Nucleophilic Addition to (3-Methylpentadienyl)iron(1+) Cations: Counterion Control of Regioselectivity; Application to the Enantioselective Synthesis of 4,5-Disubstituted Cyclohexenones

Subhabrata Chaudhury and William A. Donaldson*

Department of Chemistry, Marquette University, P. O. Box 1881, Milwaukee, WI 53201-1881

Supporting Information

Tricarbonyl(3-methylpentadienyl)iron(1+) hexafluorophosphate (1a). To an ice-cold solution of tricarbonyl(3-methyl-2,4-pentadien-1-ol)iron (**3a**)[1] (0.700 g, 3.33 mmol) in ether (10 mL) and acetic anhydride (1 mL) was added drop-wise an ice-cold solution of acetic anhydride (3 mL) and hexafluorophosphoric acid (60% w/w solution, 1 g). The mixture was stirred for 15 min, during which time a pale yellow precipitate formed. The mixture was added drop-wise to a large excess of ether (200 mL) and the resultant precipitate was collected by vacuum filtration. The solid was washed with additional ether and dried under high vacuum to afford **1a** as a pale yellow amorphous solid (0.926 g, 82%). mp 130-135 °C (dec.); IR (KBr) 2119, 2068 cm^{-1}; ^1H NMR (d_6-acetone) δ 6.49 (t, J = 11.5 Hz, 2H), 3.81 (dd, J = 10.1, 3.2 Hz, 2H), 2.87 (s, 3H), 2.44 (dd, J = 12.6, 2.9 Hz, 2H),; ^{13}C NMR (d_6-acetone, 23 °C) δ 117.9, 104.5, 64.2, 22.4 (the signal for the metal carbonyls was not observed); Anal. Calcd for $C_9H_9O_3PF_6Fe$: C, 29.53; H, 2.48. Found: C, 29.32; H, 2.50.

Dicarbonyl(3-methylpentadienyl)(triphenylphosphine)iron(1+) hexafluorophosphate (1b). To a solution of tricarbonyl(ethyl 3-methyl-2E,4-pentadienoate)iron (**2a**)[1] (5.49 g, 19.6 mmol) in acetone (130 mL) was added triphenylphosphine (5.66 g, 21.6 mmol), followed by trimethylamine N-oxide dihydrate (4.35 g, 39.2 mmol). The mixture as heated at reflux for 2 h, cooled to room temperature, filtered through a pad of celite and concentrated. The crude residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 20:1 to 5:1 gradient) to afford **2b** as a bright golden-yellow semi-solid (7.22 g, 77 %). IR (neat) 1987, 1930, 1701 cm^{-1}; ^1H NMR ($CDCl_3$, 70 °C) δ 7.58 (br t, J = 8.6 Hz, 6H), 7.05-7.03 (m, 9H), 4.43 (br t, J = 7.6 Hz,

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[1] Adams, C. M.; Cerioni, G.; Hafner, A.; Kalchhauser, H.; von Philipsborn, W.; Prewo, R.; Schwenk, A. *Helv. Chim. Acta* **1988**, *71*, 1116-1142.

1H), 4.00 (m, 2H), 2.61 (s, 3H), 1.29 (m, 1H), 1.02 (t, J = 7.2 Hz, 3H), 0.42 (s, 1H), –0.15 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 212.8 (d, J_{CP} = 18.9 Hz), 173.7, 135.5 (d, J_{CP} = 40.1 Hz), 133.2 (d, J_{CP} = 10.9 Hz), 129.9, 128.3 (d, J_{CP} = 9.8 Hz), 101.2, 88.4, 59.6, 42.8, 31.9, 18.9, 14.5. This material was used in the next step without further characterization. To a solution of **2b** (5.44 g, 10.6 mmol) in CH_2Cl_2 (160 mL), cooled in a dry-ice/acetone bath, was added, via syringe, a solution of DIBAL in hexanes (1.0M, 32.0 mL, 32.0 mmol). The reaction mixture was stirred at 78 °C for 90 min. After this time, methanol (15 mL) was added, followed by water. The layers were separated, and the aqueous layer was extracted several times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated. The crude residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 5:1 to 1:1 gradient) to afford **3b** as a bright yellow oil (4.55 g, 91 %). IR (neat) 3379, 1969, 1907 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55-7.50 (m, 6H), 7.36 (br m, 9H), 4.20 (br m, 1H), 3.81 (br d, J = 7.4 Hz, 2H), 2.15 (s, 3H), 1.64 (br m, 1H), 0.91 (m, 1H), 0.53 (br t, J = 7.3 Hz, 1H), –0.13 (br t, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 214.5 (d, J_{CP} = 22.3 Hz), 136.1 (d, J_{CP} = 38.9 Hz), 133.1 (d, J_{CP} = 10.8 Hz), 129.7 (d, J_{CP} = 2.3 Hz), 128.2 (d, J_{CP} = 9.2 Hz), 99.0, 86.5, 62.8, 56.2, 40.9, 14.4. This material was used in the next step without further characterization. To an ice-cold solution of acetic anhydride (5 mL) and hexafluorophosphoric acid (60% w/w solution, 1.5 mL) was added an ice-cold solution of **3b** (2.72 g, 5.76 mmol) and acetic anhydride (2.5 mL) in ether (35 mL). The mixture was stirred for 30 min, during which time a bright yellow precipitate formed. The mixture was added drop-wise to a large excess of ether (300 mL), and the resultant precipitate was collected by vacuum filtration. The solid was washed with additional ether and dried under high vacuum to afford **1b** as a pale yellow solid (3.23 g, 93 %). mp 160-161 °C; IR (KBr) 2054, 2006 cm^{-1}; ^{1}H NMR ($CDCl_3$, 23 °C) δ 7.70-7.35 (m, 15H), 5.37 (br m, 2H), 2.37 (br s, 3H), 1.80 (br m, 2H), 1.47 (br m, 2H); ^{1}H NMR (d_6-acetone, –70 °C) δ 7.72-7.65 (m, 15H), 6.07 (br t, J = 10.8 Hz, 1H), 5.54 (dd, J = 17.4, 10.3 Hz, 1H), 3.75 (br d, J = 10.0 Hz, 1H), 2.52 (s, 3H), 2.45 (m, 1H), 1.63 (br m, 2H); ^{13}C NMR (d_6-acetone, 23 °C) δ 133.9 (d, J_{CP} = 11.3 Hz), 133.1 (d, J_{CP} = 3.0 Hz), 130.9, 130.4 (d, J_{CP} = 10.6 Hz), 116.4 (d, J_{CP} = 1.6 Hz), 101.5, 62.3, 22.2; Anal. Calcd for $C_{26}H_{24}O_2P_2F_6Fe$: C, 52.02; H, 4.03. Found: C, 51.80; H, 4.10.

Reaction of 1a with lithium dimethyl malonate (4a). To an ice cold stirring solution of dimethyl malonate (0.326 g, 2.47 mmol) in THF (10 mL) was added a solution of butyl lithium

in hexanes (2.5M, 1.0 mL, 2.5 mmol) and the mixture was stirred for 30 min. The generated dimethyl malonate anion was then transferred to an ice-cold solution of cation **1a** (0.500 g, 1.37 mmol) in THF (25 mL). The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was warmed to room temperature and then water (20 mL) was added. The mixture was extracted several times with ether, and the combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexane-ethyl acetate = 10:1) to afford **4a** as a golden yellow liquid (0.380 g, 80 %). IR (Neat) 2046, 1966, 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (br t, J = 8.4 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.29 (dd, J = 8.8, 6.1 Hz, 1H), 2.40 (ddd, J = 10.5, 4.2, 1.5 Hz, 1H), 2.17 (m, 1H), 2.09 (s, 3H), 1.73 (dd, J = 7.6, 3.3 Hz, 1H), 1.61 (ddd, J = 14.3, 10.4, 8.9 Hz, 1H), 1.28 (dd, J = 9.2, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.6, 169.1, 168.9, 104.2, 90.8, 57.1, 54.3, 52.8, 52.7, 37.7, 29.0, 25.7. Anal. Calcd for $C_{14}H_{16}O_7Fe$: C, 47.75; H, 4.59. Found: C, 48.01; H, 4.78.

Reaction of 1a with sodium dimethyl malonate (6). To an ice cold stirring suspension of NaH (0.037 g, 0.923 mmol) in dry THF (10 mL) was added dimethyl malonate (0.081 g, 0.615 mmol). The mixture was stirred at 0 °C for 10 min, and then solid cation **1a** (0.150 g, 0.410 mmol) was added in one portion and the reaction mixture was stirred for 2 h at room temperature. During this time a yellow-brown turbidity began to appear. The reaction mixture was diluted with CH_2Cl_2, a saturated solution of methanolic $NaHCO_3$ (20 mL) was added, and this mixture was stirred overnight at room temperature. Water (20 mL) was added and the mixture was extracted several times with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 5:1) to afford **6** as a light yellow liquid (0.090 g, 91%). IR (Neat) 1734, 1676 cm^{-1}; ^1H NMR (C_6D_6) δ 6.11 (dd, J = 10.1, 6.1 Hz, 1H), 5.81 (d, J = 10.1 Hz, 1H), 3.31 (d, J = 10.9 Hz, 1H), 3.23 (s, 3H), 3.20 (s, 3H), 3.03 (m, 1H), 2.47 (dd, J = 16.7, 3.8 Hz, 1H), 2.31 (m, 1H), 2.10 (dd, J = 16.7, 13.5 Hz, 1H), 0.55 (d, J = 7.4 Hz, 3H); ^{13}C NMR (C_6D_6) δ 195.6, 167.9, 167.8, 153.5, 127.9, 54.6, 52.2, 52.1, 37.5, 37.3, 31.6, 12.2. FAB-HRMS m/z 247.1148 (calcd for $C_{12}H_{16}O_5Li$ m/z 247.1158).

Reaction of 1a with lithium dimethyl malonate/12-crown-4 (6). To a solution lithium dimethyl malonate in THF [freshly prepared from dimethyl malonate (0.216 g, 1.64 mmol) and butyl lithium] was added 12-crown-4 (0.440 g, 2.50 mmol), and the resultant solution stirred for

15 min. To this solution was added solid cation **1a** (0.300 g, 0.820 mmol). The reaction mixture was worked up in a fashion similar to that for the reaction of **1a** with sodium dimethyl malonate. Purification by column chromatography (SiO_2, hexane–ethyl acetate = 5:1) gave **6** (0.165 g, 84 %), which was identified by comparison of its ^1H NMR spectral data with that previously obtained.

Reaction of 1a with sodium dimethyl malonate/$ZnCl_2$ (4a). A solution sodium dimethyl malonate in THF [freshly prepared from dimethyl malonate (0.072 g, 0.55 mmol) and sodium hydride] was transferred by cannula to a flask containing anhydrous $ZnCl_2$ (0.148 g, 1.09 mmol). A white turbidity immediately appeared. The reaction mixture was stirred at 0 °C for 30 min, and then solid cation **1a** (100 mg, 0.272 mmol) was added in one portion. The reaction mixture was stirred for 2 h at room temperature and worked up in a fashion similar to that for the reaction of **1a** with lithium dimethyl malonate. Purification by column chromatography (SiO_2, hexane–ethyl acetate = 10:1) gave **5a** (70 mg, 63 %), which was identified by comparison of its ^1H NMR spectral data with that previously obtained.

Reaction of 1a with lithium dimethyl methylmalonate (5a). The reaction of cation **1a** (0.200 g, 0.546 mmol) with lithium dimethyl methylmalonate was carried out in a fashion similar to the reaction of **1a** with lithium dimethyl malonate. Purification of the residue by column chromatography (SiO_2, hexane-ethyl acetate = 10:1) gave **5a** as a golden yellow liquid (0.090 g, 45 %). IR (Neat) 2046, 1969, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.32 (br t, J = 8.6 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 2.28 (dd, J = 14.2, 3.7 Hz, 1H), 2.13 (m, 1H), 1.72 (dd, J = 7.7, 3.5 Hz, 1H), 1.53 (dd, J = 14.1, 11.4 Hz, 1H), 1.37 (s, 3H), 1.29 (dd, J = 9.4, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.9, 172.4, 172.3, 105.2, 90.5, 55.4, 55.1, 52.8, 52.6, 37.8, 36.0, 25.8, 20.0.

Reaction of 1a with sodium dimethyl methylmalonate (5a and 7). The reaction of cation **1a** (0.200 g, 0.546 mmol) with sodium dimethyl methylmalonate was carried out in a fashion similar to the reaction of **1a** with sodium dimethyl malonate. Purification of the residue by column chromatography (SiO_2, hexane-ethyl acetate = 5:1) gave **5a** (0.070 g, 34 %) as an oil followed by **7** (0.076 g, 55 %) as a light yellow liquid. The diene complex **5a** was identified by comparison of its ^1H NMR spectral data with that previously obtained. **7**: IR (Neat) 2956, 1731,

1681 cm^{-1}; ^1H NMR (C_6D_6) δ 6.20 (dd, J = 10.1, 6.1 Hz, 1H), 5.86 (d, J = 10.1 Hz, 1H), 3.26 (s, 3H), 3.21 (s, 3H), 3.00 (dt, J = 14.1, 4.1 Hz, 1H), 2.72 (dd, J = 16.3, 4.1 Hz, 1H), 2.57 (dd, J = 16.3, 14.4 Hz, 1H), 2.12 (m, 1H), 1.32 (s, 3H), 0.68 (d, J = 7.1 Hz, 3H); ^{13}C NMR (C_6D_6) δ 197.6, 171.6, 171.5, 153.8, 127.6, 56.0, 52.0, 51.9, 41.3, 37.1, 31.8, 18.9, 12.0. FAB-HRMS *m/z* 261.1313 (calcd for $C_{13}H_{18}O_5Li$ *m/z* 261.1314).

Reaction of 1b with sodium dimethyl malonate (4b). To an ice cold stirring suspension of NaH (0.030 g, 0.748 mmol) in dry THF (10 mL) was added dimethyl malonate (0.089 g, 0.680 mmol). The mixture was stirred at 0 °C for 10 min. Solid cation (0.200g, 0.333 mmol) was added to the malonate anion solution in one portion and the reaction mixture was stirred at room temperature for 1 h. Water (20 mL) was added, the reaction mixture was stirred for an additional 10 min, and then extracted several times with ethyl acetate. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 10:1) to afford **4b** as a golden yellow liquid (0.181 g, 93 %). IR (neat) 1973, 1912 cm^{-1}; ^1H NMR (C_6D_6, 50 °C) δ 7.56- 7.49 (m, 6H), 6.05- 6.93 (m, 9H), 4.27 (dt, J = 8.1, 4.5 Hz, 1H), 3.38 (dd, J = 8.1, 6.1 Hz, 1H), 3.33 (s, 3H), 3.31 (s, 3H), 2.49 (m, 1H), 2.35 (dd, J = 10.0, 2.3 Hz, 1H), 2.03 (s, 3H), 1.92 (m, 1H), 1.32 (dt, J = 8.5, 3.2 Hz, 1H), 1.13 (m, 1H); ^{13}C NMR (C_6D_6) δ 211.5 (d, J_{CP} = 6 Hz), 214.8 (d, J_{CP} = 22.5), 169.3, 169.1, 137.6 (d, J_{CP} = 37.5 Hz), 133.4 (d, J_{CP} = 15.0 Hz), 129.7, 128.5, 101.0, 94.4, 55.0, 52.0, 51.9, 50.7, 39.8, 29.9, 24.6. Anal. Calcd for $C_{31}H_{31}O_6PFe$: C, 63.49; H, 5.34. Found: C, 63.78; H, 5.64.

Reaction of 1a with lithium methyl cyclohexanecarboxylate (8). To a cold (–78 °C), magnetically stirring solution of diisopropylamine (0.070 g, 0.69 mmol) in dry THF (3 mL) under N_2 was slowly added a solution of *n*-BuLi (2.5 M in hexanes, 0.3 mL 0.7 mmol) and stirred for 10 min. To the LDA solution was added methyl cyclohexanecarboxylate (0.071 g, 0.50 mmol) and the mixture was stirred for an additional 30 min at –78 °C. Solid cation **1a** (0.183 g, 0.500 mmol) was added to the anion solution in one portion and the reaction mixture was stirred for 1 h at –78 °C and then 1 h at room temperature. During this time a yellow turbidity began to appear. The reaction mixture was quenched with 1M HCl solution (10 mL) and then extracted several times with ether. The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes-ethyl

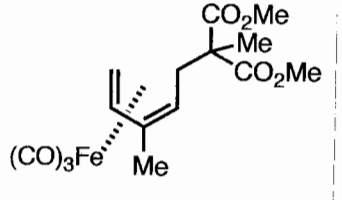
acetate = 10:1) to afford an inseparable mixture (6:1 ratio) of 2- and 3-cyclohexenones **8a/b** (0.100 g, 80%). IR (neat) 2941, 2858, 1724, 1678 cm^{-1}; **8a** (2-cyclohexenone): ^1H NMR ($CDCl_3$) δ 6.91 (dd, J = 10.1, 6.4 Hz, 1H), 5.86 (d, J = 10.1 Hz, 1H), 3.68 (s, 3H), 2.59 (m, 1H), 2.50 (m, 1H), 2.20 (m, 1H), 2.11 (m, 1H), 1.59 (m, 3H), 1.24 (m, 5H), 1.01 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 200.8, 176.0, 156.8, 127.3, 51.8, 42.9, 46.0, 35.6, 33.0, 32.7, 32.4, 25.8, 23.6, 23.3, 12.3. **8b**: ^1H NMR ($CDCl_3$, partial) δ 5.62 (m, 1H), 3.60 (s, 3H), 2.70 (m, 1H), 1.78 (br s, 3H); ^{13}C NMR ($CDCl_3$, partial) δ 211.1, 135.5, 123.2, 52.7, 51.7, 49.3, 41.8, 39.5, 32.5, 32.3, 25.6, 25.5, 23.8, 23.6. FAB-HRMS m/z 257.1735 (calcd for $C_{15}H_{22}O_3Li$ m/z 257.1729).

Reaction of cation 1a with potassium phthalimide (9a/b). To a solution of cation **1a** (0.300 g, 0.820 mmol) in acetone (6 mL) under N_2 at room temperature was added solid potassium phthalimide (0.228 g, 1.23 mmol) in one portion. The reaction mixture was stirred at room temperature for 18 h and then concentrated to dryness. The solid residue was extracted with CH_2Cl_2 several times. The combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated. The crude residue was redissolved in acetonitrile (10 mL) and then a pinch of CAN was added. This mixture was stirred for 1h at room temperature and then water (10 mL) was added. The reaction mixture was extracted several times with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexanes-ethyl acetate = 5:1) to afford an inseparable mixture (2.5:1 ratio) of 2- and 3-cyclohexenones **9a/b** as an oil (72 mg, 34%). IR (Neat) 2969, 1772, 1709 cm^{-1}; Anal. Calcd for $C_{15}H_{13}NO_3 \cdot ½H_2O$: C, 68.17; H, 5.34; N, 5.30. Found: C, 68.33; H, 5.28; N, 5.07. **9a** (2-cyclohexenone): ^1H NMR ($CDCl_3$) δ 7.77 (m, 2H), 7.67 (m, 2H), 6.92 (dd, J = 10.1, 5.3 Hz, 1H), 6.10 (d, J = 10.1 Hz, 1H), 4.90 (dt, J = 12.8, 5.1 Hz, 1H), 3.80 (dd, J = 17.0, 12.8 Hz, 1H), 2.88-2.78 (m, 1H), 2.63 (dd, J = 17.0, 4.8 Hz, 1H), 1.17 (d, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 197.4, 168.8, 153.0, 134.5, 131.9, 129.1, 123.7, 50.0, 37.5, 35.0, 14.3. **9b** (3-cyclohexenone): ^1H NMR ($CDCl_3$, partial) δ 5.70 (br m, 1H), 5.06 (br t, J = 6.5 Hz, 1H), 2.92 (m, 1H), 2.84 (m, 1H), 1.65 (m & s, 4H); ^{13}C NMR ($CDCl_3$, partial) δ 206.0, 168.1, 131.8, 130.2, 49.8, 43.6, 39.4, 20.5.

Reaction of 1a with sodium bis[(–)-8-phenylmenthyl] malonate (13). The reaction of cation **1a** (0.200 g, 0.546 mmol) with sodium bis[(–)-8-phenylmenthyl] malonate was carried out in a

fashion similar to the reaction of **1a** with sodium dimethyl malonate. Purification of the residue by column chromatography (SiO_2, hexane-ethyl acetate = 5:1) gave **13** (0.190 g, 95%) as an off-white foam. Recrystallization from CH_3CN/H_2O gave a crystalline solid. mp 52-55 °C; $[\alpha]^{20}_D$ = –12 (c 0.20, hexanes); $[\alpha]^{20}_{589}$ = –25 (c 0.20, hexanes); IR (Neat) 3055, 1742, 1676 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31 (m, 4H), 7.25 (m, 4H), 7.16 (m, 2H), 6.95 (dd, *J* = 10.1, 6.0 Hz, 1H), 5.95 (d, *J* = 10.1 Hz, 1H), 4.91 (dt, *J* = 10.8, 4.4 Hz, 1H), 4.82 (dt, *J* = 8.3, 4.3 Hz, 1H), 2.87 (d, *J* = 11.3 Hz, 1H), 2.72 (m, 2H), 2.15 (d, *J* = 9.1 Hz, 2H), 2.04-1.50 (m, 10H), 1.43 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H), 1.23-0.93 (m, 9H), 0.97 (d, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.88 d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 197.9, 168.1, 166.9, 155.6, 151.2, 150.6, 128.3, 128.2, 125.8, 54.7, 50.4, 41.5, 41.4, 40.3, 40.2, 36.8, 35.9, 34.8, 25.4, 24.7, 22.8, 22.0, 14.3, 12.6. Anal. Calcd for $C_{42}H_{56}O_5$: C, 78.70; H, 8.82. Found: C, 78.67; H, 8.91.

Reduction of chiral cyclohexenone 13. To a solution of **13** (150 mg, 0.234 mmol) in methanol (10 mL) was added cerium (III) chloride (87 mg, 0.23 mmol) and sodium borohydride (28 mg, 0.74 mmol). The reaction mixture was stirred for 30 min at room temperature and then quenched with water. The resultant mixture was extracted several times with CH_2Cl_2 and the combined extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate = 5:1) to afford **14** as a light yellow oil (103 mg, 69 %). ^1H NMR ($CDCl_3$) δ 7.33 (m, 4H), 7.31 (m, 4H), 7.17 (m, 2H), 5.72 (ddd, *J* = 10.1, 5.9, 1.7 Hz, 1H), 5.60 (d, *J* = 10.1 Hz, 1H), 4.88 (m, 2H), 4.27 (br t, *J* = 8.0 Hz, 1H), 2.98 (d, *J* = 10.6 Hz, 1H), 2.53 (m, 2H), 2.09-1.83 (m, 10H), 1.74 (m, 2H), 1.48 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.23-0.93 (m, 6H), 0.89 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 168.9, 167.2, 150.9, 150.6, 134.8, 129.6, 128.3, 128.2, 125.9, 125.8, 125.6, 125.5, 68.2, 55.6, 50.7, 50.5, 41.7, 41.4, 40.6, 40.4, 35.3, 34.6 (two signals), 31.8, 31.6, 31.5, 30.9, 30.7, 30.6, 29.9, 27.6, 27.4, 24.1, 23.8, 22.9, 22.0, 15.0, 14.3. FAB-HRMS *m/z* 649.4443 (calcd for $C_{42}H_{58}O_5Li$ *m/z* 649.4444).



5a

^{1}H NMR

(300 MHz, $CDCl_3$)

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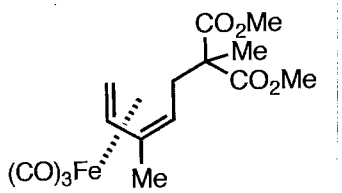

5a

^{13}C NMR

(75 MHz, $CDCl_3$)

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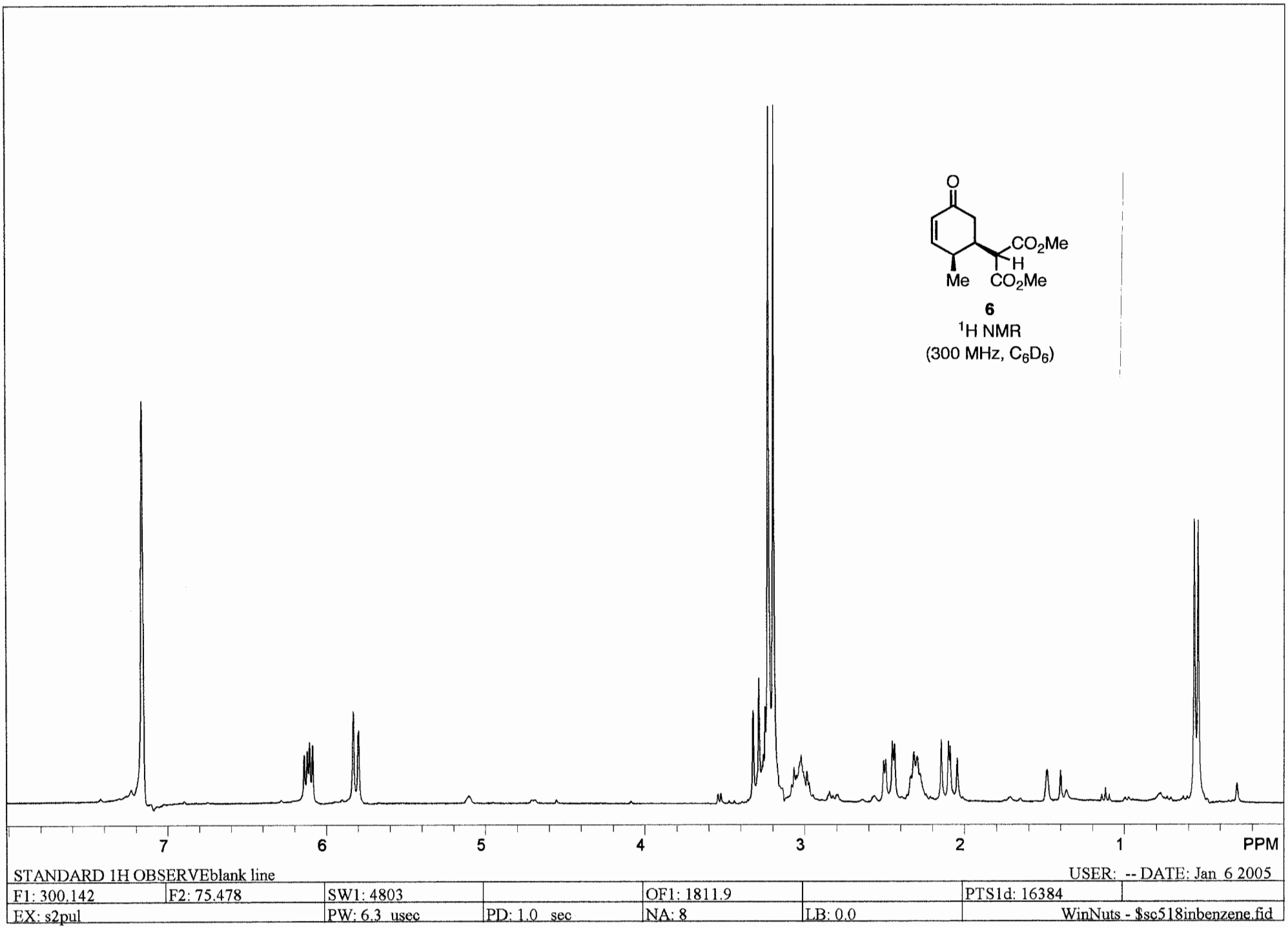

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F1: 300.142	F2: 75.478	SW1: 4803		OF1: 1811.9		PTS1d: 16384	
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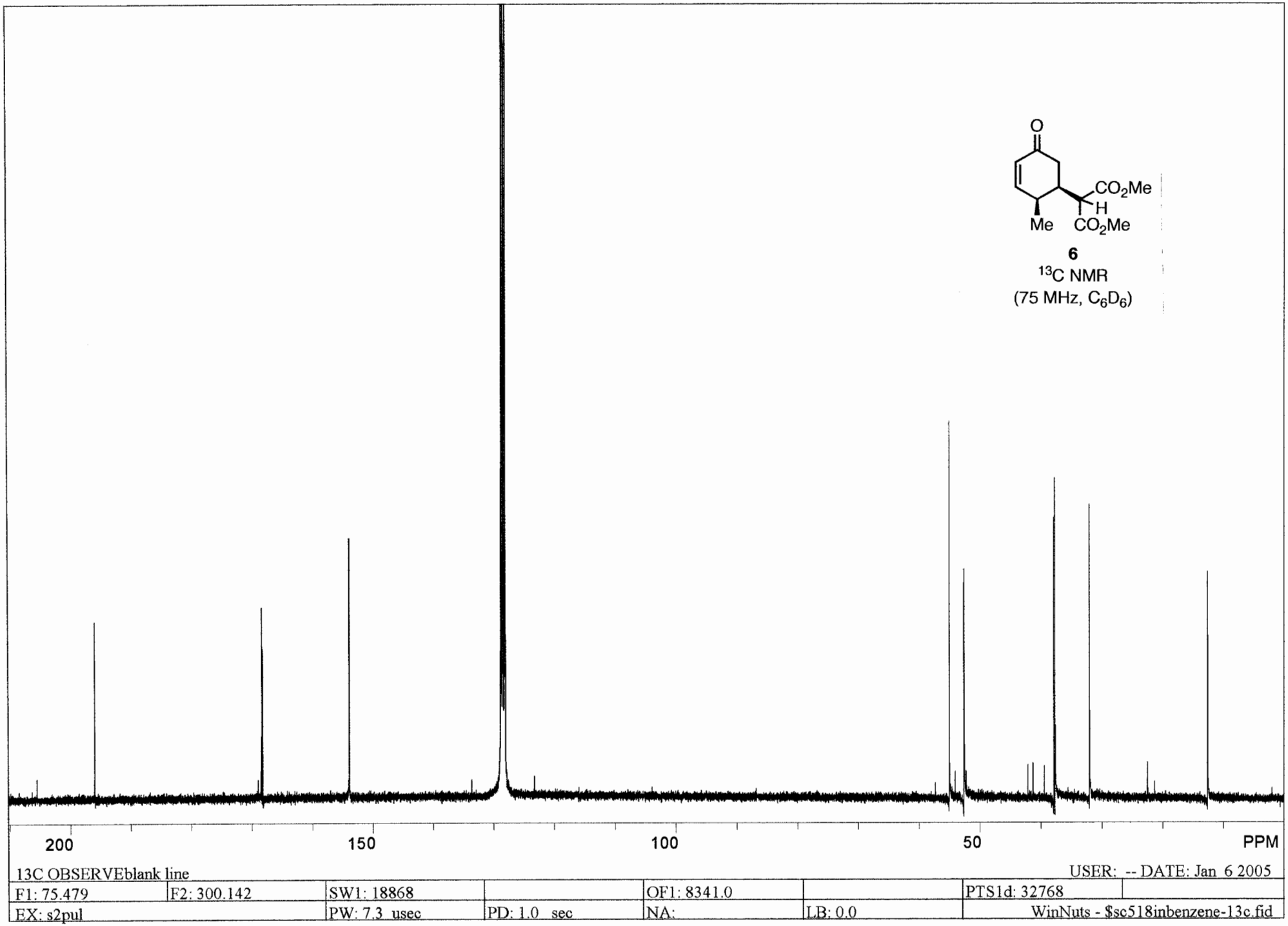
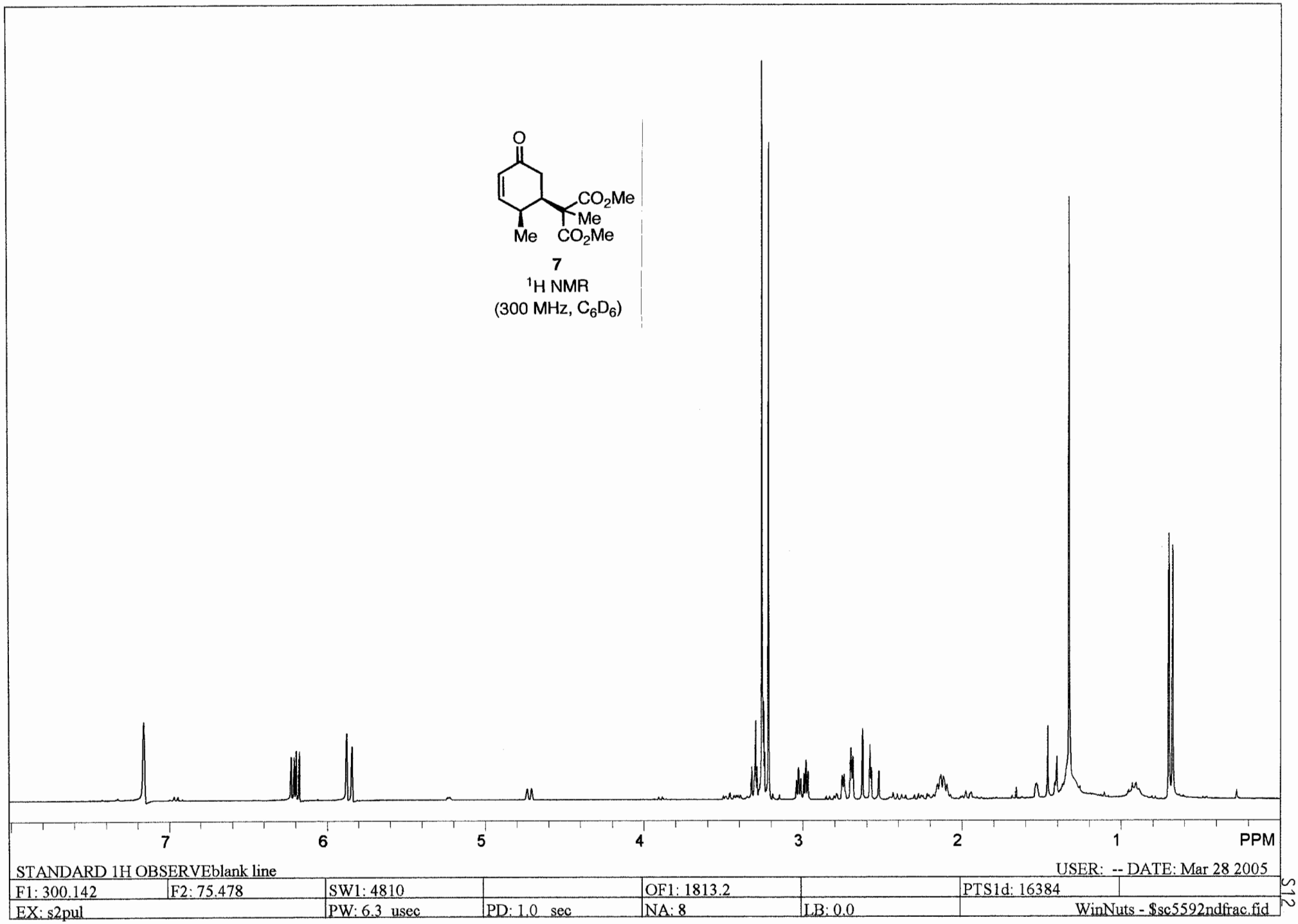
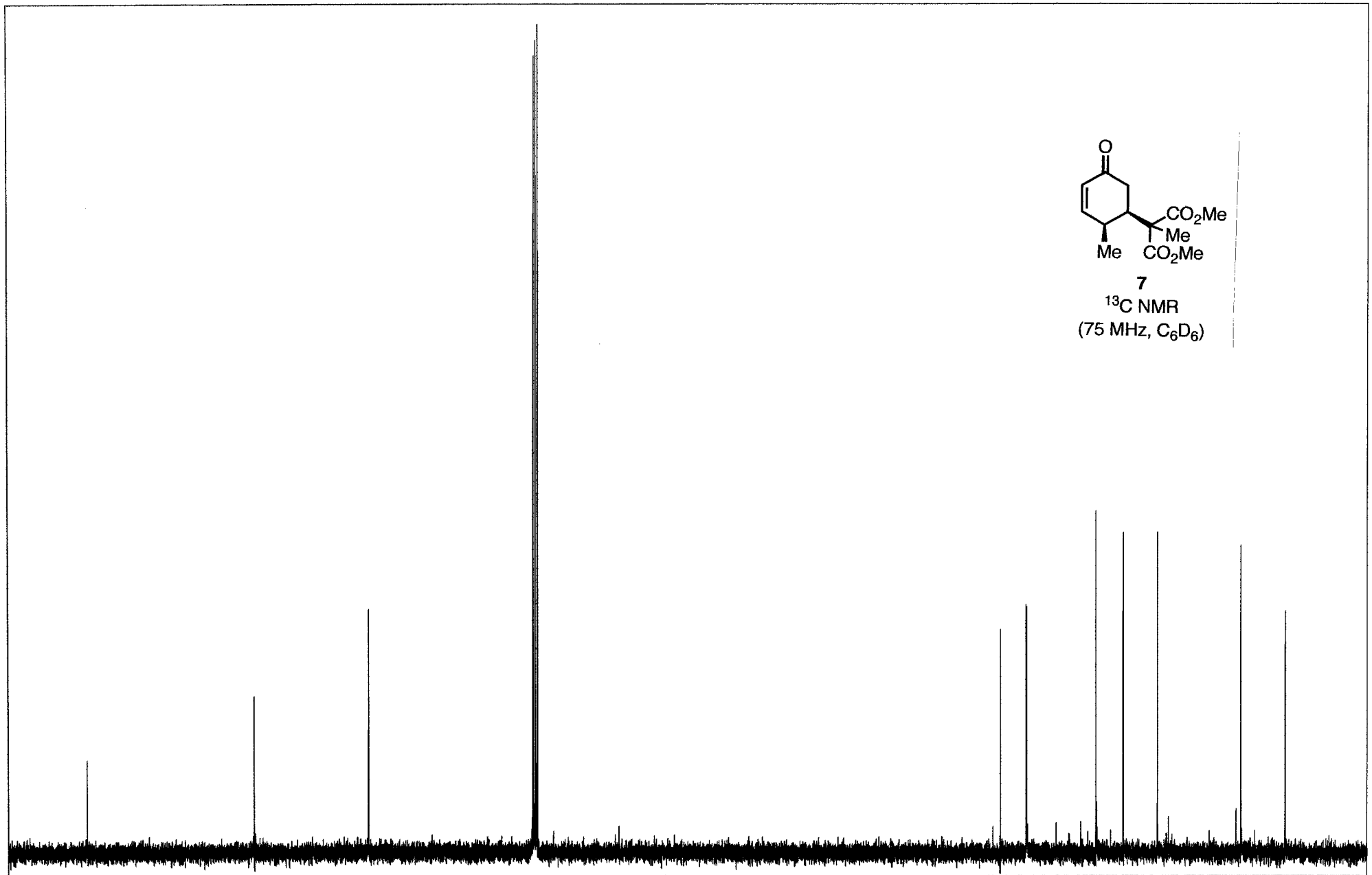


13C OBSERVEblank line USER: -- DATE: Jan 6 2005

F1: 75.479	F2: 300.142	SW1: 18868		OF1: 8341.0		PTS1d: 32768	
EX: s2pul		PW: 7.3 usec	PD: 1.0 sec	NA:	LB: 0.0	WinNuts - $sc518inbenzene-13c.fid	

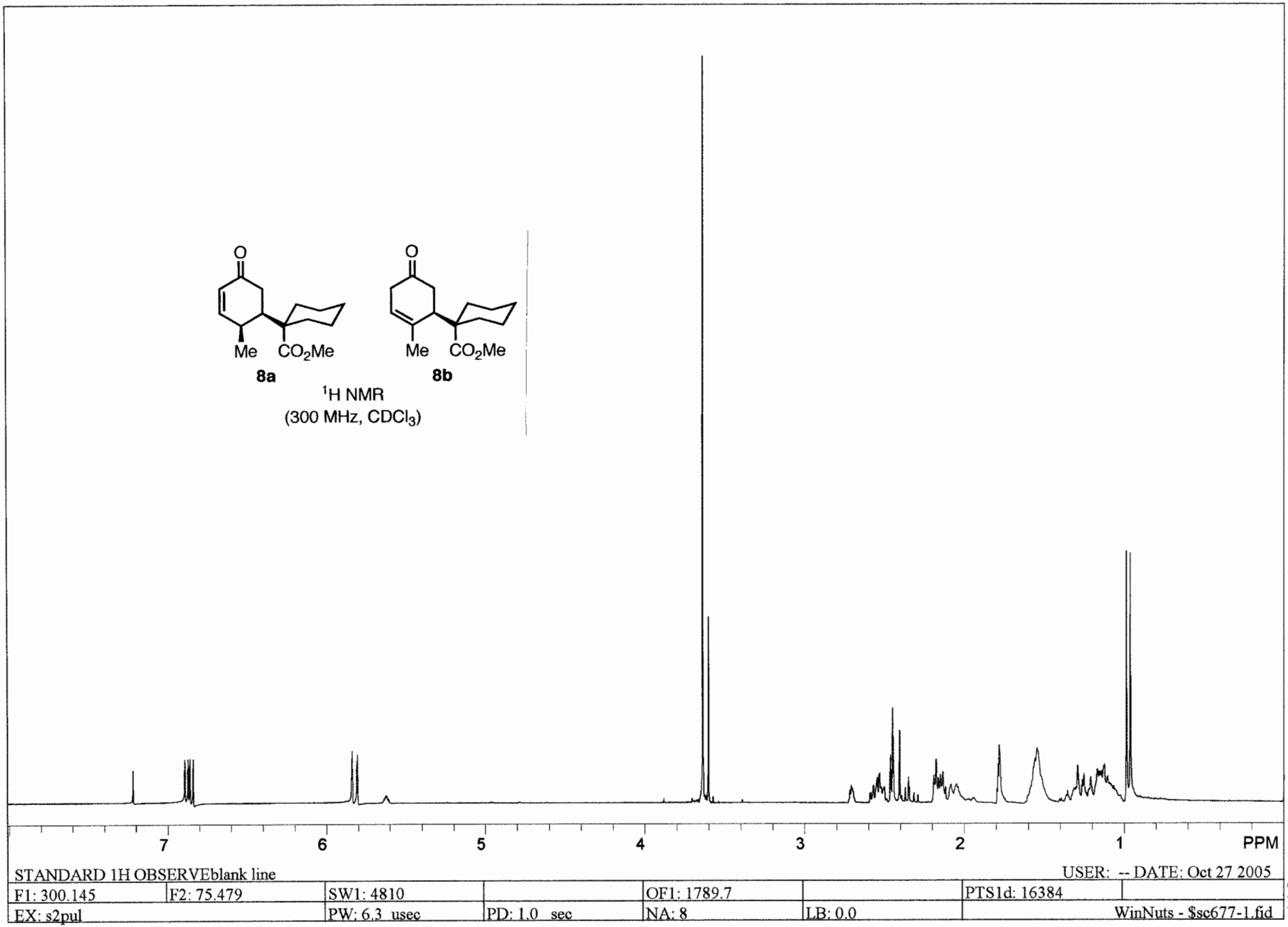

O
CO2Me
Me
Me
CO2Me
7
1H NMR
(300 MHz, C6D6)
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVEblank line
USER: -- DATE: Mar 28 2005
F1: 300.142
F2: 75.478
SW1: 4810
OF1: 1813.2
PTS1d: 16384
EX: s2pul
PW: 6.3 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $sc5592ndfrac.fid

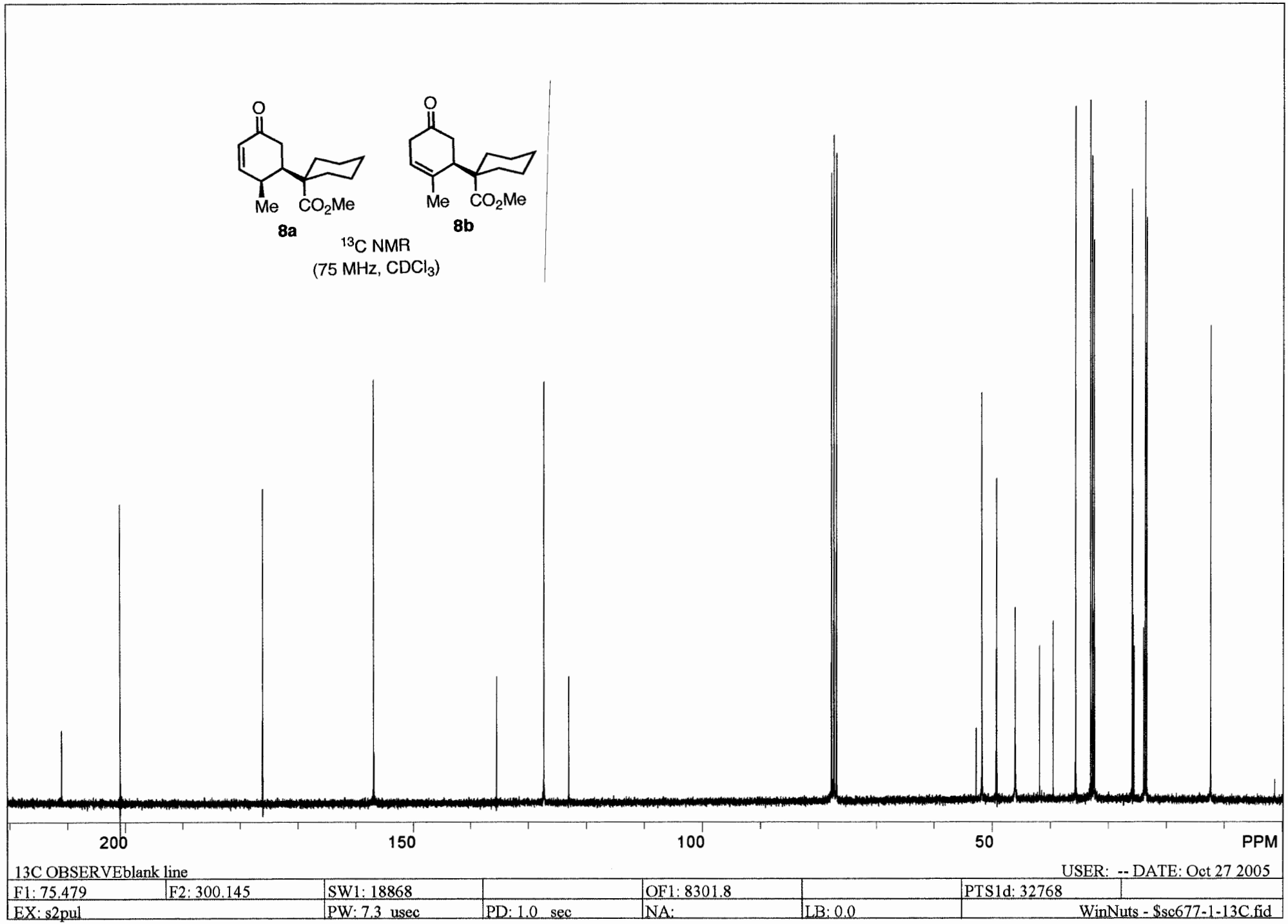


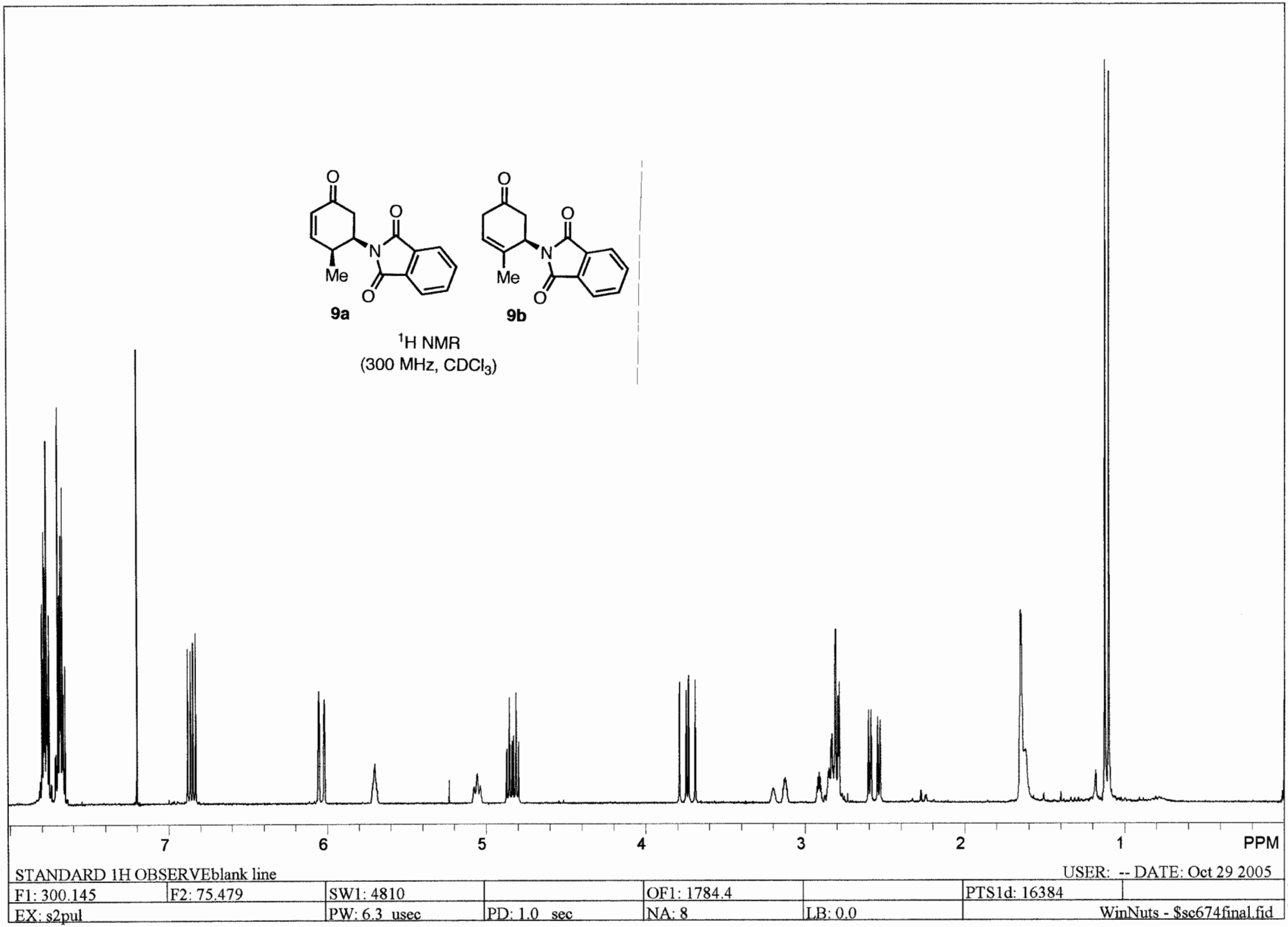
13C OBSERVEblank line

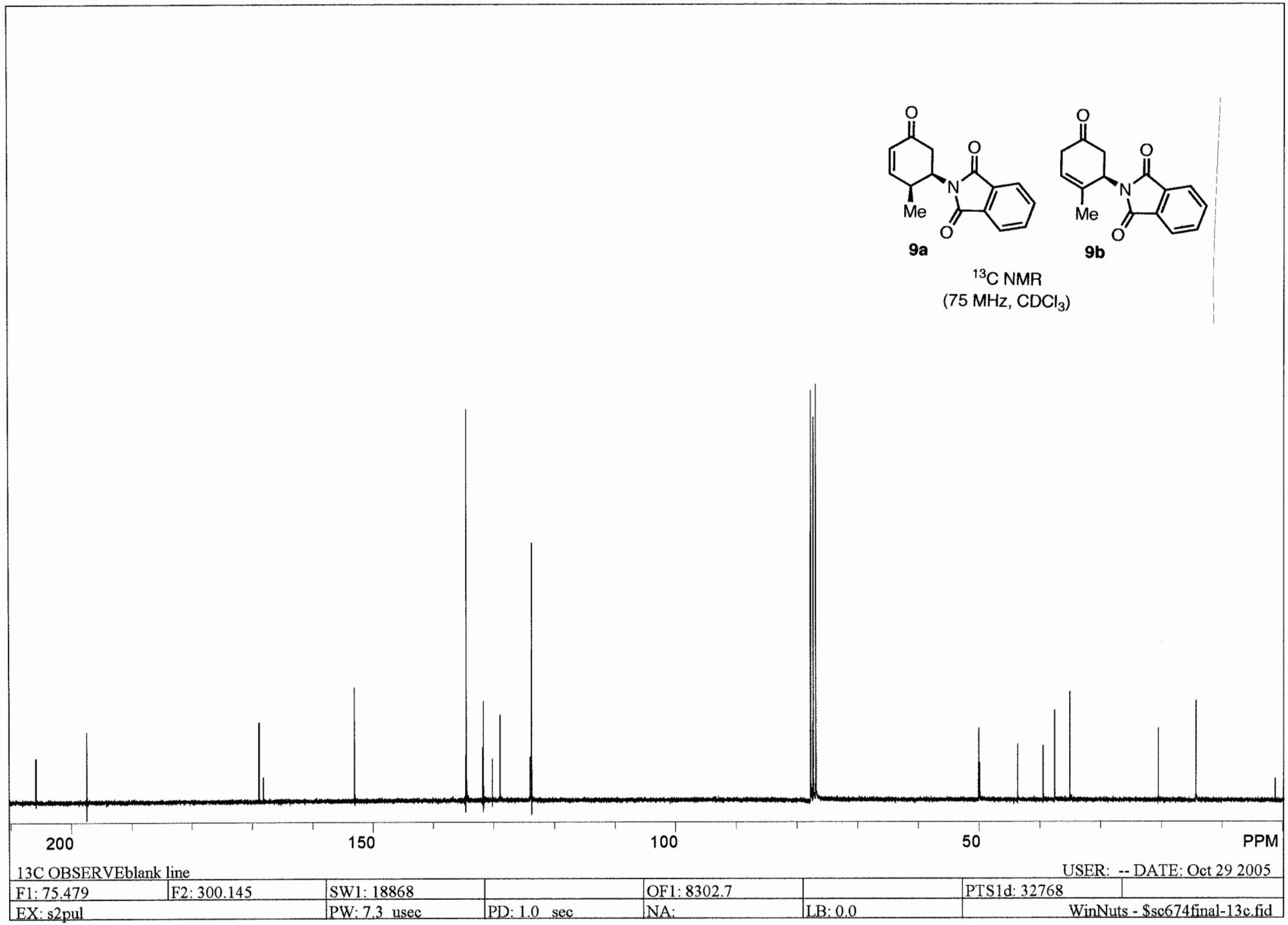
USER: -- DATE: Mar 28 2005

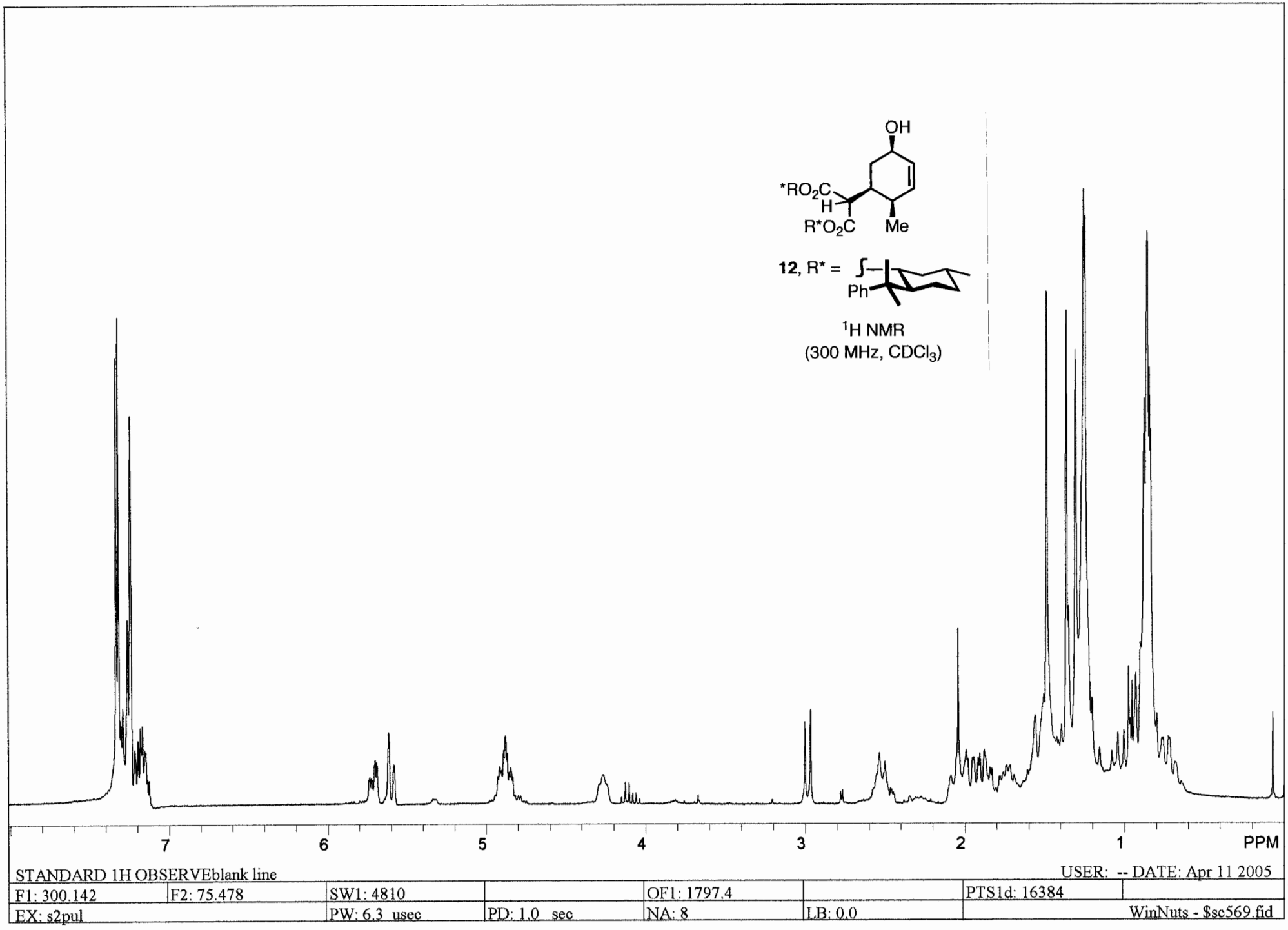
F1: 75.479	F2: 300.142	SW1: 18868		OF1: 8339.3		PTS1d: 32768	
EX: s2pul		PW: 7.3 usec	PD: 1.0 sec	NA: 256	LB: 0.0	WinNuts - $sc559-2ndfrac-13cd6.fid	


O
Me
CO2Me
8a
O
Me
CO2Me
8b
1H NMR
(300 MHz, CDCl3)
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVEblank line
USER: -- DATE: Oct 27 2005
F1: 300.145
F2: 75.479
SW1: 4810
OF1: 1789.7
PTS1d: 16384
EX: s2pul
PW: 6.3 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $sc677-1.fid


O
Me
CO2Me
8a
O
Me
CO2Me
8b
13C NMR
(75 MHz, CDCl3)
200
150
100
50
PPM
13C OBSERVEblank line
USER: -- DATE: Oct 27 2005
F1: 75.479
F2: 300.145
SW1: 18868
OF1: 8301.8
PTS1d: 32768
EX: s2pul
PW: 7.3 usec
PD: 1.0 sec
NA:
LB: 0.0
WinNuts - $sc677-1-13C.fid


O
O
N
Me
O
9a
O
O
N
Me
O
9b
^{1}H NMR
(300 MHz, $CDCl_3$)
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVEblank line
USER: -- DATE: Oct 29 2005
F1: 300.145
F2: 75.479
SW1: 4810
OF1: 1784.4
PTS1d: 16384
EX: s2pul
PW: 6.3 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $sc674final.fid


O
O
N
Me
O
9a
O
O
N
Me
O
9b
^{13}C NMR
(75 MHz, $CDCl_3$)
200
150
100
50
PPM
13C OBSERVEblank line
USER: -- DATE: Oct 29 2005
F1: 75.479
F2: 300.145
SW1: 18868
OF1: 8302.7
PTS1d: 32768
EX: s2pul
PW: 7.3 usec
PD: 1.0 sec
NA:
LB: 0.0
WinNuts - $sc674final-13c.fid


OH
*RO2C
H
R*O2C
Me
12, R* =
Ph
1H NMR
(300 MHz, CDCl3)
7
6
5
4
3
2
1
PPM
STANDARD 1H OBSERVEblank line
USER: -- DATE: Apr 11 2005
F1: 300.142
F2: 75.478
SW1: 4810
OF1: 1797.4
PTS1d: 16384
EX: s2pul
PW: 6.3 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $sc569.fid