Electronic and Steric Effects on the Rate of the Traceless Staudinger Ligation

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General. Reagent chemicals were obtained from commercial suppliers, and reagent grade solvents were used without further purification. Anhydrous THF, DMF, and CH_2Cl_2 were from a CYCLE-TAINER® solvent delivery system (Baker). Procedures were performed at room temperature (<23 °C) unless indicated otherwise. Reactions were monitored by thin-layer chromatography with visualization by UV light or staining with $KMnO_4$, ninhydrin, or I_2. Compound purification was carried out with flash chromatography on silica gel, which had a mesh of 230–400 (ASTM) and a pore size of 60 Å. The removal of solvents and other volatile materials "under reduced pressure" refers to the use of a rotary evaporator at water-aspirator pressure (<20 torr) and a water bath of <40 °C.

Instrumentation. NMR spectra were acquired at ambient temperature with a Bruker AC-300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz) at the University of Wisconsin Chemistry Department Nuclear Magnetic Resonance Facility or a Bruker DMX-400 Avance spectrometer (^1H, 400 MHz; ^{13}C, 100.6 MHz; ^{31}P, 161 MHz) or Bruker Avance DMX-500 spectrometer (^1H, 500 MHz; ^{13}C, 125.7 MHz; ^{31}P, 202 MHz) at the National Magnetic Resonance Facility at Madison (NMRFAM) or a Varian Inova 500 (^1H, 500 MHz; ^{13}C, 125.7 MHz; ^{31}P, 202 MHz) spectrometer at the University of Wisconsin Nuclear Magnetic Resonance Facility. Carbon-13 and phosphorus-31 spectra were proton-decoupled, and phosphorus-31 spectra were referenced against an external standard of deuterated phosphoric acid (0 ppm).

Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) in the Mass Spectrometry Facility in the Department of Chemistry.

$HP(O)(p\text{-}OCH(CH_3)_2\text{-}C_6H_4)_2$ (35). Bromide **34** (4 g, 18.6 mmol) was dissolved in anhydrous THF (50 mL) under Ar(g) in a flame-dried round-bottom flask equipped with a reflux condenser. To facilitate generation of the Grignard reagent, a catalytic amount of I_2 was added to the solution. Crushed magnesium turnings (678 mg, 27.9 mmol) were then added to this solution, and the resulting solution was heated to reflux for 2 h to generate the Grignard reagent. In a separate flame-dried round-bottom flask, diethyl phosphite (718 µL, 5.58 mmol) was dissolved in anhydrous THF (2 mL), and cooled to 0 °C with an ice/water bath. The solution of Grignard reagent was added dropwise to this solution, and the resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then quenched with water (2 mL), and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and the resulting solution was washed with water and brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:1 v/v acetone:CH_2Cl_2) to give phosphine−borane complex **35** as a colorless oil in 67% yield. **Spectra data.** ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62−7.56 (m, 4H), 8.01 (d, J = 476.2 Hz, 1H), 6.98−6.95 (m, 4H), 4.62 (sept, J = 6.0 Hz, 2H), 1.36 (d, J = 6.1 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 161.51, 132.94 (d, J = 12.7 Hz), 122.65 (d, J = 108 Hz), 116.08 (d, J = 13.4 Hz), 70.21, 22.07 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 20.79 ppm; MS (ESI) m/z 637.2827 ($2MNa^+$ [$C_{18}H_{23}O_3PNa^+$] = 637.2848).

$HP(O)(p\text{-}NMe_2\text{-}C_6H_4)_2$ (36). Phosphine oxide **36** was synthesized according to reports published previously.[1] **Spectral data.** Spectral data were as reported previously.[1]

$BH_3{\cdot}HP(p\text{-}OCH(CH_3)_2\text{-}C_6H_4)_2$ (37). Phosphine oxide **35** (1.18 g, 3.7 mmol) was dissolved in 1:1 v/v THF/ CH_2Cl_2 (11 mL). DIBAL (1 M in CH_2Cl_2, 18.5 mL) was added to the solution dropwise over a period of 5 min, and the resulting mixture was stirred for 20 min at room temperature. CH_2Cl_2 (25 mL) was added, and the resulting solution was cooled to 0 °C with an ice/water bath. NaOH (2 N, 10 mL) was added dropwise, followed by brine (6 mL). The solution was stirred for 5 min, then poured into a separatory funnel and the organic layer was separated and dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure to a 30 mL volume. This solution was cooled to 0 °C with an ice/water bath, and borane·dimethyl sulfide complex (10 M in THF, 444 μL) was added dropwise to the reaction mixture. The resulting solution was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **37** as a colorless oil in 97% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58−7.53 (m, 4H), 6.94−6.91 (m, 4H), 6.24 (dq, J = 377.7 Hz, 1H), 4.59 (sept, J = 6.1 Hz, 2H), 1.34 (d, J = 5.9 Hz, 12H), 1.48−0.57 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.91, 134.86 (d, J = 11.3 Hz), 116.97 (d, J = 108 Hz), 116.40 (d, J = 10.0 Hz), 70.20, 22.12 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 1.56 ppm; MS (ESI) *m/z* 339.1649 (MNa^+ [$C_{18}H_{26}BO_2PNa^+$] = 339.1661).

BH_3·HP(*p*-NMe_2-C_6H_4)$_2$ (38). Bis-[4-dimethylaminophenyl]-phosphine was synthesized from phosphine oxide **36** according to previously published reports.[1] Bis-[4-dimethylaminophenyl]-phosphine (2.88 g, 10.56 mmol) was then dissolved in anhydrous CH_2Cl_2 (85 mL) and cooled to 0 °C with an ice/water bath. Borane·dimethyl sulfide complex (10 M in THF, 3.2 mL) was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, 1:1:3 v/v/v dichloromethane:ethyl acetate:hexane) to give phosphine−borane complex **38** as a white solid in 62% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51−7.46 (m, 4H), 6.71−6.66 (m, 4H), 5.75 (q, J = 6.5 Hz, 1H), 2.99 (s, 12H), 1.40−0.50 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 152.34, 134.27, 134.17, 112.20, 40.28 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −4.74 ppm; MS (ESI) *m/z* 309.1660 (MNa^+ [$C_{16}H_{24}BN_2PNa^+$] = 309.1668).

BH_3·HP(*p*-CH_3-C_6H_4)$_2$ (39). Di-*p*-tolylphosphine (10 g, 46.7 mmol) was dissolved in anhydrous THF (100 mL), and the resulting solution was cooled to 0 °C with an ice/water bath. Borane THF complex (1 M in THF, 51.3 mL) was added dropwise to the solution, and the mixture was stirred at 0 °C for 1 h, warmed to room temperature and stirred for an additional 1 h. Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel, 50% v/v CH_2Cl_2 in hexane) to give phosphinothioester **39** as a white solid in 95% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56−7.50 (m, 4H), 7.26−7.24 (m, 4H), 6.25 (bq, J = 378 Hz, 7.1 Hz, 1H), 2.38 (s, 6H), 1.48−0.54 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 142.28, 133.09 (d, J = 10.7 Hz), 130.02 (d, J = 9.9 Hz), 123.18 (d, J = 60.7 Hz), 21.74 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ −0.50 ppm; MS (ESI) *m/z* 251.1129 (MNa^+ [$C_{14}H_{18}BPNa^+$] = 251.1137).

BH_3·HOCH$_2$P(*p*-OCH(CH_3)$_2$-C_6H_4)$_2$ (40). Phosphine−borane complex **37** (1.15 g, 3.62 mmol) was dissolved in THF (30 mL). Formaldehyde (37% v/v in H_2O; 2.21 mL) was added to this solution, followed by potassium hydroxide (207 mg, 3.69 mmol). The resulting solution was stirred overnight at room temperature, after which the organic solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (15 mL), and the organic layer was washed with brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **40** as a pale yellow oil in 70% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64−7.60 (m, 4H), 6.95−6.93 (m, 4H), 4.60 (sept, J = 5.8 Hz, 2H), 4.35 (d, J = 6.5 Hz, 2H), 2.00−1.96 (m, 1H), 1.35 (d, J = 6.0 Hz, 12H), 1.40−0.40 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.94, 134.65 (d, J = 9.5

Hz), 116.33 (d, J = 61.0 Hz), 116.22 (d, J = 10.6 Hz), 70.20, 61.04 (d, J = 43.3 Hz), 22.13 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 14.78 ppm; MS (ESI) m/z 369.1776 (MNa^+ [$C_{19}H_{28}BO_3PNa^+$] = 369.1767).

BH_3·$HOCH_2P$(*p*-NMe_2-C_6H_4)$_2$ (41). Phosphine−borane complex **38** (1.89 g, 6.59 mmol) was dissolved in THF (50 mL). Formaldehyde (37% v/v in H_2O; 4.03 mL) was added to this solution, followed by potassium hydroxide (380 mg, 6.79 mmol). The resulting solution was stirred overnight at room temperature, after which the organic solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (25 mL), and the organic layer was washed with brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:1:3 v/v/v dichloromethane:ethyl acetate:hexane) to give phosphine−borane complex **41** as a pale green solid in 92% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57−7.52 (m, 4H), 6.73−6.70 (m, 4H), 4.28 (d, J = 6.0 Hz, 2H), 2.99 (s, 12H), 2.05 (bs, 1H), 1.35−0.50 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 152.34, 133.99 (d, J = 10.3 Hz), 112.17 (d, J = 11.4 Hz), 111.33 (d, J = 64.6 Hz), 61.13 (d, J = 41.4 Hz), 40.19 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 12.80 ppm; MS (ESI) m/z 339.1764 (MNa^+ [$C_{17}H_{26}BN_2OPNa^+$] = 339.1774).

BH_3·$HOCH_2P$(*p*-CH_3-C_6H_4)$_2$ (42). Phosphine−borane complex **39** (2.29 g, 10.04 mmol) was dissolved in THF (84 mL). Formaldehyde (37% v/v in H_2O; 6.13 mL) was added to this solution, followed by potassium hydroxide (573 mg, 10.24 mmol). The resulting mixture was stirred overnight at room temperature, after which the organic solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (30 mL), and the organic layer was washed with brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **42** as a colorless oil in 83% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62−7.57 (m, 4H), 6.28−6.26 (m, 4H), 4.38 (d, J = 6.6 Hz, 2H), 2.39 (s, 6H), 2.11−2.09 (bm, 1H), 1.39−0.49 (bq, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 142.36, 132.85 (d, J = 8.3 Hz), 129.95 (d, J = 9.2 Hz), 123.49 (d, J = 57.1 Hz), 60.69 (d, J = 42.1 Hz), 21.71 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 16.50 ppm; MS (ESI) m/z 281.1246 (MNa^+ [$C_{15}H_{20}BOPNa^+$] = 281.1243).

BH_3·$MsOCH_2P$(*p*-$OCH(CH_3)_2$-C_6H_4)$_2$ (43). Triethylamine (531 μL, 3.81 mmol) was added to a solution of phosphine−borane **40** (879 mg, 2.54 mmol) in CH_2Cl_2 (23 mL), and this solution was cooled to 0 °C with an ice/water bath. Methanesulfonyl chloride (275 μL, 3.55 mmol) was added dropwise, and the resulting solution was allowed to warm slowly to room temperature overnight. The solution was washed with 0.5 N HCl and brine, and the combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **43** as a yellow oil in 83% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66−7.61 (m, 4H), 6.98−6.95 (m, 4H), 4.81 (d, J = 2.0 Hz, 2H), 4.61 (sept, J = 6.0 Hz, 2H), 2.89 (s, 3H), 1.35 (d, J = 6.1 Hz, 12H), 1.40−0.40 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 161.32, 134.85 (d, J = 9.7 Hz), 116.38 (d, J = 10.3 Hz), 115.48 (d, J = 63 Hz), 70.27, 65.40 (d, J = 39 Hz), 37.59, 22.07 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 15.49 ppm; MS (ESI) m/z 447.1546 (MNa^+ [$C_{20}H_{30}BO_5PSNa^+$] = 447.1542).

BH_3·$MsOCH_2P$(*p*-NMe_2-C_6H_4)$_2$ (44). Triethylamine (1.25 mL, 9.0 mmol) was added to a solution of phosphine−borane **41** (1.90 g, 6.0 mmol) in CH_2Cl_2 (55 mL), and this solution was cooled to 0 °C with an ice/water bath. Methanesulfonyl chloride (651 μL, 8.4 mmol) was added dropwise, and the resulting solution was allowed to warm slowly to room temperature overnight. The solution was washed with 0.1 N HCl and brine, and the combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:1:3 v/v/v dichloromethane:ethyl acetate:hexane) to give phosphine−borane complex **44** as a white solid in 95% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.55 (m, 4H), 6.77−6.75 (m, 4H), 4.78 (d, J = 2.3 Hz, 2H), 3.02 (s, 12H), 2.86 (s, 3H), 1.40−0.50 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 152.47, 134.15 (d, J = 11.8 Hz), 111.99 (d, J = 9.5 Hz), 109.48 (d, J = 67.6 Hz), 66.23 (d, J = 38.9 Hz), 40.49, 37.66 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 13.39 ppm; MS (ESI) *m*/*z* 417.1567 (MNa^+ [$C_{18}H_{28}BN_2O_3PSNa^+$] = 417.1549).

BH_3·$MsOCH_2P$(*p*-CH_3-C_6H_4)$_2$ (45). Triethylamine (1.74 mL, 12.5 mmol) was added to a solution of phosphine−borane **42** (2.15 mg, 8.33 mmol) in CH_2Cl_2 (75 mL), and this solution was cooled to 0 °C with an ice/water bath. Methanesulfonyl chloride (903 µL, 11.67 mmol) was added dropwise, and the resulting solution was allowed to warm slowly to room temperature overnight. The solution was washed with 0.5 N HCl and brine, and the combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **45** as a colorless oil in 93% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63−7.59 (m, 4H), 7.32−7.29 (m, 4H), 4.86 (d, J = 2.2 Hz, 2H), 2.89 (s, 3H), 2.41 (s, 6H), 1.47−0.48 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 143.42, 133.12 (d, J = 8.7 Hz), 130.19 (d, J = 10.1 Hz), 121.98 (d, J = 60.7 Hz), 65.05 (d, J = 38.7 Hz), 37.71, 21.86 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 17.26 ppm; MS (ESI) *m*/*z* 359.1002 (MNa^+ [$C_{16}H_{22}BO_3PSNa^+$] = 359.1018).

BH_3·$AcSCH_2P$(*p*-$OCH(CH_3)_2$-C_6H_4)$_2$ (46). Potassium thioacetate (290 mg, 2.54 mmol) was added to a solution of phosphine−borane complex **43** (898 mg, 2.12 mmol) in anhydrous DMF (20 mL) under Ar(g). The resulting solution was stirred overnight at room temperature, after which the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (10 mL), and the resulting solution was washed with water and brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 50% v/v CH_2Cl_2 in hexanes) to give phosphine−borane complex **46** as a yellow oil in 53% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62−7.57 (m, 4H), 6.93−6.91 (m, 4H), 4.59 (sept, J = 6.1 Hz, 2H), 3.63 (d, J = 6.8 Hz, 2H), 2.26 (s, 3H), 1.34 (d, J = 5.9 Hz, 12H), 1.40−0.50 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 193.81, 161.36, 134.84 (d, J = 9.6 Hz), 116.37 (d, J = 10.3 Hz), 115.52 (d, J = 63.0 Hz), 70.30, 65.49 (d, J = 38.9 Hz), 37.62, 22.09 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ 15.75 ppm; MS (ESI) *m*/*z* 427.1656 (MNa^+ [$C_{21}H_{30}BO_3PSNa^+$] = 427.1644).

BH_3·$AcSCH_2P$(*p*-NMe_2-C_6H_4)$_2$ (47). Potassium thioacetate (780 mg, 6.83 mmol) was added to a solution of phosphine−borane complex **44** (2.24 g, 5.69 mmol) in anhydrous DMF (50 mL) under Ar(g). The resulting solution was stirred overnight at room temperature, after which the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (30 mL), and the resulting solution was washed with water and brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:1:3 v/v/v dichloromethane:ethyl acetate:hexane) to give phosphine−borane complex **47** as a pale yellow oil in 24% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.50 (m, 4H), 6.71−6.68 (m, 4H), 3.60 (d, J = 6.9 Hz, 2H), 2.99 (s, 12H), 2.26 (s, 3H), 1.40−0.50 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6

MHz) δ 194.09, 152.16, 133.53 (d, J = 9.6 Hz), 112.32 (d, J = 65 Hz), 111.81 (d, J = 12.7 Hz),, 40.02, 30.22, 25.01 (d, J = 35.8 Hz) ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ 12.38 ppm; MS (ESI) m/z 397.1646 (MNa^+ [$C_{19}H_{28}BN_2OPSNa^+$] = 397.1651).

BH_3·$AcSCH_2P$(*p*-CH_3-C_6H_4)$_2$ (48). Potassium thioacetate (1.06 mg, 9.25 mmol) was added to a solution of phosphine−borane complex **45** (2.59 mg, 7.71 mmol) in anhydrous DMF (70 mL) under Ar(g). The resulting solution was stirred overnight at room temperature, after which the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (30 mL), and the resulting solution was washed with water and brine. The combined organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give phosphine−borane complex **48** as an orange solid in 62% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.55 (m, 4H), 7.26−7.24 (m, 4H), 3.67 (d, J = 10.0 Hz, 2H), 2.38 (s, 6H), 2.25 (s, 3H), 1.47−0.44 (bm, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 193.62, 142.37, 132.52 (d, J = 8.7 Hz), 129.79 (d, J = 11.5 Hz), 124.47 (d, J = 57.2 Hz), 30.23, 24.15 (d, J = 36.6 Hz), 21.70 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ 17.65 ppm; MS (ESI) m/z 339.1118 (MNa^+ [$C_{17}H_{22}BOPSNa^+$] = 339.1120).

$AcSCH_2P$(*p*-$OCH(CH_3)_2$-C_6H_4)$_2$ (49). Phosphine−borane complex **46** (549 mg, 1.36 mmol) was dissolved in degassed toluene (12 mL) under Ar(g). DABCO (183 mg, 1.63 mmol) was added, and the resulting solution was heated to 40 °C for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with 1 N HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:1:18 v/v/v dichloromethane:ethyl acetate:hexane) to give phosphinothioester **49** as a colorless oil in 98% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.32 (m, 4H), 6.87−6.85 (m, 4H), 4.56 (sept, J = 6.0 Hz, 2H), 3.44 (d, J = 3.4 Hz, 2H), 2.29 (s, 3H), 1.33 (d, J = 6.0 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 195.26, 159.07, 134.48 (d, J = 20.2 Hz), 127.71 (d, J = 10.8 Hz), 116.05 (d, J = 8.3 Hz), 69.93, 30.54, 26.73 (d, J = 23.2 Hz), 22.34 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ −18.51 ppm.

$AcGlySCH_2P$(*p*-CH_3-C_6H_4)$_2$ (9). Phosphine **51** (250 mg, 0.82 mmol) was dissolved in degassed MeOH (8 mL). NaOH (33 mg, 0.82 mmol) was added to the solution, and the resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification in the coupling with *N*-acetylglycine. In a separate round-bottom flask, *N*-acetylglycine (101 mg, 0.86 mmol) was dissolved in anhydrous DMF (8 mL). HOBT (111 mg, 0.82 mmol) was added, followed by *N,N′*-diisopropylcarbodiimide (128 μL, 0.82 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (0.82 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:2:7 EtOAc:hexanes:CH_2Cl_2) to give phosphinothioester **9** as a colorless oil in 78% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 7.6 Hz, 4H), 7.17 (d, J = 7.7 Hz, 4H), 6.00 (bm, 1H), 4.17 (d, J = 5.7 Hz, 2H), 3.49 (d, J = 3.6 Hz, 2H), 2.39 (s, 6H), 2.03 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 196.40, 170.42, 139.47, 133.32 (d, J = 12.2 Hz), 132.83 (d, J = 20.1 Hz), 129.59 (d, J = 7.7 Hz), 49.25, 25.75 (d, J = 24.1 Hz), 23.12, 21.50 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −16.80 ppm.

AcGlySCH$_2$P(*p*-OCH(CH$_3$)$_2$-C$_6$H$_4$)$_2$ (11). NaOH (42.4 mg, 1.06 mmol) was added to a solution of phosphine **49** (414 mg, 1.06 mmol) dissolved in degassed MeOH (10 mL). The resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 N HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification. In a separate round-bottom flask, *N*-acetylglycine (128 mg, 1.09 mmol) was dissolved in anhydrous DMF (10 mL). HOBT (141 mg, 1.04 mmol) was added, followed by 1,3-diisopropylcarbodiimide (163 μL, 1.04 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (363 mg, 1.04 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 3:3:4 v/v/v ethyl acetate:CH_2Cl_2:hexane) to give phosphinothioester **11** as a colorless oil in 78% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37−7.31 (m, 4H), 6.90−6.86 (m, 4H), 5.96 (bs, 1H), 4.56 (sept, J = 6.2 Hz, 2H), 4.18 (d, J = 5.6 Hz, 2H), 3.45 (d, J = 3.4 Hz, 2H), 2.03 (s, 3H), 1.34 (d, J = 6.1 Hz, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 196.46, 170.47, 159, 04, 134.39 (d, J = 20.8 Hz), 127.34 (d, J = 11.3 Hz), 116.03 (d, J = 8.4 Hz), 69.88, 49.27, 26.16 (d, J = 22.7 Hz), 23.08, 22.13 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ −18.42 ppm.

AcGlySCH$_2$P(*p*-NMe$_2$-C$_6$H$_4$)$_2$ (12). To deprotect the phosphine, phosphine−borane complex **47** (746 mg, 1.99 mmol) was dissolved in degassed toluene (19 mL) under Ar(g). DABCO (268 mg, 2.39 mmol) was added, and the resulting solution was heated to 40 °C for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with 1 M citrate buffer (pH 4.0). The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. To deprotect the thiol, the crude phosphine was dissolved in degassed MeOH (15 mL). NaOH (76 mg, 1.89 mmol) was added, and the resulting solution was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M citrate buffer (pH 4.0). The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification in the coupling with *N*-acetylglycine. In a separate round-bottom flask, *N*-acetylglycine (233 mg, 1.99 mmol) was dissolved in anhydrous DMF (15 mL). HOBT (255 mg, 1.89 mmol) was added, followed by *N,N′*-diisopropylcarbodiimide (297 μL, 1.89 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (1.89 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 4% v/v MeOH in CH_2Cl_2) to give phosphinothioester **12** as a colorless oil in 70% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33−7.29 (m, 4H), 6.70−6.68 (m, 4H), 5.96 (bs, 1H), 4.18 (d, J = 5.6 Hz, 2H), 3.46 (d, J = 3.9 Hz, 2H), 2.96 (s, 12H), 2.03 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 196.67, 151.60, 134.09, 124.58, 112.44, 111.43, 49.30, 40.40, 26.51 (d, J = 23 Hz), 23.23 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −19.35 ppm.

AcAlaSCH$_2$P(*p*-CH$_3$-C$_6$H$_4$)$_2$ (15). Phosphine **51** (287 mg, 0.95 mmol) was dissolved in degassed MeOH (9 mL). NaOH (38 mg, 0.95 mmol) was added to the solution, and the resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification in the coupling with *N*-acetylalanine. In a separate round-bottom flask, *N*-acetylalanine (131 mg, 1.0 mmol) was dissolved in anhydrous DMF (9 mL). HOBT (128 mg, 0.95 mmol) was added to the resulting solution, followed by *N,N'*-diisopropylcarbodiimide (149 μL, 0.95 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (0.95 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:2:7 EtOAc:hexanes:CH_2Cl_2) to give phosphinothioester **15** as a colorless oil in 75% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (d, J = 7.6 Hz, 4H), 7.15 (d, J = 7.6 Hz, 4H), 6.14 (d, J = 7.8 Hz, 1H), 4.67 (dq, J = 7.6 Hz, 1H), 3.46−3.44 (m, 2H), 2.34 (s, 6H), 1.98 (s, 3H), 1.29 (d, J = 7.1 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.17, 169.87, 139.34, 133.45 (d, J = 10.7 Hz), 132.86 (d, J = 19.2 Hz), 129.51 (d, J = 5.8 Hz), 55.07, 25.81 (d, J = 24.1 Hz), 23.26, 21.46, 19.01 ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ −16.35 ppm.

AcAlaSCH$_2$P(*p*-OCH(CH$_3$)$_2$-C$_6$H$_4$)$_2$ (17). NaOH (53.3 mg, 1.33 mmol) was added to a solution of phosphine **49** (521 mg, 1.33 mmol) dissolved in degassed MeOH (13 mL). The resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 N HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification. In a separate round-bottom flask, *N*-acetylalanine (174 mg, 1.33 mmol) was dissolved in anhydrous DMF (11 mL). HOBT (171 mg, 1.27 mmol) was added, followed by 1,3-diisopropylcarbodiimide (198 μL, 1.27 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (441 mg, 1.27 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 3:3:4 v/v/v ethyl acetate:CH_2Cl_2:hexane) to give phosphinothioester **17** as a colorless oil in 72% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.31 (m, 4H), 6.87−6.85 (m, 4H), 5.88 (d, 1H), 4.69 (q, J = 7.4 Hz, 1H), 4.56 (sept, J = 6.4 Hz, 2H), 3.44−3.42 (m, 2H), 2.00 (s, 3H), 1.33 (d, J = 6.0 Hz, 12H), 1.31 (d, J = 7.1 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.27, 170.05, 158.88, 134.21 (d, J = 21.4 Hz), 127.32, 158.85 (d, J = 7.3 Hz), 69.74, 55.00, 26.09 (d, J = 22.9 Hz), 23.07, 22.03, 18.63 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −17.77 ppm.

AcAlaSCH$_2$P(*p*-NMe$_2$-C$_6$H$_4$)$_2$ (18). Phosphine−borane complex **47** (581 mg, 1.55 mmol) was dissolved in degassed toluene (14 mL) under Ar(g). DABCO (209 mg, 1.86 mmol) was added, and the resulting solution was heated to 40 °C for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with 1 M citrate buffer (pH 4.0). The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. To deprotect the thiol, the crude phosphine was dissolved in degassed MeOH (14 mL). NaOH (59.2 mg, 1.48 mmol) was added, and the resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M citrate buffer (pH 4.0). The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification. In a separate round-bottom flask, *N*-acetylalanine (203.7 mg, 1.55 mmol) was dissolved in anhydrous DMF (19 mL). HOBT (200 mg, 1.48 mmol) was added, followed by 1,3-diisopropylcarbodiimide (232 μL, 1.48 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (574 mg, 1.48 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h.

The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 4% v/v MeOH in CH_2Cl_2) to give phosphinothioester **18** as a white solid in 65% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34−7.31 (m, 4H), 6.72−6.69 (m, 4H), 5.91 (bd, J = 7.4 Hz, 1H), 4.72 (q, J = 8.4 Hz, 1H), 3.46−3.43 (m, 2H), 2.98 (s, 12H), 2.01 (s, 3H), 1.34 (d, J = 7.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.34, 169.62, 150.88, 133.81 (d, J = 19.4 Hz), 122.08, 112.19 (d, J = 6.7 Hz), 54.90, 41.99, 40.20, 26.48 (d, J = 34.1 Hz), 19.06 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −19.06 ppm.

AcSCH₂P(*p*-CH₃-C₆H₄)₂ (51). Phosphine−borane complex **48** (300 mg, 0.95 mmol) was dissolved in degassed toluene (9 mL) under Ar(g). DABCO (117 mg, 1.04 mmol) was added, and the resulting solution was heated to 40 °C for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with 1 M HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue (**51**) was a colorless oil (98% yield) and was judged to be sufficiently pure by NMR spectroscopy. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (t, J = 7.7 Hz, 4H), 7.16 (d, J = 7.7 Hz, 4H), 3.48 (d, J = 3.5 Hz, 2H), 2.35 (s, 6H), 2.29 (s, 3H) ppm; ^{31}P NMR ($CDCl_3$, 161 MHz) δ −17.032 ppm.

AcGlySCH₂P(*p*-Cl-C₆H₄)₂ (52). The thioacetate of phosphine **3** [2] (373 mg, 1.09 mmol) was dissolved in degassed MeOH (10 mL). NaOH (44 mg, 1.09 mmol) was added to the solution, and the resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification in the coupling with *N*-acetylglycine. In a separate round-bottom flask, *N*-acetylglycine (141 mg, 1.2 mmol) was dissolved in anhydrous DMF (10 mL). HOBT (147 mg, 1.09 mmol) was added, followed by *N,N′*-diisopropylcarbodiimide (170 µL, 1.09 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (1.09 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 1:2:7 EtOAc:hexanes:CH_2Cl_2) to give phosphinothioester **52** as a colorless oil in 81% yield. **Spectral data.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.29 (m, 4H), 6.30 (bm, 1H), 4.14 (d, J = 5.8 Hz, 2H), 3.46 (d, J = 4.0 Hz, 2H), 2.02 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 196.08, 170.54, 135.98, 134.80 (d, J = 15.8 Hz), 134.13 (d, J = 20.7 Hz), 129.16 (d, J = 7.4 Hz), 49.19, 25.32 (d, J = 24.4 Hz), 23.08 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −16.27 ppm.

AcGlySCH₂P(*p*-OCH₃-C₆H₄)₂ (53). The thioacetate of phosphine **2** [2] (668 mg, 2.0 mmol) was dissolved in degassed MeOH (20 mL). NaOH (80 mg, 2.0 mmol) was added to the solution, and the resulting mixture was allowed to stir under Ar(g) for 1.5 h. The solvent was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and this solution was washed with 1 M HCl and brine. The organic extracts were dried over anhydrous $MgSO_4$(s), filtered, and concentrated under reduced pressure. The resulting residue was used without further purification in the coupling with *N*-acetylglycine. In a separate round-bottom flask, *N*-acetylglycine (211 mg, 1.8 mmol) was dissolved in anhydrous DMF (18 mL). HOBT (236 mg, 1.8 mmol) was added, followed by *N,N′*-diisopropylcarbodiimide (281 µL, 1.8 mmol). The resulting mixture was stirred for 20 min, and freshly deprotected phosphinothiol from above was added (1.8 mmol). The reaction mixture was allowed to stir under Ar(g) for 4 h. The solvent was then removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 70% v/v EtOAc in hexanes) to give phosphinothioester **53** as a white solid in 85% yield.

Spectral data. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (t, J = 8.0 Hz, 4H), 6.89 (d, J = 8.4 Hz, 4H), 4.15 (d, J = 5.6 Hz, 2H), 3.80 (s, 6H), 3.45 (d, J = 3.6 Hz, 2H), 2.02 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 196.42, 170.47, 160.73, 134.31 (d, J = 22.3 Hz), 127.72 (d, J = 9.1 Hz), 114.57 (d, J = 7.3 Hz), 55.41, 49.25, 26.14 (d, J = 23.8 Hz), 23.15 ppm; ^{31}P NMR ($CDCl_3$ with D_3PO_4 standard, 161 MHz) δ −18.26 ppm.

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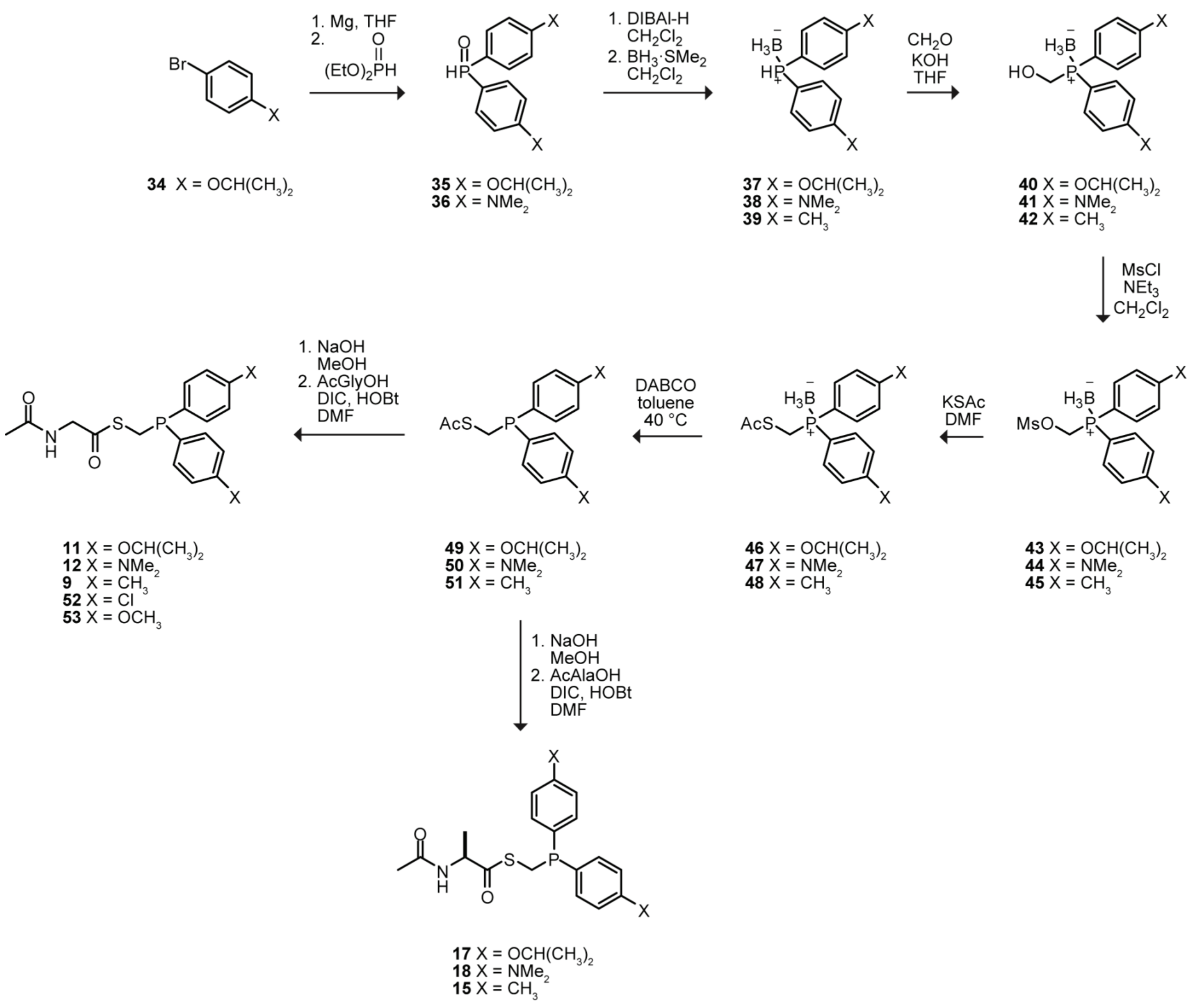
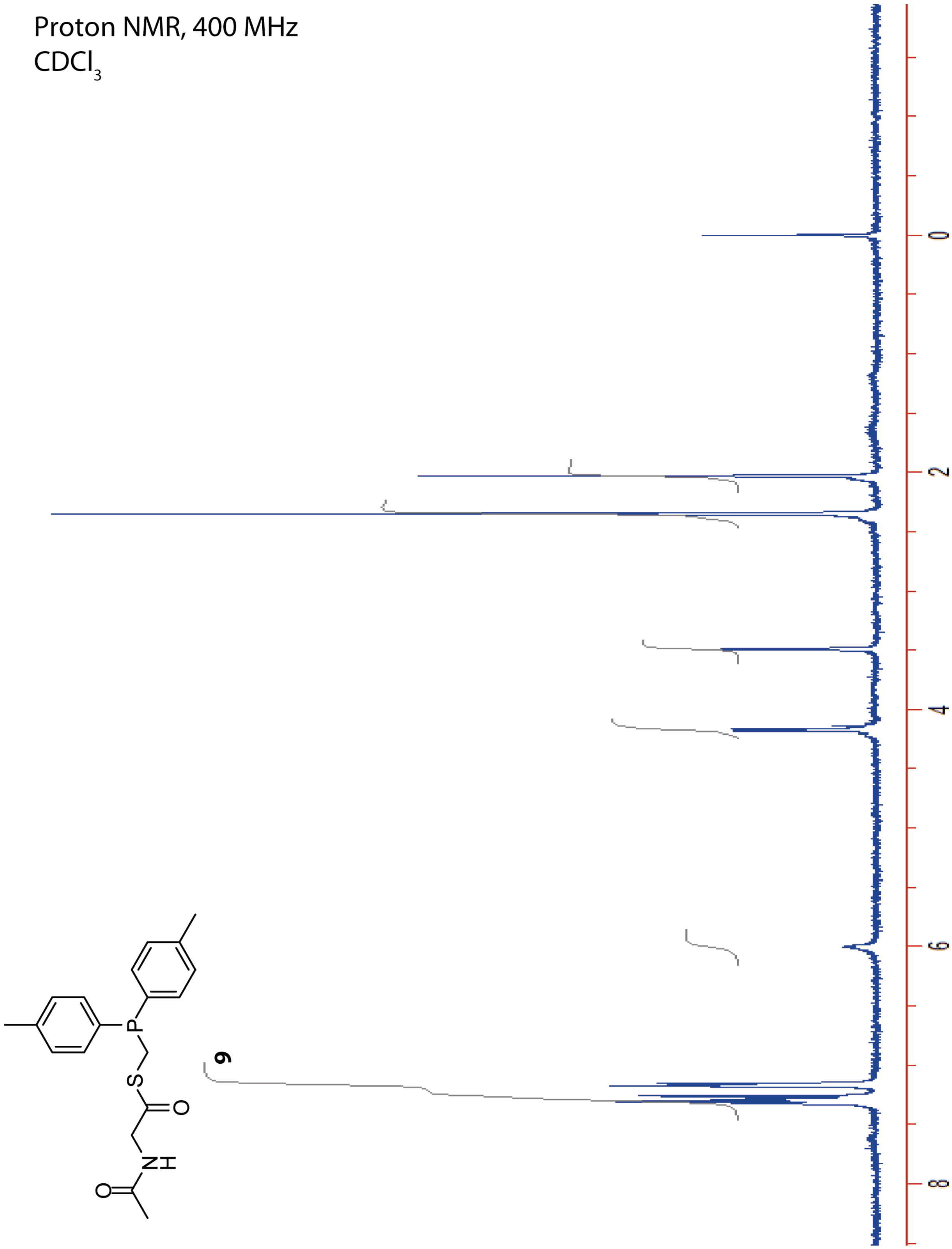


Scheme S1. Synthetic route to phosphinothioesters **15**, **17**, and **18**.

Proton NMR, 400 MHz
$CDCl_3$



9

Carbon-13 NMR, 100.6 MHz
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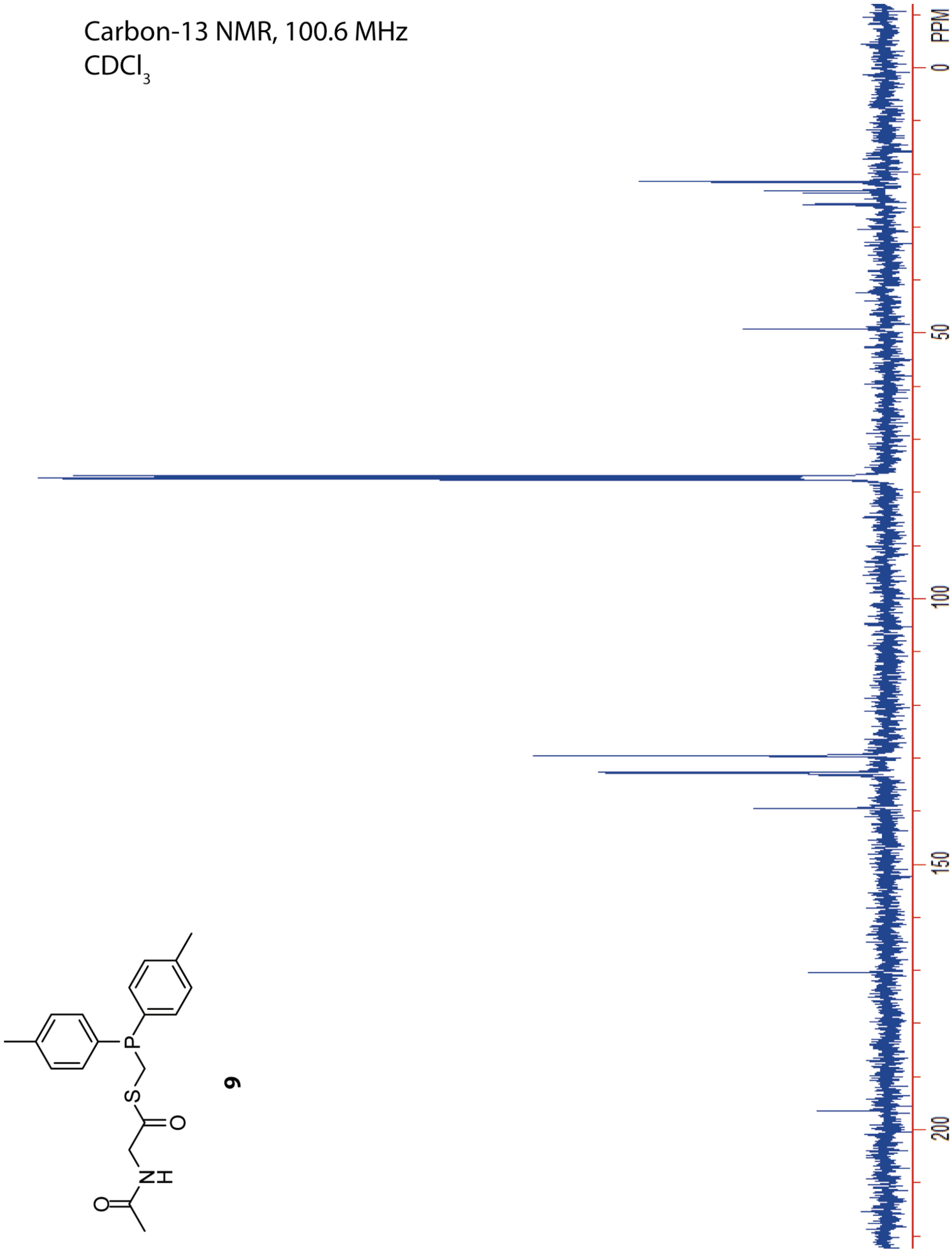

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Phosphorus-31 NMR, 121 MHz
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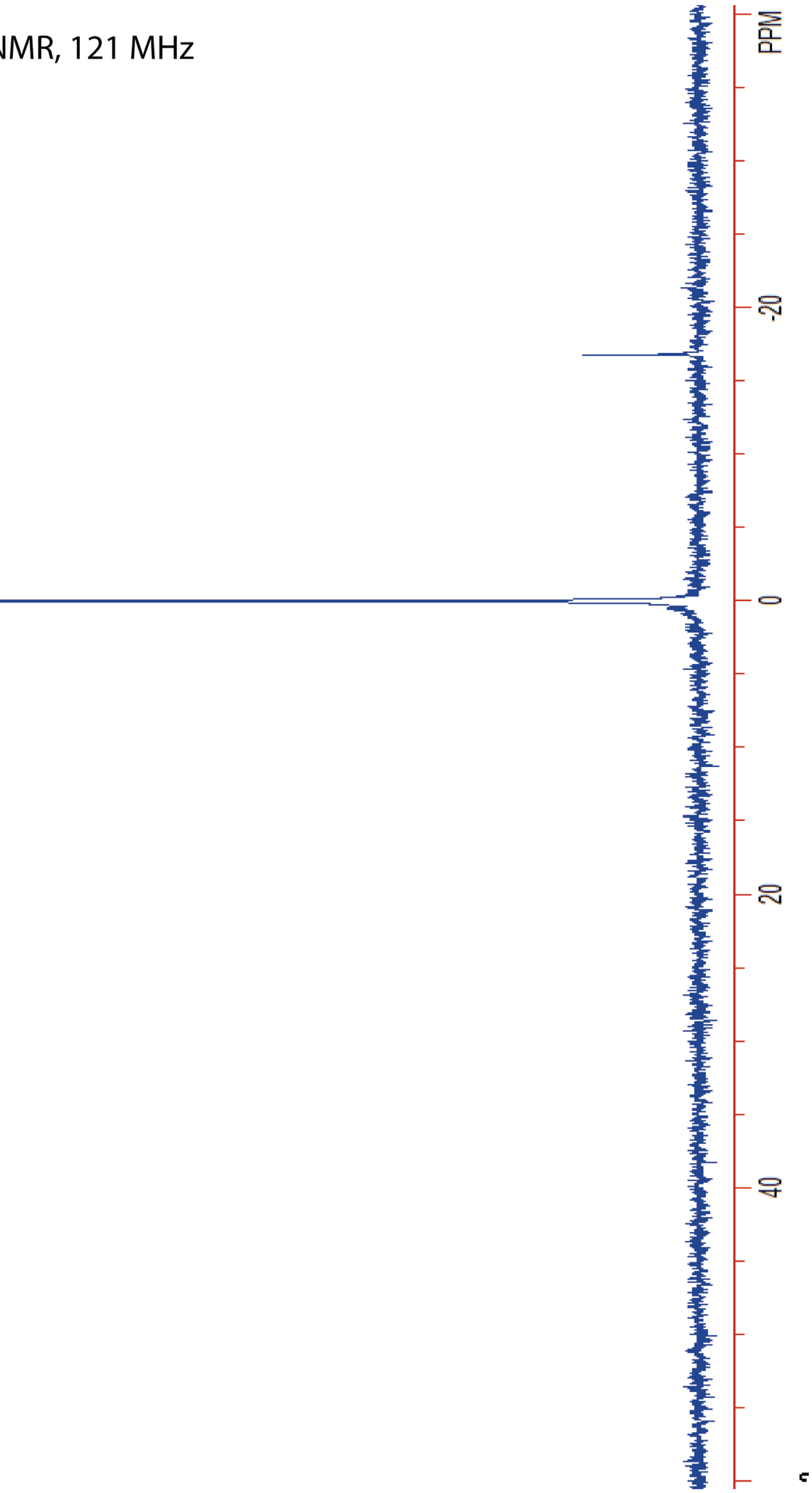

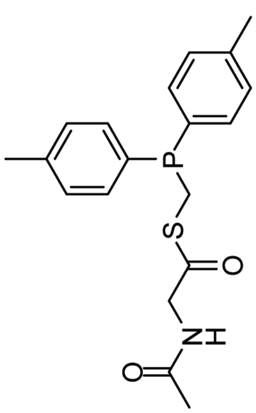

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Proton NMR, 400 MHz
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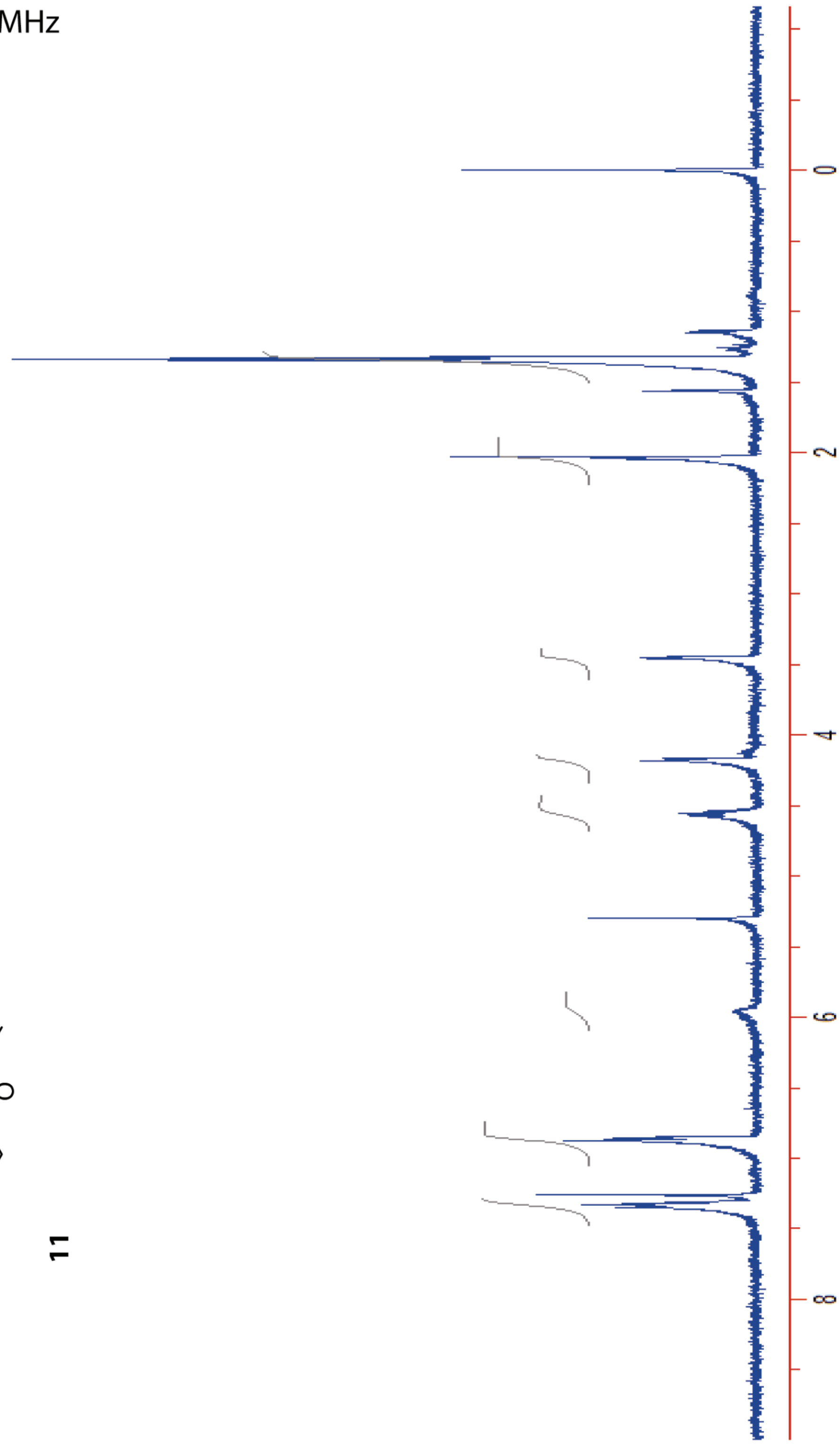

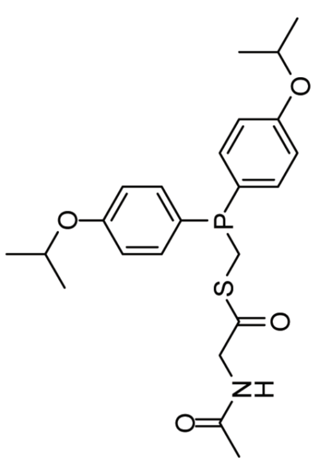

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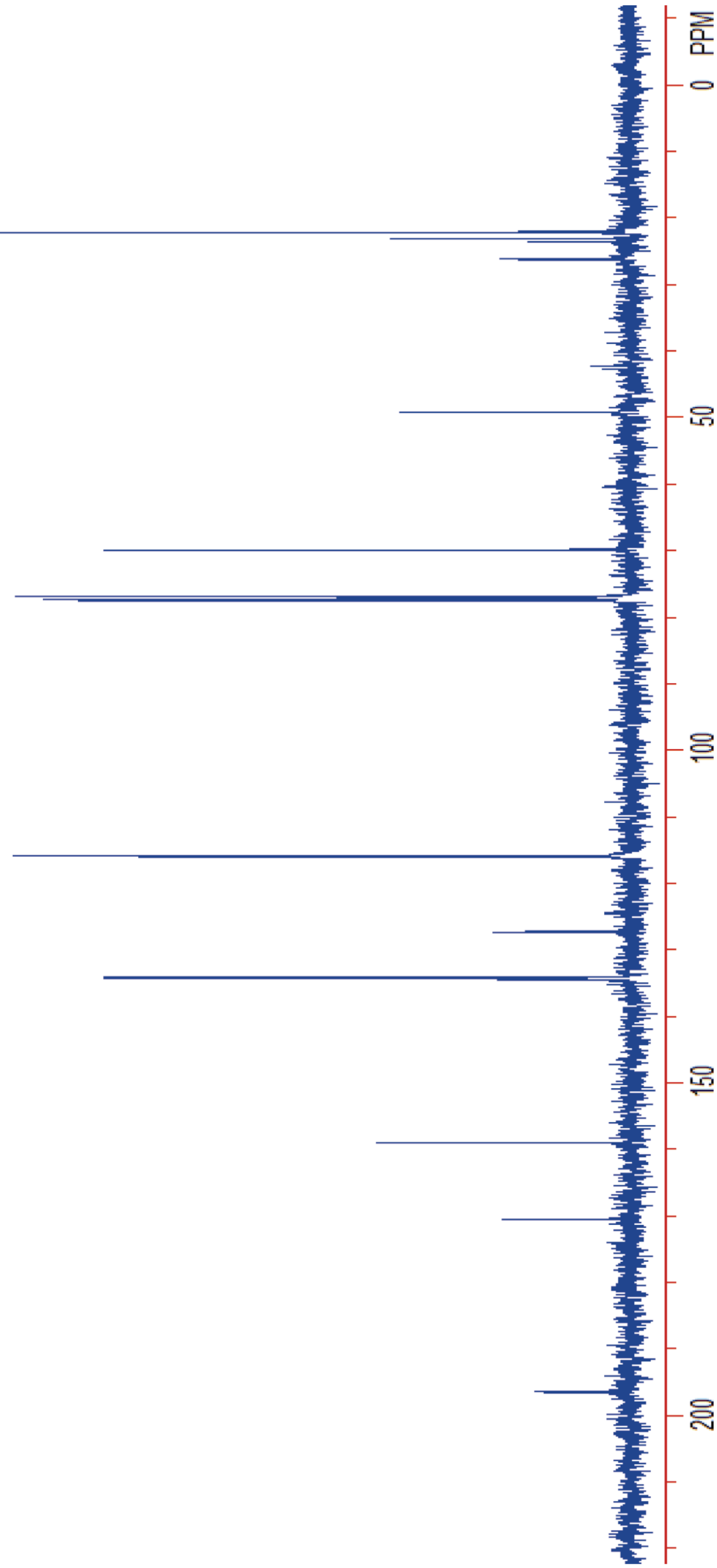
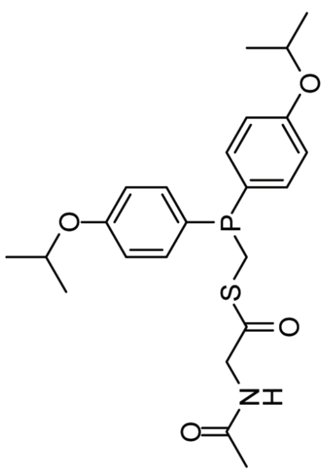
Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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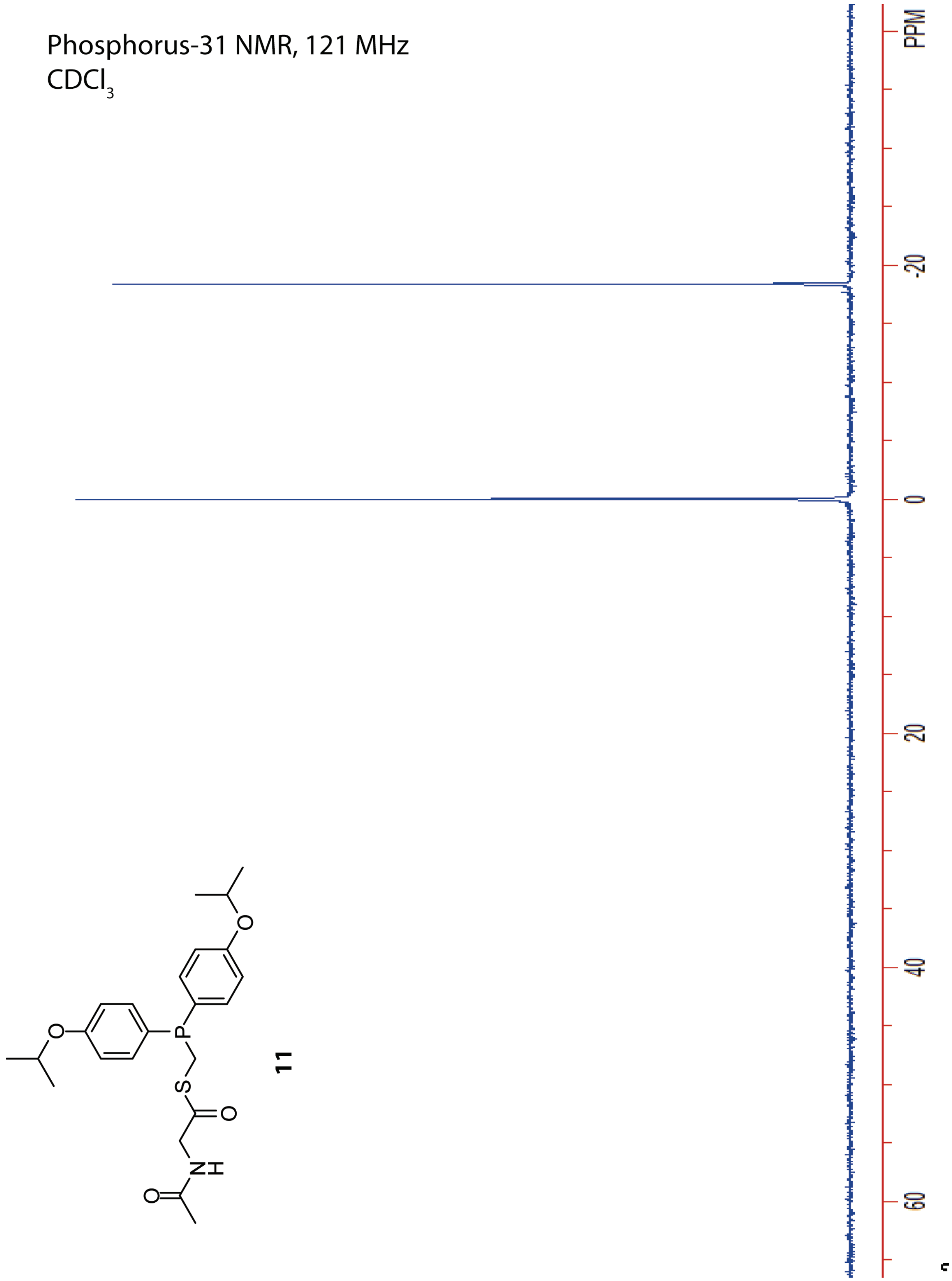
Phosphorus-31 NMR, 121 MHz
$CDCl_3$



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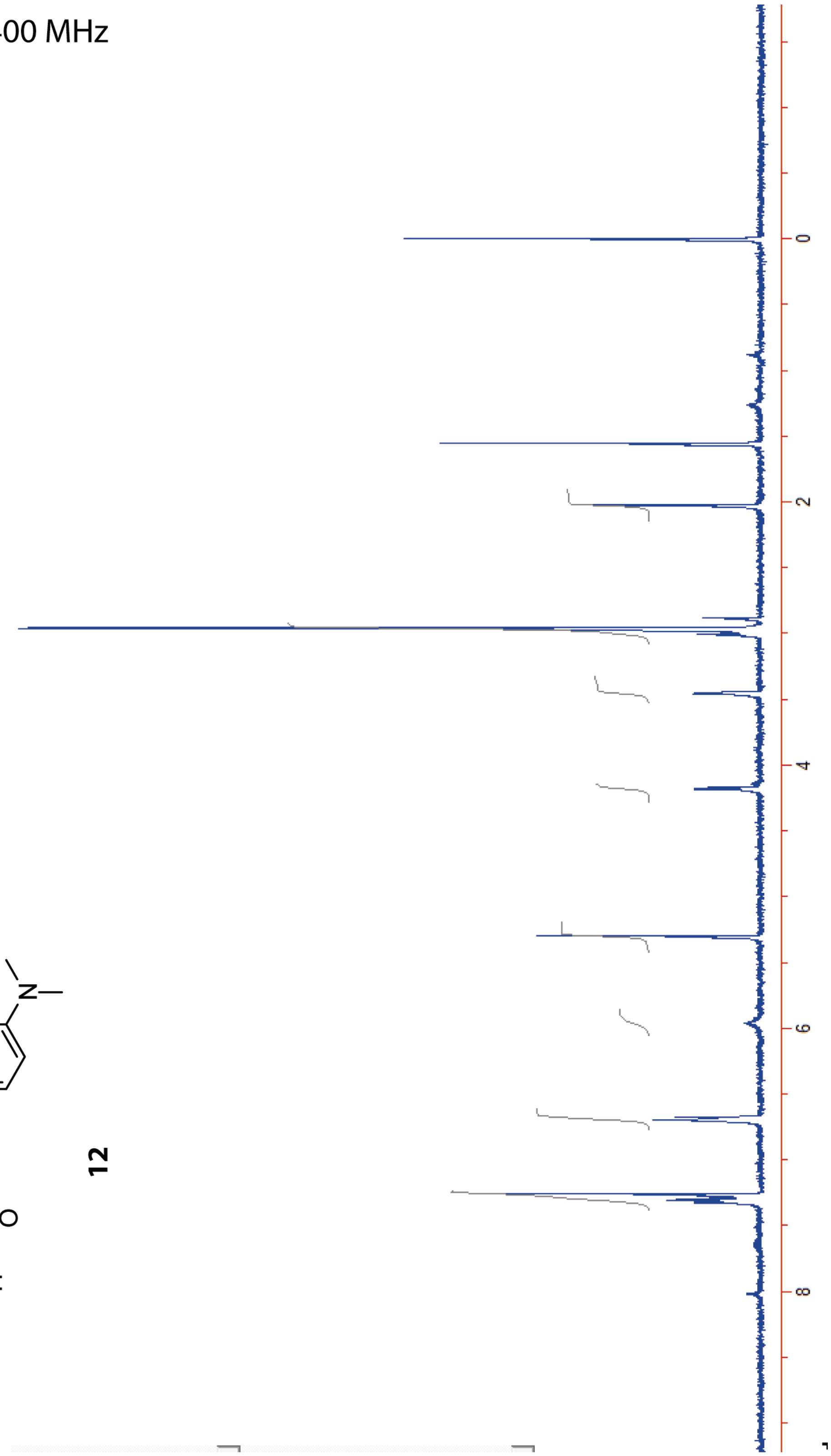
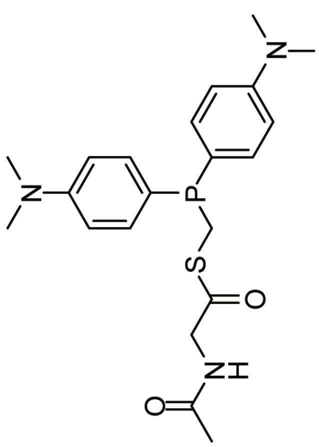
Proton NMR, 400 MHz
$CDCl_3$





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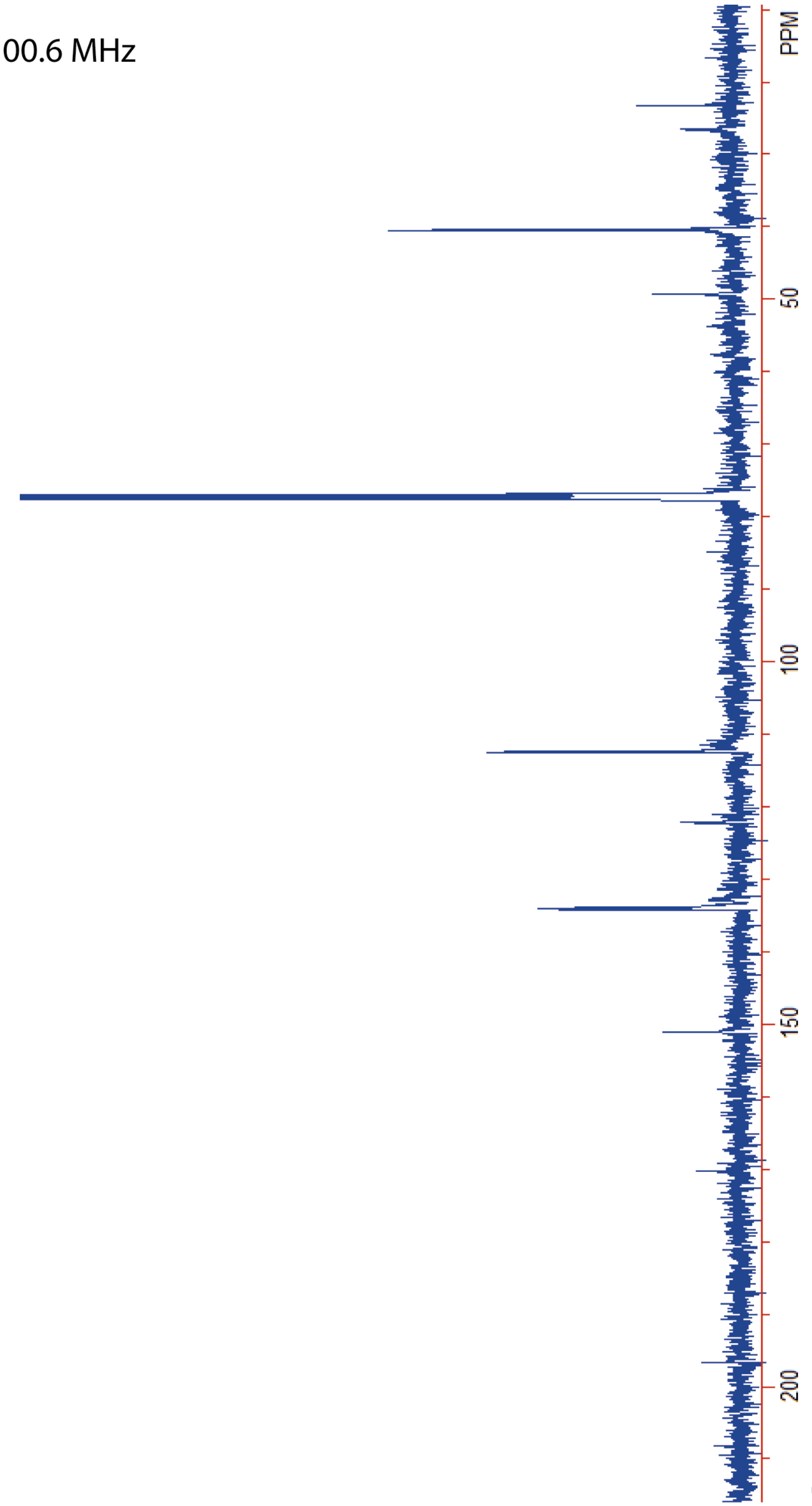
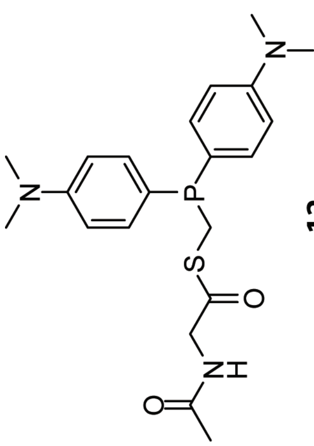
Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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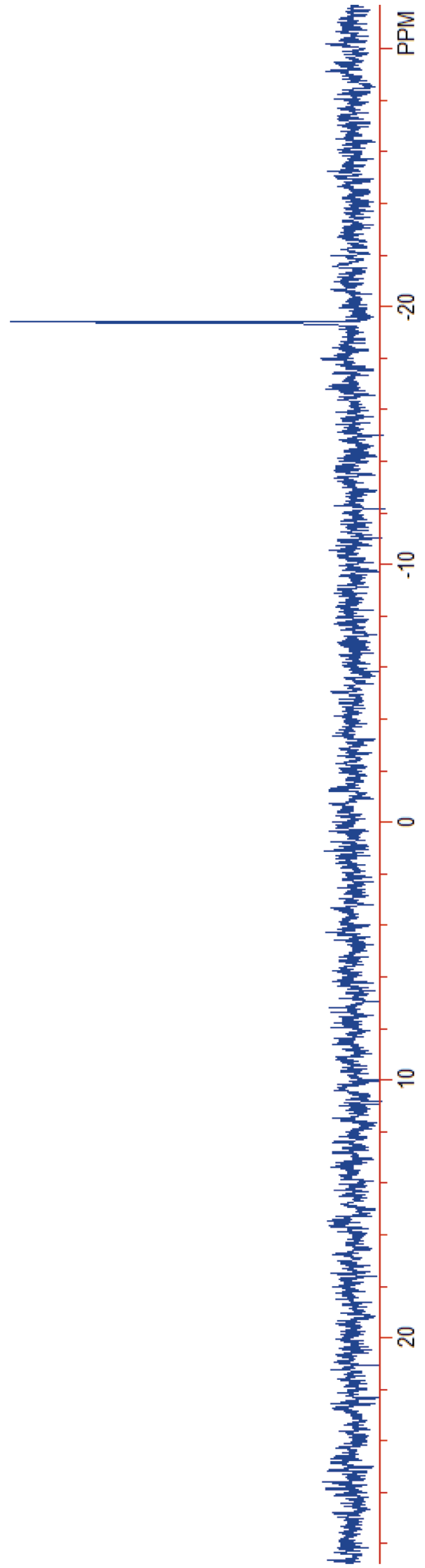
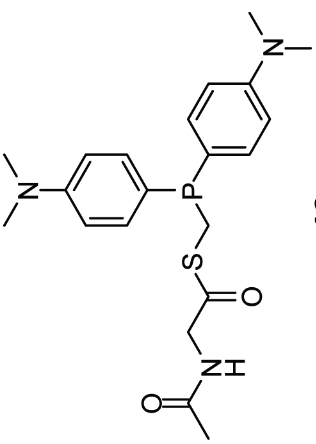
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





12

Proton NMR, 400 MHz
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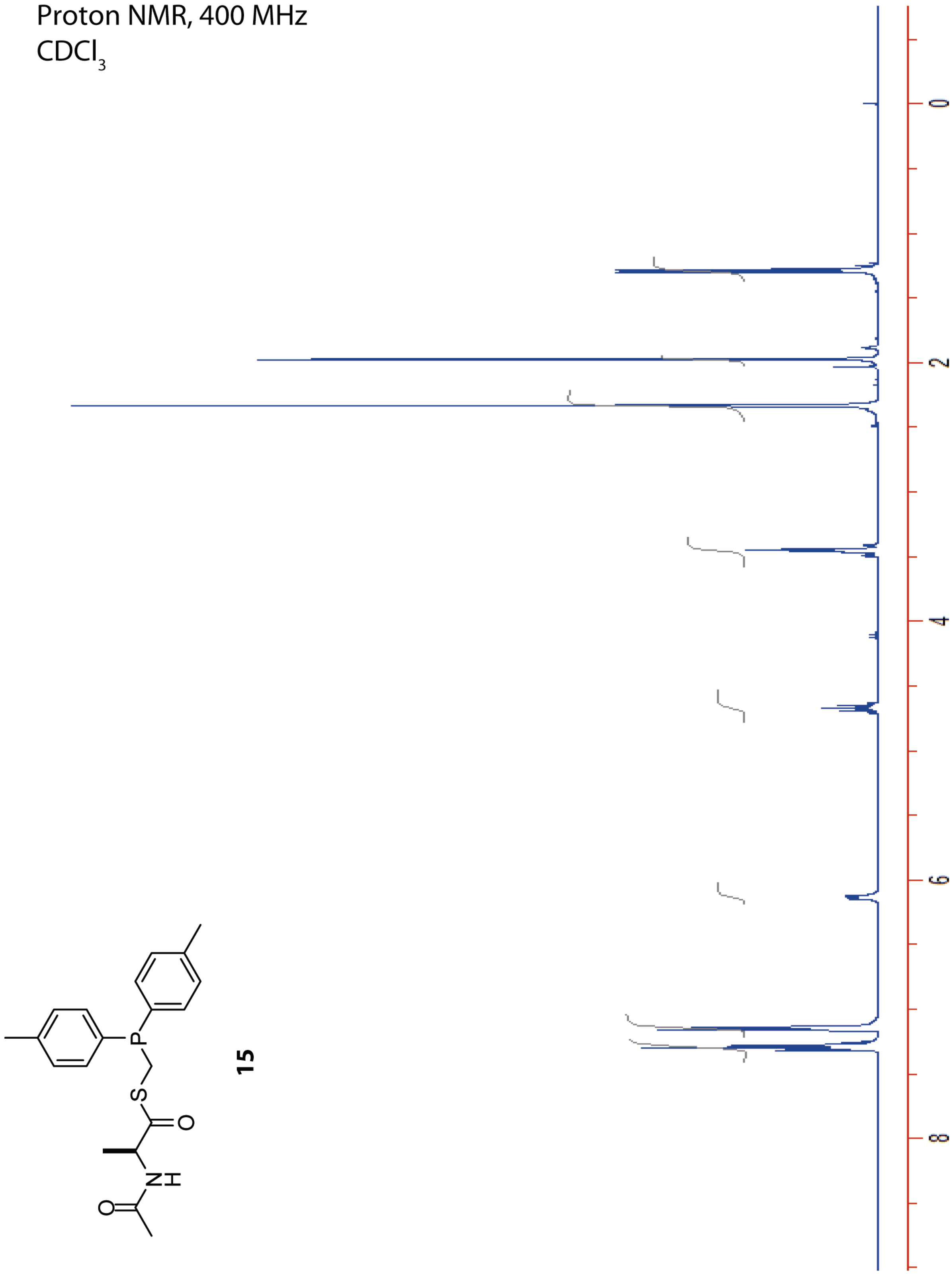

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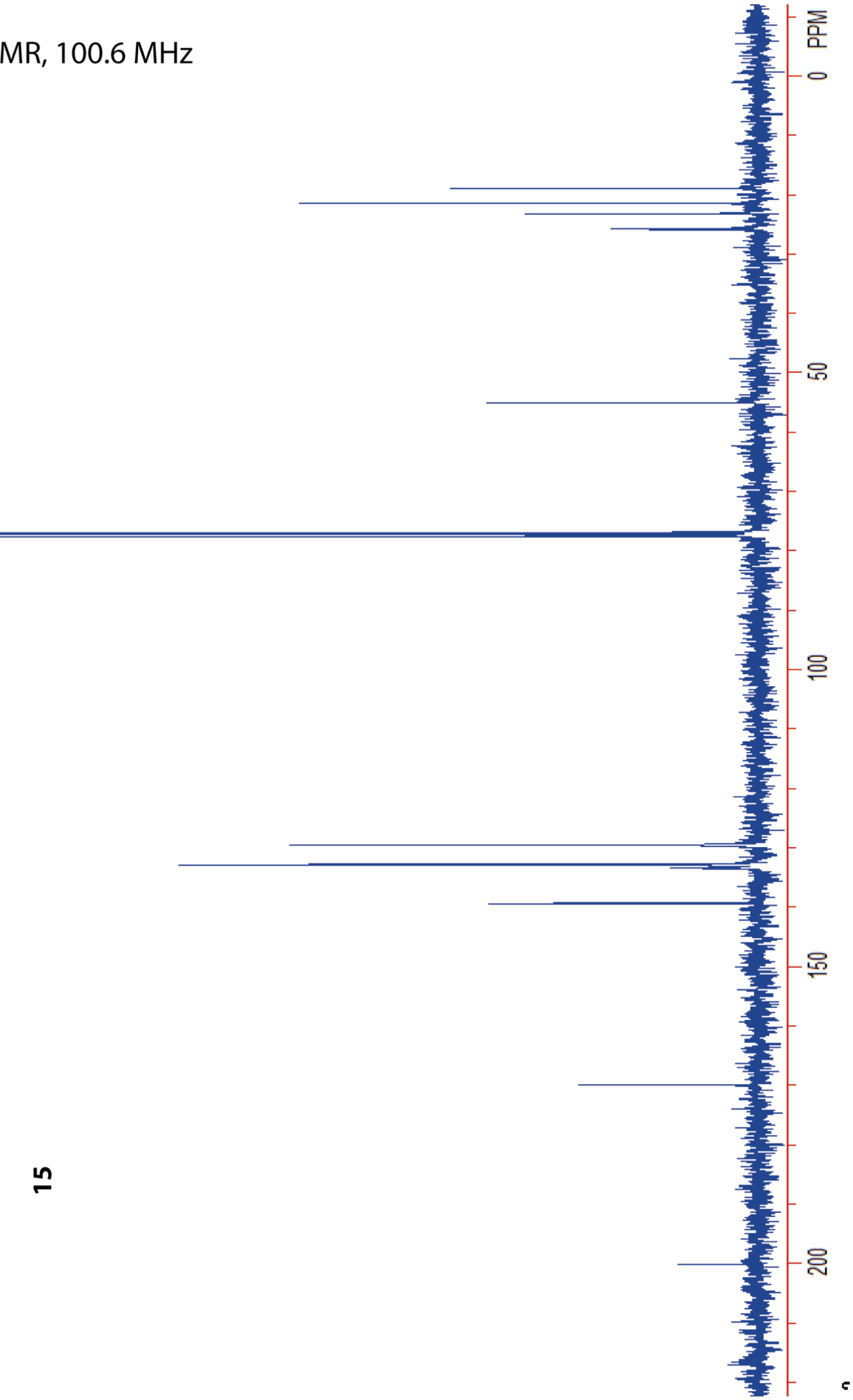
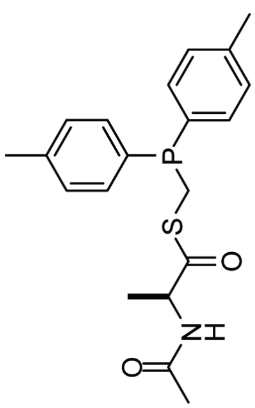
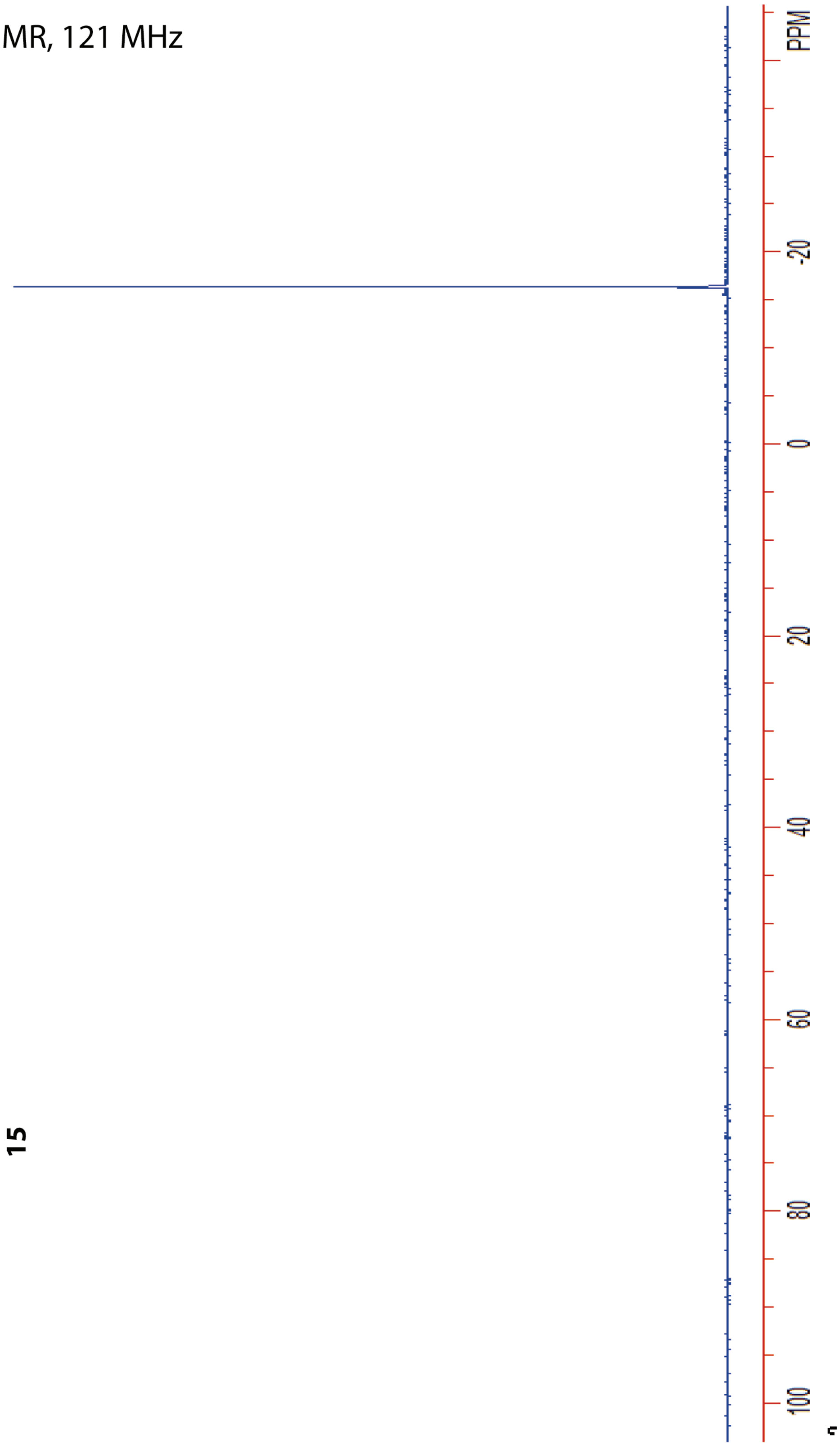
Carbon-13 NMR, 100.6 MHz
$CDCl_3$

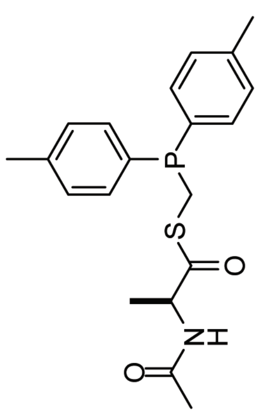




15

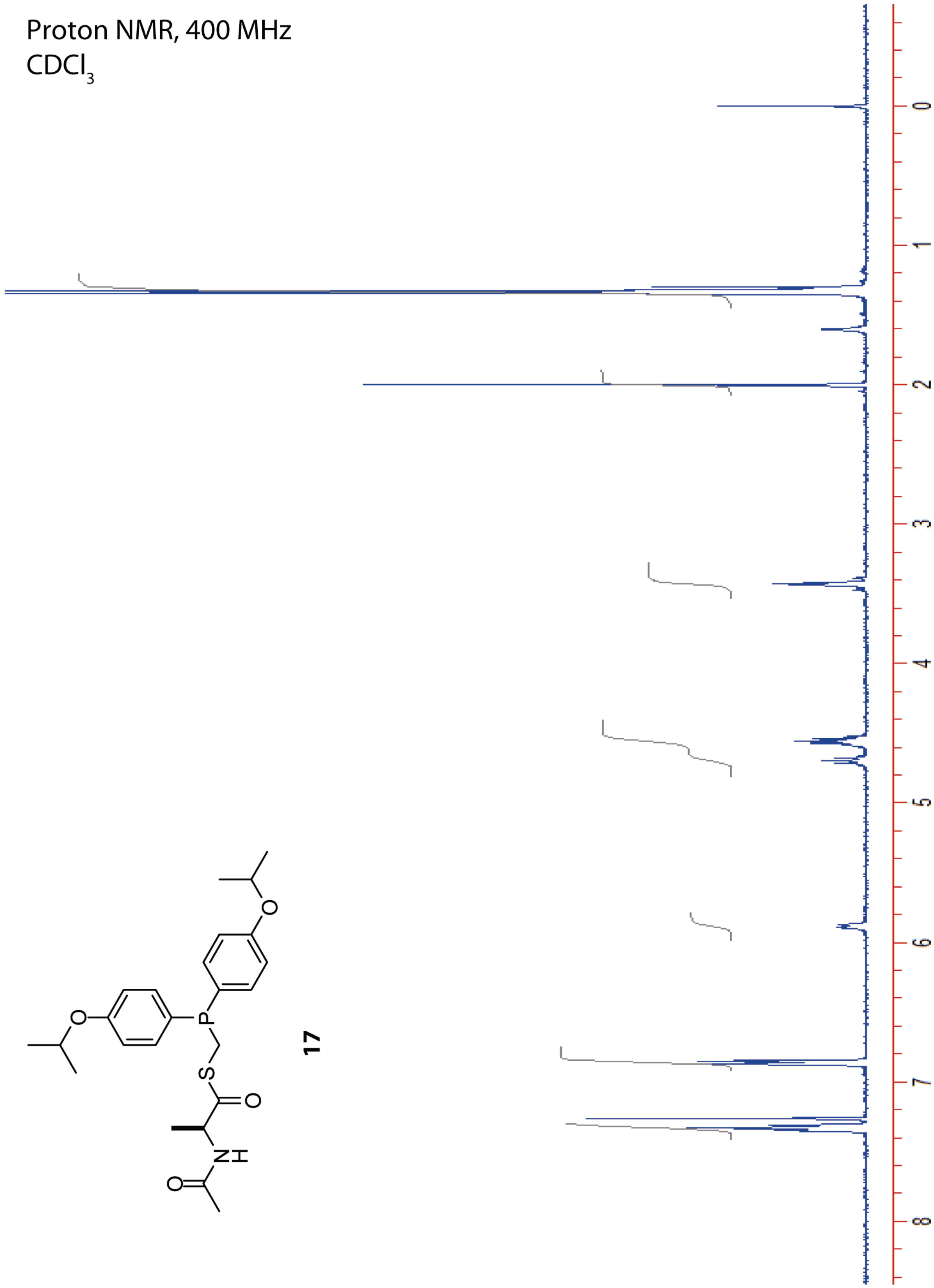
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





15

Proton NMR, 400 MHz
$CDCl_3$



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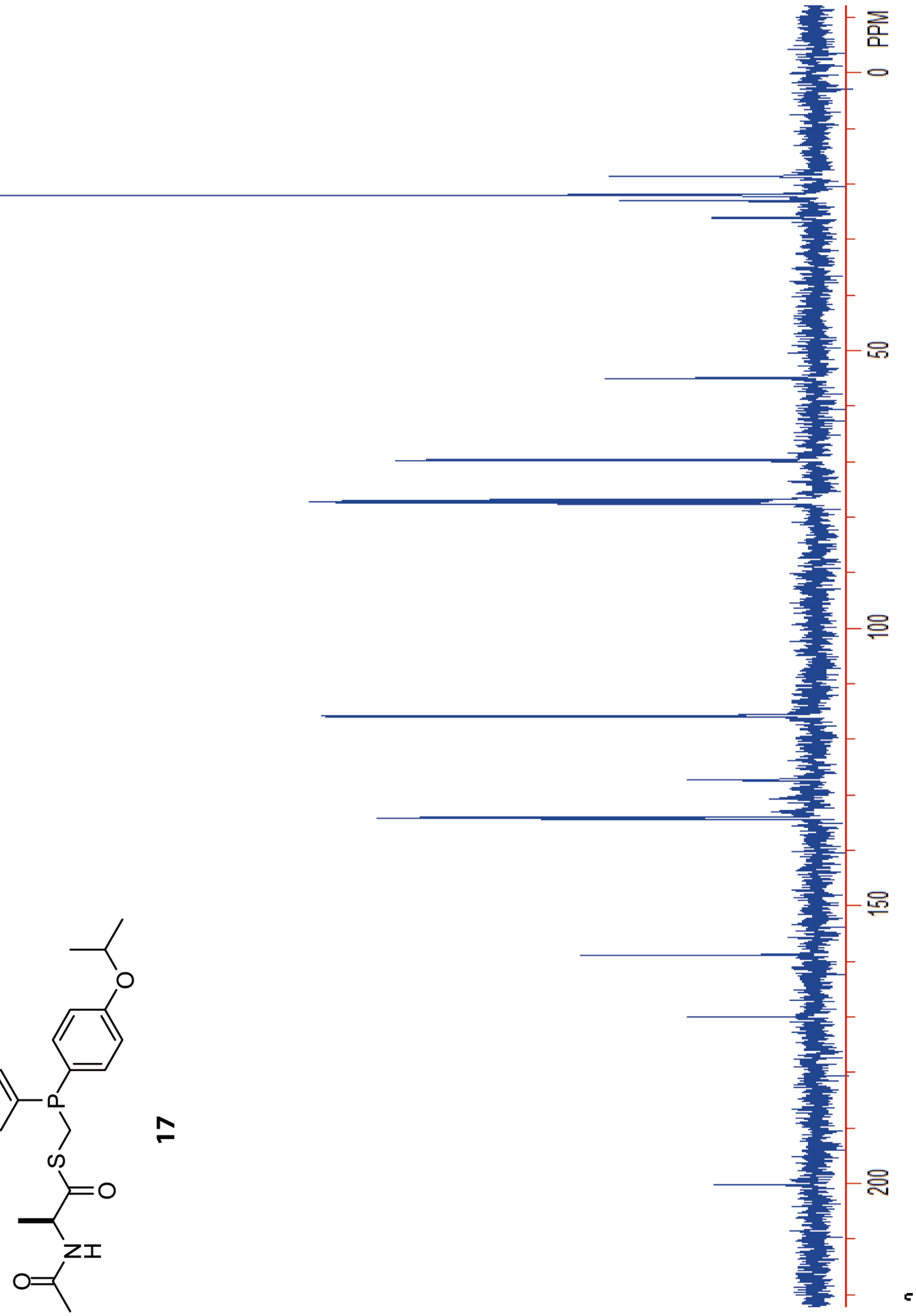
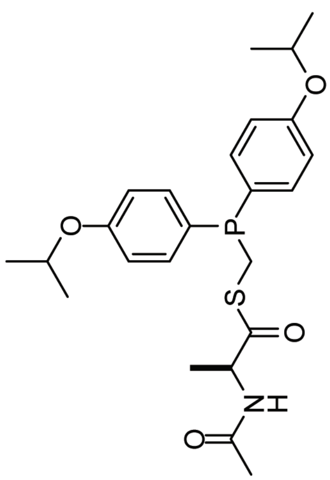
Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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Phosphorus-31 NMR, 121 MHz
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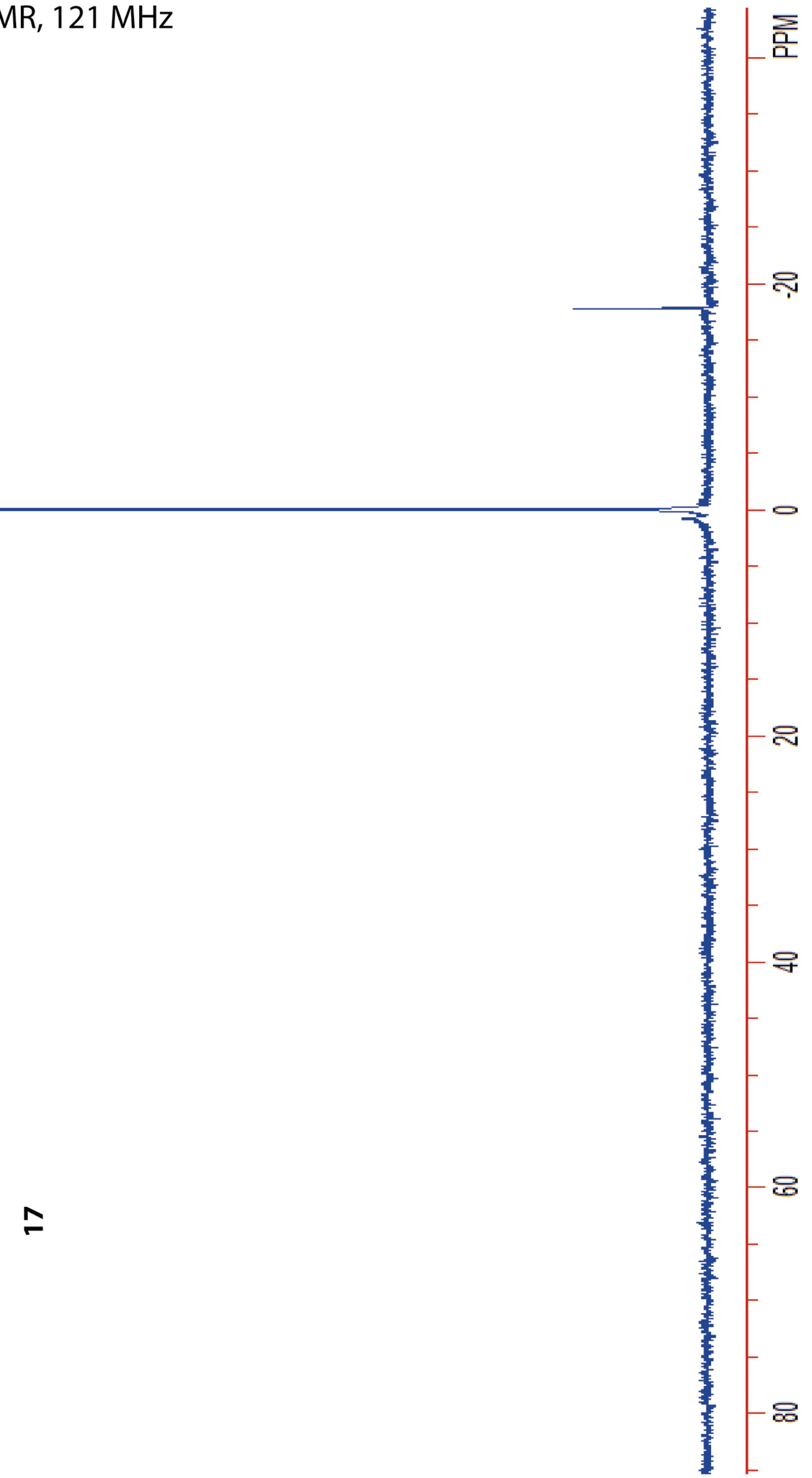

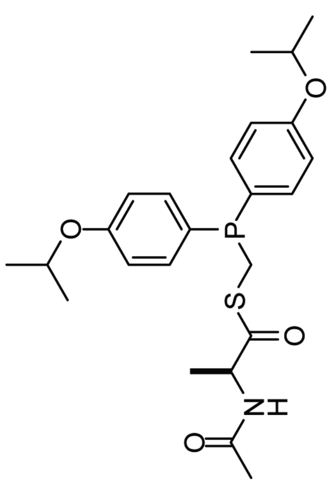

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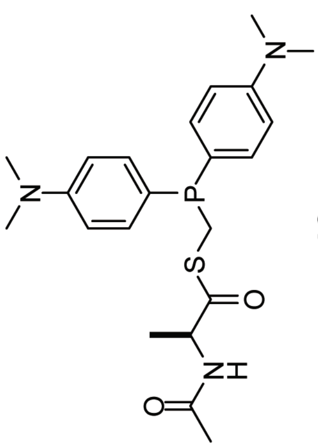
Proton NMR, 400 MHz
$CDCl_3$



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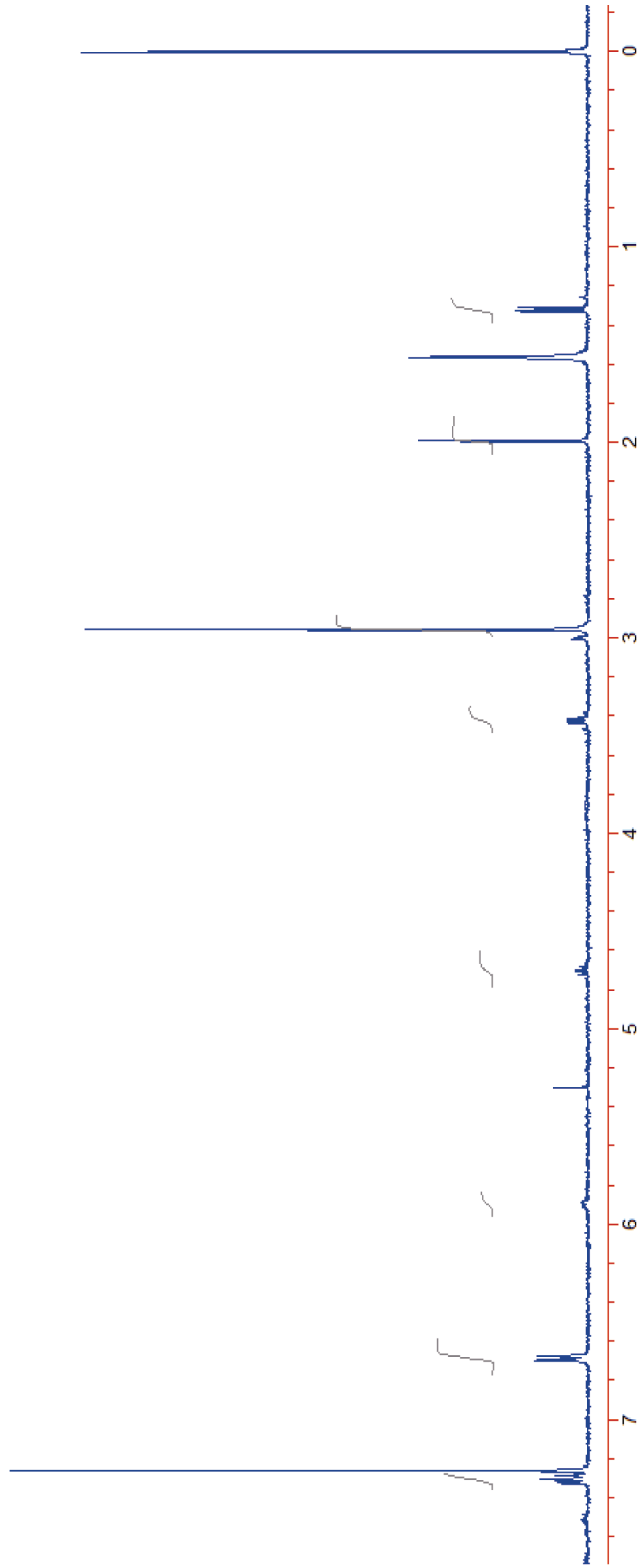
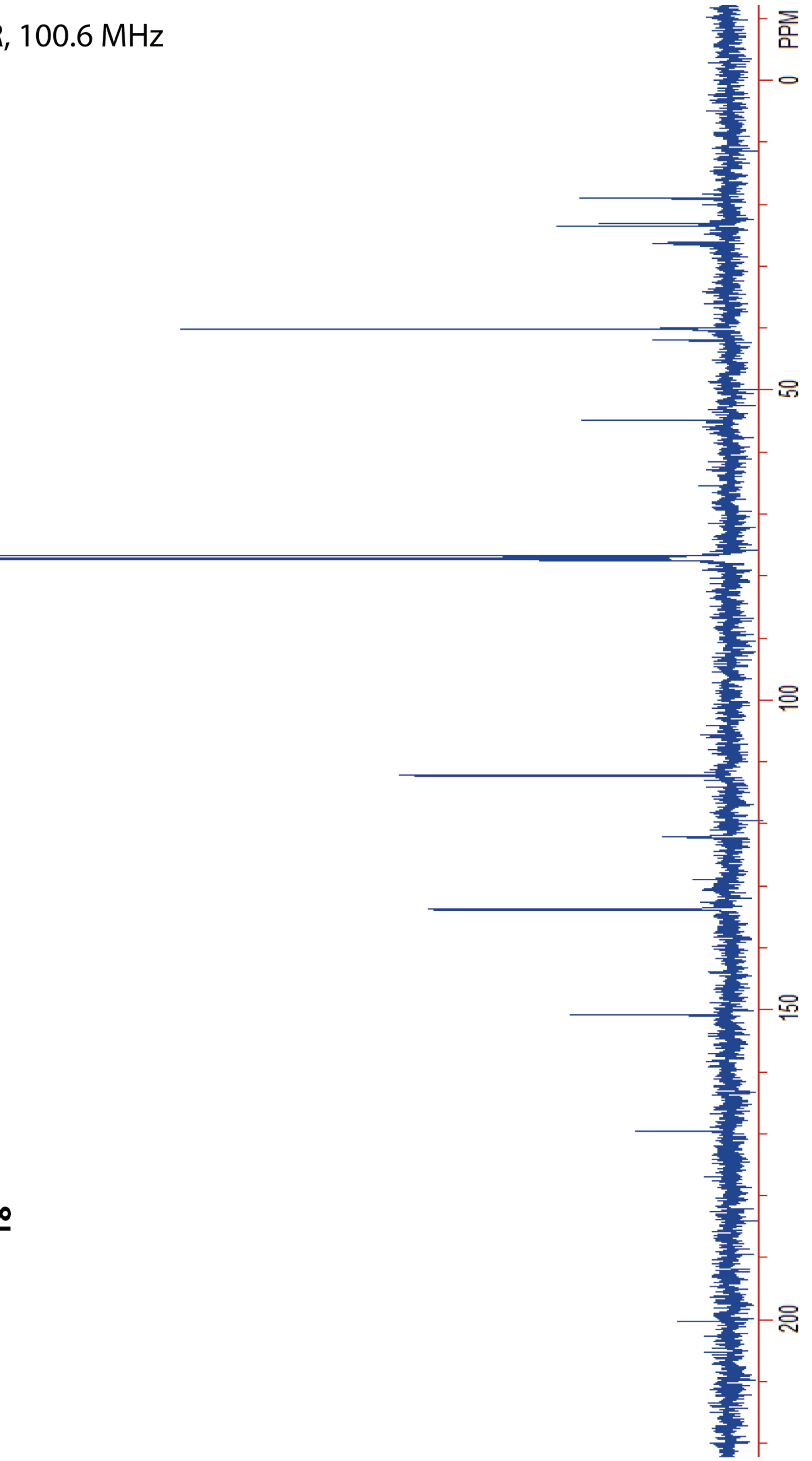
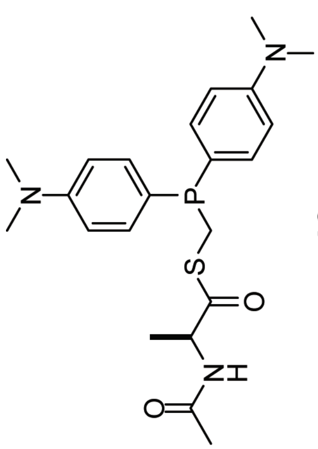


Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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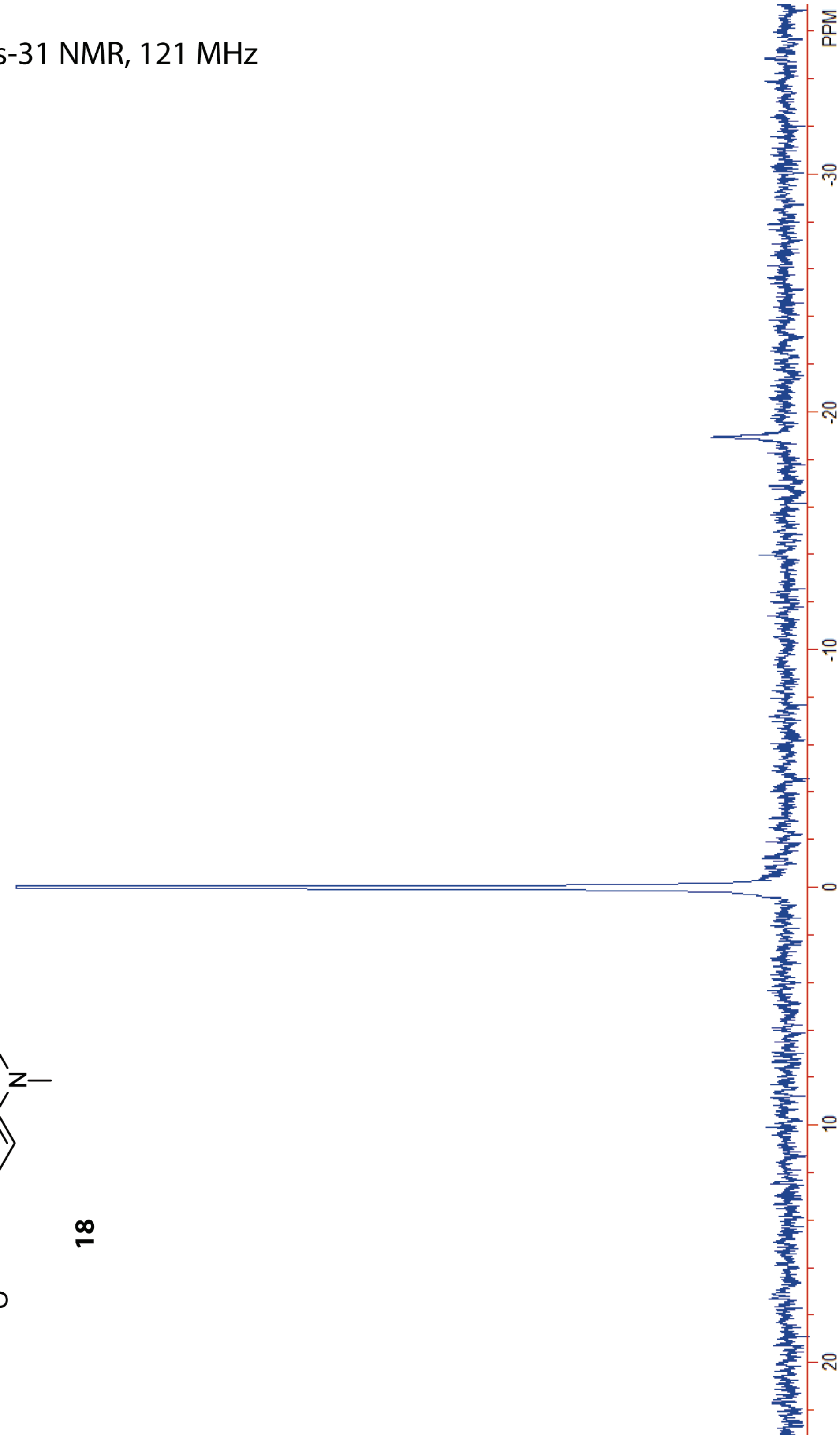
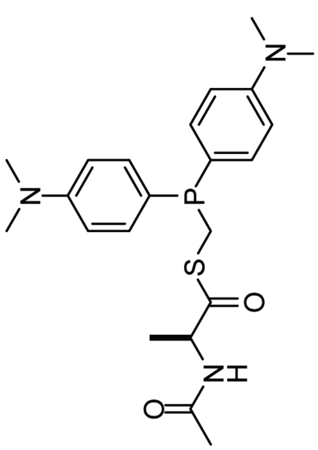
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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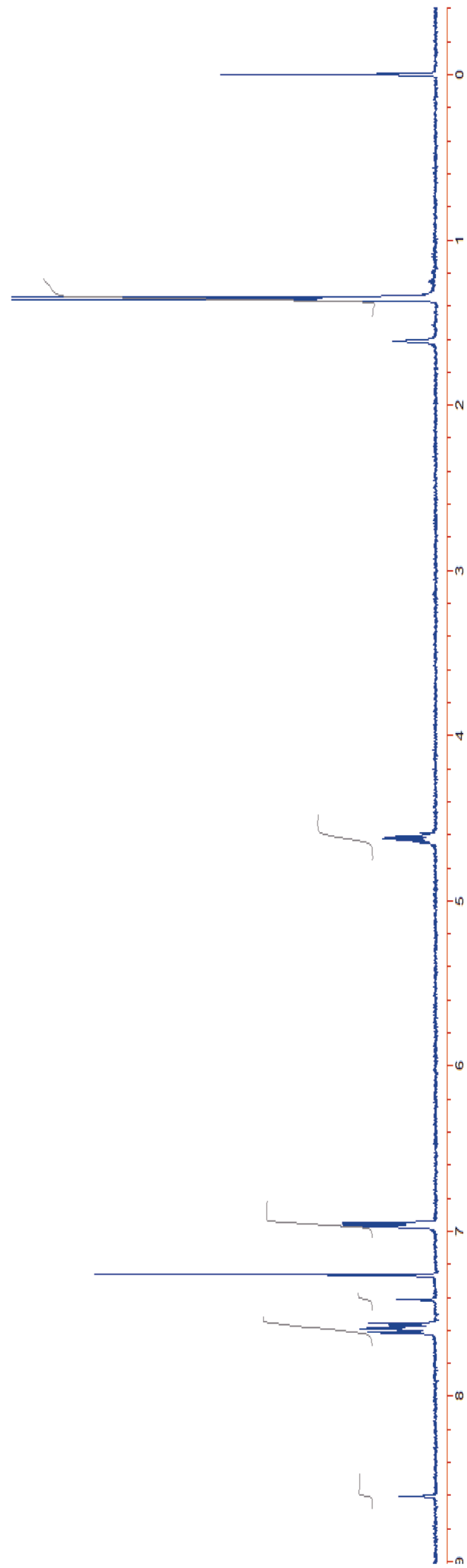
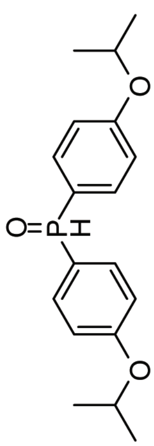
Proton NMR, 400 MHz
$CDCl_3$

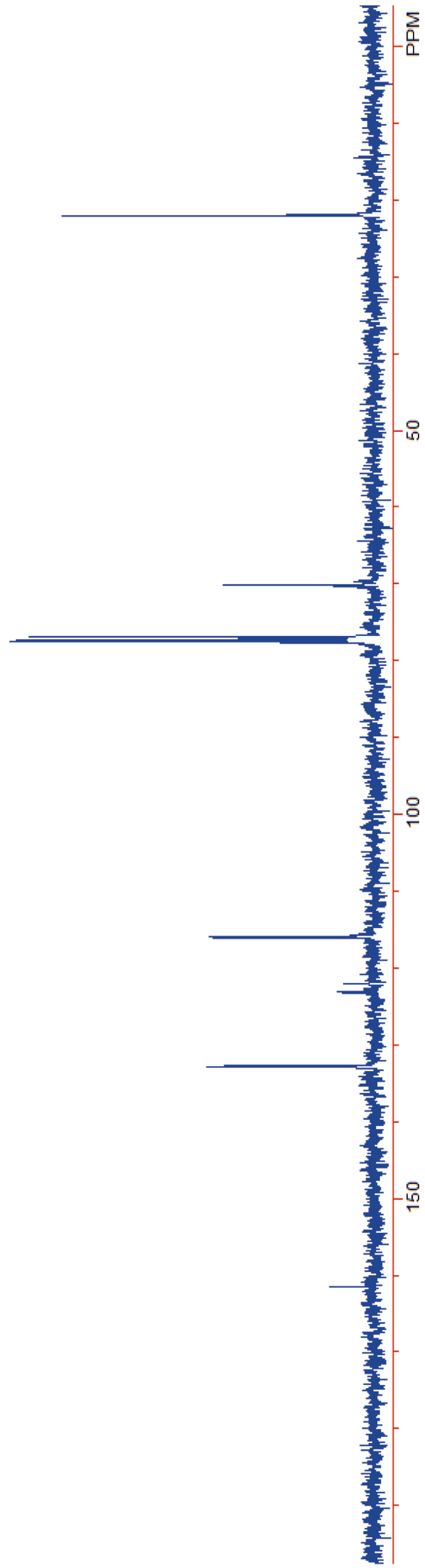


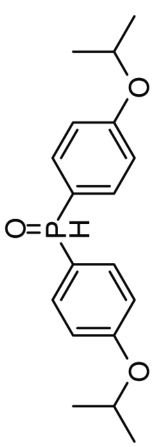


35

Supplementary Material for Organic & Biomolecular Chemistry

Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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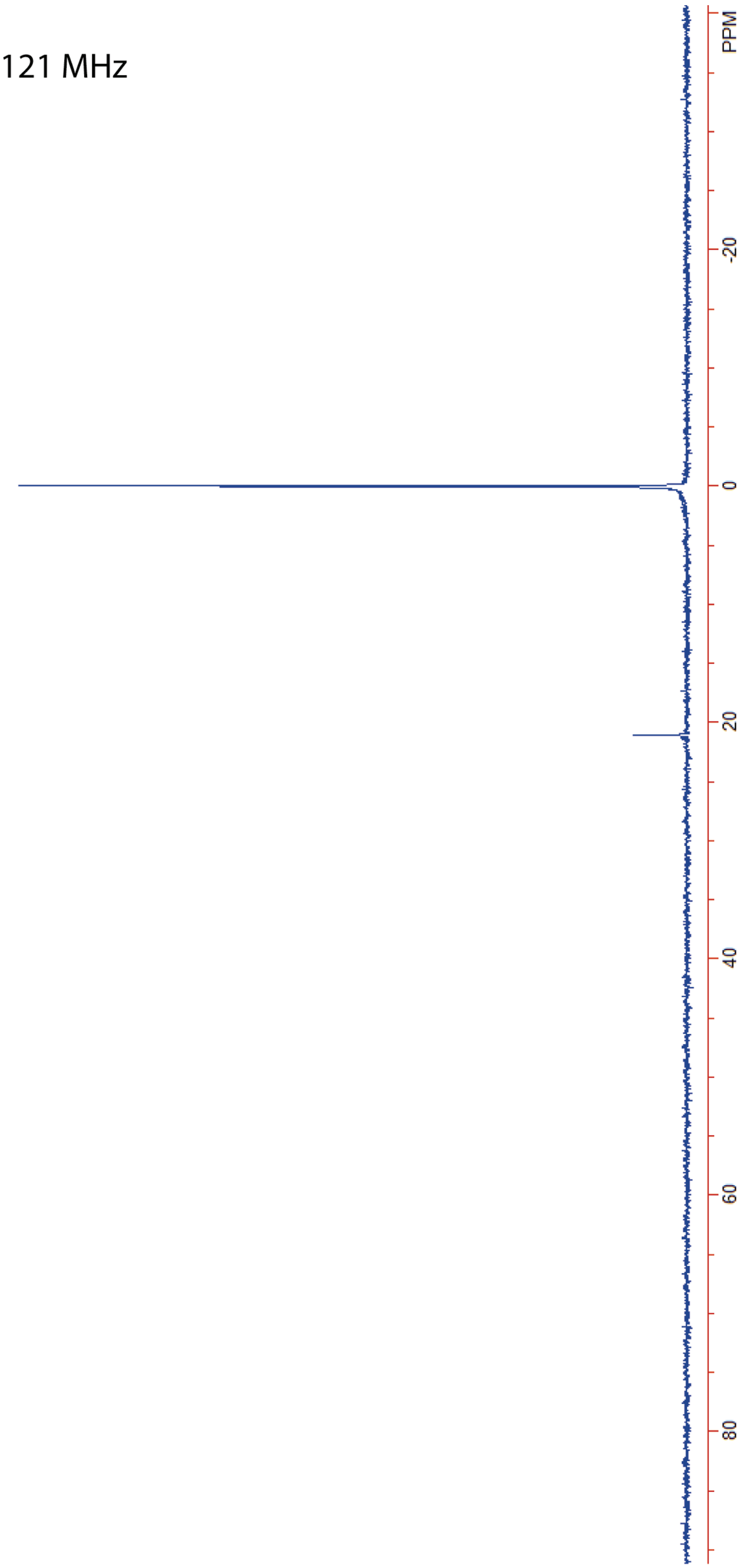
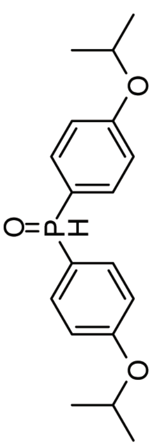
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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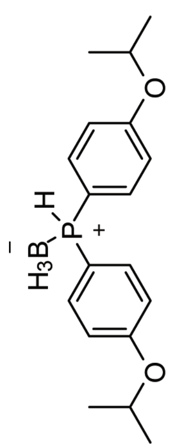
Proton NMR, 400 MHz
$CDCl_3$



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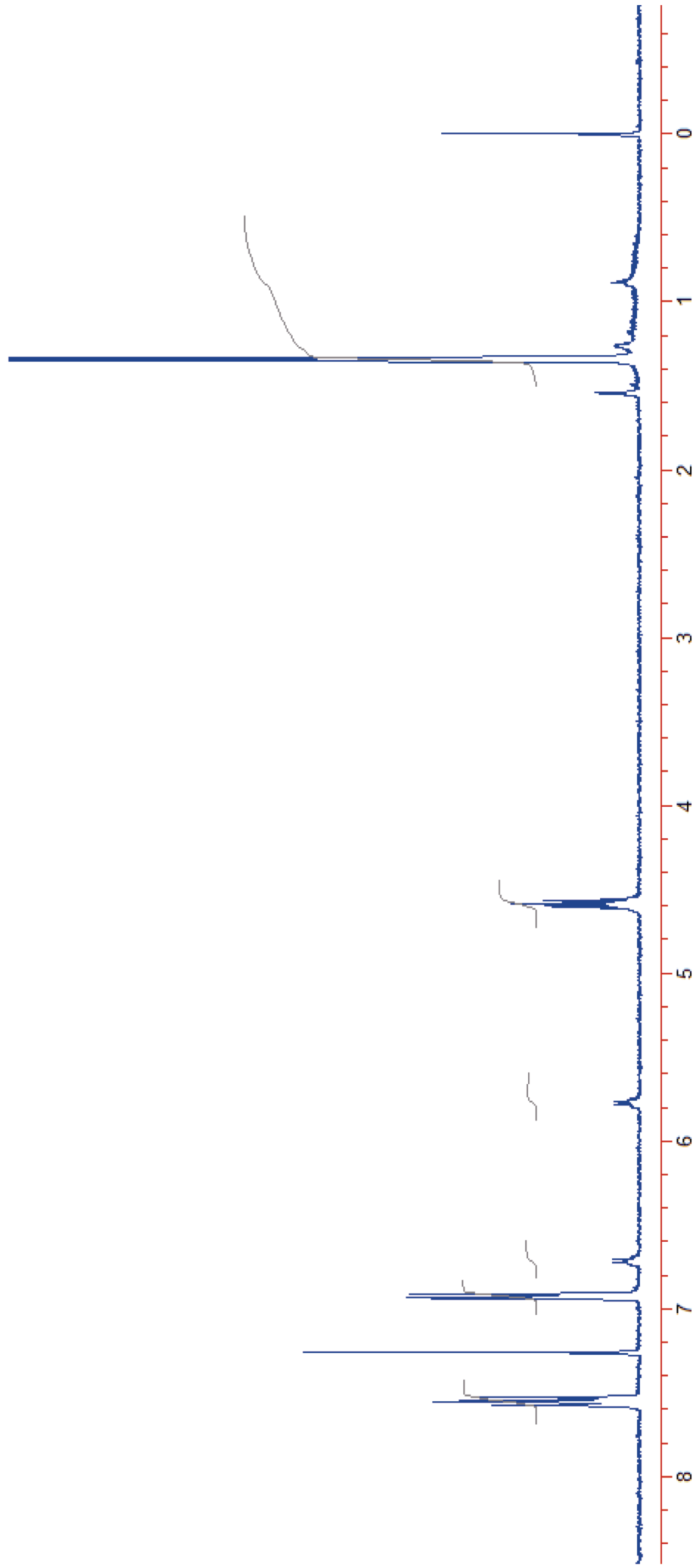
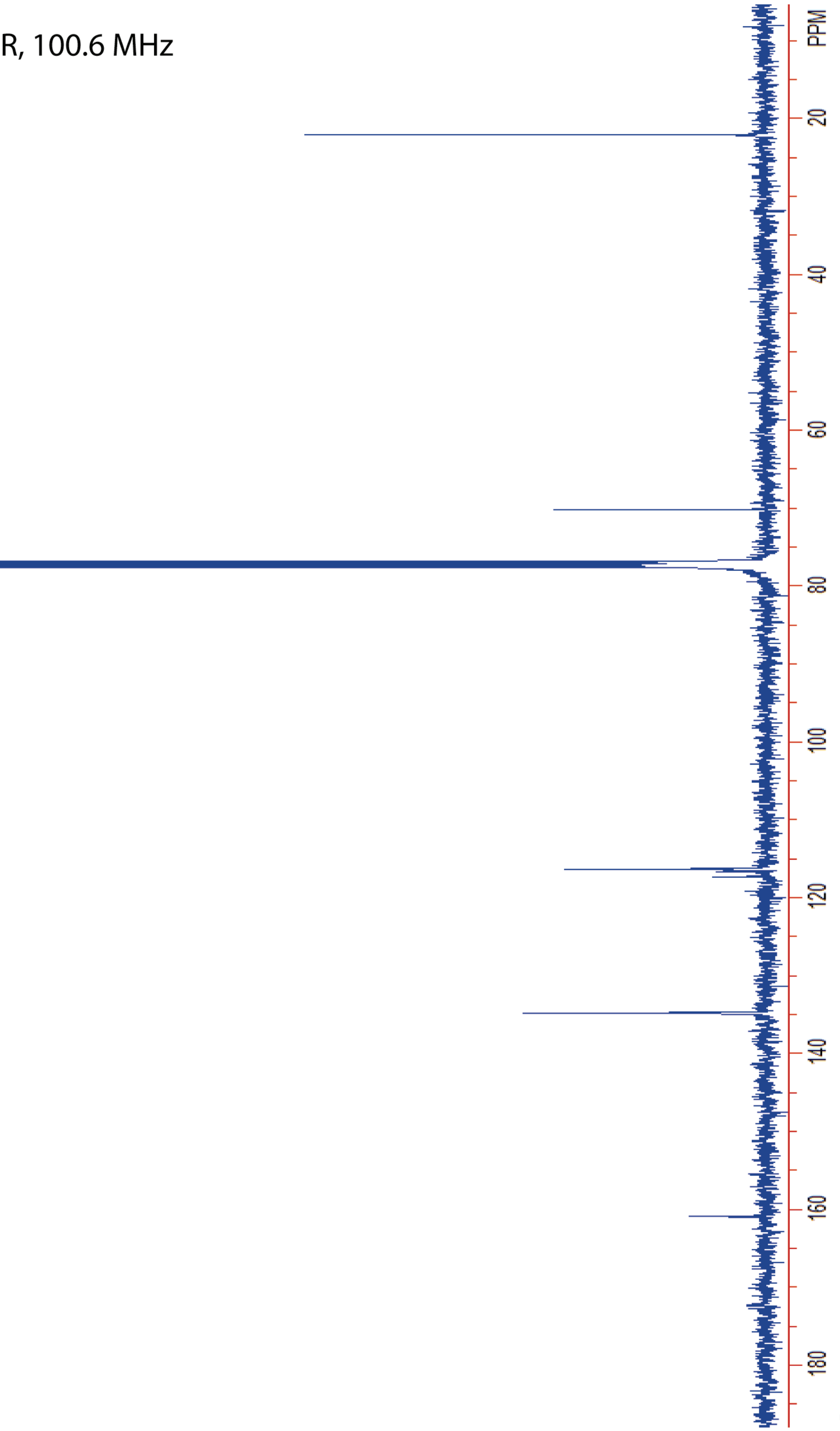
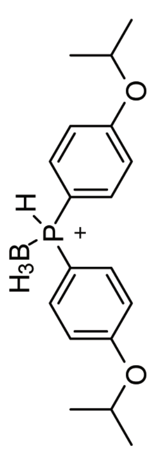


Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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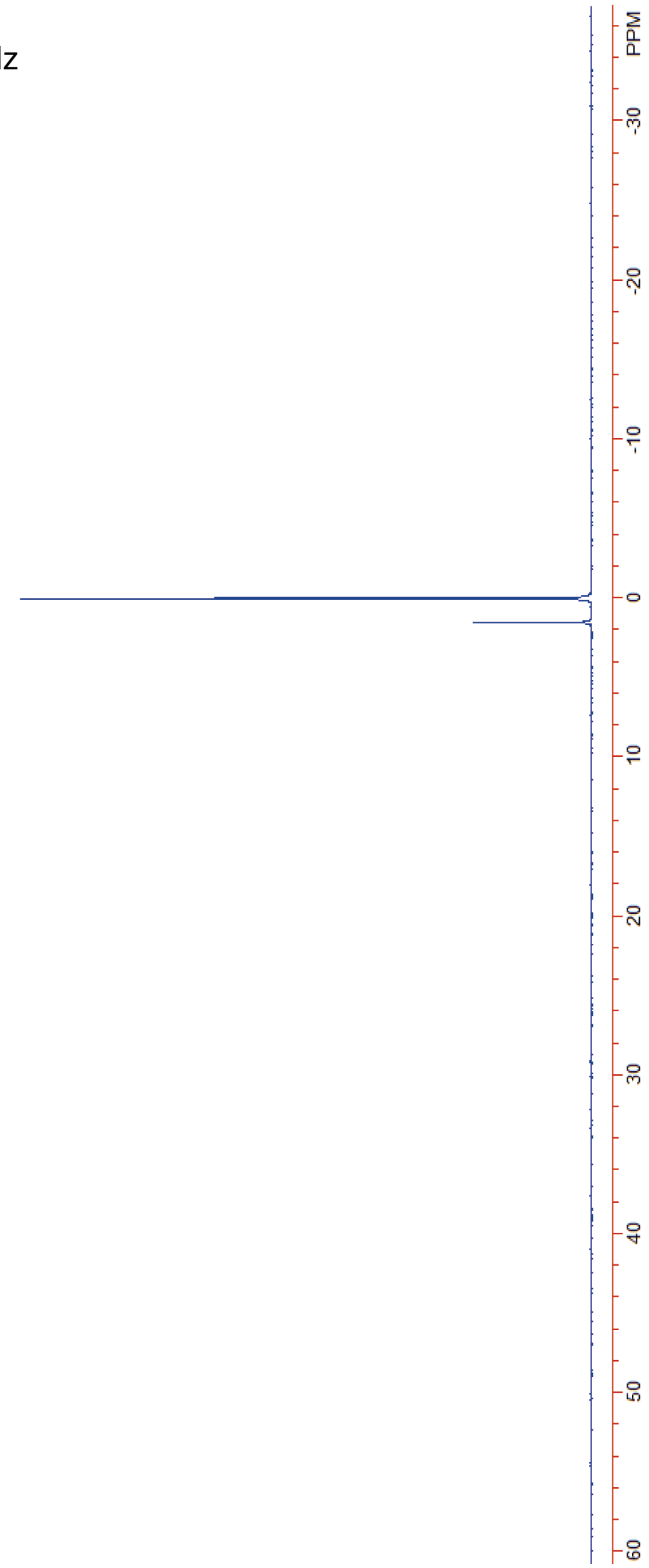
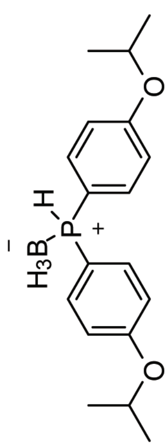
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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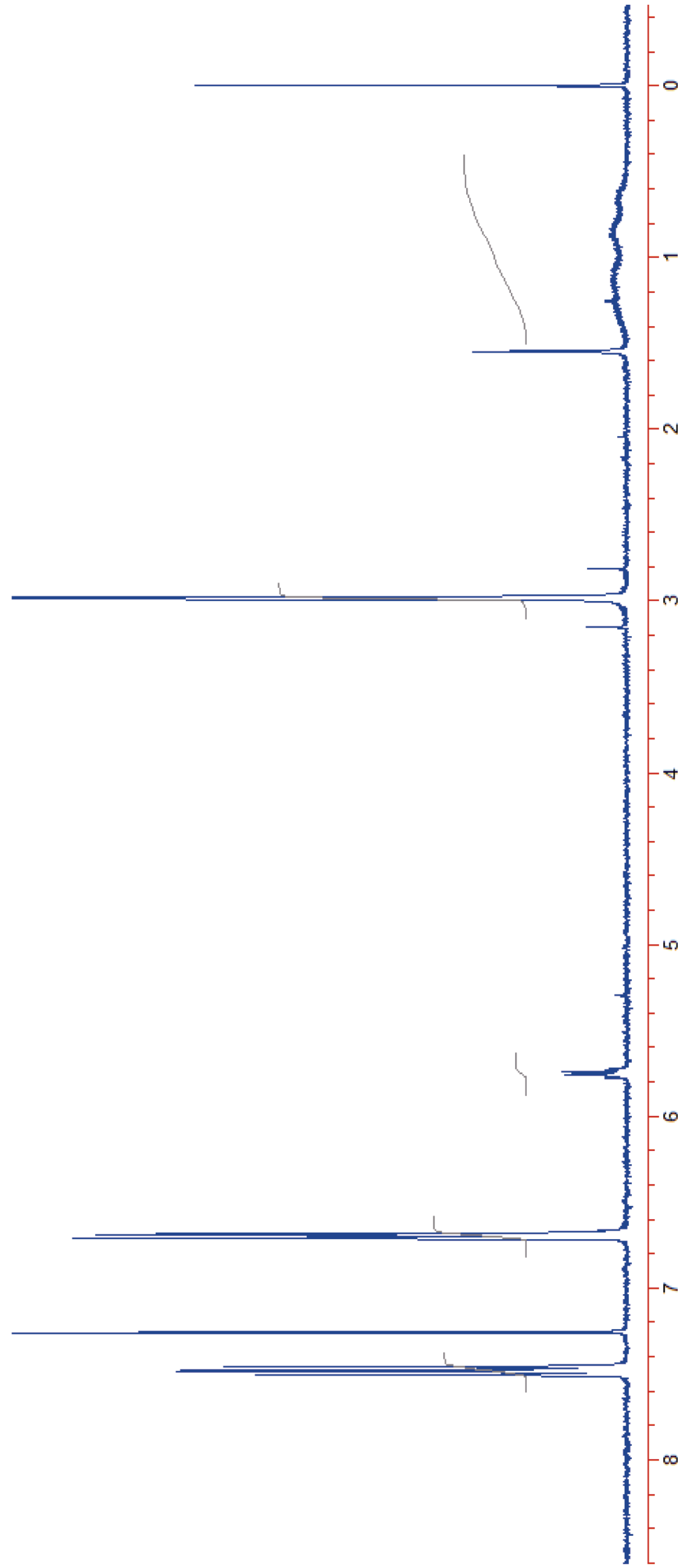
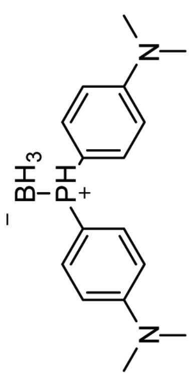
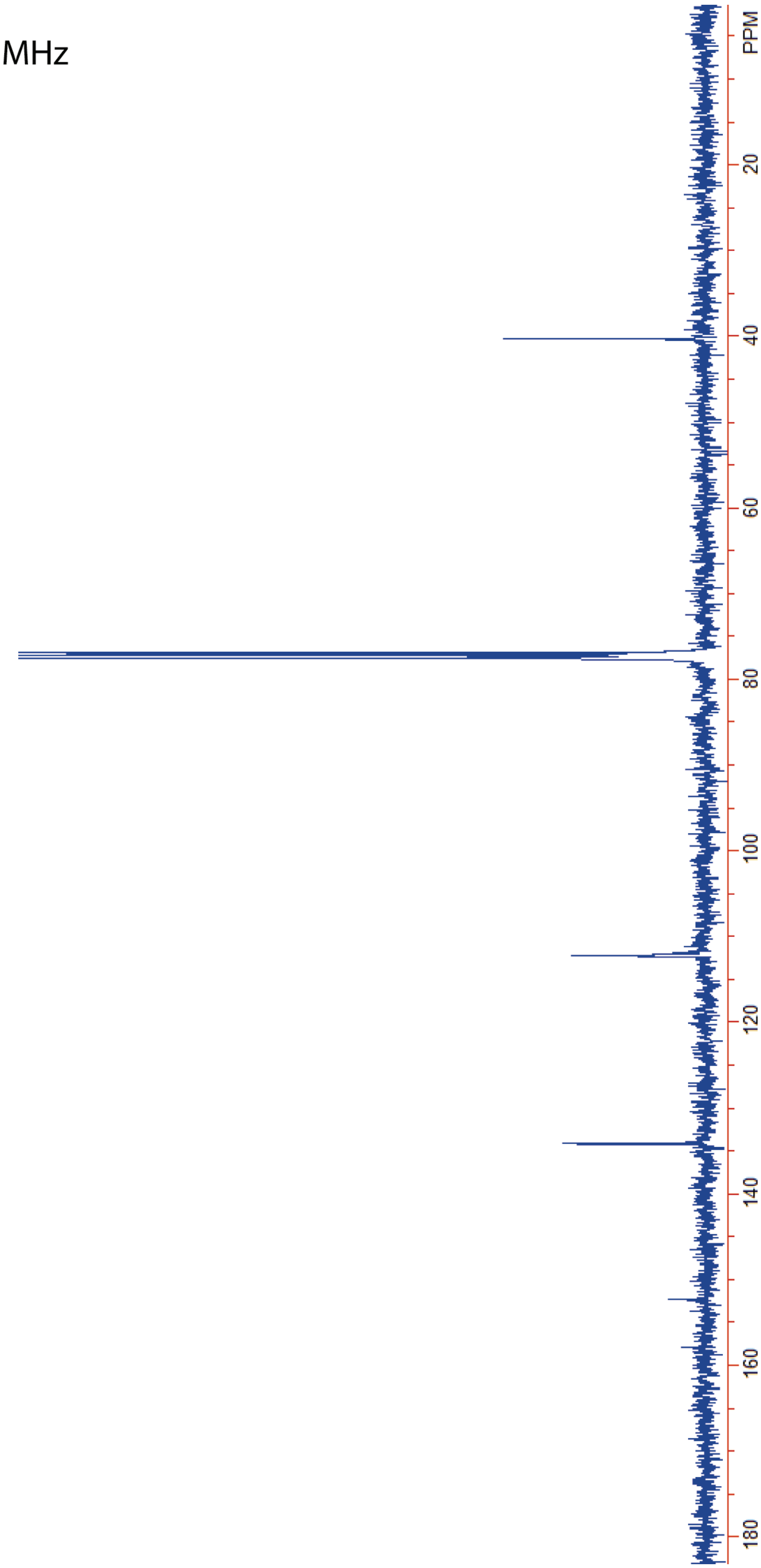
Proton NMR, 400 MHz
$CDCl_3$

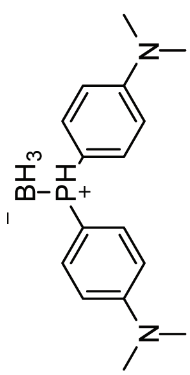




38

Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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Phosphorus-31 NMR, 121 MHz
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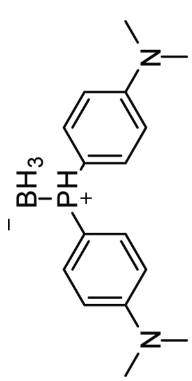

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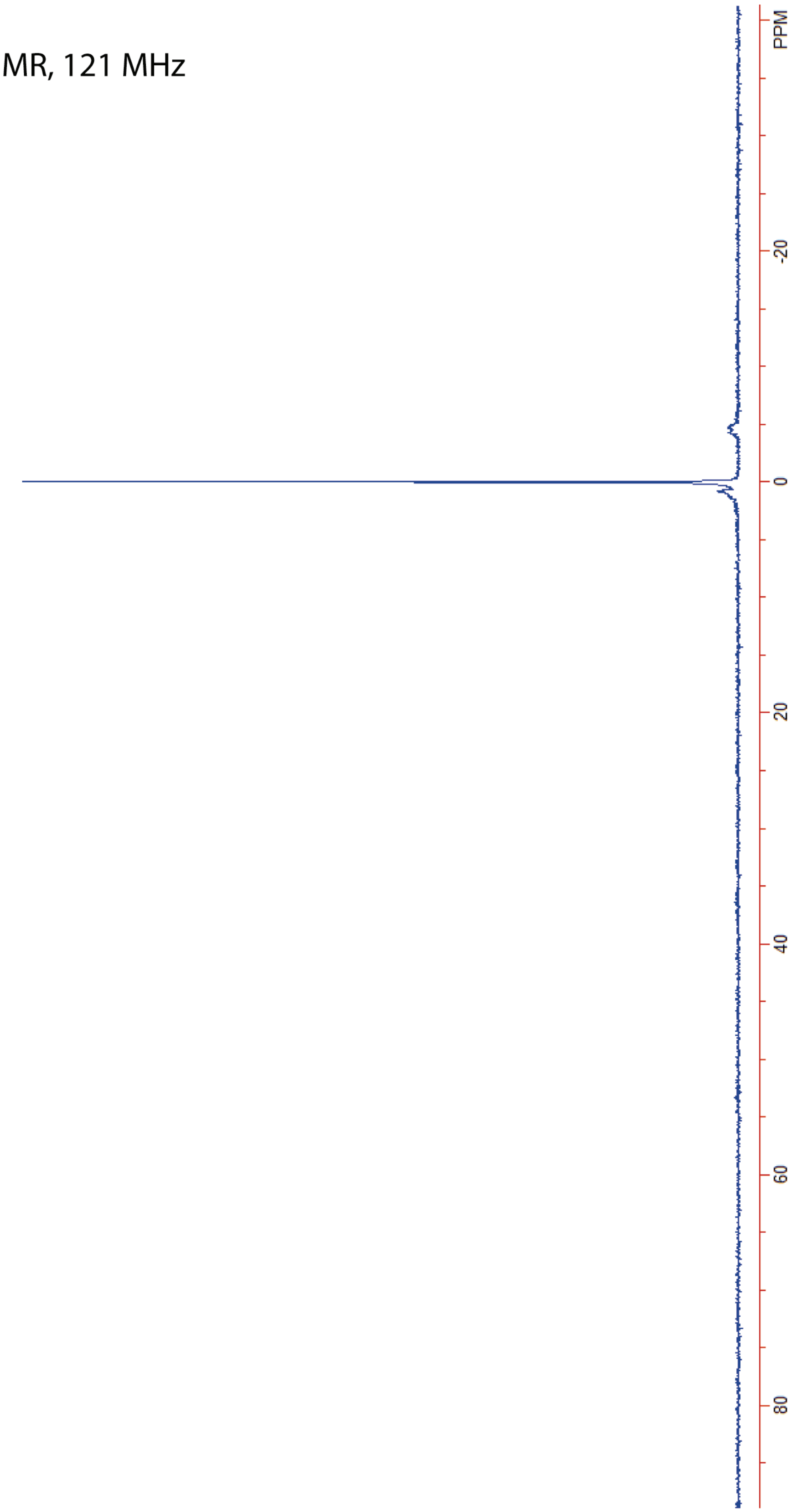
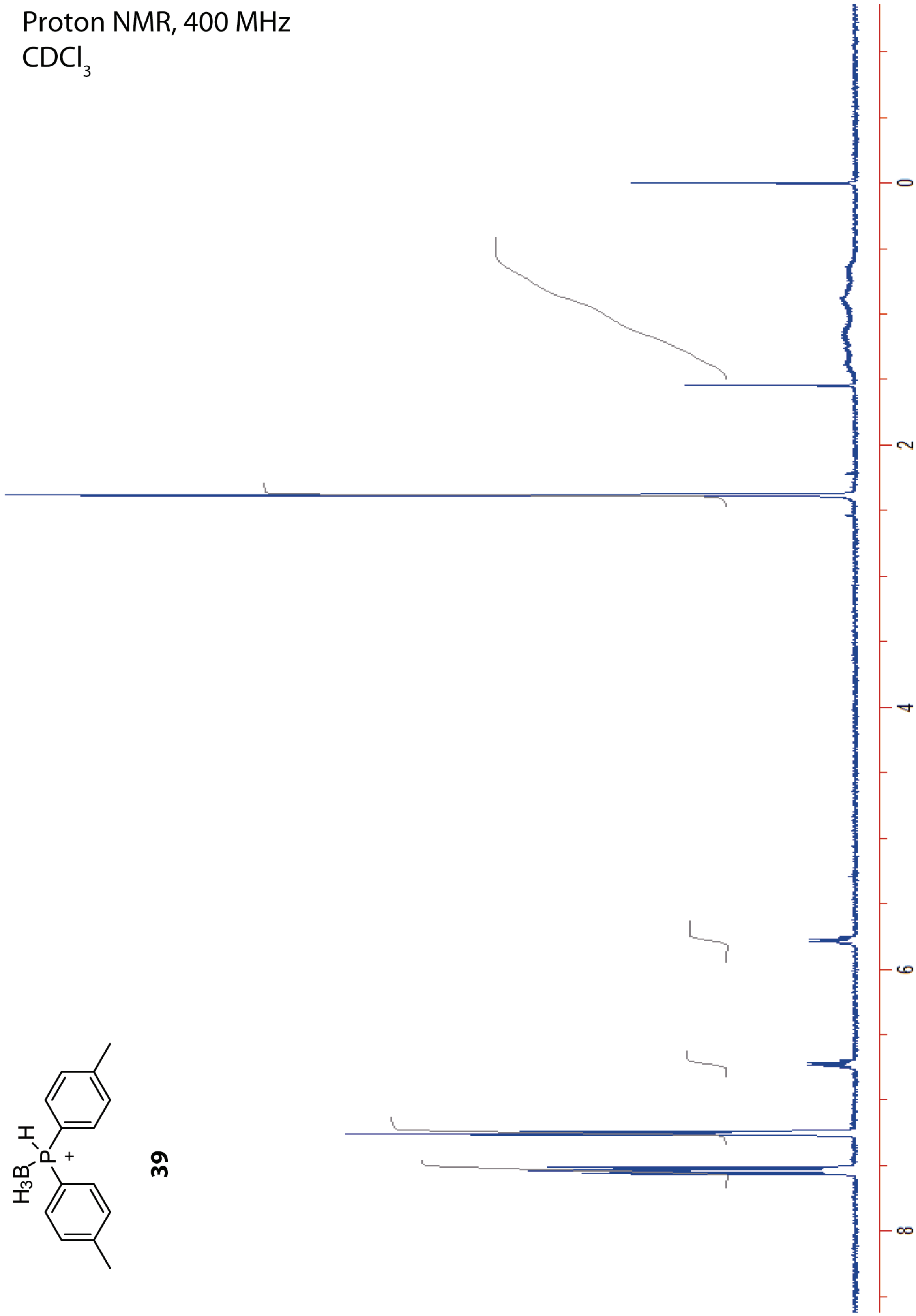


Proton NMR, 400 MHz
$CDCl_3$



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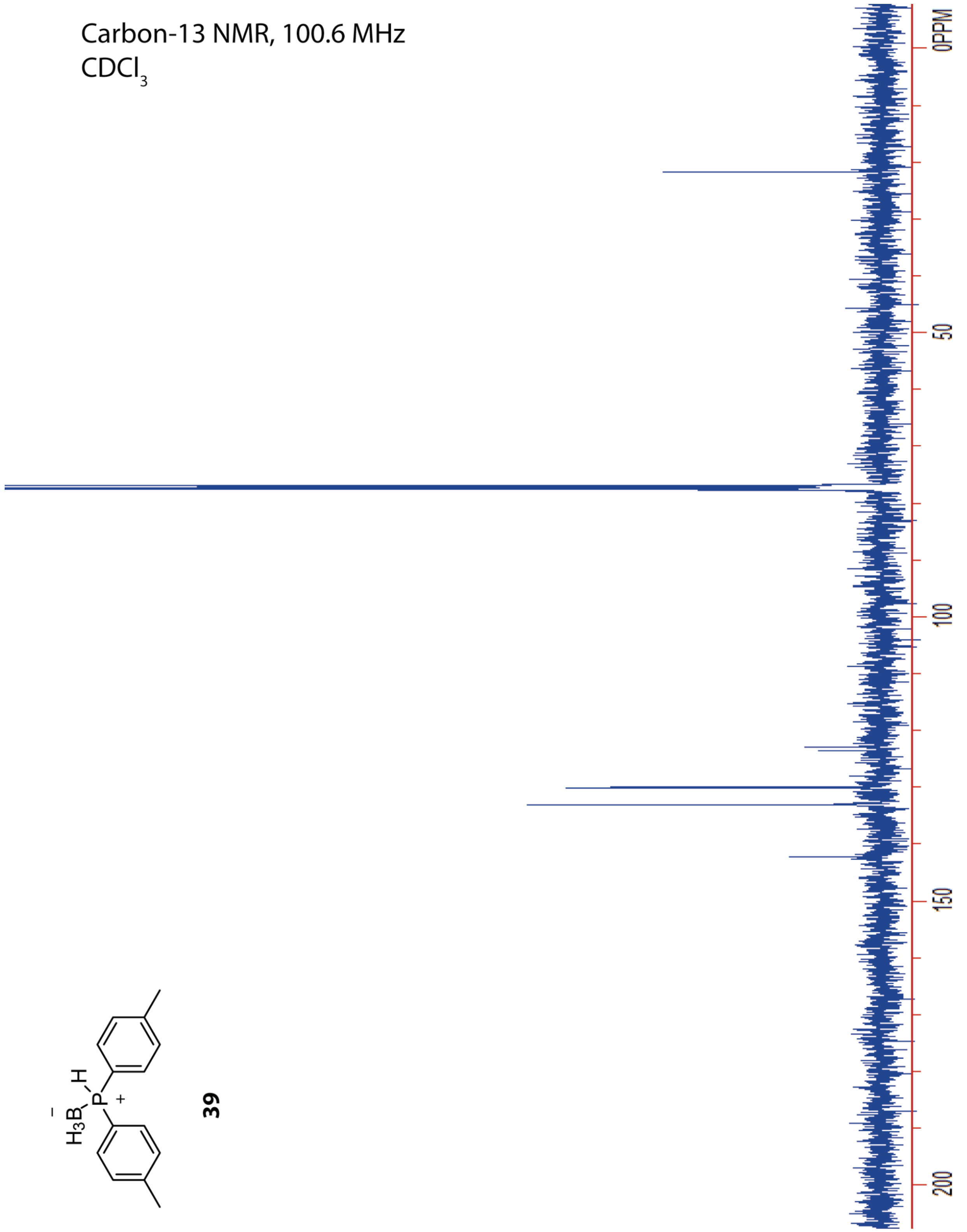
Carbon-13 NMR, 100.6 MHz
$CDCl_3$



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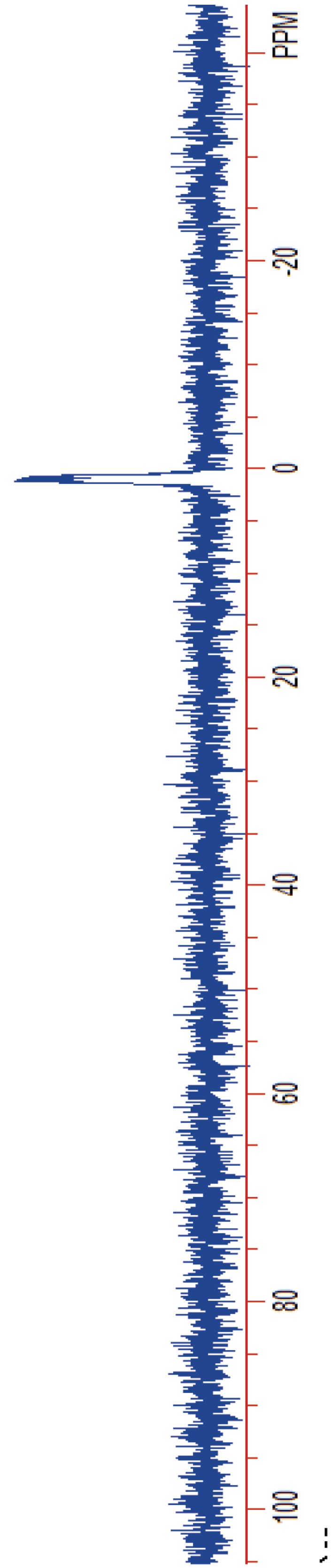
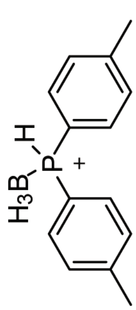
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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Proton NMR, 400 MHz
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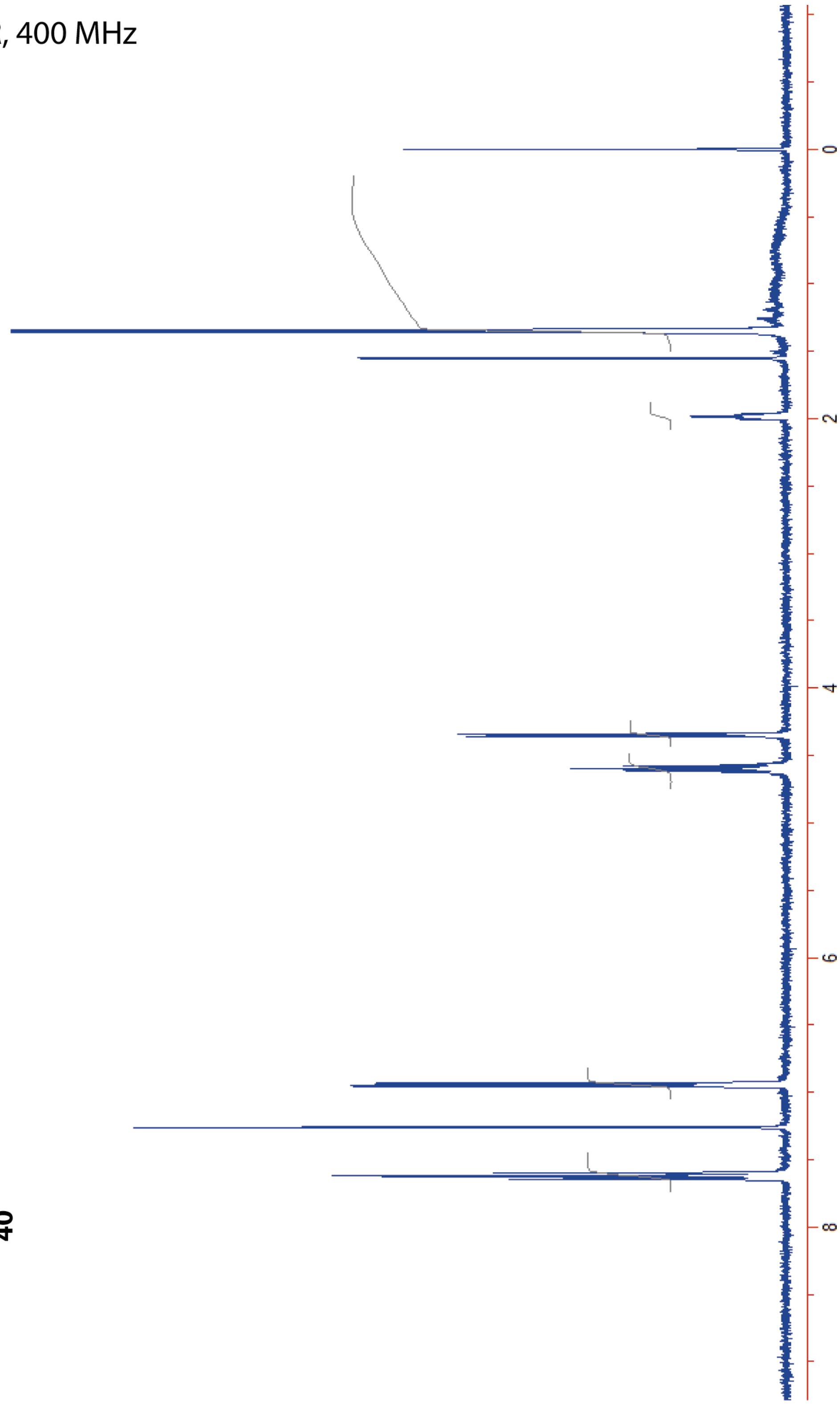

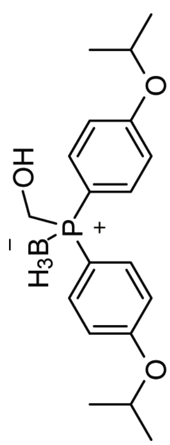

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Carbon-13 NMR, 100.6 MHz
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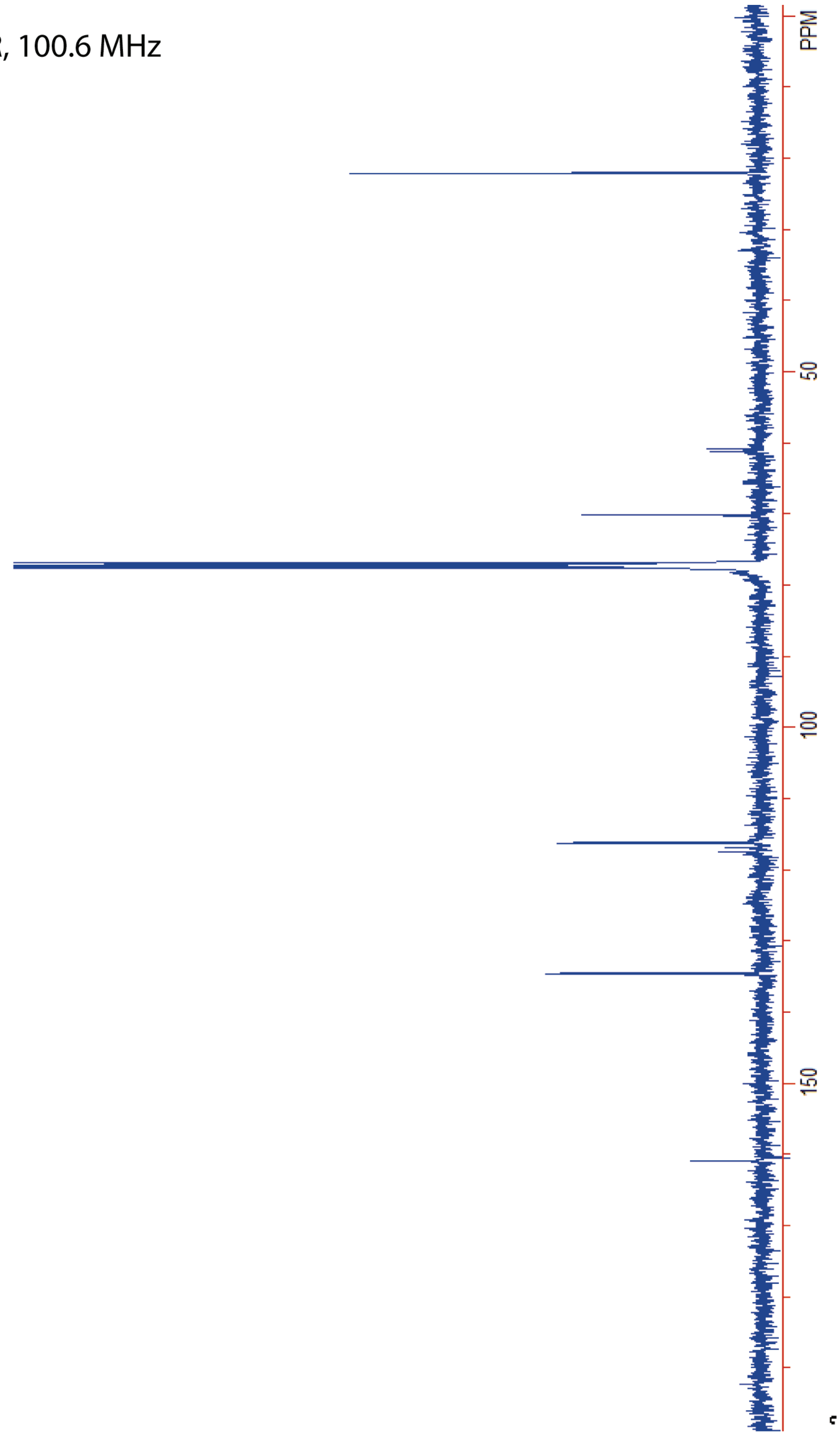

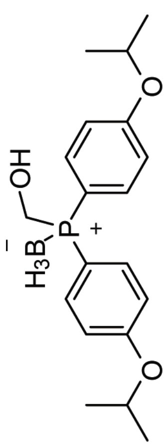

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Phosphorus-31 NMR, 121 MHz
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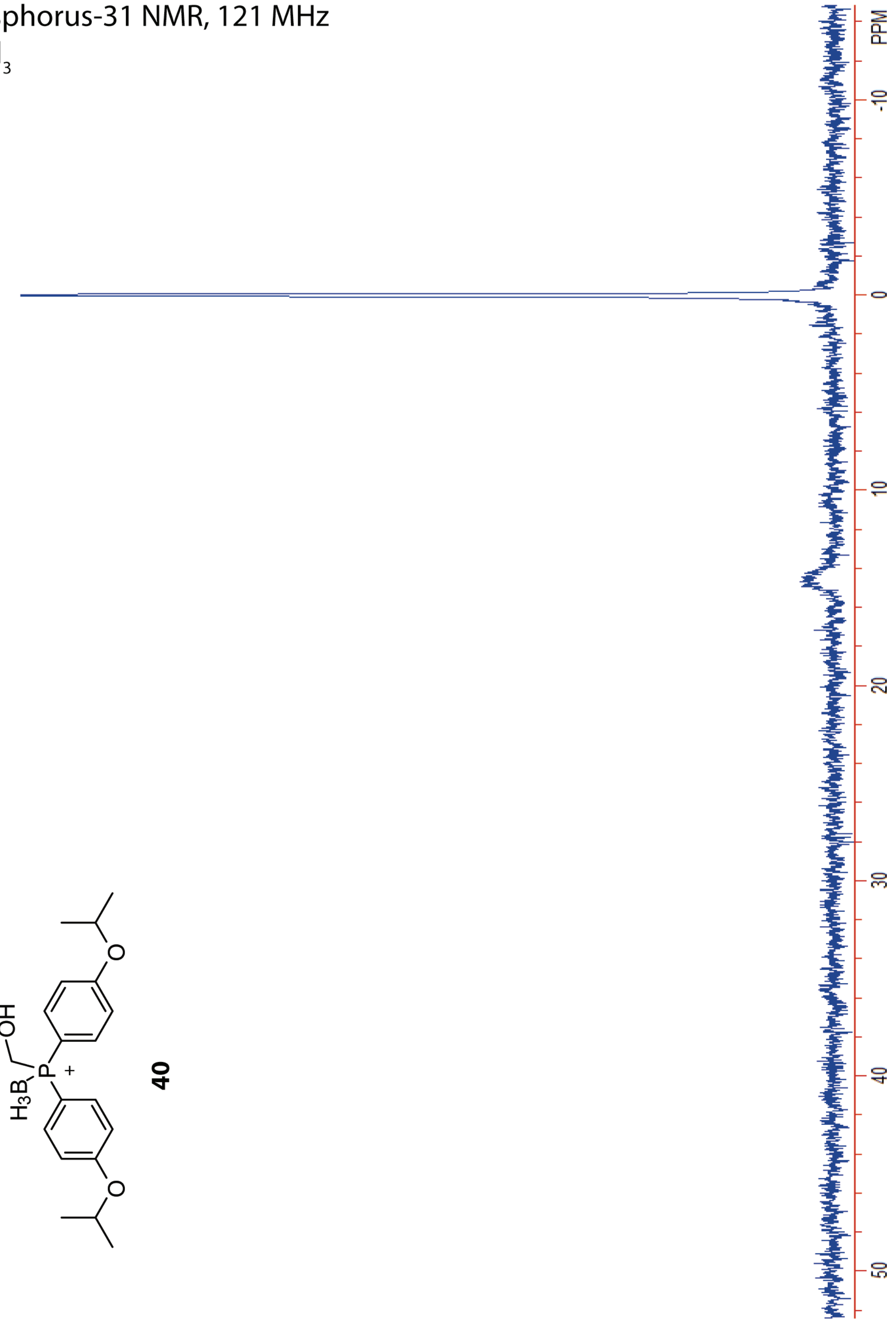

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Proton NMR, 400 MHz
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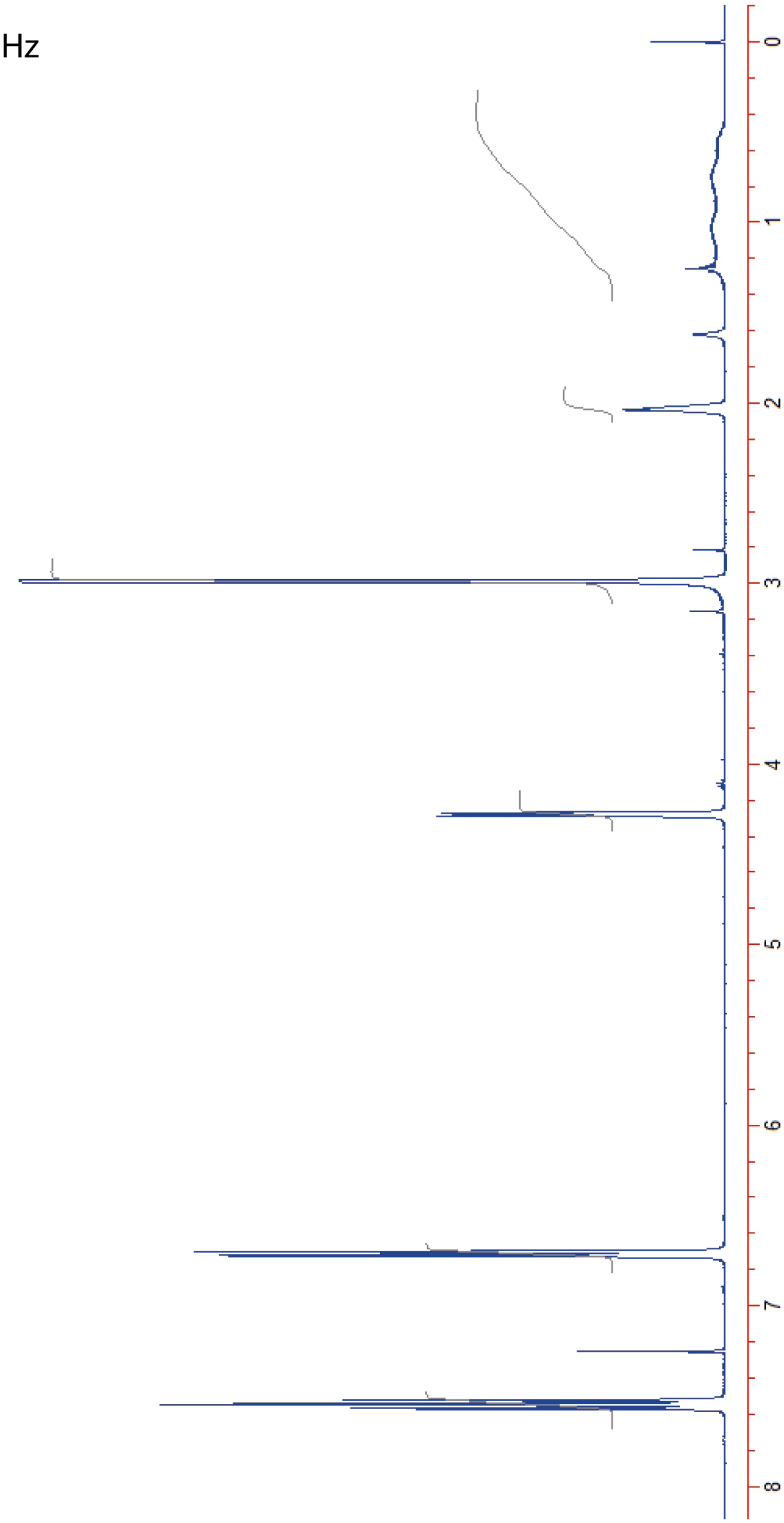

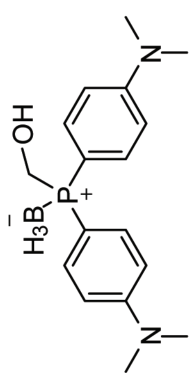

41

Carbon-13 NMR, 100.6 MHz
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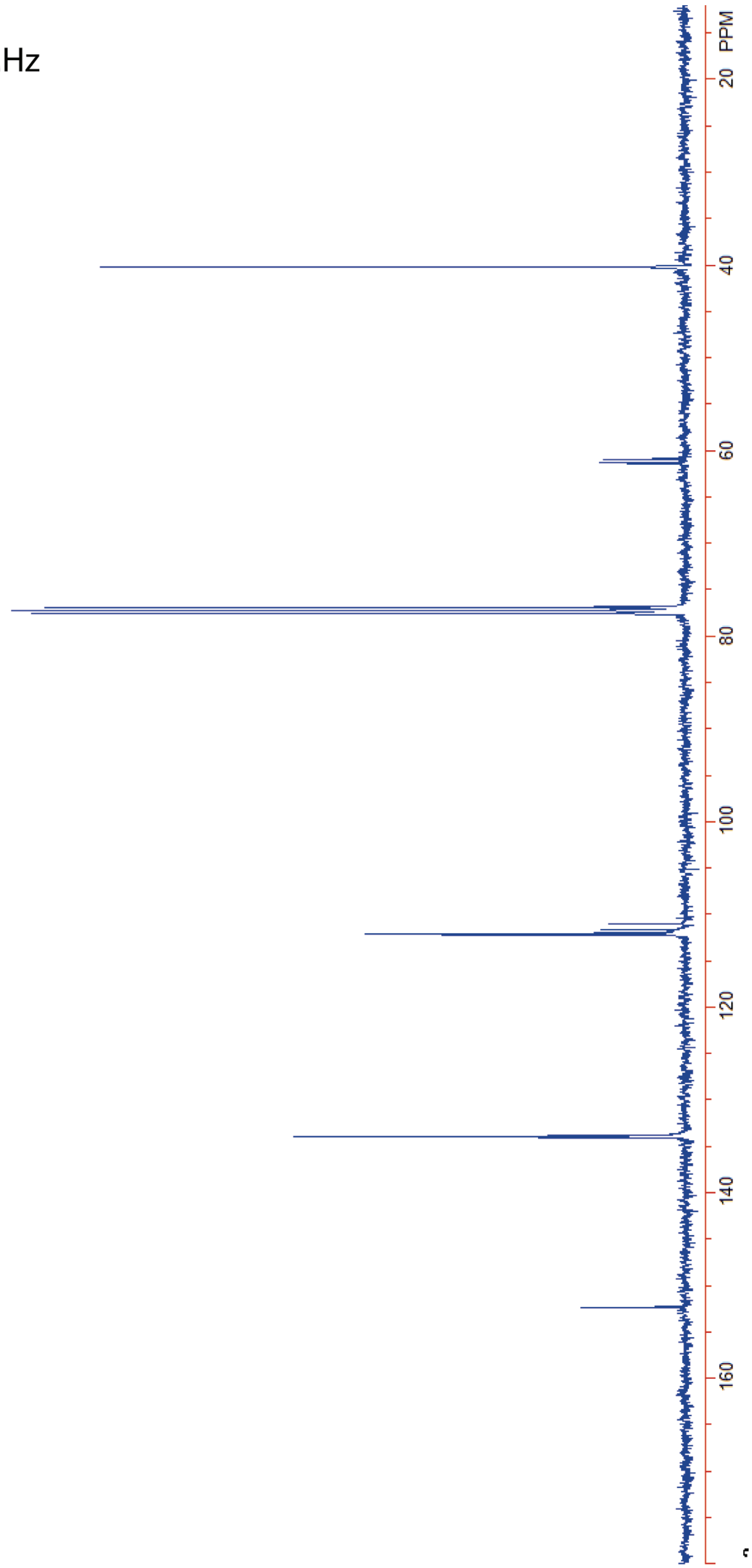

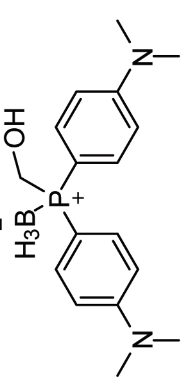

41

Phosphorus-31 NMR, 121 MHz
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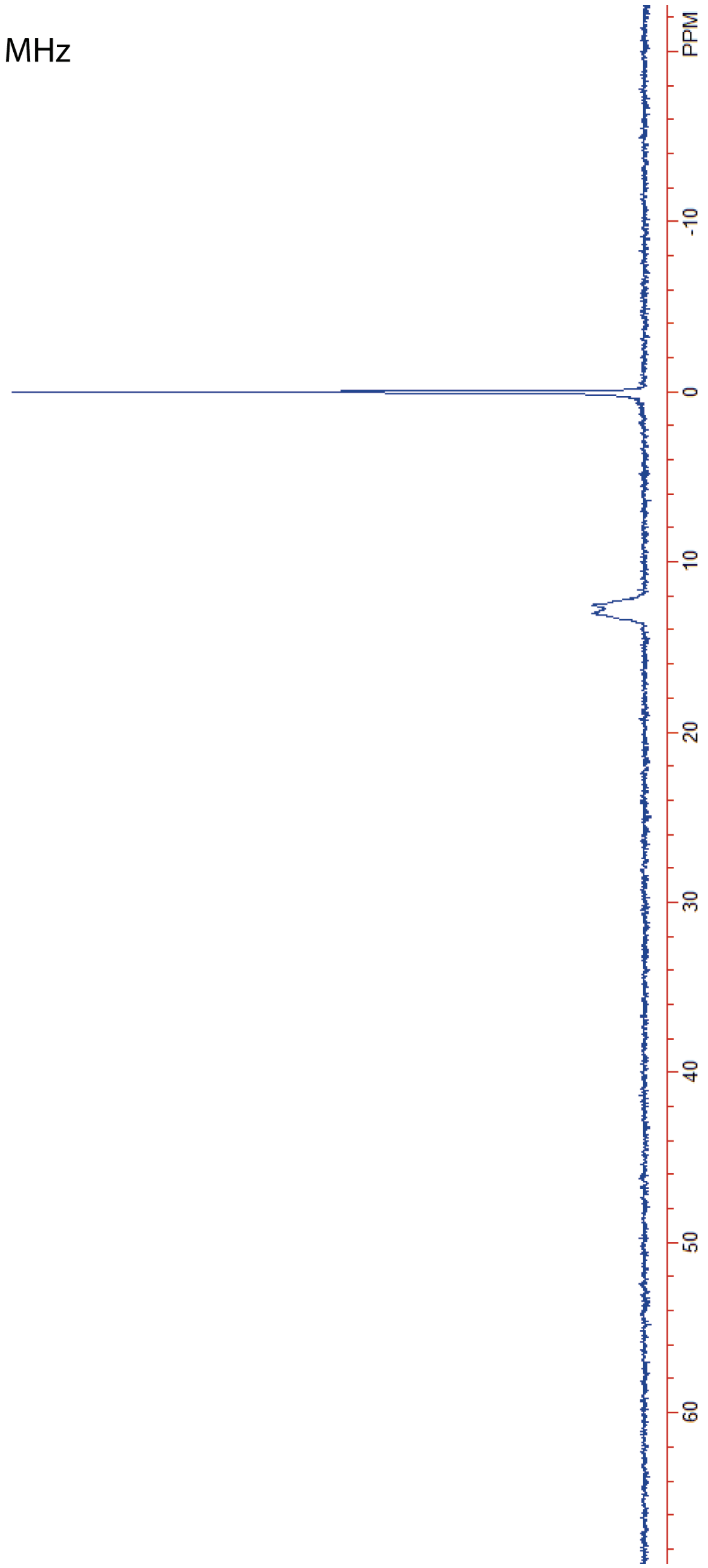

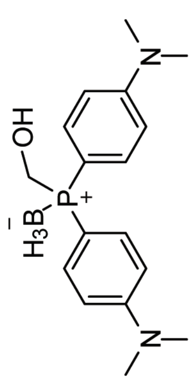

41

Proton NMR, 400 MHz
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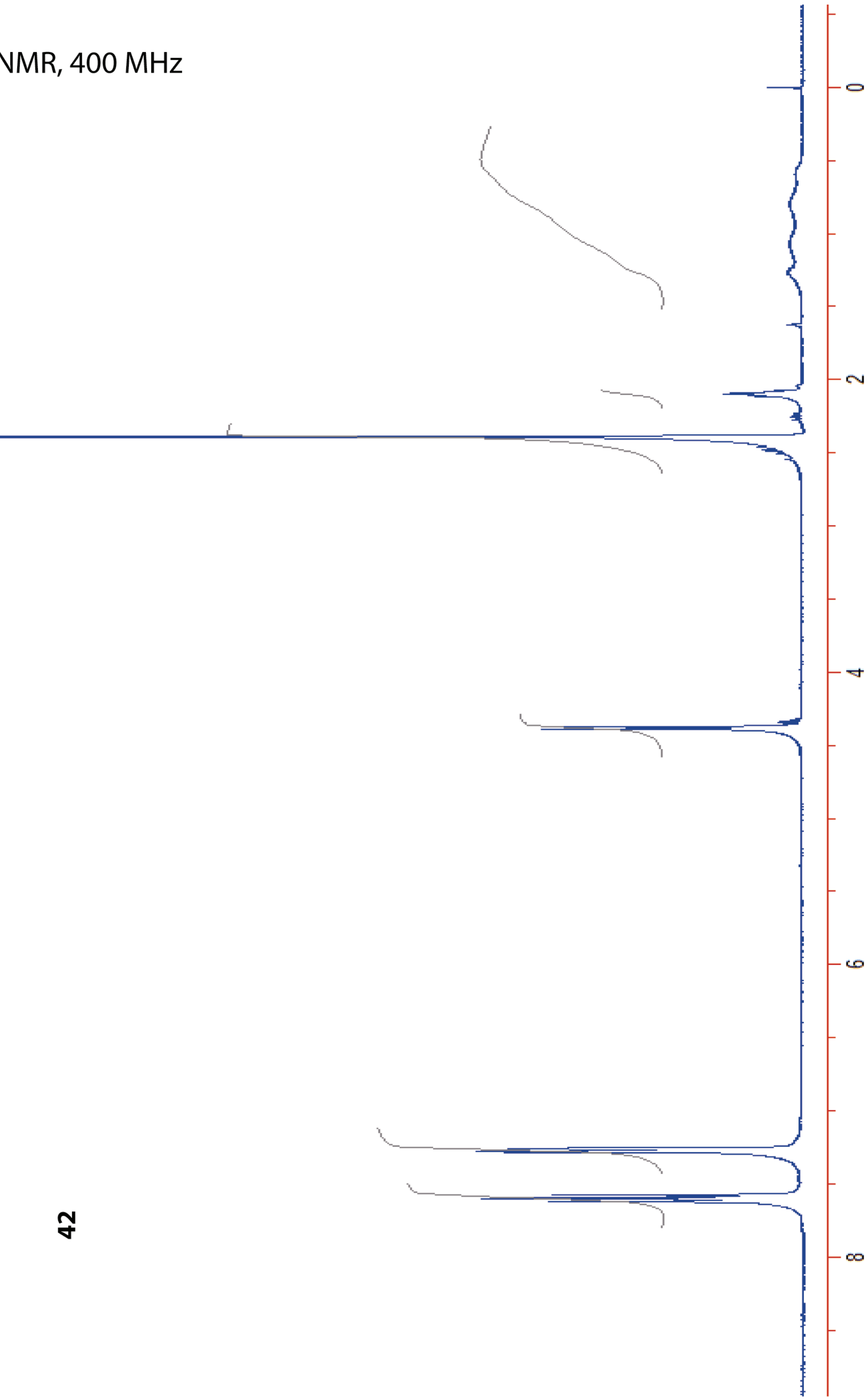

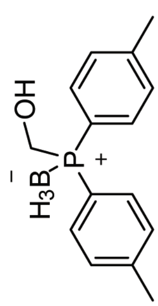

42

Carbon-13 NMR, 100.6 MHz
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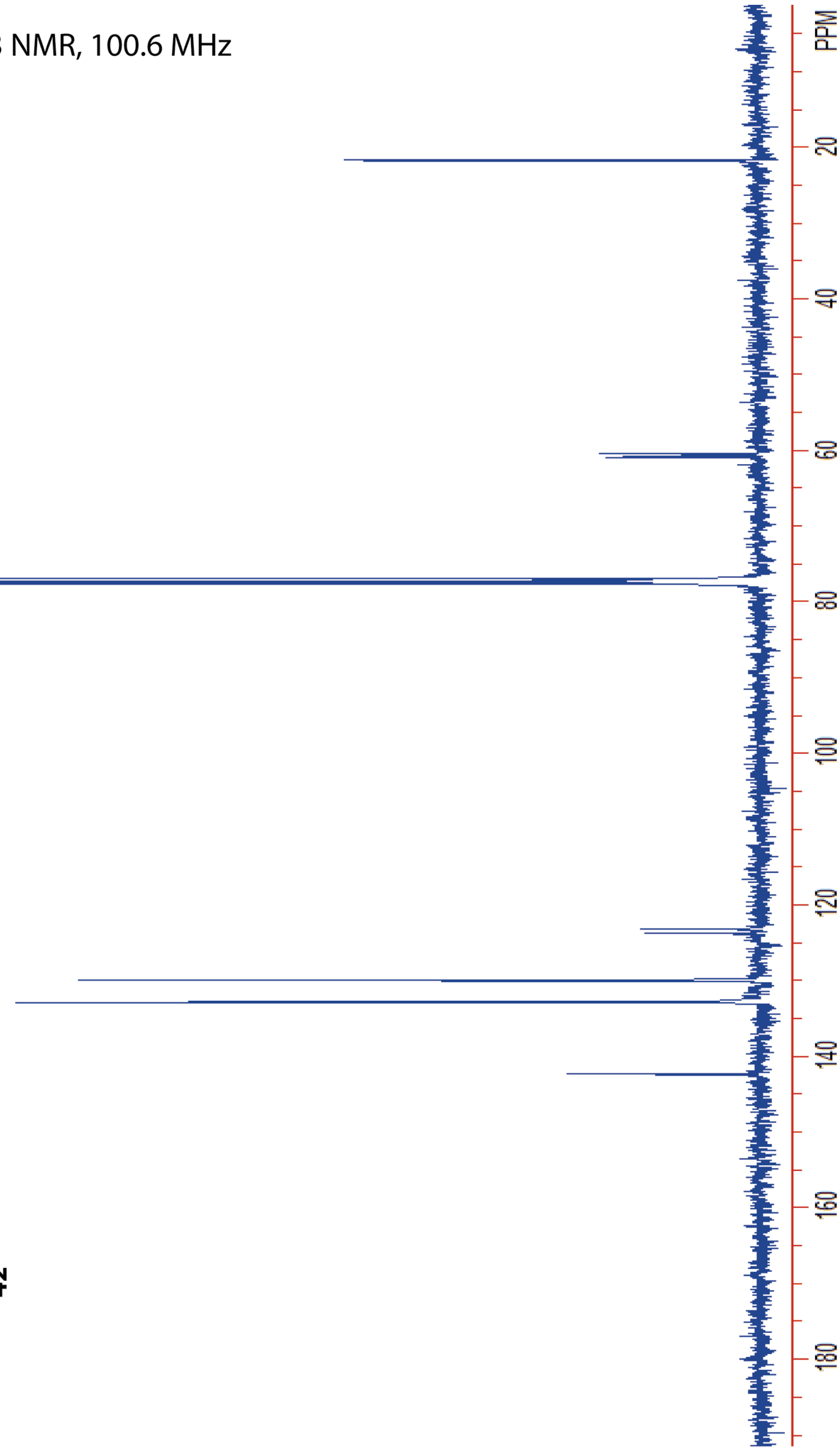

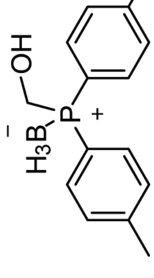

42

Phosphorus-31 NMR, 121 MHz
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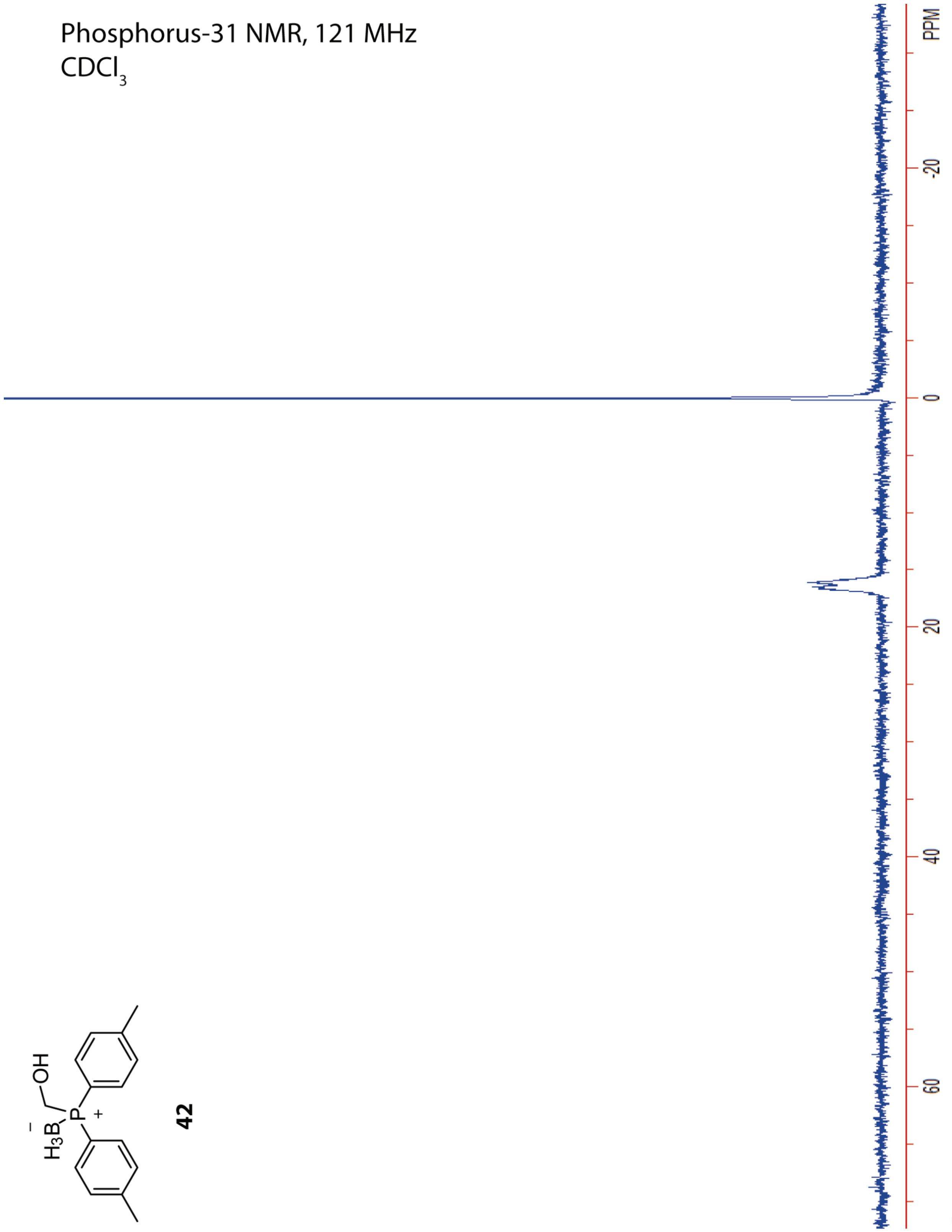

42

Proton NMR, 400 MHz
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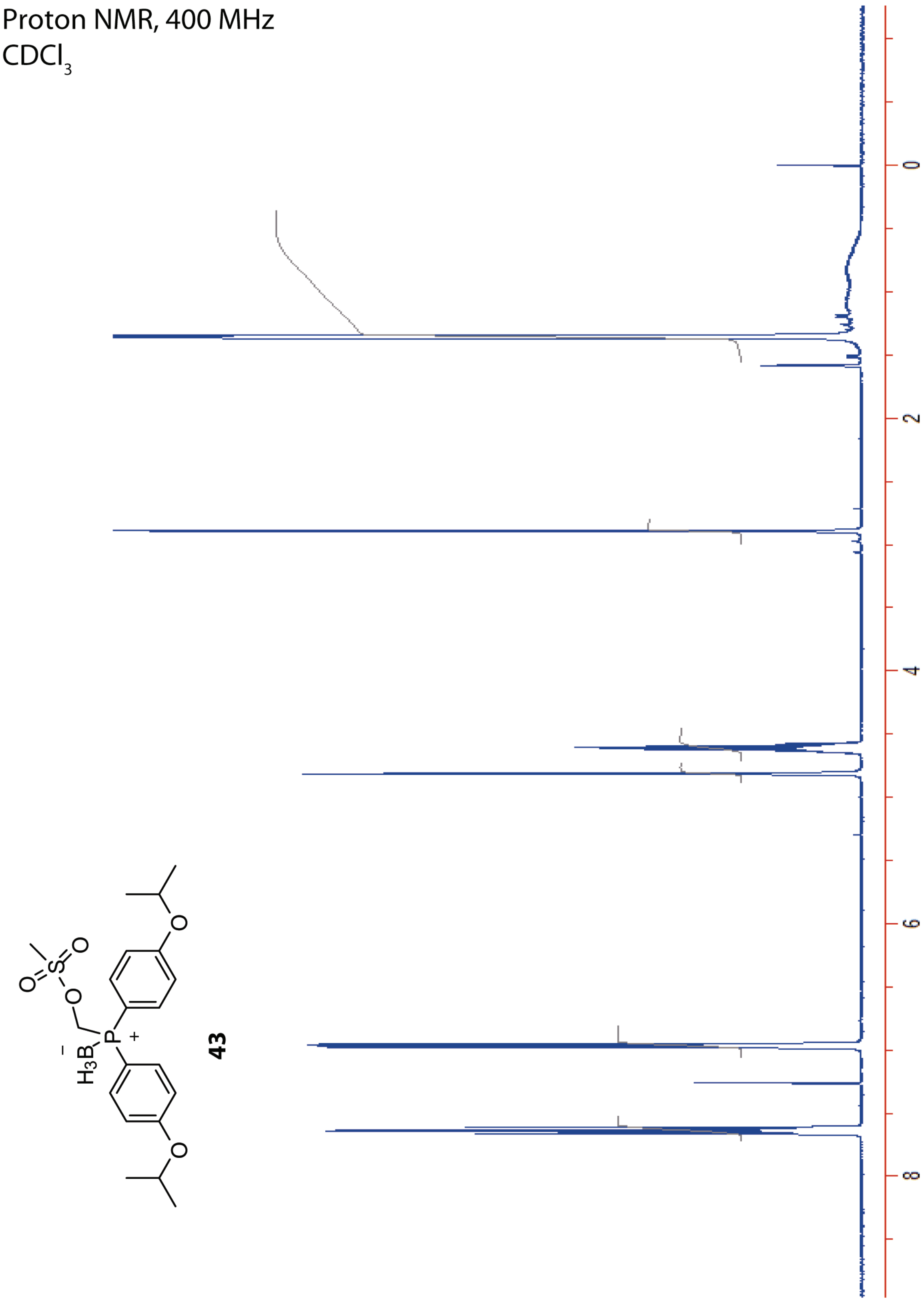

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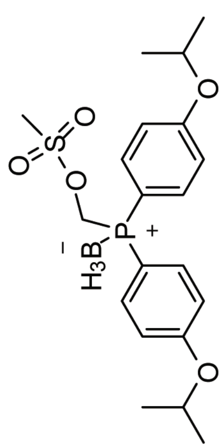
Carbon-13 NMR, 100.6 MHz
$CDCl_3$



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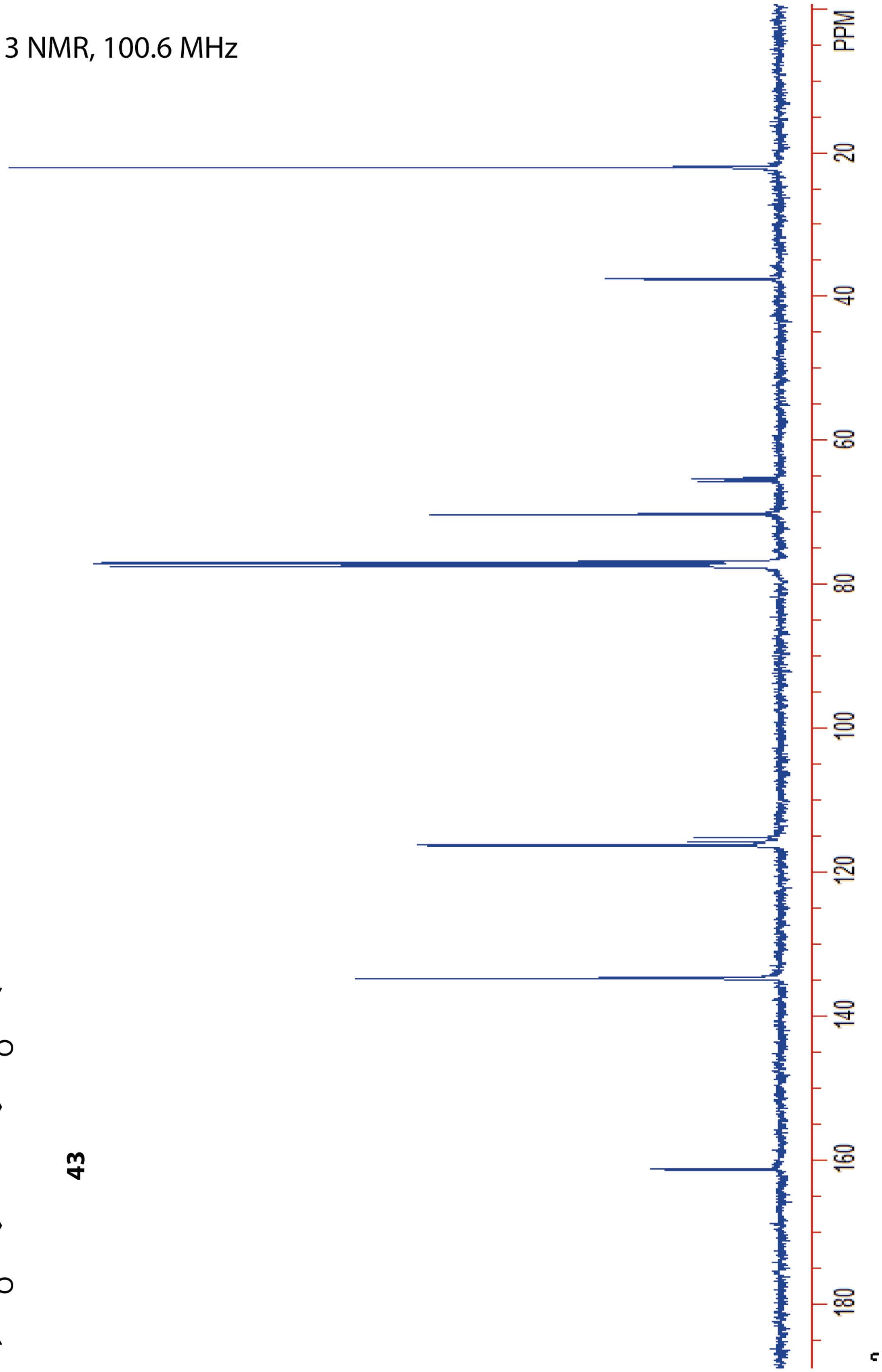

Phosphorus-31 NMR, 121 MHz
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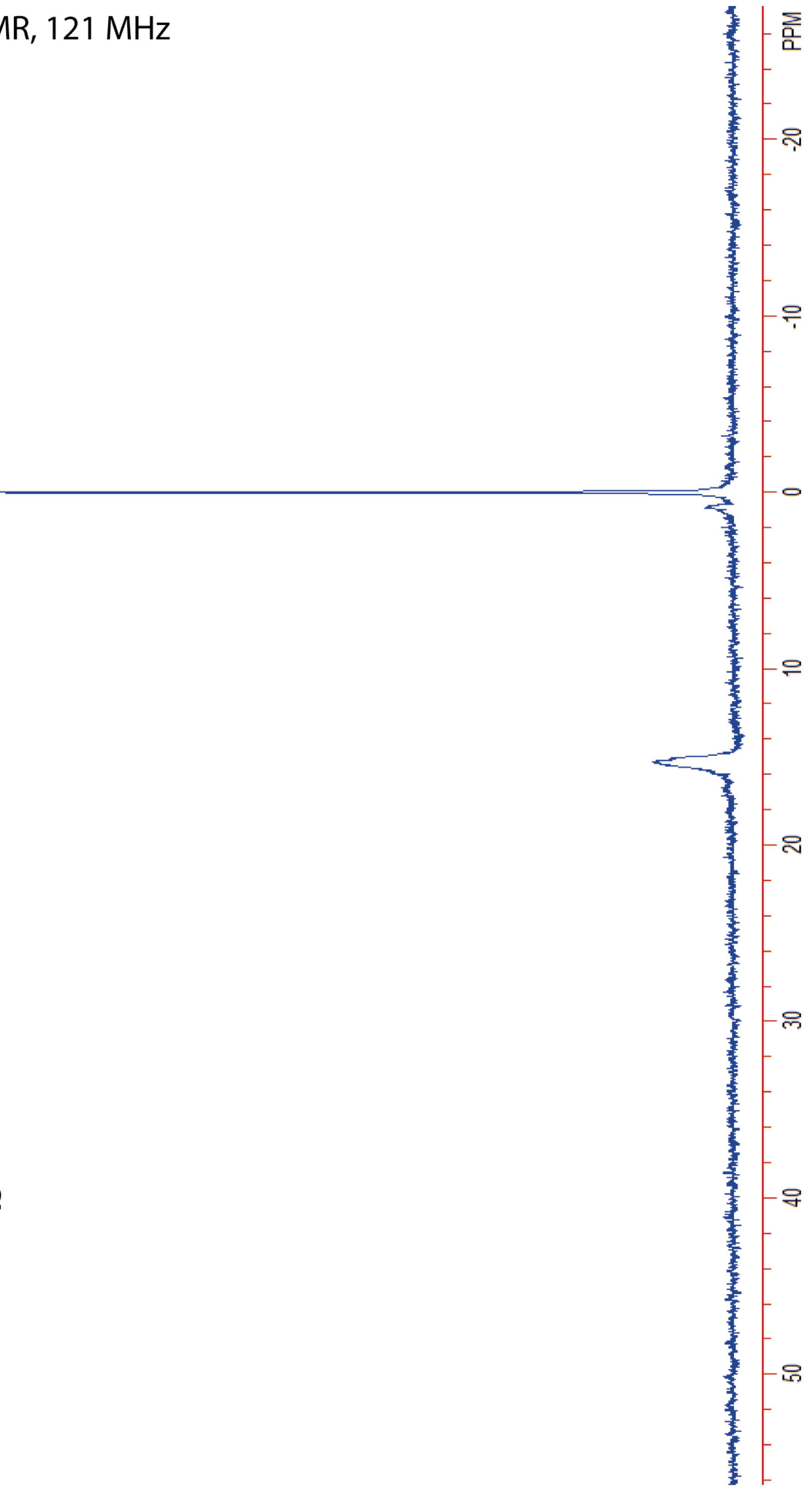

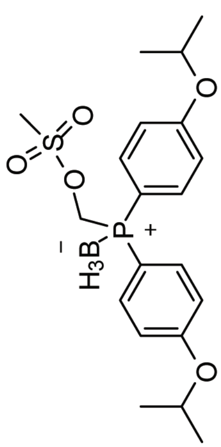

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Proton NMR, 400 MHz
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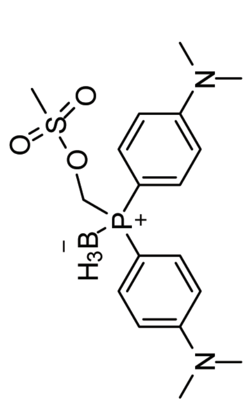

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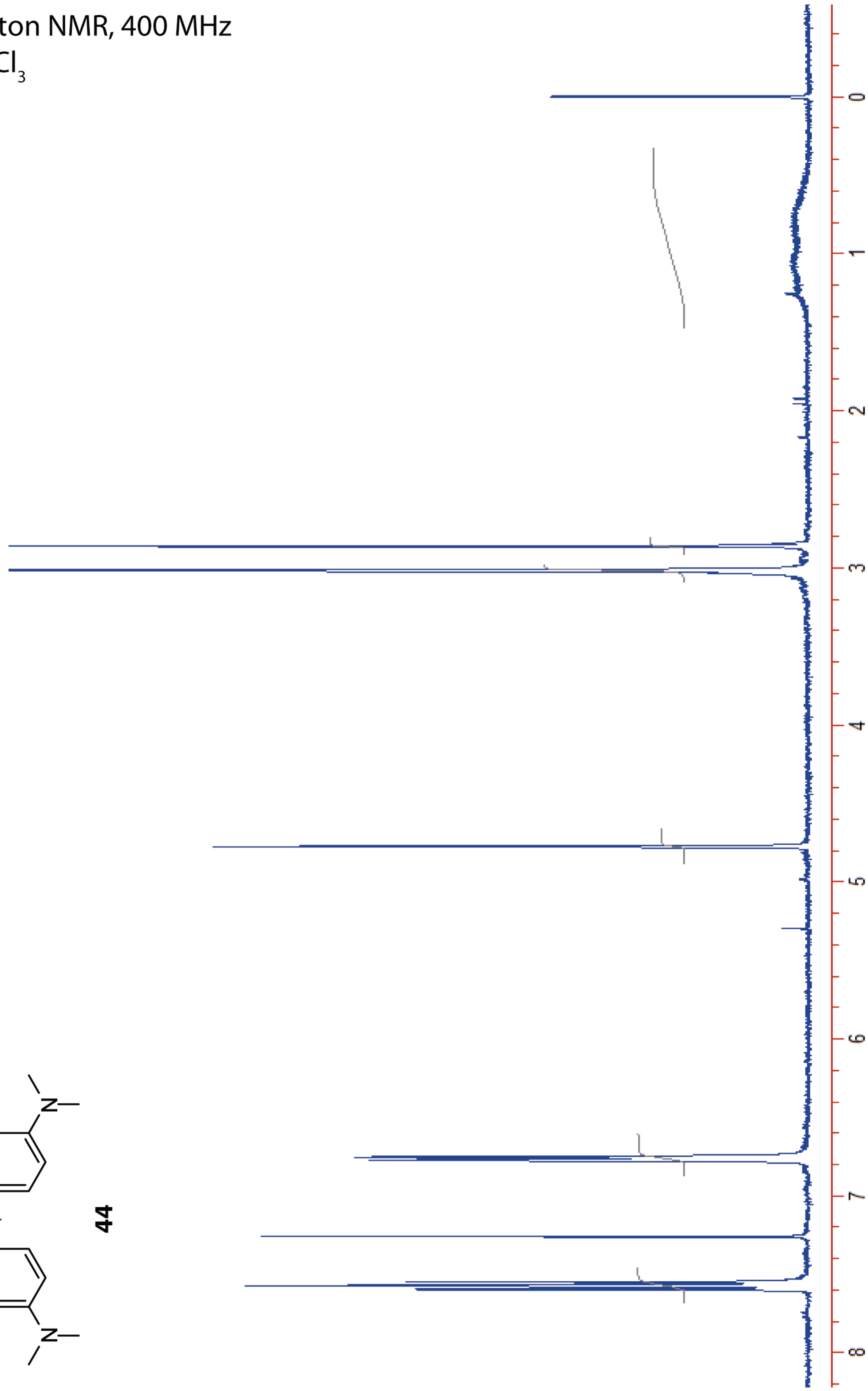

Carbon-13 NMR, 100.6 MHz
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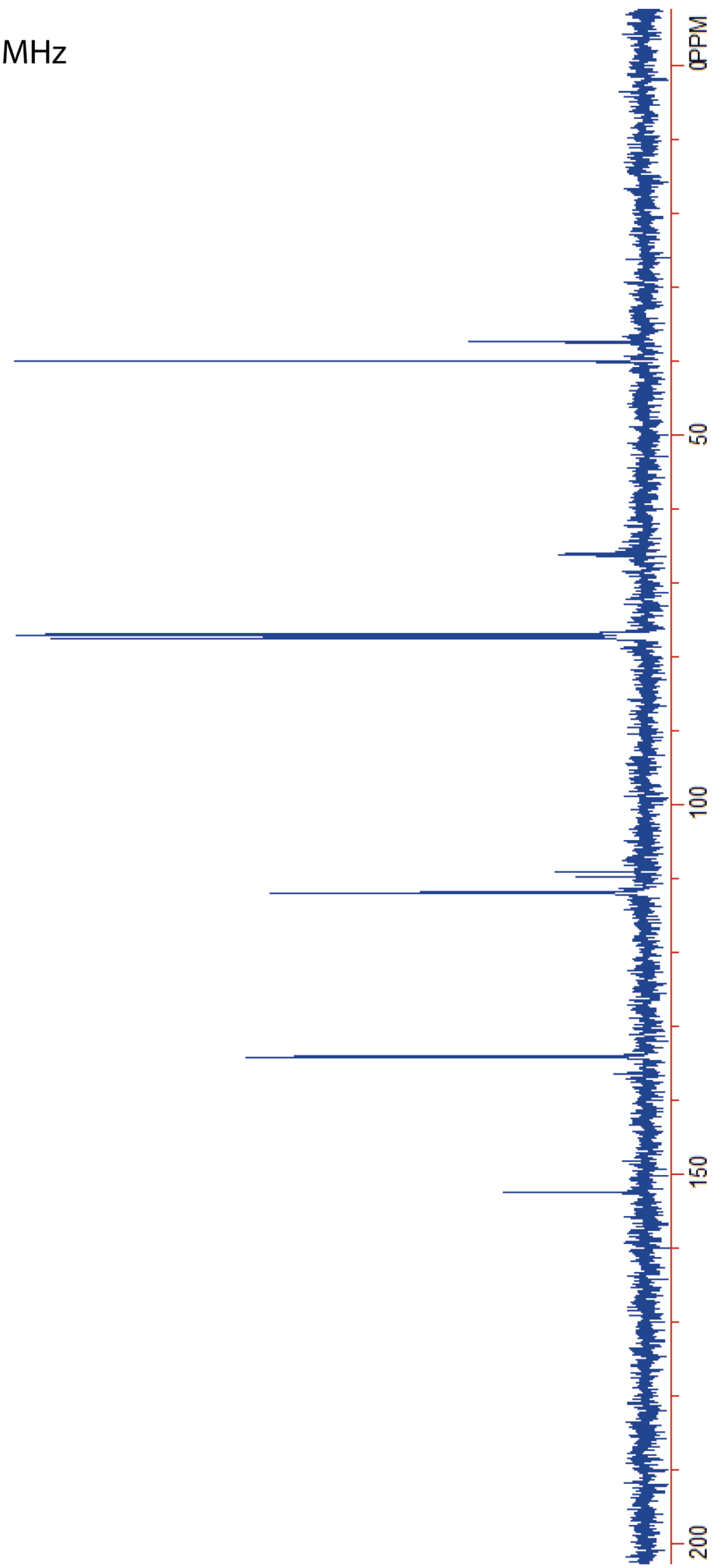

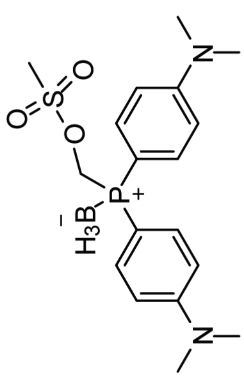

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Phosphorus-31 NMR, 121 MHz
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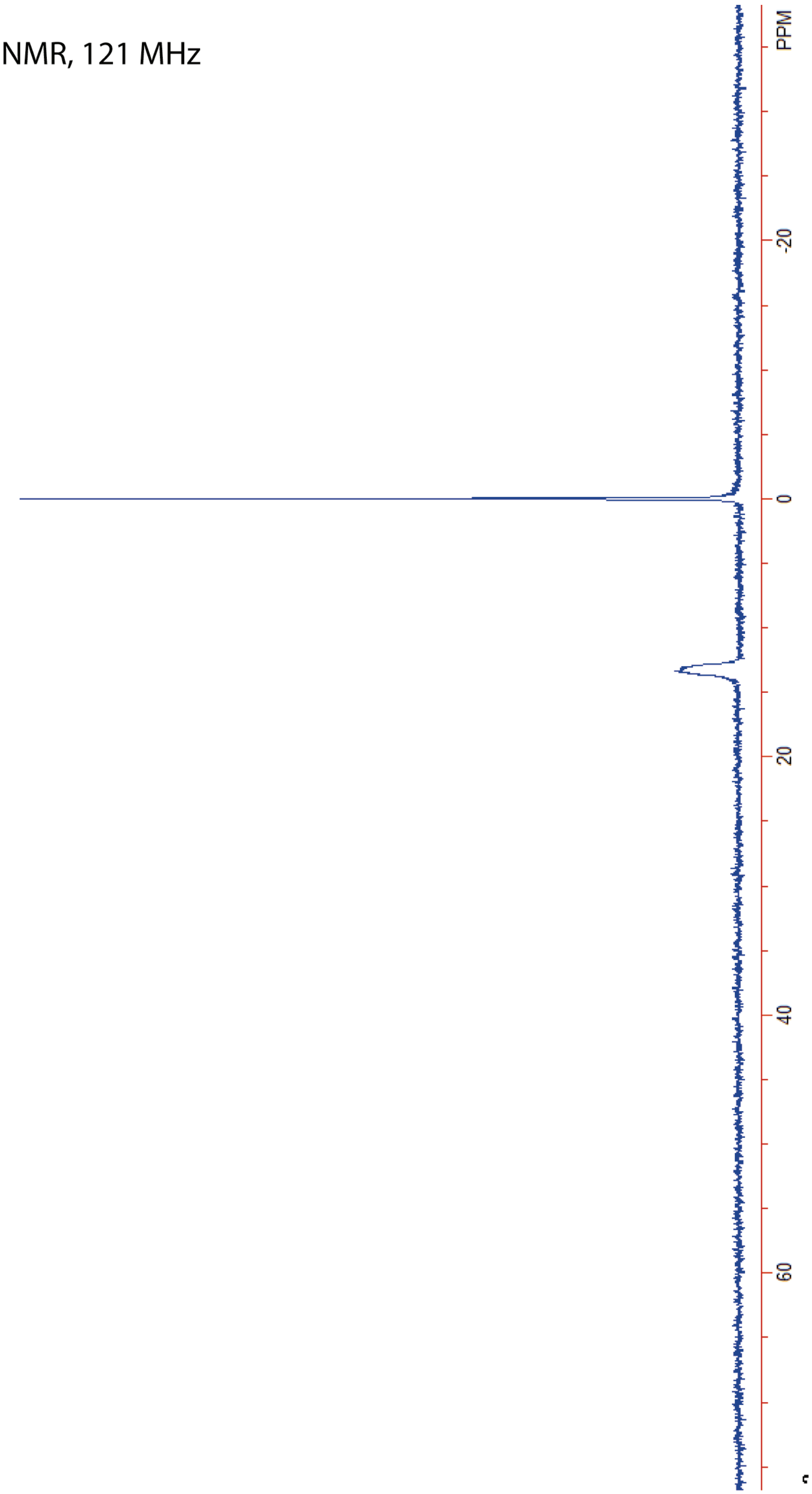

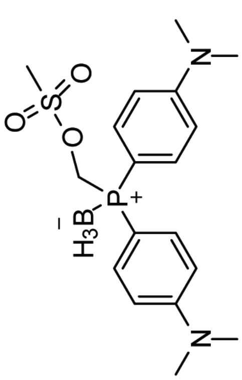

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Proton NMR, 400 MHz
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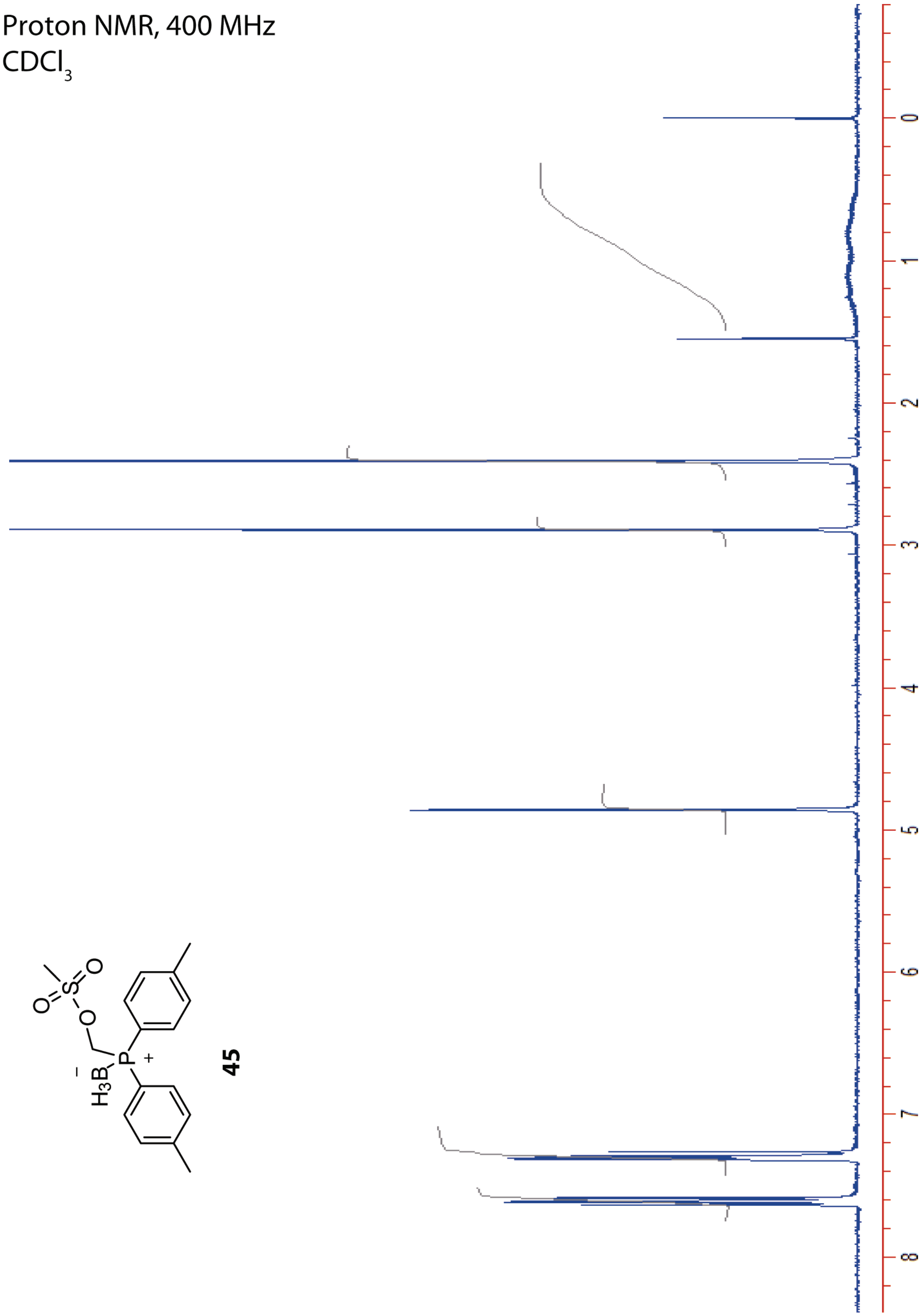

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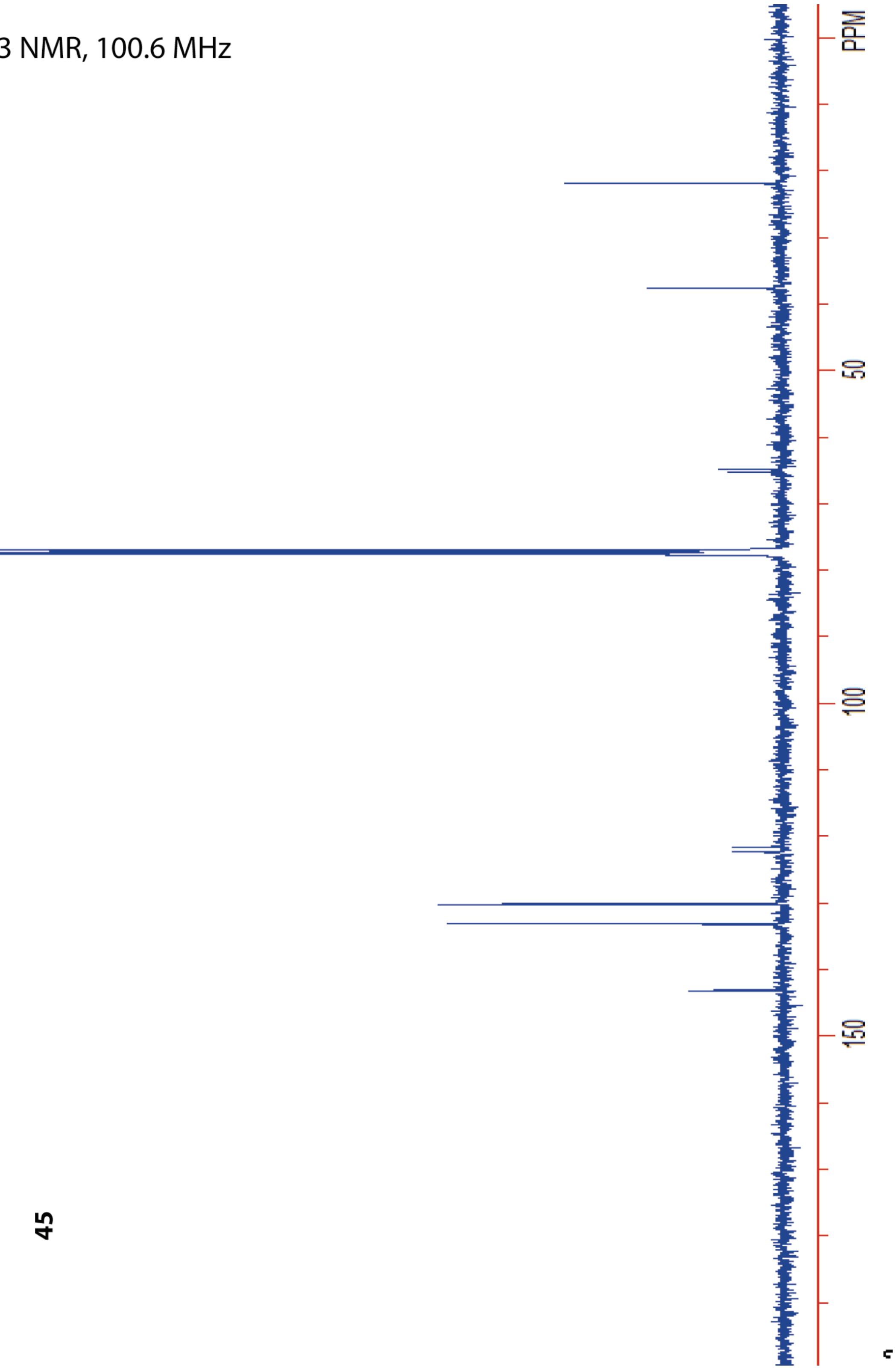
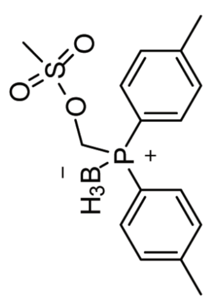
Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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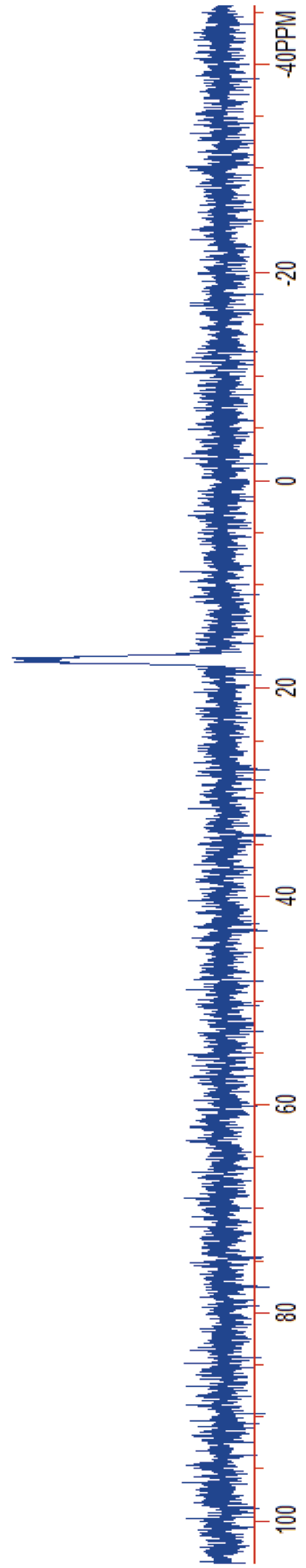
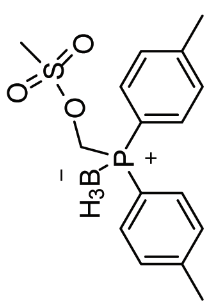
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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Proton NMR, 400 MHz
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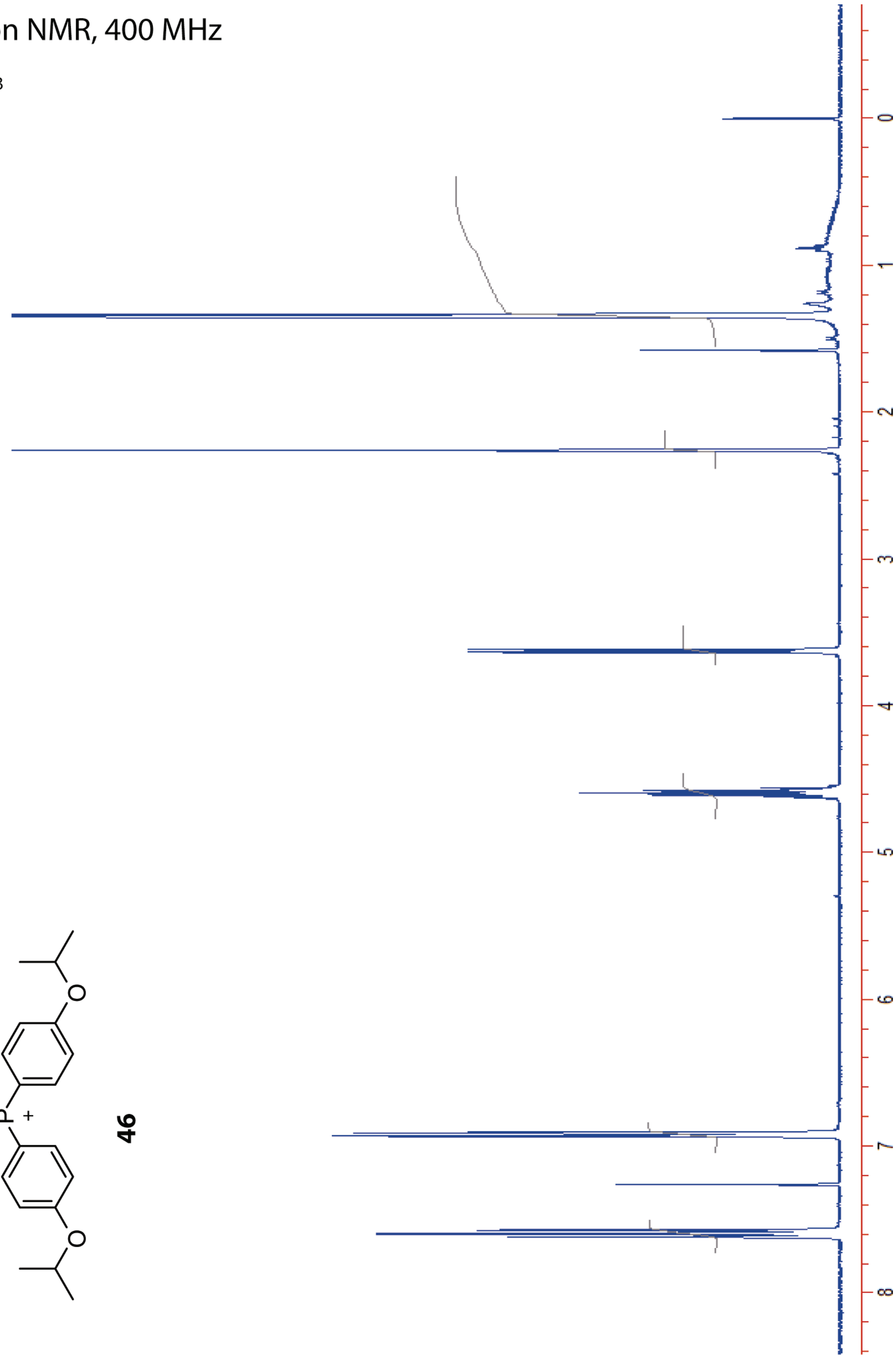

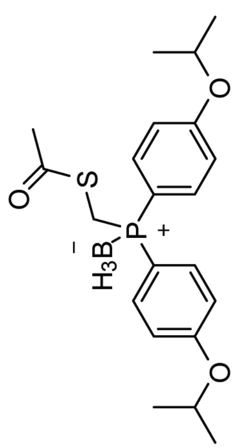

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Carbon-13 NMR, 100.6 MHz
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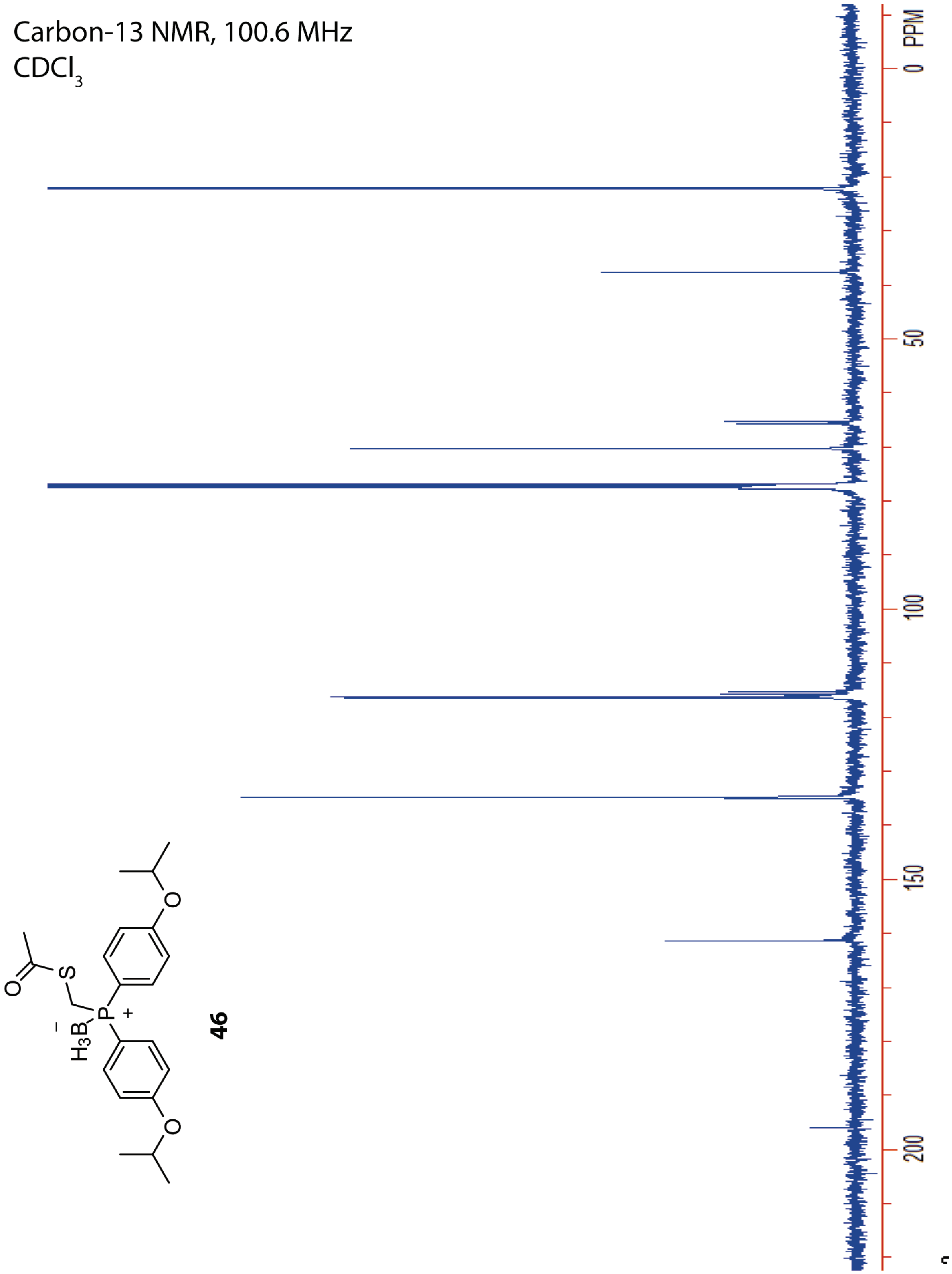

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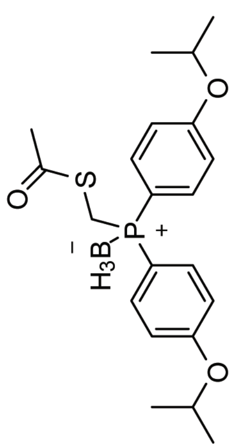
Supplementary Material for Organic & Biomolecular Chemistry

Phosphorus-31 NMR, 121 MHz
$CDCl_3$



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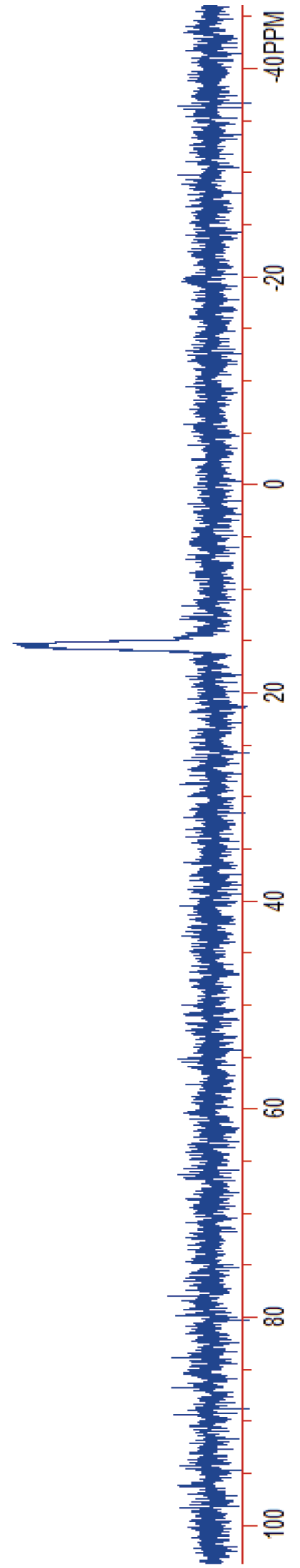
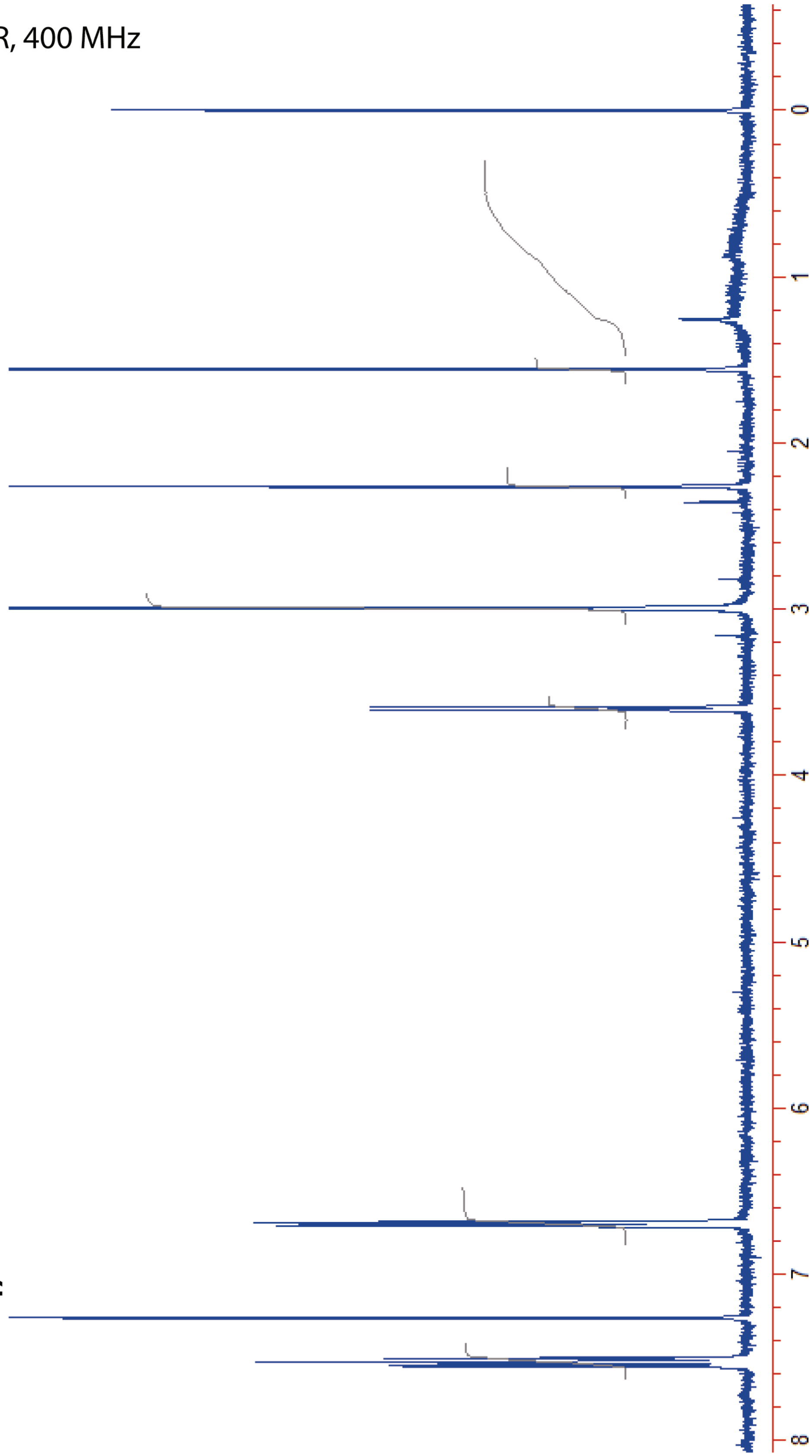
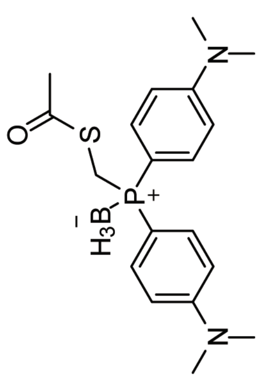


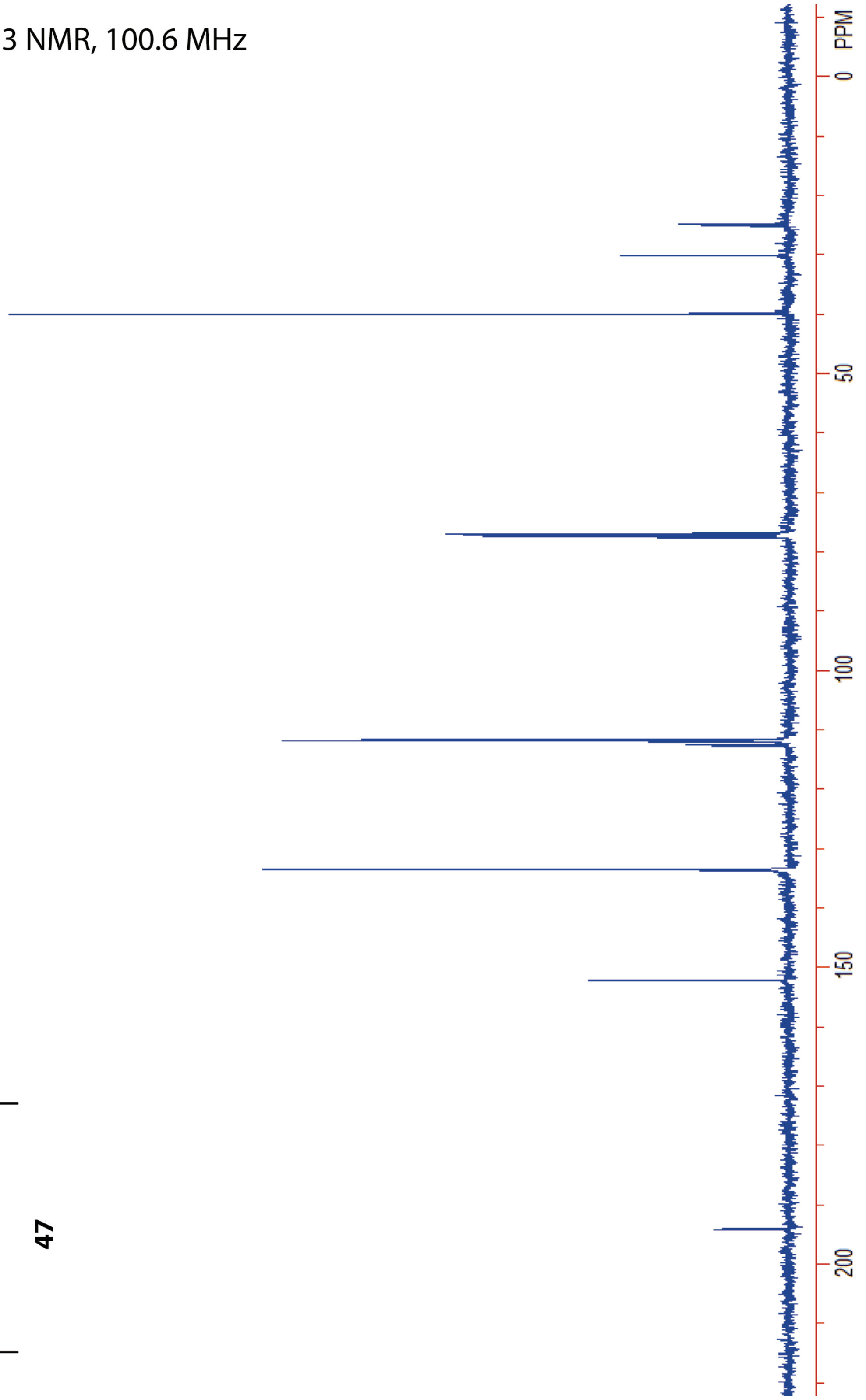
Proton NMR, 400 MHz
$CDCl_3$

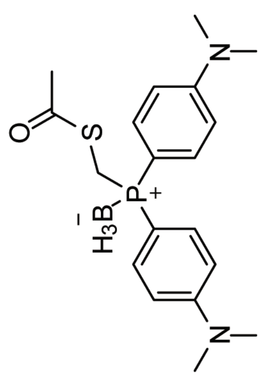




47

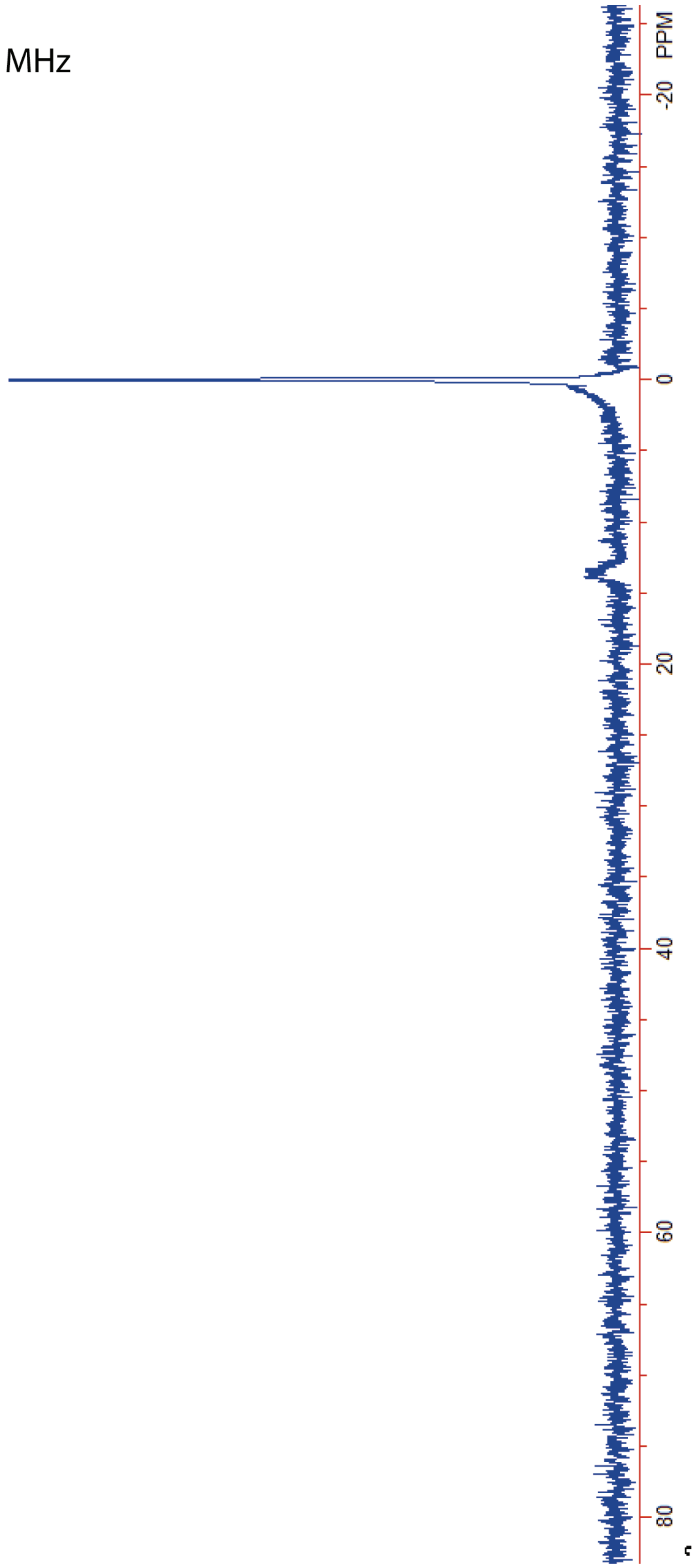
Carbon-13 NMR, 100.6 MHz
$CDCl_3$

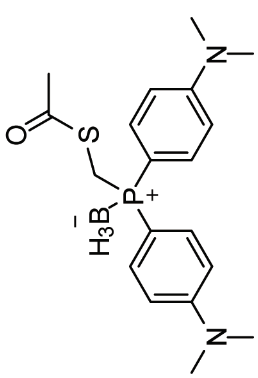




47

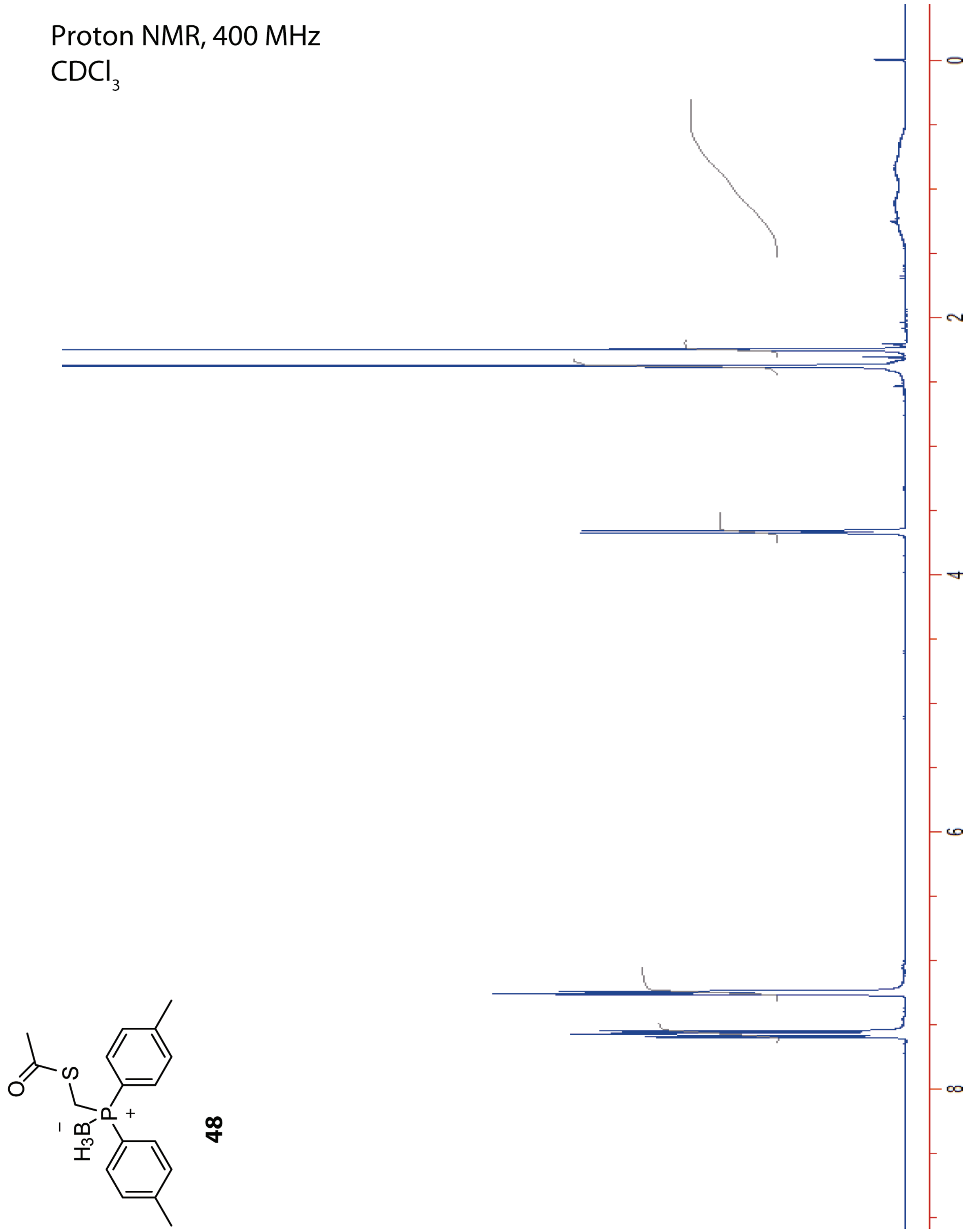
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





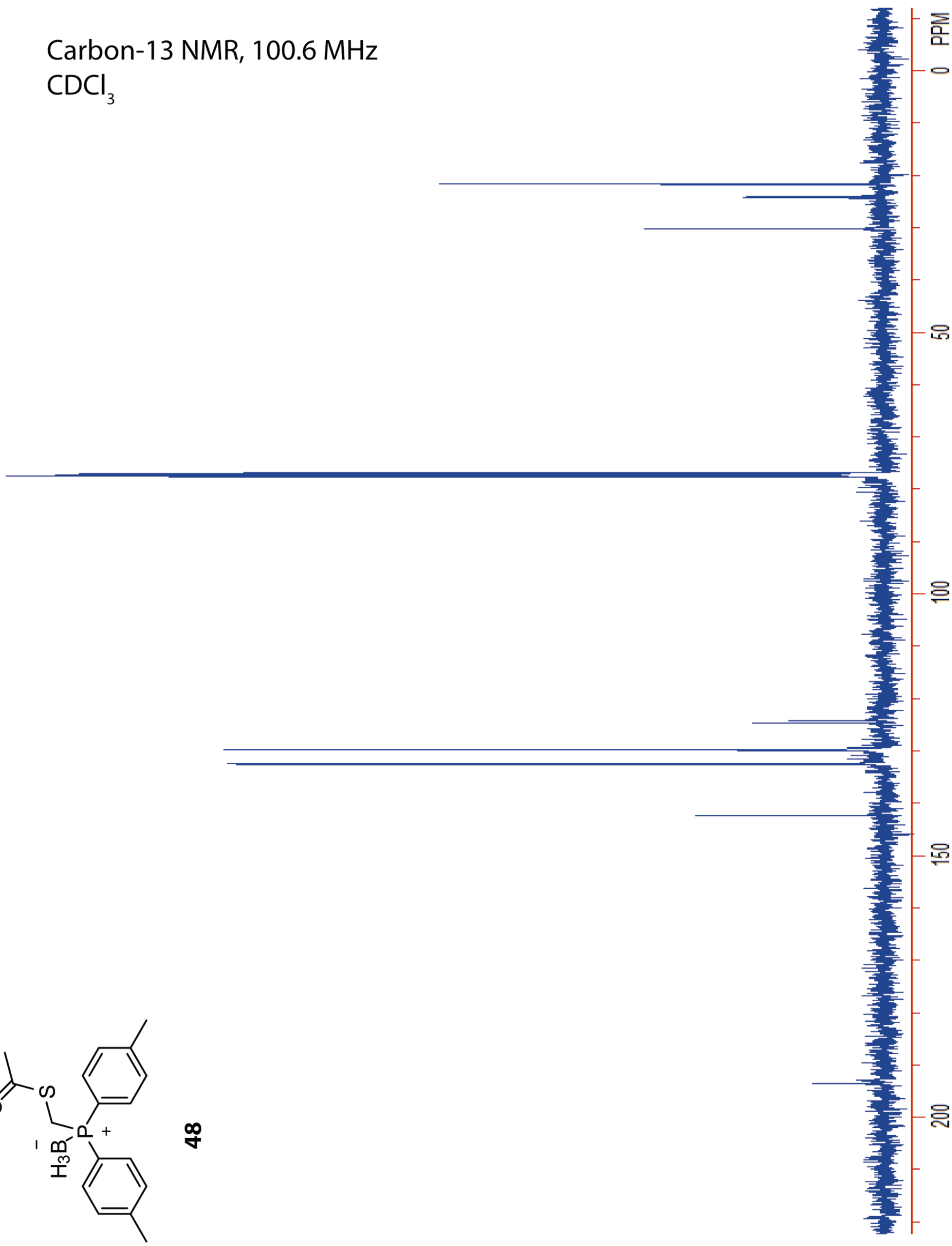
47

Proton NMR, 400 MHz
$CDCl_3$



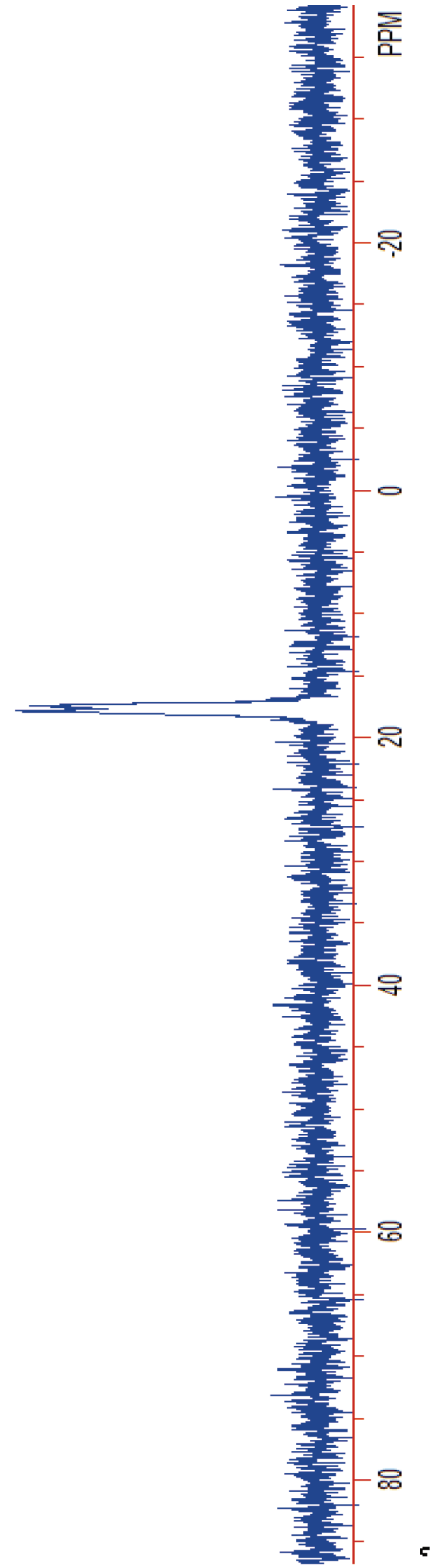
48

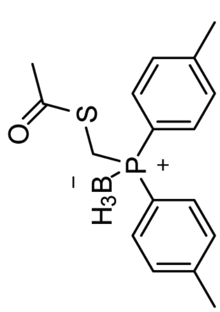
Carbon-13 NMR, 100.6 MHz
$CDCl_3$



48

Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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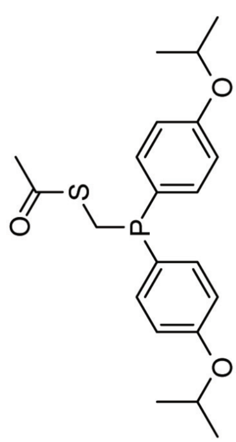
Proton NMR, 400 MHz
$CDCl_3$



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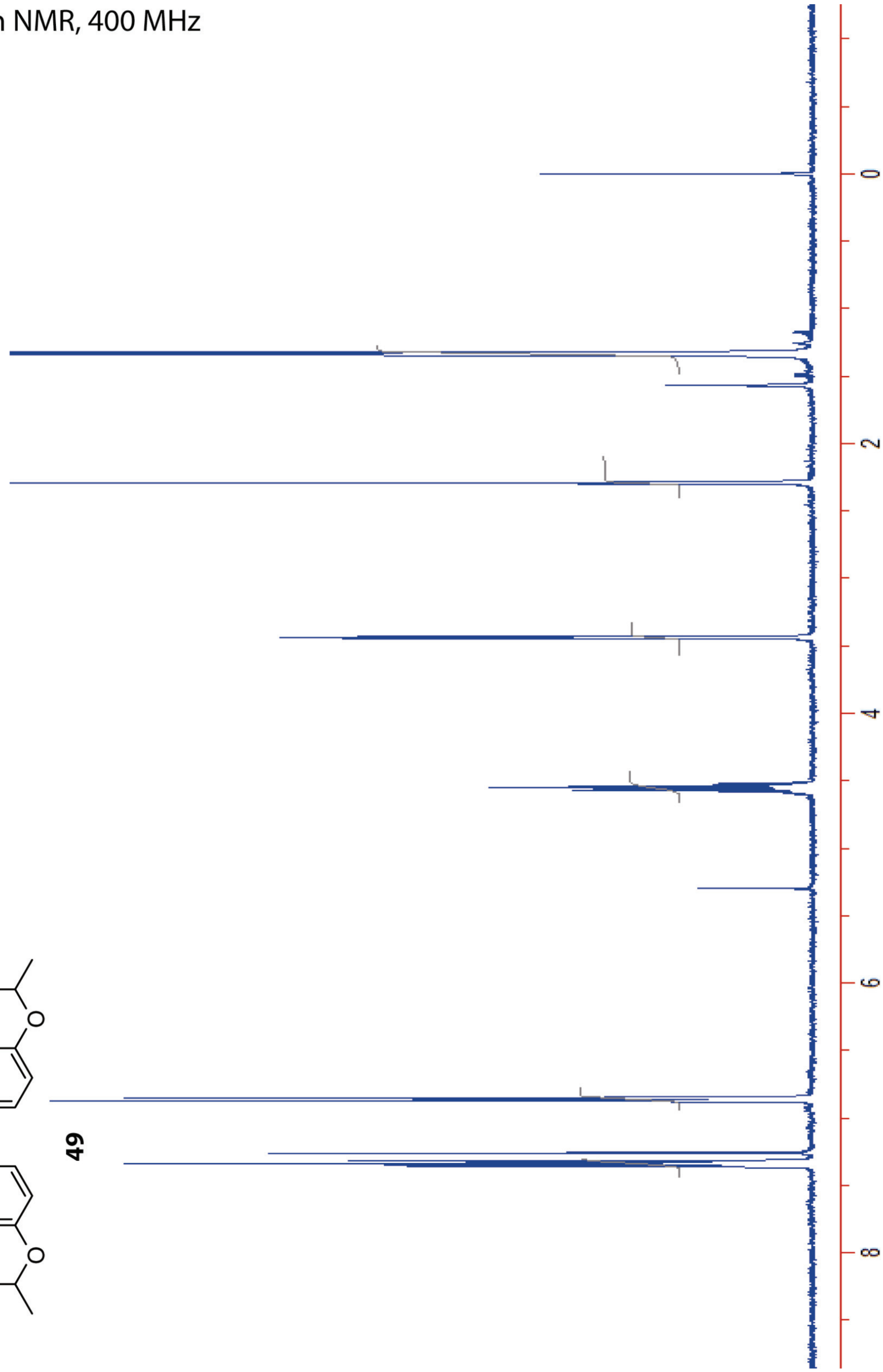
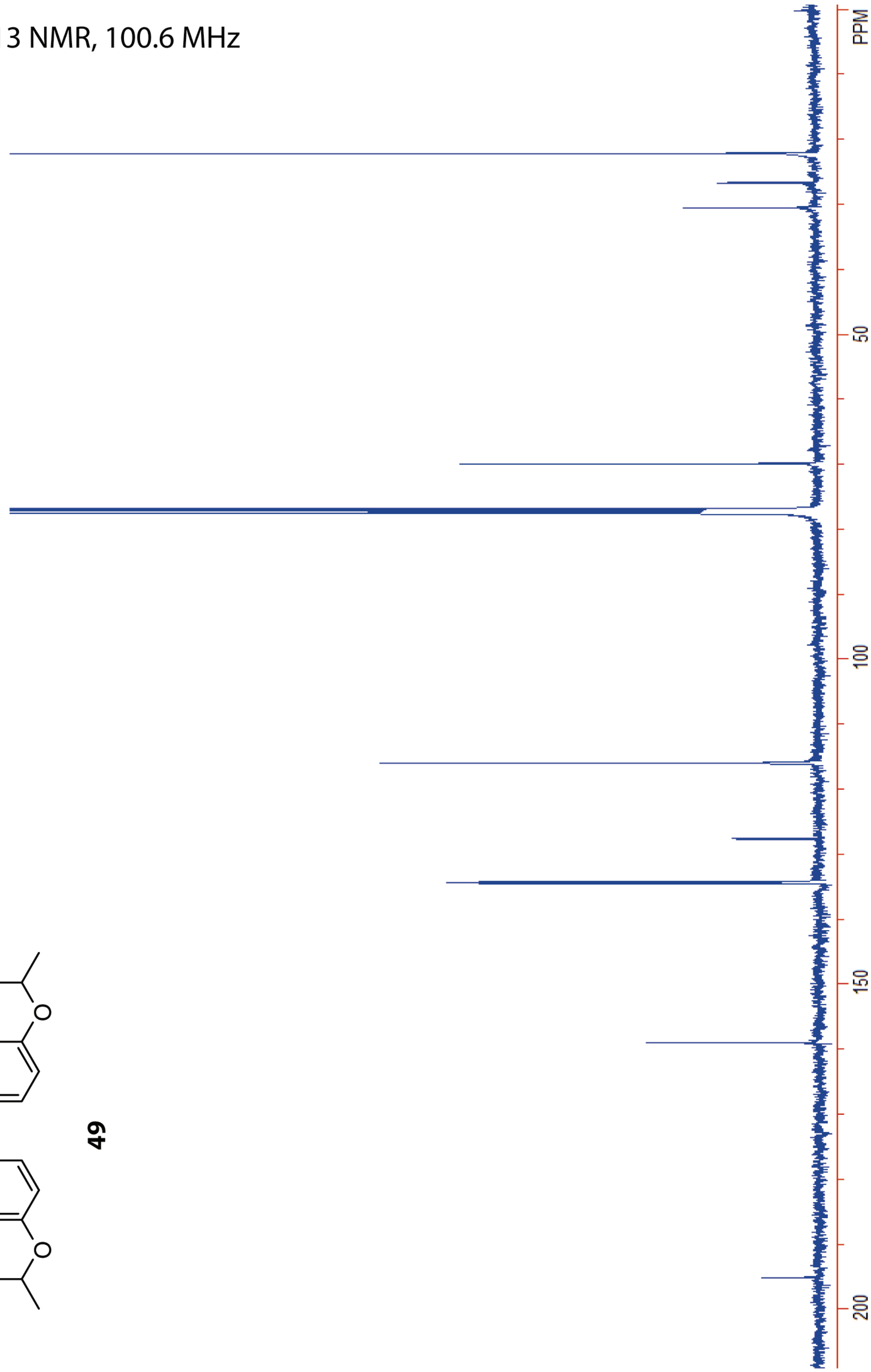
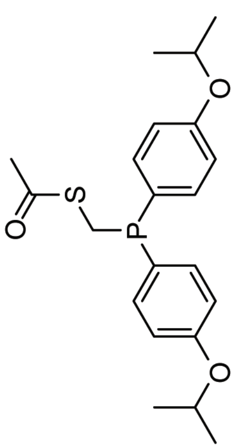


Carbon-13 NMR, 100.6 MHz
$CDCl_3$





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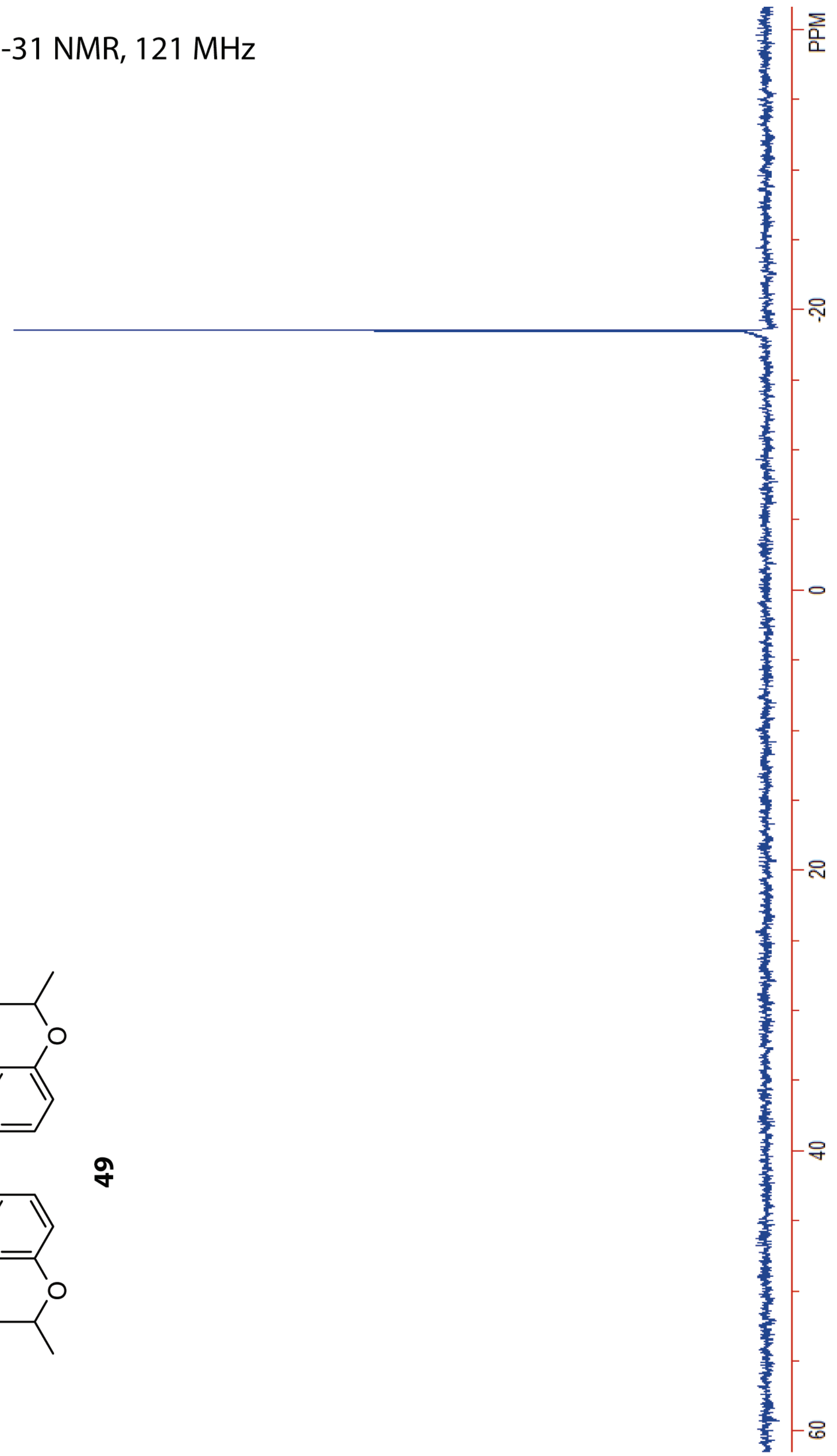
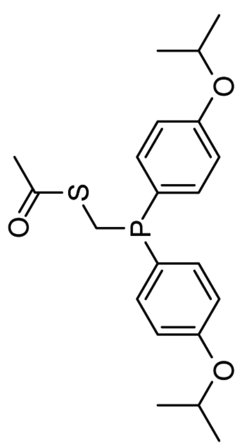
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





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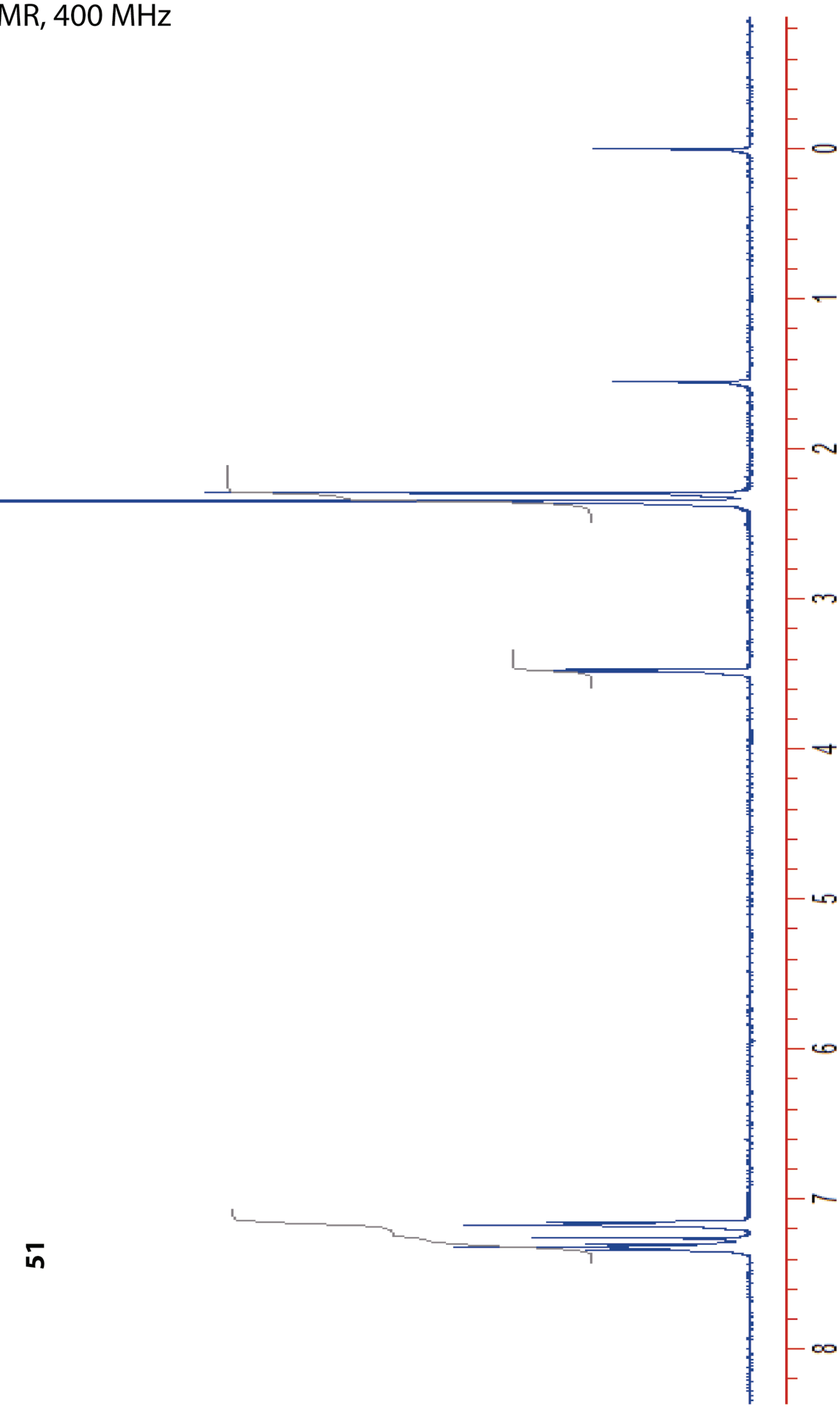
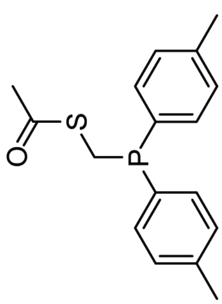
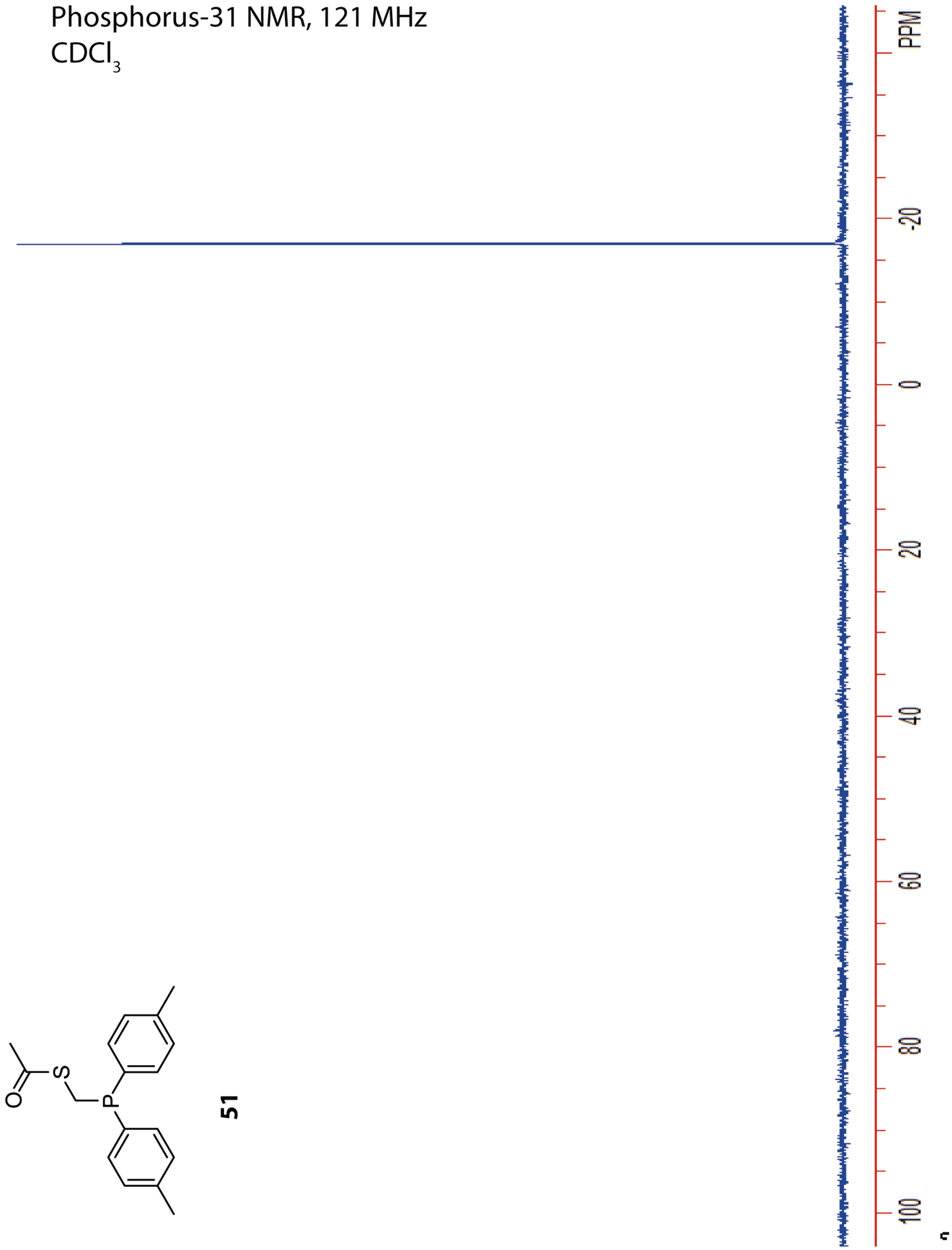
Proton NMR, 400 MHz
$CDCl_3$





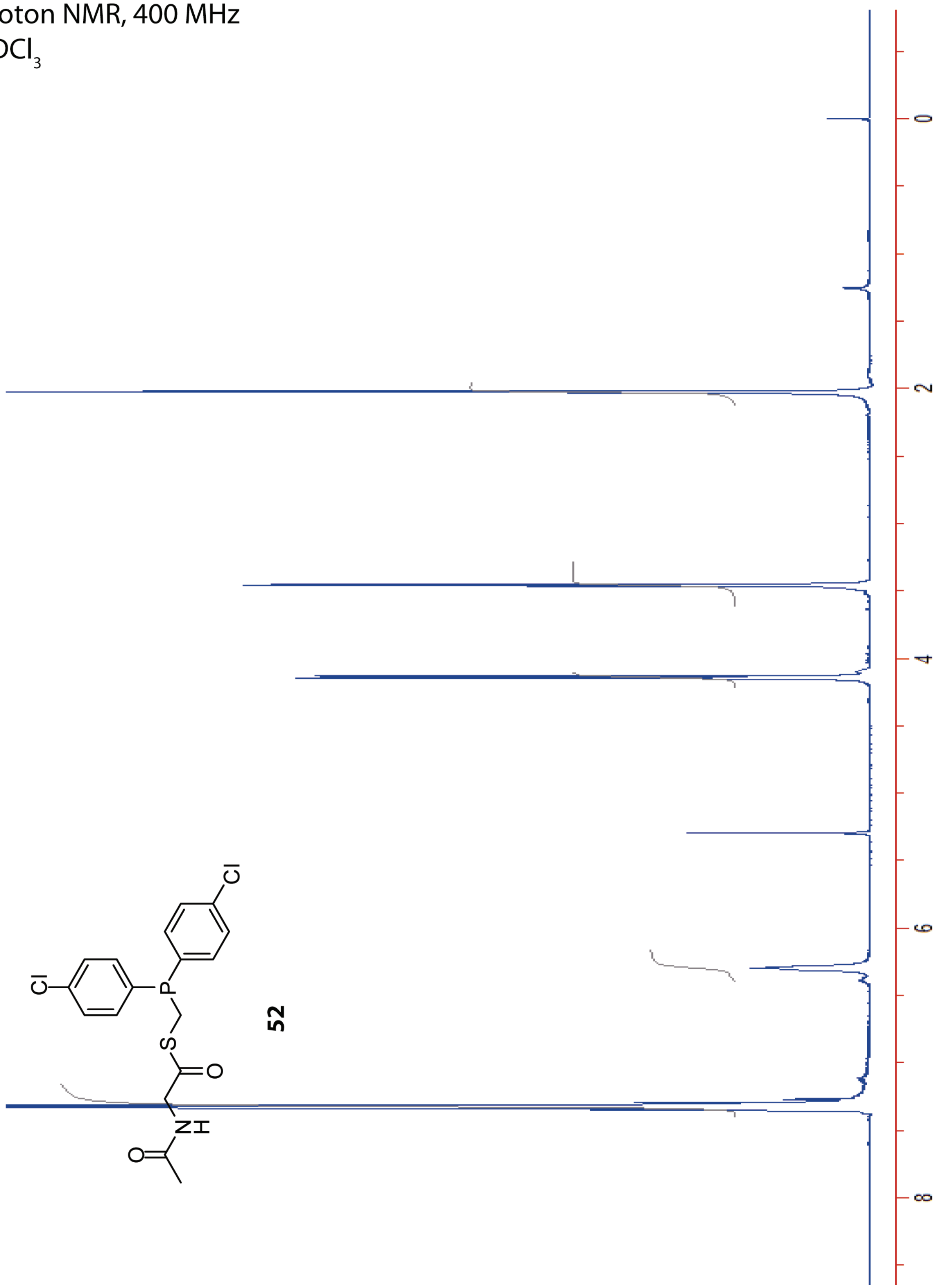
51

Phosphorus-31 NMR, 121 MHz
$CDCl_3$



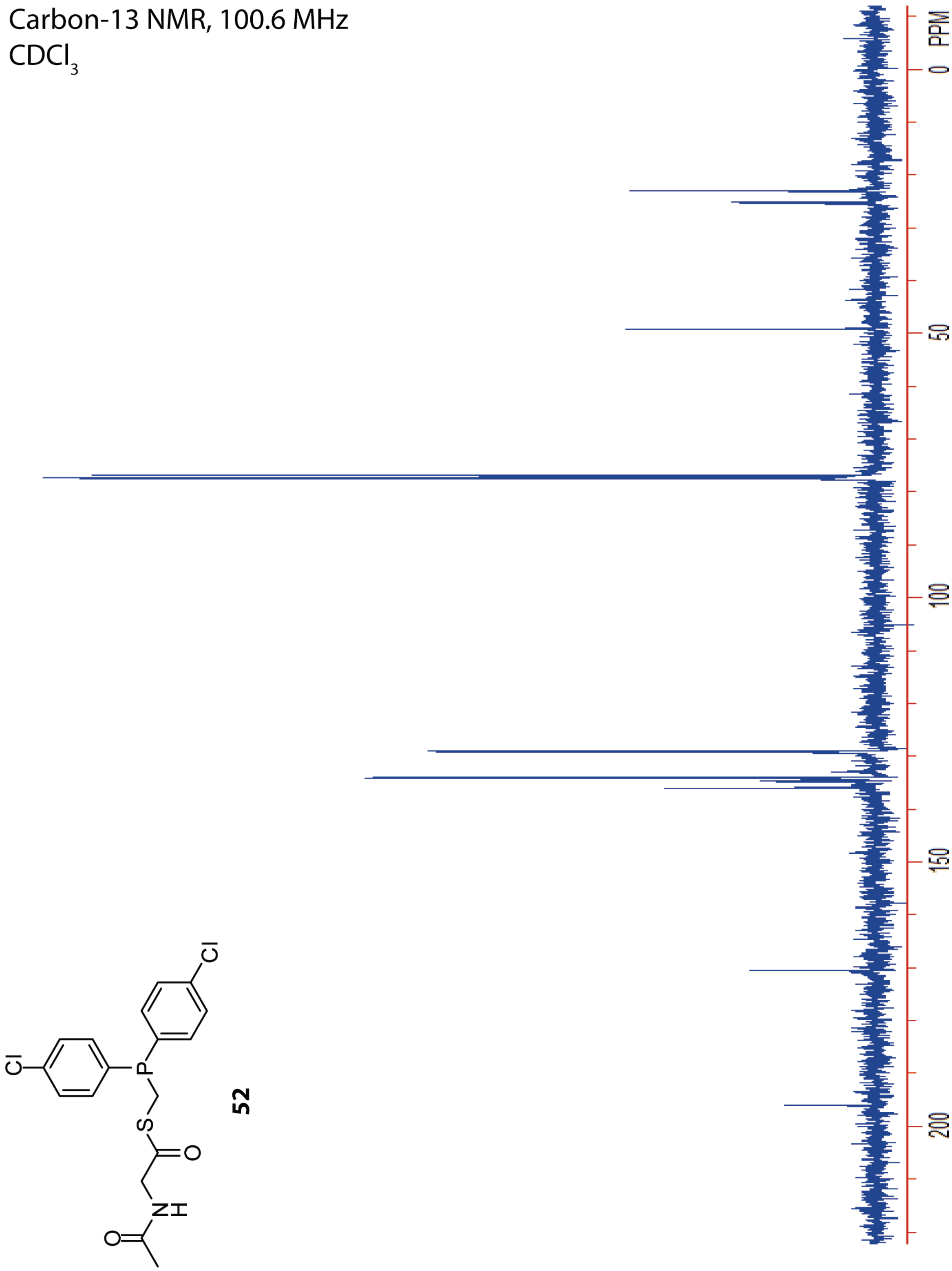
51

Proton NMR, 400 MHz
$CDCl_3$



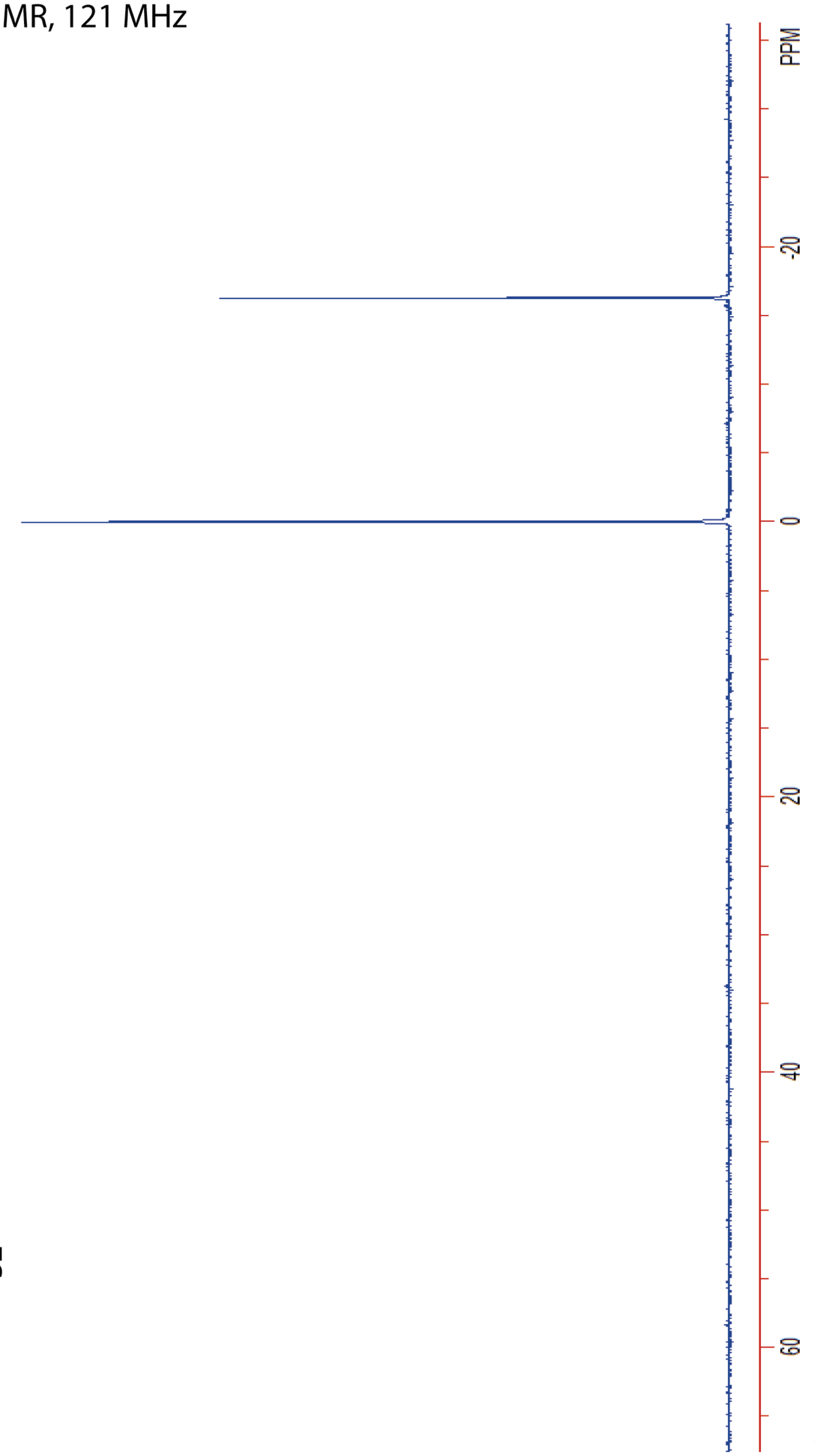
52

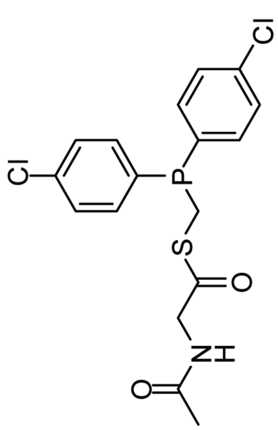
Carbon-13 NMR, 100.6 MHz
$CDCl_3$



52

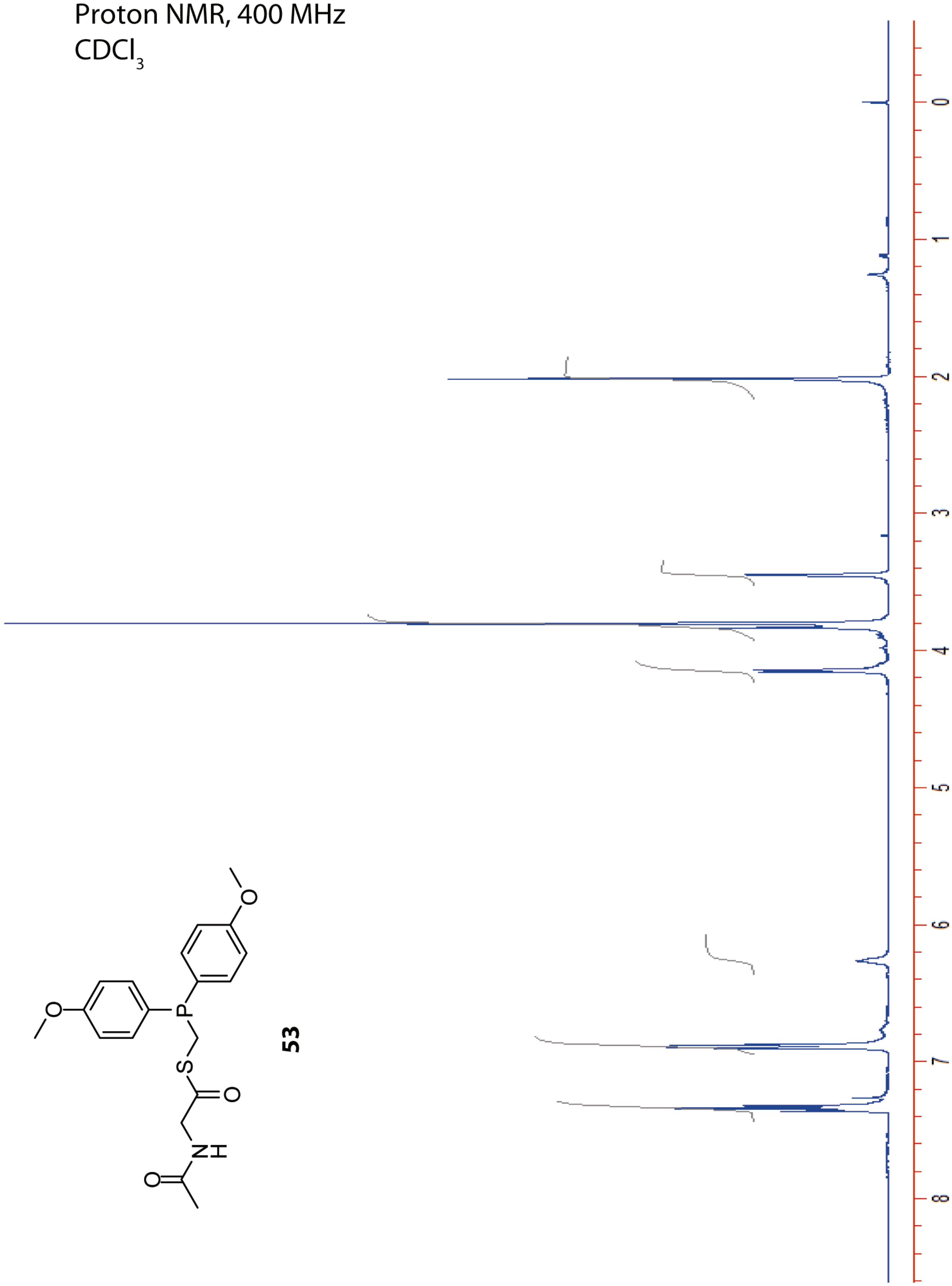
Phosphorus-31 NMR, 121 MHz
$CDCl_3$





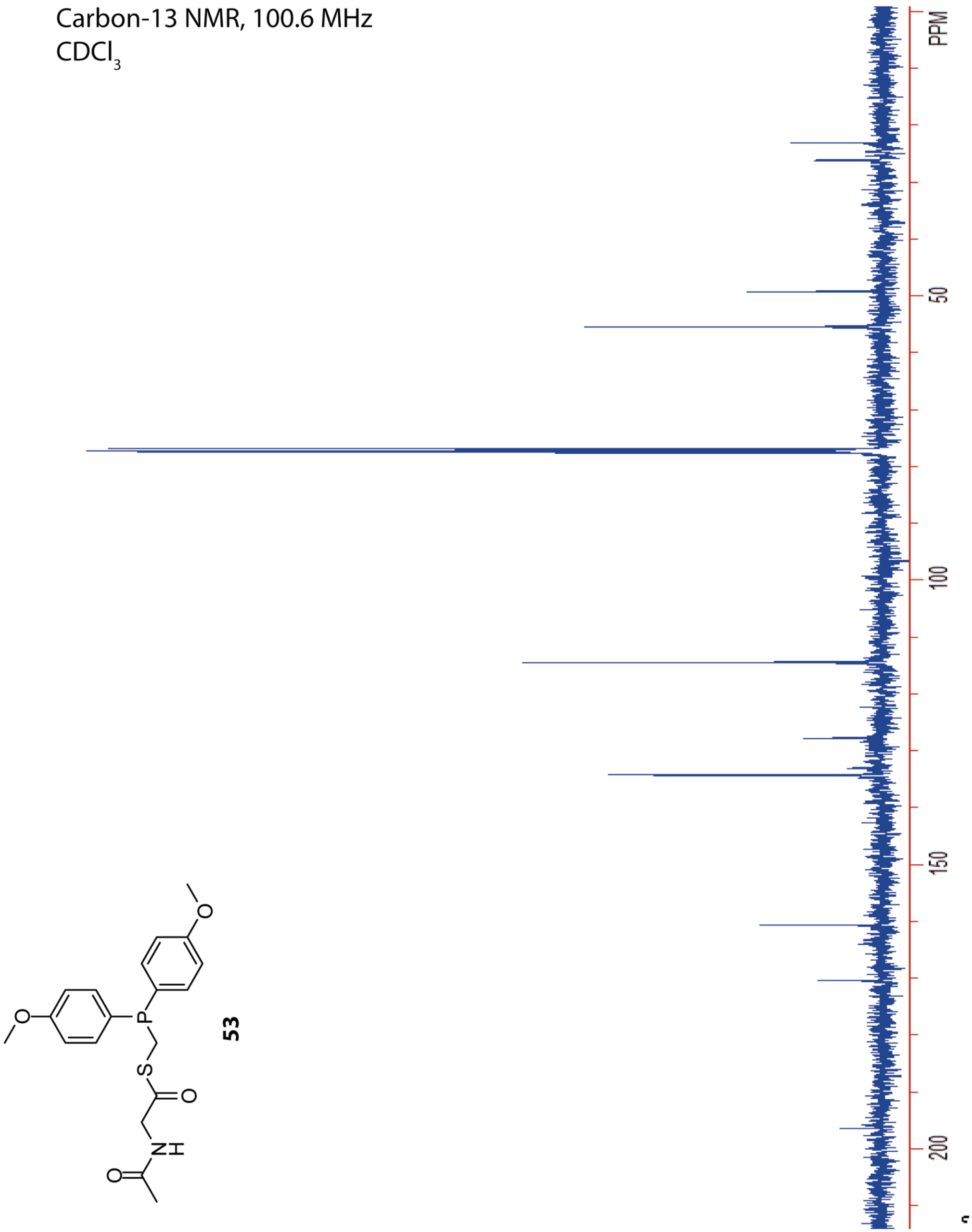
52

Proton NMR, 400 MHz
$CDCl_3$



53

Carbon-13 NMR, 100.6 MHz
$CDCl_3$



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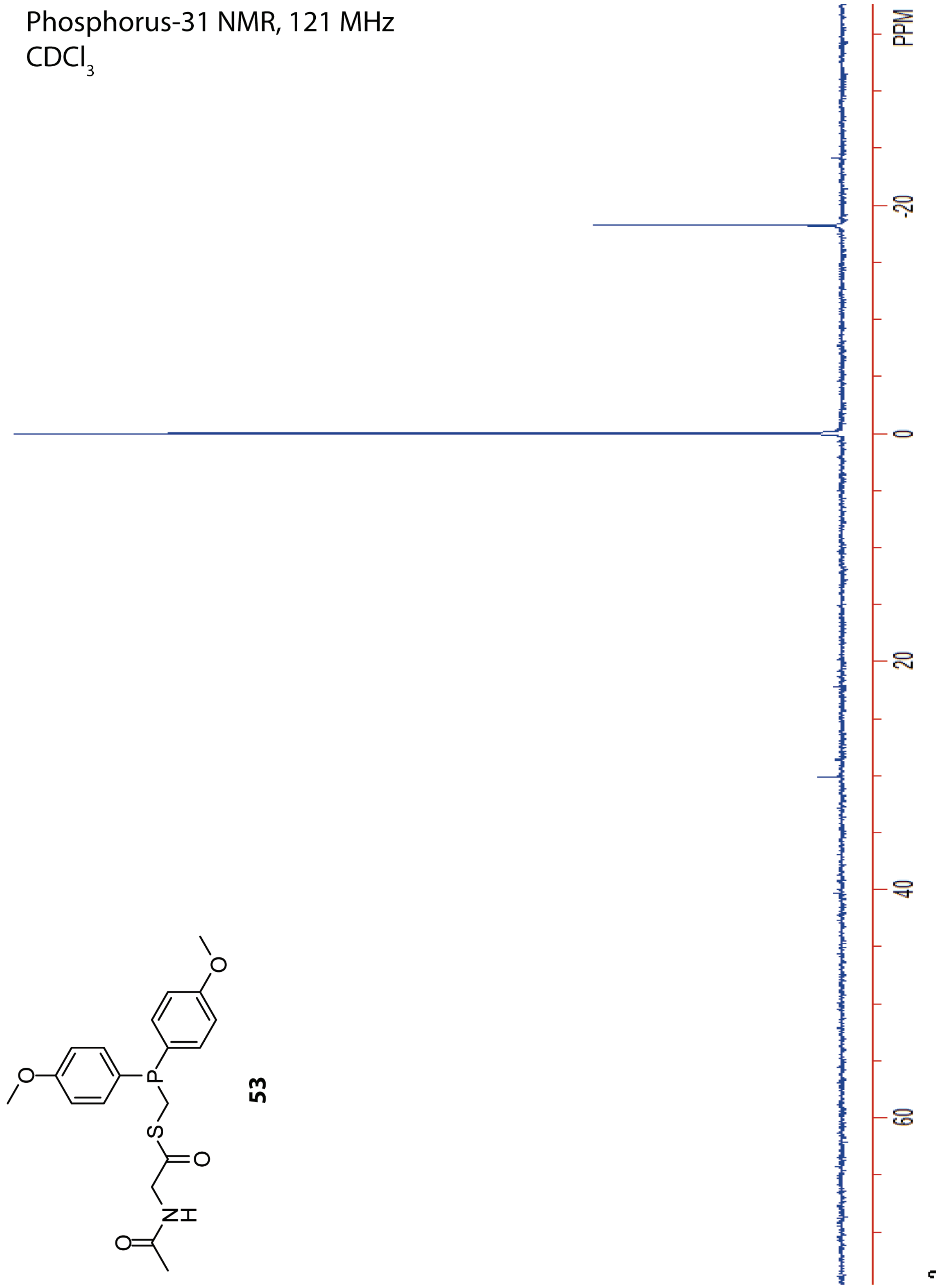
Phosphorus-31 NMR, 121 MHz
$CDCl_3$



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