Synthesis of Quaternary Carbon Centers via Hydroformylation

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Supporting Information

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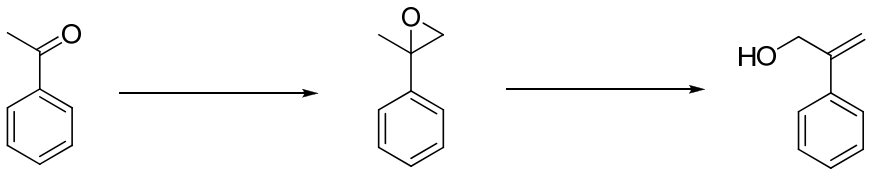
General Considerations

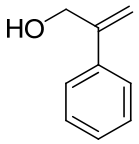
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Flash column chromatography was performed using EMD Silica Gel 60 (230-400 mesh) and ACS grade solvents as received from Fisher Scientific. All experiments were performed in oven or flame dried glassware under an atmosphere of nitrogen or argon using standard syringes, except where otherwise noted. All reactions were run with dry, degassed solvents dispensed from a Glass Contour Solvent Purification System (SG Water, USA LLC). ^{1}H and ^{13}C were performed on either a Varian Unity INOVA 400 MHz or a Varian 500 MHz instrument. Deuterated solvents were purchased from Cambridge Isotope Labs and stored over 3Å molecular sieves. All NMR chemical shifts are reported in ppm relative to residual solvent for ^{1}H and ^{13}C. Coupling constants are reported in Hz. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), br s (broad singlet). All IR spectra were gathered on a Bruker Alpha FT-IR equipped with a single crystal diamond ATR module and values are reported in cm^{-1}. HRMS data were generated in Boston College facilities. Hydroformylation was performed in an Argonaut Technologies Endeavor Catalyst Screening System using 1:1 H_2/CO supplied by Airgas, Inc.

Substrate Syntheses and Characterizations

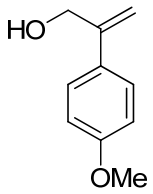


General Procedure A. The substrates were synthesized from the corresponding ketone precursors according to modified literature procedure[1, 2]: To a stirring solution of corresponding ketone substrate (40 mmol) and diiodomethane (4.8 mL, 60 mmol) in anhydrous THF (100 mL) under nitrogen. Methyllithium (27 mL of 3.0 M in diethoxymethane, 80 mmol) was added dropwise at 0 ℃. After stirring at 0 ℃ for 30 min, the mixture was stirred for one additional hour at room temperature. The resulting mixture was treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvents were removed to afford crude epoxide, which was used without further purification. To a stirring solution of dry diisopropylamine (8.5 mL, 60 mmol) in anhydrous Et_2O (60 mL), n-butyllithium (38 mL of 1.6 M in hexanes, 60 mmol) was added at room temperature under nitrogen. The solution was stirred for 45 min, and then a solution of the crude epoxide in anhydrous Et_2O (80 mL) was added dropwise via syringe pump over a period of 1 h. The solution was stirred at room temperature overnight, followed by refluxing for 4 h. The reaction was quenched with aqueous ammonium chloride and extracted with Et_2O (3 × 50 mL), the combined organic layers were washed with 1.0 N HCl (30 mL), aqueous sodium carbonate (30

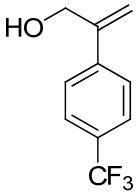
mL) and brine (30 mL), dried over $MgSO_4$ and concentrated. Flash column chromatography (Hex/EtOAc = 8:1) followed by vacuum distillation (bulb-to-bulb) afforded pure alcohol product.



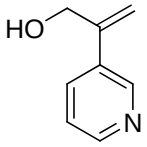
2-Phenylprop-2-en-1-ol. The alcohol was synthesized from acetophenone and was obtained as a colorless liquid (1.3 g, 24 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.46-7.43 (m, 2H), 7.38-7.29 (m, 3H), 5.48 (s, 1H), 5.36 (d, 1H, *J* = 0.8), 4.51 (s, 2H), 2.58 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.1, 138.4, 128.4, 127.8, 125.9, 112.3, 64.6; **IR**: 3332, 1495, 1444, 1024, 902, 778, 705 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{11}O$ $[M+H]^+$: 135.08099, found: 135.08081.



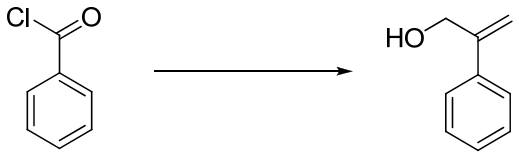
2-(4-Methoxyphenyl)prop-2-en-1-ol. The alcohol was synthesized from 4'-methoxyacetophenone and was obtained as a white solid (2.0 g, 31 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.39 (d, 2H, *J* = 9.2), 6.87 (d, 2H, *J* = 9.2), 5.38 (d, 1H, *J* = 0.6), 5.24 (d, 1H, *J* = 0.9), 4.50 (s, 2H), 3.80 (s, 3H), 1.54 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 159.4, 146.6, 130.8, 127.2, 113.9, 111.1, 65.2, 55.3; **IR**: 3240, 1515, 1253, 1186, 1110, 1029, 897, 838 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.09155, found: 165.09171.



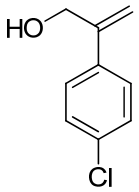
2-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol. The alcohol was synthesized from 4'-(trifluoromethyl)acetophenone and was obtained as a white solid (2.3 g, 28 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.59 (d, 2H, *J* = 8.4), 7.54 (d, 2H, *J* = 8.4), 5.53 (d, 1H, *J* = 0.8), 5.44 (d, 1H, *J* = 1.0), 4.54 (d, 2H, *J* = 5.6), 1.66 (t, 1H, *J* = 2.0); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 146.1,142.1, 129.9 (q, *J* =32.0), 126.4, 125.4, 123.8 (q, *J* = 205.4), 114.8, 64.8 ; **IR**: 3320, 1326, 1166, 1117, 1068, 845 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{10}F_3O$ $[M+H]^+$: 203.06837, found: 203.06881.



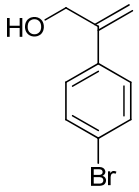
2-(pyridin-3-yl)prop-2-en-1-ol. The alcohol was synthesized from 3-acetylpyridine and was obtained as a colorless liquid (0.63 g, 12 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.66 (d, 1H, *J* = 2.0), 8.49-8.48 (m, 1H), 7.79-7.77 (m, 1H), 7.29-7.26 (m, 1H), 5.51 (d, 1H, *J* = 0.7), 5.48 (d, 1H, *J* = 1.2), 4.54 (s, 2H), 3.57 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.6, 147.3, 144.7, 134.6, 133.8, 123.4, 114.4, 64.4; **IR**: 3212, 1414, 1024, 908, 815, 700, 632 cm^{-1}; **HRMS** (DART-TOF) calcd. for C_8H_9NO $[M+H]^+$: 136.07624, found: 136.07601.



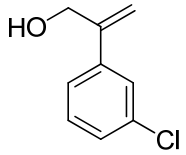
General Procedure B. Substrates were synthesized from the corresponding benzoyl chloride precursors according to literature procedure[3]: To a stirring solution of lithium bromide (3.8 g, 44 mmol), corresponding benzoyl chloride (20 mmol) and chloroiodomethane (3.2 mL, 44 mmol) in anhydrous THF (60 mL) under nitrogen, methyllithium (15 mL of 3.0 M in diethoxymethane, 46 mmol) was added dropwise over 30 min at −78 ℃. After stirring at −78 ℃ for 1 h, the mixture was warmed to room temperature and stirred overnight. Lithium iodide (2.7 g, 20 mmol) was added and solution was stirred for additional 40 h. The reaction was quenched with aqueous ammonium chloride and the solvent was removed. The residue was extracted with Et_2O (3 × 50 mL). Combined organic layers were washed with 0.5 M aqueous sodium thiosulfate (30 mL) and aqueous sodium bicarbonate (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Flash column chromatography (Hex/EtOAc = 8:1), followed by vacuum distillation (bulb-to-bulb), afforded pure alcohol product.



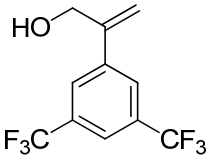
2-(4-Chlorophenyl)prop-2-en-1-ol. The alcohol was synthesized from 4-chlorobenzoyl chloride and was obtained as a colorless liquid (0.91 g, 27 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36 (d, 2H, *J* = 8.8), 7.30 (d, 2H, *J* = 8.8), 5.44 (d, 1H, *J* = 0.8), 5.34 (d, 1H, *J* = 1.2), 4.48 (dd, 2H, *J* = 0.8, 1.2), 2.03 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 146.1, 136.9, 133.7, 128.6, 127.4, 113.3, 64.9; **IR**: 3338, 1493, 1091, 1012, 909, 832 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{10}Cl_1O$ $[M+H]^+$: 169.04202, found: 169.04258.



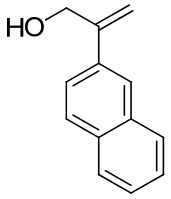
2-(4-Bromophenyl)prop-2-en-1-ol. The alcohol was synthesized from 4-bromobenzoyl chloride and was obtained as a slightly yellow solid (1.3 g, 30 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.45 (d, 2H, *J* = 8.4), 7.30 (d, 2H, *J* = 8.4), 5.45 (d, 1H, *J* = 0.8), 5.34 (d, 1H, *J* = 1.2), 4.48 (s, 2H), 1.77 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 146.1, 137.4, 131.6, 127.7, 121.9, 113.3, 64.8; **IR**: 3326, 1488, 1072, 1007, 907, 828 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{10}Br_1O$ $[M+H]^+$: 212.99150, found: 212.99138.



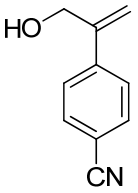
2-(3-Chlorophenyl)prop-2-en-1-ol. The alcohol was synthesized from 3-chlorobenzoyl chloride and was obtained as a colorless liquid (0.78 g, 23 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.42 (s, 1H), 7.33-7.24 (m, 3H), 5.47 (d, 1H, *J* = 0.4), 5.38 (d, 1H, *J* = 0.4), 4.50 (s, 2H), 1.61 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 146.1, 140.4, 134.4, 129.7, 127.9, 126.3, 124.2, 114.0, 64.9; **IR**: 3318, 2924, 1593, 1562, 1478, 1044, 911, 789, 690 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{10}Cl_1O$ $[M+H]^+$: 169.04202, found: 169.04174.



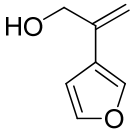
2-(3,5-Bis(trifluoromethyl)phenyl)prop-2-en-1-ol. The alcohol was synthesized from 3,5-bis(trifluoromethyl)benzoyl chloride and was obtained as a colorless liquid (1.3 g, 24 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.88 (s, 2H), 7.79 (s, 1H,), 5.60 (s, 1H), 5.54 (t, 1H, *J* = 1.2), 4.56 (s, 2H), 2.28 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.8, 140.7, 131.8 (q, *J* = 33.5), 126.3, 123.2 (q, *J* = 271.6), 121.5, 116.4, 64.7 ; **IR**: 3328, 1375, 1274, 1171, 1120, 897, 846, 700, 682 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_9F_6O$ $[M+H]^+$: 271.05576, found: 271.05627.



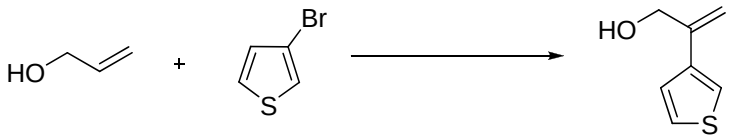
2-(Naphthalen-2-yl)prop-2-en-1-ol. The alcohol was synthesized from 2-naphthoyl chloride and was obtained as a white solid (0.68 mg, 19 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87 (s, 1H), 7.84-7.79 (m, 3H), 7.60 (dd, 1H, *J* = 2.0, 8.4), 7.47-7.44 (m, 2H), 5.61 (d, 1H, *J* = 0.8), 5.45 (d, 1H, *J* = 1.2), 4.66 (s, 2H), 1.63 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.0, 135.6, 133.3, 133.0, 128.2, 128.1, 127.5, 126.2, 126.1, 124.8, 124.3, 113.2, 65.2; **IR**: 3302, 1091, 1044, 901, 860, 824, 746, 480 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{13}H_{13}O$ $[M]^+$: 184.08881, found: 184.08846.



4-(3-Hydroxyprop-1-en-2-yl)benzonitrile. The alcohol was synthesized from 4-cyanobenzoyl chloride and was obtained as a colorless liquid (760 mg, 24 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.67-7.65 (m, 2H), 7.60-7.57 (m, 2H), 5.61 (d, 1H, *J* = 0.6), 5.53 (d, 1H, *J* = 0.6), 4.57 (s, 2H), 1.81 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.7, 143.1, 132.3, 126.8, 118.8, 115.9, 111.3, 64.6; **IR**: 3414, 2227, 1605, 1504, 1403, 1105, 1016, 914, 842, 542 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{10}NO$ $[M+H]^+$: 160.07624, found: 160.07571.

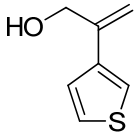


2-(furan-3-yl)prop-2-en-1-ol. The alcohol was synthesized from 3-furoyl chloride and was obtained as a light yellow liquid (0.96 g, 39 %). Characterization data of this compound was previously reported.[4]

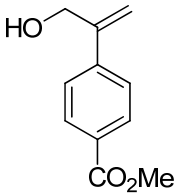


General Procedure C. Substrates were synthesized from allyl alcohol and the corresponding aryl bromide precursors according to literature procedure[5]. To the oven dried 25 mL round

bottomed flask charged with palladium(II) acetate (90 mg, 0.40 mmol) and 1,3-bis(diphenylphosphino)propane (330 mg, 0.80 mmol), corresponding aryl bromide (10 mmol, see below), solvent (20 mL, see below), 2-propen-1-ol (3.4 mL, 50 mmol) and triethylamine (2.2 mL, 16 mmol) were added under nitrogen. After stirring at 125 ℃ for 30 h, reaction was cooled to room temperature and 1.0 N HCl (100 mL) was added, followed by stirring at rt for 1 h. Aqueous sodium carbonate (100 mL) was added and reaction was stirred for additional 10 min. The resulting mixture was extracted with CH_2Cl_2 (3 × 80 mL). Combined organic layers were washed with H_2O (30 mL) and brine (30 mL), dried over Na_2SO_4, and solvent was removed. Flash column chromatography (Hex/EtOAc = 8:1) afforded pure alcohol product.



2-(Thiophen-3-yl)prop-2-en-1-ol. The alcohol was synthesized from 3-bromothiophene with anhydrous [bmim][BF_4] as solvent and was obtained as a white solid (210 mg, 15 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.24 (m, 3H), 5.48 (s, 1H), 5.30 (s, 1H), 4.49 (s, 2H), 1.57 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.0, 139.7, 125.6, 120.8, 111.4, 79.2, 65.2; **IR**: 3333, 3104, 2923, 1461, 1106, 1038, 901, 872, 790, 730, 602 cm^{-1}; **HRMS** (DART-TOF) calcd. for C_7H_9OS $[M+H]^+$: 141.03741, found: 141.03739.



Methyl 4-(3-hydroxyprop-1-en-2-yl)benzoate. The alcohol was synthesized from methyl 4-bromobenzoate with anhydrous [bmim][BF_4] and anhydrous DMSO (1:1) as solvent and was obtained as a slightly yellow solid (810 mg, 42 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.03 (d, 2H, *J* = 7.0), 7.41 (d, 2H, *J* = 7.0), 5.59 (s, 1H), 5.48 (s, 1H), 4.58 (d, 2H, *J* = 5.5), 3.93 (s, 3H), 1.59 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 166.8, 146.5, 143.0, 129.8, 129.5, 126.0, 114.7, 64.8, 52.1; **IR**: 3315, 1718, 1432, 1284, 1193, 1099, 905, 722 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.08647, found: 193.08643.

Optimization of Branch Selective Hydroformylation

General Hydroformylation Procedure A. The oven dried glass reaction vial was placed in the Endeavor, and 2-phenylprop-2-en-1-ol (20 mg, 0.15 mmol) was added. The Endeavor was

sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (1.6 mg, 6.0×10^{-3} mmol, 4.0 mol %), ligand **1** (8.6 mg, 3.0×10^{-2} mmol, 20 mol %), p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol, 0.20 mol %) and benzene (to total volume of 1 mL) was injected, followed by injection of additional benzene (0.5 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at corresponding temperature (see below) for 10 minutes. Stirring was stopped, the Endeavor was charged with corresponding pressure (see below) of H_2/CO, stirring was re-initiated at 700 rpm., and the Endeavor was maintained at a constant temperature (see below) and pressure (see below) of H_2/CO for 12 h. The Endeavor was vented to ambient pressure and cooled to ambient temperature. The reaction mixture was removed from the Endeavor and concentrated. The residue was redissolved in t-butanol (0.75 mL) and 2-methyl-2-butene (0.16 mL, 1.5 mmol, 10.0 eq.) followed by addition of a solution of $NaClO_2$ (80 %, 68 mg, 0.60 mmol, 4.0 eq.) and NaH_2PO_4 (72 mg, 0.60 mmol, 4.0 eq.) in H_2O (0.4 mL). The solution was stirred at room temperature overnight. The resulting mixture was concentrated and redissolved in EtOAc (0.75 mL), followed by addition of 10 % HCl (0.18 ml) and brine (0.18 mL). The solution was extracted with EtOAc (3 × 5 mL). Combined organic layers were dried over $MgSO_4$, filtered and solvent was removed. 1,3,5-Trimethoxybenzene (100 μL of 0.15 M in $CDCl_3$, 0.015 mmol) was added as standard and ^{1}H NMR was taken to analyze yields and selectivities.

General Hydroformylation Procedure B. The oven dried glass reaction vial was placed in the Endeavor, and 2-phenylprop-2-en-1-ol (80 mg, 0.60 mmol) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), triphenylphosphine (13 mg, 4.8×10^{-2} mmol, 8.0 mol %) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 45 ℃ for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature and pressure of 45 ℃ and 400 psi H_2/CO for 12 h. The Endeavor was vented to ambient pressure and cooled to ambient temperature. The reaction was removed from the Endeavor and concentrated. 1,3,5-Trimethoxybenzene (400 μL of 0.15 M in $CDCl_3$, 0.060 mmol) was added as standard and ^{1}H NMR was taken to analyze conversion.

General Hydroformylation Procedure C. The oven dried glass reaction vial was placed in the Endeavor, and 2-phenylprop-2-en-1-ol (80 mg, 0.60 mmol) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), triphenylphosphine (13 mg, 4.8×10^{-2} mmol, 8.0 mol %) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 75 ℃ for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature and pressure of 75 ℃ and 400 psi H_2/CO for 12 h. The Endeavor was vented to ambient pressure and cooled to ambient

temperature. The reaction was removed from the Endeavor and concentrated. The residue was redissolved in t-butanol (3 mL) and 2-methyl-2-butene (0.64 mL, 6.0 mmol, 10.0 eq.) followed by addition of a solution of $NaClO_2$ (80 %, 270 mg, 2.4 mmol, 4.0 eq.) and NaH_2PO_4 (290 mg, 2.4 mmol, 4.0 eq.) in H_2O. The solution was stirred at room temperature overnight. The resulting mixture was concentrated and redissolved in EtOAc (3 mL), followed by addition of 10 % HCl (0.75 ml) and brine (0.75 mL). The solution was extracted with EtOAc (3 × 20 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. ^{1}H NMR was taken to analyze selectivity. Flash column chromatography (Hex/EtOAc = 8/1) was performed to determine isolated yields.

Table 1, Entry 1:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure C. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of < 2:98. Linear product was isolated as a white solid (64.0 mg, 66 %).

Table 1, Entry 2:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 200 psi CO/H_2 at 35 ℃. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 96:4 and yield of 54 %.

Table 1, Entry 3:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 200 psi CO/H_2 at 45 ℃. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 95:5 and yield of 61 %.

Table 1, Entry 4:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 200 psi CO/H_2 at 55 ℃. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 95:5 and yield of 50 %.

Table 1, Entry 5:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 50 psi CO/H_2 at 45 ℃. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 89:11 and yield of 38 %.

Table 1, Entry 6:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 100 psi CO/H_2 at 45 ℃. Analysis of crude mixture after oxidation by ^1H NMR showed a b:l selectivity of 94:6 and yield (53 %).

Table 1, Entry 7:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure A with 400 psi CO/H_2 at 45 ℃. Analysis of crude mixture after oxidation by ^1H NMR showed a b:l selectivity of 97:3 and yield of 70 %.

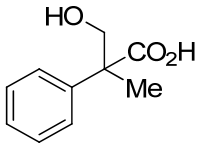
Table 1, Entry 8:

2-Phenylprop-2-en-1-ol was hydroformylated using General Procedure B. Analysis of crude mixture after hydroformylation by ^1H NMR showed 0% conversion.

Hydroformylation Using Ligand 1 and Product Characterizations

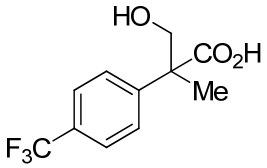
General Hydroformylation Procedure. The oven dried glass reaction vial was placed in the Endeavor, and corresponding alcohol substrate (0.60 mmol, see below) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), ligand **1** (34 mg, 0.12 mmol, 20 mol %), p-toluenesulfonic acid (see below) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 35 ℃ (or 45 ℃, see below) for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature (see below) and pressure (see below) of H_2/CO for 12 h (or 16 h, see below). The Endeavor was vented to ambient pressure and cooled to ambient temperature. The reaction was removed from the Endeavor and concentrated. The residue was redissolved in t-butanol (3 mL) and 2-methyl-2-butene (0.64 mL, 6.0 mmol, 10.0 eq.) followed by addition of a solution of $NaClO_2$ (80 %, 270 mg, 2.4 mmol, 4.0 eq.) and NaH_2PO_4 (290 mg, 2.4 mmol, 4.0 eq.) in H_2O. The solution was stirred at room temperature overnight. The resulting mixture was concentrated and redissolved in EtOAc (3 mL), followed by addition of 10 % HCl (0.75 ml) and brine (0.75 mL). The solution was extracted with EtOAc (3 × 20 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated. ^1H NMR was taken to analyze selectivities. Flash column chromatography (Hex/EtOAc = 4/1) afforded pure branched products.

Table 1, Entry 7:



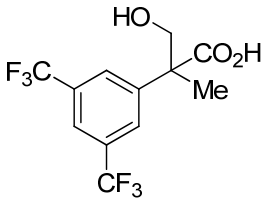
3-Hydroxy-2-methyl-2-phenylpropanoic acid. 2-Phenylprop-2-en-1-ol (80 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed selectivity (b:l = 97:3). Branched product was isolated as a white solid (79 mg, 73 %)**.** **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36-7.24 (m, 5H), 6.98 (br s, 1H), 4.09 (d, 1H, *J* = 11.6), 3.66 (d, 1H, *J* = 11.2), 1.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.2, 139.5, 128.7, 127.6, 126.3, 69.1, 52.4, 20.0; **IR**: 2982, 1701, 1239, 1026, 698 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{16}NO_3$ $[M+NH_4]^+$: 198.11302, found: 198.11247.

Table 2, Entry 1:



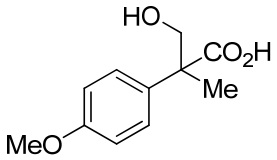
3-Hydroxy-2-methyl-2-(4-(trifluoromethyl)phenyl)propanoic acid. 2-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (120 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 96:4. Branched product was isolated as a white solid (126 mg, 85 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.54 (d, 2H, *J* = 8.5), 7.41 (d, 2H, *J* = 8.5), 7.12 (br s, 1H), 4.00 (d, 1H, *J* = 11.5), 3.66 (d, 1H, *J* = 11.5), 1.61 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 180.4, 143.6, 129.9 (q, *J* = 32.5), 126.9, 125.6, 123.9 (q, *J* = 270.1), 68.7, 52.5, 20.2; **IR**: 2946, 1708, 1328, 1167, 1124, 1066, 1016, 837 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{12}F_3O_3$ $[M+H]^+$: 249.07385, found: 249.07392.

Table 2, Entry 2:



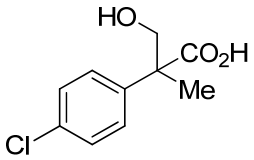
2-(3,5-Bis(trifluoromethyl)phenyl)-3-hydroxy-2-methylpropanoic acid. 2-(3,5-Bis(trifluoromethyl)phenyl)prop-2-en-1-ol (160 mg, 0.60 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (152 mg, 80 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.86 (s, 3H), 4.06 (d, 1H, *J* = 11.5), 3.89 (d, 1H, *J* = 11.5), 1.75 (s, 3H); **^{13}C NMR** (Acetone d-6, 125 MHz) δ 174.6, 145.3, 130.9 (q, *J* = 32.9), 127.9, 123.7 (q, *J* = 270.1), 120.6, 67.6, 52.5, 20.1; **IR**: 2924, 1711, 1373, 1287, 1187, 1132 cm^{-1}; **HRMS** (DART-TOF) calcd. For $C_{12}H_{14}F_6NO_3$ $[M+NH_4]^+$: 334.08779, found: 334.08865.

Table 2, Entry 3:



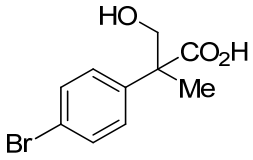
3-Hydroxy-2-(4-methoxyphenyl)-2-methylpropanoic acid. 2-(4-Methoxyphenyl)prop-2-en-1-ol (98 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 35 ℃ for 16 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (83 mg, 66 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.21 (d, 2H, *J* = 8.5), 6.99 (br s, 1H), 6.81 (d, 2H, *J* = 8.5), 4.00 (d, 1H, *J* = 11.5), 3.72 (s, 3H), 3.56 (d, 1H, *J* = 11.5), 1.58 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 181.3, 158.9, 131.5, 127.4, 114.1, 69.1, 55.2, 51.6, 20.1; **IR**: 2937, 1703, 1514, 1253, 1187, 1029, 829 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{18}NO_4$ $[M+NH_4]^+$: 228.12358, found: 228.12384.

Table 2, Entry 4:



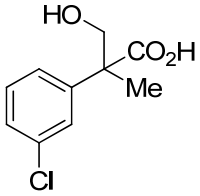
2-(4-Chlorophenyl)-3-hydroxy-2-methylpropanoic acid. 2-(4-Chlorophenyl)prop-2-en-1-ol (100 mg, 0.60 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol) at 35 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 97:3. Branched product was isolated as a white solid (78 mg, 60 %)**. ^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.33-7.24 (m, 4H), 6.54 (br s, 1H), 4.04 (d, 1H, *J* = 11.2), 3.66 (d, 1H, *J* = 11.6), 1.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.6, 138.1, 133.6, 128.8, 127.8, 68.9, 52.0, 20.1; **IR**: 2941, 1702, 1494, 1260, 1098, 1034, 1013, 824 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{15}Cl_1NO_3$ $[M+NH_4]^+$: 232.07405, found: 232.07432.

Table 2, Entry 5:



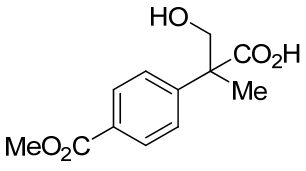
2-(4-Bromophenyl)-3-hydroxy-2-methylpropanoic acid. 2-(4-Bromophenyl)prop-2-en-1-ol (130 mg, 0.60 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol) at 35 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 94:6. Branched product was isolated as a white solid (110 mg, 71 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, 1H, *J* = 8.8), 7.22 (d, 1H, *J* = 8.8), 7.05 (br s, 1H), 4.03 (d, 1H, *J* = 11.6), 3.66 (d, 1H, *J* = 11.6), 1.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.7, 138.5, 131.8, 128.1, 121.8, 68.8, 52.0, 20.0; **IR**: 2938, 1703, 1491, 1398, 1241, 1034, 1009, 820 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{15}Br_1NO_3$ $[M+NH_4]^+$: 276.02353, found: 276.02357.

Table 2, Entry 6:



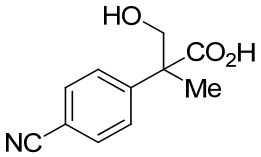
2-(3-Chlorophenyl)-3-hydroxy-2-methylpropanoic acid. 2-(3-Chlorophenyl)prop-2-en-1-ol (100 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 35 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (99 mg, 77 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.33 (s, 1H), 7.27-7.20 (m, 3H), 7.25 (br s, 1H), 4.04 (d, 1H, *J* = 11.2), 3.66 (d, 1H, *J* = 11.6), 1.63 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.3, 141.6, 134.6, 129.9, 127.8, 126.7, 124.6, 68.7, 52.2, 20.0; **IR**: 2982, 1703, 1244, 1035, 698 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{12}Cl_1O_3$ $[M+H]^+$: 215.04750, found: 215.04853.

Table 2, Entry 7:



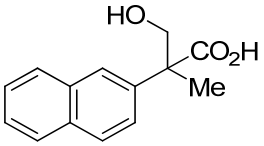
3-Hydroxy-2-(4-(methoxycarbonyl)phenyl)-2-methylpropanoic acid. Methyl 4-(3-hydroxyprop-1-en-2-yl)benzoate (120 mg, 0.60 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (106 mg, 74 %). **^{1}H NMR** (Acetone d-6, 400 MHz) δ 7.96 (d, 2H, *J* = 8.6), 7.53 (d, 2H, *J* = 8.6), 4.10 (d, 1H, *J* = 10.8), 3.86 (s, 3H), 3.84 (d, 1H, *J* = 10.8), 1.62 (s, 3H); **^{13}C NMR** (Acetone d-6, 100 MHz) δ 175.2, 166.1, 147.3, 129.2, 128.7, 126.7, 67.9, 52.5, 51.4, 20.2; **IR**: 2952, 1719, 1437, 1282, 1194, 1115, 1018, 707 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{12}H_{15}O_5$ $[M+H]^+$: 239.09195, found: 239.09209.

Table 2, Entry 8:



2-(4-Cyanophenyl)-3-hydroxy-2-methylpropanoic acid. 4-(3-Hydroxyprop-1-en-2-yl)benzonitrile (96 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (82 mg, 67 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40 (br s, 1H), 7.64 (d, 2H, *J* = 8.4), 7.48 (d, 2H, *J* = 8.4), 4.02 (d, 1H, *J* = 11.2), 3.76 (d, 1H, *J* = 11.2), 1.66 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 179.5, 145.0, 132.4, 127.4, 118.3, 111.6, 68.5, 52.6, 20.2; **IR**: 3362, 2240, 1721, 1220, 1034, 836, 677, 558 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{12}NO_3$ $[M+H]^+$: 206.08172, found: 206.08261.

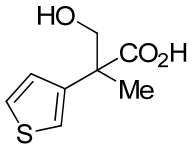
Table 2, Entry 9:



3-Hydroxy-2-methyl-2-(naphthalen-2-yl)propanoic acid. 2-(Naphthalen-2-yl)prop-2-en-1-ol (110 mg, 0.60 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (500 μL of 6.0×10^{-4} M in benzene, 3.0×10^{-4} mmol) at 35 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 95:5. Branched product was isolated as a white solid (117 mg, 85 %). **^{1}H NMR** (Acetone d-6, 500 MHz) δ 7.94-7.87 (m, 4H), 7.61-7.59 (m, 1H), 7.51-7.49 (m, 2H), 5.15-3.23 (br s, 1H), 4.28 (d, 1H, *J* = 10.5), 4.19 (br s, 1H), 3.95 (d, 1H, *J* = 11.0), 2.81 (s, 1H), 1.77 (s, 3H); **^{13}C NMR** (Acetone d-6, 125 MHz) δ 175.9, 139.4, 133.5, 132.5,

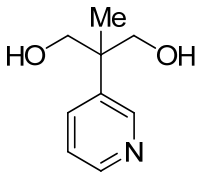
128.0, 127.8, 127.4, 126.0, 125.9, 125.0, 125.0, 68.2, 52.4, 20.4; **IR**: 2921, 1697, 1027, 816, 751, 477 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{14}H_{18}NO_3$ $[M+NH_4]^+$: 248.12867, found: 248.12972.

Table 2, Entry 10:



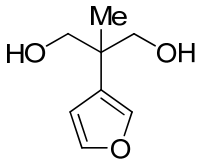
3-Hydroxy-2-methyl-2-(thiophen-3-yl)propanoic acid. 2-(Thiophen-3-yl)prop-2-en-1-ol (84 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 95:5. Branched product was isolated as a white solid (78 mg, 70 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.32-7.31 (m, 1H), 7.24 (d, 1H, *J* = 1.5), 7.13-7.12 (m, 1H), 6.87 (br s, 1H), 4.11 (d, 1H, *J* = 11.2), 3.72 (d, 1H, *J* = 11.2), 1.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 180.3, 140.5, 126.3, 125.9, 121.7, 68.7, 50.1, 20.6; **IR**: 2925, 1698, 1222, 1029, 871, 782, 684 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_8H_{10}O_3S$ $[M+NH_4]^+$: 204.06944, found: 204.07035.

Table 2, Entry 11:



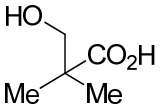
2-methyl-2-(pyridin-3-yl)propane-1,3-diol. 2-(pyridin-3-yl)prop-2-en-1-ol (20 mg, 0.15 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (0.50 mL of 6.0×10^{-4} M in benzene, 0.30×10^{-3} mmol) at 45 ℃ for 12 h. Reduction with $NaBH_4$ (17 mg, 0.45 mmol) and MeOH (3.0 mL) at rt for 2h was performed instead of oxidation. Analysis of crude mixture after reduction by ^{1}H NMR showed a b:l selectivity of 98:2. Branched product was isolated as a white solid (17 mg, 68 %). **^{1}H NMR** (Methanol d-4, 500 MHz) δ 8.65 (d, 1H, *J* = 1.7), 8.39 (dd, 1H, *J* = 1.5, 4.9), 7.96-7.94 (m, 1H), 7.43-7.40 (m, 1H), 3.84 (d, 2H, *J* = 11.0), 3.75 (d, 2H, *J* = 11.0), 1.37 (s, 3H); **^{13}C NMR** (Methanol d-4, 125 MHz) δ 147.7, 146.0, 140.7, 135.9, 123.4, 77.0, 43.8, 18.8; **IR**: 3346, 2812, 1416, 1020, 820, 713, 632 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{14}NO_2$ $[M+H]^+$: 168.10245, found: 168.10277.

Table 2, Entry 12:



2-(furan-3-yl)-2-methylpropane-1,3-diol. 2-(furan-3-yl)prop-2-en-1-ol (37 mg, 0.30 mmol) was hydroformylated with 0.05 mol % p-toluenesulfonic acid (0.25 mL of 6.0×10^{-4} M in benzene, 0.15×10^{-3} mmol) at 55 ℃ for 16 h. Reduction with $NaBH_4$ (34 mg, 0.90 mmol) and MeOH (6.0 mL) at rt for 2h was performed instead of oxidation. Analysis of crude mixture after reduction by ^{1}H NMR showed a b:l selectivity of > 98:2. Branched product was isolated as a white solid (30 mg, 64 %). **^{1}H NMR** (Methanol d-4, 500 MHz) δ 7.42 (t, 1H, *J* = 1.8), 7.38 (dd, 1H, *J* = 1.0, 1.5), 6.46 (dd, 1H, *J* = 1.0, 2.0), 3.65 (d, 2H, *J* = 10.8), 3.61 (d, 2H, *J* = 10.8), 1.22 (s, 3H); **^{13}C NMR** (Methanol d-4, 125 MHz) δ 142.2, 139.0, 128.8, 109.0, 67.1, 40.0, 18.8; **IR**: 3363, 2934, 2879, 1027, 875, 789, 601 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_8H_{13}O_3$ $[M+H]^+$: 157.08647, found: 157.08589.

Table 2, Entry 13:

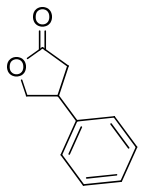


3-hydroxy-2,2-dimethylpropanoic acid. 2-methylprop-2-en-1-ol (43 mg, 0.60 mmol) was hydroformylated with 0.20 mol % p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol) at 45 ℃ for 12 h. Analysis of crude mixture after oxidation by ^{1}H NMR showed a b:l selectivity of 76:24. Branched product was isolated as a white solid (35 mg, 49 %). **^{1}H NMR** (Acetone d-6, 500 MHz) δ 3.57 (s, 2H), 1.16 (s, 6H); **^{13}C NMR** (Acetone d-6, 125 MHz) δ 117.8, 68.8, 43.8, 21.4; **IR**: 2933, 1692, 1236, 1044 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_5H_{14}NO_3$ $[M+NH_4]^+$: 136.09737, found: 136.09743.

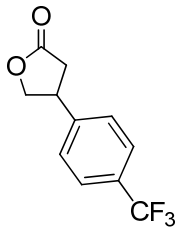
Linear Product Syntheses and Characterizations

General Procedure. The oven dried glass reaction vial was placed in the Endeavor, and corresponding alcohol substrates (0.60 mmol) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), triphenylphosphine (13 mg, 4.8×10^{-2} mmol, 8.0 mol %) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 75 ℃ for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature and pressure of 75 ℃ and 400 psi H_2/CO for

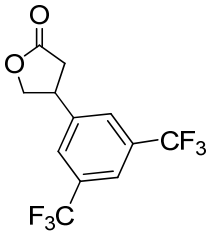
16 h. The Endeavor was vented to ambient pressure and cooled to ambient temperature. The sample was removed and concentrated. The crude residue was dissolved in CH_2Cl_2 (9 mL) and pyridinium chlorochromate (390 mg, 1.8 mmol, 3.0 eq.), sodium acetate (25 mg, 0.30 mmol, 0.50 eq.), and 3Å molecular sieves (1.2 g, 4-8 mesh) were added and the solution was agitated on an orbital shaker for 12 hours. Flash column chromatography (Hex/EtOAc = 8/1) afforded pure products.



4-Phenyldihydrofuran-2(3*H*)-one (83 mg, 85 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.39 (t, 2H, *J* = 7.6), 7.31 (t, 1H, *J* = 7.3), 7.25 (d, 2H, *J* = 7.6), 4.69 (dd, 1H, *J* = 7.8, 9.1), 4.28 (dd, 1H, *J* = 8.1, 9.1), 3.80 (m, 1H), 2.94 (dd, 1H, *J* = 8.8, 17.6), 2.69 (dd, 1H, *J* = 9.0, 17.4); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 176.3, 139.4, 129.2, 127.7, 126.7, 74.0, 41.1, 35.7; **IR** 1759, 1156, 1007, 760, 702 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.07590, found 163.07652.

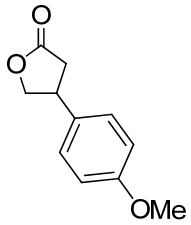


4-(4-(Trifluoromethyl)phenyl)dihydrofuran-2(3H)-one (118 mg, 85 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.61 (d, 2H, *J* = 8.4), 7.35 (d, 2H, *J* = 8.2), 4.70-4.65 (dd, 1H, *J* = 7.8, 9.2), 4.29-4.24 (dd, 1H, *J* = 7.6, 9.2), 3.88-3.80 (m, 1H), 2.95 (dd, 1H, *J* = 8.8, 17.4), 2.65 (dd, 1H, *J* = 8.4, 17.6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 175.7, 143.7, 130.1 (q, *J* = 32.5), 127.2, 126.1, 123.9 (q, *J* = 270.5), 73.4, 40.8, 35.5; **IR** 1771, 1324, 1164, 1117, 1066, 1018, 833 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{10}F_3O_2$ $[M+H]^+$: 231.06329, found 231.06376.

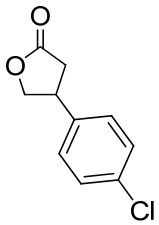


4-(3,5-Bis(trifluoromethyl)phenyl)dihydrofuran-2(3H)-one (130 mg, 72 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.86 (s, 1H), 7.28 (s, 2H), 4.77 (dd, 1H, *J* = 8.1, 9.0), 4.34 (dd, 1H, *J* = 8.1, 9.3),

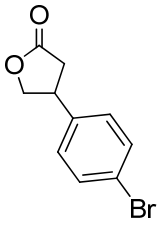
3.98 (m, 1H), 3.06 (dd, 1H, *J* = 8.8, 17.6), 2.73 (dd, 1H, *J* = 8.8, 17.6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 174.9, 142.1, 132.7 (q, *J* = 34.4), 127.1, 123.0 (q, *J* = 271.1), 121.9, 72.9, 40.8, 35.3; **IR** 1786, 1374, 1276, 1170, 1110, 1030, 899, 842, 707, 682 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{12}H_9F_6O_2$ $[M+H]^+$: 299.05067, found 299.05024.



4-(4-Methoxyphenyl)dihydrofuran-2(3H)-one (74 mg, 64 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.13 (d, 2H, *J* = 8.8), 6.90 (d, 2H, *J* = 8.8), 4.62 (dd, 1H, *J* = 8.1, 9.1), 4.20 (dd, 1H, *J* = 8.1, 9.1), 3.79 (s, 3H), 3.72 (m, 1H), 2.88 (dd, 1H, *J* = 8.6, 17.4), 2.61 (dd, 1H, *J* = 9.3, 17.4); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 176.4, 159.0, 131.3, 127.7, 114.5, 74.2, 55.3, 40.4, 35.9; **IR** 1765, 1511, 1454, 1254, 1164, 1014, 838, 602, 554 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.08647, found 193.08682.

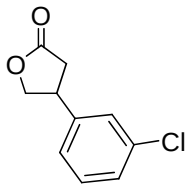


4-(4-Chlorophenyl)dihydrofuran-2(3H)-one (73 mg, 62 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31 (d, 2H, *J* = 8.6), 7.29 (d, 2H, *J* = 8.4), 4.63 (dd, 1H, *J* = 7.8, 9.2), 4.20 (dd, 1H, *J* = 7.6, 9.0), 3.79-3.70 (m, 1H), 2.90 (dd, 1H, *J* = 8.8, 17.6), 2.60 (dd, 1H, *J* = 8.8, 17.4); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 176.0, 138.0, 133.5, 129.3, 128.1, 73.7, 40.5, 35.6; **IR** 1774, 1485, 1425, 1161, 1093, 1011, 832, 680, 511, 496 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{10}ClO_2$ $[M+H]^+$: 197.03693, found 197.03745.

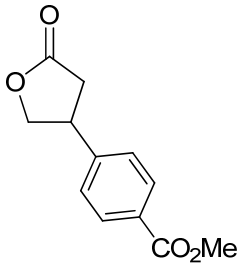


4-(4-Bromophenyl)dihydrofuran-2(3H)-one (110 mg, 76 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.49 (d, 2H, *J* = 8.6), 7.12 (d, 2H, *J* = 8.3), 4.66 (dd, 1H, *J* = 7.8, 9.0), 4.23 (dd, 1H, *J* = 7.6, 9.1),

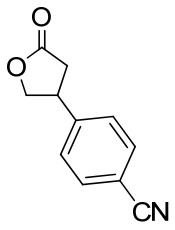
3.76 (m, 1H), 2.92 (dd, 1H, *J* = 8.6, 17.4), 2.62 (dd, 1H, *J* = 8.8, 17.6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 175.9, 138.6, 132.3, 128.4, 121.6, 73.7, 40.6, 35.6; **IR** 1764, 1486, 1422, 1154, 1010, 825, 539, 491 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{10}BrO_2$ $[M+H]^+$: 240.98642, found 240.98681.



4-(3-Chlorophenyl)dihydrofuran-2(3H)-one (95 mg, 81 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.31 (m, 1H), 7.24 (s, 1H), 7.14 (d, 2H, *J* = 8.3), 4.68 (dd, 1H, *J* = 7.8, 9.0), 4.27 (dd, 1H, *J* = 7.6, 9.0), 3.79 (m, 1H), 2.95 (dd, 1H, *J* = 8.5, 17.3), 2.66 (dd, 1H, *J* = 8.8, 17.6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 175.9, 141.6, 135.0, 127.9, 127.1, 124.9, 73.6, 40.7, 35.5; **IR** 1773, 1598, 1480, 1164, 1083, 1019, 907, 785, 729, 693, 441 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{10}ClO_2$ $[M+H]^+$: 197.03693, found 197.03729.

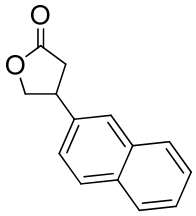


Methyl 4-(5-oxotetrahydrofuran-3-yl)benzoate (63 mg, 48 %)**. ^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.01 (d, 2H, *J* = 8.5),7.30 (d, 2H, *J* = 8.5), 4.67 (dd, 1H, *J* = 7.8, 9.0), 4.26 (dd, 1H, *J* = 7.8, 9.3), 3.89 (s, 3H), 3.86-3.83 (m, 1H), 2.94 (dd, 1H, *J* = 8.8, 17.6), 2.66 (dd, 1H, *J* = 8.8, 17.4); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 175.9, 166.5, 144.7, 130.4, 129.6, 126.8, 73.5, 52.2, 41.0, 35.4; **IR** 1778, 1717, 1280, 1168, 1109, 1019 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{12}H_{13}O_4$ $[M+H]^+$: 221.08138, found 221.08169.

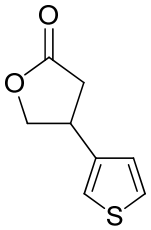


4-(5-Oxotetrahydrofuran-3-yl)-benzonitrile (82 mg, 72 %). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.65 (d, 2H, *J* = 8.2), 7.34 (d, 2H, *J* = 8.4), 4.67 (dd, 1H, *J* = 7.8, 9.2), 4.25 (dd, 1H, *J* = 7.4, 9.2),

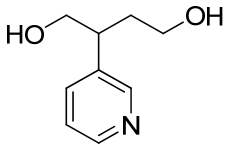
3.84 (m 1H), 2.96 (dd, 1H, *J* = 8.8, 17.4), 2.63 (dd, 1H, *J* = 8.4, 17.6); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.4, 145.0, 133.0, 127.6, 118.3, 111.8, 73.2, 41.0, 35.4; **IR** 2225, 1763, 1609, 1507, 1166, 1013, 832, 729, 561 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{11}H_{10}NO_2$ $[M+H]^+$: 188.07115, found 188.07101.



4-(Naphthalen-2-yl)dihydrofuran-2(3H)-one (97 mg, 76 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.87 (m, 3H), 7.69 (s, 1H), 7.54 (m, 2H), 7.35 (d, 1H, *J* = 8.3), 4.74 (dd, 1H, *J* = 7.8, 9.0), 4.38 (dd, 1H, *J* = 7.8, 9.0), 3.95 (m, 1H), 3.01 (dd, 1H, *J* = 8.8, 17.6), 2.80 (dd, 1H, *J* = 9.0, 17.6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 176.4, 136.8, 133.4, 132.7, 129.1, 127.7, 126.7, 126.3, 125.5, 124.5, 73.9, 41.2, 35.7; **IR** 1759, 1158, 1006, 831, 749, 477 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{14}H_{13}O_2$ $[M+H]^+$: 213.09155, found 213.09151.

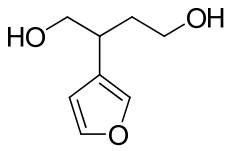


4-(Thiophen-3-yl)dihydrofuran-2(3H)-one (50 mg, 50 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.38-7.36 (m, 1H), 7.11-7.10 (m, 1H), 7.00-6.99 (m, 1H), 4.64 (dd, 1H, *J* = 7.8, 9.0), 4.26 (dd, 1H, *J* = 7.8, 9.0), 3.90-3.86 (m, 1H), 2.91 (dd, 1H, *J* = 8.6, 17.4), 2.64 (dd, 1H, *J* = 8.6, 17.4); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 176.2, 140.1, 127.2, 125.8, 121.0, 73.5, 36.8, 35.6; **IR** 1770, 1167, 1017, 783 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_8H_9O_2S$ $[M+H]^+$: 169.03232, found 169.03152.

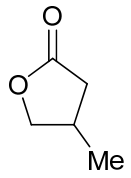


2-(pyridin-3-yl)butane-1,4-diol (19 mg, 75 %). 2-(pyridin-3-yl)prop-2-en-1-ol (20 mg, 0.15 mmol) was hydroformylated. Reduction with $NaBH_4$ (17 mg, 0.45 mmol) and MeOH (3.0 mL) at rt for 2h was performed instead of oxidation. **^{1}H NMR** (Methanol d-4, 500 MHz) δ 8.46 (s, 1H), 8.41(d, 1H, J = 3.7), 7.80-7.78 (m, 1H), 7.43-7.40 (m, 1H), 3.78-3.72 (m, 2H), 3.55-3.51 (m, 1H), 3.45-3.40 (m, 1H), 3.03-2.99 (m, 1H), 2.10-2.03 (m, 1H), 1.87-1.80 (m, 1H); **^{13}C NMR**

(Methanol d-4, 125 MHz) δ 149.0, 146.7, 139.3, 136.3, 123.8, 65.7, 59.1, 42.3, 34.3; **IR** 3260, 2925, 2855, 1427, 1050, 1028, 713 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_9H_{13}NO_2$ $[M+H]^+$: 168.10245, found 168.10230.

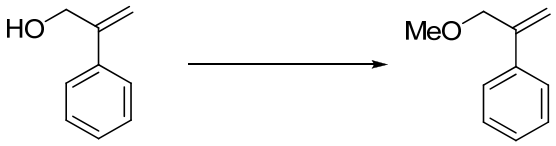


2-(furan-3-yl)butane-1,4-diol (33 mg, 70 %). 2-(furan-3-yl)prop-2-en-1-ol (37 mg, 0.30 mmol) was hydroformylated. Reduction with $NaBH_4$ (34 mg, 0.90 mmol) and MeOH (6.0 mL) at rt for 2h was performed instead of oxidation. **^{1}H NMR** (Methanol d-4, 500 MHz) δ 7.44 (t, 1H, *J* = 1.7), 7.36 (dd, 1H, *J* = 0.7, 1.5), 6.38-6.37 (m, 1H), 3.67-3.56 (m, 3H), 3.53-3.48 (m, 1H), 2.88-2.83 (m, 1H), 2.01-1.94 (m, 1H), 1.73-1.66 (m, 1H); **^{13}C NMR** (Methanol d-4, 125 MHz) δ 142.7, 139.5, 125.8, 109.2, 65.8, 59.5, 35.3, 34.4; **IR** 3334, 2929, 1157, 1025, 874, 786, 724, 601, 542 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_8H_{13}O_3$ $[M+H]^+$: 157.08647, found 157.08586.



4-methyldihydrofuran-2(3H)-one (37 mg, 62 %). Characterization data of this compound was previously reported.[6]

Synthesis of Methyl Ether

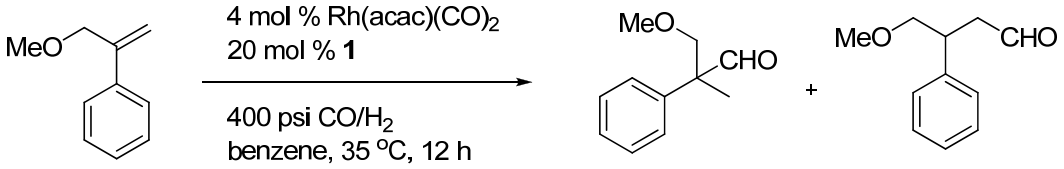


(3-Methoxyprop-1-en-2-yl)benzene was synthesized from 2-phenylprop-2-en-1-ol according to literature procedure[7]: To a flame-dried round bottom flask, sodium hydride (36 mg, 1.5 mmol) was added under nitrogen. Iodomethane (110 μL, 1.8 mmol) and anhydrous THF (2 mL) were added and solution was stirred at 45 ℃. A solution of 2-phenylprop-2-en-1-ol (150 μL, 1.2 mmol) in anhydrous THF (1 mL) was added dropwise and reaction was stirred at 45 °C for 30 min. The resulting mixture was allowed to cool to rt and H_2O (1 mL) was added, followed by extraction with Et_2O (3 × 5 mL). Combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Flash column chromatography (Hex/EtOAc = 30:1) afforded pure product as

colorless liquid (156 mg, 88 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.50-7.48 (m, 2H), 7.38-7.27 (m, 3H), 5.55 (t, 1H, *J* = 0.4), 5.35 (m, 1H), 4.34 (d, 2H, *J* = 0.4), 3.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 144.2, 138.8, 128.4, 127.8, 126.0, 114.4, 74.6, 57.9; **IR**: 2924, 1121, 1092, 905, 779, 708 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{10}H_{13}O$ $[M+H]^+$: 149.09664, found: 149.09655.

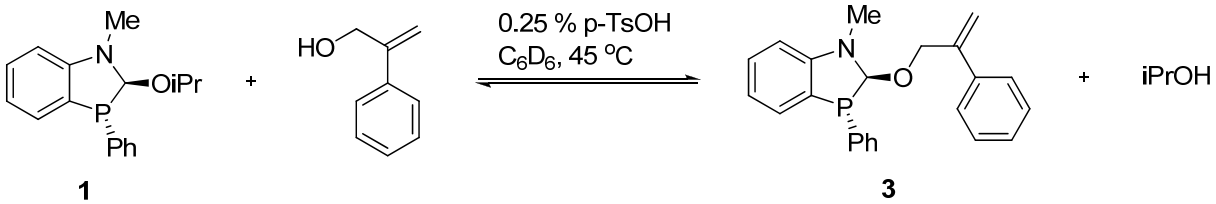
Control Reaction of Methyl Ether

Figure SI-1:



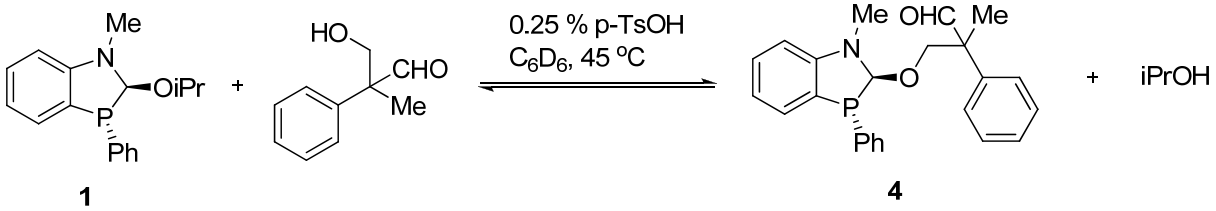
The oven dried glass reaction vial was placed in the Endeavor, and (3-methoxyprop-1-en-2-yl)benzene (89 mg, 0.60 mmol) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), ligand **1** (34 mg, 0.12 mmol, 20 mol %), p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M in benzene, 1.2×10^{-3} mmol, 0.20 mol %) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 45 ℃ for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature and pressure of 45 ℃ and 400 psi H_2/CO respectively for 12 h. The Endeavor was vented to ambient pressure and cooled to ambient temperature. The reaction was removed from the Endeavor and concentrated. 1,3,5-Trimethoxybenzene (400 μL of 0.15 M in $CDCl_3$, 0.06 mmol) was added as standard and ^{1}H NMR showed > 99% substrate and 0% conversion.

Binding Study of Ligand 1

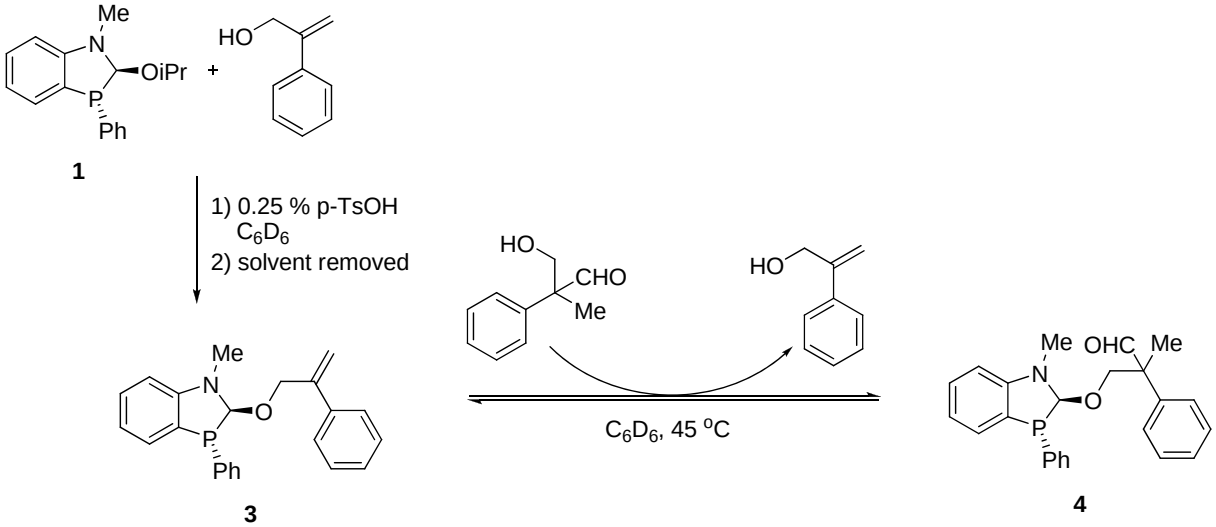


Ligand **1** (5.7 mg, 2.0×10^{-2} mmol) was dissolved in benzene d-6 (1 mL) in an NMR tube under

N_2. p-toluenesulfonic acid (0.10 mL of 5.0×10^{-4} M in benzene d-6, 5.0×10^{-5} mmol) was added to solution, followed by addition of 2-phenylprop-2-en-1-ol (13 mg, 0.10 mmol) and iPrOH (46 μL, 0.60 mmol). Solution was heated at 45℃ overnight. Analysis of the reaction by ^{1}H NMR showed **3**:**1** = 38:62, leading to Keq_1= 4.0.



Ligand **1** (5.7 mg, 2.0×10^{-2} mmol) was dissolved in benzene d-6 (1 mL) in an NMR tube under N_2. p-toluenesulfonic acid (0.10 mL of 5.0×10^{-4} M in benzene d-6, 5.0×10^{-5} mmol) was added to solution, followed by addition of 3-hydroxy-2-methyl-2-phenylpropanal (16 mg, 0.10 mmol, isolated from hydroformylation) and iPrOH (23 μL, 0.30 mmol). Solution was heated at 45℃ overnight. Analysis of the reaction by ^{1}H NMR showed **4**:**1** = 41:59.
Note: Ignoring minor aldehyde dimerization, Keq_2 was calculated to be 2.3.

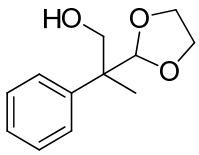


Ligand **1** (11 mg, 4.0×10^{-2} mmol), 2-phenylprop-2-en-1-ol (13 mg, 0.10 mmol) and p-toluenesulfonic acid (0.20 mL of 5.0×10^{-4} M in benzene d-6, 1.0×10^{-4} mmol) were dissolved in benzene d-6 (1 mL) under N_2. Solution was allowed to stand at rt for 10 min, and then solvent was removed under vacuum. The residue was redissolved in benzene d-6 (1 mL), and ^{1}H NMR analysis of solution showed **1a** was formed (> 99%). 3-hydroxy-2-methyl-2-phenylpropanal (16 mg, 0.10 mmol, isolated from hydroformylation) was added, and mixture was heated at 45℃

overnight. Analysis of the reaction by ^{1}H NMR showed **4**:**3** = 39:61.
Note: Ignoring minor aldehyde dimerization, Keq_3 was calculated to be 0.57. This result matches the calculated Keq from binding study experiments 1 and 2 (Keq_2 / Keq_1 = Keq_3; 2.3 / 4.0 = 0.58).

Hydroformylation using Ligand 1 and Acetal Protection

Hydroformylation and Acetal Protection Procedure. The oven dried glass reaction vial was placed in the Endeavor, and 2-phenylprop-2-en-1-ol (80 mg, 0.60 mmol) was added. The Endeavor was sealed and purged with nitrogen (4 × 100 psi). A solution of dicarbonylacetylacetonato rhodium (I) (6.2 mg, 2.4×10^{-2} mmol, 4.0 mol %), ligand **1** (34 mg, 0.12 mmol, 20 mol %), p-toluenesulfonic acid (2.0 mL of 6.0×10^{-4} M, 1.2×10^{-3} mmol, 0.20 mol %) and benzene (to total volume of 4 mL) was injected, followed by injection of additional benzene (2 mL) to wash the injection port. The Endeavor was purged with nitrogen (1 × 100 psi), stirring was started at 250 rpm, and the Endeavor was heated to and held at 45 ℃ for 10 minutes. Stirring was stopped, the Endeavor was charged with 400 psi H_2/CO, stirring was re-initiated at 700 rpm, and the Endeavor was maintained at a constant temperature and pressure of 45 ℃ and 400 psi H_2/CO respectively for 12 h. The Endeavor was vented to ambient pressure and cooled to ambient temperature. The reaction was removed from the Endeavor and concentrated. The residue was redissolved in benzene (0.6 mL). Ethylene glycol (74 μL, 1.3 mmol) and a few crystals of p-toluenesulfonic acid were added. The reaction was refluxed for 3 h. The resulting mixture was cooled to room temperature and solvent was removed. Flash column chromatography (Hex/EtOAc = 6/1) afforded the pure product as colorless liquid.



2-(1,3-Dioxolan-2-yl)-2-phenylpropan-1-ol (90.2 mg, 72 %). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.49-7.47 (m, 2H), 7.38-7.35 (m, 2H), 7.28-7.25 (m, 1H), 5.16 (s, 1H), 4.03-3.85 (m, 6H), 2.31 (t, 1H, *J* = 6.2), 1.42 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.8, 128.4, 127.0, 126.8, 108.5, 68.2, 65.3, 65.0, 46.5, 17.1; **IR**: 3458, 2884, 1107, 1028, 767, 699 cm^{-1}; **HRMS** (DART-TOF) calcd. for $C_{12}H_{17}O_3$ $[M+H]^+$: 209.11777, found: 209.11798.

References

(1) Concellon, J. M.; Cuervo, H.; Fernandez-Fano, R. *Tetrahedron* **2001**, 57, 8983.
(2) Gajewski, J. J.; Gee, K. R.; Jurayj, J. *J. Org. Chem.* **1990**, 55, 1813.

(3) Prager, R. H.; Schafer, K.; Hamon, D. P. G.; Massy-Westropp, R. A. *Tetrahedron*, **1995**, 51, 11465.
(4) Arns, S.; Barriault, L. *J. Org. Chem.* **2006**, 71, 1809.
(5) Pei, W.; Mo, J.; Xiao, J. *J. Organomet. Chem.* **2005**, 690, 3546.
(6) Sharma, V.; Kelly, G. T.; Watanabe, C. M. H. *Org. Lett.* **2008**, 10, 4815.
(7) Lightburn, T. E.; Dombrowski, M. T.; Tan, K. L. *J. Am. Chem. Soc.* **2008**, 130, 9210.

Spectra

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Operator: klt
File: xs-1-92-pure
VNMRS-500 "nmr17"

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 Pulse 45.0 degrees
 Acq. time 2.049 sec
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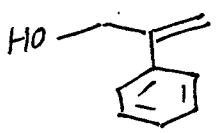
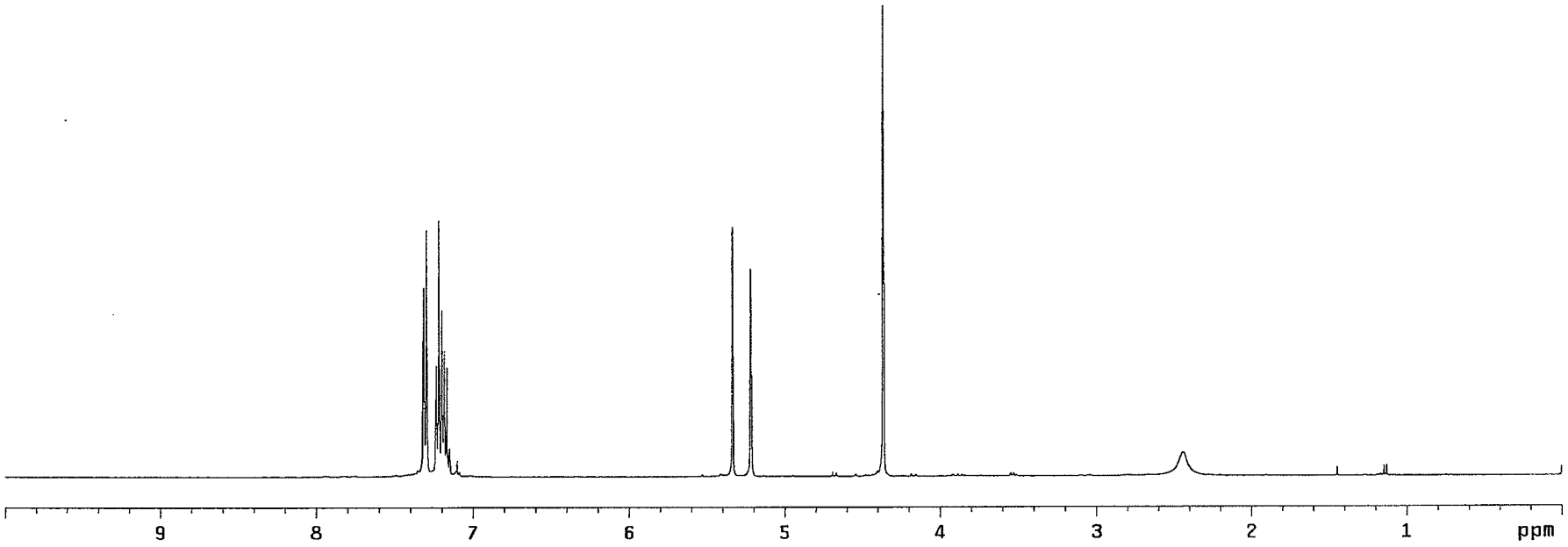
FT size 65536
Total time 0 min, 30 sec





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Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #8, Operator: xixi
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VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
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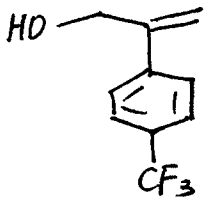

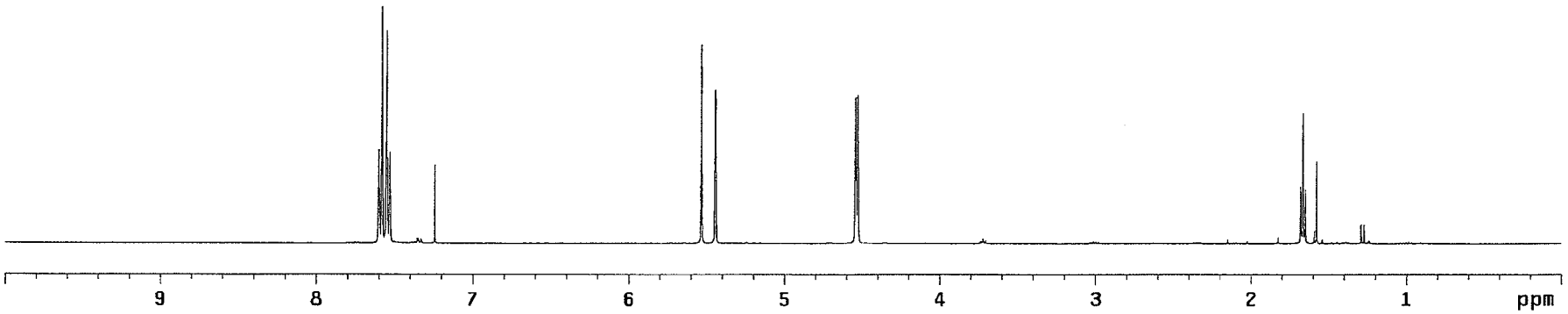

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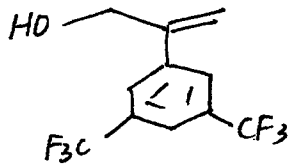
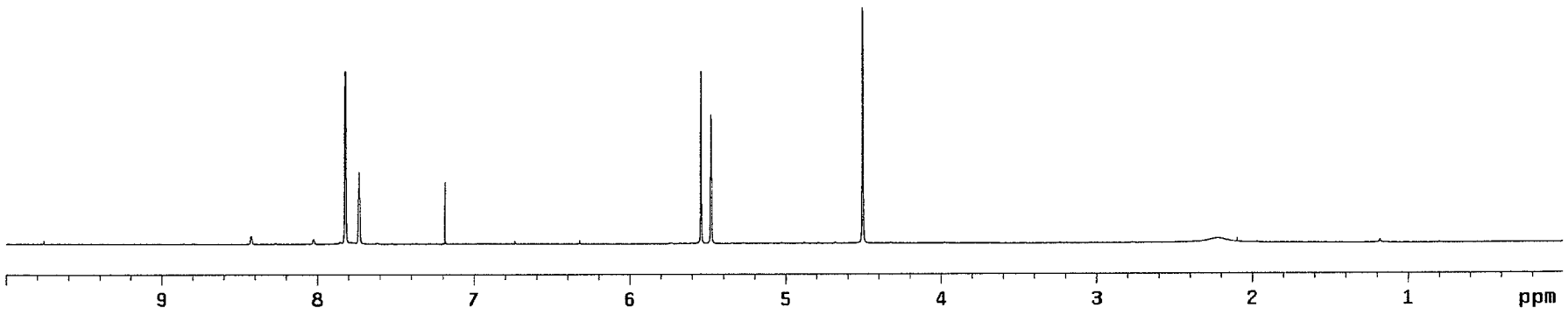
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #10, Operator: xixi
File: xs-2-7.4_2_7_01
VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663001 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec





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Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #9, Operator: xixi
File: xs-2-7.3_2_7_01
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7662995 MHz
DATA PROCESSING
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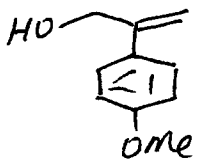
FT size 65536
Total time 0 min, 30 sec



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VNMRS-500 "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
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FT size 65536
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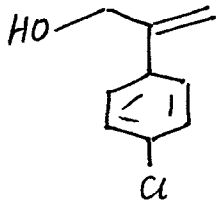

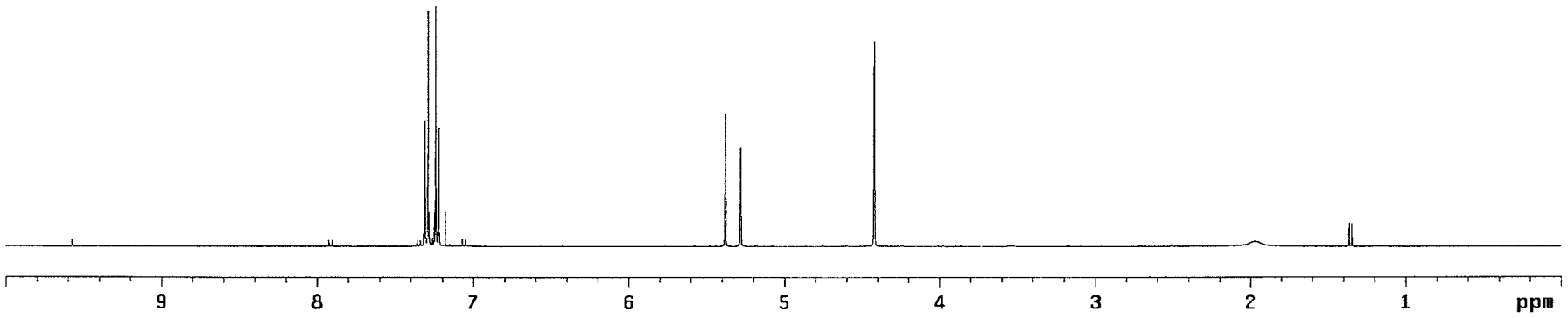

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Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #11, Operator: xixi
File: xs-2-7.5_2_7_01
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663023 MHz
DATA PROCESSING
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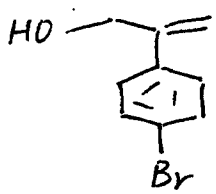
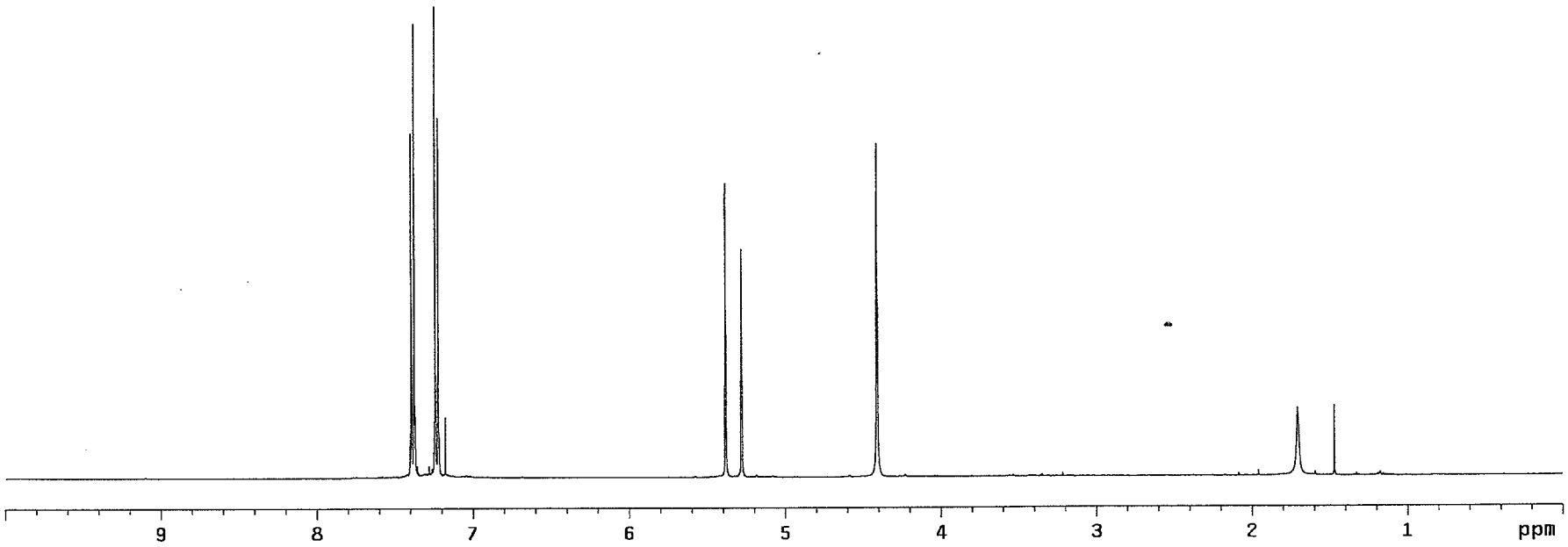
FT size 65536
Total time 0 min, 30 sec





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 Relax. delay 1.000 sec
 Pulse 45.0 degrees
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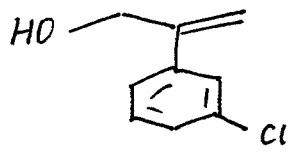

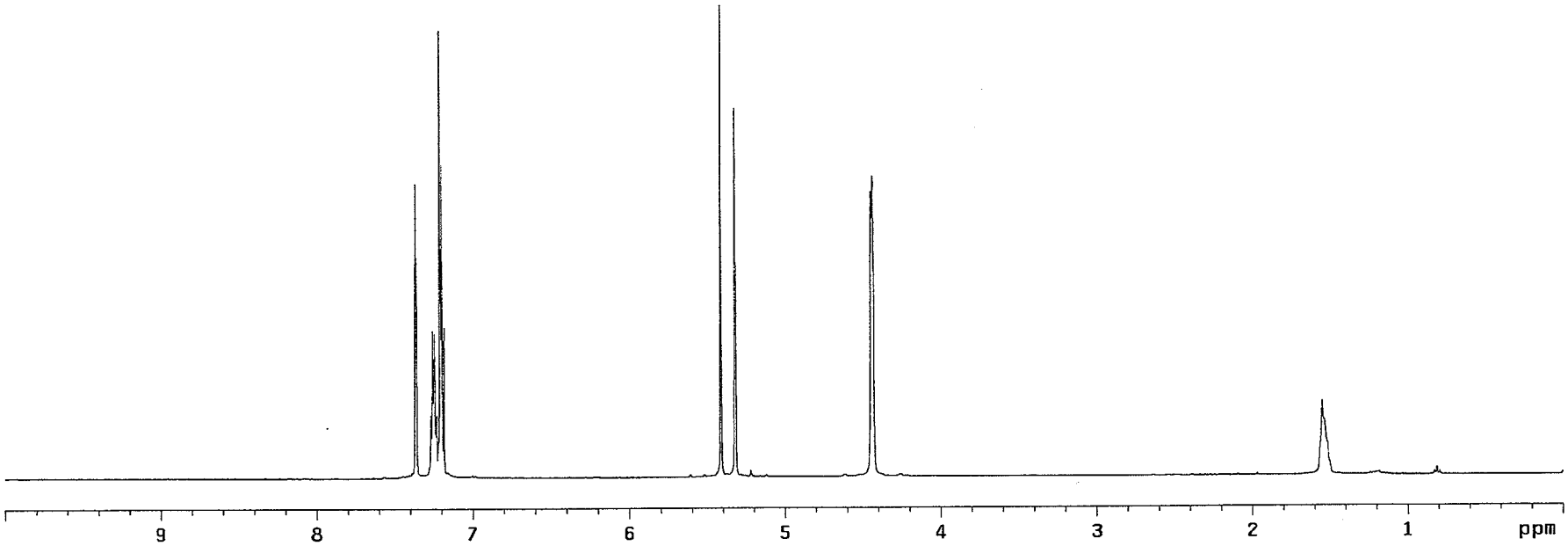

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Acq. time 2.049 sec
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DATA PROCESSING
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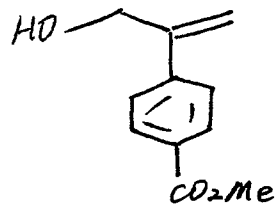
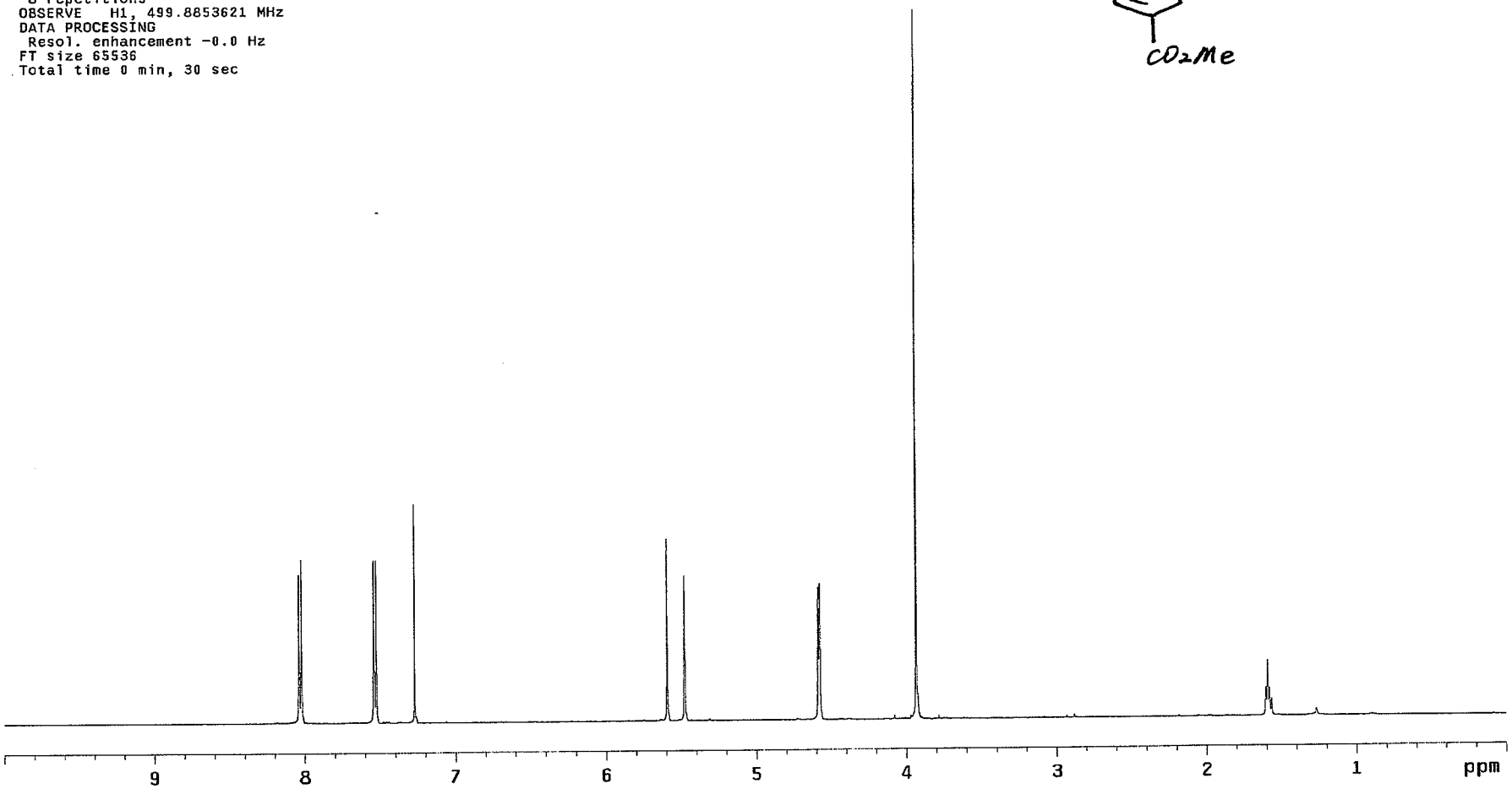
FT size 65536
Total time 0 min, 30 sec





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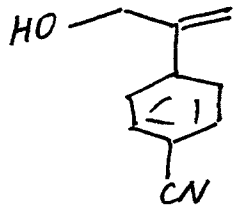

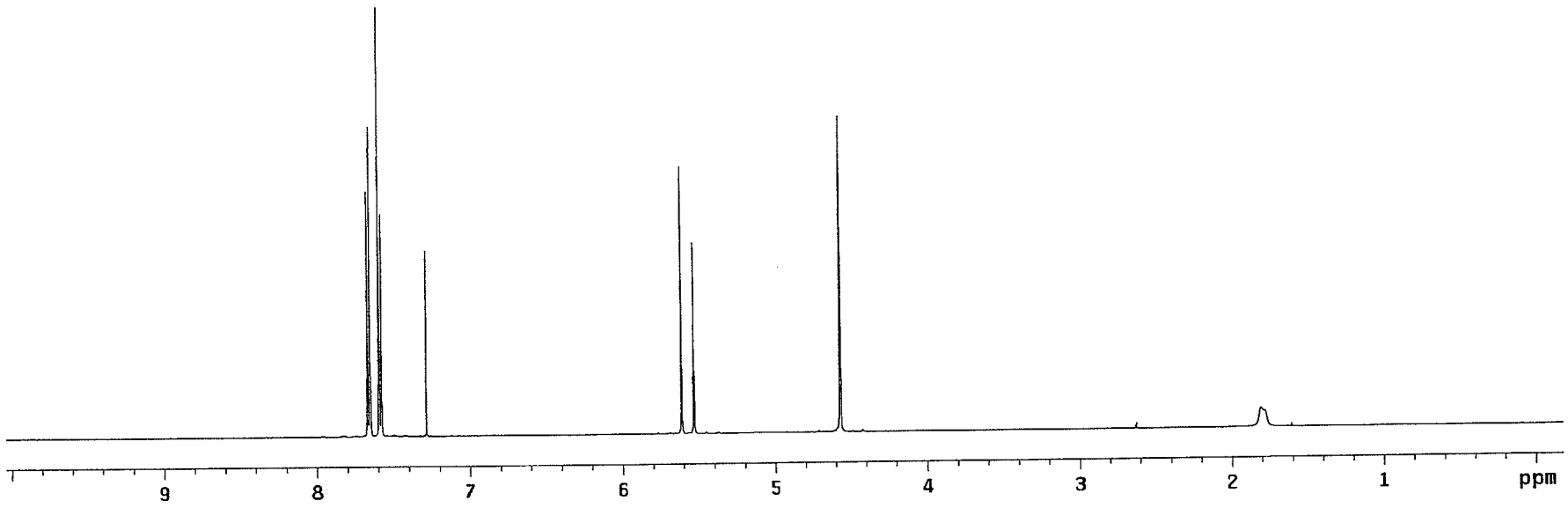

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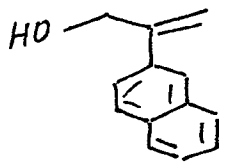
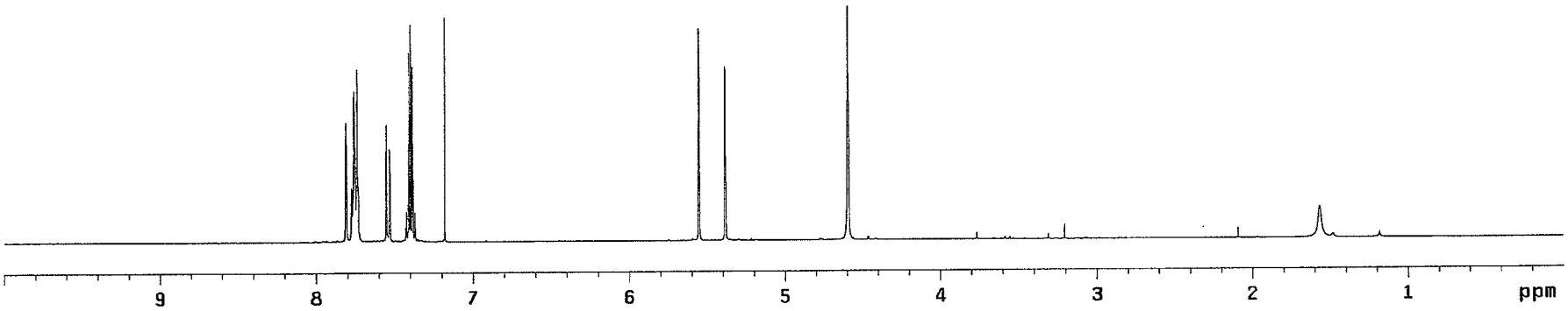
Total time 0 min, 30 sec





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Pulse 45.0 degrees
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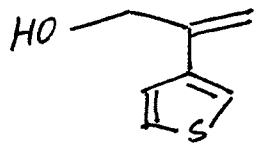
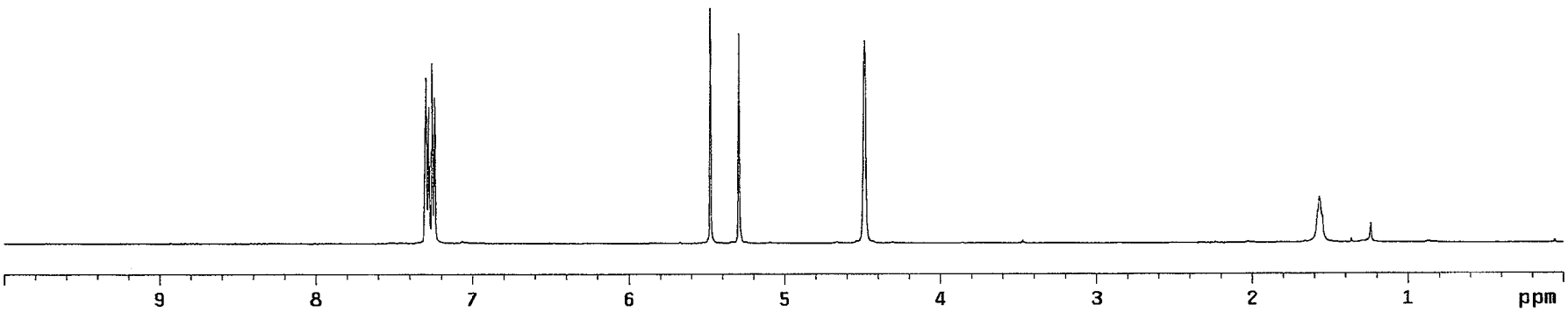
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7662768 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec

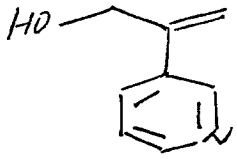


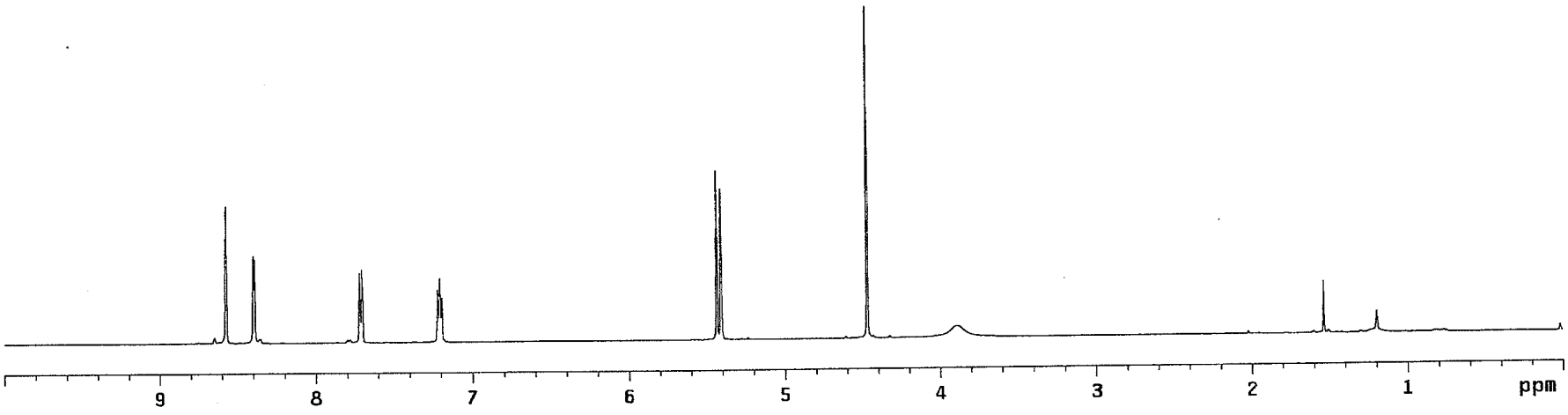


Sample: xs-1-224-pure
File: exp

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr11"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE H1, 499.7720124 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec



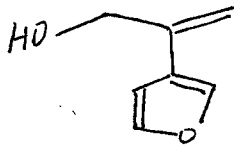


Sample: xs-2-113-pure
File: exp

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr11"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720124 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec



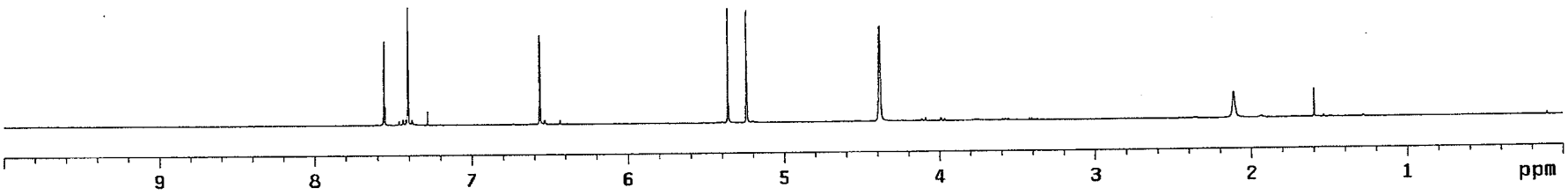


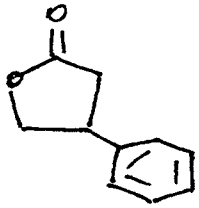
Table 1, Entry 7:
linear product

R=H

Sample: KF-2-015-R=H
File: home/All/klt/KF/KF-2-015-R=H.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: KF-2-015-R=H
VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



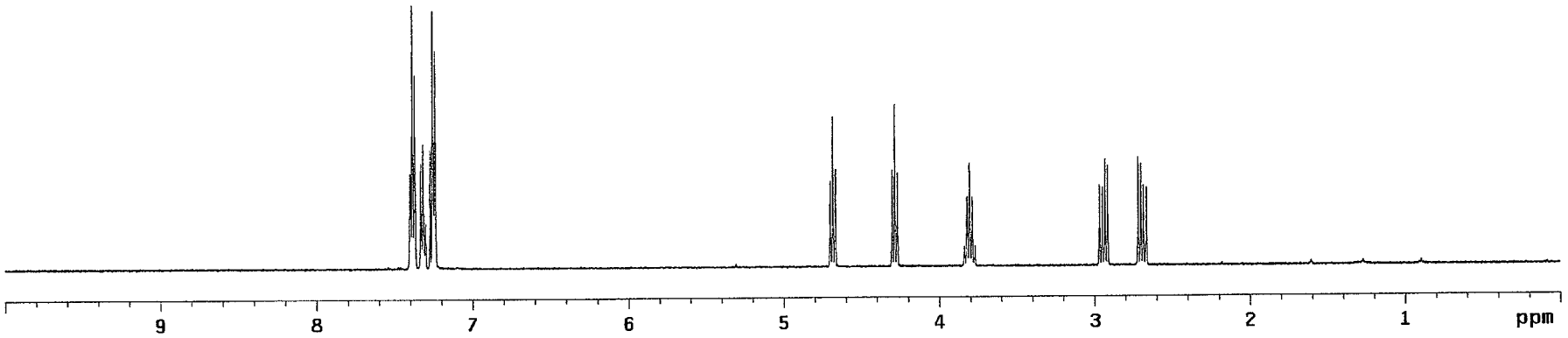


Table 1. Entry 7:
crude

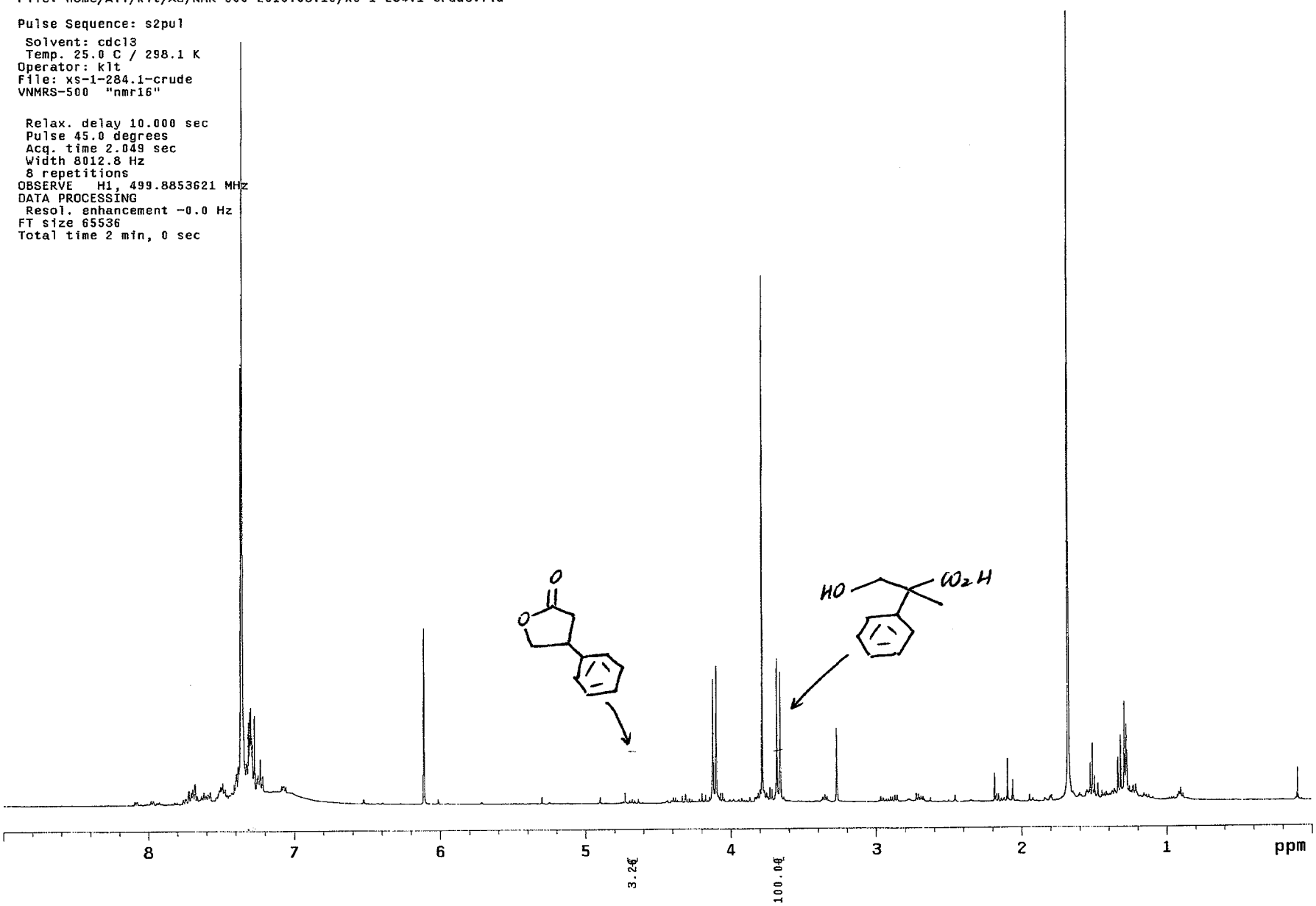
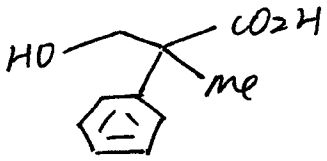


Table 1 . Entry 7:
branched product

Sample: xs-1-248-check
File: home/All/klt/XS/Printout/xs-1-248-check.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-248-check
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663013 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



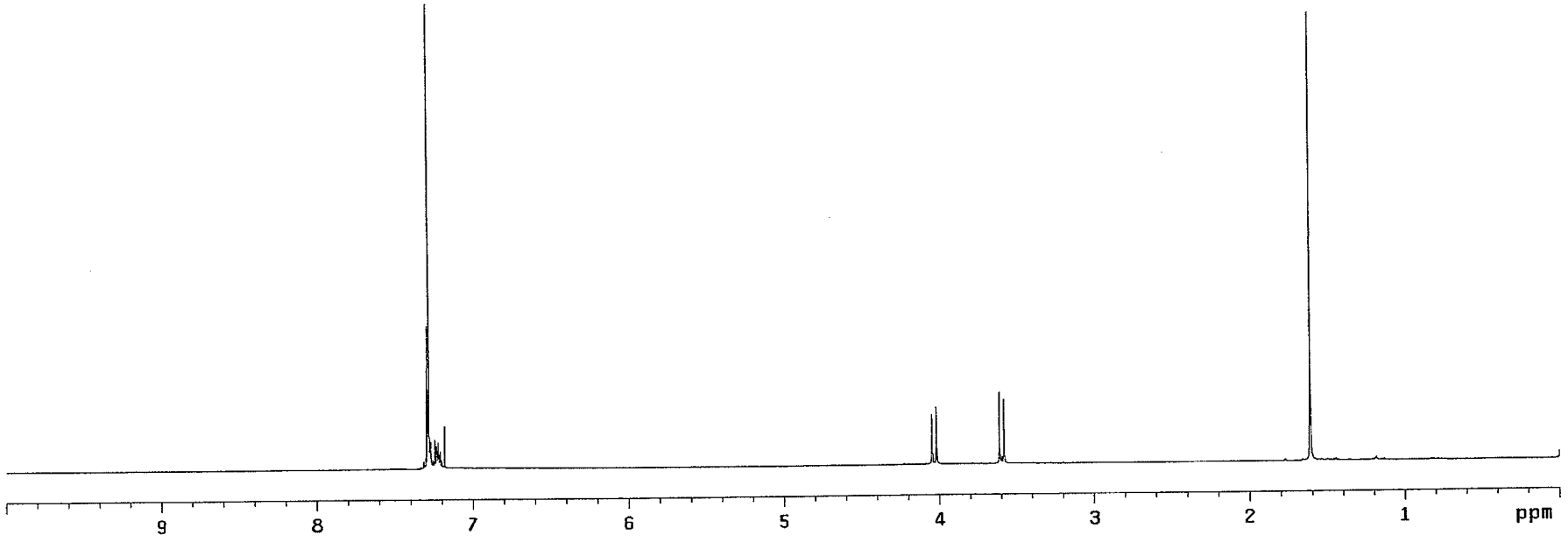


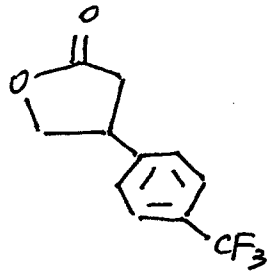
Table 2. Entry 1:

linear product

```
Sample: KF-2-015-R=CF3_H
Sample ID: /home/walkup/kwame/23_KF-2-015-R=CF3_H_2_015_01
File: home/All/klt/KF/KF-2-015-R=CF3_H_2_015_01.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Sample #23, Operator: kwame
File: KF-2-015-R=CF3_H_2_015_01
VNMRS-500  "nmr16"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.7662768 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec
```



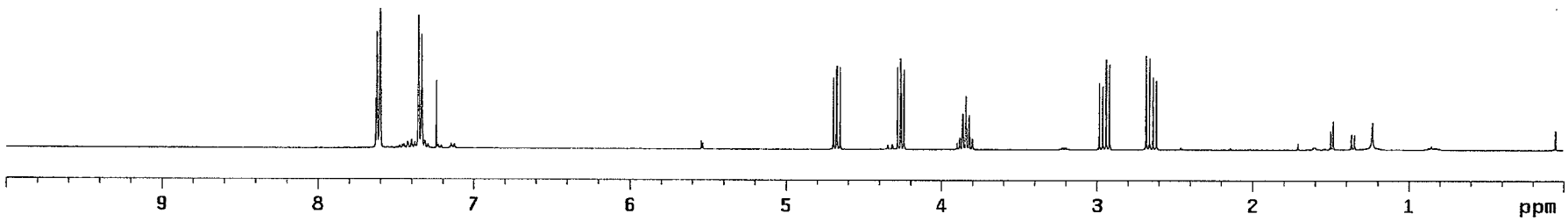


Table 2. Entry 1:
crude

Sample: xs-1-284.2-crude
File: home/All/klt/XS/NMR 500 2010.03.19/xs-1-284.2-crude.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-284.2-crude
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

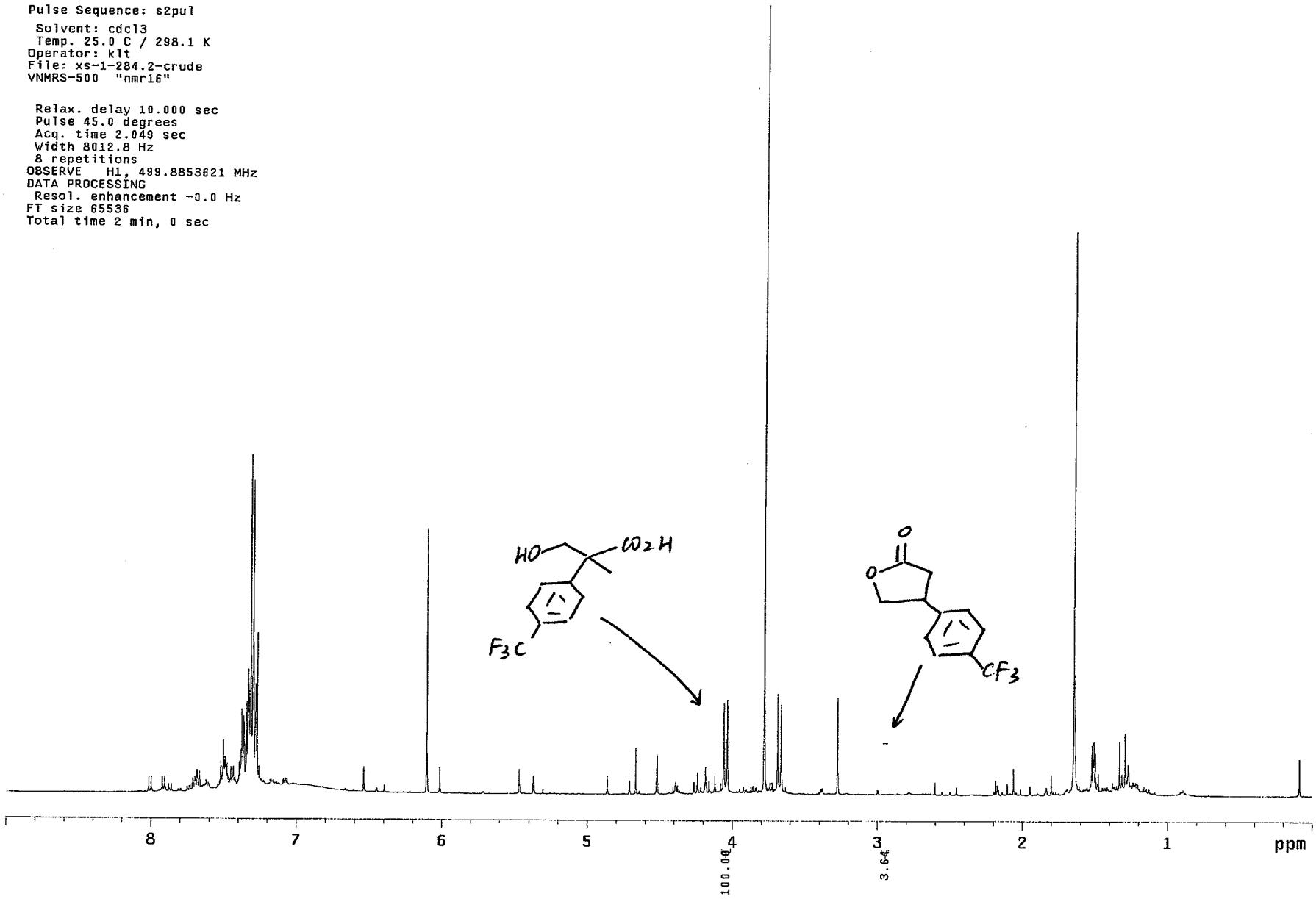


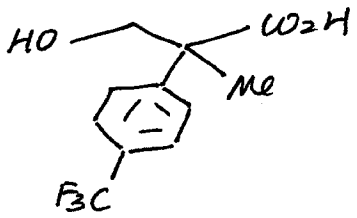
Table 2. Entry 1:
branched product

Sample: xs-1-255.3
File: home/All/klt/XS/Printout/xs-1-255.3.fid

Pulse Sequence: s2pul

Solvent: c6d6
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-255.3
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8854080 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



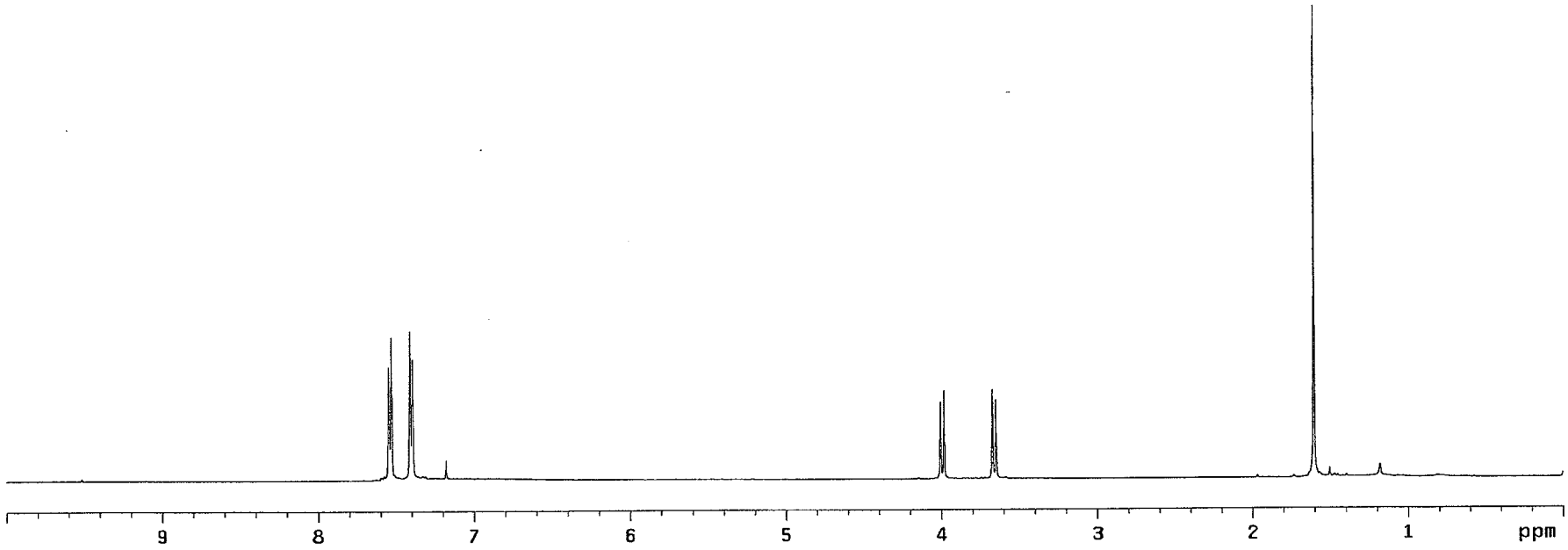
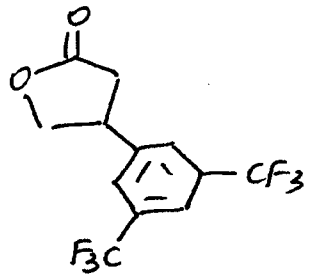


Table 2. Entry 2:
linear product

```
Sample: KF-2-056
File: home/All/klt/KF/KF-2-056.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: klt
File: KF-2-056
VNMRS-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7720124 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec
```



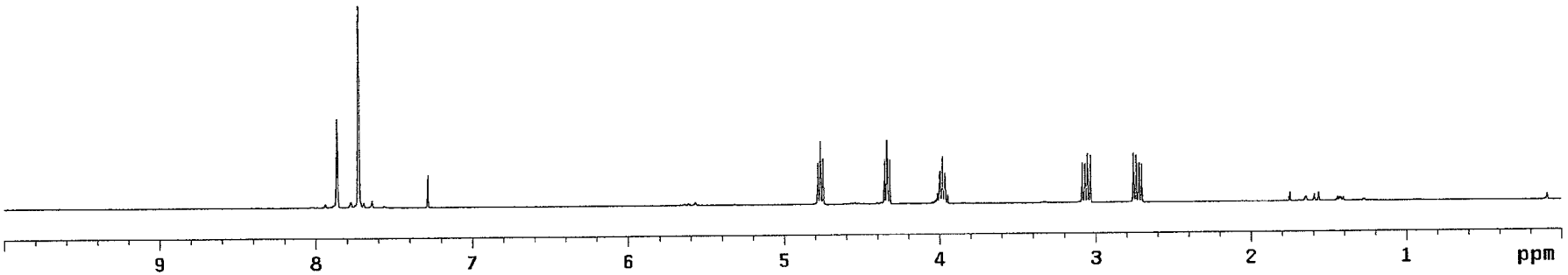


Table 2. Entry 2:
crude

Sample: xs-1-291.3-crude
Sample ID: s_20100210_01
File: home/All/klt/XS/Old NMR 500 2010.03.19/xs-1-291.3-crude.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: klt
File: xs-1-291.3-crude
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720124 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 10 sec

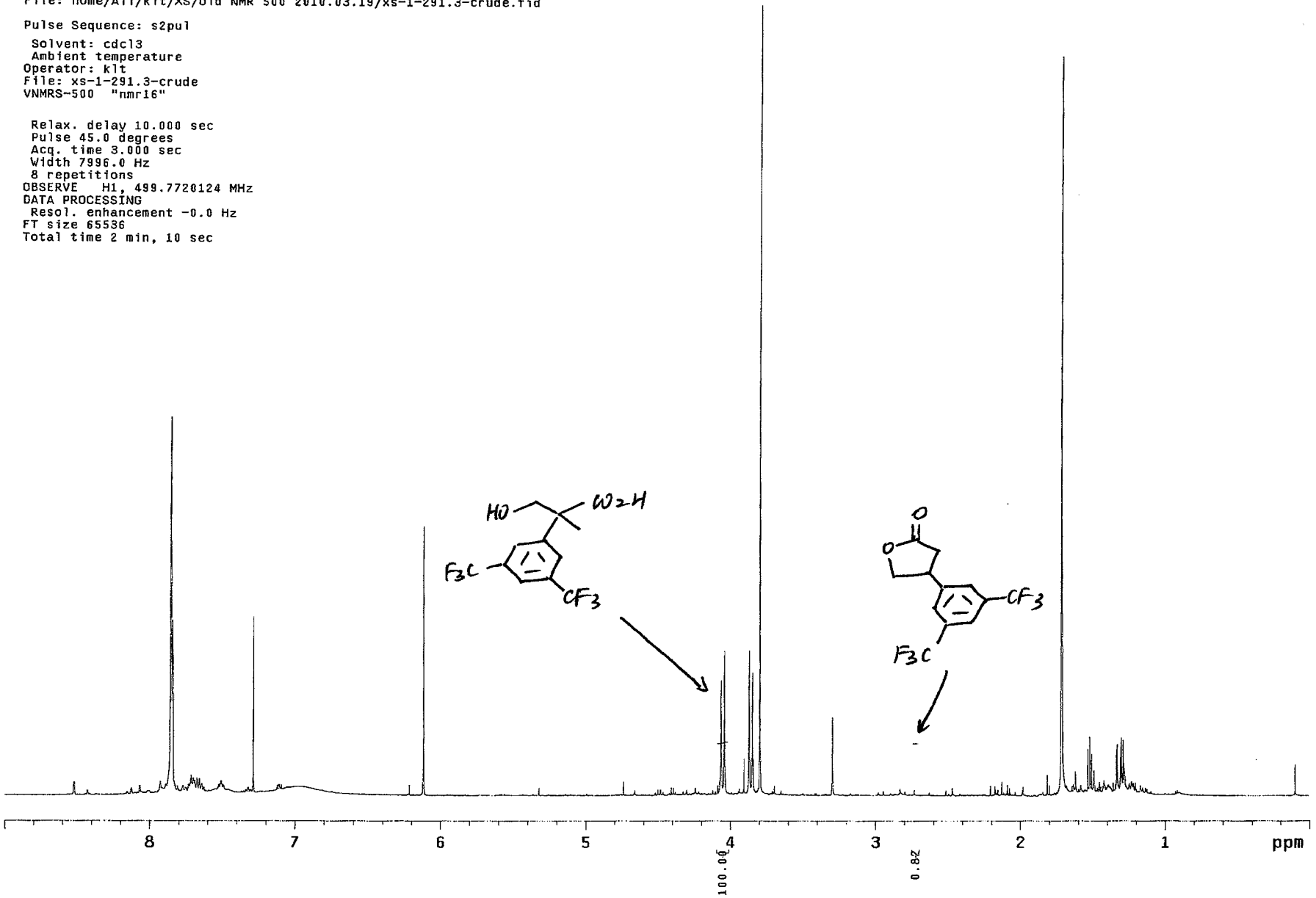


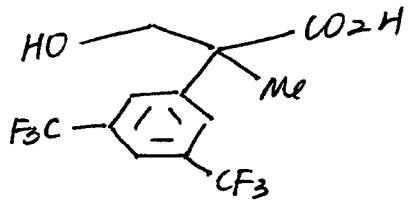
Table 2, Entry 2:
branched product

Crude

Sample: xs-1-291-pure
File: home/All/klt/XS/Printout/xs-1-291-pure.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-291-pure
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8854033 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



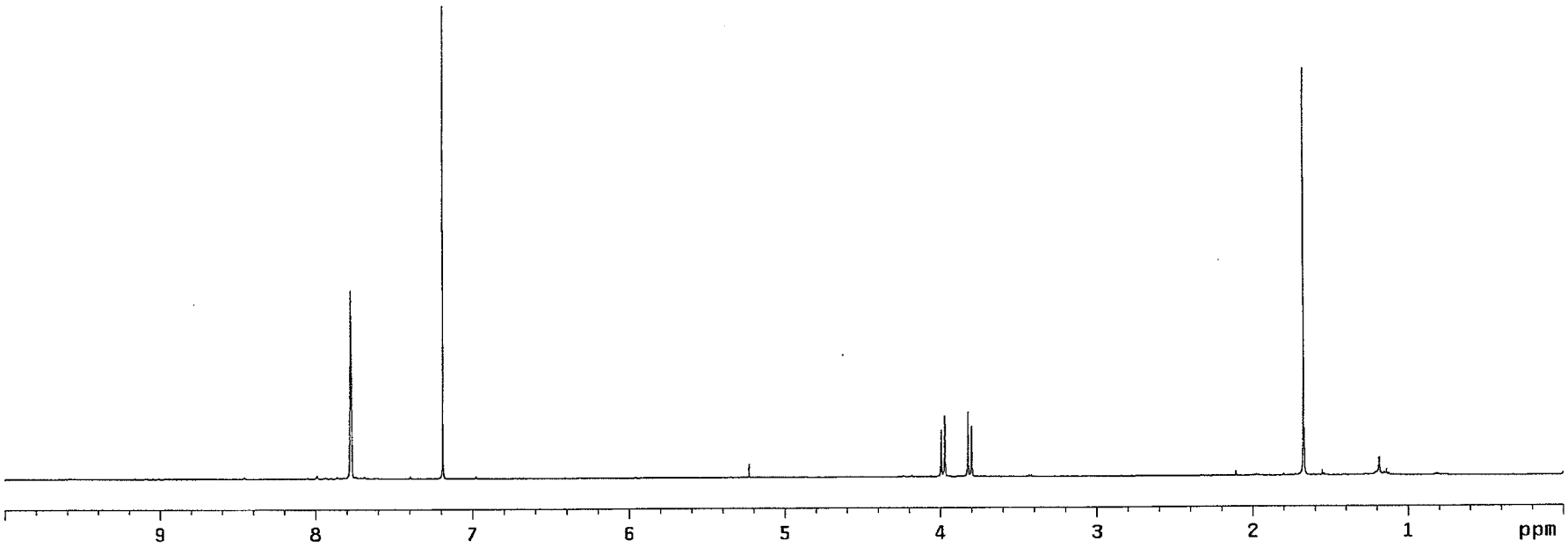


Table 2. Entry 3:
linear product

R=OMe

Sample: KF-2-015-R=OMe
File: home/All/klt/KF/KF-2-015-R=OMe.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: KF-2-015-R=OMe
VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec

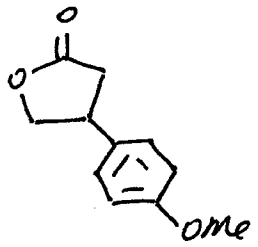


Table 2. Entry 3:

crude

Sample: xs-2-15-crude
File: home/All/klt/XS/NMR 500 2010.03.19/xs-2-15-crude.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-15-crude
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

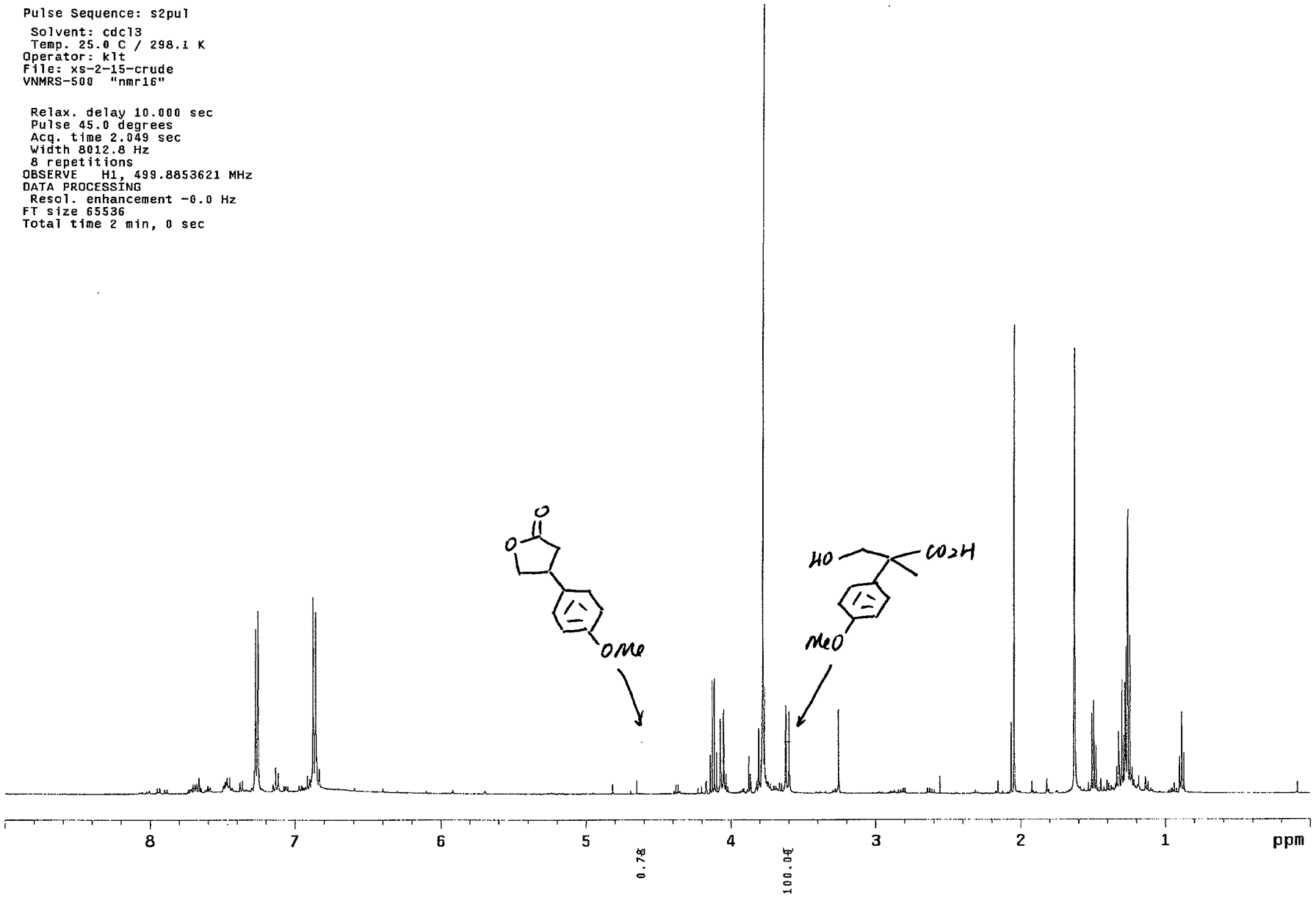
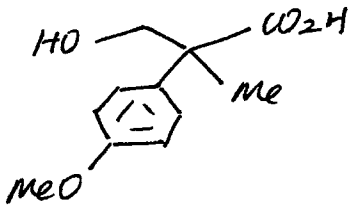


Table 2. Entry 3
branched product

```
Sample: xs-1-255.4
File: home/All/klt/XS/Printout/xs-1-255.4.fid

Pulse Sequence: s2pul
 Solvent: c6d6
 Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-255.4
VNMRS-500  "nmr17"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE    H1, 499.8854067 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```



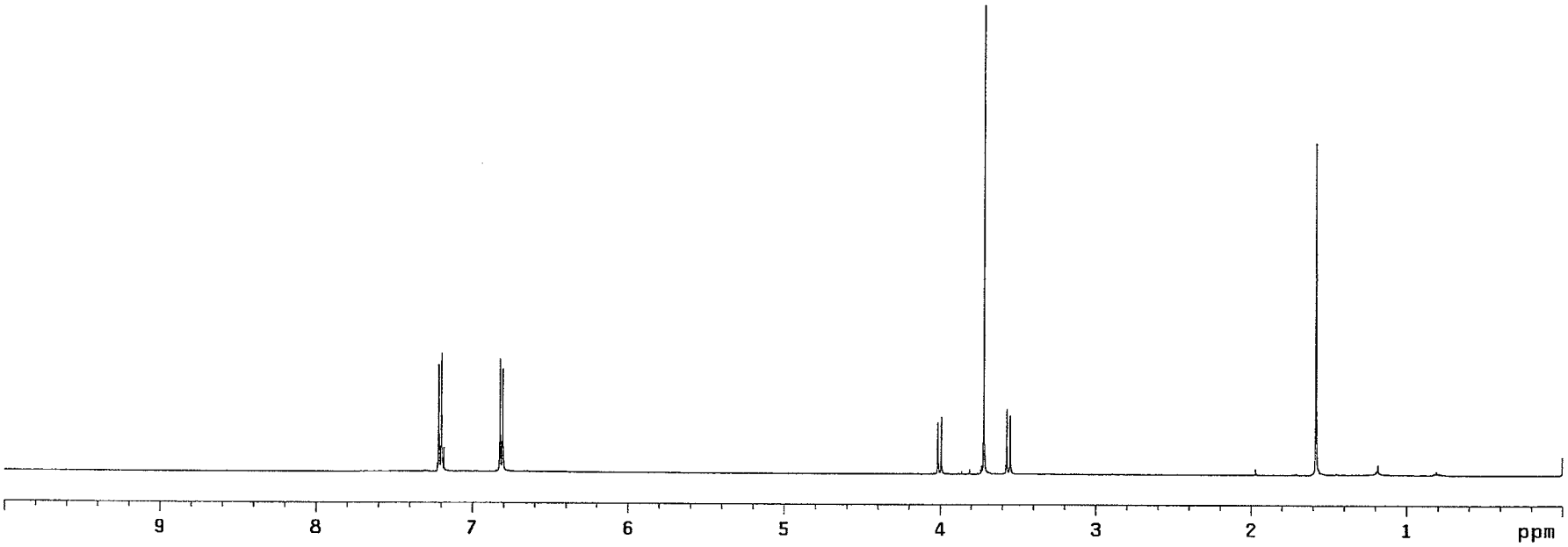


Table 2, Entry 4

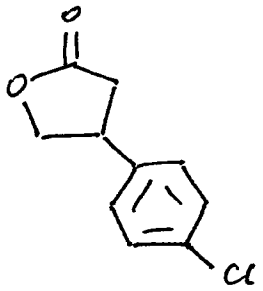
linear product

```
Sample: KF-2-015-R=Cl
Sample ID: /home/walkup/kwame/22_KF-2-015-R=Cl_2_015_01
File: home/All/klt/KF/KF-2-015-R=Cl_2_015_01.fid

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Sample #22, Operator: kwame
File: KF-2-015-R=Cl_2_015_01
VNMRS-500  "nmr16"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE    H1, 399.7662768 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec
```



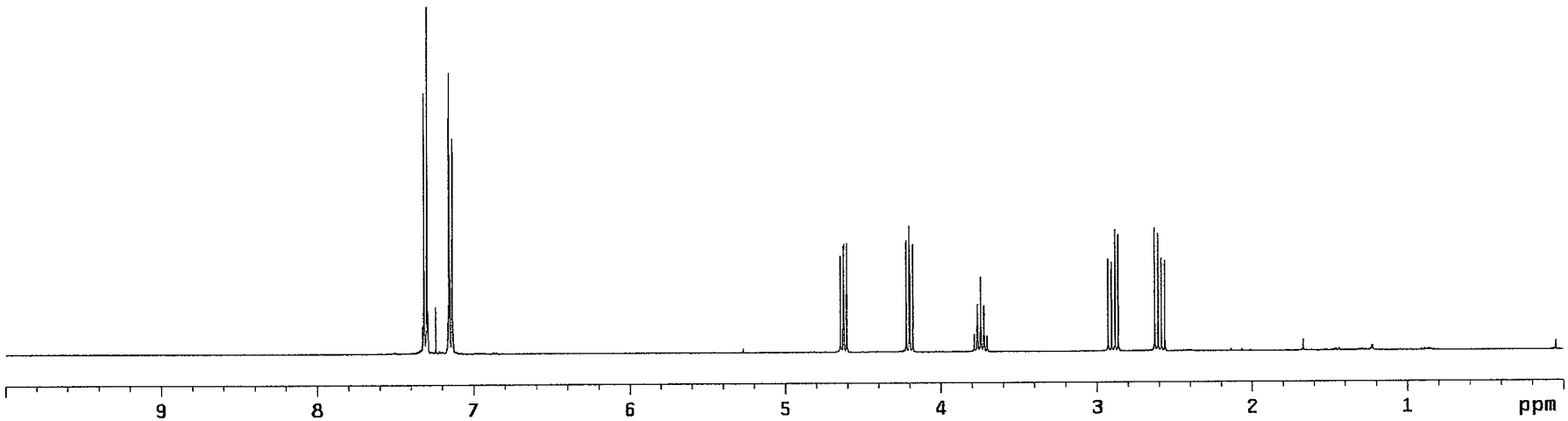


Table 2. Entry 4: crude

Sample: xs-2-14-crude
File: home/All/klt/XS/NMR 500 2010.03.19/xs-2-14-crude.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-14-crude
VNMRS-500 "nmr16"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

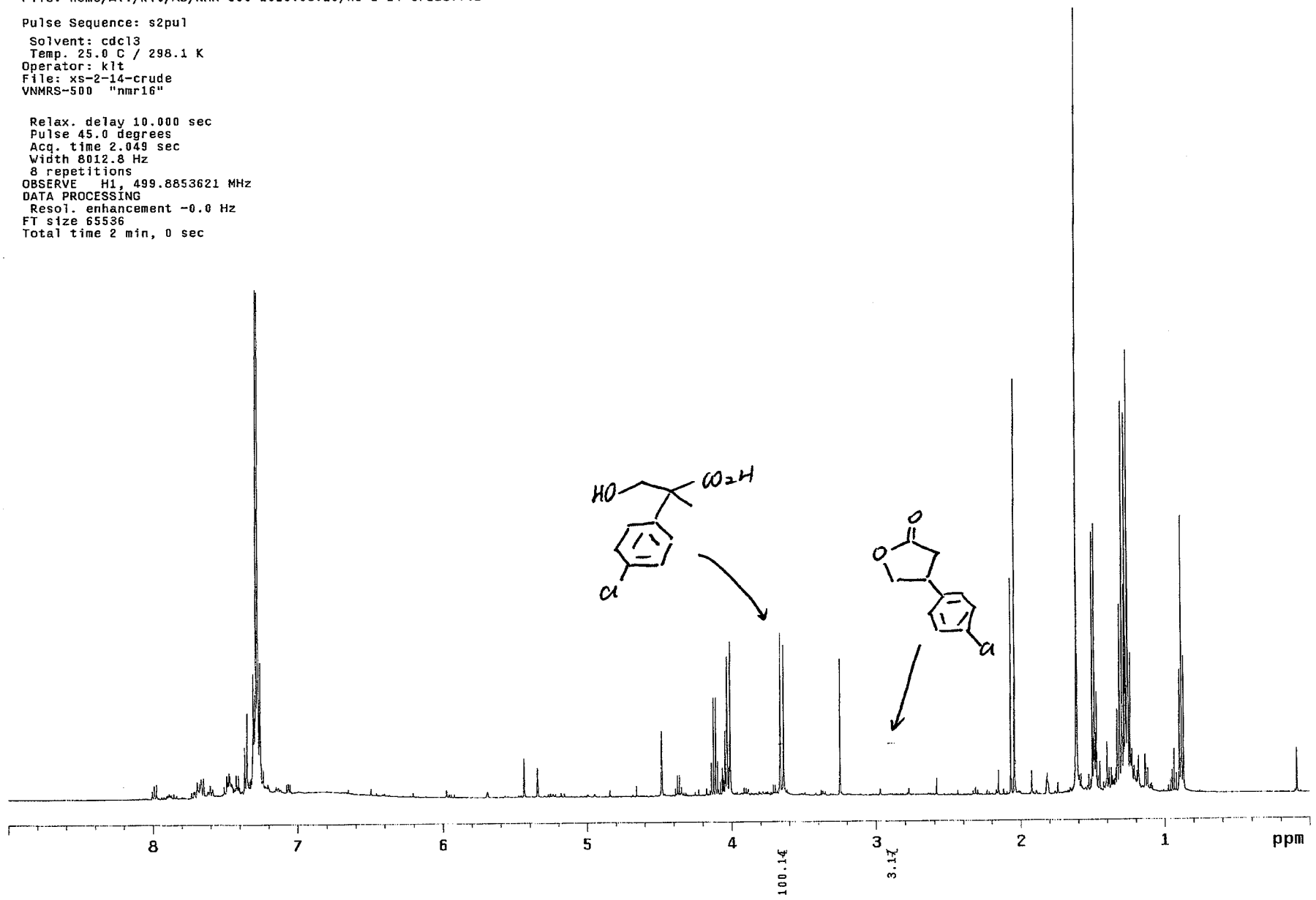
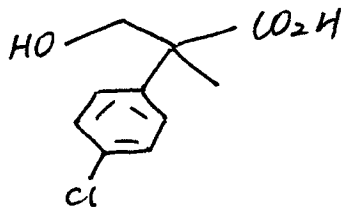


Table 2. Entry 4
branched product

```
Sample: xs-1-289.1-pure-C
Sample ID: /home/walkup/xixi_5_xs-1-289.1-pure-C___01
File: home/All/klt/XS/Printout/xs-1-289.1-pure.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Sample #5, Operator: xixi
File: xs-1-289.1-pure
VNMRS-500  "nmr17"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.7662986 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```



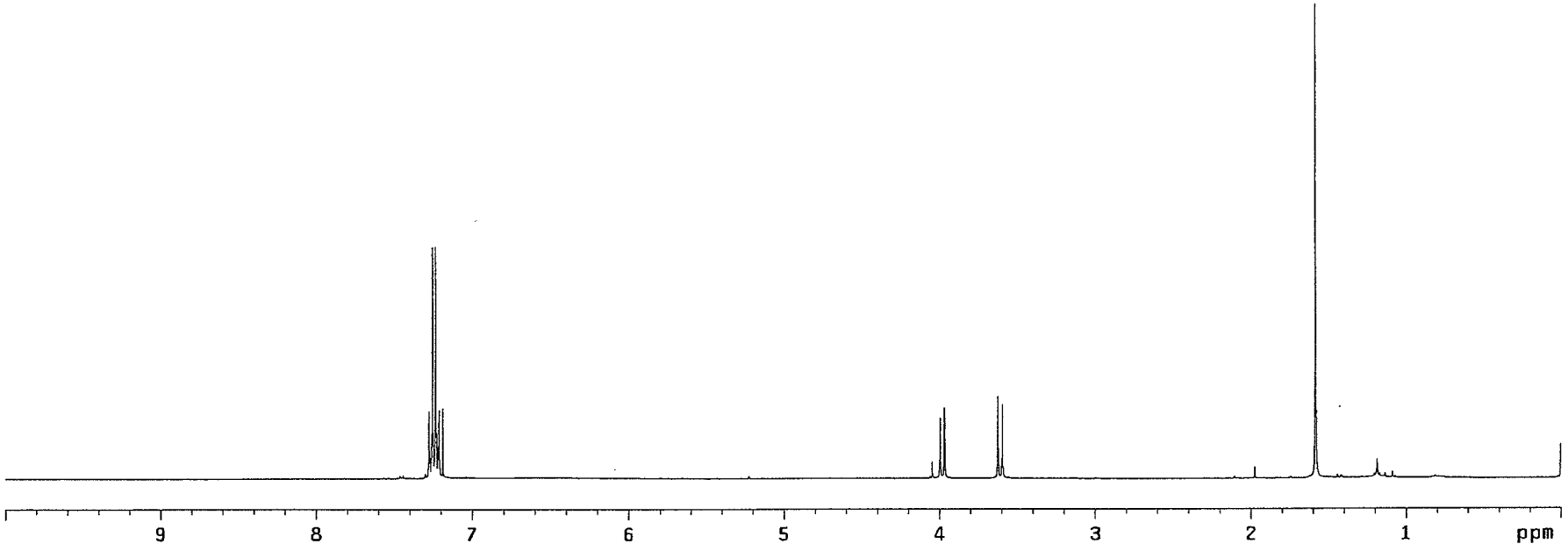


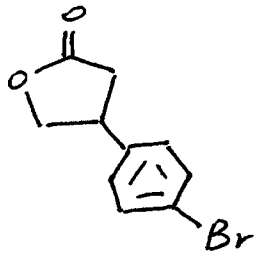
Table 2. Entry 5
linear product.

purified

Sample: xs-1-276
File: home/All/klt/XS/Backup 2010.04.13/xs-1-276-purified.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-276-purified
VNMRS-500 "nmr16"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 50 sec



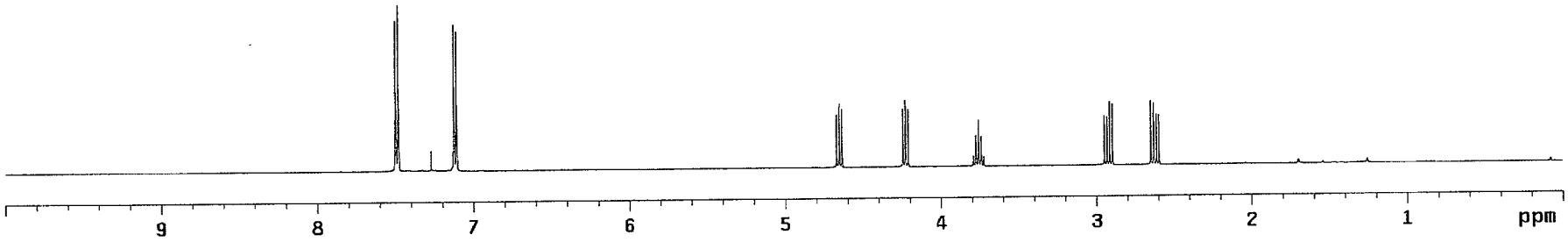


Table 2. Entry 5: crude

Sample: KF-2-040.1
File: home/All/klt/KF/KF-2-040.1.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: KF-2-040.1
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

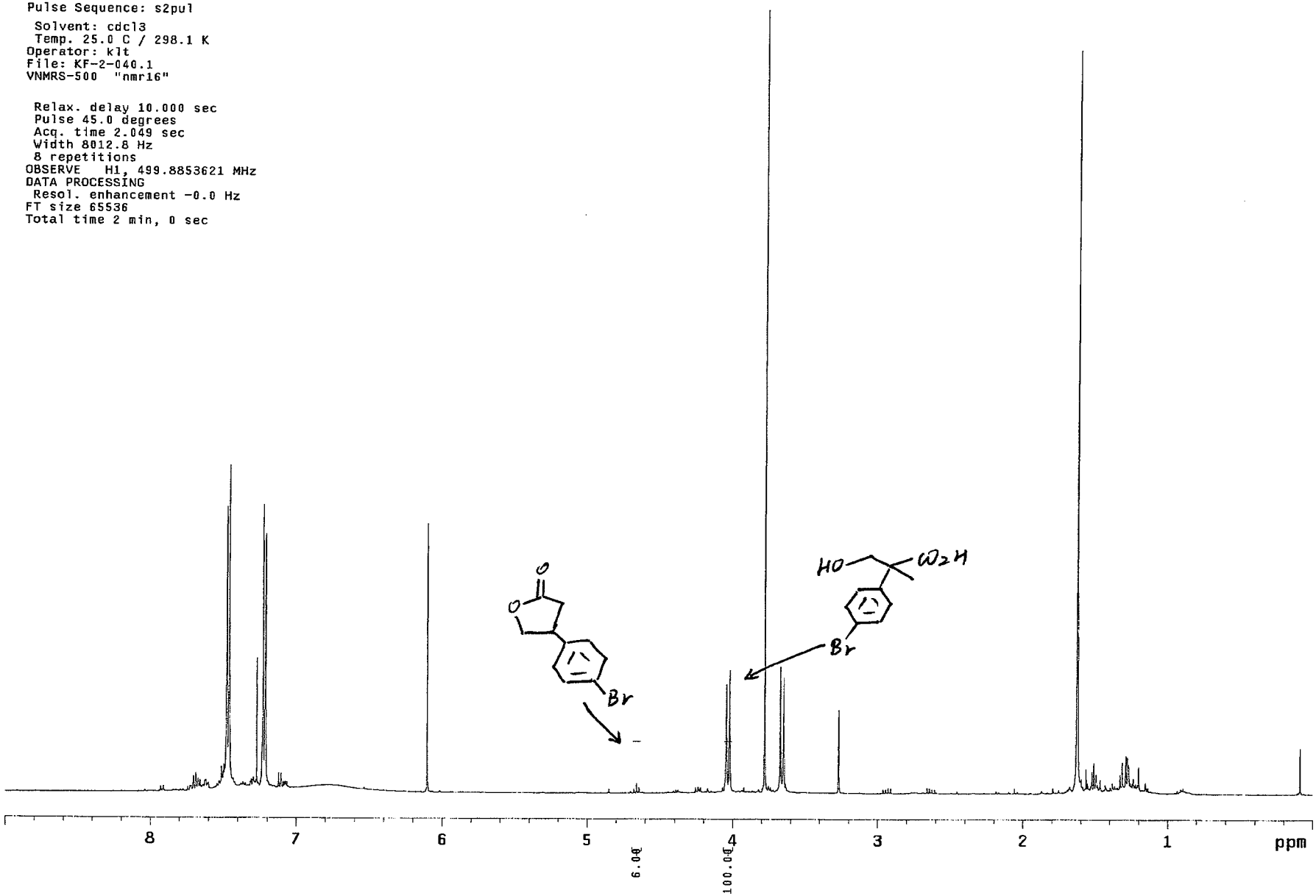
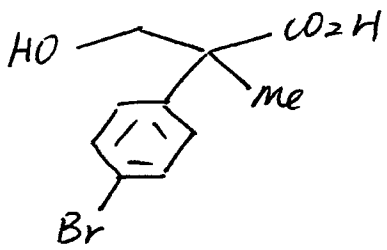


Table 2. Entry 5:
branched product

Sample: xs-1-275.1-pure
File: home/All/klt/XS/Printout/xs-1-275.1-pure.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-1-275.1-pure
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7662987 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



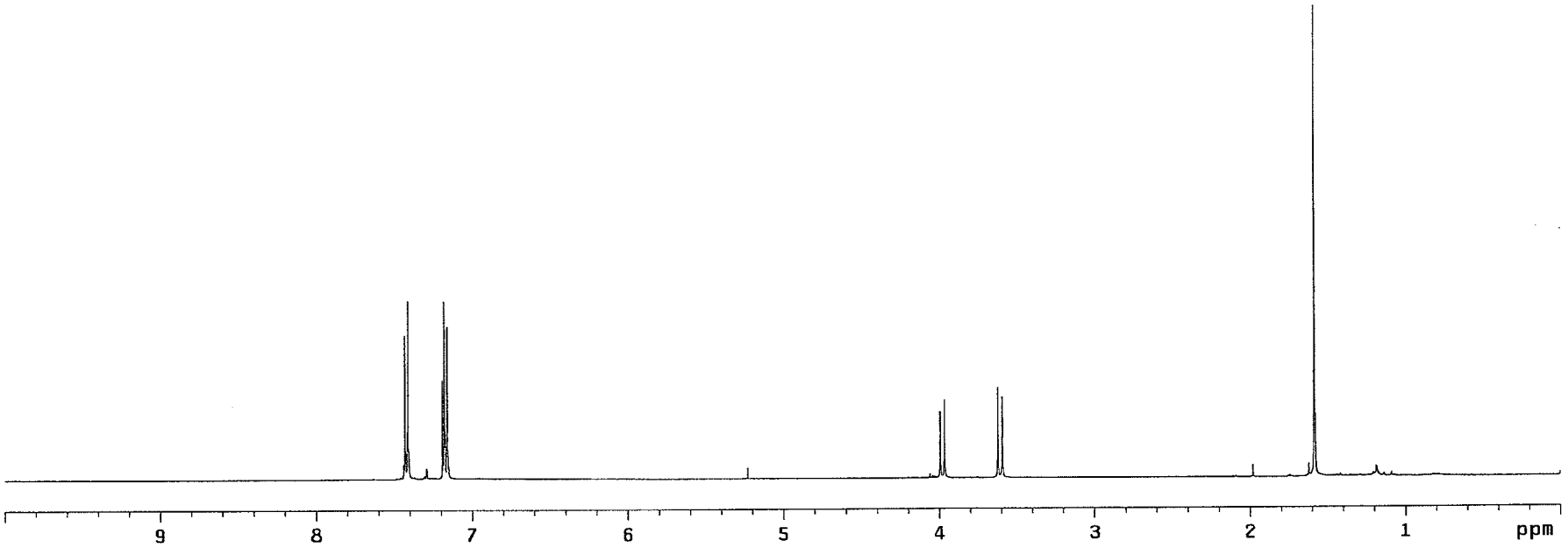
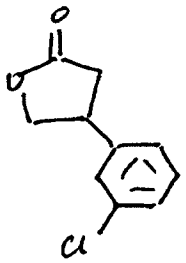


Table 2. Entry 6:
linear product

```
Sample: KF-2-055
File: home/All/klt/KF/KF-2-055.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: klt
File: KF-2-055
VNMRS-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7720124 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec
```



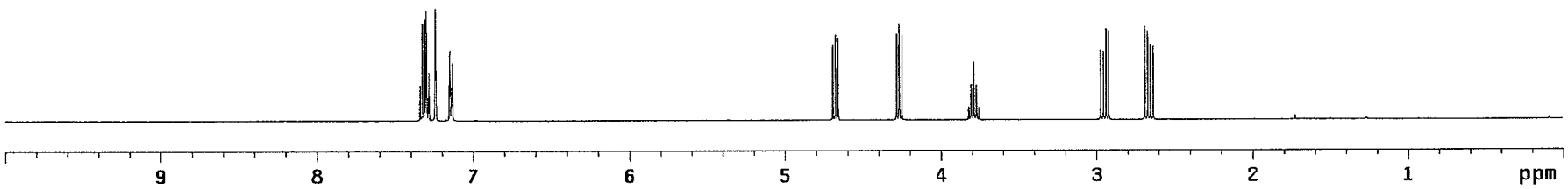


Table 2. Entry 6 :

crude

Sample: KF-2-048-2
Sample ID: /home/walkup/kwame/25_KF-2-048-2_2_048_01
File: home/All/klt/KF/KF-2-048-2_2_048_01.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #25, Operator: kwame
File: KF-2-048-2_2_048_01
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7662768 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

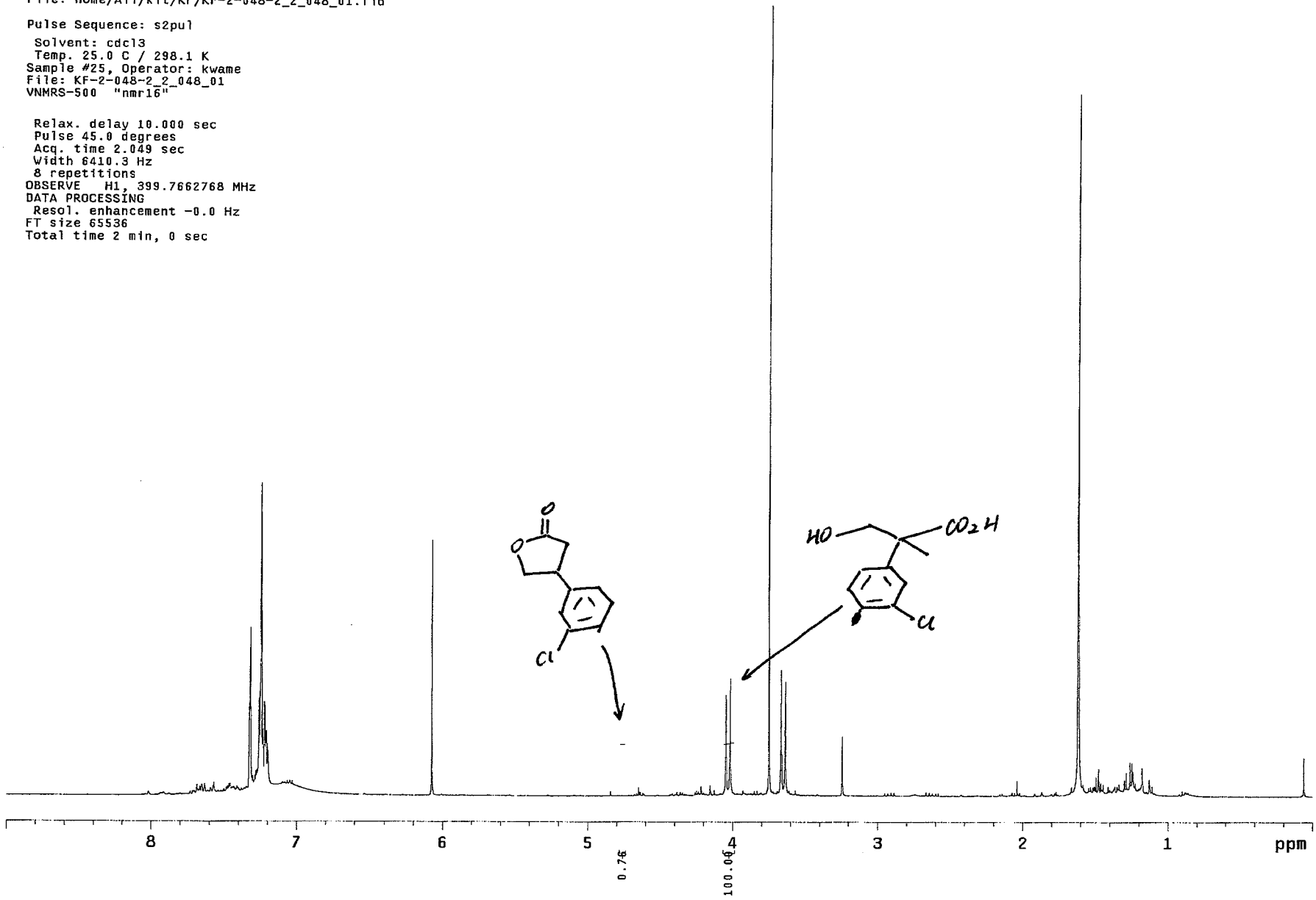
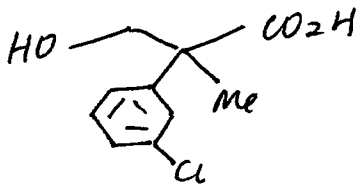


Table 2, Entry 6:
branched product

Sample: KF-2-060
File: exp

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500 "nmr15"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



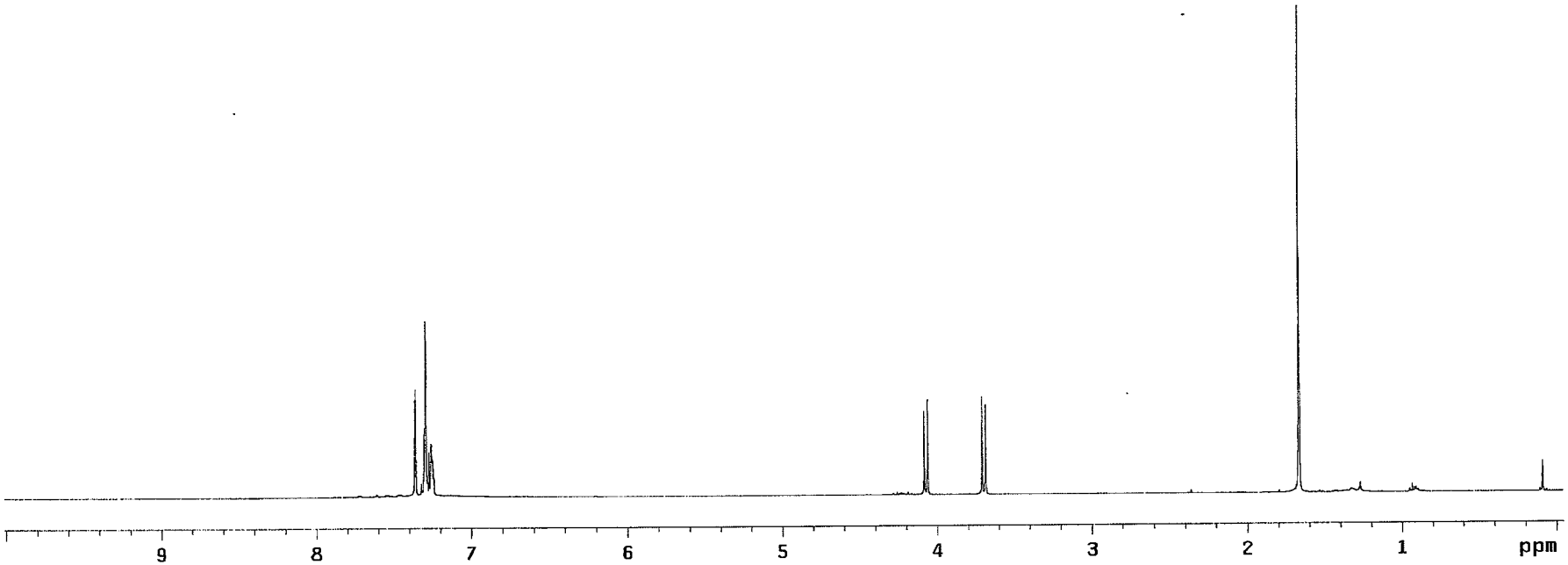
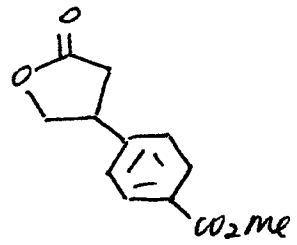


Table 2. Entry 7:
linear product

```
Sample: xs-2-36-f58-75
File: exp

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500  "nmr15"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE   H1, 499.8853621 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```



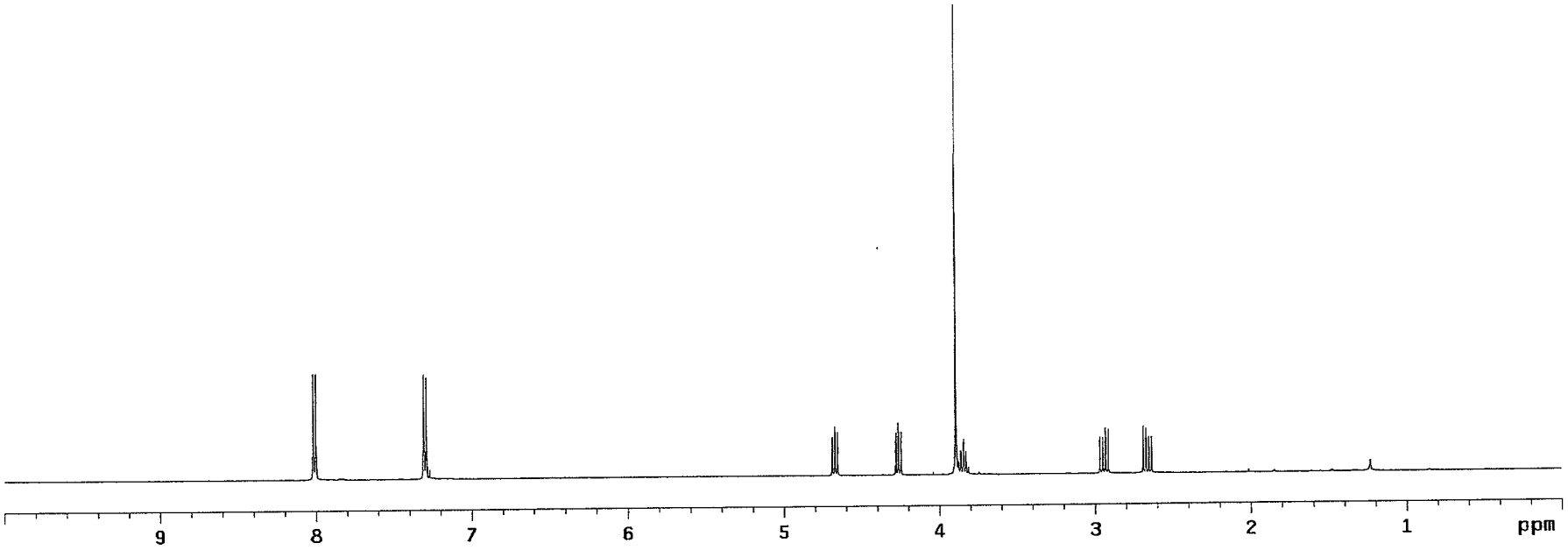


Table 2. Entry 7:
crude

Sample: xs-2-40-crude
File: home/All/klt/XS/xs-2-40-crude.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-40-crude
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec

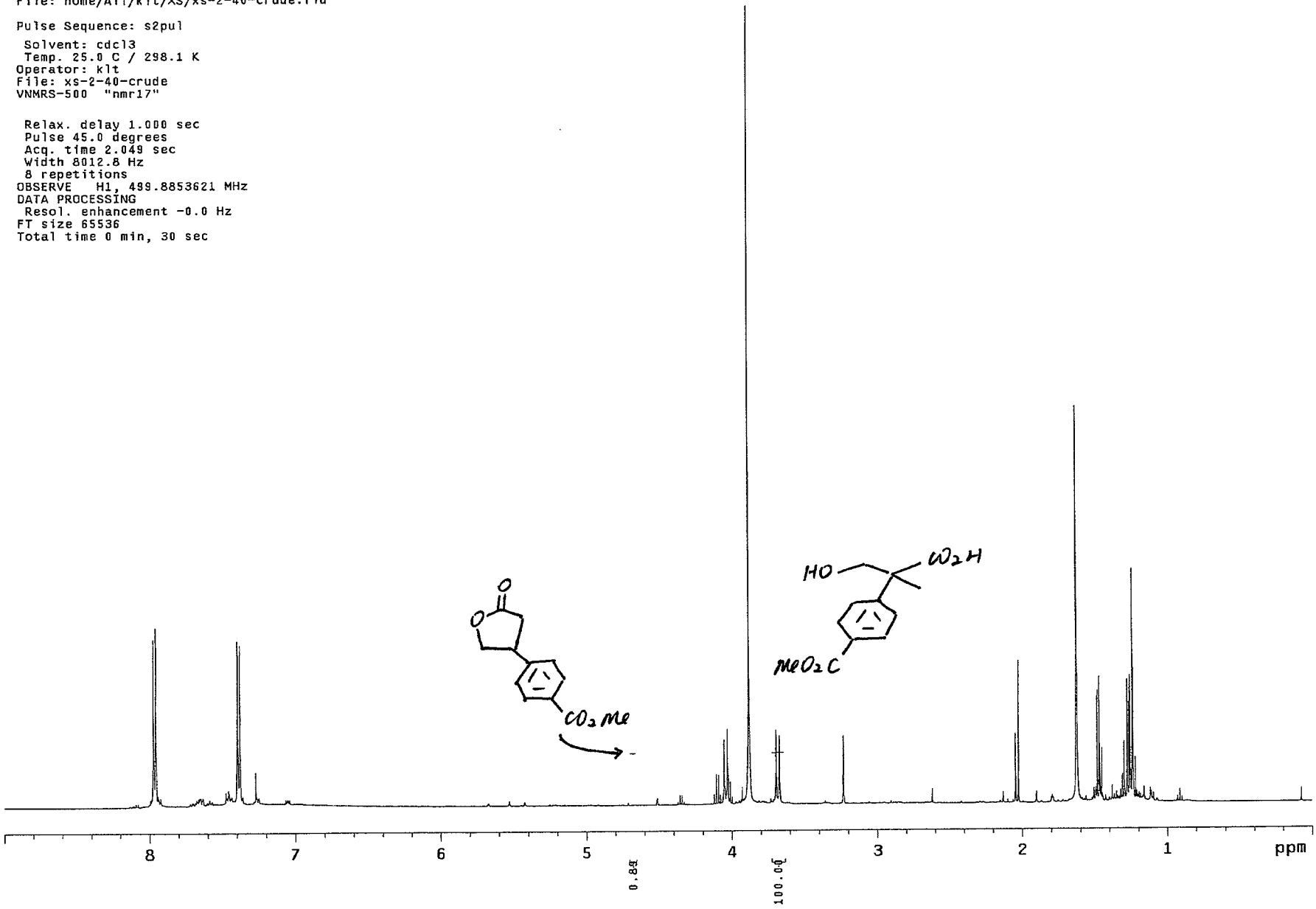
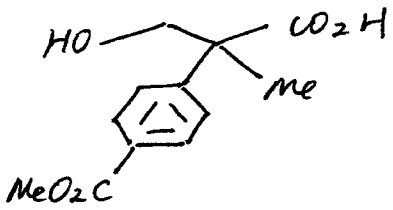


Table 2, Entry 7:
branched product

```
Sample: xs-2-40-pure
Sample ID: /home/walkup/xixi/xs-2-40-pure___01
File: home/All/klt/XS/xs-2-40-pure___01.fid

Pulse Sequence: s2pul
 Solvent: acetone
 Temp. 25.0 C / 298.1 K
Sample #5, Operator: xixi
File: xs-2-40-pure___01
VNMRS-500  "nmr17"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.7683516 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```



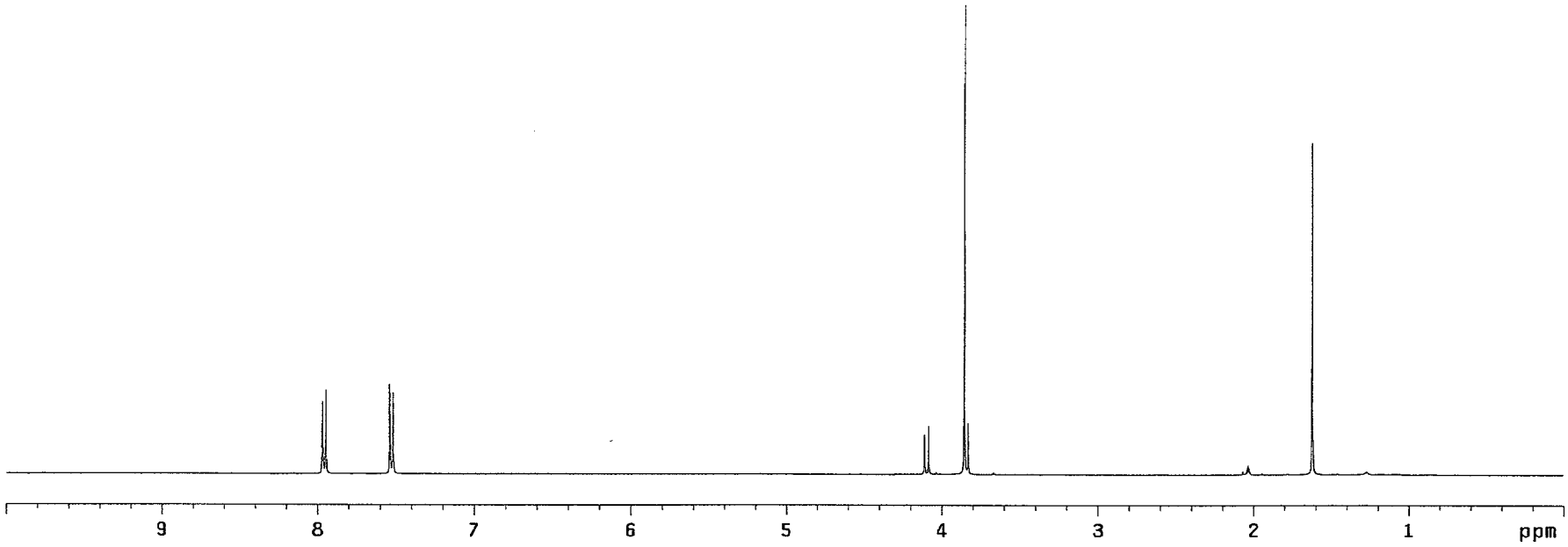
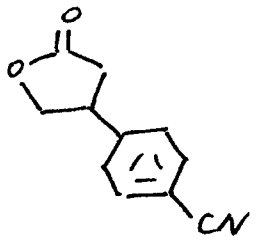


Table 2, Entry 8:
linear product

```
Sample: KF-2-047
Sample ID: /home/walkup/kwame/28_KF-2-047_2_47_01
File: home/All/klt/KF/KF-2-047_2_47_01.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Sample #28, Operator: kwame
File: KF-2-047_2_47_01
VNMRS-500  "nmr16"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 8 repetitions
OBSERVE   H1, 399.7662768 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec
```



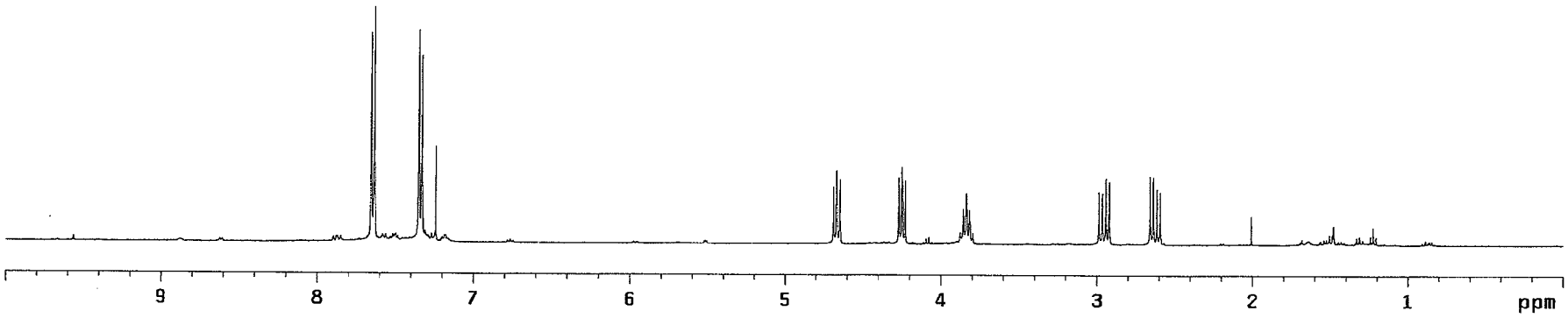


Table 2. Entry 8:

crude

Sample: KF-2-049-3
Sample ID: /home/walkup/kwame/42_KF-2-049-3_2_049_01
File: home/All/klt/KF/KF-2-049-3_2_049_01.fid

Pulse Sequence: s2pul

Solvent: c6d6
Temp. 25.0 C / 298.1 K
Sample #42, Operator: kwame
File: KF-2-049-3_2_049_01
VNMRS-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663128 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

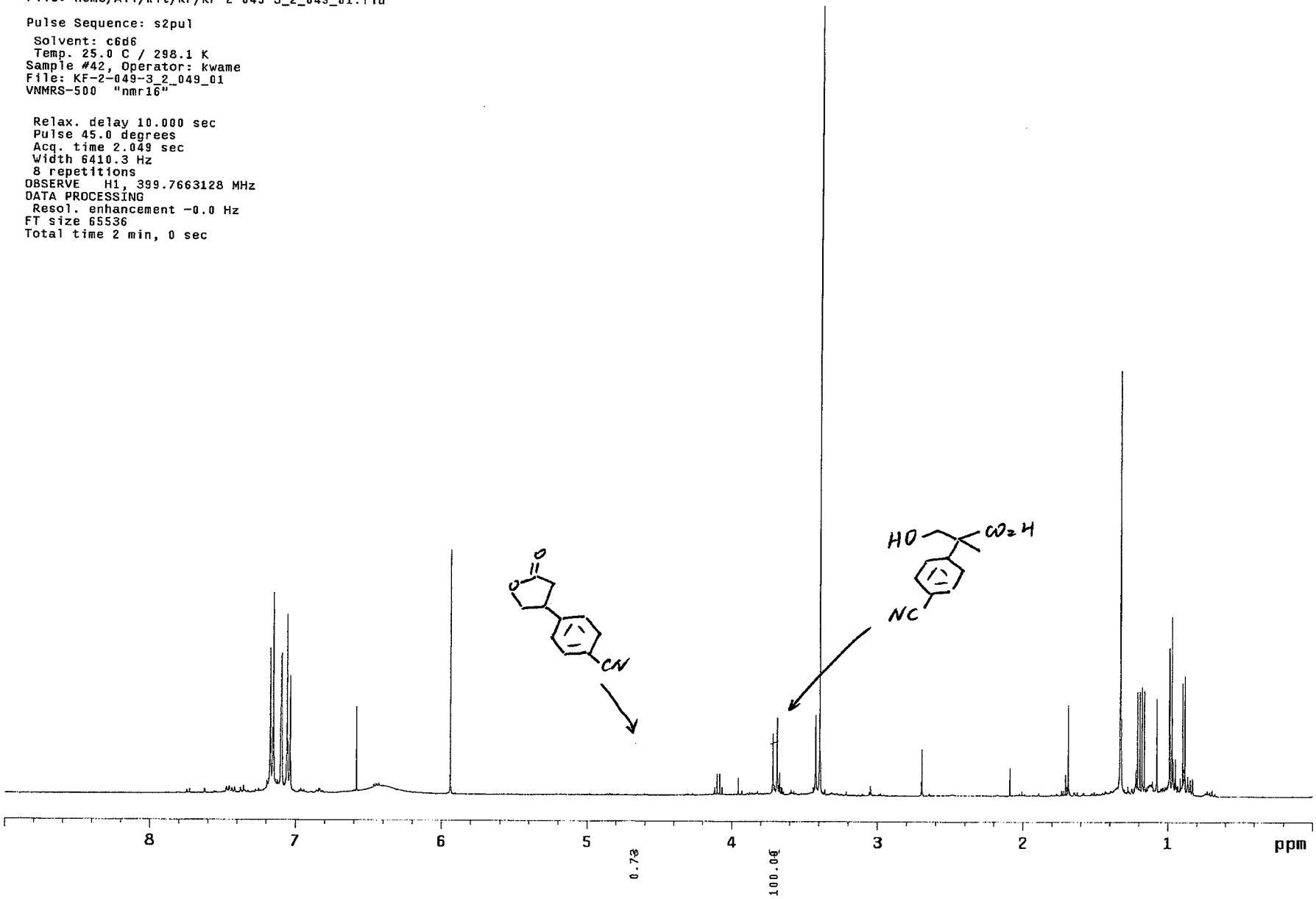


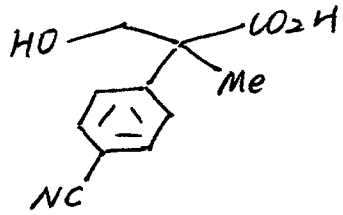
Table 2. Entry 8:

branched product

Sample: KF-2-059
File: /home/klt/vnmrsys/data/KF/KF-2-059.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: klt
File: KF-2-059
VNMRS-500 "nmr15"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec



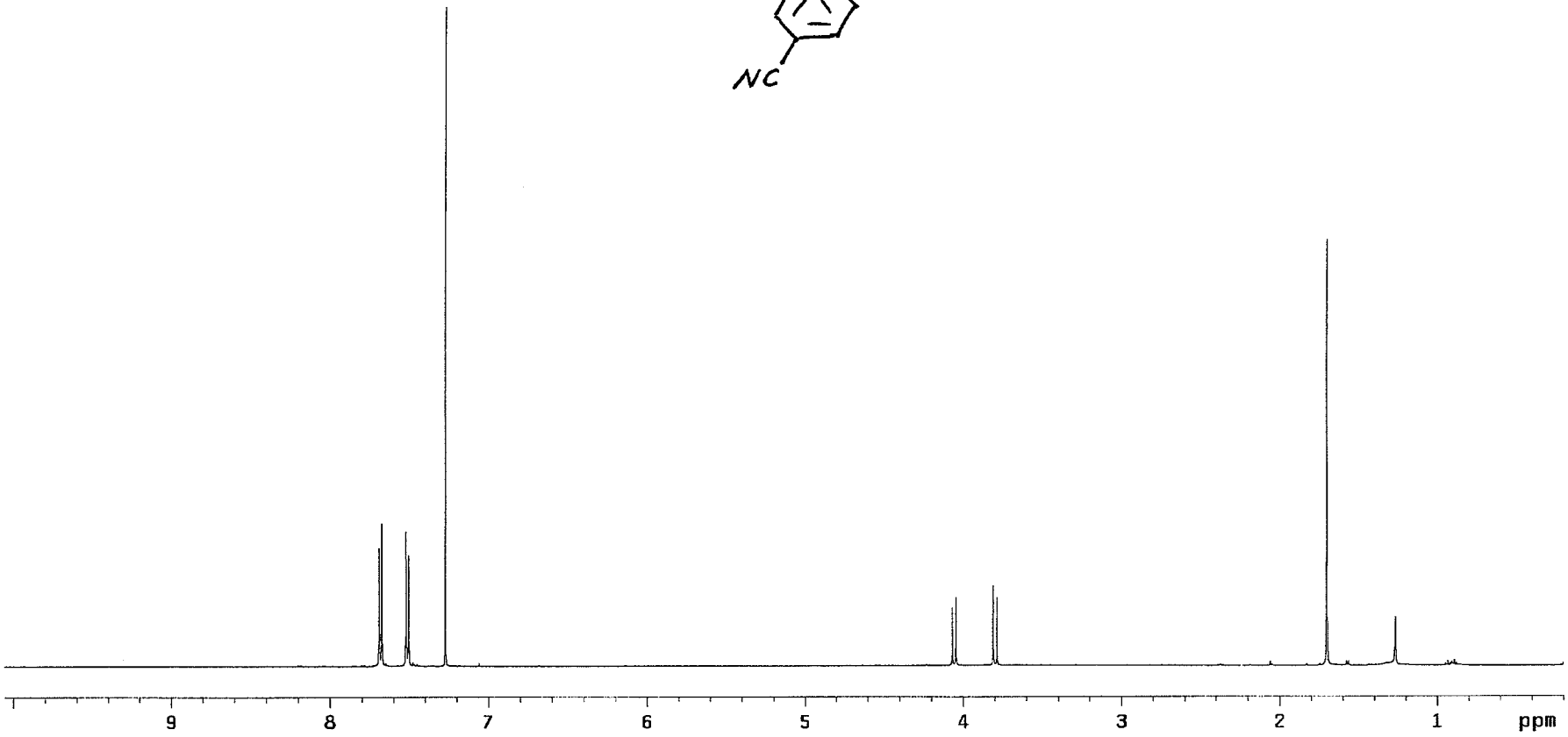


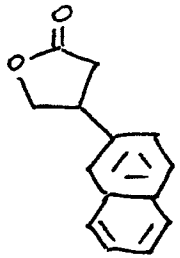
Table 2. Entry 9:

linear product

```
Sample: KF-2-057
File: home/All/klt/KF/KF-2-057.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: klt
File: KF-2-057
VNMRS-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7720124 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec
```



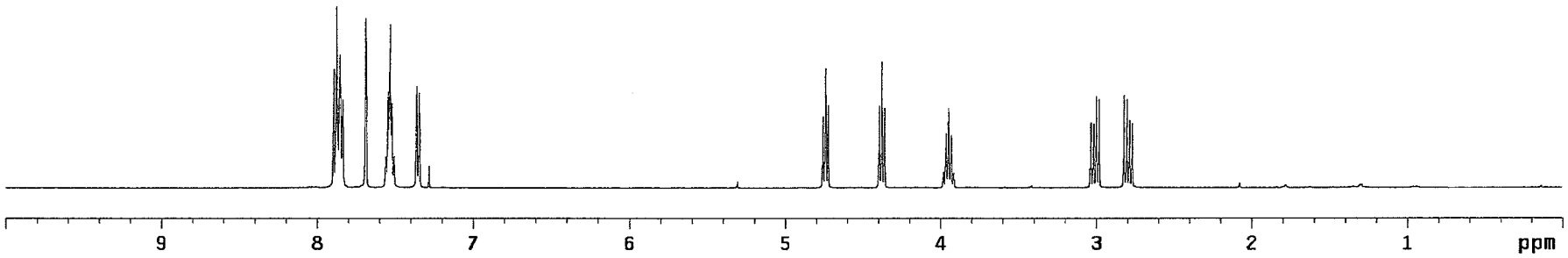


Table 2. Entry 9: crude

Sample: xs-2-20-crude
File: home/All/klt/XS/NMR 500 2010.03.19/xs-2-20-crude.fid

Pulse Sequence: s2pul
Solvent: acetone
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-20-crude
VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8879565 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec

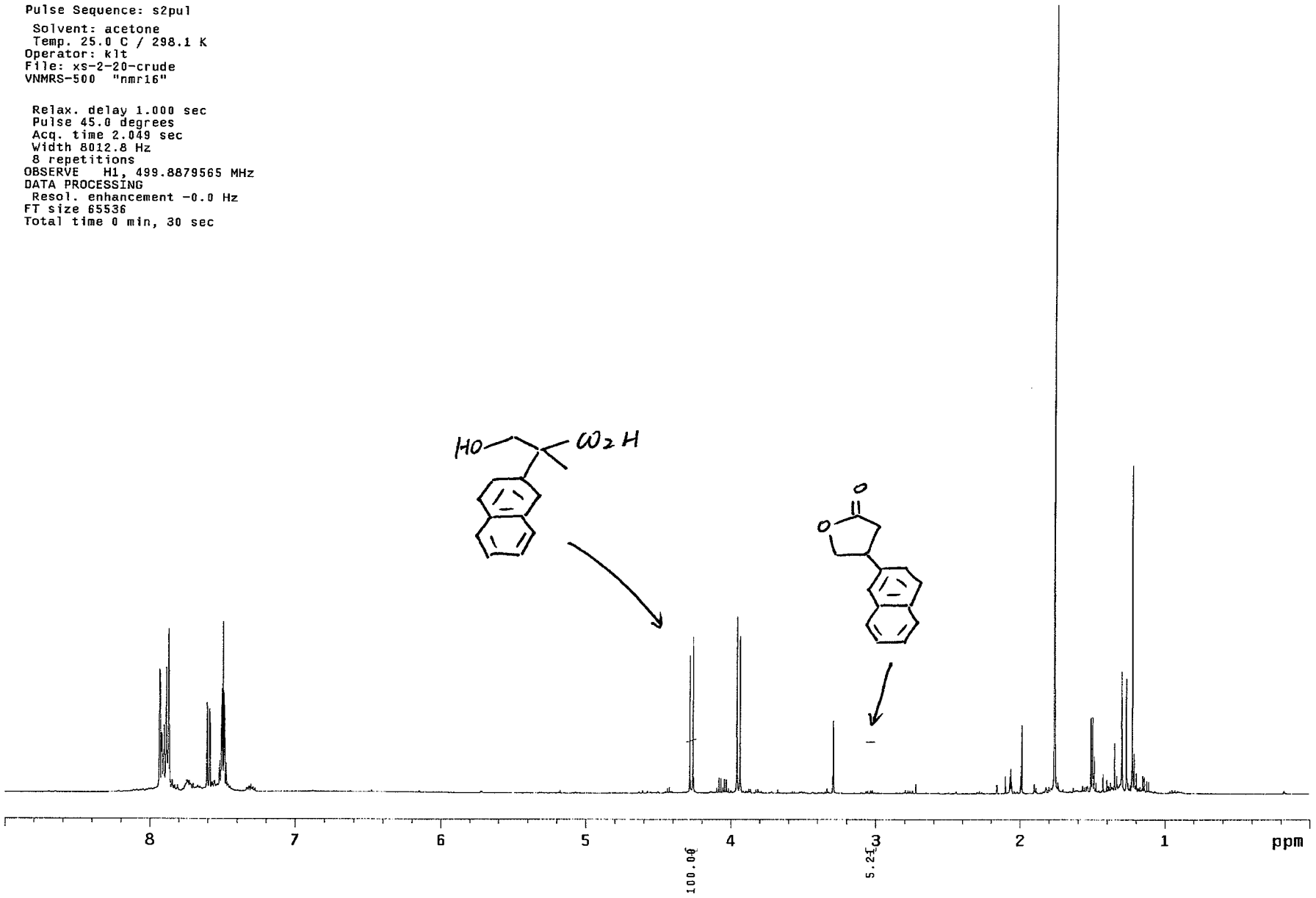


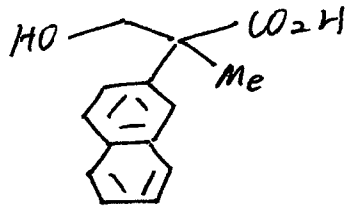
Table 2. Entry 9:

branched product

```
Sample: xs-2-6-pure
File: exp

Pulse Sequence: s2pul
 Solvent: acetone
 Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500  "nmr15"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE    H1, 499.8879565 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```



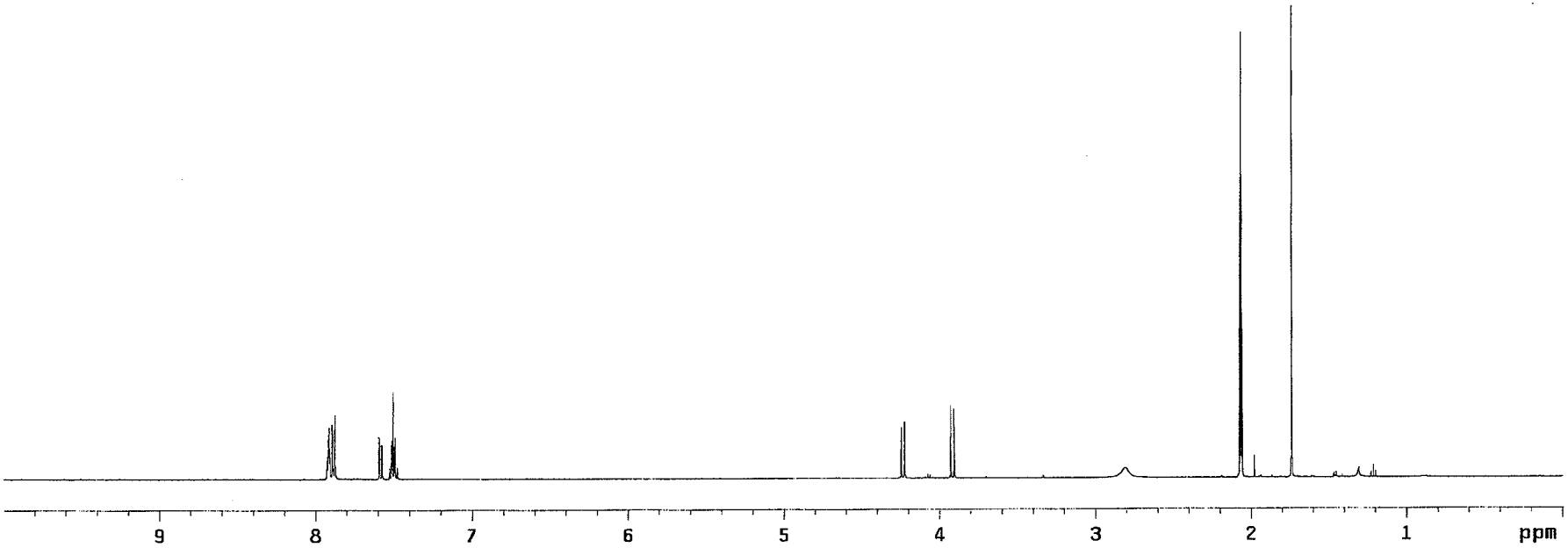


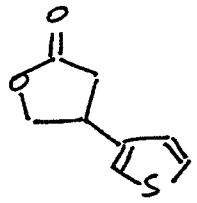
Table 2, Entry 10:
linear product

Sample: xs-2-37-pure
File: home/All/klt/XS/xs-2-37-pure.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-37-pure
VNMRS-500 "nmr17"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



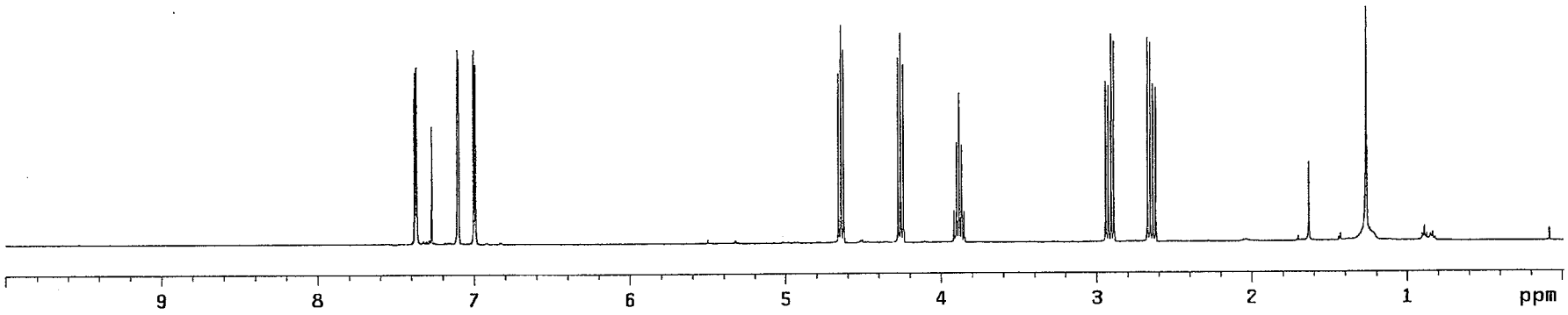


Table 2. Entry 10: crude

Sample: xs-2-39-crude
File: exp

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500 "nmr15"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

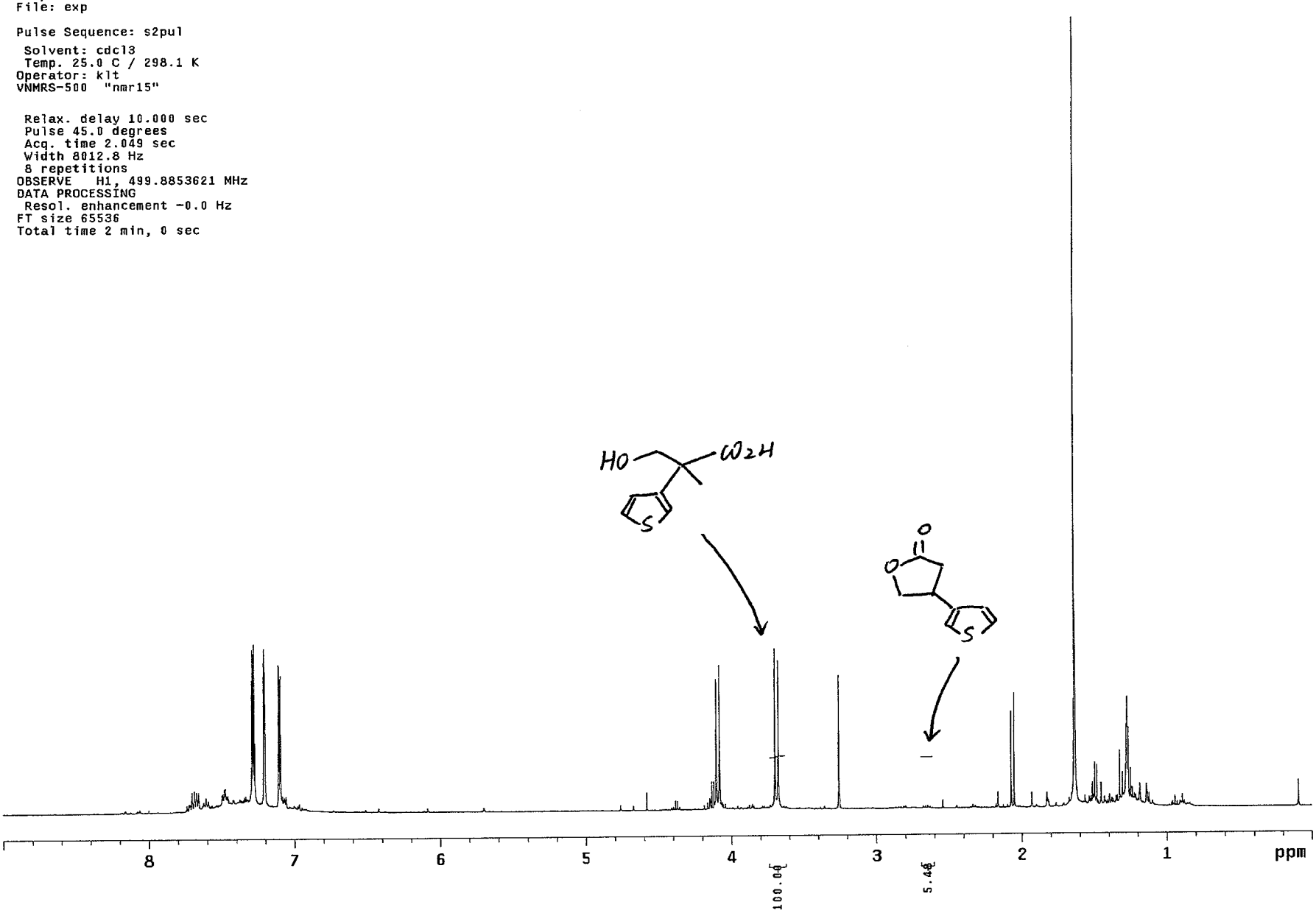


Table 2. Entry 10:

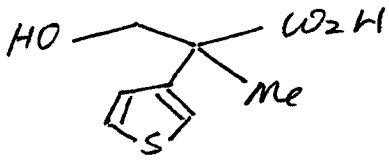
branched product

Sample: xs-2-34-pure
File: exp

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500 "nmr15"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



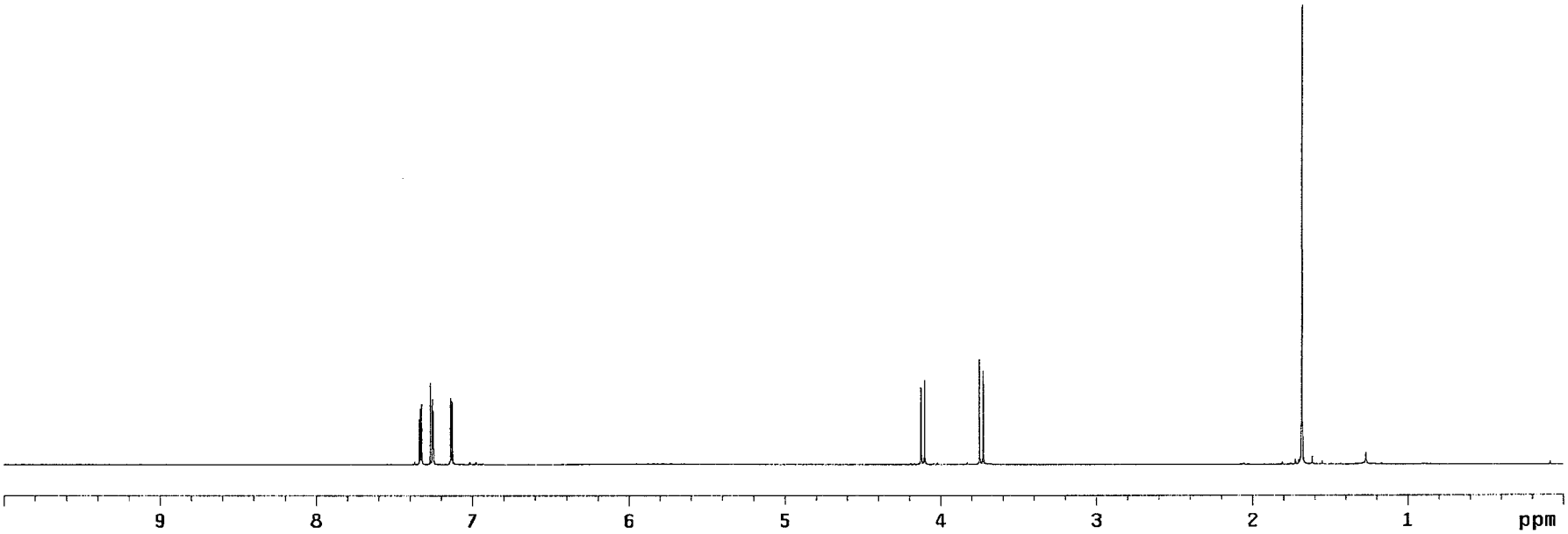


Table 2. Entry 11:
linear product

Sample Name:
xs-2-119.2-pure
Archive directory:

Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cd3od
Data collected on: Jul 14 2010

Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7739815 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 40 sec

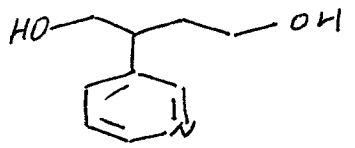


Table 2. Entry 11: crude

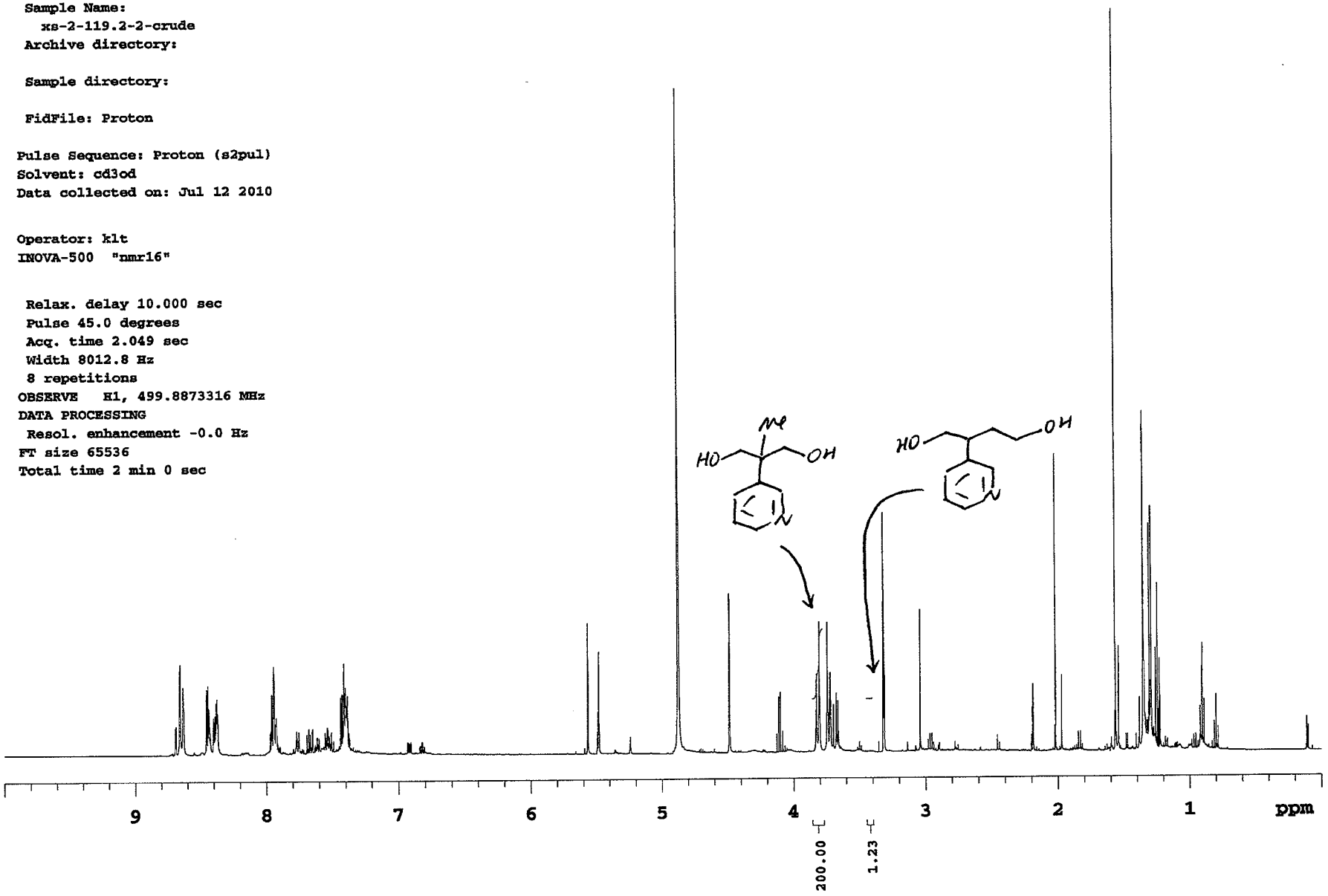


Table 2. Entry 11:
branched product

Sample Name:
xs-2-115.2-pure
Archive directory:

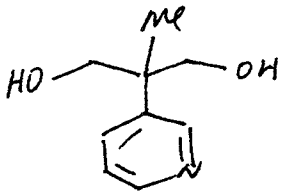
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cd3od
Data collected on: Jul 14 2010

Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7739815 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 40 sec



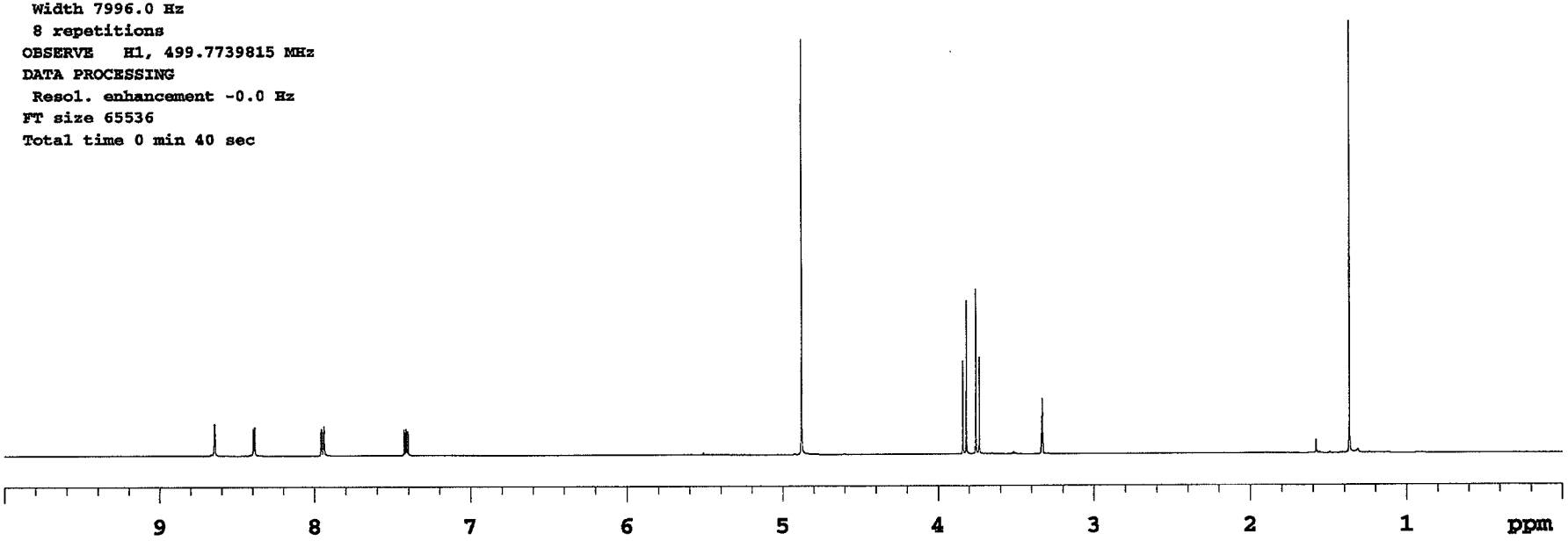


Table 2. Entry 12:
linear product

Sample: xs-2-126-pure
File: /home/klt/XS/xs-2-126-pure-CD3OD.fid

Pulse Sequence: s2pul

Solvent: cd3od
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-126-pure-CD3OD
INOVA-500 "nmr11"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7739815 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec

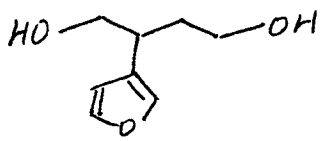


Table 2. Entry 12: crude

Sample Name:
xs-2-124.1-crude-red
Archive directory:

Sample directory:

FidFile: xs-2-124.1-crude-red

Pulse Sequence: Proton (s2pul)
Solvent: cd3od
Data collected on: Jul 15 2010

Operator: klt
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8873316 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 30 sec

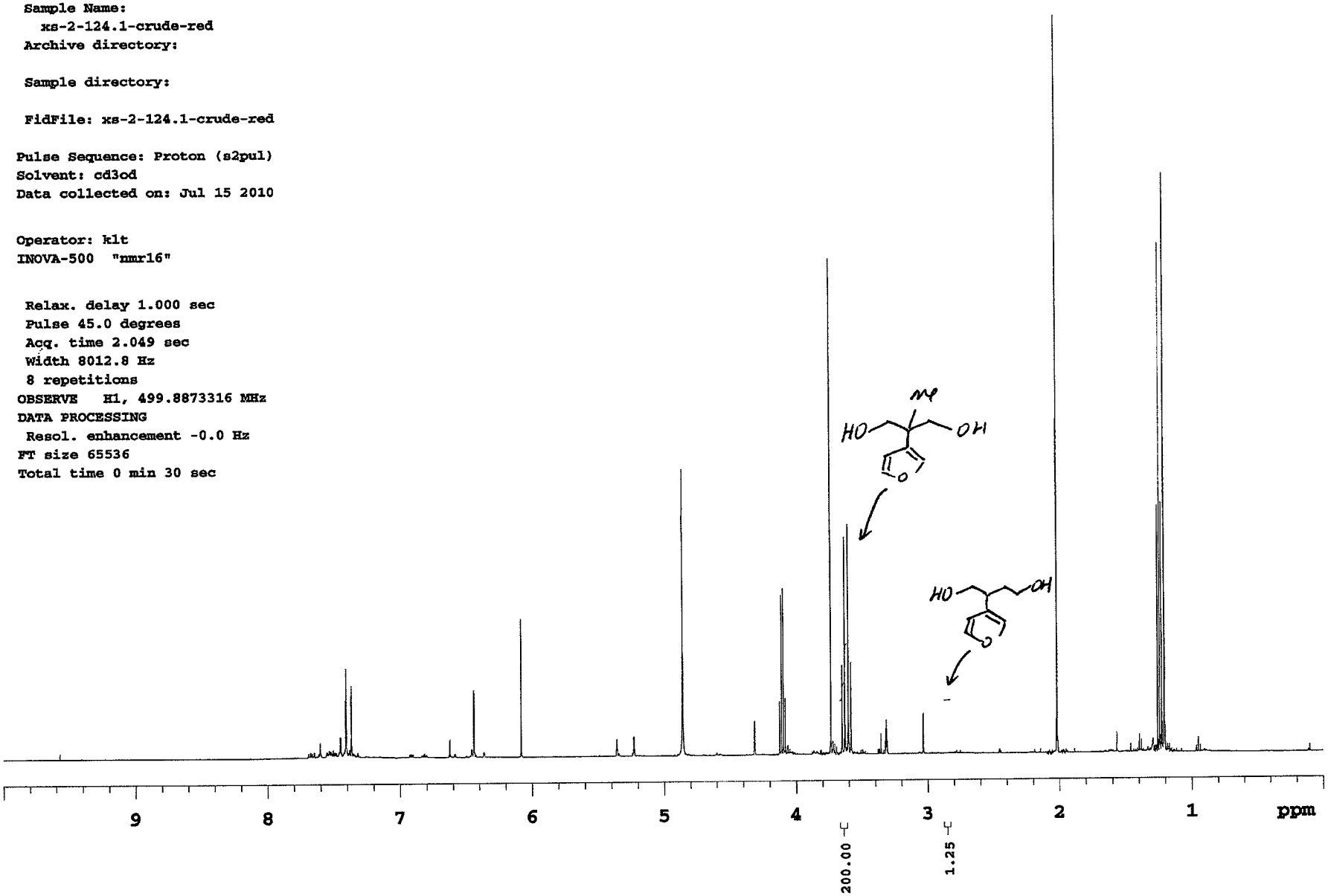
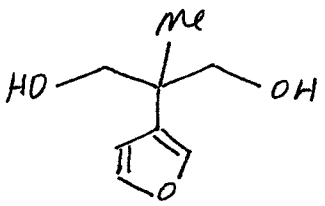


Table 2. Entry 12:
branched product

```
Sample: xs-2-124.2-pure
File: exp

Pulse Sequence: s2pul
 Solvent: cd3od
 Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500  "nmr11"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7739815 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 40 sec
```



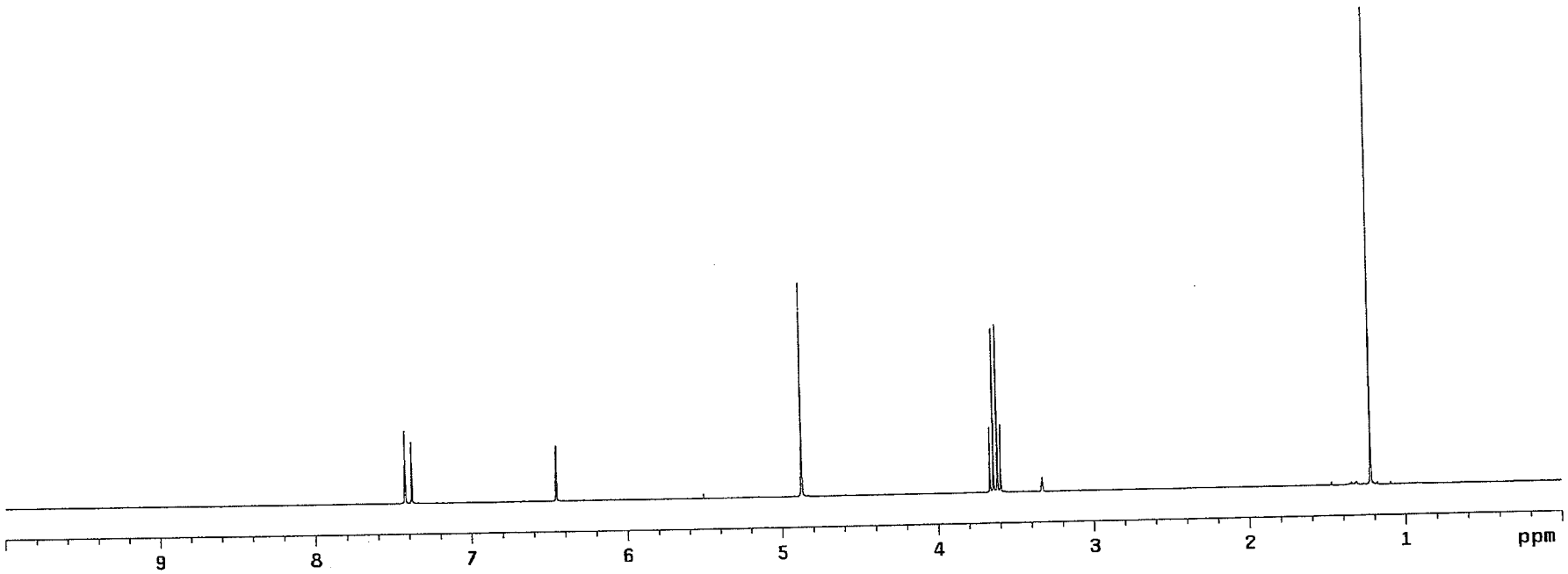


Table 2, Entry 13:
crude

Sample: xs-2-52-crude
File: exp

Pulse Sequence: s2pul
 Solvent: acetone
 Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500 "nmr15"

 Relax. delay 10.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE H1, 499.8879565 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min, 0 sec

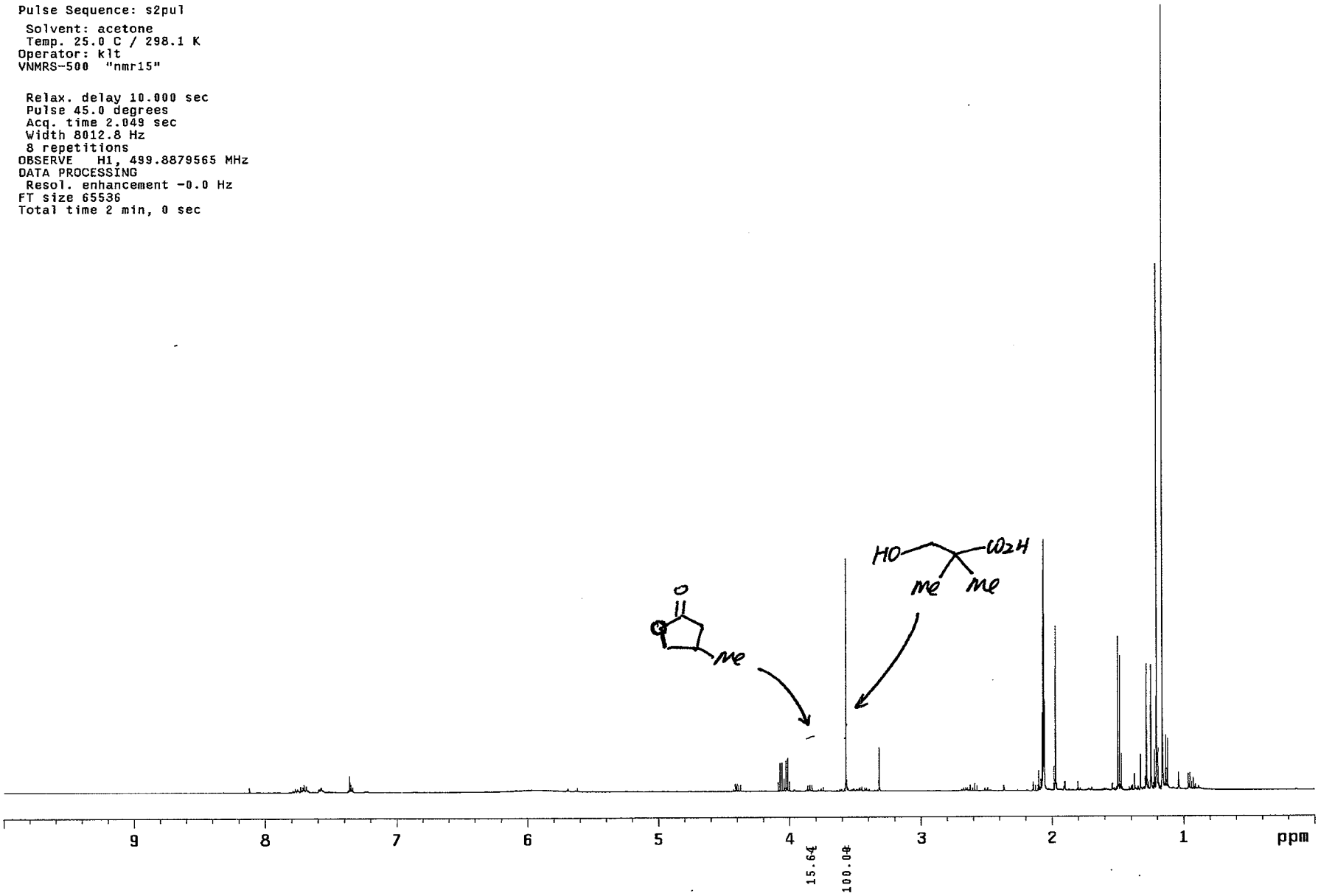
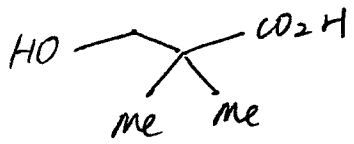


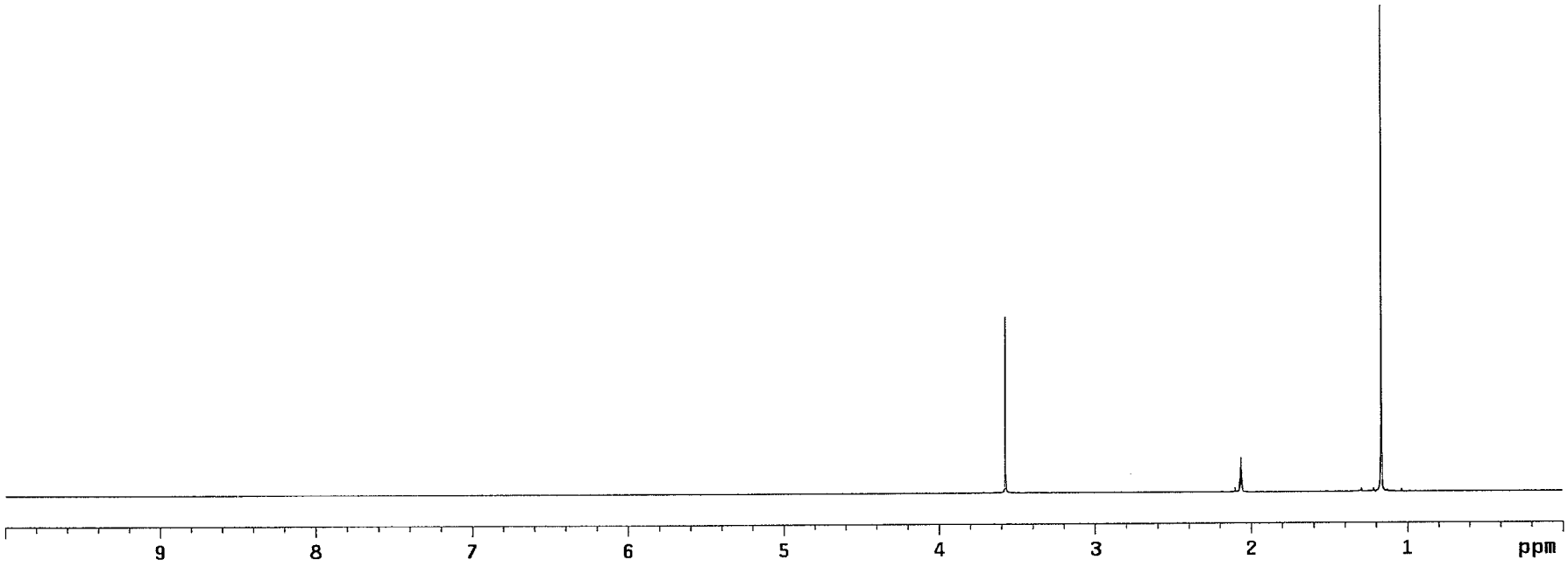
Table 2. Entry 13:
branched product

```
Sample: xs-2-45.3-f6-15-pure
File: exp

Pulse Sequence: s2pul
 Solvent: acetone
 Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500  "nmr15"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 8 repetitions
OBSERVE   H1, 499.8879565 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec
```

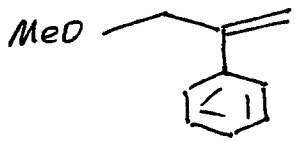




Sample: xs-2-23-pure
File: exp

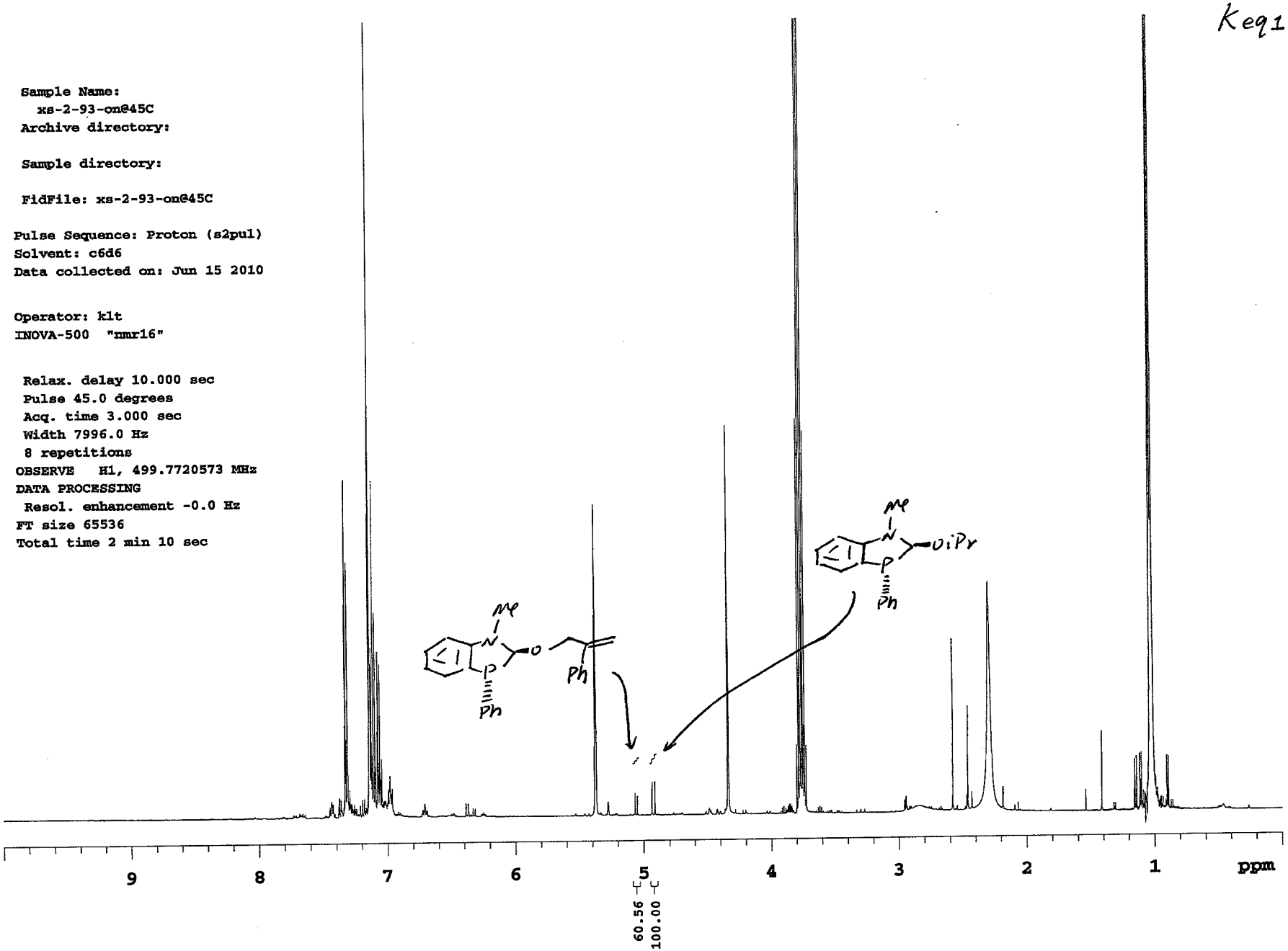
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
VNMRS-500 "nmr15"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8853621 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec



Binding Study

Keq1



Binding Study:

Keq2

Sample Name:
xs-2-94-on@45C
Archive directory:

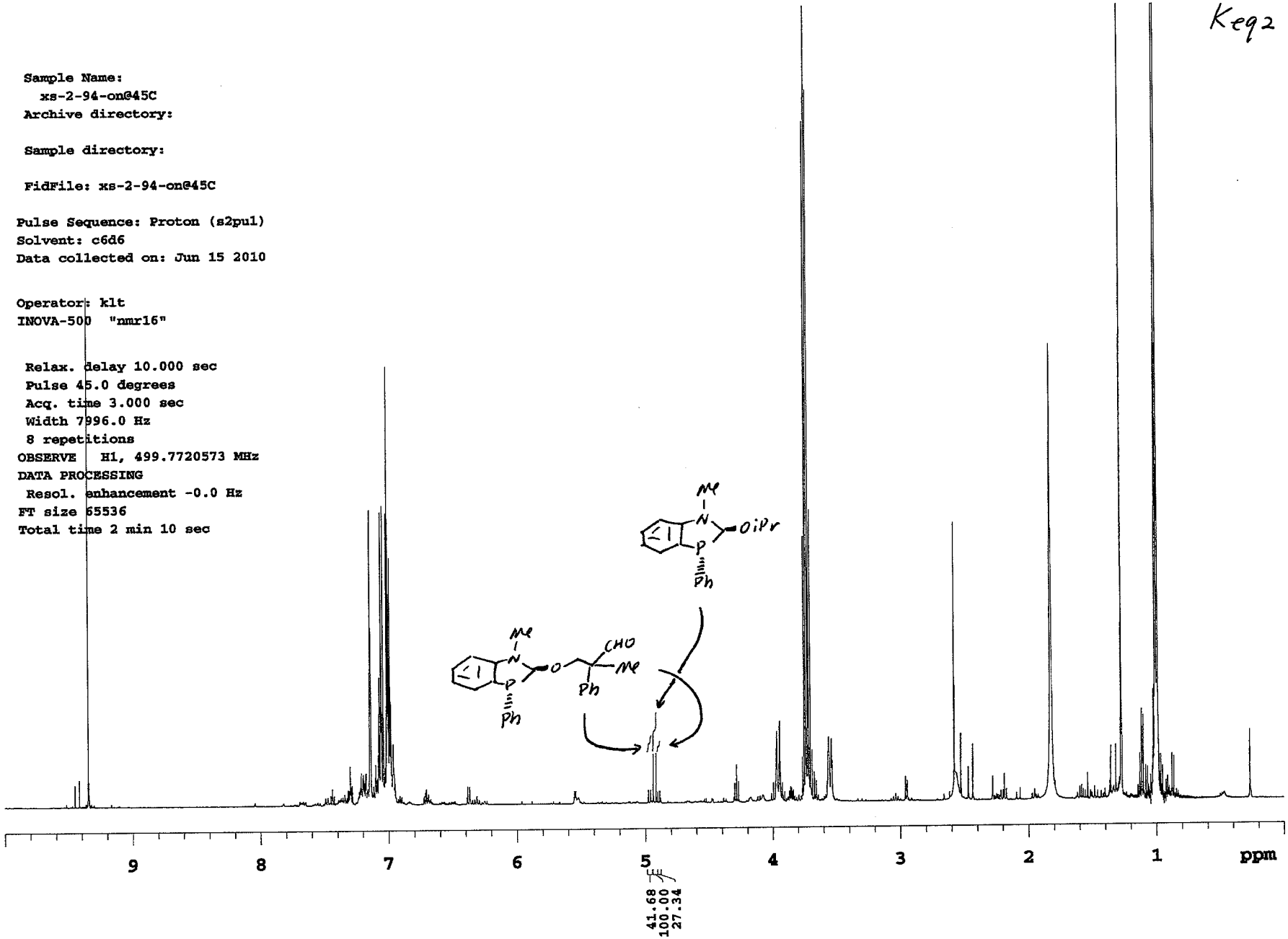
Sample directory:

FidFile: xs-2-94-on@45C

Pulse Sequence: Proton (s2pul)
Solvent: c6d6
Data collected on: Jun 15 2010

Operator: klt
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7720573 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 10 sec



Binding Study
Keq 3
before aldehyde addition.

Sample Name:
xs-2-89-1.5h@45C
Archive directory:

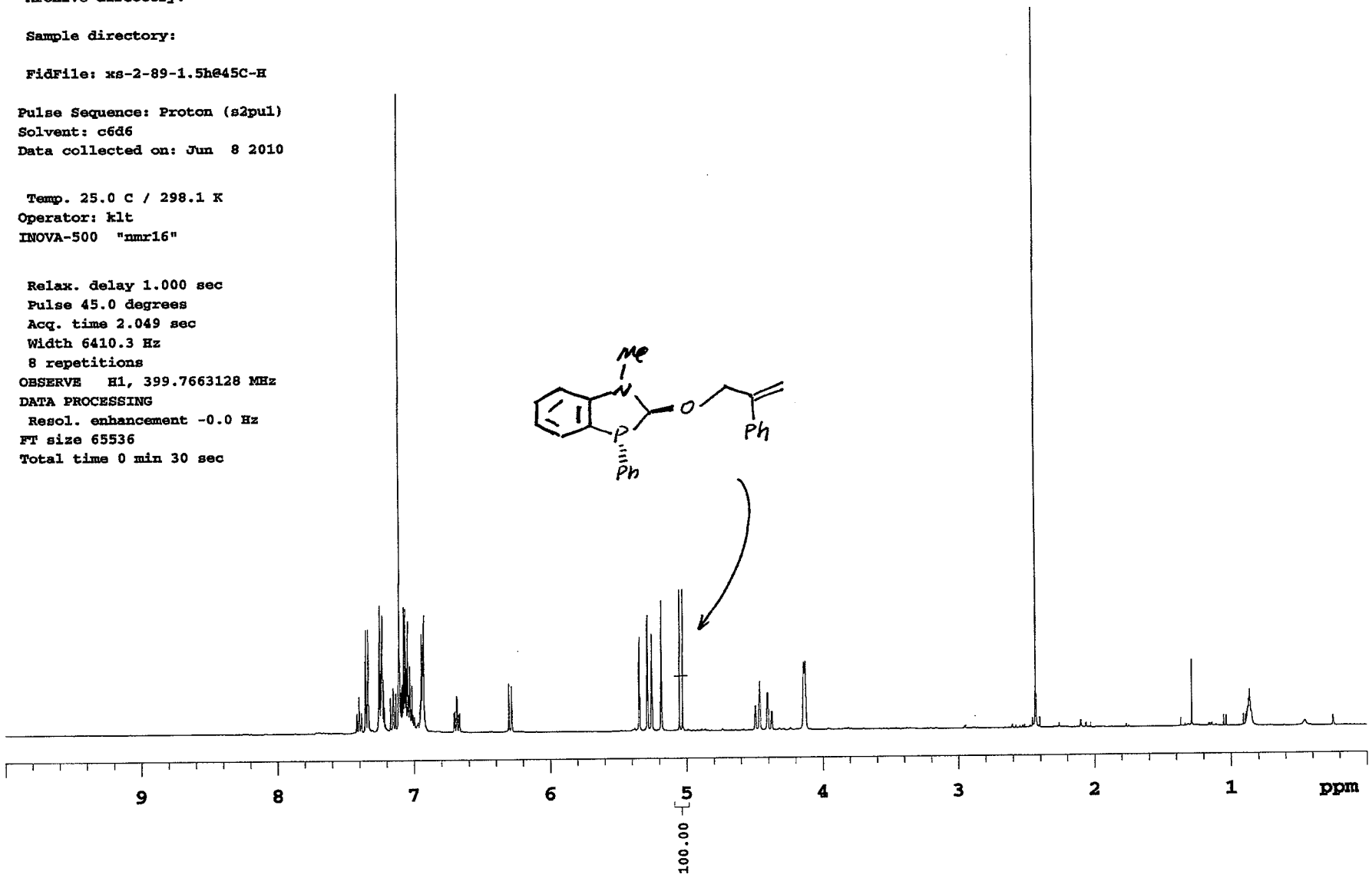
Sample directory:

FidFile: xs-2-89-1.5h@45C-H

Pulse Sequence: Proton (s2pul)
Solvent: c6d6
Data collected on: Jun 8 2010

Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663128 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 30 sec



Binding Study

Keq 3

aldehyde product added

Sample Name:
xs-2-89-2-on@45
Archive directory:

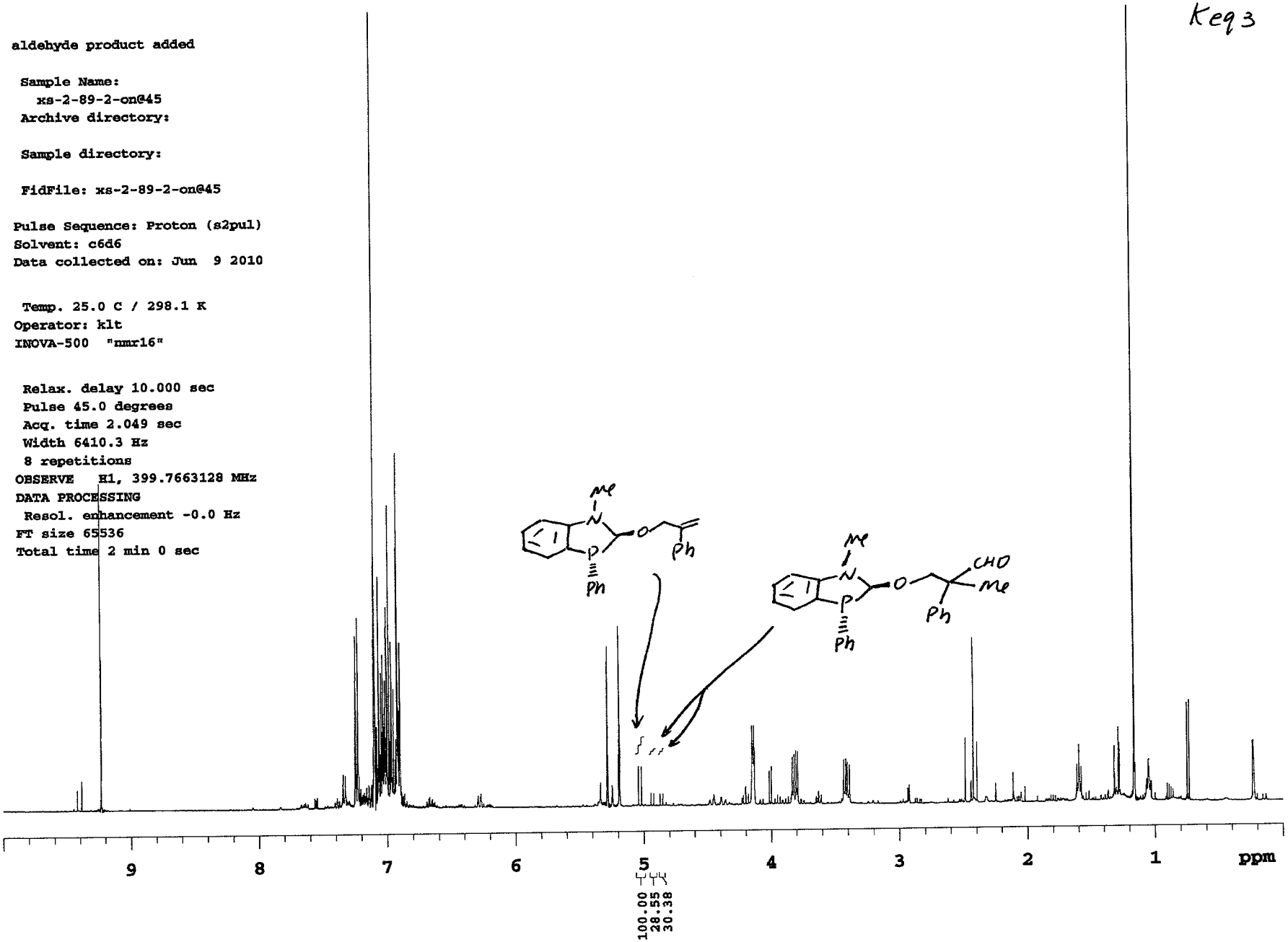
Sample directory:

FidFile: xs-2-89-2-on@45

Pulse Sequence: Proton (s2pul)
Solvent: c6d6
Data collected on: Jun 9 2010

Temp. 25.0 C / 298.1 K
Operator: klt
INOVA-500 "nmr16"

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7663128 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 2 min 0 sec



Sample: xs-2-3-pure
File: /home/klt/vnmrsys/data/XS/xs-2-3-pure.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: klt
File: xs-2-3-pure
VNMRS-500 "nmr15"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
8 repetitions
OBSERVE H1, 499.8854048 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 30 sec