Synthesis of the Oxygenated Pactamycin Core

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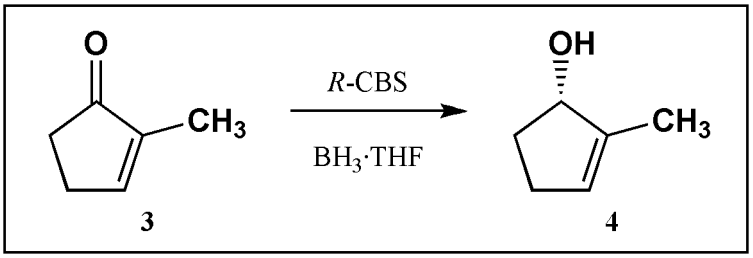
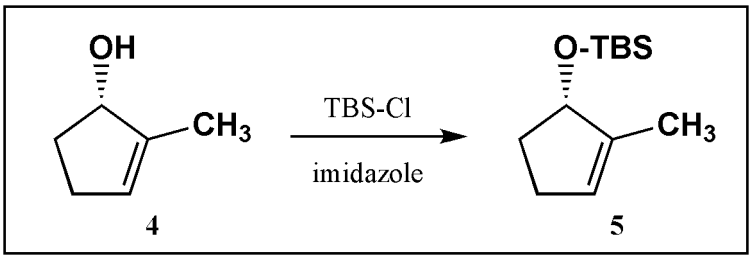
Supporting Information

Page



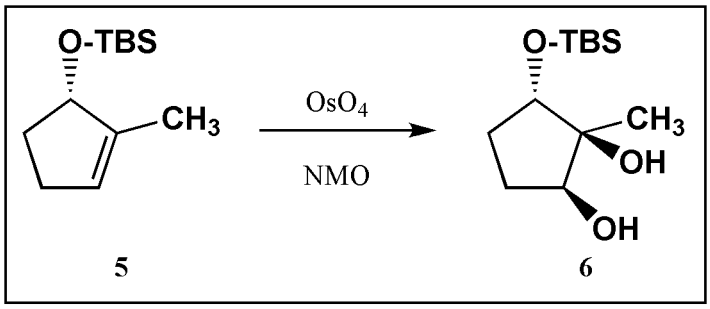
Compound 4. A solution of (*R*)-2-methyl-CBS-oxazaborolidine (1.0 M in toluene, 20.0 mL, 20.0 mmol) and 1.0 M borane-THF in THF (20.0 mL, 20.0 mmol) in 40.0 mL of additional dry THF was stirred at 0 °C. Solutions of **3** (9.61 g, 100 mmol) in 80.0 mL of dry THF, and 50.0 mL (50.0 mmol) of 1.0 M BH_3·THF in 30.0 mL of dry

THF, were added simultaneously over a 30 min period. The reaction mixture was allowed to warm slowly to room temperature, and then was quenched carefully by addition of 60 mL of water. The mixture was stirred for 2 h, and then extracted with ether (3 × 80 mL). The combined organic extract was washed sequentially with saturated ammonium chloride (80 mL) and brine (80 mL), dried with anhydrous magnesium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 14% ethyl acetate in hexanes (R_f = 0.25), to give 5.3 g (54%) of **4** as a colorless oil, the NMR spectra of which match the literature values. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.53 (s, 1 H), 4.58 (br s, 1 H), 2.43 – 2.27 (m, 2 H), 2.23 – 2.15 (m, 1 H), 1.78 (s, 3 H), 1.73 – 1.66 (m, 1 H), 1.43 (br s, OH); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 141.6, 128.1, 80.0, 34.2, 29.9, 13.8. The crude Mosher ester derivative of **4** was analyzed by ^{1}H and ^{19}F NMR spectroscopy, and *ee* values of >90% were obtained by integration of the methoxy and trifluoromethyl signals, respectively. Copies of the ^{1}H and ^{19}F NMR (CF_3 region expanded) spectra are attached below.

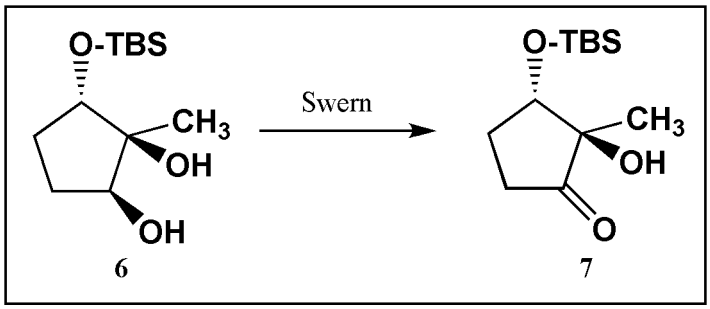


Compound 5. A solution of **4** (1.96 g, 20.0 mmol) in 60 mL of dry dichloromethane was stirred at 0 °C under a nitrogen atmosphere. To this solution was added *tert*-butyldimethylsilyl chloride (3.62 g, 24 mmol, 1.2 equiv) and imidazole (2.72 g, 40 mmol, 2.0 equiv). The turbid reaction mixture was allowed to stir overnight at room temperature. Water (30 mL) was added, and the organic layer was reserved. The aqueous layer was further extracted with dichloromethane (2 × 30 mL). The combined organic layer was washed with brine (30 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with hexanes (R_f = 0.35), to afford **5** (4.25 g, quantitative yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.46 (s, 1 H), 4.65 (br s, 1 H), 2.40 – 2.12 (m, 3 H), 1.71 (s, 3

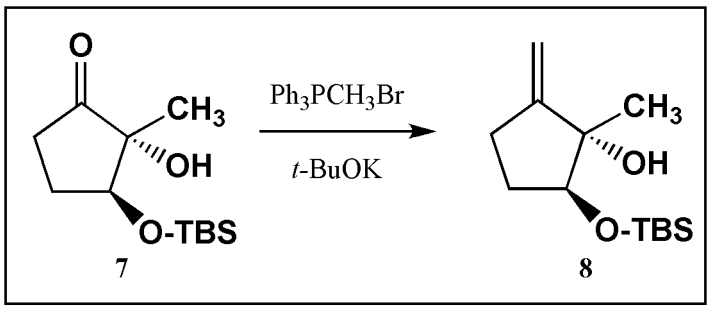
H), 1.70 – 1.63 (m, 1 H), 0.92 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 141.9, 126.7, 80.1, 34.4, 29.8, 26.1, 18.5, 14.0, -4.2, -4.5; ESI-MS *m/z* 213 MH^+.



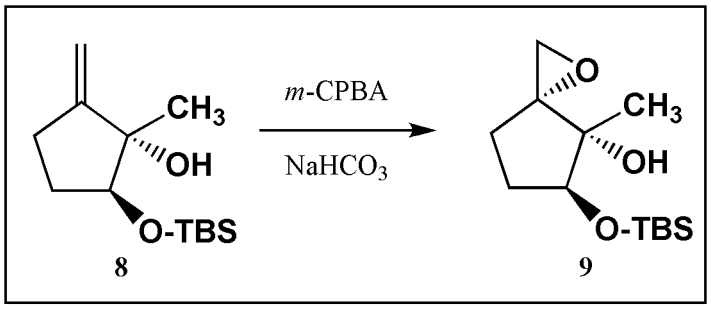
Compound 6. A solution of **5** (3.0 g, 14.1 mmol) in a mixture of acetone and water (32 mL / 2 mL) was stirred at 0 °C. 4-Methylmorpholine N-oxide (NMO, 3.3 g, 28.2 mmol, 2.0 equiv) was added, followed by an aqueous solution of osmium tetraoxide (4% wt in water, *d* = 1.04, 6 mL, 0.98 mmol, 0.07 equiv). The reaction mixture was allowed to warm slowly to room temperature, and then was stirred at room temperature for another 6 h. Sodium sulfite (5 g) was added, and the reaction mixture was stirred for 1 h. The mixture was concentrated to approximately half volume, and the residue was partitioned between dichloromethane (30 mL) and water (15 mL). The organic layer was reserved, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layer was washed with brine (30 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 20 % ethyl acetate in hexanes (R_f = 0.25), to afford **6** as a colorless oil (3.23 g, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98 (dd, *J* = 5.0, 6.6 Hz, 1 H), 3.88 – 3.84 (m, 1 H), 2.16 – 2.03 (m, 4 H, including 2 OH), 1.59 – 1.52 (m, 1 H), 1.43 – 1.36 (m, 1 H), 1.19 (s, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 80.3, 78.6, 76.7, 30.0, 28.9, 25.9, 20.3, 18.2, -4.4, -4.7; ESI-MS *m/z* 229 M – OH.



Compound 7. A solution of 1.05 mL (12 mmol, 1.2 equiv) of oxalyl chloride in 25 mL of dichloromethane was stirred at –78 °C. A solution of 1.73 mL (24 mmol, 2.4 equiv) of DMSO in 10 mL of dichloromethane was added, keeping the temperature below –65 °C. After 10 min, a solution of **6** (2.46 g, 10 mmol) in 20 mL of dichloromethane was added slowly, again keeping the temperature below –65 °C. After 30 min, a solution of 7 mL (50 mmol, 5.0 equiv) of triethylamine in 20 mL of dichloromethane was added dropwise, and the resulting mixture was stirred at –78 °C for 30 min, and then allowed to stir at room temperature overnight. The resulting yellow reaction mixture was added to 50 mL of water, the organic layer was reserved, and the aqueous layer was further extracted with dichloromethane (3 × 30 mL). The combined organic layer was washed with brine (30 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 10 % ethyl acetate in hexanes (R_f = 0.25), to provide 2.08 g (85% yield) of **7** as a white solid, mp 51 – 53 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.10 (dd, J = 6.4, 7.6 Hz, 1 H), 2.53 – 2.45 (m, 1 H), 2.38 (s, 1 OH), 2.29 – 2.12 (m, 2 H), 1.80 – 1.70 (m, 1 H), 1.18 (s, 3 H), 0.91 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 217.8, 79.8, 76.7, 32.8, 27.2, 25.9, 18.2, 17.6, -4.5, -4.6; ESI-MS *m/z* 267 MNa^+.



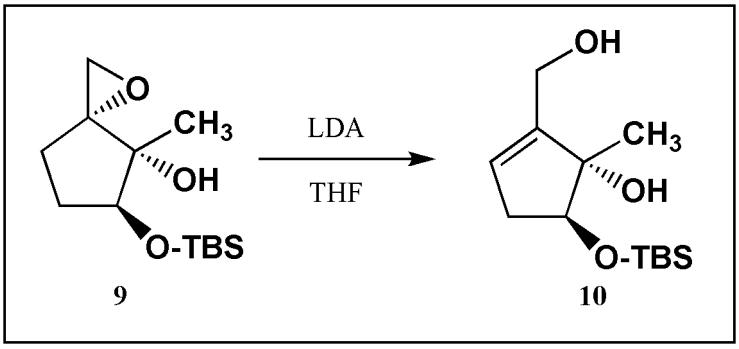
Compound 8. A suspension of dry methyltriphenylphosphonium bromide (4.3 g, 12.0 mmol, 2.6 equiv) in 20 mL of dry THF was treated at room temperature with 11.1 mL (11.1 mmol, 2.4 equiv) of a 1.0 M potassium *tert*-butoxide solution in THF, added dropwise. After 30 min, the reaction mixture was cooled to 0°C, and a solution of 1.12 g (4.6 mmol) of **7** in 15 mL of dry THF was added dropwise. The reaction mixture was stirred at room temperature for 1 h, and then quenched with 15 mL of aqueous ammonium chloride. Following extraction with ether (3 × 30 mL), the combined organic layer was washed with brine (15 mL), dried with anhydrous magnesium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 5% ethyl acetate in hexanes (R_f = 0.3), to afford **8** as a colorless oil (0.91 g, 82 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.13 (t, J = 2.6 Hz, 1 H), 4.93 (t, J = 2.2 Hz, 1 H), 3.88 (dd, J = 6.6, 6.6 Hz, 1 H), 2.51 – 2.32 (m, 2 H), 1.97 – 1.89 (m, 1 H), 1.57 – 1.49 (m, 1 H), 1.47 (s, 1 OH), 1.24 (s, 3 H), 0.89 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 155.5, 106.9, 80.6, 80.5, 30.0, 26.8, 26.0, 21.8, 18.2, -4.4, -4.5; ESI-MS *m/z* 265 MNa^+.



8 9

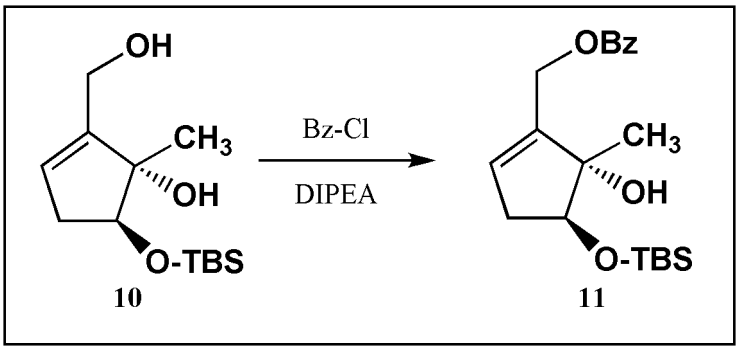
Compound 9. A solution of **8** (0.8 g, 3.3 mmol) in 30 mL of dichloromethane was stirred at 0 °C. Sodium bicarbonate (555 mg, 6.6 mmol, 2.0 equiv) was added, followed by a solution of 1.12 g of *m*-chloroperoxybenzoic acid (*m*-CPBA, 77%, 5.0 mmol, 1.5 equiv) in 15 mL of dichloromethane (pre-dried with anhydrous sodium sulfate). The reaction mixture was allowed to stir at room temperature overnight. A solution of 500 mg of sodium sulfite in 10 mL of water was added, and the mixture was stirred for 15 min. The organic layer was reserved, and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layer was washed with brine (15 mL), dried with anhydrous sodium sulfate, and then concentrated. The product was

purified by flash chromatography on silica, eluting with 5% ethyl acetate in hexanes (R_f = 0.2), to afford 0.85 g (quantitative yield) of **9** as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98 (t, J = 7.4 Hz, 1 H), 2.84 (d, J = 8 Hz, 1 H), 2.83 (d, J = 8 Hz, 1 H), 2.28 – 2.20 (m, 1 H), 2.12 – 2.03 (m, 2 H, including 1 OH), 1.70 – 1.62 (m, 1 H), 1.56 – 1.46 (m, 1 H), 1.12 (s, 3 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 79.7, 76.5, 66.6, 49.6, 28.5, 26.0, 25.8, 18.3, 17.9, -4.5, -4.6; ESI-MS *m/z* 281 MNa^+.

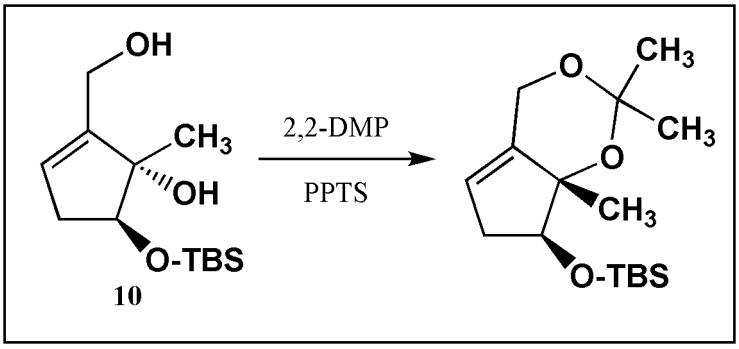


9 10

Compound 10. A solution of 1.64 mL of diisopropylamine (11.6 mmol, 6.0 equiv) in 10 mL of dry THF was stirred at 0 °C under a nitrogen atmosphere. A solution of 3.86 mL (9.65 mmol, 5.0 equiv) of 2.5 M *n*-butyllithium in hexanes was dropwise. After 20 min, a solution of 0.5 g (1.93 mmol) of **9** in 10 mL of dry THF was added slowly, while keeping the temperature at 0 °C. The reaction mixture was allowed to stir at room temperature overnight, then was poured onto ice (15 g) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 33% ethyl acetate in hexanes (R_f = 0.2), to provide **10** as a white solid (0.4 g, 80% yield), mp 68–70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.59 (s, 1 H), 4.33 (d, J = 12.4 Hz, 1 H), 4.22 – 4.17 (m, 2 H), 2.57 – 2.51 (m, 1 H), 2.21 (br s, 1 OH), 2.06 – 2.01 (m, 2 H, including 1 OH), 1.26 (s, 3 H), 0.91 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 145.6, 124.6, 85.1, 82.6, 60.2, 37.9, 26.0, 20.0, 18.3, -4.4, -4.5; ESI-MS *m/z* 281 MNa^+.

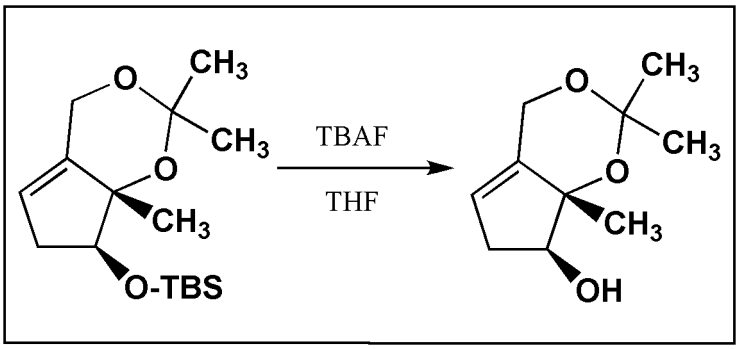


Compound 11. A solution of 0.78 g (3.0 mmol) of **10** in 30 mL of dry dichloromethane was stirred at 0 °C under a nitrogen atmosphere. Benzoyl chloride (0.38 mL, 3.3 mmol, 1.1 equiv) was added, followed by 1.05 mL (6.0 mmol, 2.0 equiv) of diisopropylethylamine. The reaction mixture was allowed to stir at room temperature overnight, was poured on ice (15 g), and then was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 8% ethyl acetate in hexanes (R_f = 0.3), to afford **11** as a colorless oil (0.98 g, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (dd, *J* = 8.0 Hz, 1.2 Hz, 2 H), 7.56 (dt, *J* = 8.0 Hz, 1.2 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 5.75 (dd, *J* = 2.8 Hz, 1.2 Hz, 1 H), 4.93 (d, *J* = 1.6 Hz, 2 H), 4.20 (t, *J* =14.8 Hz, 1 H), 2.57 – 2.51 (m, 1 H), 2.13 – 2.06 (m, 2 H, including 1 OH), 1.29 (s, 3 H), 0.92 (s, 9 H), 0.11 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.4, 142.5, 133.0, 130.0, 129.5, 128.3, 127.0, 83.8, 82.5, 61.2, 37.9, 26.0, 20.2, 18.3, -4.4, -4.5; ESI-MS *m/z* 385 MNa^+.

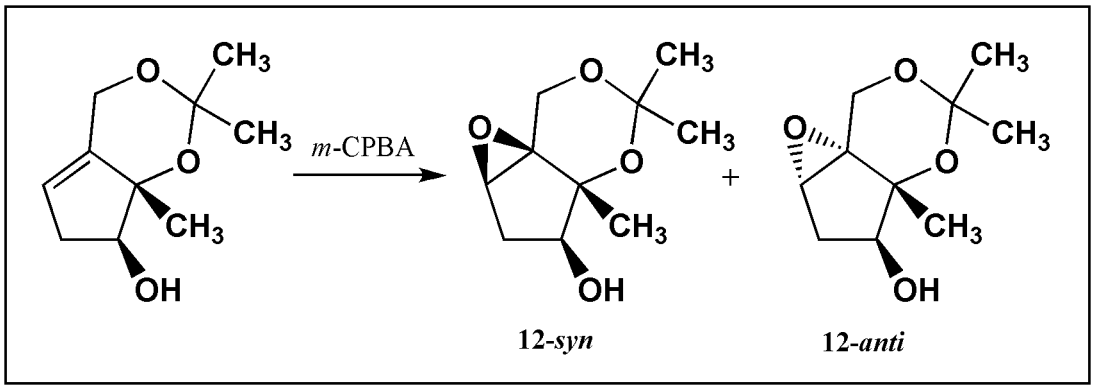


Ketalization/desilylation of 10. A mixture of 300 mg (1.16 mmol) of the allylic diol **10**, 10 mL of dry DMF, 2.85 mL (23.2 mmol, 20 equiv) of 2,2-dimethoxypropane,

146 mg (0.58 mmol, 0.5 equiv) of pyridinium *p*-toluenesulfonate, and 300 mg of 4-Å molecular sieves was heated in a sealed tube at 80 °C for 2 days. The reaction mixture was cooled, and then filtered through a Celite pad, rinsing with dichloromethane (2 × 10 mL). The combined filtrate was concentrated, and the residue was dissolved in 30 mL of EtOAc. The organic solution was washed sequentially with saturated aqueous sodium bicarbonate (2 × 10 mL) and brine (10 mL), dried with anhydrous sodium sulfate, and then concentrated. The product was purified by flash chromatography on silica, eluting with 2% ethyl acetate in hexanes (R_f = 0.25), to afford the acetonide product as a colorless oil (194 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.38 (s, 1 H), 4.61 (dd, J = 14.6 Hz, 2.2 Hz, 1 H), 4.41 (d, J = 14.8 Hz, 1 H), 4.19 (t, J = 8.2 Hz, 1 H), 2.42 – 2.36 (m, 1 H), 2.07 – 1.97 (m, 1 H), 1.38 (s, 6 H), 1.23 (s, 3 H), 0.90 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 140.4, 119.0, 99.1, 83.6, 83.1, 60.9, 37.5, 29.1, 27.3, 26.3, 19.8, 18.7, -4.1, -4.4; ESI-MS *m/z* 322 MNa^+.

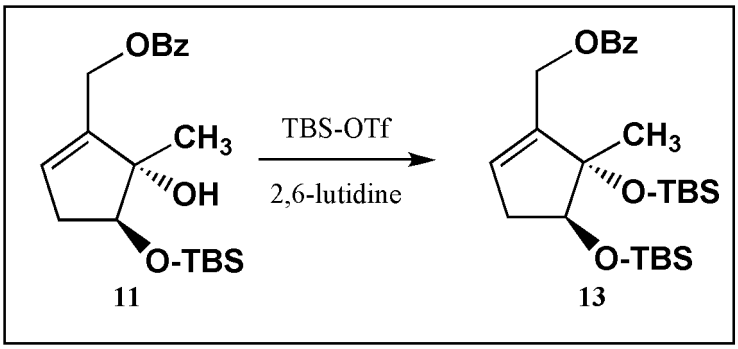


A solution of 160 mg (0.54 mmol) of the acetonide in 6 mL of THF was treated with 1.08 mL (1.0 M solution in THF, 1.08 mmol, 2.0 equiv) of tetra-*n*-butylammonium fluoride (TBAF) solution, added dropwise. After 3 h, the solvent was evaporated, and the residue was purified by column chromatography on silica, eluting with 20% ethyl acetate in hexanes (R_f = 0.3) to afford the homoallylic alcohol product as a colorless oil (90 mg, 91% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.40 (s, 1 H), 4.66 – 4.60 (m, 1 H), 4.45 (d, J = 14.0 Hz, 1 H), 4.25 (t, J = 8.2 Hz, 1 H), 3.20 (br s, OH), 2.55 – 2.49 (m, 1 H), 2.10 – 2.05 (m, 1 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 139.6, 119.0, 99.5, 83.5, 82.7, 60.6, 36.0, 29.0, 26.5, 19.5; ESI-MS *m/z* 186 MH^+.

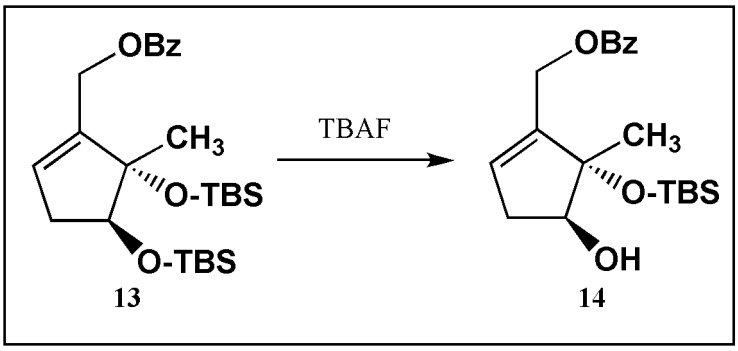


Epoxy Alcohols 12-*Anti* and 12-*Syn*. A solution of 300 mg (1.63 mmol) of the homoallylic alcohol described above in 6 mL of dichloromethane was stirred at 0 °C. A solution of 585 mg (2.61 mmol) of 77% *m*-CPBA in 10 mL of dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 2 days. A 10% aqueous sodium thiosulfate solution (10 mL) was added, and the resulting heterogeneous mixture was vigorously stirred for 5 min. The organic layer was reserved, and the aqueous layer was further extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed sequentially with saturated aqueous sodium bicarbonate (10 mL) and brine (10 mL), dried with anhydrous sodium sulfate, and then concentrated. The product was purified by flash chromatography on silica, eluting with mixtures of ethyl acetate and hexanes (20 – 35%). For the 1st product (a little more polar than the starting material), elution with 20% EtOAc in hexanes (R_f = 0.28) afforded the **12-*syn*** as a white solid (115 mg, 35%), mp 67–69 °C. For the 2nd band (the more polar isomer), elution with 35% EtOAc in hexanes (R_f = 0.25) gave **12-*anti*** as a white solid (79 mg, 24% yield), mp 59–61 °C. Crystals of **12-*anti*** suitable for x-ray analysis were grown by slow diffusion of petroleum ether into a toluene solution. Compound **12-*syn***: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.23 (d, *J* = 11.6 Hz, 1 H), 3.92 (d, *J* = 12.0 Hz, 1 H), 3.66 (br s, 1 H), 3.51 (s, 1 H), 2.39 (dd, *J* = 15.4, 6.6 Hz, 1 H), 2.00 (d, *J* = 15.6 Hz, 1 H), 1.70 (br s, OH), 1.54 (s, 3 H), 1.45 (s, 3 H), 1.39 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 100.7, 80.8, 77.6, 65.5, 65.1, 59.0, 35.9, 29.6, 26.5, 17.2; ESI-MS *m/z* 223 MNa^+, 423 M_2Na^+. Compound **12-*anti***: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.57 (d, *J* = 12.8 Hz, 1 H), 4.00 (d, *J* = 12.4 Hz, 1 H), 3.92 (t, *J* = 7.6 Hz, 1 H), 3.63 (s, 1 H), 2.42 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.25 – 2.35

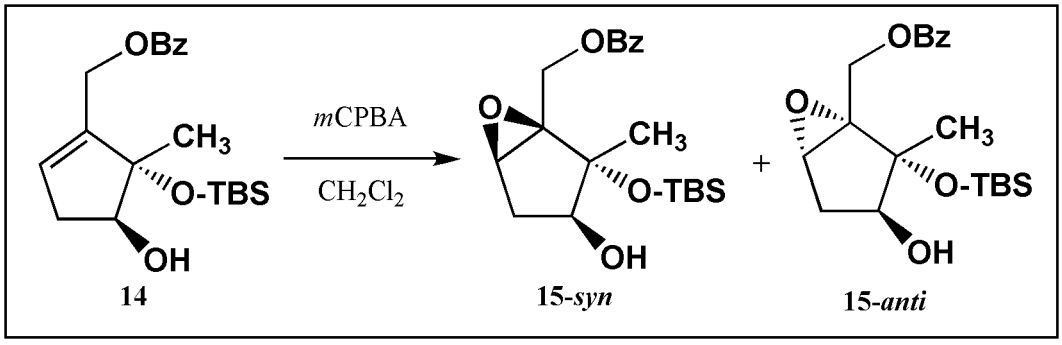
(m, 1 H), 1.73 (br s, OH), 1.59 (s, 3 H), 1.47 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 100.8, 78.3, 73.8, 64.0, 62.3, 57.9, 33.8, 30.7, 25.1, 18.3.



Compound 13. A solution of 0.4 g (1.1 mmol) of **11** in 6 mL of dry DMF was stirred at 0 °C under a nitrogen atmosphere. 2,6-Lutidine (1.28 mL, 11 mmol, 10 equiv) was added, followed by 1.52 mL (6.6 mmol, 6 equiv) of *tert*-butyldimethylsilyl trifluoromethanesulfonate. The reaction mixture was stirred for 3 h while the temperature was allowed to rise slowly to room temperature, and then was quenched by addition of 10 mL of saturated aqueous sodium bicarbonate. The mixture was extracted with EtOAc (3 × 15 mL). The combined organic layer was washed sequentially with water (3 × 10 mL) and brine (10 mL), dried with anhydrous sodium sulfate, and then concentrated. The product was purified by flash chromatography on silica, eluting with 4% ethyl acetate in hexanes (R_f = 0.3), to afford **13** as a colorless oil (0.5 g, 95% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (dd, J = 7.6 Hz, 1.6 Hz, 2 H), 7.56 (tt, J = 7.6 Hz, 1.6 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 5.65 (dd, J = 2.8 Hz, 1.2 Hz, 1 H), 4.94 – 4.83 (m, 2 H), 4.24 (t, J = 7.0 Hz, 1 H), 2.58- 2.51 (m, 1 H), 2.09 – 2.02 (m, 1 H), 1.35 (s, 3 H), 0.92 (s, 9 H), 0.87 (s, 9 H), 0.13 (s, 3 H), 0.12 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.1, 144.0, 132.8, 130.2, 129.5, 128.3, 124.1, 86.5, 82.6, 61.4, 38.2, 26.1, 26.0, 20.5, 18.3, 18.2, -1.8, -1.9, -3.5, -4.4; ESI-MS *m/z* 499 MNa^+.

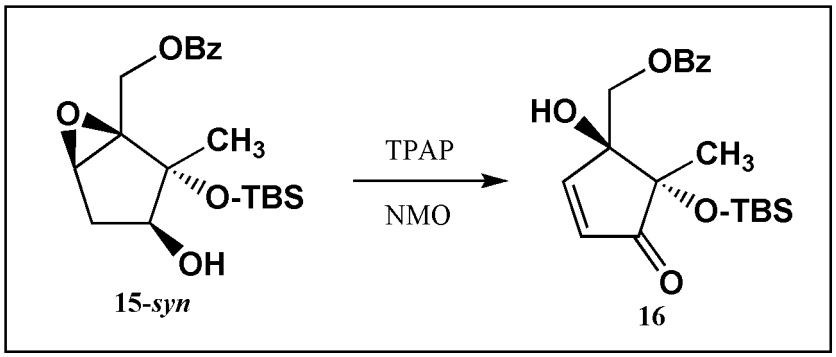


Compound 14. A solution of **13** (280 mg, 0.59 mmol) in 6 mL of dry THF was stirred at 0 °C. TBAF (0.71 mL of a 1.0 M solution in THF, 1.2 equiv) was added dropwise. The reaction mixture was allowed to stir at room temperature overnight. After concentration, the residue was partitioned between 20 mL of ethyl acetate and 10 mL of water. The organic layer was reserved, and the aqueous layer was further extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 12% ethyl acetate in hexanes (R_f = 0.25), to afford **14** as a colorless oil (0.2 g, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (dd, *J* = 7.6 Hz, 1.6 Hz, 2 H), 7.56 (tt, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 5.75 (dd, *J* = 3.0 Hz, 1.4 Hz, 1 H), 4.93 – 4.85 (m, 2 H), 4.28 (dd, *J* = 14.0 Hz, 7.2 Hz, 1 H), 2.69 – 2.63 (m, 1 H), 2.14 – 2.06 (m, 1 H), 1.70 (d, *J* = 6.0 Hz, 1 OH), 1.36 (s, 3 H), 0.88 (s, 9 H), 0.15 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.1, 144.3, 132.9, 130.1, 129.5, 128.3, 123.8, 85.5, 82.1, 61.1, 37.5, 25.9, 20.3, 18.3, -2.1, -2.3; ESI-MS *m/z* 385 MNa^+.

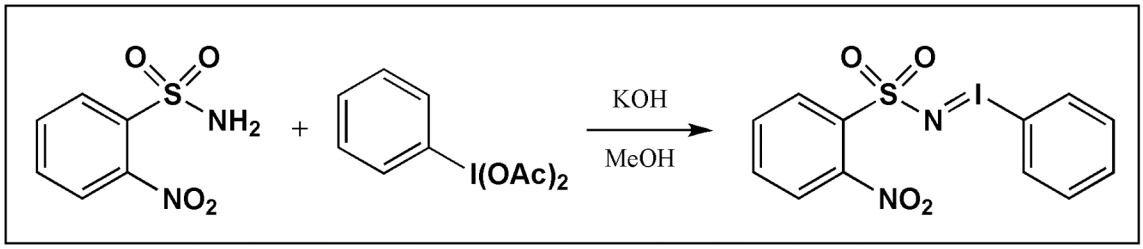


Epoxy Alcohols 15-*Syn* and 15-*Anti*. A solution of 140 mg (0.39 mmol) of **14** in 4 mL of dry dichloromethane was stirred at –20 °C. One mL (0.51 mmol, 1.3 equiv) of an

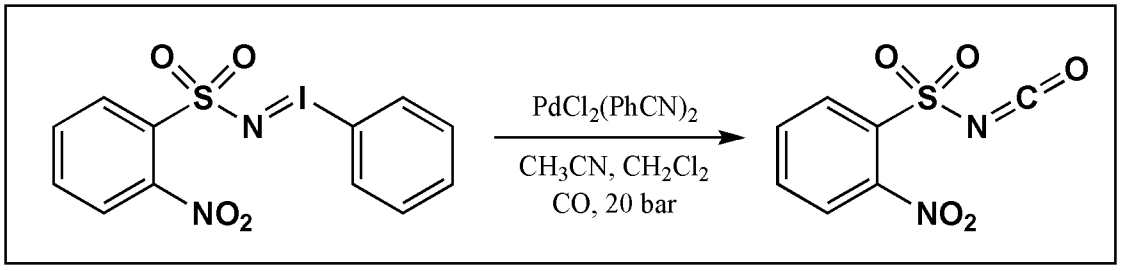
m-CPBA solution in dichloromethane (457 mg of 77% *m*-CPBA, 2.04 mmol, in 4 mL of dry dichloromethane) was added dropwise. The reaction mixture was allowed to stir at –20 °C until all the starting material was consumed, about 2.5 days. The reaction mixture was quenched with 3 mL of 10% aqueous sodium thiosulfate. The organic layer was reserved, and the aqueous layer was further extracted with dichloromethane (2 × 5 mL). The combined organic layer was washed sequentially with saturated aqueous sodium bicarbonate solution (5 mL) and brine (5 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with mixtures of ethyl acetate and hexanes. For the major product **15-*syn*** (the less polar of the two isomeric products, but a little more polar than the starting material), 10% ethyl acetate in hexanes was used to elute product (R_f = 0.20) as a colorless oil (109 mg, 74%). For the minor isomer **15-*anti*** (more polar isomer), 16% ethyl acetate in hexanes was used (R_f = 0.20, 12 mg, 8% yield). The major isomer **15-*syn***: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (dd, *J* = 7.8 Hz, 1.2 Hz, 2 H), 7.57 (tt, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 4.97 (d, *J* = 12.6 Hz, 1 H), 4.48 (d, *J* = 12.6 Hz, 1 H), 3.69 (s, 1 H), 3.66 (br, 1 H), 2.31 (dd, *J* = 14.6 Hz, 5.8 Hz, 1 H), 2.18 (br s, OH), 2.05 (d, *J* = 14.6 Hz, 1 H), 1.59 (s, 3 H), 0.86 (s, 9 H), 0.14 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.4, 133.4, 129.9 (2C), 128.7, 82.3, 78.7, 69.4, 62.0, 60.7, 35.5, 25.9, 18.8, 18.2, -2.0, -2.2; ESI-MS *m/z* 379 MH^+. The minor isomer **15-*anti***: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, *J* = 6.4 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 4.82 (d, *J* = 13.2 Hz, 1 H), 4.60 (d, *J* = 12.4 Hz, 1 H), 4.01 (q, *J* = 6.8 Hz, 1 H), 3.49 (s, 1 H), 2.47 (dd, *J* = 14.0 Hz, 7.2 Hz, 1 H), 1.57 (d, *J* = 5.6 Hz, OH), 1.53 (dd, *J* = 14.0 Hz, *J* = 8.8 Hz, 1 H), 1.32 (s, 3 H), 0.89 (s, 9 H), 0.16 (s, 3 H), 0.15 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.0, 133.1, 129.60, 129.56, 128.3, 81.7, 75.3, 66.7, 60.3, 57.0, 33.6, 25.9, 18.8, 18.3, -2.2, -2.4; ESI-MS *m/z* 379 MH^+, 401 MNa^+.



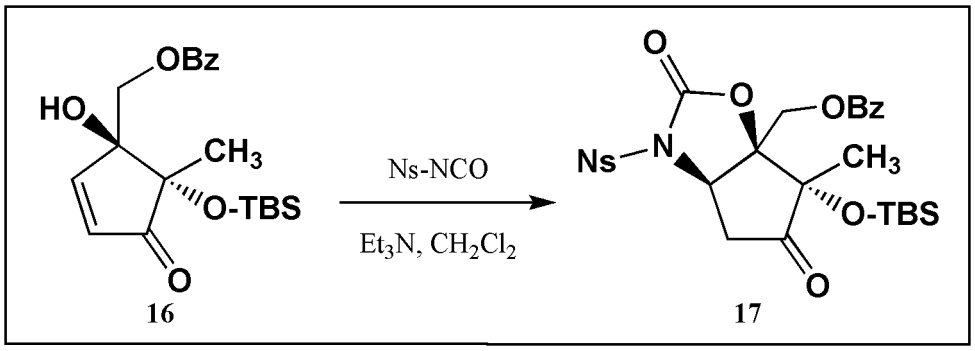
Compound 16. A solution of 250 mg (0.66 mmol) of **15-*syn*** in 15 mL of dichloromethane was treated with 4-methylmorpholine-N-oxide (NMO, 155 mg, 1.32 mmol, 2.0 equiv) in one portion, followed by a catalytic amount of tetra-*n*-propylammonium perruthenate (TPAP, 46 mg, 0.13 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature for 2 h. During this period, the starting material was consumed and two products were formed, according to TLC analysis: one less polar than the starting material, and one more polar. Hexanes (15 mL) was added to the reaction mixture, and the mixture was filtered through a Celite pad, washing with 15 mL of 1:1 dichloromethane / hexanes. The combined filtrate was concentrated. TLC analysis indicated that the less polar spot, presumably the epoxy ketone, had disappeared. The crude product was purified by flash chromatography on silica, eluting with 16% ethyl acetate in hexanes, to afford **16** (R_f = 0.20) as a white solid (216 mg, 87% yield), mp 114 – 116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 8.0 Hz, 2 H), 7.58 (t, J = 7.4 Hz, 1 H), 7.45 (t, J = 7.8 Hz, 2 H), 7.37 (d, J = 6.8 Hz, 1 H), 6.29 (d, J = 5.6 Hz, 1 H), 4.77 (d, J = 11.6 Hz, 1 H), 4.24 (d, J = 12.0 Hz, 1 H), 2.94 (br s, OH), 1.40 (s, 3 H), 0.88 (s, 9 H), 0.28 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 206.0, 167.3, 160.1, 133.7, 132.4, 130.0, 129.6, 128.8, 84.1, 82.4, 69.6, 26.1, 22.7, 18.7, -2.0, -2.6; IR (neat) 3460, 1727 cm^{-1}; ESI-MS *m/z* 399 MNa^+; FAB-HRMS calcd for $C_{20}H_{29}O_5Si$ 377.1784, found 377.1776.



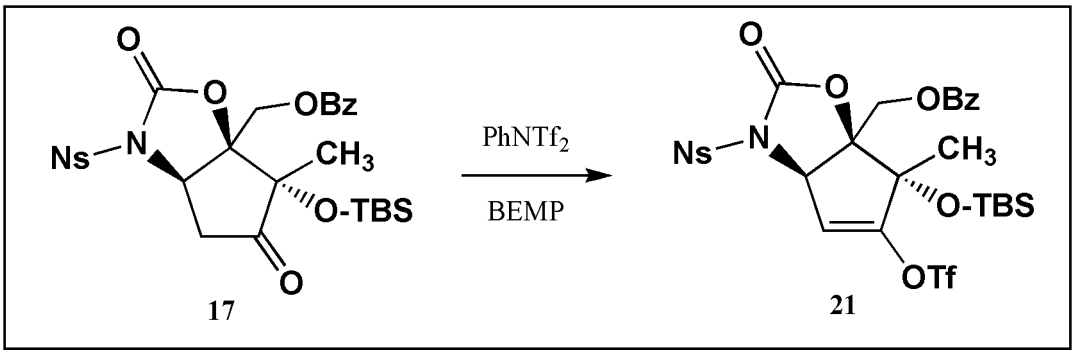
[*N*-(2-nitrophenylsulfonyl)imino]phenyliodinane. Iodobenzene diacetate (6.44 g, 20.0 mmol) was added to a stirred mixture of potassium hydroxide (2.81 g, 50.0 mmol, 2.5 equiv) and 2-nitrobenzenesulfonamide (4.04 g, 20 mmol, 1.0 equiv) in 80 mL of dry methanol, while keeping the temperature at 0 °C. The reaction mixture was allowed to stir overnight. The supernatant was filtered, washed with distilled water, and then dried at room temperature in a vacuum desiccator for 2 days to afford 5.09 g (63% yield) of the product as a white powder, mp 130–132 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 1 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.44 – 7.36 (m, 2 H), 7.27 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 147.5, 137.1, 133.9, 131.9, 131.4, 131.2, 130.7, 129.7, 123.3, 117.5; ESI-MS: 405 MH^+.



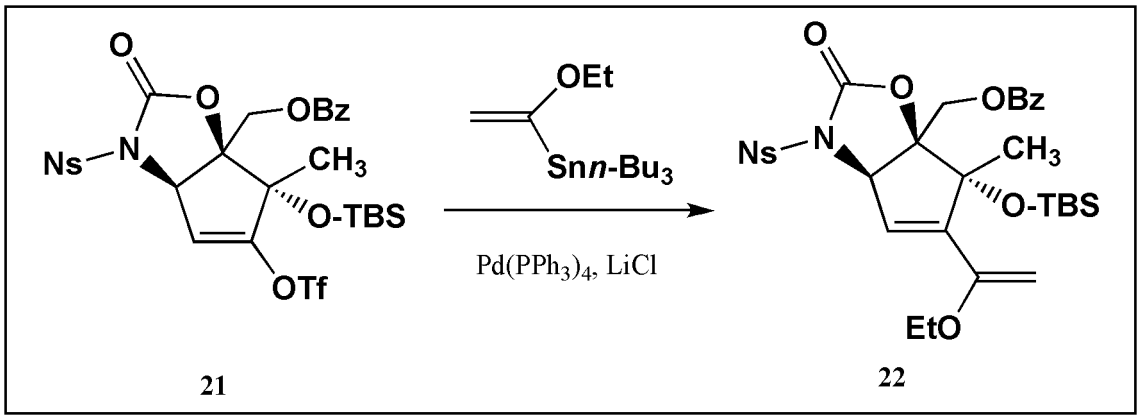
2-Nitrobenzenesulfonylisocyanate Stock Solution. A 45 mL stainless steel Parr reactor was charged with 5.4 g (13.4 mmol) of [*N*-(2-nitrophenylsulfonyl)imino]phenyliodinane, 134 mg (0.35 mmol, 0.025 equiv) of bis(benzonitrile)palladium (II) chloride, 20 mL of dry dichloromethane, and 0.2 mL of dry acetonitrile. The reactor was pressurized to 20 bar with carbon monoxide and stirred for 2.5 days at room temperature. The tea-brown-colored liquid was transferred to a 50 mL flask for use as a stock solution of (moisture sensitive) 2-nitrobenzenesulfonyl isocyanate.



Compound 17. A solution of **16** (20 mg, 0.053 mmol) in 1 mL of dry dichloromethane was stirred at 0 °C. 2-Nitrobenzenesulfonyl isocyanate stock solution (0.3 mL, prepared as above) was added, followed by 15 uL (0.106 mmol, 2.0 equiv) of triethylamine. The reaction mixture was allowed to stir at room temperature overnight. Dichloromethane (10 mL) was added to the solution, which was then cooled to 0 °C and quenched with 2 ml of saturated aqueous ammonium chloride. The organic layer was reserved, and the aqueous layer was further extracted with dichloromethane (2 × 4 mL). The combined organic extract was washed with brine (4 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 20% ethyl acetate in hexanes (R_f = 0.25), to provide **17** as a white solid (29 mg, 90% yield), mp 69–71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (dd, *J* = 7.4 Hz, 1.2 Hz, 1 H), 7.80 – 7.67 (m, 4 H), 7.47 – 7.43 (m, 2 H), 7.22 – 7.18 (m, 2 H), 5.07 (dd, *J* = 9.6 Hz, 2.8 Hz, 1 H), 5.05 (d, *J* = 12.4 Hz, 1 H), 4.57 (d, *J* = 12.4 Hz, 1 H), 3.37 (dd, *J* = 19.6 Hz, 9.6 Hz, 1 H), 2.80 (dd, *J* = 19.4 Hz, 2.6 Hz, 1 H), 1.54 (s, 3 H), 0.90 (s, 9 H), 0.18 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 207.2, 165.2, 149.9, 147.5, 135.6, 134.5, 132.9, 132.2, 130.0, 129.2, 129.0, 128.4, 124.5, 87.6, 79.8, 63.6, 58.0, 41.9, 25.7, 18.3, 16.0, -2.2, -3.6; IR (neat) 1798, 1766, 1729, 1546 cm^{-1}; ESI-MS *m/z* 627 MNa^+; FAB-HRMS calcd for $C_{27}H_{33}O_{10}SSi$ 605.1625, found 605.1598.

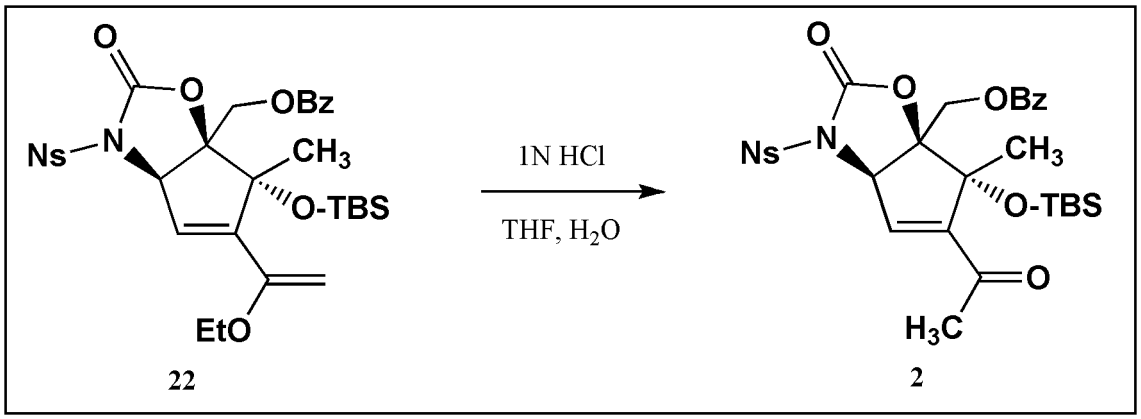


Compound 21. A solution of 86 mg (0.142 mmol) of **17** and 152 mg (0.426 mmol, 3.0 equiv) of *N*-phenyl-bis(trifluoromethanesulfonimide) in 3 mL of dry THF was stirred at 0 °C. 2-*tert*-Butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (BEMP, 82 uL, 0.284 mmol, 2.0 equiv) was added slowly. The reaction mixture was allowed to stir at room temperature overnight, cooled to 0 °C, and then was quenched by addition of 3 mL of brine. Following extraction with ethyl acetate (3 × 10 mL), the combined organic layer was washed with brine (5 mL), dried with anhydrous sodium sulfate, and then concentrated. The crude product was purified by flash chromatography on silica, eluting with 20% ethyl acetate in hexanes (R_f = 0.25), to provide **21** as a white solid (105 mg, quantitative yield), mp 152–154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (d, J = 8.4 Hz, 1 H), 7.80 – 7.65 (m, 4 H), 7.45 – 7.37 (m, 2 H), 7.16 – 7.12 (m, 2 H), 6.15 (d, J = 2.0 Hz, 1 H), 5.49 (d, J = 1.6 Hz, 1 H), 5.00 (d, J = 13.2 Hz, 1 H), 4.45 (d, J = 12.4 Hz, 1 H), 1.65 (s, 3 H), 0.92 (s, 9 H), 0.21 (s, 6 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 165.2, 154.1, 149.6, 147.5, 135.5, 134.3, 132.8, 132.2, 130.1, 129.2, 129.0, 128.3, 124.4, 119.9, 116.8, 112.4, 87.7, 83.7, 64.04, 63.99, 25.7, 20.2, 18.4, -2.2, -2.7; IR (neat) 1797, 1731, 1658 , 1547 cm^{-1}; ESI-MS *m/z* 759 MNa^+; FAB-HRMS calcd for $C_{28}H_{32}F_3N_2O_{12}S_2Si$ 737.1118, found 737.1102.



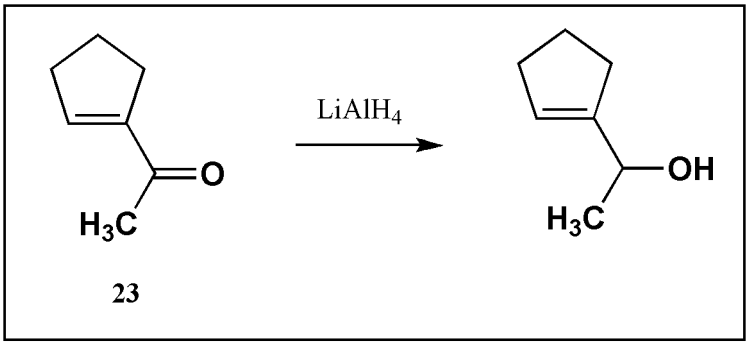
21 22

Compound 22. A solution of **21** (20 mg, 0.027 mmol), lithium chloride (2.3 mg, 0.054 mmol, 2.0 equiv), tetrakis(triphenylphosphine)palladium (3.1 mg, 0.0027 mmol, 0.1 equiv), and tri-*n*-butyl(1-ethoxy-vinyl)tin (64 *u*L, 0.189 mmol, 7.0 equiv) in 0.5 mL of THF was stirred at room temperature for 1 h, then was heated at reflux for 18 h. The black suspension was cooled to room temperature, diluted with 10 mL of ethyl acetate, filtered, and then washed sequentially with brine (10 mL) and 5% aqueous ammonium hydroxide (2 mL). The organic solution was dried over anhydrous sodium sulfate, and then concentrated. The product was purified by using preparative silica TLC, eluting with 26% ethyl acetate in hexanes, to give **22** as a white solid (13 mg, 73% yield), mp 96–98 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (d, *J* = 6.4 Hz, 1 H), 7.75 (t, *J* = 7.4 Hz, 1 H), 7.64 – 7.61 (m, 3 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 2 H), 6.29 (d, *J* = 1.6 Hz, 1 H), 5.39 (d, *J* = 2.4 Hz, 1 H), 5.01 (d, *J* = 12.4 Hz, 1 H), 4.49 (d, *J* = 2.4 Hz, 1 H), 4.45 (d, *J* = 12.4 Hz, 1 H), 4.24 (d, *J* = 2.4 Hz, 1 H), 3.79 (q, *J* = 7.2 Hz, 2 H), 1.75 (s, 3 H), 1.37 (t, *J* = 7.0 Hz, 3 H), 0.90 (s, 9 H), 0.16 (s, 3 H); 0.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 165.4, 155.3, 150.4, 148.6, 147.5, 135.1, 134.2, 132.5, 131.9, 130.5, 129.4, 129.1, 128.2, 127.4, 124.2, 91.4, 88.0, 86.9, 66.6, 64.4, 63.2, 26.0, 22.9, 18.6, 14.6, -2.1, -2.3; ESI-MS *m/z* 631 MH^+, 681 MNa^+.



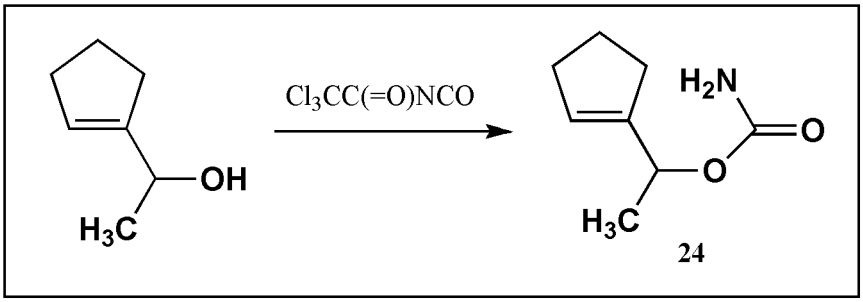
22 2

Compound 2. A mixture of **22** (10 mg, 0.0152 mmol), 0.5 mL of THF, and 0.15 mL of 1 N hydrochloric acid was stirred at room temperature for 3 h, then partitioned between 5 mL of ethyl acetate and 1 mL of water. The organic layer was dried with anhydrous sodium sulfate, and then concentrated. The product was purified by flash chromatography on silica, eluting with 15% ethyl acetate in hexanes (R_f = 0.2), to afford **2** as a white solid (8 mg, 83% yield), mp 112–114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (dd, J = 8.2 Hz, 1.4 Hz, 1 H), 7.78 – 7.74 (m, 1 H), 7.65 – 7.60 (m, 3 H), 7.42 – 7.38 (m, 1 H), 7.32 – 7.29 (m, 1 H), 7.12 – 7.08 (m, 2 H), 6.90 (d, J = 2.0 Hz, 1 H), 5.54 (d, J = 1.6 Hz, 1 H), 5.13 (d, J = 13.2 Hz, 1 H), 4.41 (d, J = 12.4 Hz, 1 H), 2.45 (s, 3 H), 1.81 (s, 3 H), 0.88 (s, 9 H), 0.22 (s, 3 H); 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 195.5, 165.3, 149.9, 148.6, 139.0, 135.5, 134.2, 132.6, 132.1, 130.1, 129.2, 129.1, 128.3, 124.3, 91.2, 86.5, 66.8, 64.3, 29.9, 28.8, 25.9, 21.2, 18.6, -2.2, -2.8; IR (neat) 1791, 1728, 1688, 1546 cm^{-1}; ESI-MS m/z 631 MH^+, 653 MNa^+; FAB-HRMS calcd for $C_{29}H_{35}N_2O_{10}SSi$ 631.1782, found 631.1782.

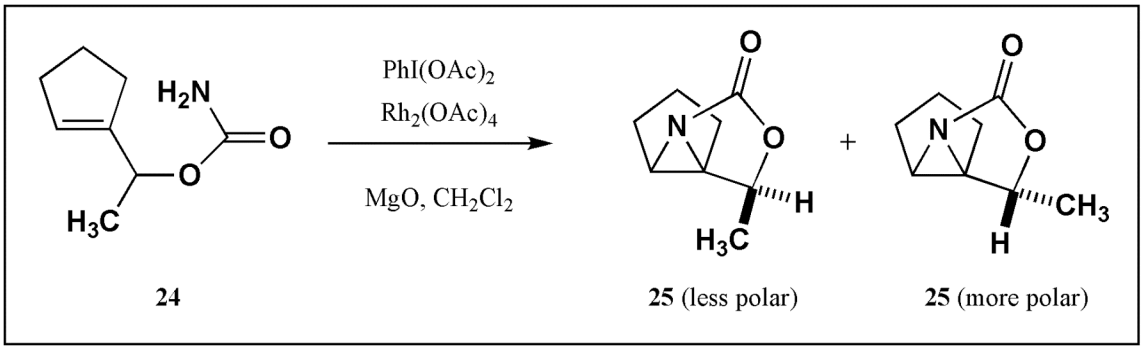


23

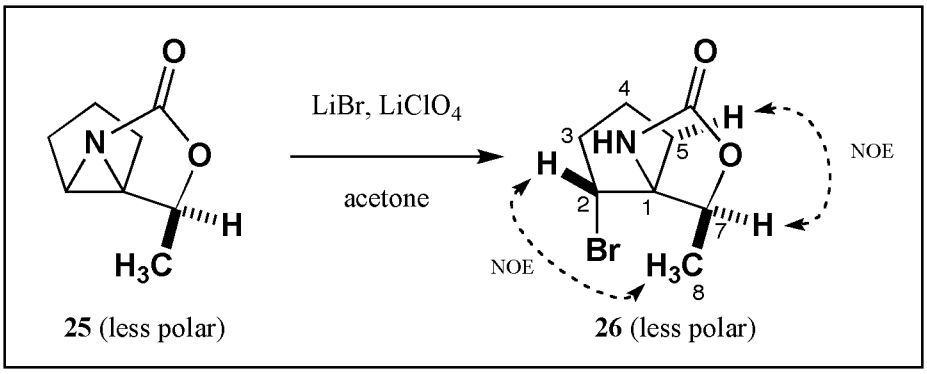
1-(1-Hydroxyethyl)cyclopentene. A solution of 5.00 g (45.4 mmol) of 1-acetylcyclopentene (**23**) in 20 mL of diethyl ether was added dropwise over a 20 min period to a stirred solution of 12.5 mL of lithium aluminum hydride (1.0 N in diethyl ether, 12.5 mmol, 0.275 equiv) in 35 mL of diethyl ether at 0 °C under a nitrogen atmosphere. The reaction mixture was allowed to stir overnight at 23 °C, was cooled to 0 °C, and then was quenched by dropwise addition of 3 mL of water. The mixture was poured into 20 mL of 1 N aq hydrochloric acid, which in turn was extracted with diethyl ether (3 X 30 mL). The combined organic extract was washed with water (30 mL) and brine (30 mL), dried over anhydrous magnesium sulfate, and then concentrated. The crude product was chromatographed on silica with ethyl acetate / hexanes as the eluant to provide 4.5 g (88%) of the racemic carbinol as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) ẟ 5.58 (br s, 1 H), 4.41 (q, *J* = 6.4 Hz, 1 H), 2.32 (t, *J* = 7.6 Hz, 4 H), 1.89 (quint, *J* = 7.6 Hz, 2 H), 1.59 (br s, OH), 1.30 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) ẟ 148.2, 124.1, 67.3, 32.3, 31.5, 23.5, 22.2.



Carbamic acid (1-cyclopentenyl)-1-ethyl ester (24). Trichloroacetylisocyanate (0.64 mL, 5.4 mmol) was added to a solution of 0.30 g (2.7 mmol) of the carbinol in 15 mL of dry dichloromethane. After 3 h, 15 mL of methanol and 2.0 g of potassium carbonate were added. The mixture was stirred at room temperature overnight, filtered through a Celite pad, and then extracted into dichloromethane (2 X 10 mL). The organic extract was concentrated and then chromatographed on silica with ethyl acetate / hexanes as the eluant to provide 0.38 g (91%) of **24** as a white solid, mp 63–64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.61 (d, J = 1.6 Hz, 1 H), 5.35 (q, J = 6.4 Hz, 1 H), 4.87 (br s, 2 NH), 2.34 – 2.27 (m, 4 H), 1.91 – 1.84 (m, 2 H), 1.33 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 156.6, 144.0, 126.0, 70.2, 32.4, 31.9, 23.3, 19.5; IR (neat) 3429, 3266, 3211, 1684 cm^{-1}; ESI-MS *m/z* 178 MNa^{+}.

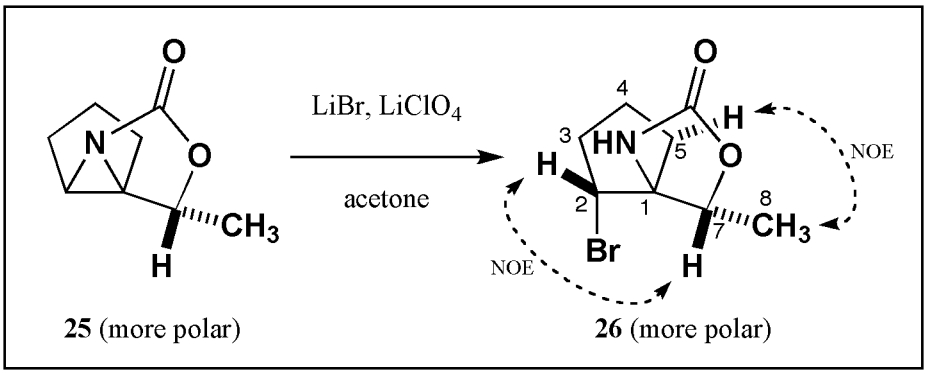


***N*-Acyl-aziridines 25.** A mixture of 0.12 g (0.77 mmol) of carbamate **24**, 161 mg (4.0 mmol) of activated MgO, 386 mg (1.2 mmol) of $PhI(OAc)_2$, 35 mg (0.08 mmol) of $Rh_2(OAc)_4$, and 6 mL of dry dichloromethane was heated at 40 °C for 12 h in a sealed tube. The reaction mixture was cooled, filtered through Celite, and then rinsed with dichloromethane (2 x 5 mL). The combined extract was concentrated and then chromatographed on silica with 30% ethyl acetate in hexanes as the eluant to give 45 mg (38%) of the less polar isomer **25**, mp 60–61 °C, and 38 mg (32%) of the more polar isomer **25**, mp 60–62 °C. Data for **25** (less polar): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.82 (q, J = 6.2 Hz, 1 H), 3.01 (d, J = 1.6 Hz, 1 H), 2.18 – 2.13 (m, 1 H), 2.04 – 1.99 (m, 1 H), 1.83 – 1.68 (m, 3 H), 1.54 – 1.48 (m, 1 H), 1.46 (d, J = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.3, 74.6, 61.1, 50.8, 27.7, 26.5, 19.9, 17.4; IR (neat) 1767 cm^{-1}; ESI-MS m/z 154 MH$^+$. Data for **25** (more polar): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88 (q, J = 6.2 Hz, 1 H), 2.96 (d, J = 2.8 Hz, 1 H), 2.18 – 2.06 (m, 2 H), 1.84 – 1.67 (m, 3 H), 1.51 – 1.44 (m, 1 H), 1.48 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.5, 74.5, 60.0, 53.4, 27.8, 25.2, 20.1, 19.5; IR (neat) 1768 cm^{-1}; ESI-MS m/z 154 MH$^+$.

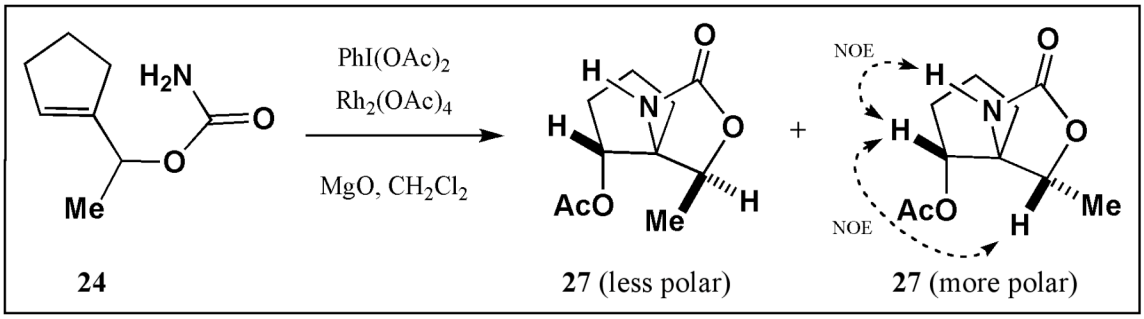


Bromo Oxazolidinone 26 (less polar). A solution of 40 mg (0.26 mmol) of **25** (less polar isomer), 95 mg (1.1 mmol) of lithium bromide, and 4 mg of lithium

perchlorate in 3 mL of dry acetone was stirred at 23 °C overnight, concentrated, and then chromatographed on silica with 40% ethyl acetate in hexanes as the eluant to afford 48 mg (79%) of **26** (less polar isomer), mp 121–123 °C: ^{1}H NMR ($CDCl_3$, 400 MHz, stereochemistry from NOESY) δ 7.23 (br s, NH), 4.54 (q, J = 6.0 Hz, H-7), 4.17 (d, J = 4.4 Hz, H-2), 2.39 – 2.22 (m, 3 H), 2.12 – 1.87 (m, 3 H), 1.59 (d, J = 5.6 Hz, H-8); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 159.4, 80.6, 72.7, 54.0, 35.2, 34.7, 18.9, 16.6; IR (neat) 3251, 3131, 1747 cm^{-1}; ESI-MS *m/z* 234 and 236 MH^+.

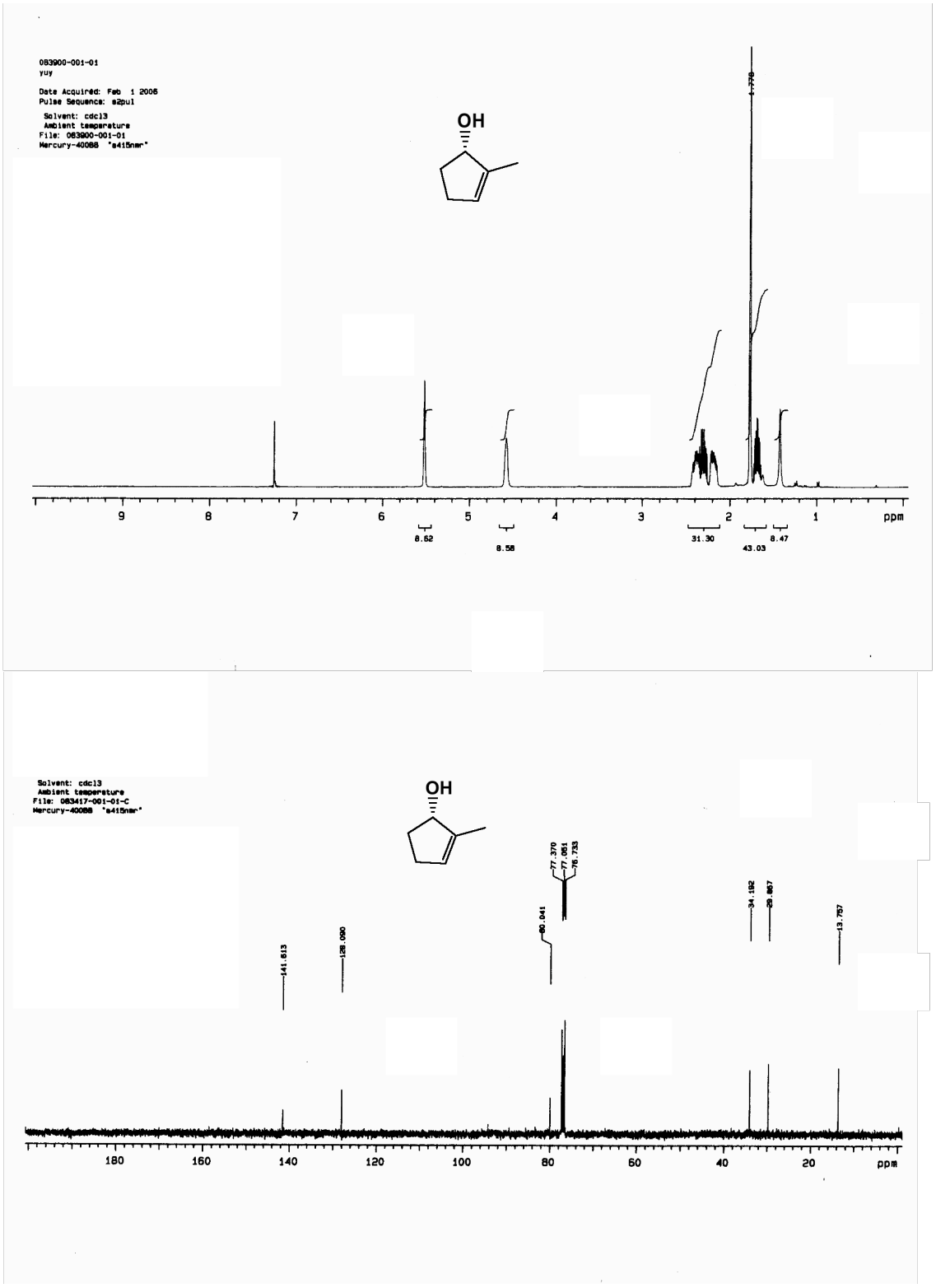


Bromo Oxazolidinone 26 (more polar). A 34 mg sample (0.22 mmol) of **25** (more polar isomer) was treated with lithium bromide and a catalytic amount of $LiClO_4$ as above. Chromatography afforded 43 mg (84%) of **26** (more polar isomer), mp 108–109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, stereochemistry from NOESY) δ 6.76 (br s, NH), 4.94 (q, J = 6.4 Hz, H-7), 4.22 (d, J = 5.2 Hz, H-2), 2.44 – 2.34 (m, 1 H), 2.30 – 2.17 (m, 2 H), 2.04 – 1.93 (m, 1 H), 1.90 – 1.72 (m, 2 H), 1.43 (d, J = 6.4 Hz, H-8); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 158.0, 78.7, 71.6, 59.7, 33.3, 29.2, 19.4, 17.9; IR (neat) 3212, 3133, 1748 cm^{-1}; ESI-MS *m/z* 234 and 236 MH^+.

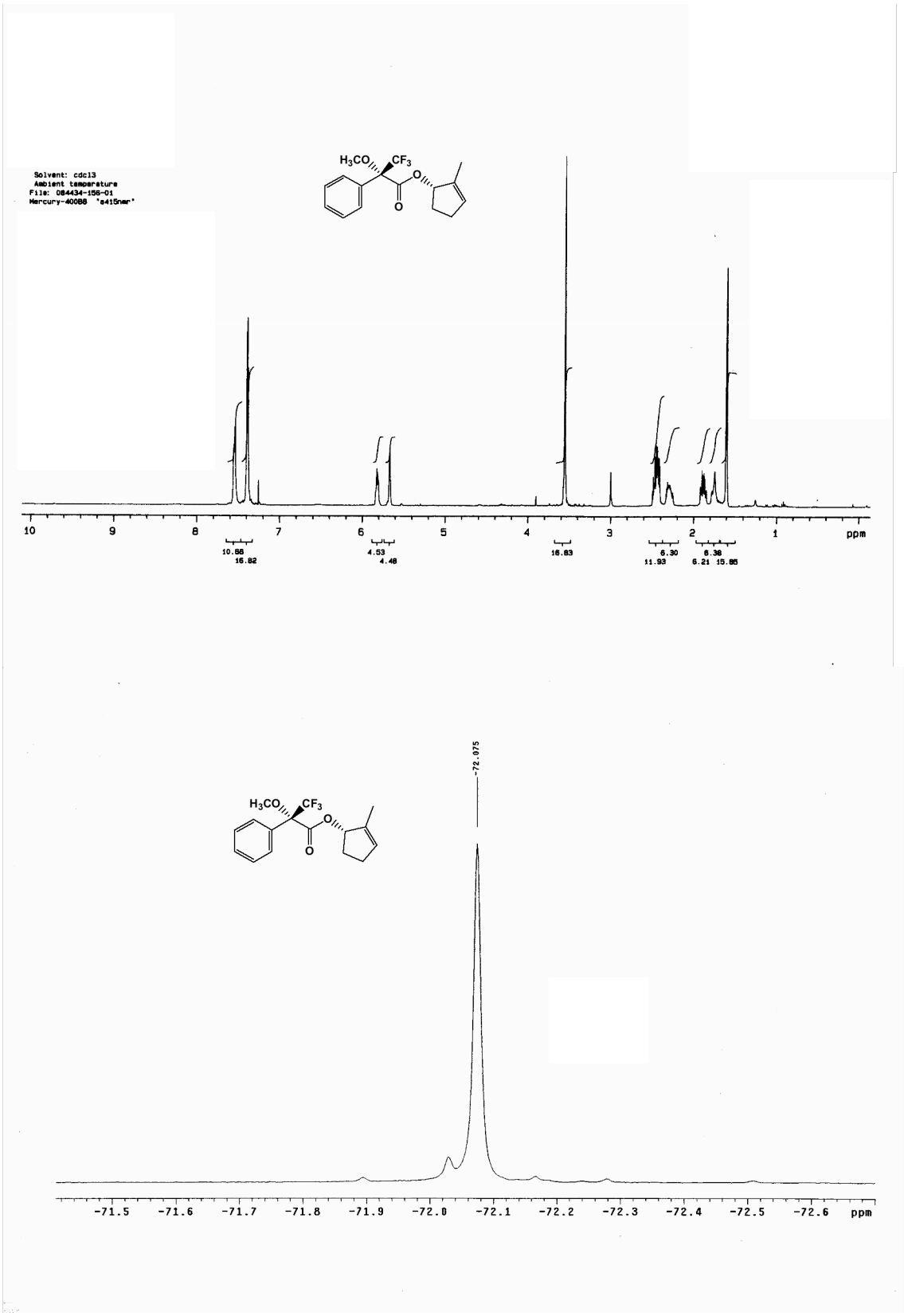


Acetoxy Oxazolidinones 27. A mixture of 0.12 g (0.77 mmol) of carbamate **24** (0.12 g, 0.77 mmol), 161 mg (4.0 mmol) of activated MgO, 386 mg (1.2 mmol) of $PhI(OAc)_2$, 35 mg (0.08 mmol) of $PhI(OAc)_2$, and 4 mL of dry dichloromethane was heated at 90 °C in a sealed tube for 4 days. The reaction mixture cooled, filtered through Celite, and then rinsed with dichloromethane (3 x 10 mL). The combined organic extract was concentrated and then chromatographed on silica with 40% ethyl acetate in hexanes as the eluant to give 51 mg (31%) of the less polar isomer **27**, mp 98–100 °C, and 66 mg (40%) of the more polar isomer **27** (structure based on NOE crosspeaks; see structure above), mp 99–101 °C. The more polar isomer of **27** forms somewhat faster than the less polar isomer under these conditions. Data for **27** (less polar isomer): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.92 (br s, NH), 5.03 (d, J = 4.4 Hz, 1 H), 4.59 (q, J = 6.4 Hz, 1 H), 2.05 (s, 3 H), 2.07 – 1.96 (m, 3 H), 1.86 – 1.78 (m, 3 H), 1.39 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 169.4, 158.8, 79.3, 78.0, 69.9, 35.9, 30.0, 21.4, 18.7, 16.7; IR (neat) 3259, 1751 cm^{-1}; ESI-MS *m/z* 214 MH^+. Data for **27** (more polar isomer): ^{1}H NMR ($CDCl_3$, 400 MHz, stereochemistry by NOESY) δ 6.88 (br s, NH), 4.97 (dd, J = 5.6, 2.8 Hz, 1 H), 4.72 (q, J = 6.4 Hz, 1 H), 2.20 – 2.11 (m, 1 H), 2.06 (s, 3 H), 1.98 – 1.91 (m, 1 H), 1.82 – 1.63 (m, 4 H), 1.38 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ170.2,

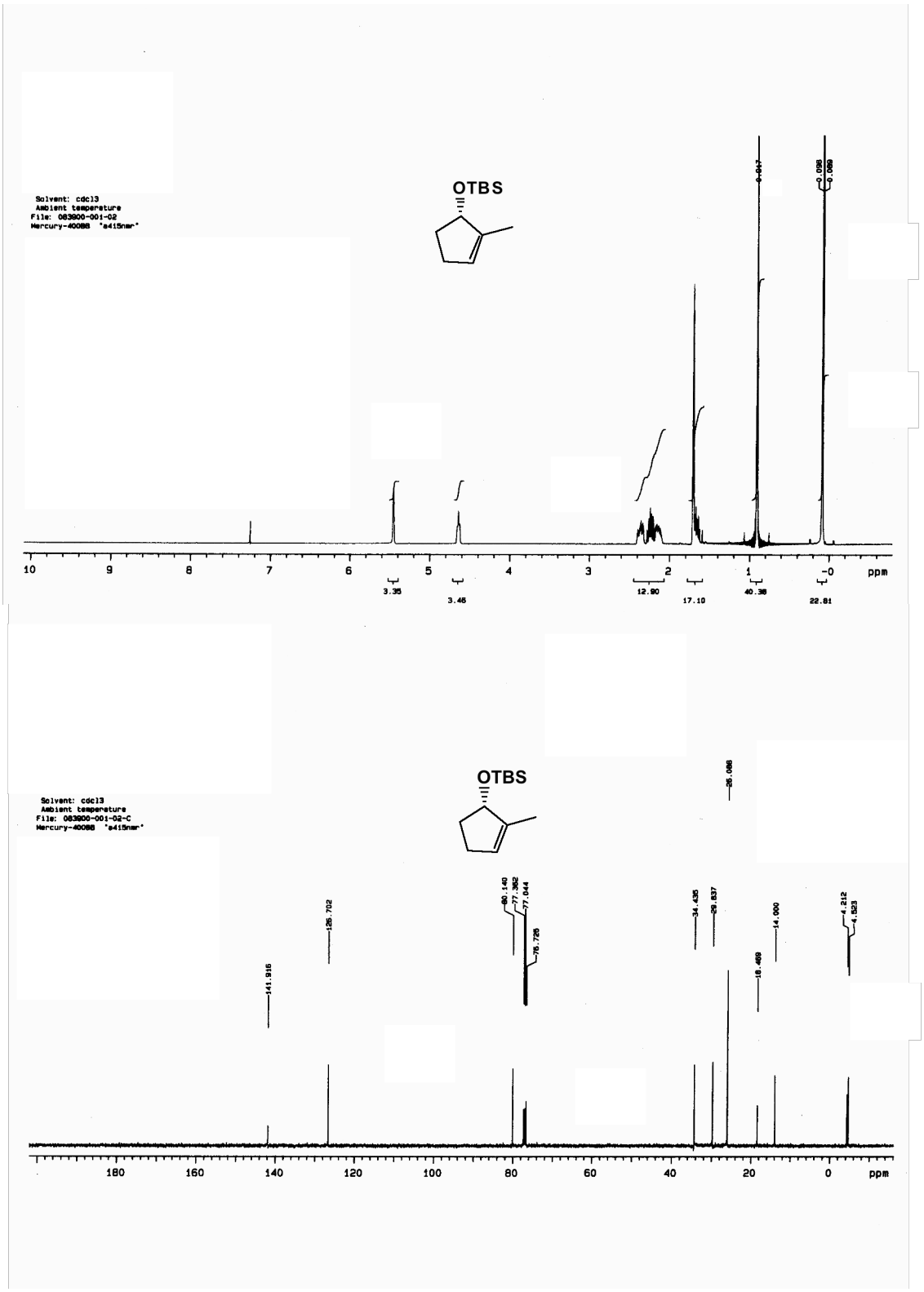
159.1, 80.5, 76.2, 70.0, 30.2, 29.3, 21.3, 19.5, 17.4; IR (neat) 3260, 1749 cm^{-1}; ESI-MS *m/z* 214 MH^+.



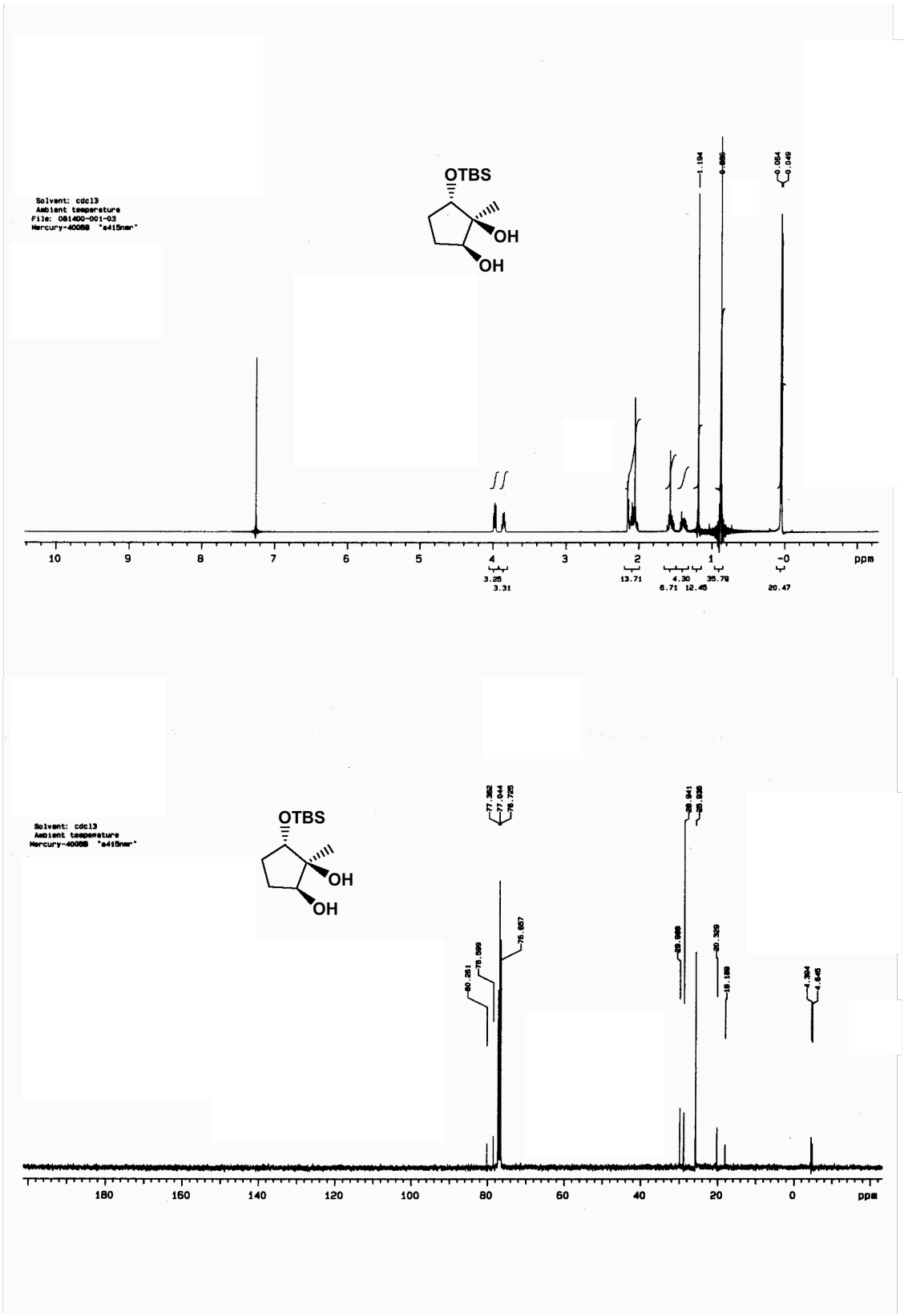
^{1}H and ^{13}C NMR spectra of **4** ($CDCl_3$)



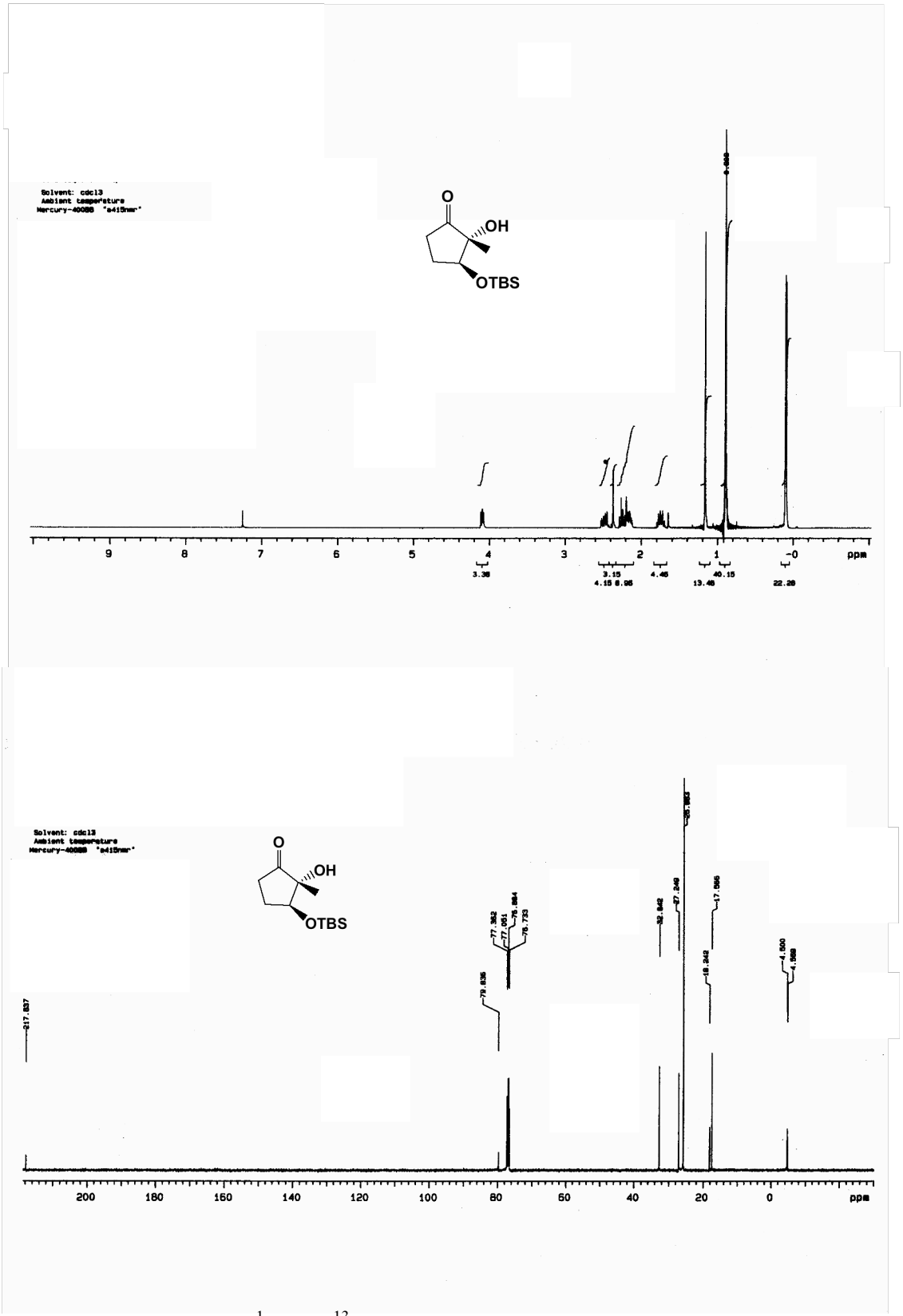
^{1}H and ^{19}F NMR spectra of the crude Mosher ester of **4** ($CDCl_3$)



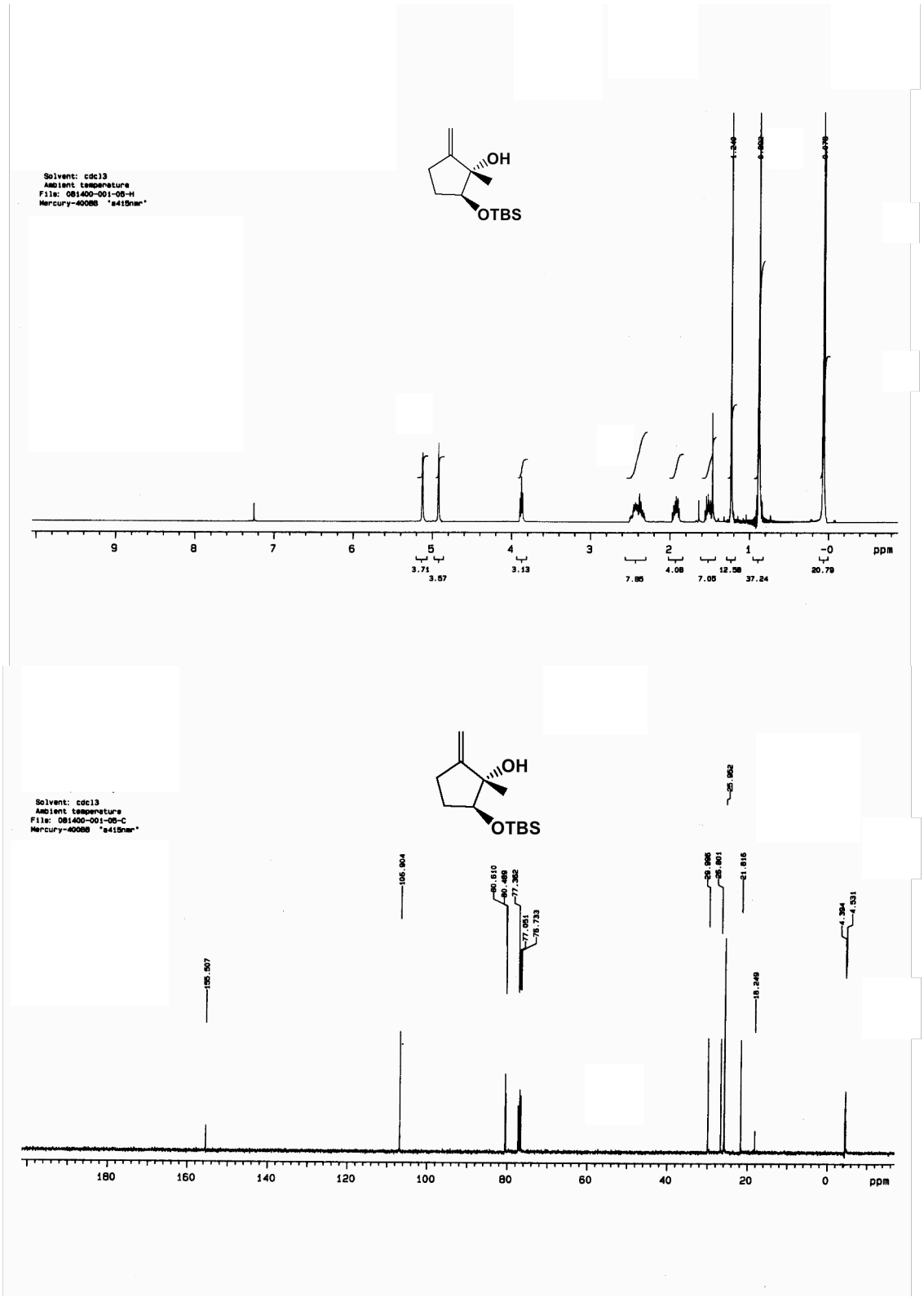
^{1}H and ^{13}C NMR spectra of **5** ($CDCl_3$)



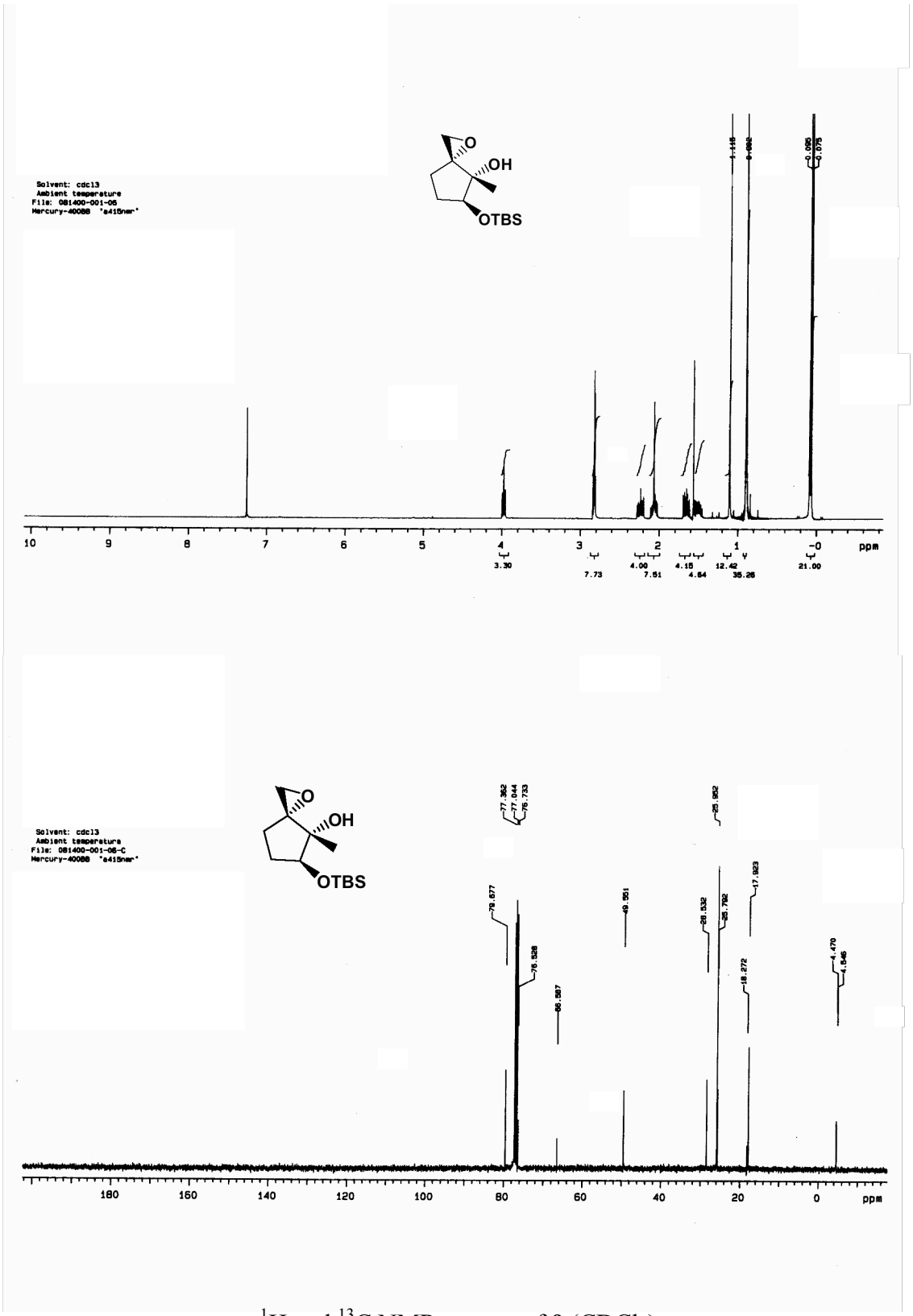
^{1}H and ^{13}C NMR spectra of **6** ($CDCl_3$)



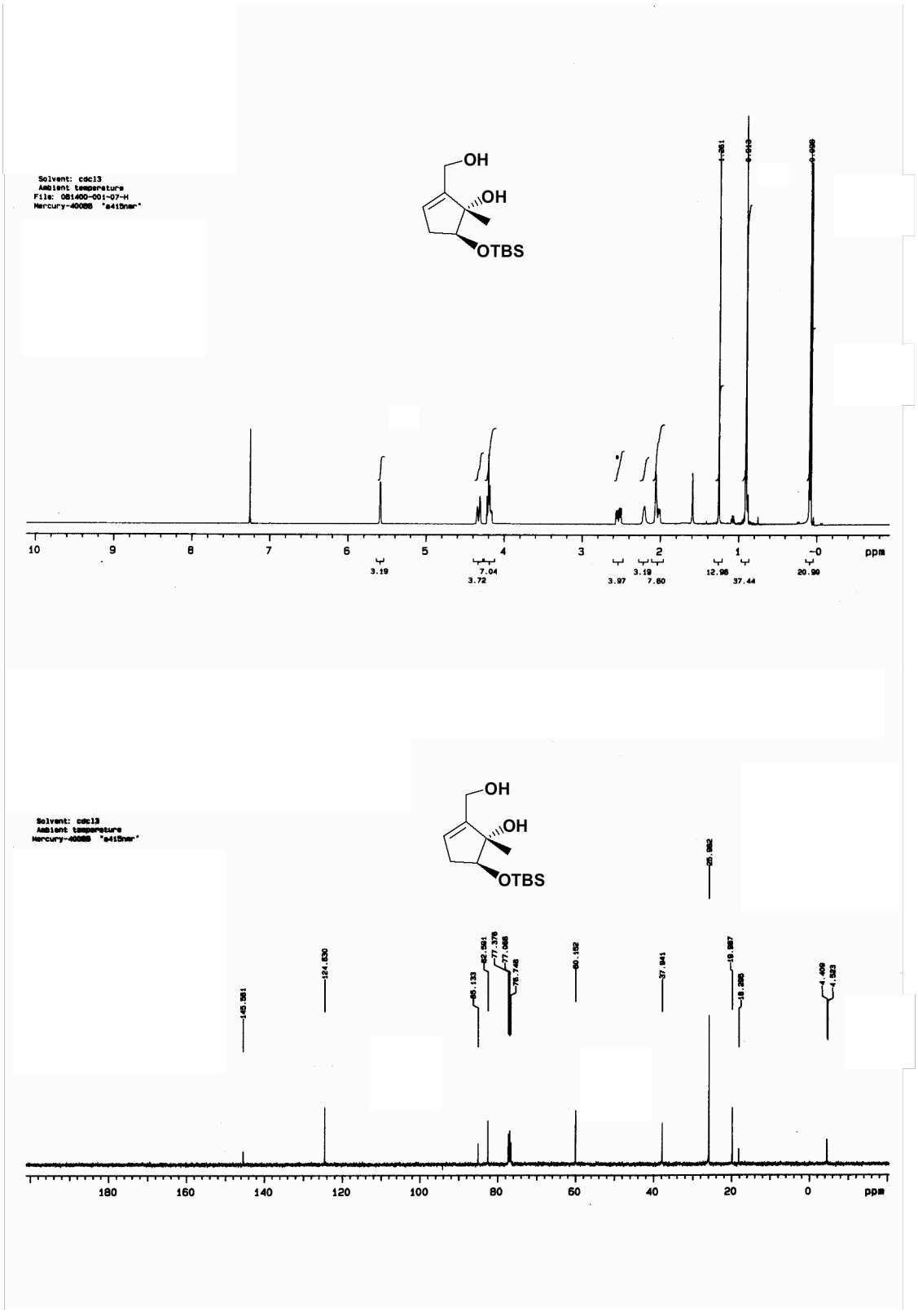
^{1}H and ^{13}C NMR spectra of **7** ($CDCl_3$)



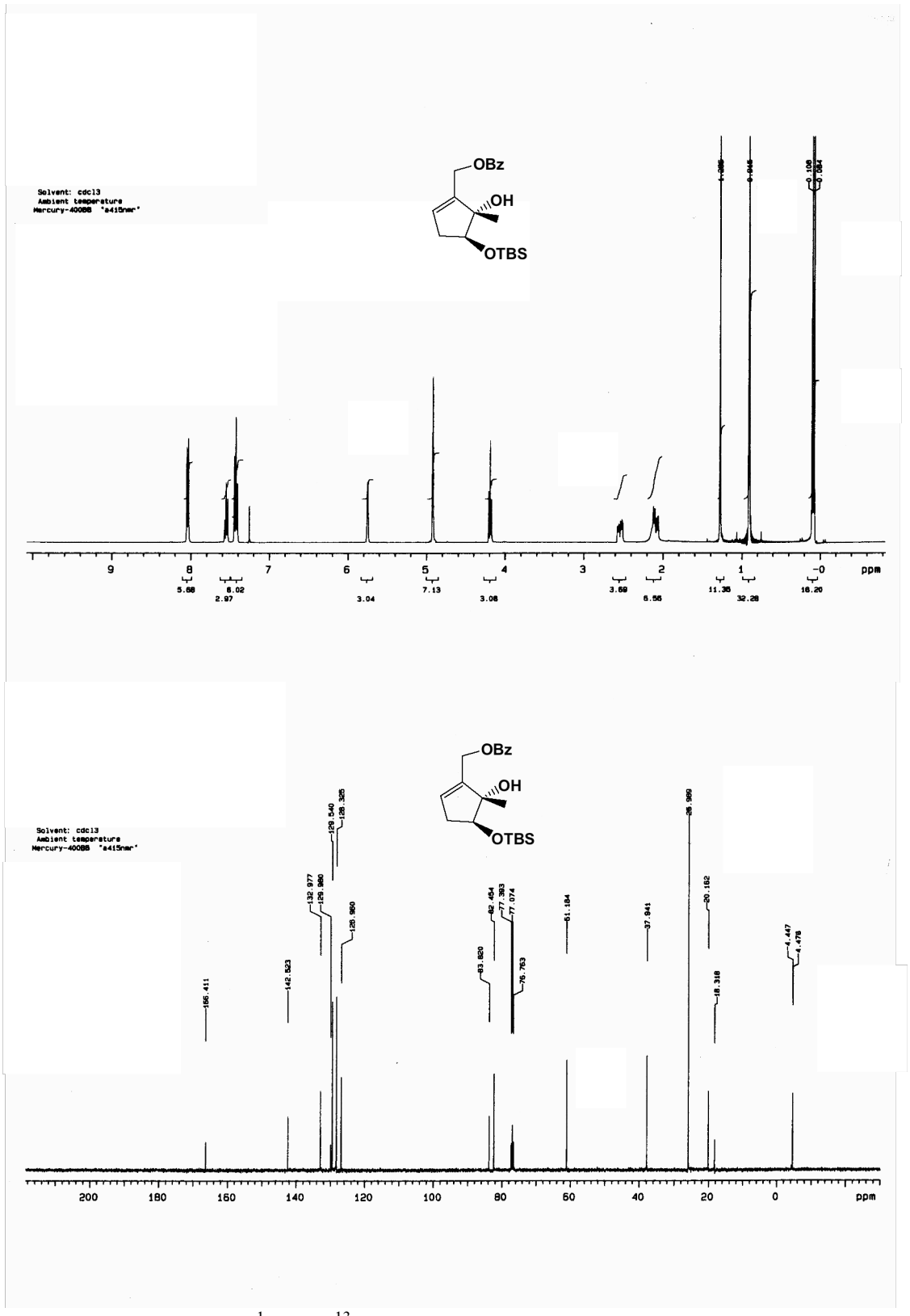
^{1}H and ^{13}C NMR spectra of **8** ($CDCl_3$)



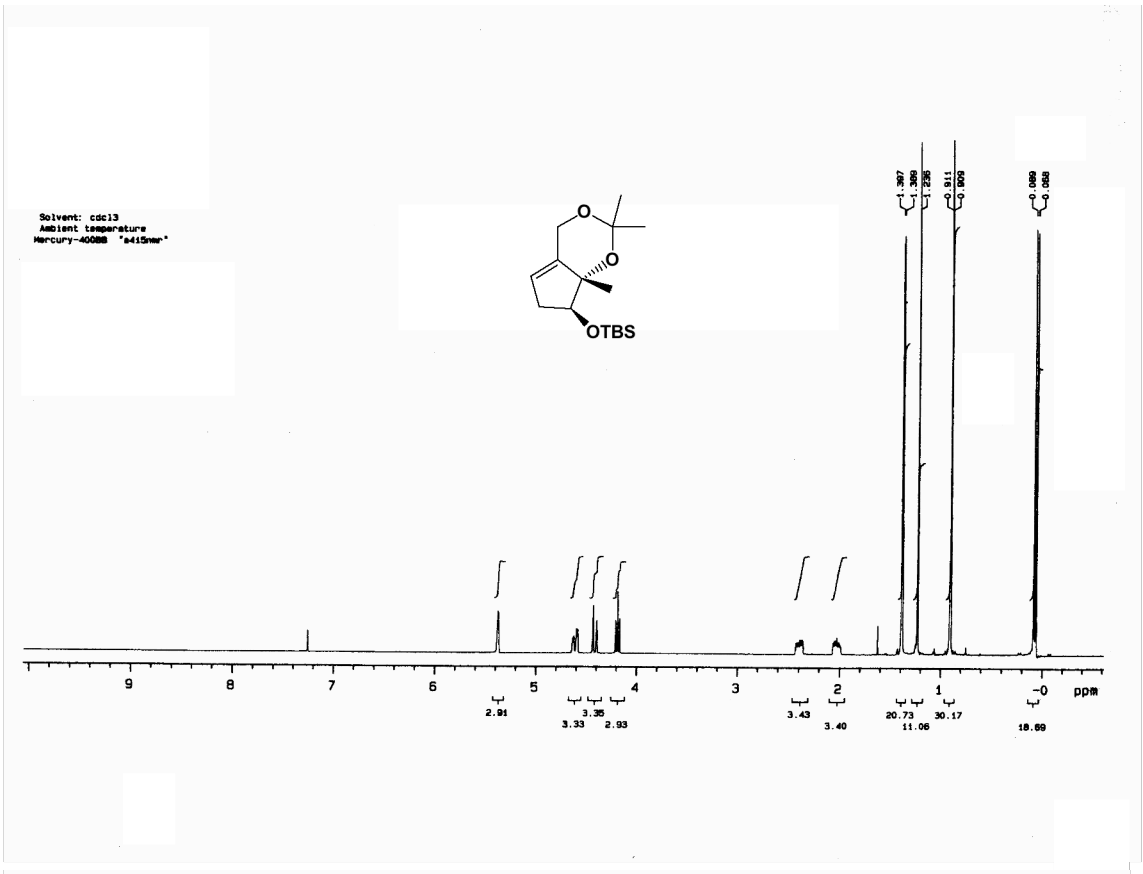
^{1}H and ^{13}C NMR spectra of **9** ($CDCl_3$)

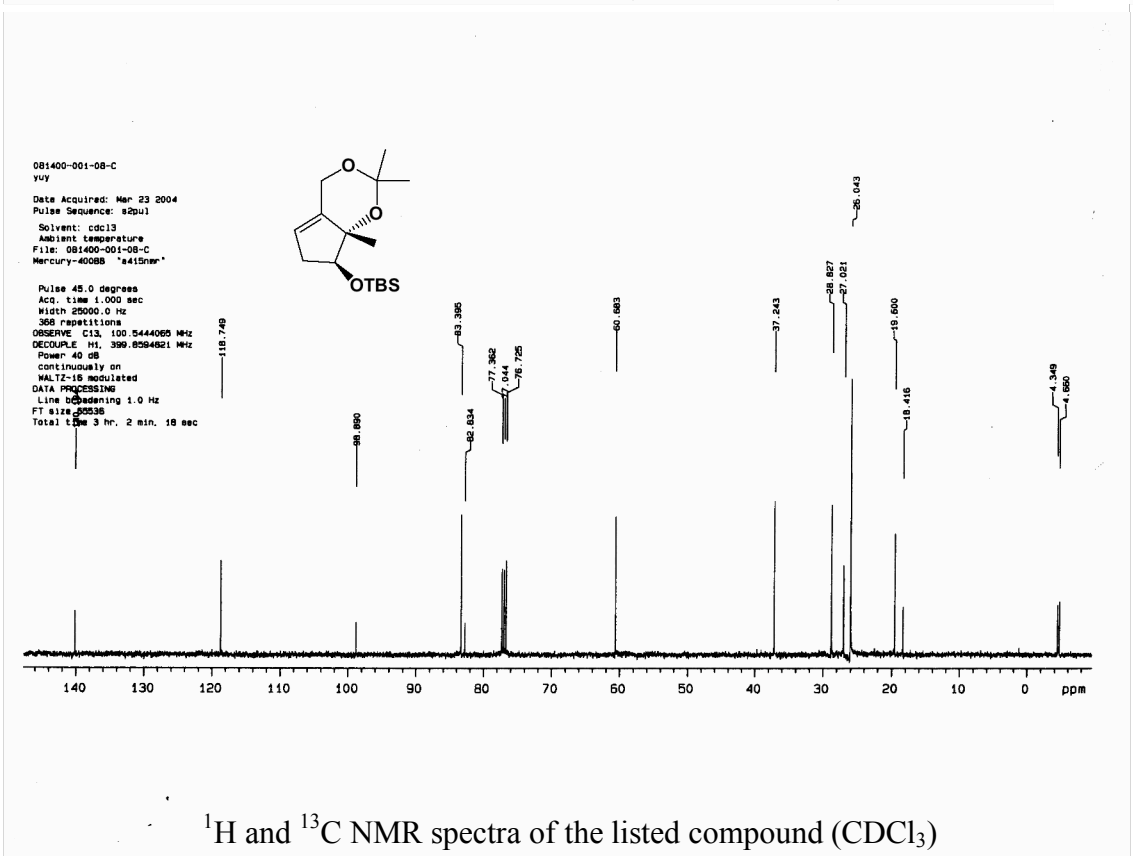


^{1}H and ^{13}C NMR spectra of **10** ($CDCl_3$)

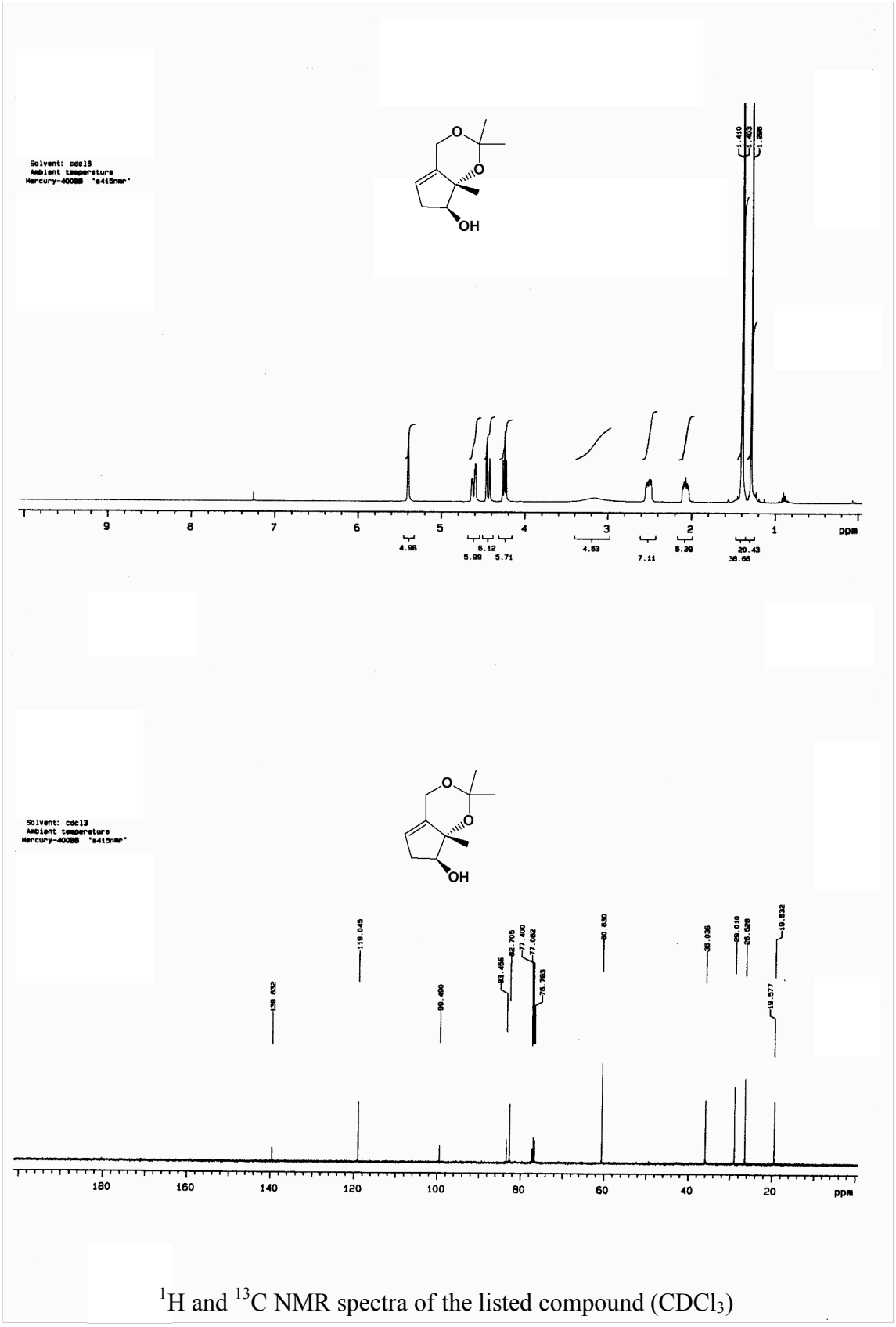


^{1}H and ^{13}C NMR spectra of **11** ($CDCl_3$)

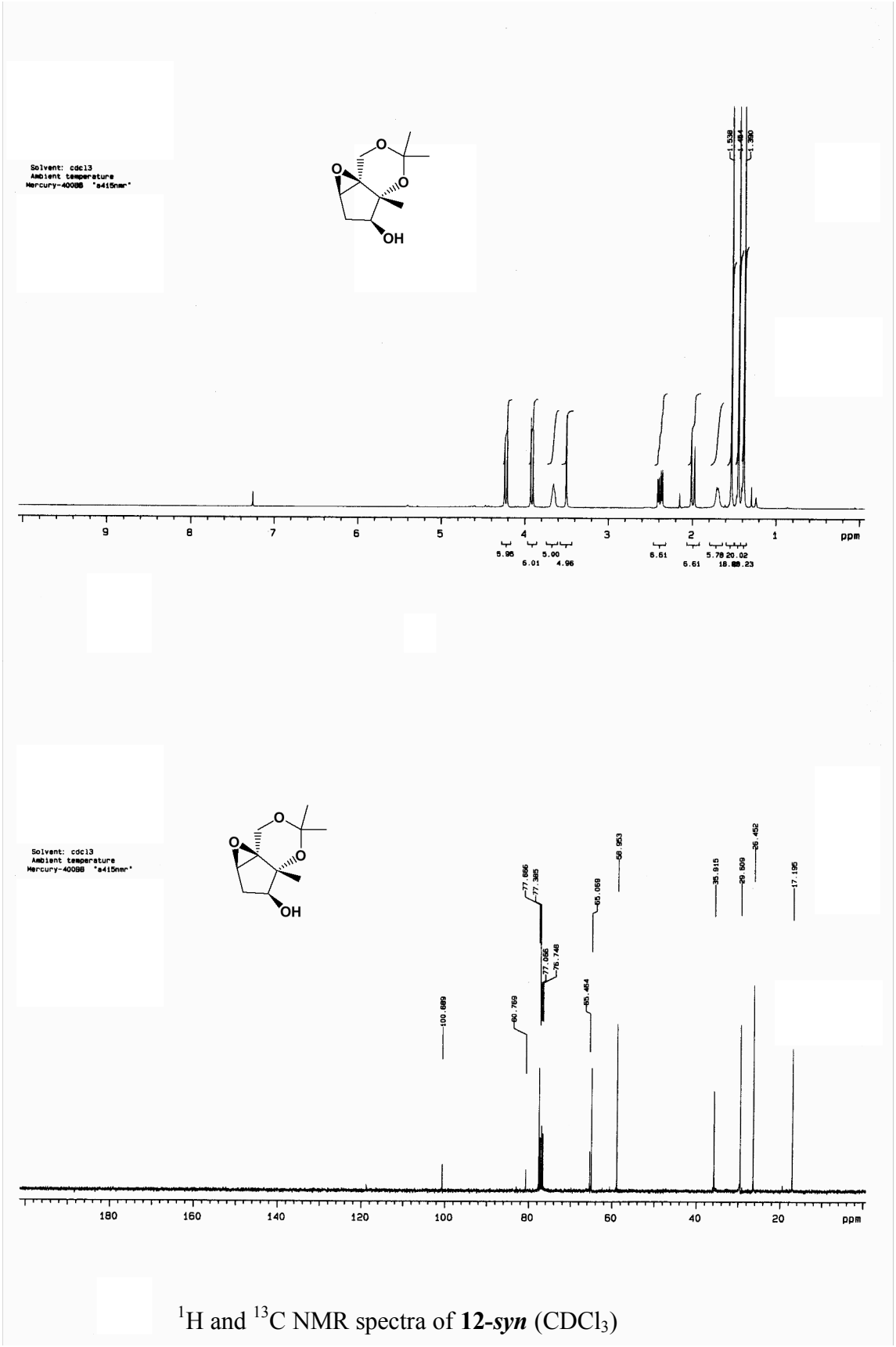




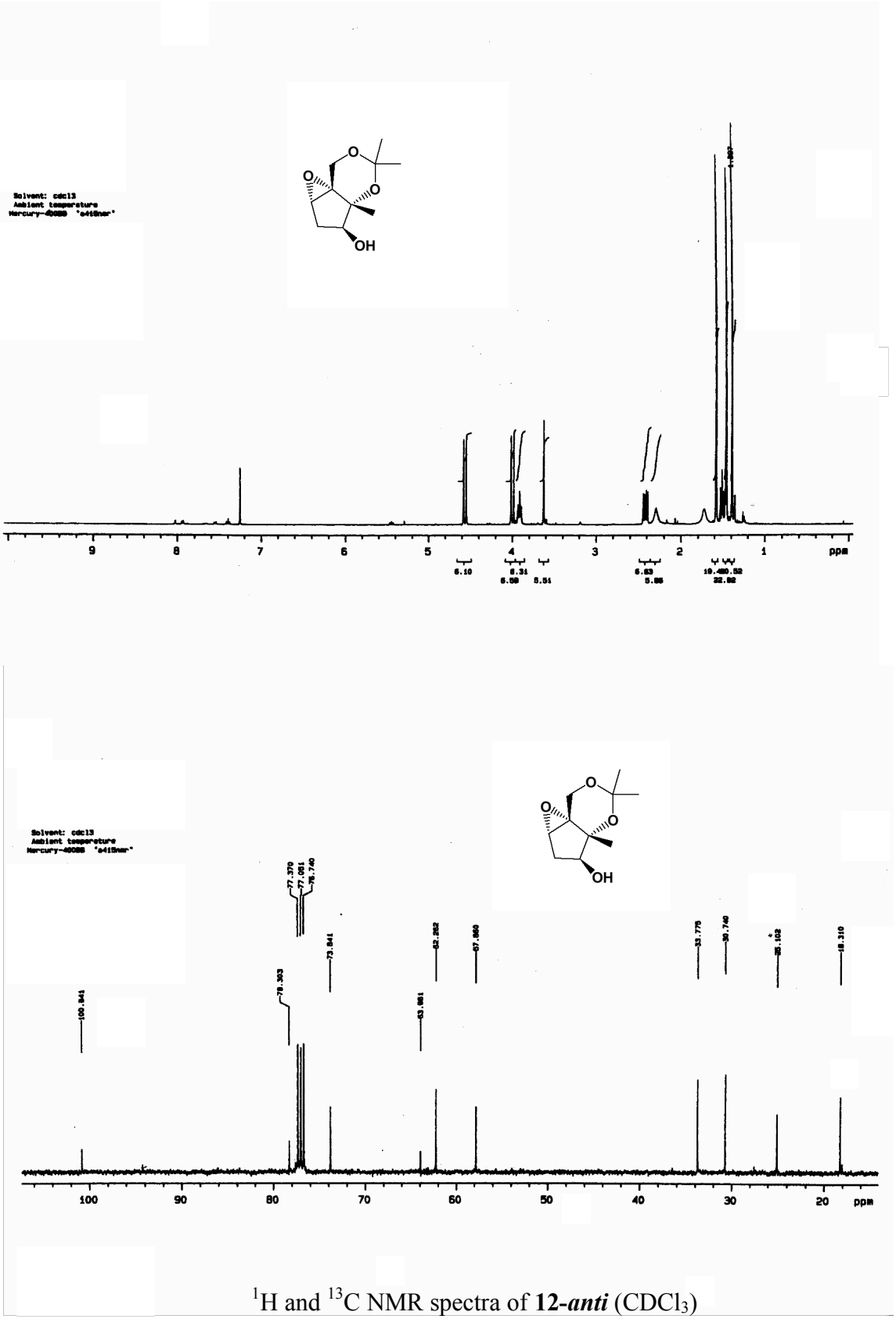
^{1}H and ^{13}C NMR spectra of the listed compound ($CDCl_3$)



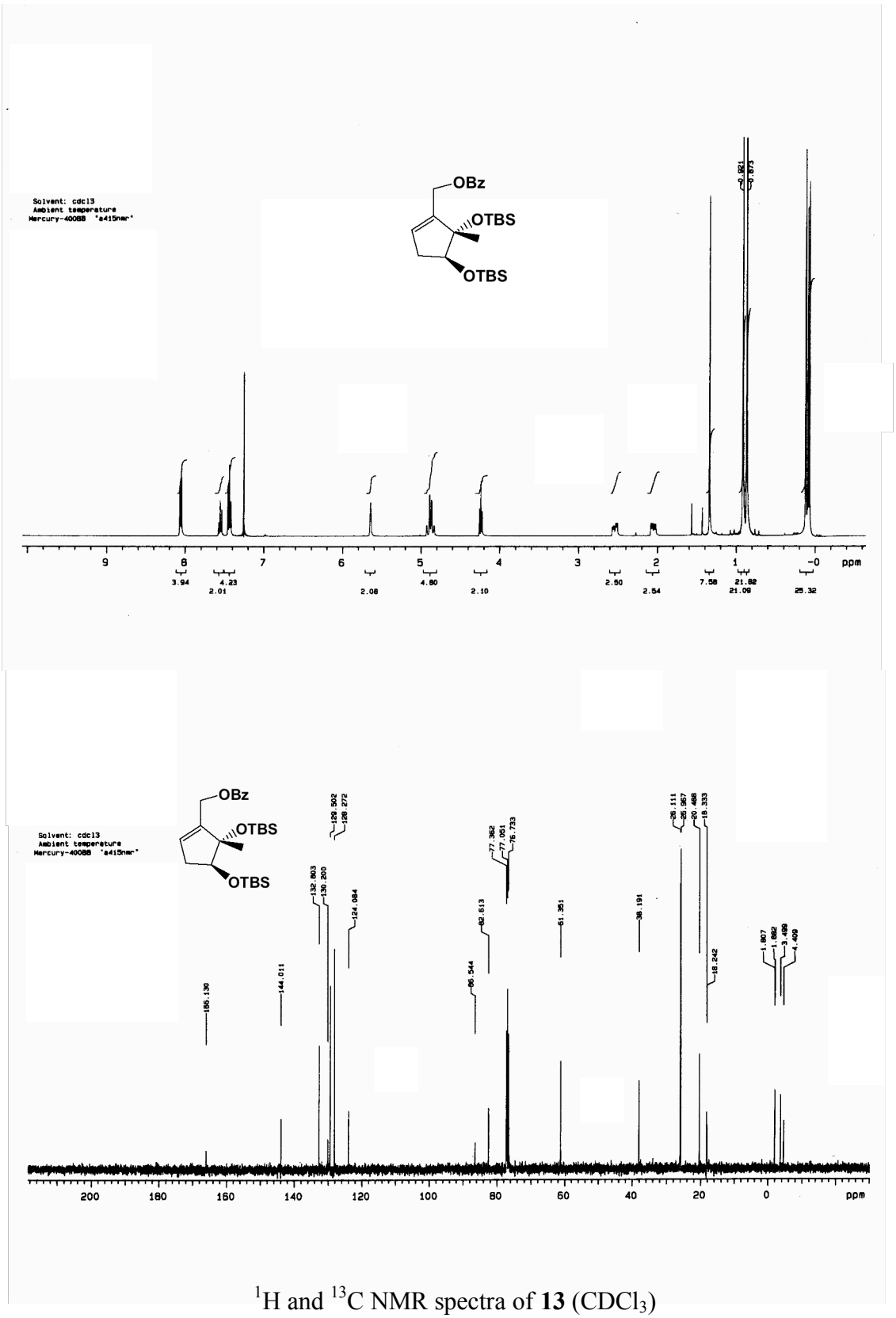
^{1}H and ^{13}C NMR spectra of the listed compound ($CDCl_3$)



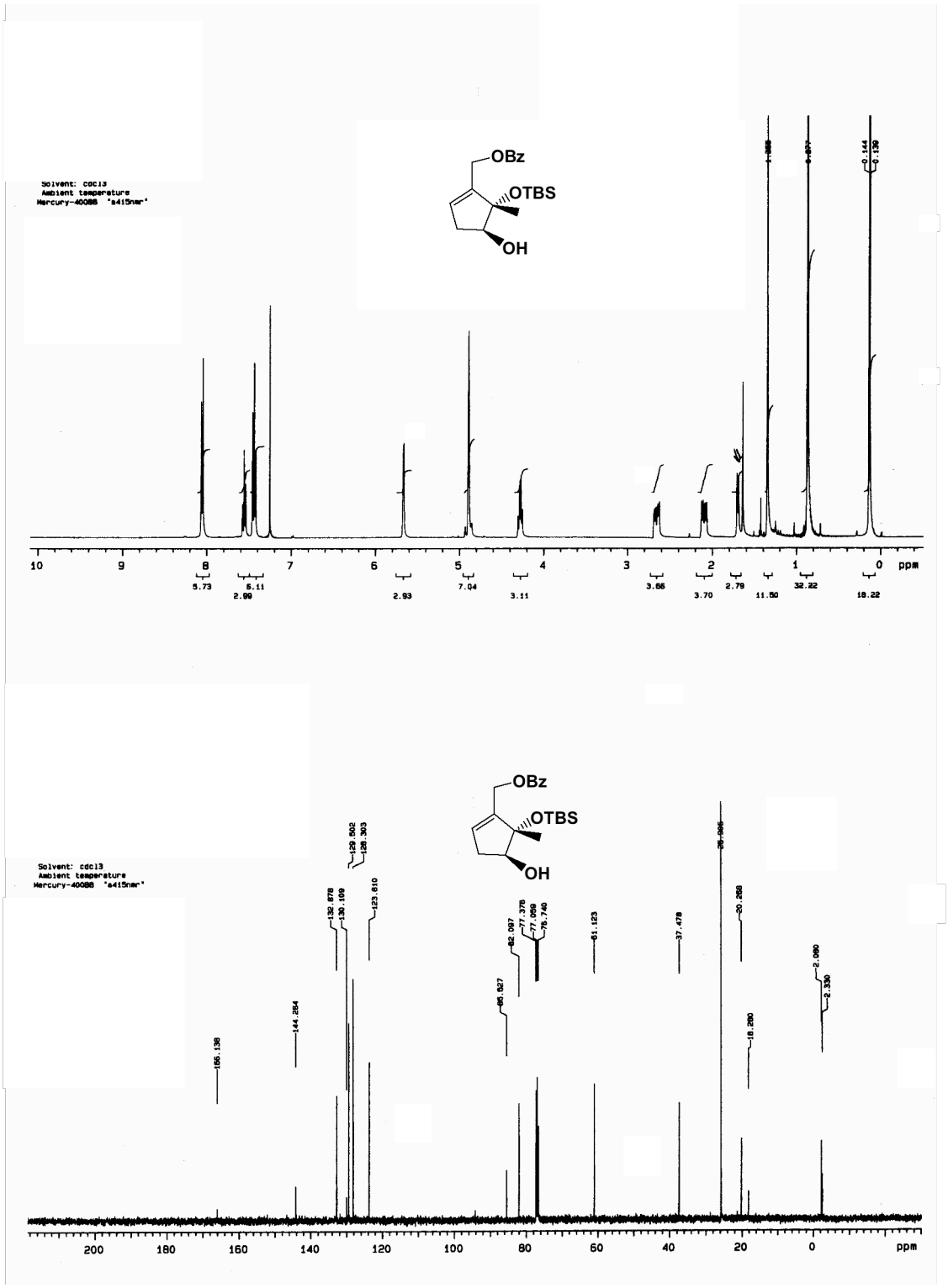
^{1}H and ^{13}C NMR spectra of **12-*syn*** ($CDCl_3$)



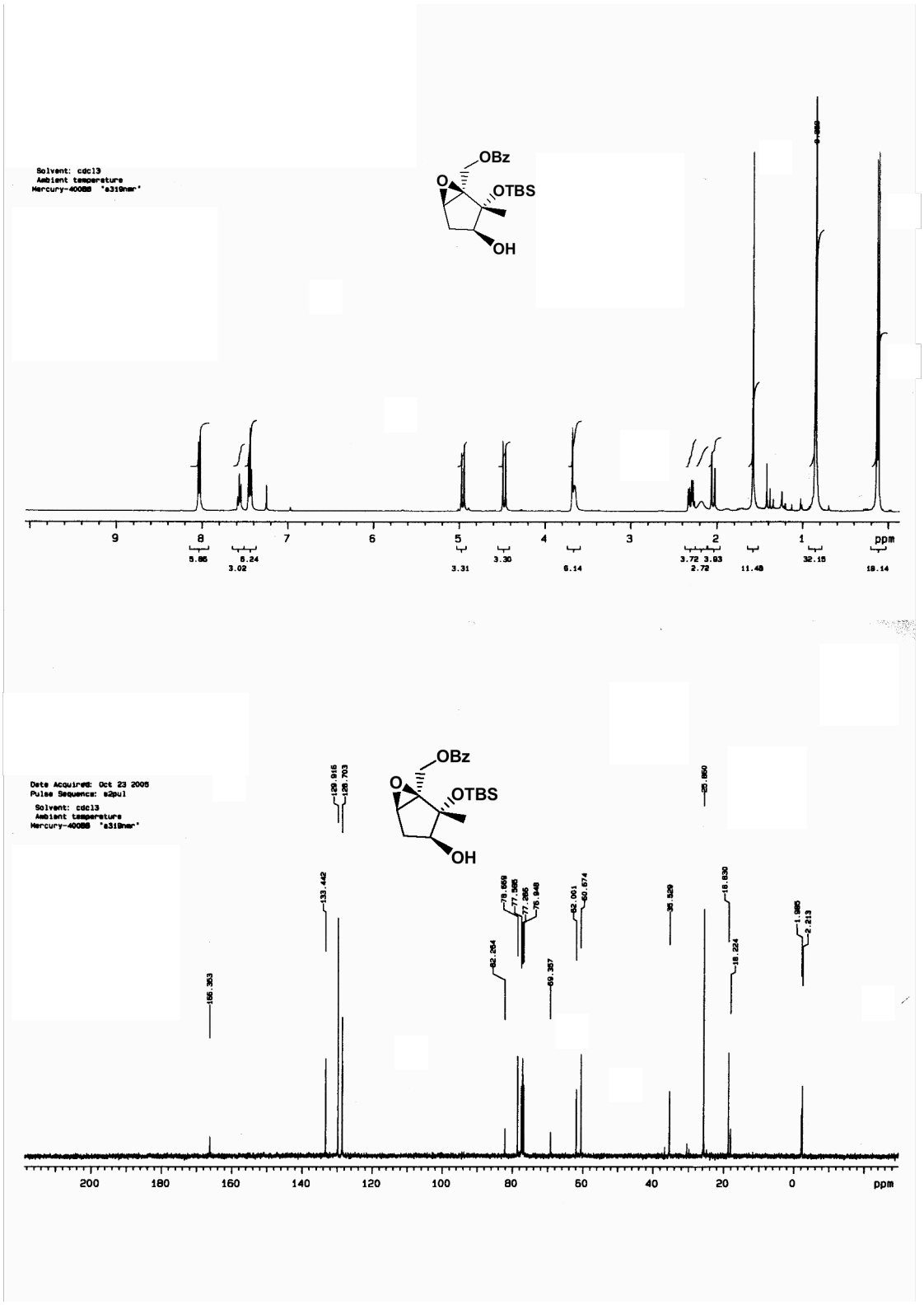
^{1}H and ^{13}C NMR spectra of **12-*anti*** ($CDCl_3$)



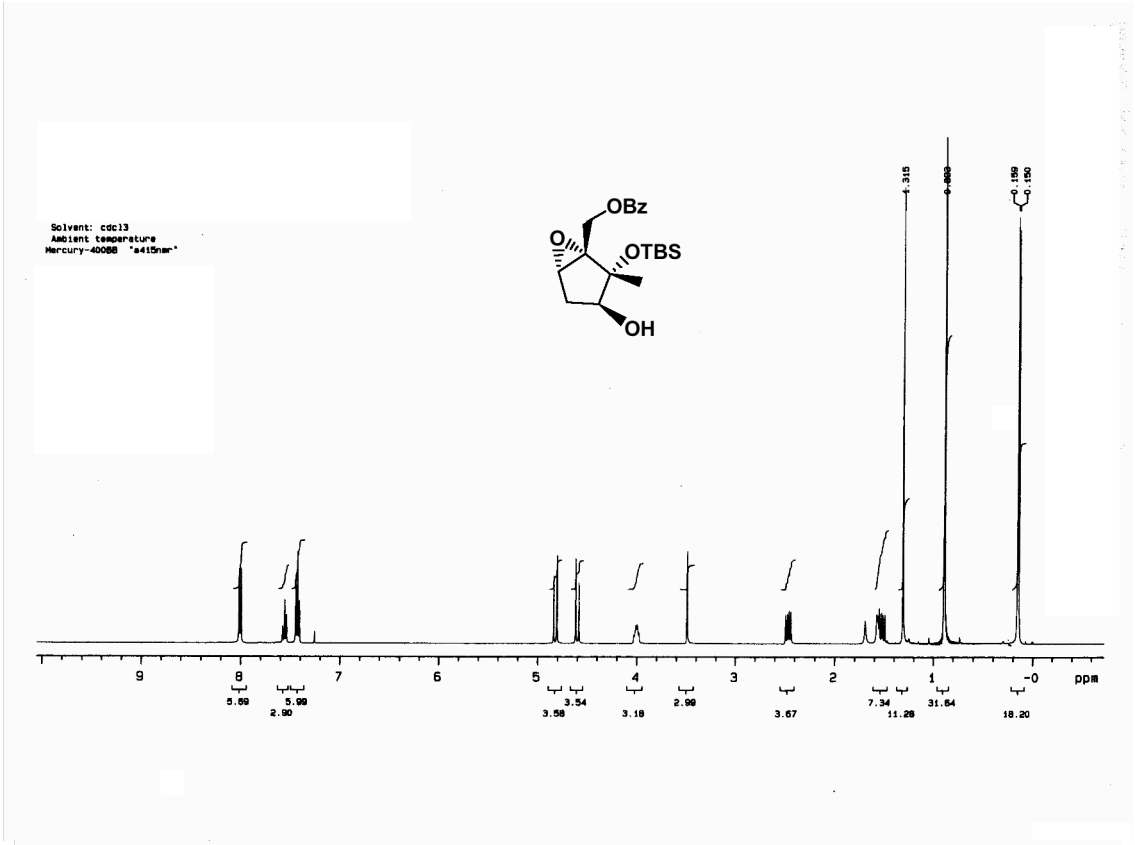
^{1}H and ^{13}C NMR spectra of **13** ($CDCl_3$)

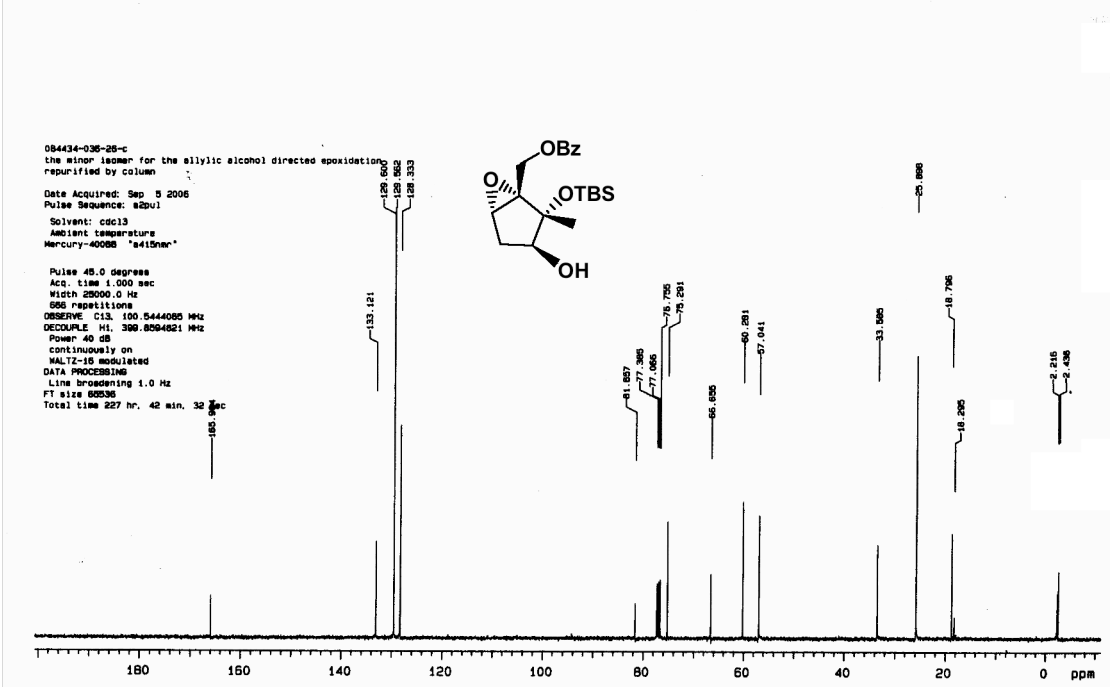


^{1}H and ^{13}C NMR spectra of **14** ($CDCl_3$)

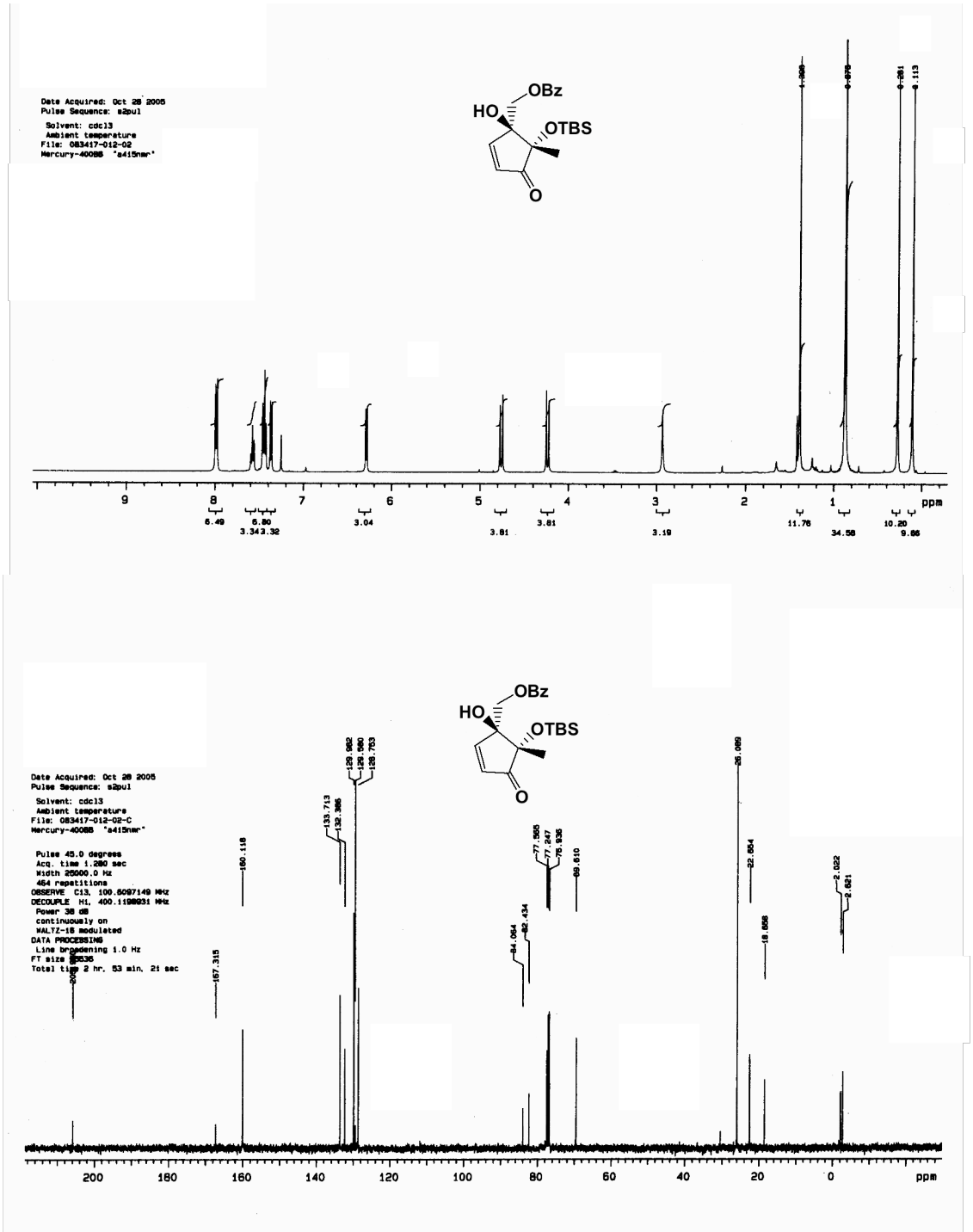


^{1}H and ^{13}C NMR spectra of **15-*syn*** ($CDCl_3$)

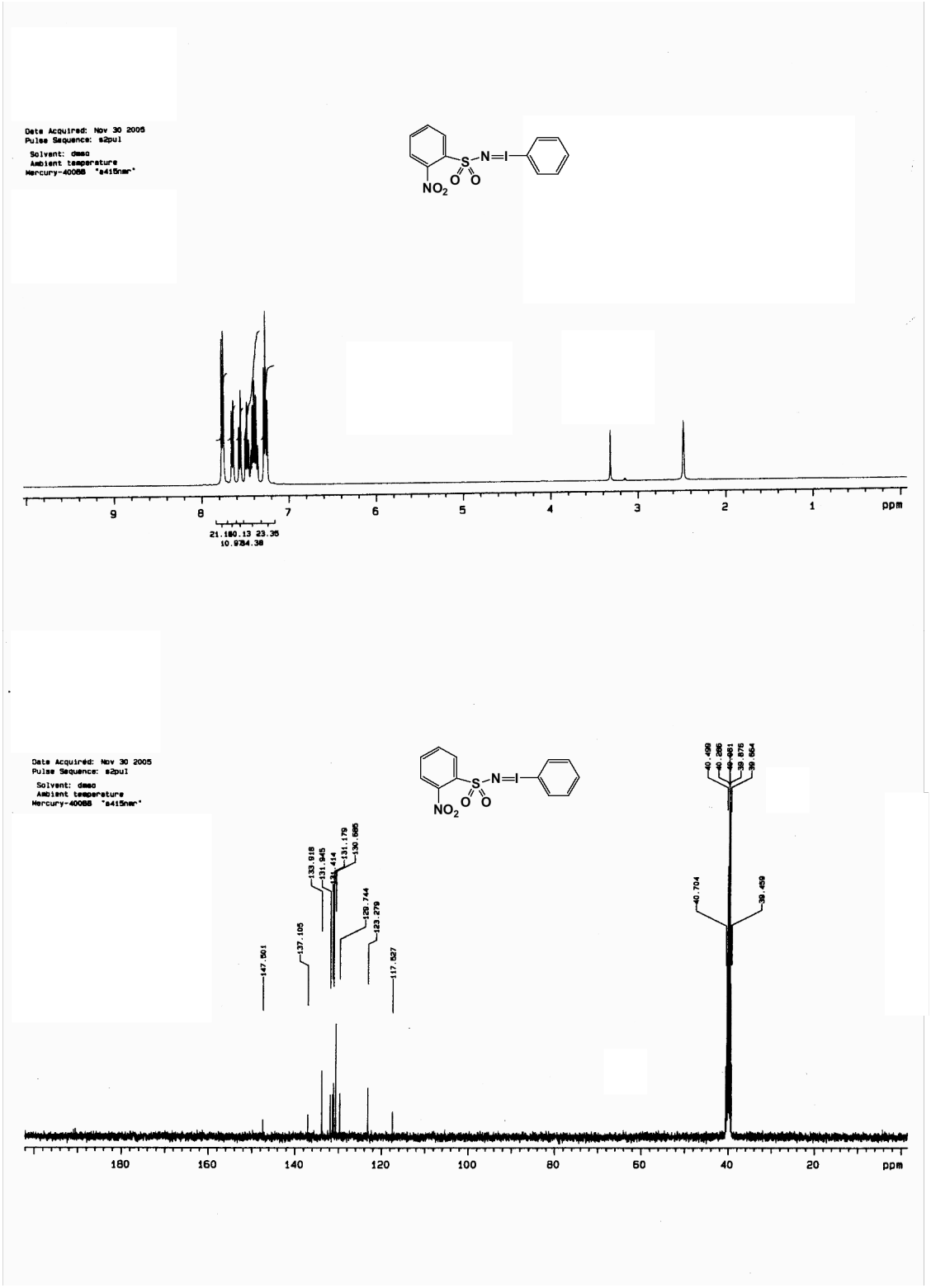




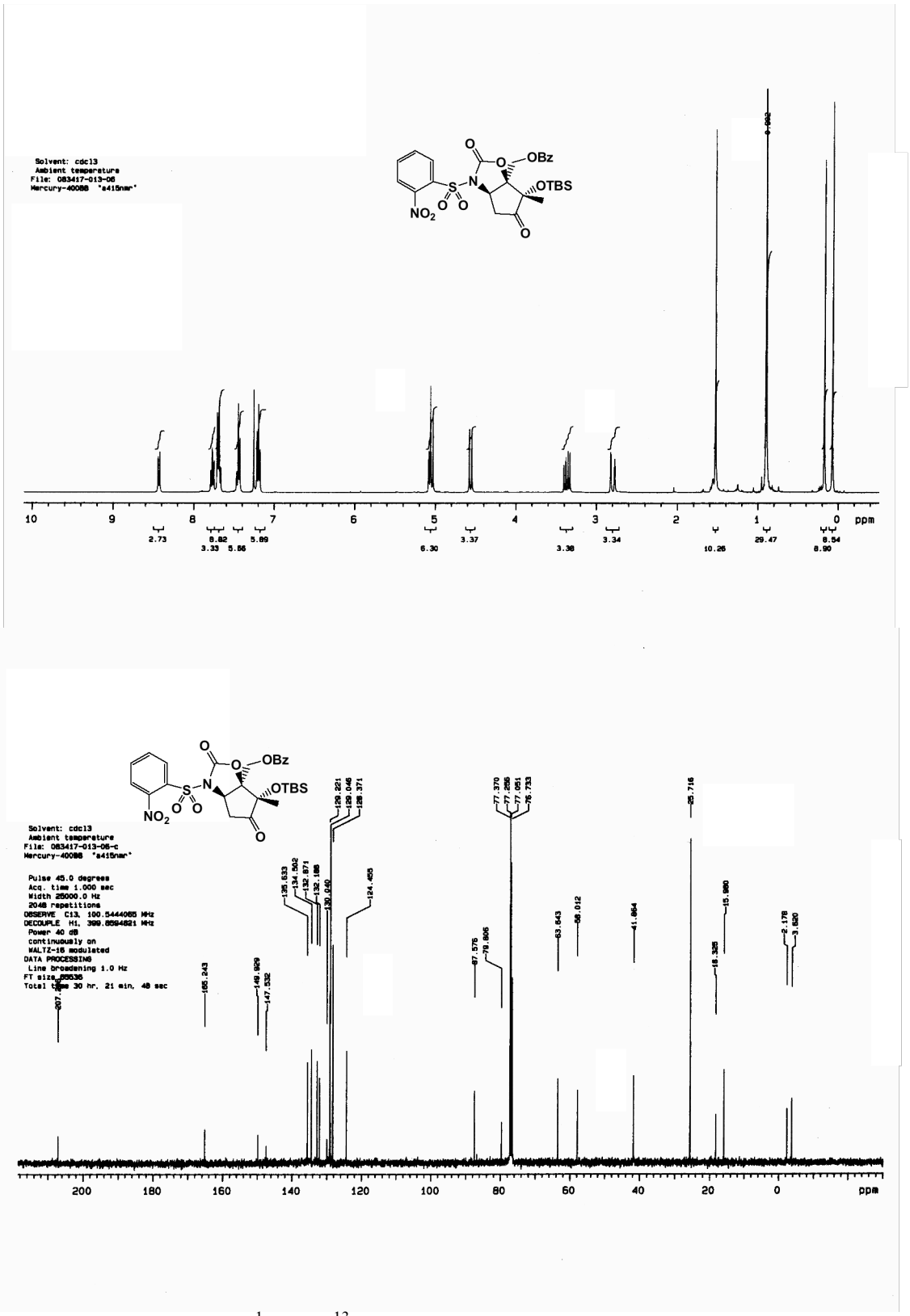
^{1}H and ^{13}C NMR spectra of **15-*anti*** ($CDCl_3$)



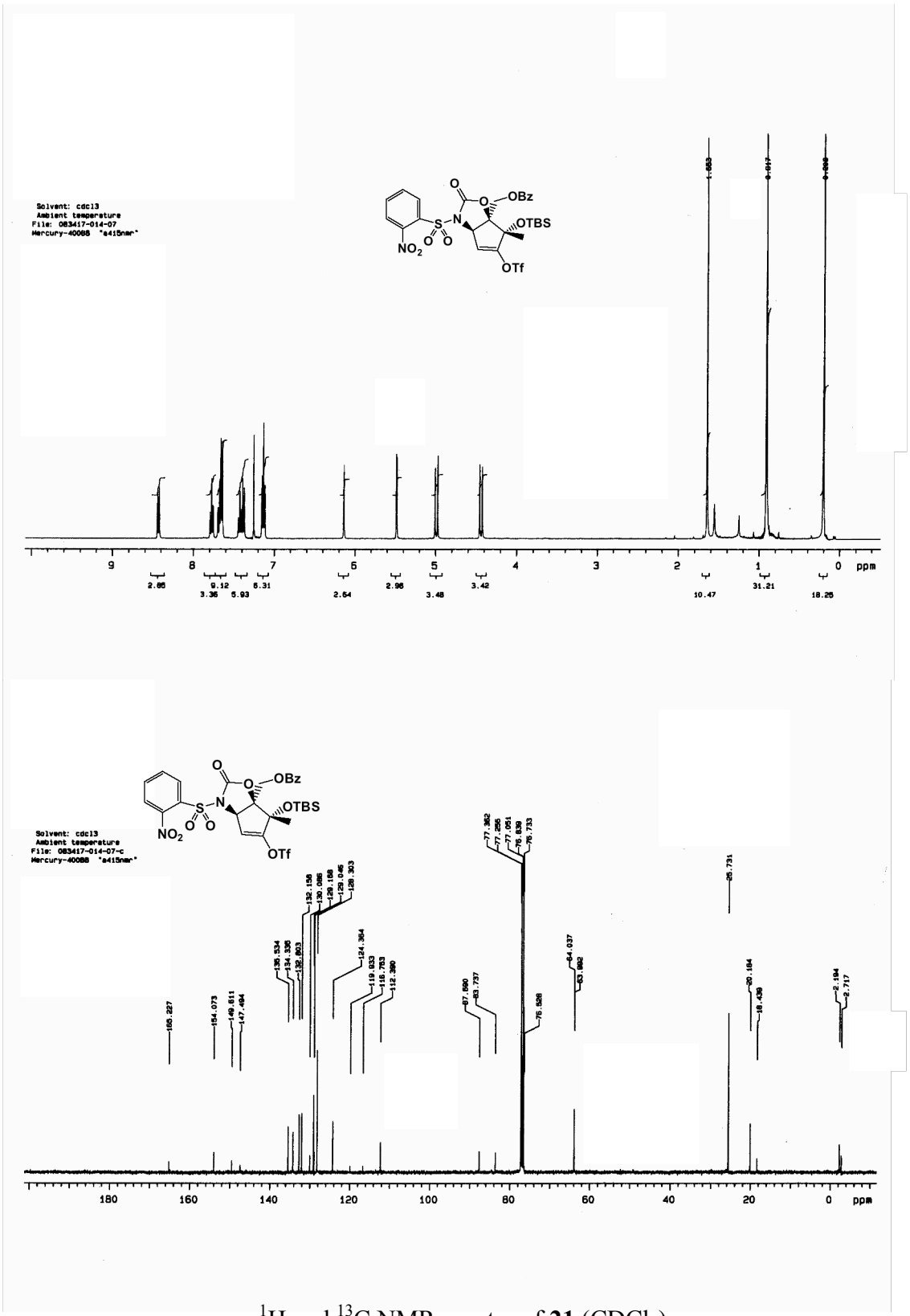
^{1}H and ^{13}C NMR spectra of **16** ($CDCl_3$)



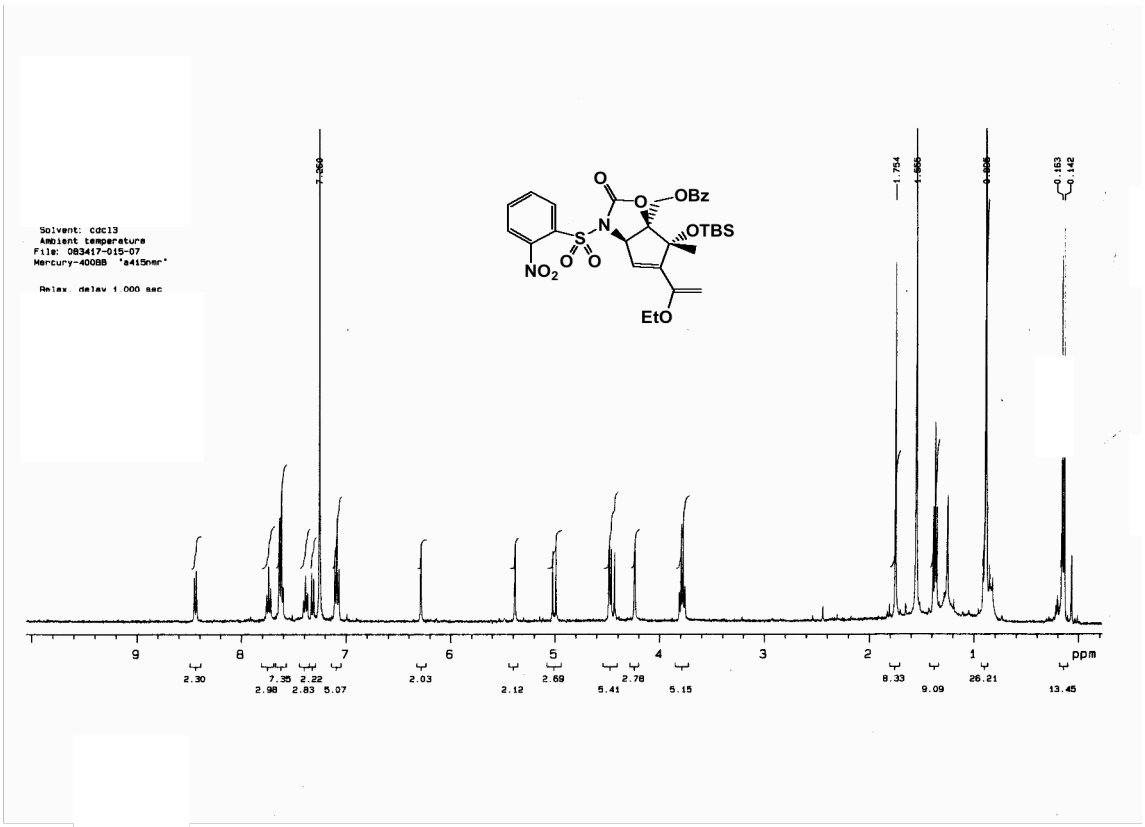
^{1}H and ^{13}C NMR spectra of [N-(2-nitrophenylsulfonyl)imino]phenyliodinane (DMSO-d_6)

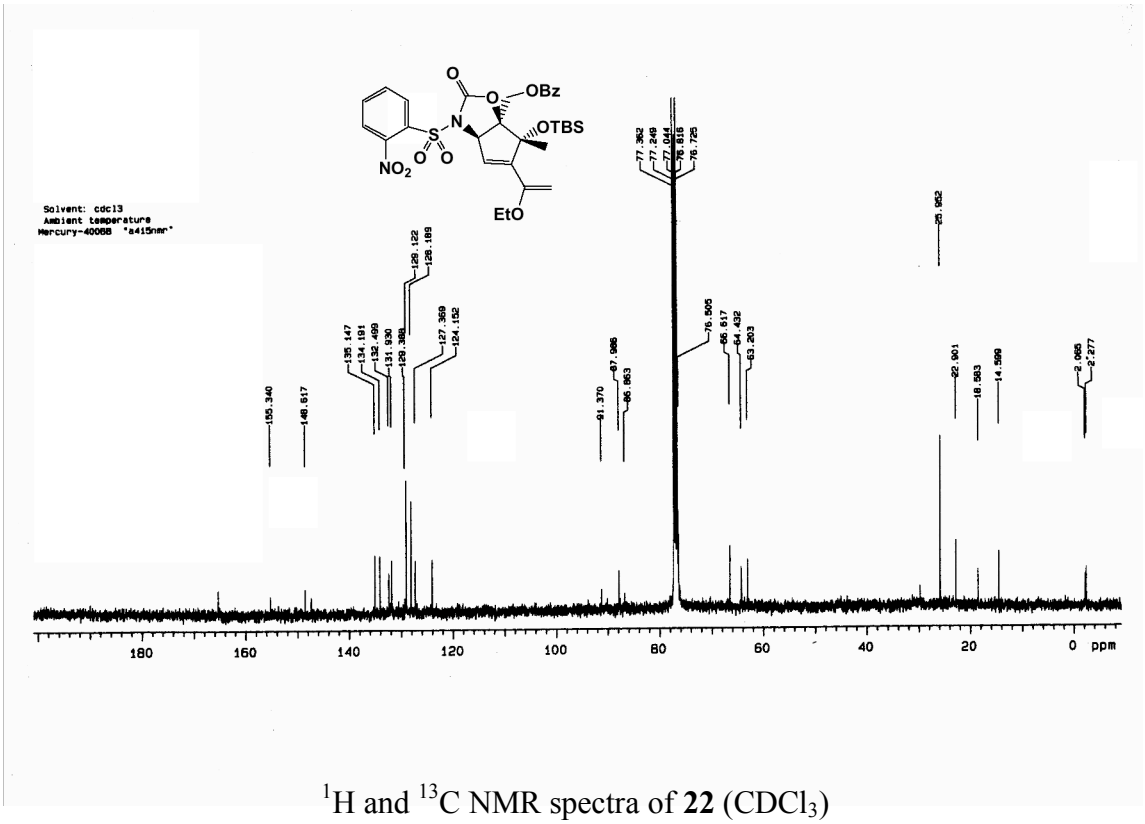


^{1}H and ^{13}C NMR spectra of **17** ($CDCl_3$)

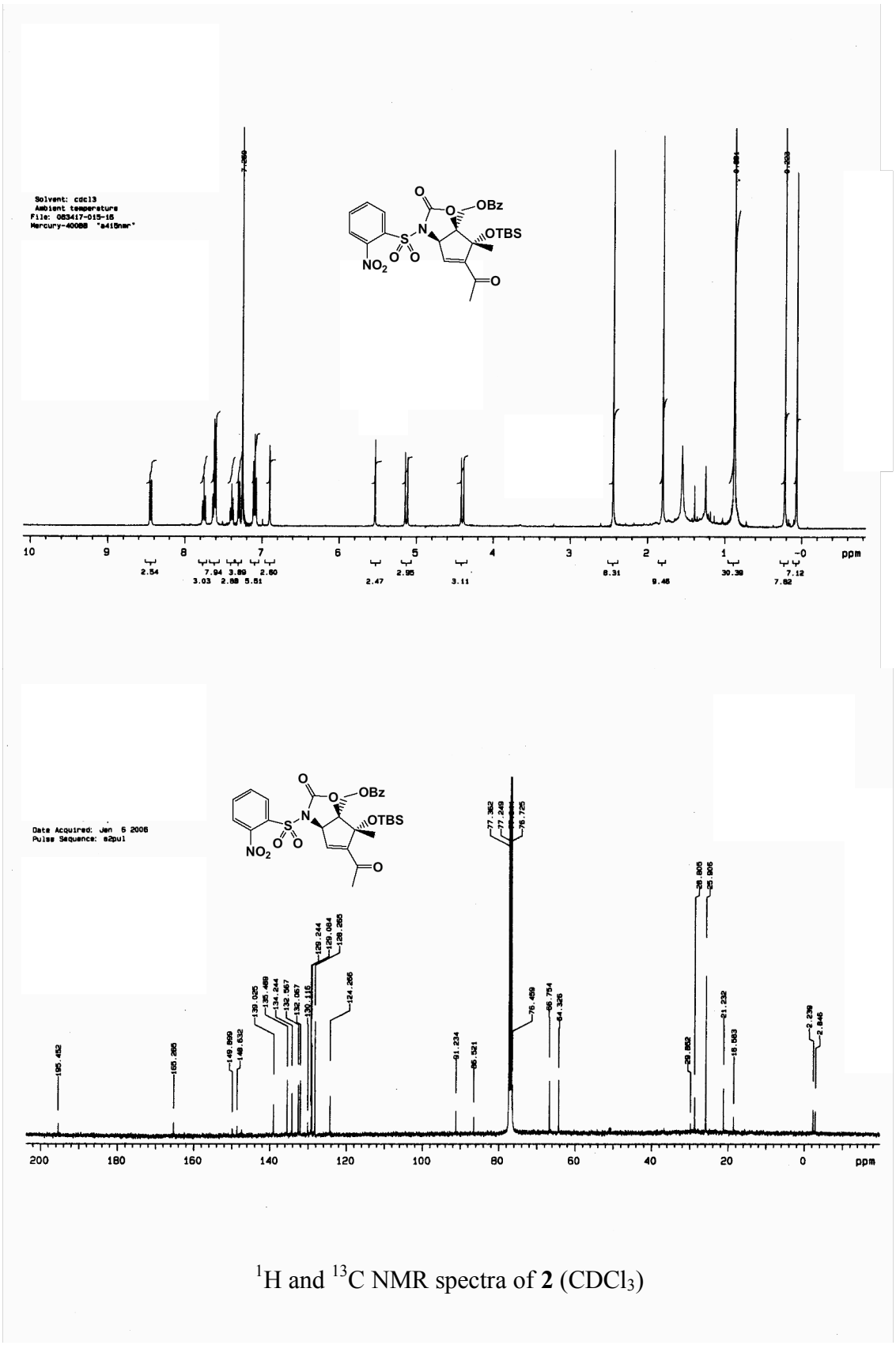


^{1}H and ^{13}C NMR spectra of **21** ($CDCl_3$)

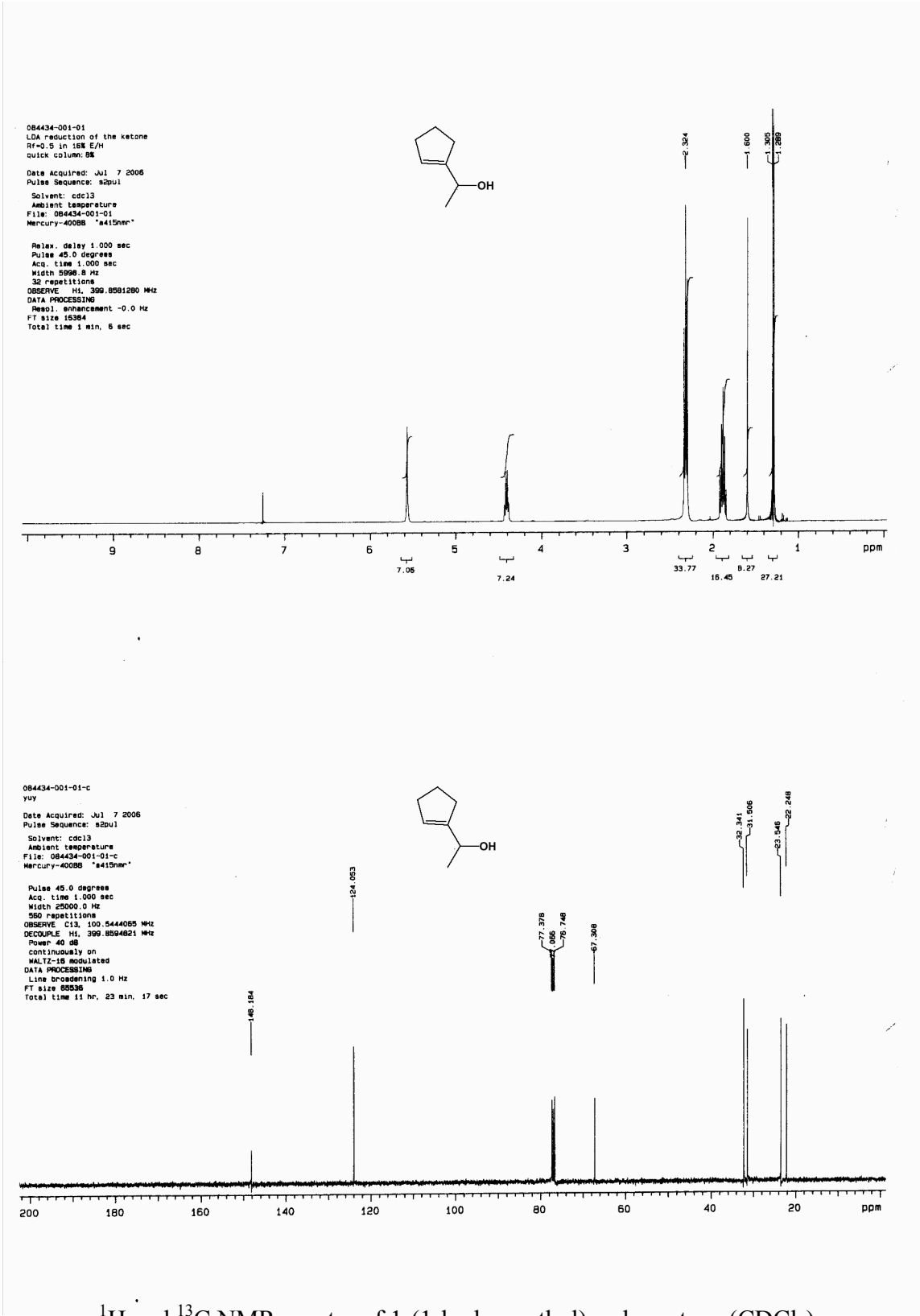




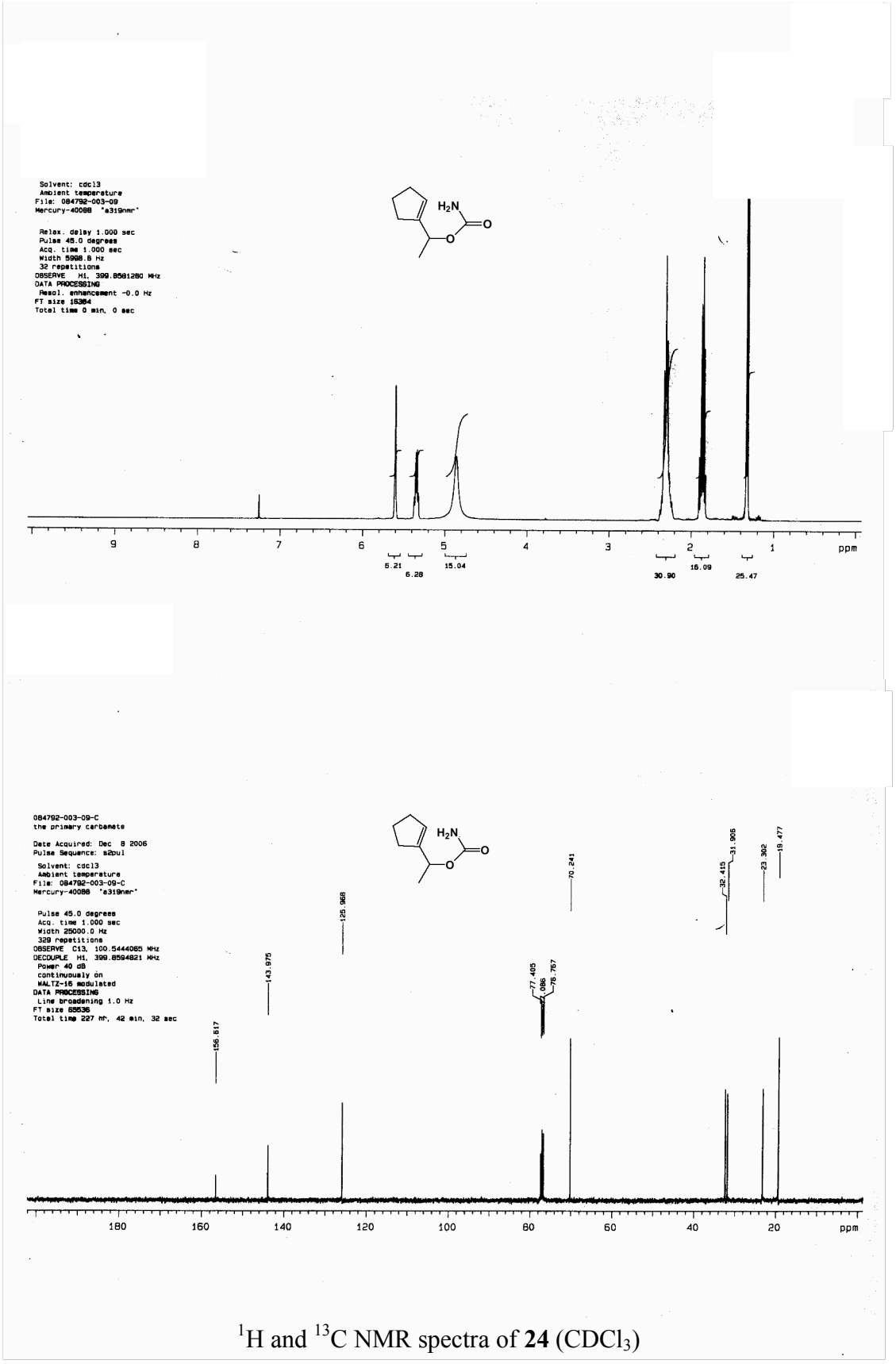
^{1}H and ^{13}C NMR spectra of **22** ($CDCl_3$)



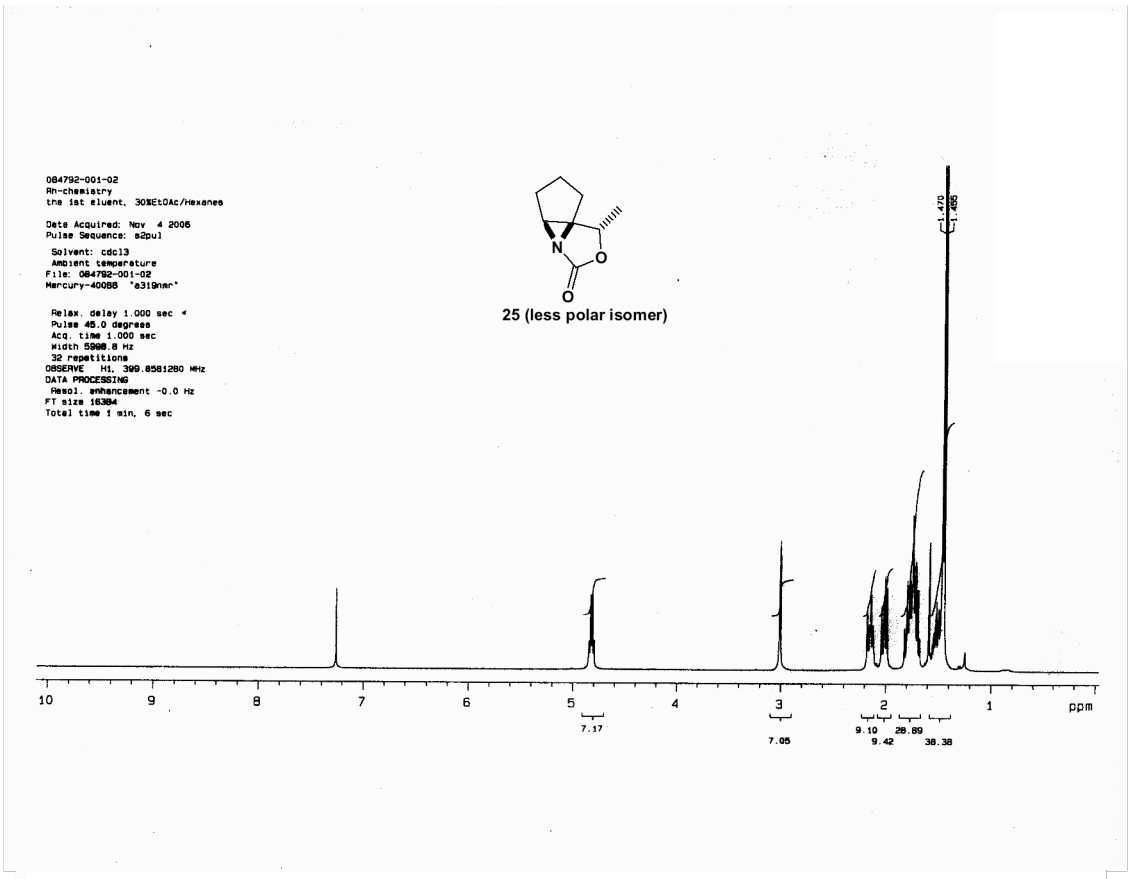
^{1}H and ^{13}C NMR spectra of **2** ($CDCl_3$)

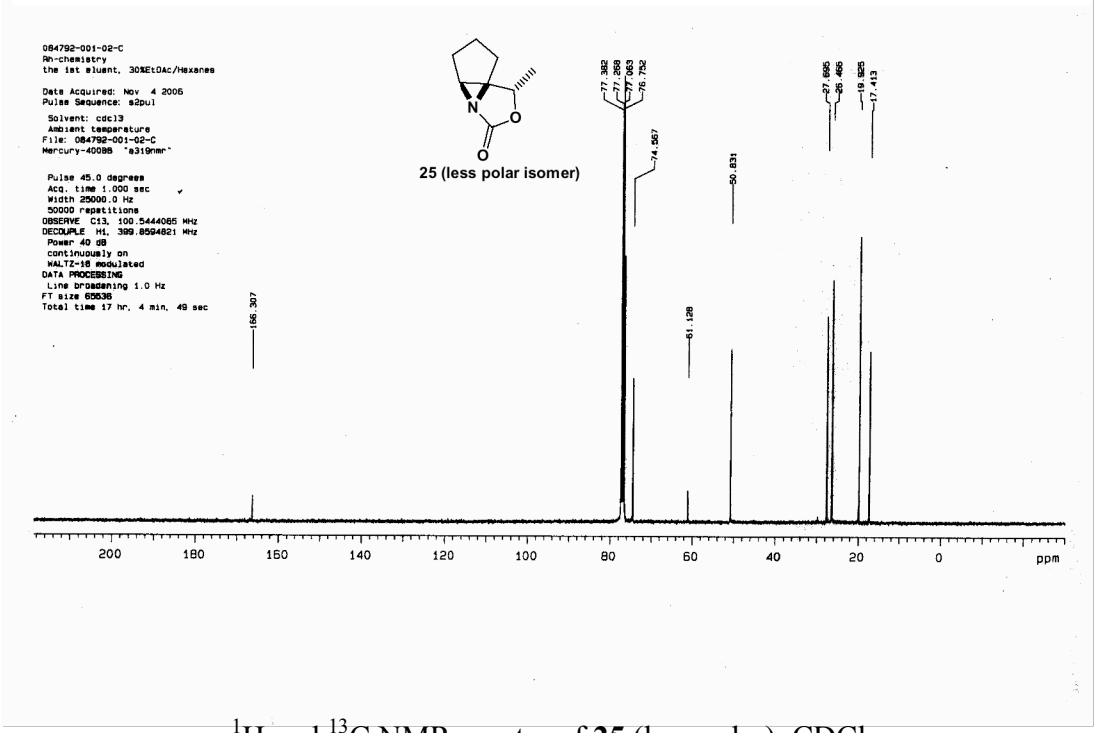


^{1}H and ^{13}C NMR spectra of 1-(1-hydroxyethyl)cyclopentene ($CDCl_3$)

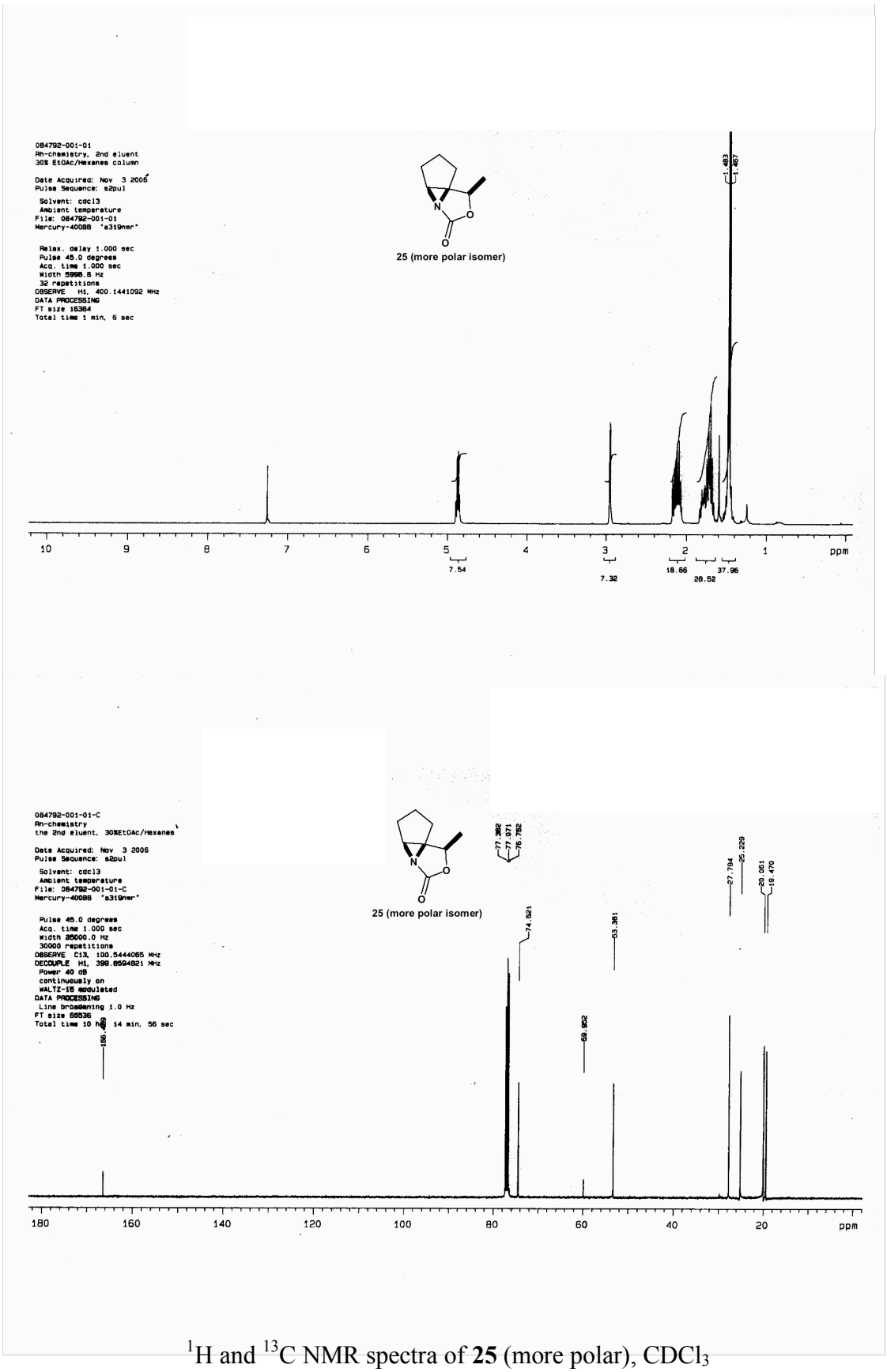


^{1}H and ^{13}C NMR spectra of **24** ($CDCl_3$)

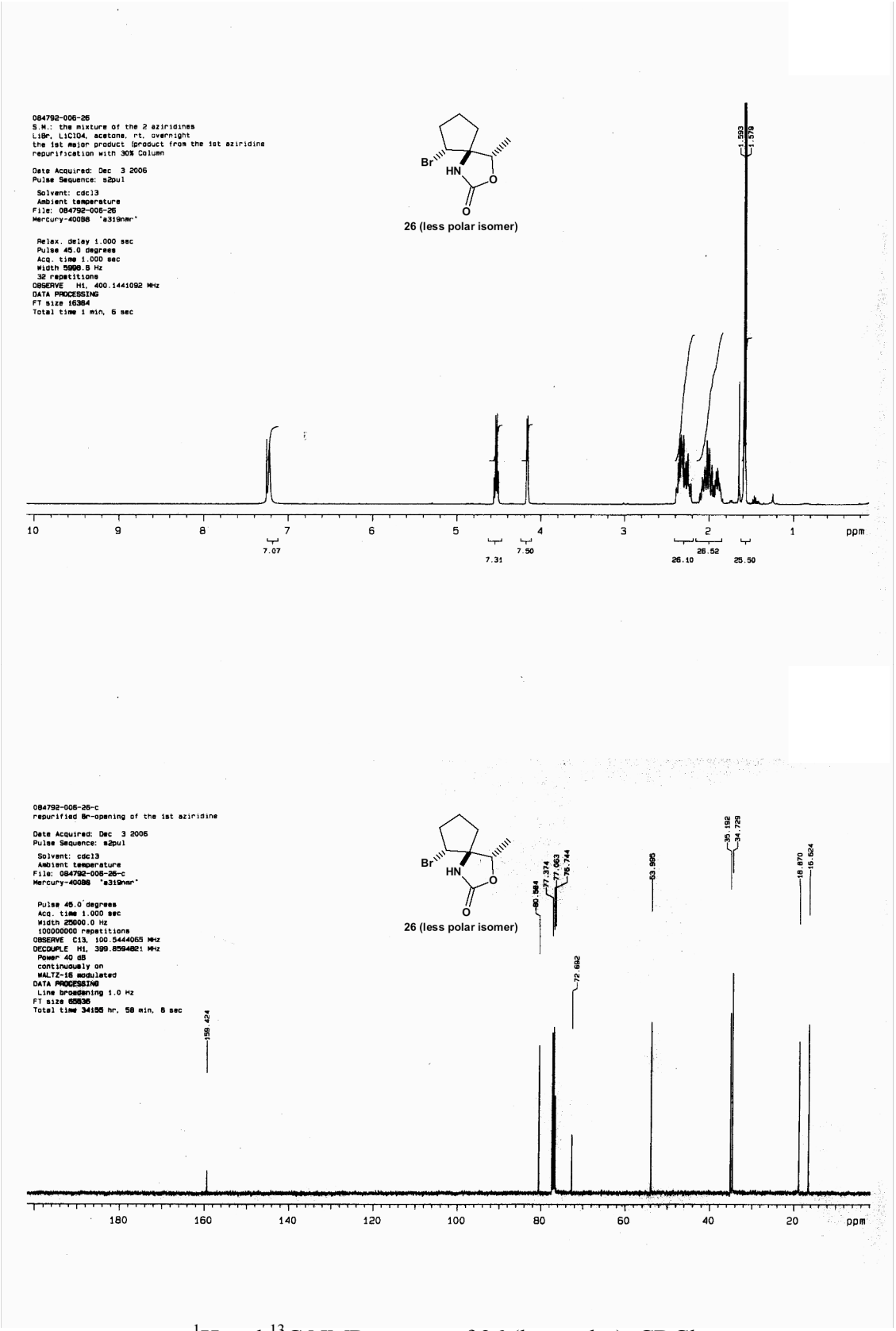




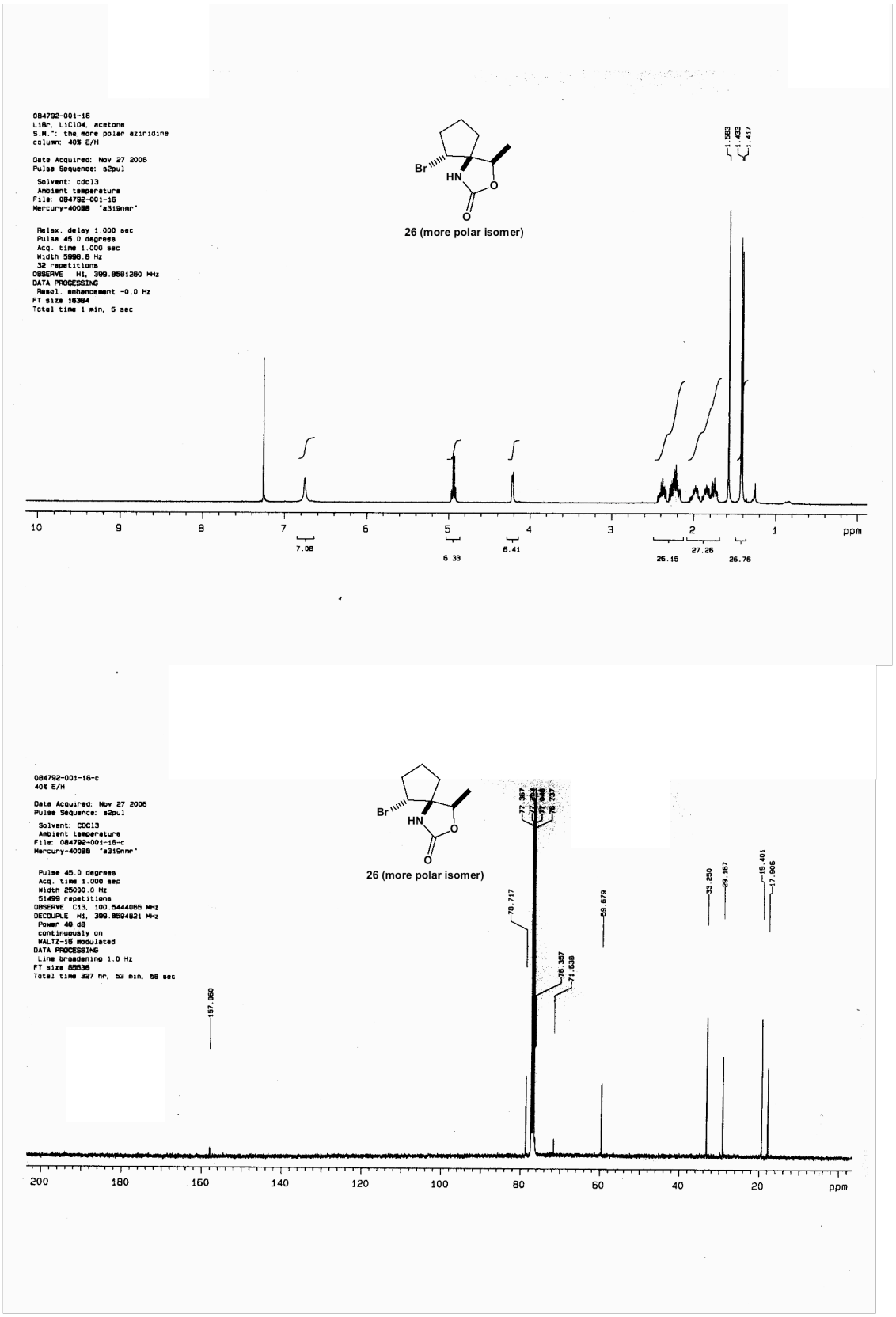
^{1}H and ^{13}C NMR spectra of **25** (less polar), $CDCl_3$



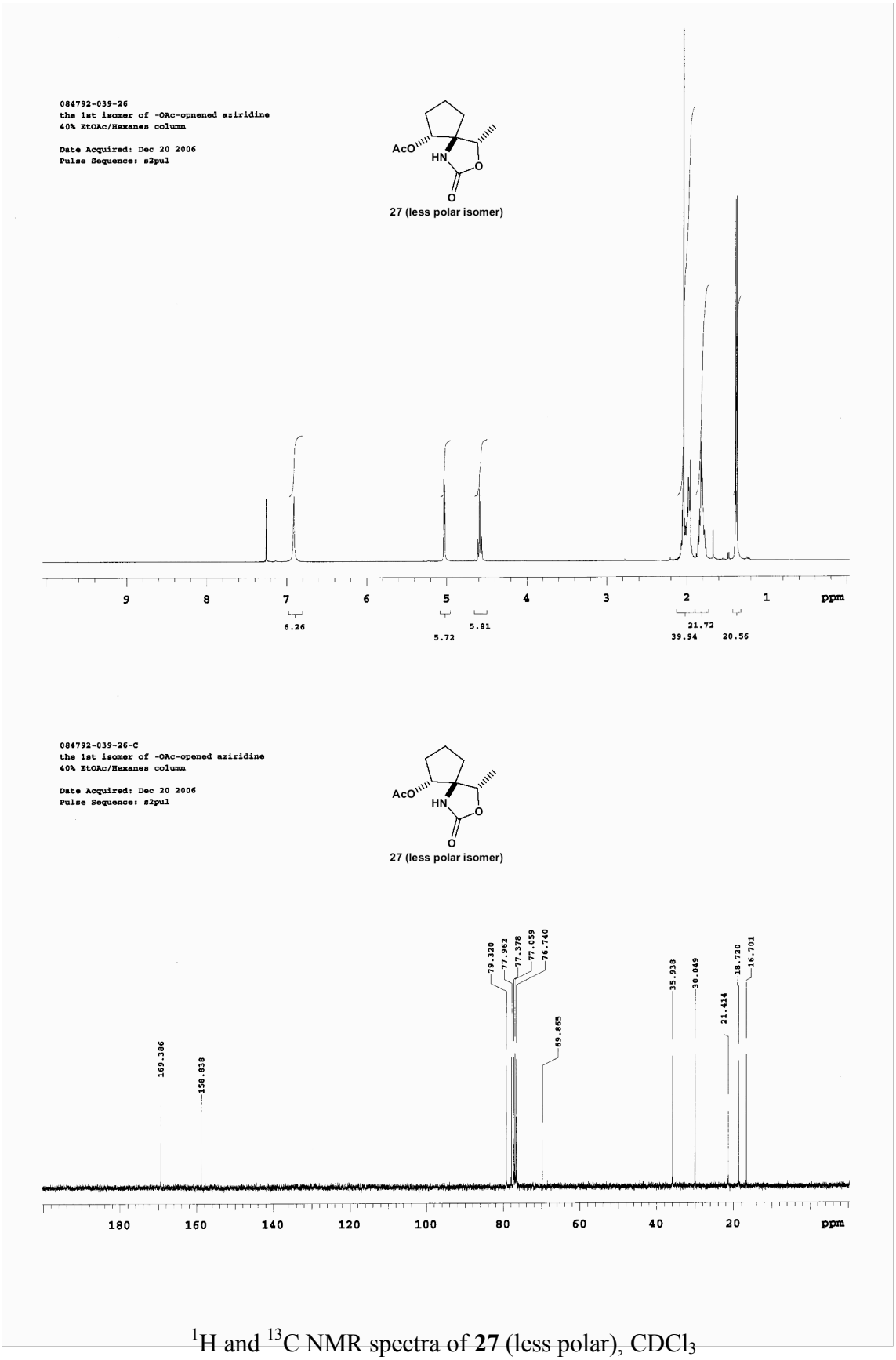
^{1}H and ^{13}C NMR spectra of **25** (more polar), $CDCl_3$



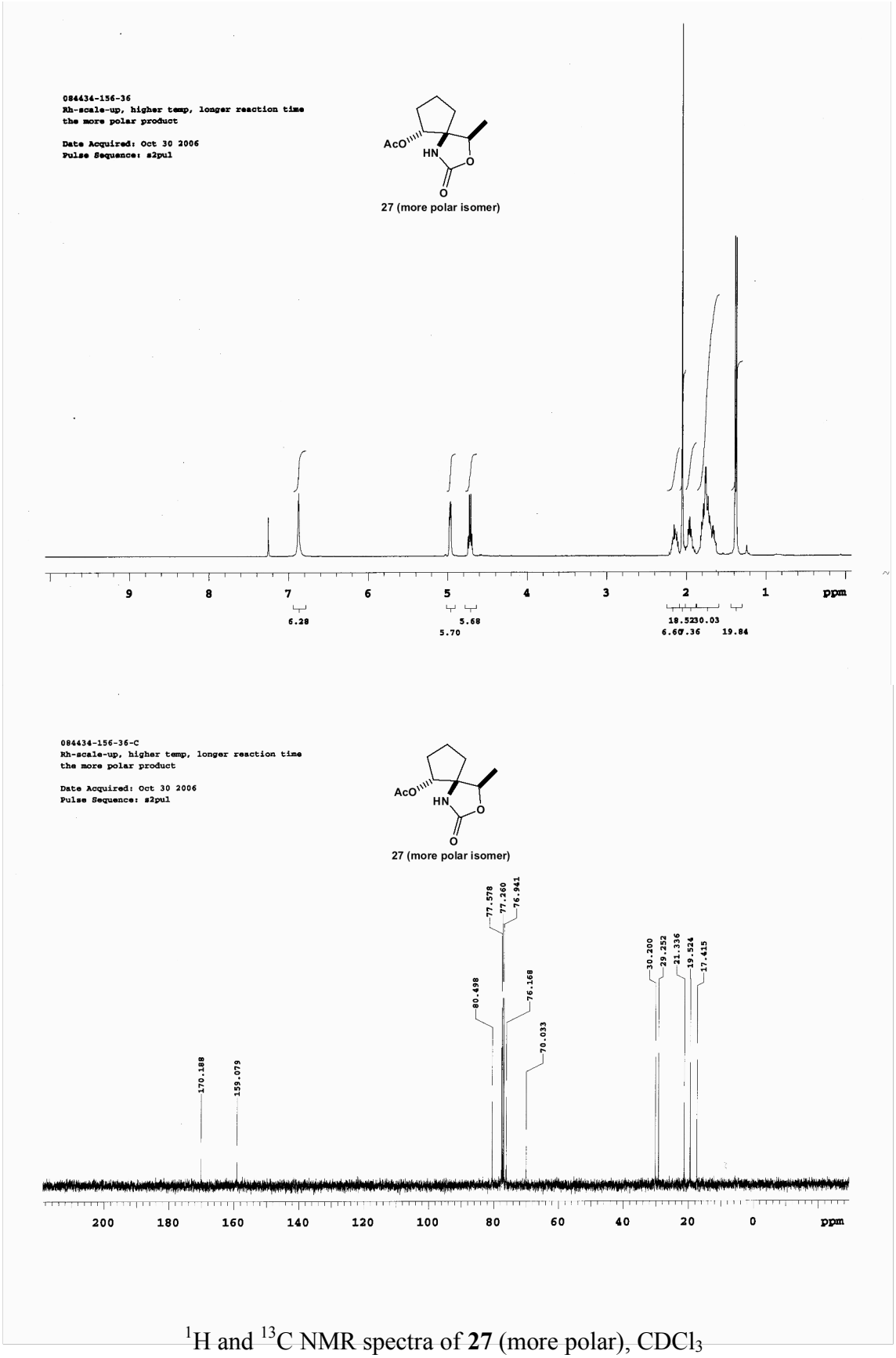
^{1}H and ^{13}C NMR spectra of **26** (less polar), $CDCl_3$



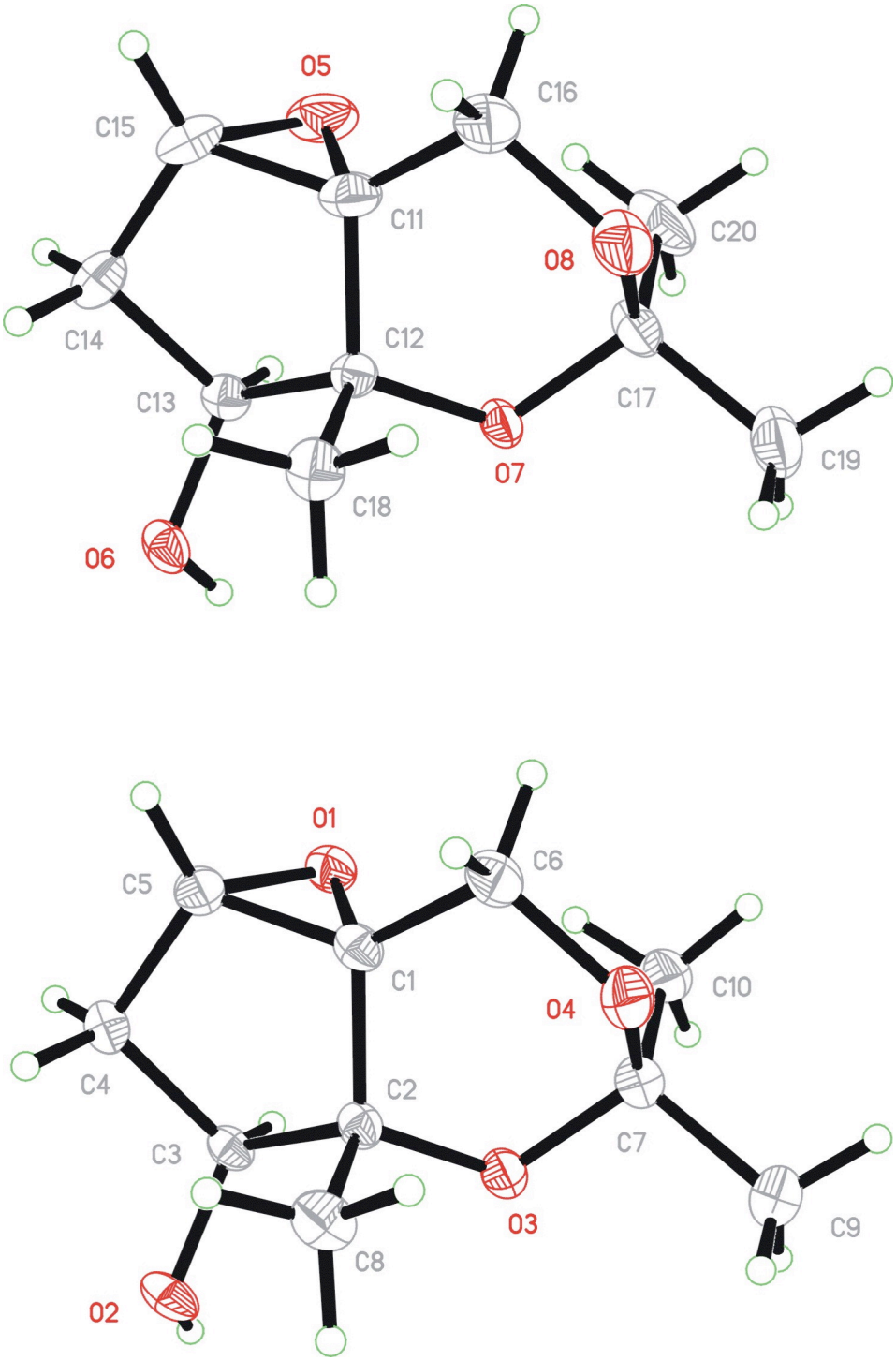
^{1}H and ^{13}C NMR spectra of **26** (more polar), $CDCl_3$



^{1}H and ^{13}C NMR spectra of **27** (less polar), $CDCl_3$



^{1}H and ^{13}C NMR spectra of **27** (more polar), $CDCl_3$



ORTEP view of **12** (two molecules in unit cell)