Supporting information for

Copper-catalyzed Reductive Coupling of Aryl Sulfonyl Chlorides with H-Phosphonates Leading to S-Aryl Phosphorothioates

Jie Bai,[a] Xiuling Cui, *[a, b] Hui Wang,[a] and Yangjie Wu*[a]

[a] Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou, 450052, P R China.

E-mail: cuixl@zzu.edu.cn; wyj@zzu.edu.cn; Tel: +86 371-67767753

[b] Xiamen Key Laboratory of Ocean and Gene Drugs, School of biomedical Sciences, and Institute of Molecular Medicine of Huaqiao University & Engineering Research Center of Molecular Medicine of Chinese Education Ministry, Fujian, Xiamen, 361021 E-mail: cuixl@hqu.edu.cn

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General Information:

All reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ^{1}H NMR spectra were recorded on a **Bruker DPX-400** (400 MHz) spectrometer with deuterated chloroform as solutions. The chemical shifts δ are reported in ppm relative to tetramethylsilane. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, J, are reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 100 MHz on **Bruker DPX-400**. The chemical shifts δ are reported relative to residual $CHCl_3$ (δ_c= 77.00 ppm). High resolution mass spectra (HRMS) were obtained on an **Agilent LC- MSD- Trap-XCT** 6450 spectrometer with micromass MS software using electrospray ionisation (ESI).

Experimental Procedure:

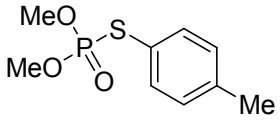
Typical Procedure for Copper-catalyzed Direct Coupling of Aryl Sulfonyl Chlorides with H-Phosphonates.

Aryl sulfonyl chloride (0.4 mmol), H-phosphonate (2.8 mmol) and $Cu(OAc)_2$ (15 mol %) were added to a 10 mL round-bottomed flask and then 2.5 mL CH_3CN was added. The reaction mixture was stirred at 140 ^{o}C for 24 h. After the reaction was complete, the mixture was evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using hexane/ethyl acetate as the eluent to give the pure product.

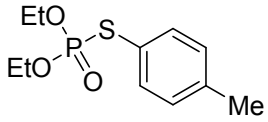
The recovery of dimethyl phosphonate 2a (^{1}H NMR yield).

When the reaction of tosyl chloride (**1a**) and dimethyl phosphonate (**2a**) (1:7) was performed in the presence of $Cu(OAc)_2$ (15 mol%) in CH_3CN at 100 ^{o}C for 24 h, the desired product was obtained in 64% yield. The reaction system was detected by NMR and **2a** was recovered in 55% yield calculated from ^{1}H NMR spectrum. The characterization was reflected (Page 76-77).

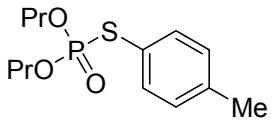
<u>Characterization of S-Aryl Phosphorothioates</u>



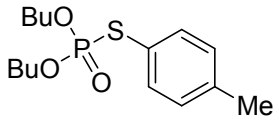
3a [1]: Colorless oil; Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J=8.0 Hz, 1.6 Hz, 2H), 7.16 (d, J=8.0 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (d, J=3.2 Hz), 134.7 (d, J=5.0 Hz), 130.3 (d, J=2.4 Hz), 122.3 (d, J=7.3 Hz), 54.3 (d, J=6.0 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.0; HRMS: m/z $[M+H]^+$ calcd for $C_9H_{14}O_3PS^+$: 233.0396; found: 233.0397.



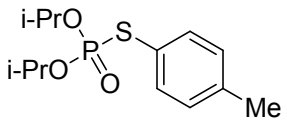
3b [2]: Colorless oil; Yield:73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J=8.0 Hz, 1.6 Hz, 2H), 7.13 (d, J=8.0 Hz, 2H), 4.23-4.08 (m, 4H), 2.32 (s, 3H), 1.28 (t, J=7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J=3.1 Hz), 134.6 (d, J=5.0 Hz), 130.2 (d, J=2.3 Hz), 122.8 (d, J=7.2 Hz), 64.0 (d, J=6.2 Hz), 21.2, 16.0 (d, J=7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.7; HRMS: m/z $[M+H]^+$ calcd for $C_{11}H_{18}O_3PS^+$: 261.0709; found: 261.0712.



3c [2c]: Colorless oil; Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J=8.2 Hz, 1.6 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 4.11-3.98 (m, 4H), 2.31 (s, 3H), 1.70-1.61 (m, 4H), 0.90 (t, J=7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2 (d, J=3.1 Hz), 134.6 (d, J=5.1 Hz), 130.1 (d, J=2.2 Hz), 122.8 (d, J=7.3 Hz), 69.4 (d, J=6.6 Hz), 23.6 (d, J=7.2 Hz), 21.2, 10.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8; HRMS: m/z $[M+H]^+$ calcd for $C_{13}H_{22}O_3PS^+$: 289.1022; found: 289.1025.

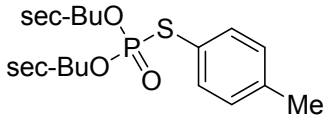


3d [3]: Colorless oil; Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (dd, J=8.2 Hz, 1.9 Hz, 2H), 7.12 (d, J=8.0 Hz, 2H), 4.15-4.01 (m, 4H), 2.32 (s, 3H), 1.64-1.56 (m, 4H), 1.38-1.28 (m, 4H), 0.88 (t, J=7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.2 (d, J=3.1 Hz), 134.6 (d, J=5.1 Hz), 130.1 (d, J=2.3 Hz), 122.9 (d, J=7.2 Hz), 67.7 (d, J=6.6 Hz), 32.2 (d, J=7.0 Hz), 21.2, 18.7, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 23.8; HRMS: m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_3PS^+$: 317.1335; found: 317.1339.

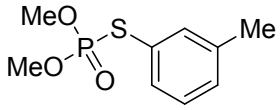


3e [2a, 2c, 3b]: Colorless oil; Yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.45 (dd, J=8.2 Hz, 1.6 Hz, 2H), 7.11 (d, J=8.0 Hz, 2H), 4.78-4.70 (m, 2H), 2.32 (s, 3H), 1.30 (d, J=6.4 Hz, 6H), 1.24 (d, J=6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.9 (d, J=3.0 Hz), 134.3 (d, J=5.3 Hz), 130.0 (d, J=2.1 Hz), 123.5 (d, J=7.1 Hz), 73.2 (d, J=6.7 Hz),

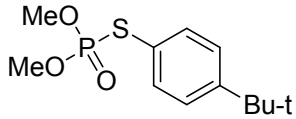
23.8 (d, J=4.0 Hz), 23.5 (d, J=5.7 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3; HRMS: m/z $[M+H]^+$ calcd for $C_{13}H_{22}O_3PS^+$: 289.1022; found: 289.1023.



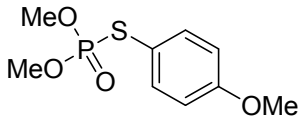
3f: Colorless oil; Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=7.2 Hz, 2H), 7.11 (d, J=7.6 Hz, 2H), 4.53 (d, J=6.8 Hz, 2H), 2.31 (s, 3H), 1.69-1.49 (m, 4H), 1.29 (d, J=6.0 Hz, 3H), 1.23 (d, J=6.0 Hz, 3H), 0.90-0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (d, J=2.8 Hz), 134.4 (d, J=5.3 Hz), 129.9 (d, J=2.1 Hz), 123.6 (d, J=7.1 Hz), 78.0-77.7 (m), 30.4 (d, J=5.0 Hz), 30.2 (d, J=6.4 Hz), 21.2 , 21.1 (d, J=2.8 Hz), 20.8 (d, J=4.2 Hz), 9.3 (d, J=4.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.7; HRMS: m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_3PS^+$: 317.1335; found: 317.1338.



3g [4]: Colorless oil; Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J=8.0 Hz, 2H), 7.22 (t, J=7.6 Hz, 1H), 7.15 (d, J=7.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 (d, J=2.3 Hz), 135.2 (d, J=5.2 Hz), 131.6 (d, J=5.2 Hz), 130.1 (d, J=3.0 Hz), 129.3 (d, J=2.3 Hz), 125.6 (d, J=7.2 Hz), 54.3 (d, J=6.1 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9; HRMS: m/z $[M+H]^+$ calcd for $C_9H_{14}O_3PS^+$: 233.0396; found: 233.0397.

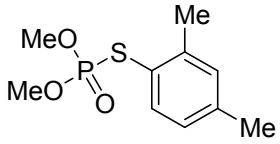


3h [5]: Colorless oil; Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=7.6 Hz, 2H), 7.34 (d, J=8.4 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J=3.2 Hz), 134.3 (d, J=5.1 Hz), 126.6 (d, J=2.2 Hz), 122.2 (d, J=7.2 Hz), 54.2 (d, J=6.0 Hz), 34.7, 31.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1; HRMS: m/z $[M+H]^+$ calcd for $C_{12}H_{20}O_3PS^+$: 275.0865; found: 275.0872.

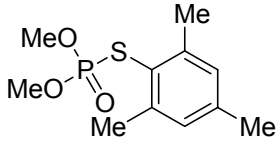


3i [3a, 6]: Colorless oil; Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J=8.6 Hz, 2.4 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 3.80 (s, 3H), 3.77 (d, J=4.0 Hz, 6H); ^{13}C NMR

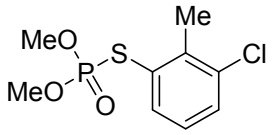
(100 MHz, $CDCl_3$) δ 160.6 (d, J=3.0 Hz), 136.4 (d, J=4.7 Hz), 116.0 (d, J=7.4 Hz), 115.1 (d, J=2.4 Hz), 55.4, 54.2 (d, J=6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.3; HRMS: m/z $[M+H]^+$ calcd for $C_9H_{14}O_4PS^+$: 249.0345; found: 249.0347.



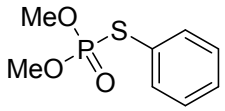
3j: Colorless oil; Yield: 64%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J=7.6 Hz, 1H), 7.06 (s, 1H), 6.96 (d, J=7.6 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.46 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2 (d, J=5.2 Hz), 139.9 (d, J=3.4 Hz), 136.3 (d, J=4.1 Hz), 131.9 (d, J=2.8 Hz), 127.8 (d, J=2.8 Hz), 121.5 (d, J=7.6 Hz), 54.3 (d, J=6.5 Hz), 21.3, 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9; HRMS: m/z $[M+H]^+$ calcd for $C_{10}H_{16}O_3PS^+$: 247.0552; found: 247.0557.



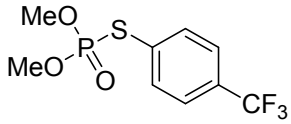
3k [7]: olorless oil; Yield: 54%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 2.53 (s, 6H), 2.25 (d, J=2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9 (d, J=4.6 Hz), 139.6 (d, J=3.8 Hz), 129.5 (d, J=3.3 Hz), 120.7 (d, J=7.9 Hz), 54.4 (d, J=7.2 Hz), 22.4, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.7; HRMS: m/z $[M+H]^+$ calcd for $C_{11}H_{18}O_3PS^+$: 261.0709; found: 261.0714.



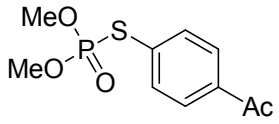
3l: Colorless oil; Yield: 69%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J=7.8 Hz, 1H), 7.36 (d, J=8.0 Hz, 1H), 7.09 (t, J=8.0 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 (d, J=5.3 Hz), 135.8 (d, J=3.0 Hz), 135.0 (d, J=4.2 Hz), 130.8 (d, J=3.1 Hz), 127.4 (d, J=7.4 Hz), 127.2 (d, J=2.8 Hz), 54.5 (d, J=6.6 Hz), 19.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8; HRMS: m/z $[M+H]^+$ calcd for $C_9H_{13}ClO_3PS^+$: 267.0006; found: 267.0009.



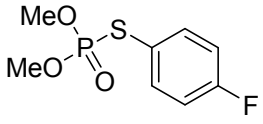
3m: Colorless oil; Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.35-7.33 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5 (d, J=5.1 Hz), 129.4 (d, J=2.2 Hz), 129.1 (d, J=2.9 Hz), 125.9 (d, J=7.0 Hz), 54.2 (d, J=6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.6; HRMS: m/z $[M+H]^+$ calcd for $C_8H_{12}O_3PS^+$: 219.0239; found: 219.0243.



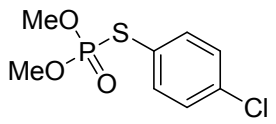
3n [3a] : Colorless oil; Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J=8.0 Hz, 2H), 7.58 (d, J=8.4 Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (d, J=5.4 Hz), 131.6-130.6 (m, J=32.8 Hz, 2.7 Hz), 131.3 (d, J=3.0 Hz), 126.3-126.2 (m), 123.7 (q, J=270.7 Hz), 54.5 (d, J=6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.1; HRMS: m/z $[M+H]^+$ calcd for $C_9H_{11}F_3O_3PS^+$: 287.0113; found: 287.0115.



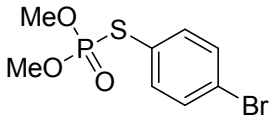
3o: Colorless oil; Yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J=8.4 Hz, 2H), 7.62 (dd, J=8.4 Hz, 1.2 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 137.2 (d, J=2.5 Hz), 134.1 (d, J=5.5 Hz), 132.5 (d, J=7.0 Hz), 129.1 (d, J=2.8 Hz), 54.5 (d, J=6.2 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.2; HRMS: m/z $[M+H]^+$ calcd for $C_{10}H_{14}O_4PS^+$: 261.0345; found: 261.0347.



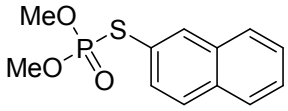
3p [3a, 8]: Colorless oil; Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.03 (t, J=8.4 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (dd, J=248.7 Hz, 3.3 Hz), 136.7 (dd, J=8.6 Hz, 5.0 Hz), 121.0 (dd, J=7.3 Hz , 3.4 Hz), 116.6 (dd, J=22.2 Hz, 2.3 Hz), 54.2 (d, J=6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3 (d, J=5.0 Hz); HRMS: m/z $[M+H]^+$ calcd for $C_8H_{11}FO_3PS^+$: 237.0145; found: 237.0147.



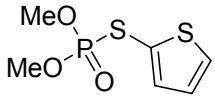
3q [1, 9]: Colorless oil; Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J=8.4 Hz, 1.6 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7 (d, J=5.2 Hz), 135.6 (d, J=3.6 Hz), 129.6 (d, J=2.3 Hz), 124.4 (d, J=7.2 Hz), 54.3 (d, J=6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.9; HRMS: m/z $[M+H]^+$ calcd for $C_8H_{11}ClO_3PS^+$: 252.9850; found: 252.9852.



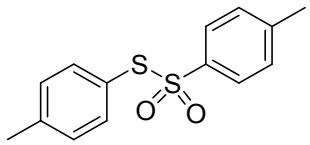
3r: Colorless oil; Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=8.0 Hz, 2H), 7.40 (d, J=8.4 Hz, 2H), 3,81 (d, J=1.2 Hz, 3H), 3.78 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3 (d, J=5.5 Hz), 131.2 (d, J=5.9 Hz), 130.8 (d, J=2.6 Hz), 126.14-126.08 (m), 54.4 (d, J=6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.7; HRMS: m/z $[M+H]^+$ calcd for $C_8H_{11}BrO_3PS^+$: 296.9344; found: 296.9345.



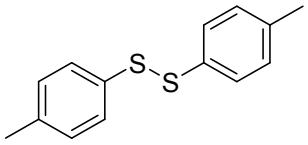
3s: Colorless oil; Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.82-7.79 (m, 3H), 7.59 (d, J=8.8 Hz, 1H), 7.52-7.49 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (d, J=6.8 Hz), 133.5 (d, J=2.3 Hz), 133.0 (d, J=2.0 Hz), 130.8 (d, J=3.9 Hz), 129.1 (d, J=1.7 Hz), 127.7, 127.1 (d, J=1.0 Hz), 126.8, 123.1 (d, J=7.5 Hz), 54.3 (d, J=6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.6; HRMS: m/z $[M+H]^+$ calcd for $C_{12}H_{14}O_3PS^+$: 269.0396; found: 269.0397.



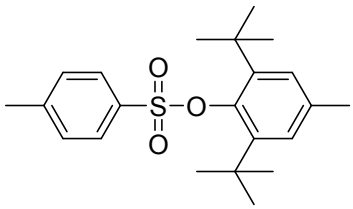
3t [10]: Colorless oil; Yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1H), 7.24-7.21 (m, 1H), 7.03 (dd, J= 5.3 Hz, 3.8 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3 (d, J= 6.5), 131.3 (d, J= 3.4), 127.9, 122.4 (d, J= 9.2), 54.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.5; HRMS m/z (ESI) calcd for $C_6H_{10}O_3PS_2^+$ $[M+H]^+$: 224.9803; found: 224.9805.



4a [11]: White solid, mp 77–78°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.0 Hz, 2H), 7.22 (t, J=8.4 Hz, 4H), 7.14 (d, J=8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.1, 140.5, 136.6, 130.3, 129.4, 127.6, 124.6, 21.7, 21.6; HRMS m/z (ESI) calcd for $C_{14}H_{15}O_2S_2^+$ $[M+H]^+$: 279.0508; found: 279.0510.



4b [12]: White solid, mp 44-45°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J=8.0 Hz, 2H), 7.12 (t, J=8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.9, 129.9, 128.6, 21.1.



5a: White solid, mp 107-108°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=8.0 Hz, 2H), 7.21 (d, J=8.0 Hz, 2H), 6.73 (s, 2H), 2.40 (s, 3H), 1.31 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 144.3, 136.0, 134.9, 129.3, 128.9, 127.7, 119.0, 34.1, 30.1, 21.6; HRMS m/z (ESI) calcd for $C_{22}H_{30}NaO_3S^+$ $[M+H]^+$: 397.1808; found: 397.1808.

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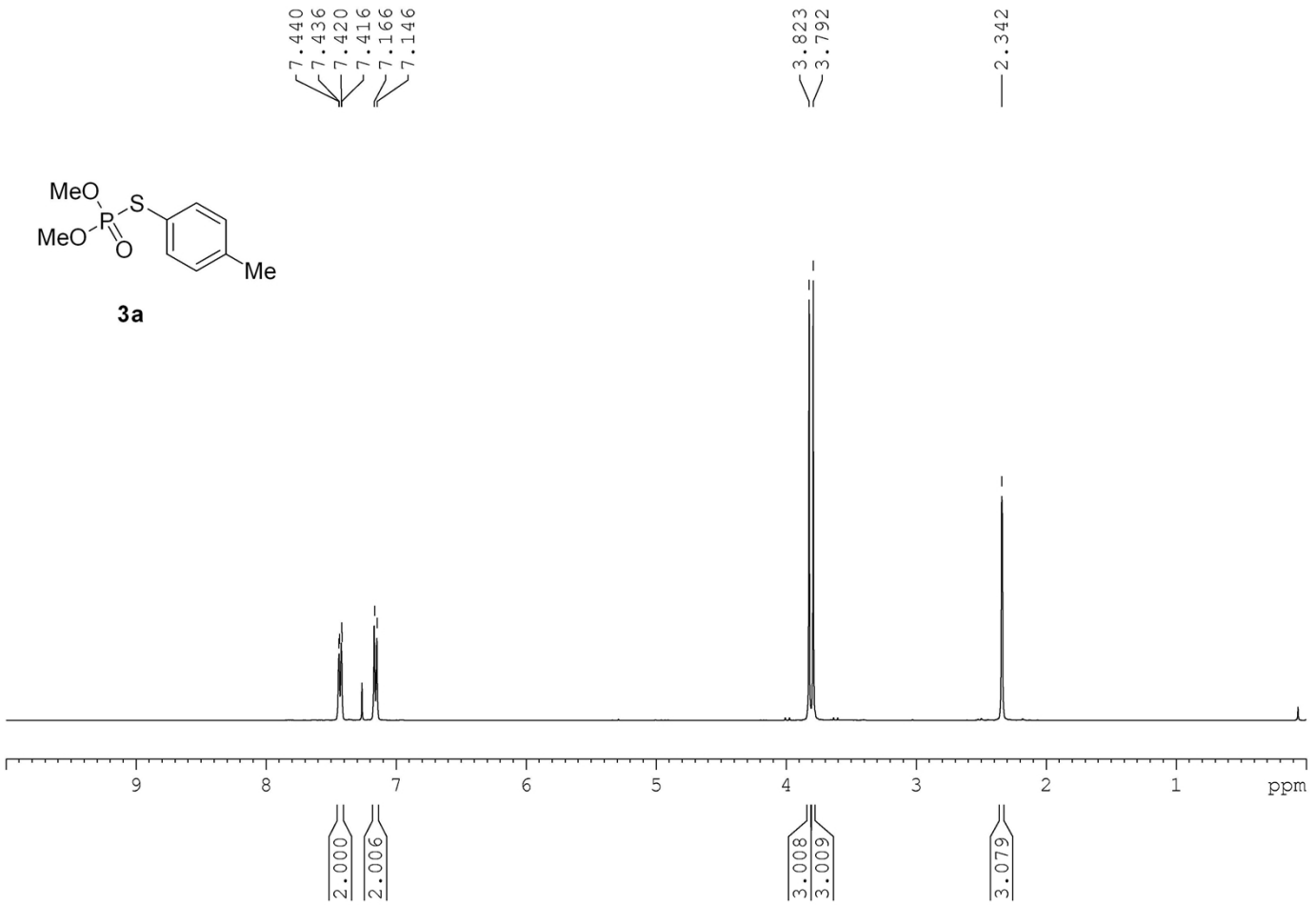
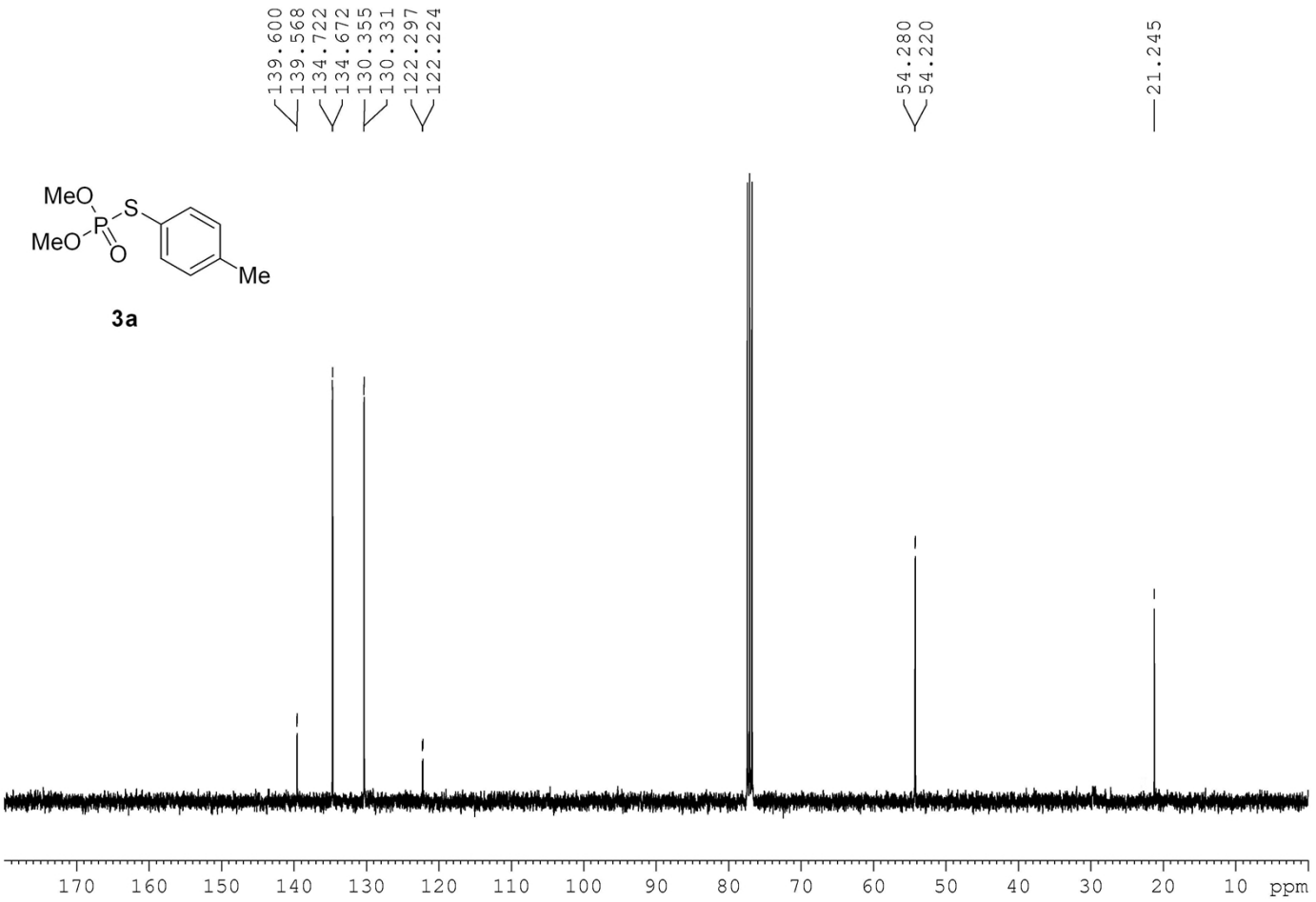
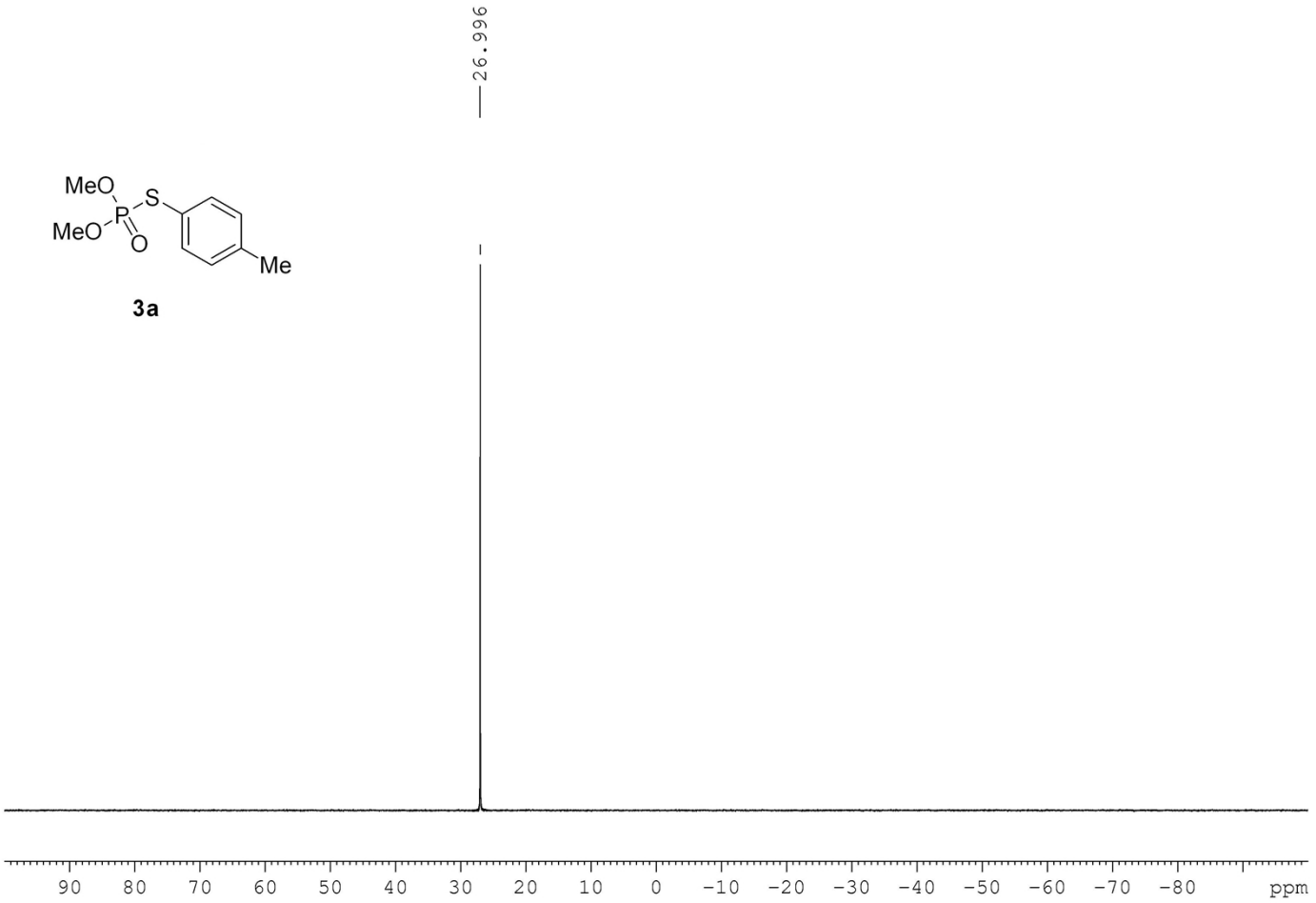


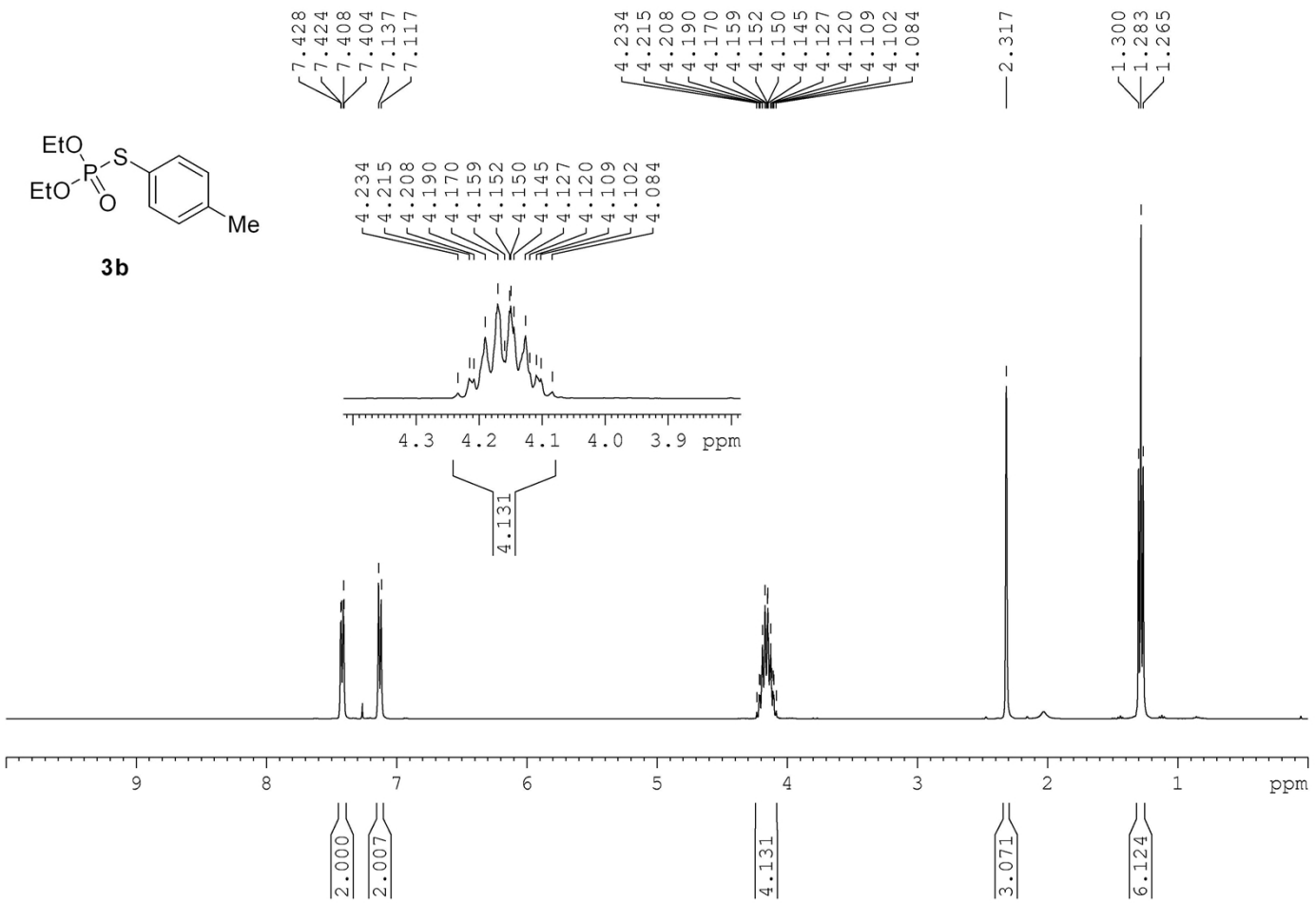
^{1}H NMR spectrum of compound **3a**



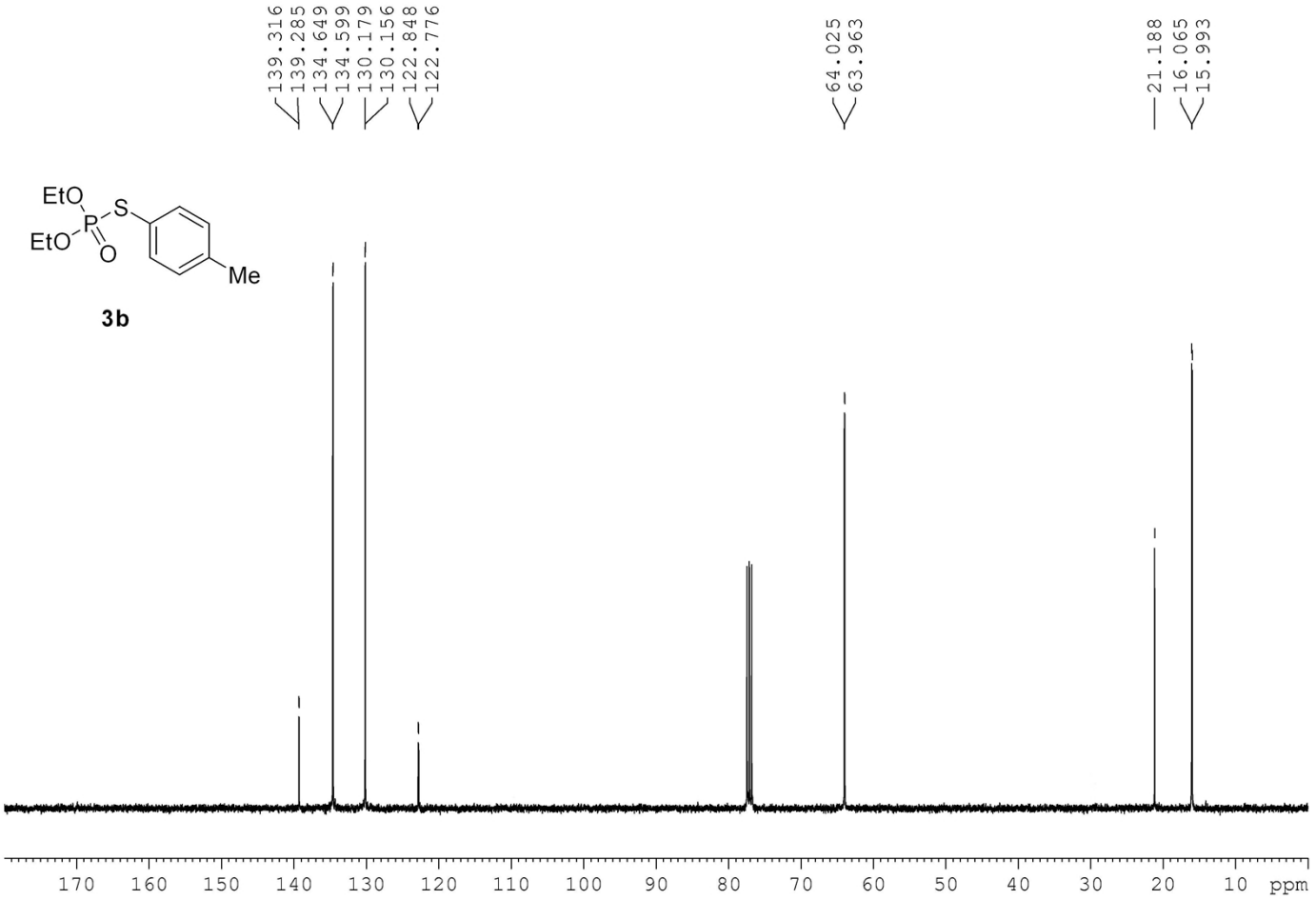
^{13}C NMR spectrum of compound **3a**



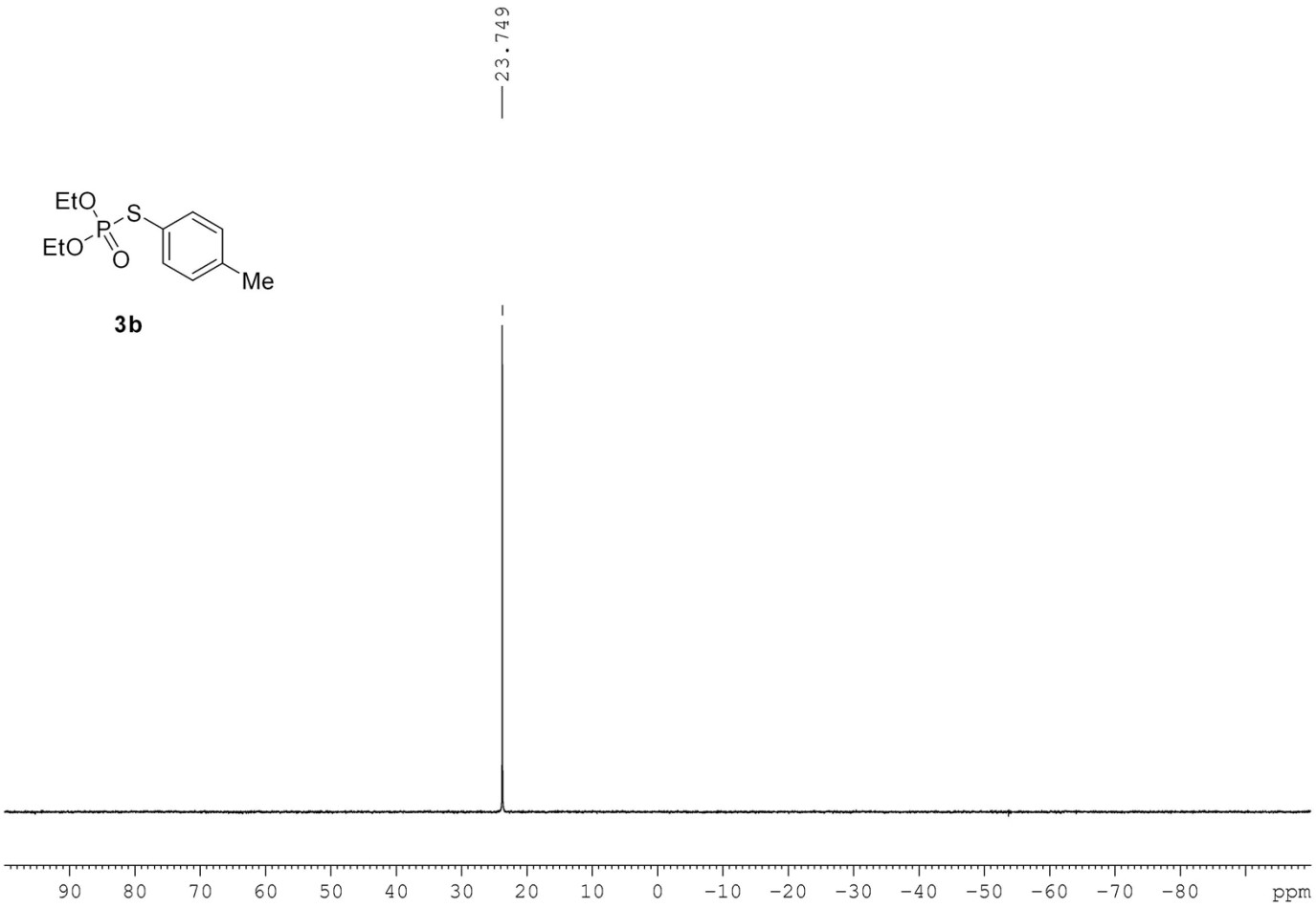
^{31}P NMR spectrum of compound **3a**



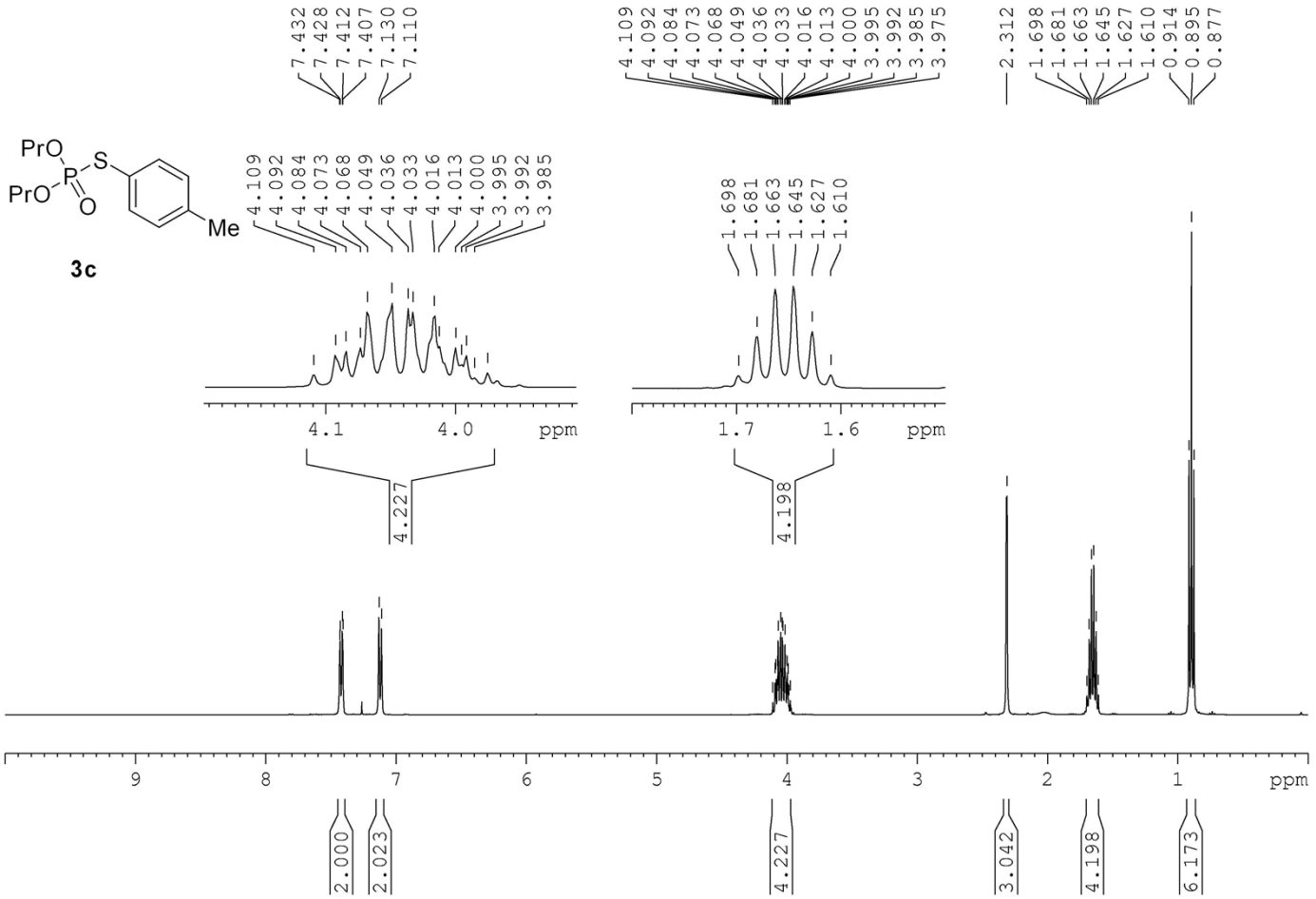
^{1}H NMR spectrum of compound **3b**



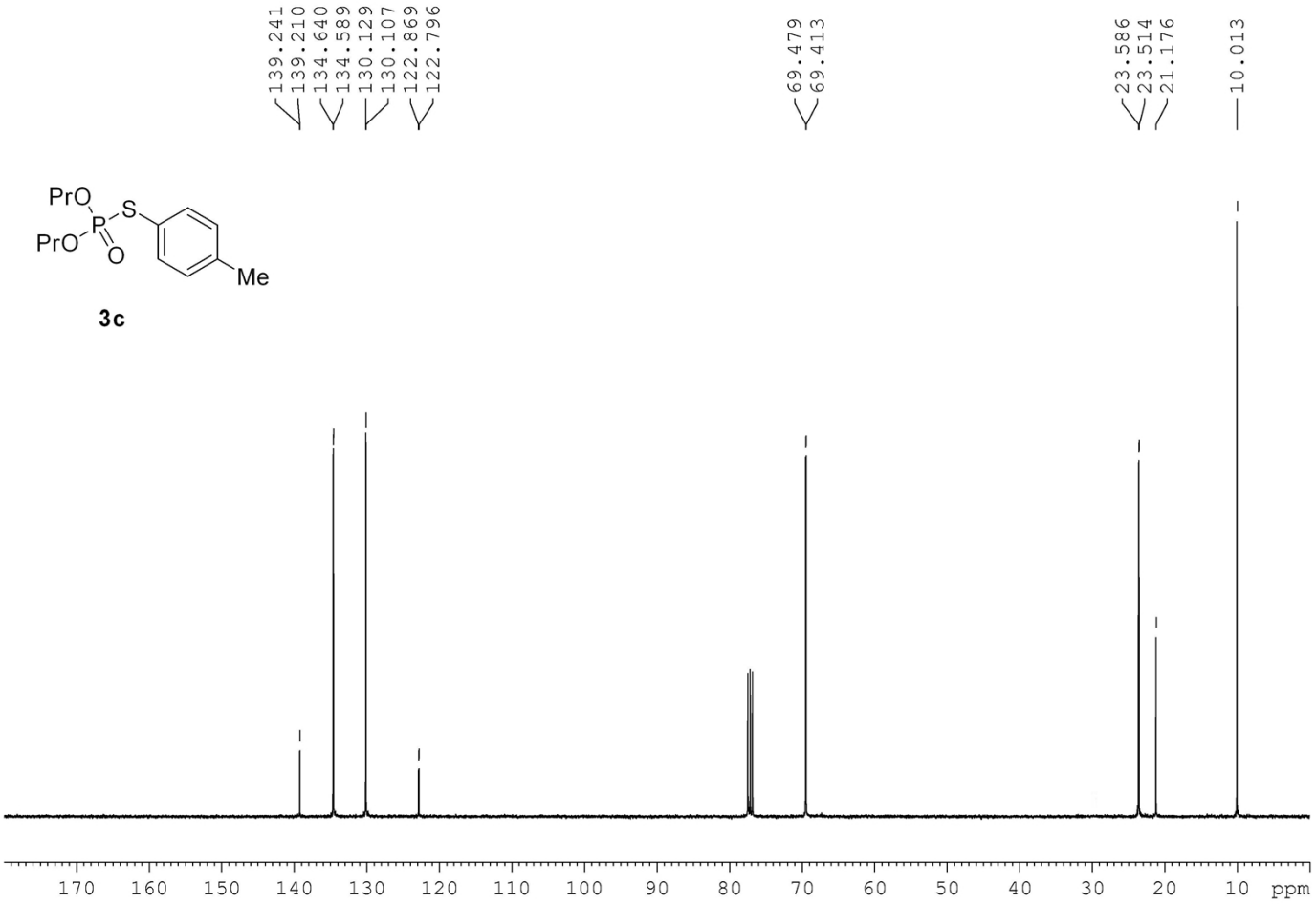
^{13}C NMR spectrum of compound **3b**



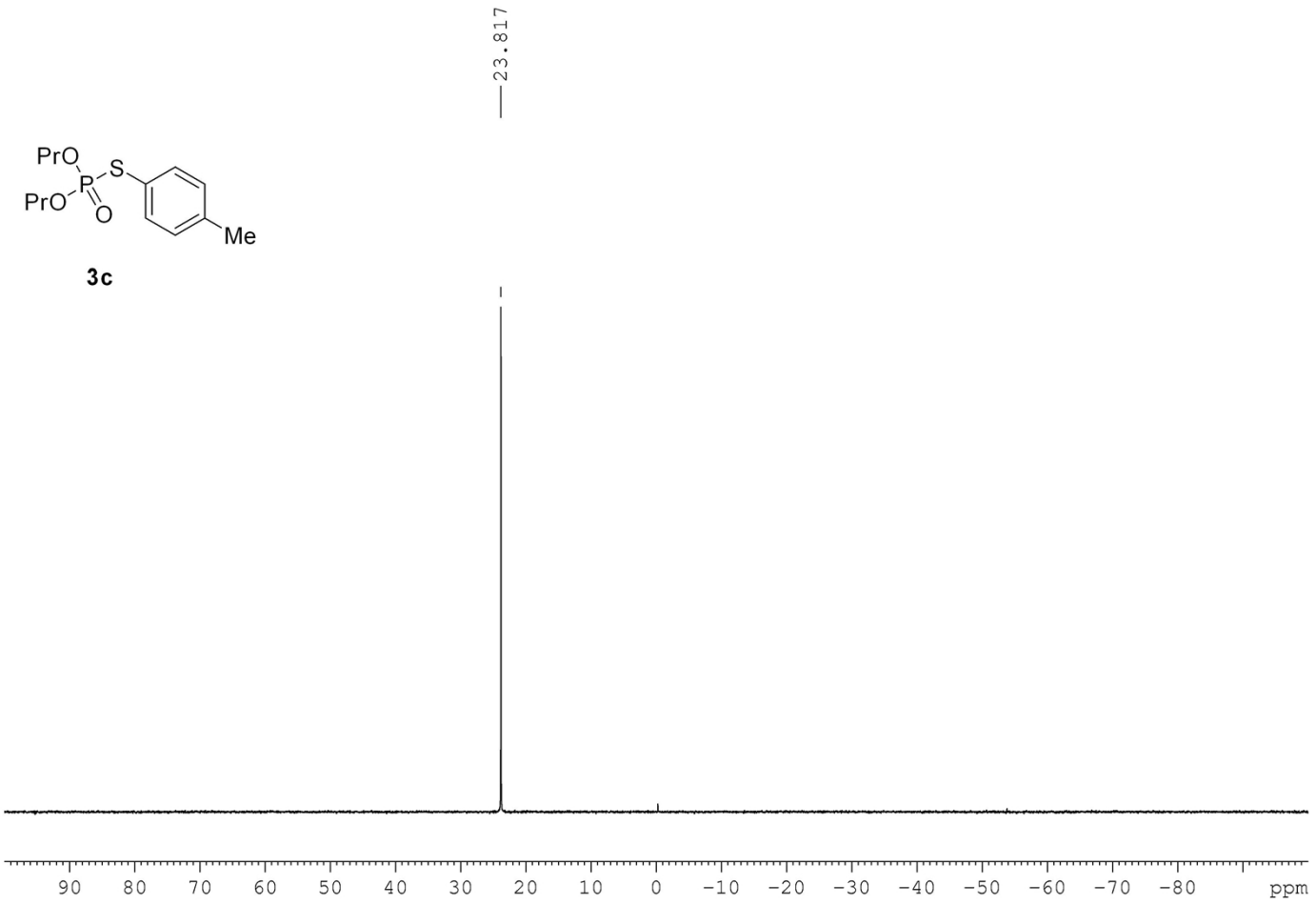
^{31}P NMR spectrum of compound **3b**



^{1}H NMR spectrum of compound **3c**



^{13}C NMR spectrum of compound **3c**



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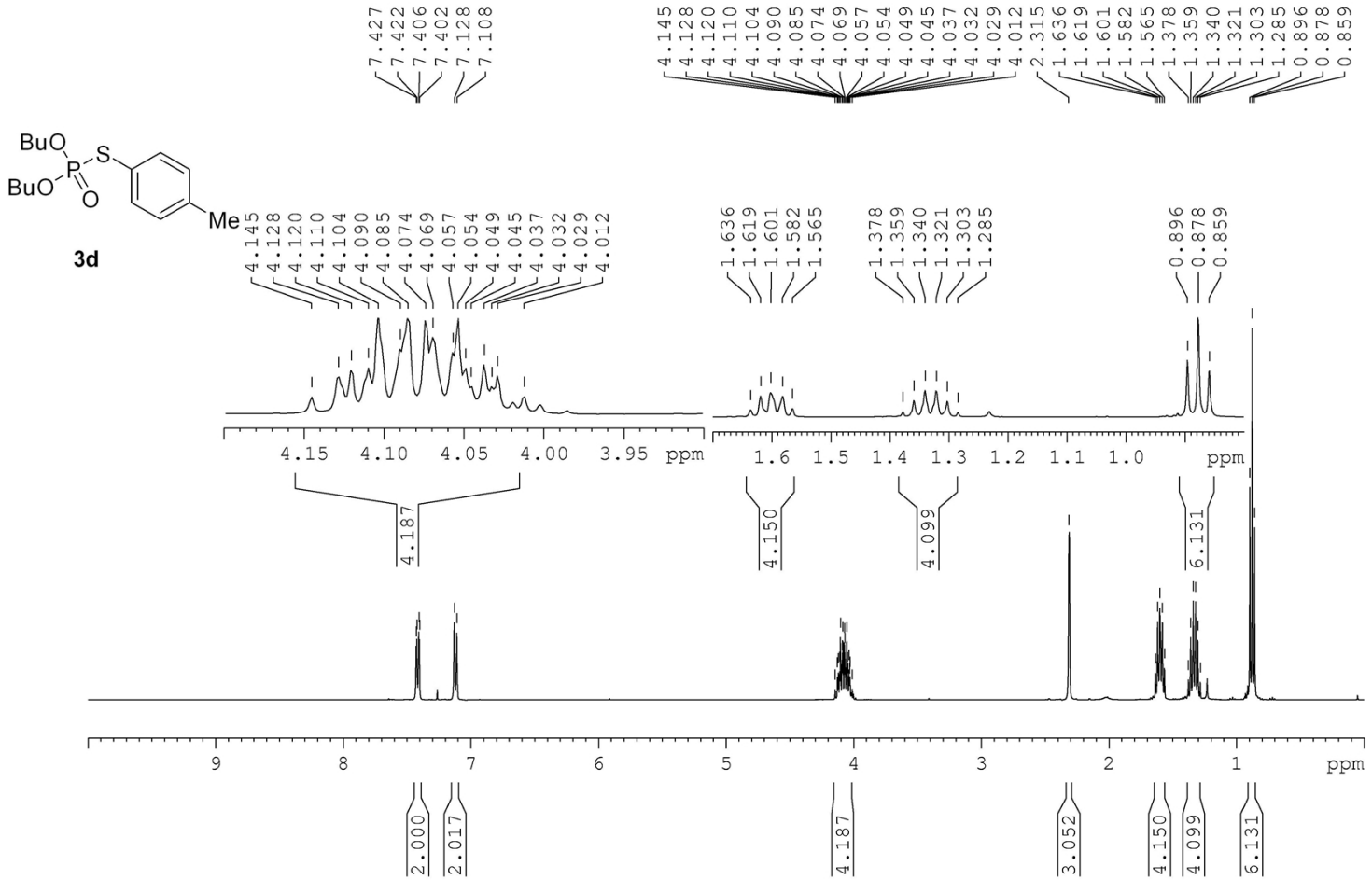

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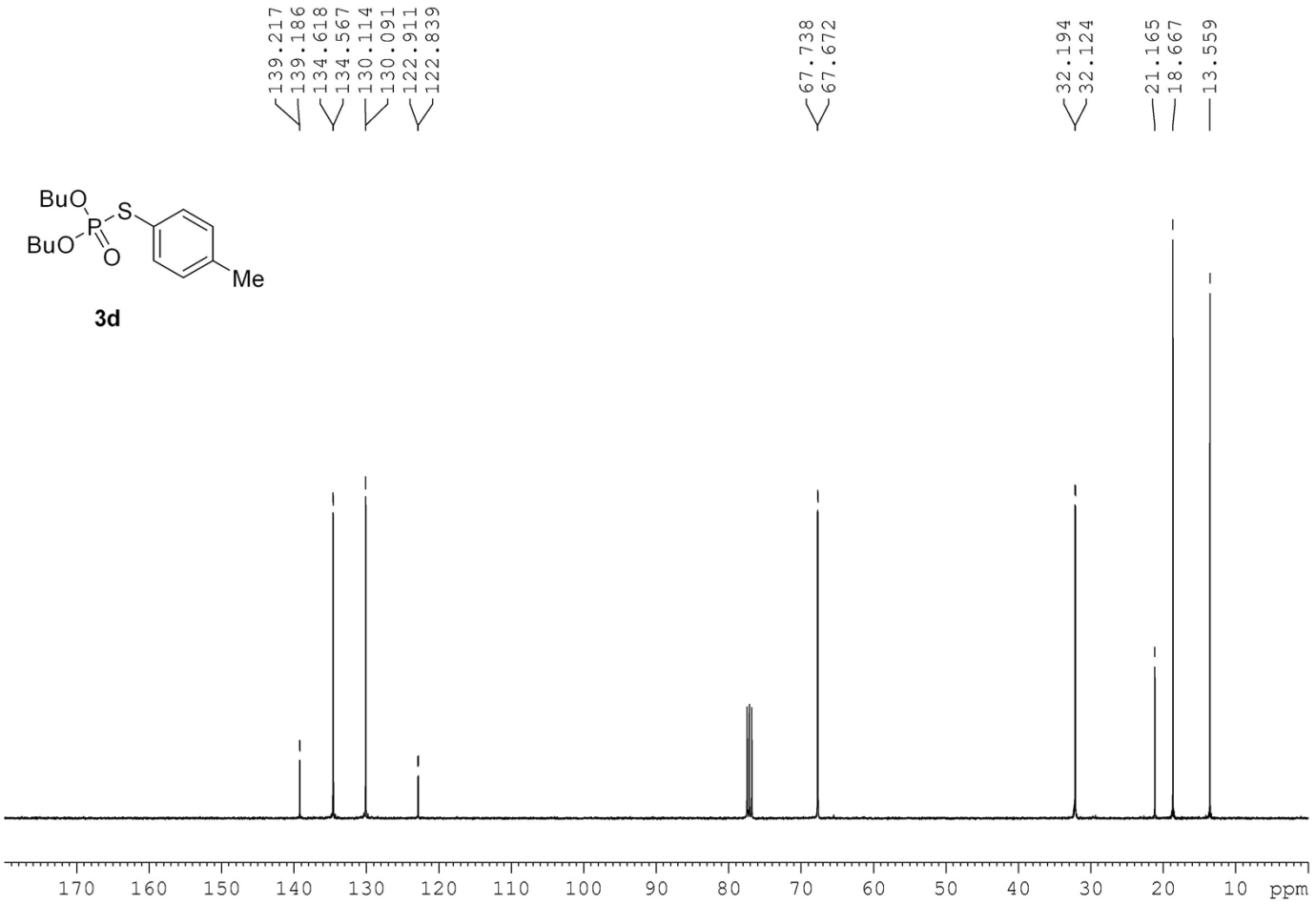
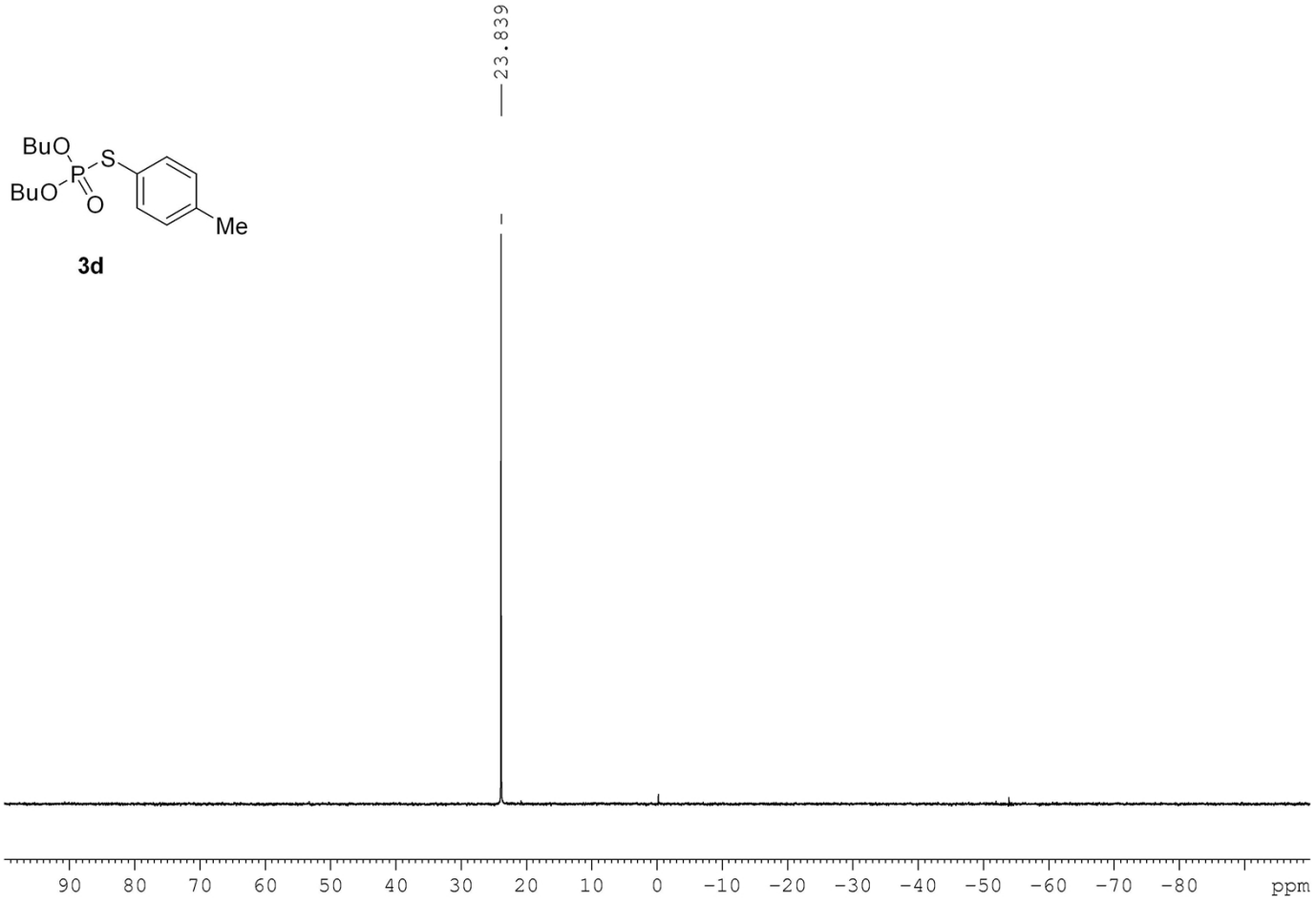
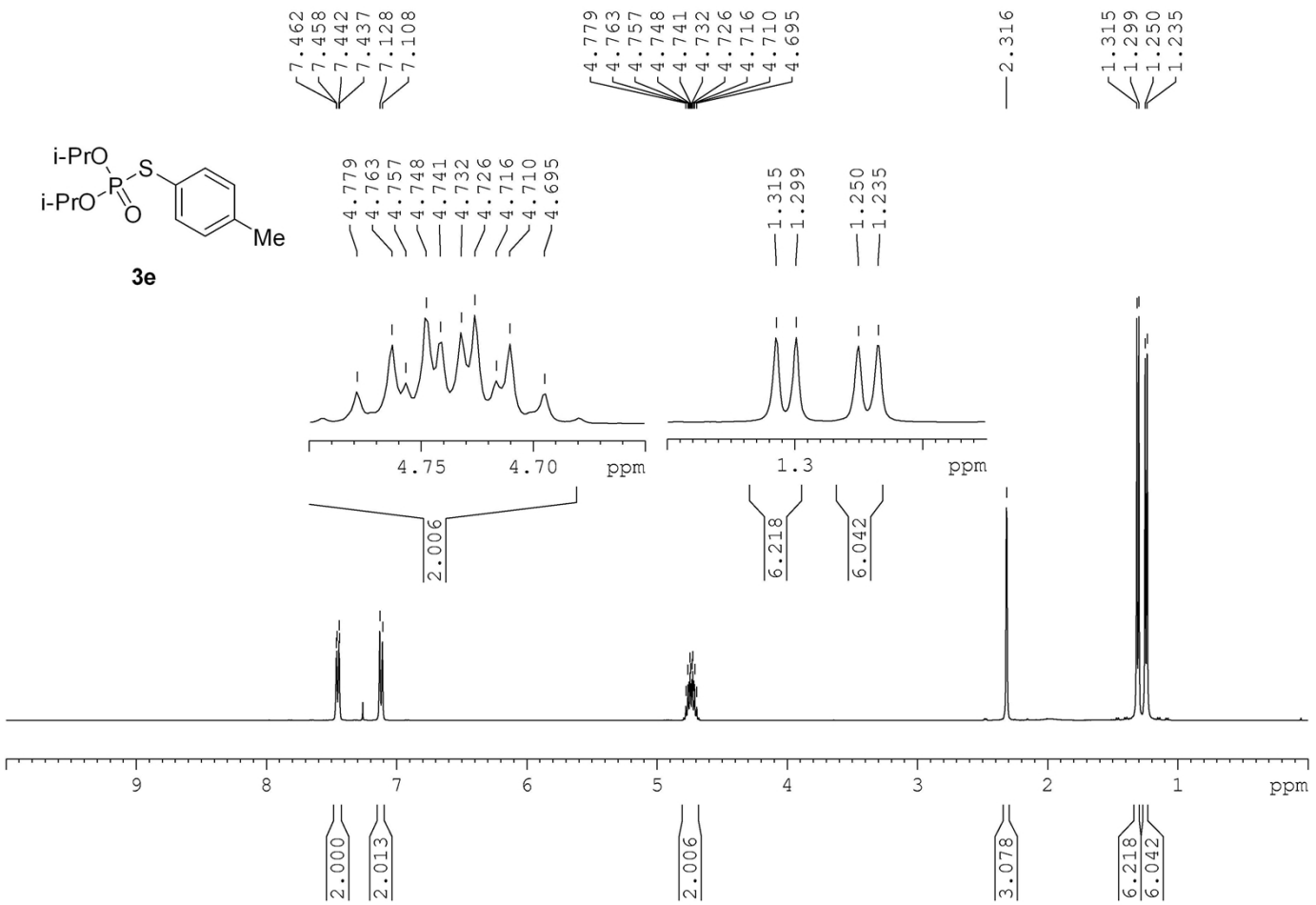


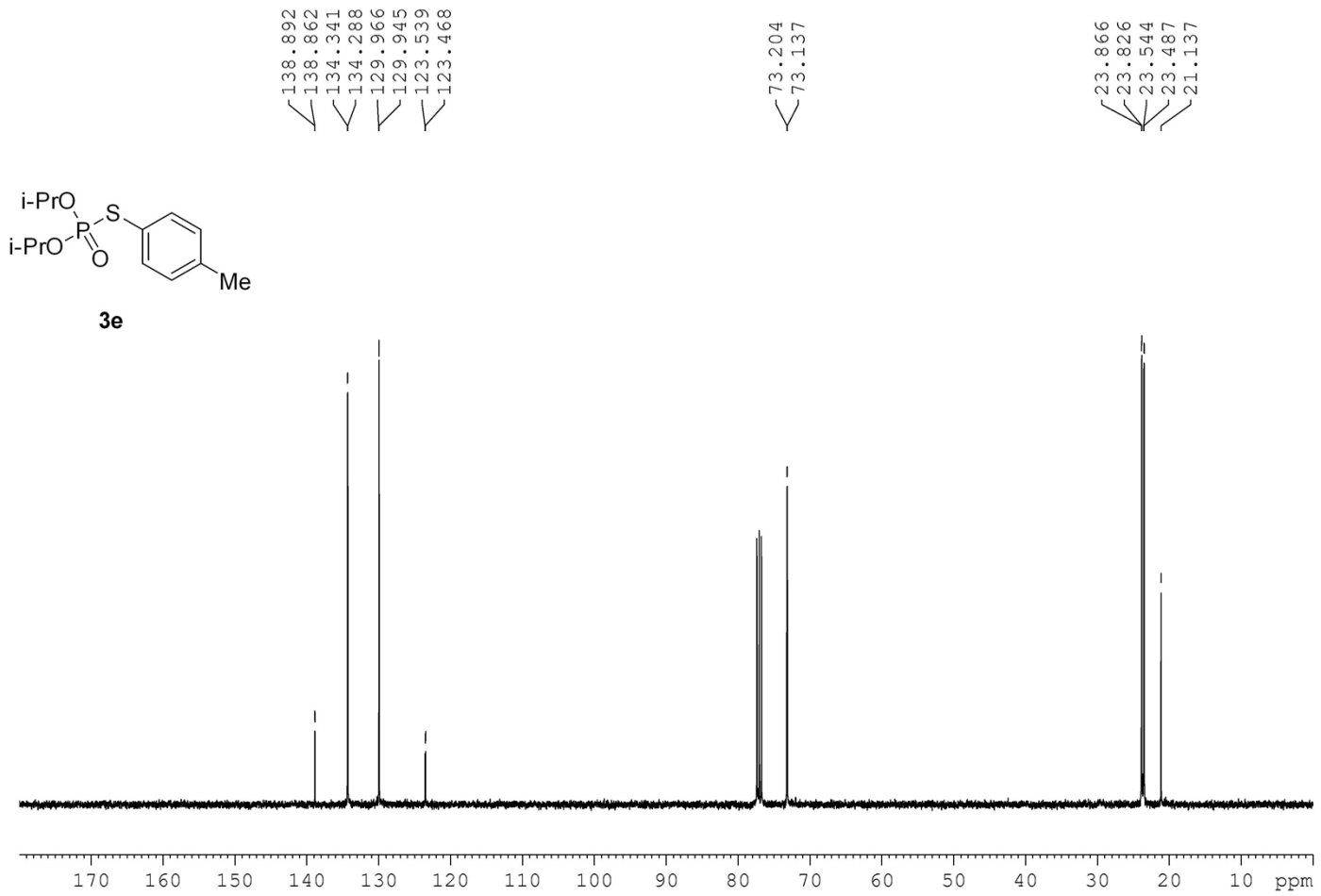
^{13}C NMR spectrum of compound **3d**



^{31}P NMR spectrum of compound **3d**



^{1}H NMR spectrum of compound **3e**



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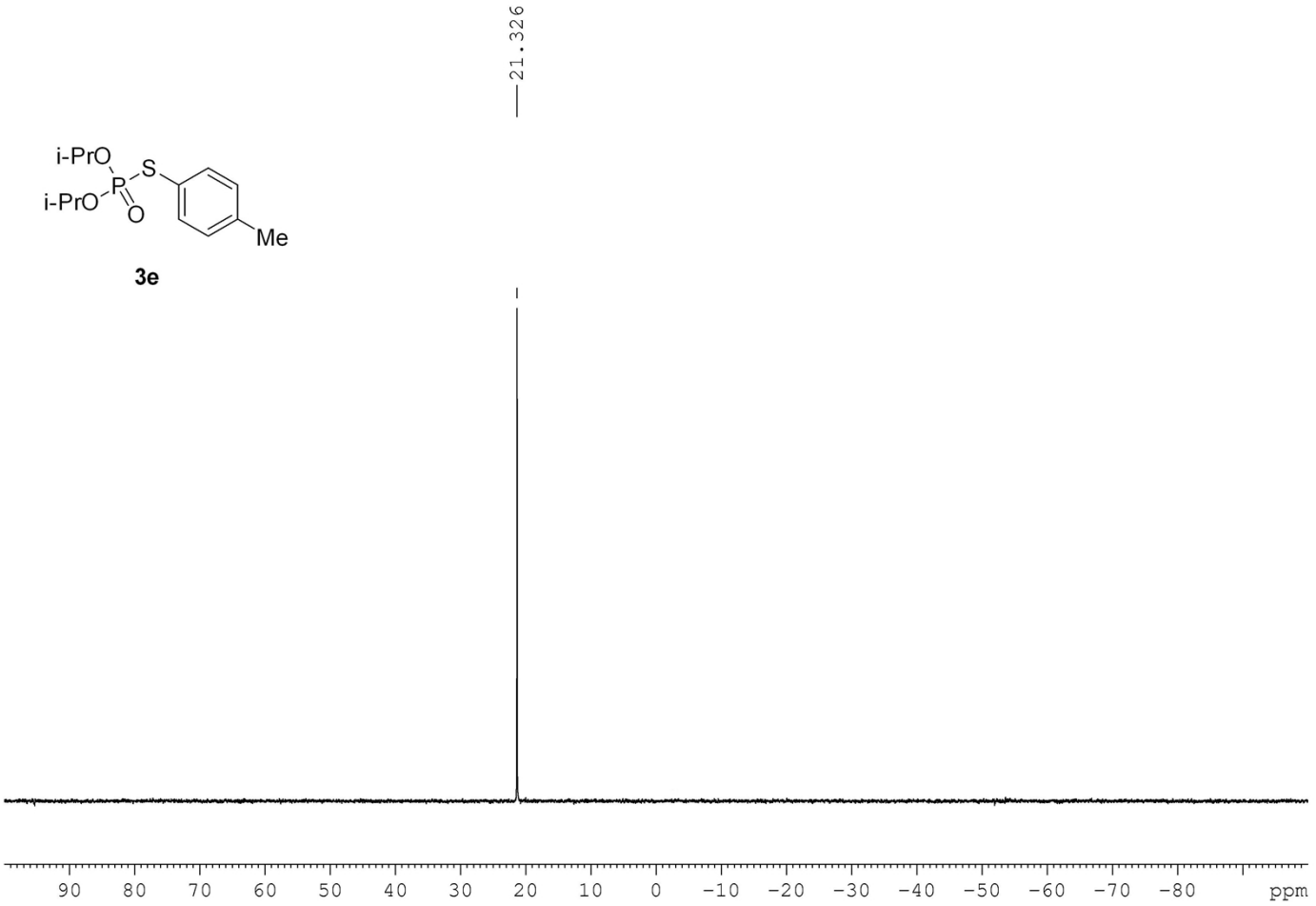

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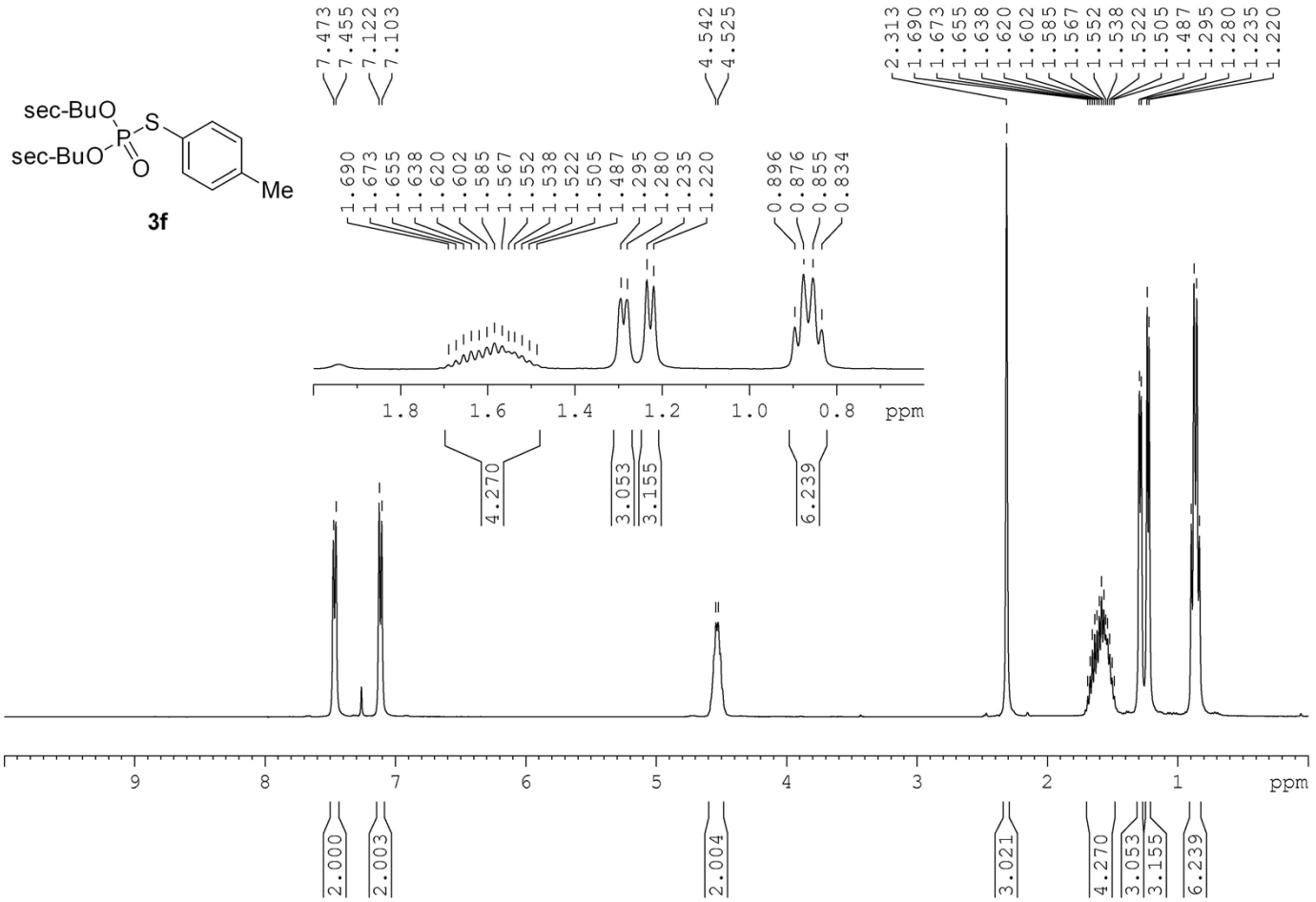

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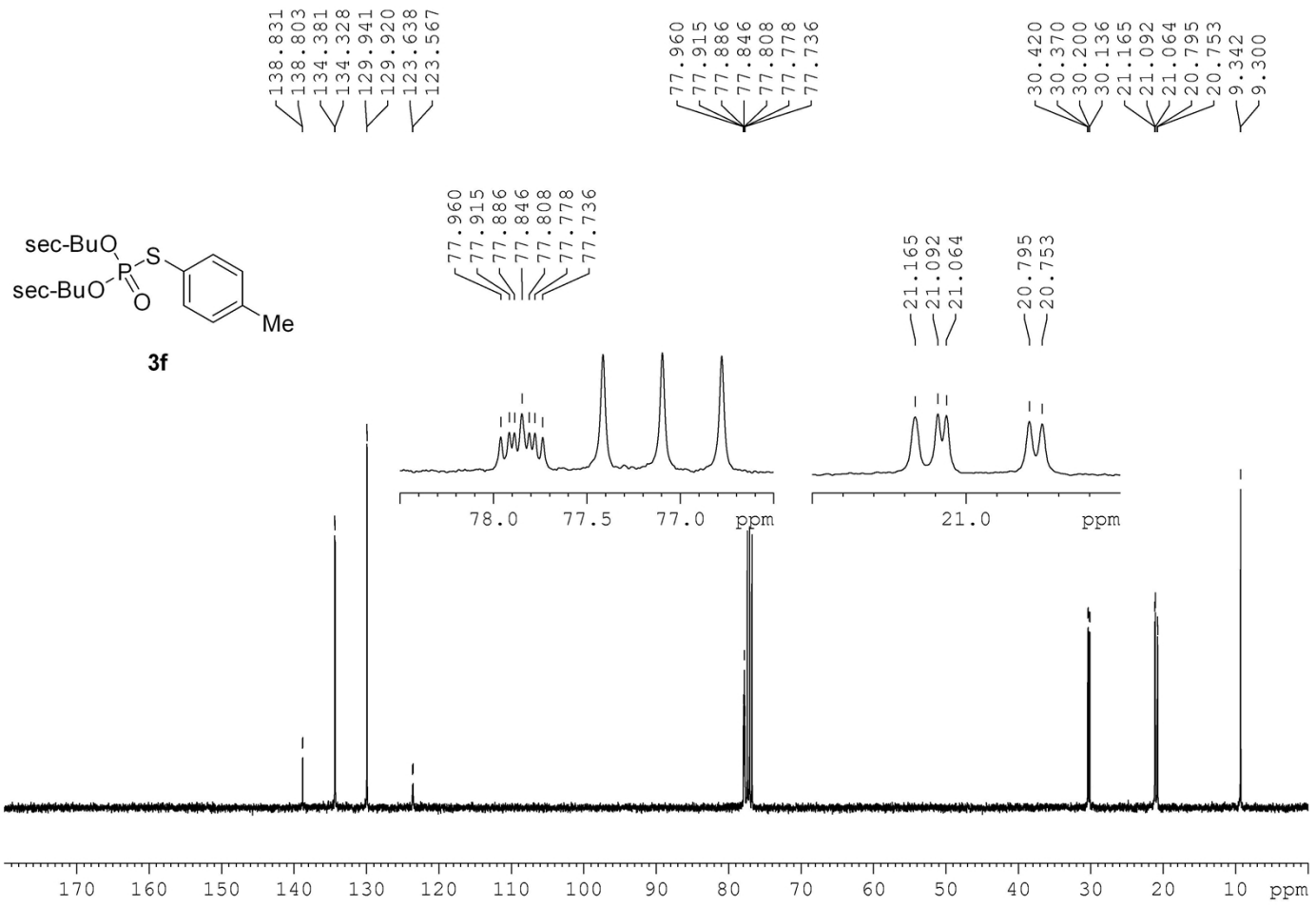
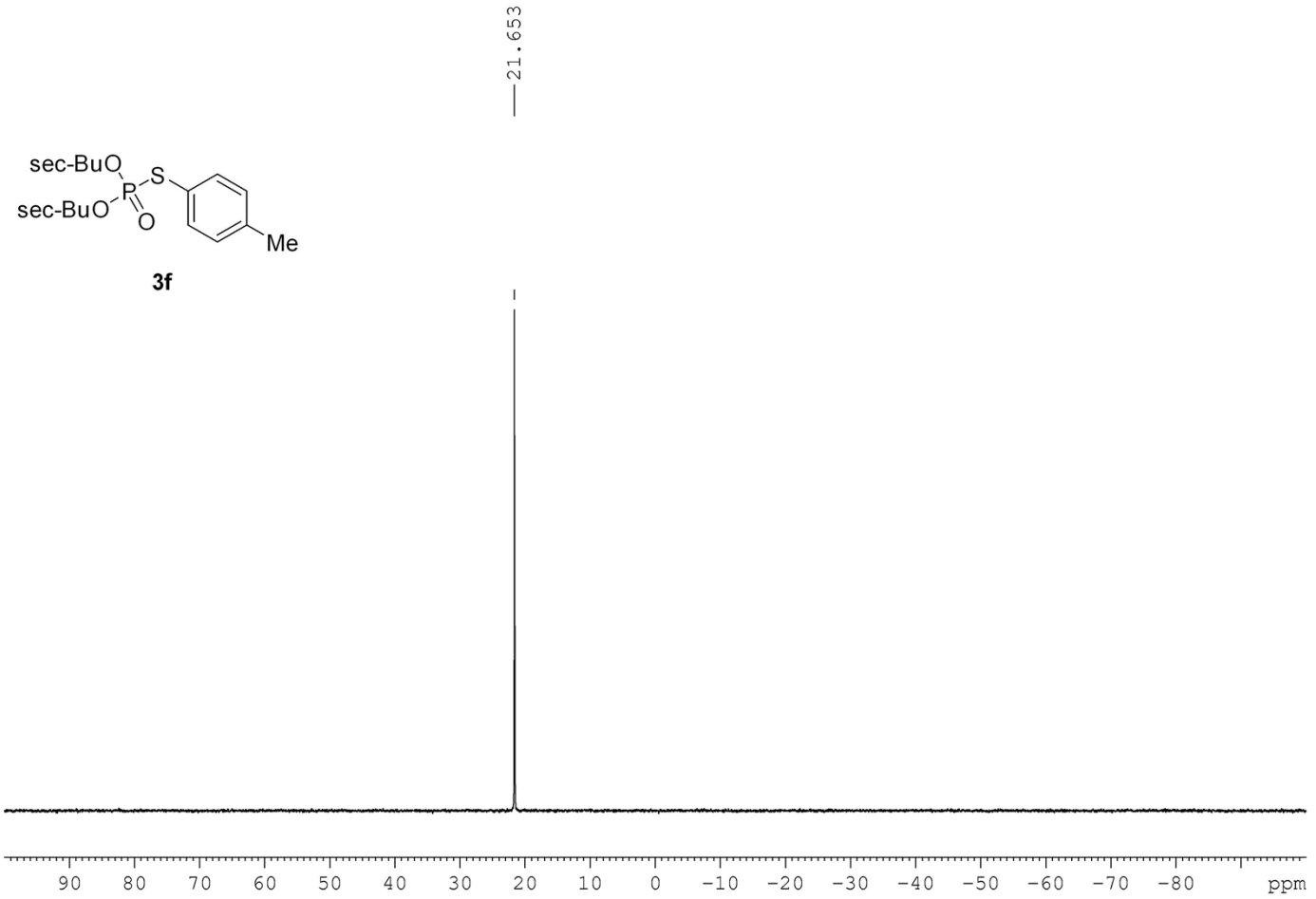
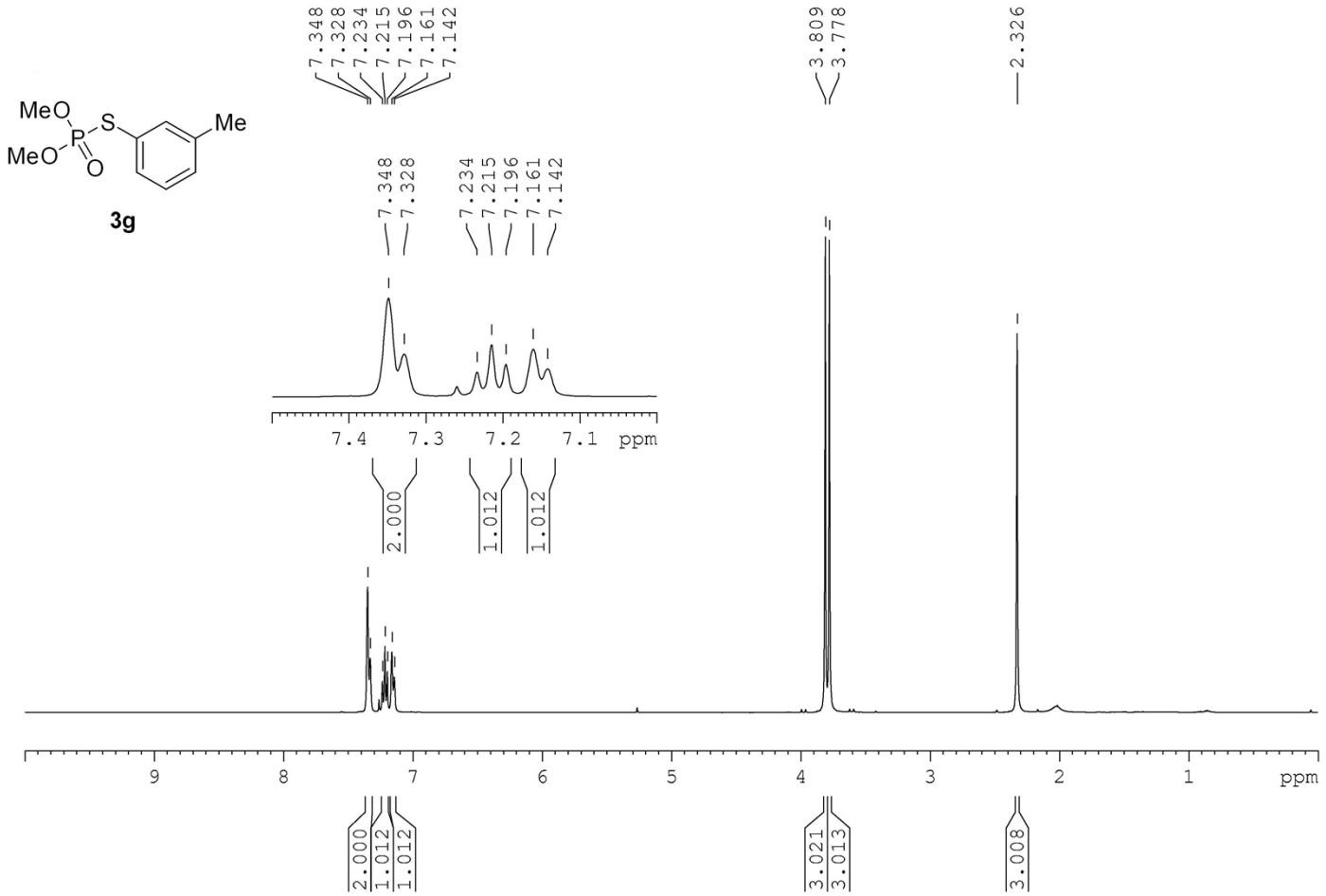


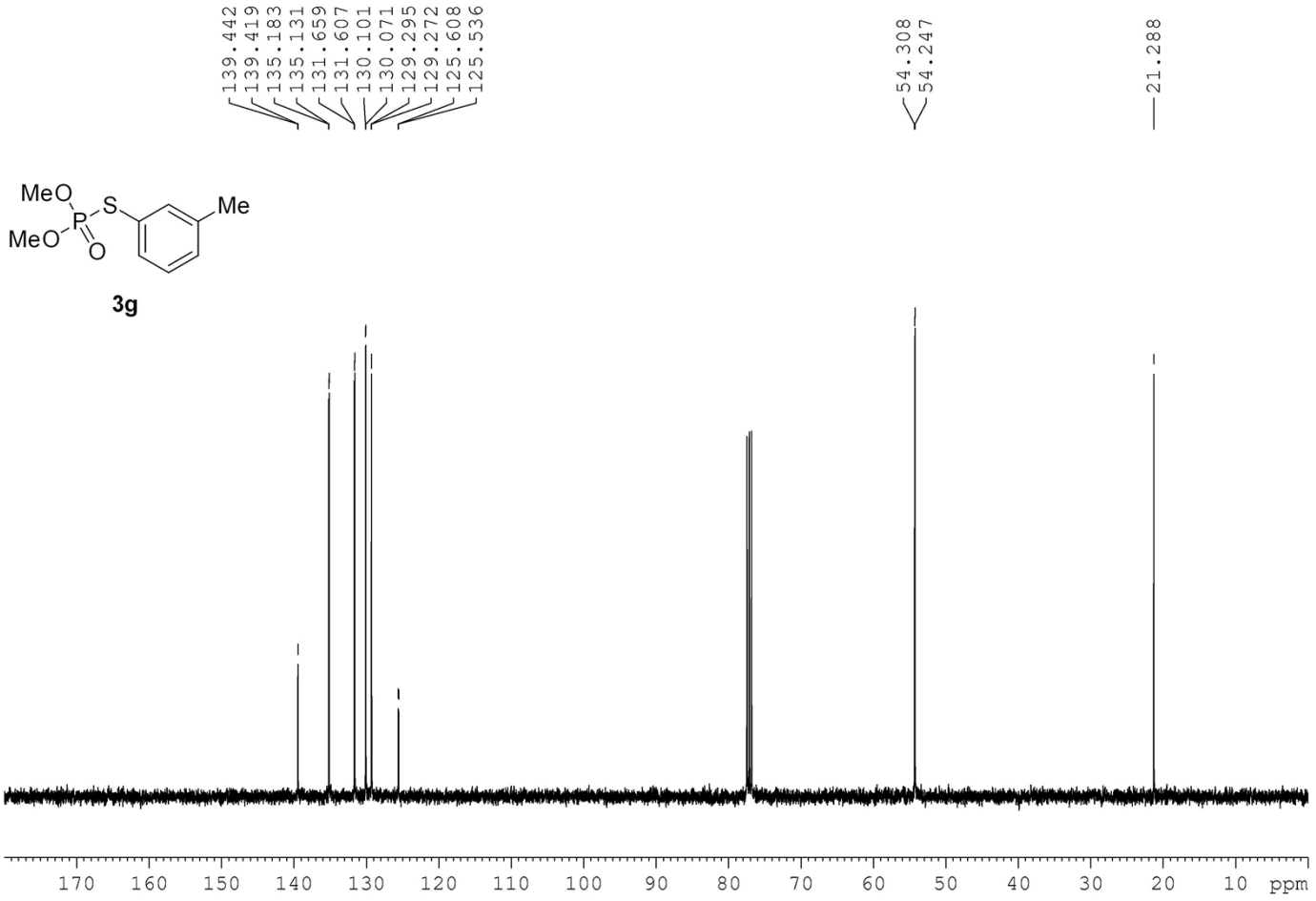
^{13}C NMR spectrum of compound **3f**



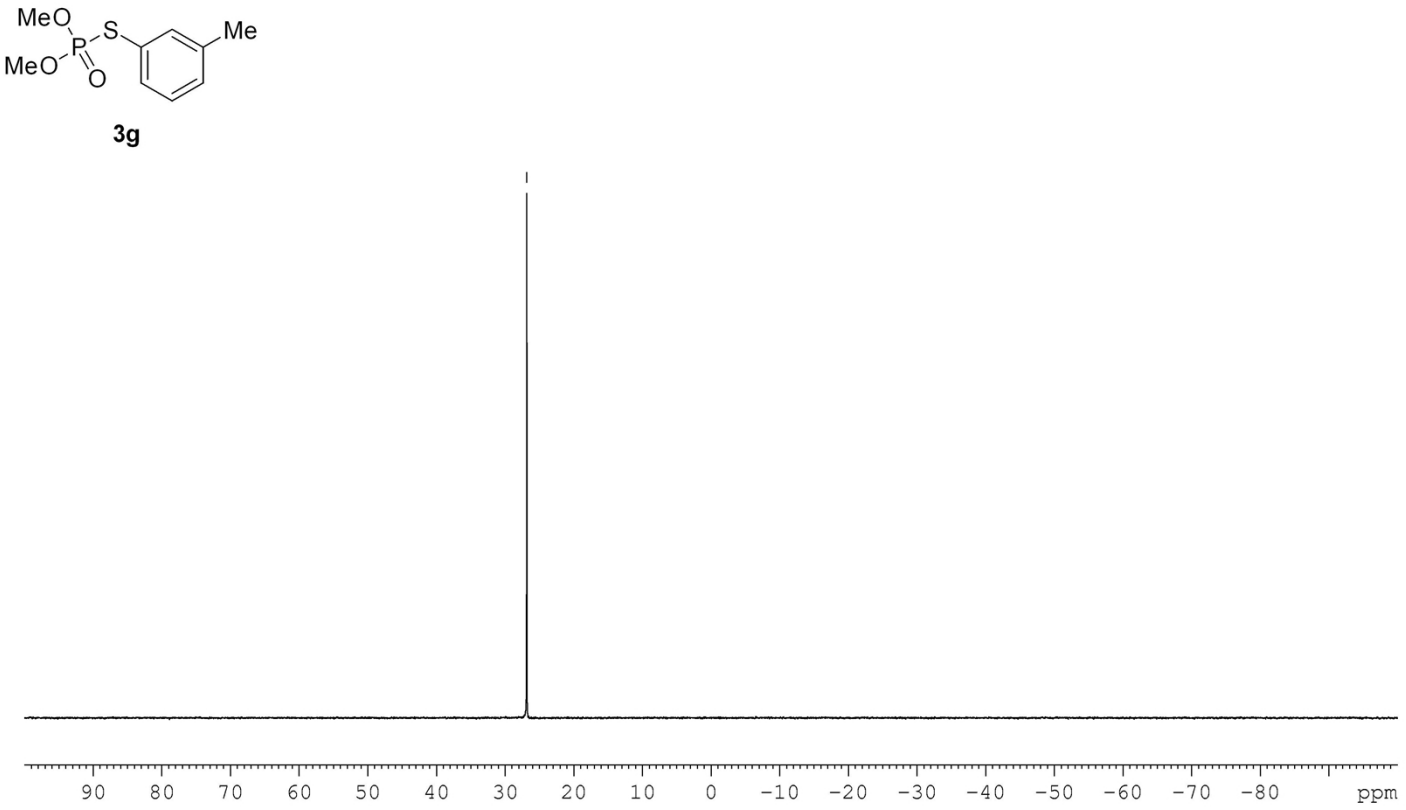
^{31}P NMR spectrum of compound **3f**



^{1}H NMR spectrum of compound **3g**

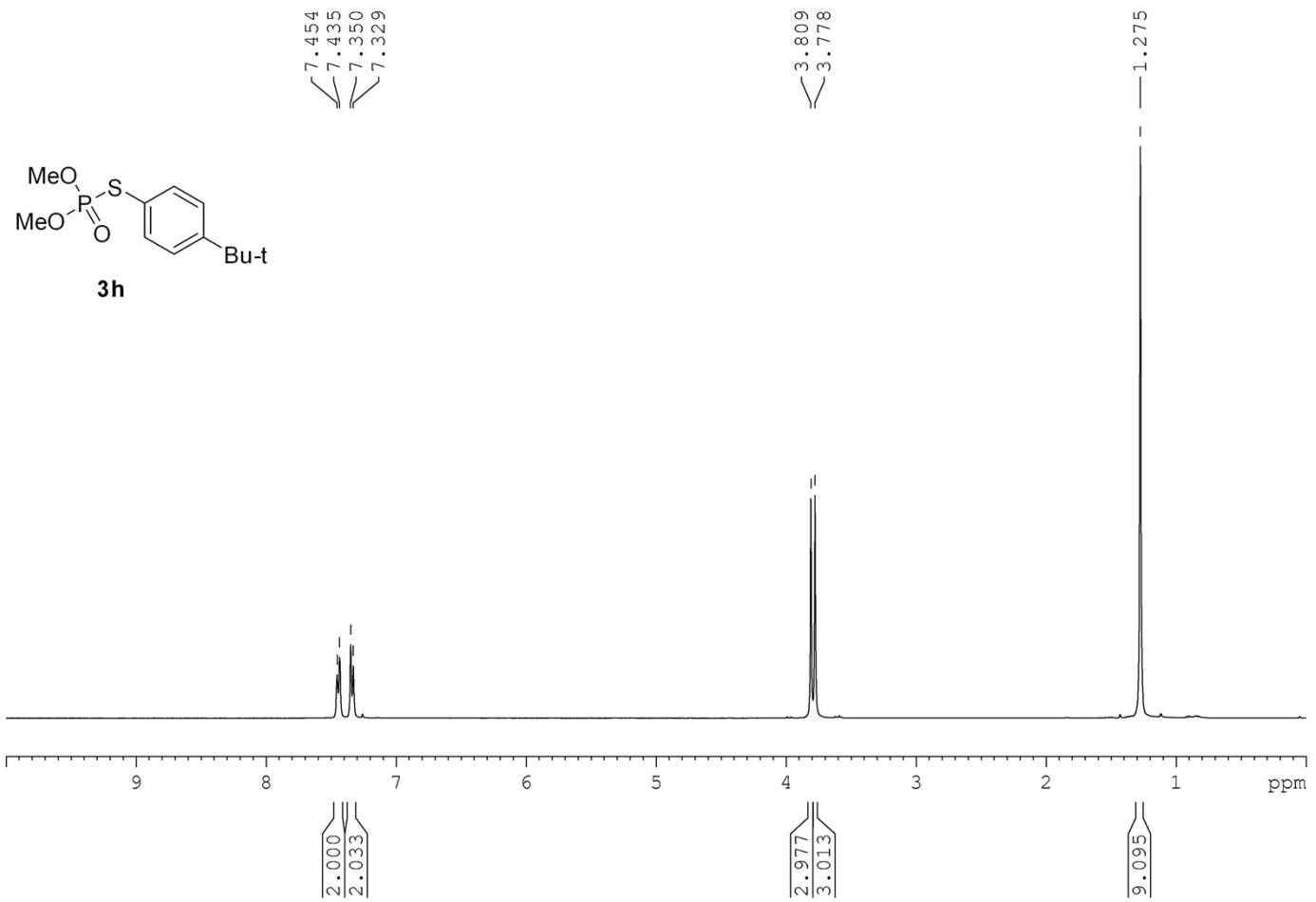


^{13}C NMR spectrum of compound **3g**

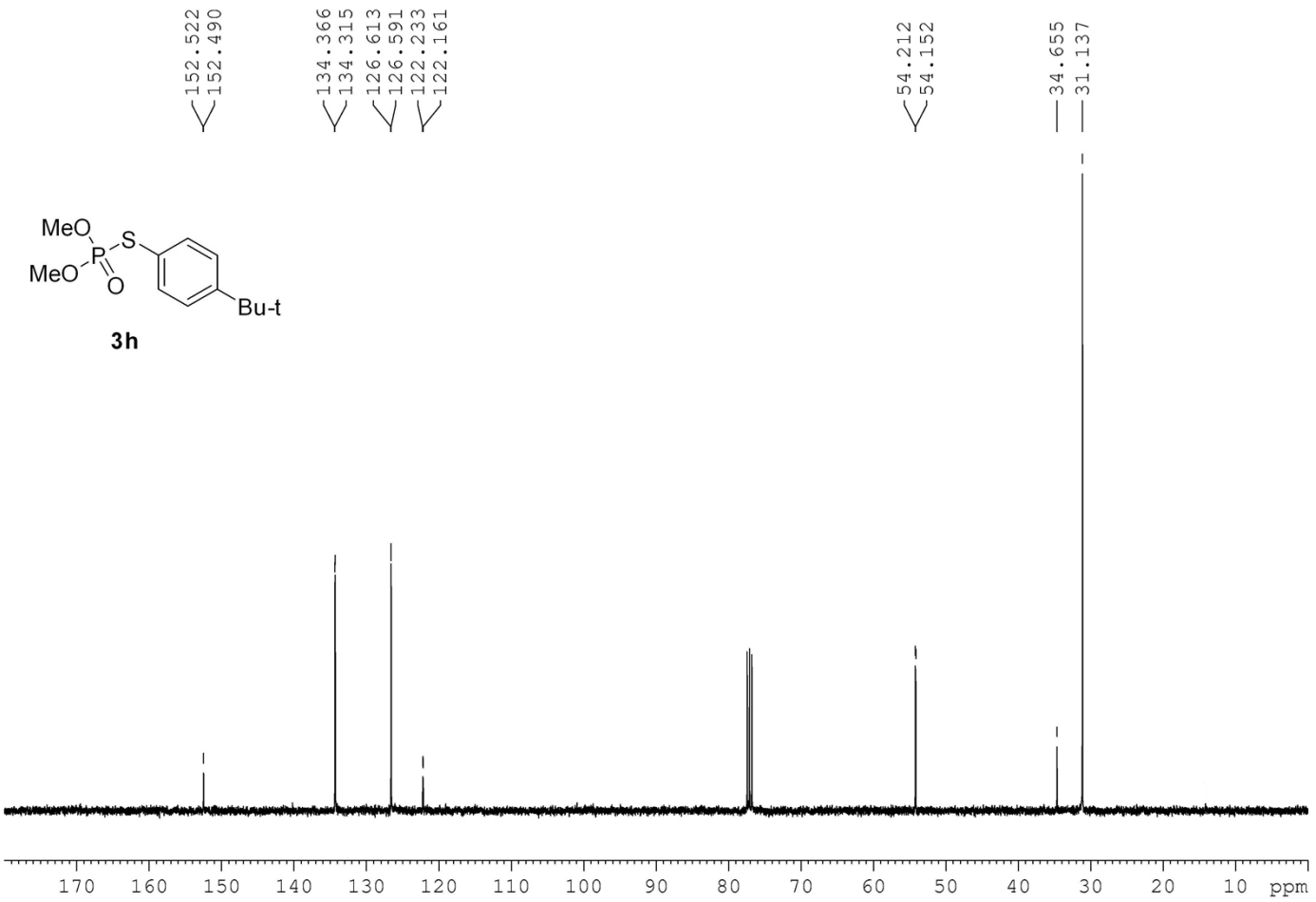


3g

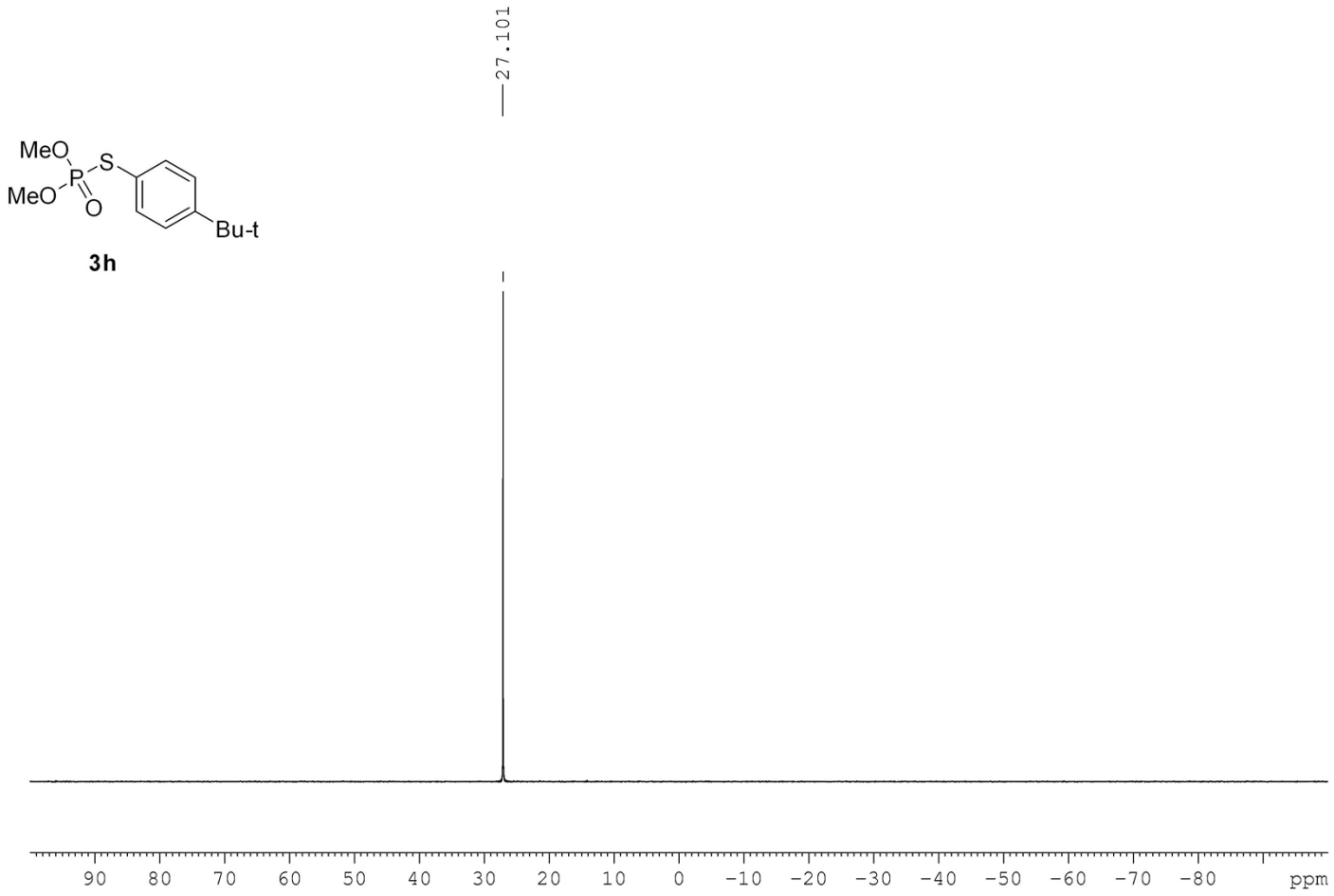
^{31}P NMR spectrum of compound **3g**



^{1}H NMR spectrum of compound **3h**



^{13}C NMR spectrum of compound **3h**



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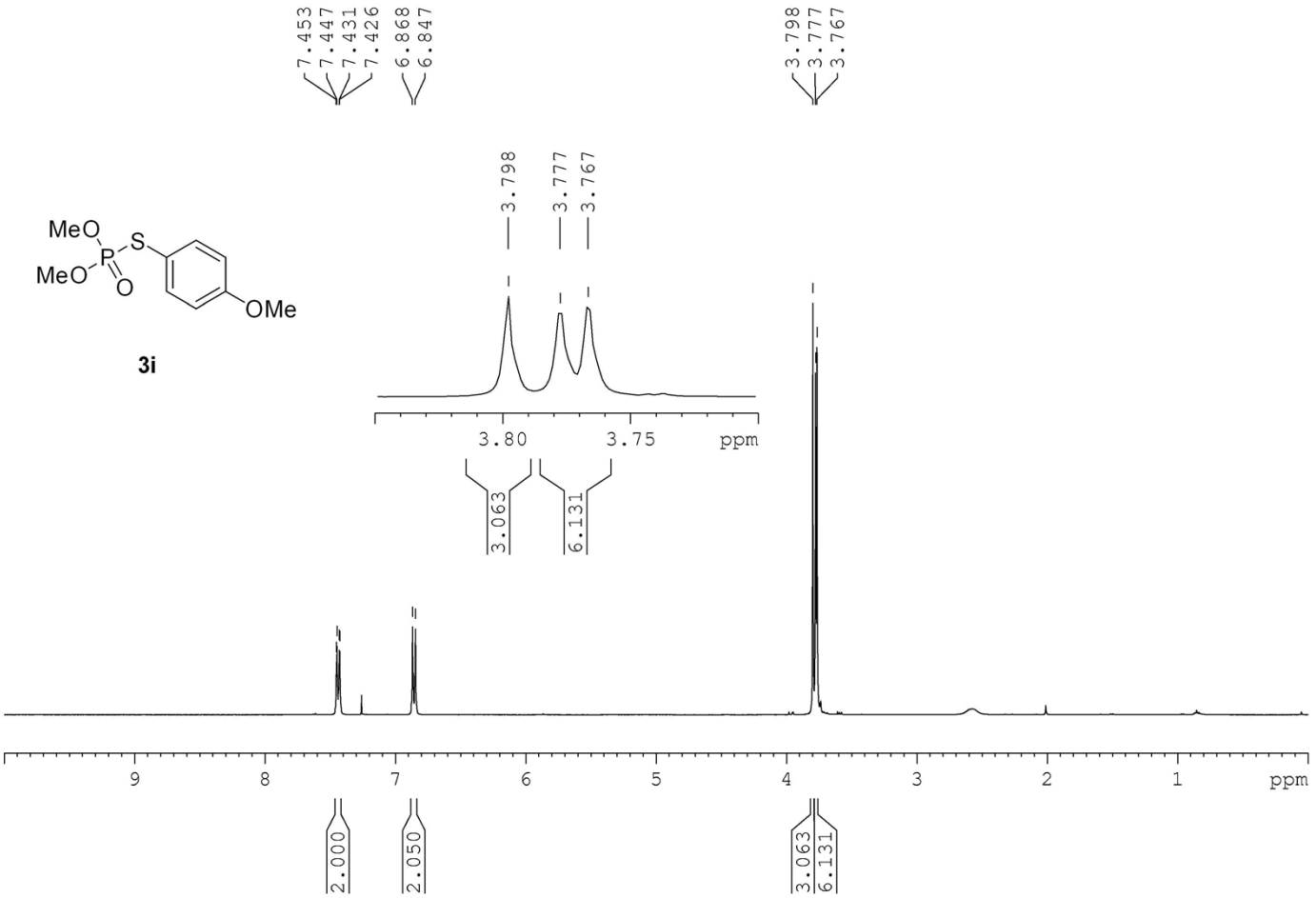
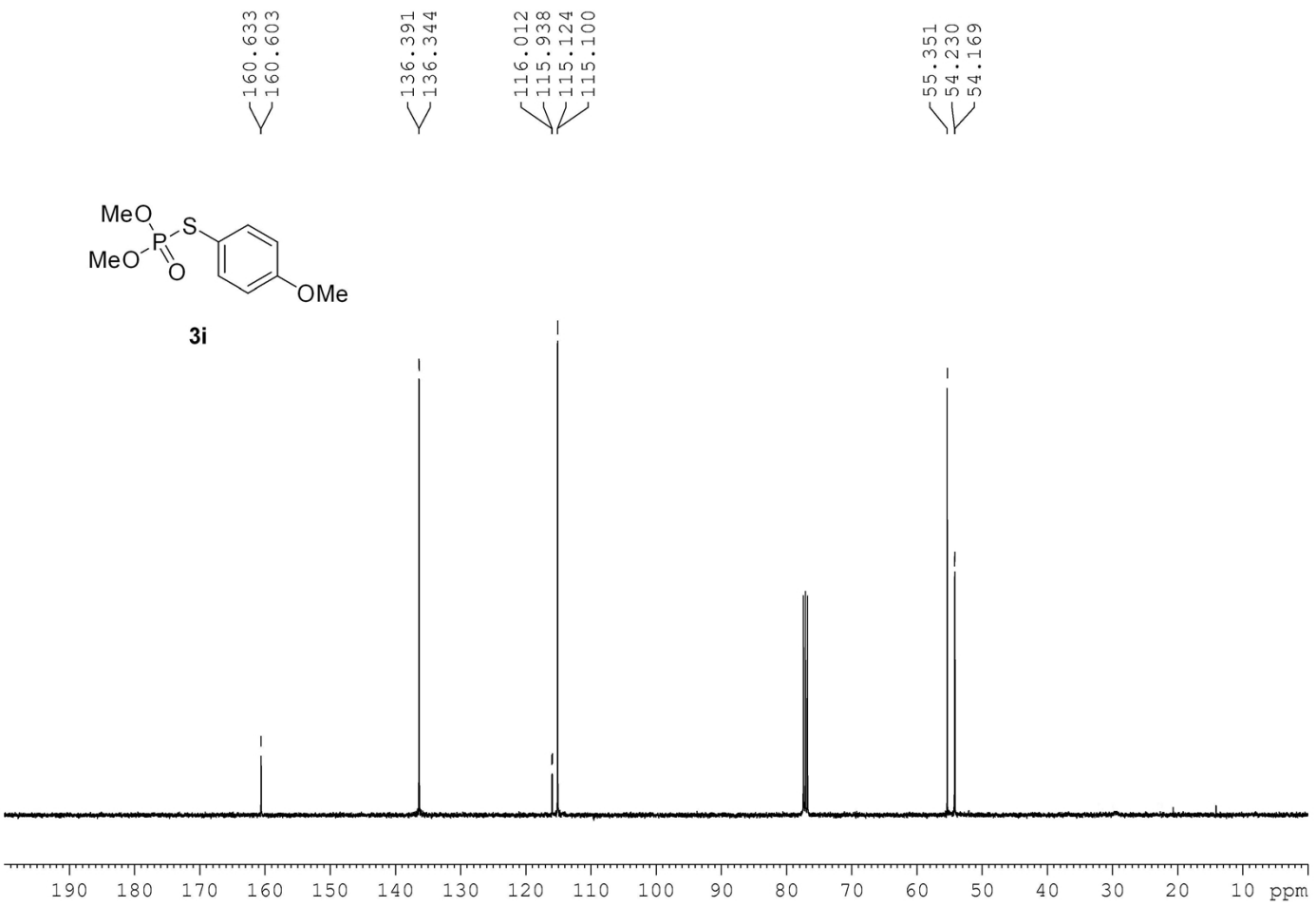
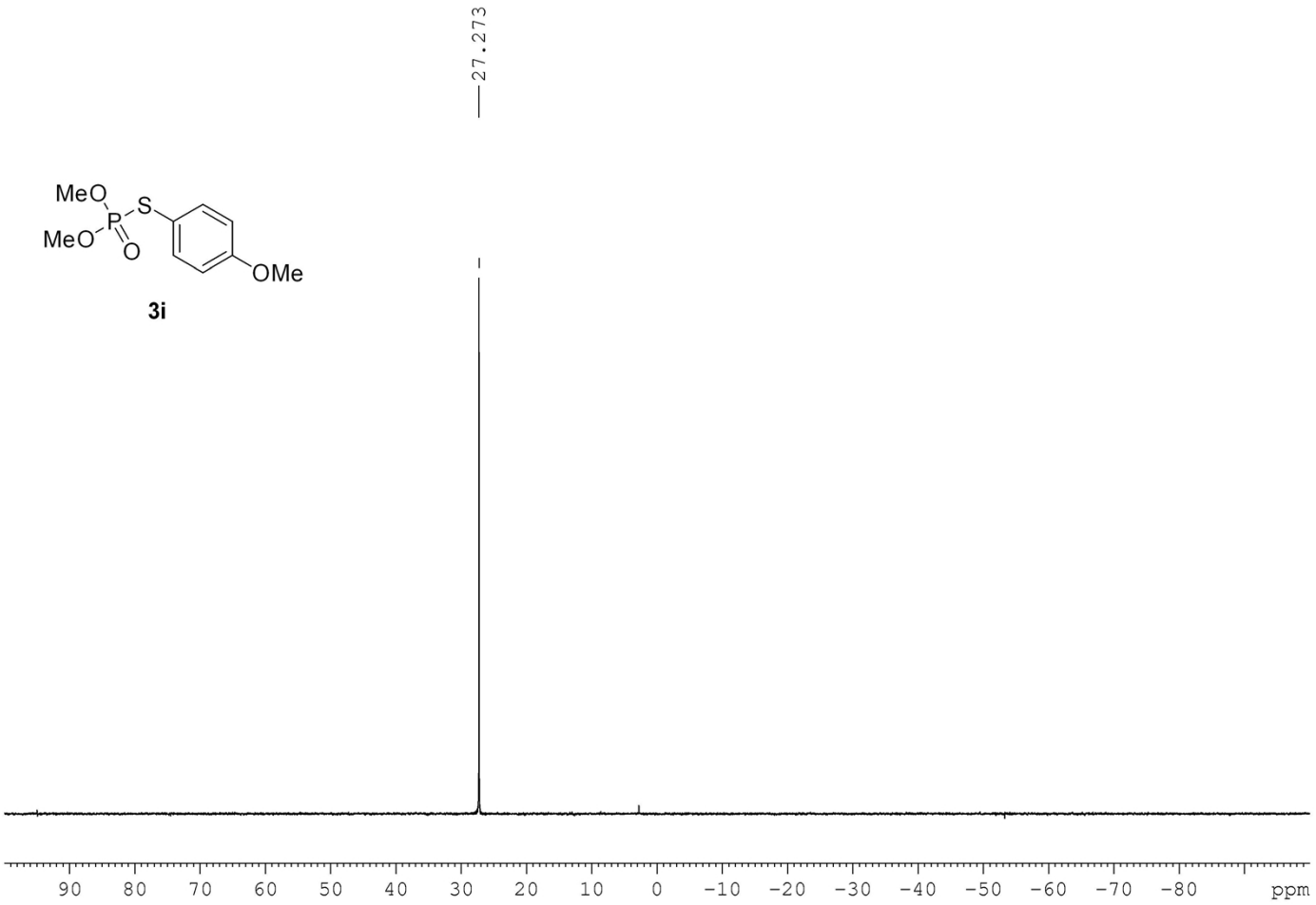


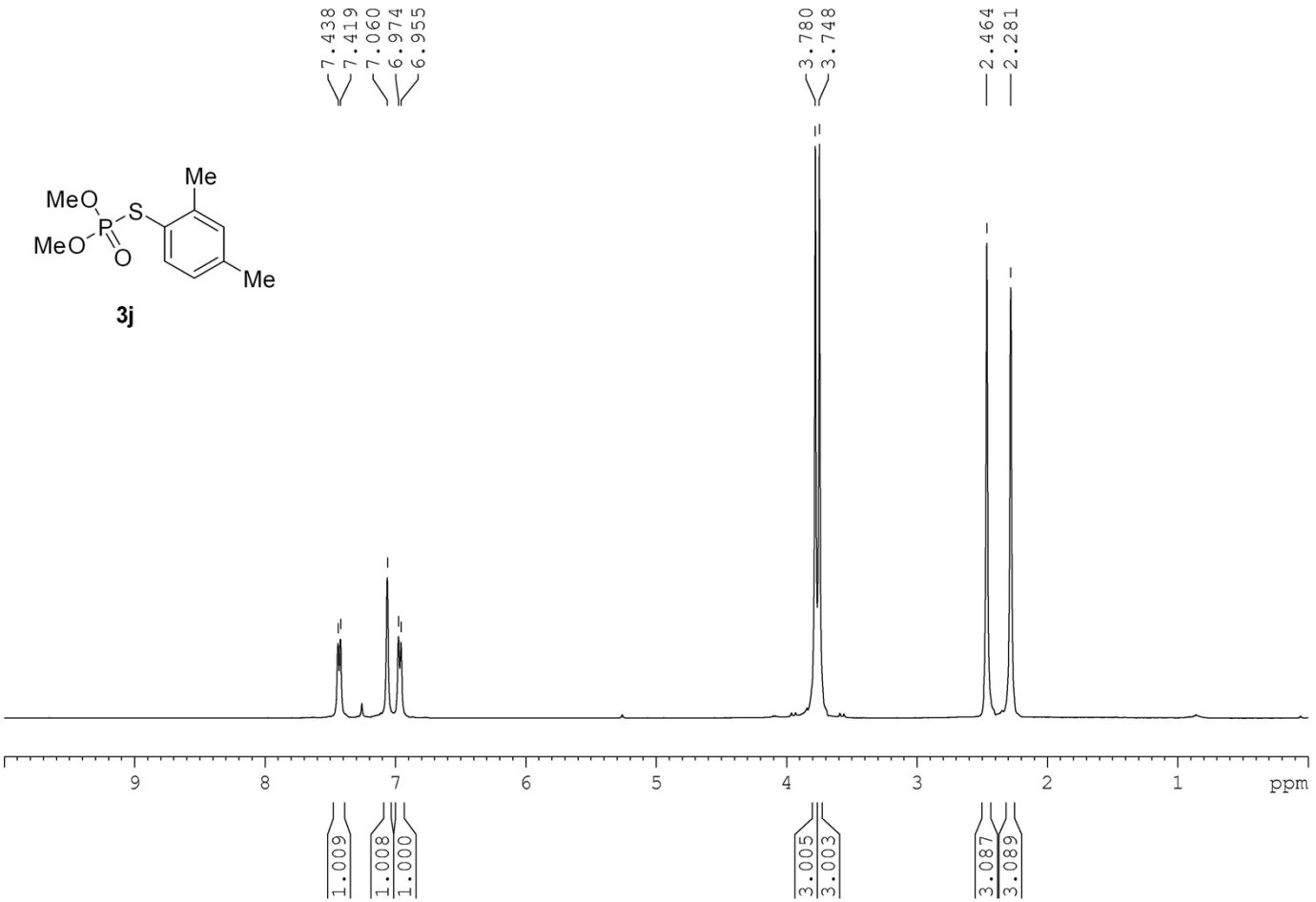
^{1}H NMR spectrum of compound **3i**



^{13}C NMR spectrum of compound **3i**



^{31}P NMR spectrum of compound **3i**



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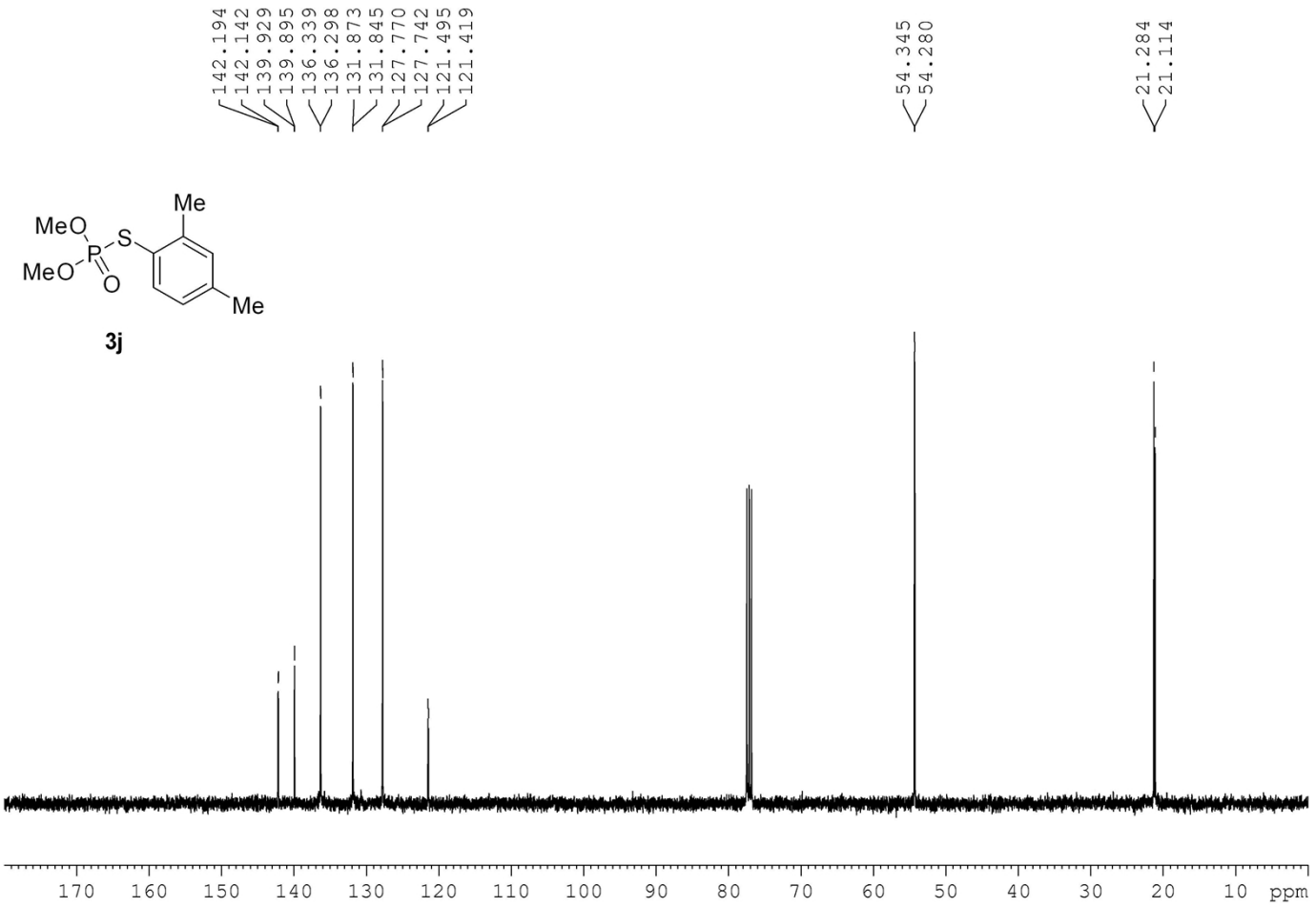

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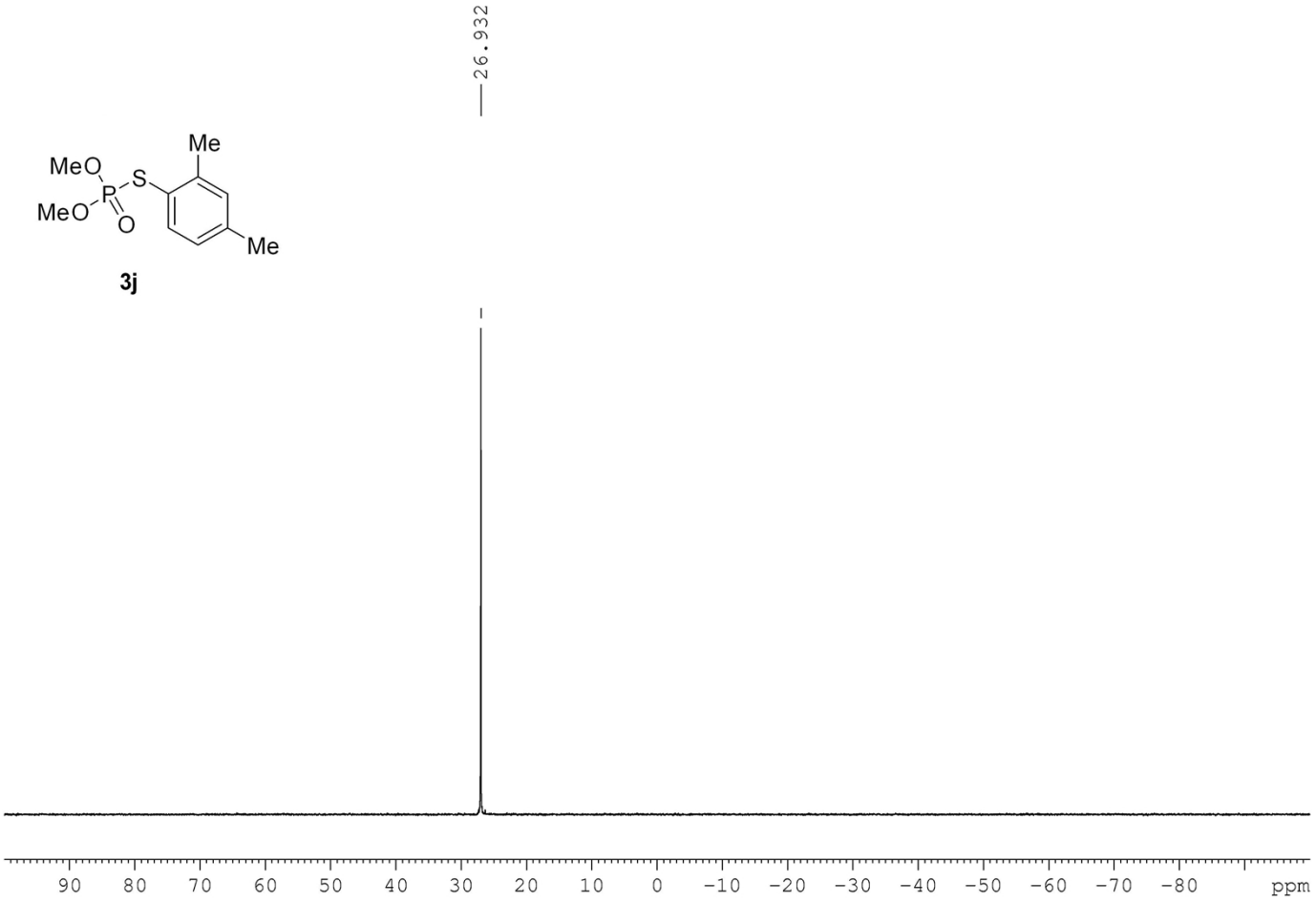
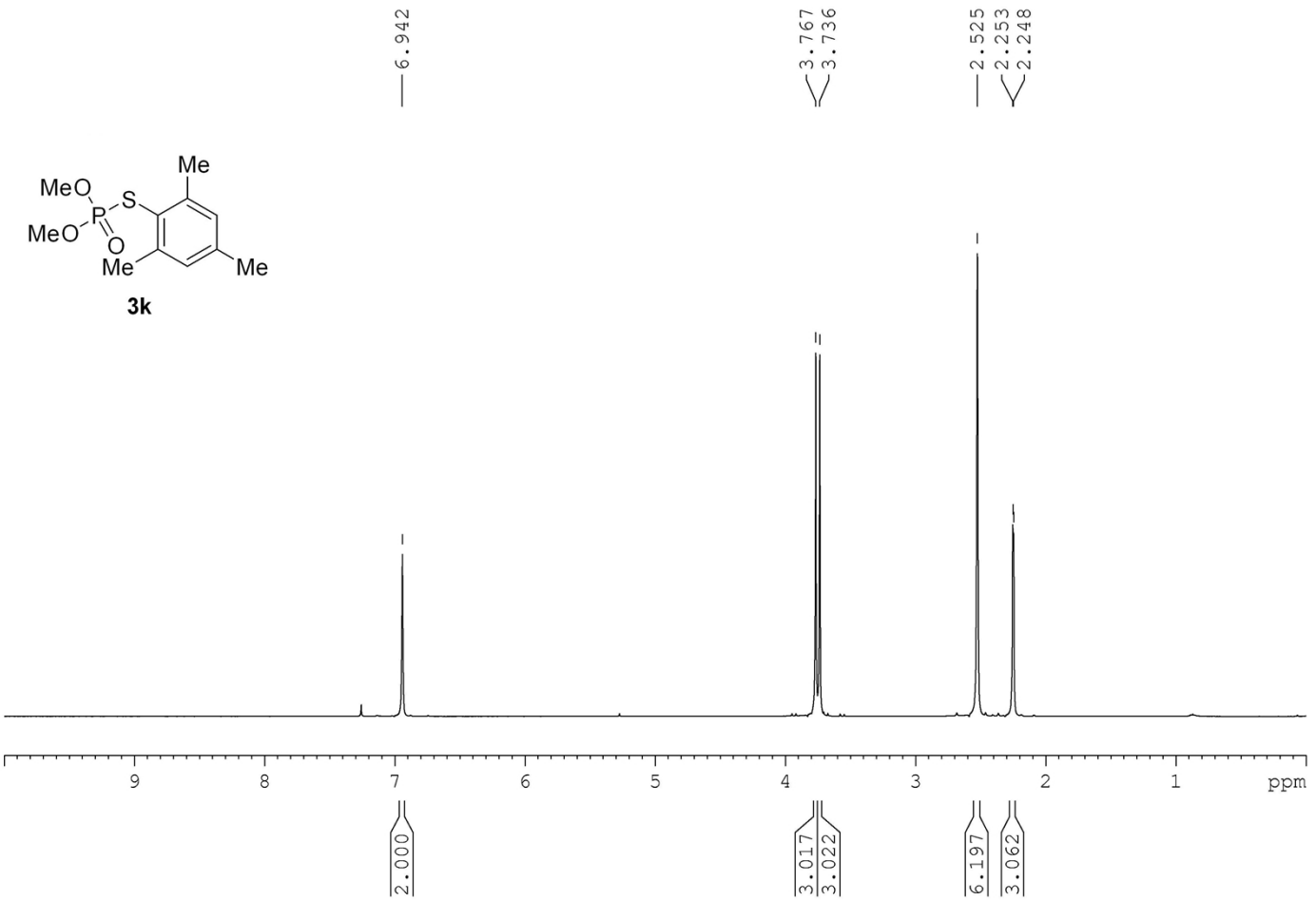
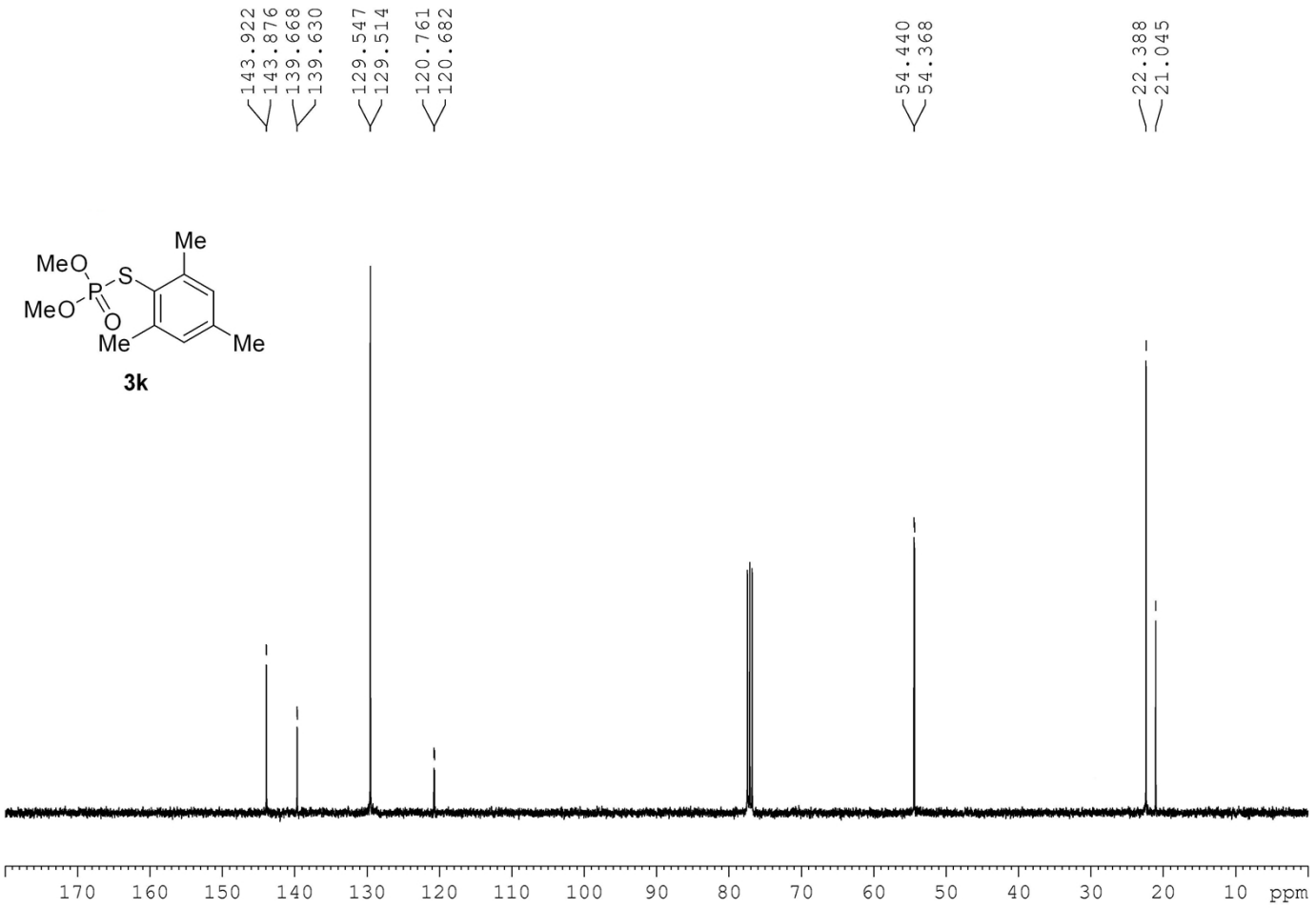


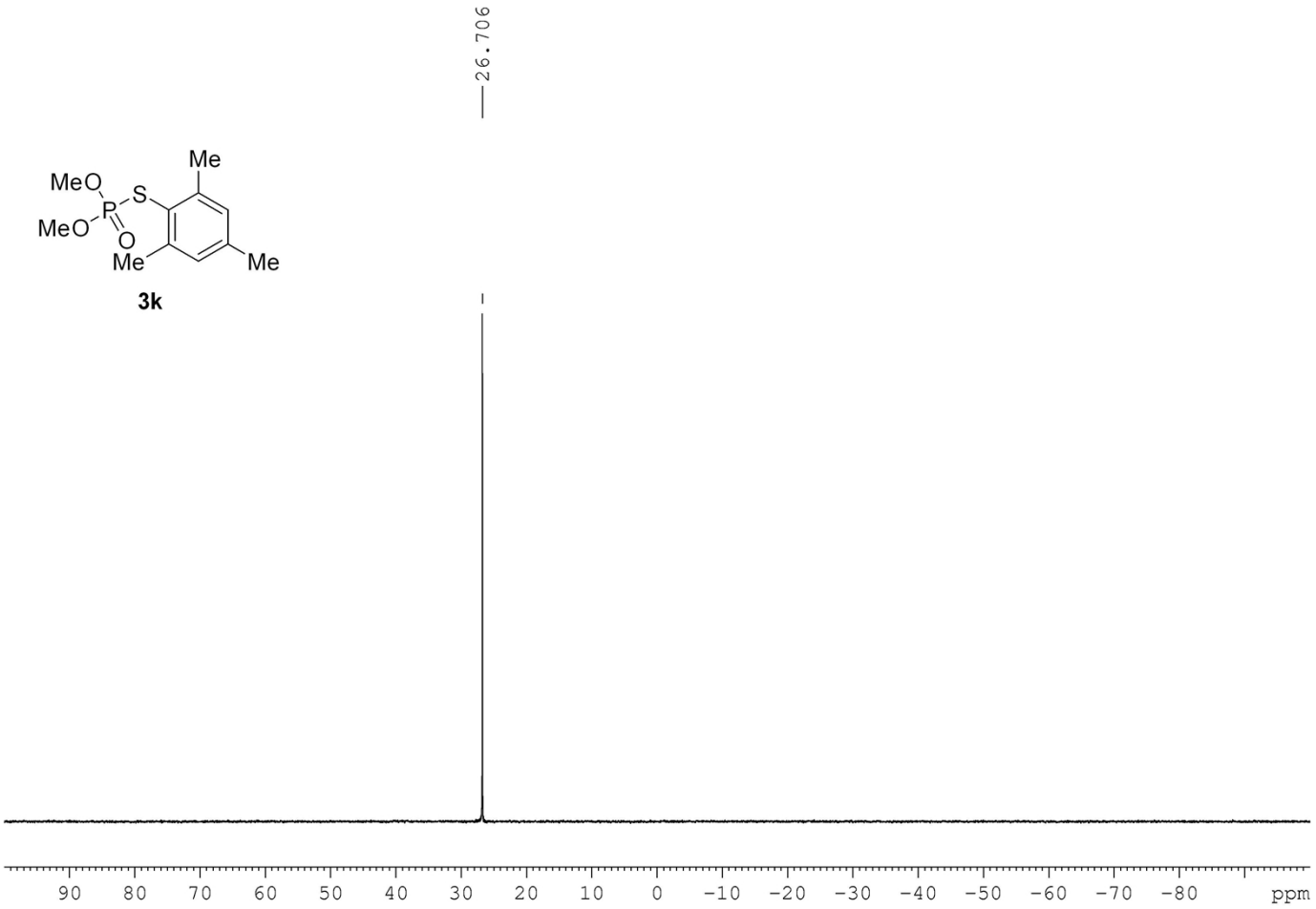
^{31}P NMR spectrum of compound **3j**



^{1}H NMR spectrum of compound **3k**



^{13}C NMR spectrum of compound **3k**



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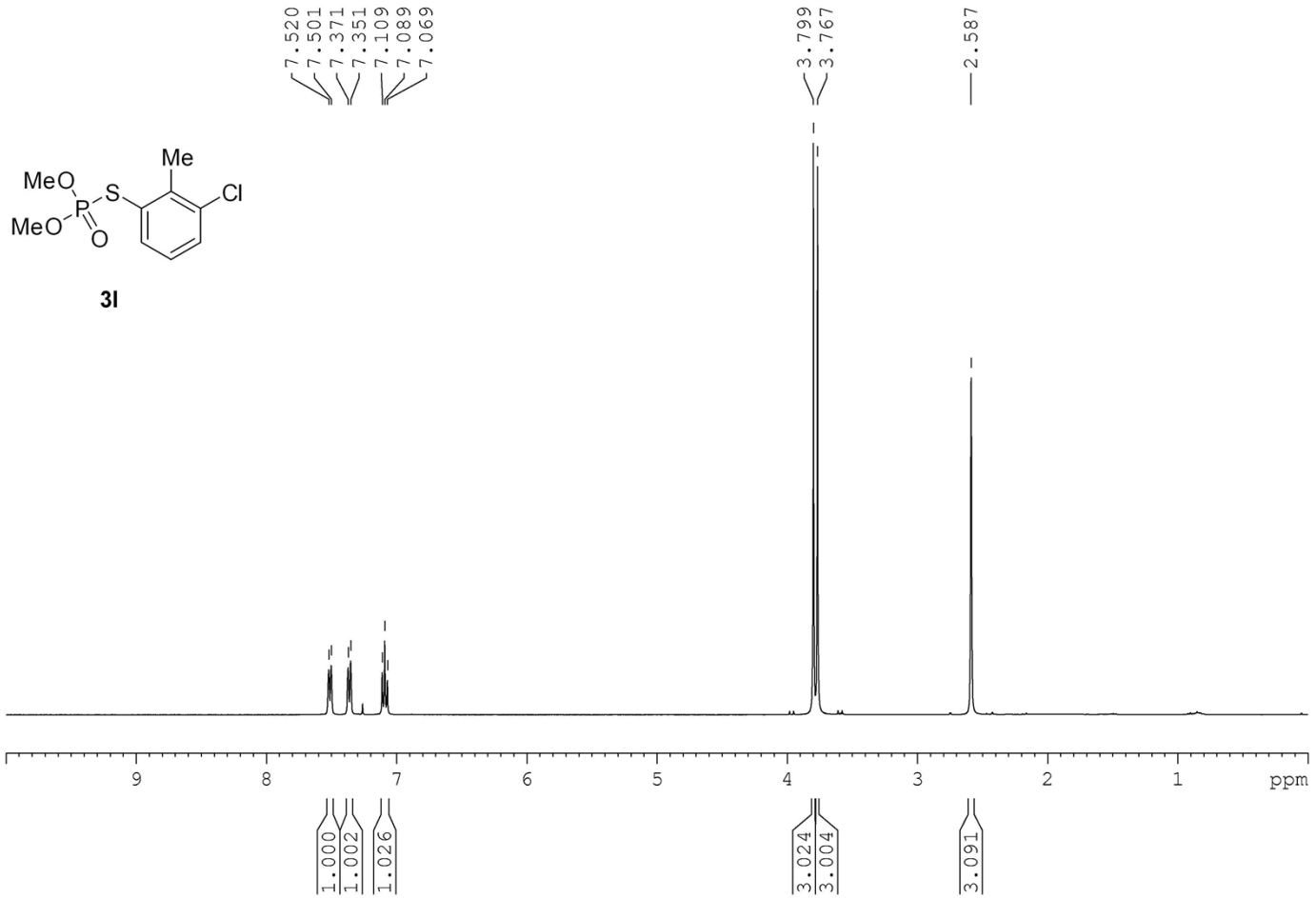
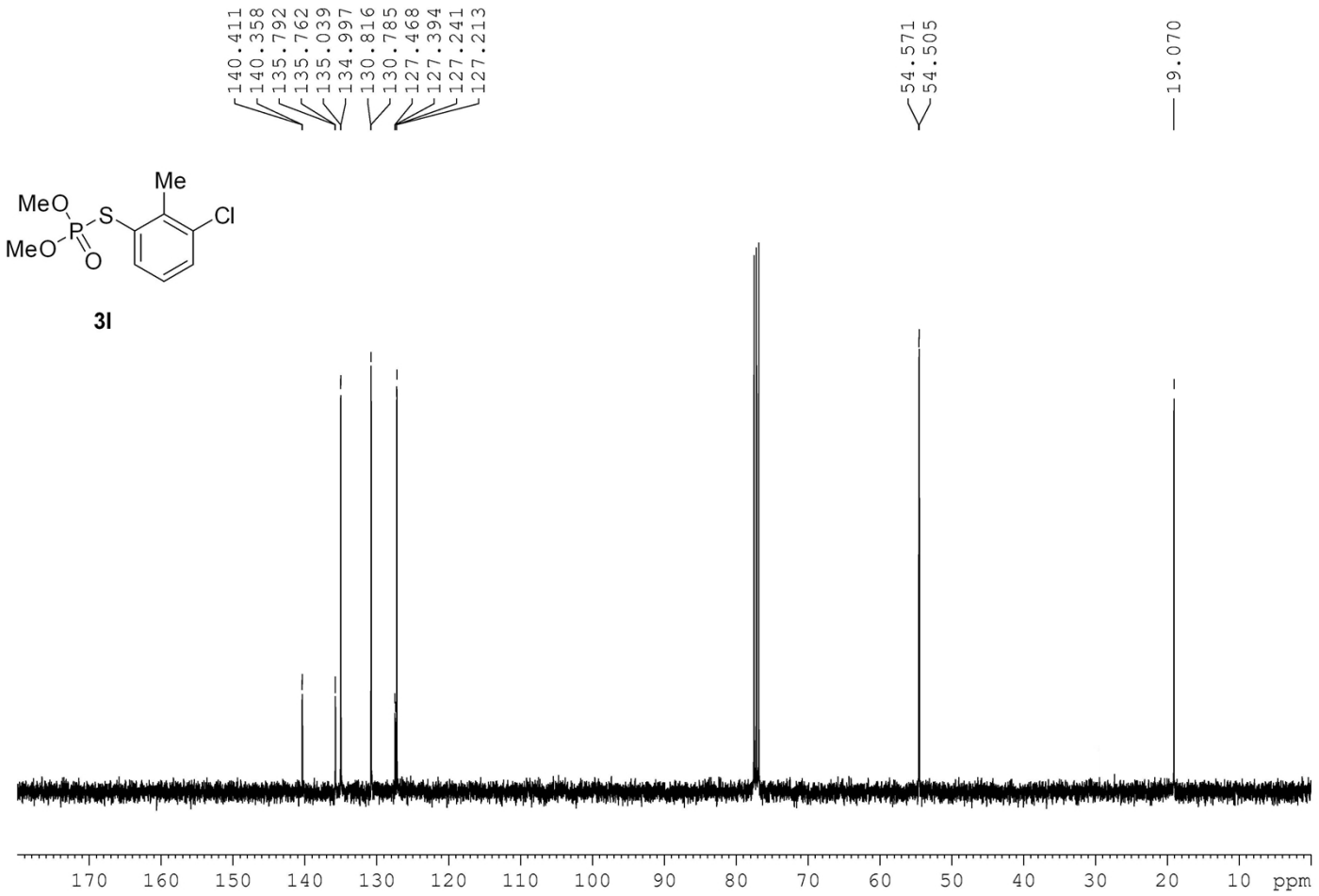
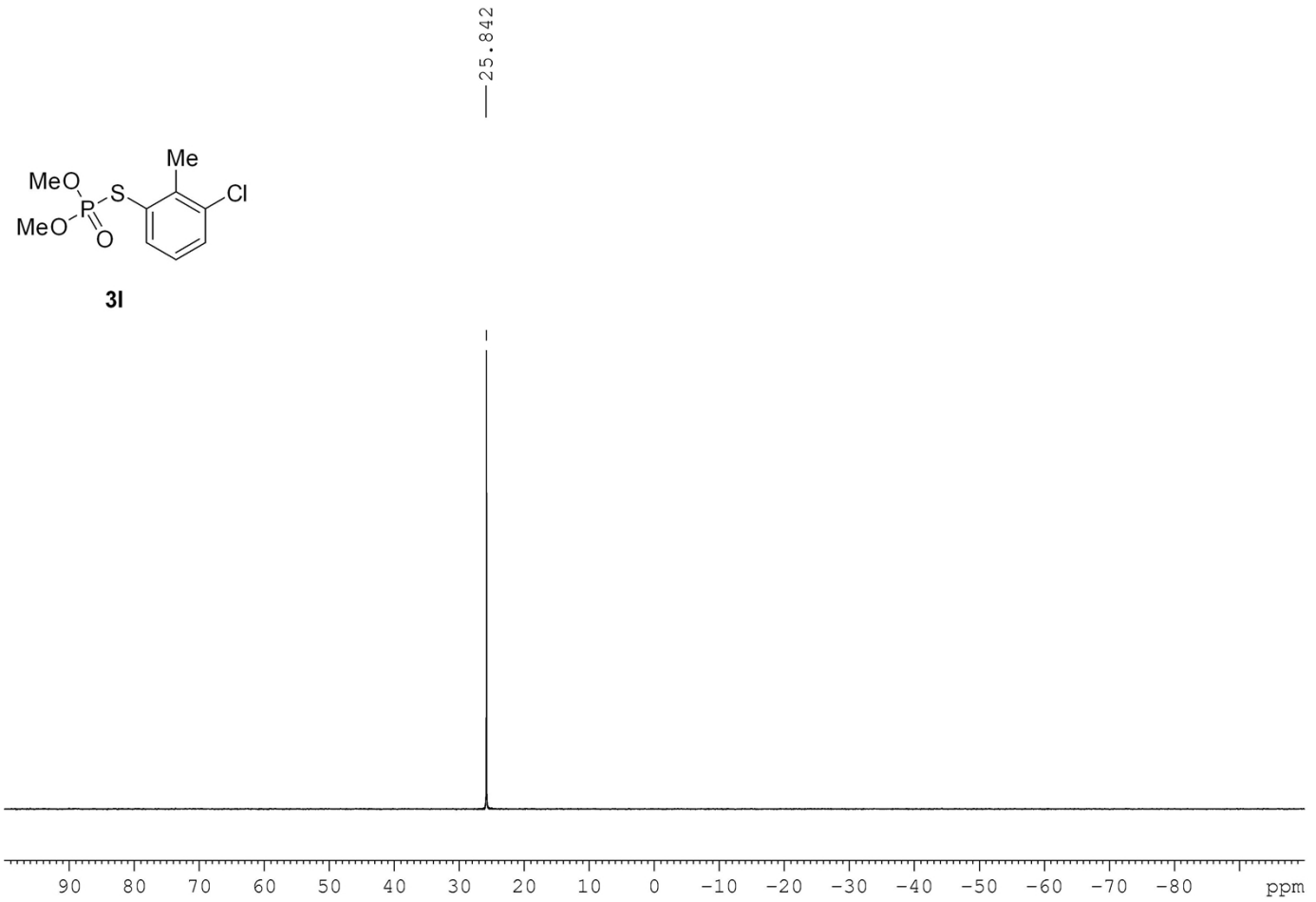


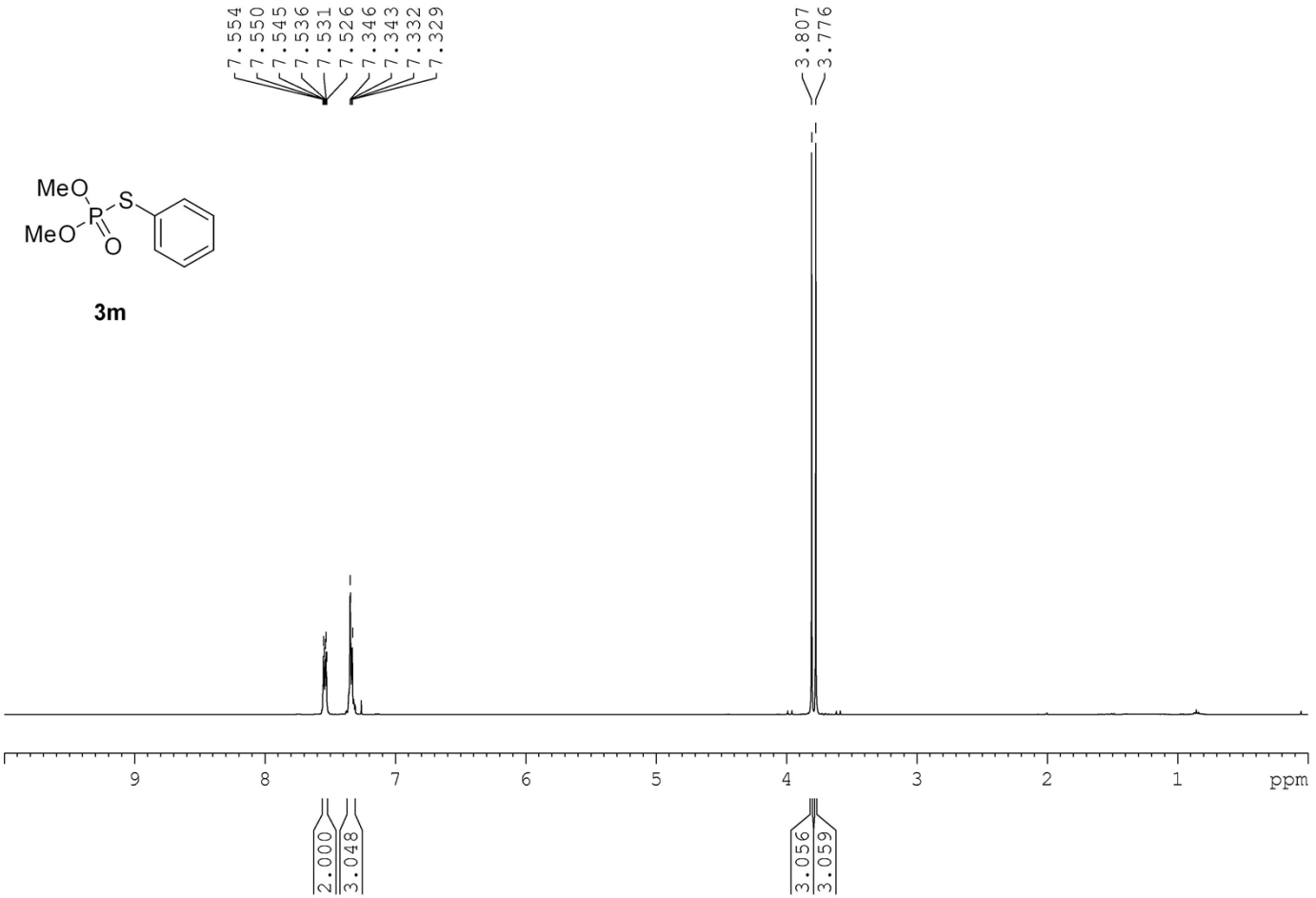
^{1}H NMR spectrum of compound **3l**



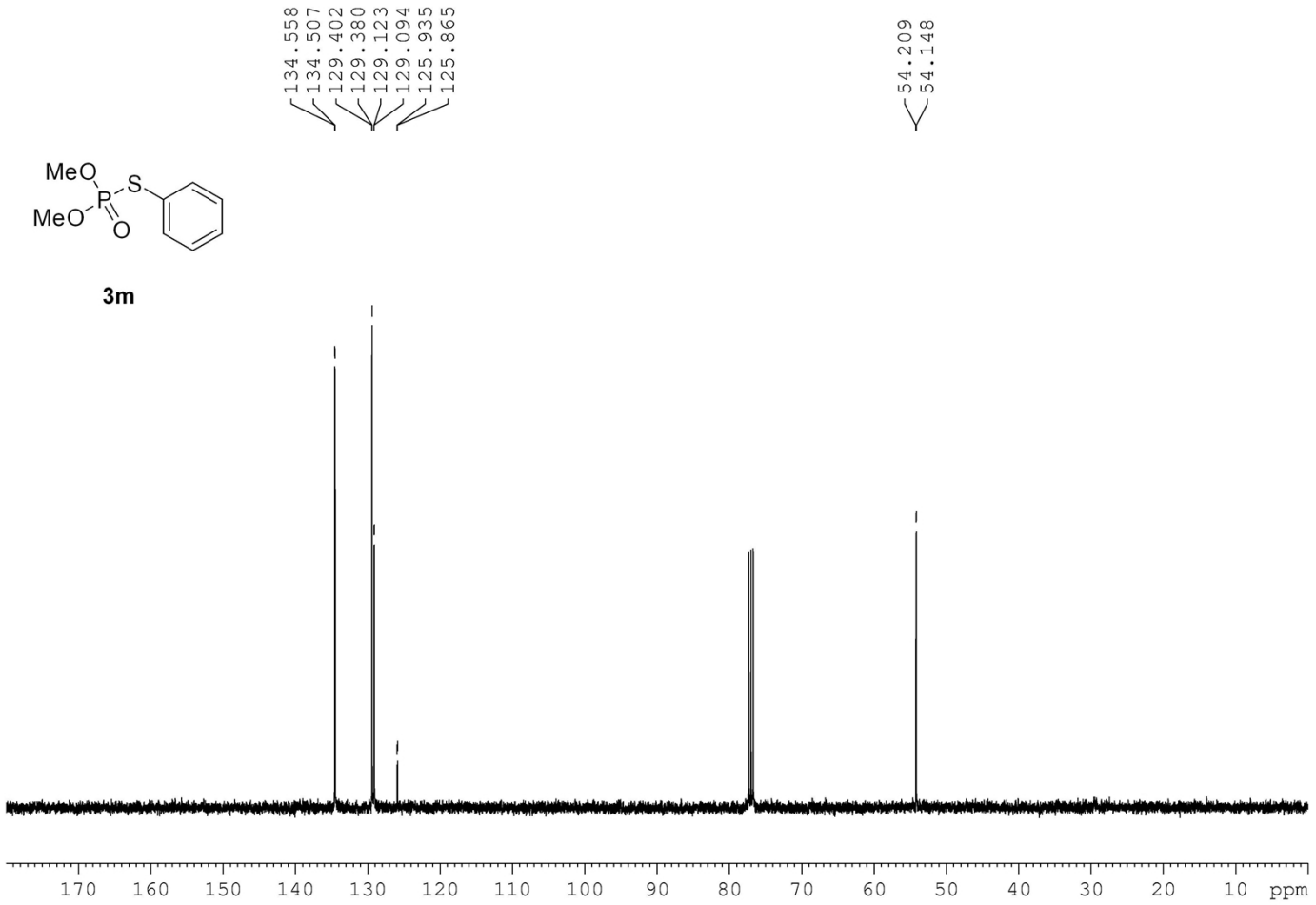
^{13}C NMR spectrum of compound **3l**



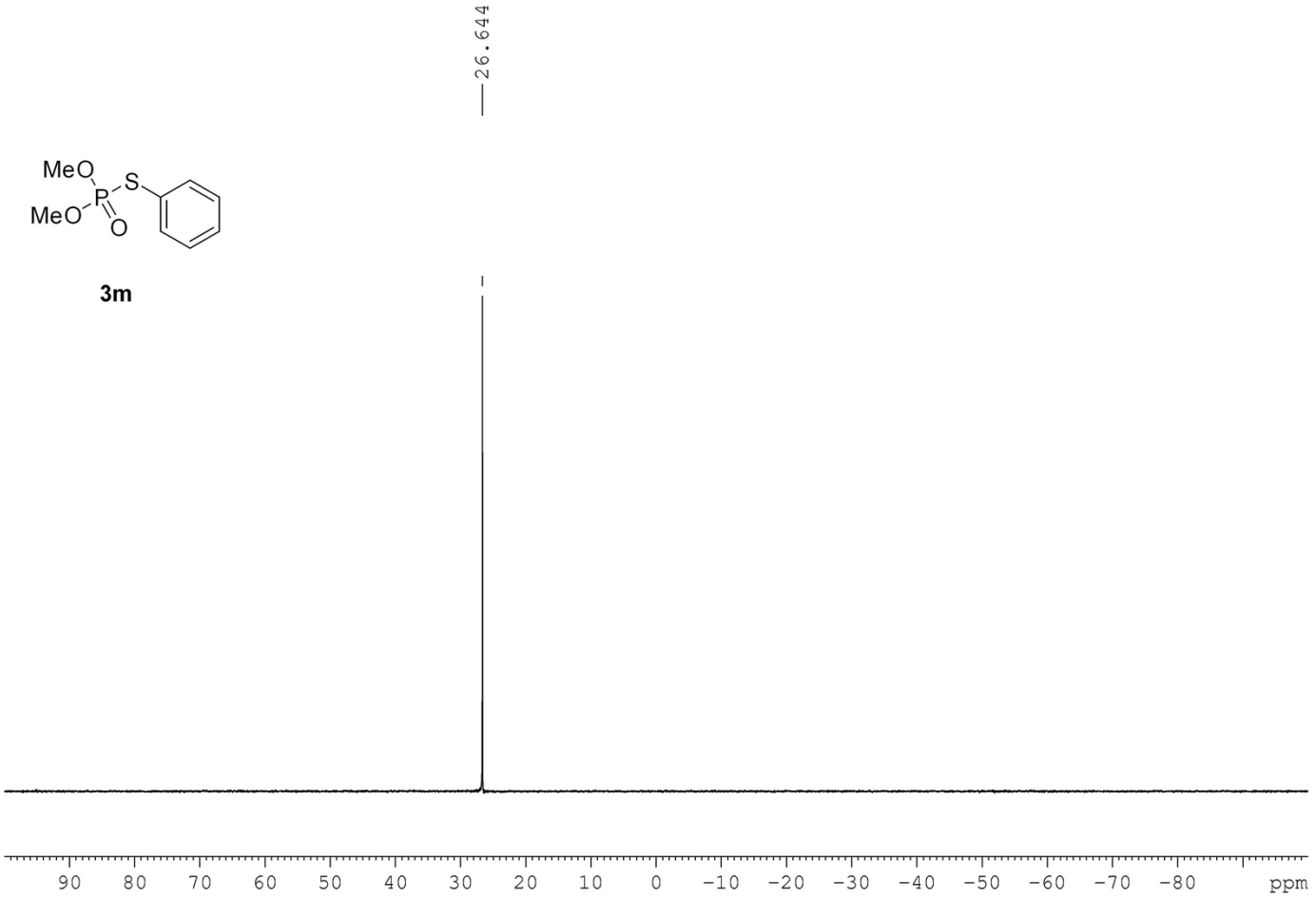
^{31}P NMR spectrum of compound **3l**



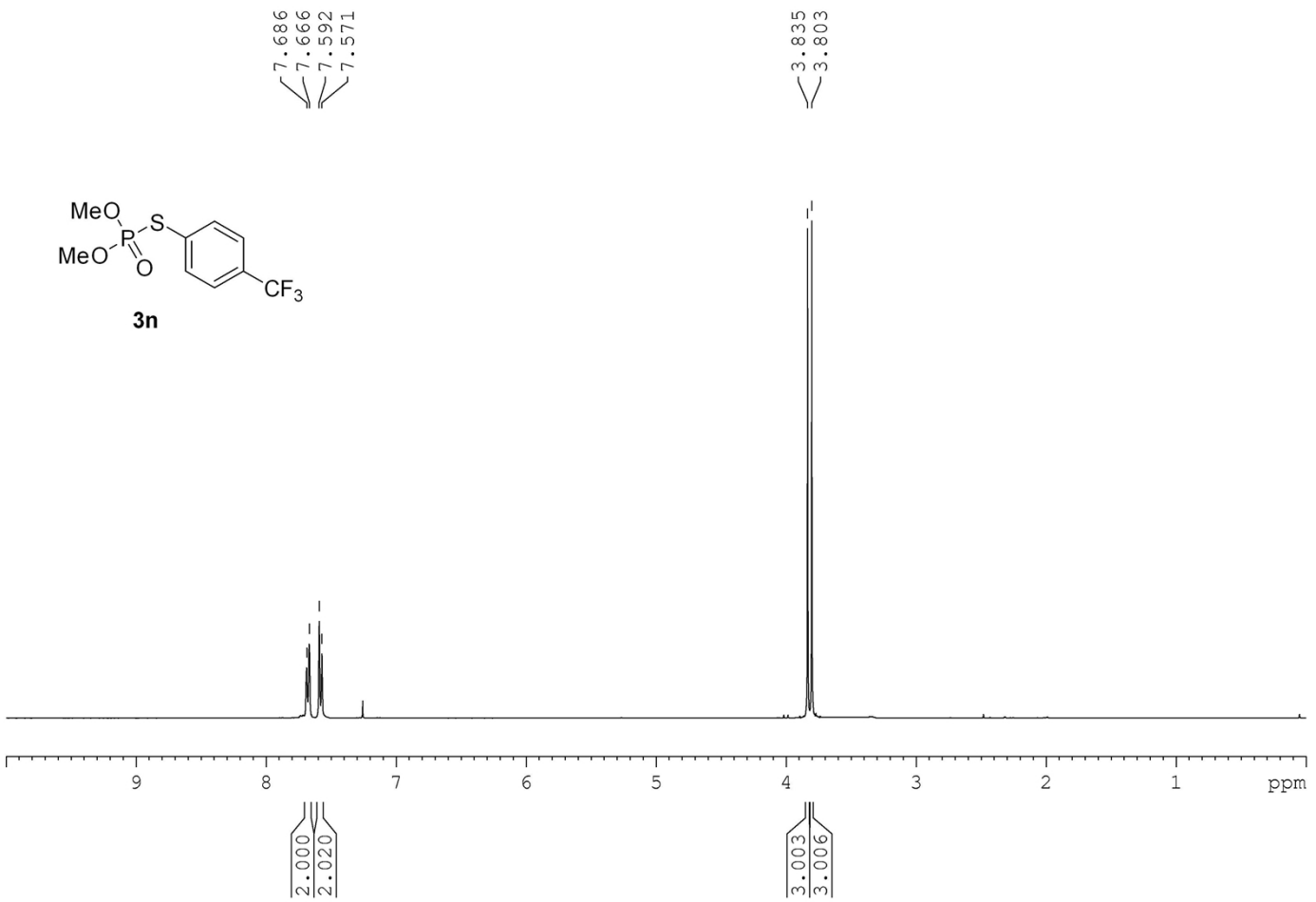
^{1}H NMR spectrum of compound **3m**



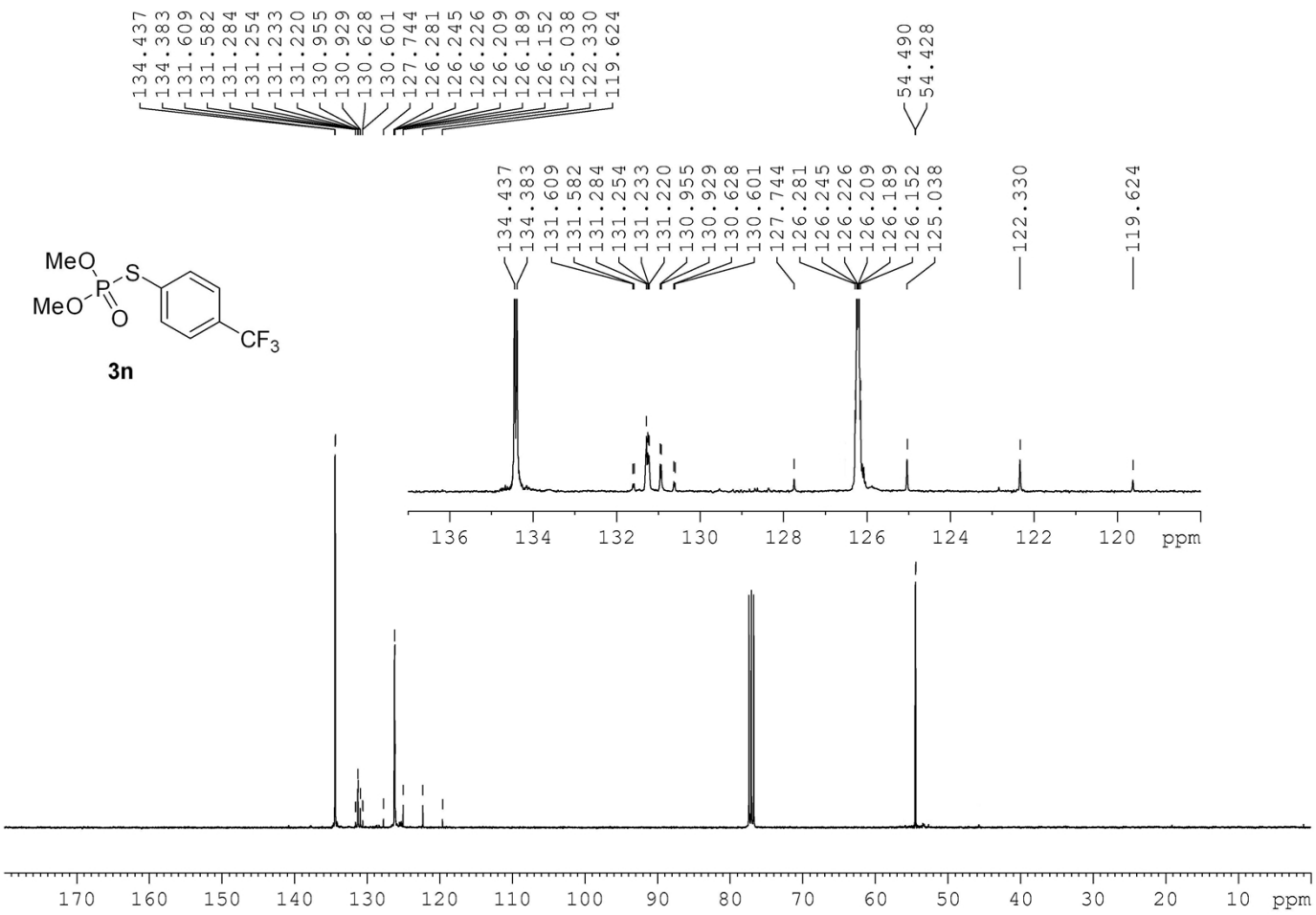
^{13}C NMR spectrum of compound **3m**



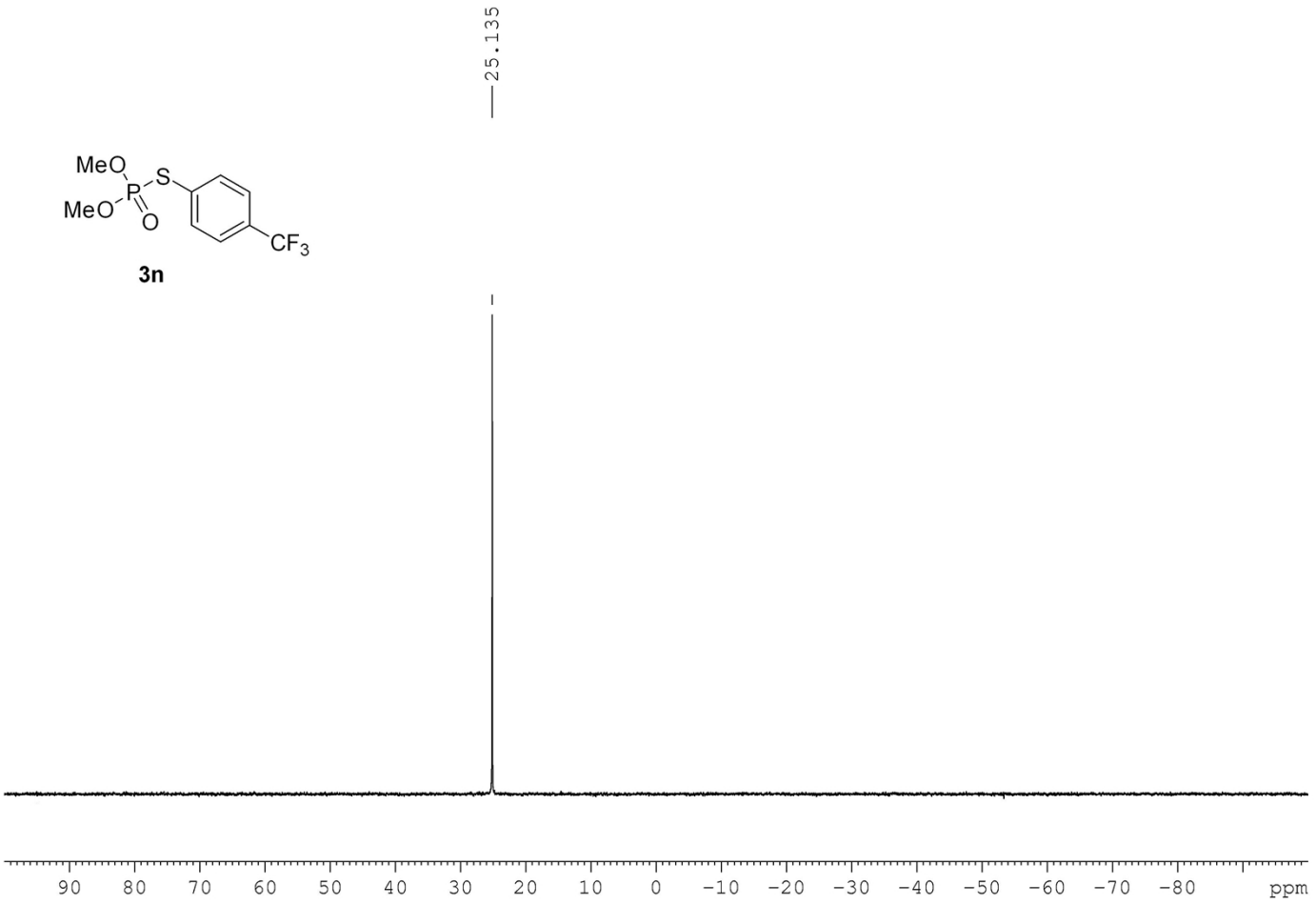
^{31}P NMR spectrum of compound **3m**



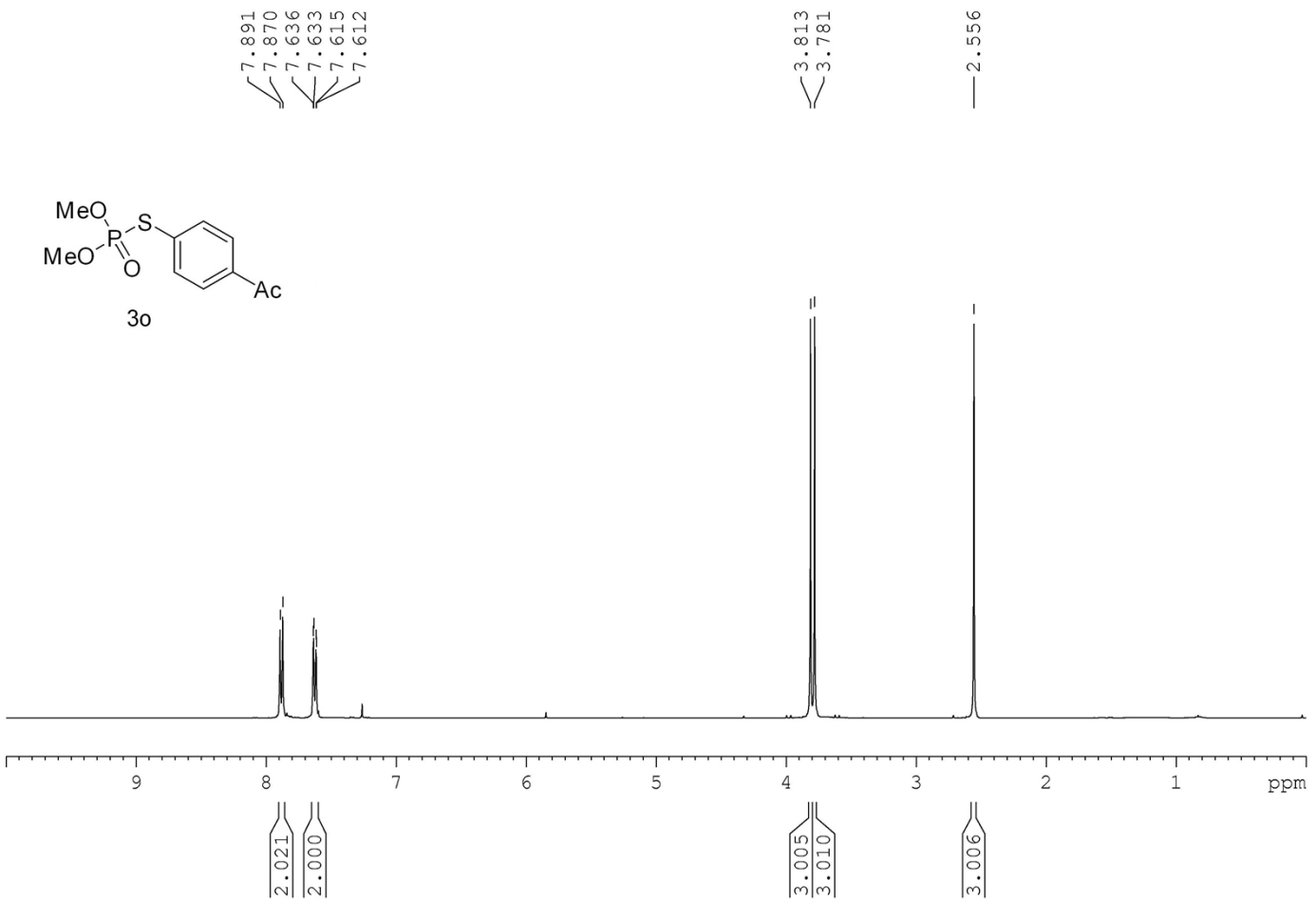
^{1}H NMR spectrum of compound **3n**



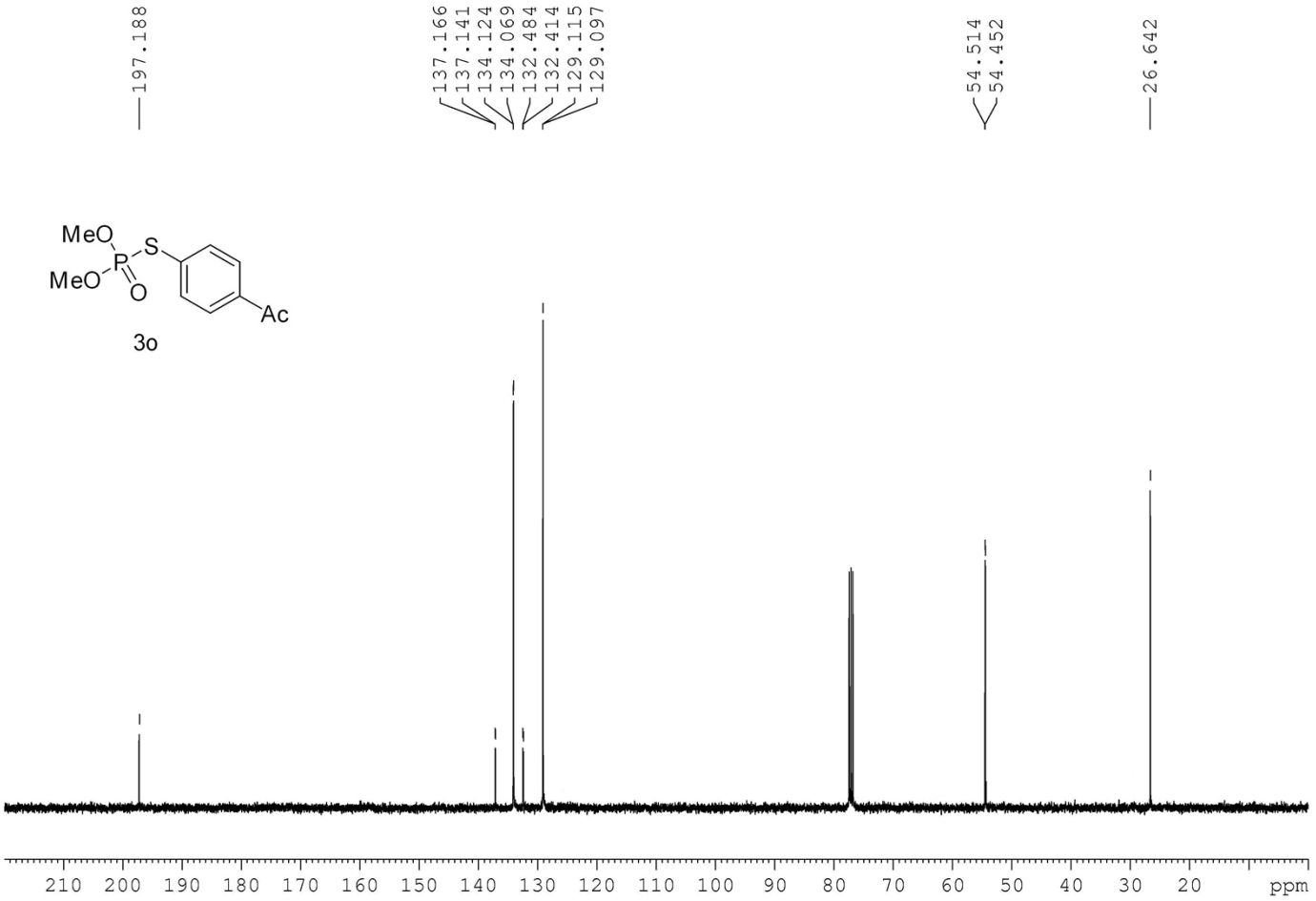
^{13}C NMR spectrum of compound **3n**



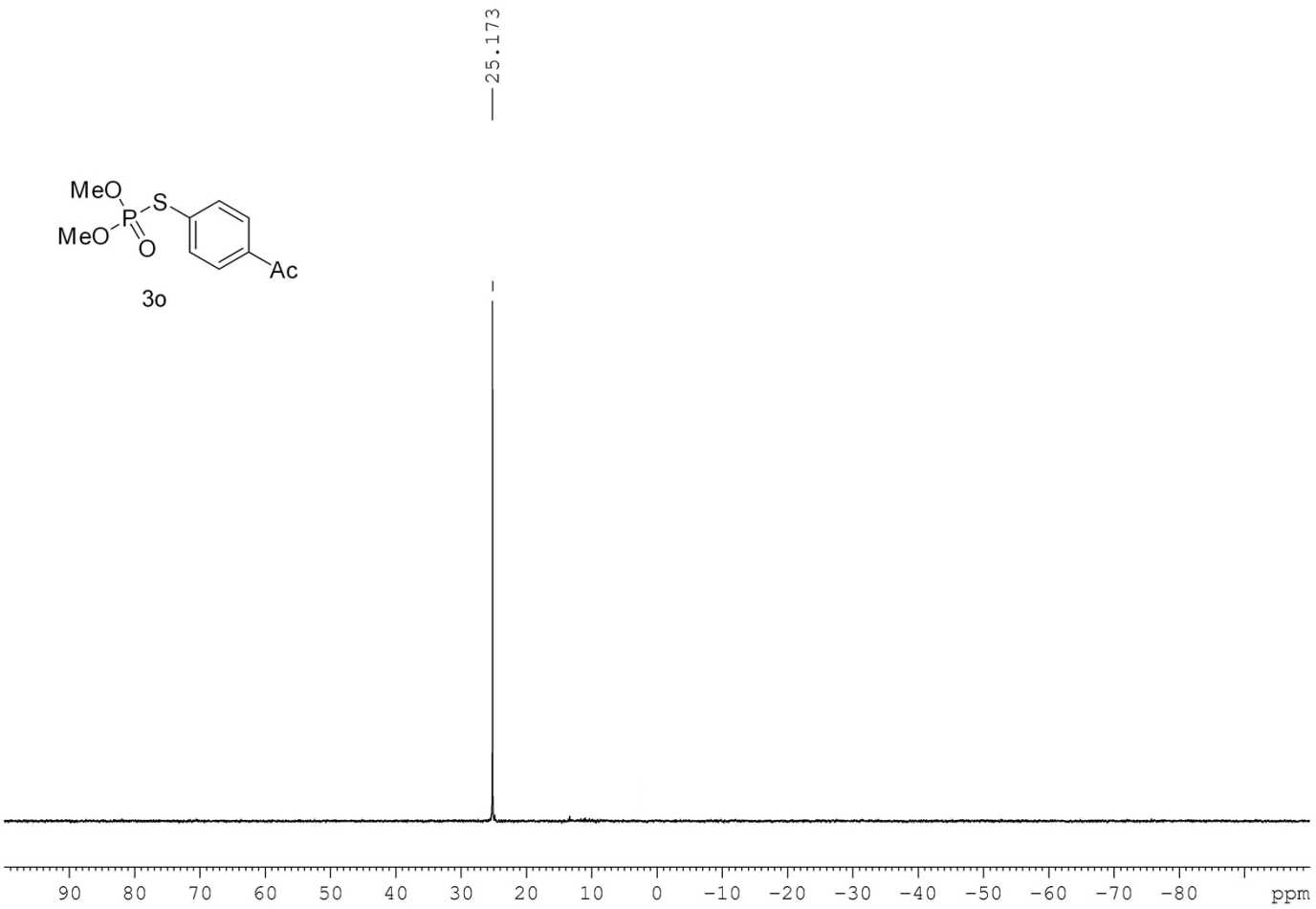
^{31}P NMR spectrum of compound **3n**



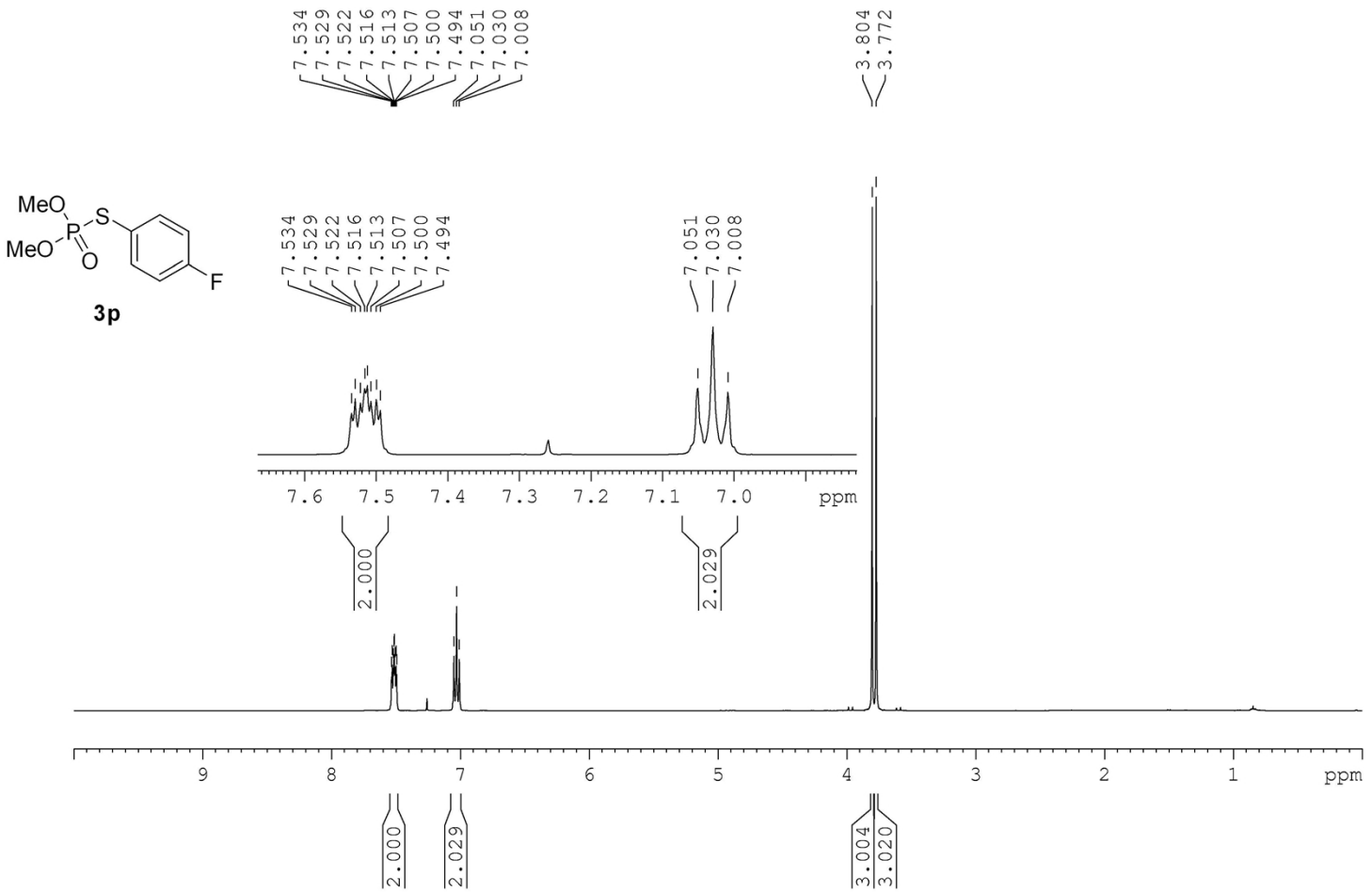
^{1}H NMR spectrum of compound **3o**



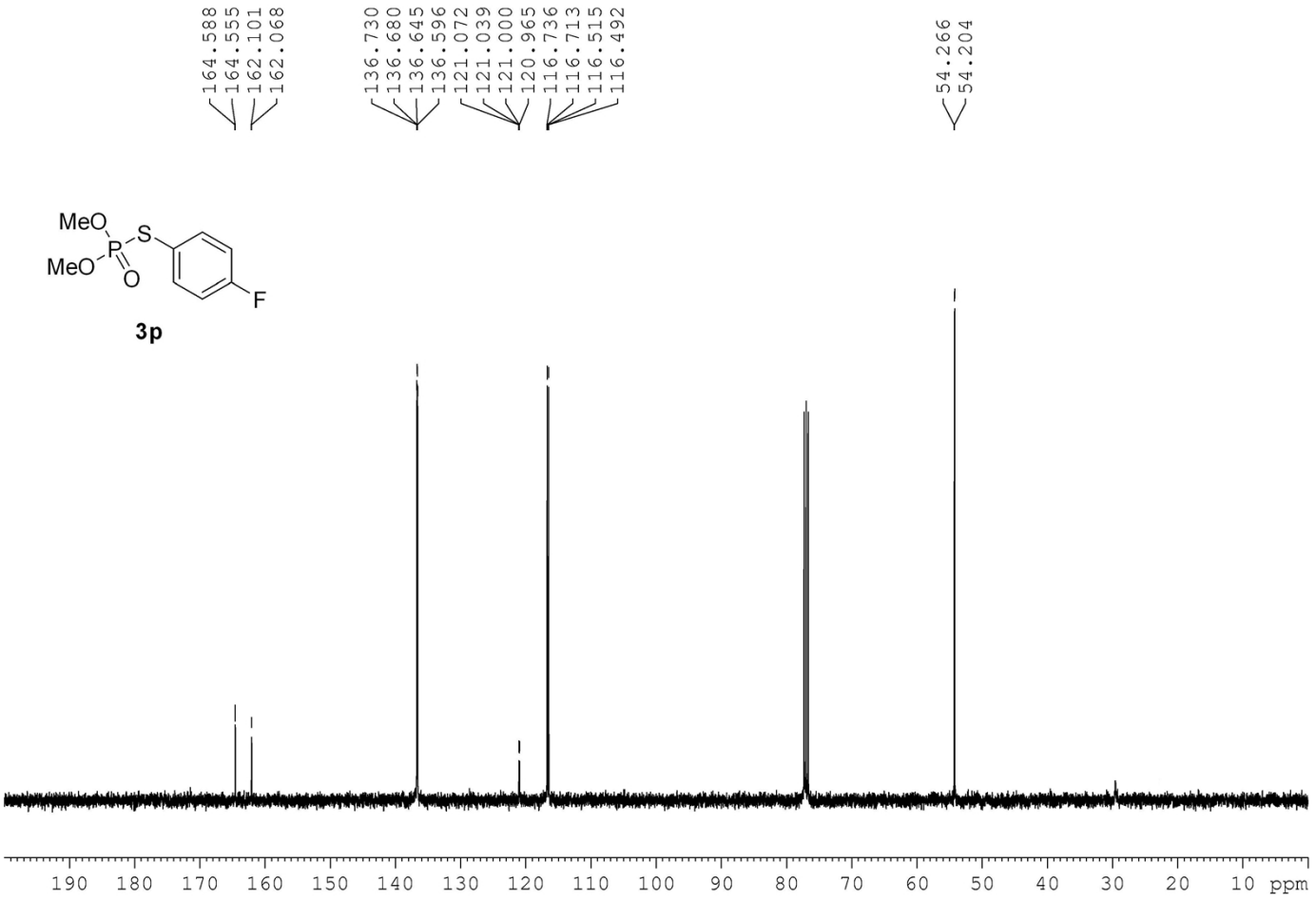
^{13}C NMR spectrum of compound **3o**



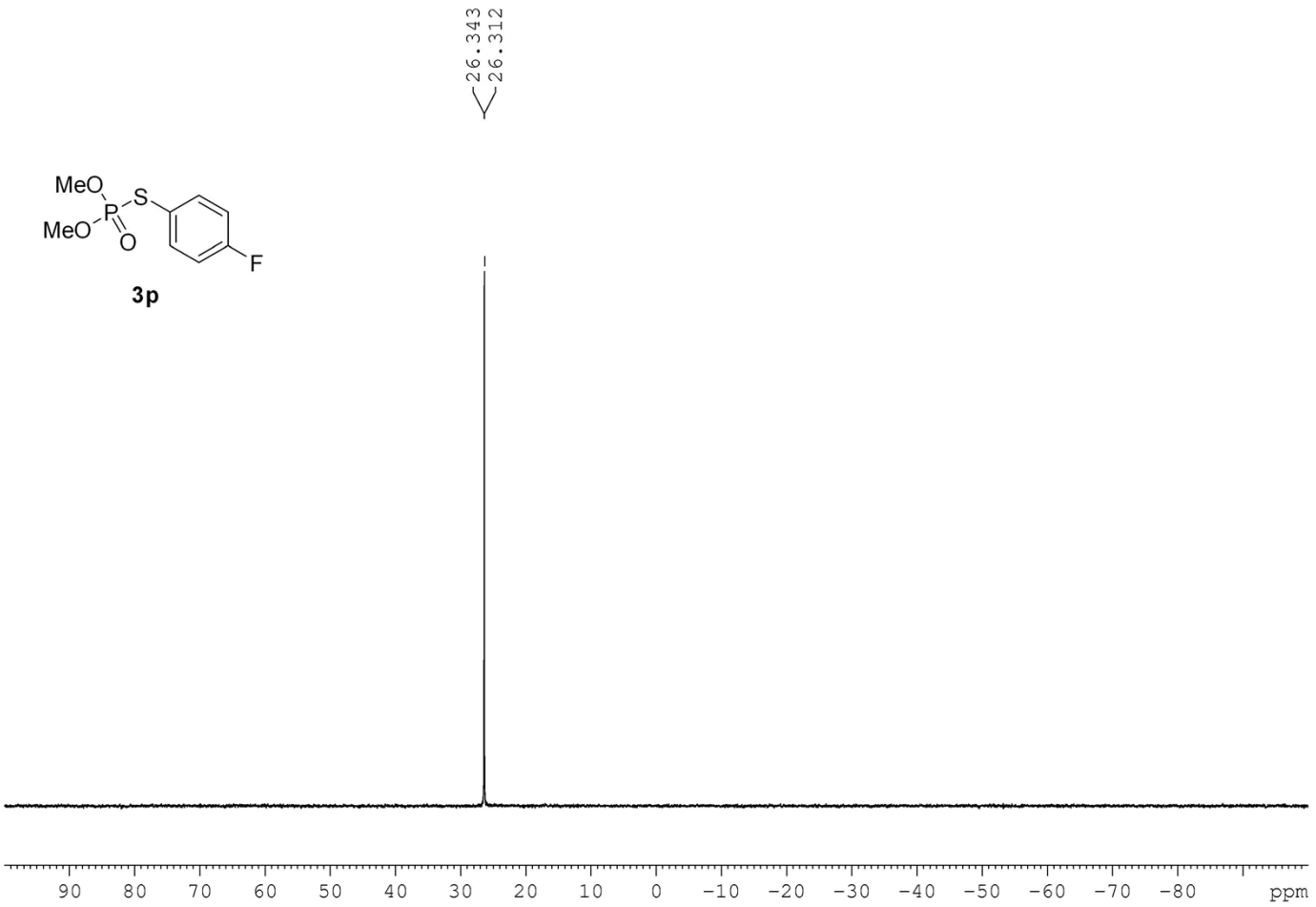
^{13}C NMR spectrum of compound **3o**



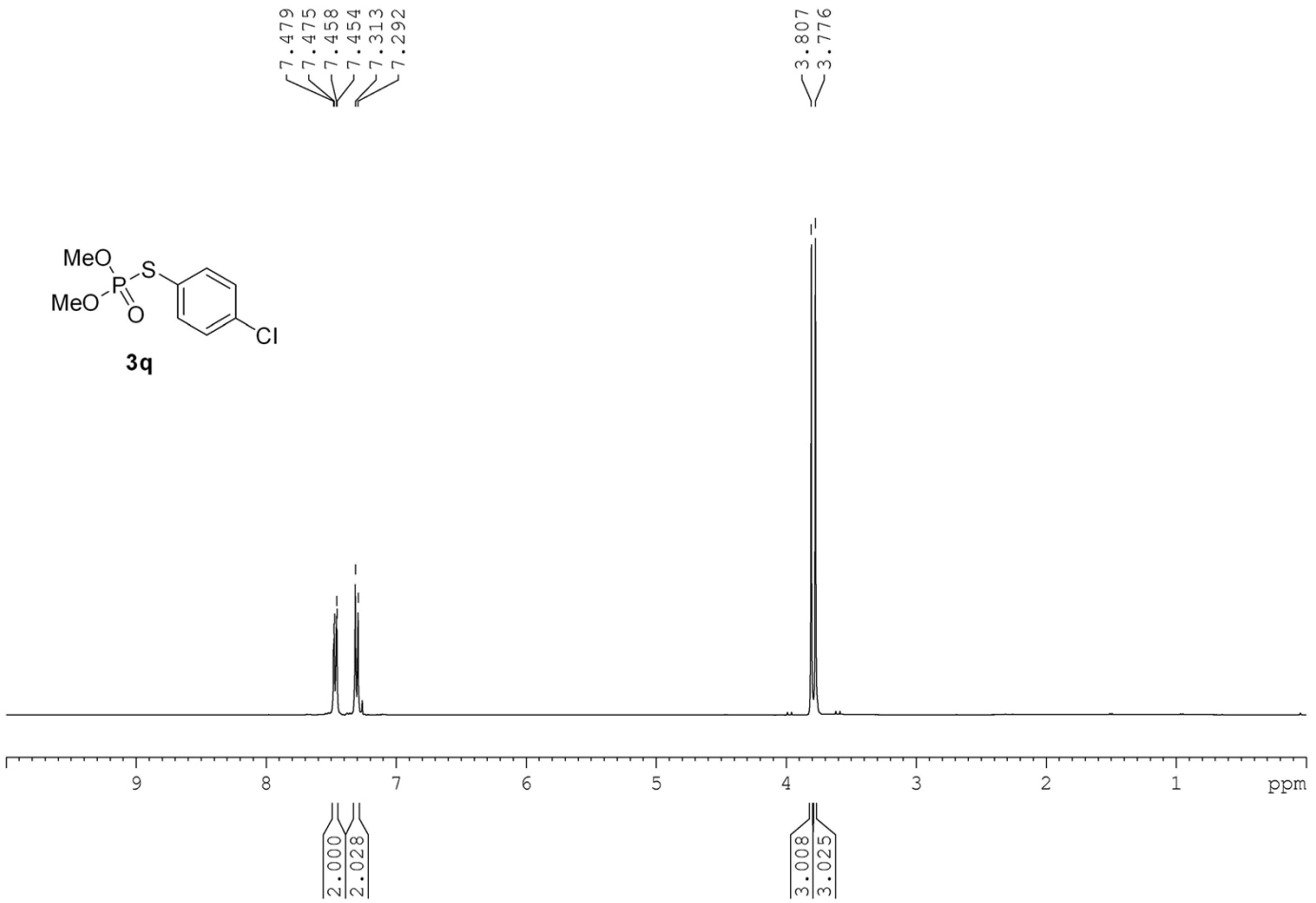
^{1}H NMR spectrum of compound **3p**



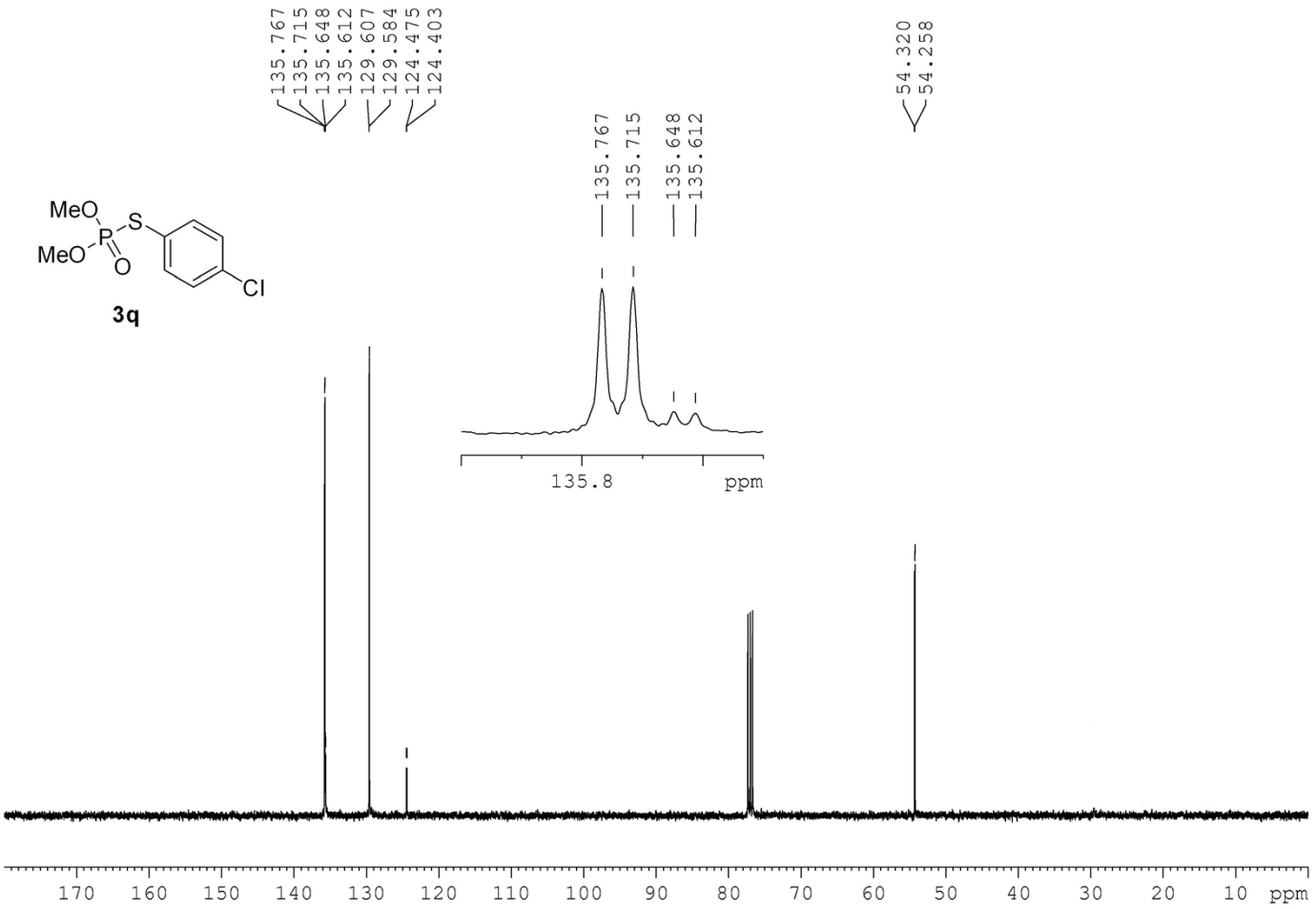
^{13}C NMR spectrum of compound **3p**



^{31}P NMR spectrum of compound **3p**

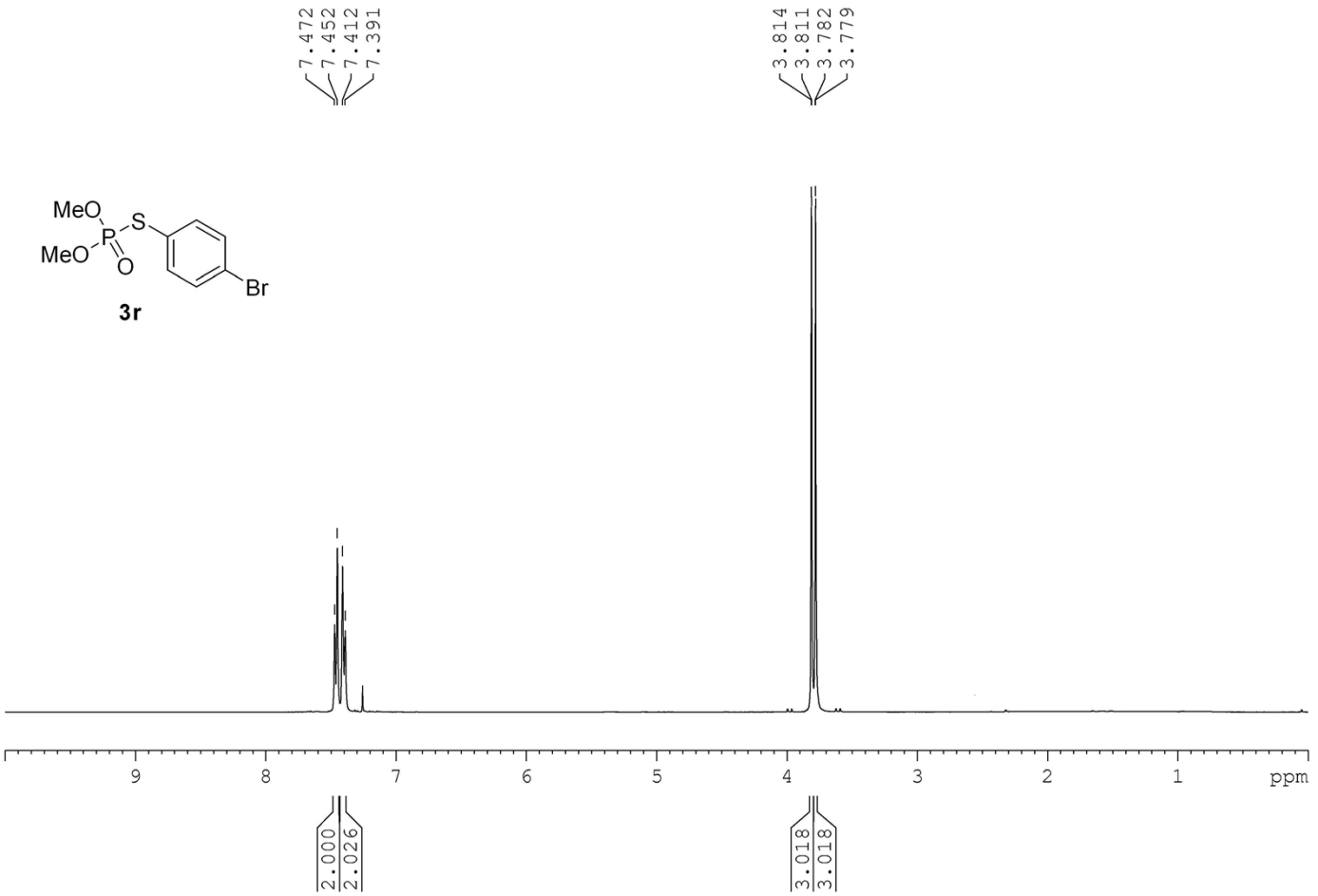


^{1}H NMR spectrum of compound **3q**

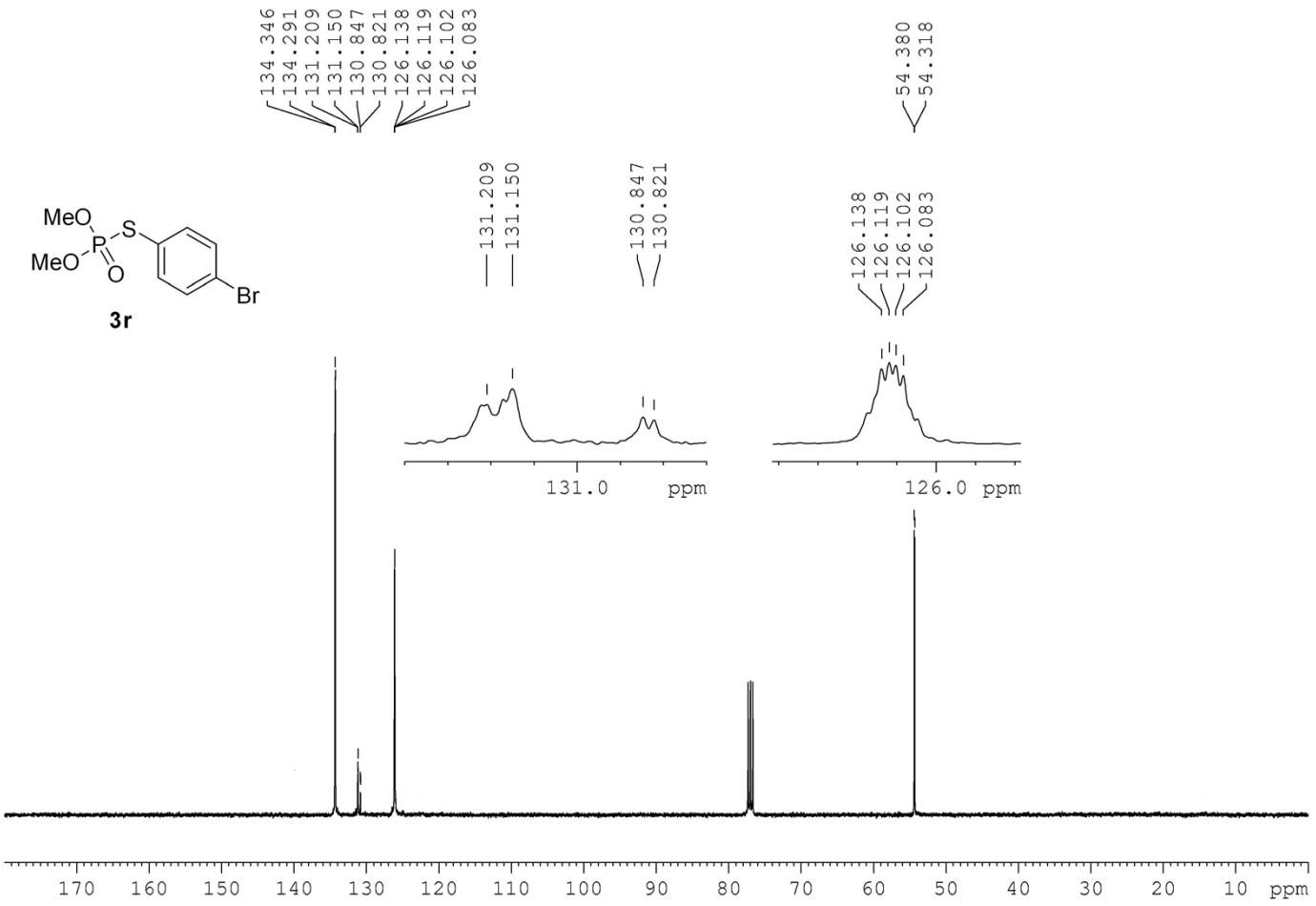


^{13}C NMR spectrum of compound **3q**

^{31}P NMR spectrum of compound **3q**

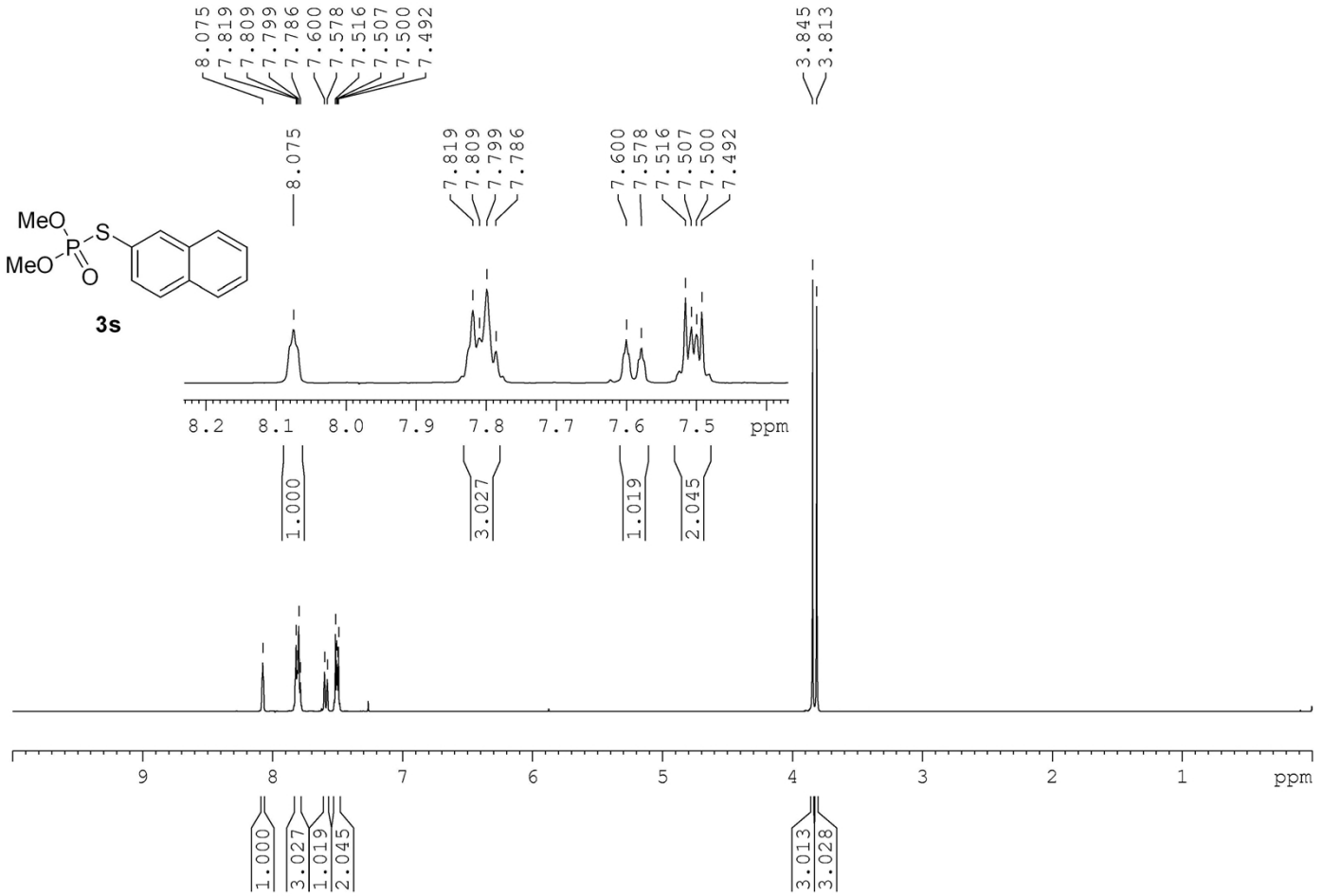


^{1}H NMR spectrum of compound **3r**

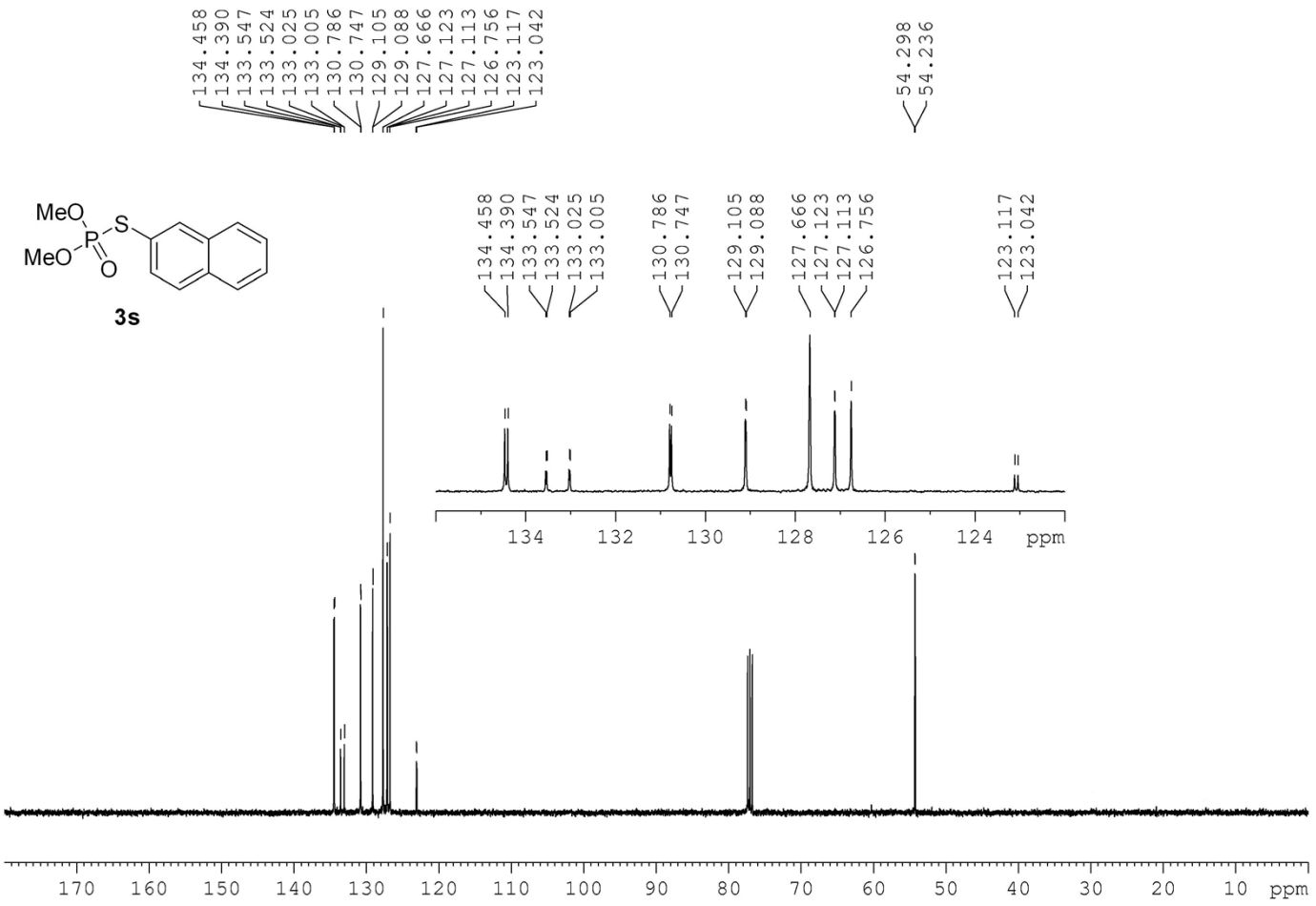


^{13}C NMR spectrum of compound **3r**

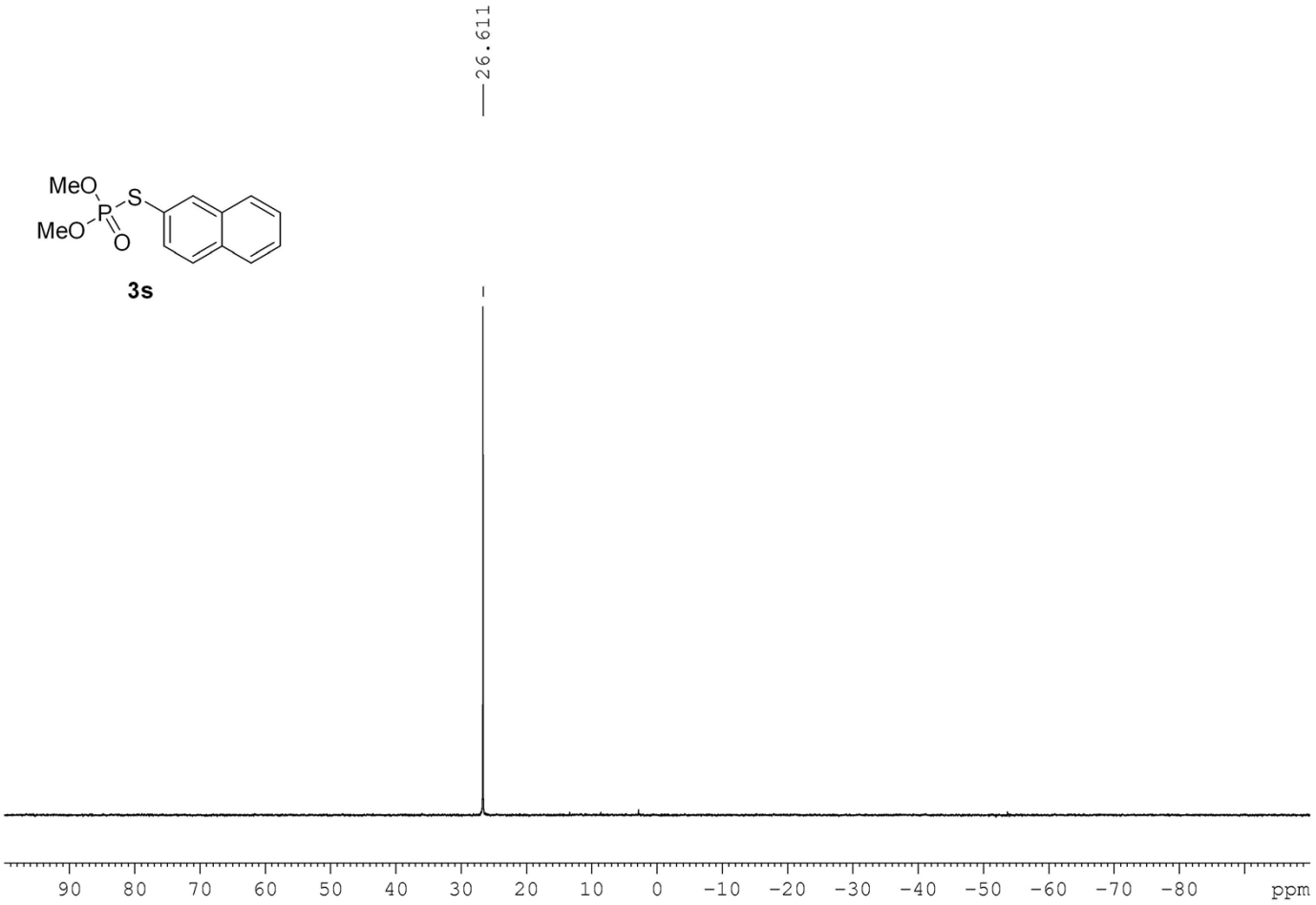
^{31}P NMR spectrum of compound **3r**



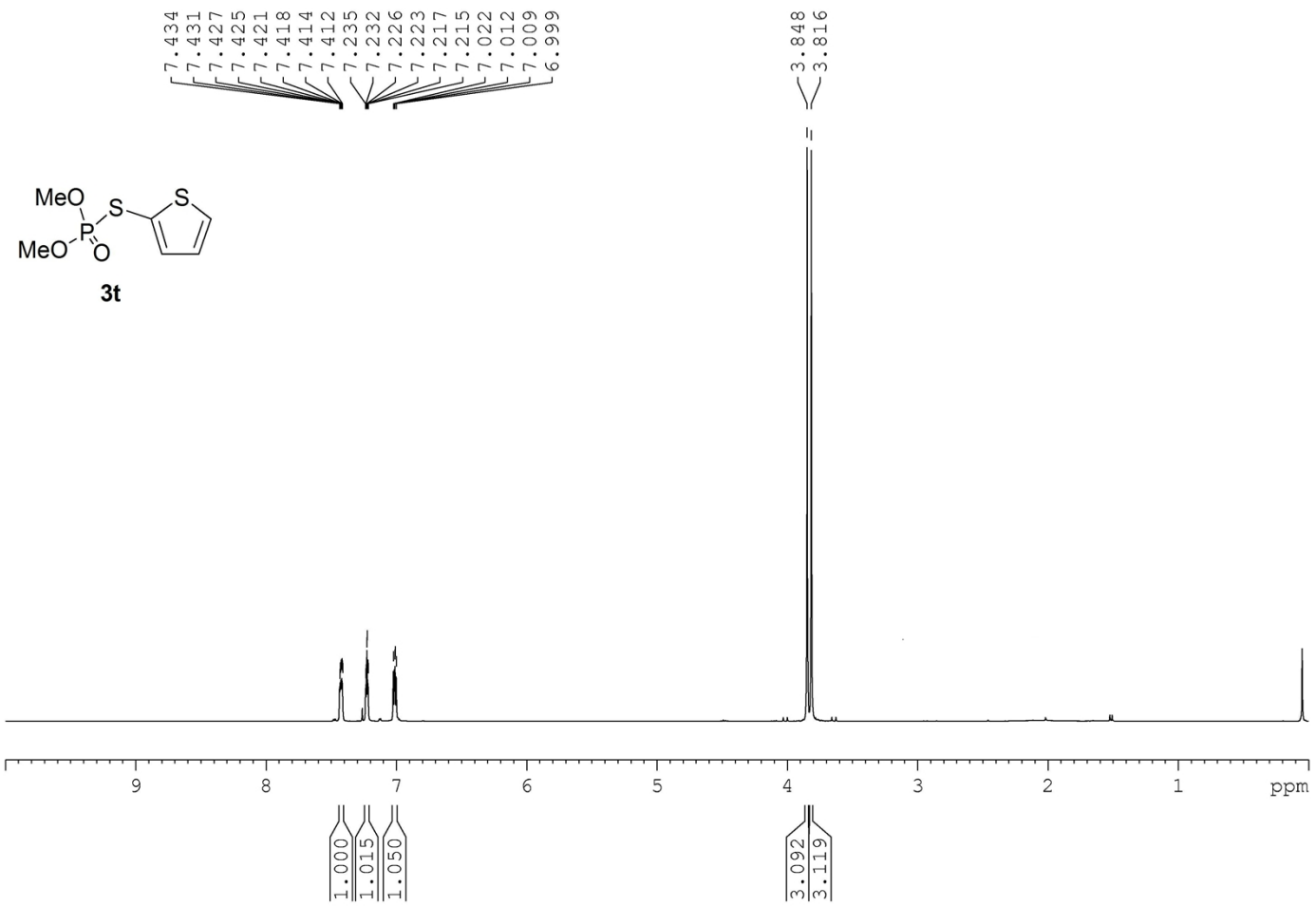
^{1}H NMR spectrum of compound **3s**



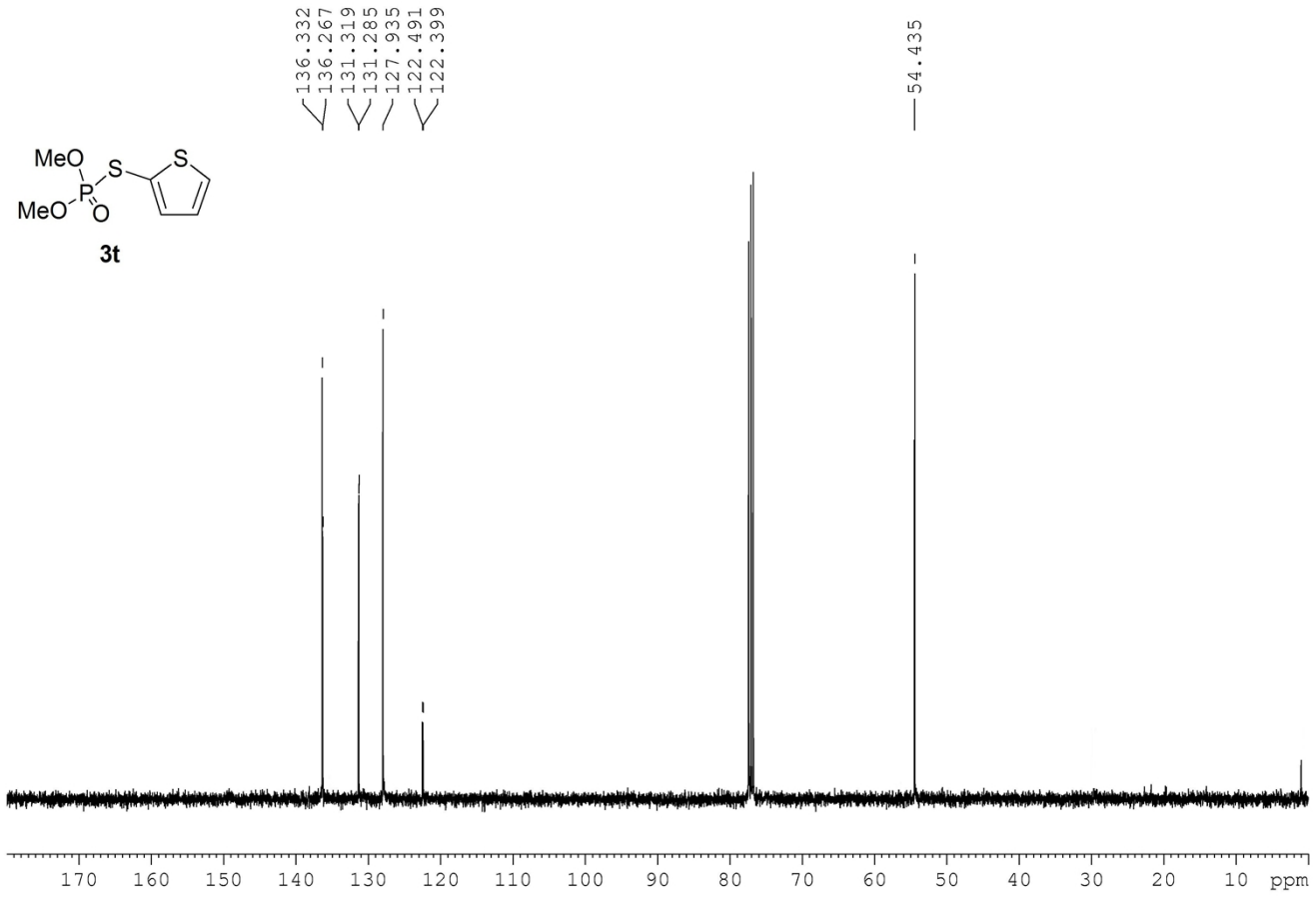
^{13}C NMR spectrum of compound **3s**



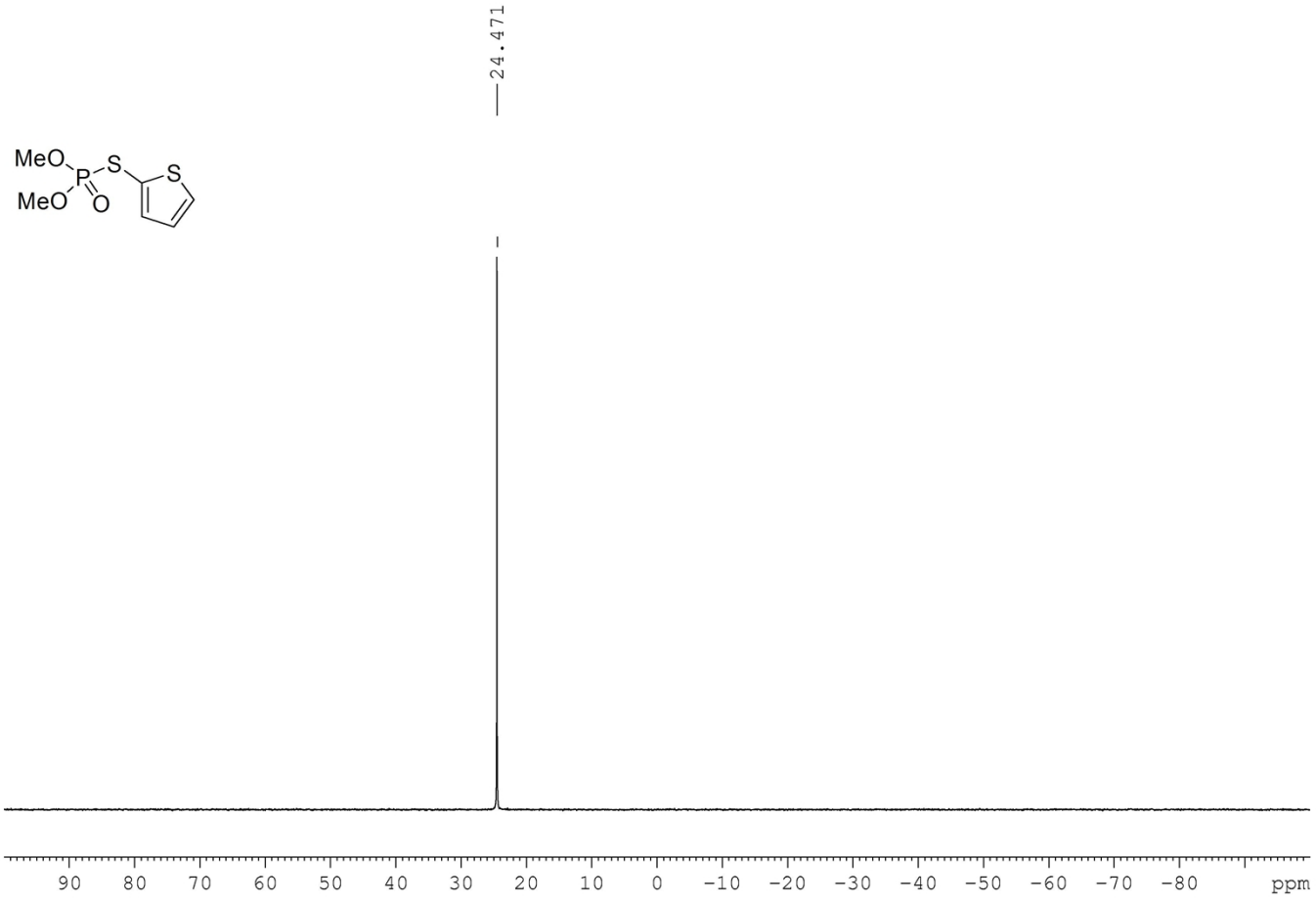
^{31}P NMR spectrum of compound **3s**



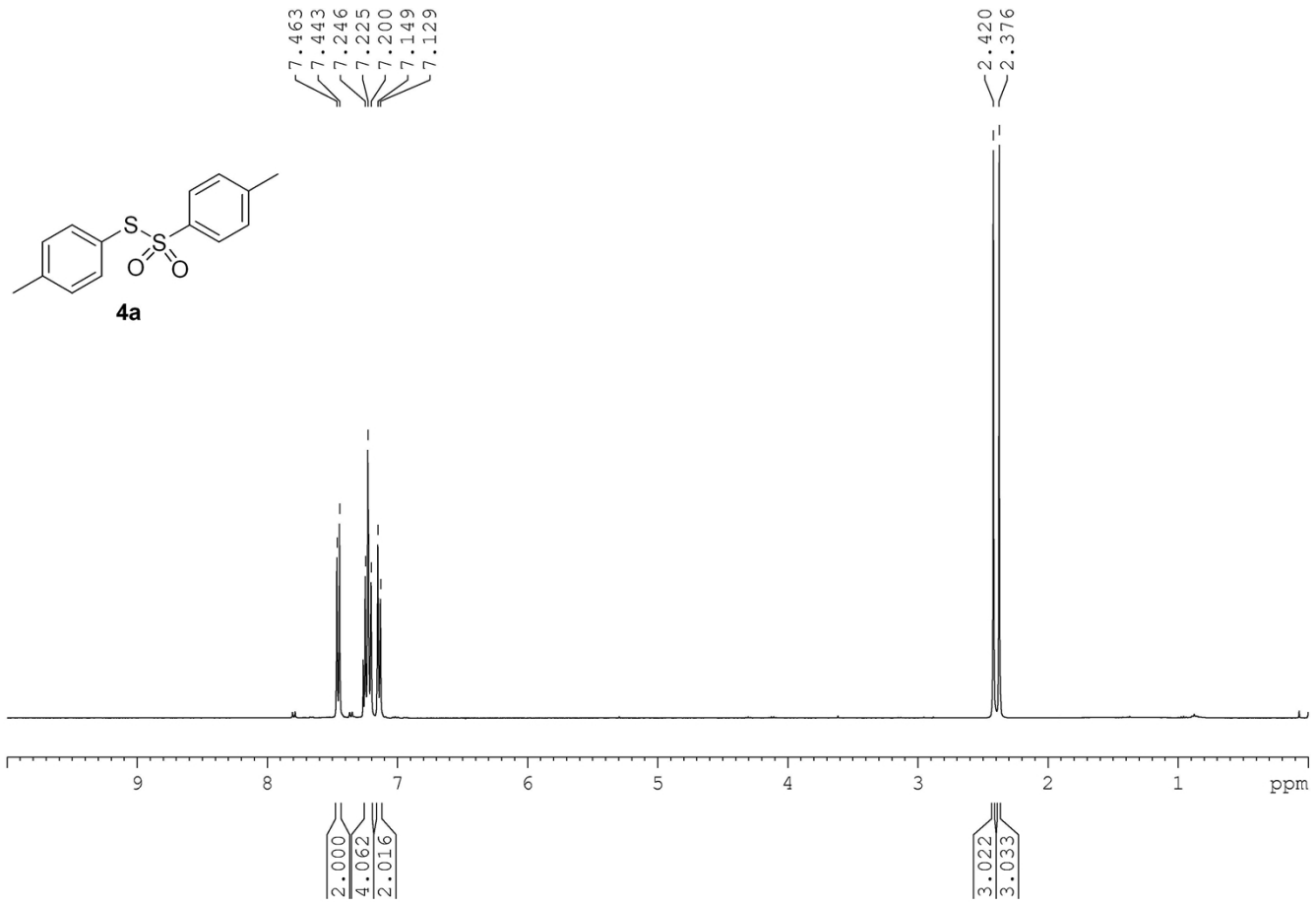
^{1}H NMR spectrum of compound **3t**



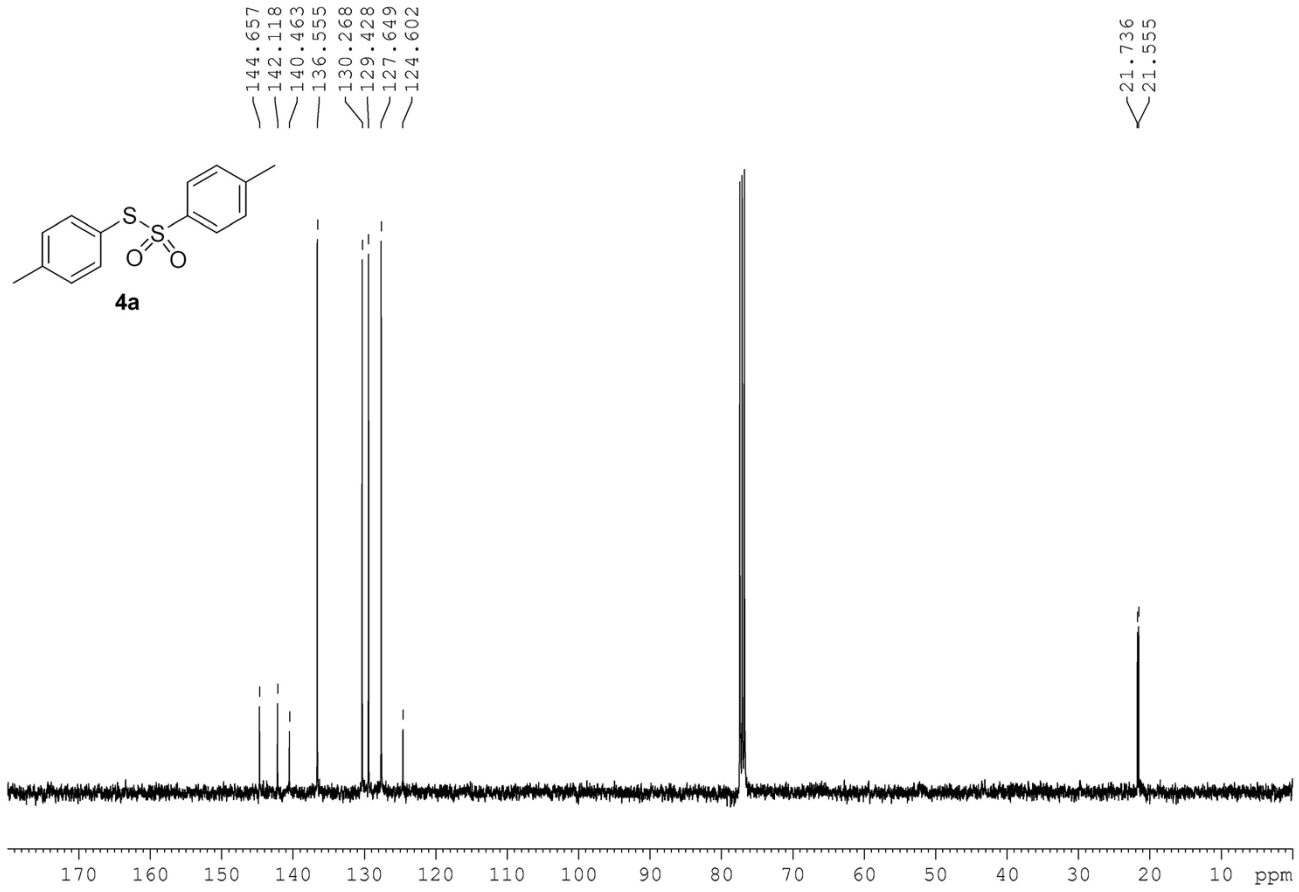
^{13}C NMR spectrum of compound **3t**



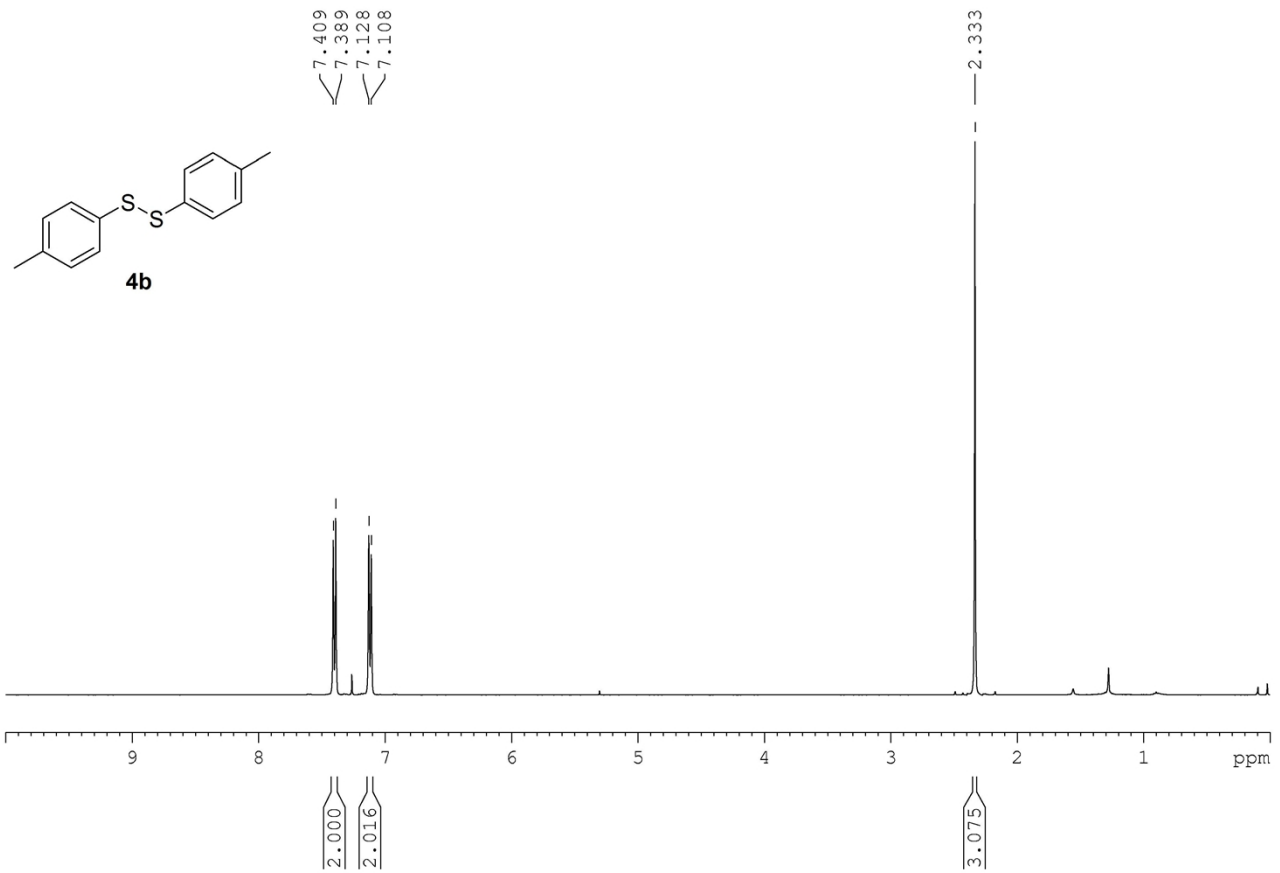
^{31}P NMR spectrum of compound **3t**



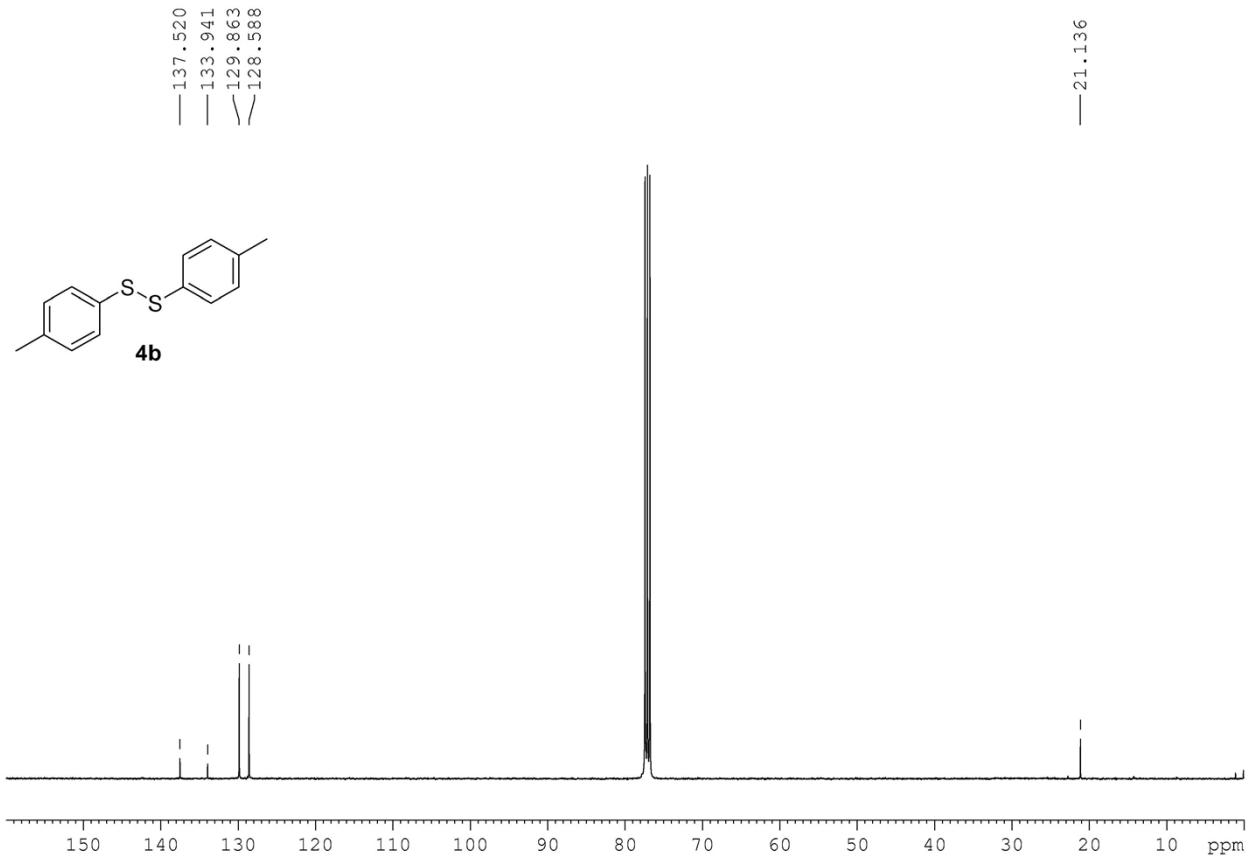
^{1}H NMR spectrum of compound **4a**



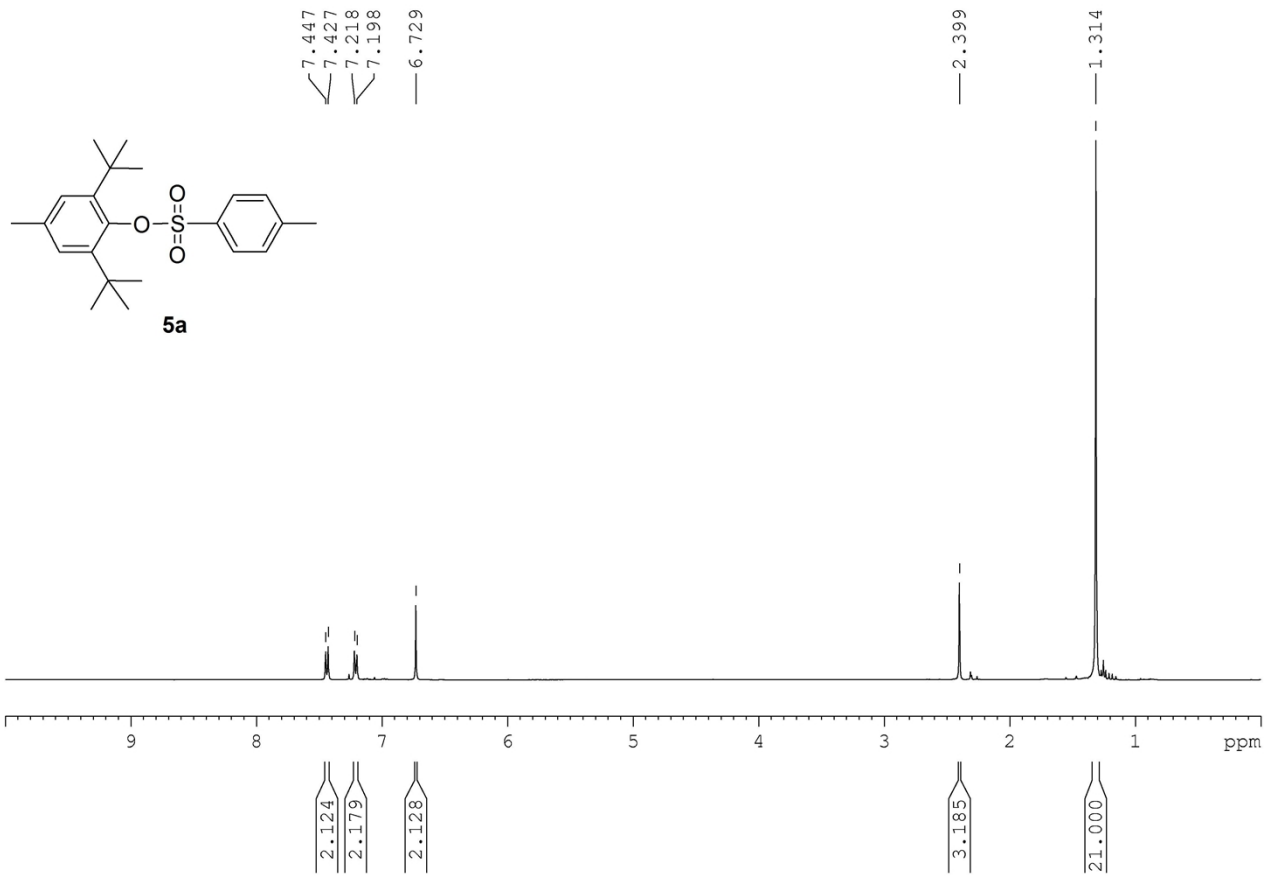
^{13}C NMR spectrum of compound **4a**



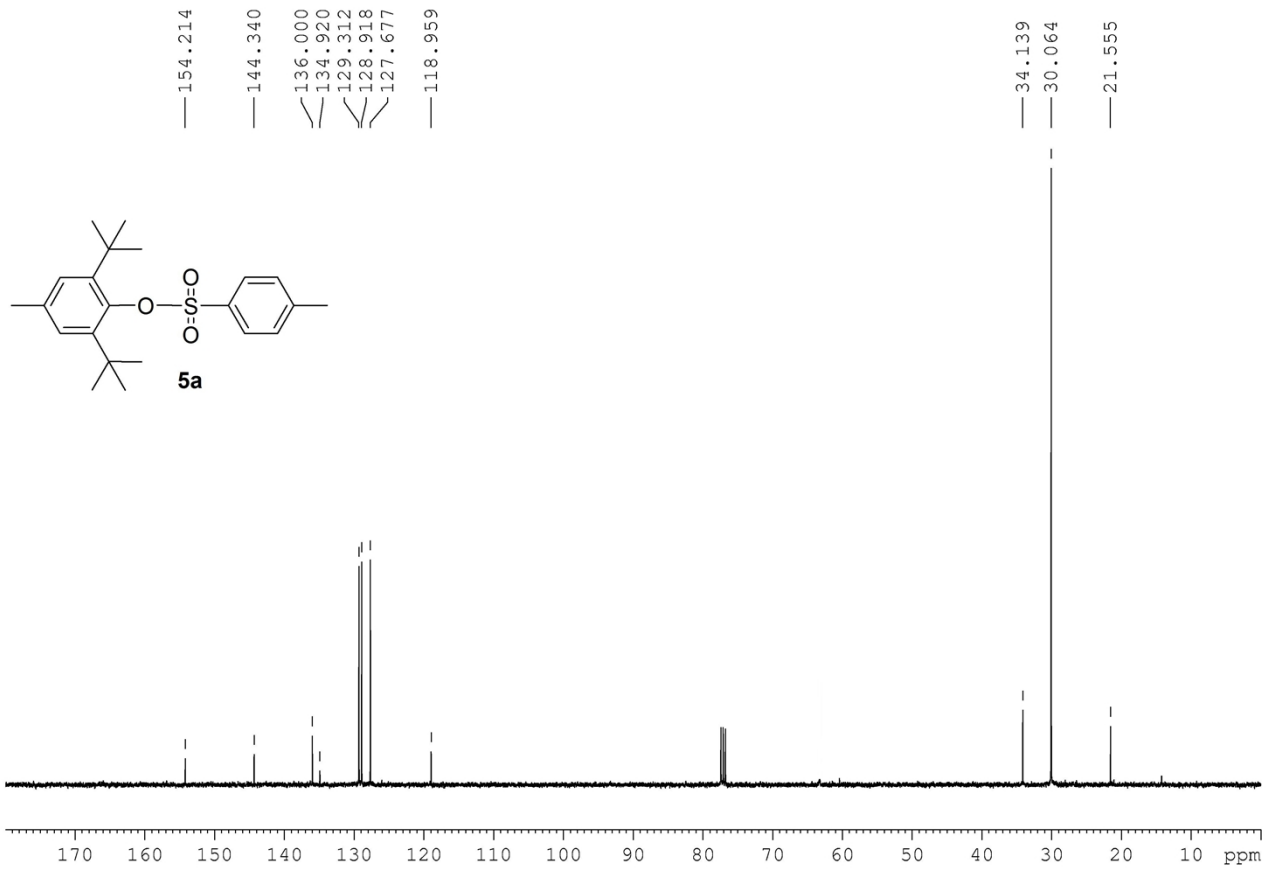
^{1}H NMR spectrum of compound **4b**



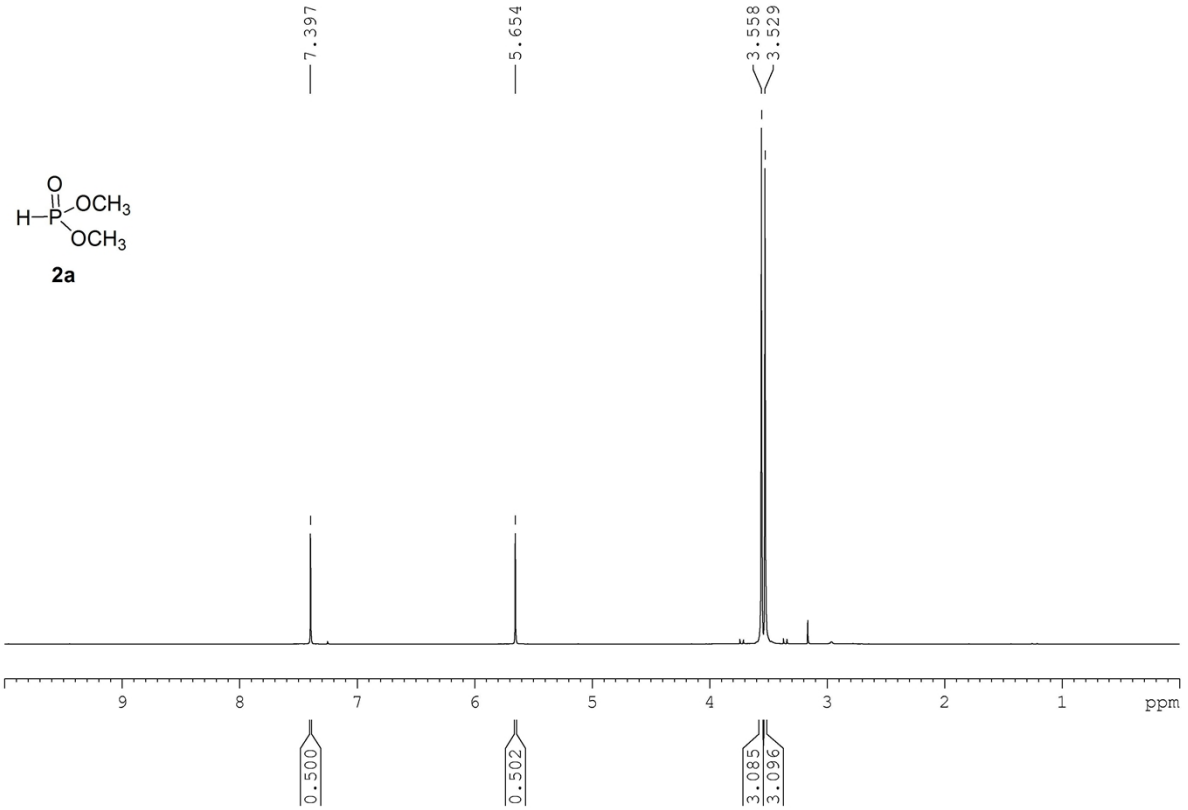
^{13}C NMR spectrum of compound **4b**



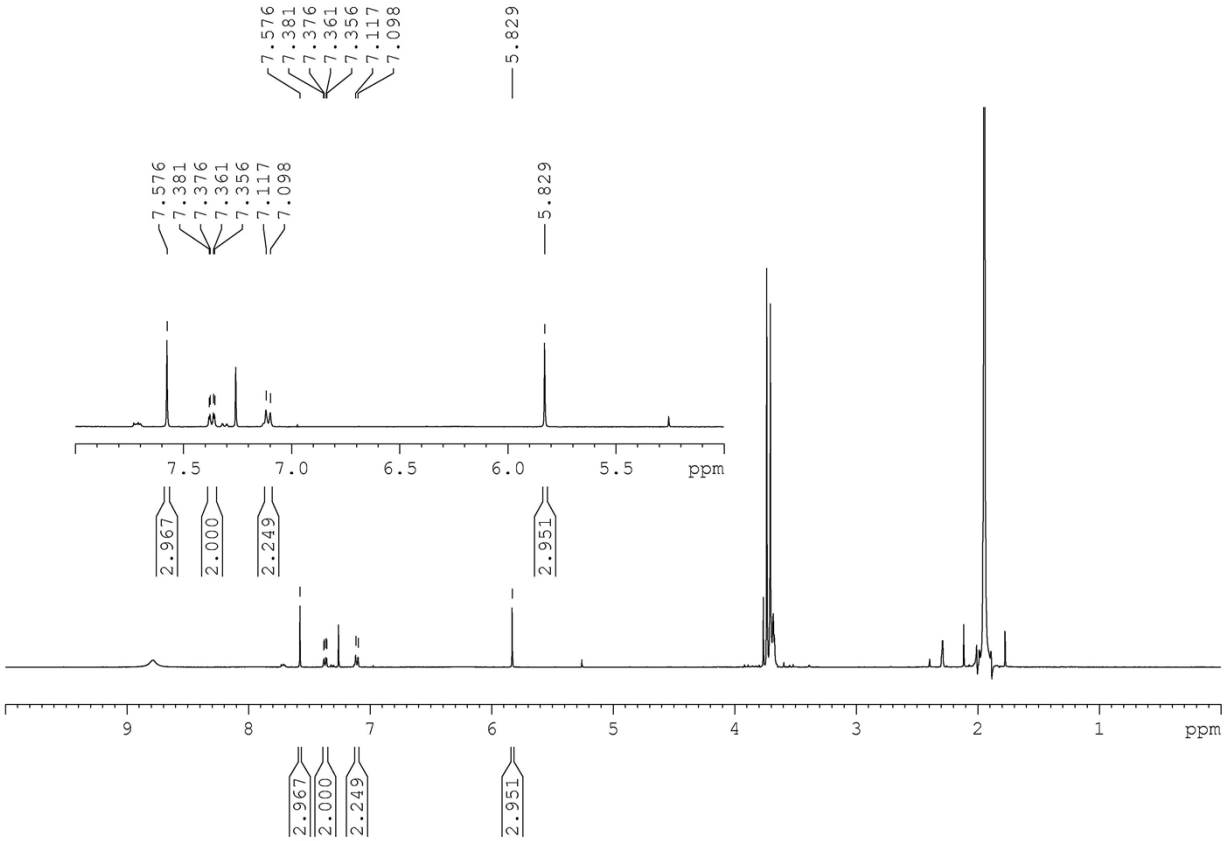
^{1}H NMR spectrum of compound **5a**



^{13}C NMR spectrum of compound **5a**



^{1}H NMR spectrum of **2a**



^{1}H NMR spectrum to show the recovery of **2a**