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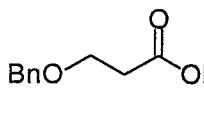
Nonracemic α-Fluoroaldehydes: Asymmetric Synthesis of 4-Deoxy-4-fluoro-D-arabinopyranose

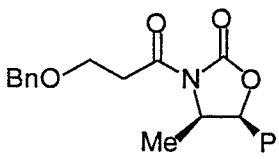
Franklin A. Davis,* Parimala V. N. Kasu, Gajendran Sundarababu and Hongyan Qi.
Department of Chemistry, Temple University, Philadelphia, PA 19122

SUPPLEMENTARY MATERIAL

General Procedure. Infrared spectra were recorded on a Mattson 4020 FTIR spectrometer using sodium chloride plates for liquids and potassium bromide disks for solids. ^1H and ^{13}C NMR spectra were referenced to $CDCl_3$ (7.26 & 77.0 ppm) using GE 300 and QE 500 MHz NMR spectrometers. ^{19}F NMR spectra were referenced to $CFCl_3$ (0.00) using QE 500 MHz NMR spectrometer. High resolution mass spectra were obtained on a Fissions ZAB HF double-focusing mass spectrometer. Column chromatography was performed on silica gel, Merck grade 60 (230-400 mesh) purchased from Aldrich Chemical Co. Analytical and preparative thin layer chromatography were performed on pre-coated silica gel plates (250 and 1000 microns) purchased from Analtech Inc. TLC plates were visualized with UV light, $KMnO_4$ solution or in an iodine chamber. Melting points were recorded on Mel-Temp apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. THF was freshly distilled under nitrogen from sodium and benzophenone and CH_2Cl_2 from CaH_2. Elemental analyses were performed by the Department of Chemistry, University of Pennsylvania.



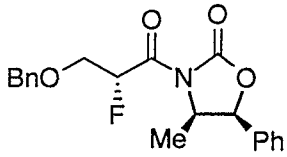
3-Benzyloxypropionic acid: In an oven dried 500 mL, one neck, round bottomed flask equipped with a rubber septum and a magnetic stir bar were placed 10 g (60 mmol) of 3-benzyloxy-1-propanol (**1**) (Aldrich) and acetone (300 mL). The reaction mixture was cooled to 0 °C and the Jones reagent was added dropwise until an orange color persisted.[1] After the reaction was complete, 1.5-2 h as monitored by TLC, the solution was filtered through Celite and concentrated. The residue was dissolved in 100 mL EtOAc, washed with H_2O (3 x 50 mL), brine (2 x 20 mL), dried ($MgSO_4$), and concentrated to afford 9.17 g (92%) of 3-benzyloxypropionic acid. An analytically pure sample was obtained by flash chromatography (EtOAc): mp 34 °C; IR (neat) 3030 (-OH), 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.67 (t, 2H, J = 6.3 Hz), 3.76 (t, 2H, J = 6.3 Hz), 4.56 (s, 2H), 7.26-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 47.3, 64.6, 73.3, 127.7, 127.8, 128.4, 137.7, 177.1. HRMS Calcd for $C_{10}H_{12}O_3$ (M^++H^+) is 181.0861; Observed (M^++H^+): 181.0864. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; Found: C, 66.61; H, 6.62.



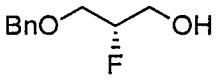
(4*R*,5*S*)-(+)-(3-benzyloxypropionoyl)-4-methyl-5-phenyl-2-oxazolidinone (2). In an oven dried 50 mL, one neck, round bottomed flask equipped with a rubber septum, argon inlet and a magnetic stir bar was placed 1.45 g (8.05 mmol) of 3-benzyloxypropionic acid and 7 mL of $SOCl_2$ (Aldrich). The reaction mixture was stirred at 0 °C for 1.5 h, warmed to rt and stirred for an additional h. The excess $SOCl_2$ was removed by co-evaporation with benzene (2 x 20 mL) and at high vacuum for 2 h to give the 3-benzyloxypropionyl chloride which was used in the next step.

In a separate oven dried 100 mL, one neck, round bottomed flask equipped with rubber septum, argon inlet and a magnetic stir bar were placed 1.39 g (7.89 mmol) of (4*R*,5*S*)-(+)-4-methyl-5-phenyl-2-oxazolidinone in THF (60 mL).[2] The solution was cooled to -78 °C and 3.1 mL (7.89 mmol, 2.5 M in hexanes) of *n*-BuLi was added dropwise *via* syringe. After stirring the reaction mixture at -78 °C for 1 h 1.56 g (7.89 mmol) of the freshly prepared 3-benzyloxypropionyl chloride in THF (20 mL) was added *via* cannula. After stirring the reaction mixture for 2 h at -78 °C the reaction mixture was quenched with

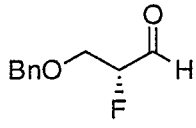
sat. NH_4Cl (5 mL) and extracted with EtOAc (30 mL). The organic phases was washed with sat. $NaHCO_3$ (2 x 20 mL), brine (2 x 20 mL), dried ($MgSO_4$), and concentrated. The product was purified by flash chromatography (25% EtOAc/hexanes) to afford 2.03 g (74%) of (+)-**2** as a thick gum; $[\alpha]^{20}_D$ + 25.1 (c 1.95, $CHCl_3$); IR (neat) 1783, 1703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (d, 3H, J = 6.6 Hz), 3.19-3.49 (m, 2H), 3.78-3.92 (m, 2H), 4.56 (s, 2H), 4.75 (m, 1H), 5.60 (d, 1H, J = 7.3 Hz), 7.22-7.48 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.4, 36.0, 54.6, 64.8, 72.9, 78.9, 125.5, 127.5, 127.6, 128.2, 128.5, 128.6, 133.1, 138.2, 153, 170.6. HRMS Calcd for $C_{20}H_{21}NO_4$ (M^++H^+) is 340.1552; Observed (M^++H^+): 340.1549 . Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13; Found: C, 70.69; H, 6.04; N, 2.22.



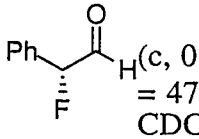
(4*R*,5*S*)-(+)-3-[2-(*R*)-fluoro-3-benzyloxypropionoyl]-4-methyl-5-phenyl-2-oxazolidinone (3). In an oven dried 250 mL, one neck, round bottomed flask equipped with rubber septum, argon inlet and a magnetic stir bar was placed 4.02 g (11.85 mmol) of **2** in THF (90 mL). The reaction mixture was cooled to -78 °C and 11.85 mL (11.85 mmol, 1.0 M in THF) of NaHMDS was added *via* syringe. After stirring the reaction mixture at -78 °C for 0.5 h it was cannulated to 4.85 g (15.4 mmol) of N-fluorobenzenesulfonimide (**NFSi**)[3] in THF (28 mL) precooled to -78 °C. The solution was stirred at this temperature for 0.5 h, quenched with sat. NH_4Cl (5 mL) and diluted with EtOAc (20 mL). After warming to rt 2 mL of sat. aqueous KI was added and the resulting I_2 solution was treated with sat. $Na_2S_2O_3$ solution until the iodine color disappears. The solution was filtered through Celite and the organic phases was washed with water (2 x 20 mL), brine (2 x 20 mL), dried ($MgSO_4$) and concentrated. The product was purified by flash chromatography (18% EtOAc/hexanes) to afford 2.83 g (68% yield, >99% de) of (+)-**3** as a thick gum: $[\alpha]^{20}_D$ +27.9 (c 0.98, CHCl3); IR (neat) 1781, 1718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (d, 3H, J = 6.6 Hz), 3.9-4.13 (m, 2H), 4.54-4.75 (m, 3H), 5.56 (d, 1H, J = 6.96 Hz), 6.11-6.22 (dm, 1H, J = 48.7 Hz), 7.26-7.44 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.9, 56.0, 69.6 (d, 1C, J = 22.4 Hz), 74.3, 80.7, 90.0 (d, 1C, J = 183.1 Hz), 126.2, 128.6, 129.1, 129.5, 129.7, 133.2, 138.2, 153.4, 167.5 (d, 1C, J = 22.4 Hz); ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -195.5 (m). HRMS Calcd for $C_{20}H_{20}FNO_4$ (M^++H^+) is 358.1457; Observed (M^++H^+): 358.1454.



(*S*)-(+)-3-Benzyloxy-2-fluoro-1-propanol (4): In an oven dried 250 mL, one neck, round bottomed flask equipped with argon inlet, rubber septum and a magnetic stir bar was placed 0.669 g (1.87 mmol) of fluoro carboximide **3** in THF (75 mL). The reaction mixture was cooled to 0 °C, 1.12 mL (2.24 mmol, 2.0 M in THF) of $LiBH_4$ was added and the solution was stirred until TLC indicated the absence of starting material (2-3 h).[3c] At this time the solution was warmed to rt, quenched with sat. NH_4Cl (5 mL) and diluted with EtOAc (30 mL). The organic phase was washed with brine (2 x 15 mL), dried ($MgSO_4$), and concentrated to give the product which was purified by flash chromatography (25% EtOAc/hexanes) to afford 0.320 g (93%) of (+)-**4** as an oil and 0.268 g (81%) of (4*R*,5*S*)-(+)-4-methyl-5-phenyl-2-oxazolidinone: $[\alpha]^{20}_D$ +5.7° (c,1.13, MeOH); IR (neat) 3410 (-OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (bt, -OH), 3.7 (dd, 1H, J_{HH}= 4.66 Hz, J_{HF} = 21.5 Hz), 3.8 (dt, 1H, J_{HH}= 4,8 Hz, J_{HF} = 23.1 Hz), 4.6 (s, 2H), 4.63-4.83 (dq, 1H, J = 53.2 Hz), 7.30-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 62.6 (d, 1C, J = 21.9 Hz), 68.5 (d, 1C, J = 22.8 Hz), 73.6, 92.3 (d, 1C, J = 172.3 Hz), 127.7, 128.4, 137.4; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -196.7 (m). HRMS Calcd for $C_{10}H_{13}FO_2$ (M^++H^+) is 185.0975; Observed (M^++H^+): 185.0977. Anal. Calcd for $C_{10}H_{13}FO_2$: C, 65.20; H, 7.11. Found: C, 65.18; H, 7.09.

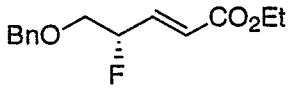


(*R*)-(+)-3-Benzyloxy-2-fluoropropionaldehyde (5): In an oven dried 25 mL, one neck, round bottomed flask equipped with an argon inlet, a rubber septum and a magnetic stir bar was placed 0.9 g (2.17 mmol) of the Dess-Martin periodinane[4] in CH_2Cl_2 (10 mL) and stirred at rt. Fluorohydrin (*S*)-**4**, 0.363 g (1.97 mmol, >97% ee) in CH_2Cl_2 (10 mL), was added *via* cannula to the reaction mixture and after 10 min. the solution was diluted with ether (20 mL), sat. $NaHCO_3$ (10 mL) and aq. $Na_2S_2O_3$ (10 mL). After stirring until the organic phase was clear it was washed with sat. $NaHCO_3$ (2 x 10 mL), aq. $Na_2S_2O_3$ (2 x 10 mL), dried ($MgSO_4$) and concentrated to give 0.341 g (95%) of (+)-**5** as an oil which was used without further purification; 94% ee, $[\alpha]^{20}_D$ +9.3° (c 2.14, $CHCl_3$); IR (neat) 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.79-3.95 (m, 2H), 4.55-4.64 (m, 2H), 4.84-5.00 (dm, 1H, J = 48.5 Hz), 7.27-7.37 (m, 5H), 9.81 (d, 1H, J = 5.9 Hz); ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -204.8 (m).

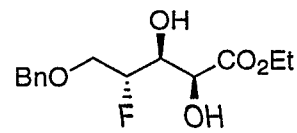


(*R*)-(-)-2-Fluorophenylacetaldehyde (6): 90% ee, $[\alpha]^{20}_D$ -34.28° (c, 0.7, $CHCl_3$); IR (neat) 1757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.65-5.80 (d, 1H, J = 47.4 Hz), 7.27-7.5 (m, 5H), 9.76 (d, 1H, J = 6.9 Hz); ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -192.5 (d, J = 53.5 Hz).

Typical procedure for determination of enantiomeric Purity:[5] In an oven dried NMR tube was placed 7 mg (0.038 mmol) of (+)-**5** in $CDCl_3$ (0.5 mL) and 6 mg (0.049 mmol) of (*R*)-(+)-α-methyl-benzylamine (98%, Aldrich) was added. Within a 2-3 min. the imine had formed as indicated by the absence of the α-fluoroaldehyde absorption in the ^{19}F NMR spectrum. The enantiomeric purity, 94% de, was determined by integration of the decoupled α-fluoroimine fluorine in the ^{19}F NMR spectra; ^{19}F NMR ($CFCl_3$ in $CDCl_3$): δ -195.0 (97%, major) and δ -195.1 (3%, minor). The enantiomeric purity of (*R*)-(-)-2-fluorophenylacetaldehyde (**6**), 90% de, was determined in a similar manner; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -182.8 (95%, major) and δ -183.2 (5%, minor).

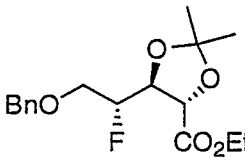


***trans*-Ethyl (4*S*)-(-)-5-benzyloxy-4-fluoro-2-pentenoate (7):** In an oven dried, 25 mL one neck, round bottomed flask equipped with an argon inlet, a rubber septum and a magnetic stir bar was placed 0.05 g (1.24 mmol) of NaH (60% dispersion in mineral oil, Aldrich) in THF (7 mL) cooled to 0 °C. Triethyl phosphonoacetate, 0.246 mL (1.24 mmol) was added slowly to the reaction mixture and the solution stirred for 45 min.[6] The reaction mixture was cooled to -78 °C and 0.21 g (1.12 mmol) of fluoroaldehyde (*R*)-**5** in THF (4 mL) was added *via* cannula; TLC indicated absence of starting material after the addition of aldehyde was complete. The reaction mixture quenched after 10 min. at -78 °C with sat. NH_4Cl (2 mL) and diluted with EtOAc (10 mL). The organic phase were washed with brine (2 x 5 mL), H_2O (2 x 5 mL), dried ($MgSO_4$) and concentrated to give the product which was purified by flash chromatography (5% EtOAc/hexanes) to give 0.203 g (71%) of (-)-**7** as an oil (the ^{19}F NMR of the crude product indicated a trans:cis ratio 92:8): $[\alpha]^{20}_D$ -21.80° (c 1.99, $CHCl_3$); IR (neat) 1718, 1667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (t, 3H, J = 7.14 Hz), 3.63-3.72 (m, 2H), 4.19-4.26 (q, 2H, J = 7.1), 4.62 (s, 2H), 5.20-5.37 (dm, 1H, J = 52.4 Hz), 6.16 (d, 1H, J = 15.8 Hz), 6.88 (m, 1H), 7.28-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2, 60.7, 70.9 (d, 1C, J = 20.4 Hz), 73.6, 90.4 (d, 1C, J = 174.0 Hz), 122.7, 127.8, 128.5, 141.3 (d, 1C, J = 18.2 Hz), 167.0; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -190.6 (m). Anal. Calcd for $C_{14}H_{17}FO_3$: C, 66.65; H, 6.79. Found: C, 66.80; H, 6.85.

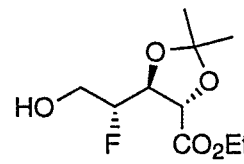


Ethyl (2*S*,3*S*,4*R*)-(+)-5-benzyloxy-4-fluoro-3,2-dihydroxy pentanoate (8): In an oven dried 50 mL, one neck, round bottomed flask equipped with a magnetic stir bar were placed

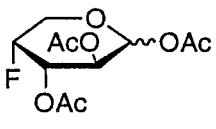
methane sulfonamide, 0.856 g (2.602 mmol) of $K_3Fe(CN)_6$, 0.071g (0.193 mmol) of $K_2OsO_4.2H_2O$, 0.399 g (2.89 mmol) of K_2CO_3 and a 1:1 ratio of *t*-BuOH/H_2O (6.4 mL).[7] The solution was cooled to 0 °C and 0.243 g (0.964 mmol) of **7** in 1:1 *t*-BuOH/H_2O (6.4 mL) was added *via* pipette and the solution stirred at 0 °C until TLC indicate the absence of starting material (<0.5 h). At this time 0.9 g of $Na_2S_2O_5$ was added to the reaction mixture, the solution was warmed to rt and diluted with CH_2Cl_2 (10 mL). The organic phase was washed with $NaHCO_3$ (2 x 5 mL), brine (2 x 5 mL), dried ($MgSO_4$) and concentrated. Purification by flash chromatography (50% EtOAc/hexanes) gave 0.263 g (96%) of **8** (94% de) as a white solid. Crystallization from ether/hexanes afforded 0.232 g (85%) of (+)-**8**; mp 70-3 °C; $[\alpha]^{20}_D$ +10.2° (c 1.08, $CHCl_3$); IR (KBr) 3462, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, *J* = 7.14), 2.67 (d, 1H, *J* = 9.1 Hz), 3.27 (d, 1H, *J* = 5.1 Hz), 3.76-3.91 (m, 2H), 4.23 (m, 1H), 4.26-4.32 (m, 2H), 4.42 (d, 1H, *J* = 4.9 Hz), 4.52-4.67 (m, 3H), 7.25-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.8, 63.0, 69.9 (d, 1C, *J* = 20.3 Hz), 71.0 (d, 1C, *J* = 26.5 Hz), 74.3 (d, 1C, *J* = 7.2 Hz), 90.8 (d, 1C, *J* = 177.0 Hz), 128.4, 128.5, 128.6, 129.1, 129.2, 138.2, 173.8; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -194.2 (m). Anal. Calcd for $C_{14}H_{19}FO_5$: C, 58.73; H, 6.69. Found: C, 58.46; H, 6.61.



4(*S*)-(+)-Carboethoxy-5(*S*)-(1(*R*)-fluoro-2-benzyloxyethyl)-2,2-dimethyl dioxolane (9): In an oven dried, one neck, round bottomed flask equipped with argon inlet, rubber septum and a magnetic stir bar were placed 0.2 g of (+)-**8**, a cat. amount of PTSA and 5 mL of 2,2-dimethoxypropane. The reaction mixture was stirred at rt until TLC indicated the absence of starting material (3 h). At this time the reaction mixture was concentrated and the product purified by flash chromatography (25% EtOAc/hexanes) to afford 0.197 g (87%) of (+)-**9** as an oil; $[\alpha]^{20}_D$ +14.33° (c 2.12, $CHCl_3$); IR (neat) 1742, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3H, *J* = 7.2 Hz), 1.43 (s, 3H), 1.46 (s, 3H), 3.67-3.83 (m, 2H), 4.15-4.25 (m, 2H), 4.46-4.60 (m, 4H), 4.72-4.85 (dm, 1H, *J* = 48.0 Hz), 7.28-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 25.8, 26.8, 61.6, 68.6 (d, 1C, *J* = 21.5 Hz), 73.5, 75.5, 77.7, 91.3 (d, 1C, *J* = 179.3), 111.8, 127.6, 128.3, 137.4, 170.5; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -197.2 (m). HRMS Calcd for $C_{17}H_{23}F0_5$ (M^++Na) is 349.1420; Observed (M^++Na): 349.1427.



4(*S*)-(+)-Carboethoxy-5(*S*)-(1(*R*)-fluoro-2-hydroxyethyl)-2,2-dimethyl dioxolane (10): In an oven dried 25 mL, one neck, round bottomed flask equipped with a magnetic stir bar was placed 0.192 g (0.59 mmoles) of (+)-**9** in ethanol (10 mL) and 0.019 g of 10% Pd/C (Aldrich). The flask was fitted with H_2 balloon and stirred at rt until TLC indicated the absence of starting material (6 h). The reaction mixture was filtered through Celite and concentrated to afford 0.136 g (97%) of (+)-**10** as an oil; $[\alpha]^{20}_D$ +7.642° (c 3.86, MeOH); IR (neat) 3497, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (t, 3H, *J* = 7.2 Hz), 1.42 (s, 3H), 1.48 (s, 3H), 2.10 (bt, -OH), 3.86-3.94 (m, 2H), 4.25-4.30 (m, 2H), 4.49 (m, 1H), 4.59 (d, 1H, *J* = 5.87), 4.62-4.73 (dq, 1H, *J* = 47.7); ^{13}C NMR ($CDCl_3$) δ 14.0, 25.6, 26.8, 61.8, 75.6, 77.4, 92.3 (d, 1C, *J* = 175.9), 112.0, 171.0; ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ -200.8 (m). HRMS Calcd for $C_{10}H_{17}F0_5$ (M^++H^+) is 237.1140; Observed (M^++H^+): 237.1138. Anal. Calcd for $C_{10}H_{17}F0_5$: C, 50.84; H, 7.25. Found: C, 50.80; H, 7.27.



1,2,3-Tri-*O*-acetyl-4-deoxy-4-fluoro-D-arabinopyranose (11): In an oven dried, one neck, round bottomed flask equipped with an argon inlet, rubber septum and magnetic stir bar was placed 0.133 g (0.563 mmol) of (+)-**10** in CH_2Cl_2 (7.2 mL) and cooled to -78 °C. Over a period of 0.5 h 1.24 mL (1.24 mmol, 1.0 M in hexanes) of DIBAL-H[8] was added to the reaction mixture *via* syringe. Soon after the addition was complete (0.5 h) TLC indicated the absence

addition was complete (0.5 h) TLC indicated the absence of starting material. The reaction mixture was stirred at -78 °C for another 2 h, quenched with MeOH (1 mL) and warmed to rt. After stirring at rt for 1 h the heterogeneous mixture was concentrated, MeOH (2 mL) added and the insoluble white solid filtered through Celite. The filtrate was concentrated and without purification 1% H_2SO_4 (10 mL) was added and the solution stirred at rt for 12 h.[9] The reaction mixture was warmed to 60 °C, until TLC indicated the absence of starting material (3 h) and neutralized at 60 °C by addition of $BaCO_3$ (approximately 5 g added over a period of 25 min.). The reaction mixture was cooled to rt, filtered, the residue was rinsed with MeOH (5 mL) and H_2O (5 mL). Concentration of the filtrate gave a yellow oil which was dried by co-evaporation with toluene. Under high vacuum the product solidified to afford 0.073 g (89%) of the water soluble crude lactol which was peracetylated for characterization as follows: in an oven dried, one neck, round bottomed flask equipped with an argon inlet, rubber septum and magnetic stir bar were placed 0.073 g (0.464 mmol) of the crude lactol, 0.44 mL (4.64 mmol) of acetic anhydride and 0.75 mL (9.28 mmol) of pyridine.[9] After 12 at rt H_2O (10 mL) was added and the solution extracted with CH_2Cl_2, dried ($MgSO_4$) and concentrated. The excess pyridine removed by co-evaporation with ethanol and the product was purified by flash chromatography (25% EtOAc/hexanes) to afford 0.123 g (79%) of **11** as viscous pale yellow oil: ^1H NMR and ^{19}F NMR showed 1:1 anomeric mixture that failed all attempts at separation. Some of the characteristic peaks for the anomers are:[10] ^1H NMR ($CDCl_3$) δ 2.01 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 5.62 (dd, α-anomer, J = 1.5, 7.5 Hz), 6.32 (d, β-anomer, J = 4 Hz); ^{19}F NMR ($CFCl_3$ in $CDCl_3$) δ anomer **1** -205.7 (m) and anomer **2** -206.6 (m). HRMS Calcd. for $C_{11}H_{15}FO_7$ (M^++Na) is 301.0702; Observed (M^++Na): 301.0699. Anal. Calcd for $C_{11}H_{15}FO_7$: C, 47.48; H, 5.43; Found: C, 47.46; H, 5.57.

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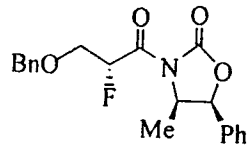
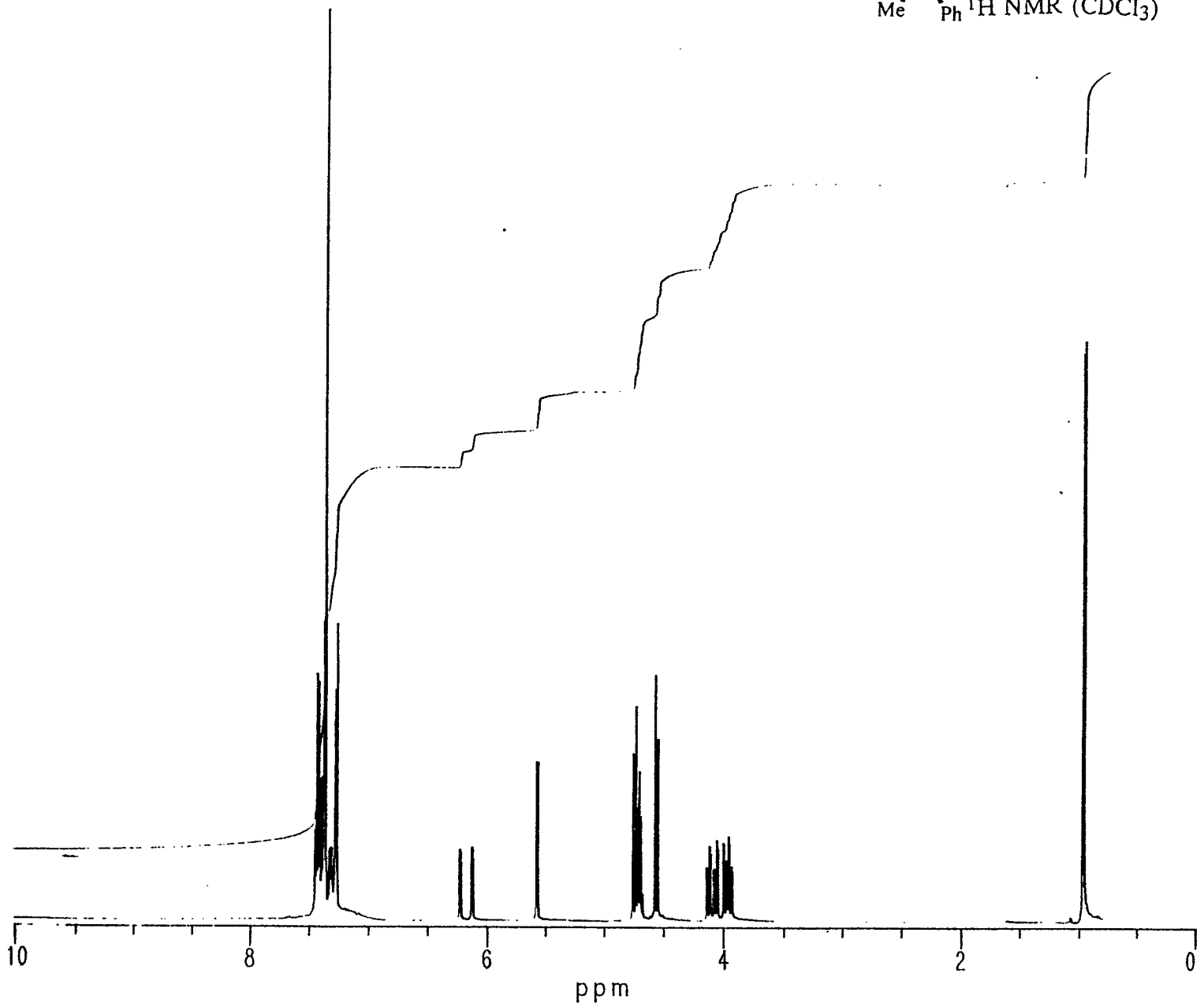
(R)-(+)-3



^{1}H NMR ($CDCl_3$)



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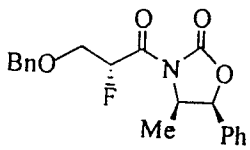

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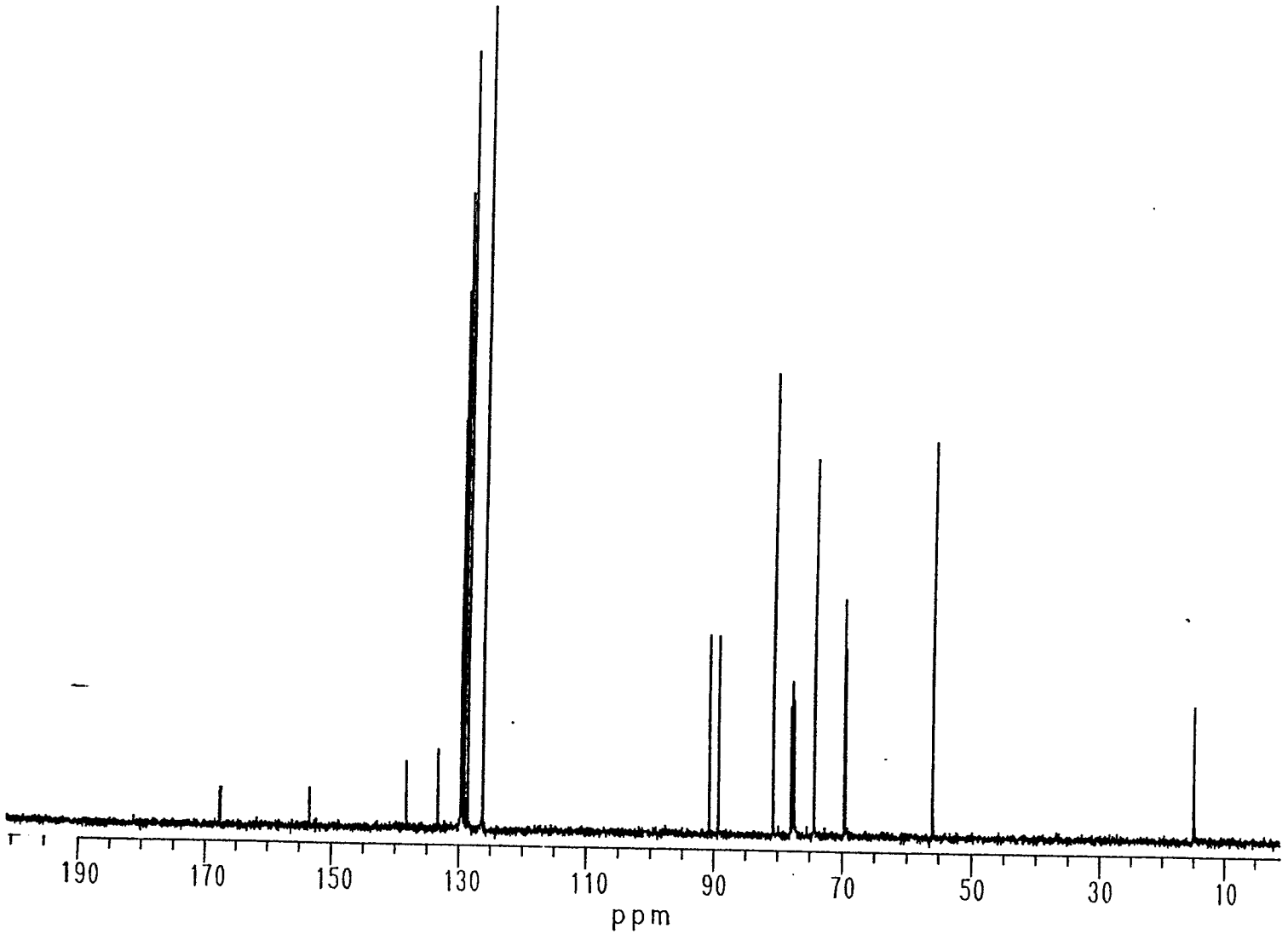

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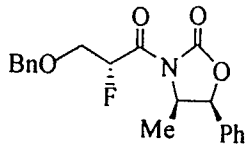
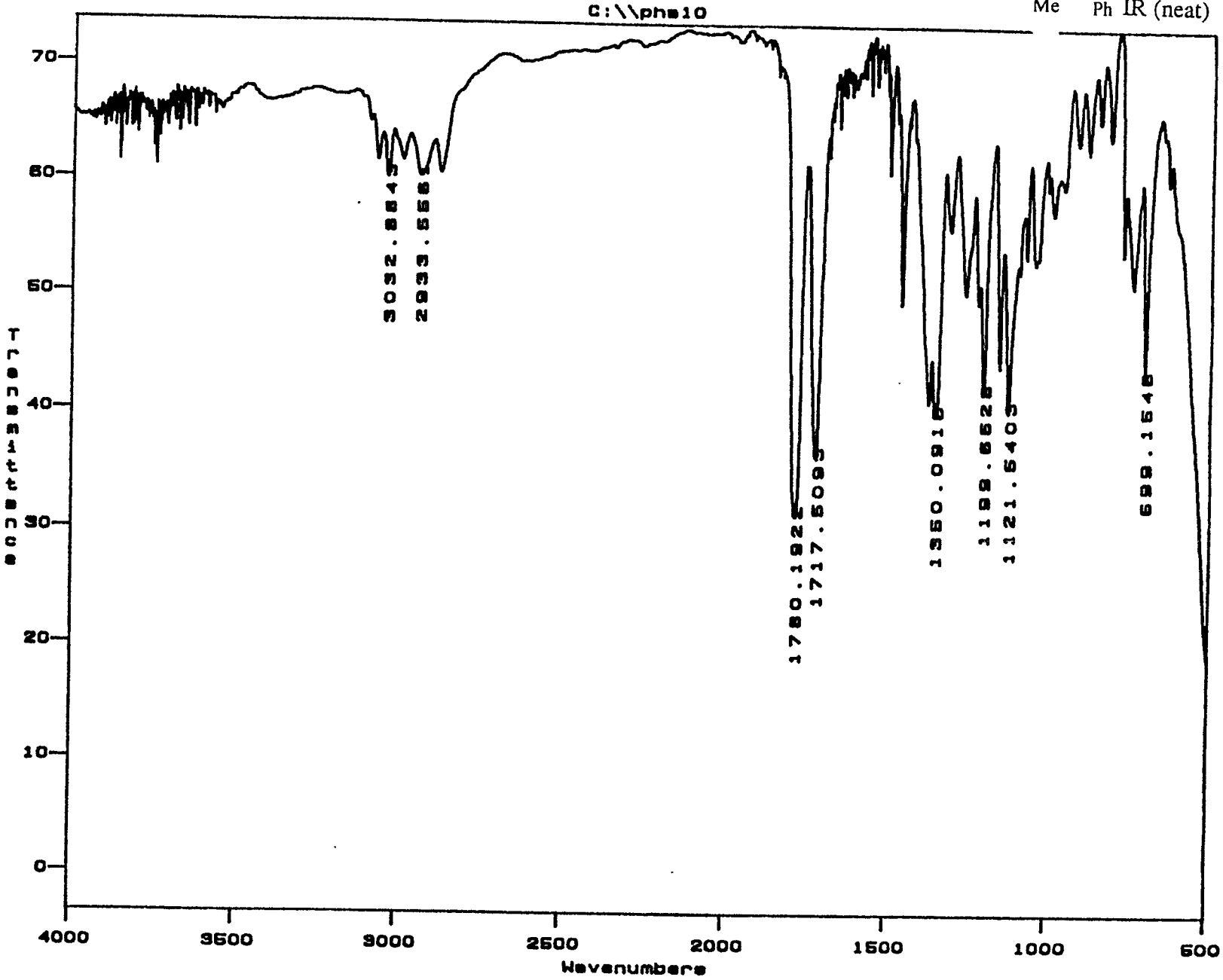


IR (neat)



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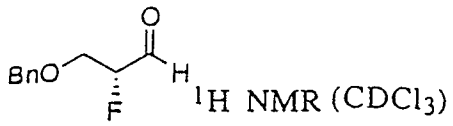

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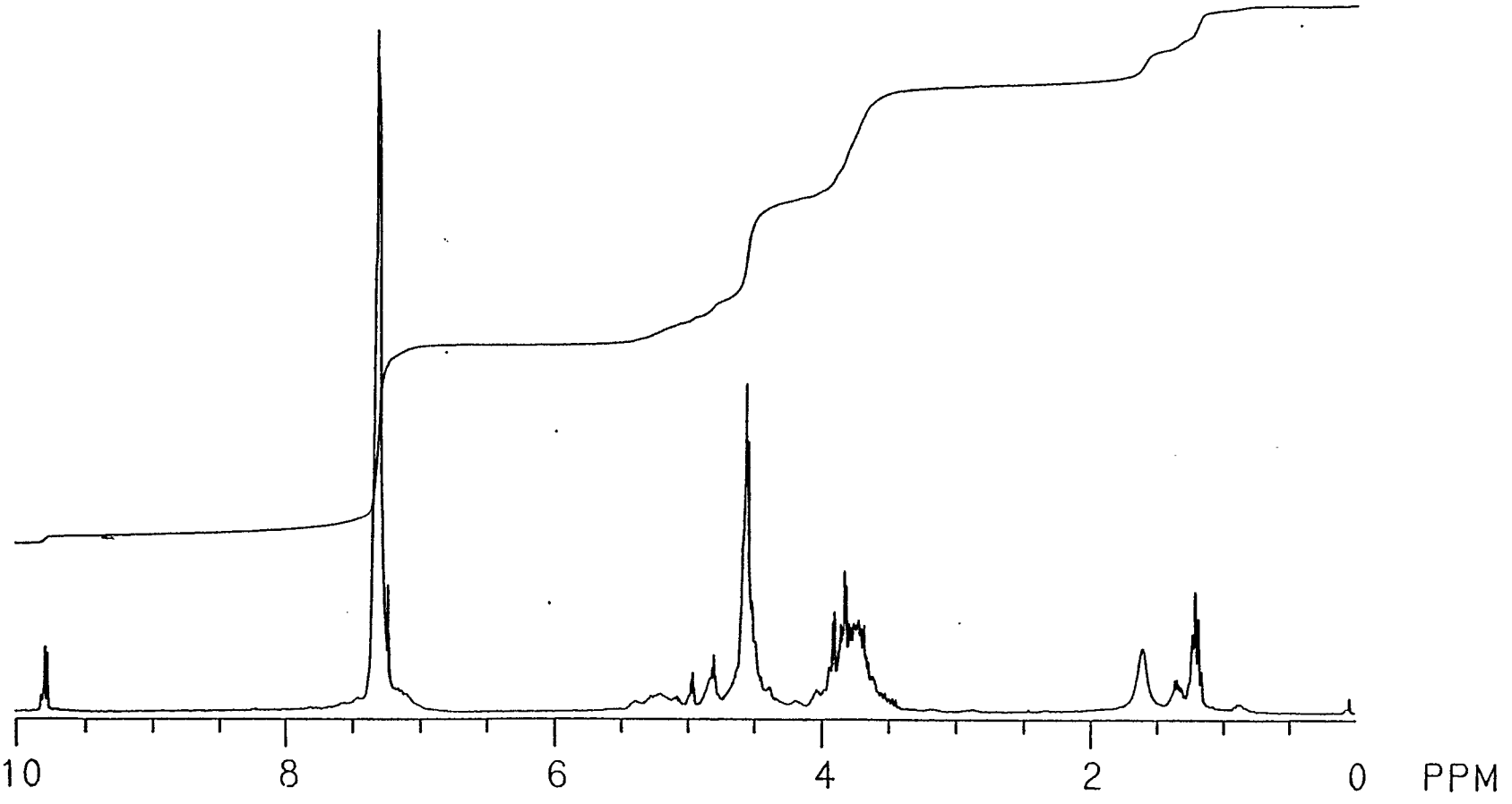
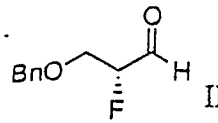


(*R*)-(+)-5



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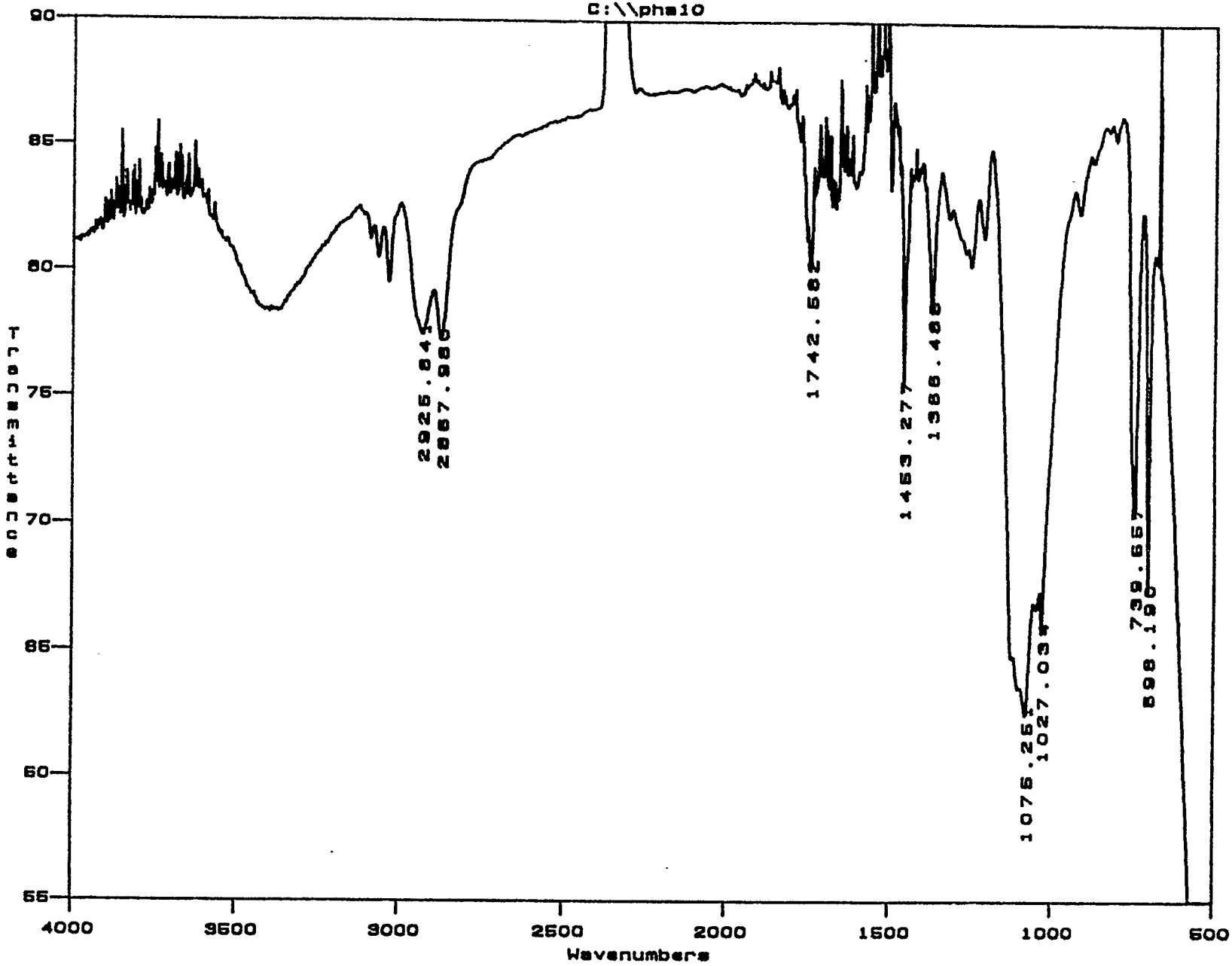

(*R*)-(-)-6

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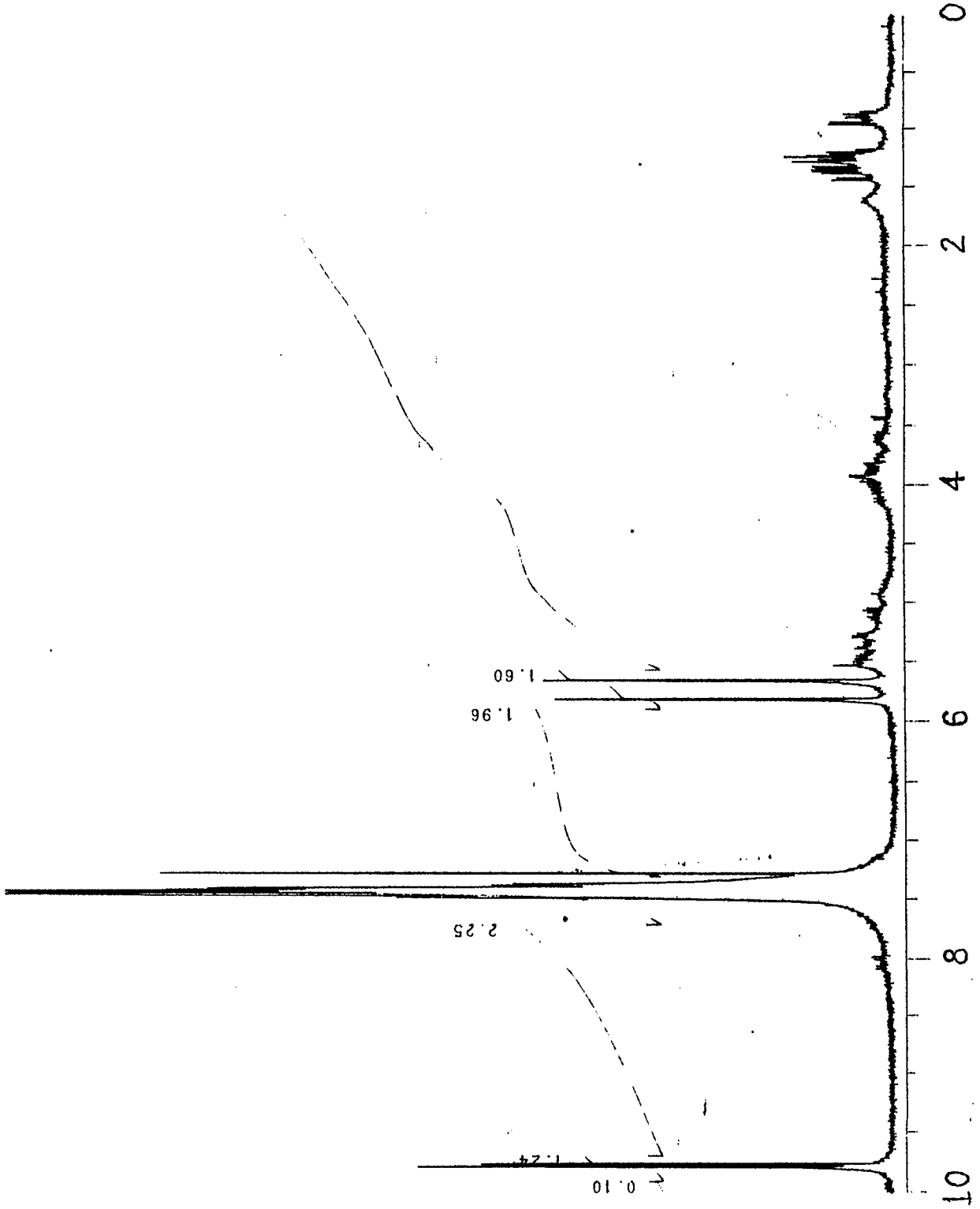
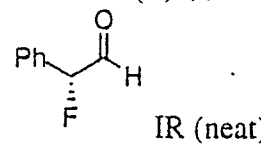


(R)-(+)-6



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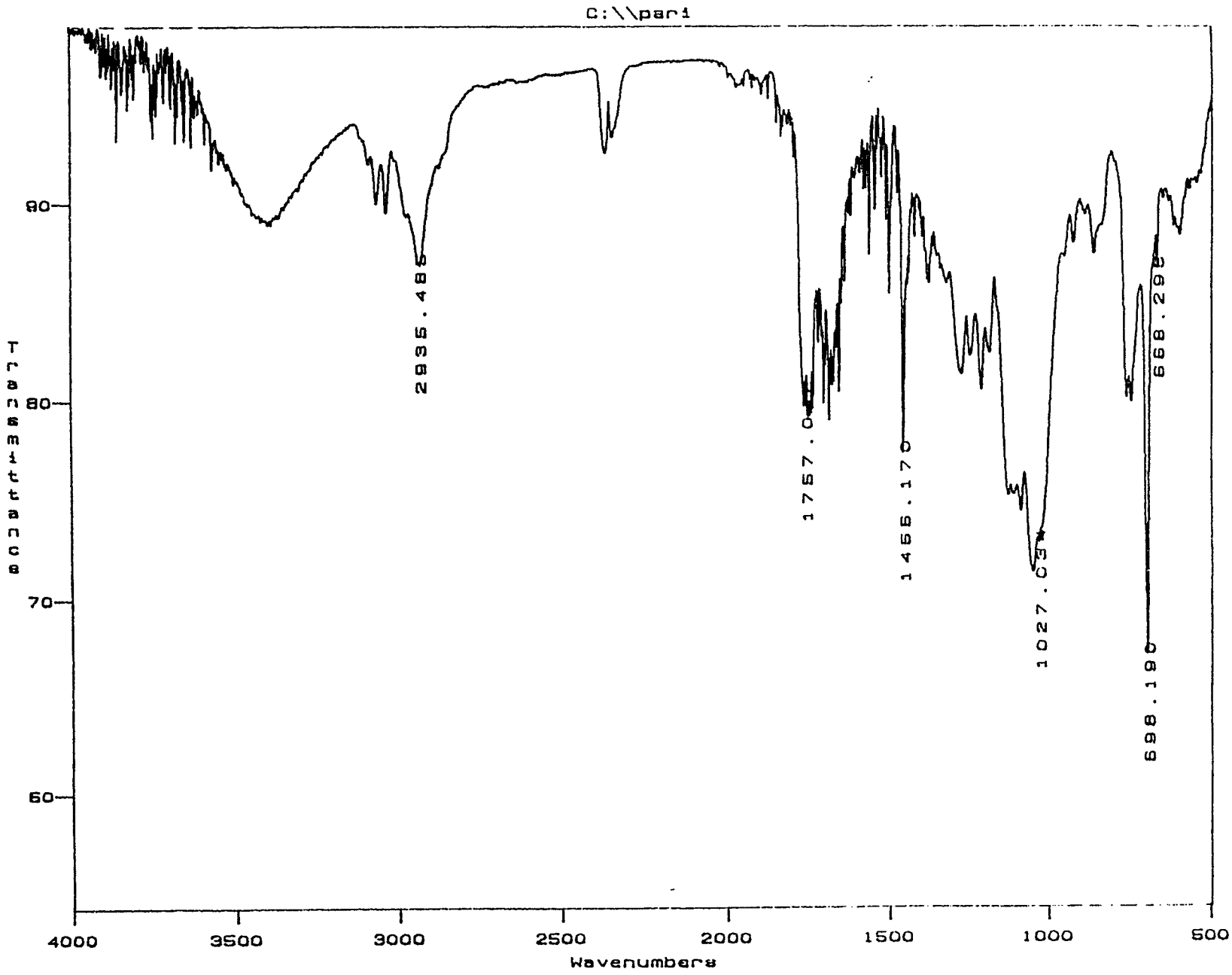
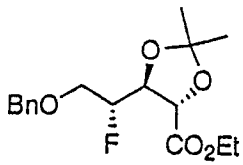


(+)-3



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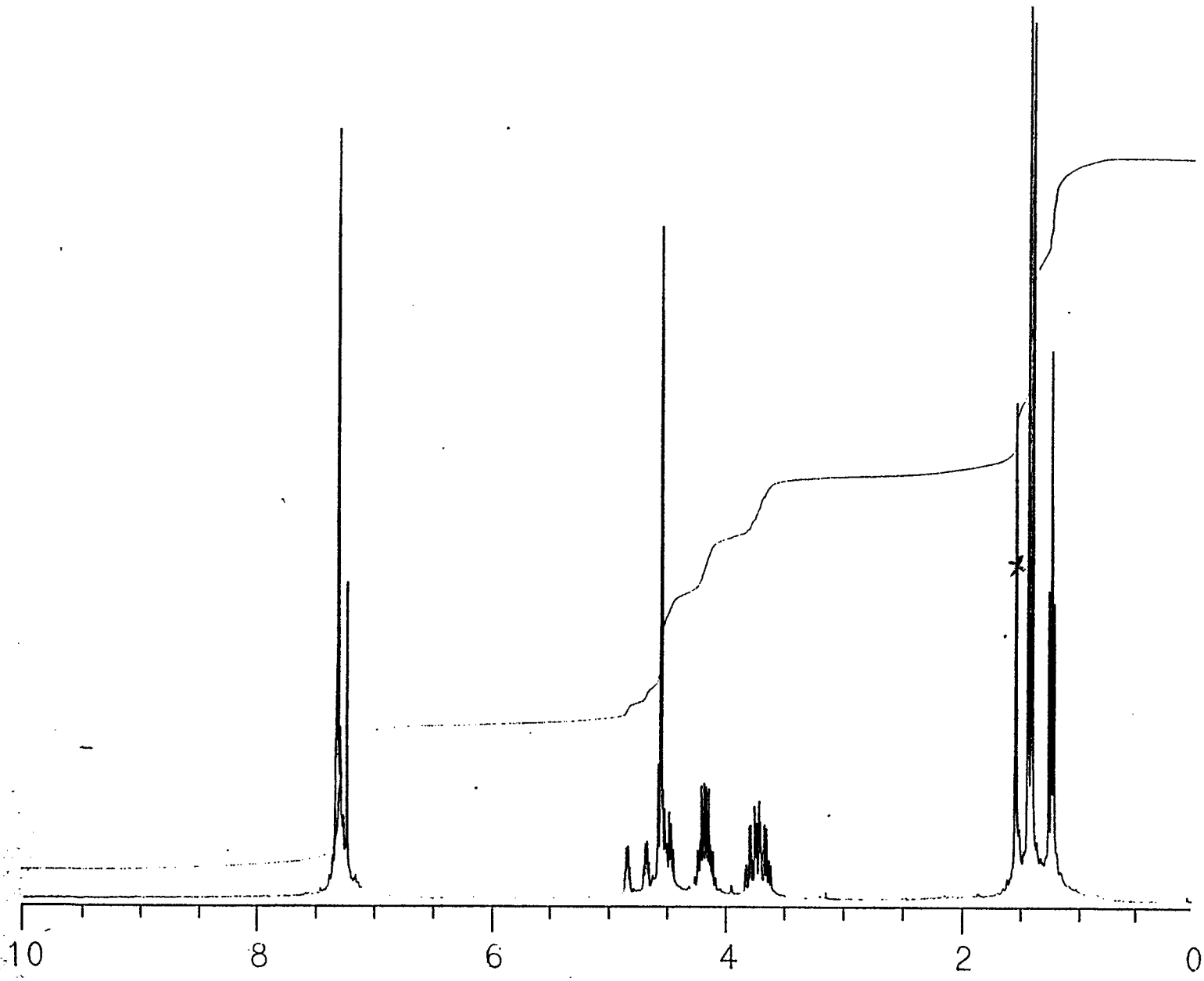
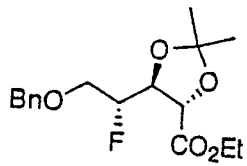
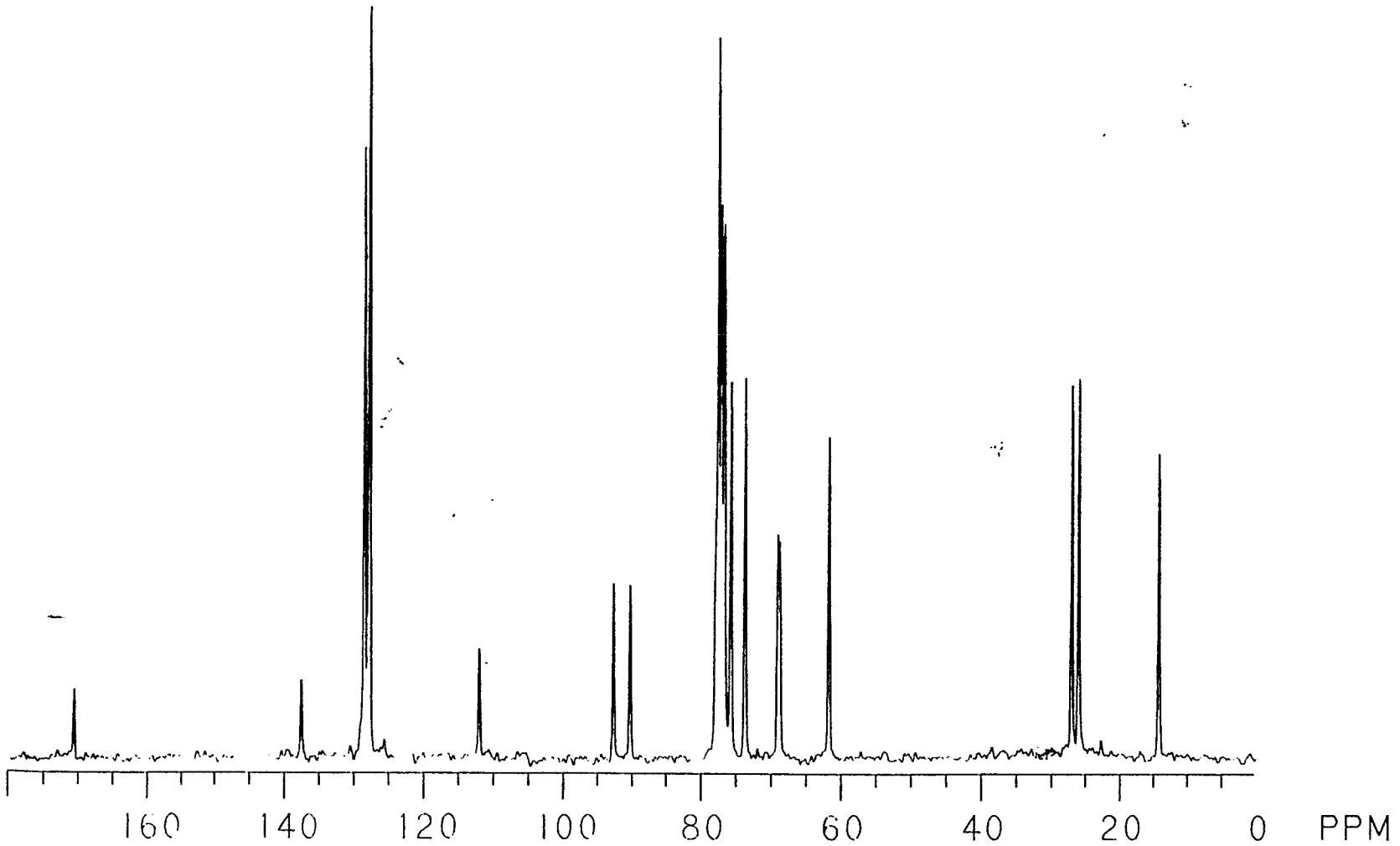


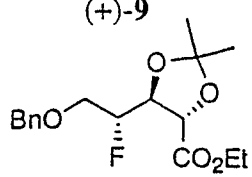
(+)-**9**



^{13}C NMR ($CDCl_3$)



(+)-9



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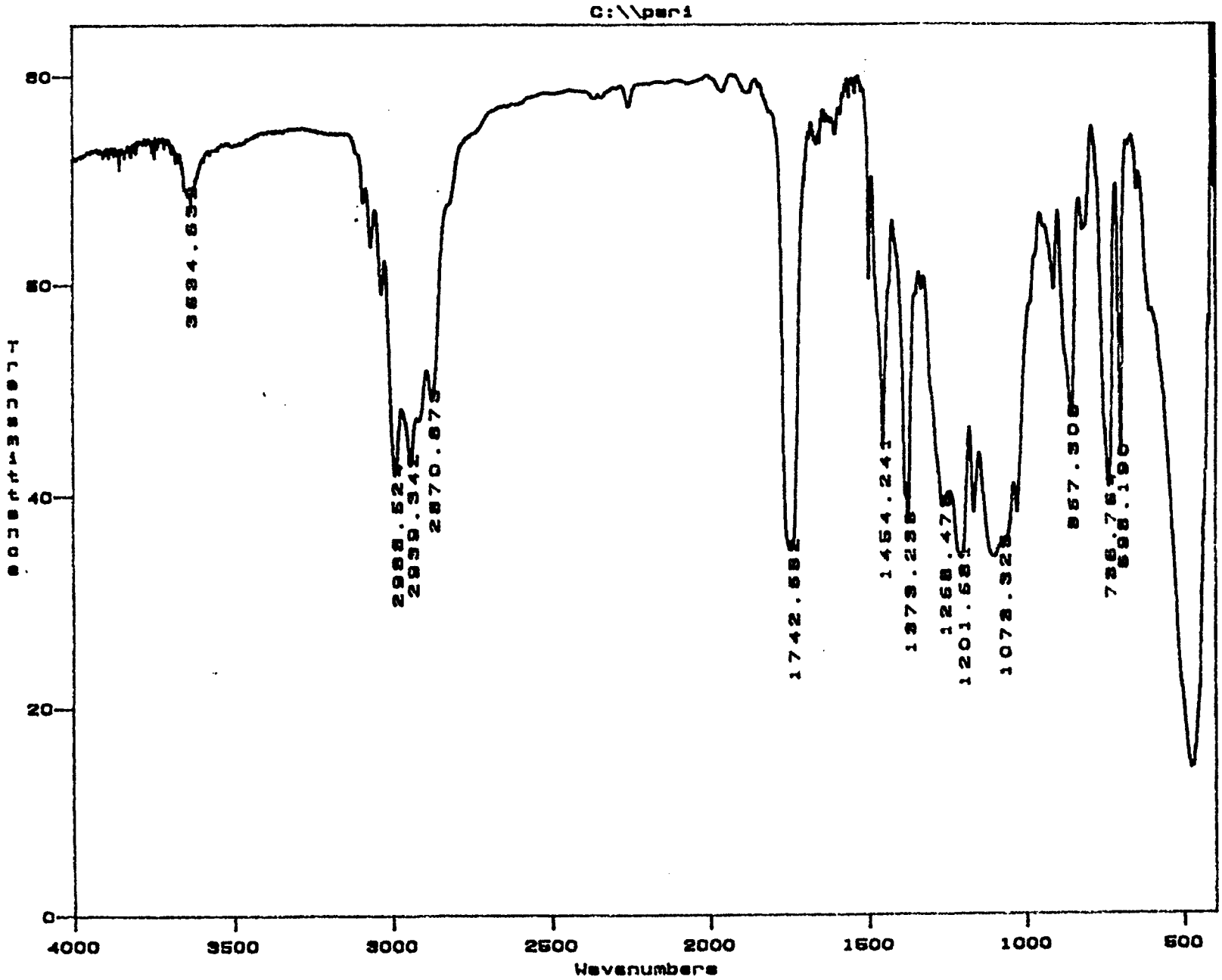

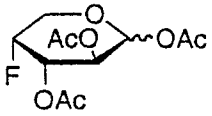

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