Highly Active in situ Catalysts for anti-Markovnikov Hydration of Terminal Alkynes

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Supporting Information

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1. General Information

Syntheses of and with air-sensitive materials were performed under argon, using freshly distilled and degassed solvents.

Analytical data were measured by in-house services at the Institute of Organic Chemistry, RWTH Aachen University. Melting points (**M.p.**) were measured with a digital thermometer, therefore "corrected" values. **MS:** *m/z* (% relative abundance). **^{1}H-NMR**: δ/ppm, *J*/Hz, referenced to tetramethylsilane. **^{13}C-NMR:** δ/ppm, *J*/Hz, referenced to tetramethylsilane. **^{31}P-NMR**: δ/ppm, *J*/Hz. **IR**: ν/cm^{-1}, intensity: s = strong, m = medium, w = weak.

The following substances were prepared according to literature procedures: 2-Chloro-4,6-diphenyl-1,3-diazine (**4**)[1], 2-chloro-6-phenyl-pyridine and 6-phenyl-2-diphenylphosphinopyridine (**L1**).[2] $NaPPh_2$ was prepared by the $Na/NH_3/PPh_3$ method[3] and careful dissolution of the residue of evaporation in THF (0.7–1 M). A solution of $LiPPh_2$ was generated from $HPPh_2$ (Strem) and BuLi in THF.

2. General Procedures for Hydration Experiments

2.1. General procedure for anti-Markovnikov hydration of terminal alkynes (preparative): A Schlenk flask was charged with [CpRu(η^6-naphthalene)]PF_6 (**C**; 1-5 mol %), pyridyl-phosphane ligand **L** (2-10 mol %, 2 equiv relative to **C**) and CH_3CN (analytical reagent, degassed, 1 mL/10 mg **C**). The mixture was heated to 60 °C for 1-6 h (1 h for **L1**; 3 h for **L2**, **L3**; 6 h for **L5**, **L6**, **L7**), then the solvent was removed in vacuo to afford a yellow powder or resin. (This in situ-catalyst is storable). A solution of the alkyne (100 mol %) and water (5 equiv relative to alkyne) in acetone (1-4 mL/mmol substrate) was added to the catalyst and the resulting solution heated to 55-60 °C. After completion of the reaction (1.5 - 15 h, according to GC-MS or TLC), the solution was allowed to cool to room temperature and the solvent removed in vacuo to afforded the crude aldehydes, which were purified by either Kugelrohr distillation or flash column chromatography (SiO_2, *t*-BuOMe/hexanes).

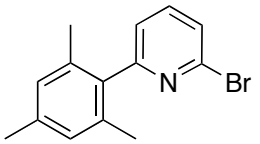
2.2. General procedure for anti-Markovnikov hydration with several ligands (kinetic runs): A Schlenk flask was charged with [CpRu(η^6-naphthalene)]PF_6 (**C**; 5 mol %) and the aza-aryl-phosphane ligand **L** (2 equiv relative to **C**, 10 mol %) and the in situ catalyst prepared as above. After removal of the solvent, the residual yellow powder or resin was carefully dried for 1 h in a high vacuum. Subsequently, a solution of 1-octyne (1 mmol, 1 equiv), H_2O (5 mmol, 5 equiv) and tetradecane (80 mg) in acetone (4 mL) was added and the resulting yellow solution kept at 45 °C (or 60 °C). Aliquots were removed at regular intervals to monitor the progress of the reaction by GC-analysis (FID-detection), based on separately determined response factors of the tetradecane standard relative to octyne and octanal.

3. Synthesis and Characterization of 2-Aryl-6-bromo-pyridines (P)

3.1. General procedure for Ni-catalyzed cross-coupling of aryl Grignard reagents and 2,6-dibromopyridine (3). A solution of the Grignard reagent (1.1–1.5 equiv) in THF was slowly added to a solution of 2,6-dibromopyridine (1.0 equiv) and [$NiCl_2(PCy)_3$] (0.2–1 mol %) in dry THF at room temperature. The reaction mixture was stirred at room temperature for 7-30 h, then quenched by careful addition NH_4Cl (aq). The aqueous phase was extracted with *t*-BuOMe or CH_2Cl_2. The combined organic phases were washed with water and dried over $MgSO_4$. Evaporation afforded crude products, which were purified by either crystallization or flash column chromatography (SiO_2).

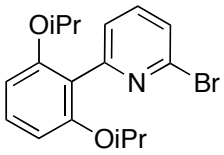
3.2. Substance data

2-Bromo-6-mesityl-pyridine (**P3**). Prepared according to the general procedure. This material contained some 2,6-dimesityl-pyridine as impurity and was used in the phosphination step without further purification.

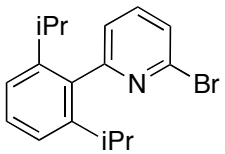


H-NMR (300 MHz, $CDCl_3$): 2.03 (s, 6 H), 2.30 (s, 3 H), 6.91 (br s, 2 H), 7.17 (d, J = 7.6 Hz, 1 H), 7.43 (d, J = 7.5, 1 H), 7.5 (t, J ≈ 7.5, 1 H). **^{13}C-NMR** (75 MHz, $CDCl_3$): 20.2 (CH_3), 21.1 (CH_3), 123.7 (CH), 126.0 (CH), 128.4 (CH), 135.6 (C), 136.3 (C), 137.9 (C), 138.5 (CH), 141.8 (C), 161.2 (C). **IR** (KBr): 3008m, 2960m, 1730m, 1610s, 1572s, 1440s, 1382s, 1277m, 1159s, 1121s, 1034s, 849s, 794s, 745s. **MS** (EI +): 275/277 (51, M^+), 274/276 (100, $[M-H]^+$), 196 (32), 181 (18), 90 (19). **HRMS** (EI): Calcd for $C_{14}H_{14}BrN$ (276.17): 275.030972, found 275.030934.

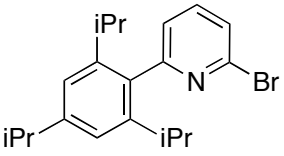
2-Bromo-6-(2,6-di-isopropoxy-phenyl)-pyridine (**P4**). According to the general procedure, with the following modifications: The Grignard reagent was prepared by ortho-metallation of 1,3-diisopropoxy-benzene with n-BuLi in hexane at 50°C for 10 h, followed by addition of a THF-solution of $MgBr_2$. **Mp.:** 77-78°C. **H-NMR** (300 MHz, $CDCl_3$): 1.18 (d, J = 6.1, 12 H), 4.42 (sept, J = 6.1, 2 H), 6.59 (d, J = 8.4, 2 H), 7.22 (d, J = 8.4, 1 H), 7.27 (d, J = 7.5, 1 H), 7.37 (d, J = 7.8, 1 H), 7.53 (t, J = 7.7, 1 H). **^{13}C-NMR** (75 MHz, $CDCl_3$): 22.1 (CH3), 71.4 (CH), 107.5 (CH), 120.9 (C), 125.3 (CH), 125.4 (CH), 129.7 (CH), 137.5 (CH), 140.5 (C), 156.2 (C), 156.9 (C). **IR** (KBr): 2976m, 2921m, 1592s, 1545m, 1459s, 1381m, 1249s, 1118s, 1062s, 785m. **MS** (EI+): 349/351 (33, M+), 334/336 (11), 265/267 (100), 249/251 (25), 186 (14). **EA** calcd for $C_{17}H_{20}BrNO_2$ (350.25) C 58.30, H 5.76, N 4.00, found C 58.43, H 5.82, N 4.11.



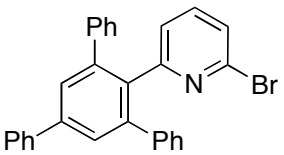
2-Bromo-6-(2,6-diisopropylphenyl)-pyridine (**P5**). According to the general procedure. White solid. **Mp:** 176-177 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$): 1.09 (d, *J* = 6.9, 6 H, CH_3), 1.14 (d, *J* = 6.9, 6 H, CH_3), 2.47 (sept, *J* = 6.9, 2 H, CH), 7.21 (d, J = 7.8, 2 H, Ar-H), 7.23 (dd, *J* = 7.4, 0.8, 1 H, Ar-H), 7.36 (t, *J* = 7.7, 1 H, Ar-H), 7.48 (dd, *J* = 8.0, 0.8, 1 H, Ar-H), 7.60 (t, *J* = 7.4, 1 H, Ar-H). **^{13}C-NMR** (100 MHz, $CDCl_3$): 22.7, 23.0, 29.3, 121.5, 122.6, 124.8, 127.7, 135.9, 136.7, 140.3, 145.1, 159.7. **IR** (KBr): 3028 (s), 2956 (m), 1569 (s), 1431 (s), 1113 (s), 1039 (s), 804 (s). **MS** (EI, 70 eV): 318.2 (100)[M^+], 302.2 (13), 287.1 (5), 273.1 (3), 260.1 (5), 238.2 (23), 196.2 (21), 180.2 (10). **HRMS** (EI) calcd for $C_{17}H_{20}BrN$: 317.077923, found: 317.077795.



2-Bromo-6-(2,4,6-triisopropylphenyl)-pyridine (**P6**).[4] Prepared according to the general procedure as white solid. Due to low solubility of the product, the reaction needed efficient stirring. Recrystallization from toluene. **Mp:** 241 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): 1.09 (d, *J* = 6.9, 6 H, CH_3), 1.14 (d, *J* = 6.9, 6 H, CH_3), 1.26 (d, *J* = 6.9, 6 H, CH_3), 2.47 (sept, *J* = 6.9, 2 H, CH), 2.91 (sept, *J* = 6.9, 1 H, CH), 7.05 (s, 2 H, Ar-H), 7.25 (dd, *J* = 7.8, 0.9, 1 H, Ar-H), 7.46 (dd, *J* = 7.9, 1.0, 1 H, Ar-H), 7.59 (t, *J* = 7.4, 1 H, Ar-H). **^{13}C-NMR** (75 MHz, $CDCl_3$): 23.8, 24.0, 24.1, 30.4, 34.4, 120.8, 123.9, 125.9, 134.9, 137.9, 141.5, 146.1, 149.3, 161.3. **IR** (KBr): 2961 (m), 2868 (m), 1574 (s), 1544 (s), 1432 (s), 1127 (s). **MS** (EI, 70 eV): 361.1 (53)[M^+], 360.1 (100), 359.1 (59), 344,1 (8). **HRMS** (EI): calcd for $C_{20}H_{26}BrN$: 359.12487, Found: 359.12486.



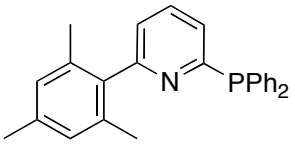
2-Bromo-6-(2,4,6-triphenyl-phenyl)-pyridine (**P7**). The compound was prepared according to the general procedure with the following modifications: 1 mol % of Ni-complex as catalyst, the reaction was stirred for 4 d at 75°C, then for 4 d at 85°C. CC (hexanes/toluene 3:2–1:1 - toluene). Yield 57% of a white crystalline powder. **Mp.:** 243-244°C. **H-NMR** (400 MHz, $CDCl_3$): 6.82 (d, J = 7.3, 1 H), 7.12 (t, J ≈ 7.0, 1 H), 7.15-7.28 (m, 11 H), 7.38 (t, J = 7.3, 1 H), 7.46 (t, J ≈ 7.5, 2 H), 7.65-7.72 (m, 4 H). **^{13}C-NMR** (100 MHz, $CDCl_3$): 125.1 (CH), 125.3 (CH), 126.5 (CH), 127.1 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.7 (CH), 129.5 (CH), 135.7 (C), 137.0 (CH), 140.1 (C), 140.3 (C), 140.9 (C), 142.3 (C), 159.5 (C). **IR** (KBr): 3031w, 1699m, 1651m, 1575m, 1558s, 1542s, 1506m, 1420m, 1129m, 767s, 698s. **MS** (EI+): 461/463 (60, M+), 460/462 (50), 383 (28), 382 (100), 354 (14), 341 (11), 183 (7). **EA** calcd for $C_{29}H_{20}BrN$ (462.38): C 75.33, H 4.36, N 3.03, found C 75.64 H 4.60, N 3.01.



4. Synthesis and Characterization of 2-Aryl-6-diphenylphosphinopyridines (L)

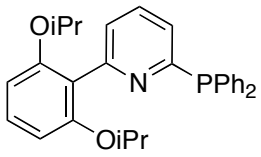
4.1. General procedure. A solution of $NaPPh_2$ (1.0 equiv) in THF was added dropwise to a solution of 2-aryl-6-bromopyridine (**P**, 1.0 equiv) in Et_2O/toluene (3:2) at 0°C. The resulting orange-yellow mixture was stirred at 0 °C for 1.5 h–1.5 d. The reaction was diluted with CH_2Cl_2 (1/3 of the reaction volume) and the resulting suspension filtered through a plug of Celite. Removal of the solvent in vacuum afforded a crude product that was purified by flash column chromatography under argon (CH_2Cl_2/hexanes, SiO_2) or recrystallization from MeOH.

6-(2,4,6-trimethylphenyl-2-diphenylphosphino-pyridine (**L3**). White solid.

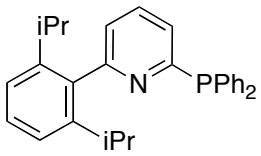


Mp: 118 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): 1.96 (s, 6 H, CH_3), 2.28 (s, 3 H, CH_3), 6.87 (s, 2 H, Ar-H), 6.97 (dt, *J* = 7.7, 0.5, 1 H, Ar-H), 7.09 (dt, *J* = 7.7, 1.0, 1 H, Ar-H), 7.31-7.43 (m, 10 H, Ar-H), 7.59 (td, *J* = 6.9, 2.0, 1 H, Ar-H). **^{13}C-NMR** (75 MHz, $CDCl_3$)**:** 20.3 (CH_3), 21.1 (CH_3), 123.3 (CH), 125.4 (d, J_{PC} =14, CH), 128.2 (CH), 128.5 (d, J_{PC} = 7, CH), 128.9 (CH), 134.3 (d, J_{PC} = 20.2, CH), 135.7 (C), 135.8 (d, J_{PC} = 2, CH), 136.5 (d, J_{PC} = 10.5, C), 137.4 (C), 137.7 (C), 160.6 (d, J_{PC} = 13, C), 164.0 (d, J_{PC} = 5, C). **^{31}P-NMR** (121 MHz, $CDCl_3$): –4.7 (s). **IR** (KBr): 3466 (m), 2917 (m), 1569 (s), 1549 (s), 1440 (s), 853 (s), 757 (s), 695 (s). **MS** (EI, 70 eV): 381.1 (100)[M^+], 302.1 (28), 287.0 (5), 195.1 (9), 183.0 (6). **EA** calcd for $C_{26}H_{24}NP$: C 81.87, H 6.34, N 3.67, found: C 82.06, H 6.03, N 3.66.

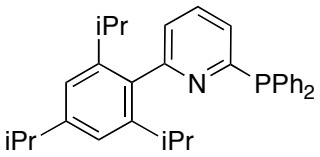
6-(2,6-Diisopropoxy-phenyl)-2-diphenylphosphino-pyridine (**L4**). White solid.



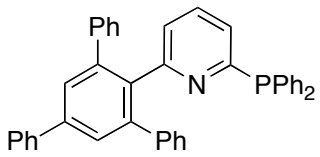
Mp: 112 °C. **^{1}H-NMR** (400 MHz, C_6D_6): δ = 0.96 (d, *J* = 6.0, 12 H, CH_3), 4.16 (sept, *J* = 6.0, 2 H, CH), 6.51 (d, *J* = 8.5, 2 H, Ar-H), 6.99 (dt, *J* = 7.5, 1.2, 1 H, Ar-H), 7.02-7.16 (m, 9 H, Ar-H), 7.52 (td, *J* = 7.6, 1.6, 4 H, Ar-H). **^{13}C-NMR** (100 MHz, C_6D_6): 22.1 (CH_3), 71.3 (CH), 108.1 (CH), 123.9 (C), 125.8 (d, J_{PC} = 17, CH), 128.4 (d, J_{PC} = 7, CH), 128.5 (CH), 129.0 (CH), 134.5 (d, J_{PC} = 20, CH), 134.7 (d, J_{PC} = 3, CH), 138.0 (d, J_{PC} = 13.0, C), 156.4 (d, J_{PC} = 13, C), 157.3 (C), 162.6 (d, J_{PC} = 5, C). **^{31}P-NMR** (160 MHz, C_6D_6): –4.8 (s). **IR** (KBr): ν = 2971 (m), 1583 (s), 1451 (s), 1373 (s), 1238 (s), 1114 (s), 1047 (s), 742 (s), 695 (m). **MS** (EI+): 455.2 (100)[M^+], 440.2 (49), 412.2 (16), 396.2 (13), 382.2 (19), 370.1 (41), 354.1 (28), 338.1 (30), 292.0 (22), 254.0 (32). **EA** calcd for $C_{29}H_{30}NO_2P$: C 76.46, H 6.64, N 3.07, found: C 76.03, H 6.70, N 3.05.



6-(2,6-Diisopropyl-phenyl)-2-diphenylphosphino-pyridine (**L5**). White solid. **Mp:** 143-144 °C. **^{1}H-NMR** (400 MHz, C_6D_6): 1.03 (d, *J* = 6.8, 6 H, CH_3), 1.09 (d, *J* = 6.8, 6 H, CH_3), 2.66 (sept, *J* = 6.9, 2 H, CH), 6.86 (dt, *J* = 7.4, 0.9, 1 H, Ar-H), 7.00 (td, *J* = 7.7, 2.2, 1 H, Ar-H), 7.03-7.10 (m, 7 H, Ar-H), 7.15 (d, J = 7.8, 2 H, Ar-H), 7.29 (t, *J* = 7.7, 1 H, Ar-H), 7.51 (td, *J* = 7.7, 1.6, 4 H, Ar-H). **^{13}C-NMR** (100 MHz, C_6D_6): 24.0 (CH_3), 24.4 (CH_3), 30.7 (CH), 122.7 (CH), 123.3 (CH), 125.9 (d, J_{PC} = 20, CH), 128.5 (d, J_{PC} = 7, CH), 128.7 (CH), 128.8 (CH), 134.4 (d, J_{PC} = 19.9, CH), 135.1 (d, J_{PC} = 3.8, CH), 137.2 (d, J_{PC} = 11.4, C), 139.0 (C), 146.4 (C), 160.8 (d, J_{PC} = 11.5, C), 163.9 (d, J_{PC} = 1.4, C). **^{31}P-NMR** (160 MHz, C_6D_6): –4.3 (s). **IR** (KBr): 3055 (s), 2957 (s), 2865 (s), 1554 (s), 1433 (s), 744 (s), 693 (s). **MS** (EI+): 423.3 (100)[M^+], 408.2 (5), 344.1 (11), 328.1 (6), 236.1 (20), 222.1 (38), 211.5 (6). **HRMS** calcd for $C_{29}H_{30}BrN$: 423.211589, found: 423.211409.



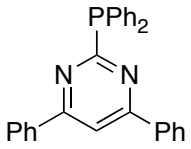
6-(2,4,6-Triisopropyl-phenyl)-2-diphenylphosphino-pyridine (**L6**). White solid. **Mp:** 198 °C. **^{1}H-NMR** (400 MHz, C_6D_6): 1.10 (d, *J* = 6.9, 6 H, CH_3), 1.17 (d, *J* = 6.9, 6 H, CH_3), 1.28 (d, *J* = 6.9, 6 H, CH_3), 2.73 (sept, *J* = 6.9, 2 H, CH), 2.86 (sept, *J* = 6.9, 1 H, CH), 6.91 (dt, *J* = 7.4, 1.2, 2 H, Ar-H), 6.99 (td, *J* = 7.7, 2.2, 1 H, Ar-H), 7.03-7.10 (m, 6 H, Ar-H), 7.19 (s, 2 H, Ar-H), 7.50-7.57 (m, 4 H, Ar-H). **^{13}C-NMR** (100 MHz, C_6D_6): 23.9 (CH_3), 24.2 (CH_3), 24.2 (CH_3), 30.7 (CH), 34.7 (CH), 120.5 (CH), 123.3 (CH), 125.7 (d, J_{PC} = 20.1, CH), 128.3 (d, J_{PC} = 7, CH), 128.6 (CH), 134.3 (d, J_{PC} = 20, CH), 134.9 (d, J_{PC} = 3.5, CH), 136.8 (C) 137.1 (d, J_{PC} = 13, C), 146.3 (C), 148.6 (C), 160.9 (d, J_{PC} = 12, C), 163.7 (d, J_{PC} = 2, C). **^{31}P-NMR** (160 MHz, C_6D_6): –4.3 (s). **IR** (KBr): 3437 (m), 2959 (s), 2868 (s), 1565 (s), 1435 (s), 745 (s). **MS** (EI, 70 eV): 466.2 (25)[M^+], 465.2 (89), 464.2 (100), 386.1 (7). **EA** calcd for $C_{32}H_{36}NP$: C 82.55, H 7.79, N 3.01, found: C 82.20, H 7.79, N 2.91.



*6-(2,4,6-Triphenyl-phenyl)-2-diphenylphosphino-pyridine (**L7**).* White solid. **Mp:** 197-198 °C. **^{1}H-NMR** (400 MHz, C_6D_6): 6.57-6.65 (m, 2 H, Ar-H), 6.82 (ddd, *J* = 6.6, 2.7, 1.9, 1 H, Ar-H), 6.96-7.10 (m, 13 H, Ar-H), 7.19-7.24 (m, 6 H, Ar-H), 7.38 (td, *J* = 7.7, 2.0, 4 H, Ar-H), 7.45 (dt, *J* = 6.8, 1.6, 2 H, Ar-H), 7.63 (s, 2 H, Ar-H). **^{13}C-NMR** (75 MHz, C_6D_6): 125.5 (CH), 126. (d, J_{PC} = 26, CH), 126.7 (CH), 127.7 (CH), 127.7 (CH), 128.0 (CH), 128.5 (CH), 128.7 (d, J_{PC} = 7, CH), 128.8 (CH), 129.1 (CH), 130.3 (CH), 134.6 (d, J_{PC} = 5, CH), 134.7 (d, J_{PC} = 20, CH), 137.8 (d, J_{PC} = 12, C), 138.5 (C), 140.9 (C), 141.4 (C), 142.2 (C), 142.9 (C), 160.1 (d, J_{PC} = 10, C), 162.5 (C). **^{31}P-NMR** (160 MHz, C_6D_6): –3.1 (s). **IR** (KBr): 3437 (m),

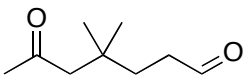
3050 (s), 1688 (s), 1557 (s), 1420 (m), 1150 (s), 693 (m). **MS** (EI, 70 eV): 567.3 (100)[M^+], 490.2 (25), 412.1 (4), 283.6 (45). **EA** calcd for $C_{41}H_{30}NP$: C 86.75, H 5.33, N 2.47, found C 87.10, H 5.36, N 2.28. **HRMS**: Calcd for $C_{41}H_{30}NP$: 567.211589, found: 567.211506.

4,6-Diphenyl-2-diphenylphosphino-1,3-diazine (**L8**). Prepared according to the general procedure, white solid. **Mp:** 104-105 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): 7.30-7.34 (m, 6 H, Ar-H), 7.35-7.41 (m, 7 H, Ar-H), 7.54-7.60 (m, 3 H, Ar-H), 7.87 (d, J = 1.4, 1 H, CH), 7.95-7.99 (m, 4 H, Ar-H). **^{13}C-NMR** (75 MHz, $CDCl_3$): 109.6 (CH), 127.2 (CH), 128.1 (d, J_{PC} = 7.6, CH), 128.8 (CH), 128.8 (CH), 130.8 (CH), 134.7 (d, J_{PC} = 19.8, CH), 136.1 (d, J_{PC} = 8, C), 137.0 (C), 160.8 (C), 163.5 (d, J_{PC} = 7, C). **^{31}P-NMR** (121 MHz, $CDCl_3$): 1.4 (s). **IR** (KBr): 3473 (m), 3057 (m), 1565 (s), 1510 (s), 1432 (s), 749 (s), 688 (s). **MS** (EI, 70 eV): 416.1 (100)[M^+], 339.1 (31), 233.1 (14), 183.0 (13). **EA** calcd for $C_{28}H_{21}N_2P$: C 80.75, H 5.08, N 6.73, found C 80.67, H 5.28, N 6.72.

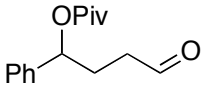


5. New Substances from Alkyne Hydration

Known substances: 4-*tert*-Butylphenyl-acetaldehyde,[5] *tert*-butyl 2-(3-oxo-propyl)-3-oxo-butanoate,[6] dimethyl 2-(3-oxopropyl)-malonate,[7] furthermore octanal, heptanal, phenylacetaldehyde (without reference).



4,4-dimethyl-6-oxo-heptanal (Table 3, entry 10). Prepared according to the general procedure. Colorless liquid of pleasant smell. **^{1}H-NMR** (400 MHz, $CDCl_3$): 1.01 (s, 6 H), 1.65-1.73 (m, 2 H), 2.14 (s, 3 H), 2.35 (s, 2 H), 2.38-2.44 (m, 2 H), 9.77 (t, J = 1.8, H). **^{13}C-NMR** (100 MHz): 27.1 (CH_3), 32.5 (CH_3), 33.0 (C), 33.4 (CH_2), 39.4 (CH_2), 53.5 (CH_2), 202.4 (C), 208.3 (C). **IR** (film): 2984w, 1684s, 1651m, 1559m, 1457m, 1266m, 754m, 668m. **MS** (EI): 156 (1, M+), 138 (12), 123 (12), 113 (55), 81 (48), 69 (40), 43 (100). **EA**: The analytical sample was oxidized to the carboxylic acid on standing in air; calcd for $C_9H_{16}O_3$: C 62.77, H 9.36, found C 62.88, H 9.51.

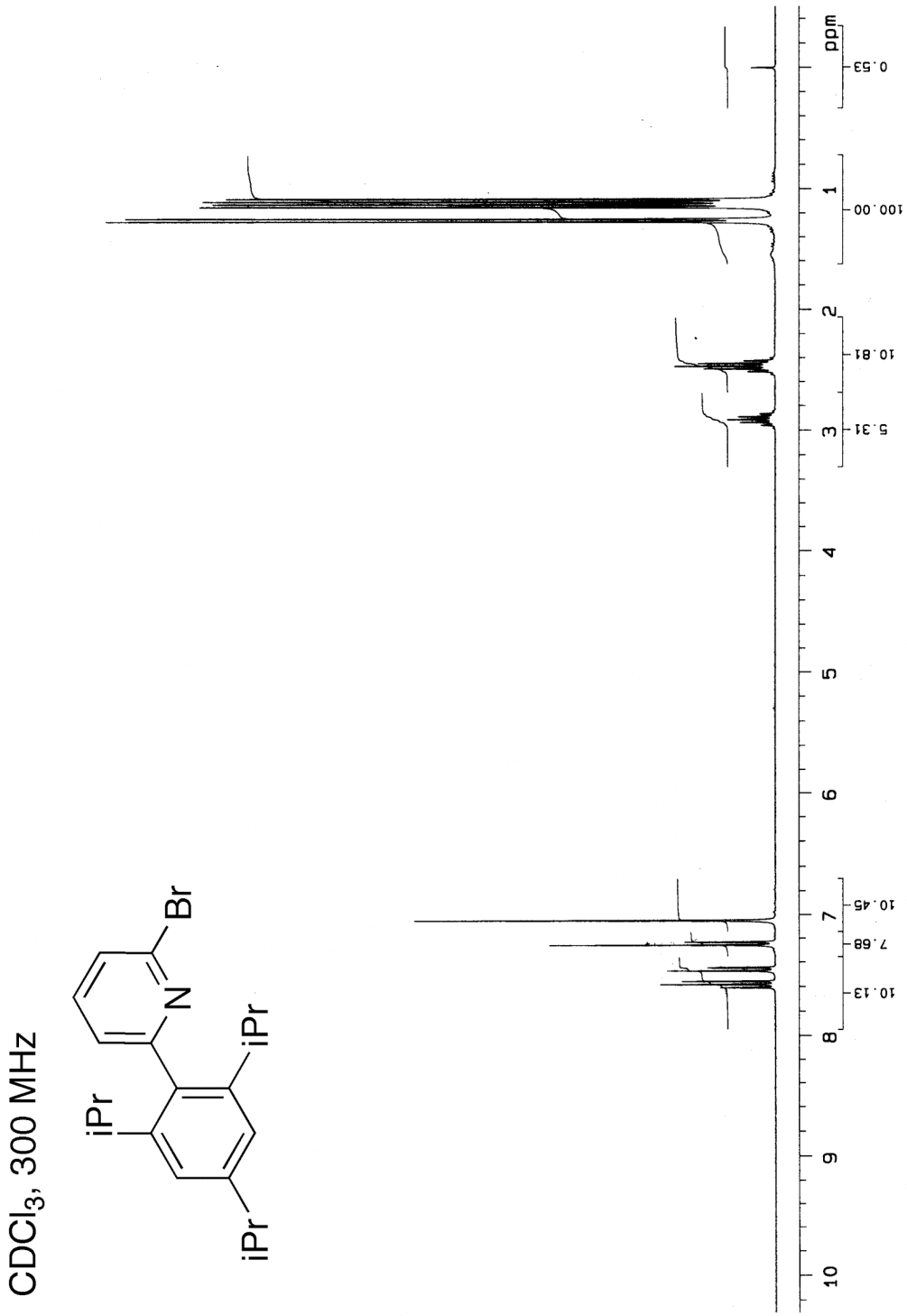


4-phenyl-4-pivaloyloxy-butanal (Table 3, entry 11). Colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): 1.21 (s, 9 H), 2.07-2.28 (m, 2 H), 2.47 (t, J = 7.5, 2 H), 5.74 (dd, J = 7.2, 6.1, 1 H), 7.24-7.40 (m, 5 H), 9.73 (t, J = 1.3, 1 H). **^{13}C-NMR** (75 MHz, $CDCl_3$): 27.1 (CH_3), 29.0 (CH_2), 38.8 (C), 39.9 (CH_2), 74.6 (CH), 126.0 (CH), 128.0 (CH), 128.6 (CH), 140.2 (C), 177.5 (C), 201.0 (C). **IR** (film): 3022w, 2976w, 1718m, 1216m, 1157m, 760s. **MS** (EI+): 248 (1, M+), 204 (40), 163 (100), 147 (67), 129 (50), 117 (85), 91 (90). **EA** calcd for $C_{15}H_{20}O$ (248.32): C 72.55, H 8.12, found C 72.00, H 8.04; calcd for M + 0.1 O (partial oxidation to carboxylic acid): C 72.09, H 8.07.

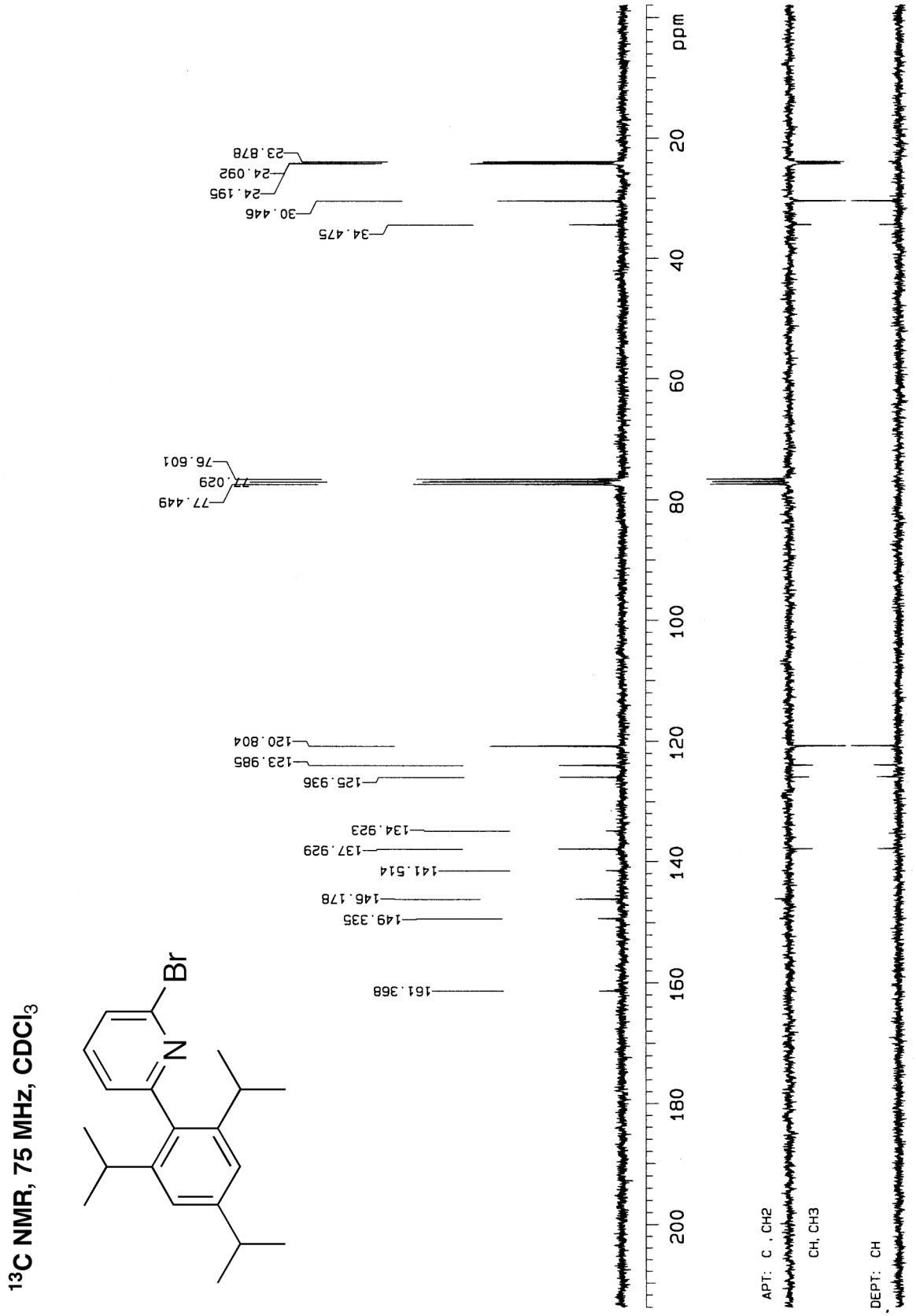
6. Selected NMR Spectra

6.1. Ligand Synthesis

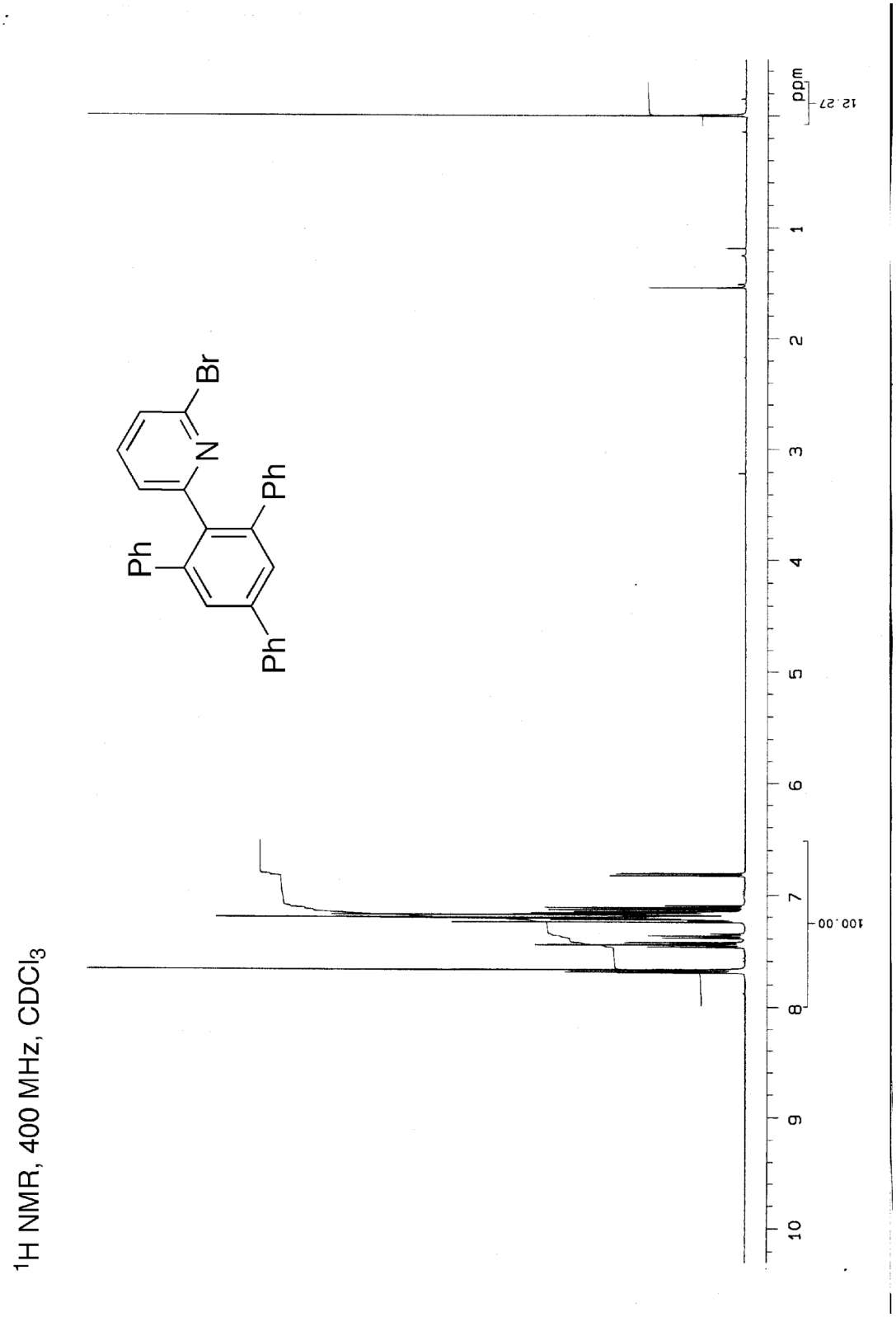
^{1}H NMR of **P6**



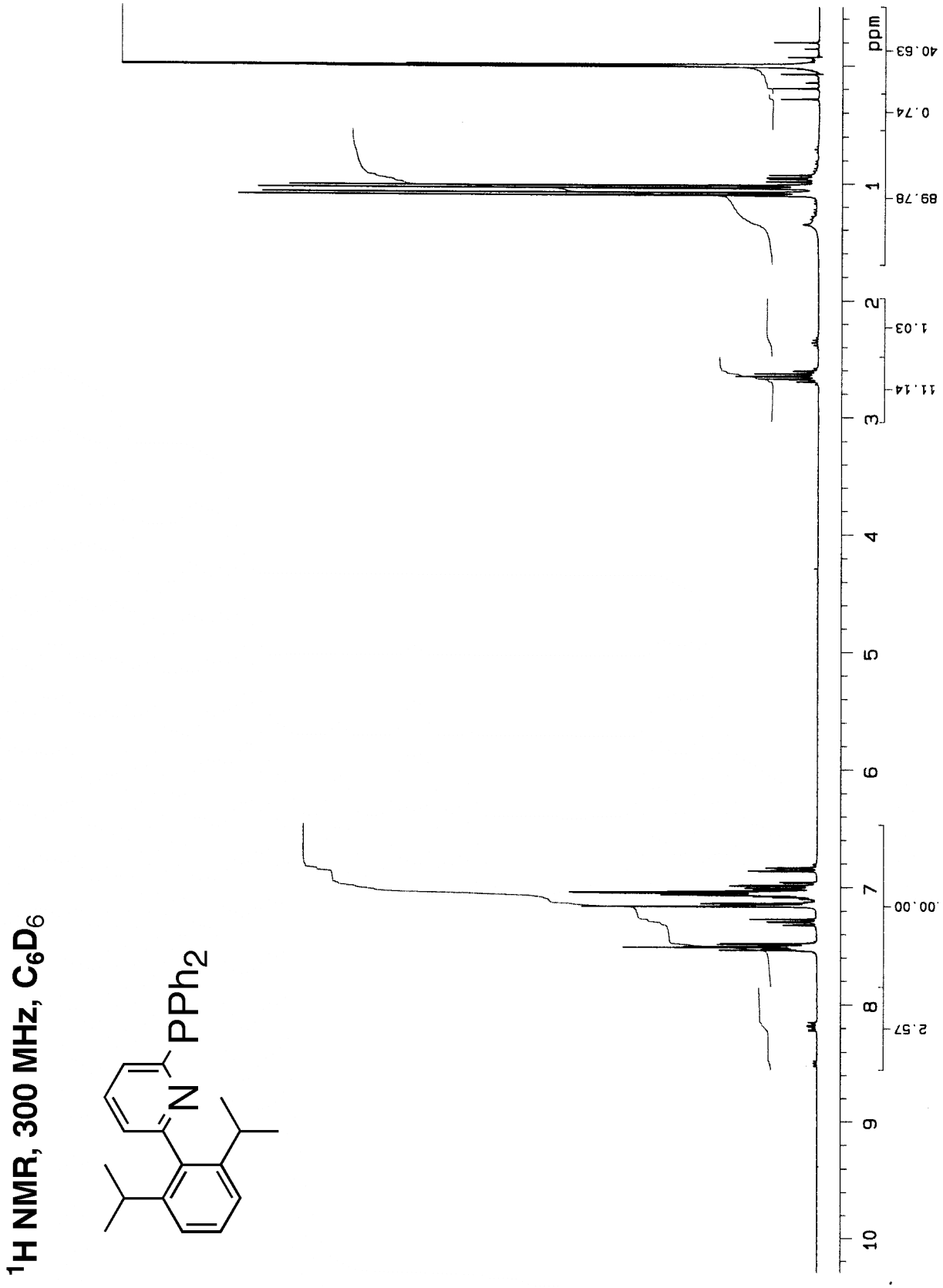
^{13}C NMR of **P6**


13C NMR, 75 MHz, CDCl3
Br
N
161.368
149.335
146.178
141.514
137.929
134.923
125.936
123.985
120.804
77.449
77.029
76.601
34.475
30.446
24.195
24.092
23.878
ppm
20
40
60
80
100
120
140
160
180
200
APT: C, CH2
CH, CH3
DEPT: CH

^{1}H NMR of **P7**

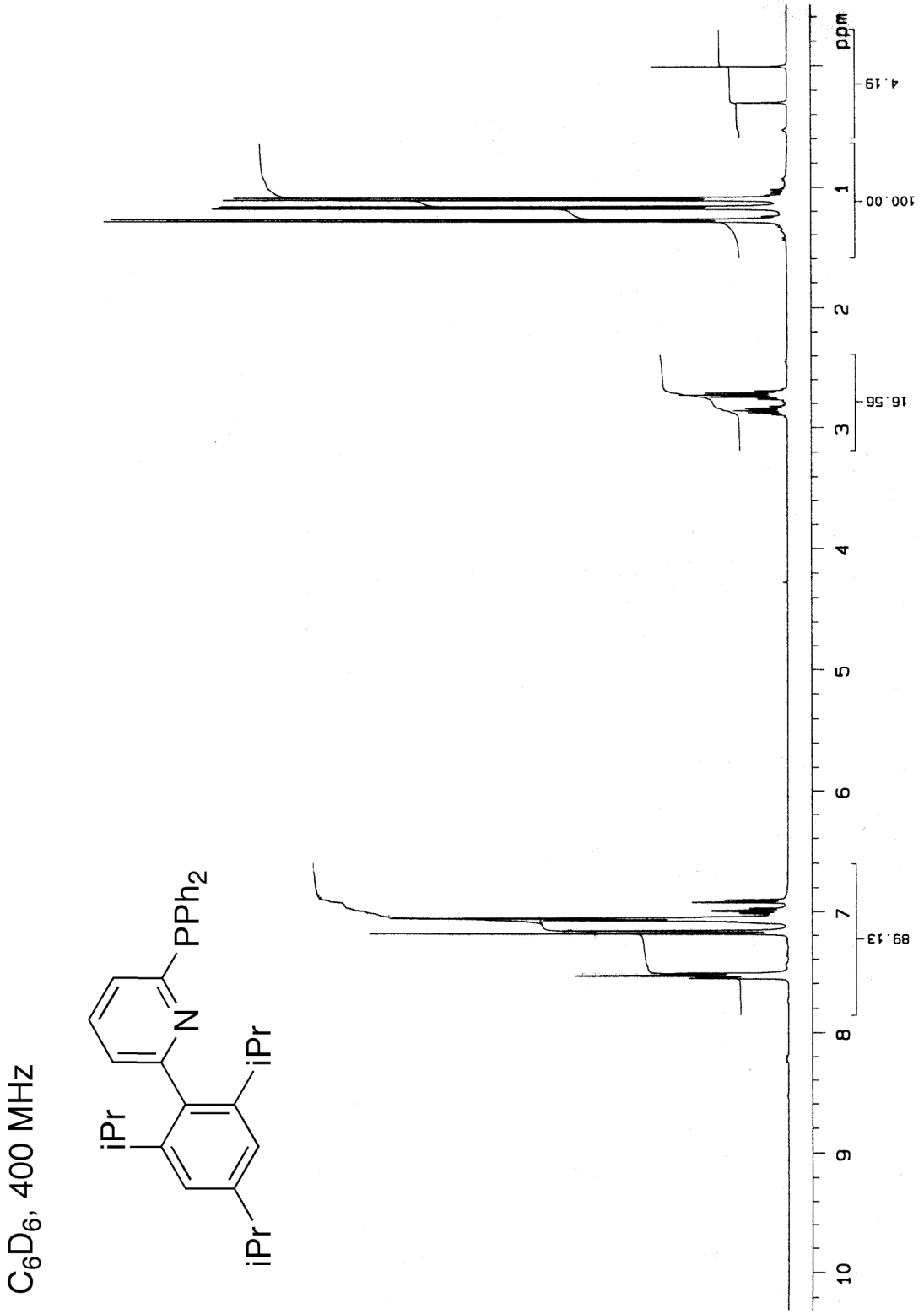


^{1}H NMR of **L5**

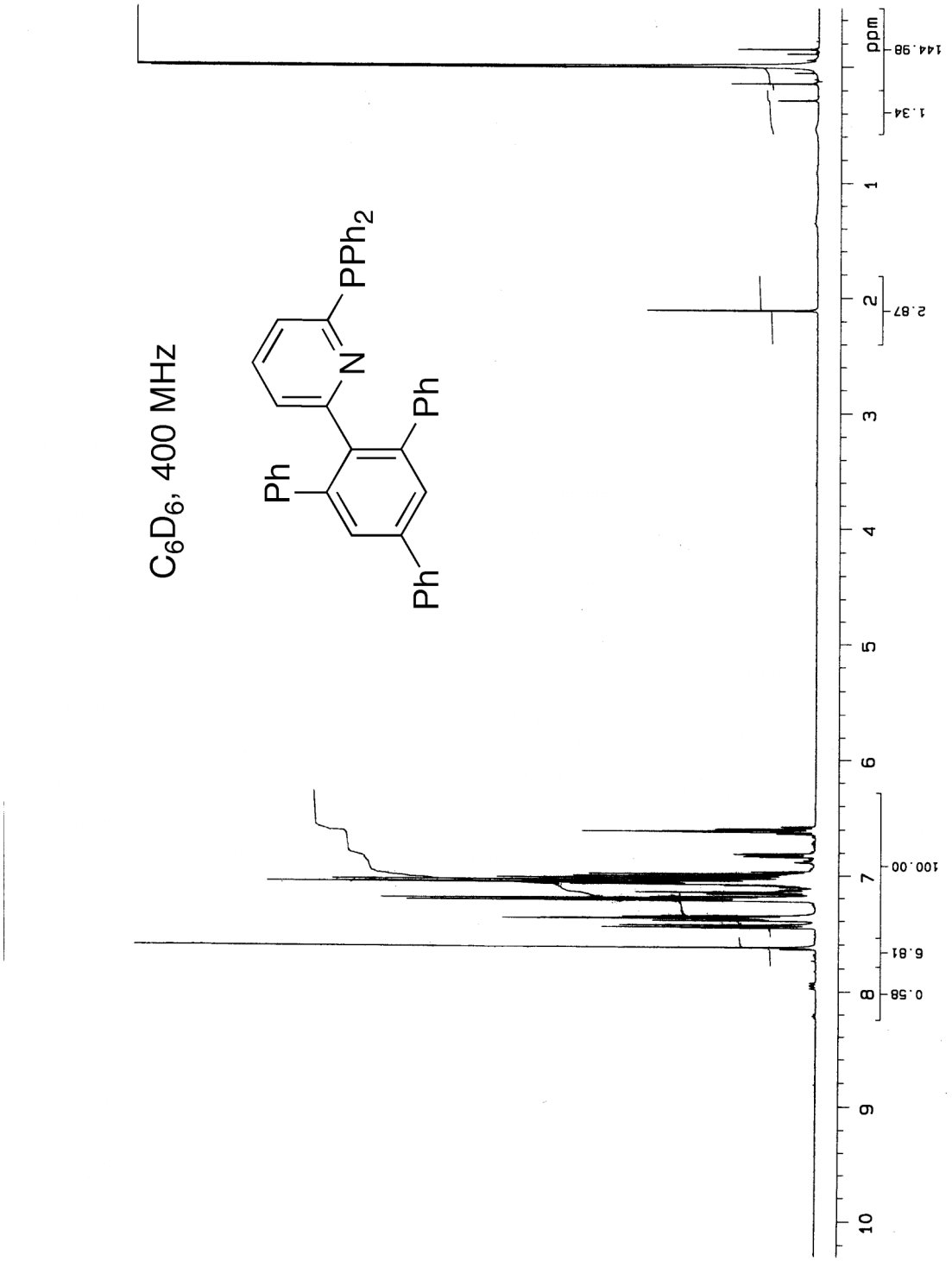


(*traces of phosphine oxide due to NMR sample oxidation*)

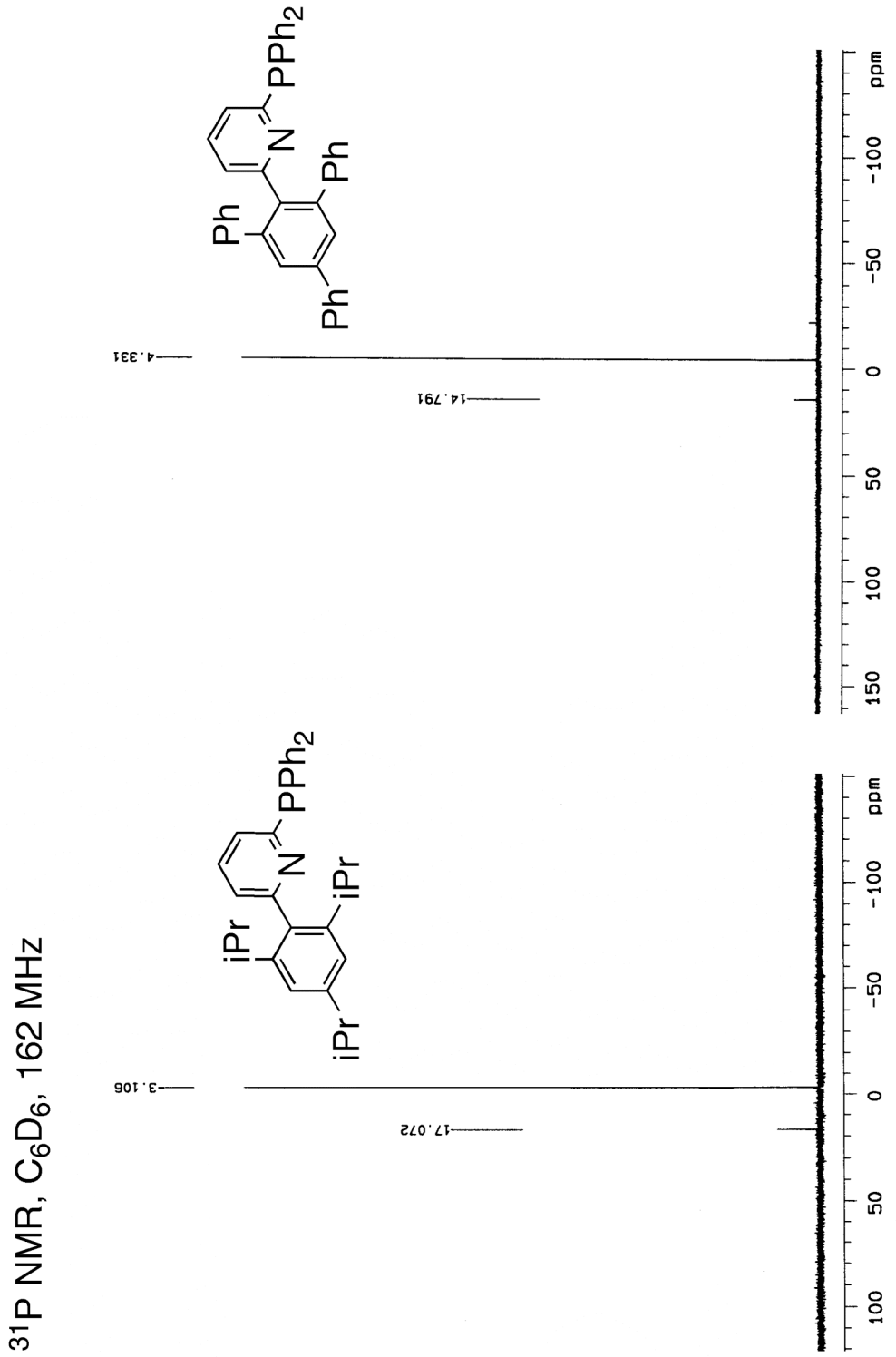
^{1}H NMR of **L6**



^{1}H NMR of **L7**

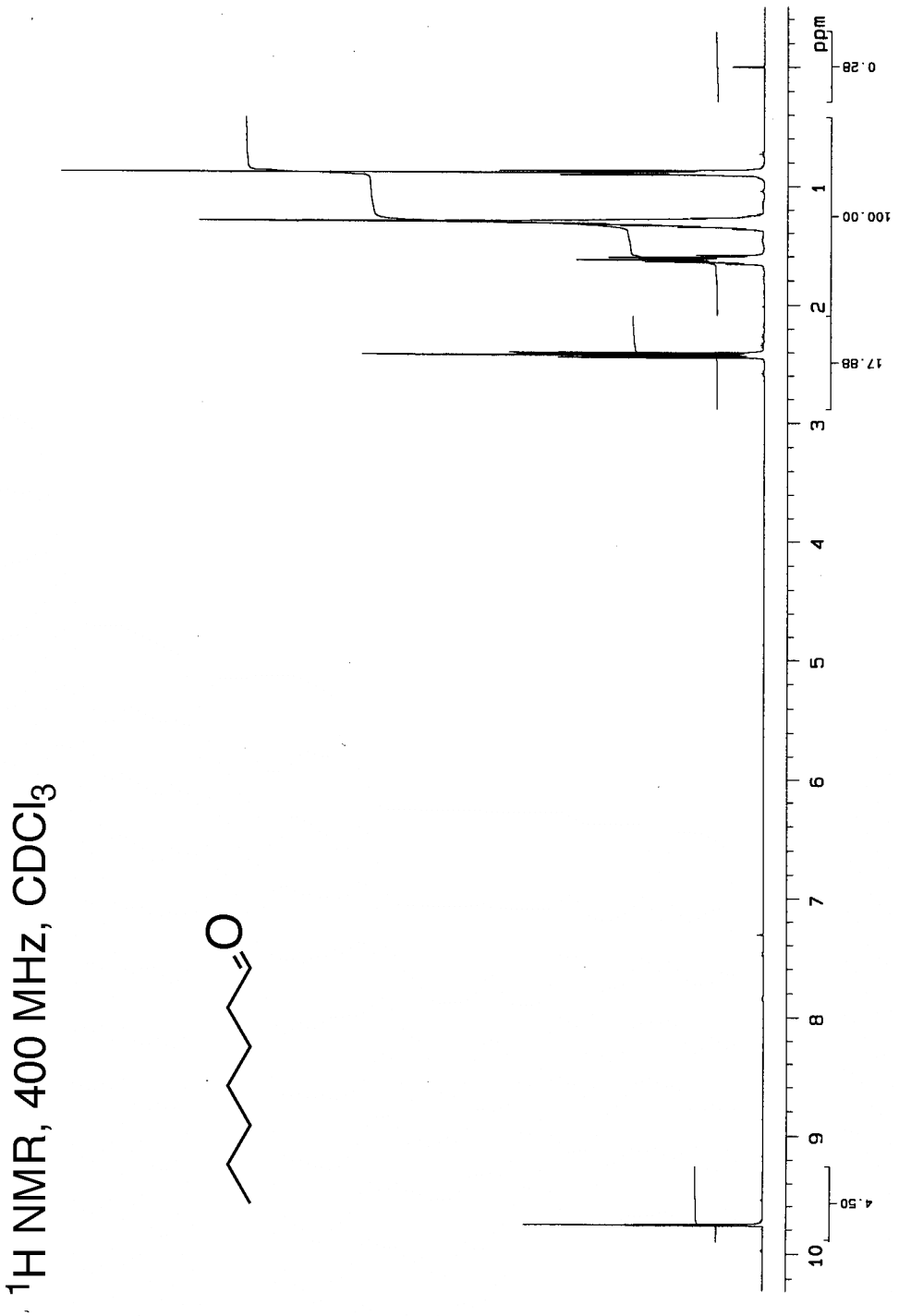

C6D6, 400 MHz
PPh2
N
Ph
Ph
Ph
ppm
144.98
1.34
2.87
100.00
6.81
0.58
1
2
3
4
5
6
7
8
9
10

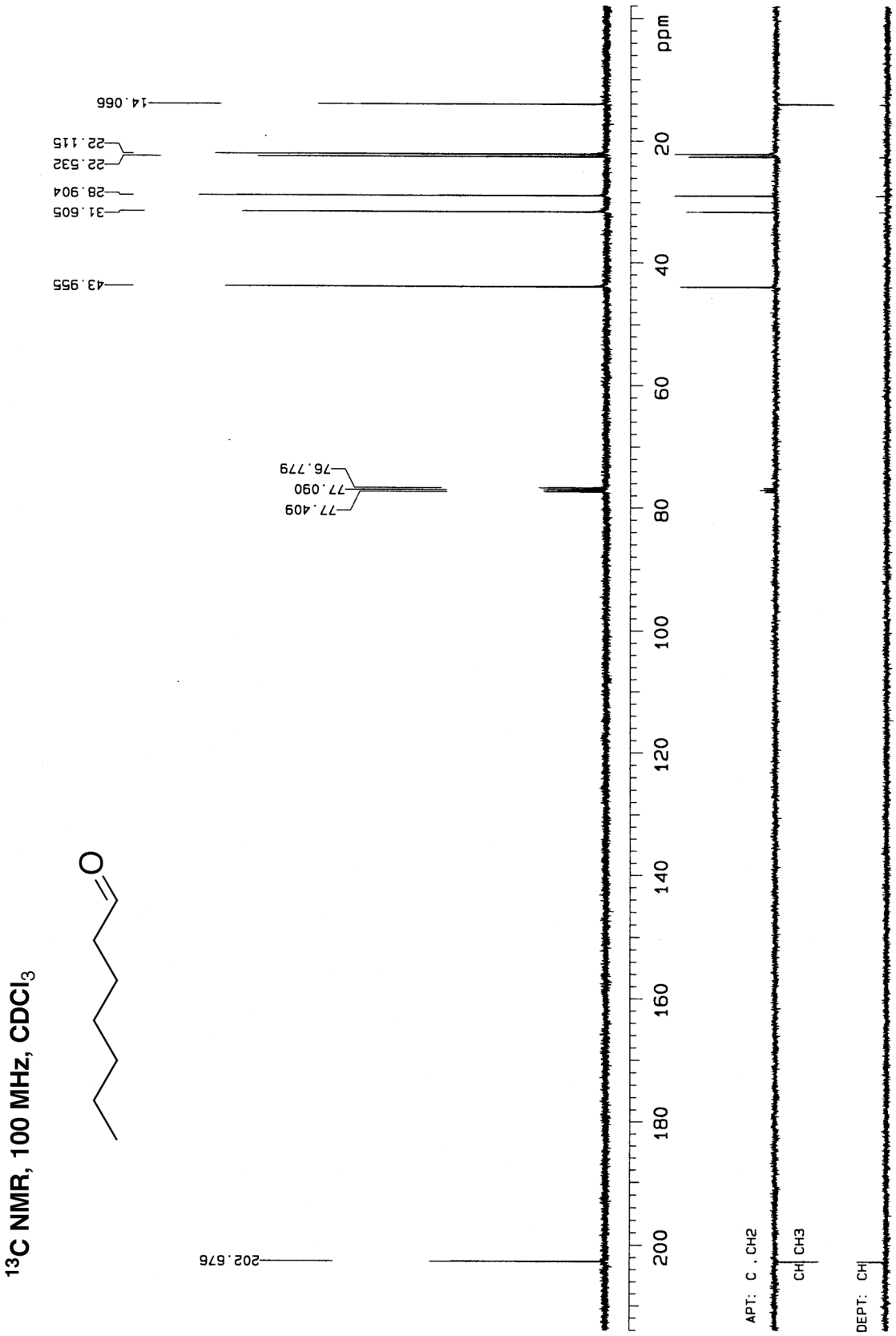
^{31}P NMR of **L6**, **L7**

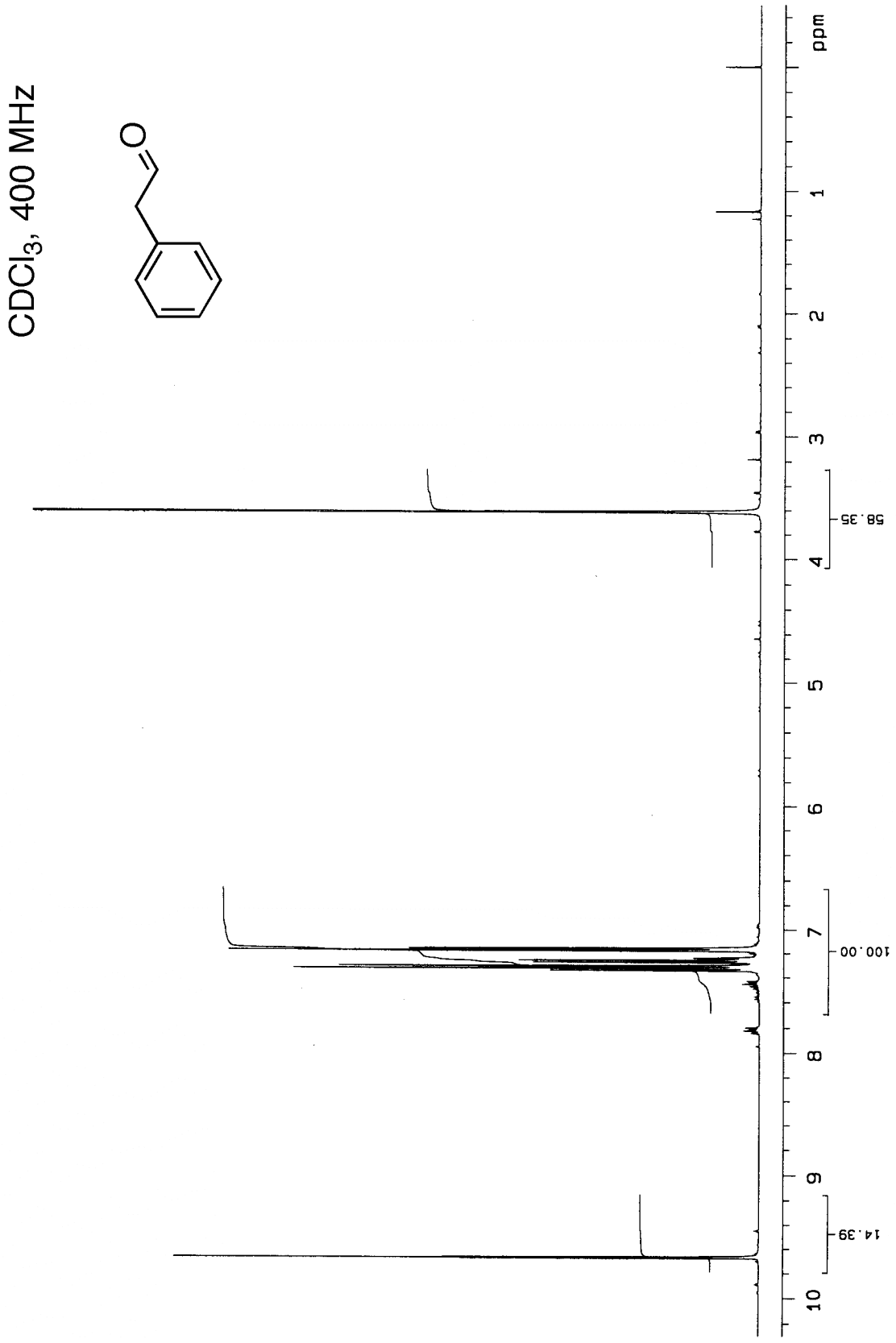


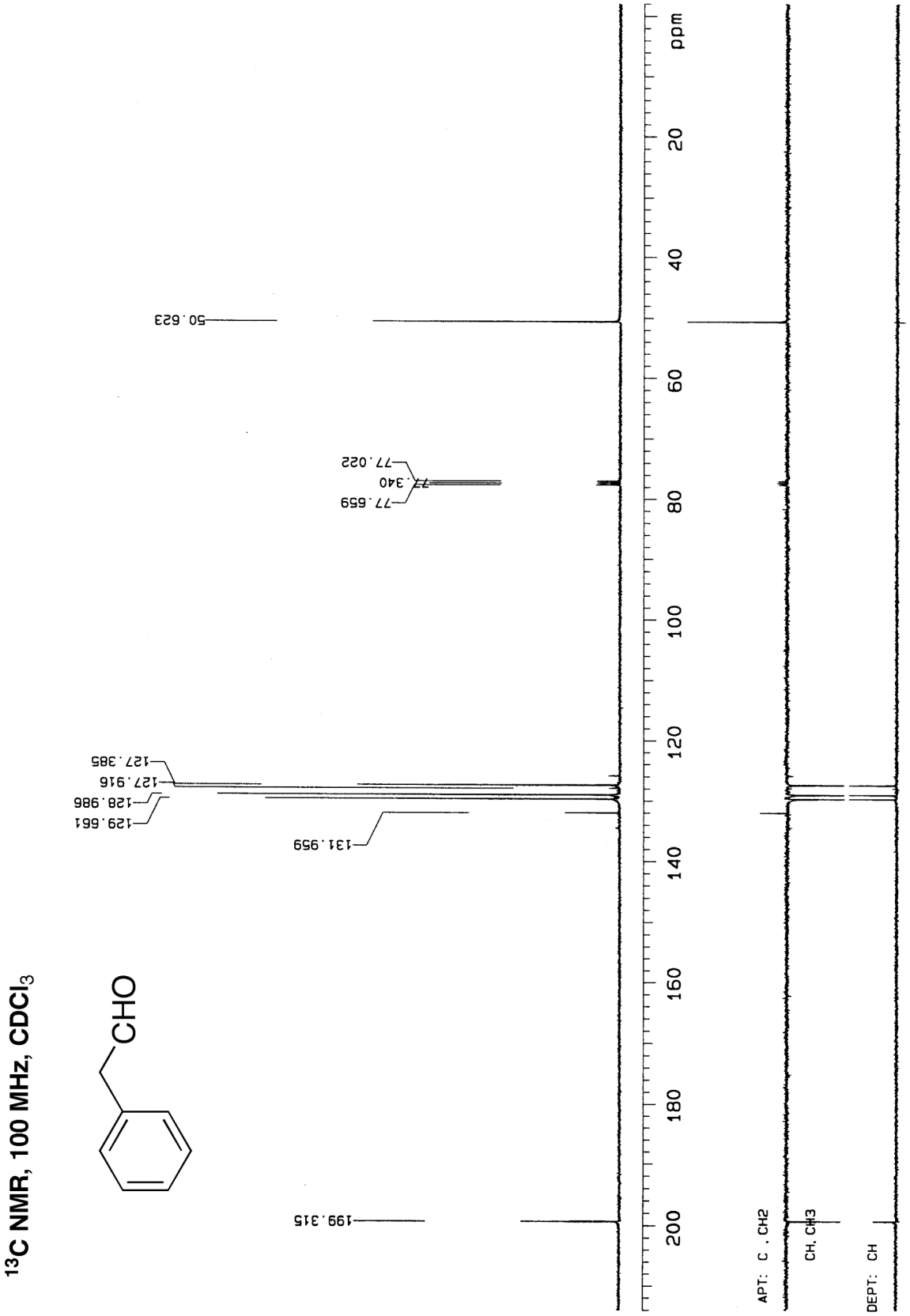
Traces of phosphine-oxide due to NMR sample oxidation in air.

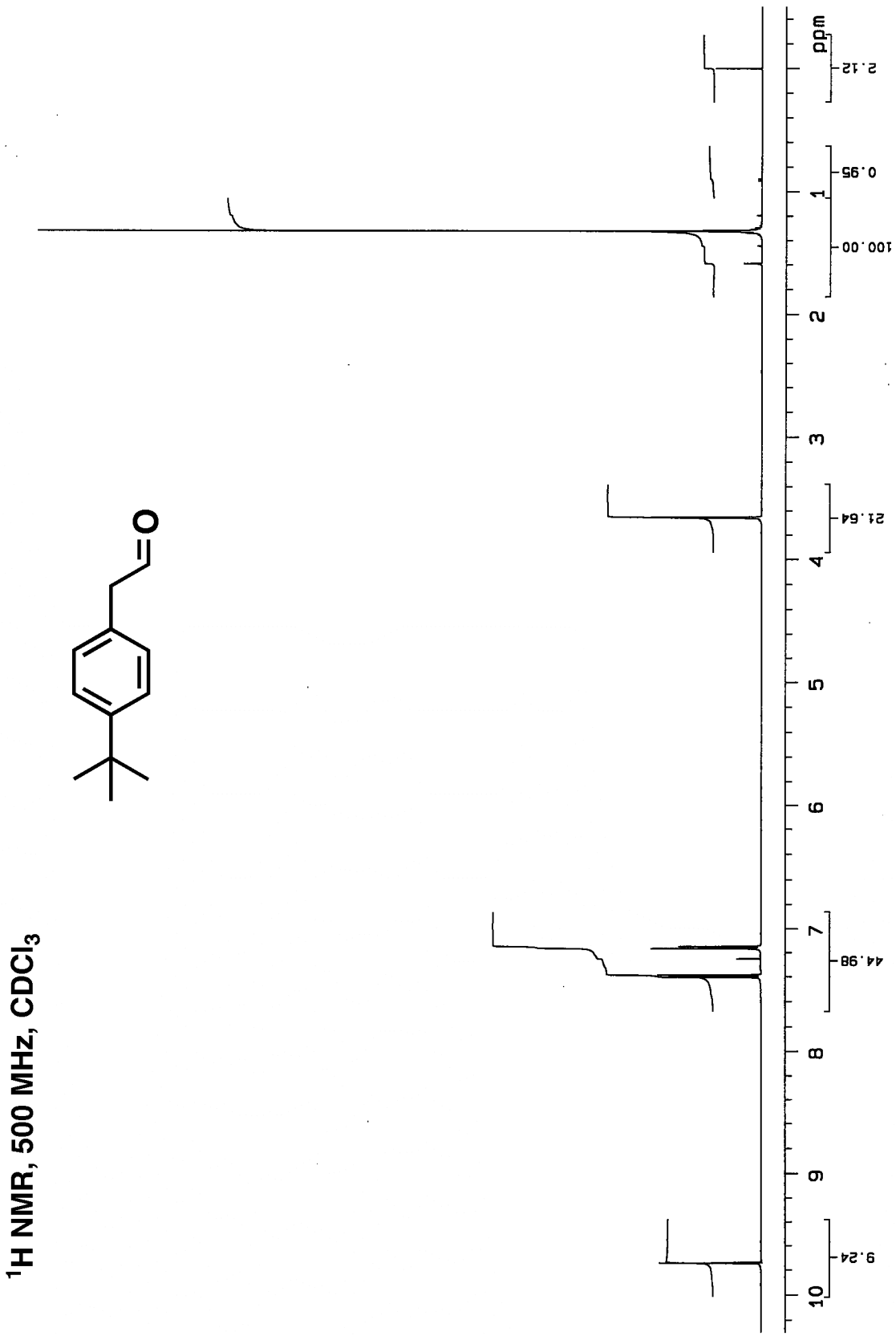
6.2. Hydration Products (Table 1 of the main article)

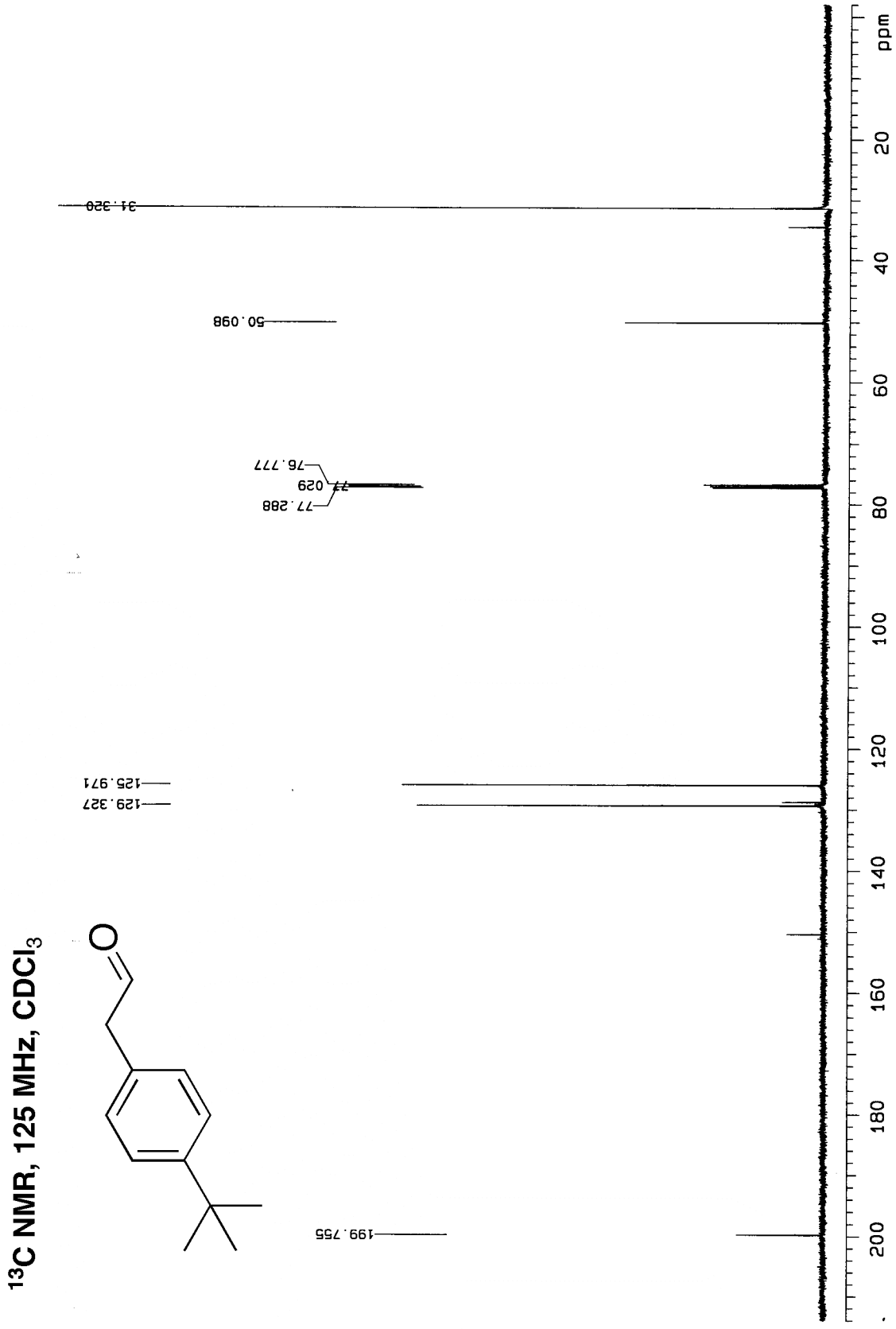


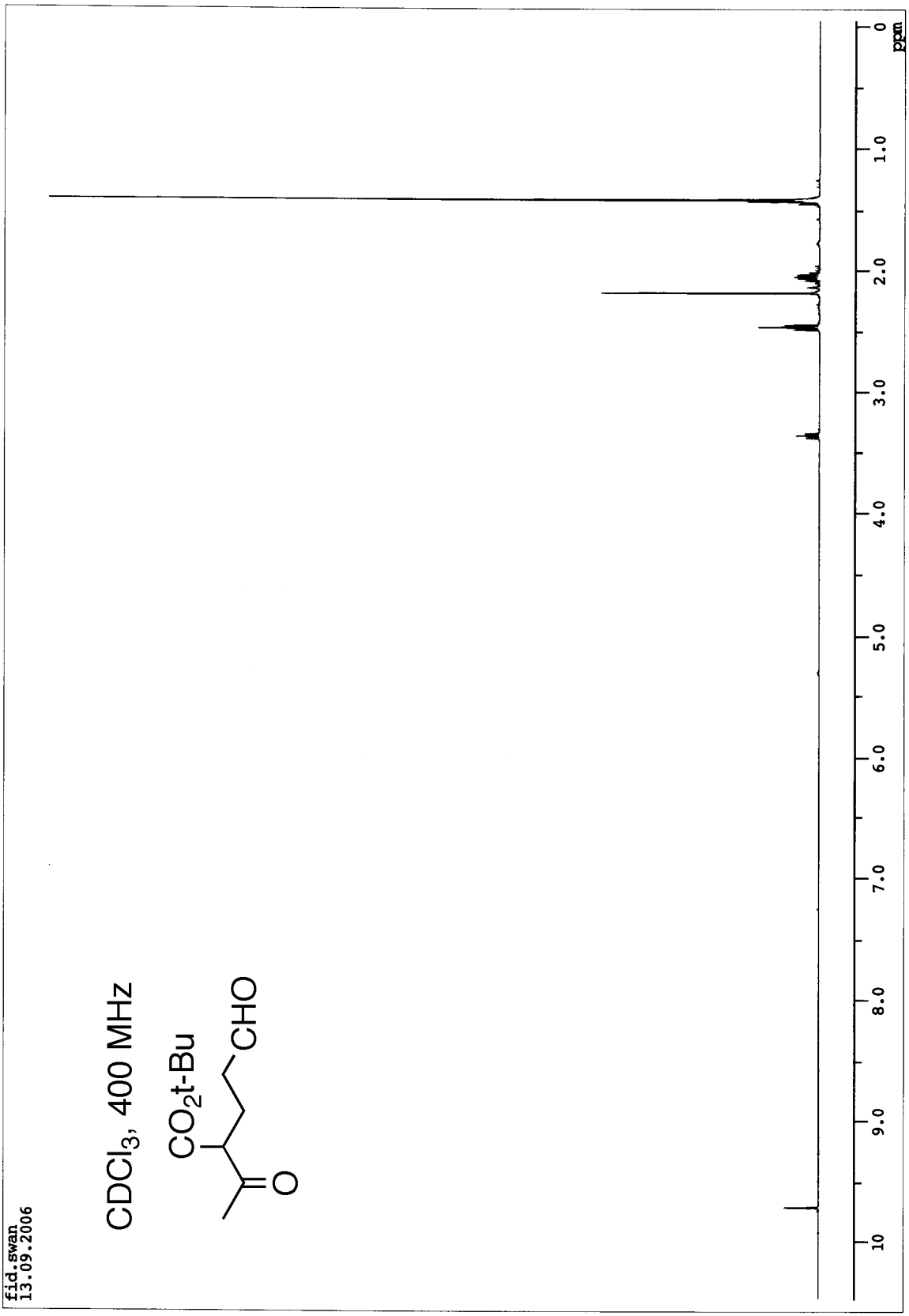

^{13}C NMR, 100 MHz, CDCl$_3$
O
202.676
77.409
77.090
76.779
43.955
31.605
28.904
22.532
22.115
14.066
ppm
20
40
60
80
100
120
140
160
180
200
APT: C , CH2
CH CH3
DEPT: CH

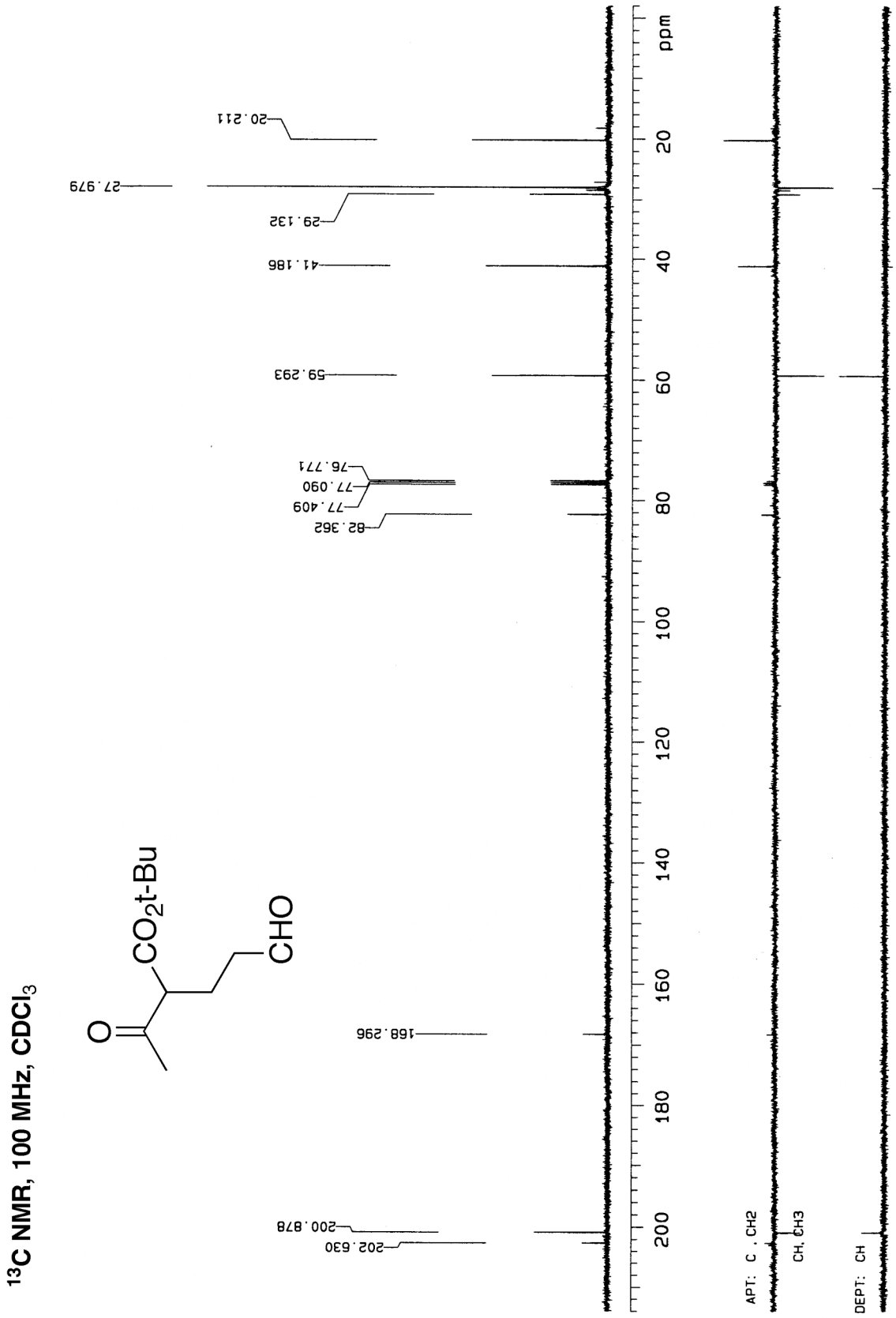

CDCl3, 400 MHz
O
ppm
1
2
3
4
5
6
7
8
9
10
58.35
100.00
14.39


^{13}C NMR, 100 MHz, $CDCl_3$
CHO
199.315
131.959
129.661
128.986
127.916
127.385
77.659
77.340
77.022
50.623
ppm
20
40
60
80
100
120
140
160
180
200
APT: C , CH2
CH, CH3
DEPT: CH

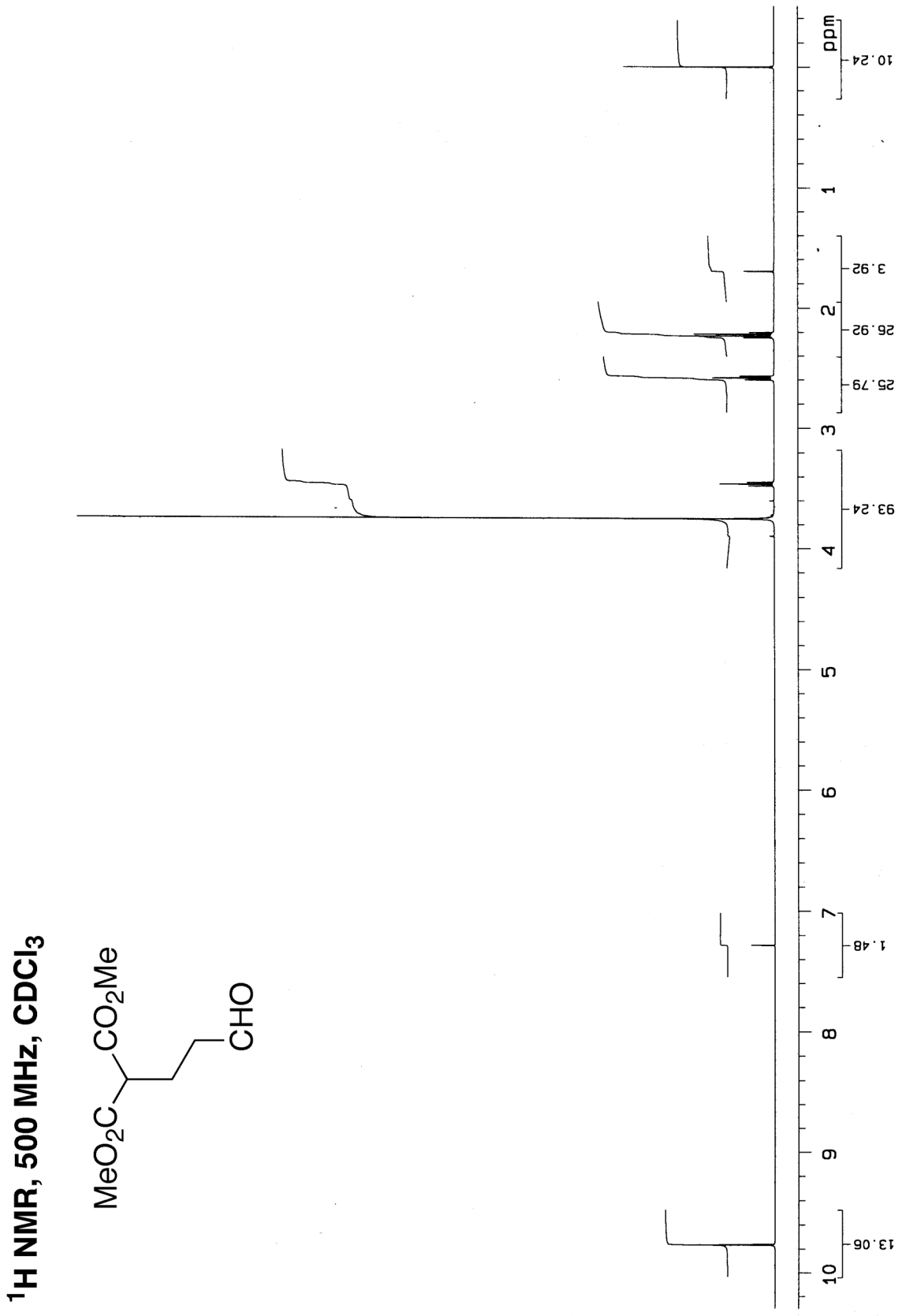

^{1}H NMR, 500 MHz, $CDCl_3$
O
ppm
2.12
0.95
100.00
21.64
44.98
9.24

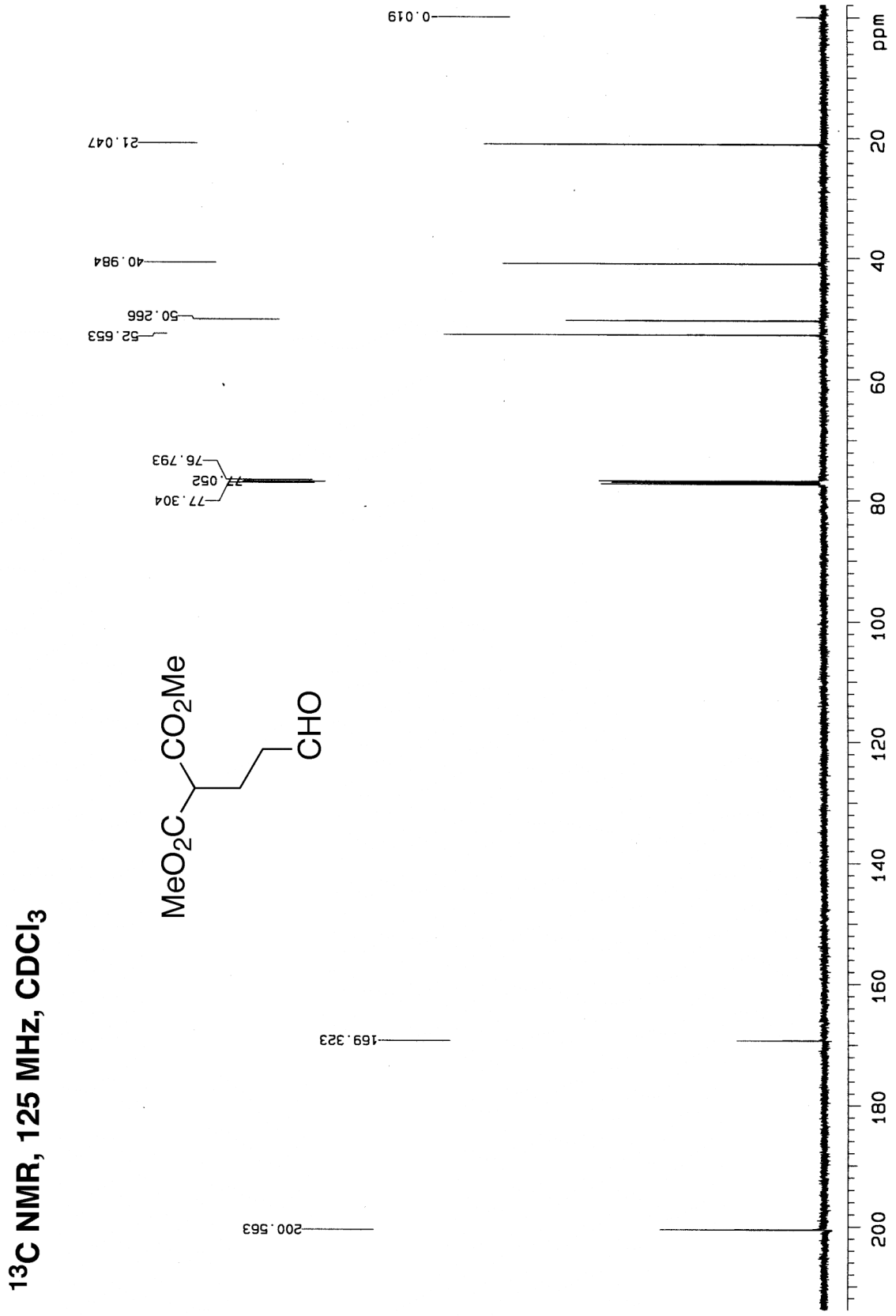

^{13}C NMR, 125 MHz, CDCl$_3$
199.755
129.327
125.971
77.288
77.029
76.777
50.098
31.320
ppm
200
180
160
140
120
100
80
60
40
20

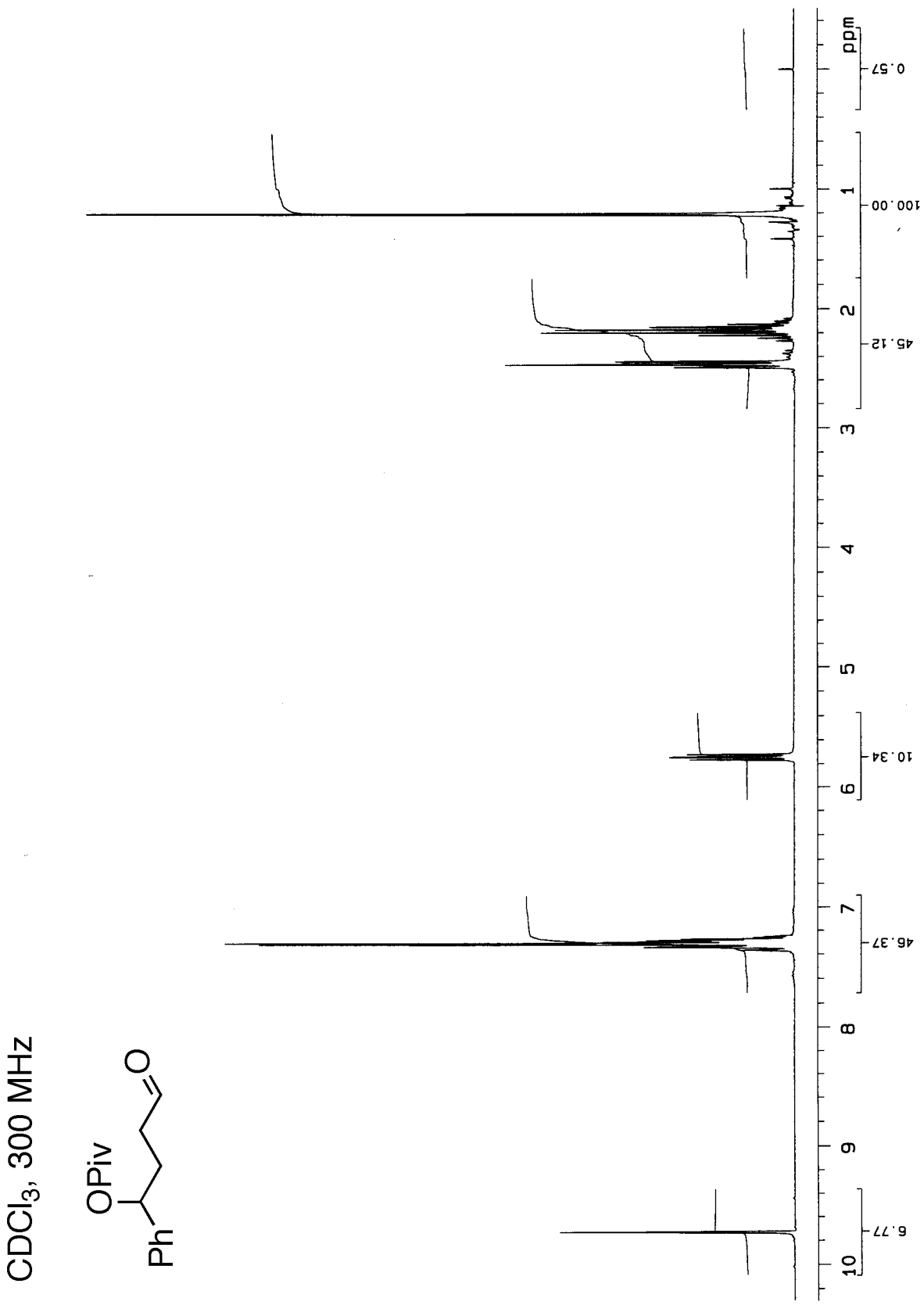

fid.swan
13.09.2006
CDCl3, 400 MHz
CO2t-Bu
CHO
O
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm

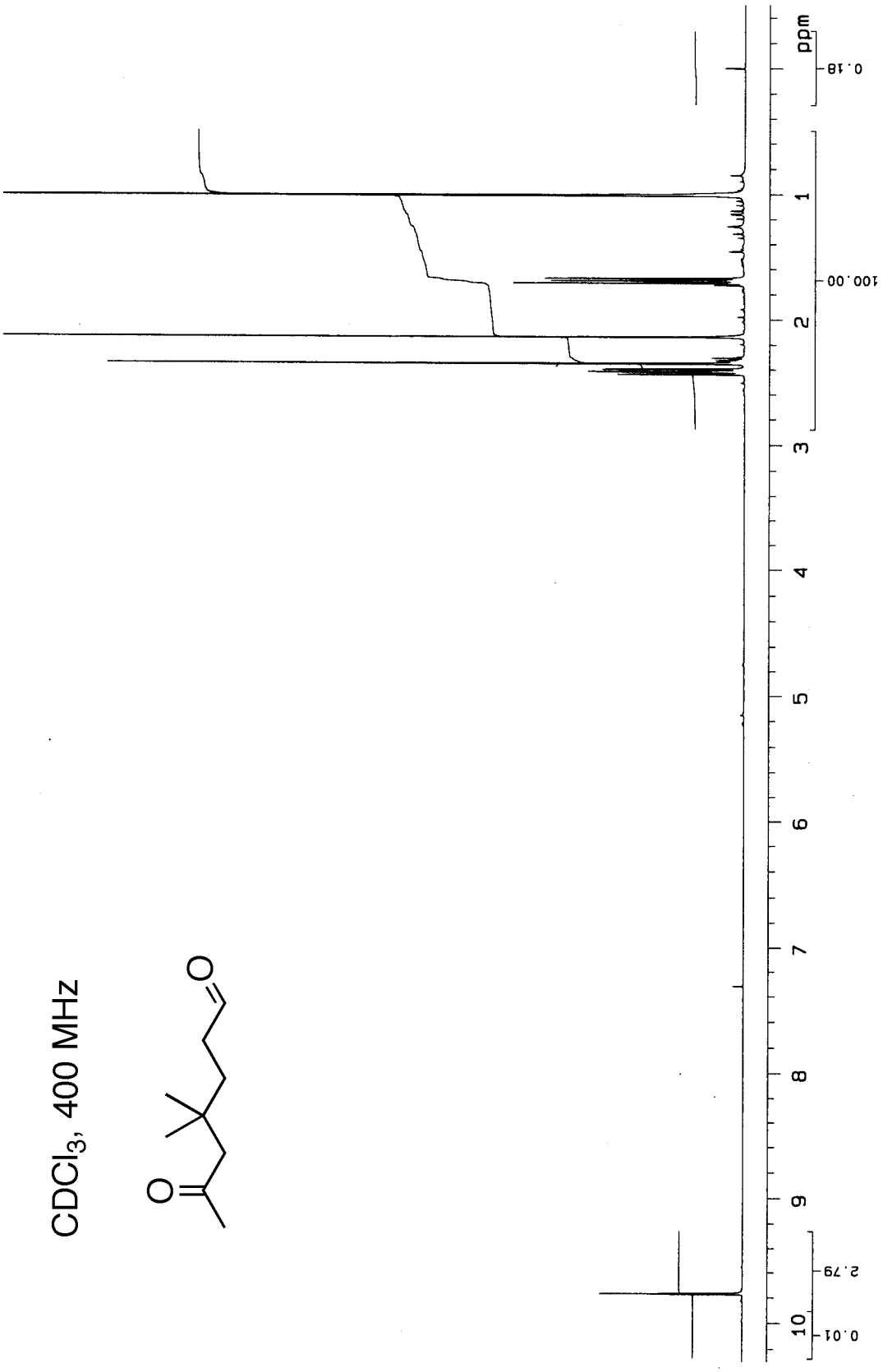

^{13}C NMR, 100 MHz, $CDCl_3$
O
CO_2t-Bu
CHO
202.630
200.878
168.296
82.362
77.409
77.090
76.771
59.293
41.186
29.132
27.979
20.211
ppm
20
40
60
80
100
120
140
160
180
200
APT: C , CH2
CH, CH3
DEPT: CH

^{1}H NMR, 500 MHz, $CDCl_3$




^{13}C NMR, 125 MHz, CDCl$_3$
MeO$_2$C
CO$_2$Me
CHO
200.563
169.323
77.304
77.052
76.793
52.653
50.266
40.984
21.047
0.019
ppm
20
40
60
80
100
120
140
160
180
200


CDCl3, 300 MHz
OPiv
Ph
O
ppm
0.57
100.00
45.12
10.34
46.37
6.77


CDCl3, 400 MHz
O
O
ppm
0.18
100.00
2.79
0.01
1
2
3
4
5
6
7
8
9
10

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