

Supporting information

Metal-Free Visible-Light-Mediated Oxidative Cross-Coupling of Thiols with P(O)H Compounds Using Air as the Oxidant

Jian-Guo Sun, Hua Yang, Ping Li,* and Bo Zhang*

*State Key Laboratory of Natural Medicines, China Pharmaceutical University,
24 Tongjia Xiang, Nanjing 210009, China*

E-mail: zb3981444@cpu.edu.cn; liping2004@126.com

Table of contents

General	S2
General procedure for visible-light-mediated oxidative cross-coupling of thiols with P(O)H compounds (GP)	S3
Physical data of the compounds	S3
Lager scale experiment	S18
Mechanistic studies	S18
References	S23
NMR spectra	S24

General

All manipulations were conducted with a standard *Schlenk* tube under air atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The P(O)H compounds **2b-2k** were prepared according to a reported method.^[1]

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F₂₅₄ plates.

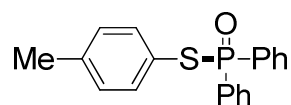
¹H NMR spectra were recorded on a *Bruker AV-300* spectrometer or a *Bruker AV-500* spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl₃ as an internal standard. ¹³C NMR spectra were obtained by the same NMR spectrometer and were calibrated with CDCl₃ ($\delta = 77.00$ ppm). ³¹P NMR spectra were recorded on a *Bruker AV-300* spectrometer and using 85% H₃PO₄ as external standard. Data for ¹H NMR are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant (Hz) and integration. Data for ¹³C NMR are reported in terms of chemical shift and multiplicity where appropriate. Mass spectra were performed on an *Agilent 6530 Q-TOF* for HRMS. The yields were determined on a *METTLER TOLEDO ME 104* balance (accuracy: 0.1 mg). Melting points (Mp) were determined on a SGW X-4B and are uncorrected.

General procedure for visible-light-mediated oxidative cross-coupling of thiols with P(O)H compounds (GP):

Thiol **1** (0.6 mmol, 2.0 equiv), P(O)H compound **2** (0.3 mmol, 1.0 equiv), and Rose Bengal (0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding product.

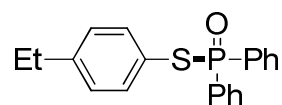
Physical data of the compounds

S-p-tolyl diphenylphosphinothioate (3aa)^[2]



According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3aa** as white solid (77.1 mg, 79%). Mp: 106-108 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.88-7.81 (m, 4H), 7.52-7.40 (m, 6H), 7.35-7.28 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.25 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.1 (d, *J* = 2.0 Hz), 135.3 (d, *J* = 3.8 Hz), 132.8 (d, *J* = 106.0 Hz), 132.2 (d, *J* = 2.0 Hz), 131.6 (d, *J* = 10.8 Hz), 129.9, 128.4 (d, *J* = 12.6 Hz), 122.3 (d, *J* = 5.9 Hz), 21.1; ³¹P NMR (121.5 MHz, CDCl₃) δ 41.36; HRMS (ESI) calculated for C₁₉H₁₈OPS [M+H]⁺ *m/z* 325.0810, found 325.0817.

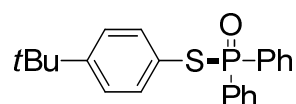
S-(4-ethylphenyl) diphenylphosphinothioate (3ba)



According to **GP** with 4-ethylbenzenethiol **1b** (82.9 mg, 0.6 mmol, 2.0 equiv),

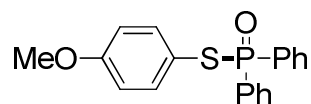
diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ba** as white solid (83.6 mg, 82%). Mp: 84-86 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88-7.81 (m, 4H), 7.51-7.39 (m, 6H), 7.37-7.31 (m, 2H), 7.02 (d, J = 7.8 Hz, 2H), 2.54 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 145.3 (d, J = 2.2 Hz), 135.4 (d, J = 3.8 Hz), 132.7 (d, J = 106.1 Hz), 132.1 (d, J = 2.8 Hz), 131.5 (d, J = 9.9 Hz), 128.7 (d, J = 1.7 Hz), 128.4 (d, J = 13.2 Hz), 122.4 (d, J = 5.6 Hz), 28.3, 15.1; $^{31}\text{P NMR}$ (121.5 MHz, CDCl_3) δ 41.49; **HRMS** (ESI) calculated for $\text{C}_{20}\text{H}_{20}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 339.0967, found 339.0973.

***S*-(4-(*tert*-butyl)phenyl) diphenylphosphinothioate (**3ca**)^[2]**



According to **GP** with 4-(*tert*-butyl)benzenethiol **1c** (100.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ca** as white solid (90.7 mg, 83%). Mp: 119-121 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.86-7.82 (m, 4H), 7.49-7.46 (m, 2H), 7.43-7.39 (m, 4H), 7.36-7.33 (m, 2H), 7.23-7.18 (m, 2H), 1.23 (s, 9H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.2 (d, J = 1.9 Hz), 135.1 (d, J = 3.9 Hz), 132.7 (d, J = 105.9 Hz), 132.1 (d, J = 3.0 Hz), 131.5 (d, J = 9.8 Hz), 128.4 (d, J = 12.6 Hz), 126.2, 122.3 (d, J = 4.8 Hz), 34.5, 31.0; $^{31}\text{P NMR}$ (121.5 MHz, CDCl_3) δ 41.56; **HRMS** (ESI) calculated for $\text{C}_{22}\text{H}_{24}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 367.1280, found 367.1290.

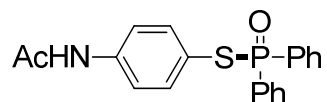
***S*-(4-methoxyphenyl) diphenylphosphinothioate (**3da**)^[2]**



According to **GP** with 4-methoxybenzenethiol **1d** (84.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3da** as white solid (88.0 mg, 86%). Mp: 132-134 °C; $^1\text{H NMR}$ (500 MHz,

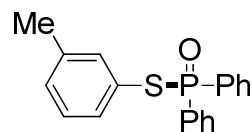
CDCl₃) δ 7.86-7.82 (m, 4H), 7.50-7.47 (m, 2H), 7.44-7.42 (m, 4H), 7.36-7.28 (m, 2H), 6.74-6.68 (m, 2H), 3.71 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.4 (d, J = 2.0 Hz), 136.9 (d, J = 2.9 Hz), 132.7 (d, J = 105.0 Hz), 132.1 (d, J = 2.9 Hz), 131.5 (d, J = 9.6 Hz), 128.4 (d, J = 12.6 Hz), 116.0 (d, J = 4.9 Hz), 114.7, 55.1; ³¹P NMR (121.5 MHz, CDCl₃) δ 41.39; HRMS (ESI) calculated for C₁₉H₁₈O₂PS [M+H]⁺ m/z 341.0760, found 341.0757.

***S*-(4-acetamidophenyl) diphenylphosphinothioate (3ea)**



According to **GP** with *N*-(4-mercaptophenyl)acetamide **1e** (100.3 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ea** as white solid (80.4 mg, 73%). Mp: 157-159 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.87 (s, 1H), 7.85-7.80 (m, 4H), 7.55-7.52 (m, 2H), 7.49-7.41 (m, 6H), 7.20 (d, J = 8.0 Hz, 2H), 2.10 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 140.5, 136.3 (d, J = 3.0 Hz), 132.6 (d, J = 2.0 Hz), 132.1 (d, J = 105.6 Hz), 131.4 (d, J = 9.6 Hz), 128.7 (d, J = 13.6 Hz), 120.4, 117.9 (d, J = 5.9 Hz), 24.3; ³¹P NMR (121.5 MHz, CDCl₃) δ 42.80; HRMS (ESI) calculated for C₂₀H₁₉NO₂PS [M+H]⁺ m/z 368.0869, found 368.0879.

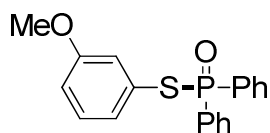
***S-m*-tolyl diphenylphosphinothioate (3fa)^[3]**



According to **GP** with 3-methylbenzenethiol **1f** (74.5 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3fa** as white solid (80.1 mg, 82%). Mp: 96-98 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.88-7.81 (m, 4H), 7.52-7.39 (m, 6H), 7.26-7.22 (m, 2H), 7.09-7.04 (m, 2H), 2.20 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.9 (d, J = 2.0 Hz), 136.0 (d, J = 3.8 Hz), 132.6 (d, J = 106.1 Hz), 132.3 (d, J = 3.8 Hz), 132.1 (d, J = 2.7 Hz), 131.5 (d, J

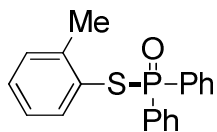
= 9.8 Hz), 129.7 (d, $J = 1.7$ Hz), 128.8 (d, $J = 1.1$ Hz), 128.4 (d, $J = 13.2$ Hz), 125.7 (d, $J = 5.0$ Hz), 21.0; ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.35; HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{18}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 325.0810, found 325.0824.

***S*-(3-methoxyphenyl) diphenylphosphinothioate (3ga)**^[3]



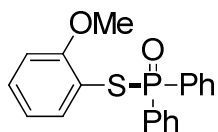
According to **GP** with 3-methoxybenzenethiol **1g** (84.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ga** as white solid (92.8 mg, 91%). Mp: 90-92 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.89-7.82 (m, 4H), 7.54-7.41 (m, 6H), 7.13-7.02 (m, 2H), 7.01-6.95 (m, 1H), 6.83-6.75 (m, 1H), 3.66 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.6, 132.6 (d, $J = 106.6$ Hz), 132.3 (d, $J = 3.3$ Hz), 131.6 (d, $J = 9.9$ Hz), 129.7 (d, $J = 1.7$ Hz), 128.5 (d, $J = 13.2$ Hz), 127.5 (d, $J = 4.4$ Hz), 127.1 (d, $J = 4.4$ Hz), 119.7 (d, $J = 3.8$ Hz), 115.7 (d, $J = 2.2$ Hz), 55.2; ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.52; HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{PS}$ $[\text{M}+\text{H}]^+$ m/z 341.0760, found 341.0754.

***S*-*o*-tolyl diphenylphosphinothioate (3ha)**



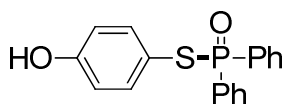
According to **GP** with 2-methylbenzenethiol **1h** (74.5 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ha** as white solid (58.1 mg, 60%). Mp: 70-72 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.85-7.78 (m, 4H), 7.52-7.39 (m, 7H), 7.18-7.11 (m, 2H), 7.02-6.98 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.8 (d, $J = 3.9$ Hz), 136.7 (d, $J = 3.9$ Hz), 132.8 (d, $J = 106.0$ Hz), 132.2 (d, $J = 2.9$ Hz), 131.4 (d, $J = 10.6$ Hz), 130.6, 129.2 (d, $J = 2.0$ Hz), 128.4 (d, $J = 12.6$ Hz), 126.4, 125.4 (d, $J = 4.9$ Hz), 21.3; ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.18; HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{18}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 325.0810, found 325.0818.

***S*-(2-methoxyphenyl) diphenylphosphinothioate (3ia)^[3]**



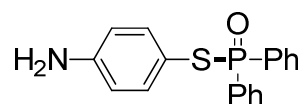
According to **GP** with 2-methoxybenzenethiol **1i** (84.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ia** as white solid (56.0 mg, 55%). Mp: 65-67 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.90-7.83 (m, 4H), 7.70-7.67 (m, 1H), 7.50-7.37 (m, 6H), 7.24-7.19 (m, 1H), 6.87-6.82 (m, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 3.61 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 159.4 (d, *J* = 3.8 Hz), 137.5 (d, *J* = 3.9 Hz), 133.1 (d, *J* = 106.6 Hz), 132.0 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 10.4 Hz), 130.6 (d, *J* = 2.2 Hz), 128.2 (d, *J* = 12.7 Hz), 121.1 (d, *J* = 1.1 Hz), 114.1 (d, *J* = 5.0 Hz), 111.1 (d, *J* = 2.2 Hz), 55.4; **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.50; **HRMS** (ESI) calculated for C₁₉H₁₈O₂PS [M+H]⁺ *m/z* 341.0760, found 341.0760.

***S*-(4-hydroxyphenyl) diphenylphosphinothioate (3ja)**



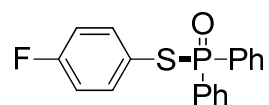
According to **GP** with 4-mercaptophenol **1j** (75.7 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ja** as white solid (75.3 mg, 77%). Mp: 137-139 °C; **¹H NMR** (300 MHz, CDCl₃) δ 9.62 (br s, 1H), 7.89-7.83 (m, 4H), 7.57-7.44 (m, 6H), 7.12-7.02 (m, 2H), 6.56-6.48 (m, 2H); **¹³C NMR** (75 MHz, CDCl₃) δ 159.1 (d, *J* = 2.3 Hz), 137.3 (d, *J* = 3.3 Hz), 132.1 (d, *J* = 106.1 Hz), 132.5 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 10.4 Hz), 128.7 (d, *J* = 12.6 Hz), 117.4 (d, *J* = 1.7 Hz), 112.1 (d, *J* = 5.5 Hz); **³¹P NMR** (121.5 MHz, CDCl₃) δ 43.12; **HRMS** (ESI) calculated for C₁₈H₁₆O₂PS [M+H]⁺ *m/z* 327.0603, found 327.0611.

***S*-(4-aminophenyl) diphenylphosphinothioate (3ka)**



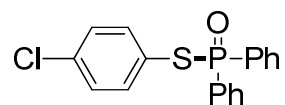
According to **GP** with 4-aminobenzenethiol **1k** (75.1 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ka** as white solid (81.5 mg, 84%). Mp: 167-169 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.86-7.80 (m, 4H), 7.51-7.39 (m, 6H), 7.19-7.10 (m, 2H), 6.48-6.40 (m, 2H), 3.62 (br s, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 147.8, 136.9 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 105.0 Hz), 132.0 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.8 Hz), 128.4 (d, *J* = 12.6 Hz), 115.5, 111.9 (d, *J* = 4.9 Hz); **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.36; **HRMS** (ESI) calculated for C₁₈H₁₇NOPS [M+H]⁺ *m/z* 326.0763, found 326.0760.

***S*-(4-fluorophenyl) diphenylphosphinothioate (3la)^[2]**



According to **GP** with 4-fluorobenzenethiol **1l** (76.9 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3la** as white solid (56.8 mg, 58%). Mp: 93-95 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.87-7.80 (m, 4H), 7.54-7.38 (m, 8H), 6.92-6.86 (m, 2H); **¹³C NMR** (75 MHz, CDCl₃) δ 163.4 (dd, *J* = 248.4, 2.2 Hz), 137.3 (dd, *J* = 8.5, 3.6 Hz), 132.4 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 106.1 Hz), 131.5 (d, *J* = 9.8 Hz), 128.5 (d, *J* = 13.2 Hz), 121.2 (dd, *J* = 5.0, 3.3 Hz), 116.2 (d, *J* = 22.0 Hz); **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.66; **HRMS** (ESI) calculated for C₁₈H₁₅FOPS [M+H]⁺ *m/z* 329.0560, found 329.0561.

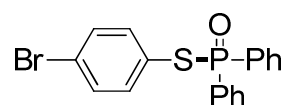
***S*-(4-chlorophenyl) diphenylphosphinothioate (3ma)^[3]**



According to **GP** with 4-chlorobenzenethiol **1m** (87.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3

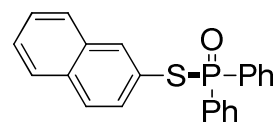
mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ma** as white solid (40.9 mg, 40%). Mp: 95-97 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.86-7.82 (m, 4H), 7.54-7.51 (m, 2H), 7.47-7.43 (m, 4H), 7.40-7.35 (m, 2H), 7.19-7.14 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 136.5 (d, *J* = 3.9 Hz), 135.5 (d, *J* = 2.0 Hz), 132.4 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 107.0 Hz), 131.6 (d, *J* = 10.8 Hz), 129.3, 128.6 (d, *J* = 13.6 Hz), 124.7 (d, *J* = 4.9 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 41.67; HRMS (ESI) calculated for C₁₈H₁₅ClOPS [M+H]⁺ m/z 345.0264, found 345.0261.

***S*-(4-bromophenyl) diphenylphosphinothioate (3na)**



According to **GP** with 4-bromobenzenethiol **1n** (113.4 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3na** as white solid (63.5 mg, 54%) (reaction time: 6 h). Mp: 93-95 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.86-7.82 (m, 4H), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 4H), 7.31 (s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 136.7 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 107.0 Hz), 132.4, 132.2, 131.5 (d, *J* = 10.8 Hz), 128.6 (d, *J* = 13.6 Hz), 125.4 (d, *J* = 4.9 Hz), 123.7 (d, *J* = 2.9 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 41.45; HRMS (ESI) calculated for C₁₈H₁₅BrOPS [M+H]⁺ m/z 388.9759, found 388.9765.

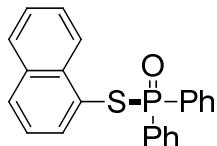
***S*-naphthalen-2-yl diphenylphosphinothioate (3oa)^[2]**



According to **GP** with naphthalene-2-thiol **1o** (96.1 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3oa** as white solid (70.1 mg, 65%). Mp: 108-110 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1H), 7.90-7.83 (m, 4H), 7.70-7.65 (m, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.49-7.35 (m, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 135.2 (d, *J* = 4.9 Hz), 133.4, 132.9,

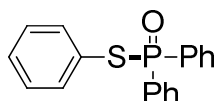
132.5 (d, $J = 106.0$ Hz), 132.2 (d, $J = 1.9$ Hz), 131.5 (d, $J = 10.6$ Hz), 131.4, 128.5, 128.4 (d, $J = 12.6$ Hz), 127.6, 127.4, 126.7, 126.3, 123.4 (d, $J = 5.9$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.63; **HRMS** (ESI) calculated for $\text{C}_{22}\text{H}_{18}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 361.0810, found 361.0819.

S-naphthalen-1-yl diphenylphosphinothioate (3pa)



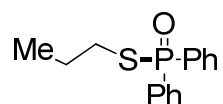
According to **GP** with naphthalene-1-thiol **1p** (96.1 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3pa** as white solid (55.8 mg, 52%). Mp: 100-102 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.39 (d, $J = 8.1$ Hz, 1H), 7.85-7.78 (m, 5H), 7.74-7.70 (m, 2H), 7.48-7.38 (m, 4H), 7.35-7.24 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.4 (d, $J = 4.9$ Hz), 134.9 (d, $J = 3.0$ Hz), 134.0, 132.5 (d, $J = 106.0$ Hz), 132.1 (d, $J = 2.9$ Hz), 131.4 (d, $J = 10.8$ Hz), 129.9 (d, $J = 2.9$ Hz), 128.3 (d, $J = 13.6$ Hz), 128.2, 126.6, 126.1, 125.9, 125.4, 123.6 (d, $J = 5.9$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.63; **HRMS** (ESI) calculated for $\text{C}_{22}\text{H}_{18}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 361.0810, found 361.0814.

S-phenyl diphenylphosphinothioate (3qa)^[3]



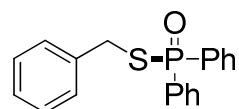
According to **GP** with benzenethiol **1q** (66.1 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3qa** as white solid (51.7 mg, 56%). Mp: 86-88 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.87-7.81 (m, 4H), 7.53-7.39 (m, 8H), 7.24-7.16 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.3 (d, $J = 3.9$ Hz), 132.5 (d, $J = 106.9$ Hz), 132.3 (d, $J = 2.9$ Hz), 131.5 (d, $J = 9.8$ Hz), 129.0, 128.9 (d, $J = 2.0$ Hz), 128.5 (d, $J = 12.8$ Hz), 126.1 (d, $J = 4.8$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 41.79; **HRMS** (ESI) calculated for $\text{C}_{18}\text{H}_{16}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 311.0654, found 311.0650.

S-propyl diphenylphosphinothioate (3ra)^[3]



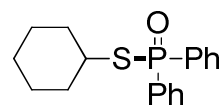
According to **GP** with propane-1-thiol **1r** (46.0 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ra** as colorless oil (37.8 mg, 46%). **¹H NMR** (300 MHz, CDCl₃) δ 7.82-7.85 (m, 4H), 7.55-7.43 (m, 6H), 2.82-2.74 (m, 2H), 1.71-1.59 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 133.5 (d, *J* = 106.0 Hz), 132.1 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 10.6 Hz), 128.5 (d, *J* = 12.6 Hz), 31.1 (d, *J* = 2.9 Hz), 24.0 (d, *J* = 4.9 Hz), 13.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 43.30; **HRMS** (ESI) calculated for C₁₅H₁₈OPS [M+H]⁺ *m/z* 277.0810, found 277.0817.

S-benzyl diphenylphosphinothioate (3sa)^[3]



According to **GP** with phenylmethanethiol **1s** (74.5 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3sa** as white solid (48.5 mg, 50%). Mp: 83-85 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.90-7.83 (m, 4H), 7.53-7.41 (m, 6H), 7.23-7.14 (m, 5H), 4.02 (d, *J* = 9.3 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 136.8 (d, *J* = 4.9 Hz), 133.1 (d, *J* = 105.9 Hz), 132.2 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 9.8 Hz), 128.9, 128.6, 128.5 (d, *J* = 4.9 Hz), 127.3, 33.1 (d, *J* = 2.0 Hz); **³¹P NMR** (121.5 MHz, CDCl₃) δ 42.83; **HRMS** (ESI) calculated for C₁₉H₁₈OPS [M+H]⁺ *m/z* 325.0815, found 325.0810.

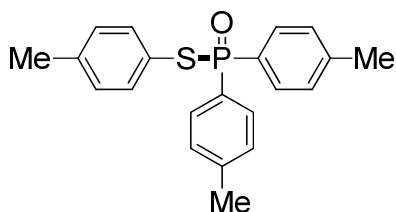
S-cyclohexyl diphenylphosphinothioate (3ta)



According to **GP** with cyclohexanethiol **1t** (69.7 mg, 0.6 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3

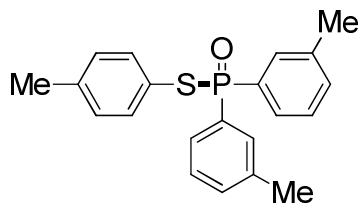
mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ta** as white solid (37.6 mg, 40%). Mp: 75-77 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.91-7.84 (m, 4H), 7.54-7.42 (m, 6H), 3.36-3.24 (m, 1H), 1.96-1.92 (m, 2H), 1.69-1.64 (m, 2H), 1.58-1.43 (m, 3H), 1.35-1.21 (m, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 134.2 (d, $J = 106.6$ Hz), 132.0 (d, $J = 2.8$ Hz), 131.4 (d, $J = 10.5$ Hz), 128.5 (d, $J = 12.6$ Hz), 44.4 (d, $J = 2.2$ Hz), 35.5 (d, $J = 3.8$ Hz), 25.7, 25.3; $^{31}\text{P NMR}$ (121.5 MHz, CDCl_3) δ 41.97; **HRMS** (ESI) calculated for $\text{C}_{18}\text{H}_{22}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 317.1123, found 317.1133.

***S-p*-tolyl di-*p*-tolylphosphinothioate (3ab)**



According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), di-*p*-tolylphosphine oxide **2b** (69.0 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ab** as colorless oil (84.5 mg, 80%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.75-7.68 (m, 4H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.23-7.20 (m, 4H), 6.99 (d, $J = 8.1$ Hz, 2H), 2.35 (s, 6H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 142.6 (d, $J = 2.8$ Hz), 138.8 (d, $J = 2.2$ Hz), 135.1 (d, $J = 3.3$ Hz), 131.5 (d, $J = 11.0$ Hz), 129.8 (d, $J = 1.7$ Hz), 129.1 (d, $J = 13.7$ Hz), 129.6 (d, $J = 108.8$ Hz), 122.7 (d, $J = 5.6$ Hz), 21.4 (d, $J = 1.1$ Hz), 21.0; $^{31}\text{P NMR}$ (121.5 MHz, CDCl_3) δ 42.01; **HRMS** (ESI) calculated for $\text{C}_{21}\text{H}_{22}\text{OPS}$ $[\text{M}+\text{H}]^+$ m/z 353.1123, found 353.1132.

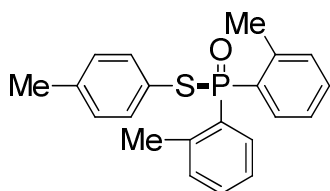
***S-p*-tolyl di-*m*-tolylphosphinothioate (3ac)**



According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv),

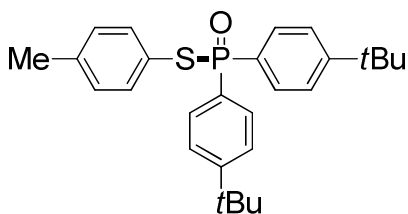
di-*m*-tolylphosphine oxide **2c** (69.0 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ac** as white solid (87.4 mg, 83%). Mp: 59-61 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.69-7.59 (m, 4H), 7.34-7.26 (m, 6H), 7.00 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 6H), 2.24 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 138.9 (d, *J* = 2.2 Hz), 138.3 (d, *J* = 12.6 Hz), 135.2 (d, *J* = 3.8 Hz), 132.9 (d, *J* = 3.3 Hz), 132.5 (d, *J* = 105.5 Hz), 132.0 (d, *J* = 9.4 Hz), 129.8 (d, *J* = 1.7 Hz), 128.5 (d, *J* = 9.4 Hz), 128.2 (d, *J* = 13.7 Hz), 122.5 (d, *J* = 5.0 Hz), 21.2, 21.0; **³¹P NMR** (121.5 MHz, CDCl₃) δ 42.00; **HRMS** (ESI) calculated for C₂₁H₂₂OPS [M+H]⁺ *m/z* 353.1123, found 353.1117.

***S-p*-tolyl di-*o*-tolylphosphinothioate (**3ad**)**



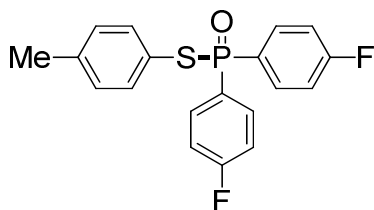
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), di-*o*-tolylphosphine oxide **2d** (69.0 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ad** as white solid (54.7 mg, 52%). Mp: 99-101 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.40-7.33 (m, 4H), 7.25-7.16 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 6H), 2.26 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 141.9 (d, *J* = 9.8 Hz), 139.0, 135.6 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 11.5 Hz), 132.1 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 12.1 Hz), 131.6 (d, *J* = 101.6 Hz), 129.8, 125.4 (d, *J* = 13.2 Hz), 122.4 (d, *J* = 5.0 Hz), 21.3 (d, *J* = 3.8 Hz), 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 43.77; **HRMS** (ESI) calculated for C₂₁H₂₂OPS [M+H]⁺ *m/z* 353.1123, found 353.1129.

***S-p*-tolyl bis(4-(*tert*-butyl)phenyl)phosphinothioate (**3ae**)**



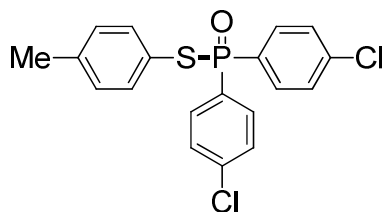
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), bis(4-(*tert*-butyl)phenyl)phosphine oxide **2e** (94.3 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ae** as white solid (45.6 mg, 35%). Mp: 120-122 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.80-7.73 (m, 4H), 7.45-7.42 (m, 4H), 7.35-7.28 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H), 1.31 (s, 18H); **¹³C NMR** (75 MHz, CDCl₃) δ 155.6 (d, *J* = 3.3 Hz), 138.8 (d, *J* = 2.2 Hz), 135.3 (d, *J* = 3.8 Hz), 131.5 (d, *J* = 10.4 Hz), 129.8 (d, *J* = 1.7 Hz), 129.7 (d, *J* = 108.2 Hz), 125.4 (d, *J* = 13.2 Hz), 122.9 (d, *J* = 5.0 Hz), 35.0, 31.0, 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.53; **HRMS** (ESI) calculated for C₂₇H₃₄OPS [M+H]⁺ *m/z* 437.2062, found 437.2063.

***S*-*p*-tolyl bis(4-fluorophenyl)phosphinothioate (**3af**)**



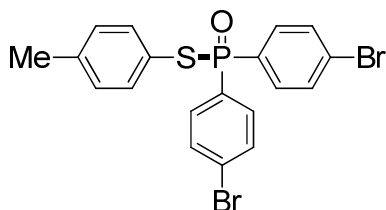
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), bis(4-fluorophenyl)phosphine oxide **2f** (71.5 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3af** as colorless oil (60.2 mg, 56%). **¹H NMR** (300 MHz, CDCl₃) δ 7.88-7.79 (m, 4H), 7.35-7.26 (m, 2H), 7.16-7.10 (m, 4H), 7.06-6.98 (m, 2H), 2.26 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 165.2 (dd, *J* = 252.8, 3.3 Hz), 139.4 (d, *J* = 2.2 Hz), 135.2 (d, *J* = 3.8 Hz), 134.1 (dd, *J* = 11.8, 9.1 Hz), 130.0, 128.4 (dd, *J* = 110.4, 2.7 Hz), 121.8 (d, *J* = 5.0 Hz), 115.9 (dd, *J* = 21.4, 14.3 Hz), 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 39.28; **HRMS** (ESI) calculated for C₁₉H₁₆F₂OPS [M+H]⁺ *m/z* 361.0622, found 361.0630.

***S*-*p*-tolyl bis(4-chlorophenyl)phosphinothioate (**3ag**)**



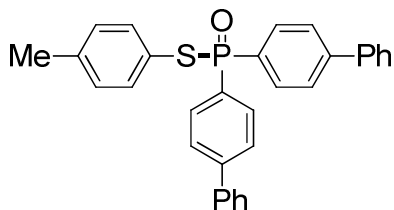
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), bis(4-chlorophenyl)phosphine oxide **2g** (81.3 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ag** as white solid (73.0 mg, 62%). Mp: 109-111 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.79-7.72 (m, 4H), 7.44-7.40 (m, 4H), 7.35-7.27 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 2.27 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 139.5 (d, *J* = 2.7 Hz), 139.1 (d, *J* = 3.9 Hz), 135.2 (d, *J* = 3.9 Hz), 132.9 (d, *J* = 11.6 Hz), 130.9 (d, *J* = 108.2 Hz), 130.1 (d, *J* = 1.7 Hz), 128.9 (d, *J* = 13.7 Hz), 121.5 (d, *J* = 5.0 Hz), 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 39.13; **HRMS** (ESI) calculated for C₁₉H₁₆Cl₂OPS [M+H]⁺ *m/z* 393.0031, found 393.0035.

***S*-*p*-tolyl bis(4-bromophenyl)phosphinothioate (**3ah**)**



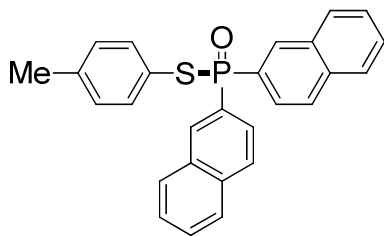
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), bis(4-bromophenyl)phosphine oxide **2h** (108.0 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ah** as white solid (60.5 mg, 42%). Mp: 132-134 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.71-7.64 (m, 4H), 7.61-7.57 (m, 4H), 7.35-7.27 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 139.6 (d, *J* = 2.2 Hz), 135.3 (d, *J* = 3.8 Hz), 133.0 (d, *J* = 11.0 Hz), 131.9 (d, *J* = 13.1 Hz), 131.4 (d, *J* = 107.7 Hz), 130.2 (d, *J* = 1.7 Hz), 127.8 (d, *J* = 3.9 Hz), 121.4 (d, *J* = 5.5 Hz), 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 39.50; **HRMS** (ESI) calculated for C₁₉H₁₆Br₂OPS [M+H]⁺ *m/z* 480.9021, found 480.9025.

***S*-*p*-tolyl di([1,1'-biphenyl]-4-yl)phosphinothioate (**3ai**)**



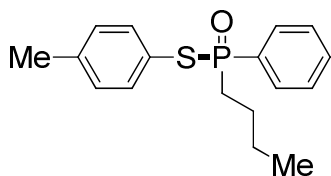
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), di([1,1'-biphenyl]-4-yl)phosphine oxide **2i** (106.3 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ai** as white solid (102.0 mg, 71%). Mp: 125-127 °C; **¹H NMR** (300 MHz, CDCl₃) δ 7.98-7.91 (m, 4H), 7.69-7.65 (m, 4H), 7.60-7.58 (m, 4H), 7.47-7.37 (m, 8H), 7.02 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 145.0 (d, *J* = 2.8 Hz), 139.7, 139.1 (d, *J* = 1.7 Hz), 135.3 (d, *J* = 3.8 Hz), 132.1 (d, *J* = 10.4 Hz), 130.6, 130.0, 128.9, 128.2, 127.2, 127.1 (d, *J* = 12.6 Hz), 122.4 (d, *J* = 5.0 Hz), 21.1; **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.09; **HRMS** (ESI) calculated for C₃₁H₂₆OPS [M+H]⁺ *m/z* 477.1436, found 477.1427.

***S-p*-tolyl di(naphthalen-2-yl)phosphinothioate (**3aj**)**



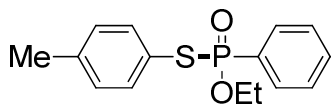
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), di(naphthalen-2-yl)phosphine oxide **2j** (90.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3aj** as colorless oil (69.8 mg, 55%). **¹H NMR** (300 MHz, CDCl₃) δ 8.48 (s, 1H), 8.43 (s, 1H), 7.90-7.82 (m, 8H), 7.59-7.49 (m, 4H), 7.41-7.35 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 2.18 (s, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 139.1 (d, *J* = 1.7 Hz), 135.3 (d, *J* = 3.8 Hz), 134.8 (d, *J* = 2.2 Hz), 133.9 (d, *J* = 9.3 Hz), 132.4 (d, *J* = 14.3 Hz), 129.9 (d, *J* = 1.1 Hz), 129.8 (d, *J* = 107.2 Hz), 129.0, 128.32, 128.30 (d, *J* = 13.2 Hz), 127.7, 126.9, 126.2 (d, *J* = 11.6 Hz), 122.2 (d, *J* = 4.9 Hz), 21.0; **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.53; **HRMS** (ESI) calculated for C₂₇H₂₂OPS [M+H]⁺ *m/z* 425.1123, found 425.1132.

***S*-*p*-tolyl butyl(phenyl)phosphinothioate (3ak)**



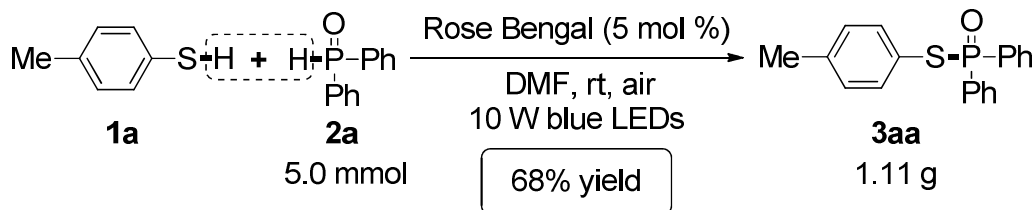
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), butyl(phenyl)phosphine oxide **2k** (54.7 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ak** as colorless oil (61.9 mg, 68%). **¹H NMR** (300 MHz, CDCl₃) δ 7.78-7.71 (m, 2H), 7.52-7.39 (m, 3H), 7.35-7.28 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H), 2.23-2.04 (m, 2H), 1.69-1.45 (m, 2H), 1.41-1.28 (m, 2H), 0.85 (d, *J* = 7.2 Hz, 2H); **¹³C NMR** (75 MHz, CDCl₃) δ 139.0 (d, *J* = 2.2 Hz), 135.3 (d, *J* = 3.3 Hz), 132.4 (d, *J* = 98.3 Hz), 131.9 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 9.9 Hz), 129.9 (d, *J* = 1.7 Hz), 128.3 (d, *J* = 12.7 Hz), 122.2 (d, *J* = 5.5 Hz), 32.7 (d, *J* = 71.0 Hz), 24.2 (d, *J* = 4.4 Hz), 23.6 (d, *J* = 15.9 Hz), 21.0, 13.4; **³¹P NMR** (121.5 MHz, CDCl₃) δ 45.29; **HRMS** (ESI) calculated for C₁₇H₂₂OPS [M+H]⁺ *m/z* 305.1123, found 305.1117.

***O*-ethyl *S*-*p*-tolyl phenylphosphonothioate (3al)**



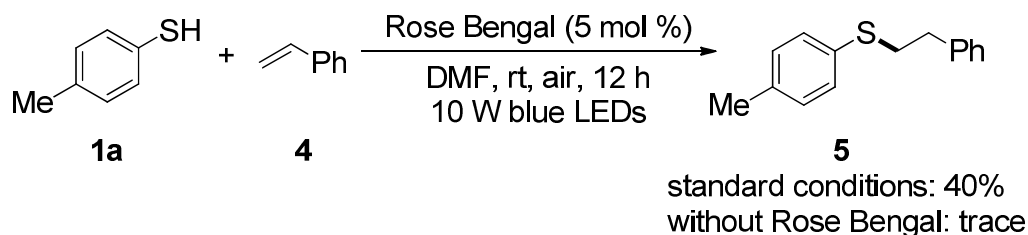
According to **GP** with 4-methylbenzenethiol **1a** (74.5 mg, 0.6 mmol, 2.0 equiv), ethyl phenylphosphinate **2l** (51.0 mg, 0.3 mmol, 1.0 equiv), and Rose Bengal (15.3 mg, 0.015 mmol, 0.05 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3al** as colorless oil (21.1 mg, 30%) (reaction time: 36 h). **¹H NMR** (300 MHz, CDCl₃) δ 7.70-7.62 (m, 2H), 7.51-7.46 (m, 1H), 7.39-7.33 (m, 2H), 7.18-7.15 (m, 2H), 7.02-6.99 (m, 2H), 4.40-4.26 (m, 2H), 2.28 (s, 3H), 1.39 (d, *J* = 7.2 Hz, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 139.1 (d, *J* = 3.3 Hz), 135.4 (d, *J* = 4.4 Hz), 132.3 (d, *J* = 3.3 Hz), 131.7 (d, *J* = 148.9 Hz), 131.4 (d, *J* = 10.4 Hz), 129.9 (d, *J* = 2.3 Hz), 128.1 (d, *J* = 14.8 Hz), 122.8 (d, *J* = 5.6 Hz), 62.3 (d, *J* = 7.1 Hz), 21.1, 16.3 (d, *J* = 6.6 Hz); **³¹P NMR** (121.5 MHz, CDCl₃) δ 41.91; **HRMS** (ESI) calculated for C₁₅H₁₈O₂PS [M+H]⁺ *m/z* 293.0760, found 293.0754.

Larger scale experiment



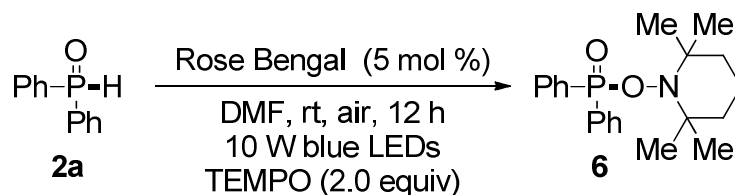
4-Methylbenzenethiol **1a** (1.24 g, 10.0 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (1.01 g, 5.0 mmol, 1.0 equiv), and Rose Bengal (254 mg, 0.25 mmol, 0.05 equiv) were placed in a 100 mL round bottom flask. Then DMF (25.0 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (50.0 mL) was added, and the mixture was extracted by EtOAc (3x50.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3aa** (1.11 g, 68%).

Mechanistic studies

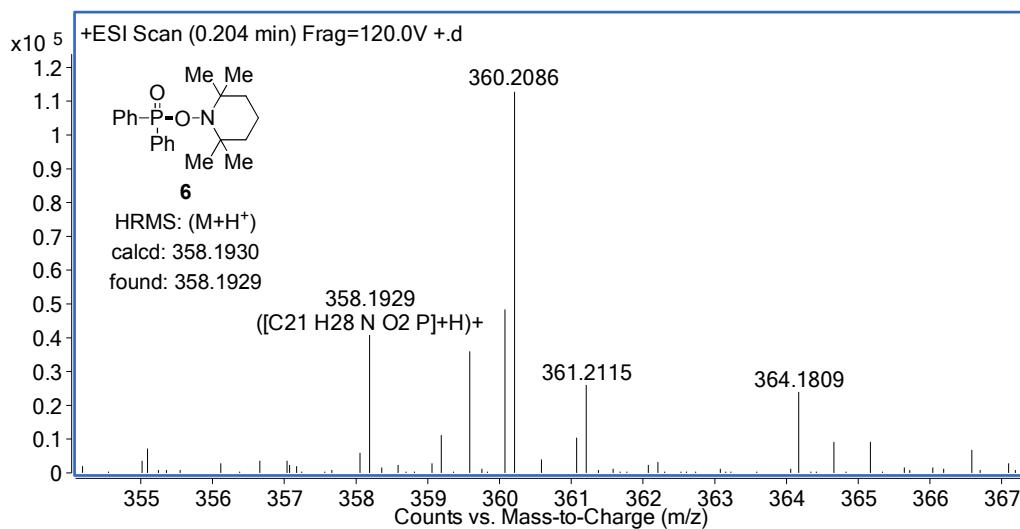


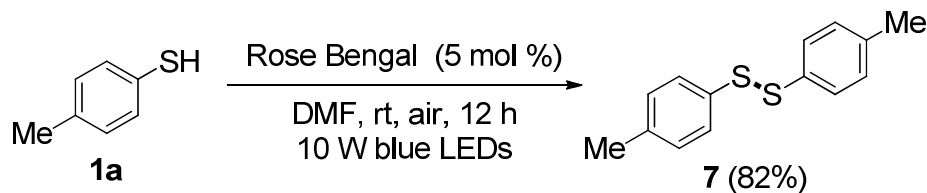
4-Methylbenzenethiol **1a** (62.1 mg, 0.50 mmol, 1.0 equiv), styrene **4** (208.3 mg, 2.0 mmol, 4.0 equiv), and Rose Bengal (25.4 mg, 0.025 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether) to afford the product **5** as colorless oil (45.7 mg, 40%). ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.26 (m, 4H), 7.22-7.16 (m, 3H), 7.14-7.06

(m, 2H), 3.12 (t, $J = 8.0$ Hz, 2H), 2.89 (t, $J = 8.0$ Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.3, 136.2, 132.5, 130.2, 129.7, 128.48, 128.45, 126.4, 35.83, 35.77, 21.0; **HRMS** (ESI) calculated for $\text{C}_{15}\text{H}_{17}\text{S}$ $[\text{M}+\text{H}]^+$ m/z 229.1045, found 229.1047. Analytical data are in agreement with those reported in the literature.^[4] In addition, when the reaction was conducted in the absence of Rose Bengal, only traces of **5** were detected.

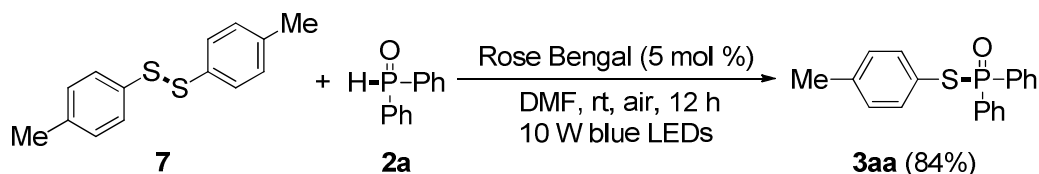


Diphenylphosphine oxide **2a** (60.9 mg, 0.30 mmol, 1.0 equiv), TEMPO (93.1 mg, 0.60 mmol, 2.0 equiv), and Rose Bengal (15.8 mg, 0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. High-resolution mass spectra analysis of this reaction mixture showed that TEMPO-trapped product **6** was formed. This result indicated that P-centered radicals are generated from diphenylphosphine oxide in the current reaction conditions.



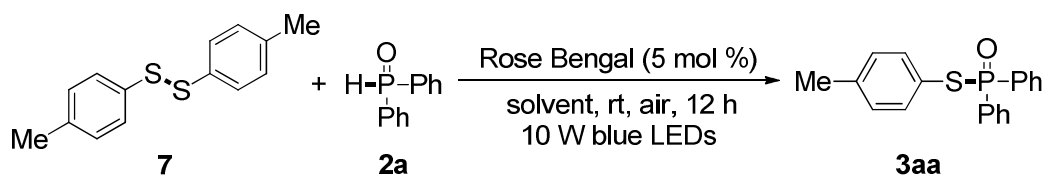


4-Methylbenzenethiol **1a** (37.9 mg, 0.30 mmol, 1.0 equiv), and Rose Bengal (15.6 mg, 0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether) to afford the product **7** as white solid (30.2 mg, 82%). ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.35 (m, 4H), 7.12-7.05 (m, 4H), 2.31 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 137.4, 134.0, 129.8, 128.6, 21.0; Analytical data are in agreement with those reported in the literature.^[5]



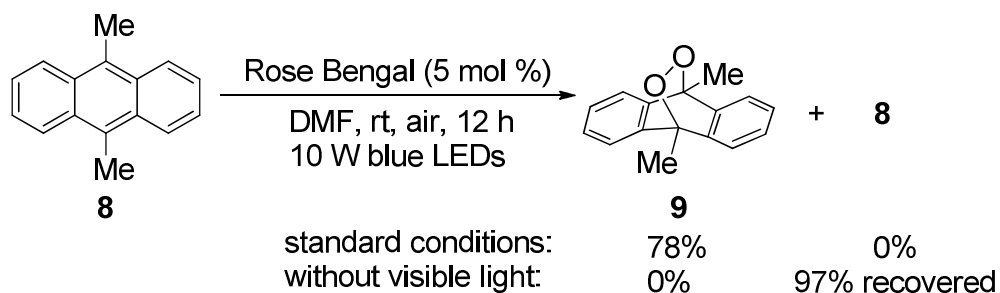
1,2-Di-*p*-tolyl disulfane **7** (148.0 mg, 0.60 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (60.7 mg, 0.30 mmol, 1.0 equiv), and Rose Bengal (15.4 mg, 0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3aa** (81.7 mg, 84%).

Control experiments



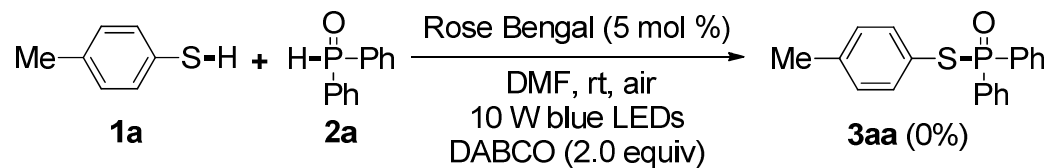
Entry	Photocatalyst	Visible light	Solvent	Atmosphere	Yield (%)
1	yes	yes	DMF	air	84
2	no	yes	DMF	air	86
3	yes	no	DMF	air	82
4	yes	yes	DMF	N ₂	82
5	no	no	DMF	N ₂	83

The above control experiments showed that the formation of **3aa** starting from **7** and **2a** did not require any help of photocatalyst, visible light, or O₂.



9,10-Dimethylanthracene (62.1 mg, 0.30 mmol, 1.0 equiv) and Rose Bengal (15.4 mg, 0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. After the reaction was completed monitored by TLC, H₂O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 40/1) to afford the endoperoxide product **9** as white solid (55.8 mg, 78%). ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.34 (m, 4H), 7.28-7.23 (m, 4H), 2.12 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 140.8, 127.3, 120.6, 79.4, 13.6; HRMS (ESI) calculated for C₁₆H₁₅O₂ [M+H]⁺ m/z 239.1067, found 239.1071. Analytical data are in

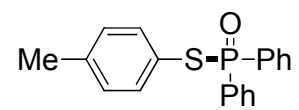
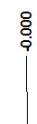
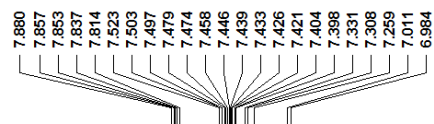
agreement with those reported in the literature.^[6] In addition, the product **9** were not observed in the dark.



4-Methylbenzenethiol **1a** (74.7 mg, 0.60 mmol, 2.0 equiv), diphenylphosphine oxide **2a** (61.2 mg, 0.30 mmol, 1.0 equiv), 1,4-diazabicyclo[2.2.2]octane (DABCO) (67.5 mg, 0.60 mmol, 2.0 equiv), and Rose Bengal (15.5 mg, 0.015 mmol, 0.05 equiv) were placed in a 10 mL *Schlenk* tube. Then DMF (1.5 mL) was added. The reaction mixture was stirred and irradiated by 10 W blue LEDs (450 nm) at room temperature under air atmosphere for 12 h. The formation of **3aa** was completely suppressed.

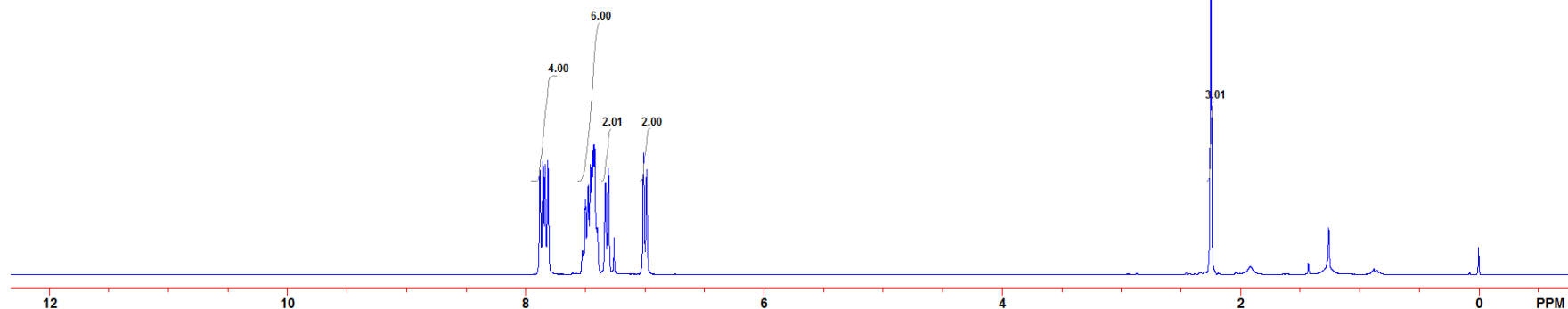
References:

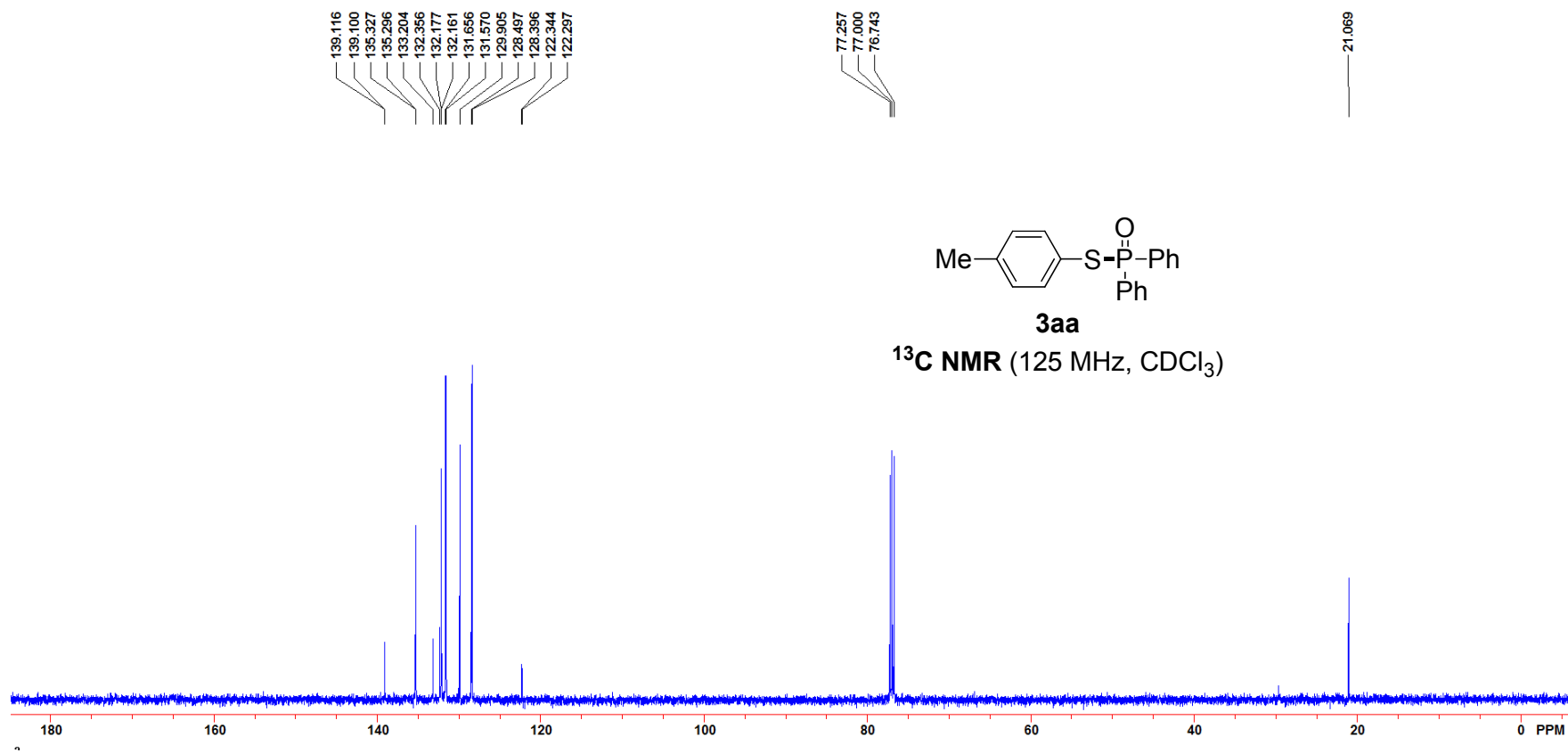
- [1] Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277.
- [2] Li, S.; Chen, T.; Saga, Y.; Han, L.-B. *RSC Adv.* **2015**, *5*, 71544.
- [3] Wang, J.; Huang, X.; Ni, Z.; Wang, S.; Wu, J.; Pan, Y. *Green Chem.* **2015**, *17*, 314.
- [4] Wang, B.; Lin, C.; Liu, Y.; Fan, Z.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 973.
- [5] Li, X.-B.; Li, Z.-J.; Gao, Y.-J.; Meng, Q.-Y.; Yu, S.; Weiss, R. G.; Tung, C.-H.; Wu, L.-Z. *Angew. Chem. Int. Ed.* **2014**, *53*, 2085.
- [6] Xu, W.-T.; Huang, B.; Dai, J.-J.; Xu, J.; Xu, H.-J. *Org. Lett.* **2016**, *18*, 3114.

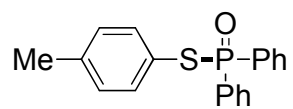


3aa

¹H NMR (300 MHz, CDCl₃)

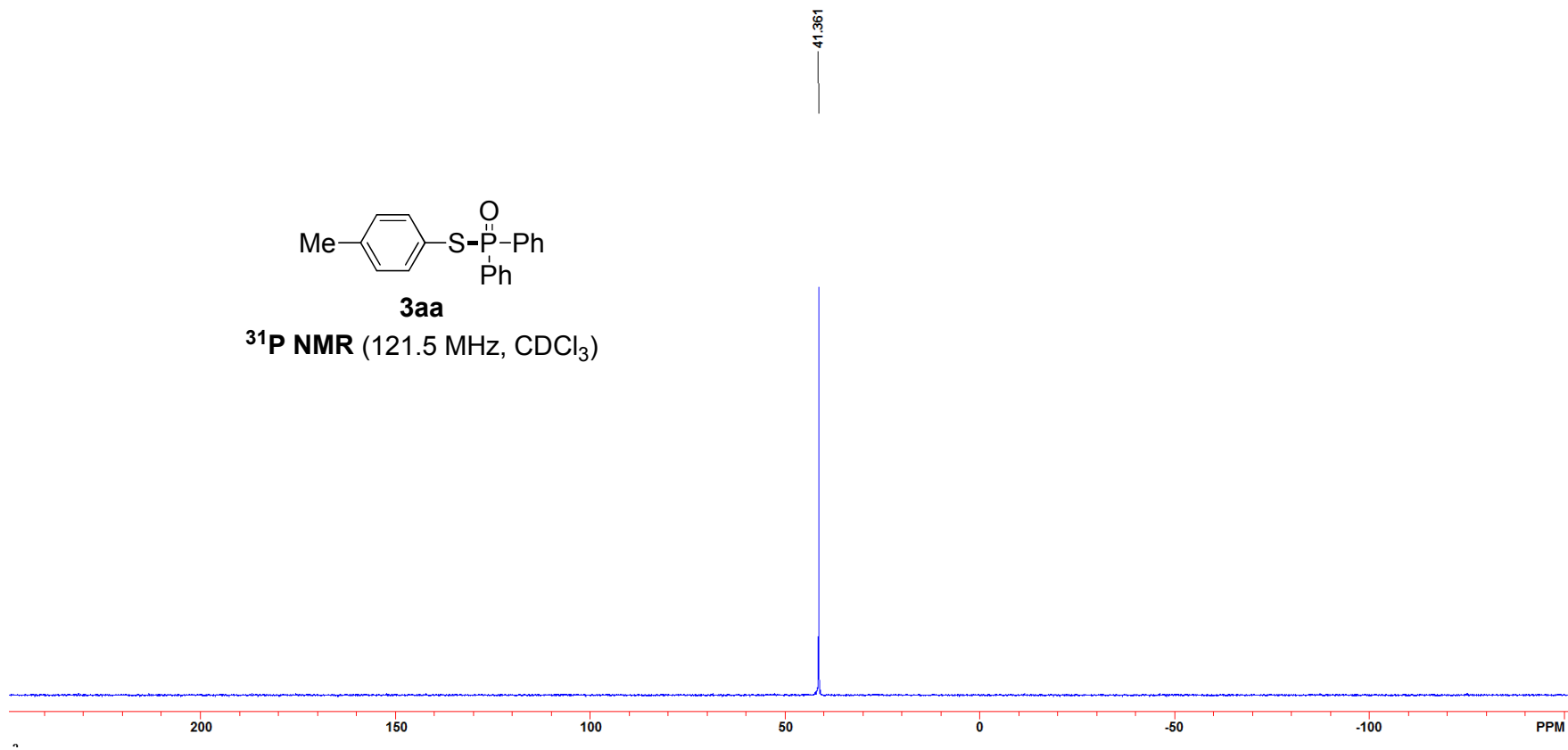


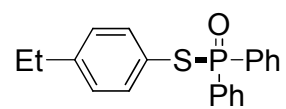
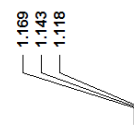
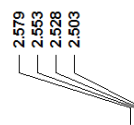
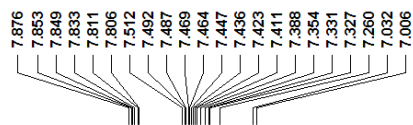




3aa

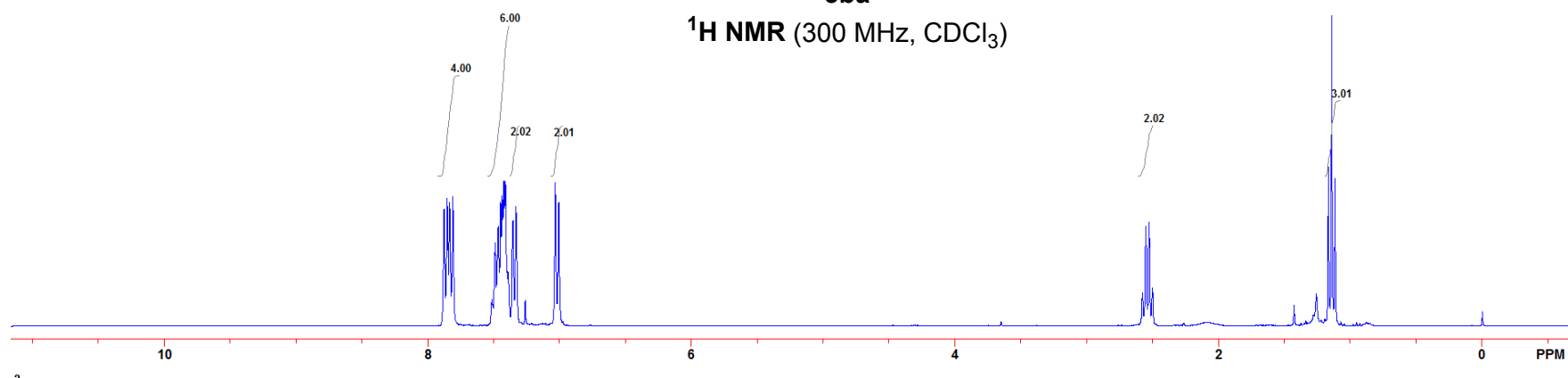
^{31}P NMR (121.5 MHz, CDCl_3)

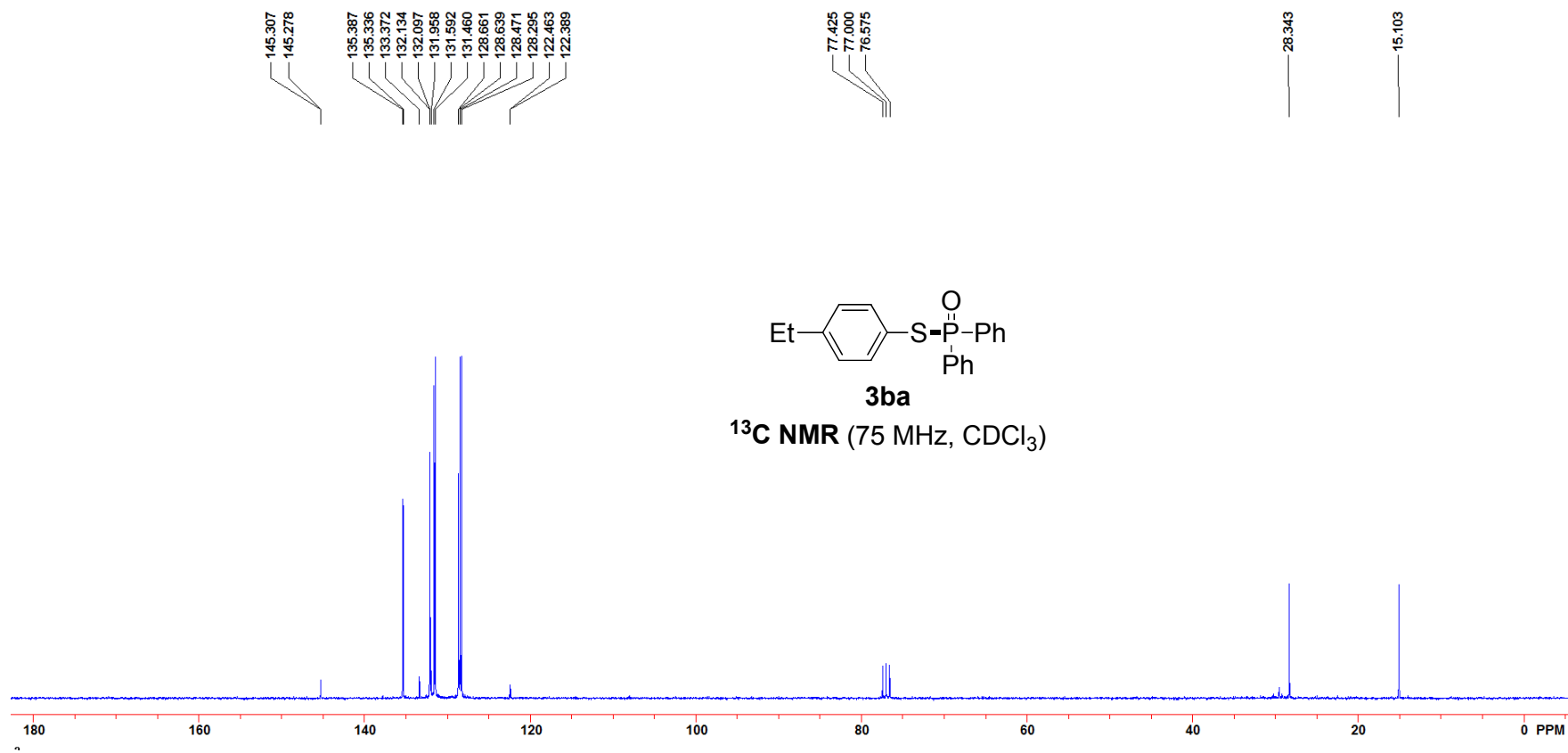


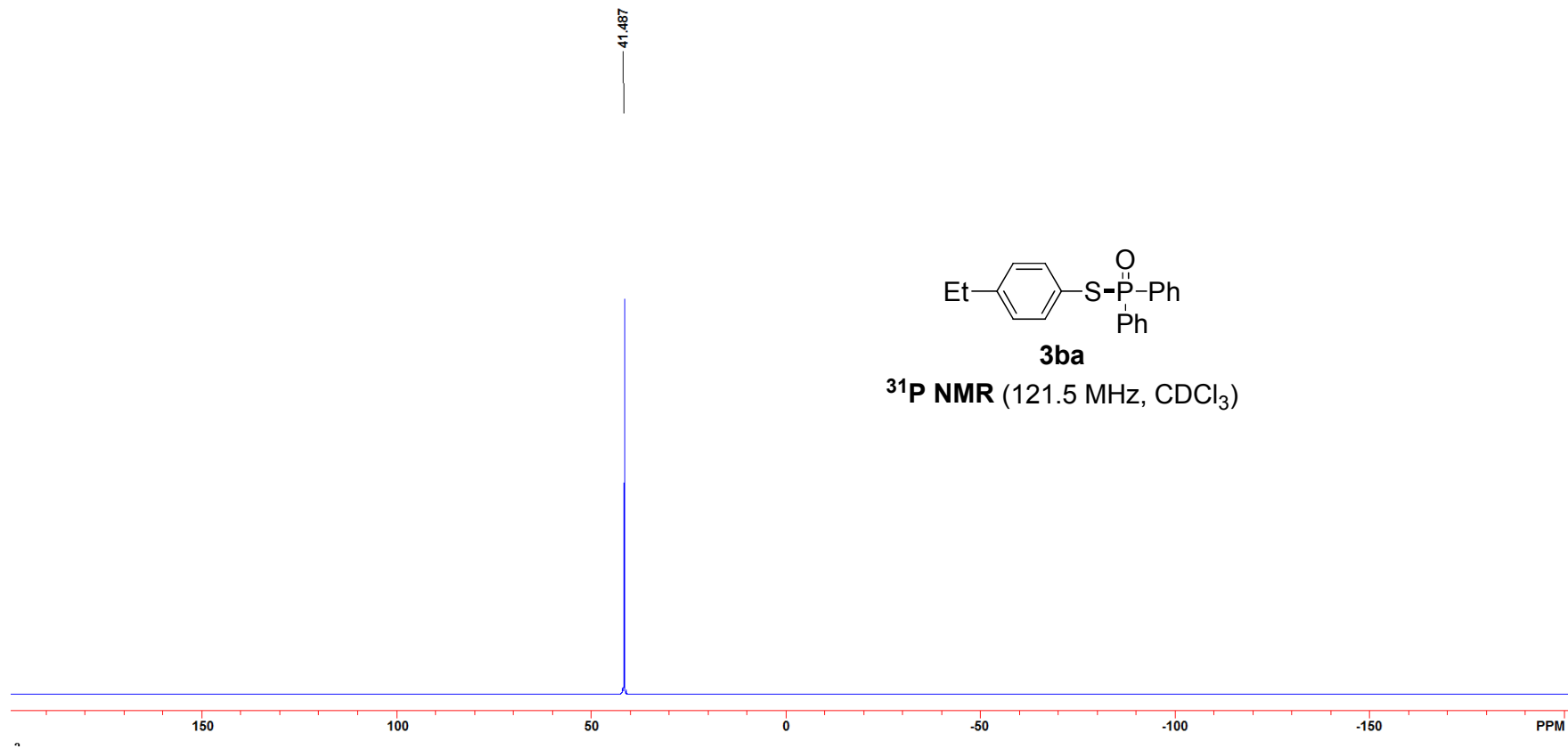


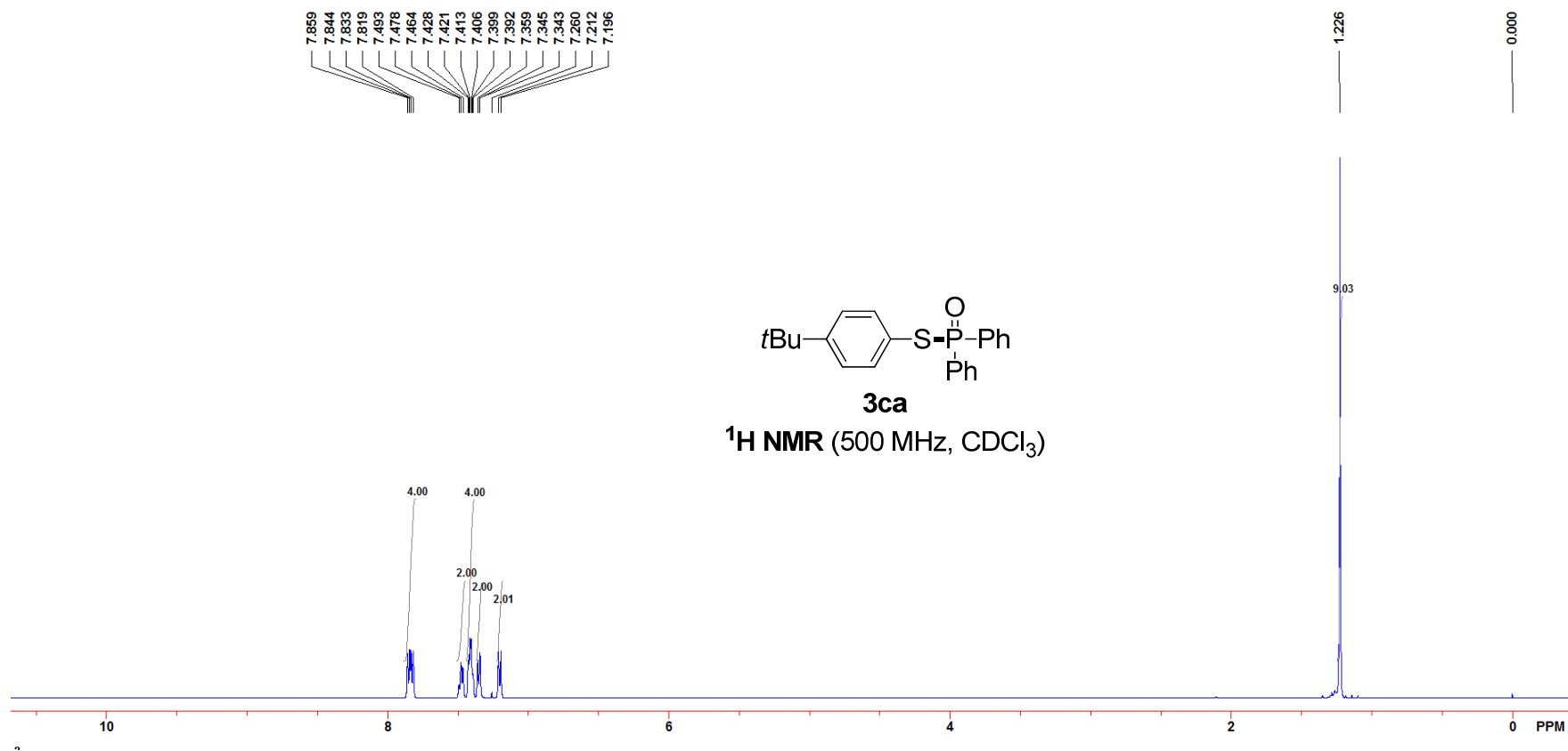
3ba

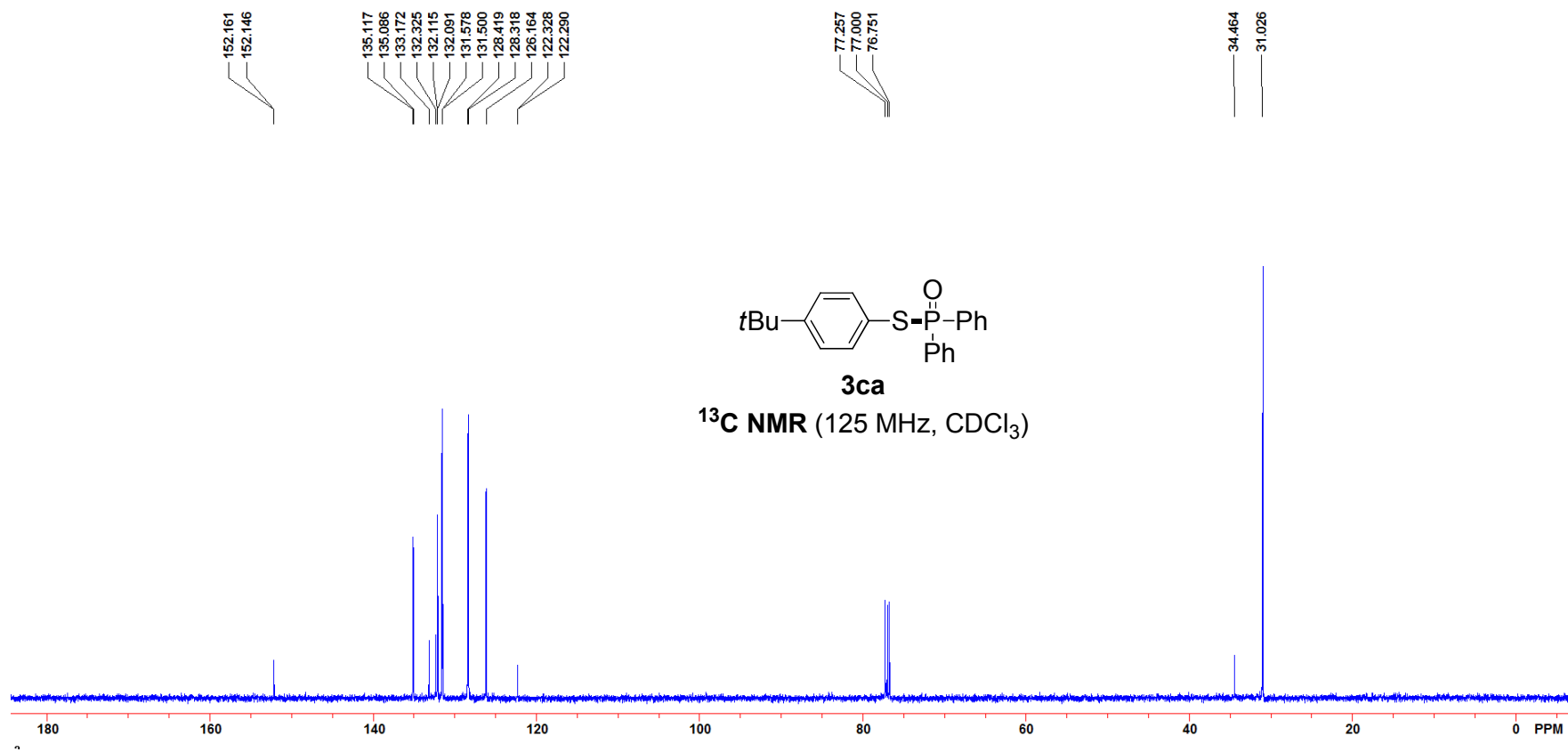
¹H NMR (300 MHz, CDCl₃)

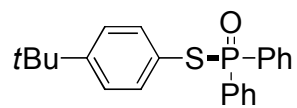






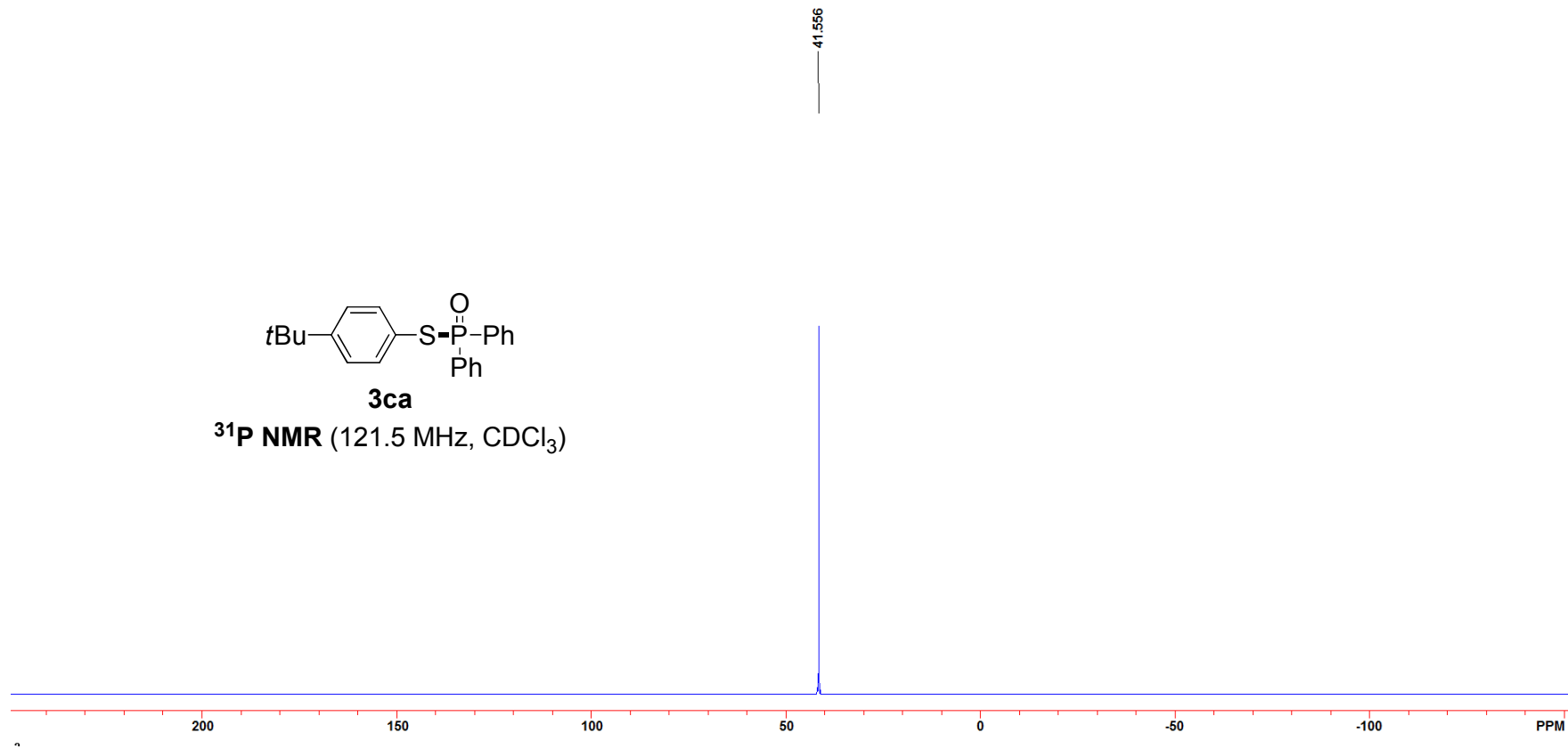


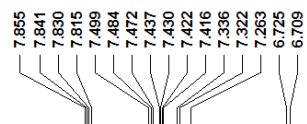




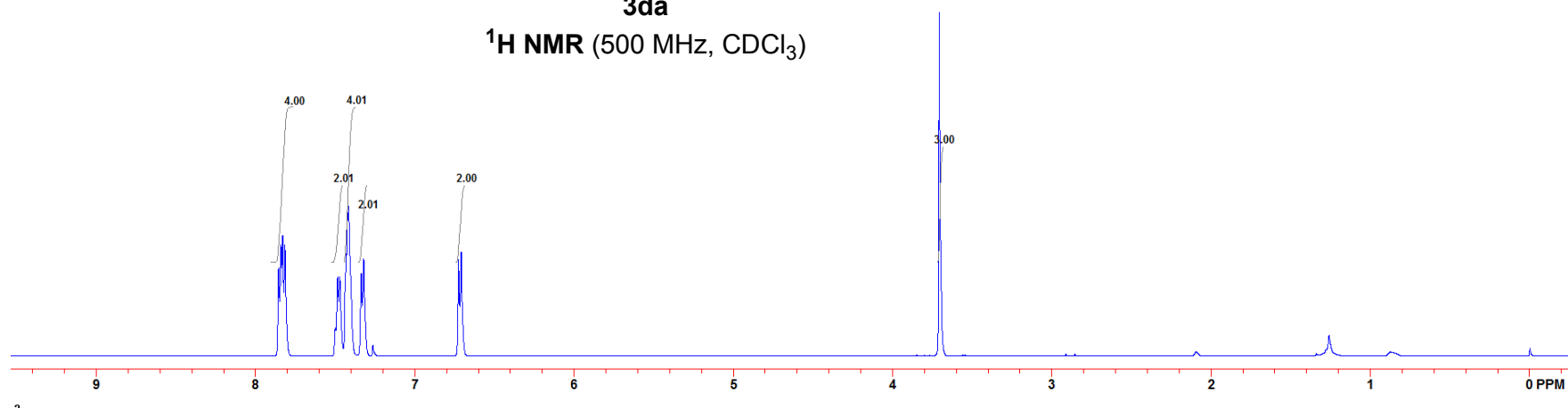
3ca

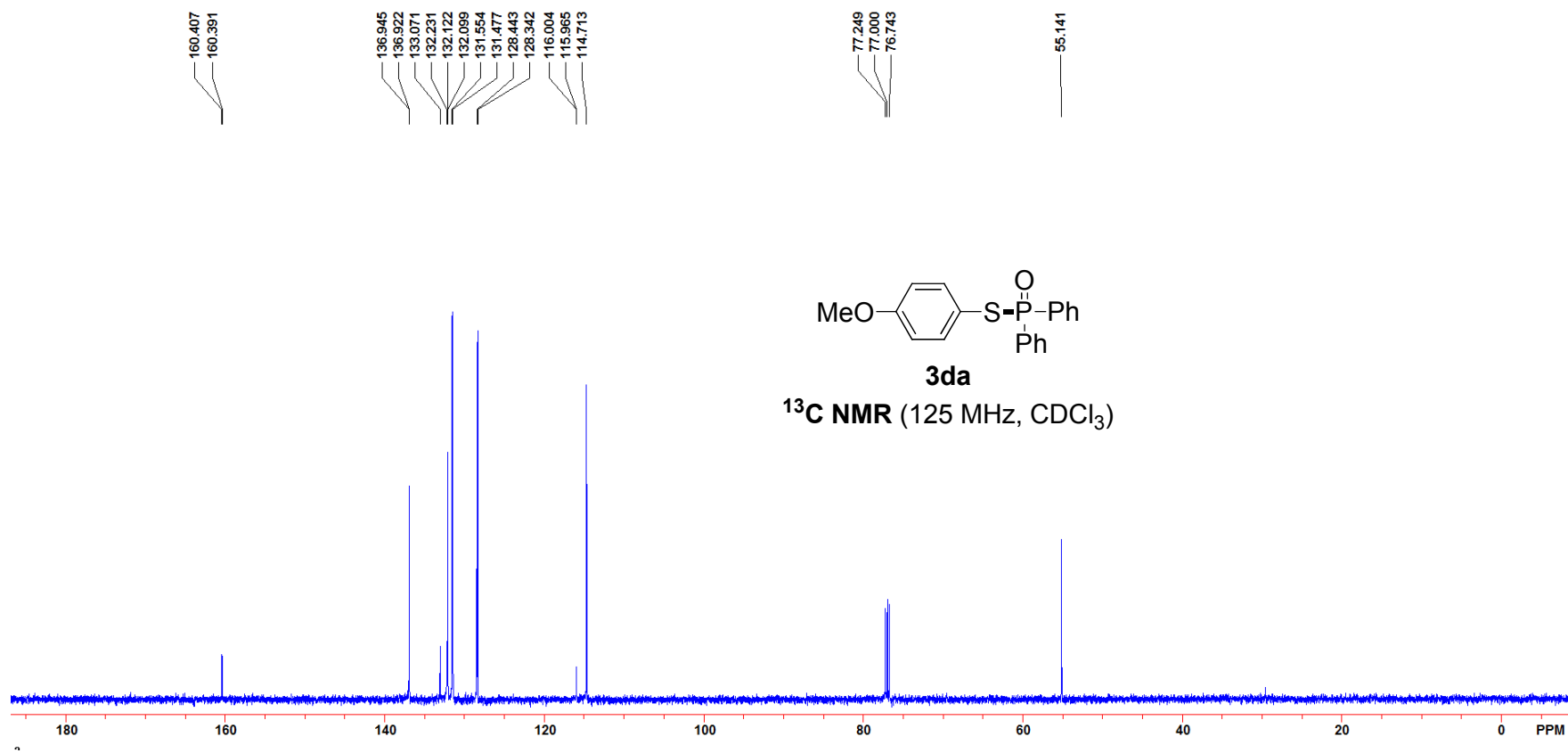
^{31}P NMR (121.5 MHz, CDCl_3)

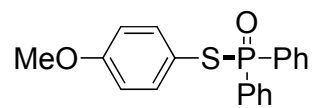




COc1ccc(cc1)S(=O)(c2ccccc2)c3ccccc3
3da
¹H NMR (500 MHz, CDCl₃)

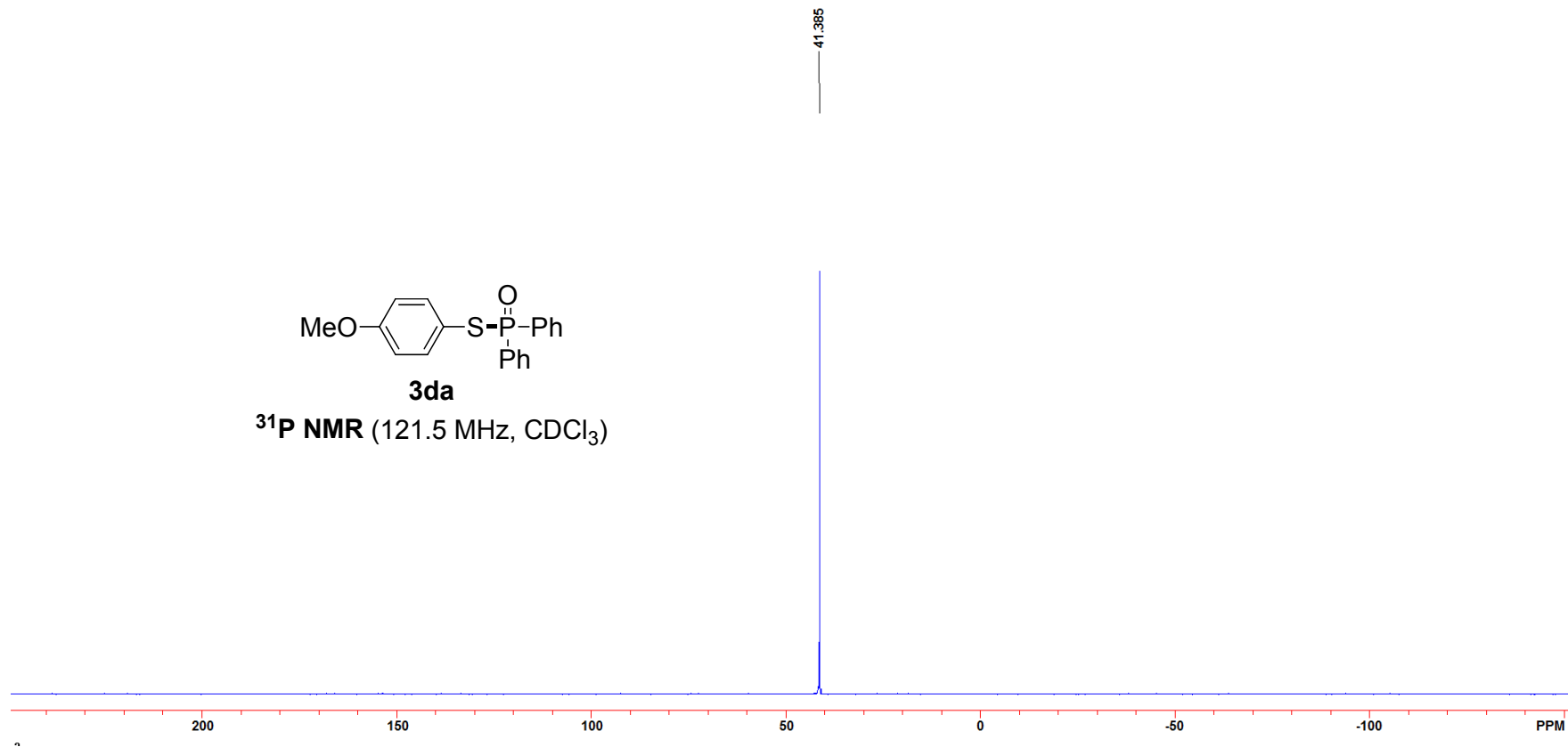


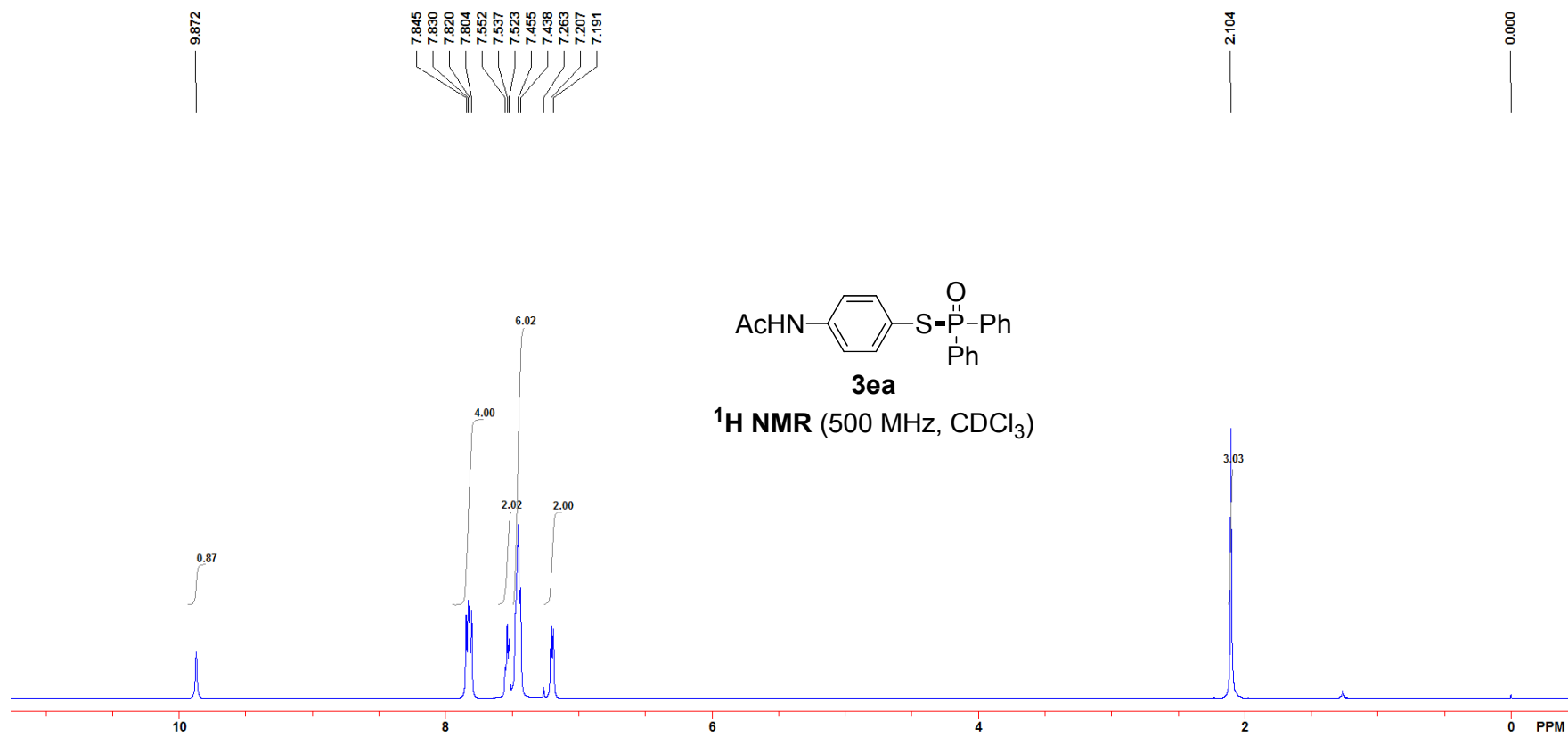


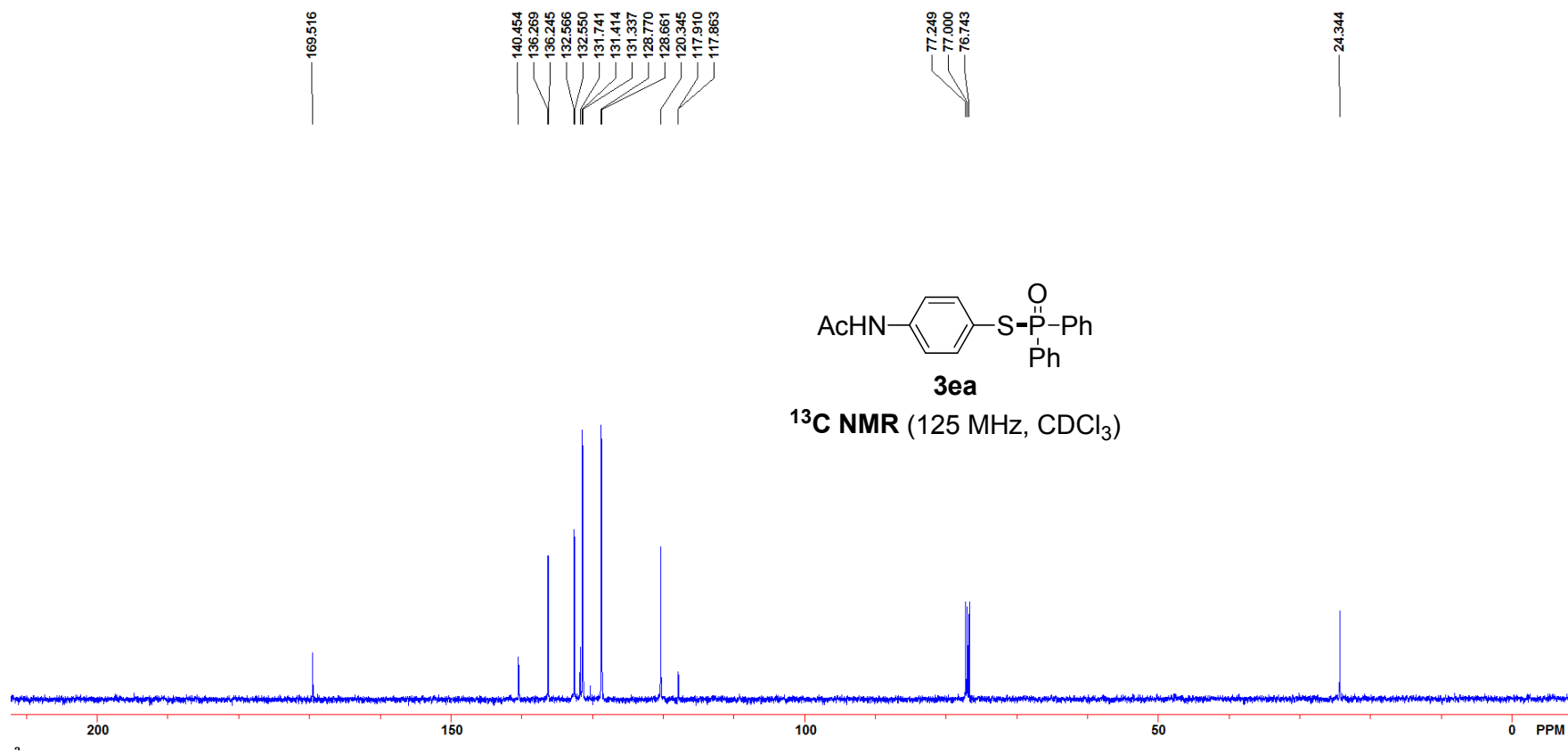


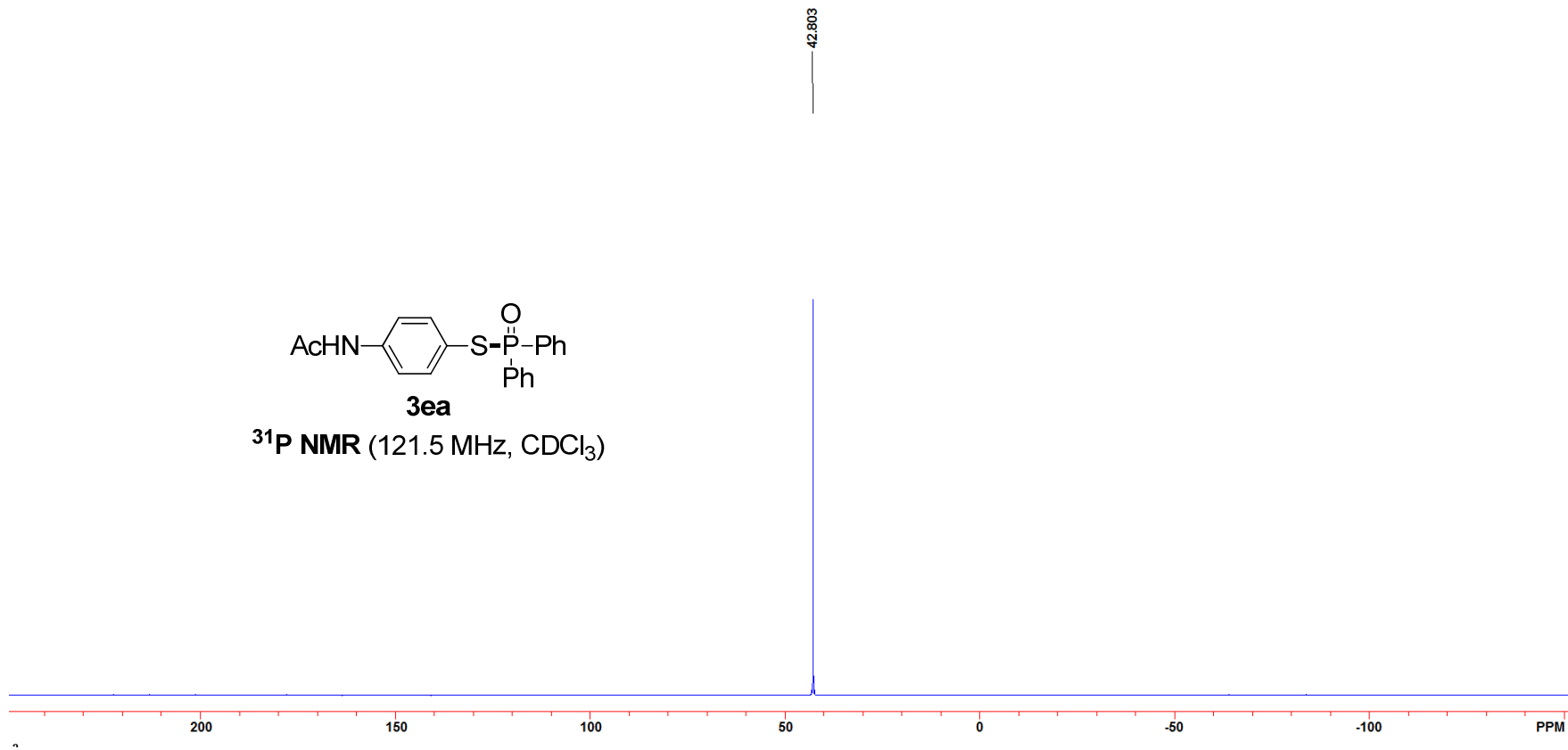
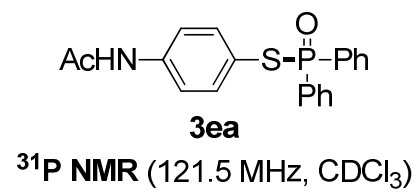
3da

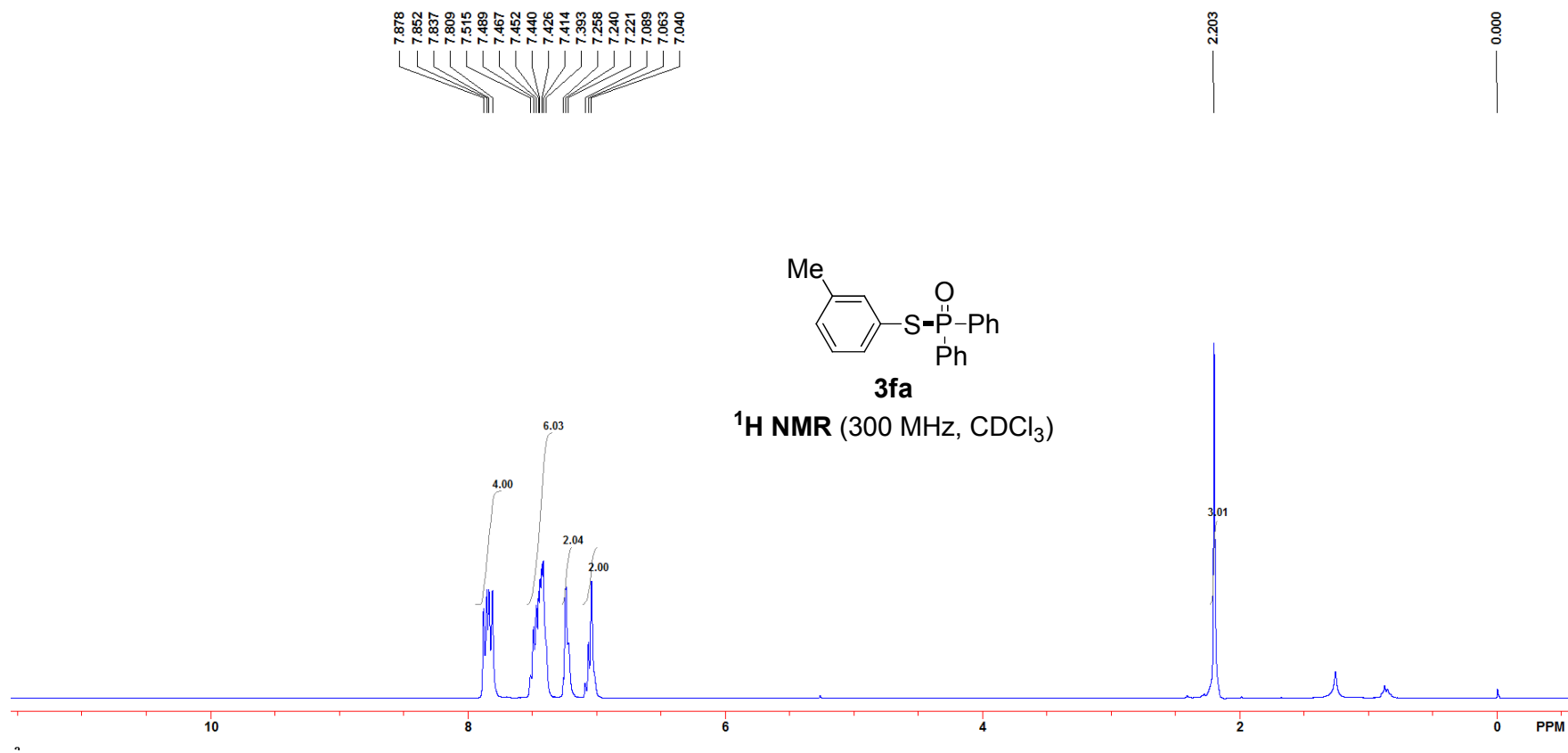
^{31}P NMR (121.5 MHz, CDCl_3)

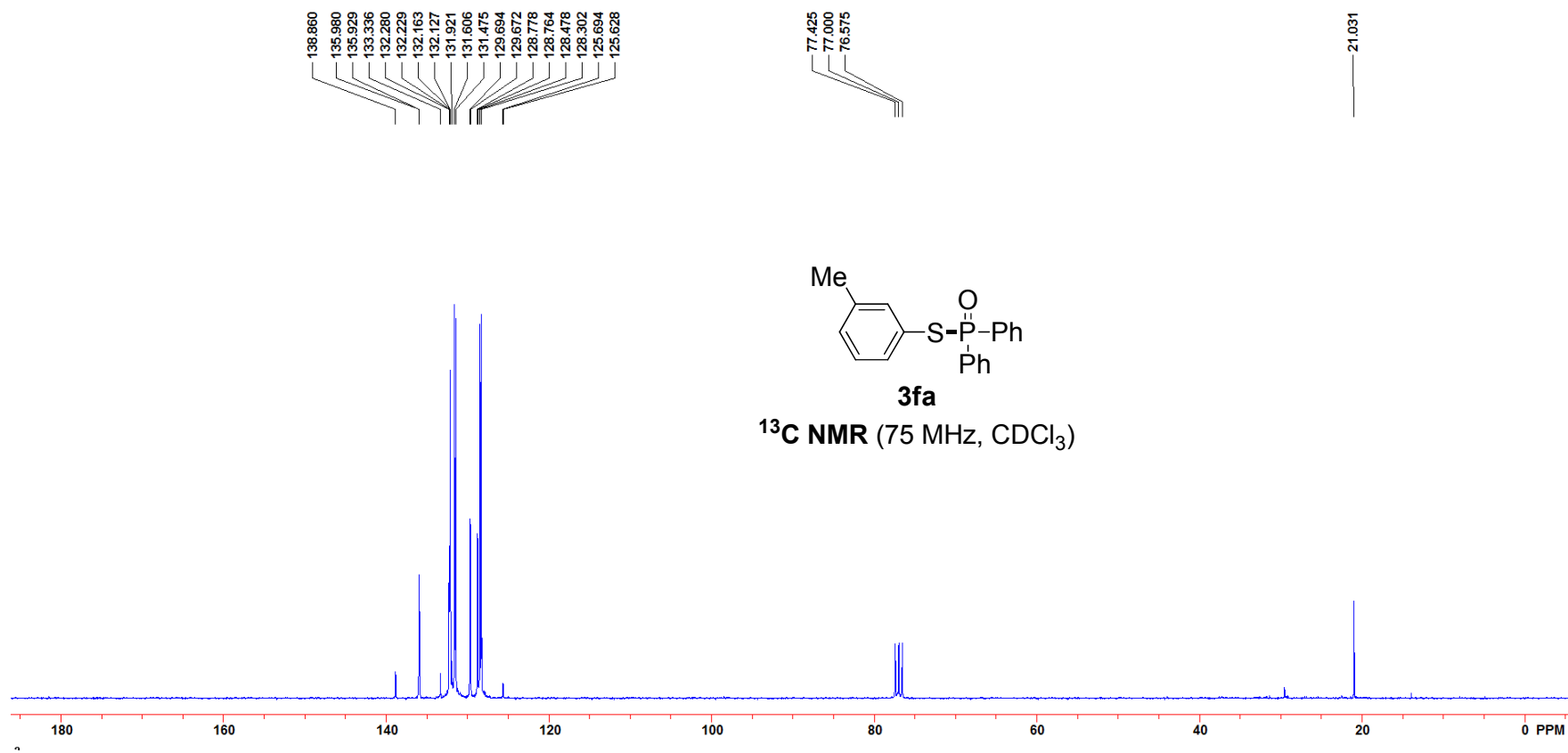


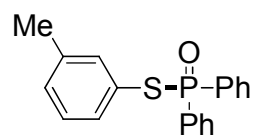






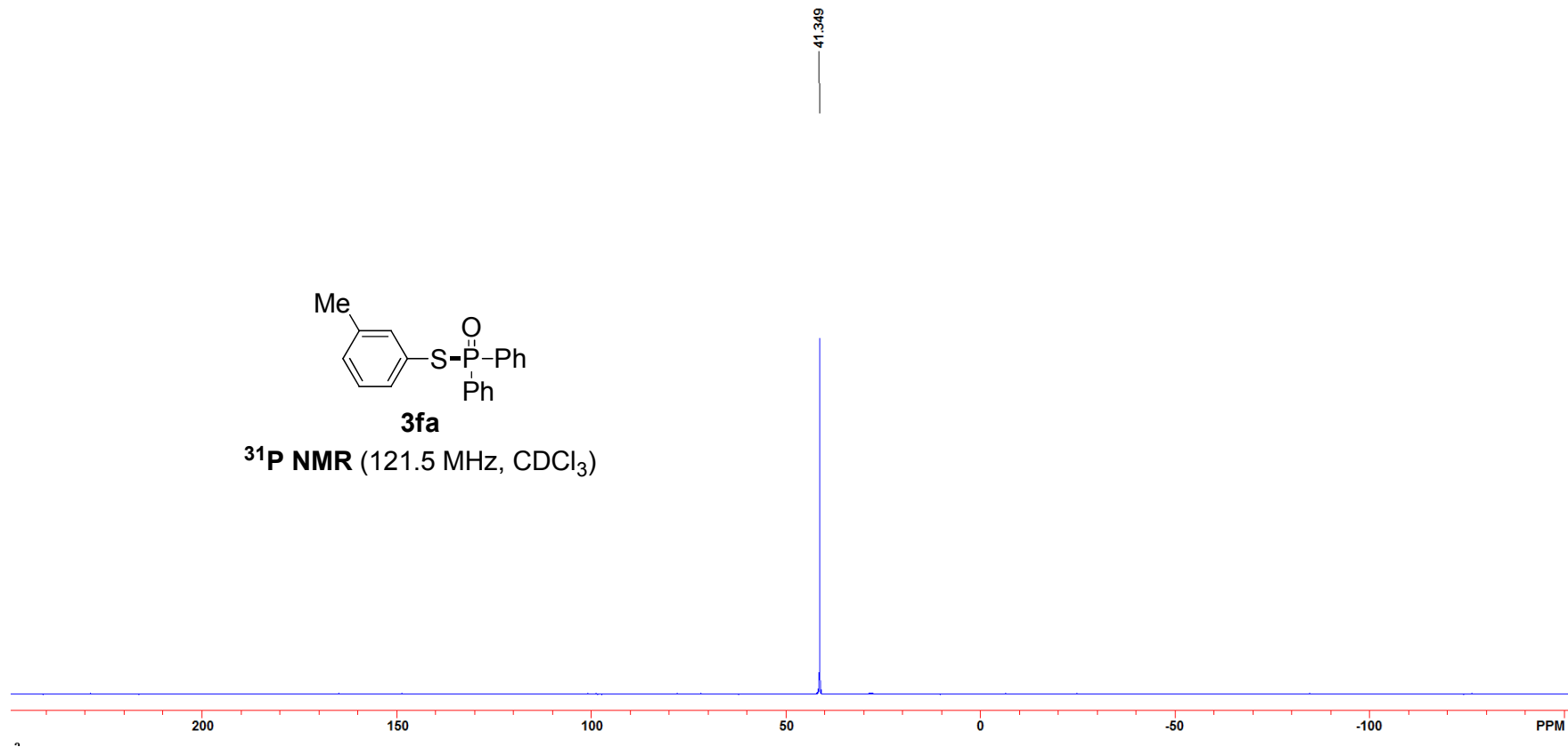


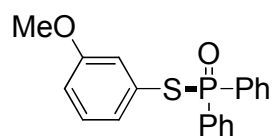




3fa

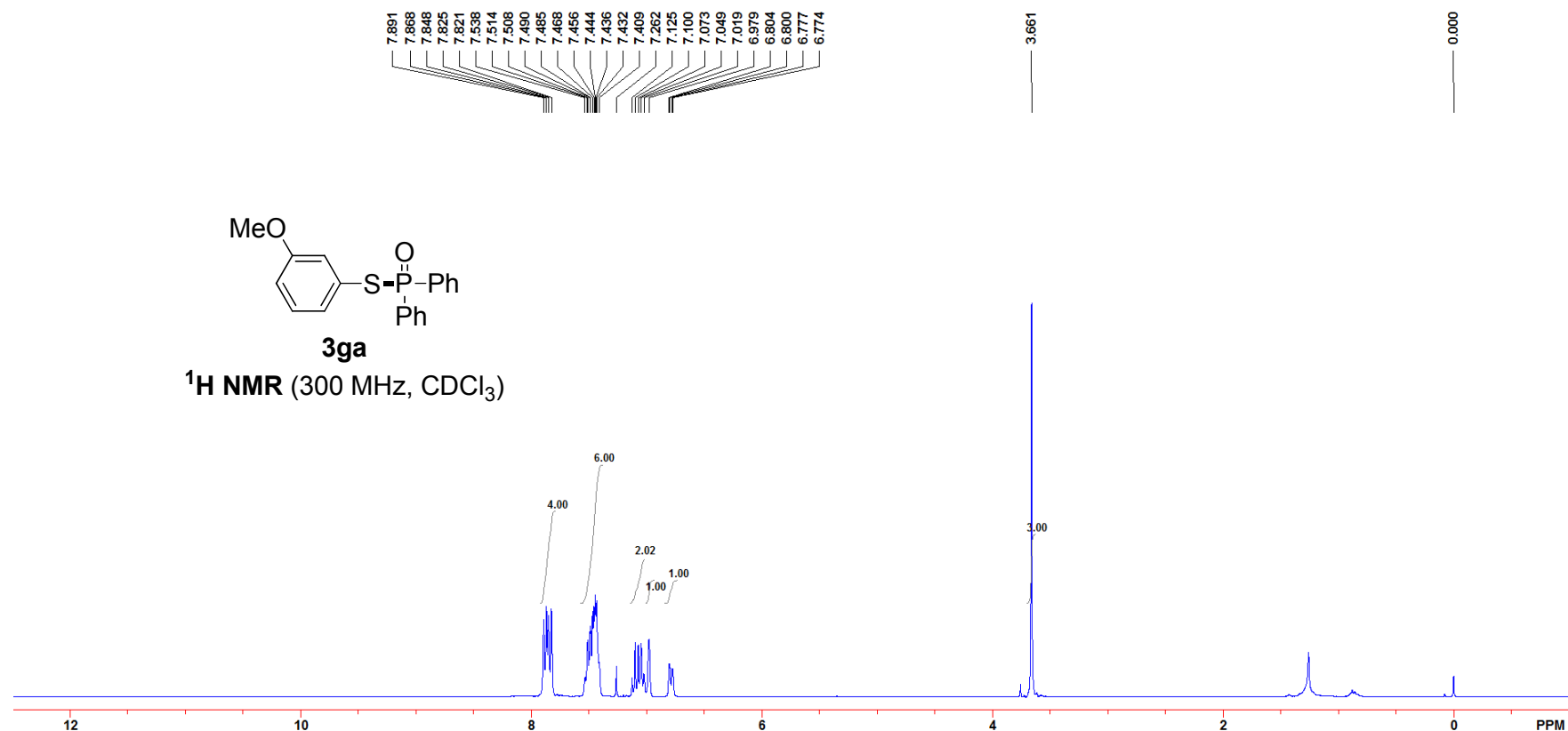
^{31}P NMR (121.5 MHz, CDCl_3)

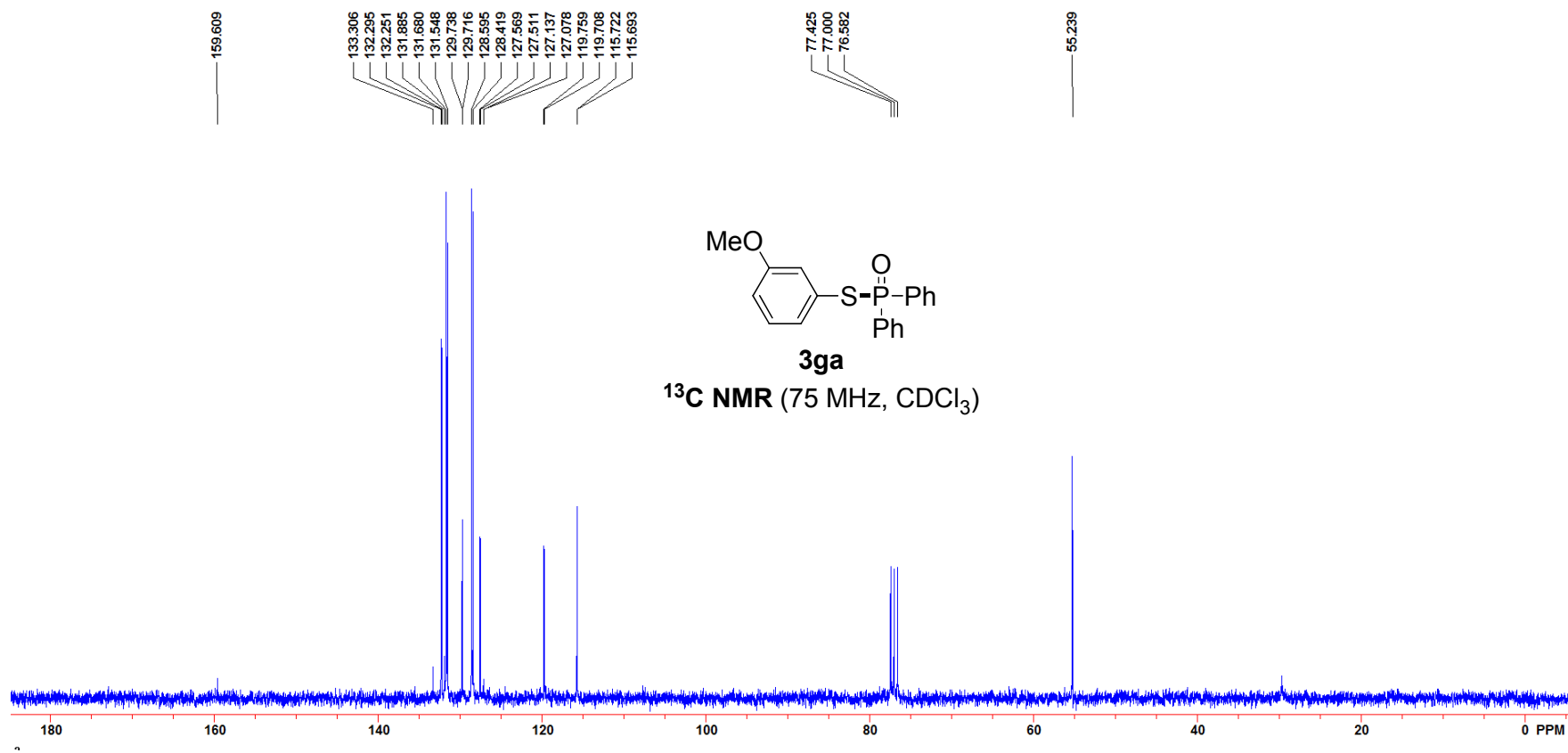


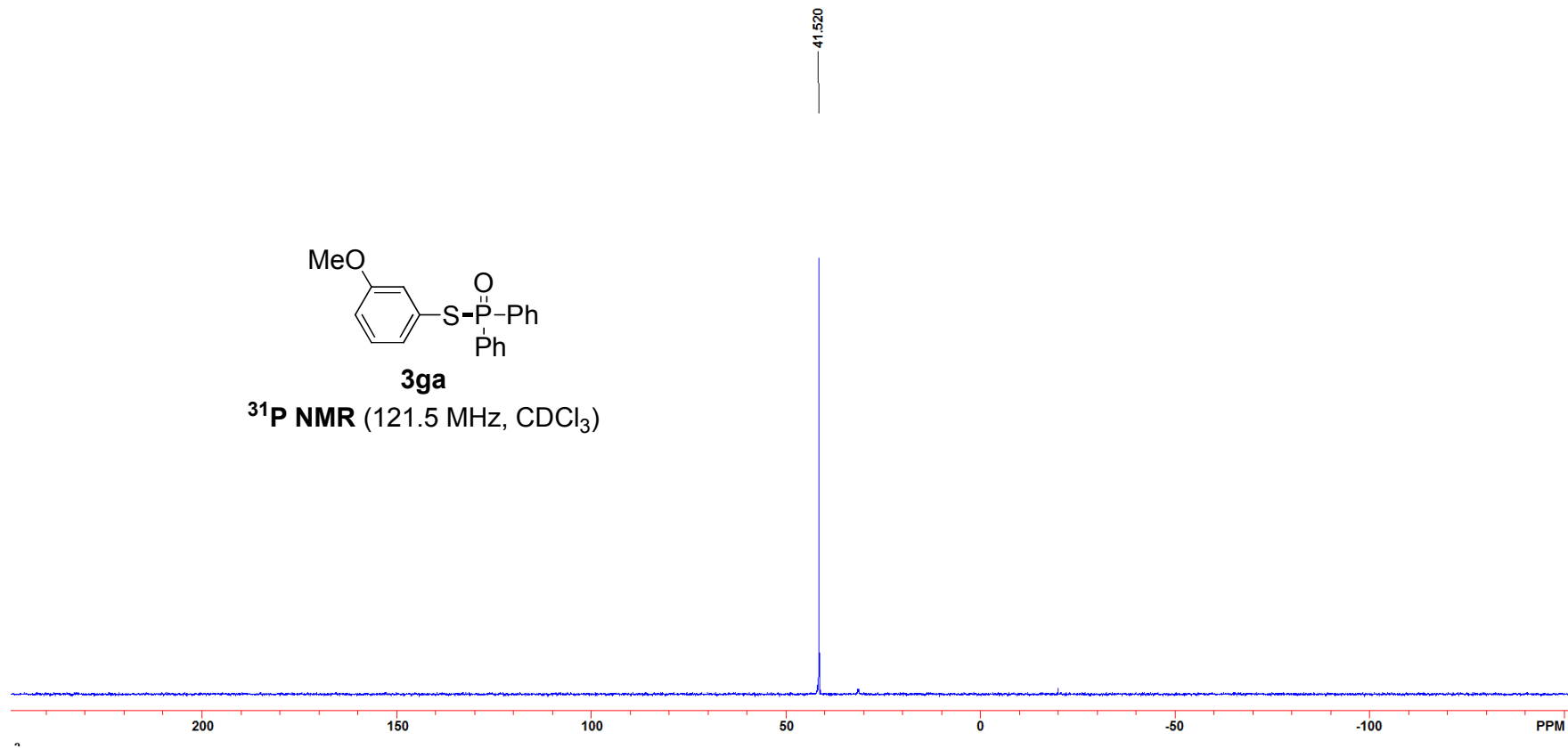
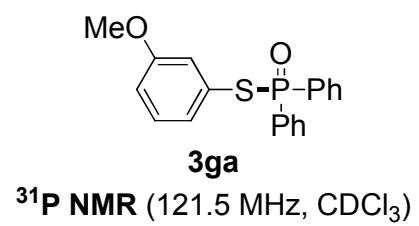


3ga

¹H NMR (300 MHz, CDCl₃)



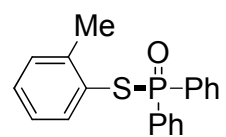




7.851
7.825
7.809
7.782
7.524
7.499
7.475
7.437
7.423
7.412
7.389
7.257
7.179
7.155
7.131
7.107
7.019
6.998
6.975

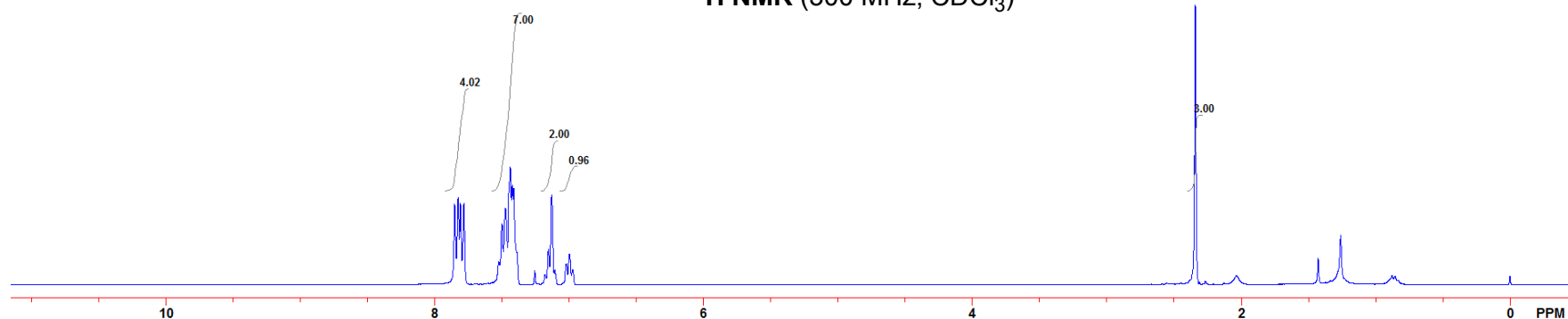
2.341

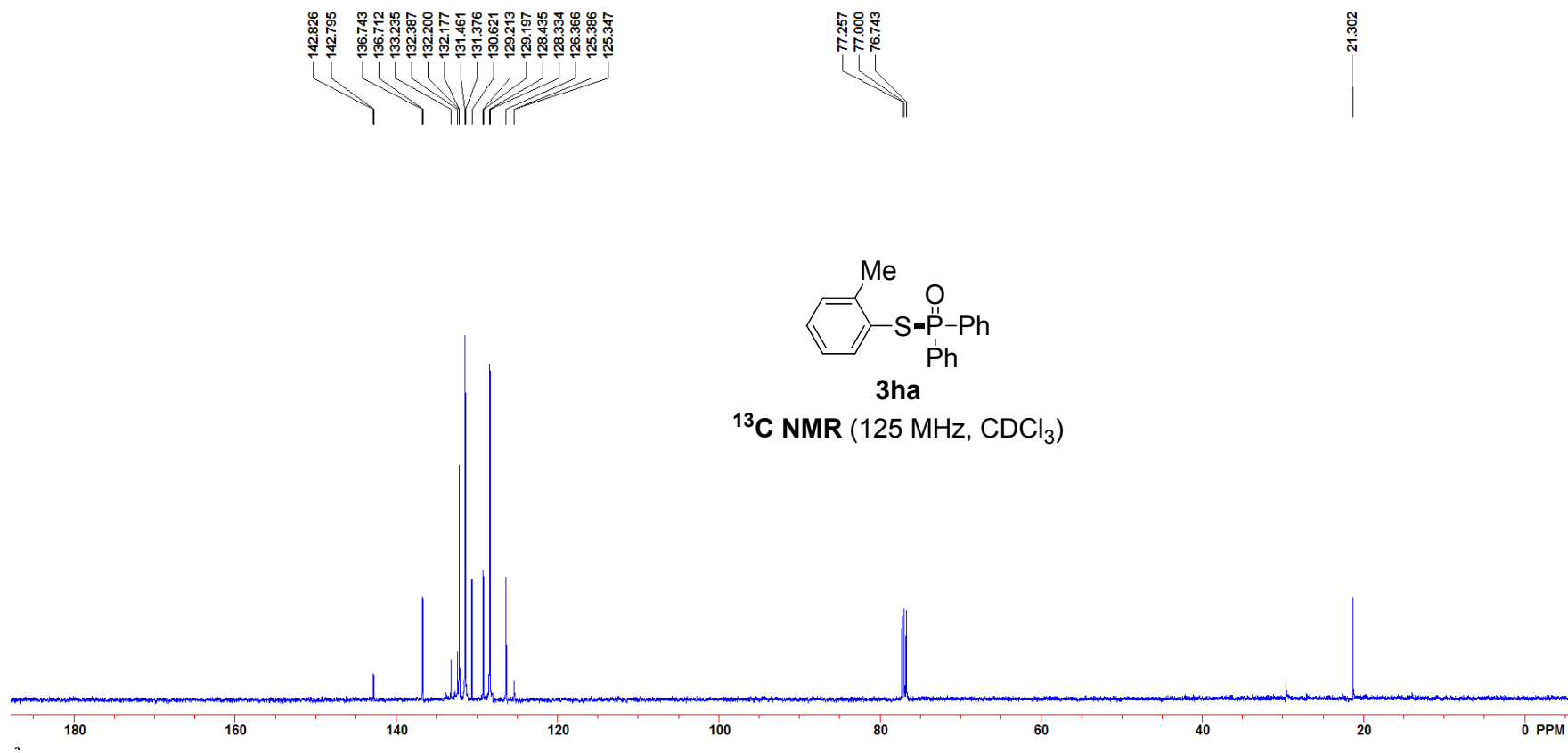
0.000

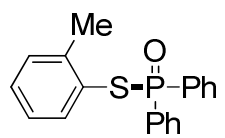


3ha

¹H NMR (300 MHz, CDCl₃)

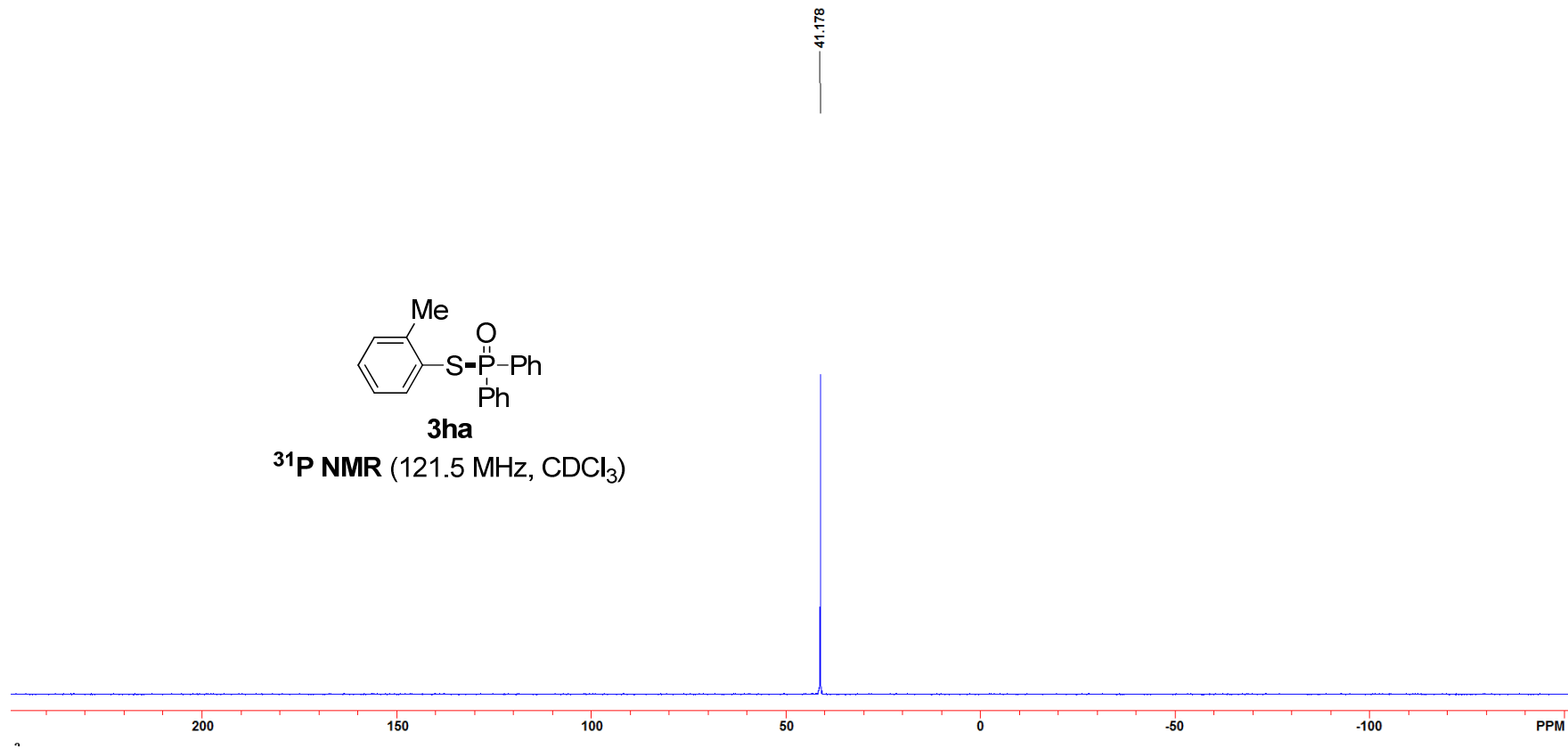


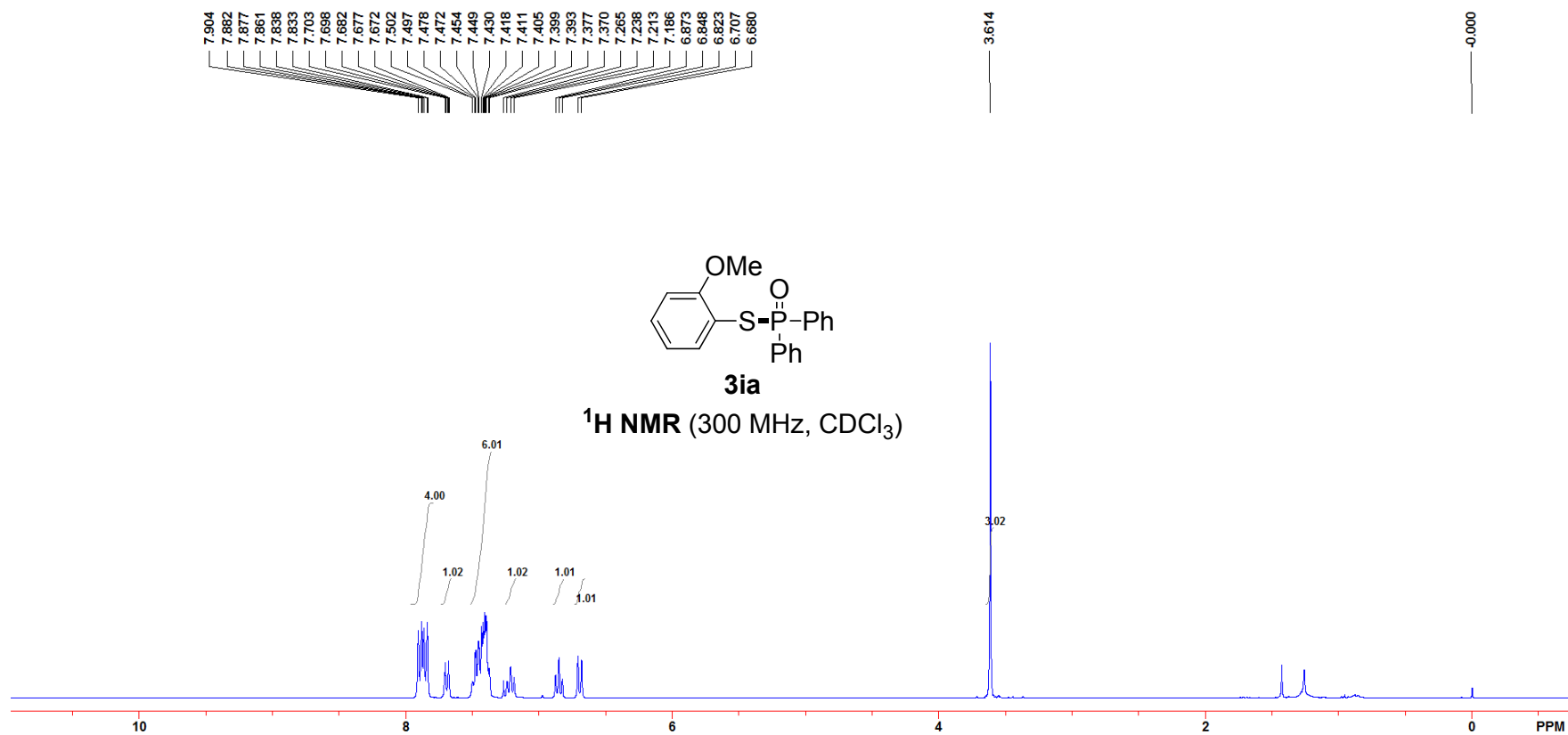


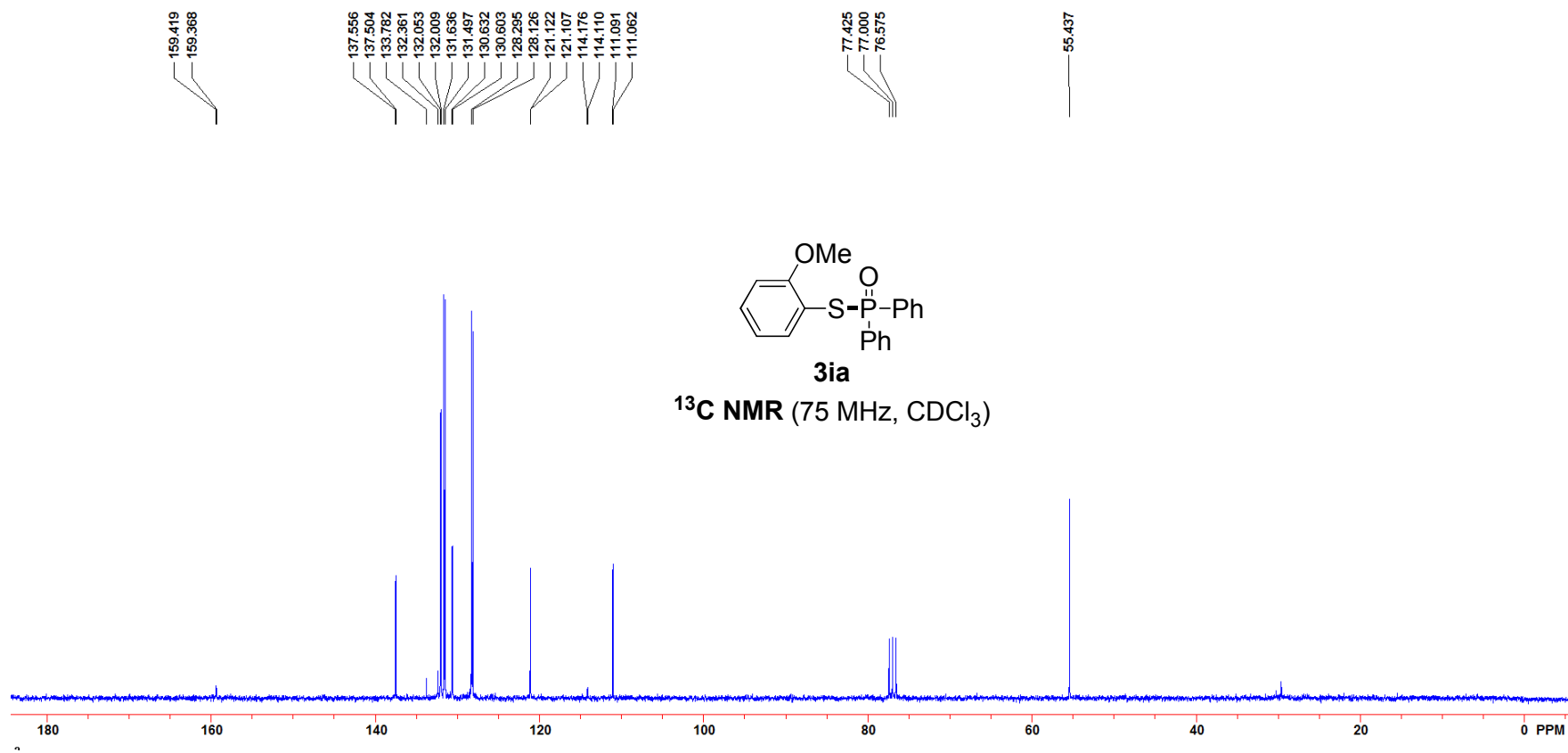


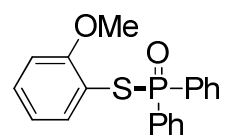
3ha

³¹P NMR (121.5 MHz, CDCl₃)



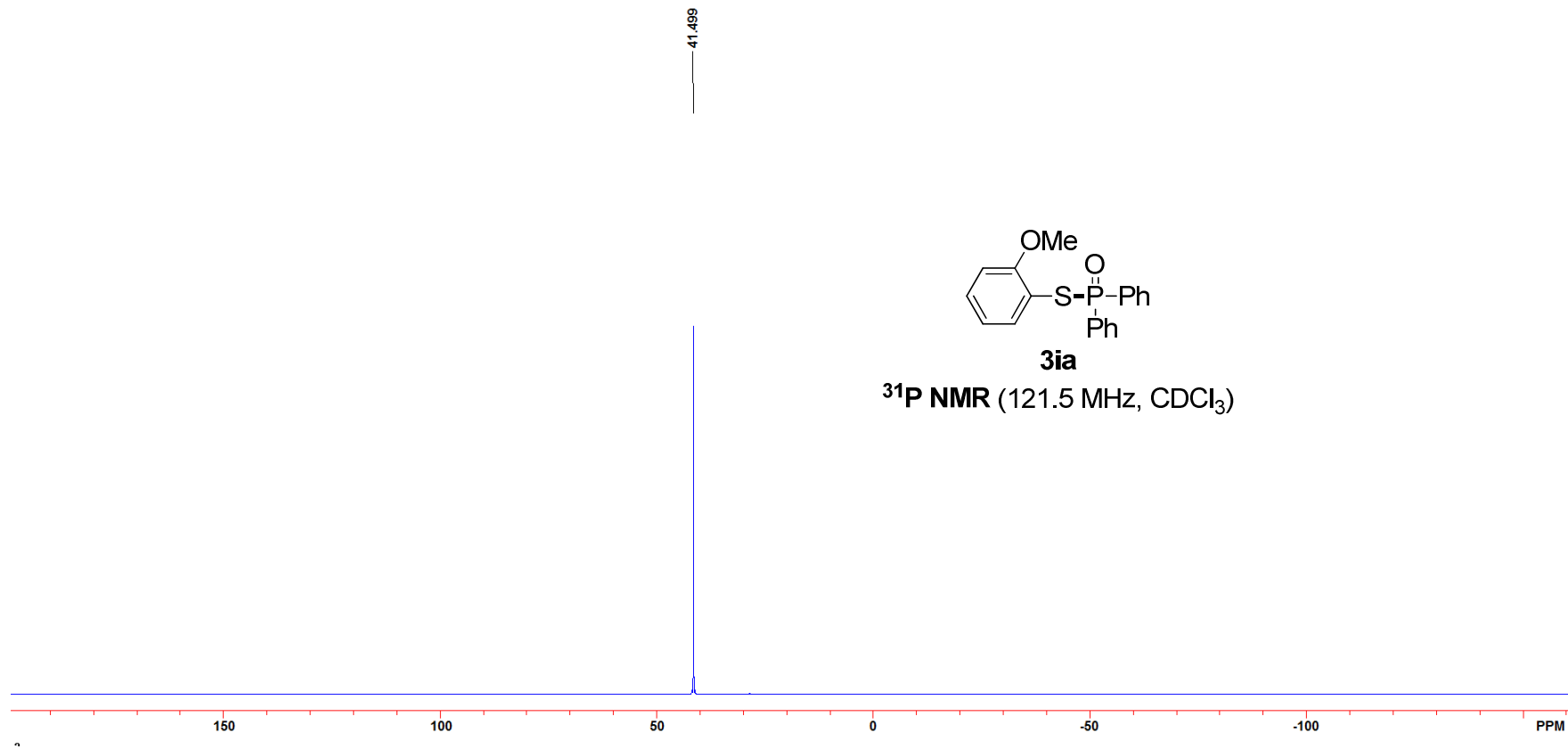


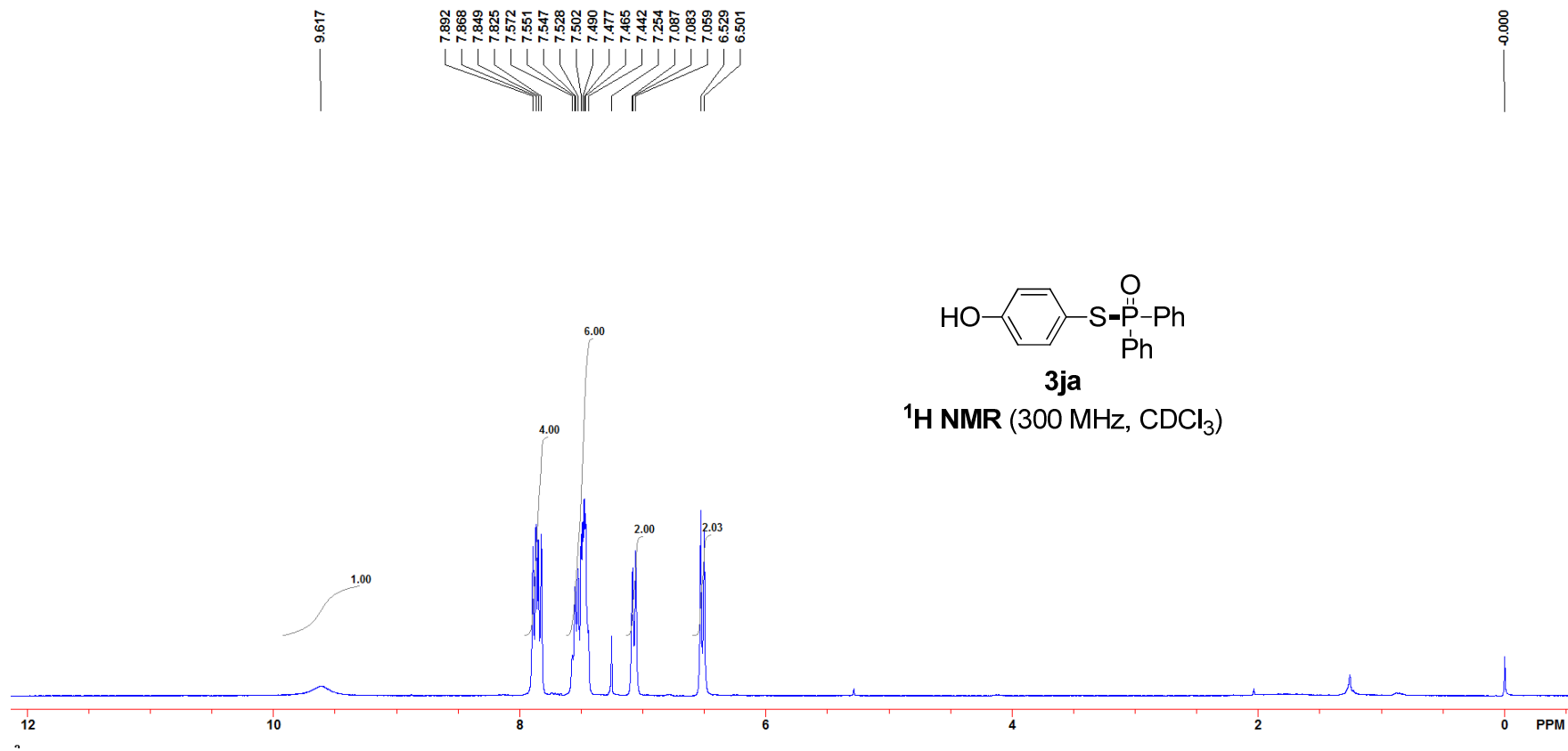


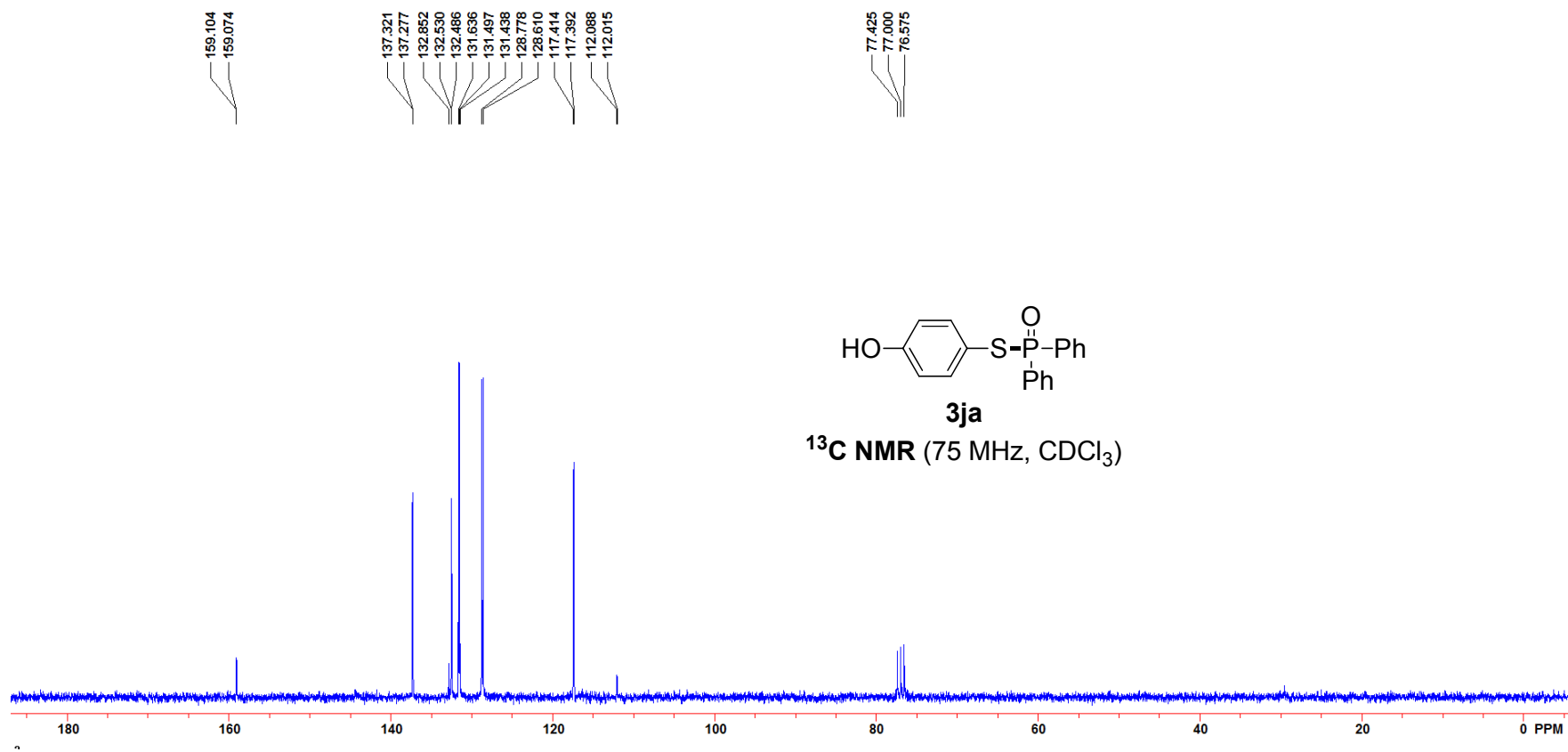


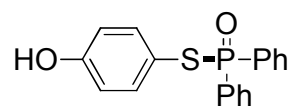
3ia

^{31}P NMR (121.5 MHz, CDCl_3)



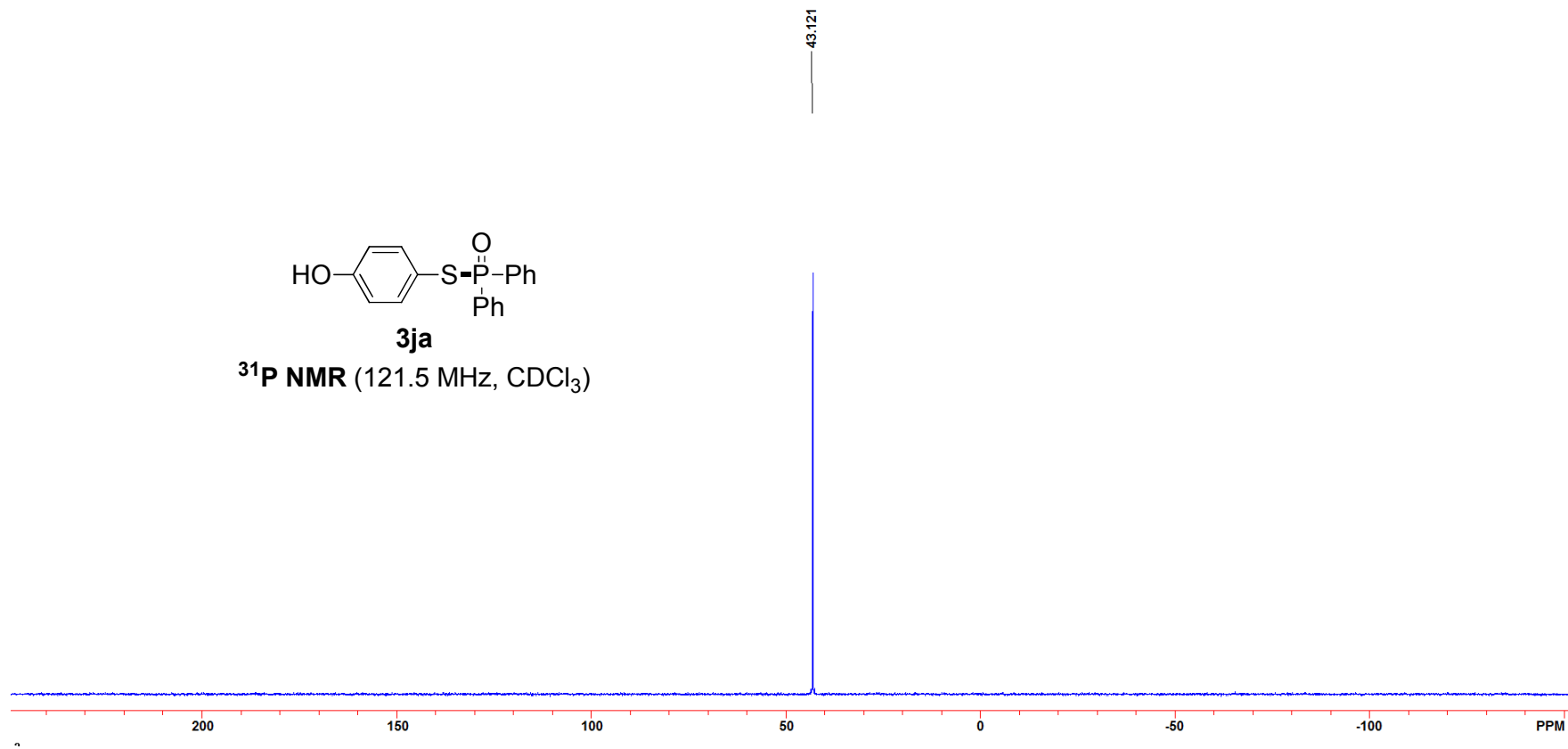


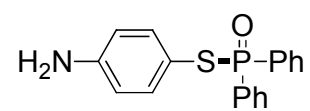
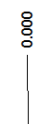
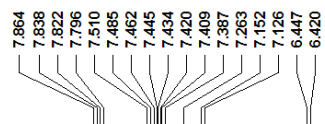




3ja

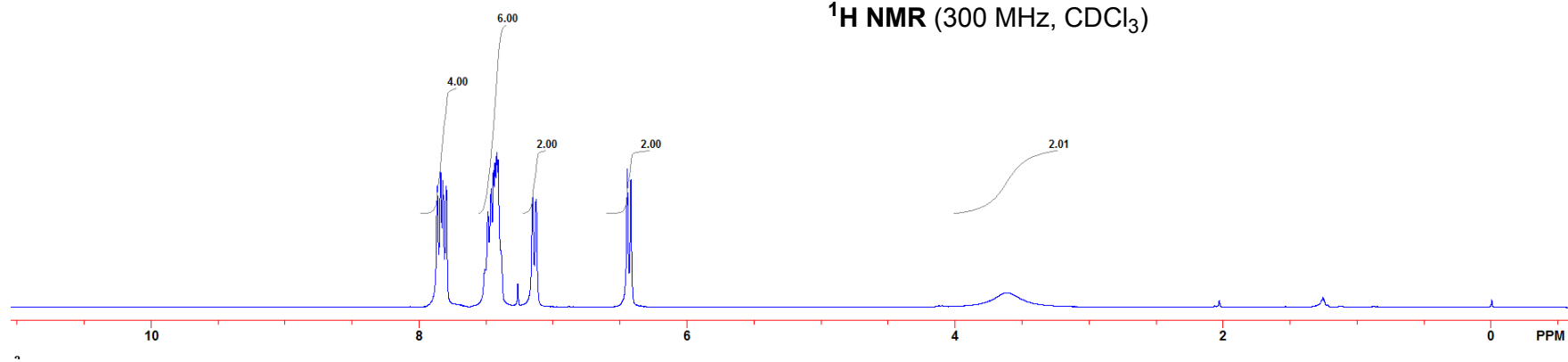
^{31}P NMR (121.5 MHz, CDCl_3)

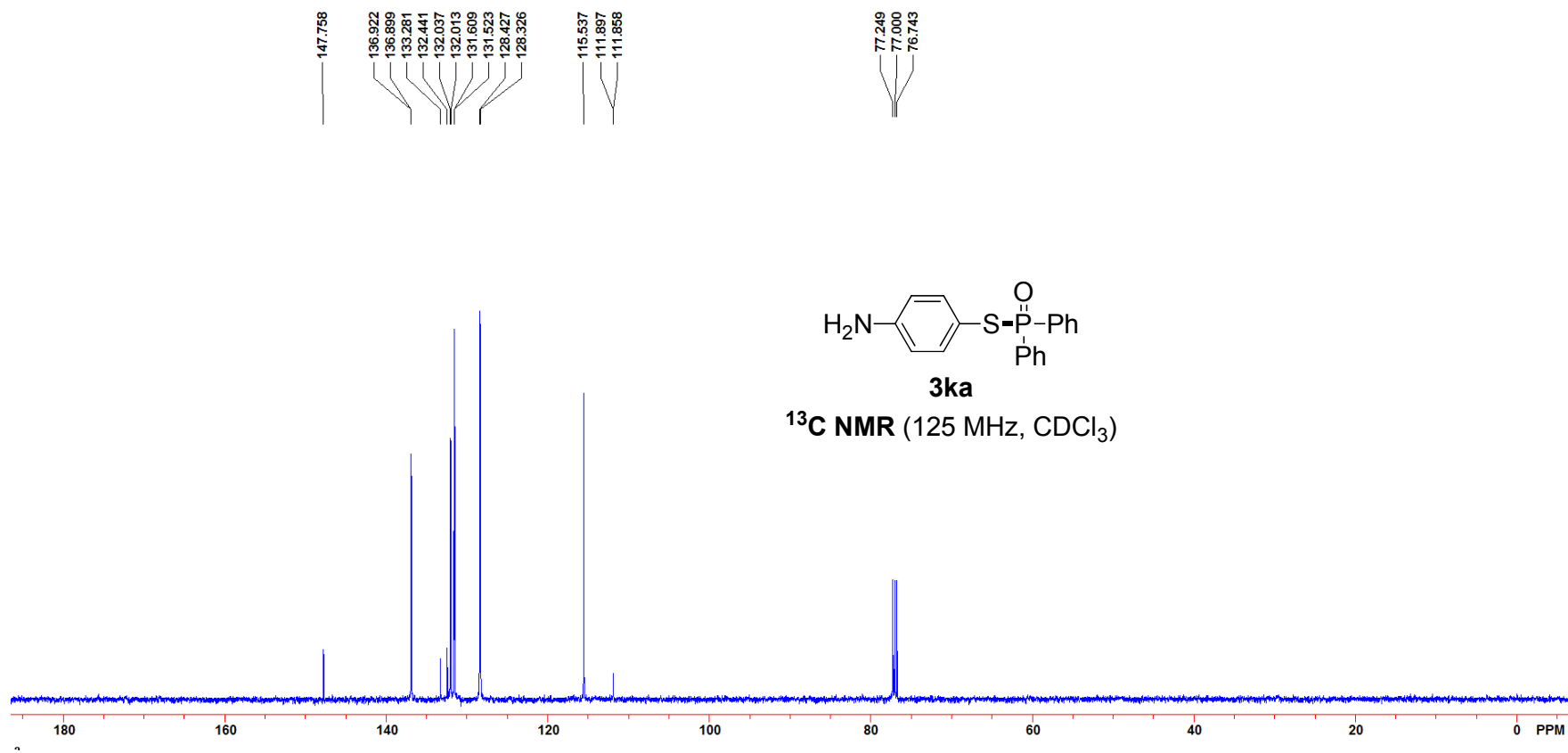


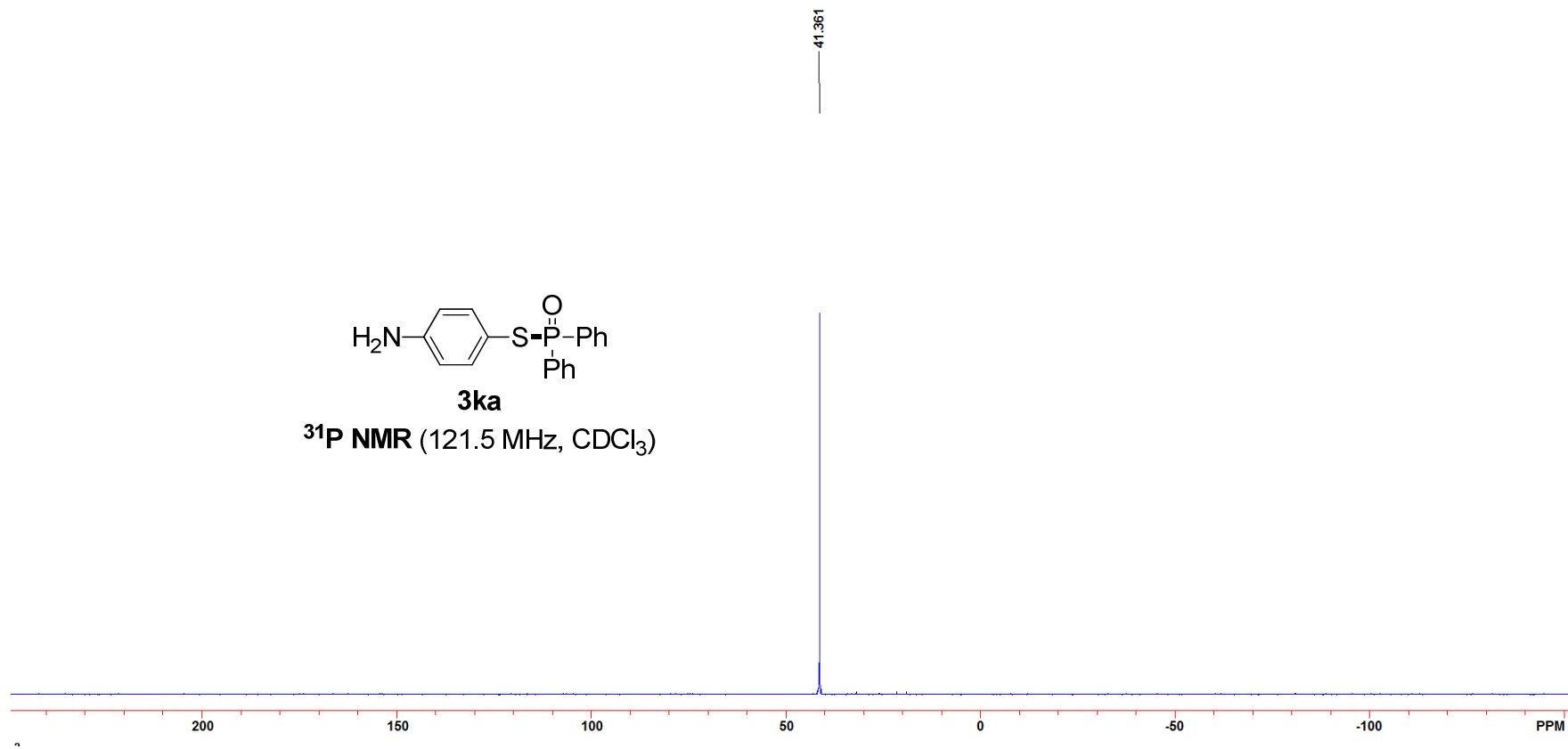
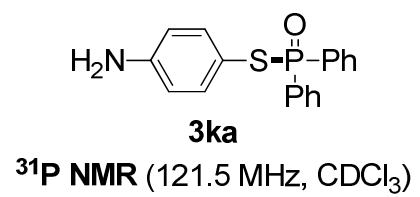


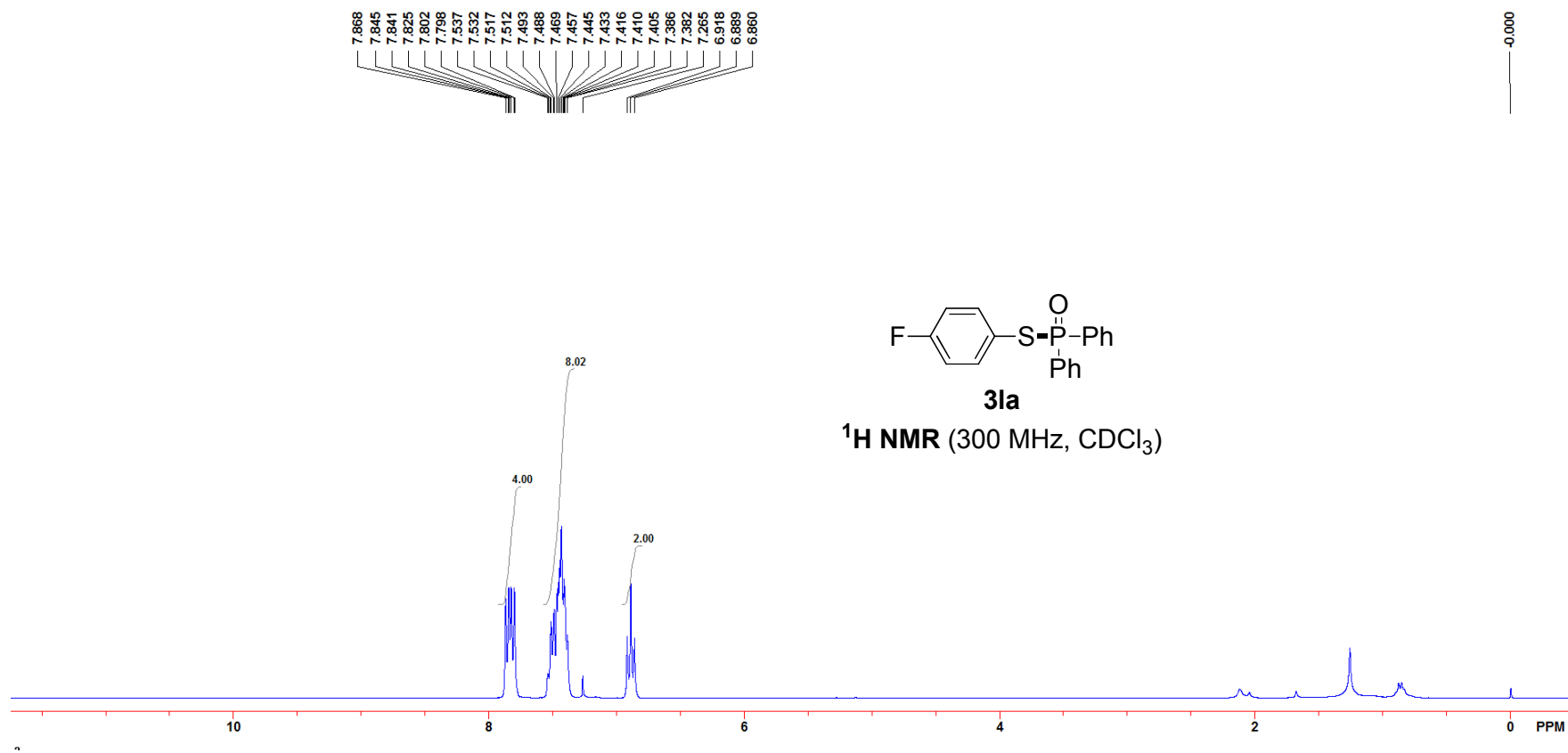
3ka

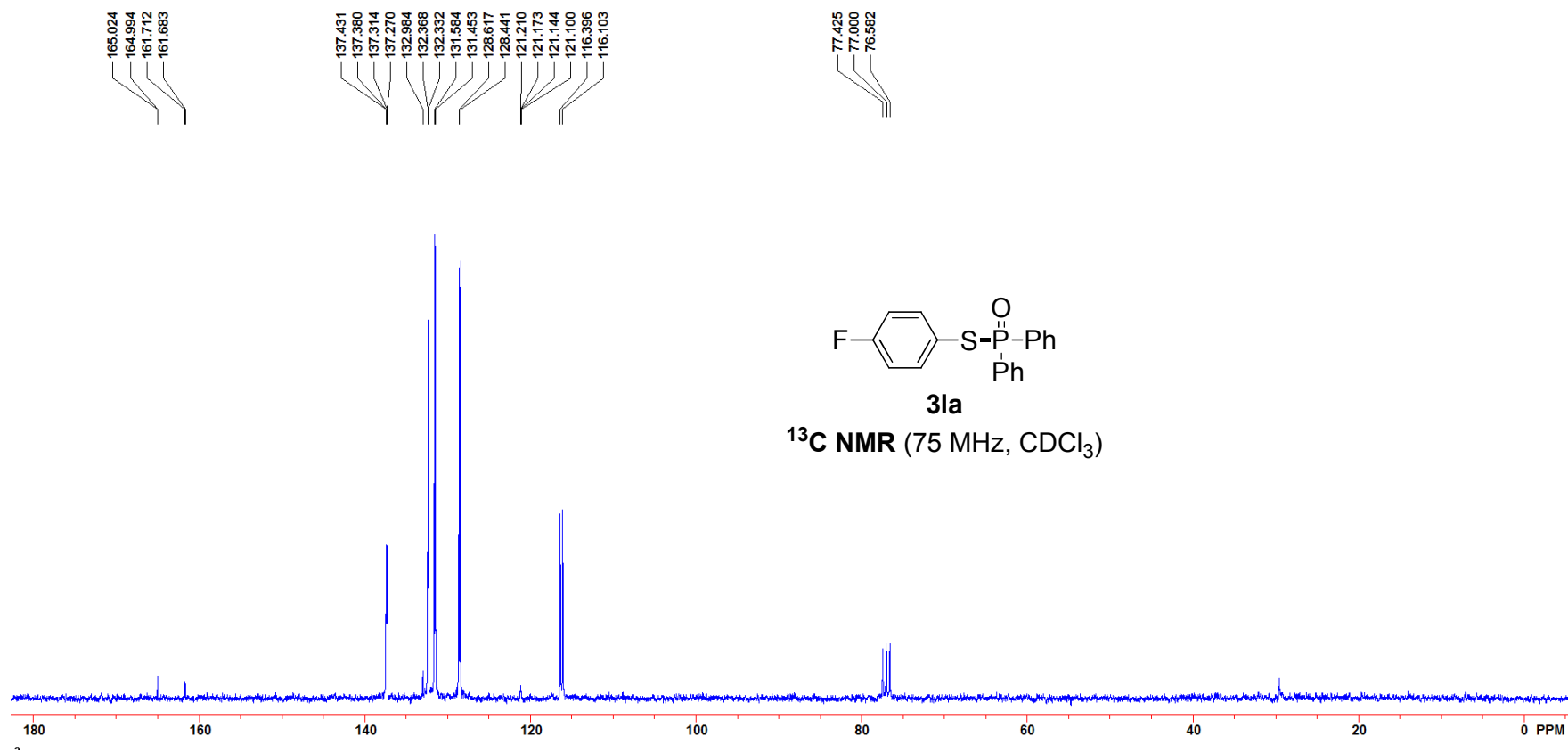
¹H NMR (300 MHz, CDCl₃)



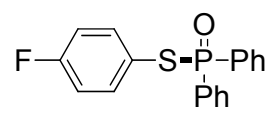






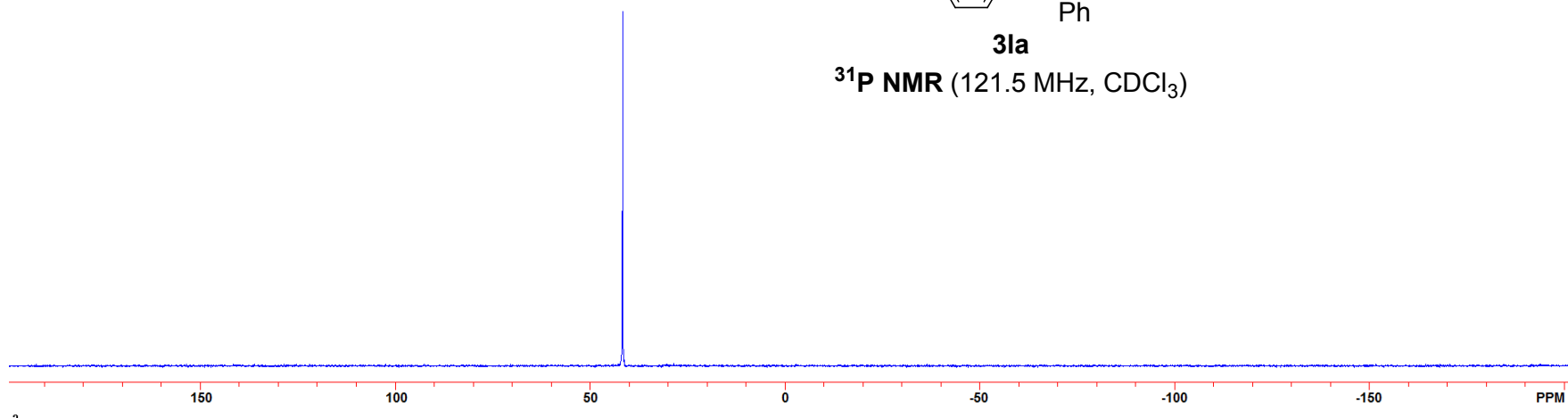


41.658



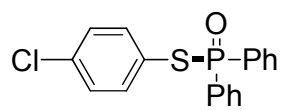
3la

^{31}P NMR (121.5 MHz, CDCl_3)



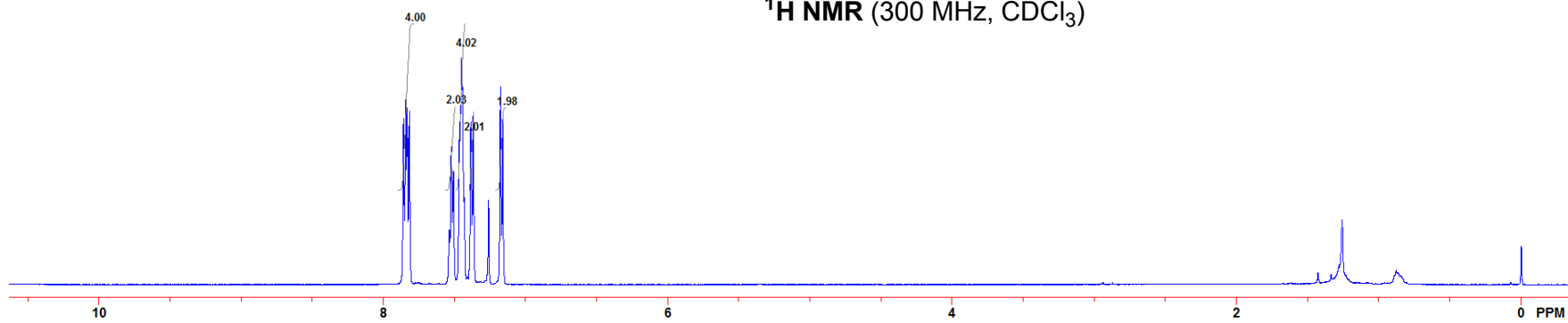
7.857
7.842
7.831
7.816
7.535
7.521
7.507
7.486
7.459
7.451
7.444
7.429
7.403
7.384
7.367
7.277
7.259
7.176
7.160

0.000



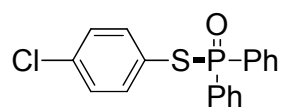
3ma

¹H NMR (300 MHz, CDCl₃)



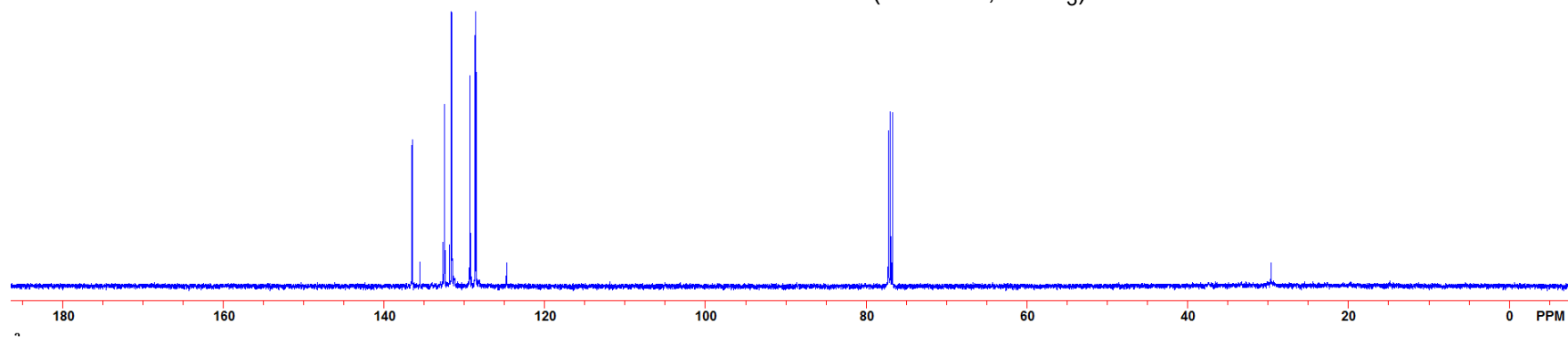
136.502
136.471
135.530
135.514
132.698
132.457
132.434
131.842
131.617
131.531
129.275
128.653
128.544
124.756
124.717

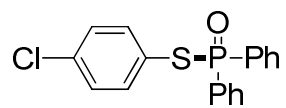
77.257
77.000
76.743



3ma

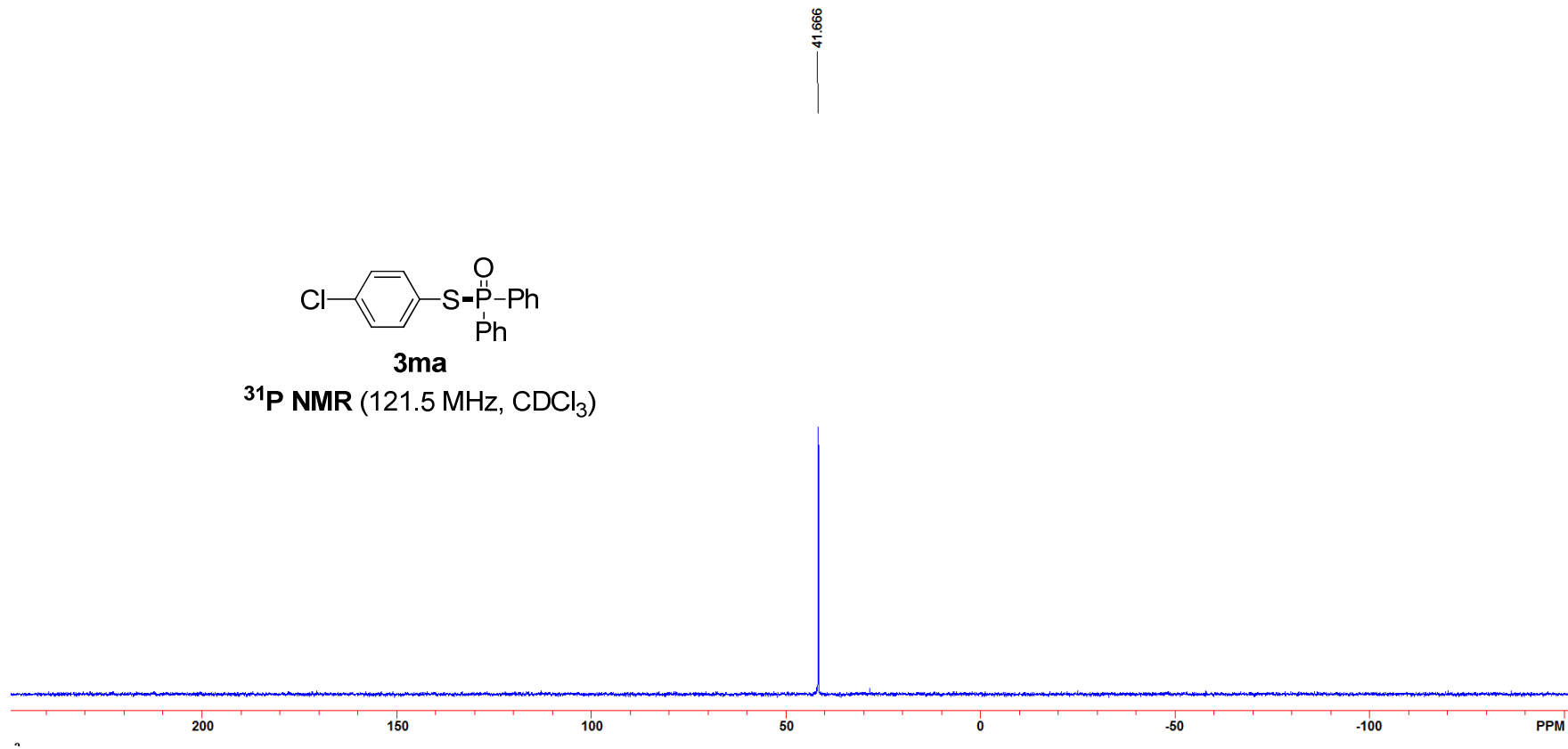
¹³C NMR (125 MHz, CDCl₃)

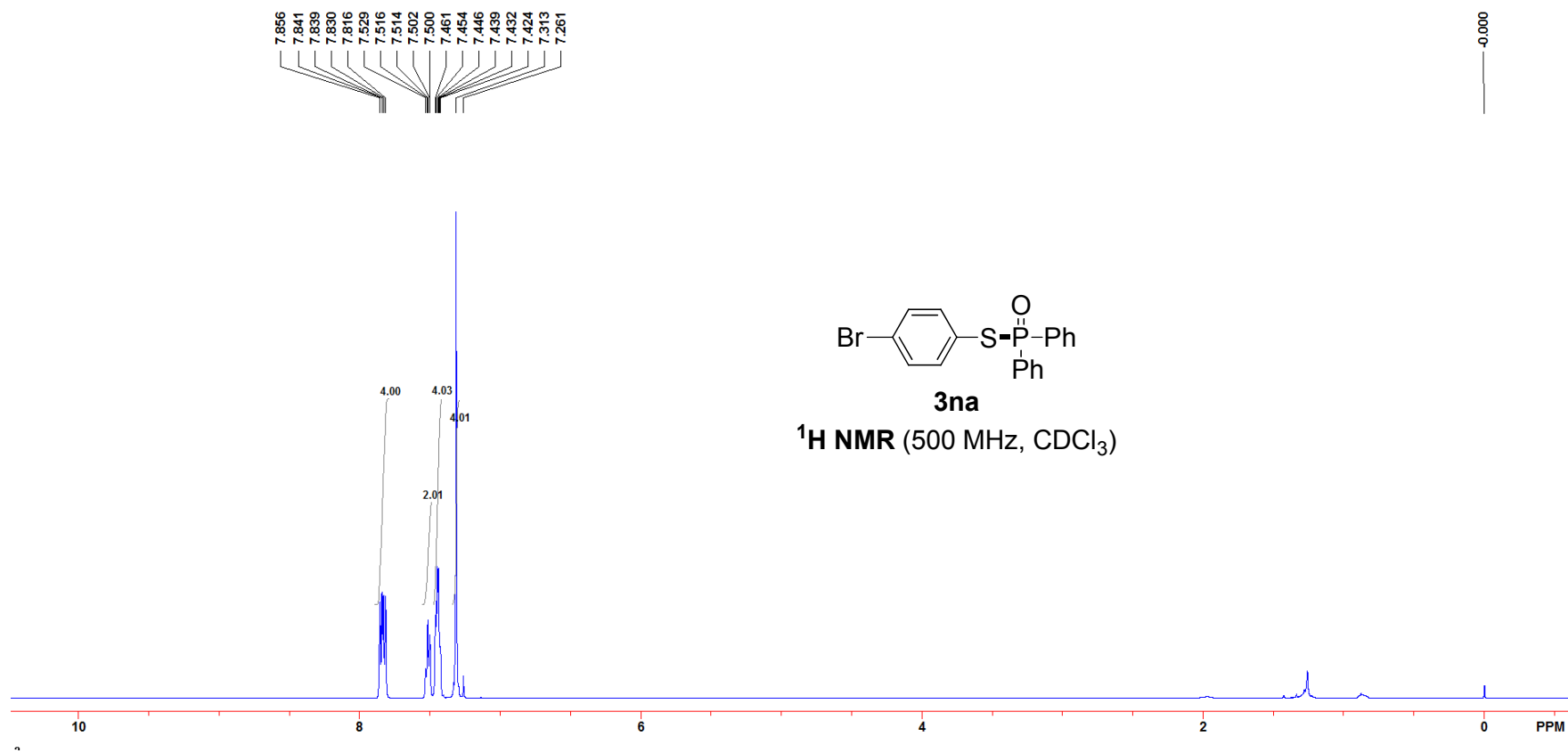


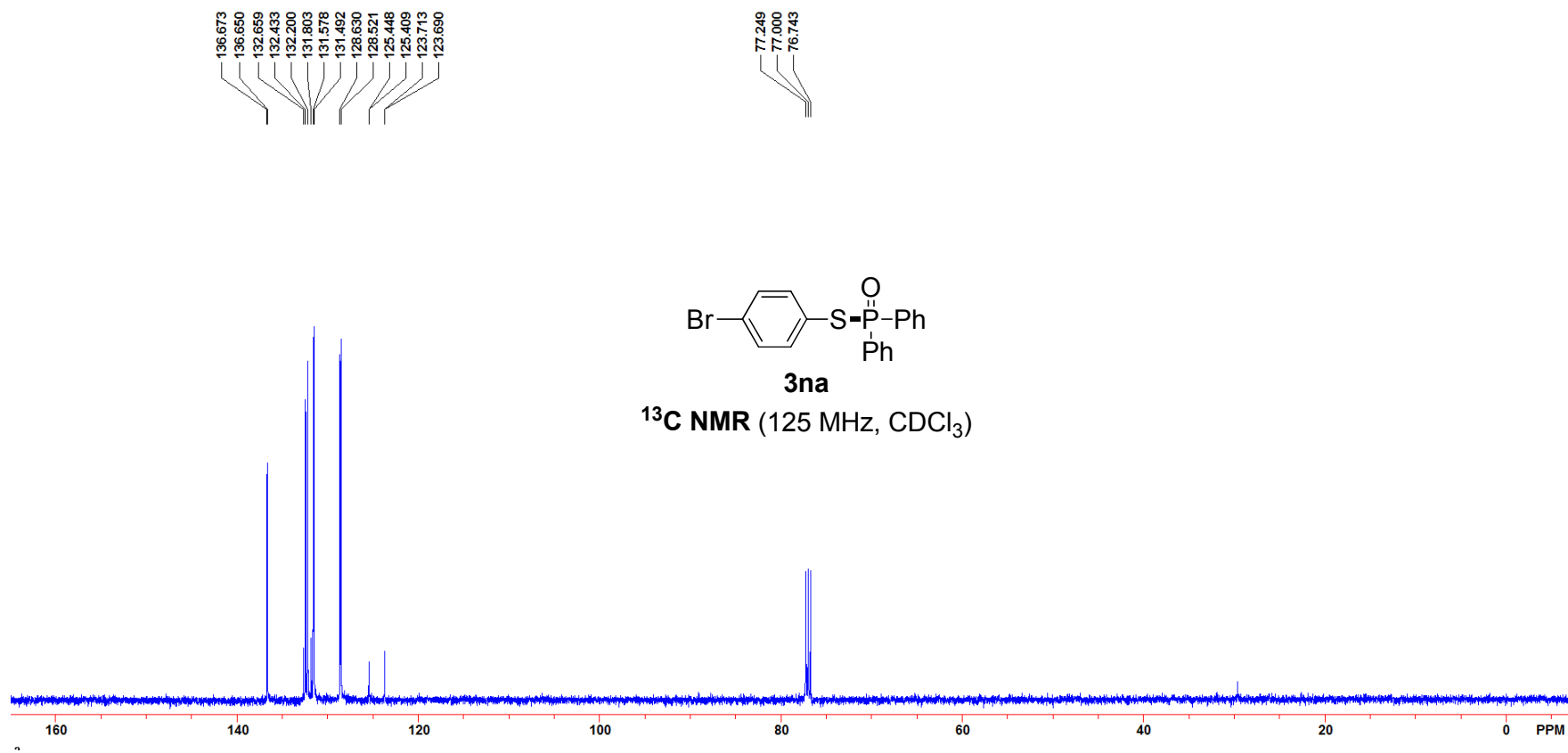


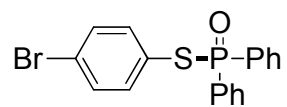
3ma

^{31}P NMR (121.5 MHz, CDCl_3)



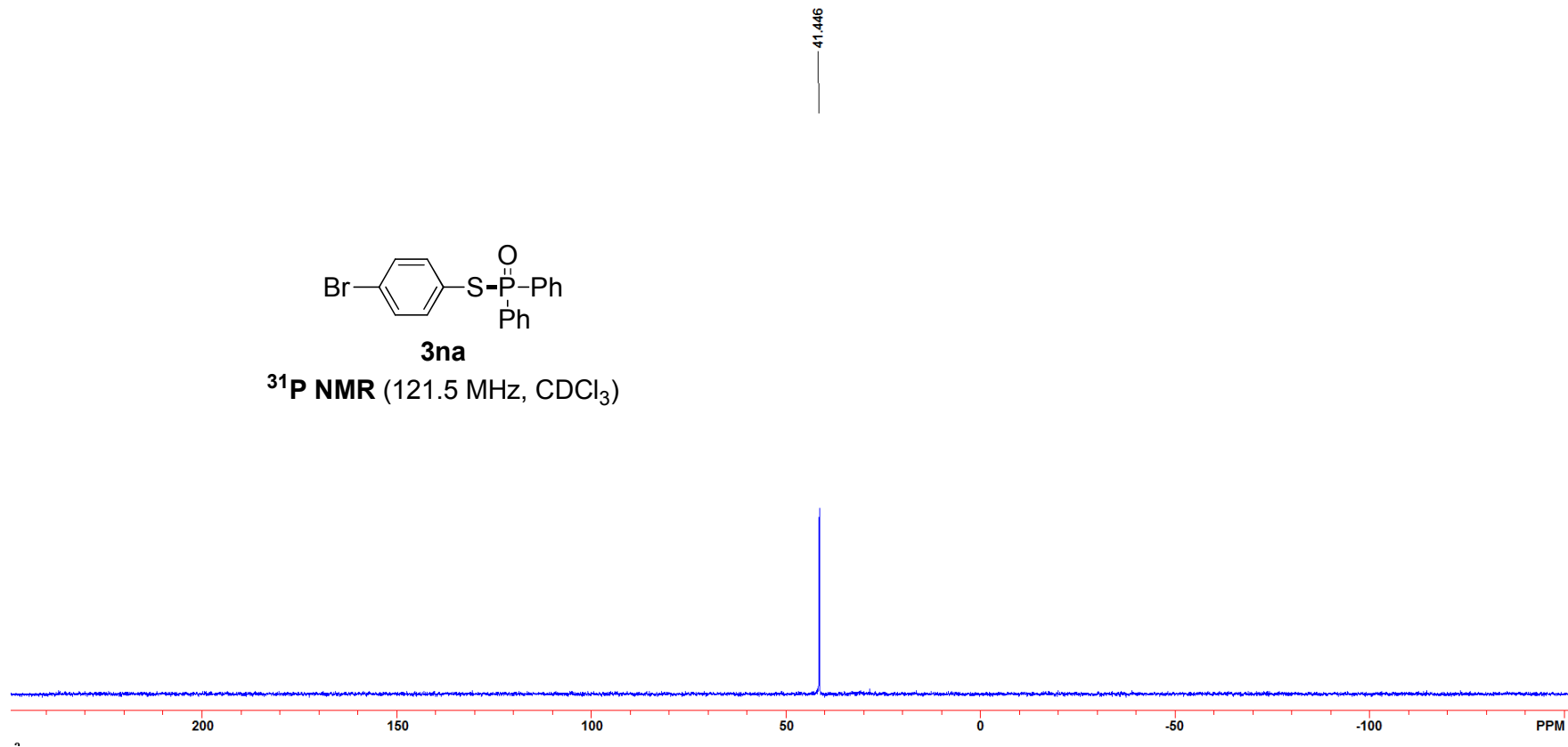


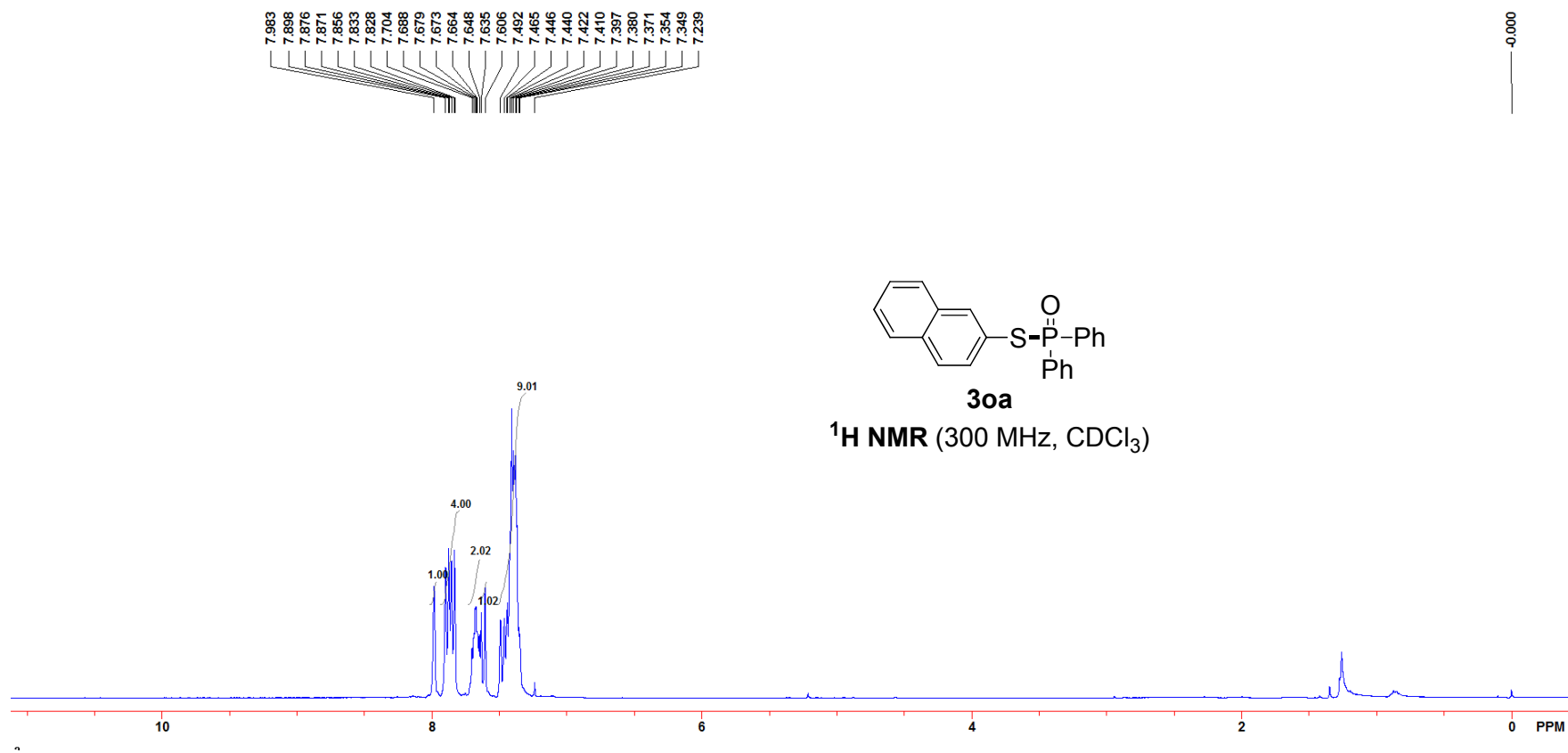


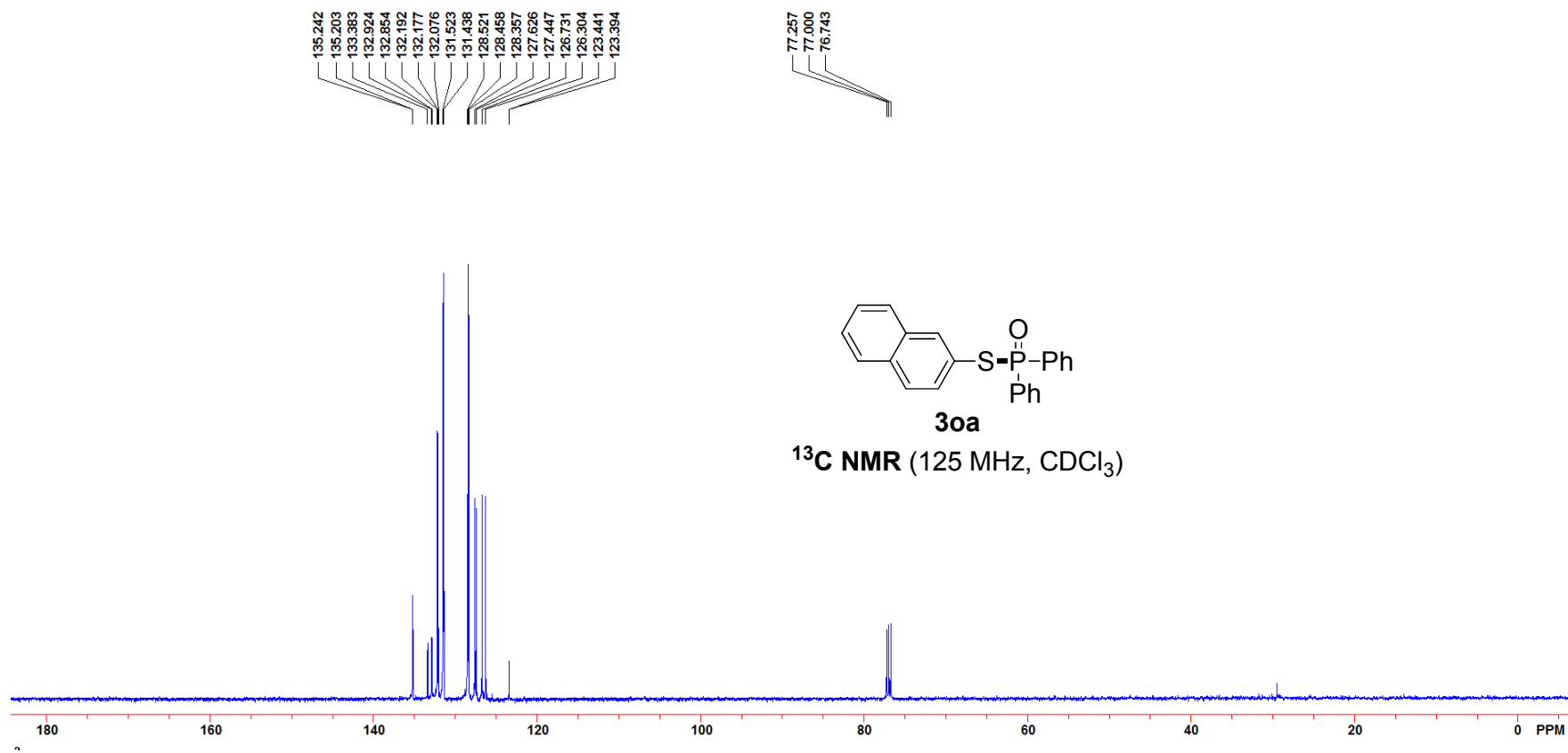


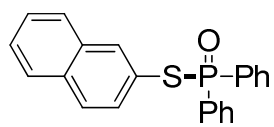
3na

^{31}P NMR (121.5 MHz, CDCl_3)



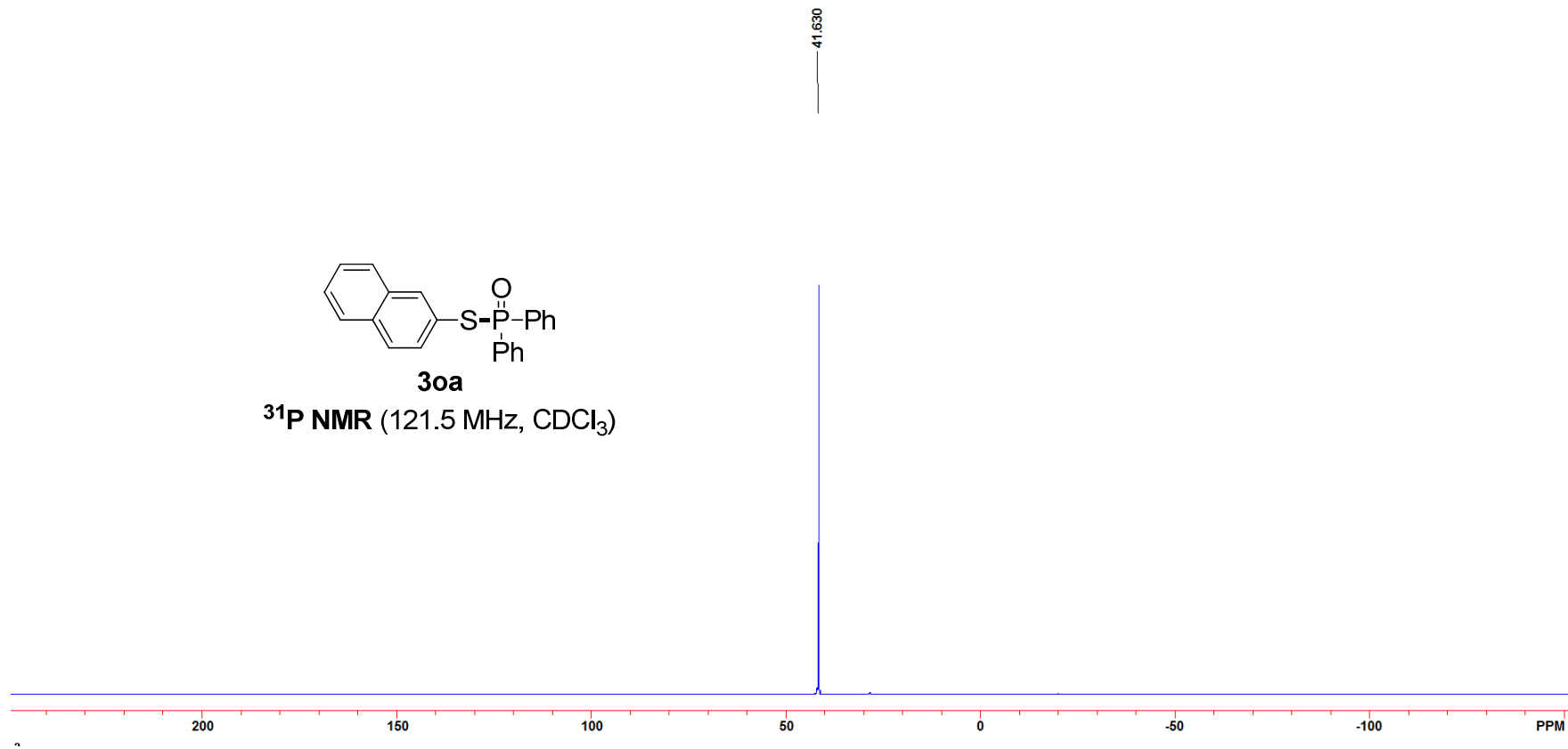


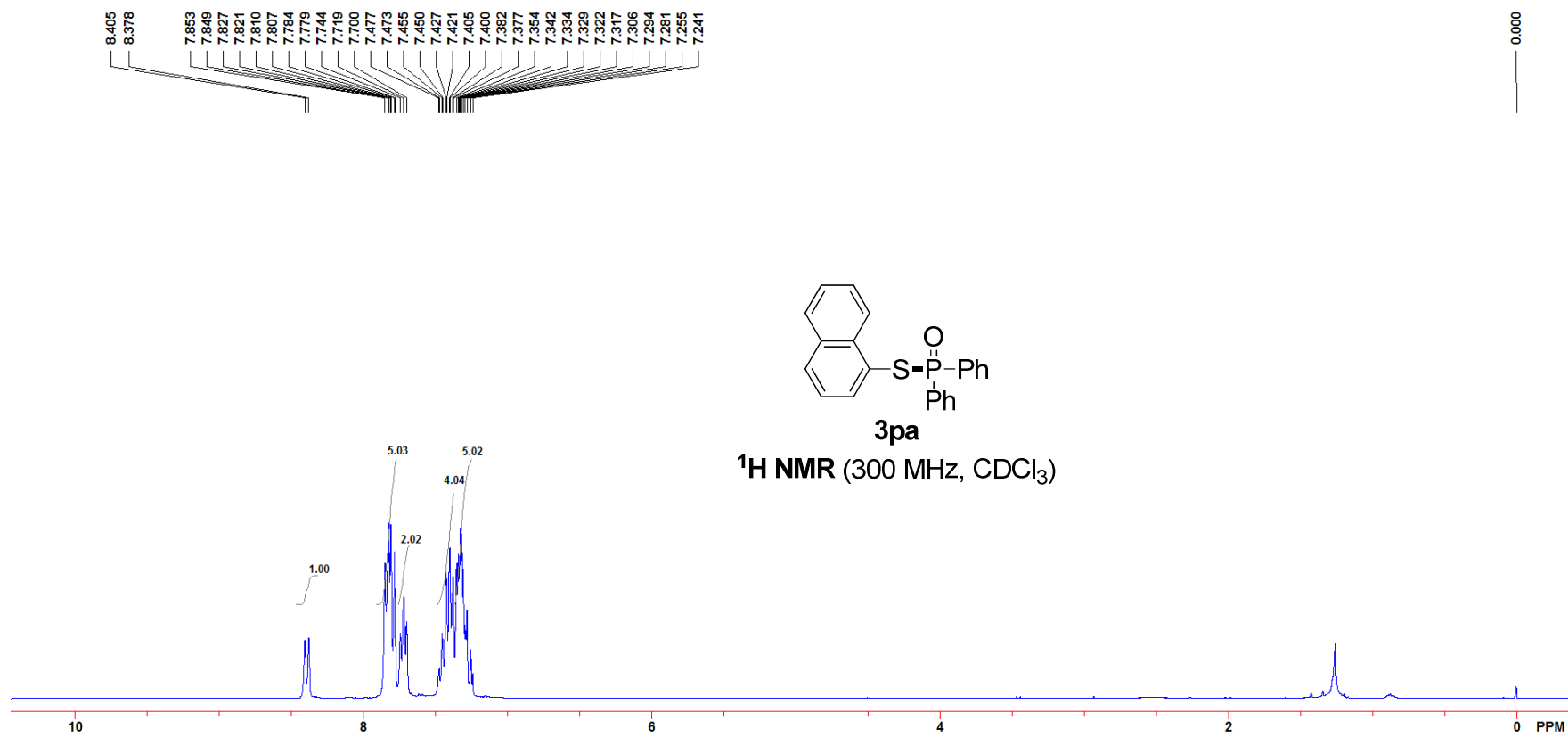


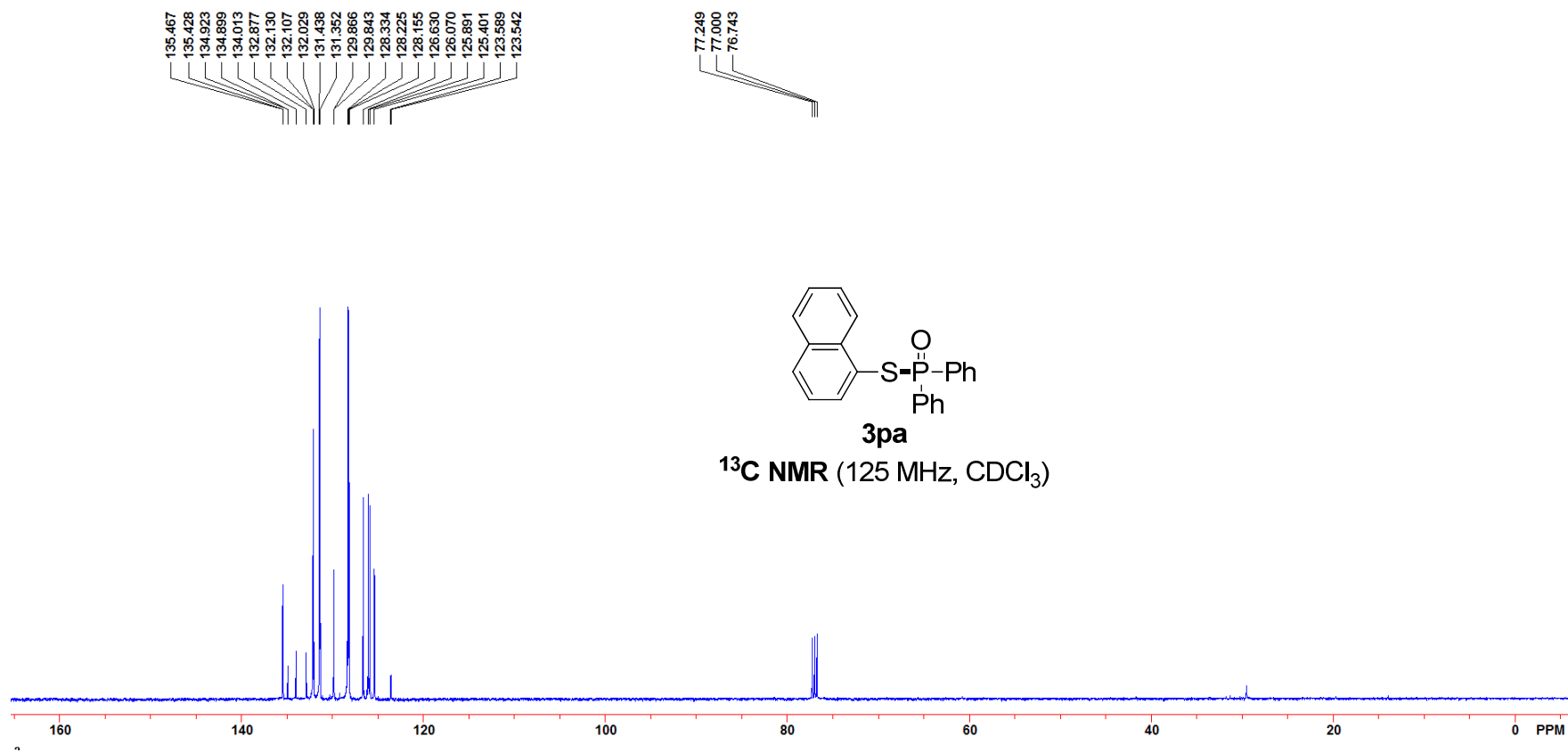


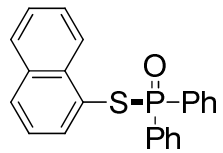
3oa

^{31}P NMR (121.5 MHz, CDCl_3)



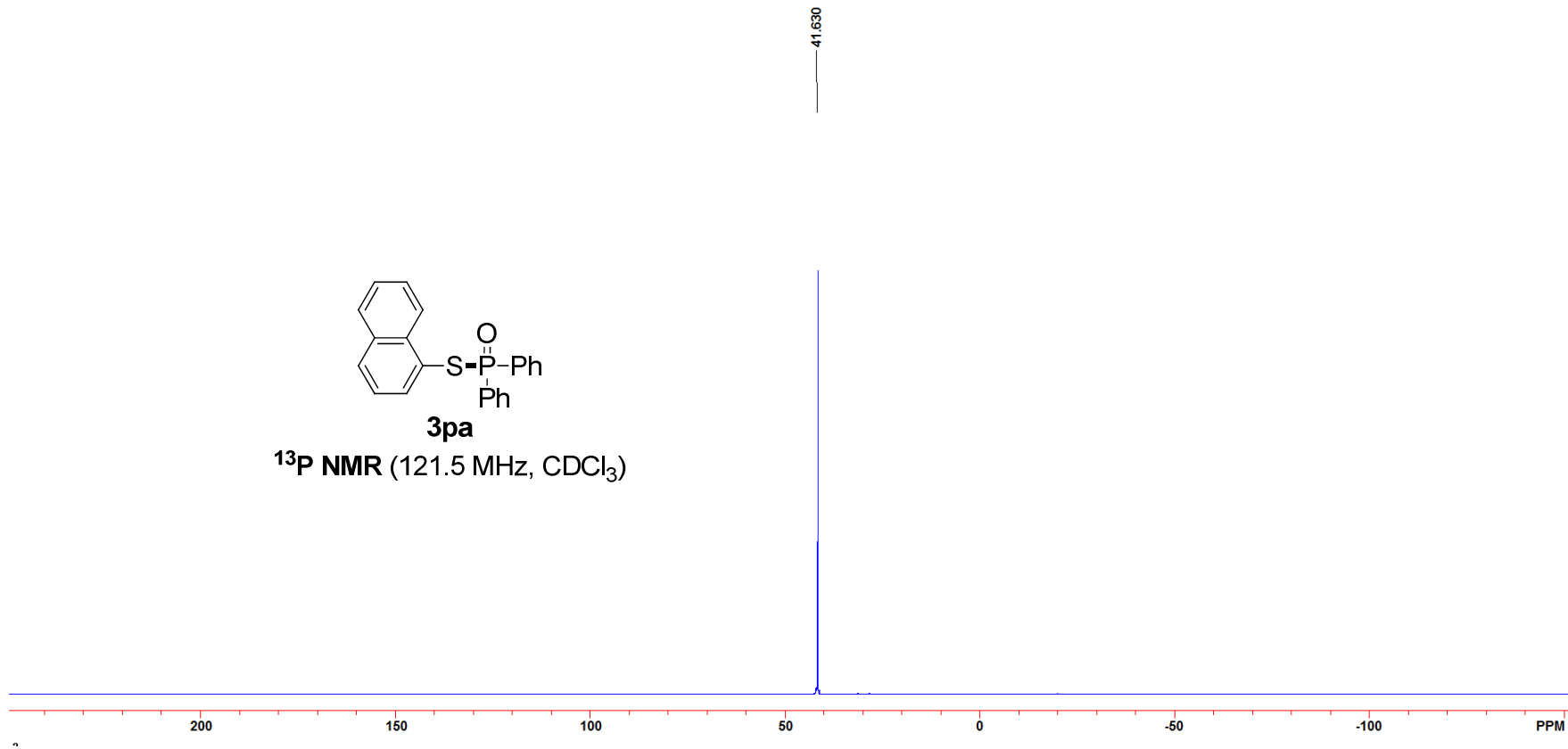


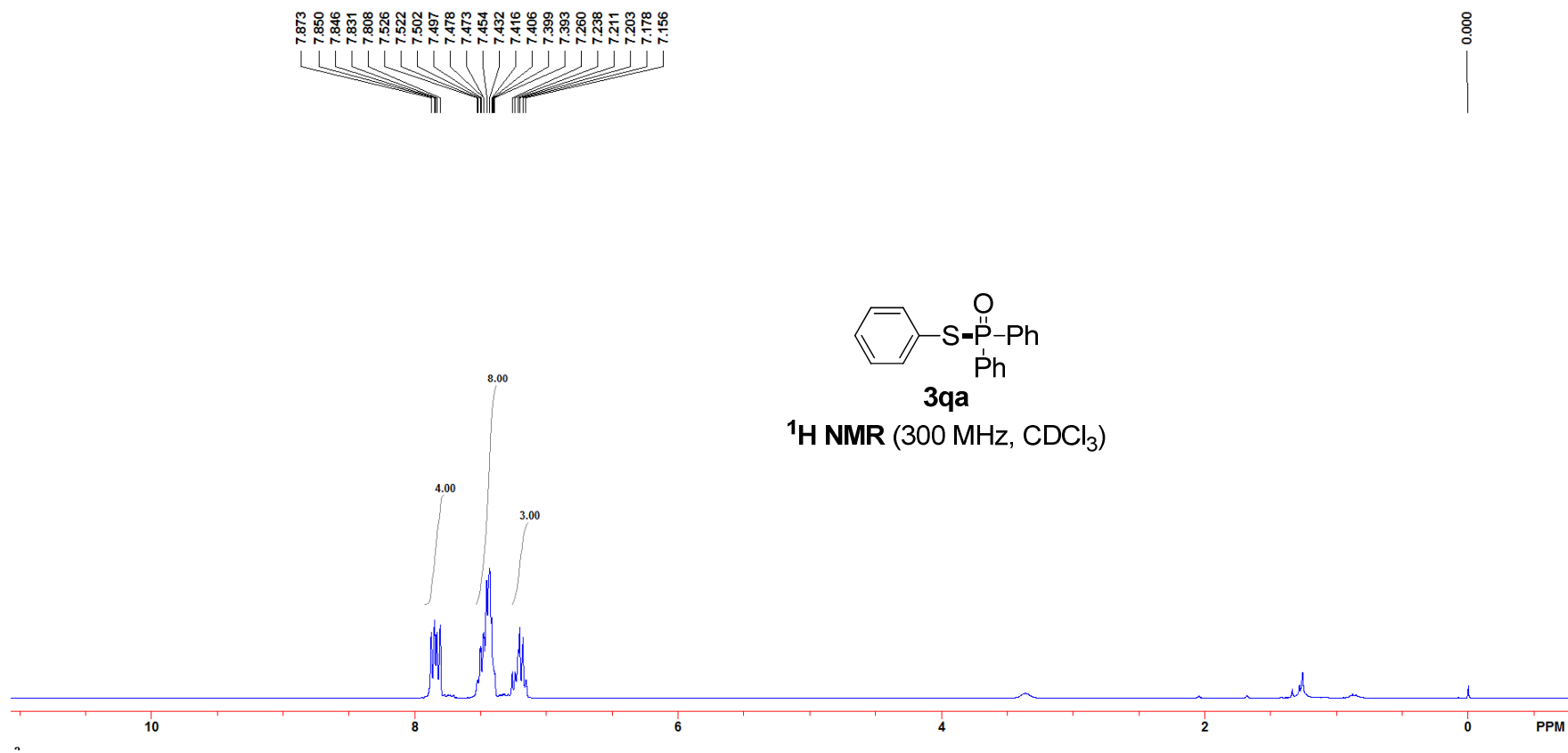




3pa

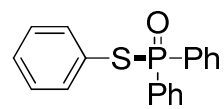
^{13}P NMR (121.5 MHz, CDCl_3)





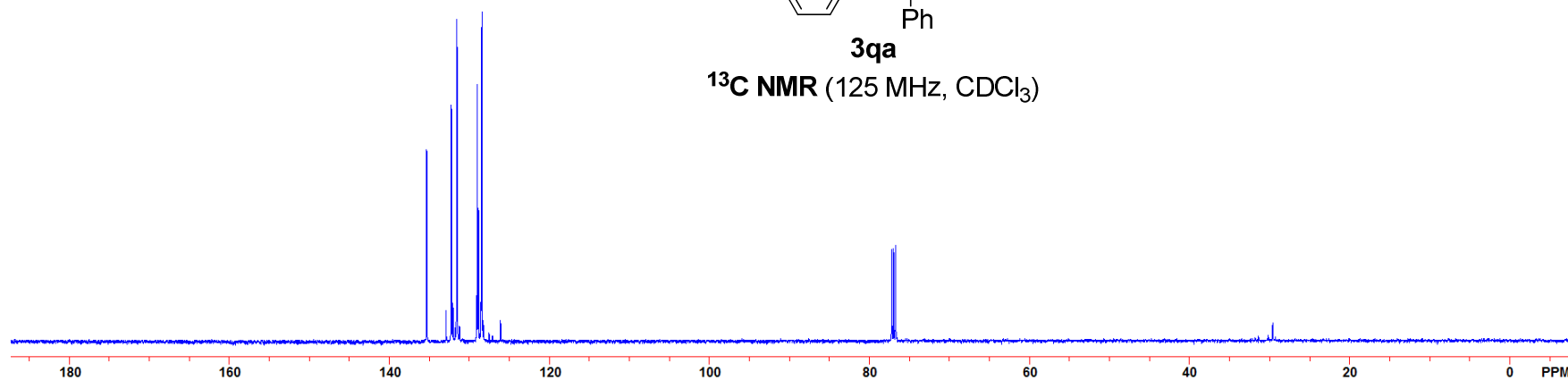
135.335
135.304
132.900
132.262
132.239
132.045
131.596
129.042
128.863
128.847
128.521
128.419
126.132
126.094

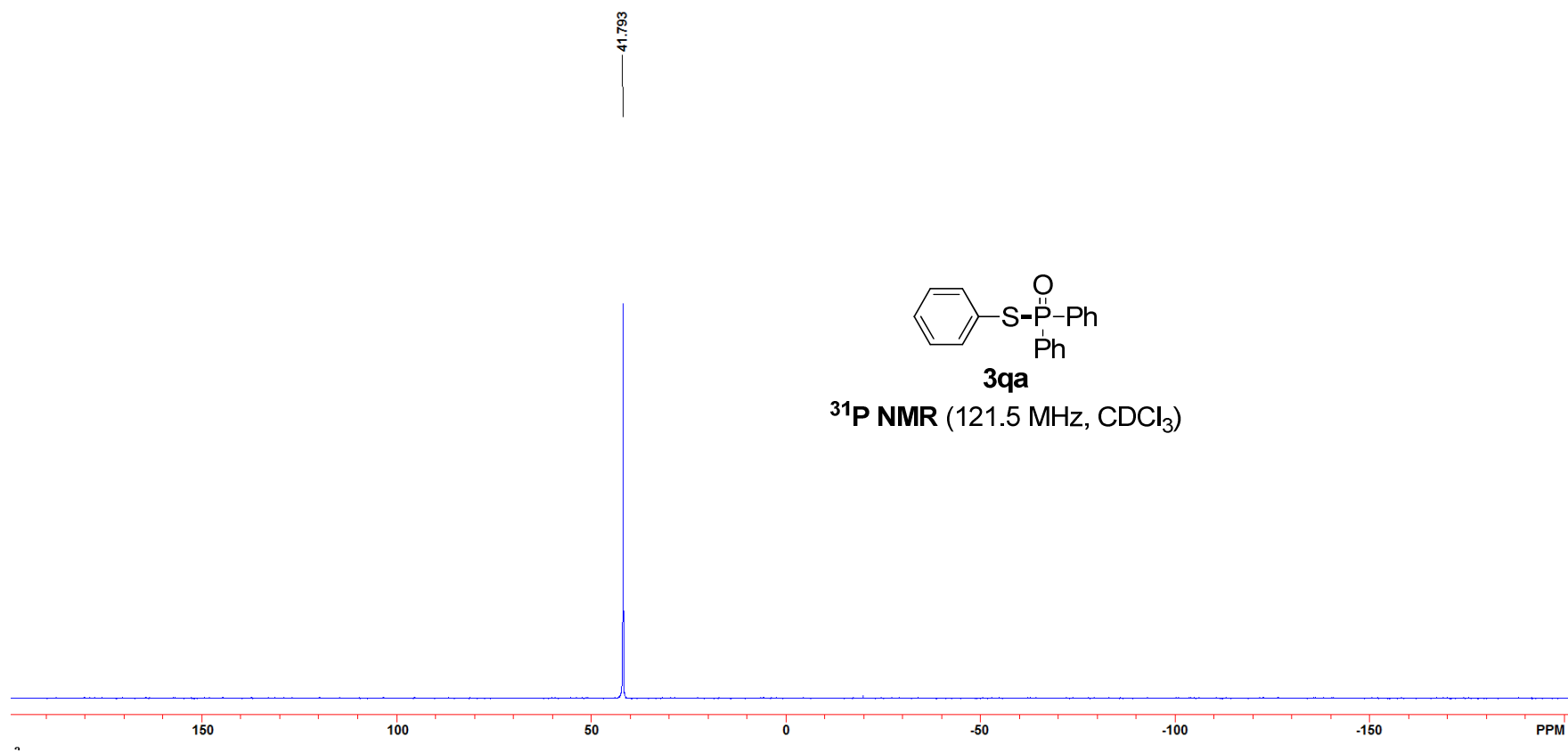
77.249
77.000
76.743

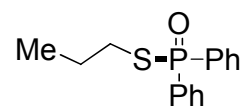
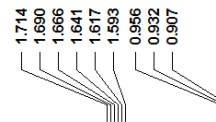
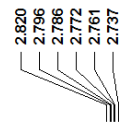
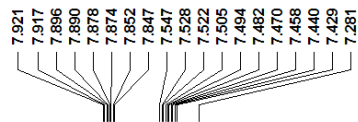


3qa

¹³C NMR (125 MHz, CDCl₃)

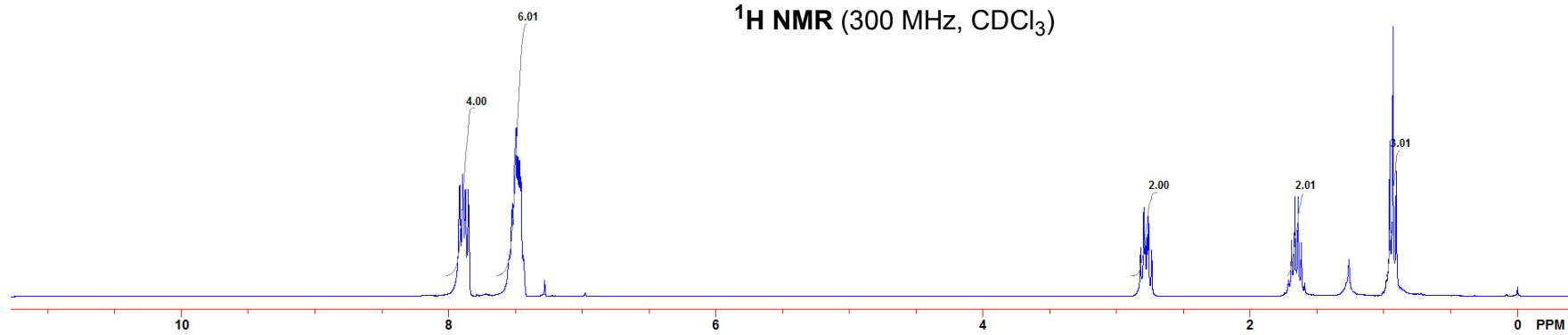


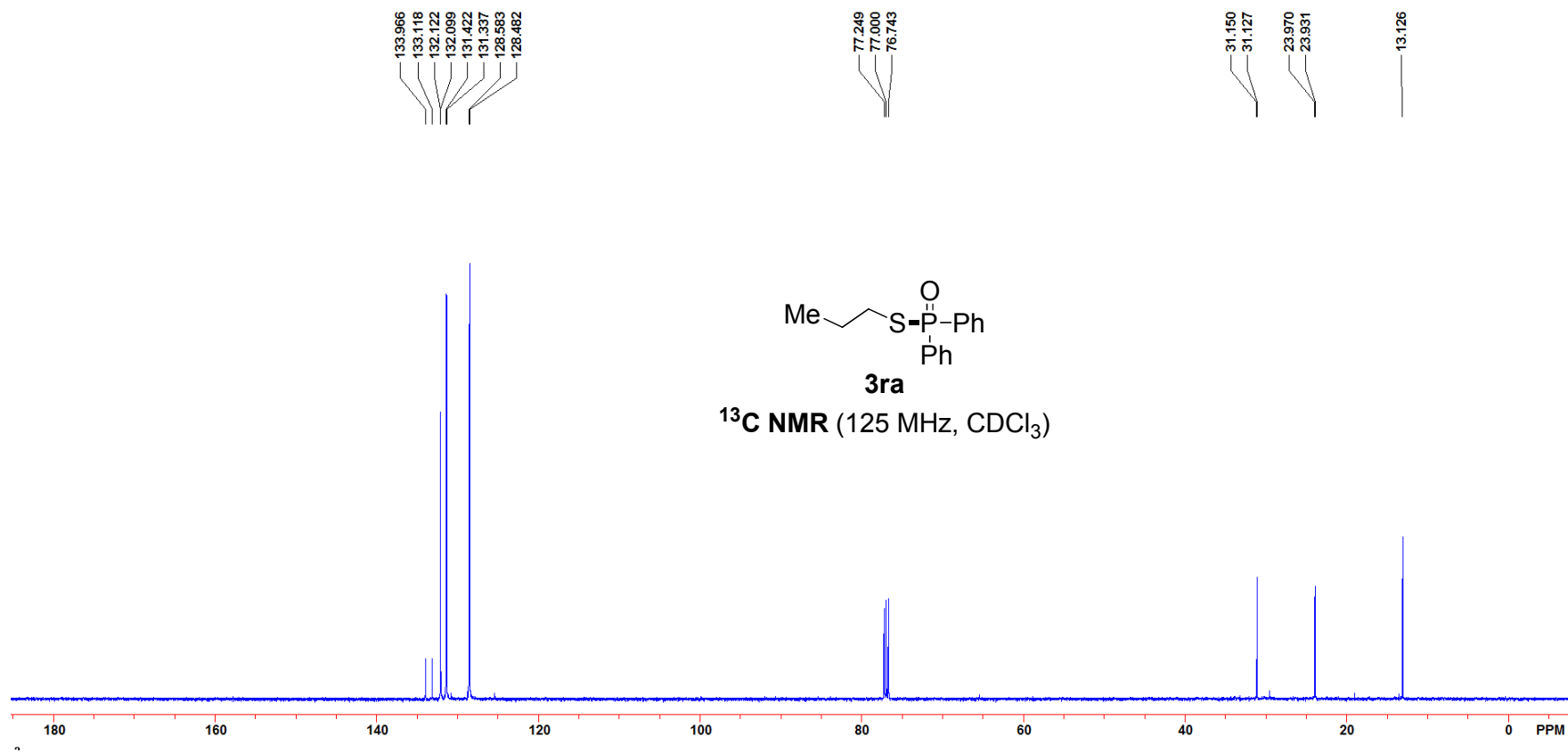


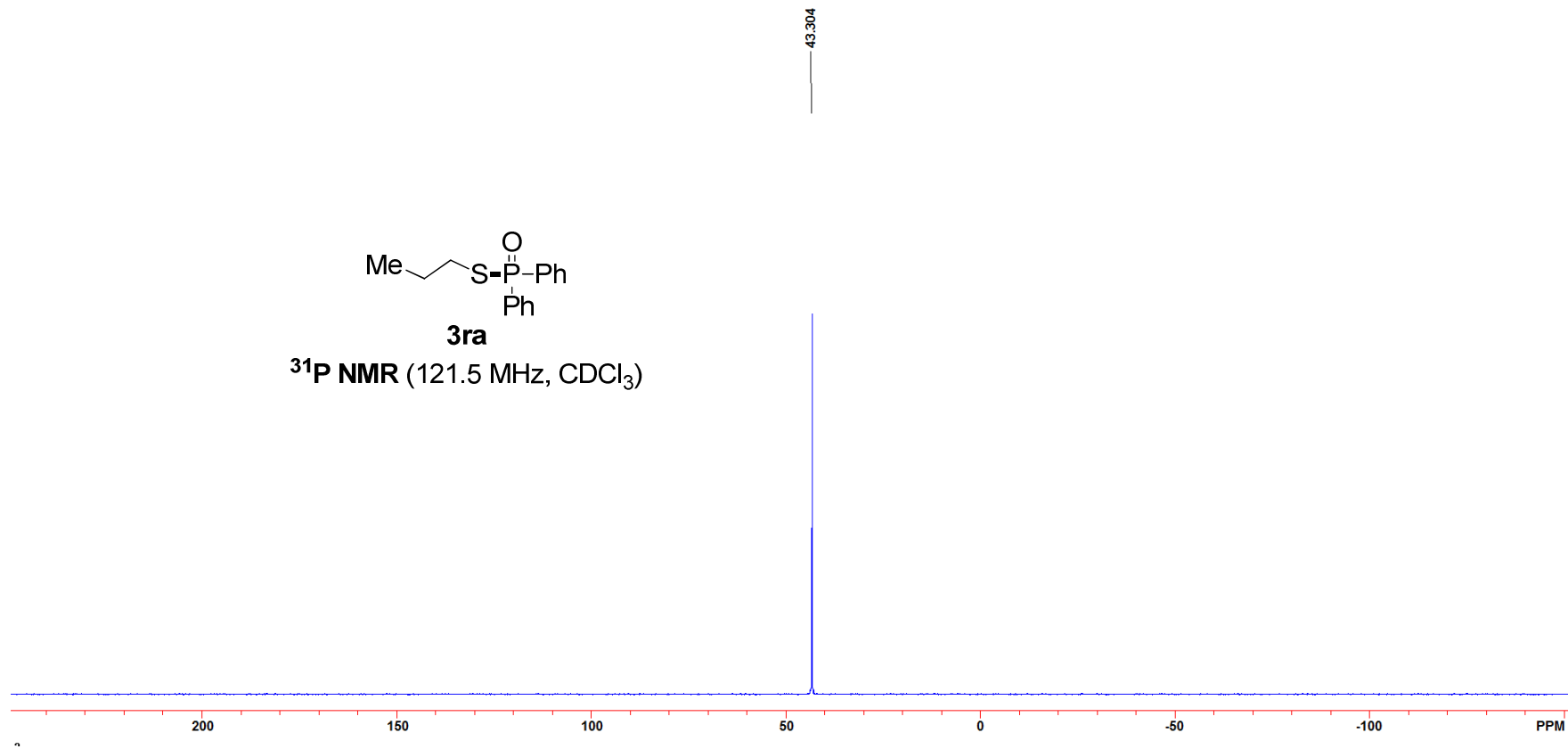
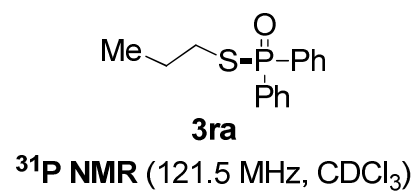


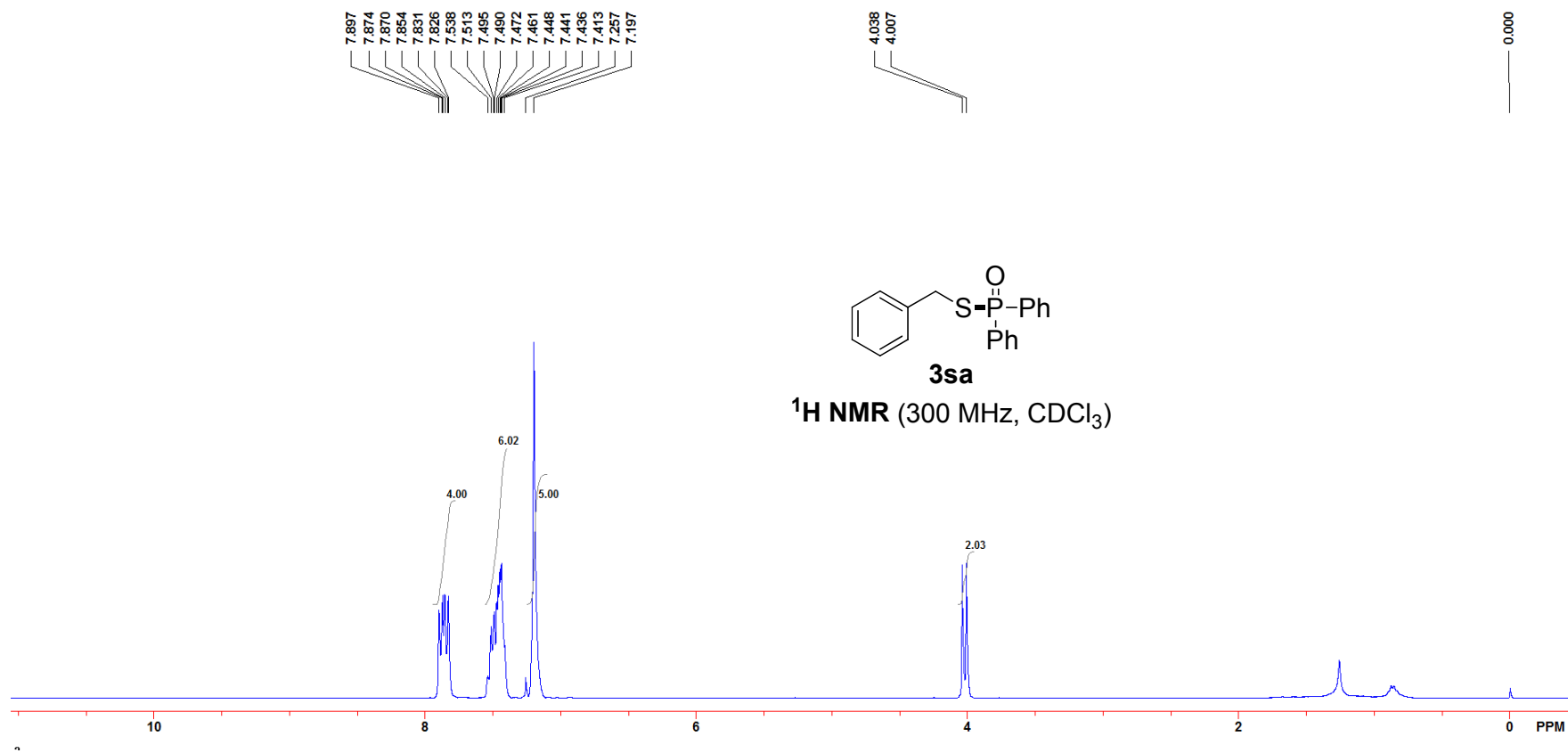
3ra

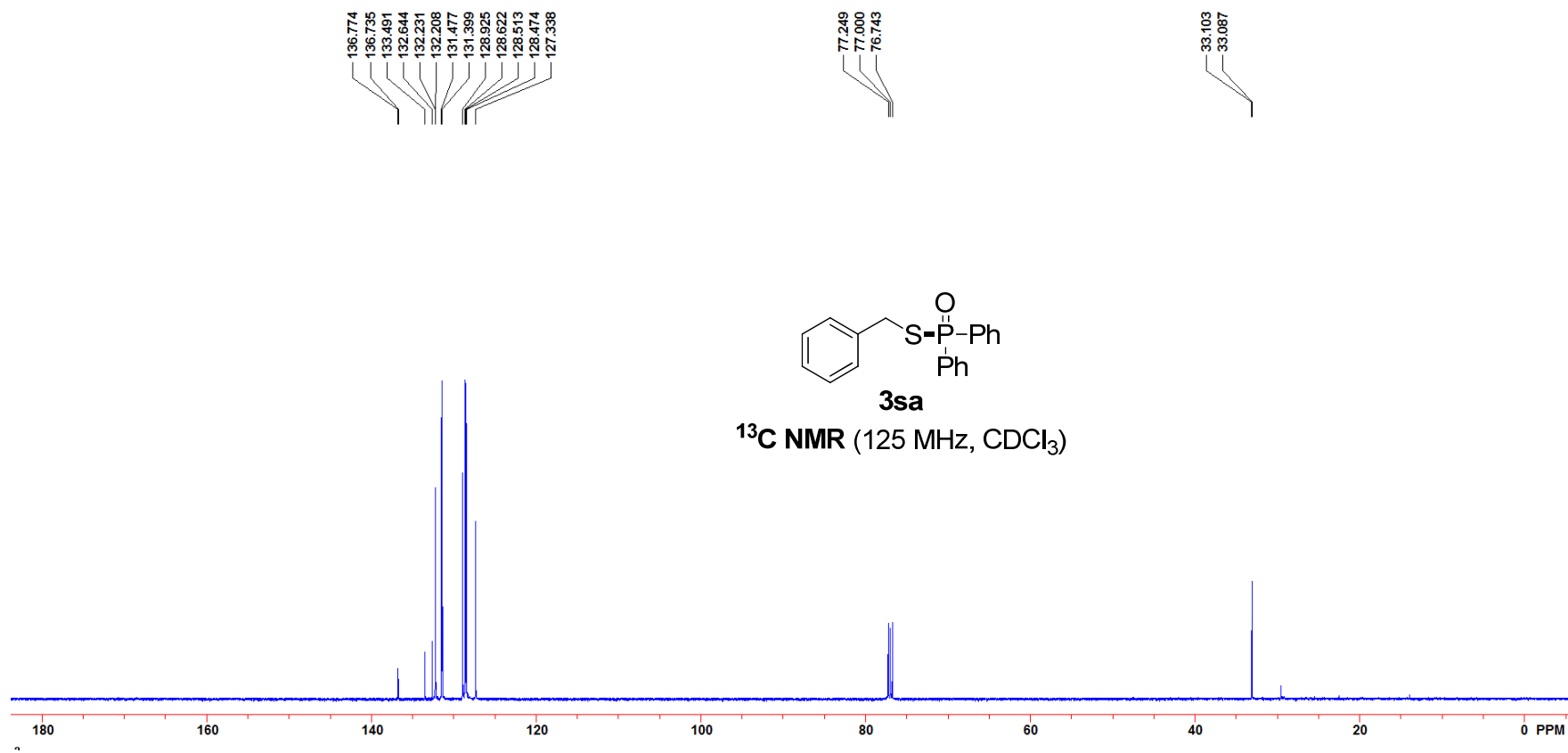
¹H NMR (300 MHz, CDCl₃)

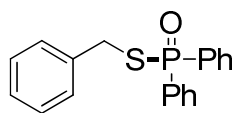






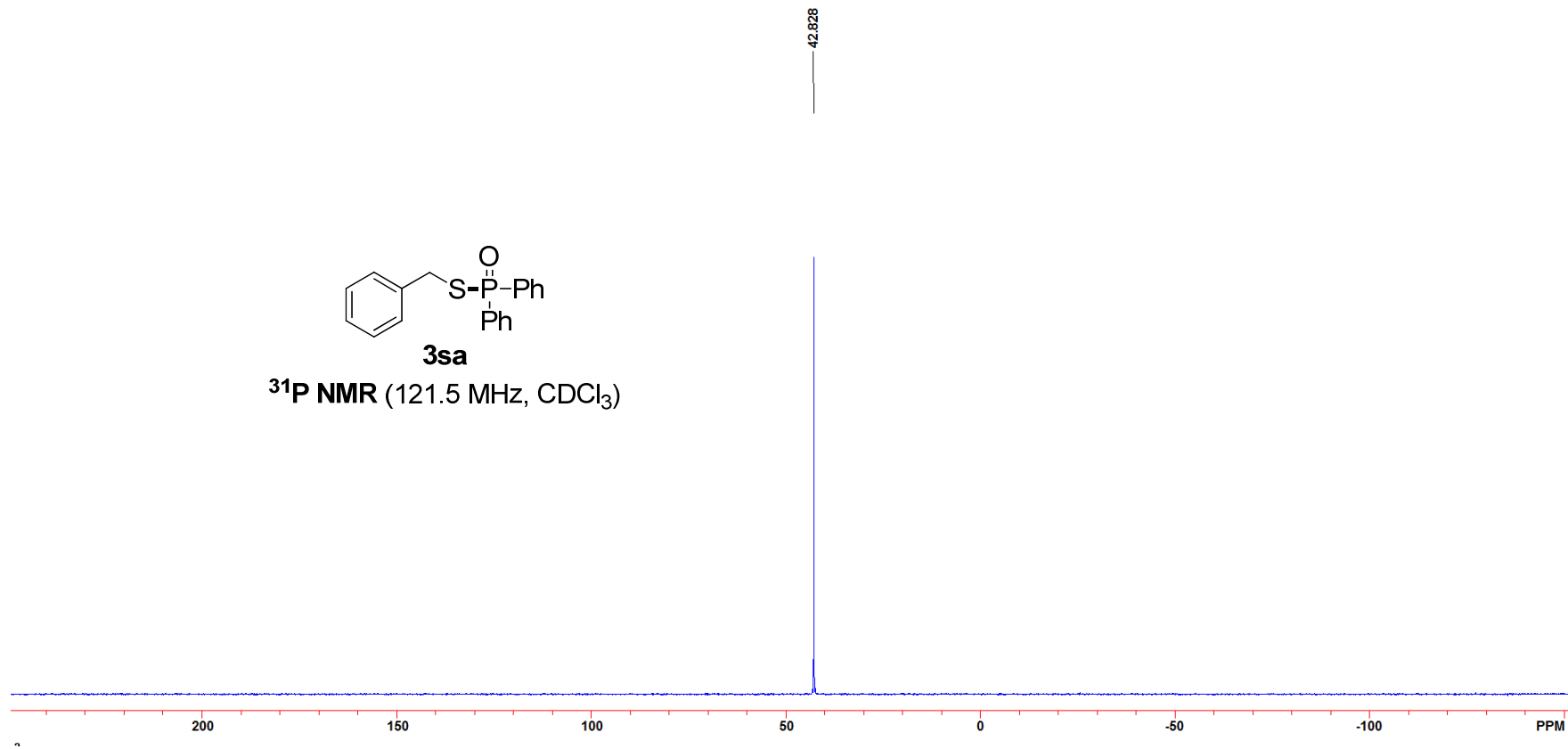


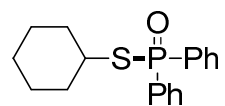
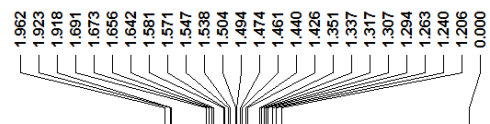
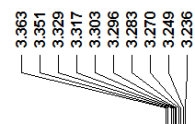
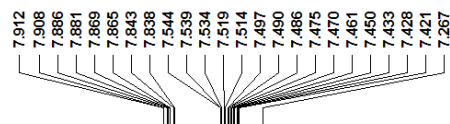




3sa

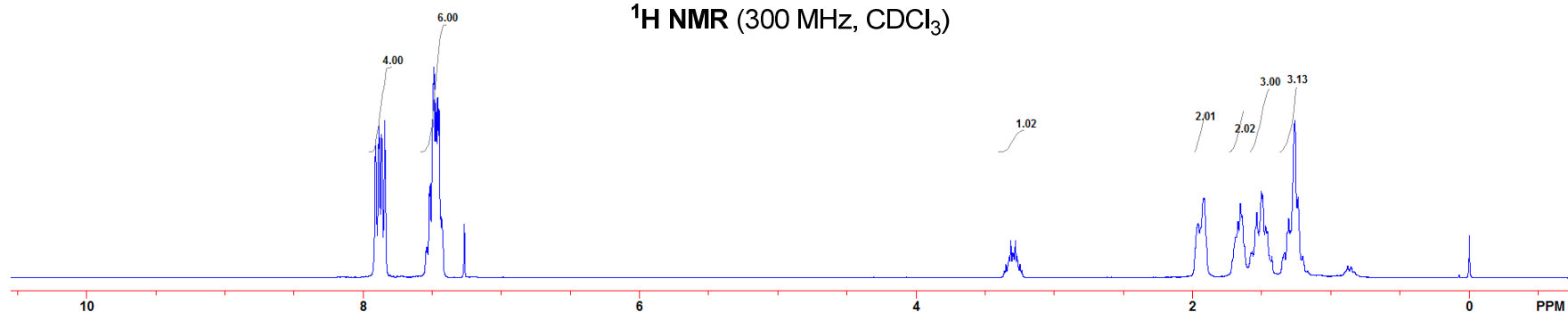
^{31}P NMR (121.5 MHz, CDCl_3)





3ta

¹H NMR (300 MHz, CDCl₃)



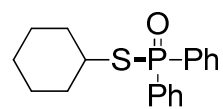
134.903
133.482
132.046
132.009
131.475
131.335
128.580
128.412

77.425
77.000
76.575

44.418
44.389

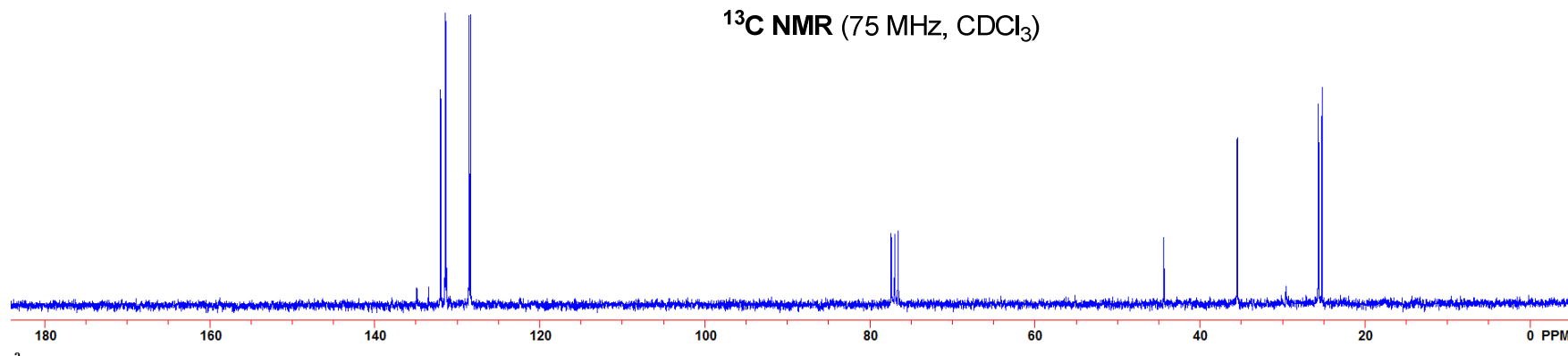
35.552
35.501

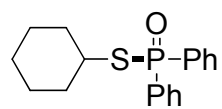
25.676
25.258



3ta

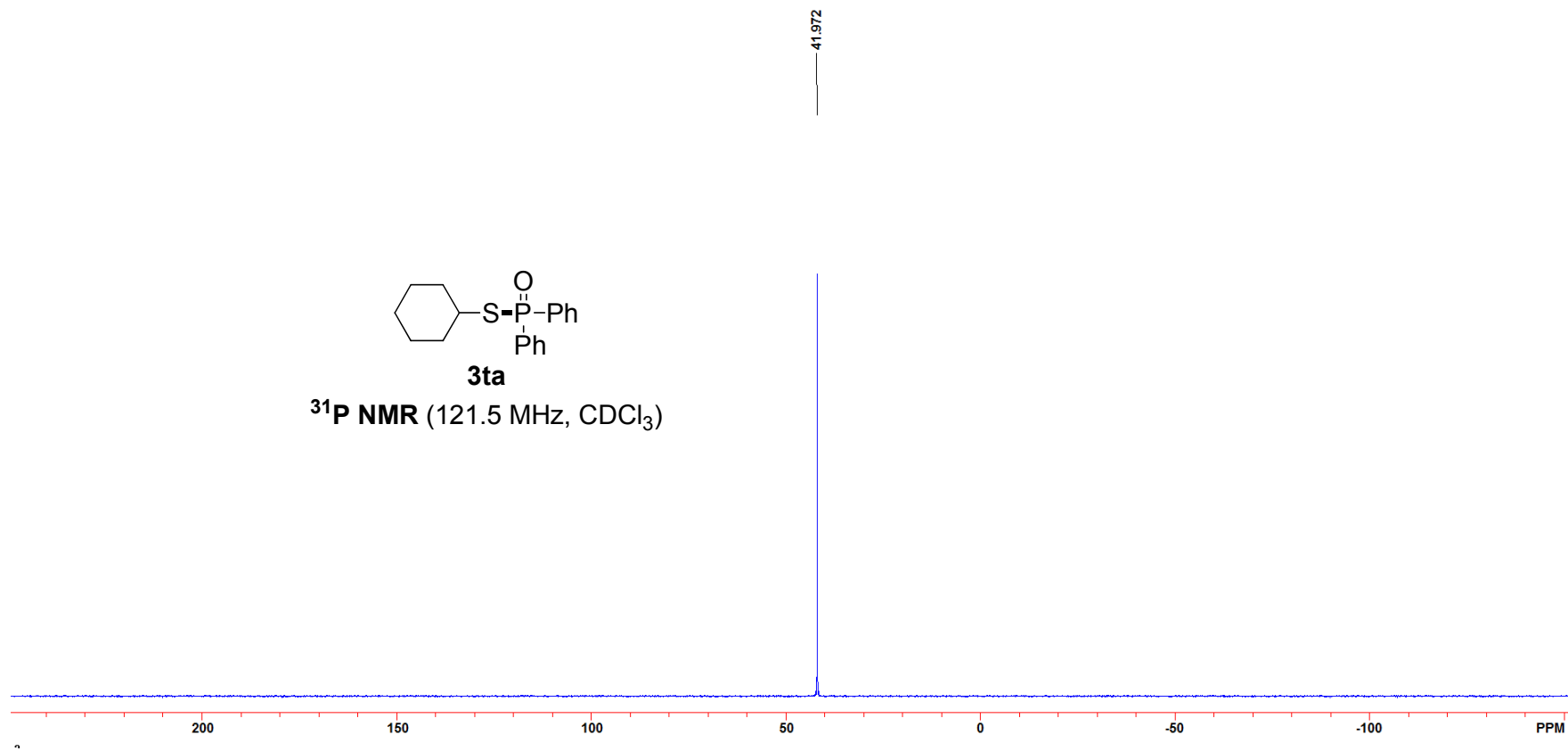
¹³C NMR (75 MHz, CDCl₃)

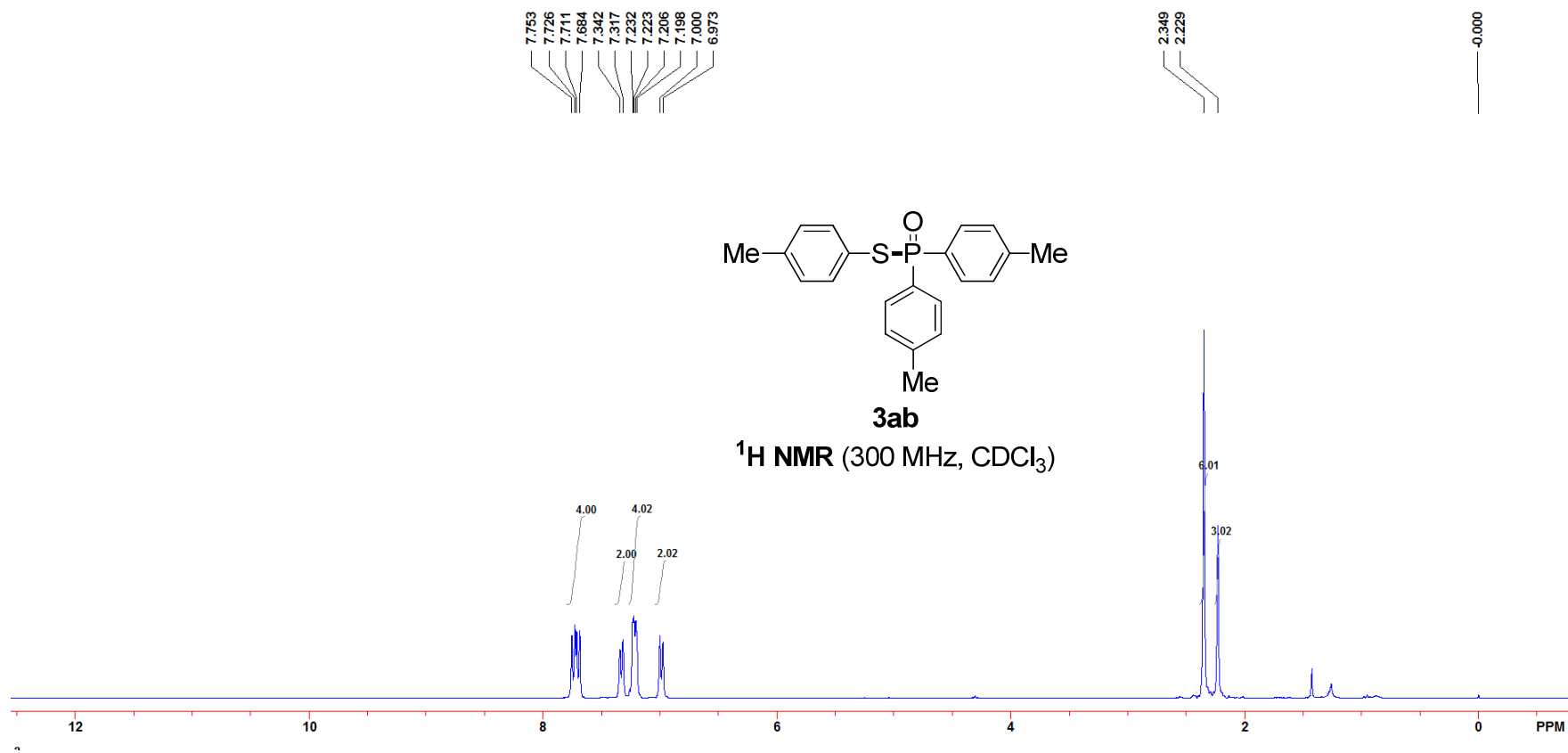


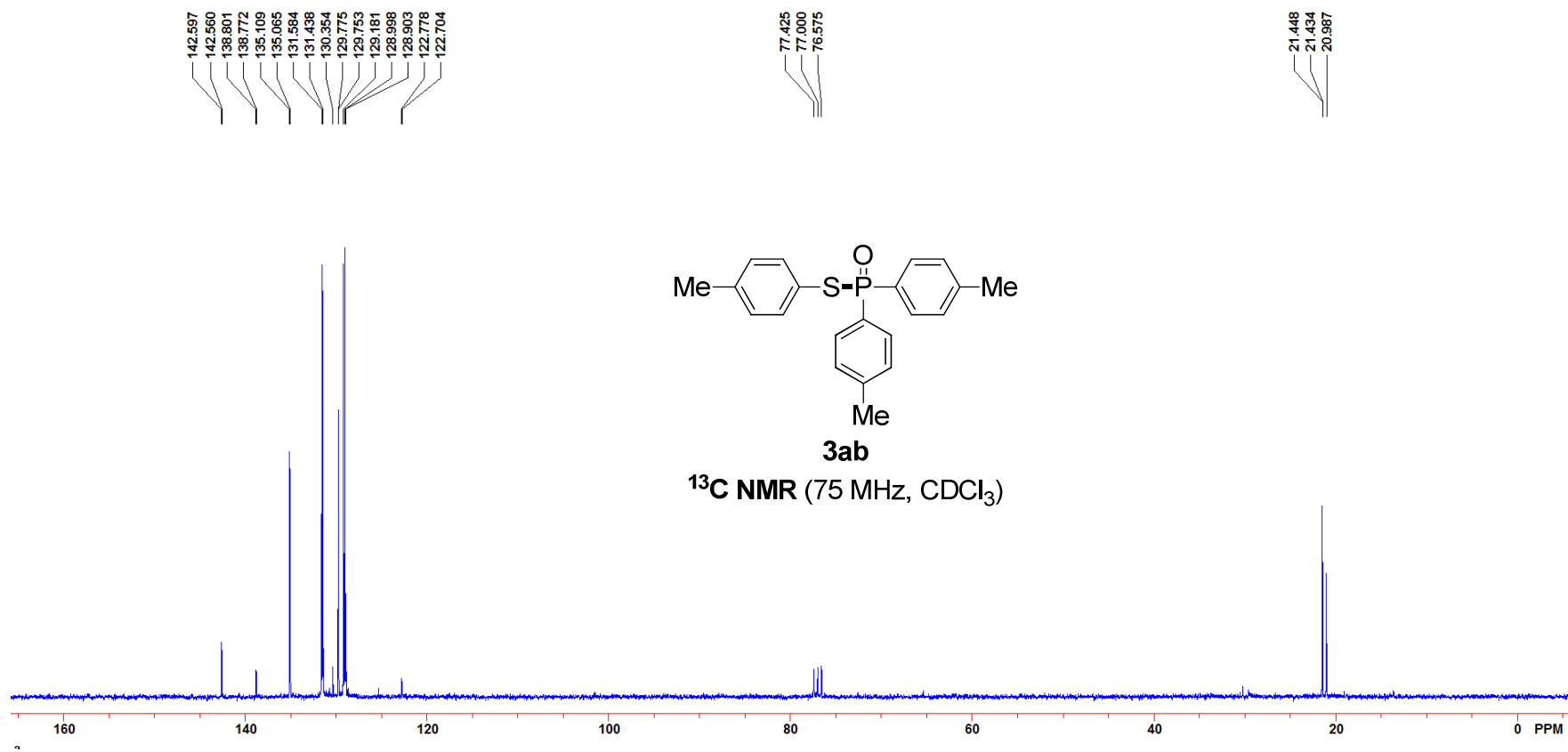


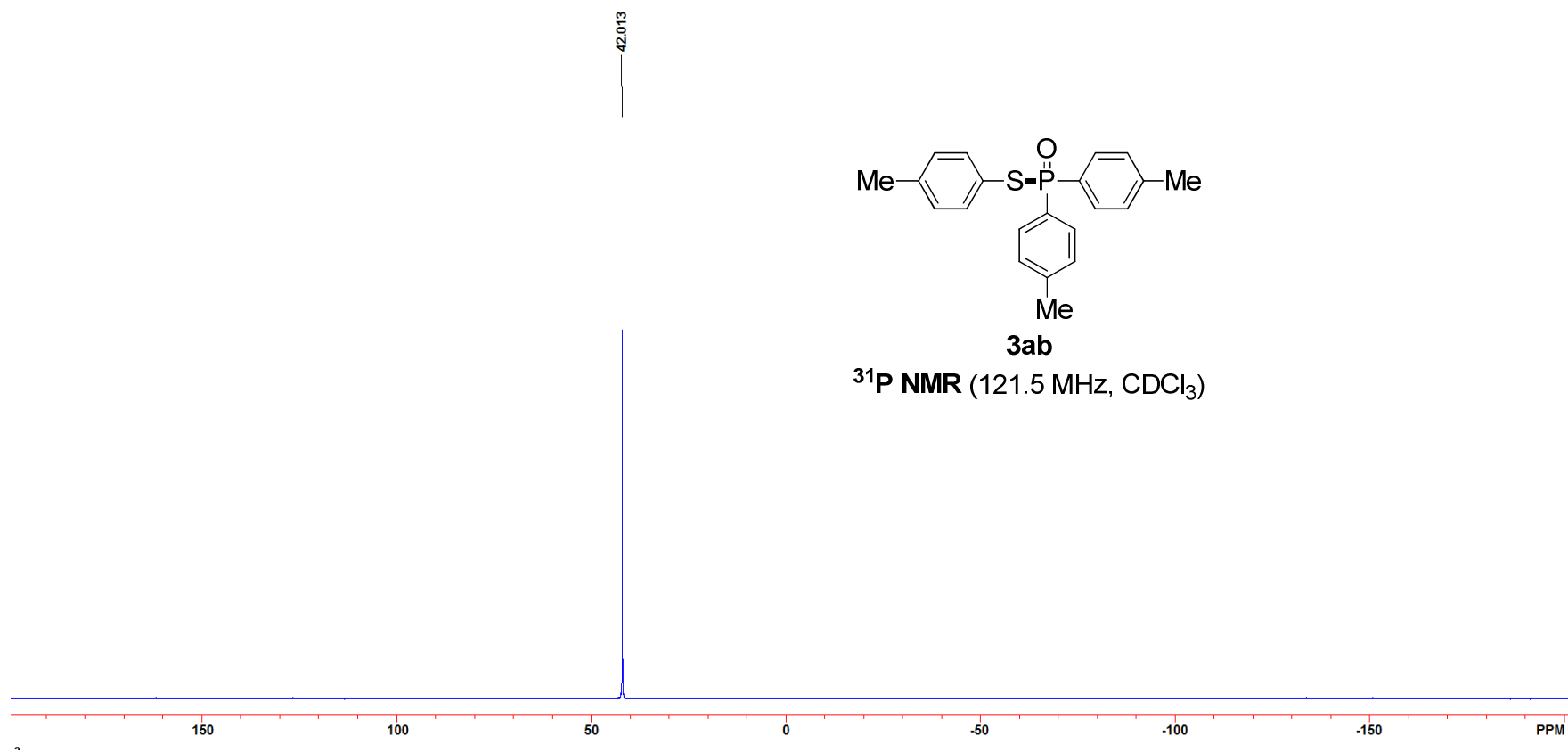
3ta

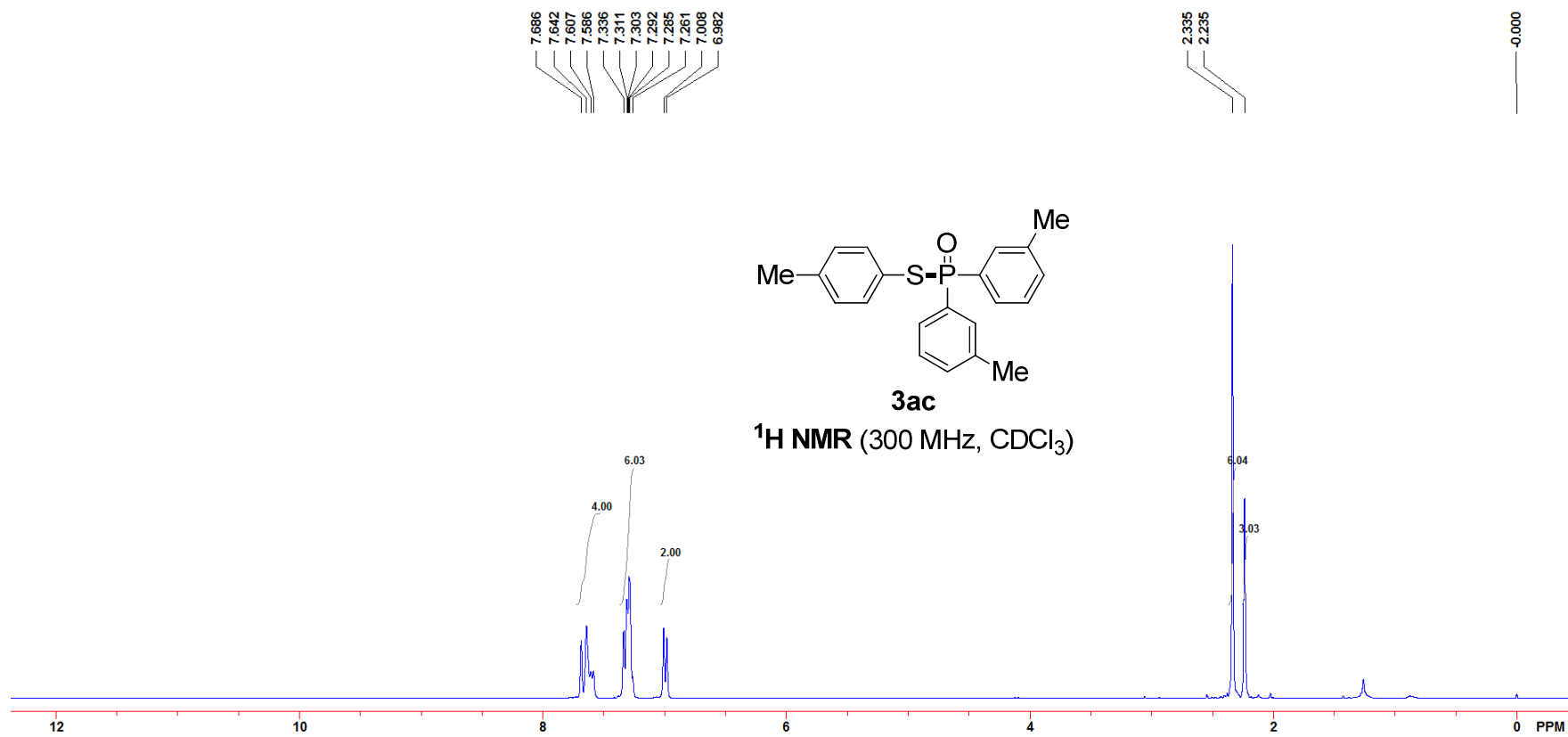
^{31}P NMR (121.5 MHz, CDCl_3)

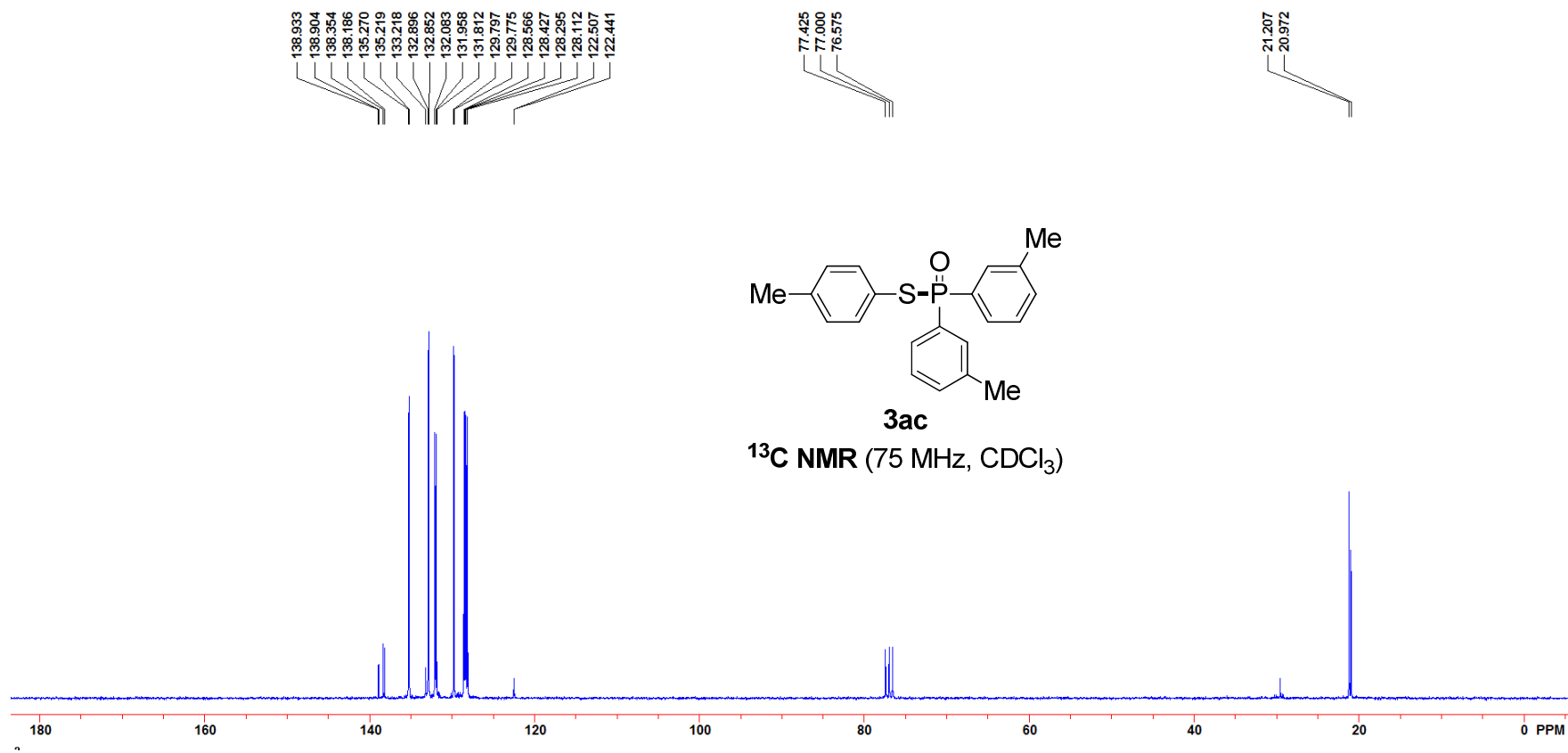


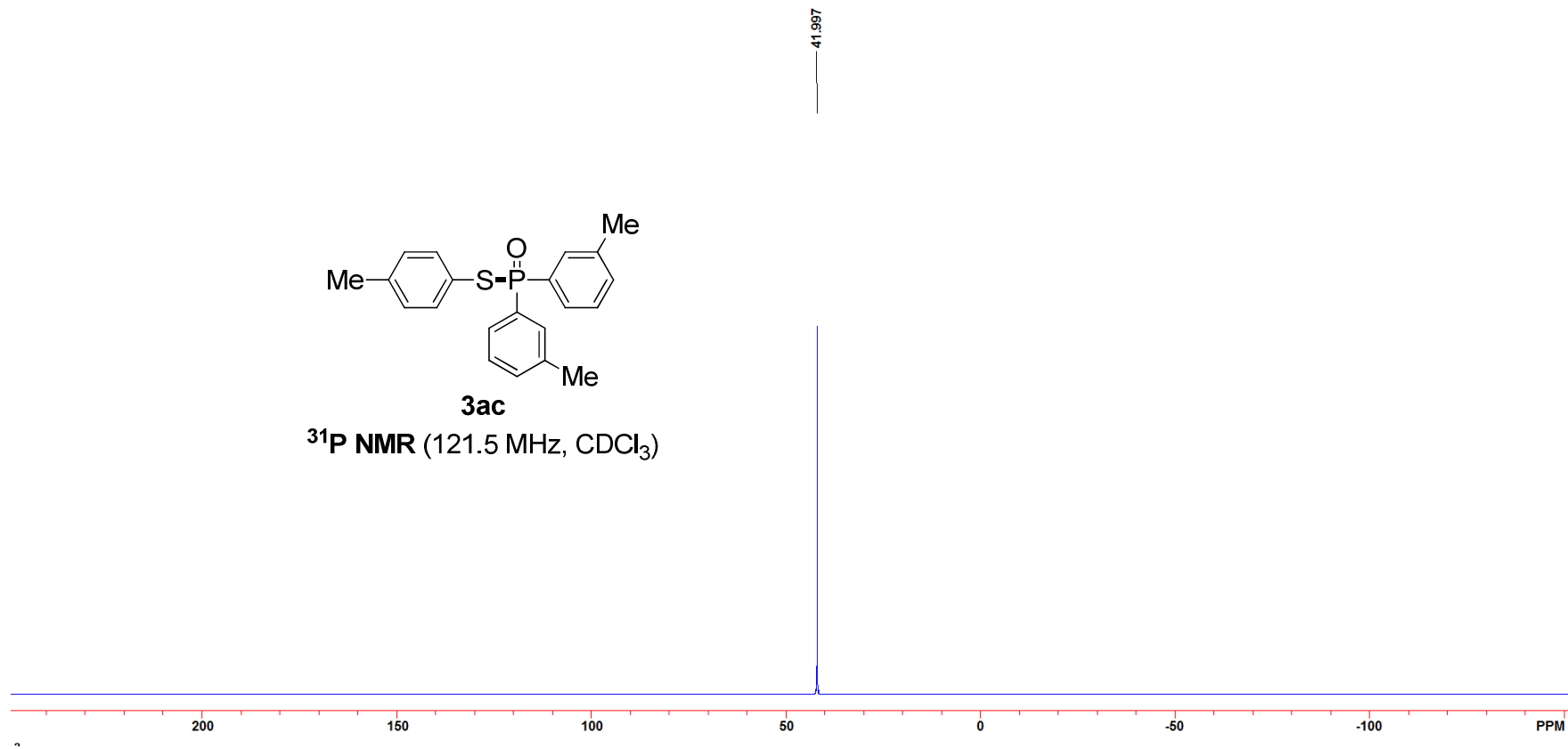
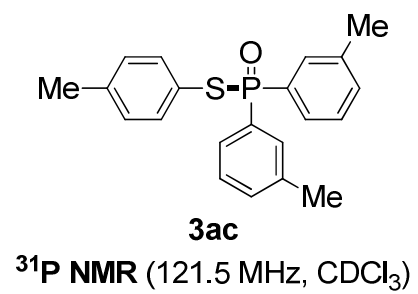


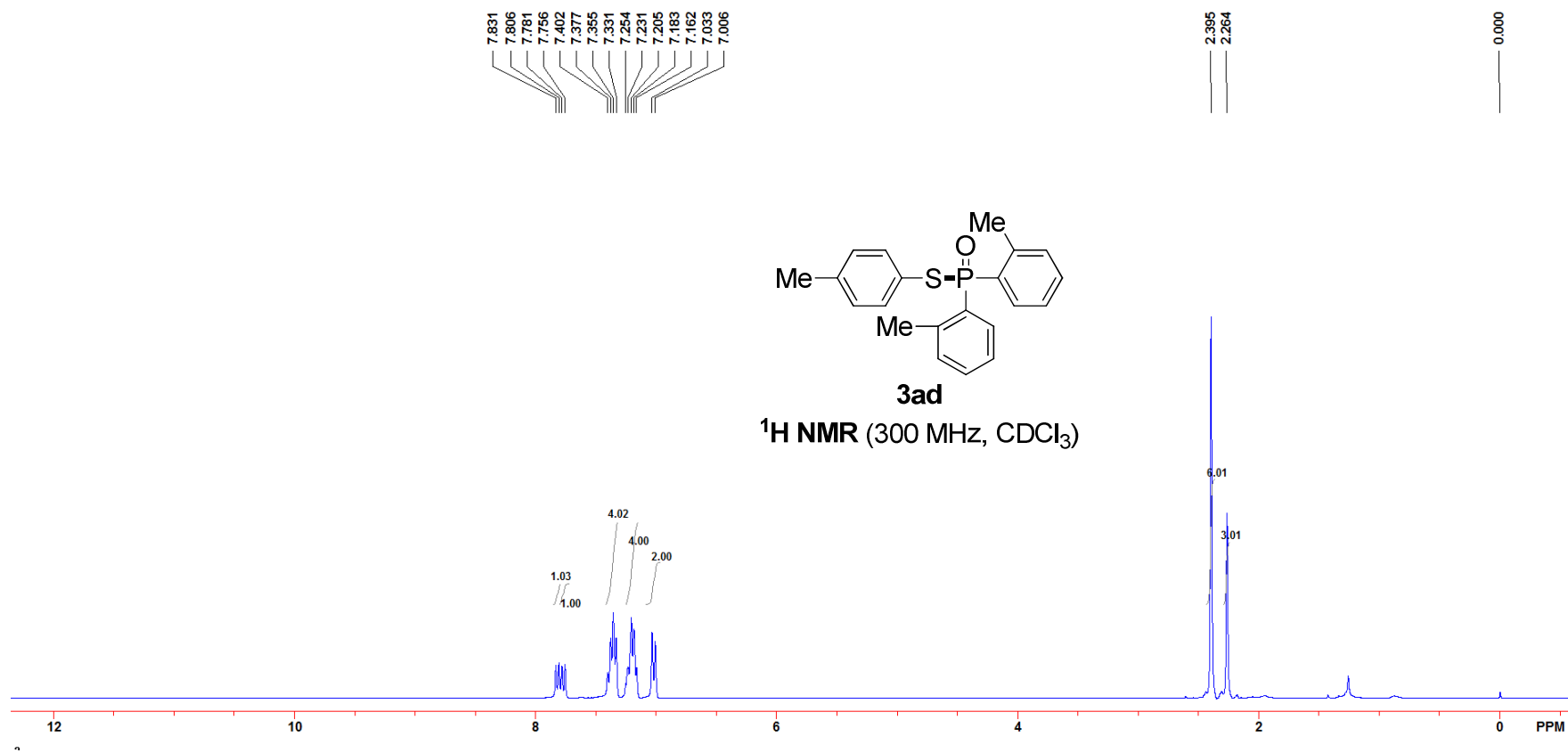


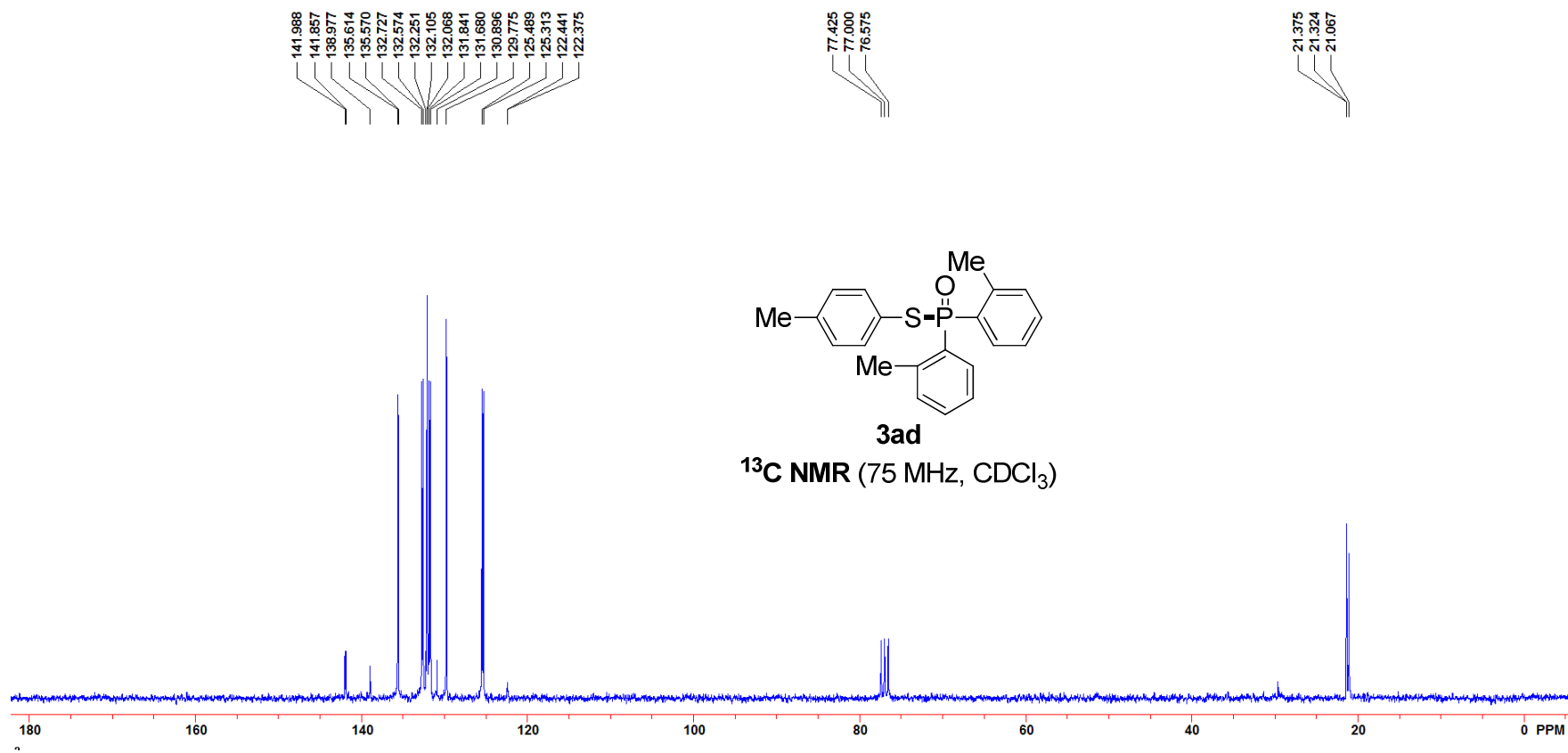


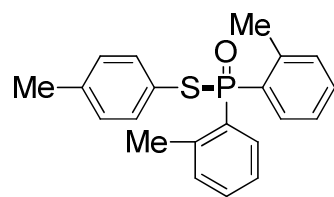






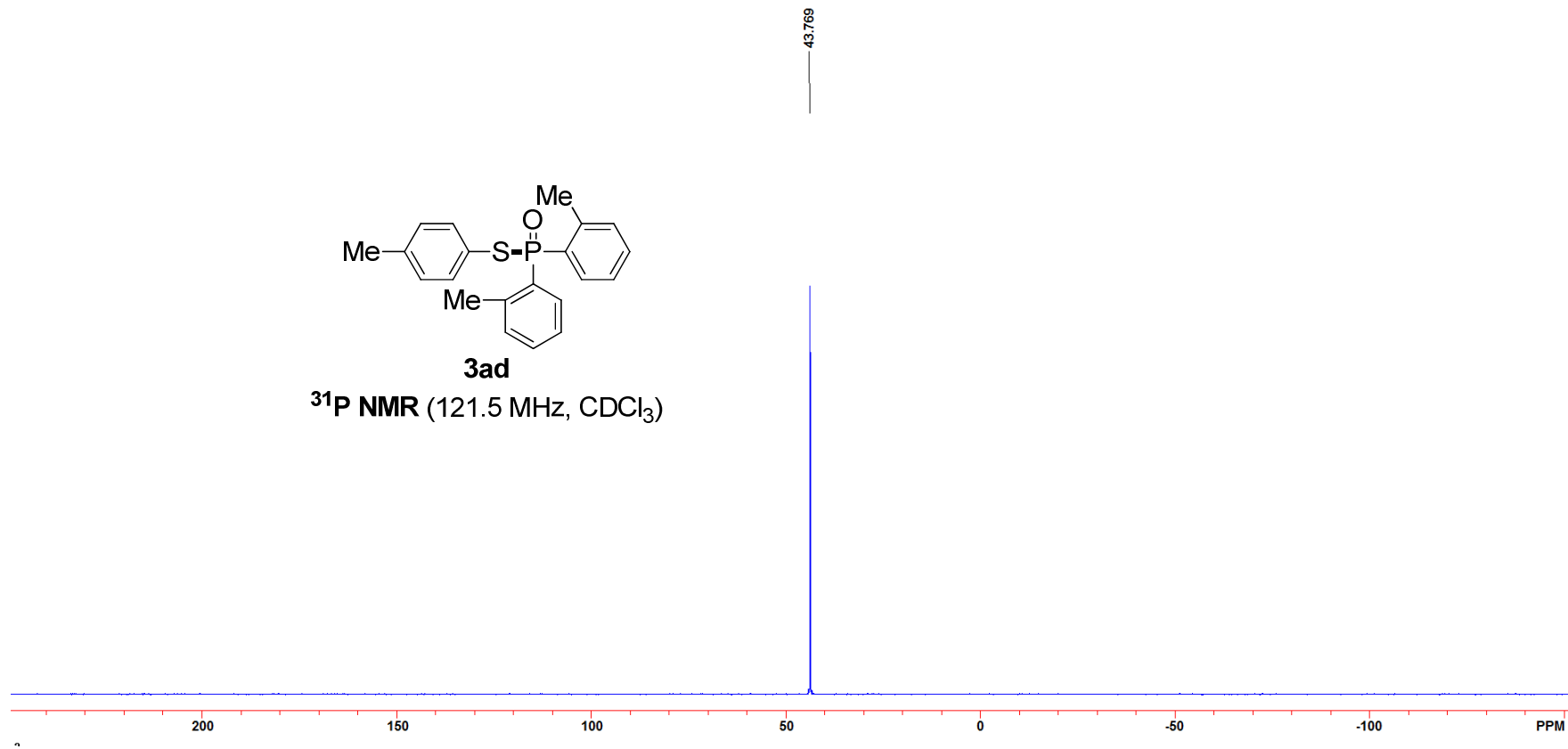


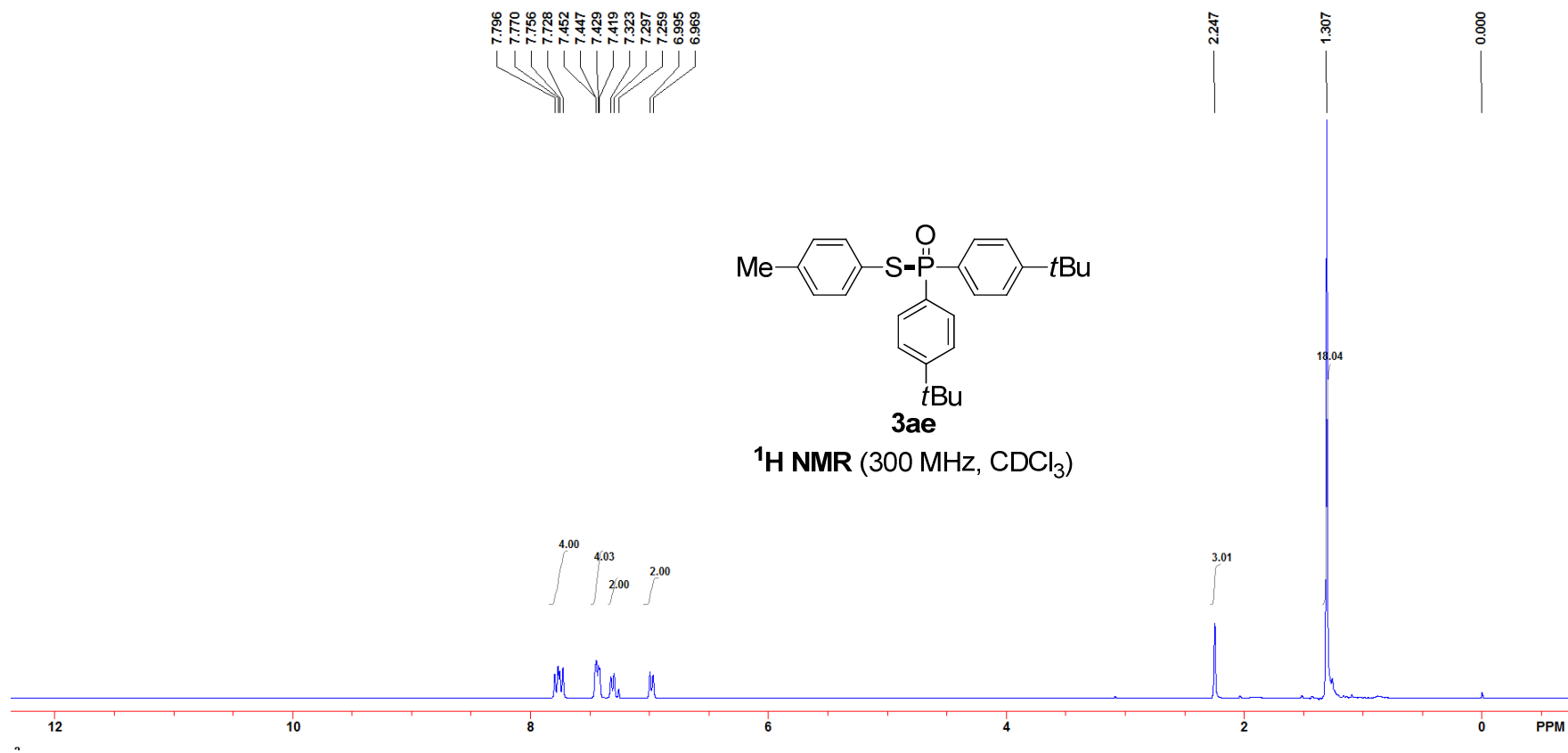


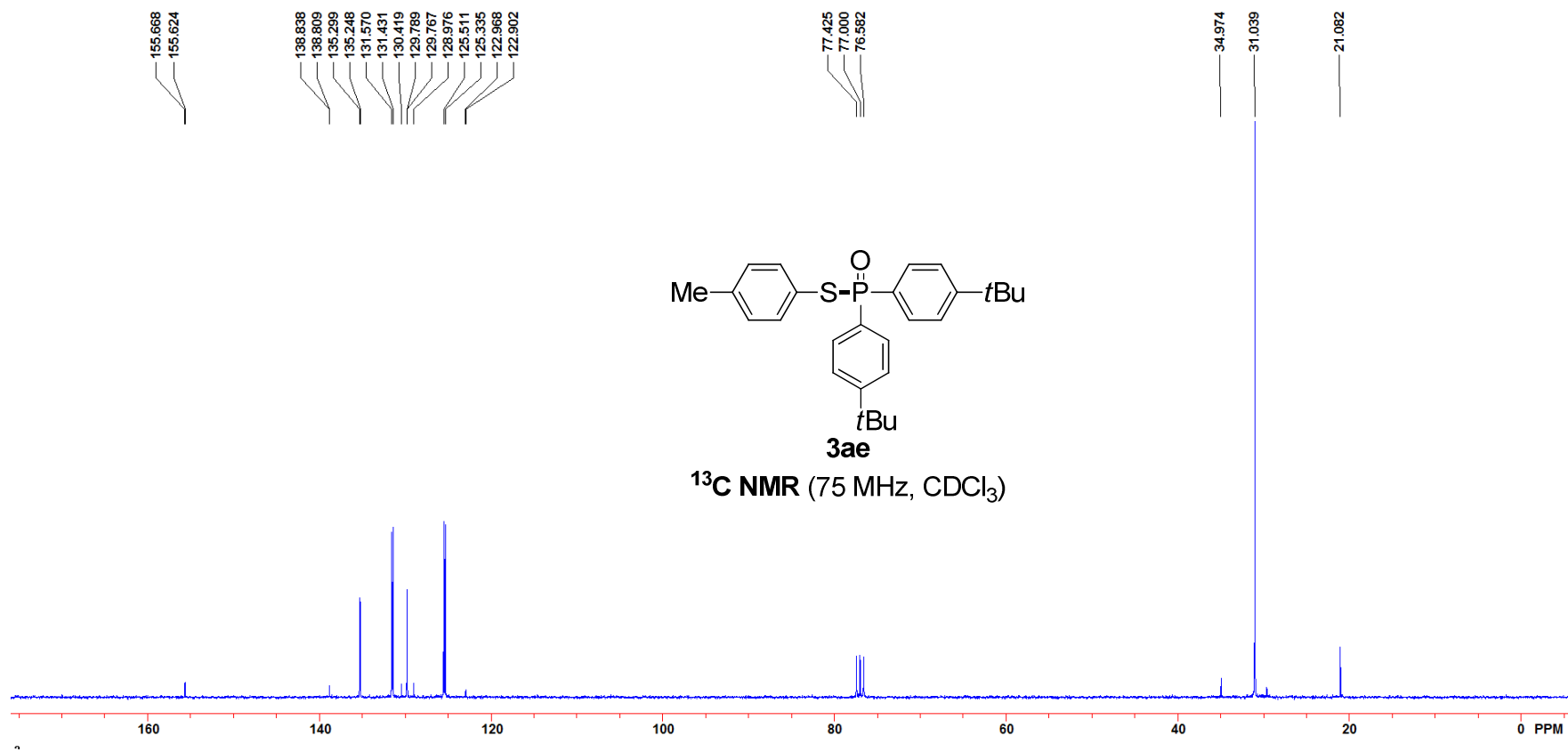


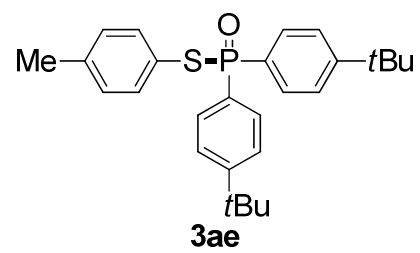
3ad

^{31}P NMR (121.5 MHz, CDCl_3)

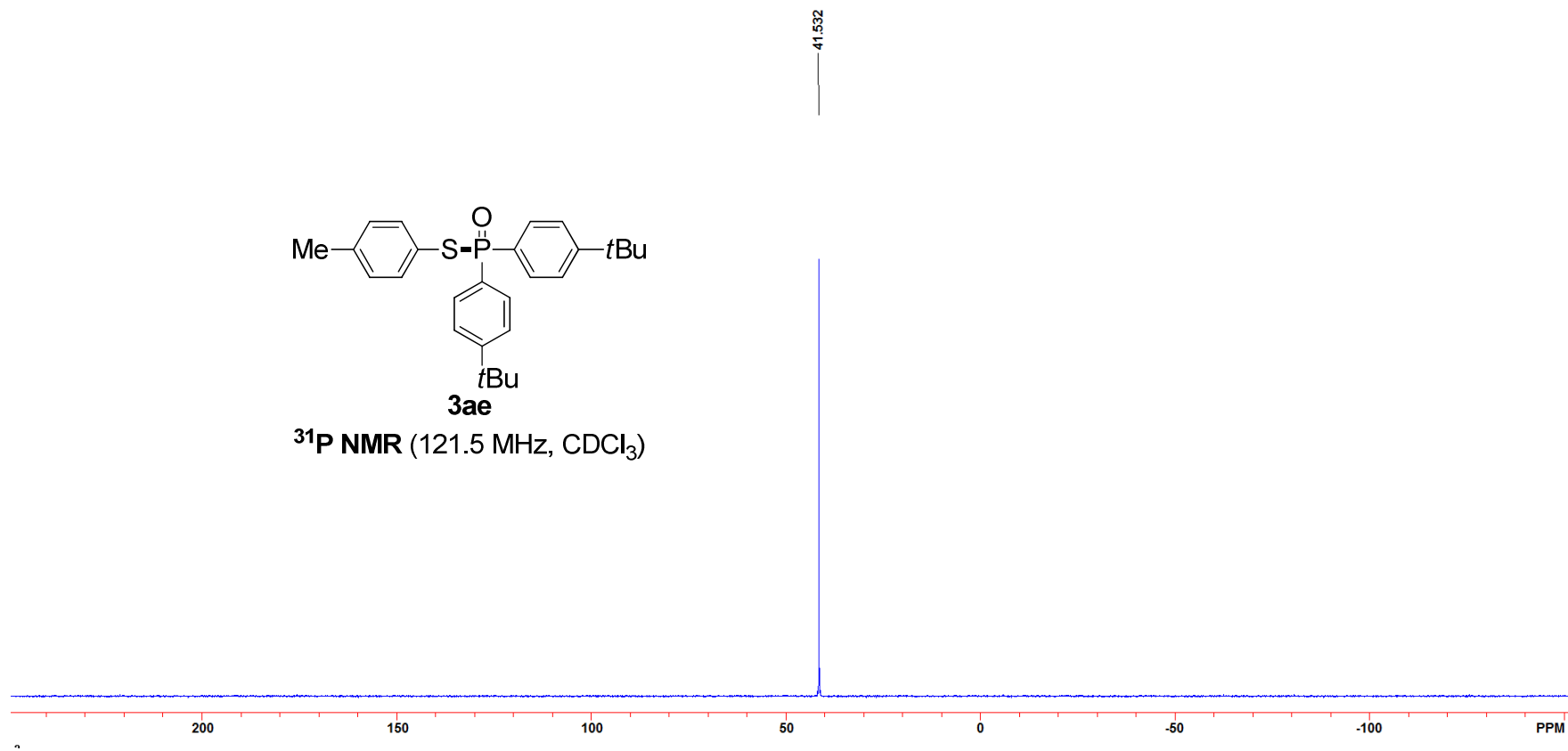


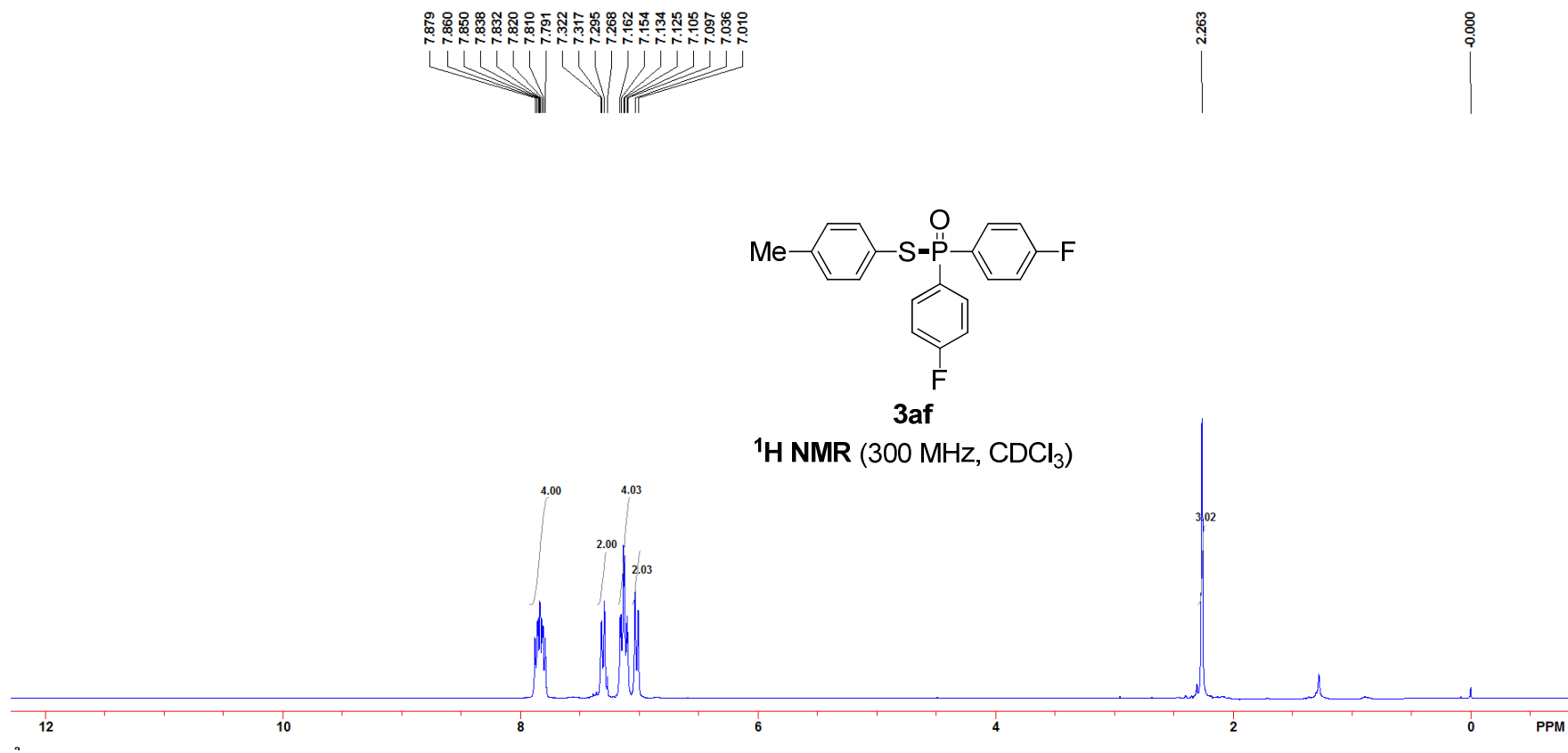


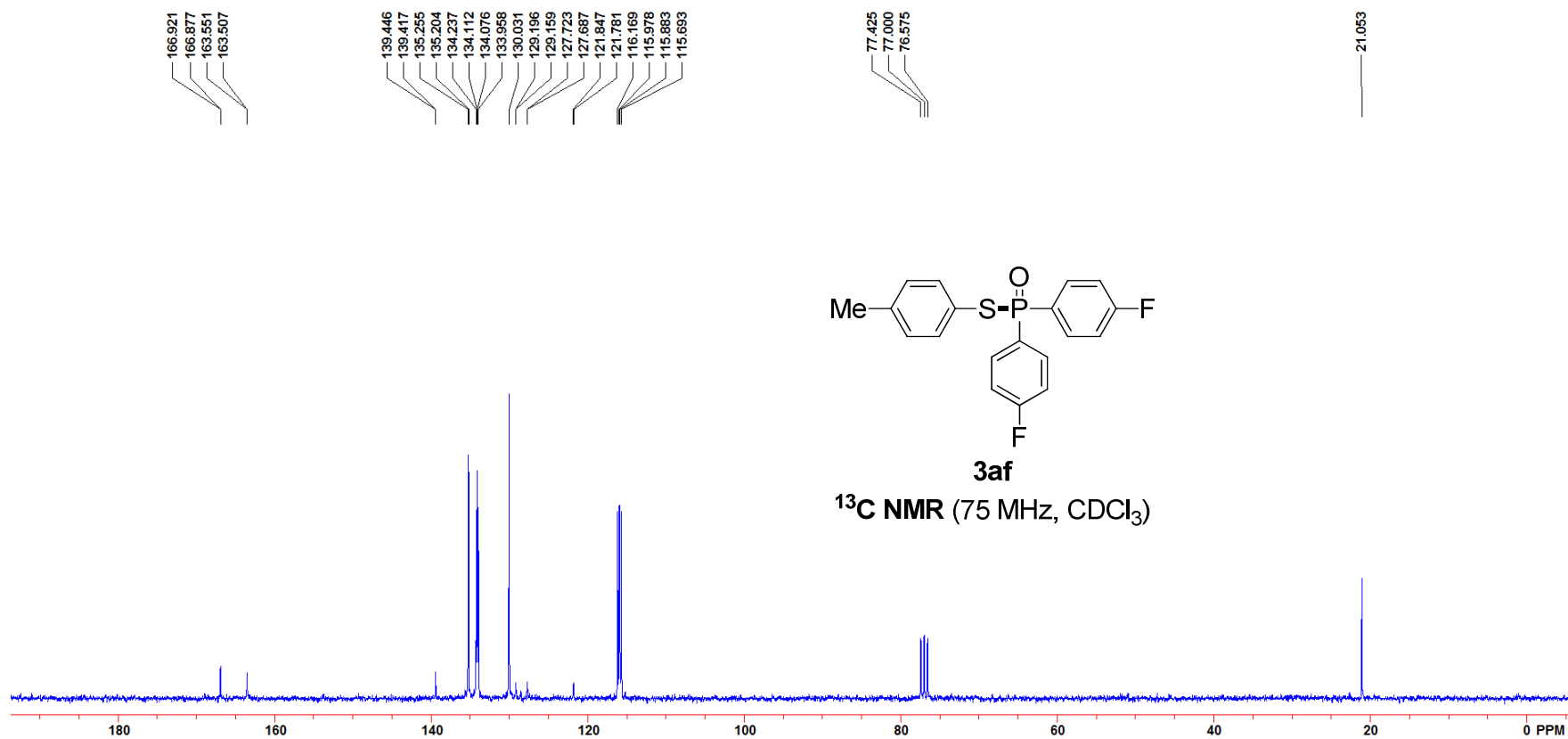


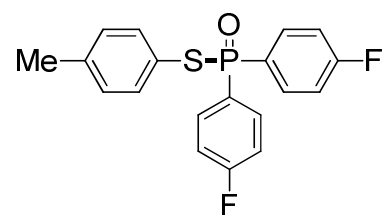


^{31}P NMR (121.5 MHz, CDCl_3)



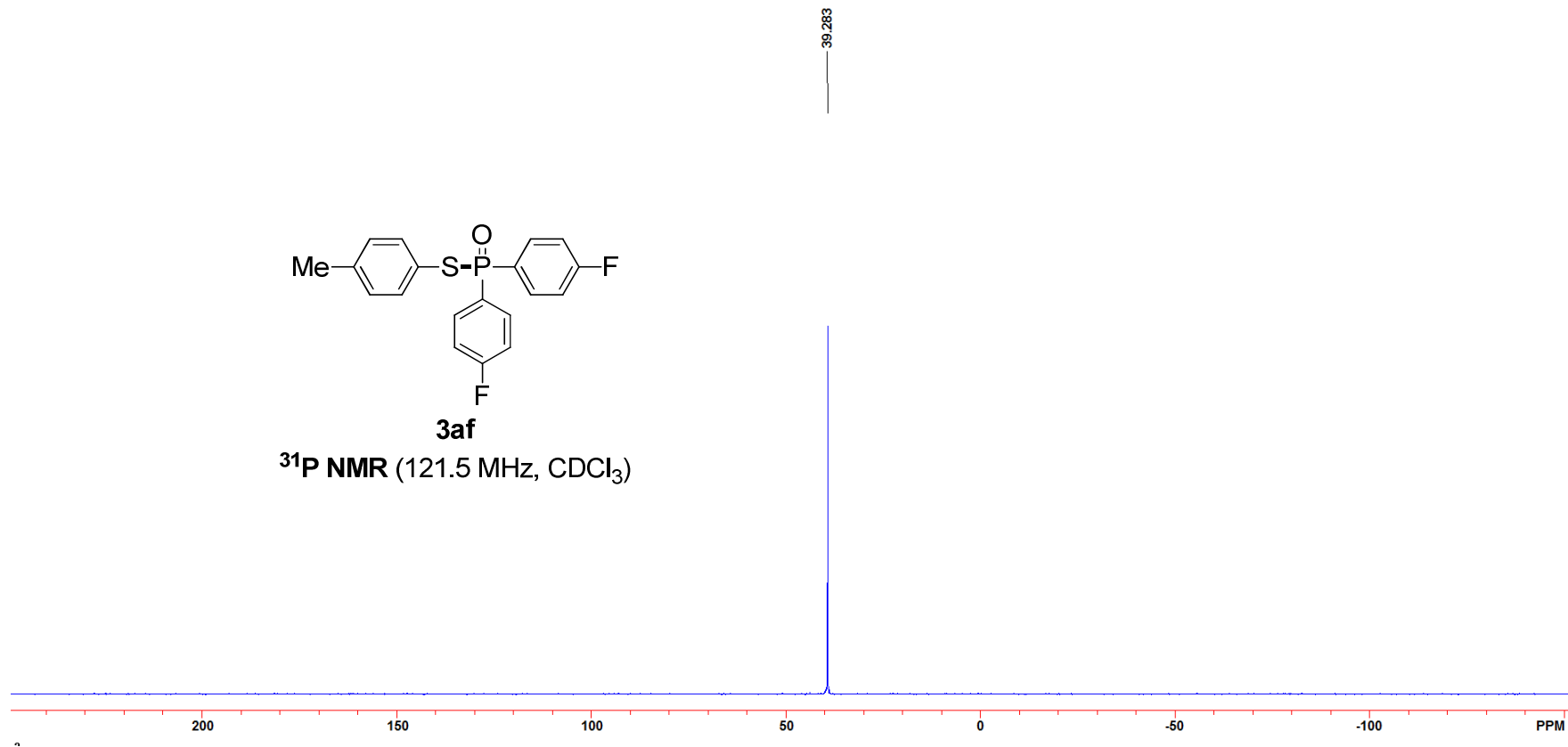






3af

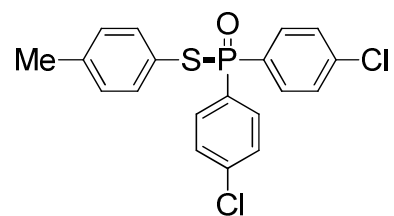
^{31}P NMR (121.5 MHz, CDCl_3)



7.789
7.761
7.748
7.720
7.436
7.428
7.409
7.400
7.320
7.297
7.267
7.042
7.016

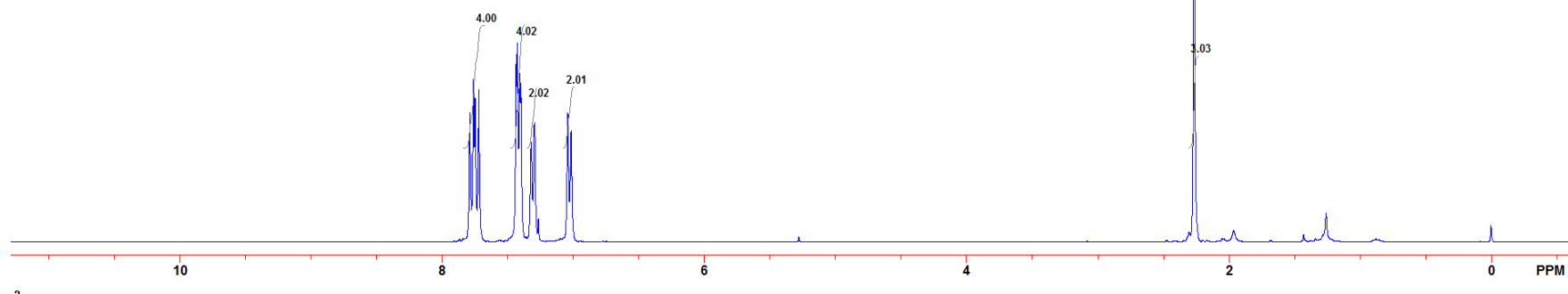
2.265

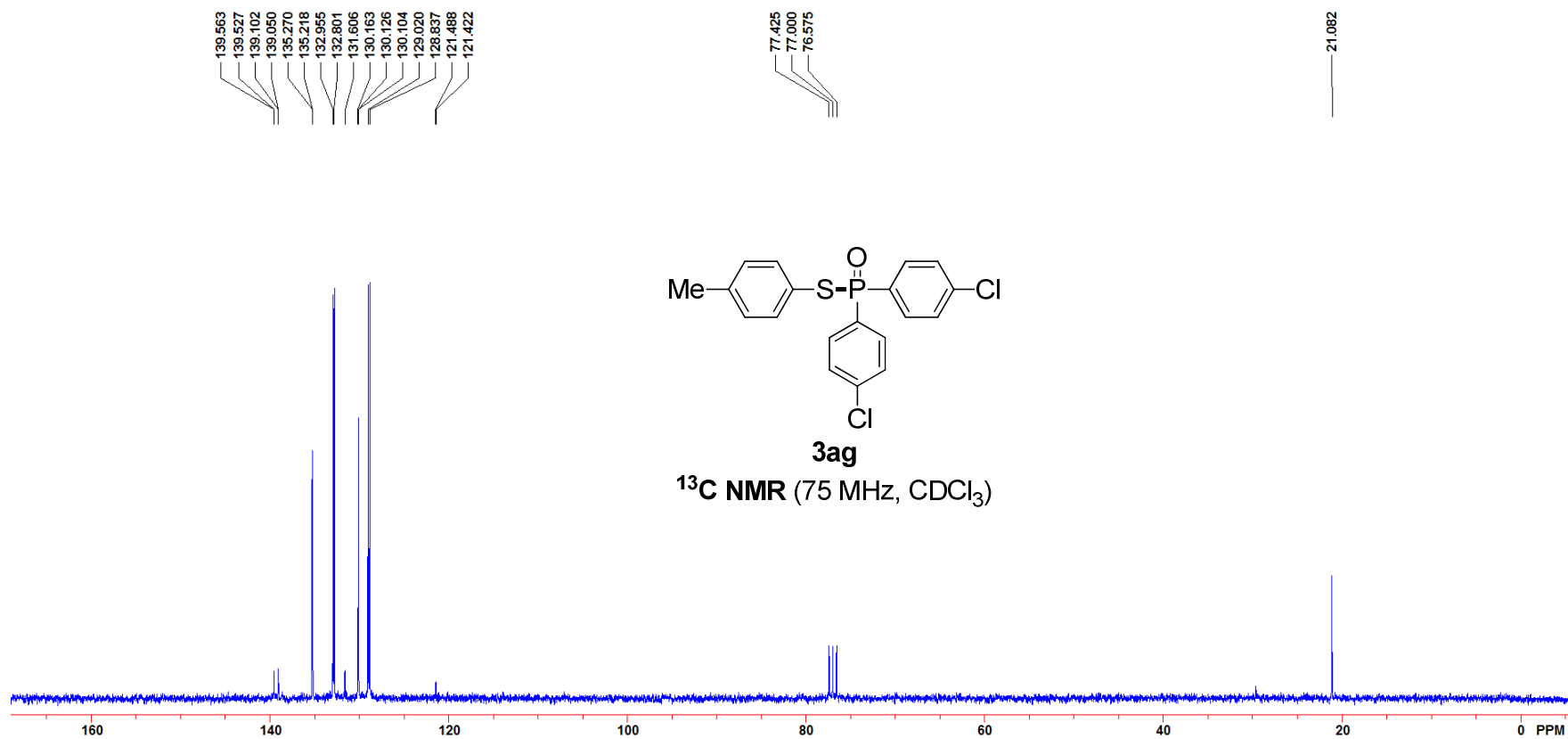
0.000

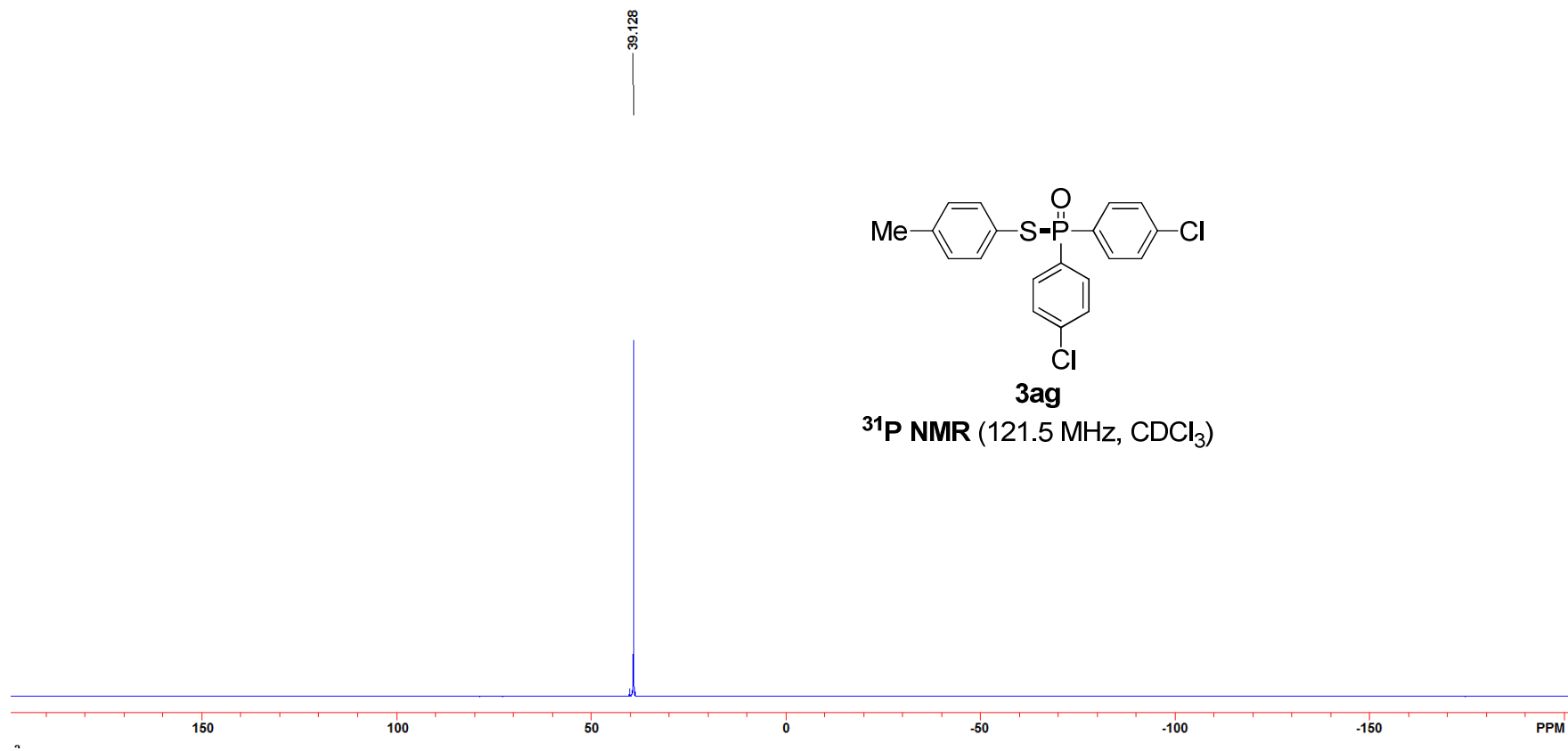


3ag

¹H NMR (300 MHz, CDCl₃)



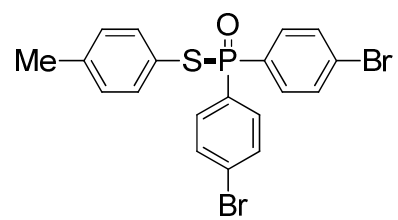




7.711
7.683
7.671
7.642
7.605
7.595
7.577
7.567
7.318
7.294
7.261
7.050
7.024

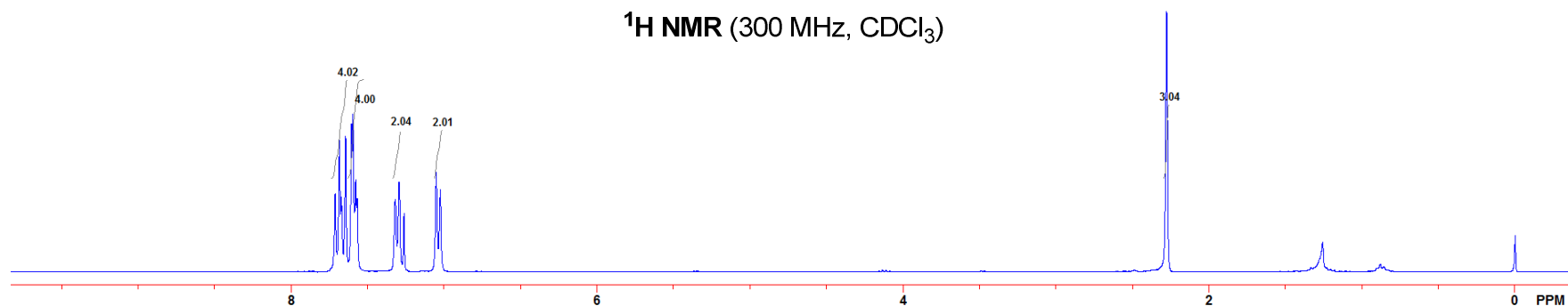
2.277

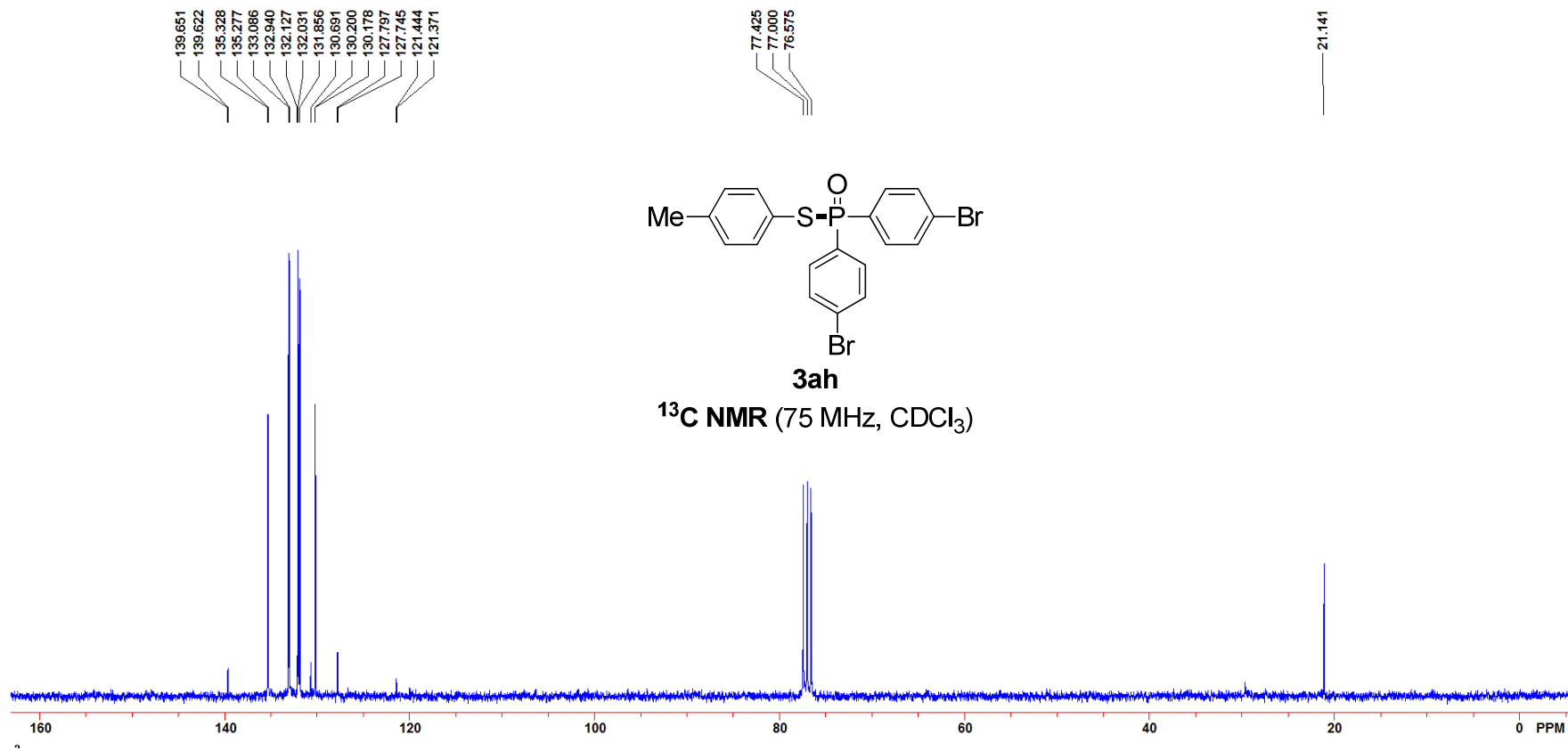
0.000

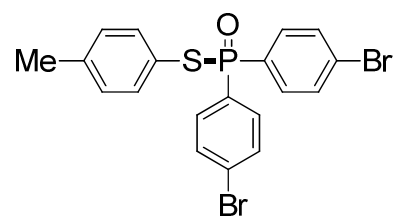


3ah

¹H NMR (300 MHz, CDCl₃)

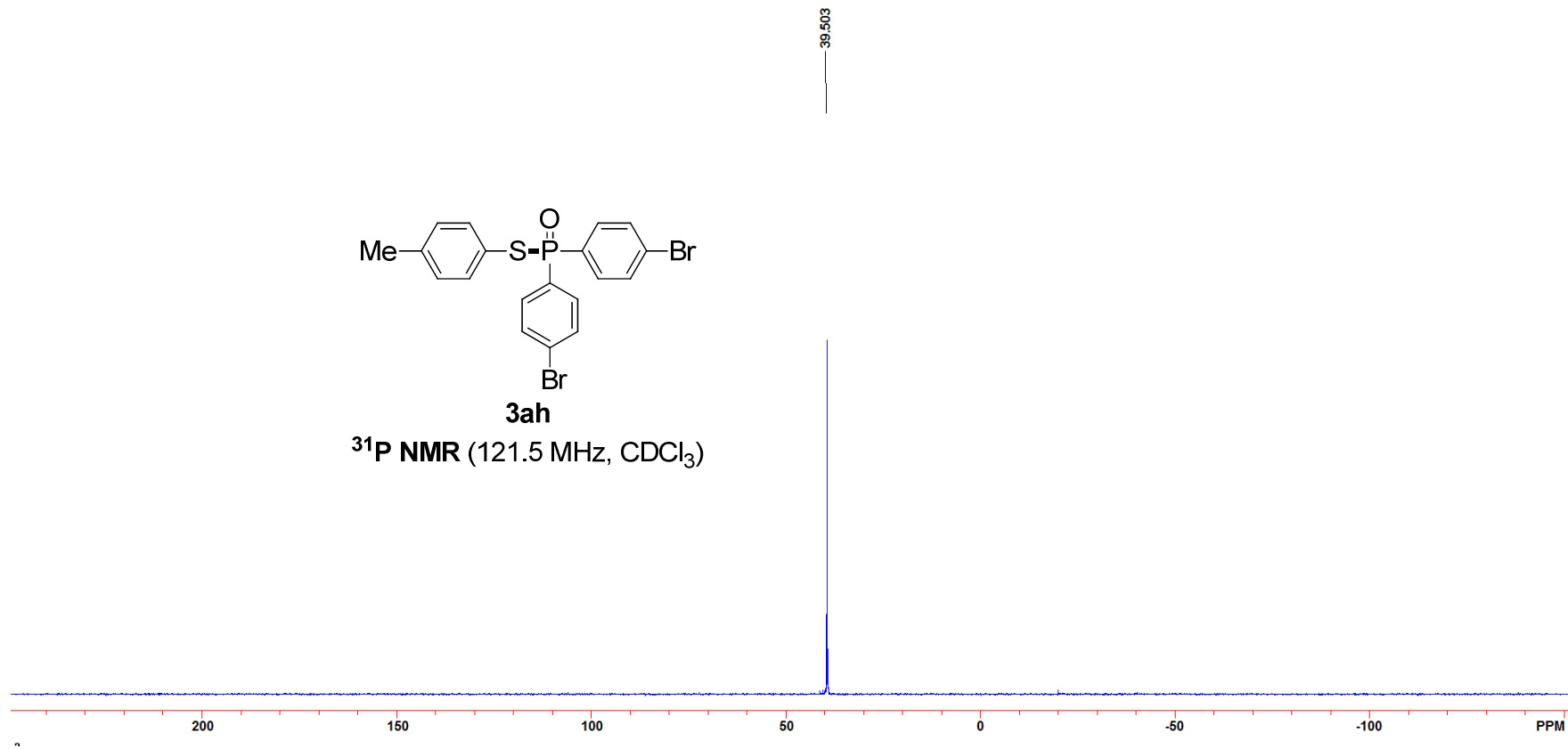






3ah

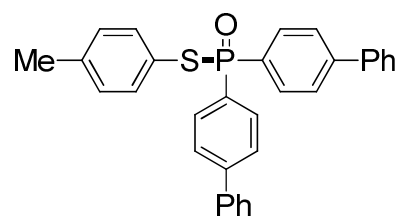
^{31}P NMR (121.5 MHz, CDCl_3)



7.981
7.954
7.940
7.912
7.887
7.877
7.859
7.850
7.599
7.576
7.469
7.446
7.421
7.396
7.372
7.240
7.033
7.007

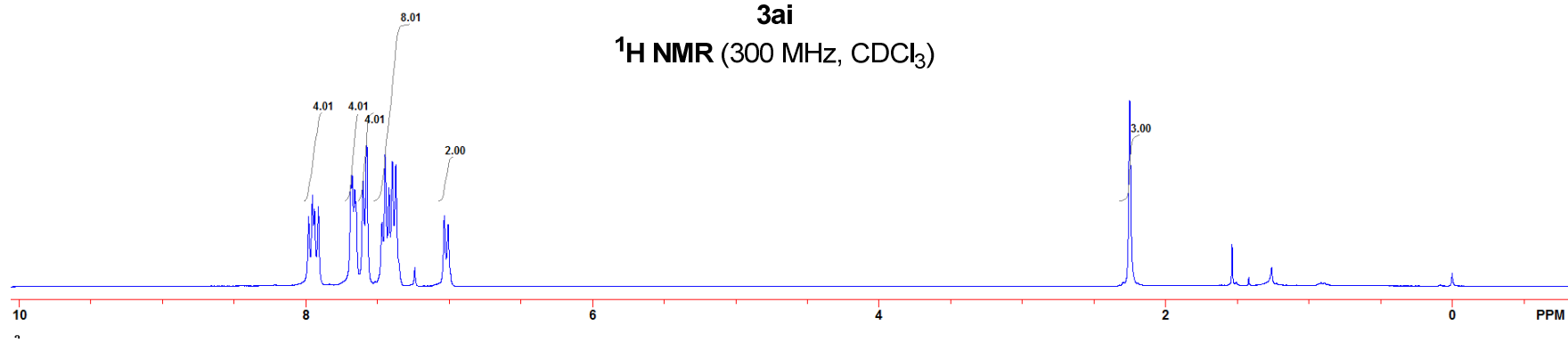
2.251

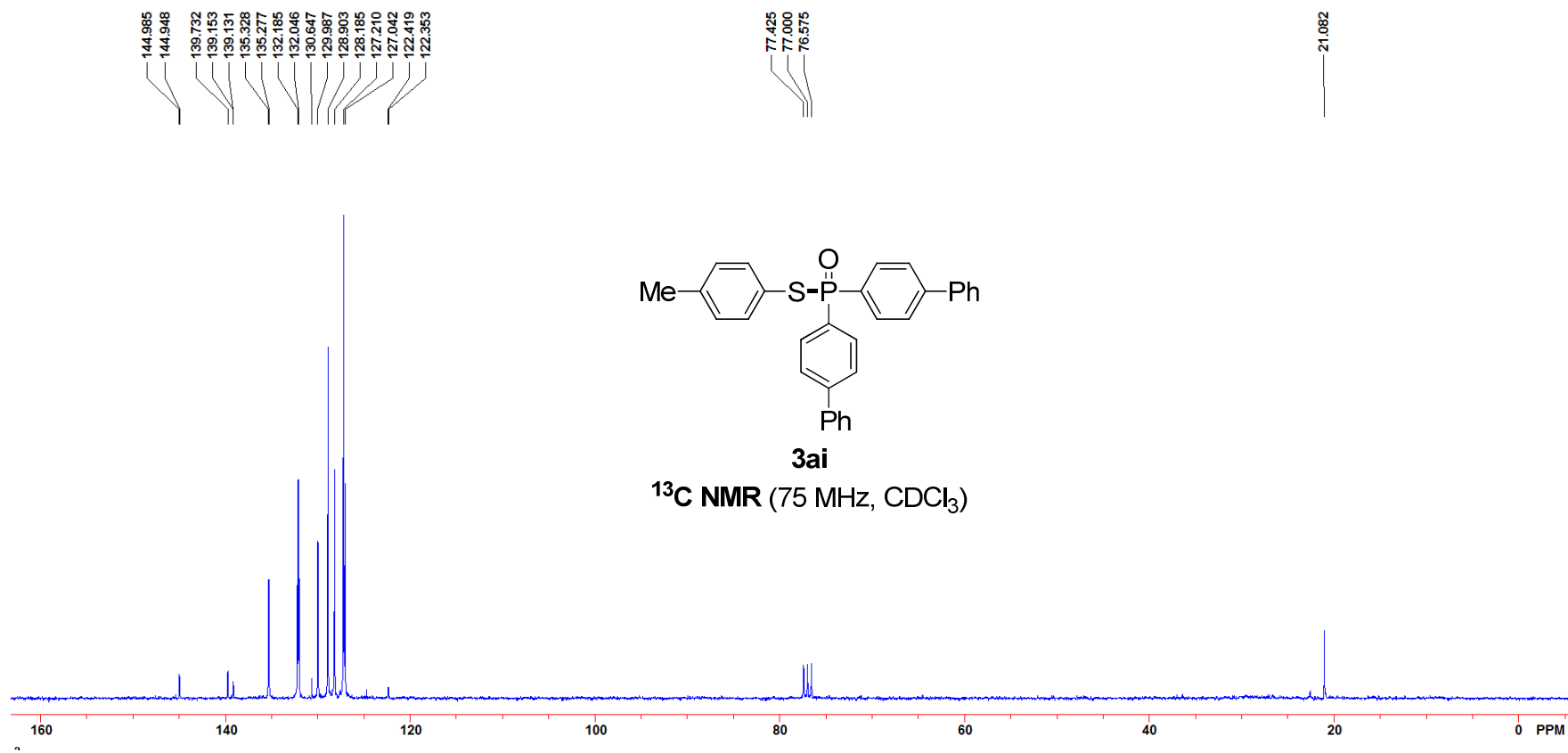
0.000

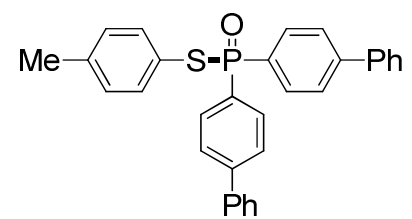


3ai

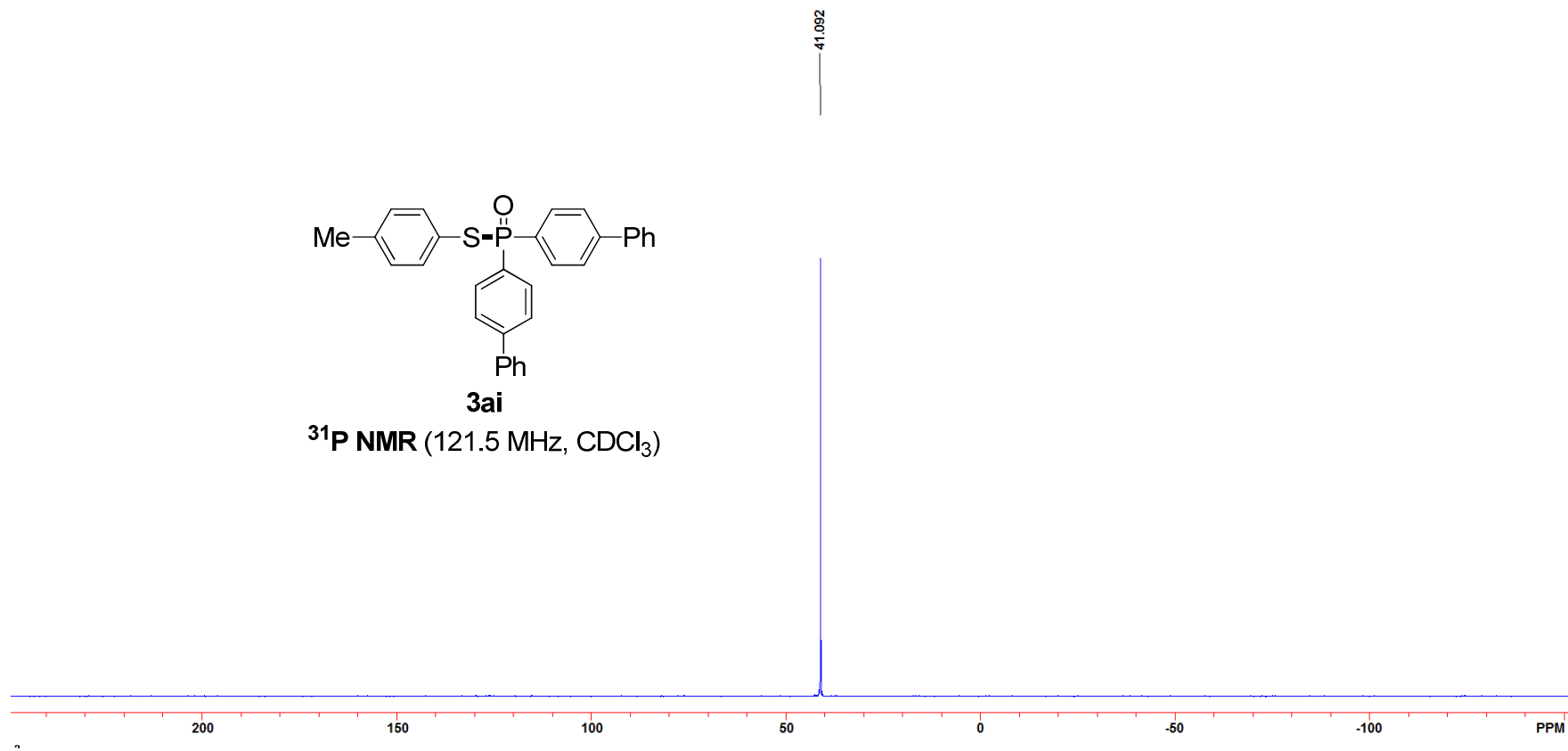
¹H NMR (300 MHz, CDCl₃)

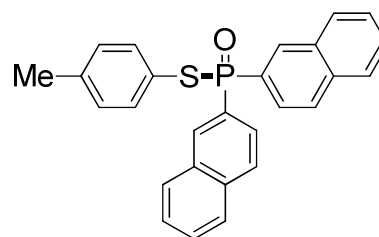
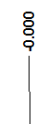
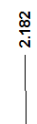
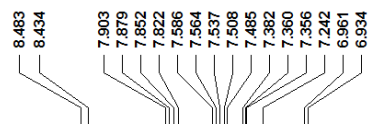






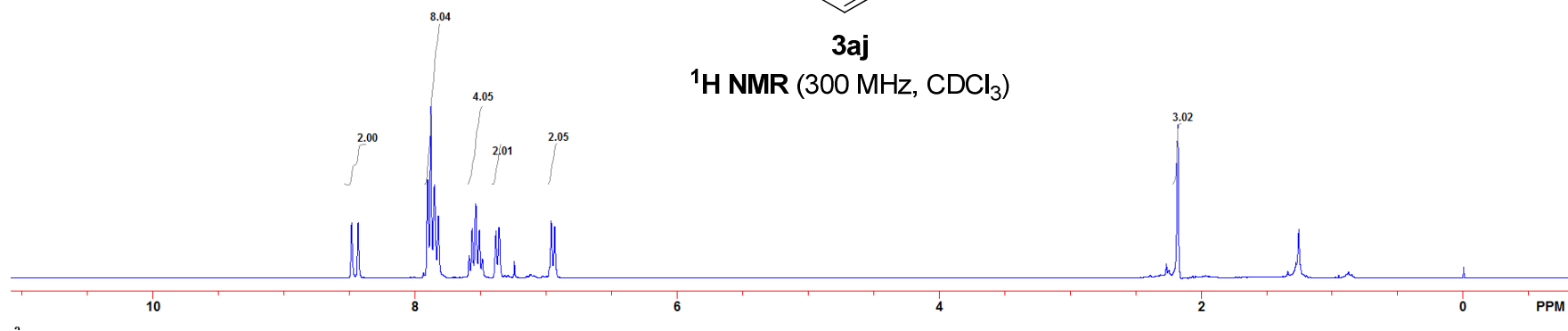
3ai
 ^{31}P NMR (121.5 MHz, CDCl_3)

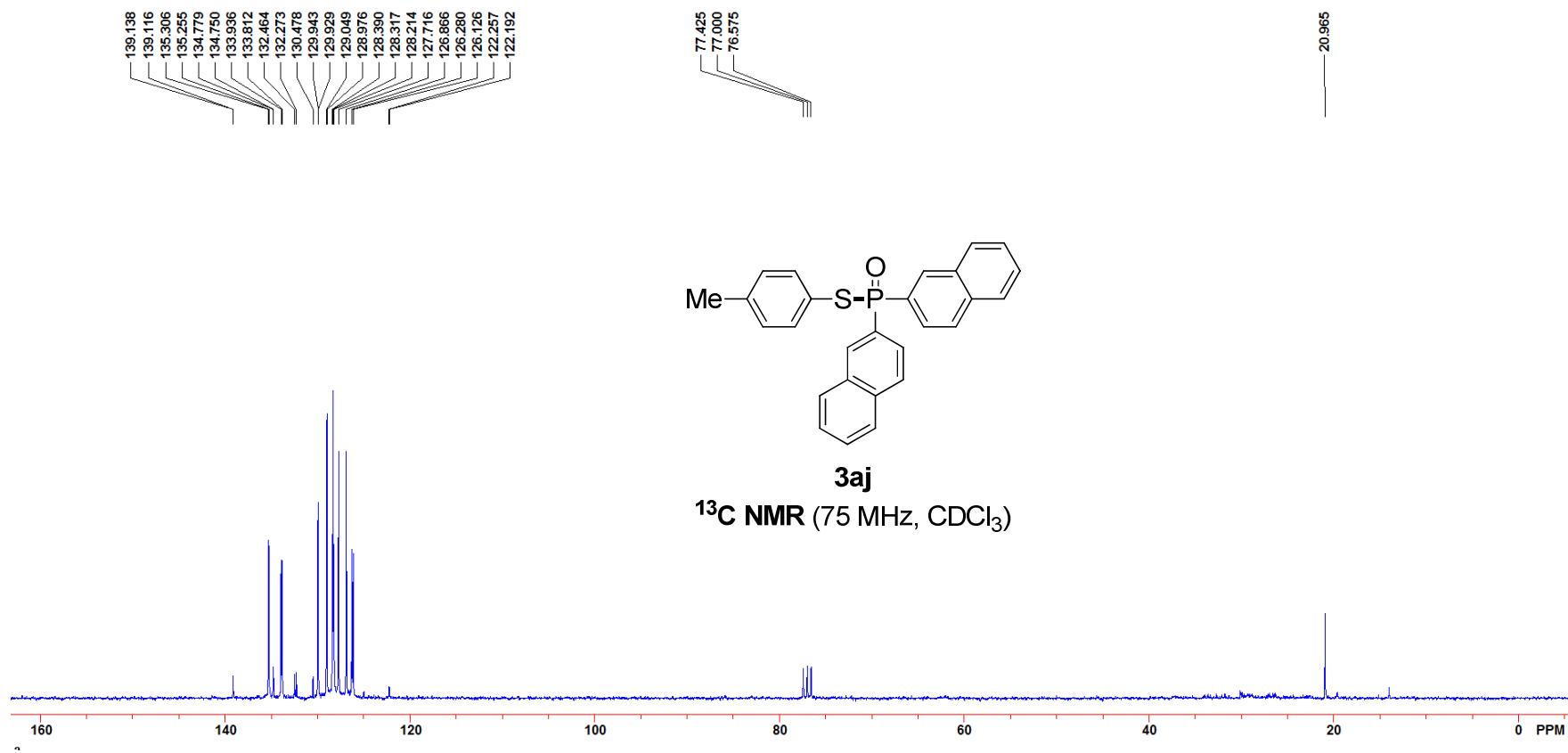


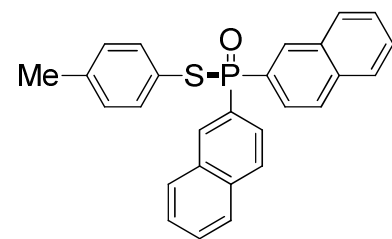


3aj

¹H NMR (300 MHz, CDCl₃)

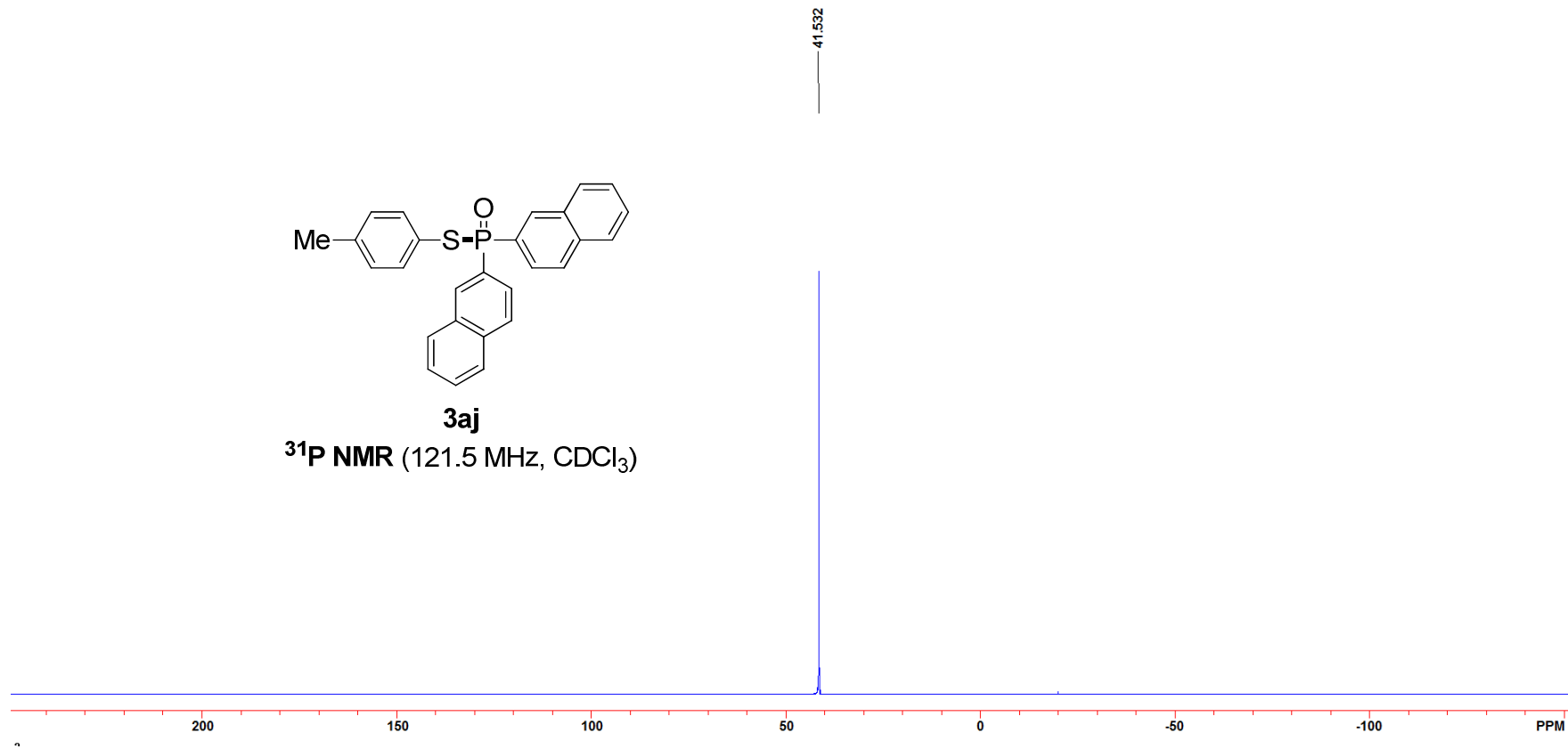


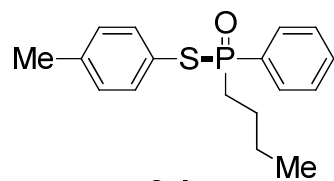
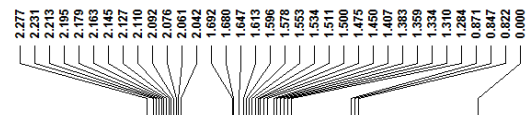
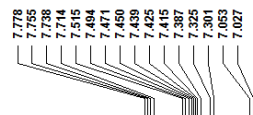




3aj

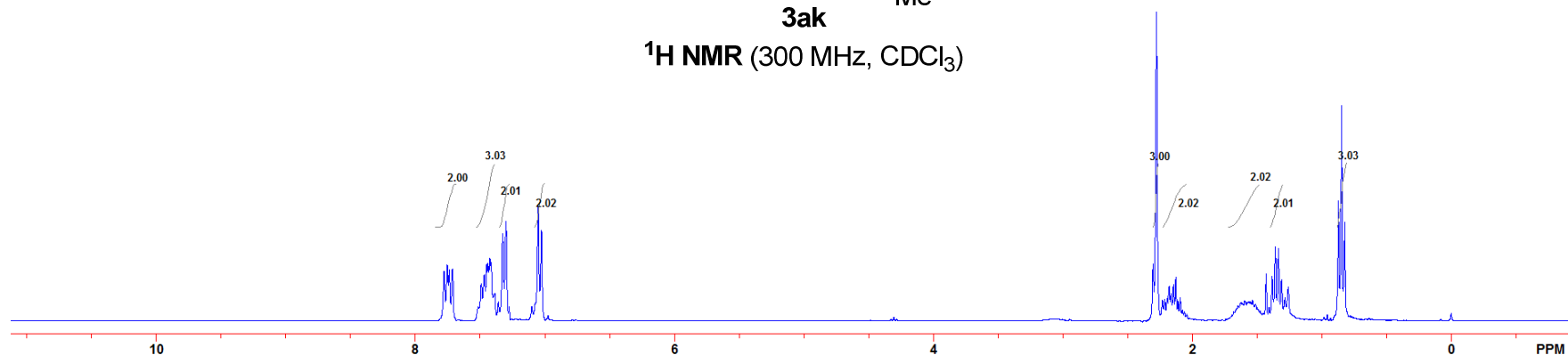
^{31}P NMR (121.5 MHz, CDCl_3)





3ak

¹H NMR (300 MHz, CDCl₃)



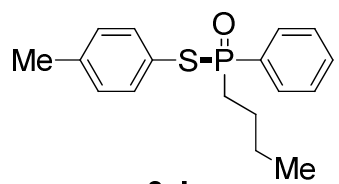
139.028
138.999
135.277
135.233
133.042
131.951
131.914
131.731
131.152
131.020
129.877
129.855
128.383
128.214
122.257
122.164

77.425
77.000
76.575

33.135
32.189

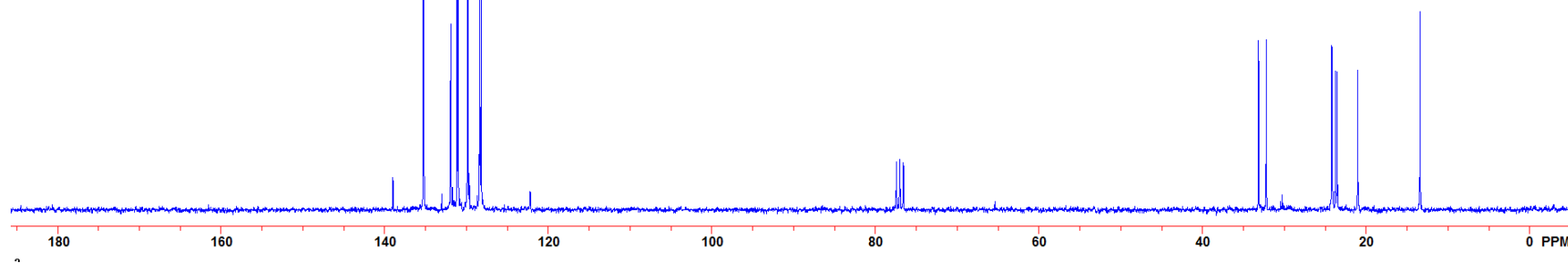
24.189
24.130
23.727
23.515
21.001

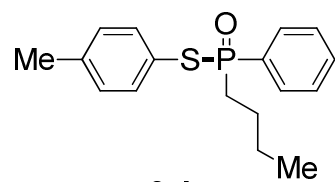
13.382



3ak

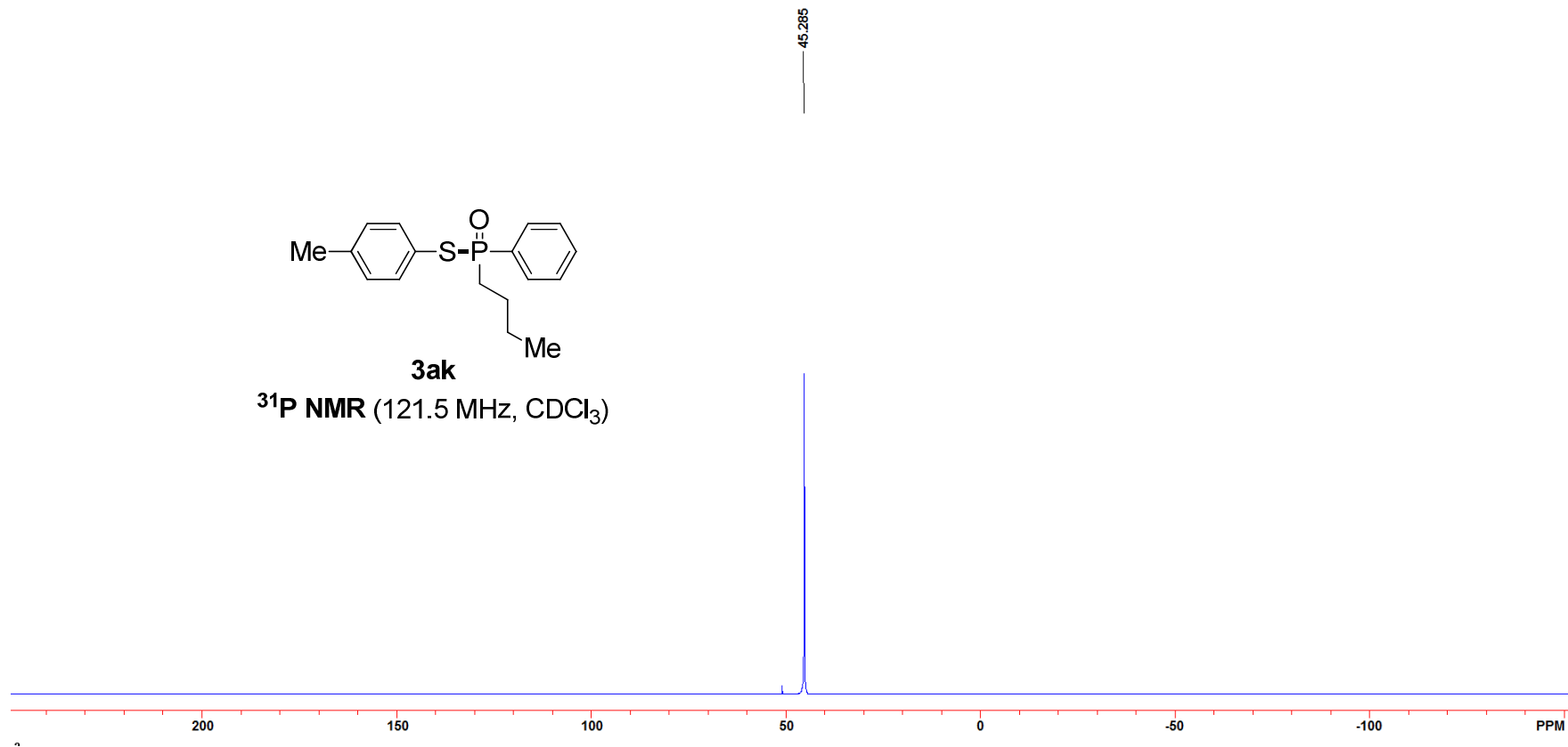
¹³C NMR (75 MHz, CDCl₃)





3ak

^{31}P NMR (121.5 MHz, CDCl_3)



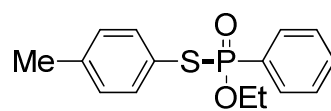
7.696
7.672
7.668
7.651
7.627
7.623
7.511
7.507
7.487
7.483
7.462
7.458
7.394
7.378
7.369
7.354
7.329
7.269
7.183
7.178
7.157
7.151
7.020
6.993

4.398
4.388
4.364
4.348
4.341
4.325
4.319
4.314
4.295
4.272
4.262

2.283

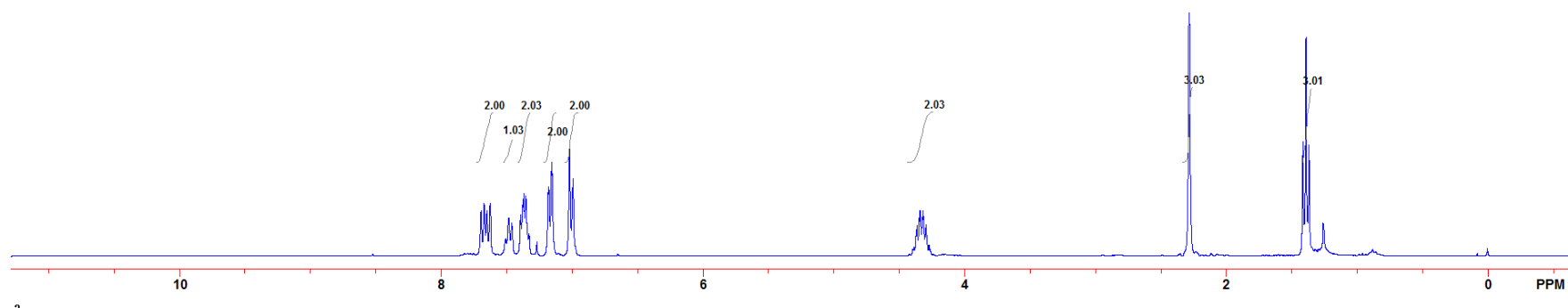
1.413
1.389
1.365

-0.000



3al

¹H NMR (300 MHz, CDCl₃)

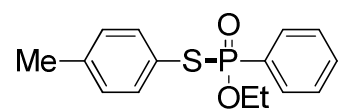


139.160
139.116
135.380
135.321
132.676
132.568
132.324
131.489
131.350
130.691
129.885
129.855
128.199
128.002
122.866
122.792

77.425
77.000
76.575

62.361
62.266

21.075
16.298
16.210



3al

¹³C NMR (75 MHz, CDCl₃)

