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Spectral Data for "Synthesis of Cyclopropanes via Organoiron Methodology: Stereoselective Preparation of Bi(cyclopropyl)s"

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Synthesis of Cyclopropanes via Organoiron Methodology:

Stereoselective Preparation of Biscyclopropanes

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Dichlorocyclopropanation of 4a (6/7): To a solution of **4a** (1.83 g, 6.27 mmol) and cetyltrimethylammonium bromide (27.6 mg, 0.076 mmol) in $CHCl_3$ (40 mL) was added 50% aqueous NaOH. The biphasic mixture was vigorously stirred at room temperature for 80 h. After this time, the mixture was diluted with water (50 mL), extracted several times with CH_2Cl_2, and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Analysis of the crude product by ^{1}H NMR spectroscopy indicated this to be a mixture of **6**, **7** and unreacted **4a** (ca. 6 : 3 : 2 by integration). Purification of the residue by column chromatography (SiO_2, hexanes–ethyl acetate = 96.5:3.5) gave a mixture of **7** and **4a** as an orange solid, followed by **6** as a yellow solid (863 mg, 2.30 mmol, 37%). Recrystallization of the mixture of **7** and **4a** gave crystals of **7** which were suitable for X-ray diffraction analysis.

6: mp 66-68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (d, J = 6.0 Hz, 1H), 1.08-1.21 (m, 2H), 1.47 (dd, J = 5.4, 7.5 Hz, 1H), 2.49 (dd, J = 1.9, 9.1 Hz, 1H), 3.03 (q, J = 6.0 Hz, 1H), 3.60 (br d, J = 6.6 Hz, 1H), 3.67 (s, 3H), 4.36 (br t, J = 5.7 Hz, 1H), 4.62 (ddd, J = 5.7, 6.6, 9.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 26.4, 38.6, 39.8, 51.6, 54.2, 61.5, 97.9, 180.0, 203.9, 210.1, 210.6.

7: mp 130-132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, J = 9.0 Hz, 1H), 1.06 (t, J = 7.2 Hz, 1H), 1.18 (dt, J = 7.5, 10.2 Hz, 1H), 1.37 (dd, J = 6.3, 9.9 Hz, 1H), 2.50-2.61 (m, 1H), 2.89-2.99 (m, 1H), 3.65-3.72 (m & s, 4H total), 4.65-4.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4,

26.3, 38.8, 40.8, 51.7, 54.9, 59.7, 64.6, 98.3, 180.4, 203.6, 210.3, 210.6. Anal. Calcd for $C_{13}H_{12}O_5Cl_2Fe$: C, 41.64; H, 3.22. Found: C, 41.69; H, 3.23.

(1*S,2*R**,3*R**,4*R**)-5,5-Dichloro-1-methoxycarbonyl-2-vinylbicyclopropane (*rac*-11):** To a solution of **6** (400 mg, 1.07 mmol) in methanol (13 mL) at room temperature was added portion-wise ceric ammonium nitrate (4.1 g, 7.5 mmol) over a period of 10 min. The mixture was stirred for an additional 10 min and then poured into brine and extracted several times with ethyl acetate. The combined organic extracts were washed with water, followed by saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated under reduced pressure to give **11** as a colorless syrup (250 mg, 1.06 mmol, 99%). **11:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28-1.42 (m, 2H), 1.52 (td, J = 4.5, 8,1 Hz, 1H), 1.70 (dd, J = 6.1, 9.4 Hz, 1H), 1.90 (t, J = 4.8 Hz, 1H), 2.26 (br dt, J = 4.8, 8.1 Hz, 1H), 3.74 (s, 3H), 5.19 (br d, J = 10.2 Hz, 1H), 5.29 (br d, J = 17.1 Hz, 1H), 5.63 (ddd, J = 8.1, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 27.5, 28.3, 29.0, 29.8, 52.2, 60.7, 118.4, 133.6, 173.0. Anal. Calcd for $C_{10}H_{12}O_2Cl_2$:0.3H_2O: C, 49.94; H, 5.28. Found: C, 49.90; H, 5.16.

Simmons-Smith cyclopropanation of 4c (8/9): To a solution of **4c** (4.31 g, 13.4 mmol) in anhydrous CH_2Cl_2 at –20 °C was added dropwise a solution of diethylzinc in hexanes (68.4 mL, 1.0 M, 68.4 mmol) followed by diiodomethane (5.4 mL, 67 mmol). The reaction mixture was allowed to gradually warm to room temperature over a 3 h period and the mixture was stirred for an additional 1 h. Saturated aqueous NH_4Cl (70 mL) was added and mixture was diluted with ether (400 mL) and 10% aqueous HCl (70 mL). The layers were separated and the organic layer was washed with saturated aqueous Na_2SO_3 (70 mL), followed by saturated aqueous $NaHCO_3$ (70 mL), brine, dried ($MgSO_4$) and concentrated under reduced pressure. Analysis of the crude product by ^{1}H NMR spectroscopy indicated this to be a mixture of **8** and **9** (4.5 : 1 by

integration). Purification of the residue by column chromatography (SiO_2, hexanes–ethyl acetate = 6.5:3.5) gave **9** as an orange oil followed by **8** as a red color syrup (3.15 g, 9.37 mmol, 70%).

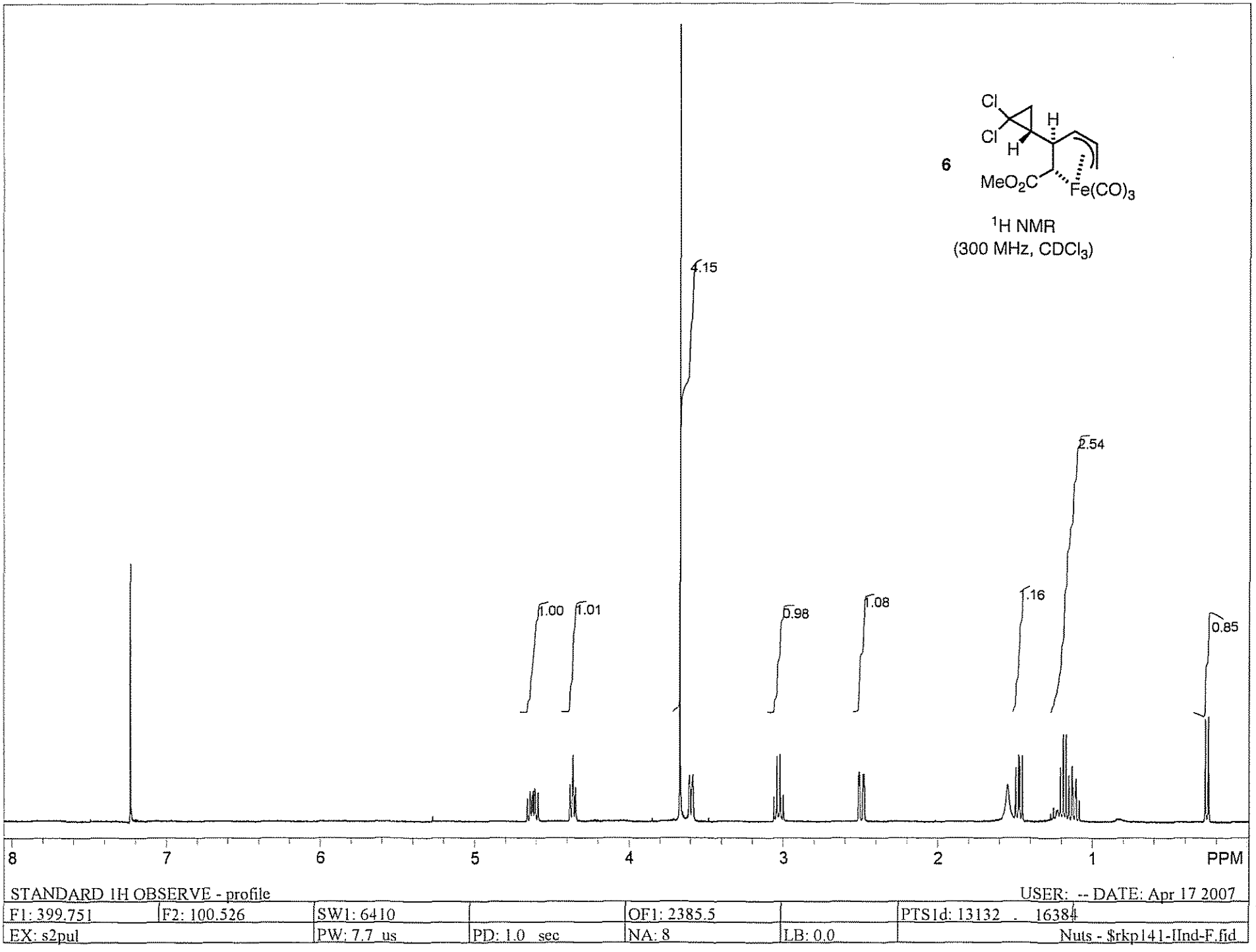
9: IR (CH_2Cl_2) 3447, 2062, 1997, 1698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, J = 8.7 Hz, 1H), 0.21-0.35 (m, 2H), 0.38-0.46 (m, 1H), 0.80 (m, 1H), 1.70 (br s, OH), 2.40-2.55 (m, 2H), 3.29 (d, J = 6.3, 2H), 3.60 (d, J = 7.2 Hz, 1H), 3.67 (s, 3H), 4.40-4.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 13.9, 19.2, 26.0, 43.0, 51.6, 54.5, 65.8, 66.4, 97.9, 181.0, 204.1, 210.7, 211.0. FAB-HRMS *m/z* 337.0363 (calcd for $C_{14}H_{17}O_6Fe$ ($M+H^+$) *m/z* 337.0375).

8: IR (CH_2Cl_2) 3447, 2067, 2002, 1698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (d, J = 9.0 Hz, 1H), 0.19-0.30 (m, 3H), 0.90-1.00 (m, 1H), 1.60 (br s, OH), 2.49 (m & dd, J = 2.4, 11.4 Hz, 2H total), 3.30 (dd, J = 7.2, 11.2 Hz, 1H), 3.41 (dd, J = 6.6., 11.1 Hz, 1H), 3.61 (d, J = 8.7 Hz, 1H), 3.67 (s, 3H), 4.50 (t, J = 7.2 Hz, 1H), 4.59 (td, J = 7.7, 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.1, 14.0, 20.4, 26.2, 42.9, 51.6, 54.6, 65.8, 66.6, 97.9, 181.0, 204.0, 210.6. FAB-HRMS *m/z* 337.0380 (calcd for $C_{14}H_{17}O_6Fe$ ($M+H^+$) *m/z* 337.0375).

(1*S,2*R**,3*R**,4*S**,6*R**)-6-Hydroxymethyl-1-methoxycarbonyl-2-vinylbicyclopropane (*rac*-12):** To a solution of **8** (690 mg, 2.05 mmol) in methanol (24 mL) at room temperature was added portion-wise ceric ammonium nitrate (7.01 g, 12.8 mmol) over a period of 10 min. The mixture was stirred for an additional 20 min and then poured into brine (30 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic extracts were washed with water (3 x 30 mL), followed by saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure to give **12** as a colorless syrup (324 mg, 1.65 mmol, 80%).

12: IR (CH_2Cl_2) 1726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.49-0.62 (m, 3H), 1.03-1.14 (m, 1H), 1.45 (td, J = 4.8, 9.3 Hz, 1H), 1.61 (t, J = 4.5 Hz, 1H), 2.18 (dt, J = 4.4, 9.0 Hz, 1H), 3.40 (dd, J = 6.9, 11.1 Hz, 1H), 3.50 (dd, J = 6.6, 11.4 Hz, 1H), 3.67 (s, 3H), 5.15 (br d, J = 10.5 Hz,

1H), 5.27 (br d, J = 17.4 Hz, 1H), 5.65 (ddd, J = 9.0, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.6, 14.8, 21.0, 27.0, 30.8, 31.5, 52.1, 66.6, 117.4, 134.7, 173.7. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.21. Found: C, 66.94; H, 8.22.



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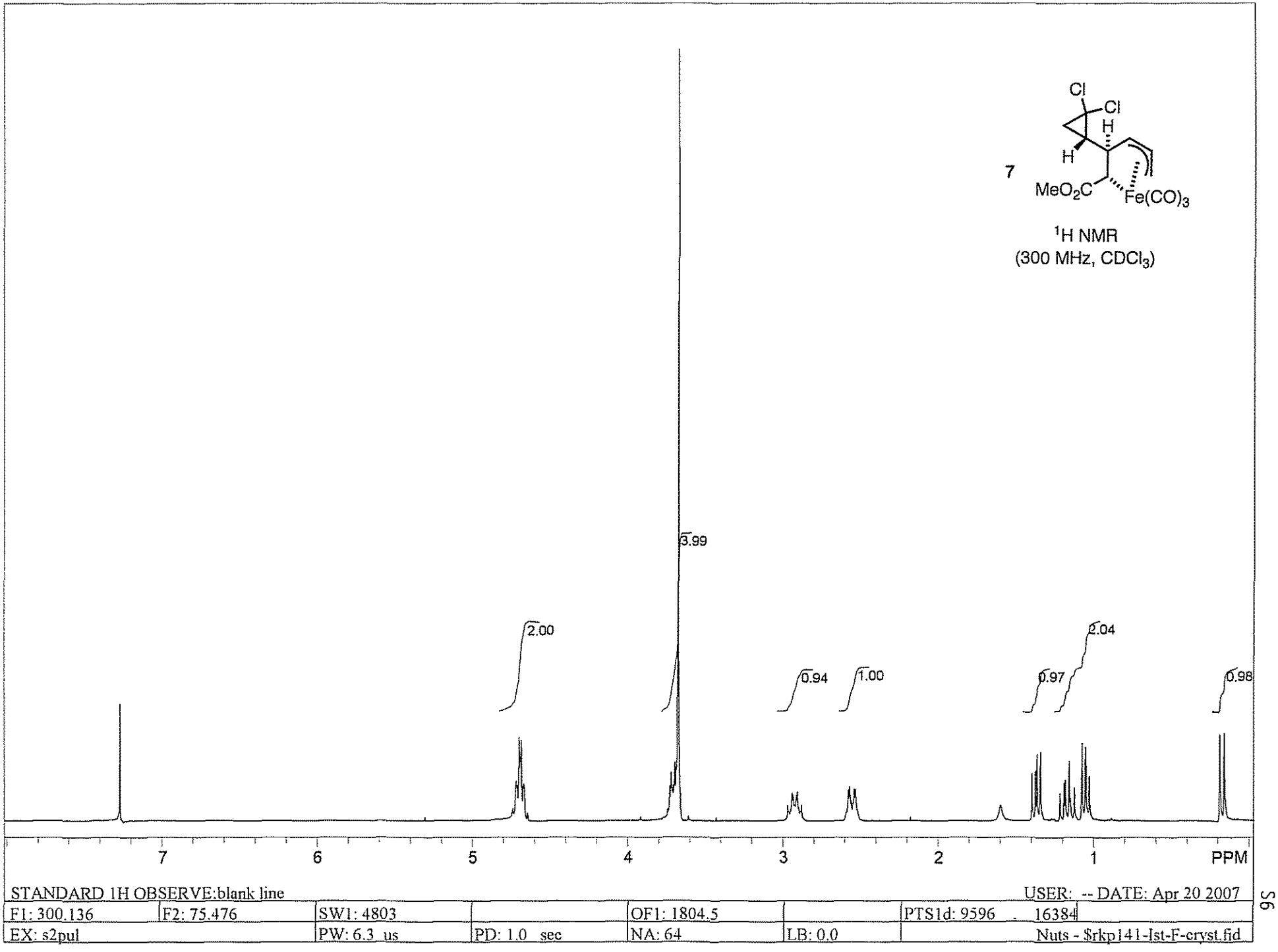
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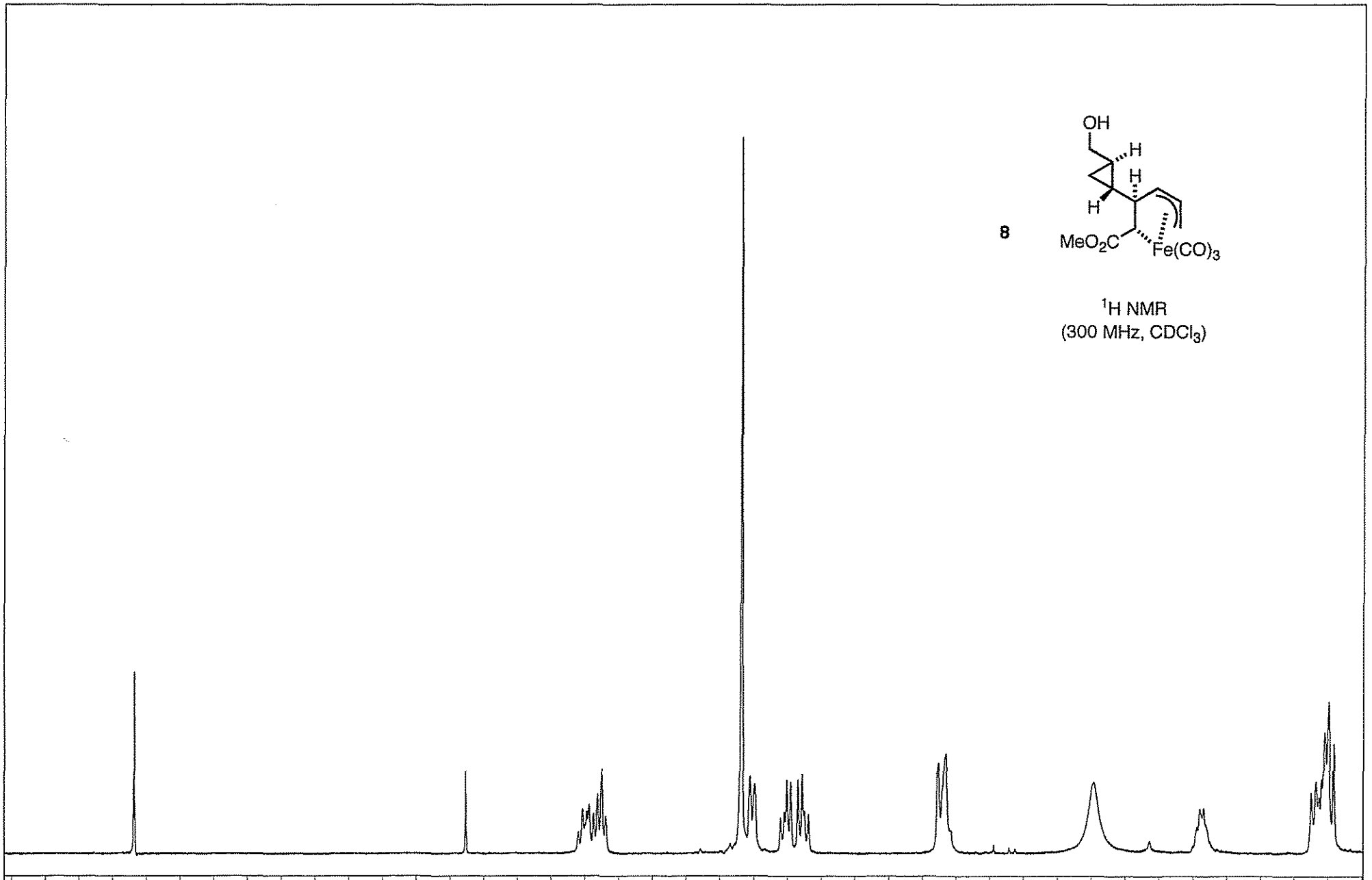
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(300 MHz, CDCl3)
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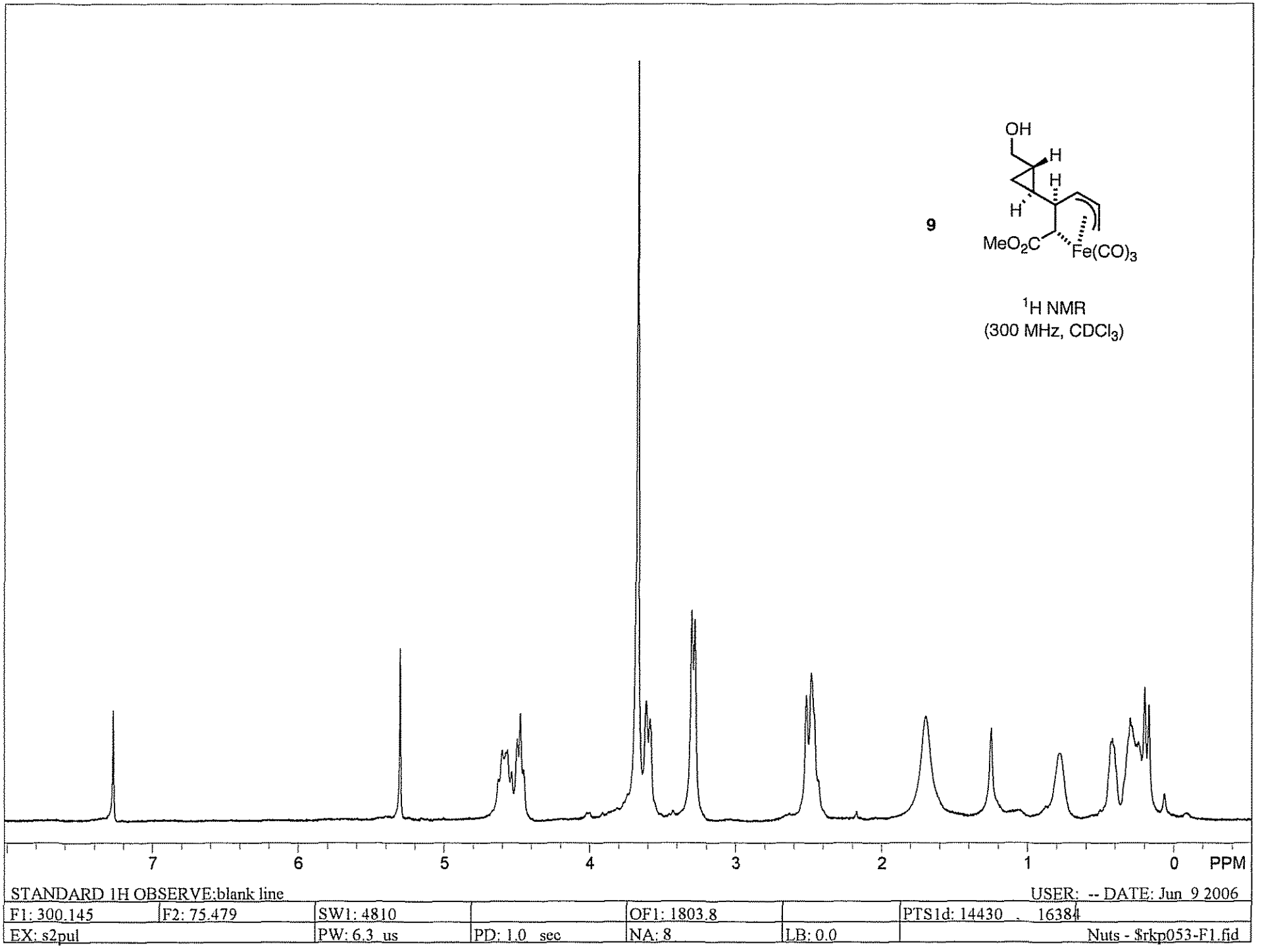
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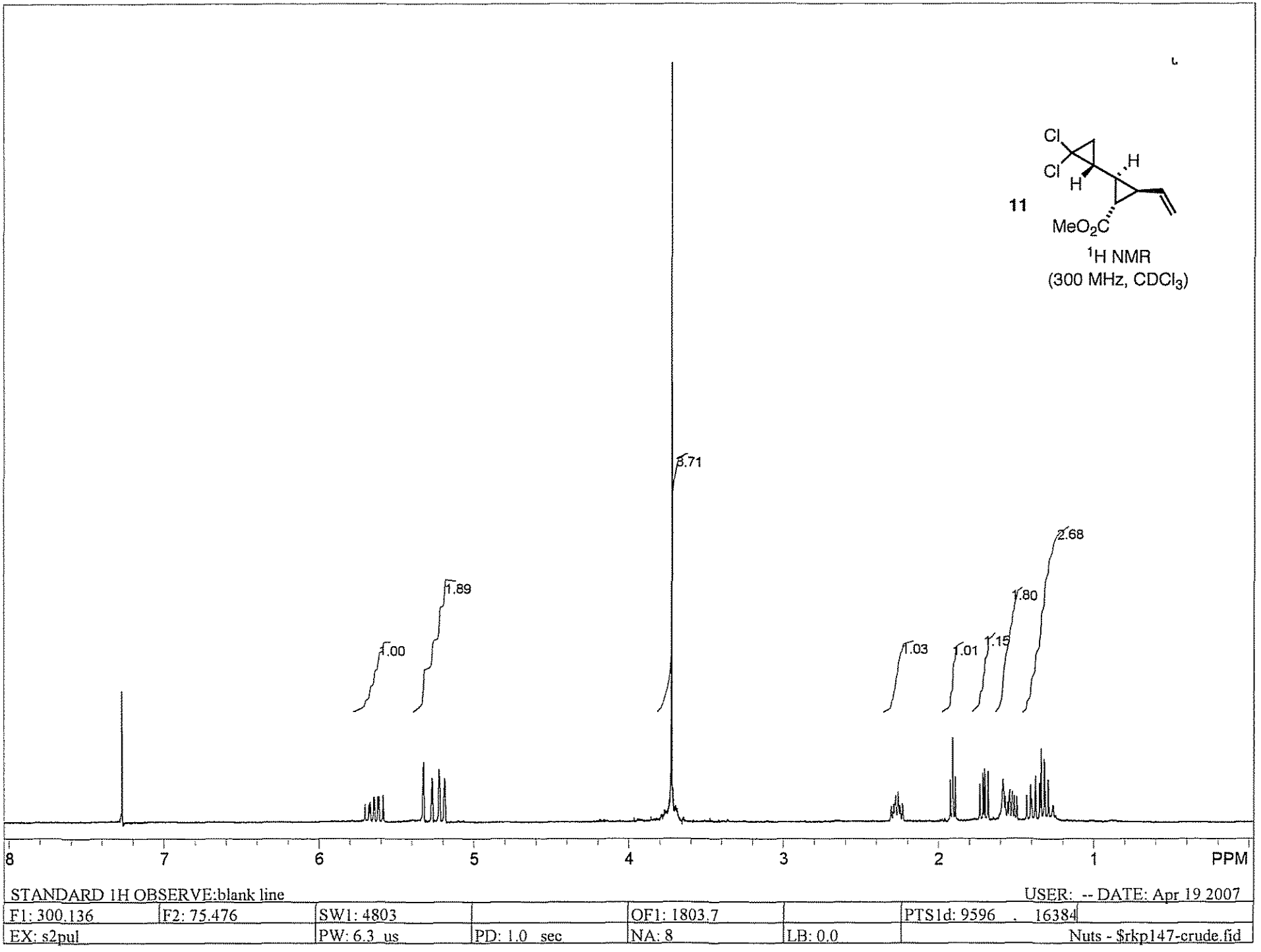
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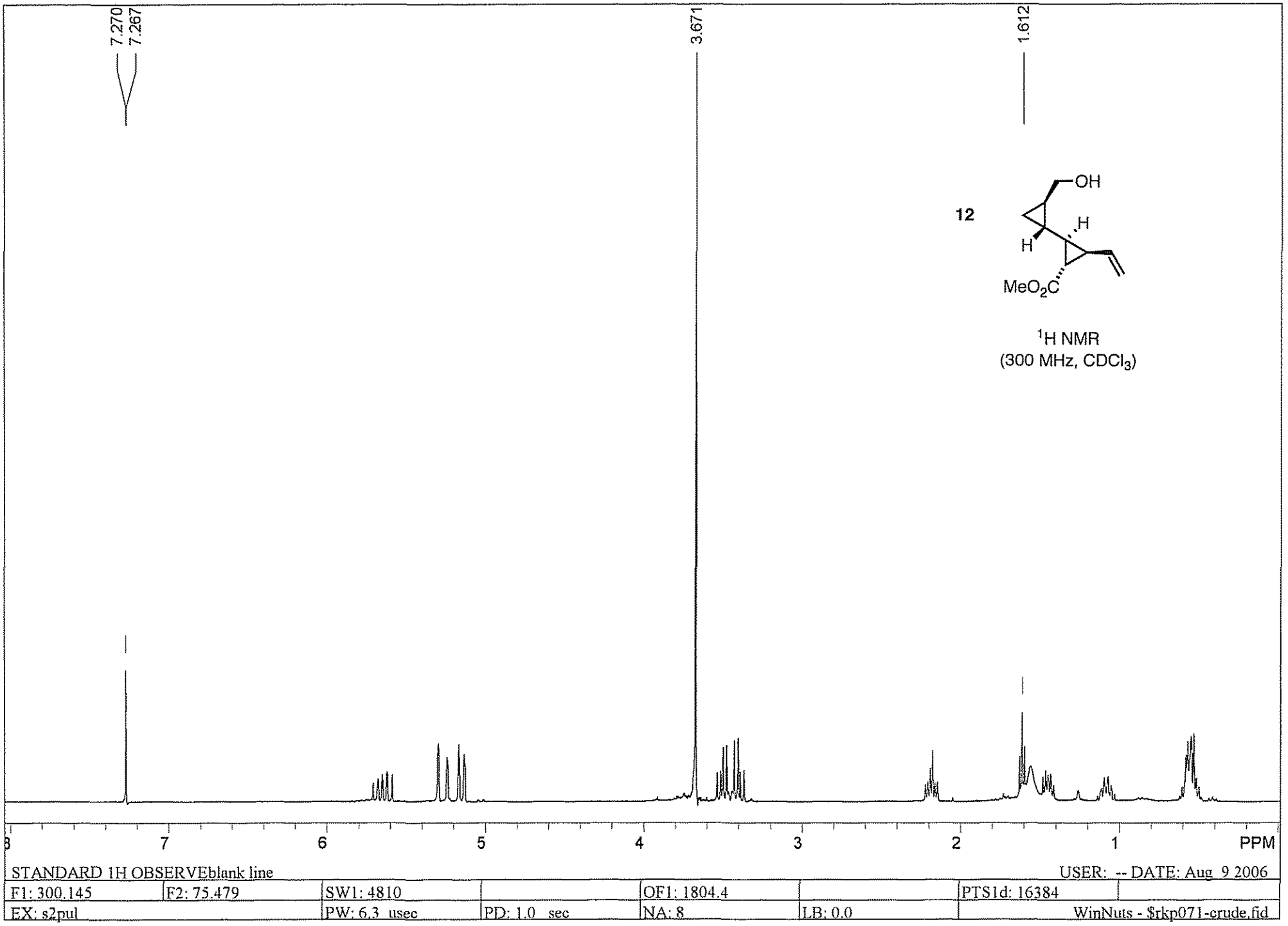
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