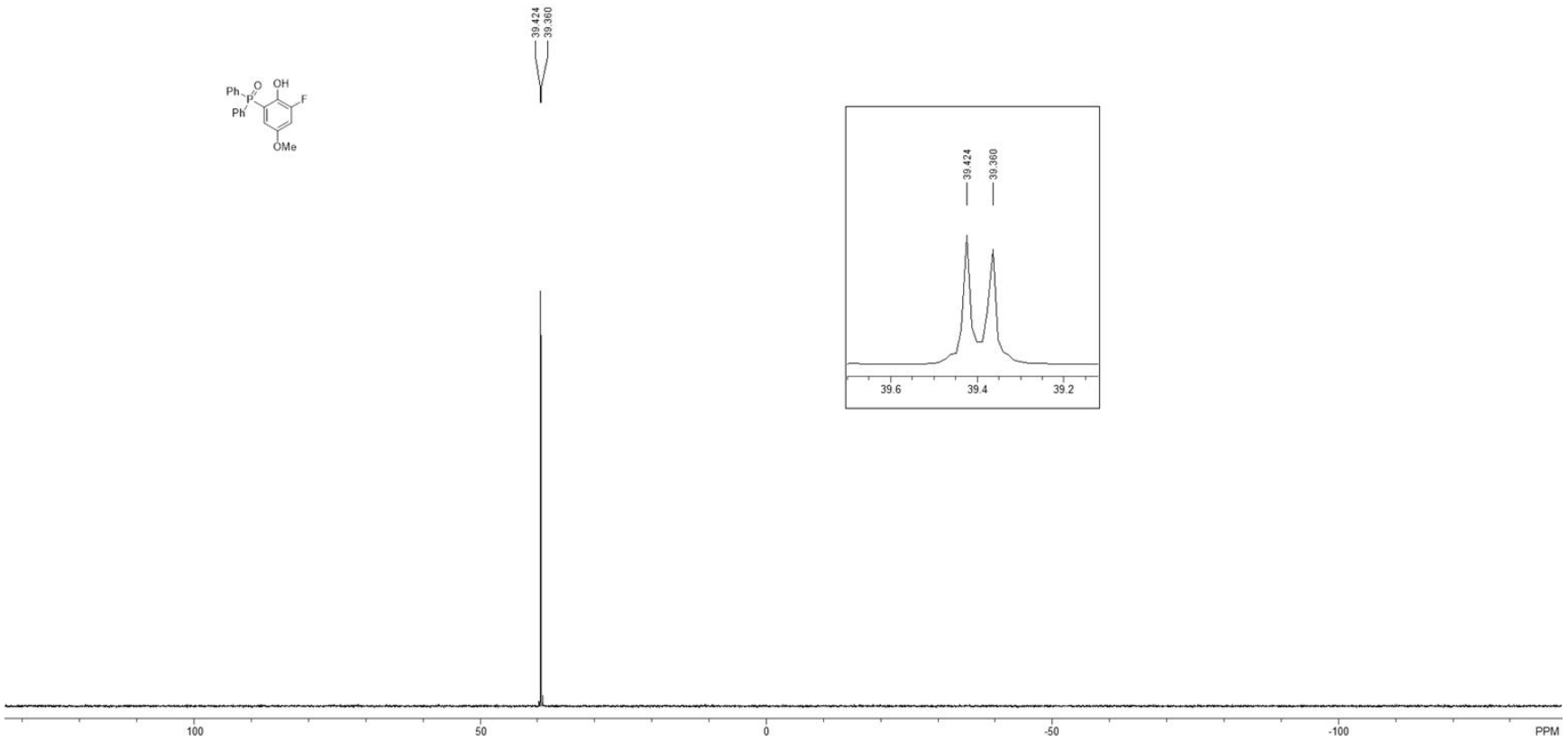
**$^{1}$H NMR of (3-fluoro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ea)**



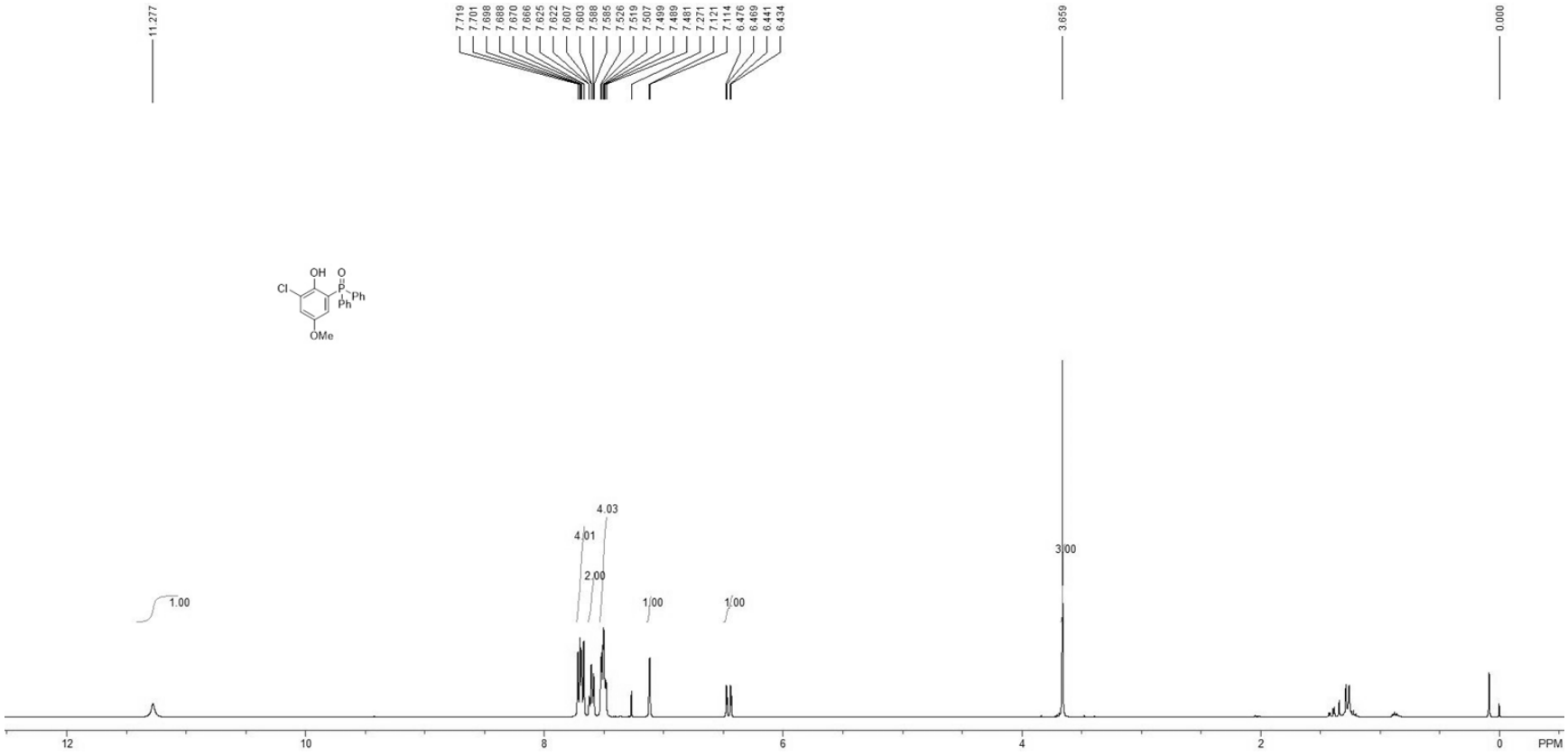
**$^{13}$C NMR of (3-fluoro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ea)**



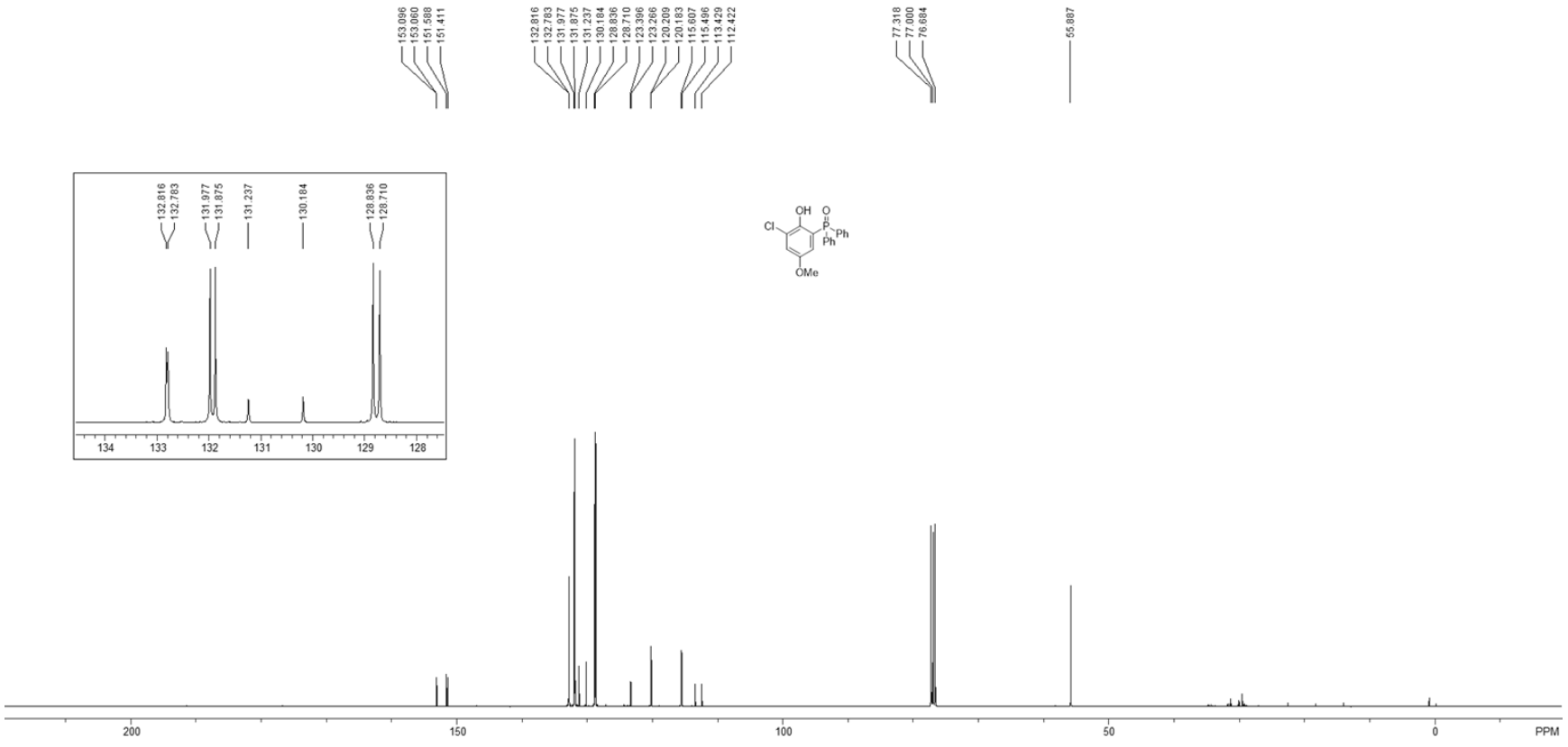
**$^{31}$P NMR of (3-fluoro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ea)**



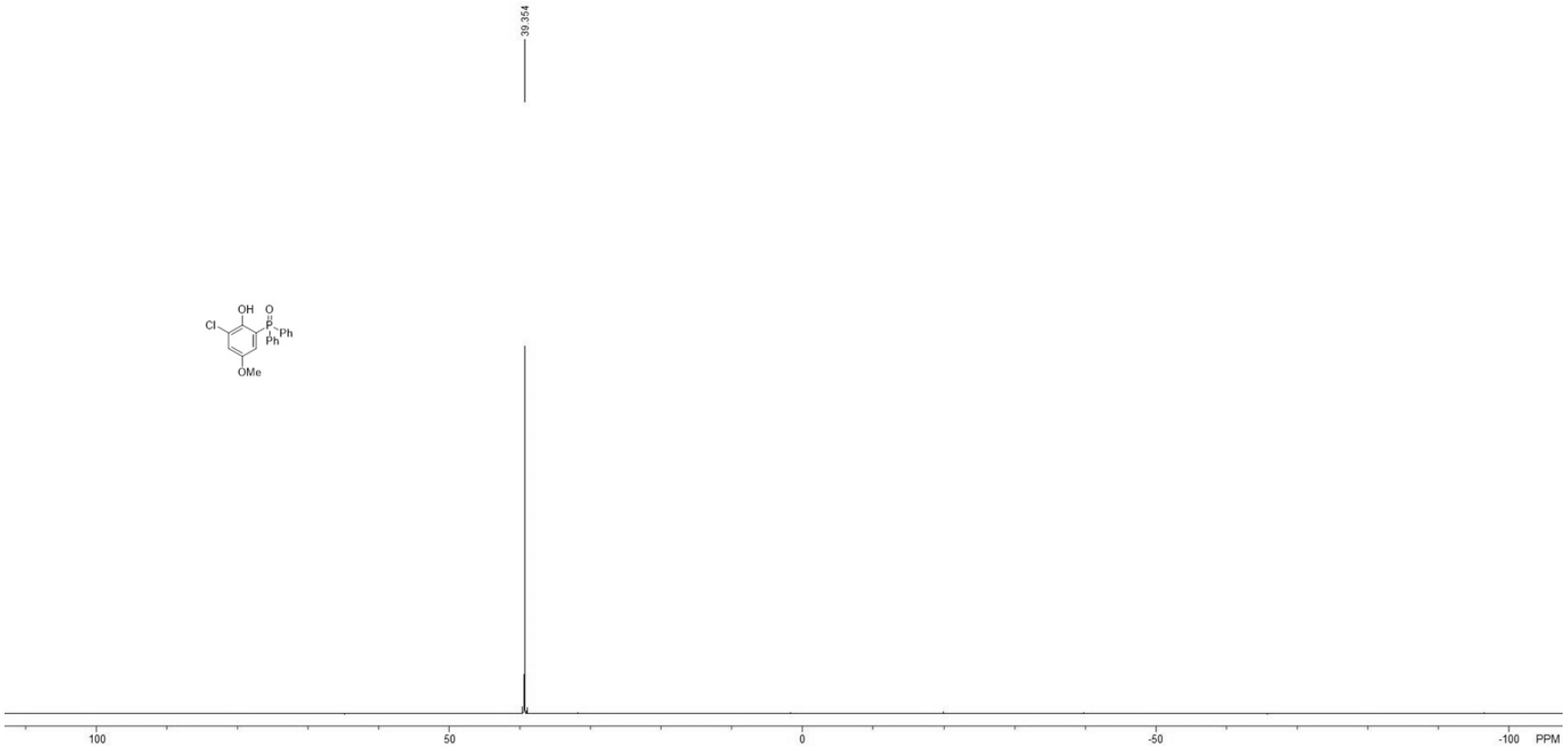
**$^{1}$H NMR of (3-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3fa)**



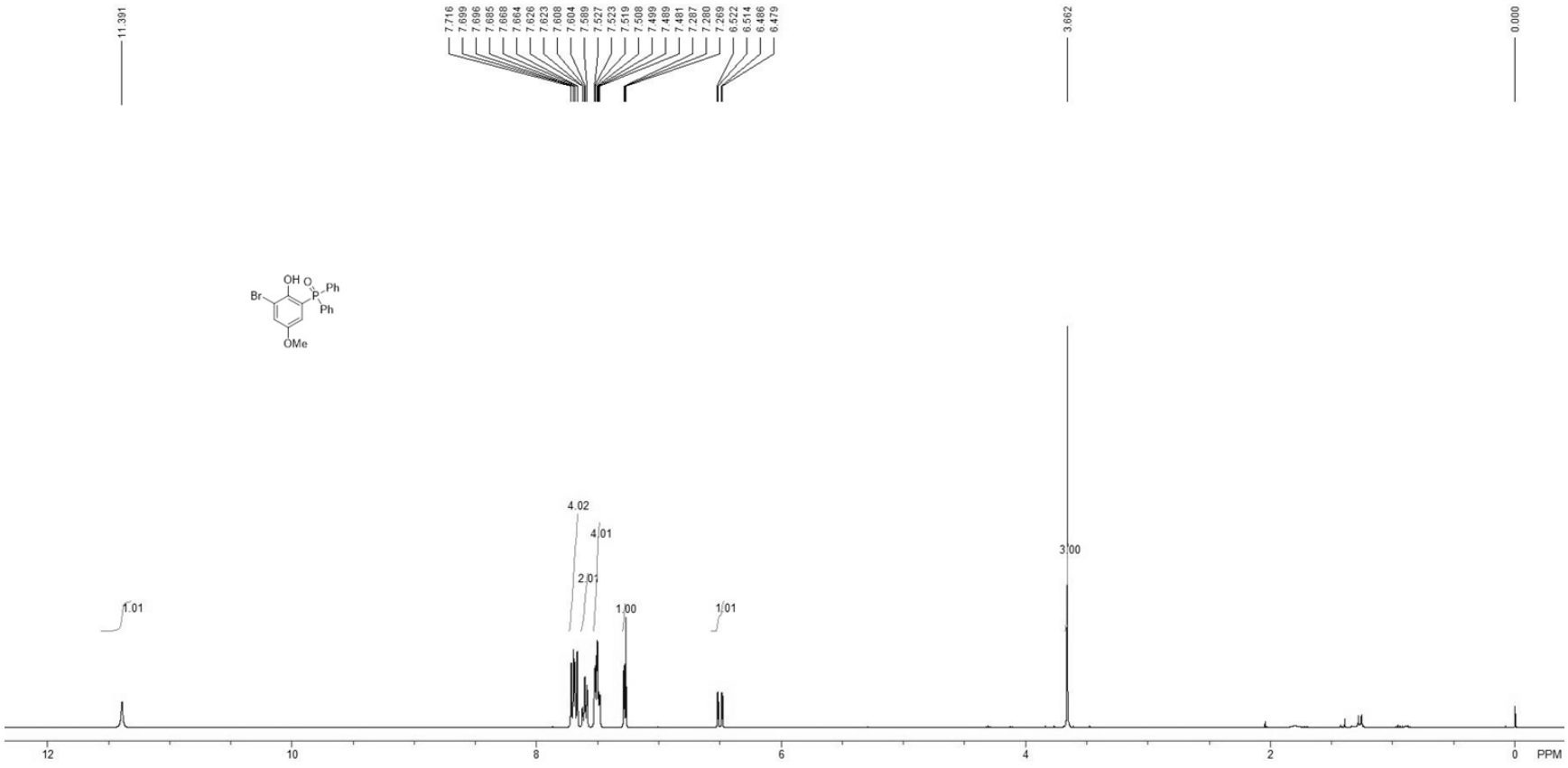
**$^{13}$C NMR of (3-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3fa)**



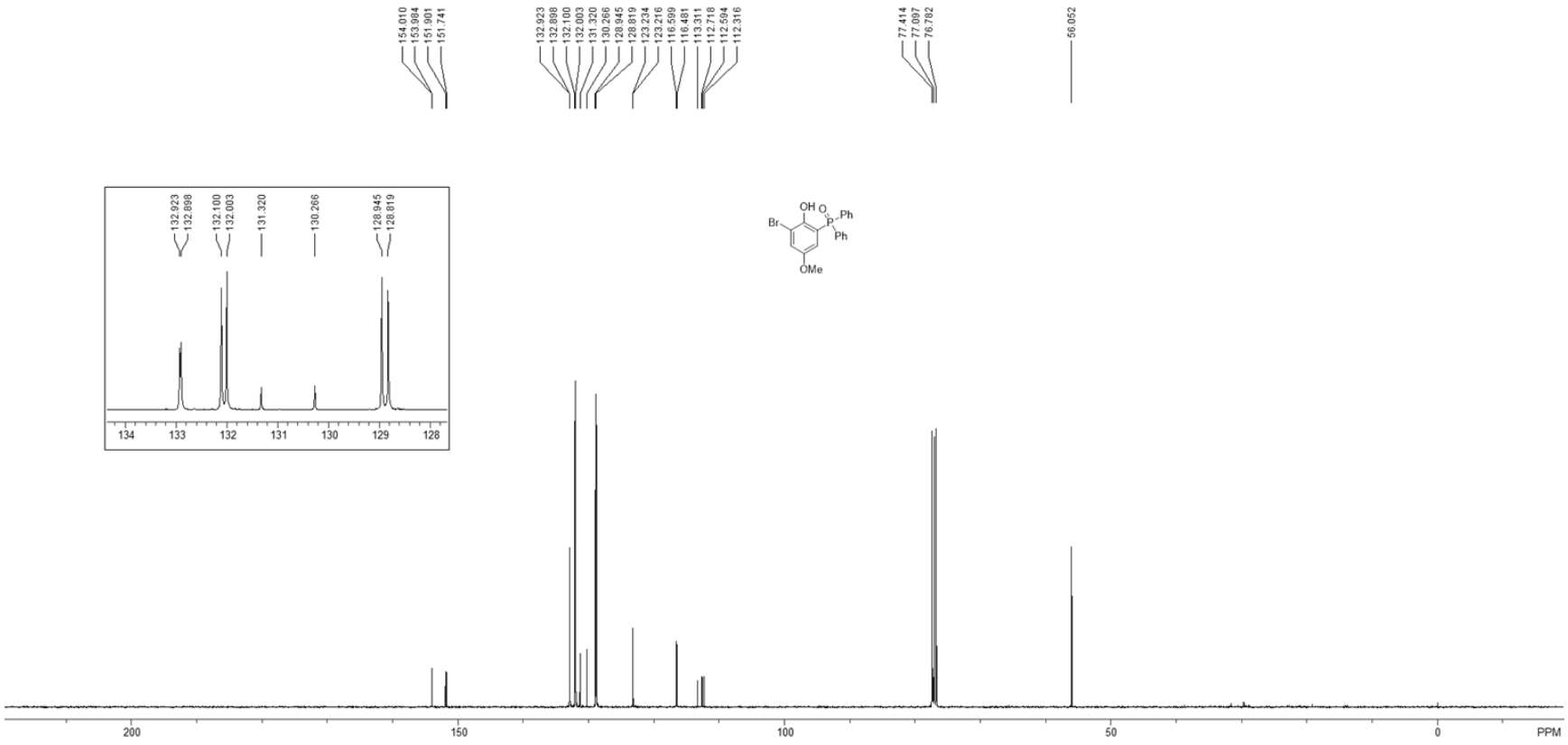
**$^{31}$P NMR of (3-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3fa)**



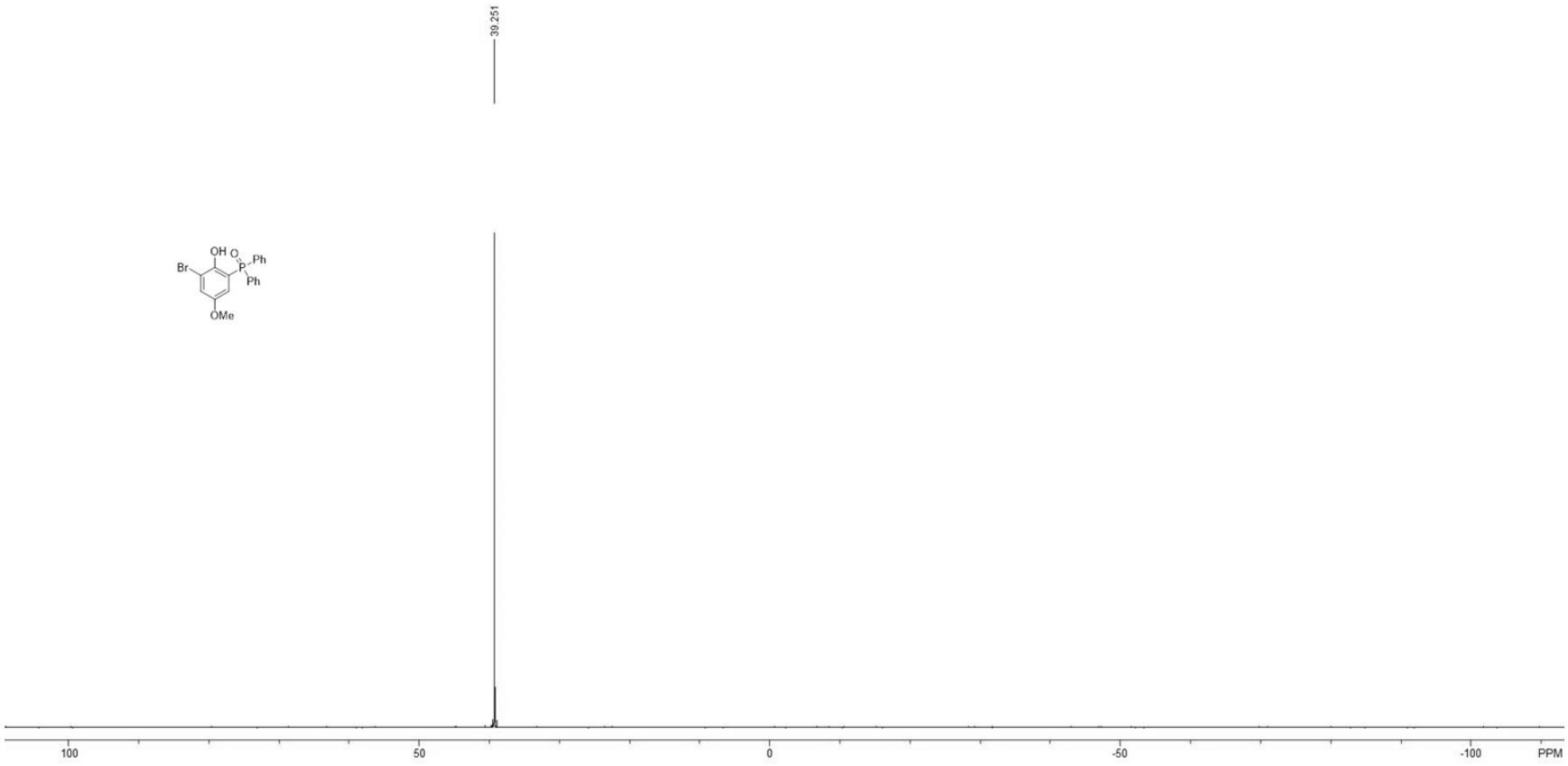
**[1]H NMR of (3-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ga)**



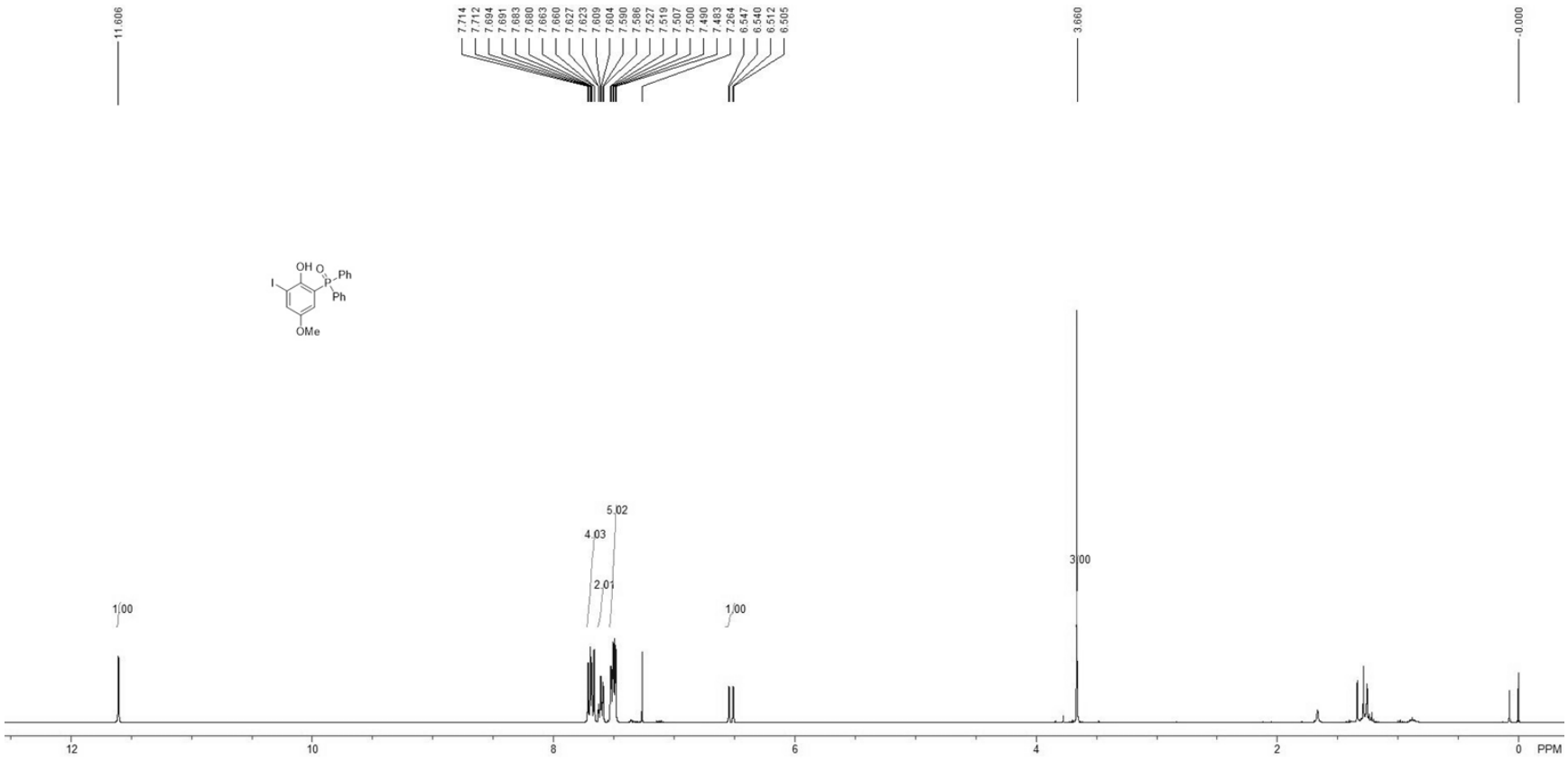
**$^{13}$C NMR of (3-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ga)**



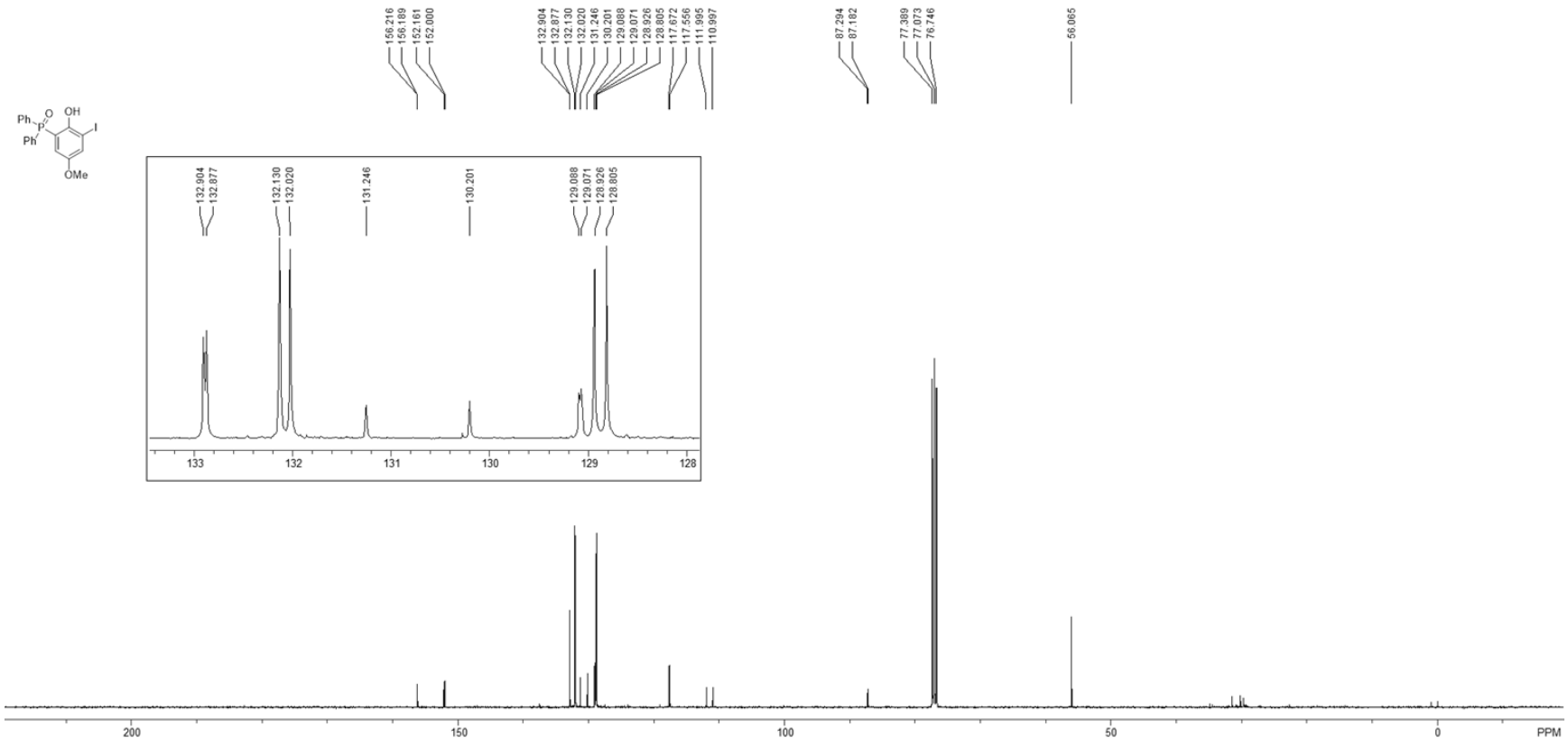
**$^{31}$P NMR of (3-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ga)**



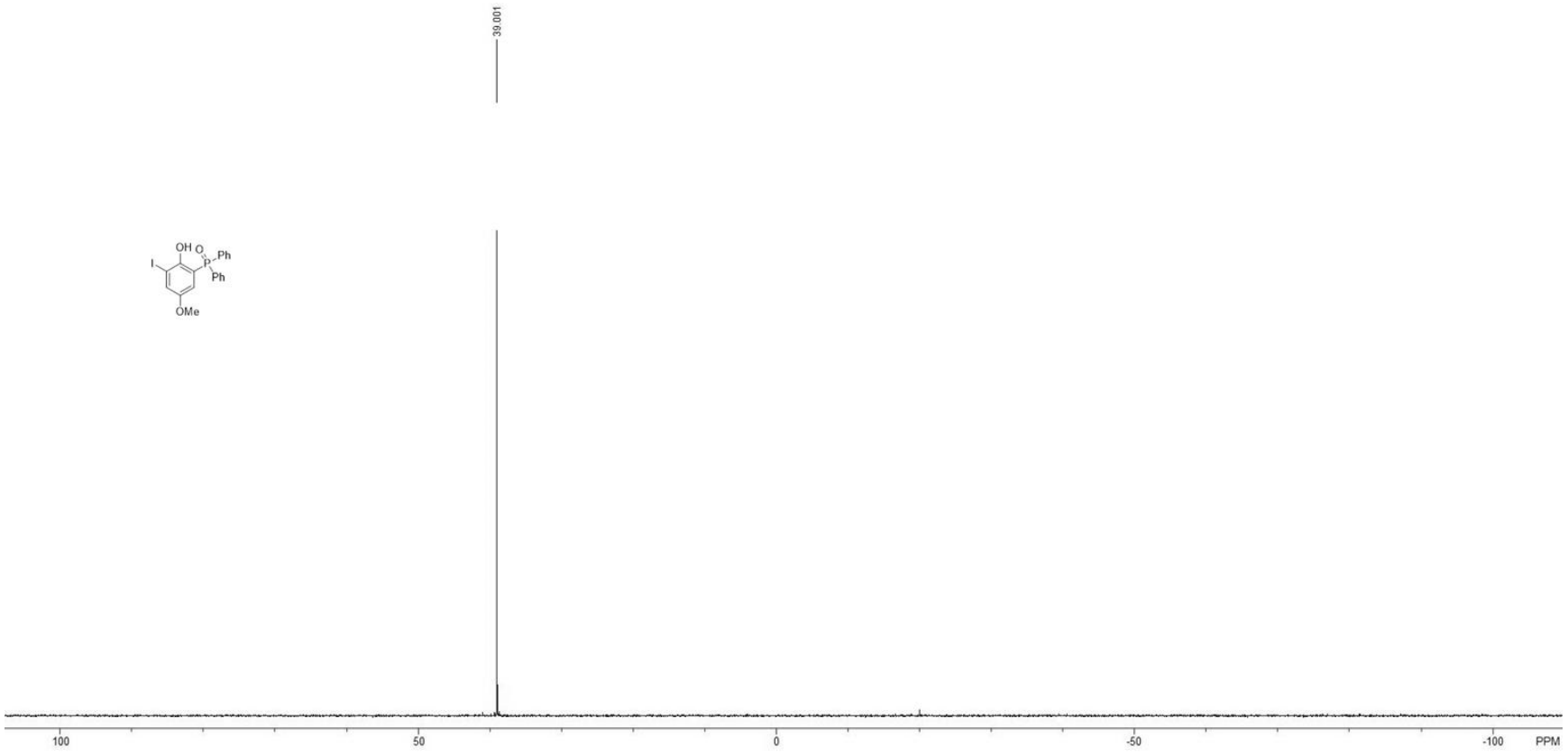
**[1]H NMR of (2-hydroxy-3-iodo-5-methoxyphenyl)diphenylphosphine oxide (3ha)**



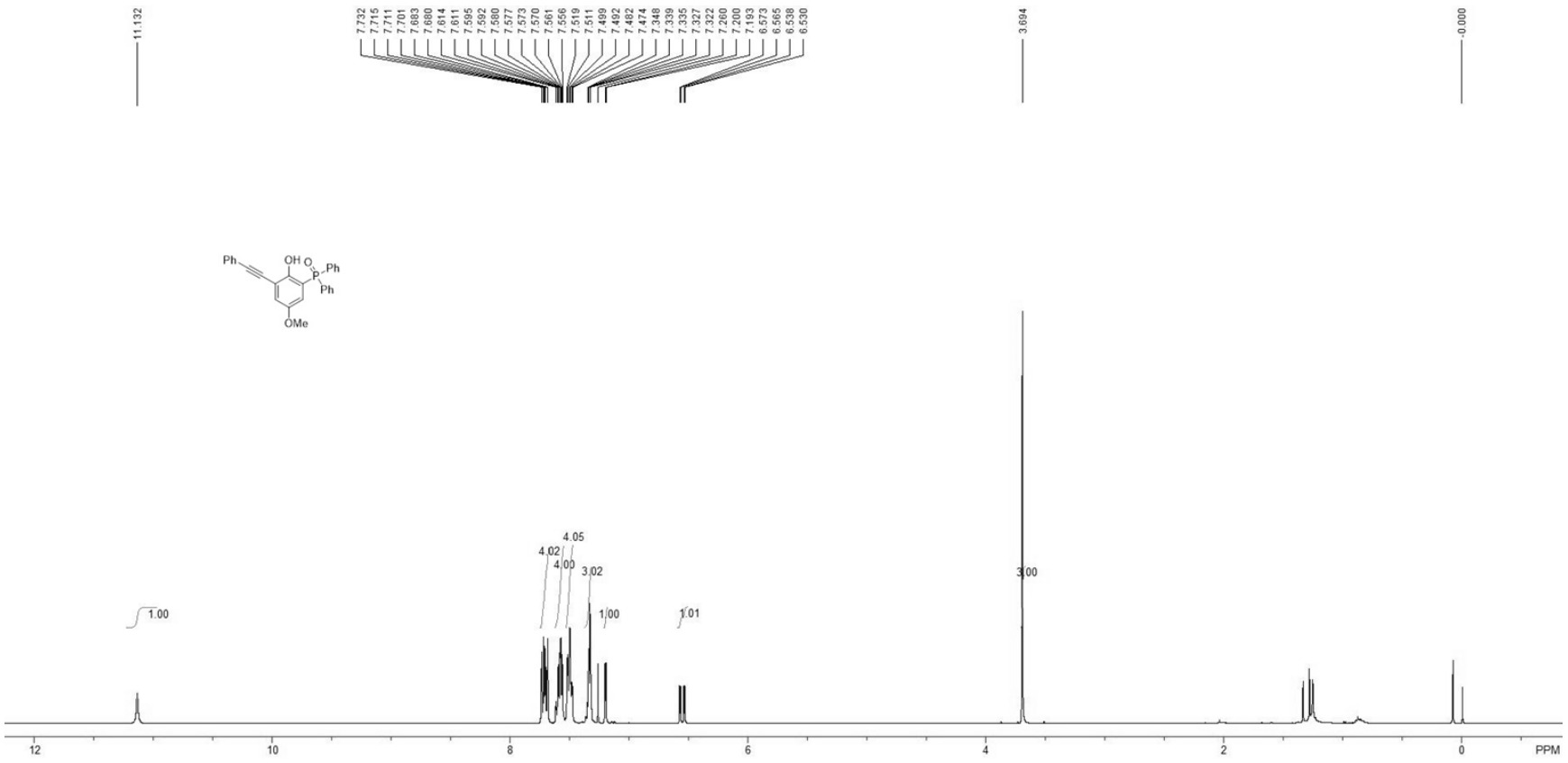
**$^{13}$C NMR of (2-hydroxy-3-iodo-5-methoxyphenyl)diphenylphosphine oxide (3ha)**



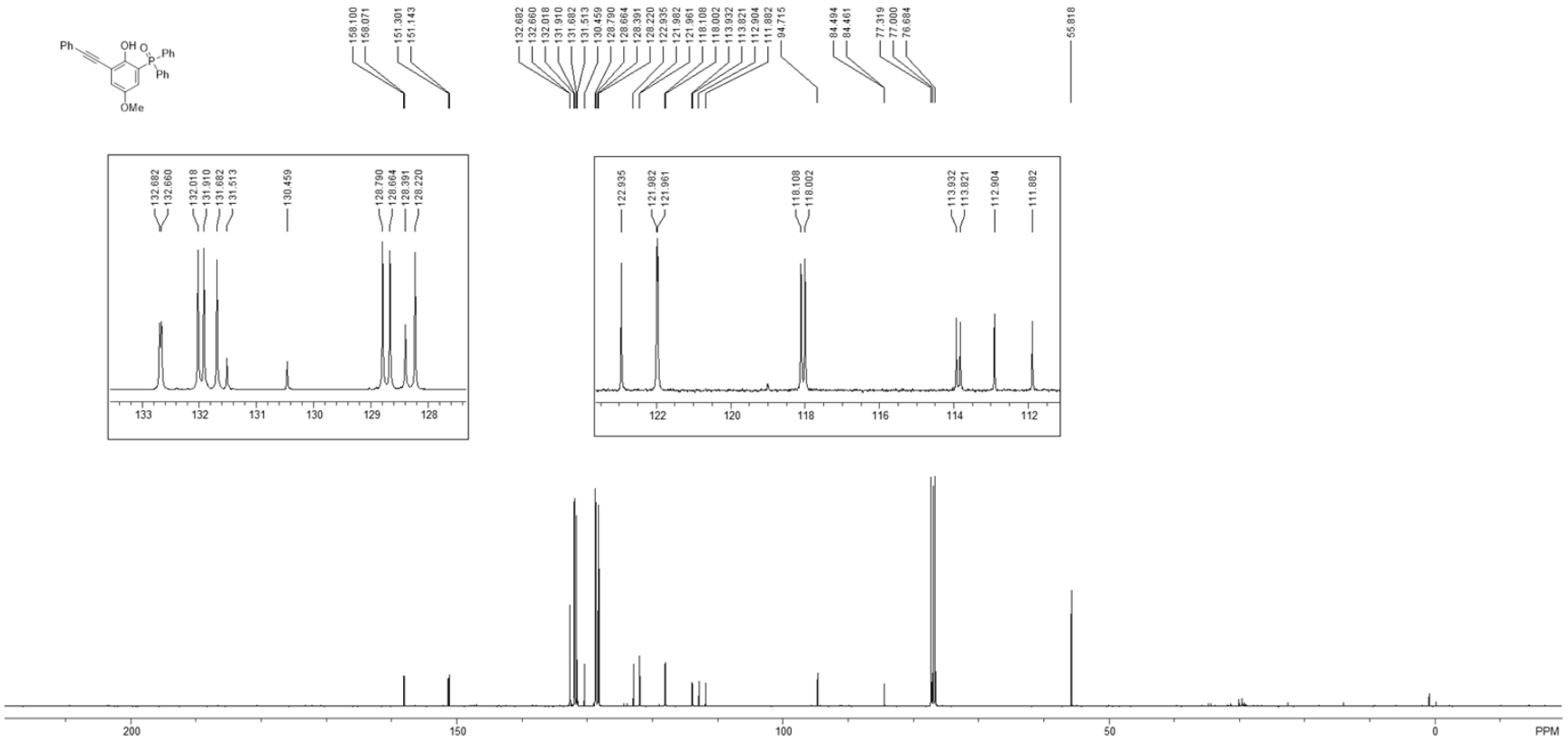
**$^{31}$P NMR of (2-hydroxy-3-iodo-5-methoxyphenyl)diphenylphosphine oxide (3ha)**



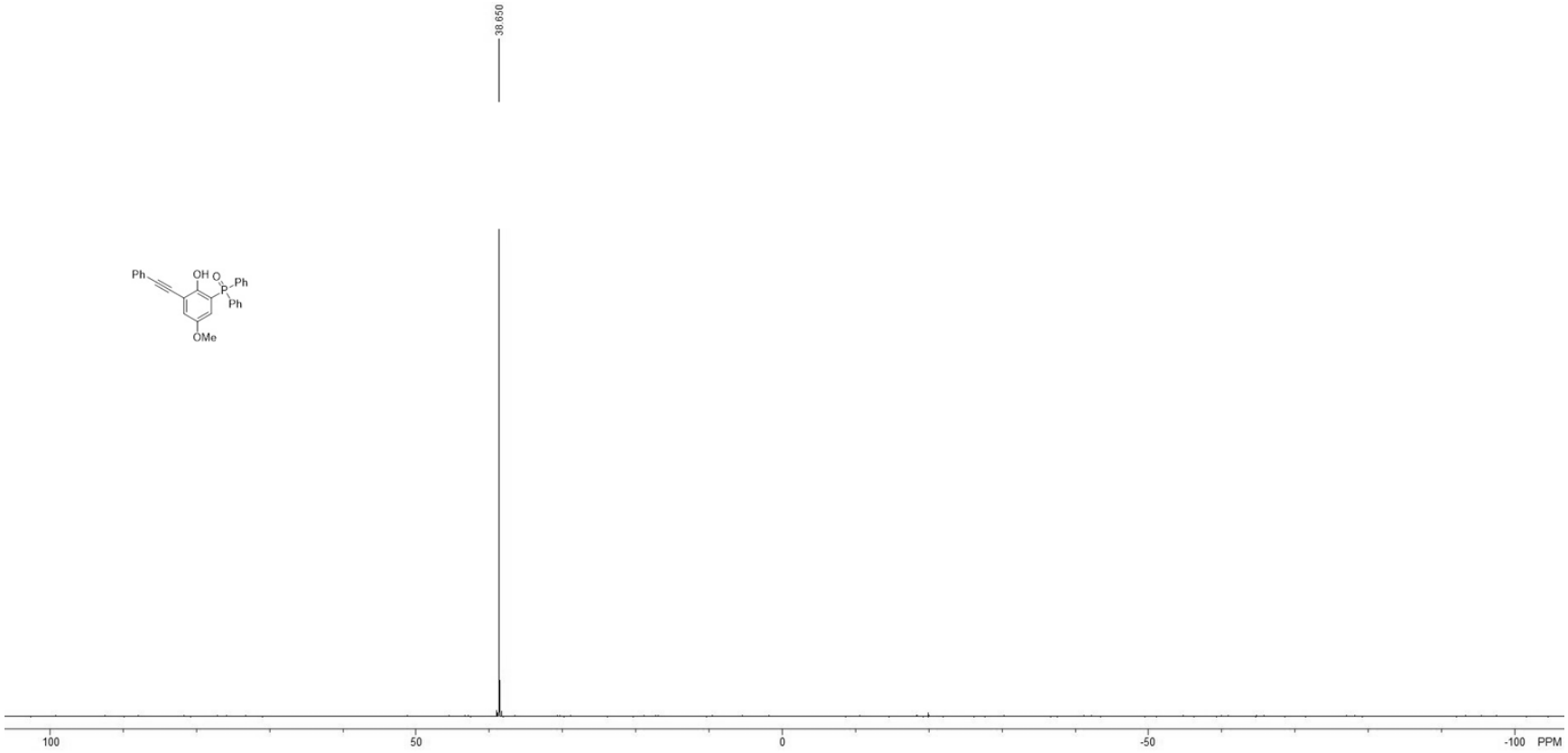
**$^{1}$H NMR of (2-hydroxy-5-methoxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (3ia)**



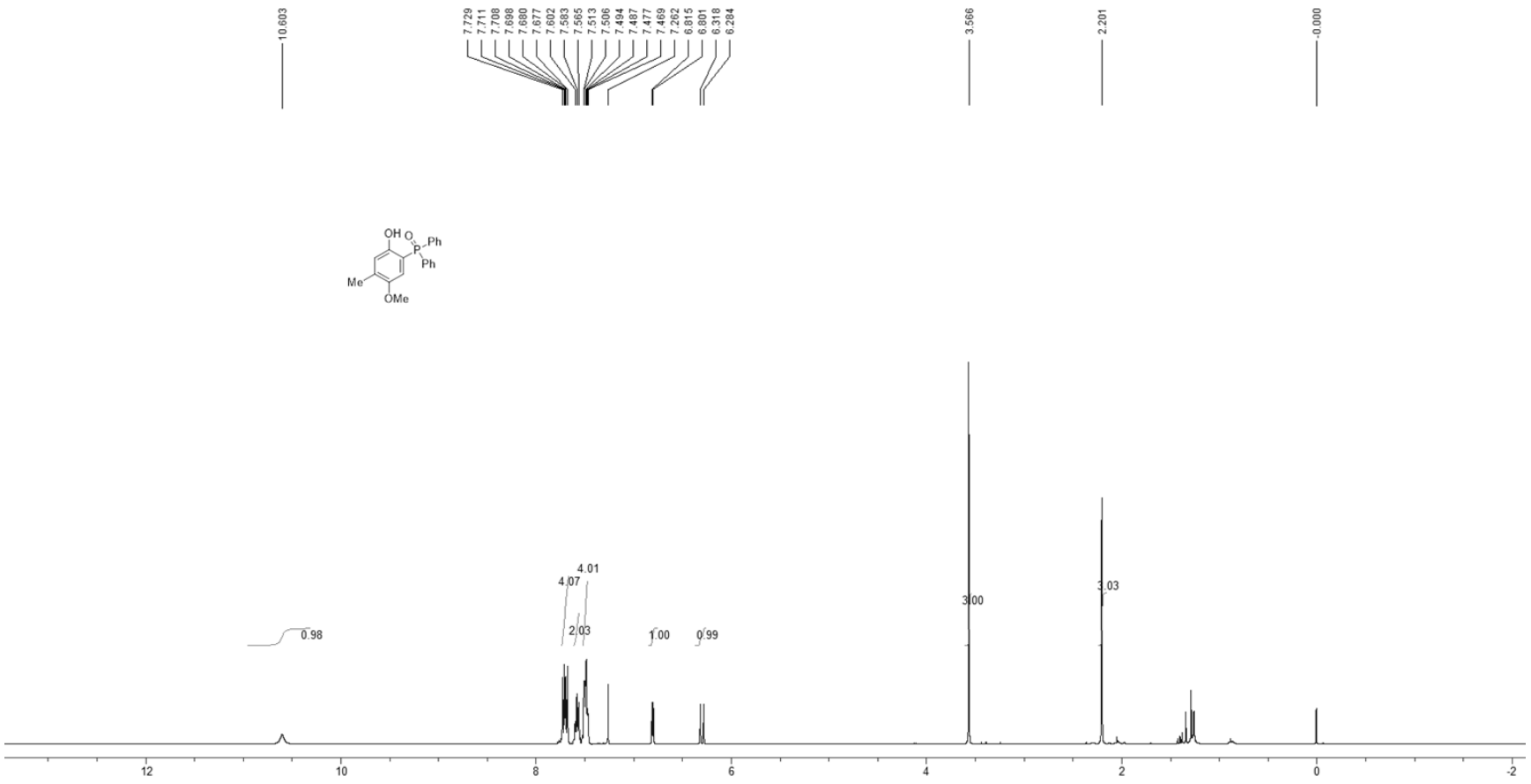
**$^{13}$C NMR of (2-hydroxy-5-methoxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (3ia)**



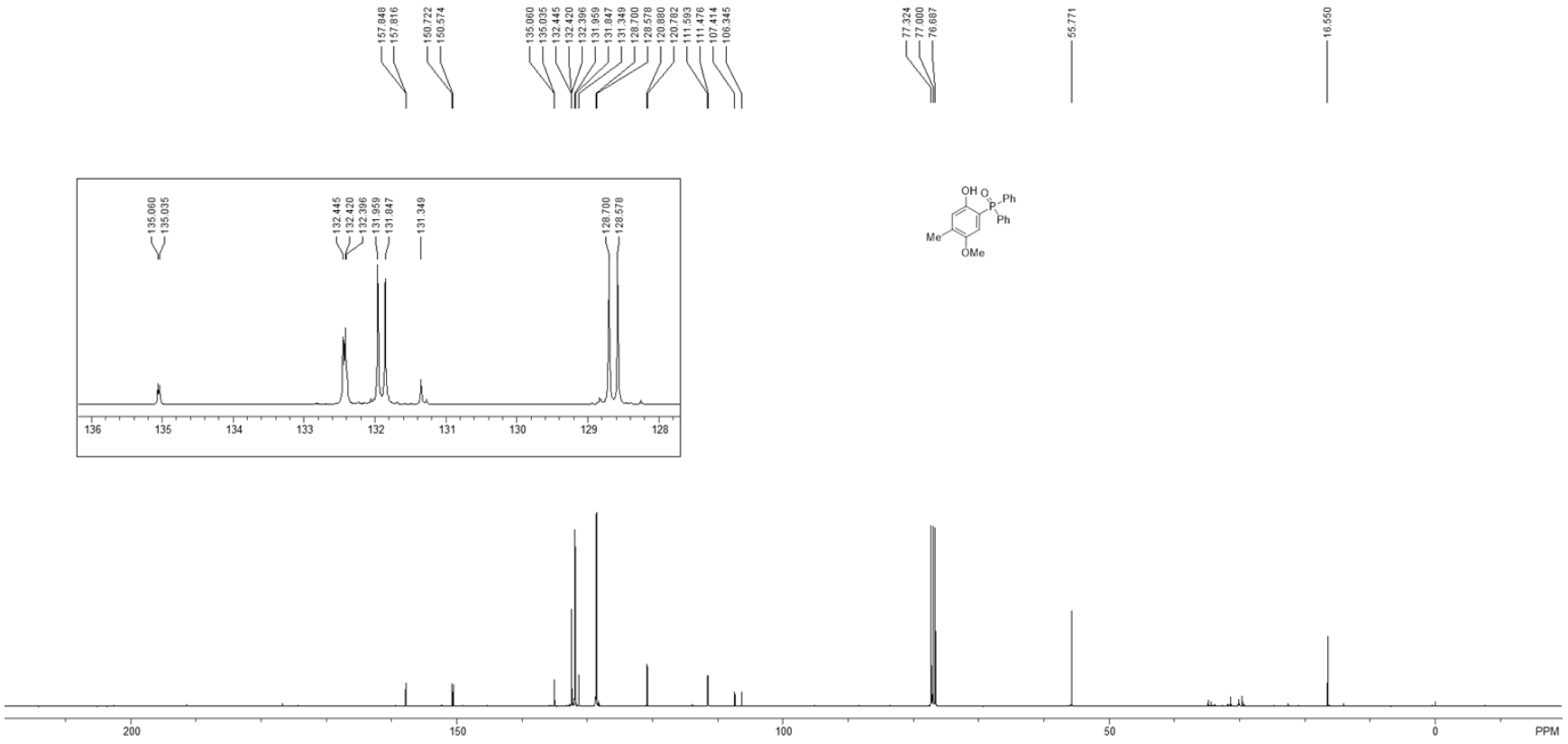
**$^{31}$P NMR of (2-hydroxy-5-methoxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (3ia)**



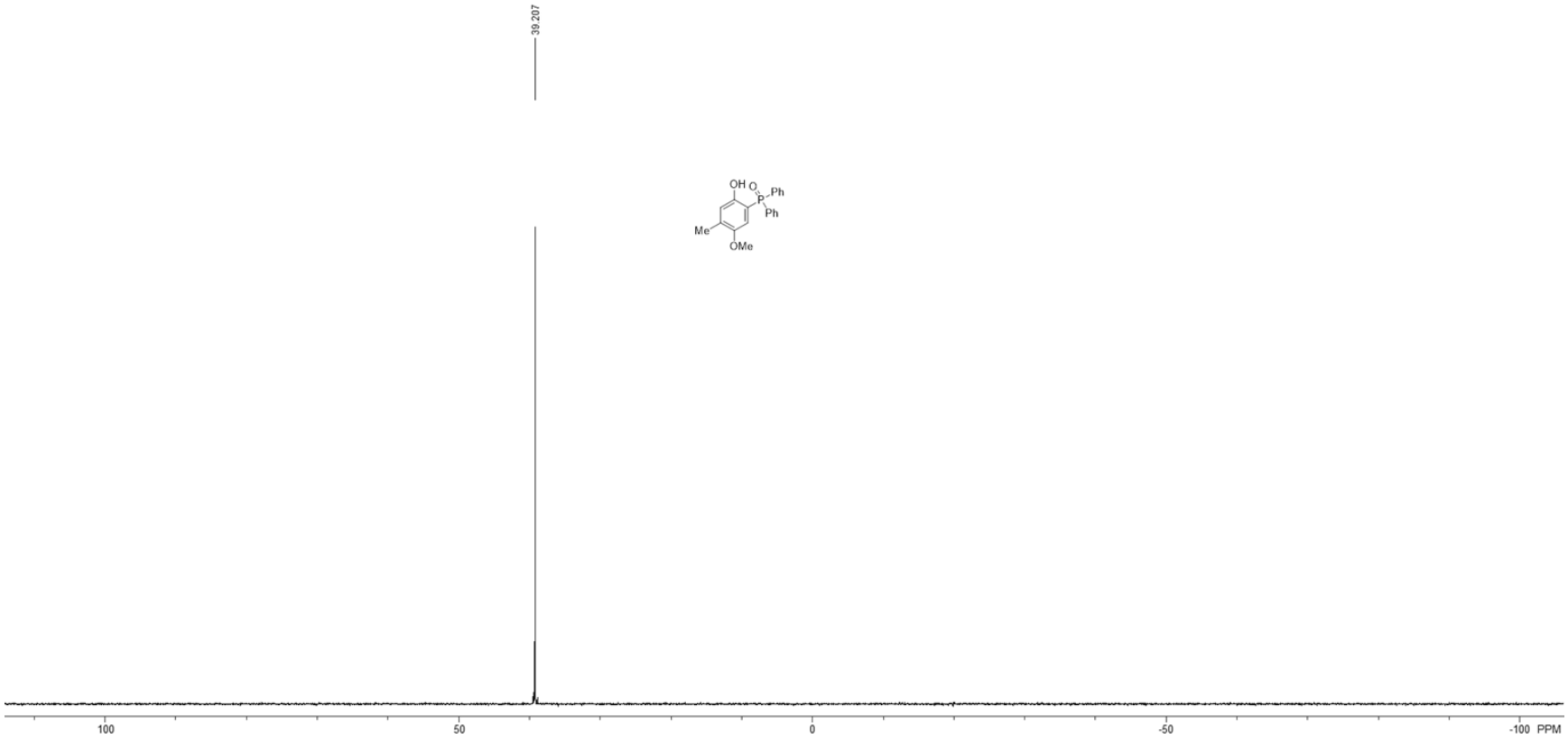
**[1]H NMR of (2-hydroxy-5-methoxy-4-methylphenyl)diphenylphosphine oxide (3ja)**



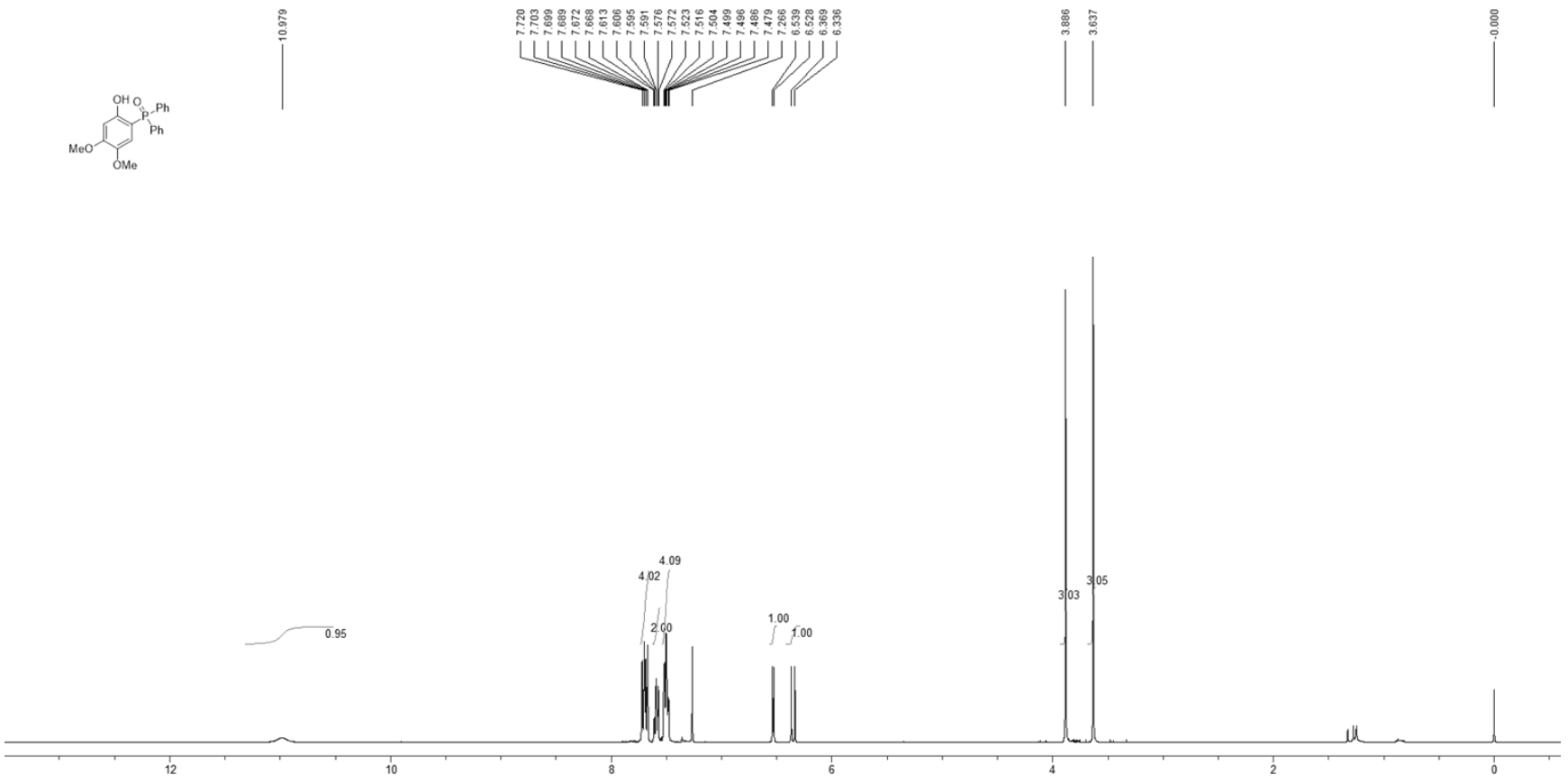
**$^{13}$C NMR of (2-hydroxy-5-methoxy-4-methylphenyl)diphenylphosphine oxide (3ja)**



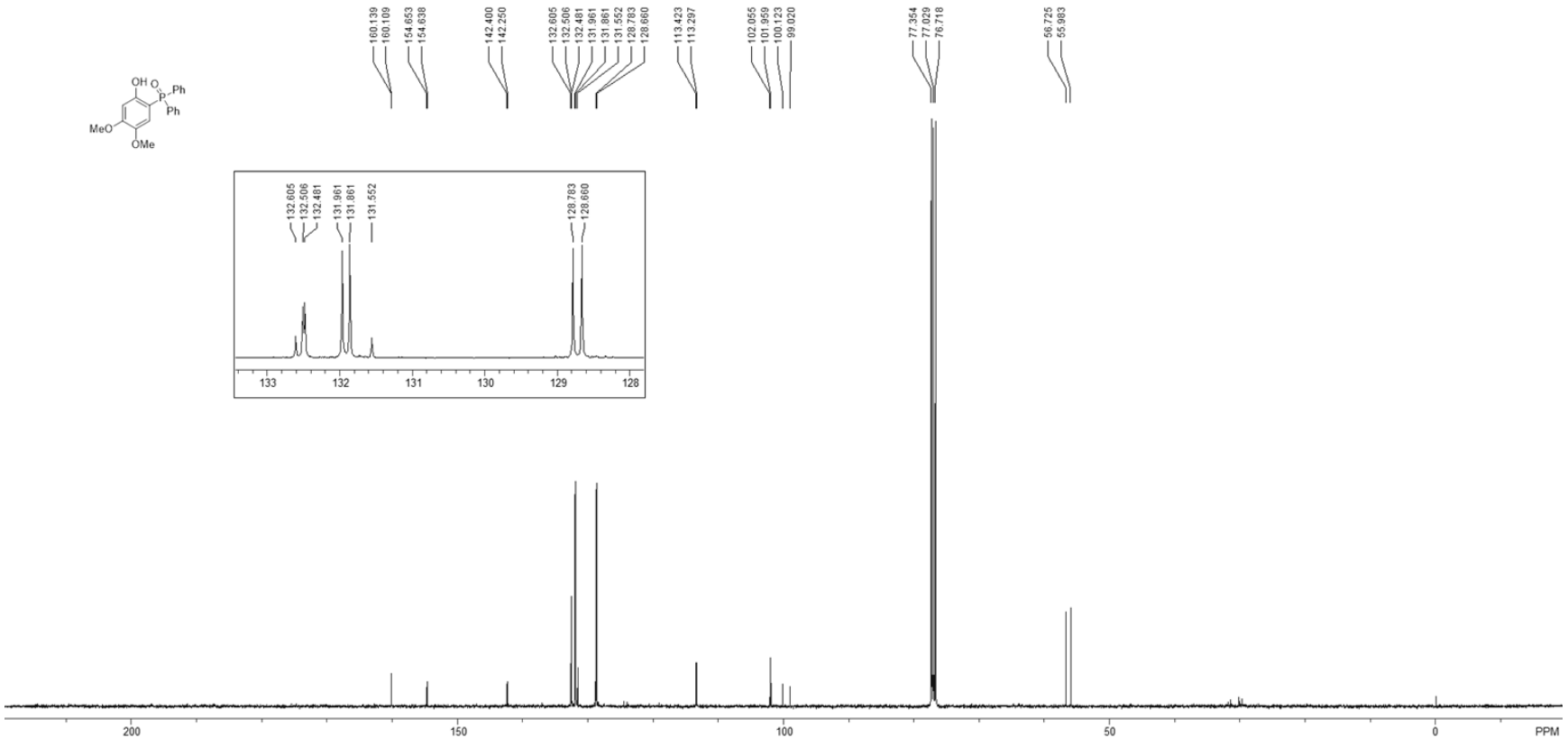
**$^{31}$P NMR of (2-hydroxy-5-methoxy-4-methylphenyl)diphenylphosphine oxide (3ja)**



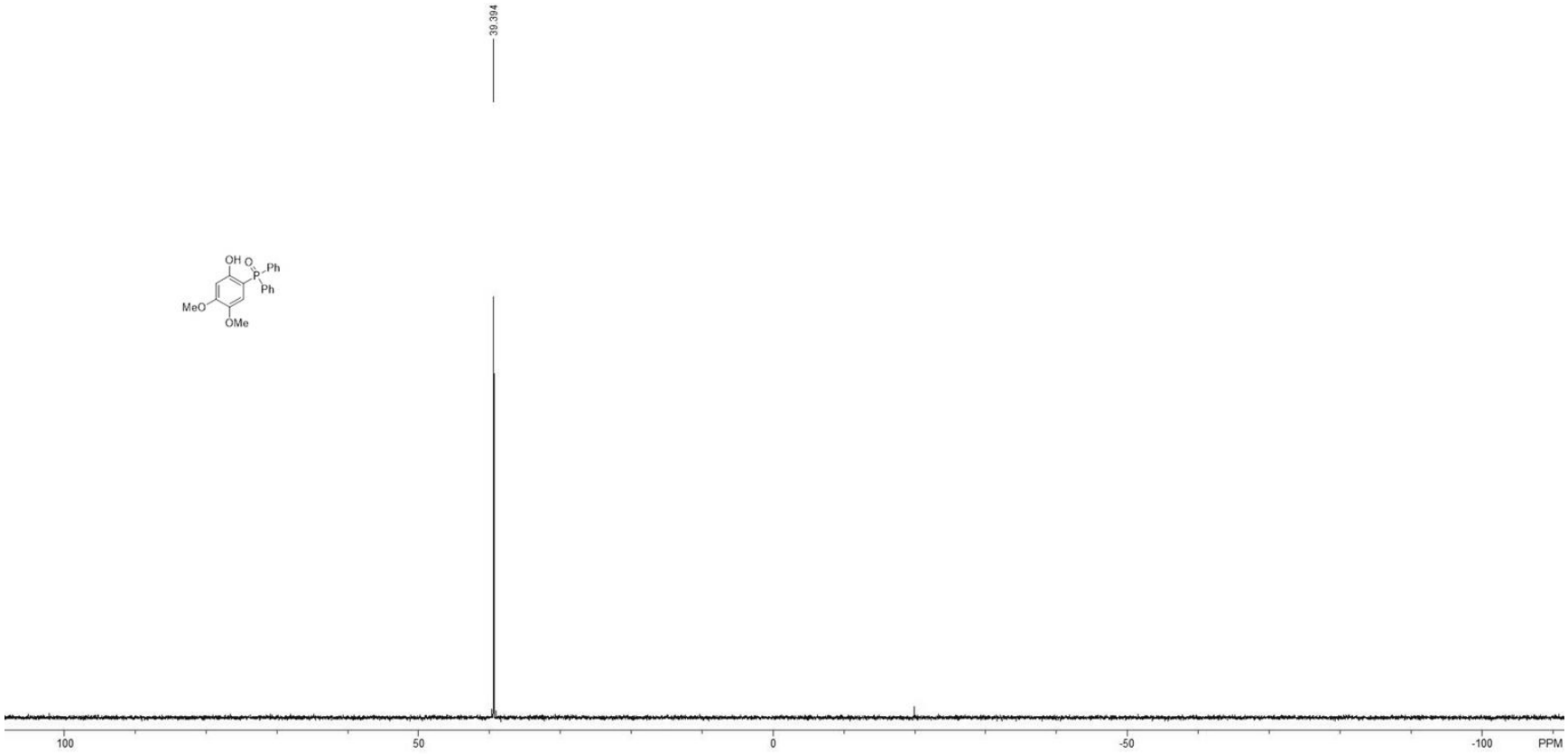
**$^{1}$H NMR of (2-hydroxy-4,5-dimethoxyphenyl)diphenylphosphine oxide (3ka)**



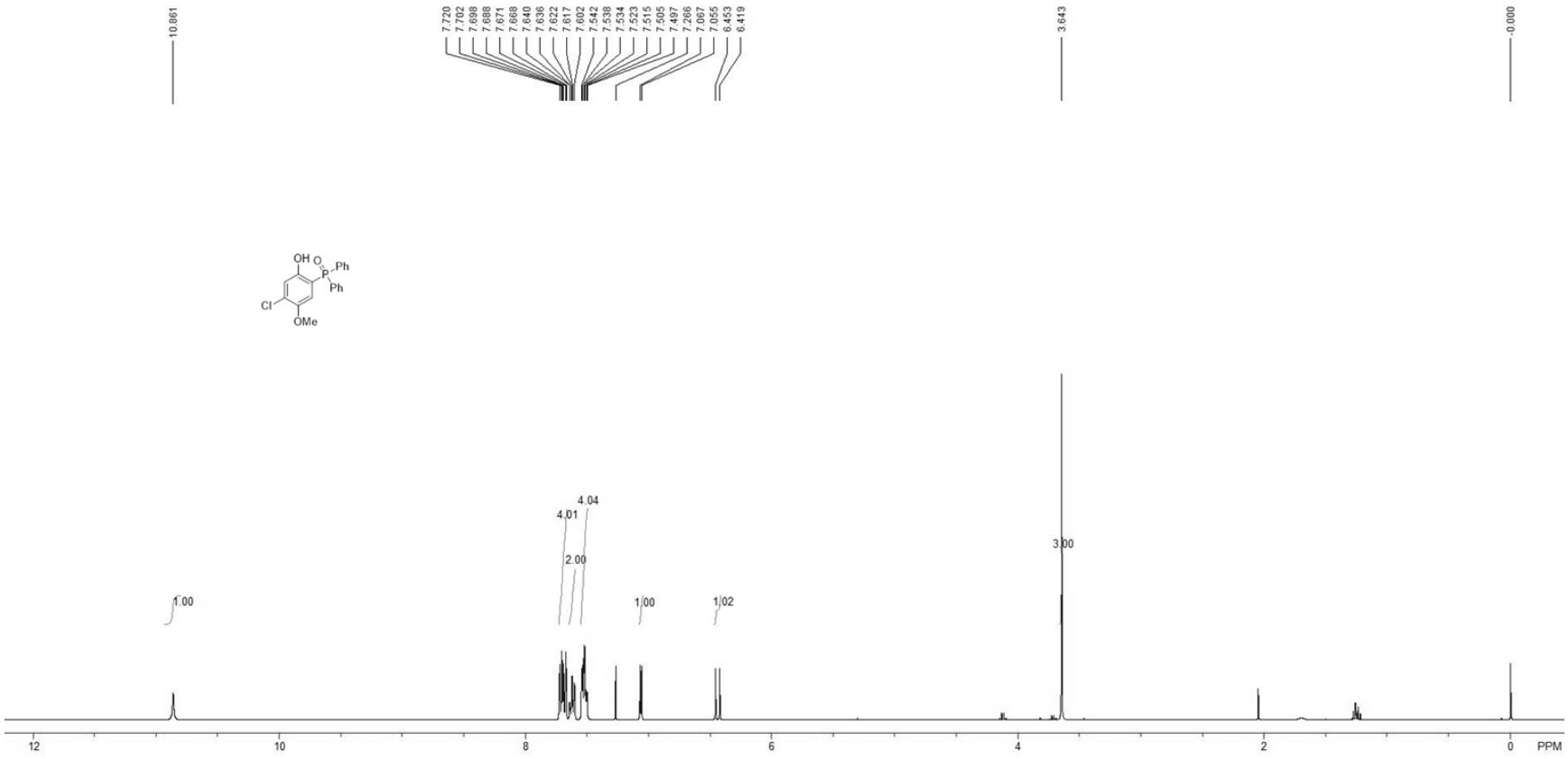
**$^{13}$C NMR of (2-hydroxy-4,5-dimethoxyphenyl)diphenylphosphine oxide (3ka)**



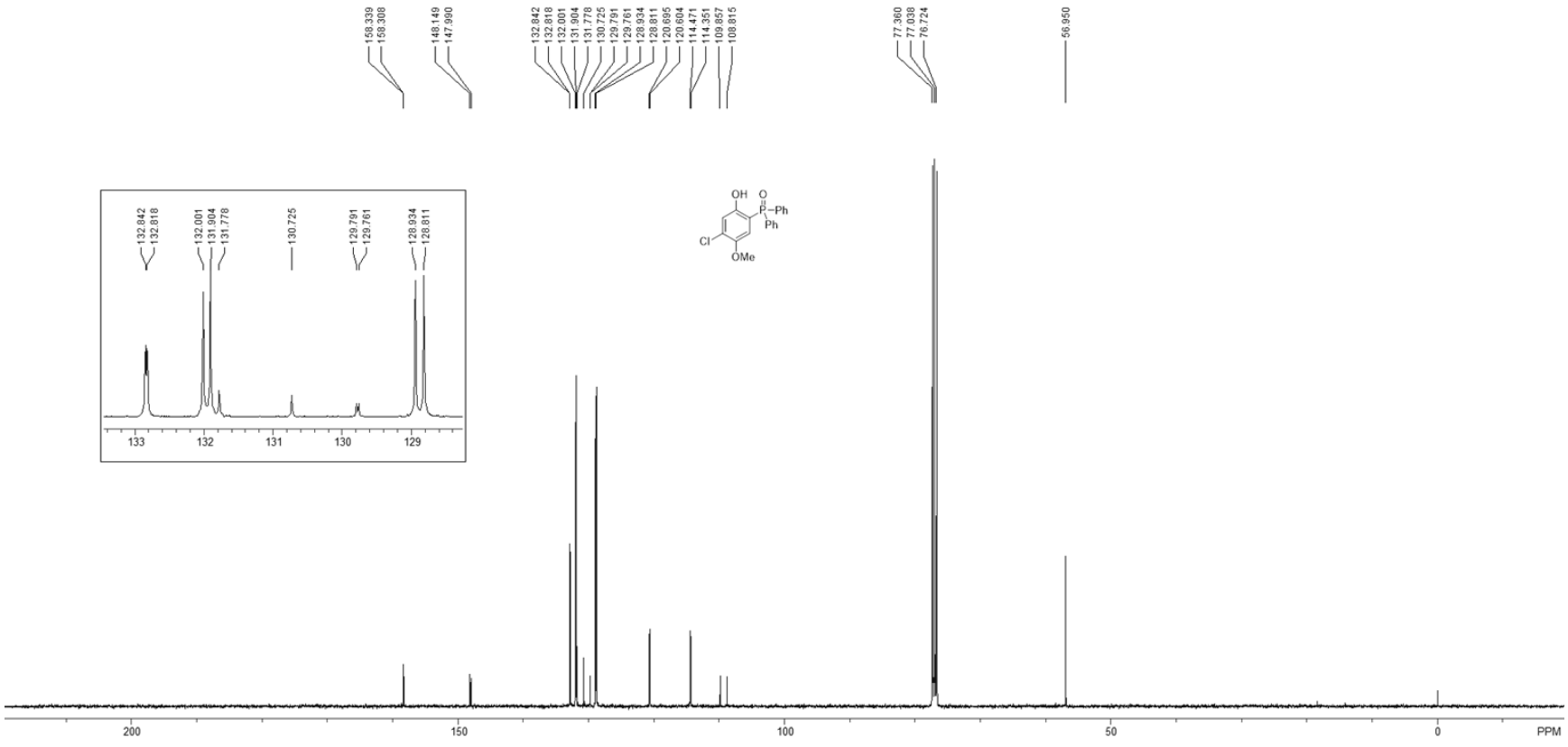
**$^{31}$P NMR of (2-hydroxy-4,5-dimethoxyphenyl)diphenylphosphine oxide (3ka)**



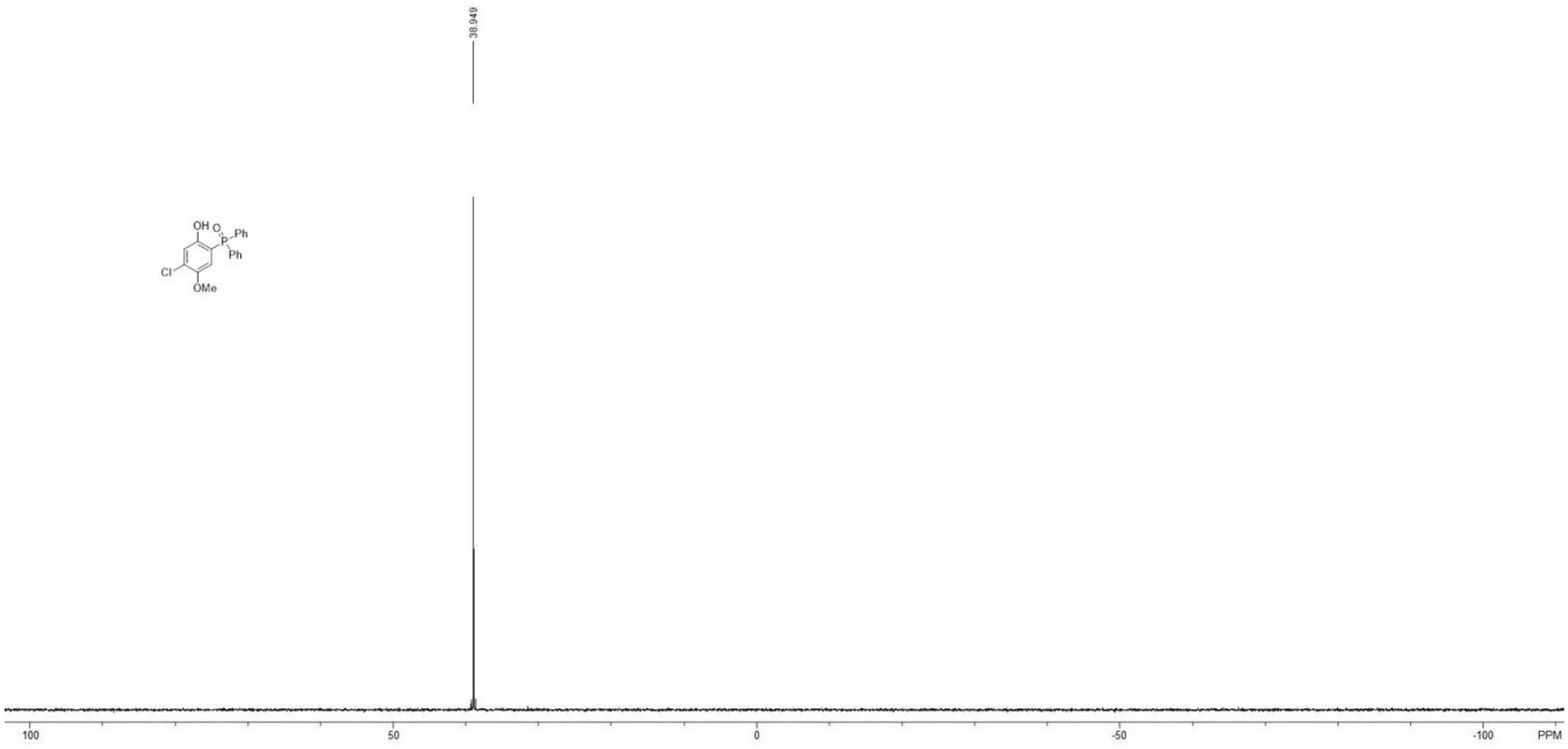
**$^{1}$H NMR of (4-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3la)**



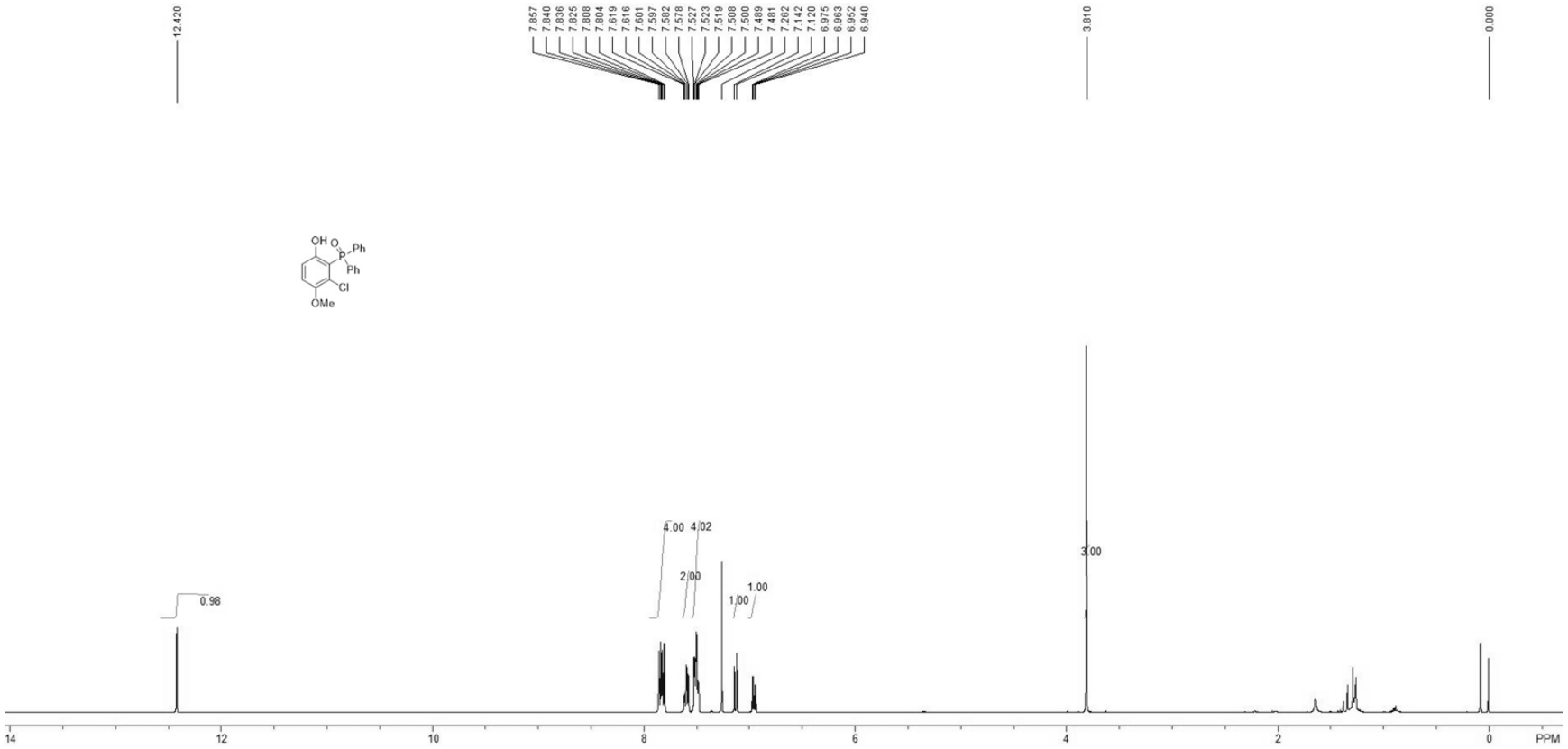
**$^{13}$C NMR of (4-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3la)**



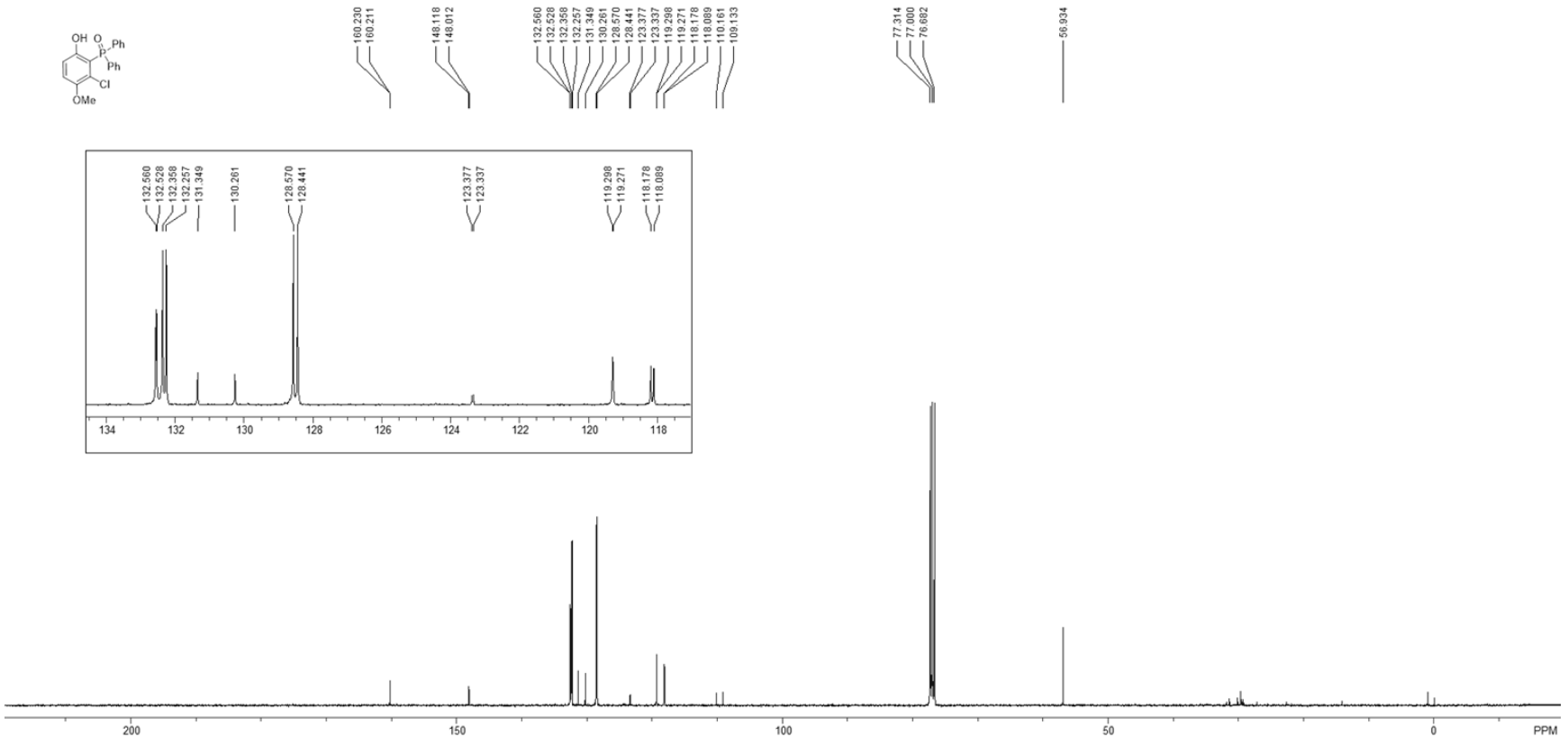
**$^{31}$P NMR of (4-chloro-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3la)**



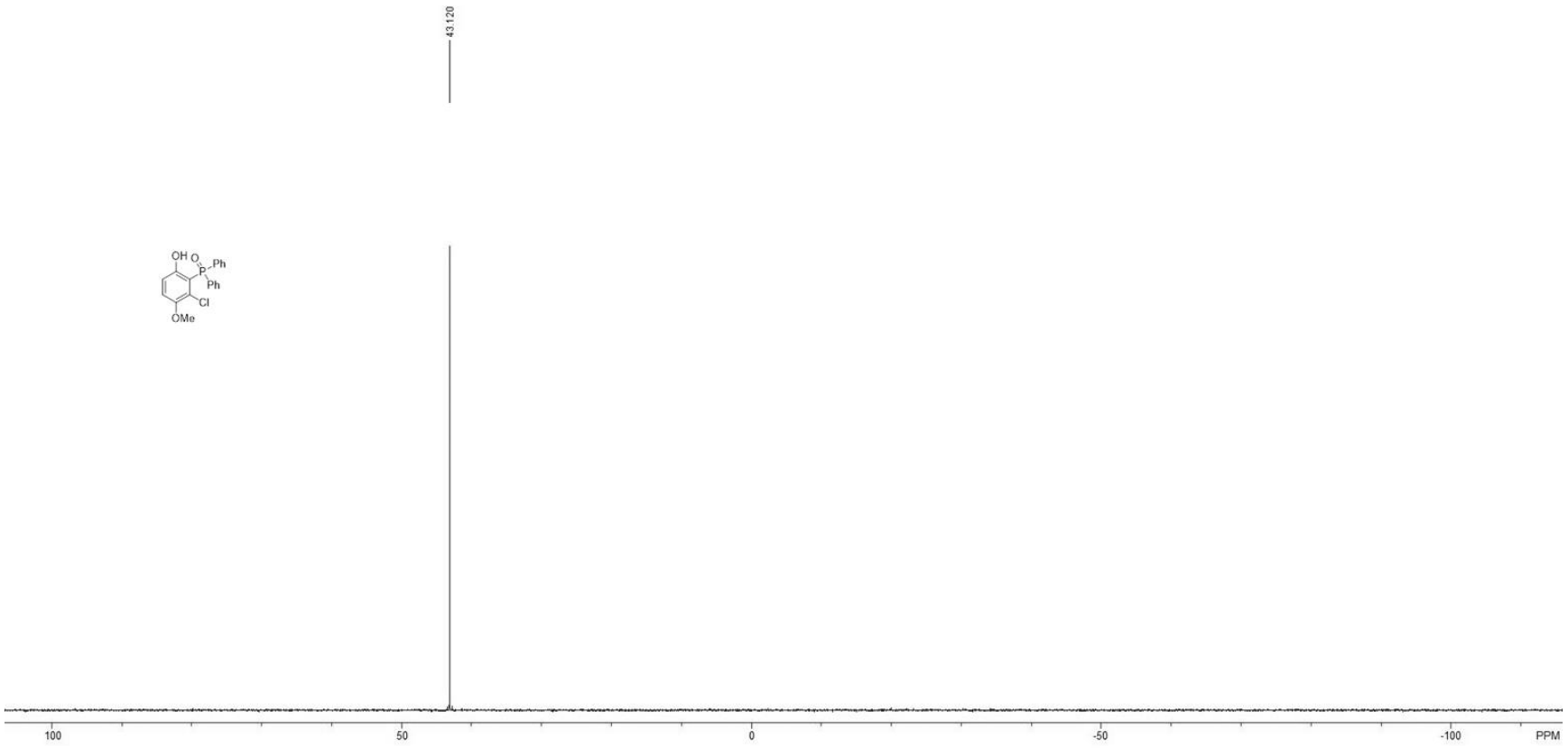
**[1]H NMR of (2-chloro-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3la')**



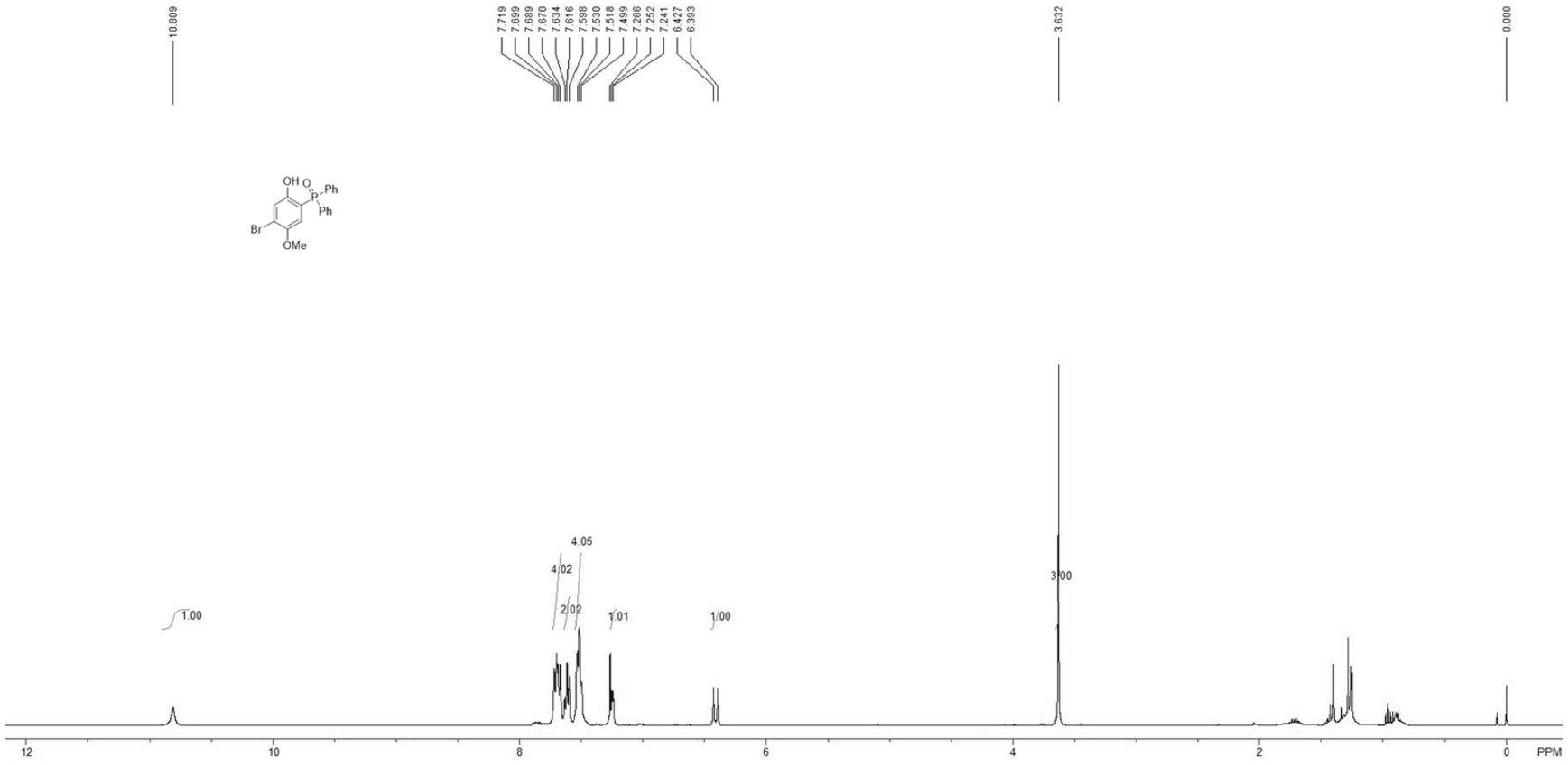
**$^{13}$C NMR of (2-chloro-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3la')**



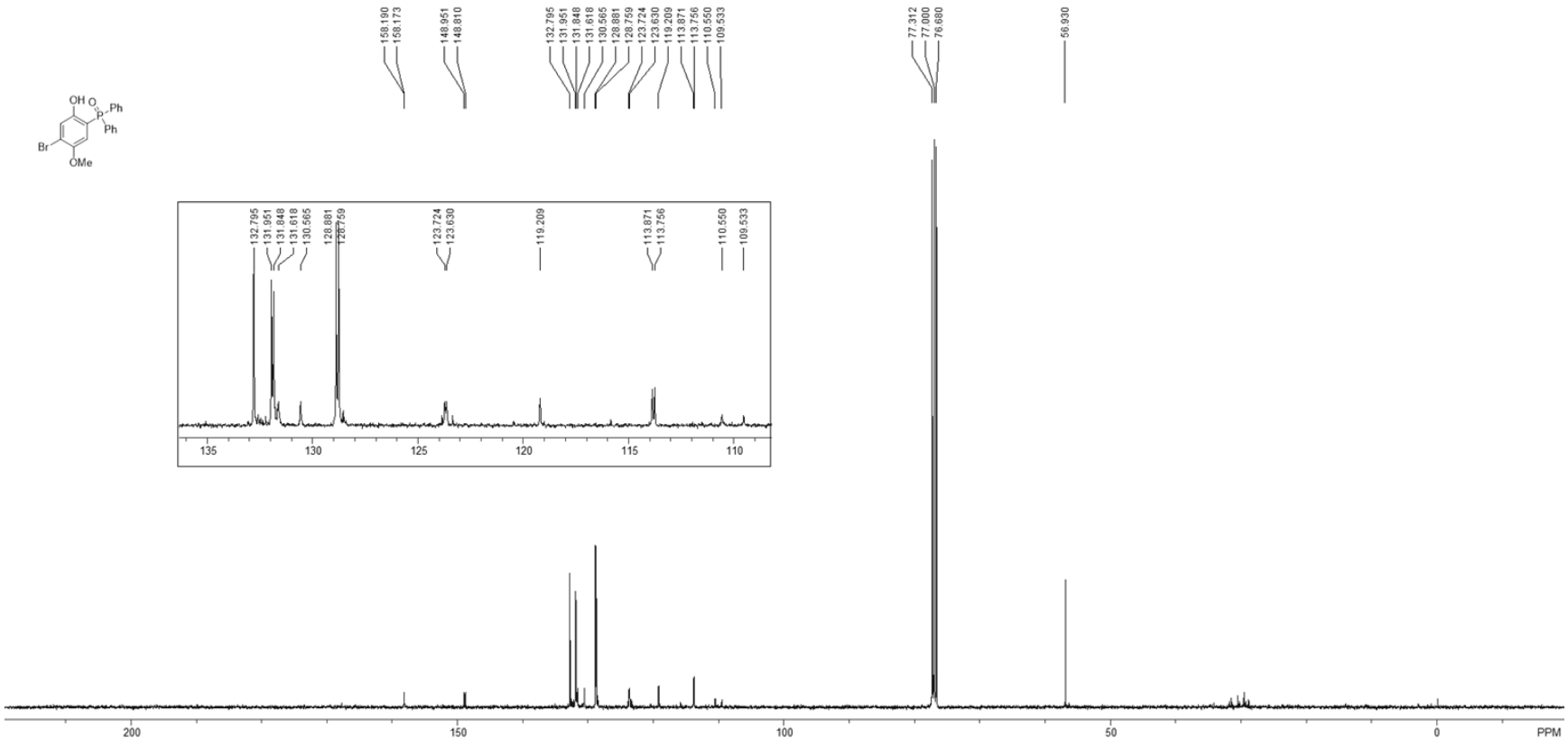
**$^{31}$P NMR of (2-chloro-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3la')**



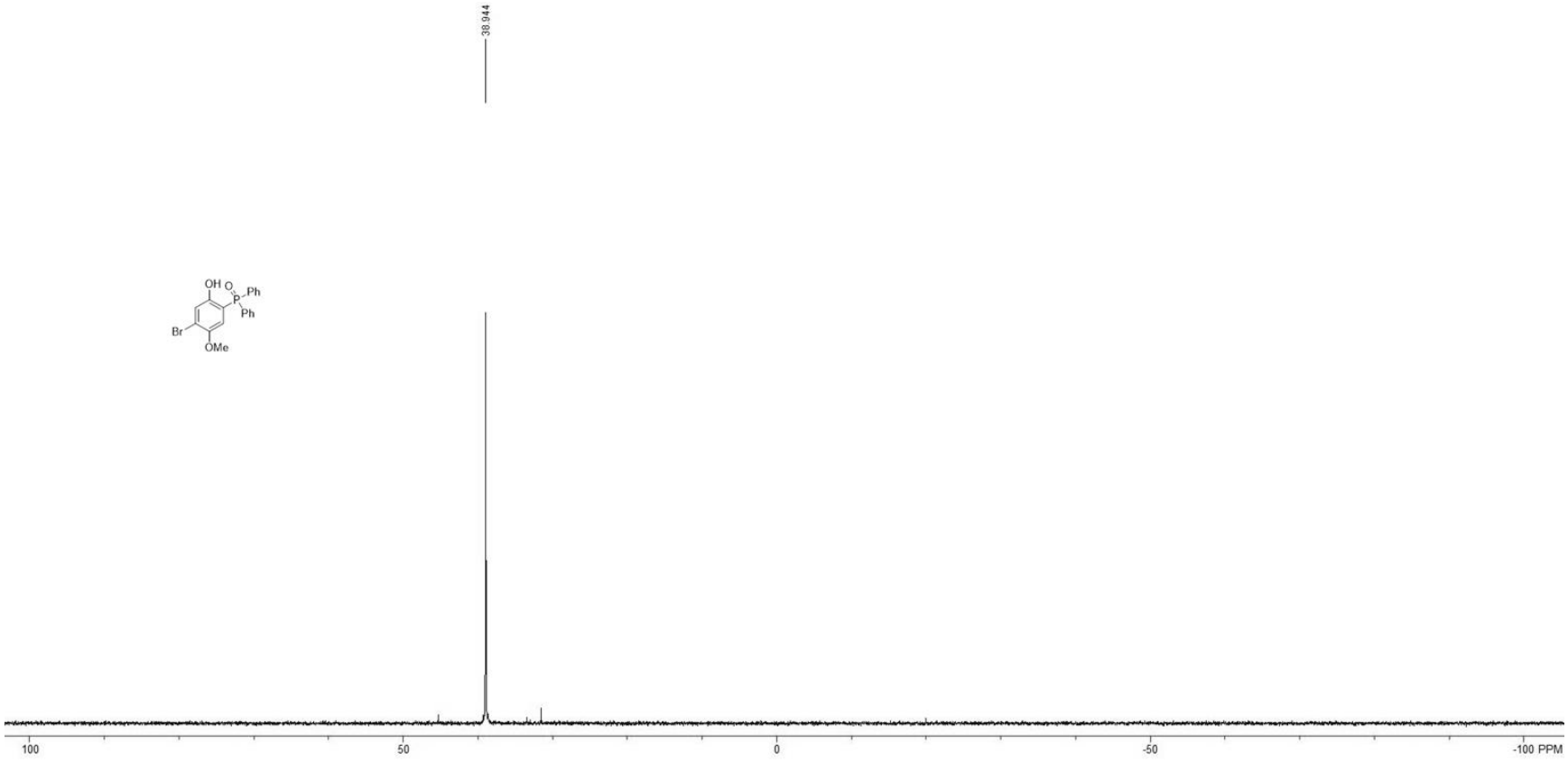
**[1]H NMR of (4-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ma)**



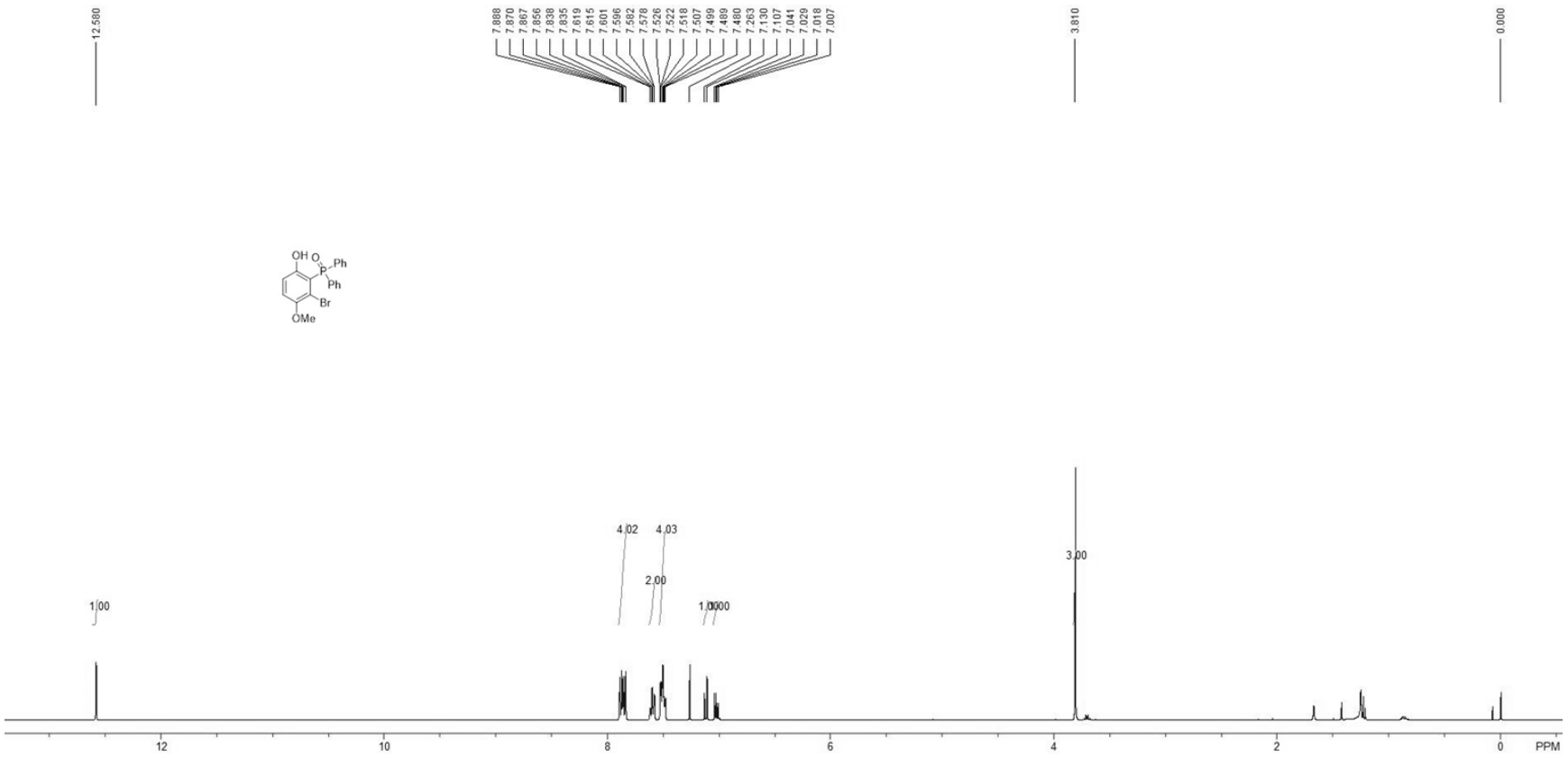
**$^{13}$C NMR of (4-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ma)**



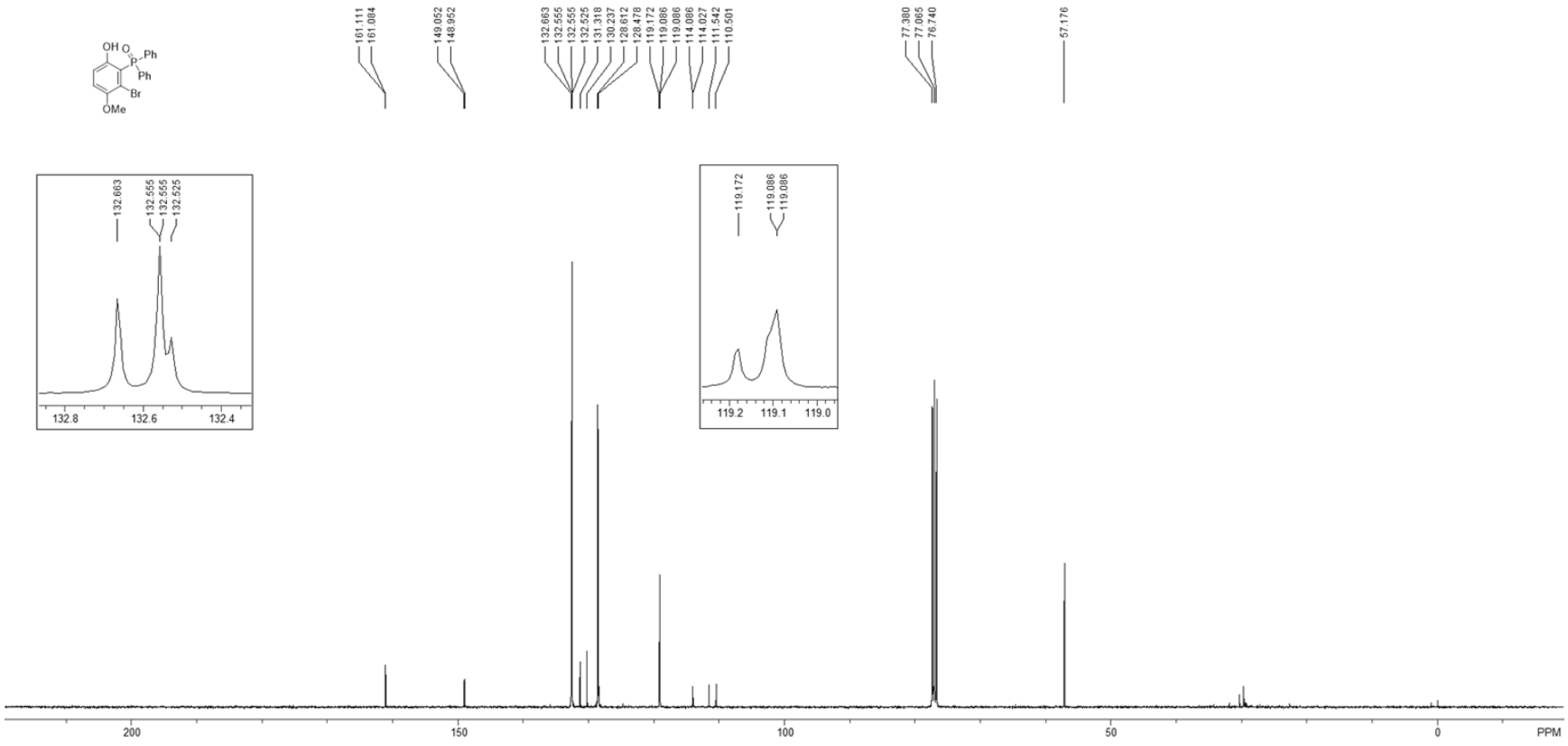
**$^{31}$P NMR of (4-bromo-2-hydroxy-5-methoxyphenyl)diphenylphosphine oxide (3ma)**



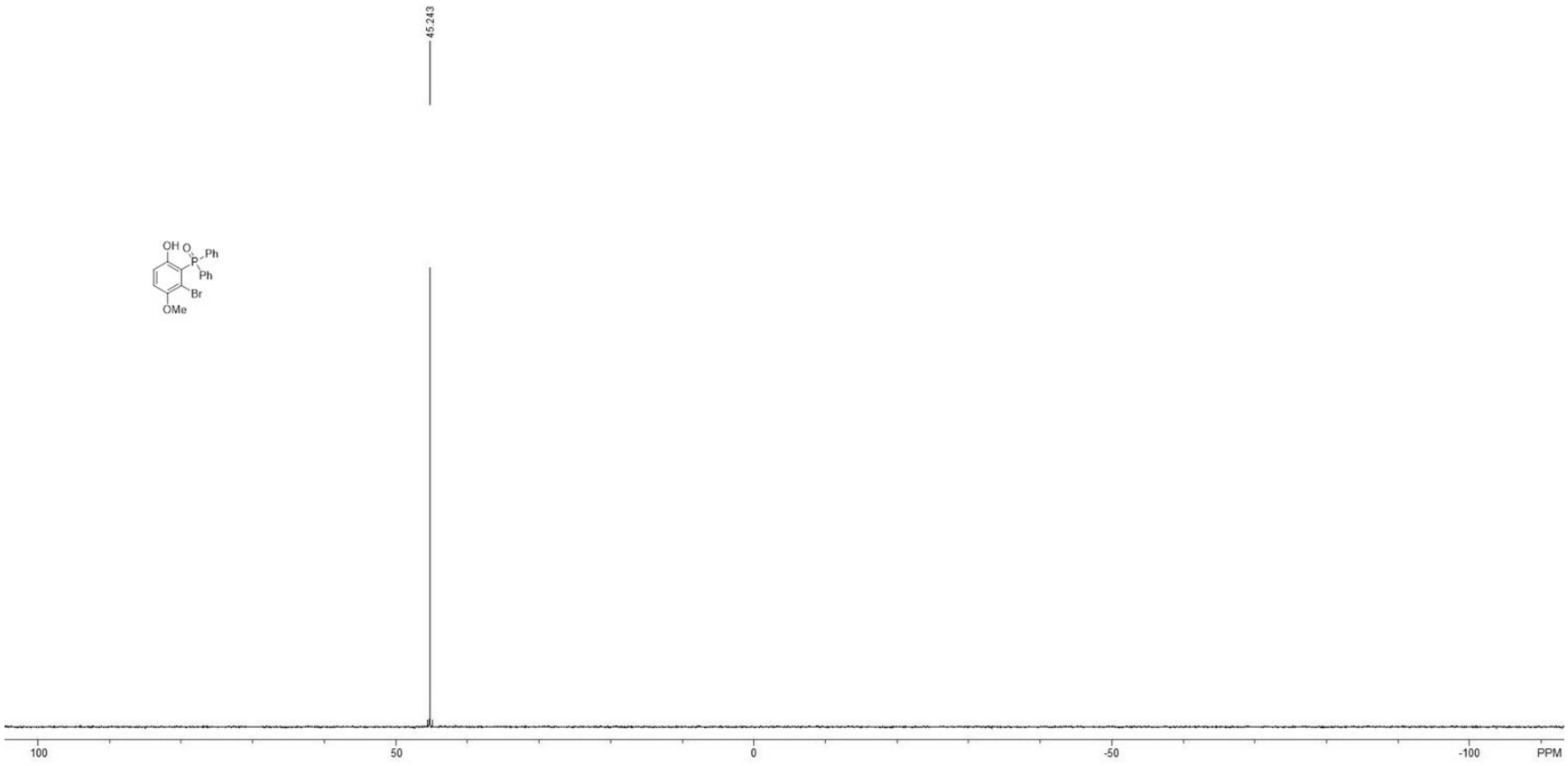
**$^{1}$H NMR of (2-bromo-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3ma')**



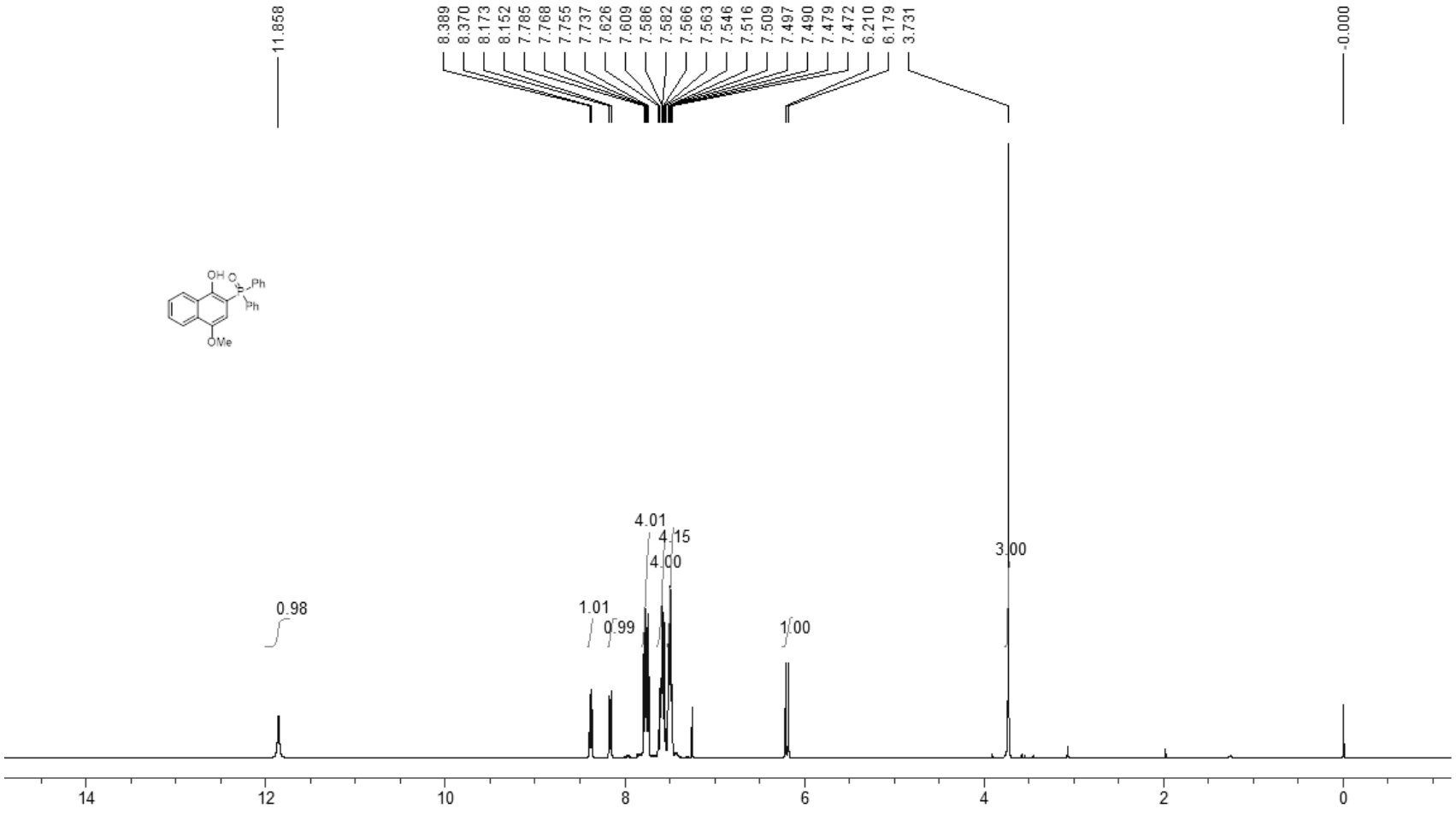
**$^{13}$C NMR of (2-bromo-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3ma')**



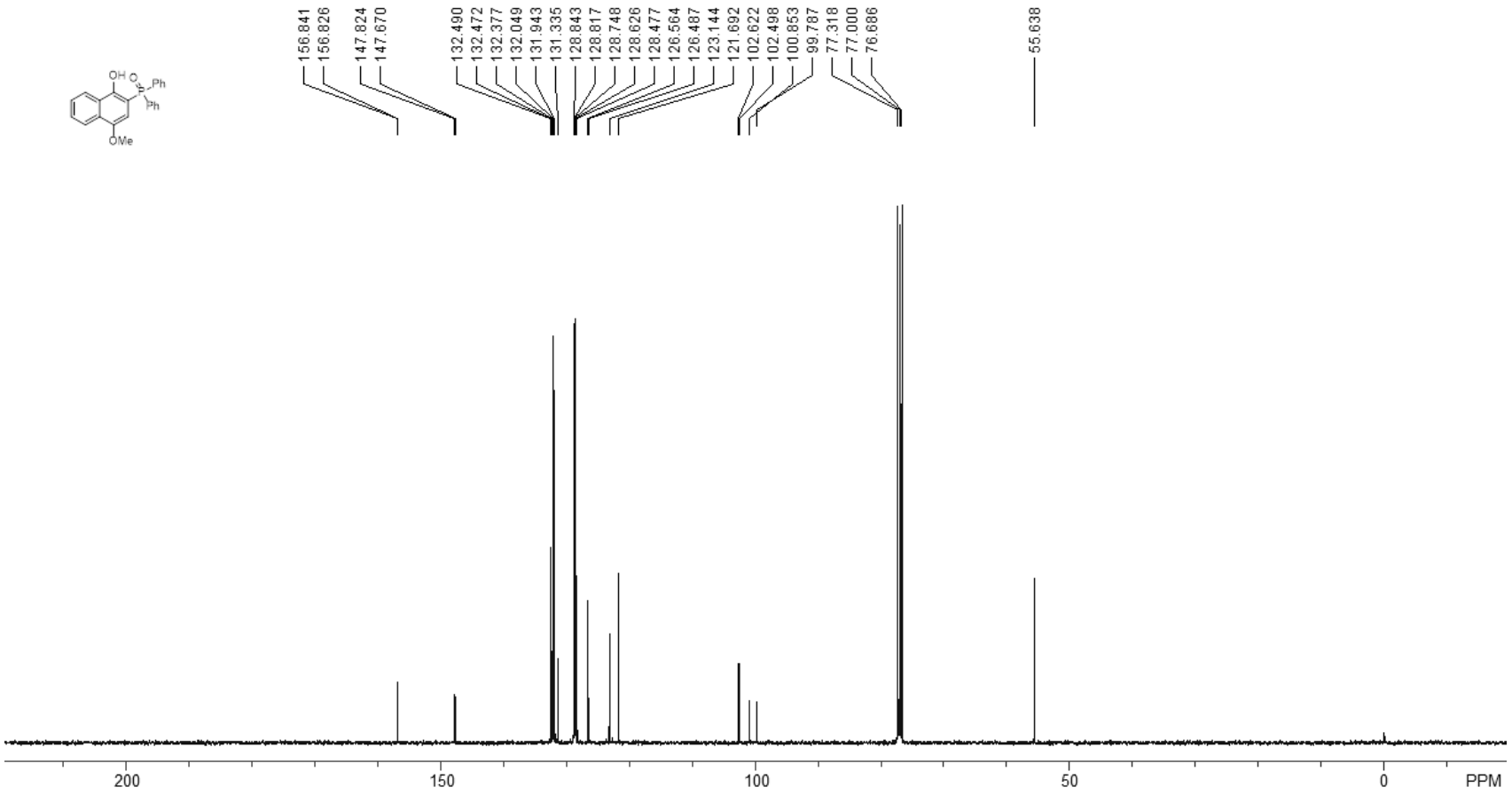
**$^{31}$P NMR of (2-bromo-6-hydroxy-3-methoxyphenyl)diphenylphosphine oxide (3ma')**



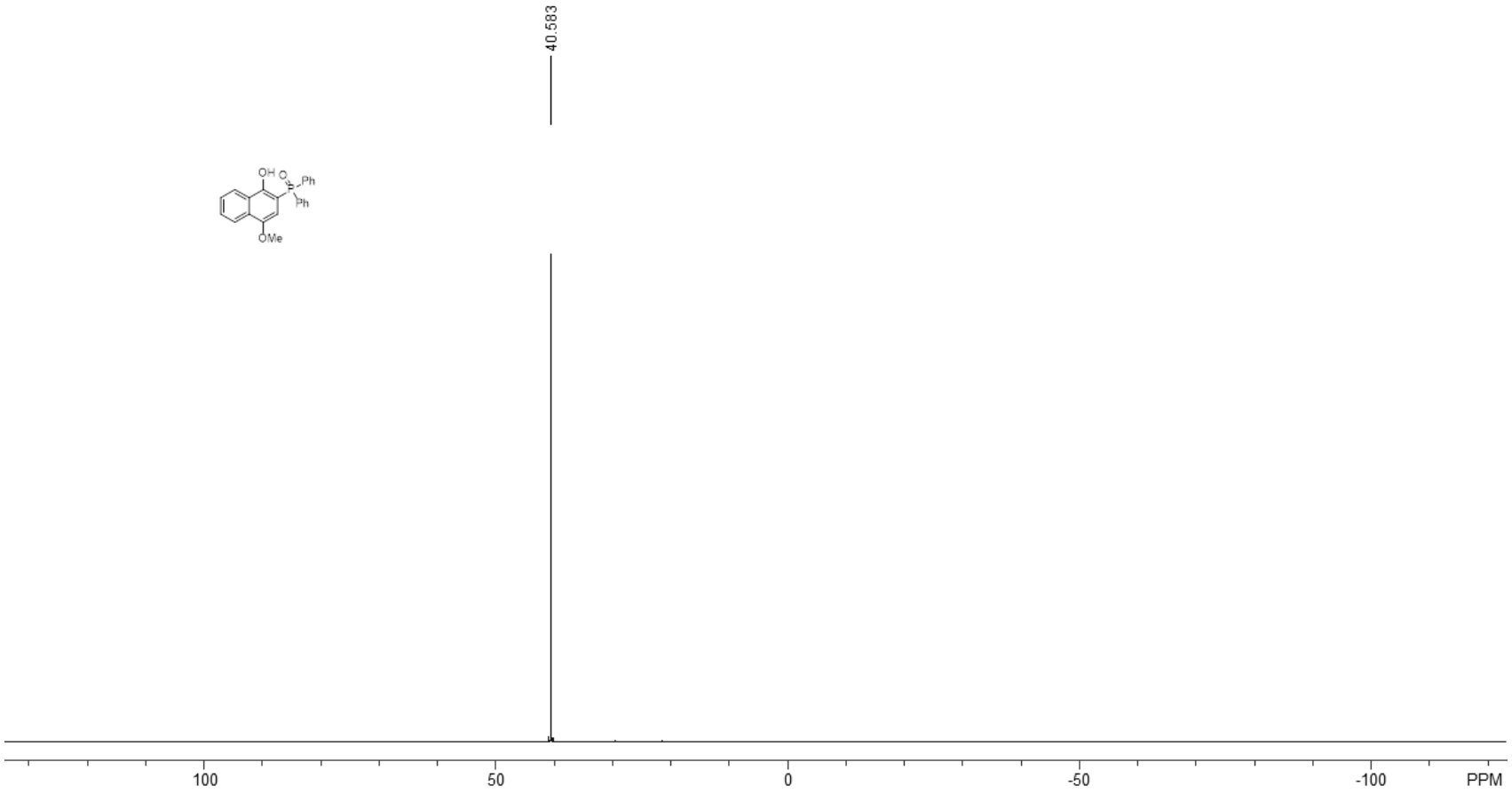
**$^{1}$H NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)diphenylphosphine oxide (3na)**



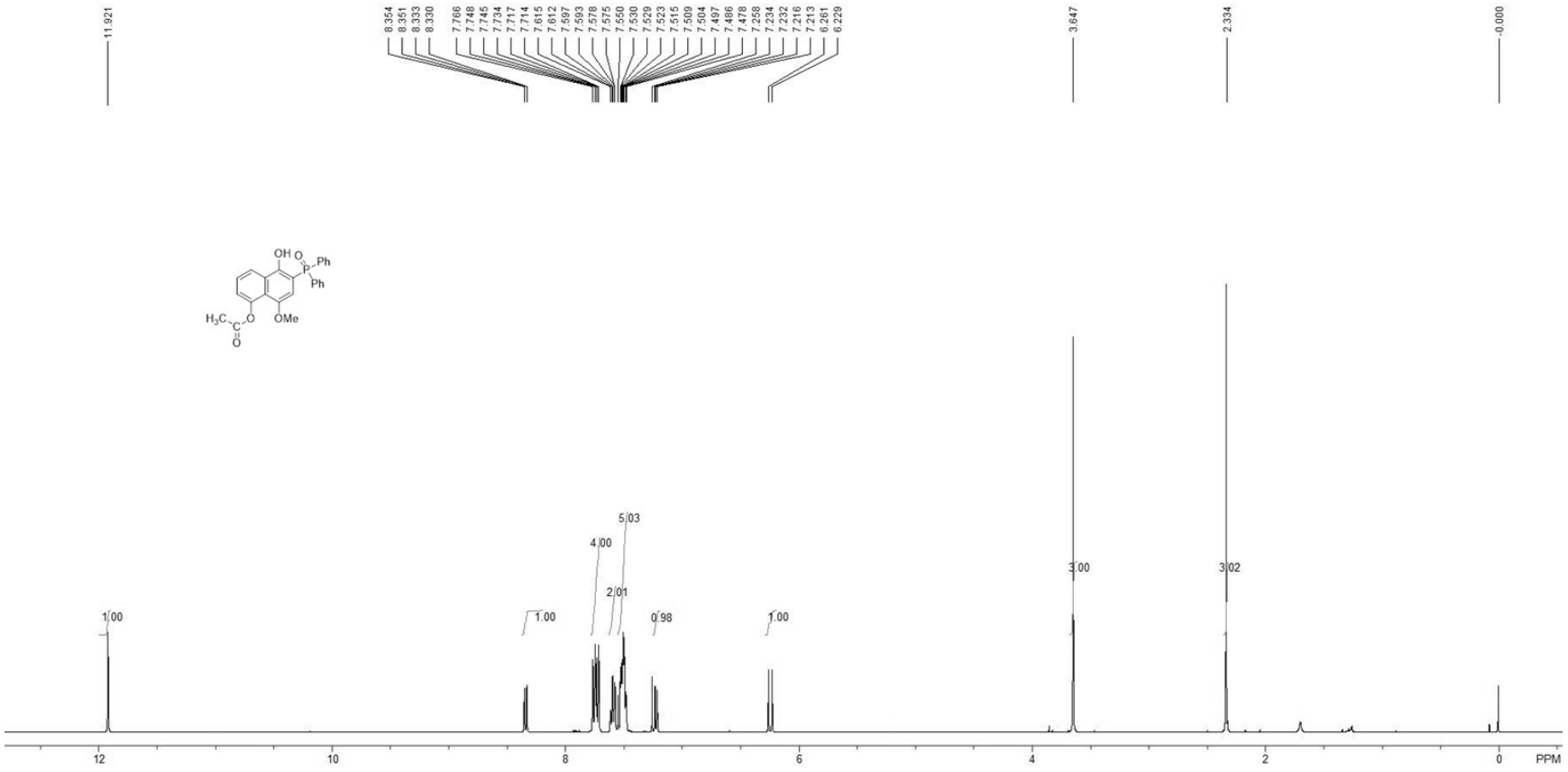
**$^{13}$C NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)diphenylphosphine oxide (3na)**



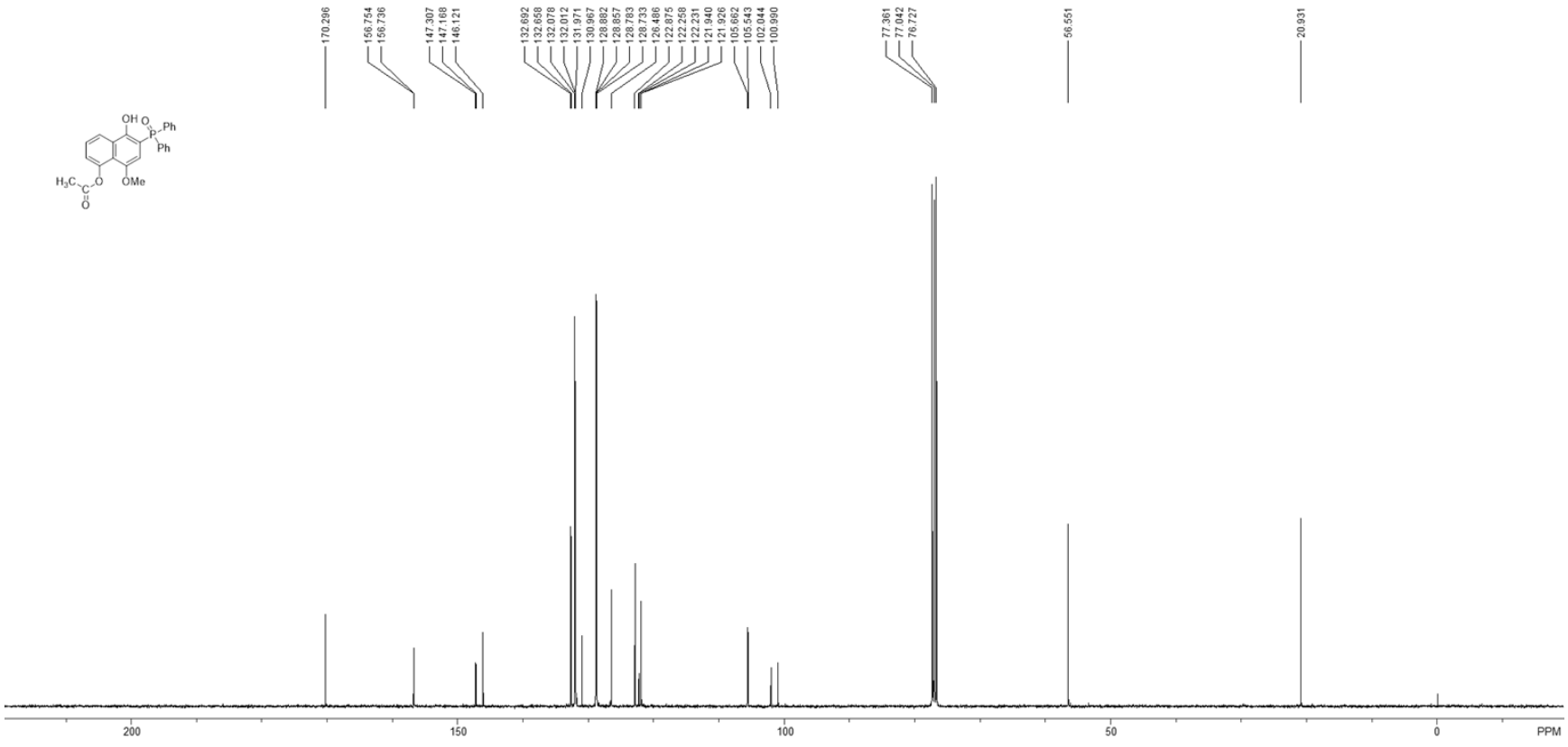
**$^{31}$P NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)diphenylphosphine oxide (3na)**



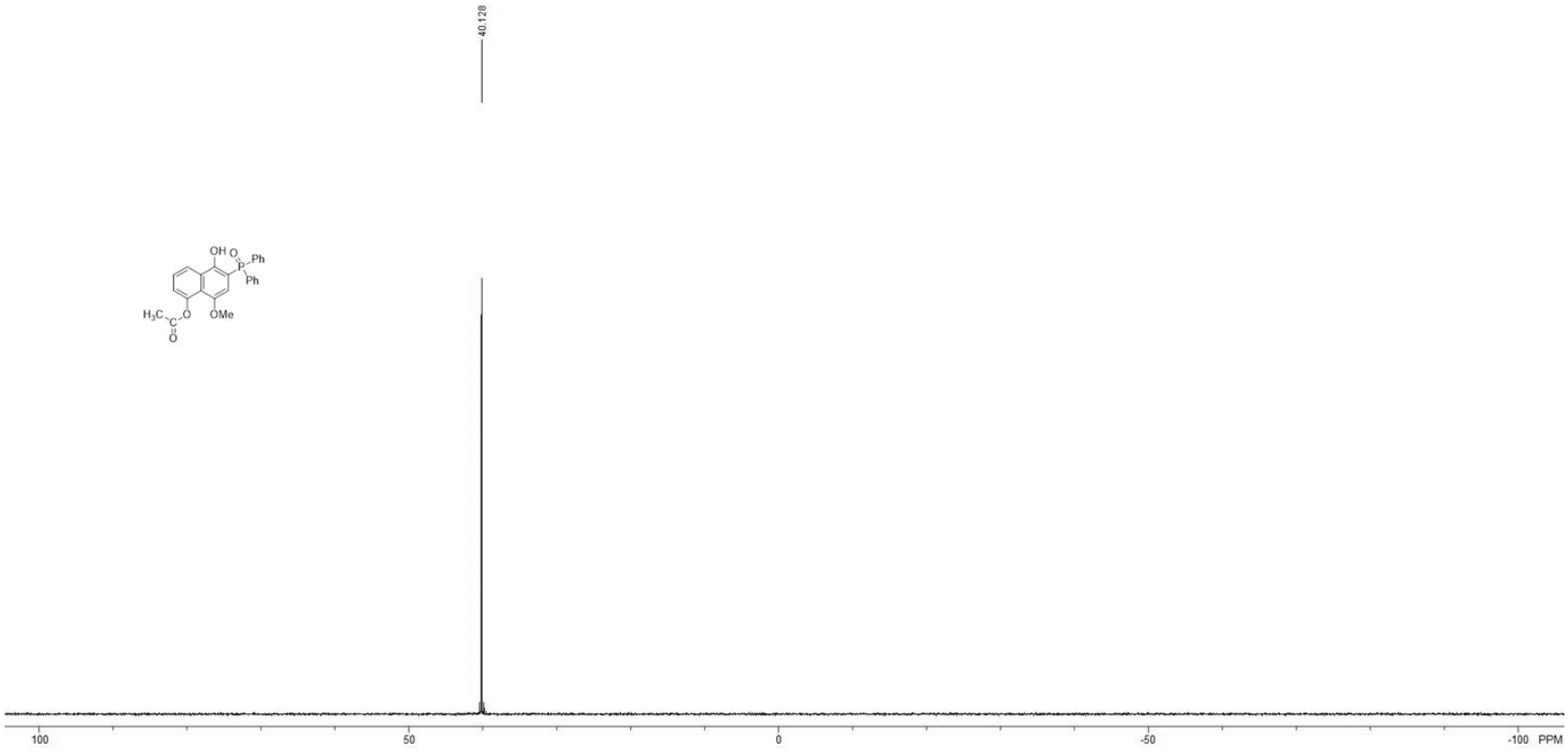
**$^{1}$H NMR of 6-(diphenylphosphoryl)-5-hydroxy-8-methoxynaphthalen-1-yl acetate (3oa)**



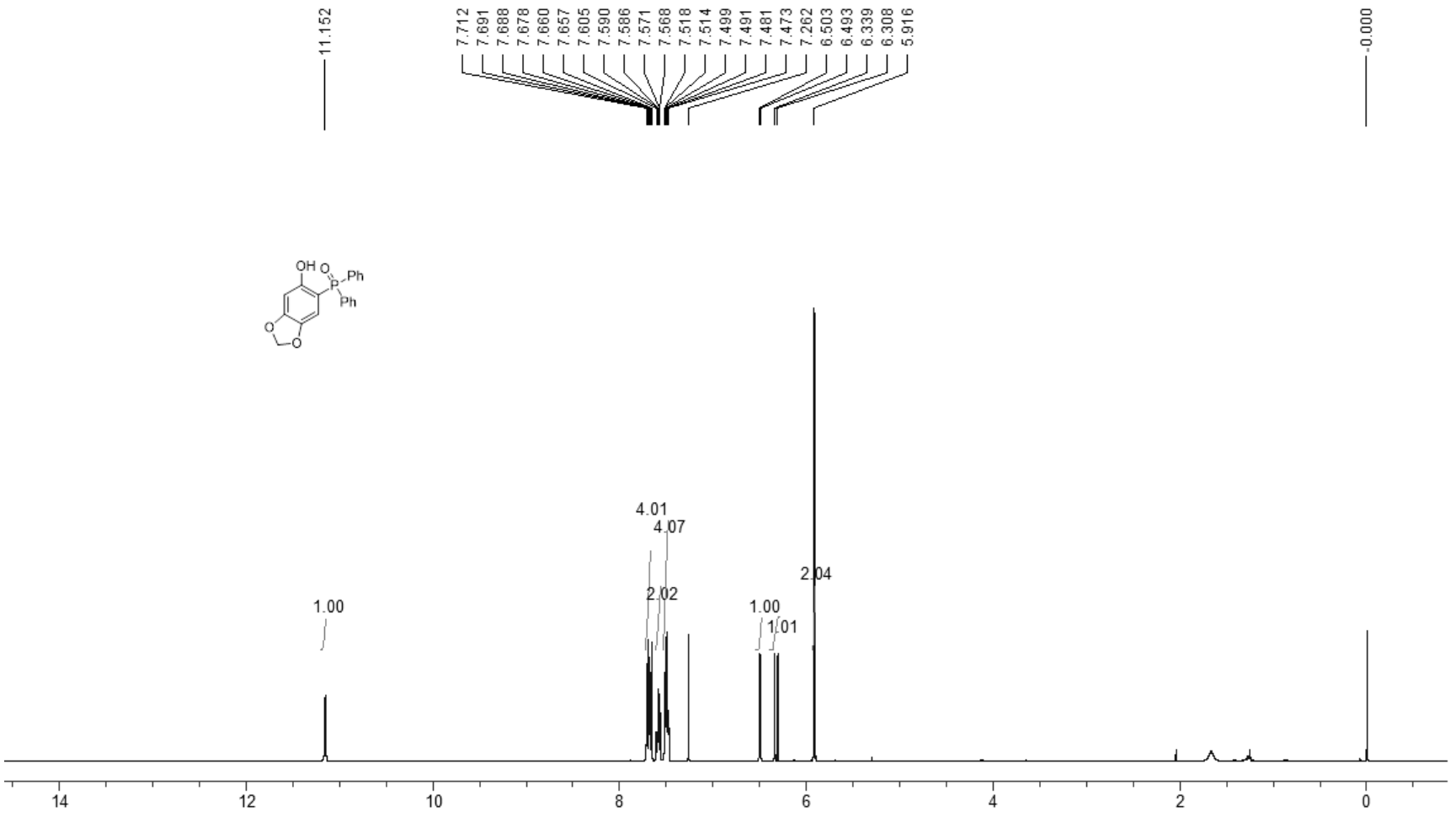
**$^{13}$C NMR of 6-(diphenylphosphoryl)-5-hydroxy-8-methoxynaphthalen-1-yl acetate (3oa)**



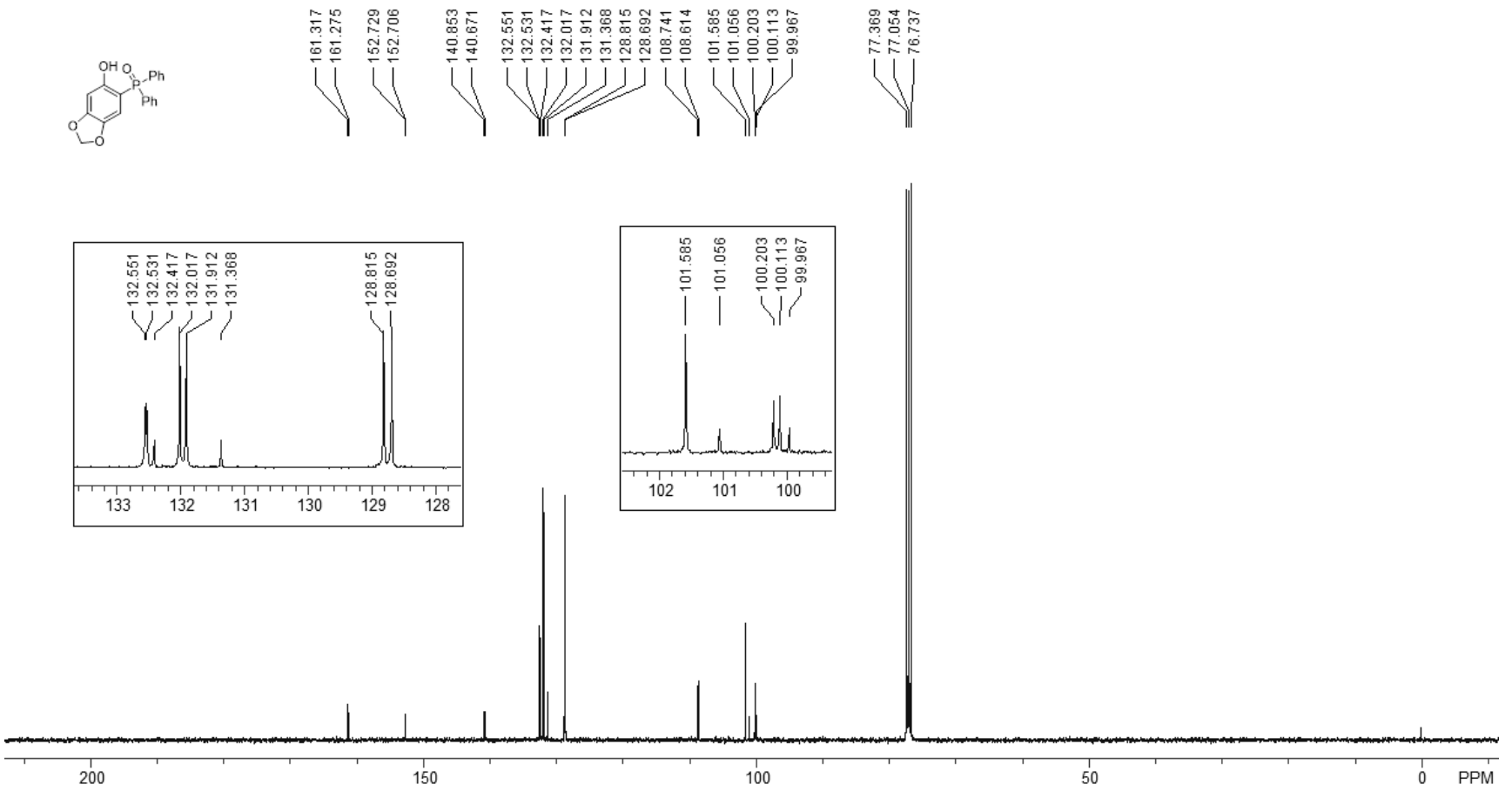
**$^{31}$P NMR of 6-(diphenylphosphoryl)-5-hydroxy-8-methoxynaphthalen-1-yl acetate (3oa)**



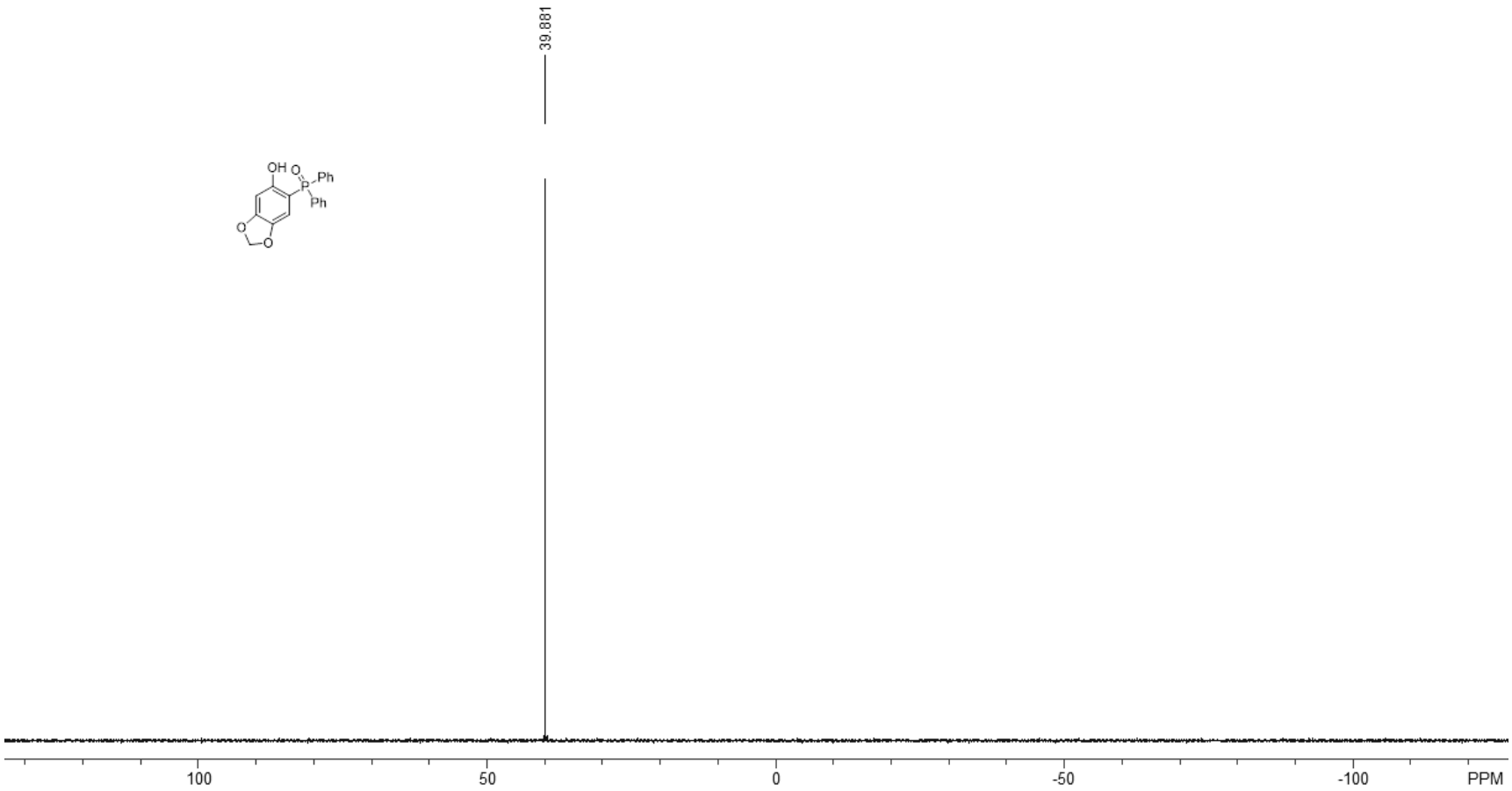
**$^{1}$H NMR of (6-hydroxybenzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (3pa)**



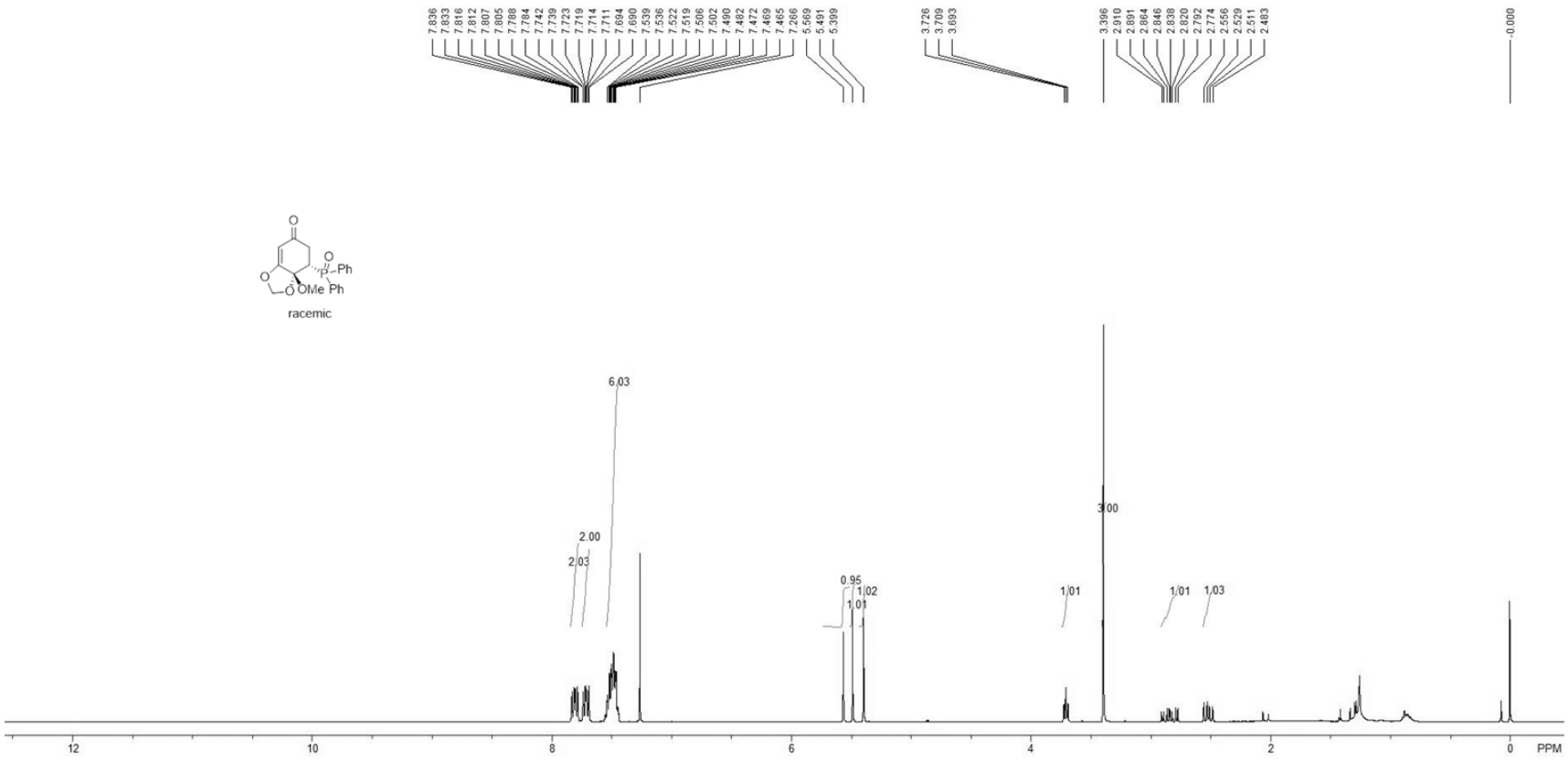
**$^{13}$C NMR of (6-hydroxybenzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (3pa)**



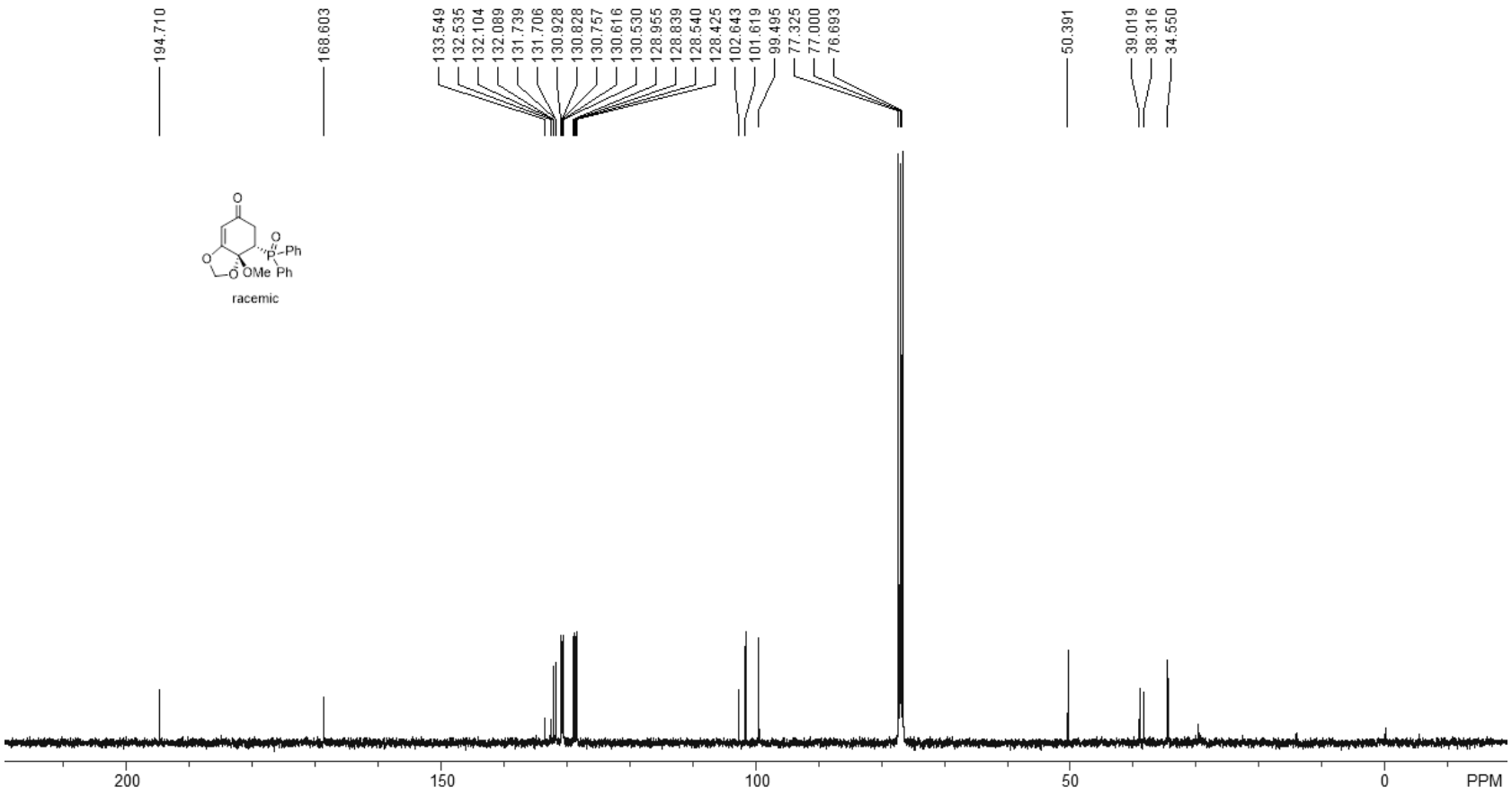
**$^{31}$P NMR of (6-hydroxybenzo[d][1,3]dioxol-5-yl)diphenylphosphine oxide (3pa)**



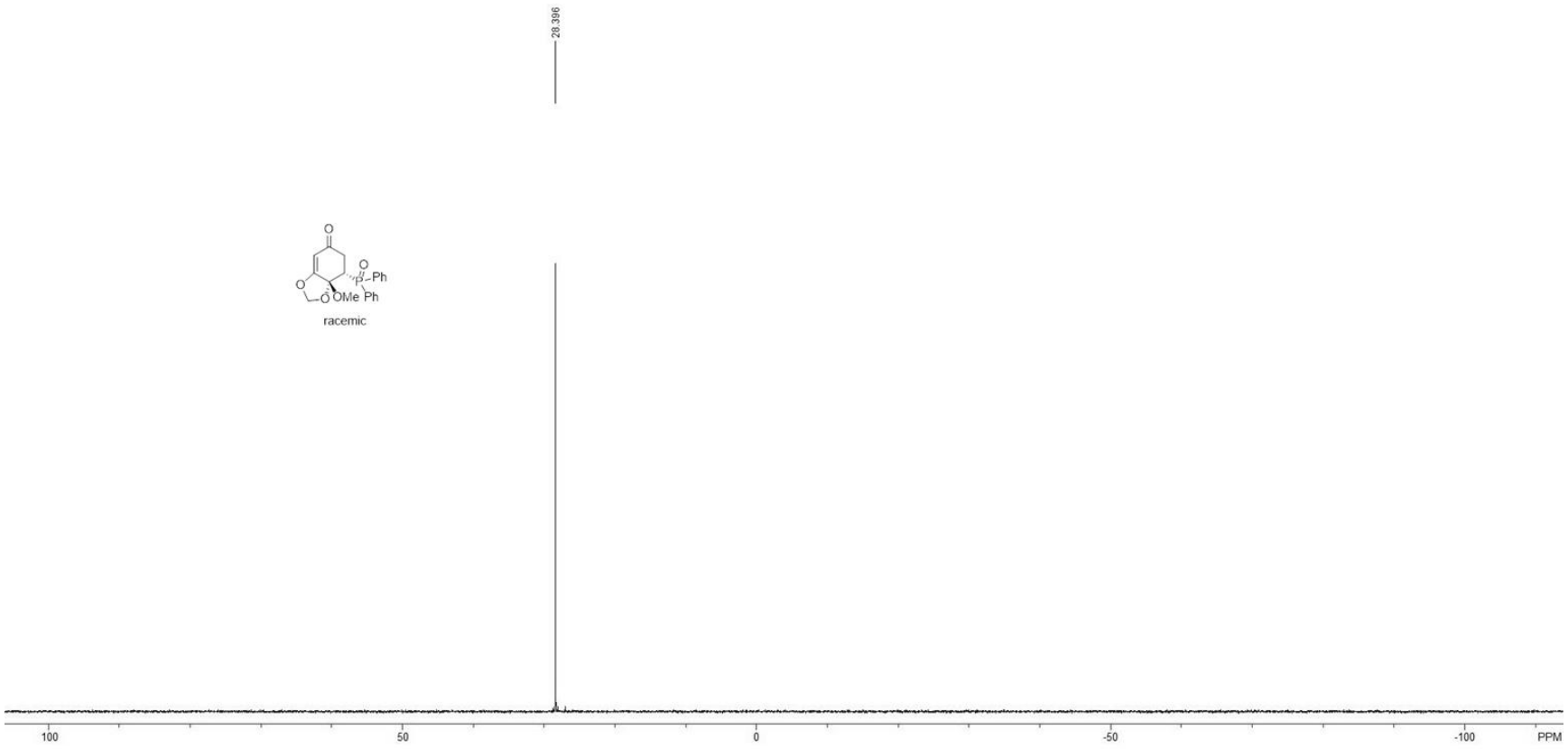
**[1]H NMR of 7-(diphenylphosphoryl)-7a-methoxy-7,7a-dihydrobenzo[d][1,3]dioxol-5(6H)-one (3pa')**



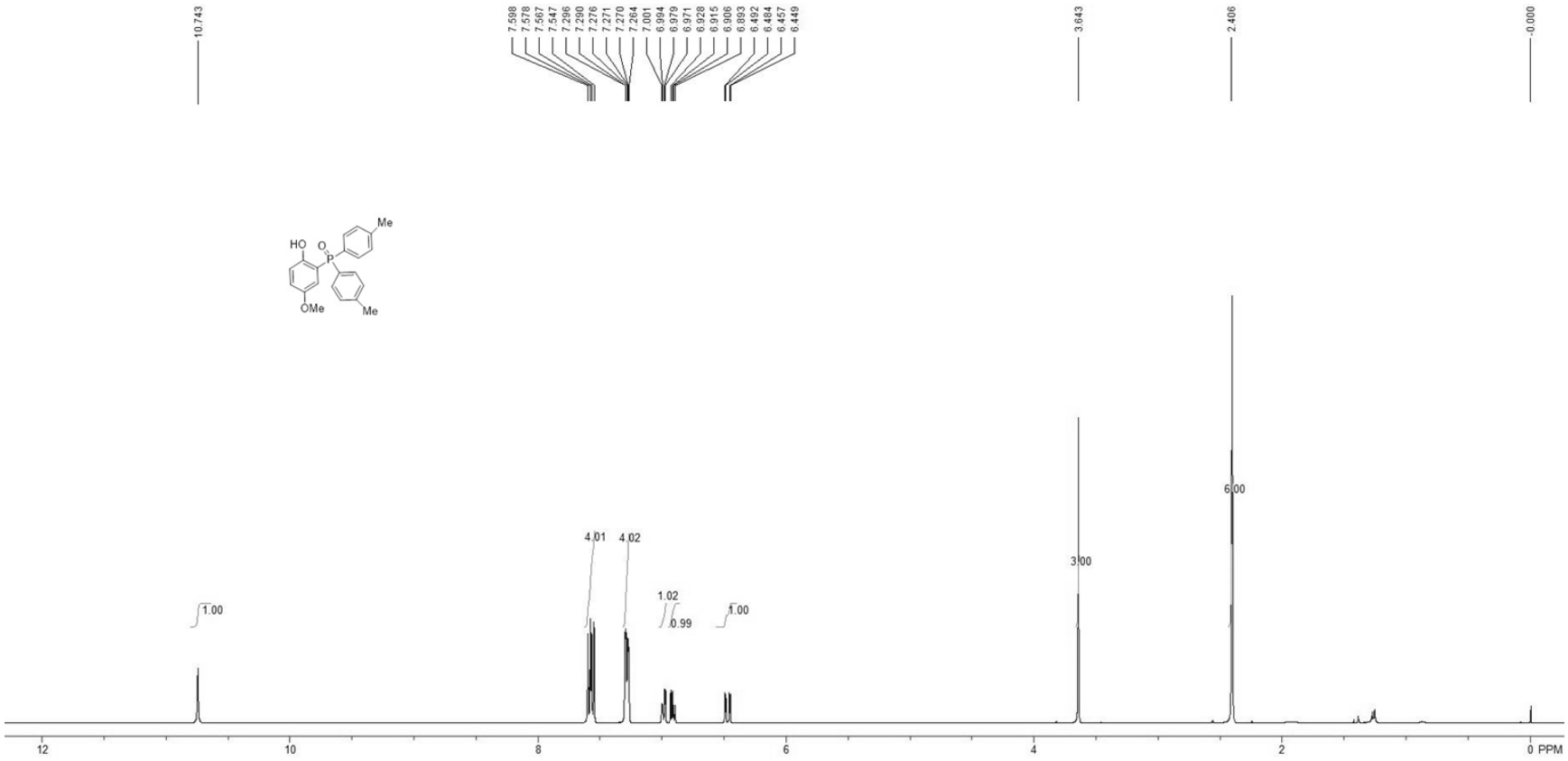
**$^{13}$C NMR of 7-(diphenylphosphoryl)-7a-methoxy-7,7a-dihydrobenzo[d][1,3]dioxol-5(6H)-one (3pa')**



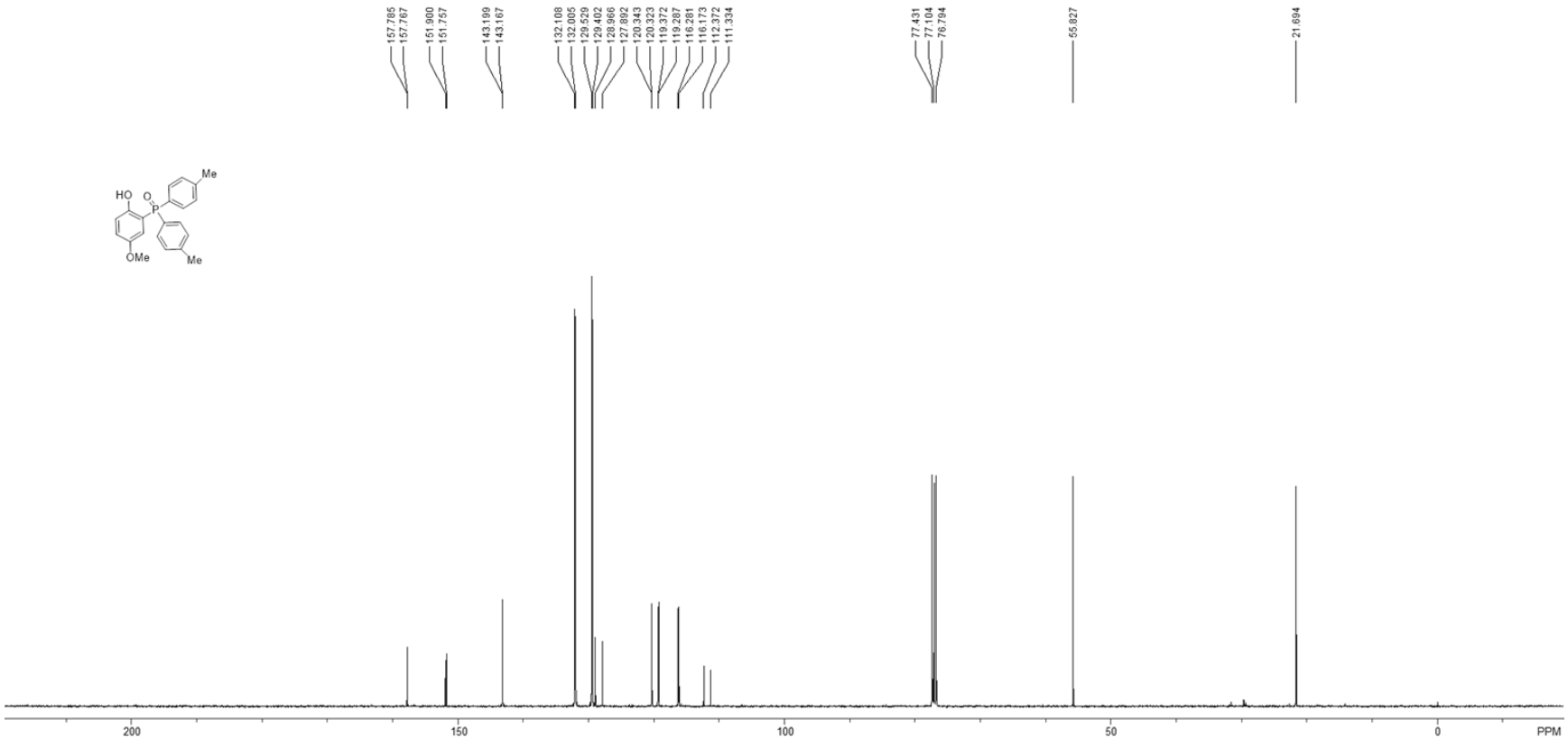
**$^{31}$P NMR of 7-(diphenylphosphoryl)-7a-methoxy-7,7a-dihydrobenzo[d][1,3]dioxol-5(6H)-one (3pa')**



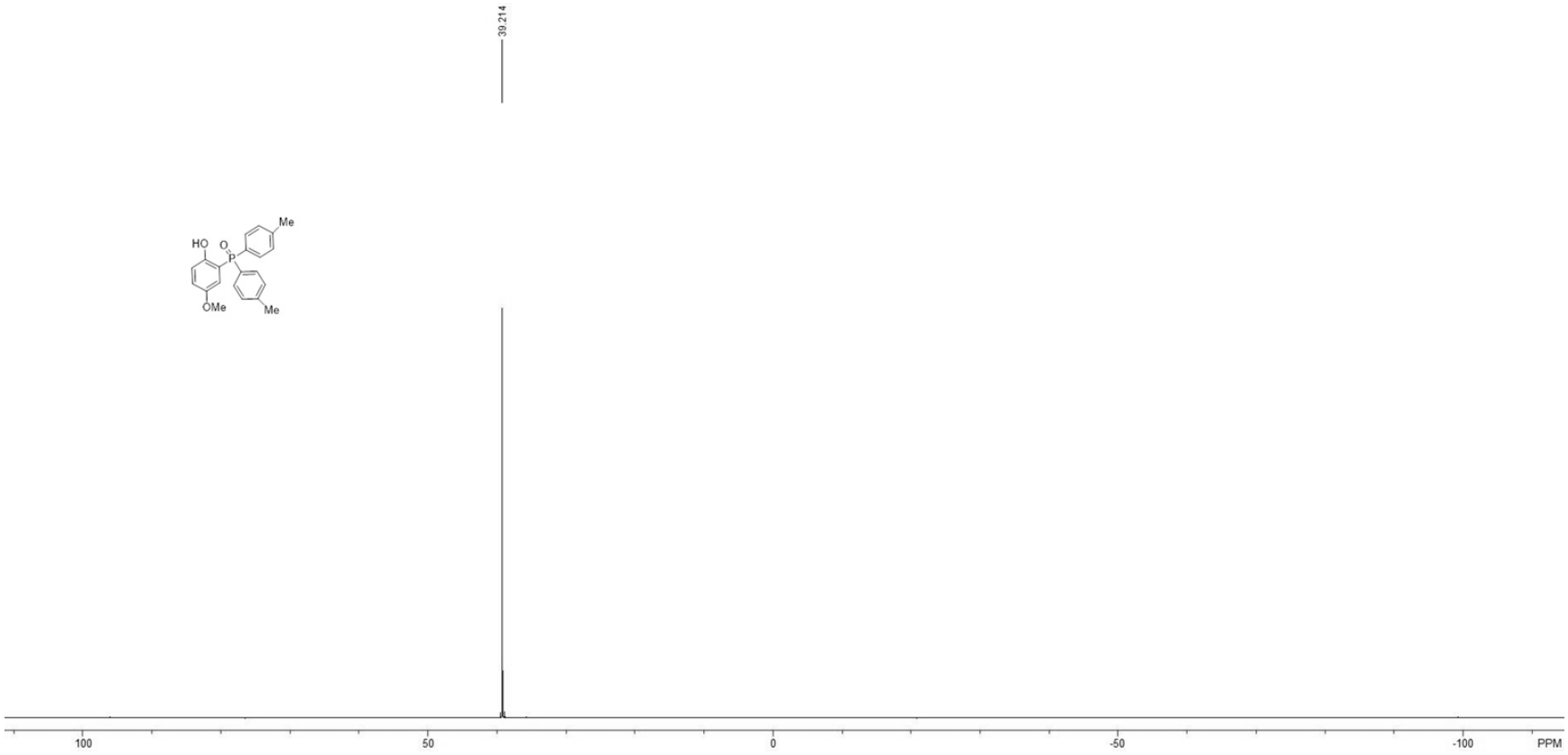
**[1]H NMR of (2-hydroxy-5-methoxyphenyl)di-p-tolylphosphine oxide (3ab)**



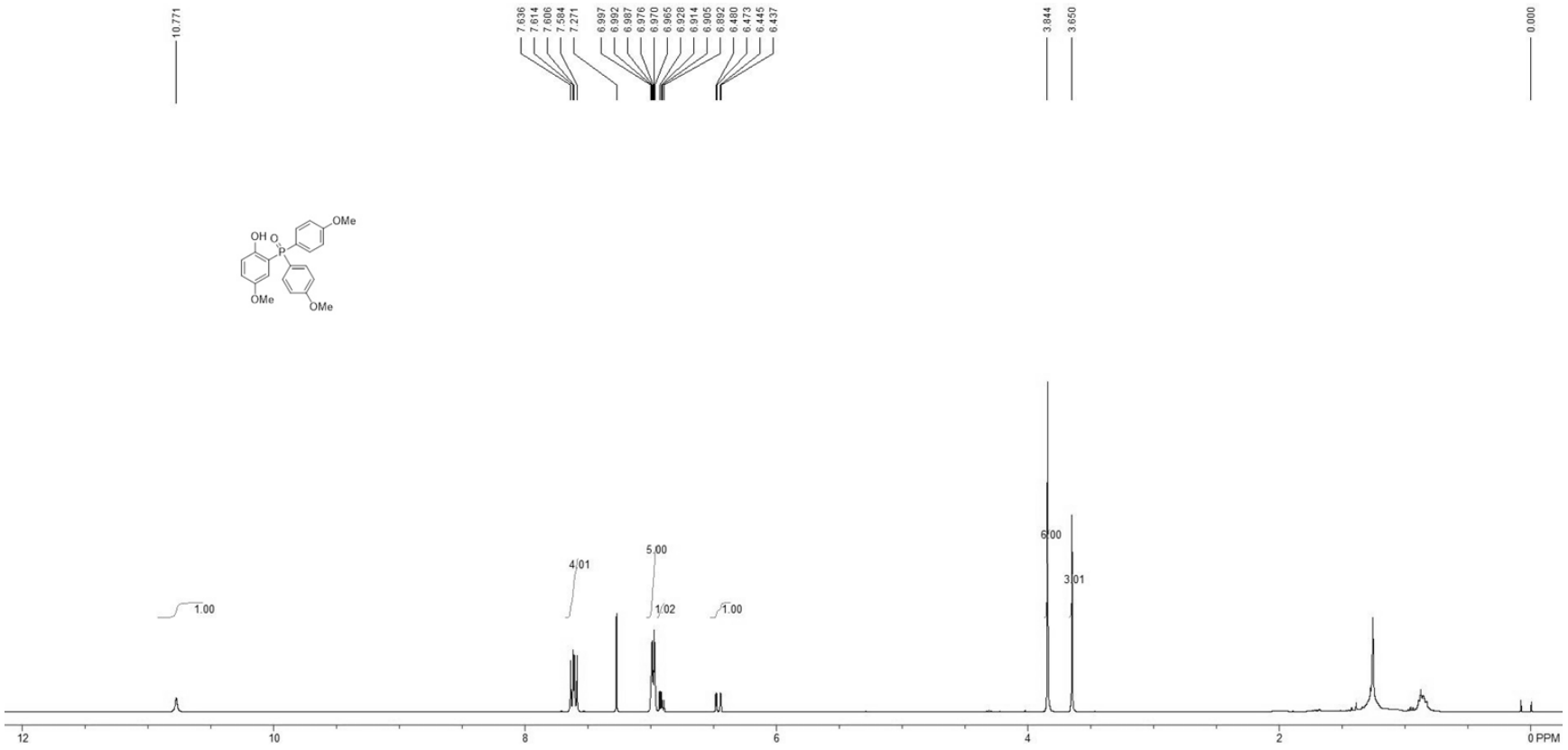
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)di-p-tolylphosphine oxide (3ab)**



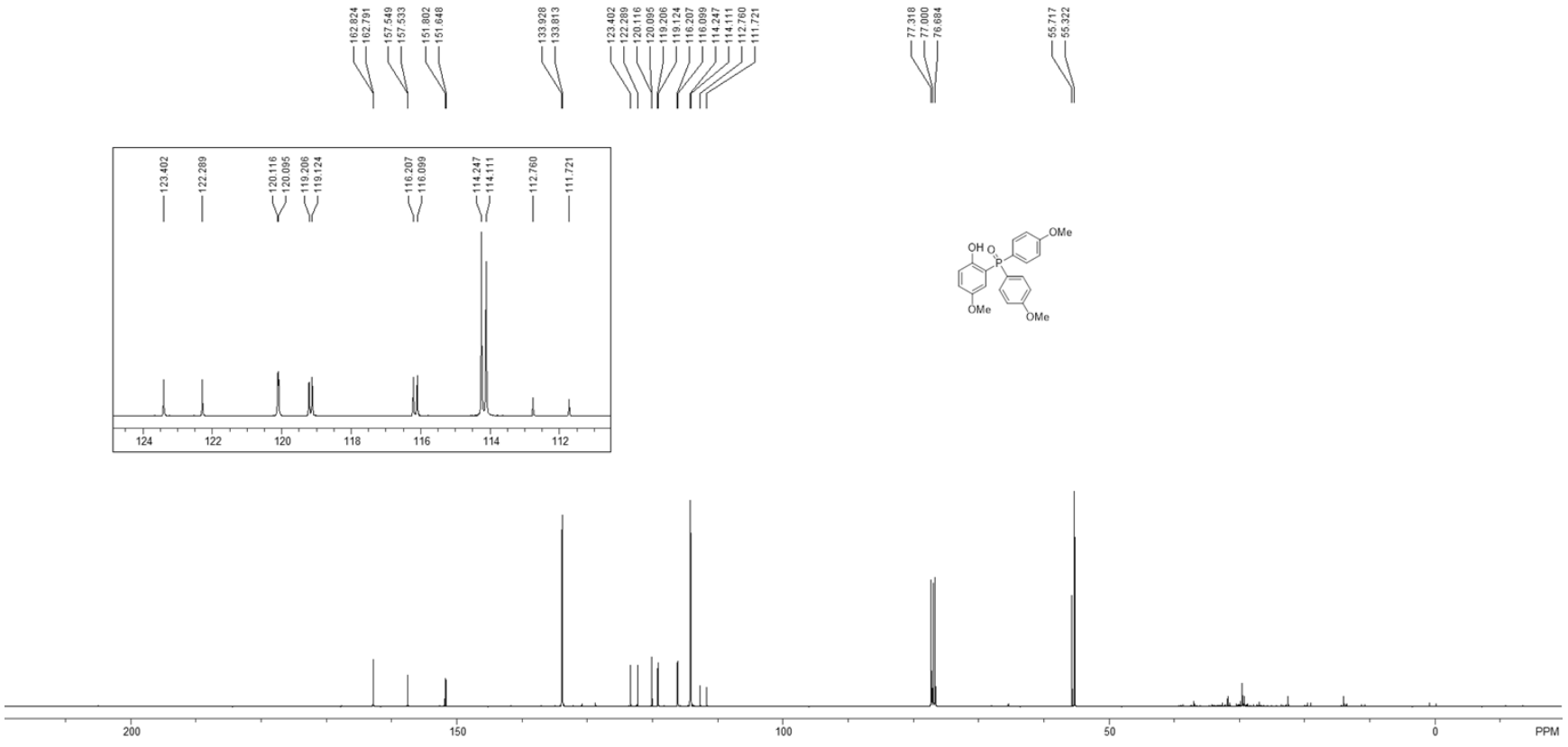
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)di-p-tolylphosphine oxide (3ab)**



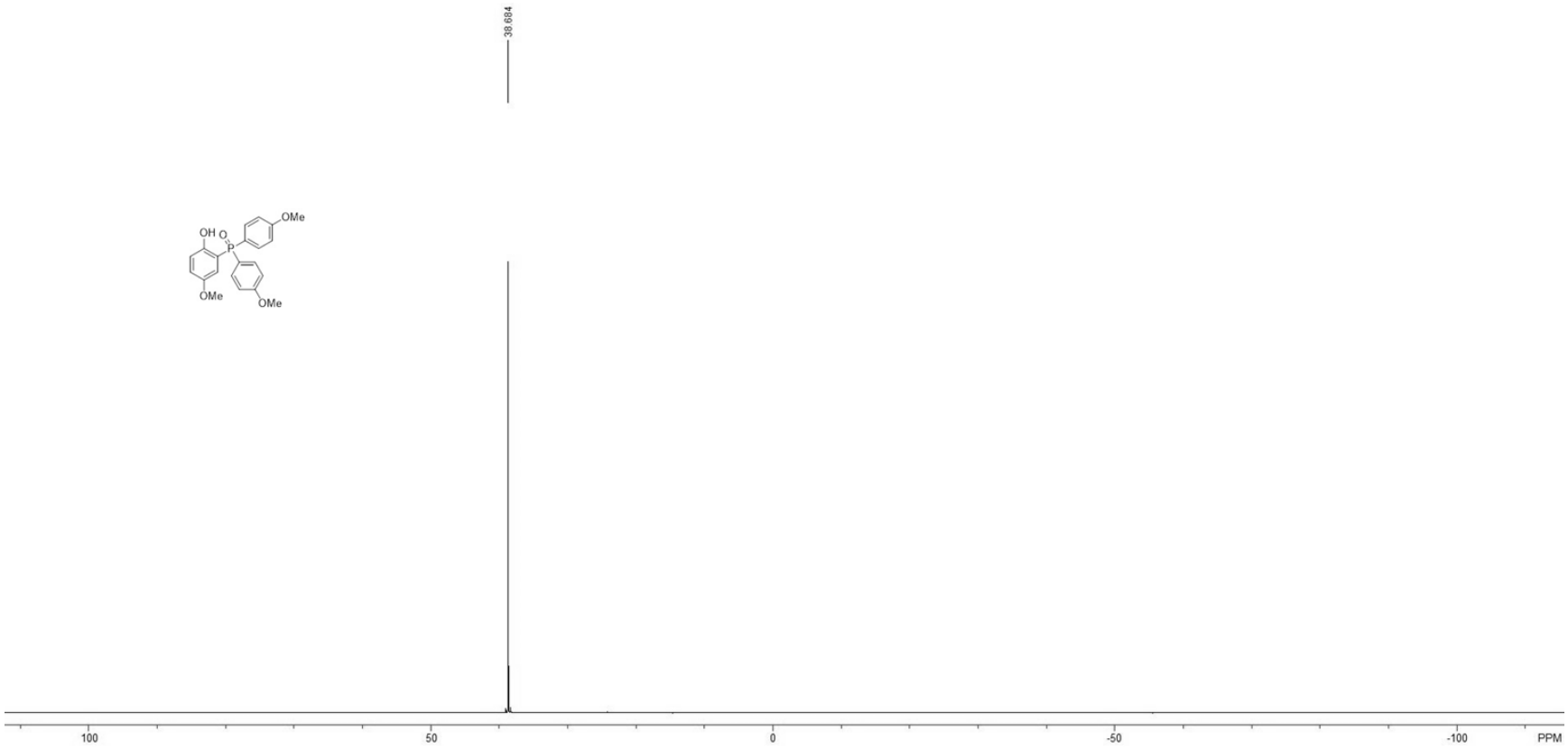
**$^{1}$H NMR of (2-hydroxy-5-methoxyphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)**



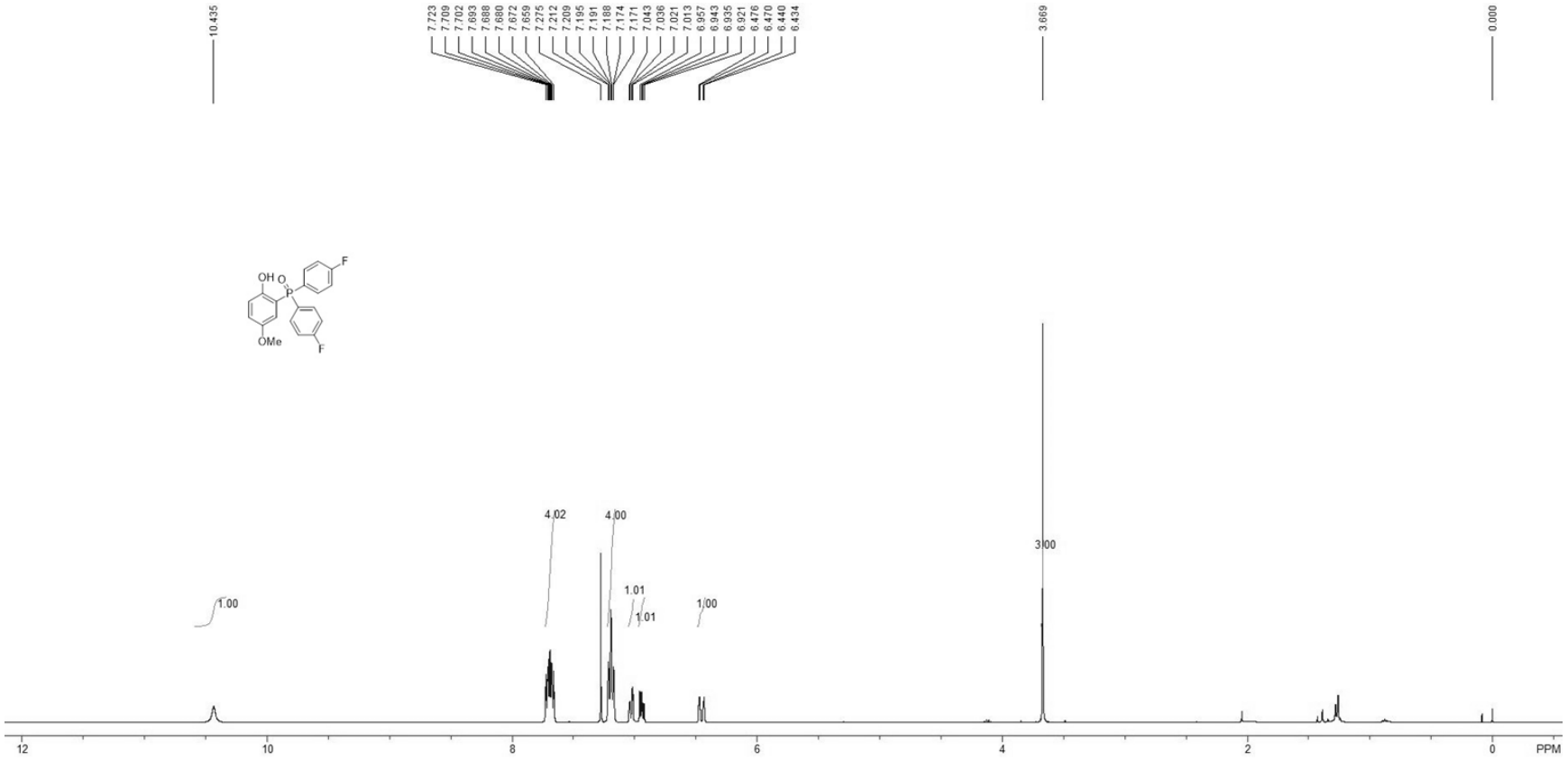
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)**



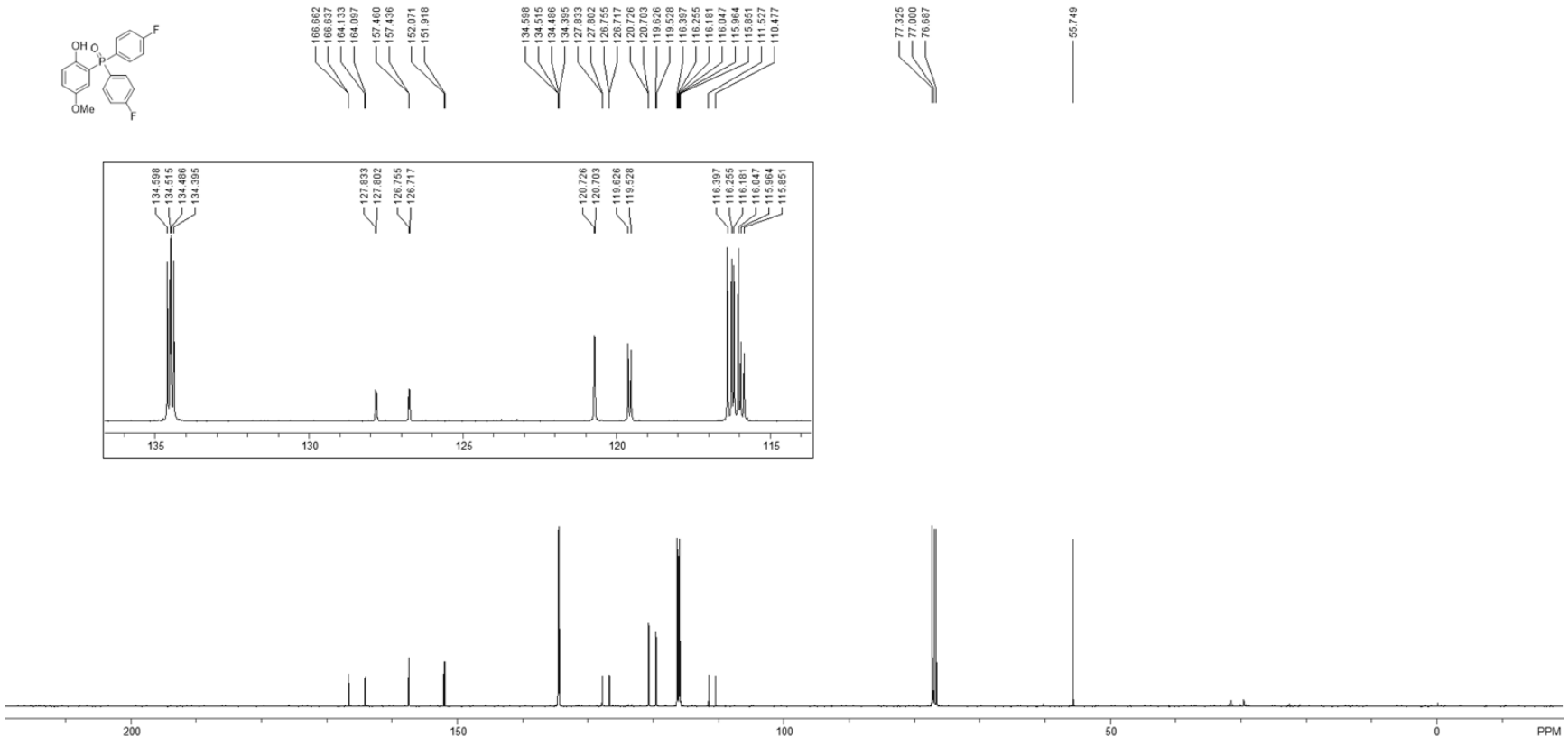
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)**



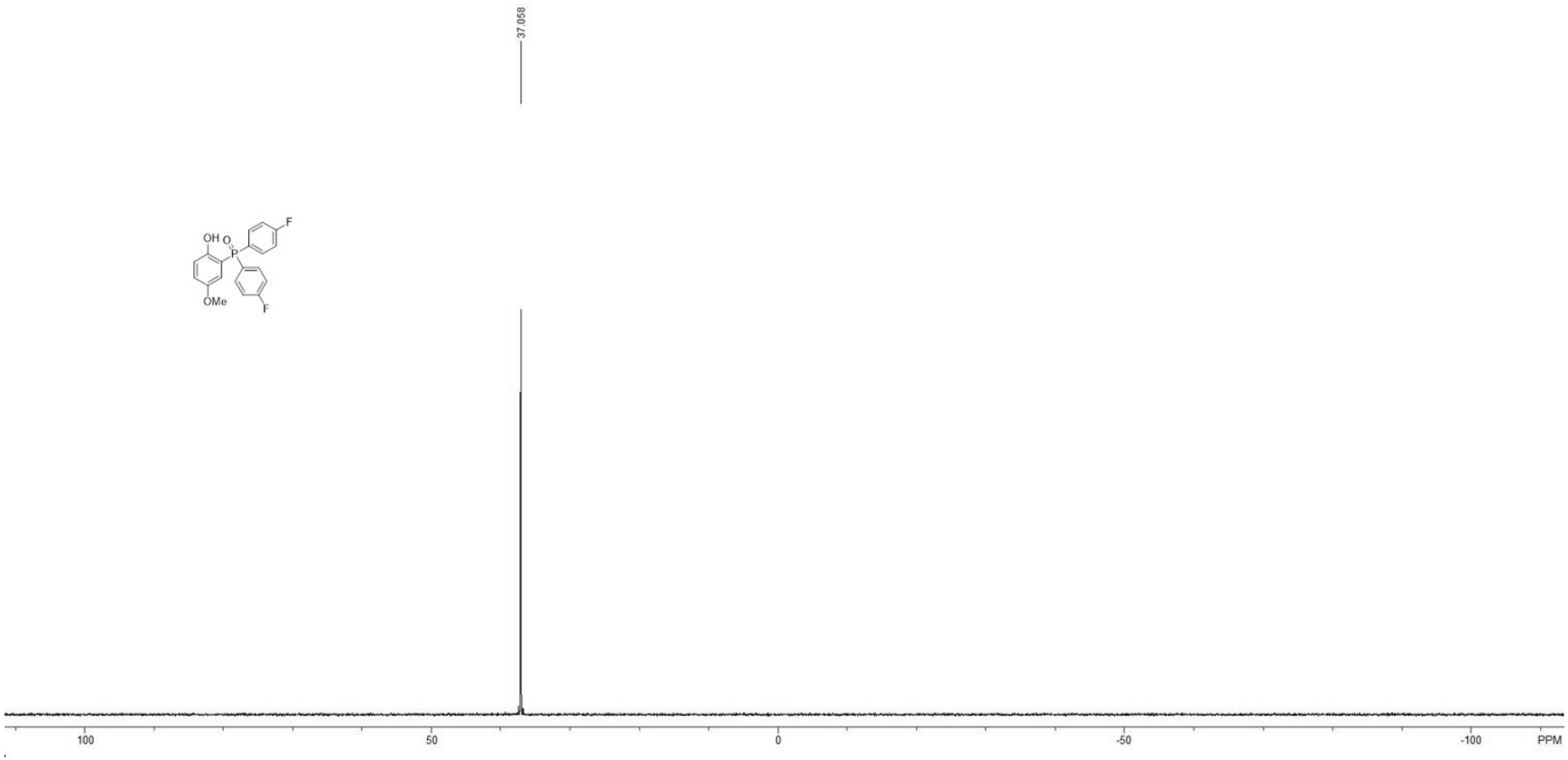
**$^{1}$H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3ad)**



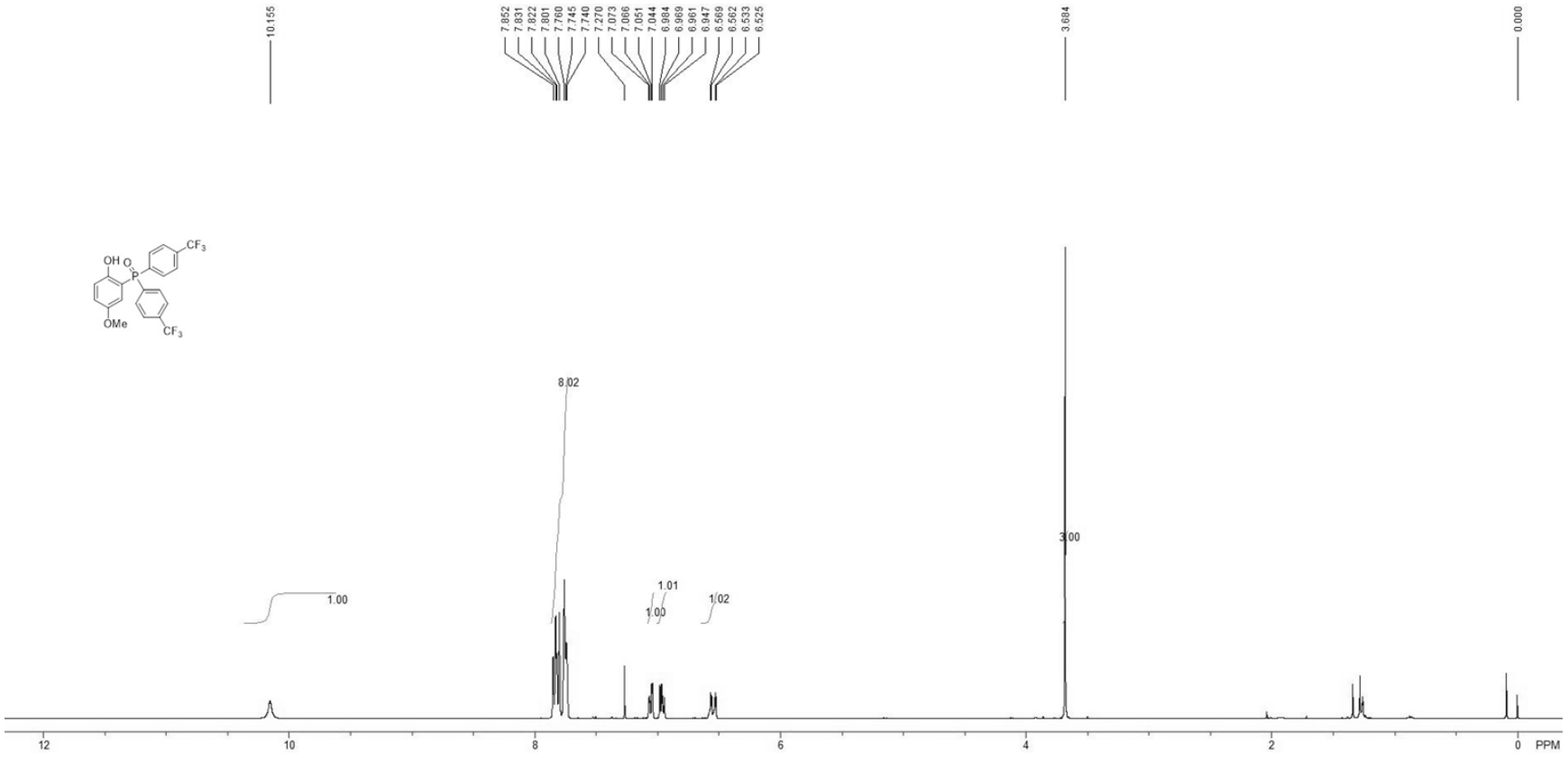
**$^{13}$C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3ad)**



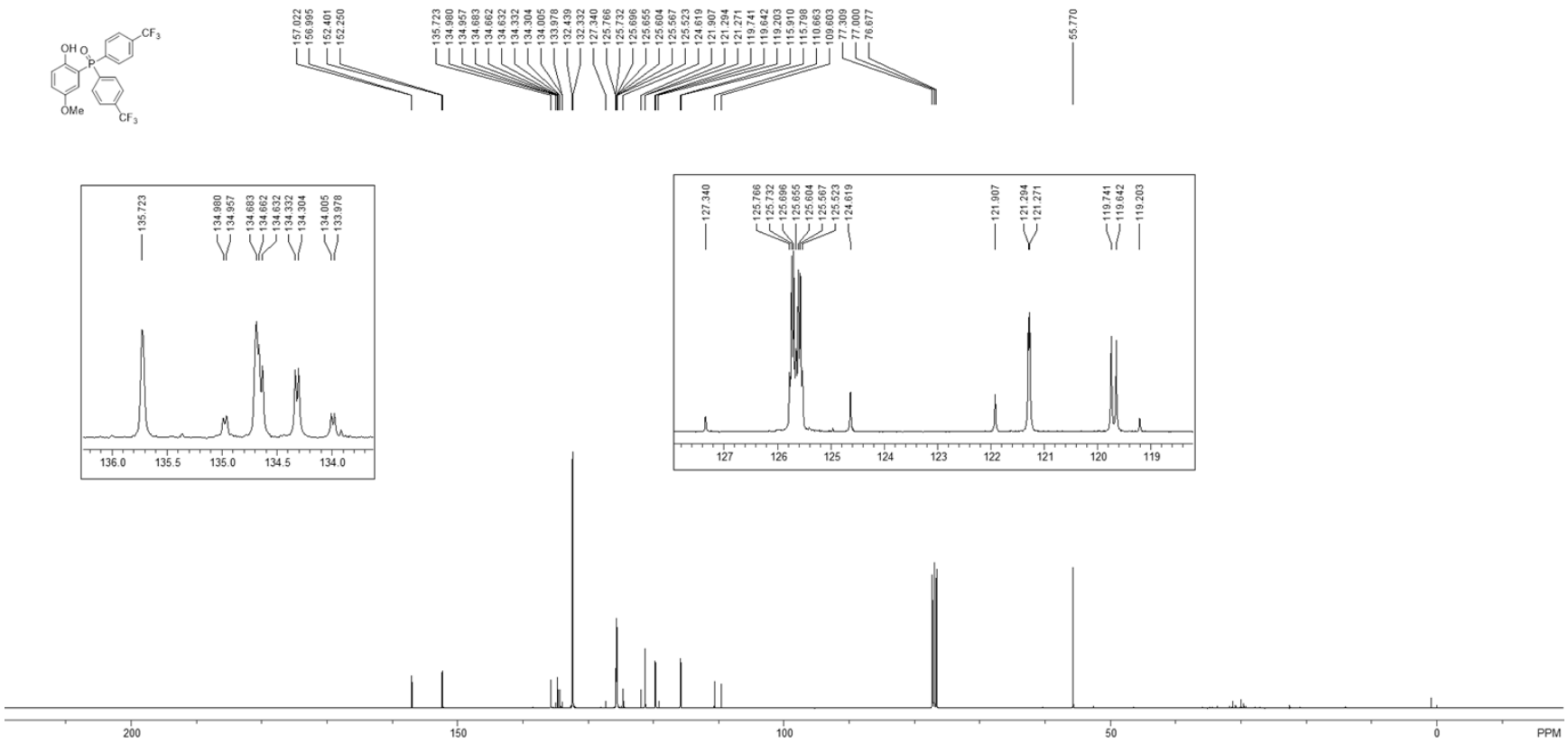
**$^{31}$P NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3ad)**



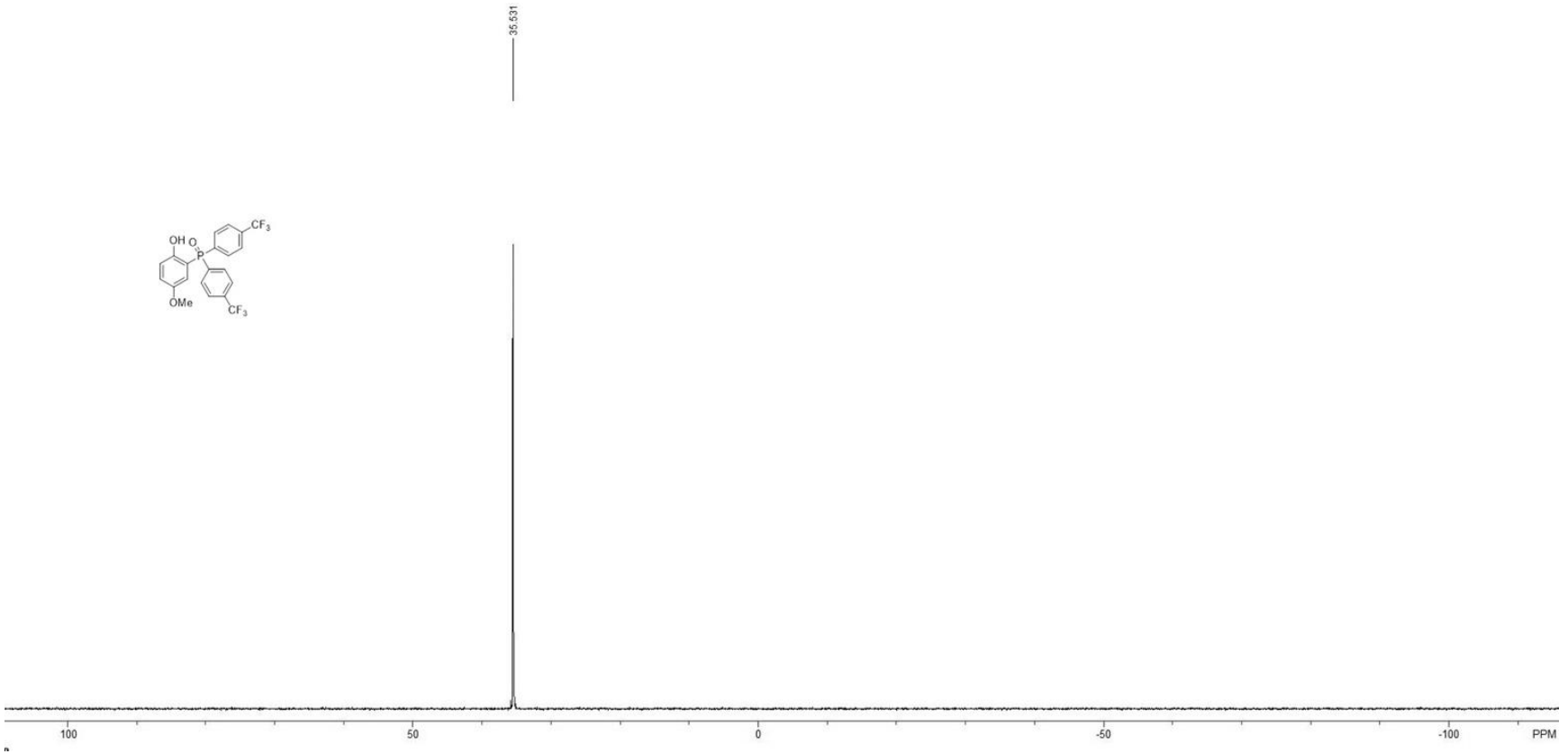
**$^{1}$H NMR of (2-hydroxy-5-methoxyphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)**



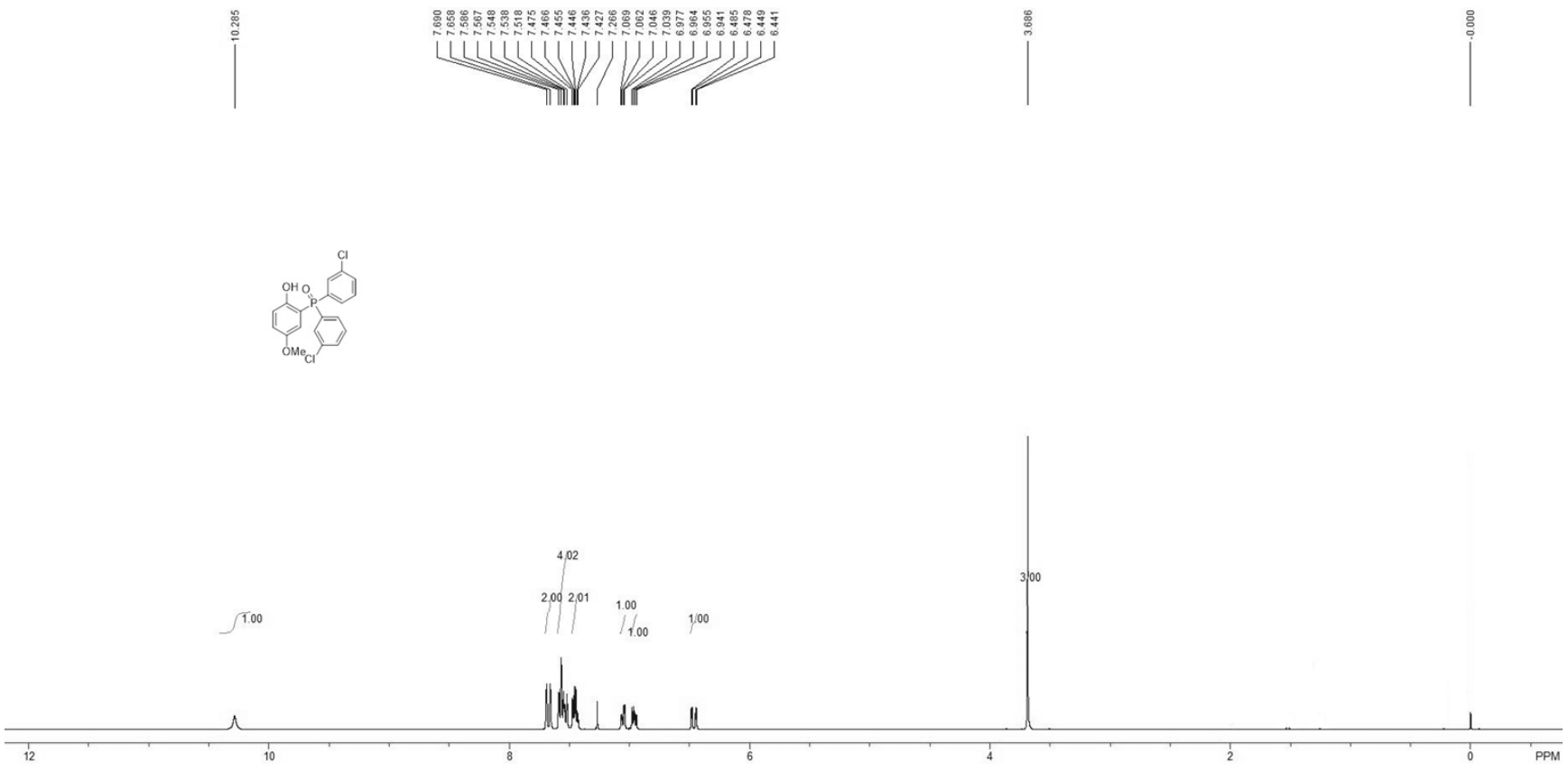
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)**



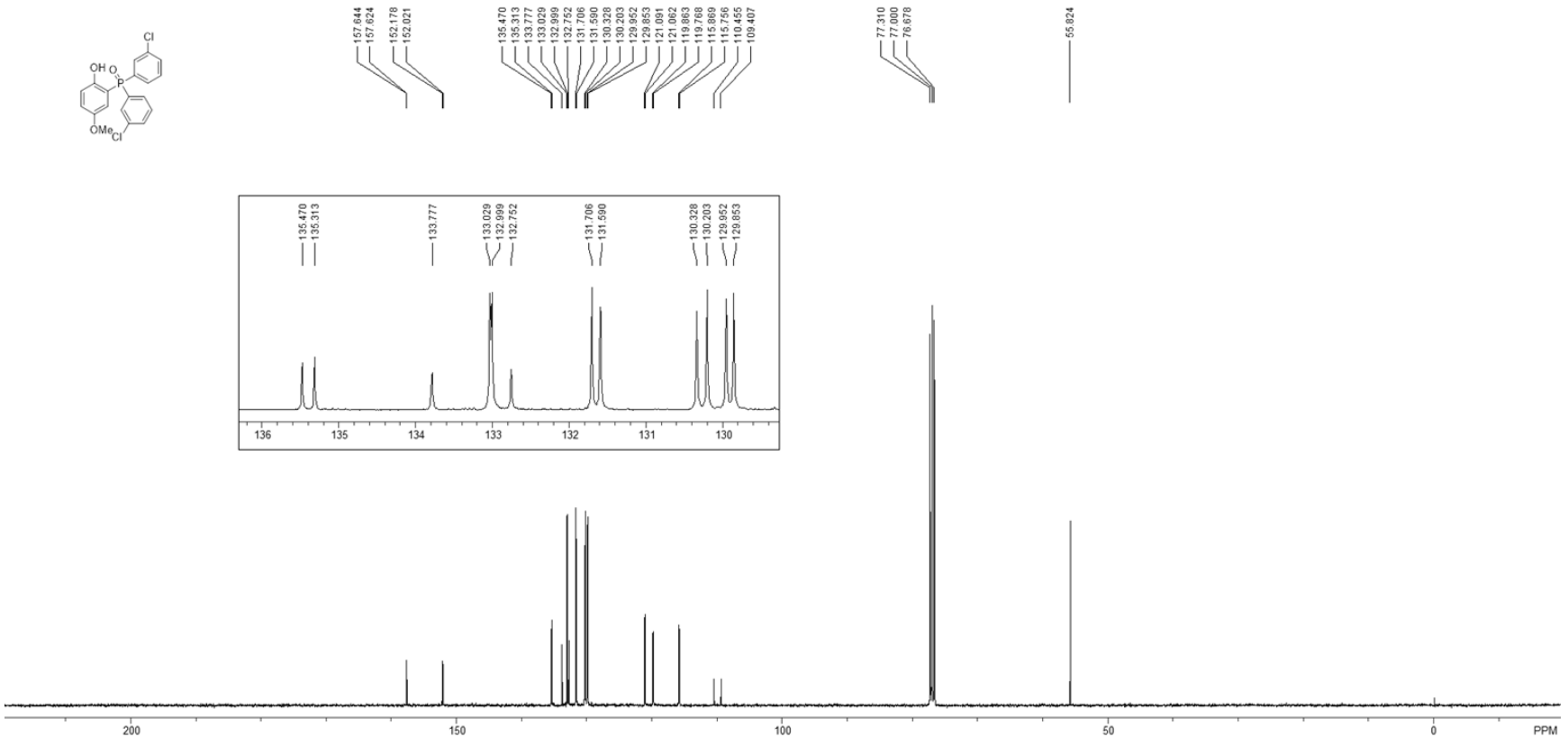
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)**



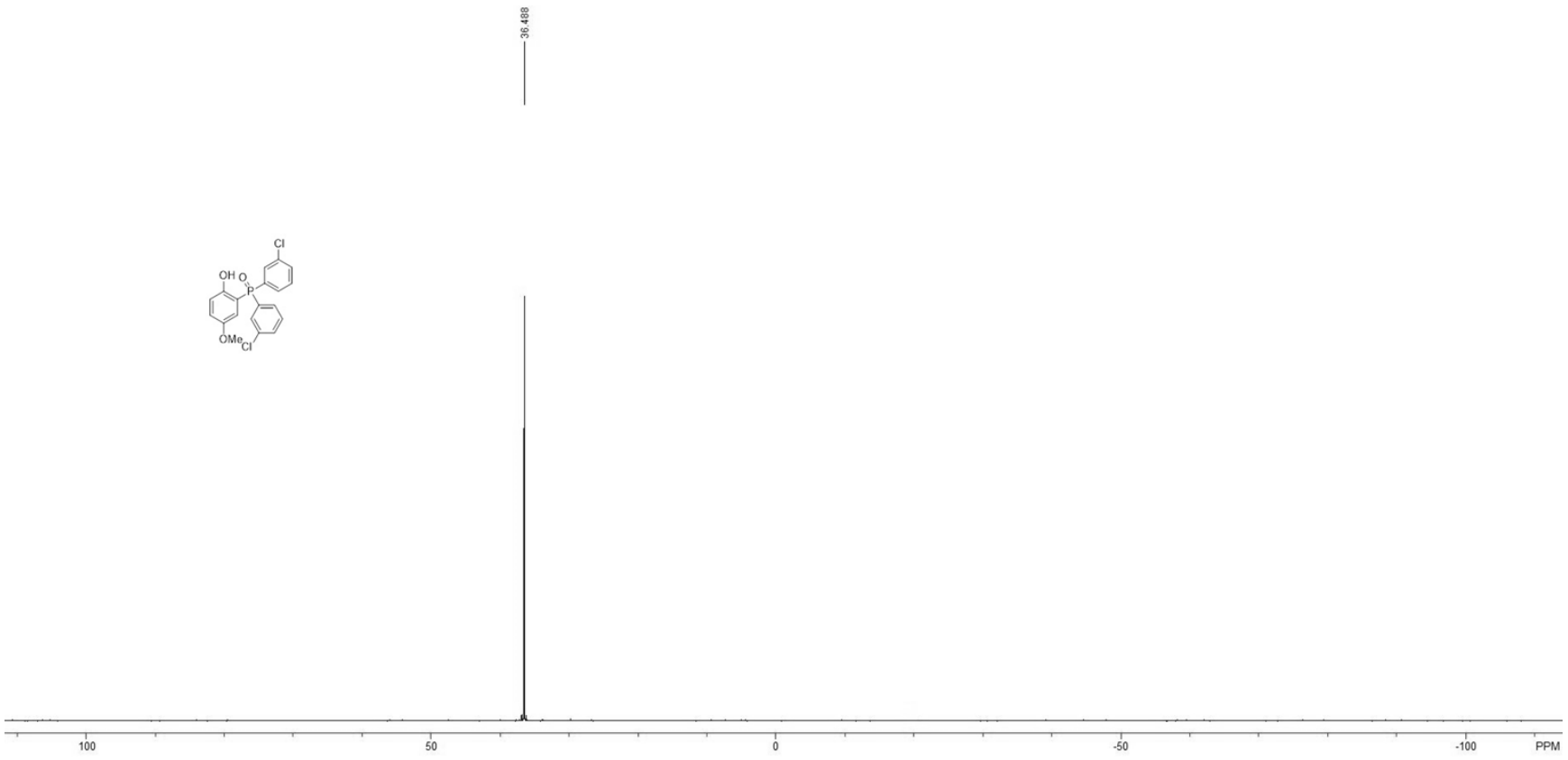
**$^{1}$H NMR of bis(3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3af)**



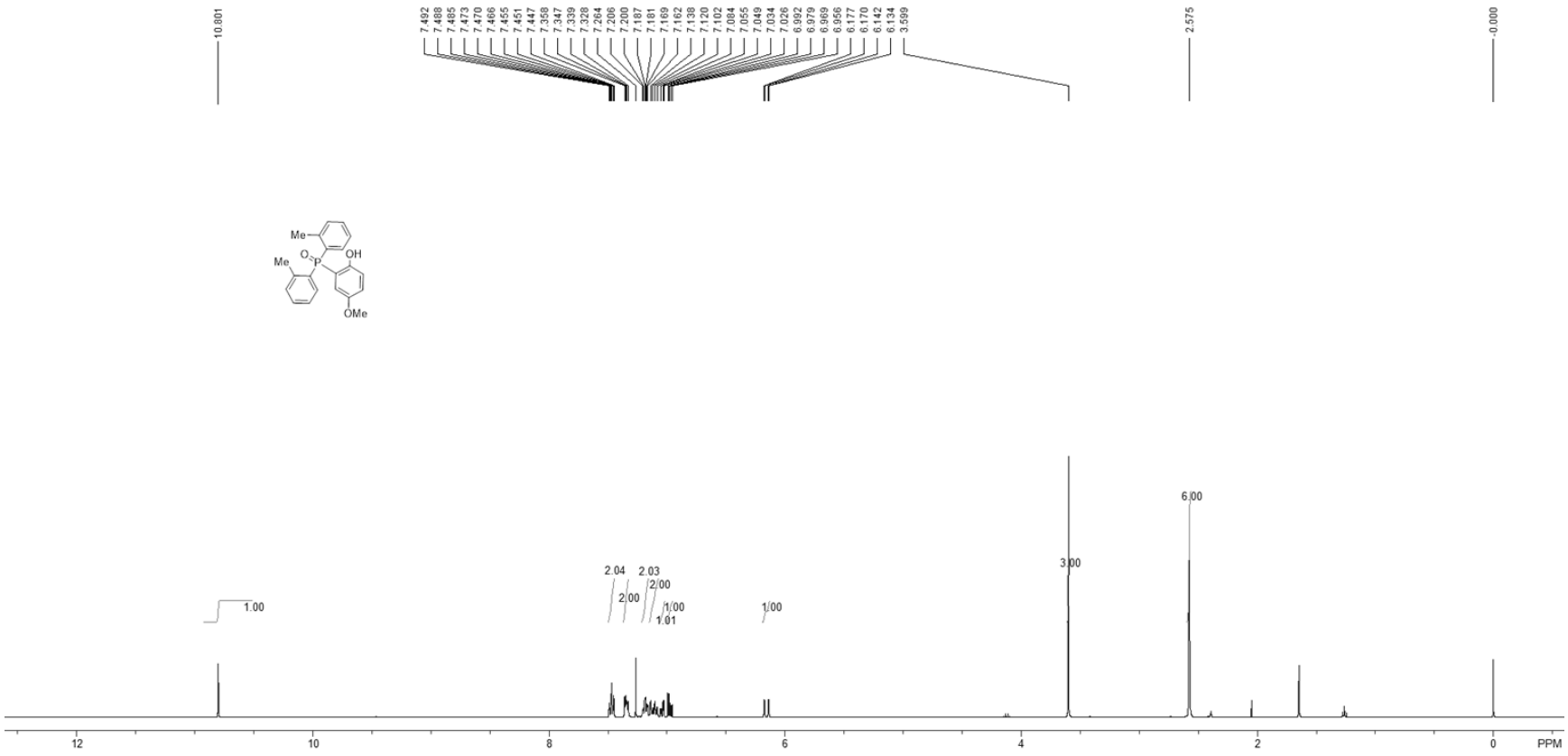
**$^{13}$C NMR of bis(3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3af)**



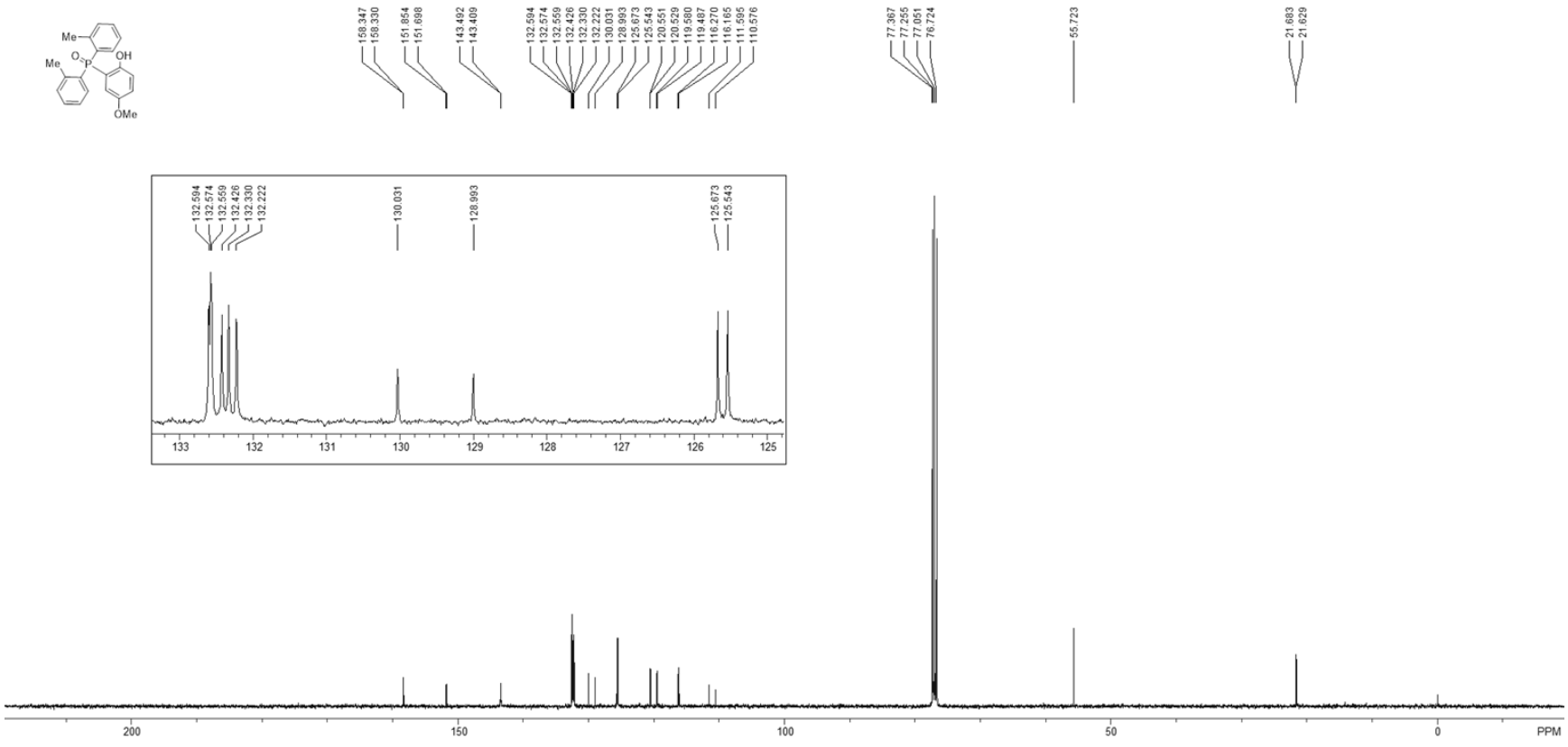
**$^{31}$P NMR of bis(3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)phosphine oxide (3af)**



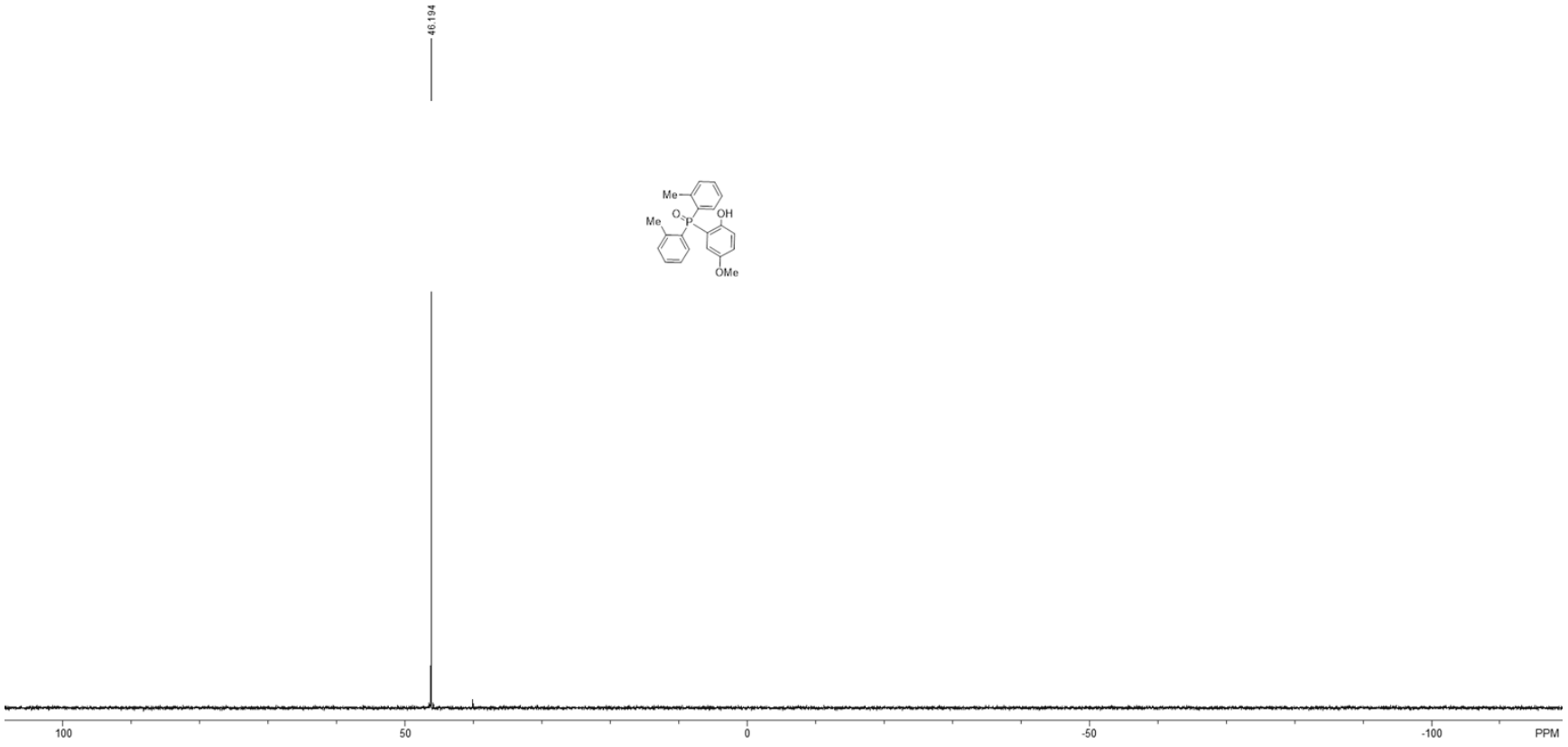
**$^{1}$H NMR of (2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ag)**



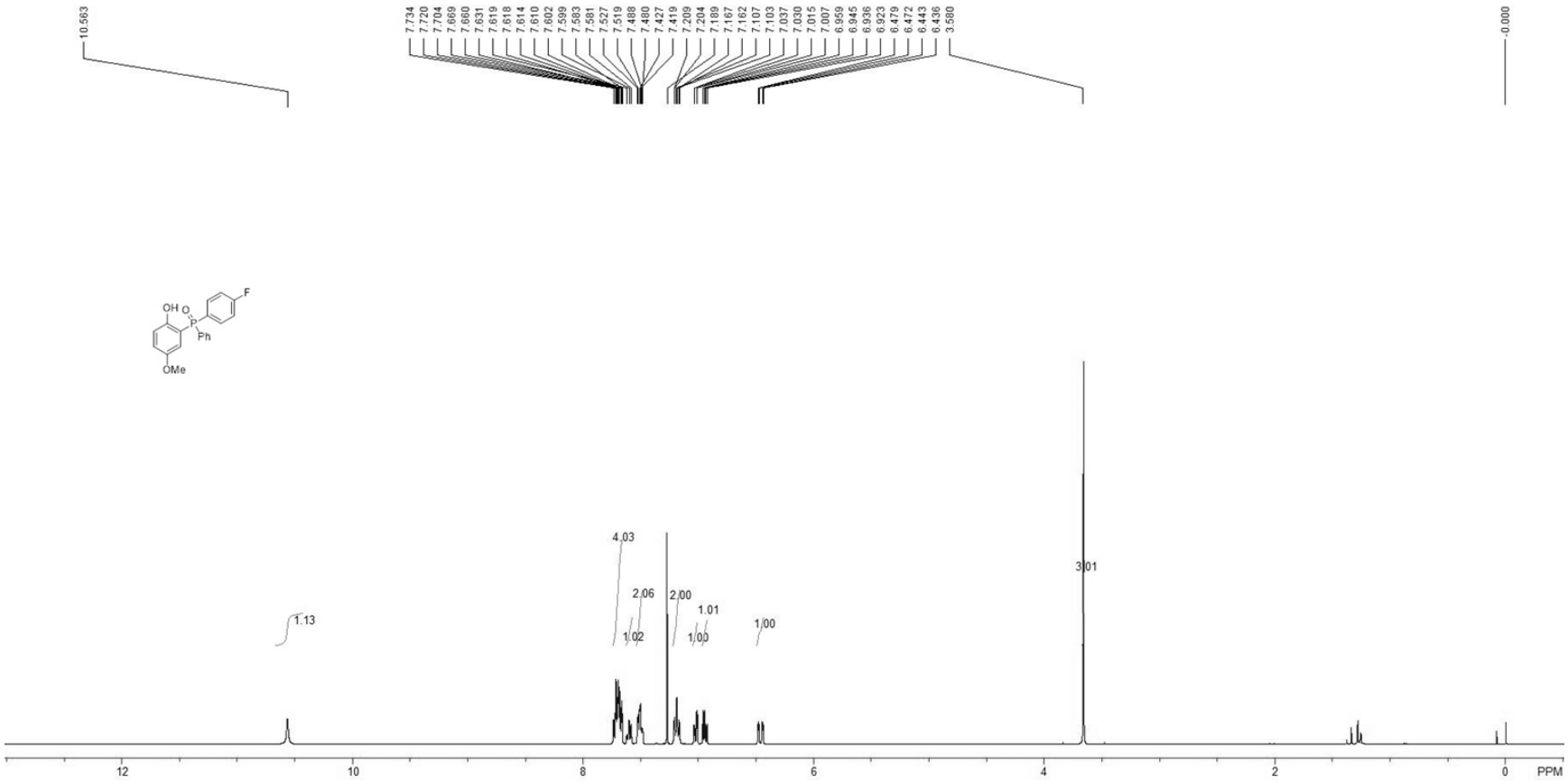
**$^{13}$C NMR of(2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ag)**



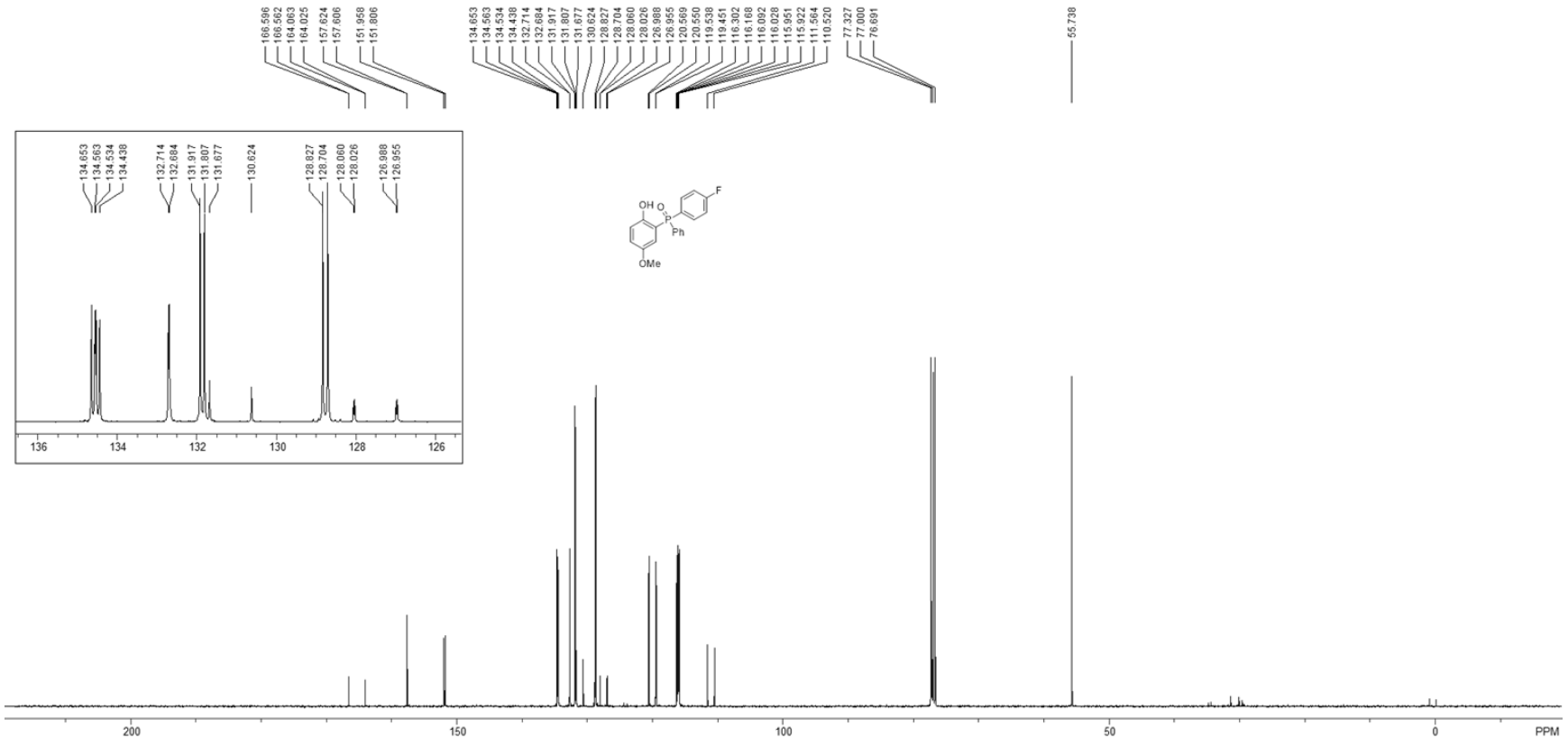
**$^{31}$P NMR of(2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ag)**



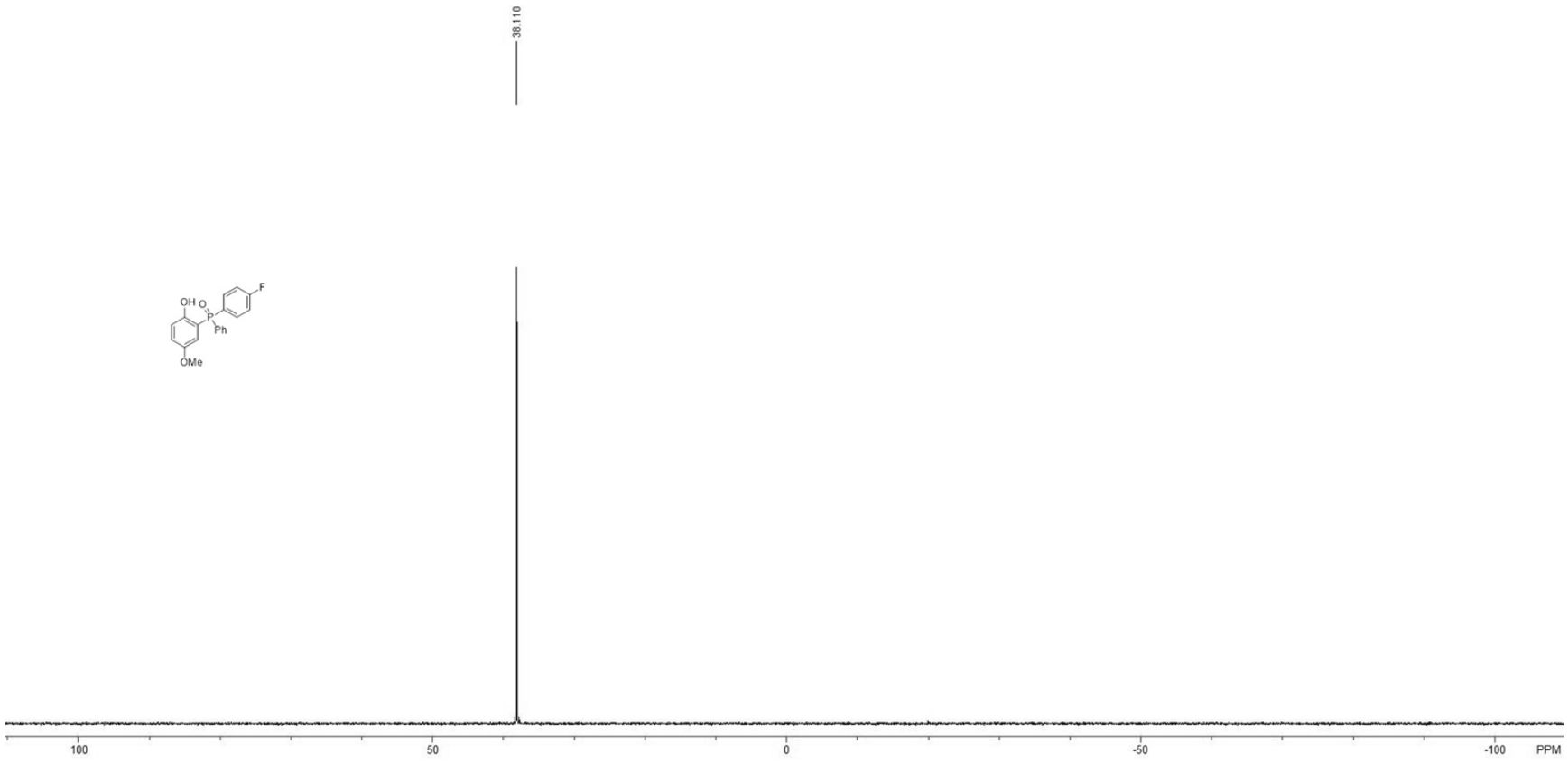
**$^{1}$H NMR of (4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ah)**



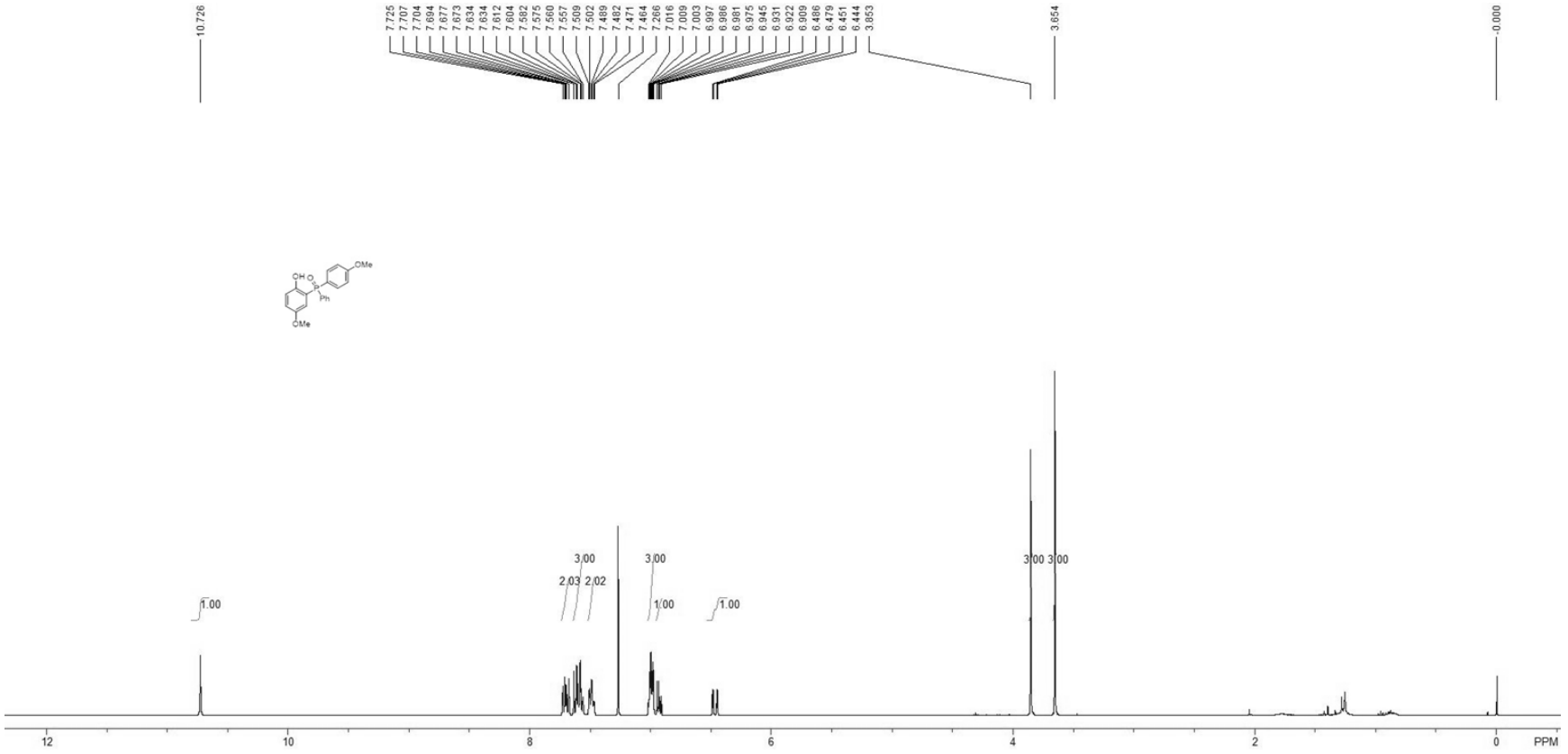
**$^{13}$C NMR of (4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ah)**



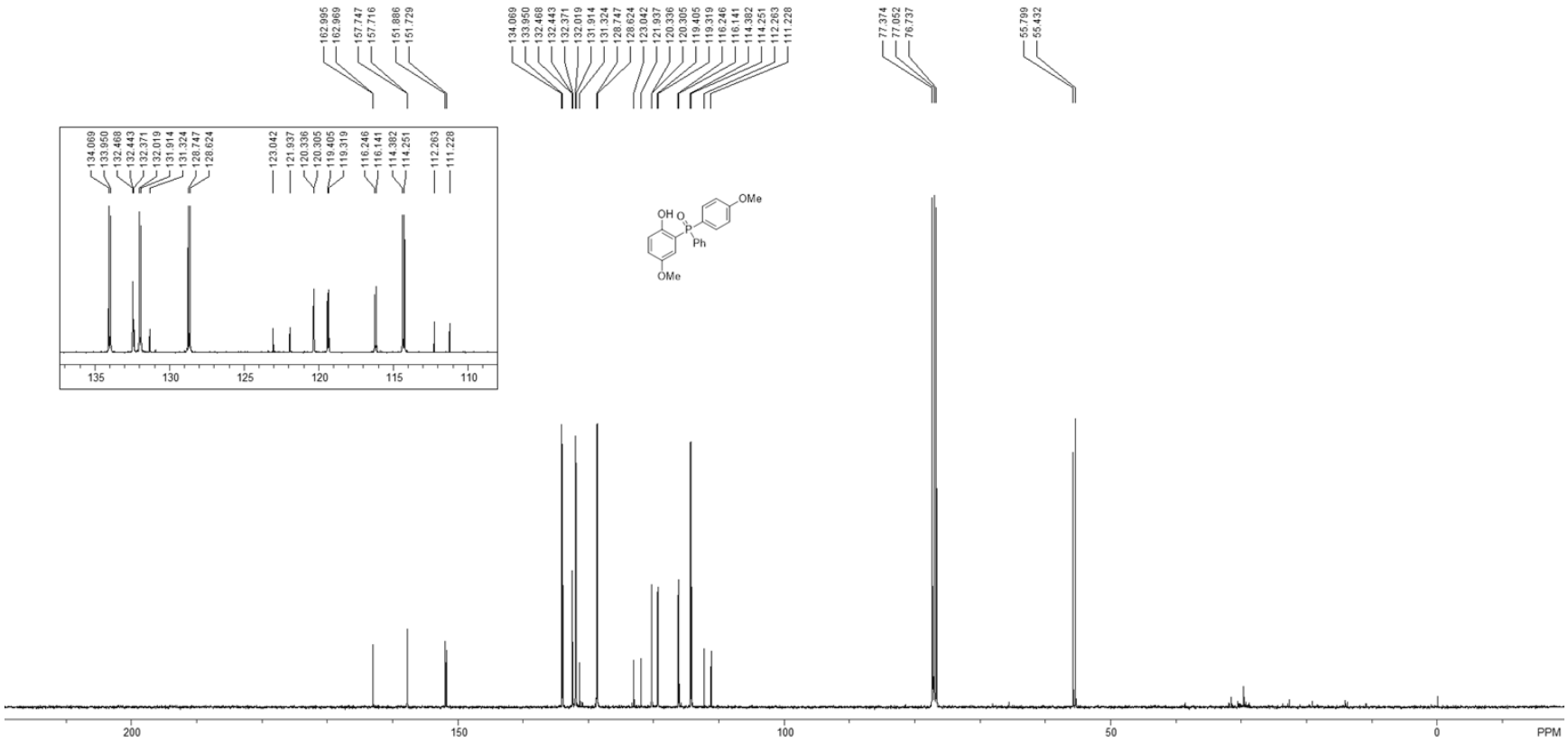
**$^{31}$P NMR of (4-fluorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ah)**



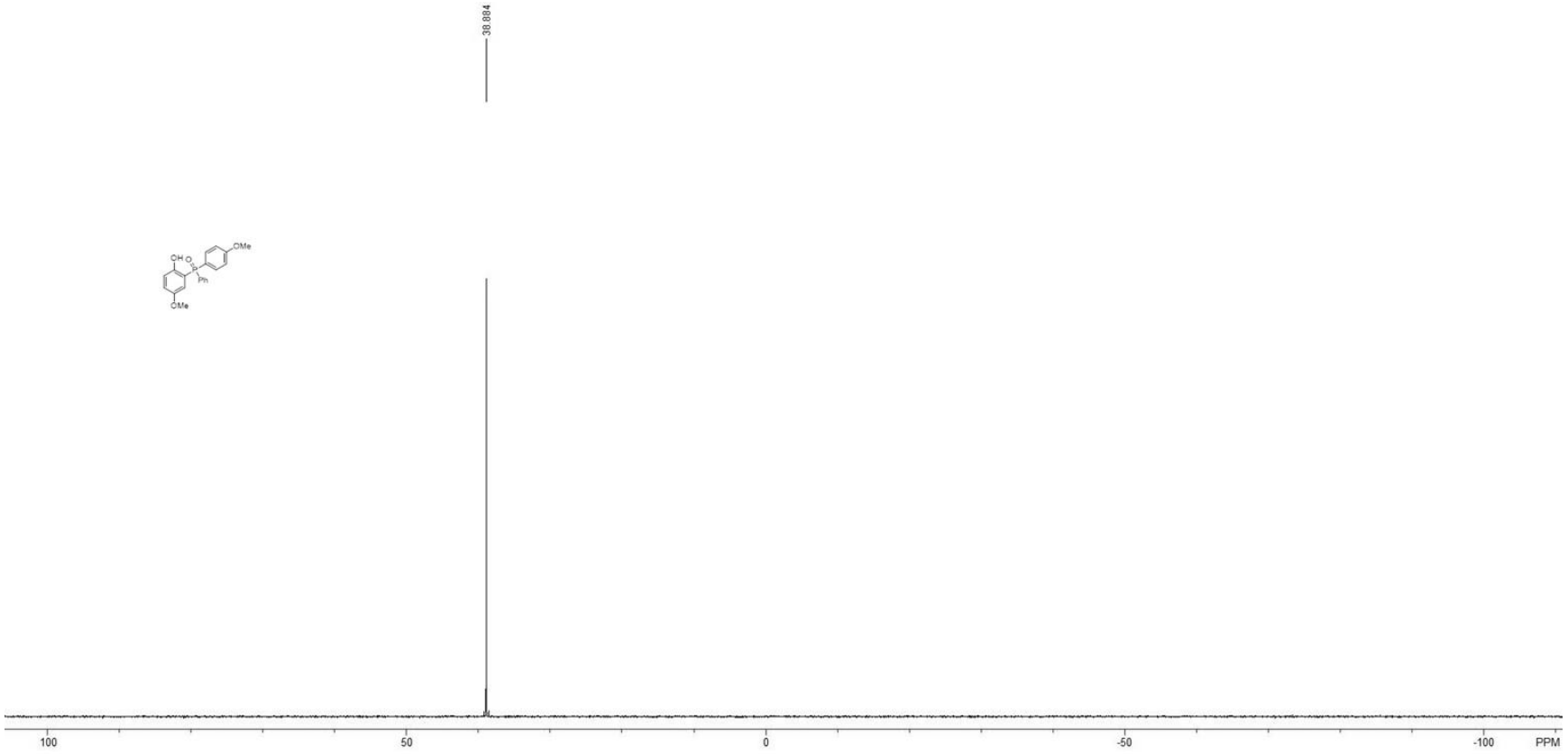
**$^{1}$H NMR of (2-hydroxy-5-methoxyphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3ai)**



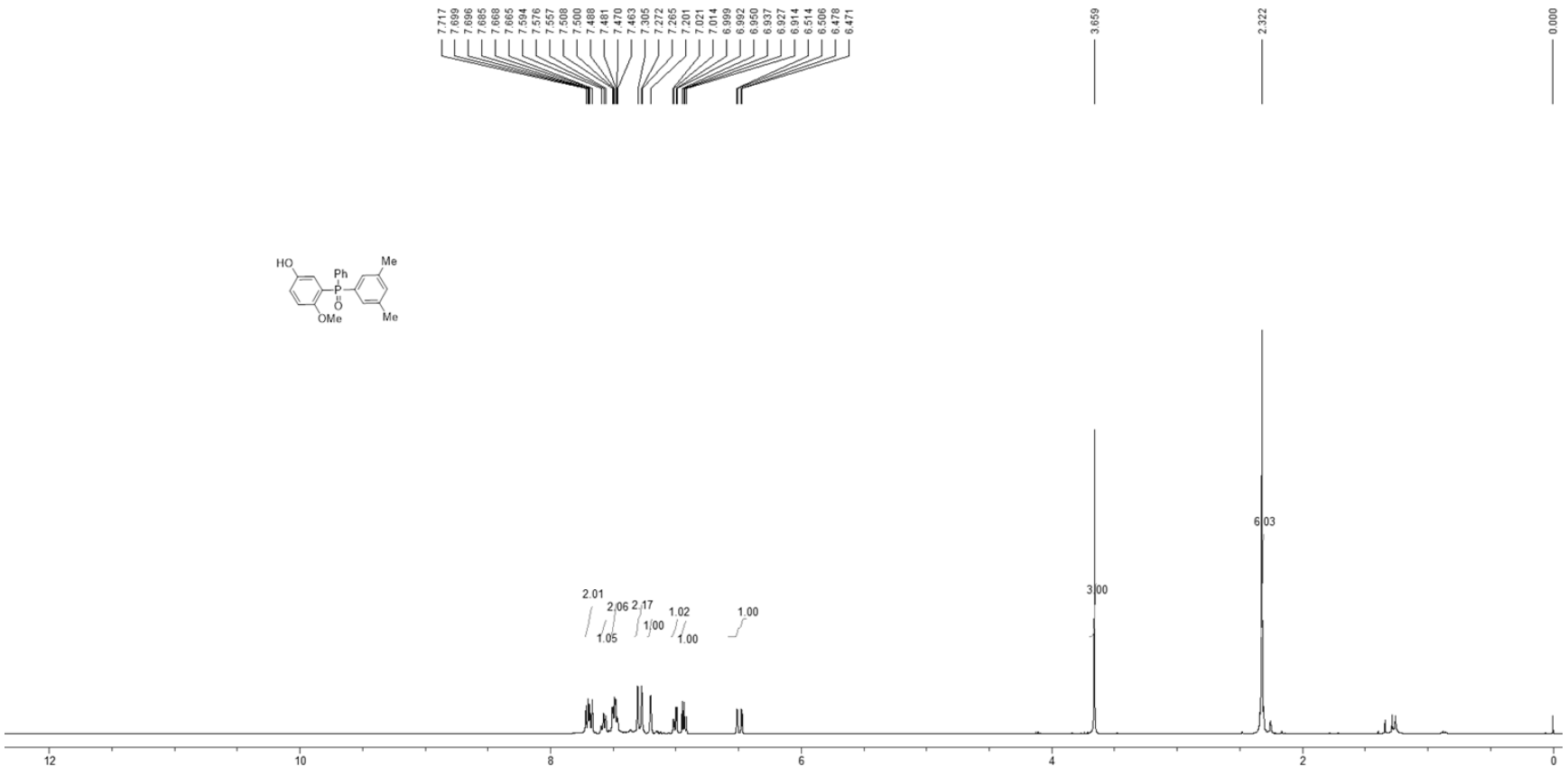
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3ai)**



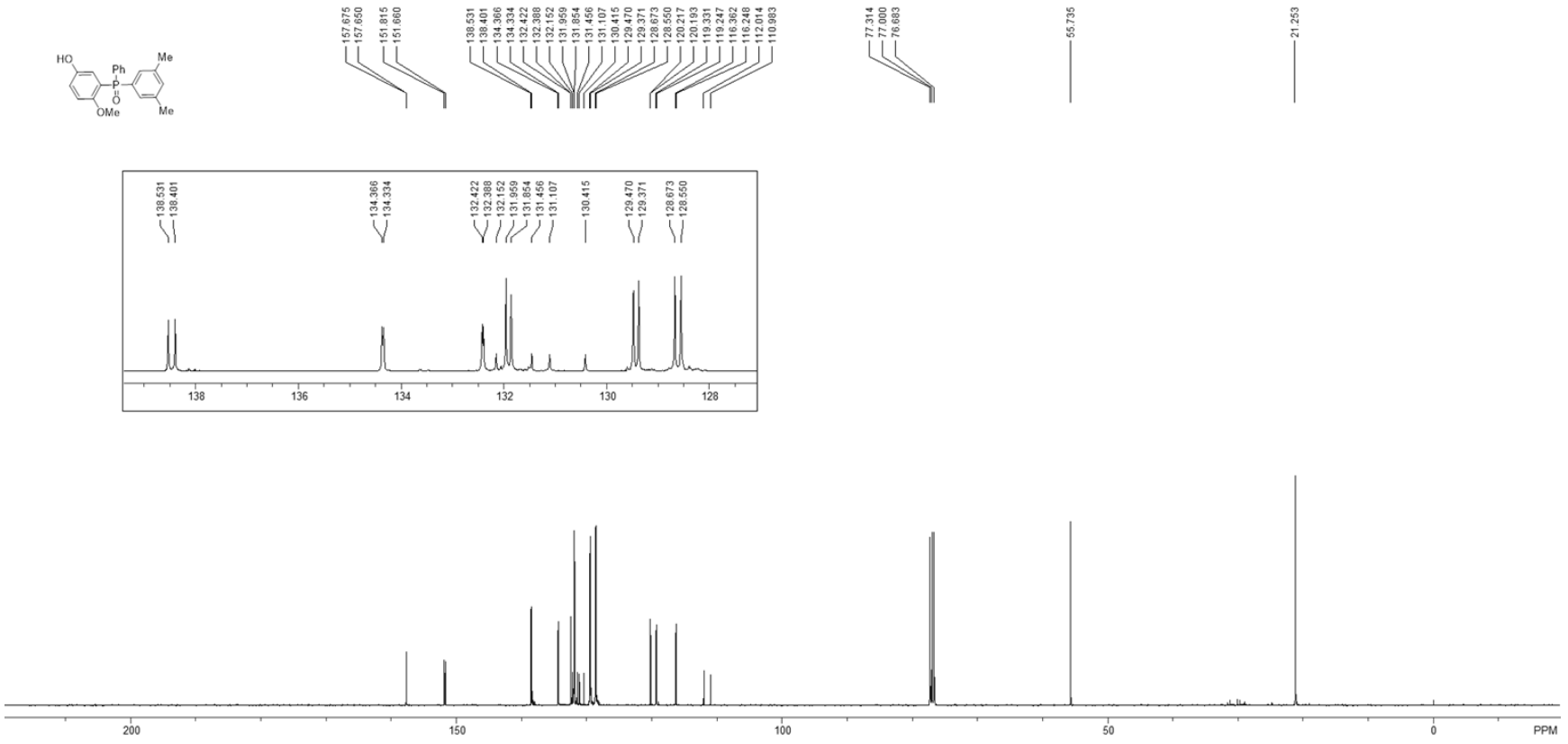
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3ai)**



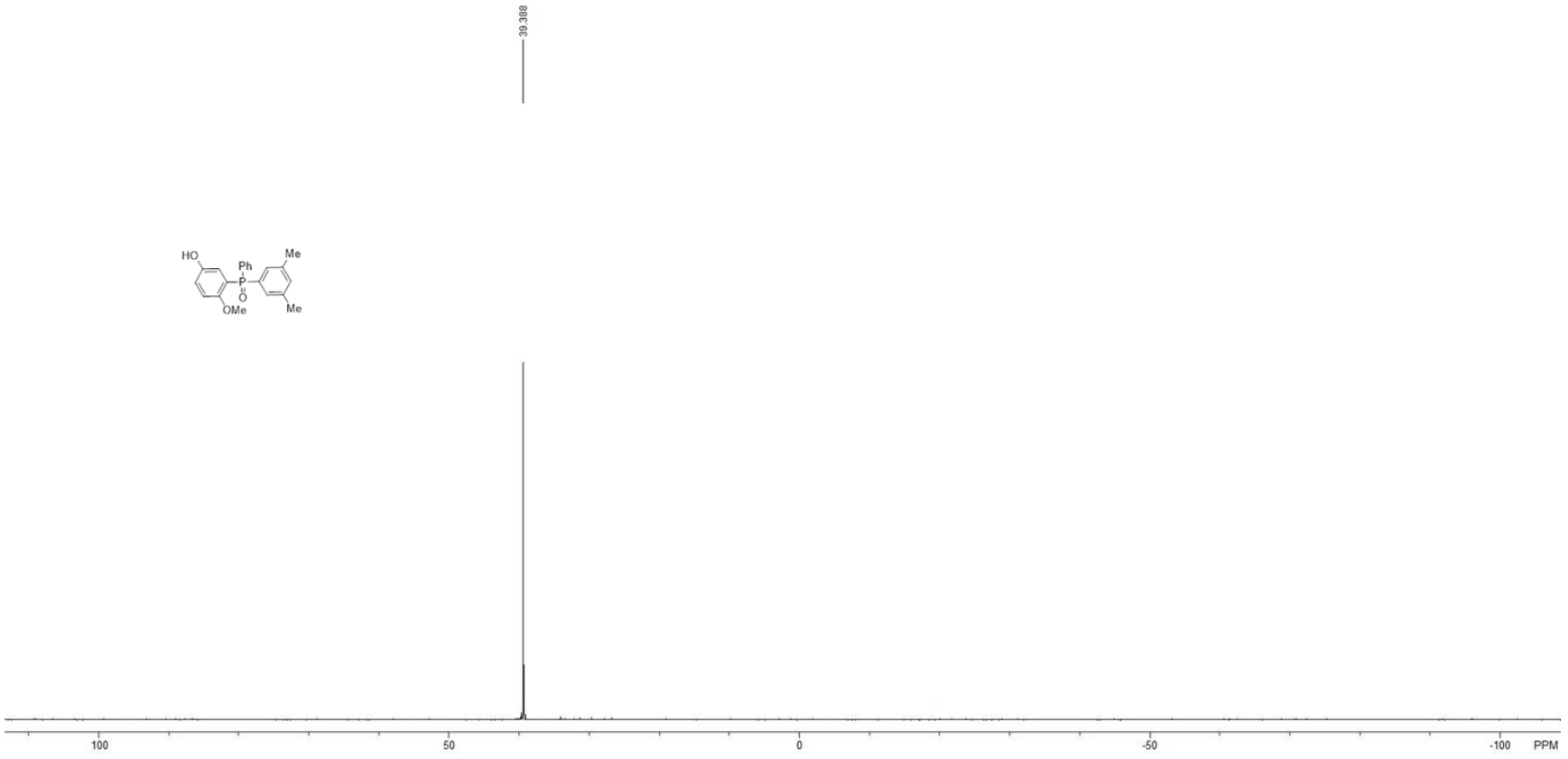
**$^{1}$H NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3aj)**



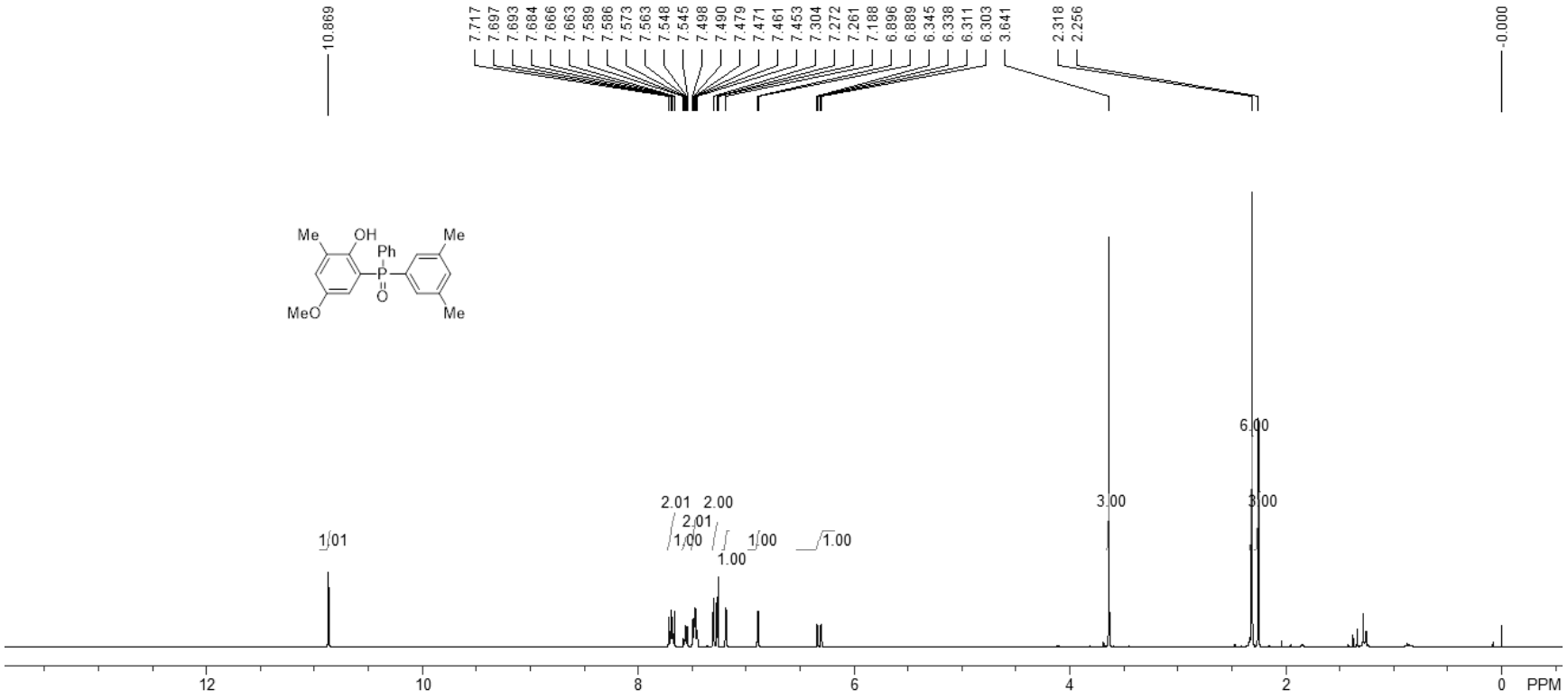
**$^{13}$C NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3aj)**



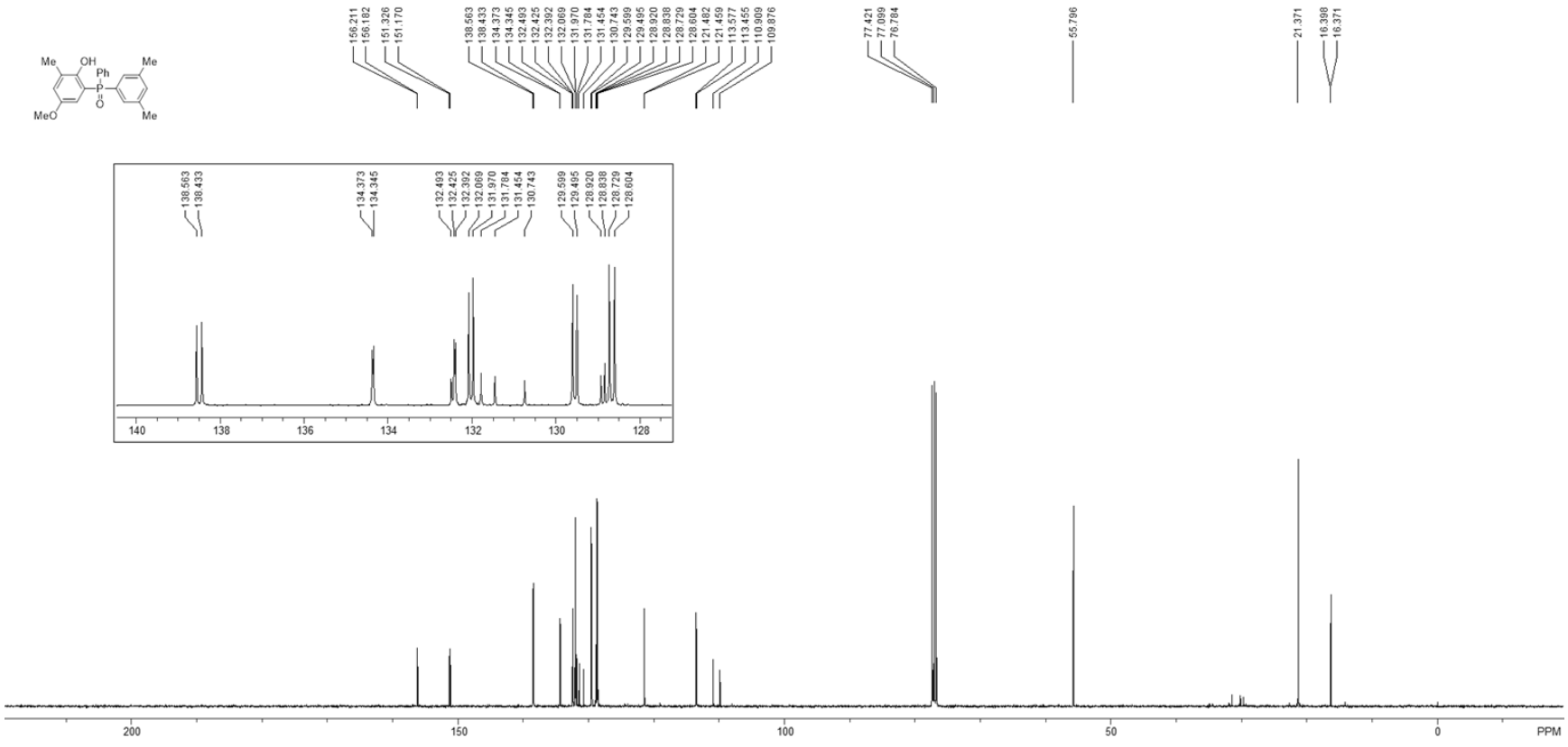
**$^{31}$P NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3aj)**



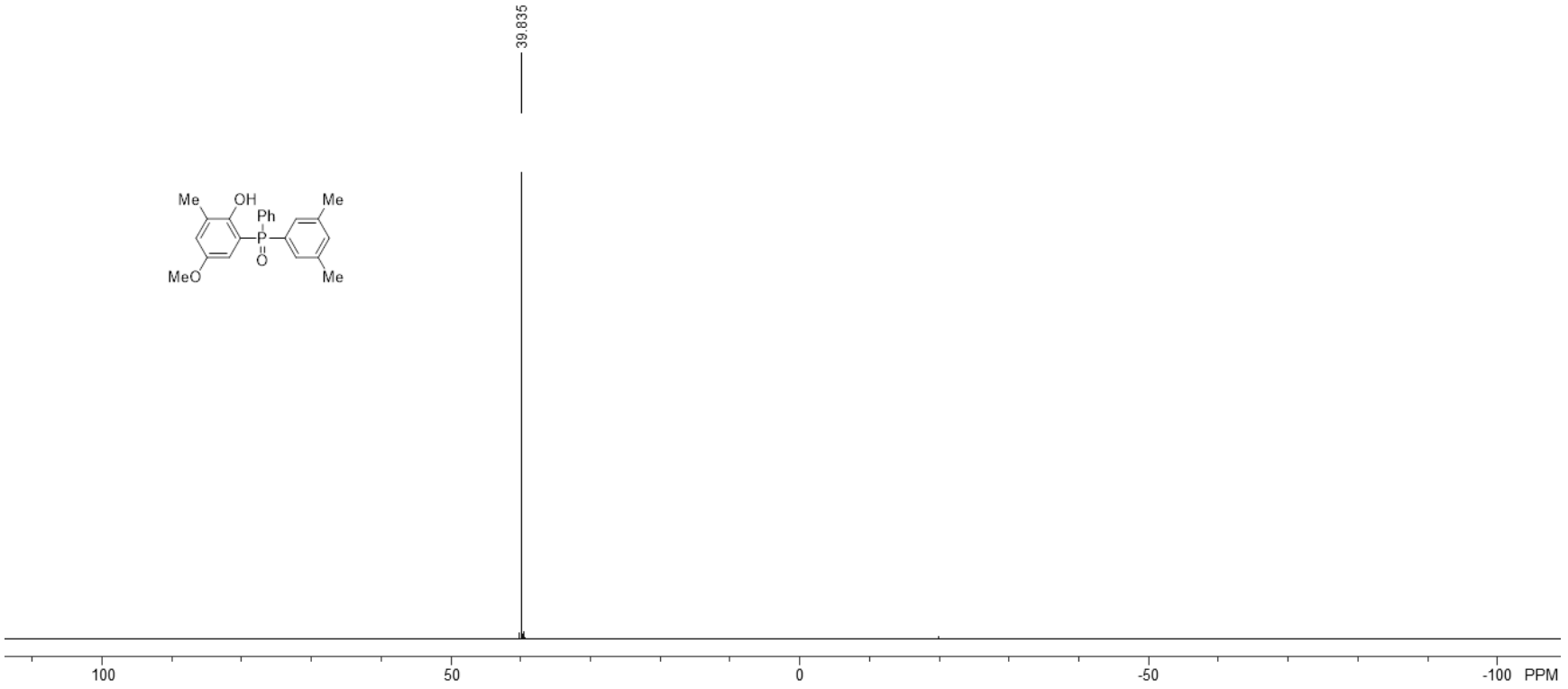
**$^{1}$H NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxy-3-methylphenyl)(phenyl)phosphine oxide (3bj)**



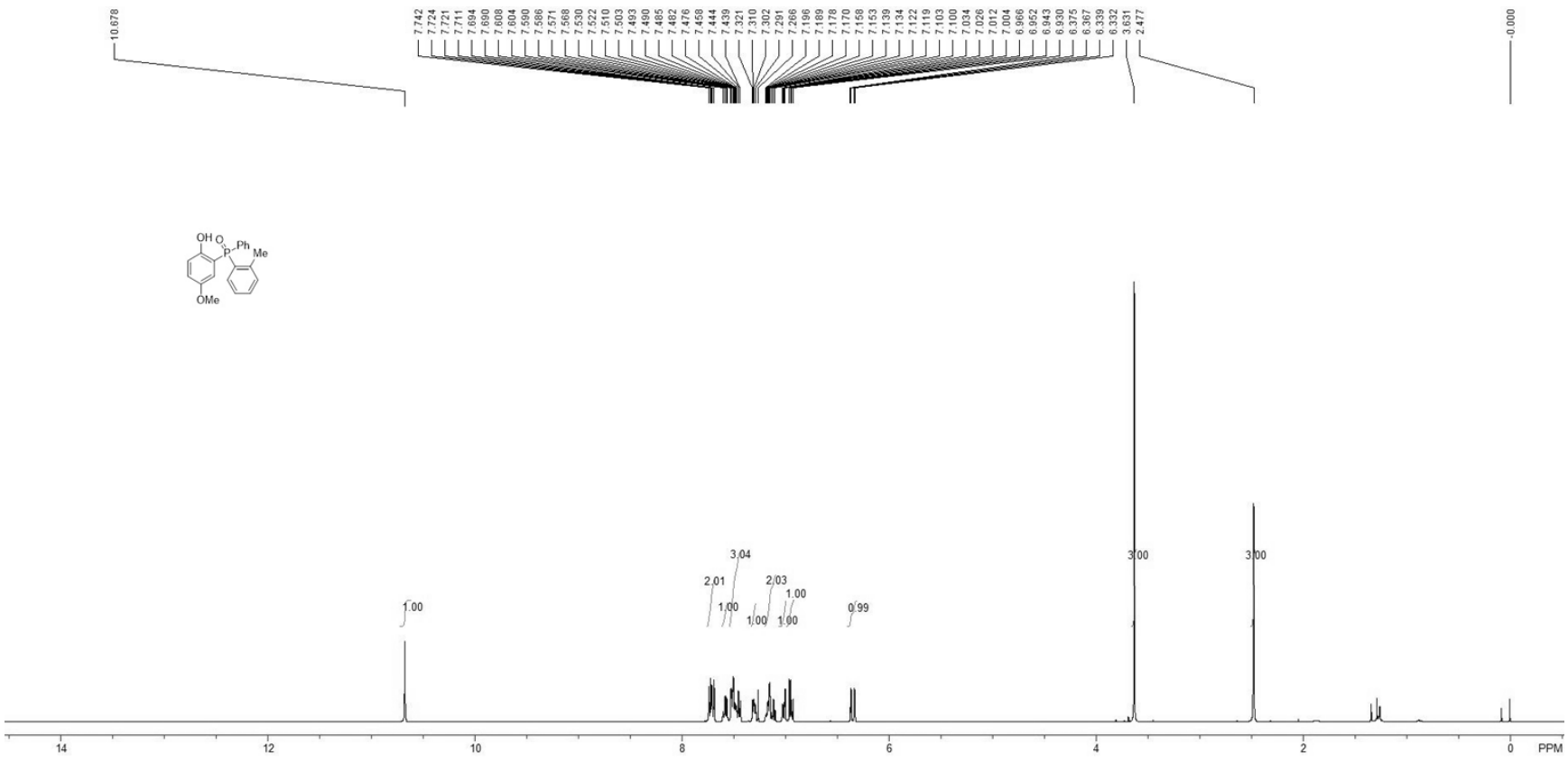
**$^{13}$C NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxy-3-methylphenyl)(phenyl)phosphine oxide (3bj)**



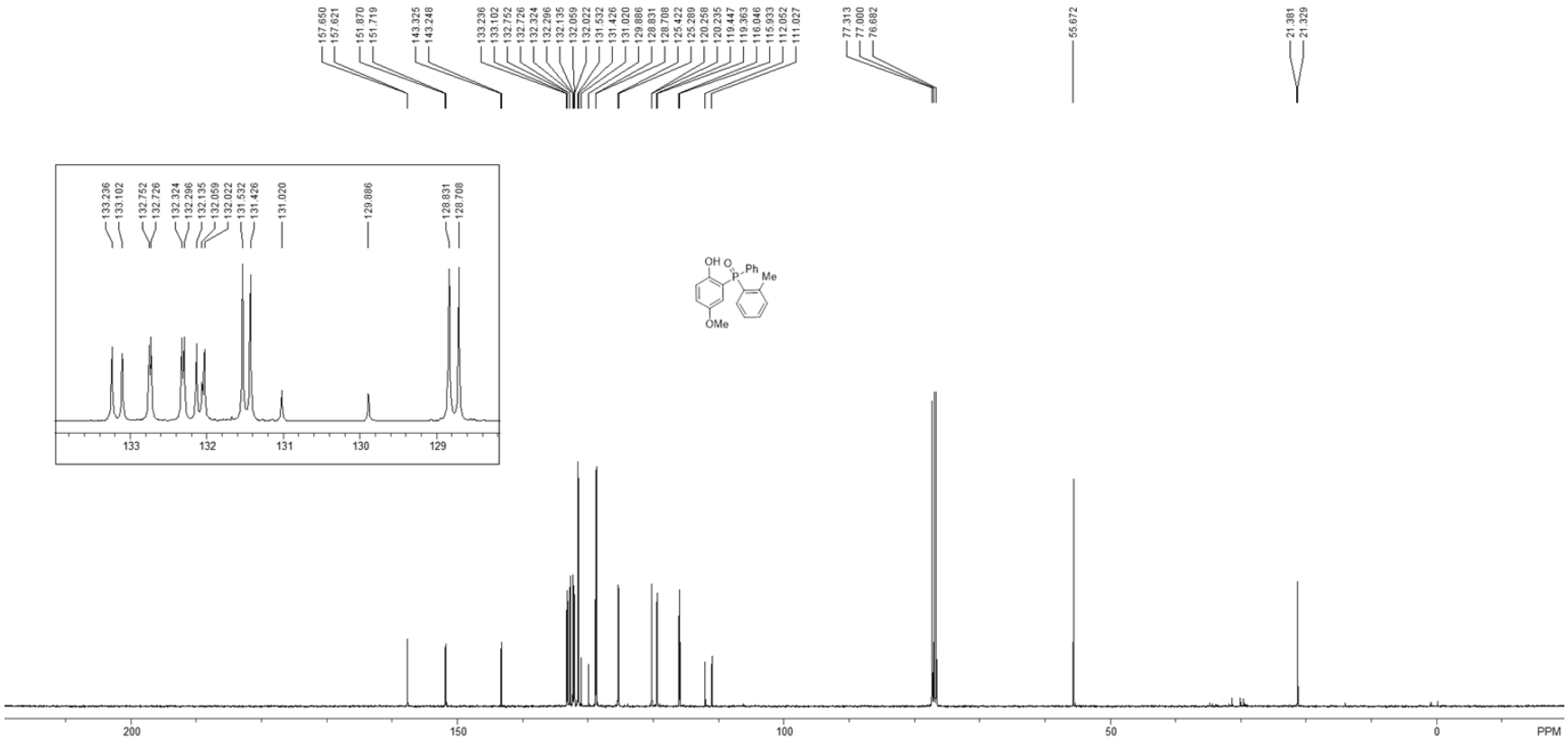
**$^{31}$P NMR of (3,5-dimethylphenyl)(2-hydroxy-5-methoxy-3-methylphenyl)(phenyl)phosphine oxide (3bj)**



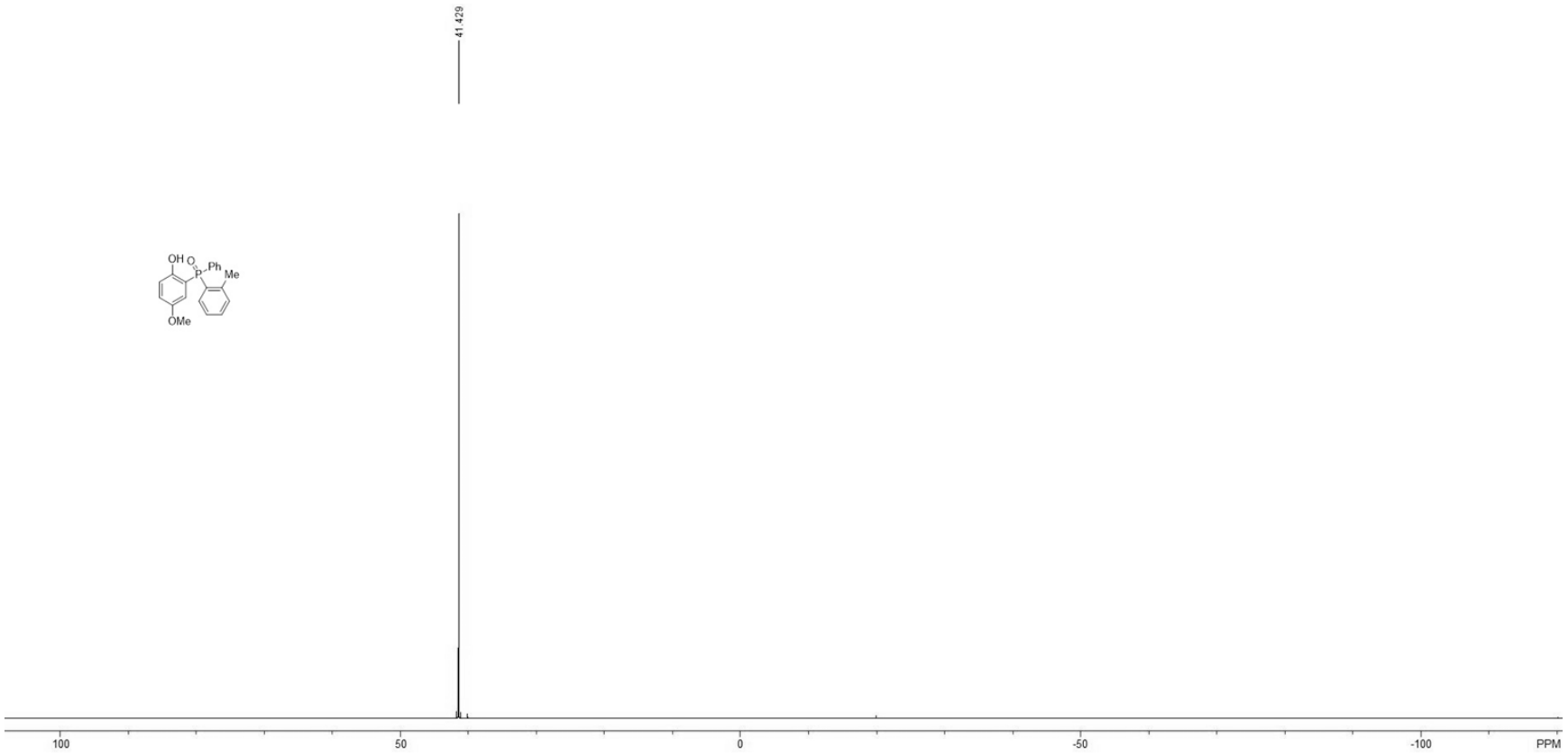
**[1]H NMR of (2-hydroxy-5-methoxyphenyl)(phenyl)(o-tolyl)phosphine oxide (3ak)**



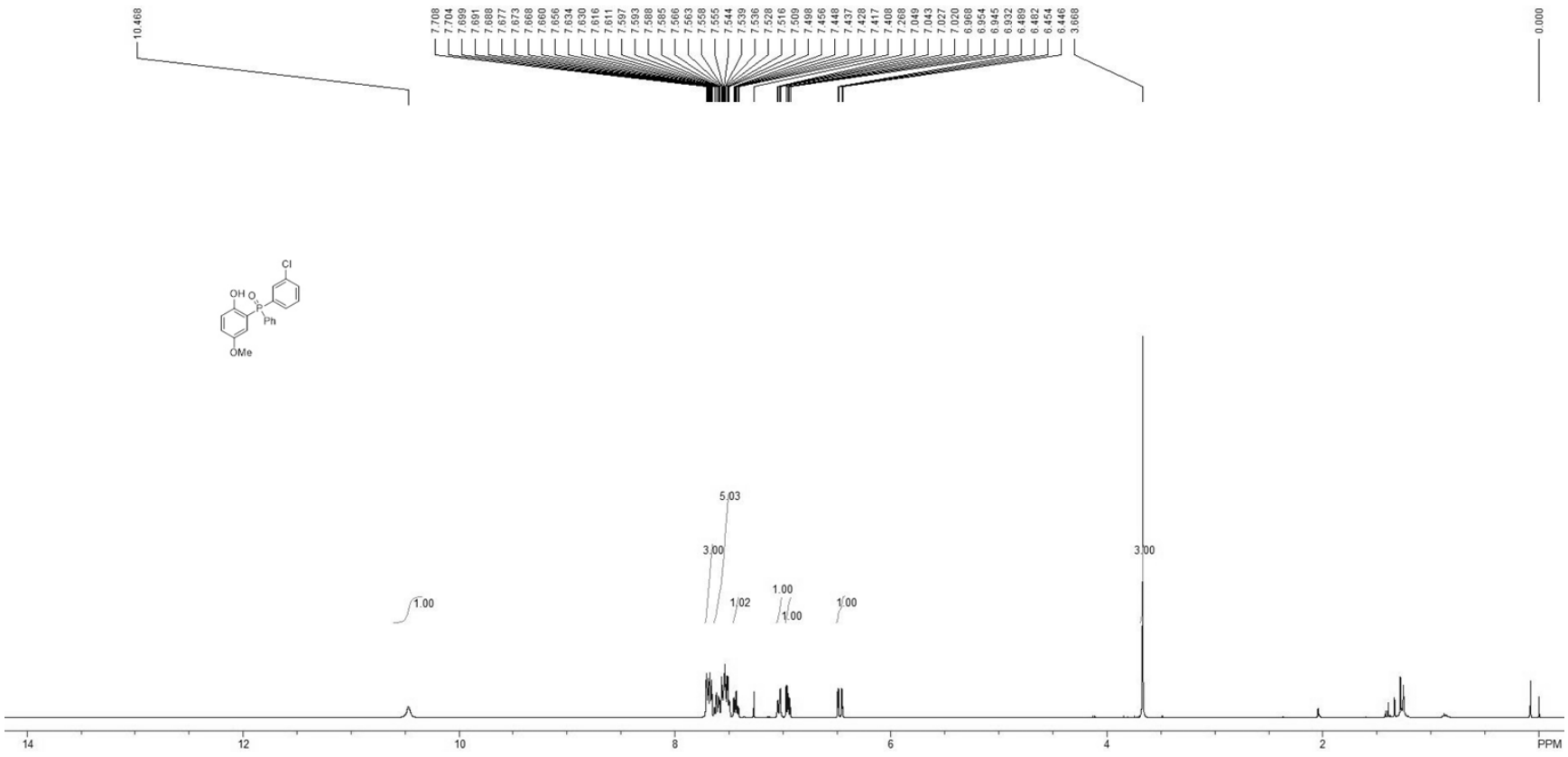
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)(phenyl)(o-tolyl)phosphine oxide (3ak)**



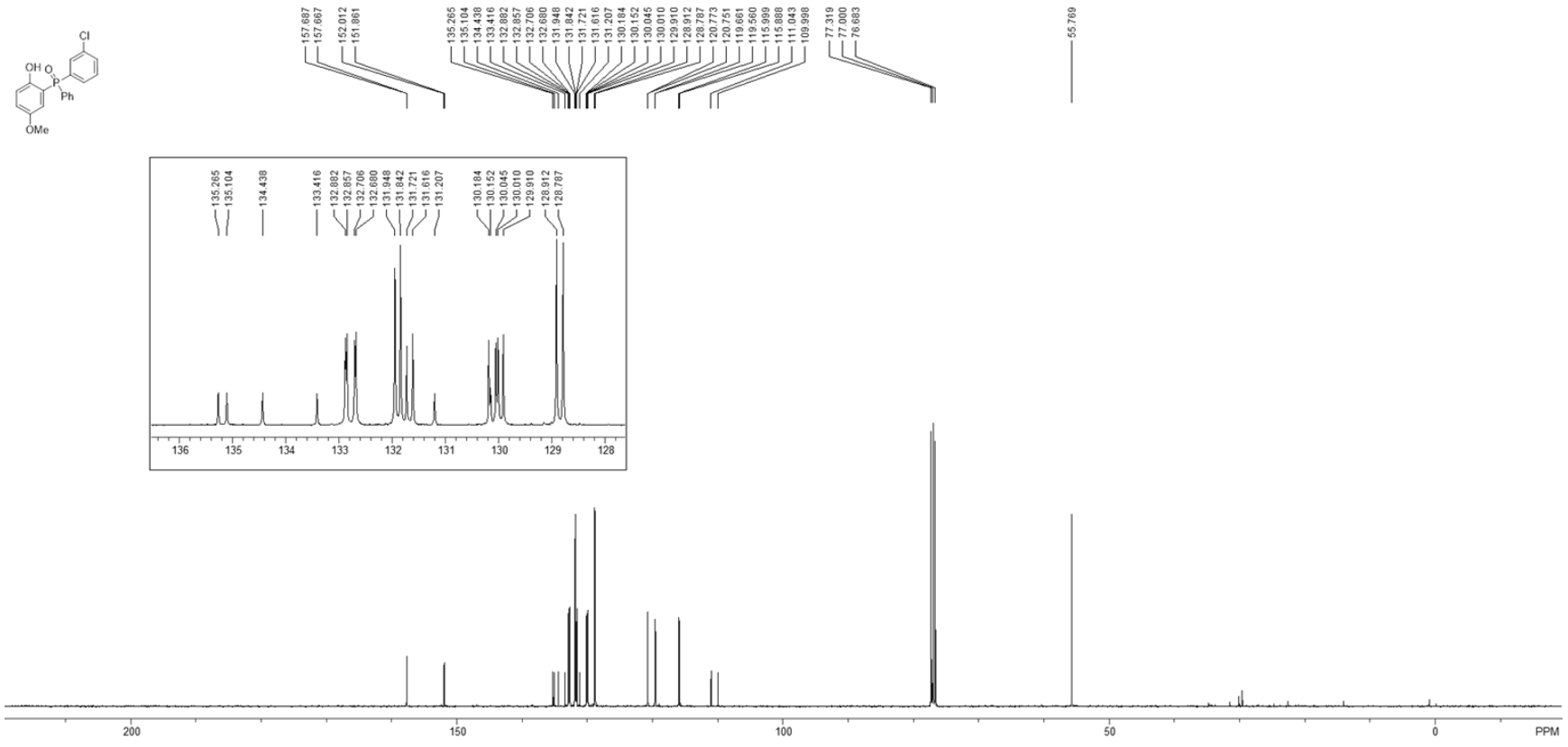
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)(phenyl)(o-tolyl)phosphine oxide (3ak)**



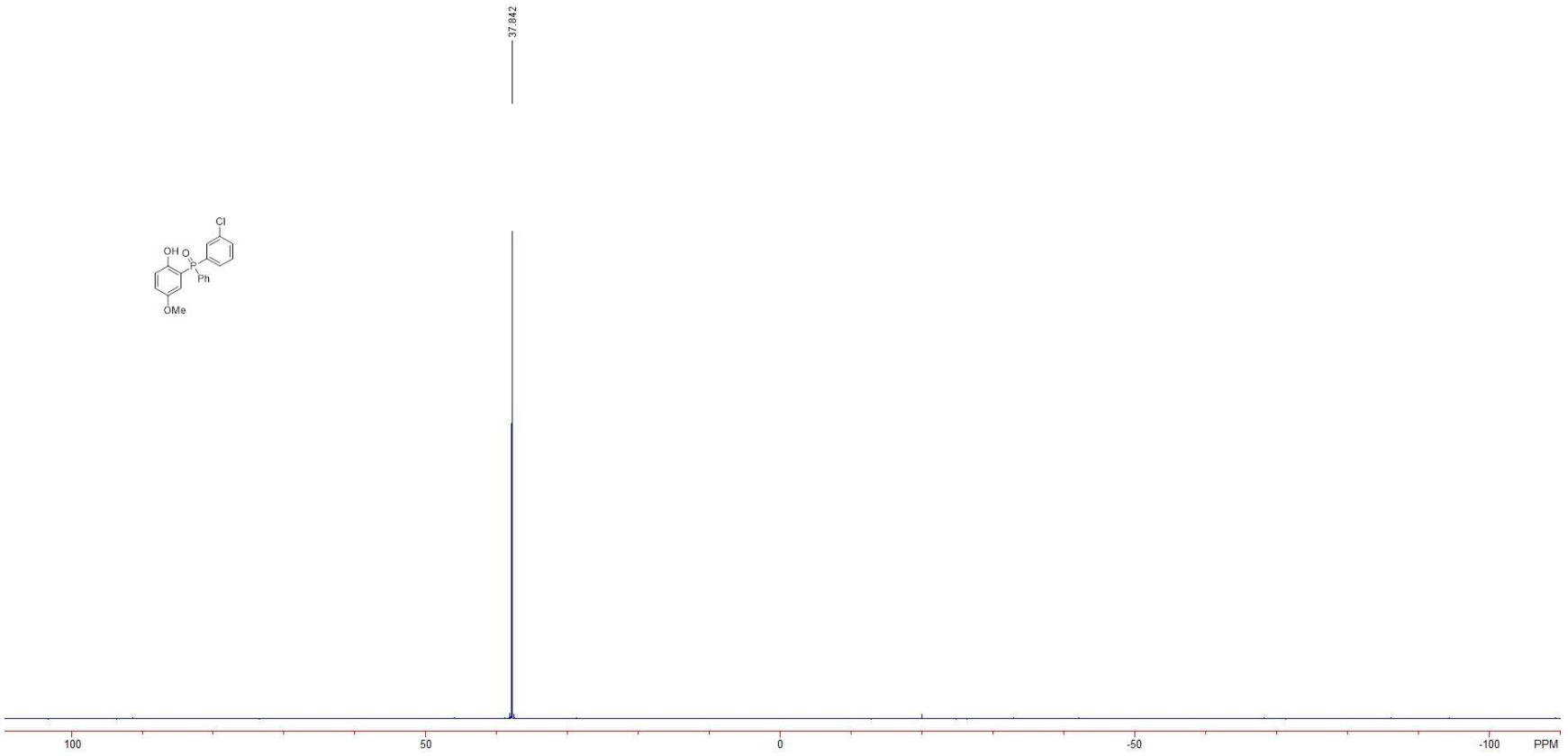
**$^{1}$H NMR of (3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3al)**



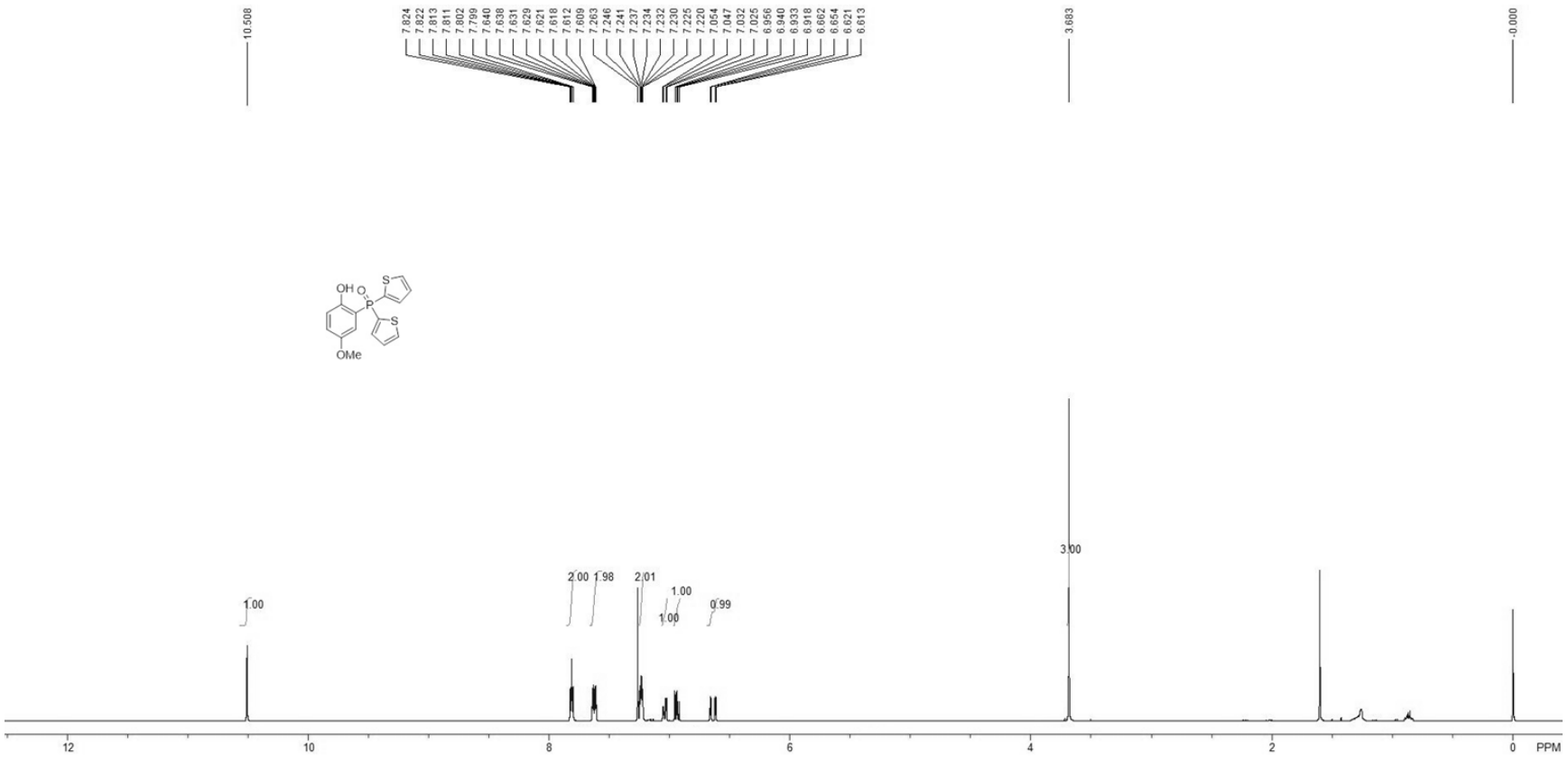
**$^{13}$C NMR of (3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3al)**



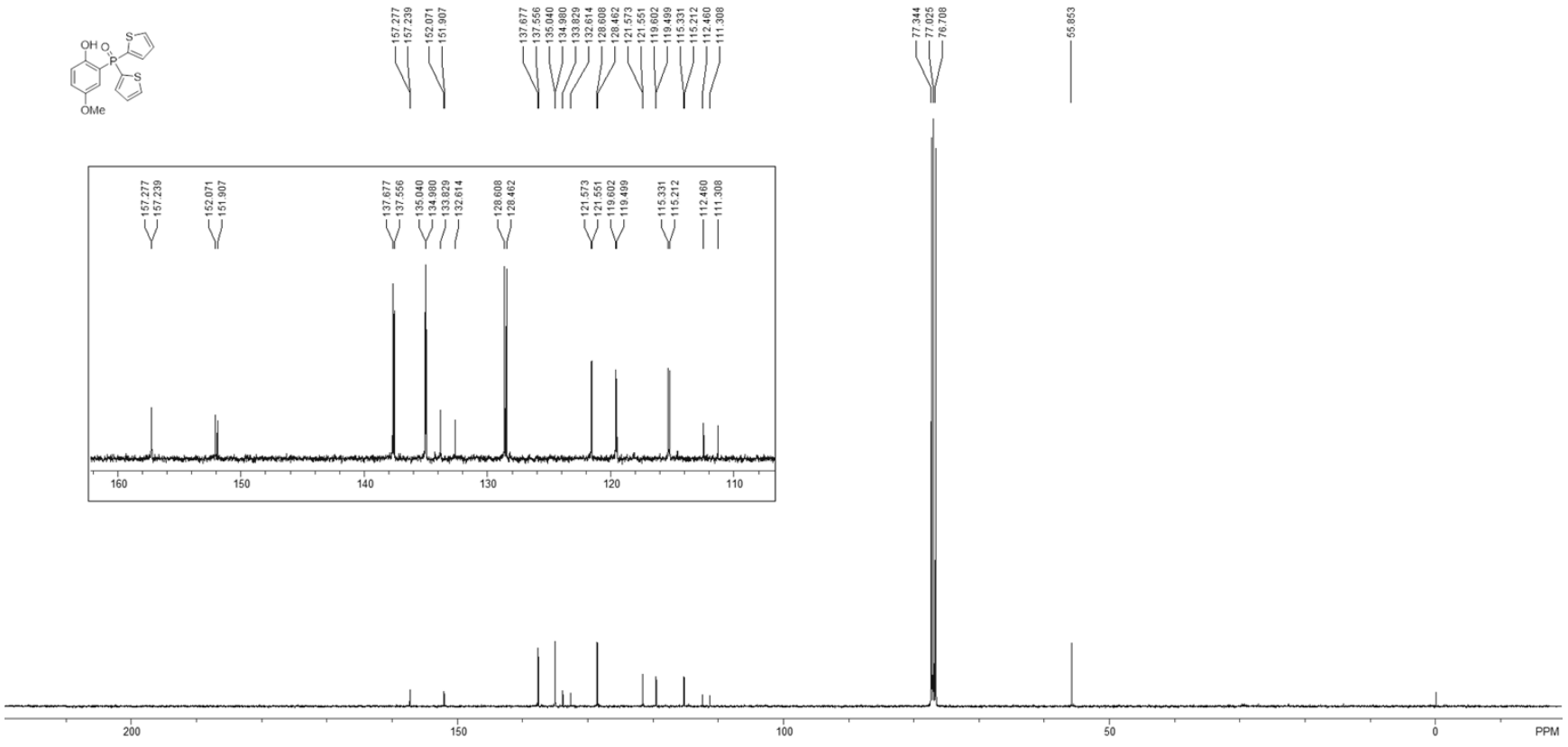
**$^{31}$P NMR of (3-chlorophenyl)(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3al)**



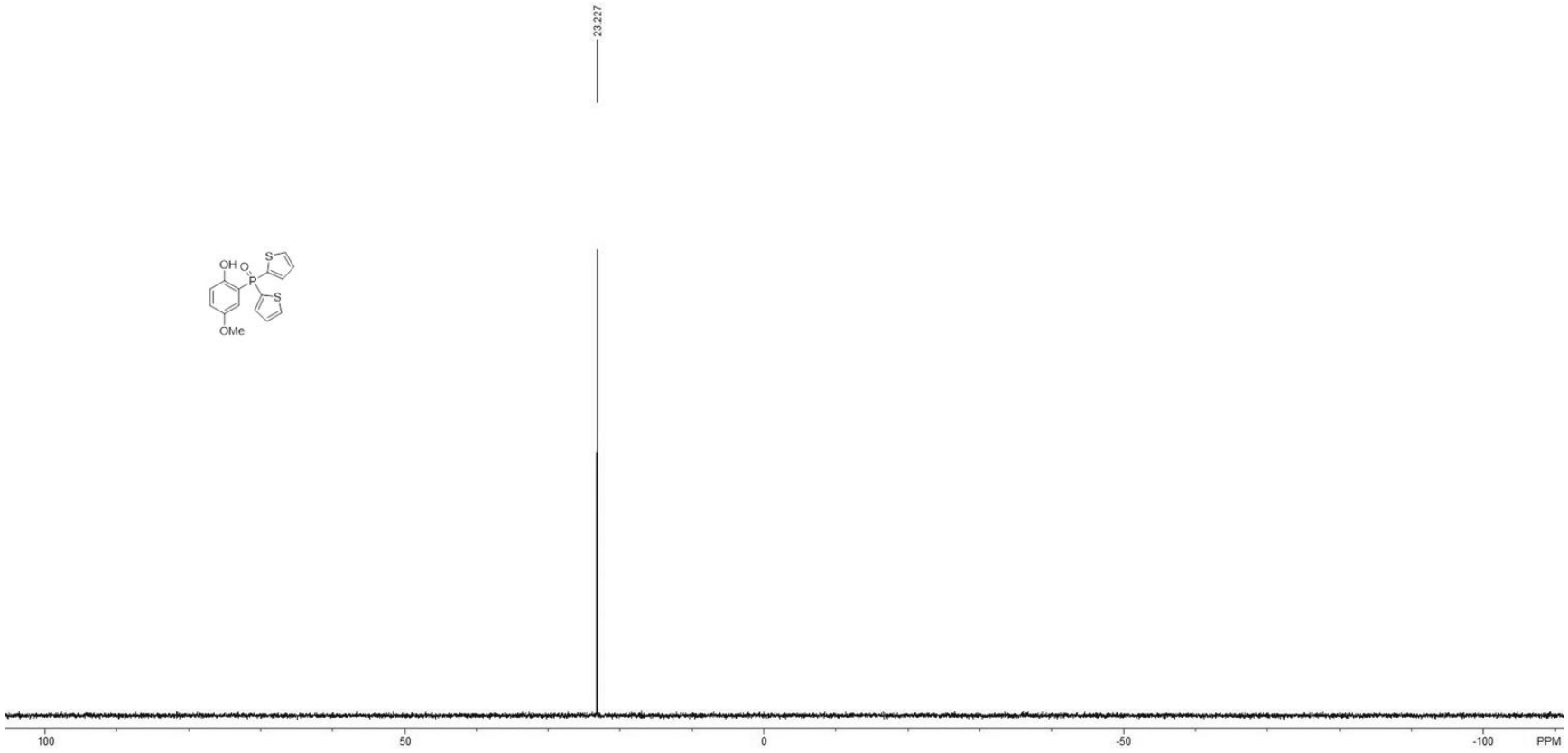
**$^{1}$H NMR of (2-hydroxy-5-methoxyphenyl)di(thiophen-2-yl)phosphine oxide (3am)**



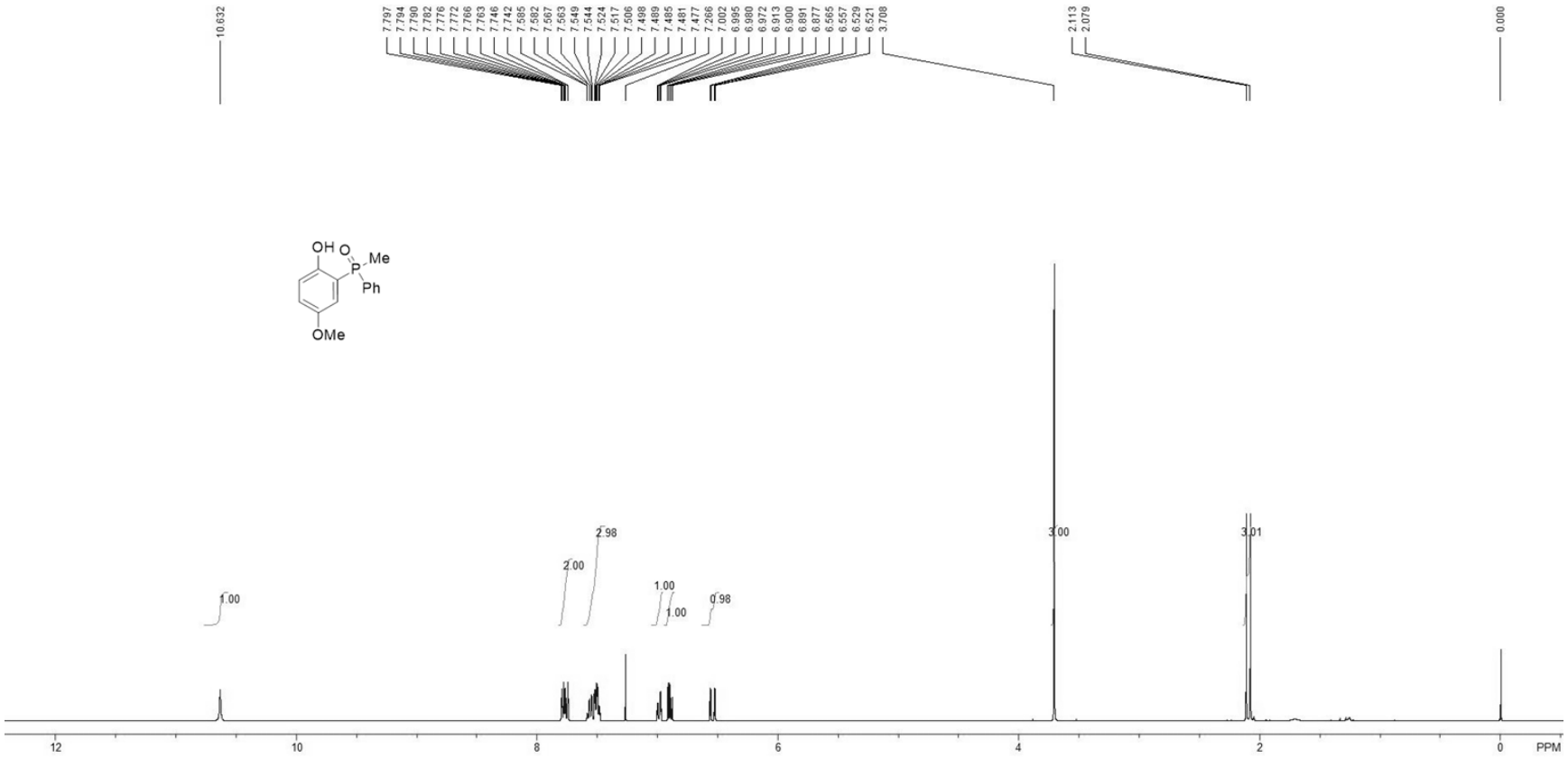
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)di(thiophen-2-yl)phosphine oxide (3am)**



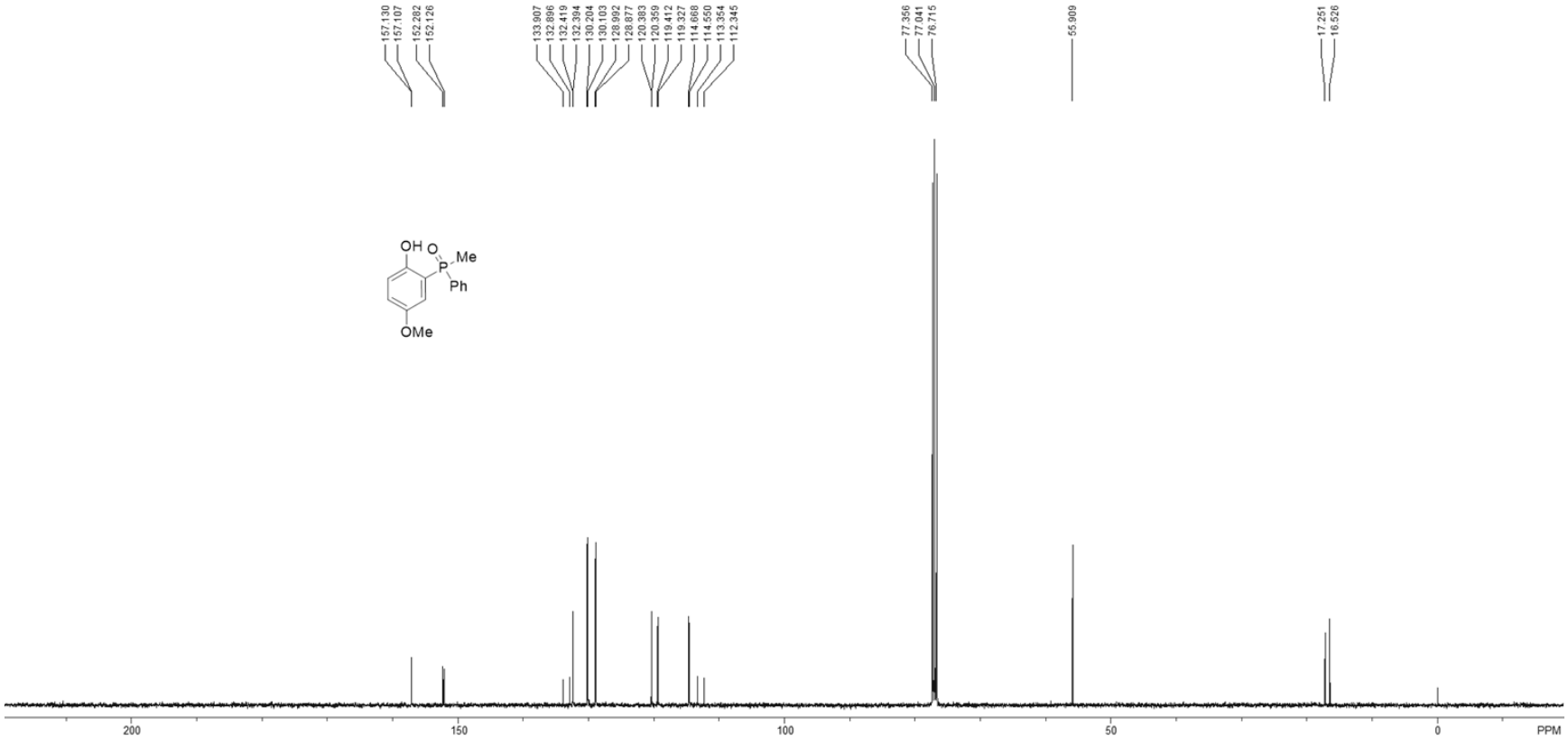
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)di(thiophen-2-yl)phosphine oxide (3am)**



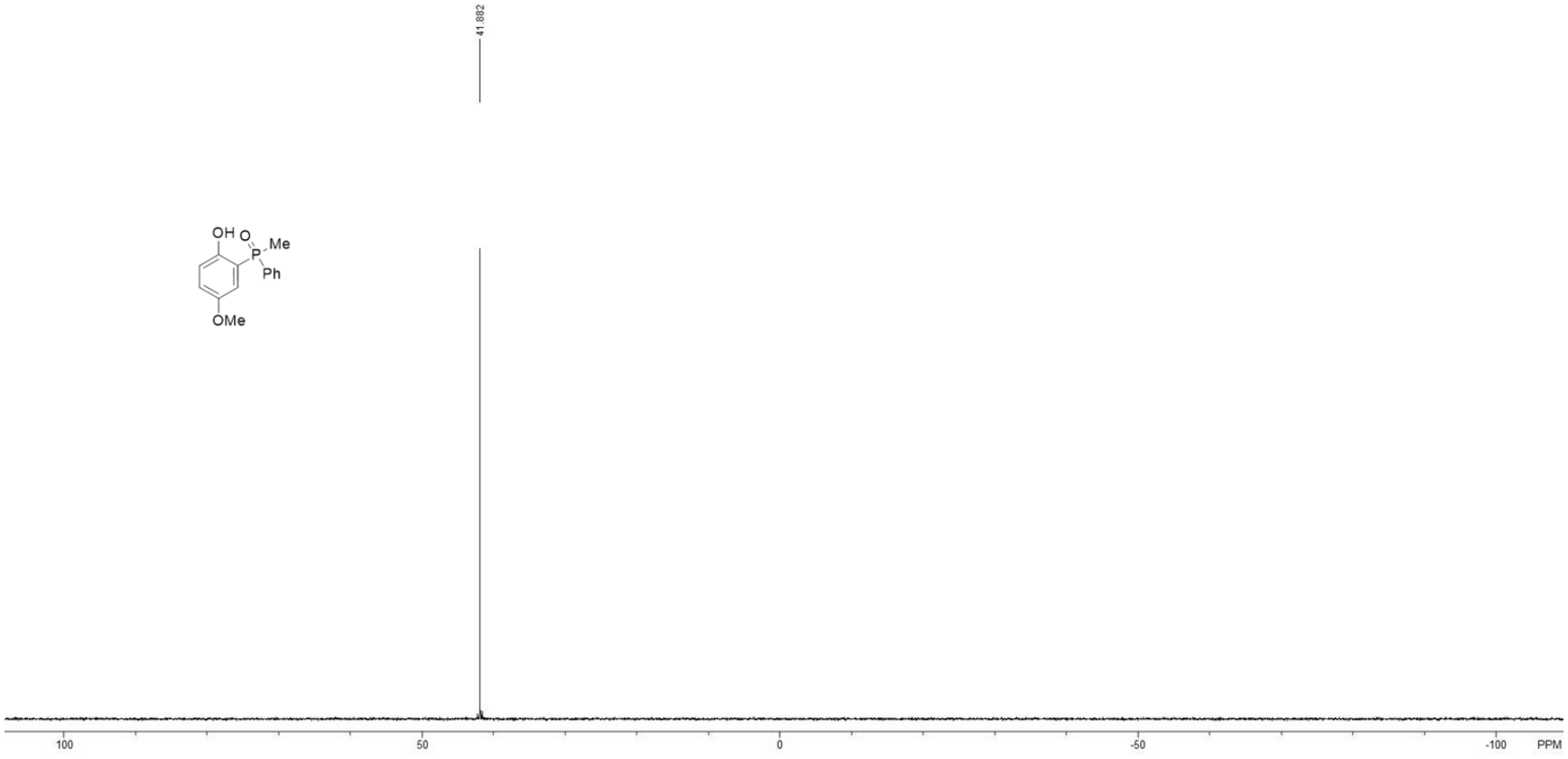
**[1]H NMR of (2-hydroxy-5-methoxyphenyl)(methyl)(phenyl)phosphine oxide (3an)**



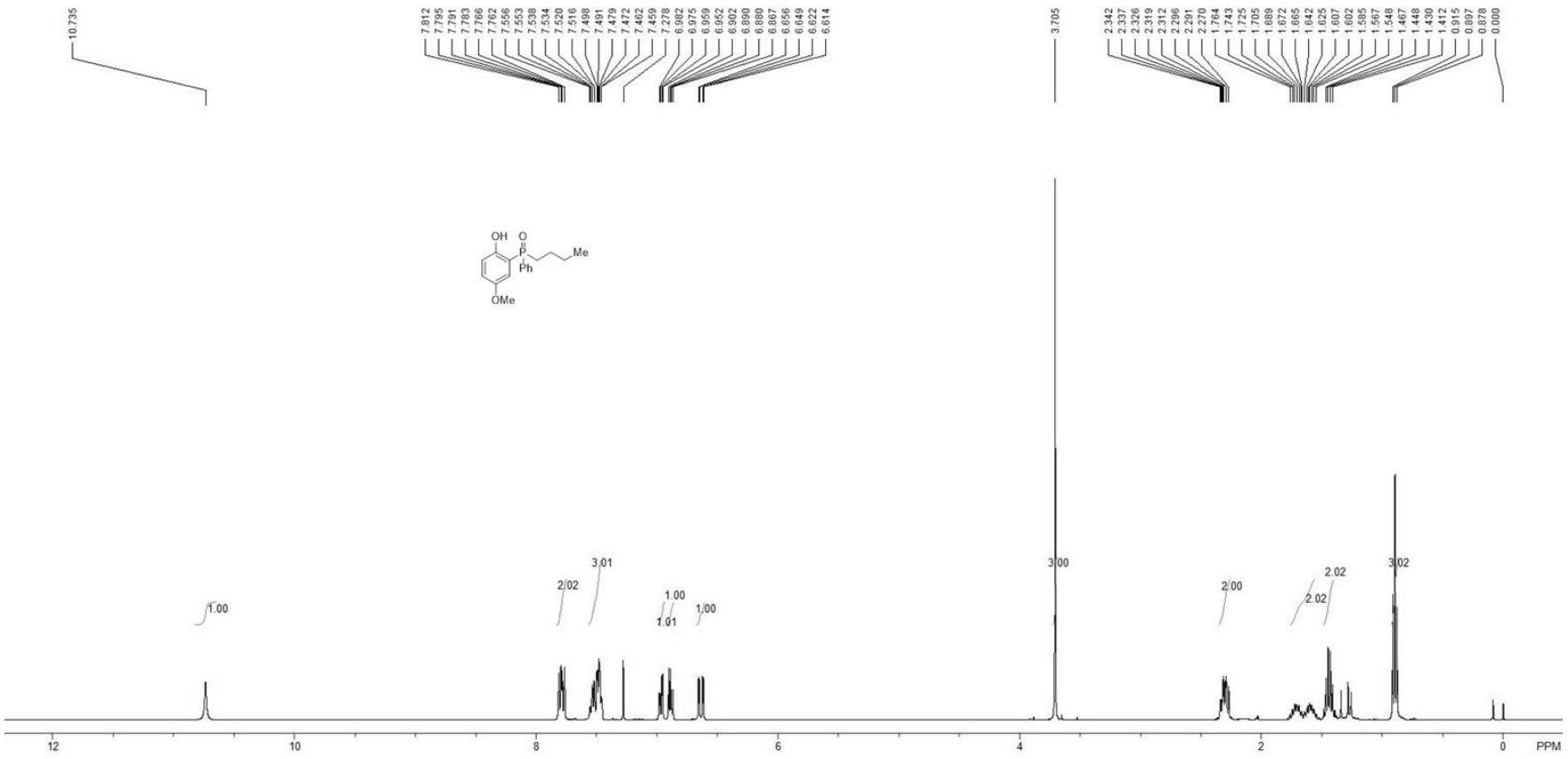
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)(methyl)(phenyl)phosphine oxide (3an)**



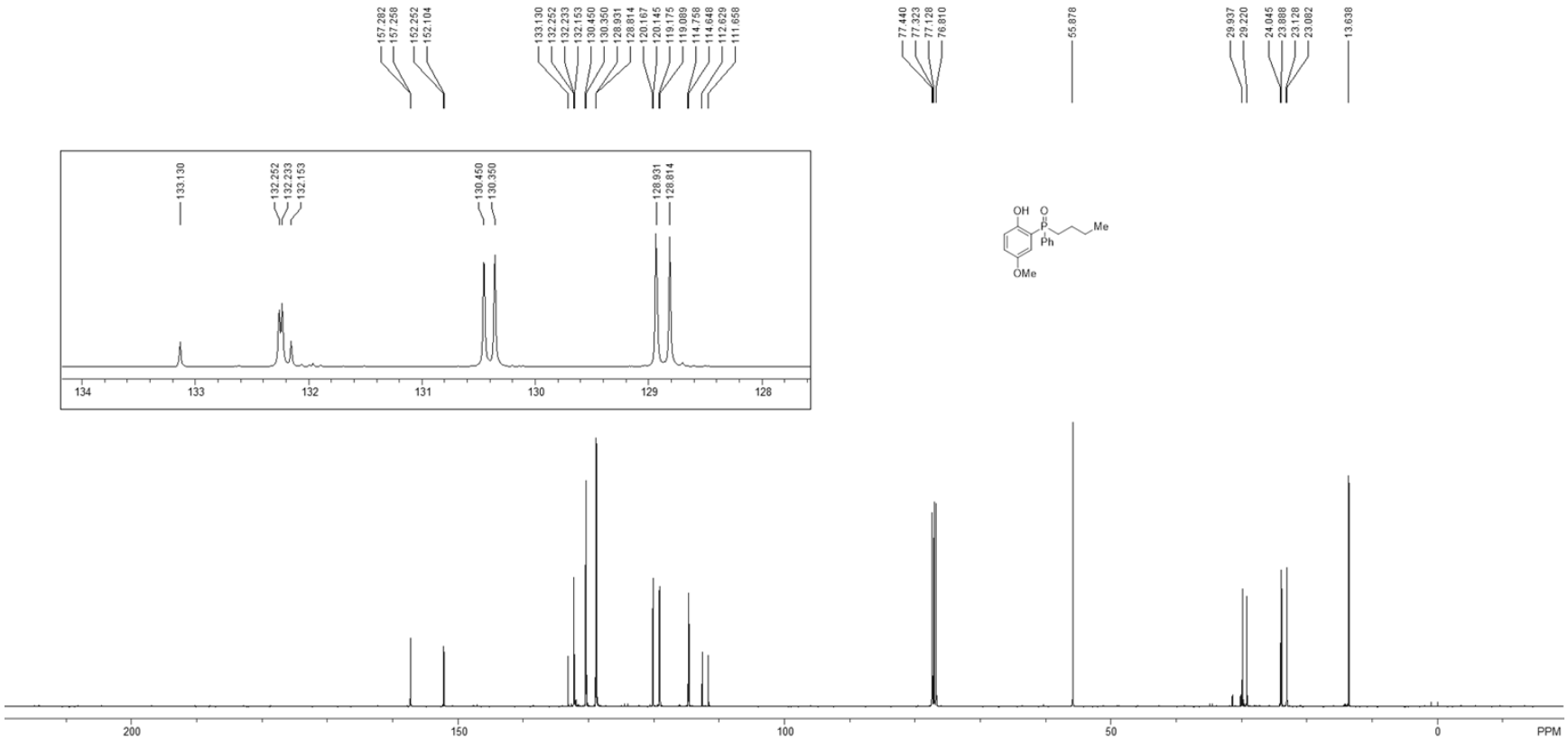
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)(methyl)(phenyl)phosphine oxide (3an)**



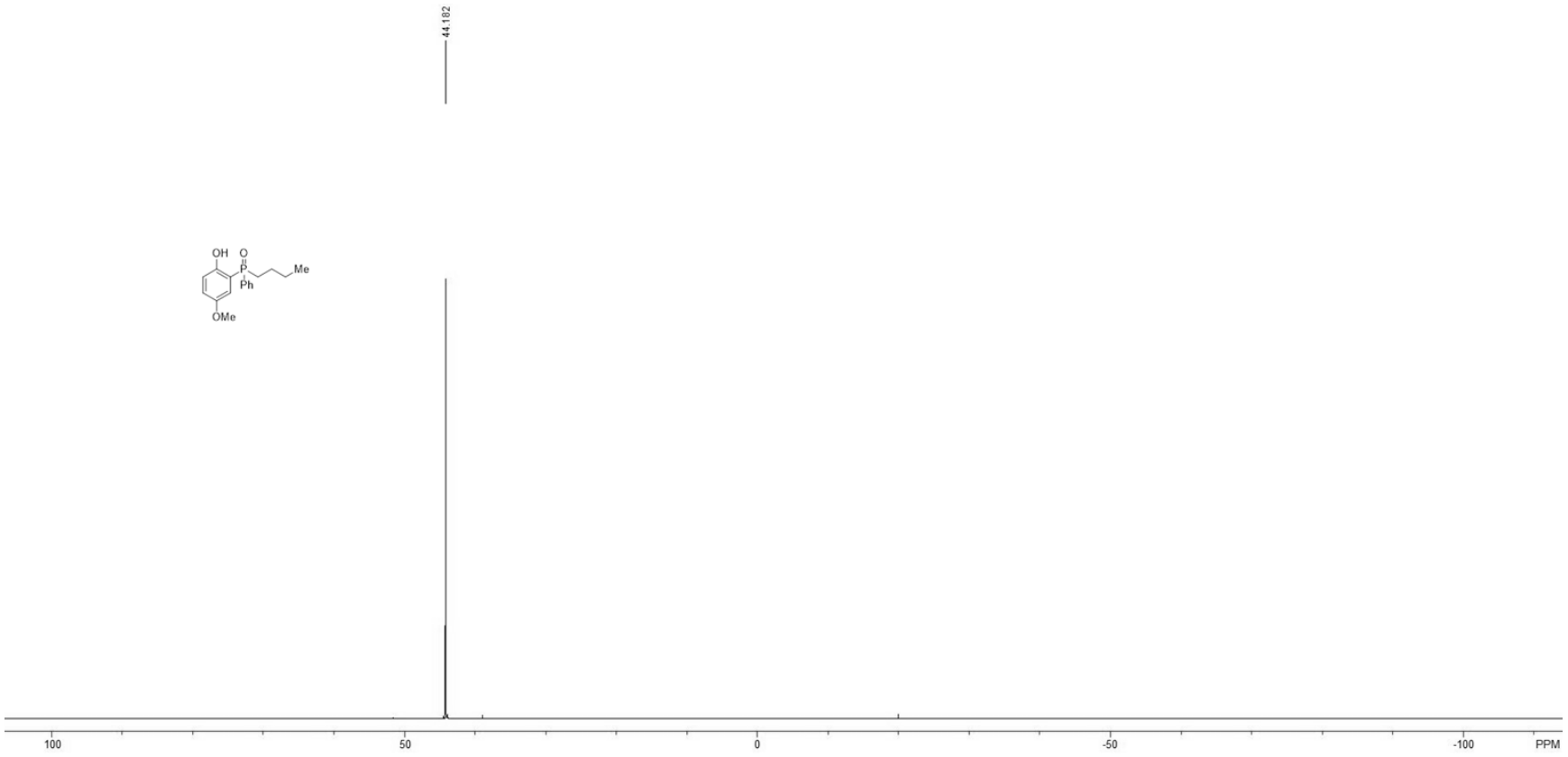
**$^{1}$H NMR of butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ao)**



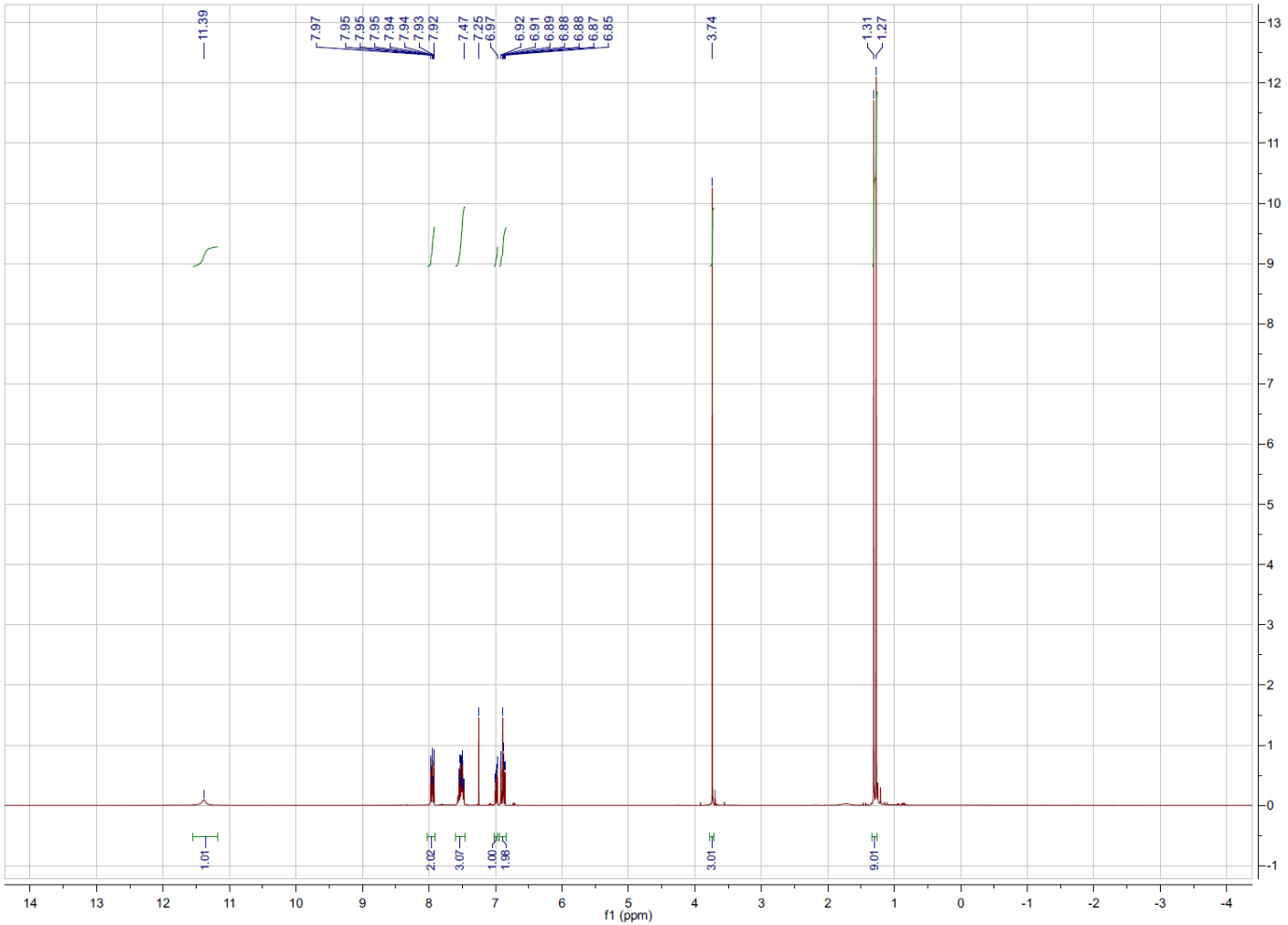
**$^{13}$C NMR of butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ao)**

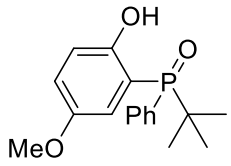


**$^{31}$P NMR of butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ao)**

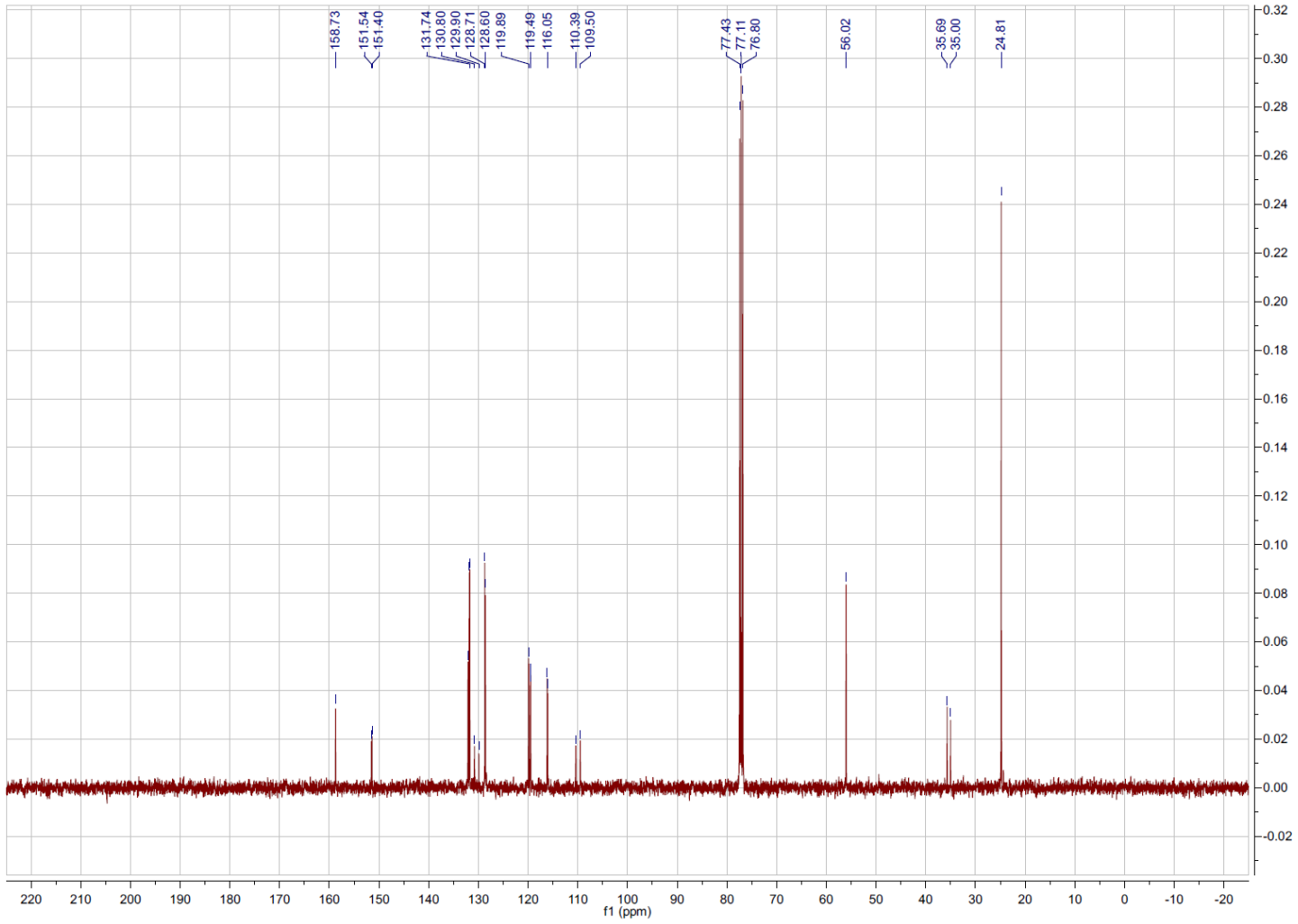


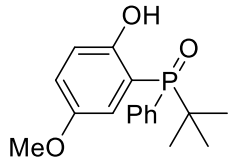
**$^{1}$H NMR of *tert*-butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ap)**



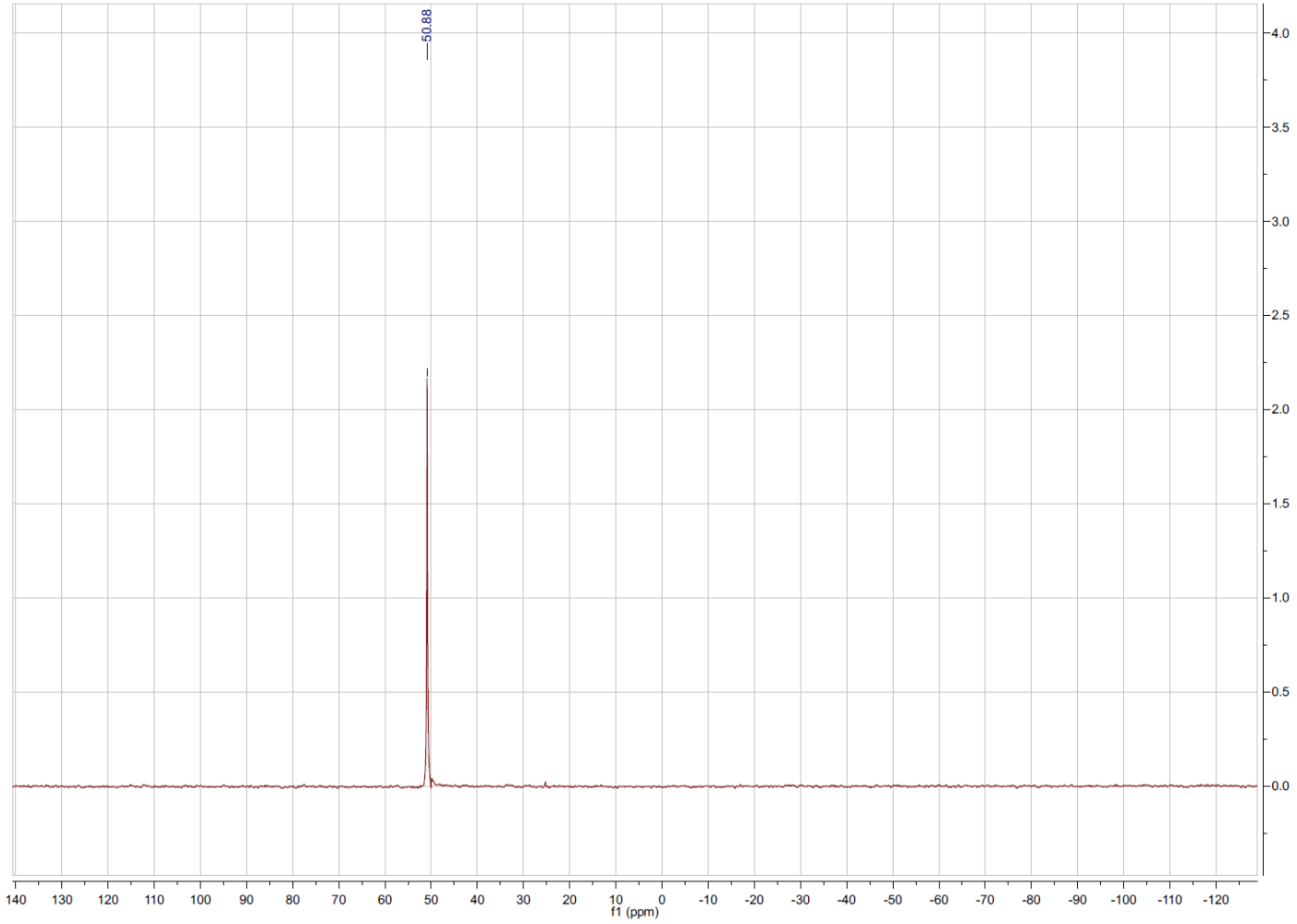



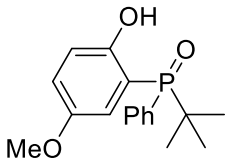
**$^{13}$C NMR of *tert*-butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ap)**



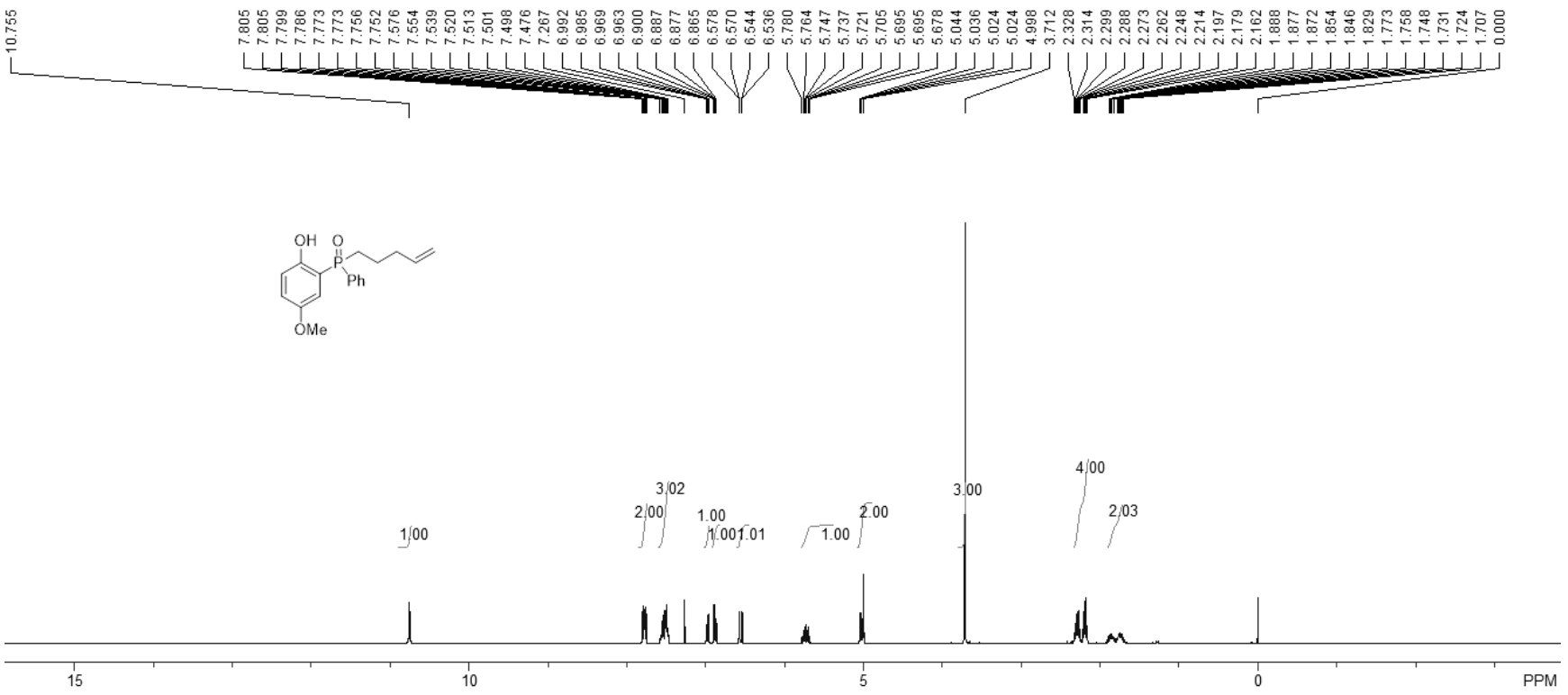



**$^{31}$P NMR of *tert*-butyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ap)**

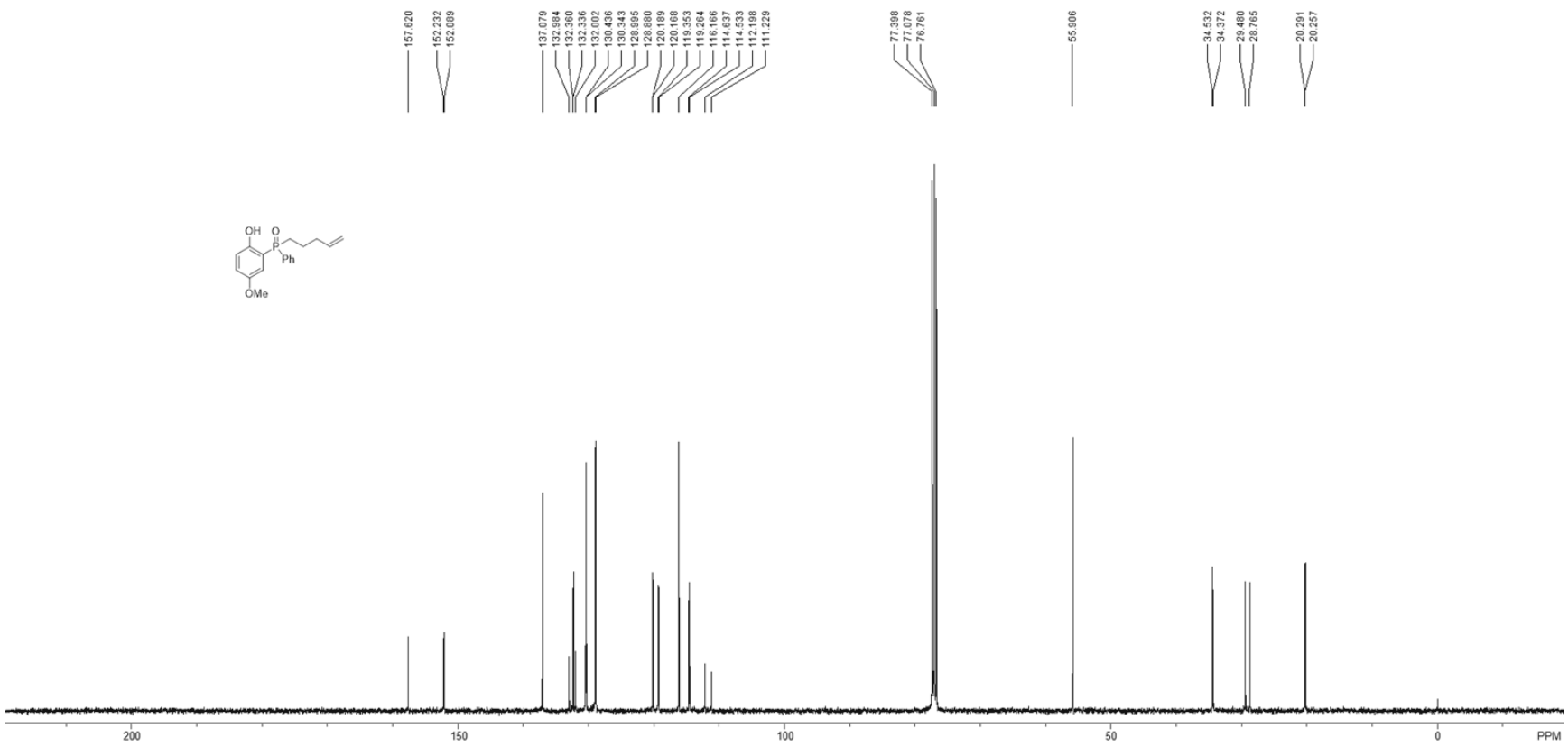


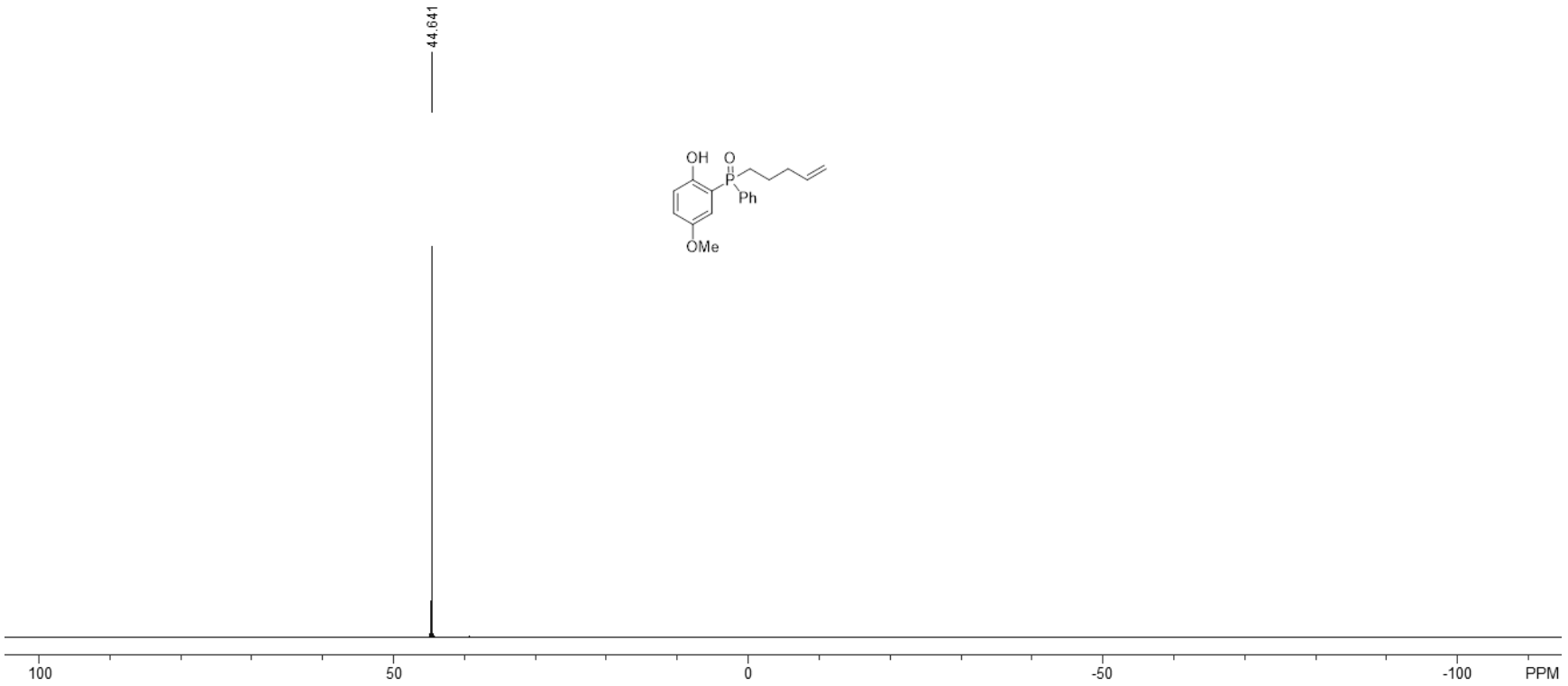
**$^{1}$H NMR of (2-hydroxy-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (3aq)**



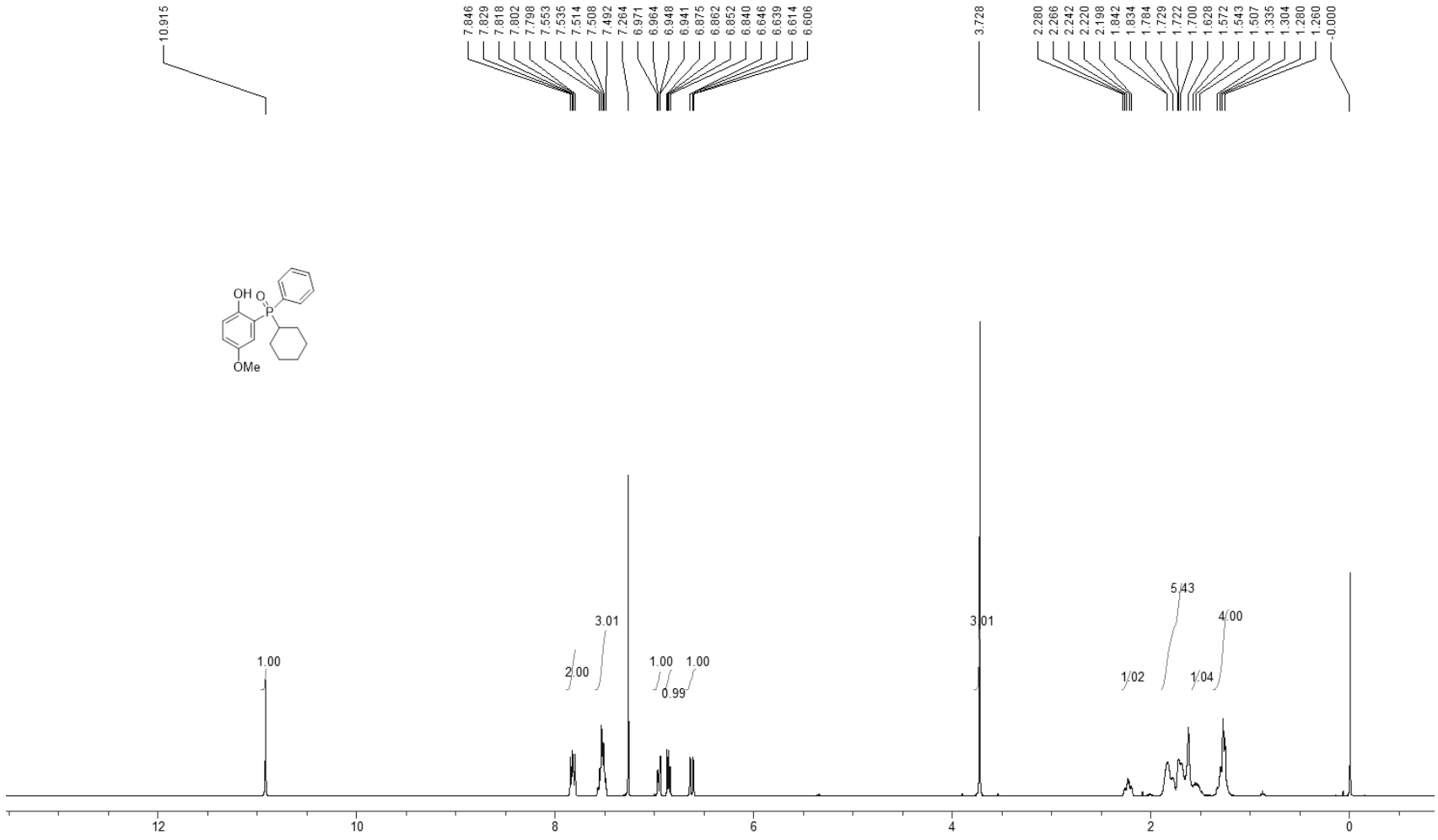
**$^{13}$C NMR of (2-hydroxy-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (3aq)**



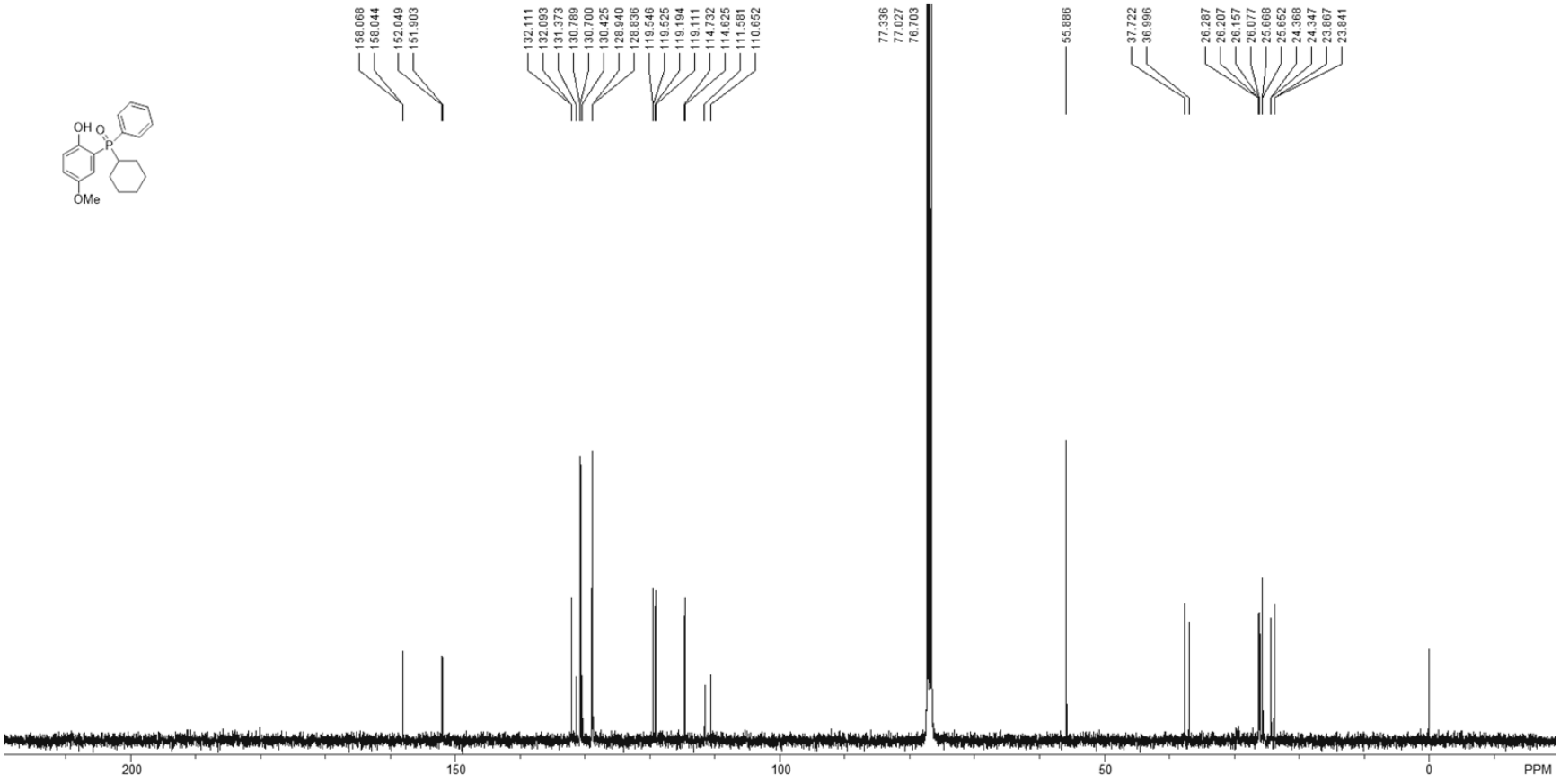
**$^{31}$P NMR of (2-hydroxy-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (3aq)**



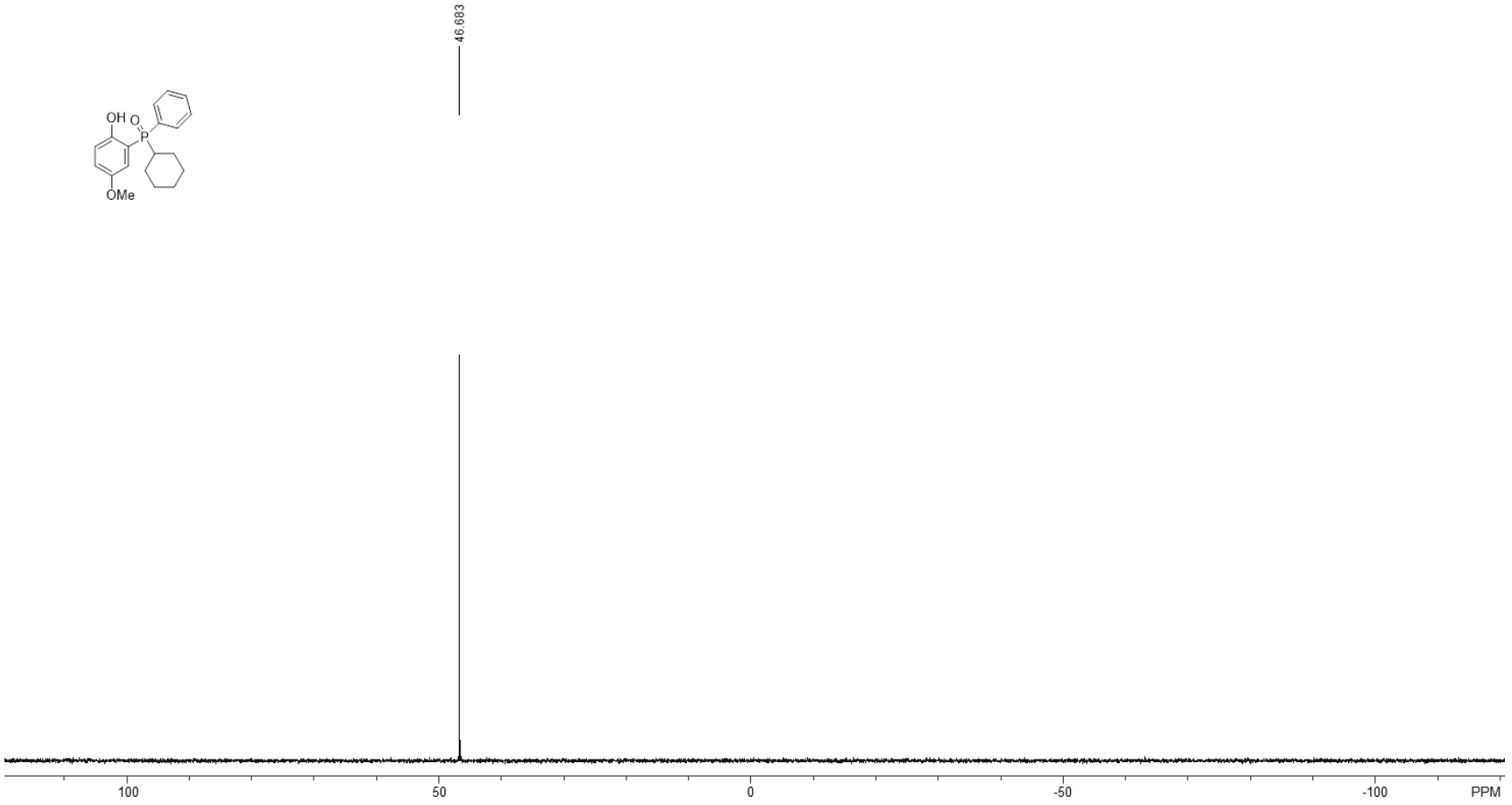
**$^{1}$H NMR of cyclohexyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ar)**



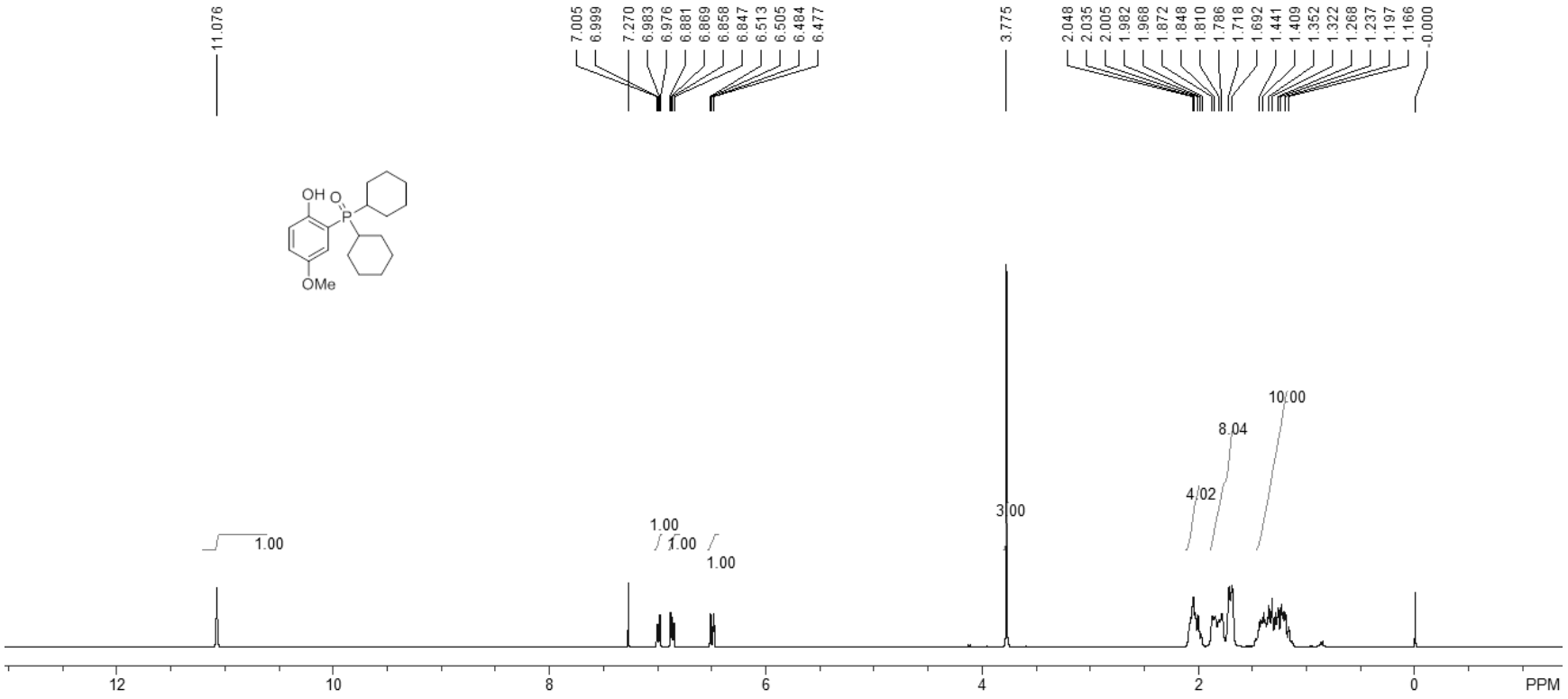
**$^{13}$C NMR of cyclohexyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ar)**



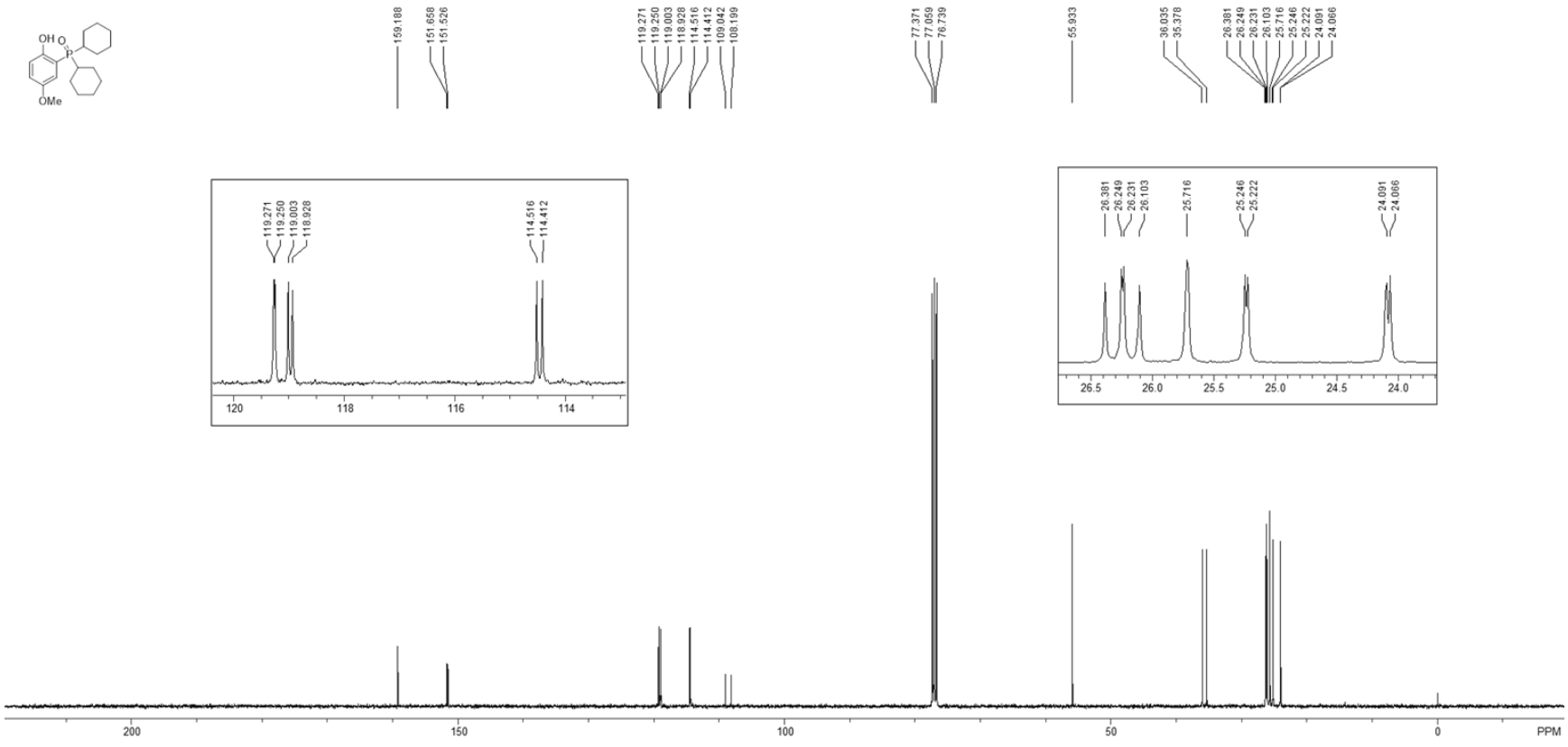
**$^{31}$P NMR of cyclohexyl(2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3ar)**



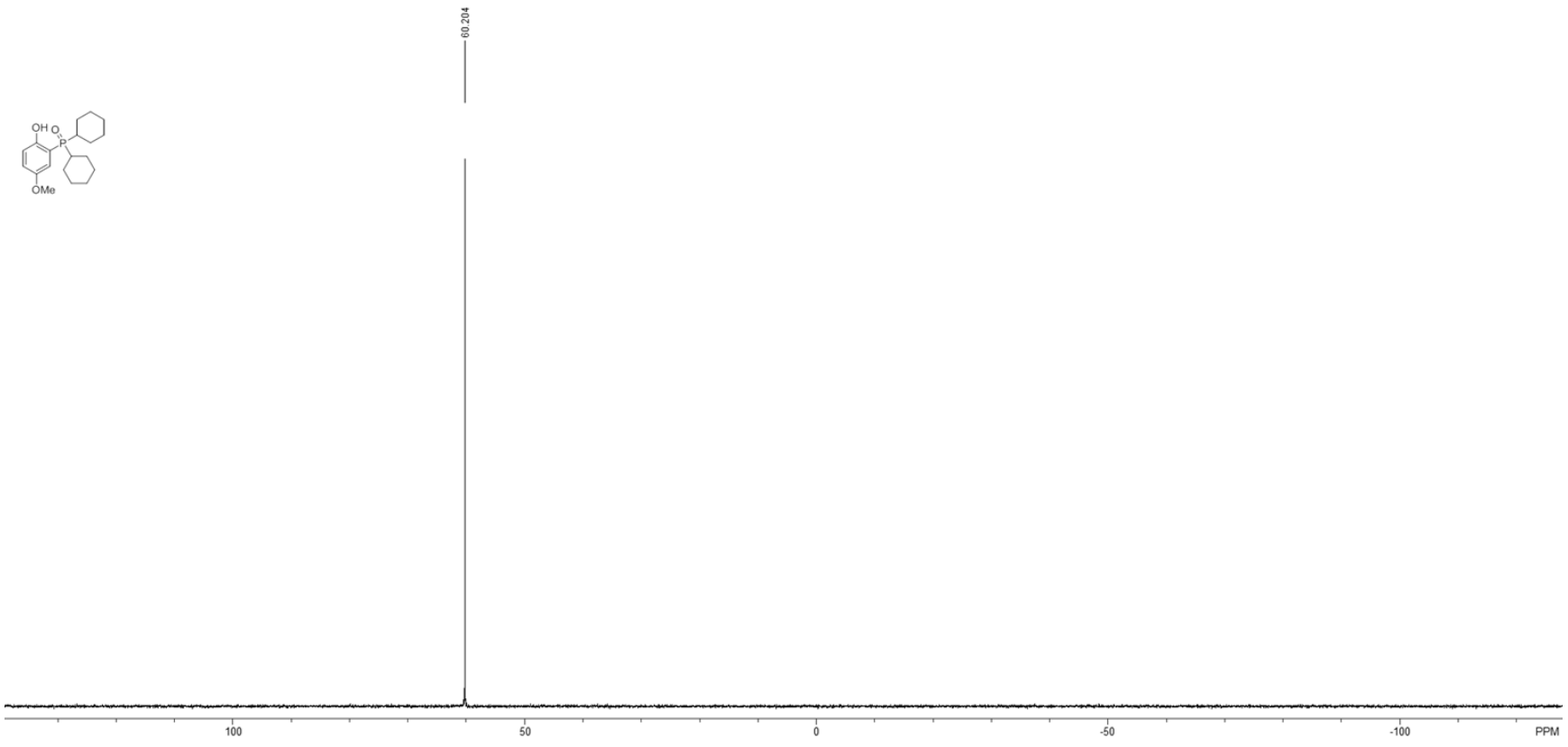
**$^{1}$H NMR of dicyclohexyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3as)**



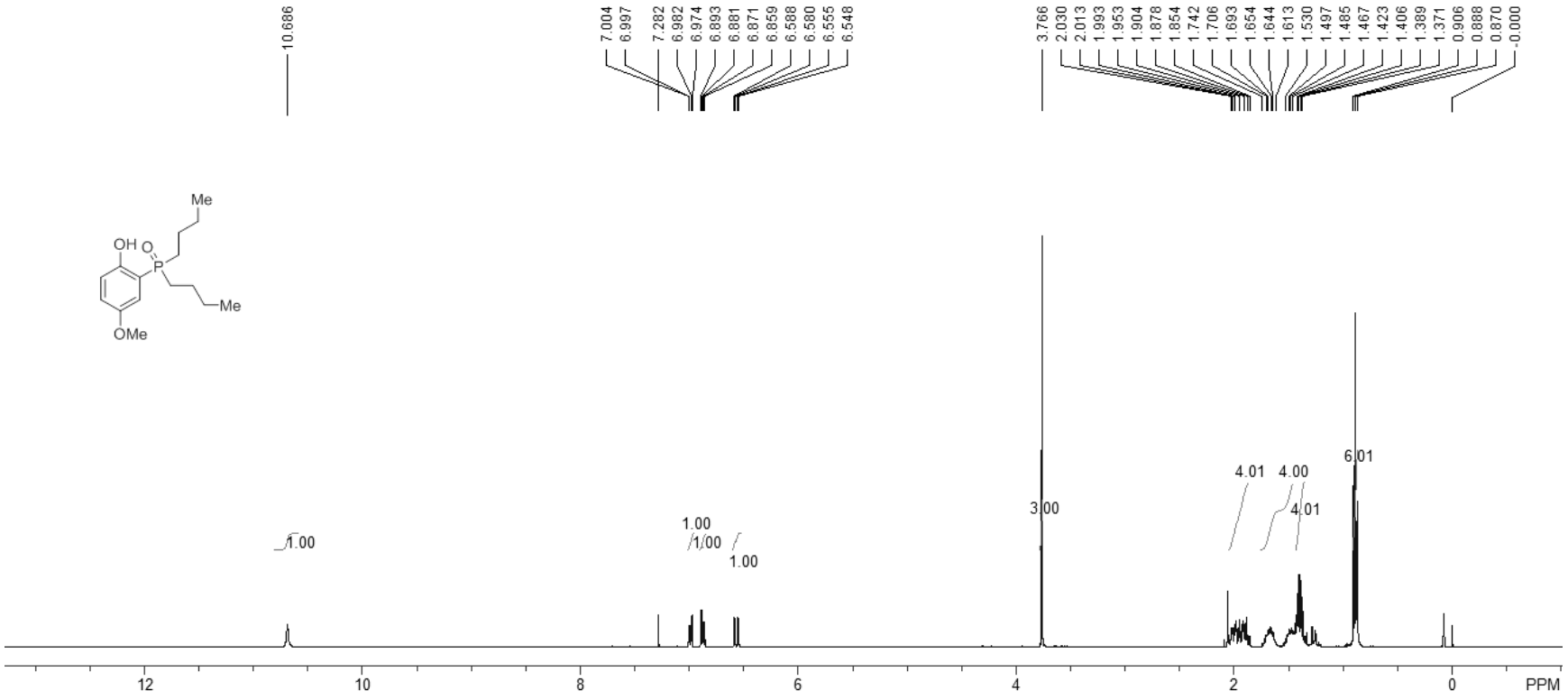
**$^{13}$C NMR of dicyclohexyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3as)**



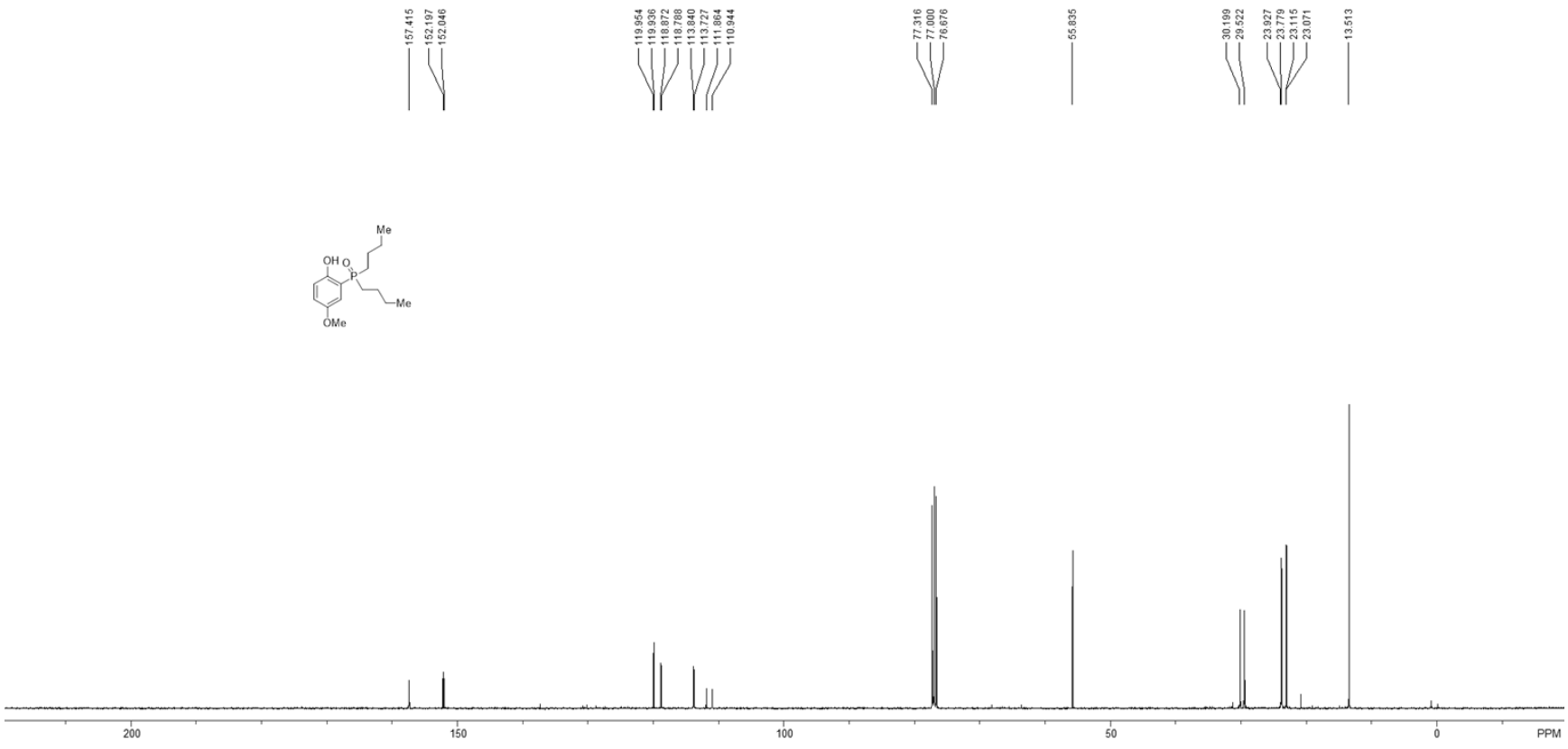
**$^{31}$P NMR of dicyclohexyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3as)**



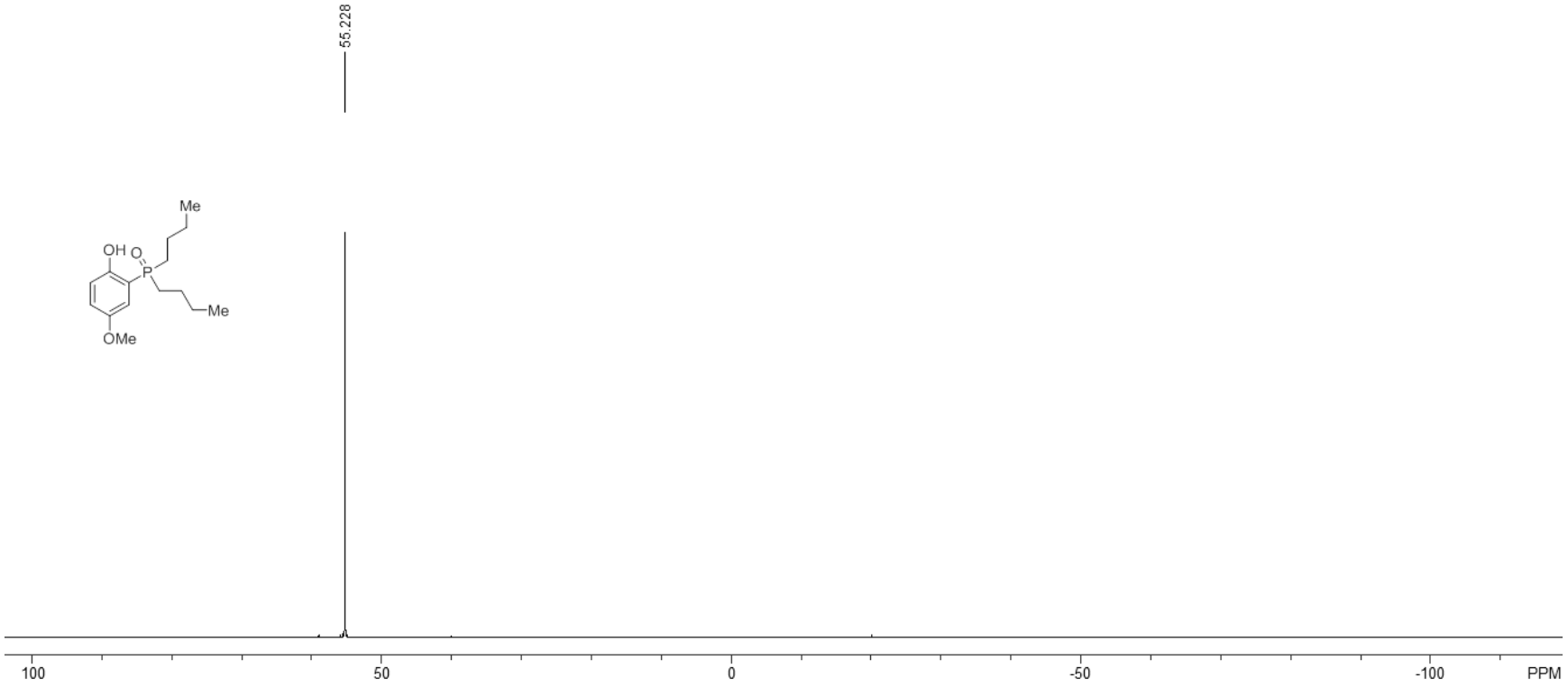
**$^{1}$H NMR of dibutyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3at)**



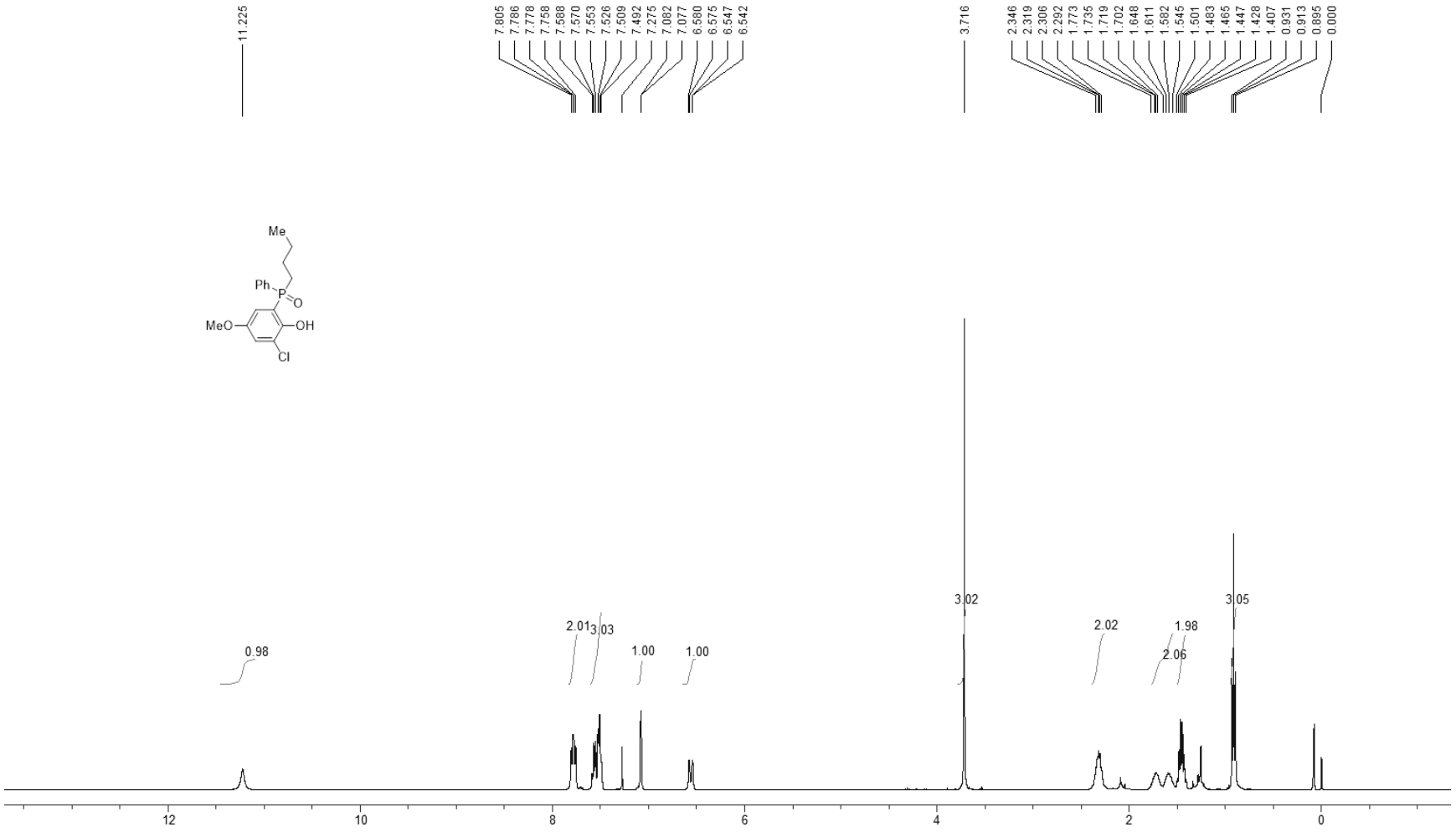
**$^{13}$C NMR of dibutyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3at)**



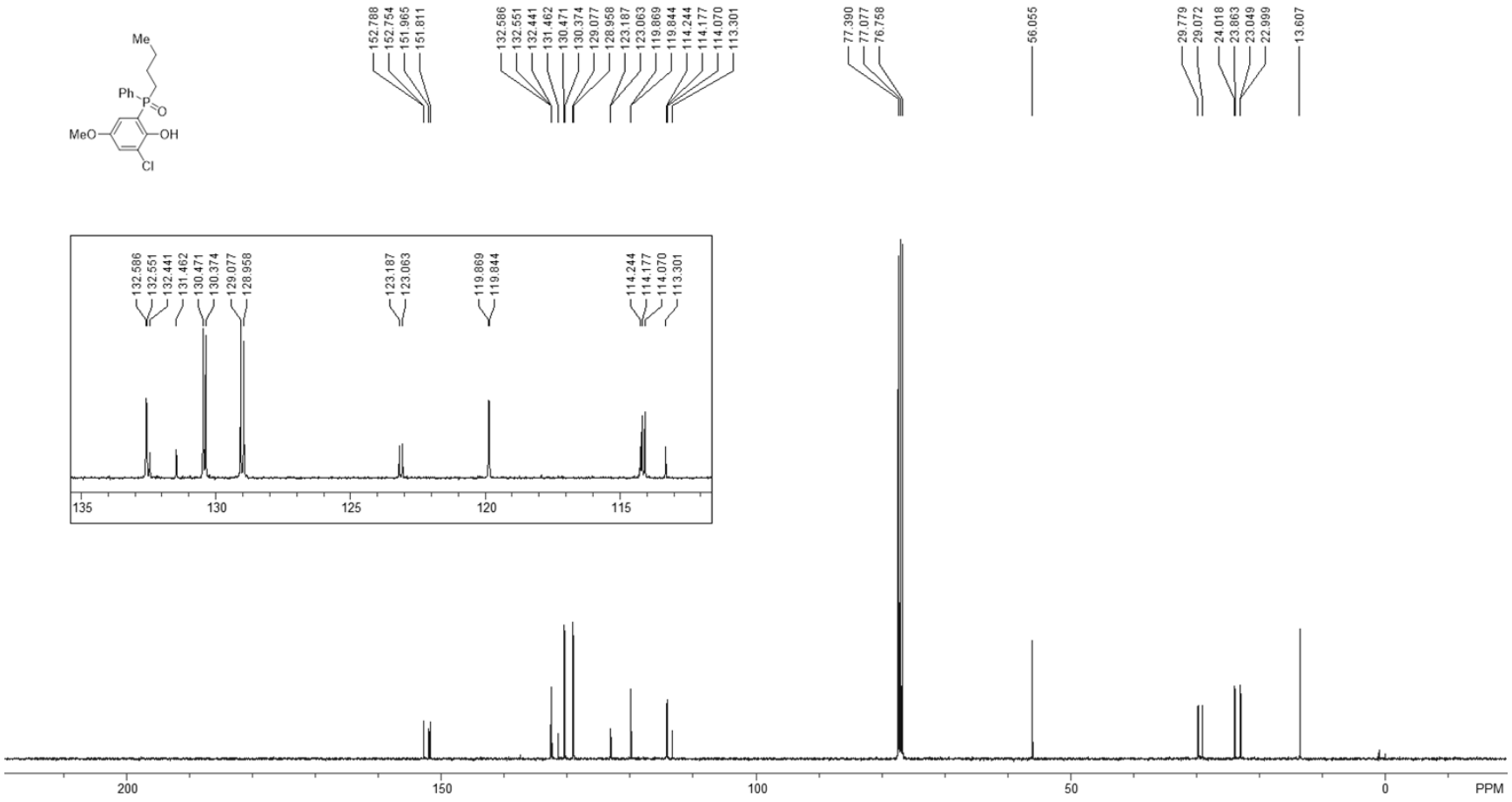
**$^{31}$P NMR of dibutyl(2-hydroxy-5-methoxyphenyl)phosphine oxide (3at)**



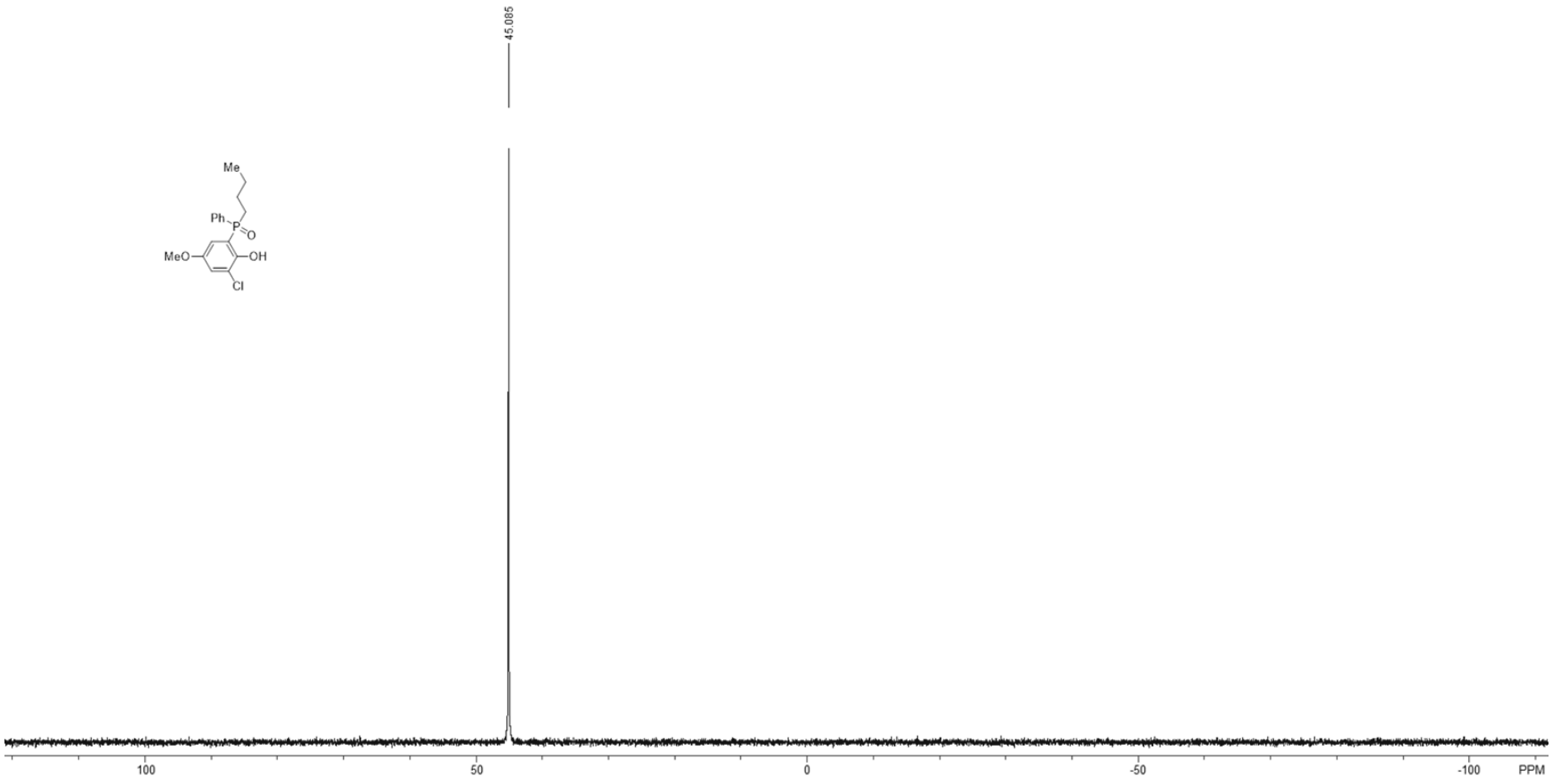
**$^{1}$H NMR of butyl(3-chloro-2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3fo)**



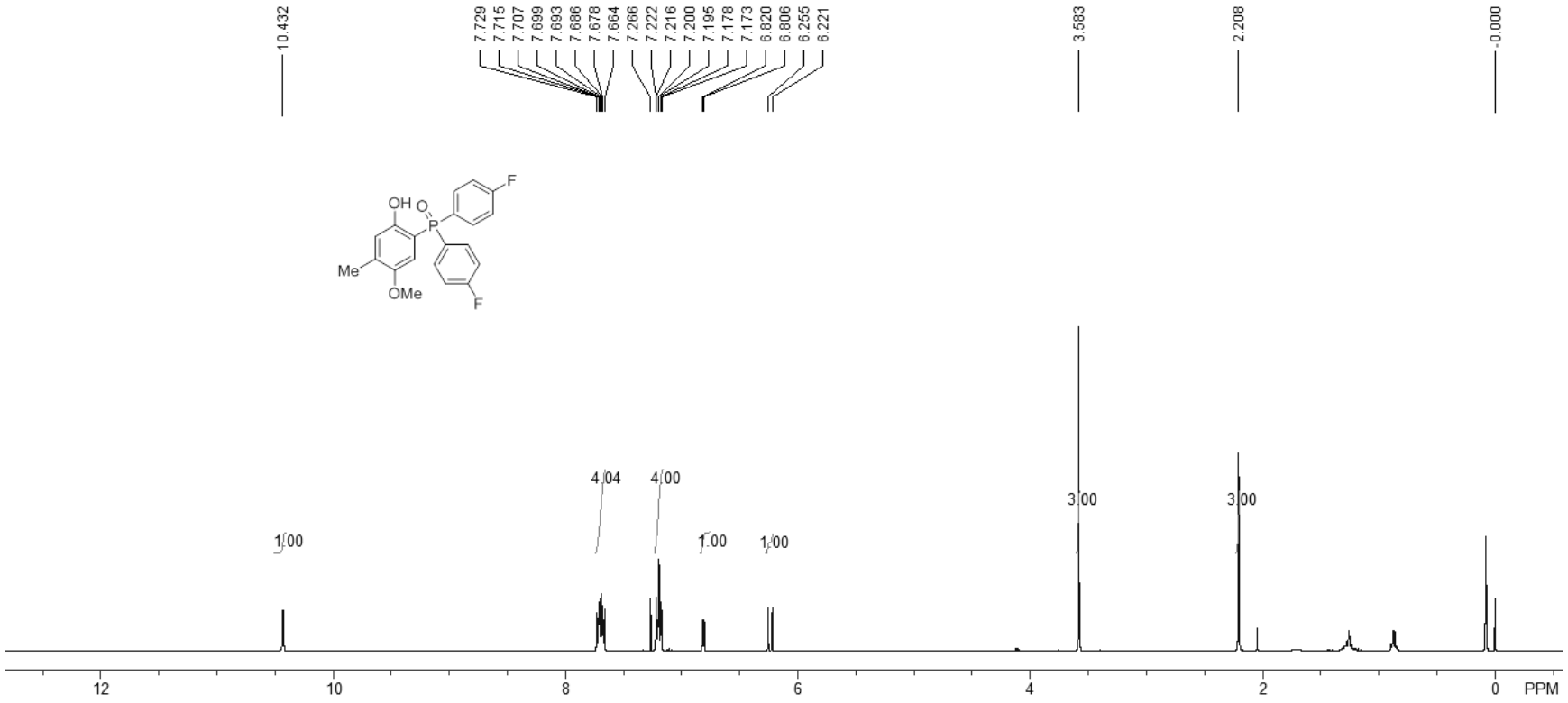
**$^{13}$C NMR of butyl(3-chloro-2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3fo)**



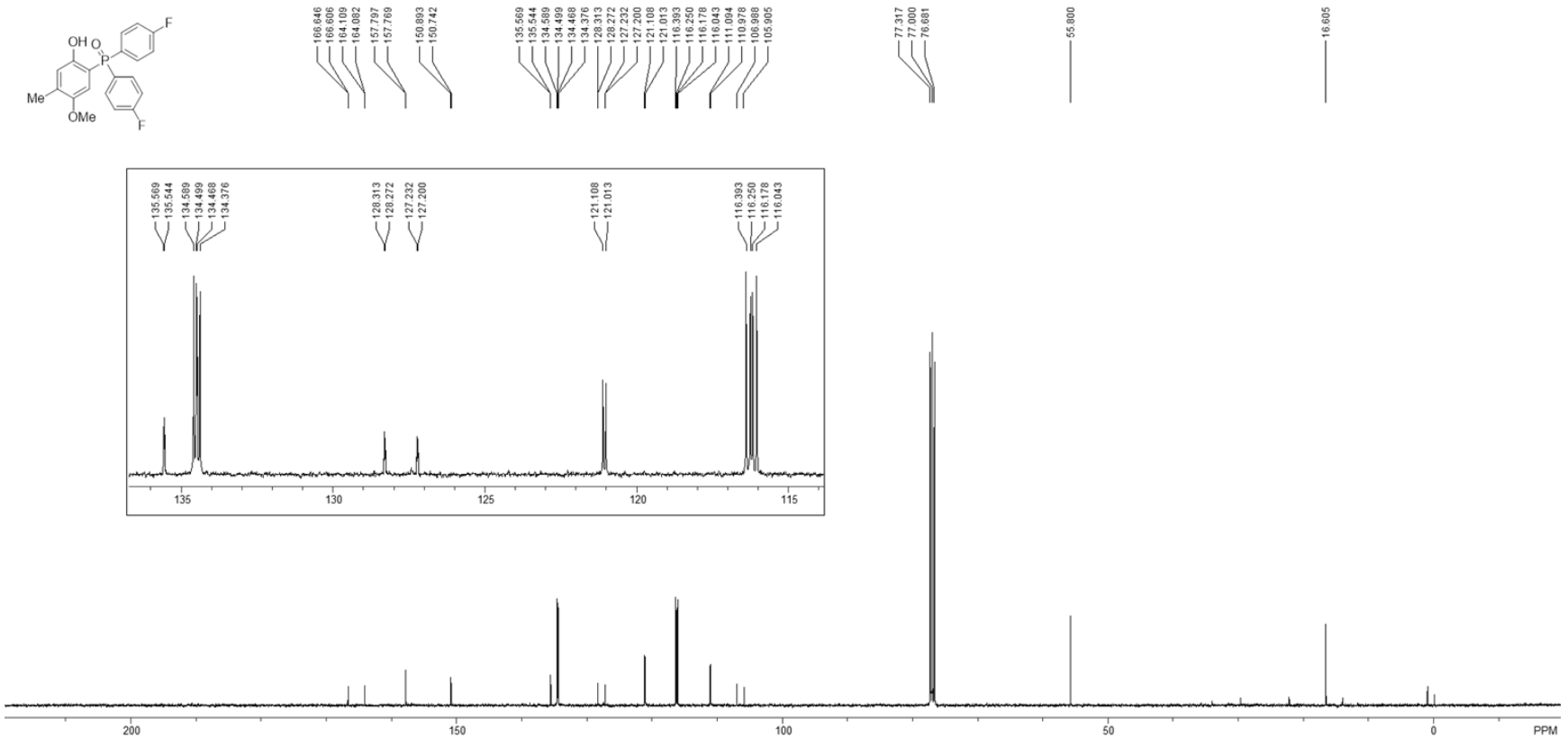
**$^{31}$P NMR of butyl(3-chloro-2-hydroxy-5-methoxyphenyl)(phenyl)phosphine oxide (3fo)**



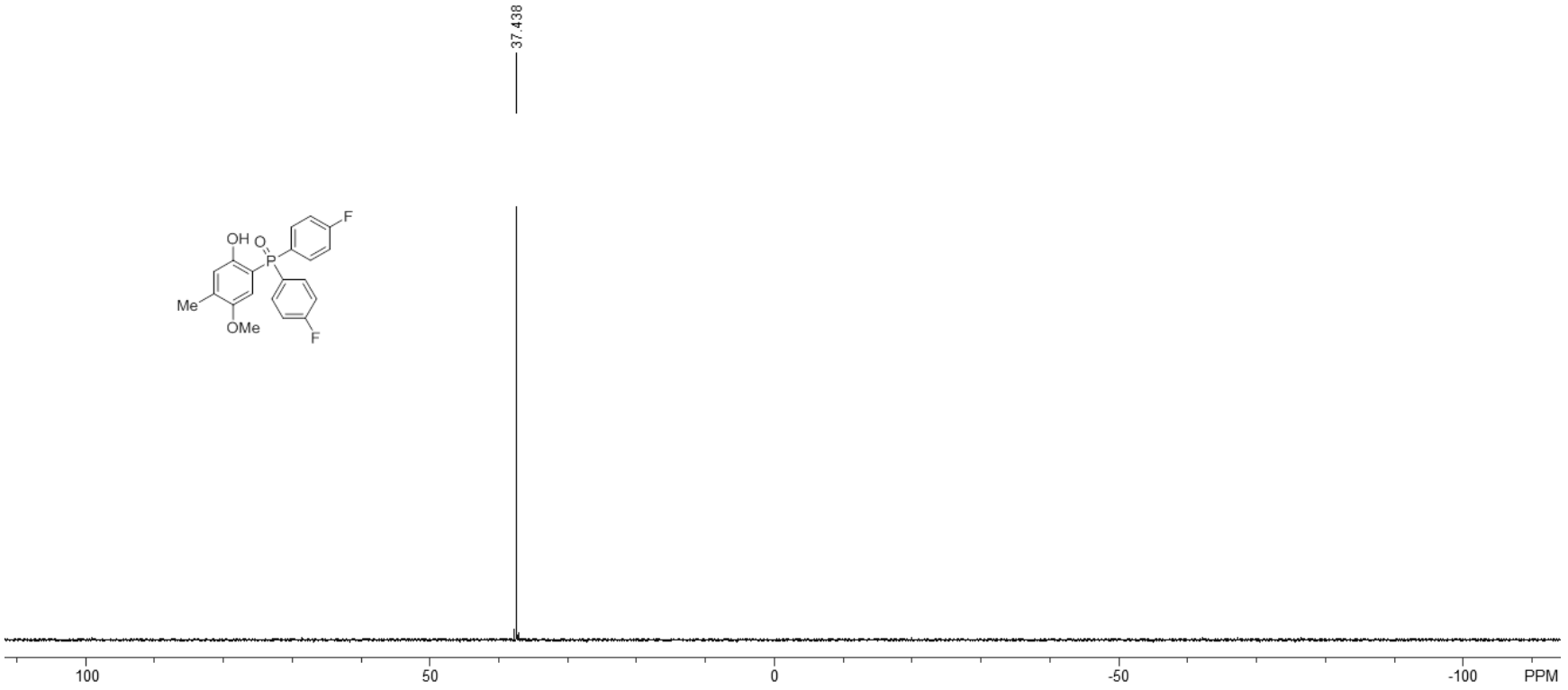
**[1]H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxy-4-methylphenyl)phosphine oxide (3jd)**



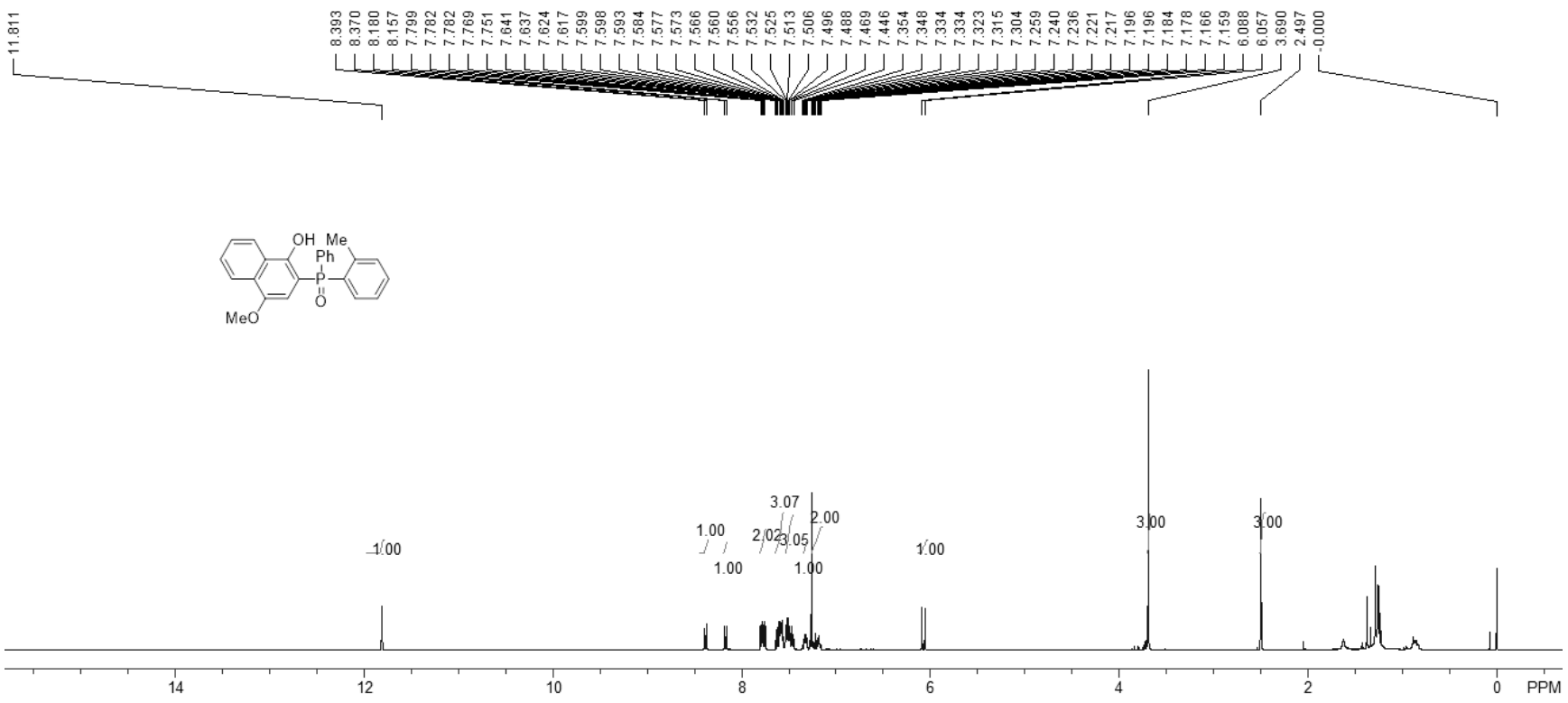
**$^{13}$C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxy-4-methylphenyl)phosphine oxide (3jd)**



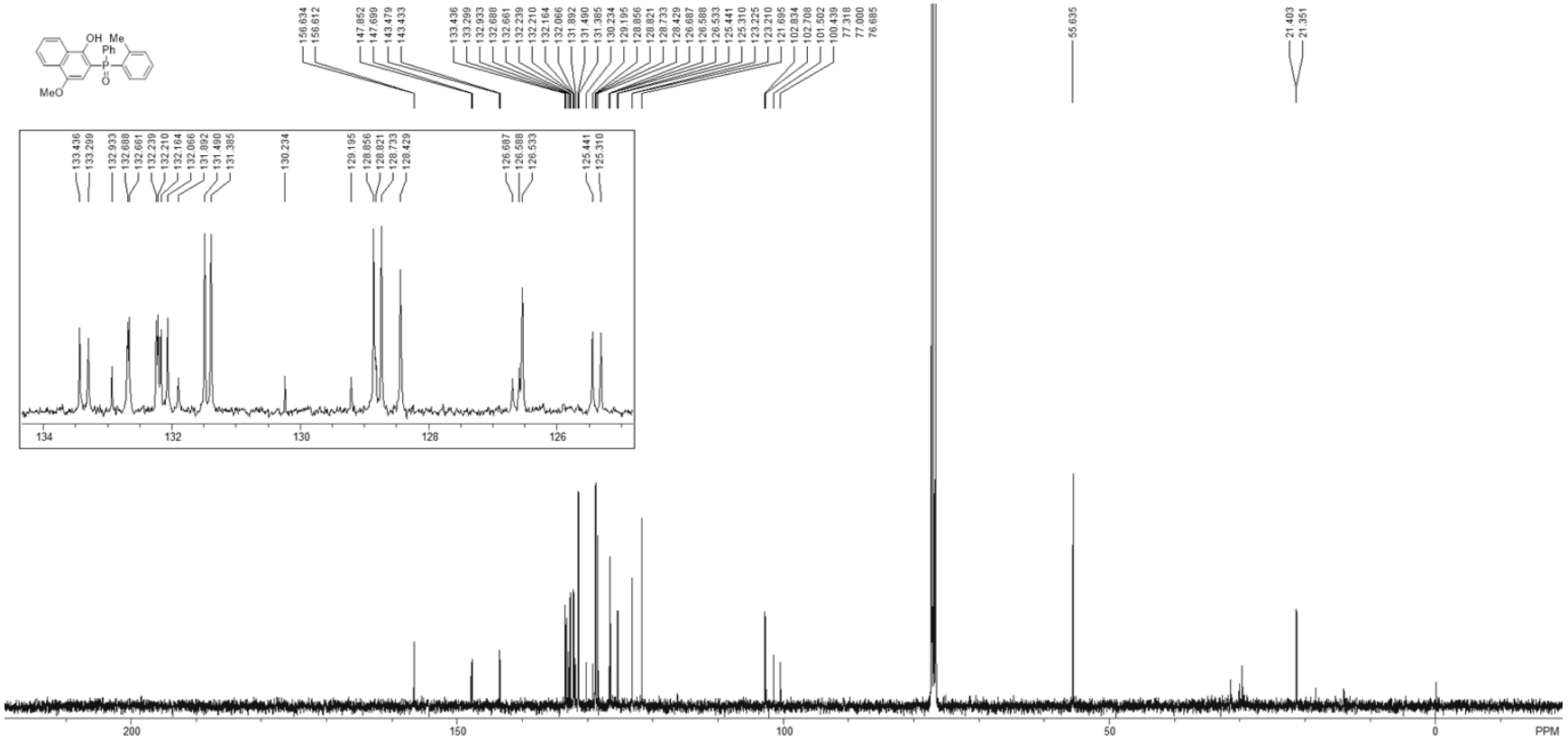
**$^{31}$P NMR of bis(4-fluorophenyl)(2-hydroxy-5-methoxy-4-methylphenyl)phosphine oxide (3jd)**



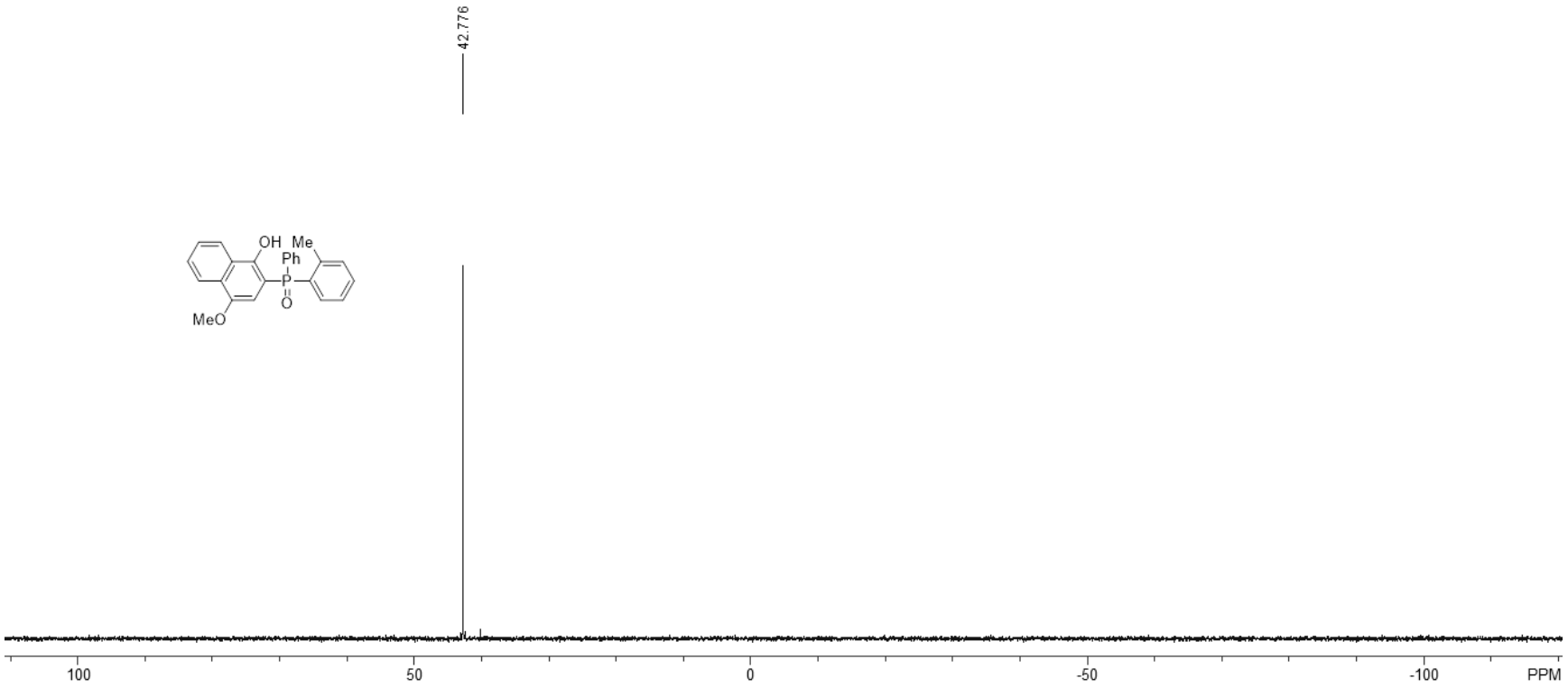
**$^{1}$H NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)(phenyl)(o-tolyl)phosphine oxide (3nk)**



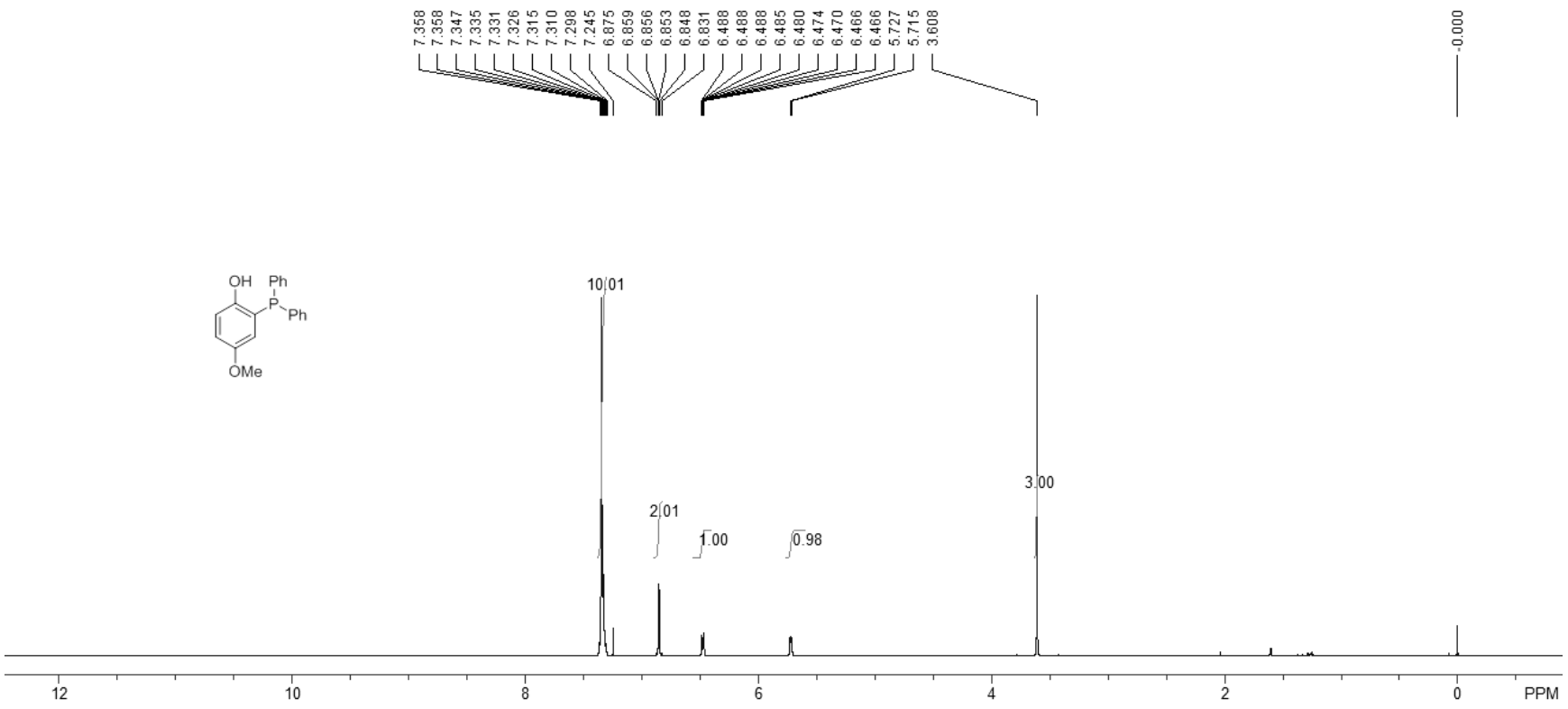
**$^{13}$C NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)(phenyl)(o-tolyl)phosphine oxide (3nk)**



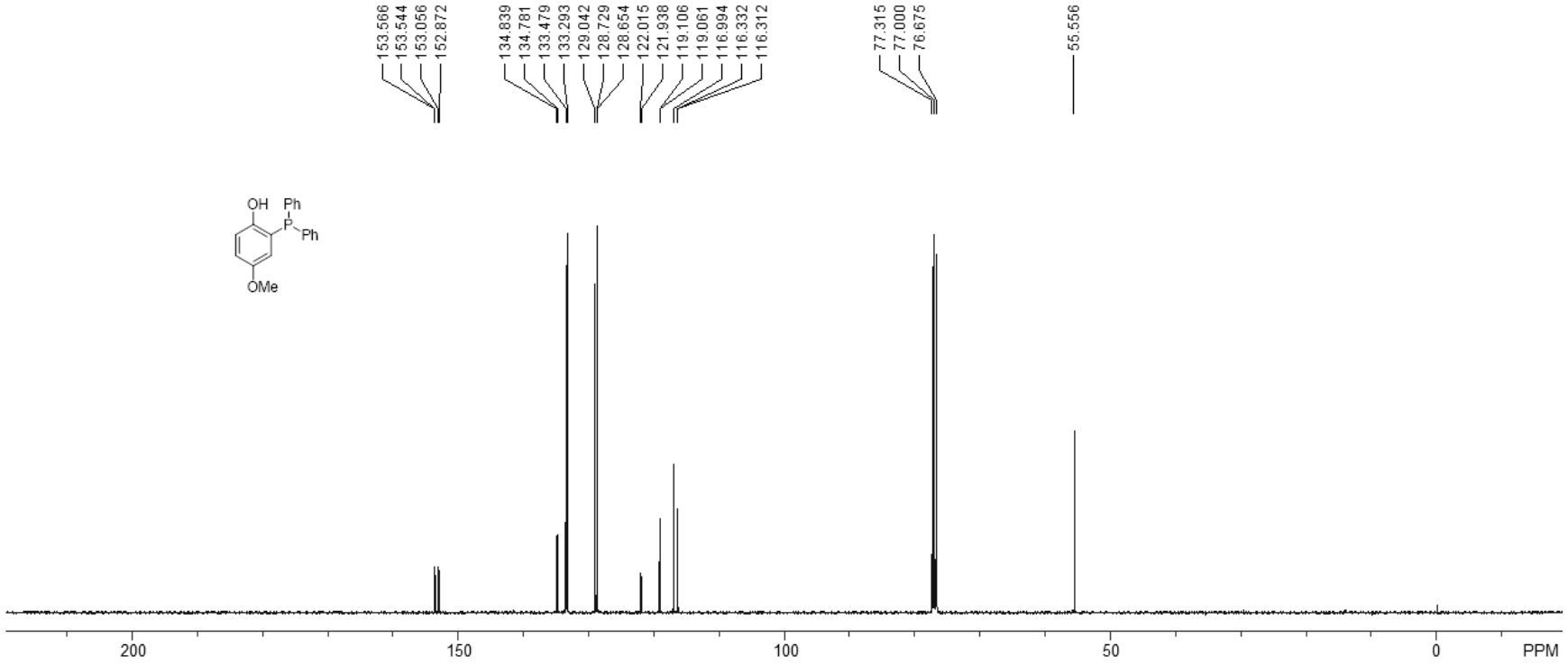
**$^{31}$P NMR of (1-hydroxy-4-methoxynaphthalen-2-yl)(phenyl)(o-tolyl)phosphine oxide (3nk)**



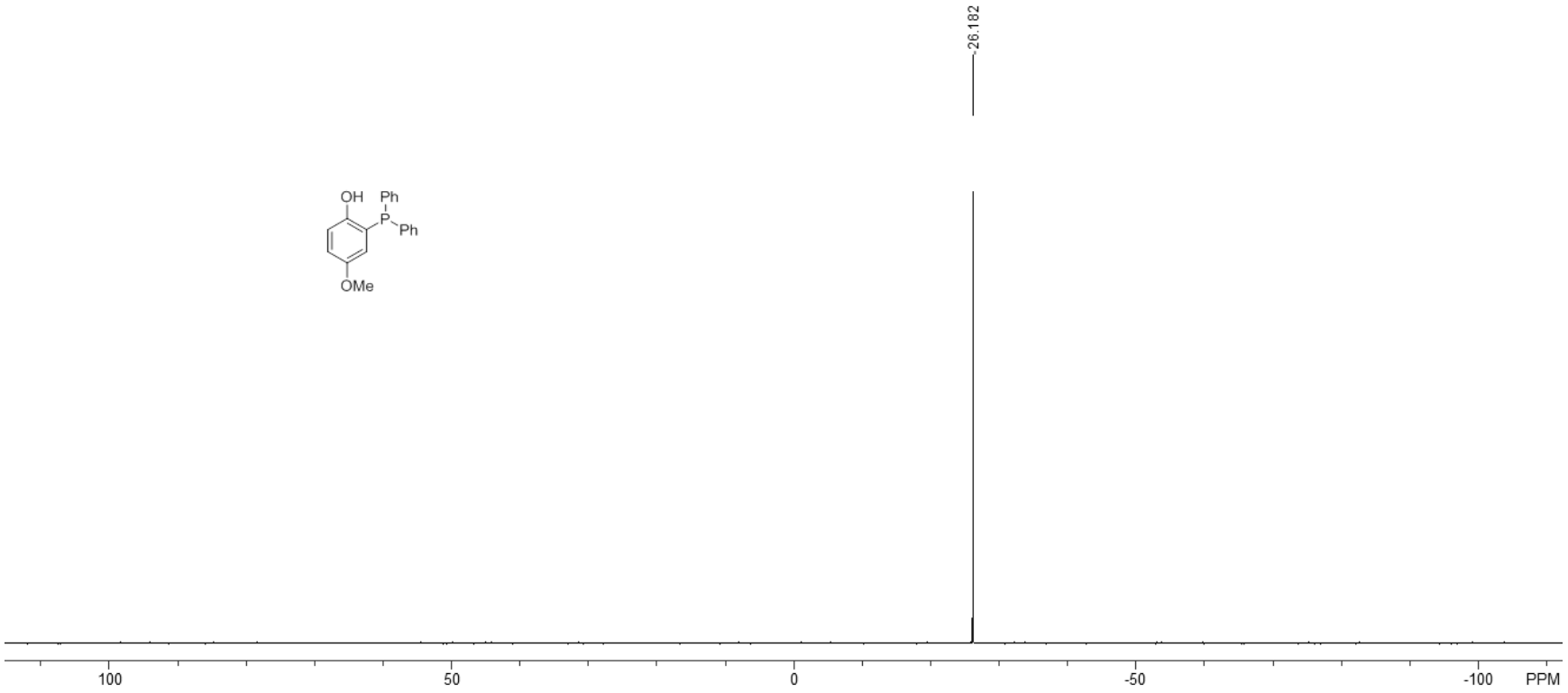
**[1]H NMR of 2-(diphenylphosphanyl)-4-methoxyphenol (5a)**



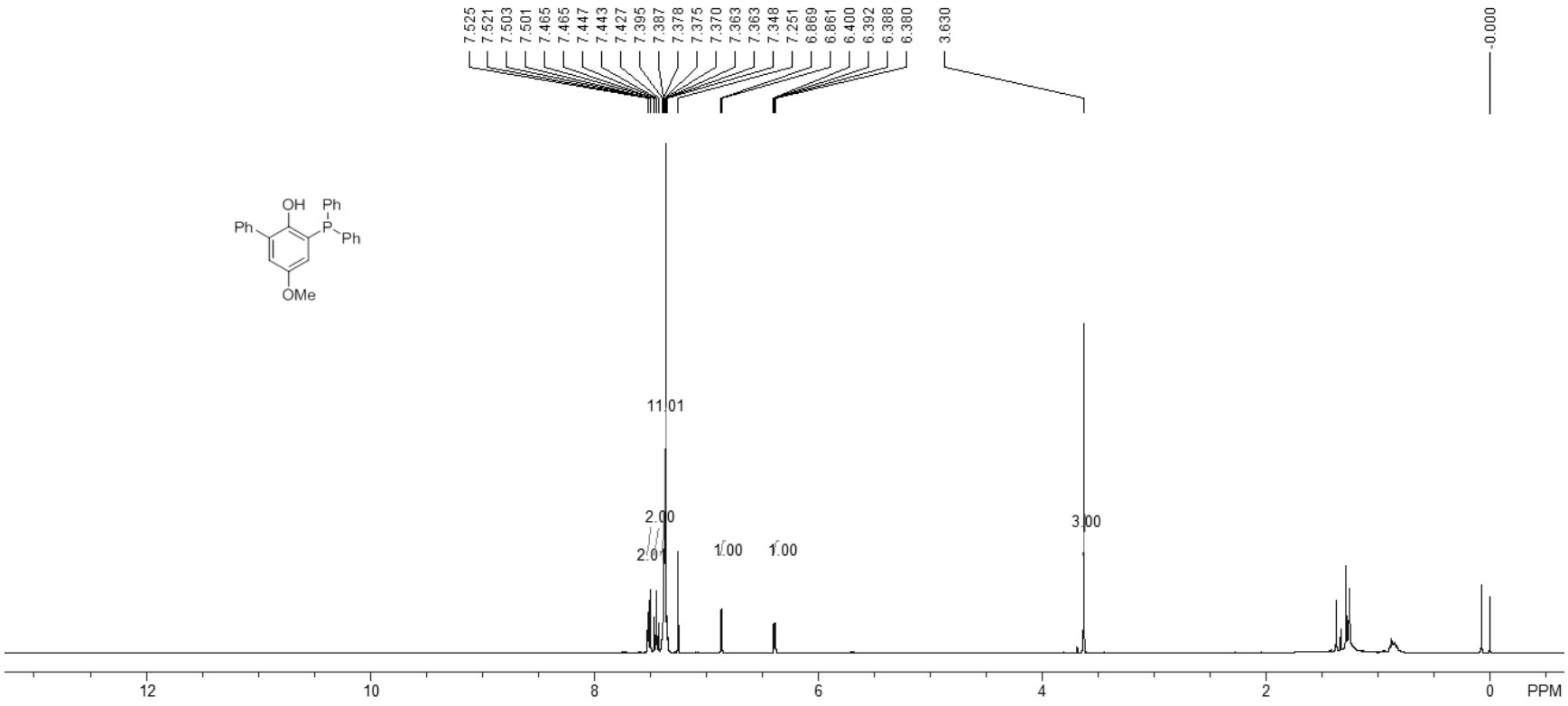
**$^{13}$C NMR of 2-(diphenylphosphanyl)-4-methoxyphenol (5a)**



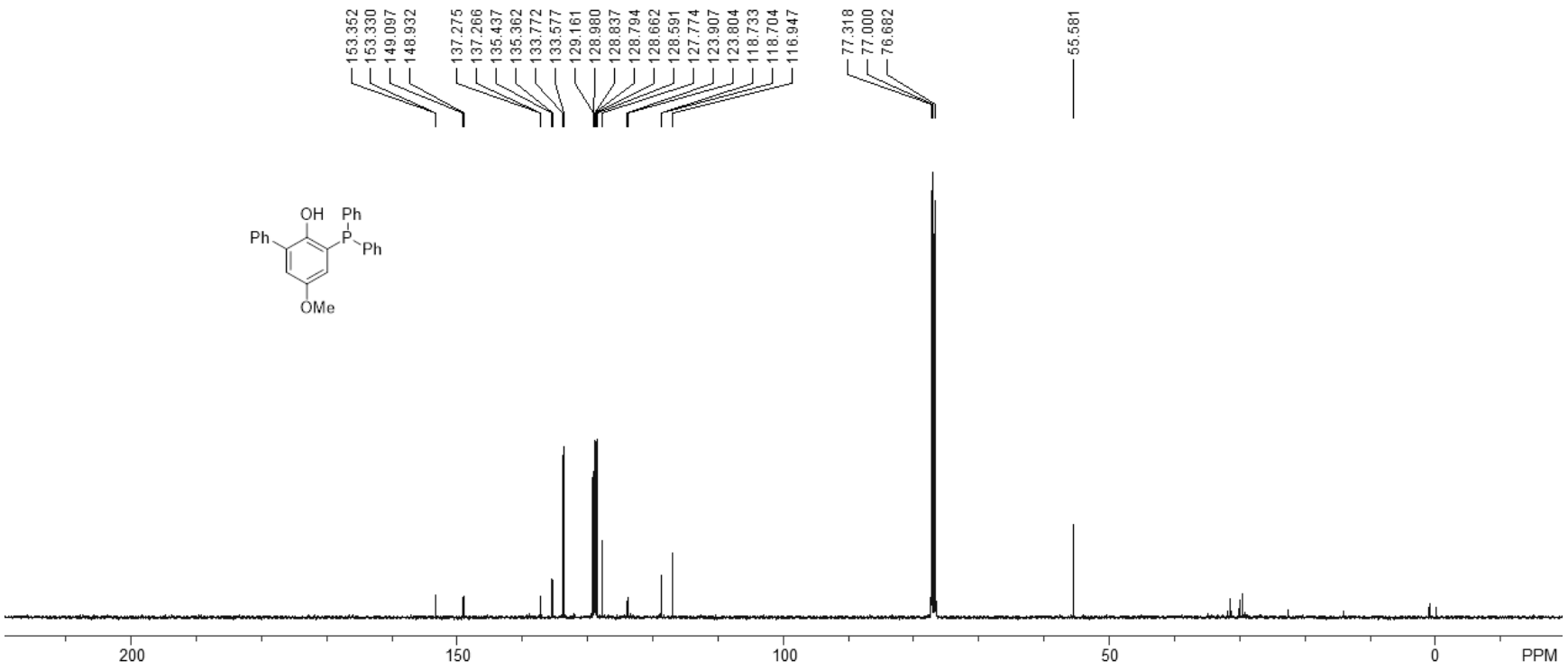
**$^{31}$P NMR of 2-(diphenylphosphanyl)-4-methoxyphenol (5a)**



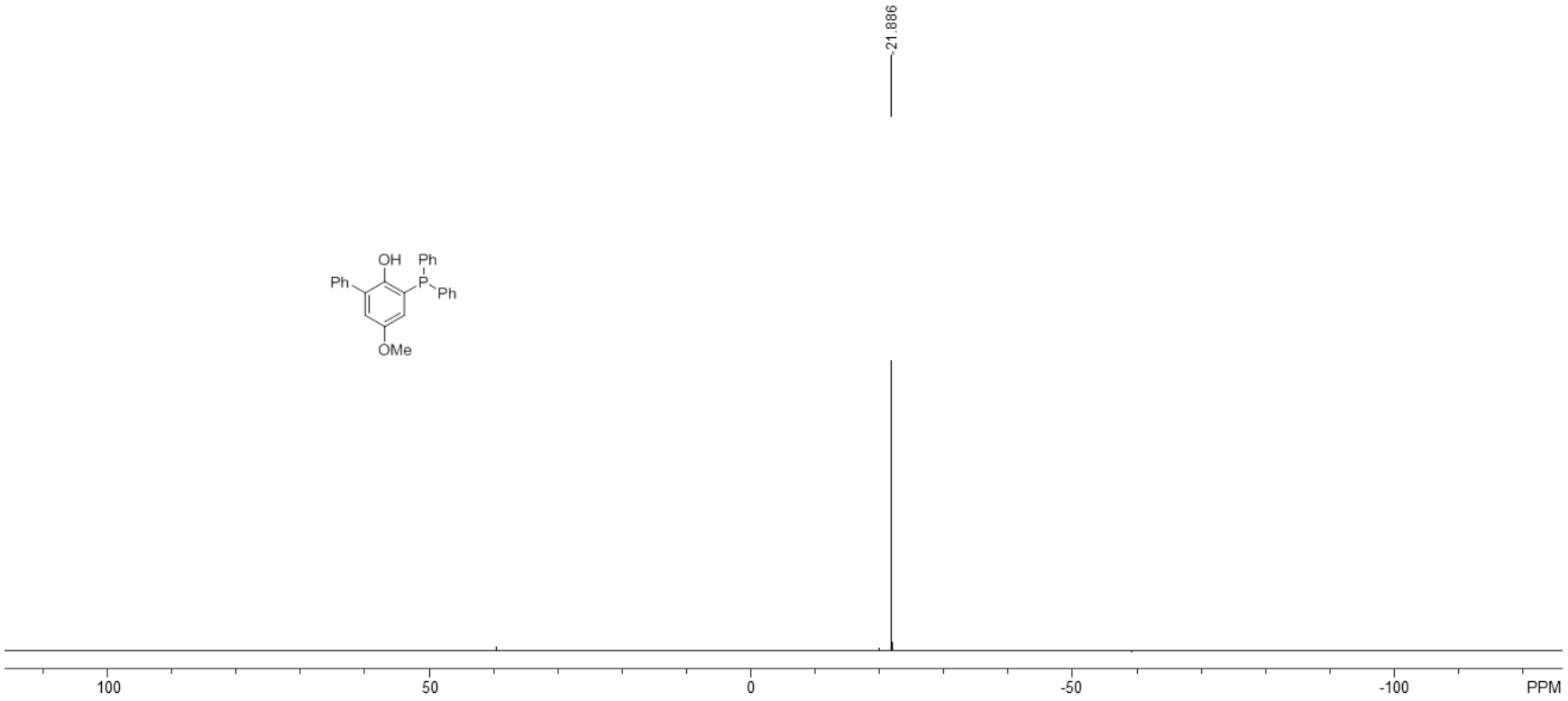
**$^{1}$H NMR of 3-(diphenylphosphanyl)-5-methoxy-[1,1'-biphenyl]-2-ol (5b)**



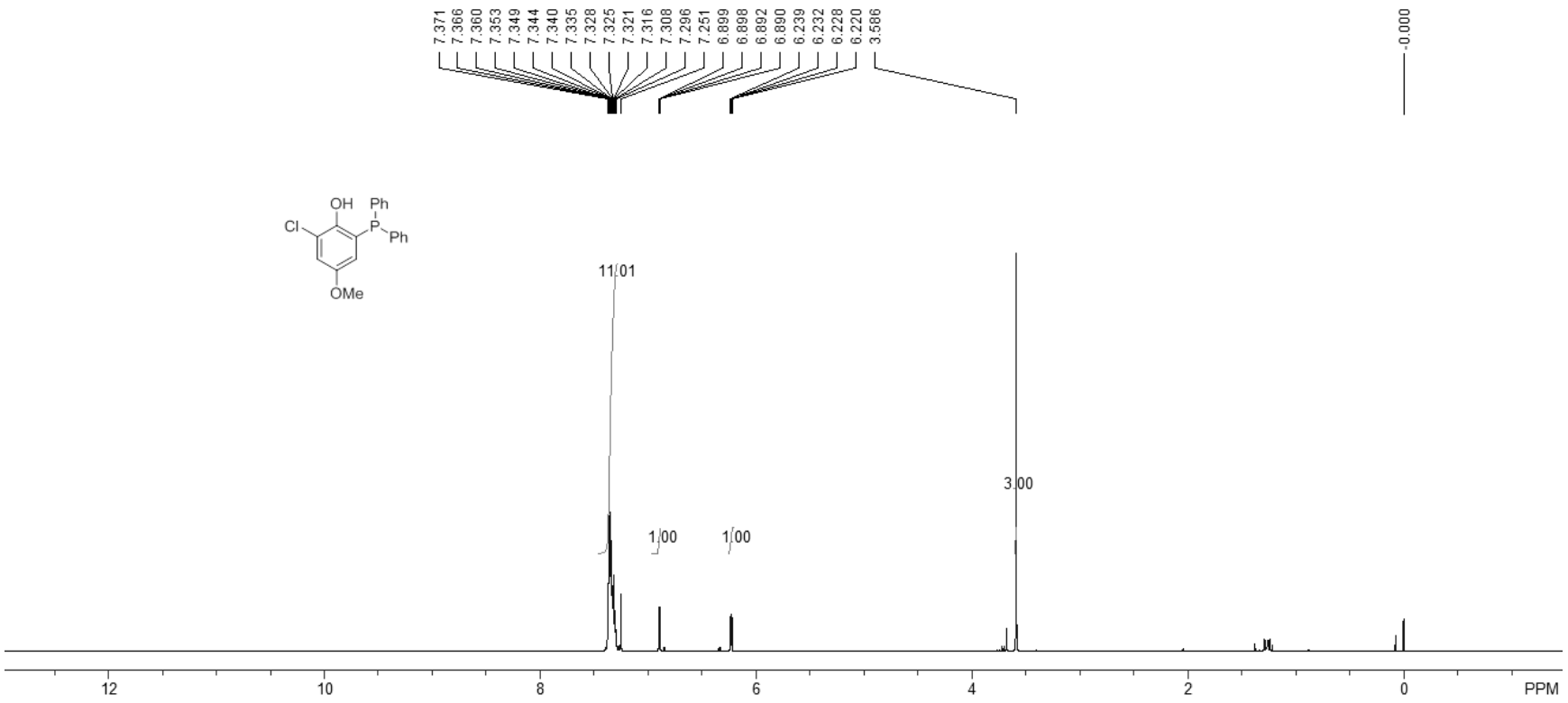
**$^{13}$C NMR of 3-(diphenylphosphanyl)-5-methoxy-[1,1'-biphenyl]-2-ol (5b)**



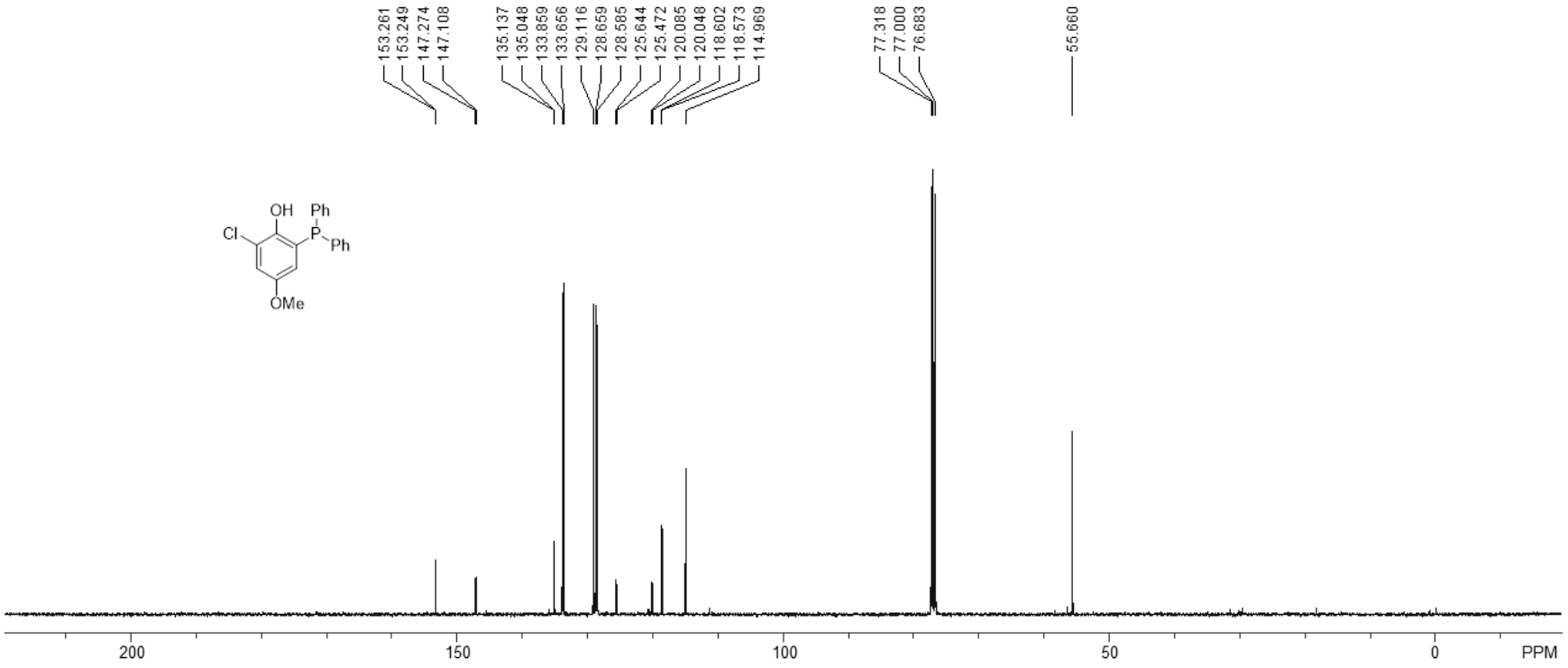
**$^{31}$P NMR of 3-(diphenylphosphanyl)-5-methoxy-[1,1'-biphenyl]-2-ol (5b)**



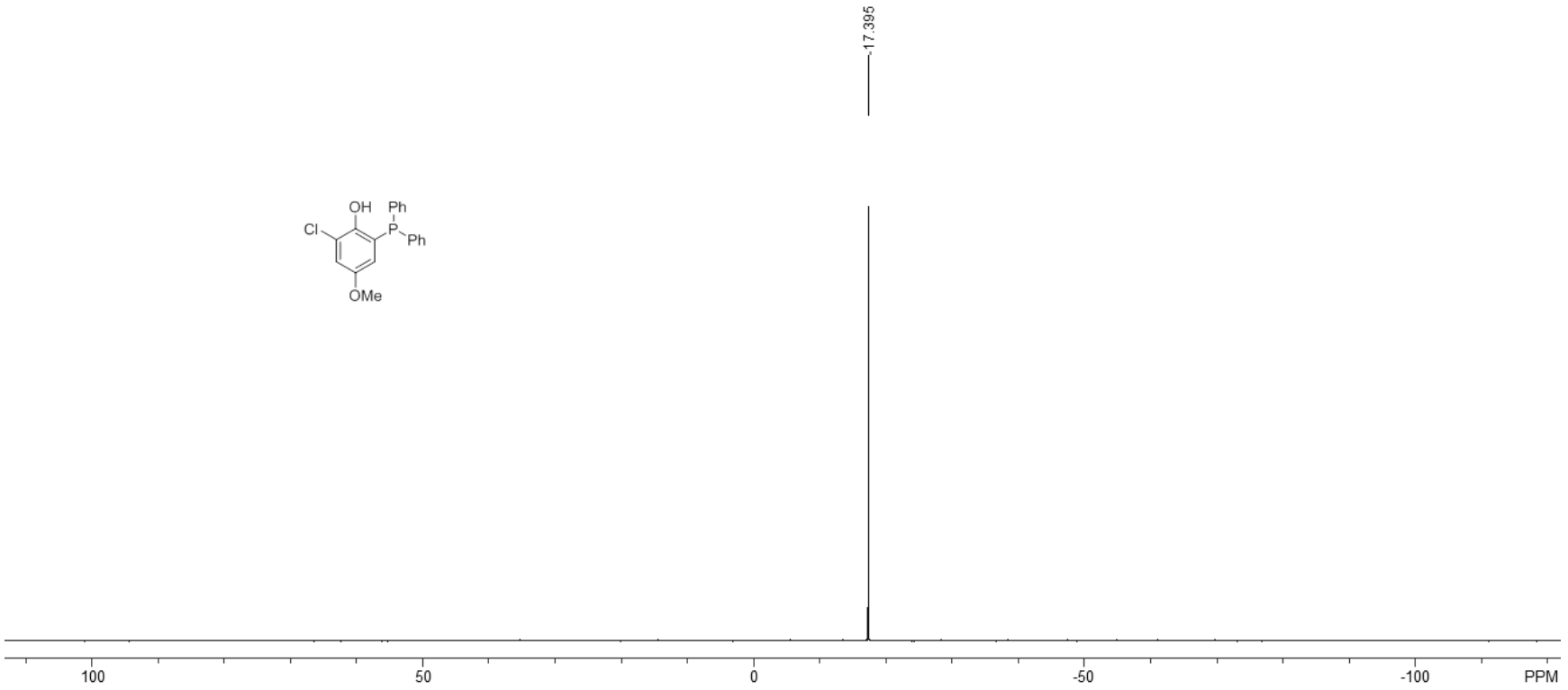
**$^{1}$H NMR of 2-chloro-6-(diphenylphosphanyl)-4-methoxyphenol (5c)**



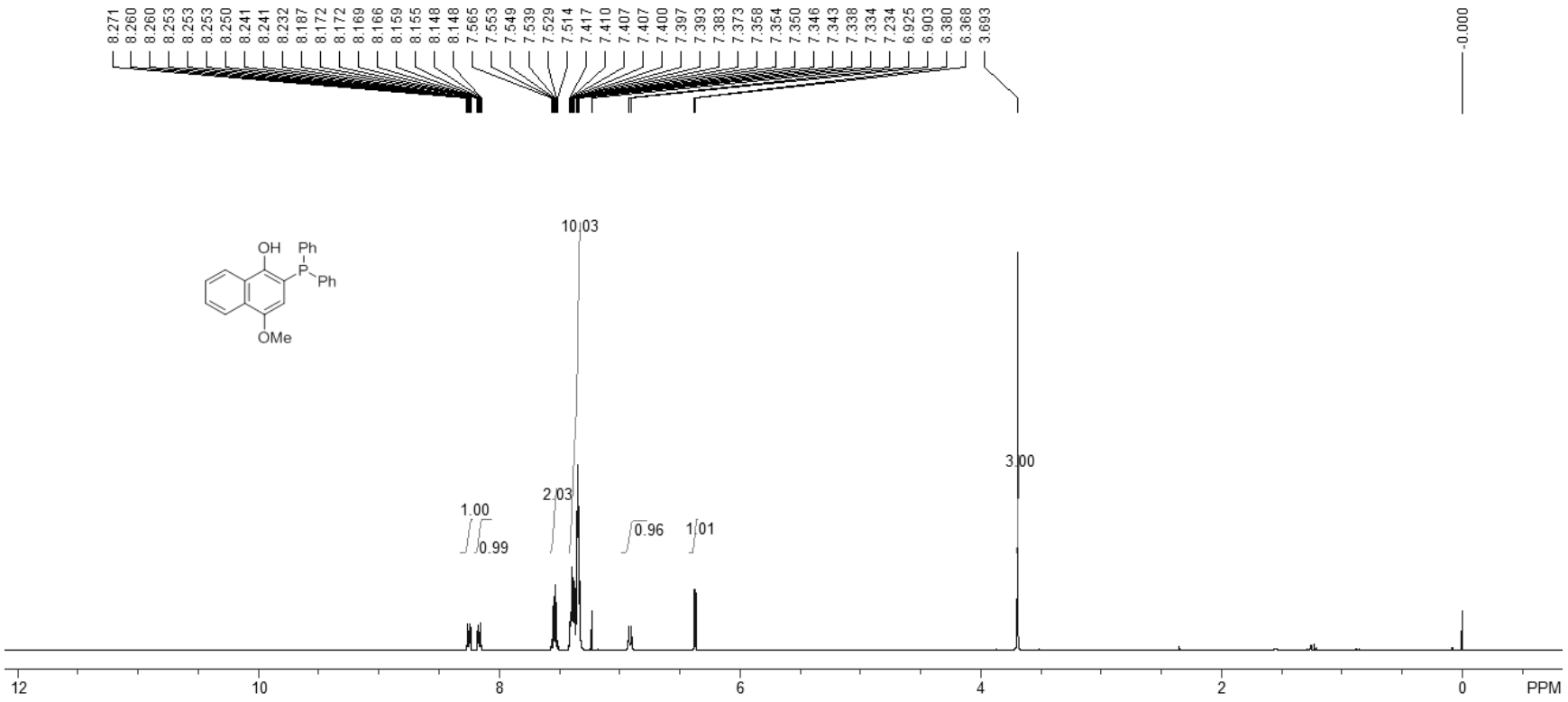
**$^{13}$C NMR of 2-chloro-6-(diphenylphosphanyl)-4-methoxyphenol (5c)**



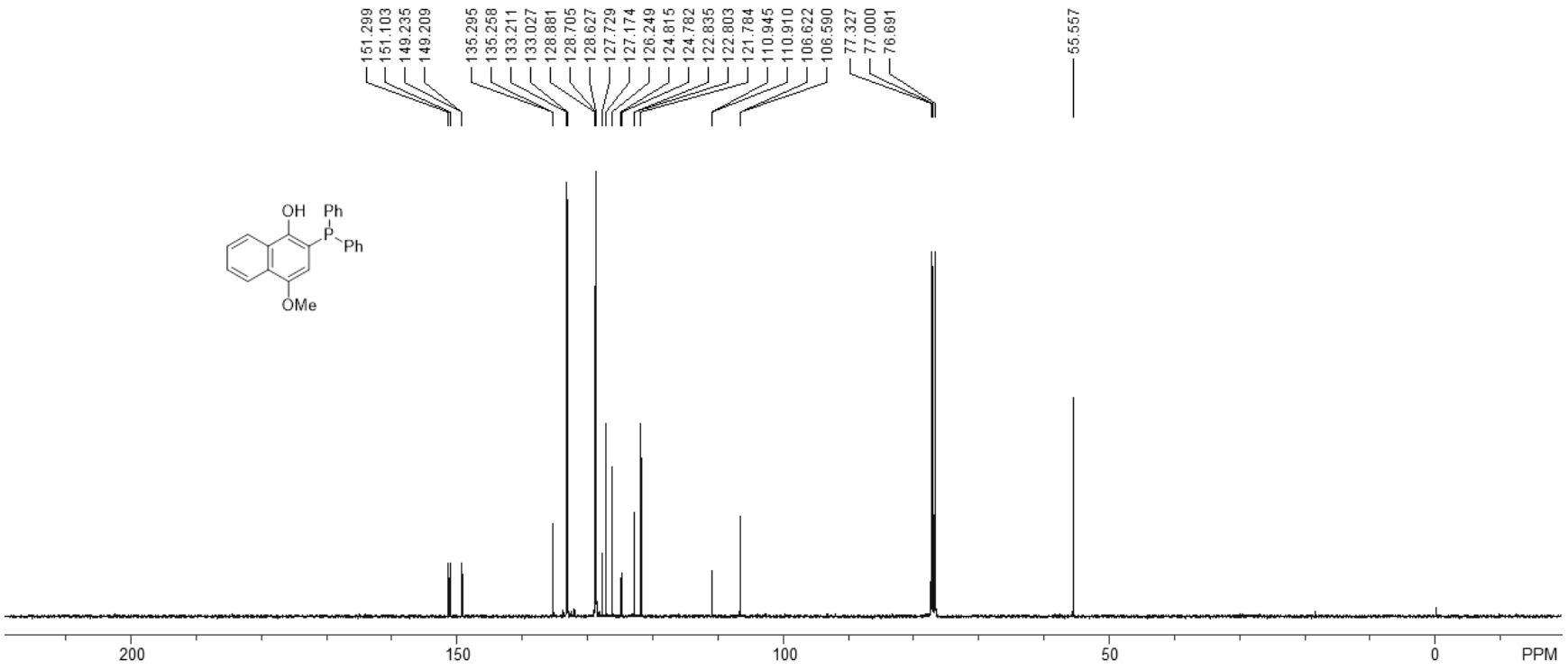
**$^{31}$P NMR of 2-chloro-6-(diphenylphosphanyl)-4-methoxyphenol (5c)**



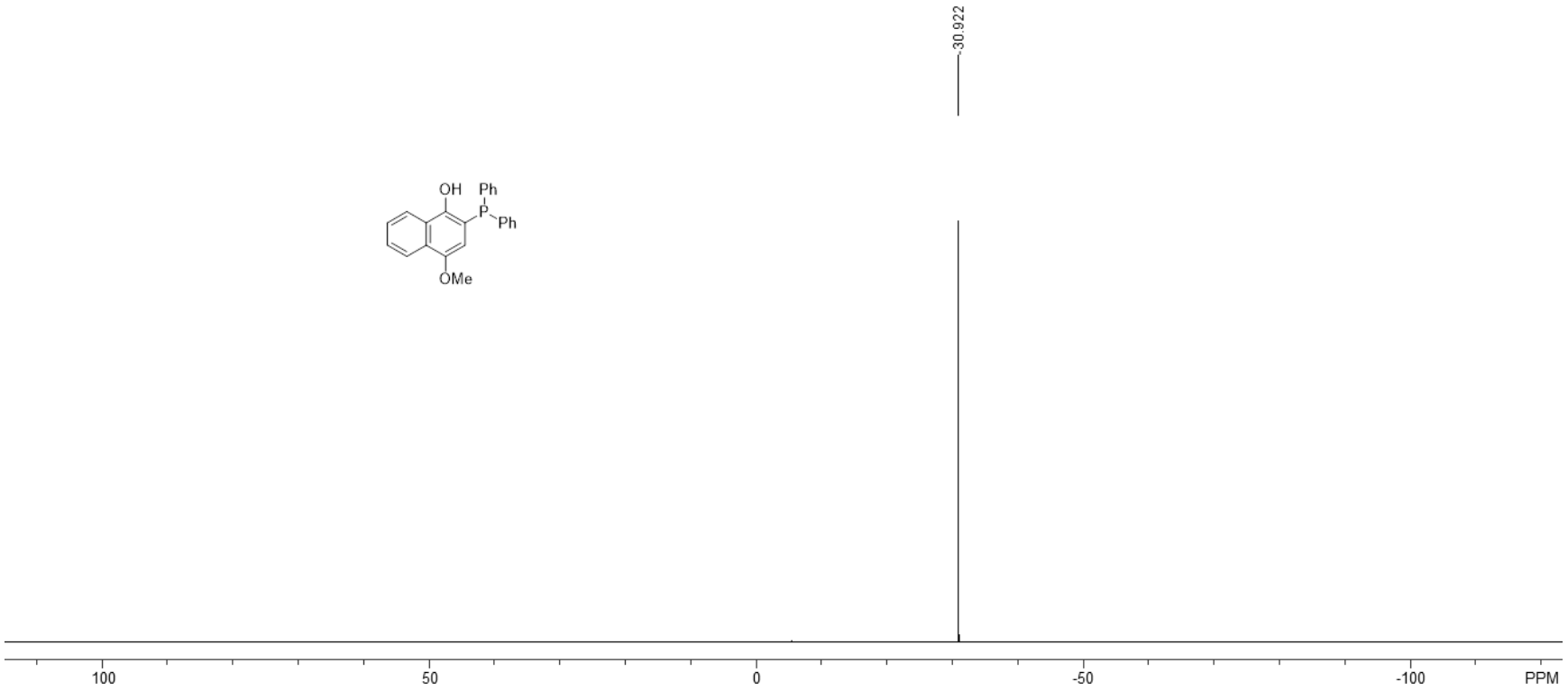
**$^{1}$H NMR of 2-(diphenylphosphanyl)-4-methoxynaphthalen-1-ol (5d)**



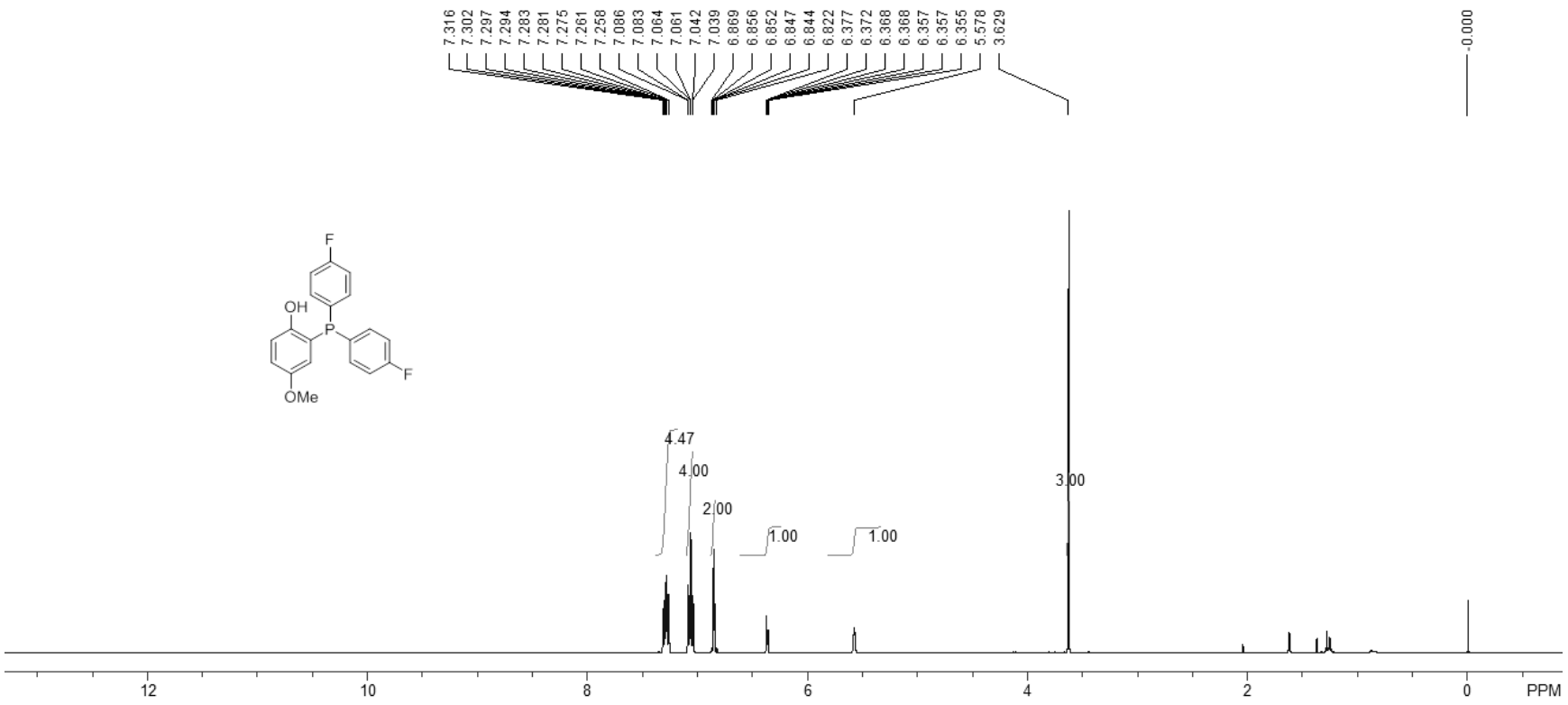
**$^{13}$C NMR of 2-(diphenylphosphanyl)-4-methoxynaphthalen-1-ol (5d)**



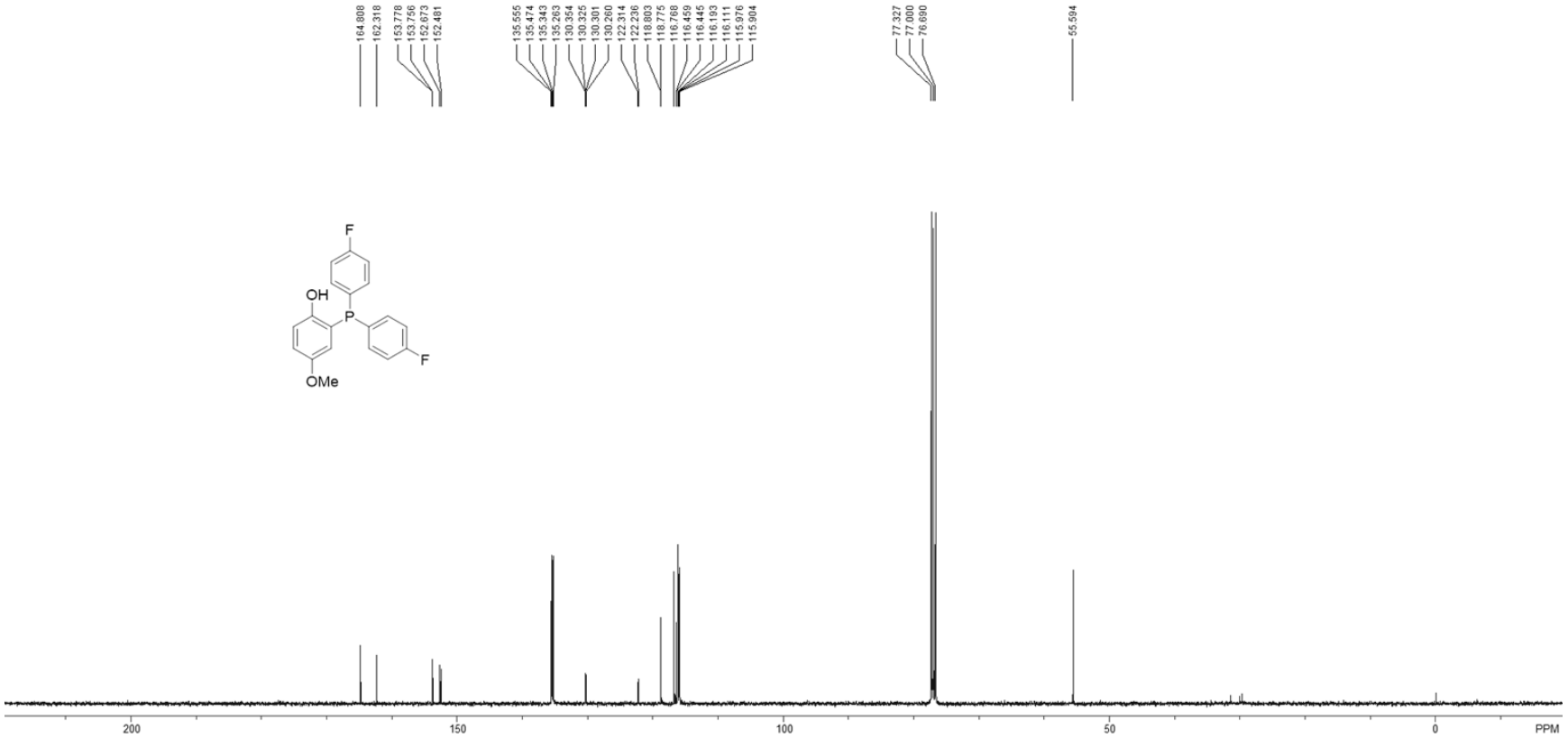
**$^{31}$P NMR of 2-(diphenylphosphanyl)-4-methoxynaphthalen-1-ol (5d)**



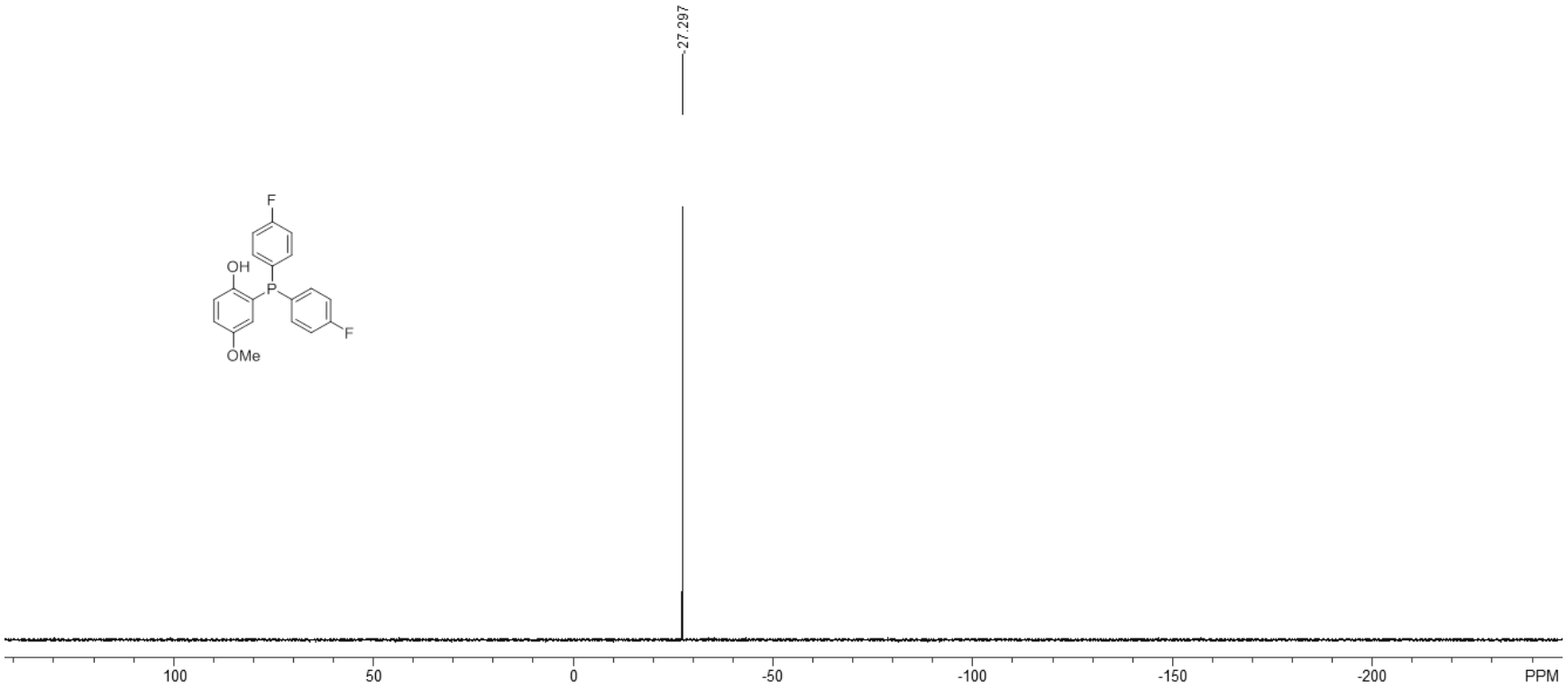
**$^{1}$H NMR of 2-(bis(4-fluorophenyl)phosphanyl)-4-methoxyphenol (5e)**



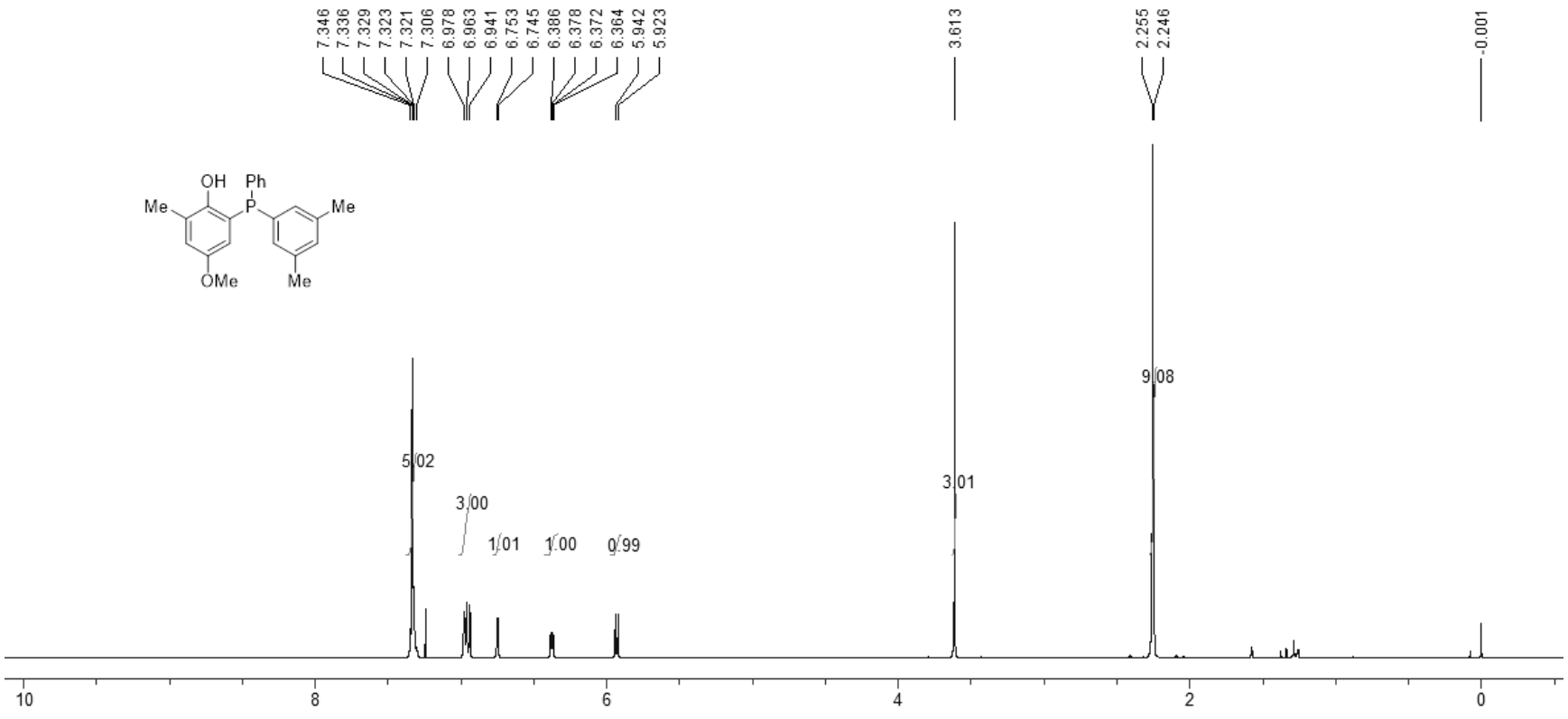
**$^{13}$C NMR of 2-(bis(4-fluorophenyl)phosphanyl)-4-methoxyphenol (5e)**



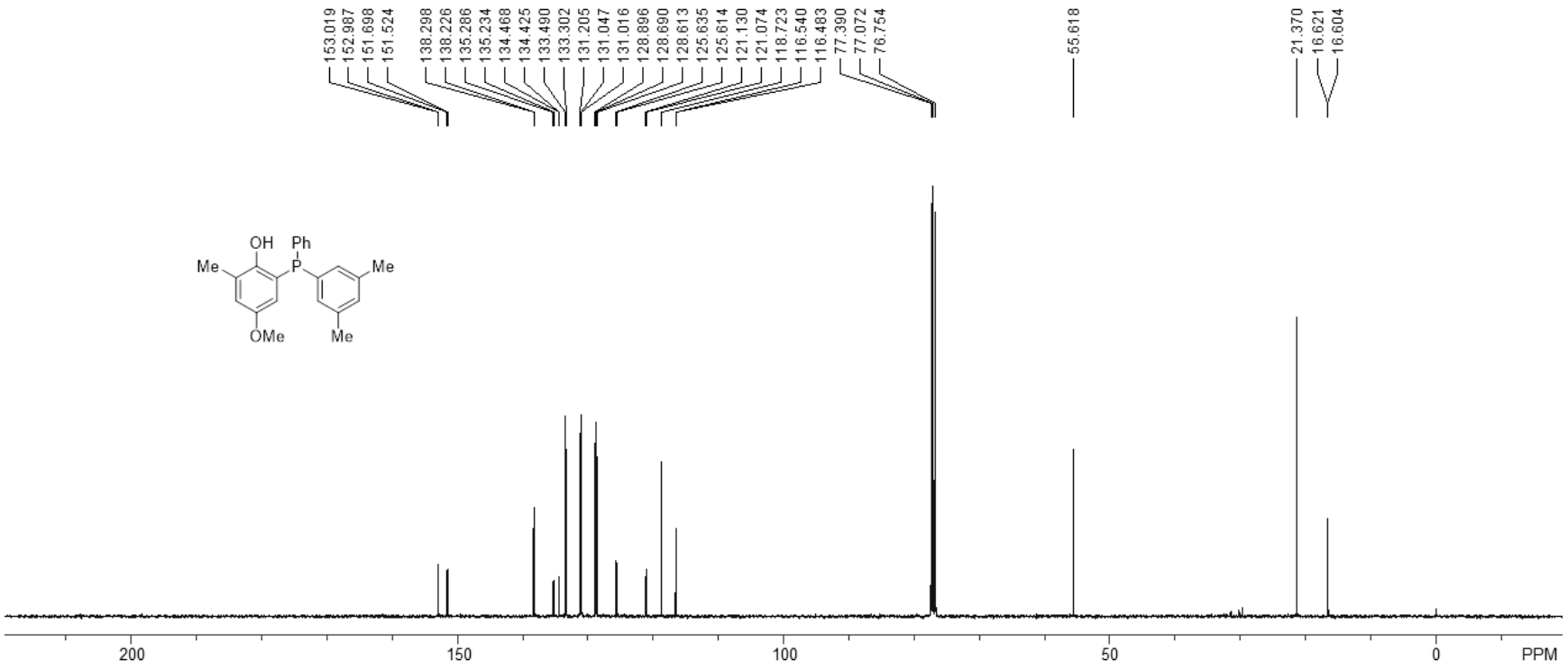
**$^{31}$P NMR of 2-(bis(4-fluorophenyl)phosphanyl)-4-methoxyphenol (5e)**



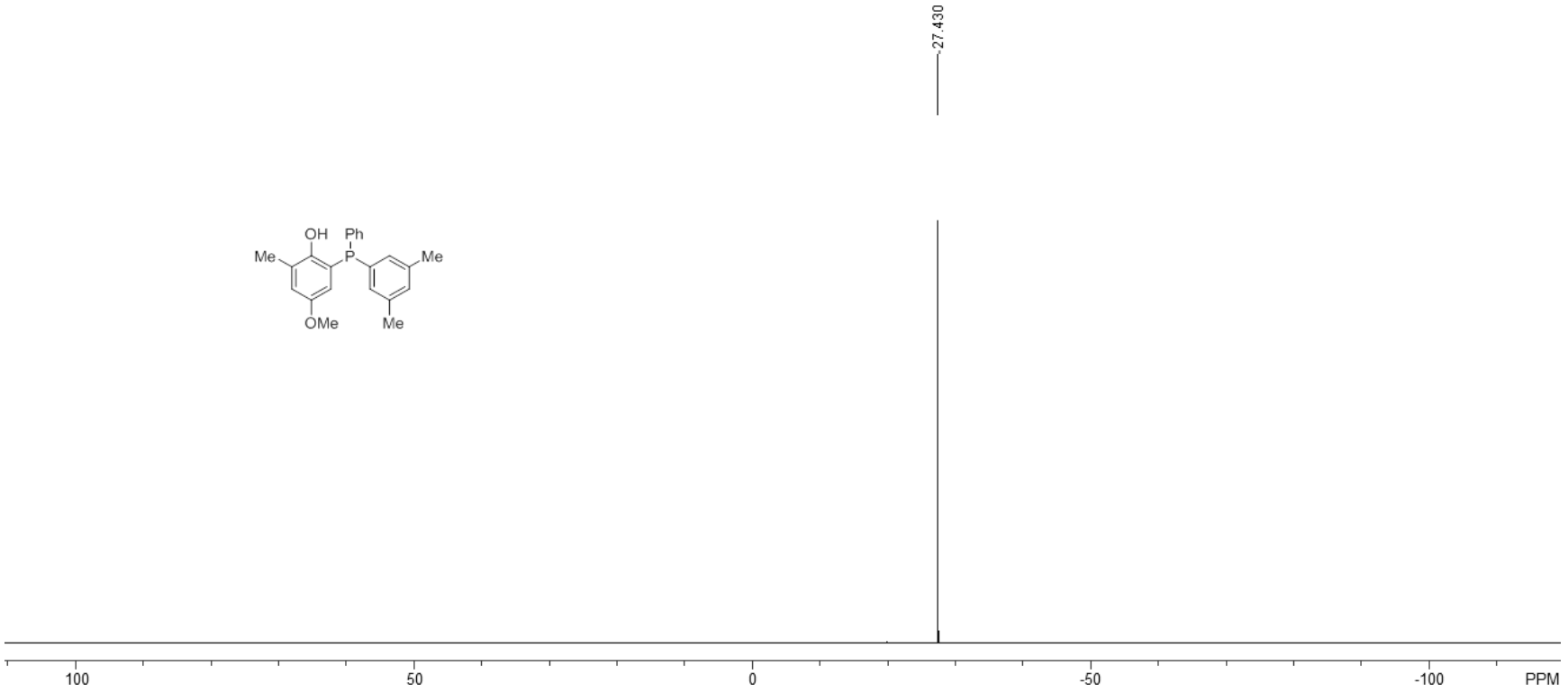
**$^{1}$H NMR of 2-((3,5-dimethylphenyl)(phenyl)phosphanyl)-4-methoxy-6-methylphenol (5f)**



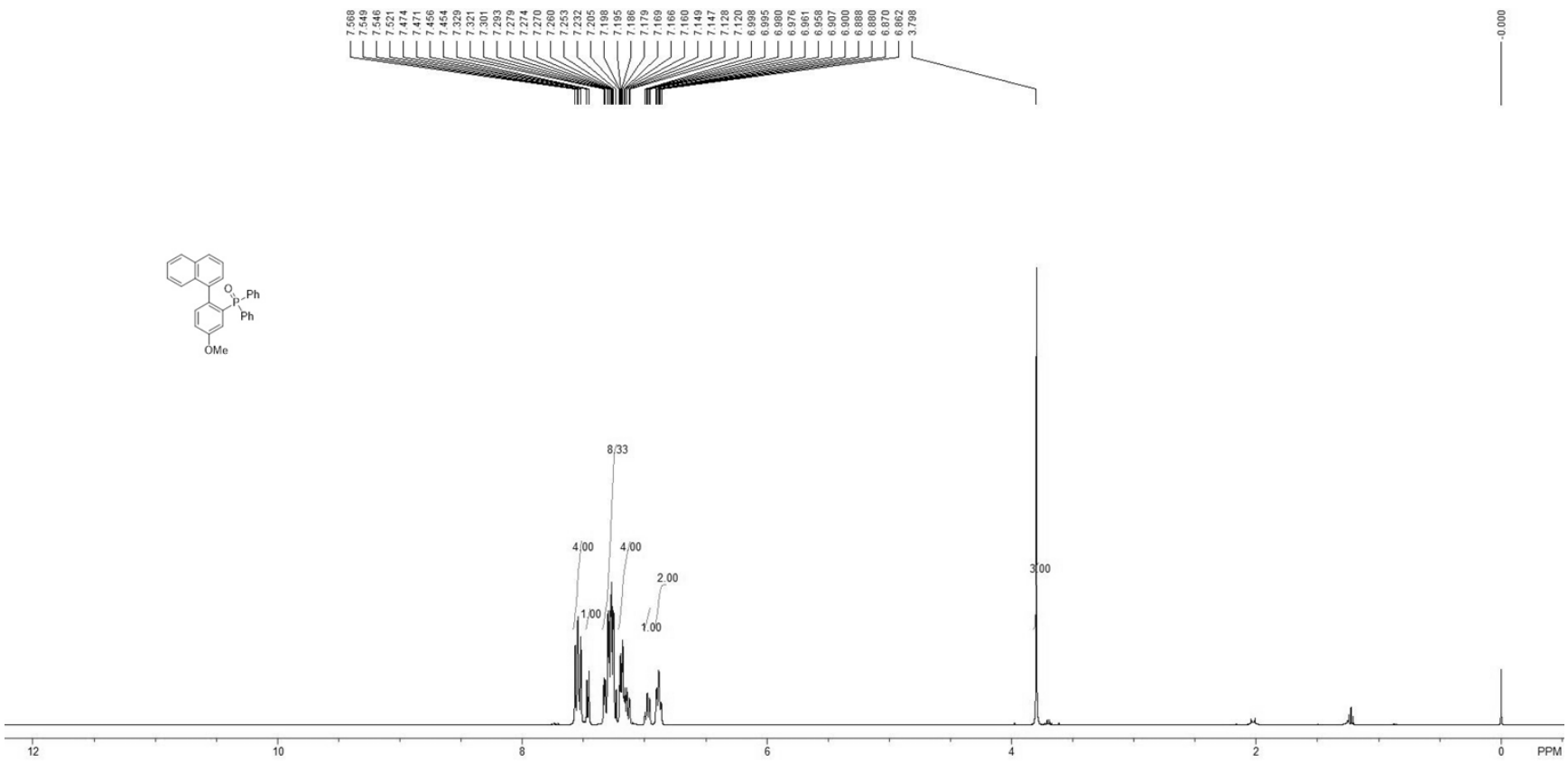
**$^{13}$C NMR of 2-((3,5-dimethylphenyl)(phenyl)phosphanyl)-4-methoxy-6-methylphenol (5f)**



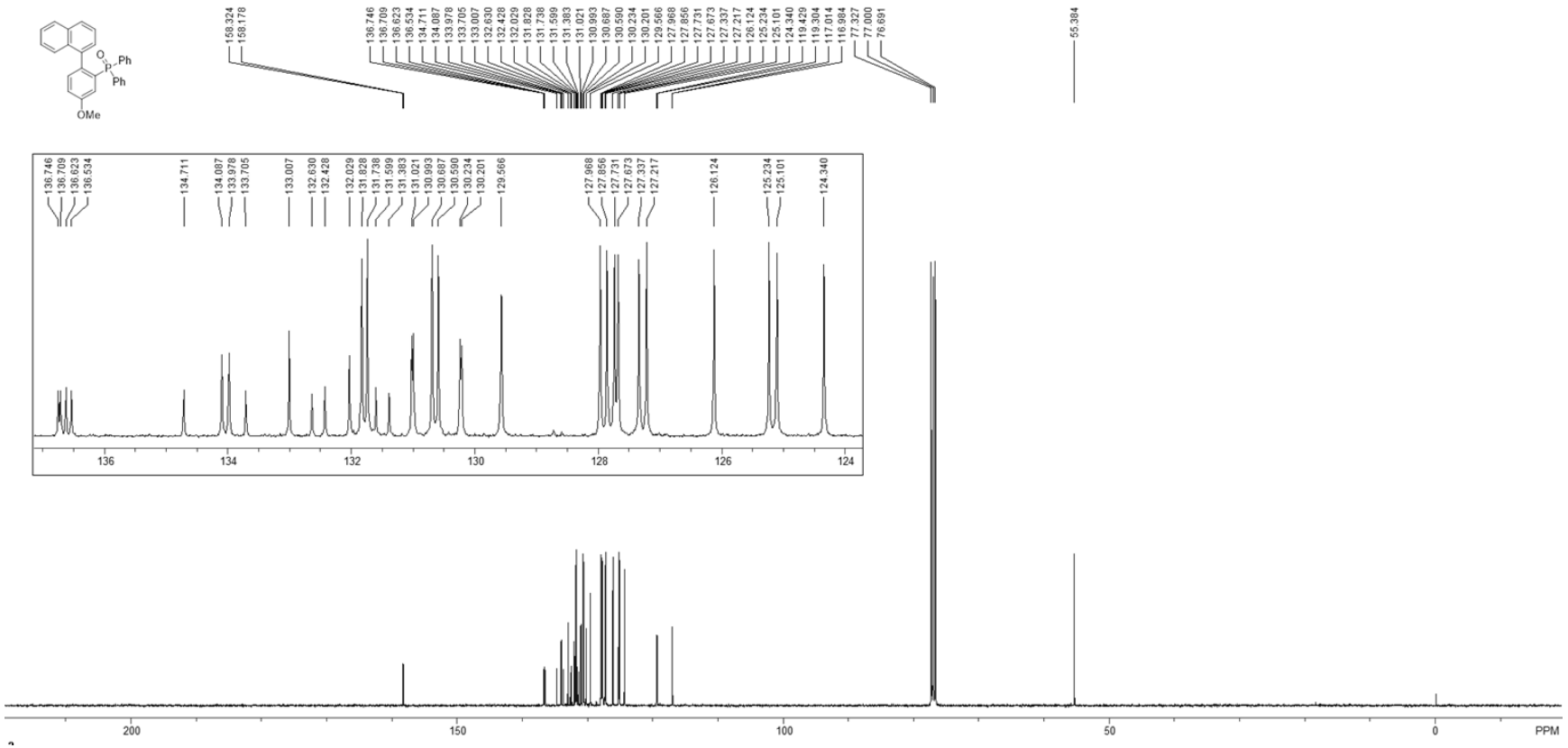
**$^{31}$P NMR of 2-((3,5-dimethylphenyl)(phenyl)phosphanyl)-4-methoxy-6-methylphenol (5f)**



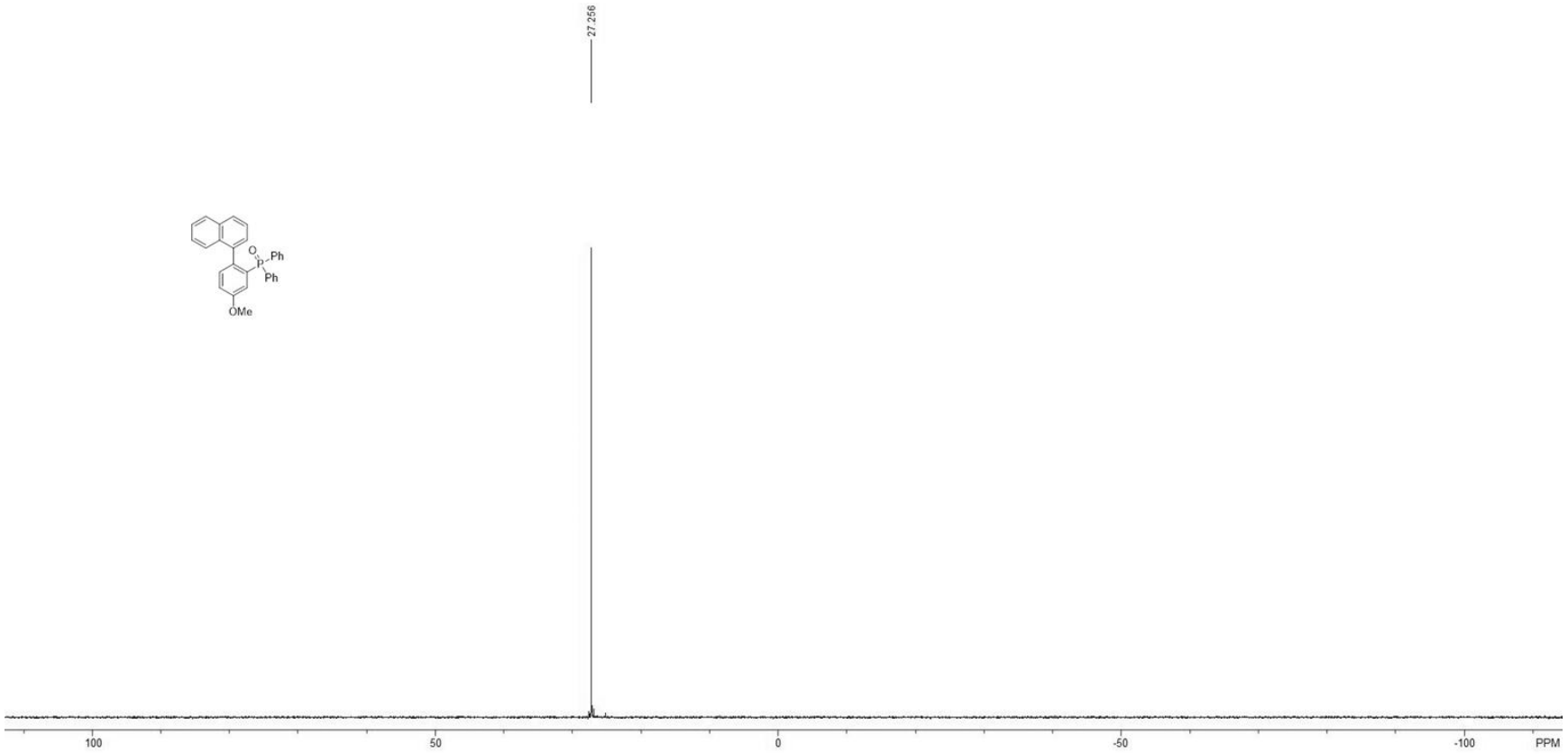
**$^{1}$H NMR of (5-methoxy-2-(naphthalen-1-yl)phenyl)diphenylphosphine oxide (6)**



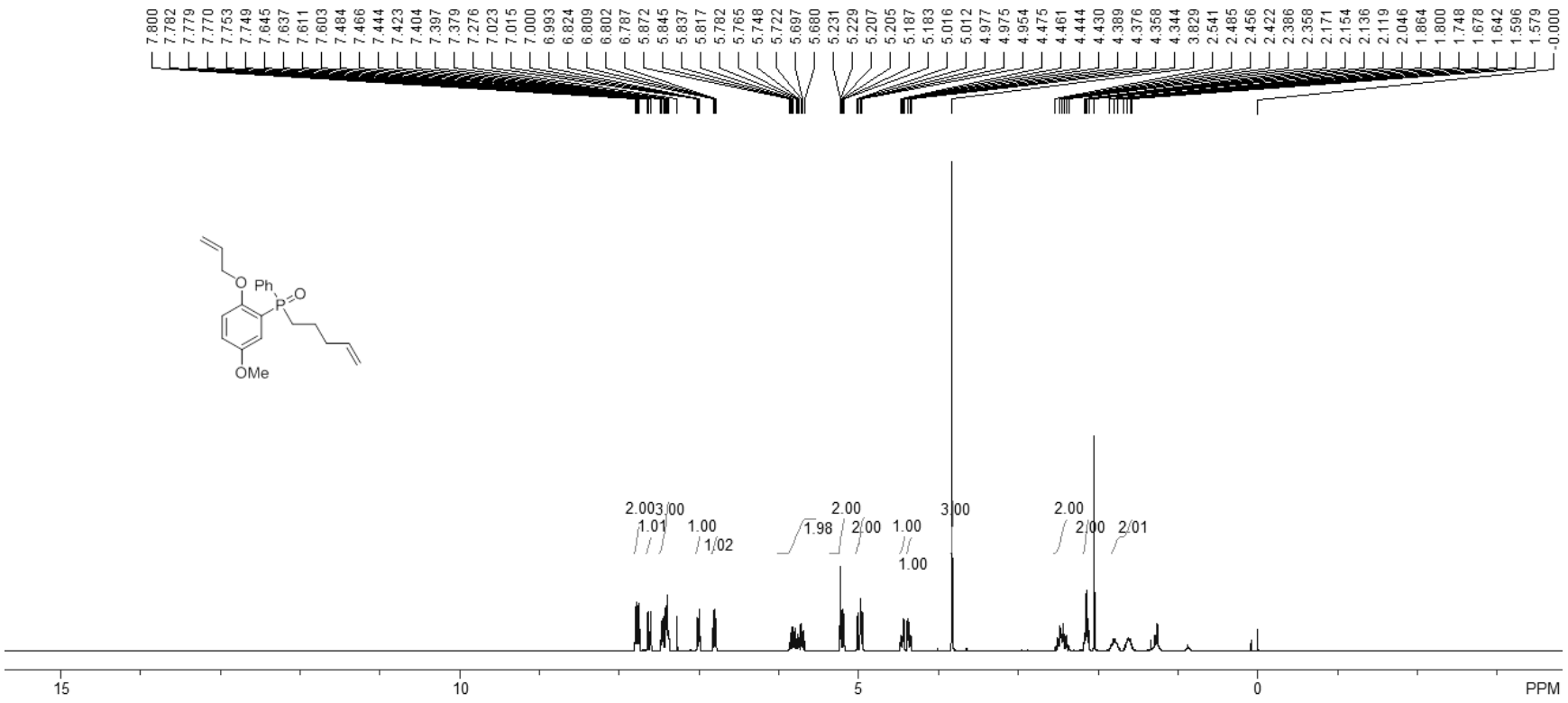
**$^{13}$C NMR of (5-methoxy-2-(naphthalen-1-yl)phenyl)diphenylphosphine oxide (6)**



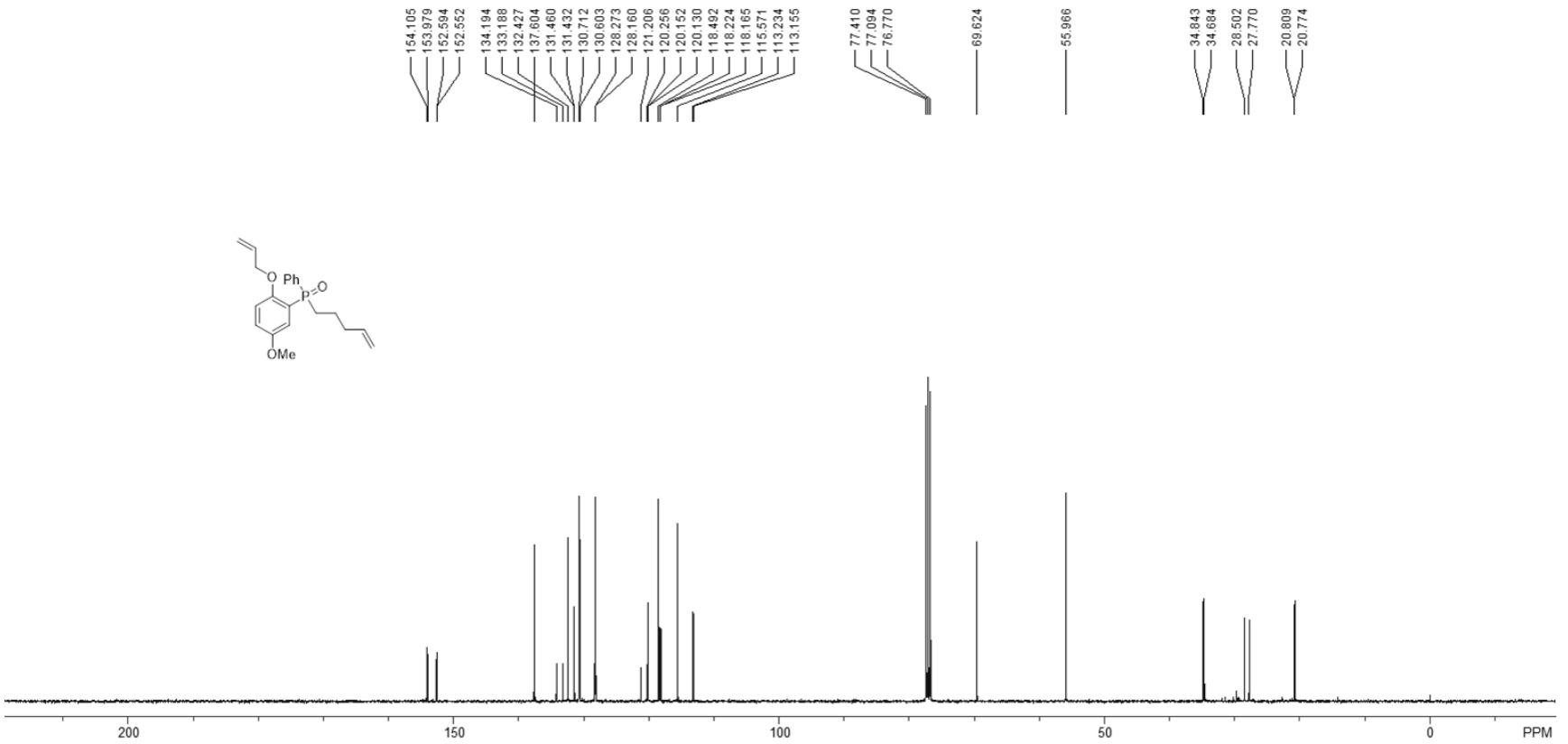
**$^{31}$P NMR of (5-methoxy-2-(naphthalen-1-yl)phenyl)diphenylphosphine oxide (6)**



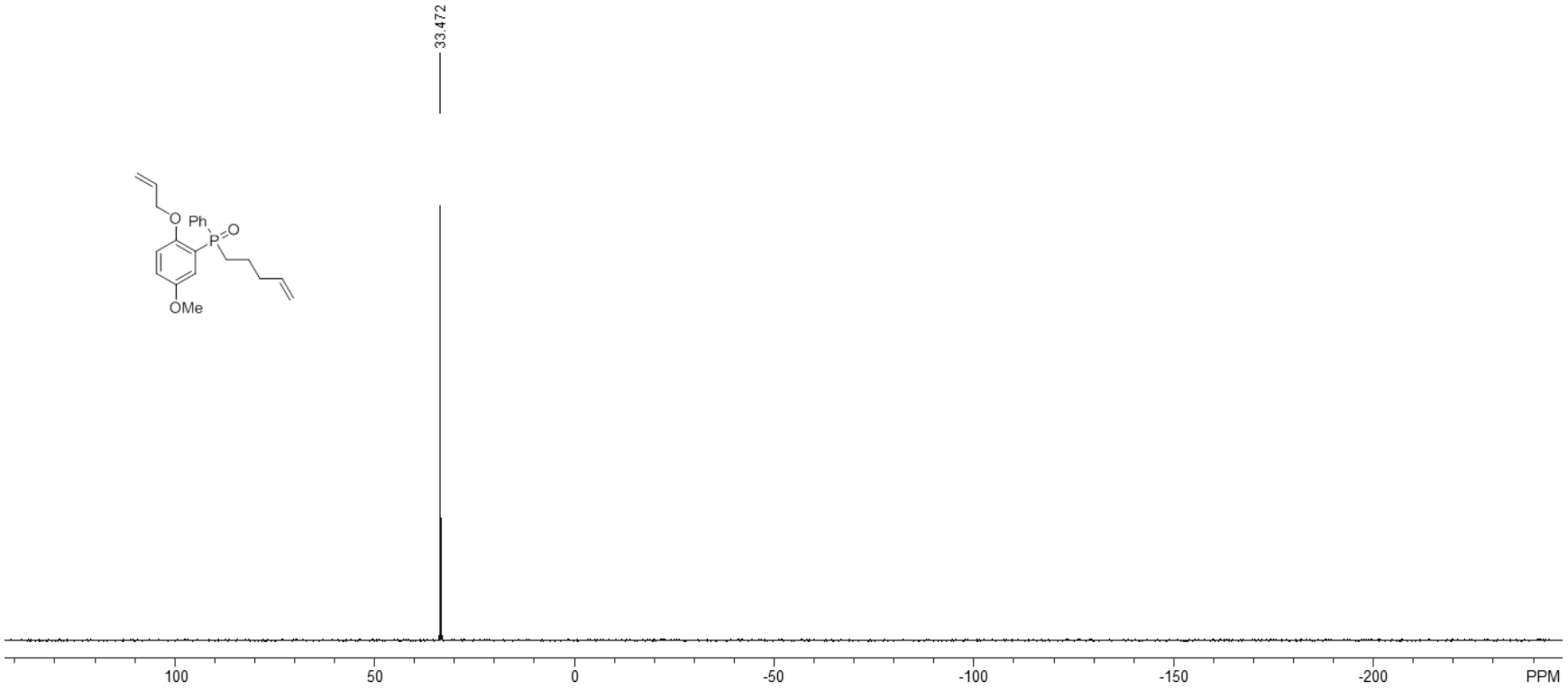
**[1]H NMR of (2-(allyloxy)-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (P-7)**



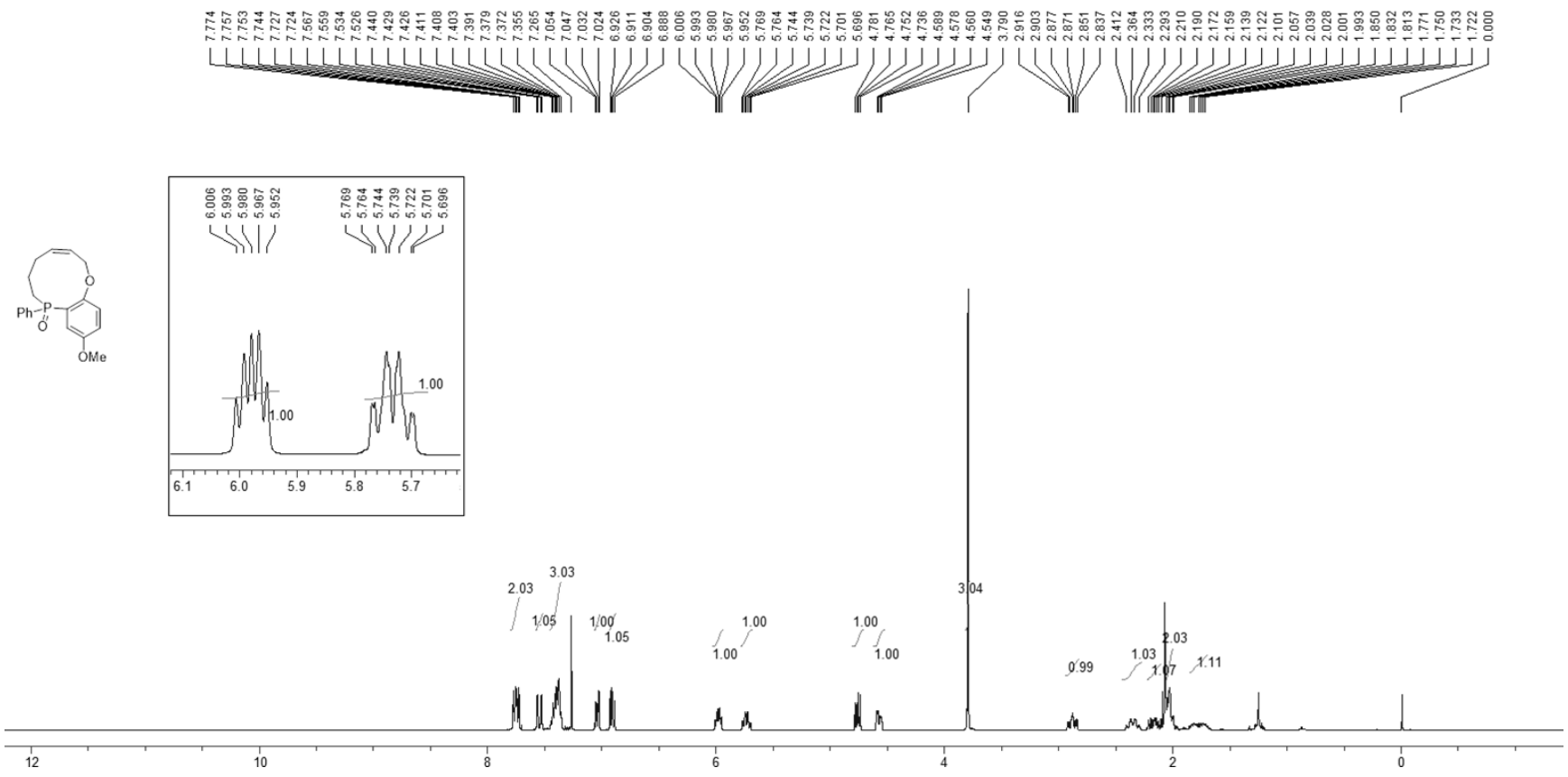
**$^{13}$C NMR of (2-(allyloxy)-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (P-7)**



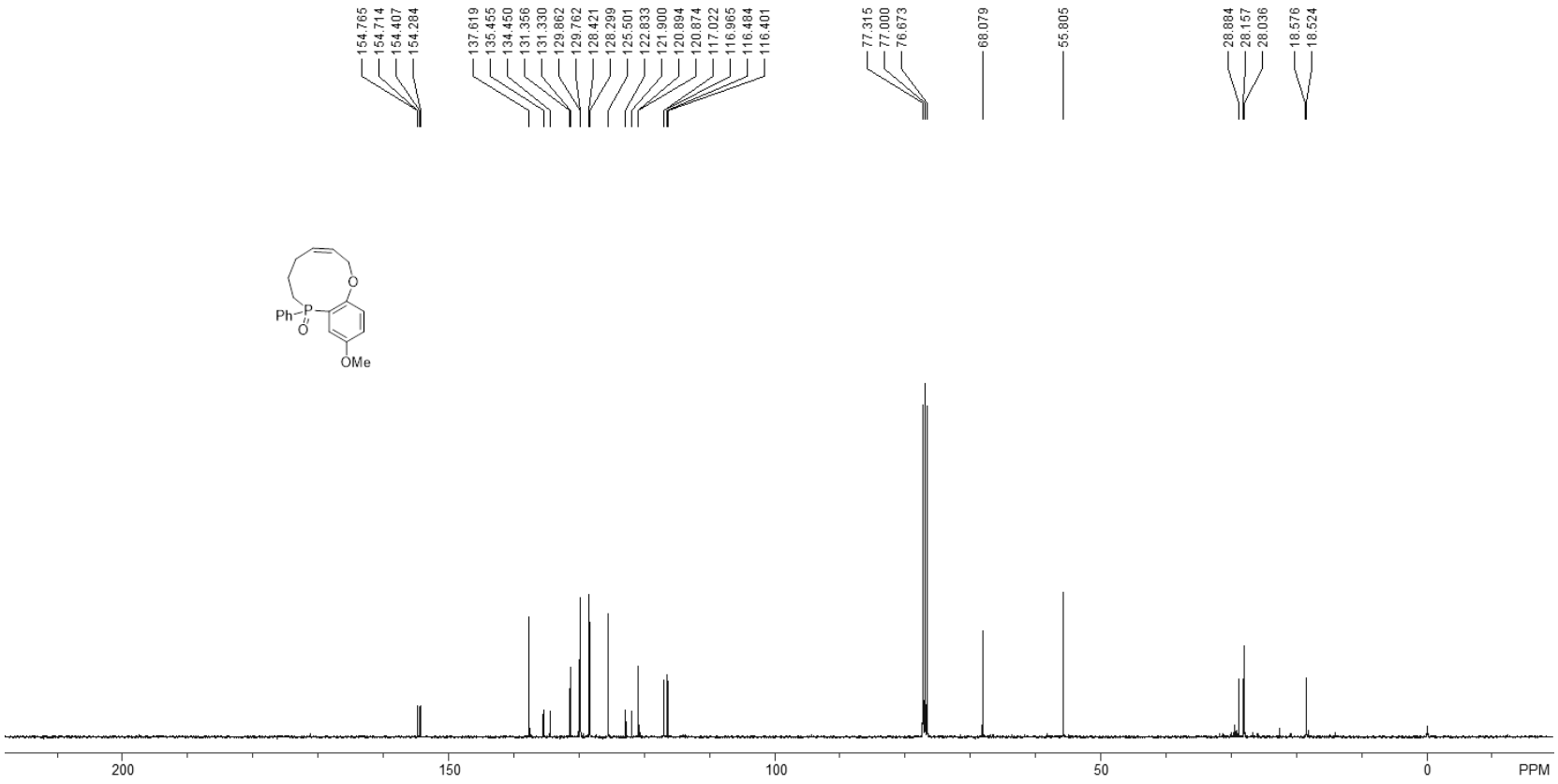
**$^{31}$P NMR of (2-(allyloxy)-5-methoxyphenyl)(pent-4-en-1-yl)(phenyl)phosphine oxide (P-7)**



**$^{1}$H NMR of (*Z*)-10-methoxy-8-phenyl-2,5,6,7-tetrahydrobenzo[b][1,4]oxaphosphecine 8-oxide (7)**



**$^{13}$C NMR of (*Z*)-10-methoxy-8-phenyl-2,5,6,7-tetrahydrobenzo[b][1,4]oxaphosphecine 8-oxide (7)**



**$^{31}$P NMR of phosphorus-macrocycle (*Z*)-10-methoxy-8-phenyl-2,5,6,7-tetrahydrobenzo[b][1,4]oxaphosphecine 8-oxide (7)**