

Synthesis and Complete stereochemical Assignment of Psymberin / Irciniastatin A

Supporting Information

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Contents

1. General Experimental.....	S1
2. Experimental Procedures.....	S2
3. X-ray Crystallography.....	S13
4. Copies of NMR Spectra.....	S24

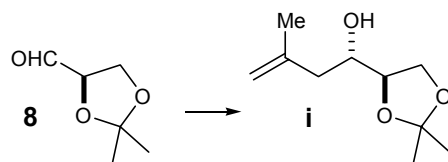
1. General Experimental

Unless otherwise noted, commercially available materials were used without further purification. All solvents were of HPLC or ACS grade. Solvents used for moisture sensitive operations were distilled from drying reagents under a nitrogen atmosphere: Et₂O and THF from sodium benzophenone ketyl; benzene and toluene from sodium; CH₂Cl₂ from CaH₂, pyridine over solid KOH, anhydrous N,N-dimethylformamide, and CH₃CN were purchased from commercial sources. Reactions were performed under an atmosphere of nitrogen with magnetic stirring unless noted otherwise. Flash chromatography (FC) was performed using *E Merck* silica gel 60 (240–400 mesh) according to the protocol of Still, Kahn, and Mitra (*J. Org. Chem.* **1978**, 43, 2923). Thin layer chromatography was performed using precoated plates purchased from *E. Merck* (silicagel 60 PF254, 0.25 mm) that were visualized using a KMnO₄ or Ce (IV) stain.

Nuclear magnetic resonance (NMR) spectra were recorded on a *Varian Inova-400* or *Mercury-300* spectrometer at operating frequencies of 400/300 MHz (¹H NMR) or 100 / 75 MHz (¹³C NMR). Chemical shifts (δ) are given in ppm relative to residual solvent (usually chloroform δ 7.26 for ¹H NMR or δ 77.23 for proton decoupled ¹³C NMR), and coupling constants (*J*) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet, whereby the prefix *app* is applied in cases where the true multiplicity is unresolved, and *br* when the signal in question is broadened.

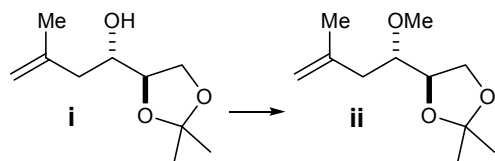
Infrared spectra were recorded on a *Perkin-Elmer I* 1000 series FTIR with wavenumbers expressed in cm⁻¹ using samples prepared as thin films between salt plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Shimadzu 2010-LCMS. Optical rotations were measured at 20 °C on a Rudolph Research Analytical Autopol[®] IV polarimeter.

2. Experimental Procedures



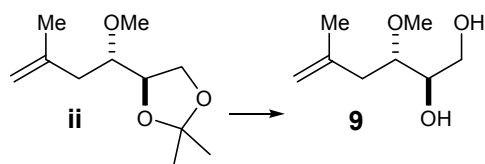
To a round bottom flask containing TMEDA (3.03 mL, 20.00 mmol) and n-BuLi (2.5 M in hexane, 8.0 mL, 20 mmol) in Et₂O (12 mL) was added under N₂ and at –78 °C 2-methylpropene (3.40 g, 60.00 mmol). The reaction was allowed to stir at –78 °C for 1 h and at room temperature overnight. The mixture obtained was added to a stirred solution of (–)-(Ipc)₂BOMe (6.34 g, 20.00 mmol) in Et₂O (20 mL) at –78 °C. After

stirring at –78 °C for 1 h and at room temperature for 1 h, the reaction was cooled to –78 °C and a solution of aldehyde **8** (Ahrendt, K. A.; Williams, R. M. *Org. Lett.* **2004**, *6*, 4539) (2.60 g, 20.00 mmol) in Et₂O (34 mL) was added dropwise. After 1 h, the reaction was quenched by adding pH 7 buffer (120 mL), MeOH (120 mL) and 30% H₂O₂ (60 mL), and stirred at room temperature for 30 min. The crude was extracted with Et₂O and the combined organic phases were washed with water and dried over MgSO₄. After concentration, the residue obtained was purified by FC (silica gel; EtOAc/hexanes 1:4) to give allylic alcohol **i** 2.6 g (70%, dr 95:5) as a colorless oil contaminated with isopinocampheol, and was used without further purification. [α]_D = +16.38 (CHCl₃, *c* = 1.0); ¹H NMR (CDCl₃) δ 1.37 (s, 3H), 1.44 (s, 3H), 1.78 (s, 3H), 2.01 (d, 1H, *J* = 2.4 Hz), 2.11 (dd, 1H, *J* = 9.4, 14.2 Hz), 2.30 (dd, 1H, *J* = 4.0, 14.2 Hz), 3.85 (m, 1H), 4.00 (m, 3H), 4.82 (s, 1H), 4.89 (s, 1H); ¹³C NMR (CDCl₃) δ 22.3, 25.3, 26.6, 41.7, 65.4, 68.8, 78.4, 109.1, 113.7, 141.9; IR ν_{max} 3477, 1219, 1066 cm^{–1}; MS (ES) calculated for C₁₀H₁₈O₃Na [MNa]⁺ 209.12, found 209.5.



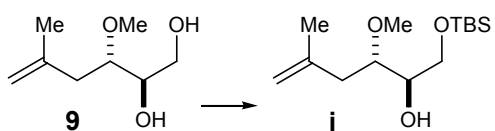
To a suspension of NaH (60% in mineral oil, 620 mg, 15.4 mmol) in THF (70 mL) was added a solution of allylic alcohol **i** (2.6 g, 13.98 mmol) in THF (14 mL) at 0 °C. After stirring at 0 °C for 30 min, MeI (1.05 mL, 16.77 mmol) was added and the reaction was allowed to stir at ambient temperature overnight. The crude was extracted with Et₂O and the combined organic phases were dried over MgSO₄, filtered and

concentrated. The residue obtained was purified by FC (silica gel, Et₂O/Hexanes 1:1) to afford methyl ether **ii** 2.52 g (90%) as a colorless volatile oil. [α]_D = +1.92 (CHCl₃, *c* = 1.0); ¹H NMR (CDCl₃) δ 1.35 (s, 3H), 1.43 (s, 3H), 1.80 (s, 3H), 2.22 (m, 2H), 3.45 (s, 3H), 3.47 (m, 1H), 3.90 (dd, 1H, *J* = 6.4, 7.6 Hz), 4.02 (app t, 1H, *J* = 6.8 Hz), 4.06 (app q, 1H, *J* = 6.4 Hz), 4.80 (d, 1H, *J* = 0.8 Hz), 4.83 (s, 1H); ¹³C NMR (CDCl₃) δ 22.9, 25.3, 26.5, 39.5, 58.8, 65.8, 77.5, 79.7, 109.0, 113.0, 142.4; IR ν_{max} 1219, 1104, 1078 cm^{–1}; MS (ES) calculated for C₁₁H₂₀O₃Na [MNa]⁺ 223.13, found 223.05.



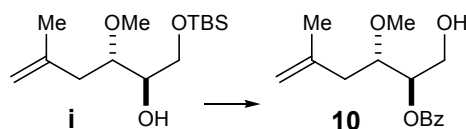
A mixture of the methyl ether **ii** (1.53 g, 7.65 mmol), PPTS (408 mg, 1.63 mmol), and water (2.55 mL) in MeOH (40 mL) was stirred at 50 °C overnight and then brought to room temperature. NaHCO₃ (600 mg, 7.14 mmol) was added and solvent was removed under reduced pressure. The residue obtained was dissolved in EtOAc (50 mL), dried with MgSO₄, filtered and concentrated. The residue obtained was

purified by FC (silica gel, EtOAc) to afford 1.13 g (93%) of compound **9** as colorless oil. [α]_D²⁴ = +29.0 (EtOAc, *c* = 0.29); ¹H NMR (CDCl₃) δ 1.78 (s, 3H), 2.17 (dd, 1H, *J* = 6.0, 14.4 Hz), 2.36 (dd, 1H, *J* = 6.9, 14.4 Hz), 2.53 (bs, 1H), 2.58 (bs, 1H), 3.41 (s, 3H), 3.52 (m, 1H), 3.68 (m, 2H), 3.77 (ddd, 1H, *J* = 1.2, 6.3, 12.0 Hz), 4.79 (bs, 1H), 4.83 (t, 1H, *J* = 1.5 Hz); ¹³C NMR (CDCl₃) δ 22.7, 38.7, 58.3, 63.0, 72.3, 81.8, 113.3, 142.2; IR ν_{max} 3391, 2919, 1646, 1448, 1094 cm^{–1}; MS (ES) calculated for C₈H₁₆O₃Na [MNa]⁺ 183.10, found 183.00.



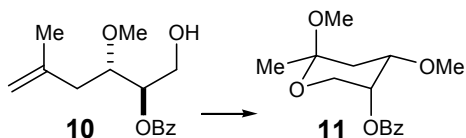
To a solution of compound **9** (640 mg, 4.0 mmol) and imidazole (408 mg, 6.0 mmol) in CH₂Cl₂ (15 mL) was added TBSCl (724 mg, 4.8 mmol) in CH₂Cl₂ (3 mL) at 0 °C. After 30 min, the reaction mixture was washed with sat. NaHCO₃ and water and dried over MgSO₄. After concentration, the residue was purified by FC (silica gel,

hexanes/EtOAc, 10:1) to give **i** 1.04 g (95%) as colorless oil. $[\alpha]_D^{22} = +8.57$ (EtOAc, $c = 0.28$); ^1H NMR (CDCl_3) δ 0.08 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.80 (s, 3H), 2.30 (m, 2H), 2.45 (d, 1H, $J = 3.3$ Hz), 3.40 (s, 3H), 3.42 (m, 1H), 3.69 (m, 3H), 4.81 (m, 2H); ^{13}C NMR (CDCl_3) δ -5.4, 18.3, 22.9, 25.9, 38.5, 58.2, 63.4, 72.7, 79.9, 112.7, 142.9; IR ν_{max} 3468, 1650, 1463, 1255, 1103 cm^{-1} ; MS (ES) calculated for $\text{C}_{14}\text{H}_{30}\text{O}_3\text{SiNa}$ $[\text{MNa}]^+$ 297.19, found 297.10.



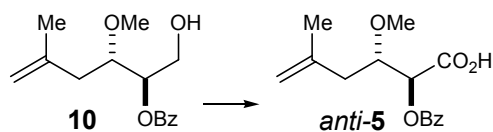
To a solution of **i** (1.00 g, 3.65 mmol) in pyridine (8 mL) was added benzoyl chloride (1.69 mL, 7.30 mmol). After 30 min at room temperature, benzoyl chloride (0.56 mL, 2.43 mmol) was added again and stirred for another 30 min. Sat. NaHCO_3 solution was added and the crude was extracted with EtOAc. The combined organic extracts were

washed with 1 N HCl and water and concentrated. 3N HCl (6 mL) was added to a solution of the crude benzoate in THF (30 mL). After stirring at room temperature for 2 h, NaHCO_3 (2.0 g) was added and the solvent was removed under reduced pressure. The residue obtained was extracted with CH_2Cl_2 and the combined organic extracts were washed with water and dried over MgSO_4 . After removal of solvent, the residue was purified by FC (silica gel, hexanes/EtOAc, 3:1) to give compound **10** (914 mg, 95%) as colorless oil. $[\alpha]_D^{24} = -26.4$ (EtOAc, $c = 0.55$); ^1H NMR (CDCl_3) δ 1.81 (s, 3H), 2.30 (dd, 1H, $J = 6.0, 14.4$ Hz), 2.42 (dd, 1H, $J = 7.5, 14.4$ Hz), 3.49 (s, 3H), 3.80 (ddd, 1H, $J = 3.9, 6.0, 7.5$ Hz), 3.92 (dd, 1H, $J = 3.9, 12.0$ Hz), 3.97 (dd, $J = 4.8, 12.0$ Hz), 4.80 (m, 1H), 4.84 (m, 1H), 5.13 (ddd, 1H, $J = 3.9, 3.9, 4.8$ Hz), 7.45 (m, 2H), 7.58 (m, 1H), 8.07 (m, 2H); ^{13}C NMR (CDCl_3) δ 22.6, 39.6, 58.9, 61.8, 76.2, 80.2, 113.5, 128.4, 129.7, 129.9, 133.2, 141.6, 166.3; IR ν_{max} 3439, 2918, 1715, 1250, 1272, 1114 cm^{-1} ; MS (ES) calculated for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{MNa}]^+$ 287.13, found 287.00; calculated for $\text{C}_{16}\text{H}_{24}\text{O}_5\text{Na}$ $[\text{MNa}+\text{MeOH}]^+$ 319.15, found 319.05.



Ozone was bubbled through a solution of compound **10** (30 mg, 114 μmol) in CH_2Cl_2 (10 mL) at -78°C until the solution became slightly blue. Me_2S (1 mL) was added and the resultant solution was stirred at room temperature overnight. After removal of solvent, the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 1:1) to give a

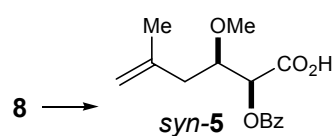
mixture of four hemiketals (24 mg, 89%) as viscous oil. To a solution of hemiketals (24 mg, 90 μmol) in MeOH (3 mL) was added $\text{HC}(\text{OMe})_3$ (0.2 mL) and a catalytic amount of $p\text{TsoH}$. After stirring at room temperature for 1 h, Et_3N (50 μL) was added and stirred for 5 min. The solvent was removed under reduced pressure and the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 3:1) to give compound **11** (20 mg, 80%) as a colorless oil. ^1H NMR (CDCl_3) δ 1.42 (s, 3H), 1.96 (dd, 1H, $J = 12.0, 12.4$ Hz), 2.06 (dd, 1H, $J = 4.8, 12.4$ Hz), 3.23 (s, 3H), 3.37 (s, 3H), 3.75 (dd, 1H, $J = 1.0, 12.8$ Hz), 3.81 (ddd, 1H, $J = 2.8, 4.8, 12.0$ Hz), 3.92 (dd, 1H, $J = 2.0, 12.8$ Hz), 5.44 (ddd, 1H, $J = 1.0, 2.0, 2.8$ Hz), 7.44 (t, 2H, $J = 7.6$ Hz), 7.56 (t, 1H, $J = 7.6$ Hz), 8.08 (d, 2H, $J = 7.6$ Hz); ^{13}C NMR (CDCl_3) δ 23.3, 37.2, 48.2, 56.1, 62.3, 66.5, 73.3, 99.7, 128.3, 129.8, 133.0, 166.2; MS (ES) calculated for $\text{C}_{15}\text{H}_{20}\text{O}_5\text{Na}$ $[\text{MNa}]^+$ 303.12, found 303.00.



To a mixture of **10** (115 mg, 435 μmol) and NaHCO_3 (73 mg, 870 μmol) in CH_2Cl_2 (6 mL) was added Dess-Martin Periodinane (369 mg, 870 μmol) at 0°C . After stirring 1 h at room temperature, ether (20 mL) and 10% $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) was added. After 5 min, the organic layer was separated and washed thoroughly with sat. NaHCO_3 and

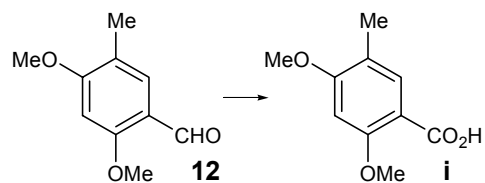
water and dried over MgSO_4 . Filtration and concentration afforded the crude aldehyde. To a mixture of the crude aldehyde, $t\text{-BuOH}$ (13 mL), water (3.3 mL) and 2-methyl-2-butene (3.3 mL) was added NaH_2PO_4 (197 mg, 1.43 mmol) and NaClO_2 (197 mg, 1.74 mmol) at 0°C . After stirring at room temperature for 1.5 h, EtOAc (30 mL) and 0.05 N NaHSO_4 (30 mL) was added. After 5 min, the crude was extracted with EtOAc and the combined organic extracts were washed with water and dried over MgSO_4 . After concentration, the residue was purified by column chromatography (silica gel, MeOH/ CH_2Cl_2 , 1:5) to give **anti-5** (105 mg, 87%) as a viscous oil. $[\alpha]_D^{22} = -13.6$ (EtOAc, $c = 0.36$); ^1H NMR (CDCl_3) δ 1.68 (s, 3H), 2.31 (dd, 1H, $J = 3.6, 14.0$ Hz), 2.41 (dd, 1H, $J = 8.4, 14.0$ Hz), 3.45 (s, 3H), 3.86 (m, 1H), 4.76 (bs, 2H), 5.45 (bs, 1H), 7.38 (m, 2H), 7.52 (m, 1H), 8.02 (m, 2H); ^{13}C NMR

(CDCl₃) δ 22.5, 38.7, 57.9, 73.7, 79.5, 113.0, 128.2, 129.4, 129.9, 133.2, 141.8, 166.1, 174.2; IR ν_{\max} 3438, 2918, 1726, 1601, 1273, 1116 cm⁻¹; MS (ES) calculated for C₁₅H₁₈O₅Na [MNa]⁺ 301.11, found 301.00.



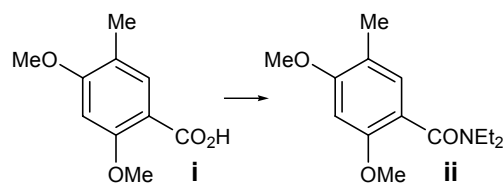
Syn-5 was synthesized from aldehyde **8** using the similar procedure as the synthesis of **anti-5**, but starting with enantiomeric borane ((+)-(Ipc)₂BOMe). ¹H NMR (CDCl₃) δ 1.75 (s, 3H), 2.33 (dd, 1H, J = 7.8, 13.8 Hz), 2.45 (dd, 1H, J = 6.6, 13.8 Hz), 3.42 (s, 3H), 4.04 (ddd, 1H, J = 2.1, 6.6, 7.8 Hz), 4.68 (bs, 1H), 4.79 (t, 1H, J = 1.5 Hz), 5.25 (d, 1H, J = 2.1 Hz), 7.42 (m, 2H), 7.55 (m, 1H), 8.09 (m, 2H); ¹³C NMR (CDCl₃)

δ 22.5, 38.2, 58.2, 73.3, 78.8, 114.1, 128.4, 129.2, 129.9, 133.3, 140.9, 166.1, 172.9; IR ν_{\max} 3446, 2938, 1726, 1602, 1266, 1107, 1072 cm⁻¹; MS (ES) calculated for C₁₅H₁₈O₅Na [MNa]⁺ 301.11, found 301.00.



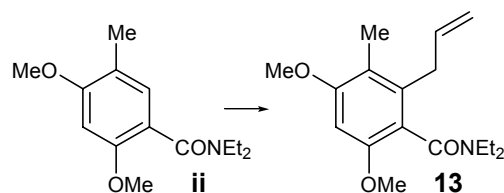
To a solution of benzaldehyde **12** (Lambooy, J. P. *J. Am. Chem. Soc.* **1956**, 78, 771) (4.19 g, 23.28 mmol) in DMSO (67 mL) were added NaH₂PO₄ (8.03 g, 58.20 mmol) in H₂O (9 mL) and NaClO₂ (5.26 g, 46.56 mmol) in H₂O (33 mL) at 10 °C. After stirring overnight at room temperature, sat Na₂CO₃ (200 mL) was added. After 5 min, the crude was extracted with EtOAc (100 mL) and the aqueous phase was

acidified with *conc.* HCl to pH 2. The white precipitate that formed was collected by filtration to give acid **i** (3.88 g, 85%). ¹H NMR (CDCl₃) δ 2.16 (s, 3H), 3.92 (s, 3H), 4.07 (s, 3H), 6.46 (s, 1H), 7.91 (1H, d, J = 0.8 Hz), 10.61 (br, 1H); ¹³C NMR (CDCl₃) δ 15.1, 55.6, 56.7, 94.1, 108.8, 120.6, 134.7, 158.2, 162.9, 165.6; IR ν_{\max} 3242, 1725, 1621, 1280, 1021, 828 cm⁻¹; MS calculated for C₁₀H₁₃O₄ [MH]⁺ 197.08, found 197.05; calculated for C₁₀H₁₂O₄Na [MNa]⁺ 219.06, found, 219.00.



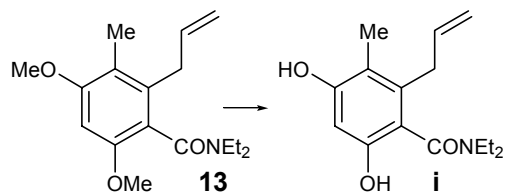
To a solution of benzoic acid **i** (3.88 g, 19.79 mmol) in benzene (110 mL) was added dropwise thionyl chloride (8.52 mL, 77 mmol) at room temperature. The reaction mixture was cooled down after refluxing for 2 h. The solvent and excess of thionyl chloride were removed under reduce pressure to give crude acid chloride. To a solution of crude acid chloride in benzene (56 mL) was added dropwise diethylamine (6.14

mL, 59.38 mmol) at 0 °C. After stirring 2 h at 0 °C and overnight at room temperature, the reaction was concentrated and the crude oil was purified by FC (silica gel, EtOAc/Hexanes/NEt₃ 9:1:0.05) to afford compound **ii** (4.82 g, 97%). ¹H NMR (CDCl₃) δ 1.03 (t, 3H, J = 7.2 Hz), 1.23 (t, 3H, J = 7.2 Hz), 2.13 (s, 3H), 3.17 (q, 2H, J = 7.2 Hz), 3.55 (q, 2H, J = 7.2 Hz), 3.81 (s, 3H), 3.85 (s, 3H), 6.41 (s, 1H), 6.95 (s, 1H); ¹³C NMR (CDCl₃) δ 12.9, 14.0, 15.2, 38.8, 42.8, 55.4, 55.9, 95.0, 118.5, 118.6, 129.2, 154.5, 158.7, 169.0; IR ν_{\max} 1614, 1462, 1207, 1143, 1033 cm⁻¹; MS (ES) calculated for C₁₄H₂₂NO₃ [MH]⁺ 252.16, found 252.10.

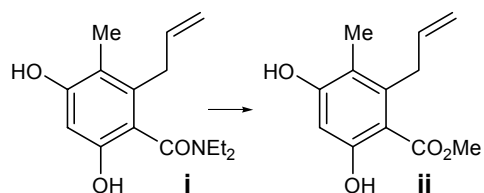


To a solution of amide **ii** (1.61 g, 6.40 mmol) in THF (16 mL) was added *sec*-BuLi (1.4 M in cyclohexane, 10.06 mL, 14.09 mmol) at -78 °C dropwise. After 1 h at -78 °C, CuBr·Me₂S (2.63 g, 12.81 mmol) was added and the reaction was allowed to warm to -15 °C. After 30 min, allylbromide (1.12 mL, 12.81 mmol) was added at -78 °C and kept at this temperature for 1 h. The reaction was warmed to room

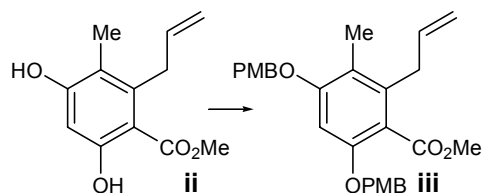
temperature, filtered through a pad of silica gel and washed with EtOAc. The filtrate was dried over MgSO₄, concentrated and purified by FC (silica gel, EtOAc/Hexanes/NEt₃ 85:15:0.5) to give (1.41 g, 76%) of compound **13**. ¹H NMR (CDCl₃) δ 1.02 (t, 3H, J = 6.8 Hz), 1.23 (t, 3H, J = 7.2 Hz), 2.09 (s, 3H), 3.04 (dt, 1H, J = 7.6 Hz), 3.15 (dt, 1H, J = 7.6 Hz), 3.24-3.40 (3H, m), 3.79 (s, 3H), 3.84 (s, 3H), 4.97 (m, 2H), 5.84 (m, 1H), 6.36 (m, 1H); ¹³C NMR (CDCl₃) δ 10.8, 12.5, 13.5, 34.7, 38.1, 42.7, 55.4, 55.5, 93.2, 115.3, 117.9, 119.2, 135.4, 136.1, 154.0, 158.3, 168.5; IR (film) 1626, 1594, 1460, 1436, 1318, 1207, 1140, 1094 cm⁻¹; MS (ES) calculated for C₁₇H₂₆NO₃ [MH]⁺ 292.19, found 292.10.



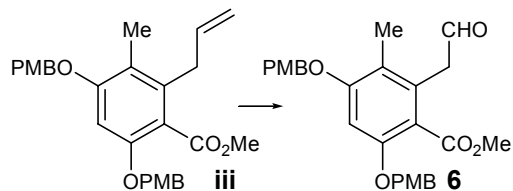
To a solution of **13** (1.00 g, 3.61 mmol) in CH_2Cl_2 (60 mL) was added a solution of BBr_3 (2.05 mL, 21.7 mmol) in CH_2Cl_2 (20 mL) at -78°C . After stirring at -78°C for 30 min, 0°C for 4 h and 25°C for 1 h, water was added at 0°C and the crude was extracted with CH_2Cl_2 . The combined extracts were washed with water, dried over MgSO_4 and concentrated. The residue obtained was purified by FC (silica gel; $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 20:1) to give **i** (730 mg, 81%) as white solid: ^1H NMR (CD_3OD) δ 1.07 (t, 3H, $J = 6.9$ Hz), 1.22 (t, 3H, $J = 6.9$ Hz), 2.04 (s, 3H), 3.11–3.45 (m, 5H), 3.65 (m, 1H), 4.98 (m, 2H), 5.82 (m, 1H), 6.28 (s, 1H); ^{13}C NMR (CD_3OD) δ 11.3, 13.1, 14.1, 36.0, 40.2, 45.0, 101.6, 116.0, 116.3, 117.5, 137.1, 137.3, 153.1, 157.8, 172.3; IR ν_{max} 3307, 1600, 1577, 1439, 1144 cm^{-1} ; MS (ES) calculated for $\text{C}_{15}\text{H}_{22}\text{NO}_3$ $[\text{MH}]^+$ 264.16, found 264.10; calculated for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}$ $[\text{MNa}]^+$ 286.14, found 286.05



To a solution of **i** (845 mg, 3.21 mmol) in CH_2Cl_2 (25 mL) was added Me_3OBF_4 (590 mg, 3.99 mmol) at room temperature. After 20 h, the reaction was concentrated and mixed with MeOH (9 mL) and saturated Na_2CO_3 solution (9 mL). After stirring at room temperature for 6 h, ether (50 mL) was added and the aqueous phase was adjusted to pH 2 using 0.5 N HCl. The crude was extracted with ether, and the combined ether extracts were washed with water and dried over MgSO_4 . After concentration, the residue obtained was purified by FC (silica gel; Hexanes/ EtOAc , 6:1) to give **ii** (520 mg, 73%) as white solid: ^1H NMR (CDCl_3) δ 2.11 (s, 3H), 3.70 (dt, 2H, $J = 1.7, 5.8$ Hz), 3.91 (s, 3H), 4.95 (m, 2H), 5.52 (s, 1H), 5.91 (m, 1H), 6.33 (s, 1H), 11.30 (s, 1H); ^{13}C NMR (CDCl_3) δ 10.9, 35.6, 52.0, 101.5, 106.1, 114.9, 117.2, 136.2, 142.1, 159.2, 161.6, 171.9; IR ν_{max} 3330, 1654, 1597, 1439, 1329, 1262, 1159 cm^{-1} ; MS (ES) calculated for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{Na}$ $[\text{MNa}+\text{MeCN}]^+$ 286.11, found 286.05

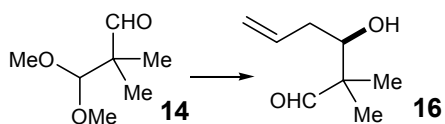


The mixture of compound **ii** (520 mg, 2.34 mmol), K_2CO_3 (971 mg, 7.03 mmol), PMBCl (953 μL , 7.02 mmol), Bu_4NI (173 mg, 0.47 mmol) and DMF (30 mL) was heated at 80°C for 20 h. Remove DMF under vacuum (5 mmHg) at 50°C , add water and the crude was extracted with CH_2Cl_2 . The combined organic extracts were washed with water, dried over MgSO_4 and concentrated. The residue obtained was purified by FC (silica gel; Hexanes/ EtOAc , 9:1) to give **iii** (990 mg, 92%) as white solid: ^1H NMR (CDCl_3) δ 2.12 (s, 3H), 3.35 (m, 2H), 3.78 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 4.93 (s, 2H), 4.97 (s, 2H), 4.99 (m, 2H), 5.85 (m, 1H), 6.46 (s, 1H), 6.91 (m, 4H), 7.27 (m, 4H); ^{13}C NMR (CDCl_3) δ 11.0, 35.0, 51.9, 55.15, 55.18, 70.1, 70.6, 97.1, 113.8, 113.9, 115.6, 117.7, 118.6, 128.6, 128.8, 128.9, 135.4, 136.9, 154.4, 158.1, 159.2, 159.3, 169.2; IR ν_{max} 2949, 1725, 1593, 1515, 1250, 1155 cm^{-1} ; MS (ES) calculated for $\text{C}_{28}\text{H}_{30}\text{O}_6\text{Na}$ $[\text{MNa}]^+$ 485.19, found 485.10.



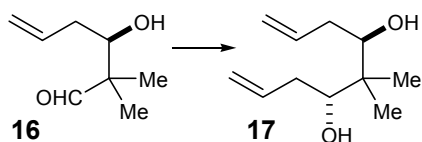
To a solution of **iii** (462 mg, 1 mmol) in THF (5 mL) and H_2O (1 mL) were added 4-methylmorpholine-*N*-oxide (234 mg, 2 mmol) and OsO_4 (0.1 M solution in *t*-BuOH, 800 μL , 0.08 mmol) at 0°C . After stirring at ambient temperature for 12 h, 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution was added. After 30 min, the crude was extracted with EtOAc and the combined organic extracts were washed with water and dried over MgSO_4 . After concentration, the residue obtained was filtered through a short column (silica gel) and washed with EtOAc . Removal of the solvent from the combined filtrate gave the crude diol. NaIO_4 (321 mg, 1.5 mmol) was added to a solution of crude diol in 90% MeOH (25 mL). After stirring at room temperature for 1 h, EtOAc (50 mL) was added and the reaction mixture was washed with water and dried over MgSO_4 . After concentration, the residue obtained was purified by FC (silica gel; $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 20:1) to give compound **6** (408 mg, 88%) as white crystals: ^1H NMR (CDCl_3) δ 2.08 (s, 3H), 3.68 (d, 2H, $J = 1.8$ Hz), 3.81 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 4.97 (s, 2H), 5.01 (s, 2H), 6.53 (s, 1H), 6.91 (m, 4H), 7.30 (m, 4H), 9.64 (t, 1H, $J = 1.8$ Hz); ^{13}C NMR (CDCl_3) δ 11.6, 45.8, 52.1, 55.2, 55.2, 70.1, 70.8, 98.2, 113.9, 114.0, 117.6, 119.5, 128.5, 128.6,

128.7, 128.8, 130.7, 155.3, 158.6, 159.3, 159.4, 168.6, 198.6; IR ν_{\max} 3000, 2951, 1722, 1594, 1515, 1250, 1156 cm^{-1} ; MS (ES) calculated for $\text{C}_{27}\text{H}_{28}\text{O}_7\text{Na}$ $[\text{MNa}]^+$ 487.17, found 487.10.



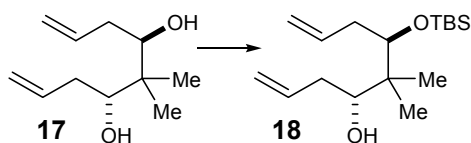
To a solution of **14** (Johnson, P. R.; White, J. D. *J. Org. Chem.* **1984**, *49*, 4424) (2.0 g, 14.1 mmol) in toluene (20 mL) was added allylsilane **15** (5.69 g, 21.1 mmol) at -15°C . After 48 h at -10°C , 0.5 N HCl (20 mL) was added to the reaction mixture and stirred at room temperature for 30 min.

The crude was extracted with ether and combined organic extracts were washed with water, sat. NaHCO_3 , brine and dried over MgSO_4 . After concentration, the residue was purified by FC (silica gel; hexanes/EtOAc, 15:1) to give **16** (1.38 g, 69%, 94% *ee*) as a colorless oil: $[\alpha]_D^{23} = +3.73$ (CH_2Cl_2 , $c = 2.0$); ^1H NMR (CDCl_3) δ 1.08 (s, 3H), 1.11 (s, 3H), 2.07 (m, 1H), 2.15 (d, 1H, $J = 3.6$ Hz), 2.32 (m, 1H), 3.78 (dt, 1H, $J = 3.6, 10.4$ Hz), 5.17 (m, 2H), 5.85 (m, 1H), 9.57 (s, 1H); ^{13}C NMR (CDCl_3) δ 16.5, 19.0, 36.2, 50.0, 73.8, 118.6, 134.9, 206.2; IR ν_{\max} 3417, 3077, 2977, 1724, 1642 cm^{-1} . MS (ES) calculated for $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Na}$ $[\text{M}_2\text{Na}]^+$ 307.19, found 307.10. The enantiomeric excess was determined from the H NMR spectrum of the Mosher ester derivative prepared with (*S*)-(-)-MTPA: major isomer has Me-resonances at 1.064 and 1.067 ppm; the minor isomer has Me-resonances at 1.094 and 1.100 ppm. Integration of the Me-resonances was used to calculate an *ee* of 94%.



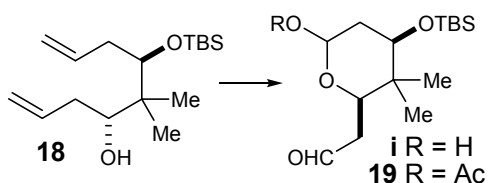
To a solution of **16** (1.30 g, 9.15 mmol) in toluene (15 mL) was added allylsilane **15** (4.93 g, 18.3 mmol) at -15°C . After kept at this temperature for 20 h, 0.5 N HCl (15 mL) was added to the reaction mixture and stirred at room temperature for 15 min. The crude was extracted with ether and the combined organic extracts were washed with water, sat. NaHCO_3 , brine and

dried over MgSO_4 . After concentration, the residue was purified by FC (silica gel; hexanes/EtOAc, 15:1) to give **17** (1.33 g, 79%, *dr* = 17:1) as white solid. $[\alpha]_D^{22} = +21.4$ (CHCl_3 , $c = 1.43$); ^1H NMR (CDCl_3) δ 0.94 (s, 6H), 2.11 (m, 2H), 2.32 (m, 2H), 3.13 (dm, 2H, $J = 3.4$ Hz), 3.57 (ddd, 2H, $J = 2.9, 3.7, 10.7$ Hz), 5.16 (m, 4H), 5.90 (m, 2H); ^{13}C NMR (CDCl_3) δ 20.9, 36.4, 40.0, 77.4, 117.6, 136.2; IR ν_{\max} 3350, 3077, 2974, 1641, 1471, 1431 cm^{-1} ; MS (ES) calculated for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{MNa}]^+$ 207.14, found 207.05. The ^{13}C NMR data matches the reported data for racemic **17** (Trieselmann, T.; Hoffmann, R. W.; Menzel, K. *Eur. J. Org. Chem.* **2002**, 1292).



To a solution of **17** (465 mg, 2.53 mmol) and 2,6-lutidine (0.44 mL, 3.80 mmol) in CH_2Cl_2 (20 mL) was added TBSOTf (0.64 mL, 2.78 mmol) at 0°C . After stirring for 10 min, MeOH (1 mL) was added and stirred for 10 min. The solvent was removed under vacuo and the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 50:1) to give **18** (692 mg,

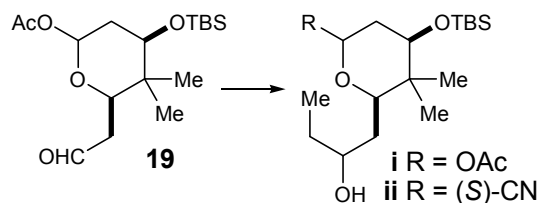
92%) as a colorless oil: $[\alpha]_D^{23} = +29.2$ (EtOAc, $c = 1.05$); ^1H NMR (CDCl_3) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.80 (s, 3H), 0.90 (s, 9H), 1.00 (s, 3H), 2.13 (m, 2H), 2.33 (m, 1H), 2.52 (m, 1H), 3.57 (dd, 1H, $J = 4.6, 6.4$ Hz), 3.87 (dd, 1H, $J = 4.1, 8.7$ Hz), 5.10 (m, 4H), 5.91 (m, 2H); ^{13}C NMR (CDCl_3) δ -4.2, -3.8, 18.1, 20.4, 23.3, 26.0, 36.4, 37.7, 41.2, 75.0, 83.2, 116.3, 116.8, 136.5, 136.8; IR ν_{\max} 3494, 3077, 2955, 1641, 1470, 1255 cm^{-1} ; MS (ES) calculated for $\text{C}_{17}\text{H}_{35}\text{O}_2\text{Si}$ $[\text{MH}]^+$ 299.24, found 299.15; calculated for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{SiNa}$ $[\text{MNa}]^+$ 321.22, found 321.15.



Ozone was bubbled through a solution of **18** (692 mg, 2.32 mmol) in CH_2Cl_2 (50 mL) at -78°C until the solution became slightly blue. Ph_3P (2.43 g, 9.28 mmol) was added and the resultant solution was stirred at room temperature overnight. After concentration, the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 10:1 to 3:1) to give hemiacetal **i** (692 mg, 99%) as viscous oil. To a solution of **i** in CH_2Cl_2

(18 mL) was added Et_3N (1.27 mL, 9.19 mmol), DMAP (50 mg) and Ac_2O (431 μL , 4.59 mmol) successively at 0°C . After 10 min, sat NaHCO_3 (20 mL) was added and the crude was extracted with ether. The combined ether extracts were washed with water, dried over MgSO_4 and concentrated. The residue obtained was purified by column chromatography (silica gel; hexanes/EtOAc, 6:1) to give **19** (633 mg, 81%) as a mixture of two epimers and was used without further separation. The compound with axial OAc has ^1H NMR (CDCl_3) δ 2.13 (s, 3H), 3.75 (dd, 1H,

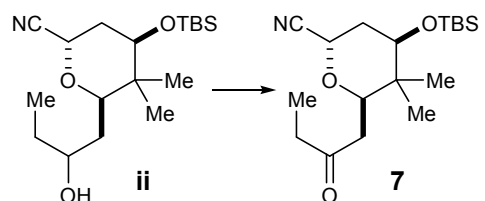
$J = 5.2, 11.3$ Hz), 4.13 (dd, 1H, $J = 2.9, 10.1$ Hz), 6.12 (dd, 1H, $J = 0.9, 3.7$ Hz), 9.71 (t, 1H, $J = 1.5$ Hz); The compound with equatorial OAc has ^1H NMR (CDCl_3) δ 2.09 (s, 3H), 3.49 (dd, 1H, $J = 4.9, 11.6$ Hz), 3.71 (dd, 1H, $J = 3.1, 9.8$ Hz), 5.68 (dd, 1H, $J = 2.8, 10.1$ Hz), 9.74 (t, 1H, $J = 2.1$ Hz); IR ν_{max} 2929, 2856, 1727, 1367, 1235, 1076, 833 cm^{-1} ; MS (ES) calculated for $\text{C}_{18}\text{H}_{36}\text{O}_6\text{SiNa}$ [$\text{MNa} + \text{MeOH}$] $^+$ 399.22, found 399.15



To a suspension of (*R,R*)-1,2-bis(trifluoromethanesulfonamido) cyclohexane in anhydrous toluene (10 mL) was added $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.16 mL, 7.32 mmol) at room temperature. After stirring at 45 $^\circ\text{C}$ for 40 min, the reaction was cooled to -78 $^\circ\text{C}$ and ZnEt_2 (1.0 M in hexanes, 7.32 mL, 7.32 mmol) was added dropwise. After 10 min, a solution of compound **19** (630 mg, 1.83 mmol) in toluene (10 mL) was added. After stirring for 8 h at -10 $^\circ\text{C}$, sat NH_4Cl (30 mL) was

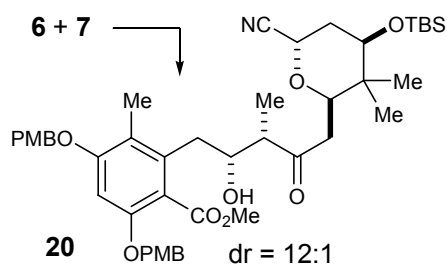
added and the reaction mixture was filtered through a pad of celite. The crude was extracted with EtOAc and the combined organic phases were washed with water and brine, dried over MgSO_4 and concentrated. The residue obtained was purified by column chromatography (silica gel; hexanes/EtOAc, 20:1) to give **i** (569 mg, 84%) as a mixture of four diastereomers and was used without further separation.

TMSCN (0.81 mL, 6.09 mmol) was added to **i** (569 mg, 1.53 mmol) and stirred at room temperature for 15 min. After cooled to 0 $^\circ\text{C}$, MeCN (20 mL), TMSCN (0.41 mL, 3.08 mmol) and ZnI_2 (114 mg, 0.36 mmol) were added successively and stirred for 40 min. Sat. NaHCO_3 solution (20 mL) was added and the reaction was extracted with EtOAc. The combined organic extracts were shaken with 1N HCl for 20 min and washed with aq. NaHCO_3 and water and dried over MgSO_4 . After concentration, the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 8:1) to give compound **ii** (471 mg, 91%) as a mixture of two alcohol epimers in the ratio of 3:1. The major isomer is a colorless oil. $[\alpha]_D^{24} = +67.6$ (EtOAc, $c = 0.55$); ^1H NMR (CDCl_3) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.81 (s, 3H), 0.87 (s, 9H), 0.89 (s, 3H), 0.93 (t, 3H, $J = 7.4$ Hz), 1.49 (m, 4H), 1.76 (ddd, 1H, $J = 1.2, 4.5, 13.8$ Hz), 1.97 (ddd, 1H, $J = 6.0, 11.7, 13.8$ Hz), 2.10 (s, 1H), 3.65 (m, 2H), 3.76 (dd, 1H, $J = 5.1, 6.6$ Hz), 4.83 (dd, 1H, $J = 1.2, 6.0$ Hz); ^{13}C NMR (CDCl_3) δ -5.1, -4.3, 10.1, 12.3, 17.9, 22.5, 25.6, 30.4, 33.5, 35.4, 39.5, 63.7, 69.7, 72.3, 78.5, 117.8; IR ν_{max} 3436, 2959, 1472, 1258, 1104, 1082, 880 cm^{-1} ; MS (ES) calculated for $\text{C}_{18}\text{H}_{35}\text{O}_3\text{NSiNa}$ [MNa] $^+$ 364.23, found 364.20. The minor is a colorless oil: $[\alpha]_D^{25} = +50.2$ (EtOAc, $c = 0.69$); ^1H NMR (CDCl_3) δ 0.06 (s, 3H), 0.07 (s, 3H), 0.85 (s, 3H), 0.88 (s, 9H), 0.89 (s, 3H), 0.94 (t, 3H, $J = 7.4$ Hz), 1.49 (m, 2H), 1.60 (dd, 1H, $J = 7.5, 10.2$ Hz), 1.68 (ddd, 1H, $J = 2.7, 3.3, 11.4$ Hz), 1.75 (ddd, 1H, $J = 1.2, 4.5, 13.5$ Hz), 1.99 (ddd, 1H, $J = 6.0, 11.4, 13.5$ Hz), 2.03 (s, 1H), 3.69 (m, 3H), 4.88 (dd, 1H, $J = 1.2, 6.0$ Hz); ^{13}C NMR (CDCl_3) δ -5.02, -4.22, 9.66, 12.35, 17.90, 22.60, 25.66, 29.76, 33.41, 35.11, 39.88, 63.81, 71.99, 72.65, 82.85, 117.35; IR ν_{max} 3306, 2857, 1461, 1082, 884 cm^{-1} ; MS (ES) calculated for $\text{C}_{18}\text{H}_{35}\text{O}_3\text{NSiNa}$ [MNa] $^+$ 364.23, found 364.20.



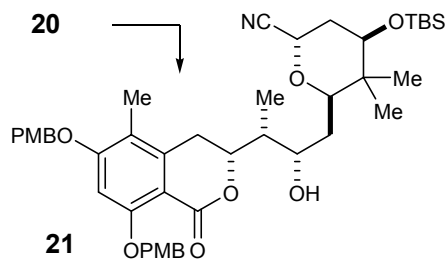
To a solution of **ii** (468 mg, 1.38 mmol) in CH_2Cl_2 (30 mL) was added Dess-Martin periodinane (2.0 g, 4.72 mmol) at 0 $^\circ\text{C}$. After stirring at ambient temperature for 3 h, 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) was added and stirred for 10 min. The reaction was extracted with CH_2Cl_2 and the combined extracts were washed with NaHCO_3 , water and dried over MgSO_4 . After concentration, the residue obtained was purified by FC (silica gel; hexanes/EtOAc, 10:1) to give compound **7** (444 mg, 95%) as

white solid: $[\alpha]_D^{24} = +40.6$ (EtOAc, $c = 0.16$); ^1H NMR (CDCl_3) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.85 (s, 3H), 0.90 (s, 9H), 0.91 (s, 3H), 1.07 (t, 3H, $J = 7.3$ Hz), 1.79 (ddd, 1H, $J = 1.5, 4.6, 13.7$ Hz), 1.98 (ddd, 1H, $J = 6.1, 11.3, 13.7$ Hz), 2.52 (m, 4H), 3.74 (dd, 1H, $J = 4.6, 11.3$ Hz), 4.07 (dd, 1H, $J = 2.8, 9.8$ Hz), 4.80 (dd, 1H, $J = 1.5, 6.1$ Hz). ^{13}C NMR (CDCl_3) δ -5.0, -4.2, 7.5, 12.5, 17.9, 22.7, 25.7, 33.6, 36.1, 39.4, 42.4, 63.7, 72.1, 77.8, 117.2, 208.4; IR ν_{max} 3402, 2958, 1716, 1462, 1256, 1099, 885 cm^{-1} .



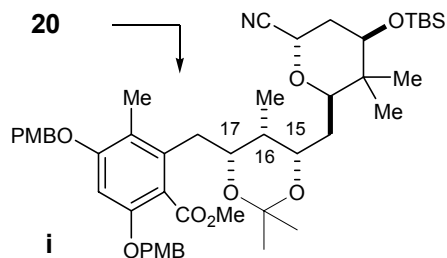
To a solution of compound **7** (100 mg, 0.296 mmol) in CH_2Cl_2 (3 mL) was added PhBCl_2 (46 μL , 0.35 mmol) at -78°C . After 20 min, DIPEA (75 μL , 0.43 mmol) was added. The reaction was stirred at -78°C for 1 h and 0°C for 1 h. Aldehyde **6** (165 mg, 0.35 mmol) in CH_2Cl_2 (1.5 mL) was added at -78°C and the reaction was kept at this temperature for 3.5 h. A mixture of MeOH (4 mL) and pH 7 buffer (4 mL) was added -78°C and the pH was adjusted to neutral using pH 8 buffer. After stirring at 0°C for 1.5 h, the reaction was extracted with CH_2Cl_2 and the combined organic phases were washed with water and dried over MgSO_4 . After concentration, the residue

was purified by FC (silica gel; $\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 20:1) to give compound **20** (210 mg, 88%, $dr = 12:1$) as a white foam: $[\alpha]_D^{24} = +42.3$ (EtOAc , $c = 0.40$); ^1H NMR (CDCl_3) δ 0.07 (s, 3H), 0.09 (s, 3H), 0.86 (s, 3H), 0.90 (s, 9H), 0.92 (s, 3H), 1.21 (d, 3H, $J = 7.0$ Hz), 1.77 (ddd, 1H, $J = 1.3, 4.6, 13.6$ Hz), 1.96 (ddd, 1H, $J = 6.0, 11.5, 13.6$ Hz), 2.17 (s, 3H), 2.57 (m, 2H), 2.73 (m, 2H), 2.88 (dd, 1H, $J = 3.3, 14.3$ Hz), 3.75 (m, 2H), 3.80 (s, 3H), 3.82 (s, 3H), 3.85 (s, 3H), 4.02 (m, 1H), 4.13 (dd, 1H, $J = 2.1, 9.0$ Hz), 4.77 (d, 1H, 5.1 Hz), 4.95 (s, 4H), 6.47 (s, 3H), 6.89 (m, 4H), 7.28 (m, 4H); ^{13}C NMR (CDCl_3) δ -5.1, -4.3, 11.4, 11.6, 12.6, 17.8, 22.6, 25.6, 33.6, 35.2, 39.2, 42.0, 52.5, 52.7, 55.1, 55.1, 63.6, 70.0, 70.7, 71.4, 72.1, 77.3, 97.2, 113.7, 113.9, 117.2, 117.3, 118.7, 128.55, 128.64, 128.7, 136.6, 155.0, 158.8, 159.2, 159.3, 170.8, 210.5; IR ν_{max} 3430, 2954, 1715, 1593, 1515, 1250, 1159, 1082 cm^{-1} ; MS (ES) calculated for $\text{C}_{45}\text{H}_{61}\text{O}_{10}\text{NSiNa}$ $[\text{MNa}]^+$ 826.40, found 826.35.



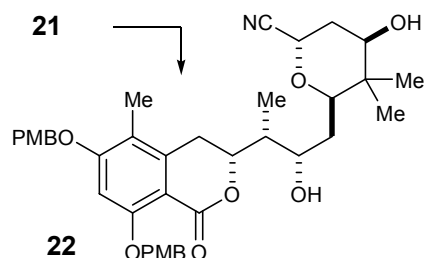
To a solution of **20** (100 mg, 125 μmol) in anhydrous THF (10 mL) was added catecholborane (1.0 M in THF, 3.74 mL, 3.74 mmol) at -78°C . After stirring at 0°C for 20 h, 2 N NaOH (12 mL) was added and the resultant reaction mixture was stirred at ambient temperature for 0.5 h. The reaction was extracted by CH_2Cl_2 and the combined organic extracts were washed with 1 N NaOH solution until the aqueous phase is colorless and then washed with water. The extracts were dried over MgSO_4 and concentrated to give a white solid in quantitative yield, which is a 8:1 mixture of compound **21** and its diastereomer. Pure compound **21** was obtained

through recrystallization from $\text{CH}_2\text{Cl}_2/\text{acetone}$. $[\alpha]_D^{22} = 39.4$ (CH_2Cl_2 , $c = 0.20$); ^1H NMR (CDCl_3) δ 0.08 (s, 3H), 0.10 (s, 3H), 0.88 (s, 3H), 0.90 (s, 9H), 0.93 (s, 3H), 1.12 (d, 3H, $J = 7.2$ Hz), 1.74 (t, 2H, $J = 6.0$ Hz), 1.79 (dd, 1H, $J = 4.6, 13.7$ Hz), 1.91 (m, 1H), 2.01 (ddd, 1H, $J = 6.2, 11.9, 13.7$ Hz), 2.10 (s, 3H), 2.83 (dd, 1H, $J = 12.0, 16.3$ Hz), 2.96 (dd, 1H, $J = 2.6, 16.3$ Hz), 3.68 (m, 2H), 3.80 (s, 3H), 3.82 (s, 3H), 4.07 (m, 1H), 4.41 (ddd, 1H, $J = 2.7, 4.9, 12.0$ Hz), 4.87 (d, 1H, $J = 5.3$ Hz), 4.98 (s, 2H), 5.09 (d, 1H, $J = 12.0$ Hz), 5.16 (d, 1H, $J = 12.0$ Hz), 6.49 (s, 1H), 6.90 (m, 4H), 7.30 (d, 2H, $J = 8.6$ Hz), 7.44 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (CDCl_3) δ -5.0, -4.2, 8.8, 11.1, 12.4, 17.9, 22.7, 25.7, 29.6, 32.9, 33.4, 40.0, 41.5, 55.2, 55.3, 63.8, 69.9, 70.9, 71.97, 72.0, 78.7, 83.0, 98.2, 107.5, 113.9, 114.0, 116.0, 117.4, 128.3, 128.5, 128.8, 141.4, 159.2, 159.5, 160.2, 161.0, 163.1; IR ν_{max} 3364, 1671, 1588, 1515, 1249, 1098 cm^{-1} ; MS (ES) calculated for $\text{C}_{44}\text{H}_{59}\text{O}_9\text{NSiNa}$ $[\text{MNa}]^+$ 796.39, found 796.50; calculated for $\text{C}_{44}\text{H}_{59}\text{NO}_9\text{SiK}$ $[\text{MK}]^+$ 812.36, found 812.45

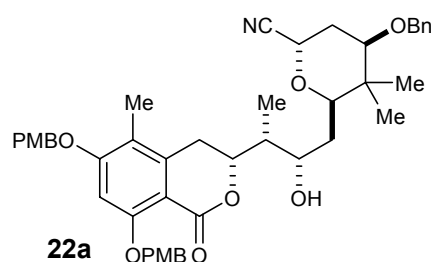


The acetonide-derivative **i** of the diol obtained from **20** by omitting a basic workup (Na,K-tartrate workup instead), was prepared for determination of the relative stereochemistry. ^{13}C NMR (CDCl_3) resonances of the acetonide Me peaks and quaternary carbon (19.5, 29.8, and 98.9 ppm) confirm the $\text{C}_{15}, \text{C}_{17}$ -syn configuration (Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, 58, 3511); the ^1H NMR H_{16} - H_{17} coupling constant of 2.4 Hz (δ 4.02 ppm) is in agreement with an equatorial disposition of H_{16} , confirming the $\text{C}_{16}, \text{C}_{17}$ -anti configuration. ^1H NMR (CD_3OD) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.87 (s, 3H), 0.92 (s, 9H), 0.95 (d, 3H, $J = 6.4$ Hz), 0.96 (s, 3H), 1.22 (s, 3H), 1.29 (s, 3H), 1.58 (m, 1H), 1.62 (m, 1H), 1.67 (m, 1H), 1.80 (ddd, 1H, $J = 1.2, 4.4, 14.0$ Hz), 2.00 (ddd, 1H, $J = 5.6, 11.6, 14.0$ Hz), 2.14 (s, 3H), 2.54 (dd, 1H, $J = 2.4, 14.4$ Hz), 3.01 (dd, 1H, $J = 8.8, 14.4$ Hz), 3.44 (dd, 1H, $J = 2.0, 11.8$ Hz), 3.69 (dd, 1H, $J = 8.4, 11.6$ Hz), 3.79 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 4.02 (ddd, 1H, $J = 2.4, 2.4, 8.8$ Hz), 4.07 (ddd,

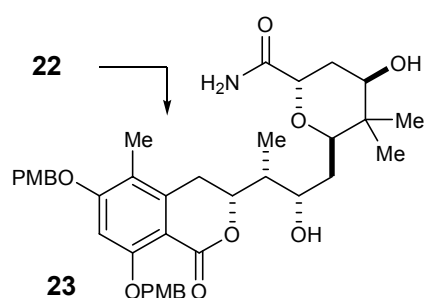
1H, $J = 1.6, 4.8, 13.2$ Hz), 4.99 (bs, 4H), 6.60 (s, 1H), 6.90 (m, 4H), 7.30 (m, 4H); ^{13}C NMR (CDCl_3) δ -5.0, -4.2, 4.8, 11.8, 12.3, 17.9, 19.5, 22.6, 25.7, 29.8, 31.2, 33.5, 33.8, 34.2, 39.8, 52.1, 55.2, 55.3, 63.7, 70.1, 70.6, 70.8, 72.4, 74.8, 77.8, 97.3, 98.9, 113.8, 113.9, 117.6, 118.2, 119.6, 128.6, 128.8, 129.0, 129.1, 137.8, 154.3, 158.0, 159.2, 159.3, 169.3; MS (ES) calculated for $\text{C}_{48}\text{H}_{67}\text{O}_{10}\text{NSiNa}$ $[\text{MNa}]^+$ 868.44, found 868.45.



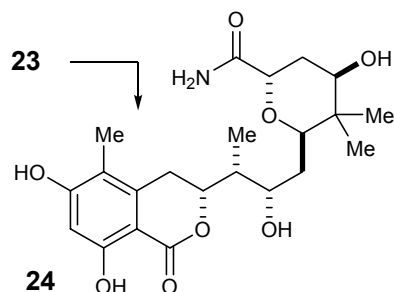
To a solution of **21** (50 mg, 65 μmol) in THF (10 mL) was added TBAF (1.0 M in THF, 100 μL , 0.1 mmol) at room temperature. After 2 h, the reaction was concentrated and the residue was purified by FC (silica gel; hexanes/EtOAc, 1:2 to EtOAc) to give **22** 43 mg (quant.) as a viscous oil. $[\alpha]_D^{26} = +33.6$ (EtOAc, $c = 0.60$); ^1H NMR (CDCl_3) δ 0.91 (s, 3H), 1.02 (s, 3H), 1.11 (d, 3H, $J = 6.8$ Hz), 1.76 (m, 2H), 1.89-2.06 (m, 3H), 2.10 (s, 3H), 2.84 (dd, 1H, $J = 12.0, 16.0$ Hz), 2.94 (dd, 1H, $J = 2.8, 16.0$ Hz), 3.68 (dd, 1H, $J = 4.6, 7.8$ Hz), 3.76 (dd, 1H, $J = 4.8, 11.6$ Hz), 3.80 (s, 3H), 3.83 (s, 3H), 4.07 (m, 1H), 4.43 (ddd, 1H, $J = 2.8, 4.4, 11.6$ Hz), 4.91 (d, 1H, $J = 4.8$ Hz), 4.98 (s, 2H), 5.10 (d, 1H, $J = 12.2$ Hz), 5.16 (d, 1H, $J = 12.2$ Hz), 6.49 (s, 1H), 6.90 (t, 4H, $J = 8.4$ Hz), 7.29 (d, 2H, $J = 8.4$ Hz), 7.43 (d, 2H, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3) δ 8.8, 11.1, 12.1, 22.2, 29.6, 32.5, 32.6, 39.5, 41.4, 55.2, 55.3, 64.0, 69.9, 70.9, 71.5, 72.0, 78.6, 82.7, 98.1, 107.4, 113.9, 114.0, 116.0, 117.2, 128.2, 128.5, 128.7, 128.8, 141.4, 159.2, 159.5, 160.2, 161.1, 163.2; IR ν_{max} 3394, 2966, 1674, 1588, 1514, 1248, 1097 cm^{-1} ; MS (ES) calculated for $\text{C}_{38}\text{H}_{45}\text{O}_9\text{NNa}$ $[\text{MNa}]^+$ 682.30, found 682.35.



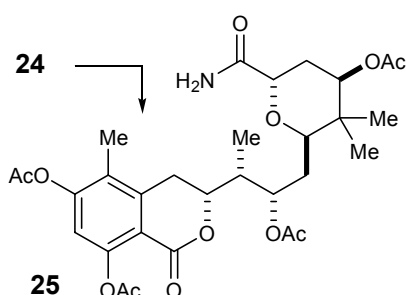
M. p. (acetone) 197 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 0.95 (s, 3H), 1.00 (s, 3H), 1.11 (d, 3H, $J = 7.2$ Hz), 1.74 (m, 2H), 1.89 (m, 1H), 1.97 (m, 1H), 2.04 (m, 1H), 2.10 (s, 3H), 2.83 (s, 1H), 2.84 (dd, 1H, $J = 12.0, 16.0$ Hz), 2.95 (dd, 1H, $J = 2.8, 16.0$ Hz), 3.44 (dd, 1H, $J = 4.6, 11.4$ Hz), 3.68 (dd, 1H, $J = 6.8, 6.8$ Hz), 3.80 (s, 3H), 3.83 (s, 3H), 4.06 (m, 1H), 4.42 (ddd, 1H, $J = 2.8, 4.8, 12.0$ Hz), 4.50 (d, 1H, $J = 11.6$ Hz), 4.63 (d, 1H, $J = 11.6$ Hz), 4.93 (d, 1H, $J = 4.8$ Hz), 4.98 (s, 2H), 5.10 (d, 1H, $J = 12.0$ Hz), 5.16 (d, 1H, $J = 12.0$ Hz), 6.49 (s, 1H), 6.90 (m, 4H), 7.28 ~ 7.45 (m, 9H); ^{13}C NMR (CDCl_3) δ 8.9, 11.1, 13.1, 22.4, 29.6, 32.6, 39.5, 41.5, 55.2, 55.3, 64.0, 69.9, 70.9, 71.9, 72.0, 78.6, 78.7, 83.3, 98.2, 107.5, 113.9, 114.0, 116.0, 117.2, 127.6, 127.8, 128.3, 128.4, 128.5, 128.7, 128.8, 138.0, 141.4, 159.2, 159.5, 160.2, 161.0, 163.1; IR ν_{max} 3369, 2963, 1669, 1513, 1247, 1097 cm^{-1} ; MS (ES) calculated for $\text{C}_{45}\text{H}_{51}\text{O}_9\text{NNa}$ $[\text{MNa}]^+$ 772.35, found 772.25.



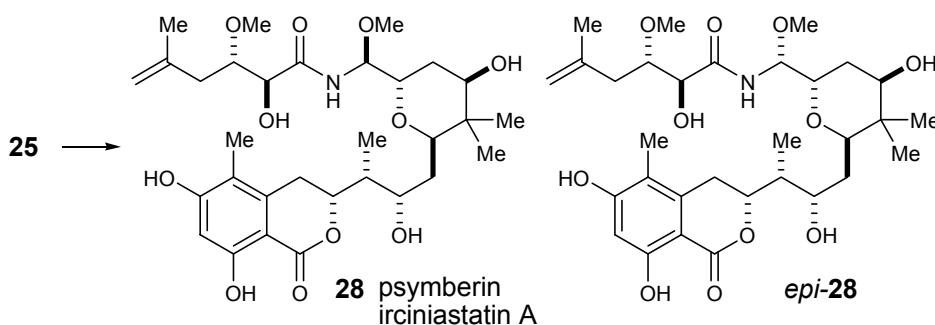
To a suspension of **22** (42 mg, 64 μmol) in 80% ethanol (8 mL) was added $[\text{PtH}(\text{PMe}_2\text{OH})(\text{PMe}_2\text{O})_2\text{H}]$ (7 mg, 16 μmol). After refluxing in air for 80 min, the reaction was cooled to room temperature. Water was added and the crude was extracted with EtOAc. The combined organic extracts were washed with water, dried over MgSO_4 and concentrated to give a residue which was purified by FC (silica gel; $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 20:1) to give **23** (42 mg, 97%) as a viscous oil. $[\alpha]_D^{27} = +37.5$ (EtOAc, $c = 0.43$); ^1H NMR (CDCl_3) δ 0.89 (s, 3H), 0.91 (s, 3H), 1.13 (d, 3H, $J = 7.2$ Hz), 1.67 (m, 2H), 1.79 (m, 1H), 1.88 (m, 1H), 2.09 (s, 3H), 2.46 (dd, 1H, $J = 3.8, 13.0$ Hz), 2.82 (dd, 1H, $J = 3.2, 16.4$ Hz), 2.89 (dd, 1H, $J = 12.0, 16.4$ Hz), 3.37 (d, 1H, $J = 8.0$ Hz), 3.41 (dd, 1H, $J = 4.4, 11.6$ Hz), 3.80 (s, 3H), 3.83 (s, 3H), 4.11 (bd, 1H, $J = 7.6$ Hz), 4.42 (ddd, 1H, $J = 3.2, 3.6, 11.6$ Hz), 4.45 (d, 1H, $J = 6.4$ Hz), 4.99 (s, 2H), 5.08 (d, 1H, $J = 12.0$ Hz), 5.16 (d, 1H, $J = 12.0$ Hz), 5.59 (bs, 1H), 6.51 (s, 1H), 6.91 (t, 4H, $J = 8.0$ Hz), 7.29 (d, 2H, $J = 8.8$ Hz), 7.42 (d, 2H, $J = 8.8$ Hz), 7.75 (bs, 1H); ^{13}C NMR (CDCl_3) δ 7.9, 11.1, 11.9, 22.5, 29.2, 29.2, 34.2, 38.6, 41.7, 55.3, 55.3, 70.0, 70.9, 71.9, 73.8, 74.1, 80.0, 81.2, 98.0, 107.0, 114.0, 114.1, 115.9, 128.1, 128.5, 128.6, 128.9, 141.3, 159.3, 159.6, 160.5, 161.3, 162.7, 174.0; IR ν_{max} 3402, 2965, 1682, 1596, 1515, 1247, 1157, 1081 cm^{-1} ; MS (ES) calculated for $\text{C}_{38}\text{H}_{47}\text{O}_{10}\text{NNa}$ $[\text{MNa}]^+$ 700.31, found 700.35.



23 → **24** 10% Pd/C (10 mg) was added to a solution of **23** (40 mg, 59 mmol) in ethanol (10 mL) and hydrogenated (H_2 , 1 atm) for 24 h. The catalyst was filtered and ethanol was removed under reduced pressure. The residue obtained was purified by FC (silica gel; $CH_2Cl_2/MeOH$ 10:1) to give **24** (26 mg) in quantitative yield as viscous oil. $[\alpha]_D^{22} = +34.0$ (EtOAc, $c = 0.20$); 1H NMR ($CDCl_3/CD_3OD$, 10/1) δ 0.85 (s, 3H), 0.88 (s, 3H), 1.09 (d, 3H, $J = 6.8$ Hz), 1.67 (m, 2H), 1.78 (ddd, 1H, $J = 6.8, 12.0, 13.2$ Hz), 1.88 (m, 1H), 2.01 (s, 3H), 2.30 (ddd, 1H, $J = 1.4, 4.6, 9.0$ Hz), 2.88 (m, 2H), 3.30 (dd, 1H, $J = 4.4, 11.6$ Hz), 3.34 (m, 1H), 4.01 (ddd, 1H, $J = 2.4, 7.8, 7.8$ Hz), 4.39 (dd, 1H, $J = 6.0$ Hz), 4.52 (ddd, 1H, $J = 4.4, 6.0, 10.0$ Hz), 5.97 (bs, 1H), 6.25 (s, 1H), 7.78 (bs, 1H); ^{13}C NMR δ 8.2, 10.3, 11.9, 22.4, 27.9, 28.9, 33.7, 38.4, 42.0, 71.3, 73.1, 73.3, 81.0, 81.1, 100.5, 114.1, 139.1, 161.8, 162.0, 162.9, 170.6, 175.1; IR ν_{max} 3401, 2967, 1659, 1651, 1376, 1254 cm^{-1} ; MS (ES) calculated for $C_{22}H_{31}O_8NNa$ $[MNa]^+$ 460.19, found 460.20.



24 → **25** To a solution of **24** (25 mg, 57 μ mol) was dissolved in pyridine (2.5 mL) was added Ac_2O (1.25 mL) at room temperature. After 20 h, EtOAc (20 mL) and sat. $NaHCO_3$ (10 mL) was added at 0 $^{\circ}C$ and stirred at room temperature for 15 min. The organic phase was separated, washed with water, 1N HCl and water, and dried over $MgSO_4$. After concentration, the residue obtained was purified by FC (silica gel; EtOAc/hexanes 2:1) to give compound **25** (32 mg, 92%) as a viscous oil. $[\alpha]_D^{22} = +48.4$ (CH_2Cl_2 , $c = 0.80$); 1H NMR ($CDCl_3$) δ 0.94 (s, 3H), 0.95 (s, 3H), 1.17 (d, 3H, $J = 7.2$ Hz), 1.79 (ddd, 1H, $J = 2.4, 4.8, 15.2$ Hz), 1.91 (ddd, 1H, $J = 5.2, 9.2, 13.6$ Hz), 2.06 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.12 (m, 1H), 2.26 (m, 2H), 2.33 (s, 3H), 2.35 (s, 3H), 2.78 (dd, 1H, $J = 12.0, 16.4$ Hz), 3.04 (dd, 1H, $J = 2.8, 16.4$ Hz), 3.46 (dd, 1H, $J = 2.4, 11.6$ Hz), 4.38 (m, 2H), 4.83 (dd, 1H, $J = 4.0, 8.4$ Hz), 5.29 (m, 1H), 5.48 (bs, 1H), 6.82 (bs, 1H), 6.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 9.4, 12.1, 14.2, 16.7, 20.8, 21.0, 21.1, 21.4, 24.2, 27.4, 28.7, 30.6, 37.0, 40.5, 72.2, 73.4, 78.3, 79.6, 115.7, 117.0, 125.7, 141.1, 150.5, 153.1, 161.5, 168.3, 169.5, 170.0, 171.0, 173.4; IR ν_{max} 3466, 2975, 1771, 1727, 1693, 1598, 1371, 1241, 1192, 1060 cm^{-1} ; MS (ES) calculated for $C_{30}H_{39}O_{12}NNa$ $[MNa]^+$ 628.24, found 628.15



To a solution of acid **anti-5** (43 mg, 155 μ mol) in CH_2Cl_2 (2.5 mL) was added oxalyl chloride (54 μ L, 620 μ mol) and a catalytic amount of DMF at 0 $^{\circ}C$. After stirring at room temperature for 2 h, solvent was removed by N_2 flushing. The acid chloride obtained was dried on vacuum pump for 5 min and dissolved in CH_2Cl_2 (770 μ L) to

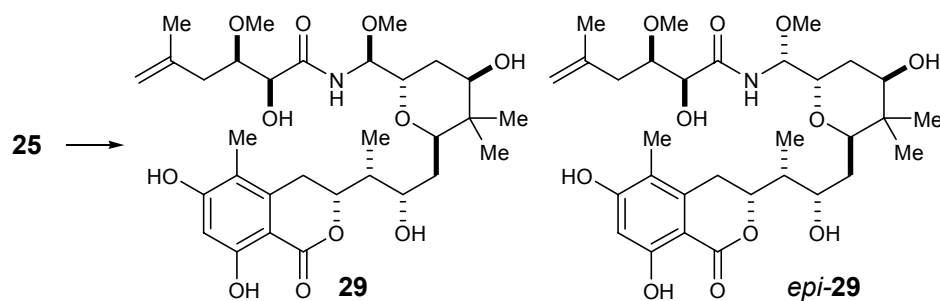
give a 0.2 M solution of compound **anti-27**.

To a mixture of compound **25** (14.5 mg, 24 μ mol) and poly(2-vinylpyridine) (30 mg, 286 μ mol) in CH_2Cl_2 (1.5 mL) was added Me_3OBF_4 (17.7 mg, 120 μ mol) at room temperature. After 1.5 h, ether (3 mL) was added and allowed to stir for 5 min to precipitate the excess Me_3OBF_4 . The reaction mixture was filtered and the solvent was removed by N_2 flushing. The residue obtained was dissolved in anhydrous toluene (2 mL) and cooled to 0 $^{\circ}C$. DIPEA (83 μ L, 0.48 mmol) and **anti-27** (0.2 M solution prepared in situ, 360 μ L, 72 μ mol) was added at 0 $^{\circ}C$ and the reaction mixture was stirred at 40 $^{\circ}C$ for 80 min. **Anti-27** (0.2 M solution in CH_2Cl_2 , 120 μ L, 24 μ mol) was added again and stirred for another 40 min and cooled to 0 $^{\circ}C$. $NaBH_4$ (45 mg) and ethanol (2 mL) was added and the reaction mixture was stirred at 0 $^{\circ}C$ for 2 h. EtOAc was added and the crude was washed with water and dried

over MgSO₄. After concentration, the residue was roughly purified by FC (silica gel, EtOAc/hexanes, 1.5:1) to give a mixture of peracetylated compounds. This mixture was dissolved in MeOH (3 mL) and 1 N LiOH (0.6 mL) was added. After stirring at room temperature for 6 h, EtOAc was added and the aqueous phase was adjusted to pH 6 using 0.05 N NaHSO₄. The crude was extracted with EtOAc and the combined organic extracts were washed with sat. NaHCO₃, water and dried over MgSO₄. After concentration, the residue was purified by FC (silica gel, CH₂Cl₂/MeOH, 20:1) to give compound **28** (5.8 mg) and *epi*-**28** (2.4 mg) in 56% total yield from **25** (ratio determined by H NMR of crude mixture: 71:29).

28: $[\alpha]_D^{23} = +25.2$ (MeOH, $c = 0.11$); ¹H NMR (CD₃OD) δ 0.89 (s, 3H), 0.97 (s, 3H), 1.09 (d, 3H, $J = 6.8$ Hz), 1.71 (s, 3H), 1.74 (m, 2H), 1.77 (ddd, 1H, $J = 6.4, 11.0, 13.2$ Hz), 1.91 (ddq, 1H, $J = 2.4, 6.0, 6.8$ Hz), 2.01 (ddd, 1H, $J = 2.8, 4.2, 13.2$ Hz), 2.08 (dd, 1H, $J = 3.2, 14.4$ Hz), 2.10 (s, 3H), 2.35 (dd, 1H, $J = 9.4, 14.4$ Hz), 2.85 (dd, 1H, $J = 12.2, 16.6$ Hz), 3.13 (dd, 1H, $J = 3.2, 16.6$ Hz), 3.21 (s, 3H), 3.35 (s, 3H), 3.50 (dd, 1H, $J = 1.6, 11.2$ Hz), 3.59 (dd, 1H, $J = 4.2, 11.0$ Hz), 3.67 (ddd, 1H, $J = 2.8, 3.2, 9.4$ Hz), 3.94 (m, 2H), 4.35 (d, 1H, $J = 2.4$ Hz), 4.49 (ddd, 1H, $J = 3.2, 6.0, 12.2$ Hz), 4.72 (bs, 1H), 4.74 (bs, 1H), 5.38 (d, 1H, $J = 8.0$ Hz), 6.25 (s, 1H); ¹H NMR (CDCl₃) δ 0.92 (s, 3H), 0.98 (s, 3H), 1.09 (d, 3H, $J = 7.2$ Hz), 1.62 (m, 2H), 1.76 (s, 3H), 1.80 (m, 1H), 1.88 (m, 1H), 2.04 (s, 3H), 2.07 (m, 1H), 2.18 (dd, 1H, $J = 4.0, 14.6$ Hz), 2.37 (dd, 1H, $J = 8.8, 14.6$ Hz), 2.82 (dd, 1H, $J = 12.0, 16.8$ Hz), 2.91 (dd, 1H, $J = 4.0, 16.8$ Hz), 3.38 (s, 6H), 3.53 (d, 1H, $J = 10.0$ Hz), 3.67 (dd, 1H, $J = 4.4, 11.8$ Hz), 3.74 (ddd, 1H, $J = 3.2, 4.0, 8.8$ Hz), 3.88 (ddd, 1H, $J = 2.4, 6.4, 8.0$ Hz), 3.95 (dm, 1H, $J = 8.8$ Hz), 4.40 (d, 1H, $J = 3.2$ Hz), 4.54 (ddd, 1H, $J = 4.0, 4.8, 12.0$ Hz), 4.80 (bs, 2H), 5.45 (dd, 1H, $J = 8.8, 10.0$ Hz), 7.09 (d, 1H, $J = 10.0$ Hz), 6.30 (s, 1H), 11.15 (bs, 1H); ¹³C NMR (CD₃OD) δ 7.7, 9.4, 12.5, 21.5, 22.2, 28.1, 29.0, 32.9, 37.2, 38.4, 41.8, 55.1, 56.1, 70.6, 71.7, 72.0, 72.8, 78.4, 80.5, 80.8, 81.2, 99.9, 111.6, 113.8, 139.7, 142.2, 162.3, 163.1, 171.0, 174.9; ¹³C NMR (CDCl₃) δ 9.2, 10.4, 13.5, 22.7, 23.0, 28.4, 29.6, 32.1, 37.5, 38.7, 42.6, 56.2, 57.9, 71.4, 73.0, 73.9, 78.2, 79.5, 80.5, 81.9, 101.3, 101.4, 113.0, 113.3, 139.6, 142.0, 161.1, 162.3, 170.5, 173.6; IR ν_{\max} 3368, 2932, 1660, 1652, 1622, 1506, 1456, 1378, 1253, 1174, 1108, 1069, 973, 896 cm⁻¹; MS (ES) calculated for C₃₁H₄₇O₁₁Na [MNa]⁺ 632.30, found 632.25.

epi-**28**: $[\alpha]_D = -19.2$ (MeOH, $c = 0.12$); ¹H NMR (CD₃OD) δ 0.89 (s, 3H), 0.97 (s, 3H), 1.13 (d, 3H, $J = 6.8$ Hz), 1.73 (m, 4H), 1.77 (s, 3H), 2.00 (m, 1H), 2.06 (s, 3H), 2.14 (dd, 1H, $J = 3.2, 14.6$ Hz), 2.34 (dd, 1H, $J = 9.2, 14.6$ Hz), 2.85 (dd, 1H, $J = 12.4, 16.8$ Hz), 3.17 (dd, 1H, $J = 3.0, 16.8$ Hz), 3.38 (s, 3H), 3.41 (s, 3H), 3.53 (dd, 1H, $J = 4.0, 8.0$ Hz), 3.58 (dd, 1H, $J = 6.0, 10.0$ Hz), 3.69 (ddd, 1H, $J = 3.2, 3.6, 9.2$ Hz), 3.93 (m, 1H), 4.11 (m, 1H), 4.35 (d, 1H, $J = 3.2$ Hz), 4.49 (ddd, 1H, $J = 3.0, 6.8, 12.4$ Hz), 4.77 (bs, 1H), 4.79 (bs, 1H), 5.48 (d, 1H, $J = 8.8$ Hz), 6.25 (s, 1H); ¹H NMR (CDCl₃) δ 0.92 (s, 3H), 0.99 (s, 3H), 1.15 (d, 3H, $J = 7.2$ Hz), 1.76 (s, 3H), 1.77 (m, 1H), 1.88 (m, 1H), 1.94 (m, 1H), 2.05 (s, 3H), 2.11 (dd, 1H, $J = 3.0, 14.4$ Hz), 2.29 (dd, 1H, $J = 8.8, 14.4$ Hz), 2.91 (dd, 1H, $J = 12.0, 16.4$ Hz), 3.02 (dd, 1H, $J = 2.8, 16.4$ Hz), 3.14 (bs, 1H), 3.41 (s, 3H), 3.42 (s, 3H), 3.63 (d, 1H, $J = 10.4$ Hz), 3.73 (m, 2H), 3.90 (m, 1H), 4.07 (m, 2H), 4.41 (bs, 1H), 4.58 (ddd, 1H, $J = 3.0, 5.2, 12.0$ Hz), 4.80 (bs, 1H), 4.83 (bs, 1H), 5.35 (dd, 1H, $J = 7.6, 9.6$ Hz), 6.00 (bs, 1H), 6.30 (s, 1H), 7.17 (d, 1H, $J = 9.6$ Hz), 11.2 (s, 1H); ¹³C NMR (CD₃OD) δ 9.9, 10.8, 13.6, 23.2, 23.5, 29.5, 30.5, 34.2, 38.9, 40.1, 42.9, 56.2, 58.1, 72.5, 72.7, 73.2, 74.5, 79.9, 80.1, 82.5, 83.1, 101.4, 101.6, 113.4, 115.2, 141.2, 144.0, 163.8, 164.9, 172.6, 176.2; IR ν_{\max} 3396, 2931, 1652, 1511, 1462, 1376, 1254, 1173, 1108, 1067 cm⁻¹; MS (ES) calculated for C₃₁H₄₇O₁₁Na [MNa]⁺ 632.30, found 632.25.



Compounds **29** and *epi*-**29** were prepared (2.4 mg, 48% yield, 75:25 ratio) from compound **25** (5 mg, 8.2 μ mol) and *syn*-**27** using the same procedure described for the synthesis of **28** and *epi*-**28**. They were inseparable, but partial separation could be achieved before acetate hydrolysis. **29** could be obtained

diastereomerically pure.

29: ^1H NMR (CD_3OD) δ 0.90 (s, 3H), 0.97 (s, 3H), 1.08 (d, 3H, $J = 7.2$ Hz), 1.64 (m, 1H), 1.70 (s, 3H), 1.78 (m, 2H), 1.88 (ddq, 1H, $J = 2.4, 6.4, 7.2$ Hz), 2.04 (m, 1H), 2.09 (s, 3H), 2.25 (dd, 1H, $J = 8.0, 14.0$ Hz), 2.37 (dd, 1H, $J = 6.0, 14.0$ Hz), 2.83 (dd, 1H, $J = 12.0, 16.8$ Hz), 3.09 (dd, 1H, $J = 3.2, 16.8$ Hz), 3.34 (s, 3H), 3.36 (s, 3H), 3.51 (dd, 1H, $J = 1.6, 10.4$ Hz), 3.60 (dd, 1H, $J = 4.4, 10.8$ Hz), 3.83 (ddd, 1H, $J = 1.8, 6.0, 8.0$ Hz), 3.93 (m, 2H), 4.01 (d, 1H, $J = 1.8$ Hz), 4.44 (ddd, 1H, $J = 3.2, 6.4, 12.0$ Hz), 4.64 (bs, 1H), 4.72 (bs, 1H), 5.41 (d, 1H, $J = 8.4$ Hz), 6.26 (s, 1H); ^1H NMR (CDCl_3) δ 0.92 (s, 3H), 1.00 (s, 3H), 1.09 (d, 3H, $J = 6.8$ Hz), 1.55 (m, 1H), 1.74 (s, 3H), 1.78 (m, 1H), 1.86 (m, 2H), 2.03 (m, 1H), 2.07 (s, 3H), 2.35 (m, 2H), 2.80 (dd, 1H, $J = 12.0, 16.4$ Hz), 2.94 (dd, 1H, $J = 3.6, 16.4$ Hz), 3.38 (s, 3H), 3.39 (s, 3H), 3.53 (d, 1H, $J = 10.0$ Hz), 3.68 (m, 1H), 3.85 (ddd, 1H, $J = 2.0, 7.6, 8.4$ Hz), 3.92 (m, 2H), 4.09 (d, 1H, $J = 2.0$ Hz), 4.25 (s, 1H), 4.53 (ddd, 1H, $J = 3.6, 5.2, 12.0$ Hz), 4.71 (bs, 1H), 4.75 (bs, 1H), 5.40 (dd, 1H, $J = 8.0, 10.4$ Hz), 6.30 (s, 1H), 7.14 (d, 1H, $J = 10.4$ Hz), 11.21 (bs, 1H); MS (ES) calculated for $\text{C}_{31}\text{H}_{47}\text{O}_{11}\text{Na}$ $[\text{MNa}]^+$ 632.30, found 632.25.

epi-**29** was obtained as a mixture with **29**. The peaks that can be identified are: ^1H NMR (CD_3OD) δ 0.90, (s, 3H), 0.97 (s, 3H), 1.14 (d, 3H, $J = 6.8$ Hz), 1.81 (s, 3H), 2.05 (s, 3H), 3.17 (dd, 1H, $J = 2.8, 16.4$ Hz), 3.36 (s, 3H), 3.37 (s, 3H), 4.07 (d, 1H, $J = 2.0$ Hz), 4.49 (ddd, 1H, $J = 2.8, 6.4, 12.0$ Hz), 5.50 (d, 1H, $J = 8.8$ Hz), 6.26 (s, 1H); ^1H NMR (CDCl_3) δ 0.92, (s, 3H), 0.98 (s, 3H), 1.15 (d, 3H, $J = 7.2$ Hz), 1.79 (s, 3H), 2.03 (s, 3H), 3.04 (dd, 1H, $J = 3.2, 16.8$ Hz), 3.37 (s, 3H), 3.41 (s, 3H), 4.57 (ddd, 1H, $J = 3.2, 5.2, 12.0$ Hz), 4.80 (bs, 1H), 4.86 (bs, 1H), 5.37 (dd, 1H, $J = 7.2, 10.0$ Hz), 6.30 (s, 1H), 7.18 (d, 1H, $J = 10.0$ Hz), 11.23 (bs, 1H).

3. X-ray Crystal Structure Data for Benzyl Ether 22a

Crystals of **22a** for X-ray analysis were obtained by slow evaporation from acetone. (colorless needles, m.p.:197 °C). X-ray data were collected using Bruker Kappa CCD (charge couple device) based diffractometer. A suitable crystal (0.2mm x 0.2mm x 0.8mm) was mounted on a glass fiber. Data were measured using phi scans of 2° per frame for 60 seconds using “collect” data collection software, Nonius 1999. The data were processed using HKL2000.¹

Based on the systematic absences the crystals were monoclinic belonging to the space group $P2_1$. The structure was solved using SHELXS-90² and refined by least-squares methods on F^2 using SHELXL-97³. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms located in the difference fourier densities were refined isotropically. The crystal was stable during data collection. The drawing depicts ORTEP⁴.

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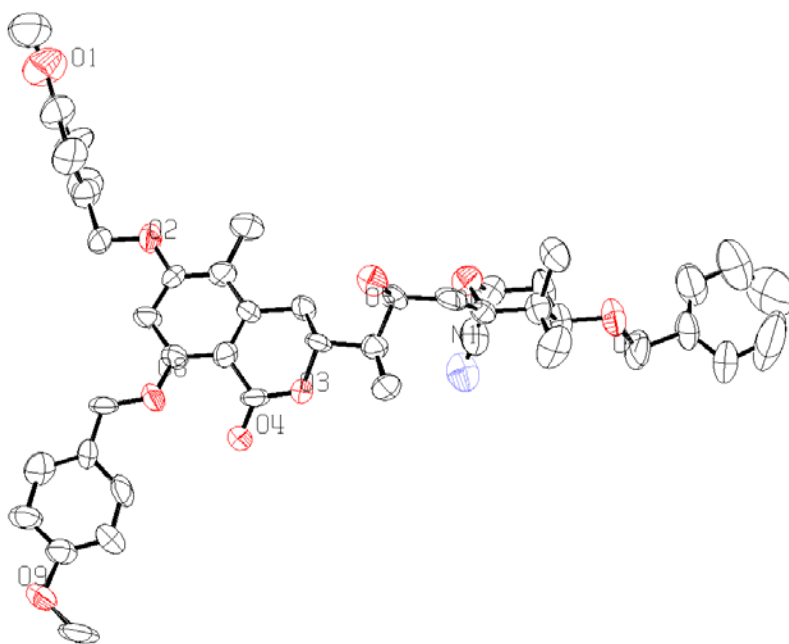


Table 1. Crystal data and structure refinement for **22a**.

Identification code	22a
Empirical formula	C ₄₈ H ₅₅ N O ₁₀
Formula weight	805.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2(1)
Unit cell dimensions	a = 6.5520(3) Å alpha = 90 deg. b = 38.4430(5) Å beta = 95.89 deg. c = 8.8450(5) Å gamma = 90 deg.
Volume	2216.11(16) Å ³
Z, Calculated density	2, 1.194 Mg/m ³
F(000)	842
Crystal size	0.2 x 0.2 x 0.8 mm ³
Theta range for data collection	2.81 to 25.27 deg.
Limiting indices	0<=h<=6, 0<=k<=45, -9<=l<=9
Reflections collected / unique	3360 / 3360 [R(int) = 0.0000]
Completeness to theta = 17.23	95.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3360 / 1 / 513
Goodness-of-fit on F ²	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0764, wR2 = 0.1872
R indices (all data)	R1 = 0.1000, wR2 = 0.2039
Absolute structure parameter	?
Largest diff. peak and hole	0.252 and -0.222 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **22a**.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U (eq)
C (46)	1050 (120)	662 (19)	4590 (100)	330 (30)
C (47)	550 (60)	635 (11)	2900 (50)	223 (15)
C (48)	3240 (70)	594 (11)	4090 (50)	248 (18)
O (10)	190 (80)	666 (12)	5680 (60)	360 (20)
C (1)	19940 (40)	4647 (7)	640 (30)	146 (10)
C (2)	17050 (40)	4950 (5)	1470 (30)	93 (7)
C (3)	17100 (30)	5194 (7)	400 (30)	106 (7)
C (4)	15630 (40)	5447 (5)	190 (20)	91 (6)
C (5)	14170 (30)	5474 (5)	1180 (30)	73 (5)
C (6)	14200 (30)	5220 (6)	2330 (20)	94 (7)
C (7)	15740 (40)	4979 (6)	2490 (30)	136 (11)
C (8)	12580 (20)	5754 (4)	1030 (20)	76 (5)
C (9)	12140 (30)	6327 (5)	2003 (18)	57 (5)
C (10)	12990 (20)	6595 (5)	2980 (19)	58 (5)
C (11)	11910 (20)	6909 (4)	3045 (17)	45 (4)
C (12)	9970 (20)	6945 (4)	2186 (19)	47 (4)
C (13)	9190 (30)	6676 (4)	1215 (19)	51 (4)
C (14)	10270 (20)	6360 (4)	1170 (18)	52 (4)
C (15)	15110 (30)	6543 (5)	3930 (20)	82 (5)
C (16)	12790 (20)	7222 (4)	3983 (17)	49 (4)
C (17)	11934 (17)	7557 (4)	3260 (16)	48 (4)
C (18)	8770 (30)	7253 (5)	2448 (19)	63 (5)
C (19)	12526 (18)	7887 (4)	4155 (17)	47 (4)
C (20)	11380 (20)	8187 (4)	3389 (19)	68 (5)
C (21)	14836 (19)	7932 (4)	4193 (18)	49 (4)
C (22)	15650 (20)	8256 (4)	4966 (17)	53 (4)
C (23)	15260 (20)	8319 (4)	6615 (17)	51 (4)
C (24)	15740 (20)	7990 (5)	8940 (20)	75 (5)
C (25)	16610 (20)	8313 (5)	9815 (17)	75 (5)
C (26)	15760 (30)	8643 (5)	9060 (20)	77 (5)
C (27)	16170 (20)	8659 (4)	7342 (19)	60 (4)
C (28)	18500 (20)	8677 (5)	7223 (19)	78 (5)
C (29)	15110 (30)	8956 (4)	6580 (20)	83 (5)
C (30)	15610 (30)	9037 (6)	11040 (30)	114 (8)
C (31)	16960 (40)	9251 (6)	12170 (20)	86 (6)
C (32)	16370 (40)	9575 (9)	12610 (40)	151 (10)
C (33)	17880 (90)	9734 (10)	13620 (60)	270 (30)
C (34)	19390 (80)	9584 (16)	14350 (50)	220 (20)
C (35)	19910 (60)	9284 (13)	13770 (40)	172 (14)
C (36)	18680 (50)	9123 (6)	12740 (40)	127 (9)
C (37)	13560 (40)	7948 (5)	9060 (20)	84 (6)
C (38)	6440 (20)	6463 (4)	-511 (19)	61 (5)
C (39)	-2060 (20)	7229 (5)	-2930 (20)	90 (6)
C (40)	4440 (20)	6596 (4)	-1288 (17)	49 (4)
C (41)	3600 (20)	6903 (4)	-871 (19)	62 (5)
C (42)	1720 (30)	7023 (4)	-1550 (20)	56 (4)
C (43)	660 (20)	6834 (5)	-2620 (20)	63 (5)
C (44)	1420 (30)	6525 (6)	-3079 (18)	71 (5)

C (45)	3280 (30)	6404 (4)	-2370 (20)	68 (5)
O (1)	18500 (30)	4695 (4)	1680 (20)	136 (6)
O (2)	13330 (15)	6030 (3)	2003 (12)	67 (3)
O (3)	9701 (14)	7529 (3)	3147 (12)	59 (3)
O (4)	6944 (17)	7289 (3)	2059 (13)	70 (3)
O (5)	15450 (13)	7939 (3)	2711 (12)	58 (3)
O (6)	16078 (14)	8003 (3)	7380 (14)	64 (3)
O (7)	16643 (17)	8938 (3)	9824 (15)	82 (4)
O (8)	7410 (15)	6736 (3)	397 (14)	66 (3)
O (9)	-1206 (18)	6912 (3)	-3388 (14)	86 (4)
N (1)	11800 (30)	7917 (5)	9251 (19)	105 (6)

Table 3. Bond lengths [Å] and angles [deg] for **22a**.

C (46)–O (10)	1.17 (8)
C (46)–C (47)	1.50 (8)
C (46)–C (48)	1.57 (7)
C (1)–O (1)	1.39 (3)
C (2)–C (7)	1.32 (3)
C (2)–C (3)	1.33 (3)
C (2)–O (1)	1.37 (2)
C (3)–C (4)	1.37 (3)
C (4)–C (5)	1.37 (2)
C (5)–C (6)	1.41 (2)
C (5)–C (8)	1.49 (2)
C (6)–C (7)	1.36 (3)
C (8)–O (2)	1.421 (17)
C (9)–C (14)	1.371 (19)
C (9)–O (2)	1.382 (19)
C (9)–C (10)	1.42 (2)
C (10)–C (11)	1.403 (19)
C (10)–C (15)	1.56 (2)
C (11)–C (12)	1.420 (19)
C (11)–C (16)	1.538 (19)
C (12)–C (13)	1.409 (19)
C (12)–C (18)	1.45 (2)
C (13)–O (8)	1.328 (16)
C (13)–C (14)	1.406 (19)
C (16)–C (17)	1.516 (19)
C (17)–O (3)	1.460 (14)
C (17)–C (19)	1.526 (19)
C (18)–O (4)	1.221 (17)
C (18)–O (3)	1.341 (18)
C (19)–C (20)	1.500 (19)
C (19)–C (21)	1.520 (18)
C (21)–O (5)	1.410 (16)
C (21)–C (22)	1.49 (2)
C (22)–C (23)	1.526 (18)
C (23)–O (6)	1.466 (17)
C (23)–C (27)	1.55 (2)
C (24)–O (6)	1.420 (18)
C (24)–C (37)	1.45 (3)
C (24)–C (25)	1.54 (2)
C (25)–C (26)	1.51 (2)
C (26)–O (7)	1.412 (19)
C (26)–C (27)	1.57 (2)
C (27)–C (29)	1.46 (2)
C (27)–C (28)	1.55 (2)
C (30)–O (7)	1.38 (2)
C (30)–C (31)	1.51 (3)
C (31)–C (36)	1.28 (3)
C (31)–C (32)	1.37 (3)
C (32)–C (33)	1.40 (4)
C (33)–C (34)	1.27 (5)
C (34)–C (35)	1.32 (5)
C (35)–C (36)	1.31 (3)
C (37)–N (1)	1.19 (2)
C (38)–O (8)	1.431 (16)

C (38) -C (40)	1.507 (19)
C (39) -O (9)	1.42 (2)
C (40) -C (41)	1.37 (2)
C (40) -C (45)	1.38 (2)
C (41) -C (42)	1.39 (2)
C (42) -C (43)	1.33 (2)
C (43) -C (44)	1.37 (2)
C (43) -O (9)	1.367 (18)
C (44) -C (45)	1.39 (2)
O (10) -C (46) -C (47)	139 (8)
O (10) -C (46) -C (48)	140 (8)
C (47) -C (46) -C (48)	80 (6)
C (46) -C (47) -C (48)	52 (3)
C (46) -C (48) -C (47)	49 (3)
C (7) -C (2) -C (3)	120 (2)
C (7) -C (2) -O (1)	117 (2)
C (3) -C (2) -O (1)	122 (3)
C (2) -C (3) -C (4)	122 (2)
C (5) -C (4) -C (3)	119.8 (19)
C (4) -C (5) -C (6)	116.7 (17)
C (4) -C (5) -C (8)	122 (2)
C (6) -C (5) -C (8)	121.6 (19)
C (7) -C (6) -C (5)	120.2 (18)
C (2) -C (7) -C (6)	121 (2)
O (2) -C (8) -C (5)	106.8 (12)
C (14) -C (9) -O (2)	123.5 (15)
C (14) -C (9) -C (10)	121.9 (17)
O (2) -C (9) -C (10)	114.6 (14)
C (11) -C (10) -C (9)	119.0 (14)
C (11) -C (10) -C (15)	120.7 (15)
C (9) -C (10) -C (15)	120.3 (15)
C (10) -C (11) -C (12)	119.2 (13)
C (10) -C (11) -C (16)	122.4 (13)
C (12) -C (11) -C (16)	118.4 (12)
C (13) -C (12) -C (11)	120.3 (13)
C (13) -C (12) -C (18)	121.9 (14)
C (11) -C (12) -C (18)	117.7 (15)
O (8) -C (13) -C (12)	116.6 (13)
O (8) -C (13) -C (14)	123.4 (14)
C (12) -C (13) -C (14)	120.0 (14)
C (9) -C (14) -C (13)	119.4 (15)
C (17) -C (16) -C (11)	109.6 (12)
O (3) -C (17) -C (16)	106.8 (12)
O (3) -C (17) -C (19)	107.3 (11)
C (16) -C (17) -C (19)	115.1 (11)
O (4) -C (18) -O (3)	115.2 (16)
O (4) -C (18) -C (12)	125.4 (16)
O (3) -C (18) -C (12)	119.4 (15)
C (20) -C (19) -C (17)	108.4 (11)
C (20) -C (19) -C (21)	112.0 (13)
C (17) -C (19) -C (21)	107.8 (11)
O (5) -C (21) -C (22)	106.6 (12)
O (5) -C (21) -C (19)	111.1 (10)
C (22) -C (21) -C (19)	114.4 (13)
C (21) -C (22) -C (23)	118.9 (13)
O (6) -C (23) -C (22)	102.7 (11)

O (6) -C (23) -C (27)	113.7 (11)
C (22) -C (23) -C (27)	115.9 (13)
O (6) -C (24) -C (37)	109.1 (14)
O (6) -C (24) -C (25)	112.0 (14)
C (37) -C (24) -C (25)	111.7 (15)
C (26) -C (25) -C (24)	110.7 (13)
O (7) -C (26) -C (25)	110.5 (14)
O (7) -C (26) -C (27)	109.1 (14)
C (25) -C (26) -C (27)	111.5 (15)
C (29) -C (27) -C (23)	108.8 (13)
C (29) -C (27) -C (28)	111.0 (15)
C (23) -C (27) -C (28)	110.5 (13)
C (29) -C (27) -C (26)	110.9 (14)
C (23) -C (27) -C (26)	105.9 (13)
C (28) -C (27) -C (26)	109.6 (13)
O (7) -C (30) -C (31)	111.4 (17)
C (36) -C (31) -C (32)	120 (2)
C (36) -C (31) -C (30)	119 (2)
C (32) -C (31) -C (30)	121 (3)
C (31) -C (32) -C (33)	112 (3)
C (34) -C (33) -C (32)	126 (4)
C (33) -C (34) -C (35)	114 (4)
C (34) -C (35) -C (36)	121 (4)
C (31) -C (36) -C (35)	123 (3)
N (1) -C (37) -C (24)	176 (2)
O (8) -C (38) -C (40)	108.7 (12)
C (41) -C (40) -C (45)	116.3 (15)
C (41) -C (40) -C (38)	121.8 (15)
C (45) -C (40) -C (38)	121.8 (15)
C (40) -C (41) -C (42)	122.0 (15)
C (43) -C (42) -C (41)	120.2 (15)
C (42) -C (43) -C (44)	120.3 (15)
C (42) -C (43) -O (9)	127.5 (17)
C (44) -C (43) -O (9)	112.2 (17)
C (43) -C (44) -C (45)	119.1 (17)
C (40) -C (45) -C (44)	122.0 (15)
C (2) -O (1) -C (1)	121 (2)
C (9) -O (2) -C (8)	117.2 (12)
C (18) -O (3) -C (17)	119.6 (12)
C (24) -O (6) -C (23)	113.0 (12)
C (30) -O (7) -C (26)	112.4 (13)
C (13) -O (8) -C (38)	119.5 (12)
C (43) -O (9) -C (39)	114.0 (14)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **22a**.
The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
C (1)	114 (18)	150 (20)	170 (30)	-6 (19)	-13 (19)	85 (17)
C (2)	16 (17)	30 (12)	120 (20)	-8 (14)	-46 (16)	52 (13)
C (3)	99 (15)	85 (17)	130 (20)	-4 (17)	4 (13)	56 (15)
C (4)	129 (17)	58 (13)	89 (16)	14 (11)	23 (15)	11 (13)
C (5)	74 (13)	64 (14)	80 (17)	-8 (13)	-1 (11)	0 (11)
C (6)	124 (17)	108 (19)	57 (15)	3 (14)	38 (12)	4 (15)
C (7)	170 (20)	140 (20)	110 (20)	47 (16)	56 (18)	137 (19)
C (8)	71 (11)	48 (12)	101 (16)	-32 (12)	-25 (10)	6 (10)
C (9)	70 (14)	76 (15)	24 (11)	1 (10)	2 (9)	-23 (13)
C (10)	50 (10)	66 (13)	57 (12)	-4 (11)	-2 (9)	31 (10)
C (11)	28 (9)	54 (12)	55 (12)	-12 (9)	7 (7)	4 (8)
C (12)	33 (10)	33 (10)	78 (13)	1 (9)	18 (9)	18 (9)
C (13)	55 (12)	34 (13)	61 (12)	-1 (9)	-10 (9)	-1 (10)
C (14)	54 (10)	35 (12)	61 (12)	-10 (8)	-20 (9)	2 (9)
C (15)	103 (14)	47 (11)	95 (15)	-3 (10)	-1 (11)	13 (9)
C (16)	55 (9)	56 (11)	35 (10)	-5 (9)	3 (8)	9 (8)
C (17)	16 (9)	84 (13)	43 (11)	4 (10)	-7 (6)	10 (7)
C (18)	48 (12)	70 (15)	68 (14)	1 (11)	-13 (9)	-13 (14)
C (19)	34 (9)	66 (12)	39 (10)	-21 (9)	-8 (7)	-4 (8)
C (20)	48 (9)	60 (11)	94 (14)	-14 (10)	-10 (9)	17 (8)
C (21)	45 (10)	58 (11)	38 (12)	-4 (9)	-26 (8)	-5 (7)
C (22)	49 (9)	64 (11)	44 (12)	12 (10)	-5 (8)	6 (8)
C (23)	59 (9)	50 (11)	44 (12)	-8 (9)	-2 (8)	4 (8)
C (24)	58 (12)	123 (17)	45 (14)	9 (12)	14 (9)	7 (10)
C (25)	107 (13)	62 (13)	46 (12)	9 (11)	-46 (9)	-35 (11)
C (26)	94 (13)	71 (13)	66 (15)	-9 (12)	14 (10)	-27 (11)
C (27)	78 (12)	39 (11)	62 (14)	2 (10)	5 (9)	4 (9)
C (28)	66 (12)	91 (13)	76 (14)	-7 (11)	-3 (9)	-36 (9)
C (29)	142 (15)	50 (12)	52 (13)	4 (10)	-8 (11)	14 (11)
C (30)	109 (15)	116 (19)	120 (20)	-64 (16)	25 (16)	-44 (13)
C (31)	129 (19)	79 (18)	46 (14)	0 (13)	-6 (13)	-5 (15)
C (32)	140 (20)	140 (30)	170 (30)	-30 (20)	-14 (19)	20 (20)
C (33)	330 (60)	120 (30)	320 (70)	-40 (30)	-150 (50)	-70 (30)
C (34)	240 (50)	280 (60)	120 (40)	-80 (40)	-30 (30)	-50 (40)
C (35)	220 (30)	230 (40)	50 (20)	-10 (20)	-30 (20)	-50 (30)
C (36)	160 (20)	76 (16)	130 (30)	8 (17)	-60 (20)	-10 (18)
C (37)	124 (19)	62 (13)	67 (14)	-3 (10)	14 (13)	-28 (13)
C (38)	32 (9)	54 (11)	95 (14)	-19 (10)	-5 (9)	-10 (8)
C (39)	59 (11)	98 (16)	108 (17)	1 (14)	-12 (10)	24 (11)
C (40)	62 (12)	40 (11)	43 (11)	-13 (9)	6 (9)	-6 (10)
C (41)	61 (11)	54 (12)	68 (13)	-24 (10)	-17 (10)	1 (9)
C (42)	66 (12)	40 (10)	58 (12)	7 (10)	-9 (10)	-1 (10)
C (43)	31 (11)	64 (15)	92 (15)	0 (12)	4 (11)	2 (10)
C (44)	53 (12)	91 (16)	62 (13)	-14 (11)	-26 (9)	11 (11)
C (45)	82 (13)	34 (11)	90 (15)	-3 (11)	9 (12)	6 (10)
O (1)	130 (12)	99 (12)	177 (18)	9 (11)	7 (12)	63 (11)
O (2)	66 (6)	46 (8)	85 (10)	3 (7)	-5 (6)	21 (7)
O (3)	51 (7)	47 (7)	75 (8)	-11 (6)	-1 (5)	8 (6)
O (4)	52 (8)	58 (7)	94 (9)	-21 (6)	-21 (6)	-1 (6)

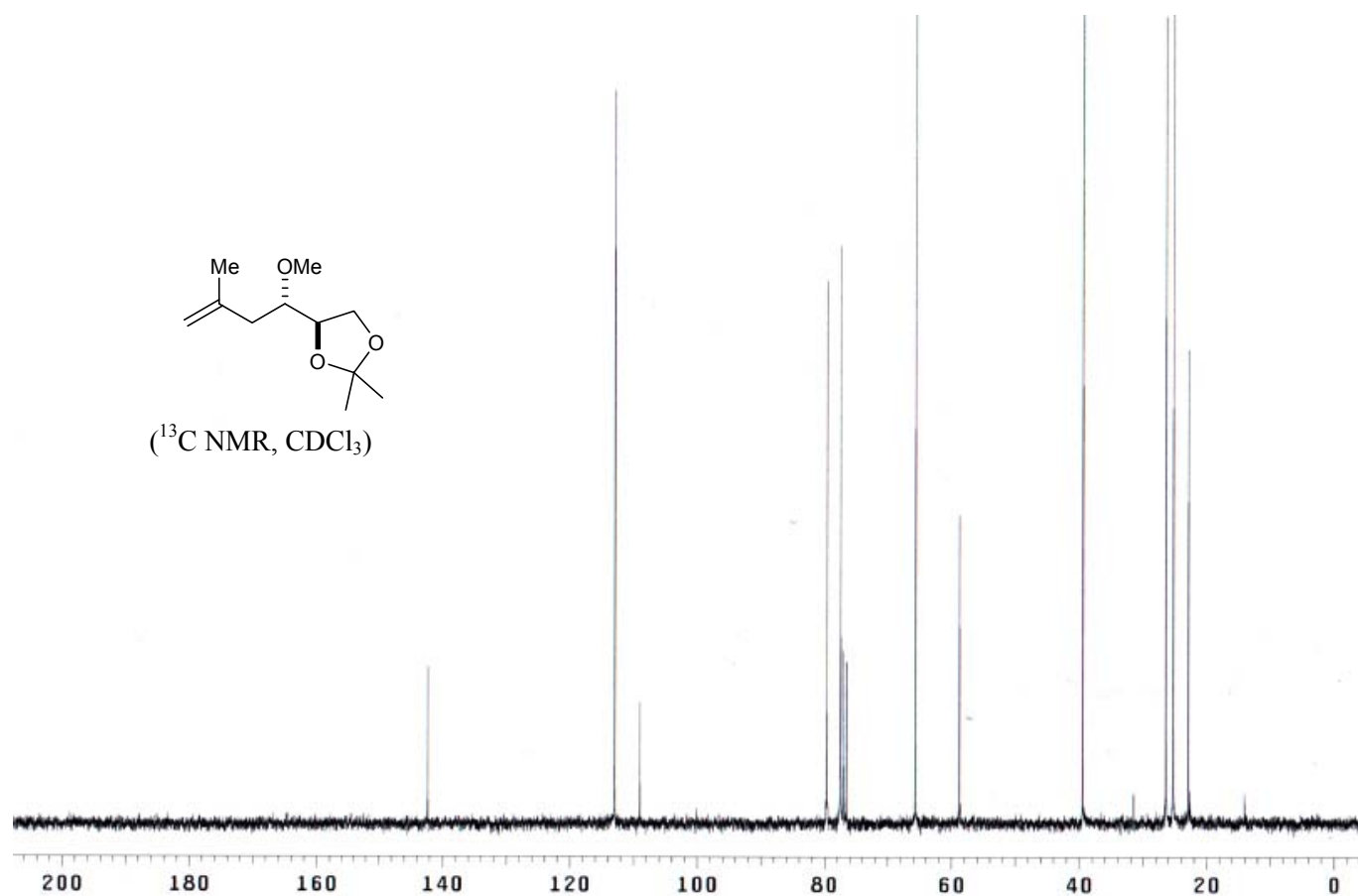
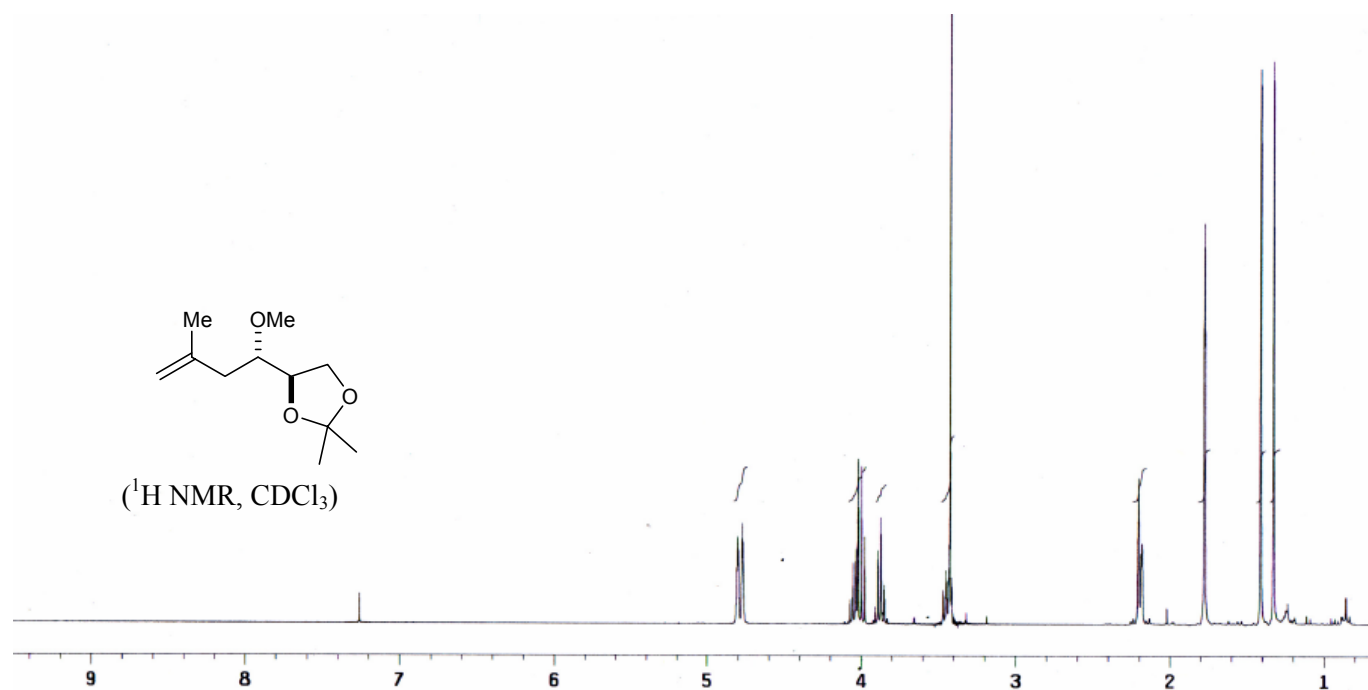
O (5)	57 (6)	86 (8)	31 (7)	1 (6)	0 (5)	-2 (5)
O (6)	66 (7)	62 (8)	61 (9)	4 (7)	-3 (6)	7 (5)
O (7)	92 (8)	84 (9)	73 (10)	-35 (7)	13 (8)	-32 (7)
O (8)	46 (7)	50 (7)	97 (9)	-5 (7)	-14 (6)	5 (6)
O (9)	67 (9)	90 (10)	94 (10)	-14 (7)	-29 (7)	6 (7)
N (1)	119 (14)	108 (14)	87 (13)	13 (10)	6 (11)	-39 (11)

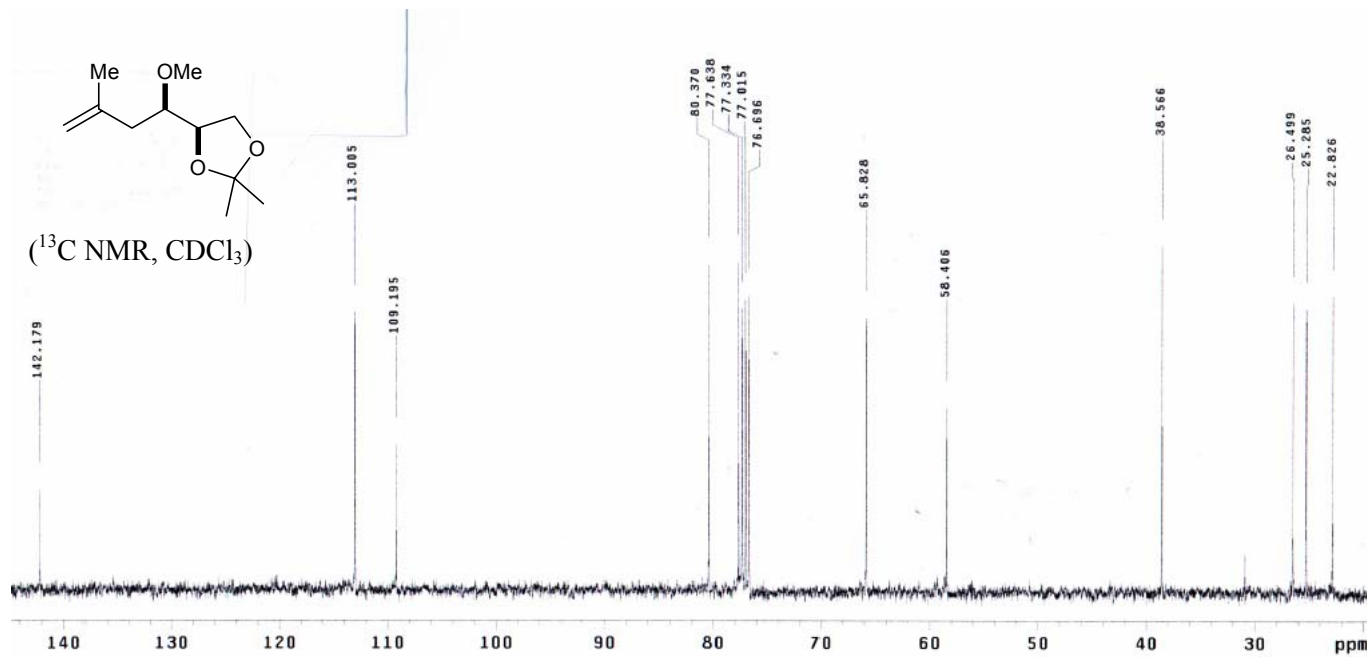
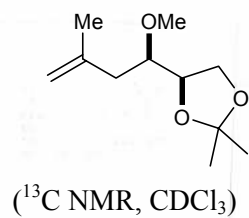
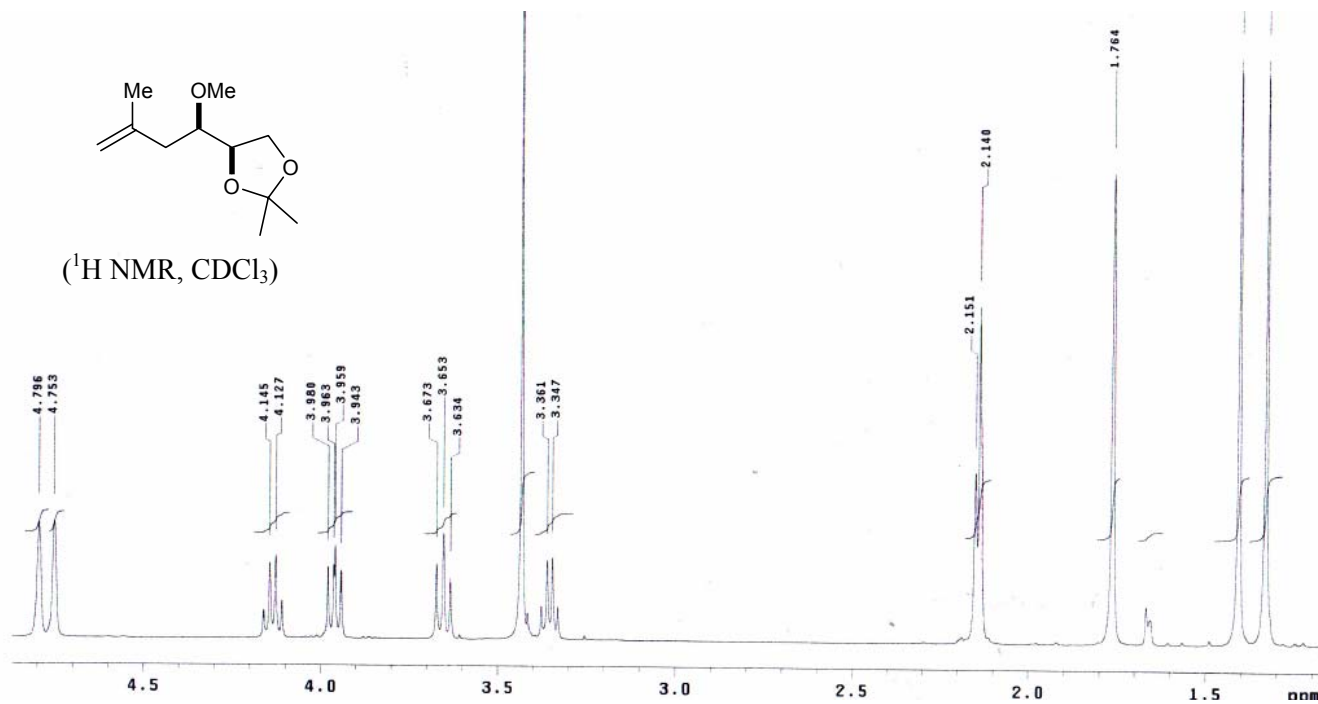
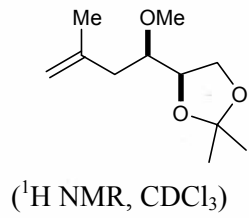
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **22a**.

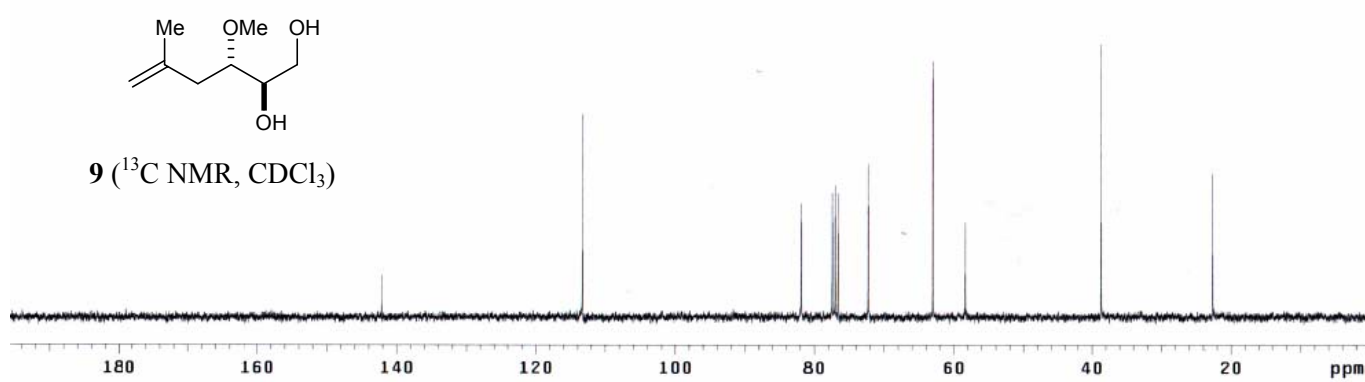
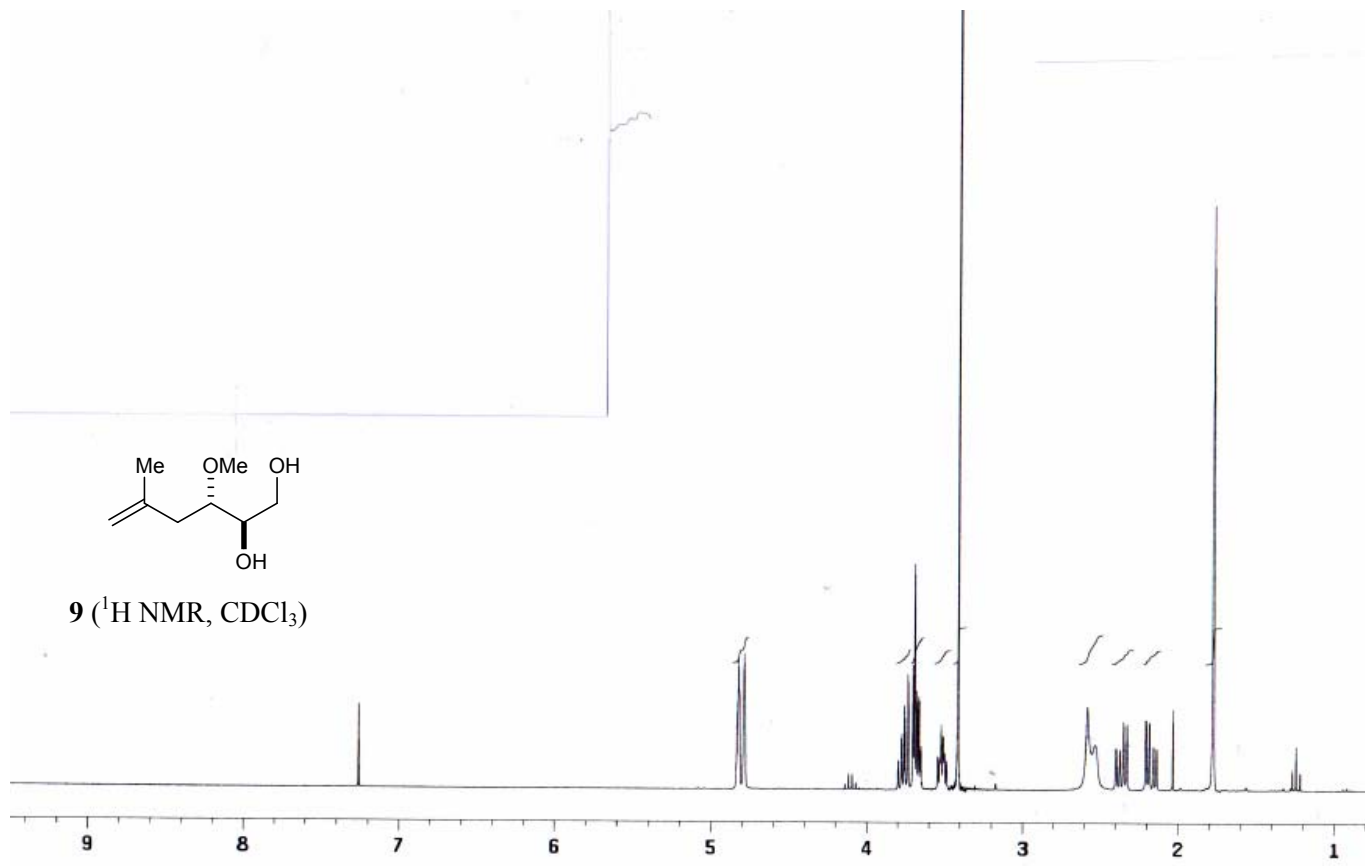
	x	y	z	U(eq)
H(47A)	-835	711	2630	334
H(47B)	697	398	2588	334
H(47C)	1471	780	2404	334
H(48A)	4263	659	4893	373
H(48B)	3423	729	3196	373
H(48C)	3389	351	3860	373
H(1A)	20831	4457	966	219
H(1B)	20738	4856	587	219
H(1C)	19245	4597	-341	219
H(3)	18165	5191	-224	127
H(4)	15629	5600	-630	109
H(6)	13181	5218	2991	113
H(7)	15853	4832	3332	163
H(8A)	12362	5834	-14	91
H(8B)	11290	5667	1327	91
H(14)	9718	6177	579	62
H(15A)	15446	6747	4530	124
H(15B)	16147	6505	3255	124
H(15C)	15046	6346	4586	124
H(16A)	12416	7205	5014	58
H(16B)	14271	7223	4023	58
H(17)	12371	7577	2237	58
H(19)	12152	7863	5195	57
H(20A)	9930	8151	3407	102
H(20B)	11691	8203	2354	102
H(20C)	11777	8399	3914	102
H(21)	15498	7732	4730	59
H(22A)	15091	8452	4372	63
H(22B)	17126	8259	4922	63
H(23)	13773	8323	6663	62
H(24)	16449	7785	9390	89
H(25)	17534	8306	10687	91
H(26)	14274	8648	9124	92
H(28A)	19159	8479	7720	117
H(28B)	19045	8886	7702	117
H(28C)	18749	8678	6172	117
H(29A)	15683	9168	7005	124
H(29B)	13674	8946	6720	124
H(29C)	15267	8948	5514	124
H(30A)	15142	8831	11537	137
H(30B)	14407	9172	10667	137
H(32)	15121	9677	12280	181
H(33)	17761	9972	13757	321
H(34)	20081	9677	15234	259
H(35)	21181	9186	14090	206
H(36)	19062	8905	12401	153
H(38A)	6192	6265	125	74
H(38B)	7326	6388	-1265	74
H(39A)	-3369	7266	-3503	134
H(39B)	-1156	7418	-3122	134

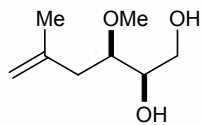
H(39C)	-2226	7220	-1869	134
H(41)	4304	7036	-107	75
H(42)	1214	7236	-1264	67
H(44)	696	6396	-3850	85
H(45)	3757	6187	-2644	82

4. Copies of NMR Spectra

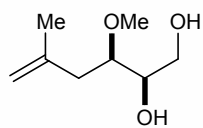
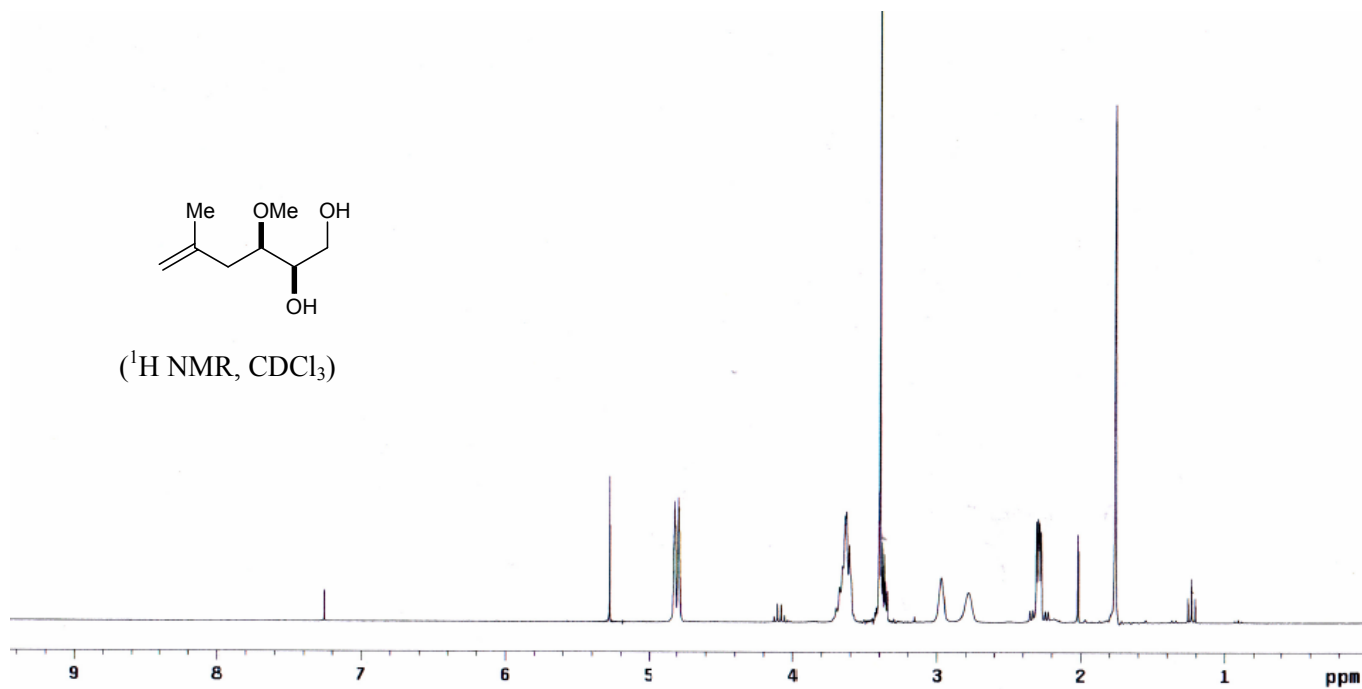




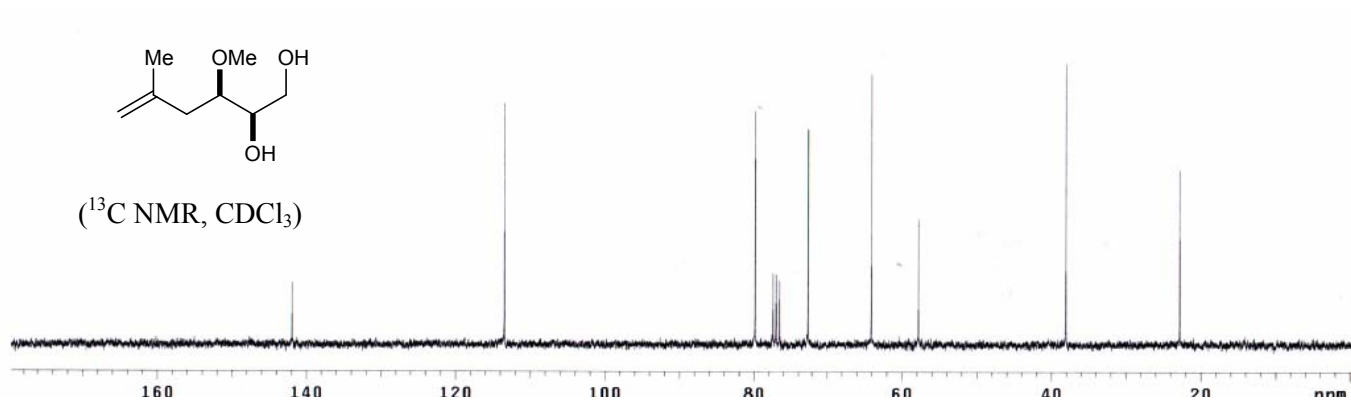


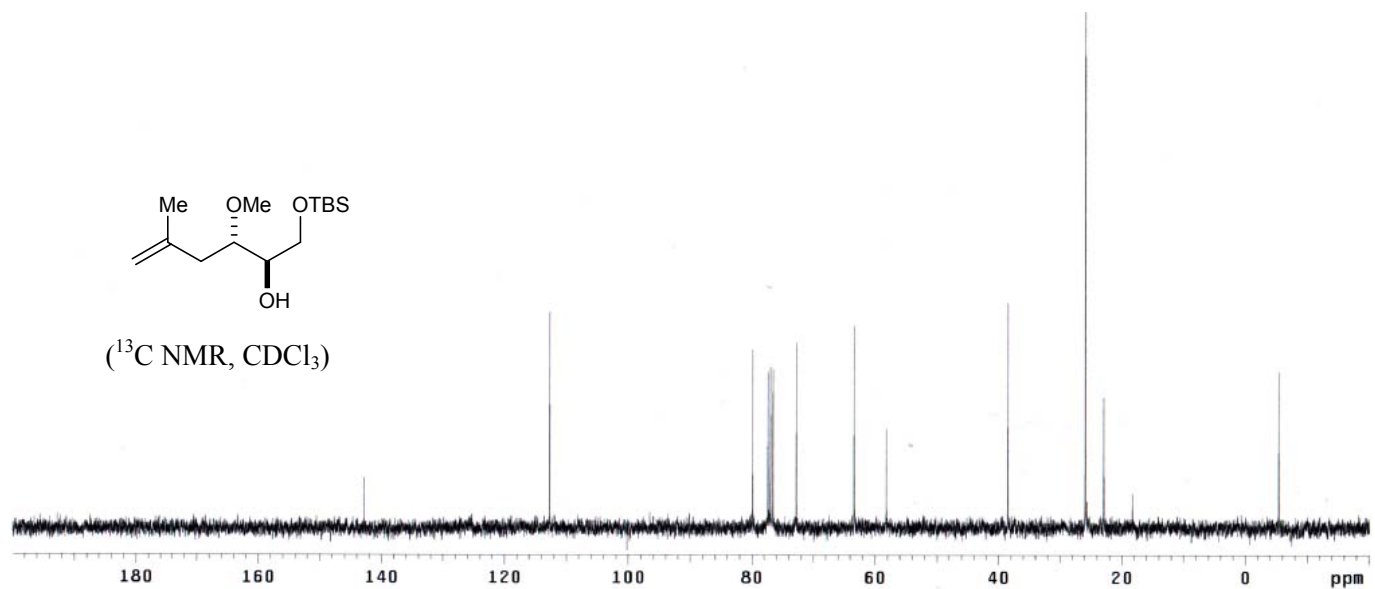
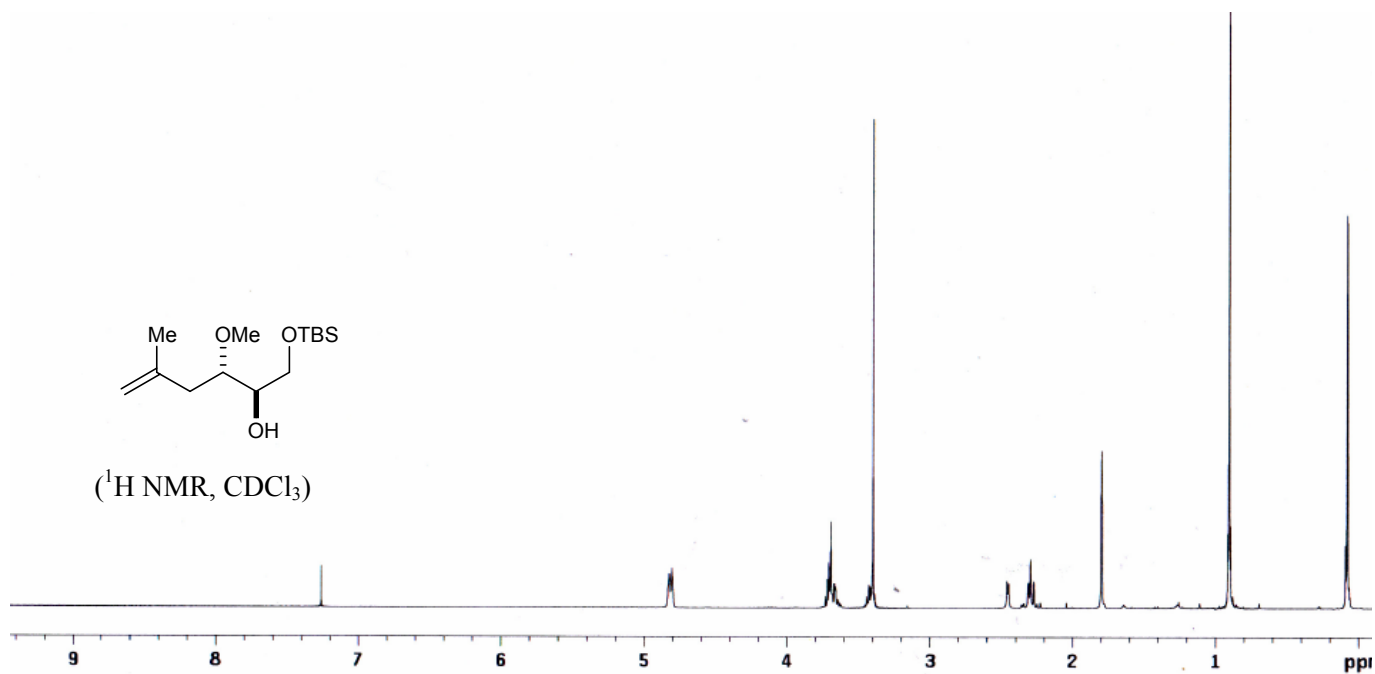


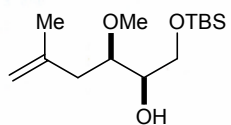
(^1H NMR, CDCl_3)



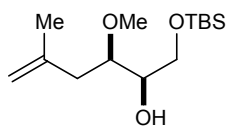
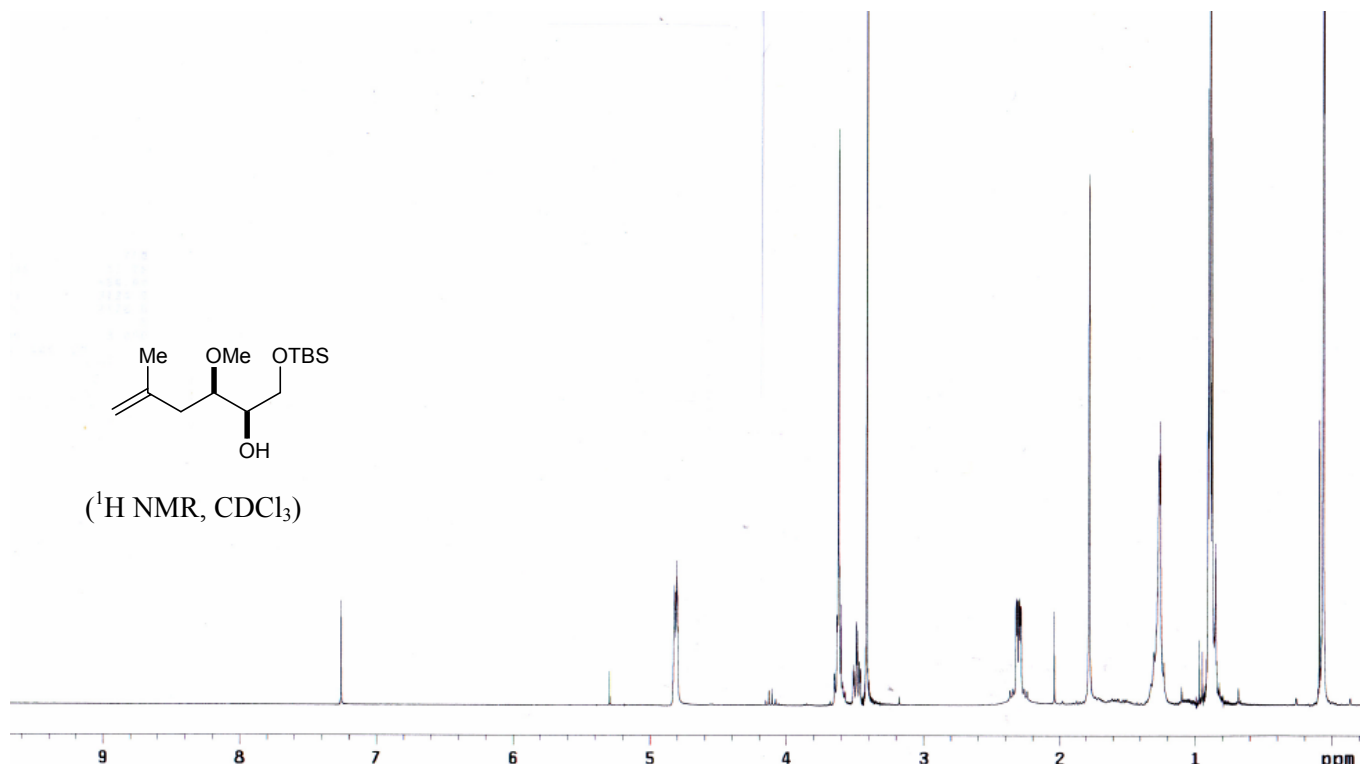
(^{13}C NMR, CDCl_3)



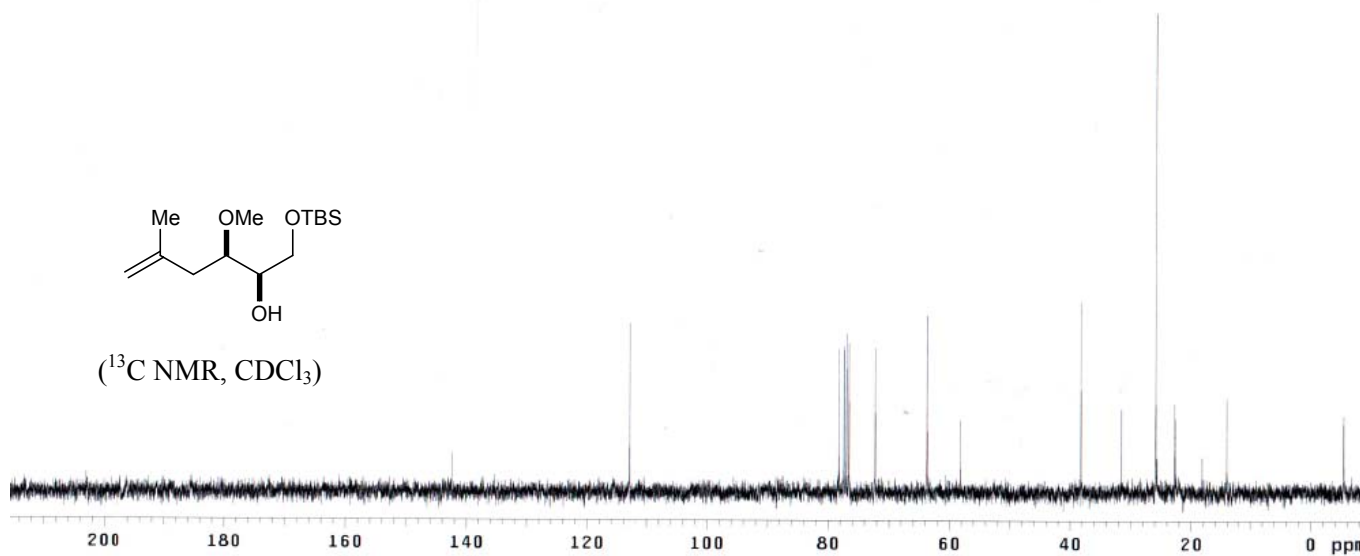


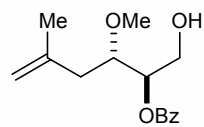


(^1H NMR, CDCl_3)

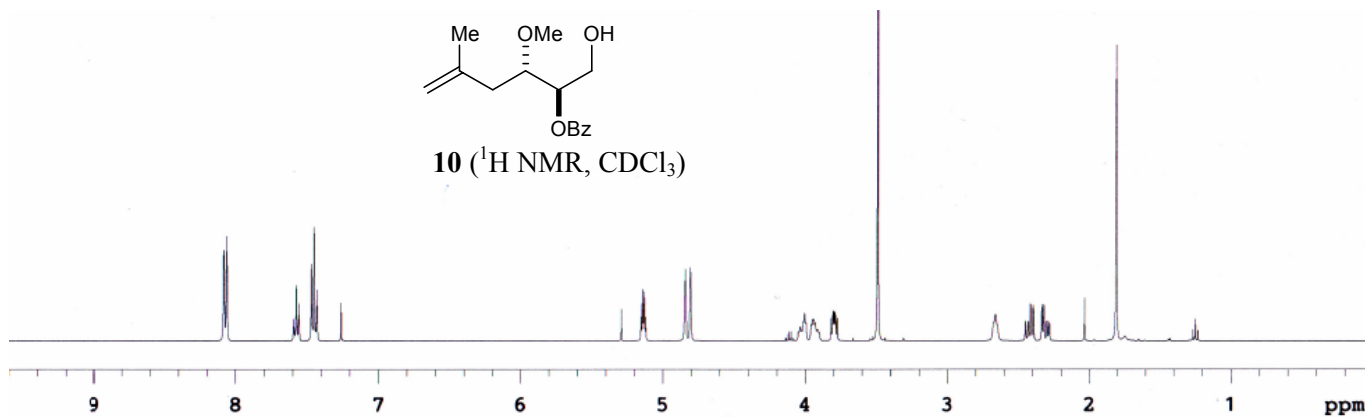


(^{13}C NMR, CDCl_3)

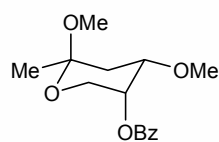
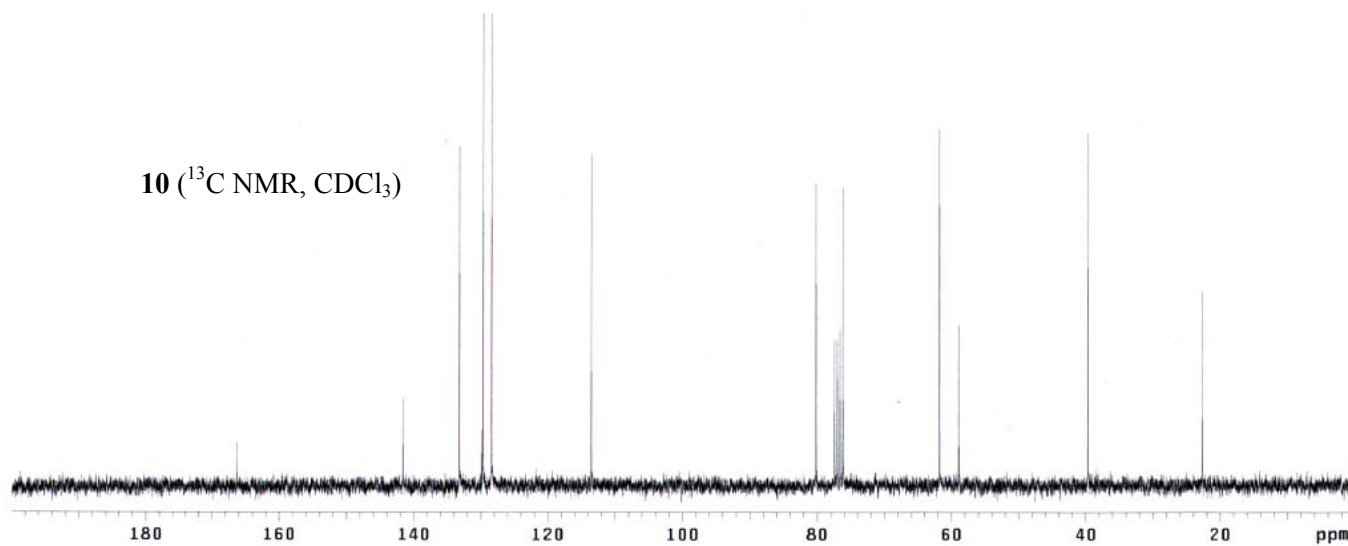




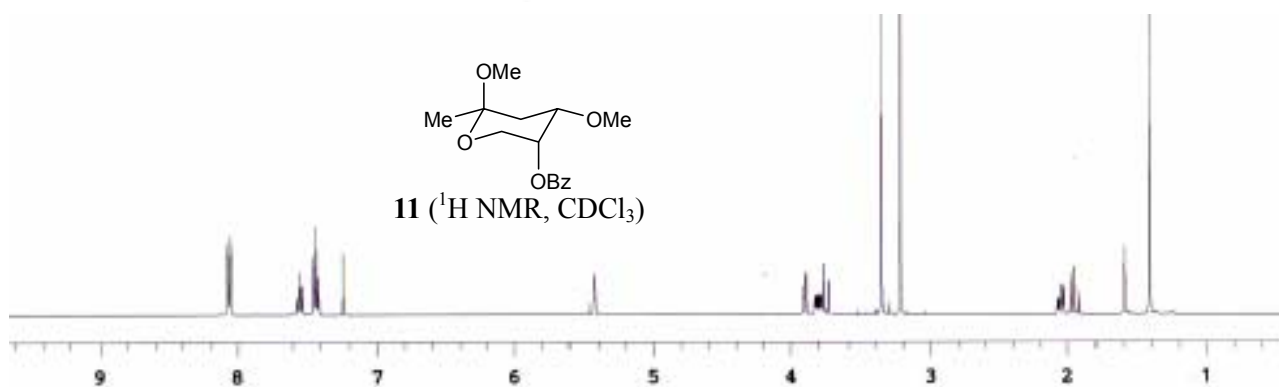
10 (^1H NMR, CDCl_3)

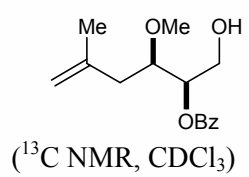


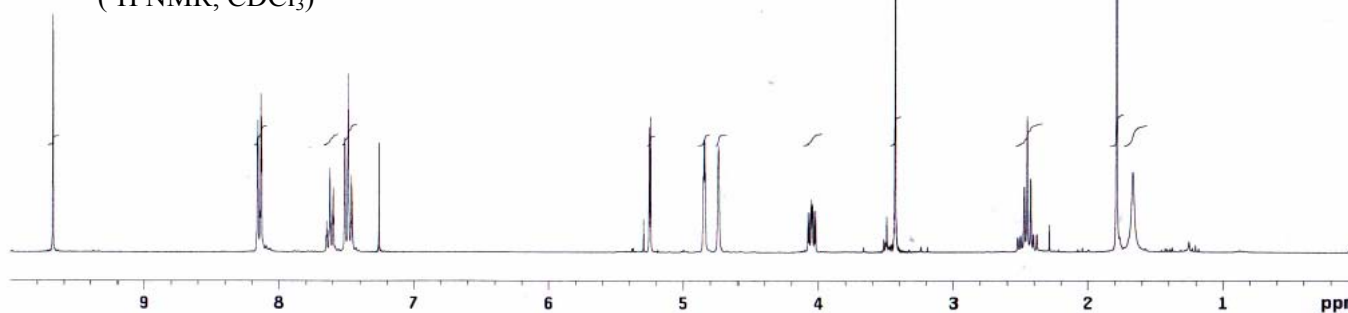
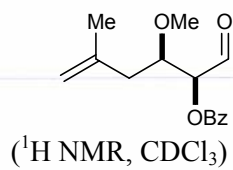
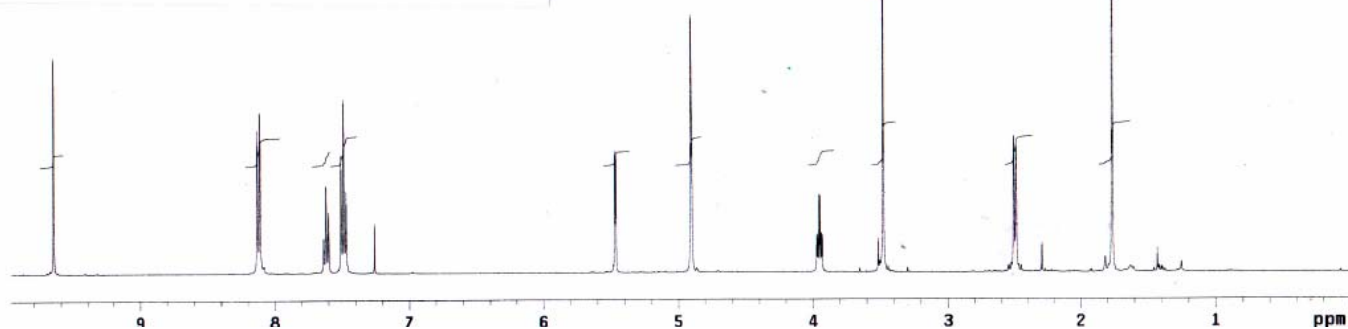
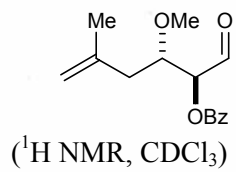
10 (^{13}C NMR, CDCl_3)

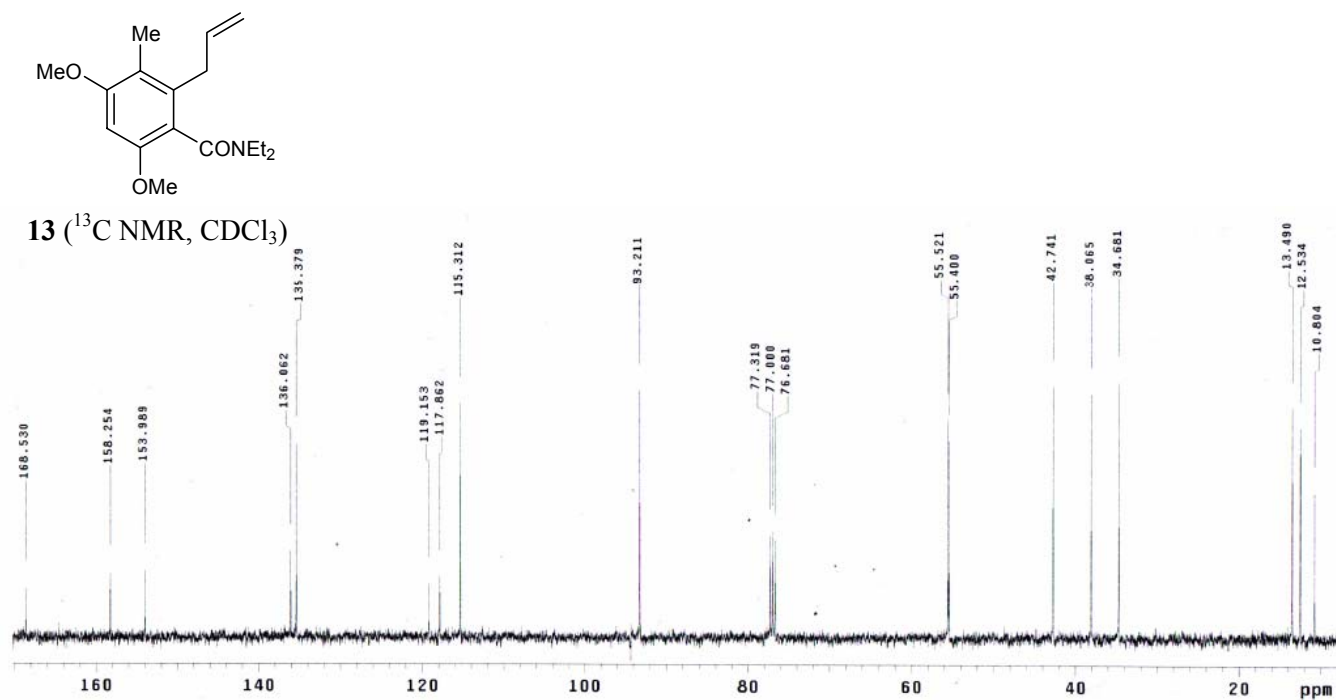
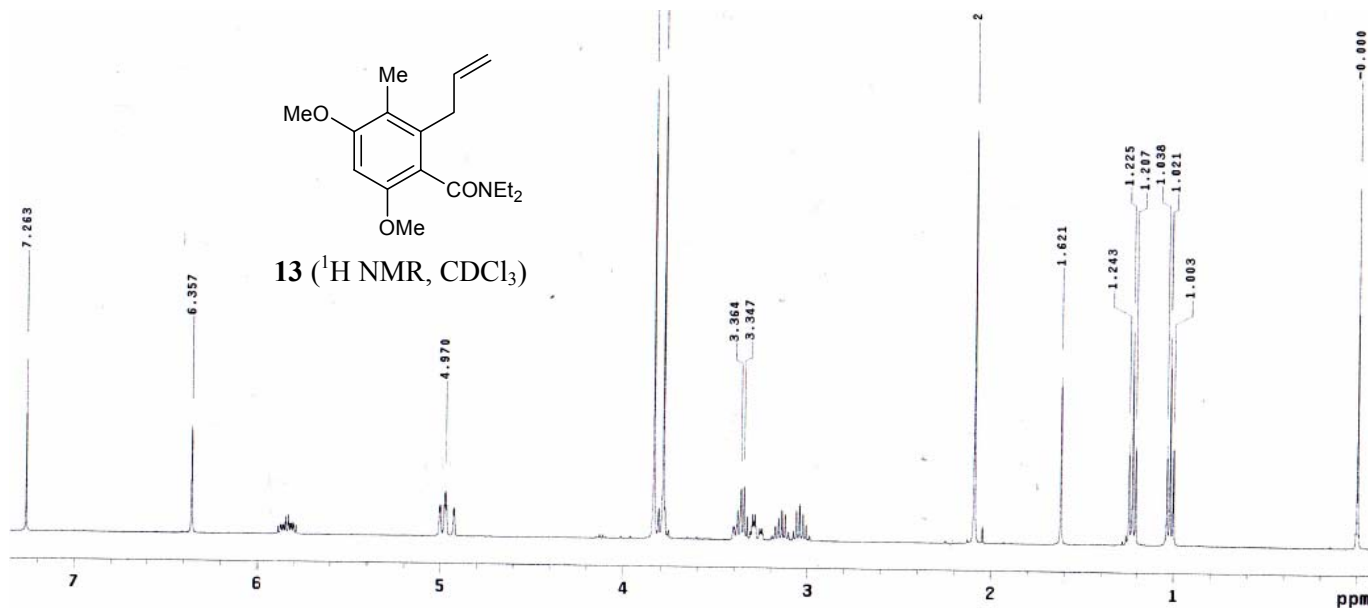


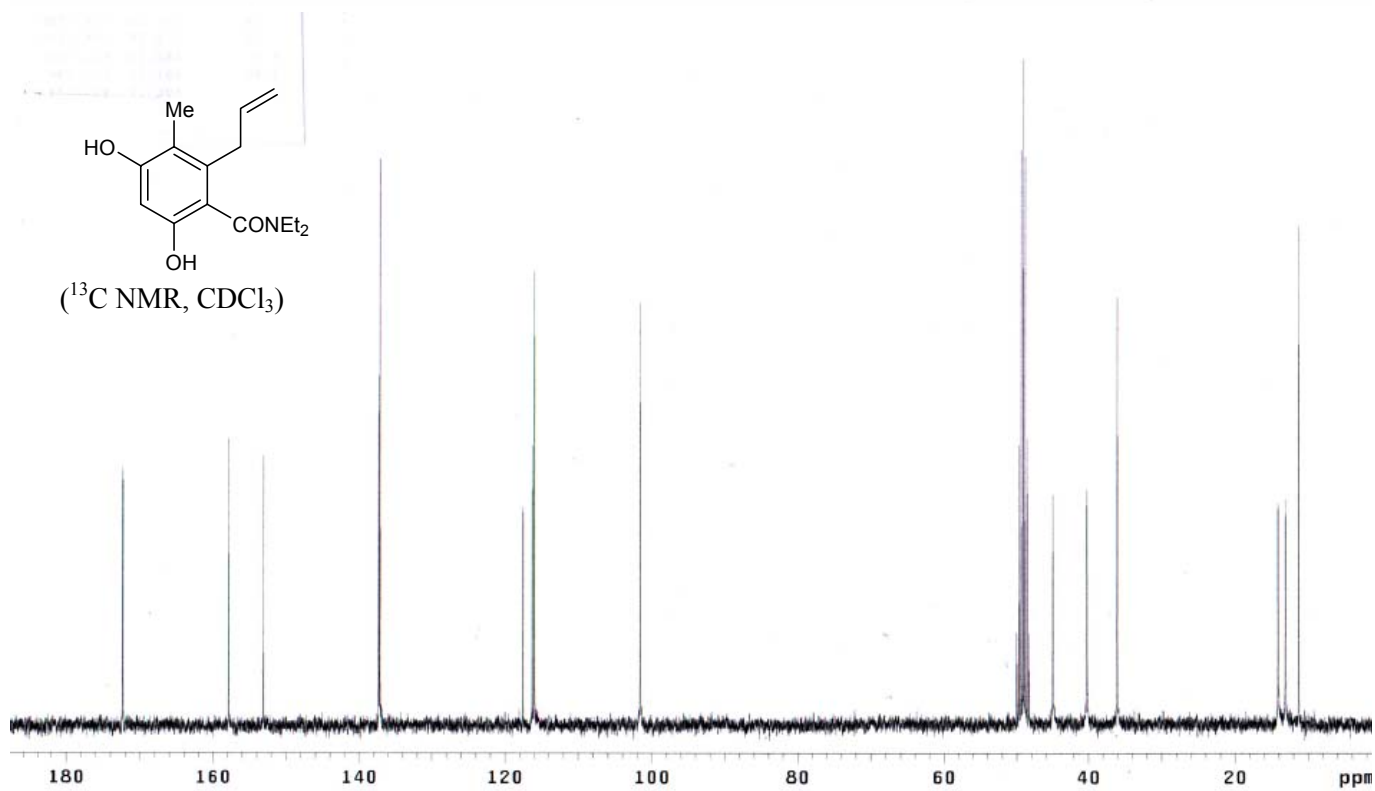
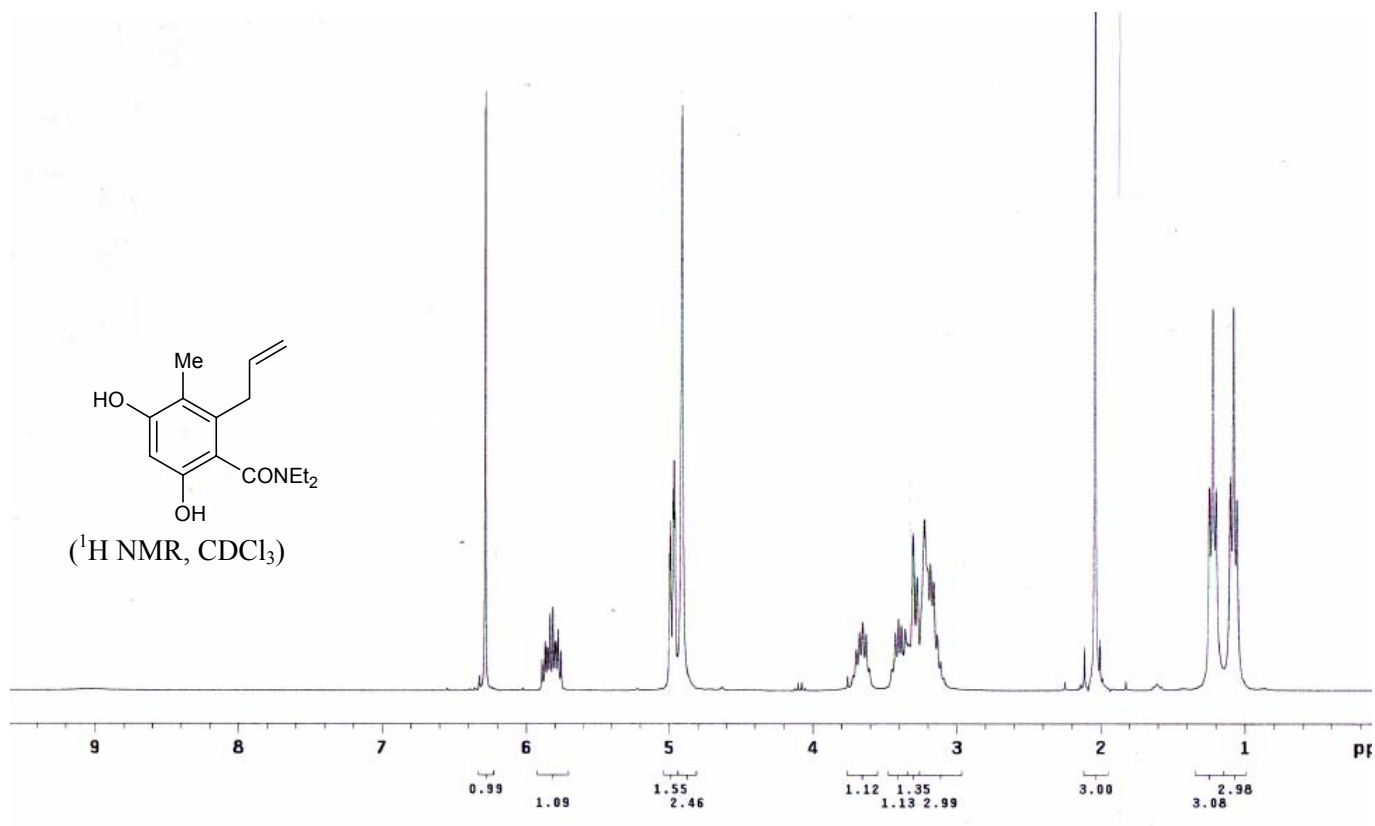
11 (^1H NMR, CDCl_3)

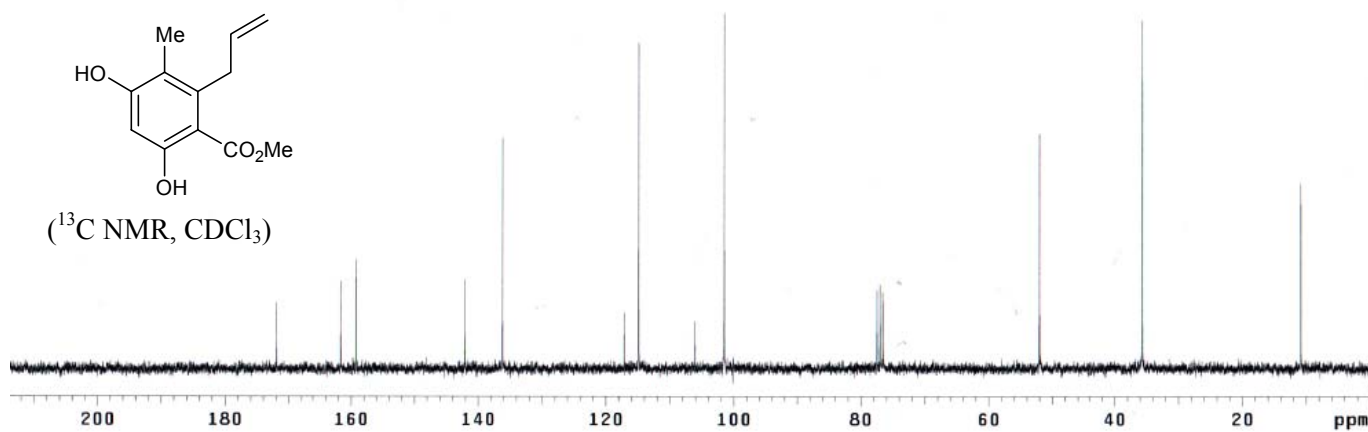
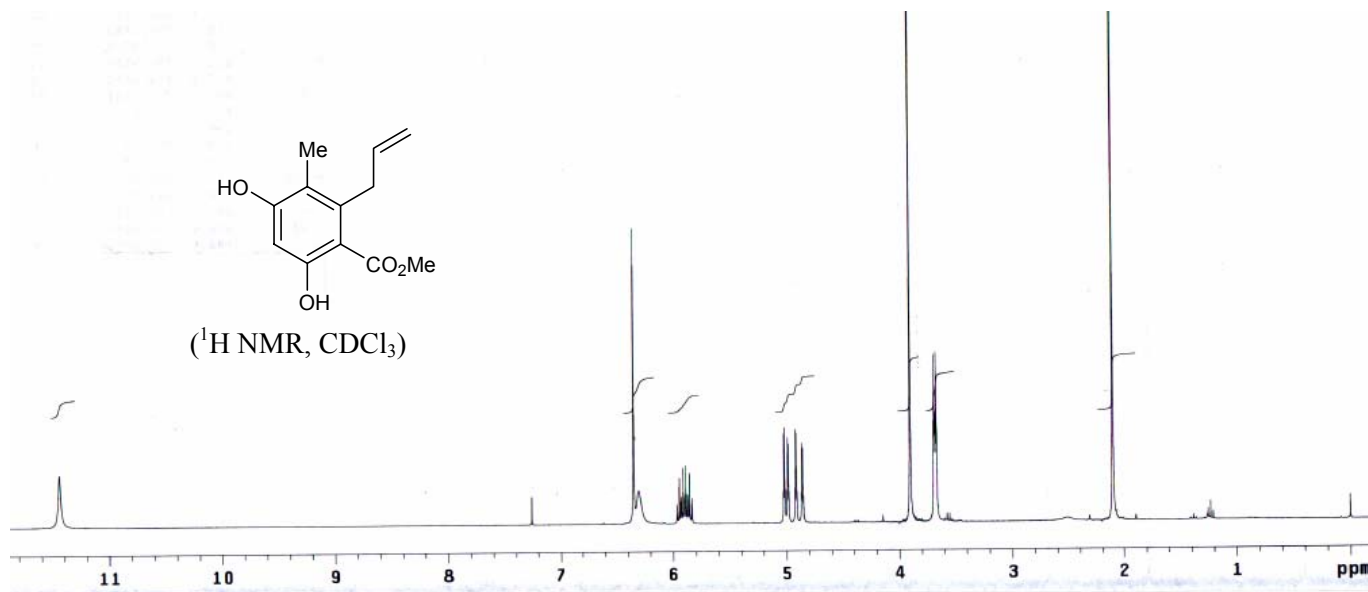


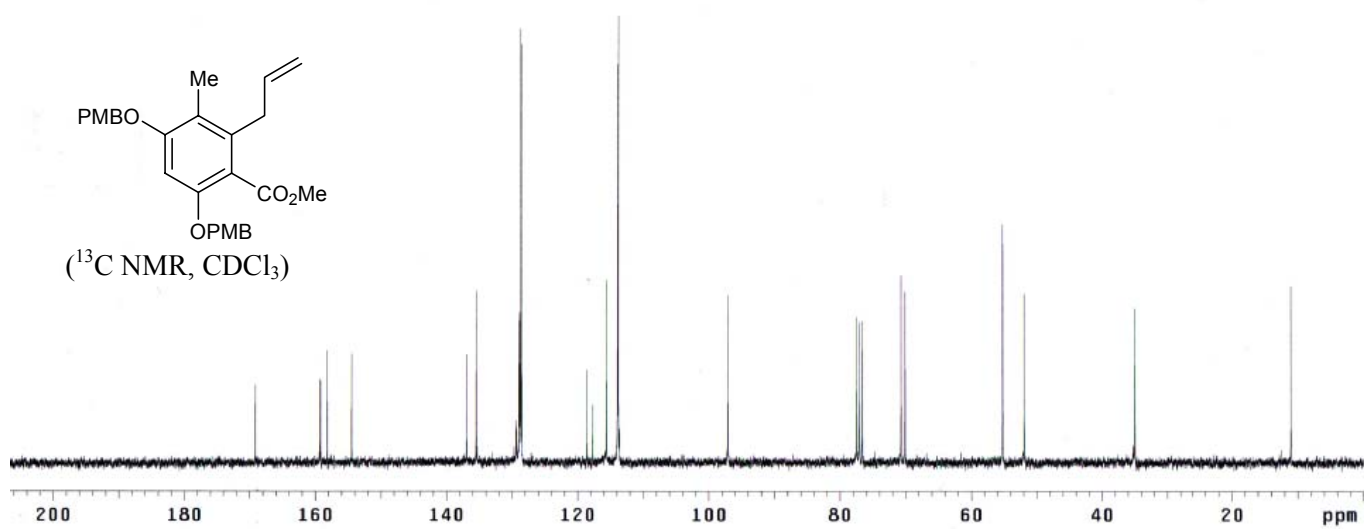
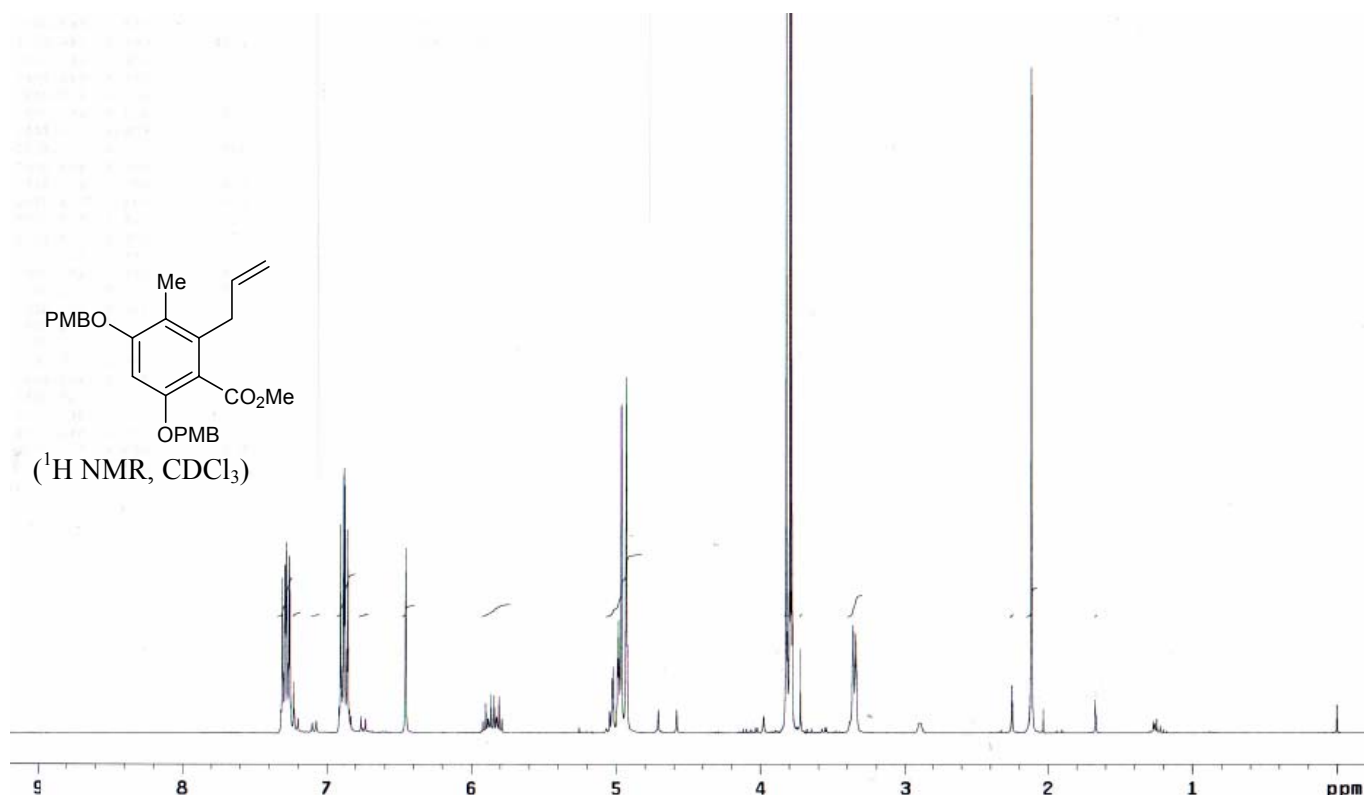


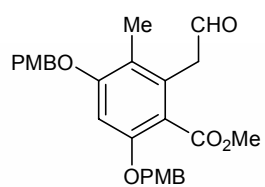




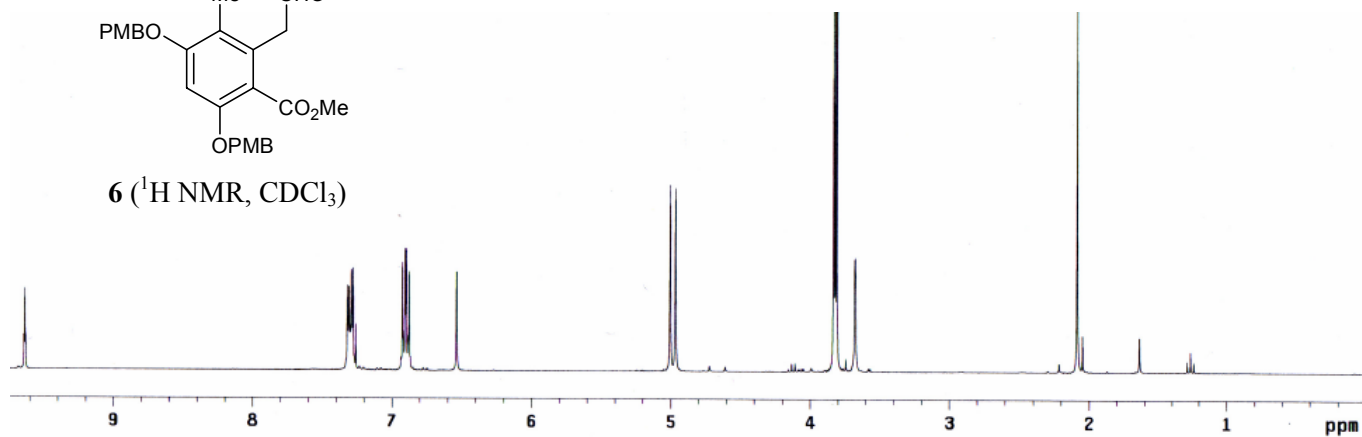




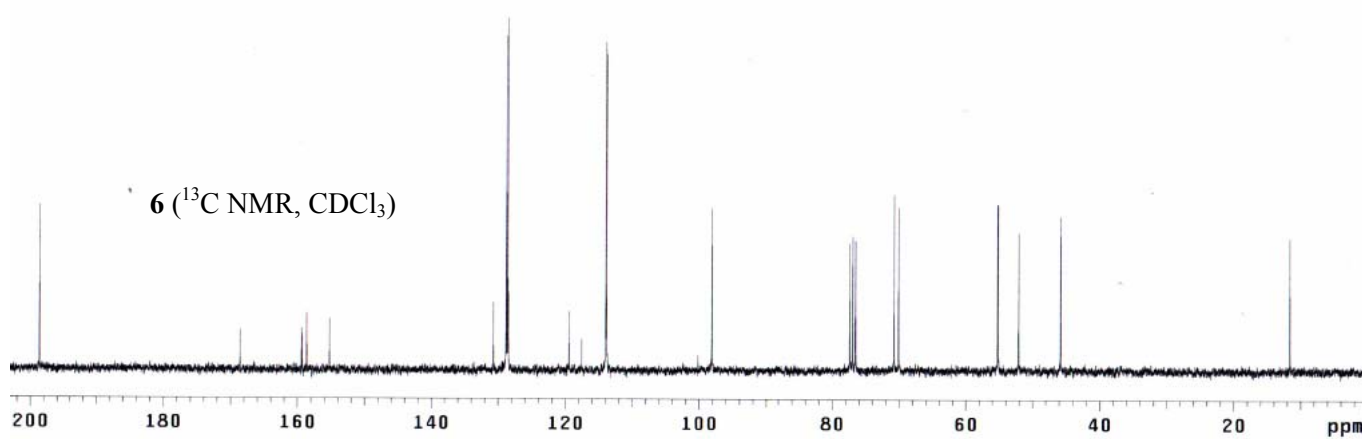


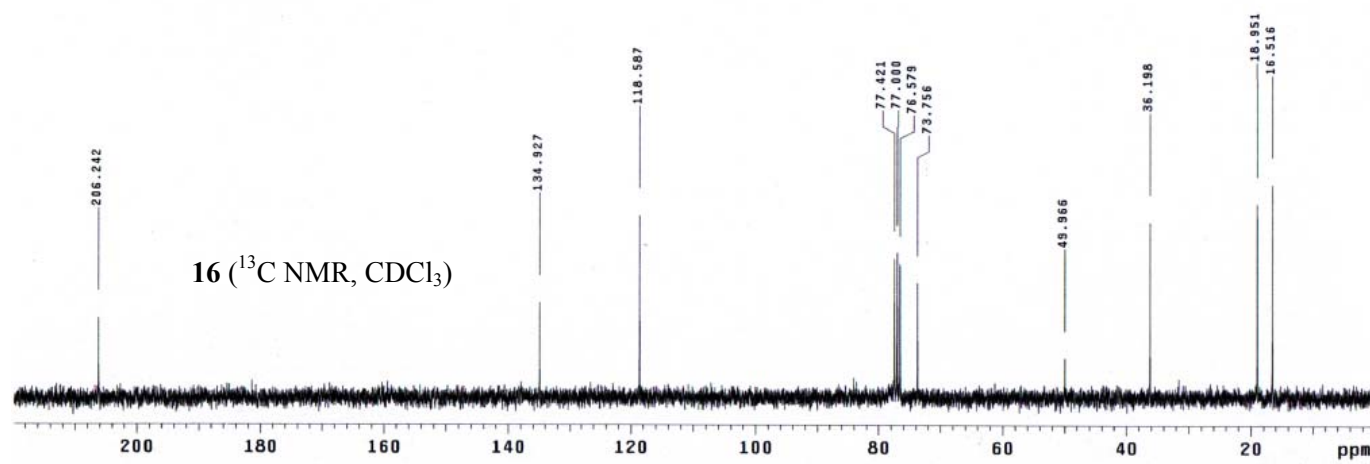
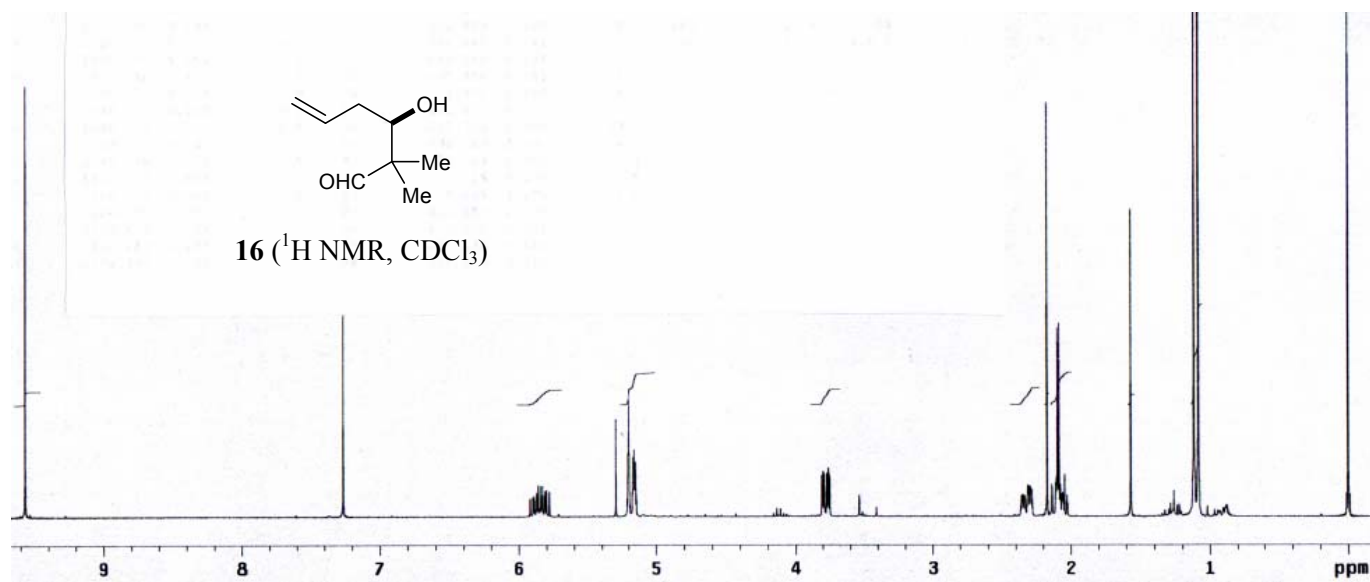


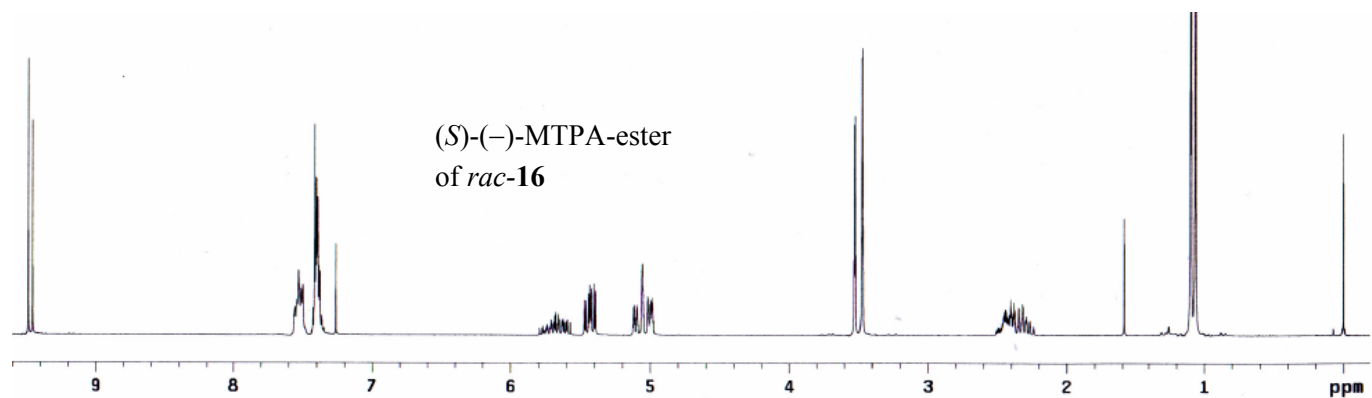
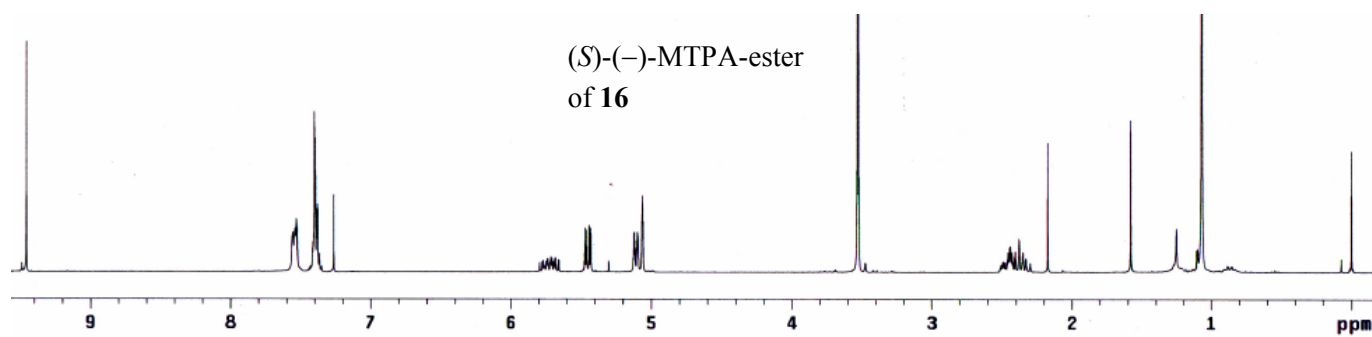
6 (¹H NMR, CDCl₃)



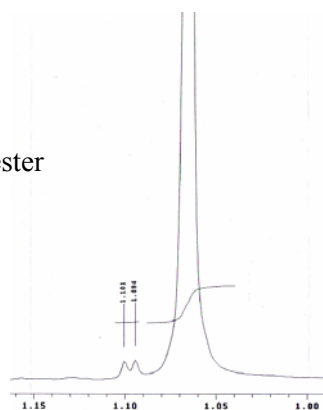
6 (¹³C NMR, CDCl₃)



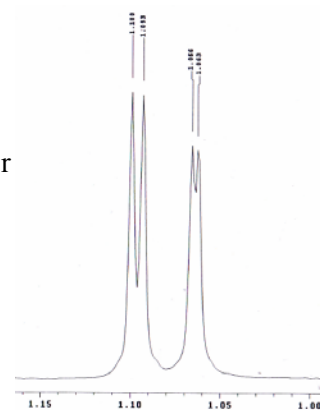


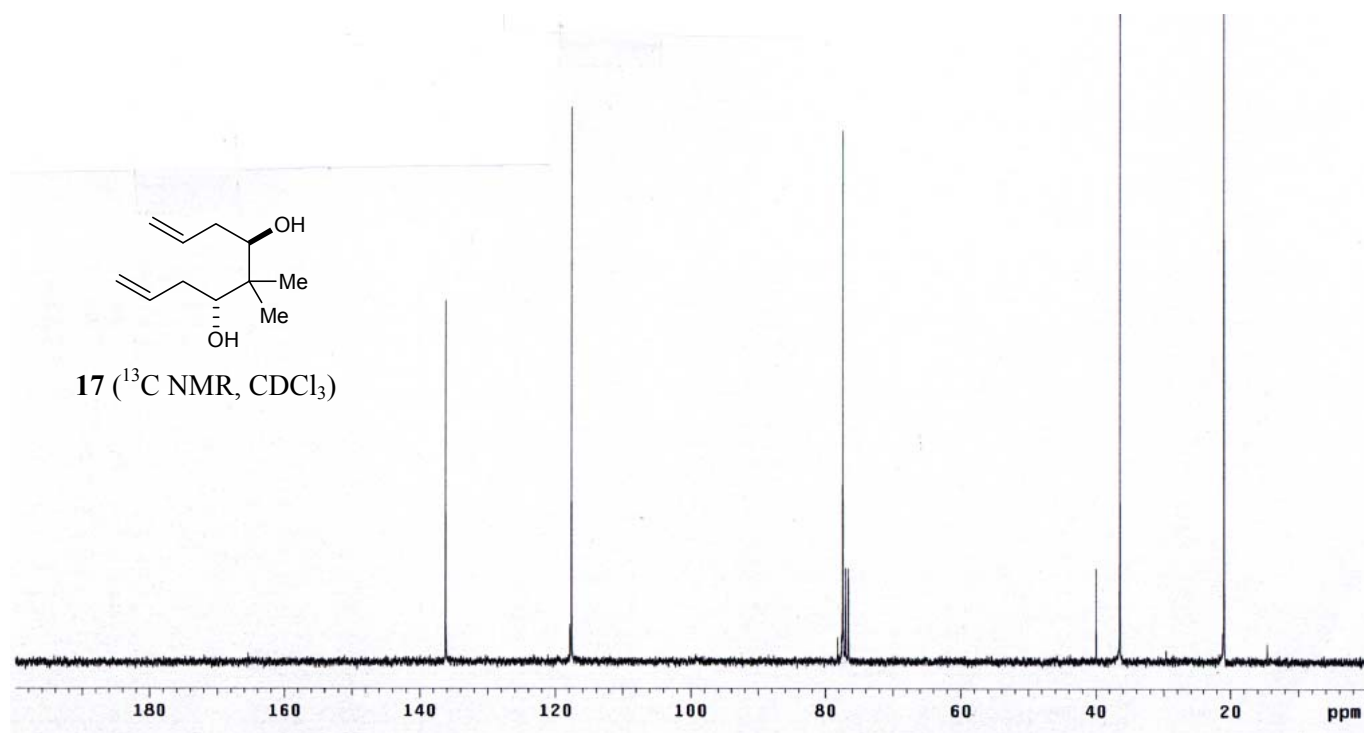
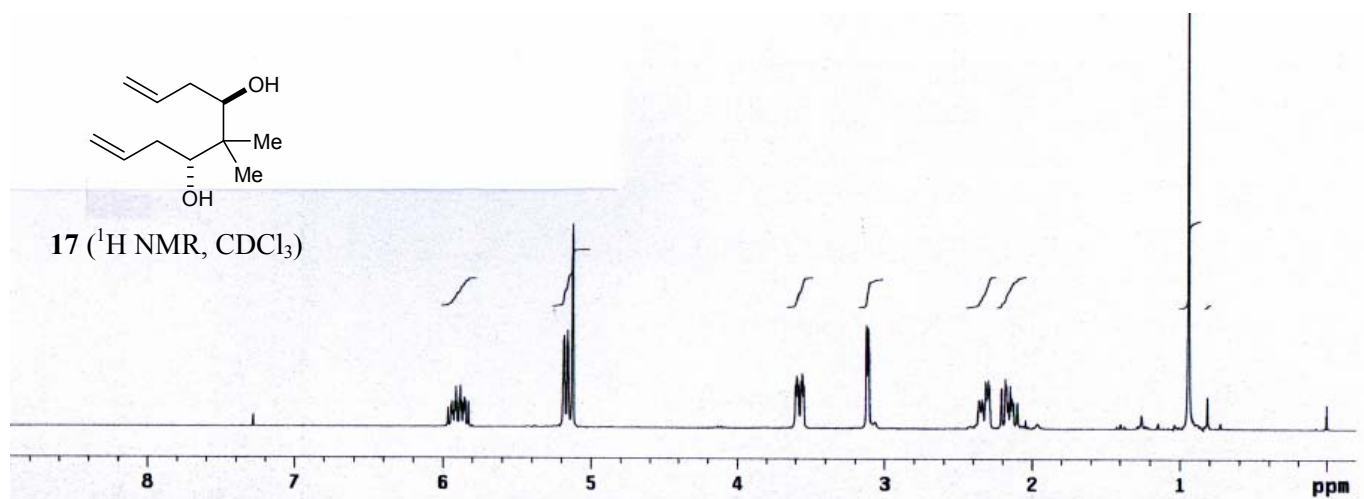


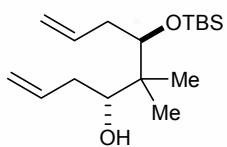
(S)-(-)-MTPA-ester
of **16**:



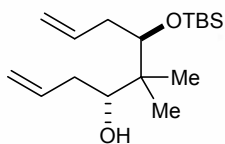
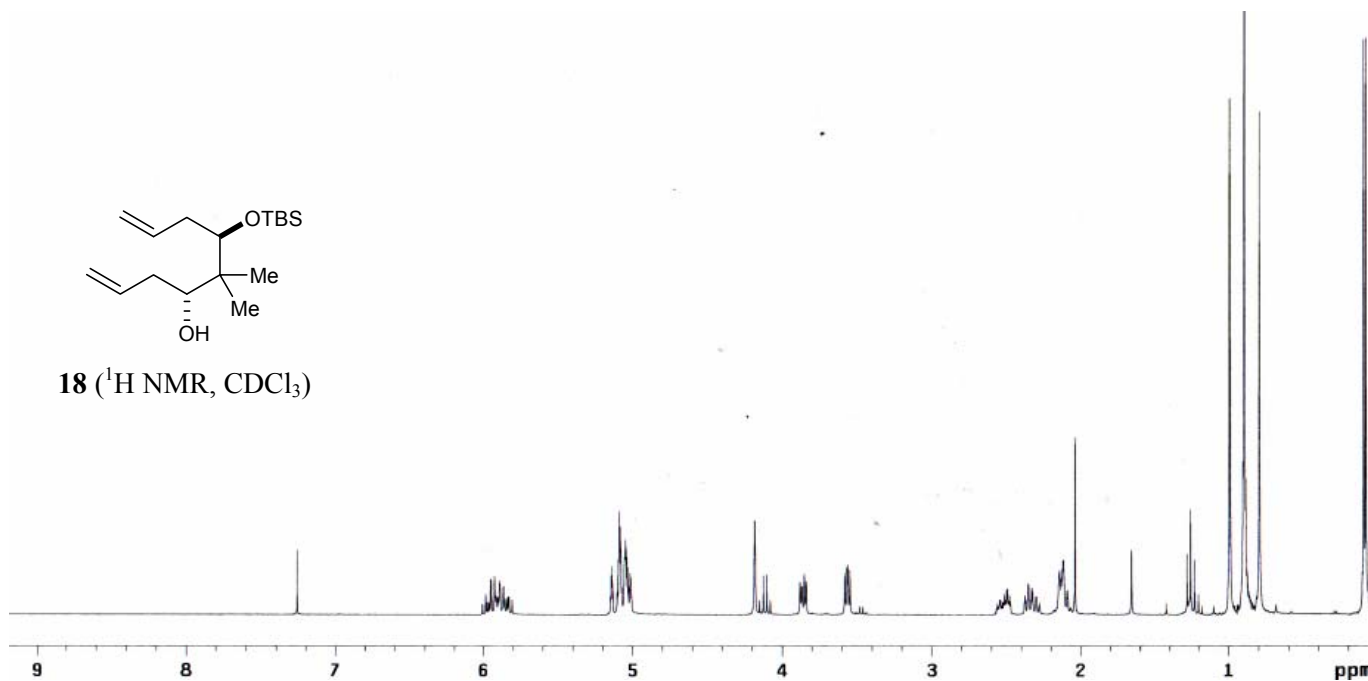
(S)-(-)-MTPA-ester
of *rac*-**16**



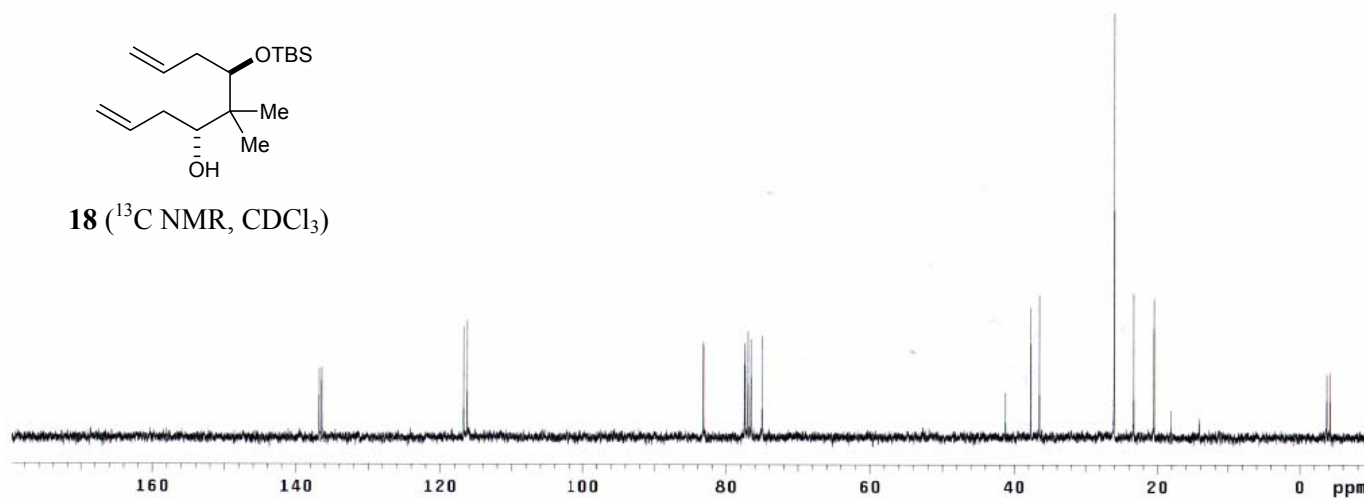


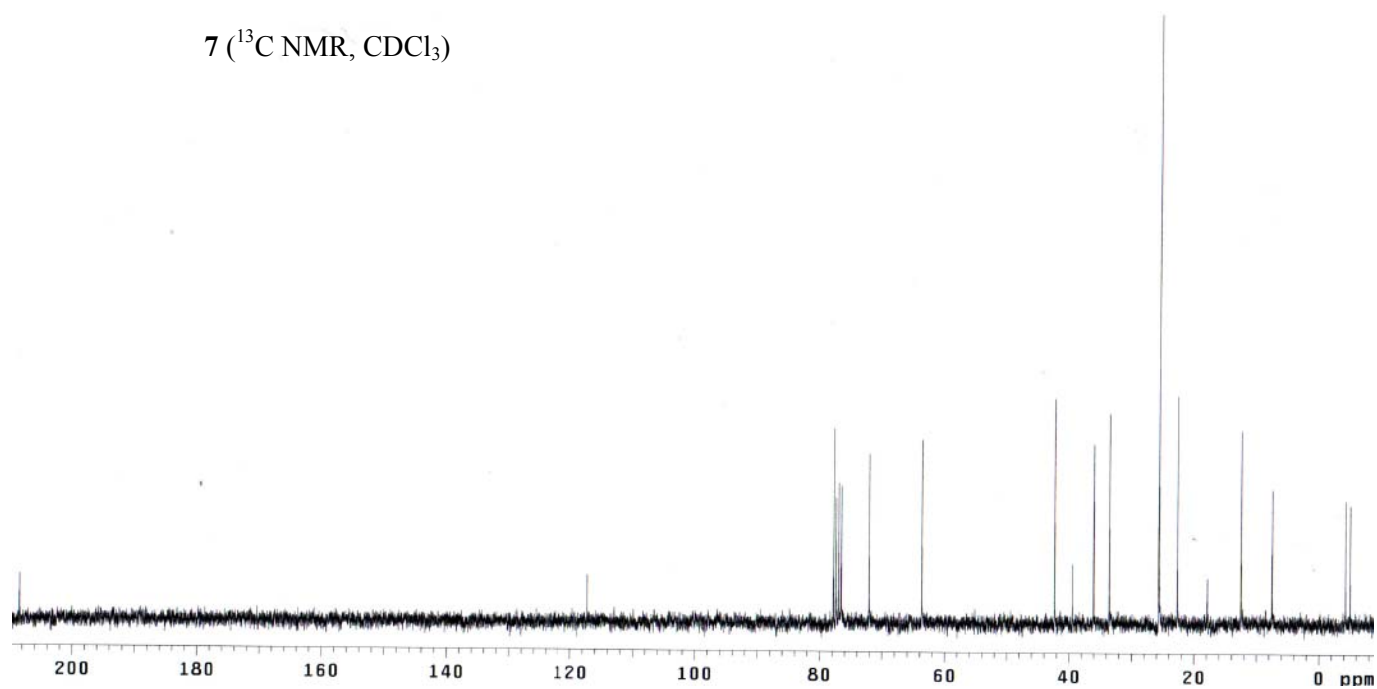
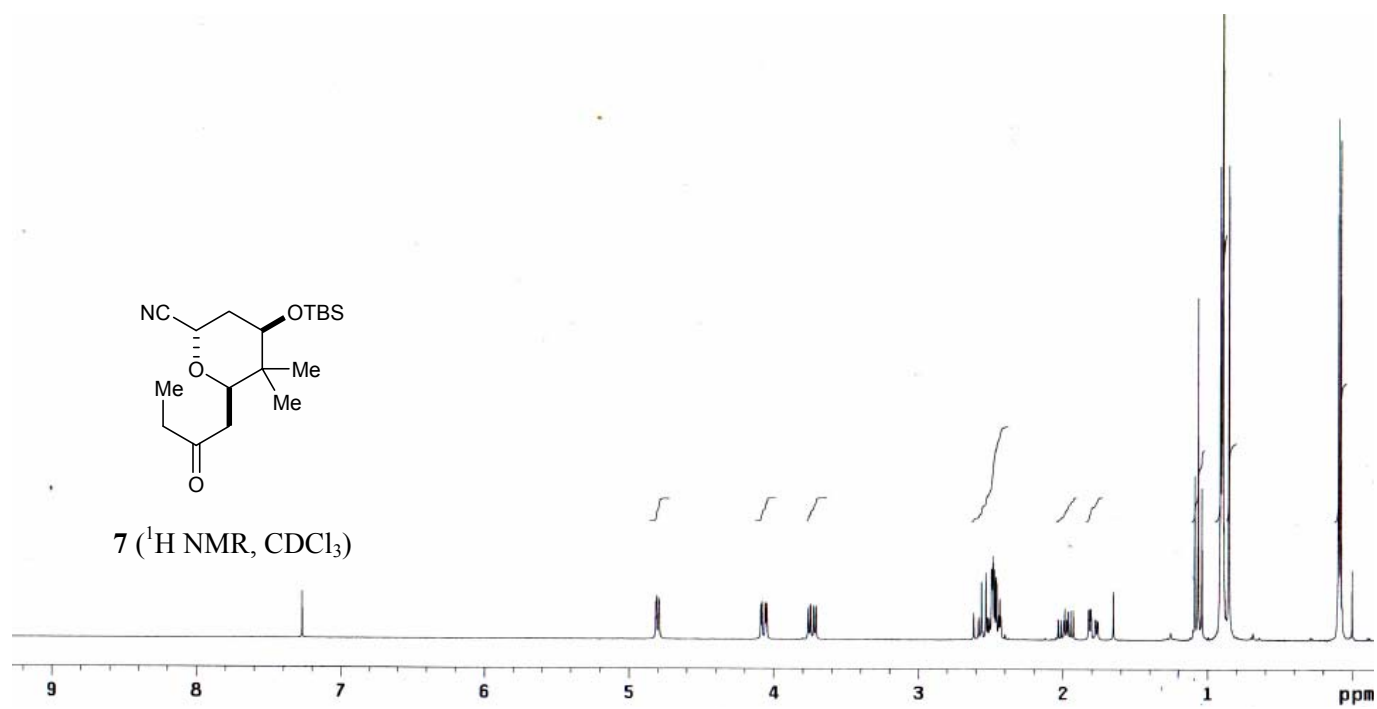


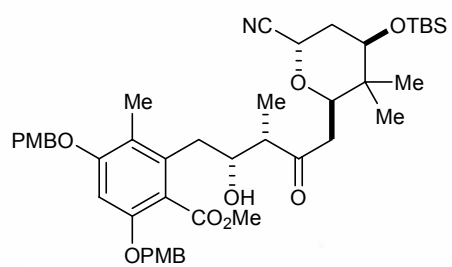
18 (^1H NMR, CDCl_3)



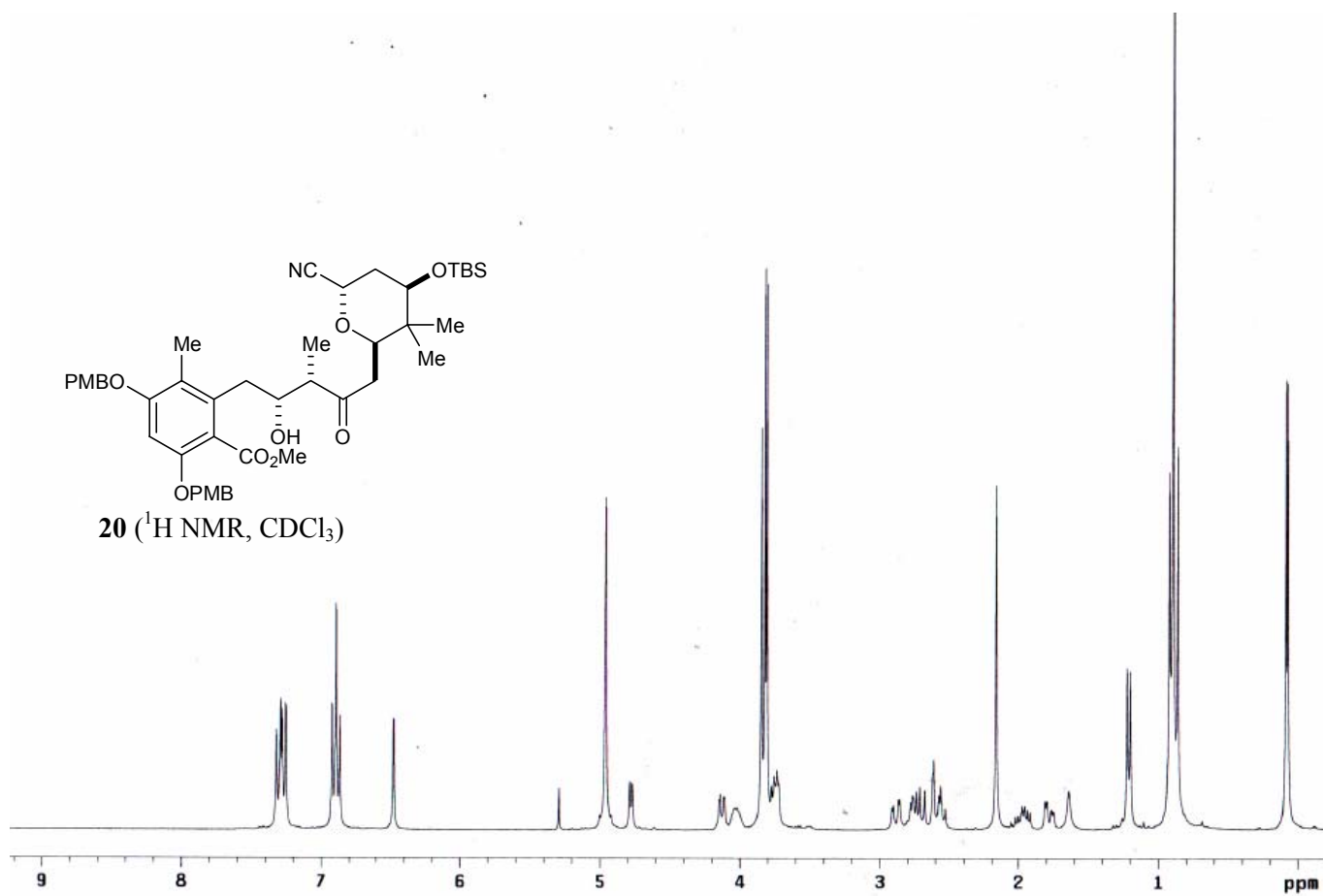
18 (^{13}C NMR, CDCl_3)



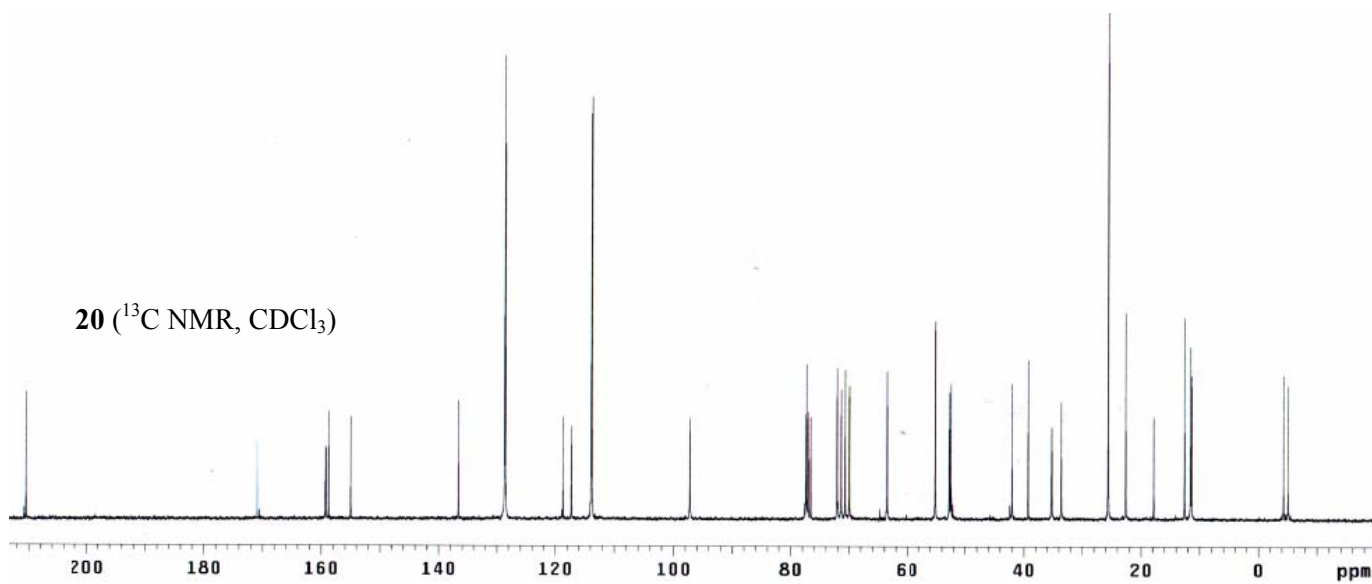


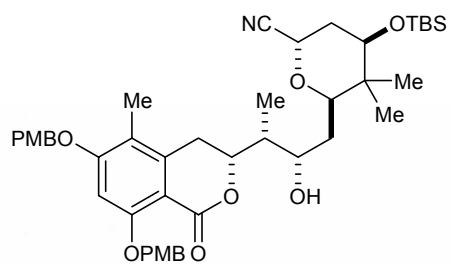


20 (¹H NMR, CDCl₃)

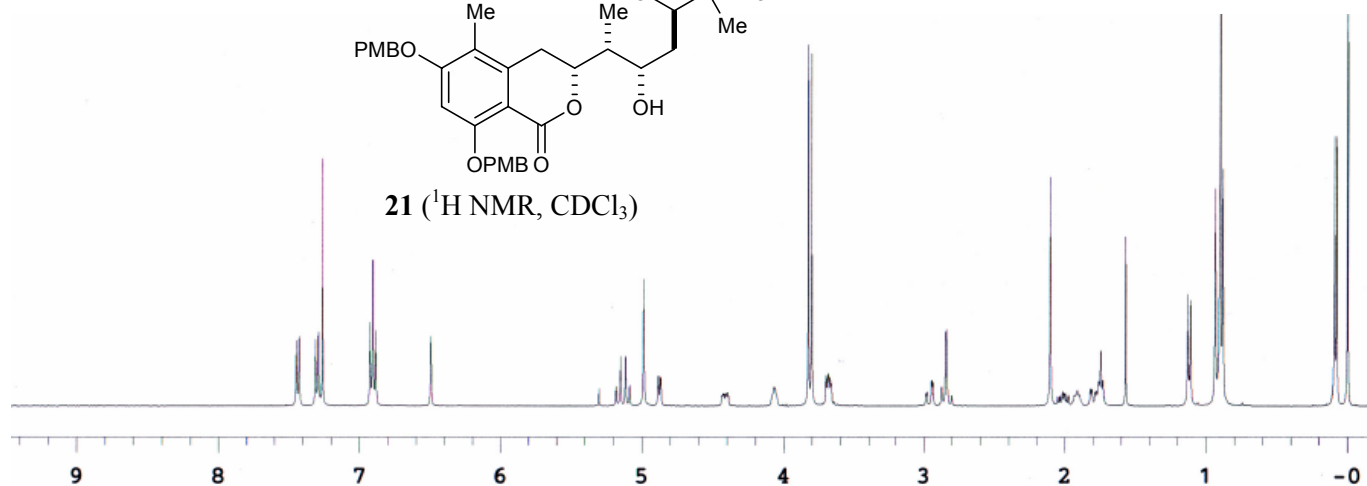


20 (¹³C NMR, CDCl₃)

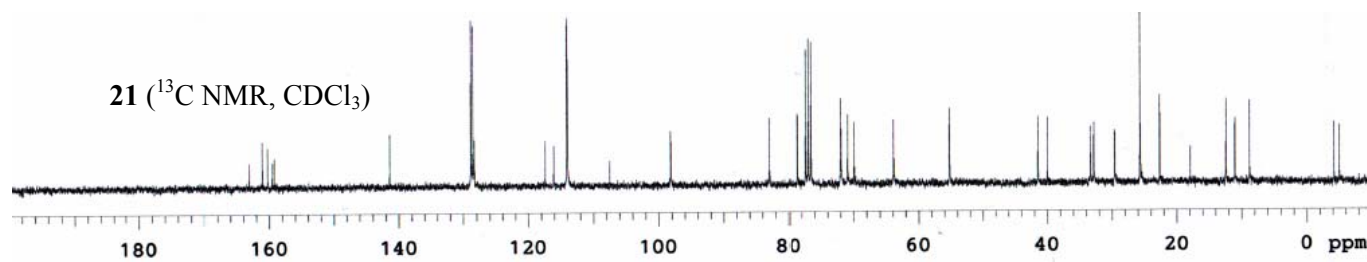


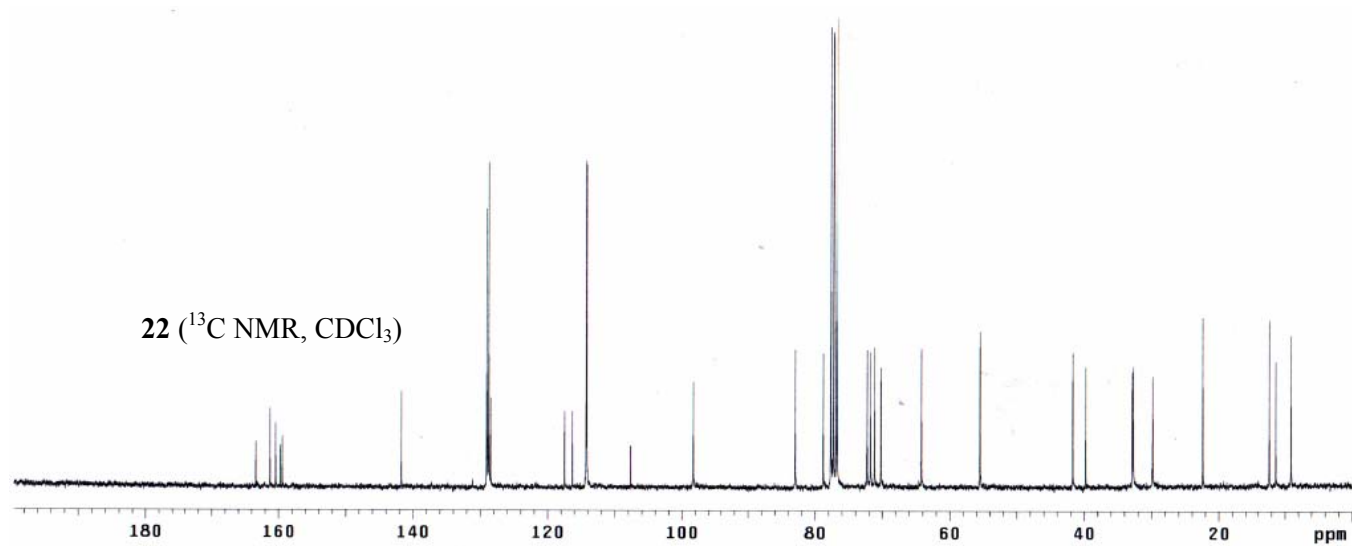
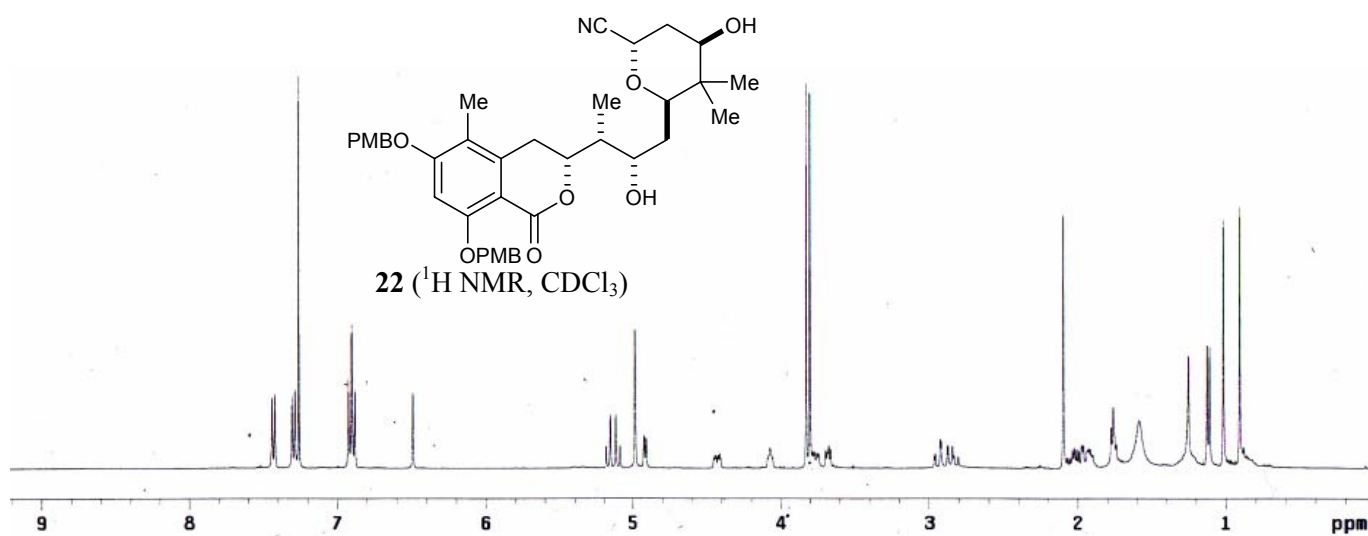


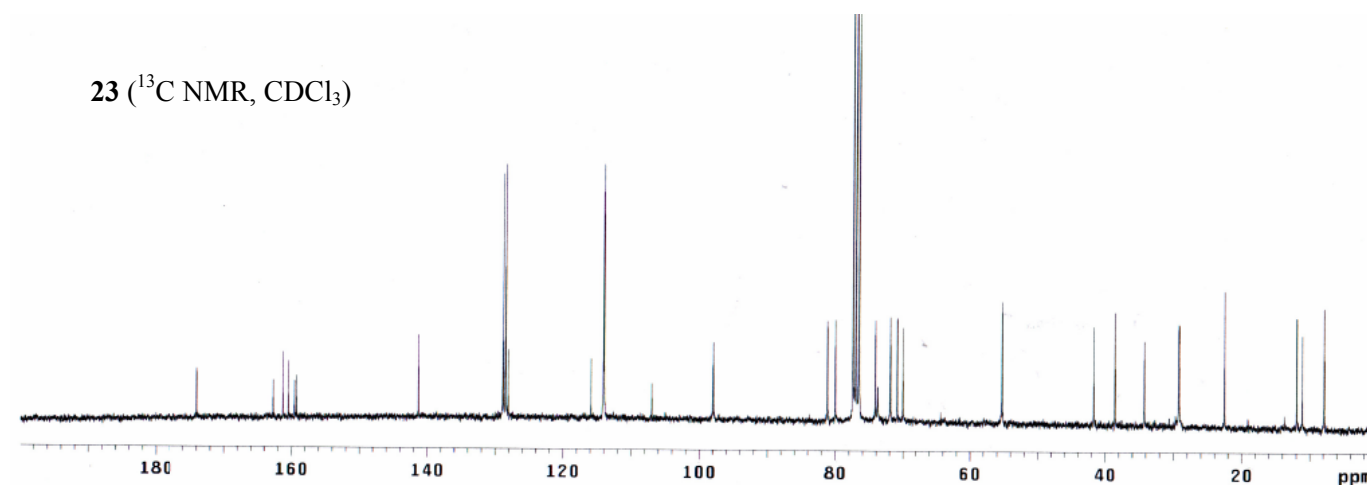
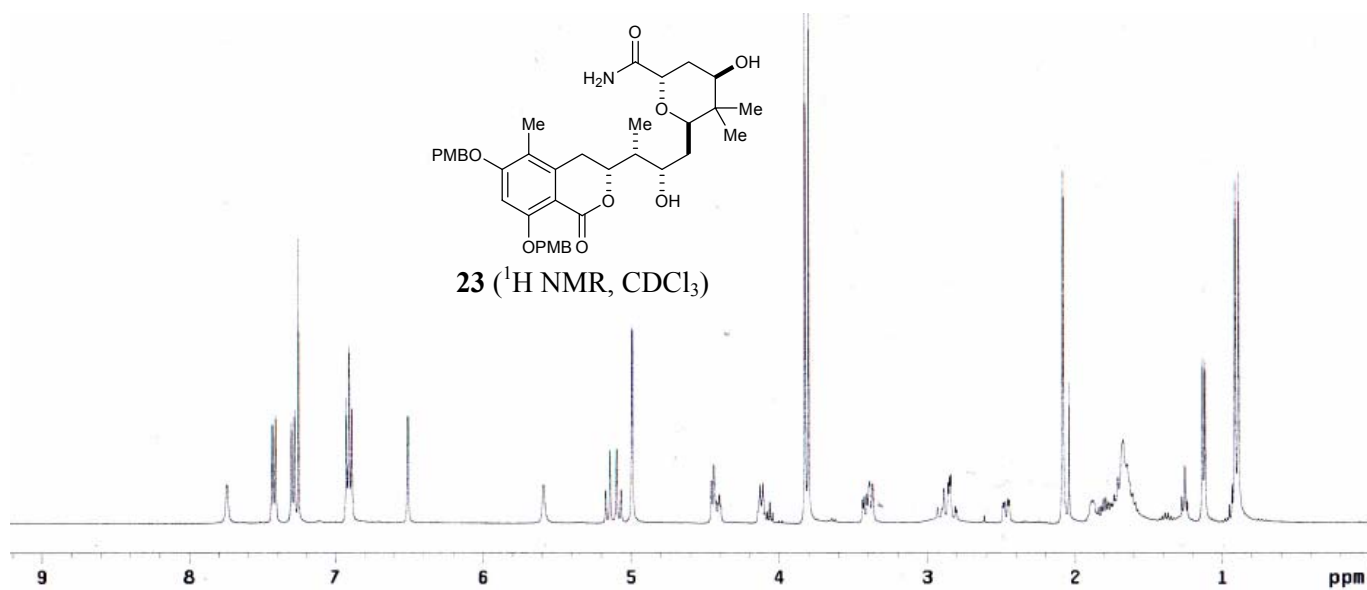
21 (^1H NMR, CDCl_3)

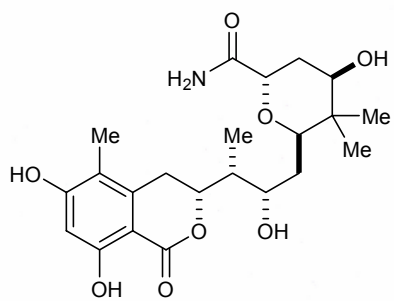


21 (^{13}C NMR, CDCl_3)

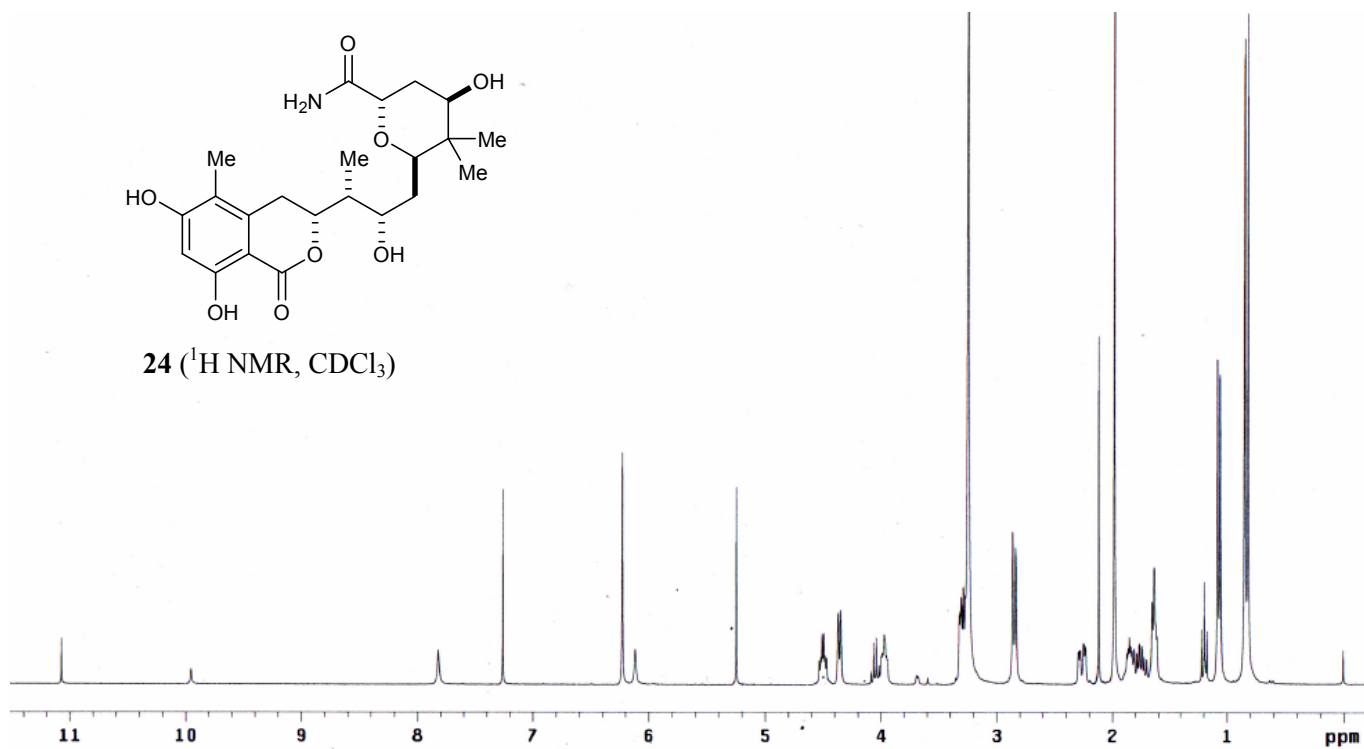




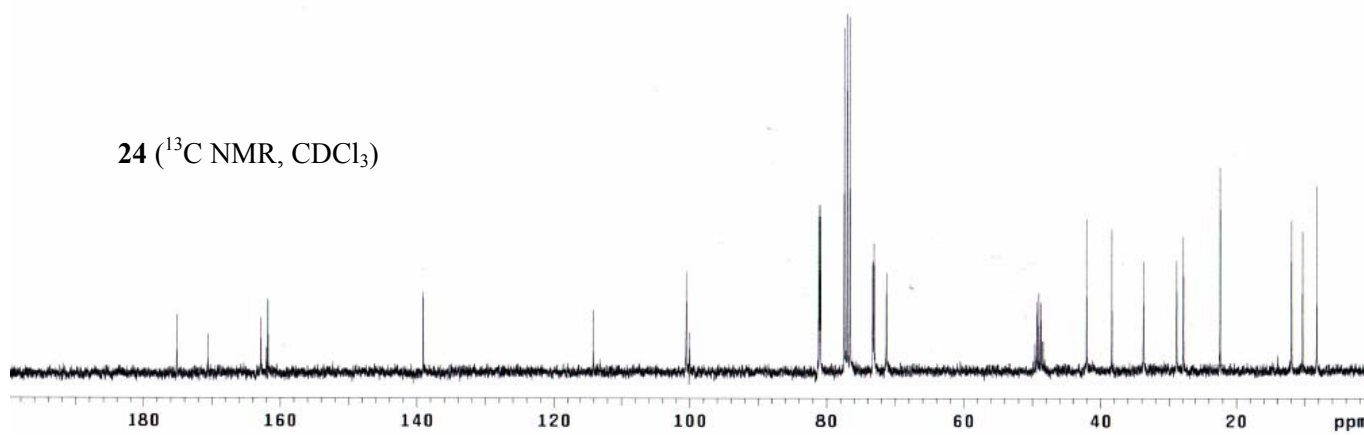


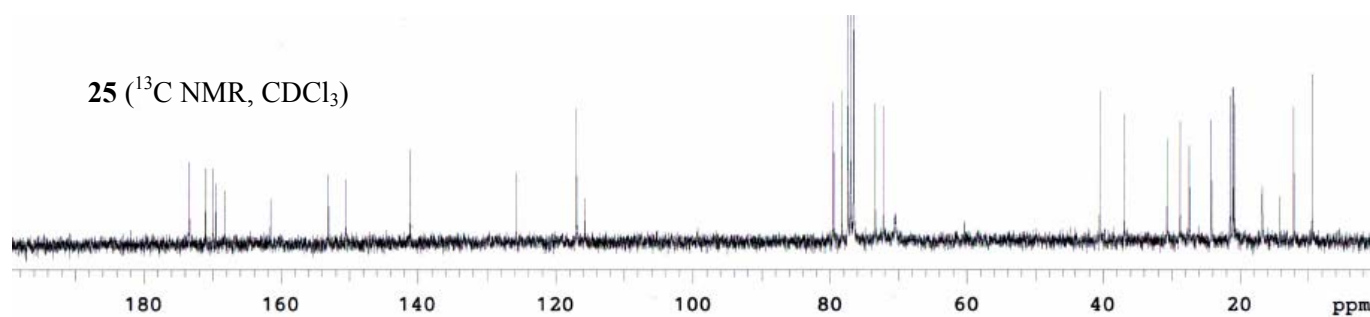
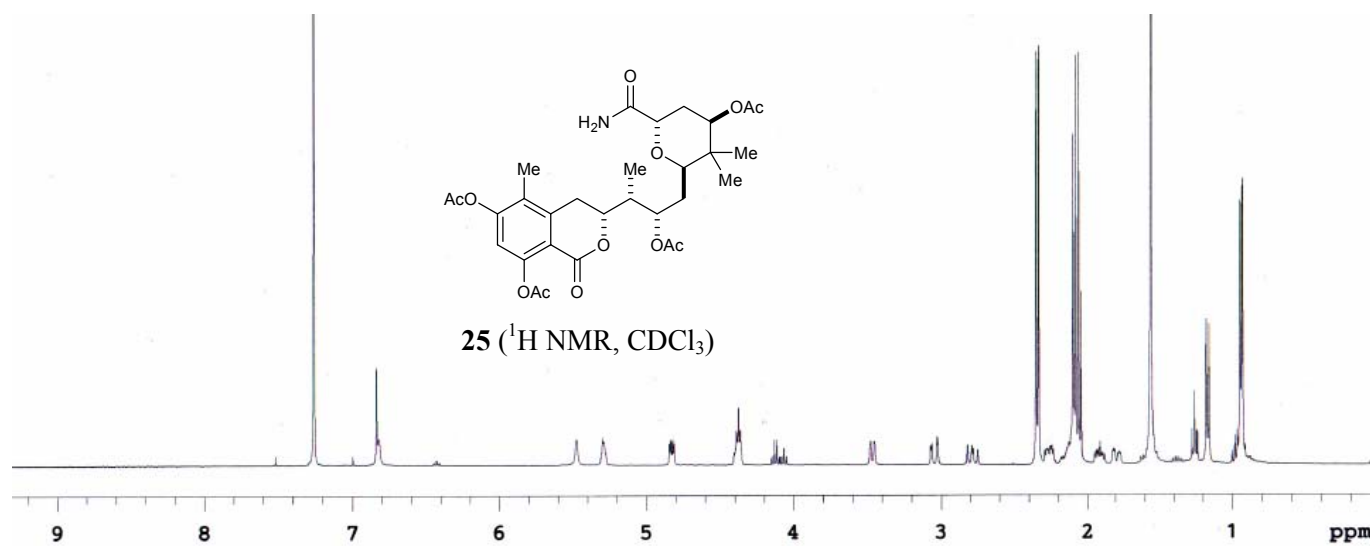


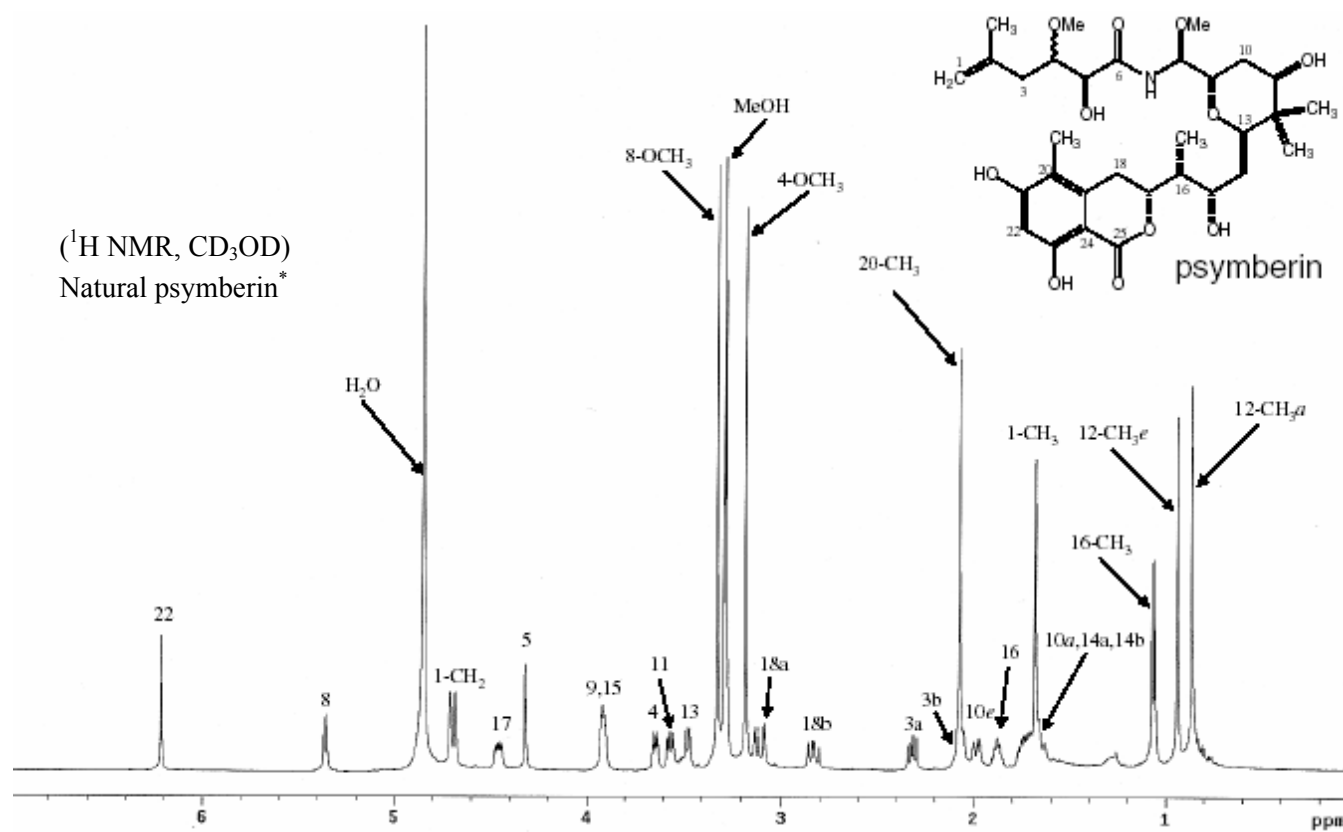
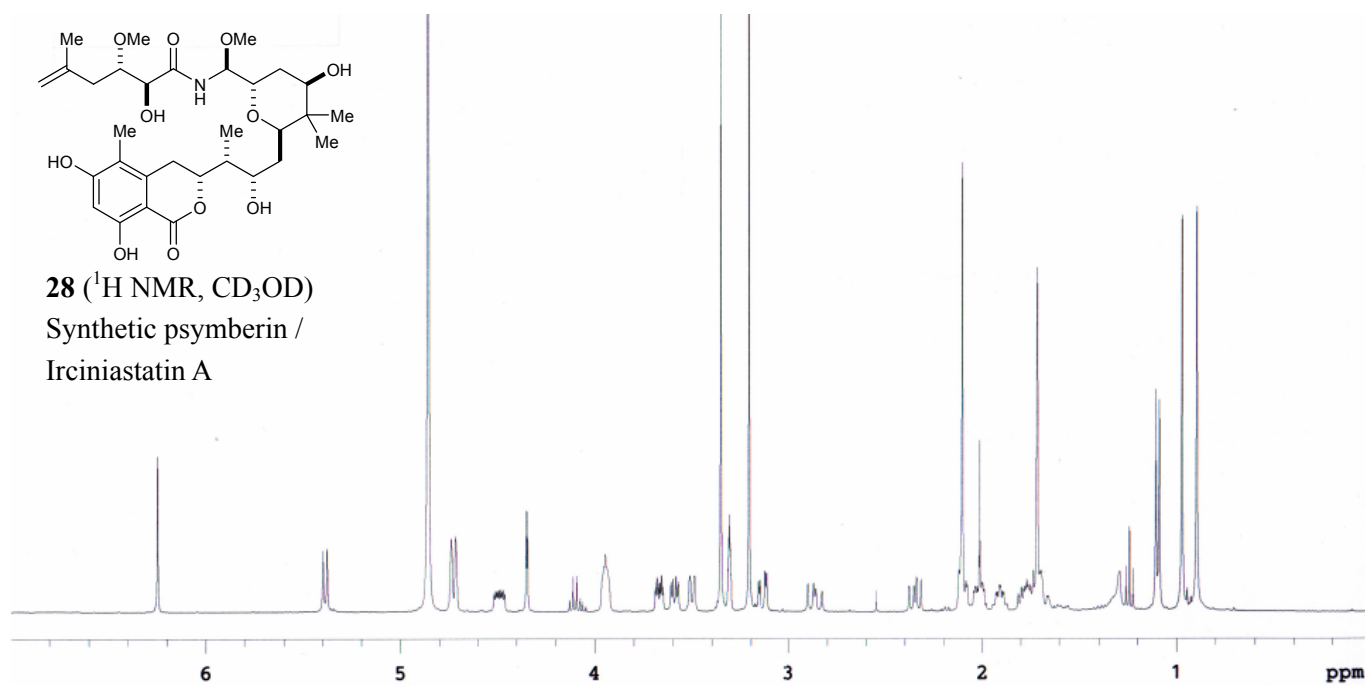
24 (^1H NMR, CDCl_3)



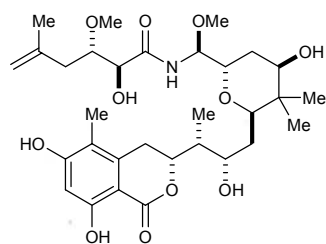
24 (^{13}C NMR, CDCl_3)







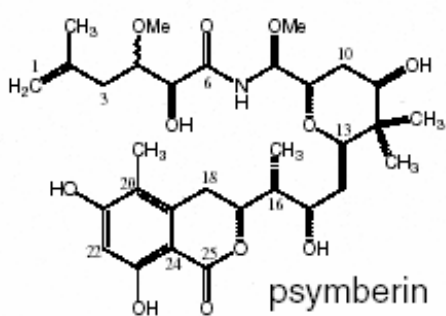
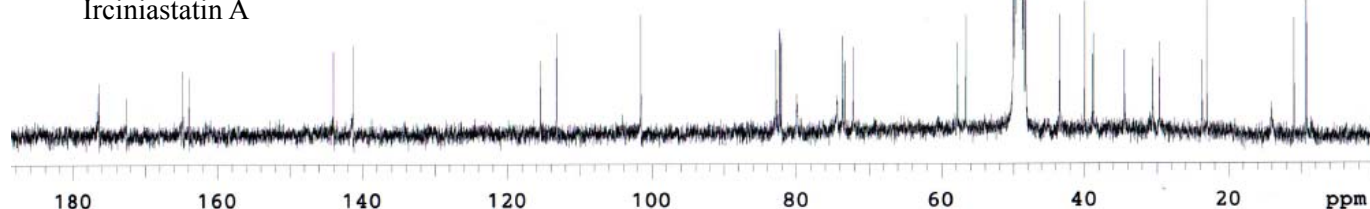
* Spectrum scanned from: Cichewicz, R. H.; Valeriote, F. A.; Crews, P. *Org. Lett.* **2004**, 6, 1951 (Supp. Info.).



28 (^{13}C NMR, CD_3OD)

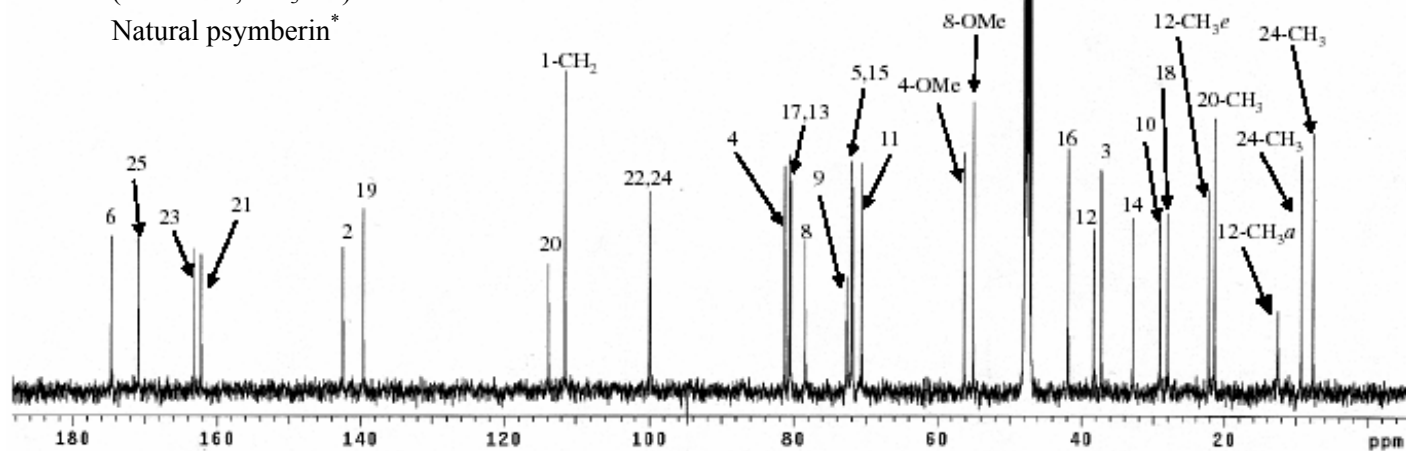
Synthetic psymberin /

Irciniastatin A

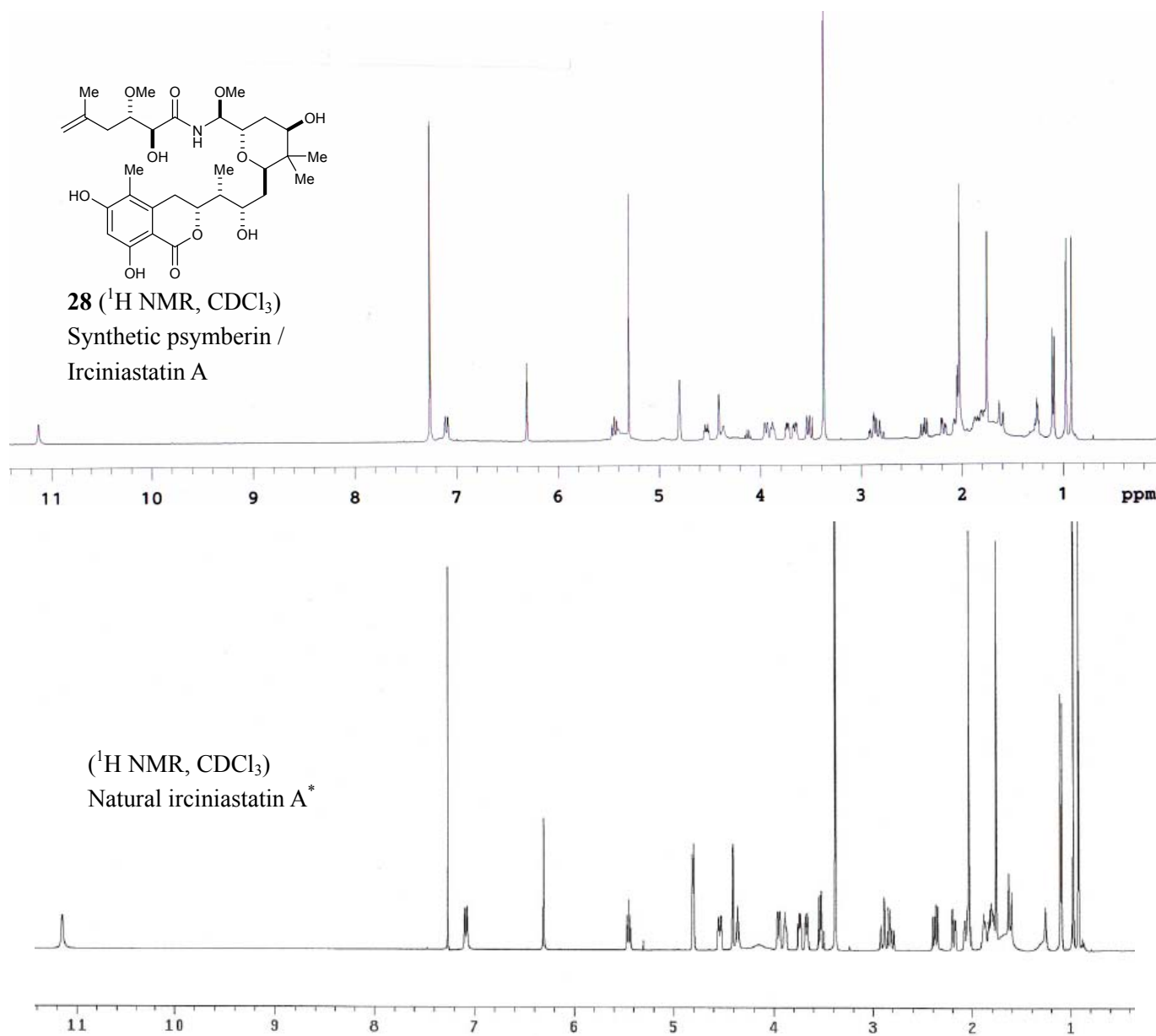


(^{13}H NMR, CD_3OD)

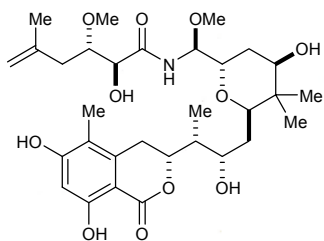
Natural psymberin*



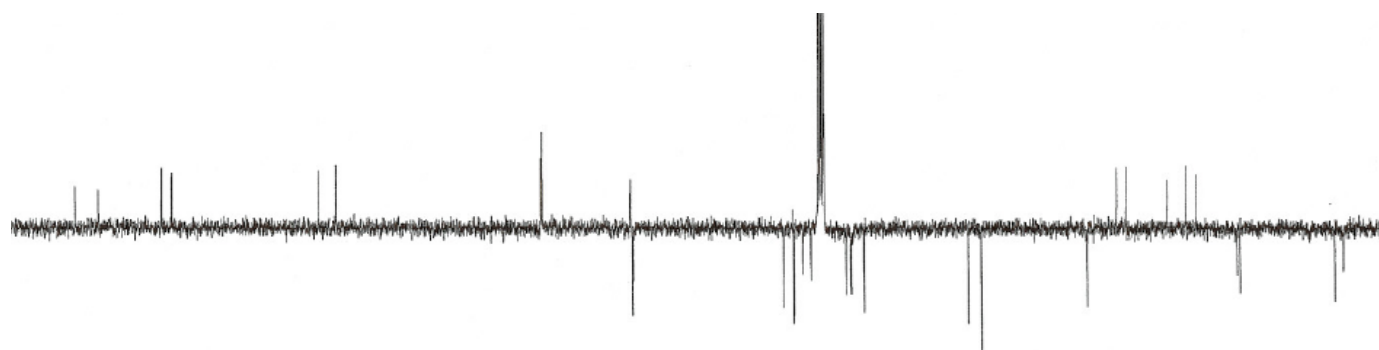
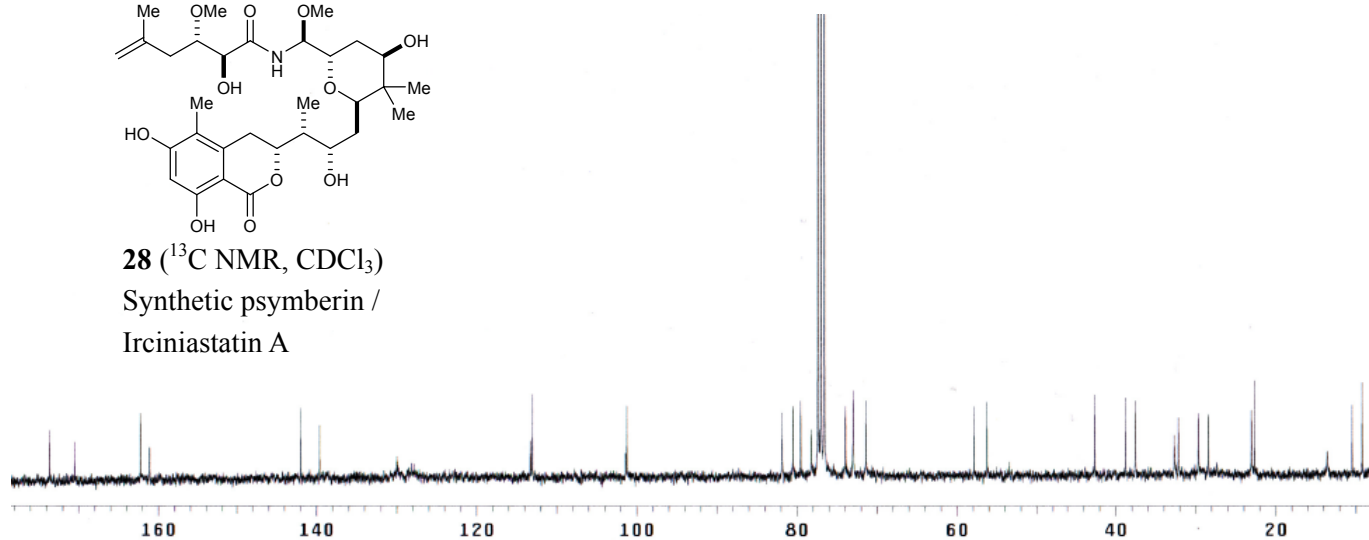
* Spectrum scanned from: Cichewicz, R. H.; Valeriote, F. A.; Crews, P. *Org. Lett.* **2004**, 6, 1951 (Supp. Info.).



*Spectrum kindly provided by Profs. Cherry Herald and George Pettit, Cancer Research Institute, Arizona State University).



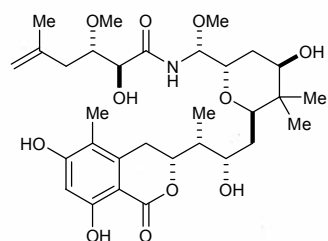
28 (^{13}C NMR, CDCl_3)
 Synthetic psymberin /
 Irciniastatin A



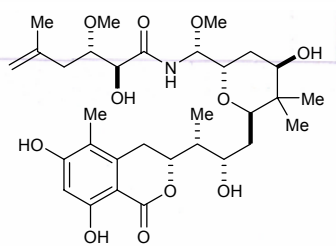
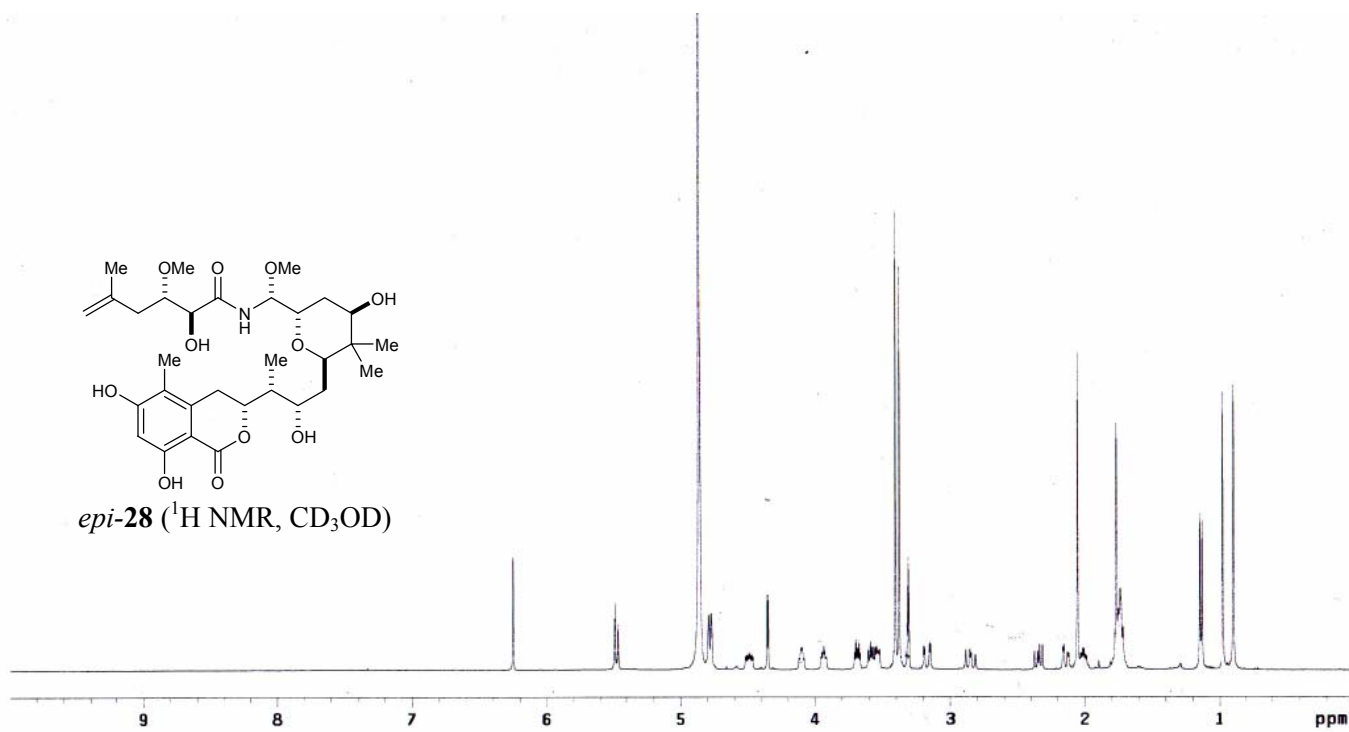
(^{13}C NMR, CDCl_3)
 Natural irciniastatin A*



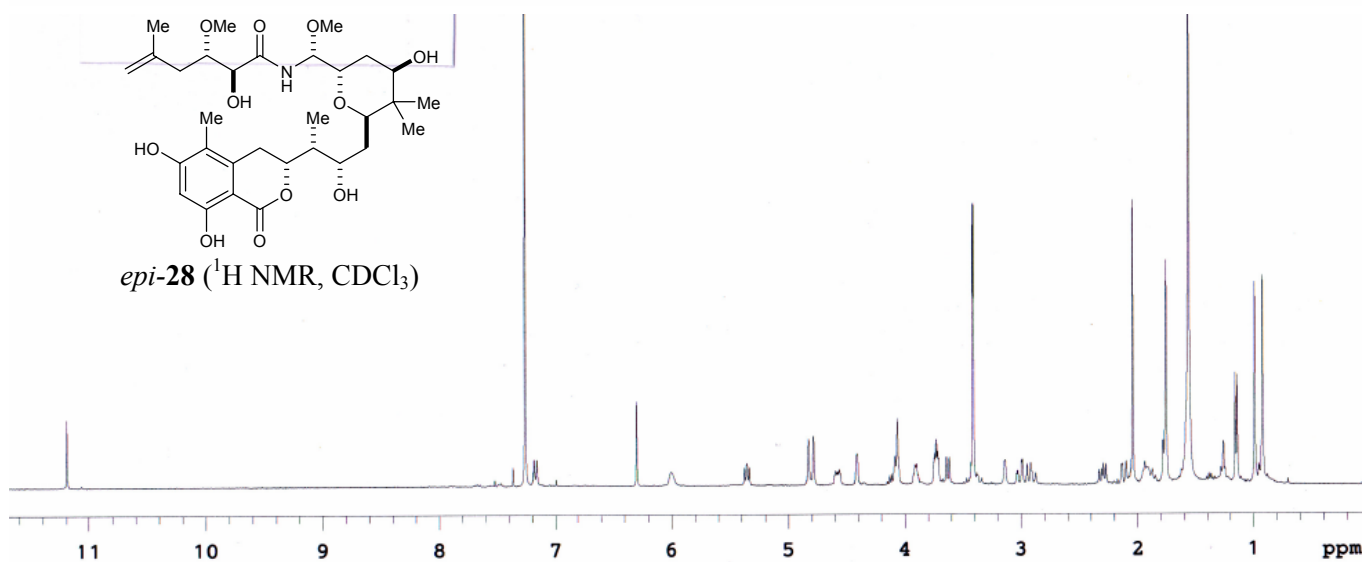
*Spectrum kindly provided by Profs. Cherry Herald and George Pettit, Cancer Research Institute, Arizona State University).

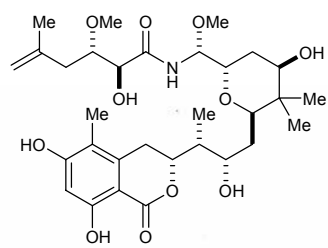


epi-28 (^1H NMR, CD_3OD)

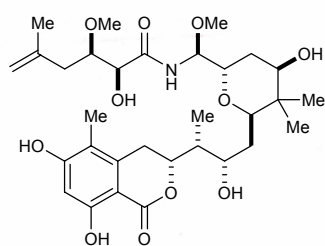
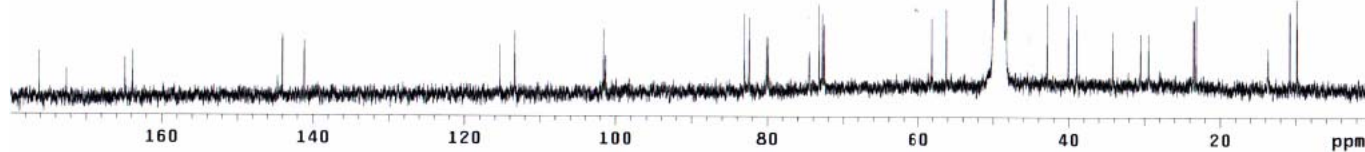


epi-28 (^1H NMR, CDCl_3)

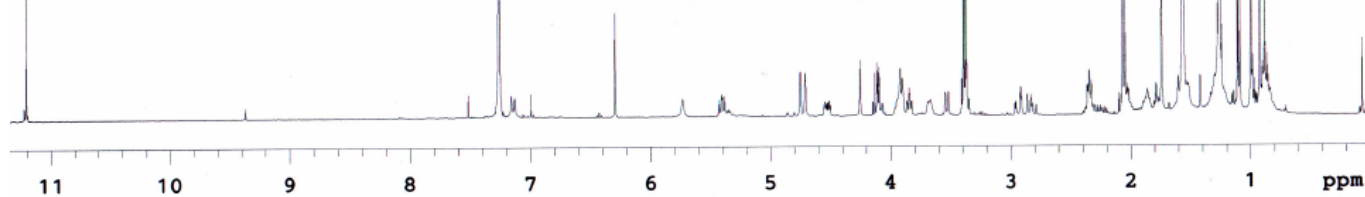


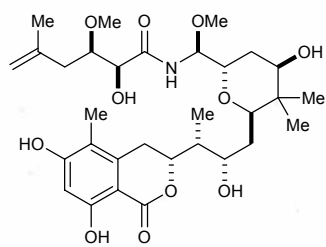


epi-28 (^{13}C NMR, CD_3OD)

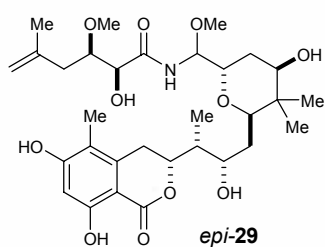
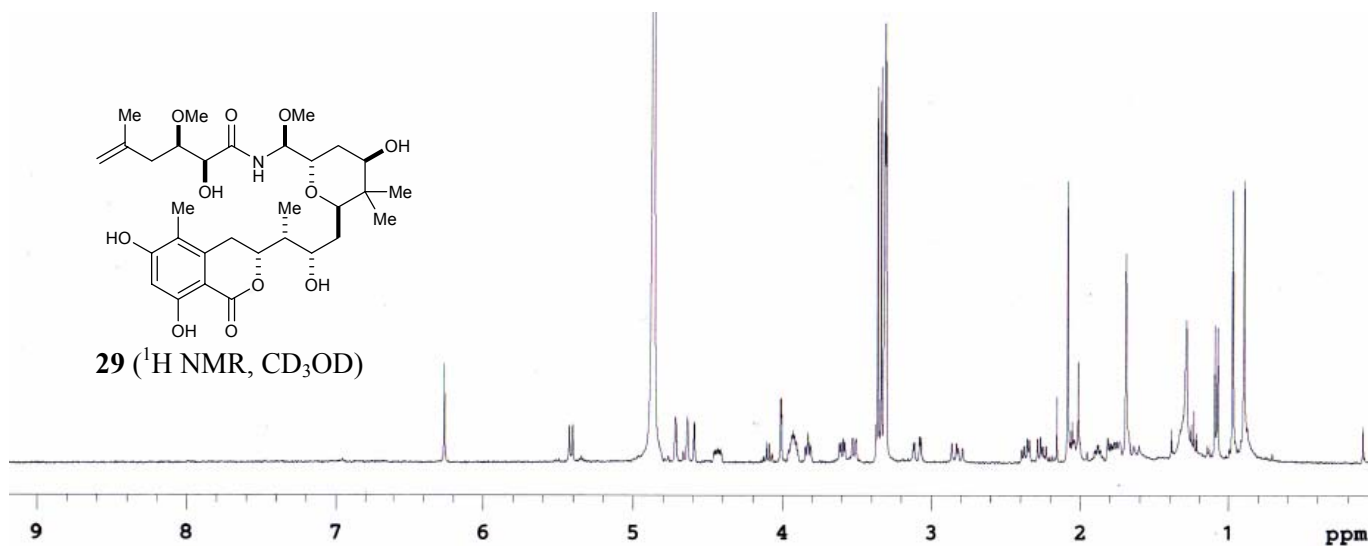


29 (^1H NMR, CDCl_3)

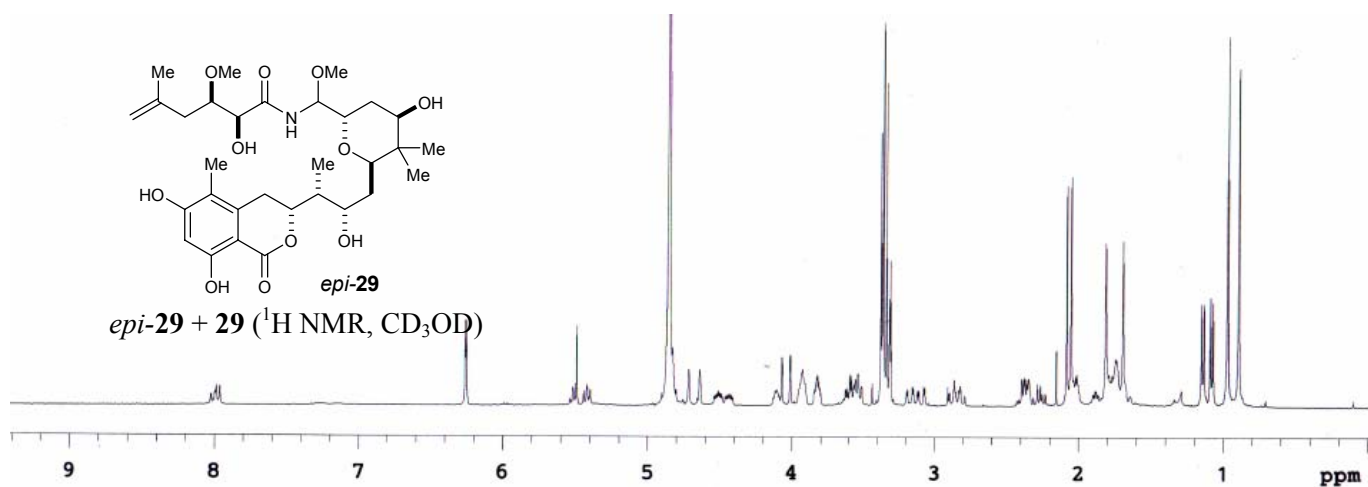




29 (^1H NMR, CD_3OD)



epi-**29** + **29** (^1H NMR, CD_3OD)



epi-**29** + **29** (^1H NMR, CDCl_3)

