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Supporting Information

Sequential Electrophilic P–C Bond Formation in Metal-Coordinated Chlorophosphines

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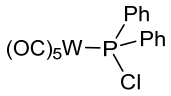
Experimental Details

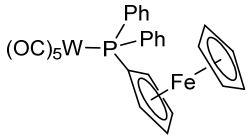
General Comments. All procedures except flash chromatography were carried out using standard Schlenk techniques or in a glovebox under nitrogen atmosphere. Diethyl ether, pentane, THF, and toluene were distilled from Na/Benzophenone. Dichloromethane, 1,2-dichloroethane and $CDCl_3$ were vacuum distilled from P_2O_5. Solvents for flash chromatography were used as received. Aluminum chloride was purified by sublimation prior to use, and stored under an inert atmosphere. The NMR spectra were recorded in 300.177 MHz (^{1}H) or 75.479 MHz (^{13}C{^{1}H}) or 121.514 MHz (^{31}P{^{1}H}) in $CDCl_3$. The ^{1}H and ^{13}C NMR spectra were referenced to internal residual solvent peaks. The ^{31}P NMR spectra were referenced to an external phosphoric acid standard. IR spectra were recorded in CH_2Cl_2. Compounds **3**, **7**, **9**, and **13** are highly sensitive, so were not isolated but treated as reactive intermediates. Full NMR spectra are given below. Compounds **11** and **12** are oils, and satisfactory elemental analysis could not be obtained. Full NMR spectra are given below. Elemental analyses on all other compounds were carried out by the Analytical and Instrumentation Laboratory in the Department of Chemistry at the University of Alberta.

a. $[W(CO)_5\{PPh_2Cl\}]$ (1). To a solution of $[W(CO)_6]$ (500 mg, 1.421 mmol) in acetonitrile (30 mL) was added $(CH_3)_3NO{\cdot}2H_2O$ (157.9 mg, 1.421 mmol), in small portions, over 20 min. The resulting yellow solution was stirred for 40 min, and the solvent was removed under reduced pressure. The residue was dissolved in toluene (5 mL) and the solvent was again removed under reduced pressure. The crude $[W(CO)_5\{CH_3CN\}]$ was dissolved in THF (40 mL), PPh_2Cl (332 μL, 1.847 mmol) was added, and the mixture was heated at 50 °C for 14 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel, 5/95 diethyl ether/petroleum ether). The pale yellow product was crystallized by cooling a saturated pentane/diethylether solution to -20 °C. Yield: 587 mg, 76%. IR (νCO, CH_2Cl_2, cm^{-1}): 2079(w), 1949(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 95.7 (s, $^1J_{PW}$ = 281 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 7.41 – 7.47 (m, 6H, Ph), 7.56 – 7.63 (m, 4H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.93 (d, $^3J_{CP}$ = 10.7 Hz, Ph), 131.15 (d, $^2J_{CP}$ = 14.6 Hz, Ph), 131.75 (d, $^4J_{CP}$ = 1.7 Hz, Ph), 138.86 (d, $^1J_{CP}$ = 32.7 Hz, *ipso*-Ph), 196.06 (d, $^2J_{CP}$ = 7.3 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 199.07 (d, $^2J_{CP}$ = 31.0 Hz, *trans*-CO). The $^{31}P\{^1H\}$ NMR spectral data match the previously published data.[1]

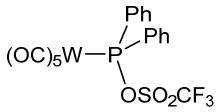


b. $[W(CO)_5\{P(C_{10}H_9Fe)Ph_2\}]$ (2). The compound $[W(CO)_5\{PPh_2Cl\}]$ (**1**, 60 mg, 0.110 mmol) and $AlCl_3$ (59 mg, 0.442 mmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 15 min at room temperature. Ferrocene (41 mg, 0.221 mmol) was added, resulting in a color change to yellow-green. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (alumina, 20/80, diethyl ether/petroleum ether). The orange product was

crystallized by cooling a saturated pentane/CH_2Cl_2 solution to -20 °C. Yield: 64 mg, 83%. IR (νCO, CH_2Cl_2, cm^{-1}): 2071(w), 1936(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 12.0 (s, $^1J_{PW}$ = 246 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 4.00 (s, 5H, FeC_5H_5), 4.26 (m, 2H, C_5H_4P), 4.53 (m, 2H, C_5H_4P), 7.40 – 7.50 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.90 (s, FeC_5H_5), 71.82 (d, $^3J_{CP}$ = 7.3 Hz, C_5H_4P), 74.06 (d, $^2J_{CP}$ = 12.4 Hz, C_5H_4P), 78.90 (d, $^1J_{CP}$ = 46.2 Hz, C_5H_4P), 128.30 (d, $^3J_{CP}$ = 9.6 Hz, Ph), 130.13 (d, $^4J_{CP}$ = 2.2 Hz, Ph), 132.69 (d, $^2J_{CP}$ = 11.9 Hz, Ph), 138.14 (d, $^1J_{CP}$ = 43.9 Hz, *ipso*-Ph), 197.60 (d, $^2J_{CP}$ = 7.3 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 199.14 (d, $^2J_{CP}$ = 21.4 Hz, $^1J_{CW}$ = 143.0 Hz, *trans*-CO). Anal. Cald for $C_{27}H_{19}O_5FePW$: C, 46.72; H, 2.76. Found: C, 46.75; H, 2.74.



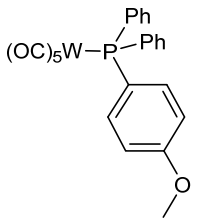
c. $[W(CO)_5\{P(OSO_2CF_3)Ph_2\}]$ (3). The compound $[W(CO)_5\{PPh_2Cl\}]$ (**1**, 25 mg, 0.046 mmol) and $AgOSO_2CF_3$ (14.2 mg, 0.55 mmol) were dissolved in CH_2Cl_2 (2 mL). This solution was stirred for 2 h, resulting in a yellow solution and a white precipitate. The solution was filtered through Celite. Conversion is quantitative by NMR spectroscopy. This air-and-moisture sensitive solution is stable for days at -20 °C or hours at room temperature. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (νCO, CH_2Cl_2, cm^{-1}): 2076(w), 1941(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 167.4 (s, $^1J_{PW}$ = 308 Hz). ^{19}F NMR ($CDCl_3$): δ -76.4 (s, OSO_2CF_3). ^1H NMR (300 Hz, $CDCl_3$): δ 7.56 – 7.70 (m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.36 (q, $^1J_{CF}$ = 319.2 Hz, OSO_2CF_3), 129.15 (d, $^3J_{CP}$ = 10.7 Hz, Ph), 131.62 (d, $^2J_{CP}$ = 15.2 Hz, Ph), 133.08 (d, $^4J_{CP}$ = 1.7 Hz, Ph), 136.99 (d, $^1J_{CP}$ = 39.4 Hz, *ipso*-Ph), 194.67 (d, $^2J_{CP}$ = 7.9 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 197.60 (d, $^2J_{CP}$ = 33.2 Hz, *trans*-CO).



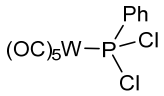
d. Reaction of $W(CO)_5\{P(OSO_2CF_3)Ph_2\}]$ (3) with ferrocene. A solution of $W(CO)_5\{P(OSO_2CF_3)Ph_2\}]$ (**3**) was prepared by dissolving $[W(CO)_5\{PPh_2Cl\}]$ (**1**, 60.0 mg, 0.110 mmol) and $AgOSO_2CF_3$ (34.0 mg, 0.132 mmol) in CH_2Cl_2 (5 mL), stirring for 2 h and filtering. This solution was added to a solution of ferrocene (41.1 mg, 0.221 mmol) in CH_2Cl_2 (1 mL), resulting in a color change to yellow-green. The solvent was removed in vacuo and the residue was purified and crystallized with the same procedure described in section **b**, leading to orange crystals of $[W(CO)_5\{P(C_{10}H_9Fe)Ph_2\}]$ (**2**). Yield: 71 mg, 92%.

e. $[W(CO)_5\{P(p\text{-}C_6H_4OCH_3)Ph_2\}]$ (4). A solution of $[W(CO)_5\{P(OSO_2CF_3)Ph_2\}]$ (**3**) was prepared by dissolving $[W(CO)_5\{PPh_2Cl\}]$ (**1**, 90.0 mg, 0.166 mmol) and $AgOSO_2CF_3$ (51.1 mg, 0.199 mmol) in CH_2Cl_2 (7 mL) as described above, and transferred to a Schlenk flask. Anisole (180 μL, 1.65 mmol) was added, the flask was sealed with a glass stopper, and the solution was stirred for 12 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/ petroleum ether), and white crystals of $[W(CO)_5\{P(p\text{-}C_6H_4OCH_3)Ph_2\}]$ (**4**) were obtained by cooling a saturated hexane solution to -20 °C. Yield: 84 mg, 82%. IR (νCO, CH_2Cl_2, cm^{-1}): 2073(w), 1938(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 20.0 (s, $^1J_{PW}$ = 243 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 3.84 (s, 3H, OCH_3), 6.96 (m, 2H, $-C_6H_4OCH_3$), 7.38 – 7.45 (m, 12H, 10H of Ph and 2H of $-C_6H_4OCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.57 (s, $-OCH_3$), 114.43 (d, $^3J_{CP}$ = 10.7 Hz, $-C_6H_4OCH_3$), 125.80 (d, $^1J_{CP}$ = 45.6 Hz, *ipso*-$C_6H_4OCH_3$), 128.79 (d, $^3J_{CP}$ = 10.1 Hz, Ph), 130.39 (d, $^4J_{CP}$ = 2.3 Hz, Ph), 132.93 (d, $^2J_{CP}$ = 11.9 Hz, Ph), 135.23 (d, $^2J_{CP}$ = 13.5 Hz, $-C_6H_4OCH_3$),

136.16 (d, $^1J_{CP}$ = 41.1 Hz, *ipso*-Ph), 161.49 (s, *ipso*-$C_6H_4OCH_3$), 197.58 (d, $^2J_{CP}$ = 7.3 Hz, *cis*-CO), 199.55 (d, $^2J_{CP}$ = 21.4 Hz, *trans*-CO). Anal. Cald for $C_{24}H_{17}O_6PW$: C, 46.78; H, 2.78. Found: C, 47.05, H, 2.82.

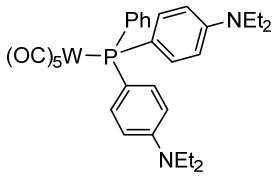


f. [W(CO)$_5${PPhCl$_2$}] (5). This compound was prepared according to the literature procedure;[2] however, purification was done using flash chromatography (silica gel, 5/95 v/v diethyl ether/petroleum ether). IR (νCO, CH_2Cl_2, cm^{-1}): 2086(w), 1962(vs). ^{31}P NMR (121 Hz, $CDCl_3$): δ 128.7 (t, $^1J_{PW}$ = 342 Hz, $^3J_{PH}$ = 13.4 Hz). ^{1}H NMR (300 Hz, $CDCl_3$): δ 7.38 – 7.57 (m, 3H, Ph), 7.79 – 7.89 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.67 (d, $^2J_{CP}$ = 17.4 Hz, Ph), 129.10 (d, $^3J_{CP}$ = 11.9 Hz, Ph), 132.91 (d, $^4J_{CP}$ = 1.7 Hz, Ph), 142.70 (d, $^1J_{CP}$ = 27.6 Hz, *ipso*-Ph), 194.88 (d, $^2J_{CP}$ = 7.9 Hz, $^1J_{CW}$ = 127.3 Hz, *cis*-CO), 198.32 (d, $^2J_{CP}$ = 45.1 Hz, *trans*-CO).



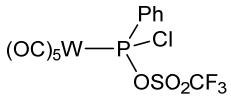
g. [W(CO)$_5${P(*p*-C$_6$H$_4$N(CH$_2$CH$_3$)$_2$)$_2$Ph}] (6). The compound [W(CO)$_5${PPhCl$_2$}] (**5**, 70 mg, 0.139 mmol) and $AlCl_3$ (55.7 mg, 0.418 mmol) were dissolved in CH_2Cl_2 (4 mL) and stirred for 15 min. *N,N*-diethyl aniline (23 μL, 0.139 mmol) was added, and the solution was stirred for 36 h. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, 10/90 v/v diethyl ether/ petroleum ether). Pale yellow crystals of [W(CO)$_5${P(*p*-C$_6$H$_4$N(CH$_2$CH$_3$)$_2$)$_2$Ph}] (**6**) were obtained by cooling a saturated solution to -20 °C. Yield: 43

mg, 42%. IR (νCO, CH_2Cl_2, cm^{-1}): 2069(w), 1935(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 15.0 (s, $^1J_{PW}$ = 240 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 1.18 (t, 12H, $^3J_{HH}$ = 6.9 Hz, -NCH_2CH_3), 3.37 (q, 8H, $^3J_{HH}$ = 6.9 Hz, -NCH_2CH_3), 6.65 (d, 4H, $^3J_{HH}$ = 8.1 Hz, $P(C_6H_4N(CH_2CH_3)_2)$), 7.27 – 7.45 (m, 9H, 4H of $P(C_6H_4N(CH_2CH_3)_2)$ and 5H of Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.78 (s, -NCH_2CH_3), 44.47 (s, -NCH_2CH_3), 111.08 (d, $^3J_{CP}$ = 10.7 Hz, -$C_6H_4N(CH_2CH_3)_2$), 119.36 (d, $^1J_{CP}$ = 49.5 Hz, *ipso*-$C_6H_4N(CH_2CH_3)_2$), 128.30 (d, $^3J_{CP}$ = 9.6 Hz, -Ph), 129.41 (s, -Ph), 132.36 (d, $^2J_{CP}$ = 11.9 Hz, -Ph), 134.98 (d, $^2J_{CP}$ = 13.5 Hz, -$C_6H_4N(CH_2CH_3)_2$), 137.47 (d, $^1J_{CP}$ = 41.7 Hz, *ipso*-Ph), 148.98 (s, *ipso*-$C_6H_4N(CH_2CH_3)_2$), 198.13 (d, $^2J_{CP}$ = 6.8 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 200.46 (d, $^2J_{CP}$ = 19.7 Hz, *trans*-CO). Anal. Cald for $C_{31}H_{33}N_2O_5PW$: C, 51.12; H, 4.57; N, 3.85. Found: C, 51.08, H, 4.58; N, 3.85.

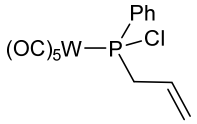


h. $[W(CO)_5\{P(OSO_2CF_3)(Cl)Ph\}]$ (7). The compound $[W(CO)_5\{PPhCl_2\}]$ (**5**, 30 mg, 0.060 mmol) and $AgOSO_2CF_3$ (18.4 mg, 0.072 mmol) were dissolved in CH_2Cl_2 (2 mL). This solution was stirred for 3 h, resulting in a yellow solution and a white precipitate. The solution was filtered through Celite. Yield is quantitative by NMR spectroscopy. This air-and-moisture sensitive solution is stable for hours at room temperature. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (νCO, CH_2Cl_2, cm^{-1}): 2091(w), 1970(vs). ^{31}P NMR (121 Hz, $CDCl_3$): δ 162.5 (t, $^1J_{PW}$ = 376 Hz, $^3J_{PH}$ = 13.1 Hz). ^{19}F NMR ($CDCl_3$): δ -75.6 (s, OSO_2CF_3). ^1H NMR (300 Hz, $CDCl_3$): δ 7.63 – 7.67 (m, 3H, Ph), 7.84 – 7.92 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.32 (q, $^1J_{CF}$ = 319.3 Hz, OSO_2CF_3), 128.87 (d, $^2J_{CP}$ = 17.4 Hz, Ph), 129.40

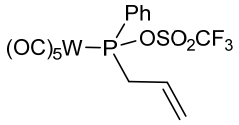
(d, $^{3}J_{CP}$ = 11.9 Hz, Ph), 133.96 (d, $^{4}J_{CP}$ = 1.7 Hz, Ph), 139.99 (d, $^{1}J_{CP}$ = 37.7 Hz, *ipso*-Ph), 193.58 (d, $^{2}J_{CP}$ = 8.5 Hz, $^{1}J_{CW}$ = 126.1 Hz, *cis*-CO), 196.50 (d, $^{2}J_{CP}$ = 46.7 Hz, *trans*-CO).



i. [W(CO)$_5${P(CH$_2$CHCH$_2$)(Cl)Ph}] (8). A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)(Cl)Ph}] (**7**) was prepared by dissolving [W(CO)$_5${PPhCl$_2$}] (**5**, 180.0 mg, 0.358 mmol) and AgOSO$_2$CF$_3$ (110.0 mg, 0.430 mmol) in CH$_2$Cl$_2$ (10 mL), stirring for 3 h and filtering. Allyl trimethylsilane (171 μL, 1.07 mmol) was added, resulting in a color change to yellow. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, 5/95 v/v diethyl ether/ petroleum ether). The pale-yellow crystals of [W(CO)$_5${P(CH$_2$CHCH$_2$)(Cl)Ph}] (**8**) was obtained by cooling a saturated hexane solution to -20 °C. Yield: 164 mg. 90%. IR (νCO, CH$_2$Cl$_2$, cm^{-1}): 2079(w), 1948(vs). ^{31}P{^{1}H} NMR (121 Hz, CDCl$_3$): δ 96.5 (s, $^{1}J_{PW}$ = 280 Hz). ^{1}H NMR (300 Hz, CDCl$_3$): δ 3.39 (m, 2H, -C*H*$_2$CHCH$_2$), 5.26 (m, 2H, -CH$_2$CHC*H*$_2$), 5.68 (m, 1H, -CH$_2$C*H*CH$_2$), 7.46 – 7.57 (m, 3H, Ph), 7.66 – 7.73 (m, 2H, Ph). ^{13}C NMR (75 MHz, CDCl$_3$): δ 48.07 (d, $^{1}J_{CP}$ = 15.2 Hz, -*C*H$_2$CHCH$_2$), 122.60 (d, $^{2}J_{CP}$ = 11.9 Hz, -CH$_2$*C*HCH$_2$), 128.23 (d, $^{3}J_{CP}$ = 6.2 Hz, -CH$_2$CH*C*H$_2$), 129.00 (d, $^{3}J_{CP}$ = 10.1 Hz -Ph), 129.50 (d, $^{2}J_{CP}$ = 13.5 Hz, -Ph), 131.49 (d, $^{4}J_{CP}$ = 2.3 Hz, -Ph), 137.29 (d, $^{1}J_{CP}$ = 29.3 Hz, *ipso*-Ph), 195.94 (d, $^{2}J_{CP}$ = 7.3 Hz, $^{1}J_{CW}$ = 133.4, *cis*-CO), 198.90 (d, $^{2}J_{CP}$ = 30.9 Hz, *trans*-CO). Anal. Cald for C$_{14}$H$_{10}$ClO$_5$PW: C, 33.07; H, 1.98. Found: C, 33.33; H, 1.99.

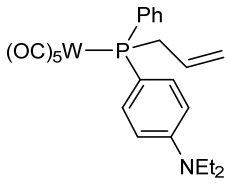


j. $[W(CO)_5\{P(CH_2CHCH_2)(OSO_2CF_3)Ph\}]$ (9). The compounds $[W(CO)_5\{P(CH_2CHCH_2)(Cl)Ph\}]$ (**8**, 70.0 mg, 0.138 mmol) and $AgOSO_2CF_3$ (42.4 mg, 0.165 mmol) were dissolved in CH_2Cl_2 (6 mL). This solution was stirred for 12 h, resulting in a yellow solution and a white precipitate. The solution was filtered through Celite. Conversion is quantitative by NMR spectroscopy. This air-and-moisture sensitive solution is stable for hours at room temperature. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (νCO, CH_2Cl_2, cm^{-1}): 2084(w), 1955(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 172.3 (s, $^1J_{PW}$ = 308 Hz). ^{19}F NMR ($CDCl_3$): δ -75.8 (s, OSO_2CF_3). ^1H NMR (300 Hz, $CDCl_3$): δ 3.56 – 3.87 (m, 2H, -CH_2CHCH_2), 5.40 (m, 2H, -CH_2CHCH_2), 5.73 (m, 1H, -CH_2CHCH_2), 7.48 – 7.62 (m, 3H, Ph), 7.70 – 7.77 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.80 (d, $^1J_{CP}$ = 18.6 Hz, -CH_2CHCH_2), 118.38 (q, $^1J_{CF}$ = 320.0 Hz, OSO_2CF_3), 124.01 (d, $^2J_{CP}$ = 13.0 Hz, -CH_2CHCH_2), 126.47 (d, $^3J_{CP}$ = 4.0 Hz, -CH_2CHCH_2), 129.35 (d, $^3J_{CP}$ = 10.1 Hz -Ph), 130.09 (d, $^2J_{CP}$ = 14.1 Hz, -Ph), 133.11 (d, $^4J_{CP}$ = 1.7 Hz, -Ph), 135.76 (d, $^1J_{CP}$ = 34.9 Hz, *ipso*-Ph), 194.68 (d, $^2J_{CP}$ = 7.3 Hz, $^1J_{CW}$ = 125.5, *cis*-CO), 197.14 (d, $^2J_{CP}$ = 33.2 Hz, *trans*-CO).



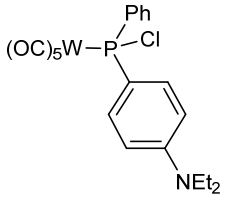
k. $[W(CO)_5\{P(p\text{-}C_6H_4N(CH_2CH_3)_2)(CH_2CHCH_2)Ph\}]$ (10). *N,N*-diethyl aniline (44.3 μL, 0.276 mmol) was added to the solution of $[W(CO)_5\{P(OSO_2CF_3)(CH_2CHCH_2)Ph\}]$ (**9**) prepared above. The solution was stirred for 15 min, resulting in a color change to pale-yellow with cloudiness. The solvent was removed in vacuo and the residue was purified by flash chromatography (alumina, 10/90 v/v diethyl ether/ petroleum ether). The pale-yellow crystals of $[W(CO)_5\{P(p\text{-}C_6H_4N(CH_2CH_3)_2)(CH_2CHCH_2)Ph\}]$ (**10**) was obtained by cooling a saturated

pentane/CH_2Cl_2 solution to -20 °C. Yield: 79 mg, 92%. IR (νCO, CH_2Cl_2, cm^{-1}): 2068(w), 1933(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 6.5 (t, $^1J_{PW}$ = 241 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 1.19 (t, 6H, $^3J_{HH}$ = 7.2 Hz, -NCH_2CH_3), 3.39 (q, 4H, $^3J_{HH}$ = 7.2 Hz, -NCH_2CH_3), 3.27 (m, 2H, -CH_2CHCH_2), 5.04 – 5.16 (m, 2H, -CH_2CHCH_2), 5.46 – 5.62 (m, 1H, -CH_2CHCH_2), 6.68 (dd, 2H, $^3J_{HH}$ = 9.0 Hz, $^5J_{HH}$ = 1.8 Hz, $P(C_6H_4N(CH_2CH_3)_2)$, 7.33 – 7.46 (m, 7H, 2H of $P(C_6H_4N(CH_2CH_3)_2)$ and 5H of Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.74 (s, -NCH_2CH_3), 39.45 (d, $^1J_{CP}$ = 24.8 Hz, -$PCH_2CH_2CH_2$), 44.48 (s, -NCH_2CH_3), 111.16 (d, $^3J_{CP}$ = 10.7 Hz, -$C_6H_4N(CH_2CH_3)_2$), 116.65 (d, $^1J_{CP}$ = 47.9 Hz, *ipso*-$C_6H_4N(CH_2CH_3)_2$, 120.80 (d, $^2J_{CP}$ = 11.9 Hz, -CH_2CHCH_2), 128.63 (d, $^3J_{CP}$ = 9.0 Hz, -Ph), 129.62 (d, $^4J_{CP}$ = 1.7 Hz, -Ph), 130.15 (d, $^3J_{CP}$ = 3.4 Hz, -CH_2CHCH_2), 131.04 (d, $^2J_{CP}$ = 10.7 Hz, -Ph), 135.06 (d, $^2J_{CP}$ = 12.9 Hz, -$C_6H_4N(CH_2CH_3)_2$), 139.07 (d, $^1J_{CP}$ = 40.0 Hz, *ipso*-Ph), 149.42 (s, *ipso*-$C_6H_4N(CH_2CH_3)_2$), 197.48 (d, $^2J_{CP}$ = 7.3 Hz, $^1J_{CW}$ = 125.8 Hz, *cis*-CO), 200.11 (d, $^2J_{CP}$ = 21.4 Hz, *trans*-CO). Anal. Cald for $C_{24}H_{24}NO_5PW$: C, 46.40; H, 3.89; N, 2.25. Found: C, 46.78, H, 4.03; N, 2.22.



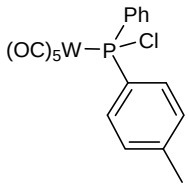
l. $[W(CO)_5\{P(Cl)(p\text{-}C_6H_4N(CH_2CH_3)_2)Ph\}]$ (11). A solution of $[W(CO)_5\{P(OSO_2CF_3)(Cl)Ph\}]$ (**7**) was prepared by dissolving $[W(CO)_5\{PPhCl_2\}]$ (**5**, 120.0 mg, 0.239 mmol) and $AgOSO_2CF_3$ (73.6 mg, 0.286 mmol) in CH_2Cl_2 (8 mL), stirring for 3 h and filtering. *N,N*-diethyl aniline (76.6 μL, 0.477 mmol) was added, and the solution was stirred for 15 min, resulting in a color change to yellow. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, 10/90 v/v diethyl ether/ petroleum ether),

leading to a pale-yellow oil. Yield: 137 mg. 93% (87% purity by NMR integration). IR (νCO, CH_2Cl_2, cm^{-1}): 2076(w), 1945(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 107.0 (s, $^1J_{PW}$ = 274 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 1.19 (t, 6H, $^3J_{HH}$ = 6.9 Hz, -NCH_2CH_3), 3.40 (q, 4H, $^3J_{HH}$ = 6.9 Hz, -NCH_2CH_3), 6.69 (dd, 2H, $^3J_{HH}$ = 8.7 Hz, $^5J_{HH}$ = 1.5 Hz, $P(C_6H_4N(CH_2CH_3)_2)$), 7.37 – 7.57 (m, 7H, 2H of $P(C_6H_4N(CH_2CH_3)_2)$ and 5H of Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.70 (s, -NCH_2CH_3), 44.61 (s, -NCH_2CH_3), 110.95 (d, $^3J_{CP}$ = 11.3 Hz, -$C_6H_4N(CH_2CH_3)_2$), 123.97 (d, $^1J_{CP}$ = 49.5 Hz, *ipso*-$C_6H_4N(CH_2CH_3)_2$), 128.51 (d, $^3J_{CP}$ = 10.1 Hz, -Ph), 129.22 (d, $^2J_{CP}$ = 12.9 Hz, -Ph), 130.22 (d, $^4J_{CP}$ = 1.7 Hz, -Ph), 133.34 (d, $^2J_{CP}$ = 16.8 Hz, -$C_6H_4N(CH_2CH_3)_2$), 142.57 (d, $^1J_{CP}$ = 47.3 Hz, *ipso*-Ph), 150.11 (s, *ipso*-$C_6H_4N(CH_2CH_3)_2$), 196.94 (d, $^2J_{CP}$ = 7.9 Hz, $^1J_{CW}$ = 125.6 Hz, *cis*-CO), 199.98 (d, $^2J_{CP}$ = 23.6 Hz, $^1J_{CW}$ = 141.9 Hz, *trans*-CO).



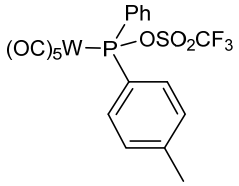
m. Reaction of $[W(CO)_5\{P(Cl)(p\text{-}C_6H_4N(CH_2CH_3)_2)Ph\}]$ (11) with allyl trimethylsilane and $AlCl_3$. Allyl trimethylsilane (62 μL, 0.390 mmol) and $[W(CO)_5\{P(Cl)(p\text{-}C_6H_4N(CH_2CH_3)_2)Ph\}]$ (**11**, 80.0 mg, 0.130 mmol) was dissolved in CH_2Cl_2 (8 mL). $AlCl_3$ (17.3 mg, 0.130 mmol) was then added to this solution, resulted in a color change from yellow to pale yellow. The solvent was removed in vacuo and the residue was purified and crystallized with the same procedure described in section **k**, leading to pale yellow crystals of $[W(CO)_5\{P(p\text{-}C_6H_4N(CH_2CH_3)_2)(CH_2CHCH_2)Ph\}]$ (**10**). Yield: 68 mg, 84%.

n. [W(CO)$_5${P(Cl)(*p*-C$_6$H$_4$CH$_3$)Ph}] (12). A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)(Cl)Ph}] (**7**) was prepared by dissolving [W(CO)$_5${PPhCl$_2$}] (**5**, 160.0 mg, 0.318 mmol) and AgOSO$_2$CF$_3$ (98.1 mg, 0.382 mmol) in CH$_2$Cl$_2$ (8 mL), stirring for 3 h and filtering. Toluene (0.507 mL, 4.77 mmol) was added and the solution was stirred for 30 h, resulting in a color change to red. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, 5/95 v/v diethyl ether/ petroleum ether), leading to a pale yellow oil. Yield: 135 mg. 76% (99% pure by NMR). IR (νCO, CH$_2$Cl$_2$, cm^{-1}): 2078(w), 1949(vs). ^{31}P{^{1}H} NMR (121 Hz, CDCl$_3$): δ 95.7 (s, $^1J_{PW}$ = 281 Hz). ^{1}H NMR (300 Hz, CDCl$_3$): δ 2.43 (s, 3H, -C*H$_3$*), 7.32 (dd, 2H, $^3J_{HH}$ = 8.1 Hz, $^5J_{HH}$ = 2.4 Hz, -C$_6$*H$_4$*CH$_3$), 7.45 – 7.68 (m, 7H, 2H of -C$_6$H$_4$CH$_3$, 5H of Ph). ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.68 (d, $^5J_{CP}$ = 1.9 Hz, -*C*H$_3$), 128.87 (d, $^3J_{CP}$ = 10.8 Hz, Ph), 129.68 (d, $^3J_{CP}$ = 11.3 Hz, -*C$_6$*H$_4$CH$_3$), 130.82 (d, $^2J_{CP}$ = 14.5 Hz, Ph), 131.54 (d, $^4J_{CP}$ = 2.1 Hz, Ph), 131.55 (d, $^2J_{CP}$ = 15.6 Hz, -*C$_6$*H$_4$CH$_3$), 135.28 (d, $^1J_{CP}$ = 34.6 Hz, *ipso*-C$_6$H$_4$CH$_3$), 139.4 (d, $^1J_{CP}$ = 33.4 Hz, *ipso*-Ph), 142.60 (d, $^4J_{CP}$ = 2.1 Hz, -*C$_6$*H$_4$CH$_3$), 196.15 (d, $^2J_{CP}$ = 7.6 Hz, $^1J_{CW}$ = 125.3 Hz, *cis*-CO), 199.25 (d, $^2J_{CP}$ = 30.7 Hz, *trans*-CO).



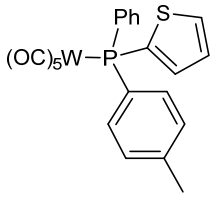
o. [W(CO)$_5${P(OSO$_2$CF$_3$)(*p*-C$_6$H$_4$CH$_3$)Ph}] (13). The compound [W(CO)$_5${P(Cl)(*p*-C$_6$H$_4$CH$_3$)Ph}] (**12**, 30 mg, 0.054 mmol) and AgOSO$_2$CF$_3$ (16.6 mg, 0.064 mmol) were dissolved in CH$_2$Cl$_2$ (2 mL). This solution was stirred for 2 h, resulting in a yellow solution and a white precipitate. The solution was filtered through Celite. Conversion is quantitative by NMR spectroscopy. This air-and-moisture sensitive solution is stable for days at -20 °C or several

hours at room temperature. This reaction was also carried out in $CDCl_3$ for NMR spectroscopy. IR (νCO, CH_2Cl_2, cm^{-1}): 2076(w), 1946(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 95.7 (s, $^1J_{PW}$ = 308 Hz). ^{19}F NMR ($CDCl_3$): δ -76.4 (s, OSO_2CF_3). ^1H NMR (300 Hz, $CDCl_3$): δ 2.47 (s, 3H, -CH_3), 7.38 (dd, 2H, $^3J_{HH}$ = 8.1 Hz, $^5J_{HH}$ = 2.4 Hz, -$C_6H_4CH_3$), 7.55 – 7.65 (m, 7H, 2H of -$C_6H_4CH_3$, 5H of Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.88 (s, -CH_3), 118.32 (q, $^1J_{CF}$ = 318.7 Hz, OSO_2CF_3), 129.11 (d, $^3J_{CP}$ = 10.1 Hz, Ph), 129.88 (d, $^3J_{CP}$ = 11.3 Hz, -$C_6H_4CH_3$), 130.86 (d, $^2J_{CP}$ = 14.1 Hz, Ph), 132.55 (d, $^2J_{CP}$ = 18.0 Hz, -$C_6H_4CH_3$), 132.65 (s, Ph), 133.05 (d, $^1J_{CP}$ = 38.9 Hz, *ipso*-$C_6H_4CH_3$), 137.76 (d, $^1J_{CP}$ = 41.7 Hz, *ipso*-Ph), 144.55 (d, $^4J_{CP}$ = 1.7 Hz, -$C_6H_4CH_3$), 194.77 (d, $^2J_{CP}$ = 7.9 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 197.80 (d, $^2J_{CP}$ = 32.6 Hz, *trans*-CO).

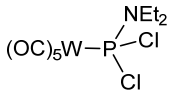


p. [W(CO)$_5${P(C$_4$H$_3$S)(*p*-C$_6$H$_4$CH$_3$)Ph}] (14). A solution of [W(CO)$_5${P(OSO$_2$CF$_3$)(*p*-C$_6$H$_4$CH$_3$)Ph}] (**13**) was prepared by dissolving [W(CO)$_5${P(Cl)(*p*-C$_6$H$_4$CH$_3$)Ph}] (**12**, 90.0 mg, 0.161 mmol) and $AgOSO_2CF_3$ (49.7 mg, 0.193 mmol) in CH_2Cl_2 (5 mL), stirring for 2 h and filtering. Thiophene (26 μL, 0.322 mmol) was added and the solution was stirred for 10 min at room temperature, resulting in a color change to red. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (alumina, 20/80 v/v diethyl ether/ petroleum ether). The pale yellow crystals of the product were obtained by cooling the saturated pentane/dichloromethane solution to -20 °C. Yield: 85 mg, 87%. IR (νCO, CH_2Cl_2, cm^{-1}): 2073(w), 1939(vs). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): δ 6.9 (s, $^1J_{PW}$ = 247 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 2.32 (s, 3H, -CH_3), 7.10 -7.38 (m, 11H, 4H of -$C_6H_4CH_3$, 5H of Ph, 2H of -C_4H_3S),

7.58 (m, 1H, -C_4H_3S). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.59 (d, $^5J_{CP}$ = 1.1 Hz, -CH_3), 128.64 (d, $^3J_{CP}$ = 10.1 Hz, -C_4H_3S), 128.75 (d, $^3J_{CP}$ = 10.1 Hz, -Ph), 129.59 (d, $^3J_{CP}$ = 10.7 Hz, -$C_6H_4CH_3$), 130.57 (d, $^4J_{CP}$ = 1.7 Hz, -Ph), 132.18 (d, $^2J_{CP}$ = 12.5 Hz, -Ph), 132.55 (d, $^2J_{CP}$ = 12.9 Hz, -$C_6H_4CH_3$), 132.80 (d, $^1J_{CP}$ = 46.2 Hz, -C_4H_3S), 133.34 (d, $^3J_{CP}$ = 3.4 Hz, -C_4H_3S), 136.89 (d, $^1J_{CP}$ = 44.5 Hz, -$C_6H_4CH_3$), 137.39 (d, $^2J_{CP}$ = 11.3 Hz, -C_4H_3S), 138.15 (d, $^1J_{CP}$ = 38.7 Hz, *ipso*-Ph), 141.15 (d, $^4J_{CP}$ = 2.3 Hz, -$C_6H_4CH_3$), 197.36 (d, $^2J_{CP}$ = 7.3 Hz, $^1J_{CW}$ = 126.1 Hz, *cis*-CO), 199.35 (d, $^2J_{CP}$ = 21.9 Hz, $^1J_{CW}$ = 144.6 Hz, *trans*-CO). Anal. Cald for $C_{22}H_{15}O_5PSW$: C, 43.59; H, 2.49; S, 5.29. Found: C, 43.75, H, 2.56; S, 5.52.



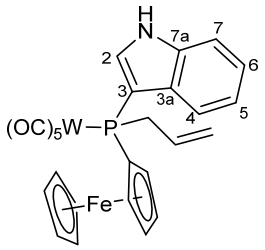
q. $[W(CO)_5\{P(Cl)_2(N(CH_2CH_3)_2)\}]$ (15). This compound was synthesized using the literature procedure.[3] IR (νCO, CH_2Cl_2, cm^{-1}): 2086(w), 1958(vs). ^{31}P NMR (121 Hz, $CDCl_3$): δ 123.8 (quintet, $^1J_{PW}$ = 373 Hz, $^3J_{PH}$ = 16.7 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 1.26 (t, 6H, $^3J_{HH}$ = 6.9 Hz, -$N(CH_2CH_3)_2$), 3.52 (dq, 4H, $^3J_{HP}$ = 16.8 Hz, $^3J_{HH}$ = 6.9 Hz, -$N(CH_2CH_3)_2$). These spectroscopic data match the previously published data.[3]



r. $[W(CO)_5\{P(CH_2CHCH_2)(C_{10}H_9Fe)(3\text{-}C_8H_5NH)\}]$ (16). The compound $[W(CO)_5\{P(Cl)_2(N(CH_2CH_3)_2)\}]$ (**15**, 200.0 mg, 0.402 mmol) and $AlCl_3$ (53.6 mg, 0.402 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred for 15 min at room temperature, resulting in the

generation of the phosphenium ion complex $[W(CO)_5\{P(Cl)(N(CH_2CH_3)_2)\}][AlCl_4]$ ($^{31}P\{^1H\}$ NMR: δ 234) with a color change from yellow to red. Allyl trimethylsilane (64 μL, 0.402 mmol) was added dropwise with vigorous stirring for 10 min at room temperature, resulting in the generation of allyl amino phosphenium ion complex $[W(CO)_5\{P(CH_2CHCH_2)(N(CH_2CH_3)_2)\}][AlCl_4]$ ($^{31}P\{^1H\}$ NMR: δ 370), with a color change to dark red. This resulting solution was first added to a CH_2Cl_2 solution of indole (61.2 mg, 0.522 mmol) and then to ferrocene (74.7 mg, 0.402 mmol) and stirred for 12 h at room temperature, resulting in a color change to lighter red. The solvent was removed in vacuo and the residue was purified by flash chromatography (alumina, 0.5/49.5/50 v/v CH_2Cl_2/diethyl ether/ petroleum ether). Orange crystals of $[W(CO)_5\{P(CH_2CHCH_2)(C_{10}H_9Fe)(3\text{-}C_8H_5NH)\}]$ (**16**) were obtained by cooling a saturated pentane/CH_2Cl_2 solution to -20 °C. Yield: 221 mg, 79%. (IR (νCO, CH_2Cl_2, cm^{-1}): 2069(w), 1932(vs). ^{31}P NMR (121 Hz, $CDCl_3$): δ -15.1 (s, $^1J_{PW}$ = 246 Hz). ^1H NMR (300 Hz, $CDCl_3$): δ 3.41 – 3.68 (m, 2H, -CH_2CHCH$_2$), 4.27 (s, 5H, FeC$_5H_5$), 4.46 – 4.57 (m, 4H, C$_5H_4$P), 5.18 – 5.29 (m, 2H, -CH$_2$CHCH_2), 5.90 (m, 1H, -CH$_2$CHCH$_2$), 7.17 (m, 1H, -C$_8H_5$NH), 7.26 (m, 1H, -C$_8H_5$NH), 7.36 (m, 1H, -C$_8H_5$NH), 7.41 (m, 1H, -C$_8H_5$NH), 7.75 (d, 1H, $^3J_{HH}$ = 7.8 Hz, -C$_8H_5$NH), 8.35 (br s, 1H, -C$_8$H$_5$NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.73 (d, $^1J_{CP}$ = 28.7 Hz, -CH$_2$CHCH$_2$), 69.79 (s, FeC_5H$_5$), 70.81 (d, J_{CP} = 7.9 Hz, C_5H$_4$P), 71.34 (d, J_{CP} = 6.2 Hz, C_5H$_4$P), 72.45 (d, J_{CP} = 7.9 Hz, C_5H$_4$P), 74.58 (d, J_{CP} = 16.3 Hz, C_5H$_4$P), 80.48 (d, $^1J_{CP}$ = 44.5 Hz, C_5H$_4$P), 110.21 (d, $^1J_{CP}$ = 52.9 Hz, C^3), 111.99 (s, C^7), 120.26 (d, $^2J_{CP}$ = 11.2 Hz, -CH$_2C$HCH$_2$), 120.84 (s, C^4), 121.64 (s, C^6), 123.20 (s, C^5), 127.77 (d, $^3J_{CP}$ = 6.8 Hz, -CH$_2$CHCH$_2$), 130.77 (d, $^2J_{CP}$ = 20.3 Hz, C^2), 132.06 (d, $^3J_{CP}$ = 5.1 Hz, C^{7a}), 137.43 (d, $^2J_{CP}$ = 7.3 Hz, C^{3a}), 198.09 (d, $^2J_{CP}$ = 6.8 Hz, $^1J_{CW}$ = 125.5 Hz, *cis*-CO), 199.34 (d, $^2J_{CP}$ = 20.8 Hz, *trans*-

CO). Anal. Cald for $[W(CO)_5\{P(CH_2CHCH_2)(C_{10}H_9Fe)(3\text{-}C_8H_5NH)\}]\cdot\frac{1}{2}\ CH_2Cl_2$: C, 43.04; H, 2.86; N, 1.89. Found: C, 43.59, H, 2.99; N, 1.93.



X-ray crystallography. X-ray quality crystals of **16** were grown by slow diffusion of pentane into a saturated $CH_2Cl_2/ClCH_2CH_2Cl$ solution at -20 °C. Crystals were mounted on glass fibres. Programs for diffractometer operation, data collection, cell indexing, data reduction and absorption correction were those supplied by Bruker AXS Inc., Madison, WI. Diffraction measurements were made on a PLATFORM diffractometer/SMART 1000 CCD using graphite-monochromated Mo-Kα radiation at -80°C. The unit cell was determined from randomly selected reflections obtained using the *SMART CCD* automatic search, center, index and least-squares routines. Integration was carried out using the program *SAINT* and an absorption correction was performed using *SADABS*. Crystal data and collection parameters are listed in Table S1. Structure solution was carried out using the *SHELX97*[4] suite of programs and the *WinGX* graphical interface.[5] Initial solutions were obtained by direct methods and refined by successive least-squares cycles. All non-hydrogen atoms were refined.

Table S1. Crystal data and structure refinement for **16**.

Empirical formula	$C_{26}H_{20}FeNO_5PW$
Formula weight	697.10
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.3798(5) Å	a= 90°.
	b = 11.4305(4) Å	b= 102.75°.
	c = 15.0127(5) Å	g = 90°.
Volume	2406.79(14) $Å^3$	
Z	4	
Density (calculated)	1.924 Mg/m^3	
Absorption coefficient	5.483 mm^{-1}	
F(000)	1352	
Crystal size	0.369 x 0.299 x 0.284 mm^3	
Theta range for data collection	1.452 to 28.821°.	
Index ranges	-18<=h<=18, -14<=k<=15, -20<=l<=19	
Reflections collected	21180	
Independent reflections	5880 [R(int) = 0.0129]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5880 / 0 / 316	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0145, wR2 = 0.0355	
R indices (all data)	R1 = 0.0153, wR2 = 0.0357	
Largest diff. peak and hole	0.589 and -0.418 $e.Å^{-3}$	

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2. A. Marinetti, S. Bauer, L. Ricard and F. Mathey, *Organometallics*, 1990, **9**, 793-798.
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4. G. M. Sheldrick, Release 97-2 ed. 1998.
5. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.

Figure S1. ^{1}H NMR spectrum of compound **3**.

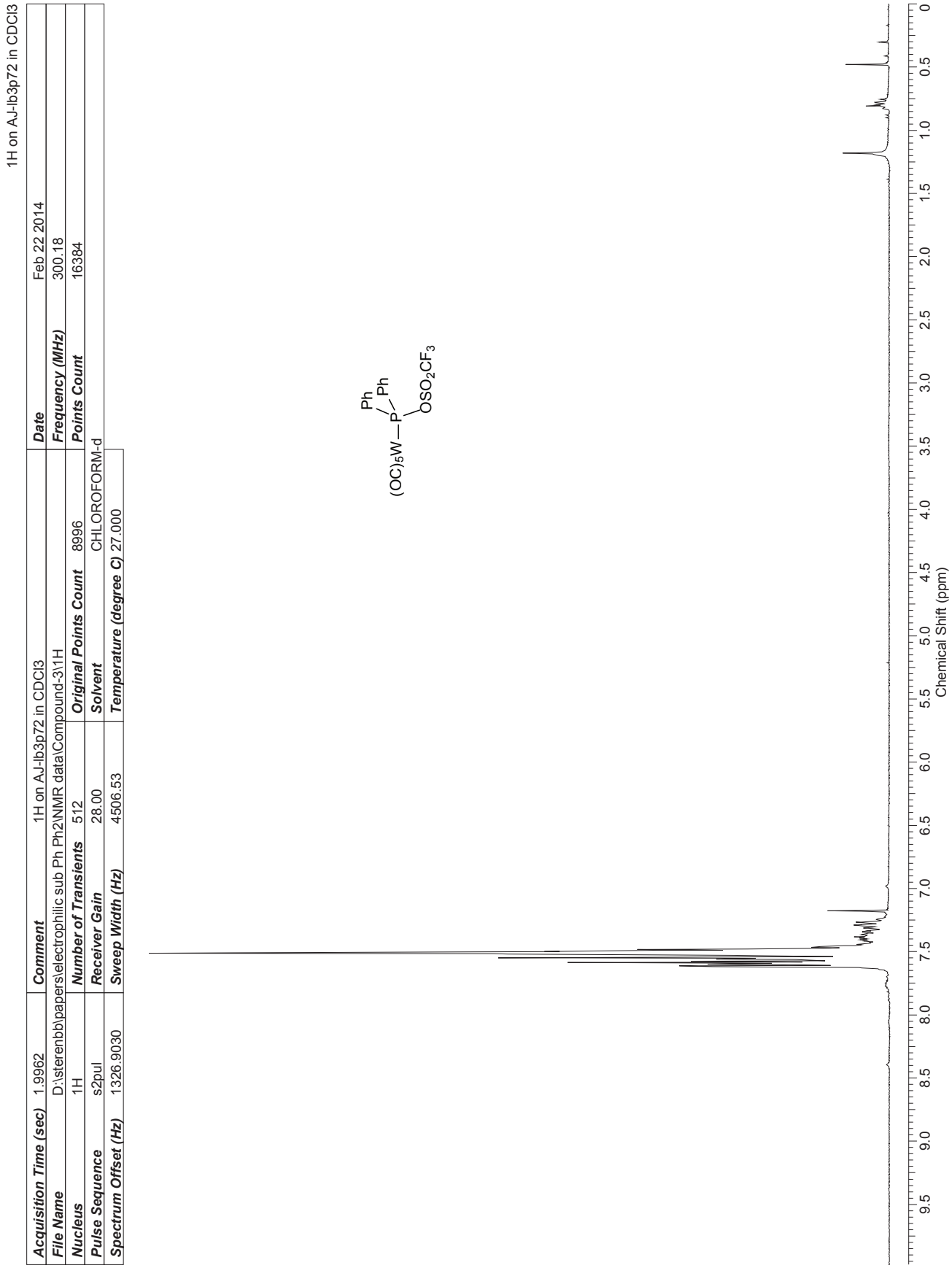


Figure S2. ^{13}C NMR spectrum of compound **3**.

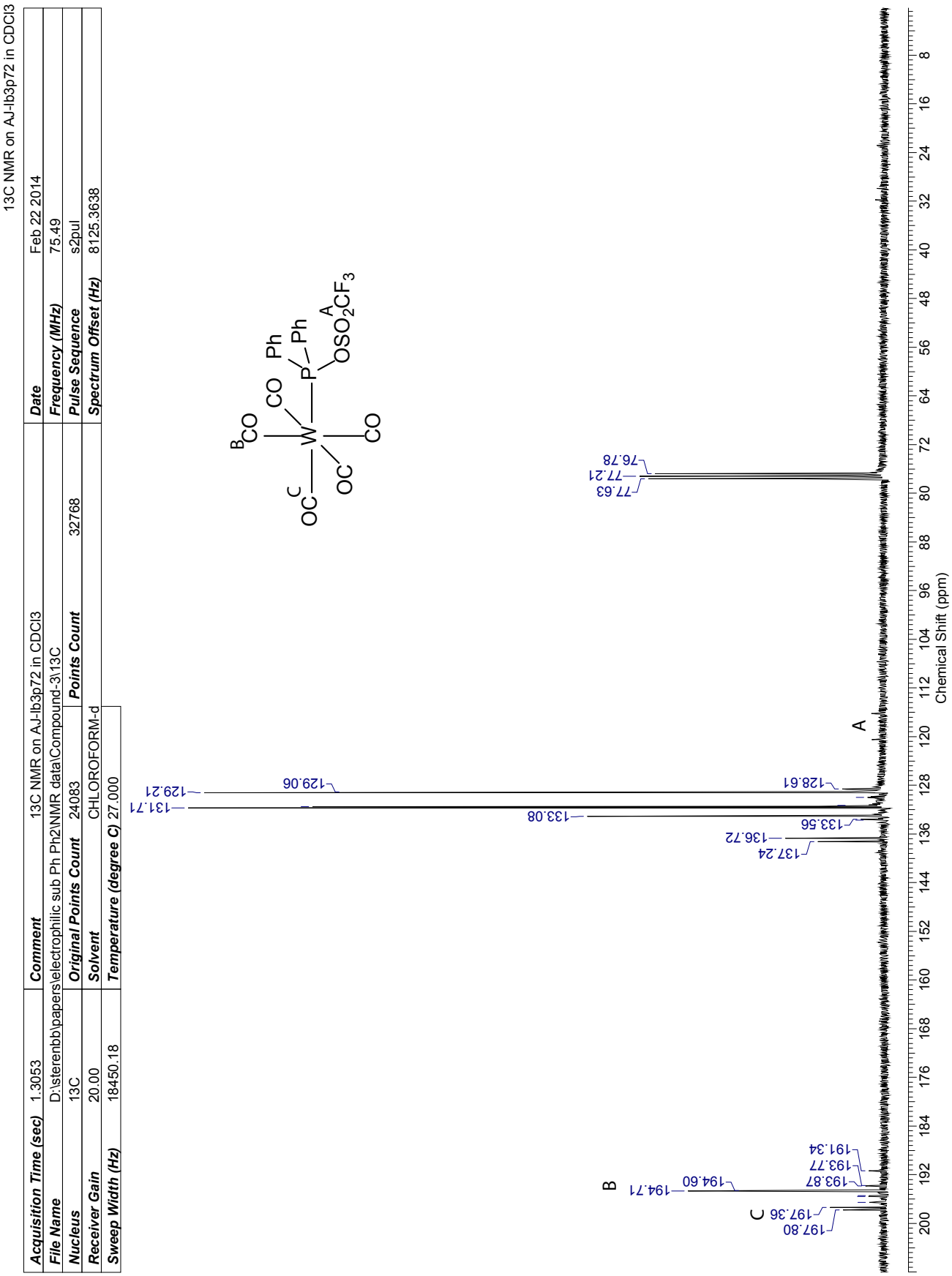


Figure S3. ^{31}P NMR spectrum of compound **3**.

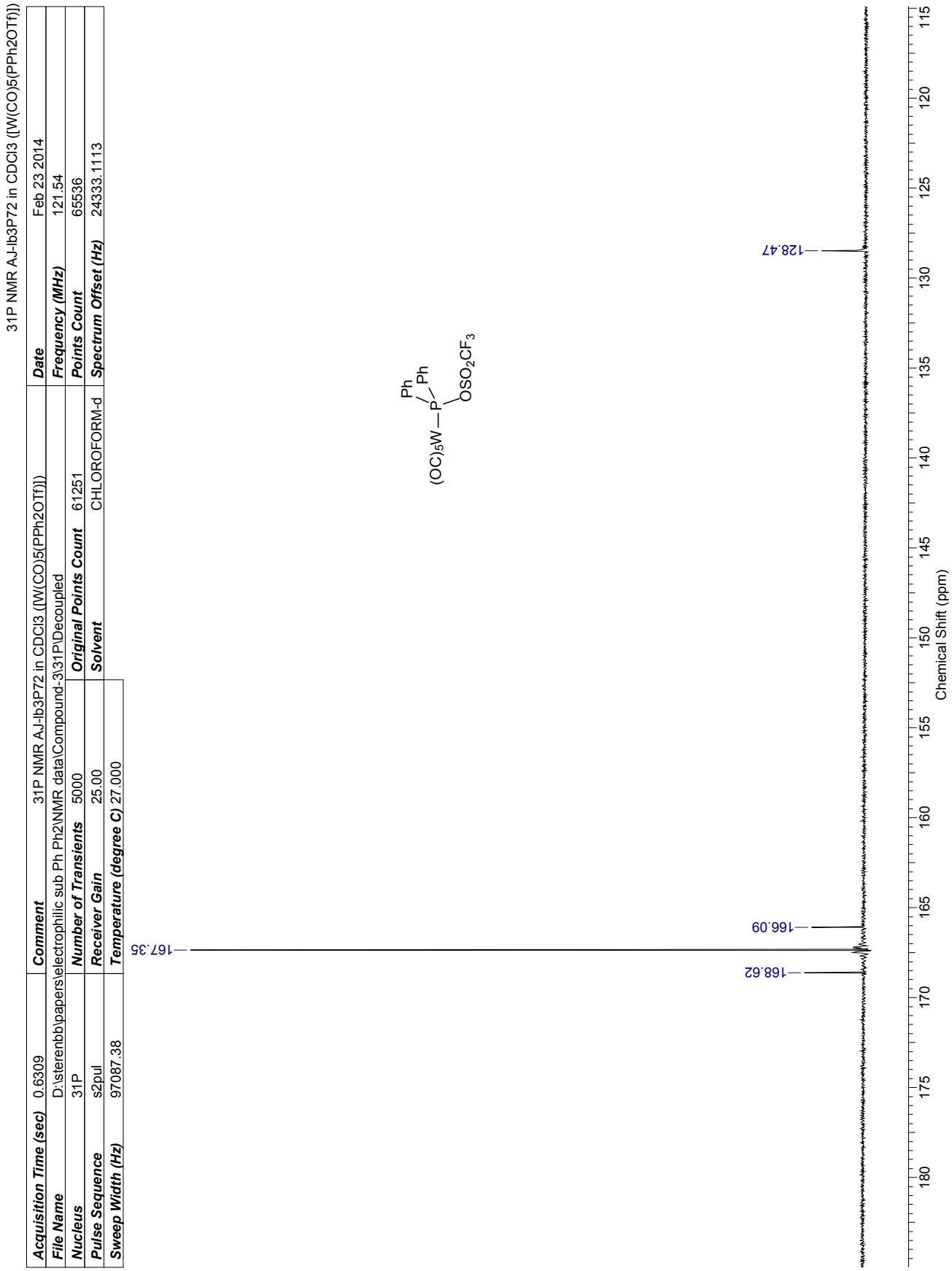


Figure S4. ^{19}F NMR spectrum of compound **3**.

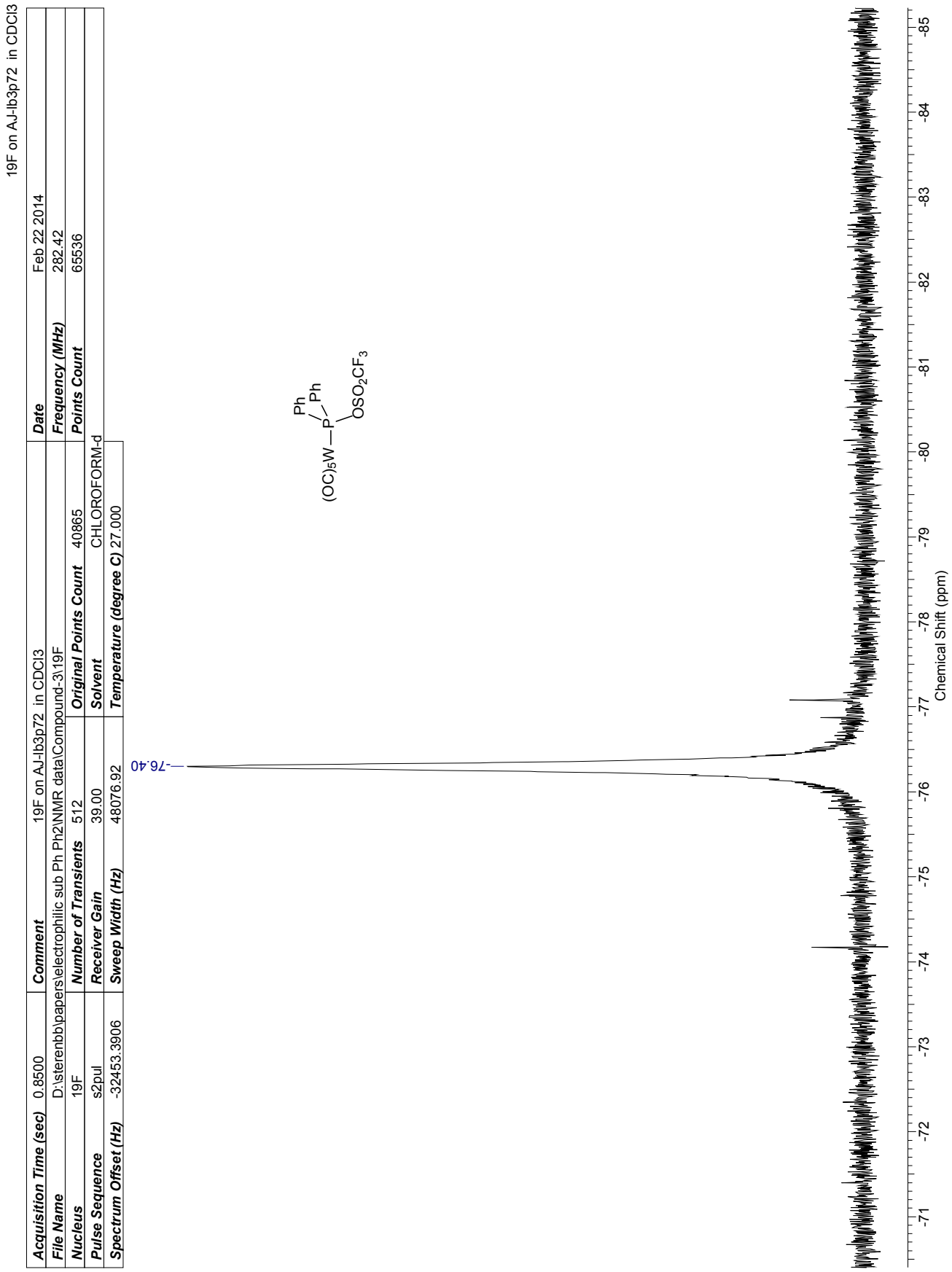


Figure S5. ^{1}H NMR spectrum of compound **7**.

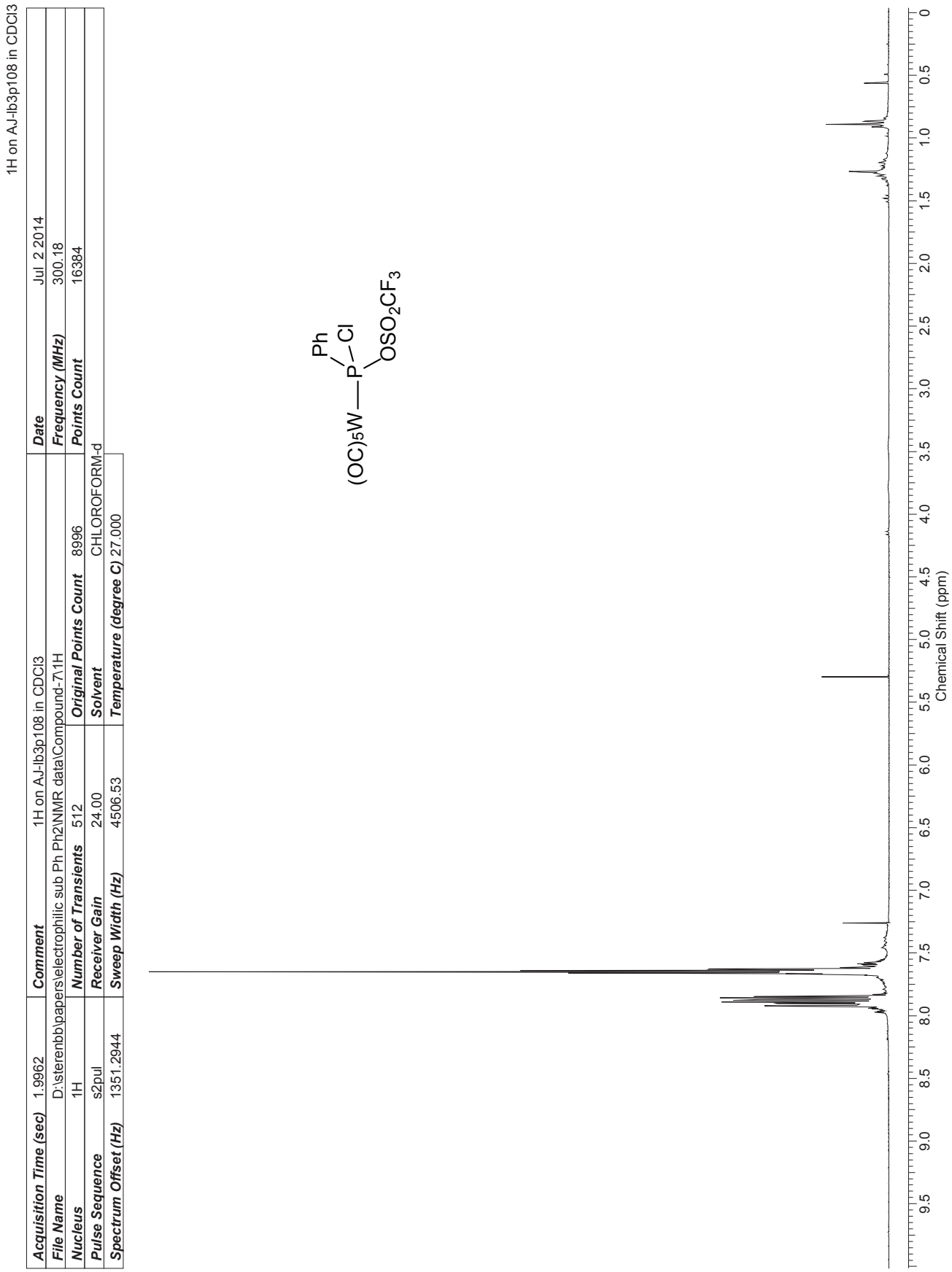


Figure S6. ^{13}C NMR spectrum of compound **7**.

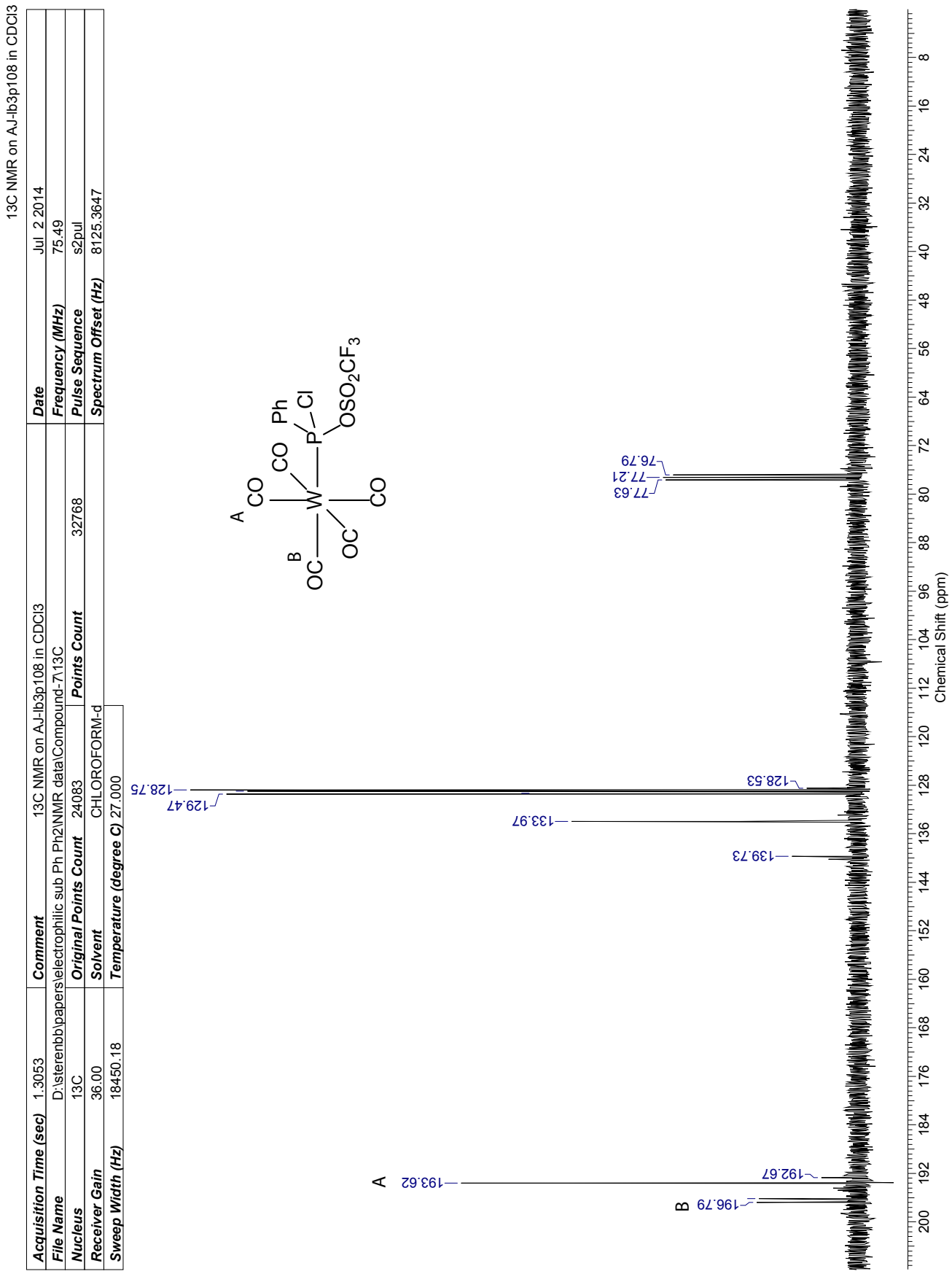


Figure S7. ^{31}P NMR spectrum of compound **7**.

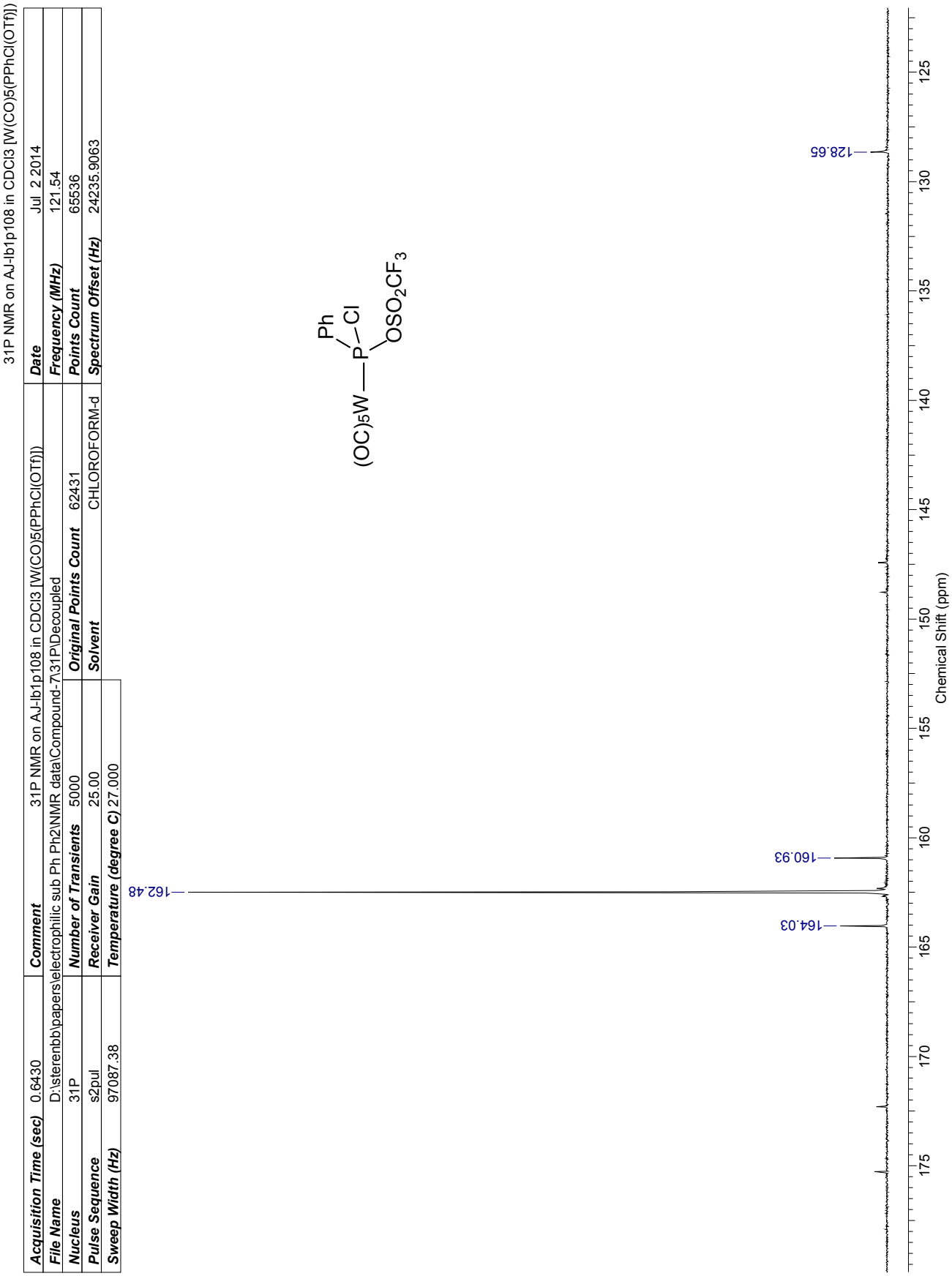


Figure S8. ^{19}F NMR spectrum of compound **7**.

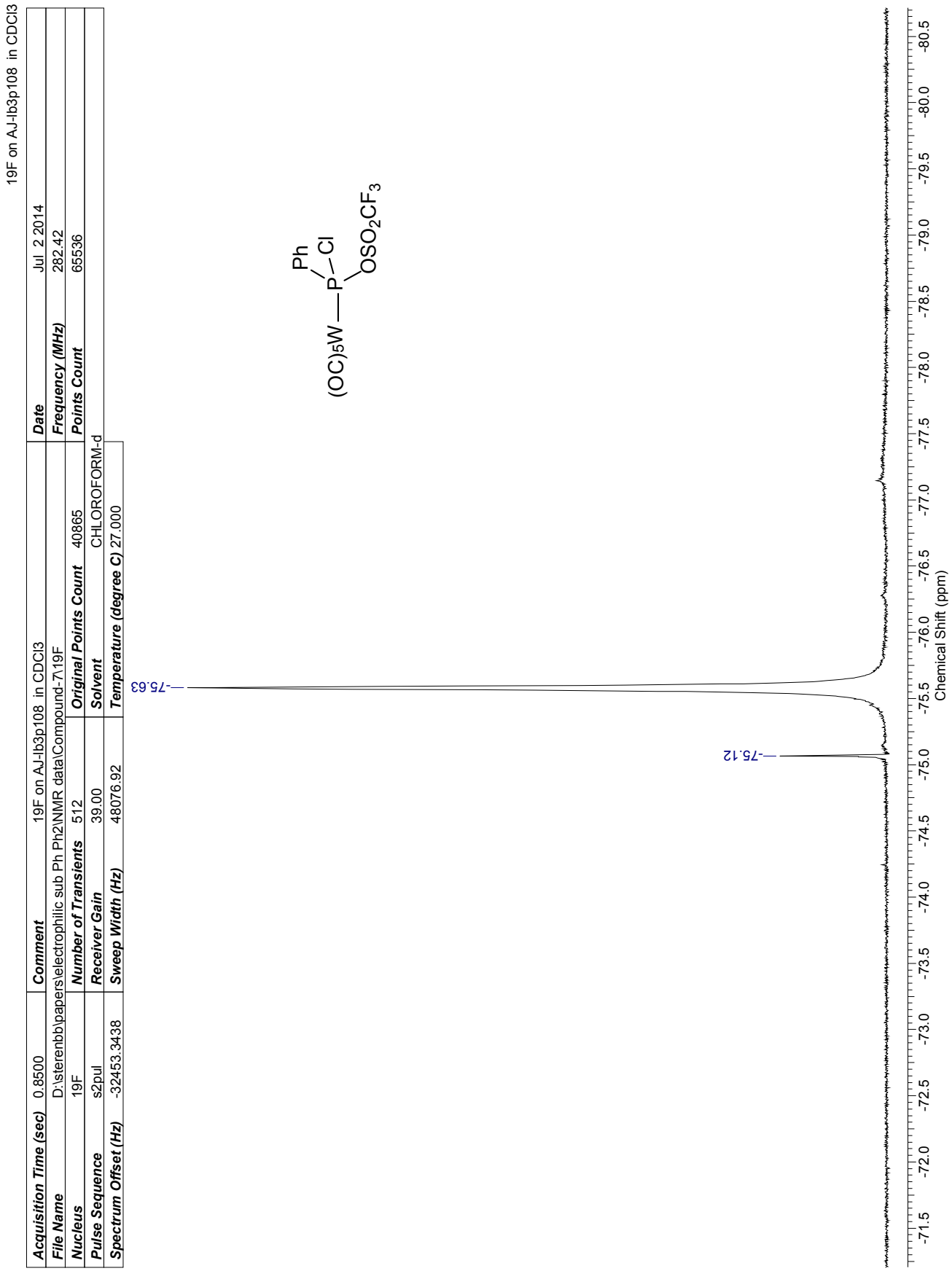
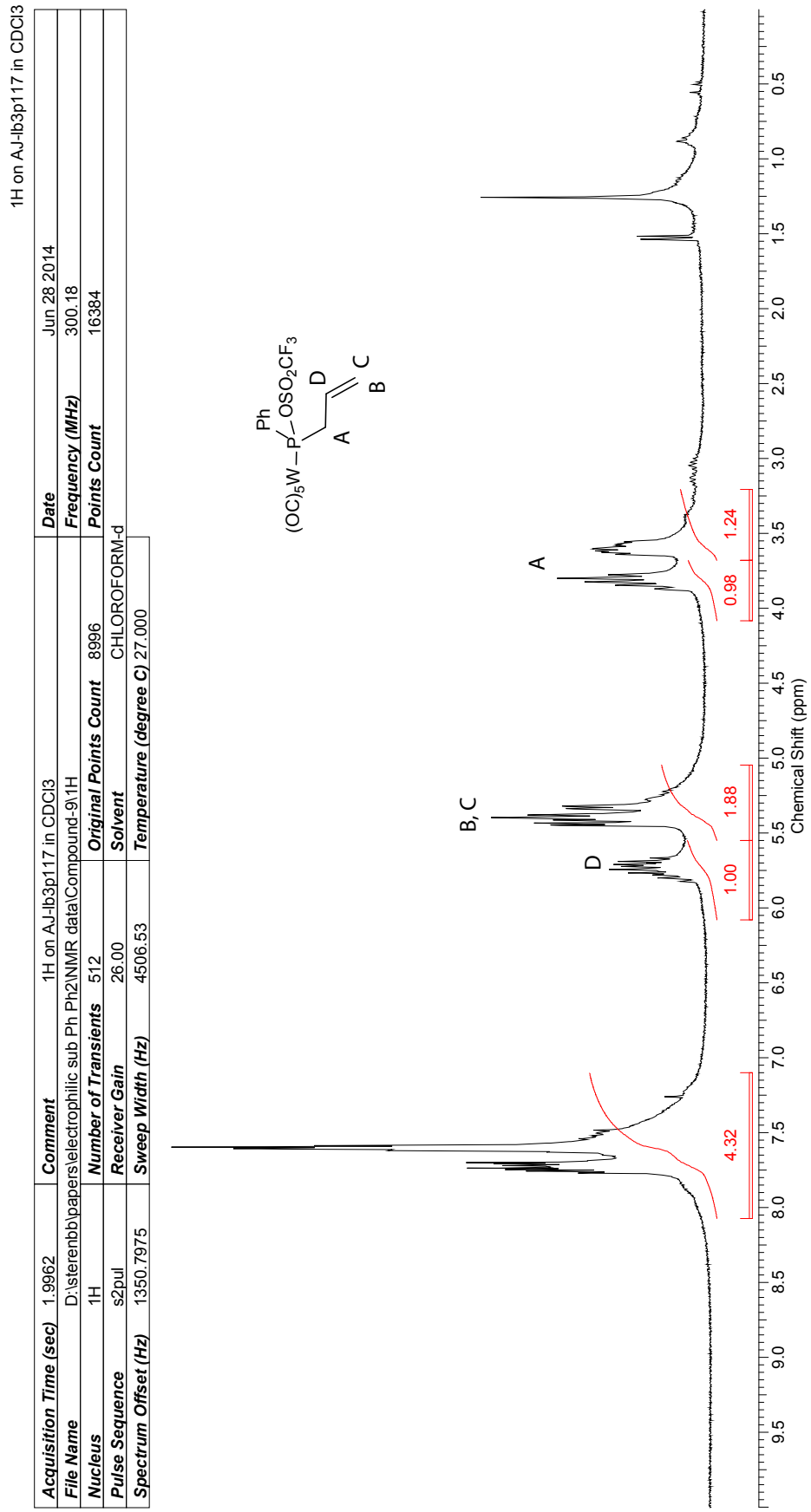


Figure S9. ^{1}H NMR spectrum of compound **9**.



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[3.21 .. 3.68]	1.240	7.56553e+8	1.240
2	[3.68 .. 4.08]	0.978	5.96482e+8	0.978
3	[5.05 .. 5.55]	1.877	1.14544e+9	1.877
4	[5.55 .. 6.08]	1.000	6.10165e+8	1.000
5	[7.10 .. 8.07]	4.318	2.63487e+9	4.318

Figure S10. ^{13}C NMR spectrum of compound **9**.

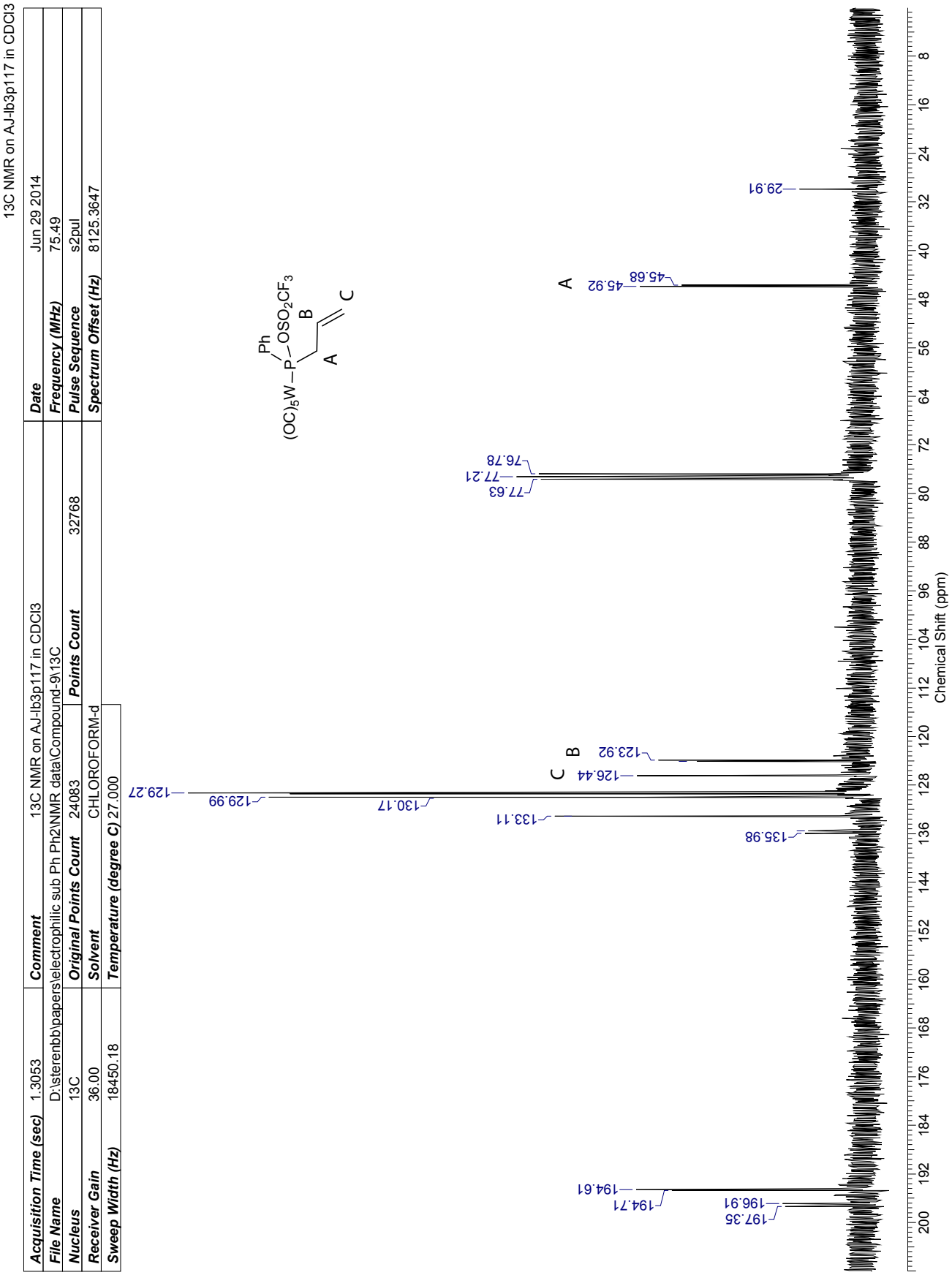


Figure S11. ^{31}P NMR spectrum of compound **9**.

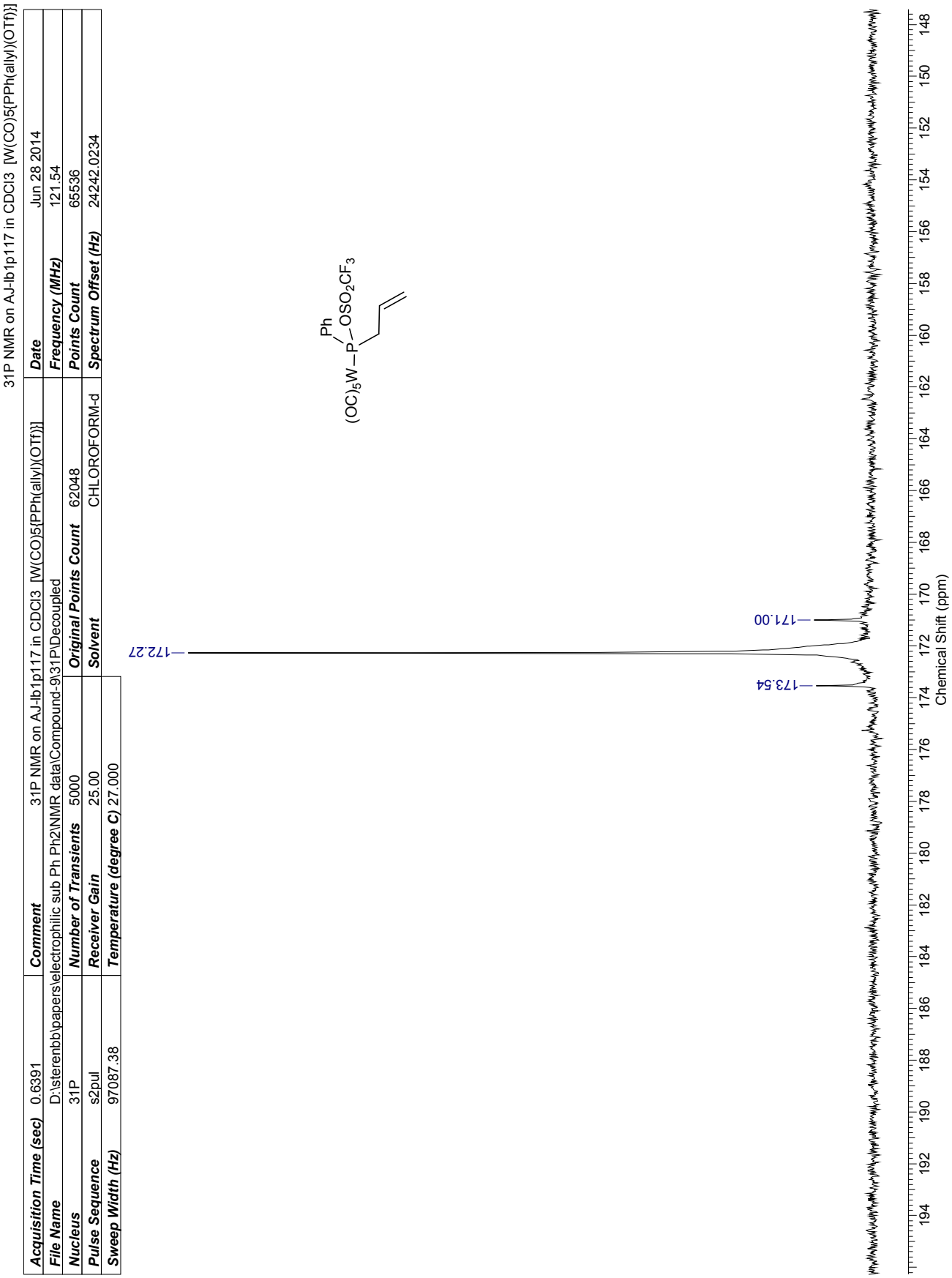


Figure S12. ^{19}F NMR spectrum of compound **9**.

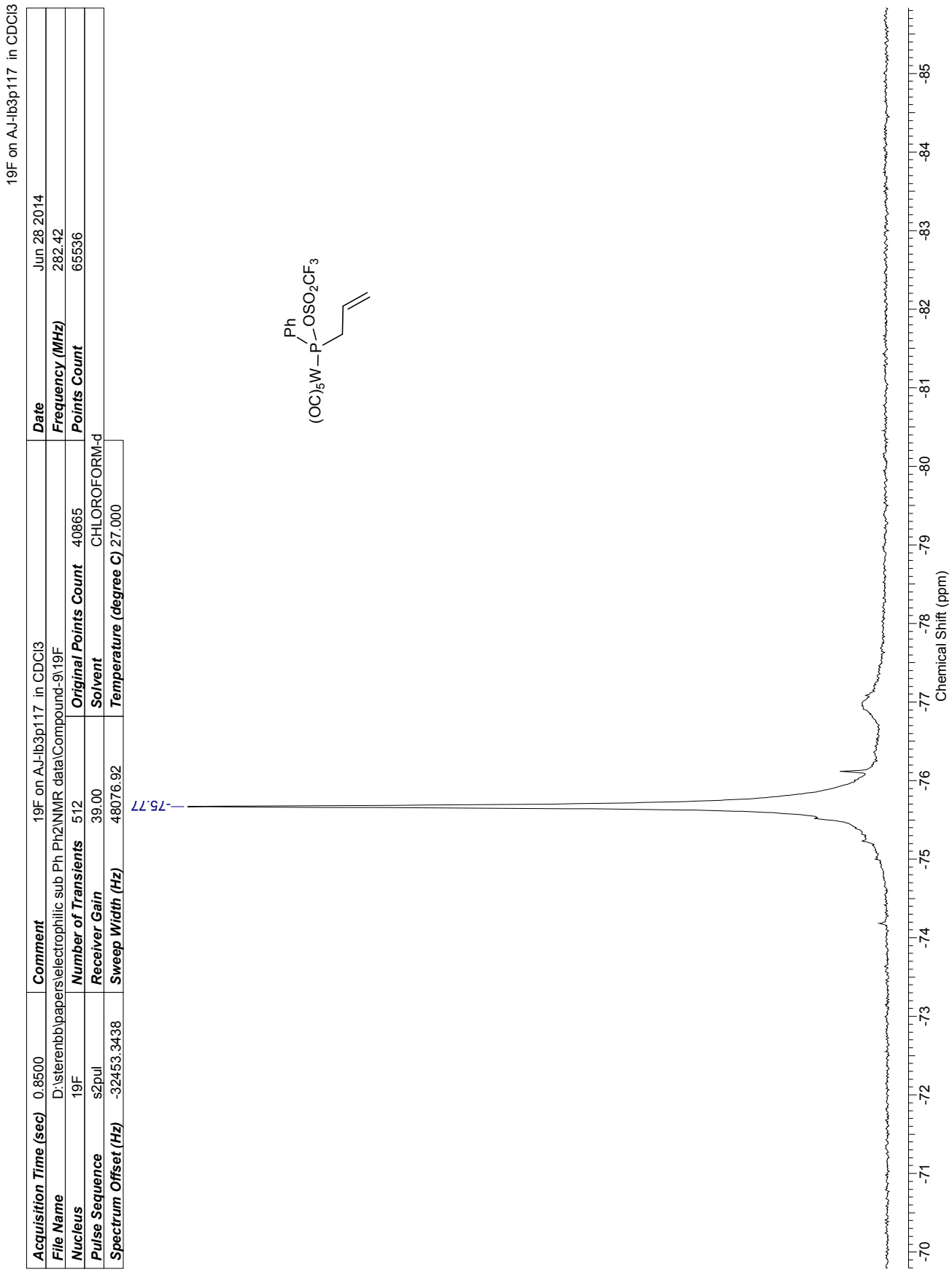


Figure S13. ^{1}H NMR spectrum of compound **11**.

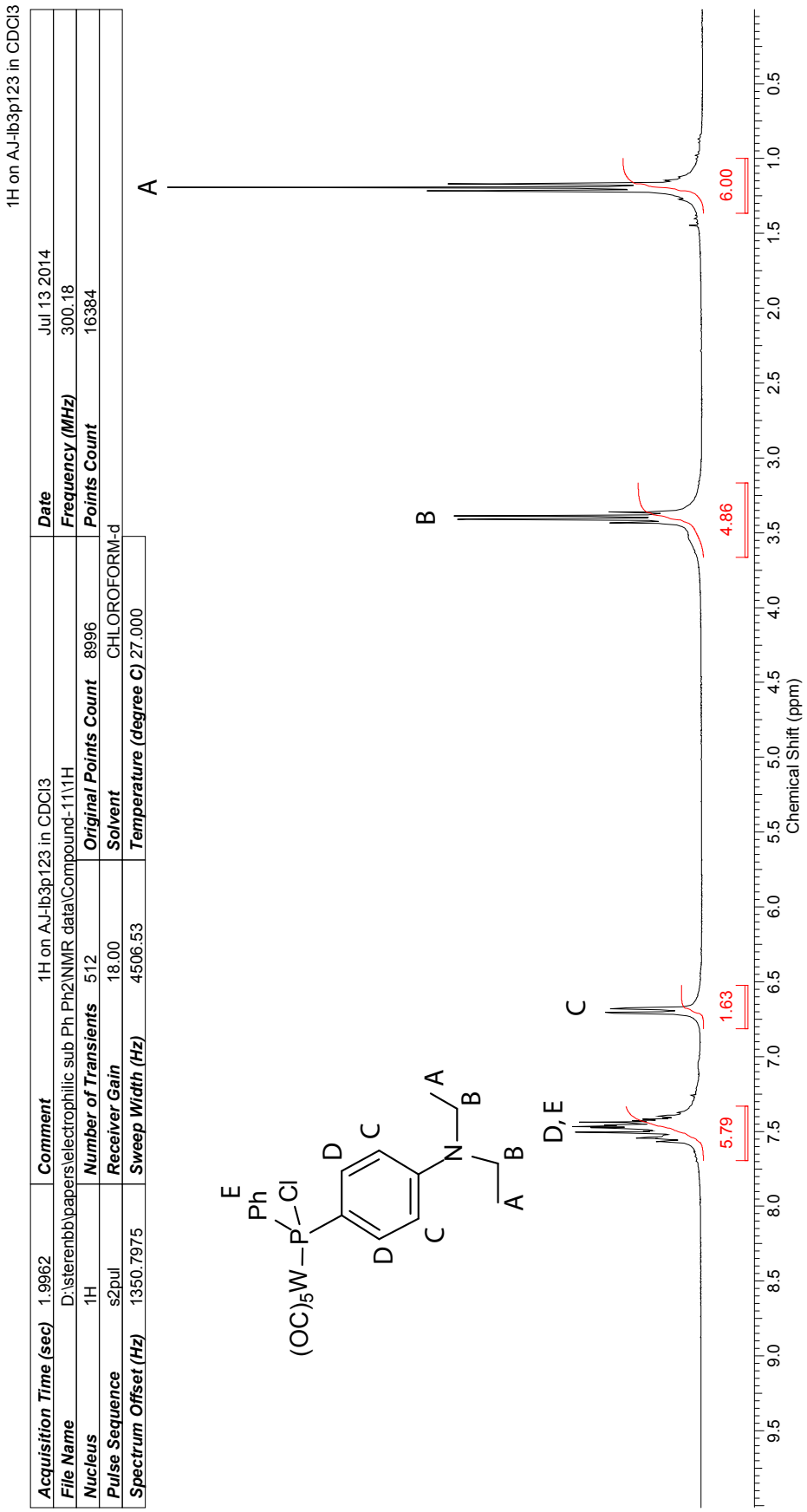


Figure S14. ^{13}C NMR spectrum of compound **11**.

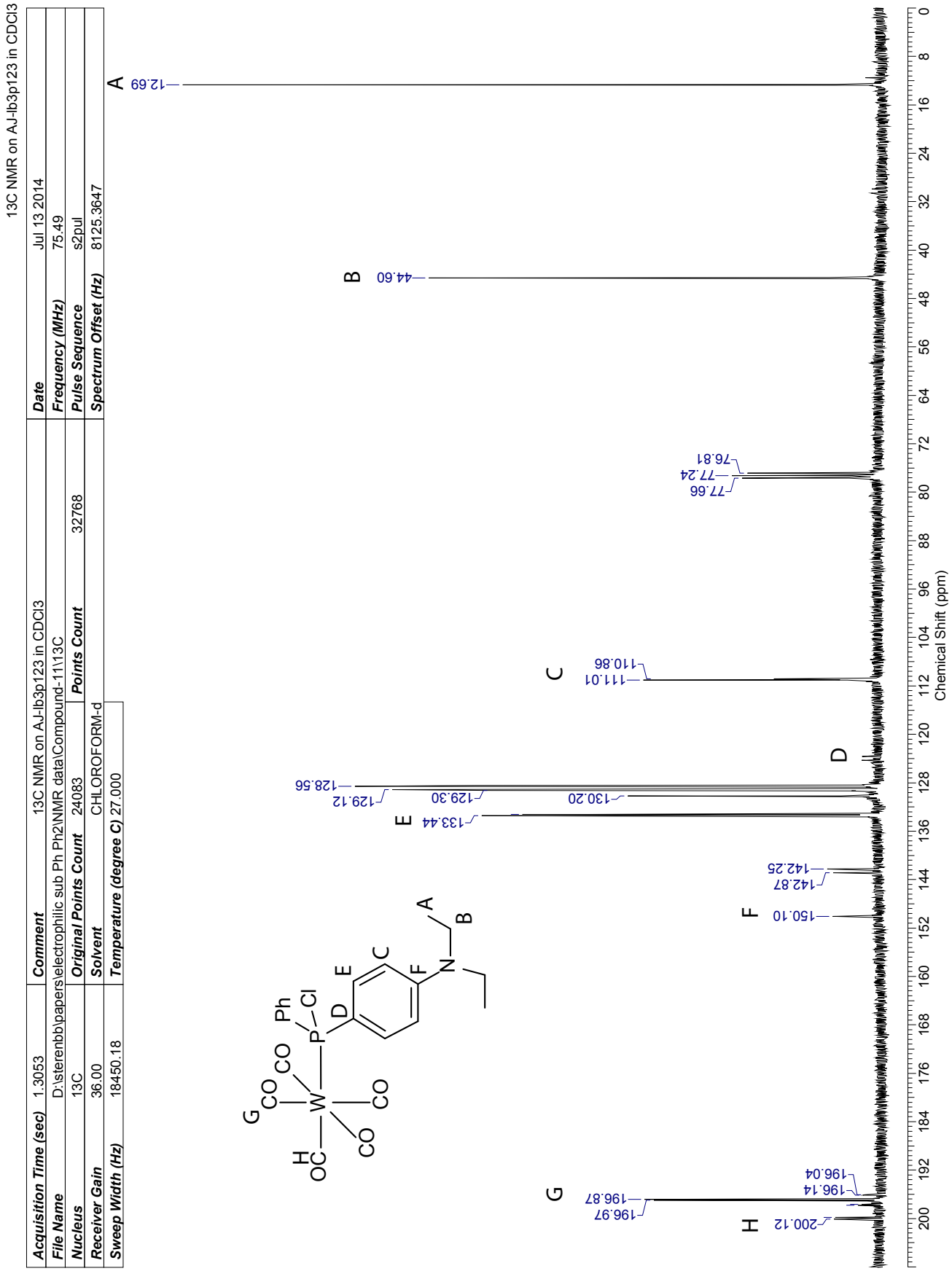


Figure S15. ^{31}P NMR spectrum of compound **11**.

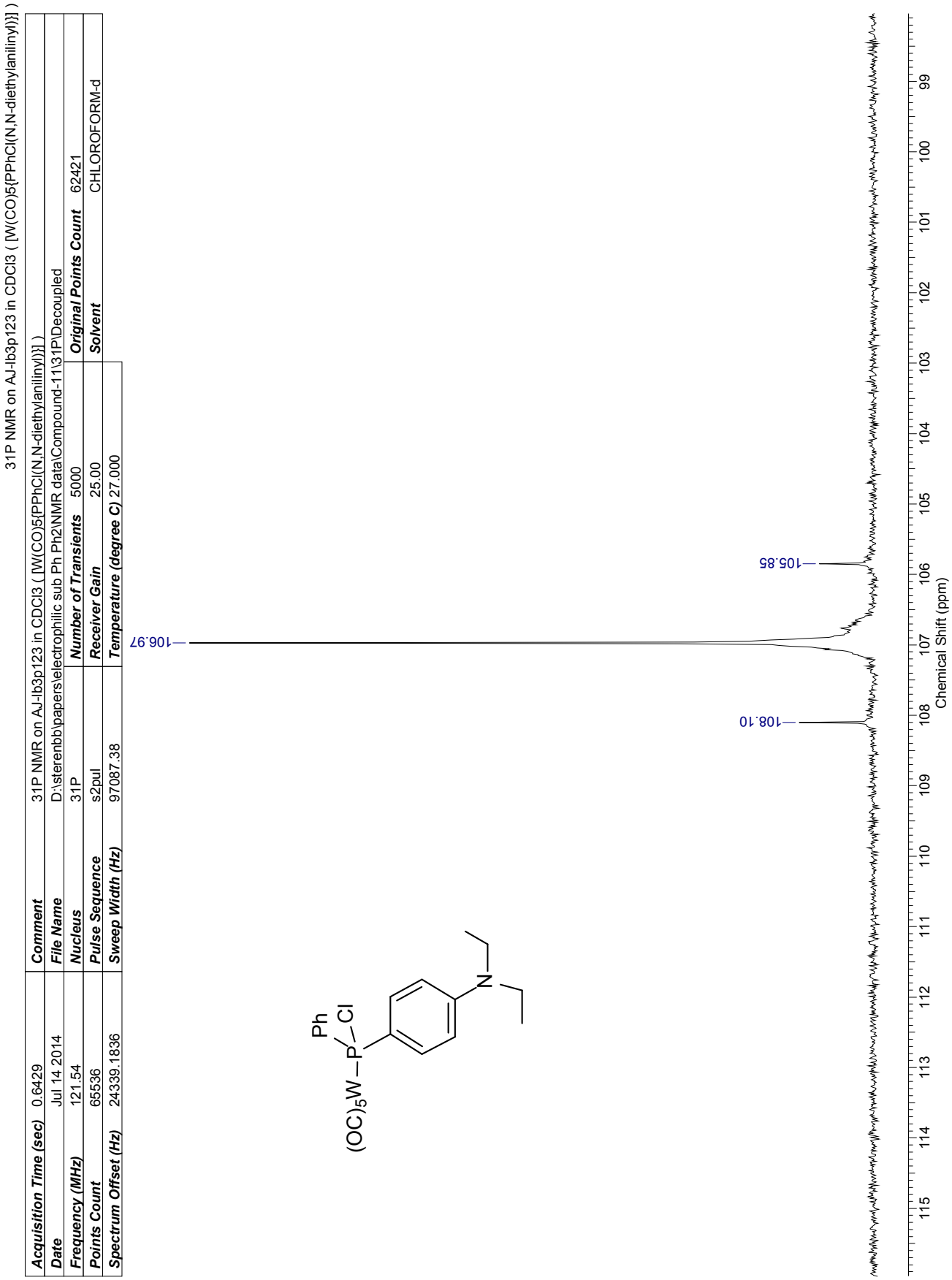


Figure S16. ^{1}H NMR spectrum of compound **12**.

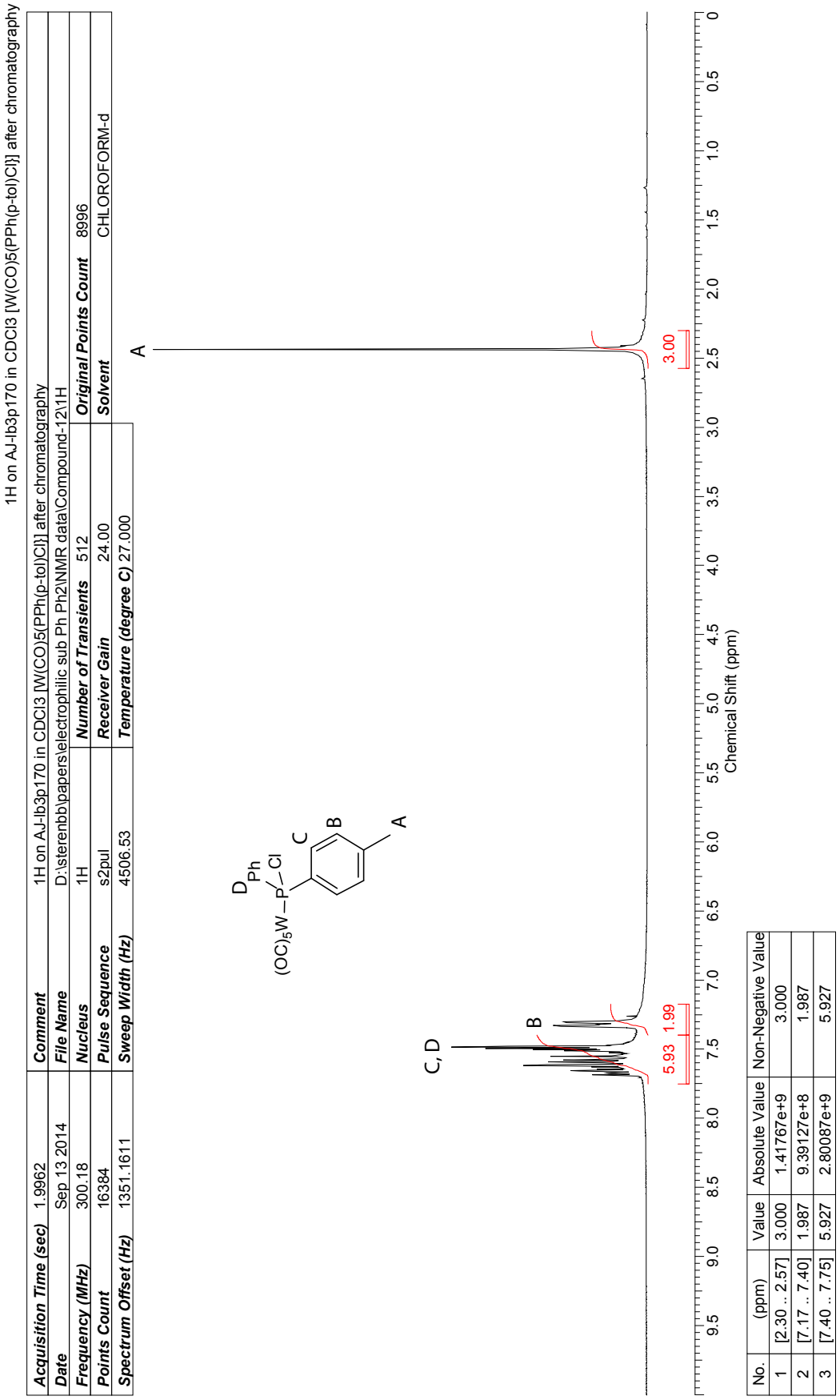


Figure S17. ^{13}C NMR spectrum of compound **12**.

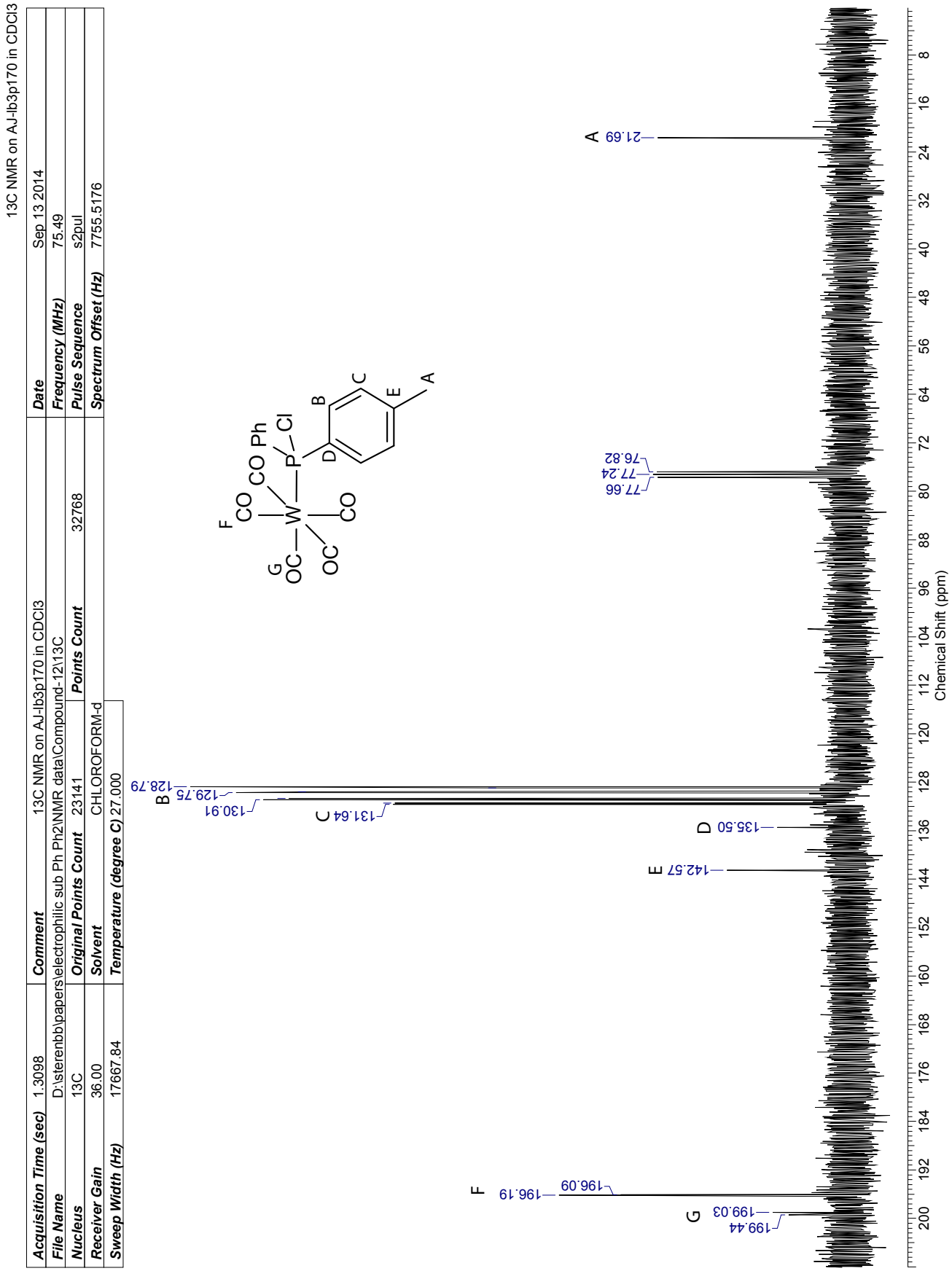


Figure S18. ^{31}P NMR spectrum of compound **12**.

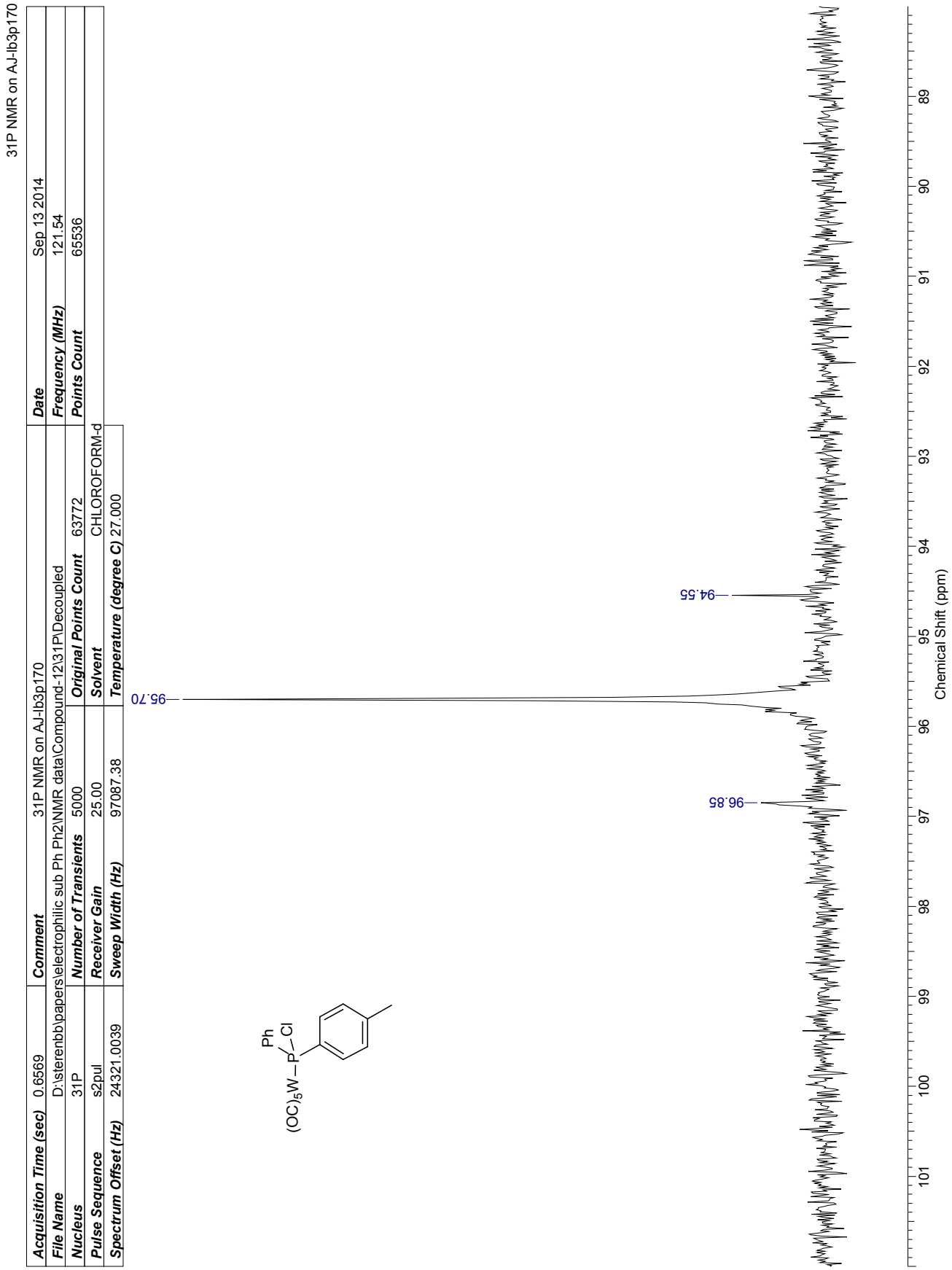


Figure S19. ^{1}H NMR spectrum of compound **13**.

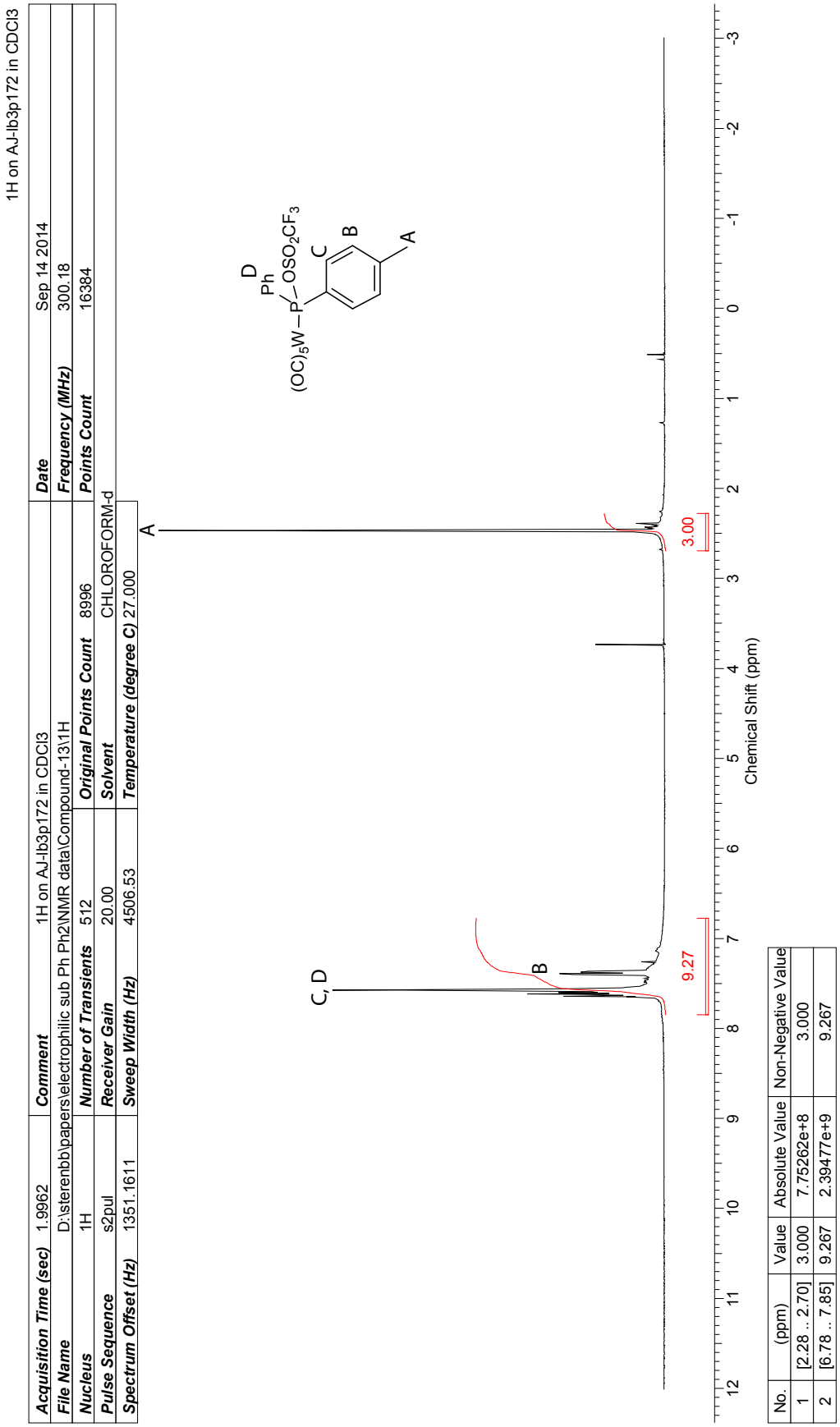


Figure S20. ^{13}C NMR spectrum of compound **13**.

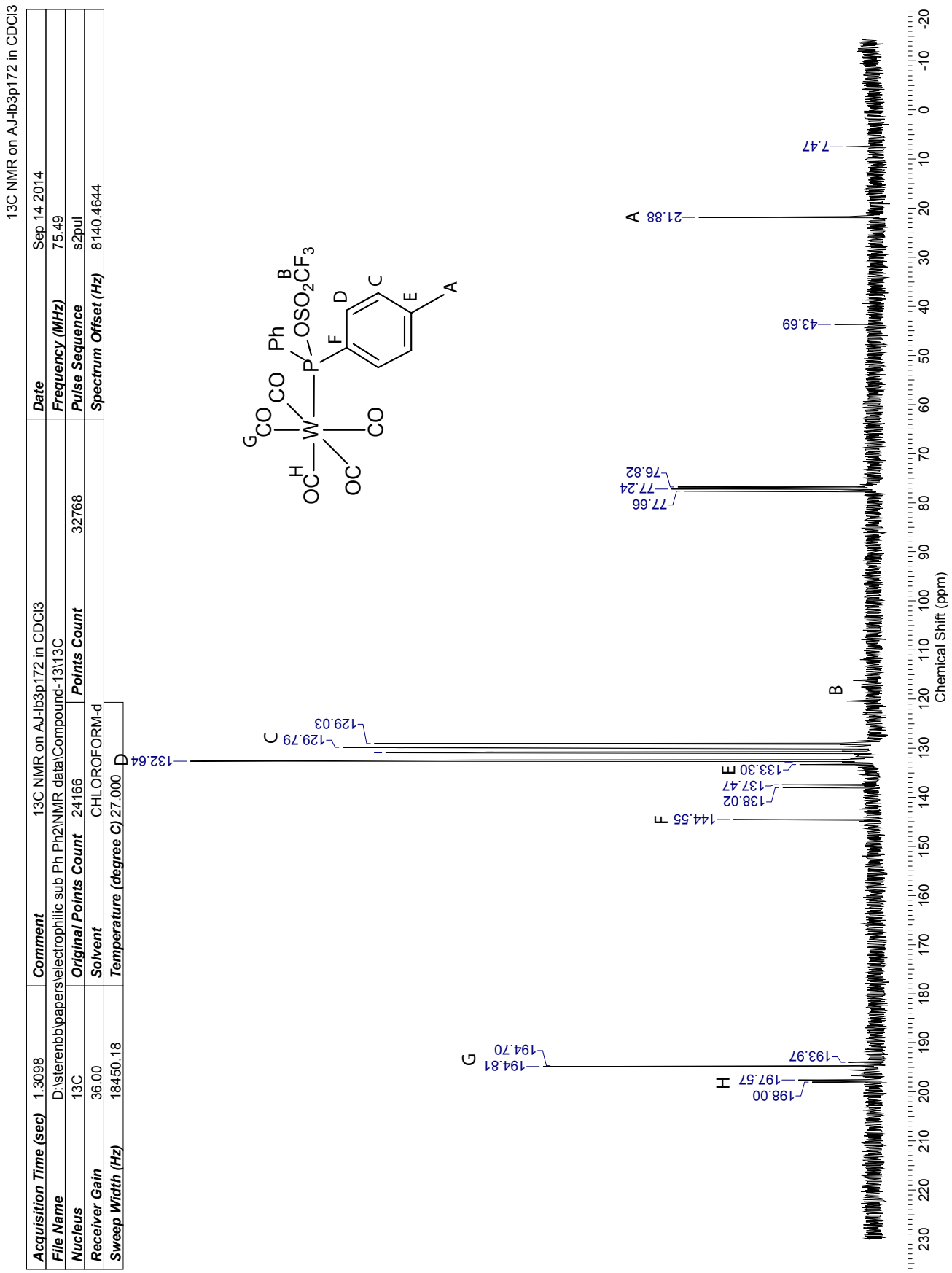


Figure S21. ^{31}P NMR spectrum of compound **13**.

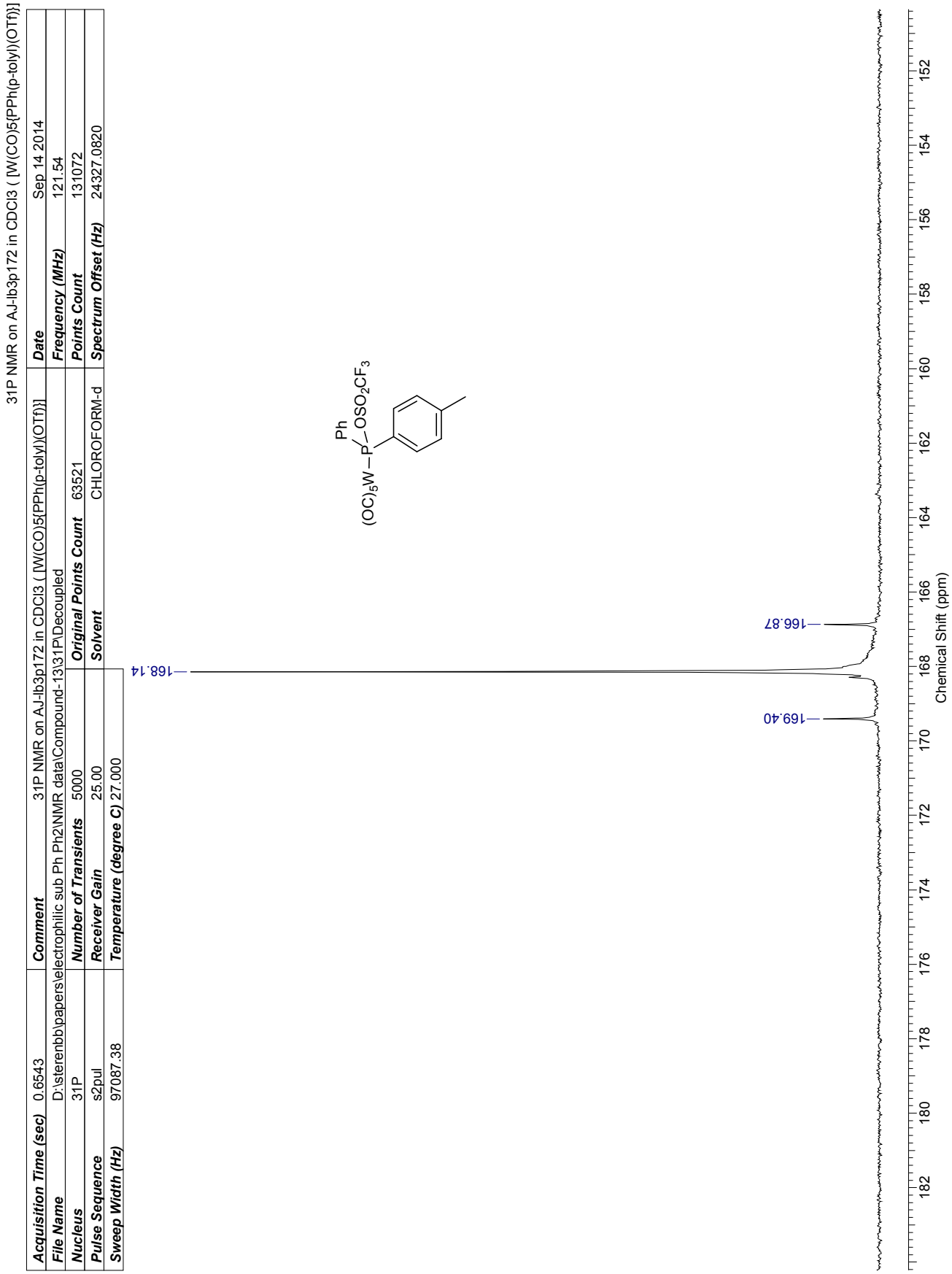
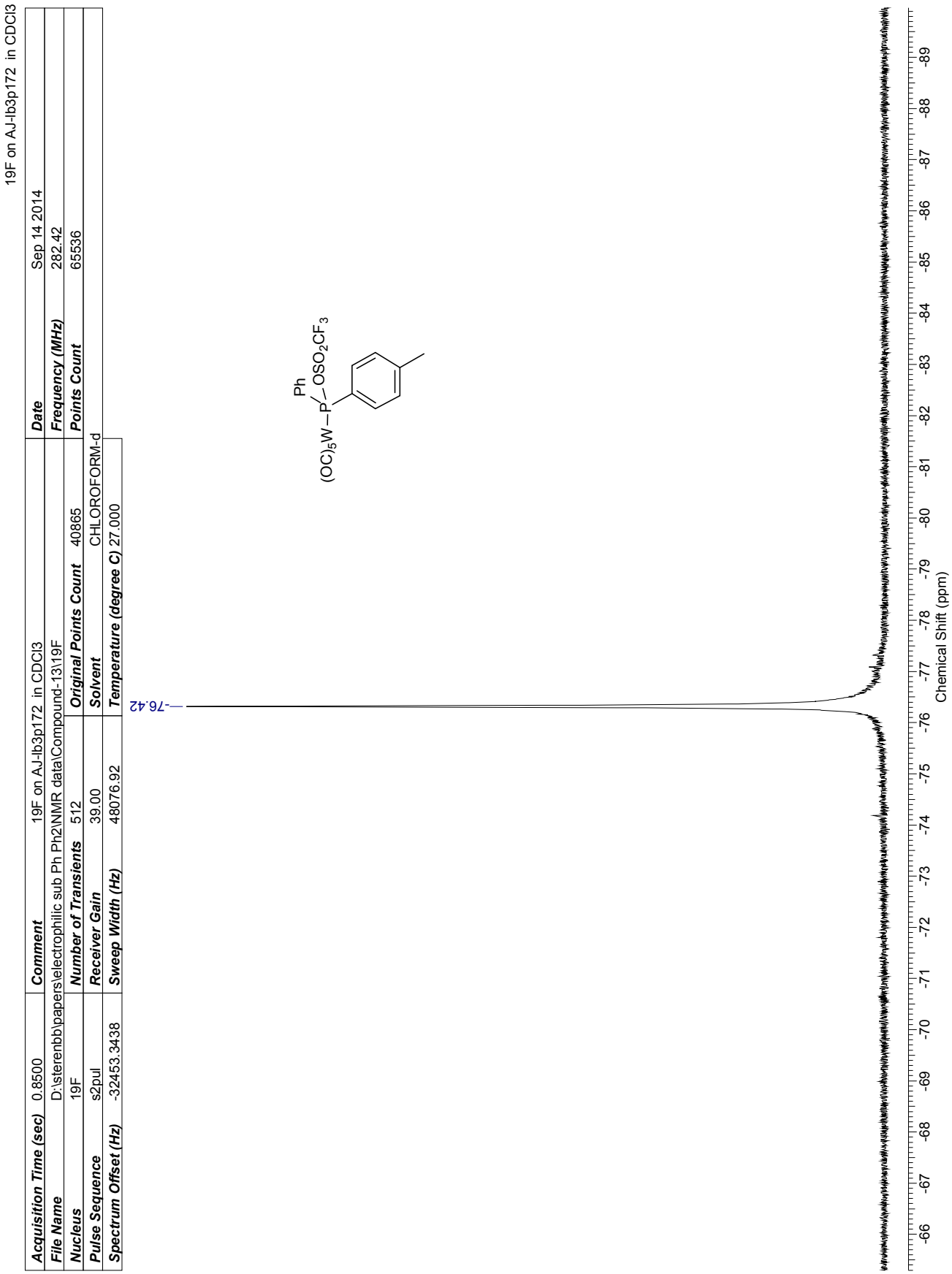



Figure S22. ^{19}F NMR spectrum of compound **13**.