Supporting information

Eosin Y-Catalyzed, Visible-Light-Promoted Carbophosphinylation of Allylic Alcohols via Radical Neophyl Rearrangement

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General

All manipulations were conducted with a standard *Schlenk* tube under a nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Allylic alcohols **1a-l** were prepared according to a reported method.[1] The P(O)H compounds **2b-g** were prepared according to a reported method.[2] The P(O)H compound **2i** was prepared according to a reported method.[3]

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F_{254} plates.

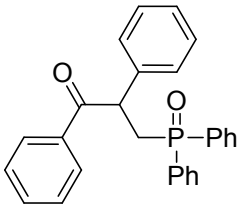
^{1}H NMR spectra were recorded on a *Bruker AV-300* spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{31}P NMR spectra were recorded on a *Bruker AV-300* spectrometer and using 85% H_3PO_4 as external standard. Data for ^{1}H 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 ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. Mass spectra were performed on an *Aglient 6530 Q-TOF* for HRMS. The yields were determined on a *METTLER TOLEDO ME 104* balance (accuracy: 0.1 mg).

General procedure for visible-light-promoted carbophosphinylation of allylic alcohols (GP)：

Allylic alcohol **1** (0.2 mmol, 1.0 equiv), P(O)H compound **2** (0.5 mmol, 2.5 equiv), and eosin Y (0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then DMA (2.0 mL) was added. The reaction mixture was stirred and irradiated by 12 W blue LEDs (450 nm) at room temperature for 24 h. After the reaction was completed monitored by TLC, H_2O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding product.

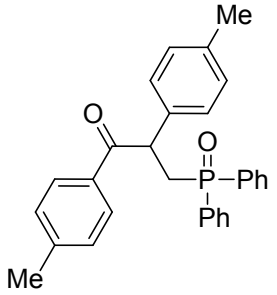
Physical data of the compounds

3-(Diphenylphosphoryl)-1,2-diphenylpropan-1-one (3aa)[4]



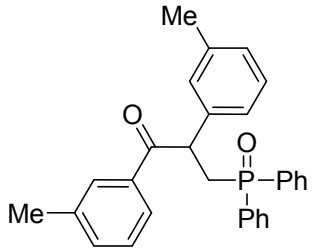
According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.1 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3aa** as white solid (62.0 mg, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89-7.81 (m, 2H), 7.72-7.66 (m, 2H), 7.63-7.57 (m, 2H), 7.39-7.22 (m, 11H), 7.11-7.00 (m, 3H), 5.35-5.27 (m, 1H), 3.54-3.43 (m, 1H), 2.82-2.71 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6 (d, *J* = 6.0 Hz), 138.3 (d, *J* = 7.1 Hz), 135.5, 133.2 (d, *J* = 40.1 Hz), 132.6, 131.8 (d, *J* = 40.1 Hz), 131.4 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 2.8 Hz), 130.4 (dd, *J* = 10.7, 9.6 Hz), 128.6 (d, *J* = 9.4 Hz), 128.2 (d, *J* =5.6 Hz), 128.1-128.0 (m), 127.0, 46.3 (d, *J* = 1.7 Hz), 33.6 (d, *J* = 70.4 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.28; **HRMS** (ESI) calculated for $C_{27}H_{24}O_2P$ $[M+H]^+$ m/z 411.1508, found 411.1510.

3-(Diphenylphosphoryl)-1,2-di-*p*-tolylpropan-1-one (3ba)[4]



According to **GP** with 1,1-di-*p*-tolylprop-2-en-1-ol **1b** (47.9 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.5 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.5 mg, 0.02 mmol, 0.1 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 (55.0 mg, 63%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.72-7.65 (m, 2H), 7.60-7.54 (m, 2H), 7.41-7.26 (m, 6H), 7.09 (d, *J* = 7.8 Hz, 4H), 6.87 (d, *J* = 7.8 Hz, 2H), 5.28-5.20 (m, 1H), 3.46-3.36 (m, 1H), 2.81-2.71 (m, 1H), 2.29 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.5 (d, *J* = 7.1 Hz), 143.7, 136.8, 135.6 (d, *J* = 7.1 Hz), 133.5 (d, *J* = 52.7 Hz), 133.1, 132.2 (d, *J* = 53.3 Hz), 131.3 (dd, *J* = 40.1, 2.7 Hz), 130.7 (dd, *J* = 9.3, 5.5 Hz), 129.5, 129.0 (d, *J* = 3.8 Hz), 128.4, 128.2 (dd, *J* = 11.6, 2.8 Hz), 46.0 (d, *J* = 1.7 Hz), 33.8 (d, *J* = 71.0 Hz), 21.5, 20.8; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.46; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1827.

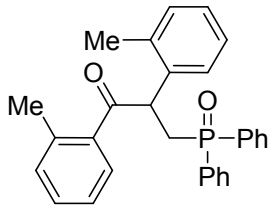
3-(Diphenylphosphoryl)-1,2-di-*m*-tolylpropan-1-one (3ca)



According to **GP** with 1,1-di-*m*-tolylprop-2-en-1-ol **1c** (47.8 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.8 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.6 mg, 0.02 mmol, 0.1 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 colourless oil (62.0 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72-7.56 (m, 6H), 7.37-7.27 (m, 6H), 7.20-7.12 (m, 2H), 7.06-6.95 (m, 3H), 6.81 (d, *J* = 7.2 Hz,

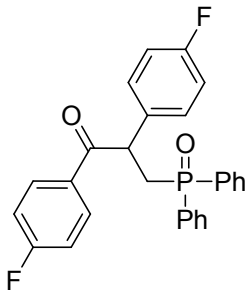
1H), 5.32-5.24 (m, 1H), 3.48-3.37 (m, 1H), 2.84-2.74 (m, 1H), 2.25 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.9 (d, J = 7.1 Hz), 138.2, 138.24, 138.21 (d, J = 7.1 Hz), 135.5, 133.5, 133.4 (d, J = 54.5 Hz), 132.0 (d, J = 53.9 Hz), 131.1 (dd, J = 22.0, 2.8 Hz), 130.4 (dd, J = 11.0, 9.3 Hz), 128.9 (d, J = 23.1 Hz), 128.4 (d, J = 23.6 Hz), 128.0 (d, J = 5.0 Hz), 129.9 (d, J = 6.1 Hz), 127.8, 125.8, 125.0, 46.3 (d, J = 1.7 Hz), 33.6 (d, J = 70.4 Hz), 21.0; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.32; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1823.

3-(Diphenylphosphoryl)-1,2-di-*o*-tolylpropan-1-one (3da)



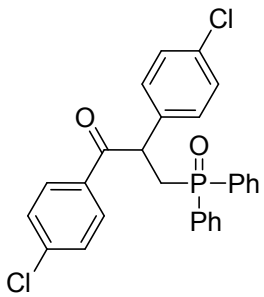
According to **GP** with 1,1-di-*o*-tolylprop-2-en-1-ol **1d** (47.7 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.5 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.8 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3da** as colourless oil (67.0 mg, 76%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.65-7.58 (m, 2H), 7.45-7.38 (m, 5H), 7.33-7.26 (m, 2H), 7.22-7.08 (m, 3H), 7.06-6.94 (m, 3H), 6.89 (d, *J* = 7.2 Hz, 1H), 5.29-5.21 (m, 1H), 3.67-3.56 (m, 1H), 2.69-2.59 (m, 1H), 2.13 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.8 (d, J = 6.6 Hz), 138.4, 137.4, 136.3, 136.0 (d, J = 7.7 Hz), 133.6 (d, J = 45.1 Hz), 132.3 (d, J = 44.6 Hz), 131.7 (d, J = 2.7 Hz), 131.4 (d, J = 2.2 Hz), 130.8 (dd, J = 23.1, 15.4 Hz), 130.6 (d, J = 2.2 Hz), 130.4, 128.4 (dd, J = 18.4, 11.8 Hz), 127.4, 127.3, 126.2, 125.2, 45.3 (d, J = 1.1 Hz), 32.8 (d, J = 70.3 Hz), 20.0, 19.6; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.35; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1824.

3-(Diphenylphosphoryl)-1,2-bis(4-fluorophenyl)propan-1-one (3ea)[4]



According to **GP** with 1,1-bis(4-fluorophenyl)prop-2-en-1-ol **1e** (49.5 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.5 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 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 (44.5 mg, 50%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.72-7.65 (m, 2H), 7.60-7.54 (m, 2H), 7.46-7.28 (m, 6H), 7.20-7.16 (m, 2H), 7.03-6.97 (m, 2H), 6.80-6.74 (m, 2H), 5.30-5.22 (m, 1H), 3.41-3.31 (m, 1H), 2.84-2.73 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.3 (d, J = 7.7 Hz), 165.5 (d, J = 253.9 Hz), 161.8 (d, J = 245.0 Hz), 133.8 (dd, J = 6.6, 3.3 Hz), 133.7, 132.6 (d, J = 36.8 Hz), 131.7 (dd, J = 7.1, 2.8 Hz), 131.44 (d, J = 18.2 Hz), 131.42 (d, J = 9.9 Hz), 130.5 (dd, J = 9.6, 5.8 Hz), 139.9 (d, J = 8.3 Hz), 128.4 (dd, J = 14.7, 11.5 Hz), 115.6 (dd, J = 21.7, 16.8 Hz), 45.7 (d, J = 1.7 Hz), 33.8 (d, J = 70.4 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 29.91; **HRMS** (ESI) calculated for $C_{27}H_{22}F_2O_2P$ $[M+H]^+$ m/z 447.1320, found 447.1323.

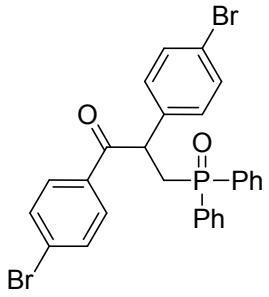
1,2-Bis(4-chlorophenyl)-3-(diphenylphosphoryl)propan-1-one (3fa)[4]



According to **GP** with 1,1-bis(4-chlorophenyl)prop-2-en-1-ol **1f** (55.9 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.4 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 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 (70.0 mg, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 (d, J

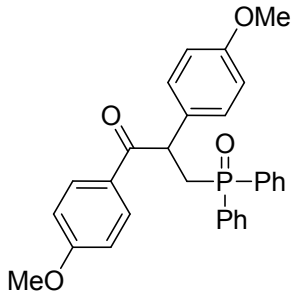
= 8.1 Hz, 2H), 7.73-7.66 (m, 2H), 7.60-7.53 (m, 2H), 7.39-7.27 (m, 8H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 5.28-5.21 (m, 1H), 3.42-3.31 (m, 1H), 2.84-2.74 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.3 (d, *J* = 7.7 Hz), 139.5, 136.3 (d, *J* = 6.6 Hz), 133.4 (d, *J* = 19.2 Hz), 132.4 (d, *J* = 29.6 Hz), 131.6 (d, *J* = 2.7 Hz), 131.3, 131.2 (d, *J* = 3.3 Hz), 130.4 (dd, *J* = 9.4, 3.3 Hz), 130.0, 129.6, 128.8 (d, *J* = 20.3 Hz), 128.3 (dd, *J* = 15.7, 11.8 Hz), 45.9 (d, *J* = 1.7 Hz), 33.5 (d, *J* = 70.3 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 29.81; **HRMS** (ESI) calculated for $C_{27}H_{22}Cl_2O_2P$ $[M+H]^+$ m/z 479.0729, found 479.0732.

1,2-Bis(4-bromophenyl)-3-(diphenylphosphoryl)propan-1-one (3ga)[4]



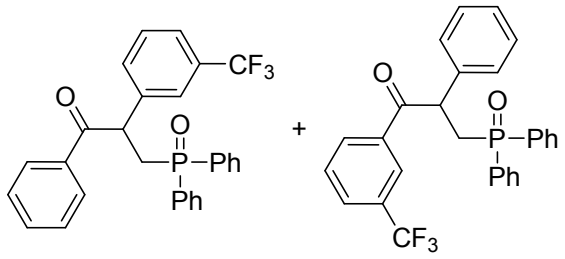
According to **GP** with 1,1-bis(4-bromophenyl)prop-2-en-1-ol **1g** (73.8 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.3 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.5 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ga** as white solid (56.7 mg, 50%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72-7.66 (m, 4H), 7.58-7.52 (m, 2H), 7.47-7.30 (m, 8H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.25-5.18 (m, 1H), 3.40-3.29 (m, 1H), 2.83-2.72 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.6 (d, J = 8.3 Hz), 136.8 (d, J = 6.5 H), 134.0, 133.1 (d, J = 74.2 H), 131.8 (d, J = 73.6 H), 132.3, 131.7, 131.3 (d, J = 2.8 Hz), 130.5 (dd, J = 9.6, 3.0 Hz), 130.2, 130.0, 128.4, 128.3 (dd, J = 12.4, 10.2 Hz), 121.6, 46.0 (d, J = 1.7 Hz), 33.5 (d, J = 70.3 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 29.57; **HRMS** (ESI) calculated for $C_{27}H_{22}Br_2O_2P$ $[M+H]^+$ m/z 566.9719, found 566.9727.

3-(Diphenylphosphoryl)-1,2-bis(4-methoxyphenyl)propan-1-one (3ha)[4]



According to **GP** with 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol **1h** (55.0 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.0 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 2/1) to afford the desired product **3ha** as white solid (57.8 mg, 61%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.71-7.65 (m, 2H), 7.60-7.54 (m, 2H), 7.43-7.27 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.25-5.17 (m, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.41-3.30 (m, 1H), 2.83-2.73 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.5 (d, *J* = 7.1 Hz), 163.2, 158.5, 131.5 (d, *J* = 2.2 Hz), 131.1, 131.0 (d, *J* = 2.2 Hz), 130.8, 130.6 (dd, *J* = 9.3, 3.8 Hz), 129.3, 128.5, 128.2 (dd, *J* = 13.2, 11.6 Hz), 114.1, 113.5, 55.3, 55.0, 45.3 (d, *J* = 1.7 Hz), 33.7 (d, *J* = 71.0 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.45; **HRMS** (ESI) calculated for $C_{29}H_{28}O_4P$ $[M+H]^+$ m/z 471.1720, found 471.1726.

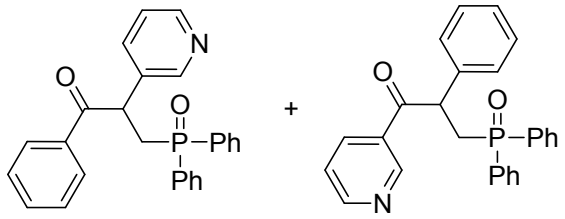
3-(Diphenylphosphoryl)-1-phenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (3ia) and 3-(diphenylphosphoryl)-2-phenyl-1-(3-(trifluoromethyl)phenyl)propan-1-one (3ia') [4]



According to **GP** with 1-phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol **1i** (56.0 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.4 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.5 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to

afford the desired product **3ia**+**3ia'** as colourless oil (55.0 mg, 57%, **3ia**/**3ia'** = 2.5:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ **3ia**: 7.89 (d, *J* = 7.5 Hz, 2H), 7.73-7.05 (m, 17H), 5.49-5.41 (m, 1H), 3.44-3.31 (m, 1H), 2.94-2.84 (m, 1H); **3ia'**: 8.07 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.73-7.05 (m, 17H), 5.33-5.25 (m, 1H), 3.59-3.48 (m, 1H), 2.82-2.74 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) **3ia**+**3ia'** CF_3-signal could not be assigned δ 197.3 (d, *J* = 8.8 Hz), 196.4 (d, *J* = 6.0 Hz), 138.8 (d, *J* = 6.0 Hz), 137.7 (d, *J* = 8.3 Hz), 136.0, 135.0, 133.5, 133.1, 132.3 (d, *J* = 12.7 Hz), 131.9, 131.7, 131.3 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.8 Hz), 130.6, 130.5 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 2.8 Hz), 130.3 (d, *J* = 4.4 Hz), 129.2, 128.9, 128.6, 128.4, 128.3, 128.2 (d, *J* = 2.7 Hz), 128.0 (d, *J* = 3.9 Hz), 127.4, 125.3 (d, *J* = 3.7 Hz), 125.3, 124.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 3.6 Hz), 121.6, 46.7 (d, *J* = 1.7 Hz), 46.0 (d, *J* = 1.7 Hz), 33.7 (d, *J* = 69.8 Hz), 33.5 (d, *J* = 70.4 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) **3ia**+**3ia'** δ 30.07, 29.62; **HRMS** (ESI) calculated for $C_{28}H_{23}F_3O_2P$ $[M+H]^+$ m/z 479.1382, found 479.1385.

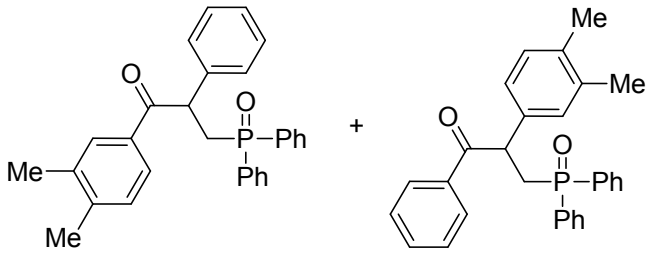
3-(Diphenylphosphoryl)-1-phenyl-2-(pyridin-3-yl)propan-1-one (3ja) and 3-(diphenylphosphoryl)-2-phenyl-1-(pyridin-3-yl)propan-1-one (3ja') [4]



According to **GP** with 1-phenyl-1-(pyridin-3-yl)prop-2-en-1-ol **1j** (42.5 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.5 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (dichloromethane/MeOH = 100/1) to afford the desired product **3ja**+**3ja'** as white solid (58.0 mg, 70%, **3ja**/**3ja'** = 2.9:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ **3ja**: 8.52 (s, 1H), 8.28 (d, *J* = 4.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.74-7.67 (m, 3H), 7.69-7.29 (m, 9H), 7.25-7.21 (m, 1H), 7.17-7.09 (m, 1H), 7.00-6.96 (m, 1H), 5.40-5.33 (m, 1H), 3.46-3.35 (m, 1H), 2.89-2.79 (m, 1H); **3ja'**: 9.02 (s, 1H), 8.63 (d, *J* = 3.9 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.69-7.29 (m, 15H), 7.17-7.09 (m, 1H), 5.26-5.17 (m, 1H), 3.59-3.49 (m, 1H), 2.75-2.70 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) **3ja**+**3ja'** δ 197.3 (d, *J* = 7.7 Hz), 153.1, 150.0, 149.8, 148.6, 136.0, 135.6, 135.0, 134.0 (d, *J* = 6.6 Hz), 133.4, 132.6, 132.1, 131.8 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 2.8 Hz), 130.8, 130.5 (dd, *J* = 9.3, 5.5 Hz), 130.6 (d, *J* = 9.4 Hz), 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 123.5, 123.2, 43.9 (d, *J* = 1.7 Hz), 33.5 (d, *J*

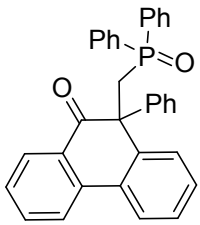
= 69.8 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) **3ja**+**3ja'** δ 30.10, 29.62; **HRMS** (ESI) calculated for $C_{26}H_{22}NO_2PNa$ $[M+Na]^+$ m/z 434.1280, found 434.1281.

1-(3,4-Dimethylphenyl)-3-(diphenylphosphoryl)-2-phenylpropan-1-one (3ka) and 2-(3,4-dimethylphenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3ka') [4]



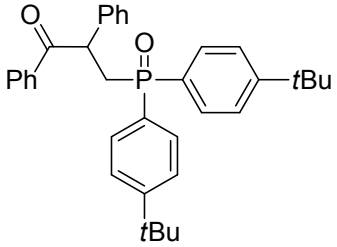
According to **GP** with 1-(3,4-dimethylphenyl)-1-phenylprop-2-en-1-ol **1k** (48.0 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.4 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ka**+**3ka'** as white solid (60.0 mg, 68%, **3ka/3ka'** = 3.3:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ **3ka**: 7.86-7.85 (m, 1H), 7.72-7.66 (m, 2H), 7.62-7.55 (m, 3H), 7.41-7.22 (m, 9H), 7.09-6.95 (m, 3H), 5.34-5.26 (m, 1H), 3.50-3.39 (m, 1H), 2.84-2.73 (m, 1H), 2.17 (s, 6H); **3ka'**: 7.72-7.66 (m, 2H), 7.62-7.55 (m, 3H), 7.41-7.22 (m, 9H), 7.09-6.95 (m, 3H), 6.84 (d, *J* = 7.5 Hz, 1H), 5.26–5.20 (m, 1H), 3.41–3.34 (m, 1H), 2.84-2.73 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ **3ka**+**3ka'** δ 197.8 (d, *J* = 7.1 Hz), 197.6 (d, *J* = 7.1 Hz), 142.4, 138.7 (d, *J* = 6.6 Hz), 136.9, 136.5, 135.62 (d, *J* = 7.2 Hz), 135.55 (d, *J* = 8.8 Hz), 133.8, 133.4, 133.1 (d, *J* = 2.8 Hz), 132.7, 132.5, 131.4 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 130.7, 130.6 (d, *J* = 9.4 Hz), 130.5, 130.4, 129.8, 129.44, 129.42, 128.7, 128.4, 128.22, 128.20, 128.16, 128.1, 128.0, 127.9 (d, *J* = 11.6 Hz), 127.0, 126.5, 125.5, 46.2 (d, *J* = 1.7 Hz), 46.1 (d, *J* = 2.2 Hz), 33.8 (d, *J* = 70.4 Hz), 33.6 (d, *J* = 70.3 Hz), 19.8, 19.54, 19.49, 19.1; **^{31}P NMR** (121.5 MHz, $CDCl_3$) **3ka**+**3ka'** δ 30.4, 30.3; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1827.

10-((Diphenylphosphoryl)methyl)-10-phenylphenanthren-9(10*H*)-one (3la)



According to **GP** with 9-(1-phenylvinyl)-9*H*-fluoren-9-ol **1l** (57.1 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 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 (40.1 mg, 41%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.02-7.97 (m, 3H), 7.61-7.51 (m, 5H), 7.45-7.40 (m, 1H), 7.36-7.20 (m, 7H), 7.11-7.08 (m, 5H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.61-4.53 (m, 1H), 3.45-3.37 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.7 (d, *J* = 1.1 Hz), 142.7, 142.5, 138.8 (d, *J* = 2.8 Hz), 136.9, 134.4 (d, *J* = 7.7 Hz), 134.2, 133.1 (d, *J* = 8.3 Hz), 131.2 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 9.3 Hz), 130.8, 130.6 (d, *J* = 7.1 Hz), 128.5, 128.4 (d, *J* = 7.1 Hz), 128.2, 128.1 (d, *J* = 2.3 Hz), 128.0, 127.7, 127.2, 127.0, 123.4, 122.9, 56.3 (d, *J* = 2.7 Hz), 40.5 (d, *J* = 69.2 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 26.66; **HRMS** (ESI) calculated for $C_{33}H_{26}O_2P$ $[M+H]^+$ m/z 485.1665, found 485.1668.

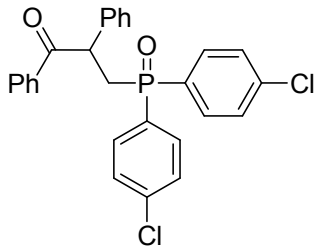
3-(Bis(4-(*tert*-butyl)phenyl)phosphoryl)-1,2-diphenylpropan-1-one (3ab)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.3 mg, 0.2 mmol, 1.0 equiv), bis(4-(*tert*-butyl)phenyl)phosphine oxide **2b** (151.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 4/1) to afford the desired product **3ab** as white solid (80.1 mg, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.66-7.50 (m, 4H), 7.41-7.21 (m, 9H), 7.09-6.98 (m, 3H), 5.34-5.26 (m, 1H), 3.49-3.38 (m, 1H), 2.82-2.70 (m, 1H), 1.27 (s, 9H), 1.23 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.9 (d, *J* = 6.6 Hz), 154.8 (d, *J* = 2.8 Hz), 154.4 (d, *J* = 2.8 Hz), 138.5 (d, *J* = 7.2 Hz), 135.6, 132.7, 130.5 (dd, *J* = 16.2, 9.7 Hz), 130.0 (d, *J*

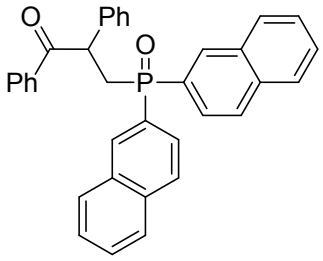
= 43.4 Hz), 128.7 (d, *J* = 44.0 Hz), 128.7, 128.2 (d, *J* = 7.2 Hz), 127.0, 124.7 (dd, *J* = 11.6, 7.1 Hz), 46.3 (d, *J* = 1.1 Hz), 34.7, 34.6, 34.1 (d, *J* = 70.4 Hz), 30.89, 30.86; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.2; **HRMS** (ESI) calculated for $C_{35}H_{40}O_2P$ $[M+H]^+$ m/z 523.2760, found 523.2770.

3-(Bis(4-chlorophenyl)phosphoryl)-1,2-diphenylpropan-1-one (3ac)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.5 mg, 0.2 mmol, 1.0 equiv), bis(4-chlorophenyl)phosphine oxide **2c** (135.6 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 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 (45.8 mg, 48%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.63-7.57 (m, 2H), 7.51-7.41 (m, 3H), 7.34-7.26 (m, 6H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.13-7.05 (m, 3H), 5.32-5.24 (m, 1H), 3.45-3.34 (m, 1H), 2.82-2.72 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.7 (d, *J* = 7.1 Hz), 138.5 (d, *J* = 3.3 Hz), 138.11 (d, *J* = 3.3 Hz), 138.07 (d, *J* = 7.1 Hz), 135.4, 133.1, 132.0 (dd, *J* = 13.5, 10.2 Hz), 130.9 (d, *J* = 56.0 Hz), 129.0, 128.9, 128.8, 128.6, 128.3 (d, *J* = 8.8 Hz), 127.4, 46.4 (d, *J* = 1.7 Hz), 33.7 (d, *J* = 71.5 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 29.4; **HRMS** (ESI) calculated for $C_{27}H_{21}Cl_2O_2PNa$ $[M+Na]^+$ m/z 501.0548, found 501.0553.

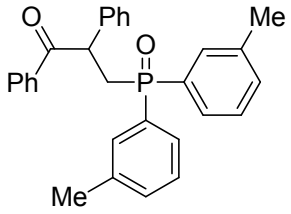
3-(Di(naphthalen-2-yl)phosphoryl)-1,2-diphenylpropan-1-one (3ad)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.7 mg, 0.2 mmol, 1.0 equiv), di(naphthalen-2-yl)phosphine oxide **2d** (151.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash

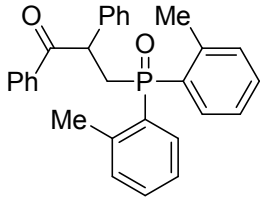
silica gel column chromatography (petroleum ether/EtOAc = 4/1) to afford the desired product **3ad** as white solid (50.2 mg, 49%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.36-8.25 (m, 2H), 7.83-7.74 (m, 8H), 7.68-7.44 (m, 6H), 7.38-7.17 (m, 5H), 7.05-7.01 (m, 2H), 6.95-6.90 (m, 1H), 5.42-5.34 (m, 1H), 3.71-3.61 (m, 1H), 3.00-2.90 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.9 (d, *J* = 6.6 Hz), 138.5 (d, *J* = 7.7 Hz), 135.5, 134.4 (d, *J* = 2.7 Hz), 134.3 (d, *J* = 2.2 Hz), 132.9, 132.8 (d, *J* = 3.8 Hz), 132.7 (d, *J* = 4.4 Hz), 132.4, 132.2, 130.5 (d, *J* = 35.7 Hz), 129.2 (d, *J* = 35.2 Hz), 128.83, 128.76, 128.7, 128.3, 128.2 (d, *J* = 9.9 Hz), 128.1, 128.0, 127.7, 127.6, 127.3, 126.7, 125.7 (d, *J* = 10.4 Hz), 125.5 (d, *J* = 11.0 Hz), 46.6 (d, *J* = 1.7 Hz), 33.8 (d, *J* = 70.4 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.60; **HRMS** (ESI) calculated for $C_{35}H_{27}O_2PNa$ $[M+Na]^+$ m/z 533.1641, found 533.1644.

3-(Di-*m*-tolylphosphoryl)-1,2-diphenylpropan-1-one (3ae)



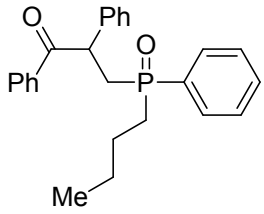
According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.4 mg, 0.2 mmol, 1.0 equiv), di-*m*-tolylphosphine oxide **2e** (115.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **3ae** as colourless oil (70.0 mg, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 12.0 Hz, 1H), 7.44-7.37 (m, 4H), 7.33-7.20 (m, 8H), 7.14-7.02 (m, 3H), 5.34-5.26 (m, 1H), 3.50-3.39 (m, 1H), 2.80-2.70 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.9 (d, *J* = 6.6 Hz), 138.6 (d, *J* = 7.7 Hz), 138.2 (d, *J* = 11.6 Hz), 138.1 (d, *J* = 11.6 Hz), 135.6, 133.2 (d, *J* = 47.3 Hz), 132.9, 132.2 (dd, *J* = 13.2, 2.8 Hz), 131.9 (d, *J* = 46.7 Hz), 131.2 (dd, *J* = 10.7, 9.1 Hz), 128.8, 128.3, 128.2 (dd, *J* = 12.7, 6.6 Hz), 127.6 (dd, *J* = 9.9, 7.8 Hz), 127.2, 46.4 (d, *J* = 1.6 Hz), 33.9 (d, *J* = 69.8 Hz), 21.2 (d, *J* = 2.8 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.69; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1826.

3-(Di-*o*-tolylphosphoryl)-1,2-diphenylpropan-1-one (3af)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.8 mg, 0.2 mmol, 1.0 equiv), di-*o*-tolylphosphine oxide **2f** (115.6 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 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 colourless oil (72.6 mg, 83%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.86-7.68 (m, 4H), 7.43-7.38 (m, 1H), 7.35-7.26 (m, 6H), 7.23-7.13 (m, 4H), 7.11-7.06 (m, 3H), 5.35-5.26 (m, 1H), 3.81-3.70 (m, 1H), 2.85-2.75 (m, 1H), 2.21 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.5 (d, *J* = 4.4 Hz), 141.3 (dd, *J* = 19.5, 9.1 Hz), 139.1 (d, *J* = 8.8 Hz), 135.6, 132.8, 132.4 (d, *J* = 9.8 Hz), 131.8-131.4 (m), 130.3 (d, *J* = 27.6 Hz), 128.9, 128.7, 128.2, 128.1, 127.2, 125.4 (dd, *J* = 11.6, 1.7 Hz), 46.0 (d, *J* = 1.1 Hz), 32.5 (d, *J* = 69.8 Hz), 21.1 (d, *J* = 4.4 Hz), 21.0 (d, *J* = 4.4 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 30.58; **HRMS** (ESI) calculated for $C_{29}H_{28}O_2P$ $[M+H]^+$ m/z 439.1821, found 439.1827.

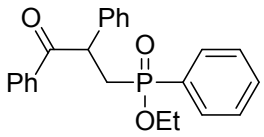
3-(Butyl(phenyl)phosphoryl)-1,2-diphenylpropan-1-one (3ag)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.5 mg, 0.2 mmol, 1.0 equiv), butyl(phenyl)phosphine oxide **2g** (91.4 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.4 mg, 0.02 mmol, 0.1 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 colourless oil (40.2 mg, 51%, d.r. = 1:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.68-7.62 (m, 2H), 7.55-7.49 (m, 2H), 7.43-7.28 (m, 14H), 7.22-7.15 (m, 4H), 7.08-6.97 (m, 4H), 5.28-5.18 (m, 2H), 3.18-3.07 (m, 1H), 3.04-2.93 (m, 1H), 2.55-2.47 (m, 1H), 2.44-2.34 (m, 1H), 1.97-1.78 (m, 2H), 1.65-1.43 (m, 4H), 1.19-1.23 (m, 6H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.2 (d, *J* = 6.6 Hz), 197.7 (d, *J* = 7.2 Hz),

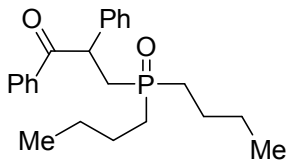
138.8 (d, J = 7.1 Hz), 138.2 (d, J = 7.7 Hz), 135.43, 135.37, 132.9, 132.8, 132.7, 131.7, 131.5, 131.2 (d, J = 2.7 Hz), 130.8 (d, J = 2.8 Hz), 130.2 (d, J = 8.8 Hz), 129.8 (d, J = 8.8 Hz), 129.8 (d, J = 8.8 Hz), 128.9, 128.7, 128.6, 128.5, 128.21, 128.18, 128.10, 128.0, 127.9, 127.3, 127.0, 46.6 (d, J = 2.2 Hz), 46.2 (d, J = 1.7 Hz), 33.9 (d, J = 65.9 Hz), 33.5 (d, J = 65.9 Hz), 30.6 (d, J = 68.2 Hz), 29.7 (d, J = 68.2 Hz), 23.62 (d, J = 14.8 Hz), 23.55 (d, J = 15.5 Hz), 23.11, 23.05, 13.2, 13.1; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 39.25, 38.92; **HRMS** (ESI) calculated for $C_{25}H_{28}O_2P$ $[M+H]^+$ m/z 391.1821, found 391.1823.

Ethyl (3-oxo-2,3-diphenylpropyl)(phenyl)phosphinate (3ah)[4]



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.4 mg, 0.2 mmol, 1.0 equiv), ethyl phenylphosphinate **2h** (177.4 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 4/1) to afford the desired product **3ah** as colourless oil (60.0 mg, 79%, d.r. = 1:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01 (d, J = 7.5 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.74-7.64 (m, 4H), 7.50-7.23 (m, 18H), 7.19-7.03 (m, 4H), 5.26-5.20 (m, 2H), 3.96-3.84 (m, 2H), 3.79-3.65 (m, 2H), 3.25-3.12 (m, 1H), 3.07-2.95 (m, 1H), 2.52-2.32 (m, 2H), 1.10 (t, J = 7.4Hz, 3H), 1.05 (t, J = 7.7 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.8 (d, J = 6.6 Hz), 197.6 (d, J = 6.6 Hz), 138.9 (d, J = 9.9 Hz), 138.2 (d, J = 9.9 Hz), 135.9, 135.7, 132.9, 132.2 (d, J = 2.8 Hz), 132.0 (d, J = 2.8 Hz), 131.6, 131.5, 131.4, 129.8 (d, J = 19.3 Hz), 128.9, 128.8, 128.7, 128.7, 128.5, 128.4, 128.31, 128.27, 128.2, 127.3, 127.2, 60.43 (d, J = 6.6 Hz), 60.39 (d, J = 6.1 Hz), 46.9 (d, J = 1.1 Hz), 46.5 (d, J = 1.7 Hz), 34.0 (d, J = 98.9 Hz), 33.8 (d, J = 98.9 Hz), 16.1 (d, J = 6.6 Hz), 16.0 (d, J = 6.6 Hz); **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 42.37, 42.07; **HRMS** (ESI) calculated for $C_{23}H_{24}O_3P$ $[M+H]^+$ m/z 379.1458, found 379.1458.

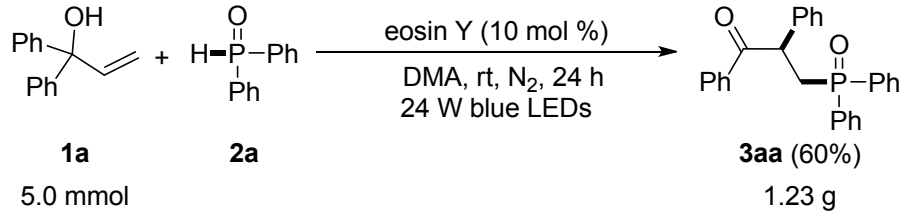
3-(Dipropylphosphoryl)-1,2-diphenylpropan-1-one (3ai)



According to **GP** with 1,1-diphenylprop-2-en-1-ol **1a** (42.3 mg, 0.2 mmol, 1.0 equiv),

dipropylphosphine oxide **2i** (81.2 mg, 0.5 mmol, 2.5 equiv), and eosin Y (13.6 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 4/1) to afford the desired product **3ai** as colourless oil (25.1 mg, 34%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.49-7.35 (m, 5H), 7.33-7.26 (m, 2H), 7.22-7.17 (m, 1H), 5.28-5.21 (m, 1H), 2.78-2.67 (m, 1H), 2.20-2.10 (m, 1H), 1.68-1.46 (m, 6H), 1.41-1.19 (m, 6H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.3 (d, *J* = 6.6 Hz), 138.9 (d, *J* = 6.6 Hz), 135.4, 132.9, 128.9, 128.7, 128.24, 128.17, 127.3, 46.5 (d, J = 2.3 Hz), 31.0 (d, J = 63.2 Hz), 31.0 (d, J = 64.9 Hz), 28.1 (d, J = 64.3 Hz), 23.9 (d, J = 8.9 Hz), 23.7 (d, J = 8.8 Hz), 23.5 (d, J = 3.3 Hz), 23.3 (d, J = 3.8 Hz), 13.3, 13.2; **^{31}P NMR** (121.5 MHz, $CDCl_3$) δ 48.26; **HRMS** (ESI) calculated for $C_{23}H_{32}O_2P$ $[M+Na]^+$ m/z 371.2134, found 371.2134.

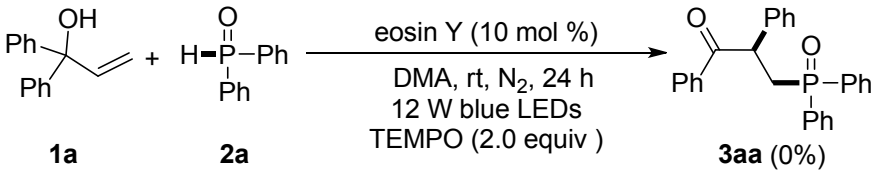
Larger scale experiment



1,1-Diphenylprop-2-en-1-ol **1a** (1.05 g, 5.0 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (2.50 g, 12.5 mmol, 2.5 equiv), and eosin Y (0.32 g, 0.5 mmol, 0.1 equiv) were placed in a dry 100 mL Schlenk tube under a nitrogen atmosphere. Then DMA (20.0 mL) was added. The reaction mixture was stirred and irradiated by 24 W blue LEDs (450 nm) at room temperature for 24 h. After the reaction was completed monitored by TLC, H_2O (50.0 mL) was added, and the mixture was extracted by EtOAc (3x50.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, 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** (1.23g, 60%).

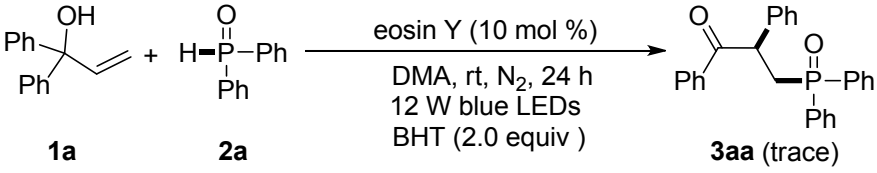
Mechanistic studies

Radical inhibition experiments:



1a **2a** **3aa** (0%)

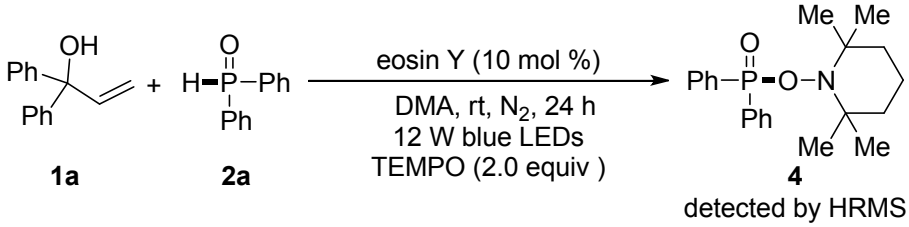
1,1-Diphenylprop-2-en-1-ol **1a** (42.5 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.2 mg, 0.5 mmol, 2.5 equiv), eosin Y (13.1 mg, 0.02 mmol, 0.1 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.4 mg, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then DMA (2.0 mL) was added. The reaction mixture was stirred and irradiated by 12 W blue LEDs (450 nm) at room temperature for 24 h. In this reaction, the formation of **3aa** was completely suppressed.



1a **2a** **3aa** (trace)

1,1-Diphenylprop-2-en-1-ol **1a** (43.0 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.3 mg, 0.5 mmol, 2.5 equiv), eosin Y (13.4 mg, 0.02 mmol, 0.1 equiv), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (88.1 mg, 0.6 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then DMA (2.0 mL) was added. The reaction mixture was stirred and irradiated by 12 W blue LEDs (450 nm) at room temperature for 24 h. In this reaction, only traces of the desired product **3aa** were observed.

Radical trapping experiments:

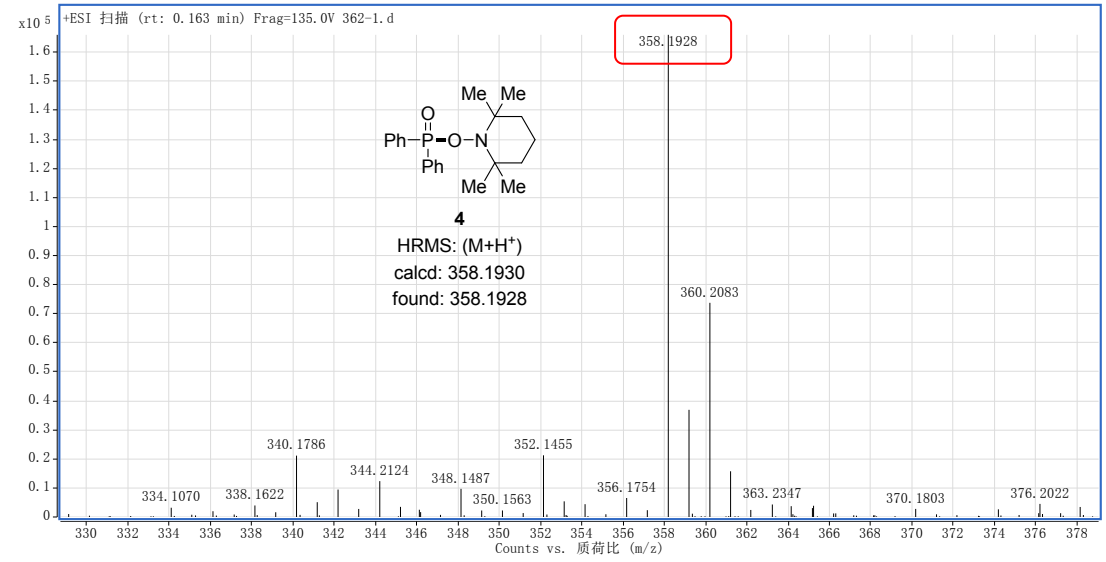


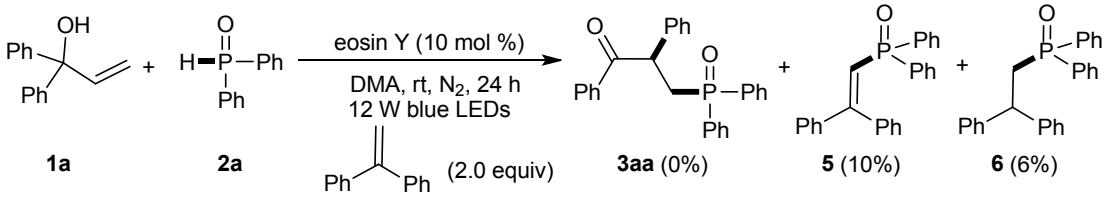
1a **2a** **4**

detected by HRMS

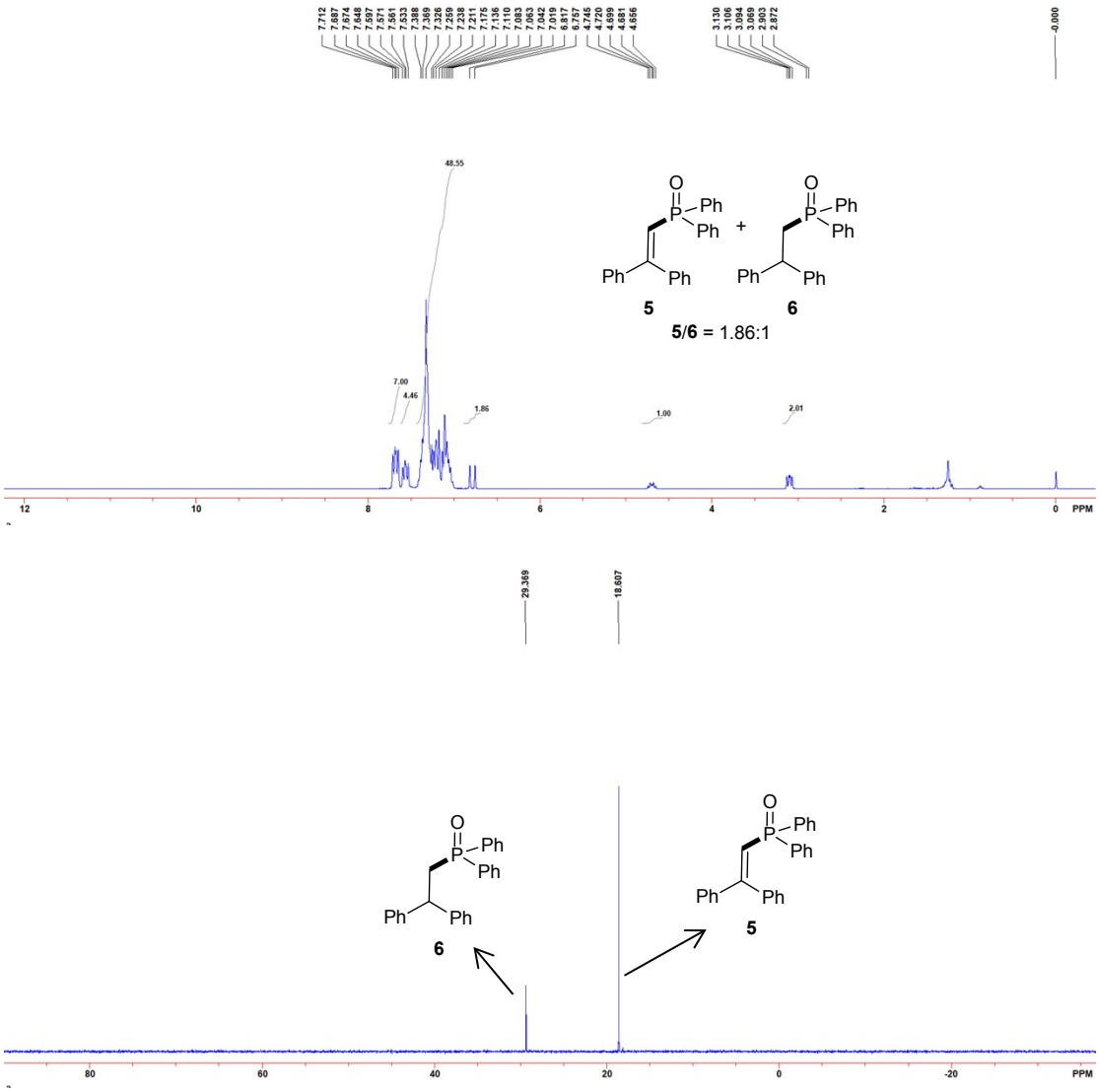
1,1-Diphenylprop-2-en-1-ol **1a** (42.6 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine

oxide **2a** (101.8 mg, 0.5 mmol, 2.5 equiv), eosin Y (13.2 mg, 0.02 mmol, 0.1 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.5 mg, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then DMA (2.0 mL) was added. The reaction mixture was stirred and irradiated by 12 W blue LEDs (450 nm) at room temperature for 24 h. High-resolution mass spectra analysis of this reaction mixture showed that TEMPO-trapped product **4** was formed.





1,1-Diphenylprop-2-en-1-ol **1a** (42.5 mg, 0.2 mmol, 1.0 equiv), diphenylphosphine oxide **2a** (101.6 mg, 0.5 mmol, 2.5 equiv), eosin Y (13.5 mg, 0.02 mmol, 0.1 equiv), and ethene-1,1-diyldibenzene (71 μL, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then DMA (2.0 mL) was added. The reaction mixture was stirred and irradiated by 12 W blue LEDs (450 nm) at room temperature for 24 h. After the reaction was completed monitored by TLC, H_2O (10.0 mL) was added, and the mixture was extracted by EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, 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 product **5** and **6** (24.0 mg, **5**/**6** = 1.86:1).[5,6]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7.238
7.211
7.175
7.136
7.110
7.083
7.063
7.042
7.019
6.817
6.757
4.745
4.720
4.699
4.681
4.656
3.130
3.106
3.094
3.069
2.903
2.872
-0.000
48.55
7.00
4.46
1.86
1.00
2.01
12
10
8
6
4
2
0
PPM
5
6
5/6 = 1.86:1
29.369
18.607
6
5
80
60
40
20
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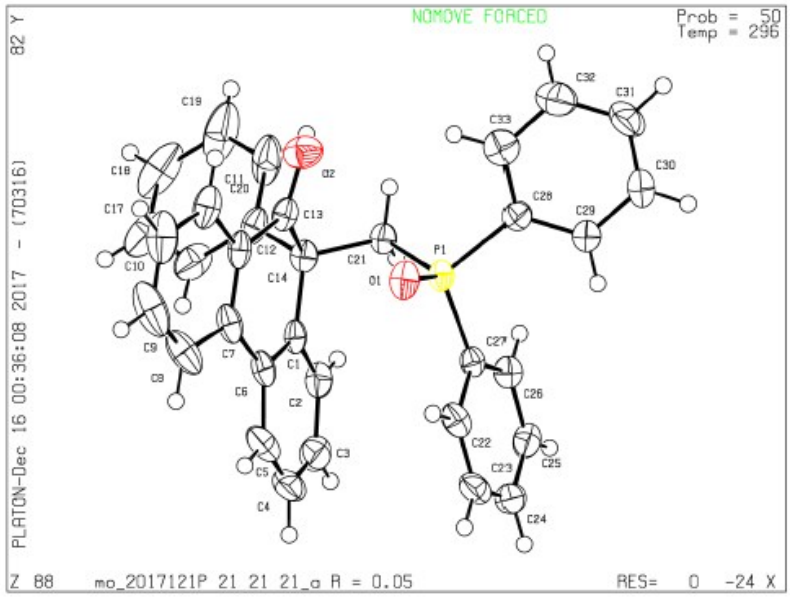
-20
PPM

Crystallographic data of 3la (CCDC: 1811785)

Datablock mo_20171213YKD_ZB_0m_a - ellipsoid plot



No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_20171213YKD_ZB_0m_a

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                  alpha=90         beta=90          gamma=90
Temperature:      296 K

                 Calculated                Reported
Volume           2452.9(8)                 2452.8(9)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C33 H25 O2 P              ?
Sum formula      C33 H25 O2 P              C33 H25 O2 P
Mr               484.50                    484.50
Dx,g cm-3        1.312                     1.312
Z                4                         4
Mu (mm-1)        0.142                     0.142
F000             1016.0                    1016.0
F000'            1016.81
h,k,lmax         13,14,21                  13,14,21
Nref             4335[ 2466]               4296
Tmin,Tmax        0.969,0.975
Tmin'            0.969

Correction method= Not given

Data completeness= 1.74/0.99      Theta(max)= 25.010

R(reflections)= 0.0459( 3943)     wR2(reflections)= 0.1304( 4296)

S = 1.033                 Npar= 325
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References:

[1] Liu, X.; Xiong, F.; Huang, X.; Xu, L.; Li, P.; Wu, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 6962.

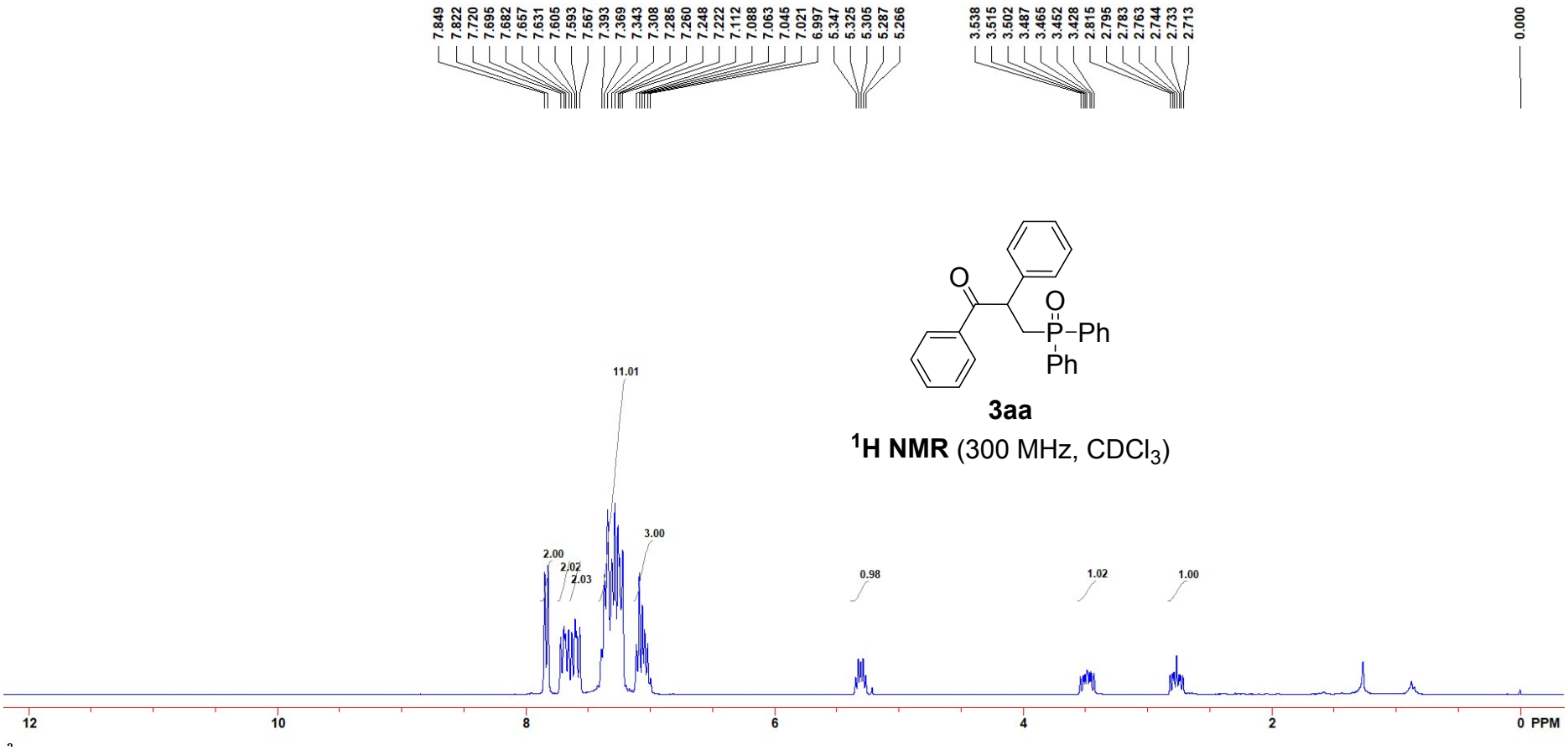
[2] Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277.

[3] Keglevich, G.; Jablonkai, E.; Balázs, L. B. *RSC Adv.* **2014**, *4*, 22808.

[4] Chu, X.-Q.; Zi, Y.; Meng, H.; Xu, X.-P.; Ji, S.-J. *Chem. Commun.* **2014**, *50*, 7642.

[5] Zhang, H.-Y.; Mao, L.-L.; Yang, B.; Yang, S.-D. *Chem. Commun.* **2015**, *51*, 4101.

[6] Isley, N. A.; Linstadt, R. T. H.; Slack, E. D.; Lipshutz, B. H. *Dalton Trans.* **2014**, *43*, 13196.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7.605
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7.248
7.222
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7.063
7.045
7.021
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5.325
5.305
5.287
5.266
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3.515
3.502
3.487
3.465
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2.795
2.783
2.763
2.744
2.733
2.713
0.000
O
O
P–Ph
Ph
3aa
1H NMR (300 MHz, CDCl3)
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2.03
3.00
0.98
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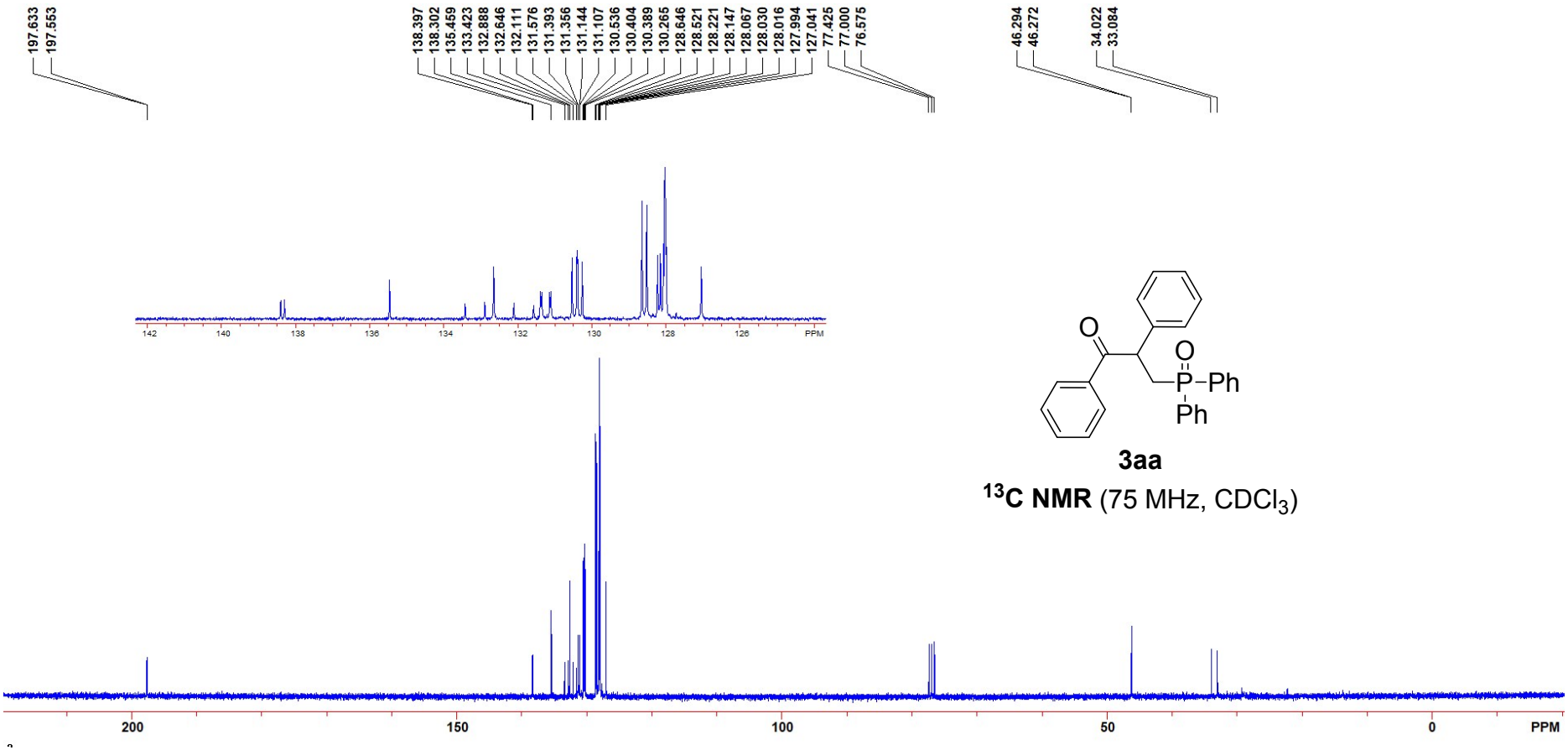
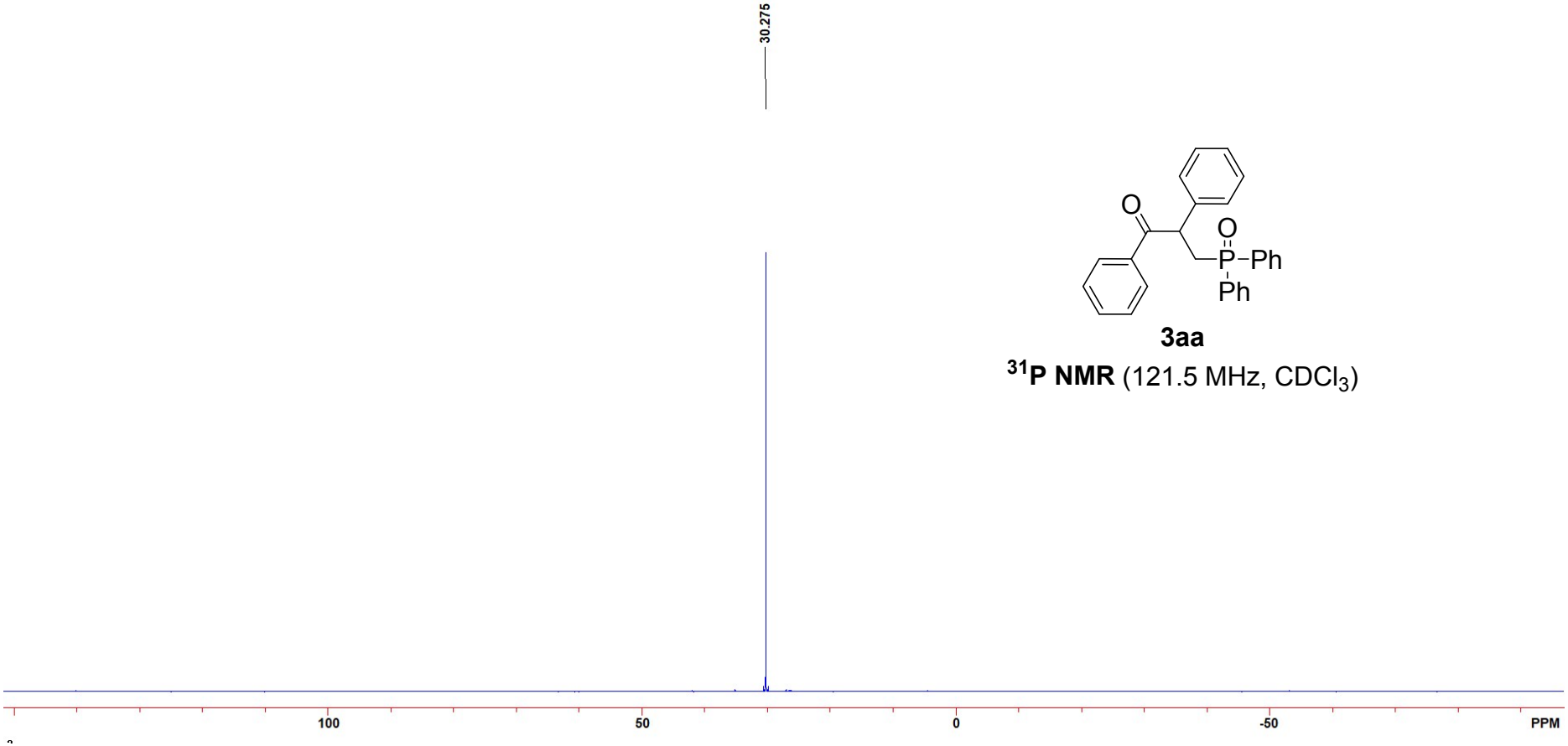
12
10
8
6
4
2
0 PPM



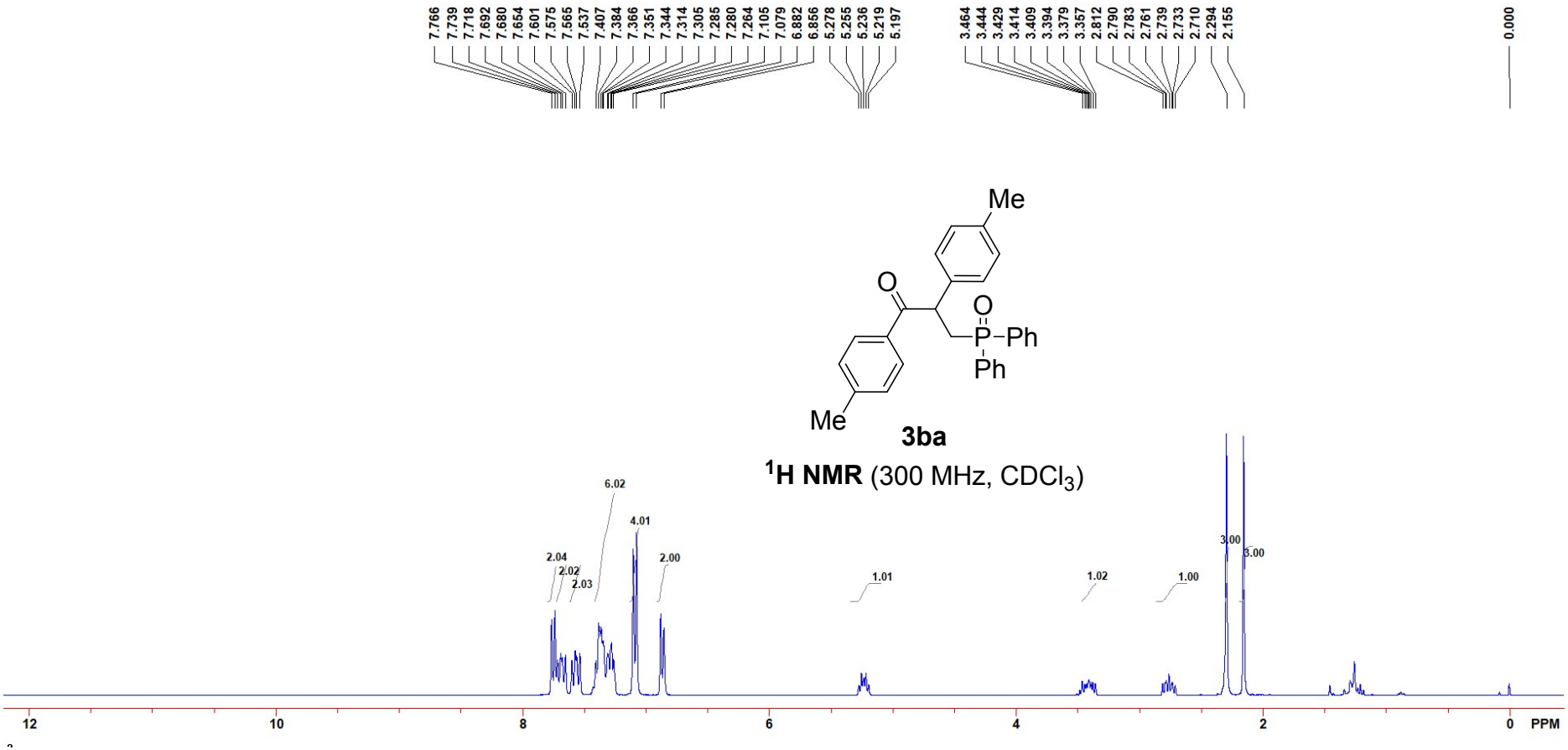
3aa

^{13}C NMR (75 MHz, $CDCl_3$)



3aa

^{31}P NMR (121.5 MHz, $CDCl_3$)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7.351
7.344
7.314
7.305
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7.280
7.264
7.105
7.079
6.882
6.856
5.278
5.255
5.236
5.219
5.197
3.464
3.444
3.429
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3.409
3.394
3.379
3.357
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2.790
2.783
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2.733
2.710
2.294
2.155
0.000
Me
O
O
P
Ph
Ph
Me
3ba
1H NMR (300 MHz, CDCl3)
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2.04
2.02
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1.02
1.00
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10
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6
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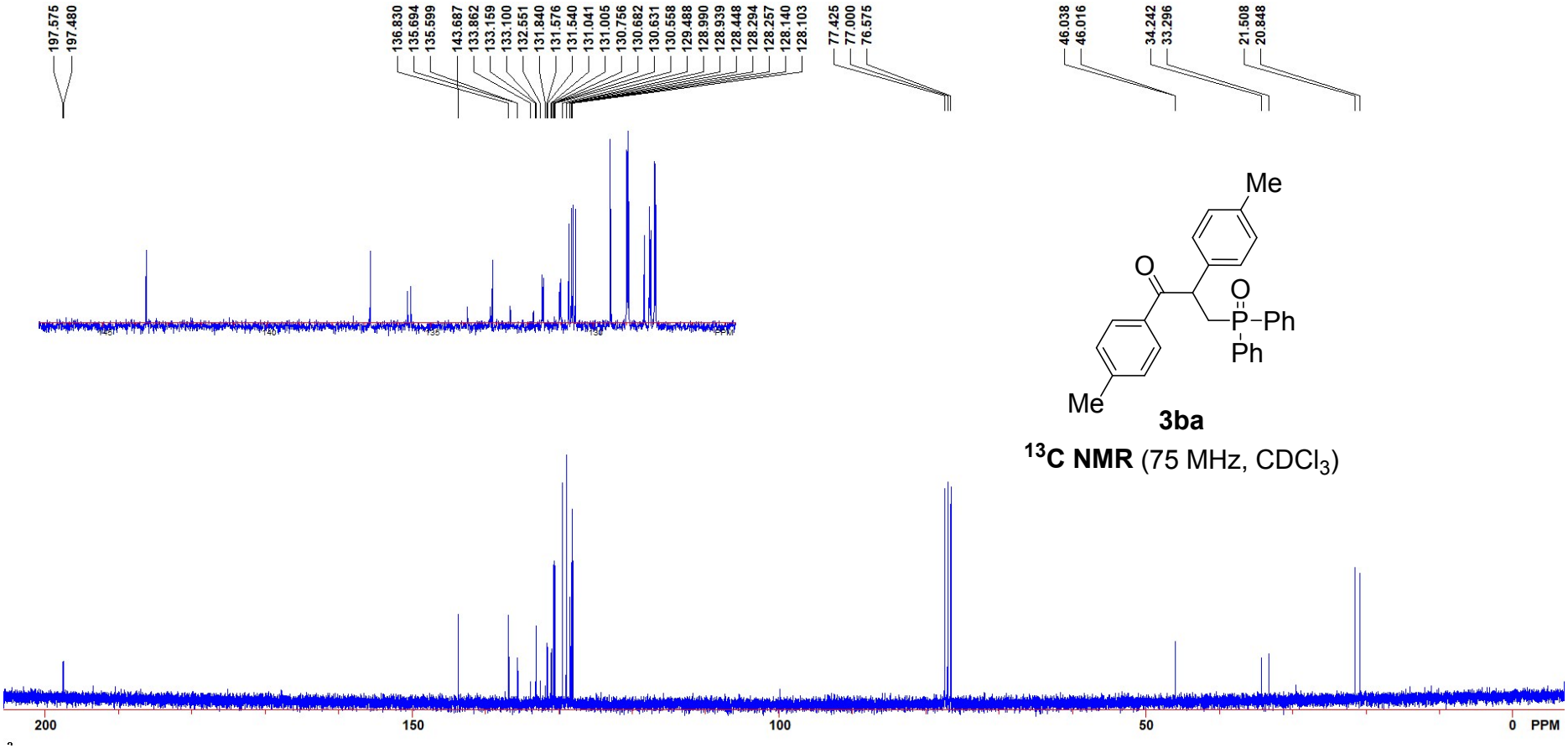
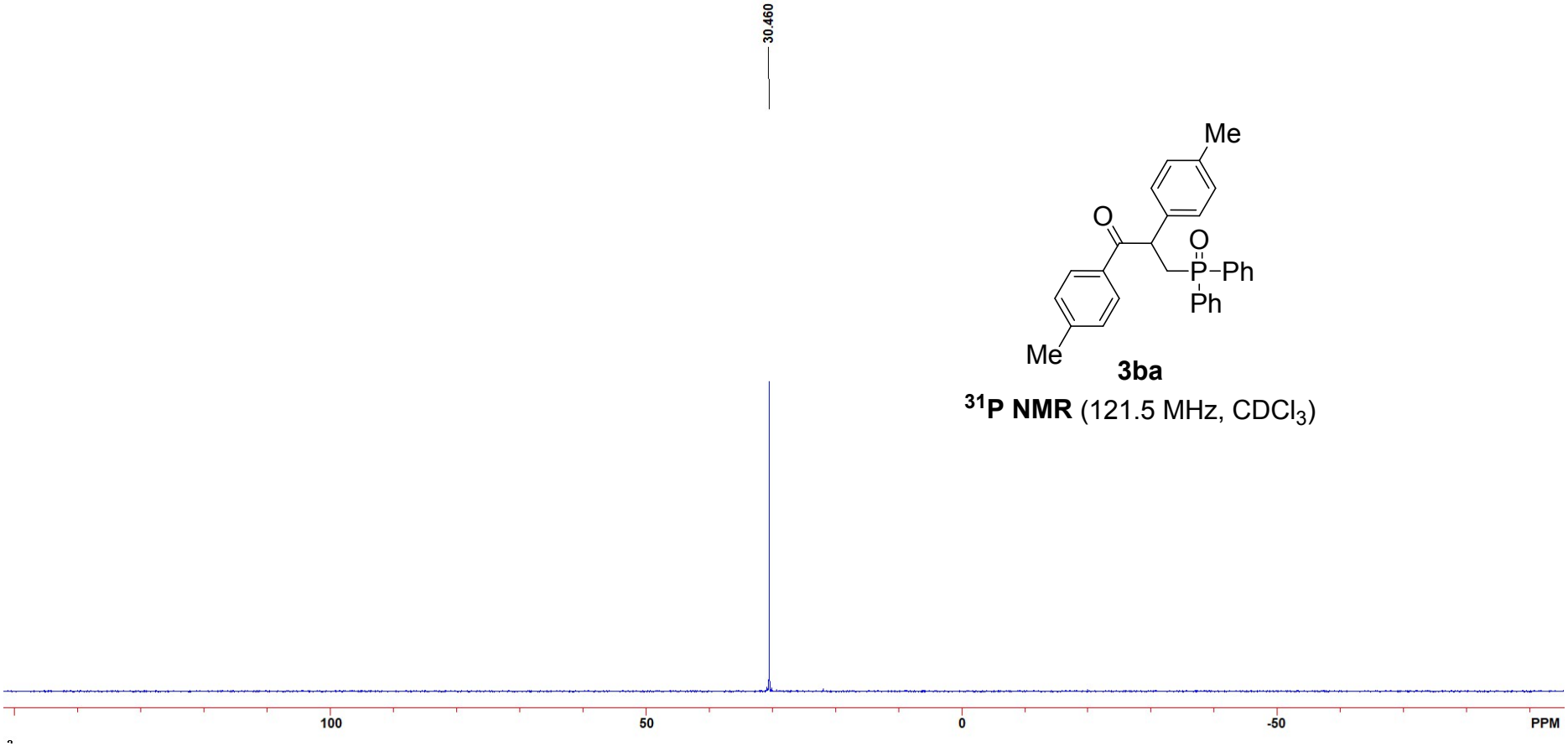
2
0
PPM



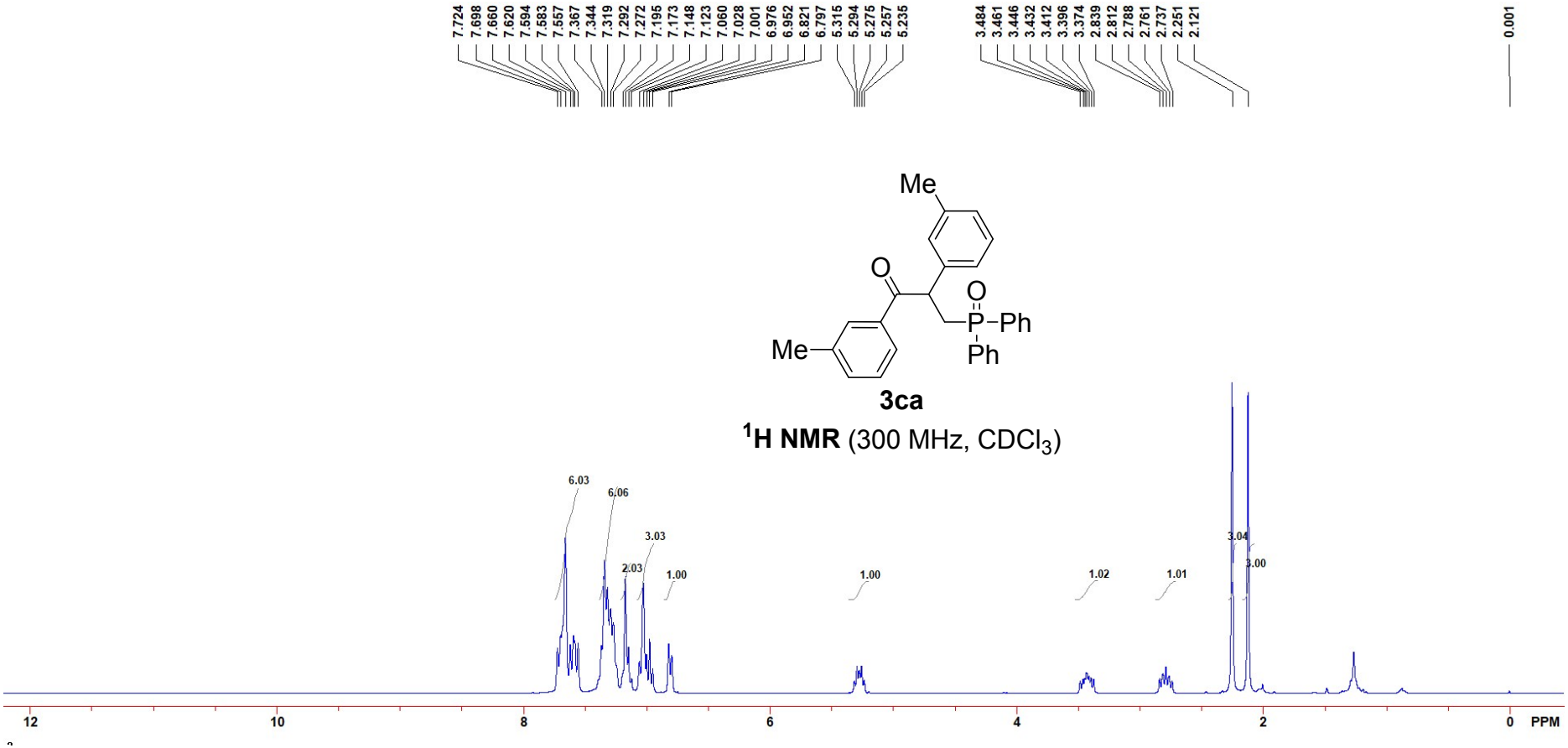
3ba

^{13}C NMR (75 MHz, $CDCl_3$)



3ba

^{31}P NMR (121.5 MHz, $CDCl_3$)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7.173
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7.028
7.001
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6.952
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5.294
5.275
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5.235
3.484
3.461
3.446
3.432
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3.396
3.374
2.839
2.812
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2.737
2.251
2.121
0.001
Me
O
O
P
Ph
Ph
Me
3ca
1H NMR (300 MHz, CDCl3)
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6.06
3.03
2.03
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1.01
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10
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6
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2
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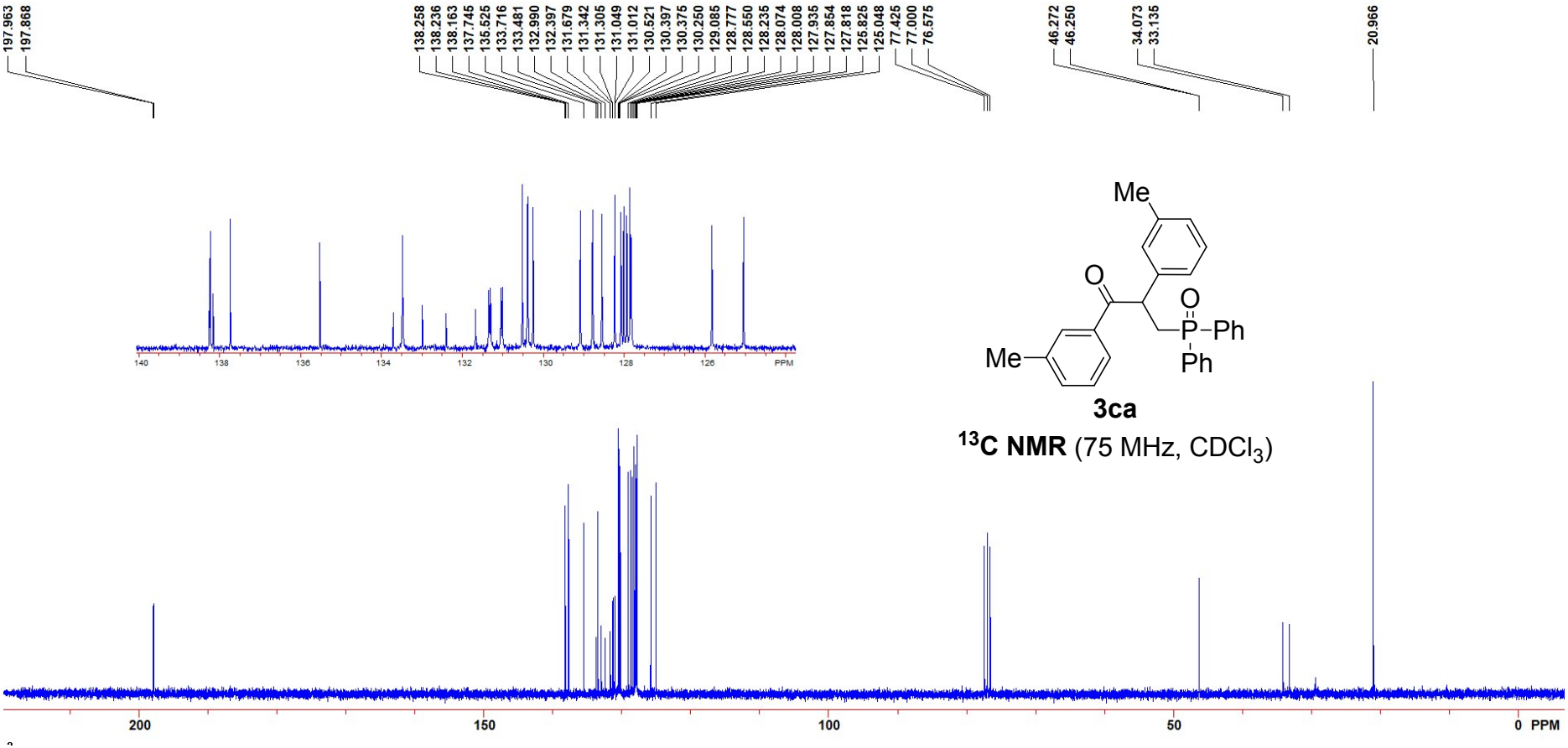
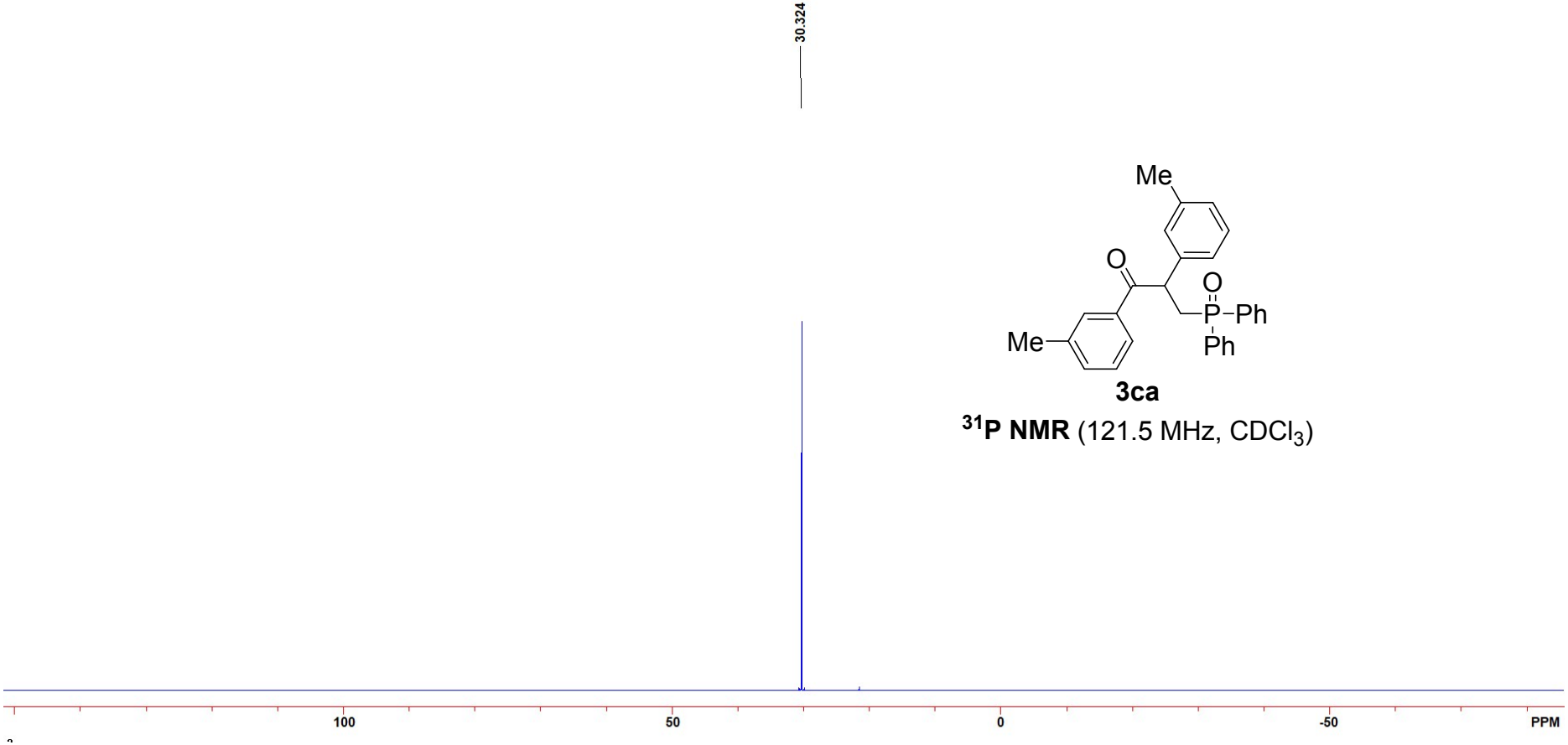
PPM



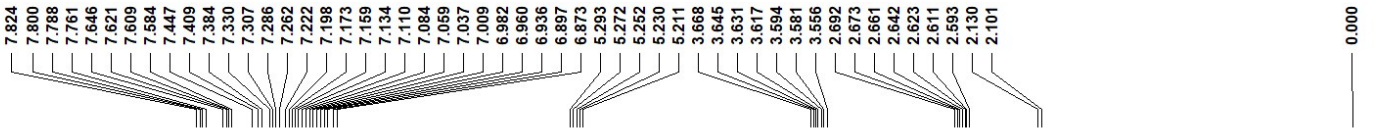
3ca

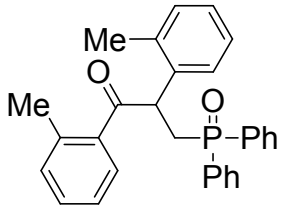
^{13}C NMR (75 MHz, $CDCl_3$)



3ca

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





3da

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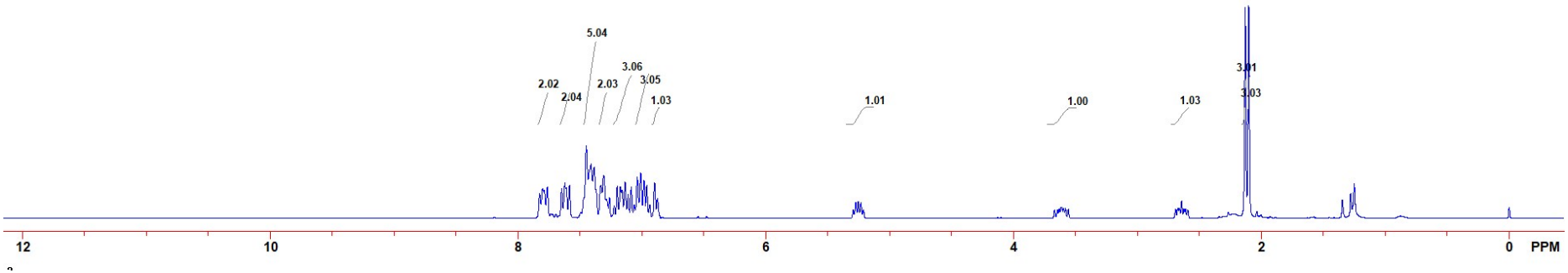
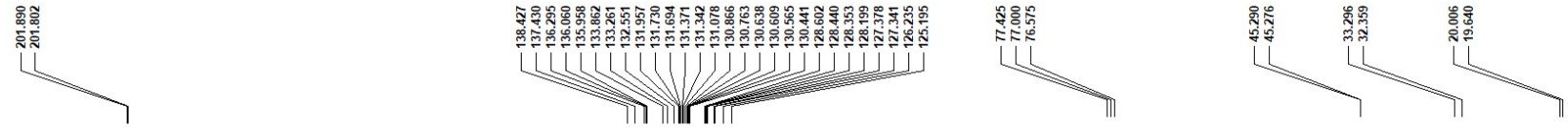
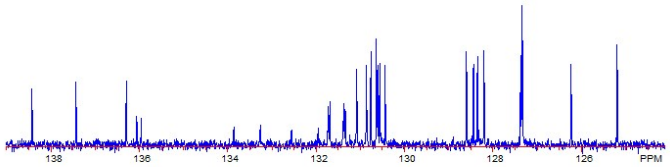
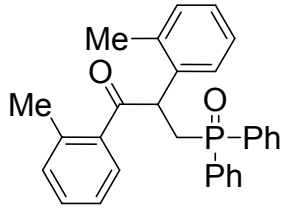


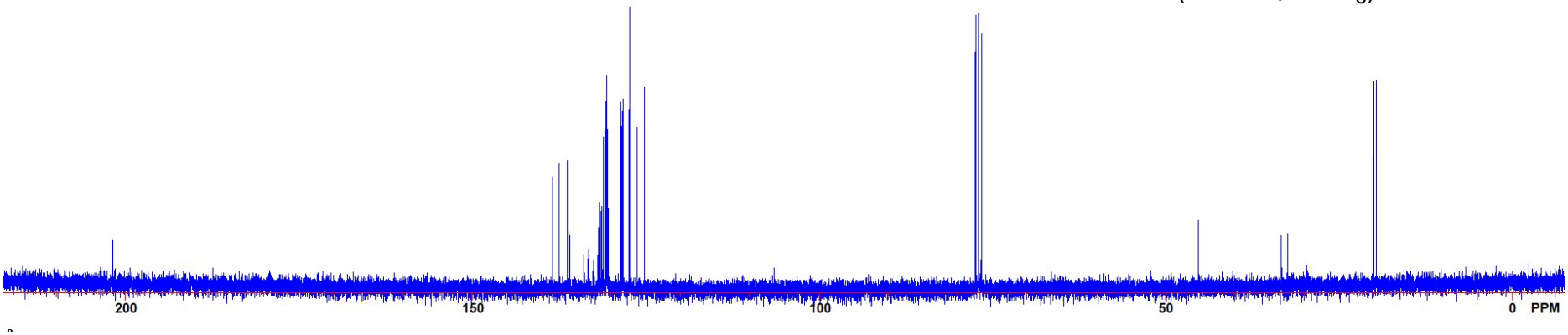


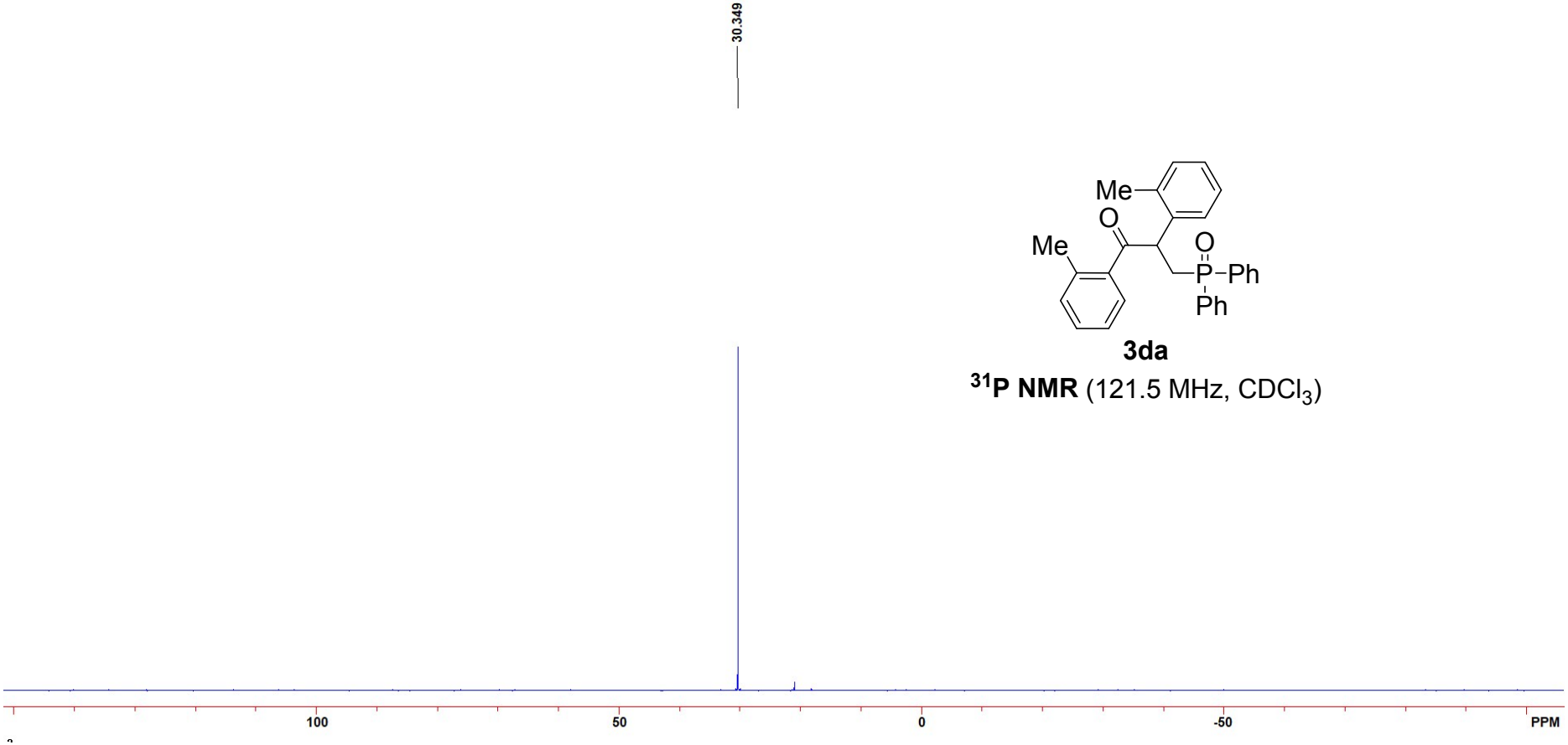




3da

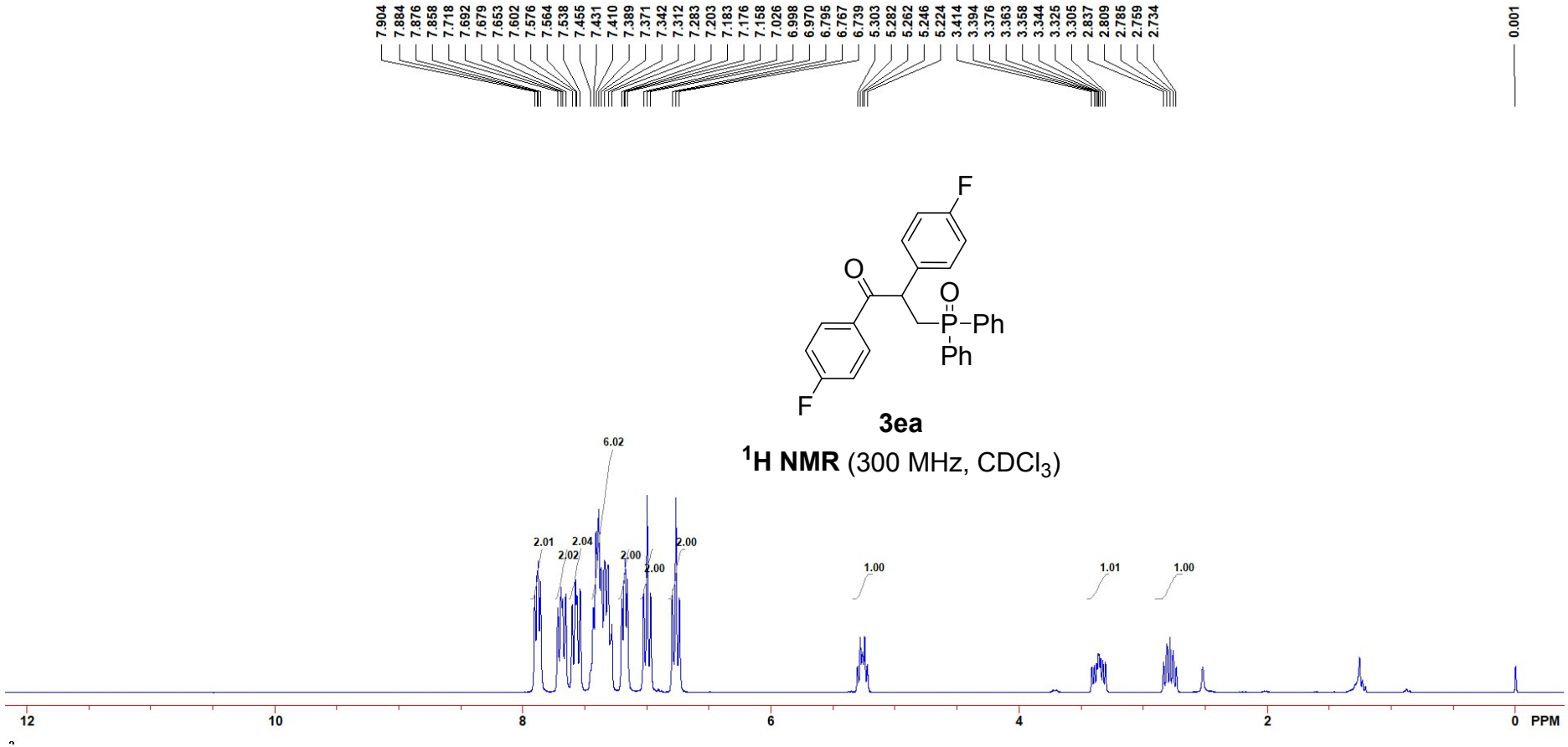
^{13}C NMR (75 MHz, $CDCl_3$)

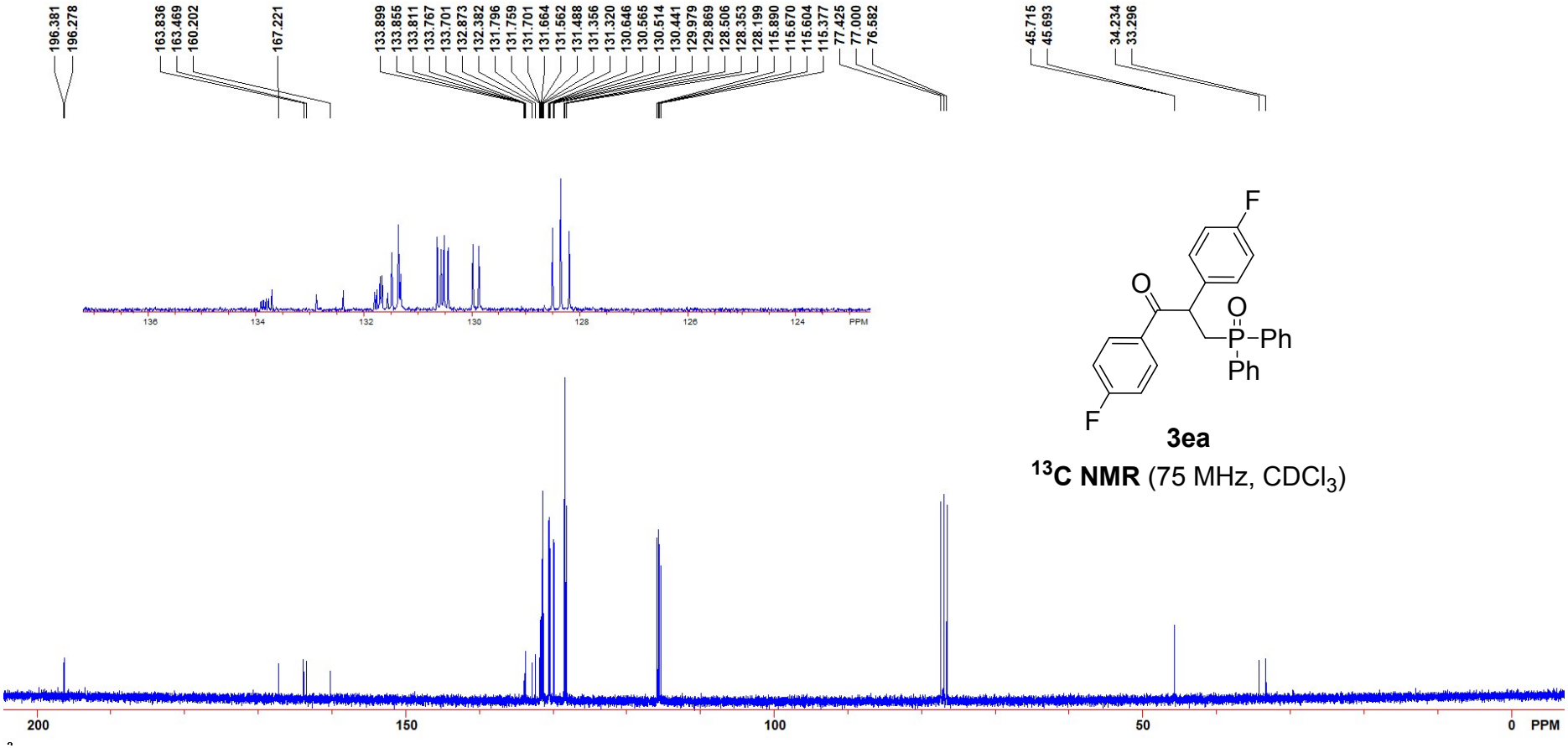




3da

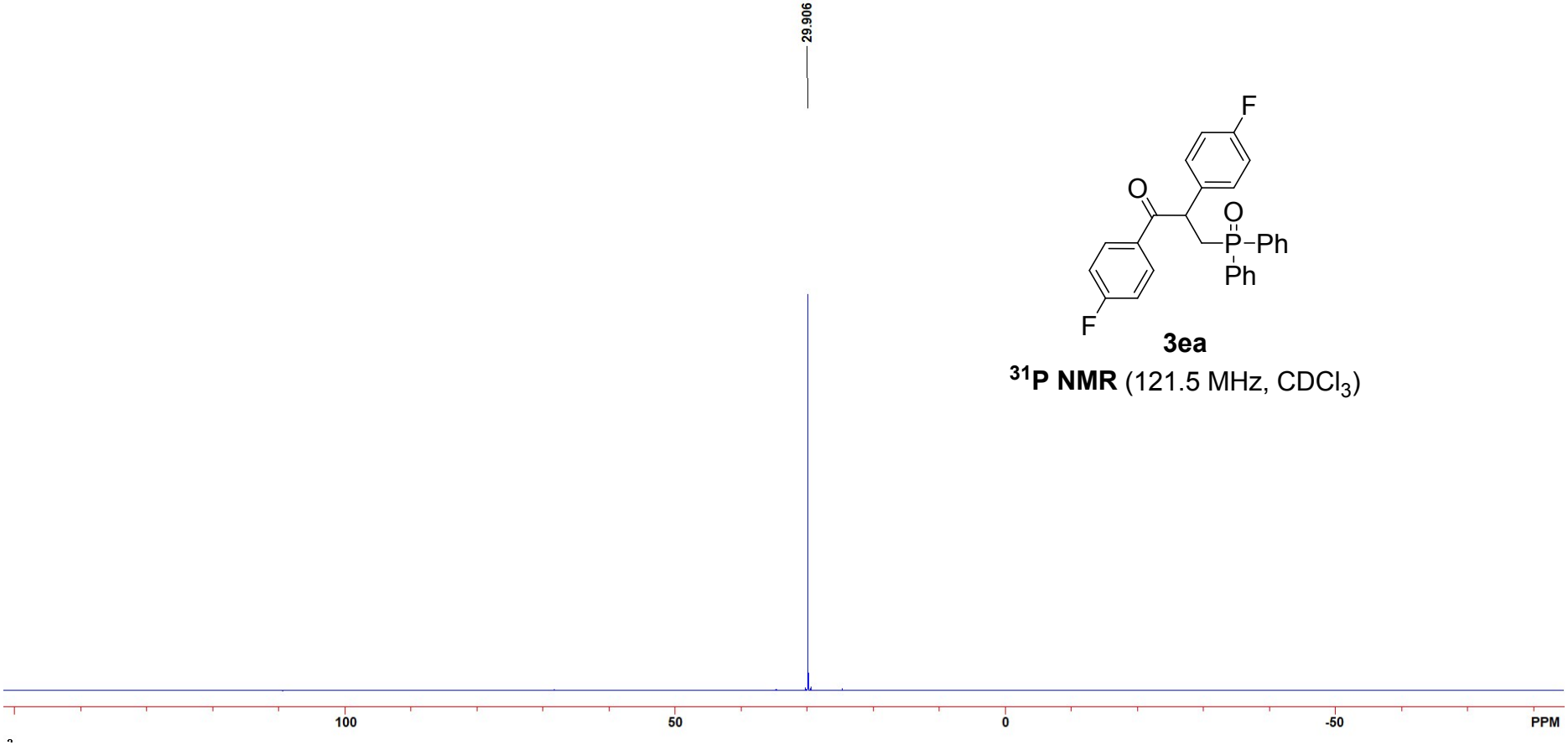
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.904
7.884
7.876
7.858
7.718
7.692
7.679
7.653
7.602
7.576
7.564
7.538
7.455
7.431
7.410
7.389
7.371
7.342
7.312
7.283
7.203
7.183
7.176
7.158
7.026
6.998
6.970
6.795
6.767
6.739
5.303
5.282
5.262
5.246
5.224
3.414
3.394
3.376
3.363
3.358
3.344
3.325
3.305
2.837
2.809
2.785
2.759
2.734
0.001
F
O
O
P
Ph
Ph
F
3ea
1H NMR (300 MHz, CDCl3)
6.02
2.01
2.02
2.04
2.00
2.00
2.00
1.00
1.01
1.00
12
10
8
6
4
2
0
PPM



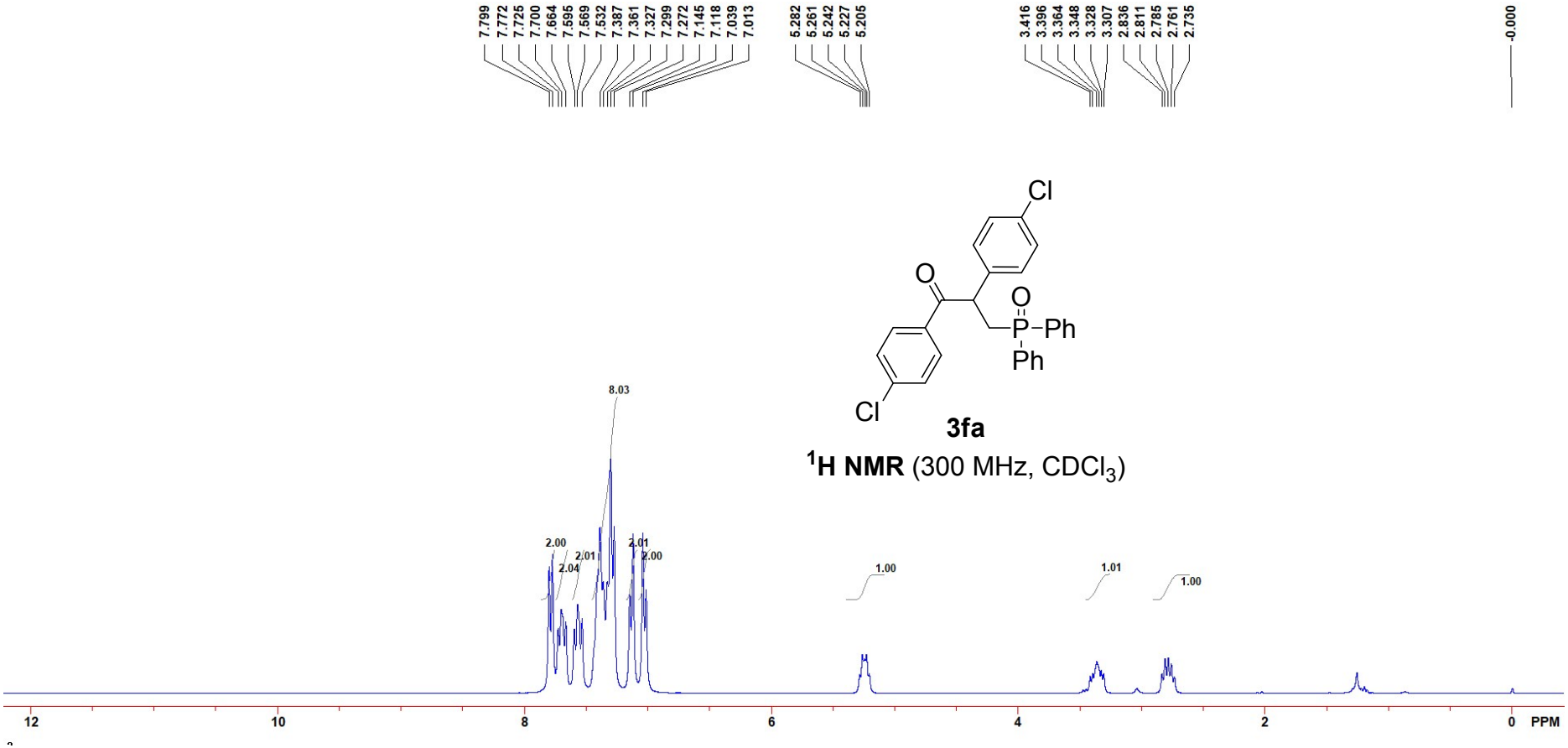
3ea

^{13}C NMR (75 MHz, $CDCl_3$)



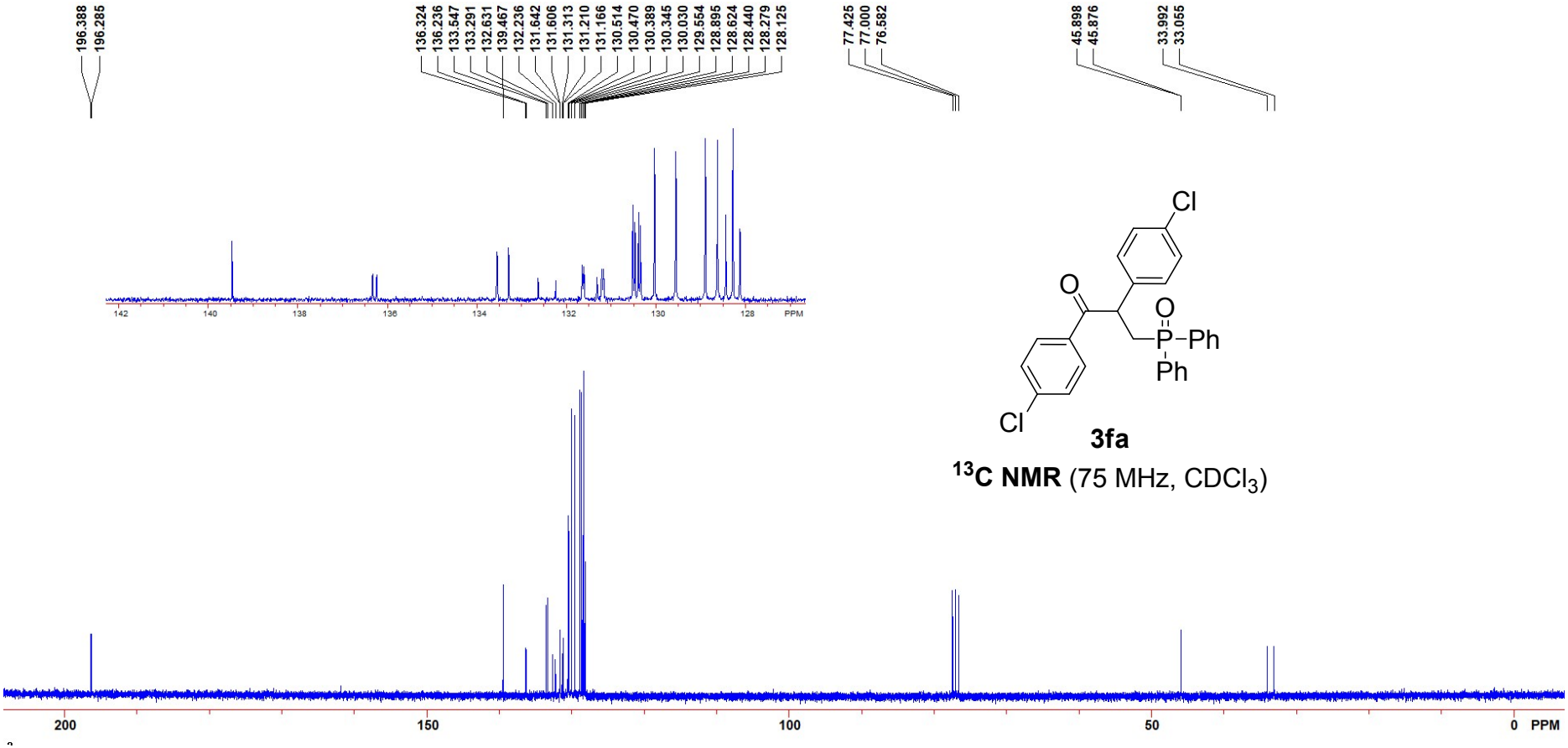
3ea

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



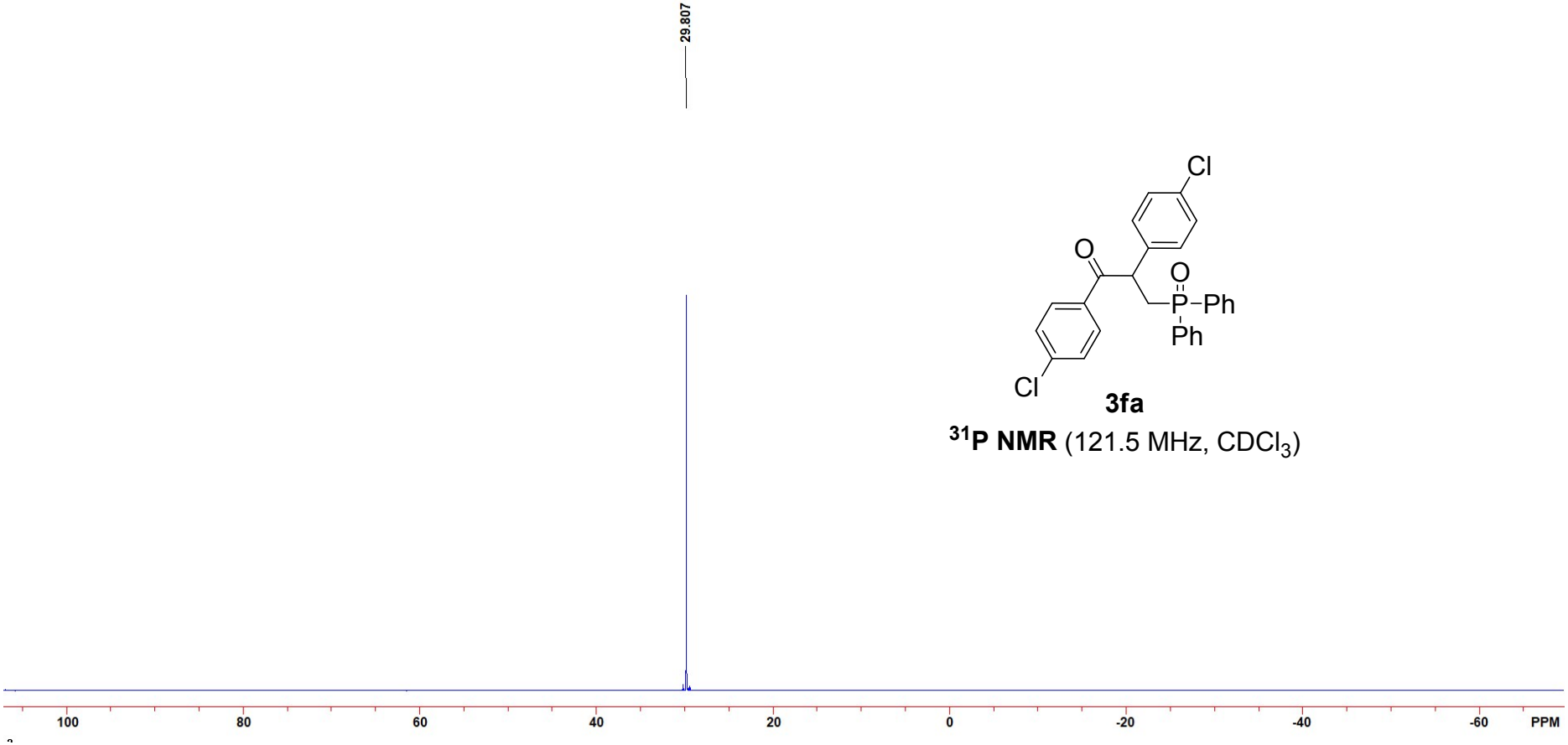
3fa

^{1}H NMR (300 MHz, $CDCl_3$)



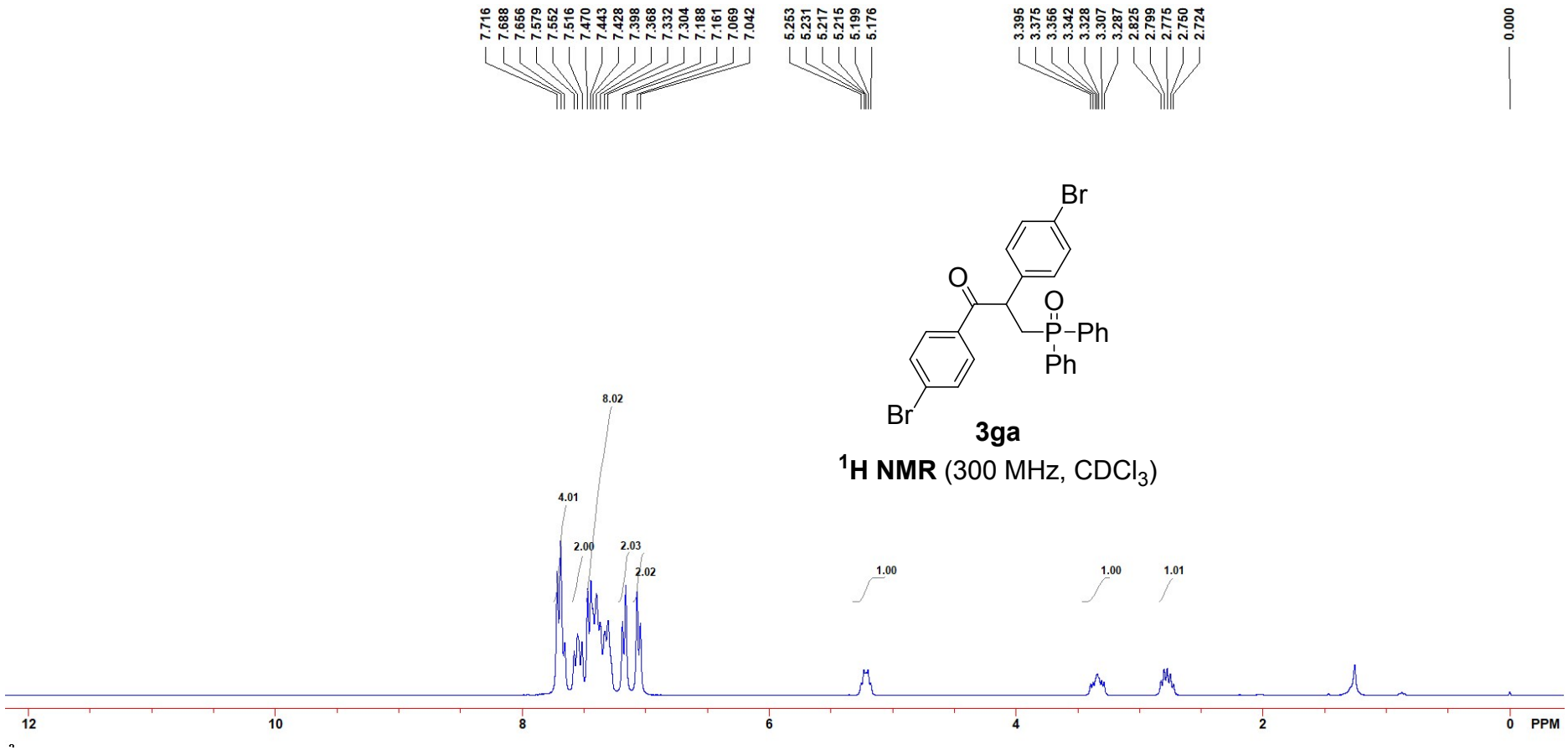
3fa

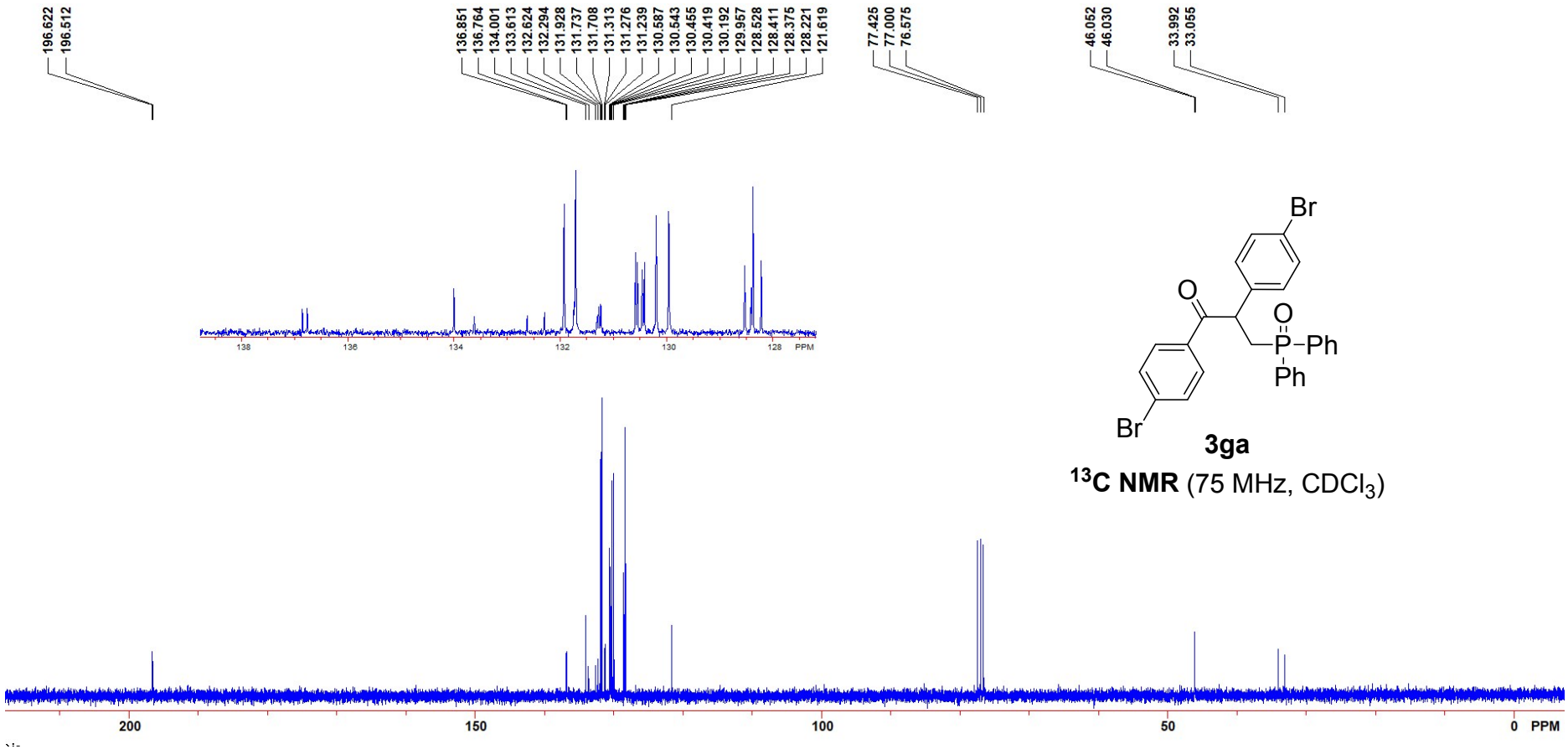
^{13}C NMR (75 MHz, $CDCl_3$)



3fa

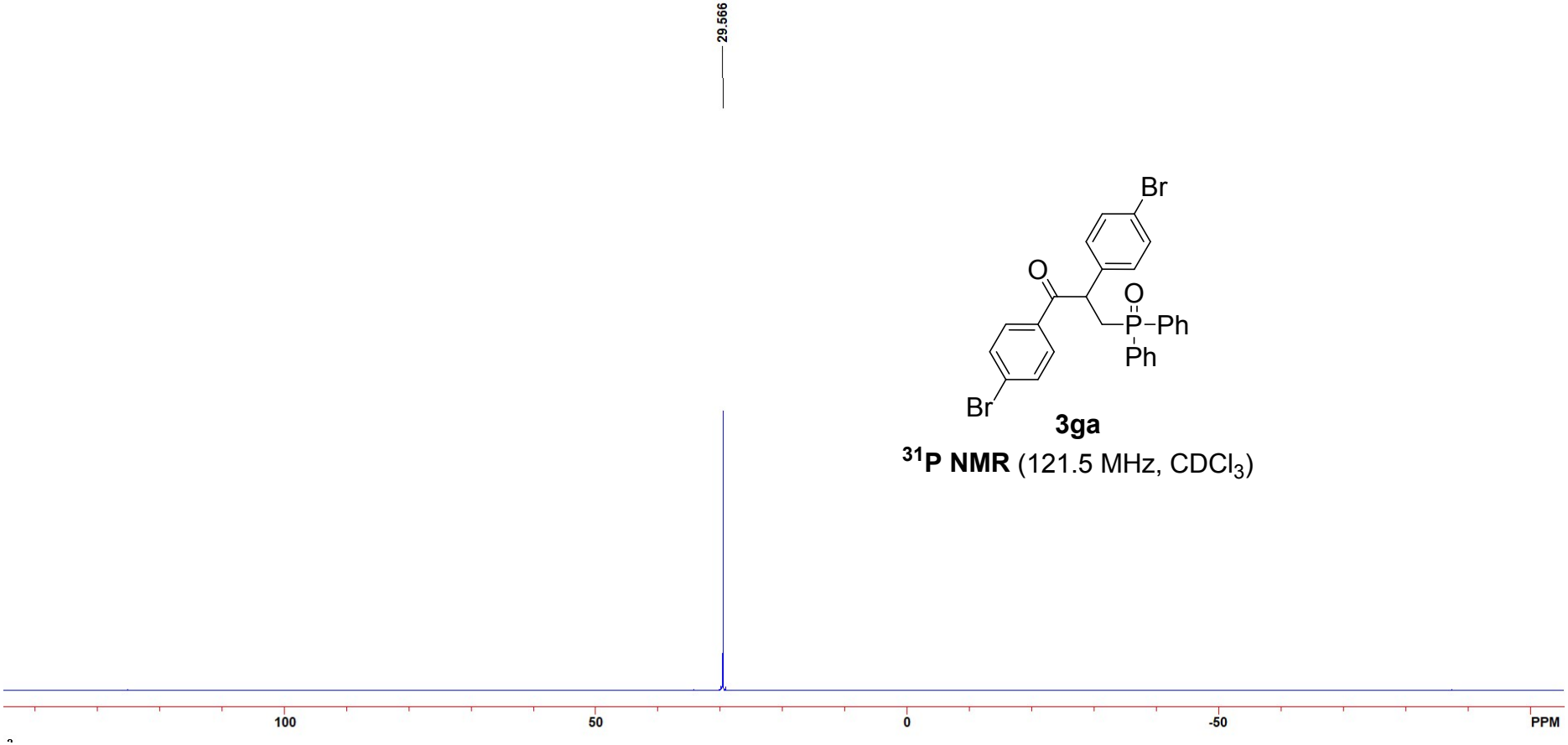
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.716
7.688
7.656
7.579
7.552
7.516
7.470
7.443
7.428
7.398
7.368
7.332
7.304
7.188
7.161
7.069
7.042
5.253
5.231
5.217
5.215
5.199
5.176
3.395
3.375
3.356
3.342
3.328
3.307
3.287
2.825
2.799
2.775
2.750
2.724
0.000
Br
O
O
P
Ph
Ph
Br
3ga
1H NMR (300 MHz, CDCl3)
8.02
4.01
2.00
2.03
2.02
1.00
1.00
1.01
12
10
8
6
4
2
0
PPM



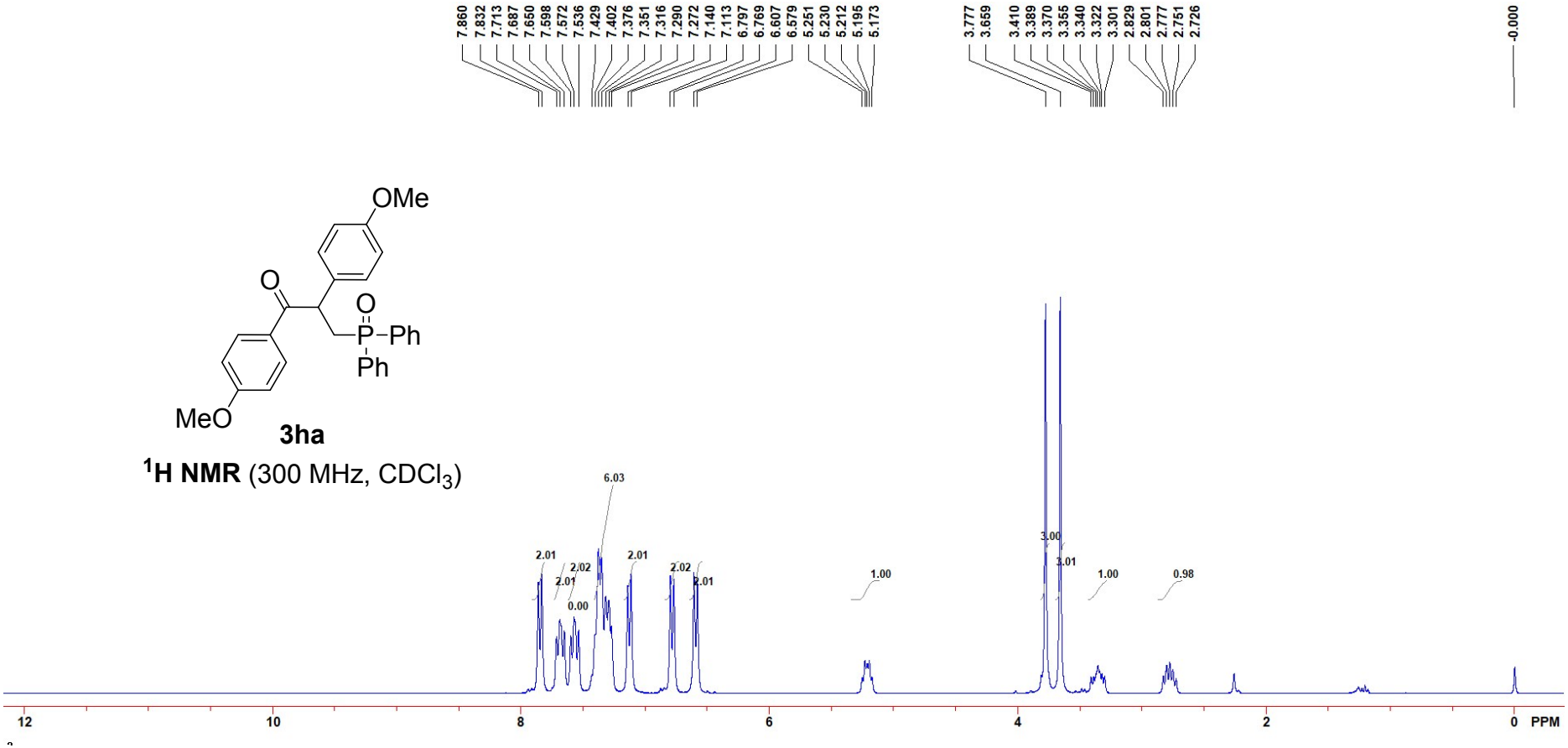
3ga

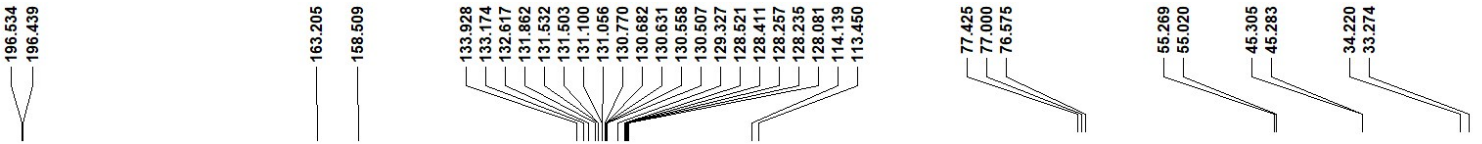
^{13}C NMR (75 MHz, $CDCl_3$)

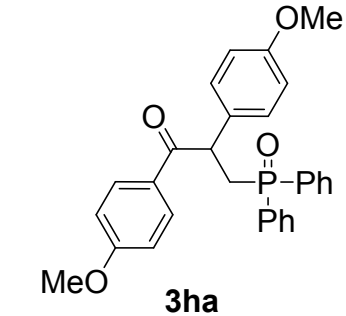


3ga

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

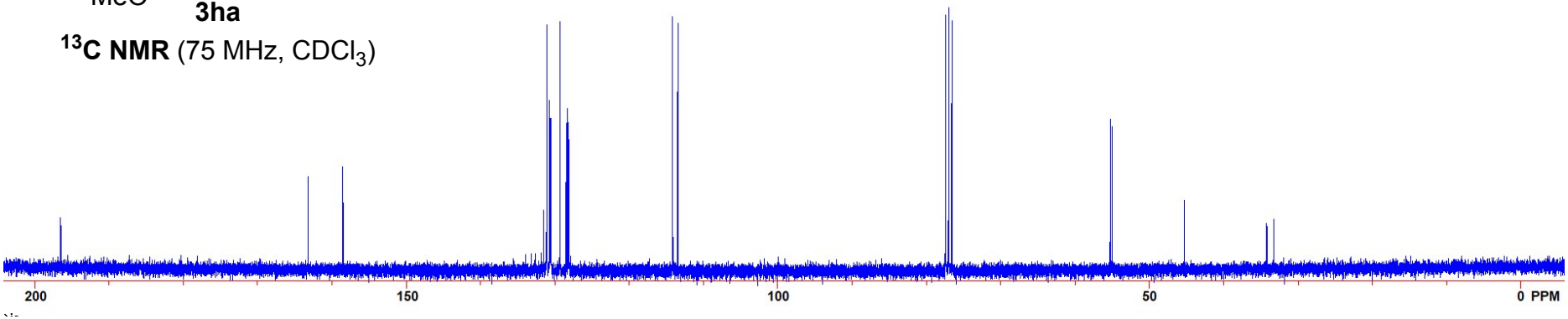

7.860
7.832
7.713
7.687
7.650
7.598
7.572
7.536
7.429
7.402
7.376
7.351
7.316
7.290
7.272
7.140
7.113
6.797
6.769
6.607
6.579
5.251
5.230
5.212
5.195
5.173
3.777
3.659
3.410
3.389
3.370
3.355
3.340
3.322
3.301
2.829
2.801
2.777
2.751
2.726
-0.000
OMe
O
O
P–Ph
Ph
MeO
3ha
1H NMR (300 MHz, CDCl3)
6.03
2.01
2.02
2.01
0.00
2.01
2.02
2.01
1.00
3.00
3.01
1.00
0.98
12
10
8
6
4
2
0
PPM

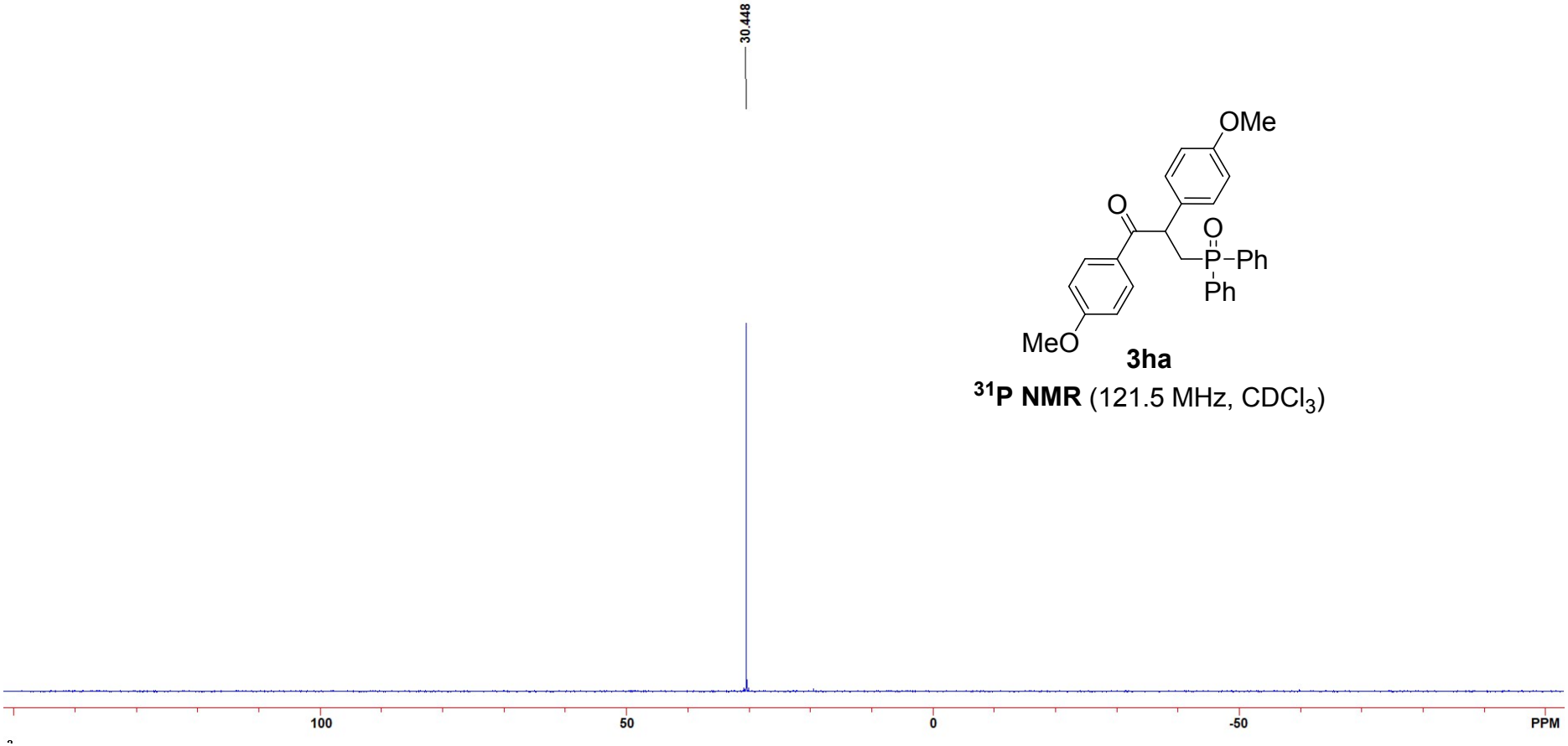




3ha

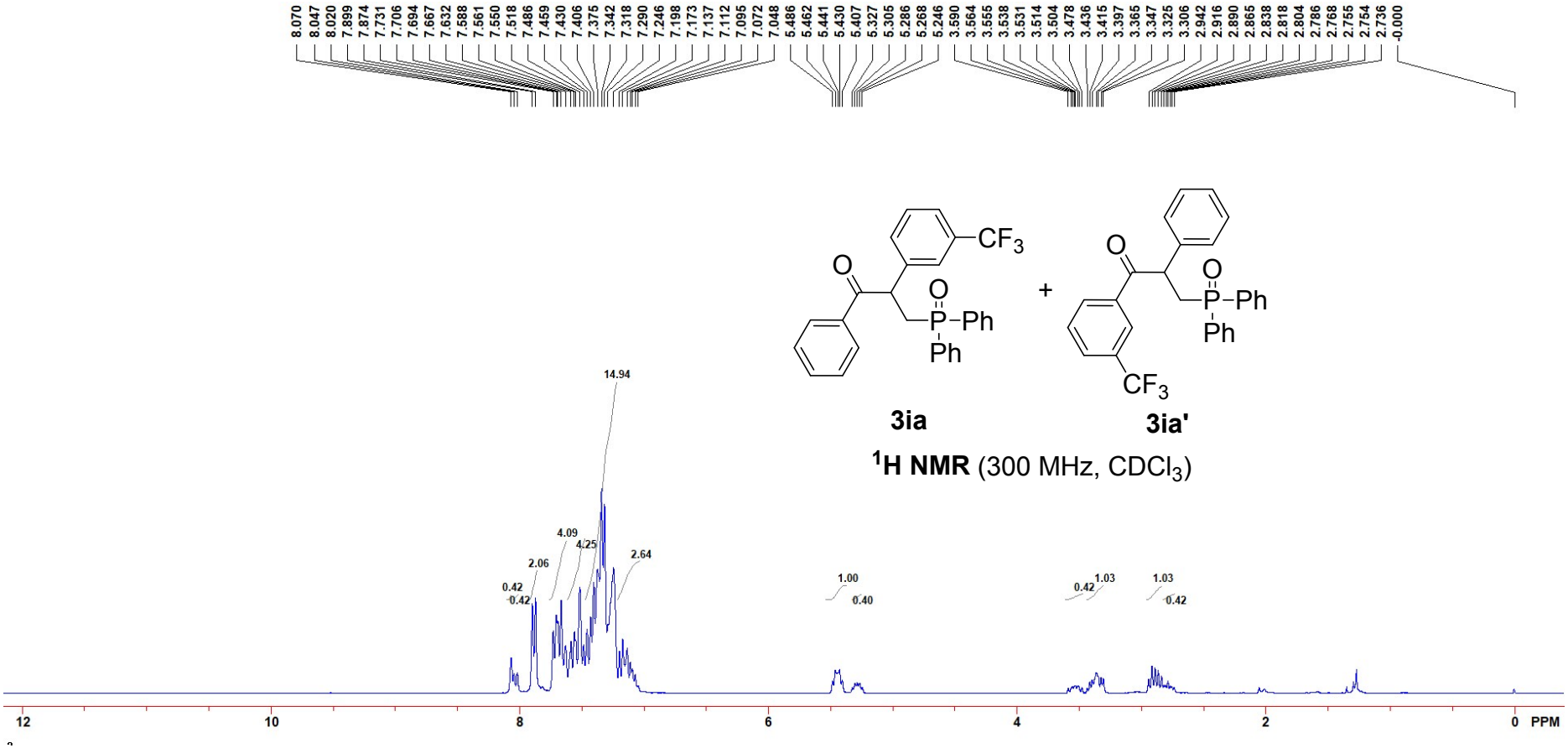
^{13}C NMR (75 MHz, $CDCl_3$)

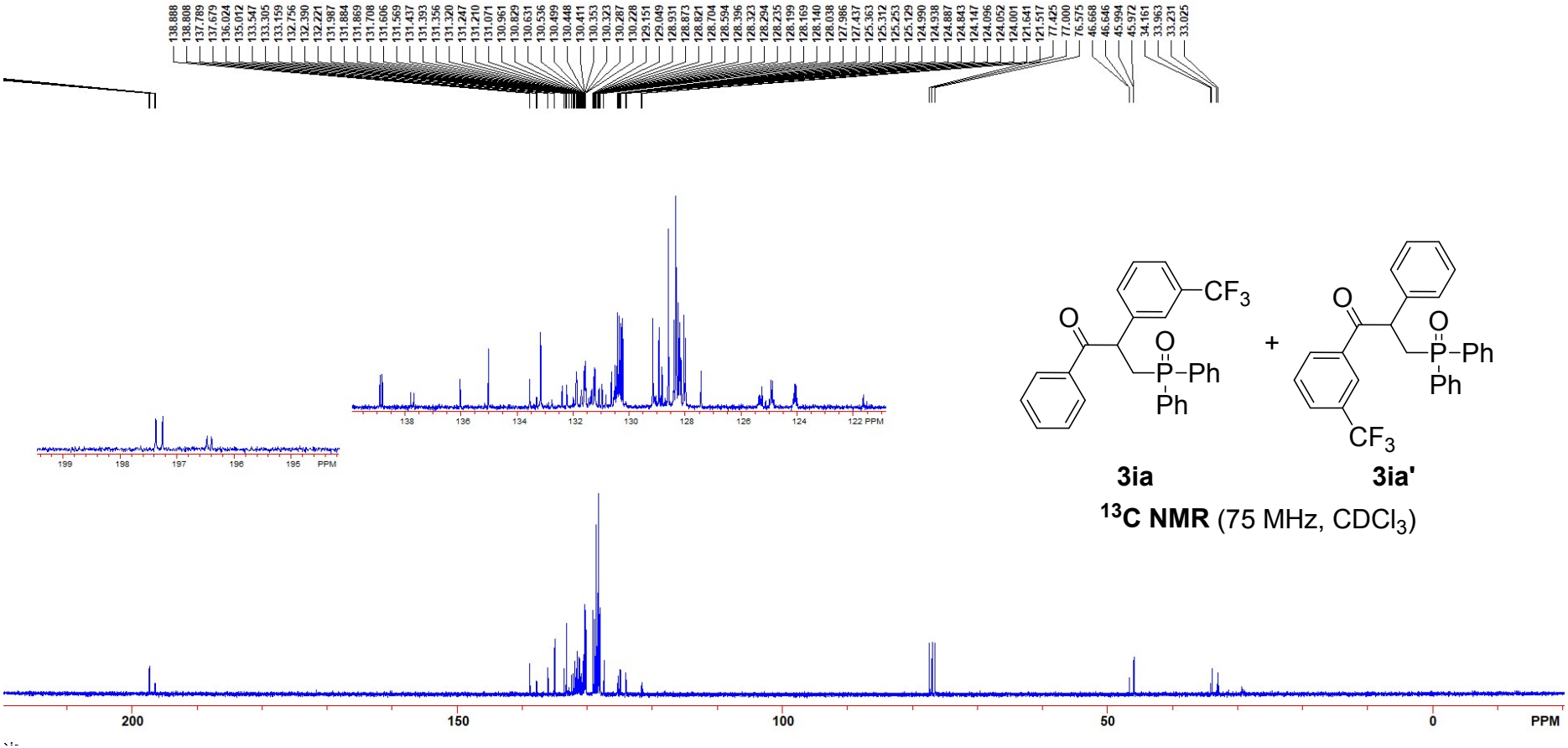


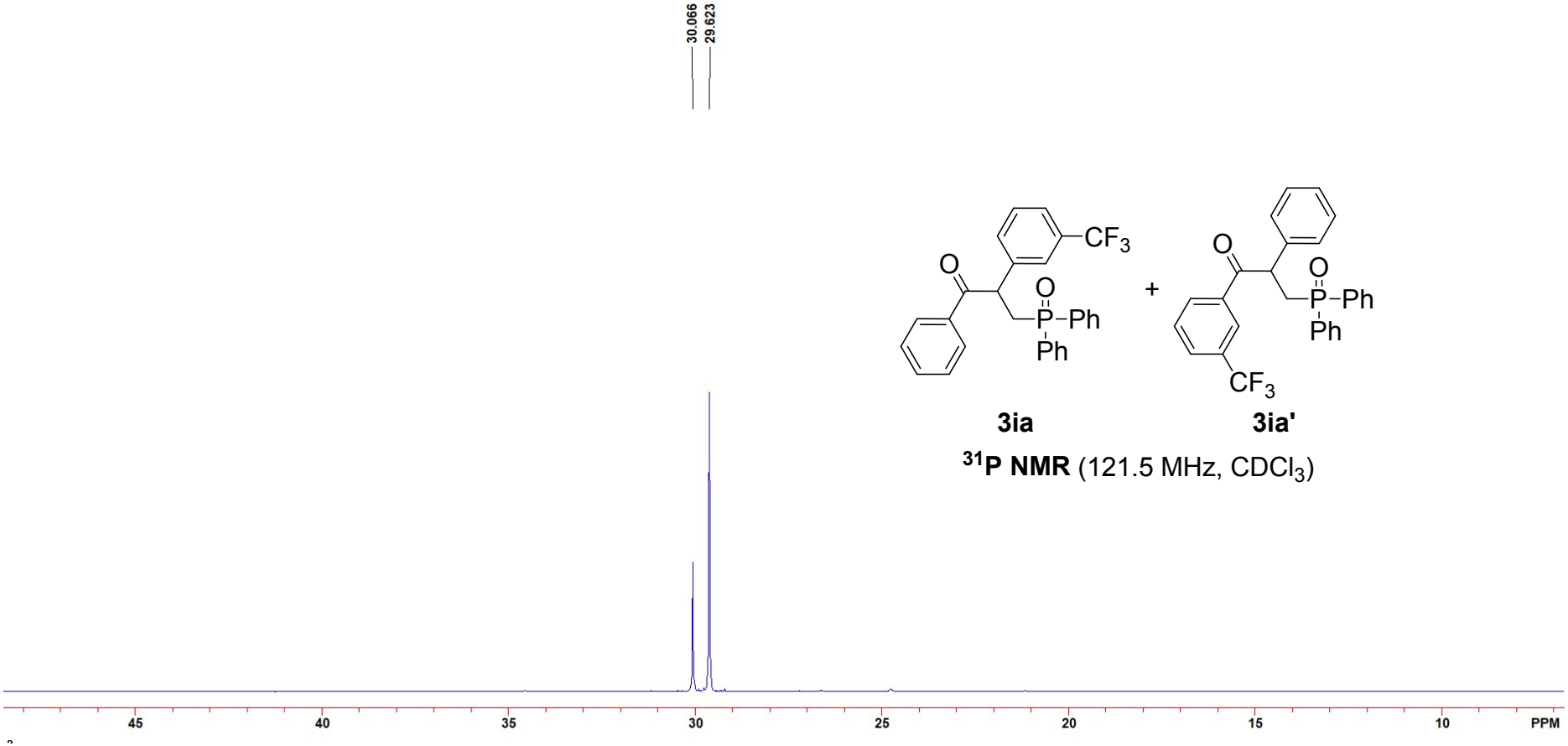


3ha

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

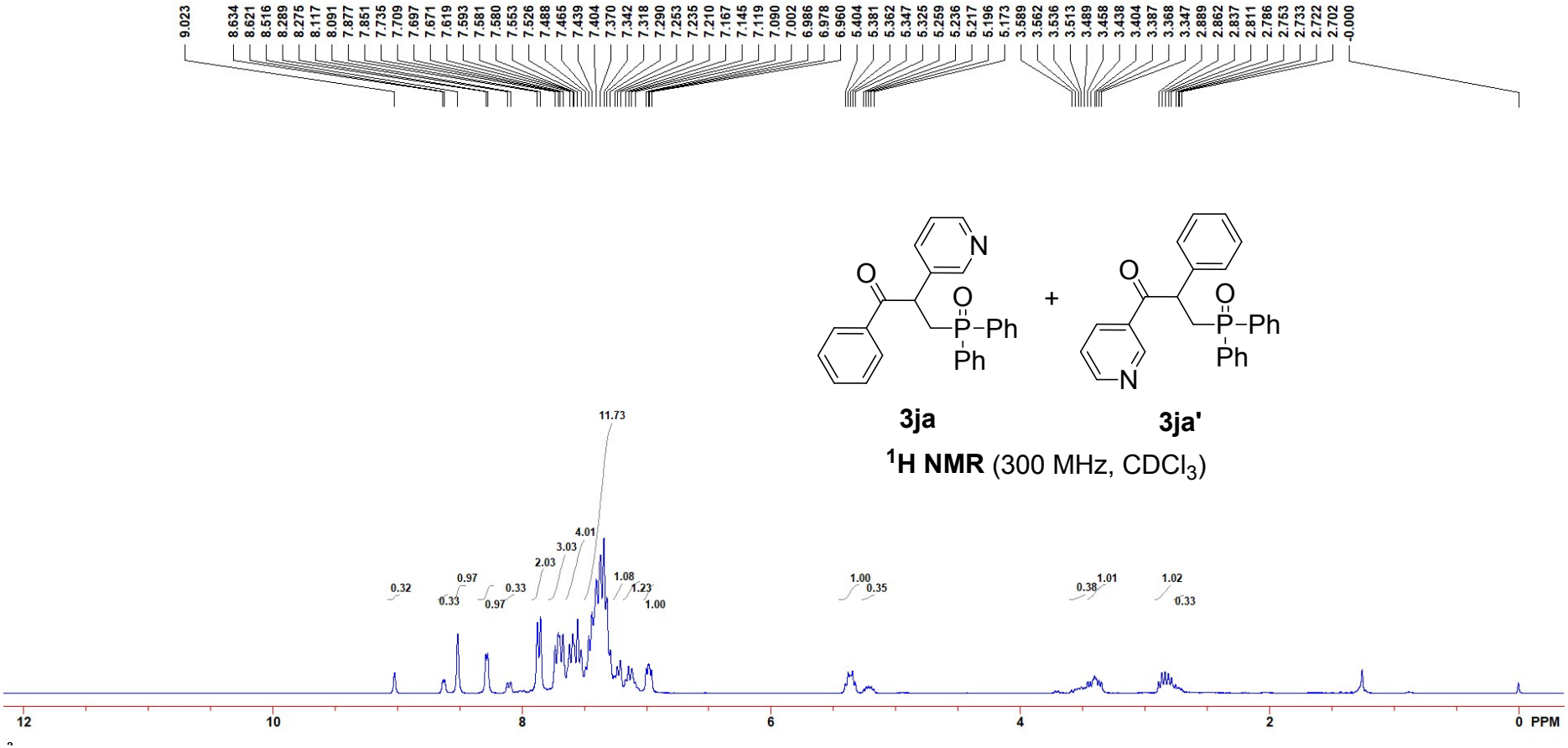

8.070
8.047
8.020
7.899
7.874
7.731
7.706
7.694
7.667
7.632
7.588
7.561
7.550
7.518
7.486
7.459
7.430
7.406
7.375
7.342
7.318
7.290
7.246
7.198
7.173
7.137
7.112
7.095
7.072
7.048
5.486
5.462
5.441
5.430
5.407
5.327
5.305
5.286
5.268
5.246
3.590
3.564
3.555
3.538
3.531
3.514
3.504
3.478
3.436
3.415
3.397
3.365
3.347
3.325
3.306
2.942
2.916
2.890
2.865
2.838
2.818
2.804
2.786
2.768
2.755
2.754
2.736
-0.000
CF3
O
O
P–Ph
Ph
+
O
O
P–Ph
Ph
CF3
3ia
3ia'
1H NMR (300 MHz, CDCl3)
14.94
4.09
4.25
2.06
2.64
0.42
0.42
1.00
0.40
0.42
1.03
1.03
0.42
12
10
8
6
4
2
0
PPM

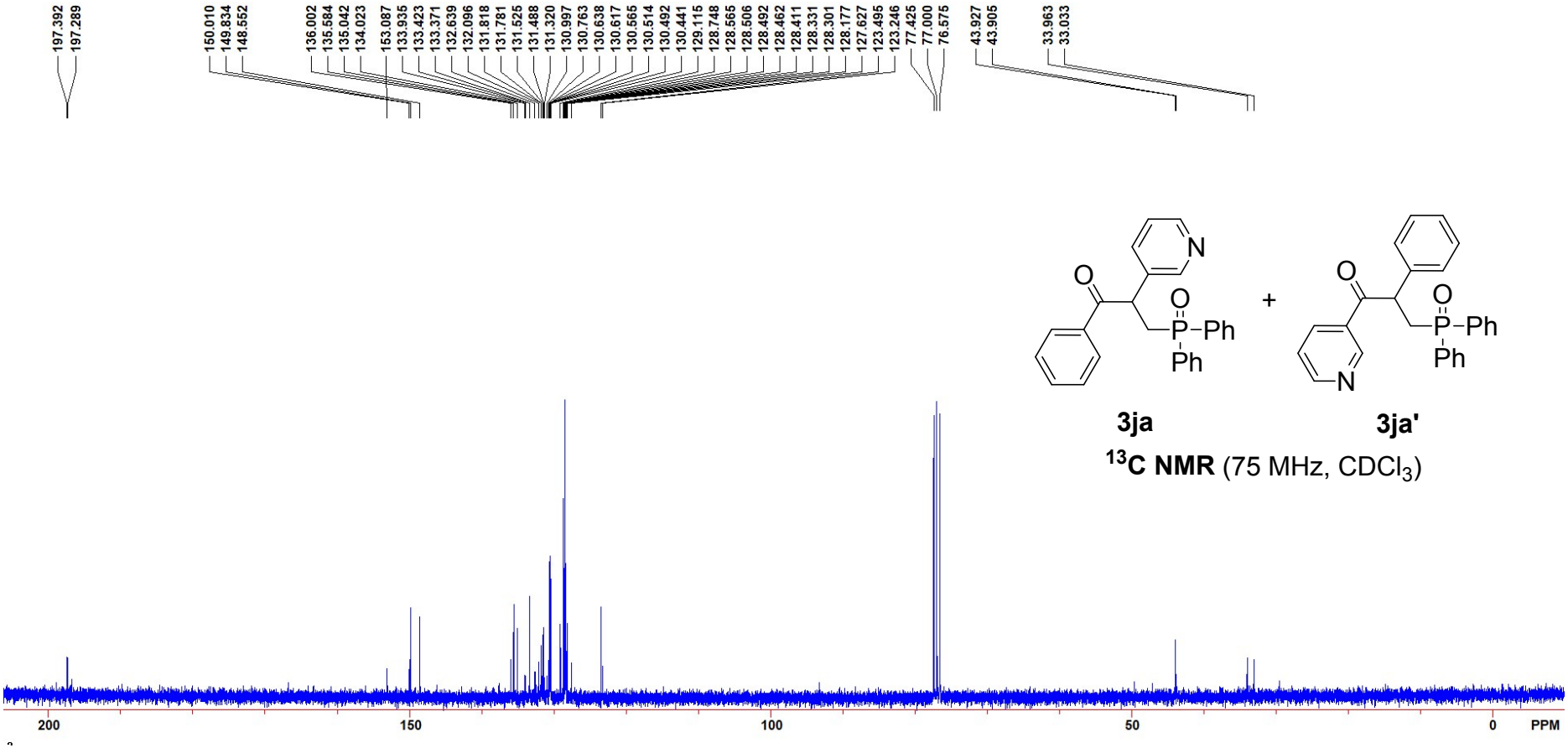

138.888
138.808
137.789
137.679
136.024
135.012
133.547
133.305
133.159
132.756
132.390
132.221
131.987
131.884
131.869
131.708
131.606
131.569
131.437
131.393
131.356
131.320
131.247
131.210
131.071
130.961
130.829
130.631
130.536
130.499
130.448
130.411
130.353
130.323
130.287
130.228
129.151
129.049
128.931
128.873
128.821
128.704
128.594
128.396
128.323
128.294
128.235
128.199
128.169
128.140
128.038
127.986
127.437
125.363
125.312
125.253
125.129
124.990
124.938
124.887
124.843
124.147
124.096
124.052
124.001
121.641
121.517
77.425
77.000
76.575
46.668
46.646
45.994
45.972
34.161
33.963
33.231
33.025
138
136
134
132
130
128
126
124
122 PPM
199
198
197
196
195
PPM
200
150
100
50
0
PPM
CF3
O
O
P–Ph
Ph
+
O
O
P–Ph
Ph
CF3
3ia
3ia'
13C NMR (75 MHz, CDCl3)



3ia **3ia'**

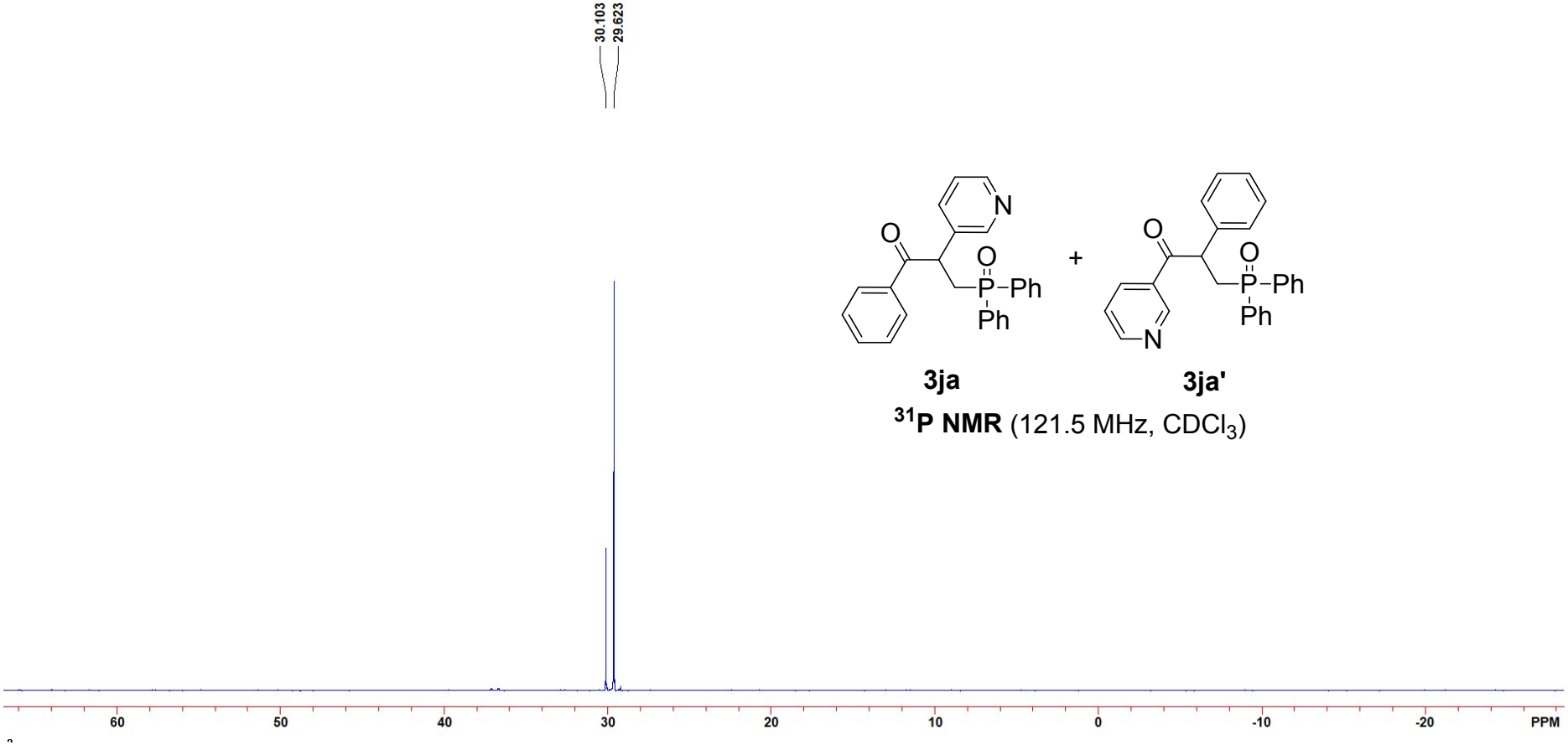
^{31}P NMR (121.5 MHz, $CDCl_3$)


9.023
8.634
8.621
8.516
8.289
8.275
8.117
8.091
7.877
7.851
7.735
7.709
7.697
7.671
7.619
7.593
7.581
7.580
7.553
7.526
7.488
7.465
7.439
7.404
7.370
7.342
7.318
7.290
7.253
7.235
7.210
7.167
7.145
7.119
7.090
7.002
6.986
6.978
6.960
5.404
5.381
5.362
5.347
5.325
5.259
5.236
5.217
5.196
5.173
3.589
3.562
3.536
3.513
3.489
3.458
3.438
3.404
3.387
3.368
3.347
2.889
2.862
2.837
2.811
2.786
2.753
2.733
2.722
2.702
-0.000
O
N
O
P–Ph
Ph
+
3ja
3ja'
1H NMR (300 MHz, CDCl3)
11.73
4.01
3.03
2.03
1.08
1.23
1.00
0.97
0.97
0.33
0.33
0.32
1.00
0.35
1.01
0.38
1.02
0.33
12
10
8
6
4
2
0 PPM



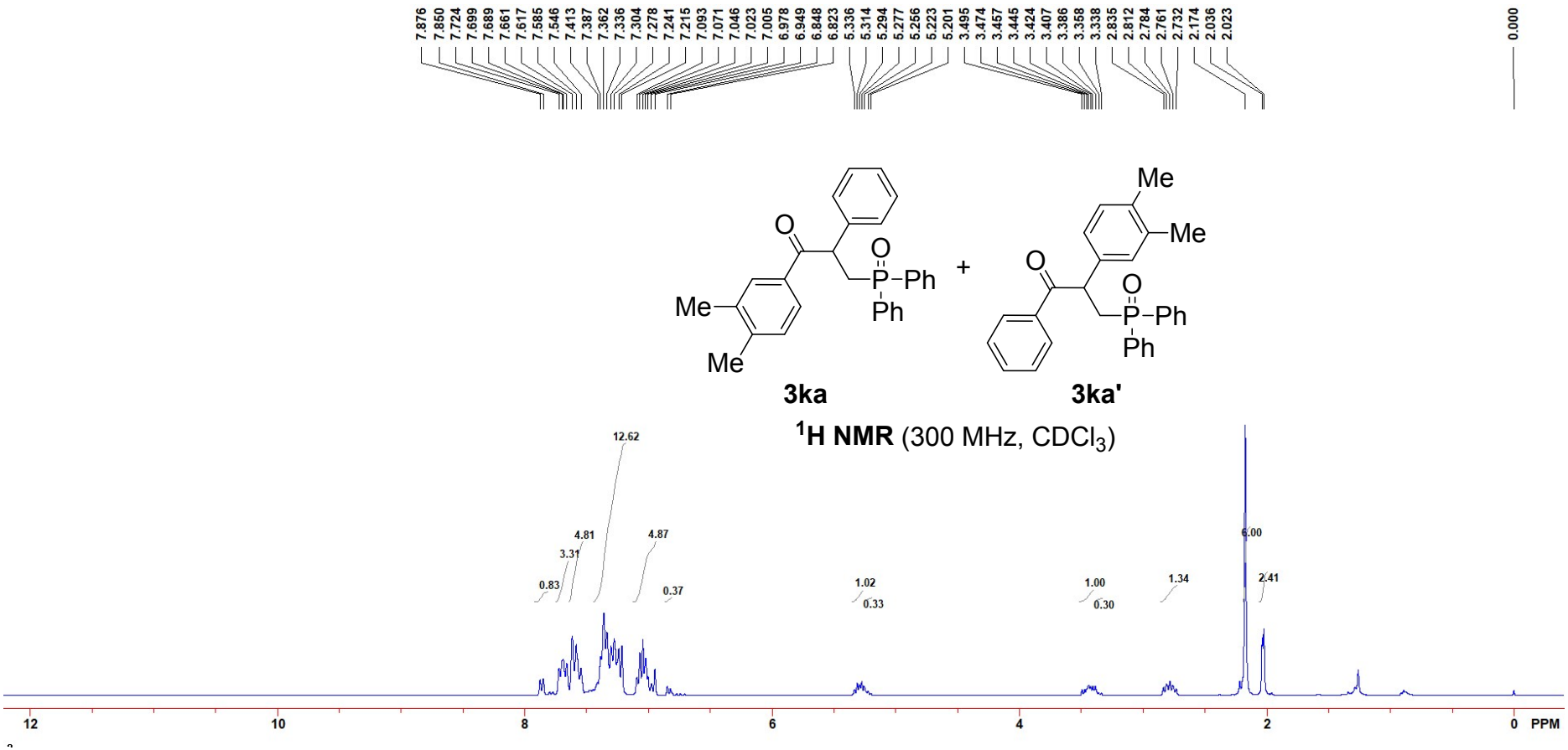
3ja **3ja'**

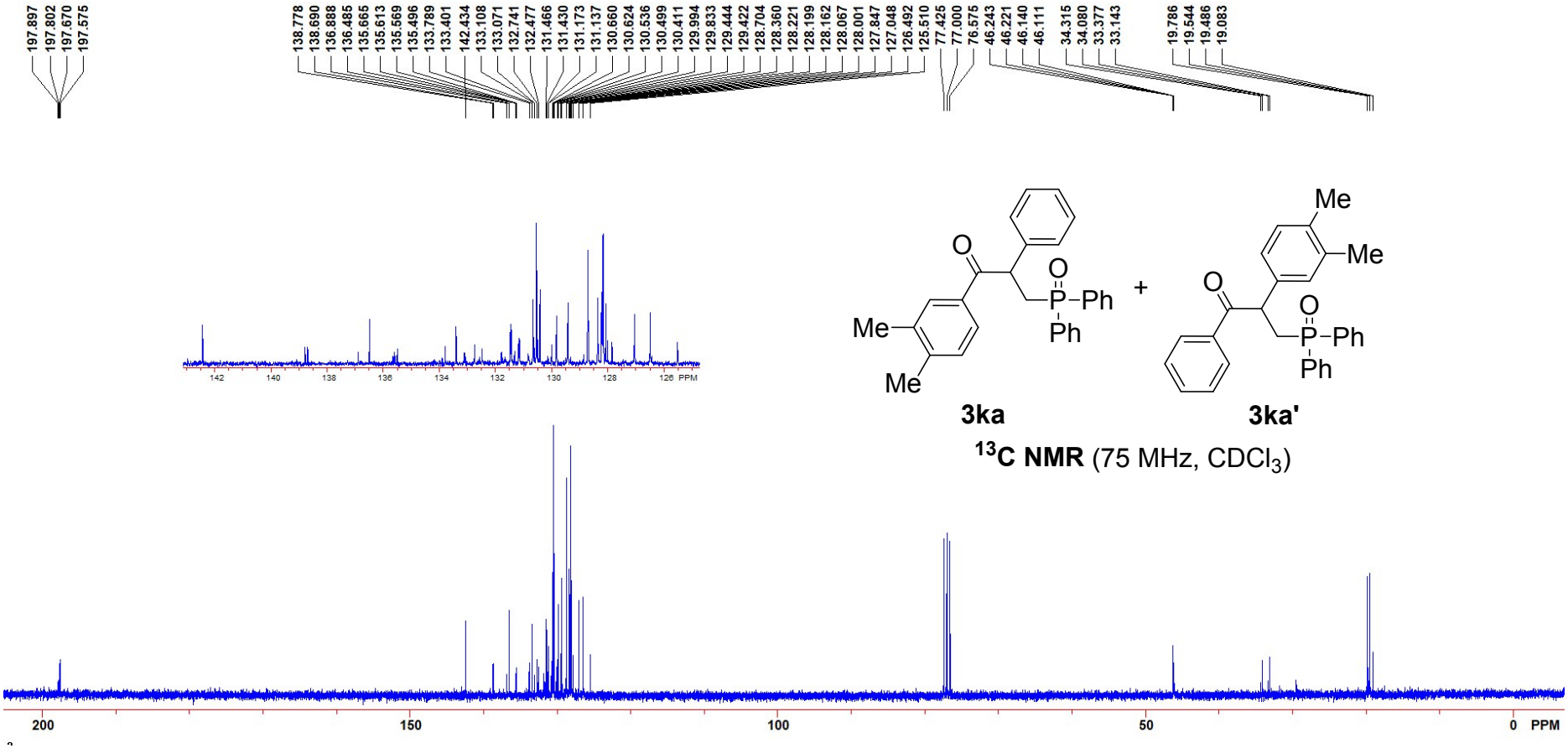
^{13}C NMR (75 MHz, $CDCl_3$)



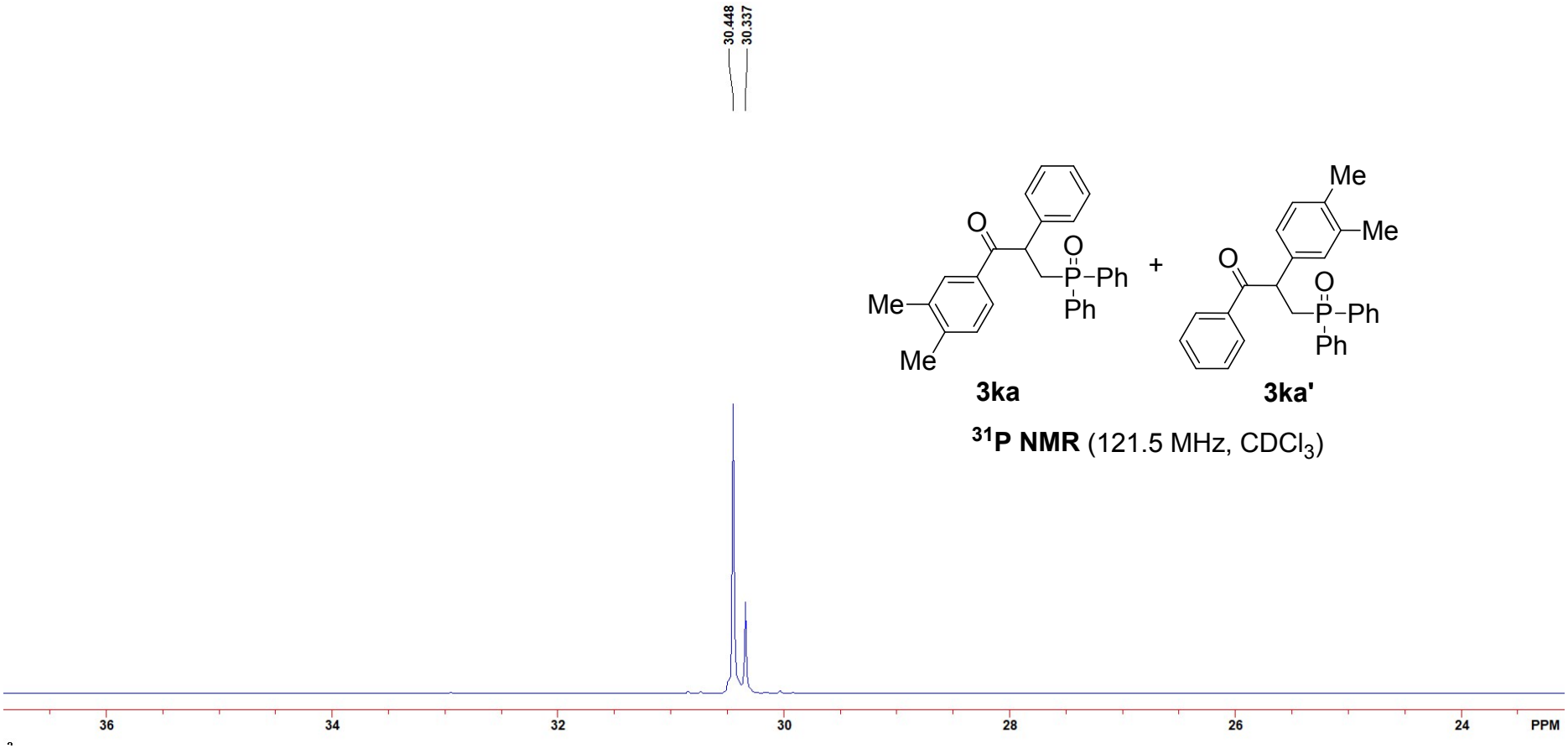
3ja **3ja'**

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


7.876
7.850
7.724
7.699
7.689
7.661
7.617
7.585
7.546
7.413
7.387
7.362
7.336
7.304
7.278
7.241
7.215
7.093
7.071
7.046
7.023
7.005
6.978
6.949
6.848
6.823
5.336
5.314
5.294
5.277
5.256
5.223
5.201
3.495
3.474
3.457
3.445
3.424
3.407
3.386
3.358
3.338
2.835
2.812
2.784
2.761
2.732
2.174
2.036
2.023
0.000
O
O
P–Ph
Ph
Me
Me
+
Me
Me
O
O
P–Ph
Ph
3ka
3ka'
1H NMR (300 MHz, CDCl3)
12.62
4.81
4.87
3.31
0.83
0.37
1.02
0.33
1.00
0.30
1.34
6.00
2.41
12
10
8
6
4
2
0
PPM

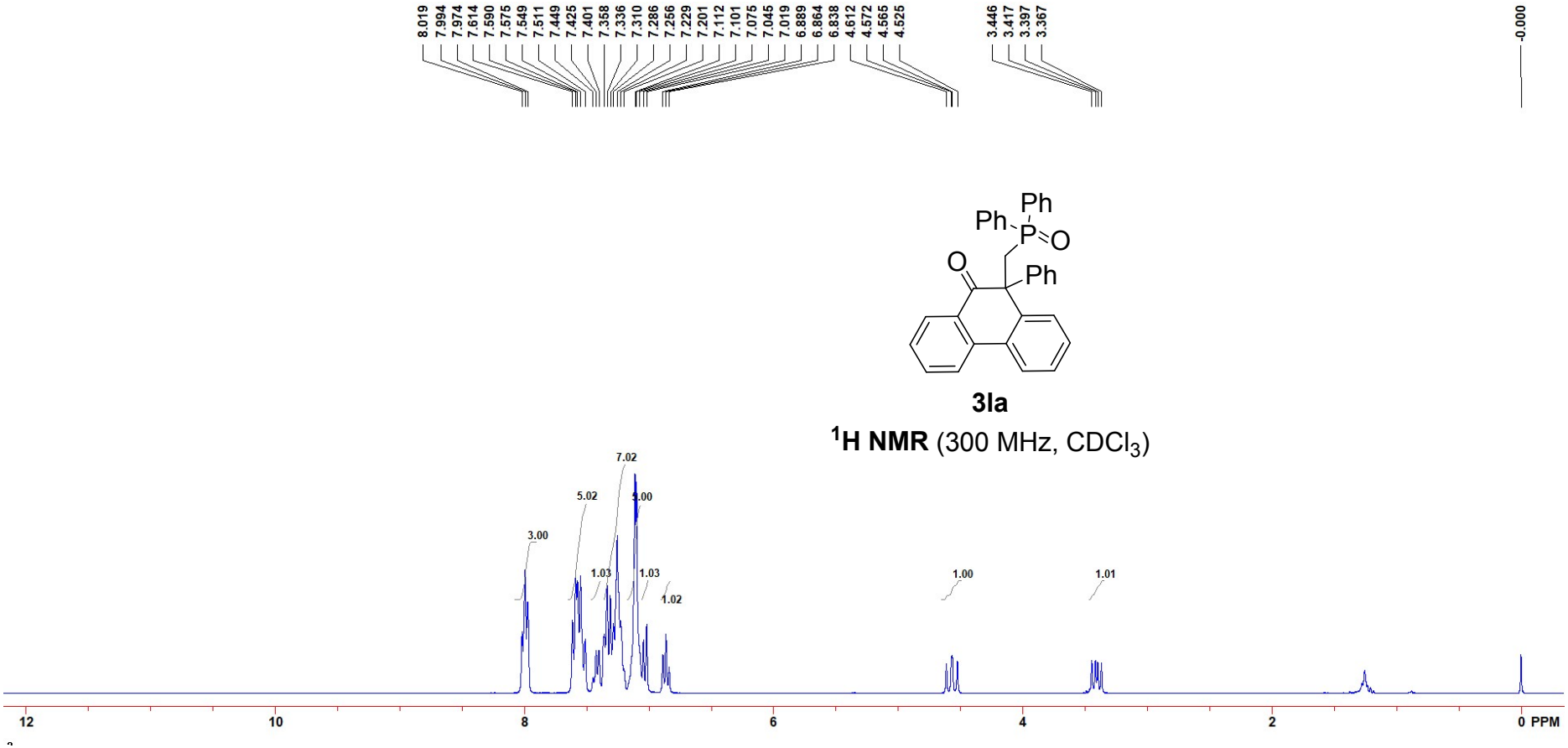


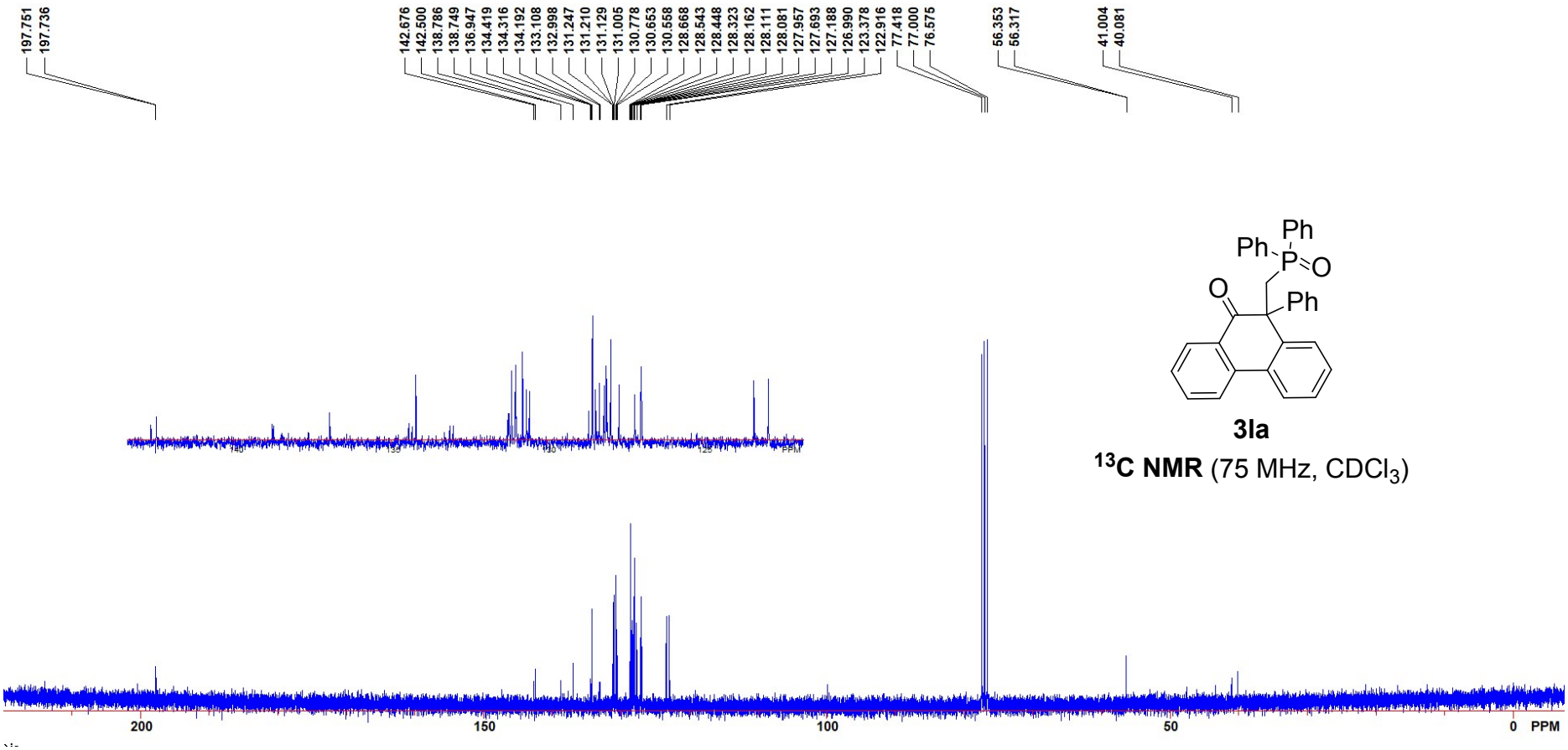
^{13}C NMR (75 MHz, $CDCl_3$)



3ka **3ka'**

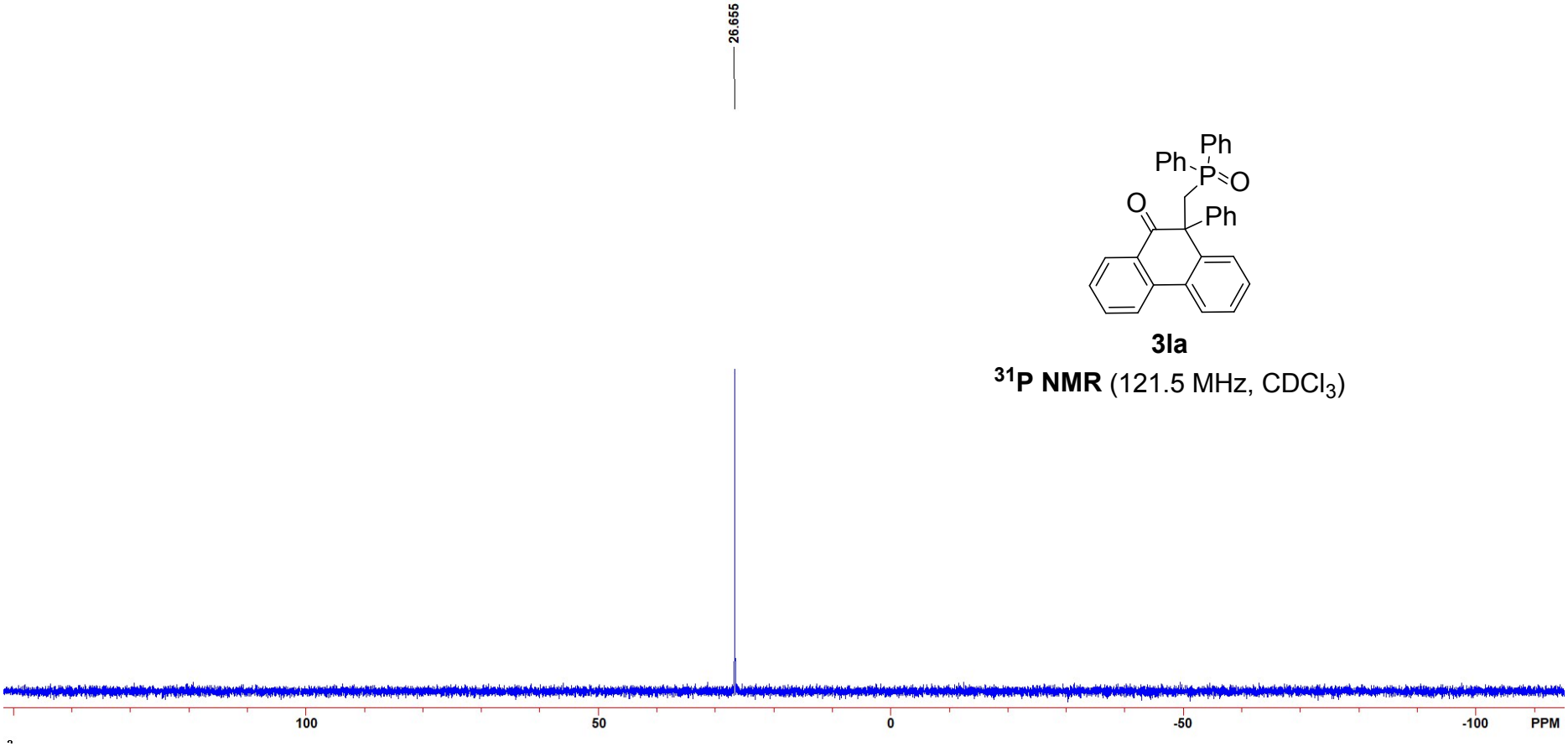
^{31}P NMR (121.5 MHz, $CDCl_3$)


8.019
7.994
7.974
7.614
7.590
7.575
7.549
7.511
7.449
7.425
7.401
7.358
7.336
7.310
7.286
7.256
7.229
7.201
7.112
7.101
7.075
7.045
7.019
6.889
6.864
6.838
4.612
4.572
4.565
4.525
3.446
3.417
3.397
3.367
-0.000
Ph
Ph
P
O
O
Ph
3la
1H NMR (300 MHz, CDCl3)
7.02
5.02
3.00
3.00
1.03
1.03
1.02
1.00
1.01
12
10
8
6
4
2
0 PPM



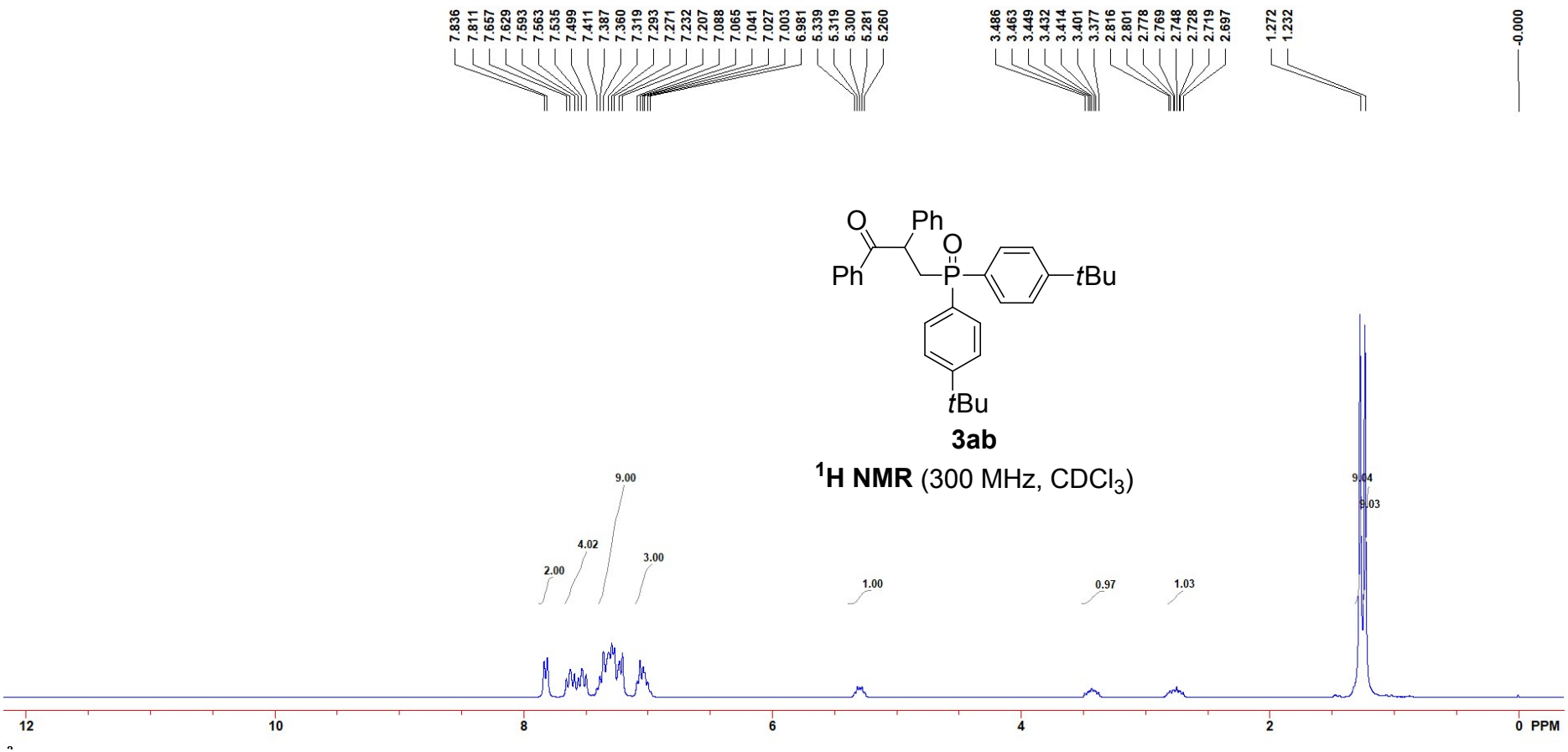
3la

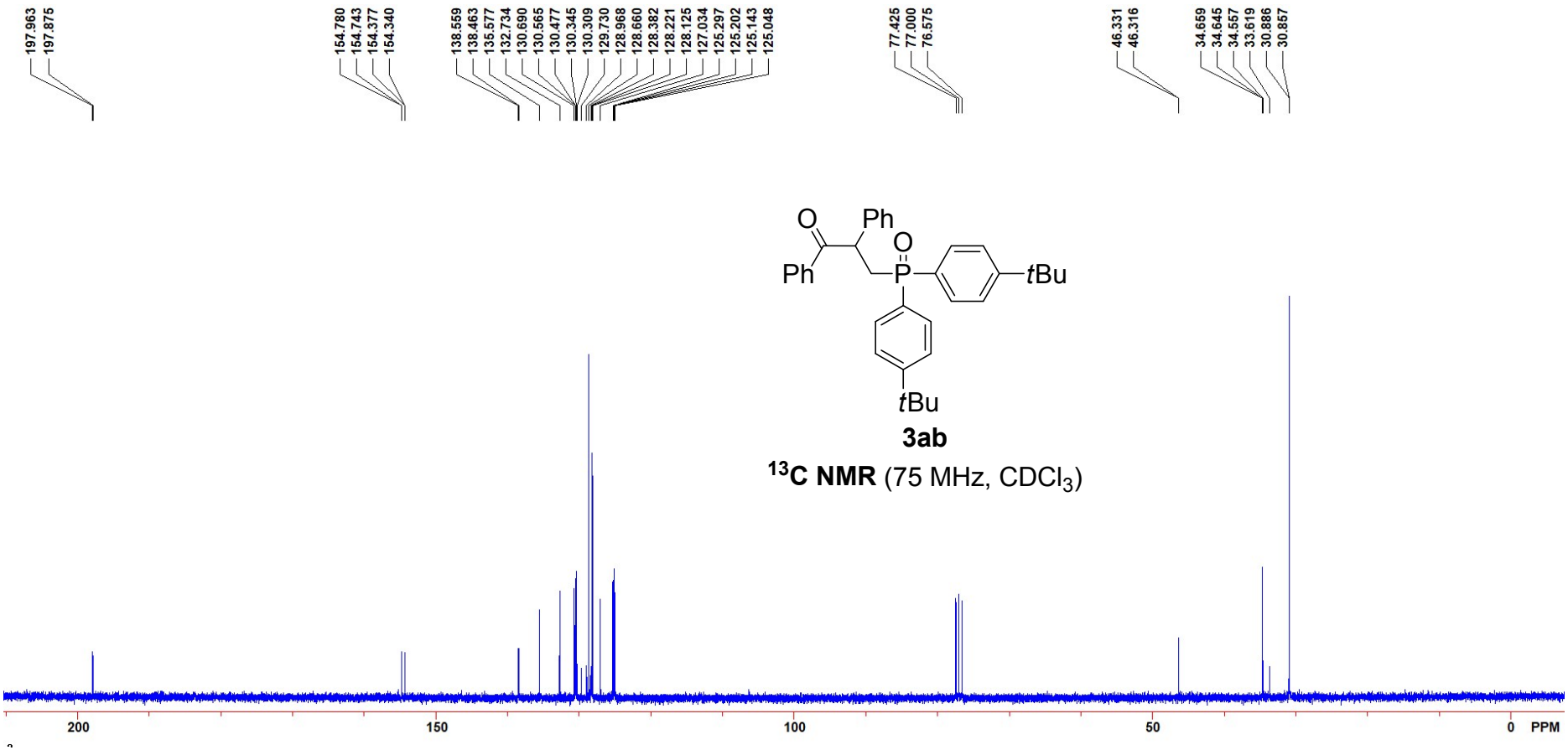
^{13}C NMR (75 MHz, $CDCl_3$)



3la

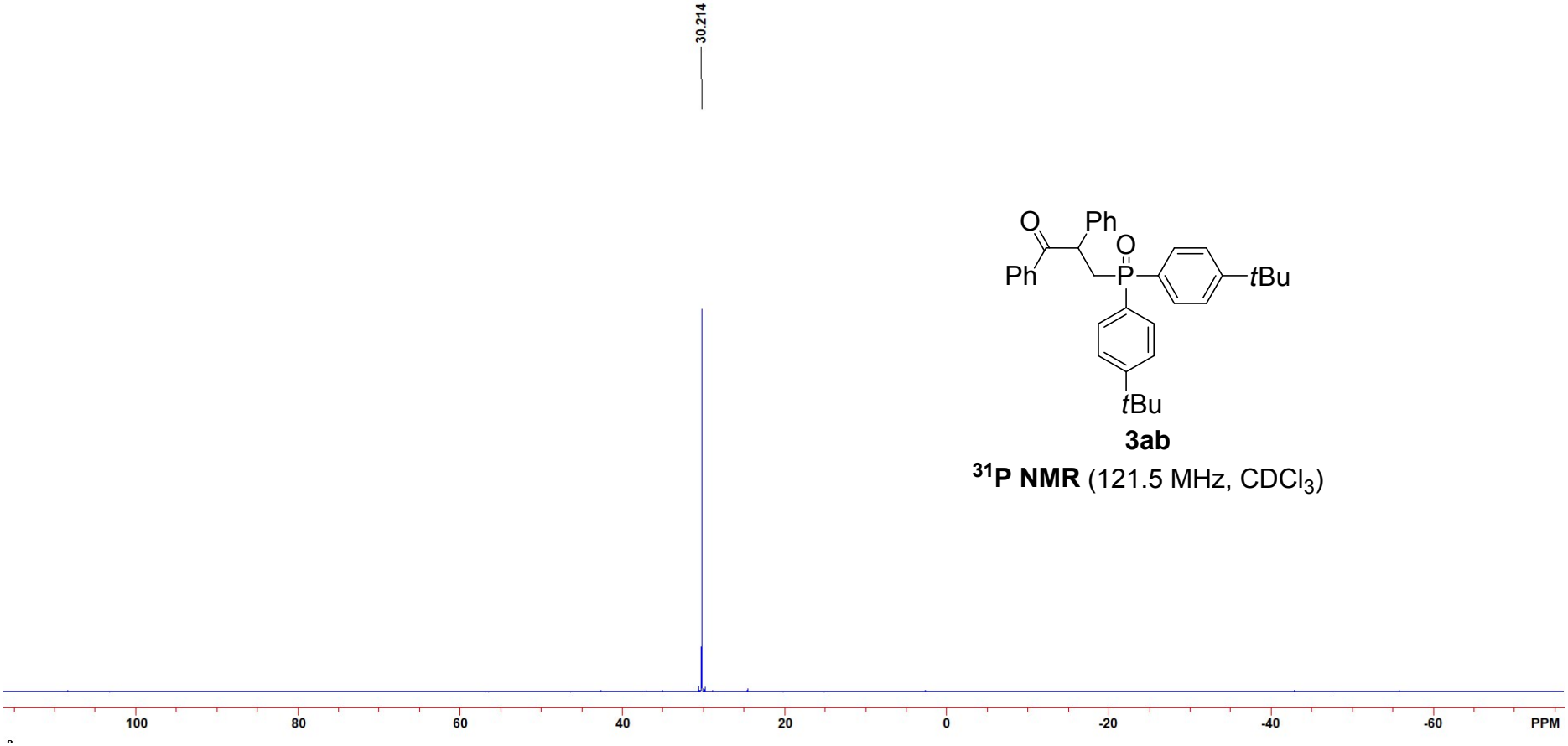
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.836
7.811
7.657
7.629
7.593
7.563
7.535
7.499
7.411
7.387
7.360
7.319
7.293
7.271
7.232
7.207
7.088
7.065
7.041
7.027
7.003
6.981
5.339
5.319
5.300
5.281
5.260
3.486
3.463
3.449
3.432
3.414
3.401
3.377
2.816
2.801
2.778
2.769
2.748
2.728
2.719
2.697
1.272
1.232
-0.000
O
Ph
O
Ph
P
tBu
tBu
3ab
1H NMR (300 MHz, CDCl3)
9.00
4.02
3.00
2.00
1.00
0.97
1.03
9.04
9.03
12
10
8
6
4
2
0 PPM



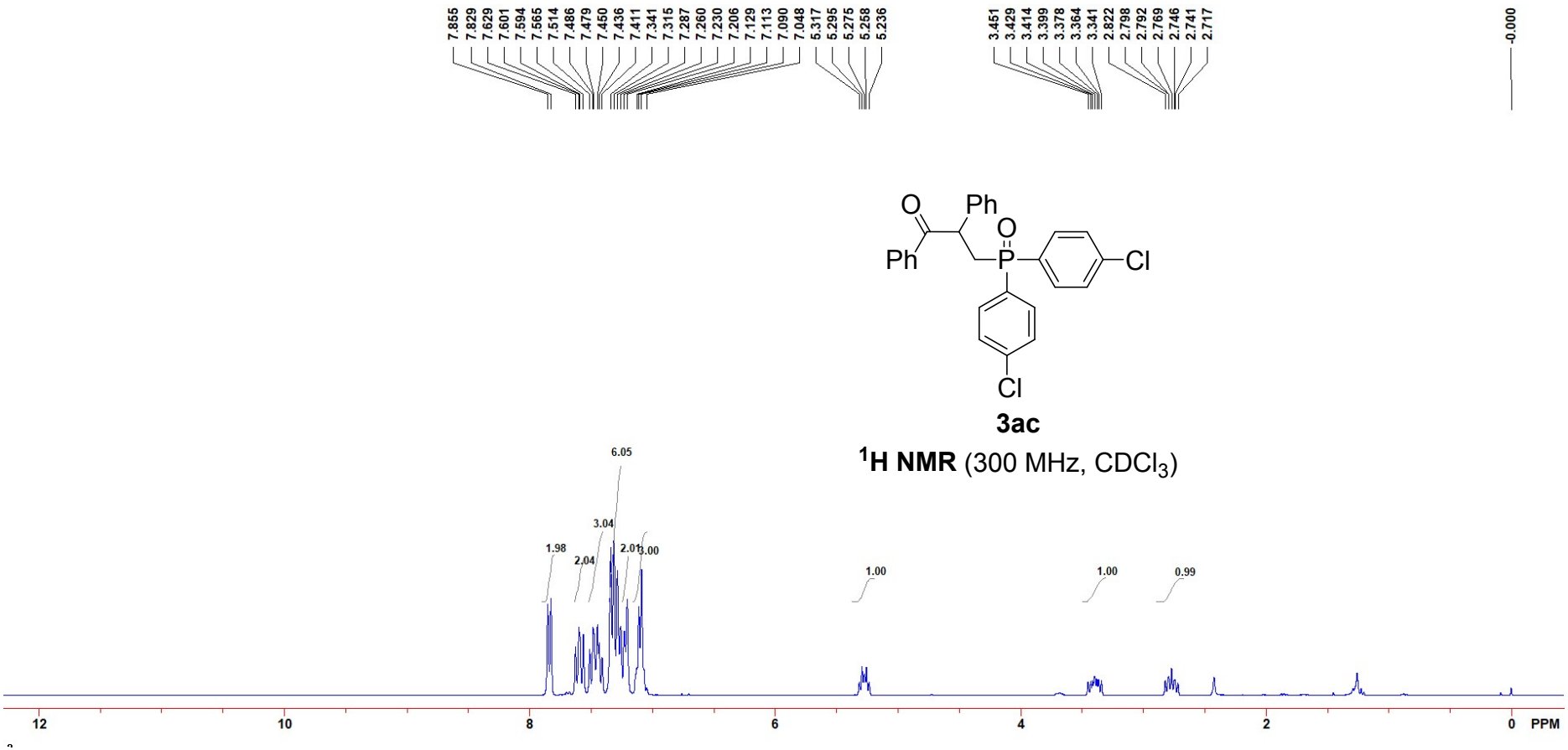
3ab

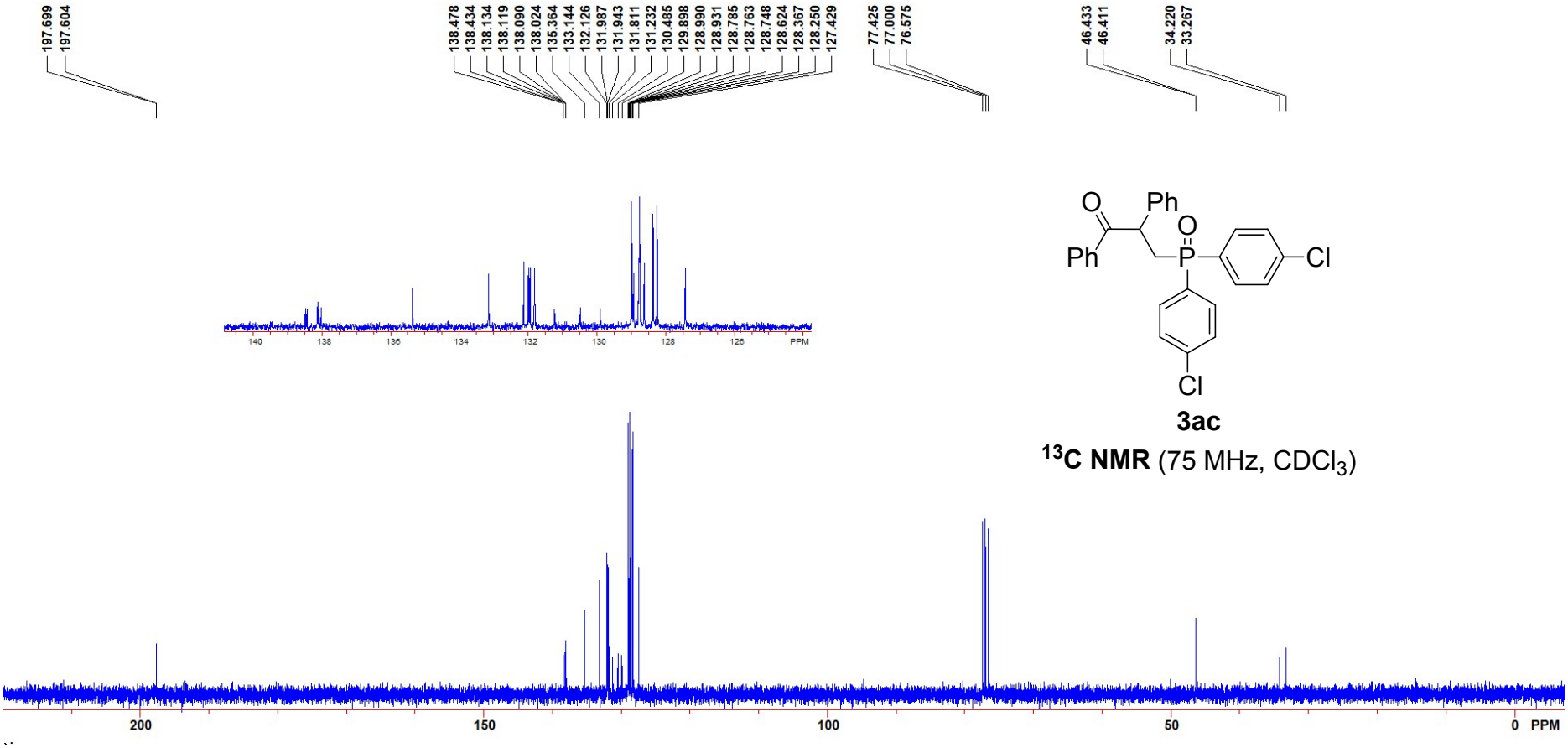
^{13}C NMR (75 MHz, $CDCl_3$)



3ab

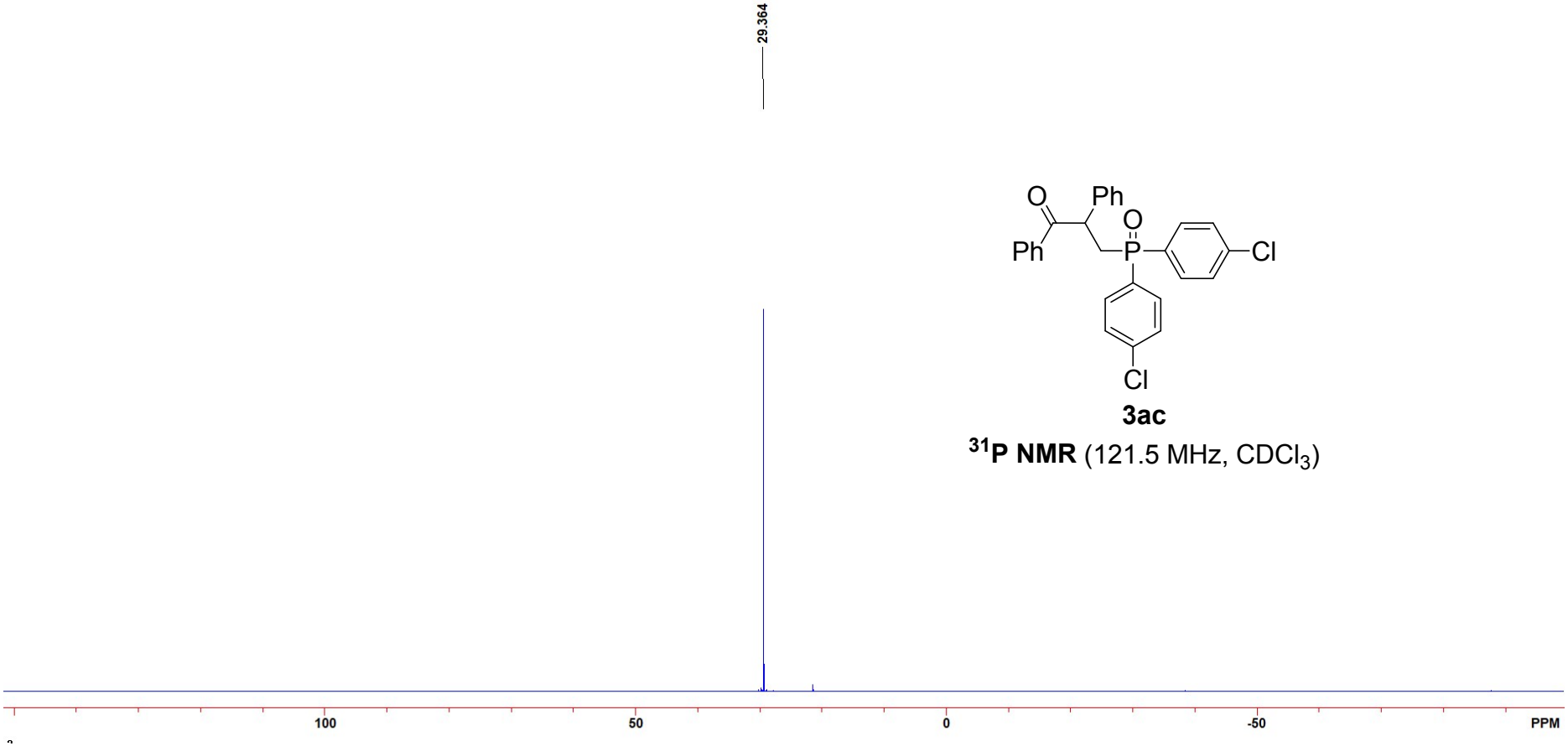
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.855
7.829
7.629
7.601
7.594
7.565
7.514
7.486
7.479
7.450
7.436
7.411
7.341
7.315
7.287
7.260
7.230
7.206
7.129
7.113
7.090
7.048
5.317
5.295
5.275
5.258
5.236
3.451
3.429
3.414
3.399
3.378
3.364
3.341
2.822
2.798
2.792
2.769
2.746
2.741
2.717
-0.000
O
Ph
O
Ph
P
Cl
Cl
3ac
1H NMR (300 MHz, CDCl3)
6.05
3.04
1.98
2.04
2.01
3.00
1.00
1.00
0.99
12
10
8
6
4
2
0
PPM



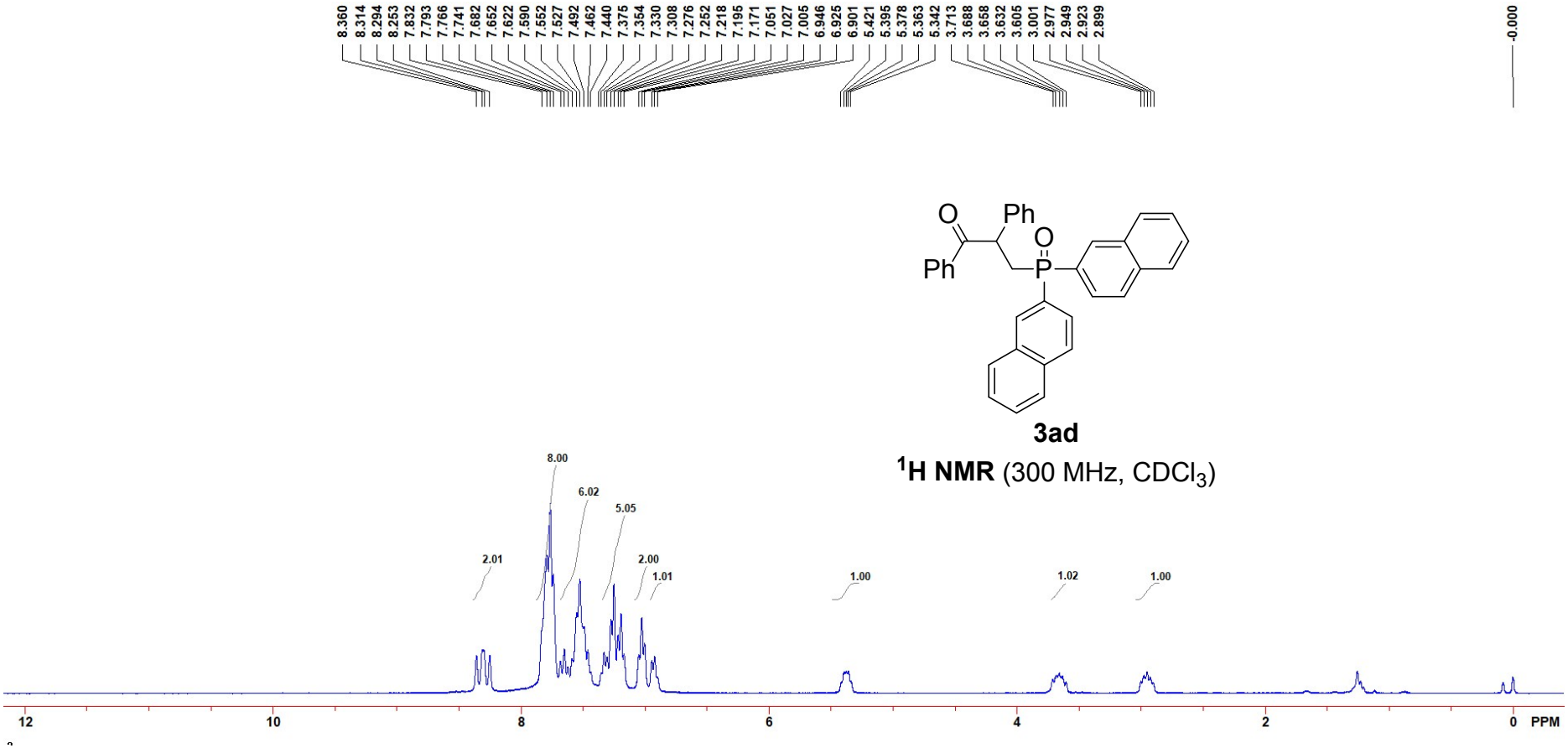
3ac

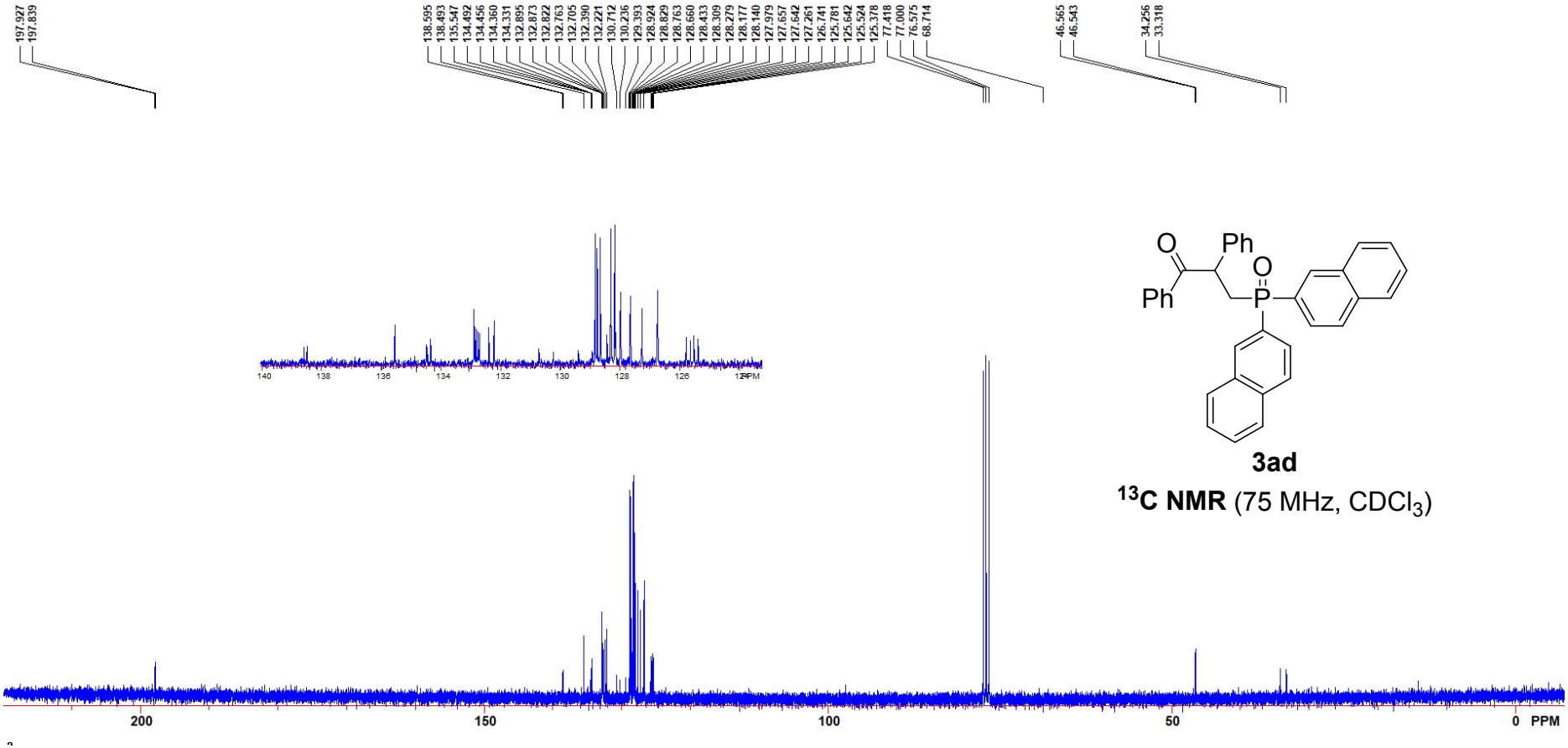
^{13}C NMR (75 MHz, $CDCl_3$)



3ac

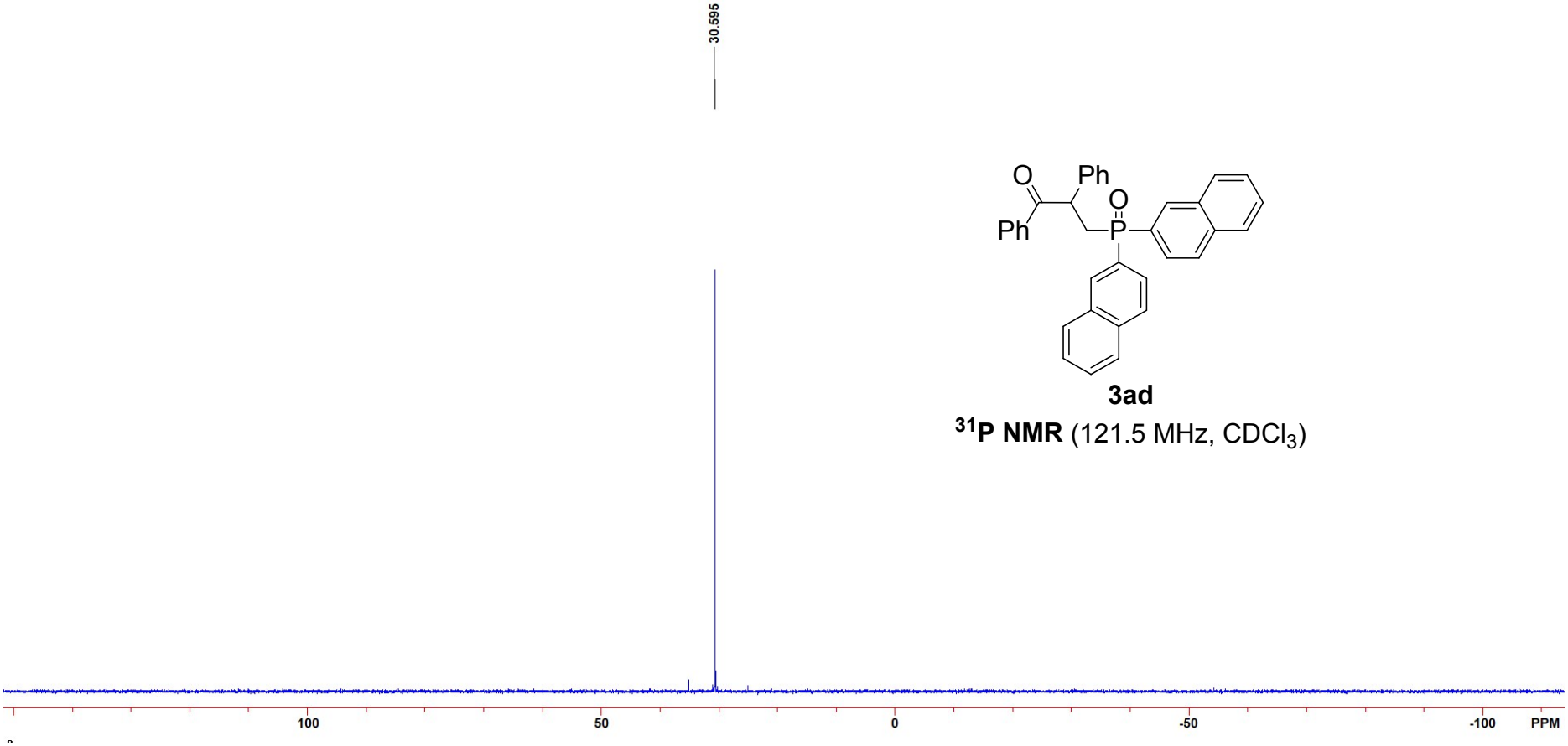
^{31}P NMR (121.5 MHz, $CDCl_3$)


8.360
8.314
8.294
8.253
7.832
7.793
7.766
7.741
7.682
7.652
7.622
7.590
7.552
7.527
7.492
7.462
7.440
7.375
7.354
7.330
7.308
7.276
7.252
7.218
7.195
7.171
7.051
7.027
7.005
6.946
6.925
6.901
5.421
5.395
5.378
5.363
5.342
3.713
3.688
3.658
3.632
3.605
3.001
2.977
2.949
2.923
2.899
-0.000
O
Ph
O
Ph
P
3ad
1H NMR (300 MHz, CDCl3)
8.00
6.02
5.05
2.01
2.00
1.01
1.00
1.02
1.00
12
10
8
6
4
2
0
PPM



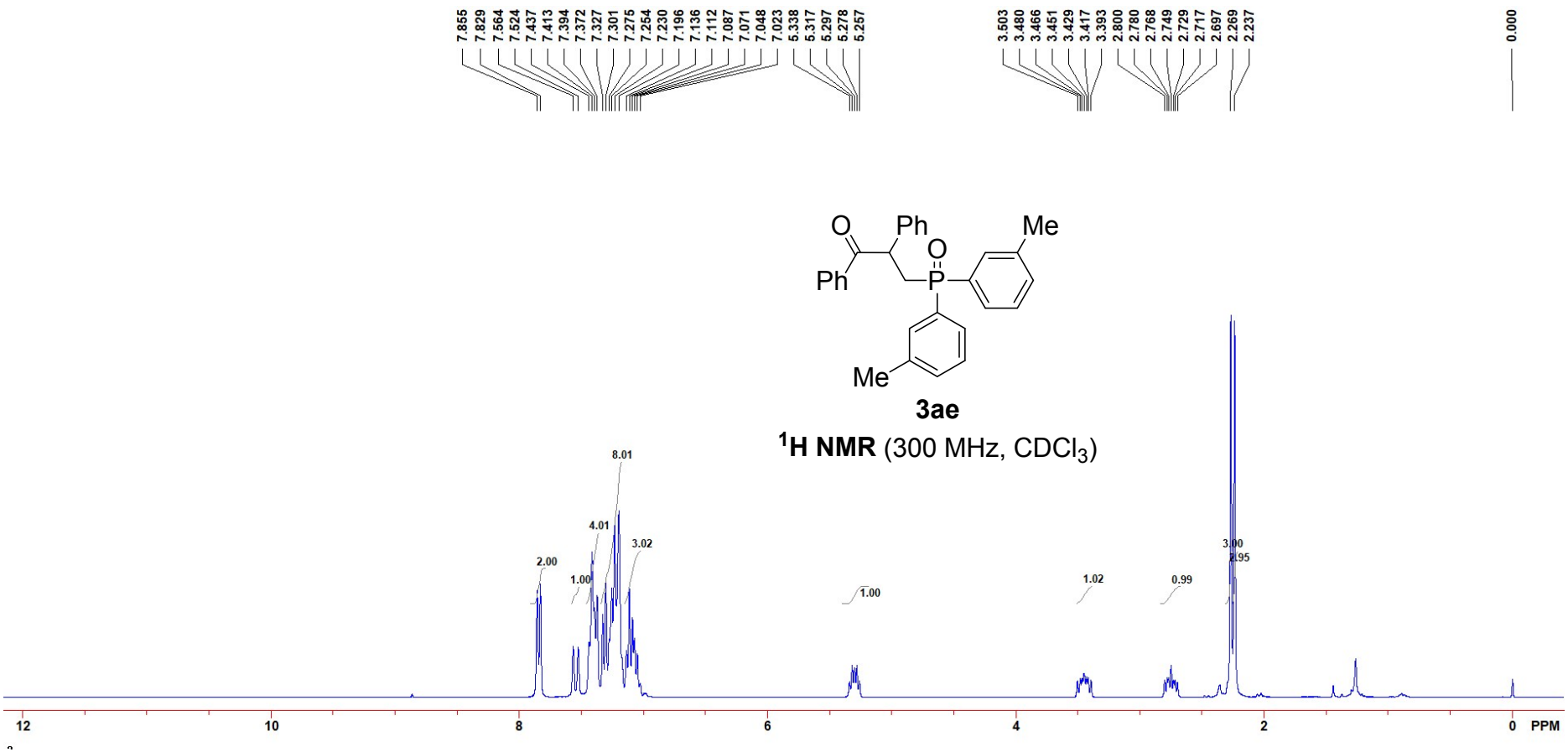
3ad

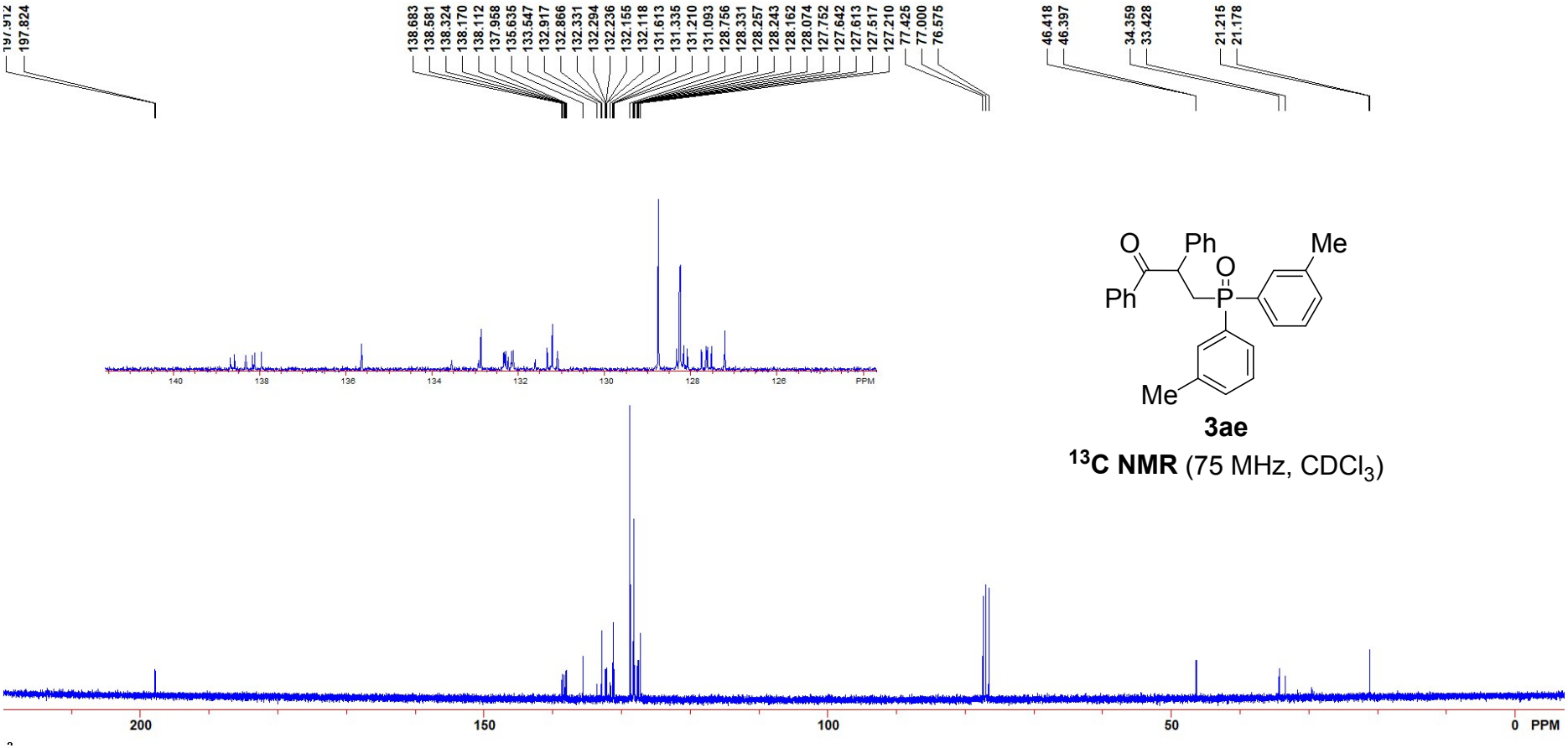
^{13}C NMR (75 MHz, $CDCl_3$)



3ad

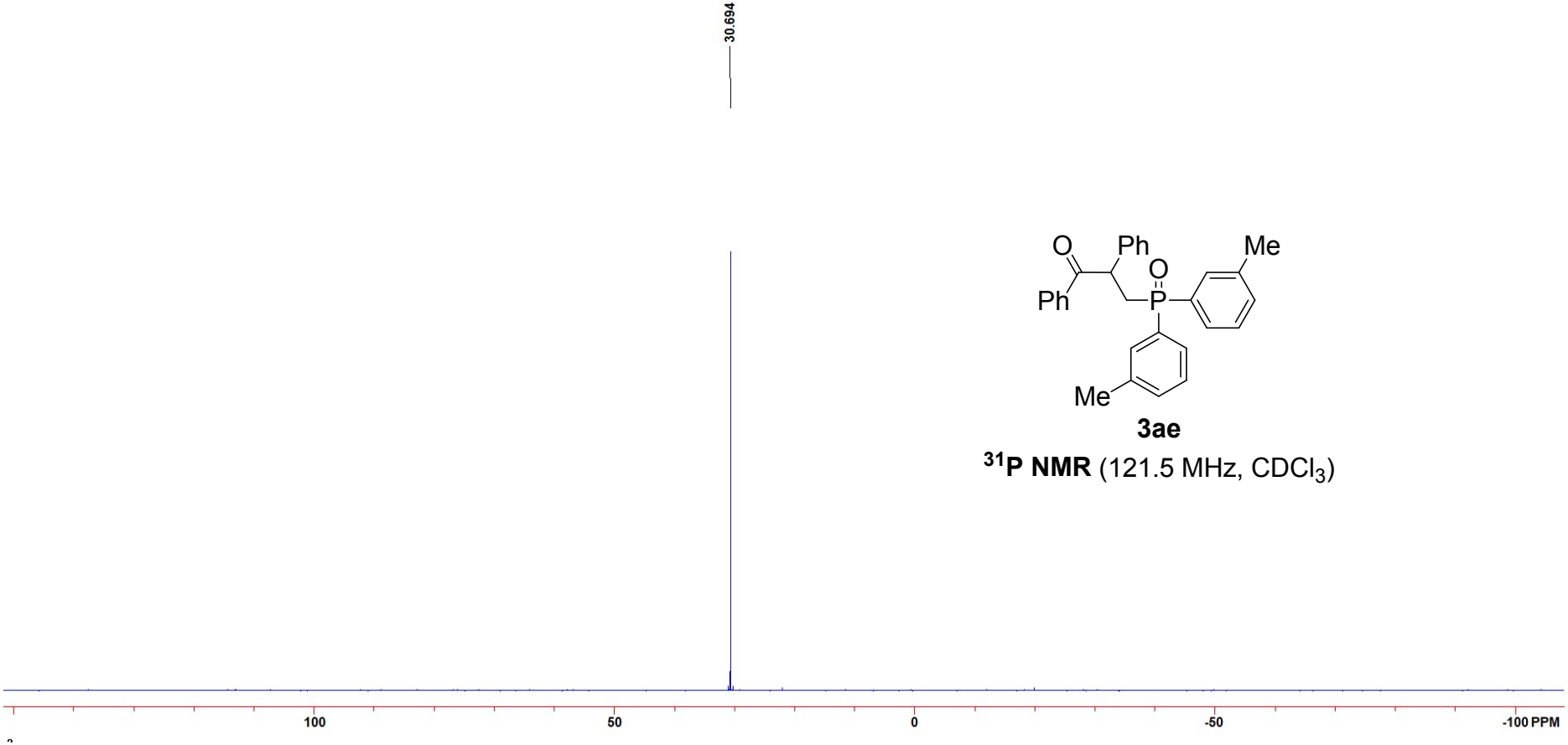
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.855
7.829
7.564
7.524
7.437
7.413
7.394
7.372
7.327
7.301
7.275
7.254
7.230
7.196
7.136
7.112
7.087
7.071
7.048
7.023
5.338
5.317
5.297
5.278
5.257
3.503
3.480
3.466
3.451
3.429
3.417
3.393
2.800
2.780
2.768
2.749
2.729
2.717
2.697
2.269
2.237
0.000
O
Ph
Me
O
Ph
P
Me
3ae
1H NMR (300 MHz, CDCl3)
8.01
4.01
3.02
2.00
1.00
1.00
1.02
0.99
3.00
2.95
12
10
8
6
4
2
0
PPM



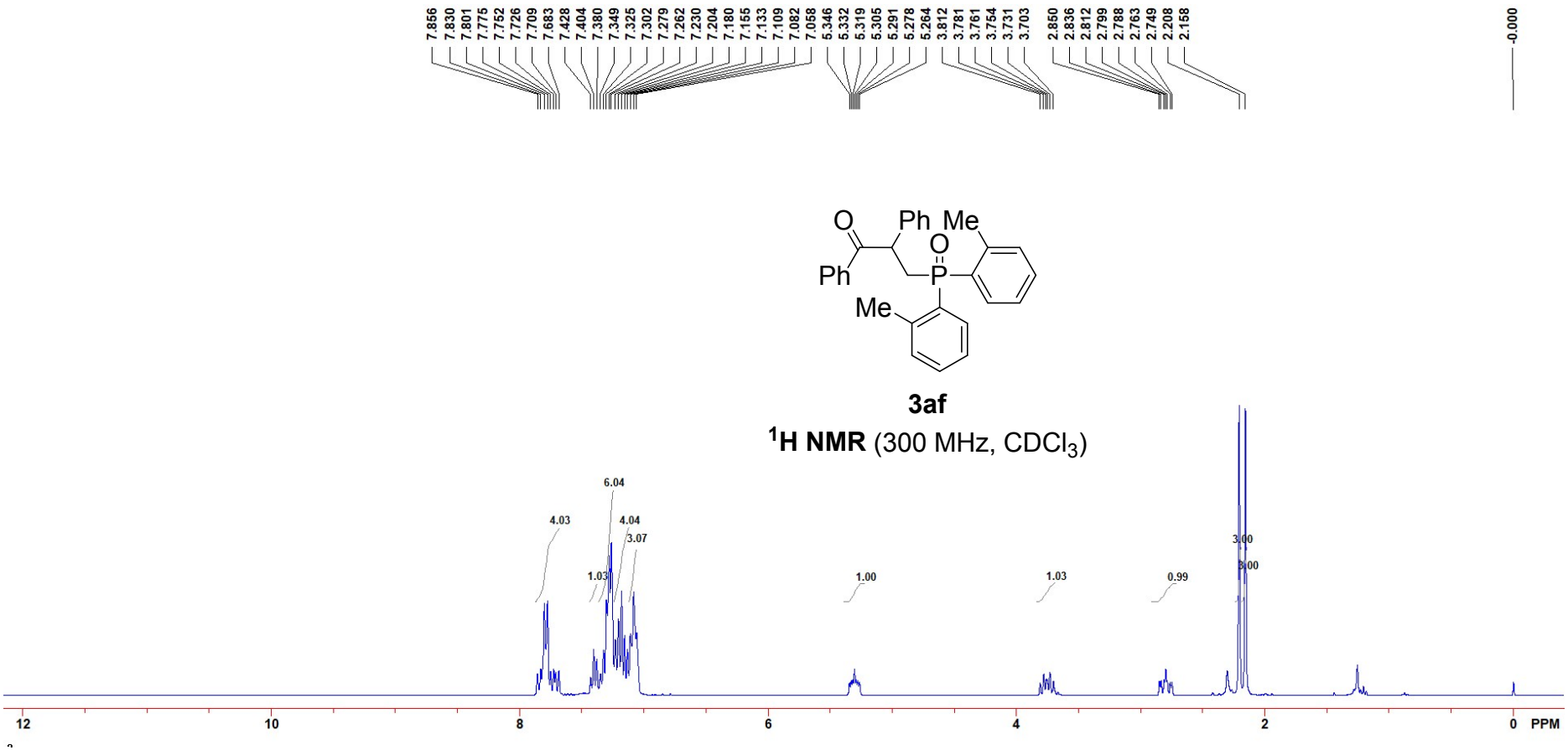
3ae

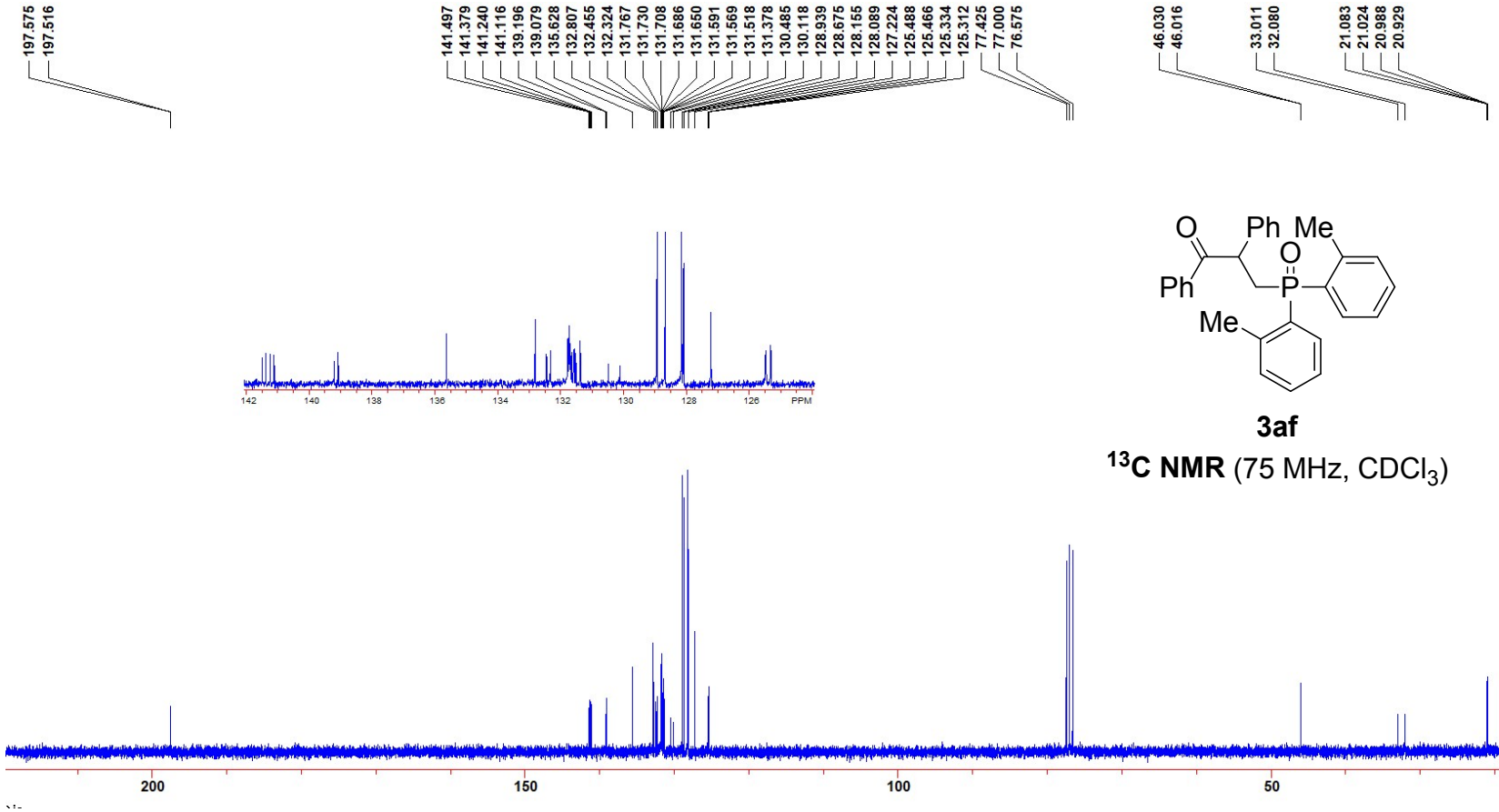
^{13}C NMR (75 MHz, $CDCl_3$)



3ae

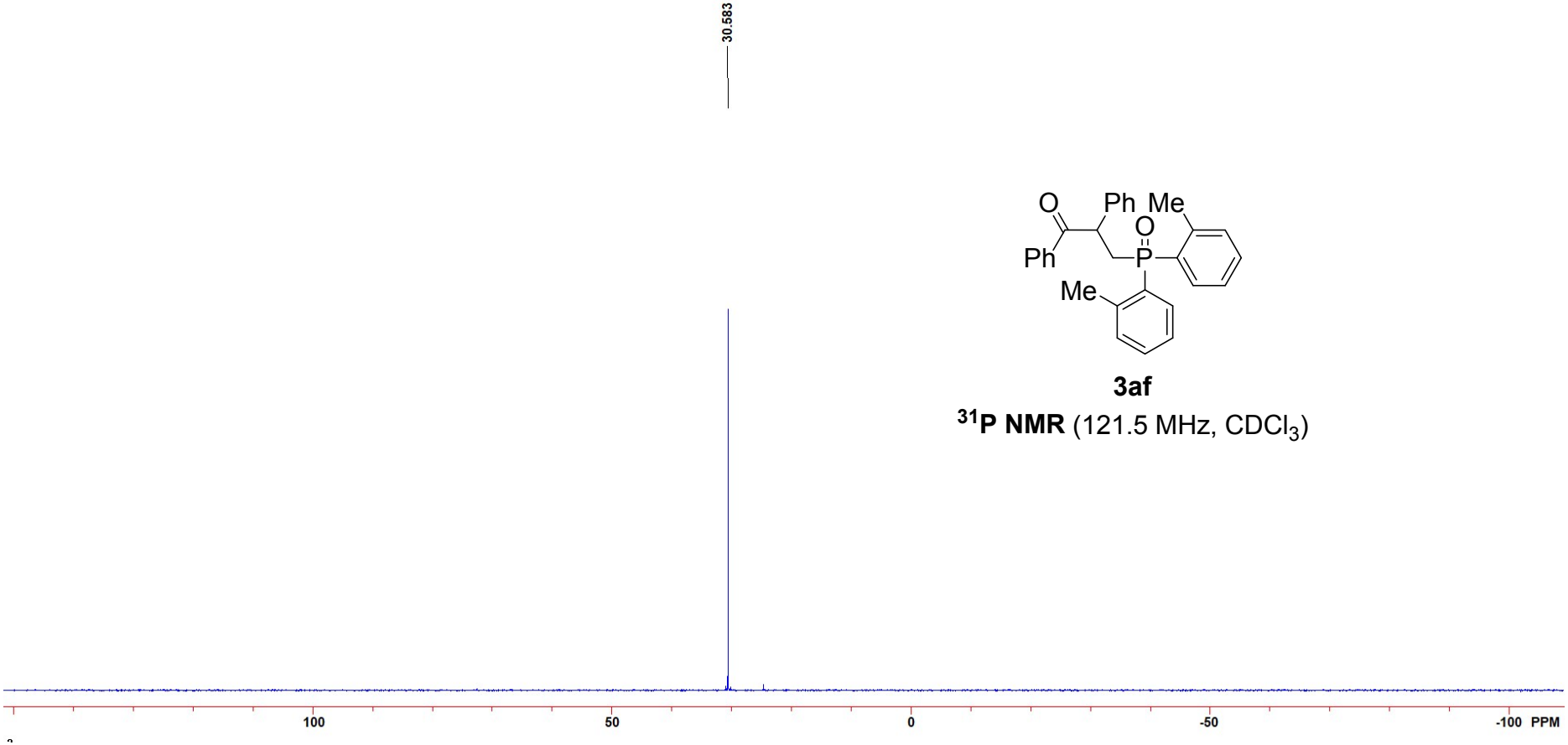
^{31}P NMR (121.5 MHz, $CDCl_3$)


7.856
7.830
7.801
7.775
7.752
7.726
7.709
7.683
7.428
7.404
7.380
7.349
7.325
7.302
7.279
7.262
7.230
7.204
7.180
7.155
7.133
7.109
7.082
7.058
6.346
5.332
5.319
5.305
5.291
5.278
5.264
3.812
3.781
3.761
3.754
3.731
3.703
2.850
2.836
2.812
2.799
2.788
2.763
2.749
2.208
2.158
-0.000
O
Ph
Me
O
Ph
P
Me
3af
1H NMR (300 MHz, CDCl3)
6.04
4.03
4.04
3.07
1.03
1.00
1.03
0.99
3.00
3.00
12
10
8
6
4
2
0
PPM



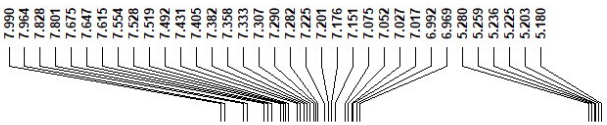
3af

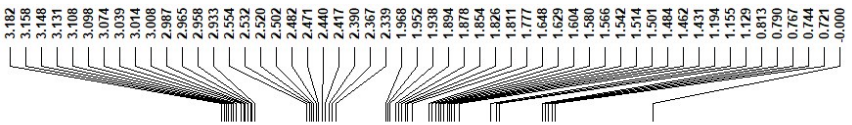
^{13}C NMR (75 MHz, $CDCl_3$)

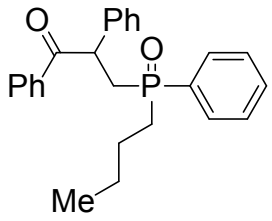


3af

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

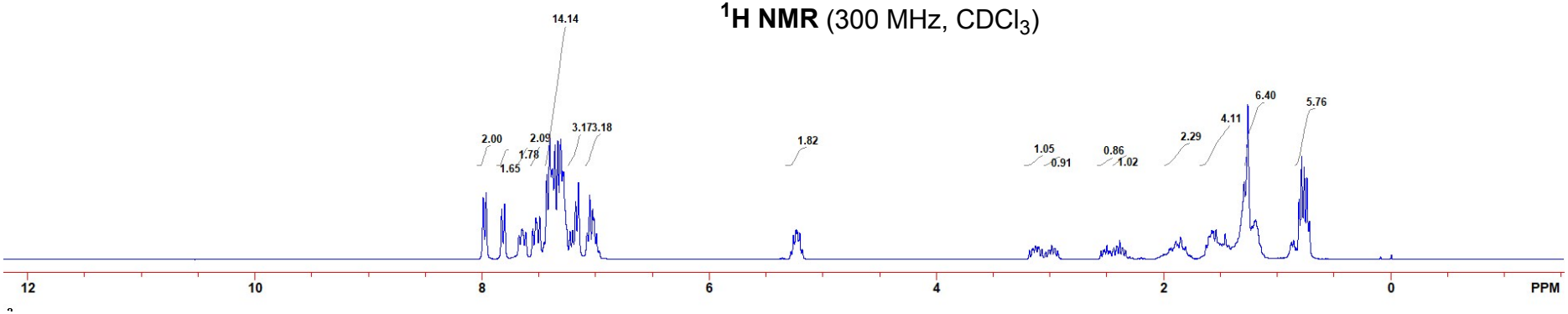


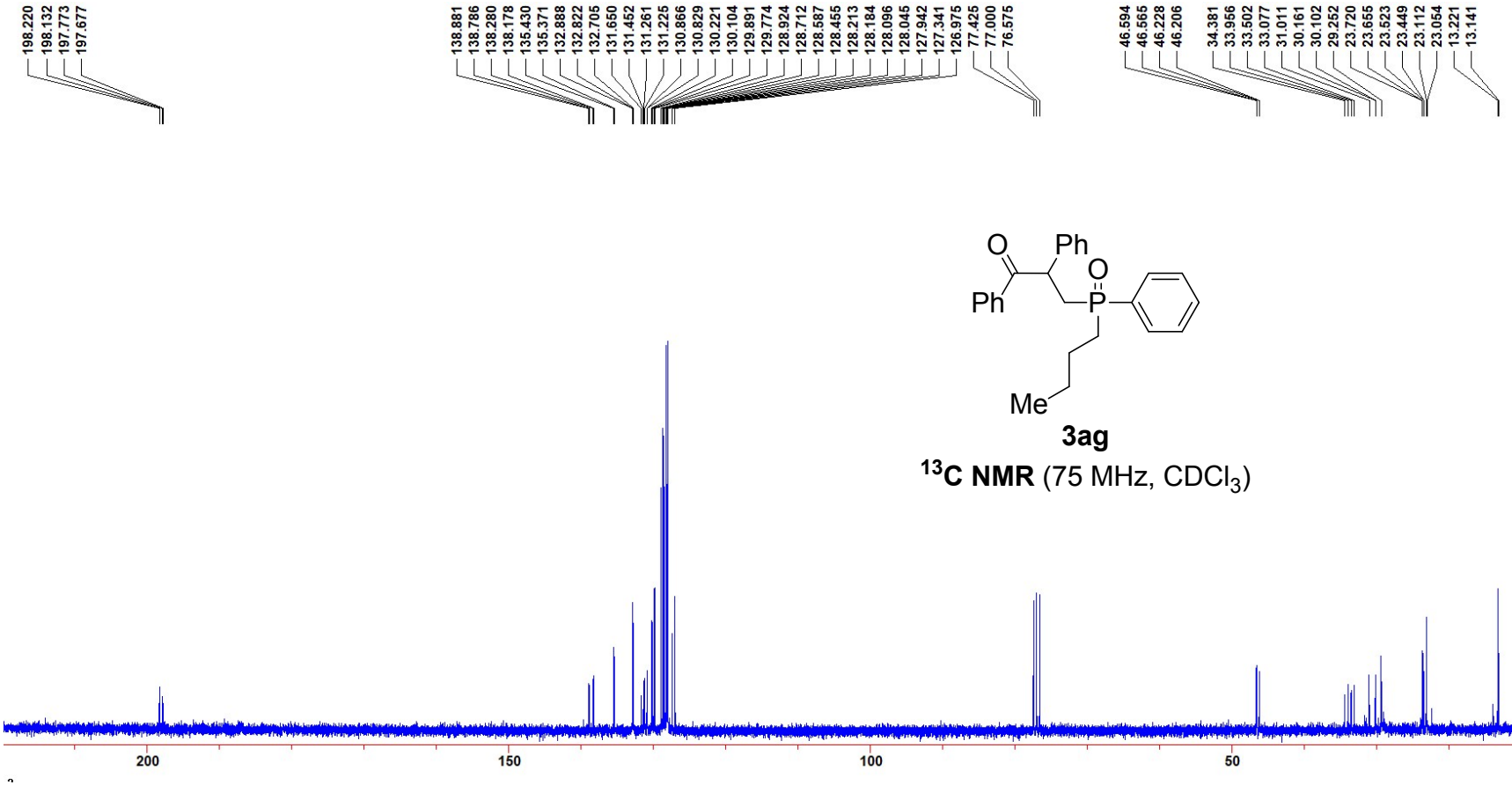




3ag

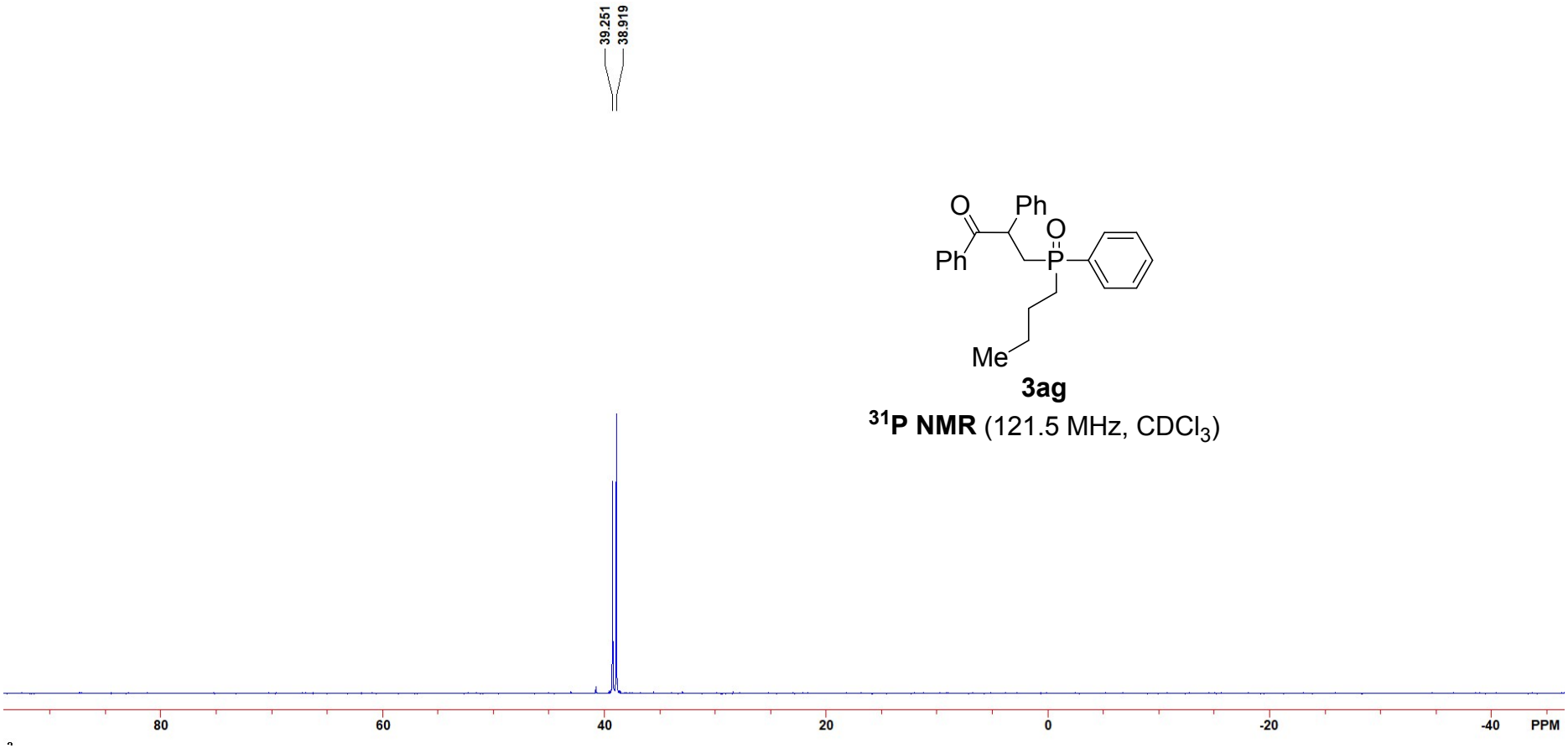
^{1}H NMR (300 MHz, $CDCl_3$)





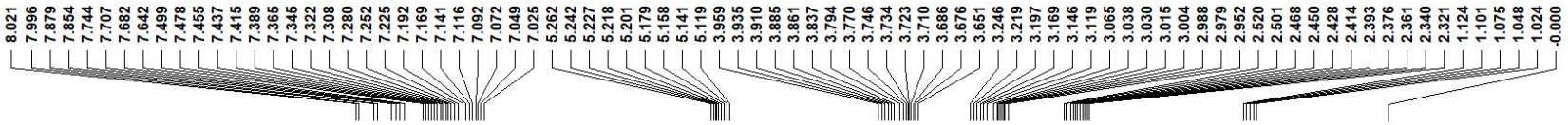
3ag

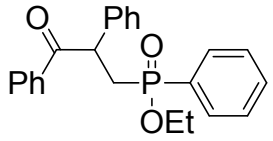
^{13}C NMR (75 MHz, $CDCl_3$)



3ag

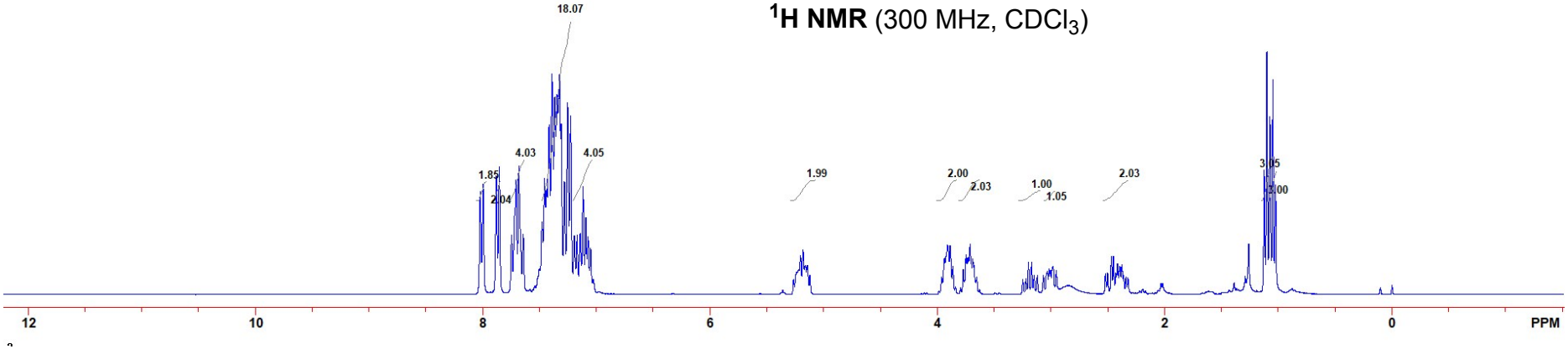
^{31}P NMR (121.5 MHz, $CDCl_3$)

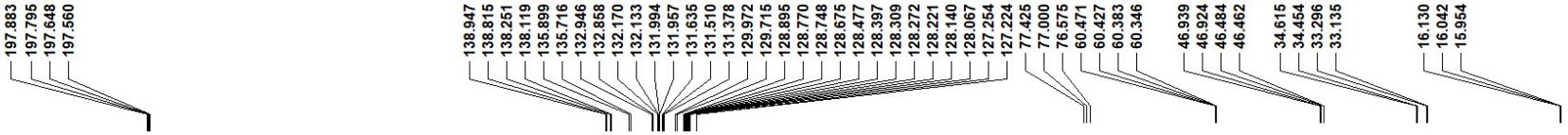


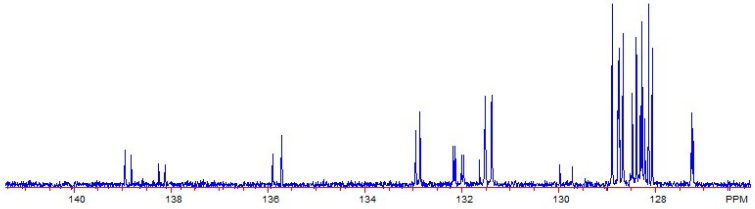


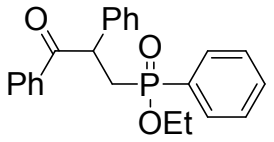
3ah

^{1}H NMR (300 MHz, $CDCl_3$)



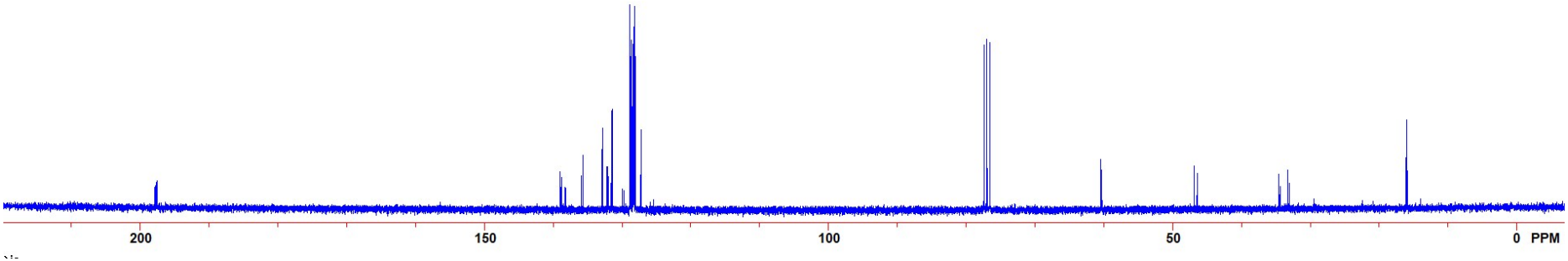


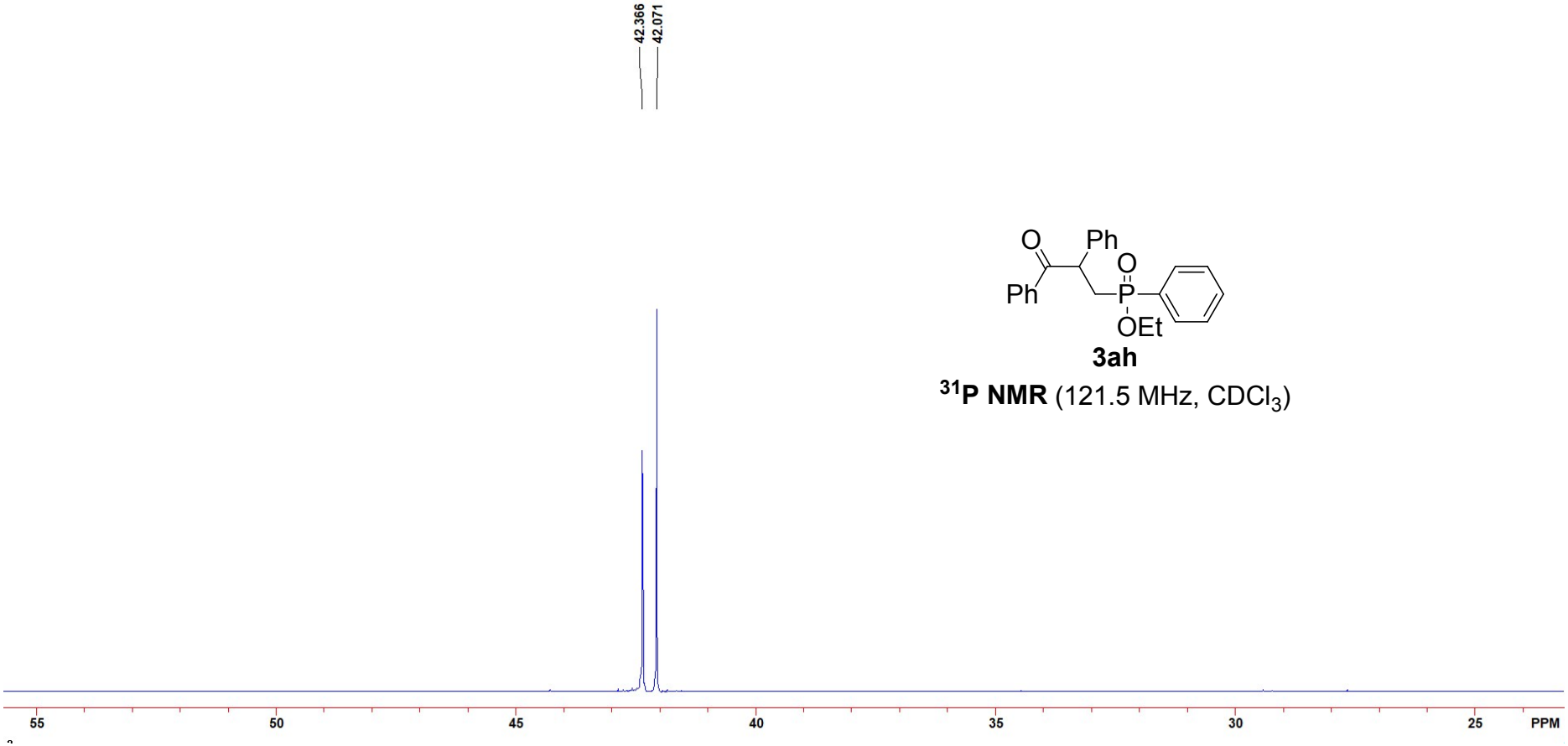




3ah

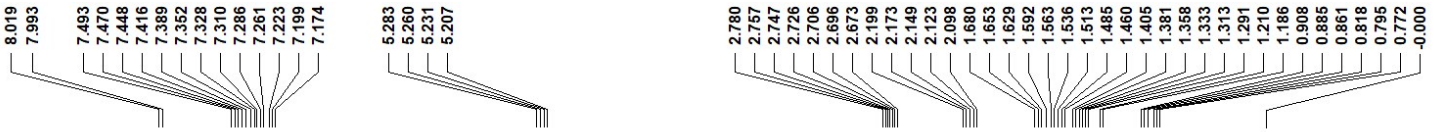
^{13}C NMR (75 MHz, $CDCl_3$)

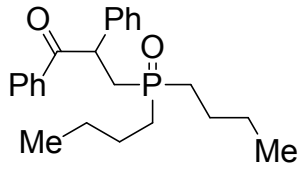




3ah

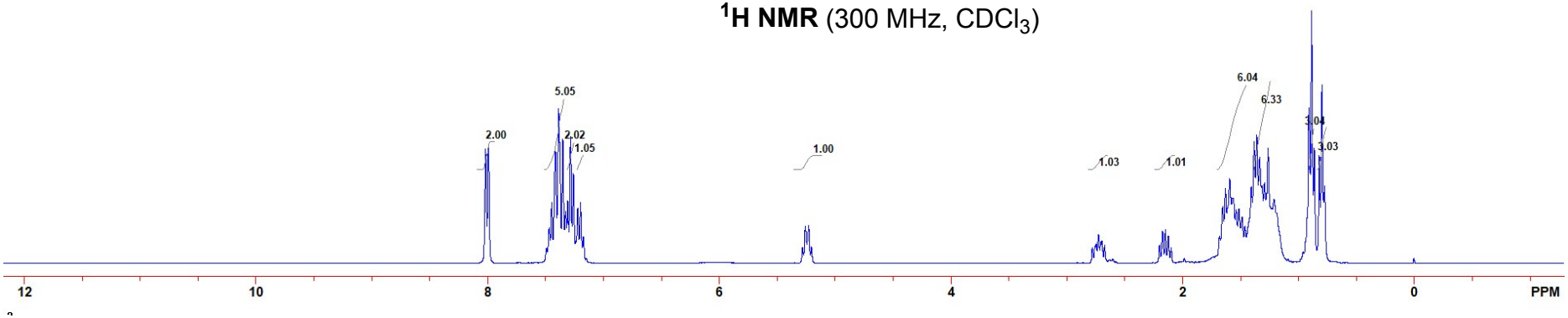
^{31}P NMR (121.5 MHz, $CDCl_3$)

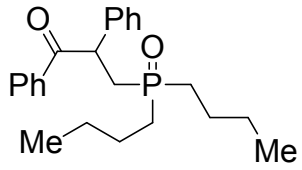




3ai

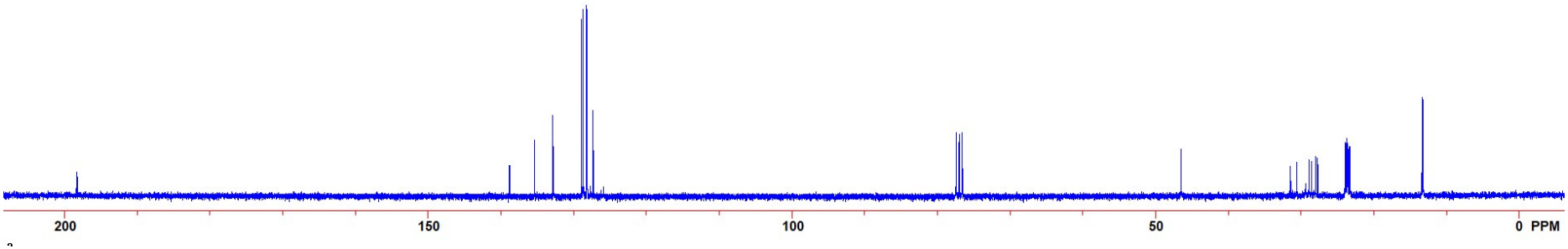
^{1}H NMR (300 MHz, $CDCl_3$)

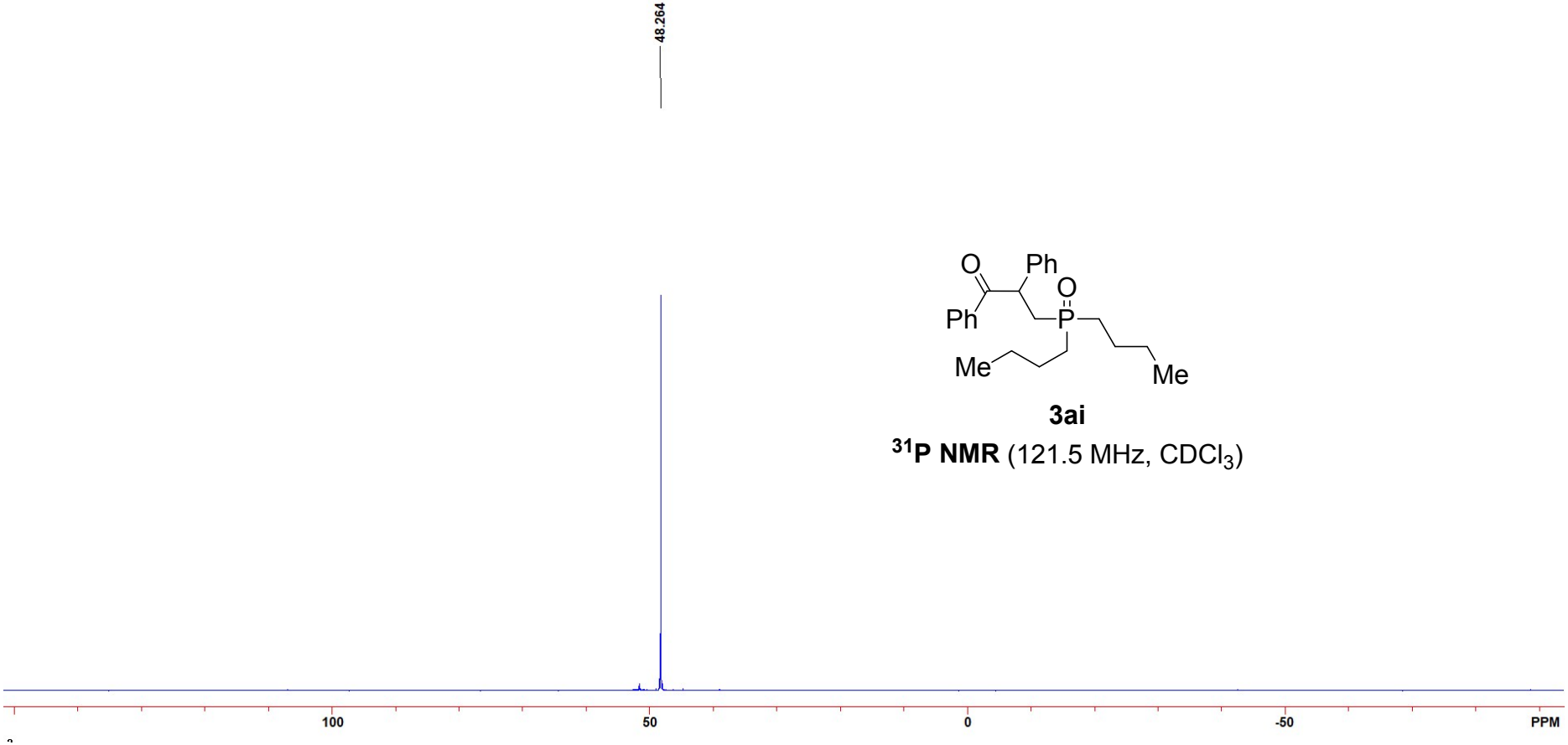




3ai

^{13}C NMR (75 MHz, $CDCl_3$)





3ai

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