

Supporting Information for

Zinc-Catalyzed Regioselective C–P Couplings of *p*-Quinol Ethers with Secondary Phosphine Oxides to Afford 2-Phosphinylphenols

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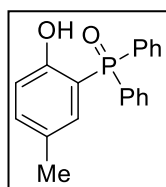
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1. General Information

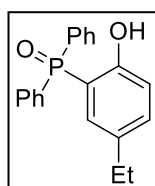
Unless otherwise specified, all reactions were performed under dry N₂ atmosphere. Anhydrous solvents were distilled prior to use: THF and toluene were distilled from sodium using benzophenone as the indicator; DCM, DMF, MeCN and DMSO were distilled from CaH₂. *p*-Quinol ethers were prepared following known procedures by oxidation of the corresponding phenols with PhI(OAc)₂ in MeOH.^[1] Secondary phosphine oxides were prepared via a known procedure.^[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. ¹H NMR spectra were recorded on a Bruker AscendTM 400 spectrometer at 400 MHz. ¹³C NMR spectra were recorded on a Bruker AscendTM 400 spectrometer at 100 MHz. ³¹P NMR spectra were recorded on a Bruker AscendTM 400 spectrometer at 160 MHz. Spectra were obtained in CDCl₃. 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 (CDCl₃, δ 7.26 ppm). Carbon chemical shifts were reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard (CDCl₃, δ 77.0 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 NanJing Tech University. The X-Ray crystallographic analysis were performed on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo K_α (λ = 0.71073 Å) radiation.

2. Experimental procedures and the characterization data of the products

General procedure for the Zn(OTf)₂-catalyzed preparation of 2-phosphinyl phenols 3: An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with Zn(OTf)₂ (7.2 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N₂ (3 cycles). Then **1** (0.2 mmol) and **2** (0.6 mmol) dissolved in 2 mL of DCE was injected. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C. After the reaction was complete (monitored by TLC, 6-48 h), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate 3/1) to afford the product **3**.



(2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa): white solid, mp. 219.3–220.6 °C, 52.5 mg (yield 85%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.96 (s, 1H), 7.72–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.48 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J*₁ = 8.4 Hz, *J*₂ = 5.2 Hz, 1H), 6.75 (dd, *J*₁ = 13.2 Hz, *J*₂ = 1.6 Hz, 1H), 2.19 (s, 3H). ³¹P NMR (CDCl₃, 162 MHz): δ = 39.5. This is a known compound.^[3]



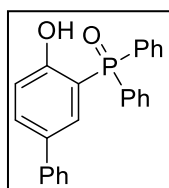
(5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba): White solid, mp. 199.3–201.2 °C, 49.0 mg (yield 76%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.96 (s, 1H), 7.72–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.47 (m, 4H), 7.25 (d, *J* = 7.6 Hz, 1H), 6.92 (dd, *J*₁ = 8.8 Hz, *J*₂ = 4.8 Hz, 1H), 6.77 (dd, *J*₁ = 13.6 Hz, *J*₂ = 2.0 Hz, 1H), 2.48 (q, *J* = 7.6

[1] a) R. M. Moriarty, O. Prakash, *Org. React.* **2001**, *57*, 327; b) A. E. Fleck, J. A. Hobart, G. W. Morrow, *Synth. Commun.* **1992**, *22*, 179.

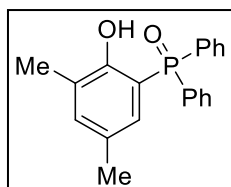
[2] R. Shen, J. Yang, H. Zhao, Y. Fu, L. Zhang, L.-B. Han, *Chem. Comm.* **2016**, *52*, 11959.

[3] D. G. Yakhvarov, K. a R. Basvani, M. s K. Kindermann, A. B. Dobrynin, I. A. Litvinov, O. g G. Sinyashin, P. G. Jones, J. Heinicke, *Eur. J. Inorg. Chem.* **2009**, 1234.

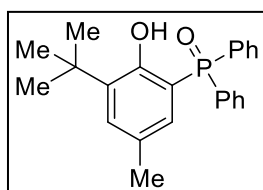
Hz, 2H), 1.11 (t, $J = 7.6$ Hz, 3H). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.6$. This is a known compound. [4]



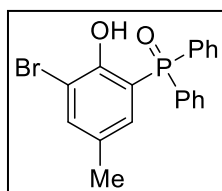
(4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca): White solid, mp. 178.8–180.2 °C, 40.7 mg (yield 55%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.26$ (s, 1H), 7.77–7.71 (m, 4H), 7.66–7.59 (m, 3H), 7.54–7.49 (m, 4H), 7.39–7.36 (m, 4H), 7.31–7.26 (m, 1H), 7.18 (dd, $J_1 = 14.0$ Hz, $J_2 = 2.4$ Hz, 1H), 7.07 (dd, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz, 1H). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.8$. This is a known compound. [5]



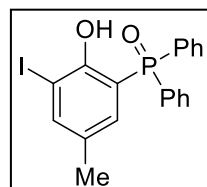
(2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da): White solid, mp. 161.3–163.1 °C, 48.6 mg (yield 75%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.08$ (s, 1H), 7.71–7.66 (m, 4H), 7.59–7.55 (m, 2H), 7.50–7.46 (m, 4H), 7.09 (s, 1H), 6.59 (d, $J = 14.0$ Hz, 1H), 2.23 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.9$ (d, $J_{P-C} = 2.4$ Hz), 136.3 (d, $J_{P-C} = 2.9$ Hz), 132.3 (d, $J_{P-C} = 13.3$ Hz), 132.0 (d, $J_{P-C} = 10.5$ Hz), 131.9 (d, $J_{P-C} = 103.0$ Hz), 128.9 (d, $J_{P-C} = 10.1$ Hz), 128.6 (d, $J_{P-C} = 12.2$ Hz), 127.5 (d, $J_{P-C} = 13.3$ Hz), 127.4 (d, $J_{P-C} = 8.3$ Hz), 109.5 (d, $J_{P-C} = 103.4$ Hz), 20.5, 15.9 (d, $J_{P-C} = 1.0$ Hz). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.9$. This is a known compound. [6]



(3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenyl phosphine oxide (3ea): 16.8 mg (yield 23%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.19$ (s, 1H), 7.71–7.66 (m, 4H), 7.60–7.56 (m, 2H), 7.51–7.46 (m, 4H), 7.22 (d, $J = 1.6$ Hz, 1H), 6.59 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.17 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.0$, 138.6 (d, $J_{P-C} = 7.0$ Hz), 132.6, 132.4, 132.1 (d, $J_{P-C} = 10.2$ Hz), 131.6, 129.4 (d, $J_{P-C} = 10.3$ Hz), 128.6 (d, $J_{P-C} = 12.4$ Hz), 127.1 (d, $J_{P-C} = 15.5$ Hz), 110.1 (d, $J_{P-C} = 102.6$ Hz), 35.1, 29.4, 20.9. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 41.0$. HRMS (ESI-TOF): $m/z = 365.1672$, calcd for $\text{C}_{23}\text{H}_{26}\text{O}_2\text{P}$ [MH^+] 365.1670



(3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa): 69.6 mg (yield 90%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.77$ (s, 1H), 7.71–7.66 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.49 (m, 5H), 6.73 (dd, $J_1 = 13.2$ Hz, $J_2 = 1.2$ Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 157.7$ (d, $J_{P-C} = 4.0$ Hz), 138.3 (d, $J_{P-C} = 2.3$ Hz), 132.7 (d, $J_{P-C} = 2.0$ Hz), 132.0 (d, $J_{P-C} = 9.7$ Hz), 131.0 (d, $J_{P-C} = 104.9$ Hz), 130.9 (d, $J_{P-C} = 9.0$ Hz), 129.4 (d, $J_{P-C} = 12.9$ Hz), 128.8 (d, $J_{P-C} = 12.3$ Hz), 112.2 (d, $J_{P-C} = 11.1$ Hz), 112.1 (d, $J_{P-C} = 100.6$ Hz), 20.2. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.5$. HRMS (ESI-TOF): $m/z = 387.0152$, calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{PBr}$ [MH^+] 387.0150.



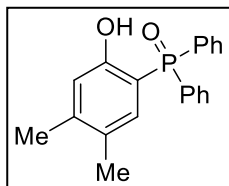
(2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga): 69.6 mg (yield 82%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.98$ (s, 1H), 7.74–7.65 (m, 5H), 7.62–7.58 (m, 2H), 7.52–7.48 (m, 4H), 6.76 (dd, $J_1 = 13.2$ Hz, $J_2 = 0.8$ Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.9$ (d, $J_{P-C} = 3.7$ Hz), 144.5 (d,

[4] S. Shuvaev, O. Kotova, V. Utochnikova, A. Vaschenko, L. Puntus, V. Baulin, N. Kuzmina, A. Tzivadze, *Inorg. Chem. Comm.* **2012**, 20, 73.

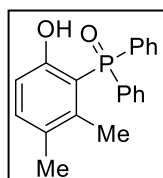
[5] S.-W. Zhang, L.-P. Lu, Y.-Y. Long, Y.-S. Li, *J. Polym. Sci. Pol. Chem.* **2013**, 51, 5298.

[6] D. Sascha, R. Carsten, F. Omrane, C. Francois, EP 2786434 A1, 2014.

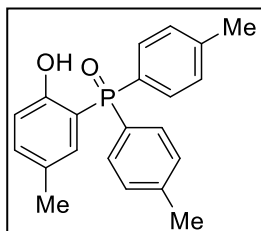
$J_{P-C} = 2.5$ Hz), 132.8 (d, $J_{P-C} = 2.4$ Hz), 132.0 (d, $J_{P-C} = 11.0$ Hz), 131.9 (d, $J_{P-C} = 9.0$ Hz), 130.9 (d, $J_{P-C} = 104.7$ Hz), 130.1 (d, $J_{P-C} = 13.6$ Hz), 128.8 (d, $J_{P-C} = 12.3$ Hz), 111.0 (d, $J_{P-C} = 100.8$ Hz), 87.2 (d, $J_{P-C} = 9.9$ Hz), 20.0. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.4$. HRMS (ESI-TOF): $m/z = 435.0015$, calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{P}$ [MH^+] 435.0011.



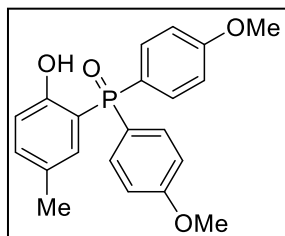
(2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha): white solid, mp. 210.7–212.2 °C, 37.3 mg (yield 58%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 10.88$ (s, 1H), 7.72–7.67 (m, 4H), 7.60–7.56 (m, 2H), 7.51–7.46 (m, 4H), 6.79 (d, $J = 4.8$ Hz, 1H), 6.69 (d, $J = 13.2$ Hz, 1H), 2.23 (s, 3H), 2.09 (s, 3H). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.4$. This is a known compound.^[7]



(6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha'): white solid, mp. 205.3–206.1 °C, 22.4 mg (yield 35%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 12.41$ (s, 1H), 7.78–7.73 (m, 4H), 7.61–7.57 (m, 2H), 7.53–7.49 (m, 4H), 7.25 (d, $J = 7.2$ Hz, 1H), 6.82 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 2.10 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 164.5$ (d, $J_{P-C} = 4.4$ Hz), 138.4 (d, $J_{P-C} = 8.8$ Hz), 136.5 (d, $J_{P-C} = 2.4$ Hz), 132.4 (d, $J_{P-C} = 2.7$ Hz), 132.3 (d, $J_{P-C} = 103.9$ Hz), 132.0 (d, $J_{P-C} = 11.2$ Hz), 128.8 (d, $J_{P-C} = 12.3$ Hz), 127.8 (d, $J_{P-C} = 10.2$ Hz), 116.8 (d, $J_{P-C} = 8.3$ Hz), 108.0 (d, $J_{P-C} = 101.4$ Hz), 20.6 (d, $J_{P-C} = 6.4$ Hz), 19.6 (d, $J_{P-C} = 1.9$ Hz). ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 44.0$. HRMS (ESI-TOF): $m/z = 323.1206$, calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{P}$ [MH^+] 323.1201

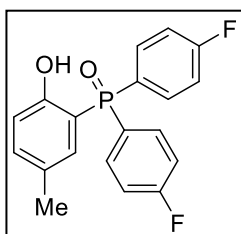


(2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab): white solid, mp. 190.0–190.8 °C, 54.3 mg (yield 81%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.03$ (s, 1H), 7.59–7.54 (m, 4H), 7.30–7.28 (m, 4H), 7.19 (d, $J = 8.4$ Hz, 1H), 6.87 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 6.73 (dd, $J_1 = 13.2$ Hz, $J_2 = 1.6$ Hz, 1H), 2.42 (s, 6H), 2.18 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.7$, 143.1, 135.1, 132.1 (d, $J_{P-C} = 10.7$ Hz), 131.5 (d, $J_{P-C} = 10.1$ Hz), 129.4 (d, $J_{P-C} = 12.8$ Hz), 128.8 (d, $J_{P-C} = 106.6$ Hz), 128.0 (d, $J_{P-C} = 14.5$ Hz), 118.4 (d, $J_{P-C} = 8.1$ Hz), 111.0 (d, $J_{P-C} = 103.1$ Hz), 21.7, 20.5. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.7$. HRMS (ESI-TOF): $m/z = 337.1356$, calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{P}$ [MH^+] 337.1357.

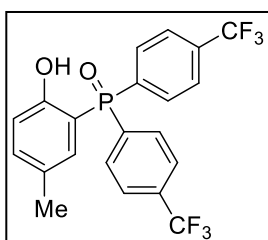


(2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl) phosphine oxide (3ac): white solid, mp. 181.1–181.8 °C, 62.0 mg (yield 84%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.05$ (s, 1H), 7.63–7.58 (m, 4H), 7.19 (d, $J = 8.0$ Hz, 1H), 7.00–6.97 (m, 4H), 6.87 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 6.72 (dd, $J_1 = 13.6$ Hz, $J_2 = 2.0$ Hz, 1H), 3.85 (s, 6H), 2.18 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 162.8$ (d, $J_{P-C} = 3.2$ Hz), 161.5 (d, $J_{P-C} = 3.4$ Hz), 135.1 (d, $J_{P-C} = 2.0$ Hz), 134.0 (d, $J_{P-C} = 11.8$ Hz), 131.6 (d, $J_{P-C} = 9.5$ Hz), 128.1 (d, $J_{P-C} = 12.7$ Hz), 123.1 (d, $J_{P-C} = 110.6$ Hz), 118.3 (d, $J_{P-C} = 8.0$ Hz), 114.2 (d, $J_{P-C} = 13.6$ Hz), 111.5 (d, $J_{P-C} = 103.9$ Hz), 55.4, 20.5. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.2$. HRMS (ESI-TOF): $m/z = 369.1266$, calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{P}$ [MH^+] 369.1256.

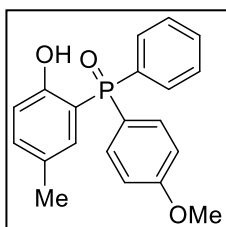
bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad): white solid, mp. 185.8–



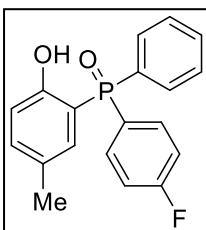
186.5 °C, 54.9 mg (yield 80%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.77 (s, 1H), 7.72–7.65 (m, 4H), 7.25–7.18 (m, 5H), 6.90 (dd, *J*₁ = 8.4 Hz, *J*₂ = 4.8 Hz, 1H), 6.68 (dd, *J*₁ = 13.6 Hz, *J*₂ = 1.6 Hz, 1H), 2.20 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 165.4 (dd, *J*_{F-C} = 252.9 Hz, *J*_{P-C} = 3.2 Hz), 161.7 (d, *J*_{P-C} = 2.8 Hz), 135.7 (d, *J*_{P-C} = 2.2 Hz), 134.5 (dd, *J*_{F-C} = 11.7 Hz, *J*_{P-C} = 9.0 Hz), 131.2 (d, *J*_{P-C} = 9.8 Hz), 128.5 (d, *J* = 12.4 Hz), 127.7 (dd, *J*_{P-C} = 108.0 Hz, *J*_{F-C} = 3.5 Hz), 118.7 (d, *J*_{P-C} = 8.8 Hz), 116.3 (dd, *J*_{F-C} = 21.6 Hz, *J*_{P-C} = 13.2 Hz), 110.2 (d, *J*_{P-C} = 105.5 Hz), 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 37.9. HRMS (ESI-TOF): *m/z* = 345.0856, calcd for C₁₉H₁₆O₂PF₂ [MH⁺] 345.0856.



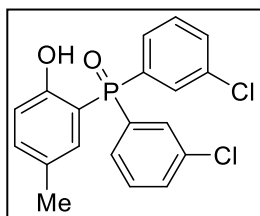
(2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae): 63.1 mg (yield 71%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.51 (s, 1H), 7.86–7.76 (m, 8H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J*₁ = 8.4 Hz, *J*₂ = 5.2 Hz, 1H), 6.75 (dd, *J*₁ = 13.6 Hz, *J*₂ = 1.2 Hz, 1H), 2.22 (s, 3H). *Due to the coupling of F-C and P-C, the ¹³C NMR spectra show complex peaks not easily interpreted. A full list of the ¹³C NMR data:* ¹³C NMR (CDCl₃, 100 MHz): δ = 161.80, 161.78, 136.31, 136.29, 136.1, 135.1, 134.76, 134.73, 134.44, 134.40, 134.11, 134.08, 132.5, 132.4, 131.1, 130.9, 128.98, 128.86, 127.4, 125.90, 125.86, 125.82, 125.79, 125.74, 125.70, 125.66, 124.7, 122.0, 119.3, 119.03, 118.95, 109.4, 108.3, 20.5. ³¹P NMR (CDCl₃, 162 MHz): δ = 36.7. HRMS (ESI-TOF): *m/z* = 445.0796, calcd for C₂₁H₁₆F₆O₂P [MH⁺] 445.0792.



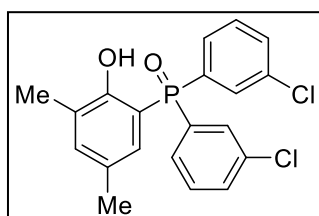
(2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl) phosphine oxide (3af): 66.9 mg (yield 94%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.03 (s, 1H), 7.72–7.67 (m, 2H), 7.63–7.56 (m, 3H), 7.51–7.47 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 2H), 6.88 (dd, *J*₁ = 8.4 Hz, *J*₂ = 4.8 Hz, 1H), 6.73 (dd, *J*₁ = 13.6 Hz, *J*₂ = 1.6 Hz, 1H), 3.86 (s, 3H), 2.18 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 162.9 (d, *J*_{P-C} = 3.2 Hz), 161.7 (d, *J*_{P-C} = 2.1 Hz), 135.2 (d, *J*_{P-C} = 2.3 Hz), 134.0 (d, *J*_{P-C} = 11.8 Hz), 132.4 (d, *J*_{P-C} = 3.2 Hz), 132.2 (d, *J* = 104.2 Hz), 132.0 (d, *J*_{P-C} = 10.0 Hz), 131.7 (d, *J*_{P-C} = 10.9 Hz), 128.7 (d, *J*_{P-C} = 11.6 Hz), 128.1 (d, *J*_{P-C} = 12.7 Hz), 122.9 (d, *J*_{P-C} = 111.0 Hz), 118.4 (d, *J*_{P-C} = 7.9 Hz), 114.3 (d, *J*_{P-C} = 12.8 Hz), 111.0 (d, *J*_{P-C} = 103.6 Hz), 55.4, 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 39.3. HRMS (ESI-TOF): *m/z* = 339.1155, calcd for C₂₀H₂₀O₃P [MH⁺] 339.1150.



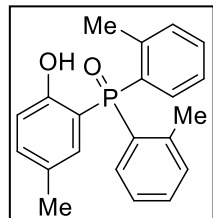
(4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl) phosphine oxide (3ag): 58.0 mg (yield 89%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.85 (s, 1H), 7.73–7.66 (m, 4H), 7.63–7.59 (m, 1H), 7.53–7.49 (m, 2H), 7.24–7.17 (m, 3H), 6.90 (dd, *J*₁ = 9.2 Hz, *J*₂ = 5.2 Hz, 1H), 6.71 (dd, *J*₁ = 13.6 Hz, *J*₂ = 1.6 Hz, 1H), 2.19 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 165.8 (dd, *J*_{F-C} = 253.1 Hz, *J*_{P-C} = 2.9 Hz), 161.7 (d, *J*_{P-C} = 2.7 Hz), 135.5 (d, *J*_{P-C} = 2.2 Hz), 134.6 (dd, *J*_{P-C} = 21.6 Hz, *J*_{F-C} = 9.1 Hz), 132.6 (d, *J*_{P-C} = 3.2 Hz), 131.9 (d, *J*_{P-C} = 9.8 Hz), 131.5 (d, *J* = 105.8 Hz), 131.3 (d, *J*_{P-C} = 9.8 Hz), 128.8 (d, *J*_{P-C} = 12.3 Hz), 128.3 (d, *J*_{P-C} = 12.4 Hz), 127.8 (d, *J*_{P-C} = 103.7 Hz), 118.6 (d, *J*_{P-C} = 8.3 Hz), 116.1 (dd, *J*_{F-C} = 21.6 Hz, *J*_{P-C} = 13.2 Hz), 111.2 (d, *J*_{P-C} = 104.8 Hz), 20.5. ³¹P NMR (CDCl₃, 162 MHz): δ = 38.7. HRMS (ESI-TOF): *m/z* = 327.0956, calcd for C₁₉H₁₇O₂PF [MH⁺] 327.0950.



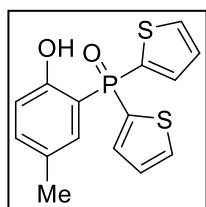
bis(3-chlorophenyl)(2-hydroxy-5-methylphenyl) phosphine oxide (3ah) : 58.0 mg (yield 77%). ^1H NMR (CDCl_3 , 400 MHz): δ = 10.62 (s, 1H), 7.68–7.64 (m, 2H), 7.60–7.52 (m, 4H), 7.49–7.44 (m, 2H), 7.26 (d, J = 4.8 Hz, 1H), 6.92 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 1H), 6.72 (d, J = 13.6 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 161.8 (d, $J_{\text{P-C}}$ = 2.5 Hz), 136.1 (d, $J_{\text{P-C}}$ = 2.2 Hz), 135.4 (d, $J_{\text{P-C}}$ = 16.4 Hz), 133.6 (d, $J_{\text{P-C}}$ = 103.0 Hz), 133.0 (d, J = 3.4 Hz), 131.7 (d, $J_{\text{P-C}}$ = 10.3 Hz), 131.1 (d, $J_{\text{P-C}}$ = 10.2 Hz), 130.3 (d, $J_{\text{P-C}}$ = 13.6 Hz), 130.0 (d, $J_{\text{P-C}}$ = 10.7 Hz), 128.7 (d, $J_{\text{P-C}}$ = 12.8 Hz), 118.9 (d, $J_{\text{P-C}}$ = 8.8 Hz), 109.1 (d, $J_{\text{P-C}}$ = 104.7 Hz), 20.6. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 37.2. HRMS (ESI-TOF): m/z = 377.0265, calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{PCl}_2$ [MH^+] 377.0265.



bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh): 54.8 mg (yield 70%). ^1H NMR (CDCl_3 , 400 MHz): δ = 10.76 (s, 1H), 7.68–7.64 (m, 2H), 7.58–7.51 (m, 4H), 7.47–7.43 (m, 2H), 7.14 (s, 1H), 6.55 (d, J = 13.2 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.1 (d, $J_{\text{P-C}}$ = 3.1 Hz), 137.0 (d, $J_{\text{P-C}}$ = 3.2 Hz), 135.4 (d, $J_{\text{P-C}}$ = 16.2 Hz), 133.9 (d, $J_{\text{P-C}}$ = 103.1 Hz), 132.9 (d, $J_{\text{P-C}}$ = 2.9 Hz), 131.7 (d, $J_{\text{P-C}}$ = 11.8 Hz), 130.3 (d, $J_{\text{P-C}}$ = 13.3 Hz), 130.0 (d, $J_{\text{P-C}}$ = 10.5 Hz), 128.5 (d, $J_{\text{P-C}}$ = 10.2 Hz), 128.1 (d, $J_{\text{P-C}}$ = 13.3 Hz), 127.9 (d, $J_{\text{P-C}}$ = 9.3 Hz), 108.1 (d, $J_{\text{P-C}}$ = 105.7 Hz), 20.6, 16.0 (d, $J_{\text{P-C}}$ = 1.4 Hz). ^{31}P NMR (CDCl_3 , 162 MHz): δ = 37.7. HRMS (ESI-TOF): m/z = 391.0426, calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{PCl}_2$ [MH^+] 391.0421.

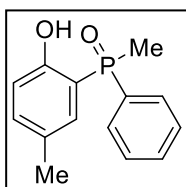


(2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ai): white solid, mp. 198.2–199.0 °C, 42.5 mg (yield 63%). ^1H NMR (CDCl_3 , 400 MHz): δ = 11.10 (s, 1H), 7.49–7.45 (m, 2H), 7.36–7.33 (m, 2H), 7.25–7.16 (m, 3H), 7.13–7.07 (m, 2H), 6.92 (dd, J_1 = 8.4 Hz, J_2 = 4.8 Hz, 1H), 6.43 (dd, J_1 = 13.6 Hz, J_2 = 1.6 Hz, 1H), 2.57 (s, 6H), 2.15 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 162.2 (d, $J_{\text{P-C}}$ = 2.8 Hz), 143.4 (d, $J_{\text{P-C}}$ = 8.4 Hz), 135.4 (d, $J_{\text{P-C}}$ = 2.3 Hz), 132.6 (d, $J_{\text{P-C}}$ = 8.5 Hz), 132.5 (d, $J_{\text{P-C}}$ = 2.7 Hz), 132.3 (d, $J_{\text{P-C}}$ = 10.6 Hz), 131.7 (d, $J_{\text{P-C}}$ = 9.8 Hz), 129.8 (d, $J_{\text{P-C}}$ = 102.7 Hz), 128.0 (d, $J_{\text{P-C}}$ = 12.6 Hz), 125.6 (d, $J_{\text{P-C}}$ = 13.2 Hz), 118.5 (d, $J_{\text{P-C}}$ = 7.8 Hz), 110.3 (d, $J_{\text{P-C}}$ = 101.8 Hz), 21.7 (d, $J_{\text{P-C}}$ = 4.8 Hz), 20.6. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 46.6. HRMS (ESI-TOF): m/z = 337.1356, calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{P}$ [MH^+] 337.1357.



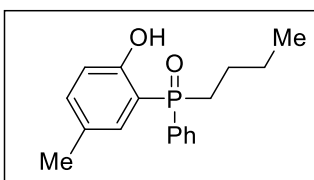
(2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj): white solid, mp. 188.4–189.8 °C, 41.6 mg (yield 65%). ^1H NMR (CDCl_3 , 400 MHz): δ = 10.76 (s, 1H), 7.79 (t, J = 4.2 Hz, 2H), 7.61–7.58 (m, 2H), 7.24–7.20 (m, 3H), 6.95–6.88 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.9 (d, $J_{\text{P-C}}$ = 3.5 Hz), 137.4 (d, $J_{\text{P-C}}$ = 11.3 Hz), 135.8 (d, $J_{\text{P-C}}$ = 2.0 Hz), 134.8 (d, $J_{\text{P-C}}$ = 6.2 Hz), 133.5 (d, $J_{\text{P-C}}$ = 120.3 Hz), 131.1 (d, $J_{\text{P-C}}$ = 10.5 Hz), 128.4 (d, $J_{\text{P-C}}$ = 14.2 Hz), 128.3 (d, $J_{\text{P-C}}$ = 13.1 Hz), 118.3 (d, $J_{\text{P-C}}$ = 8.2 Hz), 111.4 (d, $J_{\text{P-C}}$ = 115.5 Hz), 20.4. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 23.7. HRMS (ESI-TOF): m/z = 321.0172, calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}_2\text{P}$ [MH^+] 321.0173.

(2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak): 40.8 mg (yield 83%). ^1H NMR



(CDCl₃, 400 MHz): δ = 10.92 (s, 1H), 7.79–7.74 (m, 2H), 7.58–7.48 (m, 3H), 7.19 (d, J = 8.0 Hz, 1H), 6.87–6.81 (m, 2H), 2.22 (s, 3H), 2.09 (d, J = 13.2 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 161.1 (d, J_{P-C} = 2.8 Hz), 135.2 (d, J_{P-C} = 2.2 Hz), 133.7 (d, J_{P-C} = 102.0 Hz), 132.3 (d, J_{P-C} = 3.0 Hz), 131.1 (d, J_{P-C} = 10.1 Hz), 130.0 (d, J_{P-C} = 9.8 Hz), 128.5 (d, J_{P-C} = 11.7 Hz), 118.4 (d, J_{P-C} = 7.8 Hz), 112.2 (d, J_{P-C} = 101.3 Hz), 20.5, 17.0 (d, J_{P-C} = 73.0 Hz). ³¹P NMR (CDCl₃, 162 MHz): δ = 42.4.

HRMS (ESI-TOF): m/z = 247.0885, calcd for C₁₄H₁₆O₂P [MH⁺] 247.0888.

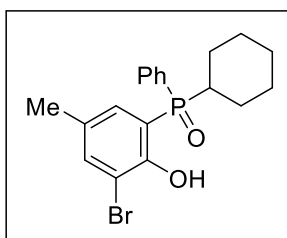


butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3al):

49.5 mg (yield 86%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.06 (s, 1H), 7.81–7.76 (m, 2H), 7.56–7.49 (m, 3H), 7.17 (d, J = 8.4 Hz, 1H), 6.86–6.81 (m, 2H), 2.33–2.25 (m, 2H), 2.23 (s, 3H), 1.74–1.56 (m, 2H), 1.50–1.41 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, 100

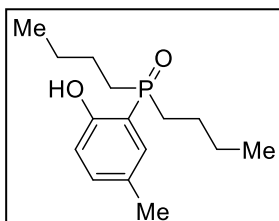
MHz): δ = 161.5, 135.0 (d, J_{P-C} = 2.3 Hz), 132.9 (d, J_{P-C} = 97.9 Hz), 132.1 (d, J_{P-C} = 3.1 Hz), 130.3 (d, J_{P-C} = 9.5 Hz), 129.8 (d, J_{P-C} = 10.4 Hz), 128.7 (d, J_{P-C} = 11.6 Hz), 128.3 (d, J_{P-C} = 11.2 Hz), 118.2 (d, J_{P-C} = 8.3 Hz), 111.2 (d, J_{P-C} = 97.4 Hz), 29.7 (d, J_{P-C} = 71.0 Hz), 23.9 (d, J_{P-C} = 14.5 Hz), 23.0 (d, J_{P-C} = 3.7 Hz), 20.5, 13.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 44.9. HRMS (ESI-TOF): m/z = 289.1361, calcd for C₁₇H₂₂O₂P [MH⁺] 289.1357.

(3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm):



63.2 mg (yield 80%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.98 (s, 1H), 7.84–7.79 (m, 2H), 7.56–7.49 (m, 3H), 7.44 (d, J = 2.0 Hz, 1H), 6.87 (dd, J_1 = 12.0 Hz, J_2 = 1.6 Hz, 1H), 2.32–2.25 (m, 1H), 2.23 (s, 3H), 1.84–1.64 (m, 6H), 1.35–1.23 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ = 157.8 (d, J_{P-C} = 3.2 Hz), 137.8 (d, J_{P-C} = 2.0 Hz), 132.2 (d, J_{P-C} = 2.8 Hz), 130.7 (d, J_{P-C} = 8.6 Hz), 130.5 (d, J_{P-C} = 94.7 Hz), 129.5 (d, J_{P-C} = 13.2 Hz), 128.95 (d, J_{P-C} = 9.4

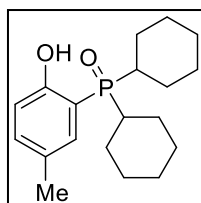
Hz), 128.89 (d, J_{P-C} = 11.4 Hz), 112.1 (d, J_{P-C} = 91.2 Hz), 111.9 (d, J_{P-C} = 10.0 Hz), 37.1 (d, J_{P-C} = 72.6 Hz), 26.1 (d, J_{P-C} = 4.2 Hz), 26.0 (d, J_{P-C} = 5.2 Hz), 25.5 (d, J_{P-C} = 1.4 Hz), 24.2 (d, J_{P-C} = 3.1 Hz), 23.7 (d, J_{P-C} = 3.1 Hz), 20.2. ³¹P NMR (CDCl₃, 162 MHz): δ = 47.4. HRMS (ESI-TOF): m/z = 393.0612, calcd for C₁₉H₂₃O₂PBr [MH⁺] 393.0619.



dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an):

33.6 mg (yield 63%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.08 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.82 (dd, J_1 = 8.8 Hz, J_2 = 4.4 Hz, 1H), 6.75 (dd, J_1 = 12.4 Hz, J_2 = 1.6 Hz, 1H), 2.27 (s, 3H), 2.01–1.84 (m, 4H), 1.72–1.63 (m, 4H), 1.43–1.38 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 162.0 (d, J_{P-C} = 2.0 Hz), 134.9 (d, J_{P-C} = 2.1 Hz), 128.7 (d, J_{P-C} = 10.0

Hz), 128.3 (d, J_{P-C} = 11.8 Hz), 118.1 (d, J_{P-C} = 7.2 Hz), 110.5 (d, J_{P-C} = 92.0 Hz), 30.3 (d, J_{P-C} = 67.4 Hz), 23.9 (d, J_{P-C} = 14.9 Hz), 23.1 (d, J_{P-C} = 4.1 Hz), 20.5, 13.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 56.0. HRMS (ESI-TOF): m/z = 269.1671, calcd for C₁₅H₂₆O₂P [MH⁺] 269.1670.

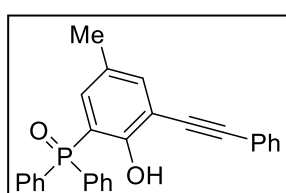


dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao):

38.2 mg (yield 60%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.33 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.81 (dd, J_1 = 8.4 Hz, J_2 = 4.0 Hz, 1H), 6.73 (dd, J_1 = 10.8 Hz, J_2 = 1.2 Hz, 1H), 2.28 (s, 3H), 2.06–2.01 (m, 4H), 1.87–1.69 (m, 8H), 1.42–1.20 (m, 10H). ¹³C NMR

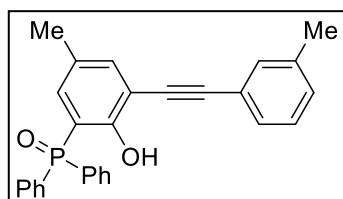
(CDCl₃, 100 MHz): δ = 163.1, 134.7 (d, J_{P-C} = 1.9 Hz), 129.2 (d, J_{P-C} = 10.0 Hz), 127.6 (d, J_{P-C} = 10.9 Hz), 118.1 (d, J_{P-C} = 7.2 Hz), 107.9 (d, J_{P-C} = 85.9 Hz), 35.7 (d, J_{P-C} = 65.6 Hz), 26.3 (d, J_{P-C} = 14.9 Hz), 26.1 (d, J_{P-C} = 11.8 Hz), 25.7, 25.2 (d, J_{P-C} = 2.9 Hz), 24.0 (d, J_{P-C} = 3.1 Hz), 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 60.5. HRMS (ESI-TOF): m/z = 321.1986, calcd for C₁₉H₃₀O₂P [MH⁺] 321.1983.

General procedure for the Zn(OTf)₂-catalyzed preparation of 2-phosphinyl phenols 6: An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with Zn(OTf)₂ (7.2 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N₂ (3 cycles). Then **5** (0.2 mmol) and **2** (0.6 mmol) dissolved in 2 mL of toluene was injected. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C. After the reaction was complete (monitored by TLC), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate 10/1 to 4/1) to afford the product **6**.



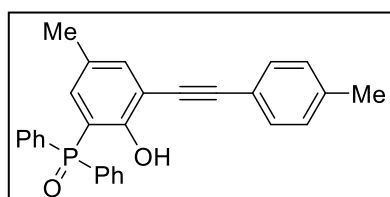
(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a):

white solid, mp 201.5–202.4 °C, 69.7 mg (yield 84%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.47 (s, 1H), 7.73–7.68 (m, 4H), 7.61–7.55 (m, 4H), 7.52–7.48 (m, 4H), 7.45 (s, 1H), 7.34–7.32 (m, 3H), 6.78 (d, J = 12.0 Hz, 1H), 2.19 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 161.9 (d, J_{P-C} = 2.8 Hz), 138.2 (d, J_{P-C} = 2.5 Hz), 132.6 (d, J_{P-C} = 3.1 Hz), 132.0 (d, J_{P-C} = 10.1 Hz), 131.9 (d, J_{P-C} = 9.6 Hz), 131.7, 130.9, 128.7 (d, J_{P-C} = 12.4 Hz), 128.23, 128.21, 128.1 (d, J_{P-C} = 12.6 Hz), 123.2, 113.2 (d, J_{P-C} = 9.5 Hz), 111.3 (d, J_{P-C} = 103.1 Hz), 94.4, 84.6 (d, J_{P-C} = 2.5 Hz), 20.3. ³¹P NMR (CDCl₃, 162 MHz): δ = 39.1. HRMS (ESI-TOF): m/z = 409.1350, calcd for C₂₇H₂₂O₂P [MH⁺] 409.1357. The structure of this compound was further confirmed by an X-ray crystallographic analysis.



(2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b):

59.2 mg (yield 70%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.43 (s, 1H), 7.73–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.47 (m, 4H), 7.44–7.35 (m, 3H), 7.21 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.78 (dd, J_1 = 13.6 Hz, J_2 = 1.6 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 161.8 (d, J_{P-C} = 3.7 Hz), 138.2 (d, J_{P-C} = 2.5 Hz), 137.8, 132.6 (d, J_{P-C} = 3.4 Hz), 132.2, 132.0 (d, J_{P-C} = 9.9 Hz), 131.3 (d, J_{P-C} = 96.5 Hz), 129.1, 128.68, 128.66 (d, J_{P-C} = 12.4 Hz), 128.1, 128.0, 123.0, 113.3 (d, J_{P-C} = 9.4 Hz), 111.3 (d, J_{P-C} = 102.2 Hz), 94.6, 84.2 (d, J_{P-C} = 2.7 Hz), 21.1, 20.3. ³¹P NMR (CDCl₃, 162 MHz): δ = 39.0. HRMS (ESI-TOF): m/z = 423.1516, calcd for C₂₈H₂₄O₂P [MH⁺] 423.1514.

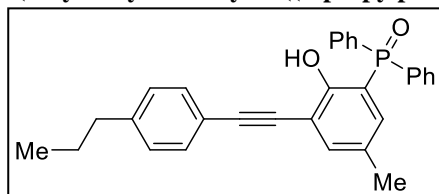


(2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c):

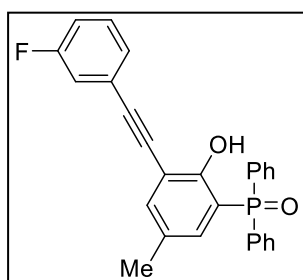
white solid, mp 181.4–182.8 °C, 57.0 mg (yield 68%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.40 (s, 1H), 7.73–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.44 (m, 7H), 7.13 (d, J = 8.0 Hz, 2H), 6.77 (dd, J_1 = 13.6 Hz, J_2 = 1.6 Hz, 1H), 2.34 (s, 3H), 2.18 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 161.8 (d, J_{P-C} = 2.9 Hz), 138.4, 138.2 (d, J_{P-C} = 3.0 Hz), 132.6 (d, J_{P-C} = 3.5 Hz), 132.0 (d, J_{P-C} = 10.6 Hz), 131.8 (d, J_{P-C} = 9.4 Hz), 131.5, 130.9, 129.0, 128.7 (d, J_{P-C} = 12.4 Hz), 128.0 (d, J_{P-C} = 12.4 Hz), 120.1, 113.4 (d, J_{P-C} = 9.5 Hz), 111.3 (d, J_{P-C} = 102.5 Hz), 94.6, 83.9 (d, J_{P-C} = 1.8 Hz), 21.5, 20.3. ³¹P NMR (CDCl₃, 162 MHz): δ = 39.0. HRMS

(ESI-TOF): $m/z = 423.1514$, calcd for $C_{28}H_{24}O_2P$ [MH^+] 423.1514.

(2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl) diphenylphosphine oxide (6d): white



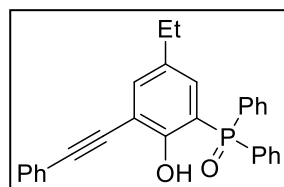
solid, mp 154.6–155.5 °C, 58.6 mg (yield 65%). 1H NMR ($CDCl_3$, 400 MHz): $\delta = 11.37$ (s, 1H), 7.73–7.68 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.44 (m, 7H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.77 (dd, $J_1 = 13.2$ Hz, $J_2 = 1.2$ Hz, 1H), 2.58 (t, $J = 7.4$ Hz, 2H), 2.19 (s, 3H), 1.68–1.58 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 161.7$ (d, $J_{P-C} = 3.2$ Hz), 143.1, 138.2 (d, $J_{P-C} = 1.9$ Hz), 132.5 (d, $J_{P-C} = 2.3$ Hz), 132.0 (d, $J_{P-C} = 9.7$ Hz), 131.8 (d, $J_{P-C} = 9.6$ Hz), 131.7, 131.3 (d, $J_{P-C} = 95.7$ Hz), 128.7 (d, $J_{P-C} = 12.4$ Hz), 128.4, 128.0 (d, $J_{P-C} = 12.5$ Hz), 120.3, 113.4 (d, $J_{P-C} = 9.5$ Hz), 111.2 (d, $J_{P-C} = 101.6$ Hz), 94.7, 83.9 (d, $J_{P-C} = 1.8$ Hz), 37.9, 24.3, 20.3, 13.7. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 38.9$. HRMS (ESI-TOF): $m/z = 451.1826$, calcd for $C_{30}H_{28}O_2P$ [MH^+] 451.1827.



(3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenyl phosphine oxide (6e): 64.5 mg (yield 76%). 1H NMR ($CDCl_3$, 400

MHz): $\delta = 11.58$ (s, 1H), 7.73–7.68 (m, 4H), 7.62–7.58 (m, 2H), 7.53–7.48 (m, 4H), 7.44 (s, 1H), 7.35–7.24 (m, 3H), 7.04–6.99 (m, 1H), 6.79 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.20 (s, 3H). *Due to the coupling of F-C and P-C, the ^{13}C NMR spectra show complex peaks not easily interpreted.* Typical signals belong to the alkyne unit: $\delta = 92.98$ (d, J_{F-C}

$= 2.7$ Hz), 85.66 (d, $J_{P-C} = 2.4$ Hz). Signals belong to the methyl group: $\delta = 20.3$. A full list of the ^{13}C NMR data: ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 163.5$, 162.2, 162.1, 161.1, 138.33, 138.31, 132.67, 132.65, 132.3, 132.2, 132.1, 132.0, 131.9, 130.8, 129.8, 129.7, 128.8, 128.7, 128.2, 128.0, 127.60, 127.58, 125.1, 125.0, 118.5, 118.3, 115.7, 115.4, 112.9, 112.8, 111.9, 110.8, 92.99, 92.96, 85.67, 85.65, 20.3. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 39.3$. HRMS (ESI-TOF): $m/z = 427.1261$, calcd for $C_{27}H_{21}O_2PF$ [MH^+] 427.1263.

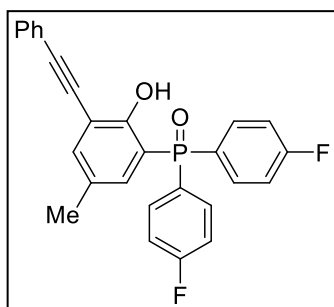


(5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide

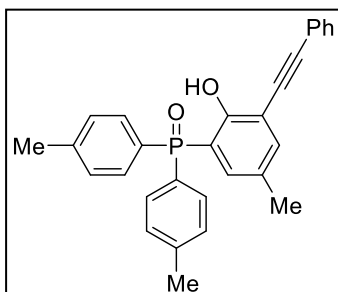
(6f): white solid, mp 238.0–239.0 °C, 53.6 mg (yield 63%). 1H NMR ($CDCl_3$, 400 MHz): $\delta = 11.43$ (s, 1H), 7.73–7.68 (m, 4H), 7.61–7.48 (m, 9H), 7.34–7.31 (m, 3H), 6.81 (dd, $J_1 = 13.2$ Hz, $J_2 = 2.0$ Hz, 1H), 2.49 (q, $J = 7.6$ Hz, 2H), 1.13 (t, $J = 7.6$, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$

162.0 (d, $J_{P-C} = 3.0$ Hz), 137.0 (d, $J_{P-C} = 3.1$ Hz), 134.5 (d, $J_{P-C} = 12.2$ Hz), 132.6 (d, $J_{P-C} = 2.8$ Hz), 131.9 (d, $J_{P-C} = 11.0$ Hz), 131.6, 131.3 (d, $J_{P-C} = 104.6$ Hz), 131.0 (d, $J_{P-C} = 10.2$ Hz), 128.7 (d, $J_{P-C} = 12.4$ Hz), 128.23, 128.19, 123.12, 113.2 (d, $J_{P-C} = 9.5$ Hz), 111.3 (d, $J_{P-C} = 102.1$ Hz), 94.3, 84.7 (d, $J_{P-C} = 2.4$ Hz), 27.6, 15.5. ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 39.1$. HRMS (ESI-TOF): $m/z = 423.1516$, calcd for $C_{28}H_{24}O_2P$ [MH^+] 423.1514.

bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g): white solid, mp 199.3–200.5 °C, 61.8 mg (yield 70%). 1H NMR ($CDCl_3$, 400 MHz): $\delta = 11.07$ (s, 1H), 7.73–7.67 (m, 4H), 7.56–7.54 (m, 2H), 7.47 (s, 1H), 7.34–7.32 (m, 3H), 7.23–7.18 (m, 4H), 6.77 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.21 (s, 3H). *Due to the coupling of F-C and P-C, the ^{13}C NMR spectra show complex peaks not easily interpreted.* Typical signals belong to the alkyne unit: $\delta = 94.75$, 84.27



(d, $J_{P-C} = 3.0$ Hz). Signals belong to the methyl group: $\delta = 20.3$. A full list of the ^{13}C NMR data: ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 166.70, 166.68, 161.49, 161.45, 138.46, 138.43, 134.65, 134.56, 134.53, 134.44, 131.79, 131.70, 131.65, 128.47, 128.36, 128.23, 127.81, 127.79, 126.73, 126.70, 123.00, 116.42, 116.28, 116.21, 116.07, 113.45, 113.36, 111.74, 110.70, 94.7, 84.28, 84.25, 20.3$. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 36.9$. HRMS (ESI-TOF): $m/z = 445.1171$, calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2\text{PF}_2$ [MH^+] 445.1169.

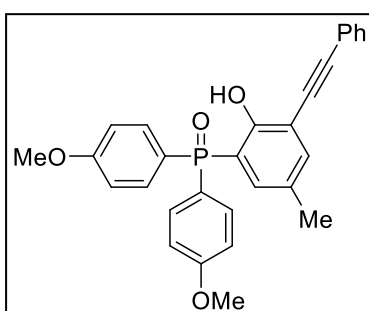


(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine

oxide (6h): white solid, mp 211.1–212.3 °C, 69.8 mg (yield 80%).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.65$ (s, 1H), 7.60–7.54 (m, 6H), 7.42 (d, $J = 2.0$ Hz, 1H), 7.33–7.25 (m, 7H), 6.76 (dd, $J_1 = 13.2$ Hz, $J_2 = 1.6$ Hz, 1H), 2.41 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.9$ (d, $J_{P-C} = 2.7$ Hz), 143.1 (d, $J_{P-C} = 2.5$ Hz), 138.0 (d, $J_{P-C} = 2.7$ Hz), 132.0 (d, $J_{P-C} = 10.6$ Hz), 131.9 (d, $J_{P-C} = 9.5$ Hz), 131.6, 129.4 (d, $J_{P-C} = 13.8$ Hz), 128.3 (d, $J_{P-C} = 107.2$ Hz), 128.1,

127.8 (d, $J_{P-C} = 12.6$ Hz), 123.2, 113.0 (d, $J_{P-C} = 9.4$ Hz), 111.8 (d, $J_{P-C} = 102.7$ Hz), 94.2, 84.8 (d, $J_{P-C} = 2.5$ Hz), 21.6, 20.3. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.4$. HRMS (ESI-TOF): $m/z = 437.1675$, calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2\text{P}$ [MH^+] 437.1670.

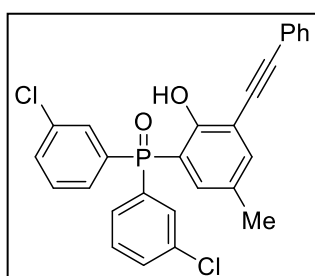


(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine

oxide (6i): 47.9 mg (yield 51%).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 11.69$ (s, 1H), 7.64–7.54 (m, 6H), 7.42 (d, $J = 1.6$ Hz, 1H), 7.35–7.31 (m, 3H), 7.00–6.97 (m, 4H), 6.74 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 3.85 (s, 6H), 2.18 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 162.9$ (d, $J_{P-C} = 3.1$ Hz), 161.9 (d, $J_{P-C} = 2.7$ Hz), 137.9 (d, $J_{P-C} = 1.8$ Hz), 133.9 (d, $J_{P-C} = 11.6$ Hz), 132.0

(d, $J_{P-C} = 9.6$ Hz), 131.6, 128.2, 127.8 (d, $J_{P-C} = 12.5$ Hz), 122.2, 114.2 (d, $J_{P-C} = 12.8$ Hz), 113.0 (d, $J_{P-C} = 9.6$ Hz), 112.2 (d, $J_{P-C} = 103.0$ Hz), 94.1, 84.9 (d, $J_{P-C} = 2.9$ Hz), 55.3, 20.3. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 39.0$. HRMS (ESI-TOF): $m/z = 469.1566$, calcd for $\text{C}_{29}\text{H}_{26}\text{O}_4\text{P}$ [MH^+] 469.1569.

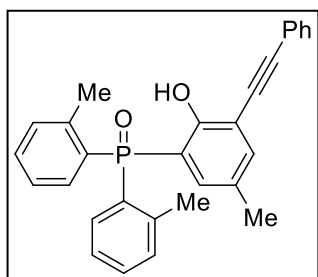


bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)

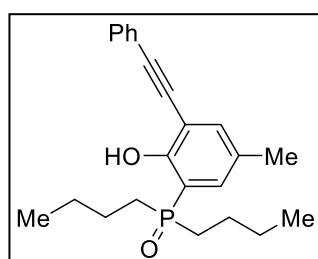
phosphine oxide (6j): 63.5 mg (yield 67%).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 10.68$ (s, 1H), 7.70–7.66 (m, 2H), 7.59–7.54 (m, 6H), 7.49–7.43 (m, 3H), 7.34–7.32 (m, 3H), 6.84 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.1$ (d, $J_{P-C} = 4.2$ Hz), 138.7 (d, $J_{P-C} = 2.8$ Hz), 135.3 (d, $J_{P-C} = 16.4$ Hz), 133.2 (d, $J_{P-C} = 103.8$ Hz), 133.0 (d, $J_{P-C} = 1.9$ Hz), 131.8 (d, $J_{P-C} = 9.7$ Hz), 131.62,

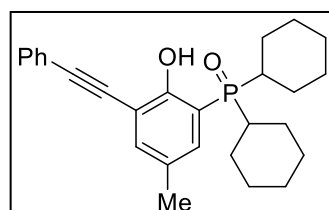
131.60 (d, $J_{P-C} = 11.0$ Hz), 131.6, 130.2 (d, $J_{P-C} = 13.2$ Hz), 129.9 (d, $J_{P-C} = 10.5$ Hz), 128.7 (d, $J_{P-C} = 13.3$ Hz), 128.4, 128.2, 122.8, 113.4 (d, $J_{P-C} = 9.7$ Hz), 110.5 (d, $J_{P-C} = 104.2$ Hz), 95.0, 84.0 (d, $J_{P-C} = 2.7$ Hz), 20.3. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta = 35.7$. HRMS (ESI-TOF): $m/z = 477.0571$, calcd for $\text{C}_{27}\text{H}_{20}\text{Cl}_2\text{O}_2\text{P}$ [MH^+] 477.0578.



(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k): 21.0 mg (yield 24%). ^1H NMR (CDCl_3 , 400 MHz): δ = 8.32–8.27 (m, 2H), 7.43–7.31 (m, 9H), 7.28–7.23 (m, 2H), 7.15 (t, J = 6.4 Hz, 2H), 6.94 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 2.39 (s, 6H), 2.24 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 149.7 (d, $J_{\text{P-C}}$ = 8.0 Hz), 141.8 (d, $J_{\text{P-C}}$ = 11.1 Hz), 133.9 (d, $J_{\text{P-C}}$ = 10.0 Hz), 133.5, 133.3, 132.5 (d, $J_{\text{P-C}}$ = 2.8 Hz), 131.5 (d, $J_{\text{P-C}}$ = 13.2 Hz), 130.2, 129.7 (d, $J_{\text{P-C}}$ = 132.7 Hz), 128.3, 125.6 (d, $J_{\text{P-C}}$ = 12.9 Hz), 123.2, 119.2 (d, $J_{\text{P-C}}$ = 5.1 Hz), 114.8 (d, $J_{\text{P-C}}$ = 6.8 Hz), 93.6, 85.6, 21.2 (d, $J_{\text{P-C}}$ = 4.3 Hz), 20.4. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 30.0. HRMS (ESI-TOF): m/z = 437.1676, calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2\text{P}$ [MH^+] 437.1670.

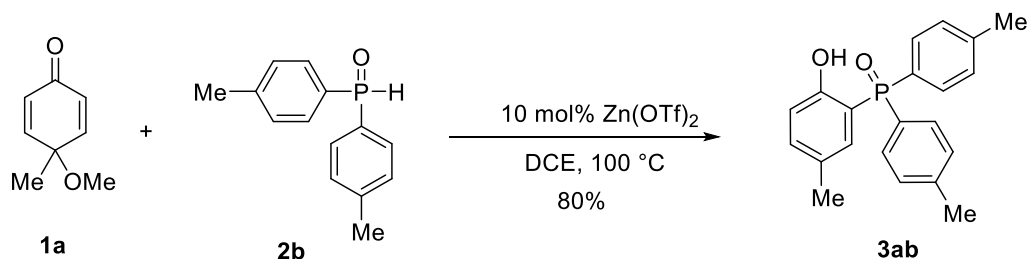


dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl) phosphine oxide (6l): 53.8 mg (yield 73%). ^1H NMR (CDCl_3 , 400 MHz): δ = 11.33 (s, 1H), 7.58–7.55 (m, 2H), 7.43 (s, 1H), 7.34–7.32 (m, 3H), 6.83 (dd, J_1 = 12.4 Hz, J_2 = 1.6 Hz, 1H), 2.28 (s, 3H), 2.04–1.85 (m, 4H), 1.73–1.63 (m, 2H), 1.52–1.36 (m, 6H), 0.89 (t, J = 7.2 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 161.7 (d, $J_{\text{P-C}}$ = 2.4 Hz), 137.8 (d, $J_{\text{P-C}}$ = 2.7 Hz), 131.7, 129.7 (d, $J_{\text{P-C}}$ = 9.8 Hz), 128.31, 128.27, 128.22, 123.1, 112.6 (d, $J_{\text{P-C}}$ = 8.5 Hz), 111.4 (d, $J_{\text{P-C}}$ = 90.5 Hz), 94.4, 84.6 (d, $J_{\text{P-C}}$ = 1.2 Hz), 30.1 (d, $J_{\text{P-C}}$ = 67.9 Hz), 23.9 (d, $J_{\text{P-C}}$ = 13.8 Hz), 23.1 (d, $J_{\text{P-C}}$ = 4.3 Hz), 20.3, 13.6. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 55.3. HRMS (ESI-TOF): m/z = 369.1987, calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{P}$ [MH^+] 369.1983.



dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl) phosphine oxide (6m): 48.1 mg (yield 57%). ^1H NMR (CDCl_3 , 400 MHz): δ = 12.03 (s, 1H), 7.57–7.55 (m, 2H), 7.43 (s, 1H), 7.34–7.31 (m, 3H), 6.74 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 2.29 (s, 3H), 2.07–2.02 (m, 4H), 1.87–1.69 (m, 8H), 1.43–1.20 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 163.4, 137.8 (d, $J_{\text{P-C}}$ = 2.2 Hz), 131.7, 129.6 (d, $J_{\text{P-C}}$ = 8.8 Hz), 128.14, 128.12, 127.4 (d, $J_{\text{P-C}}$ = 10.5 Hz), 123.3, 112.9 (d, $J_{\text{P-C}}$ = 9.0 Hz), 108.4 (d, $J_{\text{P-C}}$ = 84.0 Hz), 94.1, 85.0 (d, $J_{\text{P-C}}$ = 2.2 Hz), 35.6 (d, $J_{\text{P-C}}$ = 65.8 Hz), 26.16 (d, $J_{\text{P-C}}$ = 3.3 Hz), 26.15 (d, $J_{\text{P-C}}$ = 28.3 Hz), 25.6, 25.1 (d, $J_{\text{P-C}}$ = 2.9 Hz), 24.0 (d, $J_{\text{P-C}}$ = 3.4 Hz), 20.3. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 60.9. HRMS (ESI-TOF): m/z = 421.2291, calcd for $\text{C}_{27}\text{H}_{34}\text{O}_2\text{P}$ [MH^+] 421.2296.

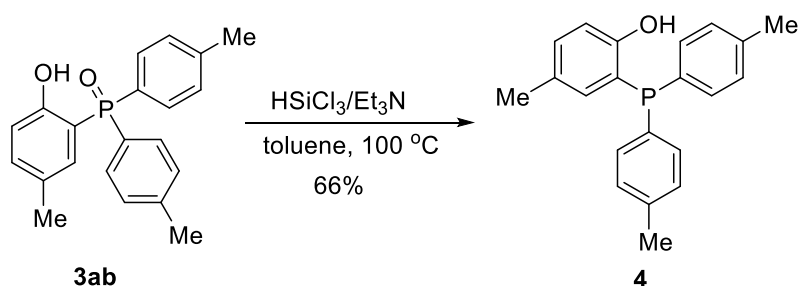
3. Experimental procedure for gram-scale synthesis of 3ab



An oven-dried 50 mL Schlenk tube containing a Teflon-coated stir bar was charged with $\text{Zn}(\text{OTf})_2$ (26.3 mg, 10 mol %) and di-p-tolylphosphine oxide **2b** (5.002 g, 21.75 mmol). The Schlenk tube was

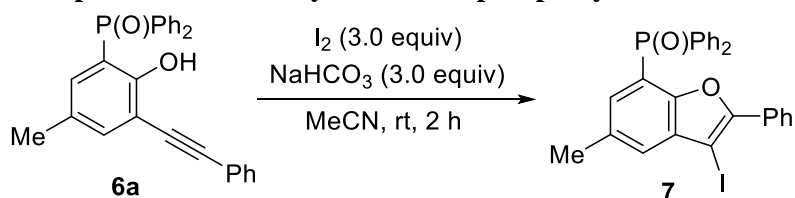
sealed and then evacuated and backfilled with N₂ (3 cycles). 15 mL DCE was injected. Then **1a** (1.000 g, 7.25 mmol) was introduced with 5 mL of DCE. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C for 6 h. The reaction mixture was cooled to room temperature, and EtOAc (20 mL) and water (20 mL) were added. The organic layer was separated, and the aqueous phase was extracted with EtOAc (20 mL ×3). The combined organic layers were washed with brine and dried over anhydrous MgSO₄. The solvent was removed under vacuum, and the product **3ab** (1.960 g, 80%) was obtained after purification by flash chromatography on silica (petroleum ether/ethyl acetate 3/1).

4. Experimental procedure for the synthesis of 2-phosphanilphenol **4**



To a solution of **3ab** (1.233 g, 4.0 mmol) and triethylamine (2.8 mL, 20 mmol) in toluene (20 mL) was added trichlorosilane (1.9 mL, 20 mmol) dropwise at 0 °C. The mixture was then stirred at 100 °C for 48 h. After the mixture was cooled to 0 °C, 1 N NaOH (aq) (20 mL) was slowly added, and the mixture was warmed to room temperature, and then stirred at 60 °C for 30 min. The mixture was cooled to room temperature, and filtered through a pad of celite eluted with ethyl acetate. The organic layer was separated, dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate 30/1–10/1) to give **4** (0.846 g, 66%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.25–7.15 (m, 8H), 7.08 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 1H), 6.82–6.79 (m, 2H), 5.99 (s, 1H), 2.35 (s, 6H), 2.17 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.9 (d, *J*_{P-C} = 16.8 Hz), 139.0, 134.7 (d, *J*_{P-C} = 5.9 Hz), 133.4 (d, *J*_{P-C} = 19.2 Hz), 132.2, 131.6 (d, *J*_{P-C} = 3.8 Hz), 130.1 (d, *J*_{P-C} = 2.4 Hz), 129.5 (d, *J*_{P-C} = 7.2 Hz), 120.9 (d, *J*_{P-C} = 6.0 Hz), 115.4 (d, *J*_{P-C} = 1.6 Hz), 21.4, 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = -29.6. HRMS (ESI-TOF): *m/z* = 321.1416, calcd for C₂₁H₂₂OP [MH⁺] 321.1408.

5. Experimental procedure for the synthesis of 7-phosphenylbenzofuran **7**



An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with **6a** (81.7mg, 0.2 mmol) NaHCO₃ (50.4, 0.6 mmol) and MeCN (2 mL). After stirring at rt for 30 min, I₂ (151.8 mg, 0.6 mmol) was added. After the reaction was complete (monitored by TLC, 2 h), the reaction was quenched with aq. Na₂S₂O₃. The mixture was extracted with EtOAc. The combined organic layers were dried over MgSO₄, filtered and concentrated. The residue was purified with silica gel column chromatography (PE/EtOAc 3/1 to 1/1) to afford compound **7** (93.6 mg, 88%). White solid, mp. 240.4–

241.0 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.87–7.77 (m, 5H), 7.68–7.64 (m, 2H), 7.58–7.53 (m, 2H), 7.48–7.44 (m, 5H), 7.37–7.33 (m, 3H), 2.53 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 153.5, 151.5 (d, J_{P-C} = 3.0 Hz), 133.4 (d, J_{P-C} = 100.1 Hz), 133.8, 133.0, 132.0 (d, J_{P-C} = 3.3 Hz), 131.9 (d, J_{P-C} = 10.2 Hz), 131.6 (d, J_{P-C} = 4.6 Hz), 129.3, 128.6, 128.4 (d, J_{P-C} = 7.3 Hz), 127.2, 126.3 (d, J_{P-C} = 2.3 Hz), 115.6 (d, J_{P-C} = 101.4 Hz), 60.6, 21.2. ^{31}P NMR (CDCl_3 , 162 MHz): δ = 23.3; HRMS (ESI-TOF): m/z = 535.0327, calcd for $\text{C}_{27}\text{H}_{21}\text{O}_2\text{PI}$ [MH^+] 535.0324.

6. 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_α (λ = 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. CCDC 1874221 and CCDC 1874220 contains the crystallographic data of compounds **3ao** and **6a** for this article. ORTEP representations (30% probability level) of the molecular structures are presented in Table S1. Crystallographic data 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 **3an** and **6a**

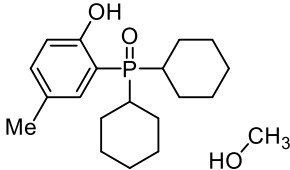
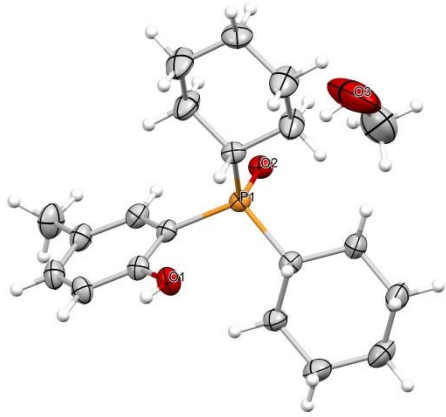
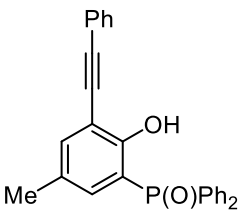
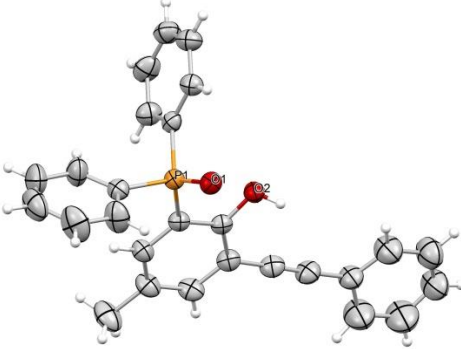
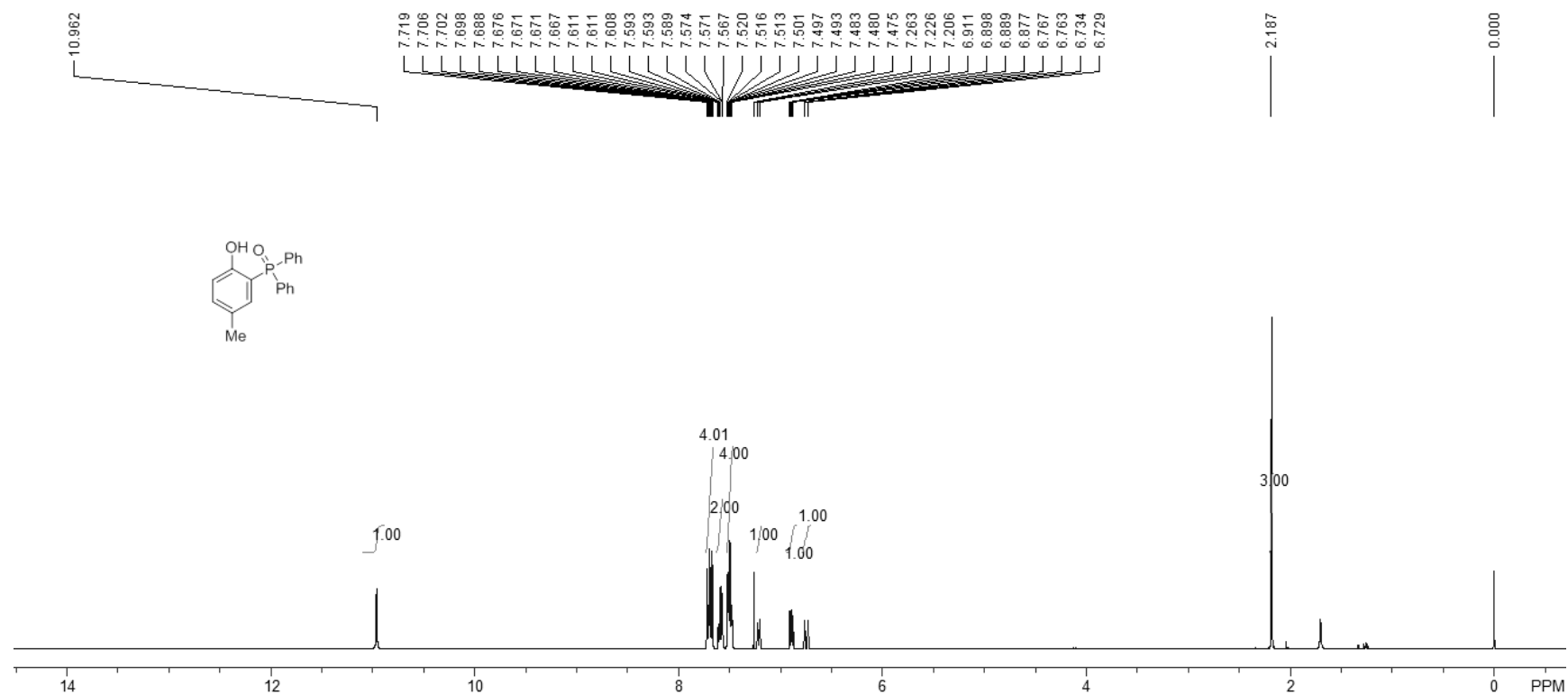
Compound	X-Ray structure	CCDC Number
 <p>3ao</p>		1874221
 <p>6a</p>		1874220

Table S2 Crystal data and structure refinements for the products

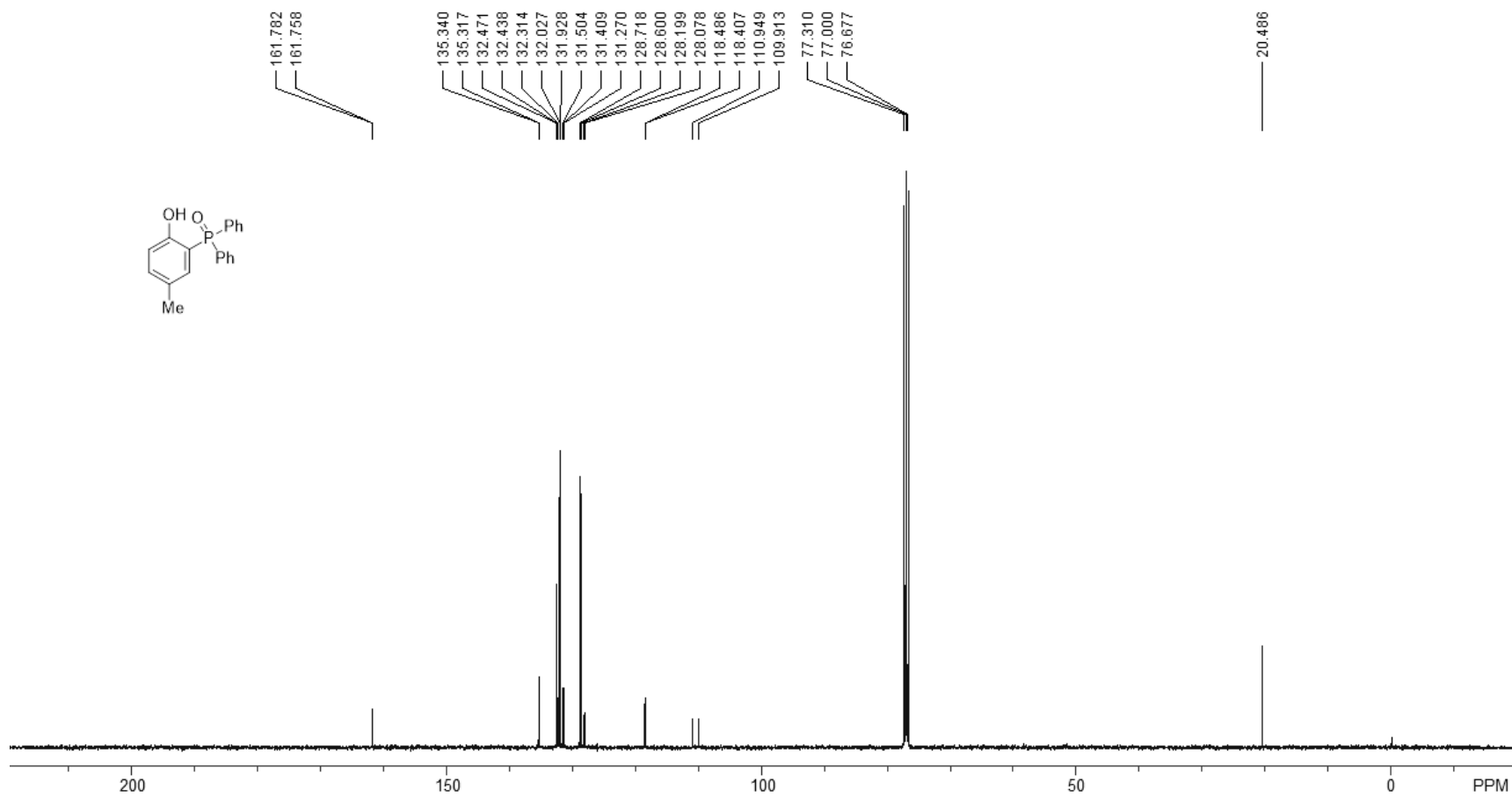
Compound	3ao	6a
Empirical formula	C ₁₉ H ₂₉ O ₂ P, CH ₄ O	C ₂₇ H ₂₁ O ₂ P
Formula weight	352.43	408.41
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>c</i>
<i>a</i> / Å	11.624(2)	15.430(3)
<i>b</i> / Å	16.463(3)	8.5473(14)
<i>c</i> / Å	10.9887(18)	20.666(14)
β / (°)	105.891(2)	127.448(9)
<i>V</i> / Å ³	2022.4(6)	2163.8(7)
<i>Z</i>	4	4
<i>D_c</i> / (g.cm ⁻³)	1.157	1.254
μ / mm ⁻¹	0.150	0.148
<i>F</i> (000)	768.0	856.0
Crystal size / mm ³	0.17 × 0.14 × 0.13	0.15 × 0.13 × 0.10
θ range / (°)	1.822~25.003	1.662~26.946
Reflections collected	14080	15509
Independent reflections	3548 (<i>R</i> _{int} = 0.0255)	4500 (<i>R</i> _{int} = 0.029)
Reflections observed (<i>I</i> > 2σ(<i>I</i>))	2912	2876
Data/restraints/parameters	3548/6/218	4300/21/217
Goodness-of-fit on <i>F</i> ²	1.080	1.054
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0472/0.1318	0.0667/0.1966
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0575/0.1386	0.0962/0.2242
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e · Å ⁻³)	0.281, -0.396	0.849, -0.473

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

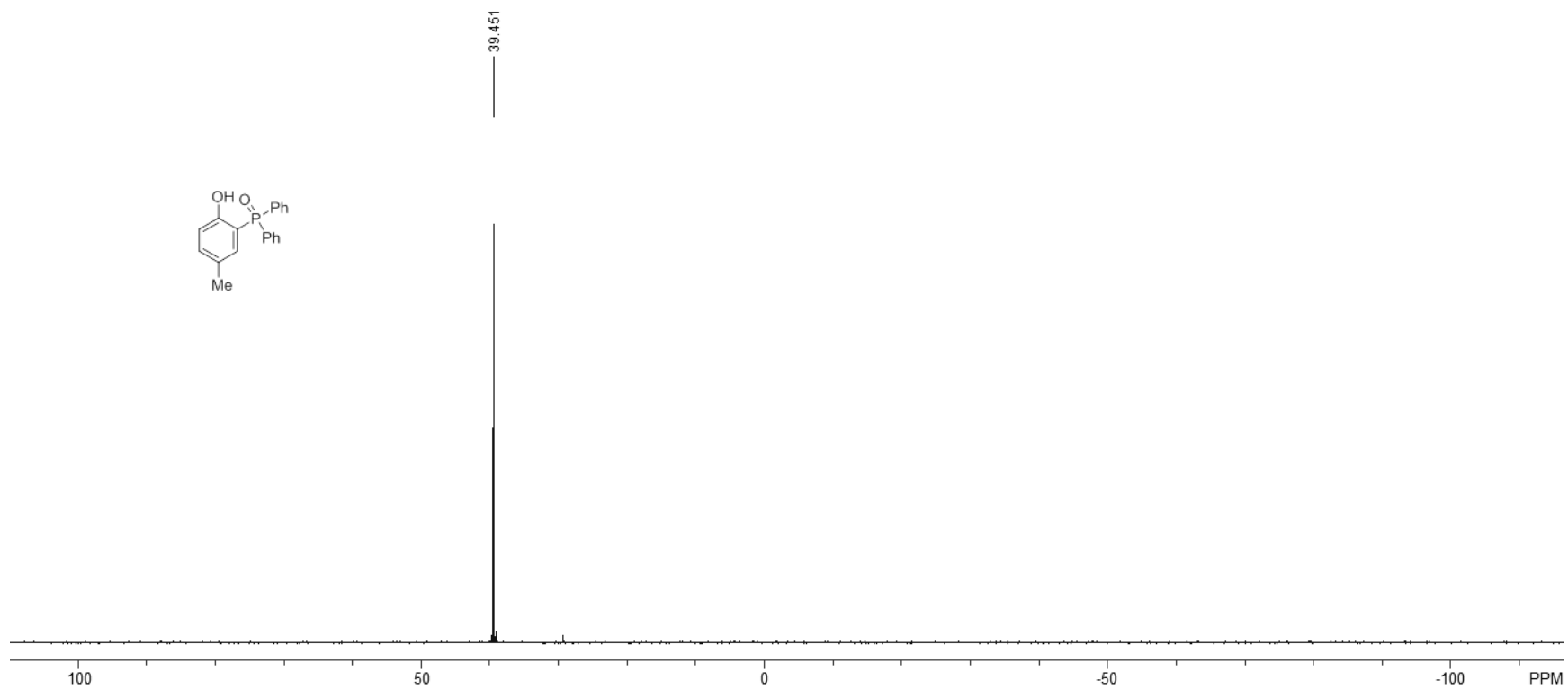
^1H NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)



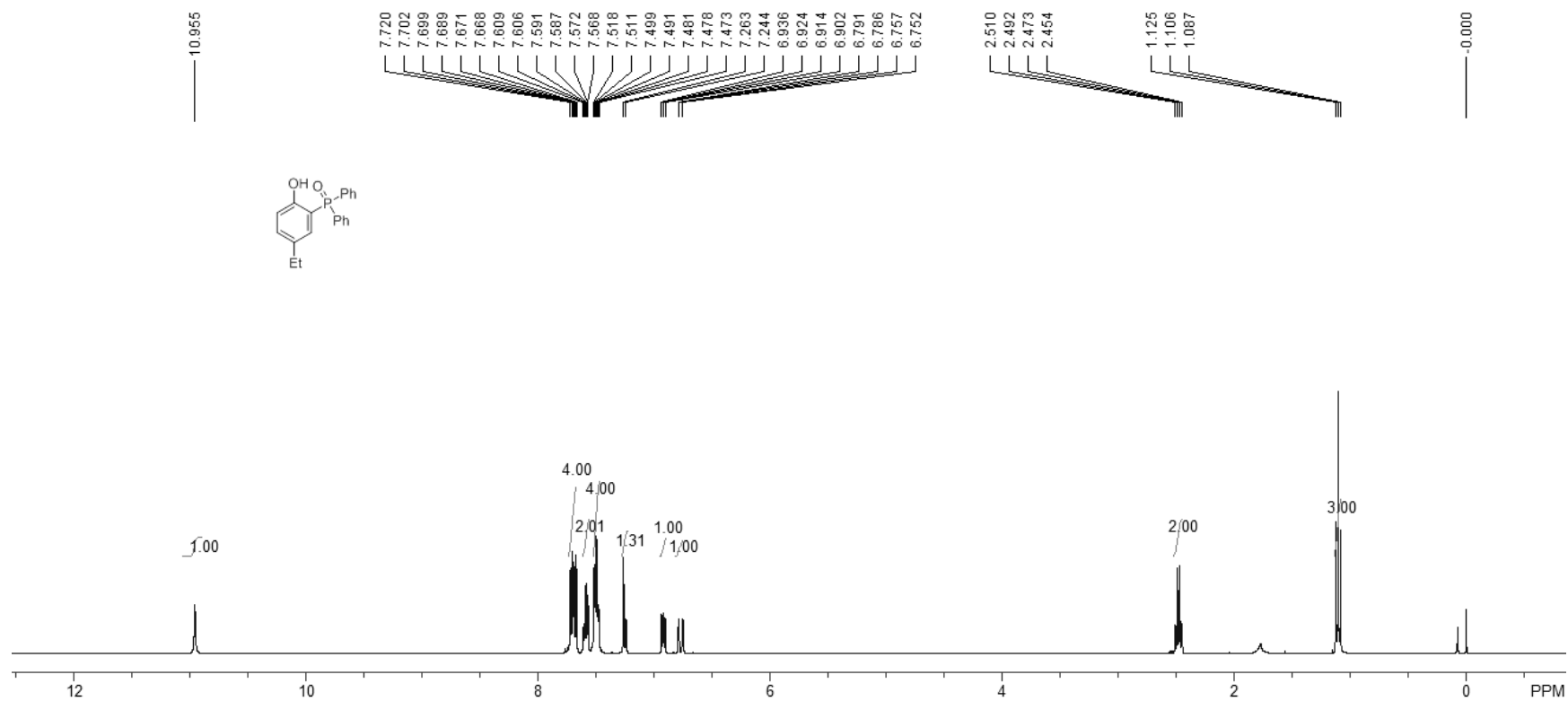
¹³C NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)



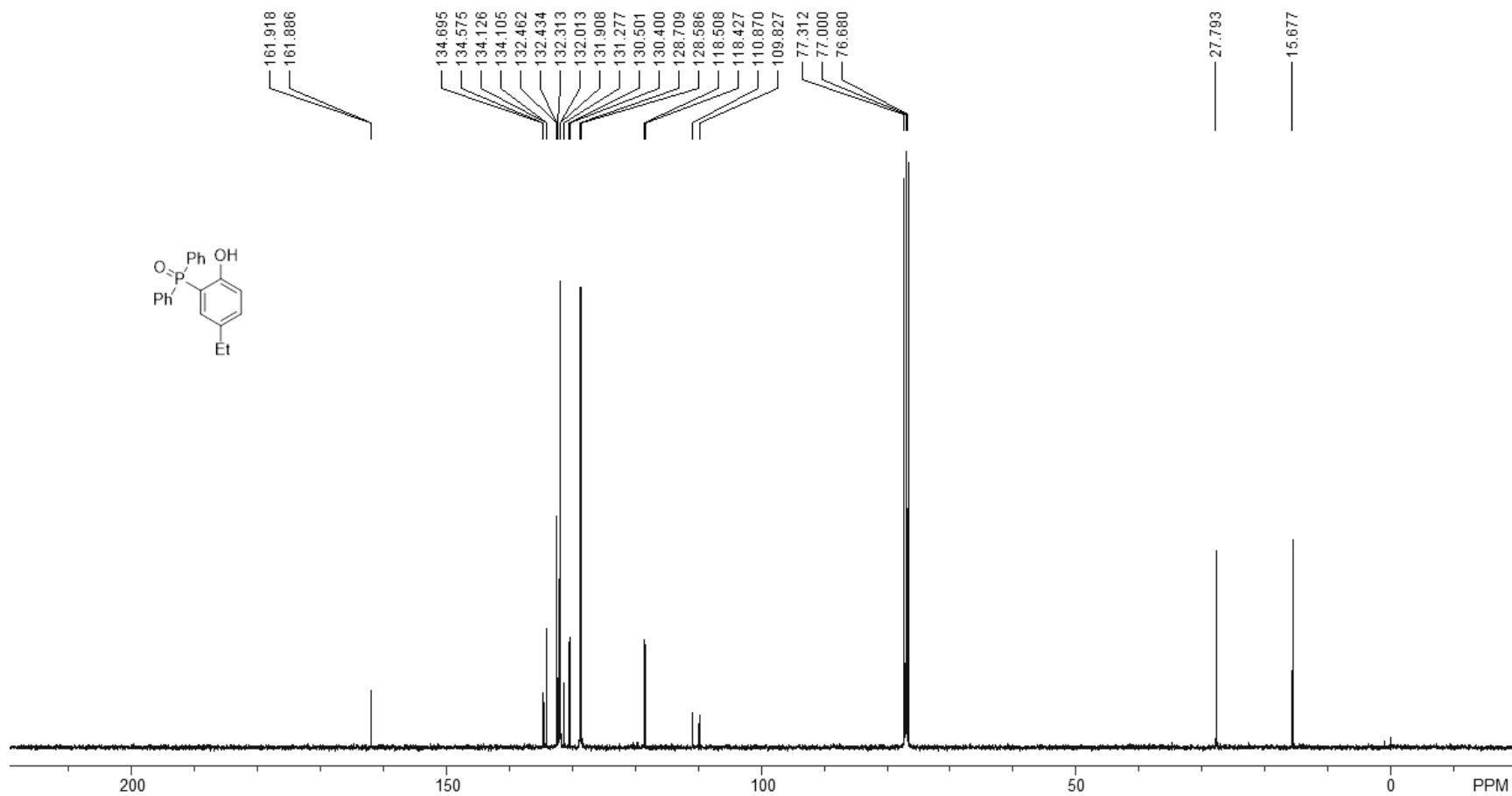
^{31}P NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)



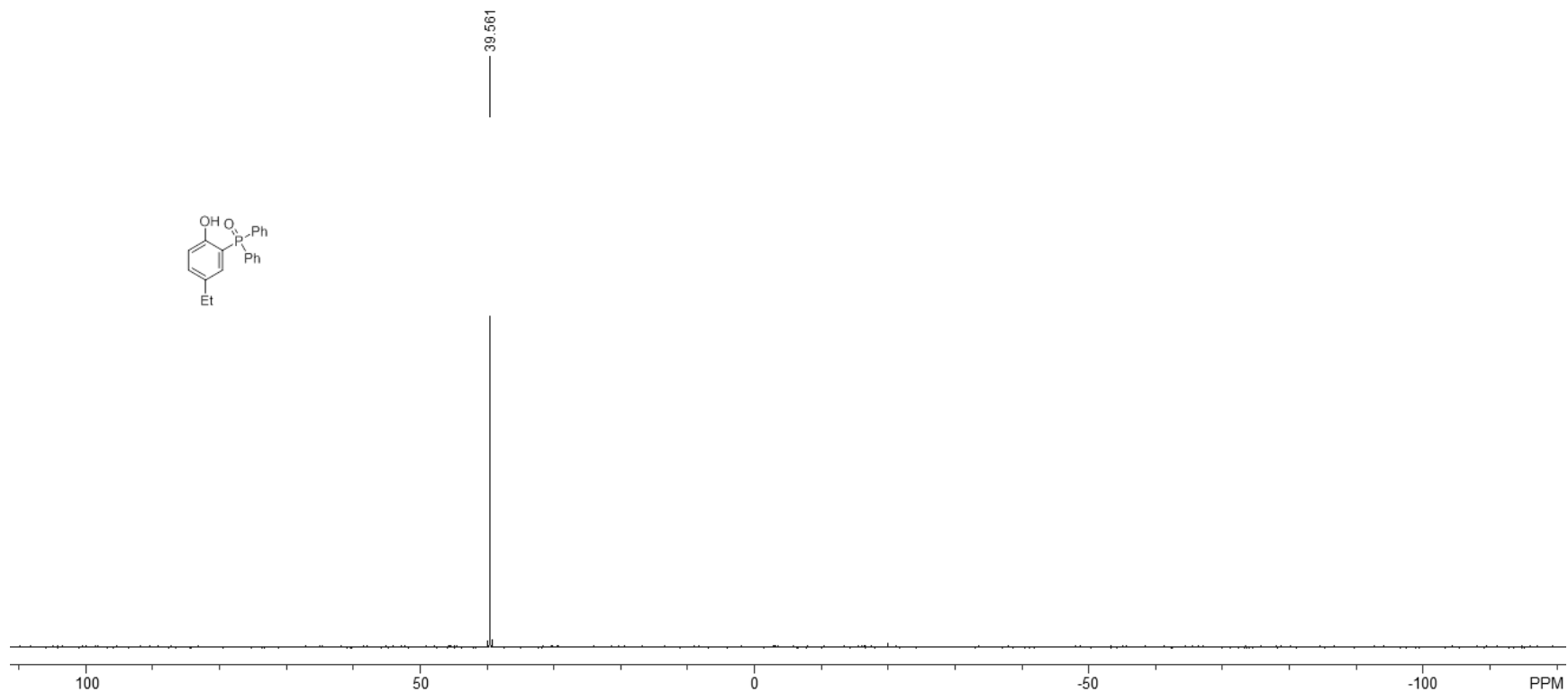
¹H NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)



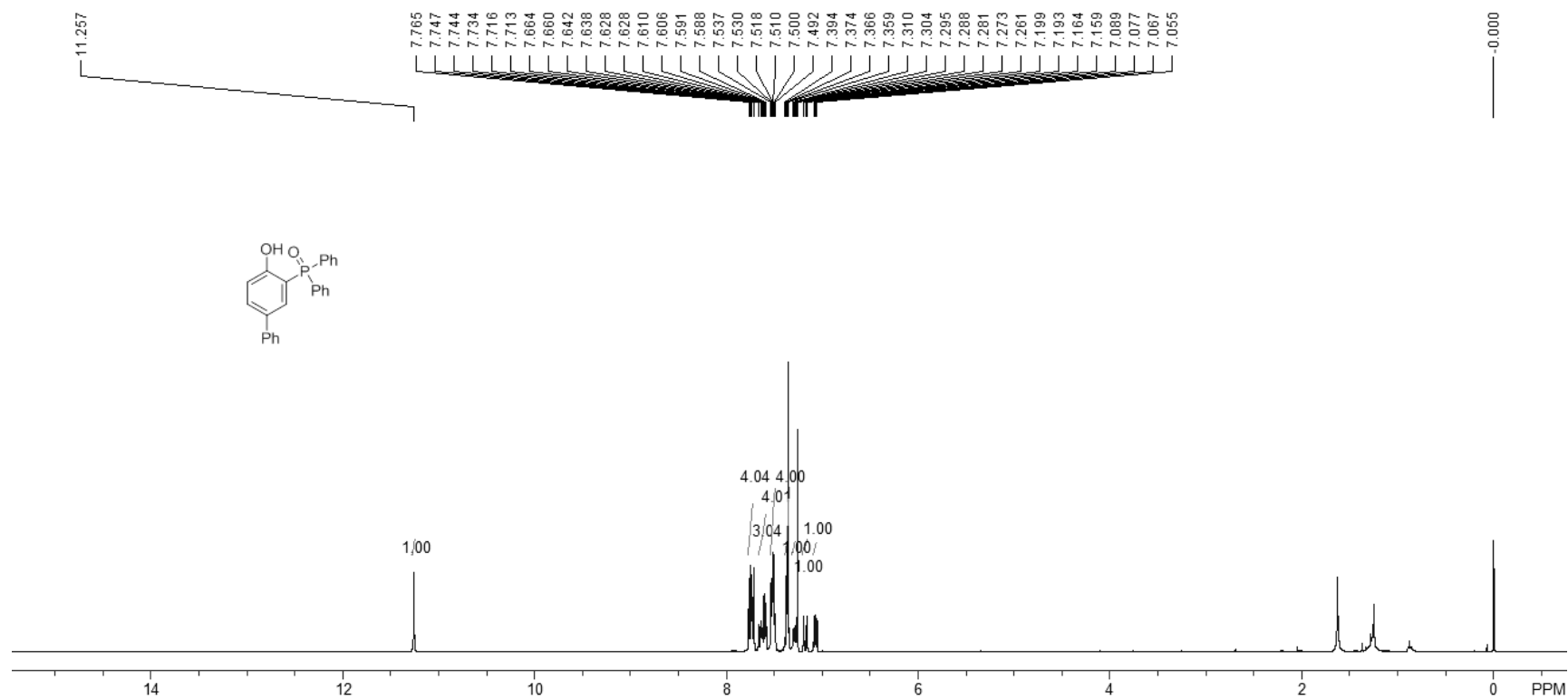
¹³C NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)



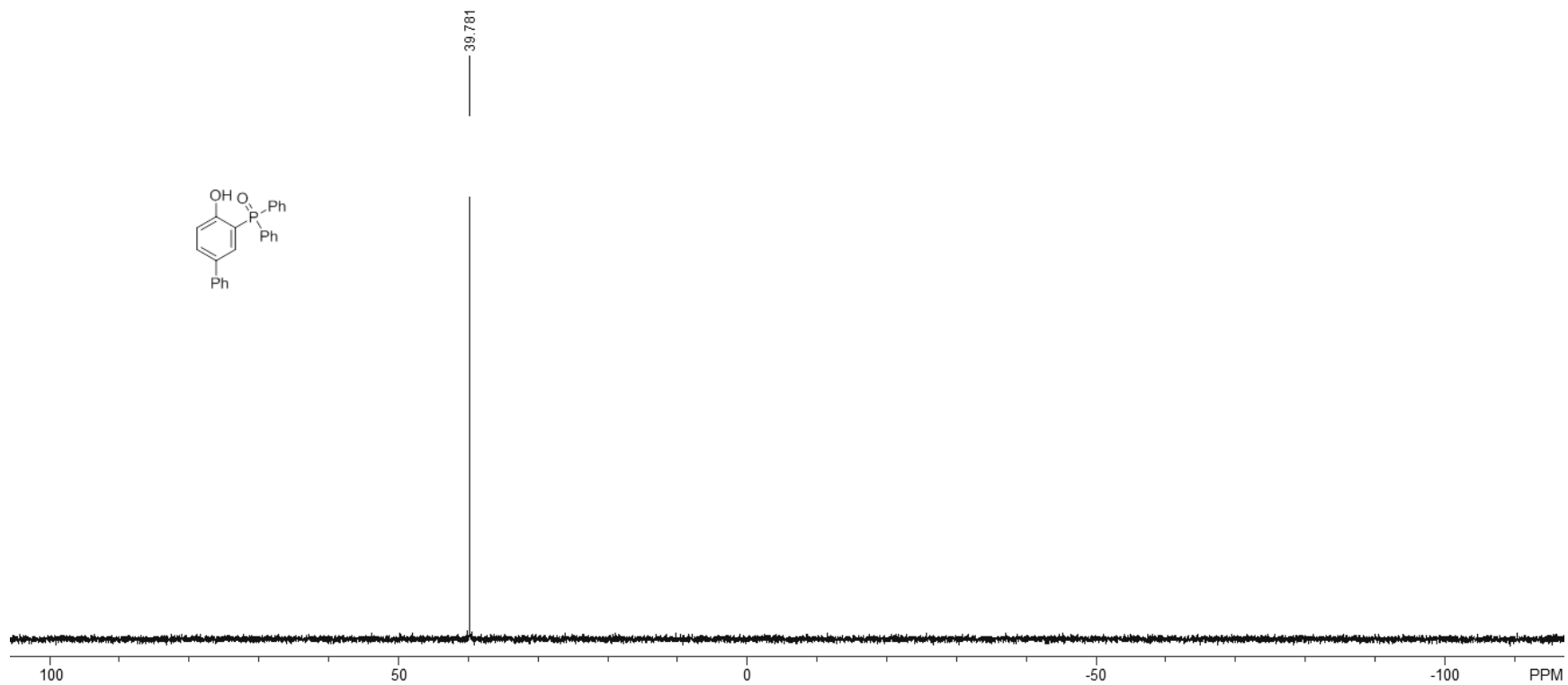
³¹P NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)



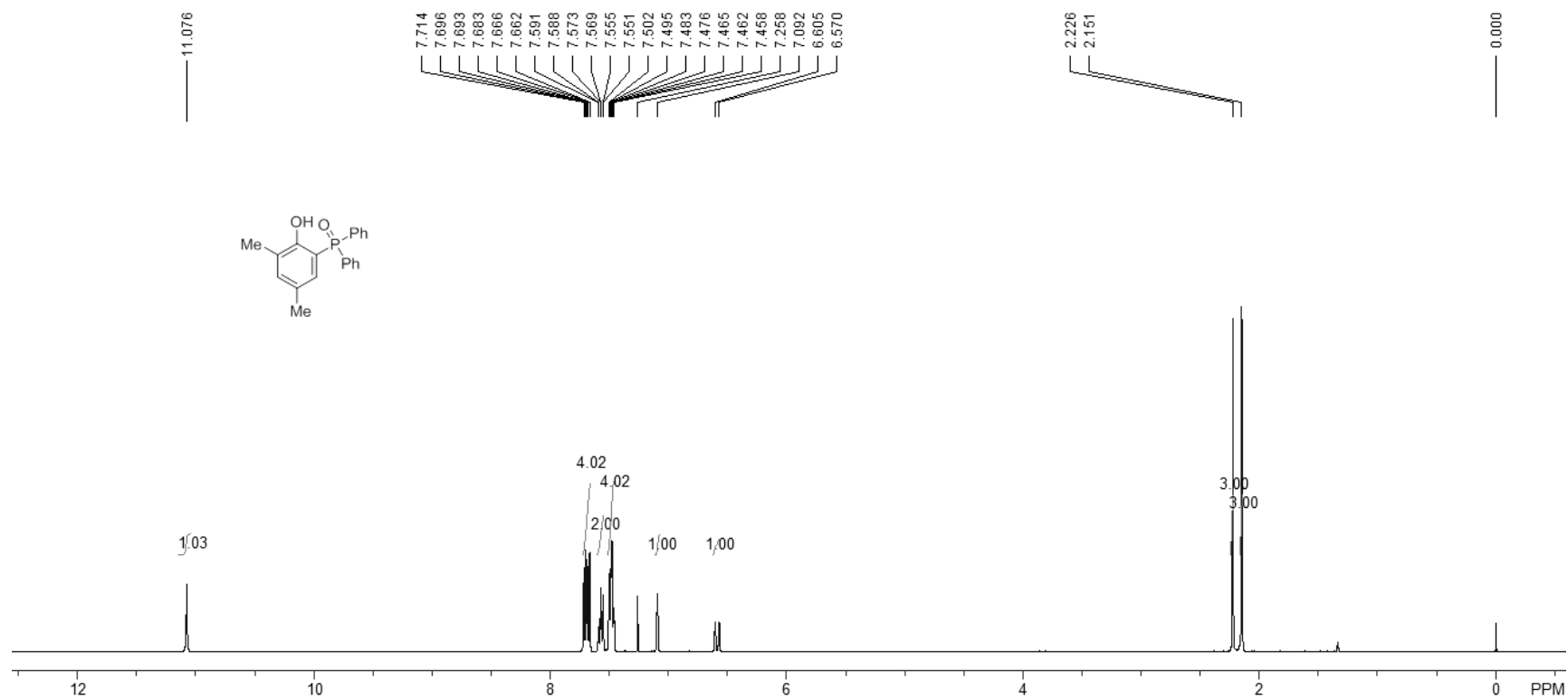
¹H NMR of (4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca)



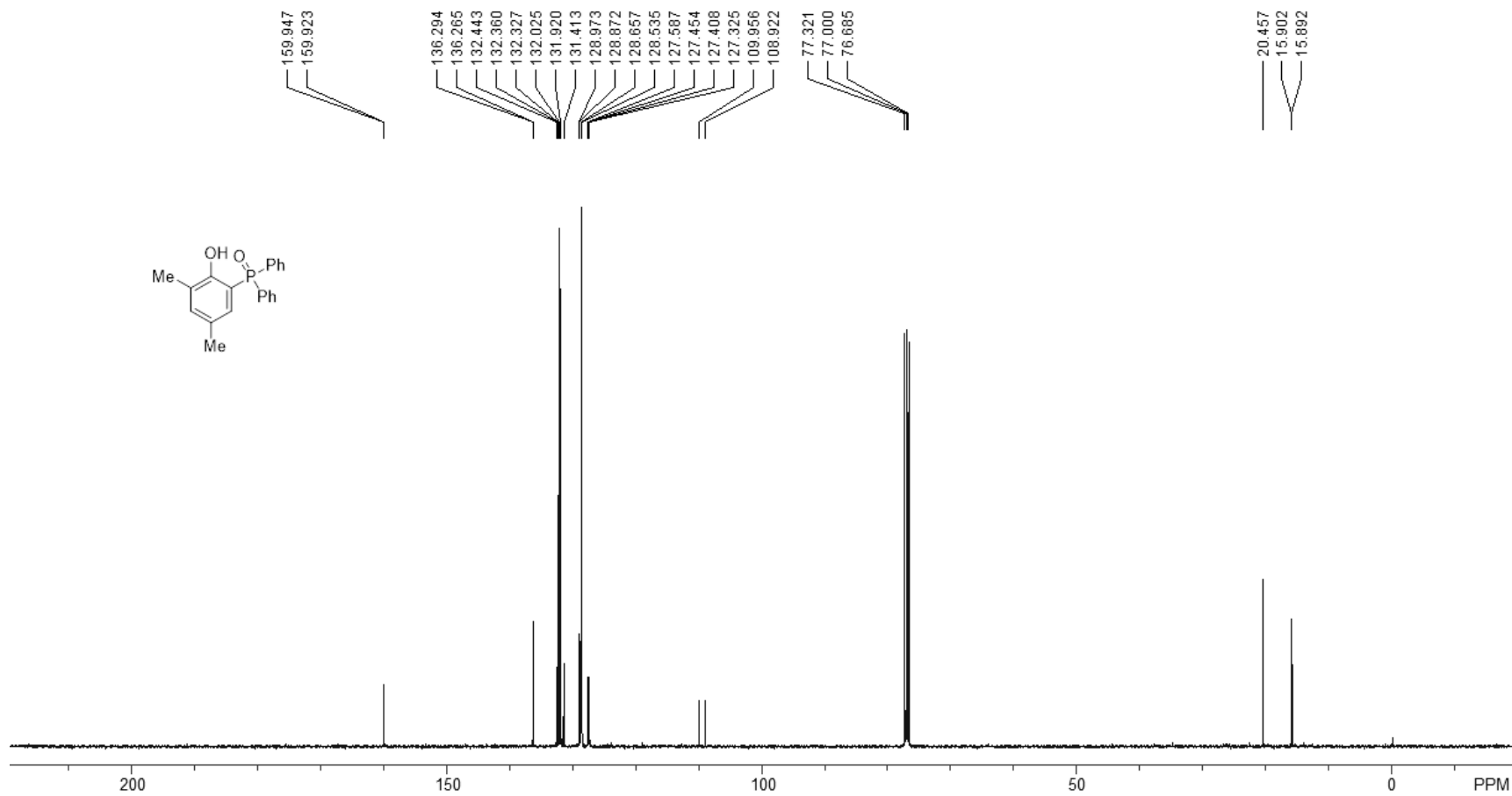
^{31}P NMR of (4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca)



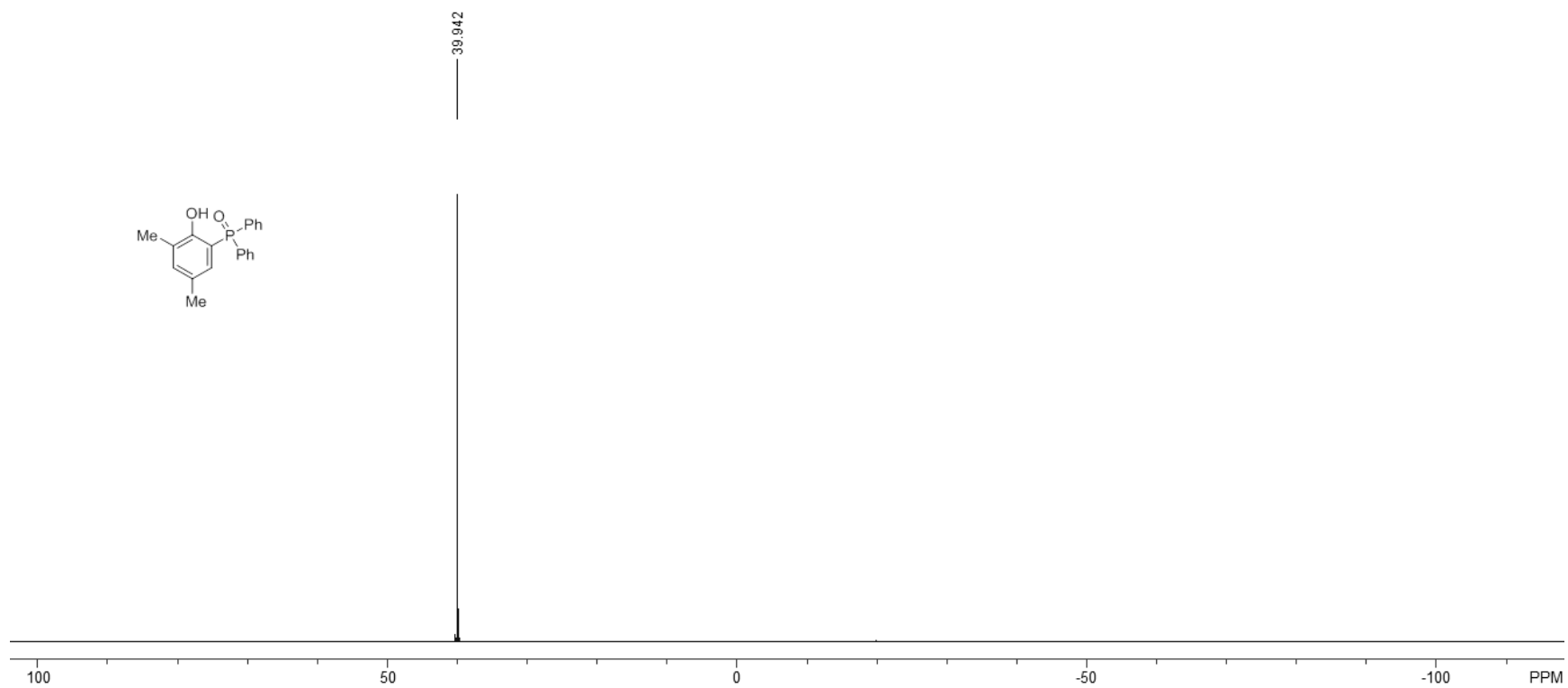
¹H NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)



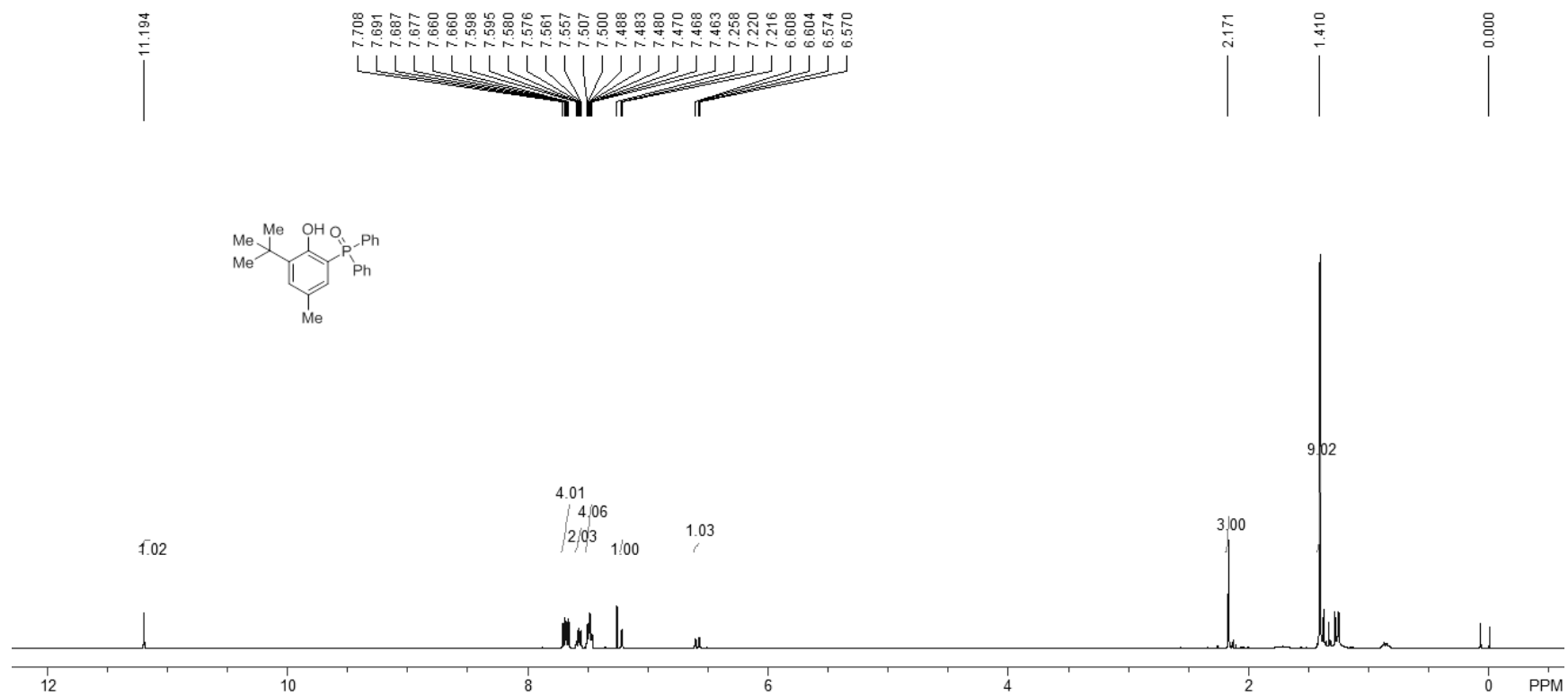
¹³C NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)



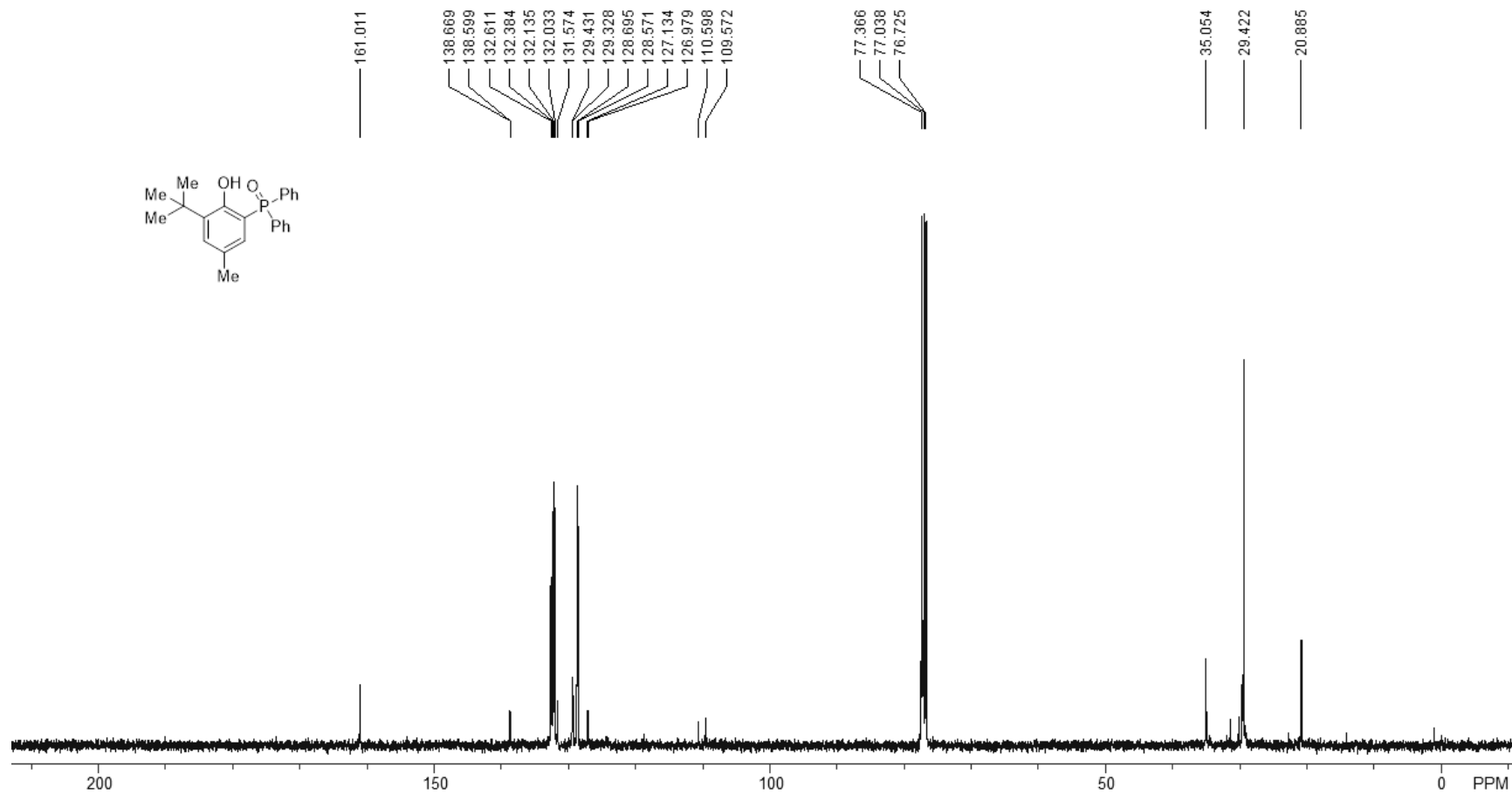
^{31}P NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)



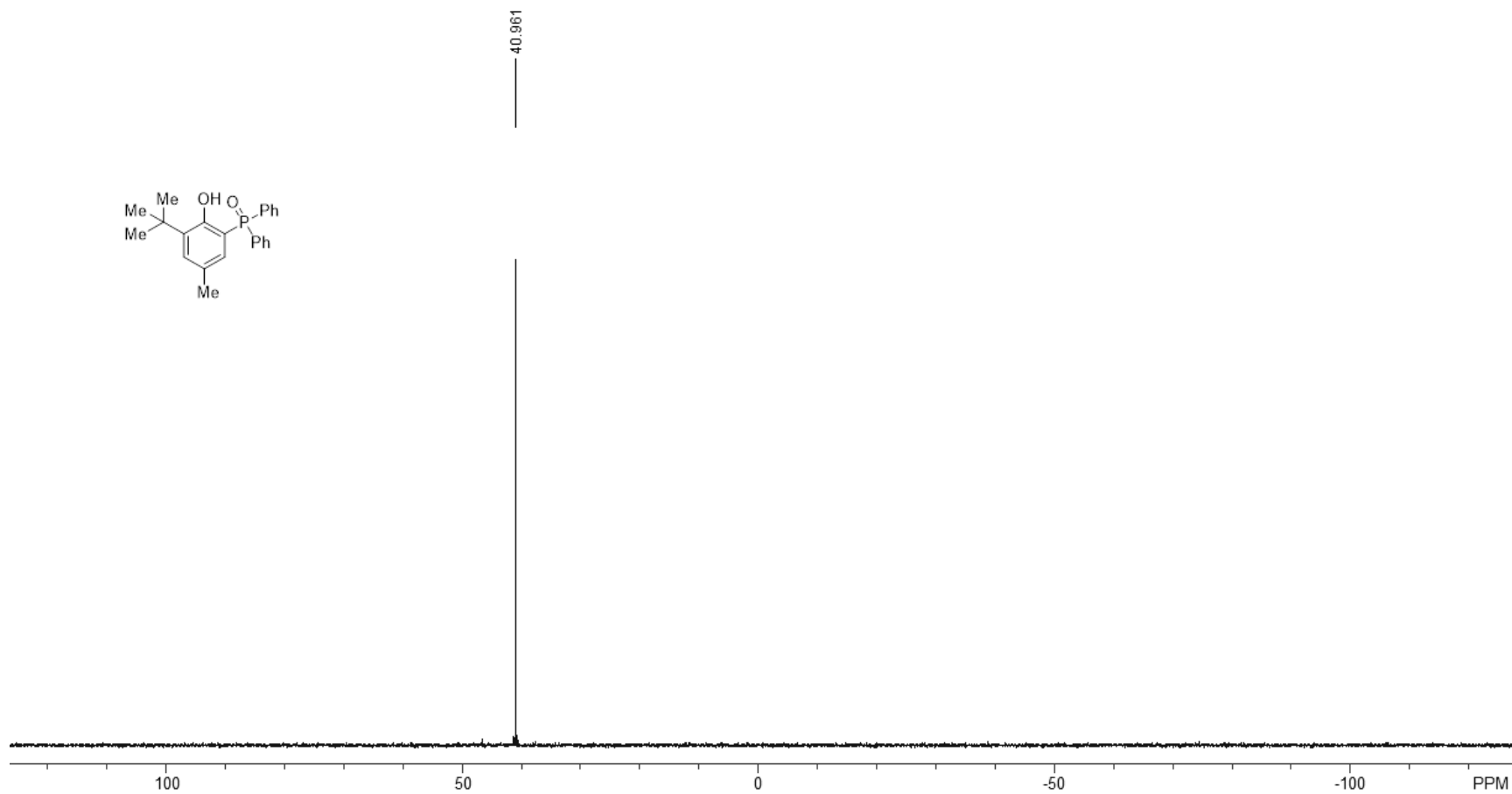
¹H NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)



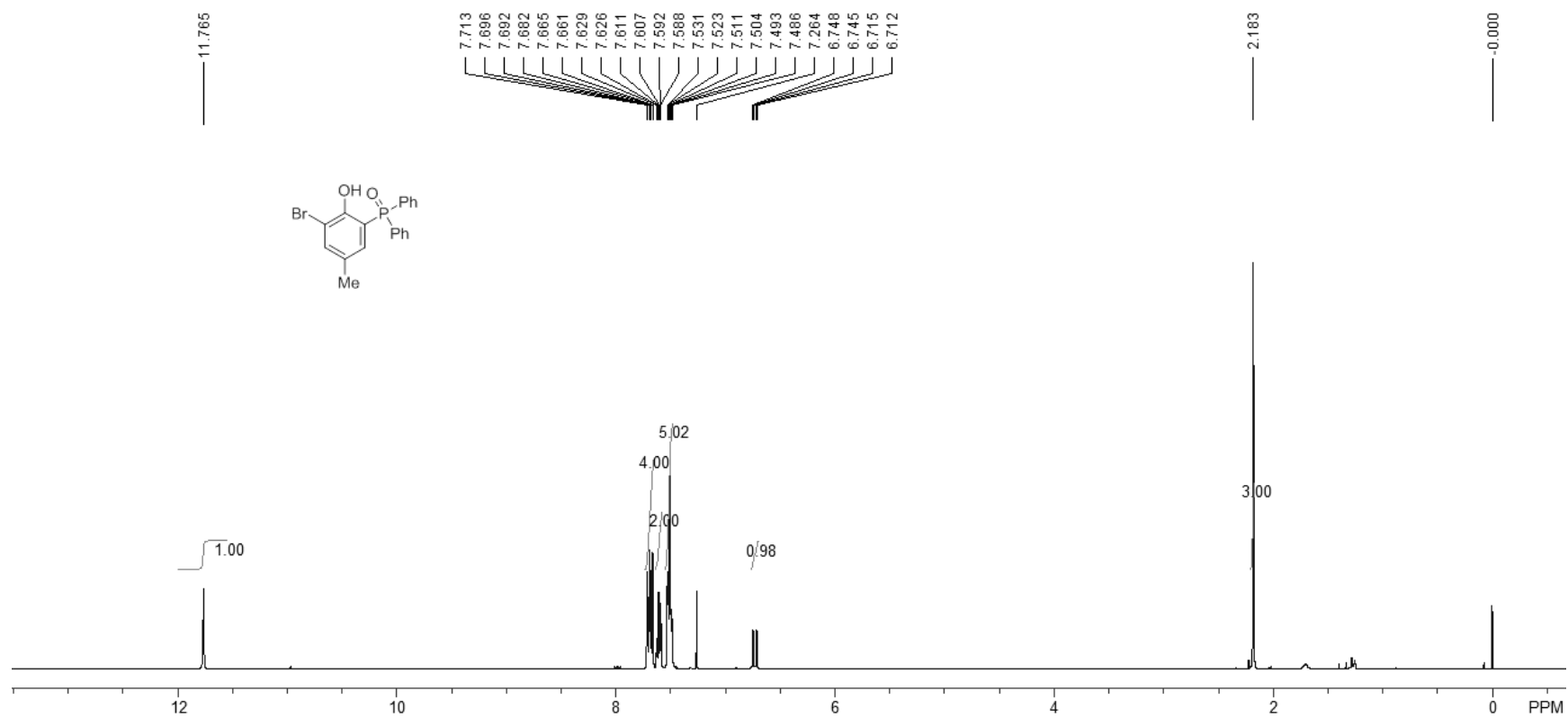
¹³C NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)



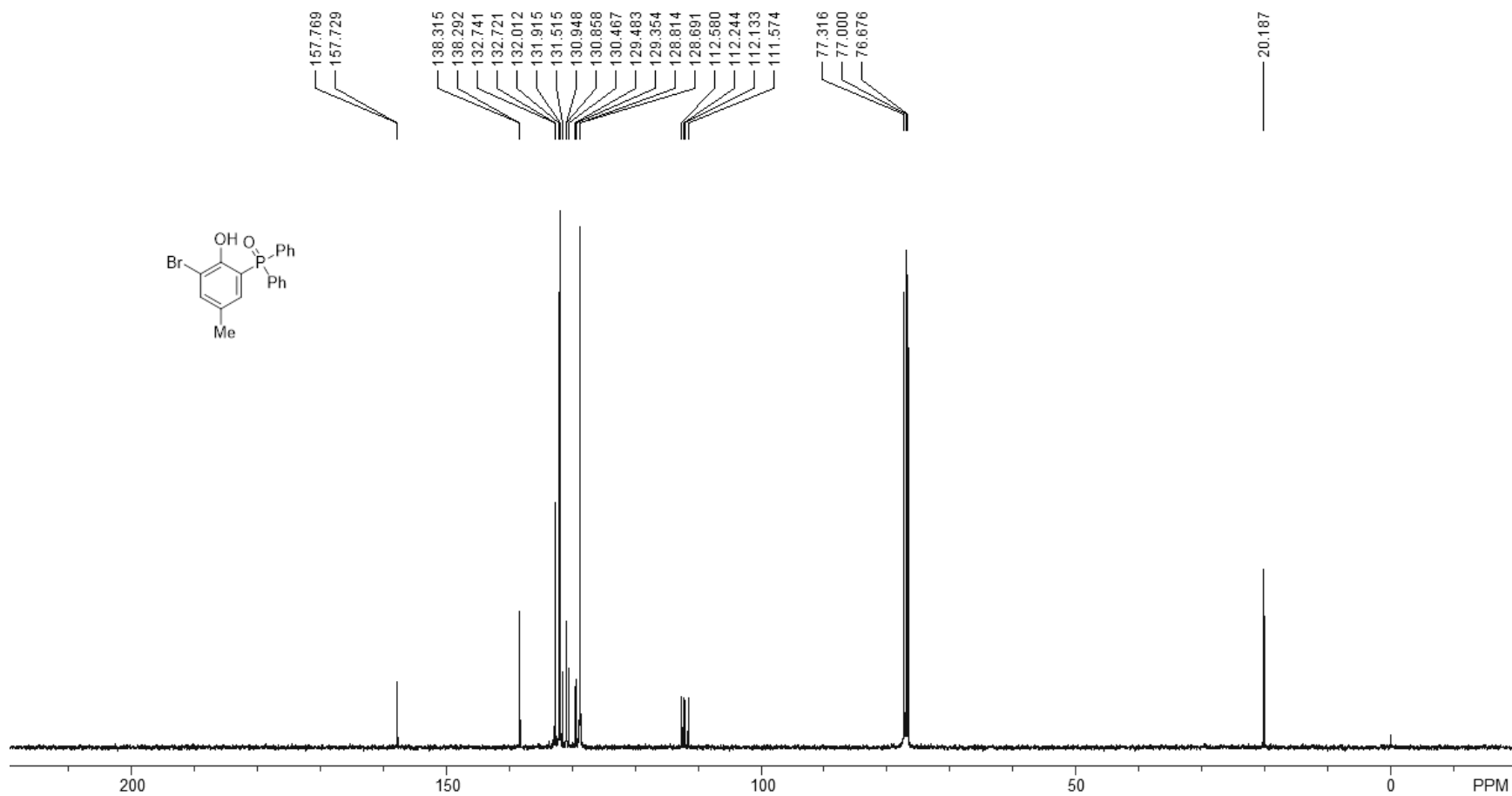
^{31}P NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)



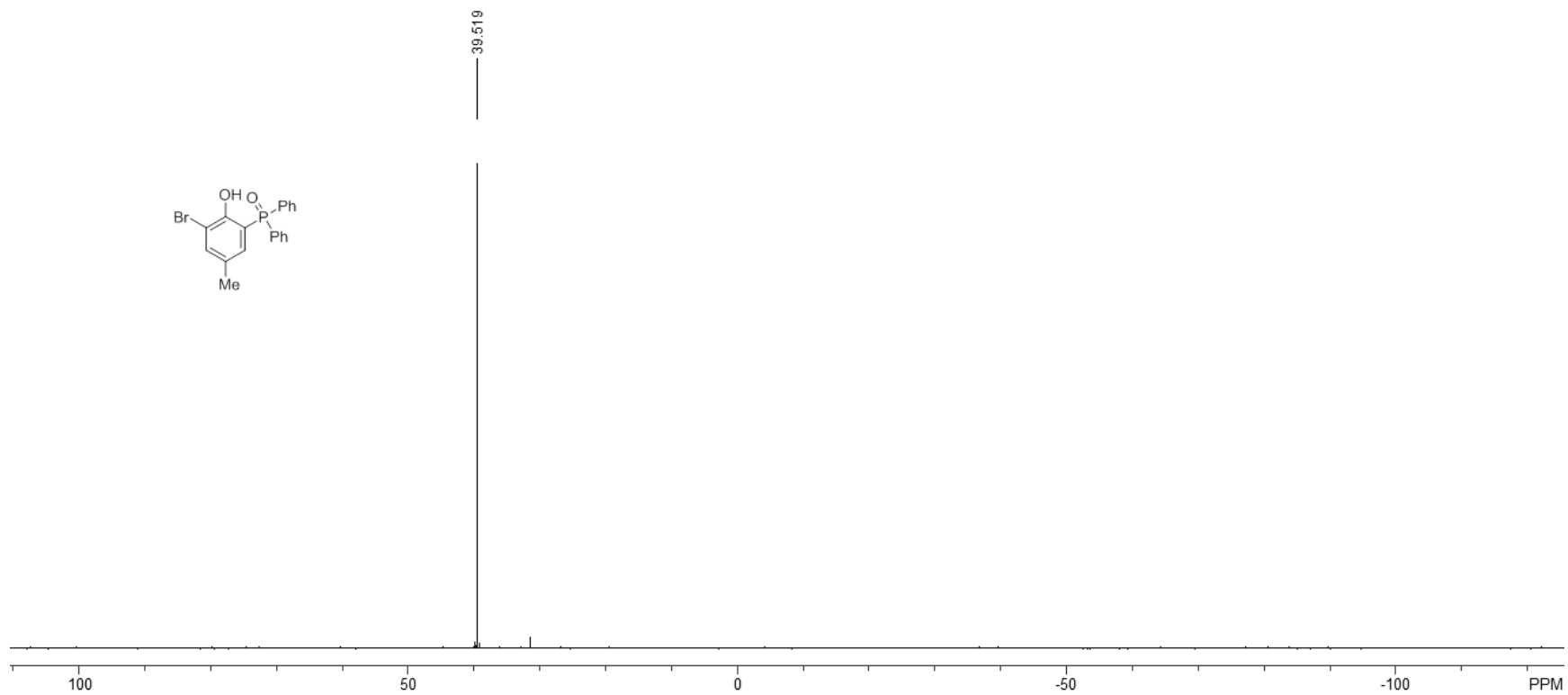
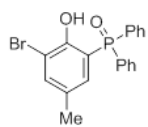
¹H NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)



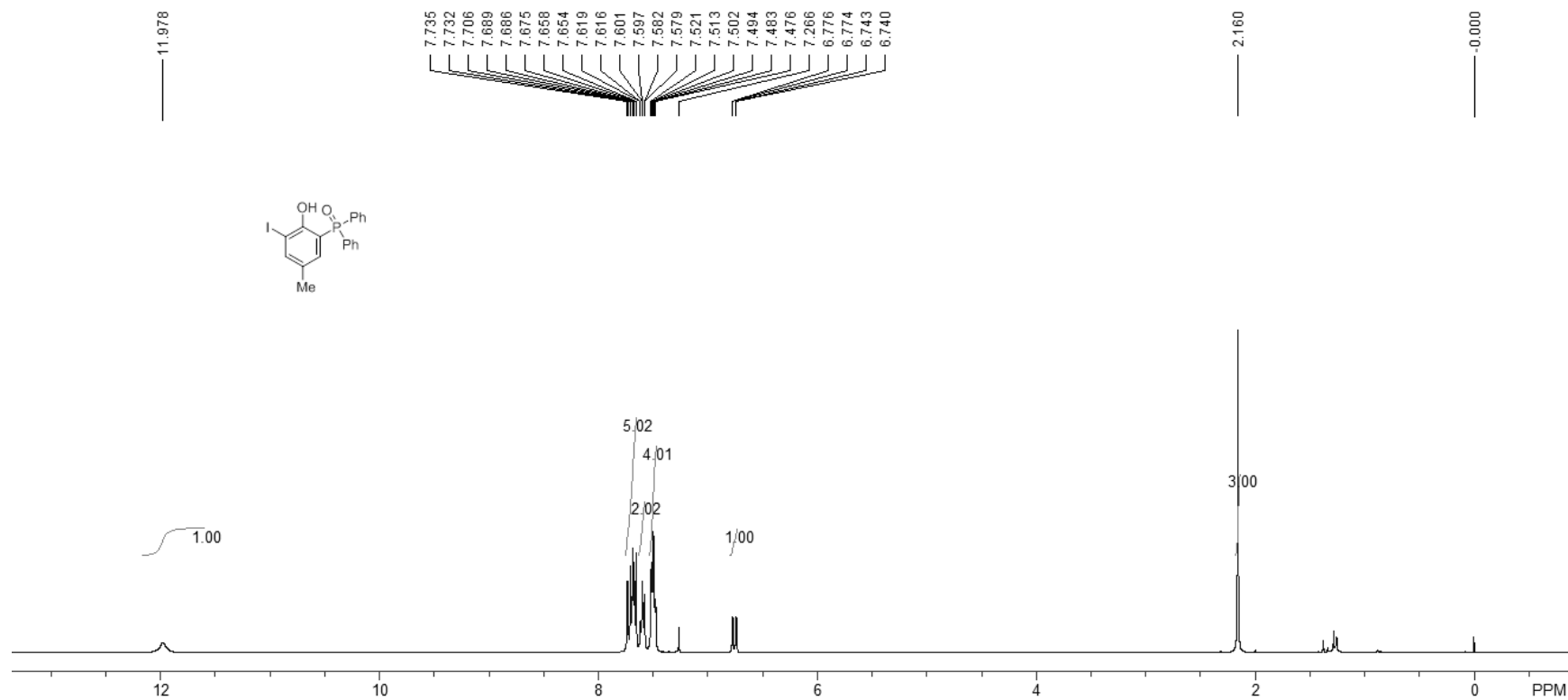
¹³C NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)



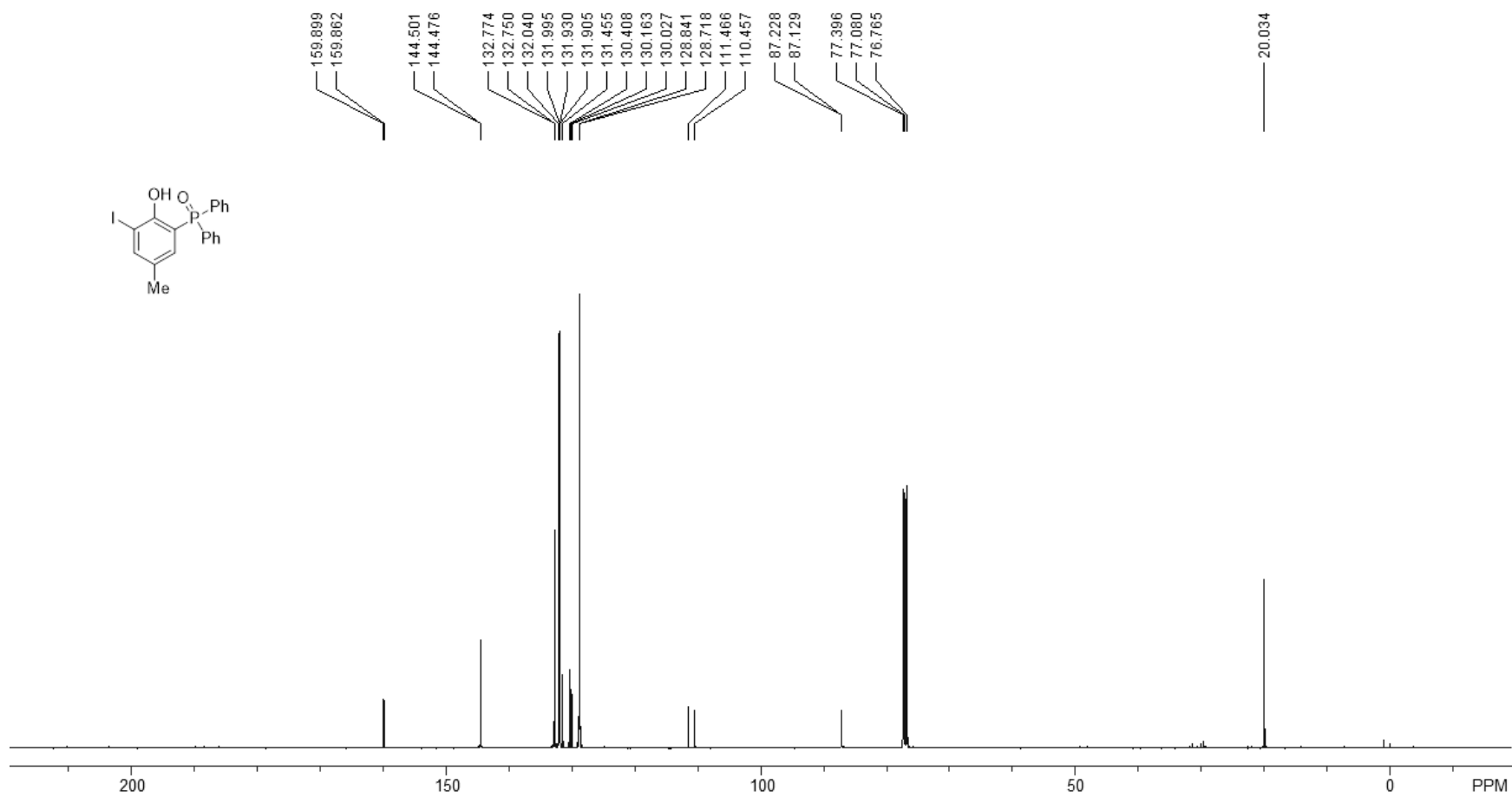
^{31}P NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)



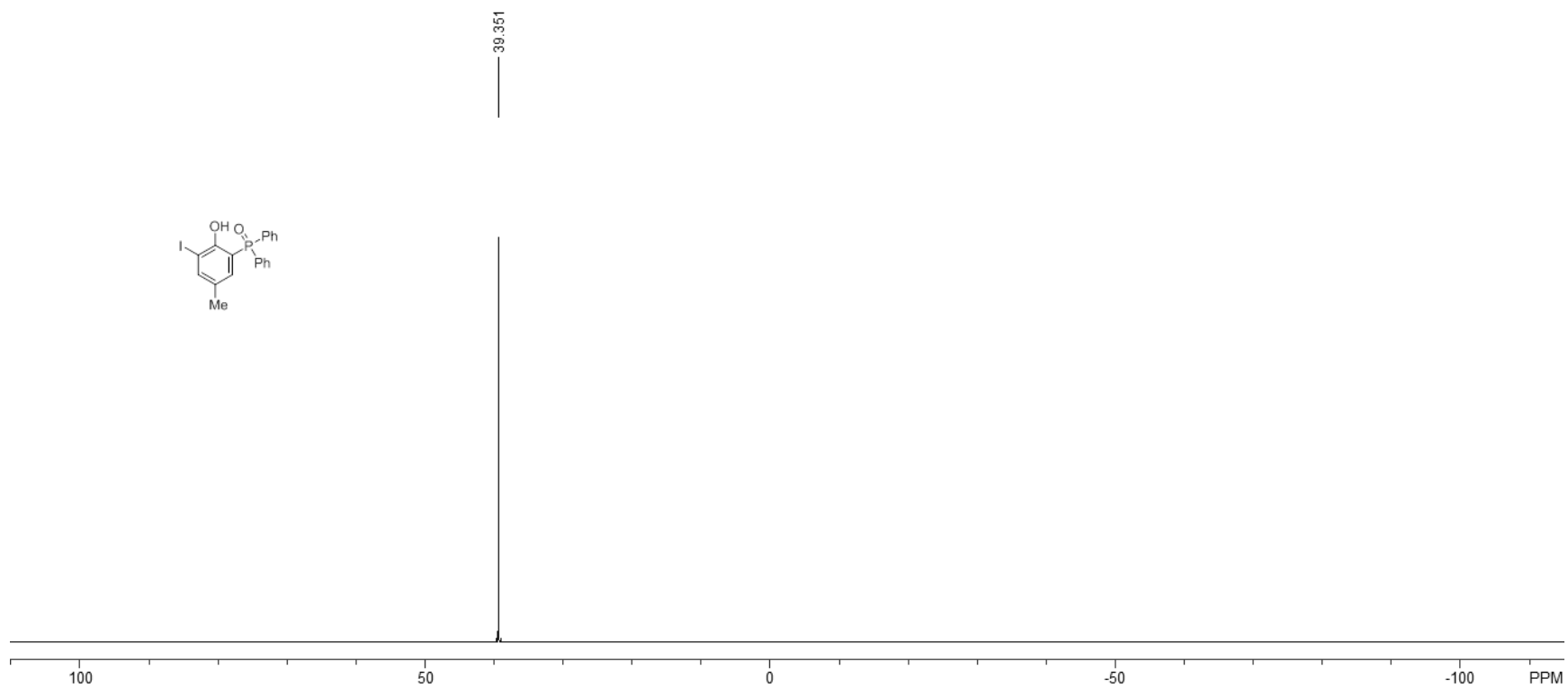
¹H NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)



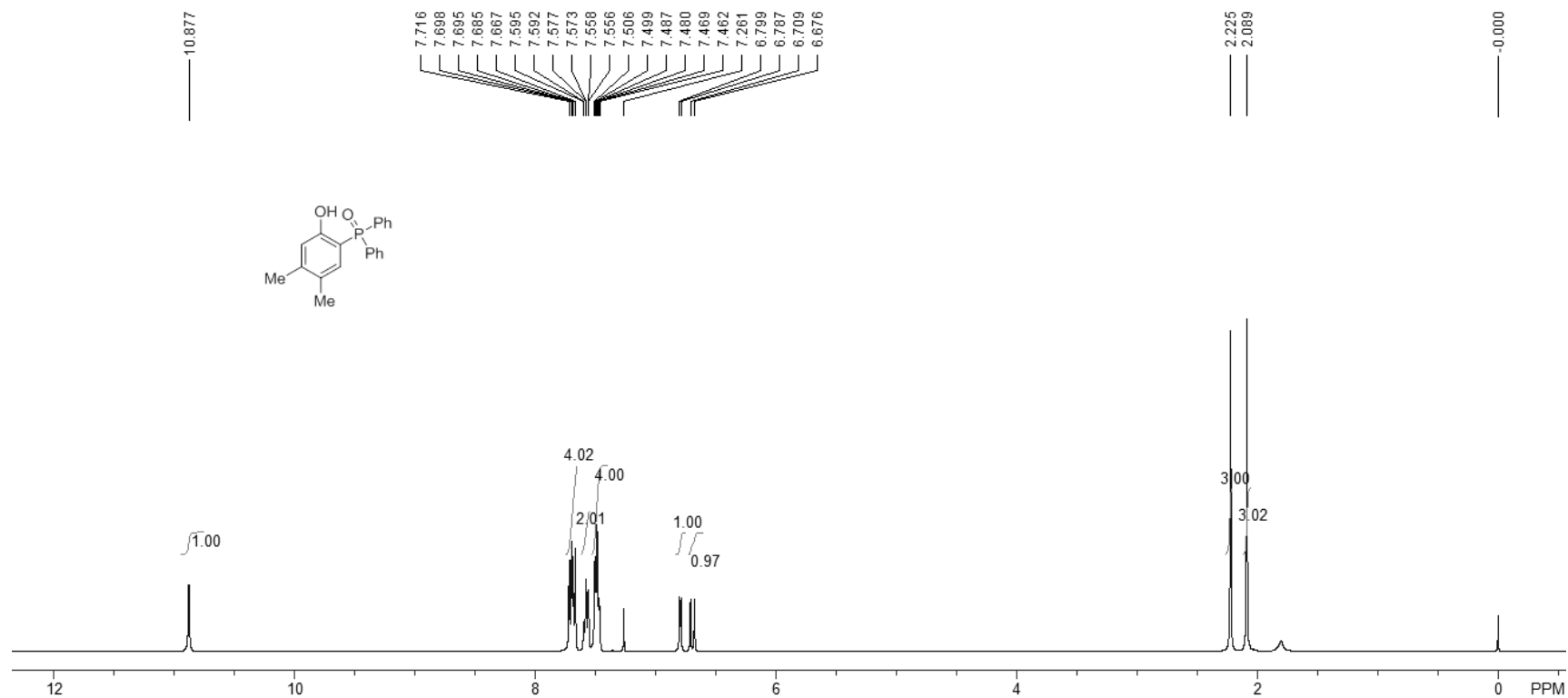
¹³C NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)



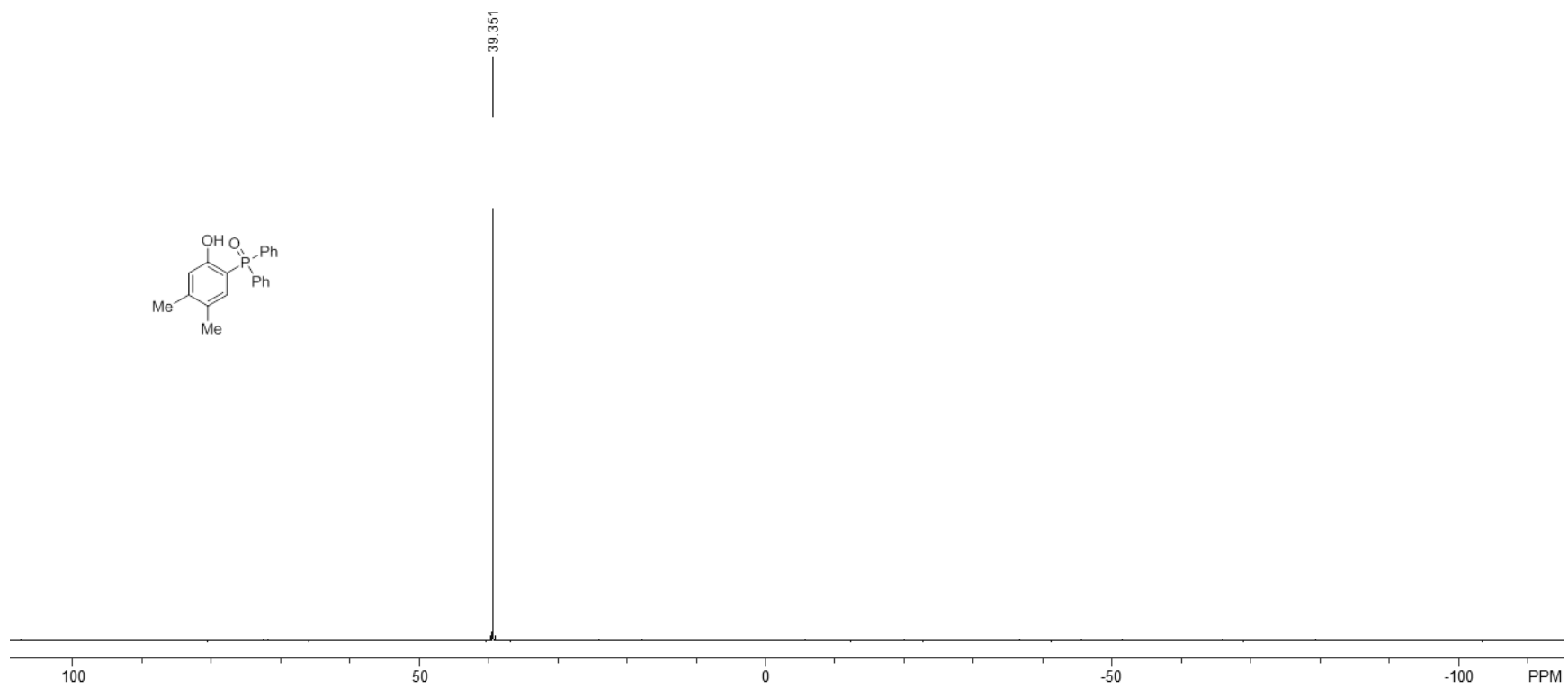
^{31}P NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)



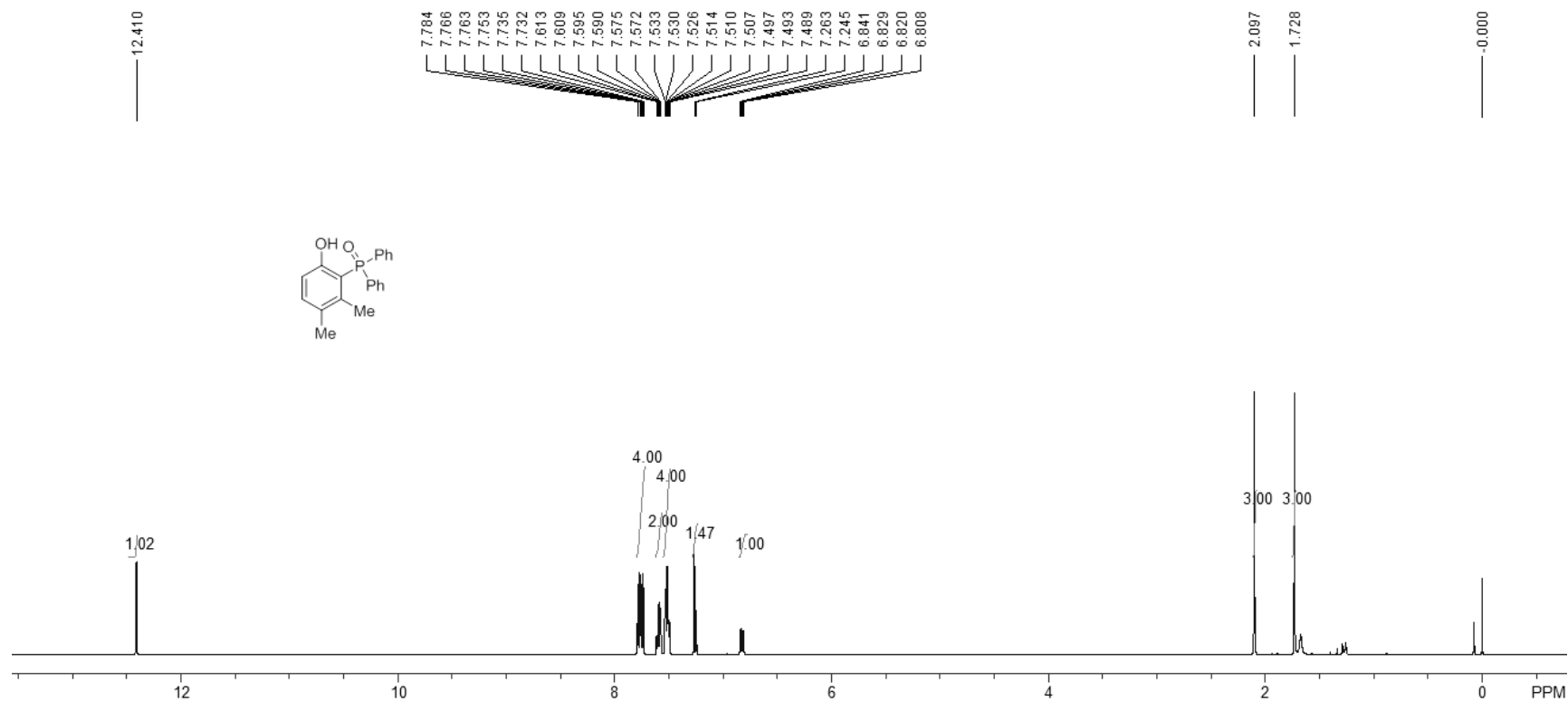
¹H NMR of (2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha)



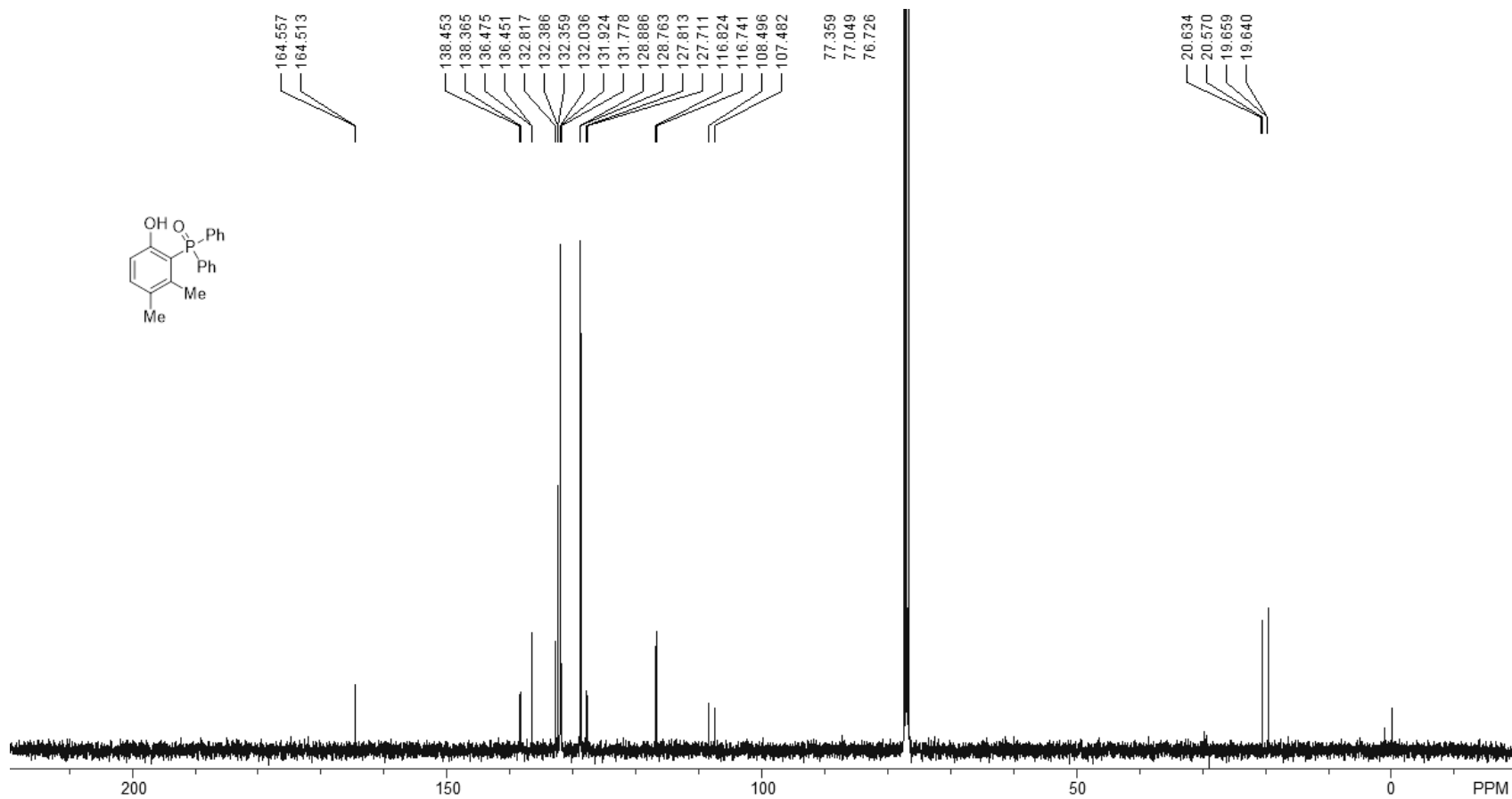
^{31}P NMR of (2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha)



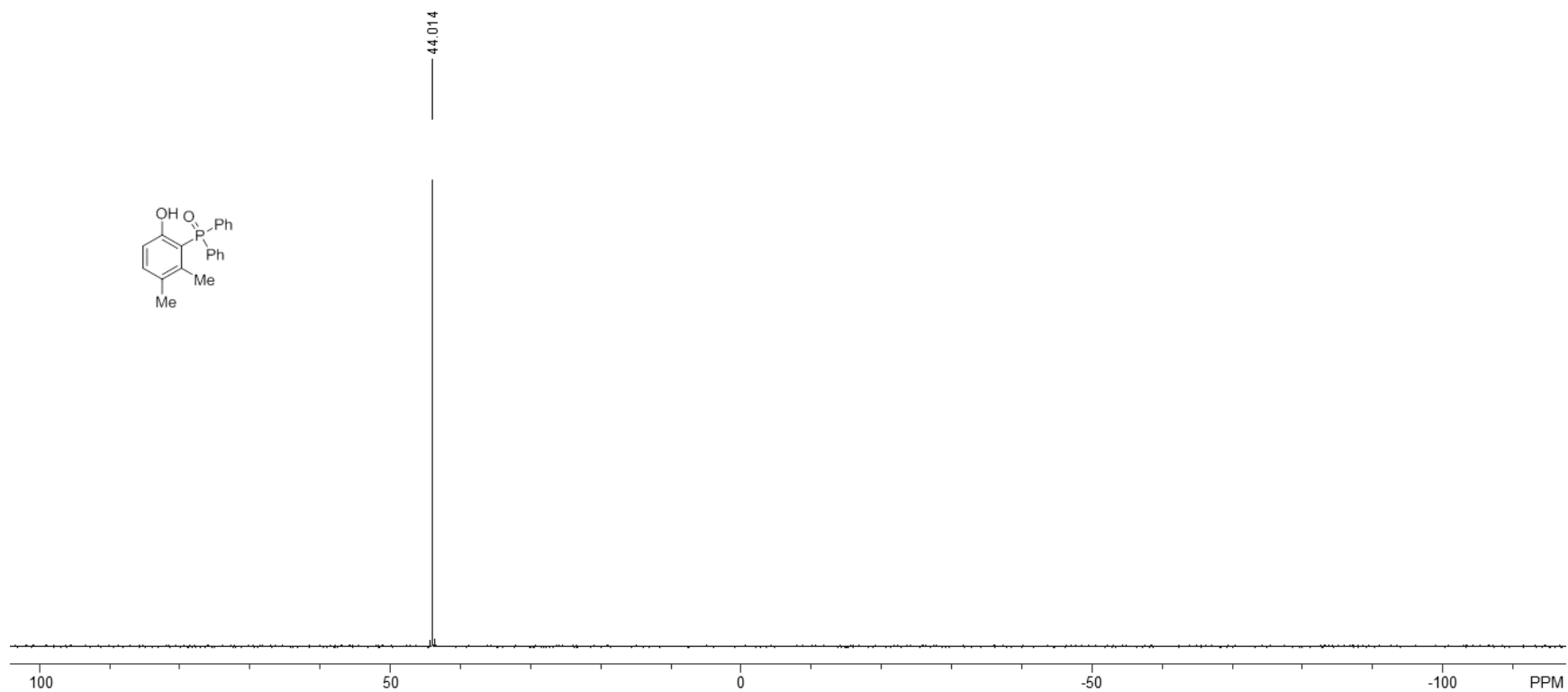
¹H NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')



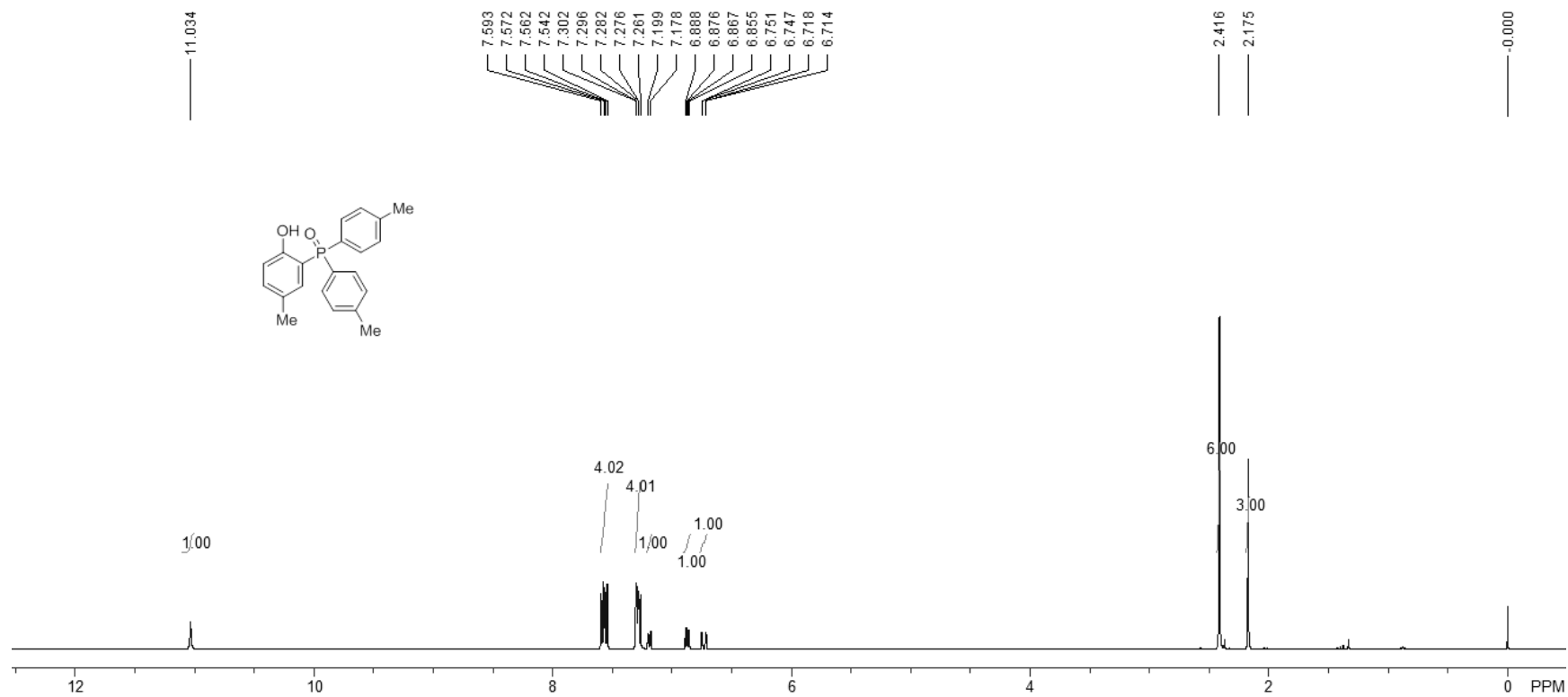
¹³C NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')



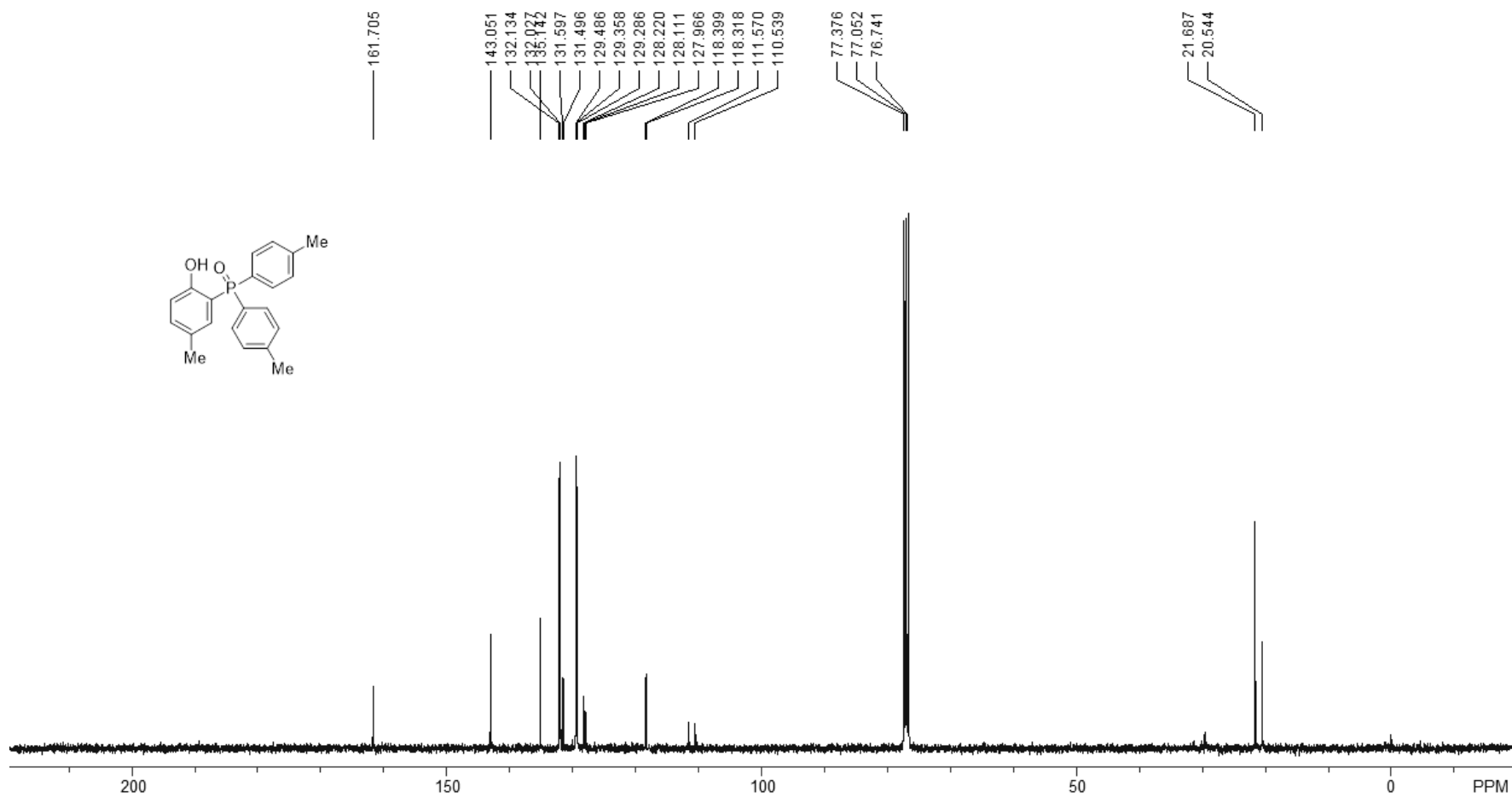
^{31}P NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')



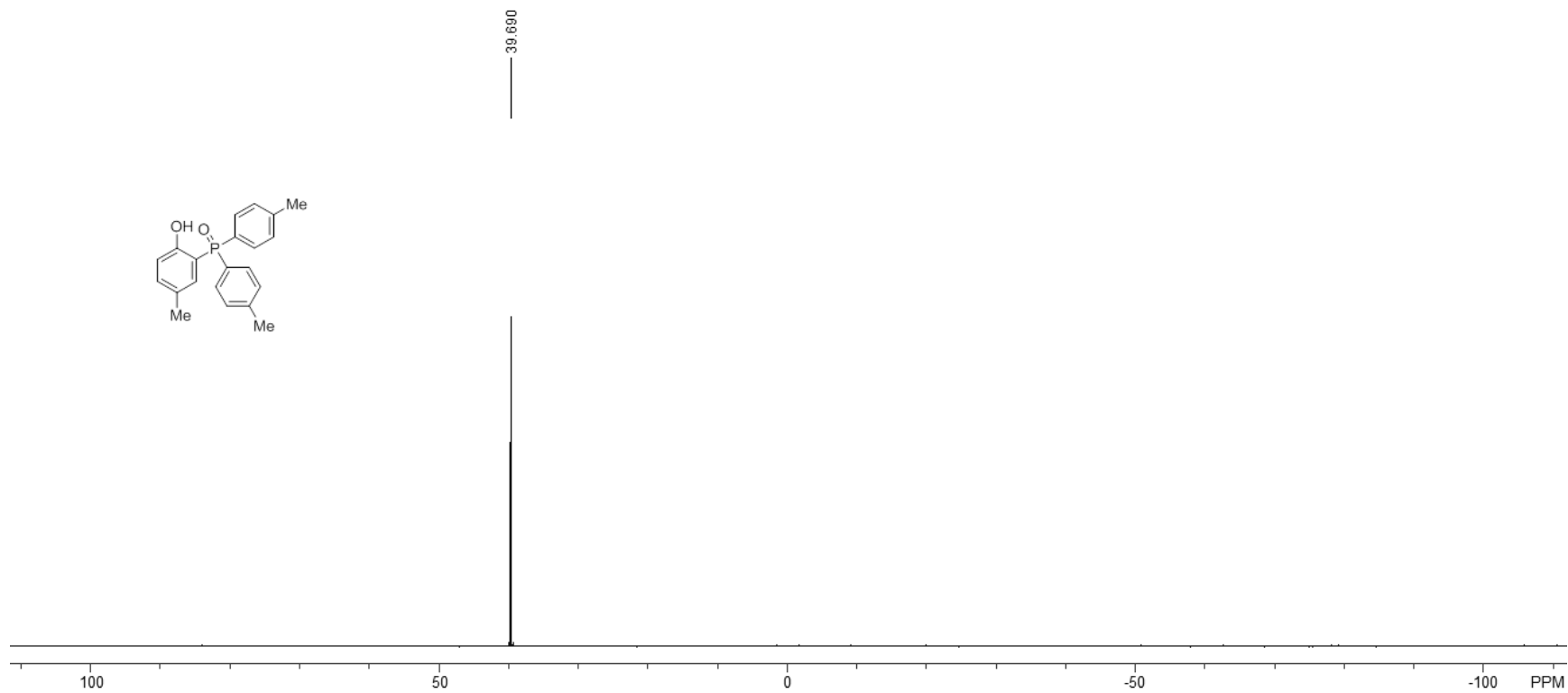
¹H NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)



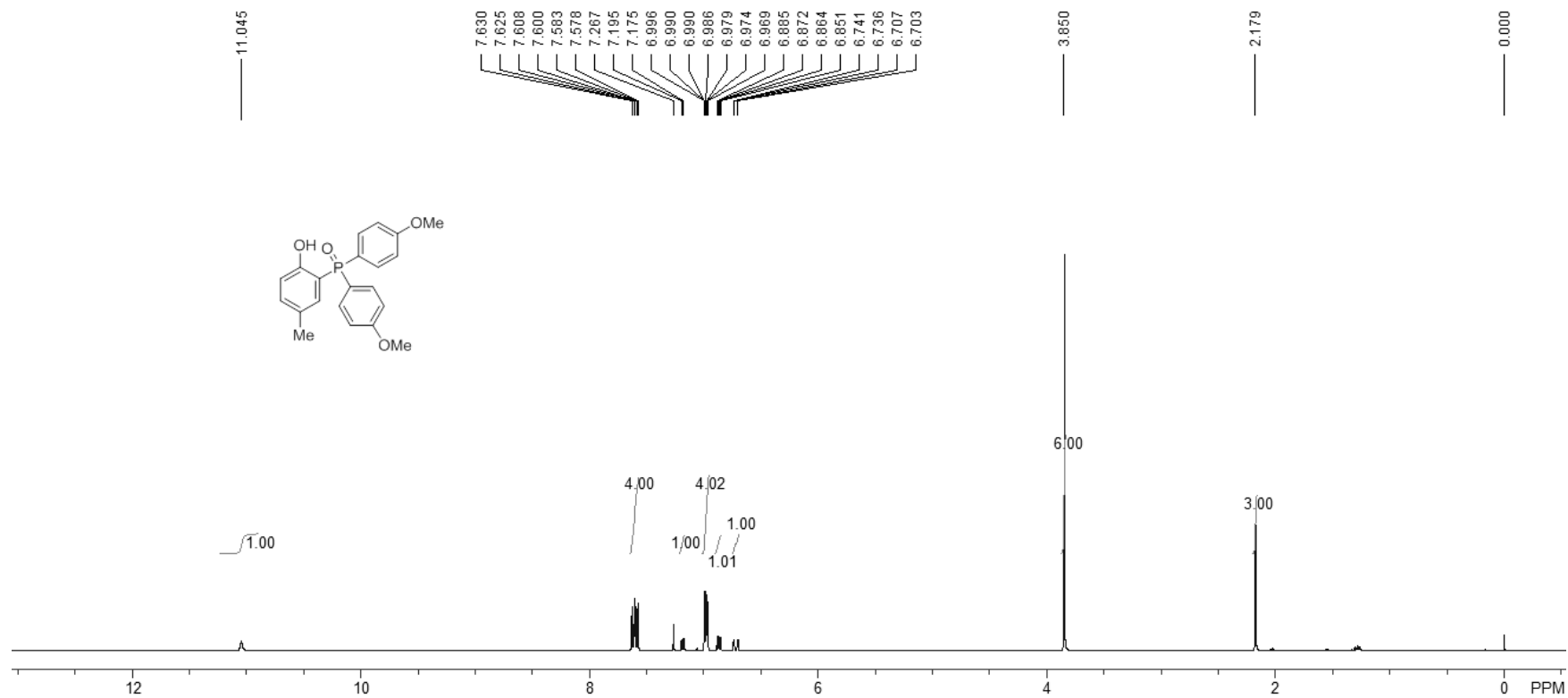
¹³C NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)



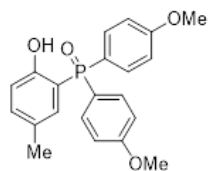
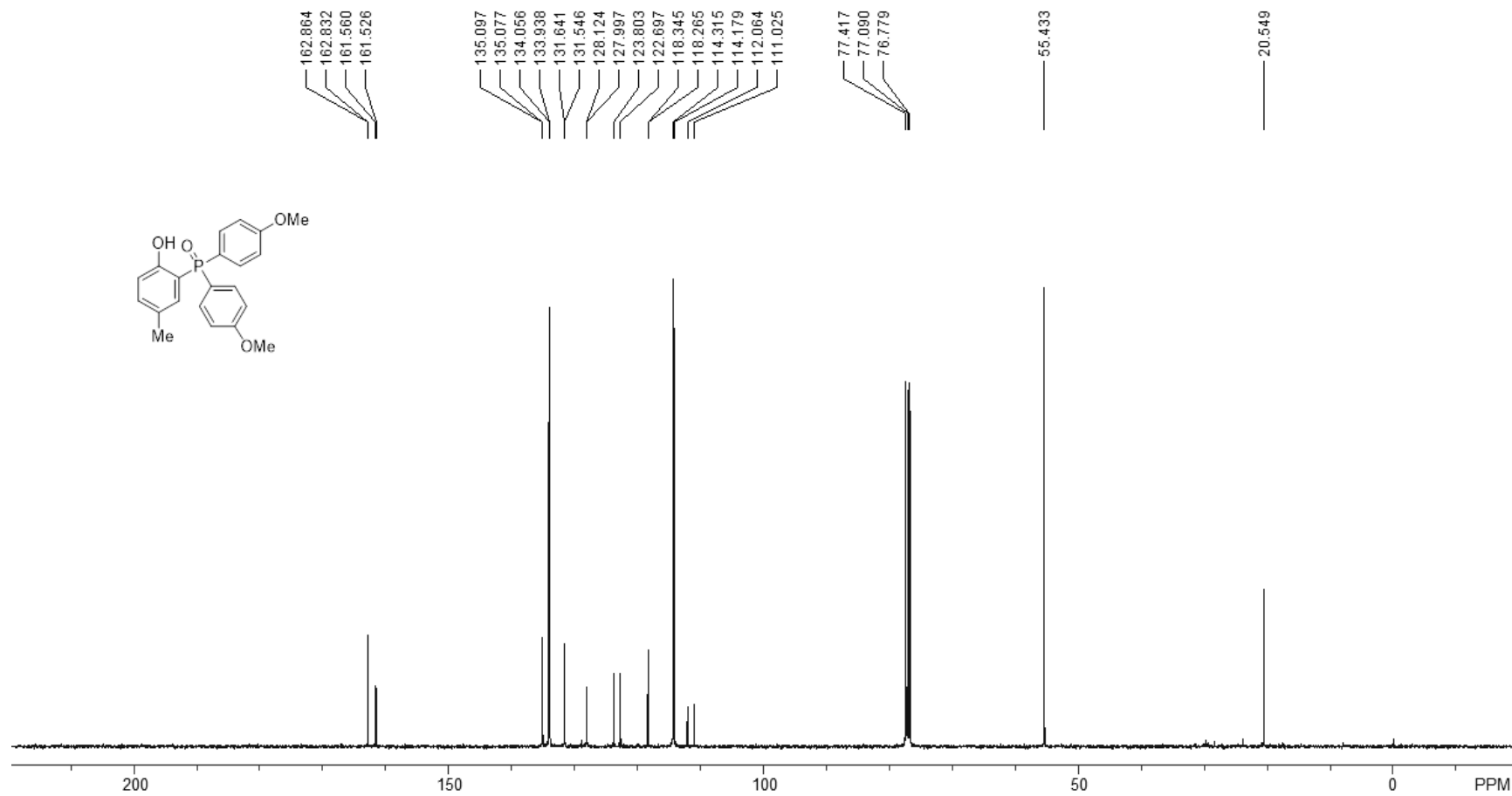
^{31}P NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)



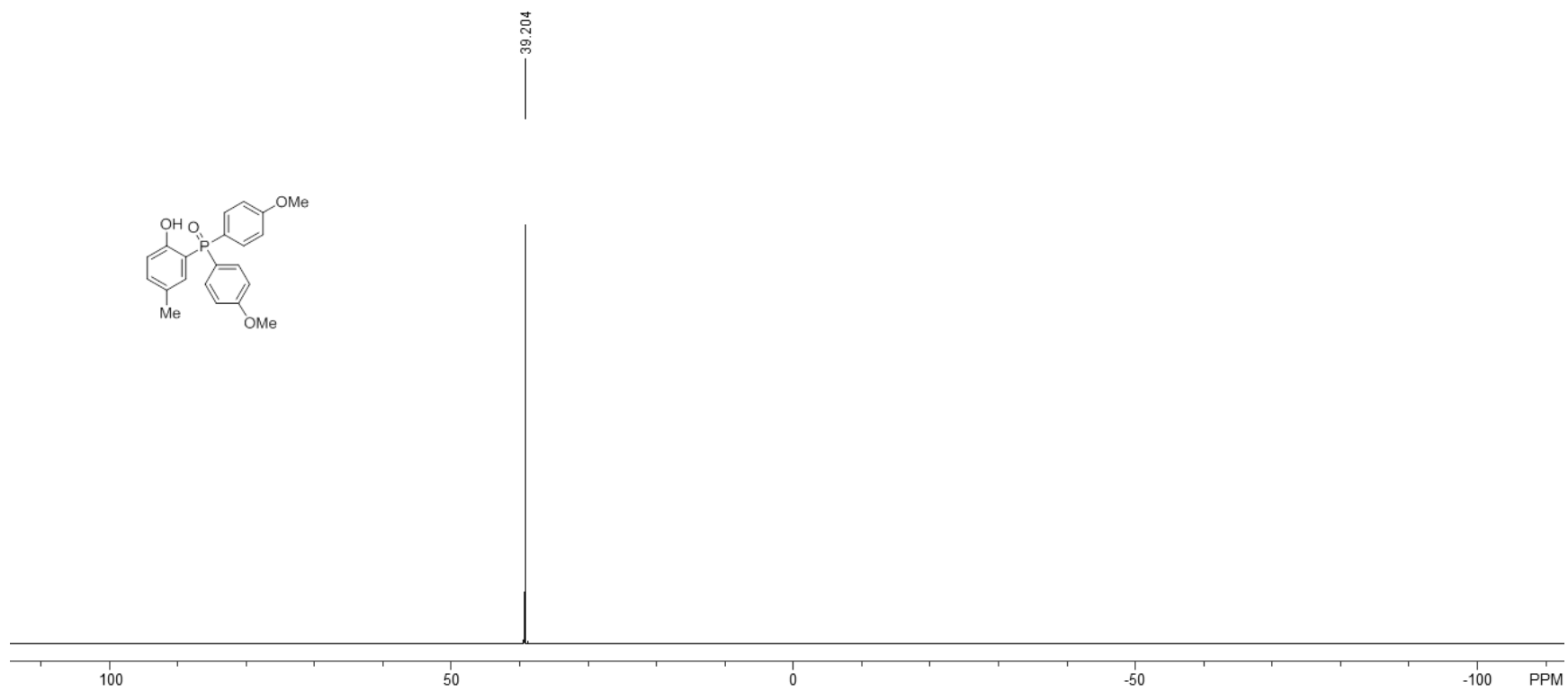
¹H NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)



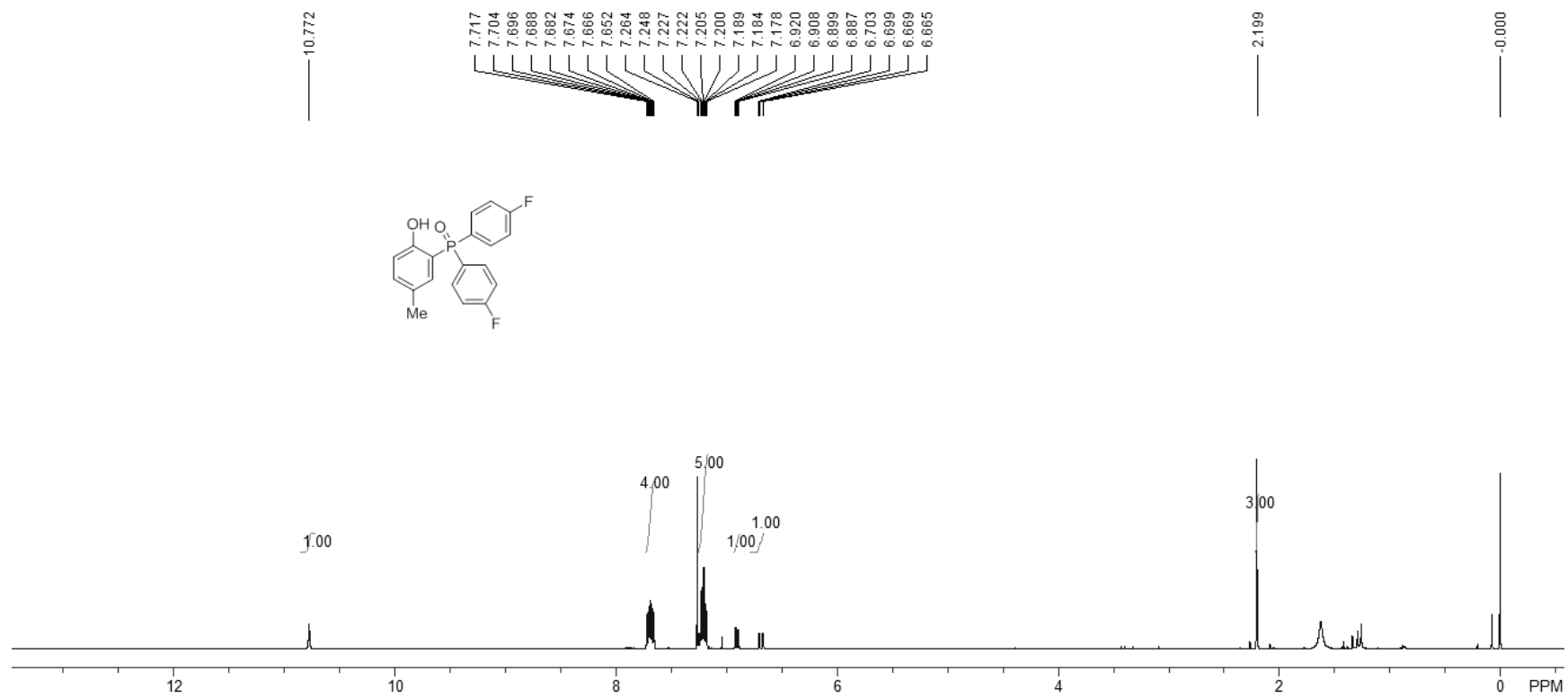
¹³C NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)



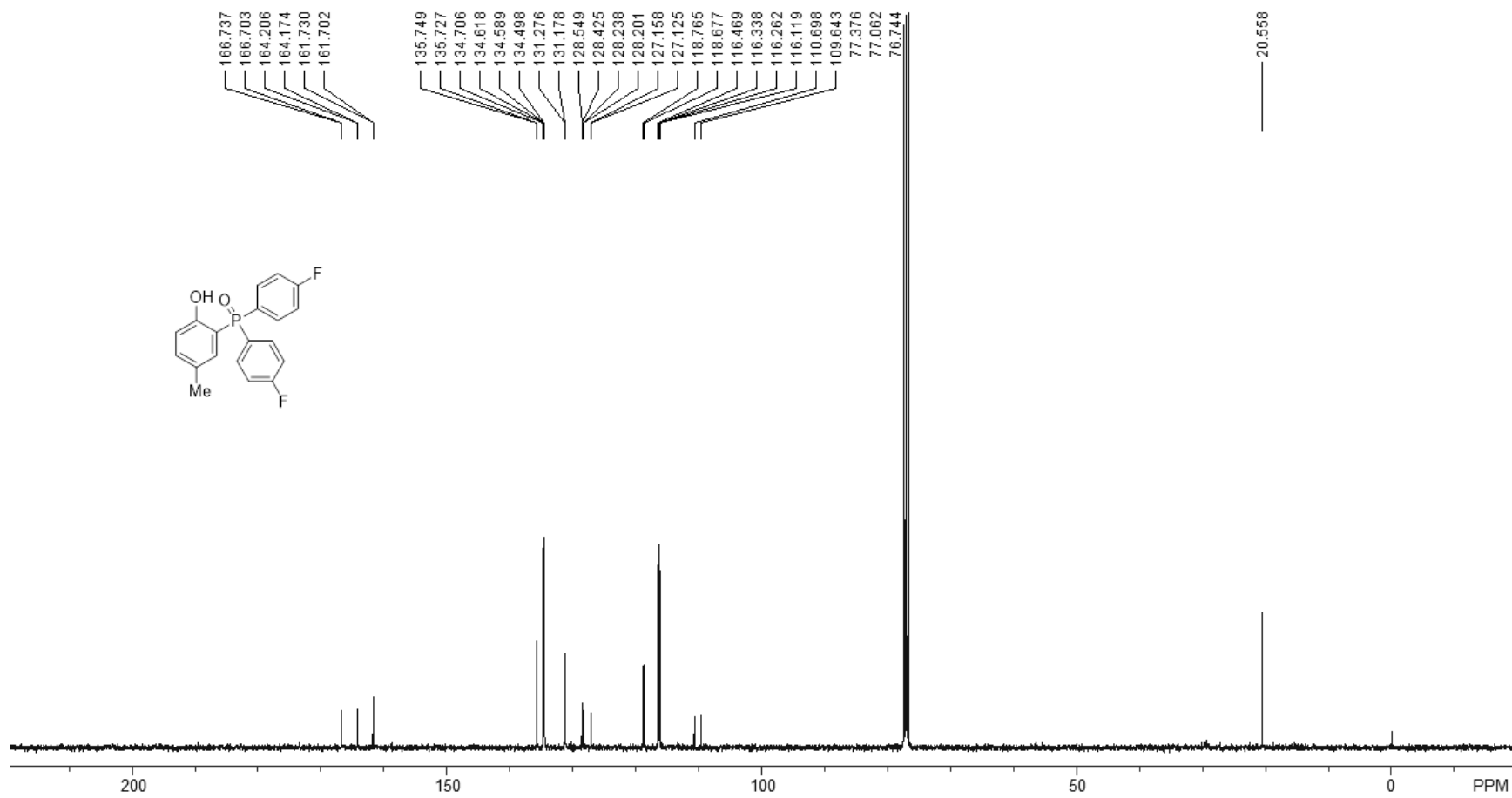
^{31}P NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)



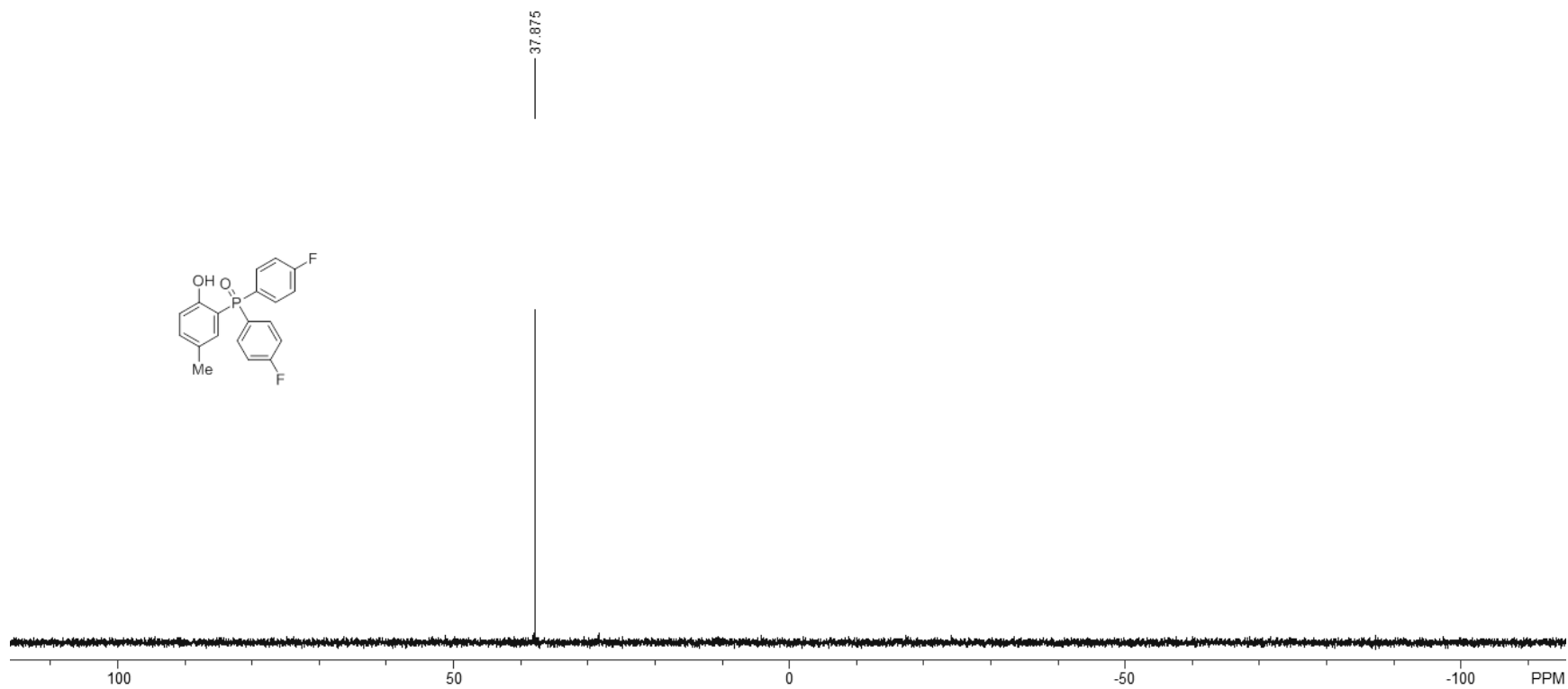
¹H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)



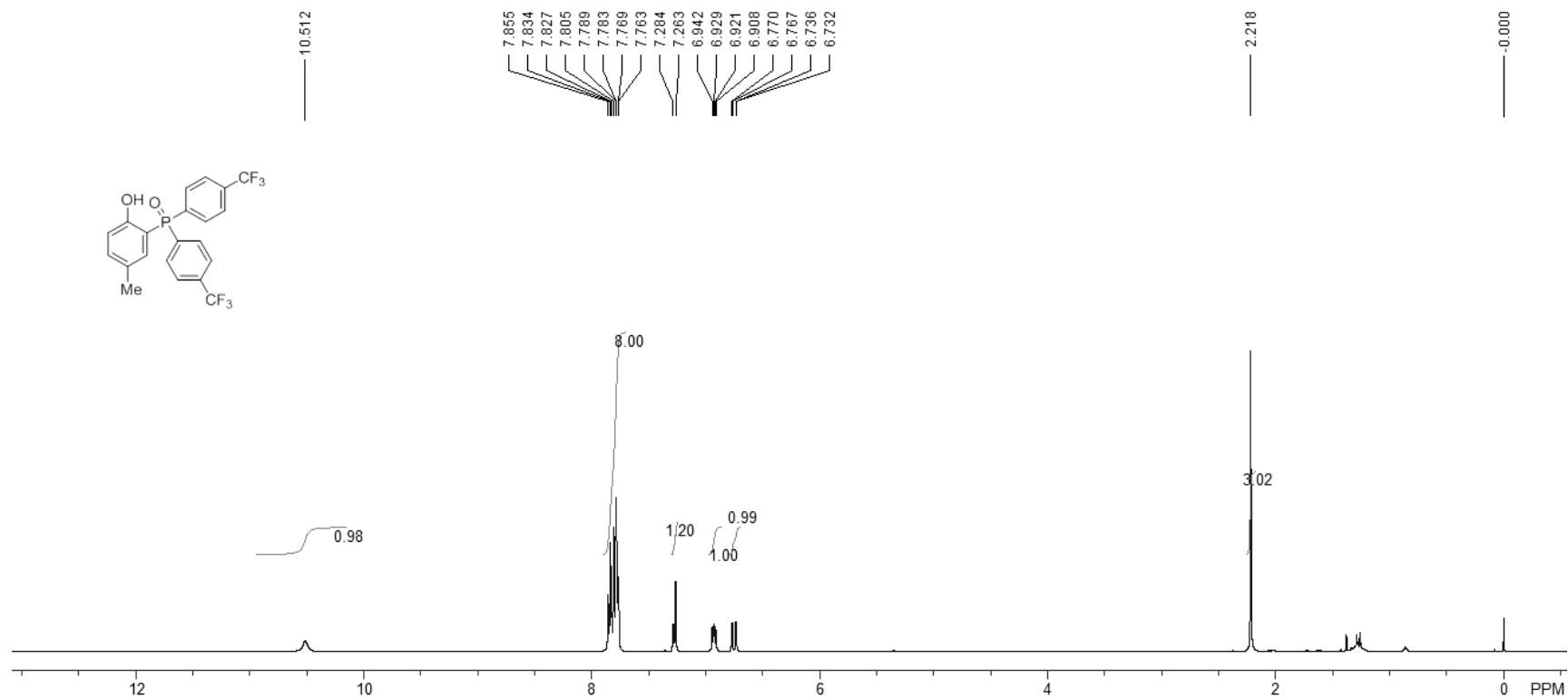
¹³C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)



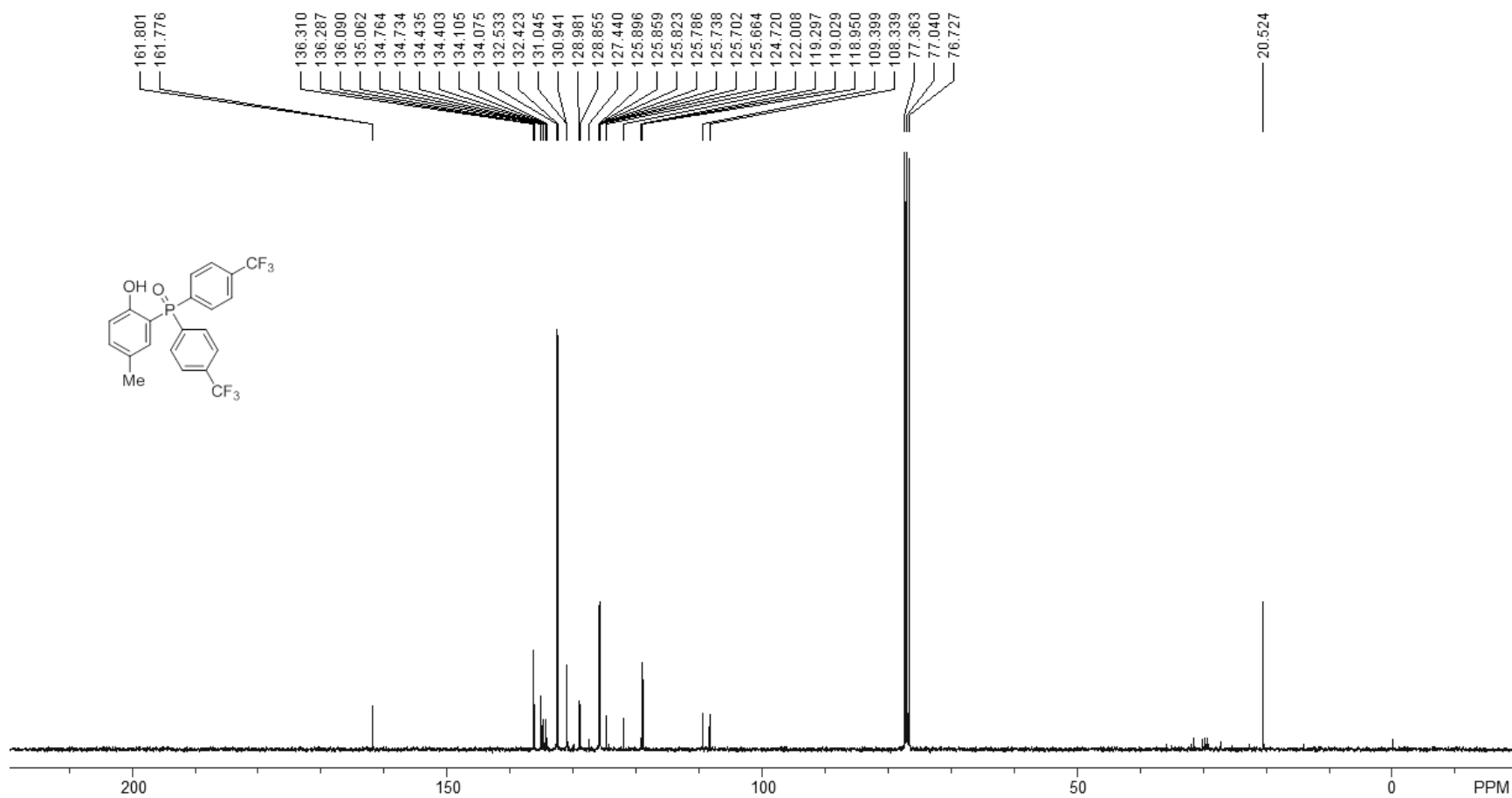
^{31}P NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)



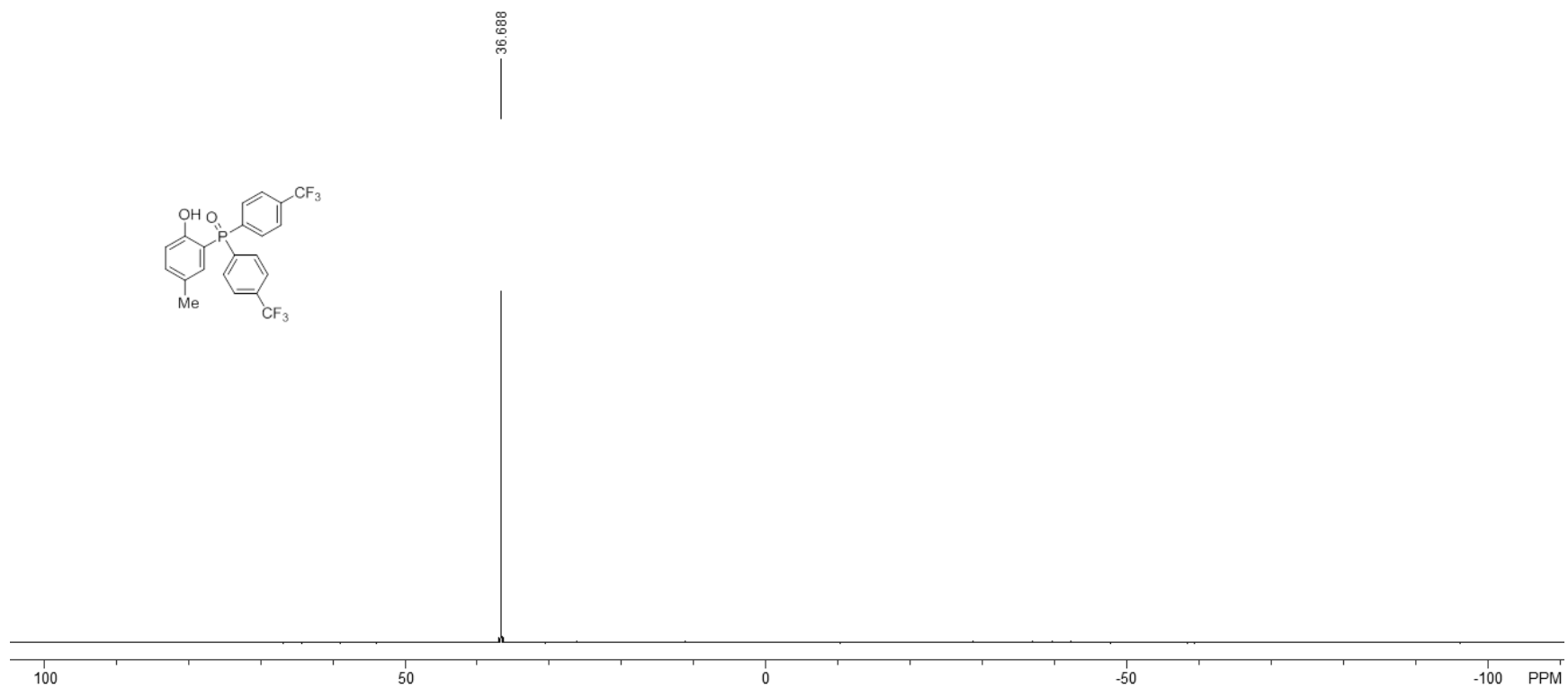
¹H NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)



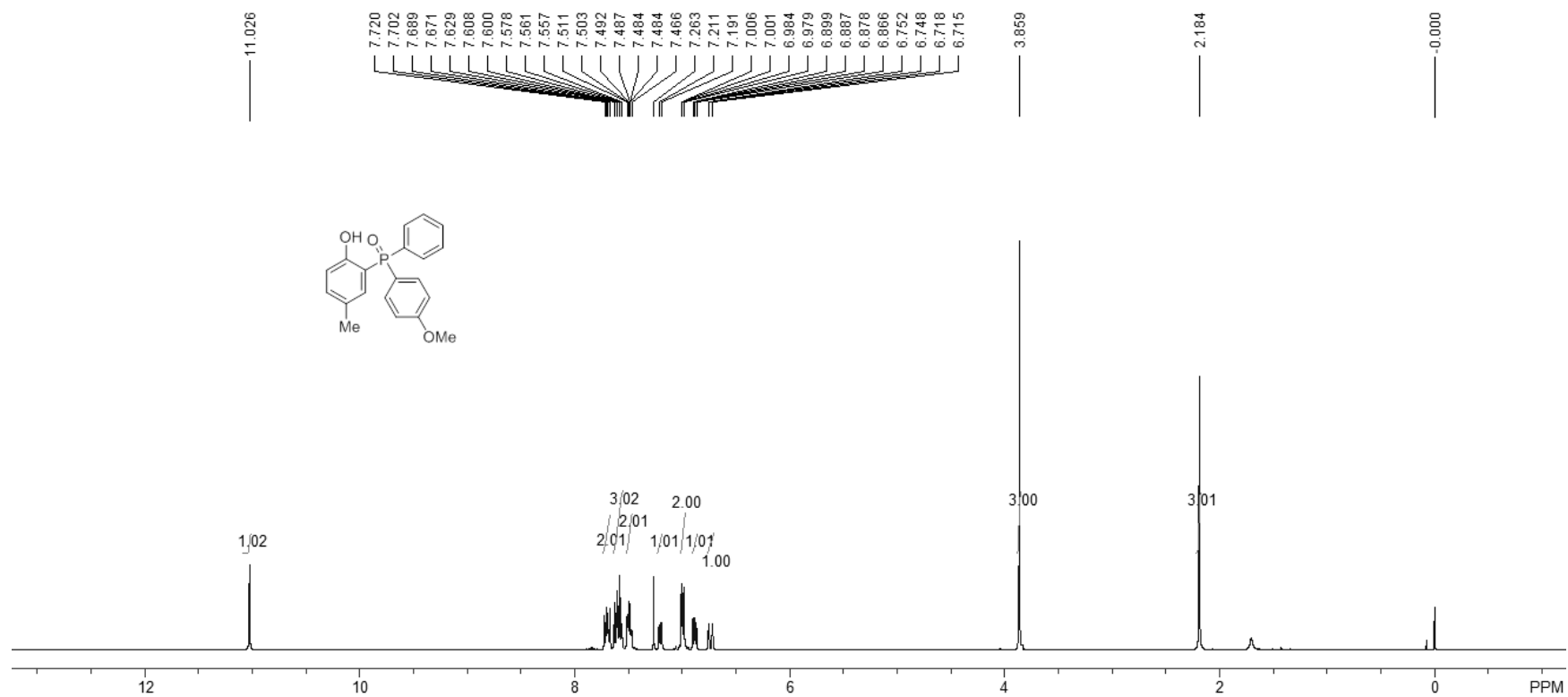
¹³C NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)



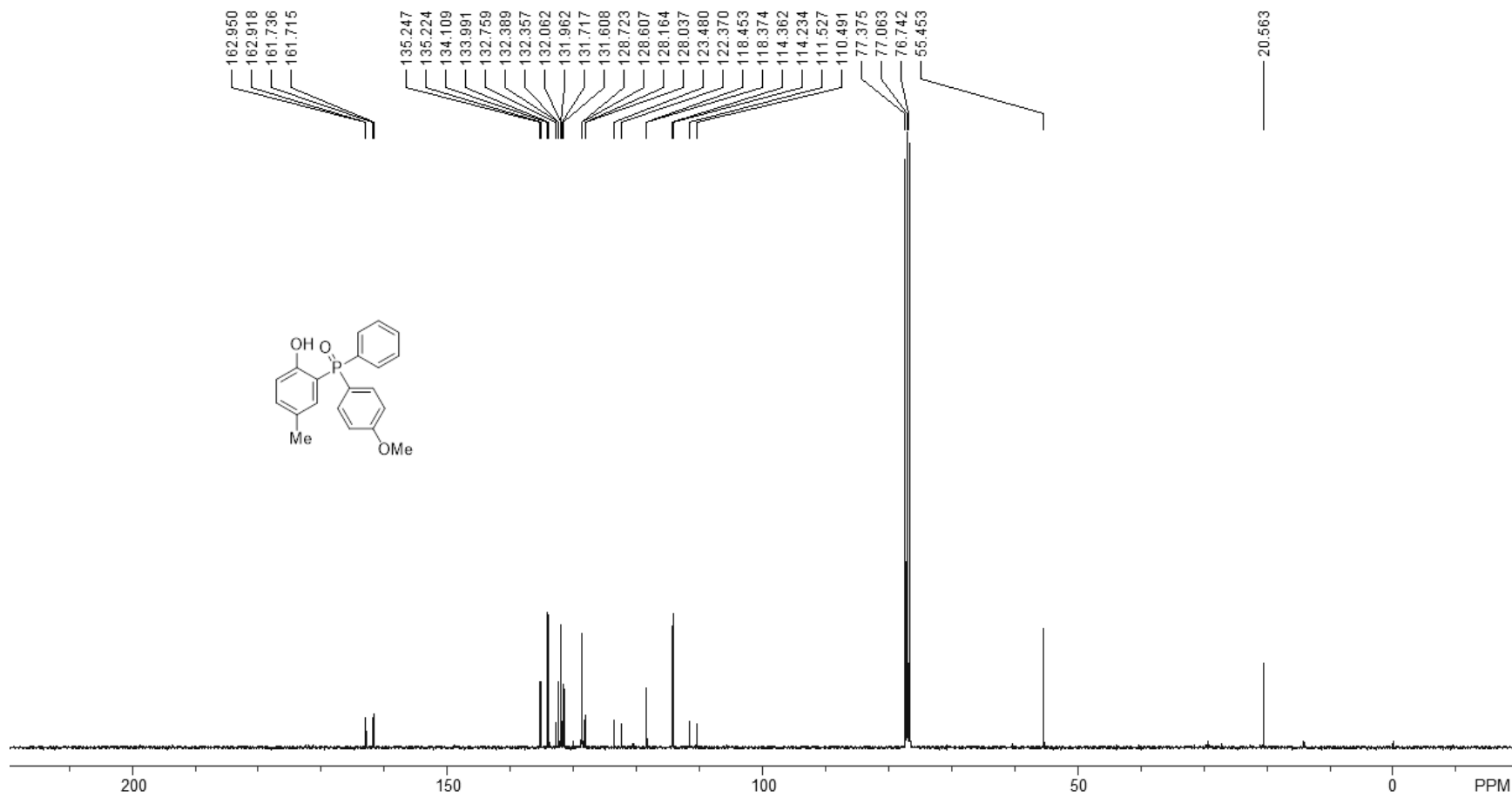
^{31}P NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)



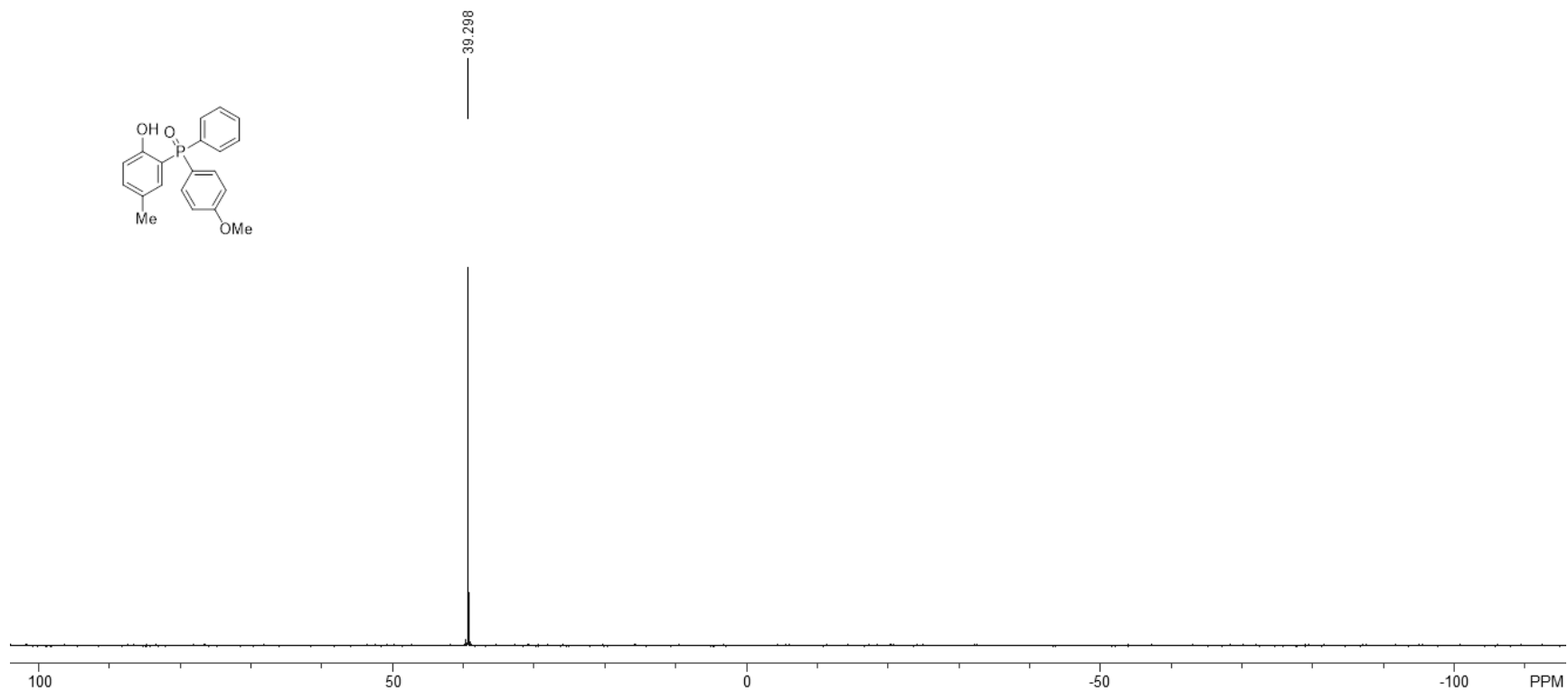
^1H NMR of (2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3af)



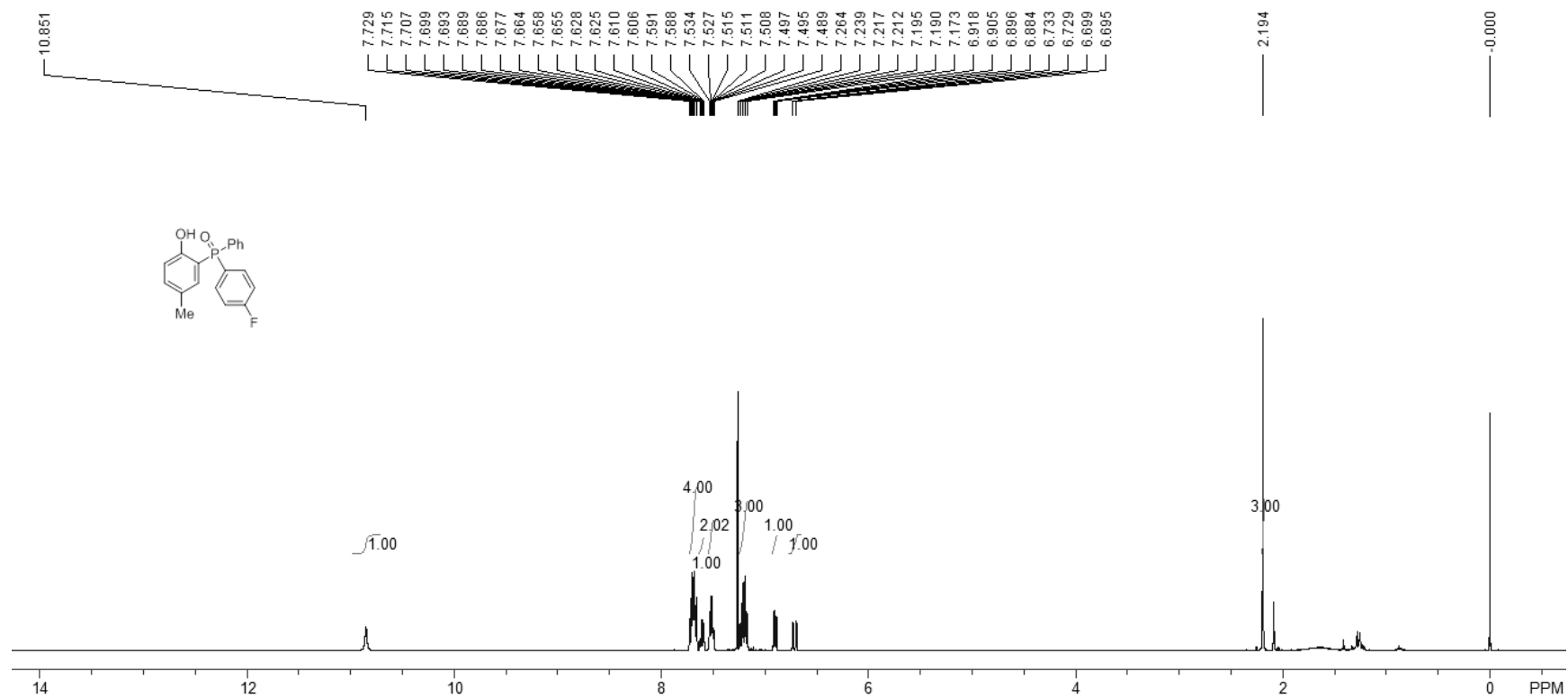
¹³C NMR of (2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3af)



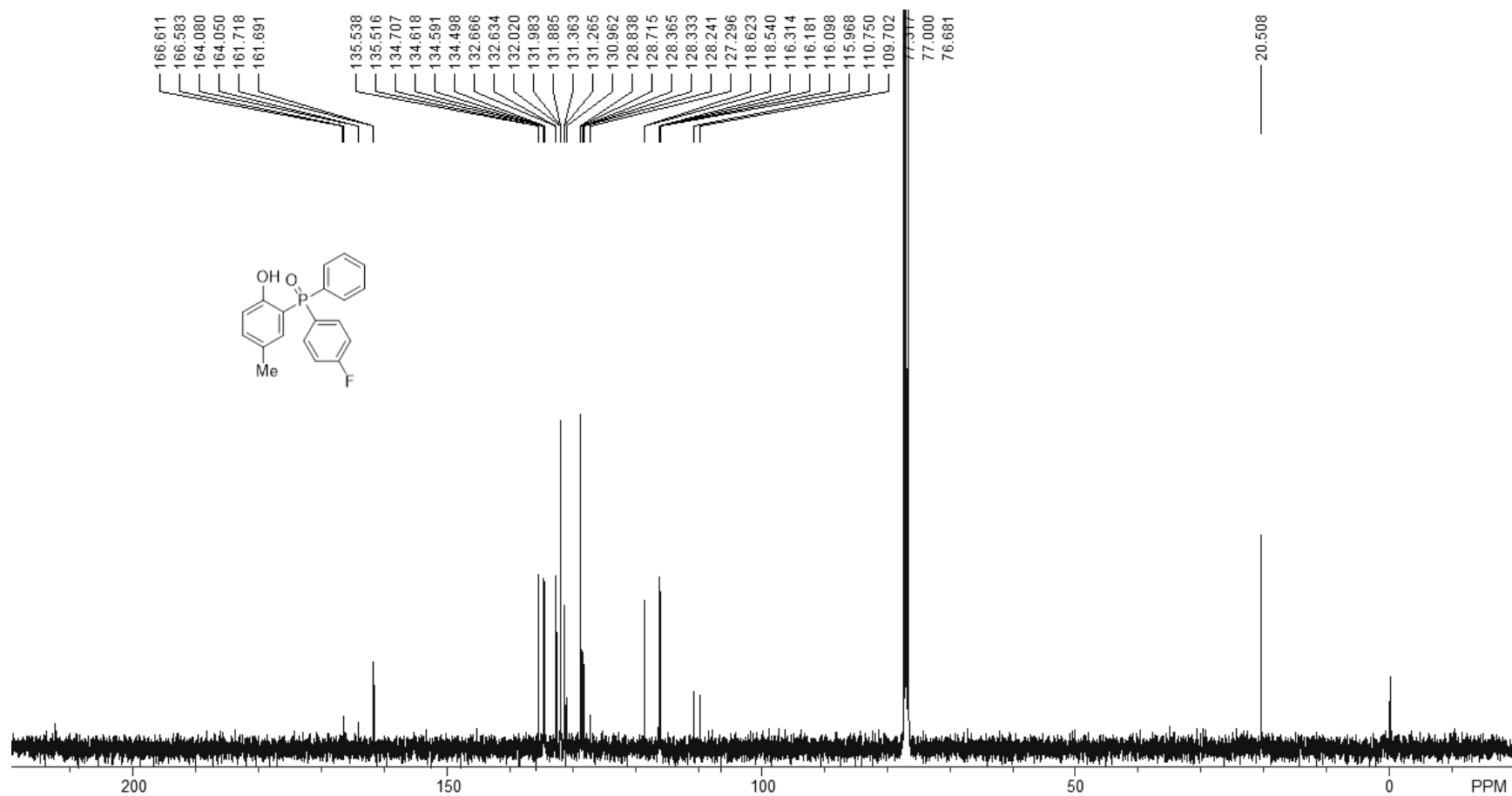
^{31}P NMR of (2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3af)



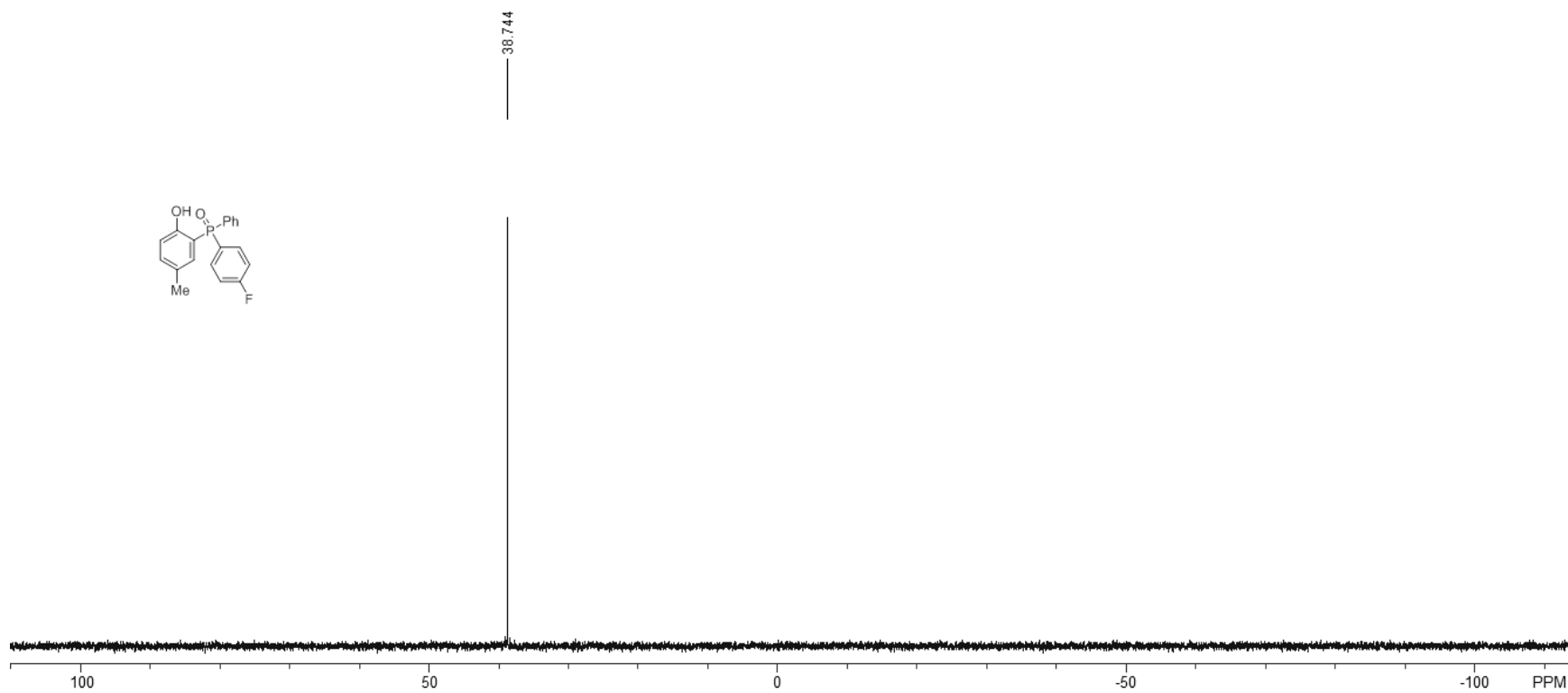
^1H NMR of (4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3ag)



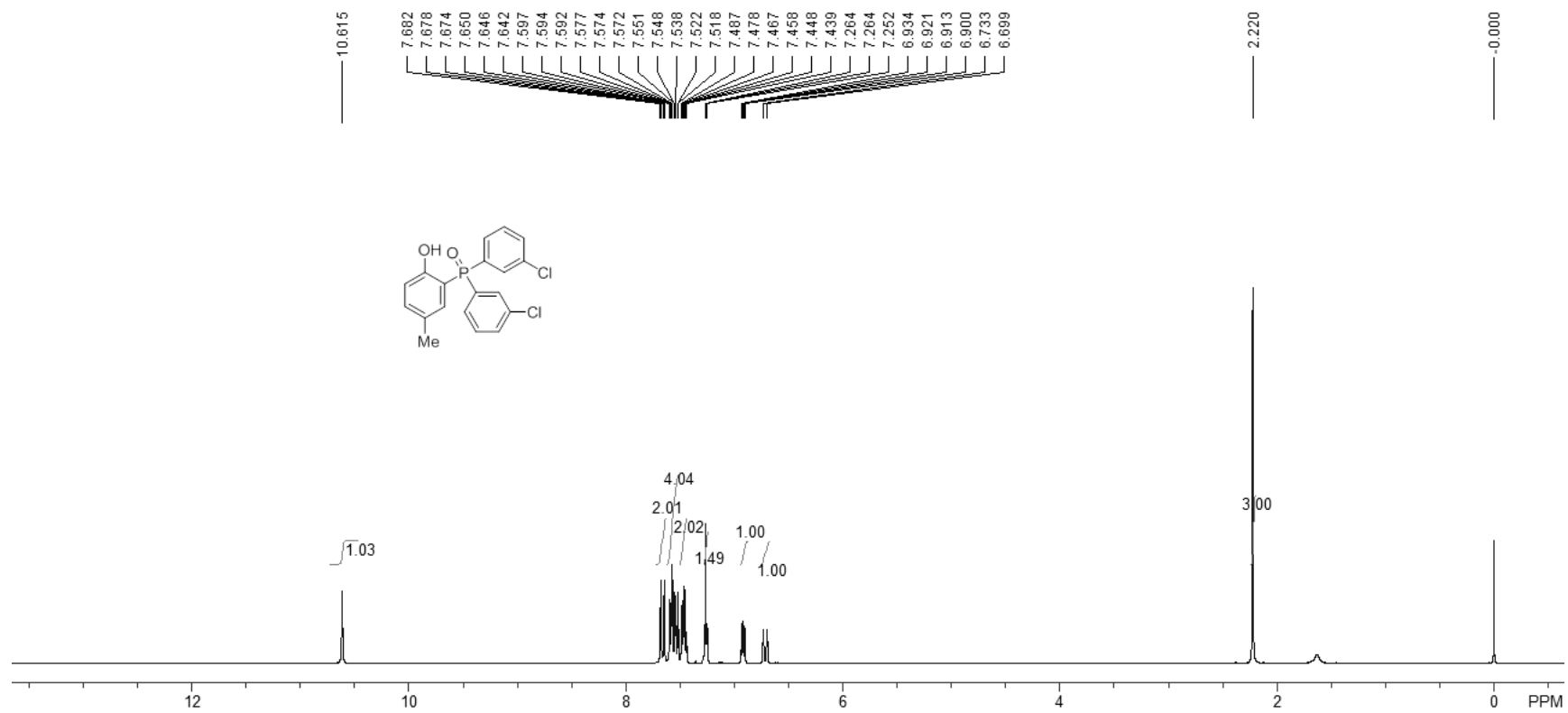
¹³C NMR of (4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3ag)



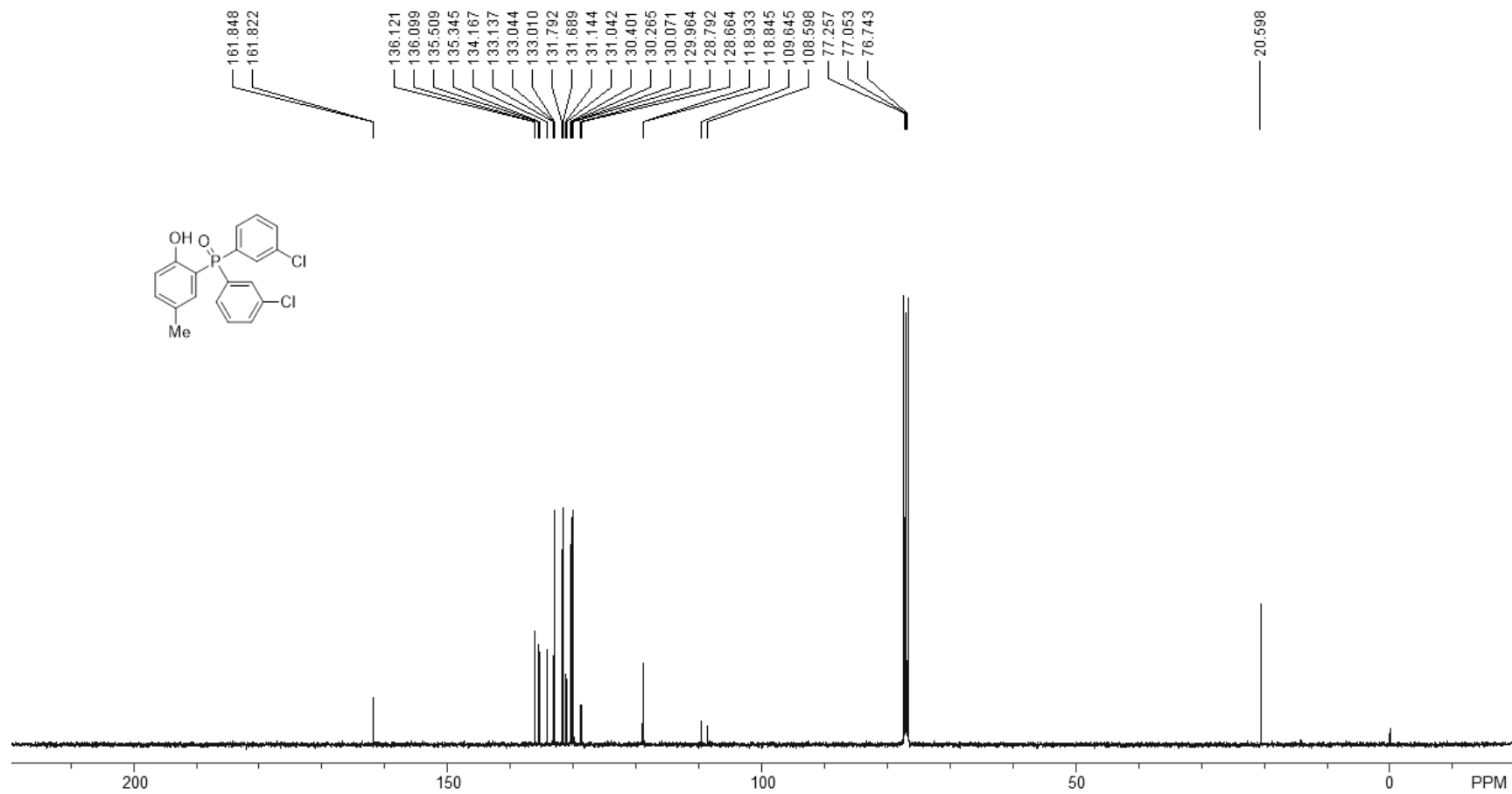
^{31}P NMR of (4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3ag)



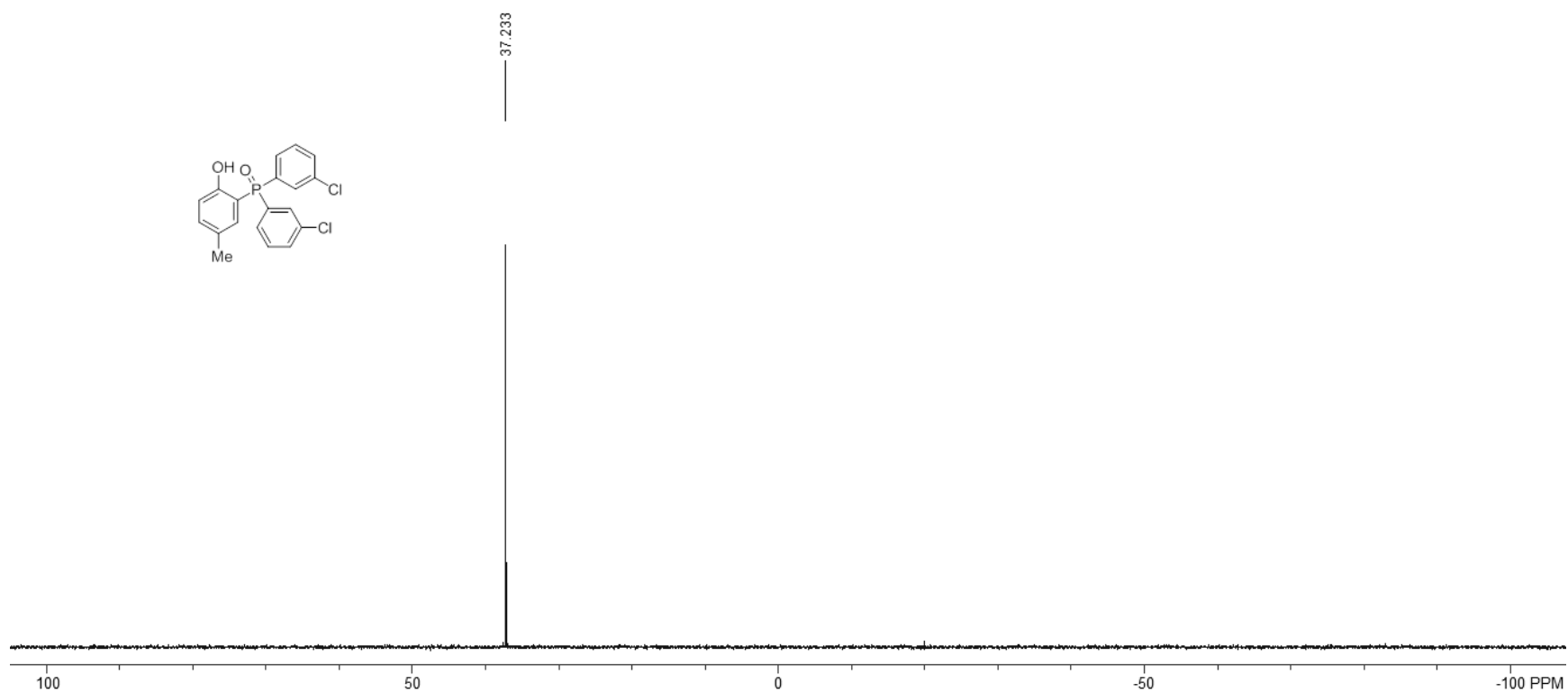
¹H NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)



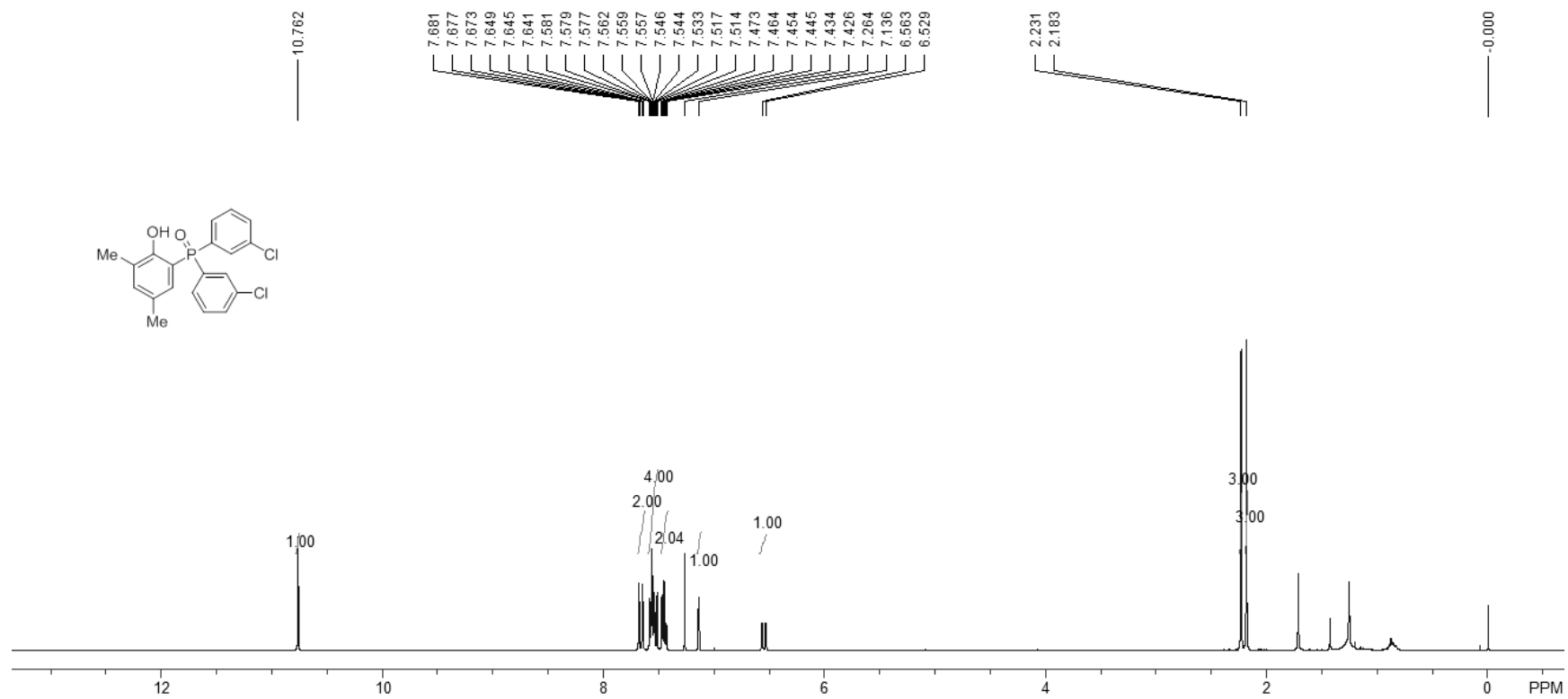
¹³C NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)



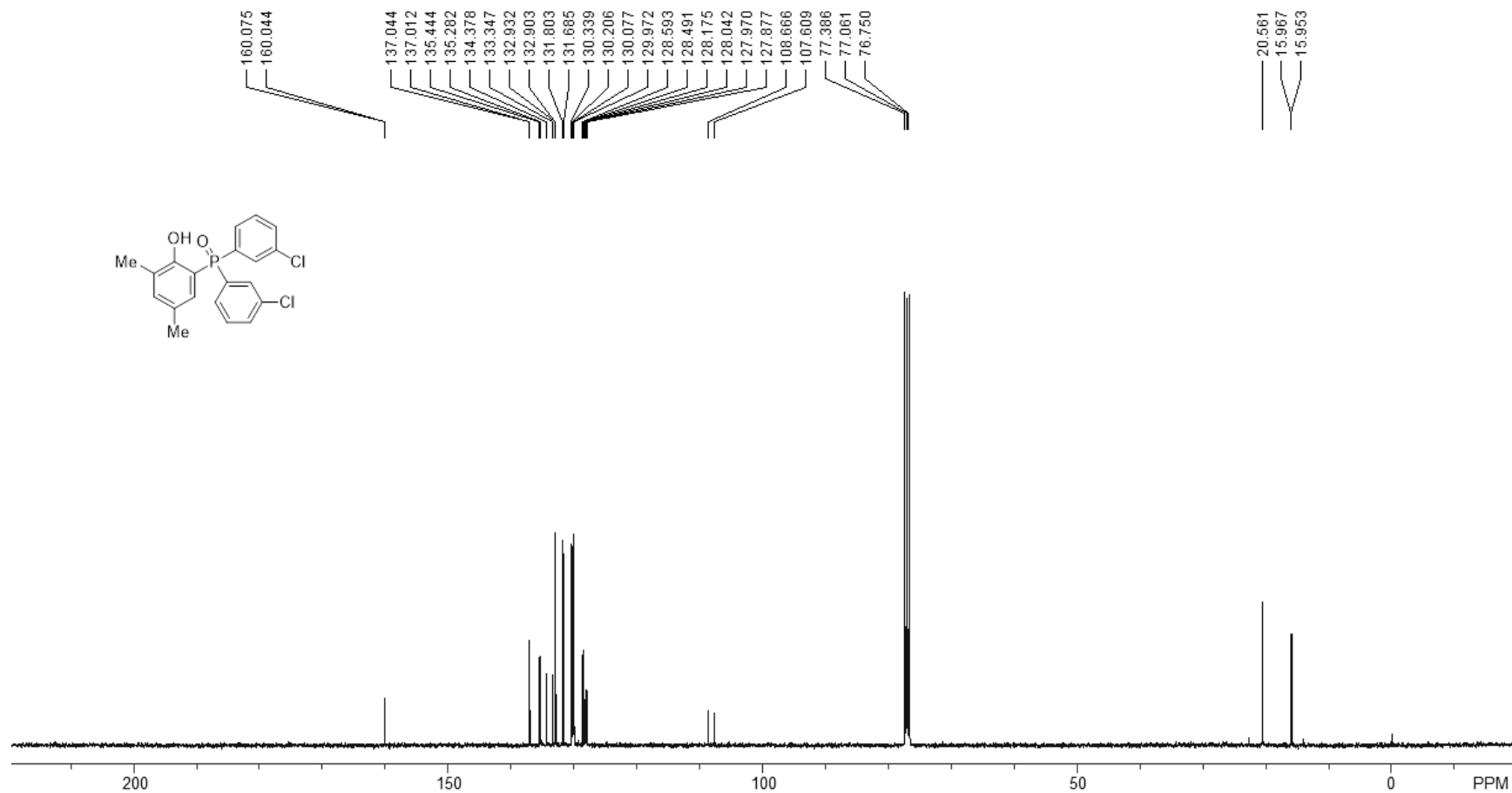
^{31}P NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)



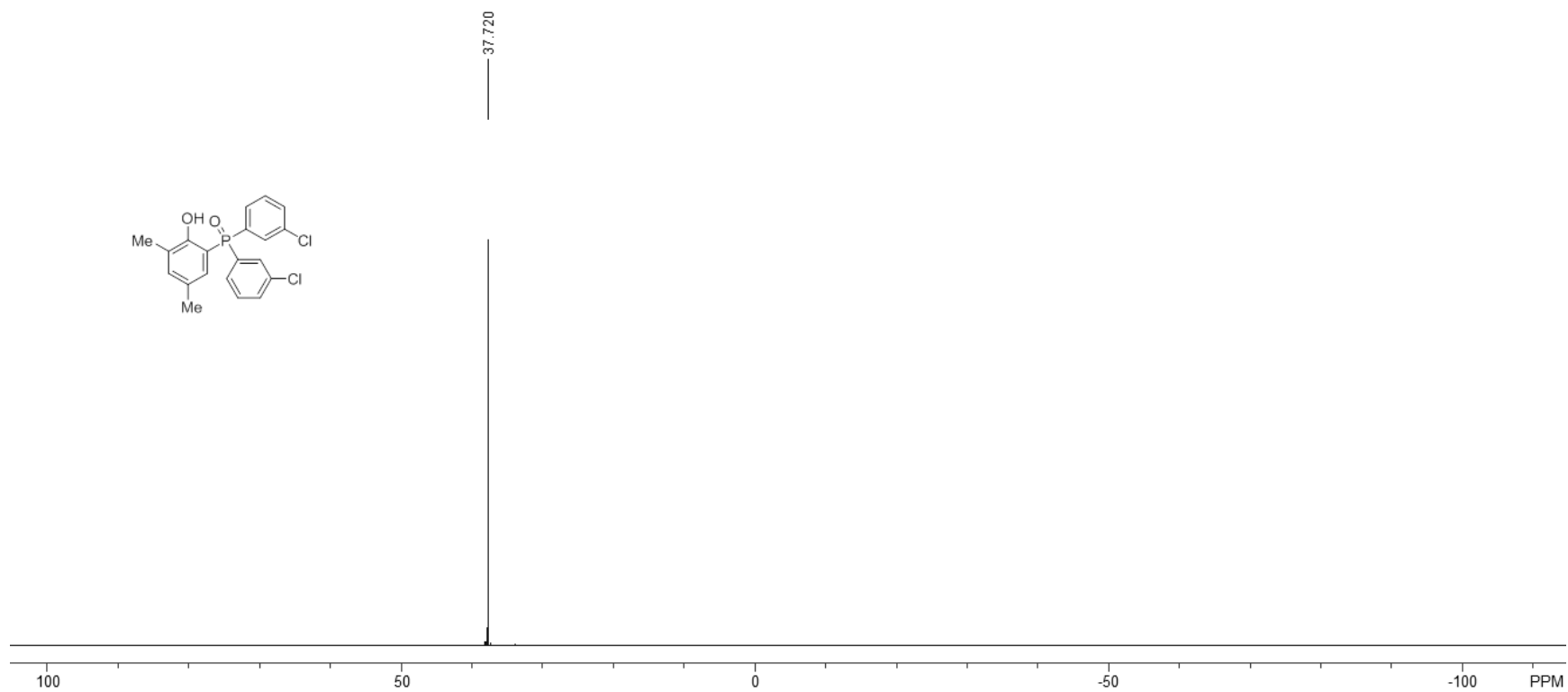
^1H NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)



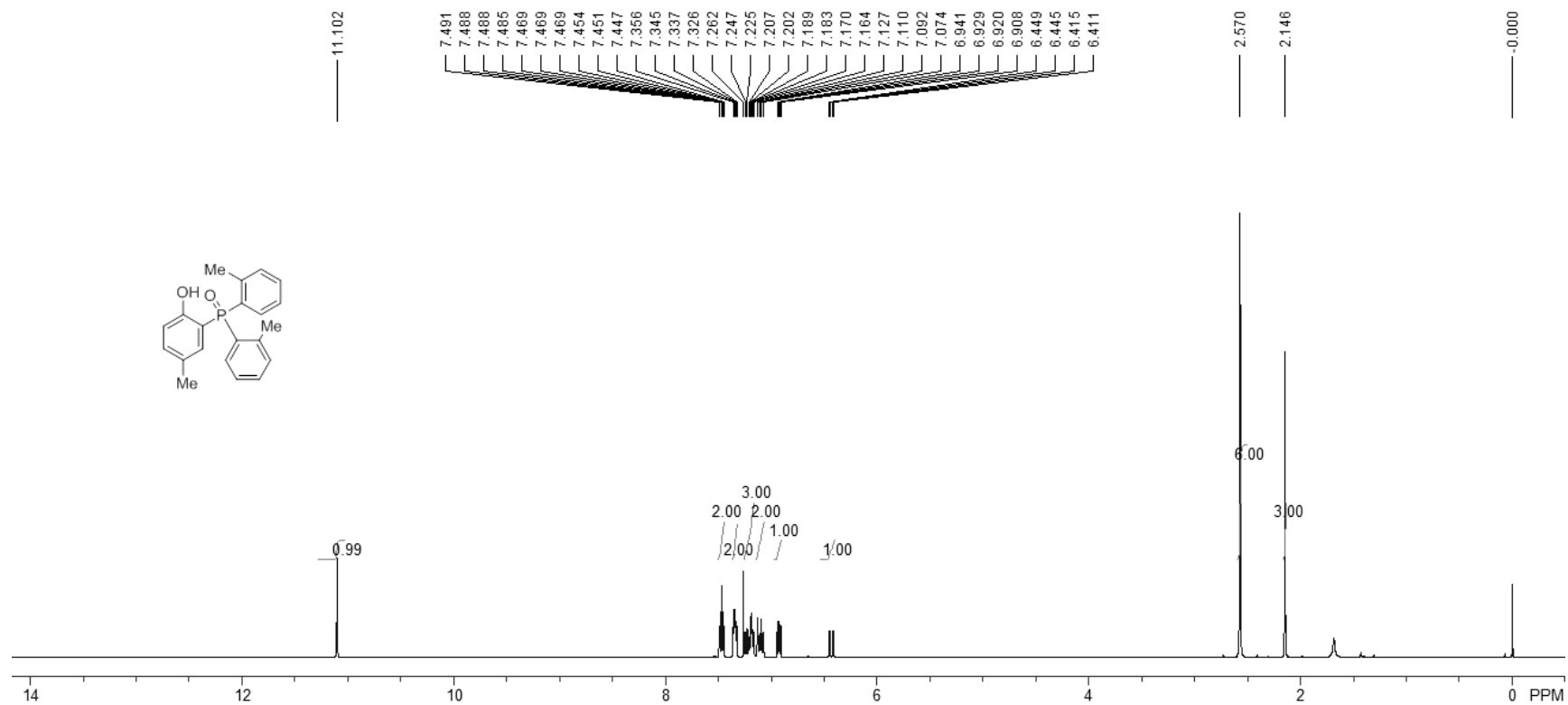
¹³C NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)



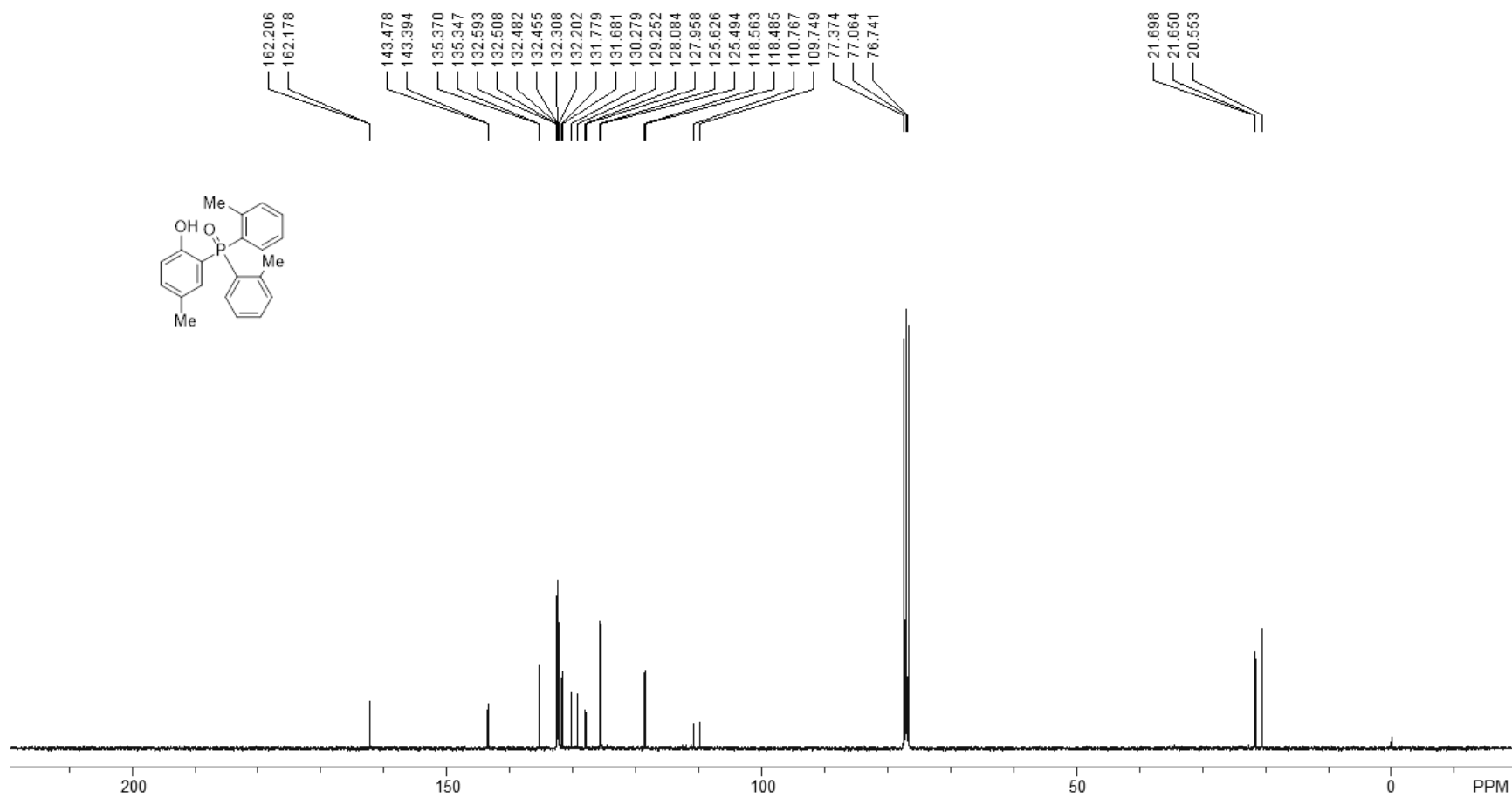
^{31}P NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)



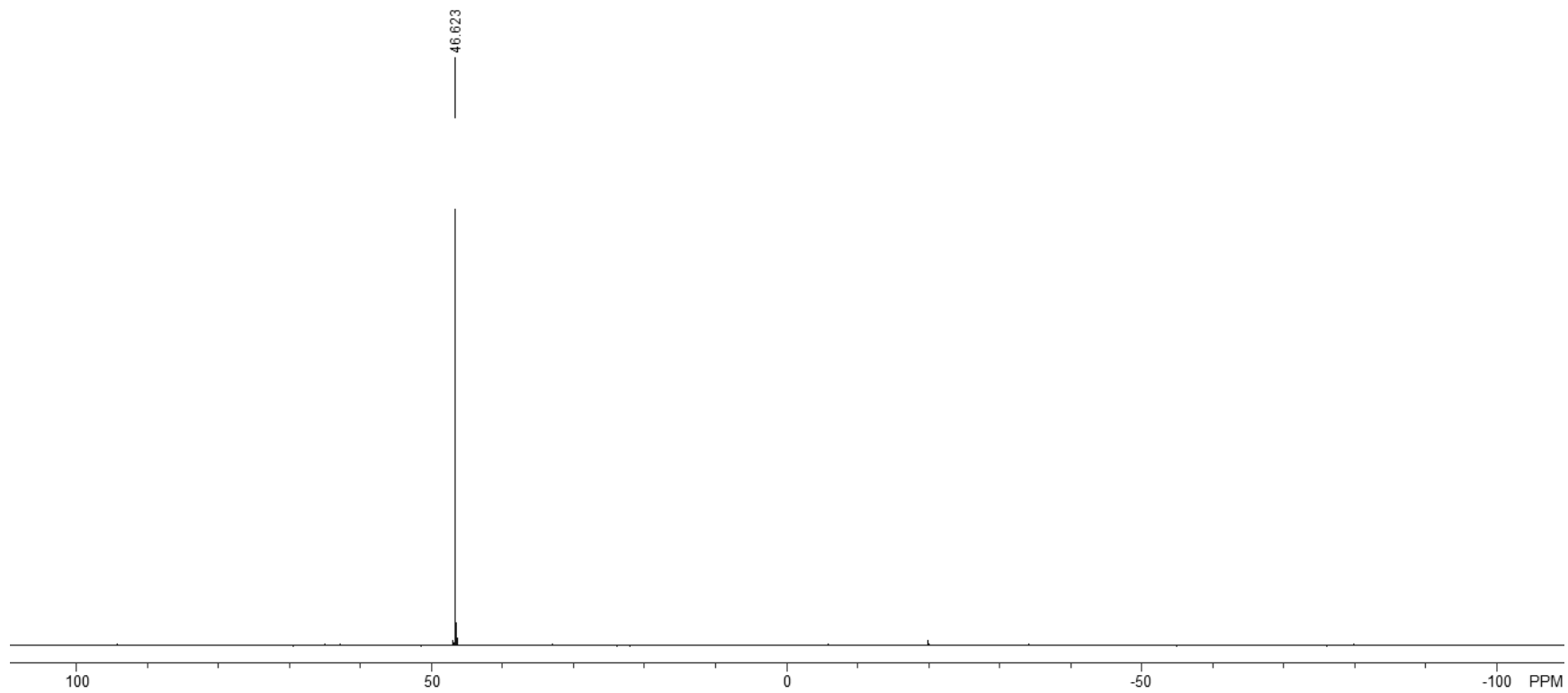
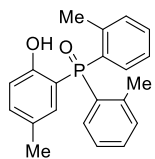
¹H NMR of (2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ai)



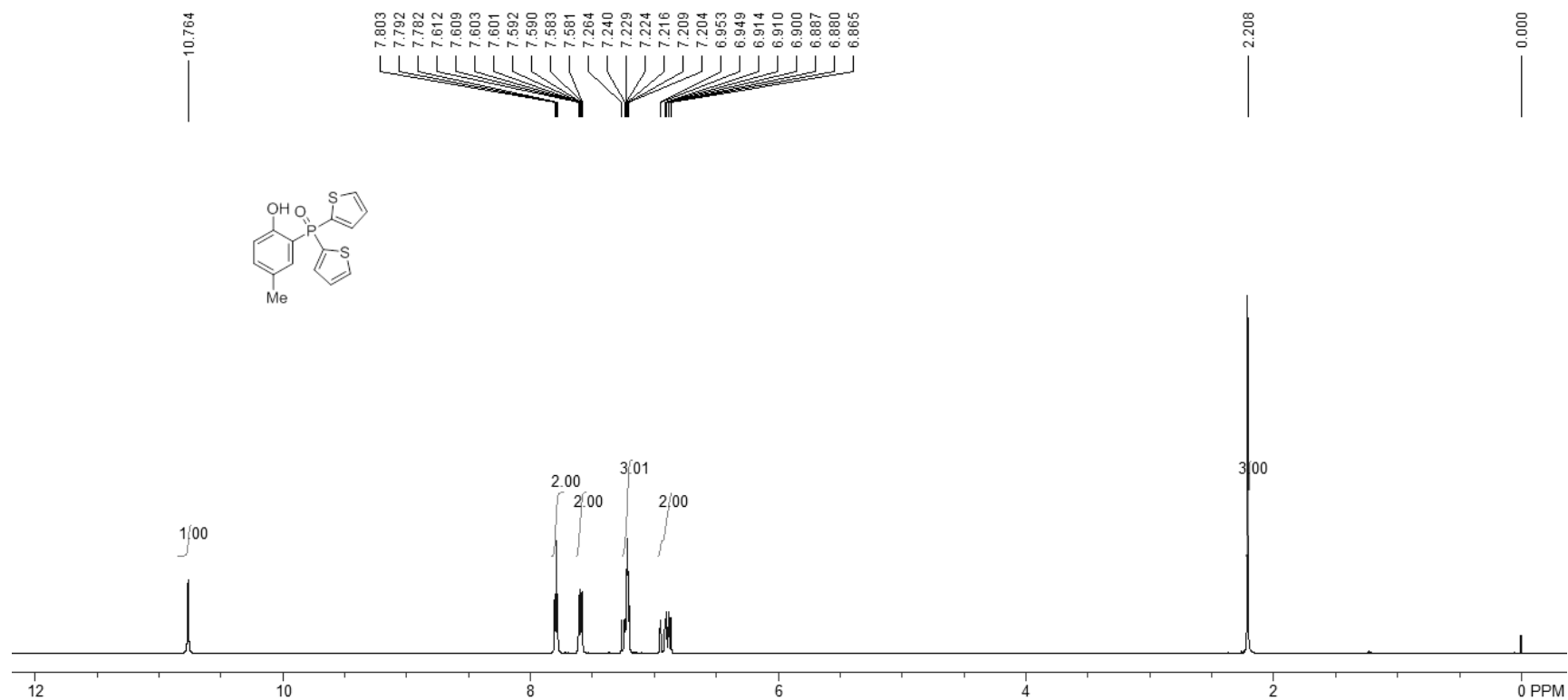
^{13}C NMR of (2-hydroxy-5-methylphenyl)di-*o*-tolylphosphine oxide (3ai)



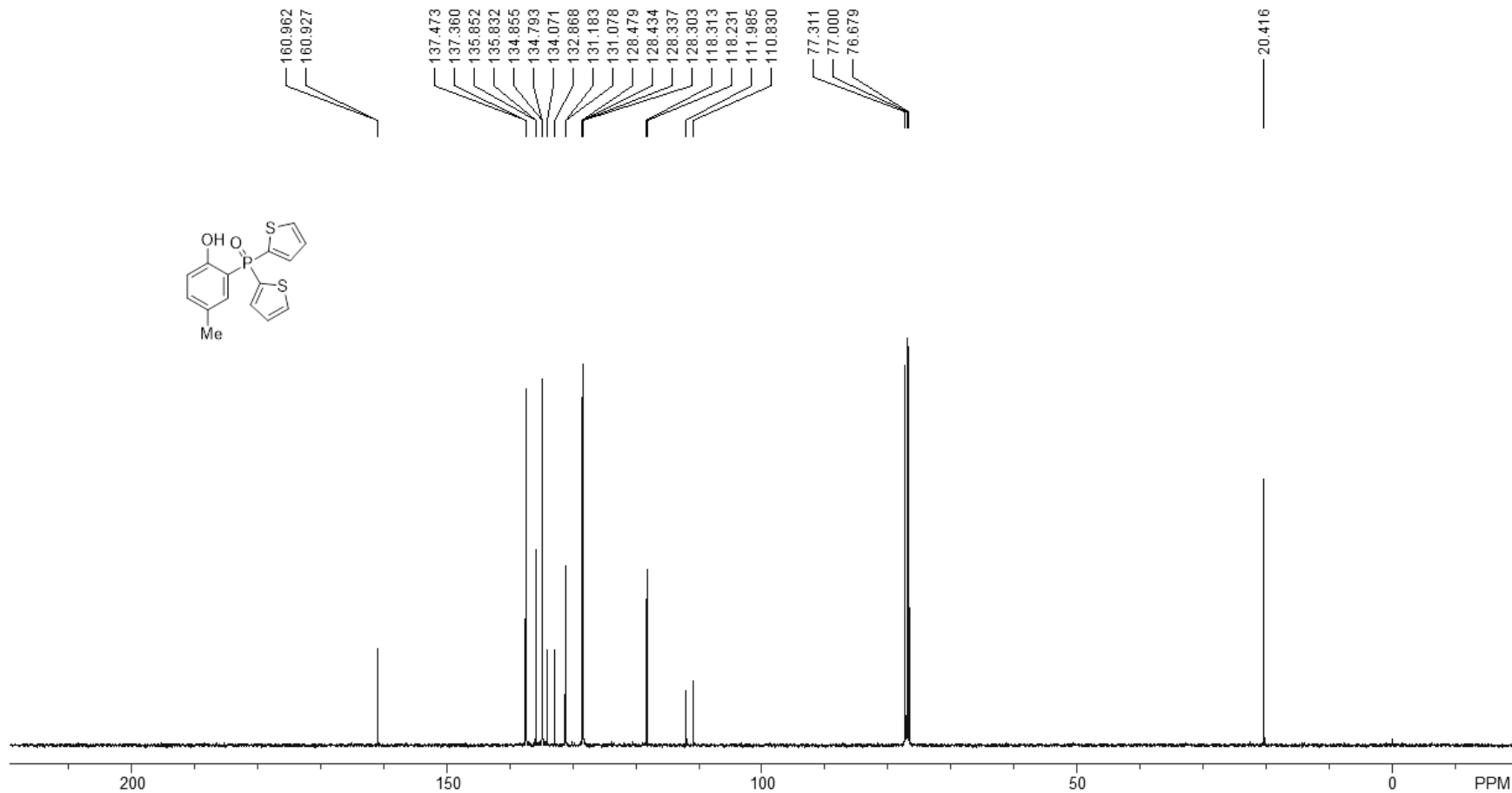
^{31}P NMR of (2-hydroxy-5-methylphenyl)di-*o*-tolylphosphine oxide (3ai)



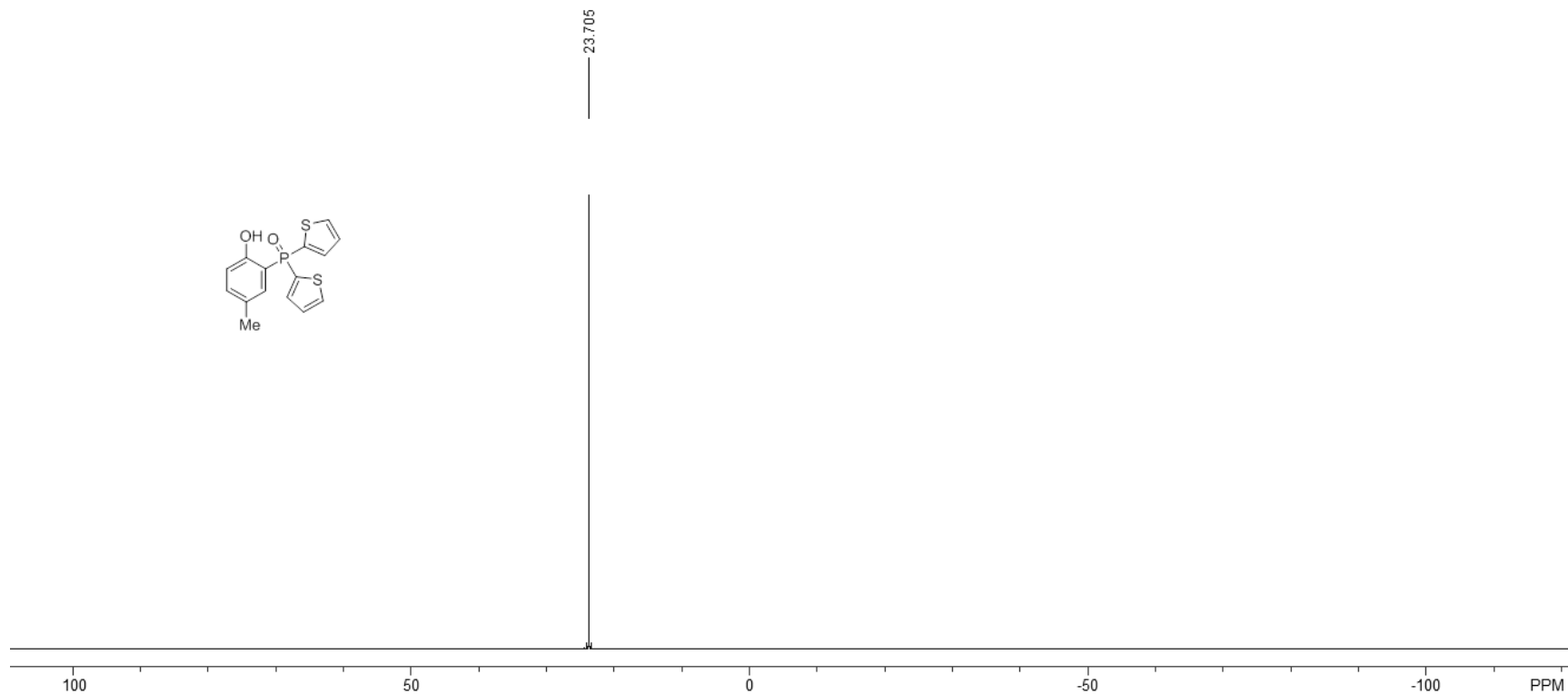
¹H NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)



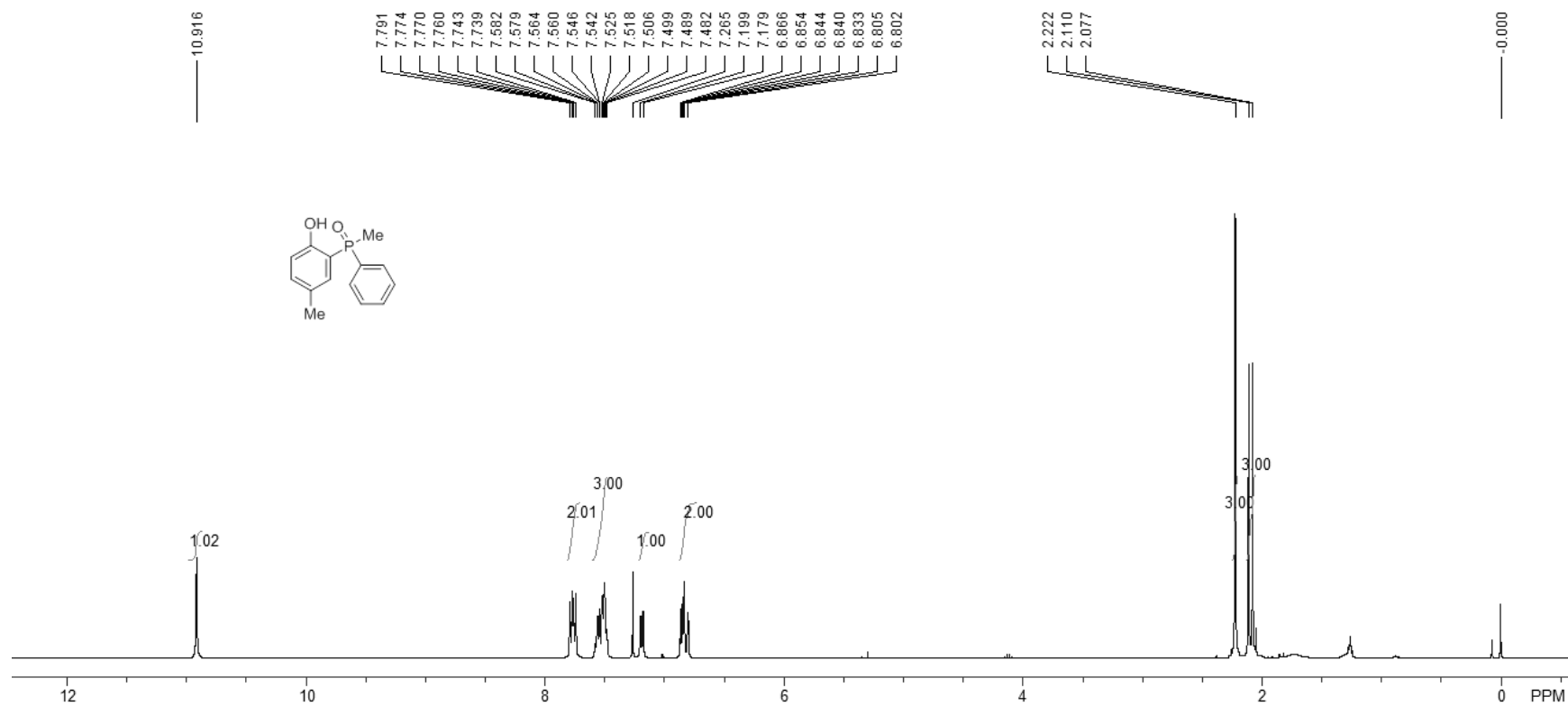
¹³C NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)



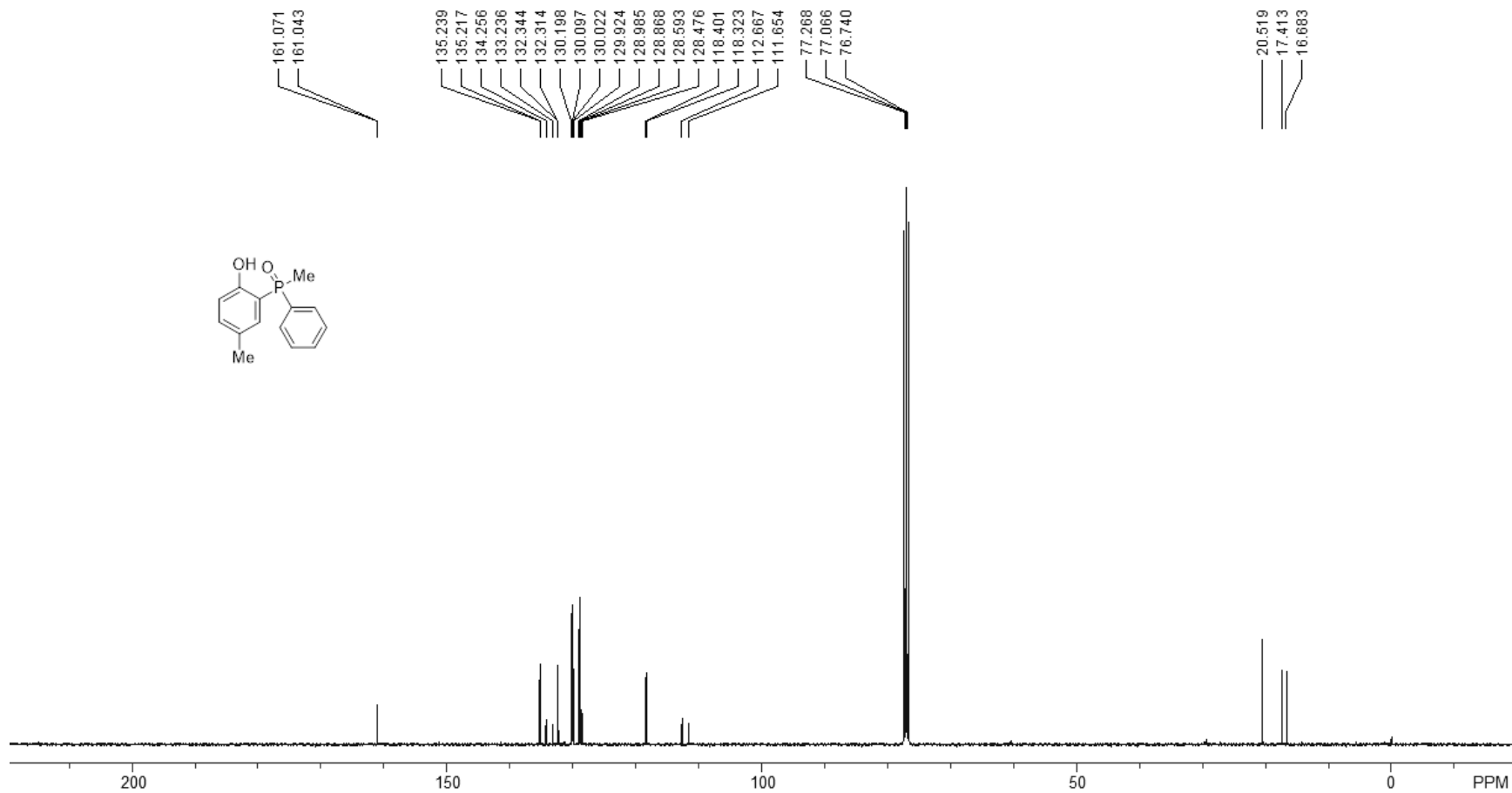
^{31}P NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)



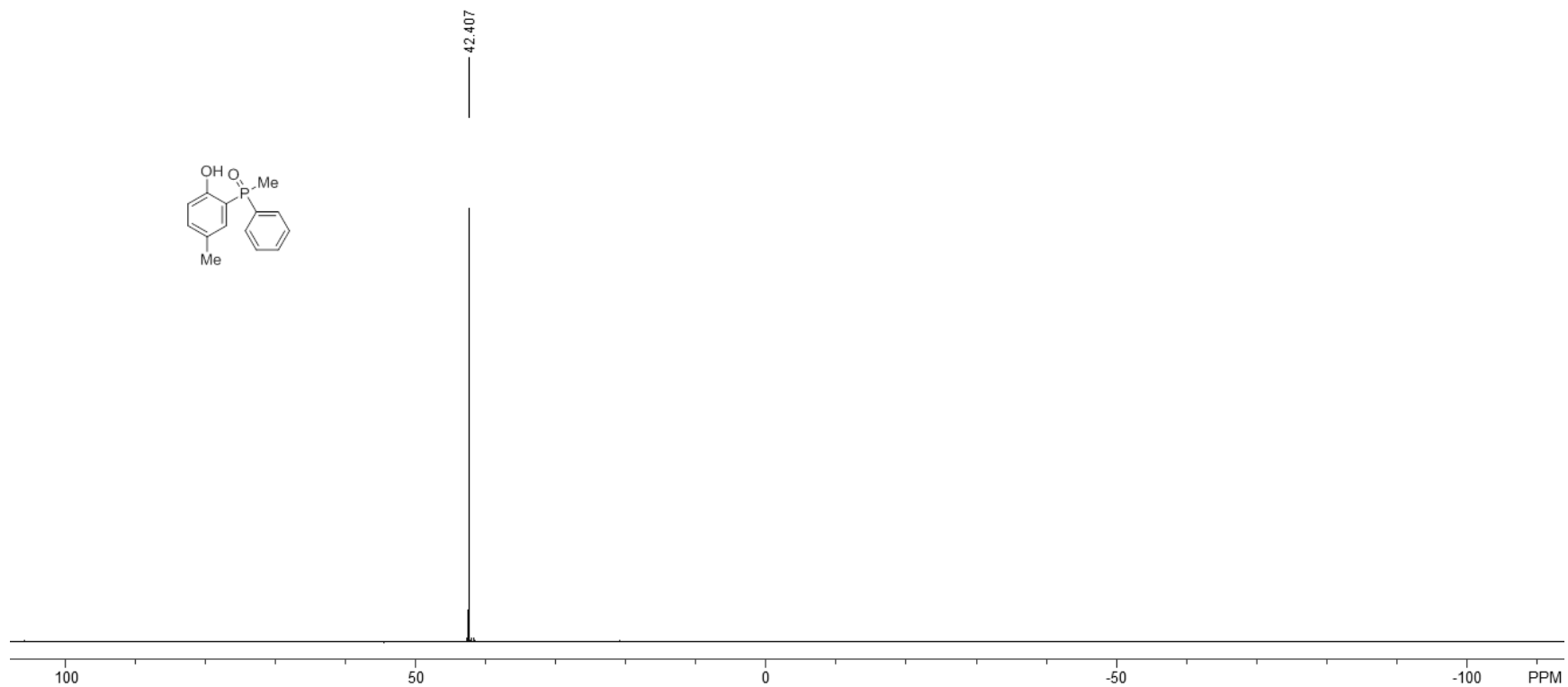
¹H NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak)



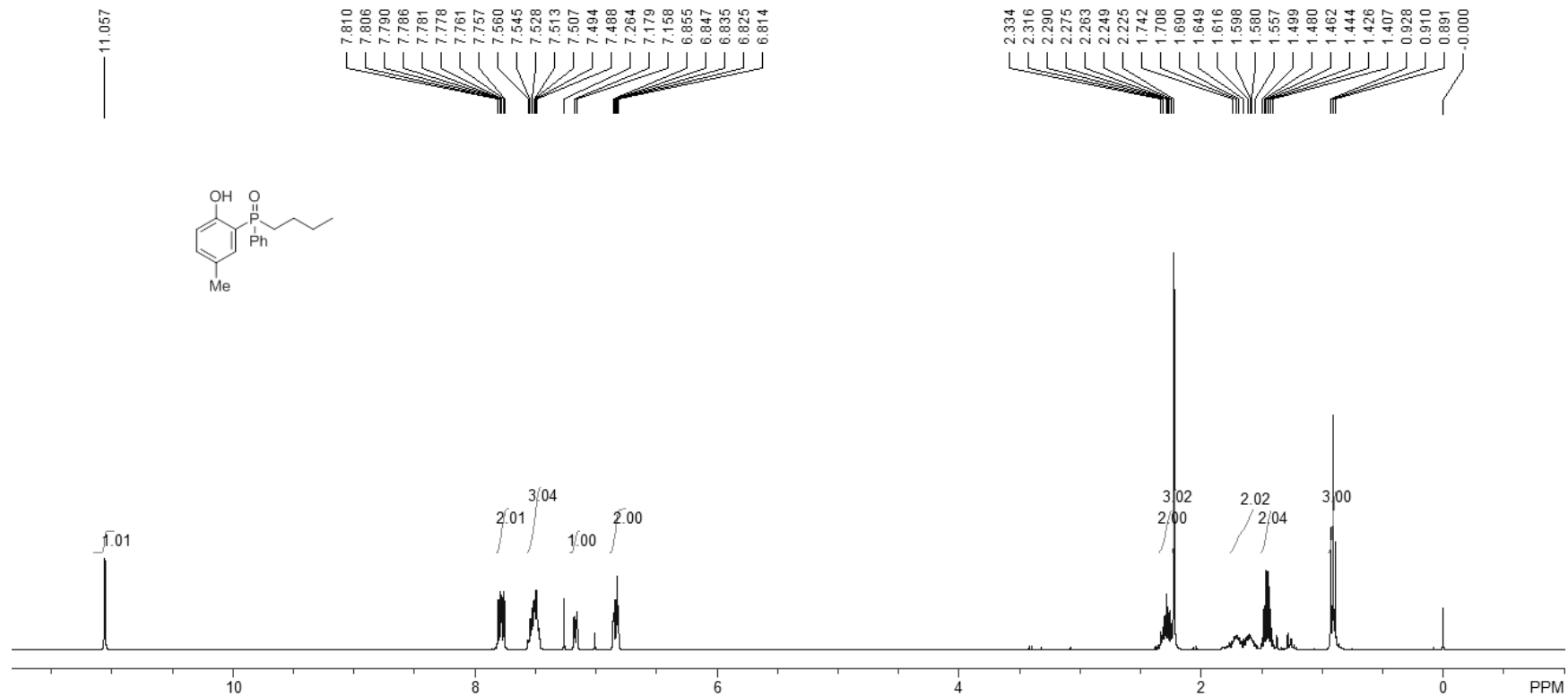
^{13}C NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak)



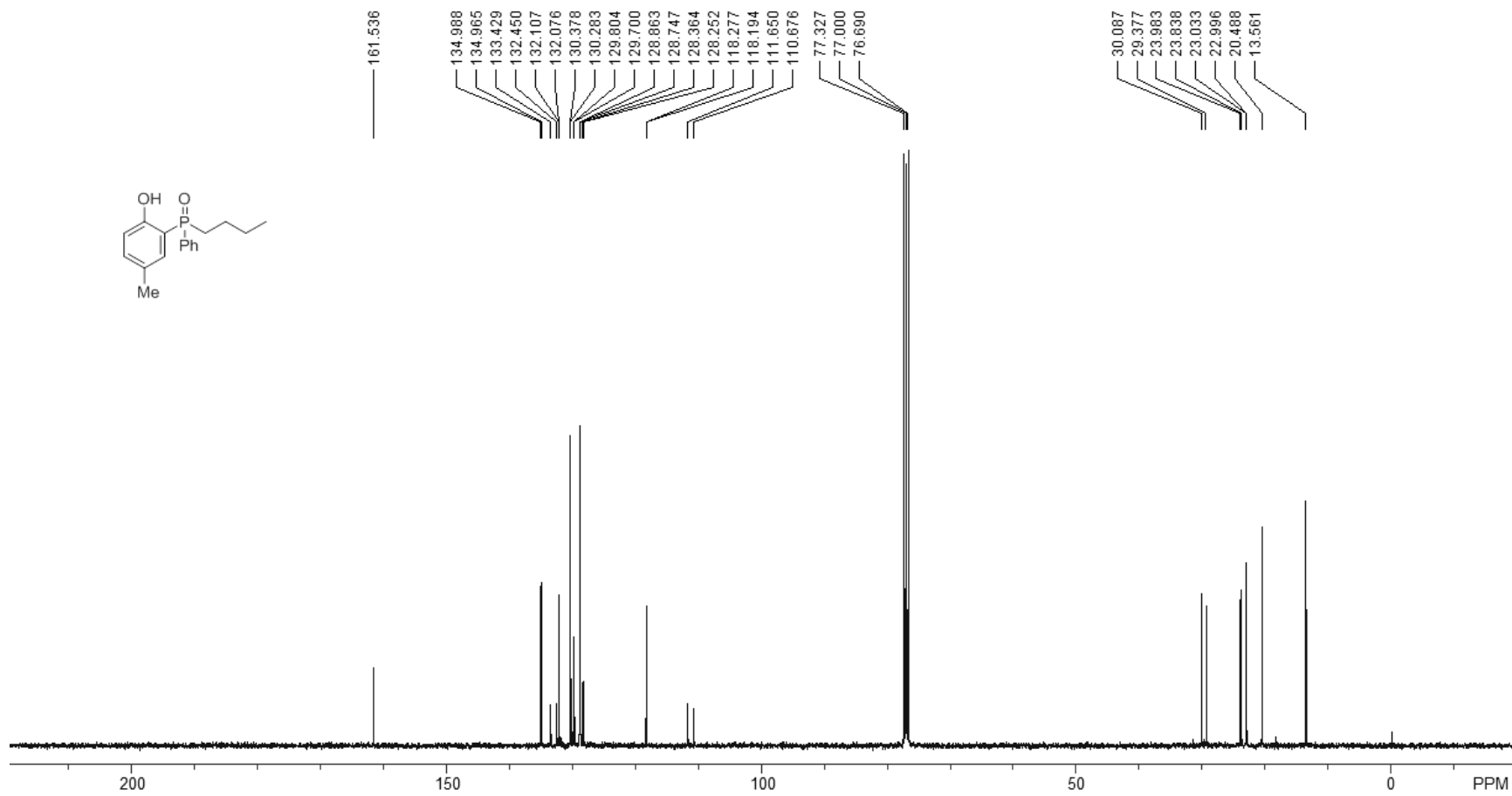
^{31}P NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak)



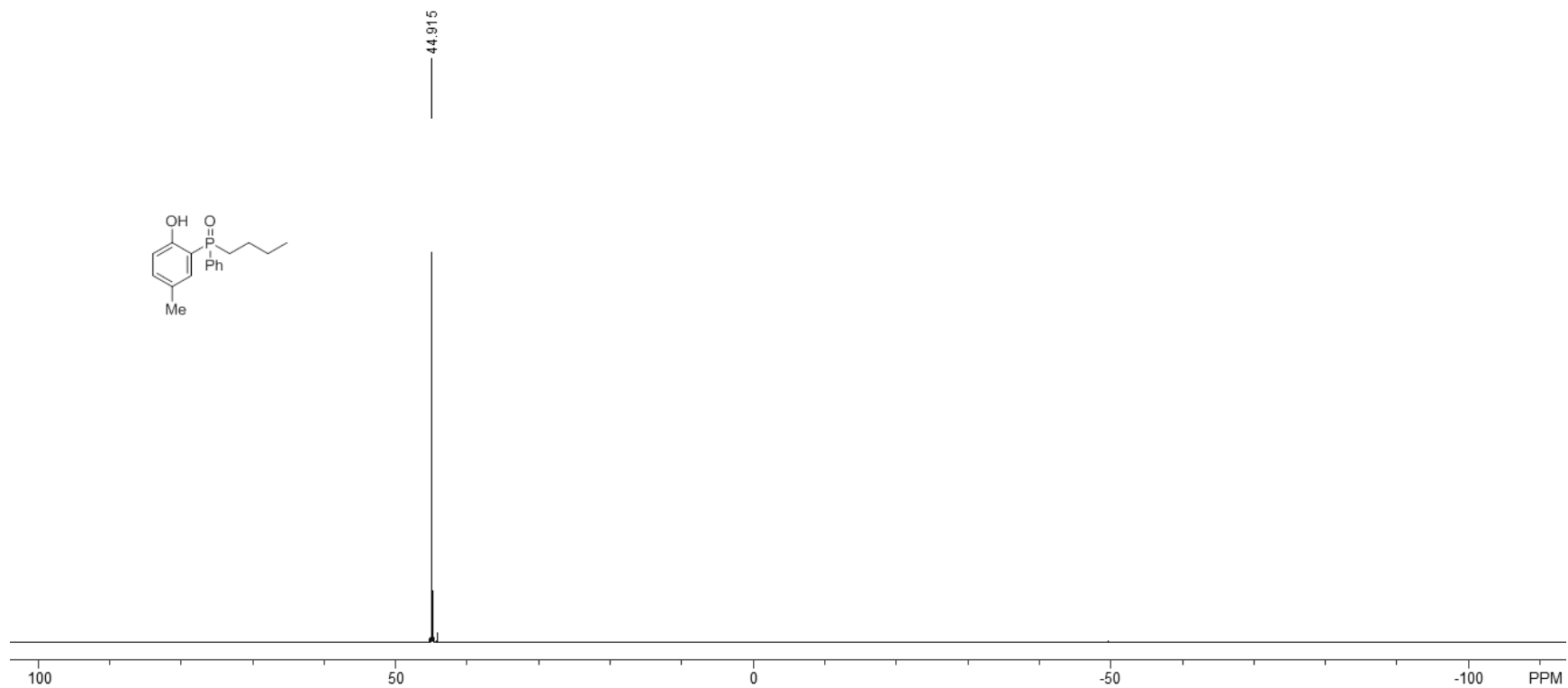
^1H NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3a)



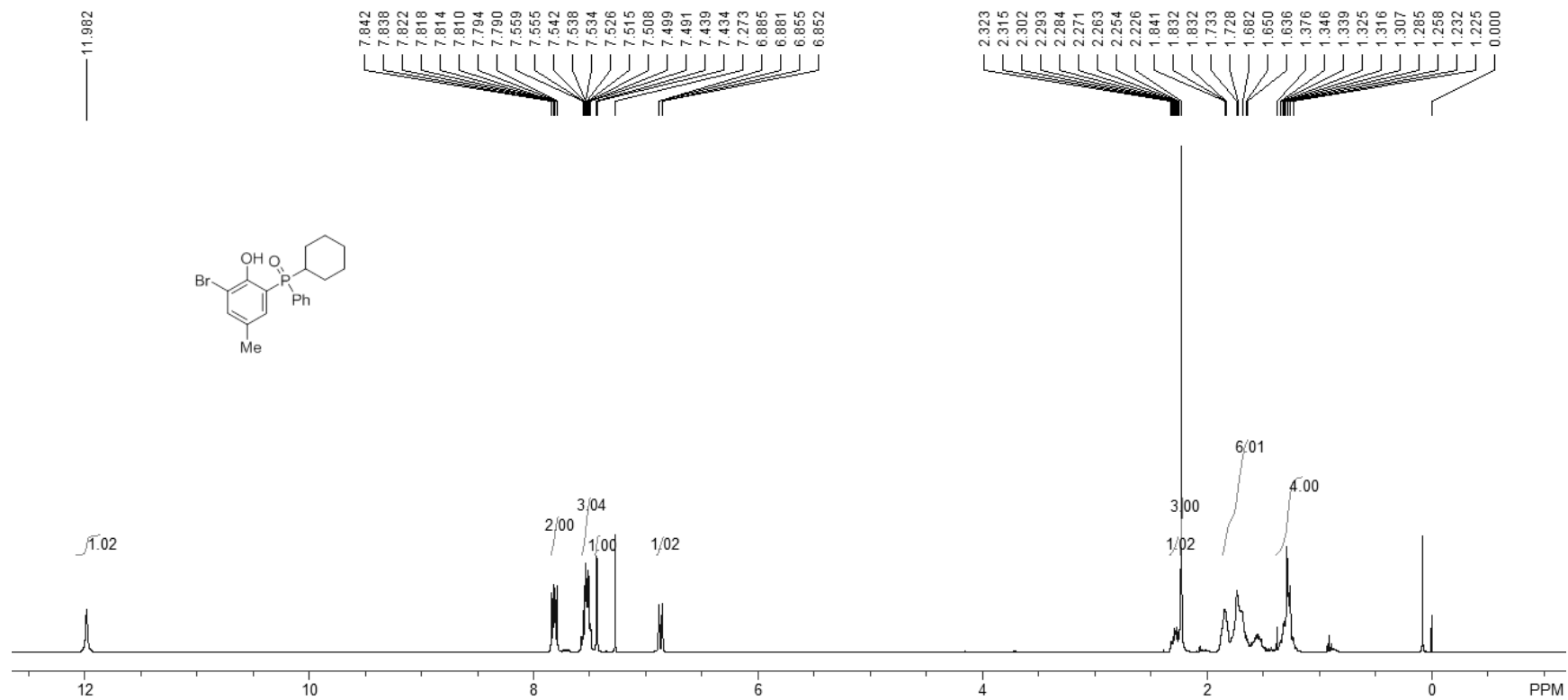
¹³C NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3a)



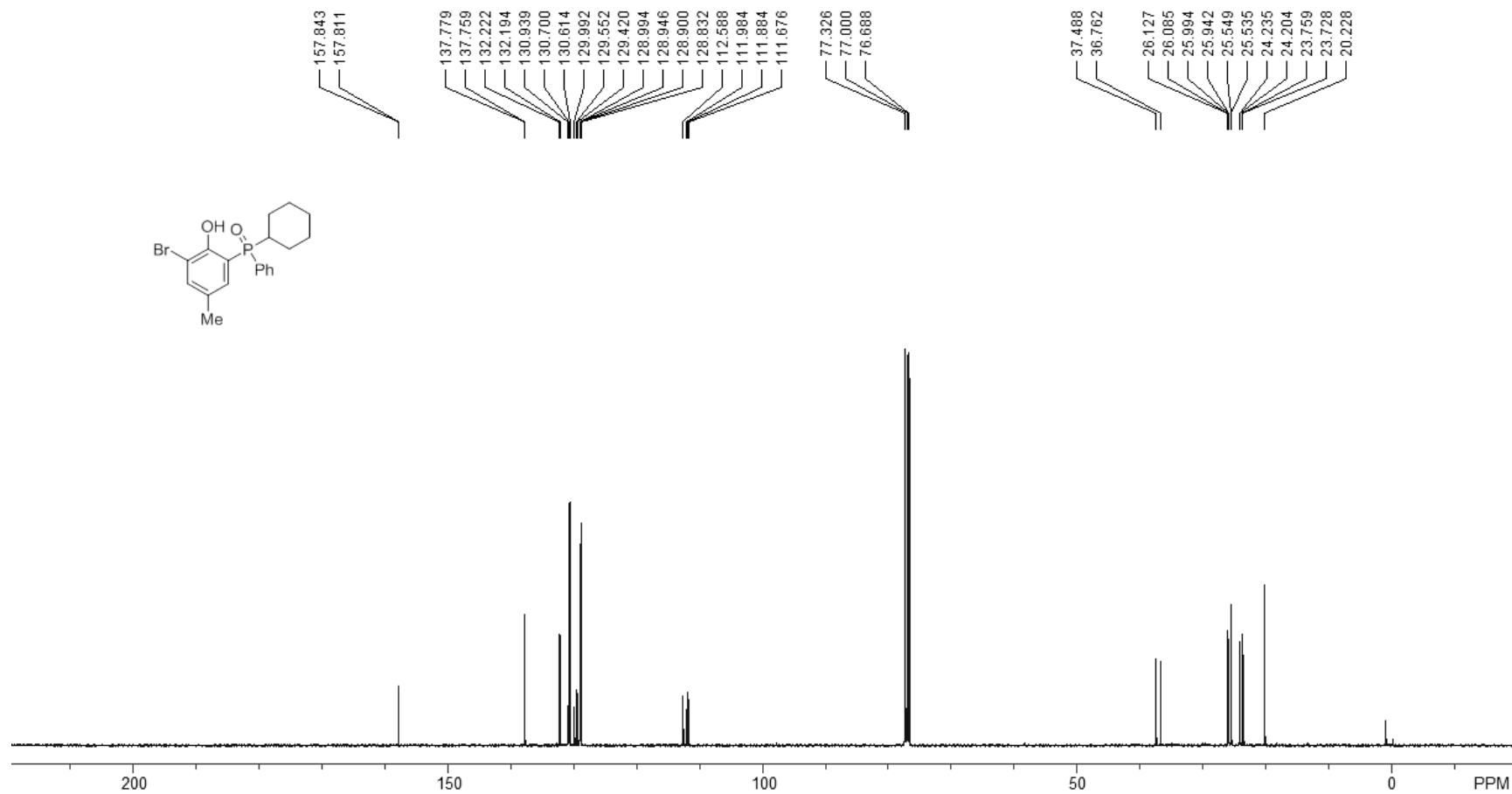
^{31}P NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3al)



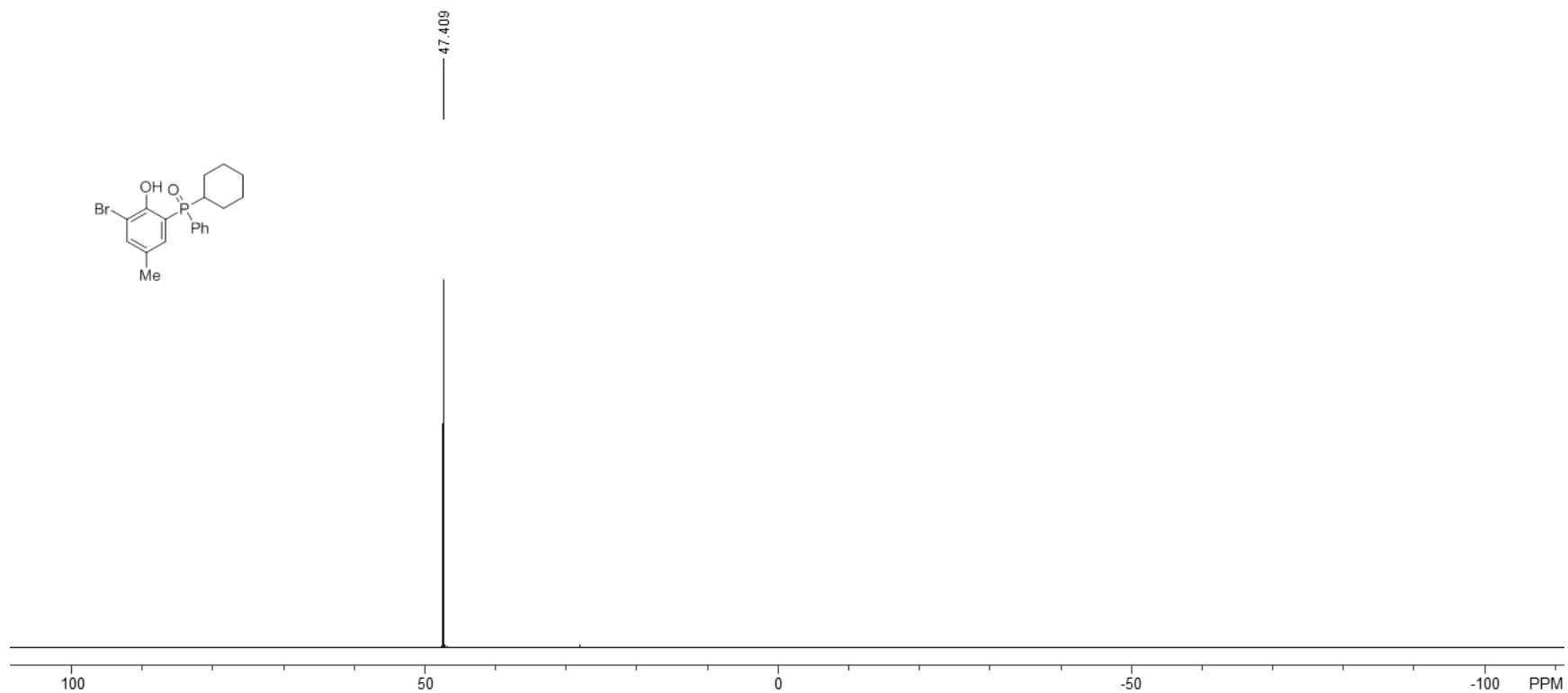
^1H NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm)



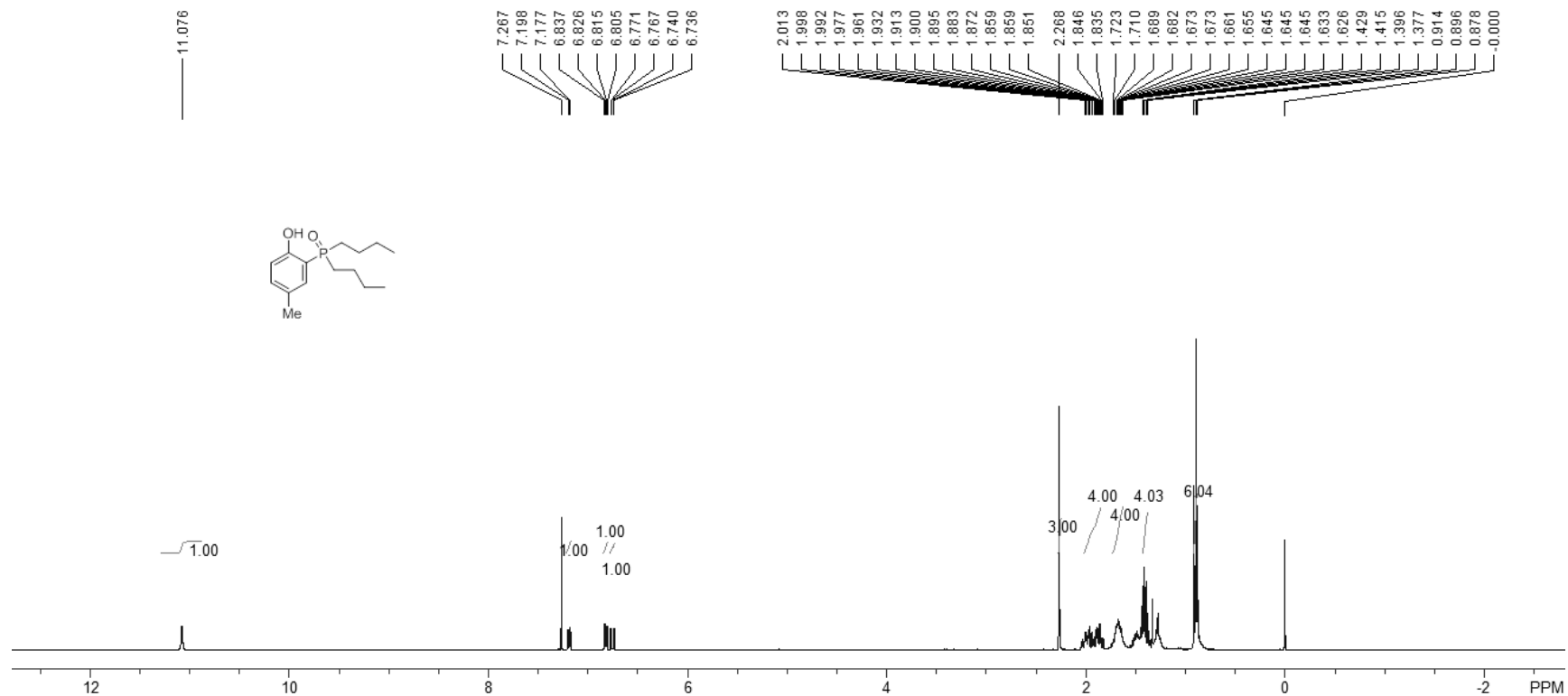
^{13}C NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm)



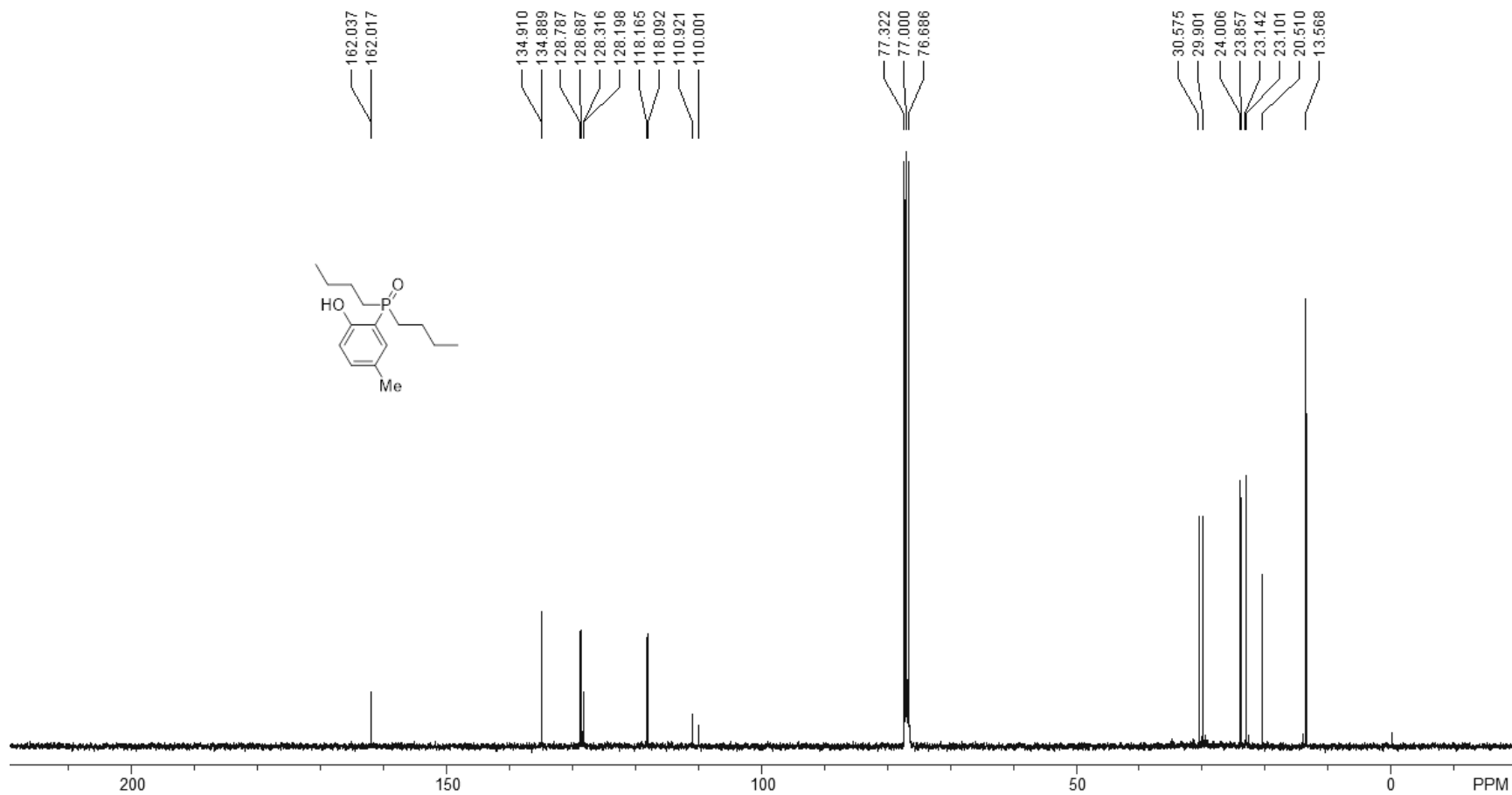
^{31}P NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm)



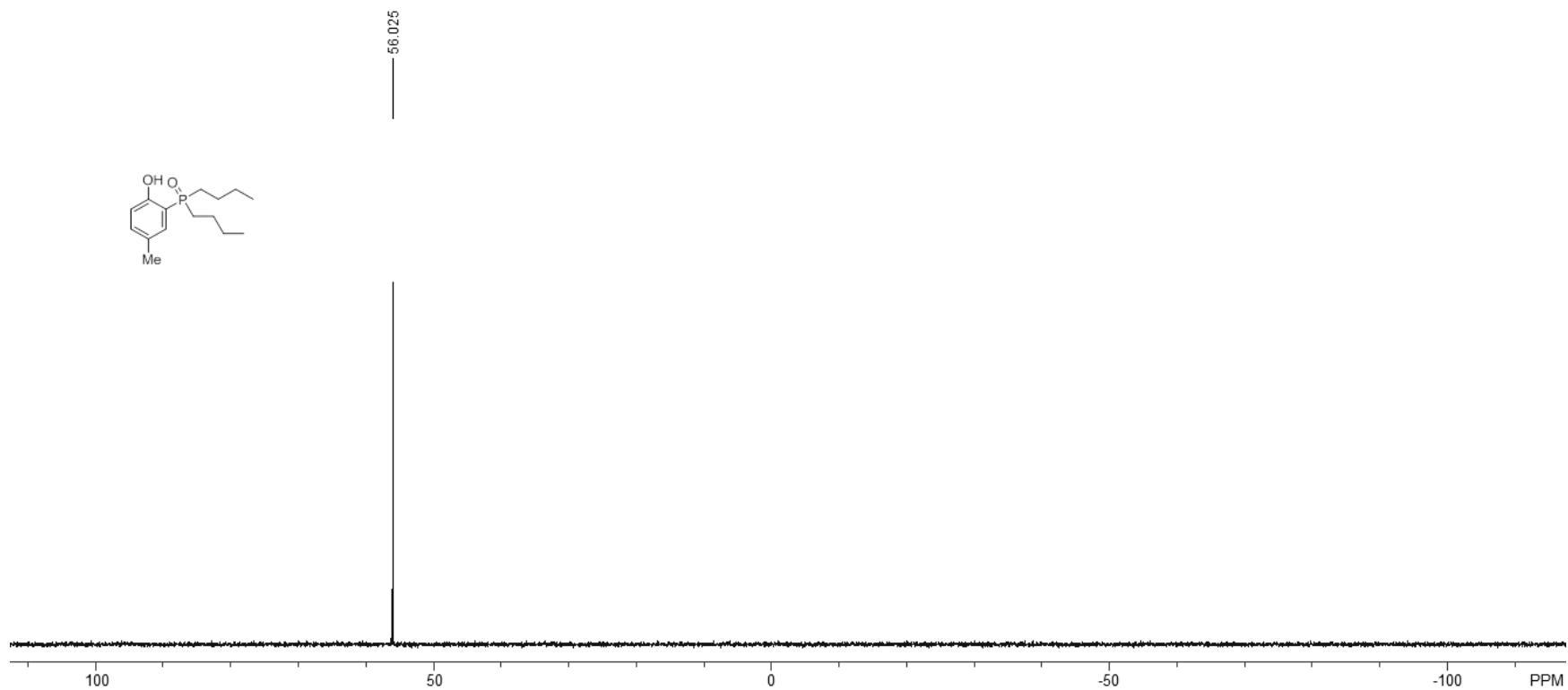
¹H NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)



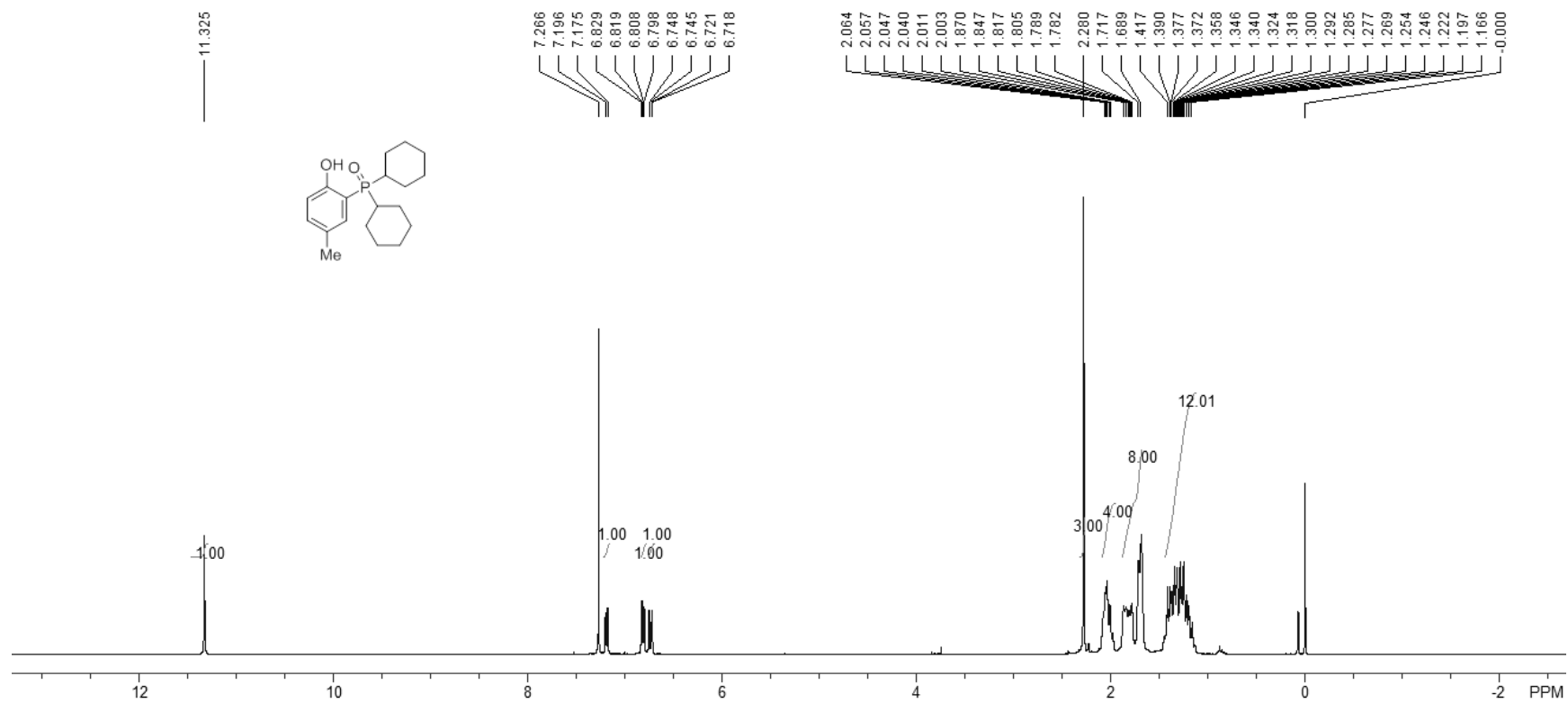
¹³C NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)



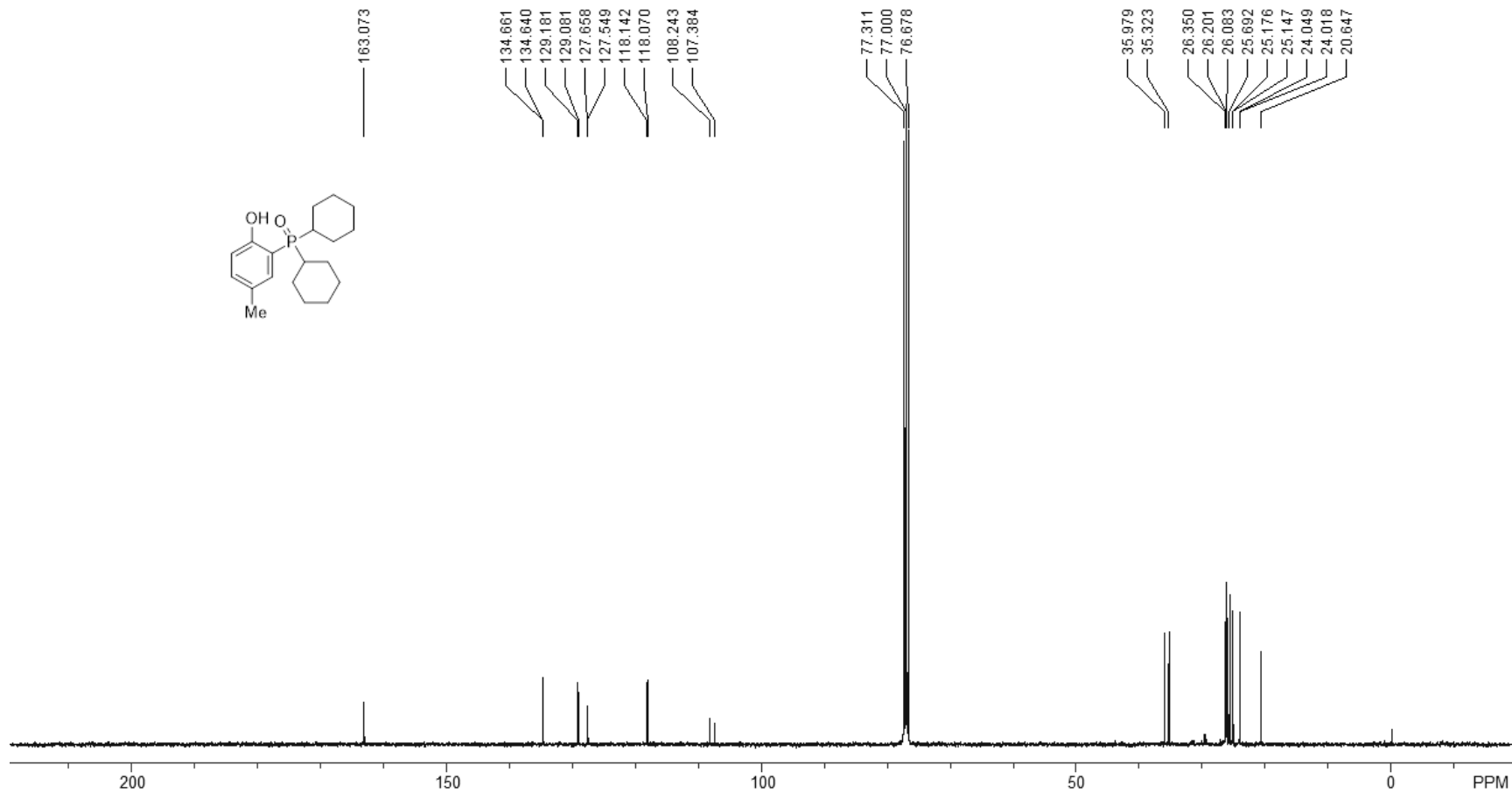
^{31}P NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)



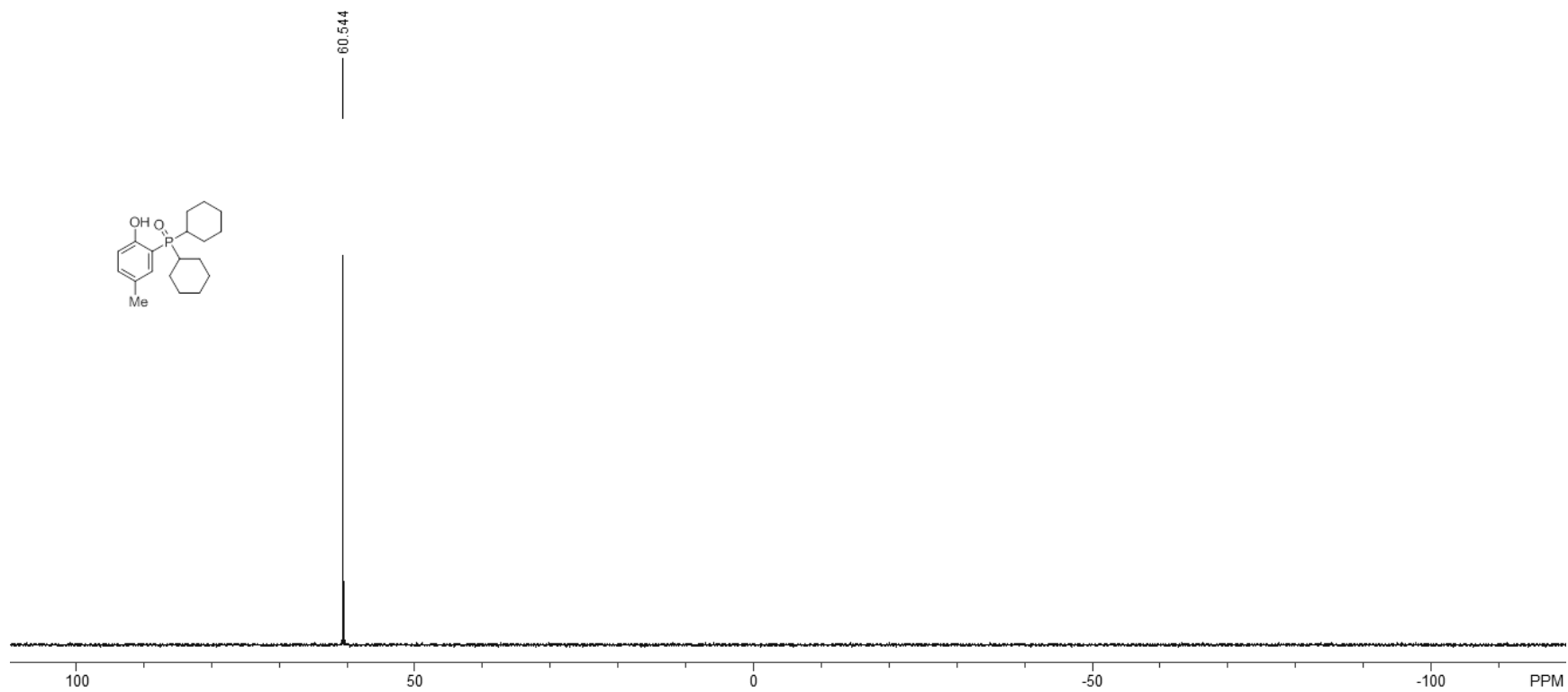
¹H NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)



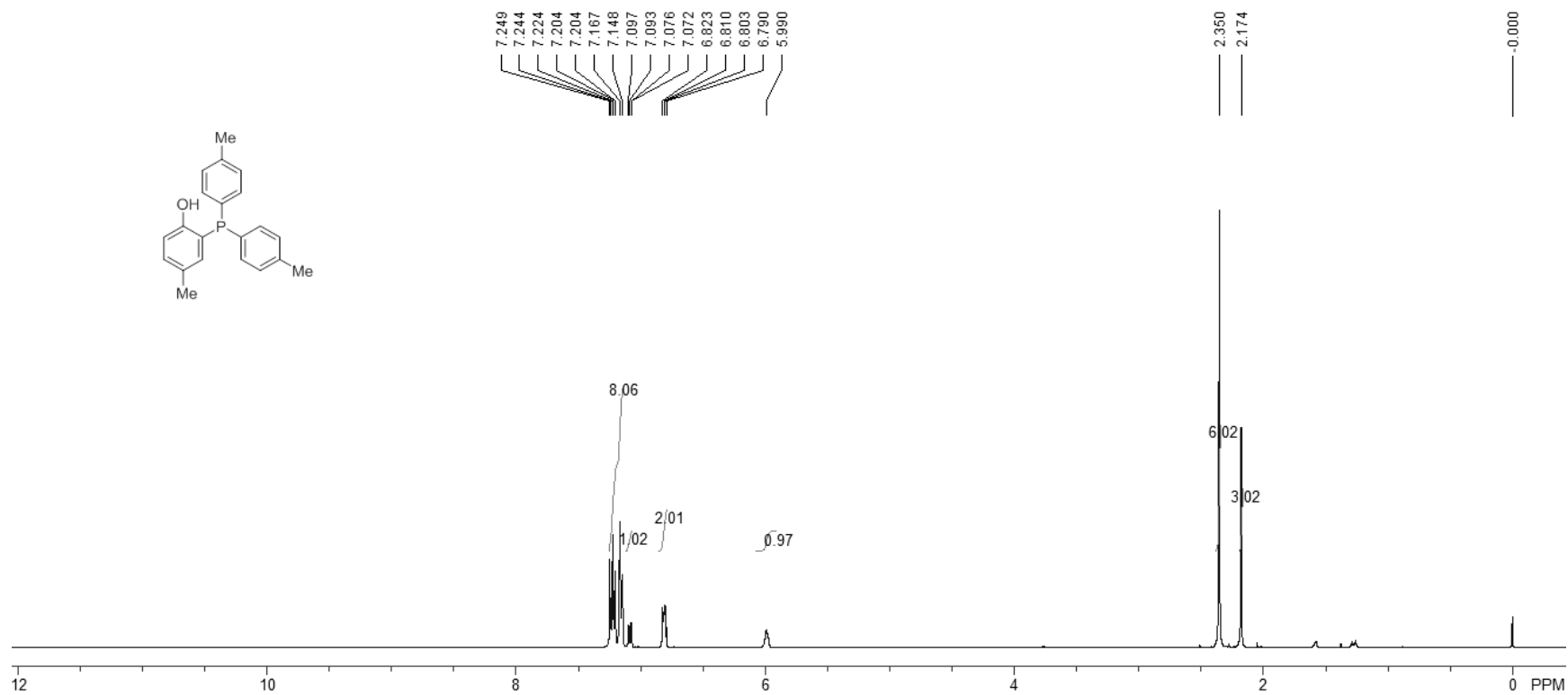
¹³C NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)



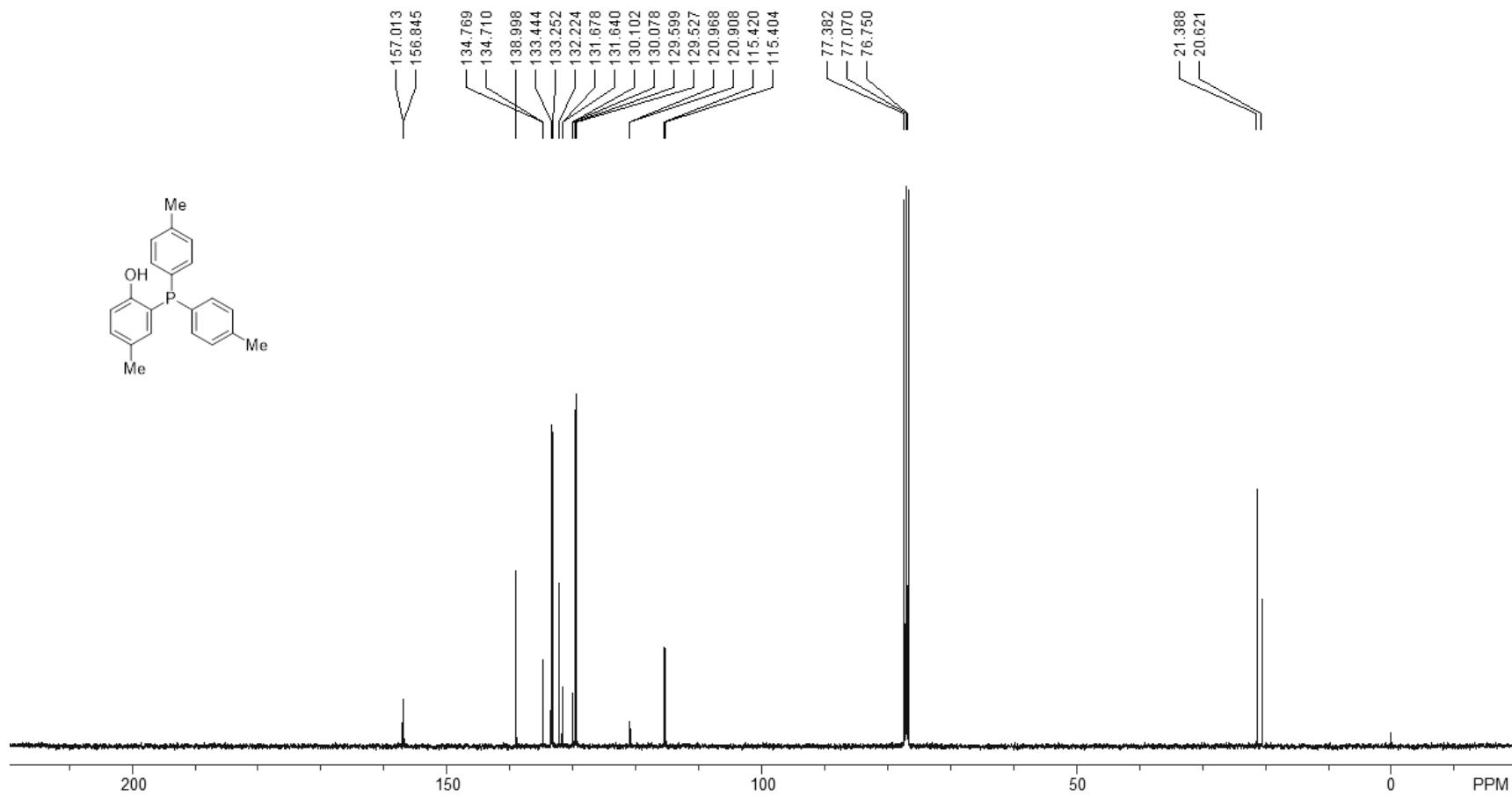
^{31}P NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)



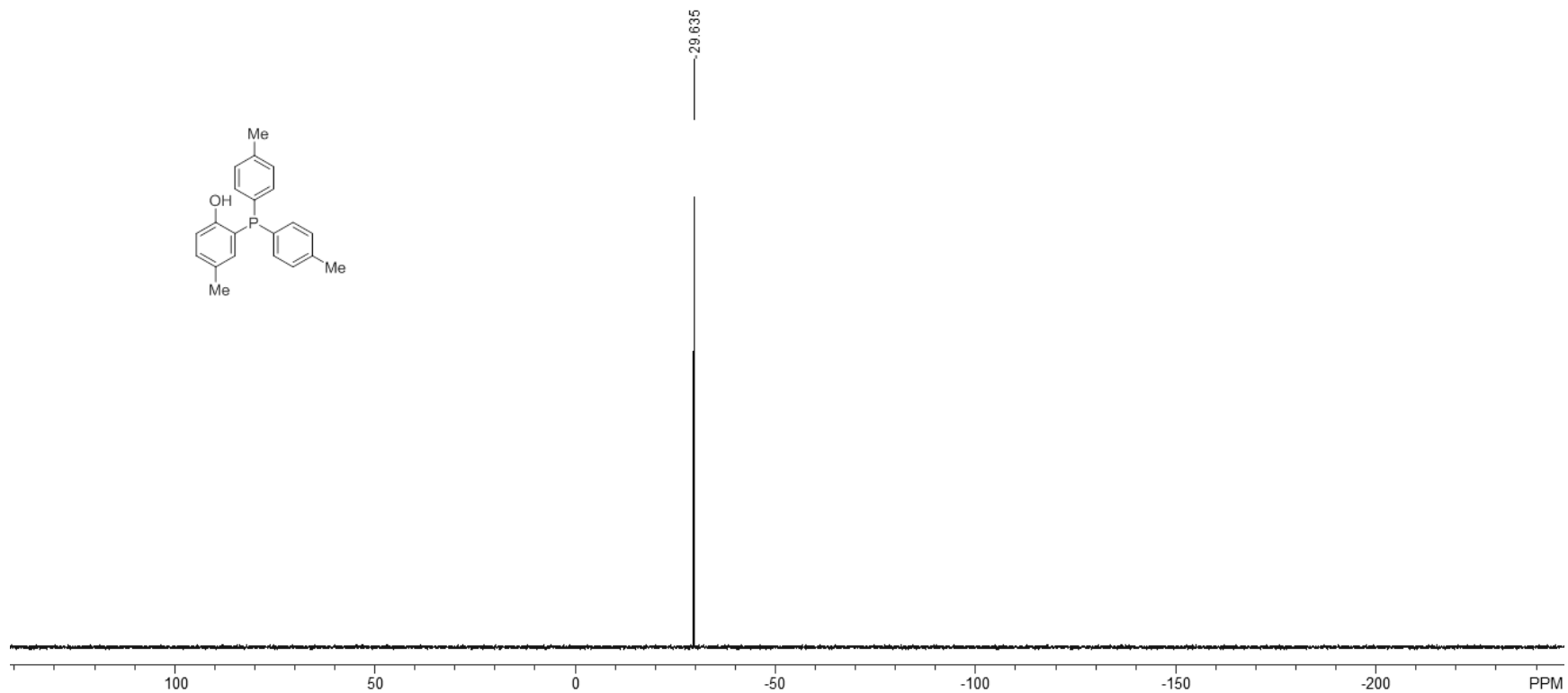
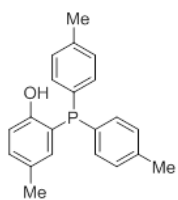
¹H NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)



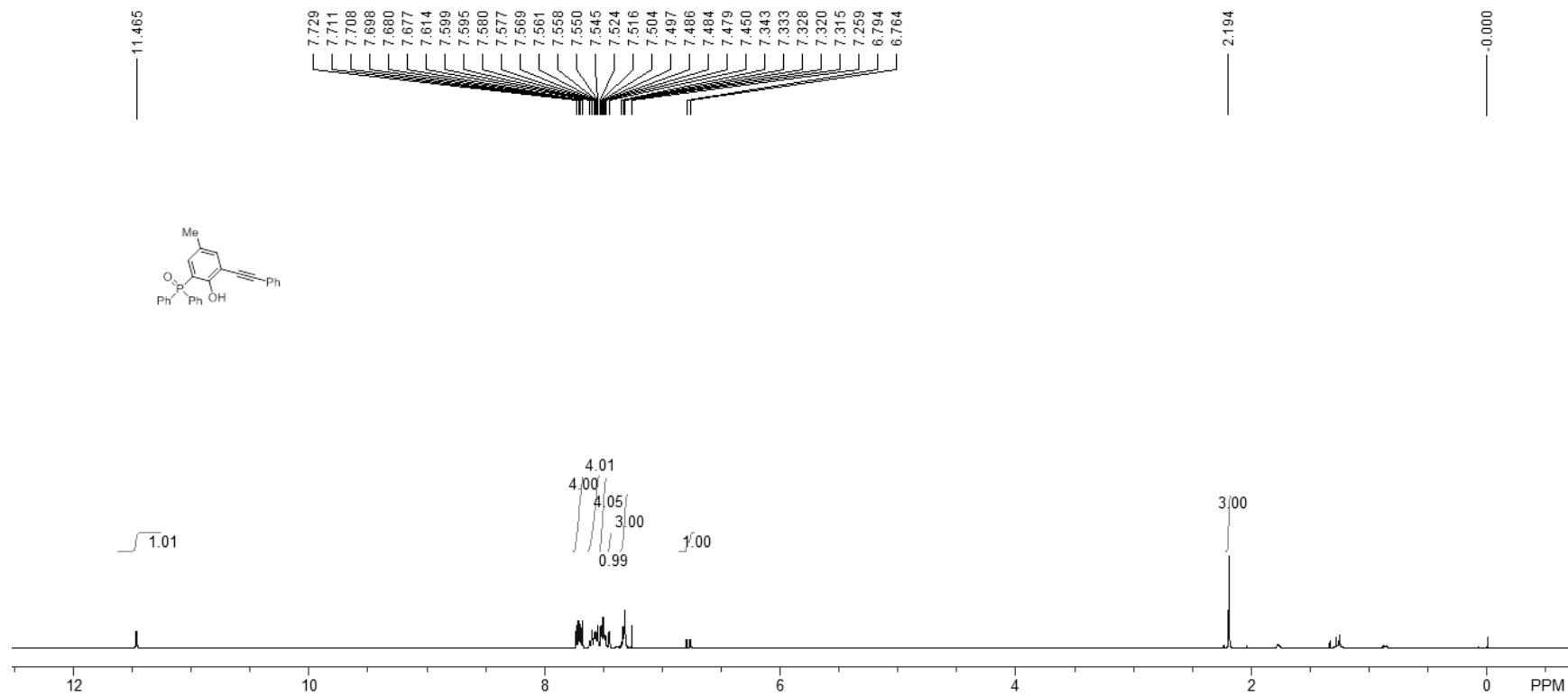
¹³C NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)



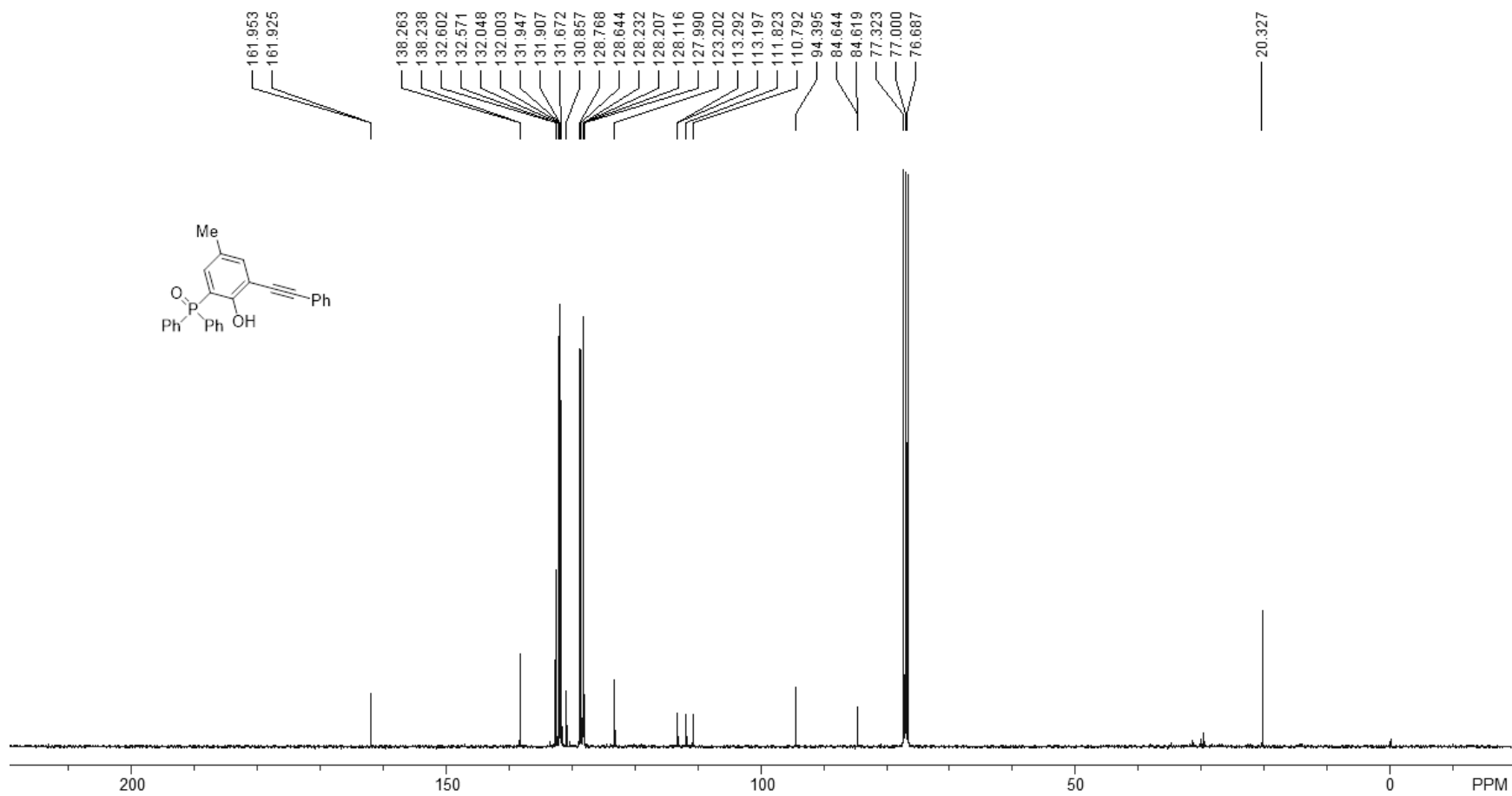
^{31}P NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)



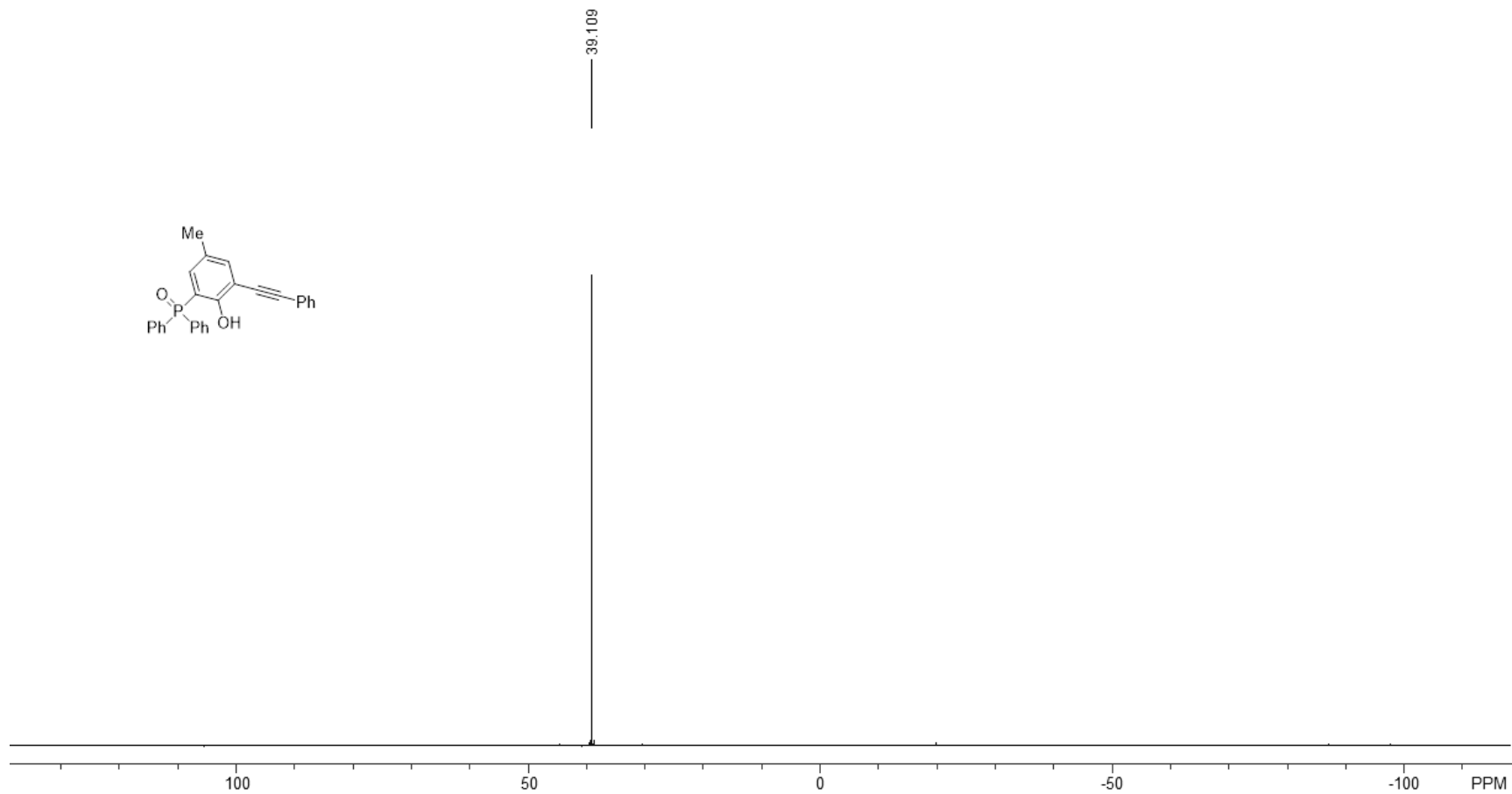
¹H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)



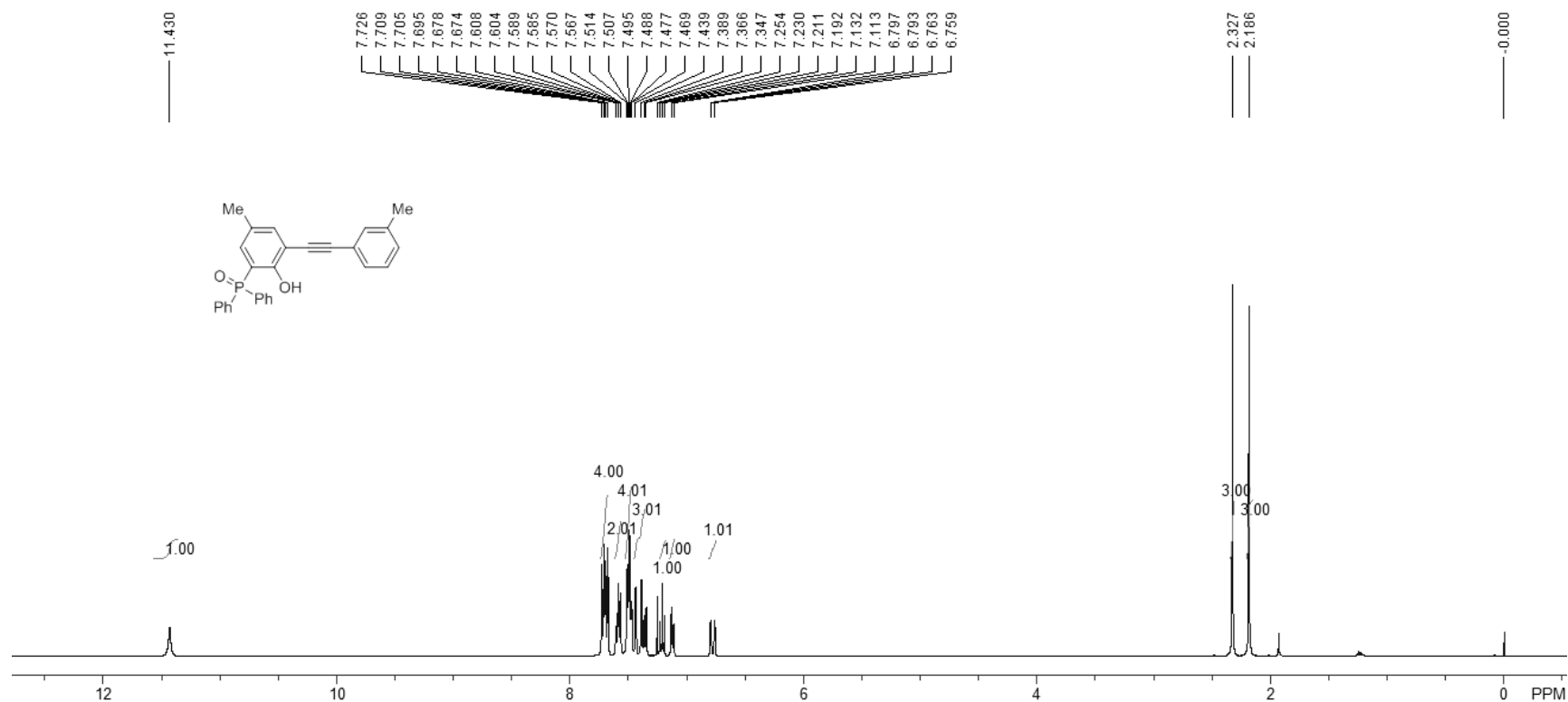
^{13}C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)



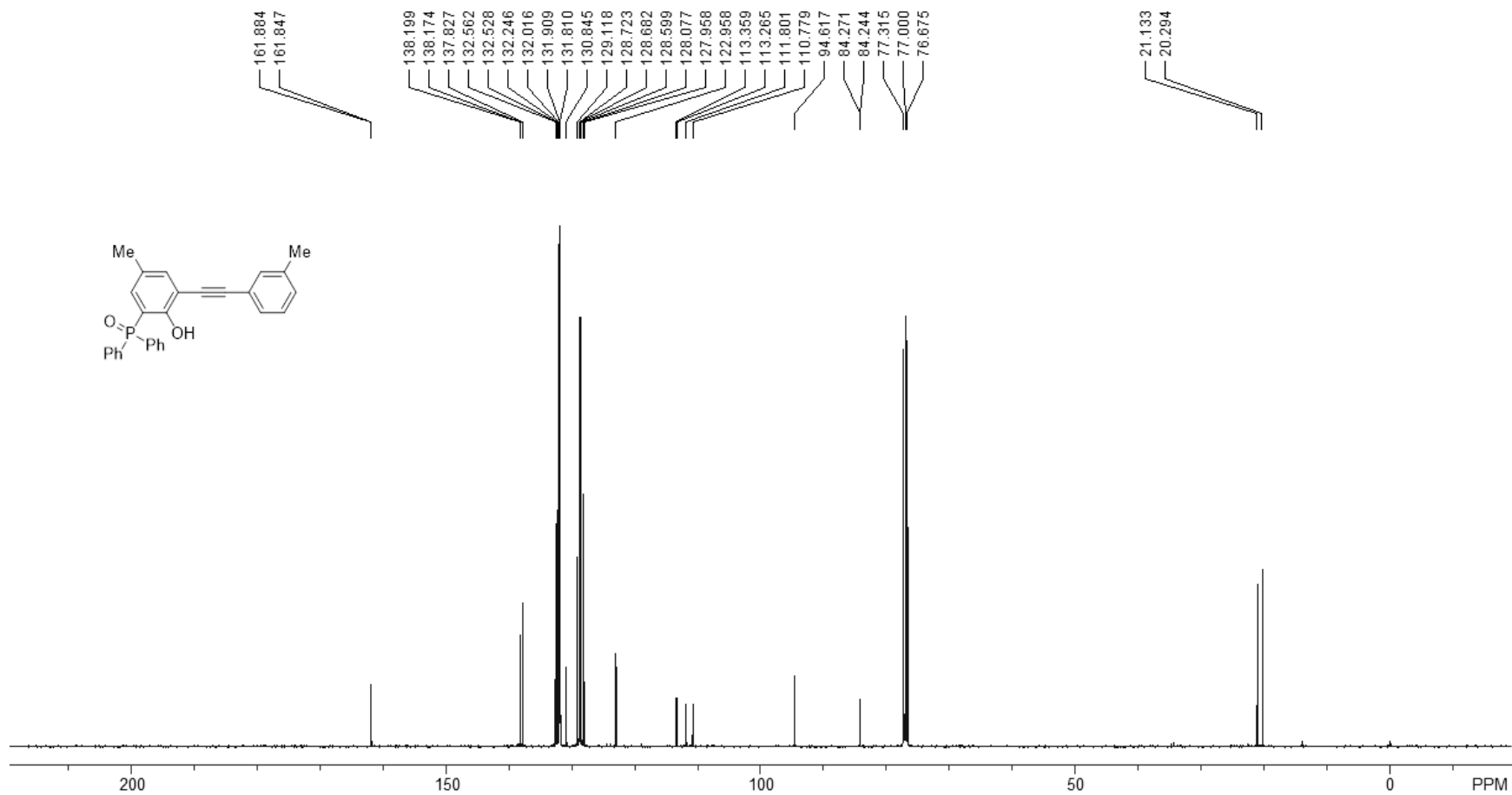
^{31}P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)



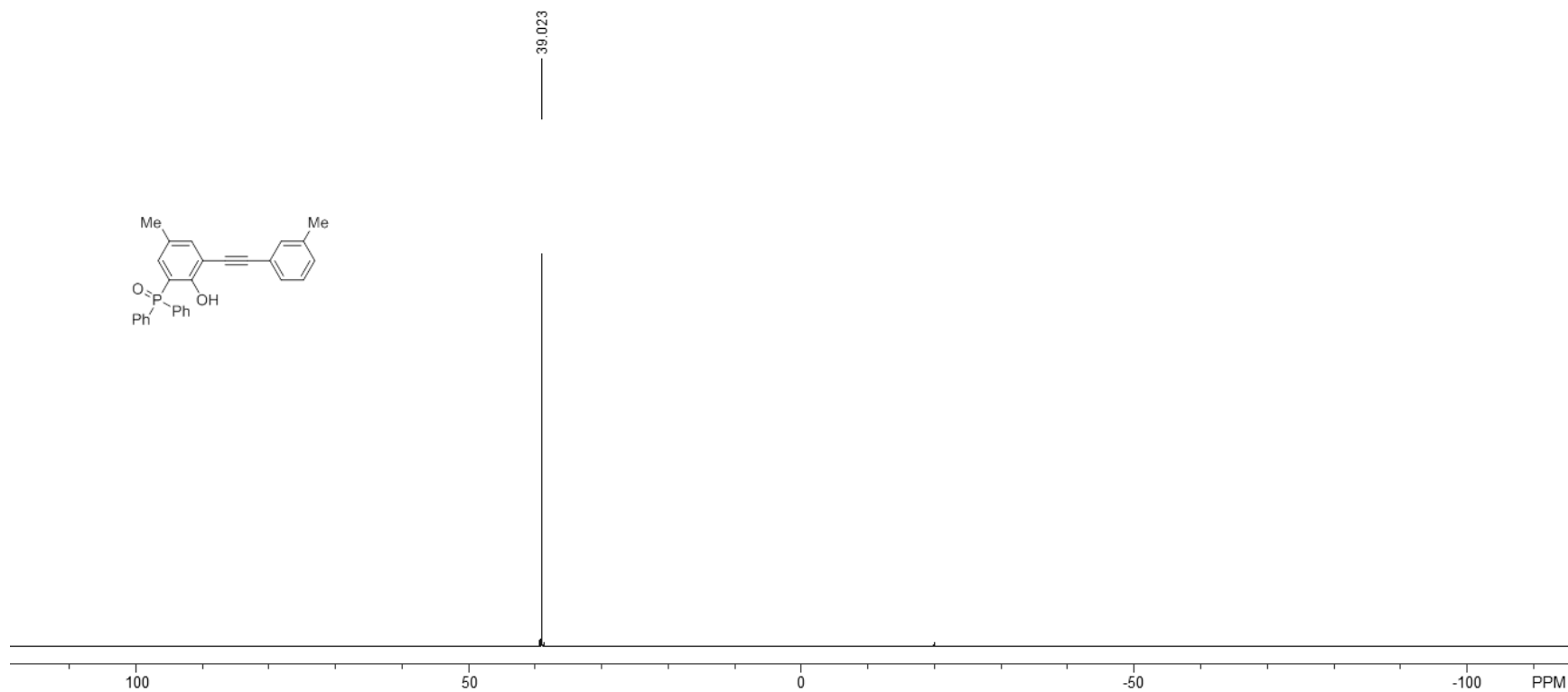
¹H NMR of (2-hydroxy-5-methyl-3-(m-tolyethynyl)phenyl)diphenylphosphine oxide (6b)



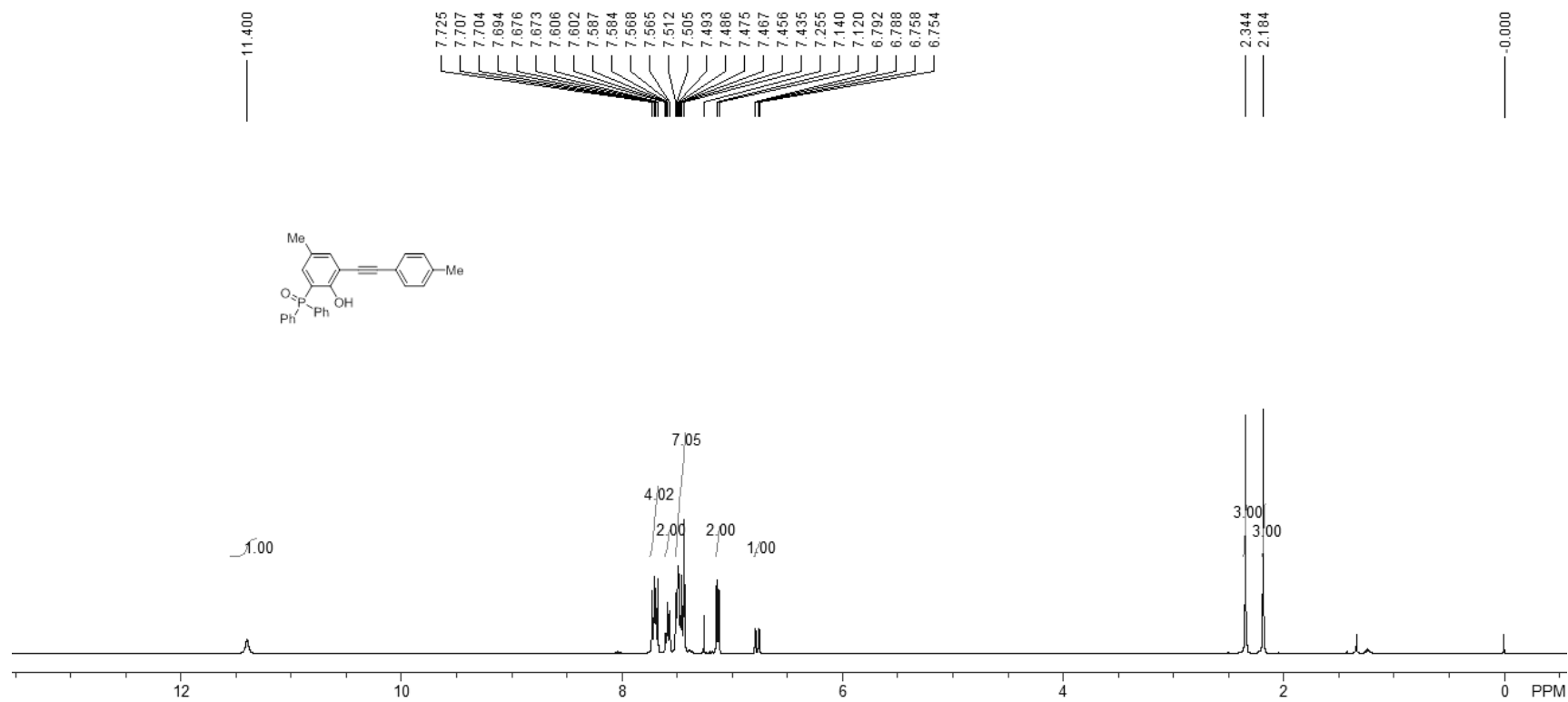
¹³C NMR of (2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b)



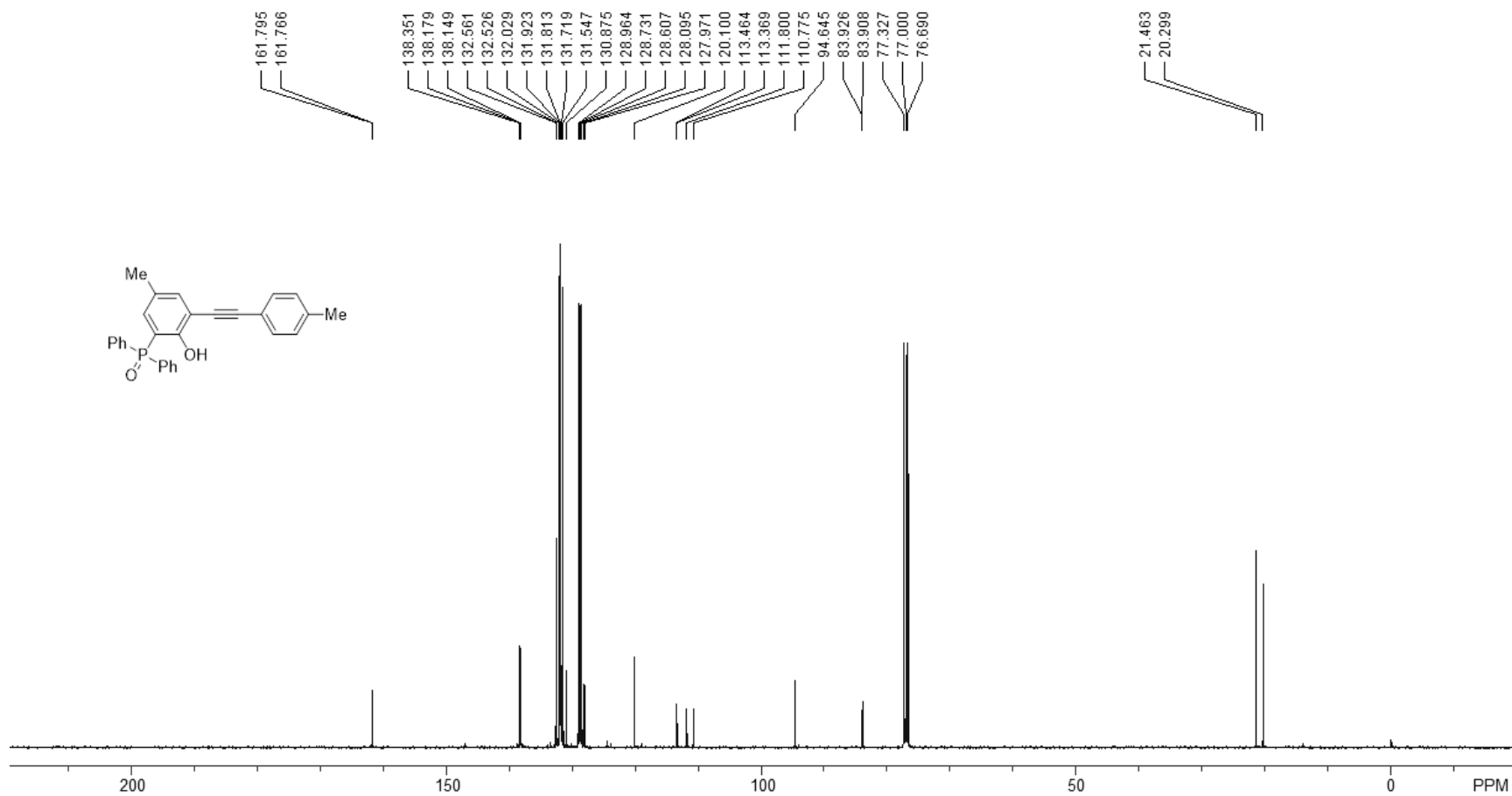
^{31}P NMR of (2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b)



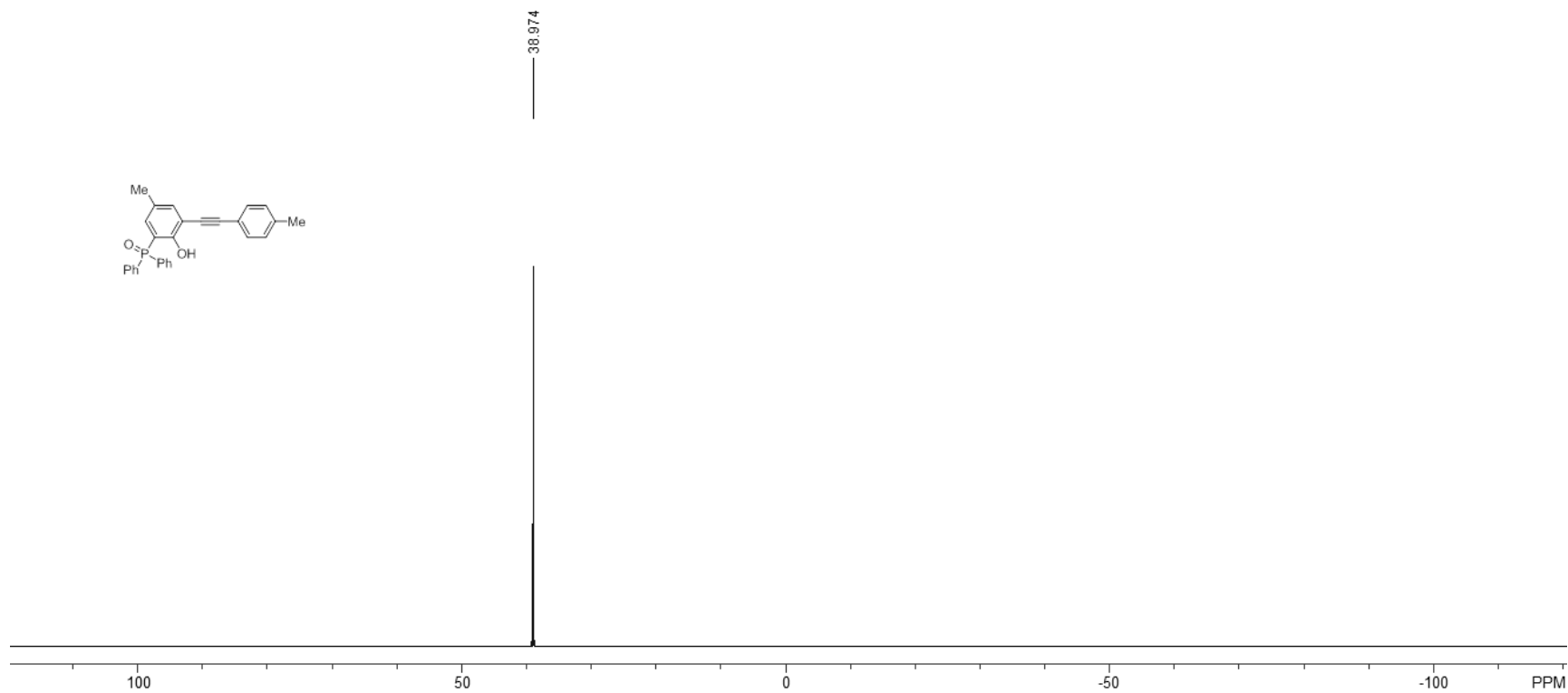
¹H NMR of (2-hydroxy-5-methyl-3-(p-tolyethynyl)phenyl)diphenylphosphine oxide (6c)



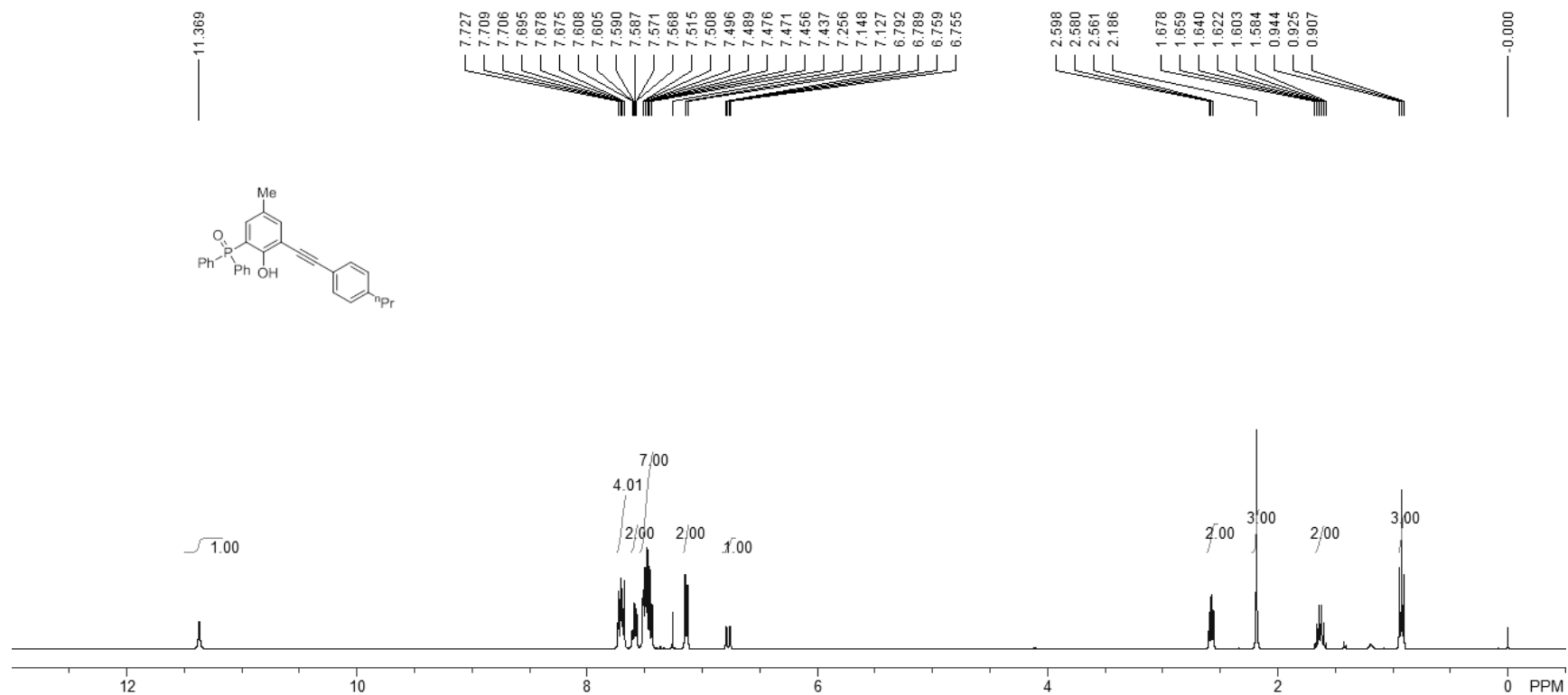
¹³C NMR of (2-hydroxy-5-methyl-3-(p-tolyethynyl)phenyl)diphenylphosphine oxide (6c)



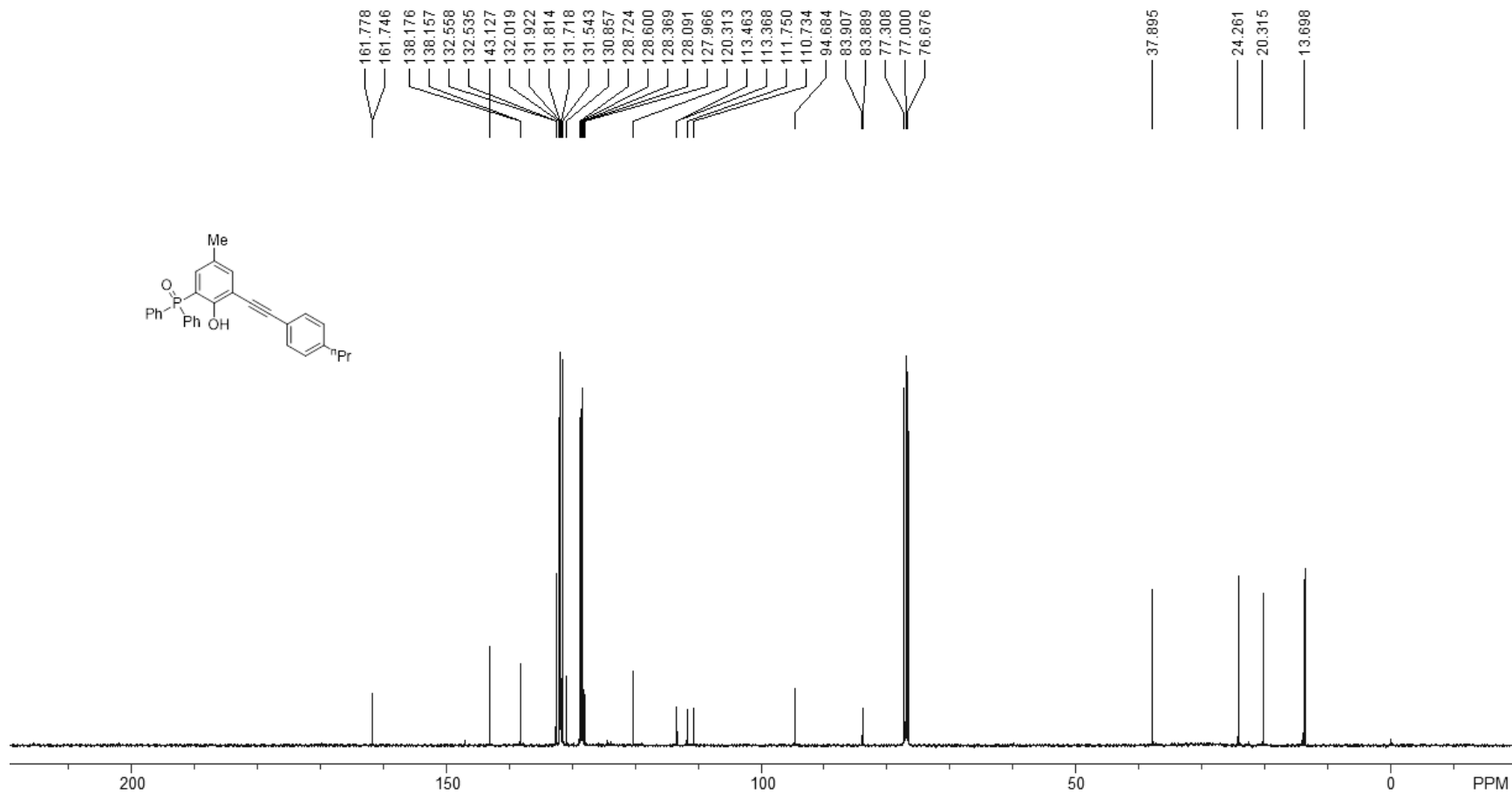
^{31}P NMR of (2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c)



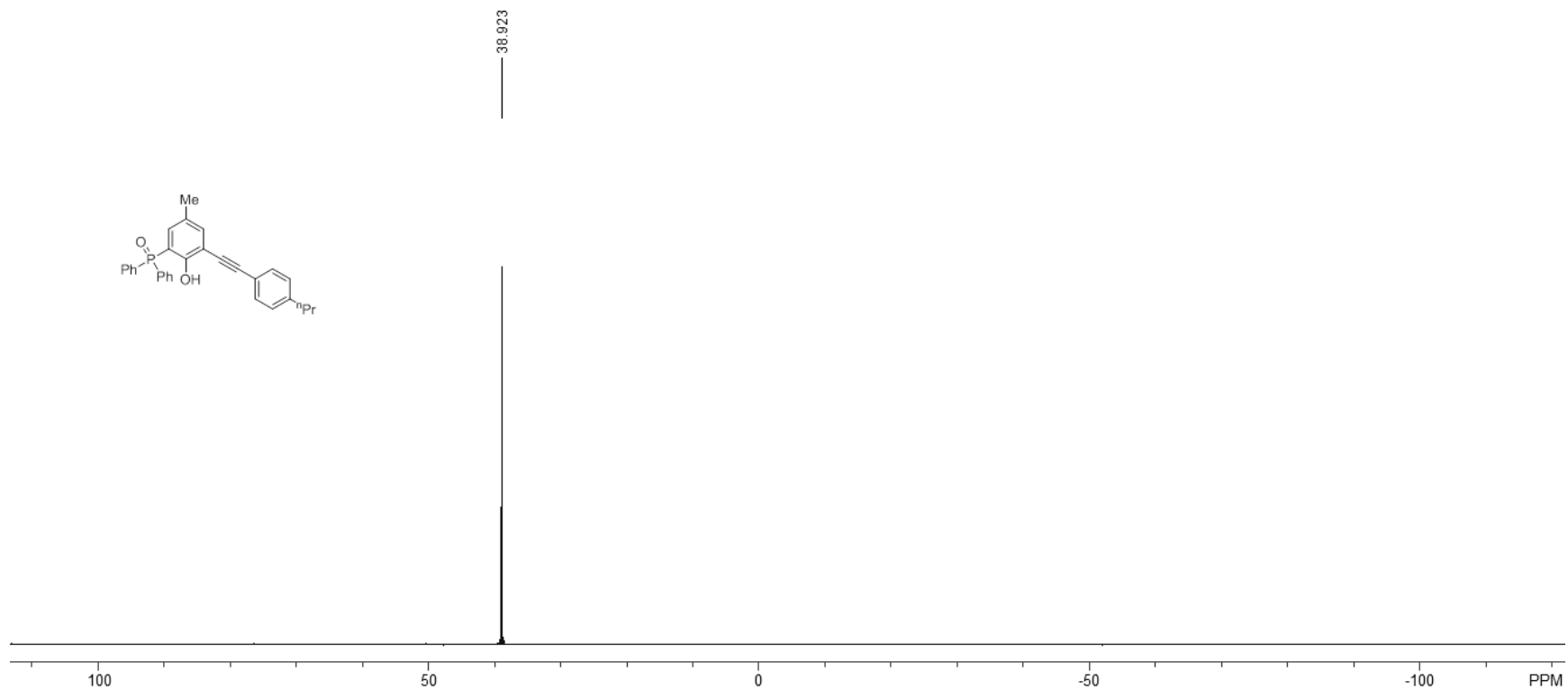
¹H NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)



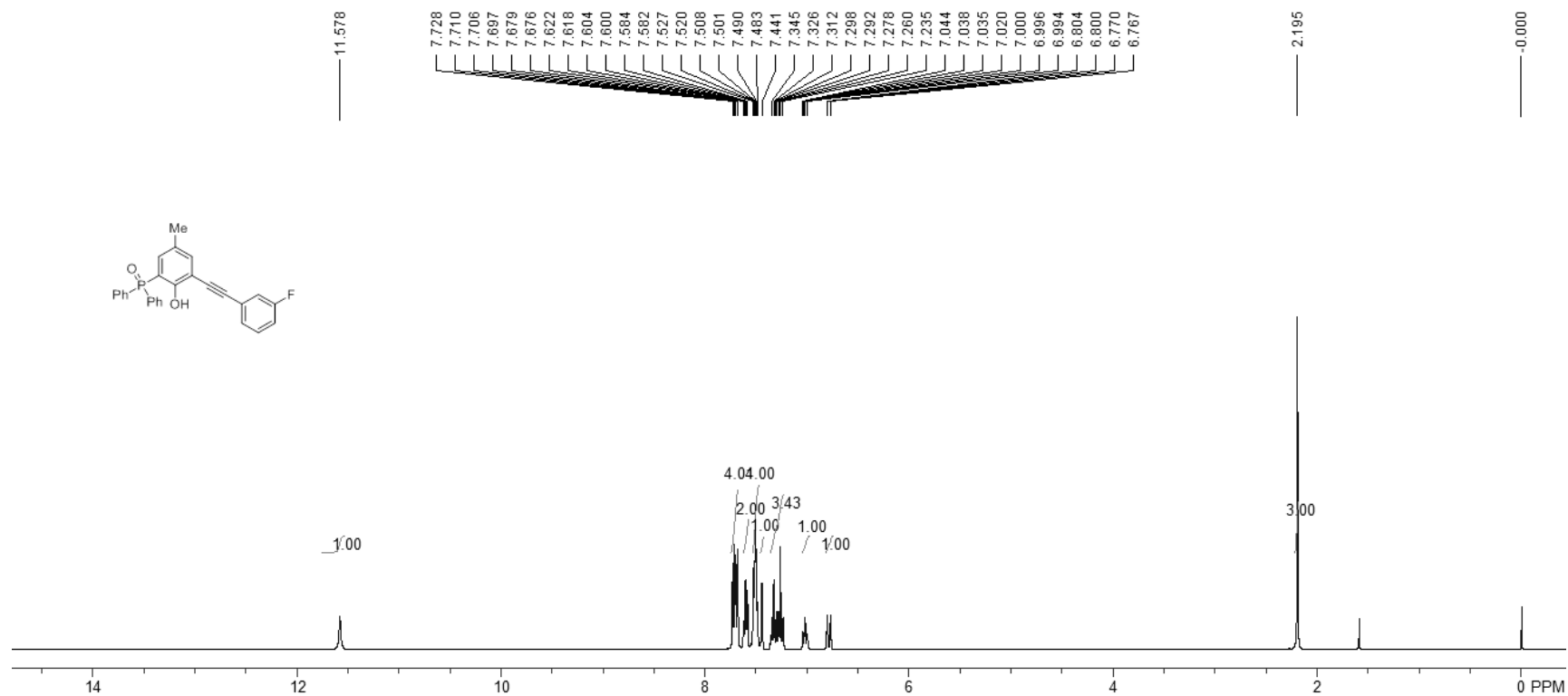
¹³C NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)



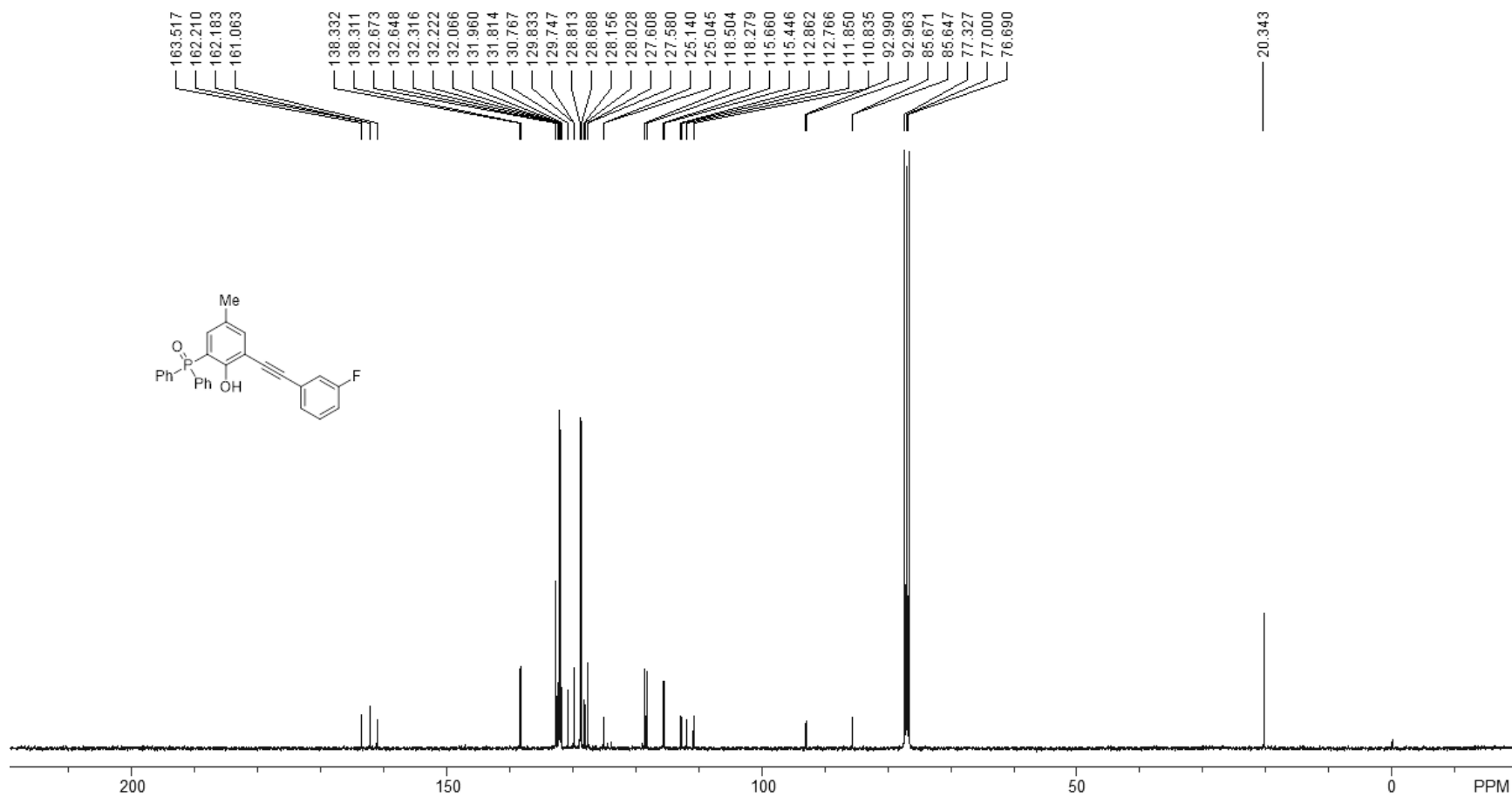
^{31}P NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)



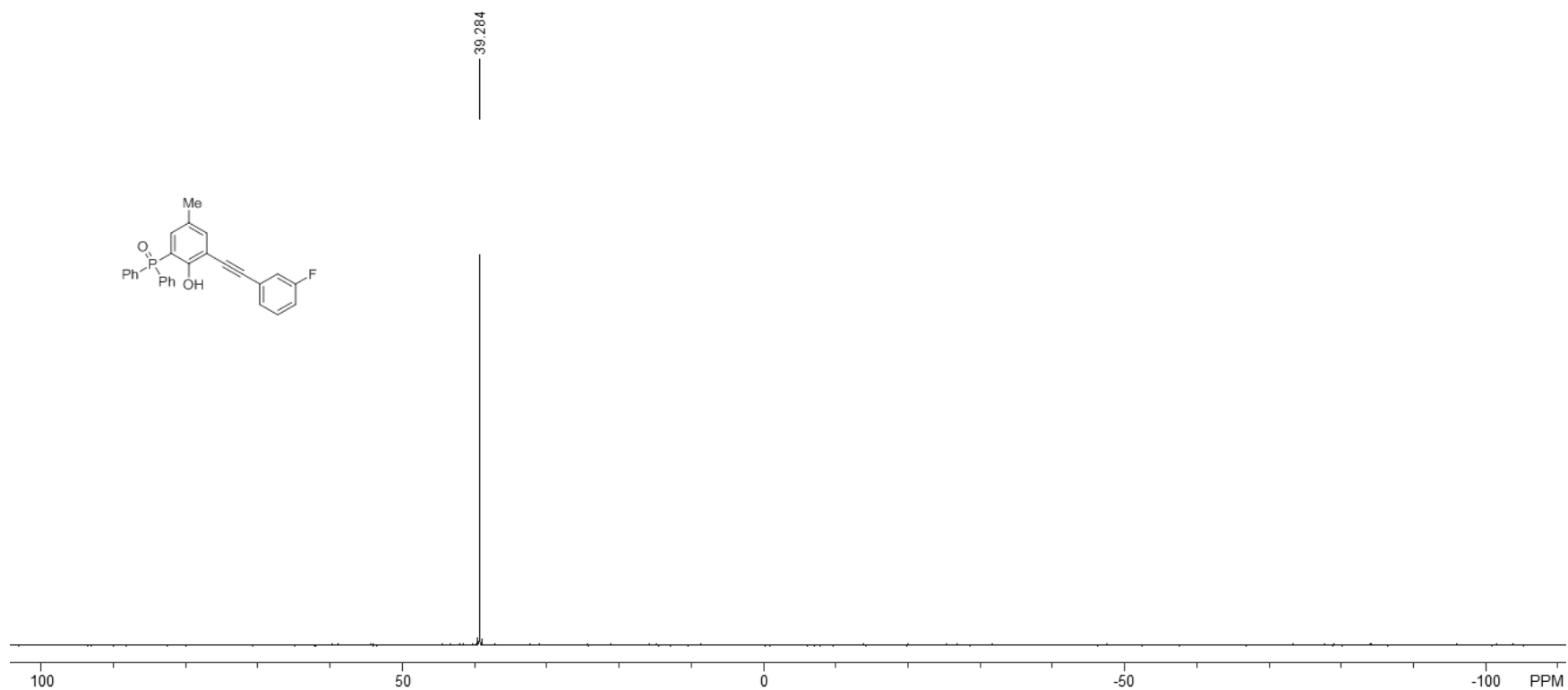
¹H NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)



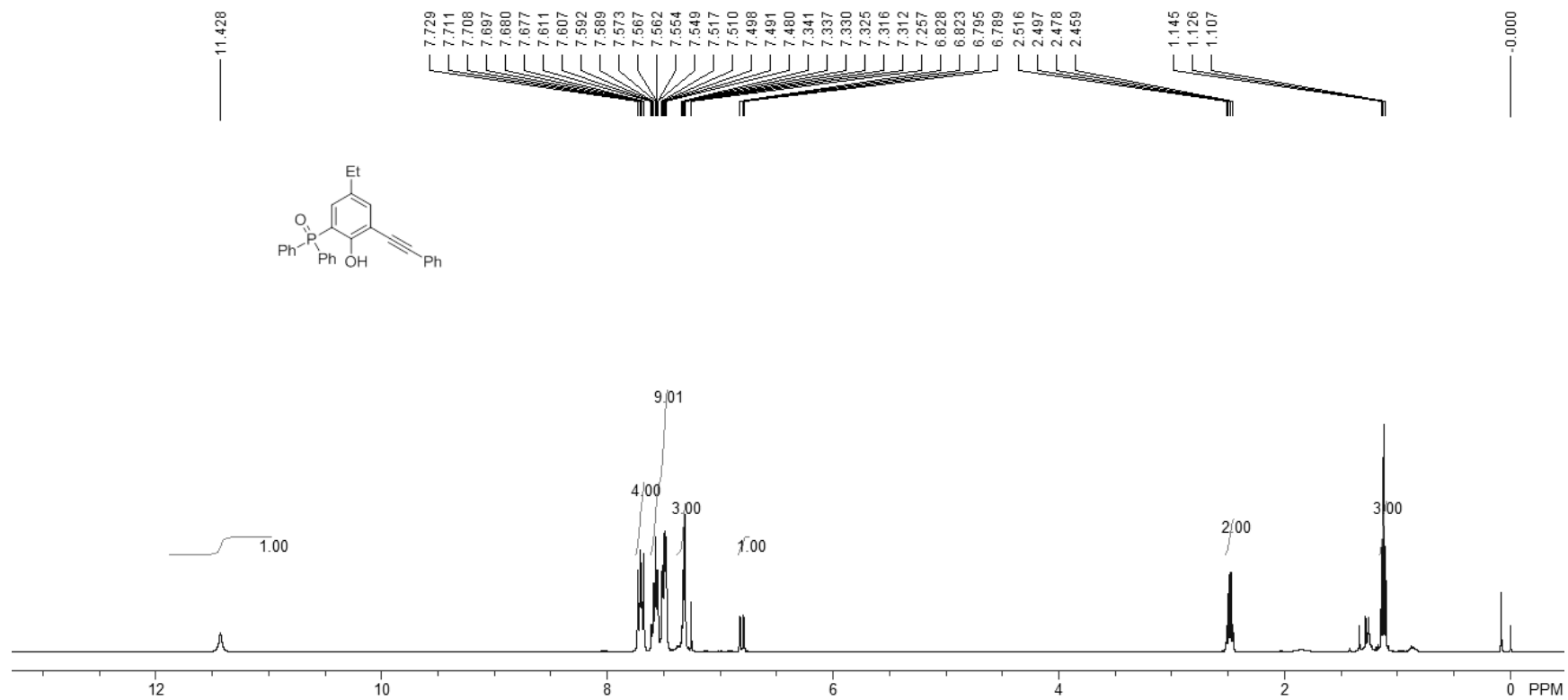
¹³C NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)



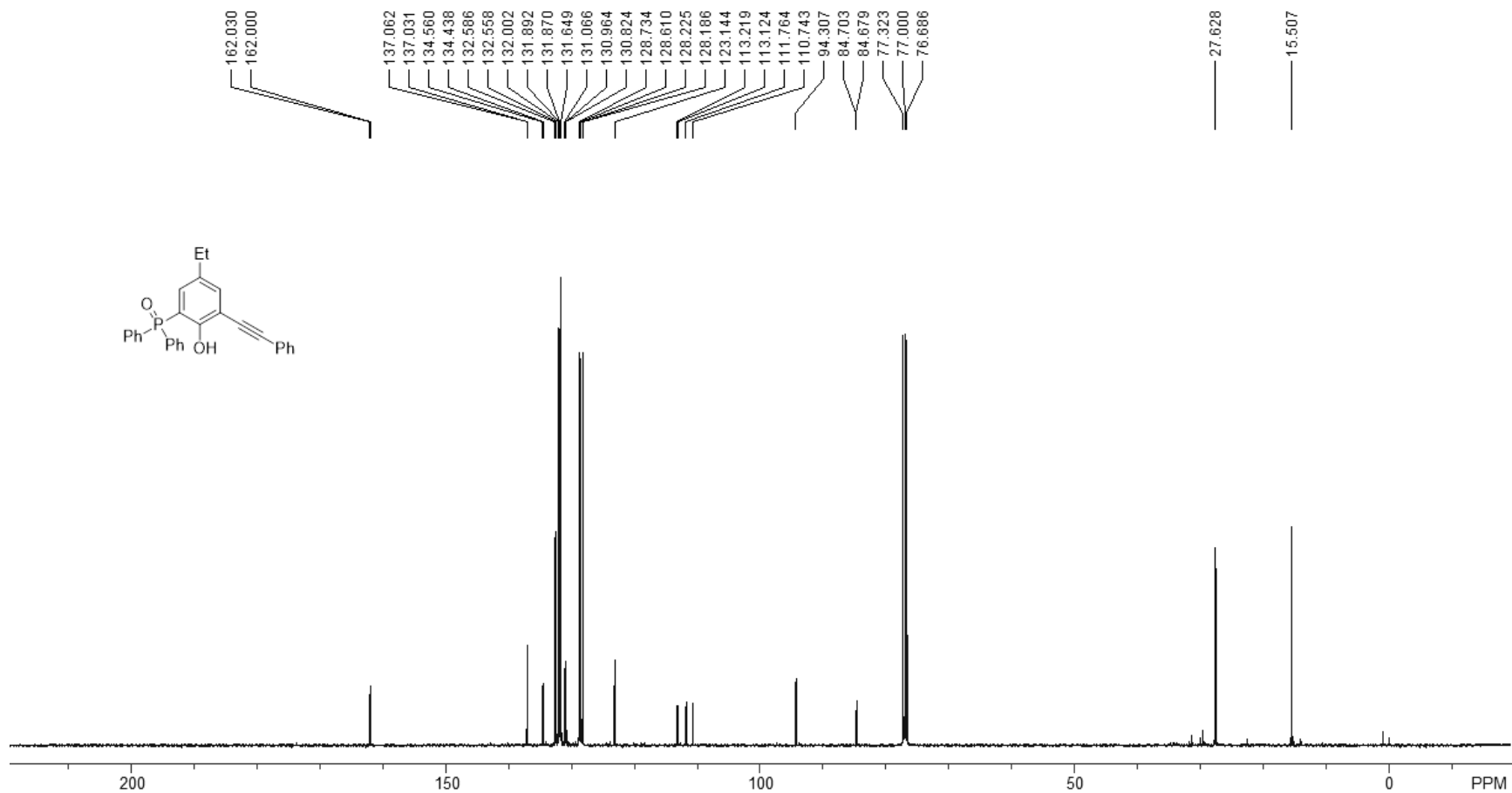
^{31}P NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)



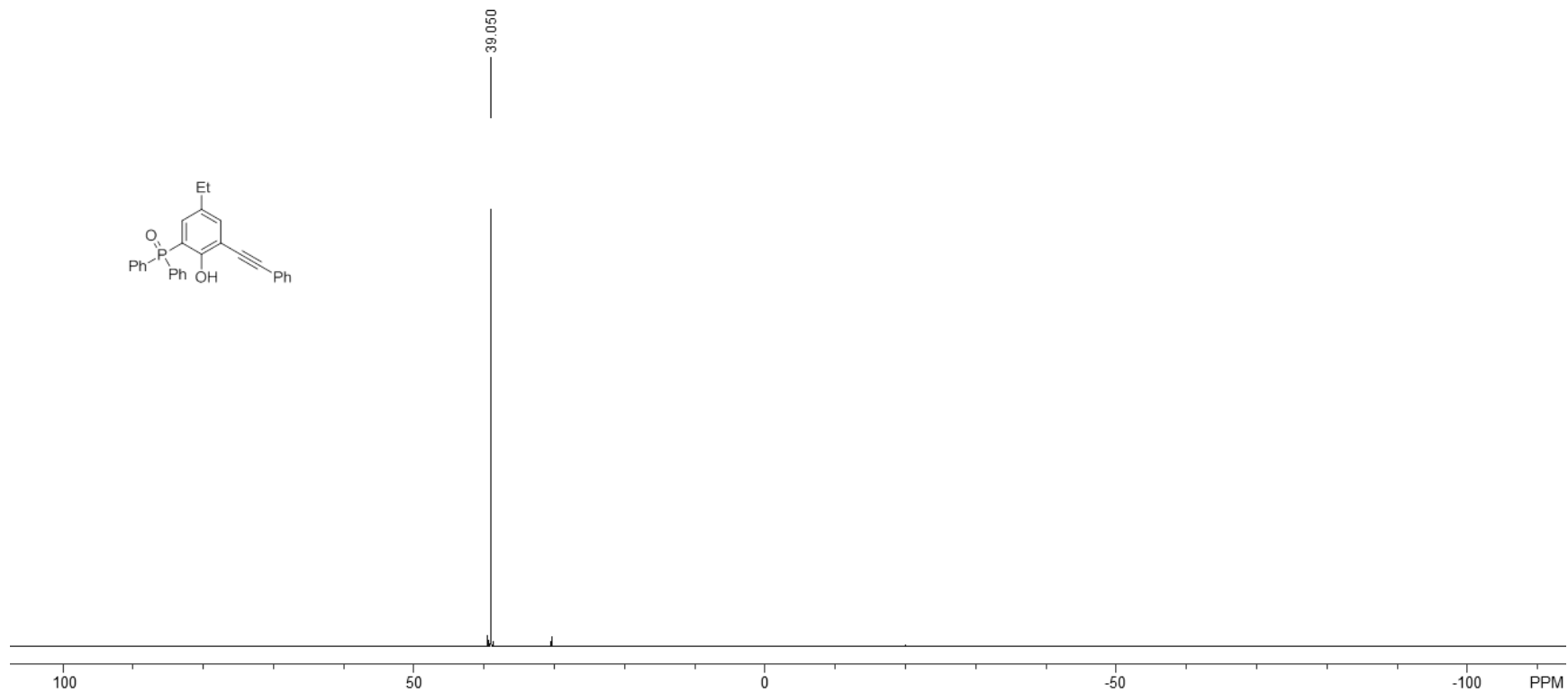
¹H NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)



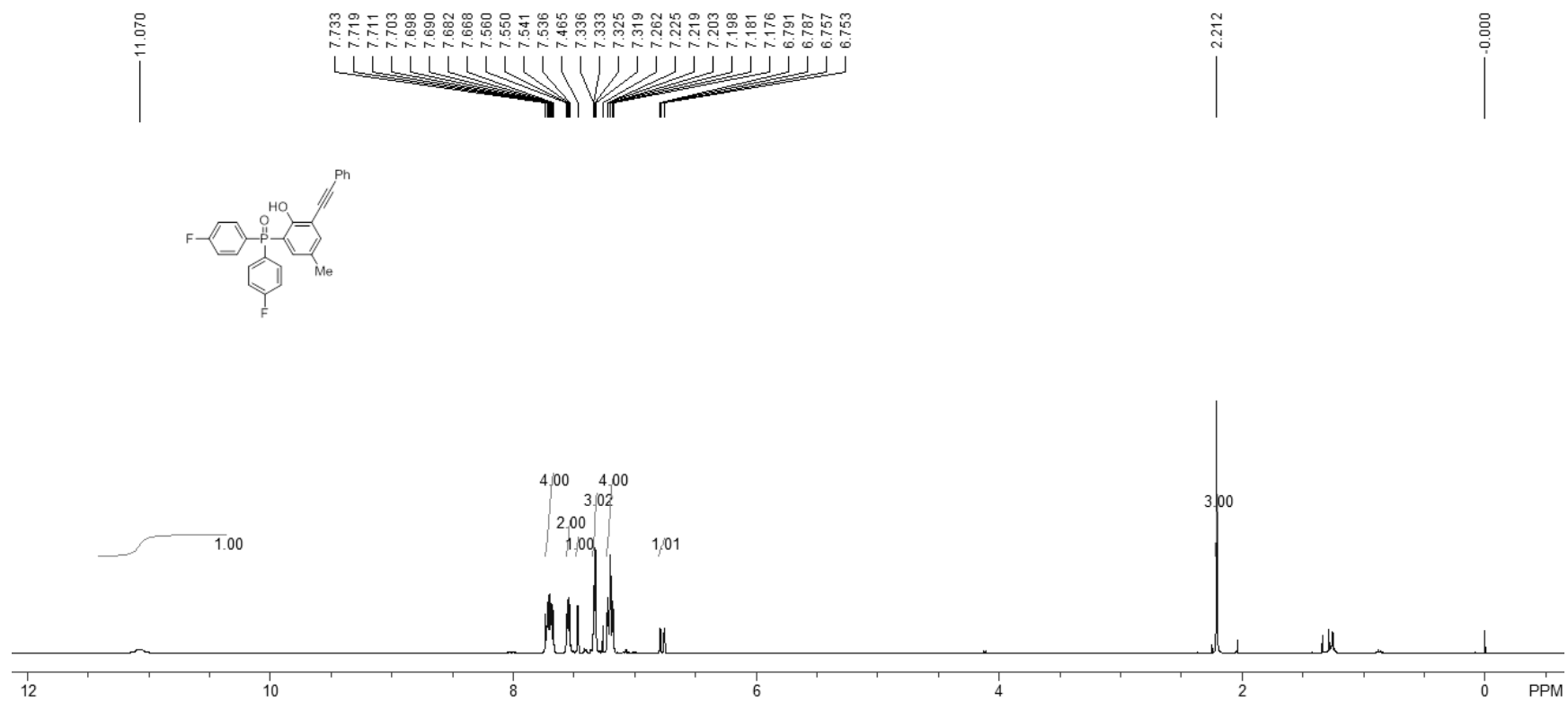
¹³C NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)



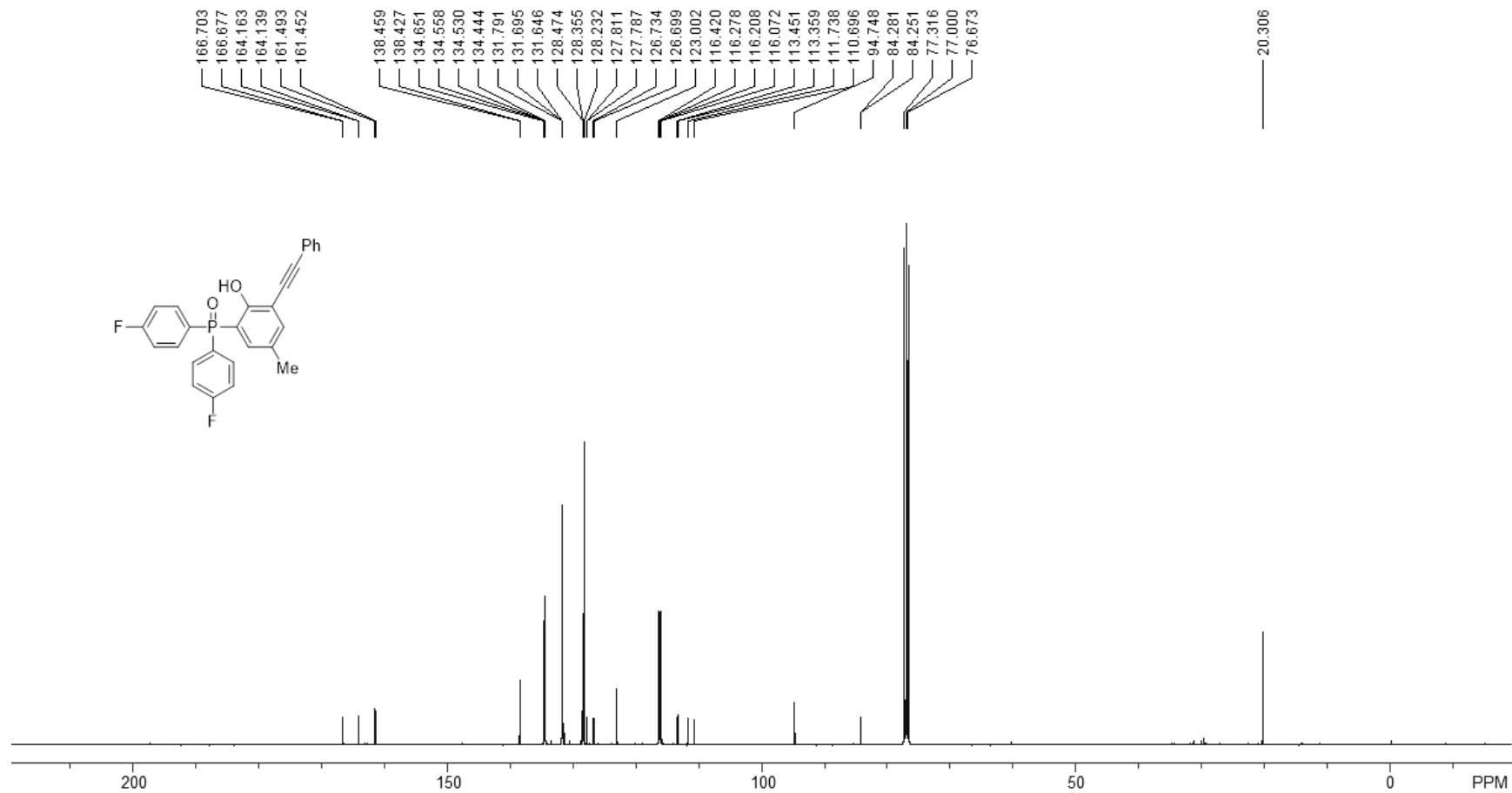
^{31}P NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)



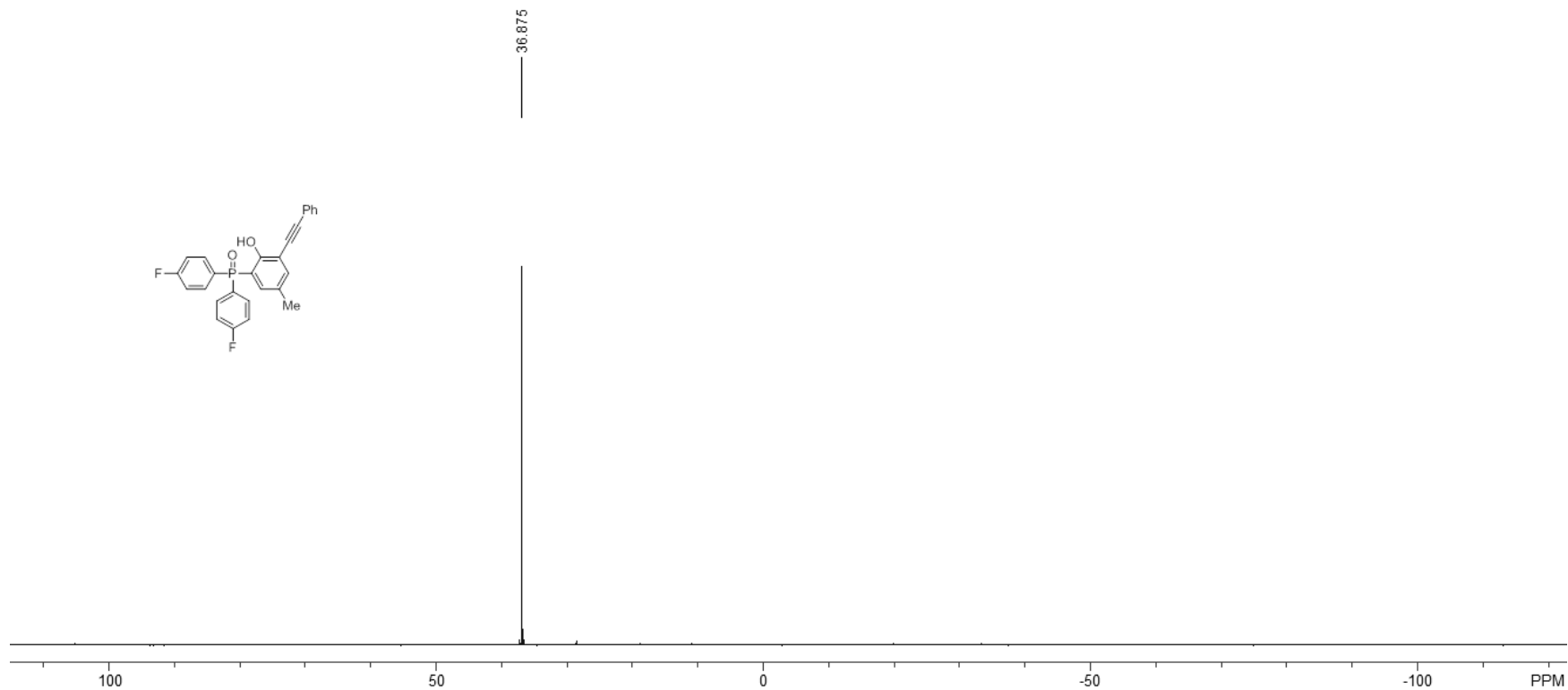
¹H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)



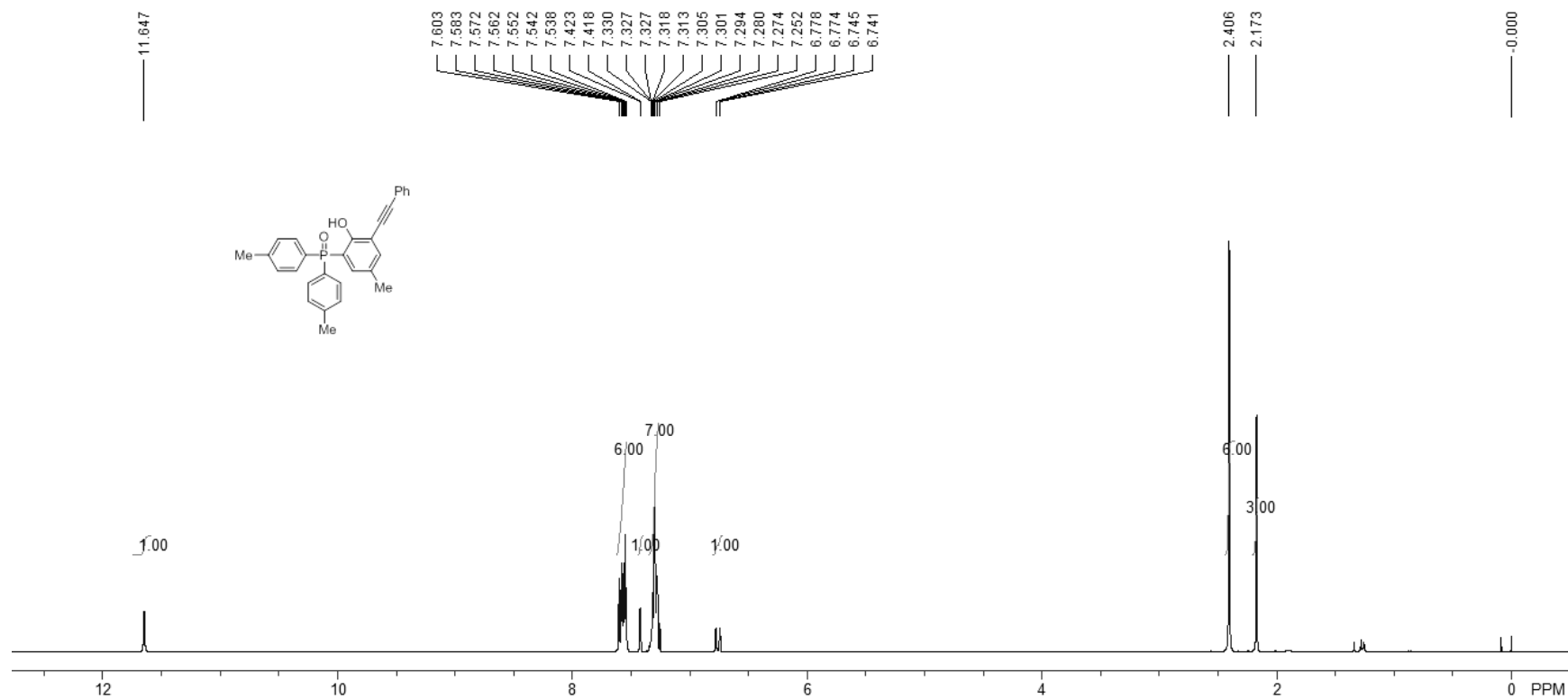
¹³C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)



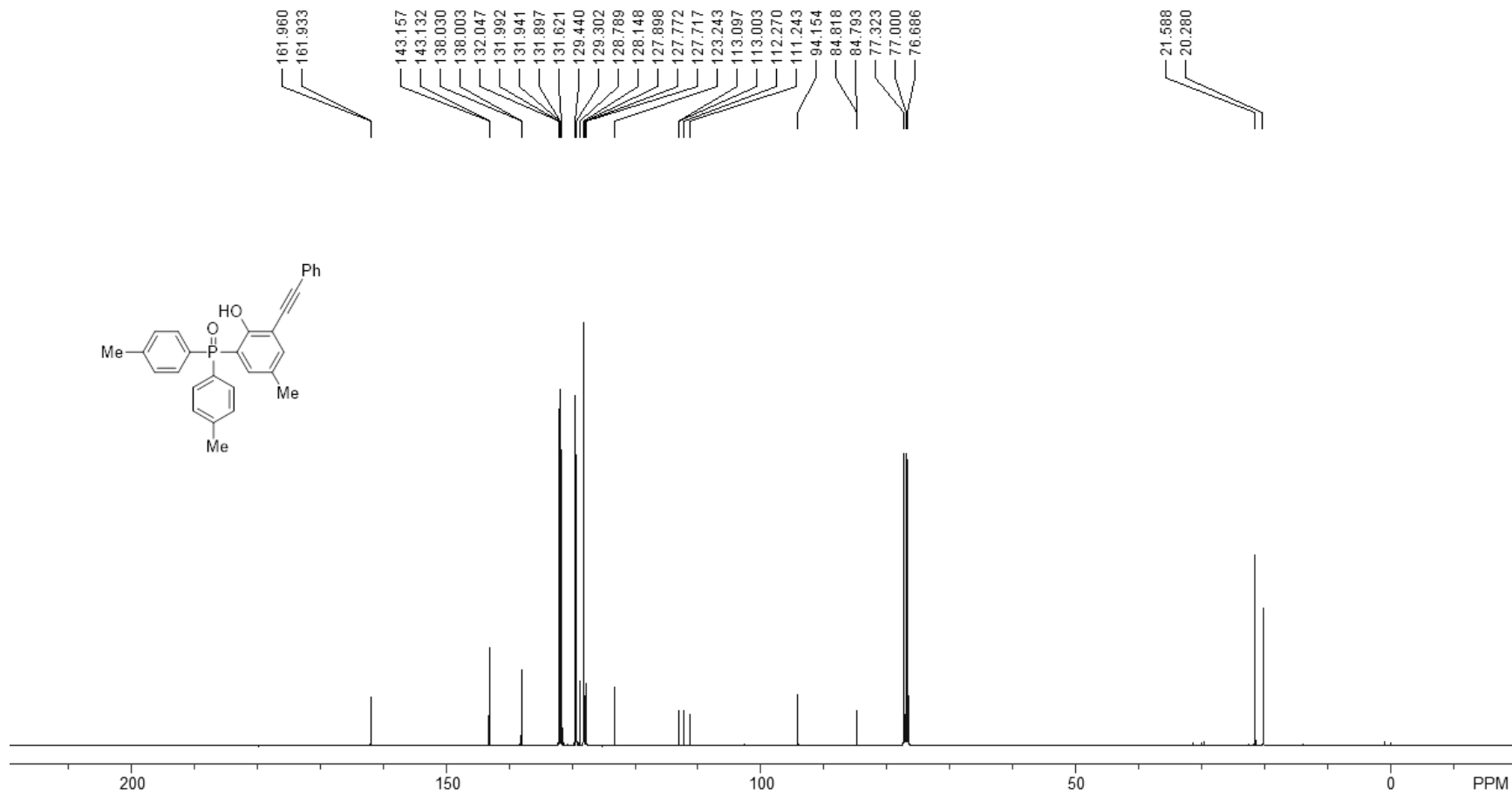
^{31}P NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)



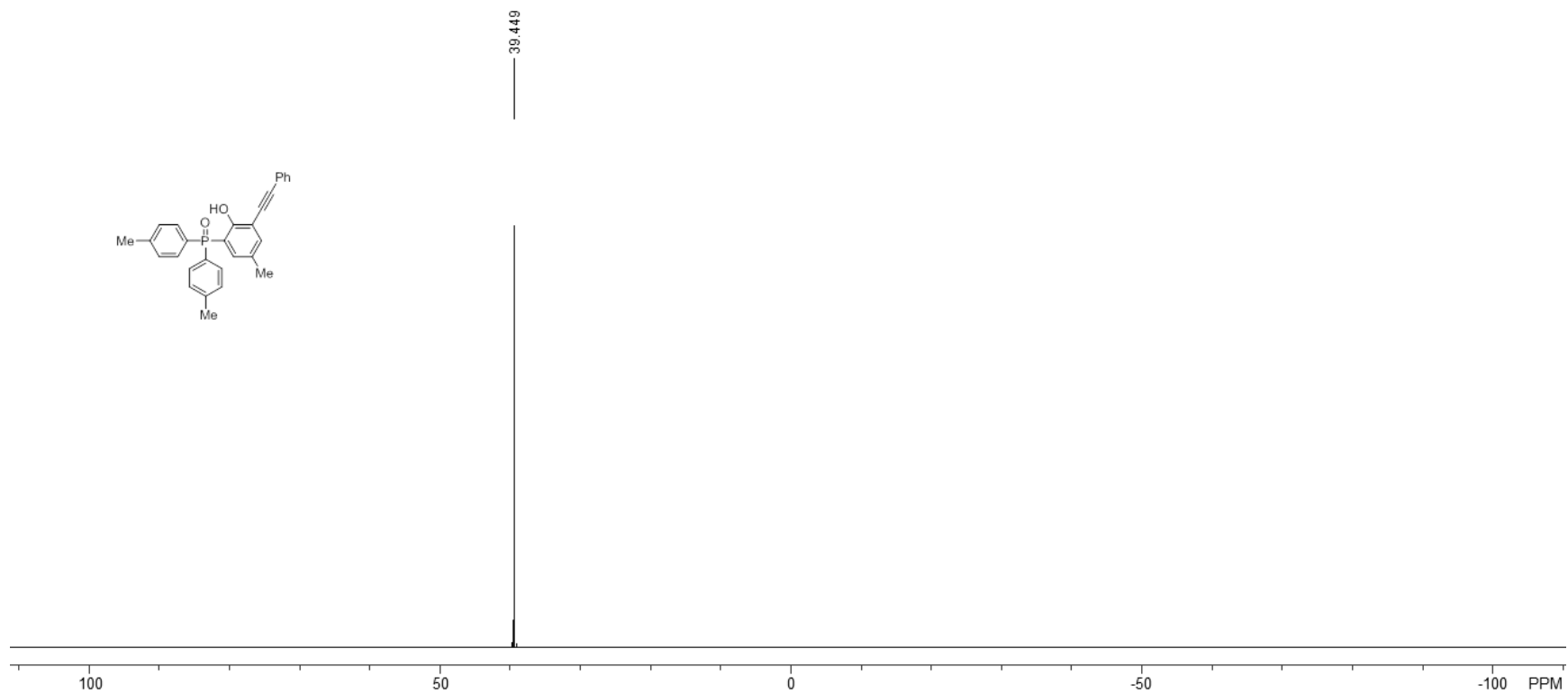
¹H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)



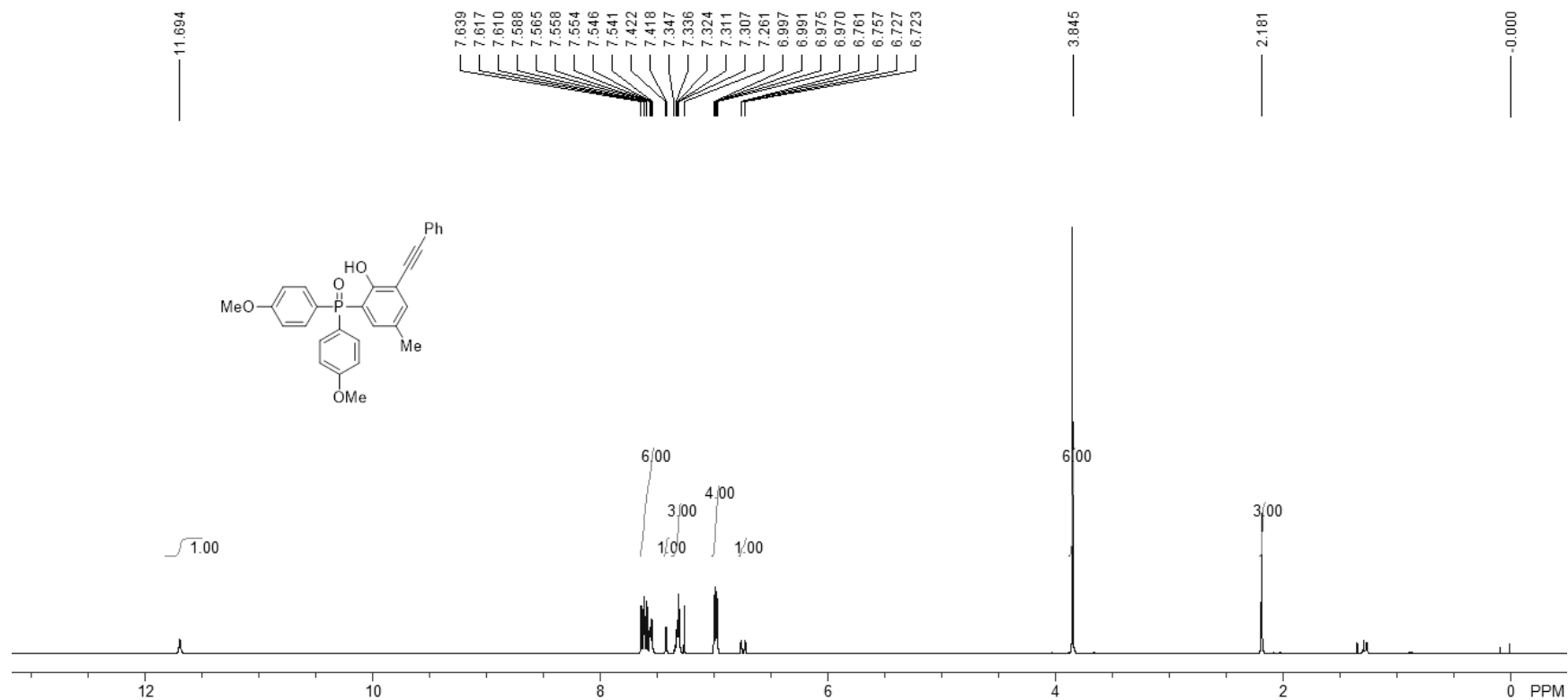
¹³C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)



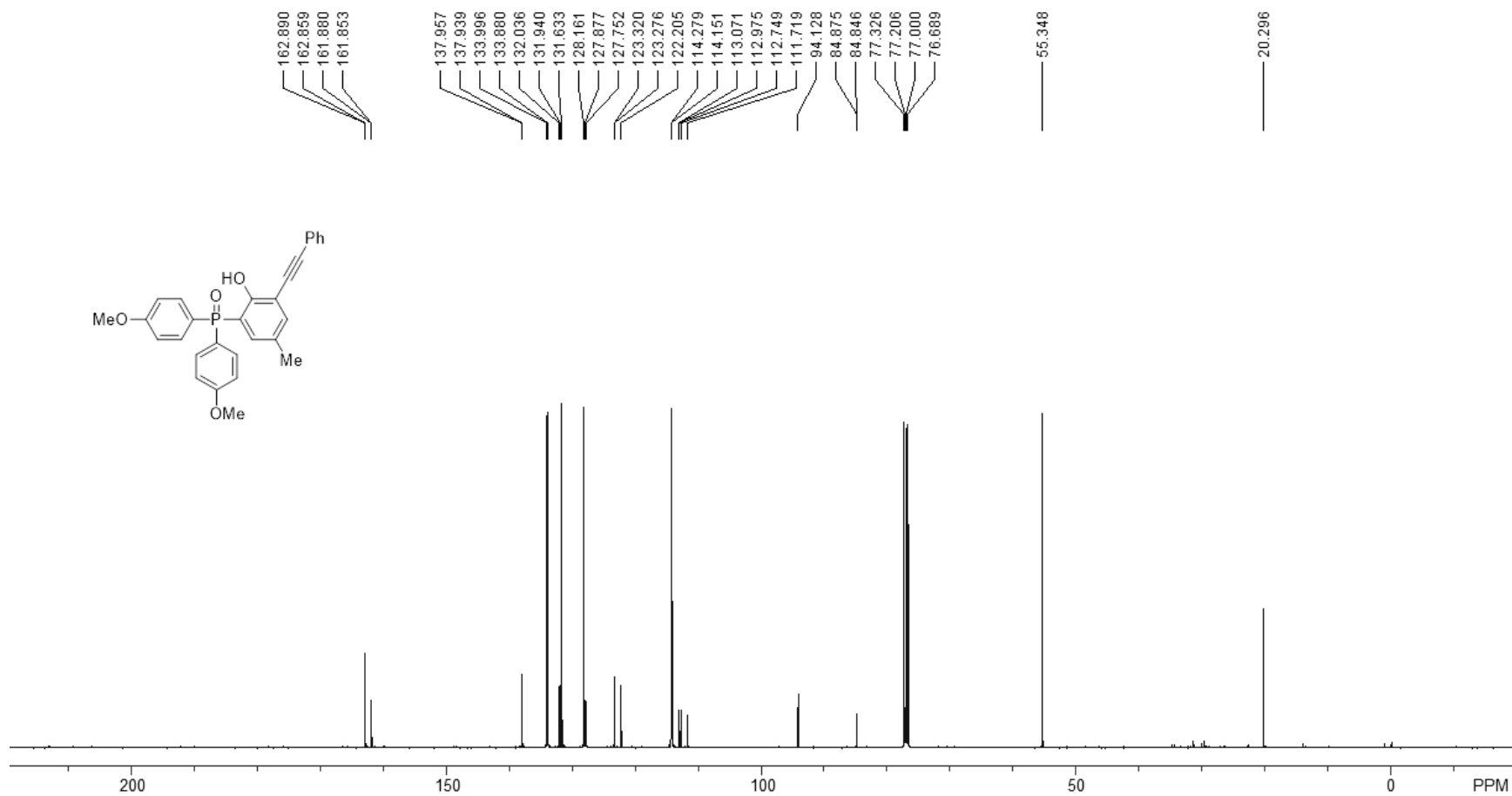
^{31}P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)



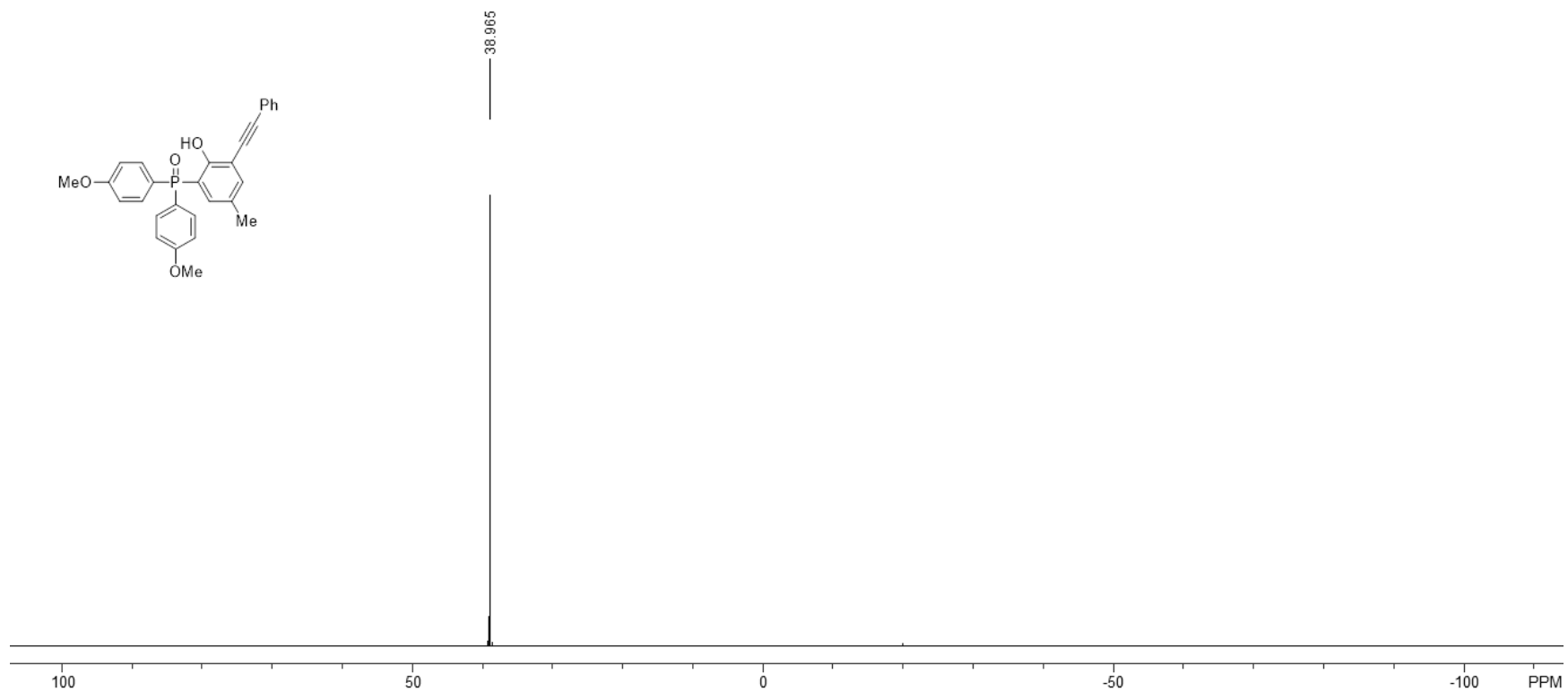
¹H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)



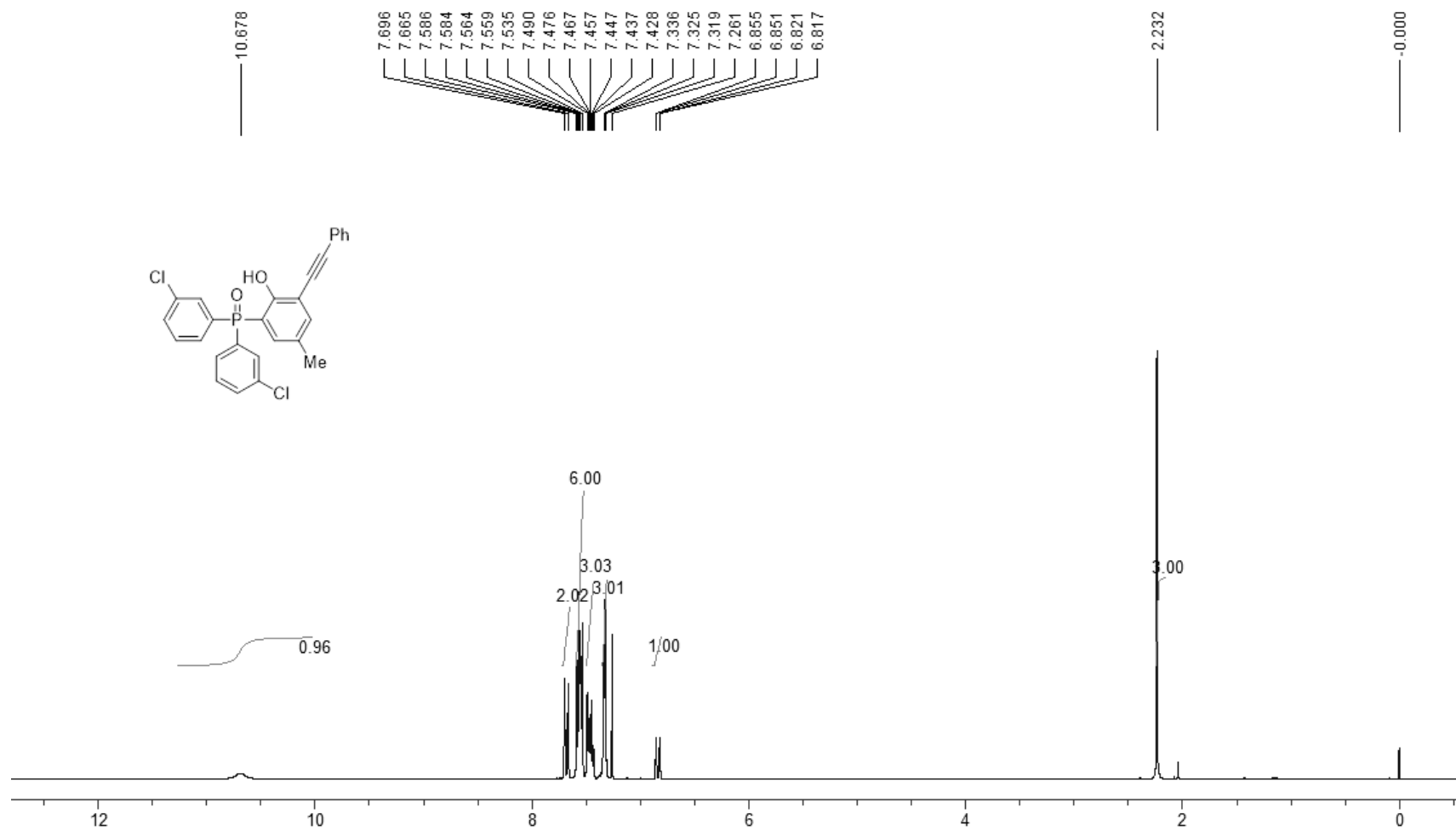
^{13}C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)



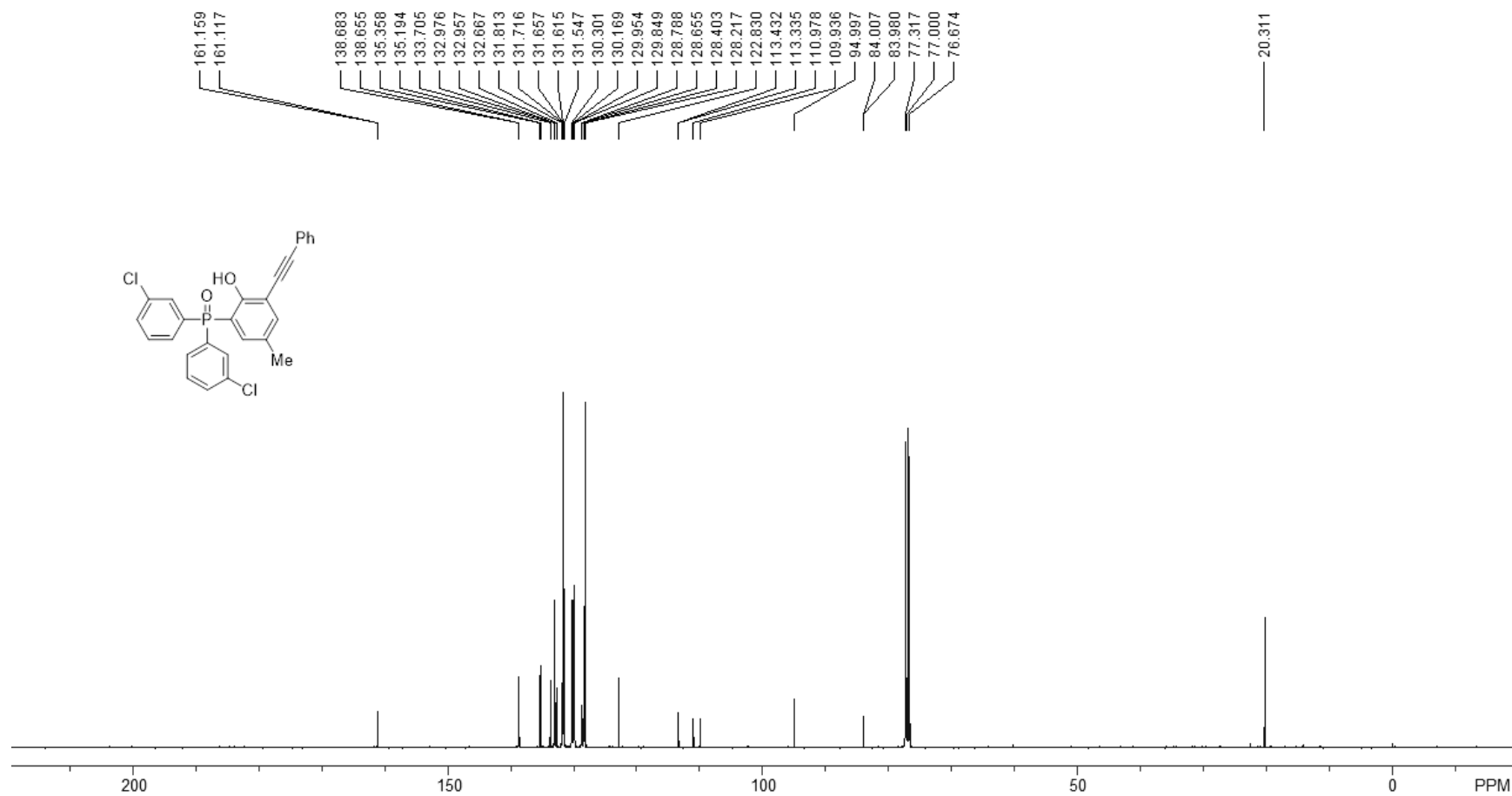
^{31}P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)



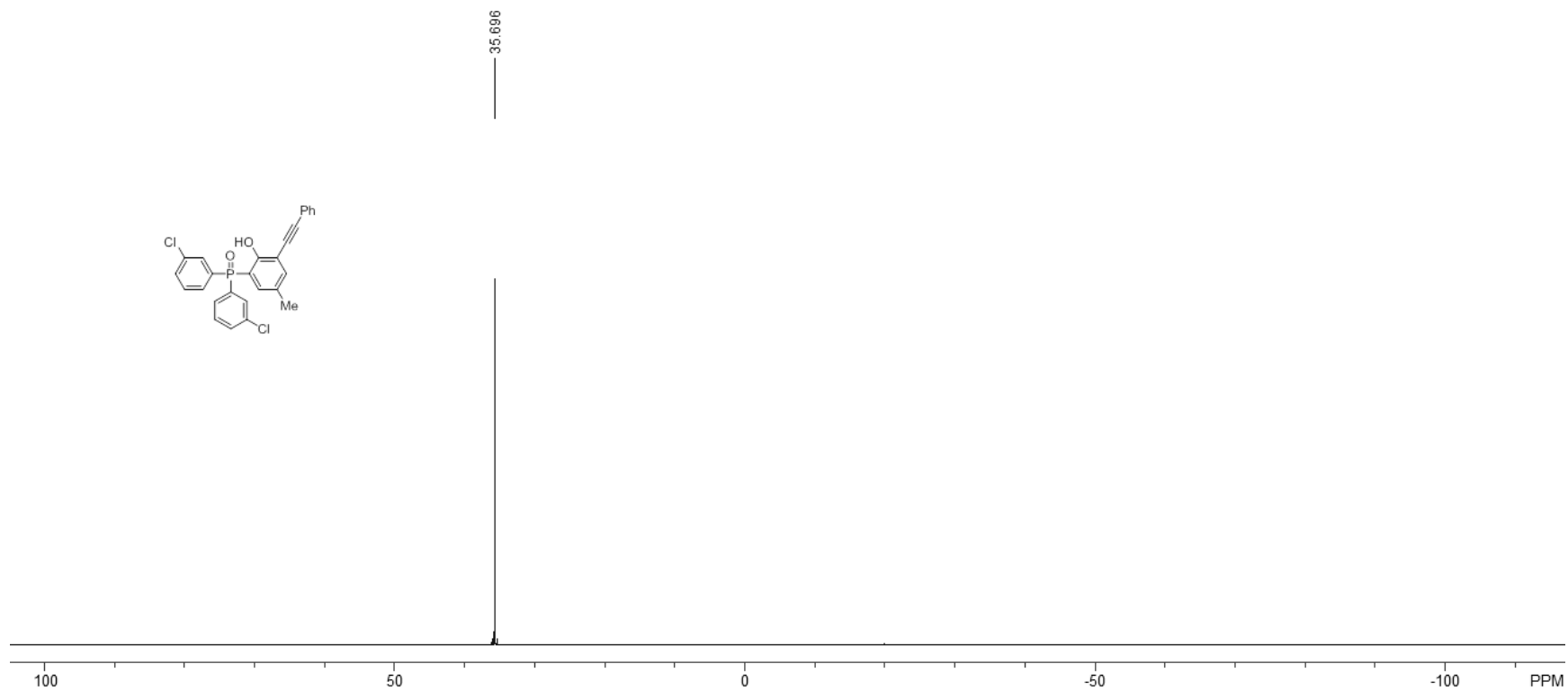
¹H NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j)



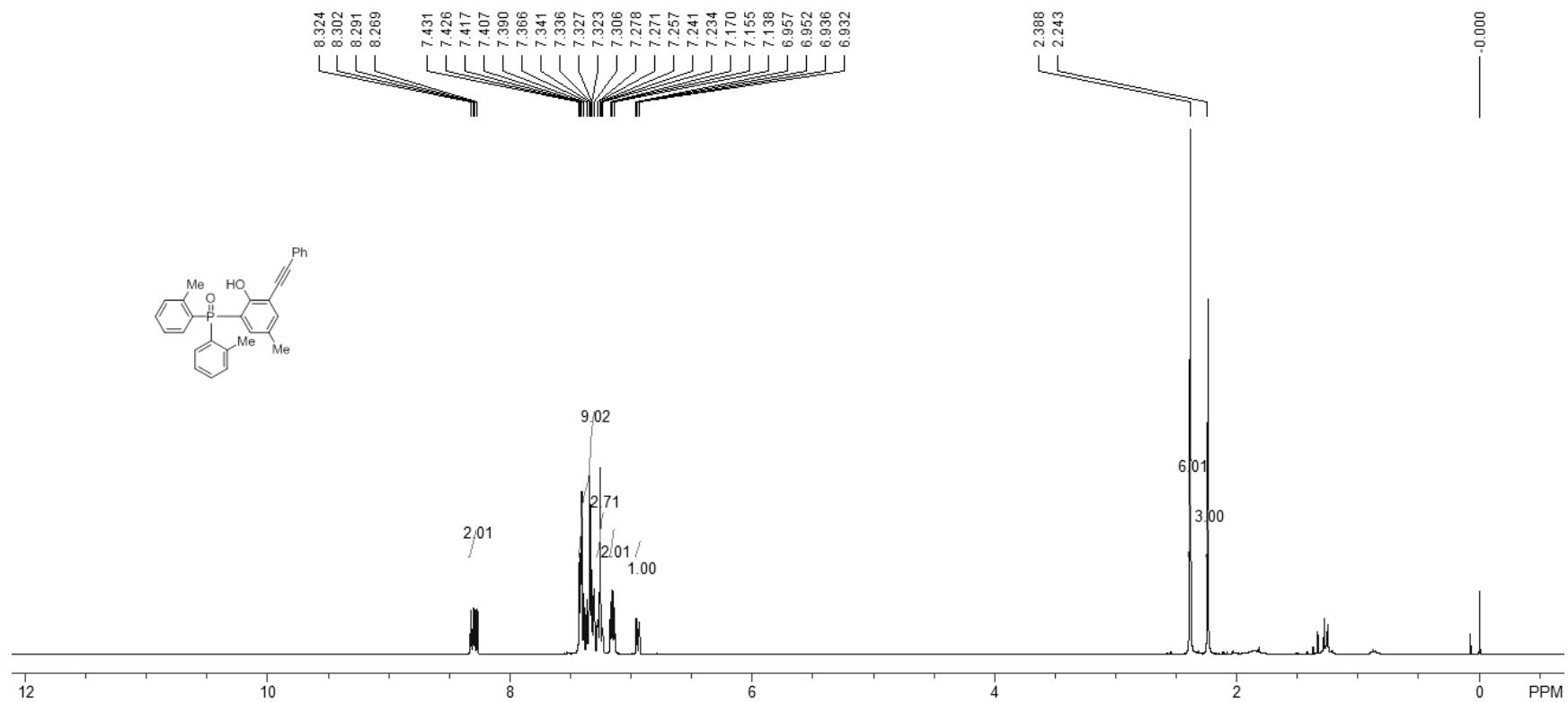
¹³C NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j)



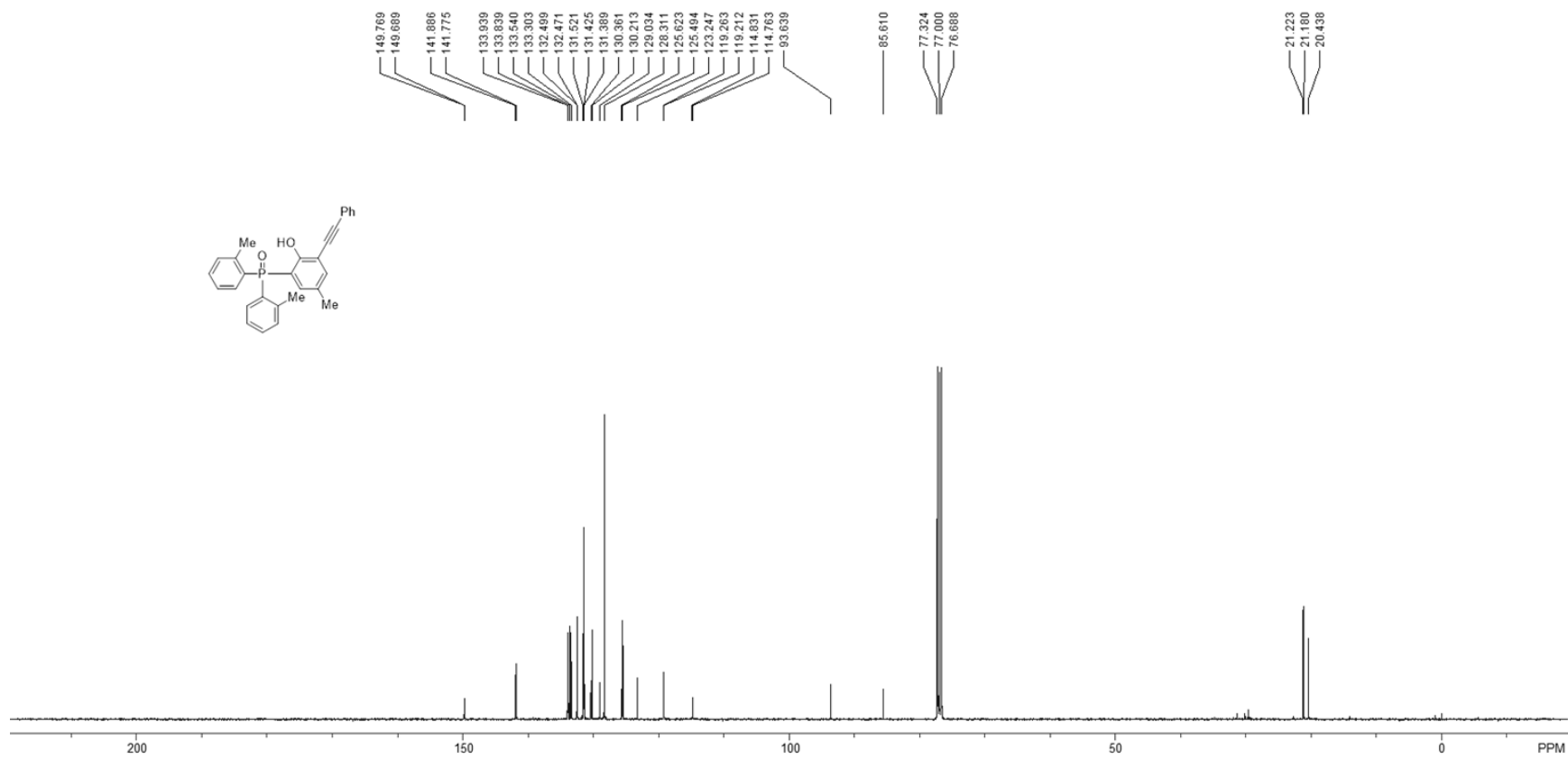
^{31}P NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j)



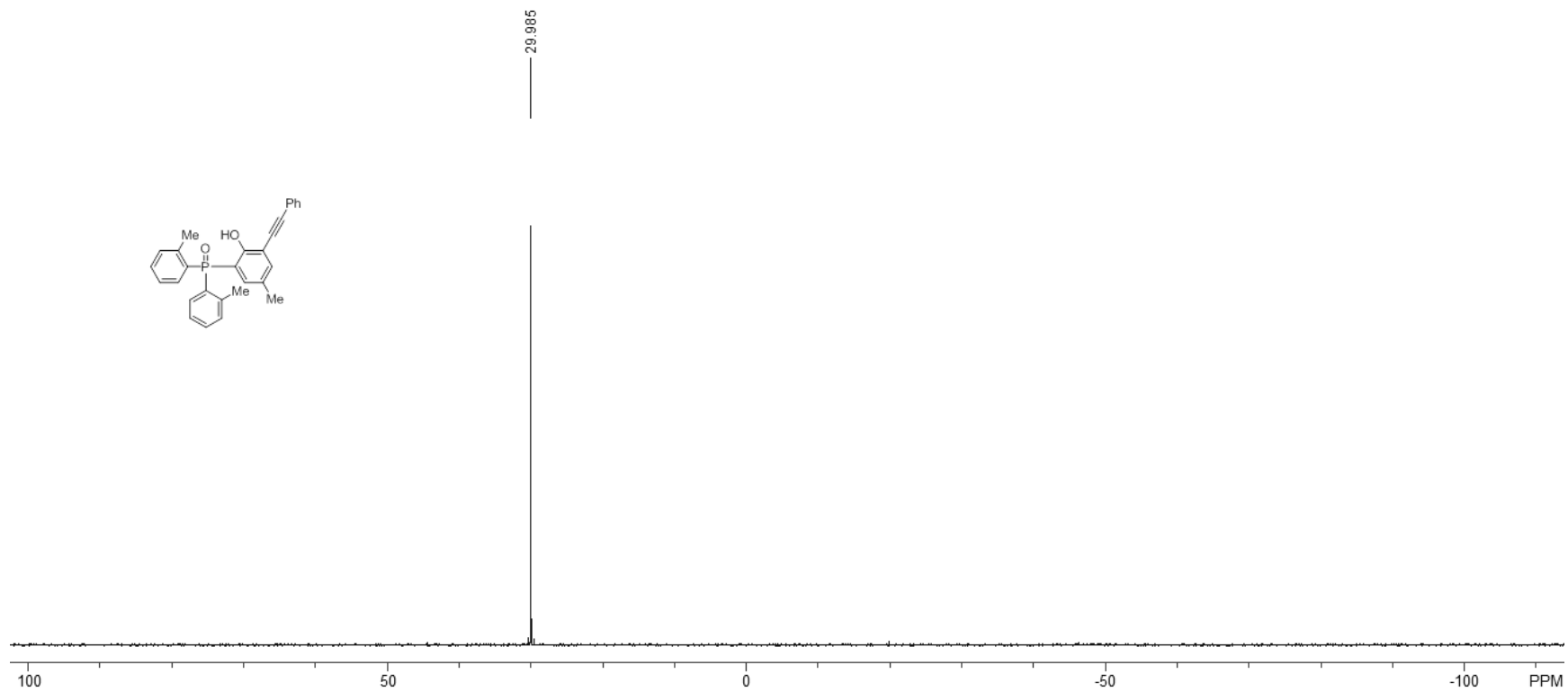
¹H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k)



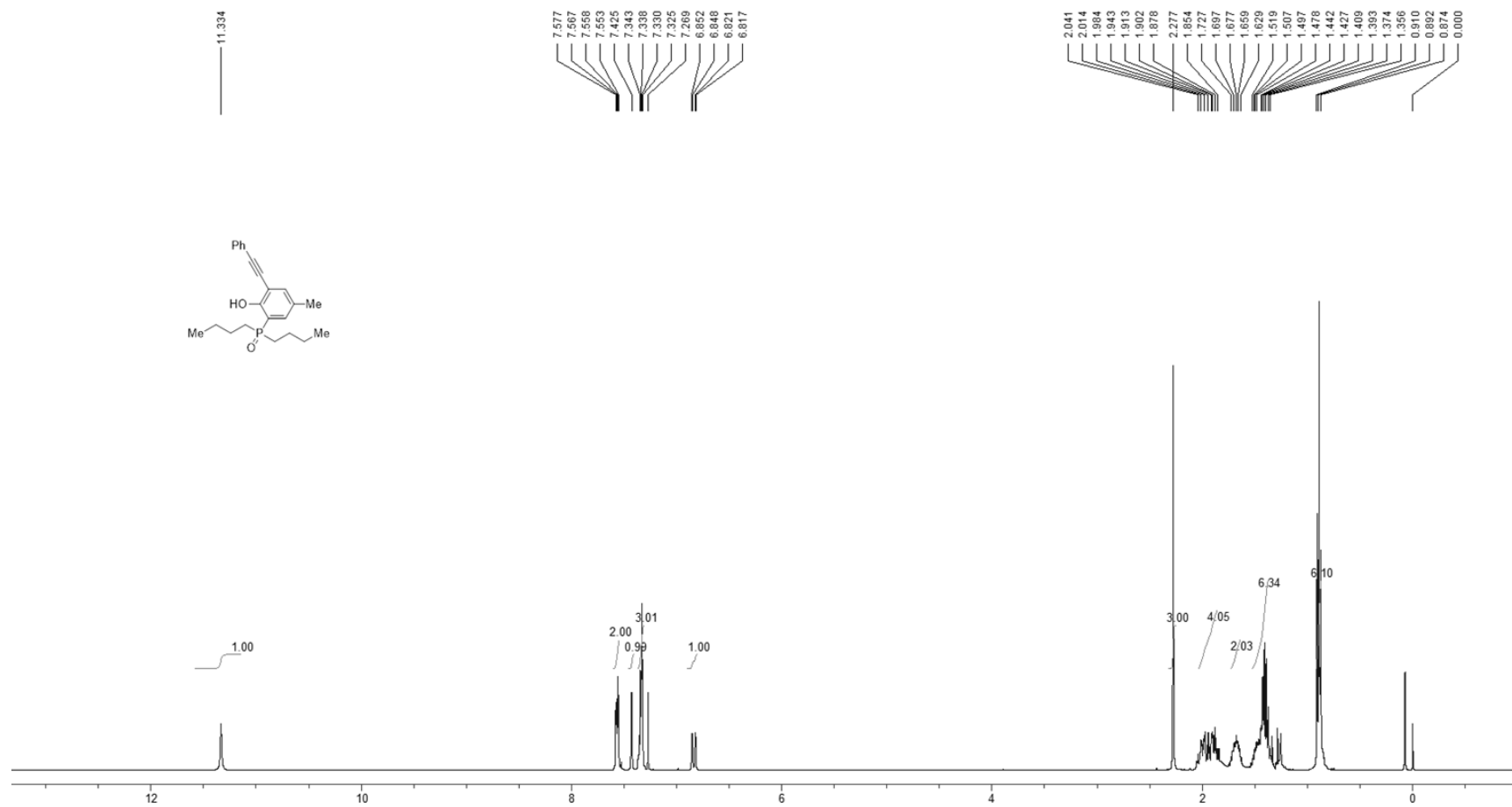
¹³C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k)



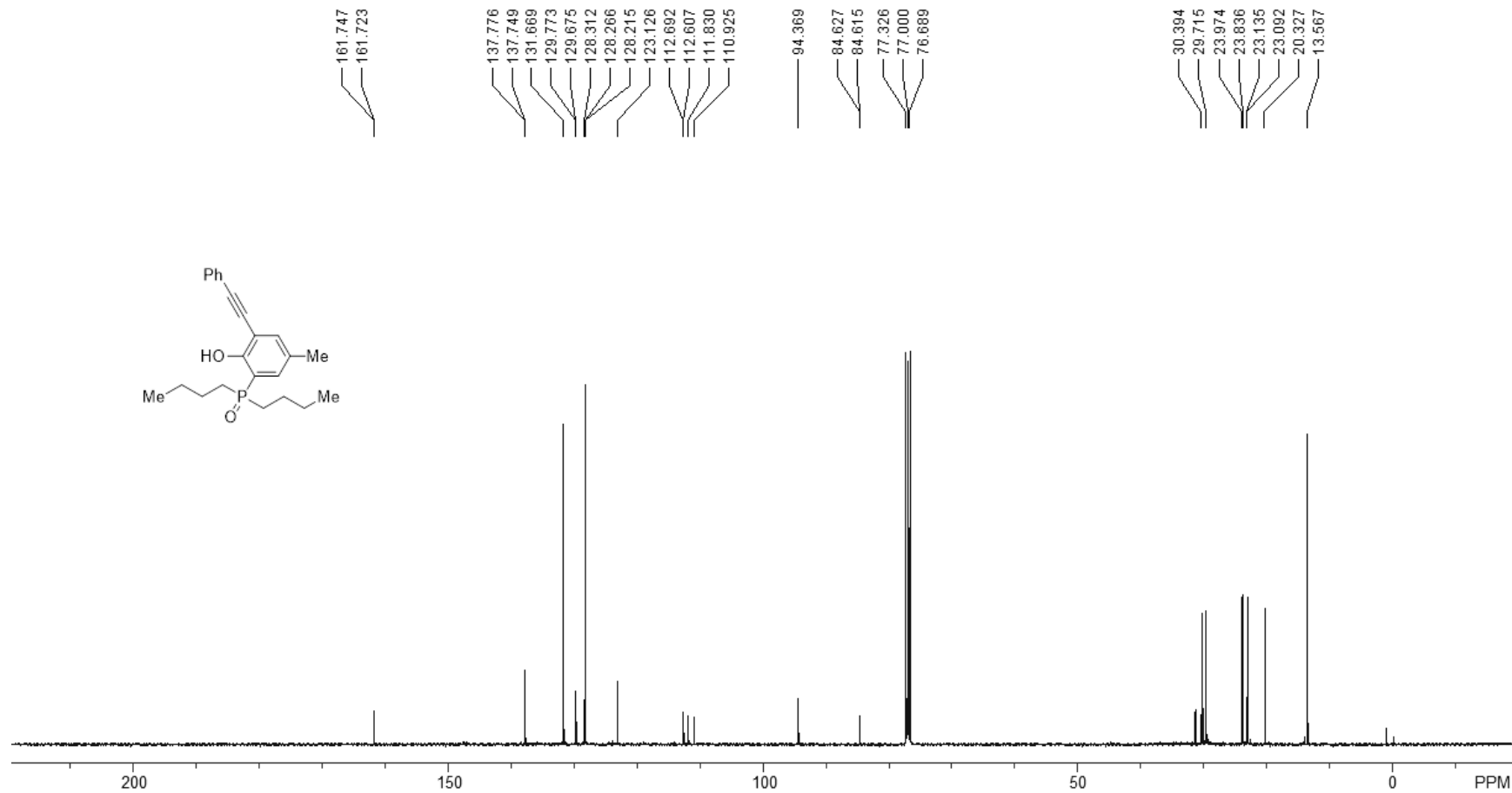
^{31}P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-*o*-tolylphosphine oxide (6k)



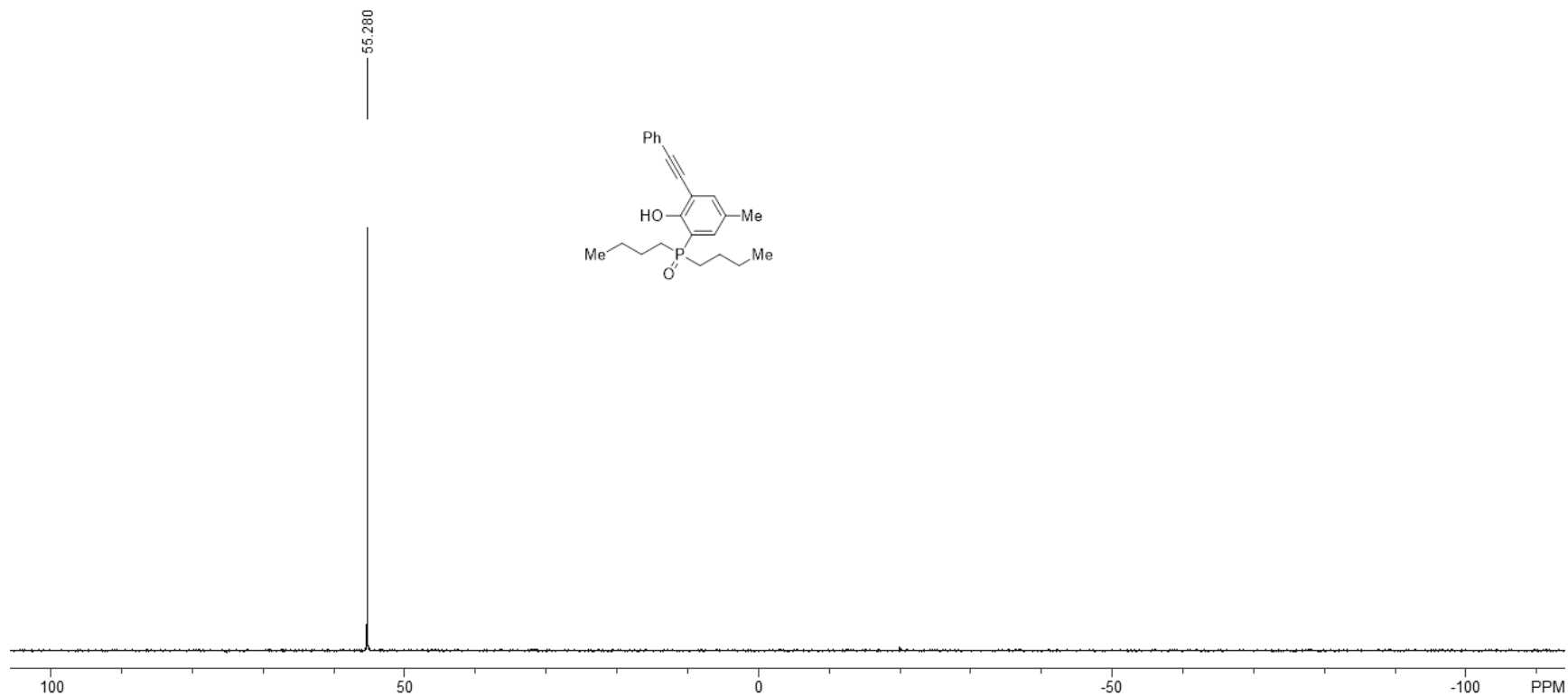
¹H NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)



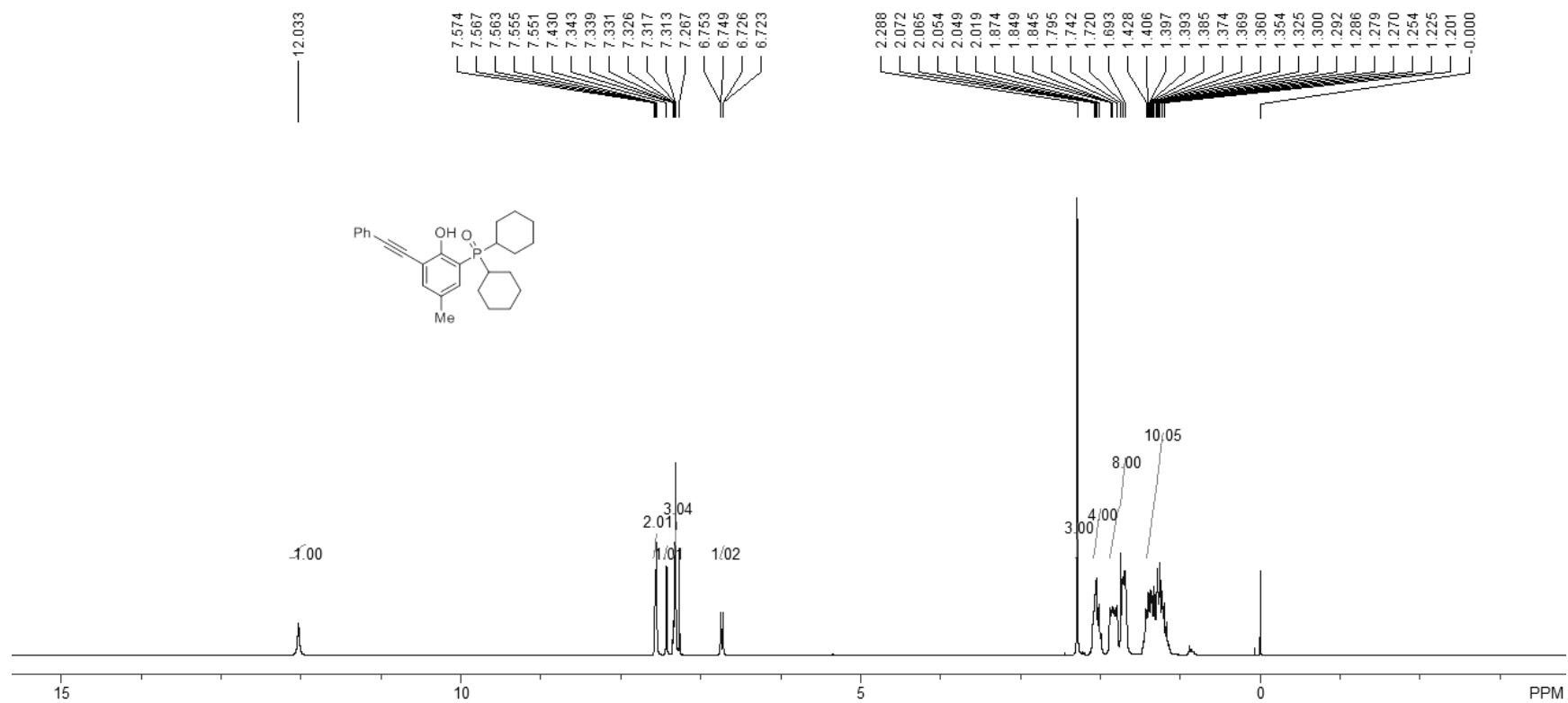
¹³C NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)



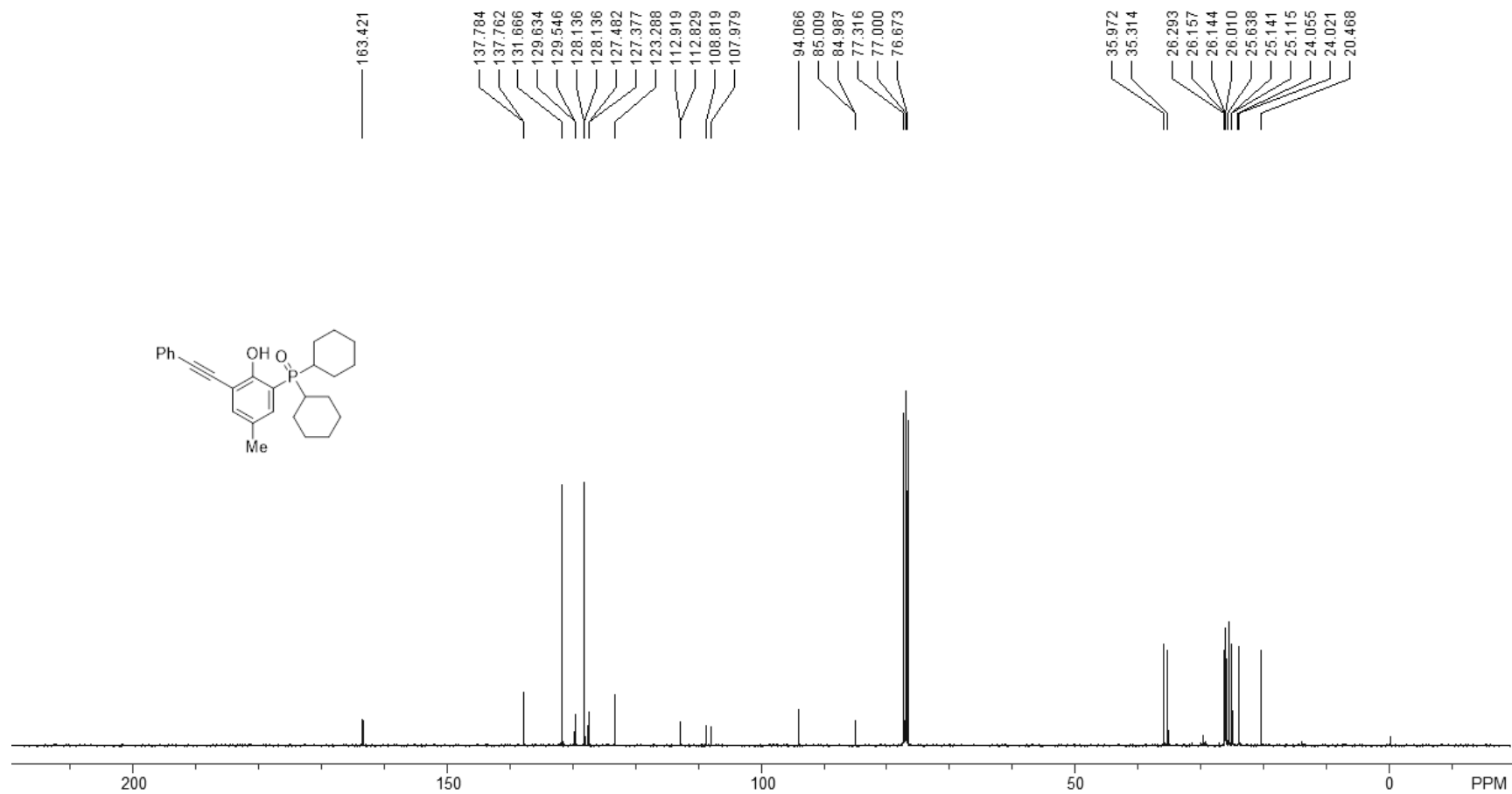
^{31}P NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)



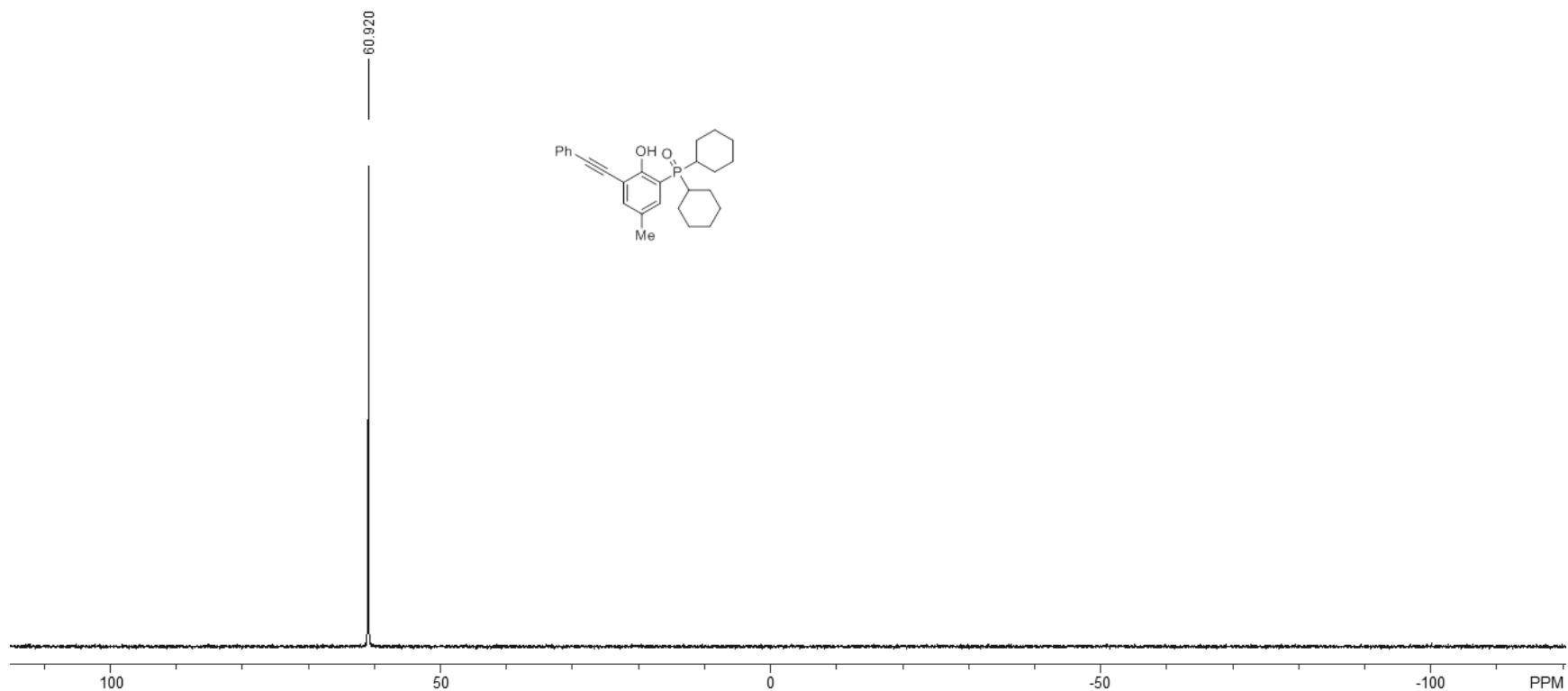
¹H NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)



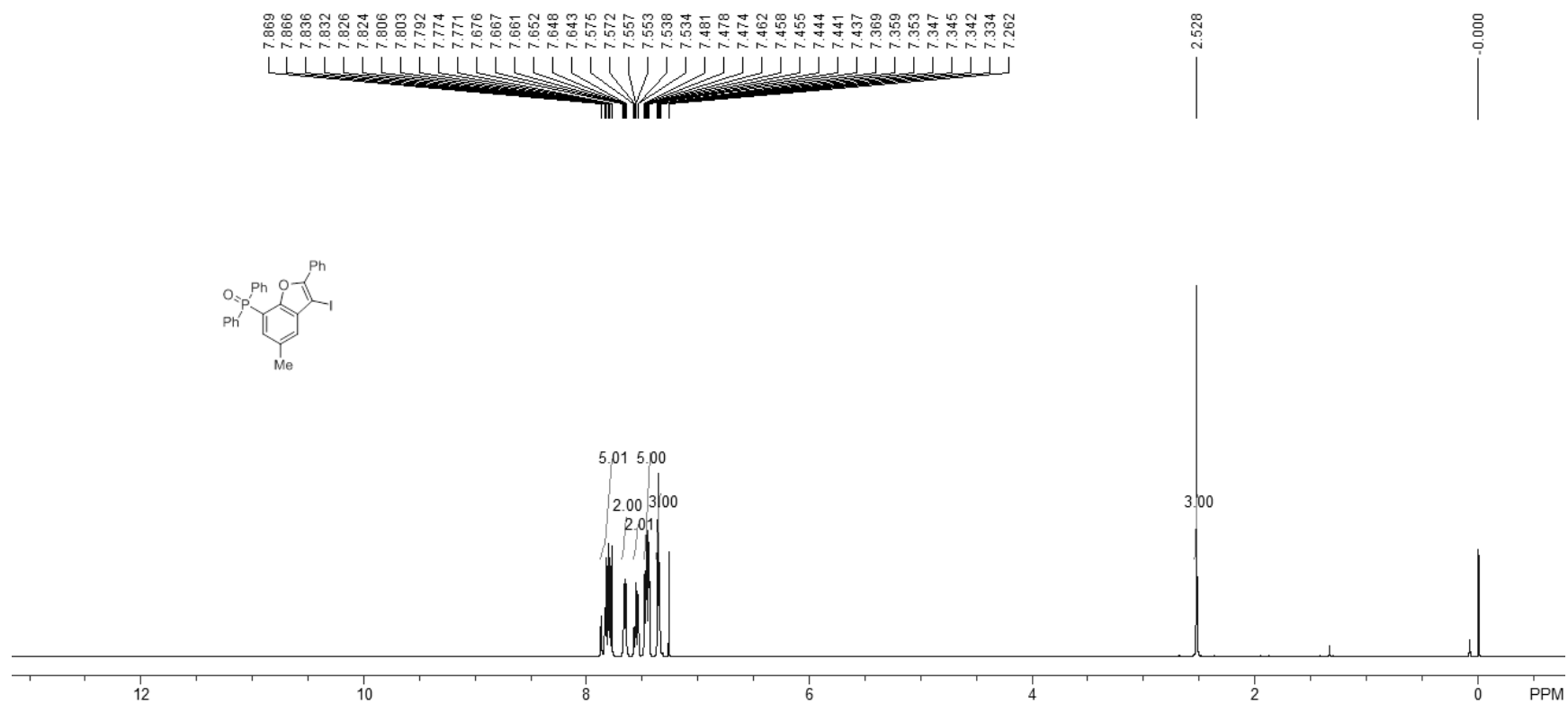
^{13}C NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)



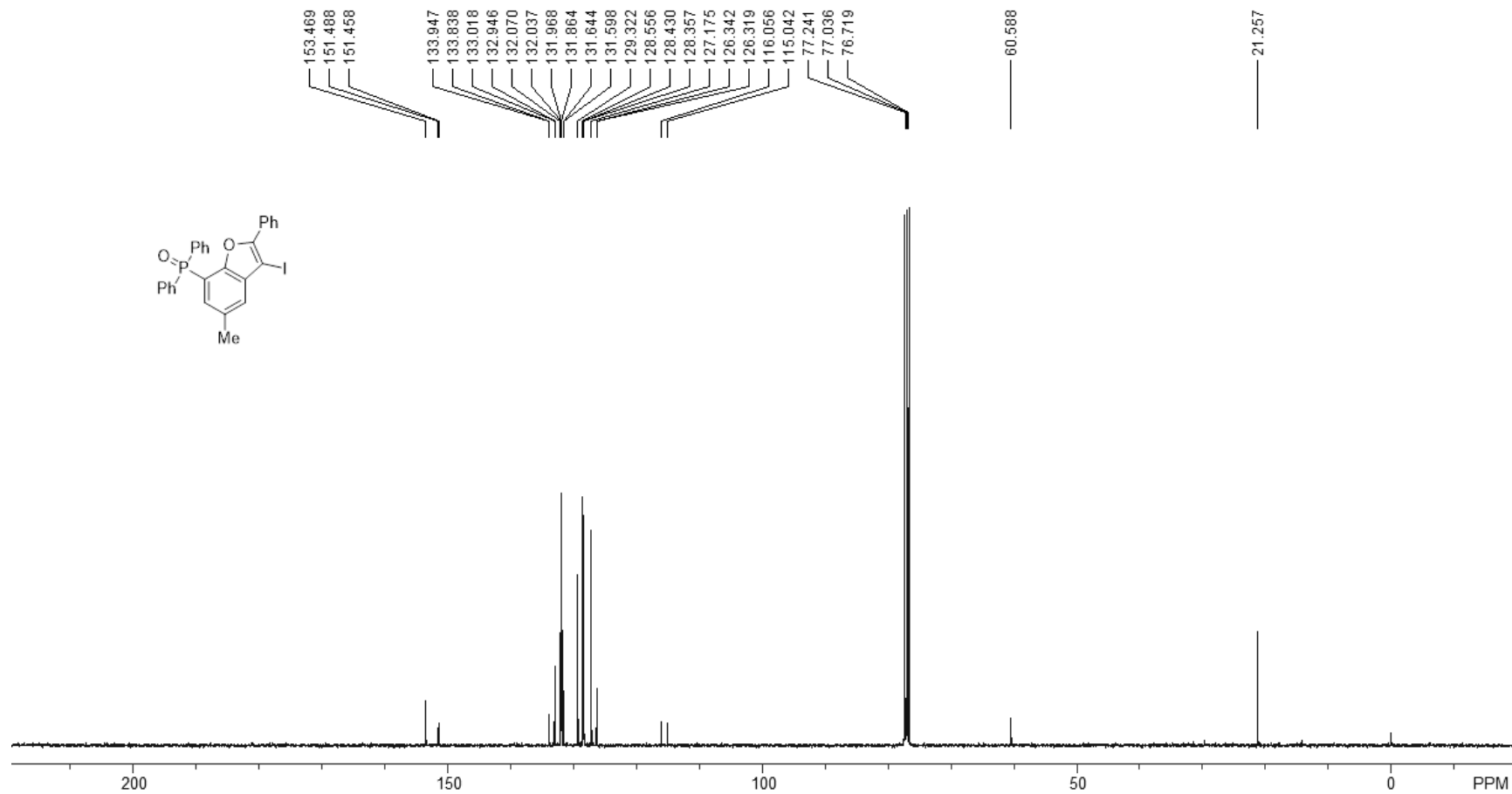
^{31}P NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)



¹H NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)



¹³C NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)



^{31}P NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)

