Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Towards tetrasubstituted furans through rearrangement and cyclodimerization of acetylenic ketones

Zhenyun Dai, Chenyong Xu, Rongqiang Tian,* Zheng Duan*

College of Chemistry, Green Catalysis Center, International Phosphorus Laboratory, International Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province, Zhengzhou University, Zhengzhou 450001, P. R. China
**E-mail:tianrq@zzu.edu.cn (R. Tian).*
**E-mail:duanzheng@zzu.edu.cn (Z. Duan).*

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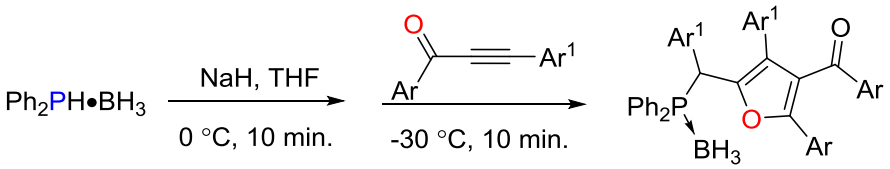
General Information

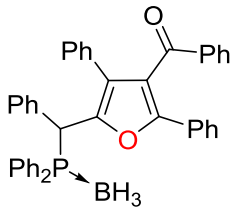
All reactions were performed under nitrogen using solvents dried by standard methods. Tetrahydrofuran (THF) were dried with sodium and distilled before use. Silica gel (200-300 mesh) were used for the chromatographic separations. **^{1}H**, **^{13}C** ,**^{11}B** and **^{31}P** nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-300 (300 MHz) or AV-400 (400 MHz) spectrometer. All coupling constants (*J* values) were reported in hertz (Hz). Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS (^{1}H). High-resolution mass spectra (HRMS) were obtained with a Waters UPLC G2-XS Q-Tof mass spectrometer (ESI, positive mode). X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4 °C/min, the thermometer was not corrected. All commercially available reagents were used without further purification. 2-chloroethylphosphine $W(CO)_5$ complex was prepared according to literature method[1]. Acetylenic ketones were prepared according to literature method[2]. Borane diphenylphosphane and borane dicyclohexylphosphane were prepared according to literature method[3].All new compounds were synthetic in small scale, and were purified by column chromatography or thin layer chromatography. The purities of the new compounds are acceptable according to NMR spectra analysis. Flammable gas was released when phosphine borane complex contact with water. The toxicity of compounds obtained in this work is unknown.

Experimental Procedures and Characterization Data



3a-3m

General Procedures and Characterization of 3a to 3m: NaH (9.6 mg, 0.24 mmol, 60% dispersion in mineral oil) was added to the solution of diphenylphosphane borane complex **1** (40 mg, 0.2 mmol) in THF (4 mL) at 0 °C. Then the mixture was stirred vigorously in an ice bath for 10 minutes. Acetylenic ketones (0.5 mmol) was added to the reaction mixture at -30 °C and kept the mixture for 10 minutes at -30 °C. Two drops of saturated aqueous NH_4Cl was added to the mixture to quench the reaction. After filtration with a silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford the desired product.

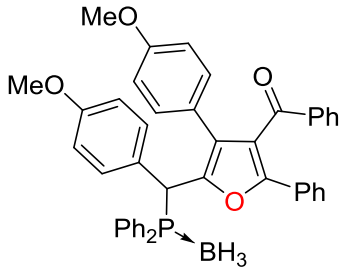


3a: 106.5 mg, 87% yield, yellow solid, R_f= 0.30 (hexane/EtOAc = 15/1), **m.p.** 119.4-120.7 ℃. **^{31}P NMR (121MHz, $CDCl_3$)** δ 27.0; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -37.2; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 – 7.59 (m, 4H), 7.58 – 7.53 (m, 3H), 7.51 – 7.41 (m, 7H), 7.39 – 7.29 (m, 8H), 7.27 – 7.19 (m, 6H), 6.94 – 6.88 (m, 2H), 5.15 (d, *J*= 15.8 Hz, 1H), 1.13 – 0.44 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.1, 152.5, 146.03, 145.98, 137.2, 134.3, 133.4, 133.33, 133.26, 133.25, 133.2, 131.4, 131.2, 130.2, 130.1, 129.8, 129.2, 128.6, 128.6, 128.52, 128.49, 128.42, 128.38, 127.9, 127.84, 127.79, 127.72, 127.5, 127.3, 126.8, 126.7, 126.6, 121.1, 43.3, 43.1. **HRMS (ESI)** Calcd for $C_{42}H_{34}BNaO_2P$ $[M+Na]^+$ 635.2282, found 635.2292.

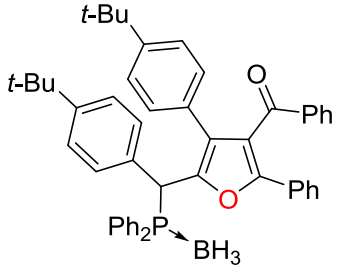
Gram scale experiment for synthesis of **3a**

NaH (6 mmol, 0.24 g) was added to the solution of diphenylphosphane borane

complex **1** (1.00 g, 5 mmol) in THF (20 mL) at 0 °C. Then the mixture was stirred vigorously in an ice bath for 10 minutes. Acetylenic ketone **2a** (2.58 g 12.5 mmol) was added to the reaction mixture at -30 °C and kept the mixture for 10 minutes at -30 °C. Saturated aqueous NH_4Cl was added to the mixture to quench the reaction. After filtration with a silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford **3a** (2.98 g) in 80% yield.

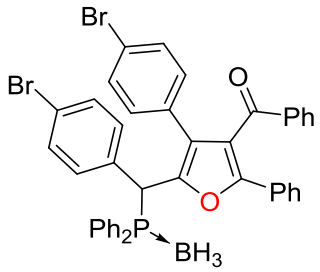


3b: 127.7 mg, 95% yield, yellow solid, R_f= 0.30 (hexane/EtOAc = 5/1), **m.p.** 152.7-153.9 ℃. **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.4; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.2; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.85 – 6.57 (m, 12H), 6.54 – 6.29 (m, 12H), 6.00 – 5.85 (m, 4H), 4.23 (d, *J* = 15.4 Hz, 1H), 2.88 (s, 6H),1.14 – 0.46 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.4, 159.2, 159.08, 152.06, 146.3, 146.2, 137.2, 135.2, 134.0, 133.6, 133.4, 133.29, 133.25, 133.2, 131.3, 130.4, 129.8, 129.5, 129.3, 128.6, 128.5, 128.2, 128.1, 127.5, 127.4, 126.5, 126.2, 126.13, 126.05, 123.4, 121.2, 114.5, 114.1, 113.9, 55.3, 55.2, 42.6, 42.2. **HRMS (ESI)** Calcd for $C_{44}H_{38}BKO_4P$ $[M+K]^+$ 711.2232, found 711.2233.

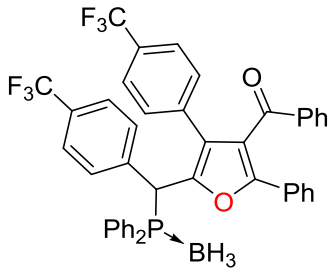


3c: 121.7 mg, 84% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1). **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.9; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -37.6; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.50 (m, 7H), 7.46 – 7.40 (m, 4H), 7.40 – 7.34 (m, 5H), 7.34 – 7.27 (m, 7H), 7.22 – 7.18 (m, 3H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.18 (d, *J* = 15.6 Hz, 1H),

1.28 (d, *J* = 9.8 Hz, 18H), 1.11 – 0.54 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.3, 152.3, 150.8, 150.7, 150.4, 146.14, 146.07, 137.4, 133.7, 133.53, 133.50, 133.42, 133.38, 133.3, 133.2, 133.1, 131.7, 131.24, 131.19, 129.9, 129.8, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.4, 126.6, 126.5, 125.5, 125.4, 124.8, 121.2, 42.8, 42.4, 34.58, 34.57, 31.4, 31.3. **HRMS (ESI)** Calcd for $C_{50}H_{50}BNaO_2P$ $[M+Na]^+$ 747.3534, found 747.3548.

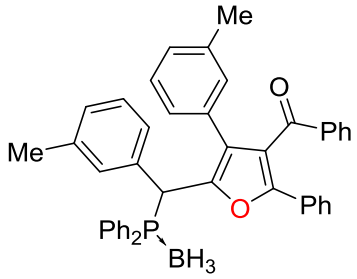


3d: 117.0 mg, 76% yield, yellow solid, R_f= 0.30 (hexane/EtOAc = 10/1), **m.p.** 95.4-96.6 ℃. **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.3; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.1; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.54 (m, 5H), 7.53 – 7.45 (m, 7H), 7.43 – 7.33 (m, 10H), 7.27 (s, 1H), 7.24 – 7.21 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 2H), 4.98 (d, *J* = 15.5 Hz, 1H),1.12 – 0.49 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.6, 152.9, 145.6, 145.6, 137.0, 133.7, 133.34, 133.25, 133.16, 133.1, 131.9, 131.8, 131.8 , 131.7, 131.62, 131.58, 130.7, 130.0, 129.7, 128.82, 128.76, 128.7, 128.6, 128.5, 127.5, 127.2, 127.0, 126.6, 126.0, 125.9, 122.31, 122.28, 122.2, 120.8, 43.1, 42.8. **HRMS (ESI)** Calcd for $C_{42}H_{32}BBr_2NaO_2P$ $[M+Na]^+$ 793.0471, found 793.0487.

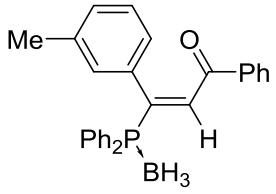


3e: 80.8 mg, 54% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1), . **^{31}P NMR (121MHz, $CDCl_3$)** δ 27.0; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.8; **^{19}F NMR (282 MHz, $CDCl_3$)** δ -63.45, -63.47; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.65 – 7.57 (m, 4H), 7.55 – 7.45 (m, 13H), 7.45 – 7.32 (m, 6H), 7.28 (s, 2H), 7.23 (s, 1H), 6.96 (d, J = 7.9 Hz, 2H), 5.09 (d, J = 15.4 Hz, 1H), 1.22 – 0.54 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**

δ 192.3, 153.4, 145.5, 138.0, 136.9, 134.8, 133.8, 133.3, 133.17, 133.1, 133.0, 131.93, 131.90, 131.75, 131.72, 130.31, 130.26, 129.7, 129.4, 129.0, 128.8, 128.7, 128.66, 128.6, 127.3, 126.9, 126.8, 126.6, 126.2, 126.14, 126.06, 125.7, 125.64, 125.56, 125.54, 122.1, 120.8, 43.5, 43.2. **HRMS (ESI)** Calcd for $C_{44}H_{32}BF_6NaO_2P$ $[M+]^+$ 711.2029 , found 711.2050.



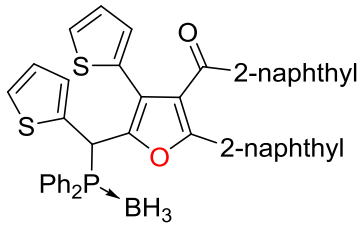
3f: 50.1 mg, 39% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1). **^{31}P NMR (121MHz, CDCl$_3$)** δ 26.5; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -39.3; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.65 – 7.49 (m, 7H), 7.48 – 7.38 (m, 5H), 7.32 (s, 6H), 7.22 – 7.18 (m, 3H), 7.17 – 7.13 (m, 2H), 7.12 – 7.06 (m, 2H), 7.01 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 7.5 Hz, 1H), 6.66 (s, 1H), 5.07 (d, J = 15.8 Hz, 1H), 2.26 (s, 3H), 2.20 (s, 3H), 1.19 – 0.51 (m, 3H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 193.2, 152.3, 146.1, 146.0, 138.01, 137.98, 137.3, 134.1, 133.43, 133.39, 133.3, 133.2, 131.30, 131.27, 131.1, 131.0, 130.9, 130.1, 129.8, 129.3, 128.6, 128.5, 128.4, 128.33, 128.31, 127.9, 127.6, 127.3, 127.2, 126.8, 126.7, 126.5, 126.2, 121.1, 43.4, 43.0, 21.5, 21.3. **HRMS (ESI)** Calcd for $C_{44}H_{38}BNaO_2P$ $[M+Na]^+$ 663.2595 , found 663.2596.



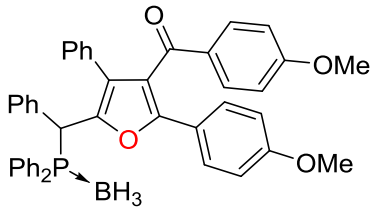
3f'

The use of 3-methylphenyl group provided **3f** in 39% yield, along with 54% (45.4 mg) Michael addition product **3f'**. Yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1). **^{31}P NMR (121MHz, CDCl$_3$)** δ 26.5; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -36.9; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.81 – 7.75 (m, 2H), 7.74 – 7.65 (m, 4H), 7.52 – 7.32 (m, 9H), 7.26 (d, J = 6.8 Hz, 1H), 6.94 – 6.84 (m, 2H), 6.76 (d, J = 7.1, 1.8 Hz, 1H), 6.69 (s, 1H), 2.05 (s, 3H), 1.50 – 0.59 (m, 3H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 192.9, 192.7, 144.3,

143.8, 141.2, 141.0, 137.3, 136.5, 134.8, 134.7, 133.7, 133.6, 131.72, 131.69, 129.84, 129.80, 129.0, 128.93, 128.87, 128.7, 128.6, 127.7, 127.4, 126.6, 126.21, 126.16, 100.0, 21.18. **HRMS (ESI)** Calcd for $C_{26}H_{28}BNaO_2P$ $[M+Na]^+$ 442.1707, found 442.1722.

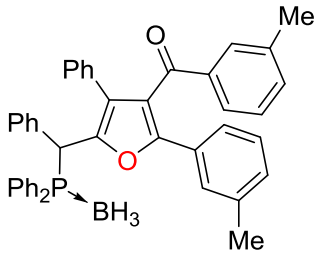


3g: 104.3 mg, 72% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 5/1). **^{31}P NMR (121MHz, $CDCl_3$)** δ 29.7; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.6; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.32 (s, 1H), 7.99 – 7.90 (m, 2H), 7.85 – 7.74 (m, 3H), 7.74 – 7.61 (m, 7H), 7.60 – 7.37 (m, 11H), 7.16 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.07 (s, 1H), 6.97 – 6.90 (m, 1H), 6.87 – 6.82 (m, 1H), 6.77 (s, 1H), 5.82 (d, *J* = 13.6 Hz, 1H),1.12 – 0.50 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.1, 151.8, 146.2, 146.1, 135.9, 135.5, 134.6, 134.0, 133.9, 133.11, 133.09, 133.07, 133.00, 132.9, 132.4, 131.91, 131.88, 131.6, 131.5, 131.17, 131.15, 130.0, 128.9, 128.8, 128.7, 128.62, 128.58, 128.5, 128.4, 128.0, 127.7, 127.63, 127.57, 127.4, 127.04, 127.02, 126.8, 126.7, 126.5, 126.43, 126.36, 126.1, 125.5, 124.4, 123.4, 121.7, 120.0, 39.2, 38.8. **HRMS (ESI)** Calcd for $C_{46}H_{34}BNaO_2PS_2$ $[M+Na]^+$ 747.1723, found 747.1744.

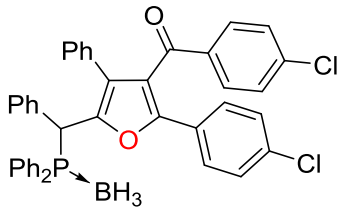


3h: 115.6 mg, 86% yield, yellow solid, R_f= 0.40 (hexane/EtOAc = 10/1), **m.p.** 91.2-92.4 ℃. **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.4; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.0; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 – 7.56 (m, 4H), 7.55 – 7.37 (m, 8H), 7.34 – 7.18 (m, 10H), 6.96 – 6.88 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.14 (d, *J* = 15.9 Hz, 1H), 3.70 (s, 2H),1.15 – 0.44 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.8, 163.9, 159.8, 152.1, 145.2, 145.2, 134.4, 133.3, 133.3, 133.2, 133.1, 132.3, 131.5, 130.4, 130.20, 130.15, 129.1, 128.7, 128.6, 128.51, 128.45, 128.2, 128.0,

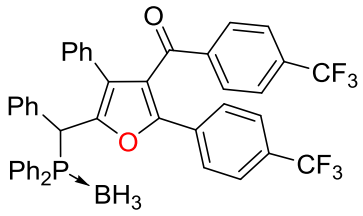
127.8, 127.7, 127.5, 127.3, 126.73, 126.65, 122.2, 119.8, 114.1, 113.7, 55.5, 55.3, 43.4, 43.0. **HRMS (ESI)** Calcd for $C_{44}H_{38}BKO_4P$ $[M+Na]^+$ 711.2232, found 711.2241.



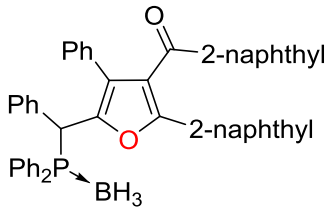
3i: 94.5 mg, 74% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1). **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.8; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -39.2; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 2H), 7.51 – 7.28 (m, 17H), 7.24 – 7.16 (m, 4H), 7.14 – 7.02 (m, 3H), 6.92-6.89 (m, 2H), 5.11 (d, J = 15.0 Hz, 1H), 2.25 (d, J = 6.0 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.3, 152.8, 145.9, 138.1, 137.3, 134.4, 134.2, 133.4, 133.3, 131.4, 130.2, 130.1, 130.0, 129.4, 129.23, 129.17, 128.62, 128.57, 128.49, 128.45, 128.4, 128.3, 127.8, 127.7, 127.4, 127.2, 126.8, 123.9, 121.2, 43.5, 43.1, 21.5, 21.2.**HRMS (ESI)** Calcd for $C_{44}H_{39}BO_2P$ $[M+H]^+$ 641.2775 , found 641.2775.



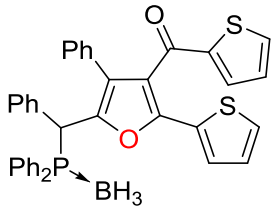
3j: 118.3 mg, 87% yield, yellow solid, R_f= 0.40 (hexane/EtOAc = 10/1), **m.p.** 166.8-167 ℃. **^{31}P NMR (121MHz, $CDCl_3$)** δ 26.4; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -38.5; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.60 – 7.51 (m, 4H), 7.51 – 7.42 (m, 5H), 7.41 – 7.35 (m, 3H), 7.35 – 7.17 (m, 14H), 6.90 – 6.83 (m, 2H), 5.12 (d, *J* = 15.7 Hz, 1H),1.16 – 0.48 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.6, 151.5, 146.44, 146.38, 140.1, 135.4, 134.7, 134.0, 133.3, 133.20, 133.16, 133.1, 131.50, 131.47, 131.44, 131.41, 131.1, 130.8, 130.1, 130.0, 129.1, 129.0, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.0, 127.83, 127.79, 127.7, 127.5, 127.1, 127.1, 126.7, 126.6, 121.0, 43.3, 43.0. **HRMS (ESI)** Calcd for $C_{42}H_{32}BCl_2NaO_2P$ $[M+Na]^+$ 703.1502, found 703.1516.



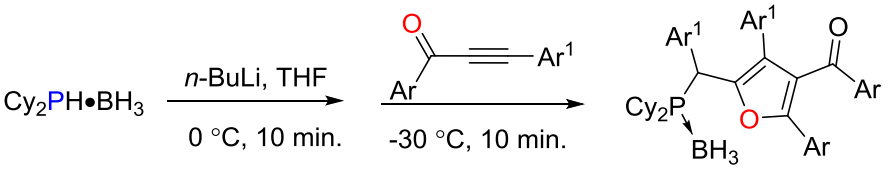
3k: 70.3 mg, 47% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 10/1). **^{31}P NMR (121MHz, CDCl$_3$)** δ 27.7; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -38.1; **^{19}F NMR (282 MHz, CDCl$_3$)** δ -63.2, -63.5; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.73 – 7.64 (m, 4H), 7.60 – 7.52 (m, 4H), 7.50 – 7.43 (m, 6H), 7.42 – 7.27 (m, 10H), 7.24 – 7.20 (m, 2H), 6.91 – 6.84 (m, 2H), 5.14 (d, J = 15.6 Hz, 1H), 1.17 – 0.66 (m, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 191.7, 151.3, 147.3, 139.6, 134.9, 134.6, 133.9, 133.4, 133.3, 133.1, 133.0, 132.2, 131.61, 131.59, 131.52 ,150.50, 130.6, 130.5, 130.3, 130.04, 130.00, 129.9, 129.2, 128.8, 128.7, 128.64, 128.57, 128.5, 128.2, 128.09, 128.07, 127.8, 127.5, 127.2, 127.0, 126.74, 126.68, 126.6, 125.8, 125.7, 125.53, 125.49, 122.5, 122.2, 122.0, 43.4, 43.1. **HRMS (ESI)** Calcd for $C_{44}H_{32}BF_6NaO_2P$ $[M+]^+$ 771.2029 , found 771.2019.



3l: 118.2 mg, 83% yield, yellow solid, R_f= 0.40 (hexane/EtOAc = 5/1), **m.p.** 118.2-119.7 ℃. **^{31}P NMR (121MHz, CDCl$_3$)** δ 27.1; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -37.9; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.20 (s, 1H), 8.05 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.77 – 7.71 (m, 3H), 7.71 – 7.58 (m, 6H), 7.52 – 7.46 (m, 5H), 7.46 – 7.32 (m, 10H), 7.31 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 5.20 (d, *J* = 15.4 Hz, 1H), 1.16 – 0.50 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 193.2, 152.3, 146.4, 146.3, 135.8, 134.7, 134.3, 133.5, 133.43, 133.40, 133.3, 133.1, 133.0, 132.6, 132.4, 131.5, 131.3, 130.19, 130.15, 129.8, 129.2, 128.74, 128.68, 128.6, 128.58, 128.55, 128.54, 128.51, 128.48, 128.3, 127.9, 127.8, 127.7, 127.6, 127.4, 127.1, 127.0, 126.7, 126.6, 126.5, 125.9, 124.6, 123.8, 121.7, 43.6, 43.3. **HRMS (ESI)** Calcd for $C_{50}H_{39}BO_2P$ $[M+H]^+$ 713.2775, found 713.2782.

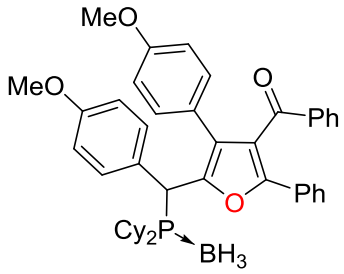


3m: 116.1 mg, 93% yield, yellow solid, R_f= 0.40 (hexane/EtOAc = 10/1), **m.p.** 101.4-102.7 ℃. **^{31}P NMR (121MHz, CDCl$_3$)** δ 27.2; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -37.9; **^{1}H NMR (300 MHz, CDCl3)** δ 7.62 – 7.53 (m, 3H), 7.51 – 7.40 (m, 5H), 7.41 – 7.25 (m, 13H), 7.15 (d, 1H), 7.02 – 6.95 (m, 3H), 6.82 – 6.77 (m, 1H), 5.14 (d, *J* = 15.1 Hz, 1H) ,1.10 – 0.50 (m, 3H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 183.8, 148.7, 145.72, 145.65, 144.3, 135.5, 135.0, 134.2, 133.4, 133.3, 133.2, 131.49, 131.46, 131.43, 131.40, 131.2, 131.1, 130.1, 130.0, 129.1, 128.8, 128.7, 128.5, 128.4, 128.0, 127.9, 127.6, 127.5, 127.2, 127.0, 126.8, 126.13, 126.06, 120.2, 43.4, 43.0. **HRMS (ESI)** Calcd for $C_{38}H_{30}BNaO_2PS_2$ $[M+Na]^+$ 647.1410, found 647.1427.

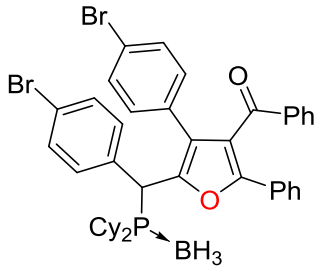


3n-3p

General Procedures and Characterization of 3n to 3p: A 10 mL Schlenk tube equipped with a stir bar and was charged sequentially with borane dicyclohexylphosphane complex (42 mg, 0.2 mmol) and THF (4 mL) under N_2 atmosphere. *n*-BuLi (0.15 mL, 0.24 mmol) was added dropwise to the solution at 0 °C, and the solution was kept at 0 °C for 10 minutes. Then solution was cooled to -30 °C. Acetylenic ketones (0.5 mmol) was added to the reaction mixture at -30 °C, and the mixture was kept at -30 °C for 10 minutes. Two drops of saturated aqueous NH_4Cl was added to the mixture to quench the reaction. After filtration with a silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford the desired product.

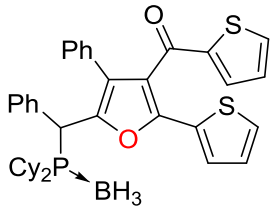


3n: 82.1 mg, 60% yield, yellow solid, R_f= 0.30 (hexane/EtOAc = 8/1), **m.p.** 208.5-209.8 ℃. **^{31}P NMR (162MHz, CDCl$_3$)** δ 38.5 ppm; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -41.8 ppm; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.24 (d, *J* = 3.4 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.60 (d, *J* = 14.5 Hz, 1H), 1.86 – 1.50 (m, 13H), 1.19 – 0.52 (m, 12H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 193.4, 159.1, 151.9, 147.51, 147.46, 137.3, 133.6, 130.8, 130.7, 130.4, 129.8, 129.5, 128.7, 128.5, 127.7, 126.6, 125.01, 124.96, 123.6, 121.6, 114.2, 114.1, 55.3, 55.2, 37.0, 36.8, 33.6, 33.3, 32.9, 32.6, 27.4, 27.32, 27.28, 27.2, 27.0, 26.0. **HRMS (ESI)** Calcd for $C_{44}H_{51}BO_4P$ $[M+H]^+$ 685.3613, found 685.3608. The single crystal of **3k** was grown from a mixture of dichloromethane and n-Hexane.

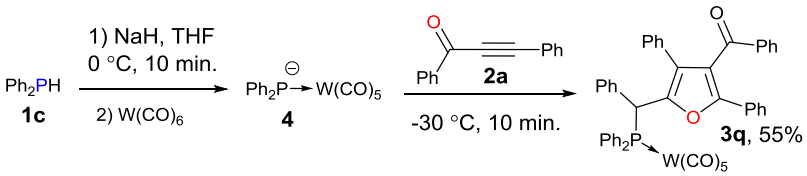


3o: 65.7 mg, 42% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 8/1). **^{31}P NMR (162MHz, CDCl$_3$)** δ 40.2; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -41.8; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.83 – 7.74 (m, 2H), 7.66 – 7.60 (m, 2H), 7.55 – 7.47 (m, 4H), 7.46 – 7.39 (m, 3H), 7.35 – 7.25 (m, 5H), 7.01 – 6.91 (m, 2H), 4.53 (d, *J* = 13.5 Hz, 1H), 1.86 – 1.56 (m, 13H), 1.19 – 0.61 (m, 12H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 192.7, 152.7, 147.0, 146.9, 137.0, 134.7, 133.8, 132.0, 131.14, 131.11, 130.8, 130.2, 129.8, 129.1, 128.9, 128.8, 128.6, 126.7, 124.9, 124.8, 122.3, 122.09, 122.07, 121.3, 37.4, 37.2, 33.6, 33.4, 32.8, 32.5, 27.5, 27.3, 27.2, 27.2, 27.13, 27.09, 25.9. **HRMS (ESI)**

Calcd for $C_{42}H_{44}BBr_2NaO_2P$ $[M+Na]^+$ 805.1410, found 805.1426.



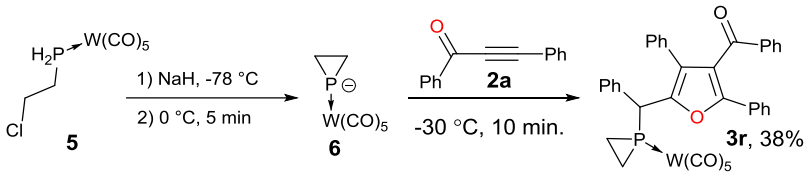
3p: 75.4 mg, 42% yield, yellow oil, R_f= 0.40 (hexane/EtOAc = 8/1). **^{31}P NMR (121MHz, $CDCl_3$)** δ 39.8; **^{11}B NMR (128 MHz, $CDCl_3$)** δ -41.9; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 4.9 Hz, 1H), 7.46 (d, *J* = 3.0 Hz, 2H), 7.42 – 7.32 (m, 6H), 7.28 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.88 – 6.83 (m, 1H), 4.70 (d, *J* = 13.7 Hz, 1H), 1.88 – 1.54 (m, 12H), 1.24 – 0.51 (m, 13H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.9, 148.3, 147.1, 147.0, 144.3, 135.7, 135.5, 135.1, 131.4, 131.3, 129.4, 129.4, 129.0, 128.8, 128.2, 127.9, 127.7, 127.7, 126.9, 126.6, 125.2, 125.2, 120.7, 37.9, 37.6, 33.4, 33.1, 32.3, 32.1, 27.3, 27.3, 27.2, 27.1, 27.0, 26.0. **HRMS (ESI)** Calcd for $C_{38}H_{42}BNaO_2PS_2$ $[M+Na]^+$ 659.2349, found 659.2356.



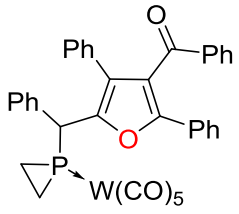
NaH (12 mg, 0.3 mmol, 60% dispersion in mineral oil) was added to the solution of diphenylphosphane (45 μL, 0.25 mmol) in THF (4 mL) at 0 °C. Then the mixture was stirred vigorously in an ice bath for 5 minutes. $W(CO)_6$ was added (88 mg, 0.25mmol) to the reaction for 30 minutes, affording compound **4**. Acetylenic ketones (129 mg, 0.625 mmol) was added to the reaction mixture at -30 °C, and the solution was kept at -30 °C for 10 minutes. Two drops of saturated aqueous NH_4Cl was added to the mixture to quench the reaction. After filtration with silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford **3q**.

3q: 126.8 mg, 55% yield, yellow oil, R_f= 0.30 (hexane/EtOAc = 8/1). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 31.8 (J_{PW}= 247.9 Hz). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.64 (m,

2H), 7.63 – 7.56 (m, 2H), 7.50 – 7.38 (m, 3H), 7.38 – 7.30 (m, 3H), 7.30 – 7.25 (m, 8H), 7.23 – 7.14 (m, 10H), 7.13 – 7.07 (m, 2H), 5.40 (d, J = 7.8 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.5, 199.3, 196.53, 196.47, 193.3, 151.92, 151.90, 147.4, 147.3, 137.2, 135.97, 135.95, 135.4, 135.03, 134.98, 134.9, 133.5, 133.1, 132.7, 132.6, 132.50, 131.45, 130.83, 130.81, 130.50, 130.45, 130.0, 129.8, 129.5, 129.2, 128.8, 128.5, 128.4, 128.34, 128.29, 128.3, 128.20, 128.16, 128.00, 127.96, 127.0, 126.9, 126.3, 121.8, 47.5, 47.4. **HRMS (ESI)** Calcd for $C_{47}H_{32}O_7PW$ $[M+H]^+$ 923.1389, found 923.1402.

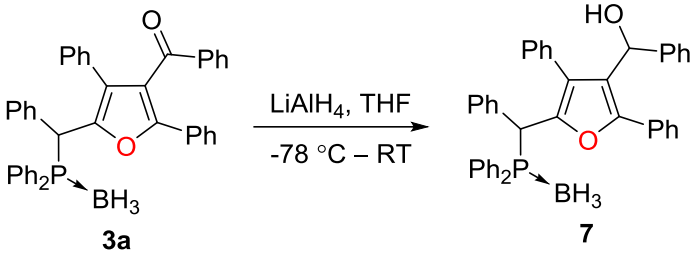


NaH (20 mg, 0.5 mmol, 60% dispersion in mineral oil) was added to the solution of 2-chloroethylphosphine $W(CO)_5$ complex **5** (84 mg, 0.2 mmol) in THF (4 mL) at -78 °C. Then the mixture was stirred vigorously in an ice bath for 5 minutes, affording compound **6**. Acetylenic ketones (103 mg, 0.5 mmol) was added to the reaction mixture at -30 °C and kept the mixture for 10 minutes at -30 °C. Two drops of saturated aqueous NH_4Cl was added to the mixture to quench the reaction. After filtration with a silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford **3r**.



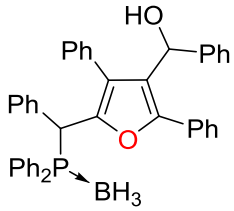
3r: 38% yield, yellow oil, R_f= 0.40 (hexane/EtOAc = 10/1). **^{31}P NMR (121 MHz, CDCl$_3$)** δ -175.6 (J_{PW}= 258.4 Hz); **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.77 (d, J = 7.3 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.46 – 7.35 (m, 6H), 7.33 – 7.26 (m, 4H), 7.24 – 7.18 (m, 4H), 7.12 – 7.04 (m, 2H), 4.44 (d, J = 7.8 Hz, 1H), 1.56 – 1.36 (m, 2H), 1.22 – 1.04 (m, 2H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 197.6, 197.1, 195.2, 195.1, 192.8, 152.8, 146.7, 146.6, 137.1, 136.0, 133.5, 130.7, 129.8, 129.3, 129.1, 129.0, 128.93, 128.85,

128.6, 128.4, 128.2, 128.1, 127.9, 127.04, 126.97, 126.6, 122.1, 44.7, 44.6, 8.1, 8.0. **HRMS (ESI)** Calcd for $C_{37}H_{26}O_7PW$ $[M+H]^+$ 797.0920, found 797.0926.



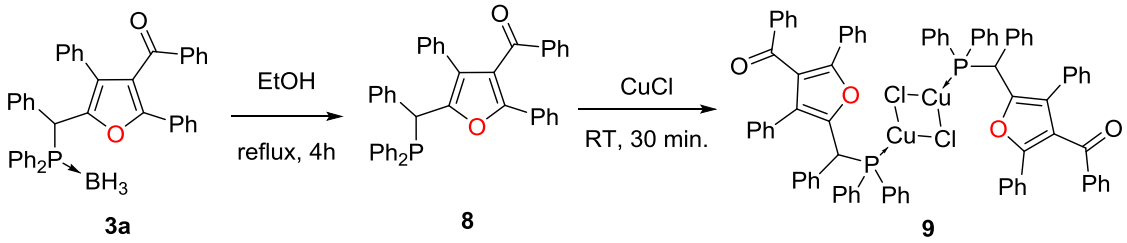
3a **7**

A 10 mL Schlenk tube equipped with a stir bar was charged sequentially with **3a** (61 mg, 0.1 mmol) and THF (3 mL) under N_2 atmosphere. $LiAlH_4$ (46 mg, 0.12 mmol) was added at -78 °C, and the mixture kept at -78 °C for 30 minutes. Then the solution was slowly warmed to room temperature. After filtration with silica gel, crude product was obtained by rotary evaporation. The residue was purified by column chromatography on silica gel to afford a pair of diastereoisomers **7** and **7′** as a yellow oil mixture（**7** : **7′**=1 : 0.55, the ratio was determined by ^{1}H NMR) .



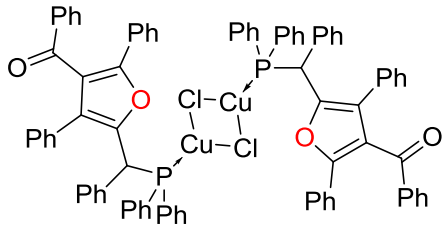
7, **7′**: 55.3 mg, 90% yield, **7** and **7′**were isolated as a mixture. Yellow oil, R_f= 0.30 (hexane/EtOAc = 8/1). **^{31}P NMR (121MHz, CDCl$_3$)** δ 21.8; **^{11}B NMR (128 MHz, CDCl$_3$)** δ -38.3; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 7.3 Hz, 1.29H, 7+7′), 7.61 – 7.50 (m, 5.71H, 7+7′), 7.48 – 7.37 (m, 8.14H, 7+7′), 7.37 – 7.27 (m, 11.71H, 7+7′), 7.26 – 7.20 (m, 9.71H, 7+7′), 7.19 – 7.08 (m, 7.42H, 7+7′), 6.77 (d, *J* = 6.7 Hz, 1.09H, 7′), 6.60 (d, *J* = 7.3 Hz, 1.99H, 7), 6.00 (s, 0.99H, 7), 5.87 (s, 0.54H, 7′), 4.93 (d, *J* = 16.0 Hz, 0.55H, 7′), 4.87 (d, *J* = 15.4 Hz, 1H, 7). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 151.2, 151.1, 150.56, 150.55, 146.8, 146.7, 145.91, 145.86, 143.2, 142.0, 134.8, 133.7, 133.62, 133.57, 133.5, 133.44, 133.37, 133.3, 132.2, 131.9, 131.38, 131.36, 131.32, 131.29, 130.4, 130.28, 130.25, 130.22, 130.17, 128.8, 128.6, 128.51, 128.48, 128.45, 128.3, 128.1, 128.0, 127.9, 127.83, 127.75, 127.7, 127.6, 127.5, 127.3, 127.1, 126.9, 126.4, 126.2, 125.9, 125.8, 122.7, 68.5, 67.9, 43.6, 43.5, 43.4, 43.2.**HRMS**

(ESI) Calcd for $C_{42}H_{36}BNaO_2P$ $[M+Na]^+$ 637.2438, found 637.2455.



3a **8** **9**

A solution of **3a** (21 mg, 0.03 mmol) in EtOH (3 mL) was refluxed for 4 h. Crude product **8** was obtained by rotary evaporation. CuCl (3 mg, 0.03 mmol) was added to a solution of **8** in CH_2Cl_2. The mixture was stirred at room temperature for 30 minutes. After filtration and rotary evaporation, **9** was obtained as yellow solid in 97 % yield (20.2 mg).



9: m.p. 112.2-113.7 ℃. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 11.1; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.6 Hz, 4H), 7.70 – 7.52 (m, 12H), 7.46 – 7.34 (m, 10H), 7.34 – 7.16 (m, 24H), 7.16 – 7.09 (m, 4H), 7.08 – 6.99 (m, 2H), 6.89 – 6.81 (m, 4H), 5.00 (d, *J* = 13.8 Hz, 2H). **HRMS (ESI)** Calcd for $C_{84}H_{63}Cl_2Cu_2O_4P_2$ $[M+H]^+$ 1393.2165, found 1393.2181. The single crystal of **9** was grown from a mixture of dichloromethane and *n*-hexane.

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[2] a) J. Sweet, S. Rajkumar, P. Dingwall, P. Knipe, *Eur. J. Org. Chem.*, 2021, 3980. b) A. S. Sharma, V. S. Sharma, H. Kaur, *ACS Appl. Nano Mater.*, 2020, **3**, 1191; c) S. Santra, K. Dhara, P. Ranjan, P. Bera, J. Dash, K. S. Mandal, *Green Chem.*, 2011, **13**, 3238; d) M. Zhang, X. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 17185; e) X. Hu, B. Zhou, H. Jin, Y. Liu, L. Zhang, *Chem. Commun.*, 2020, **56**, 7297; f) L. Zhang, Y. Chu. P. Ma, S. Zhao, Q. Li, B. Chen, X. Hong, J. Sun, *Org. Biomol. Chem.*, 2020, **18**, 1073.

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X-Ray Crystallographic Studies

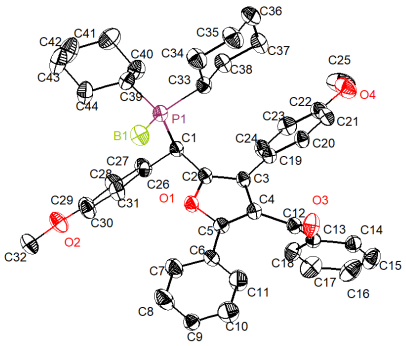


Figure S1. X-ray crystal structures of **3n** (CCDC 2239712, thermal ellipsoids shown at 30% probability level).

Table S1. Crystal data and structure refinement for **3n.**

Identification code	**3n**
Empirical formula	$C_{44}H_{50}BO_4P$
Formula weight	684.62
Temperature/K	300.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.982(2)
b/Å	15.999(3)
c/Å	21.423(4)

α/°	90.00(3)
β/°	90.00(3)
γ/°	90.00(3)
Volume/Å^3	3764.2(12)
Z	4
ρ_{calc}g/cm^3	1.208
μ/mm^{-1}	0.115
F(000)	1464.0
Crystal size/mm^3	0.12 × 0.11 × 0.13
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.168 to 49.99
Index ranges	-12 ≤ h ≤ 13, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25
Reflections collected	58243
Independent reflections	6619 [R_{int}= 0.0958, R_{sigma}= 0.0752]
Data/restraints/parameters	6619/0/451
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1= 0.0465, wR_2= 0.1068
Final R indexes [all data]	R_1= 0.0666, wR_2= 0.1182
Largest diff. peak/hole / e Å^{-3}	0.14/-0.17
Flack parameter	-0.02(8)

Table S2. Bond Lengths for 3n.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.859(4)	C29	C28	1.387(6)
P1	C33	1.846(4)	C29	C30	1.377(6)
P1	C39	1.826(4)	C6	C7	1.370(6)
P1	B1	1.938(5)	C6	C11	1.360(6)
O1	C5	1.362(5)	C22	C23	1.365(7)
O1	C2	1.371(4)	C22	C21	1.375(6)
O2	C29	1.369(5)	C20	C21	1.373(5)
O2	C32	1.420(5)	C27	C28	1.364(6)
O3	C12	1.224(5)	C33	C38	1.524(5)
O4	C22	1.368(5)	C33	C34	1.520(6)
O4	C25	1.418(7)	C14	C15	1.359(6)
C19	C24	1.382(5)	C18	C17	1.366(6)
C19	C20	1.389(5)	C39	C40	1.511(6)
C19	C3	1.468(5)	C39	C44	1.511(6)
C5	C4	1.360(5)	C38	C37	1.522(6)
C5	C6	1.456(5)	C15	C16	1.360(8)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C12	C4	1.480(5)	C9	C8	1.357(8)
C12	C13	1.475(5)	C9	C10	1.348(7)
C26	C1	1.526(5)	C40	C41	1.510(6)
C26	C31	1.377(5)	C17	C16	1.372(8)
C26	C27	1.388(5)	C37	C36	1.492(7)
C4	C3	1.441(5)	C34	C35	1.526(7)
C1	C2	1.490(5)	C44	C43	1.521(7)
C13	C14	1.394(6)	C7	C8	1.367(7)
C13	C18	1.381(6)	C36	C35	1.511(8)
C31	C30	1.390(6)	C11	C10	1.381(6)
C2	C3	1.353(5)	C41	C42	1.485(8)
C24	C23	1.390(6)	C43	C42	1.498(8)

Table S3. Bond Angles for 3n.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	B1	115.3(2)	C11	C6	C7	116.6(4)
C33	P1	C1	104.16(18)	O4	C22	C21	115.0(4)
C33	P1	B1	109.5(2)	C23	C22	O4	125.1(4)
C39	P1	C1	106.82(19)	C23	C22	C21	119.9(4)
C39	P1	C33	107.1(2)	C21	C20	C19	120.9(4)
C39	P1	B1	113.3(2)	C4	C3	C19	126.9(3)
C5	O1	C2	107.9(3)	C2	C3	C19	127.7(3)
C29	O2	C32	117.2(3)	C2	C3	C4	105.4(3)
C22	O4	C25	117.1(4)	C28	C27	C26	121.3(4)
C24	C19	C20	117.8(3)	C27	C28	C29	120.7(4)
C24	C19	C3	121.3(3)	C29	C30	C31	119.7(4)
C20	C19	C3	120.9(3)	C22	C23	C24	119.7(4)
O1	C5	C6	115.0(3)	C38	C33	P1	118.5(3)
C4	C5	O1	108.9(3)	C34	C33	P1	110.6(3)
C4	C5	C6	136.0(4)	C34	C33	C38	110.4(4)
O3	C12	C4	121.5(4)	C15	C14	C13	120.4(5)
O3	C12	C13	120.7(4)	C17	C18	C13	120.4(4)
C13	C12	C4	117.8(3)	C20	C21	C22	120.4(4)
C31	C26	C1	122.5(3)	C40	C39	P1	117.1(3)
C31	C26	C27	117.8(3)	C44	C39	P1	114.4(3)
C27	C26	C1	119.8(3)	C44	C39	C40	109.8(4)
C5	C4	C12	129.4(3)	C37	C38	C33	110.8(4)
C5	C4	C3	107.5(3)	C14	C15	C16	119.9(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C4	C12	123.1(3)	C10	C9	C8	117.9(5)
C26	C1	P1	115.3(2)	C41	C40	C39	112.2(4)
C2	C1	P1	111.3(3)	C18	C17	C16	119.6(5)
C2	C1	C26	112.4(3)	C36	C37	C38	111.7(4)
C14	C13	C12	119.1(4)	C15	C16	C17	121.0(5)
C18	C13	C12	122.0(3)	C33	C34	C35	112.3(4)
C18	C13	C14	118.8(4)	C39	C44	C43	111.7(5)
C26	C31	C30	121.5(4)	C8	C7	C6	121.7(5)
O1	C2	C1	116.8(3)	C37	C36	C35	109.4(4)
C3	C2	O1	110.3(3)	C9	C8	C7	121.1(5)
C3	C2	C1	132.9(3)	C6	C11	C10	121.5(5)
C19	C24	C23	121.2(4)	C42	C41	C40	111.7(5)
O2	C29	C28	116.1(4)	C9	C10	C11	121.2(5)
O2	C29	C30	124.9(4)	C42	C43	C44	111.5(5)
C30	C29	C28	119.0(4)	C41	C42	C43	111.2(5)
C7	C6	C5	121.1(4)	C36	C35	C34	111.2(5)
C11	C6	C5	122.3(4)				

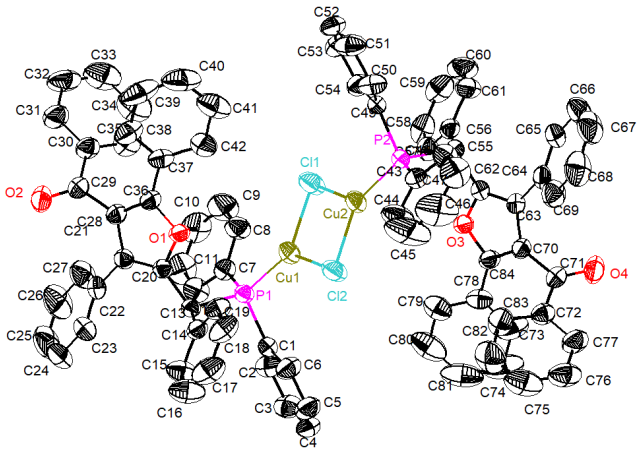


Figure S2. X-ray crystal structures of **9** (CCDC 2239716, thermal ellipsoids shown at 30% probability level).

Table S4. Crystal data and structure refinement for **9.**

Identification code	**9**
Empirical formula	$C_{84}H_{62}Cl_2Cu_2O_4P_2$
Formula weight	1395.370
Temperature/K	299.00

Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.6011(3)
b/Å	21.4880(4)
c/Å	16.3102(3)
α/°	90
β/°	105.866(1)
γ/°	90
Volume/Å^3	6945.1(2)
Z	4
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.787
F(000)	2886.3
Crystal size/mm^3	0.184× 0.11 × 0.13
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.6 to 50
Index ranges	-26 ≤ h ≤ 26, -27 ≤ k ≤ 27, -19 ≤ l ≤ 21
Reflections collected	147072
Independent reflections	12224 [R_{int}= 0.0458, R_{sigma}= 0.0256]
Data/restraints/parameters	12224/0/847
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.1175
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1282
Largest diff. peak/hole / e Å^{-3}	0.60/-0.66

Table S5. Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	Cu2	2.2815(7)	C49	C50	1.383(4)
Cl2	Cu1	2.3061(8)	C54	C53	1.394(4)
Cl1	Cu2	2.2837(8)	C40	C41	1.368(7)
Cl1	Cu1	2.2974(8)	C40	C39	1.340(7)
Cu2	Cu1	2.9384(4)	C70	C63	1.444(3)
Cu2	P2	2.1692(6)	C70	C84	1.356(4)
Cu1	P1	2.1733(6)	C70	C71	1.493(3)
O1	C20	1.378(3)	C53	C52	1.364(5)
O1	C36	1.371(3)	C47	C48	1.370(4)
O3	C62	1.373(3)	C47	C46	1.339(6)
O3	C84	1.373(3)	C13	C14	1.513(3)
O2	C29	1.210(3)	C13	C20	1.487(3)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C71	1.211(3)	C15	C14	1.383(4)
P1	C13	1.887(2)	C15	C16	1.400(5)
P1	C7	1.822(2)	C41	C42	1.378(4)
P1	C1	1.827(2)	C63	C64	1.477(4)
P2	C49	1.832(2)	C66	C67	1.353(6)
P2	C43	1.831(2)	C66	C65	1.395(4)
P2	C55	1.882(2)	C68	C69	1.388(5)
C72	C73	1.376(4)	C68	C67	1.368(6)
C72	C77	1.388(4)	C7	C8	1.382(4)
C72	C71	1.487(4)	C7	C12	1.389(4)
C62	C63	1.366(3)	C2	C1	1.382(4)
C62	C55	1.488(3)	C2	C3	1.387(4)
C23	C24	1.405(5)	C26	C27	1.383(5)
C23	C22	1.387(4)	C26	C25	1.357(6)
C30	C31	1.383(4)	C39	C38	1.396(5)
C30	C35	1.386(4)	C43	C48	1.385(4)
C30	C29	1.488(4)	C43	C44	1.375(4)
C51	C50	1.380(4)	C18	C17	1.359(5)
C51	C52	1.369(5)	C74	C75	1.375(6)
C19	C14	1.380(4)	C1	C6	1.388(4)
C19	C18	1.387(4)	C16	C17	1.364(6)
C57	C56	1.377(4)	C21	C20	1.353(3)
C57	C58	1.388(4)	C21	C28	1.446(3)
C5	C4	1.376(5)	C21	C22	1.475(3)
C5	C6	1.382(4)	C56	C55	1.519(3)
C4	C3	1.370(5)	C82	C83	1.384(5)
C61	C60	1.402(5)	C77	C76	1.374(5)
C61	C56	1.385(4)	C46	C45	1.379(6)
C11	C10	1.371(5)	C28	C36	1.358(4)
C11	C12	1.387(4)	C28	C29	1.490(3)
C10	C9	1.360(5)	C58	C59	1.358(5)
C31	C32	1.388(5)	C45	C44	1.384(5)
C73	C74	1.396(5)	C84	C78	1.463(4)
C81	C80	1.378(7)	C69	C64	1.388(4)
C81	C82	1.356(7)	C64	C65	1.382(4)
C35	C34	1.388(5)	C27	C22	1.381(4)
C32	C33	1.346(6)	C38	C37	1.381(4)
C33	C34	1.351(6)	C36	C37	1.462(4)
C80	C79	1.395(5)	C79	C78	1.376(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C9	C8	1.384(4)	C42	C37	1.378(4)
C24	C25	1.348(6)	C76	C75	1.331(6)
C60	C59	1.360(5)	C83	C78	1.386(4)
C49	C54	1.380(4)			

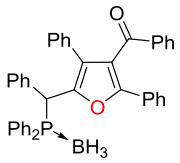
Table S6. Bond Angles for 9.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	Cl2	Cu2	79.66(3)	C25	C26	C27	120.4(4)
Cu1	Cl1	Cu2	79.79(3)	C13	C14	C19	122.3(2)
Cl1	Cu2	Cl2	100.85(3)	C15	C14	C19	118.5(3)
Cu1	Cu2	Cl2	50.54(2)	C15	C14	C13	119.2(2)
Cu1	Cu2	Cl1	50.308(19)	C7	C8	C9	120.6(3)
P2	Cu2	Cl2	131.73(3)	C38	C39	C40	120.9(4)
P2	Cu2	Cl1	127.09(3)	C48	C43	P2	124.4(2)
P2	Cu2	Cu1	174.42(2)	C44	C43	P2	116.7(2)
Cl1	Cu1	Cl2	99.70(3)	C44	C43	C48	118.9(3)
Cu2	Cu1	Cl2	49.804(18)	C17	C18	C19	120.3(3)
Cu2	Cu1	Cl1	49.90(2)	C75	C74	C73	119.8(4)
P1	Cu1	Cl2	129.21(3)	C2	C1	P1	124.63(19)
P1	Cu1	Cl1	130.73(3)	C6	C1	P1	116.54(19)
P1	Cu1	Cu2	175.18(2)	C6	C1	C2	118.8(2)
C36	O1	C20	107.05(18)	C43	C48	C47	121.1(3)
C84	O3	C62	107.41(18)	C17	C16	C15	120.5(3)
C13	P1	Cu1	117.90(7)	C28	C21	C20	105.6(2)
C7	P1	Cu1	113.71(8)	C22	C21	C20	127.3(2)
C7	P1	C13	100.94(11)	C22	C21	C28	127.0(2)
C1	P1	Cu1	111.22(8)	C7	C12	C11	120.2(3)
C1	P1	C13	103.23(10)	C33	C34	C35	120.5(4)
C1	P1	C7	108.82(11)	C61	C56	C57	118.7(2)
C49	P2	Cu2	110.64(7)	C55	C56	C57	122.3(2)
C43	P2	Cu2	114.73(8)	C55	C56	C61	119.0(2)
C43	P2	C49	106.93(11)	C2	C3	C4	120.9(3)
C55	P2	Cu2	116.61(8)	C83	C82	C81	119.9(4)
C55	P2	C49	104.87(10)	C13	C20	O1	116.09(19)
C55	P2	C43	102.07(11)	C21	C20	O1	110.6(2)
C77	C72	C73	118.1(3)	C21	C20	C13	133.1(2)
C71	C72	C73	122.9(2)	C76	C77	C72	121.2(3)
C71	C72	C77	119.0(3)	C45	C46	C47	120.0(3)

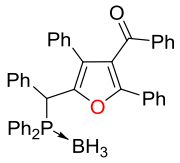
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C63	C62	O3	110.2(2)	C36	C28	C21	107.1(2)
C55	C62	O3	116.56(19)	C29	C28	C21	126.4(2)
C55	C62	C63	133.0(2)	C29	C28	C36	126.5(2)
C22	C23	C24	119.6(3)	C59	C58	C57	120.3(3)
C35	C30	C31	118.8(3)	C44	C45	C46	120.8(4)
C29	C30	C31	119.9(3)	C70	C84	O3	109.6(2)
C29	C30	C35	121.3(3)	C78	C84	O3	116.7(2)
C52	C51	C50	120.1(3)	C78	C84	C70	133.7(2)
C18	C19	C14	120.9(3)	C64	C69	C68	120.6(3)
C58	C57	C56	120.8(3)	C69	C64	C63	120.4(3)
C6	C5	C4	119.9(3)	C65	C64	C63	121.5(3)
C3	C4	C5	119.6(3)	C65	C64	C69	118.1(3)
C56	C61	C60	119.6(3)	C22	C27	C26	120.8(3)
C12	C11	C10	119.8(3)	C21	C22	C23	121.1(2)
C9	C10	C11	120.7(3)	C27	C22	C23	118.3(3)
C32	C31	C30	119.5(4)	C27	C22	C21	120.6(2)
C74	C73	C72	119.9(3)	C16	C17	C18	119.9(3)
C82	C81	C80	120.8(4)	C62	C55	P2	108.24(15)
C34	C35	C30	119.8(4)	C56	C55	P2	111.20(16)
C33	C32	C31	121.0(4)	C56	C55	C62	115.5(2)
C34	C33	C32	120.3(4)	C37	C38	C39	119.2(4)
C79	C80	C81	119.6(4)	C28	C36	O1	109.6(2)
C8	C9	C10	119.9(3)	C37	C36	O1	116.6(2)
C25	C24	C23	120.7(3)	C37	C36	C28	133.8(2)
C59	C60	C61	120.6(3)	C68	C67	C66	120.1(3)
C54	C49	P2	123.11(19)	C49	C50	C51	120.9(3)
C50	C49	P2	117.92(19)	C78	C79	C80	119.9(4)
C50	C49	C54	118.7(2)	C53	C52	C51	119.8(3)
C53	C54	C49	119.9(3)	C58	C59	C60	120.0(3)
C39	C40	C41	120.4(4)	C30	C29	O2	121.8(2)
C84	C70	C63	107.3(2)	C28	C29	O2	120.8(2)
C71	C70	C63	125.3(2)	C28	C29	C30	117.4(2)
C71	C70	C84	127.4(2)	C37	C42	C41	120.5(3)
C52	C53	C54	120.6(3)	C1	C6	C5	120.8(3)
C46	C47	C48	120.2(3)	C45	C44	C43	119.1(3)
C14	C13	P1	112.54(16)	C36	C37	C38	120.5(3)
C20	C13	P1	108.96(15)	C42	C37	C38	119.1(3)
C20	C13	C14	114.27(19)	C42	C37	C36	120.4(3)
C16	C15	C14	119.9(3)	C26	C25	C24	120.2(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C42	C41	C40	119.9(4)	C64	C65	C66	120.6(3)
C70	C63	C62	105.5(2)	C75	C76	C77	120.3(4)
C64	C63	C62	127.1(2)	C72	C71	O4	121.4(2)
C64	C63	C70	127.3(2)	C70	C71	O4	120.4(2)
C65	C66	C67	120.4(4)	C70	C71	C72	118.2(2)
C67	C68	C69	120.3(4)	C78	C83	C82	120.5(4)
C8	C7	P1	117.3(2)	C79	C78	C84	120.9(3)
C12	C7	P1	123.9(2)	C83	C78	C84	119.7(3)
C12	C7	C8	118.7(2)	C83	C78	C79	119.4(3)
C3	C2	C1	119.9(3)	C76	C75	C74	120.6(3)

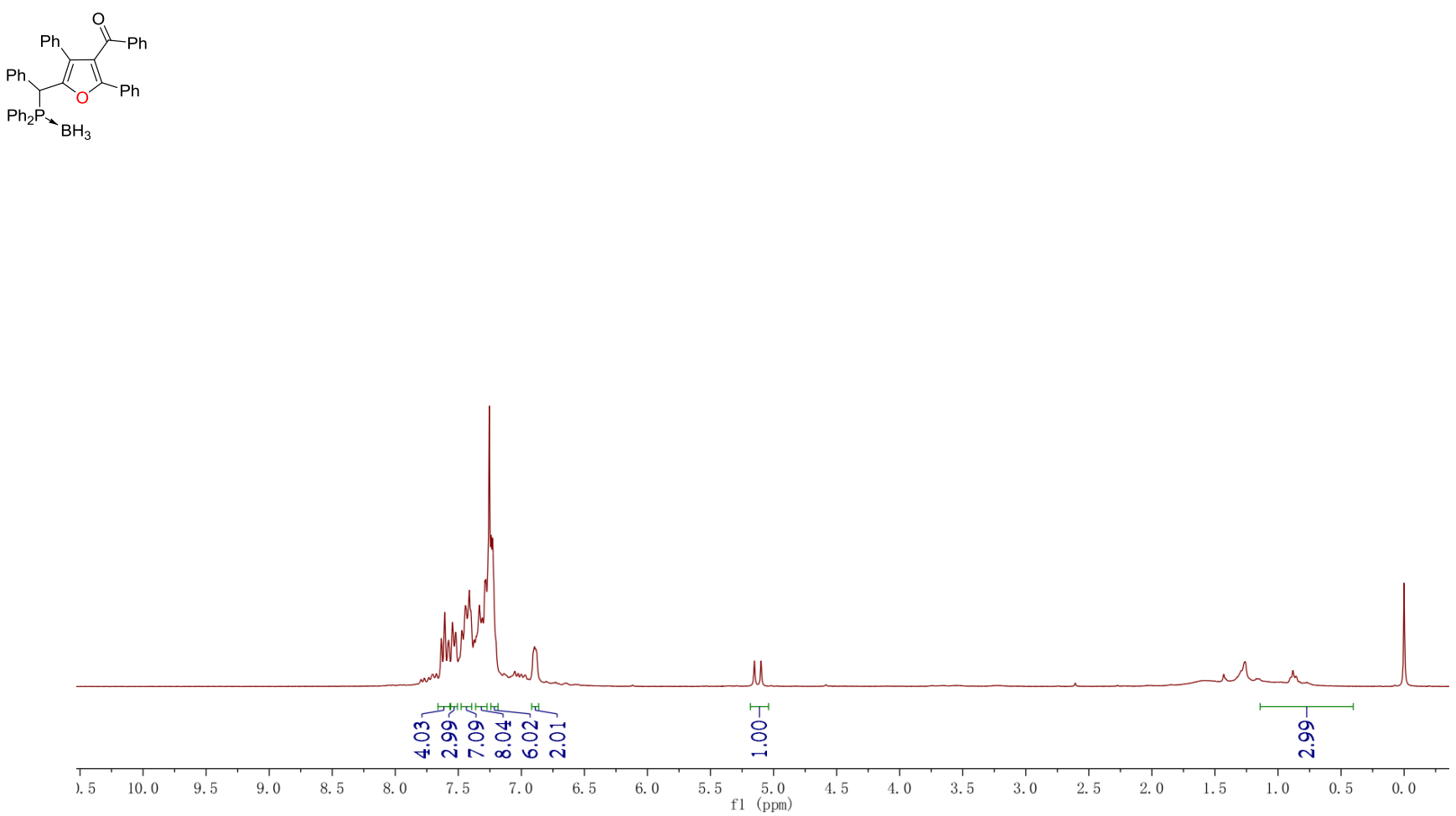
NMR Spectra



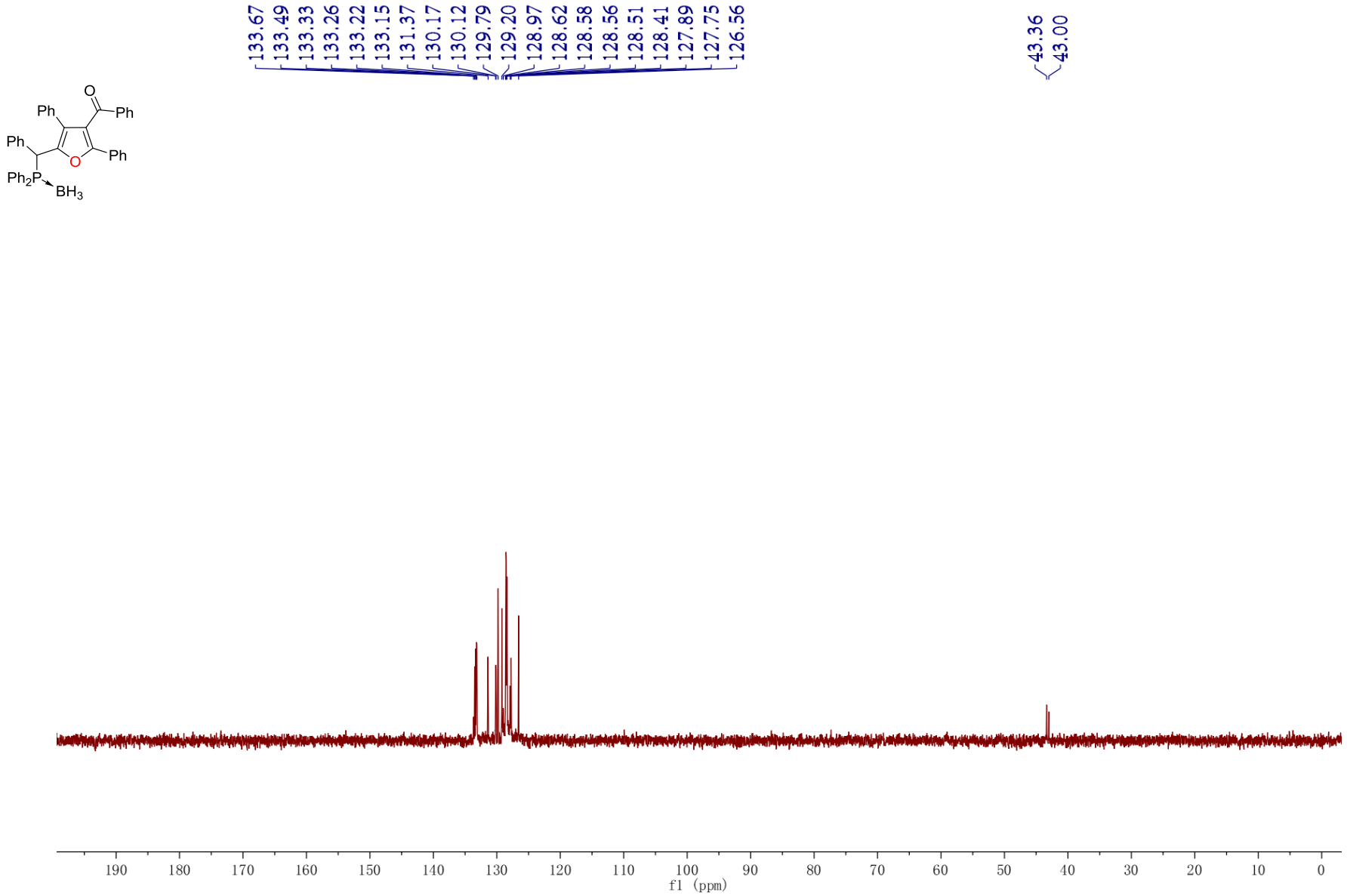
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3a**



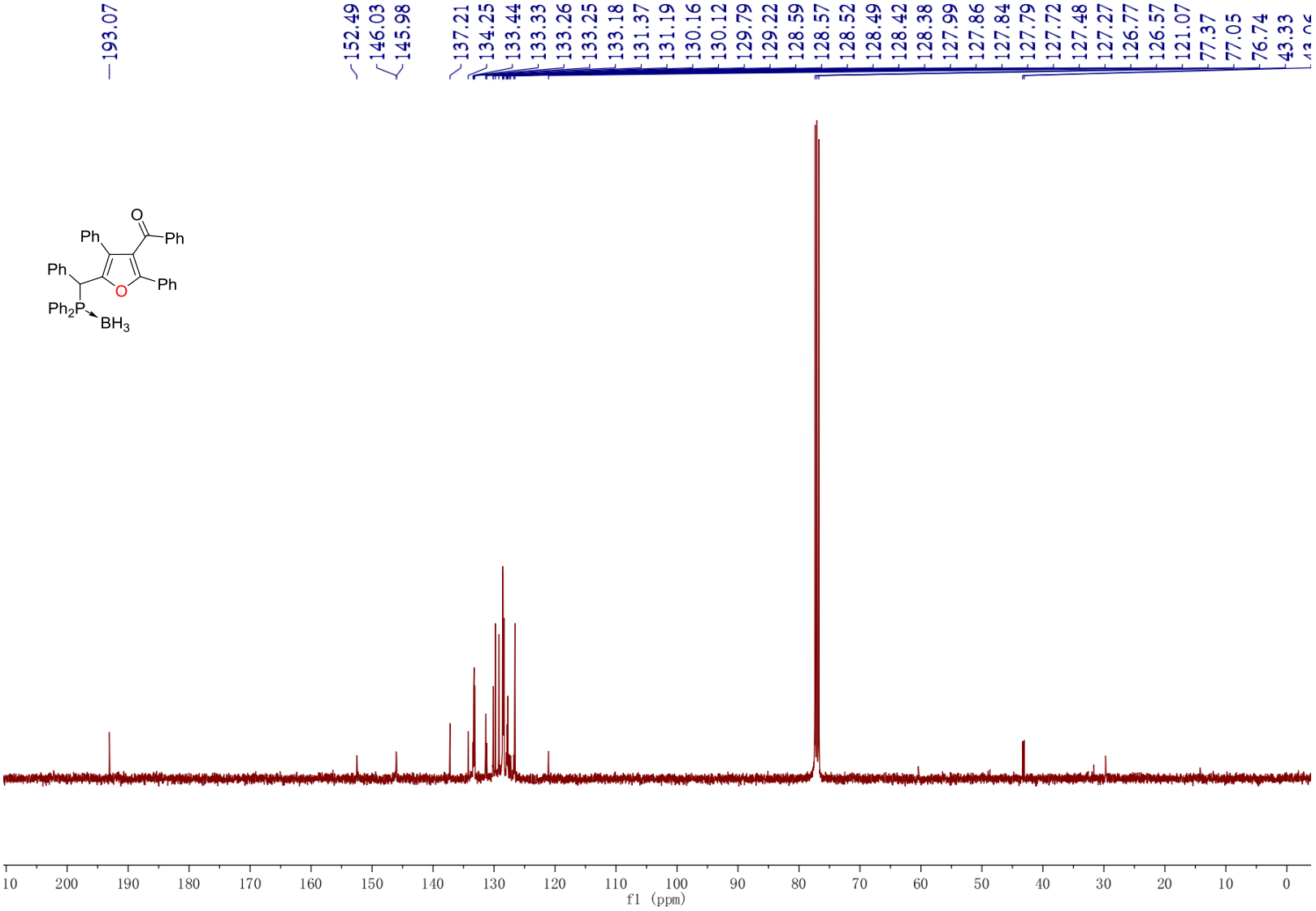
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3a**



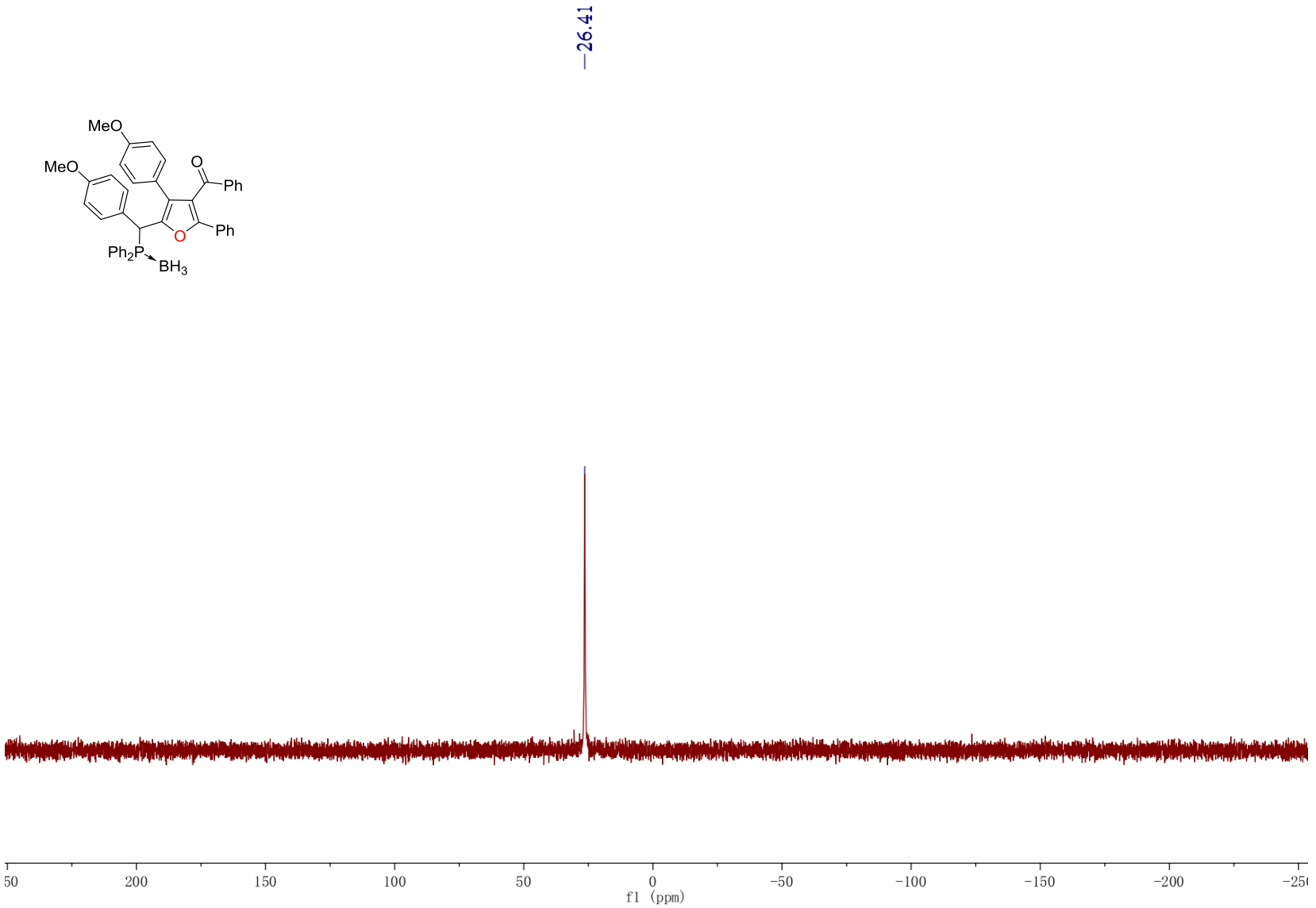
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3a**



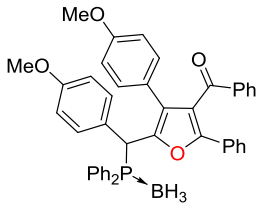
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3a**



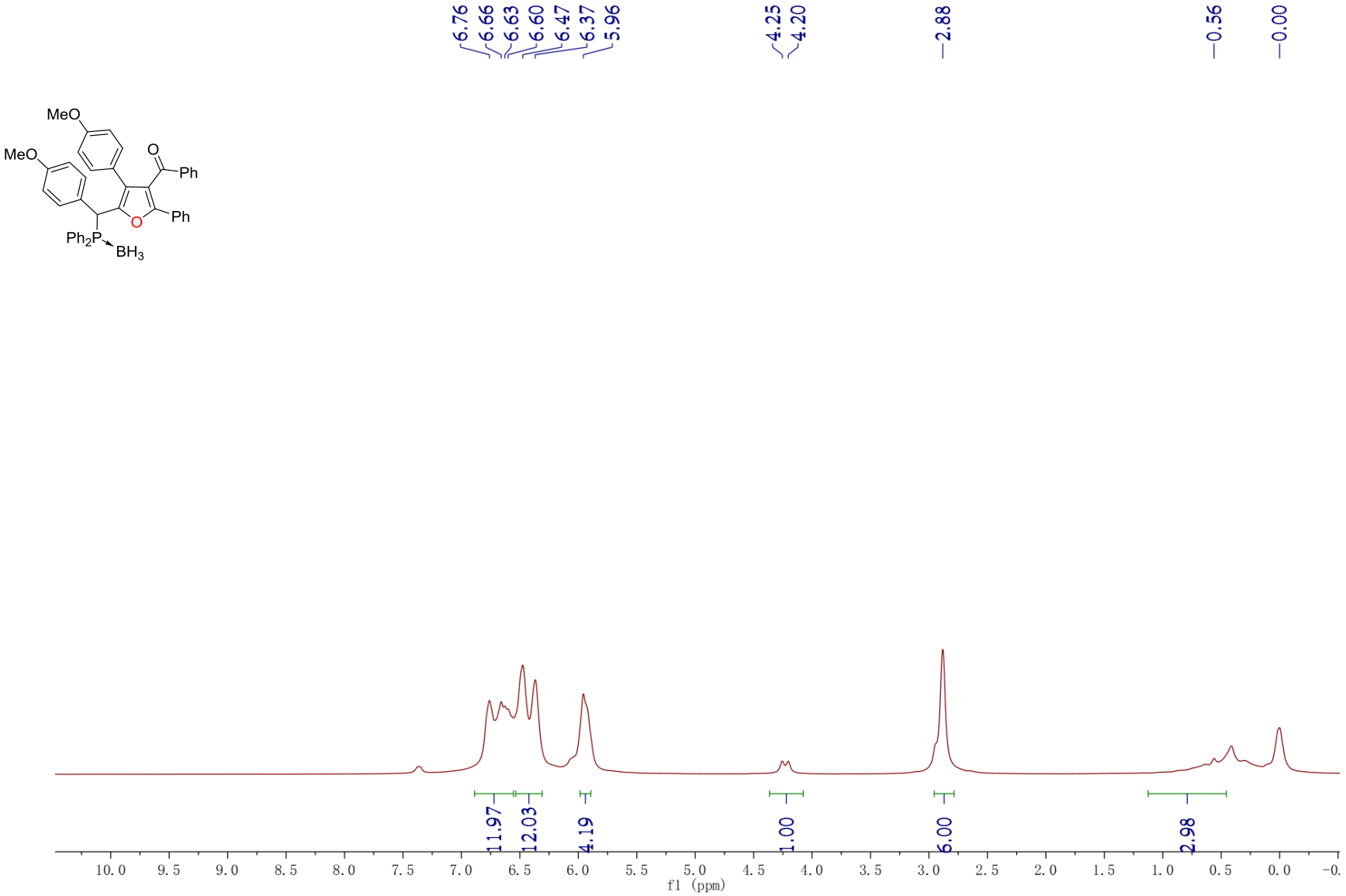
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3a**



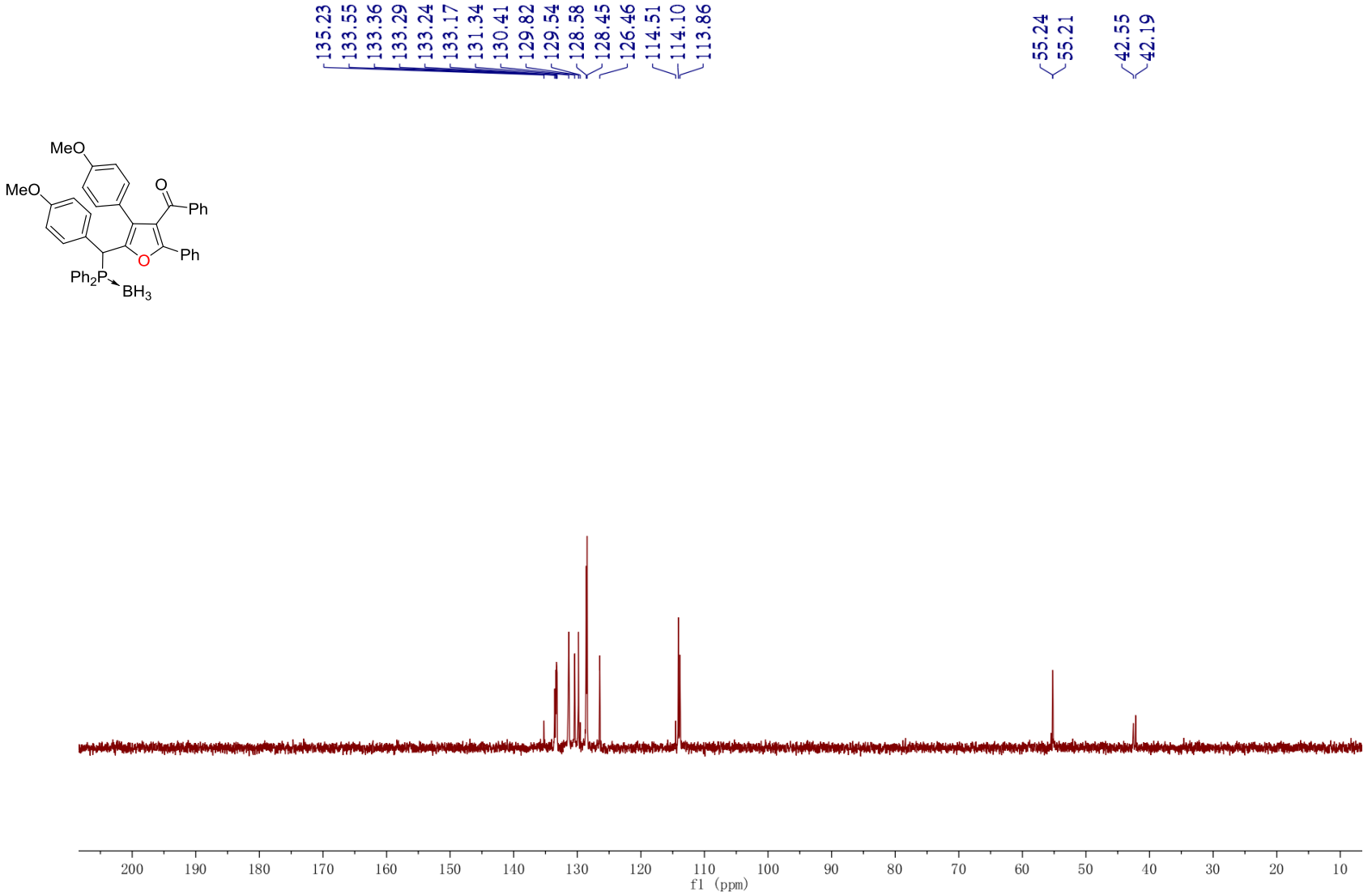
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3b**



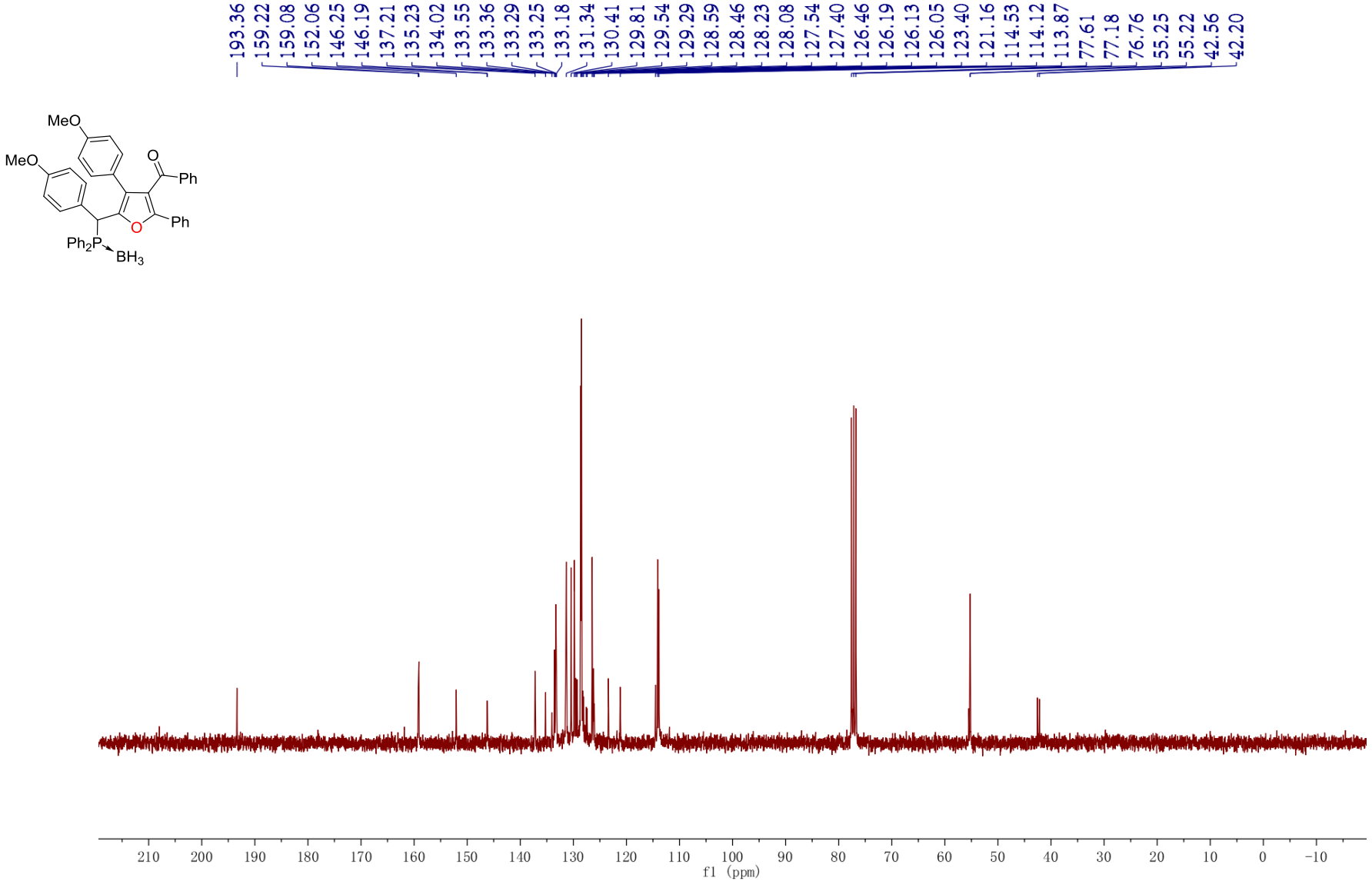
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3b**



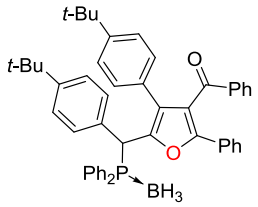
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3b**



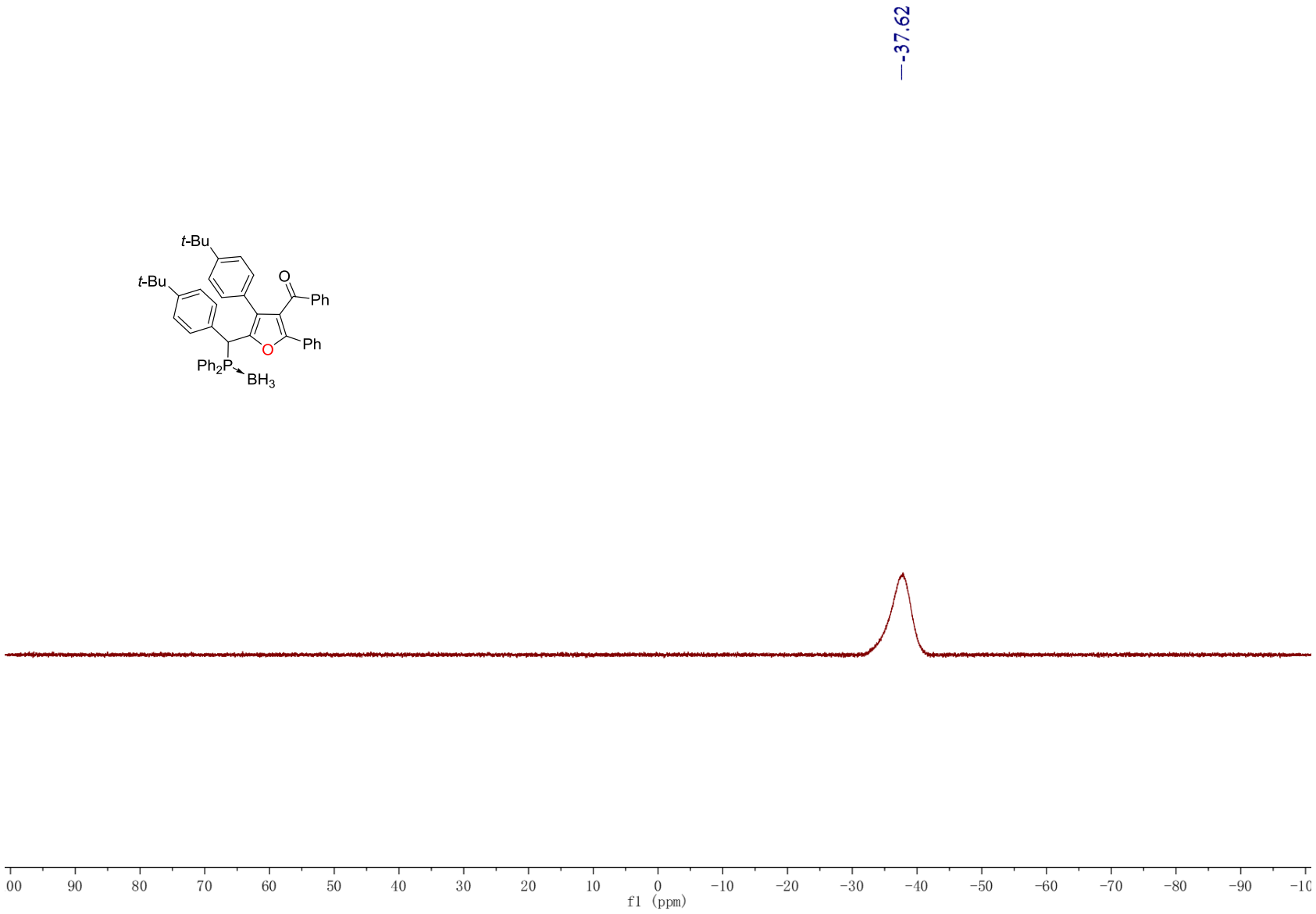
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3b**



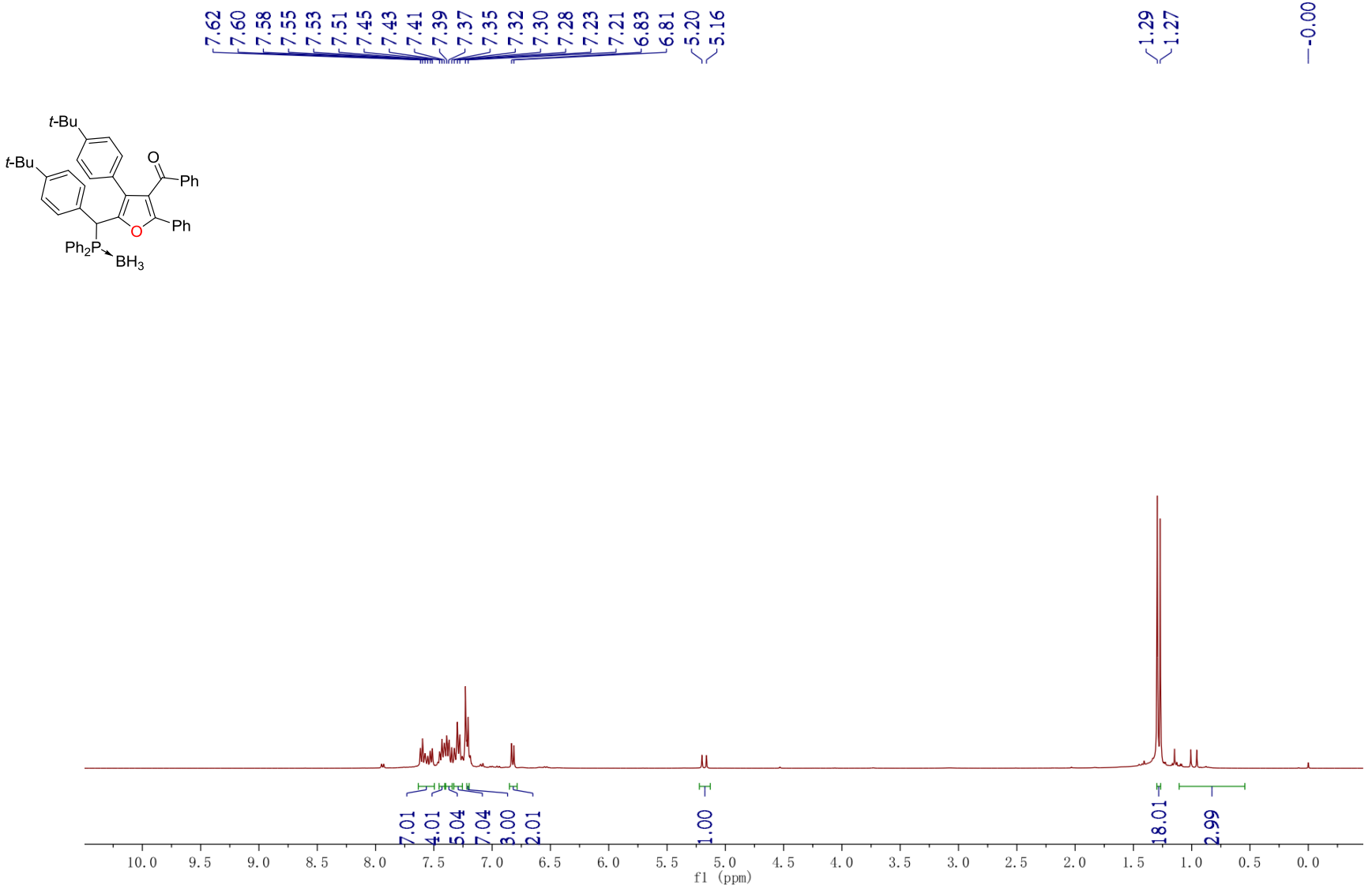
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3b**



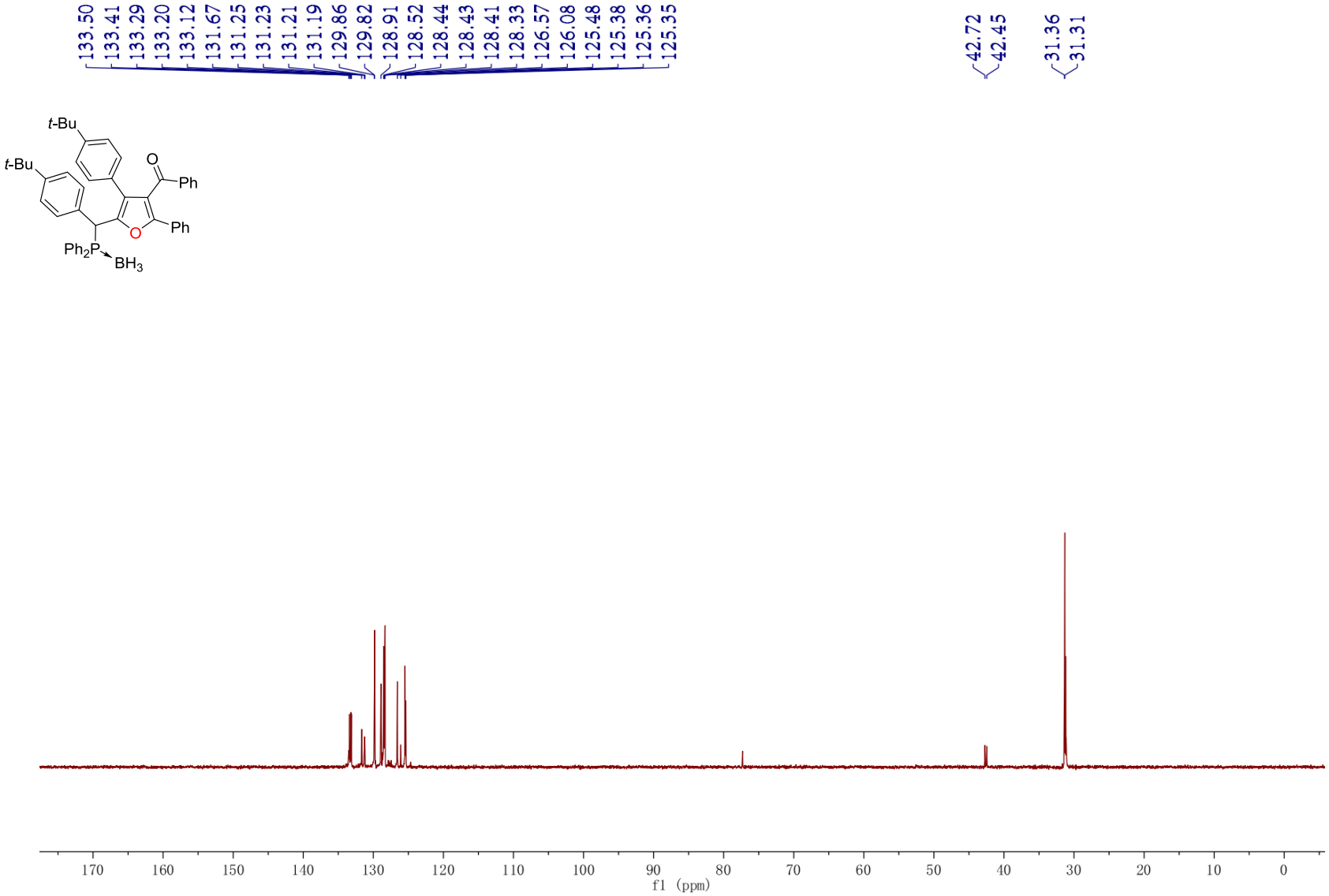
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3c**



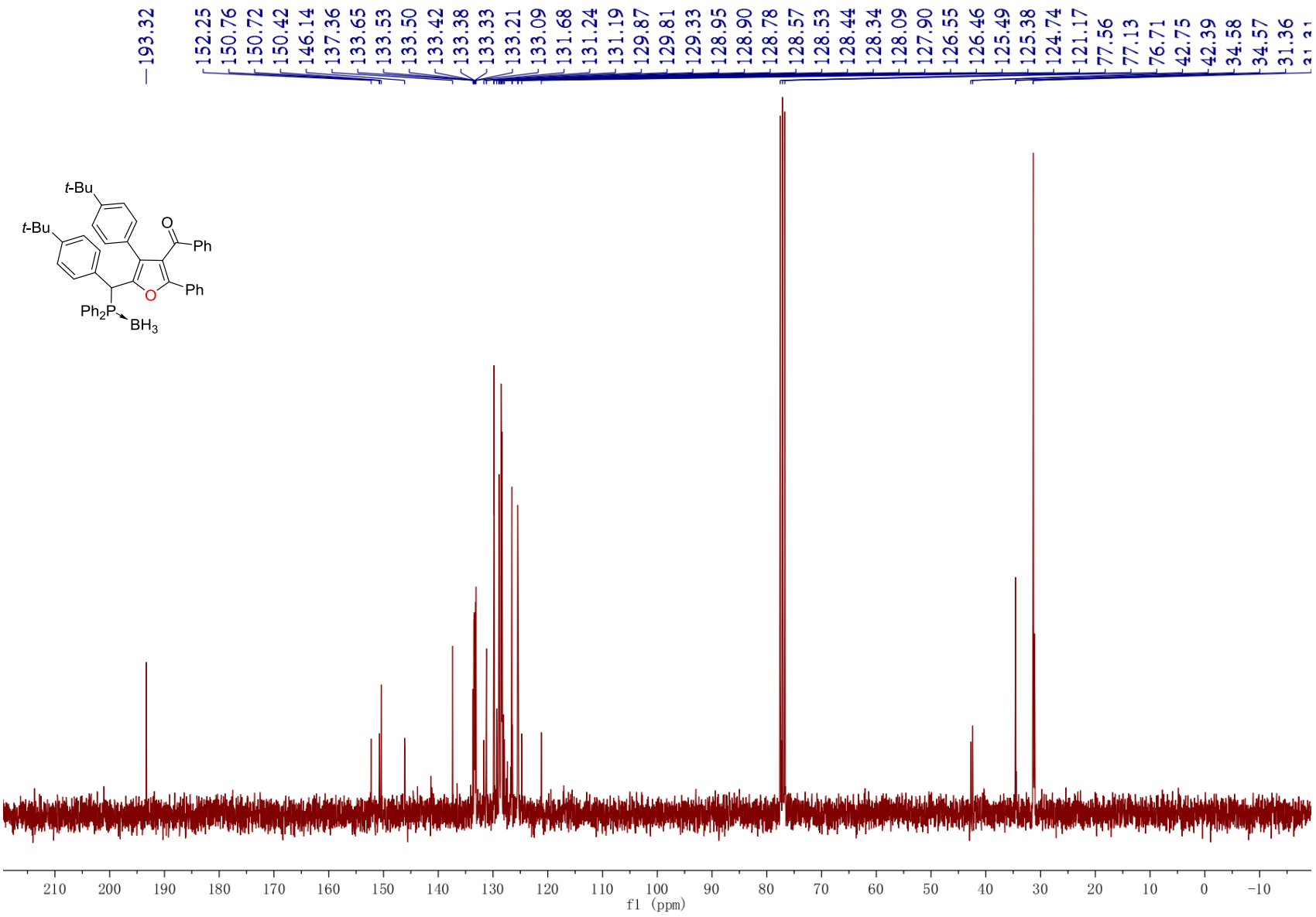
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3c**



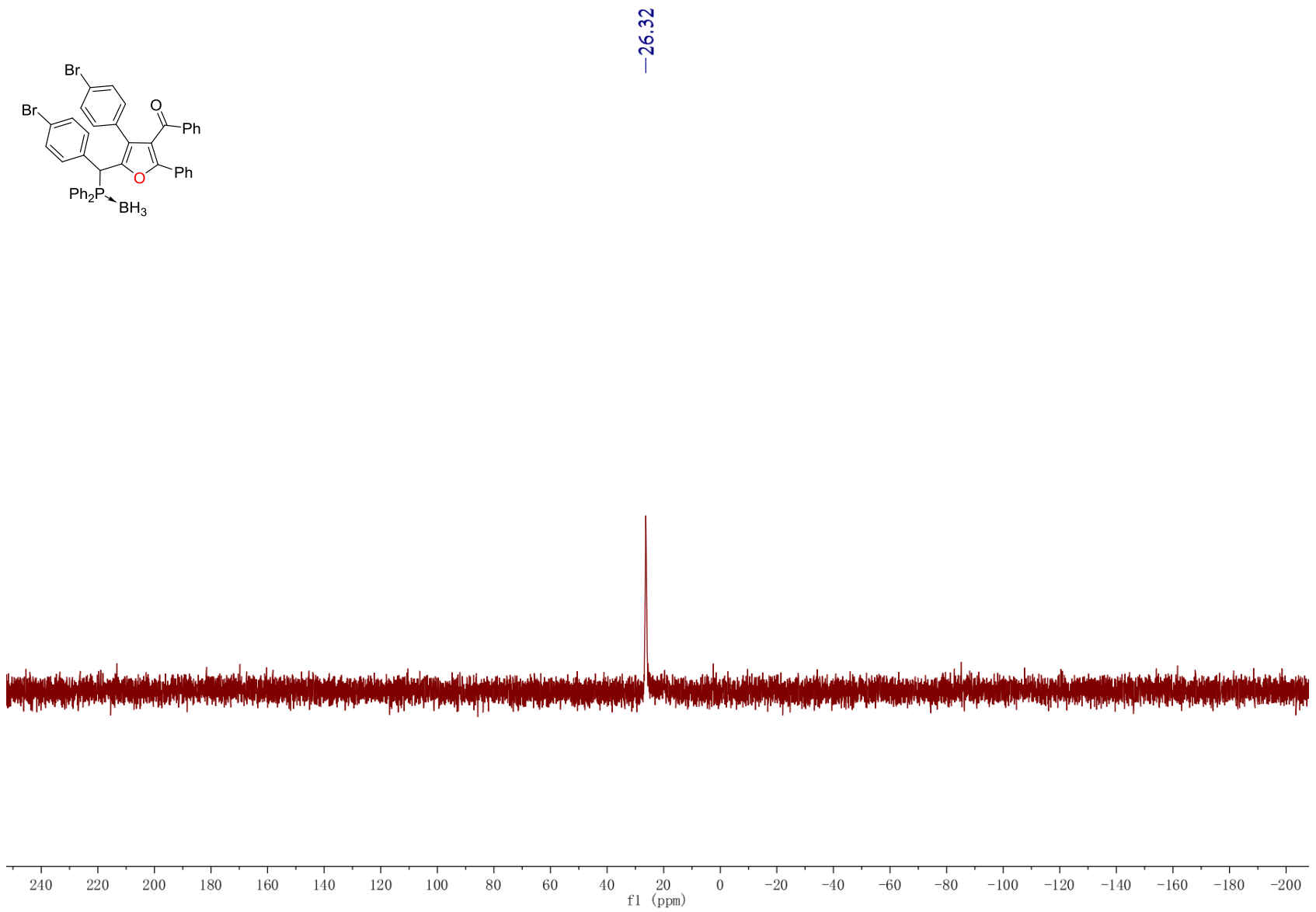
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3c**



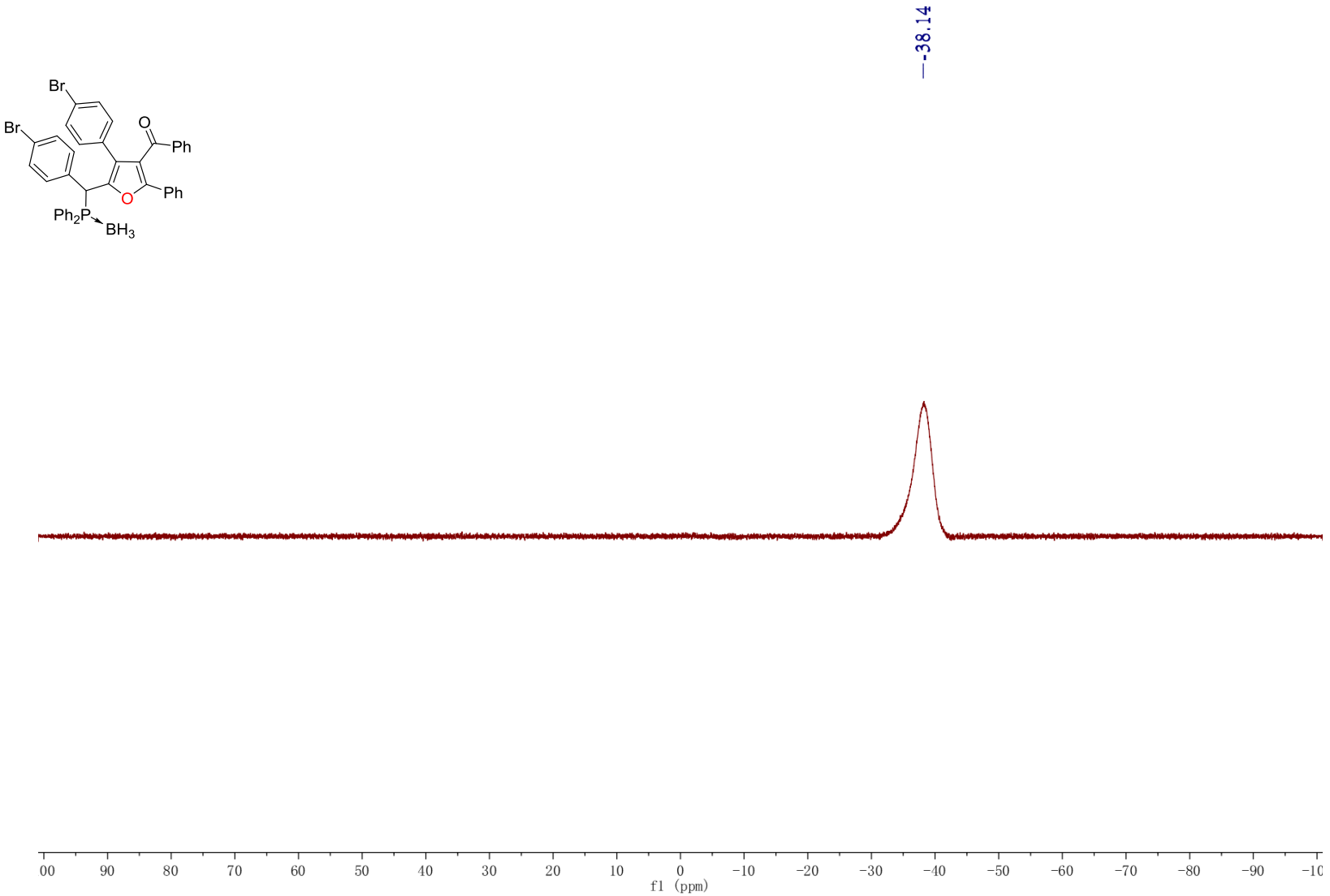
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3c**



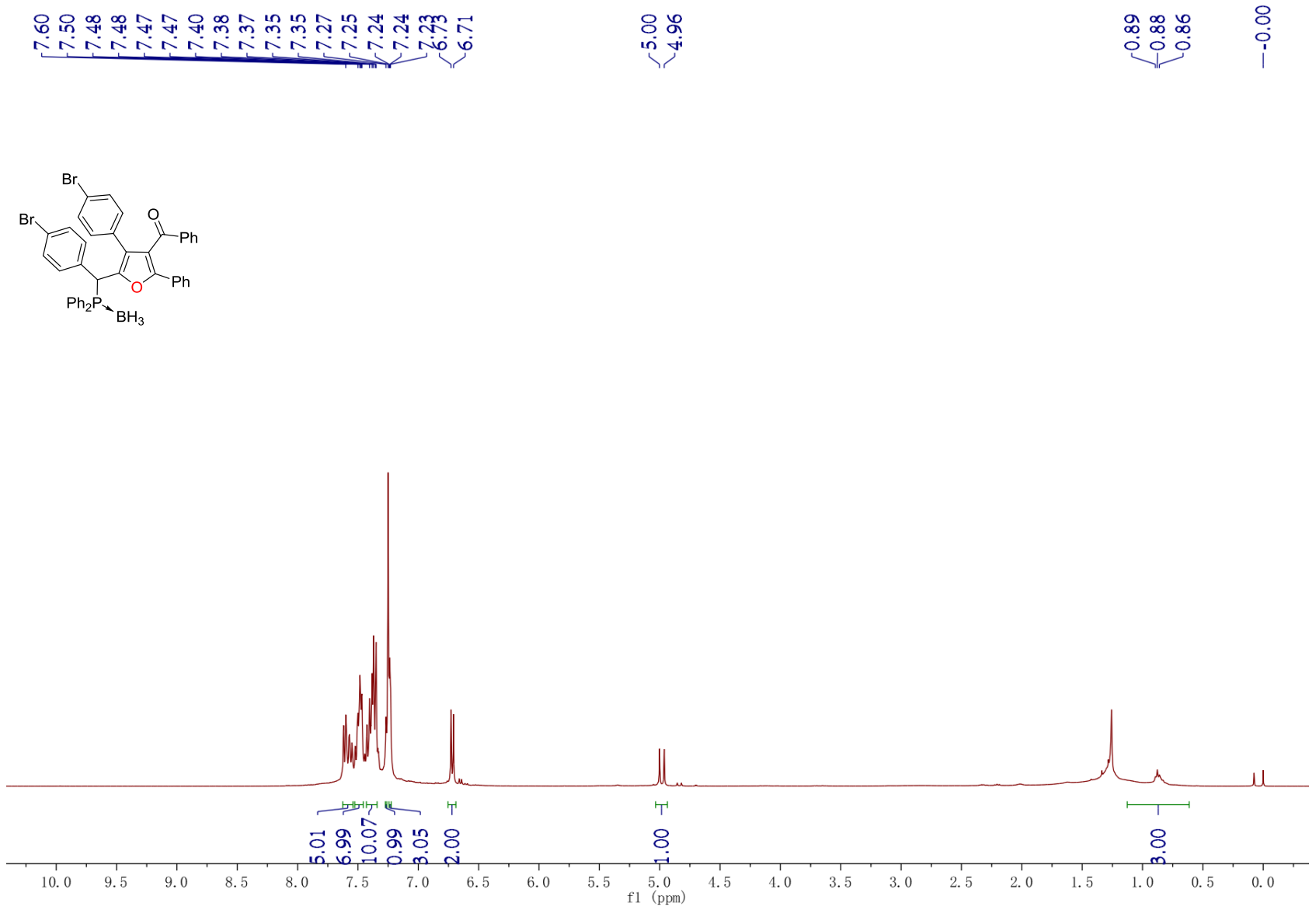
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3c**



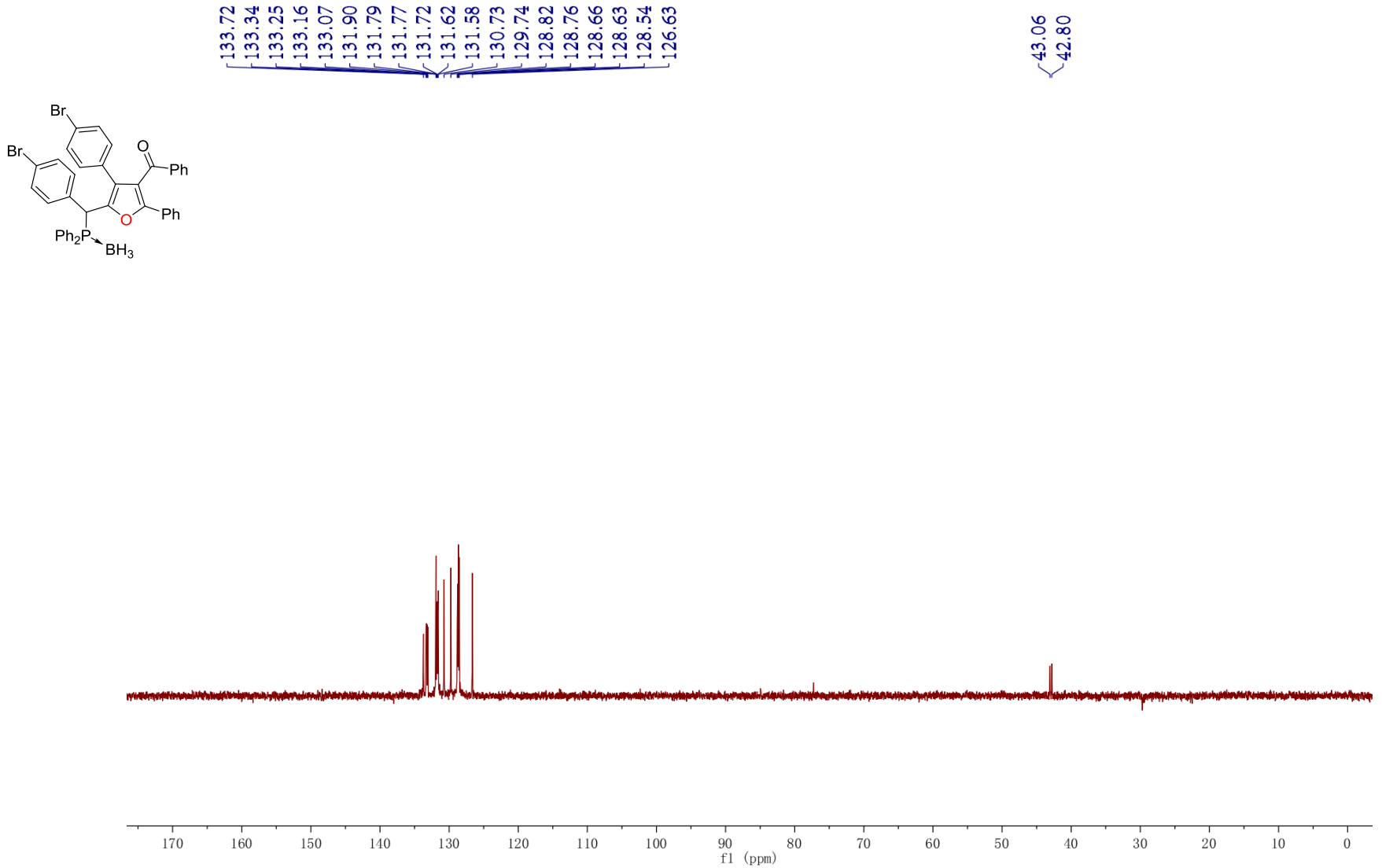
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3d**



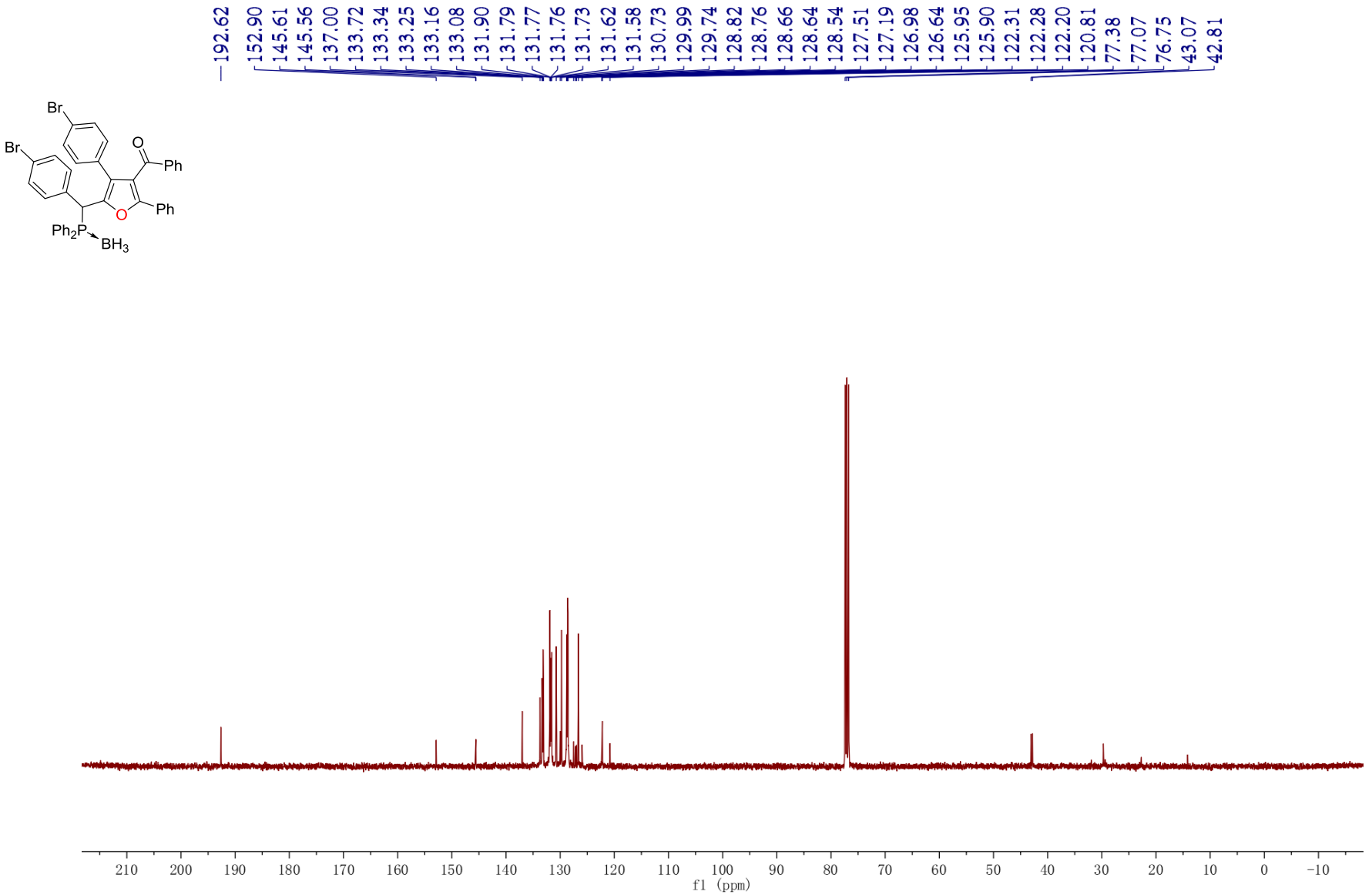
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3d**



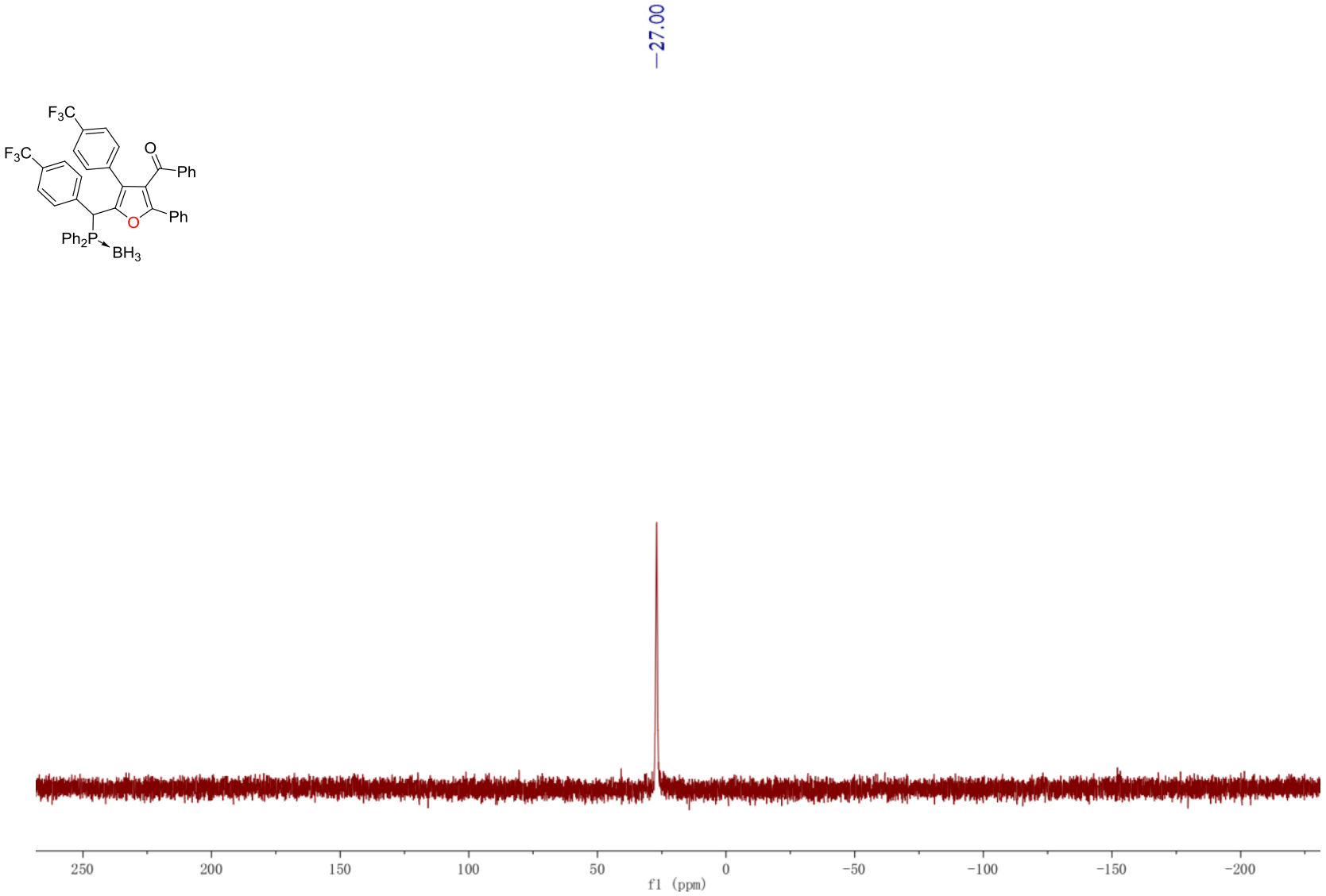
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3d**



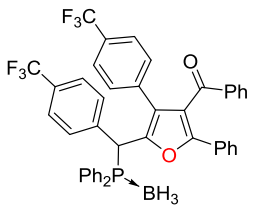
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3d**



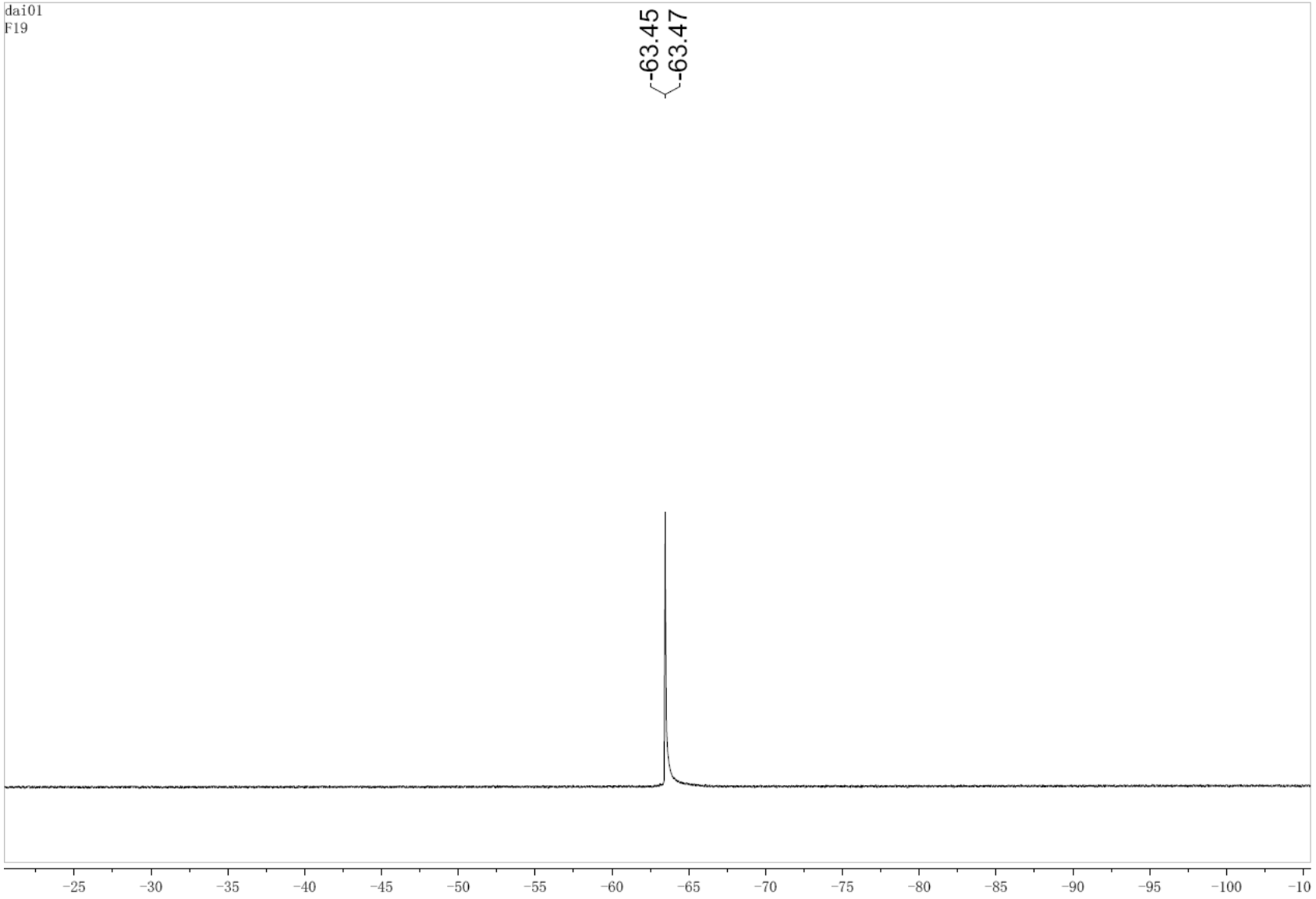
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3d**



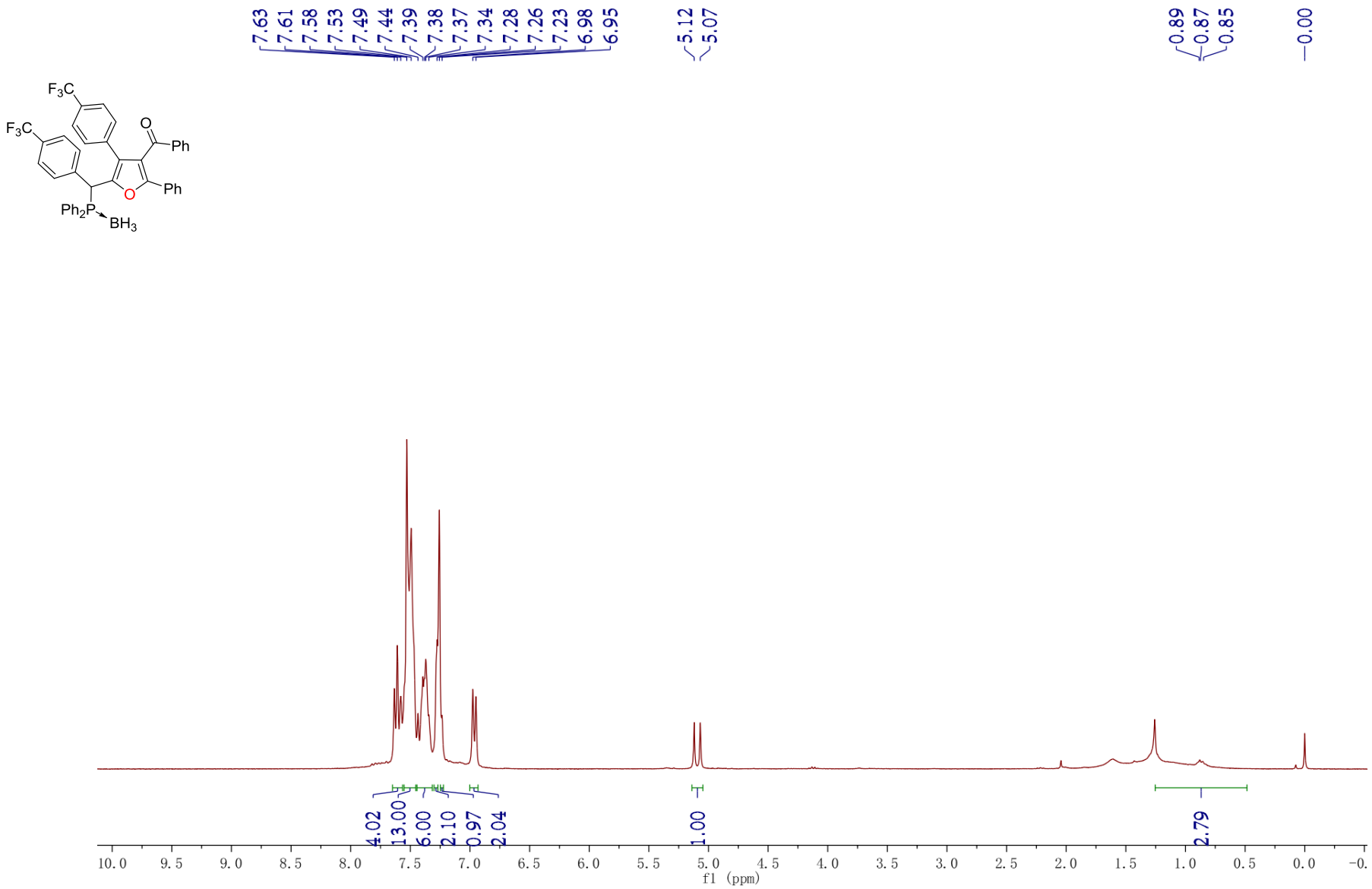
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3e**



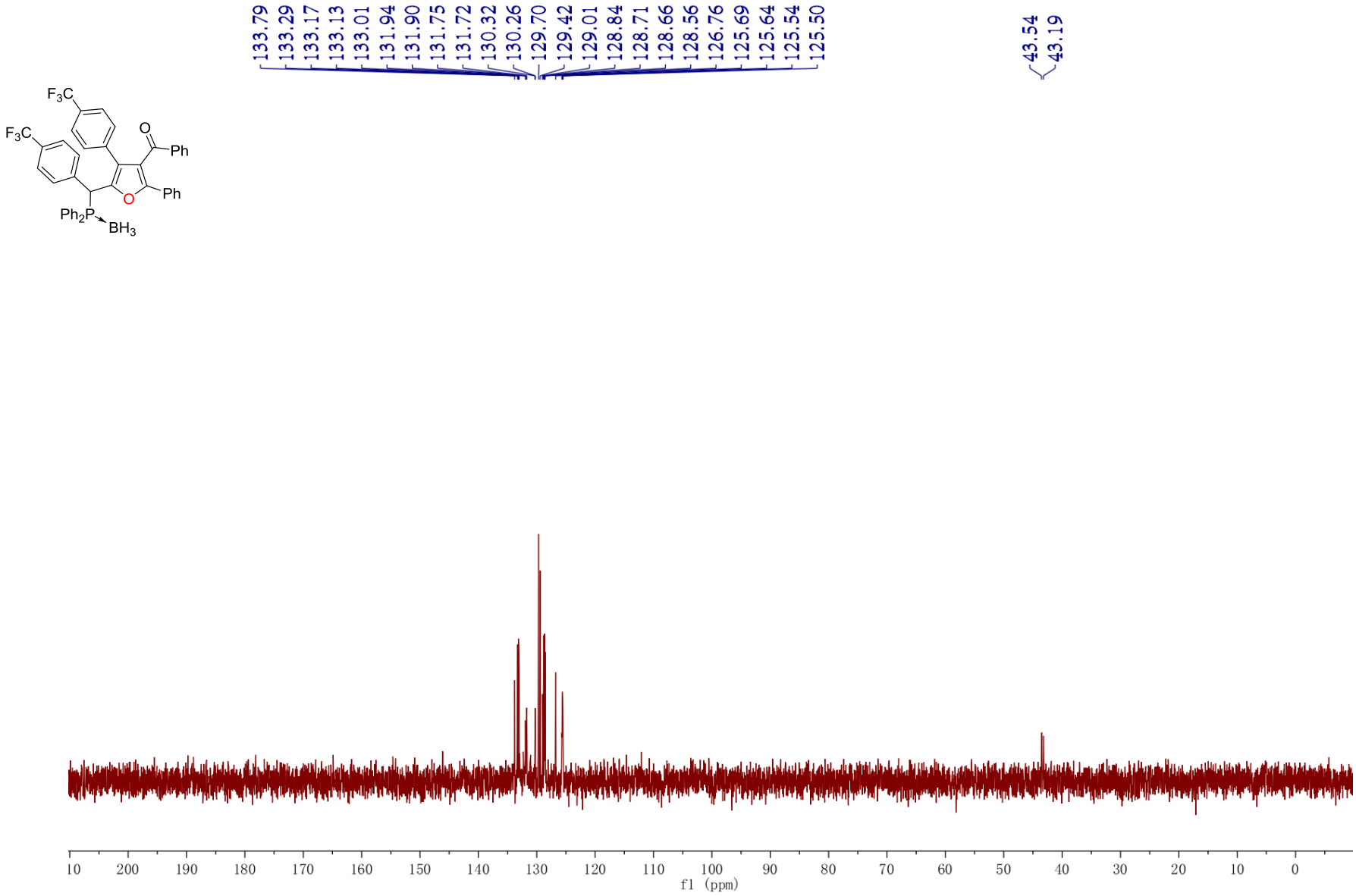
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3e**



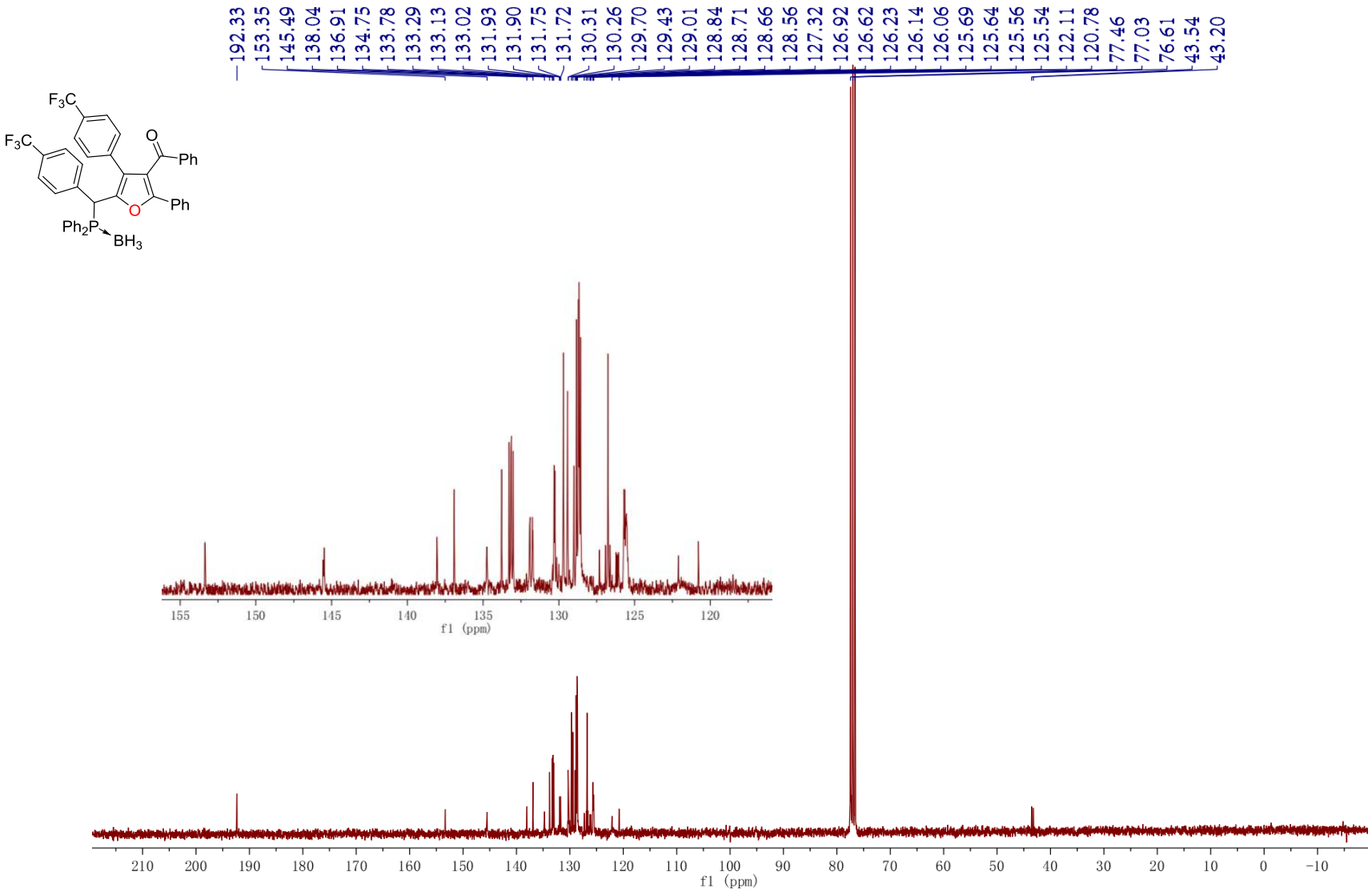
^{19}F NMR ($CDCl_3$, 282 MHz) of compound **3e**



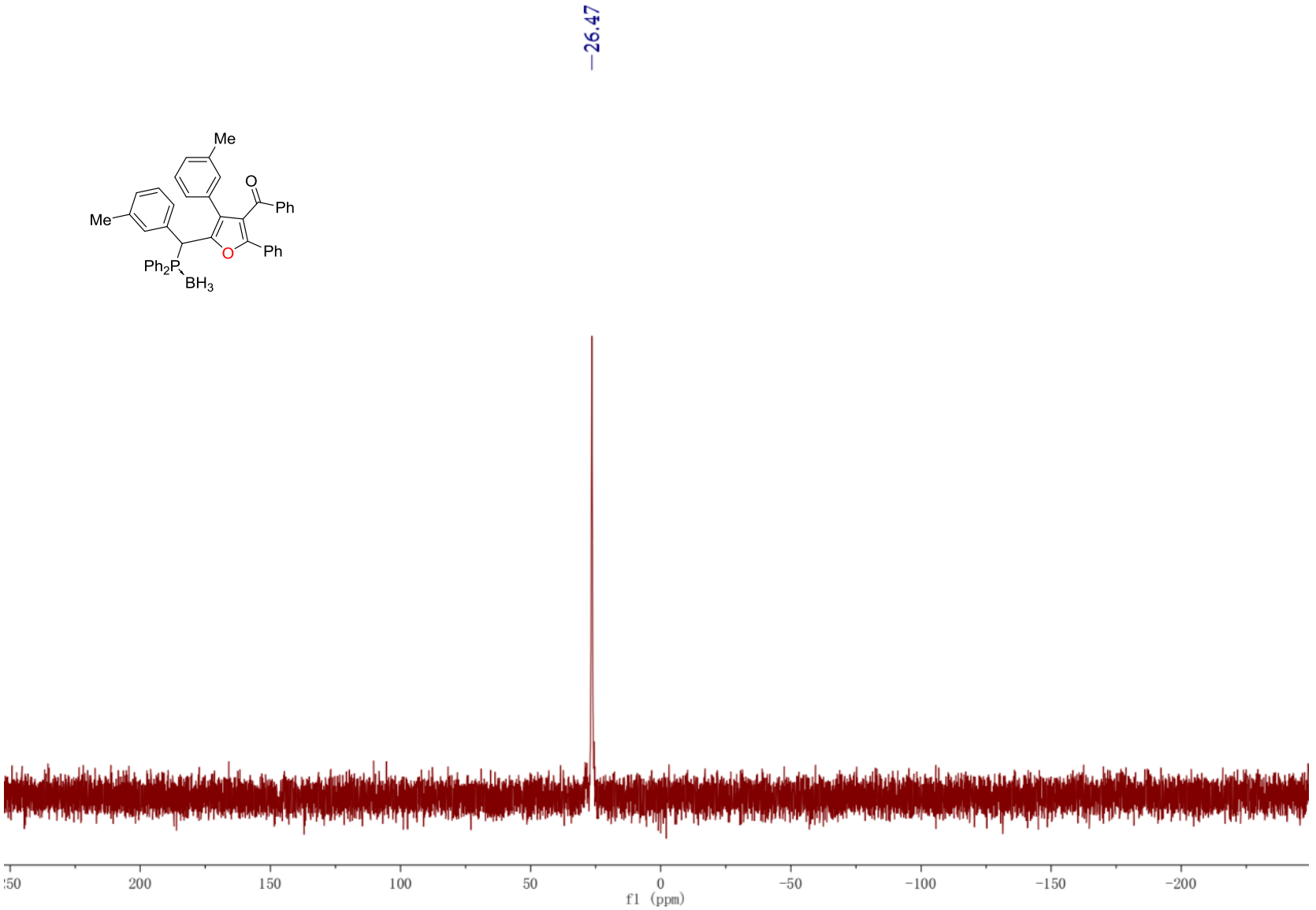
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3e**



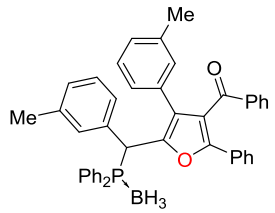
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3e**



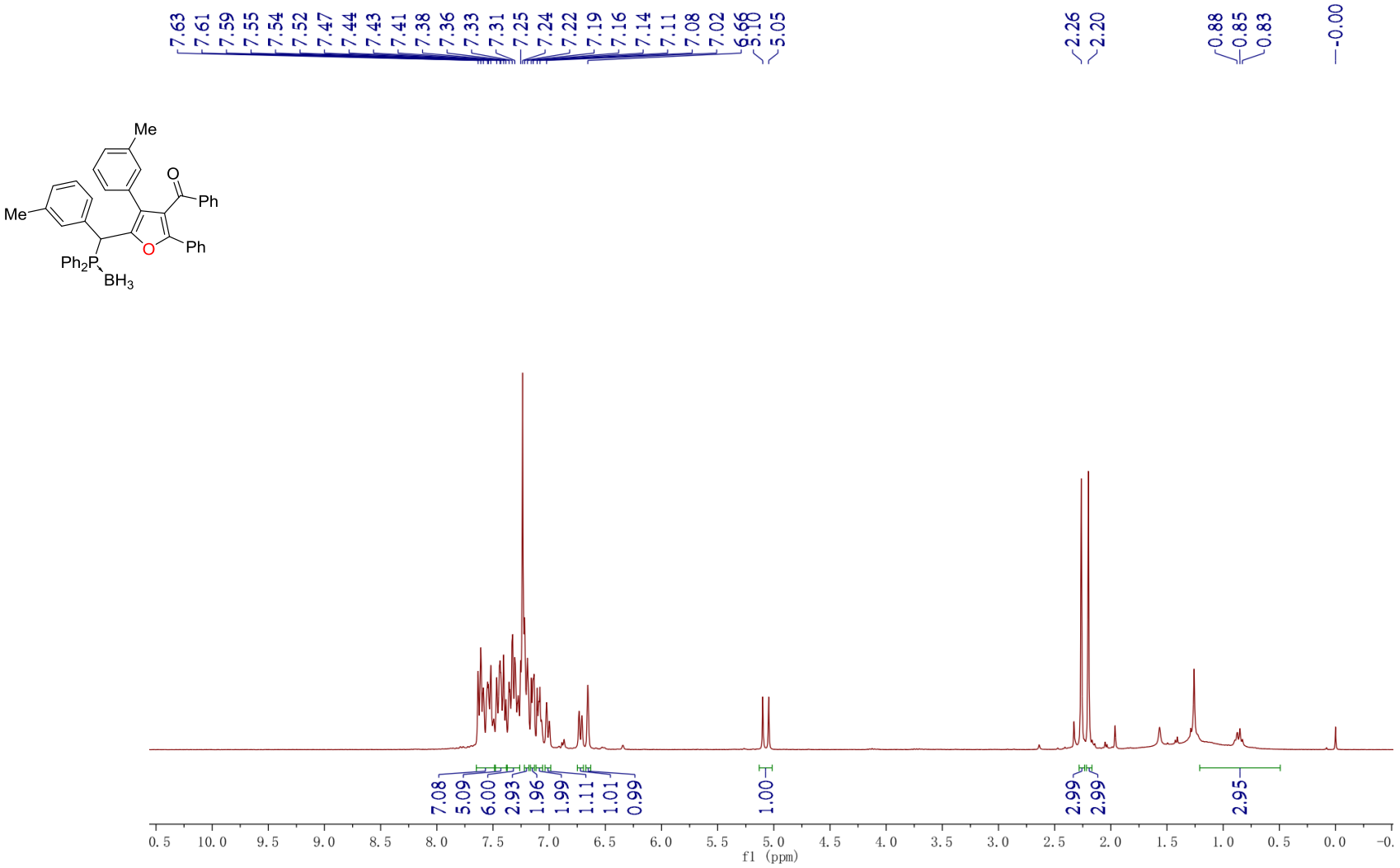
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3e**



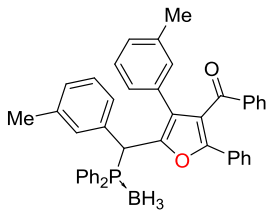
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3f**



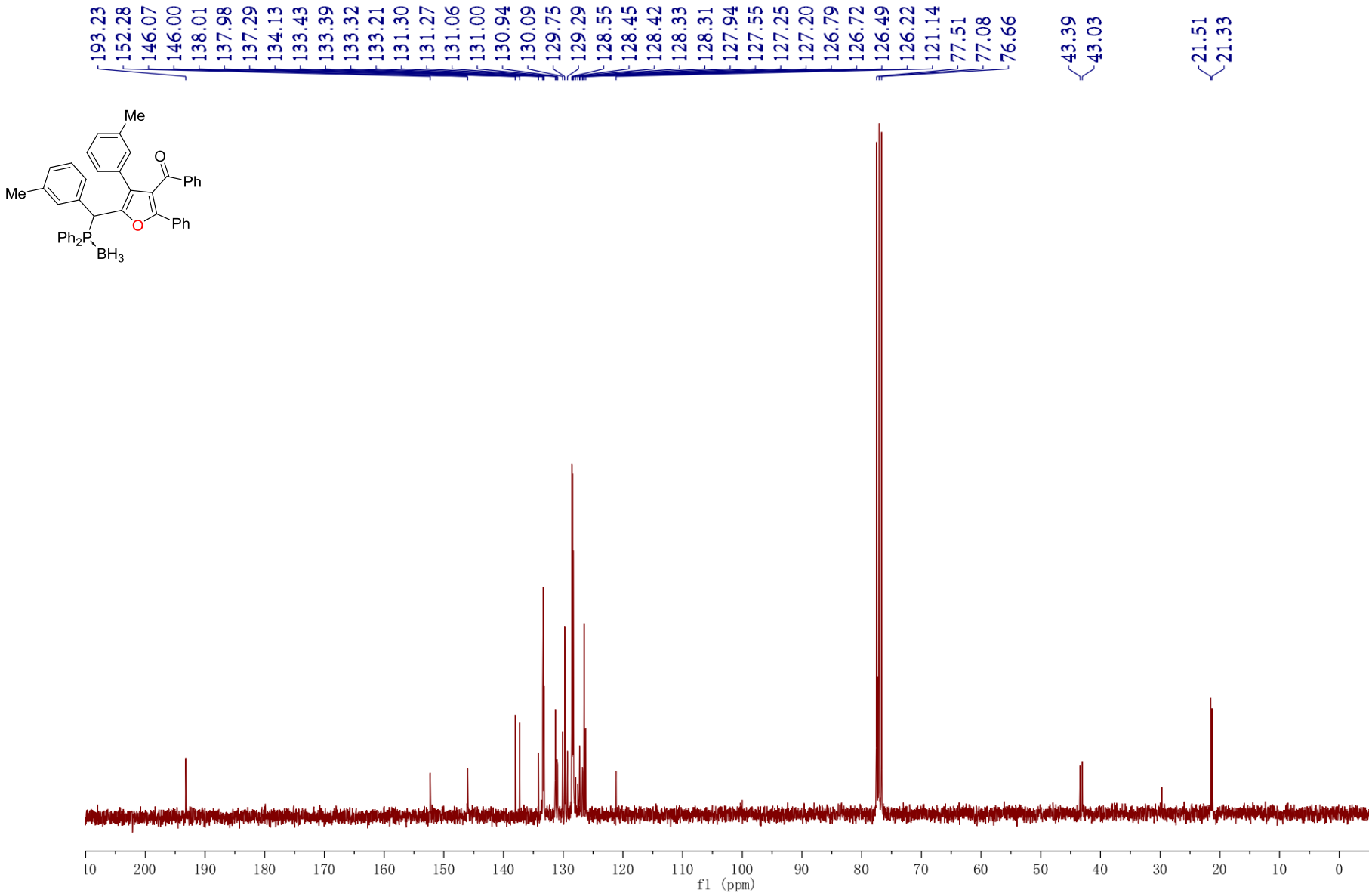
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3f**



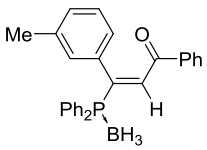
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3f**



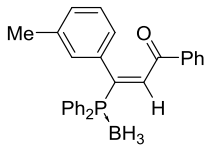
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3f**



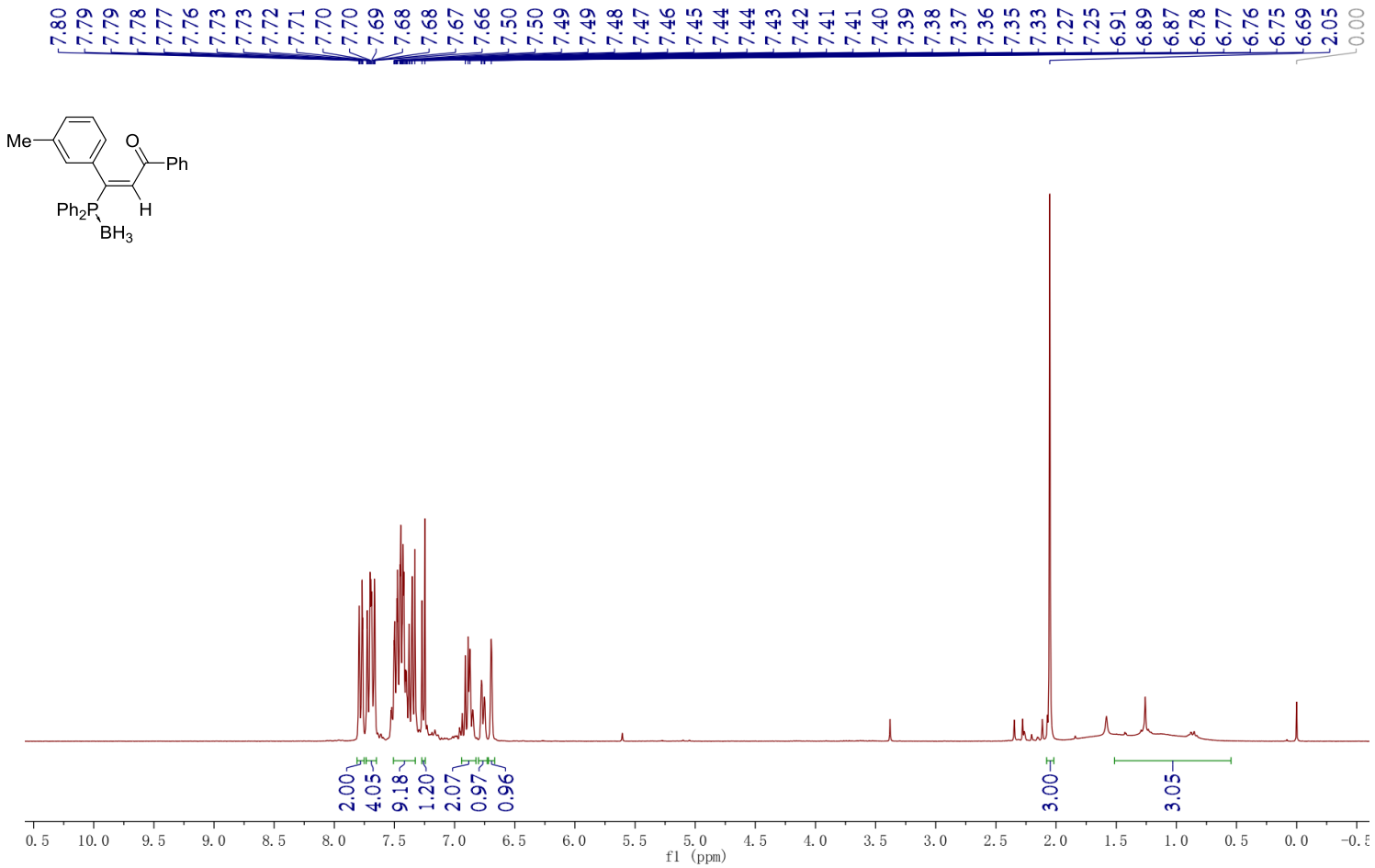
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3f**



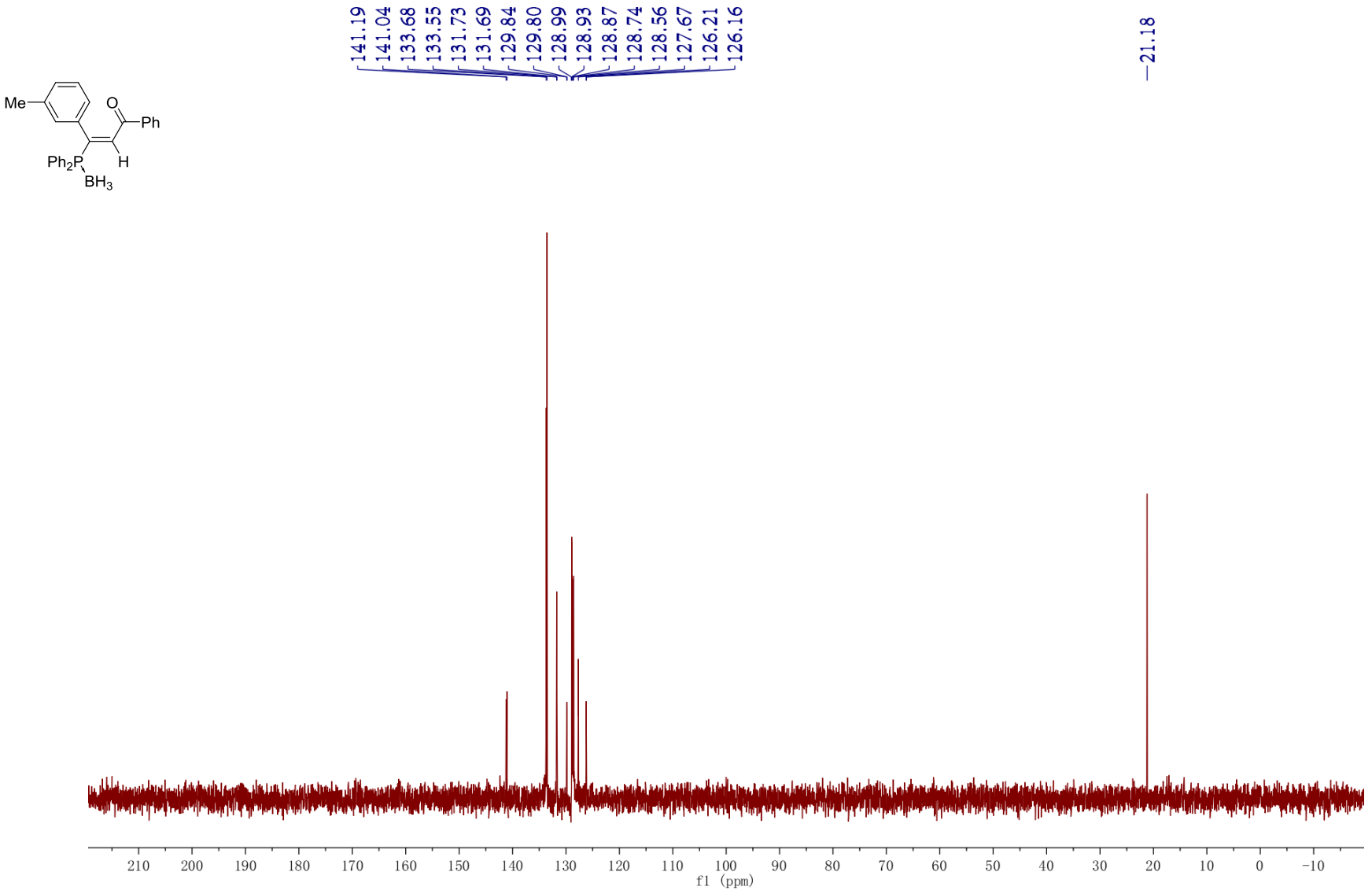
^{31}P $\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of compound **3f'**



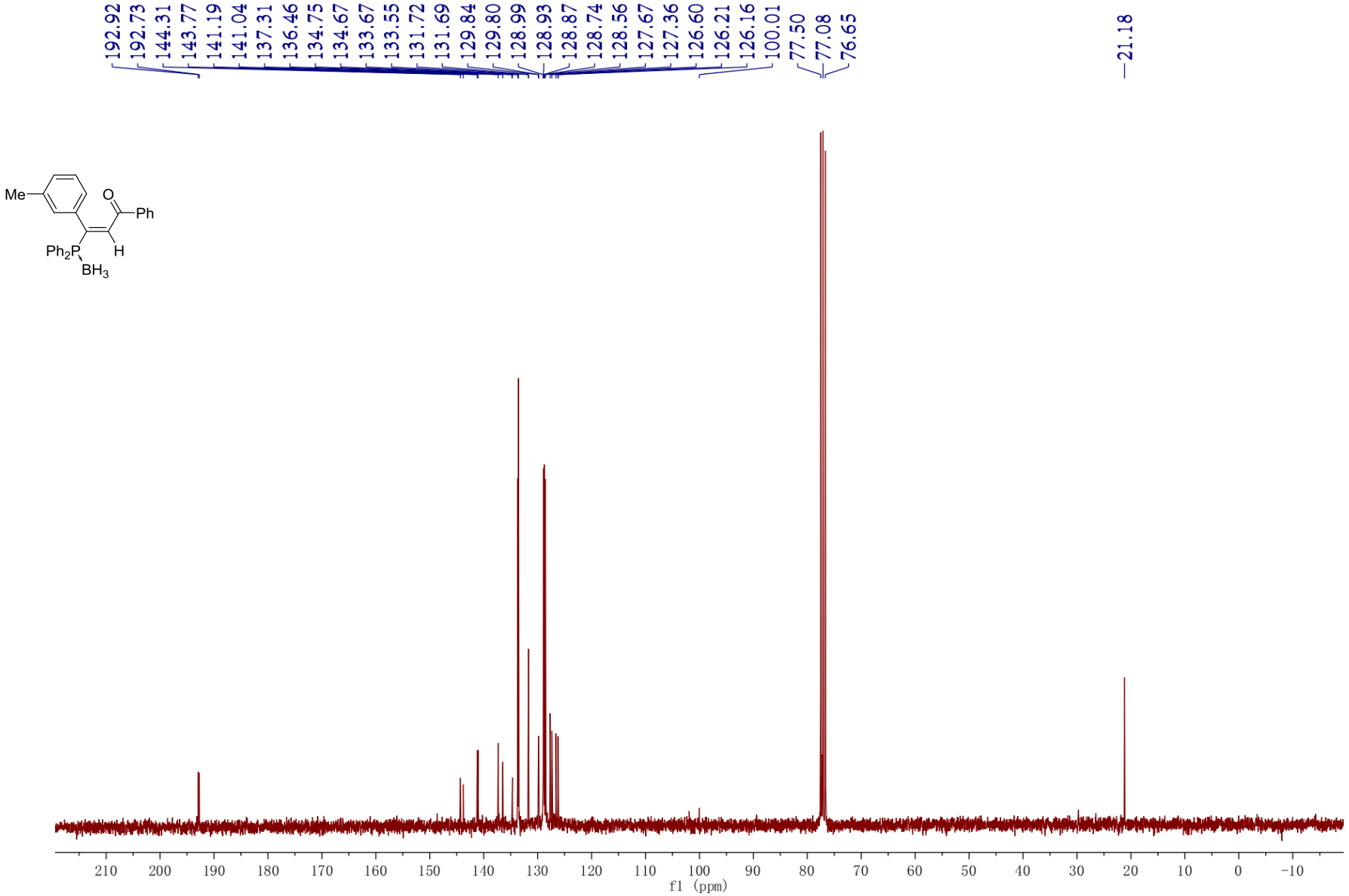
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3f'**



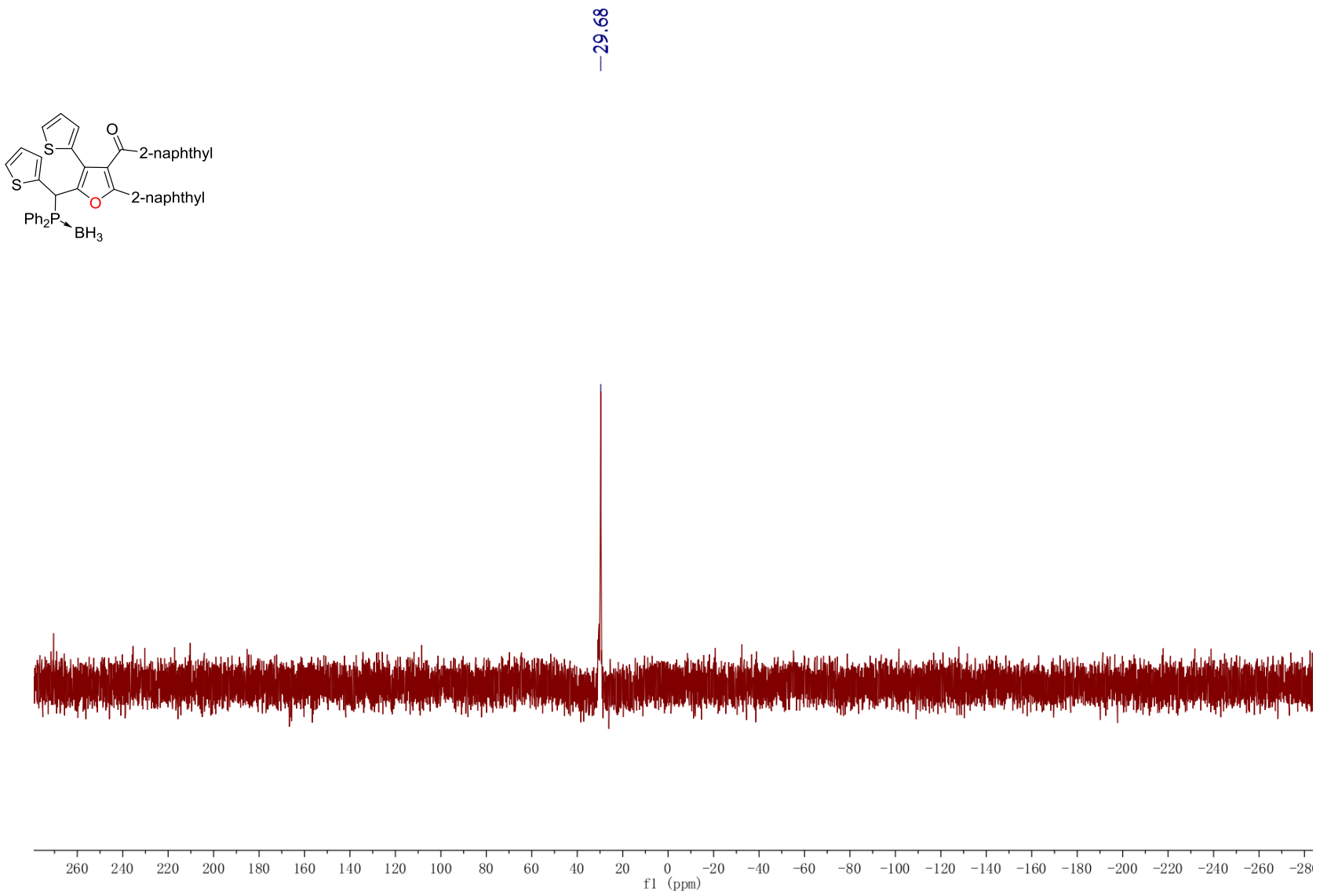
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3f'**



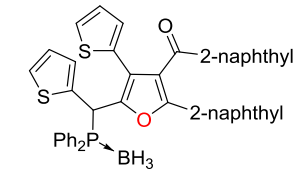
Dept 135 NMR ($CDCl_3$, 101 MHz) of compound **3f'**



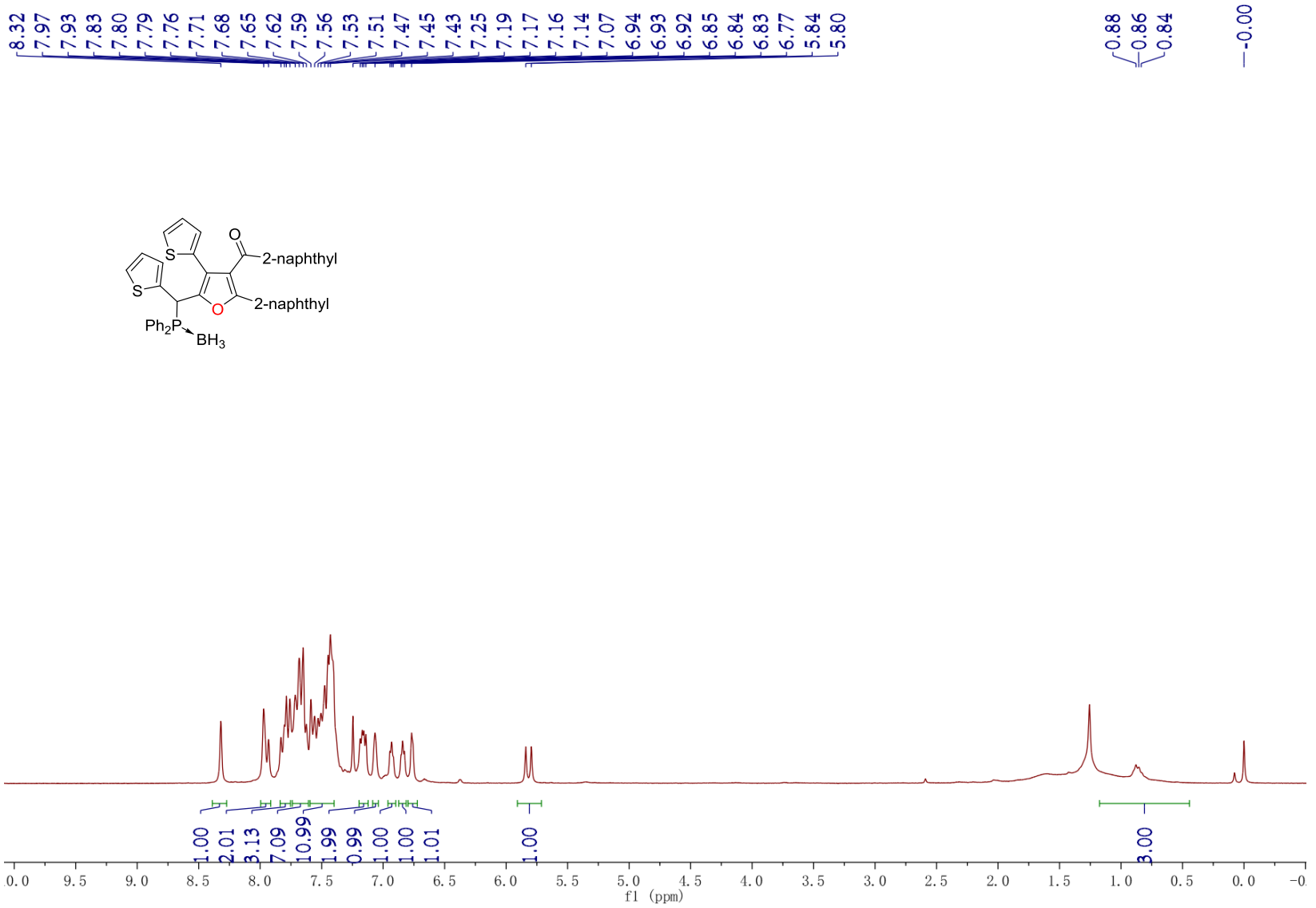
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3f'**



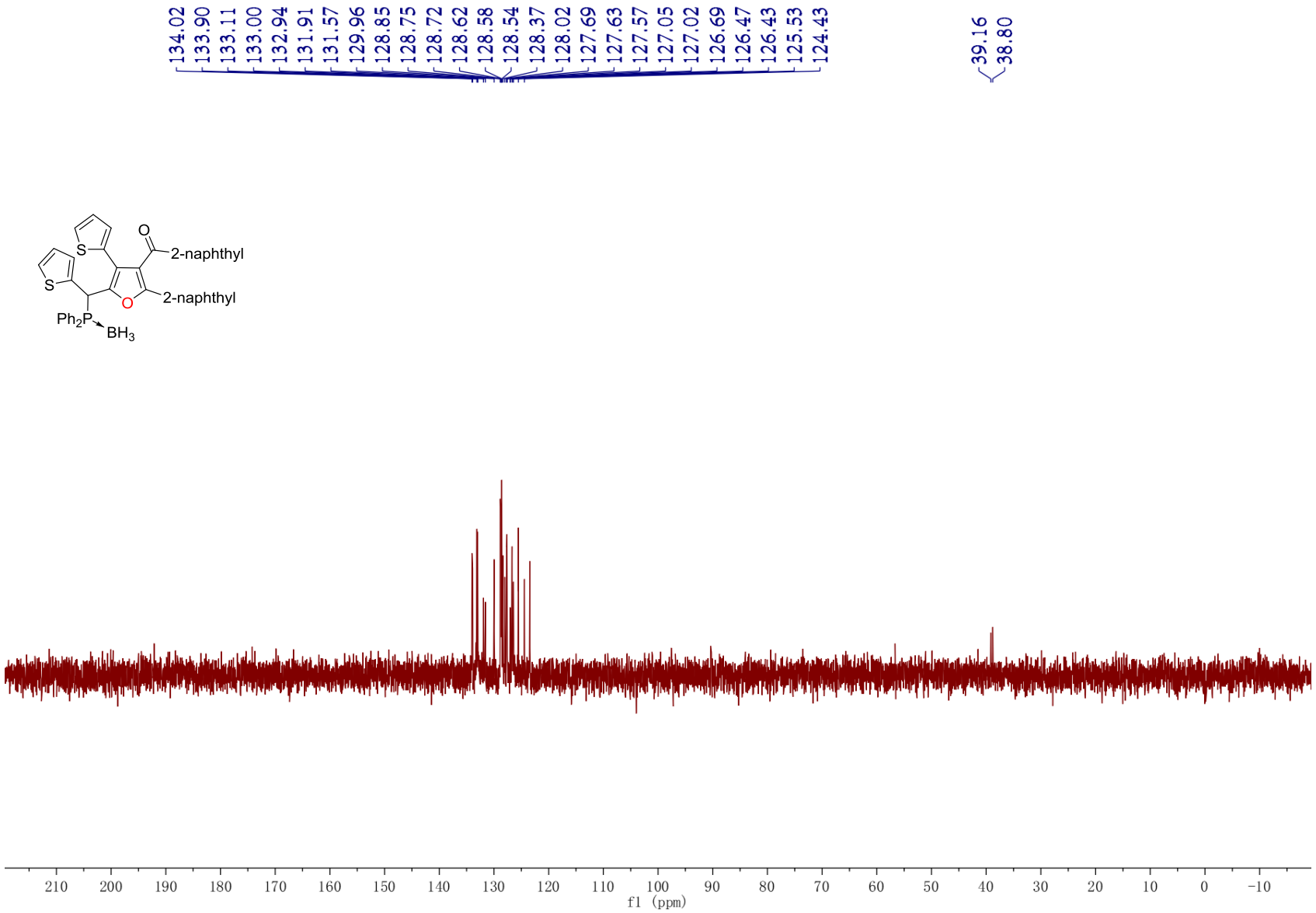
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3g**



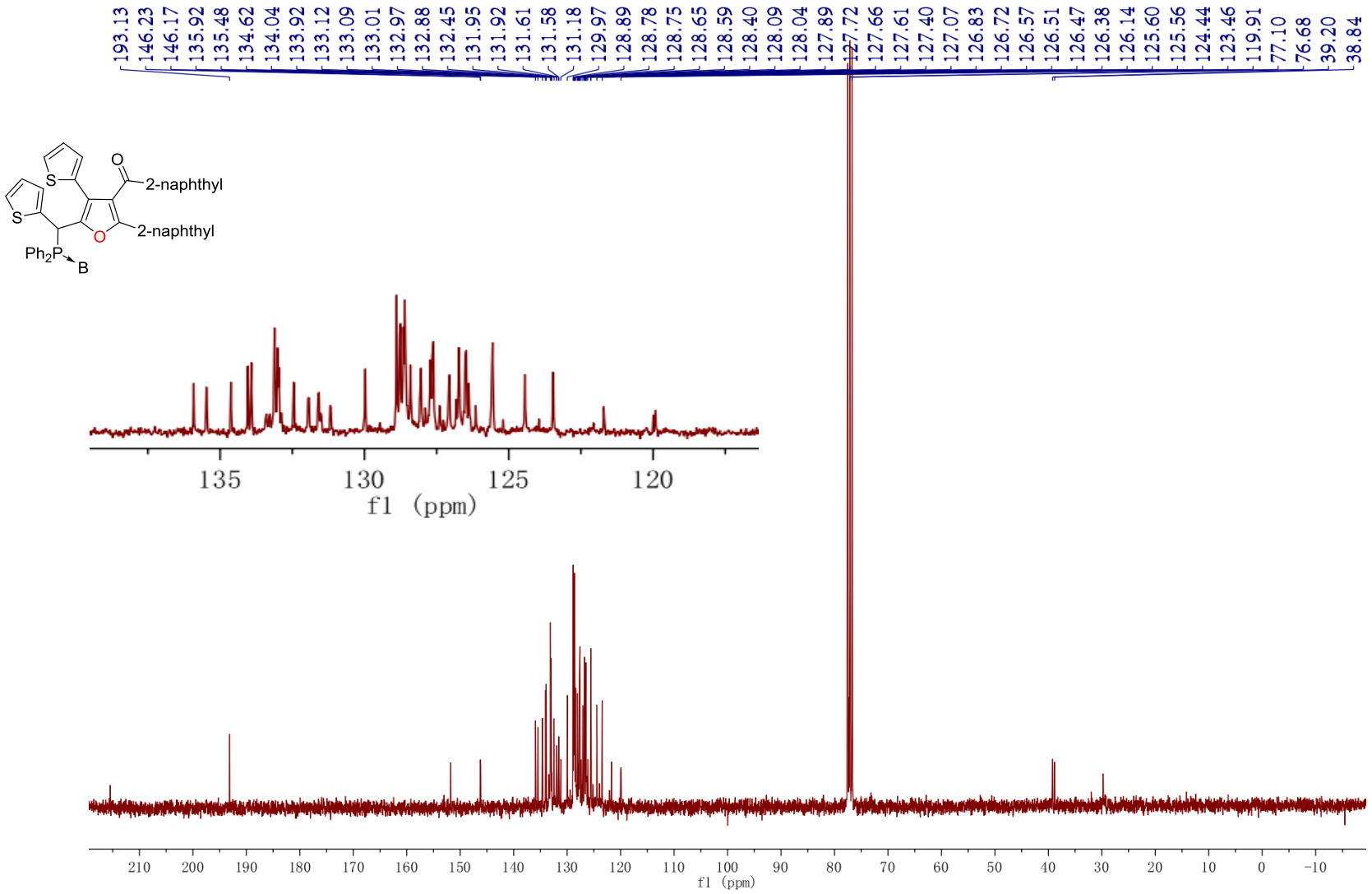
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3g**



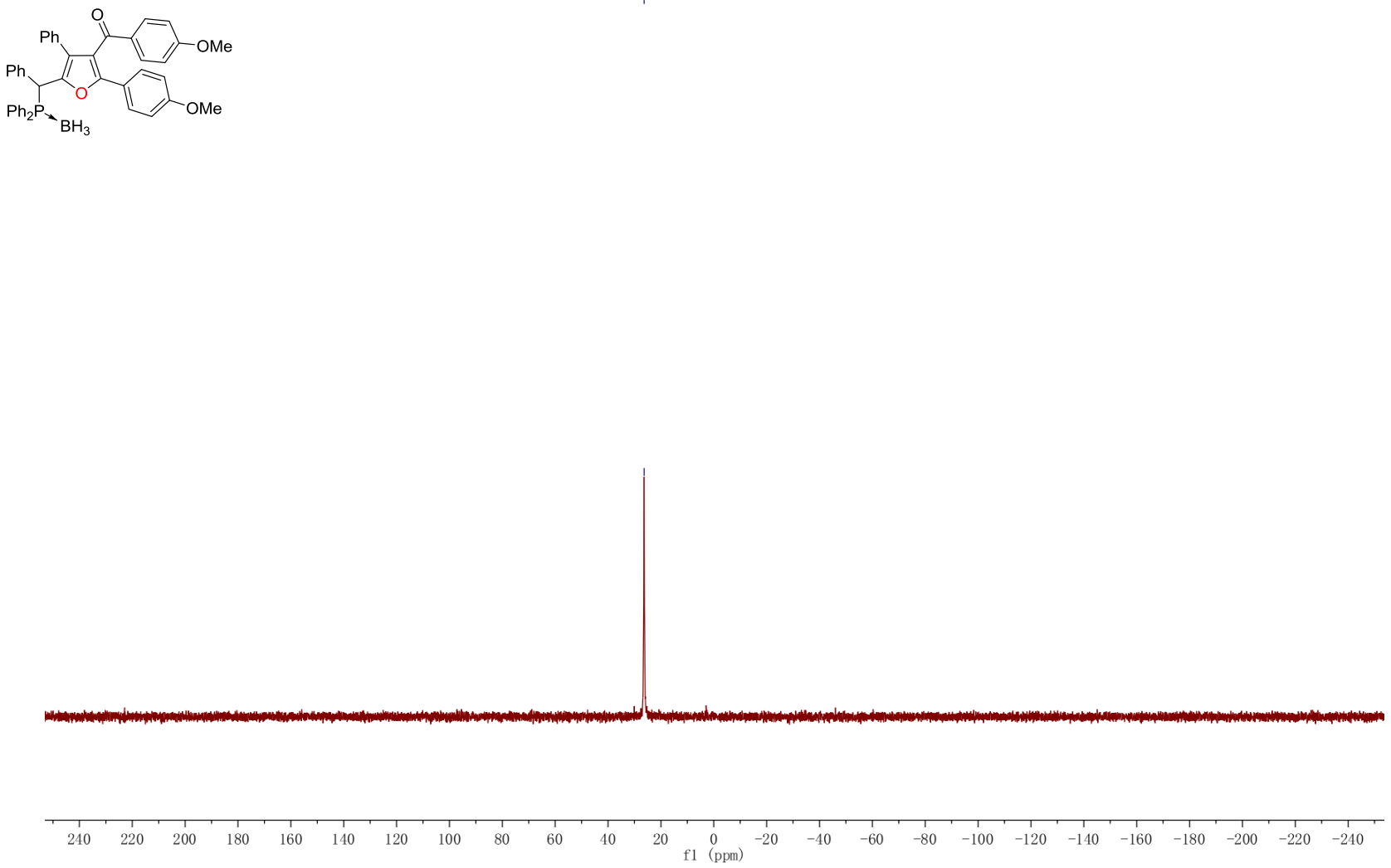
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3g**



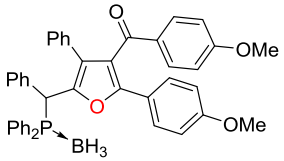
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3g**



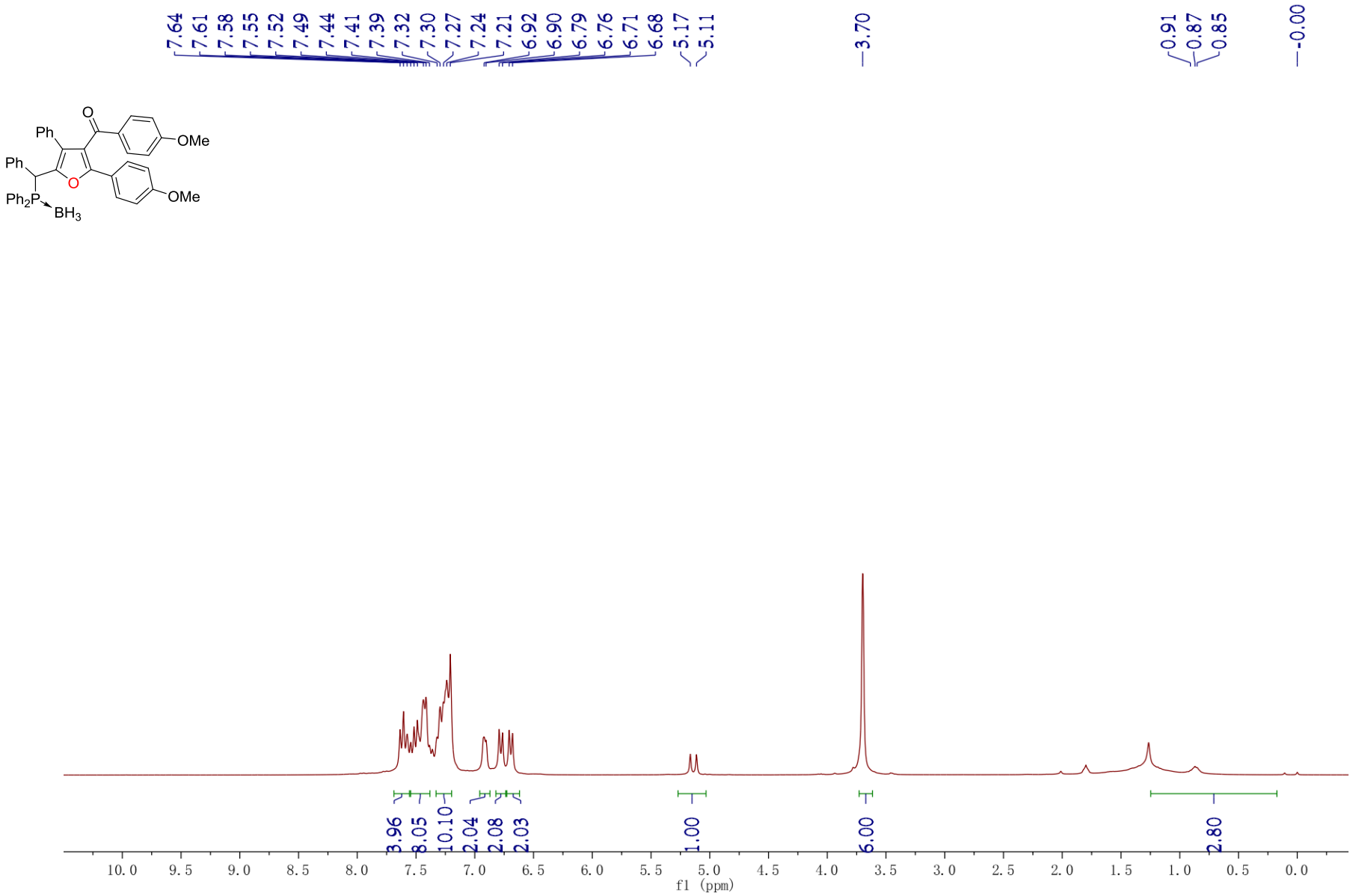
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3g**



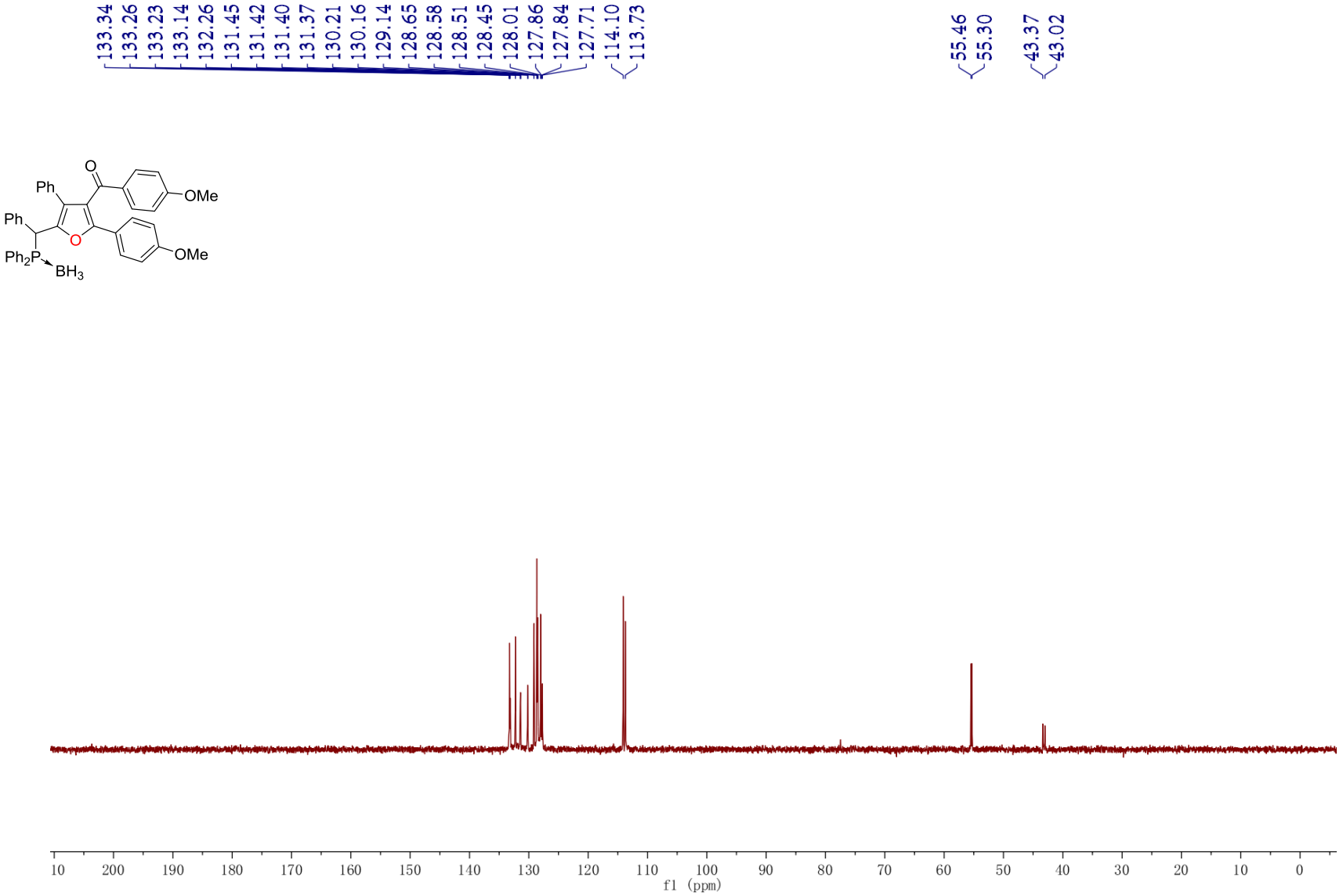
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3h**



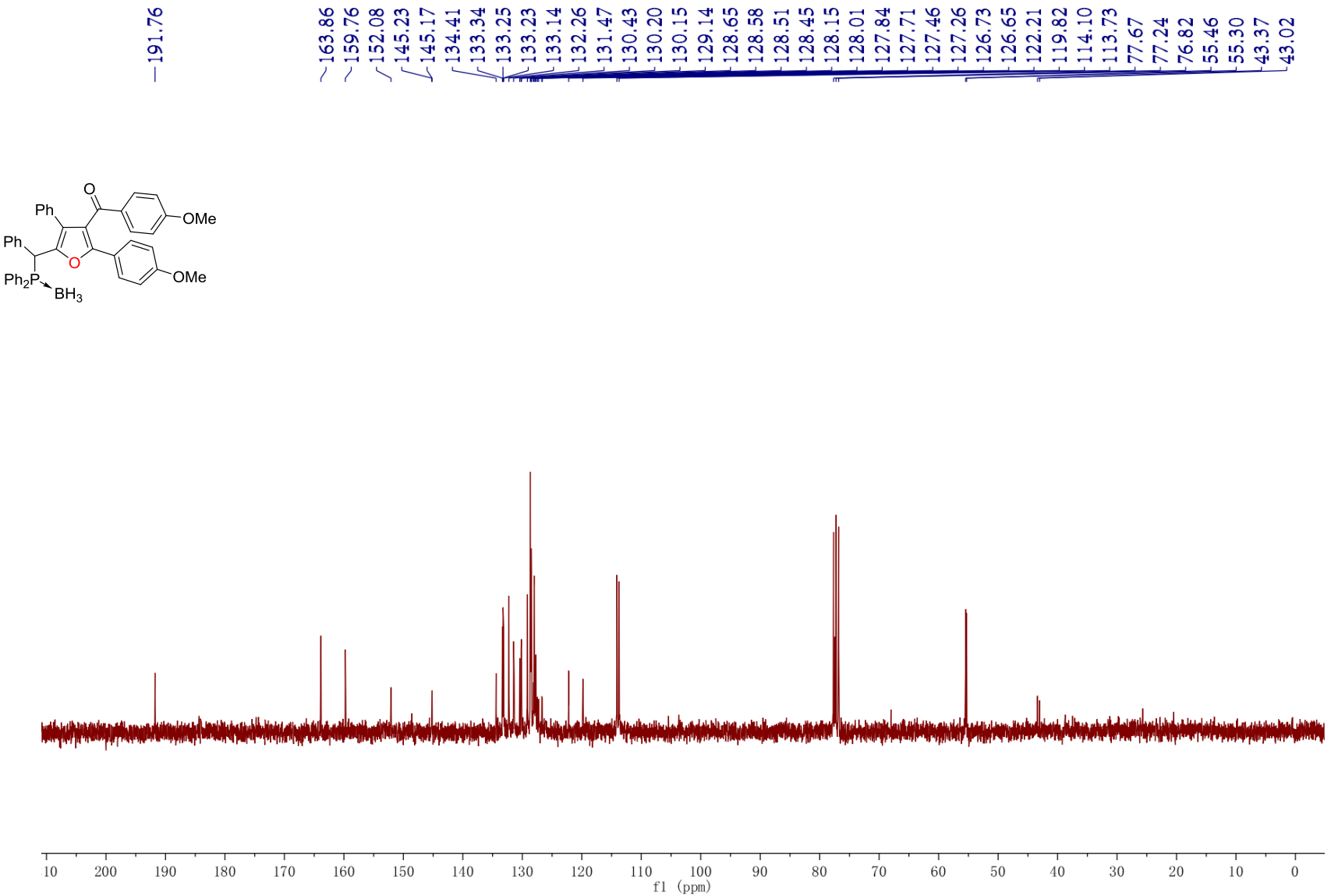
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3h**



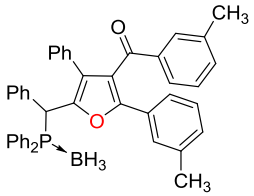
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3h**



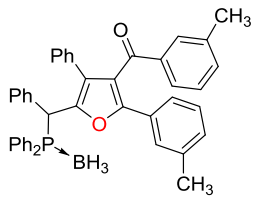
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3h**



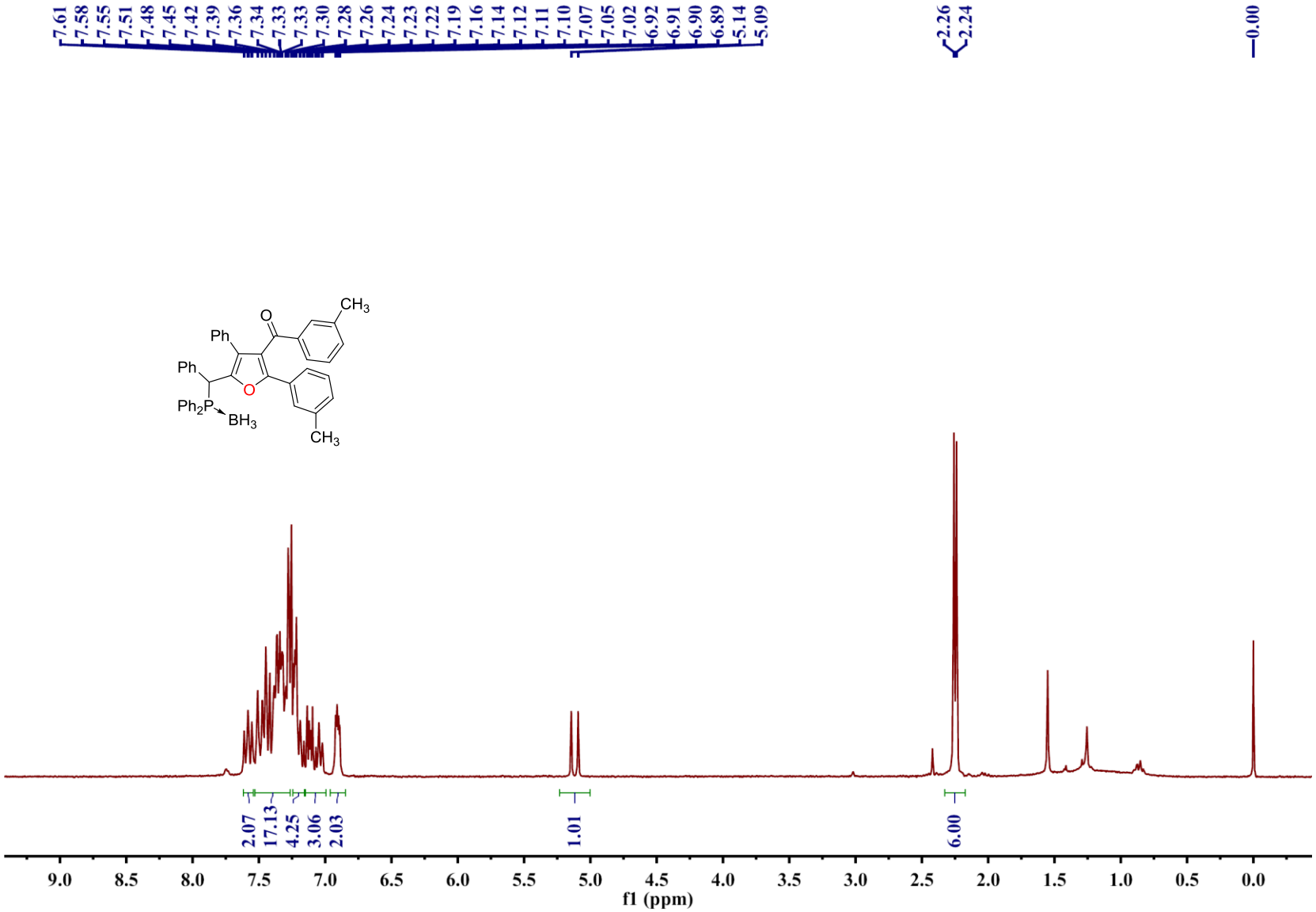
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3h**



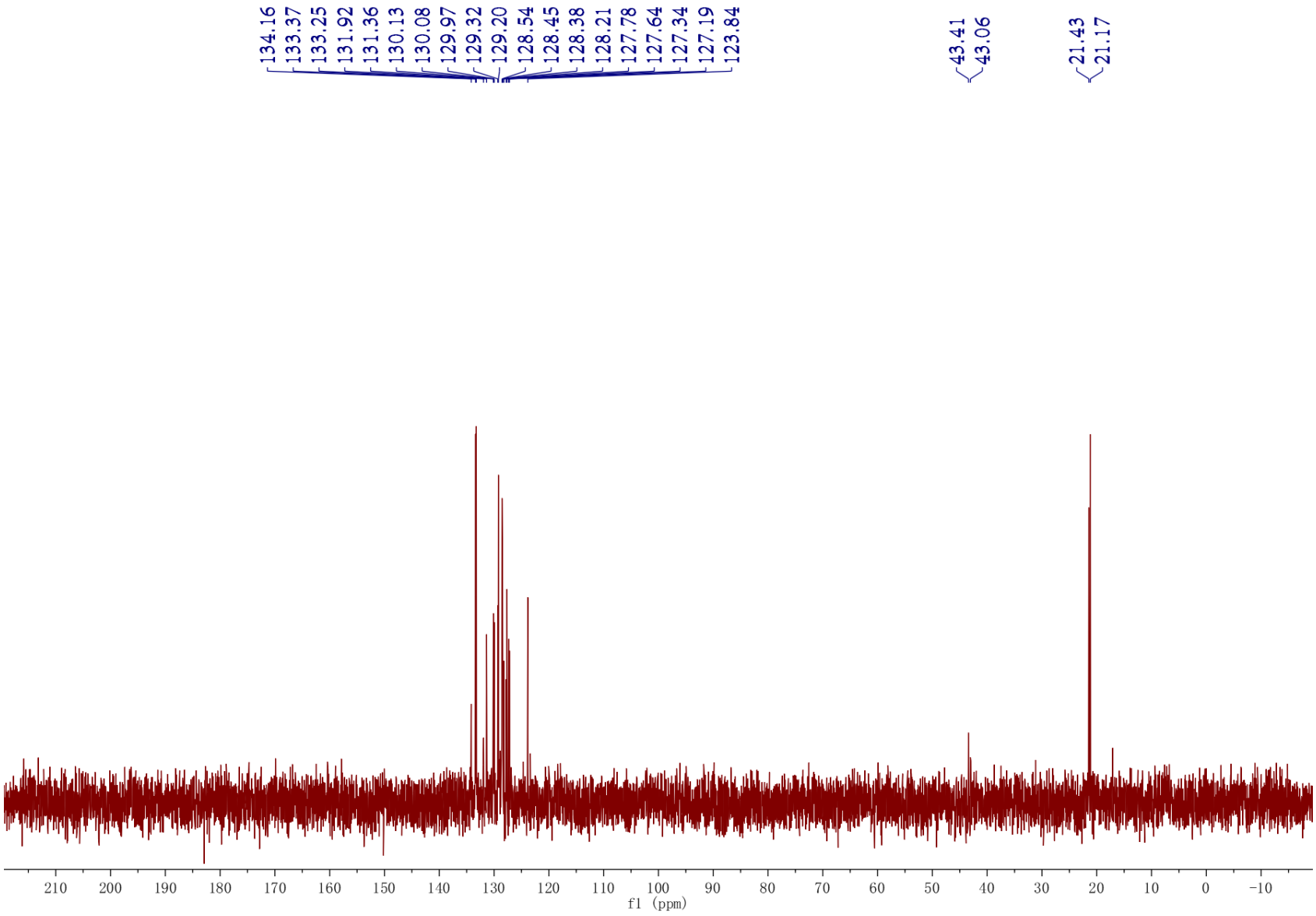
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3i**



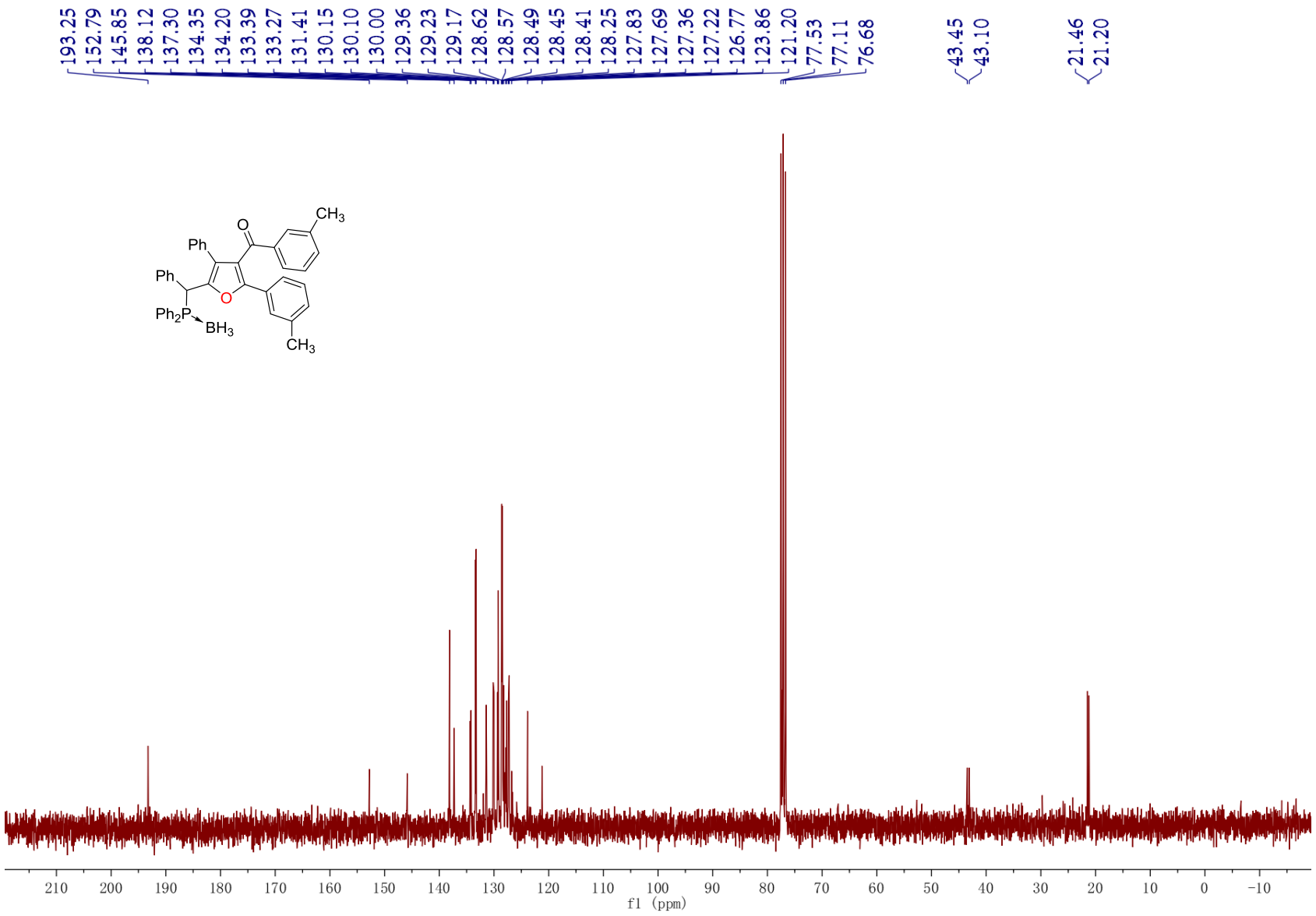
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3i**



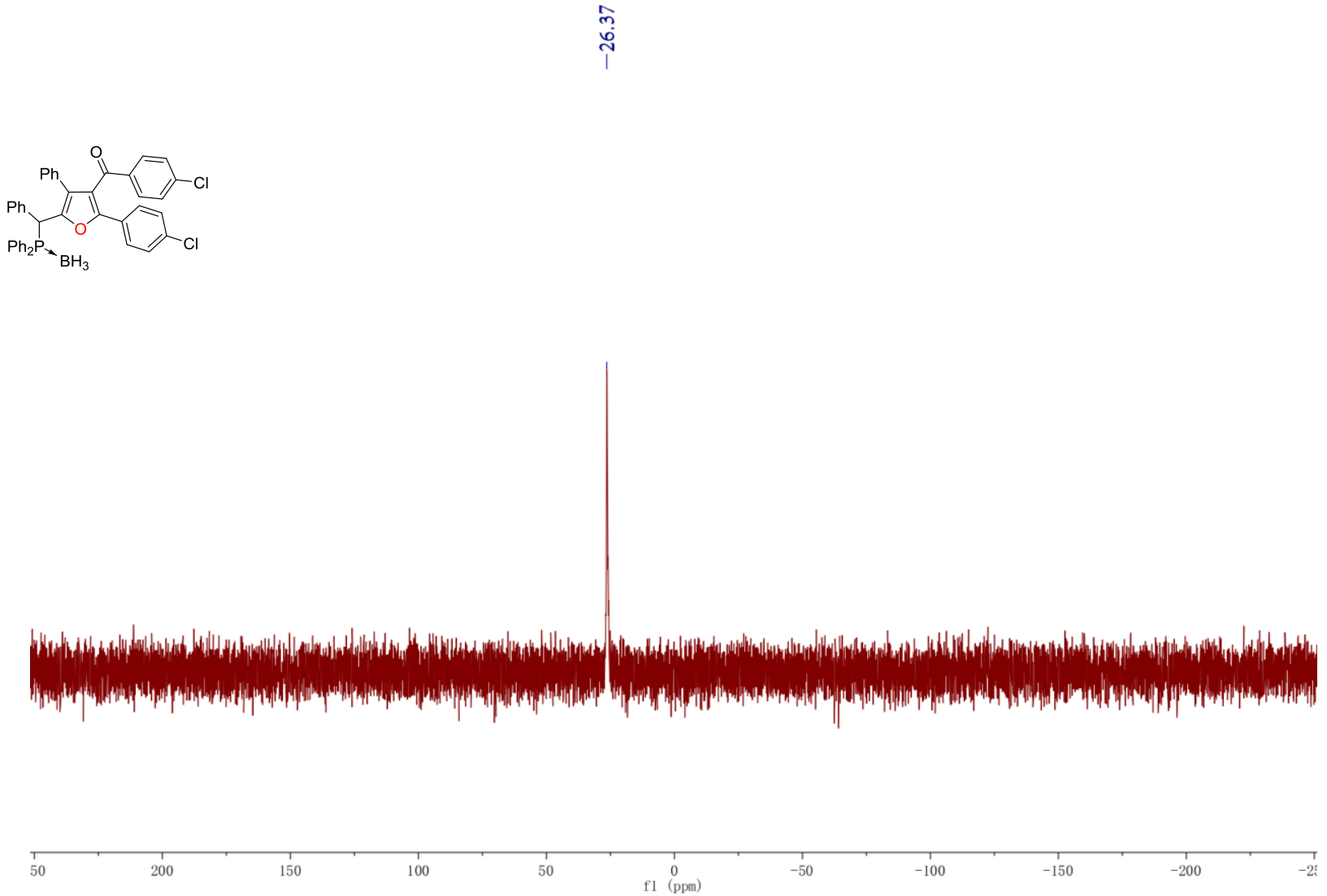
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3i**



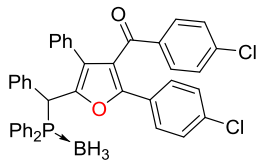
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3i**



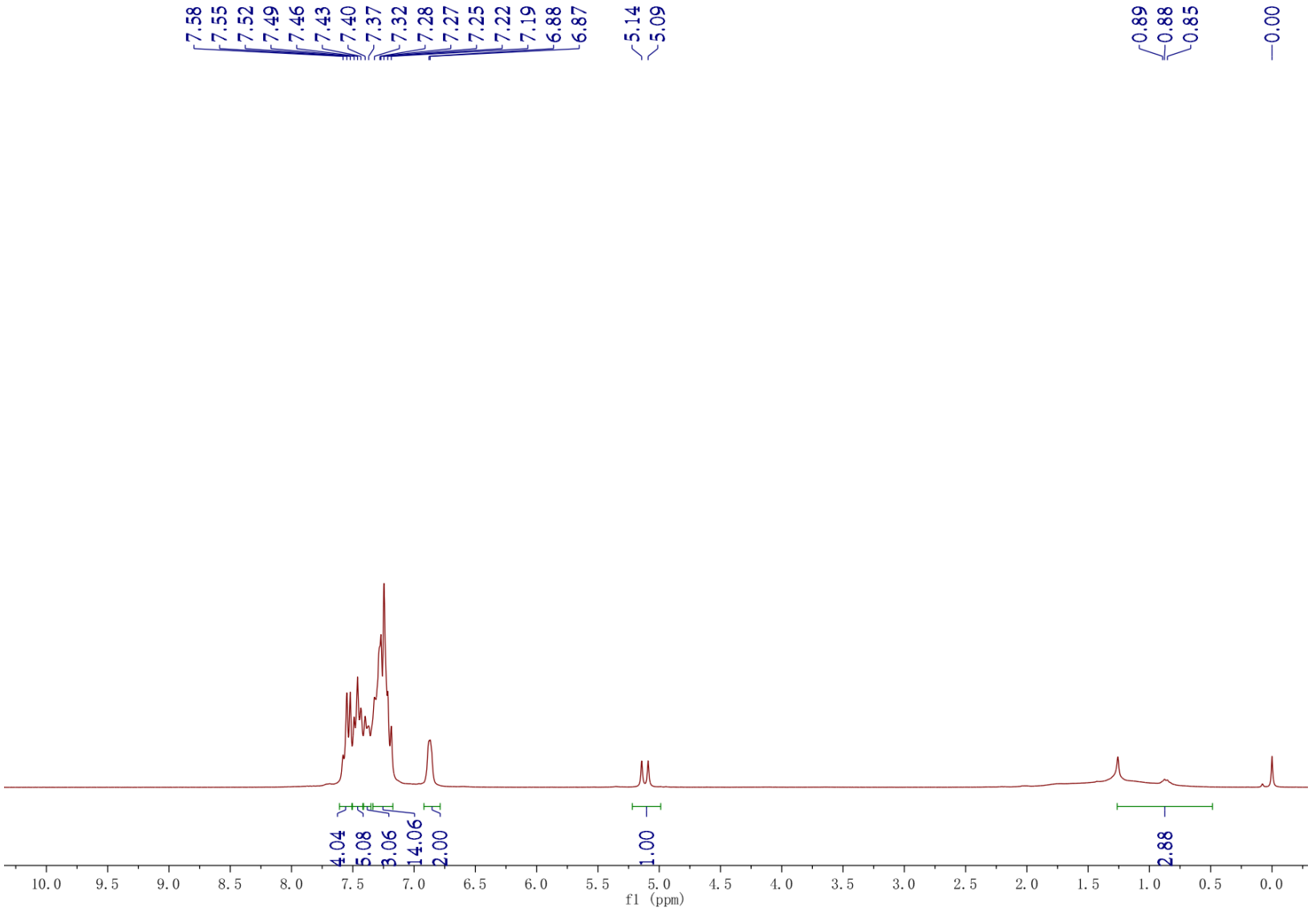
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3i**



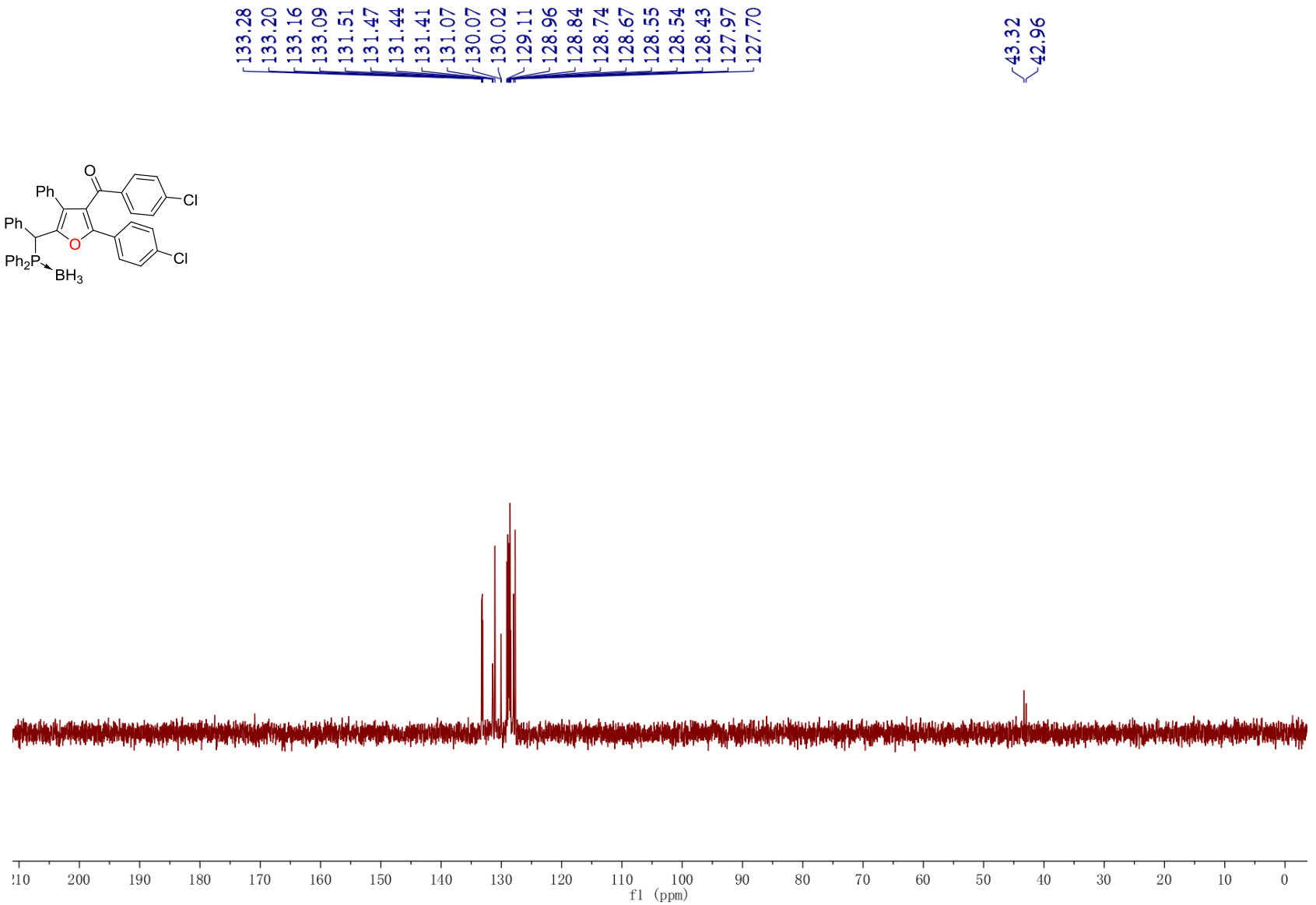
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3j**



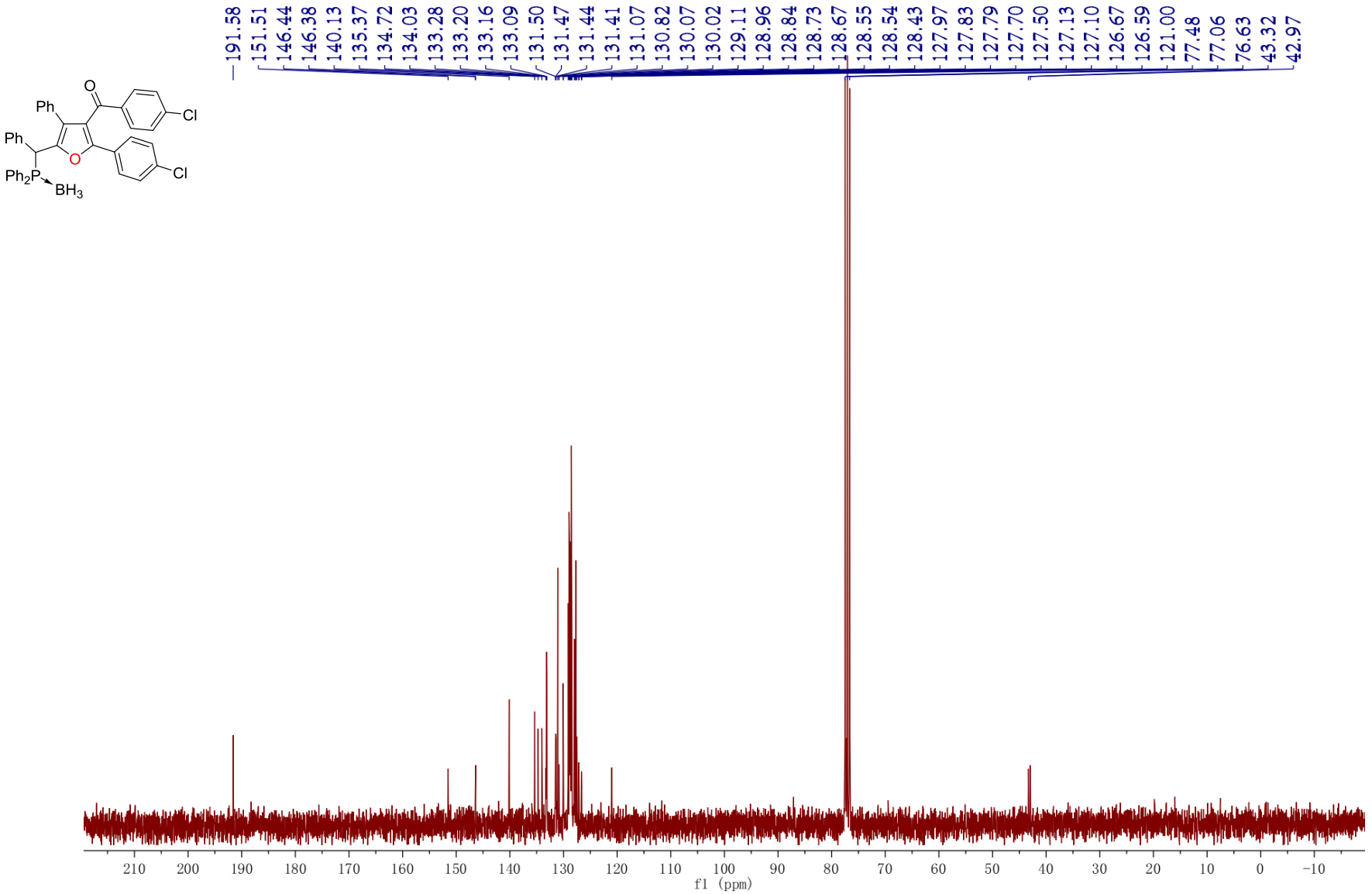
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3j**



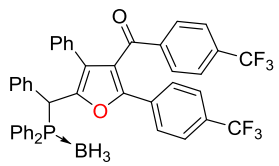
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3j**



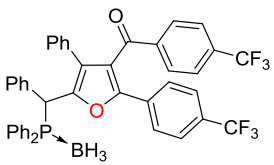
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3j**



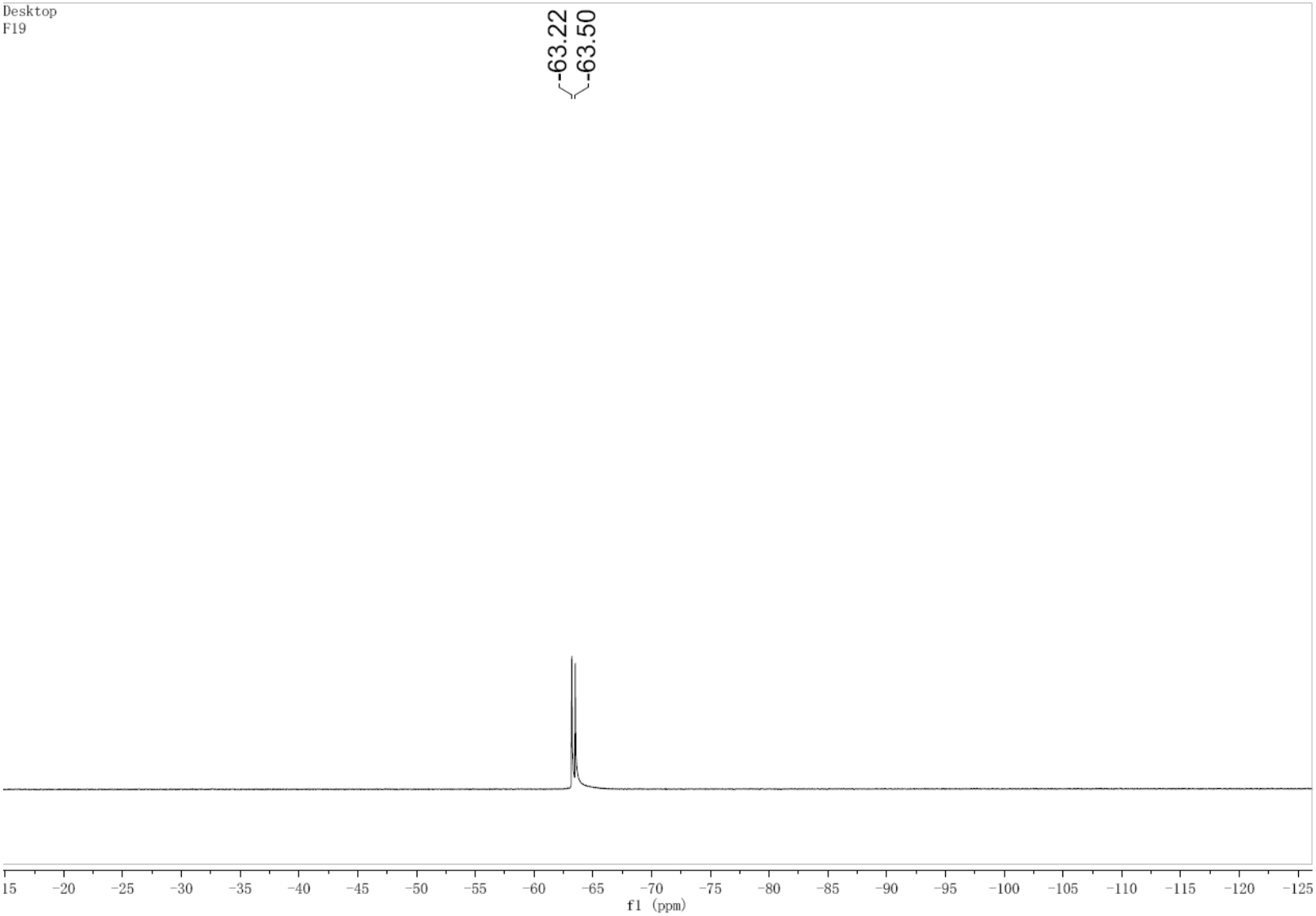
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3j**



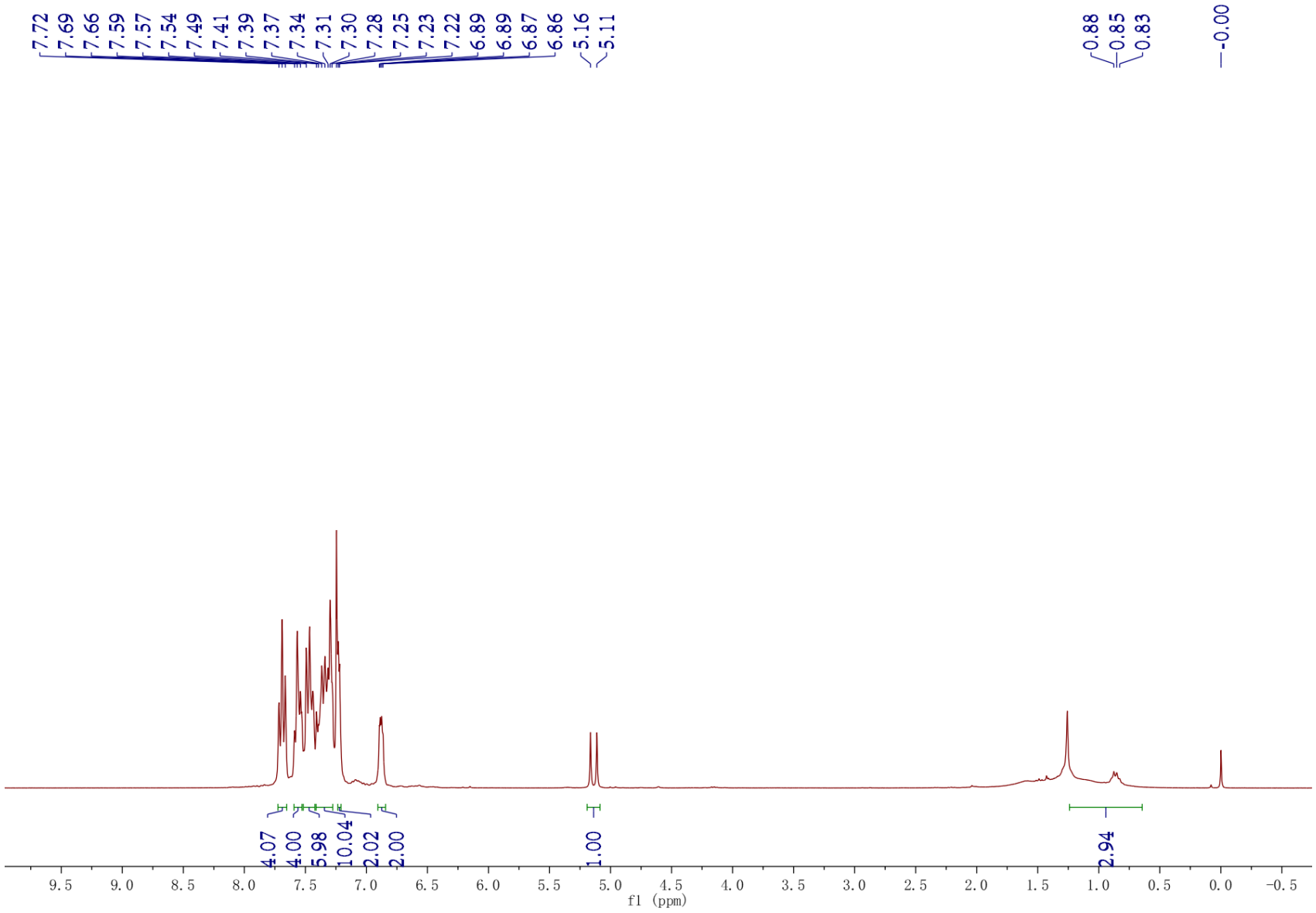
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3k**



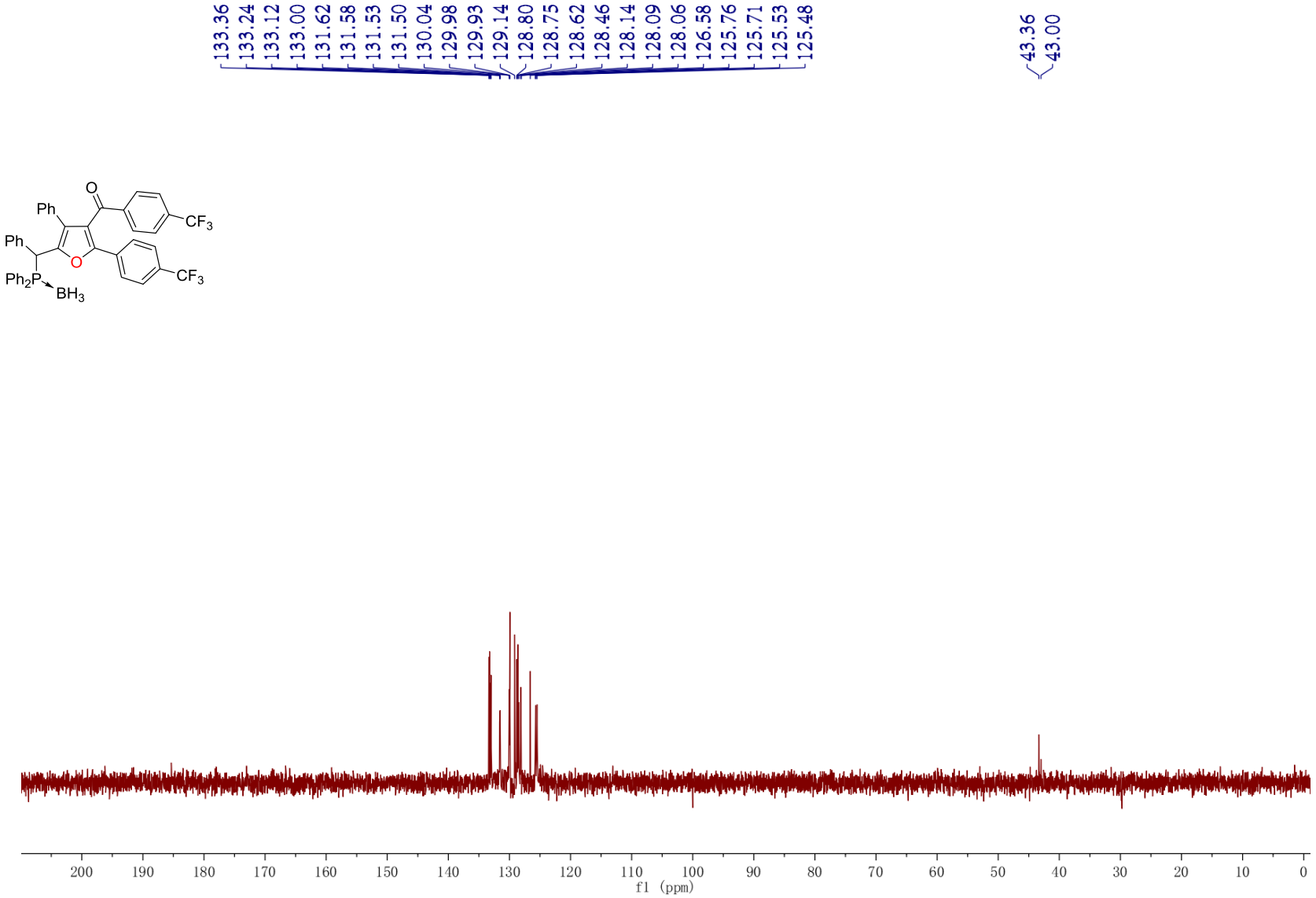
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3k**



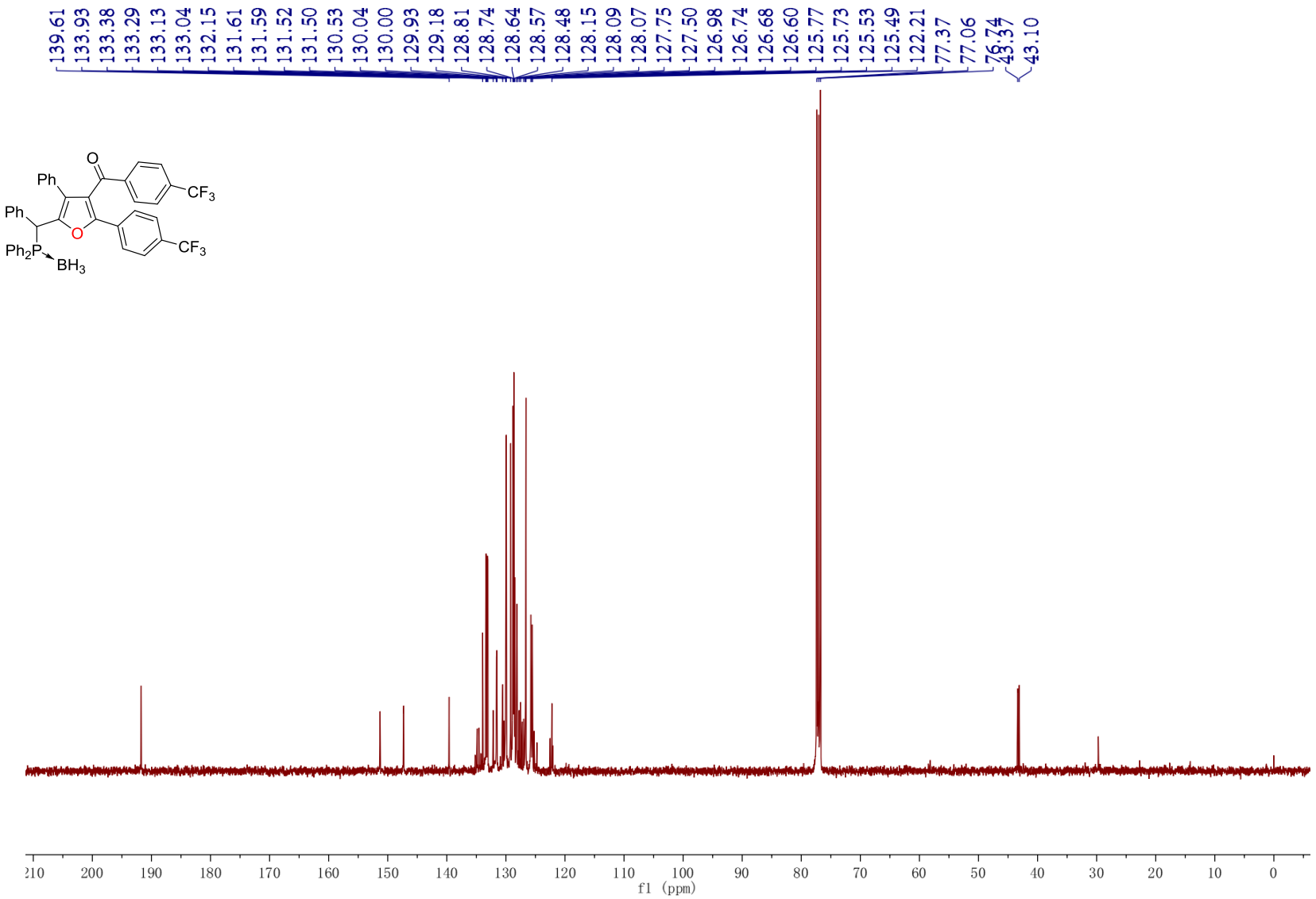
^{19}F NMR ($CDCl_3$, 282 MHz) of compound **3k**



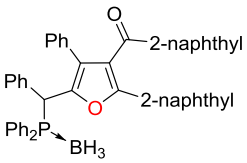
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3k**



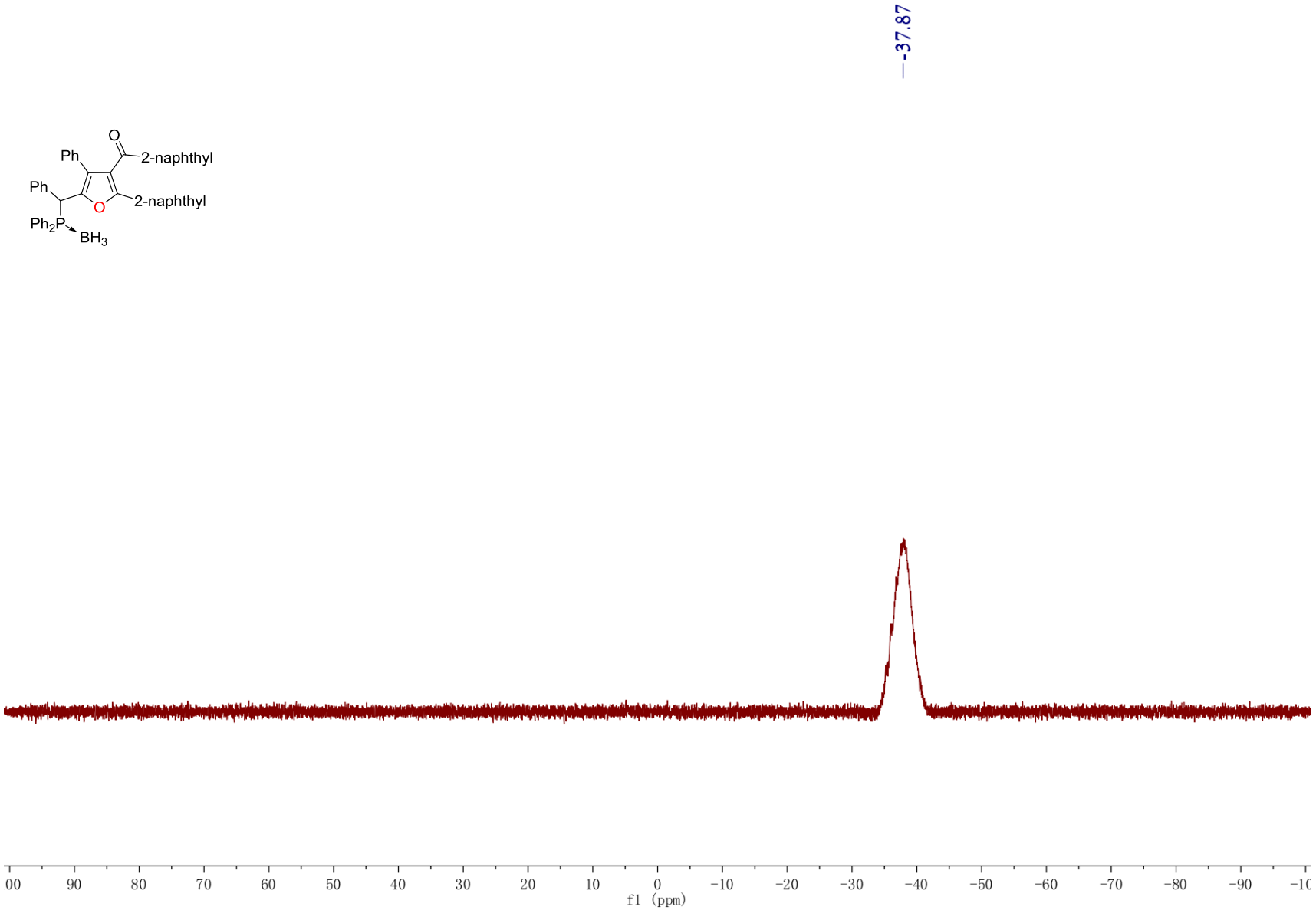
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3k**



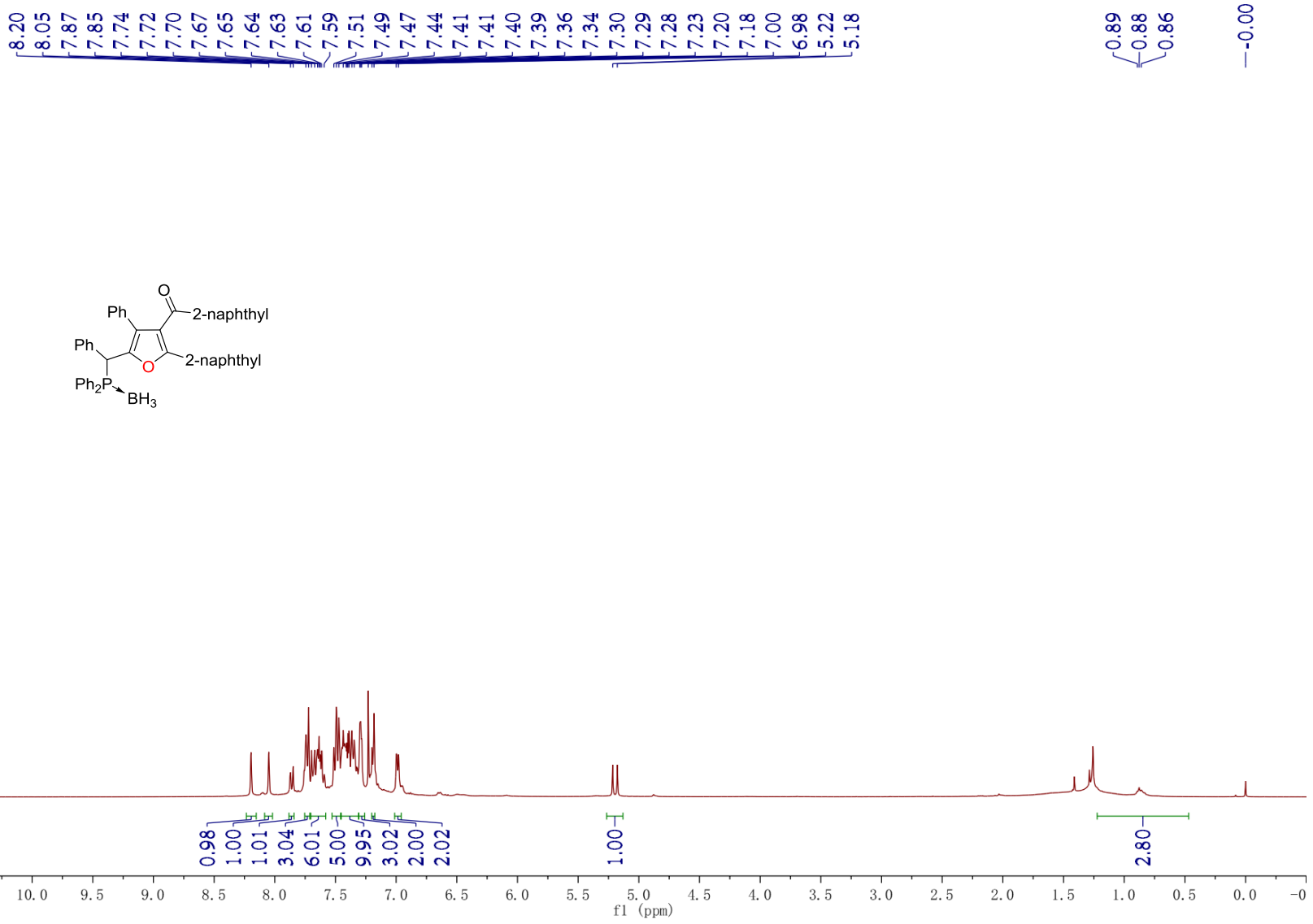
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3k**



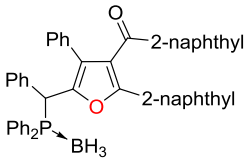
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3l**

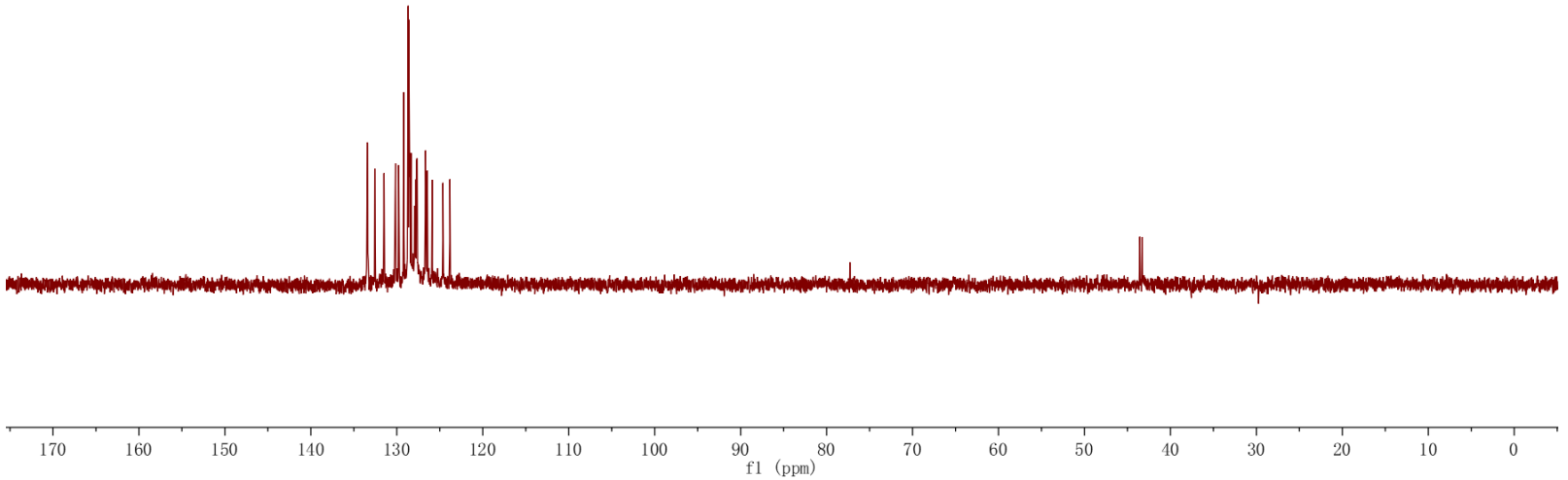


^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3l**

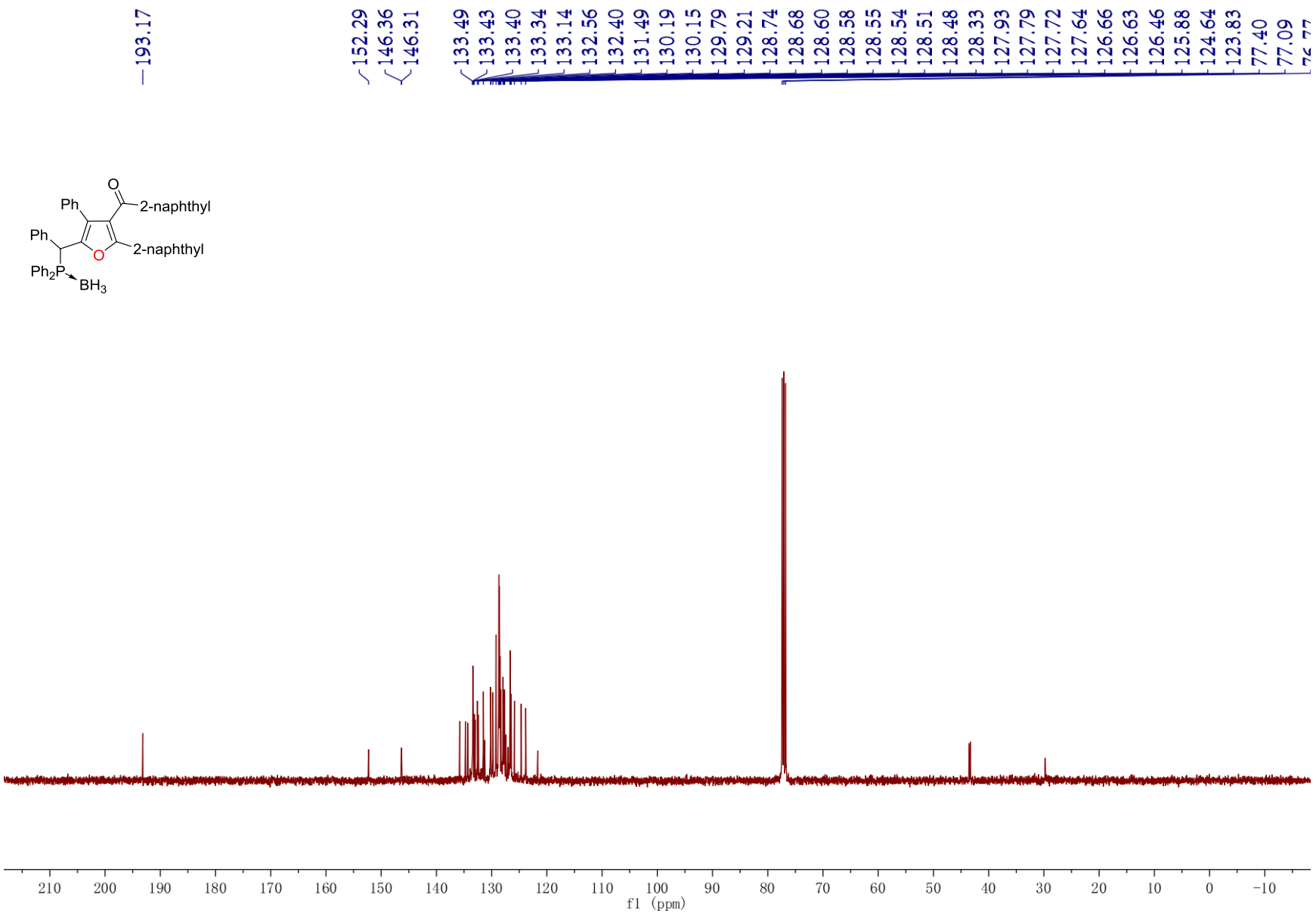


^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3l**

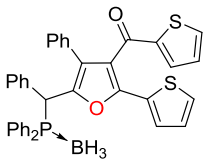


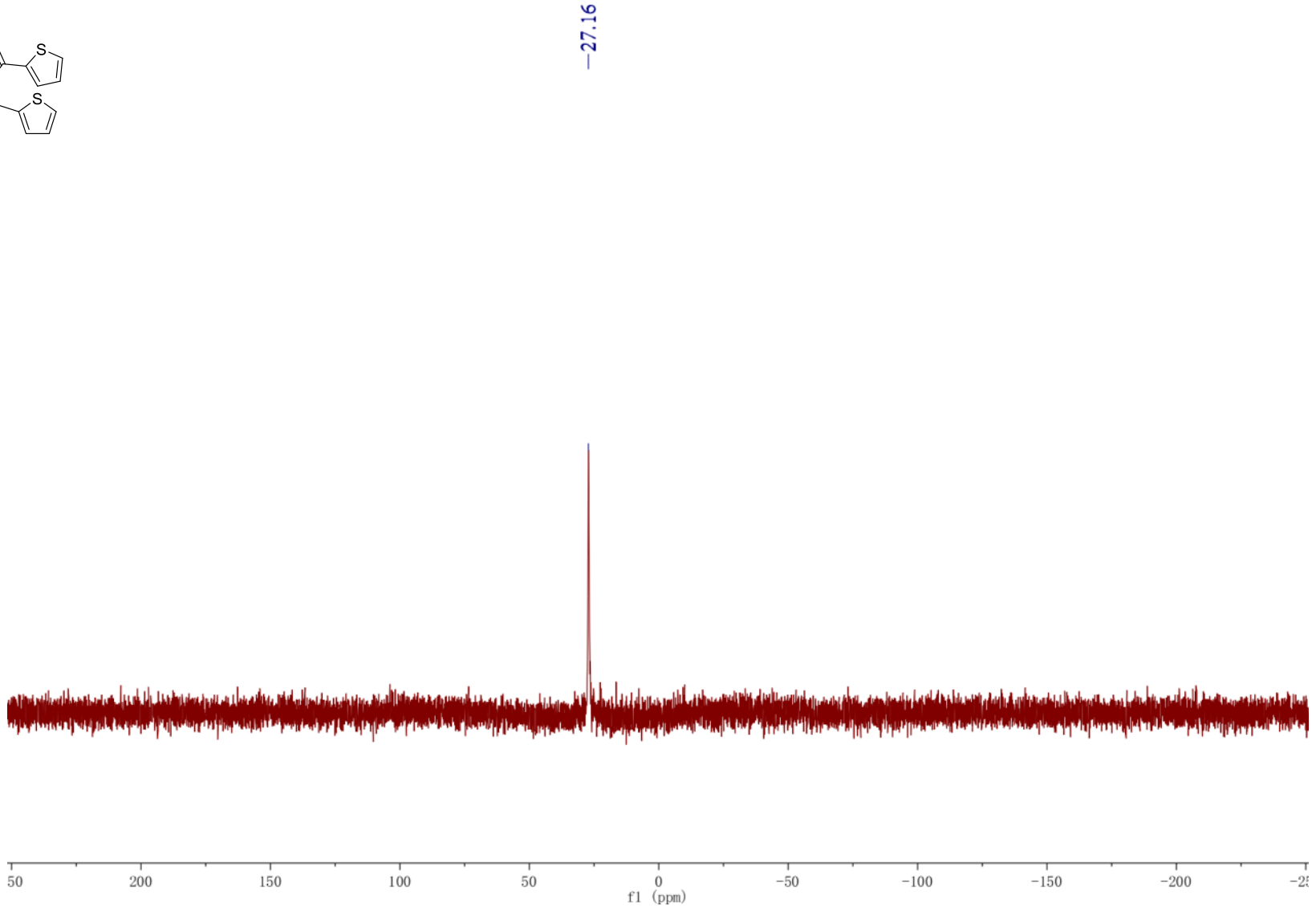


Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3l**

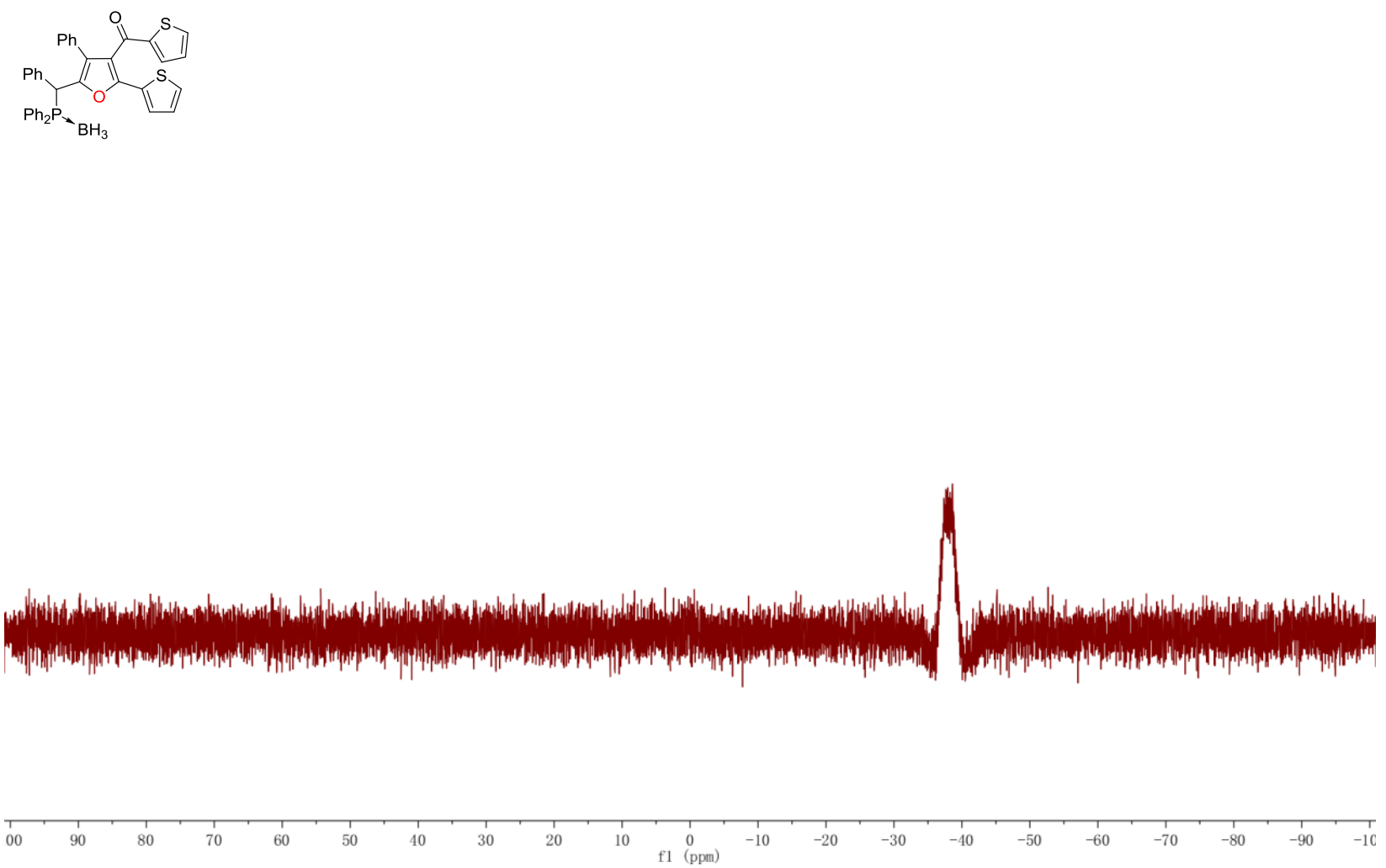


^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3l**

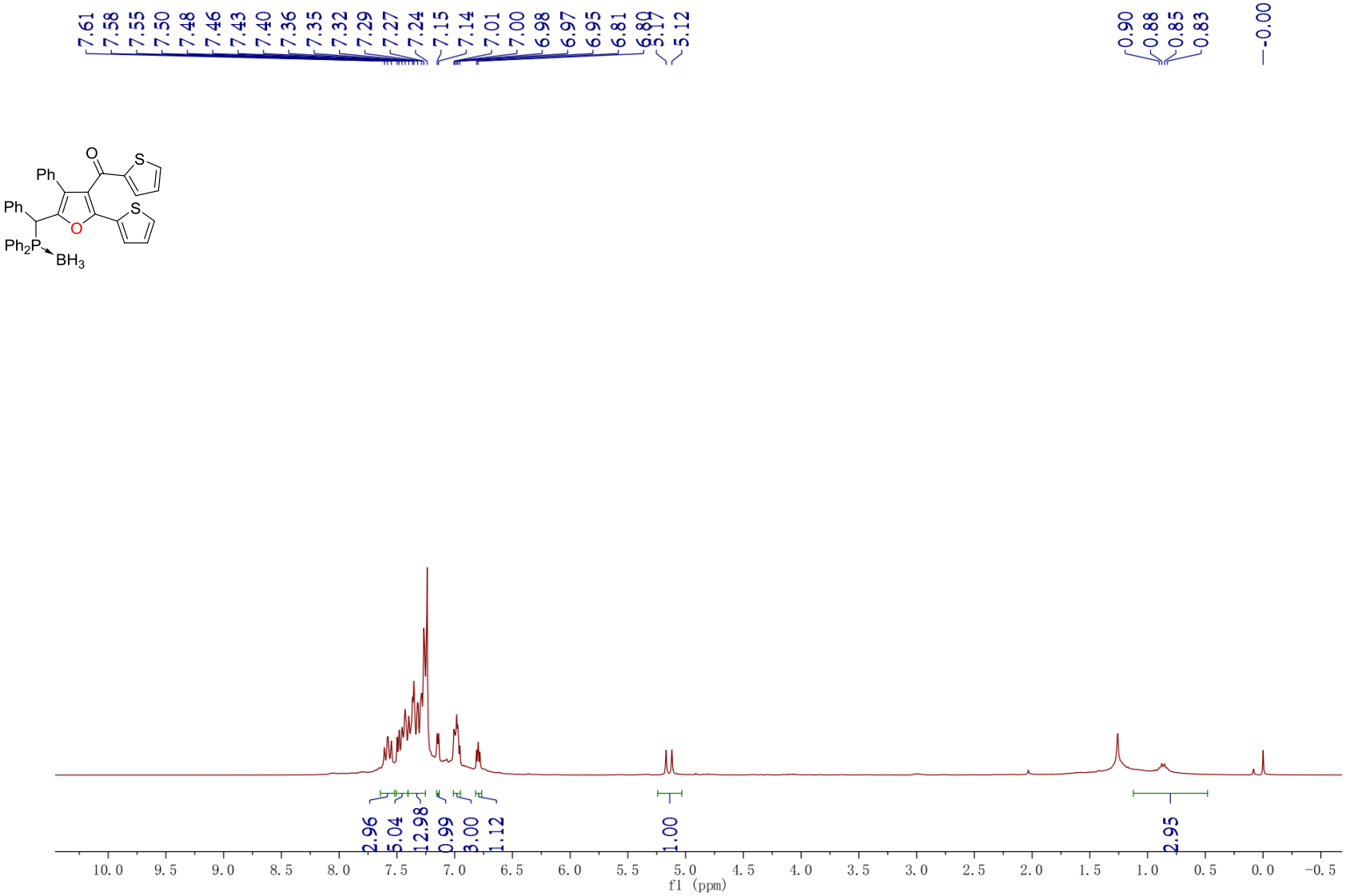




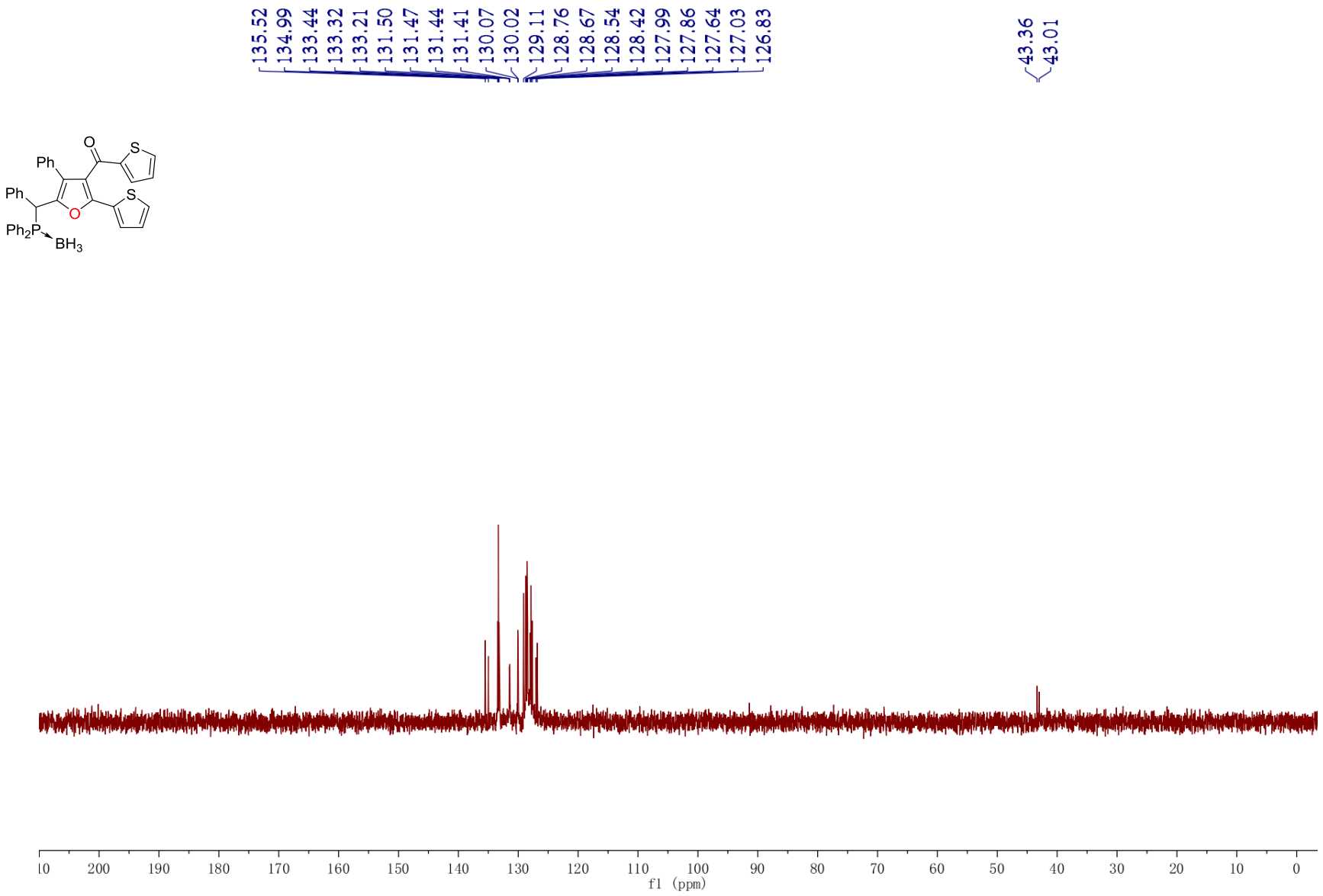
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3m**



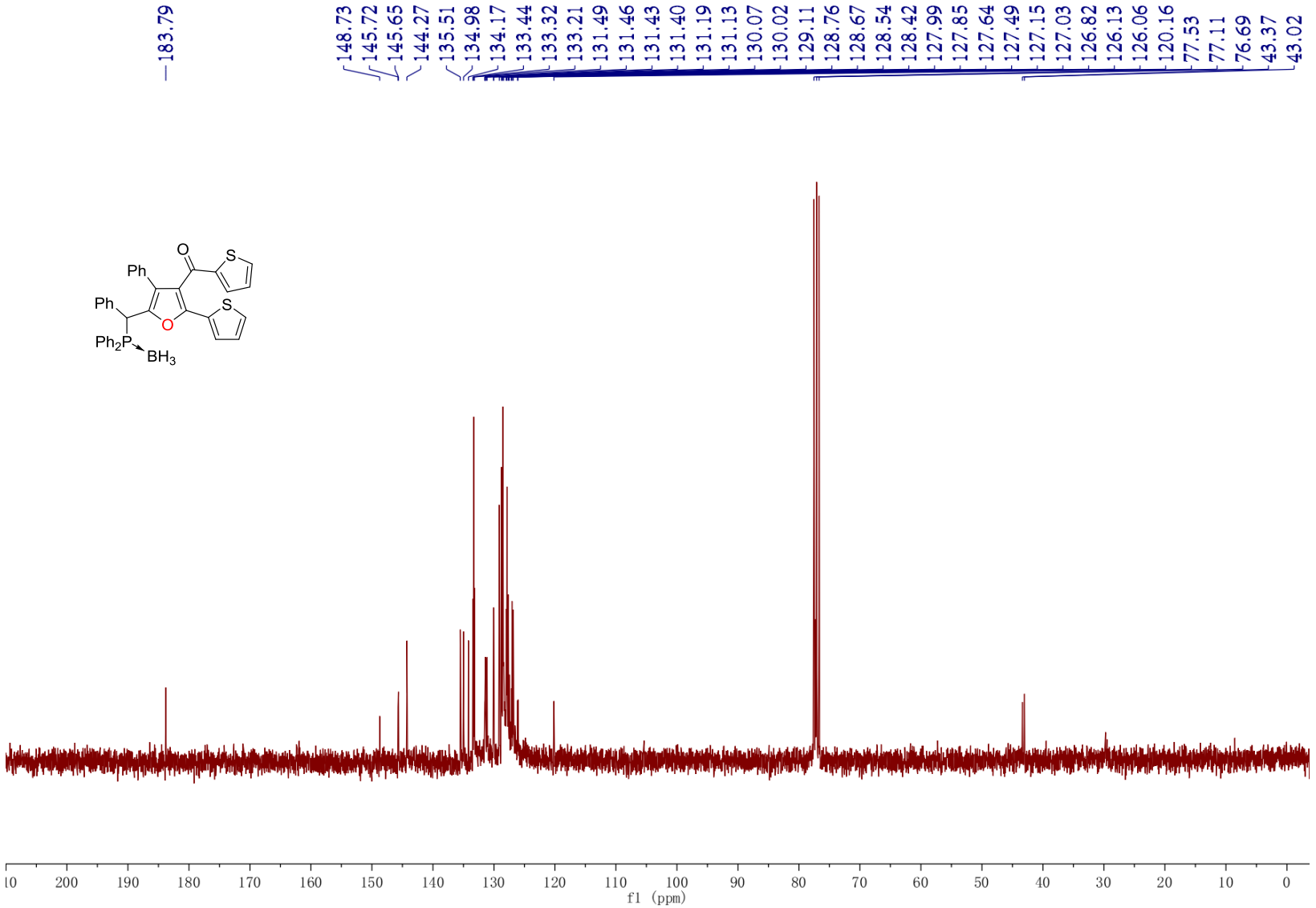
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3m**



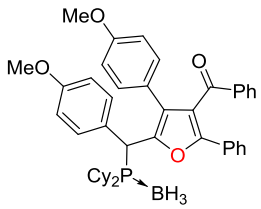
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3m**



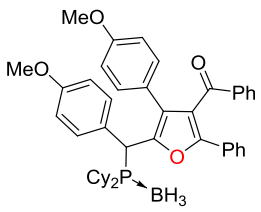
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3m**



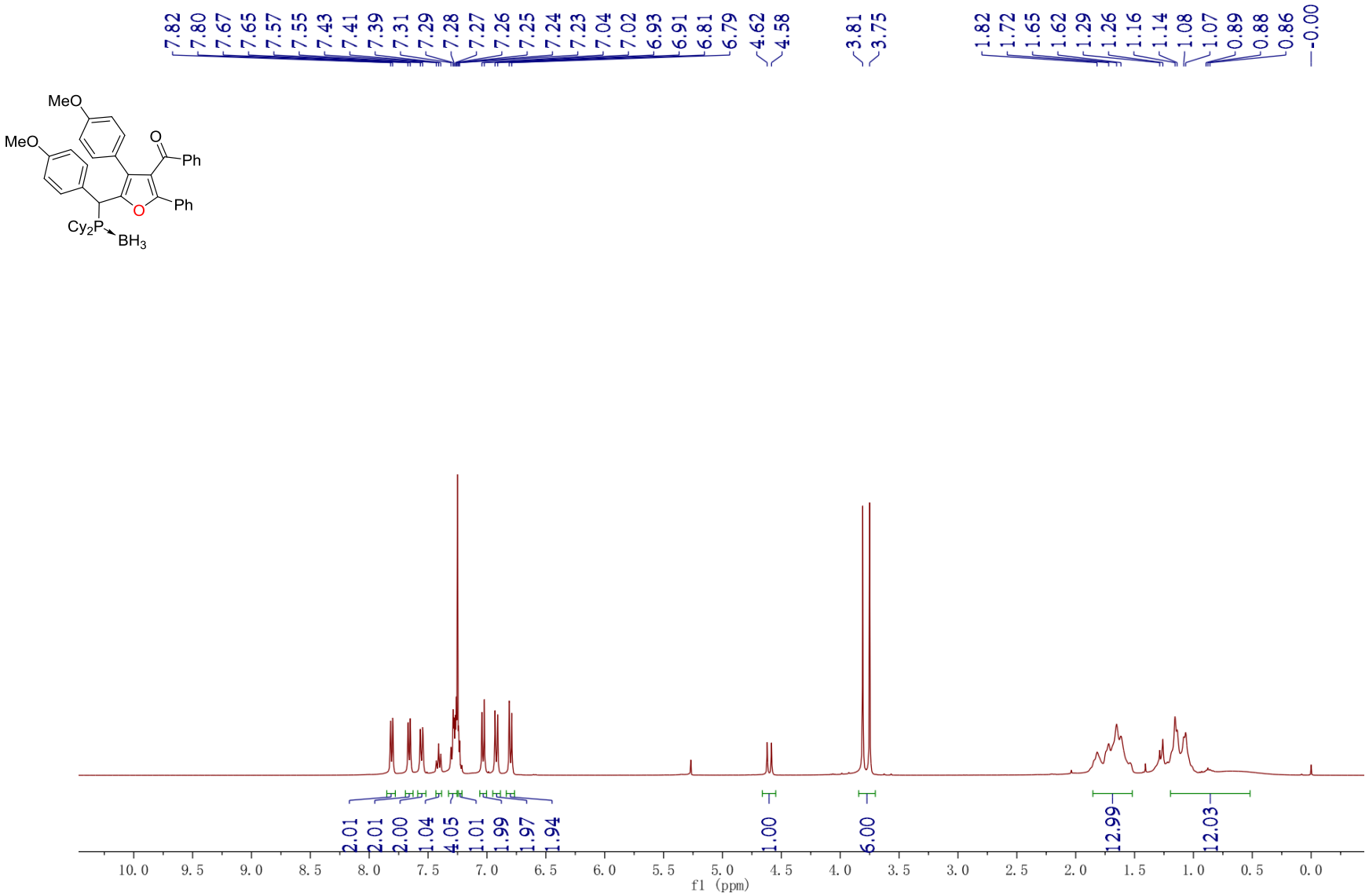
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3m**



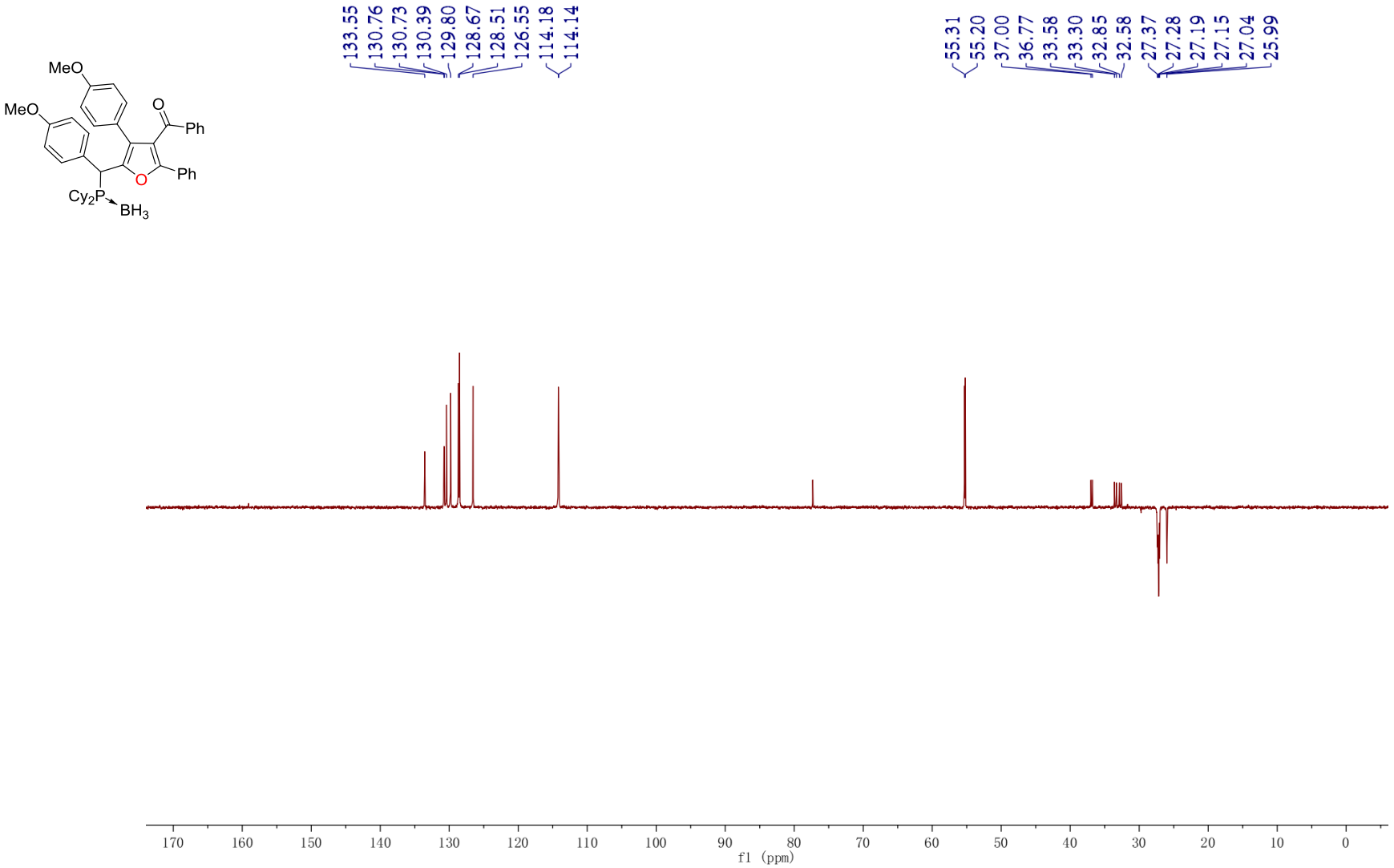
^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz) of compound **3n**



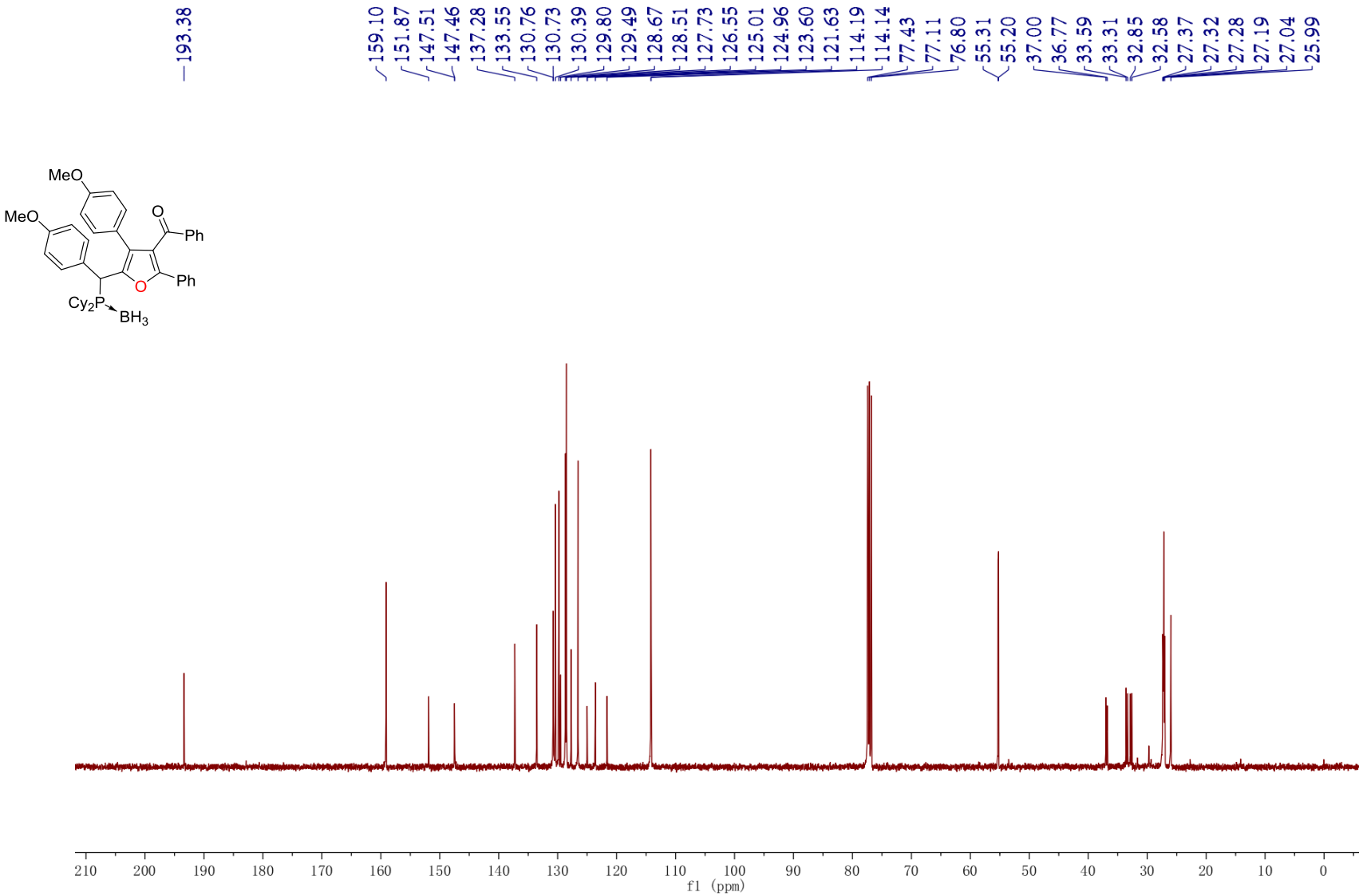
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3n**



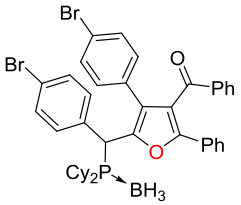
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3n**



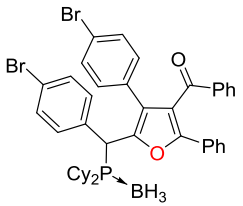
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3n**



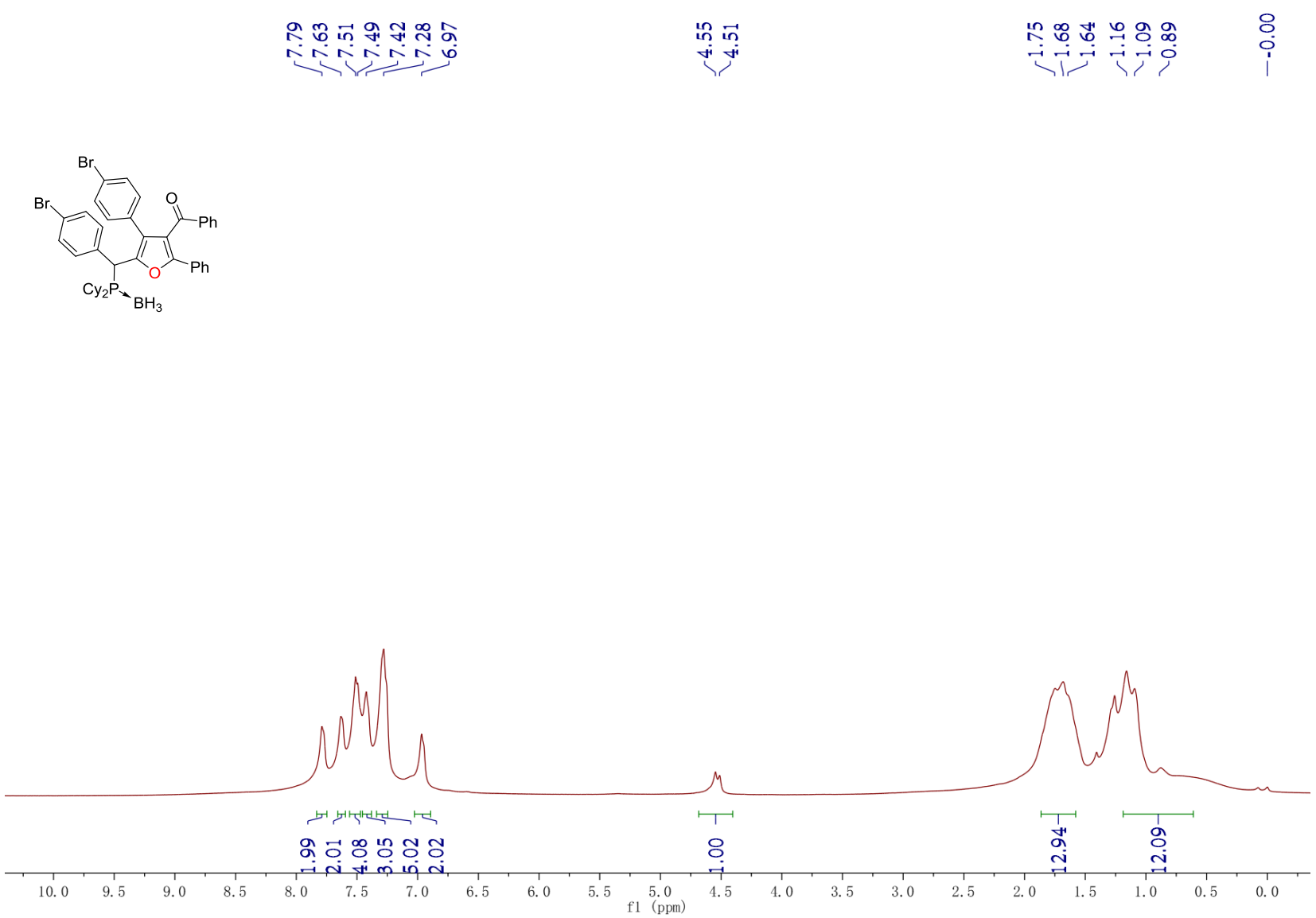
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3n**



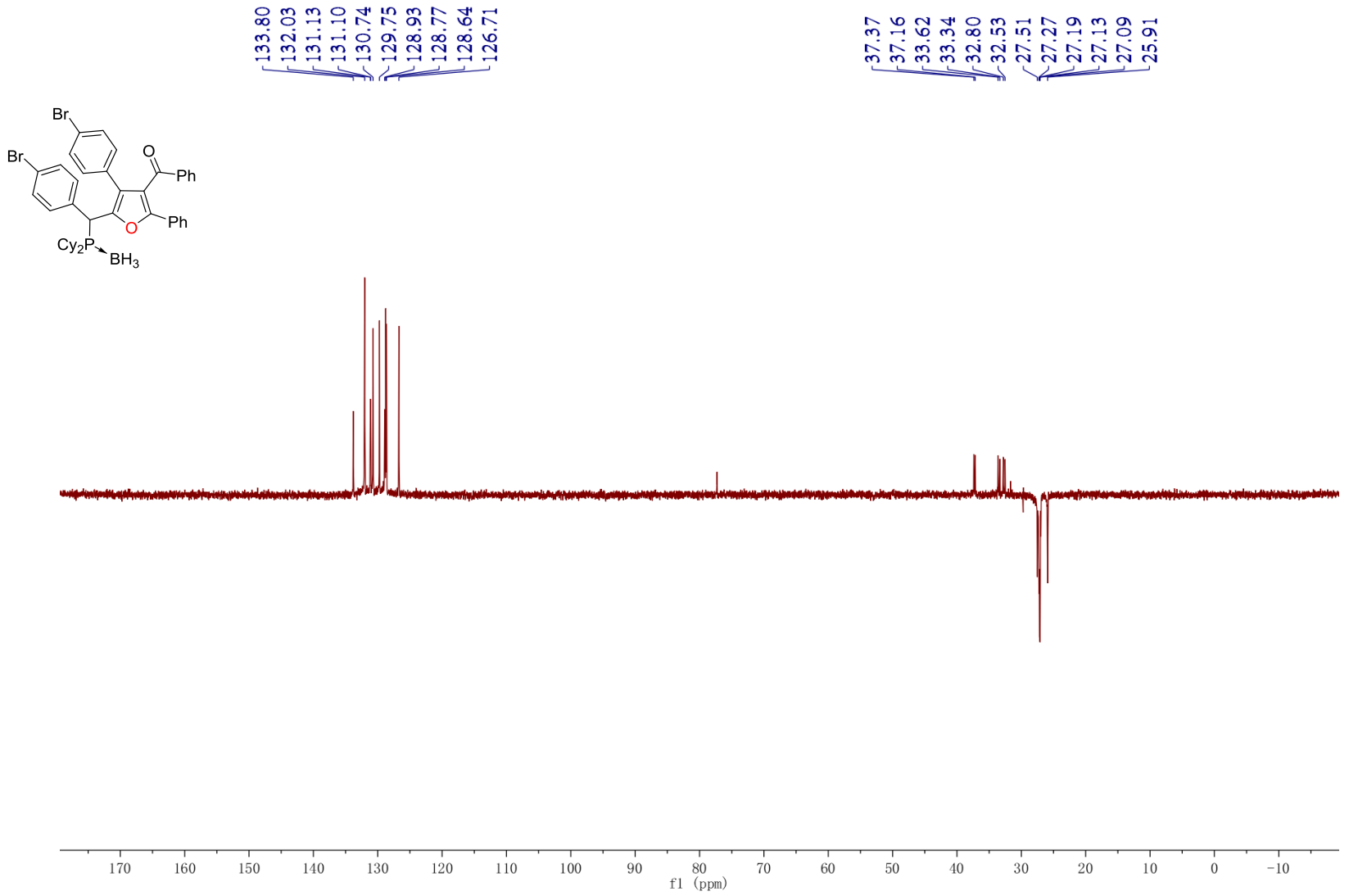
^{31}P {^{1}H} NMR ($CDCl_3$, 162 MHz) of compound **3o**



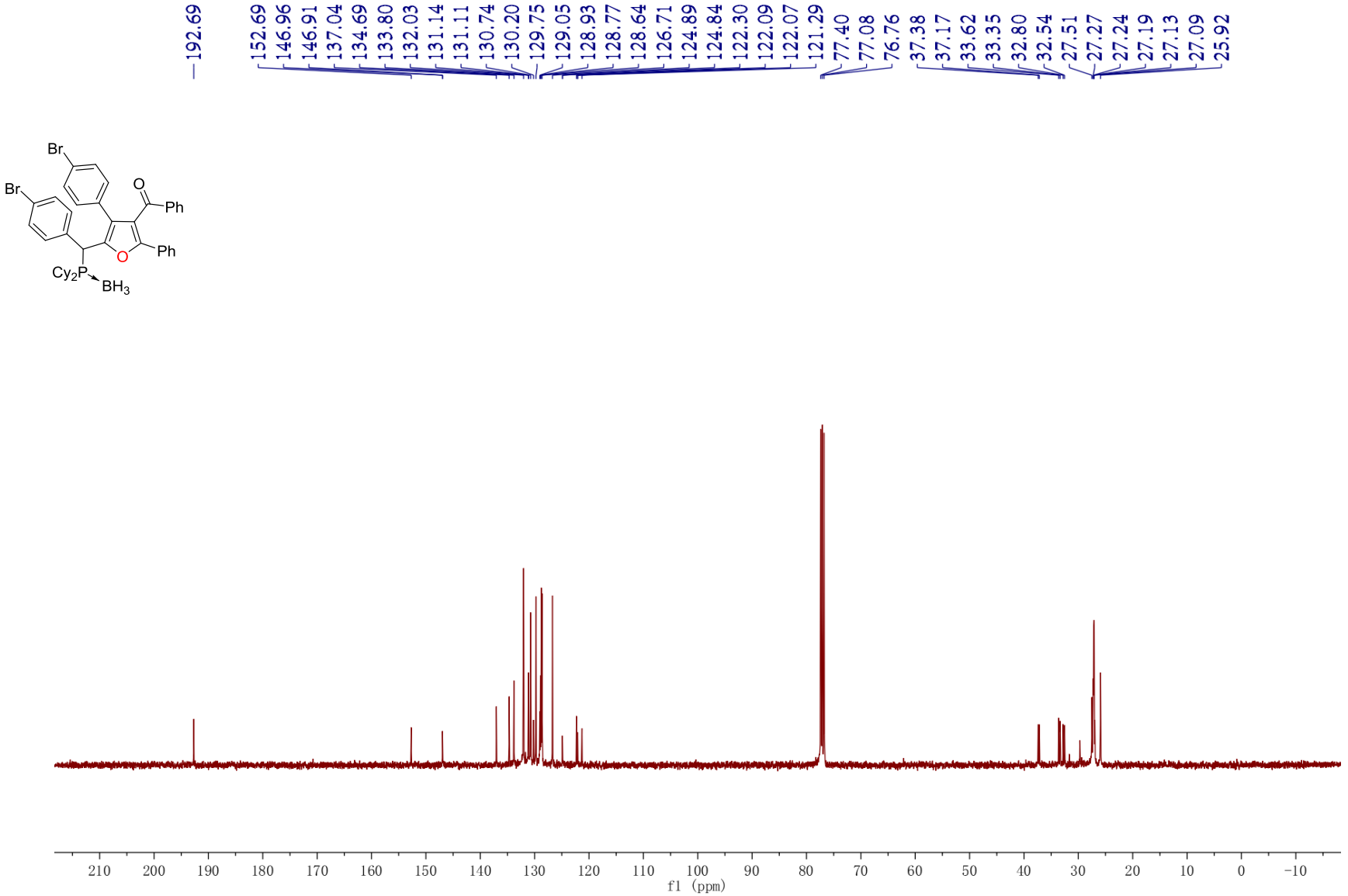
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3o**



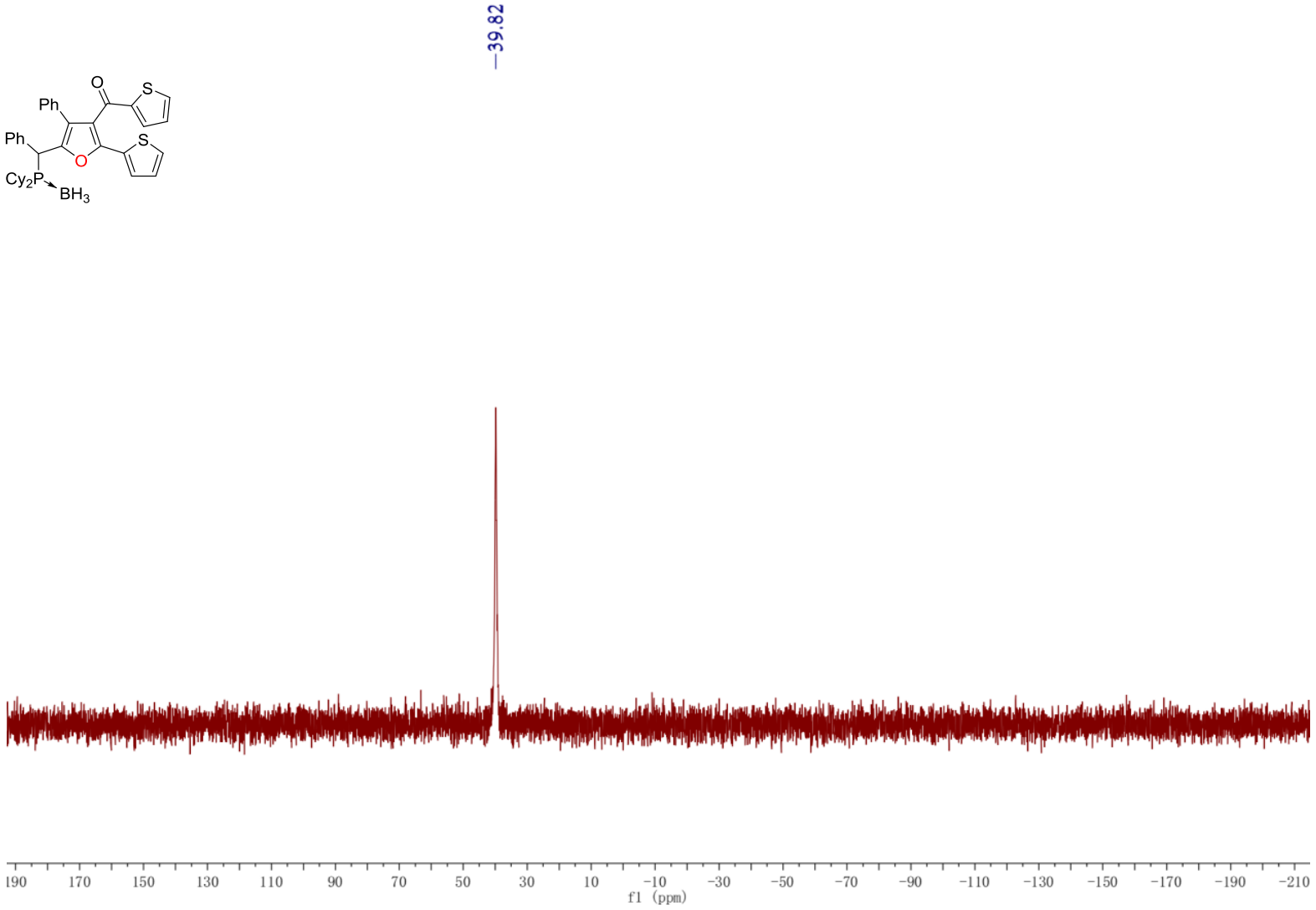
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3o**



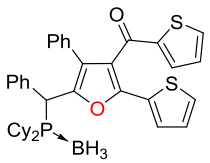
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3o**



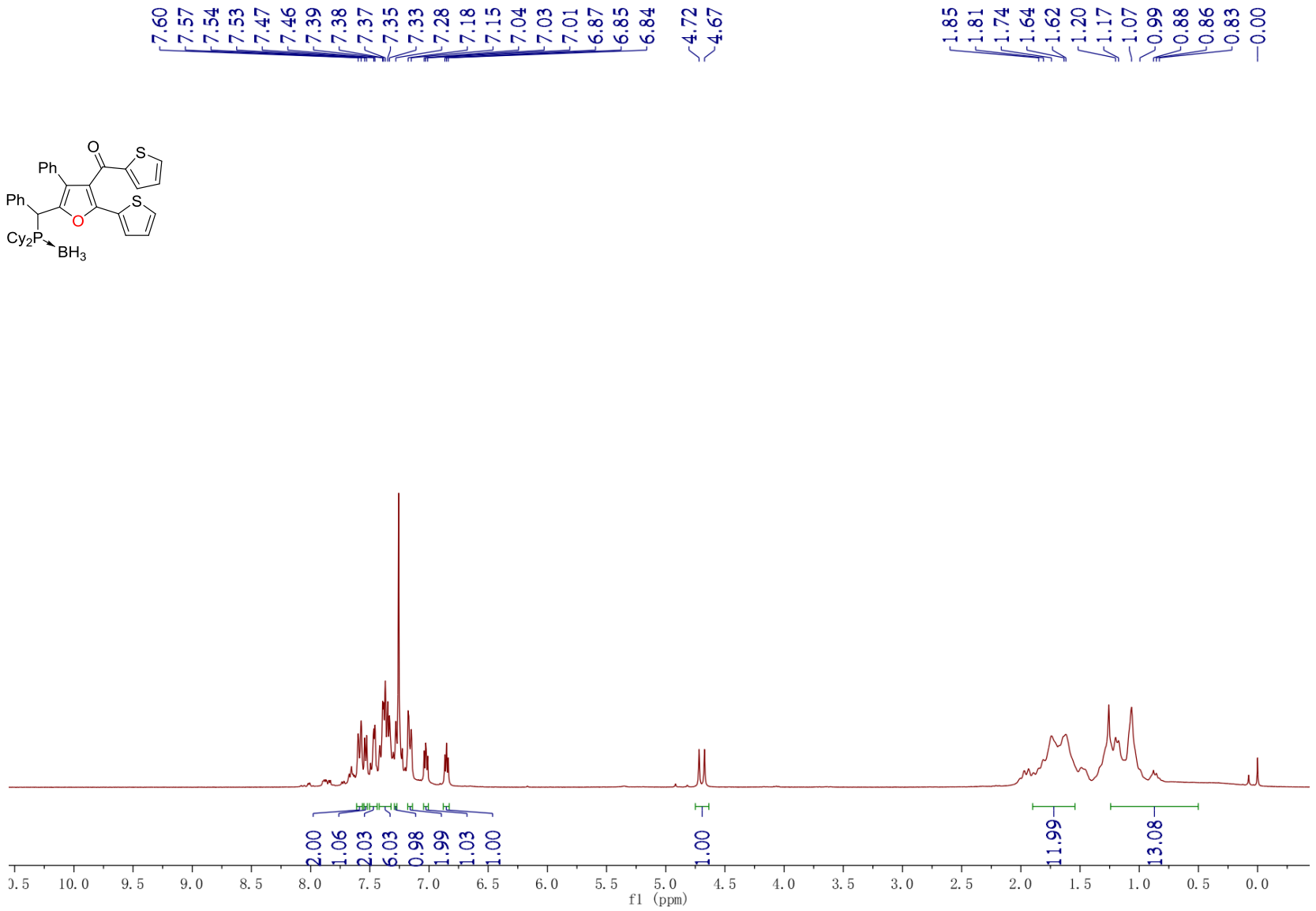
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3o**



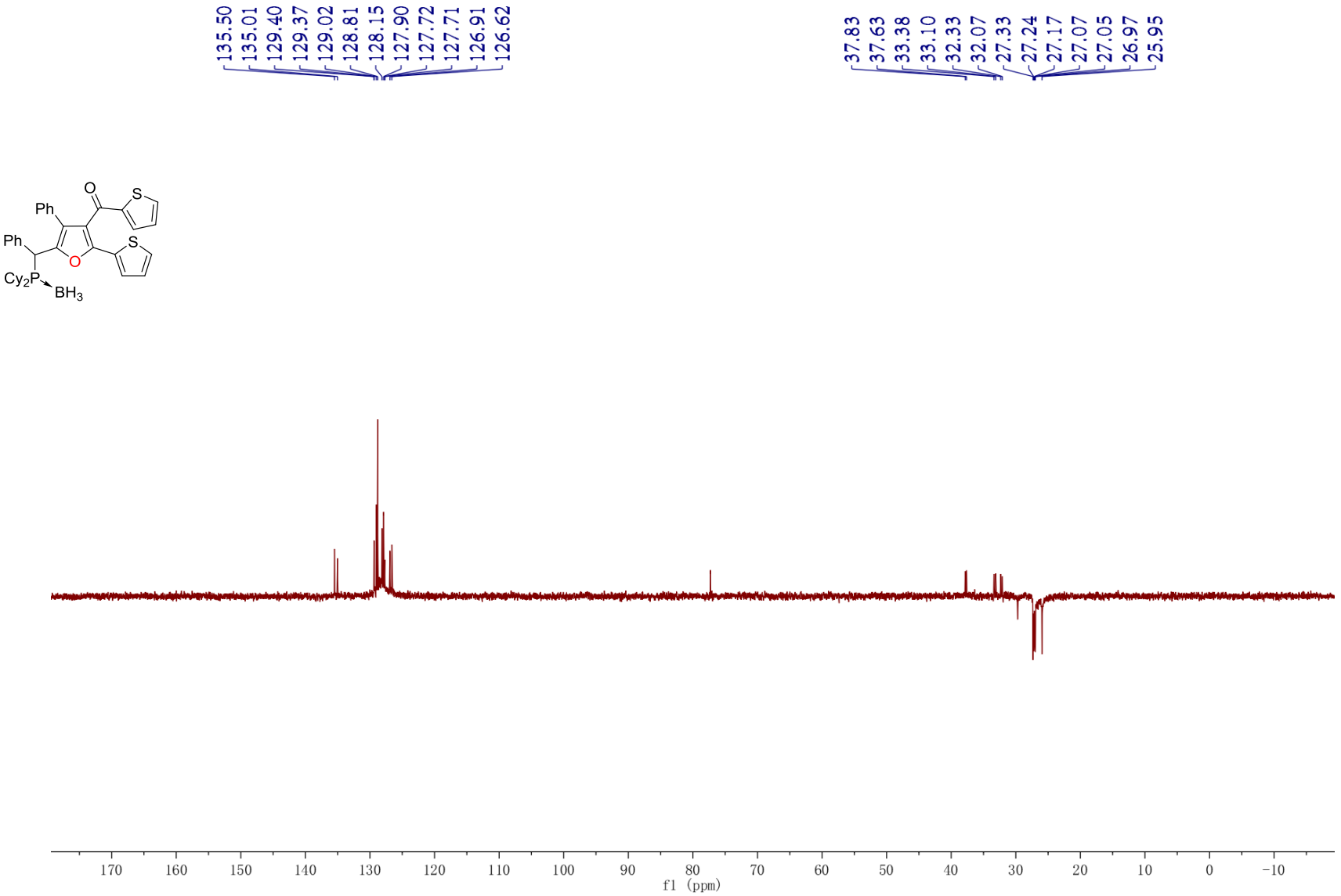
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3p**



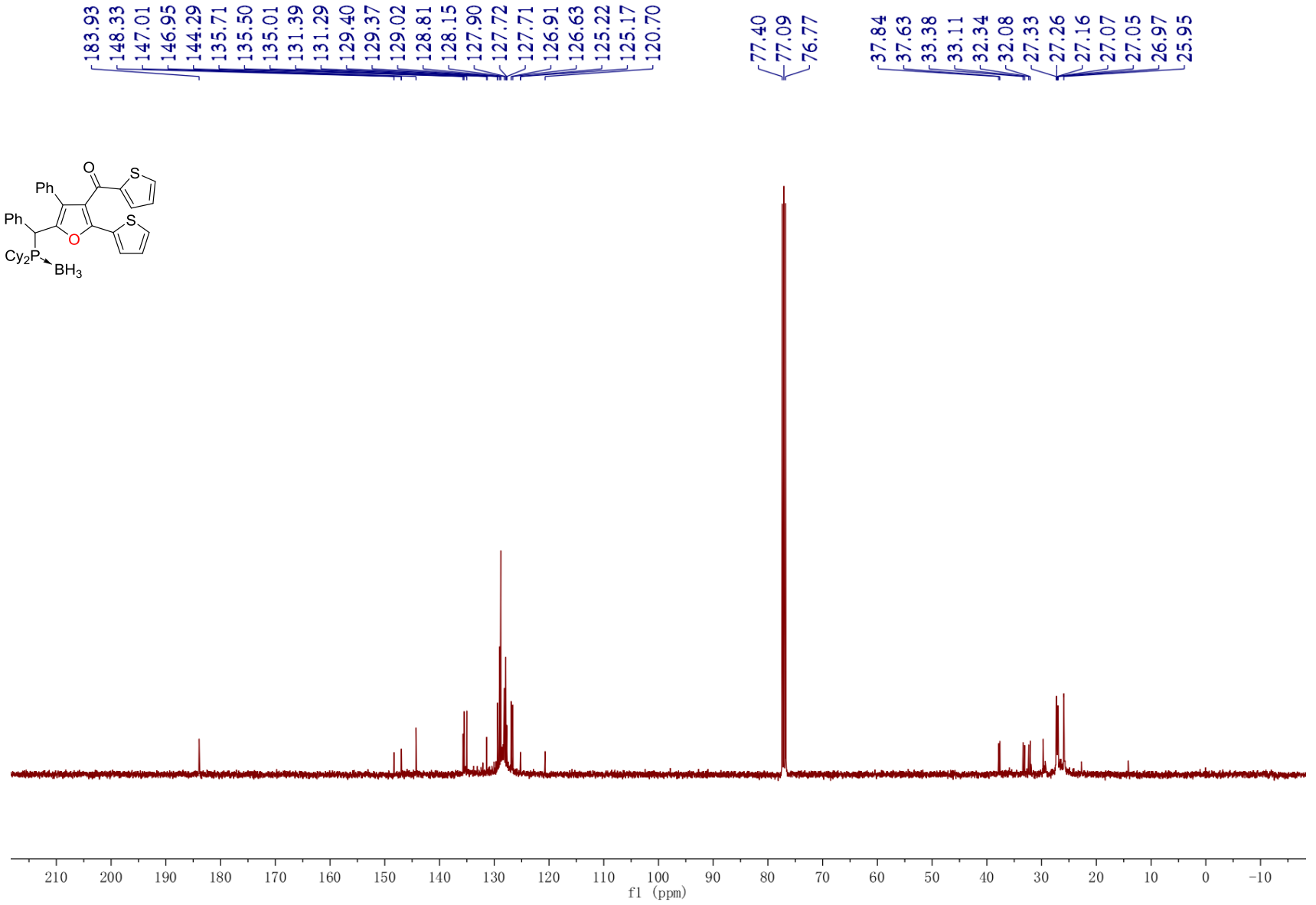
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **3p**



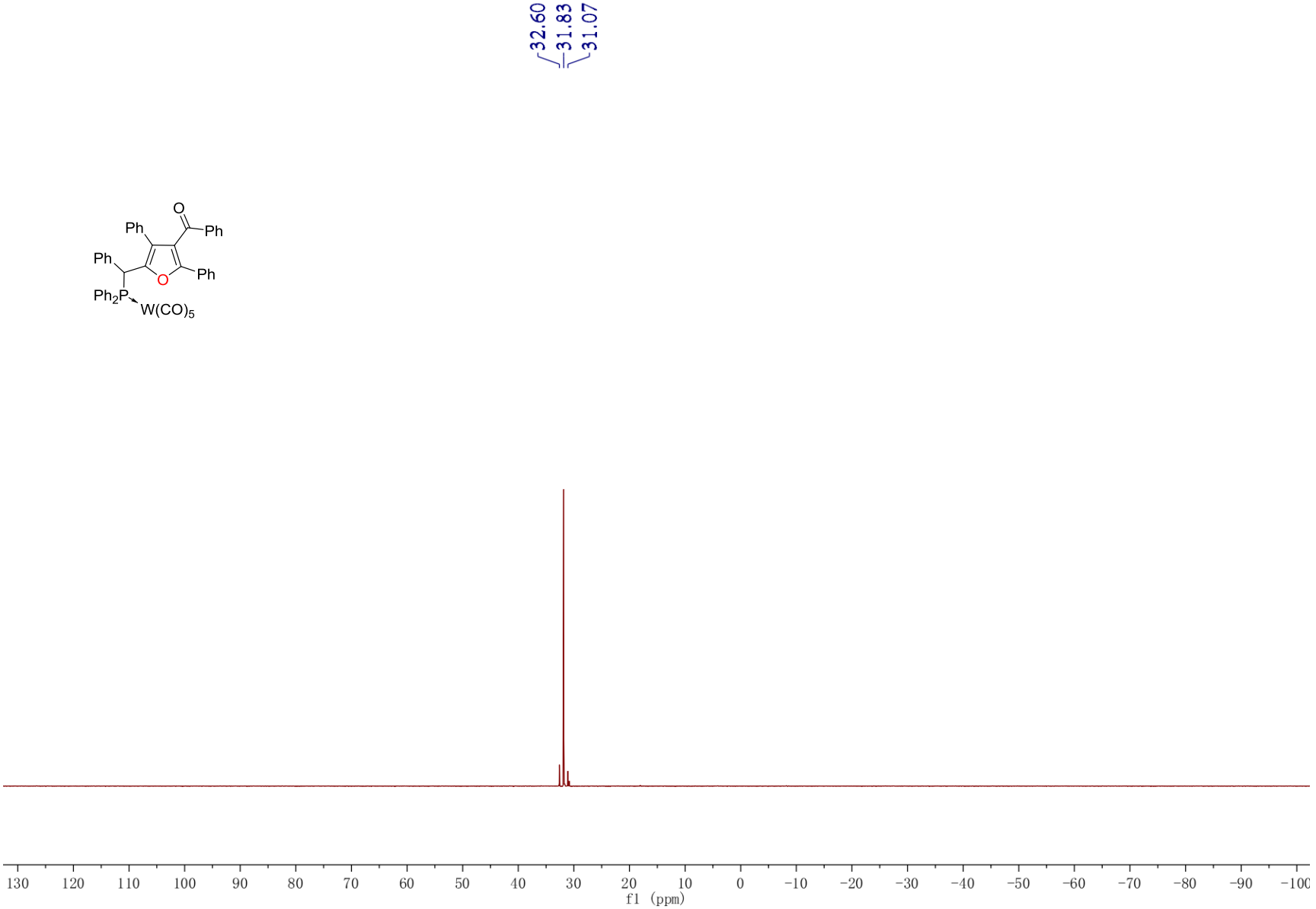
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **3p**



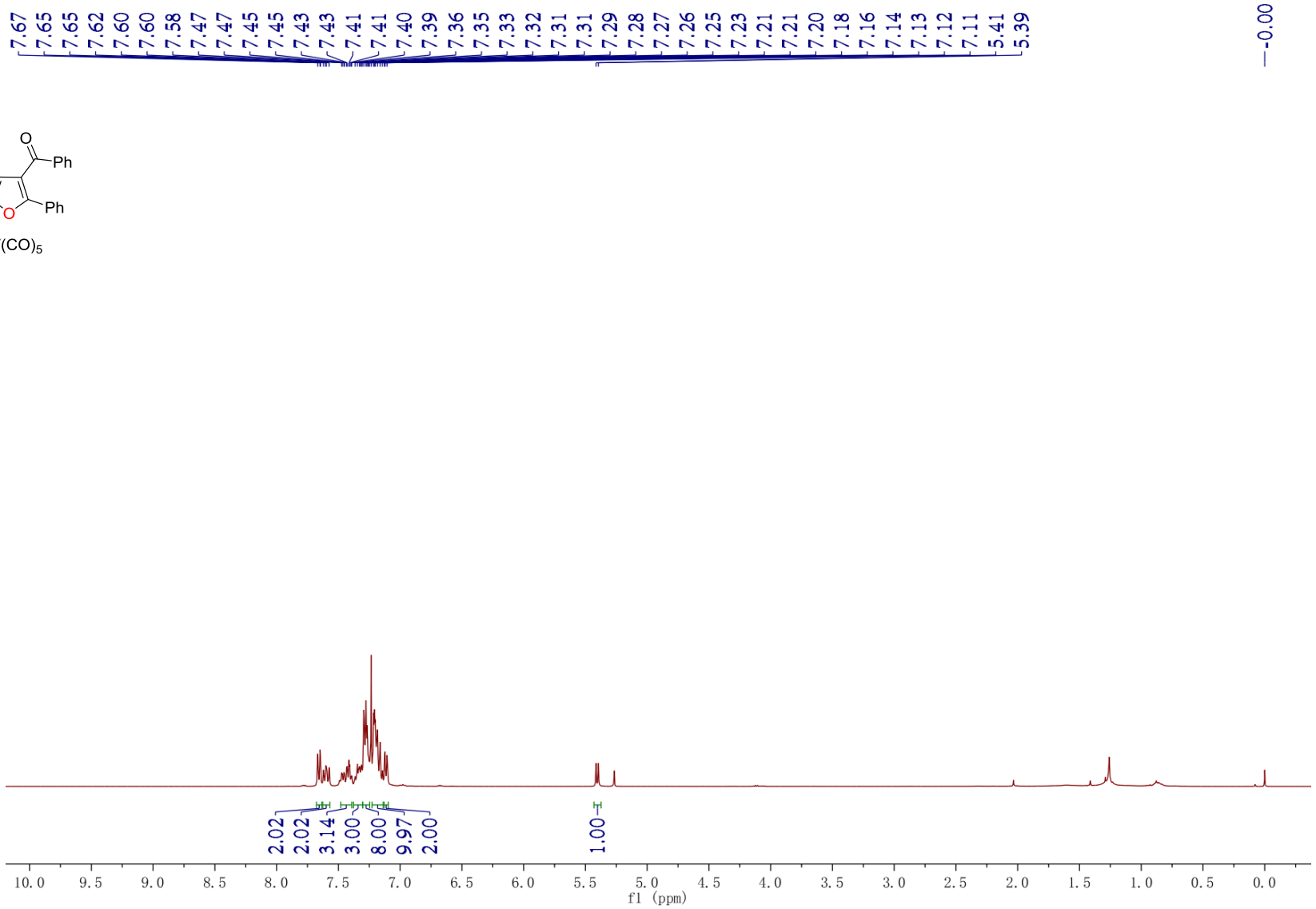
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3p**



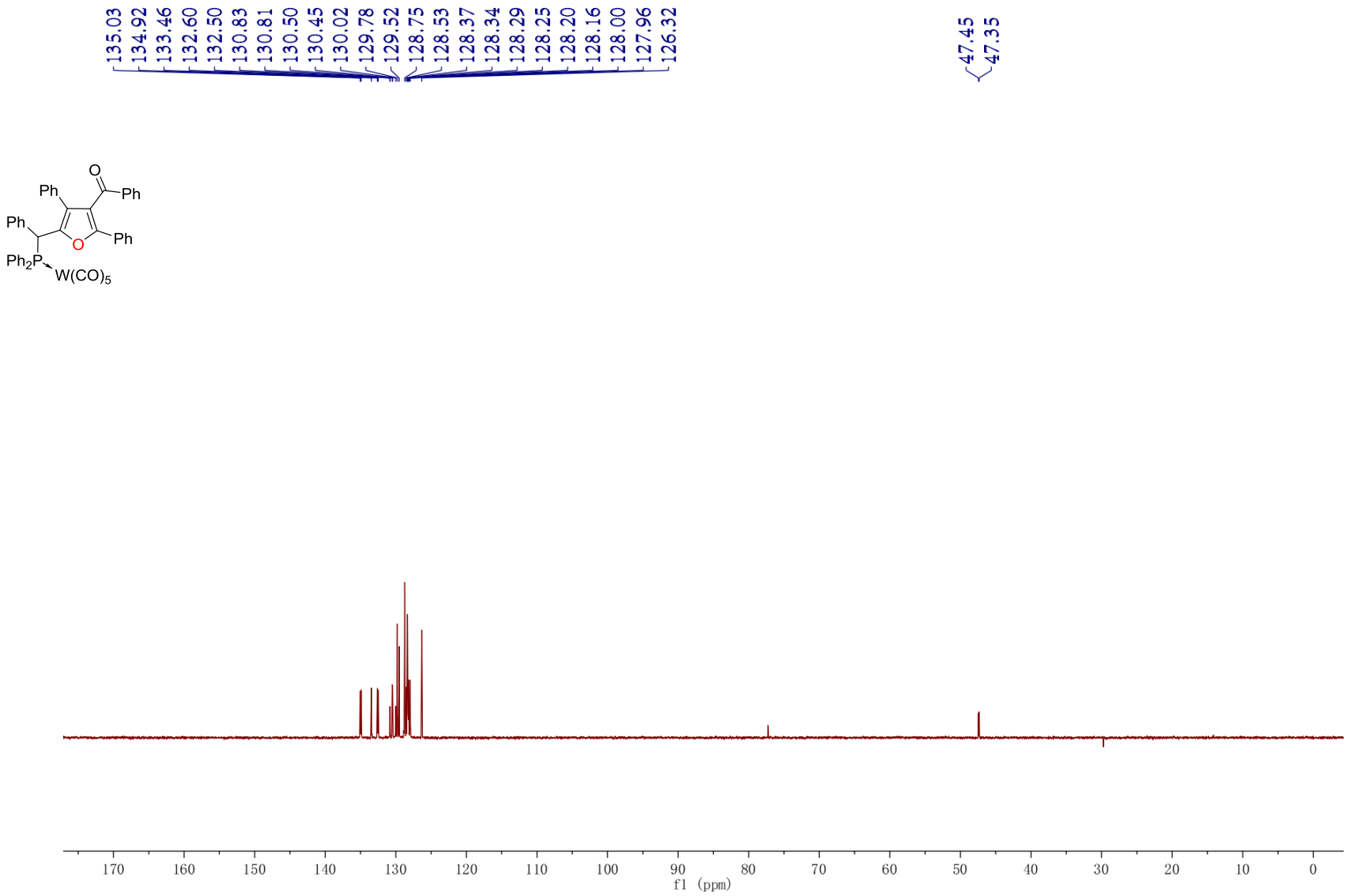
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3p**



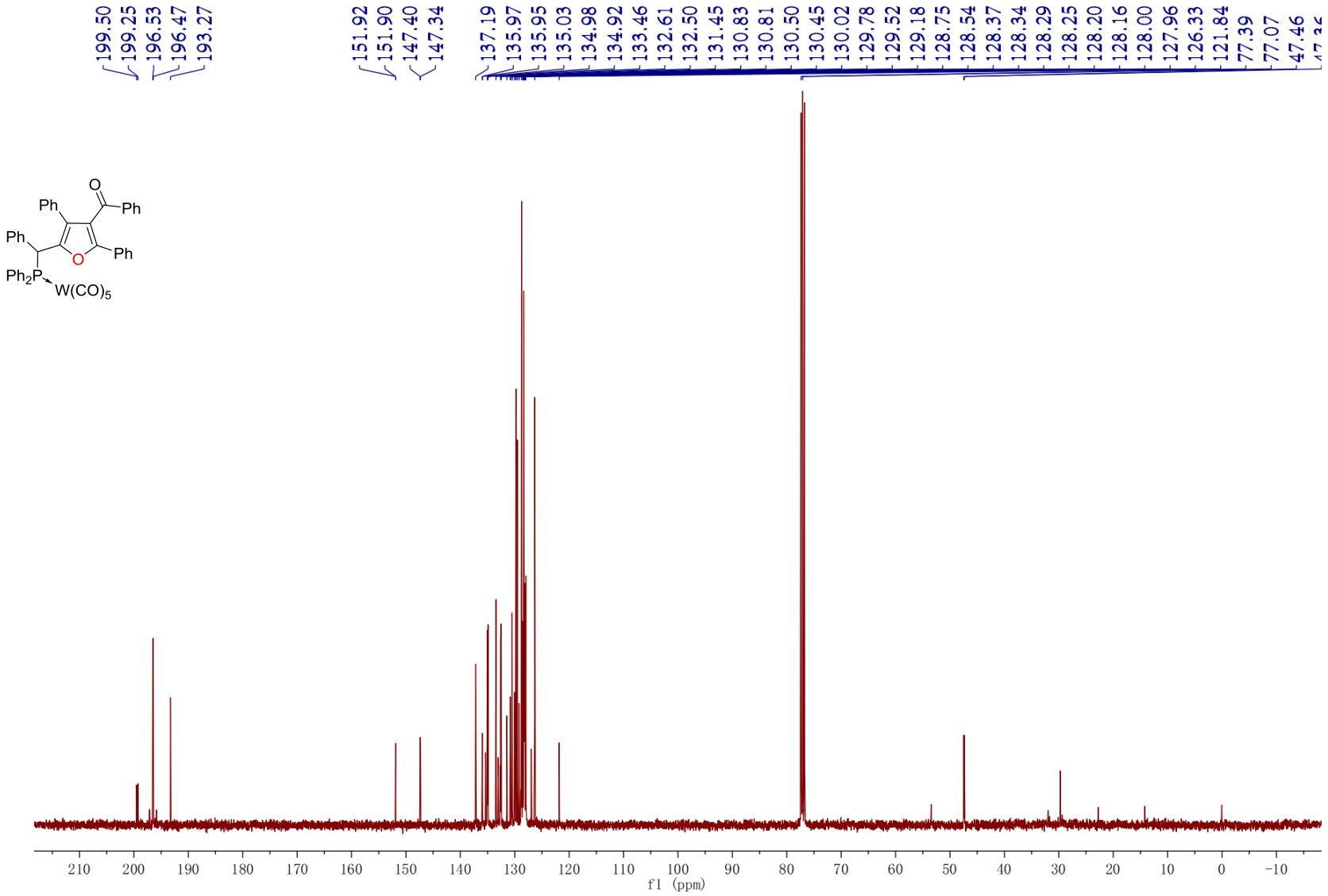
^{31}P $\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) of compound **3q**



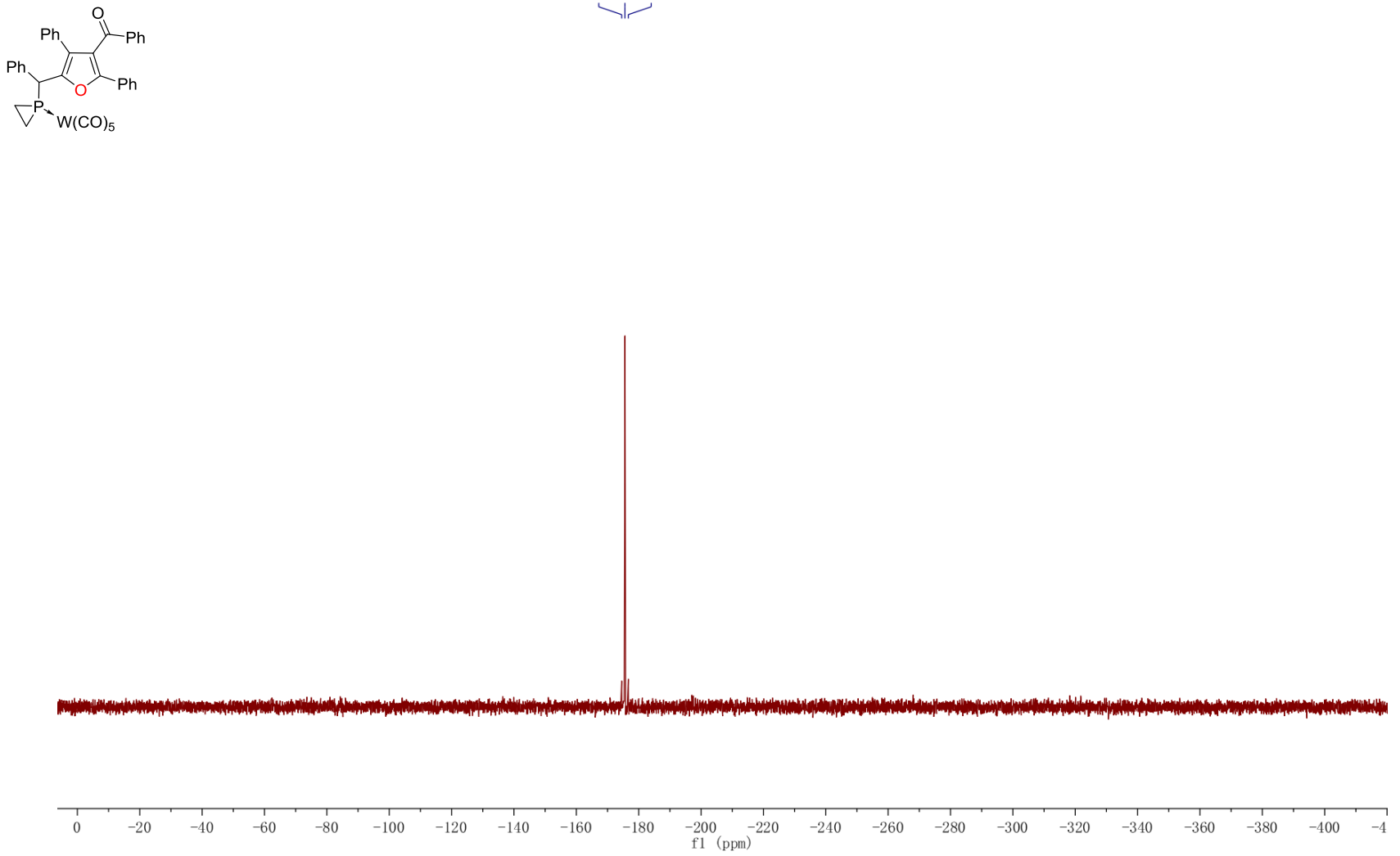
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3q**



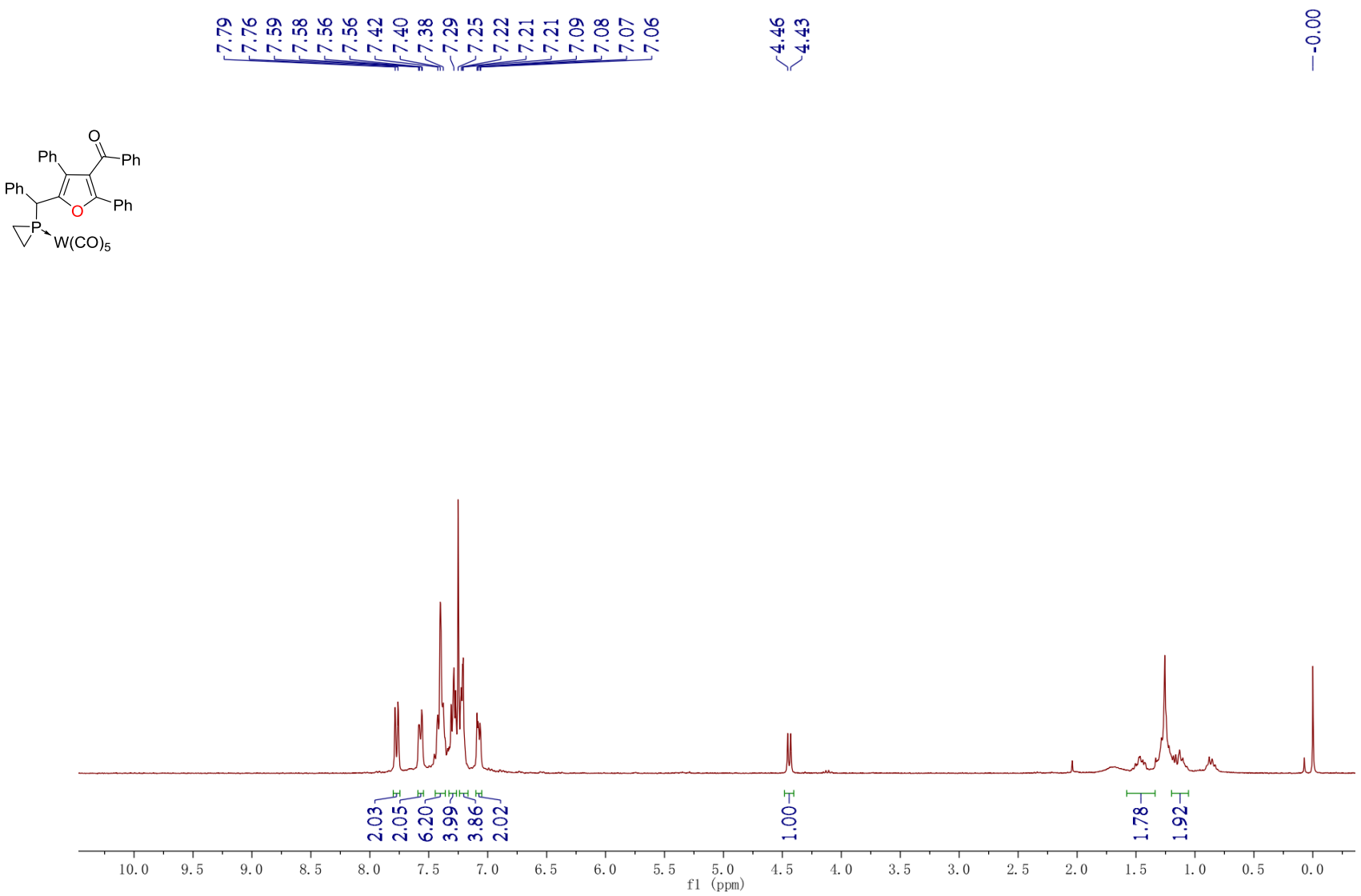
Dept 135 NMR ($CDCl_3$, 101 MHz) of Compound **3q**



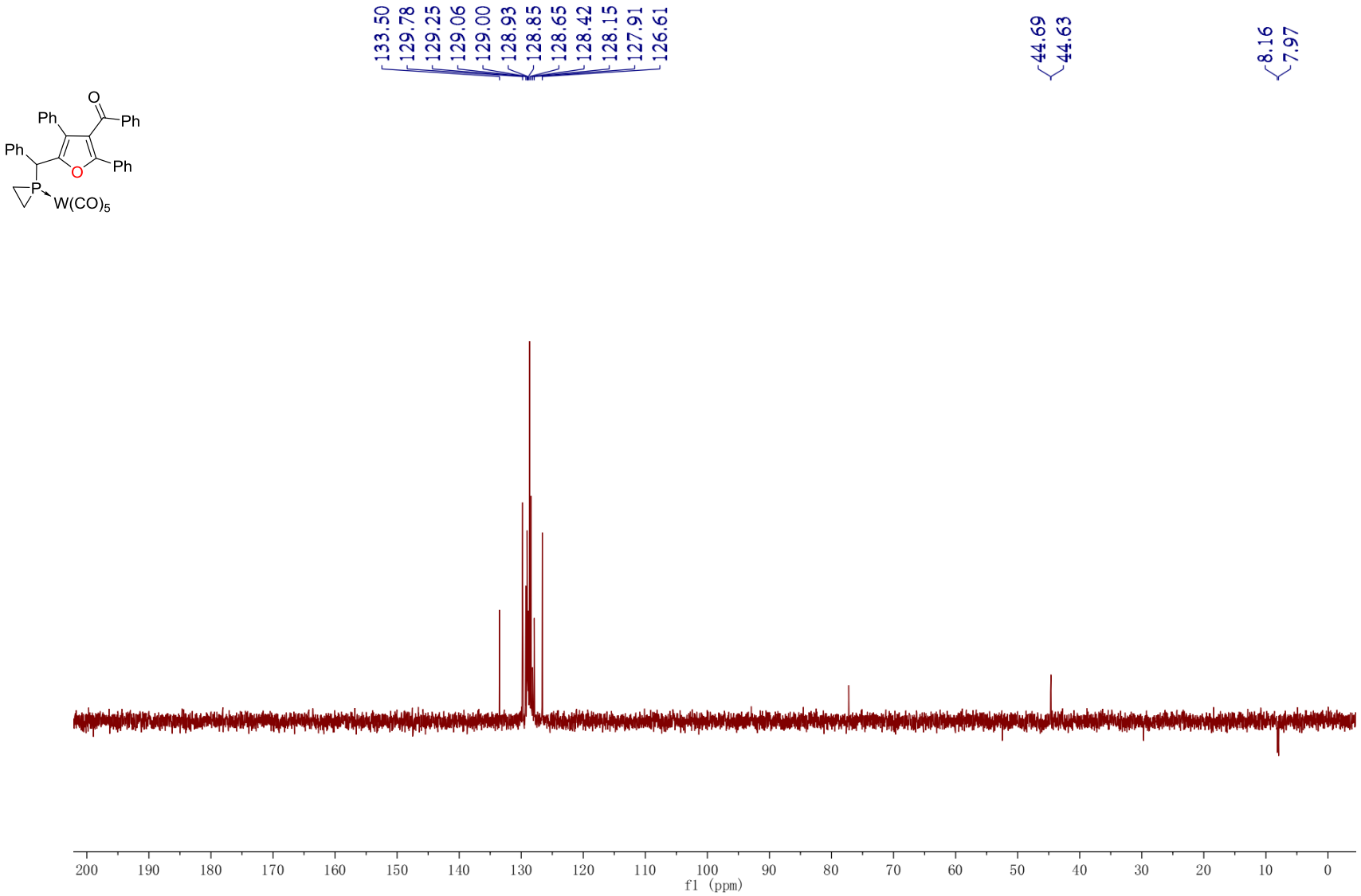
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **3q**



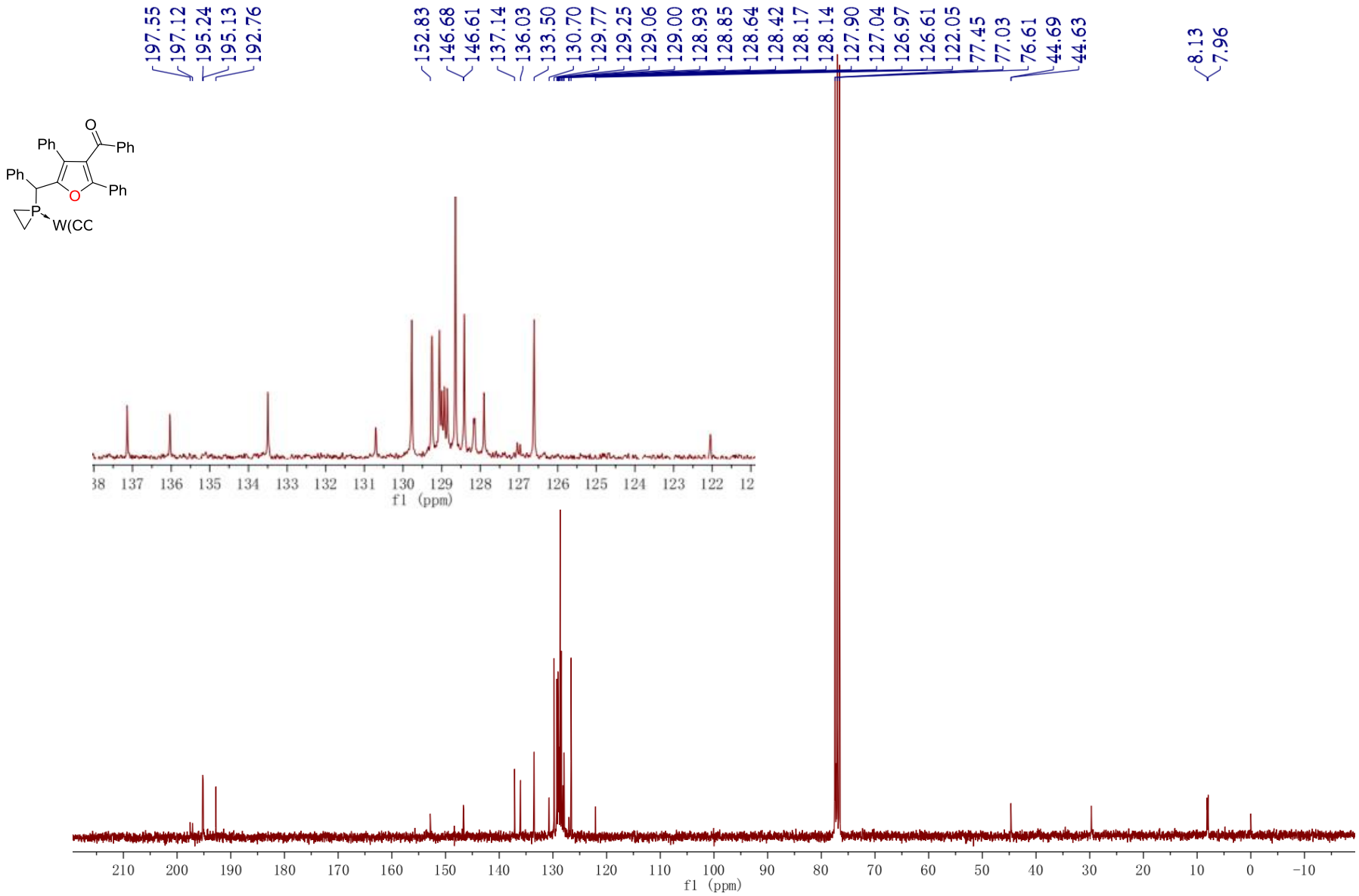
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **3r**



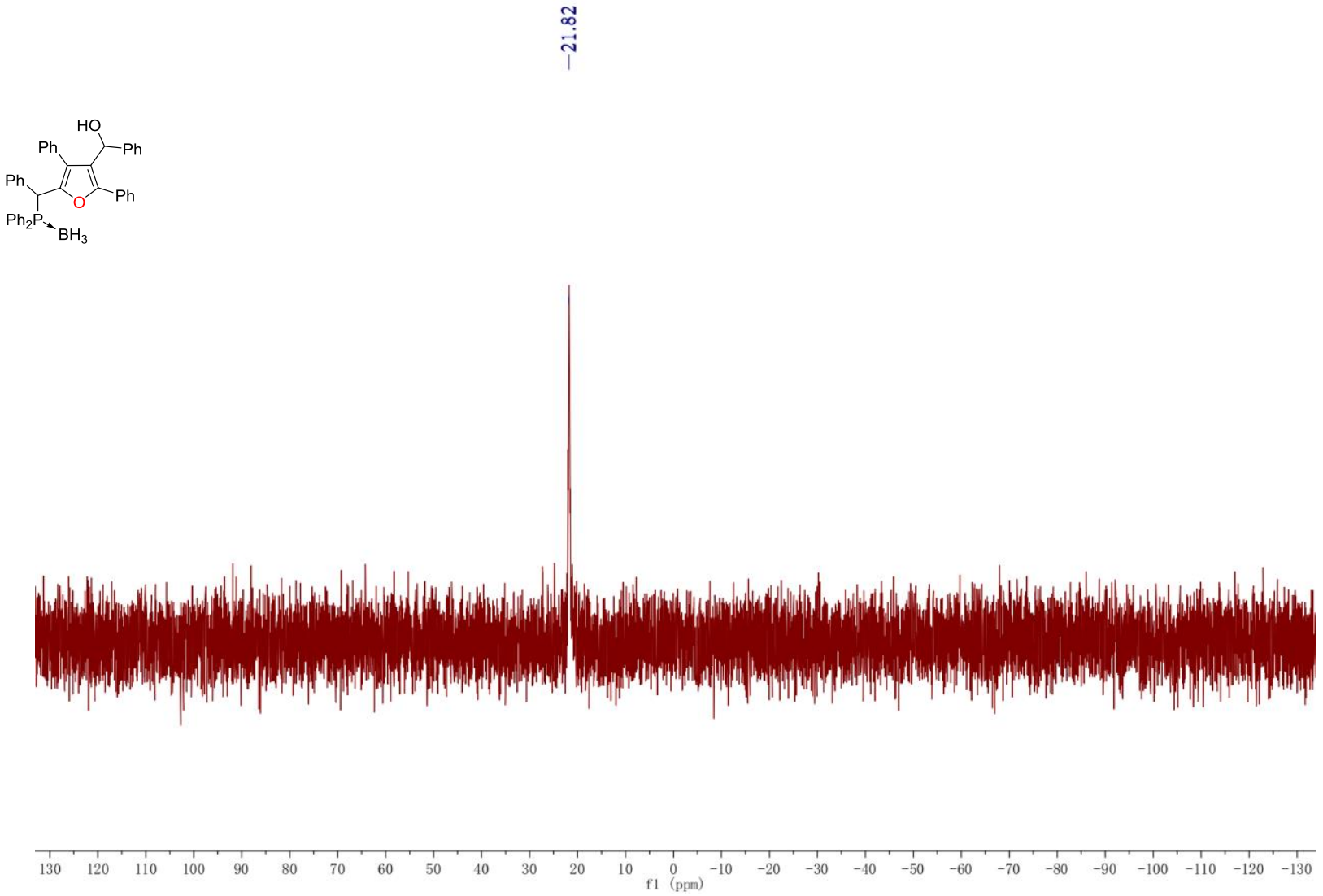
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **3r**



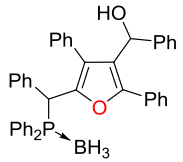
Dept 135 NMR ($CDCl_3$, 75 MHz) of Compound **3r**



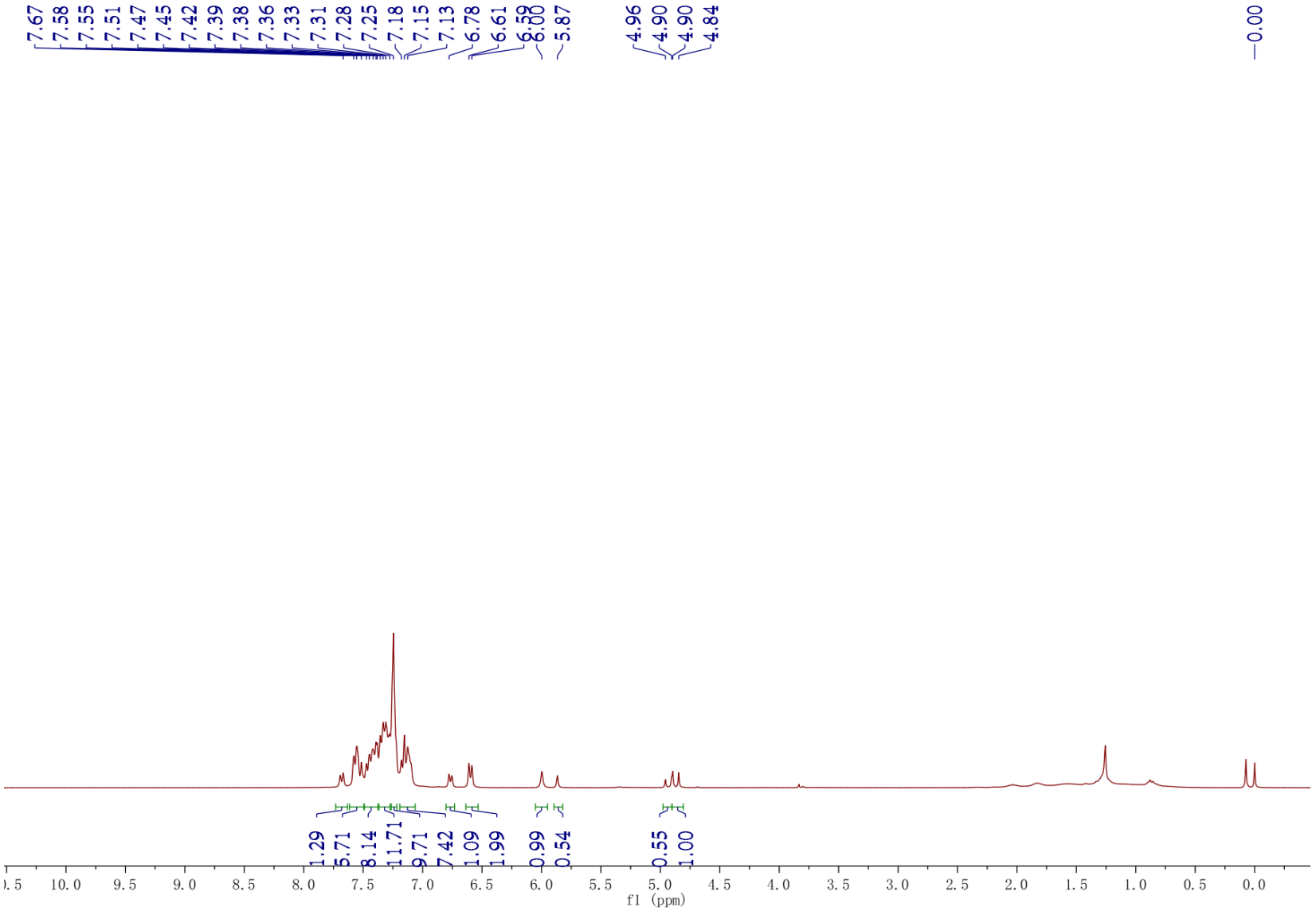
^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) of compound **3r**



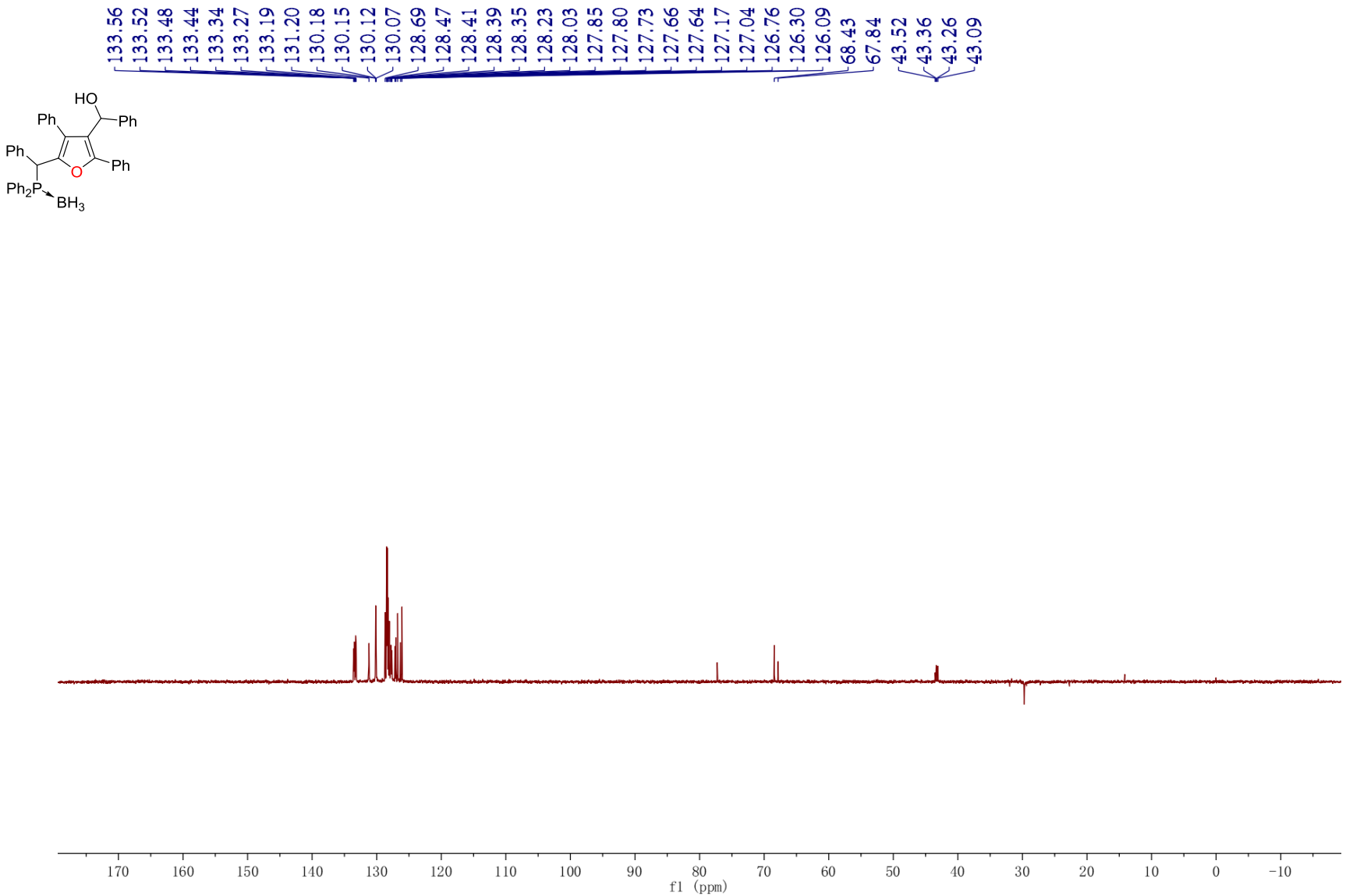
^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of compound **7**



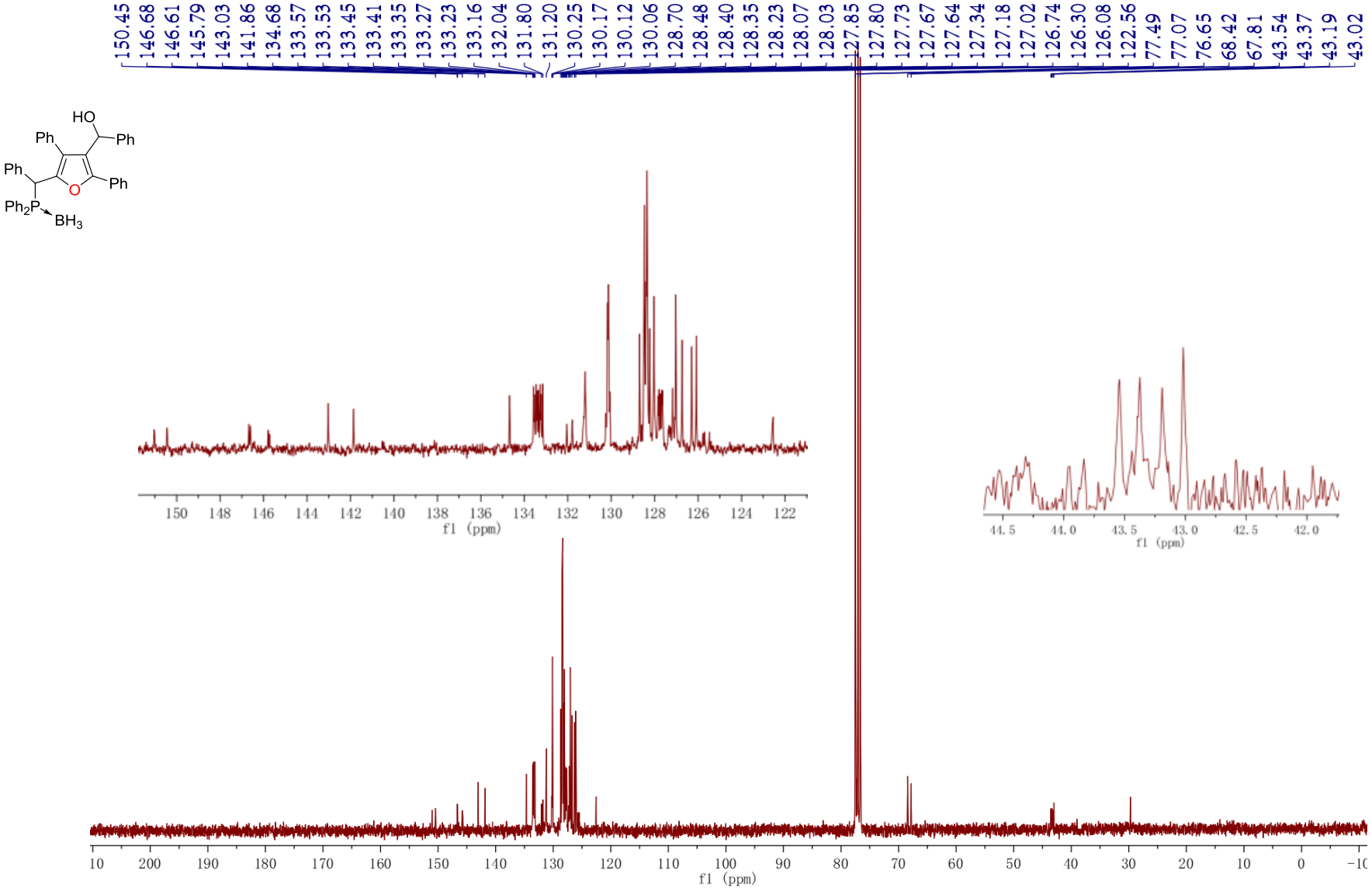
^{11}B {^{1}H} NMR ($CDCl_3$, 128 MHz) of compound **7**



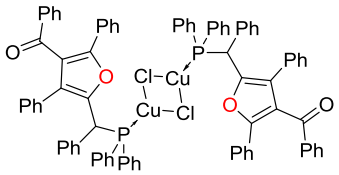
^{1}H NMR ($CDCl_3$, 300 MHz) of compound **7**



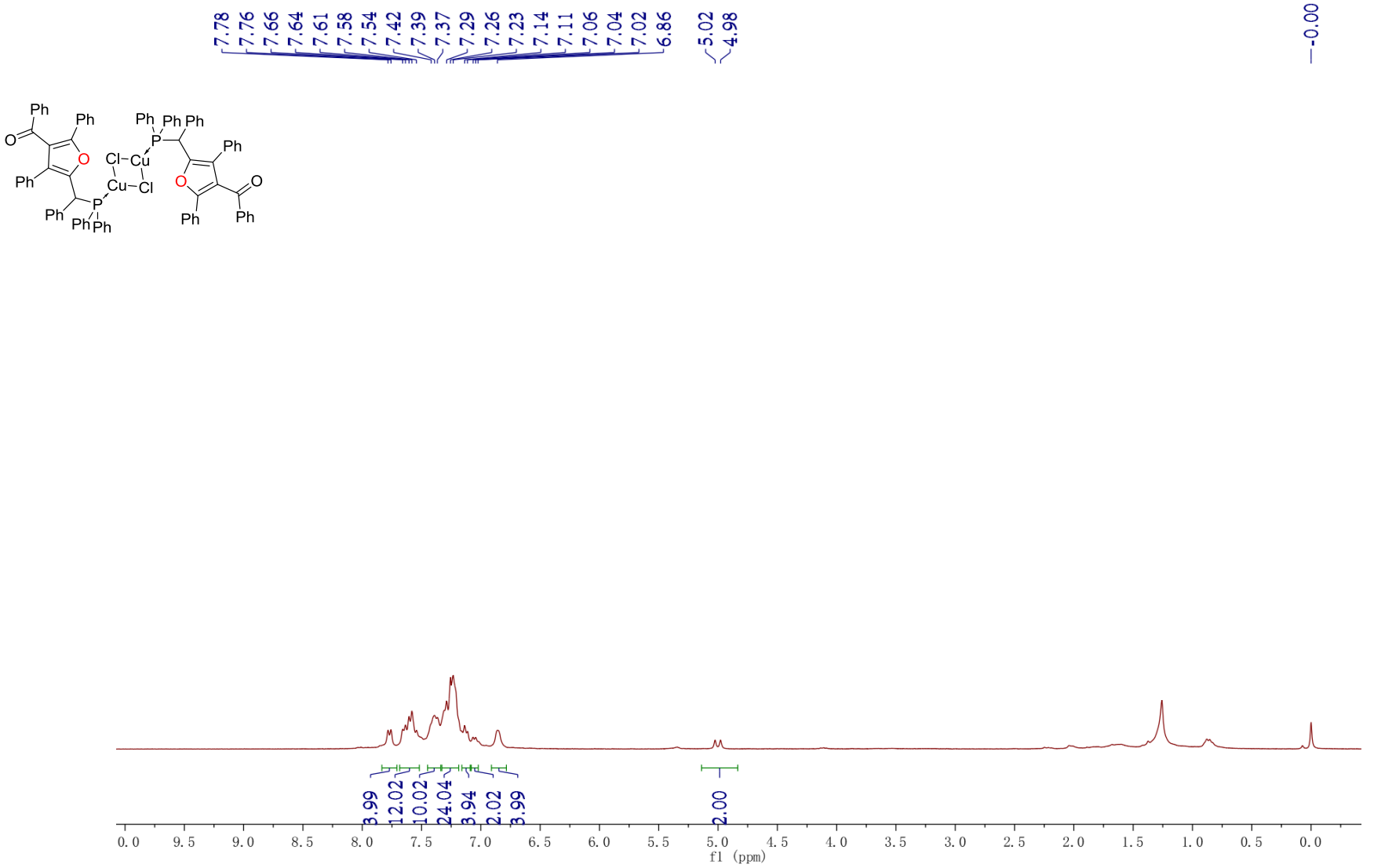
Dept 135 NMR ($CDCl_3$, 101 MHz) of compound **7**



^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz) of compound **7**



^{31}P $\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) of compound **9**



^{1}H NMR ($CDCl_3$, 300 MHz) of compound **9**