Supporting information.

Reactions were performed under nitrogen or argon atmosphere with flame-dried glassware. All solvents were distilled shortly before use: 1,4-dioxane, ether and tetrahydrofurane (THF) from sodium/benzophenone ketyl; acetonitrile, benzene, dichloromethane, dimethylsulfoxide (DMSO), hexane and toluene from calcium hydride; methanol from magnesium/iodine. Most amines were dried over calcium hydride and distilled. Cesium carbonate, cesium iodide, chromium (II) chloride, lithium carbonate and sodium iodide were dried with a heat gun under nitrogen flow. All other starting materials and reagents were obtained commercially and used as such or purified by standard means. All solvents and reagents purified or dried were stored under nitrogen. Thin-layer chromatography were carried out on precoated glass plates with silica gel 60F-250 (Merck). Materials were detected by visualization under an ultraviolet lamp and by dipping into phosphomolybdic acid (10% in ethanol) or molybdic ammonium nitrate solution, followed by heating on a hot plate. For flash chromatography, Merck Kieselgel silica gel 60 (230-400 Mesh) was used. Optical rotation ($[\alpha]_D$) values were obtained with a Perkin-Elmer 141 polarimeter. The infrared (IR) spectra were recorded on a ν-scale in cm^{-1}, on a Perkin-Elmer 1600 FT-IR spectrometer. ^1H (300 MHz) NMR and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AC-300 instrument. For ^1H NMR, the following abbreviations were used: br broad; s singlet; d doublet; t triplet; q quadruplet; qn quintet; and m multiplet. Chemical shifts are reported in ppm δ units, relative to $CHCl_3$ (7.26 ppm) as internal standard. Proton decoupled ^{13}C NMR spectra used $CDCl_3$ as internal standard. When necessary, decoupling experiments and 2D techniques were applied. Mass spectra (MS) were obtained on a VG Micromass ZAB-2F instrument. Crystallographic analyses were performed on a Enraf-Nonius CAD-4 diffractometer (Mo Kα radiation; λ=0.70930 Å).

(2*Z*,8*E*)-(6*S*,7*S*)-3,7-Dimethyl-9-iodo-2-methoxymethyl-6-(triisopropylsilyloxy)nona-2,8-dien-1-ol (5)

To a solution of amide 7 (387 mg, 0.69 mmol) in THF (6.1 mL) at -78°C, was added DIBALH (1.5 M in toluene, 2.30 mL, 3.46 mmol). The mixture was stirred for 1h at -78°C then acetone (200 μL) was added. After an additional 5 min stirring at -78°C, the solution was added to a mixture of hexane (7 mL) and tartaric acid (1.0 M, 11 mL) under vigorous stirring (continued for 30 min) then layers were separated. Aqueous layer was extracted with ether (3×6 mL). Combined organic layers were washed with brine (15 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude **5** was used in the next step without any further purification. For characterization purpose, a small quantity was purified by flash chromatography (20% EtOAc in hexane) to afford **8** as a pale yellow oil. $[\alpha]^{23}_D$ -17.6 (c = 2.010, CH_2Cl_2). IR (film, ν cm^{-1}): 2943.0, 2865.6, 1729.4, 1464.0, 1055.2, 841.2. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 9.85 (1H, s, $-C\underline{H}O$), 4.31 (1H, td, J = 6.5, 3.0 Hz, $-C\underline{H}(OTIPS)-$), 4.17 (2H, s, $-C\underline{H_2}OTBDMS$), 3.98 (2H, s, $-C\underline{H_2}OCH_3$), 3.30 (3H, s, $C\underline{H_3}O-$), 2.51 (1H, qd, J = 7.0, 3.0 Hz, $-C\underline{H}(CH_3)CHO$), 2.22-2.00 (2H, m, $-C\underline{H_2}C(CH_3)=$), 1.78 (3H, s, $-C(C\underline{H_3})=$), 1.72-1.55 (2H, m, $-C\underline{H_2}CH(OTIPS)-$), 1.09 (3H, d, J = 7.0 Hz, $-CH(C\underline{H_3})CHO$), 1.05 (21H, s, $-Si(C\underline{H}(C\underline{H_3})_2)_3$), 0.90 (9H, s, $-C(C\underline{H_3})_3$), 0.07 (6H, s, $-Si(C\underline{H_3})_2-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 205.18, 137.37, 130.26, 72.99, 69.15, 60.11, 57.95, 50.96, 33.40, 30.85, 25.99, 18.64, 18.17, 12.83, 7.42, -5.33. MS (*m/e*): 457 ($M^+ - C_3H_7$), 443 ($M^+ - C_4H_9$). HR-MS calcd for $C_{27}H_{56}O_4Si_2$ ($M^+ - C_3H_7$): 457.3169; found: 457.3160 ± 0.0013.

To a suspension of chromous chloride (II) (850 mg, 6.9 mmol) in THF (2.3 mL) at 22°C, was added a solution of crude aldehyde **8** and iodoform (815 mg, 2.07 mmol) in 1,4-dioxane (4 mL, + 2×0.3 mL rinse). The solution was stirred for 30 min at 22°C, treated with ether (8 mL), brine (6 mL) and water (6 mL) then layers were separated. Aqueous layer was saturated with NaCl then extracted with ether (3×6 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude **9** was used in the next step without any further purification. For characterization purpose, a small quantity was purified by flash chromatography (7% acetone in toluene) to afford **9** as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.66 (1H, dd, J = 14.5, 7.1 Hz, $-C\underline{H}=CHI$), 6.01 (1H, dd, J = 14.8, 0.5 Hz, $=C\underline{H}I$), 4.18 (2H, s, $-C\underline{H_2}OTBDMS$), 3.98 (2H, s, $-C\underline{H_2}OCH_3$), 3.76 (1H, td, J = 6.0, 3.5 Hz, $-C\underline{H}(OTIPS)-$), 3.31 (3H, s, $C\underline{H_3}O-$), 2.42 (1H, qnd, J = 7.1, 3.2 Hz, $-(CH_3)C\underline{H}CH=$), 2.22-1.98 (2H, m, $-C\underline{H_2}C(CH_3)=$), 1.77 (3H, s, $-C(C\underline{H_3})=$), 1.60-1.41 (2H, m, $-C\underline{H_2}CH(OTIPS)-$), 1.07 (21 H, s, $-Si(C\underline{H}(C\underline{H_3})_2)_3$), 0.99 (3H, d, J = 6.9 Hz, $-(C\underline{H_3})CHCH=$), 0.91 (9H, s, $-C(C\underline{H_3})_3CH=$), 0.07 (6H, s, $-Si(C\underline{H_3})_2-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 149.30, 138.12, 129.84, 76.00, 74.77, 69.14, 60.16, 57.95, 45.21, 32.91, 30.90, 26.00, 18.68, 18.48, 18.29, 12.99, -5.26.

To a solution of crude protected alcohol **9** in MeOH (6.9 mL) at 22°C, was added APTS (13 mg, 0.069 mmol). The mixture was stirred for 30 min at 22°C, treated $NaHCO_3$ (3 mL, satd) and concentrated under vacuum. Ether (6 mL) and water (6 mL) were added then layers were separated. Aqueous layer was extracted with ether (3×4 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (25% EtOAc in hexane) to afford **5** (268 mg, 76% for 3 steps) as a pale yellow oil. $[\alpha]^{23}_D$ -9.9 (c = 1.120, CH_2Cl_2). IR (film, ν cm^{-1}): 3432.4, 2940.8, 2866.9, 1461.3, 1378.9, 1091.5, 675.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.61 (1H, dd, J = 14.5, 7.5 Hz, $-C\underline{H}=CHI$), 5.99 (1H, d, J = 14.5 Hz, $=C\underline{H}I$), 4.14 (2H, s, $-C\underline{H_2}OH$), 4.03 (2H, s, $-C\underline{H_2}OCH_3$), 3.73 (1H, td, J = 6.0, 4.0 Hz, $-C\underline{H}(OTIPS)-$), 3.31 (3H, s, $C\underline{H_3}O-$), 2.38 (1H, qd, J = 7.0, 4.0 Hz, $-C\underline{H}(CH_3)CH=$), 2.31 (1H, br s, $O\underline{H}$), 2.19-2.00 (2H, m, $-C\underline{H_2}C(CH_3)=$), 1.72 (3H, s, $-C(C\underline{H_3})=$), 1.59-1.38 (2H, m, $-C\underline{H_2}CH(OTIPS)-$), 1.04 (21H, s, $-Si(C\underline{H}(C\underline{H_3})_2)_3$), 0.96 (3H, d, J = 7.0 Hz, $-CH(C\underline{H_3})CH=$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 149.23, 138.15, 129.34, 75.71, 74.88, 71.84, 61.32, 58.25, 45.17, 33.13, 30.63, 18.51, 18.23, 13.47, 12.95. MS (*m/e*): 510 (M^+), 467 ($M^+ - C_3H_7$). HR-MS calcd for $C_{22}H_{43}O_3SiI$ ($(M - H_2O)NH_4^+$): 510.2264; found: 510.2259 ± 0.0015. HR-MS calcd for $C_{22}H_{42}O_2SiI$ ($(M - H_2O)H^+$): 493.1999; found: 493.1994 ± 0.0015.

tert-Butyl (6*E*,8*E*,14*Z*)-(10*S*,11*S*)-10,14-dimethyl-16-hydroxy-15-methoxymethyl-3-oxo-11-(triisopropylsilyloxy)hexadeca-6,8,14-trienoate (10)

To a solution of iodide **5** (370 mg, 0.73 mmol) and stannane **6** (537 mg, 1.1 mmol) in degassed DMF (7.5 mL), was added bis(acetonitrile)palladium (II) chloride (19 mg, 0.073 mmol). The mixture was degassed again and stirred for 2h at 22°C. NH_4OH (10%, 10 mL) was added and the mixture was stirred until a clear solution with a black precipitate. Ether (5 mL) was added, layers were separated, then aqueous layer was extracted with ether (4×5 mL). Combined organic layers were washed with brine (15 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (15% EtOAc in hexane) to afford **10** (311 mg, 74%) as a pale yellow oil. $[\alpha]^{23}_D$ -7.0 (c = 1.060, CH_2Cl_2). IR (film, ν cm^{-1}): 3446.0, 2942.6, 2866.7, 1736.2, 1715.9, 1462.6, 1368.5, 1251.6, 1151.0, 1093.8, 993.2, 678.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.98 (1H, dd, J = 14.5, 10.0 Hz, $-CH{=}C\underline{H}CH{=}CH-$), 5.94 (1H, dd, J = 14.5, 10.0, $-CH{=}CHC\underline{H}{=}CH-$), 5.65 (1H, dd, J = 14.5, 7.0 Hz, $-CH(CH_3)C\underline{H}{=}$), 5.50 (1H, dt, J = 14.5, 7.0 Hz, $-CH_2C\underline{H}{=}$), 4.12 (2H, s, $-C\underline{H}_2OH$), 4.01 (2H, s, $-C\underline{H}_2OCH_3$), 3.70 (1H, q, J = 5.0 Hz, $-C\underline{H}(OTIPS)-$), 3.29 (5H, s, $-COC\underline{H}_2CO-$ and $C\underline{H}_3O-$), 2.57 (2H, t, J = 7.0 Hz, $-CH_2C\underline{H}_2CO-$), 2.45-2.24 (3H, m, $=CHC\underline{H}_2-$ and $-(CH_3)C\underline{H}CH{=}$), 2.17 (1H, td, J = 12.5, 6.0 Hz, $-\underline{H}CHC(CH_3){=}$), 2.05 (1H, td, J = 12.5, 5.5 Hz, $HC\underline{H}C(CH_3){=}$), 1.70 (3H, s, $-C(C\underline{H}_3){=}$), 1.56-1.33 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.41 (9H, s, $-C(C\underline{H}_3)_3$), 1.02 (21H, s, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$), 0.95 (3H, d, J = 6.9 Hz, $-(C\underline{H}_3)CHCH{=}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 202.59, 166.42, 138.62, 135.55, 131.65, 129.90, 129.32, 129.04, 81.95, 76.62, 71.93, 61.51, 58.28, 50.68, 43.00, 41.62, 34.00, 30.61, 28.32, 27.97, 26.41, 18.27, 15.06, 12.99. MS (*m/e*): 598 (MNH_4^+), 580 (M^+). HR-MS calcd for $C_{33}H_{60}O_6Si$ (MNH_4^+): 598.4503; found: 598.4505 ± 0.0018.

(4*E*,6*E*,12*Z*)-(8*S*,9*S*,15*R*)-15-(*tert*-Butoxy)carbonyl-8,12-dimethyl-13-methoxymethyl-9-(triisopropylsilyloxy)cyclopentadeca-4,6,12-trien-1-one and (4*E*,6*E*,12*Z*)-(8*S*,9*S*,15*S*)-15-(*tert*-butoxy)carbonyl-8,12-dimethyl-13-methoxymethyl-9-(triisopropylsilyloxy)cyclopentadeca-4,6,12-trien-1-one (12)

To a solution of alcohol **10** (1.00 g, 1.73 mmol) in THF (17 mL) at 22°C, was added triphenylphosphine (499 mg, 1.90 mmol) and hexachloroacetone (210 μL, 1.38 mmol). The mixture was stirred for 40 min at 22°C, treated with ether (15 mL) and water (15 mL) then layers were separated. Aqueous layer was extracted with ether (3×10 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified rapidly by flash chromatography (5% EtOAc in hexane) to afford **11** (956 mg, 92%) as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.07-5.93 (2H, m, $-CH{=}C\underline{H}C\underline{H}{=}CH-$), 5.67 (1H, dd, J = 14.5, 7.0 Hz, $-(CH_3)CHC\underline{H}{=}$), 5.54 (1H, dt, J = 14.5, 7.0, $-CH_2C\underline{H}{=}$), 4.16 (1H, dAB, J = 11.0 Hz, $-\underline{H}CHCl$), 4.11 (1H, dAB, J = 11.0 Hz, $-HC\underline{H}Cl$), 3.98 (2H, s, $-C\underline{H}_2OCH_3$), 3.79-3.72 (1H, m, $-C\underline{H}(OTIPS)-$), 3.32 (2H, s, $-COC\underline{H}_2CO-$), 3.30 (3H, s, $C\underline{H}_3O-$), 2.60 (2H, t, J = 7.0 Hz, $-CH_2C\underline{H}_2CO-$), 2.48-2.17 (4H, m, $=CHC\underline{H}_2-$, $-(CH_3)C\underline{H}CH{=}$ and $-\underline{H}CHC(CH_3){=}$), 2.09 (1H, td, J = 12.5, 5.5 Hz, $-HC\underline{H}C(CH_3){=}$), 1.76 (3H, s, $-C(C\underline{H}_3){=}$), 1.67-1.41 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.45 (9H, s, $-C(C\underline{H}_3)_3$), 1.05 (21H, s, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$), 0.99 (3H, d, J = 7.0 Hz, $-CH(C\underline{H}_3)CH{=}$).

To a suspension of cesium carbonate (2.71 g, 8.3 mmol) and cesium iodide (2.17 g, 8.3 mmol) in acetone (350 mL) at 60°C, was added over 15h (with a syringe pump) a solution of chloride **11** (956 mg, 1.60 mmol) in acetone (10 mL). The mixture was cooled down to 22°C and concentrated under vacuum. Ether (160 mL) and water (300 mL) were added then layers were separated. Aqueous layer was extracted with ether (3×160 mL). Combined organic layers were washed with brine (400 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (15% EtOAc in hexane) to afford **12** (749 mg, 79% for 2 steps) as a pale yellow oil. $[\alpha]^{23}_D$ +5.1 (c = 1.085 CH_2Cl_2). IR (film, ν cm^{-1}): 2942.1, 2886.1, 1732.2, 1710.9, 1643.0, 1367.7, 12484.4, 1144.4, 1092.3, 933.0, 678.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 1:1 mixture of C15 epimers, non-assigned stereochemistry, split signals identified by a half integration, i.e. H/2: 6.04-5.89 (2H, m, $-CH{=}C\underline{H}C\underline{H}{=}CH-$), 5.62-5.44 (2H, m, $-C\underline{H}{=}CHCH{=}C\underline{H}-$), 3.90-3.32 (4H, m, $-C\underline{H}_2OCH_3$, $-C\underline{H}(OTIPS)-$ and $-COC\underline{H}(CO_2t\text{-}Bu)-$), 3.26 (3H/2, s, $C\underline{H}_3O-$), 3.23 (3H/2, s, $C\underline{H}_3O-$), 2.72-2.14 (8H, m, $-(CH_3)C\underline{H}CH{=}$, $-C\underline{H}_2C\underline{H}_2CO-$, $-HC\underline{H}C(CH_3){=}$ and $-C\underline{H}_2C(CH_2OCH_3){=}$), 2.00 (1H/2, td, J = 12.5, 4.5 Hz, $-\underline{H}CHC(CH_3){=}$), 1.90 (1H/2, td, J = 13.0, 5.0 Hz, $-HC\underline{H}C(CH_3){=}$), 1.70 (3H, s, $-C(CH_3){=}$), 1.68-1.42 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.45 (9H/2, s, $-C(C\underline{H}_3)_3$), 1.42 (9H/2, s, $-C(C\underline{H}_3)_3$), 1.11-1.05 (24H, m, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$ and $-CH(C\underline{H}_3)CH{=}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 207.63, 207.35, 137.74, 137.35, 135.17, 134.73, 133.14, 132.93, 130.35, 130.26, 129.88, 126.24, 125.70, 81.19, 80.99, 77.07, 76.59, 70.59, 70.47, 61.32, 60.87, 57.67, 46.18, 44.55, 40.39, 39.69, 34.63, 33.52, 30.75, 28.91, 28.54, 28.34, 27.96, 18.30, 12.95. MS (*m/e*): 562 (M^+). HR-MS calcd for $C_{33}H_{58}O_5Si$ (M^+): 562.4053; found: 562.4047 ± 0.0017.

(4*E*,6*E*,12*Z*)-(8*S*,9*S*)-8,12-Dimethyl-13-methoxymethyl-9-(triisopropylsilyloxy)cyclopentadeca-4,6,12-trien-1-one (13)

To a solution of β-ketoester **12** (745 mg, 1.32 mmol) in 2,4,6-collidine (13 mL) at 22°C, was added dihydrated lithium iodide (2.38 g, 13.2 mmol). The mixture was heated to 100°C for 15 h, cooled down to 22°C, concentrated under vacuum and coevaporated with toluene (4×15 mL). Ether (10 mL) and water (15 mL) were added then layers were separated. Aqueous layer was extracted with ether (3×10 mL). Combined organic layers were washed with NH_4Cl (2×20 mL), with a sodium thiosulfate solution (1M, 2×15 mL), with brine (15 mL), then dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (10% EtOAc in hexane) to afford **13** (439 mg, 72%) as a pale yellow oil. $[\alpha]^{23}_{D}$ -2.8 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2942.5, 2865.8, 1709.6, 1462.2, 1101.0, 1062.2, 992.7. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.98 (1H, dd, J = 14.5, 10.0 Hz) and 5.90 (1H, dd, J = 14.5, 10.0 Hz) ($-CH=C\underline{H}C\underline{H}=CH-$), 5.60-5.47 (2H, m, $-C\underline{H}=CHCH=C\underline{H}-$), 3.81 (1H, dAB, J = 10.5, $-\underline{H}CHOCH_3$), 3.75 (1H, dAB, J = 10.5, $-HC\underline{H}OCH_3$), 3.60 (1H, dt, J = 7.5, 4.0 Hz, $-C\underline{H}(OTIPS)-$), 3.24 (3H, s, $C\underline{H}_3O-$), 2.49-1.99 (9H, m, $-(CH_3)C\underline{H}CH=$ and $-C\underline{H}_2C\underline{H}_2COC\underline{H}_2C\underline{H}_2CH=$), 2.05-1.99 (2H, m, $-C\underline{H}_2C(CH_3)=$), 1.66 (3H, s, $-C(C\underline{H}_3)=$), 1.56-1.48 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.05 (21H, s, $Si(C\underline{H}(C\underline{H}_3)_2)_3$), 1.02 (3H, d, J = 7.0 Hz, $-(C\underline{H}_3)CHCH=$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 213.54, 136.28, 134.98, 132.55, 130.02, 129.32, 128.42, 76.55, 71.95, 57.92, 45.07, 44.92, 41.74, 34.21, 30.08, 28.96, 24.92, 18.29, 13.01. MS (*m/e*): 462 (M^+). HR-MS calcd for $C_{28}H_{50}O_3Si$ (M^+): 462.3529; found: 462.3525 ± 0.0014.

(4*E*,6*E*,12*Z*)-(8*S*,9*S*)-8,12-Dimethyl-13-hydroxymethyl-9-(triisopropylsilyloxy)cyclopentadeca-4,6,12-trien-1-one (15)

To a solution of methylether **13** (455 mg, 0.98 mmol), were added sodium iodide (740 mg, 4.9 mmol) 15-crown-5 ether (975 mg, 4.9 mmol) in CH_2Cl_2 (110 mL) under argon at 22°C. The mixture was stirred for 5 min then cooled to -78°C. A solution of bromodimethylborane (1.0 M, 6.88 mL, 6.88 mmol), diluted in CH_2Cl_2 (10 mL) was added over 35 min (with a syringe pump). The mixture was stirred for 10 min at -78°C, then treated with ether (60 mL). The resulting mixture was stirred for 10 min at -78°C, then 20 min at 22°C. DMF (110 mL) and sodium acetate (1.61 g, 19.7 mmol) were added. The mixture was stirred for 6h at 55°C then treated with water (200 mL) and extracted with a 1:5 ether/hexane mixture (4×80 mL). Combined organic layers were washed with brine (500 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was used in the next step without any further purification. For characterization purpose, a small quantity was purified by flash chromatography (15% EtOAc in hexane) to afford **14** as a pale yellow oil. $[\alpha]^{23}_{D}$ -10.5 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2943.4, 2866.1, 1738.2, 1710.4, 1462.6, 1230.5, 1103.7, 1062.8, 994.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.02 (1H, dd, J = 14.5, 10.5 Hz) and 5.92 (1H, dd, J = 14.5, 10.5 Hz)($-CH=C\underline{H}C\underline{H}=CH-$), 5.63 - 5.36 (1H, m, $=C\underline{H}CH_2-$), 5.54 (1H, dd, J = 14.5, 8.5, $-(CH_3)CHC\underline{H}=$), 4.50 (2H, s, $CH_3CO_2C\underline{H}_2-$), 3.64 (1H, dt, J = 7.5, 4.0 Hz, $-C\underline{H}(OTIPS)-$), 2.49-2.03 (11H, m, $-C\underline{H}_2C\underline{H}_2COC\underline{H}_2C\underline{H}_2CH=$, $-C\underline{H}_2C(CH_3)=$ and $-(CH_3)C\underline{H}CH=$), 2.03 (3H, s, $C\underline{H}_3CO_2-$), 1.68 (3H, s, $-C(C\underline{H}_3)=$), 1.57-1.50 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.07 (21H, s, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$), 1.05 (3H, d, J = 7.0, $-(C\underline{H}_3)CHCH=$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 213.16, 171.27, 137.89, 135.05, 132.60, 129.97, 129.33, 126.21, 76.43, 63.51, 45.04, 44.71, 41.80, 33.96, 30.08, 28.97, 24.16, 21.07, 18.30, 12.95. MS (*m/e*): 490 (M^+). HR-MS calcd for $C_{29}H_{50}O_4Si$ (M^+): 490.3478; found: 490.3481 ± 0.0014.

To a solution of crude acetate **14** in MeOH (20 mL) at 22°C, was added potassium carbonate (3.40 g, 24.5 mmol). The mixture was stirred for 15 h at 22°C, then treated with (20 mL), and volatiles were concentrated under vacuum. Aqueous layer was extracted with ether (3×10 mL). Combined organic layers were washed with brine (20 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (20 to 40% EtOAc in hexane) to afford **15** (330 mg, 75% for 2 steps) as a pale yellow oil. $[\alpha]^{23}_{D}$ -4.7 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 3430.5, 2943.5, 2866.2, 1707.2, 1458.3, 1103.1, 1062.4, 992.7, 677.8. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.01 (1H, dd, J = 14.5, 10.5 Hz) and 5.92 (1H, dd, J = 14.5, 10.5 Hz)($-CH=C\underline{H}C\underline{H}=CH-$), 5.60-5.55 (1H, m, $=C\underline{H}CH_2-$), 5.52 (1H, dd, J = 14.5, 9.0 Hz, $-(CH_3)CHC\underline{H}=$), 4.06 (1H, dAB, J = 12.0 Hz, $-\underline{H}CHOH$), 4.02 (1H, dAB, J = 12.0 Hz, $-HC\underline{H}OH$), 3.62 (1H, dt, J = 7.5, 3.5 Hz, $-C\underline{H}(OTIPS)-$), 2.49-2.12 (9H, m, $-C\underline{H}_2C\underline{H}_2COC\underline{H}_2C\underline{H}_2CH=$ and $-(CH_3)C\underline{H}CH=$), 2.05-1.99 (2H, m, $-C\underline{H}_2C(CH_3)=$), 1.69 (3H, s, $-C(C\underline{H}_3)=$), 1.56-1.48 (3H, m, $-C\underline{H}_2CH(OTIPS)-$ and $-O\underline{H}$), 1.07 (21H, s, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$), 1.04 (3H, d, J = 7.0 Hz, $-(C\underline{H}_3)CHCH=$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 213.58, 135.23, 134.97, 132.52, 131.09, 129.99, 129.34, 76.48, 61.86, 45.04, 41.80, 34.18, 30.05, 28.84, 24.40, 18.25, 12.88. MS (*m/e*): 430 ($M^+ - H_2O$). HR-MS calcd for $C_{27}H_{48}O_3Si$ ($M^+ - H_2O$): 430.3267; found: 430.3273 ± 0.0013.

(4*E*,6*E*,12*Z*)-(8*S*,9*S*)-8,12-Dimethyl-13-formyl-9-(triisopropylsilyloxy)cyclopentadeca-4,6,12-trien-1-one (4)

To a solution of alcohol **15** (1.78 g, 3.96 mmol) in CH_2Cl_2 (41 mL) at 22°C, was added Dess-Martin periodinane (2.02 g, 4.76 mmol). The mixture was stirred at 22°C for 20 min, then treated with ether (60 mL), $NaHCO_3$ (30 mL, satd) sodium thiosulfate (2.3 g, 14.5 mmol). The mixture was stirred for 15 min (until homogenous) then layers were separated. Aqueous layer was extracted with CH_2Cl_2 (3×15 mL). Combined organic layers were washed with $NaHCO_3$ (50 mL), with NH_4Cl (50 mL, satd), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by recrystallization in hexane to afford **4** (1.56 g, 88%) as a white solid. $[\alpha]^{23}_{D}$ +2.8 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2944.1, 2866.3, 1711.1, 1667.1, 1463.6, 1099.8, 1062.4, 994.5. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 10.05 (1H, s, $-C\underline{H}O$), 6.03 (1H, dd, J = 14.5, 10.5 Hz) and 5.93 (1H, dd, J = 14.5, 10.5 Hz)($-CH=C\underline{H}C\underline{H}=CH-$), 5.59 (1H, dd, J = 14.5, 8.0 Hz, $-(CH_3)CHC\underline{H}=$), 5.63-5.53 (1H, m, $=C\underline{H}CH_2-$), 3.75 (1H, dt, J = 7.5, 4.0 Hz, $-C\underline{H}(OTIPS)-$), 2.51-2.06 (11H, m, $-C\underline{H}_2C\underline{H}_2COC\underline{H}_2C\underline{H}_2CH=$, $-C\underline{H}_2C(CH_3)=$ and $-(CH_3)C\underline{H}CH=$), 2.14 (3H, s, $-C(C\underline{H}_3)=$), 1.66-1.59 (2H, m, $-C\underline{H}_2CH(OTIPS)-$), 1.09 (21H, s, $-Si(C\underline{H}(C\underline{H}_3)_2)_3$), 1.07 (3H, d, J = 7.0 Hz, $-(C\underline{H}_3)CHCH=$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 221.47, 191.34, 159.54, 135.74, 134.58, 132.48, 130.19, 129.65, 75.89, 45.06, 44.51, 41.26, 32.72, 30.86, 30.11, 19.72, 18.29, 18.14, 17.49, 12.93. MS (*m/e*): 446 (M^+). HR-MS calcd for $C_{27}H_{46}O_3Si$ (M^+): 446.3216; found: 446.3222 ± 0.0013.

(3*S*,11*R*)-17,19-Dinor-8-epi-11-hydroxy-3-(triisopropylsilyloxy)aphidicol-6-en-16-one (3)

To a preconditioned pyrex tube (washed with NH_4OH satd, rinsed three times with distilled water then three times with distilled acetone, and flame dried under vacuum) was added macrocyclic aldehyde **4** (50 mg, 0.11 mmol) then toluene (2 mL, by rinsing the tube's walls). The solution was degassed by freezing in liquid nitrogen (under nitrogen), pumped under vacuum and slowly melted under vacuum (4 cycles, caution to bumping). Under nitrogen, triethylamine (47 μL, 0.34 mmol) was added then the tube was frozen again (in liquid nitrogen), pumped under vacuum, sealed with a flame and allowed to warm up slowly to 22°C. It was then heated to 220°C for 30h, cooled to 22°C and broke. The solution was poured in a flask and the tube was rinsed with ether (4×2 mL). The combined organic phases were concentrated under vacuum. Crude product was purified by flash chromatography (10% EtOAc in hexane) to afford **3** (41 mg, 81%) as a pale yellow oil. $[\alpha]^{23}_D$ -66.8 (c = 0.650, $CHCl_3$). IR (film, ν cm^{-1}): 3440, 2940, 2865, 1710. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.69 (1H, dAB, J = 9.5 Hz) and 5.64 (1H, dmAB, J = 9.5 Hz)(-CH=CH-), 4.35 (1H, br d, J = 4.5 Hz, -CH(OH)-), 3.30 (1H, td, J = 9.5, 5.0 Hz, -CH(OTIPS)-), 2.69 (1H, t, J = 5.5 Hz, -HCHC(=O)-), 2.55 (1H, br t, J = 9.5 Hz), 2.49-2.26 (3H, m), 2.06 (1H, dd, J = 14.0, 10.0 Hz), 1.81-1.72 (2H, m) and 1.71-0.80 (7H, m)(other CH and CH_2), 1.08 (21H, s, $-Si(CH(CH_3)_2)_3$), 1.07 (3H, d, J = 8.5 Hz, $-CH(CH_3)-$), 0.93 (3H, s, $-(CH_3)C(CH_2-)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 214.43, 132.93, 78.93, 77.56, 57.09, 49.44, 46.78, 41.17, 40.17, 38.31, 35.32, 31.17, 30.71, 27.11, 18.32, 17.59, 12.92. MS (*m/e*): 403 ($M^+ - C_3H_7$). HR-MS calcd for $C_{24}H_{39}O_3Si$ ($M^+ - C_3H_7$): 403.2668; found: 403.2665 ± 0.0012.

(16*Z*)-(3*S*,11*R*)-8-Epi-17-methoxy-19-nor-3-(triisopropylsilyloxy)aphidicola-6,16-dien-11-ol and (16*E*)-(3*S*,11*R*)-8-epi-17-methoxy-19-nor-3-(triisopropylsilyloxy)aphidicola-6,16-dien-11-ol (16)

To a suspension methoxymethyltriphenylphosphonium chloride (425 mg, 1.24 mmol) in THF (6 mL) at -78°C, was added KHMDS (0.50 M in toluene, 2.43 mL, 1.22 mmol). The mixture was stirred at -78°C for 5 min, 30 min at 0°C then cooled at -78°C. A solution of ketone **3** (54.3 mg, 0.122 mmol) in THF (2 mL, 2×0.5 mL rinse) was added by canula. The mixture was stirred for 5 min at -78°C then 2h at 0°C. Ether (3 mL) and water (7 mL) were added then layers were separated. Aqueous layer was extracted with ether (3×4 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product purified by flash chromatography (7% EtOAc in hexane) to afford **16** (54.8 mg, 95%) as a white foam. $[\alpha]^{23}_D$ -63.4 (c = 1.380, CH_2Cl_2). IR (film, ν cm^{-1}): 3467.0, 2942.6, 2865.8, 1462.5, 1125.8, 1101.9, 883.6, 667.5. ^1H NMR (300 MHz, $CDCl_3$, δ ppm) ~1:1 mixture of isomers, non-assigned stereochemistry, split signals identied by a half integration, i.e. H/2: 6.00 (1H/2, d, J = 1.5 Hz, $=CHOCH_3$), 5.79 (1H/2, d, J = 2.0 Hz, $=CHOCH_3$), 5.66-5.62 (1H, m) and 5.55 (1H, dt, J = 9.0, 3.0 Hz) (-CH=CH-), 3.98-3.73 (1H, m, -CH(OH)-), 3.58 (3H/2, s, $-OCH_3$), 3.52 (3H/2, s, $-OCH_3$), 3.29-3.18 (2H, m, -CH(OTIPS)- and another CH), 2.63 (1H/2, dd, J = 15.0, 5.5 Hz) and 2.42-1.14 (14H, m)(other CH and CH_2), 1.07 (21H, s, $-Si(CH(CH_3)_2)_3$, 1.05 (3H, d, J =6.0 Hz, $-CH(CH_3)-$), 0.90 (3H, s, $-(CH_3)C(CH_2-)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 141.62, 133.85, 133.65, 132.41, 115.77, 77.75, 76.59, 75.95, 59.56, 50.06, 46.74, 45.08, 40.81, 40.55, 40.08, 38.56, 33.82, 32.79, 32.46, 31.23, 28.38, 27.22, 23.65, 19.78, 18.31, 18.16, 17.65, 12.92, 12.28. MS (*m/e*): 474 (M^+). HR-MS calcd for $C_{29}H_{50}O_3Si$ (M^+): 474.3529; found: 474.3538 ± 0.0014.

(3*S*,11*R*,16*R*)-17,17-Dimethoxy-8-epi-19-nor-3-(triisopropylsilyloxy)aphidicol-6-ene-11,16-diol (17) and (3*S*,11*R*,16*R*)-17,17-dimethoxy-8-epi-19-noraphidicol-6-ene-3,11,16-triol (18)

To a solution of *m*-CPBA (235 mg, 1.36 mmol) in CH_2Cl_2 (45 mL) at 22°C, was added lithium carbonate (405 mg, 5.45 mmol). The mixture was stirred for 30 min at -78°C then was added a solution of methyl enol ether **16** (259 mg, 0.545 mmol) in CH_2Cl_2 (5 mL + 2×2.5 mL rinse). The mixture stirred for 3 h at -78°C then treated with sodium thiosulfate (2.16 g, 13.6 mmol). The mixture was stirred for 10 min at -78°C, then water (23 mL) was added and the mixture was warmed up to 22°C. Layers were separated and aqueous layer was extracted with CH_2Cl_2 (3×15 mL). Combined organic layers were washed with water (40 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude epoxides mixture was used in the next step without any further purification.

To a solution of crude epoxides mixture in MeOH (20 mL) at 22°C, was added APTS (105 mg, 0.545 mmol). The mixture was stirred for 15h at 22°C, then treated with $NaHCO_3$ (5 mL, satd) and volatiles were concentrated under vacuum. Ether (5 mL) and water (5 mL) were added then layers were separated. Aqueous layer was extracted with ether (2×4 mL) and with EtOAc (2×4 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (60% EtOAc in hexane) to afford **17** (20.6 mg, 7%) as a white foam, and **18** (179 mg, 90%) as a white foam. **17:** $[\alpha]^{23}_D$ -130 (c = 0.300, CH_2Cl_2). IR (film, ν cm^{-1}): 3393.7, 2942.4, 2866.4, 1462.7, 1079.6. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.65-5.52 (2H, m, -CH=CH-), 4.08 (1H, s, $-CH(OCH_3)_2$), 3.89 (1H, d, J = 4.0 Hz, -CH(OH)-), 3.51 (3H, s, $-(CH_3O)CH(OCH_3)$), 3.50 (3H, s, $-(CH_3O)CH(OCH_3)$), 3.28 (1H, td, J = 9.0, 4.0 Hz, -CH(OTIPS)-), 2.25 (1H, t, J = 5.0 Hz), 2.20-1.99 (2H, m), 1.87 (1H, dd, J = 12.5, 10.5 Hz) and 1.77-1.25 (10H, m) (other CH and CH_2), 1.07 (21H, s, $-Si(CH(CH_3)_2)_3$), 1.05 (3H, d, J = 5.0 Hz, $-CH(CH_3)-$), 0.90 (3H, s, $-(CH_3)C(CH_2-)-$). ^{13}C NMR

(75 MHz, $CDCl_3$, δ ppm): 132.95, 131.64, 107.76, 78.67, 71.94, 57.20, 57.14, 41.68, 39.33, 39.13, 38.93, 36.58, 28.77, 28.48, 26.57, 24.48, 23.82, 18.38, 18.27, 18.15, 12.89, 12.26. MS (*m/e*): 479 (M^+ - C_3H_7). HR-MS calcd for $C_{30}H_{54}O_2Si$ (M^+ - C_3H_7): 479.3193; found: 479.3196 ± 0.0014. **18:** $[\alpha]^{23}_D$ -76.8 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 3342.1, 2445.0, 1458.6, 1079.2. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.63 (1H, dm, J = 9.0 Hz) and 5.55 (1H, dt, J = 9.0, 3.0 Hz) (-C$\underline{H}$=C$\underline{H}$-), 4.09 (1H, s, -C$\underline{H}$(OCH_3)$_2$), 3.91 (1H, d, J = 4.5 Hz, -C$\underline{H}$(OH)-), 3.52 (3H, s, -(C$\underline{H}_3$O)CH(OCH_3)), 3.51 (3H, s, -(CH_3O)CH(OC$\underline{H}_3$)), 3.14 (1H, td, J = 9.0, 5.0 Hz, -C$\underline{H}$(OH)CH_2-), 2.25 (1H, t, J = 5.0 Hz), 2.20-2.02 (2H, m), 1.88 (1H, dd, J = 13.5, 10.0 Hz) and 1.79-1.25 (10H, m) (other C$\underline{H}$ and C$\underline{H}_2$), 1.07 (3H, d, J = 6.0 Hz, -CH(C$\underline{H}_3$)-), 0.90 (3H, s, -(C$\underline{H}_3$)C(CH_2-)-). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 133.43, 132.27, 107.93, 78.57, 77.51, 76.30, 57.20, 57.14, 48.28, 46.58, 41.57, 39.27, 39.07, 38.72, 31.91, 30.52, 28.80, 28.11, 23.40, 17.01. MS (*m/e*): 334 (M^+ - CH_3OH). HR-MS calcd for $C_{21}H_{34}O_5$ (M^+ - CH_3OH): 334.2144; found: 334.2149 ± 0.0010.

(3*S*,11*R*,16*R*)-17,17-Dimethoxy-8-epi-19-noraphidicol-6-ene-3,11,16-triol (18)

Procedure from enol ether **16**: see previous procedure. Procedure from silylether **17**: To a solution of silylether **17** (13.9 mg, 26.6 μmol) in THF (1 mL) at 22°C, was added TBAF (1.0 M min THF, 665 μL, 665 μmol). The mixture was stirred for 40h at 22°C, then treated with ether (0.5 mL) and water (1 mL) then layers were separated. Aqueous layer was extracted with ether (3×0.5 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (5% MeOH in EtOAc) to afford **18** (6.5 mg, 67%) as a white foam (characterization given after the previous procedure).

(3*S*,11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-3-imidazolecarbonyl-19-noraphidicol-6-ene (19)

To a solution of triol **18** (179 mg, 0.488 mmol) in benzene (14 mL) at 22°C, was added imidazole (400 mg, 2.44 mmol). The mixture was heated to reflux for 2h, then cooled to 22°C and treated with water (14 mL). The layers were separated and the aqueous layer was extracted with ether (2×7 mL) and with EtOAc (2×7 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (EtOAc) to afford **19** (228.3 mg, 96%) as a white foam. $[\alpha]^{23}_D$ -33.7 (c =1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2964.0, 1750.2, 1469.1, 1394.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 8.13 (1H, s, Im-$\underline{H}$), 7.42 (1H, s, Im-$\underline{H}$), 7.06 (1H, s, Im-H), 5.68-5.58 (2H, m, -C$\underline{H}$=C$\underline{H}$-), 4.67-4.56 (2H, m, -C$\underline{H}$(OC(=O)O-)-) and -C$\underline{H}$(OC(=O)Im)-) 4.15 (1H, s, -C$\underline{H}$(OCH_3)$_2$), 3.56 (3H, s, -(C$\underline{H}_3$O)CH(OCH_3), 3.50 (3H, s, -(CH_3O)CH(OC$\underline{H}_3$)), 2.58 (1H, t, J = 5.0 Hz), 2.51 (1H, dd, J = 14.0, 10.5 Hz), 2.25 (1H, t, J = 8.5 Hz) and 2.11-1.45 (11H, m) (other C$\underline{H}$ and C$\underline{H}_2$), 1.03 (3H, d, J = 6.0 Hz, -CH(C$\underline{H}_3$)-), 0.97 (3H, s, -(C$\underline{H}_3$)C(CH_2-)-). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 149.17, 148.45, 133.11, 131.68, 130.61, 117.07, 108.49, 87.37, 83.13, 82.23, 58.66, 57.79, 51.01, 46.42, 39.94, 38.32, 36.18, 33.91, 31.86, 28.18, 26.38, 25.97, 24.80, 17.99, 16.78. MS (*m/e*): 486 (M^+). HR-MS calcd for $C_{26}H_{34}N_2O_7$ (M^+): 486.2366; found: 486.2372 ± 0.0014. mp: 111°C.

(3*S*,11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-19-noraphidicol-6-en-3-ol (20)

To a solution of carbamate **19** (169 mg, 0.33 mmol) in THF (10 mL) at 0°C, was added NaOH (0.1 N, 5.6 mL, 0.56 mmol) previously cooled to 0°C. The mixture was stirred for 1.5 h at 0°C, treated with NH_4Cl (10 mL, satd) then layers were separated. Aqueous layer was extracted with ether (3×8 mL) and with EtOAc (3×8 mL). Combined organic layers were washed with water (25 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (100% EtOAc) to afford **20** (120.6 mg, 88%) and **18** (8.1 mg, 7%, characterization previously described) as a white foam. **20:** $[\alpha]^{23}_D$ -67.3 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 3433.8, 2926.0, 1743.3, 1462.4, 1083.6. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.61-5.54 (2H, m, -C$\underline{H}$=C$\underline{H}$-), 4.58 (1H, d, J = 5.5 Hz, -C$\underline{H}$(OC(=O)O-)-), 4.12 (1H, s, -C$\underline{H}$(OCH_3)$_2$), 3.53 (3H, s, -(C$\underline{H}_3$O)CH(OCH_3)), 3.48 (3H, s, -(CH_3O)CH(OC$\underline{H}_3$)), 3.14-3.06 (1H, m, -C$\underline{H}$(OH)-), 2.52 (1H, t, J = 5.5 Hz), 2.46 (1H, dd, J = 14.0, 10.5 Hz), 2.19 (1H, t, J = 9.5 Hz) and 2.05-1.39 (12H, m)(other C$\underline{H}$ and C$\underline{H}_2$), 1.04 (3H, d, J = 5.5 Hz, -CH(C$\underline{H}_3$)-), 0.88 (3H, s, -(C$\underline{H}_3$)C(CH_2-)-). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 149.37, 132.84, 132.39, 108.47, 87.44, 82.39, 76.03, 58.57, 57.77, 51.07, 46.39, 39.89, 39.26, 38.47, 33.98, 32.28, 30.36, 28.20, 25.94, 24.74, 18.02, 16.93. MS (*m/e*): 392 (M^+). HR-MS calcd for $C_{22}H_{32}O_6$ (M^+): 392.2199; found: 392.2202 ± 0.0011. mp: 101°C.

(11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-19-noraphidicol-6-en-3-one (21)

The procedure for the formation of **4** was applied for the oxidation of alcohol **20** (121 mg, 0.307 mmol) in CH_2Cl_2 (10 mL) with Dess-Martin periodinane (380 mg, 0.90 mmol) during 30 min at 22°C. Flash chromatography (20% EtOAc in hexane) afforded **21** (111.4 mg, 93%) as a white foam. $[\alpha]^{23}_D$ -65.2 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2936.7, 1747.8, 1709.5. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.69 (1H, dm, J = 9.5 Hz) and 5.63 (1H, dt, J = 9.5, 3.0 Hz) (-C$\underline{H}$=C$\underline{H}$-), 4.68 (1H, d, J = 5.5 Hz, -C$\underline{H}$(OC(=O)O-)-), 4.16 (1H, s, -C$\underline{H}$(OCH_3)$_2$), 3.58 (3H, s, -(C$\underline{H}_3$O)CH(OCH_3)), 3.51 (3H, s, -(CH_3O)CH(OC$\underline{H}_3$)), 2.64-2.13 (14H, m, other C$\underline{H}$ and C$\underline{H}_2$), 1.25 (3H, s, -(C$\underline{H}_3$)C(CH_2-)-), 1.10 (3H, d, J = 6.5 Hz, -CH(C$\underline{H}_3$)-). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 211.92, 149.06, 133.19, 132.44, 108.40, 87.31, 82.16, 58.63, 57.78, 51.07, 49.54, 45.06, 39.91, 38.45, 37.51, 34.34, 33.85, 28.11, 25.92, 24.69, 17.59, 12.79. MS (*m/e*): 390 (M^+). HR-MS calcd for $C_{22}H_{30}O_6$ (M^+): 390.2042; found: 390.2044 ± 0.0011.

(11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-19-noraphidicolan-3-one (22)

To a solution of alkene **21** (20 mg, 51.2 mmol) in EtOAc (2 mL) at 22°C, was added palladium (10% on charcoal, ~1 mg), then hydrogen was bubbled (big flow for initial purging, then slow bubbling) during 18h. The mixture was filtered on a celite plug (1 cm), washed with EtOAc and concentrated under vacuum. The crude **22** (20.1 mg, 100%) was pure and did not require any further purification. $[\alpha]^{23}_{D}$ -74.5 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2936.7, 1746.5, 1708.4, 1126.1, 1081.0. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4.84 (1H, d, J = 6.0 Hz, $-C\underline{H}(OC(=O)O-)-$), 4.07 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.48 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.42 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 2.54-2.42 (2H, m), 2.26 (1H, dd, J = 14.5, 9.0 Hz), 2.25-2.13 (2H, m), 2.00-1.60 (8H, m) and 1.51-1.11 (5H, m)(other $C\underline{H}$ and $C\underline{H}_2$), 1.34 (3H, s, $-(C\underline{H}_3)C(CH_2-)-$), 0.92 (3H, d, J = 6.5 Hz, $-CH(C\underline{H}_3)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 212.16, 149.17, 108.40, 87.34, 81.57, 58.55, 57.74, 48.54, 47.79, 44.37, 37.47, 37.26, 35.73, 33.10, 29.17, 27.50, 26.71, 25.92, 24.74, 17.95, 11.62. MS (*m/e*): 392 (M^+). HR-MS calcd for $C_{22}H_{32}O_6$ (M^+): 392.2199; found: 392.2209 ± 0.0011.

(11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-19-noraphidicol-1-en-3-one (23)

To a solution of ketone **22** (10.1 mg, 25.9 μmol) in THF (1 mL) at -78°C, was added chlorotrimethylsilane (50 μL, 388 μmol) then LDA (2.0 M, 129 μL, 259 μmol). The mixture was stirred for 20 min at -78°C, treated with ether (1 mL) and water (1 mL) then layers were separated. Aqueous layer was extracted with ether (4×1 mL). Combined organic layers were washed with water (5 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. Crude silyl enol ether was used in the next step without any further purification.

To a solution of crude silyl enol ether in acetonitrile (1 mL) at 22°C, was added palladium (II) acetate (29 mg, 129 μmol). The mixture was stirred for 15h at 22°C, then filtered on a silica gel plug (2 cm), washed with a 1:1 mixture of EtOAc and hexane (5×2 mL) and concentrated under vacuum. Crude product was purified by flash chromatography (20% EtOAc in hexane) to afford **23** (7.9 mg, 80% for 2 steps) as a white foam. $[\alpha]^{23}_{D}$ -80.8 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 2937.7, 1747.7, 1677.0, 1128.9, 1081.4. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.79 (1H, d, J = 10.5 Hz, $-C\underline{H}=CHC(=O)-$), 5.81 (1H, d, J = 10.5 Hz, $=C\underline{H}(C(=O)-$), 4.84 (1H, d, J = 5.5 Hz, $-C\underline{H}(OC(=O)-)-$), 4.12 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.53 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.46 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 2.58 (1H, t, J = 5.5 Hz, $-C\underline{H}(CH(O-)-)-$), 2.38-2.23 (2H, m) and 2.07-1.20 (11H, m)(other $C\underline{H}$ and $C\underline{H}_2$), 1.28 (3H, s, $-(C\underline{H}_3)C(CH=)-$), 1.06 (3H, d, J = 6.5 Hz, $-CH(C\underline{H}_3)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 200.59, 155.71, 125.73, 108.42, 87.42, 81.03, 58.64, 57.77, 48.5, 43.00, 41.12, 39.12, 37.90, 33.36, 28.77, 26.57, 25.87, 25.25, 24.37, 17.54, 11.27. MS (*m/e*): 390 (M^+). HR-MS calcd for $C_{22}H_{30}O_6$ (M^+): 390.2042; found: 390.2048 ± 0.0011.

(11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-18-hydroxyaphidicol-1-en-3-one (24)

The procedure for the formation of **23** was applied for the enolization of ketone **23** (30.4 mg, 78 μmol) in THF (4 mL) with chlorotrimethylsilane (148 μL, 1.17 mmol) and LDA (2.0 M, 390 μL, 780 μmol) during 30 min at -78°C. Flash chromatography (20% EtOAc in hexane) afforded silyl enol ether intermediate (28.5 mg, 79%) as a white foam. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 5.68 (1H, d, J = 8.5 Hz, $=C\underline{H}C(OTMS)-$), 5.48 (1H, d, J = 8.5 Hz, $-C\underline{H}=CHC(OTMS)-$), 4.79 (1H, d, J = 6.0 Hz, $-C\underline{H}(OC(=O)O-)-$), 4.30 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.56 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.49 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 2.65-2.56 (1H, m), 2.29 (1H, dd, J = 14.0, 9.0 Hz), 2.02-1.56 (7H, m) and 1.40-1.02 (3H, m)(other $C\underline{H}$ and $C\underline{H}_2$), 2.55 (1H, t, J = 6.5 Hz, $-C\underline{H}(CH(O-)-)-$), 1.60 (3H, d, J = 1.5 Hz, $=C(C\underline{H}_3)-$), 1.11 (3H, s, $-(C\underline{H}_3)C(CH_2-)-$), 0.14 (9H, s, $-Si(C\underline{H}_3)_3$).

To a solution of silyl enol ether intermediate (9.3 mg, 20.1 μmol) in CH_2Cl_2 (2.5 mL) at -78°C under argon, was bubbled formaldehyde [produced by depolymerisation of paraformaldehyde (25 mg, 800 μmol), placed in a flask dipped in an oil bath at 150°C or below[20], and carried by argon flow through a glass tube passed through septa and dipped into reaction mixture] during 3 to 5 min at -78°C. A prepared solution of tetra-*n*-butylammonium difluorotriphenylsilicate (0.70 M in CH_2Cl_2, 115 μL, 80.4 mmol) was added. Formaldehyde bubbling was continued for an additional 3 to 5 min, then the mixture was stirred for 20 min at -78°C without bubbling. The solution was warmed to 22°C over 45 min then treated with brine (1 mL) and water (1 mL). The layers were separated and the aqueous layer was extracted with ether (2×2 mL) and with EtOAc (2×2 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by flash chromatography (80% EtOAc in hexane) to afford **24** (5.7 mg, 68%) as a white foam, plus hydrolyzed starting material **23** (1.9 mg, 17%) as a white foam. **24:** $[\alpha]^{23}_{D}$ -43.6 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 3462.1, 2942.0, 1748.7, 1670.0, 1082.2 ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.79 (1H, d, J = 10.5 Hz, $-C\underline{H}=CHC(=O)-$), 5.84 (1H, d, J = 10.5 Hz, $=C\underline{H}(C(=O)-$), 4.80 (1H, d, J = 5.5 Hz, $-C\underline{H}(OC(=O)-)-$), 4.14 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.87 (1H, d, J = 11.5 Hz, $-\underline{H}CHOH$), 3.56 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.49 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 3.39 (1H, d, J = 11.5 Hz, $-HC\underline{H}OH$), 2.61 (1H, t, J = 5.5 Hz, $-C\underline{H}(CH(O-)-)-$), 2.42 (1H, dd, J = 12.0, 7.0 Hz), 2.32 (1H, dd, J = 14.5, 9.5 Hz), 2.10-1.36 (10H, m) and 1.29-1.17 (3H, m)(other $C\underline{H}$, $C\underline{H}_2$ and $O\underline{H}$), 1.41 (3H, s) and 1.05 (3H, s)($-(C\underline{H}_3)C(CH=)-$ and $-(C\underline{H}_3)C(CH_2OH)-$). ^{13}C NMR

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[20] Higher temperatures should be avoided to prevent protic impurities contamination: (a) Stork, G.; d'Angelo, J.; *J. Am. Chem. Soc.*, **1974**, *96*, 7114-7116; (b) Maruoka, K.; Concepcion, A.B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H.; *J. Am. Chem. Soc.*, **1993**, *115*, 3943-3949.

(75 MHz, $CDCl_3$, δ ppm): 204.83, 156.12, 124.78, 108.45, 87.46, 80.47, 65.37, 58.69, 57.78, 49.87, 49.23, 40.82, 37.81, 34.44, 33.52, 28.61, 26.75, 26.03, 25.47, 19.64, 18.49, 16.79. MS (*m/e*): 420 (M^+). HR-MS calcd for $C_{23}H_{32}O_7$ (M^+): 420.2148; found: 420.1255 ± 0.0013.

(11*R*,16*R*)-11,16-Carbonyldioxy-17,17-dimethoxy-8-epi-18-hydroxyaphidicolan-3-one (25)

The procedure for the formation of **22** was applied for the reduction of enone **24** (16.1 mg, 38.3 mmol) in EtOAc (1.5 mL) with palladium (10% on charcoal,~1 mg) and hydrogen (50 psi) in a bomb during 7h at 22°C. Flash chromatography (80% EtOAc in hexane) afforded **25** (12.1 mg, 75%) as a white foam. $[\alpha]^{23}_D$ -74.9 (c = 1.000, CH_2Cl_2). IR (film, ν cm^{-1}): 3448.1, 2942.0, 1742.8, 1128.6, 1067.7. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4.89 (1H, d, J = 5.5 Hz, $-C\underline{H}(OC(=O)-)-$), 4.13 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.65 (1H, d, J = 11.5 Hz, $-\underline{H}CHOH$), 3.55 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.48 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 3.24 (1H, d, J = 11.5 Hz, $-HC\underline{H}OH$), 2.73 (1H, dt, J = 14.0, 9.0 Hz), 2.55 (1H, t, J = 6.0 Hz, $-C\underline{H}(CH(O-)-)-$), 2.31 (1H, dd, J = 14.5, 9.0 Hz), 2.21-2.11 (1H, m), 2.05-1.92 (1H, m), 1.83 (2H, dd, J = 9.0, 4.5 Hz) and 1.80-1.16 (13H, m)(other $C\underline{H}$, $C\underline{H}_2$ and $O\underline{H}$), 1.45 (3H, s) and 1.17 (3H, s)($-(C\underline{H}_3)C(CH_2CH_2-)-$ and $-(C\underline{H}_3)C(C(=O)-)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 217.72, 156.30, 108.45, 87.39, 81.10, 66.06, 58.61, 57.74, 52.94, 38.36, 37.93, 37.65, 35.23, 34.93, 33.34, 29.08, 27.70, 26.05, 24.86, 20.31, 19.65, 17.89. MS (*m/e*): 422 (M^+). HR-MS calcd for $C_{22}H_{34}O_7$ (M^+): 422.2304; found: 422.2308 ± 0.0013.

(3*S*,11*R*,16*R*)-17,17-Dimethoxy-8-epi-aphidicolane-3,11,16,18-tetraol (26) and (3*R*,11*R*,16*R*)-17,17-dimethoxy-8-epi-aphidicolane-3,11,16,18-tetraol (27)

To *t*-butyllithium (1.59 M in pentane, 375 mL, 595 μmol) at 0°C, was added DIBALH (1.0 M in hexane, 595 μL, 595 μmol). The mixture was vigorously stirred for 2 min at 0°C, then diluted with dry hexane (10 mL) and ether (10mL). The mixture was stirred for an addition 10 min at 0°C, then a portion (2.8 mL, corresponding to 83 μmol of *t*-butyllithium and 83 μmol of DIBALH) of this solution was placed in a flask at -78°C. A solution of ketone **25** (3.5 mg, 8.3 μmol) in THF (250 μL) was added and the mixture was stirred for 1h at -78°C then allowed to warm up to 22°C over 2.5h. Water (1 mL) and aqueous tartaric acid (1 M, 1 mL) were added, then layers were separated. Aqueous layer was extracted with CH_2Cl_2 (5×2 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by preparative chromatography (5% MeOH in EtOAc) to afford **26** (0.6 mg, 19%) as a white solid, plus **27** (0.6 mg, 19%) as a white solid. **Tetraol 26:** $[\alpha]^{23}_D$ -33.0 (c = 0.060, CH_2Cl_2). IR (film, ν cm^{-1}): 3381.7, 2924.8, 1731.6, 1470.0, 1079.5. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4.81 (1H, br s, $-O\underline{H}$), 4.18 (1H, br s, $-CH(C\underline{H}(OH)-)-$), 4.06 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.76-3.73 (1H, m, $-\underline{H}CHOH$), 3.51-3.35 (3H, m, $-CH_2C\underline{H}_{ax}(OH)-$, $-HC\underline{H}OH$ and $-O\underline{H}$), 3.51 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.50 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 3.28 (1H, br s, $-O\underline{H}$), 2.29 (1H, massif $-O\underline{H}$), 2.21 (1H, t, J = 5.5, $-C\underline{H}(CH(OH)-)-$), 2.18-2.08 (3H, m), 1.93 (1H, tt, J = 12.5, 2.5 Hz) and 1.75-0.96 (12H, m)(other $C\underline{H}$ and $C\underline{H}_2$), 1.20 (3H, s) and 0.81 (3H, s)($-(C\underline{H}_3)C(CH_2CH_2-)-$ and $-(C\underline{H}_3)C(CH(OH)-)-$). MS (*m/e*): 366 ($M^+$ - CH_2OH). HR-MS calcd for $C_{21}H_{35}O_5$ (M^+ - CH_2OH): 366.2406; found: 366.2404 ± 0.0011. **Tetraol 27:** $[\alpha]^{23}_D$ -80.3 (c = 0.053, CH_2Cl_2). IR (film, ν cm^{-1}): 3381.9, 2929.6, 1715.1, 1455.4, 1191.1, 1075.3. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4.14 (1H, d, J = 5.0 Hz, $-CH(C\underline{H}(OH)-)-$), 4.04 (1H, s, $-C\underline{H}(OCH_3)_2$), 3.63 (1H, d, J = 10.0 Hz, $-\underline{H}CHOH$), 3.58-3.54 (1H, m, $-CH_2C\underline{H}_{eq}(OH)-$), 3.51 (3H, s, $-(C\underline{H}_3O)CH(OCH_3)$), 3.50 (3H, s, $-(CH_3O)CH(OC\underline{H}_3)$), 3.39 (1H, d, J = 10.0 Hz, $-HC\underline{H}OH$), 2.21 (1H, t, J = 5.5 Hz, $-C\underline{H}(CH(OH)-)-$), 2.11-2.00 (1H, m) and 2.71-1.02 (15H, m)(other $C\underline{H}$, $C\underline{H}_2$ and $O\underline{H}$), 1.18 (3H, s) and 1.02 (3H, s) ($-(C\underline{H}_3)C(CH_2CH_2-)-$ and $-(C\underline{H}_3)C(CH(OH)-)-$). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 107.44, 78.61, 77.99, 77.19, 76.06, 72.03, 57.16, 46.83, 43.00, 41.23, 37.88, 37.50, 33.01, 29.76, 29.67, 28.30, 27.85, 27.28, 24.07, 20.80, 19.78, 11.40. MS (*m/e*): 366 (M^+ - CH_2OH). HR-MS calcd for $C_{21}H_{35}O_5$ (M^+ - CH_2OH): 366.2406; found: 366.2400 ± 0.0011.

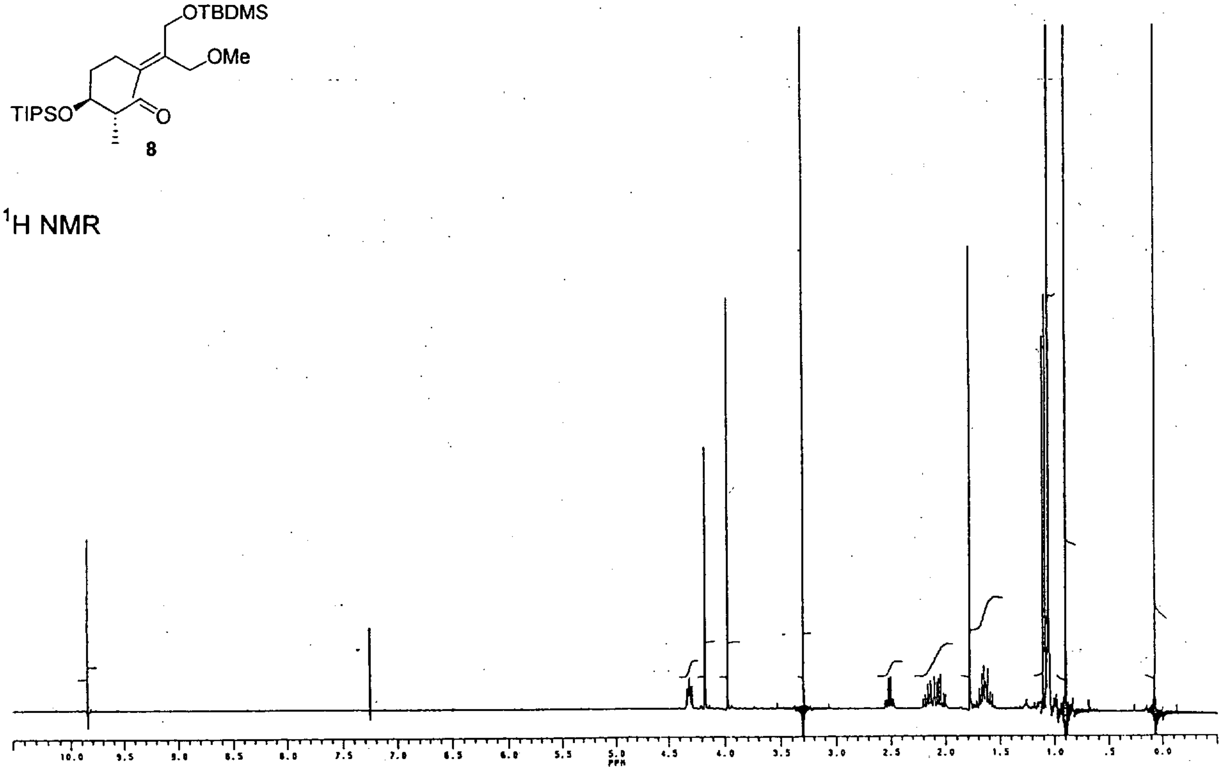
(11*R*)-8-Epi-11-hydroxyaphidicoline (2)

To a solution of acetal **27** (0.8 mg, 2.0 μmol) in THF (250 μL) at 22°C, was added HCl (1 N, 250 μL). The mixture was stirred for 15h at 22°C, treated with EtOAc (1 mL), water (0.5 mL) and K_2CO_3 (until no bubbling), then layers were separated. Aqueous layer was extracted with EtOAc (3×1 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude aldehyde was used in the next step without any further purification (seemed to be quantitative according to TLC analysis).

To a solution of crude aldehyde in EtOH (95%, 0.5 mL) at 22°C, was added sodium borohydride (a few grains). The mixture was stirred for 2.5h at 22°C, then treated with NH_4Cl (0.5 mL, satd) and layers concentrated under vacuum. Water (1 mL) and EtOAc (1 mL) were added and the layers were separated. Aqueous layer was extracted with EtOAc (6×1 mL). Combined organic layers were dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by preparative chromatography (5% MeOH in EtOAc) to afford **2** (0.4 mg, 57% for 2 steps) as white solid. $[\alpha]^{23}_D$ -75.0 (c = 0.020, CH_2Cl_2). IR (film, ν cm^{-1}): 3363.5, 2921.4, 2852.0, 1416.1, 1295.0, 1050.8. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4.48 (1H, d, J = 5.5 Hz) and 4.30-3.35 (9H, m)(2×$-C\underline{H}(OH)-$, 2×$-C\underline{H}_2OH$ and 4×$-O\underline{H}$), 2.17 (1H, tm, J = 6.0 Hz, $-C\underline{H}(CH(OH)-)-$), 1.75-0.80 (23H, m, other $C\underline{H}$, $C\underline{H}_2$, $C\underline{H}_3$ and $O\underline{H}$). MS (*m/e*): 323 (M^+ - CH_2OH). HR-MS calcd for $C_{19}H_{31}O_4$ (M^+ - CH_2OH): 323.2222; found: 323.2230 ± 0.0010.

(11*R*)-8-Epi-11-hydroxy-3,18;16,17-bis(isopropylidene)aphidicoline (28)

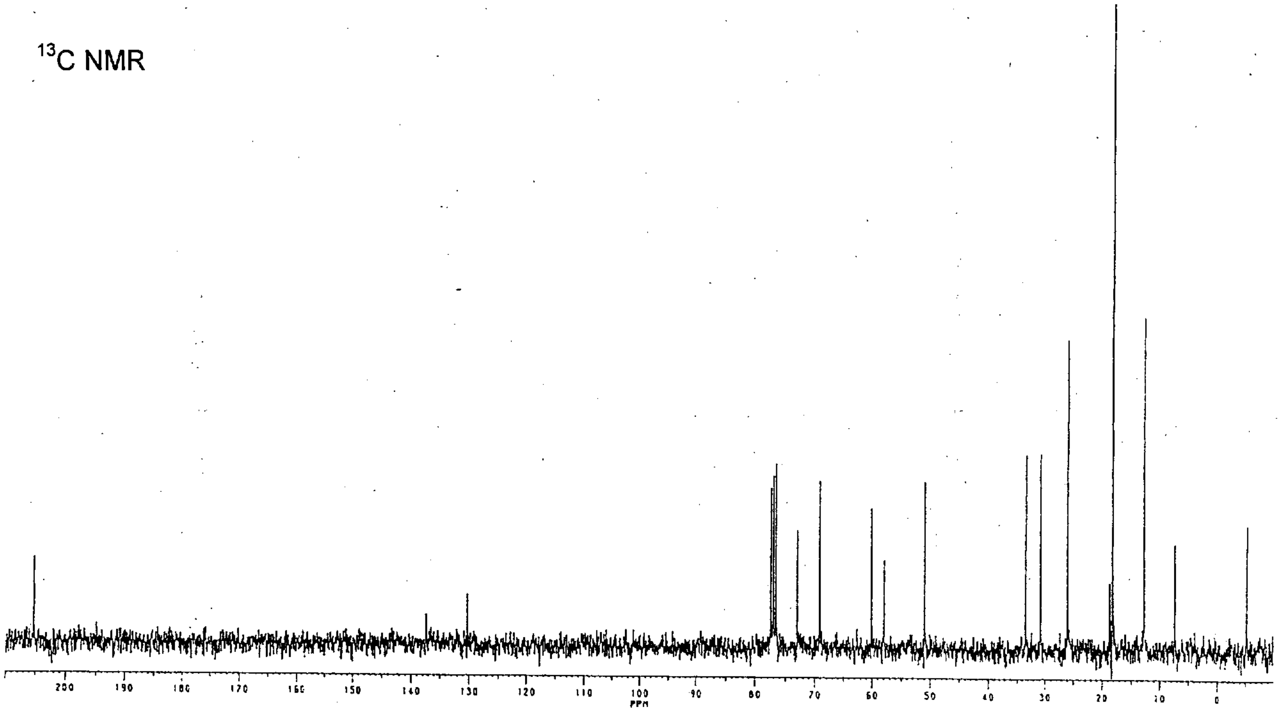
To a solution of pentaol **2** (0.3 mg, 0.8 μmol) in CH_2Cl_2 (300 μL) at 22°C, was added APTS (1 crystal) and 2,2-dimethoxypropane (14 μL, 110 μmol). The mixture was stirred for 5h at 22°C, then treated with water (2 drops) and $NaHCO_3$ (satd, 2 drops) and vigorously for 5 min at 22°C. CH_2Cl_2 (2 mL) was added and the mixture was dried over magnesium sulfate, filtered and concentrated under vacuum. Crude product was purified by preparative chromatography (50% EtOAc in hexane) to afford **28** (0.3 mg, 80%) as a white solid. IR (film, ν cm^{-1}): 2924.4, 2853.7, 1372.0, 1091.2, 1058.7. ^{1}H NMR(300 MHz, $CDCl_3$, δ ppm): 4.55 (1H, d, J = 8.5 Hz, -O$\underline{H}$), 4.18 (1H, ddt, J = 7.5, 5.0, 1.0 Hz, -C$\underline{H}$(OH)-), 3.80 (1H, d, J = 8.5 Hz), 3.61 (1H, d, J = 8.5 Hz) and 3.45-3.43 (2H, m)(2×-C$\underline{H}_2$O-), 3.40 (1H, dm, J = 3.5 Hz, -$CH_2C\underline{H}$(O-)-), 2.38-2.26 (1H, m), 2.11-1.97 (1H, m) and 1.79-0.81 (20H, m)(other C$\underline{H}$, C$\underline{H}_2$, C$\underline{H}_3$ and O$\underline{H}$), 2.15 (1H, tm, J = 6.0 Hz, -C$\underline{H}$(CH(OH)-)-), 1.24 (12H, br s, 2×-OC(C$\underline{H}_3)_2$)O-). MS (*m/e*): 435 (MH^+), 377 (MH^+ - CH_3COCH_3), 359 (MH^+ - CH_3COCH_3 - H_2O), 301 (MH^+ - 2×CH_3COCH_3 - H_2O), 283 (MH^+ - 2×CH_3COCH_3 - 2×H_2O).

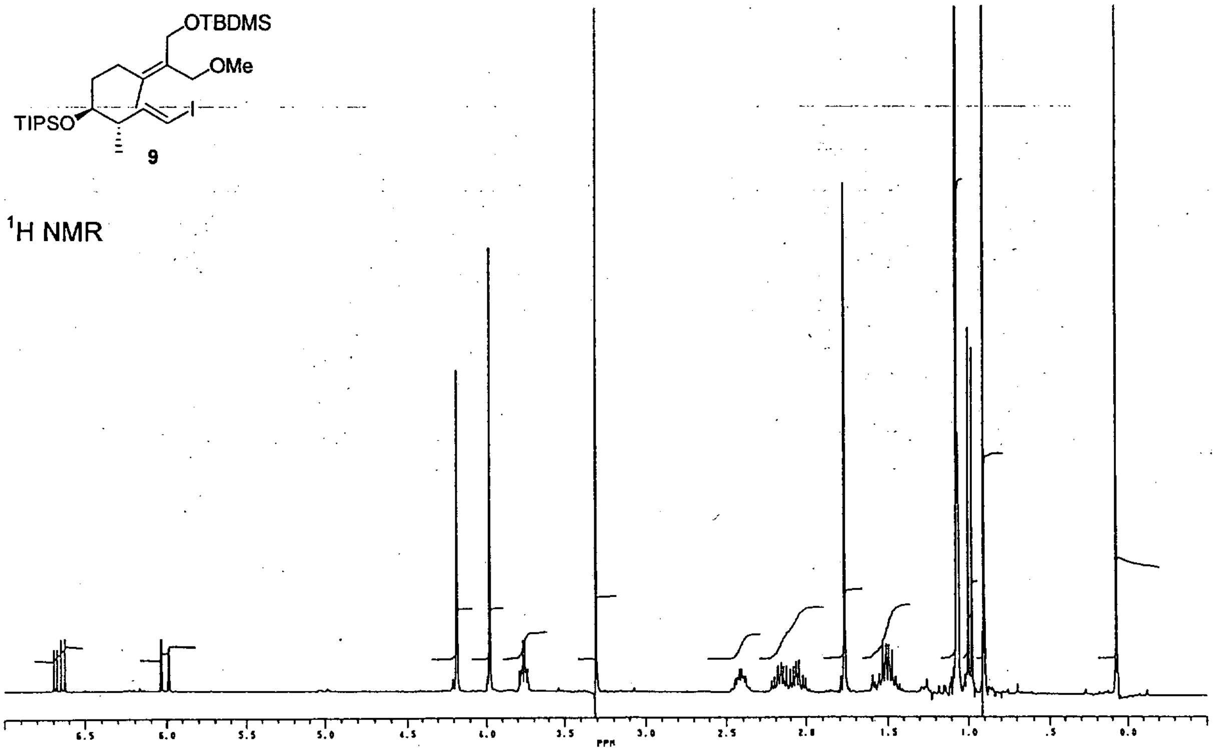


8

^{1}H NMR

^{13}C NMR

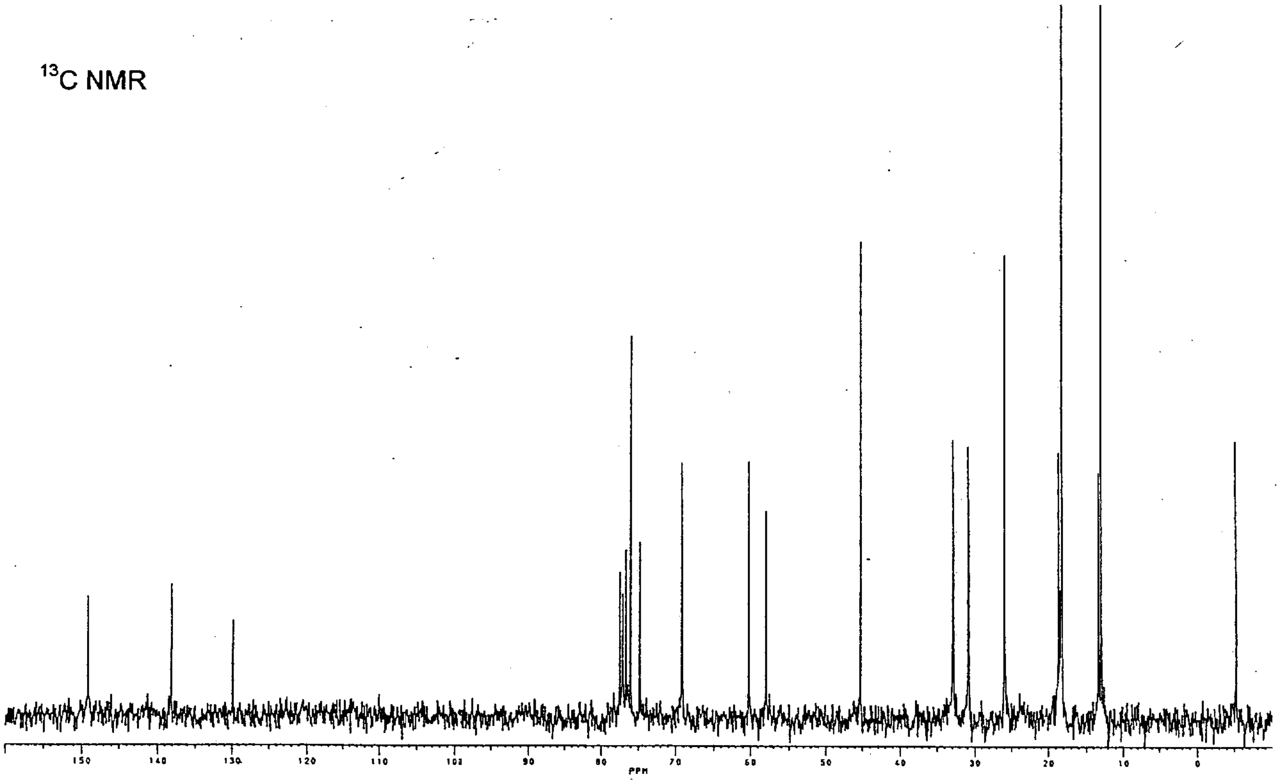


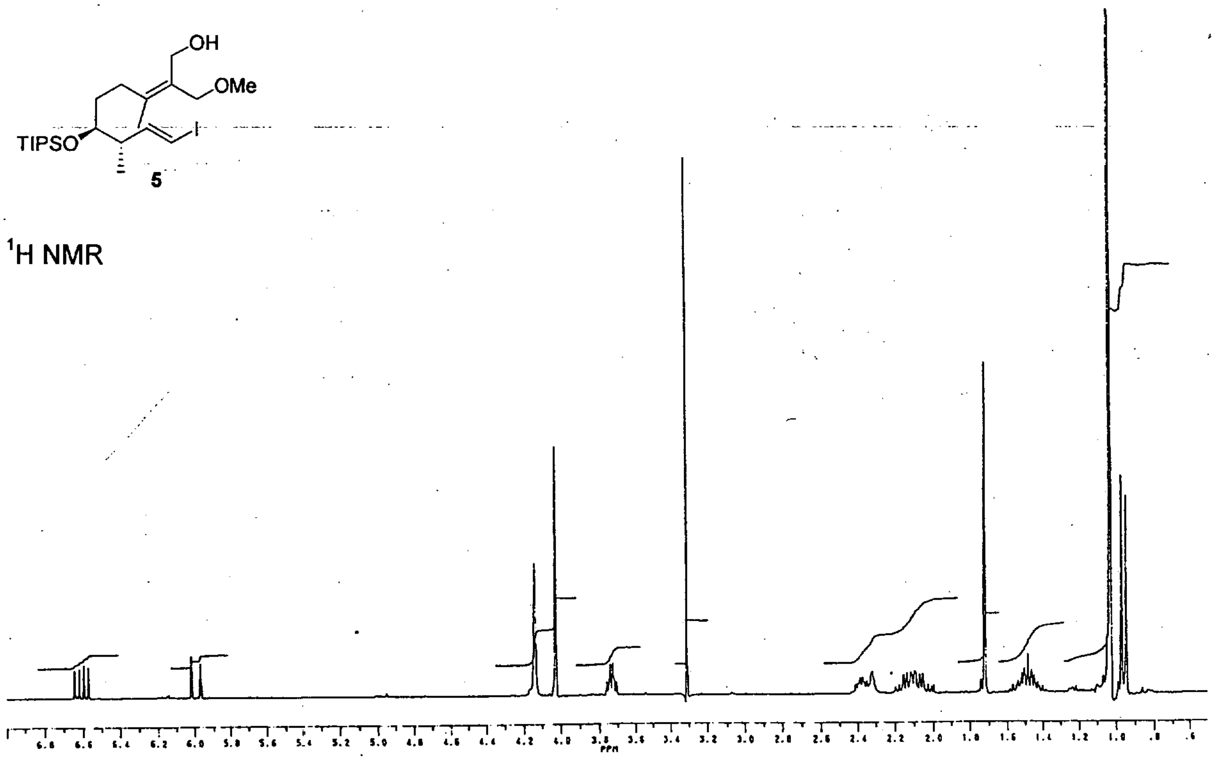


9

¹H NMR

¹³C NMR

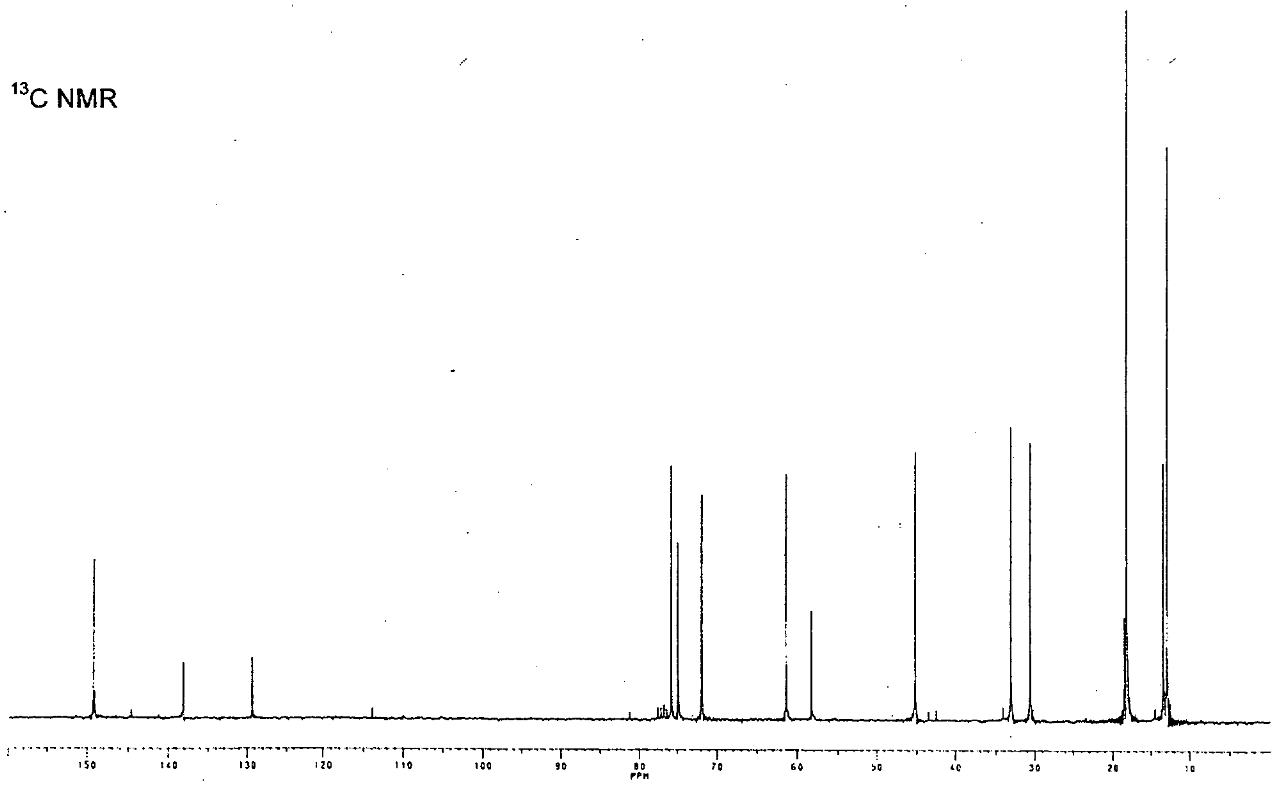


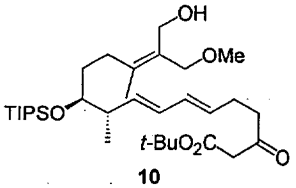


5

^{1}H NMR

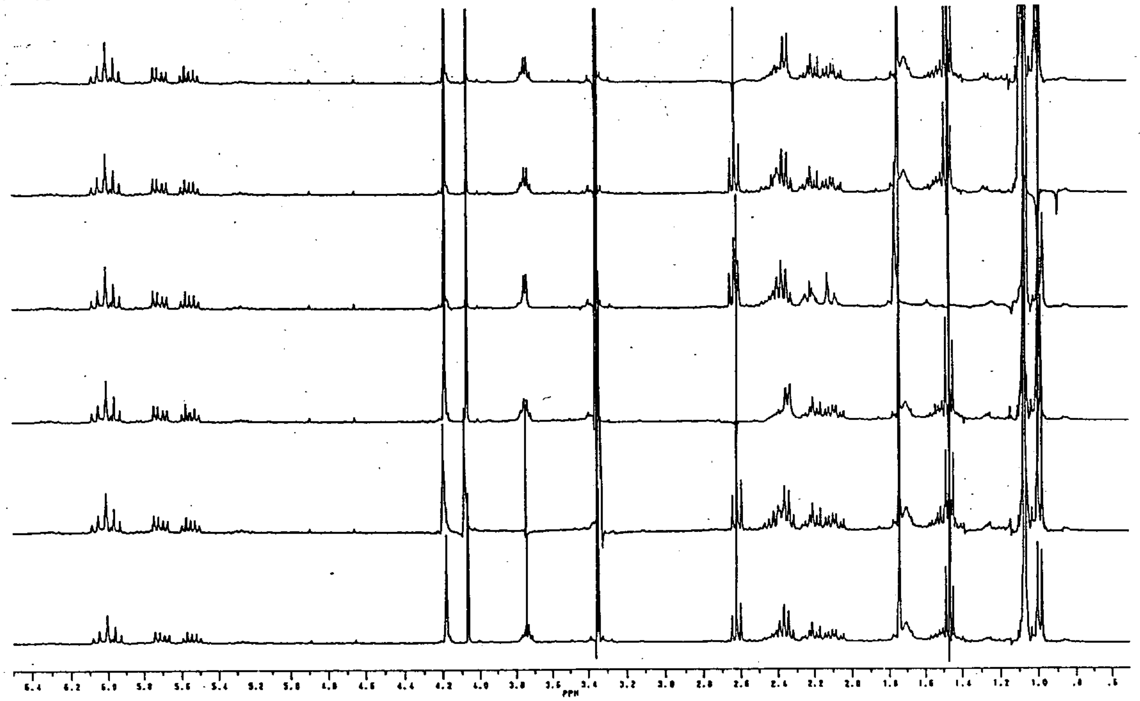
^{13}C NMR





10

^{1}H NMR



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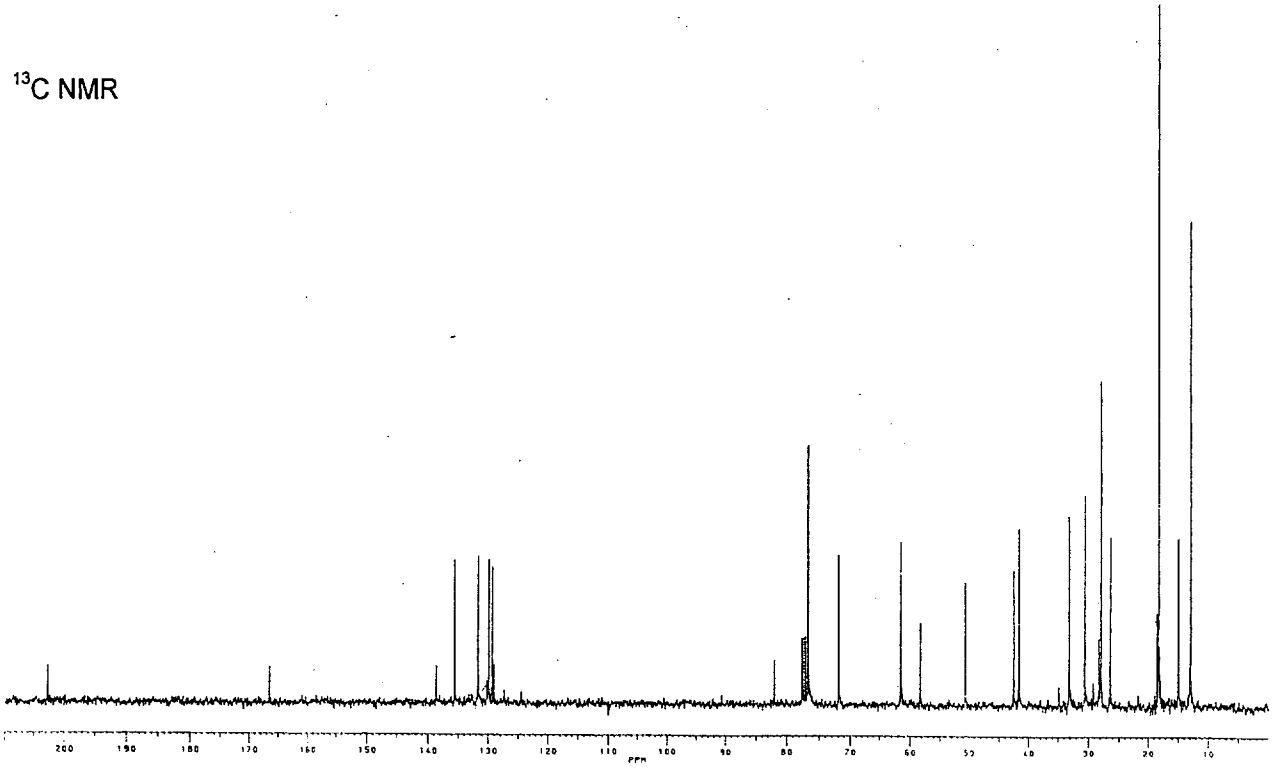
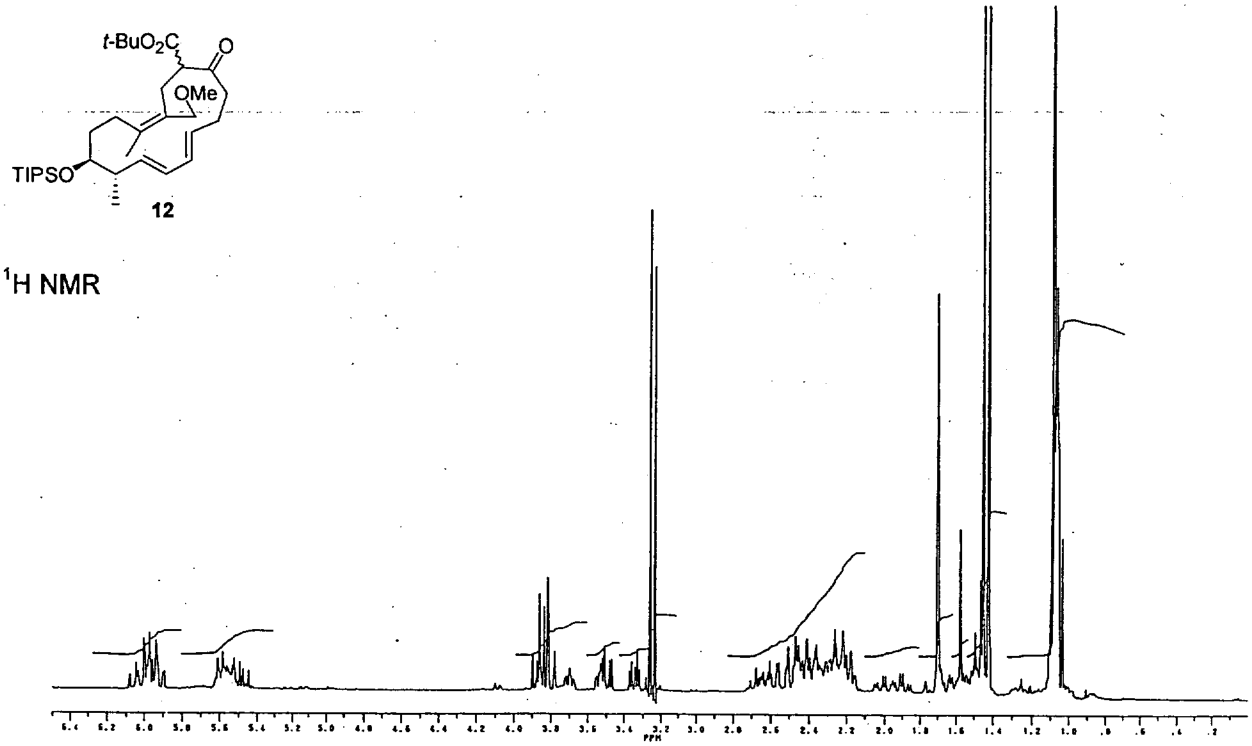
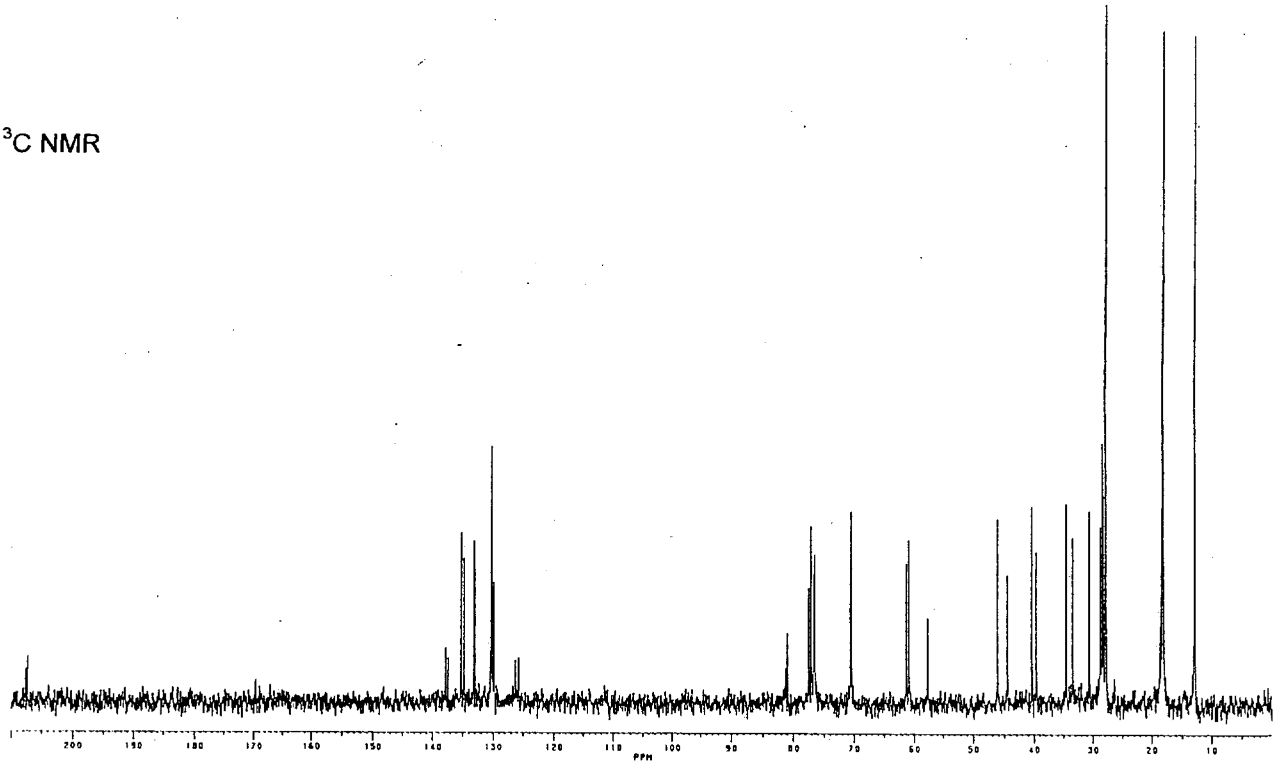




12

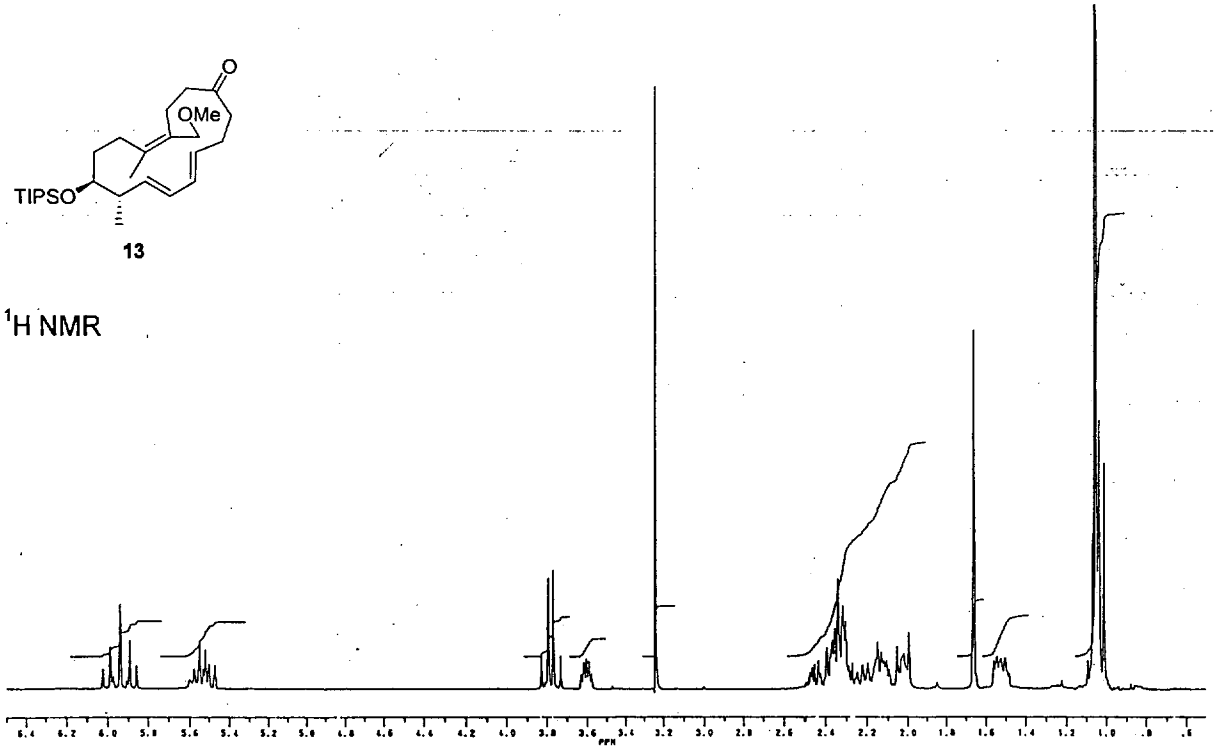
^{1}H NMR

^{13}C NMR

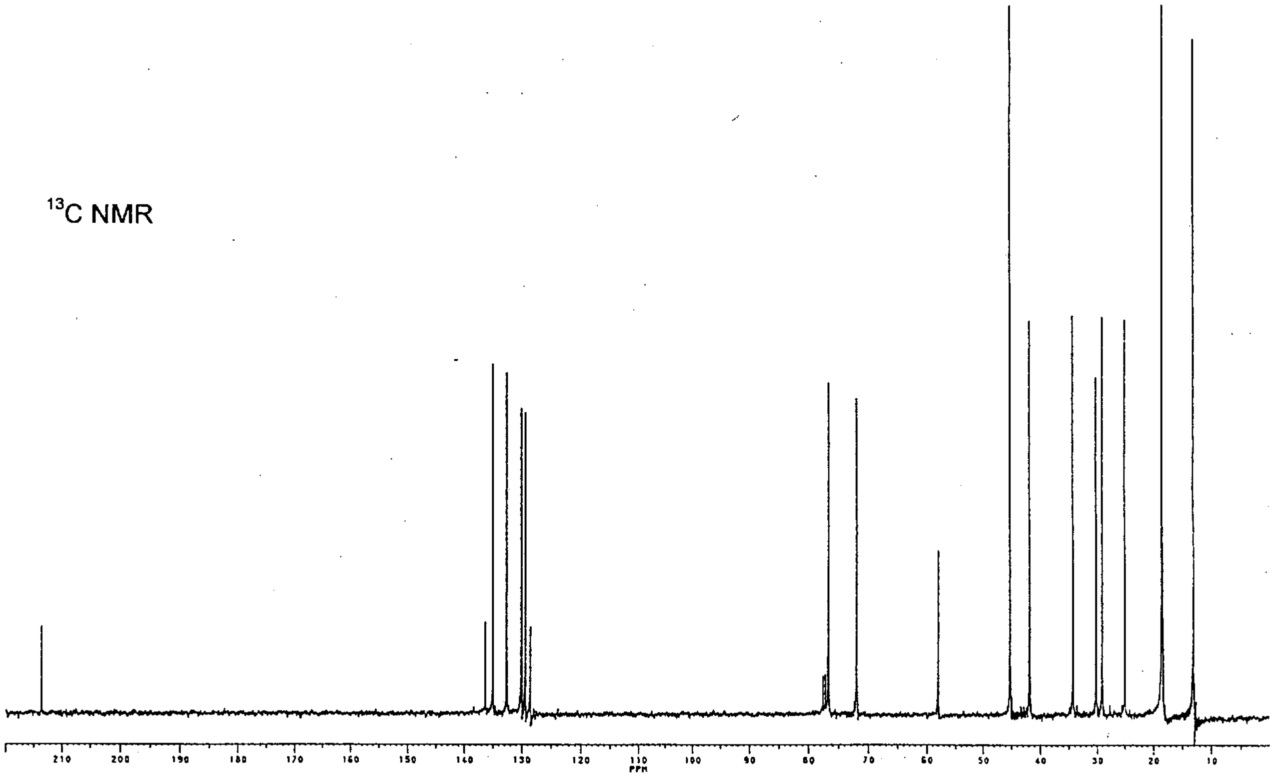


13

^{1}H NMR

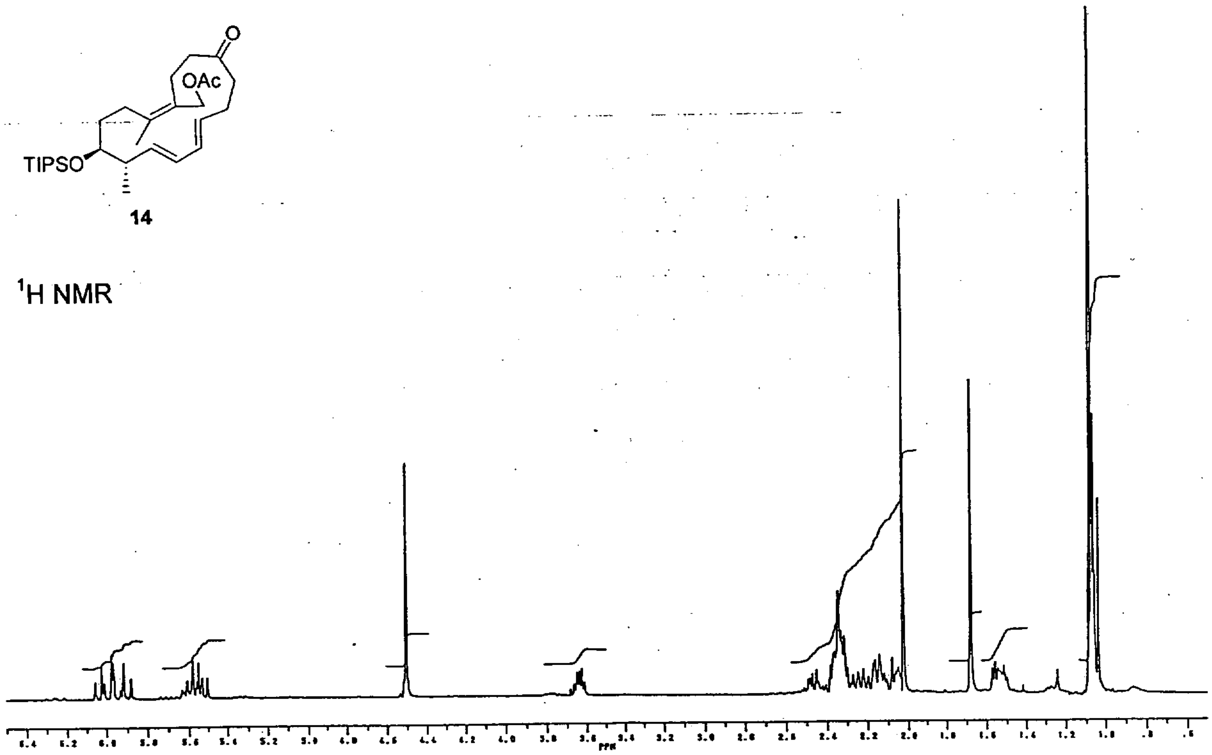


^{13}C NMR

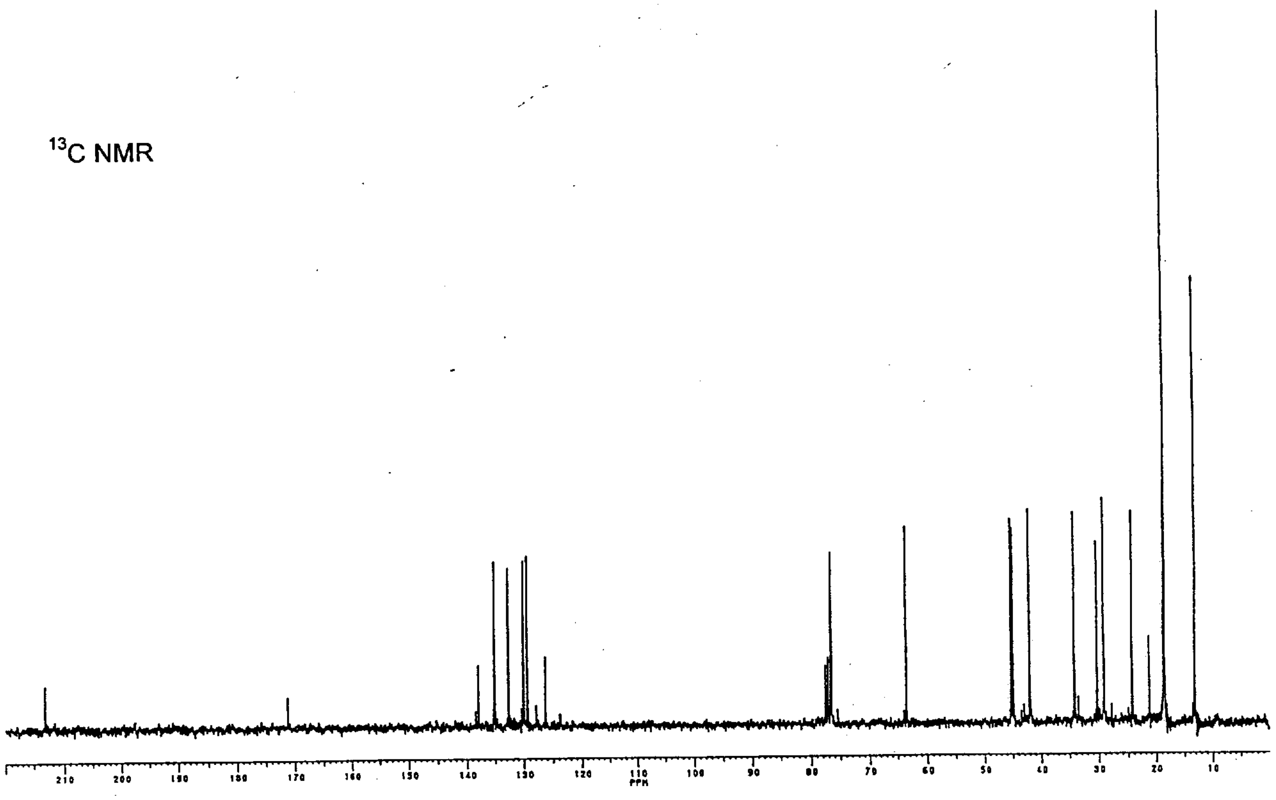


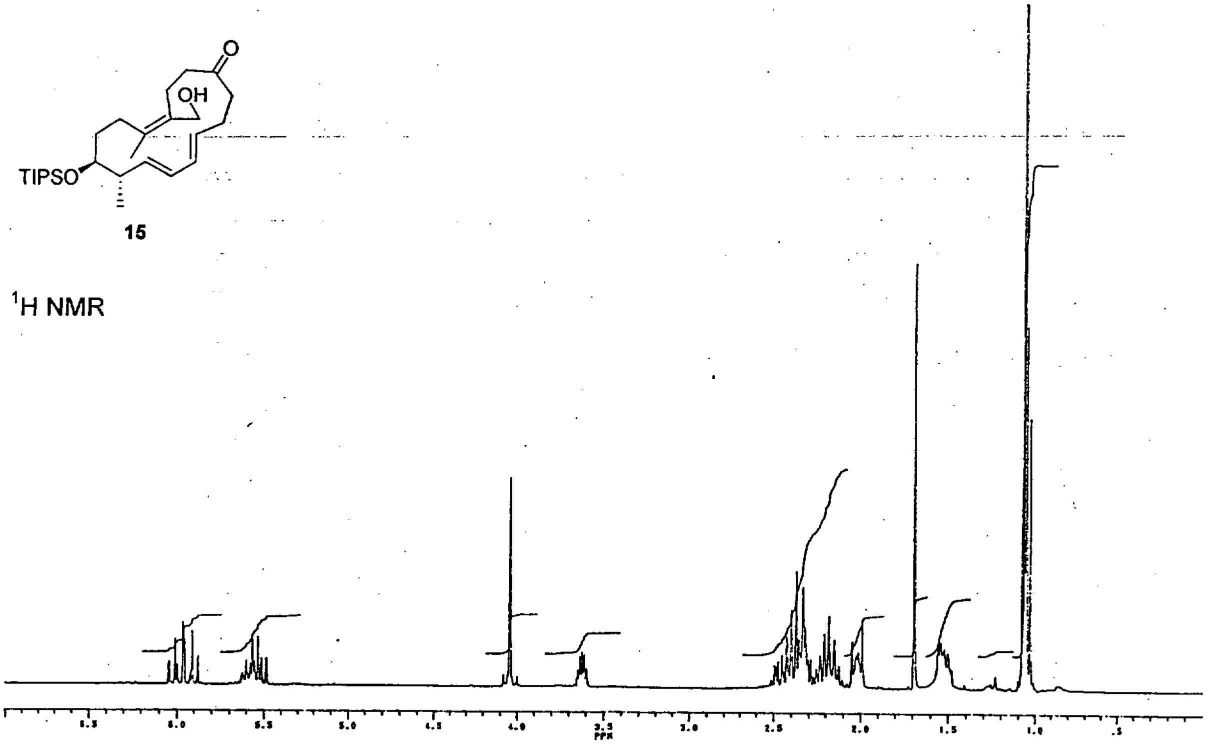
14

^{1}H NMR



^{13}C NMR

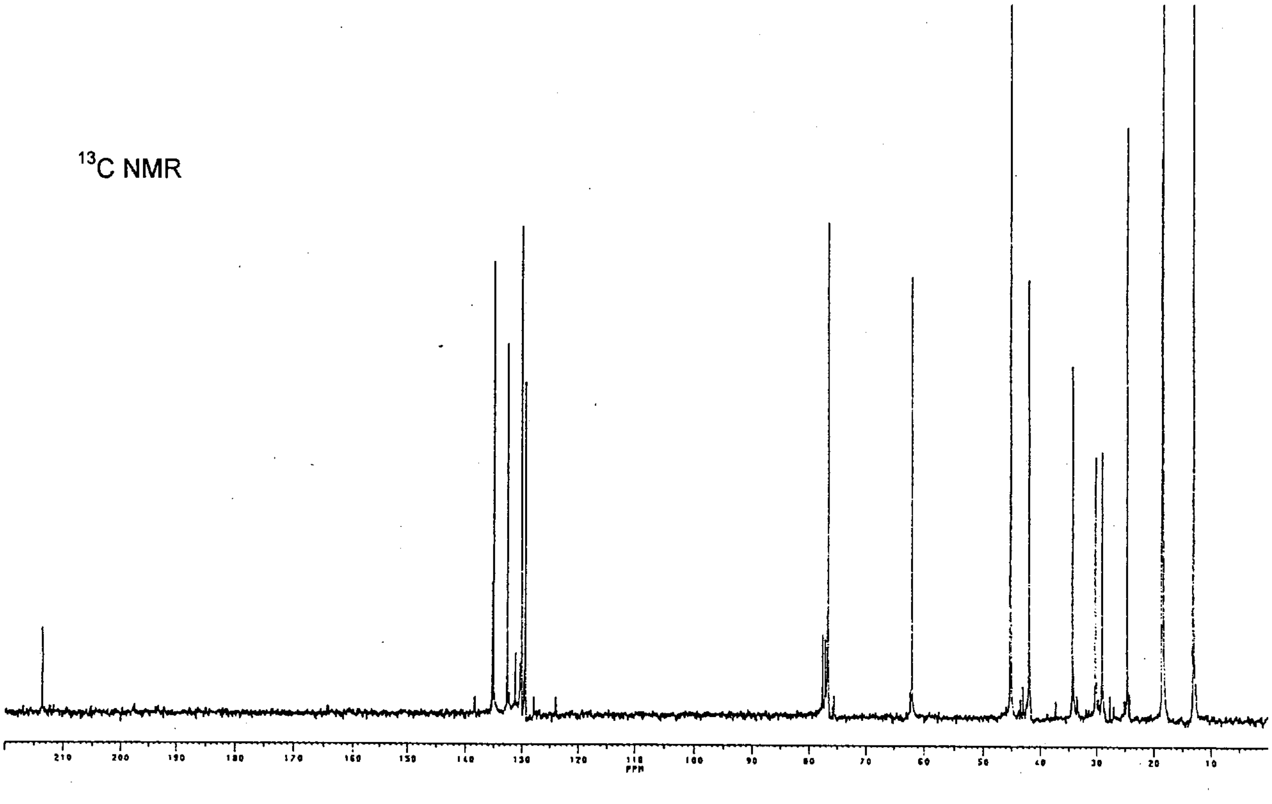




15

^{1}H NMR

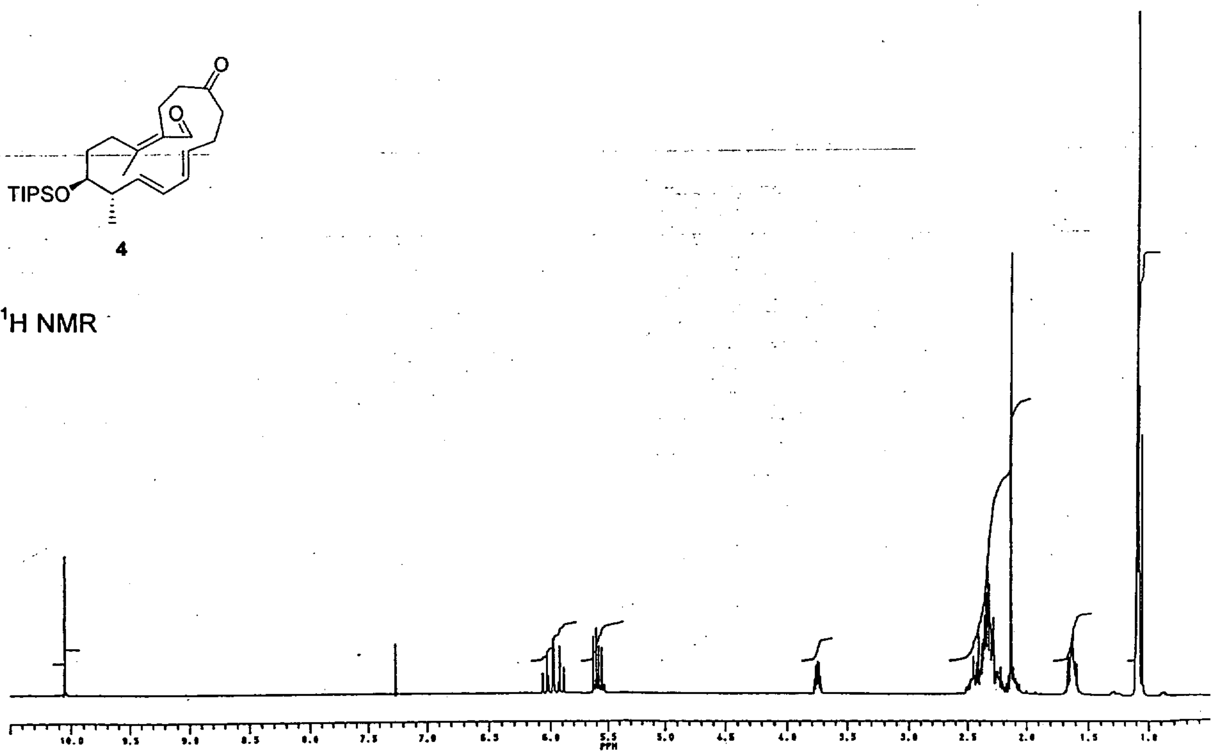
^{13}C NMR



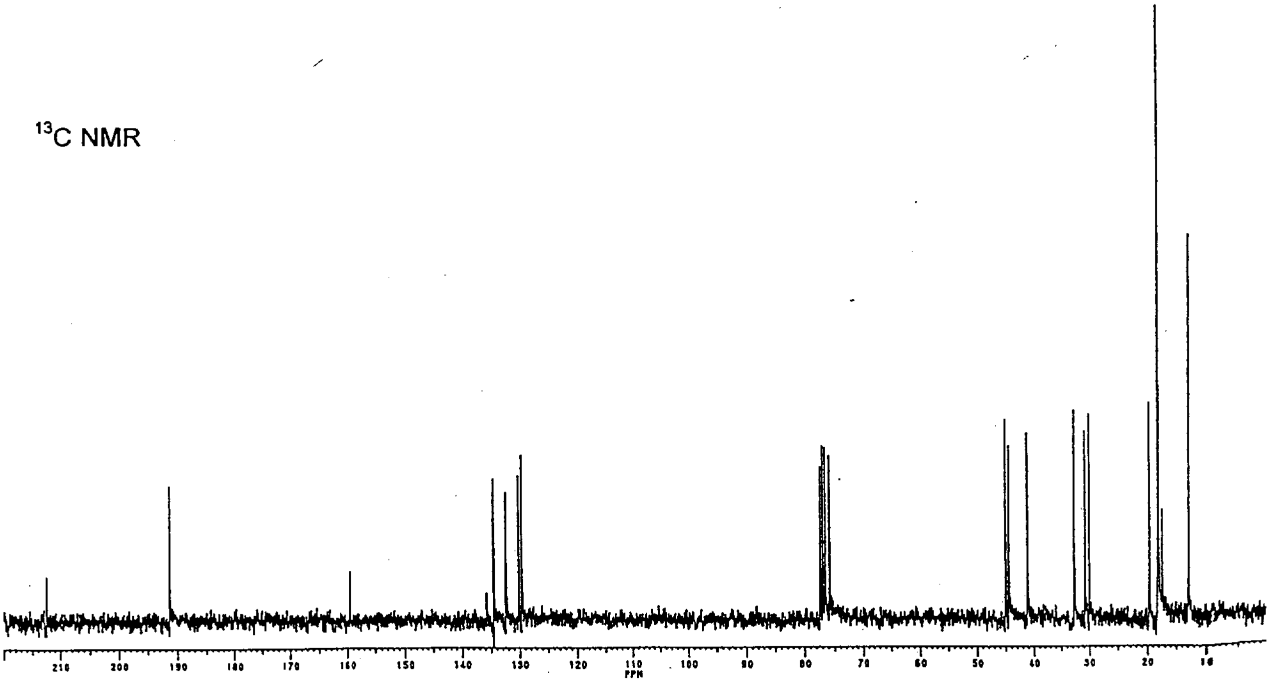
9

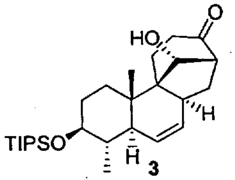
4

^{1}H NMR



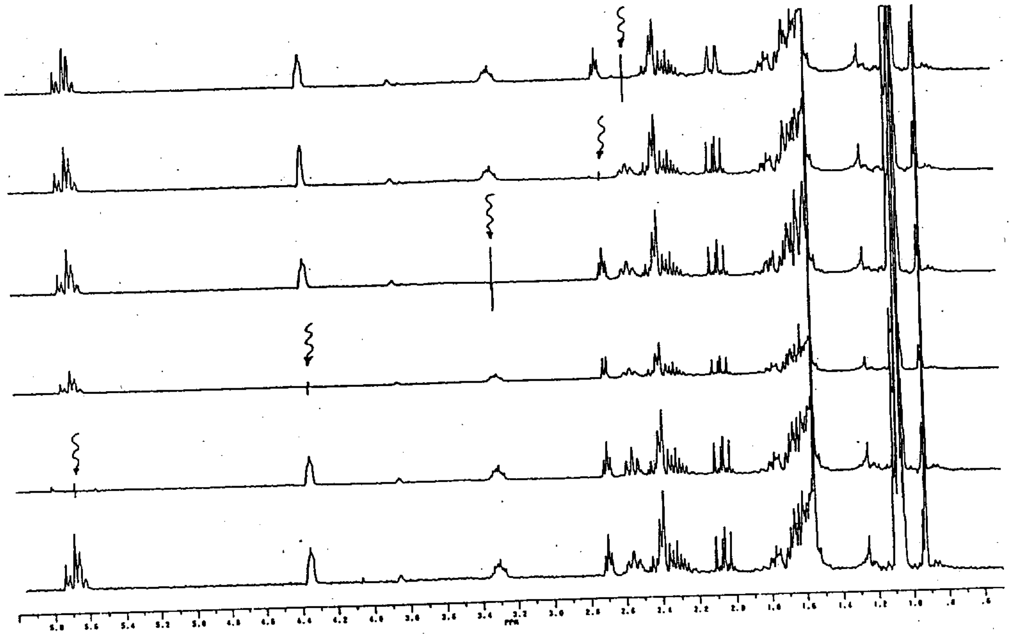
^{13}C NMR



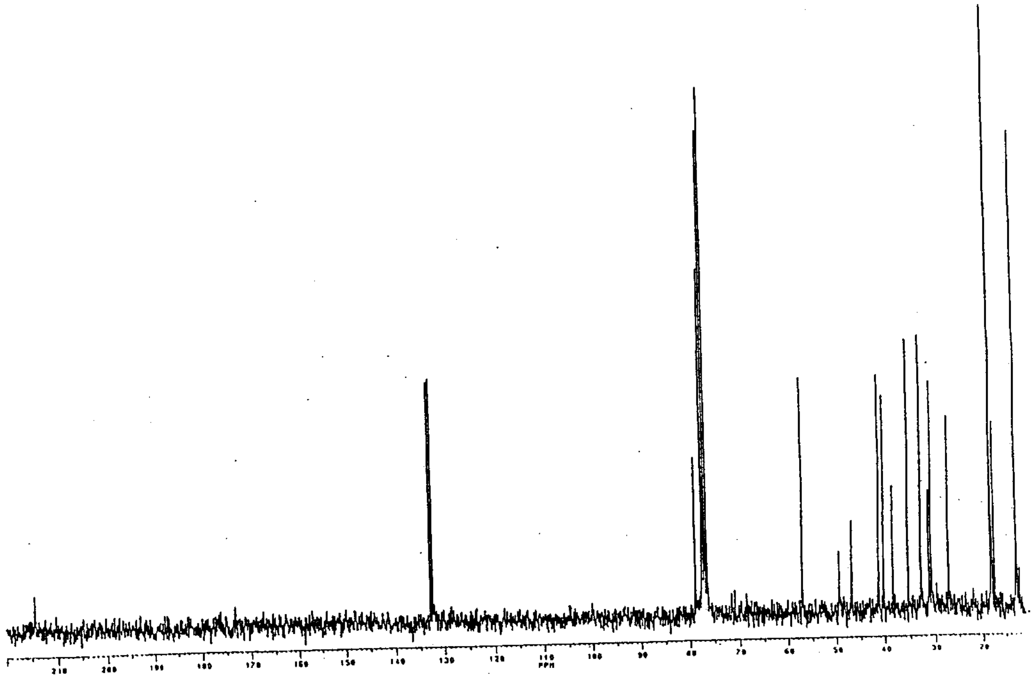


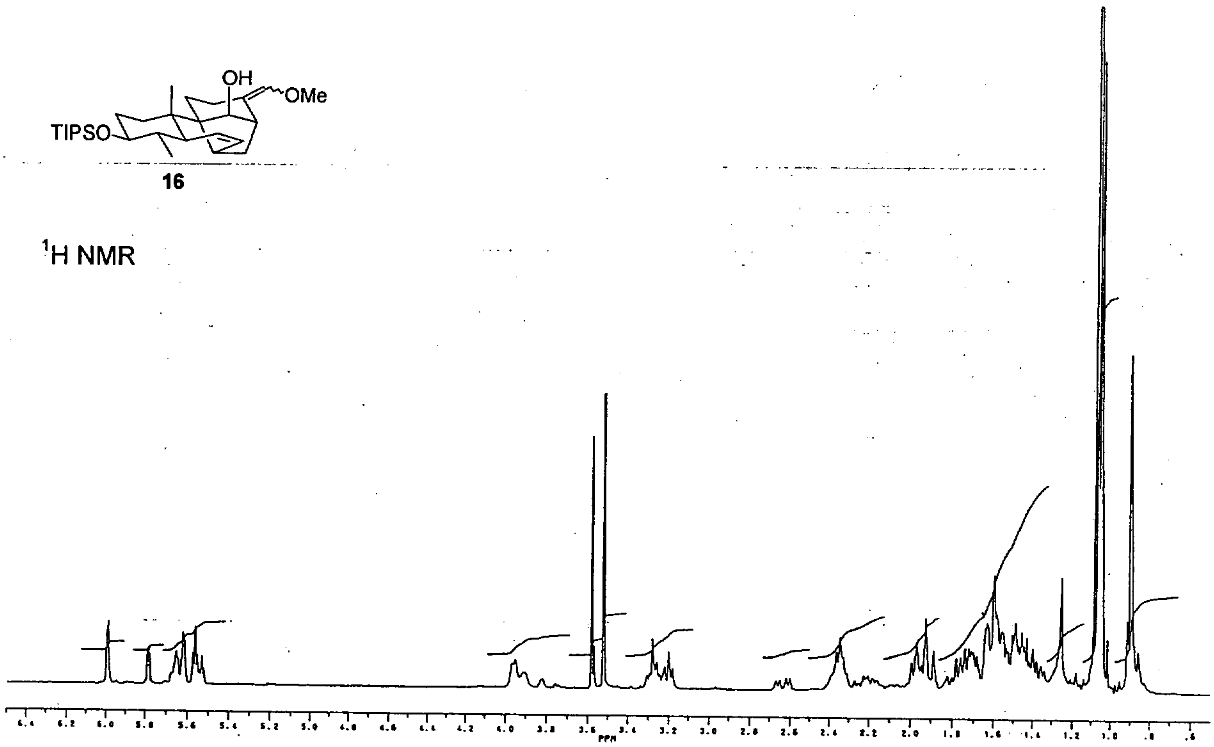
3

¹H NMR



¹³C NMR

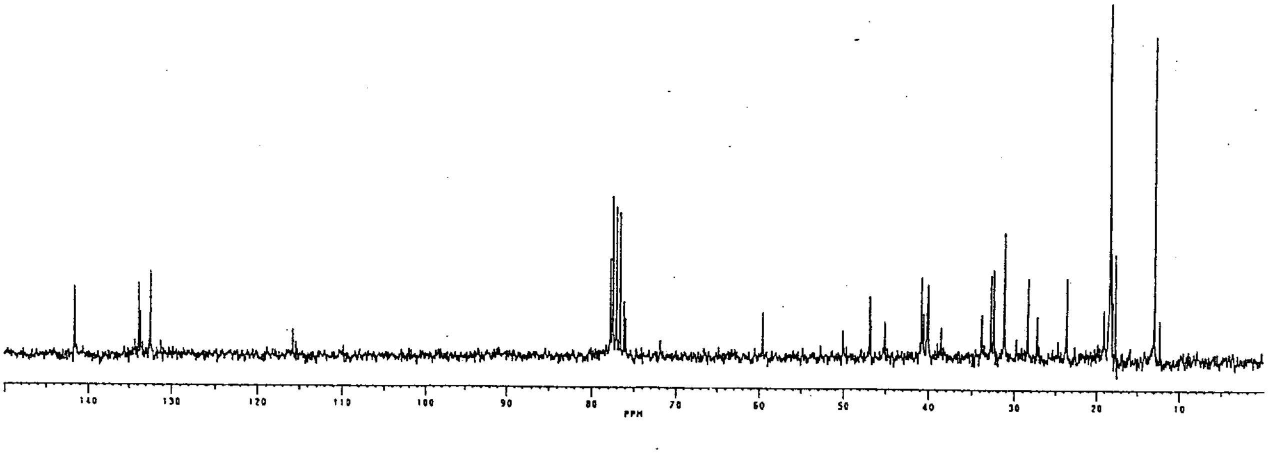


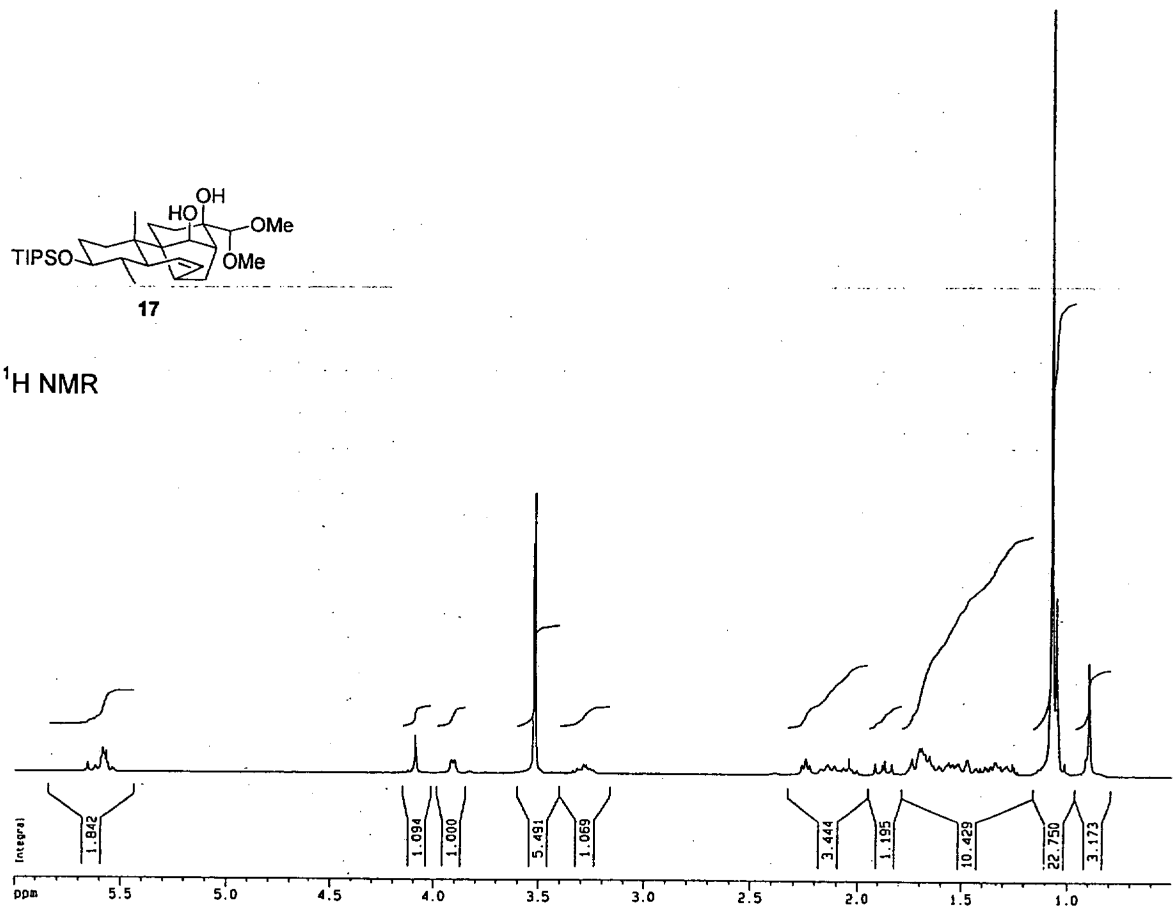


16

^{1}H NMR

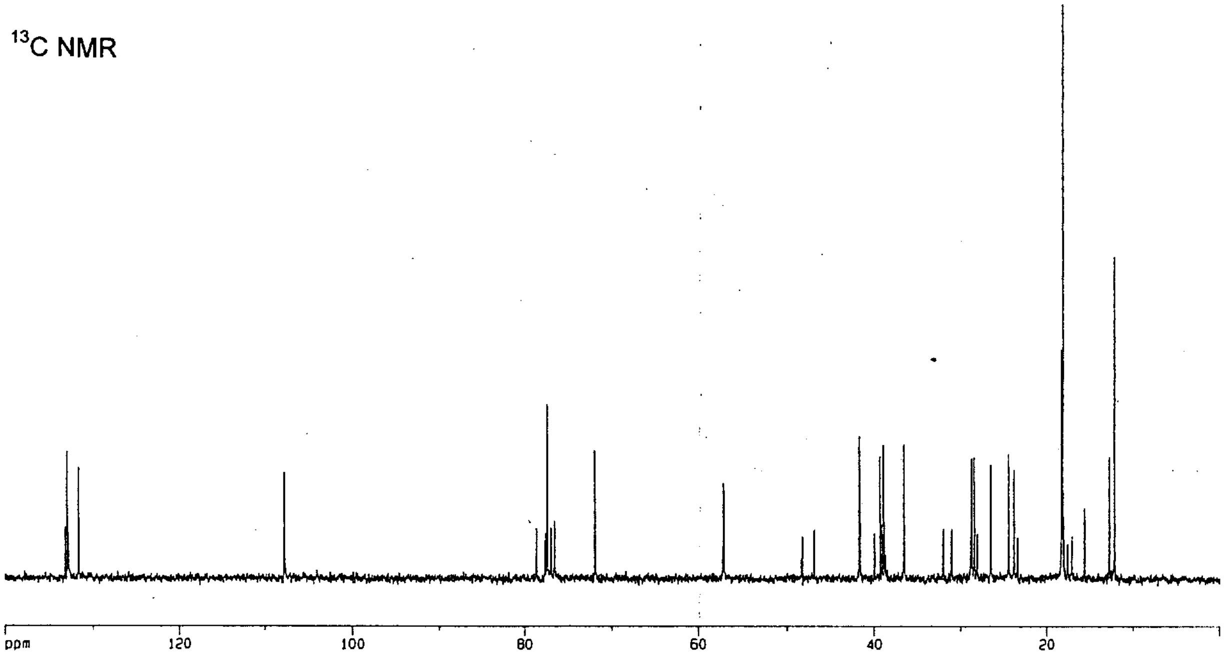
^{13}C NMR



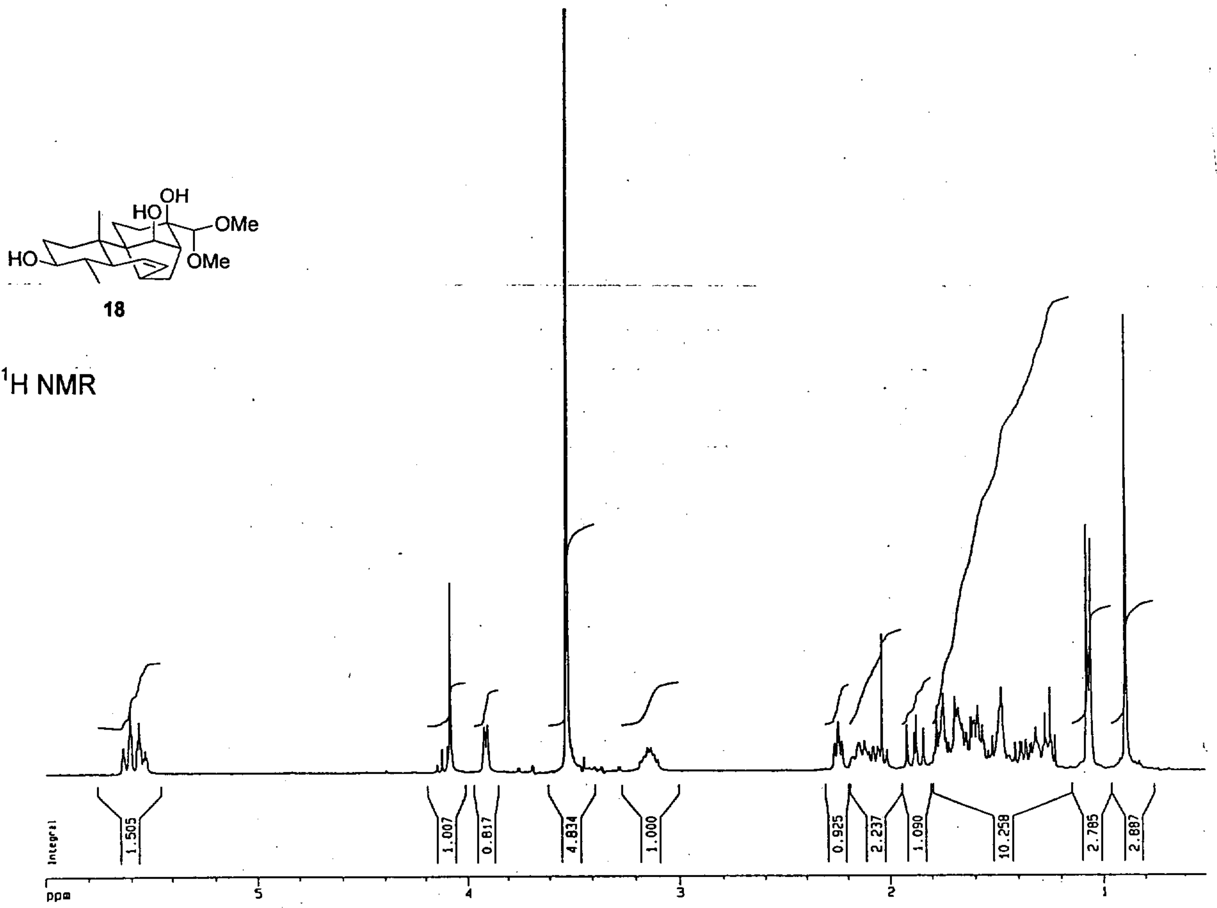


17

^{1}H NMR



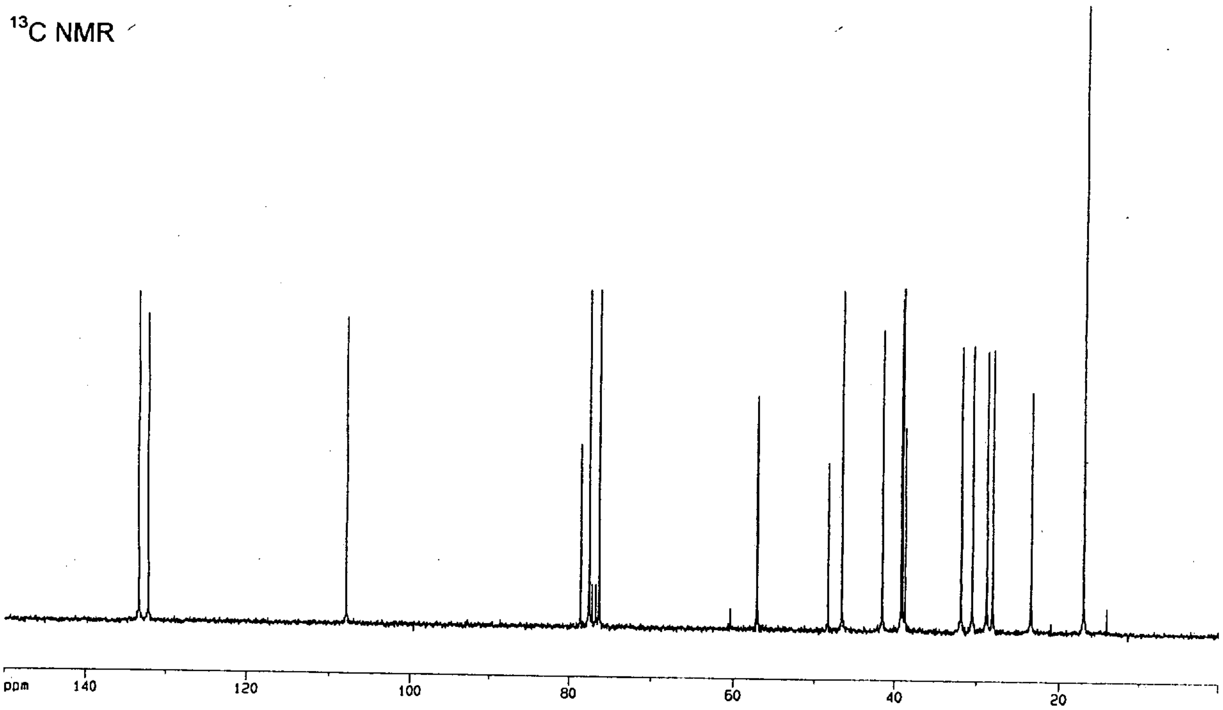
^{13}C NMR

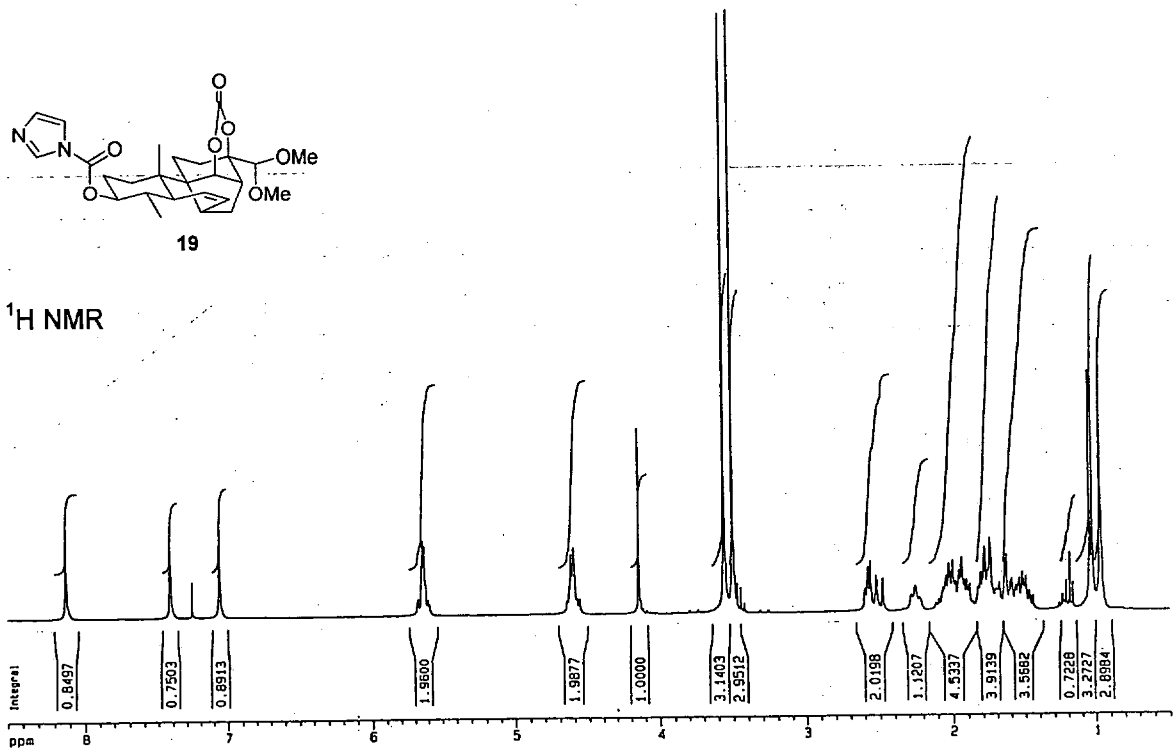


18

^{1}H NMR

^{13}C NMR

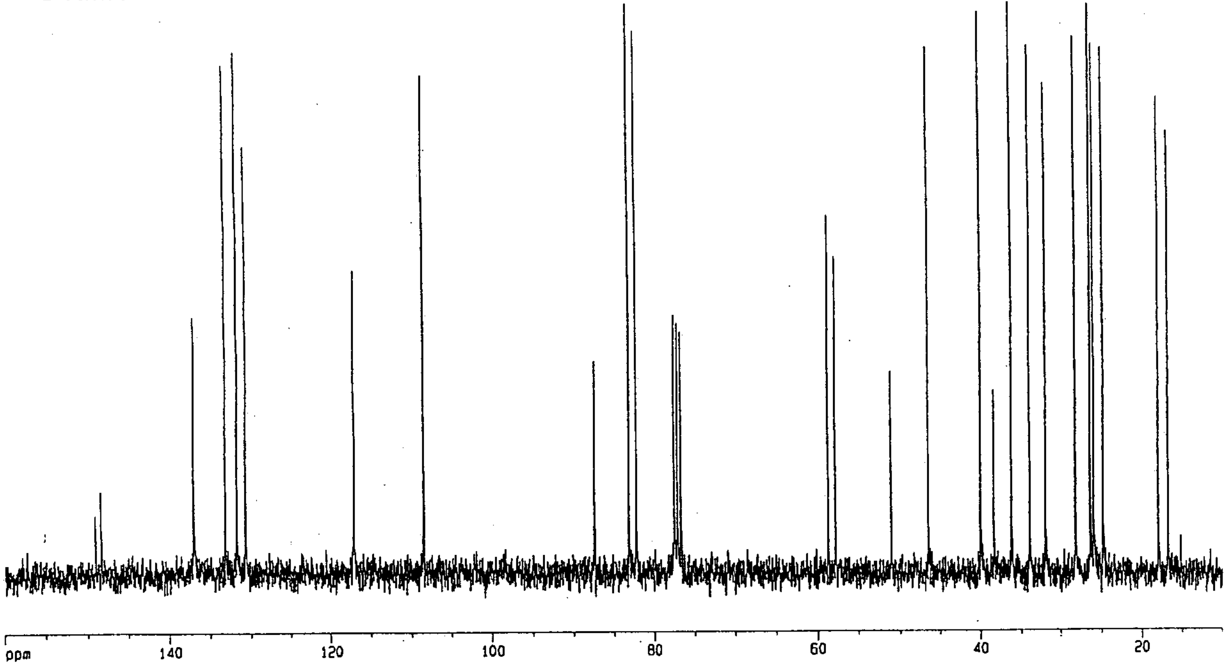


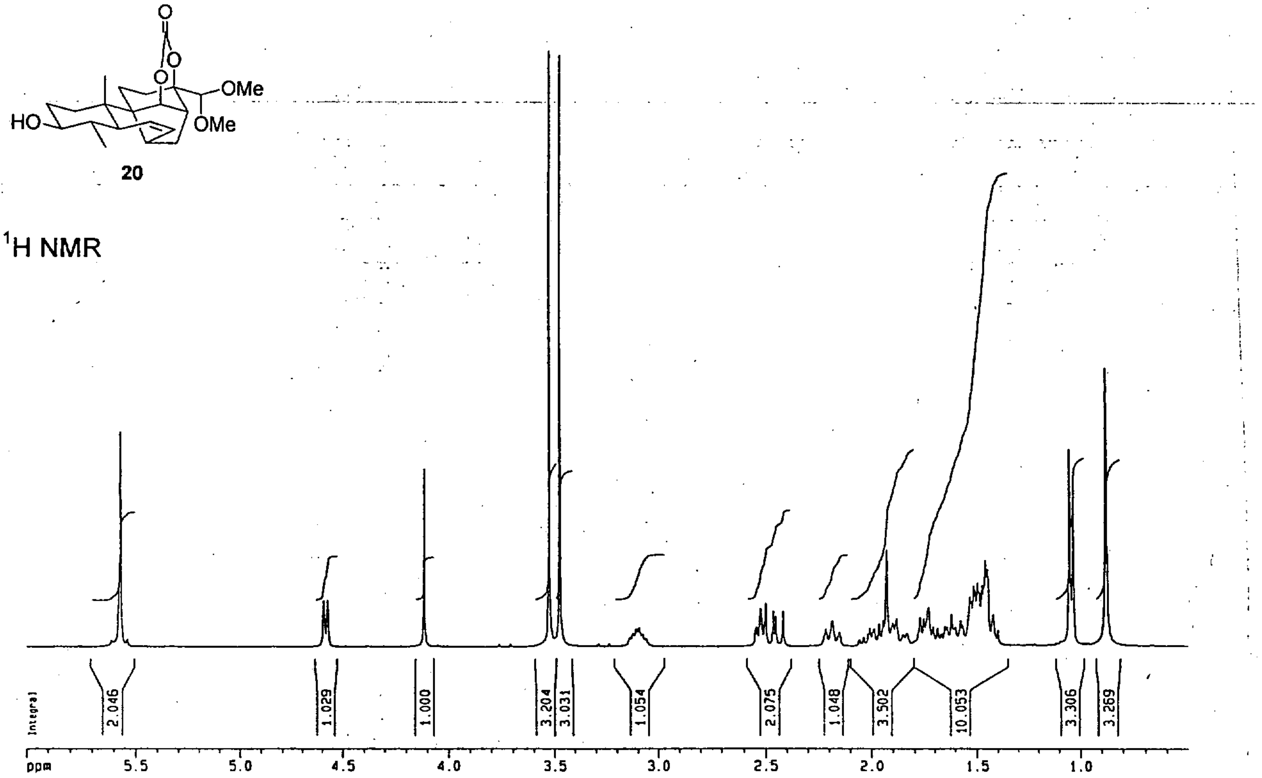


19

^{1}H NMR

^{13}C NMR

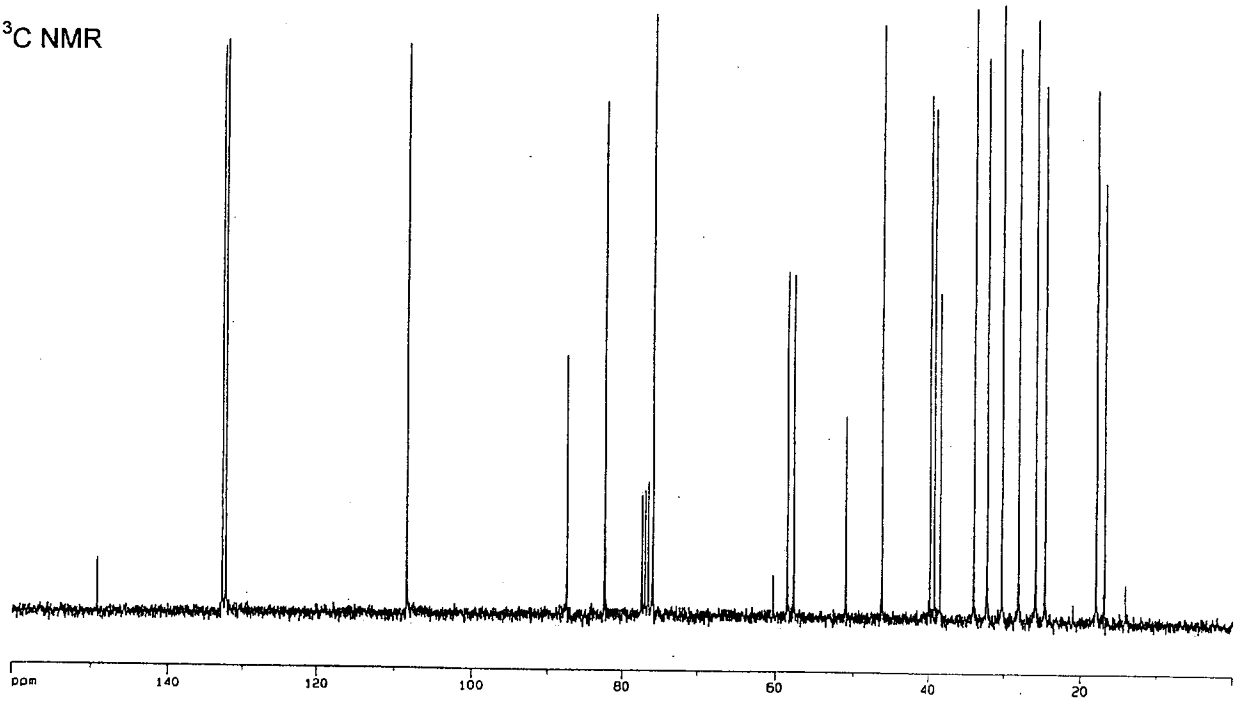


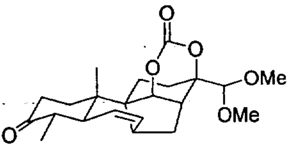


20

^{1}H NMR

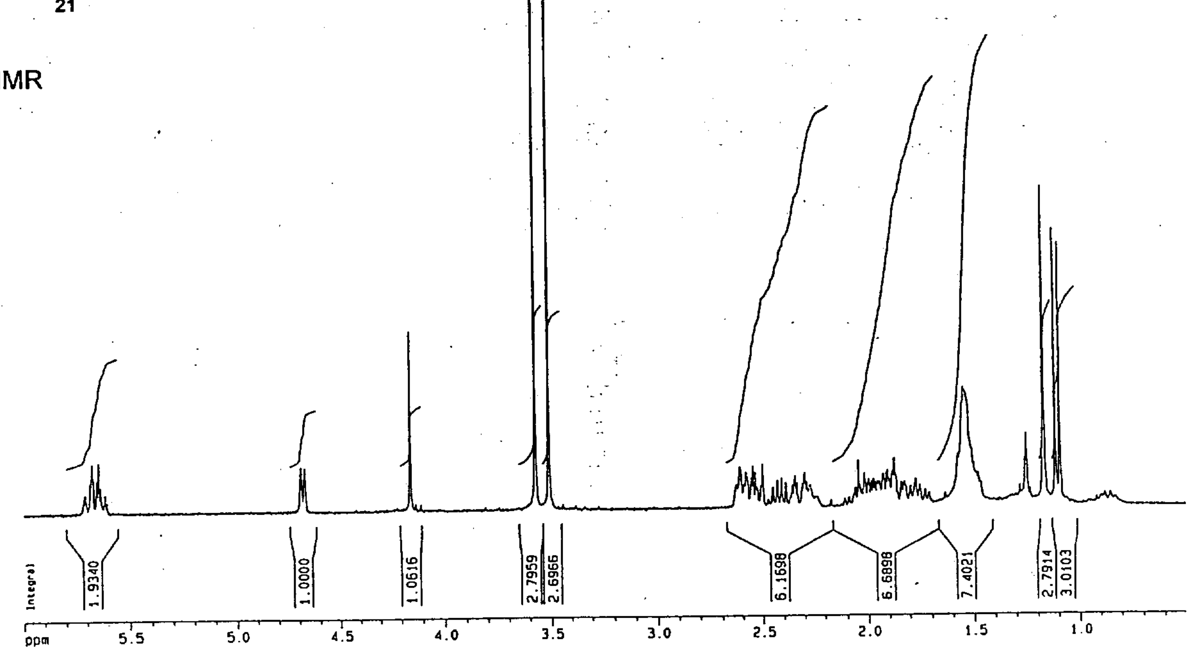
^{13}C NMR



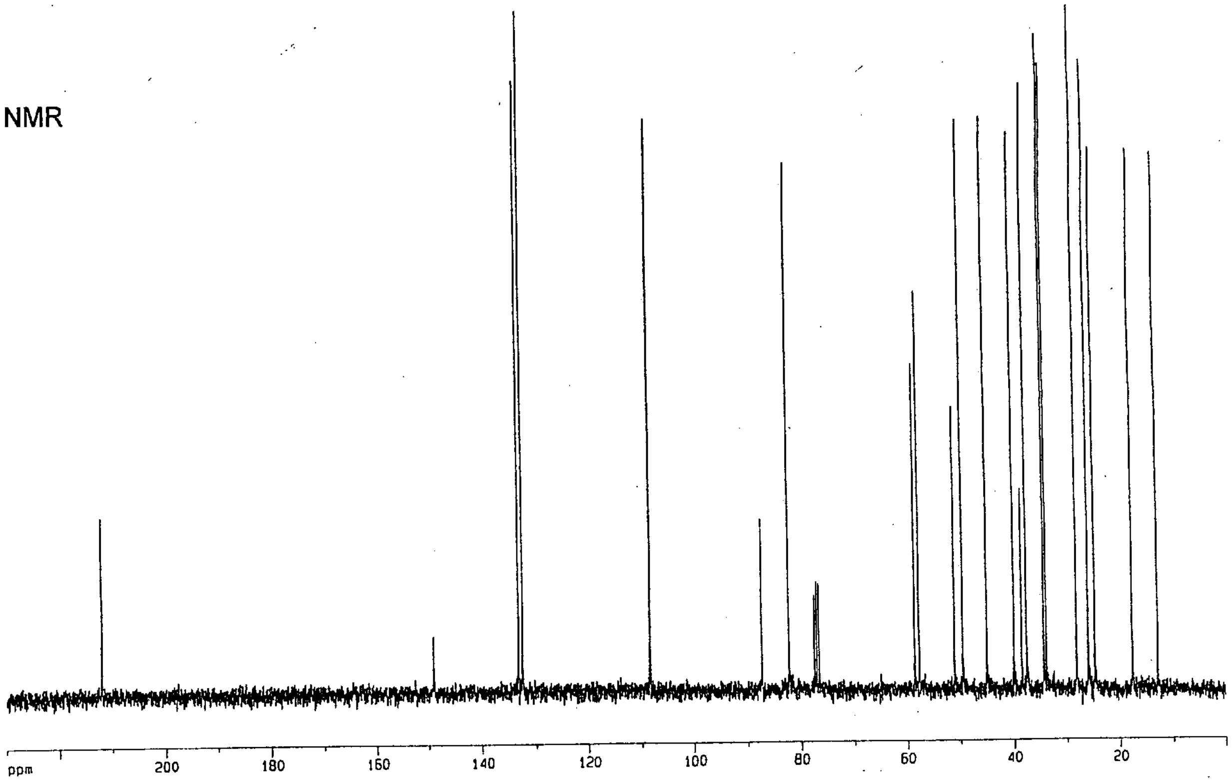


21

^{1}H NMR

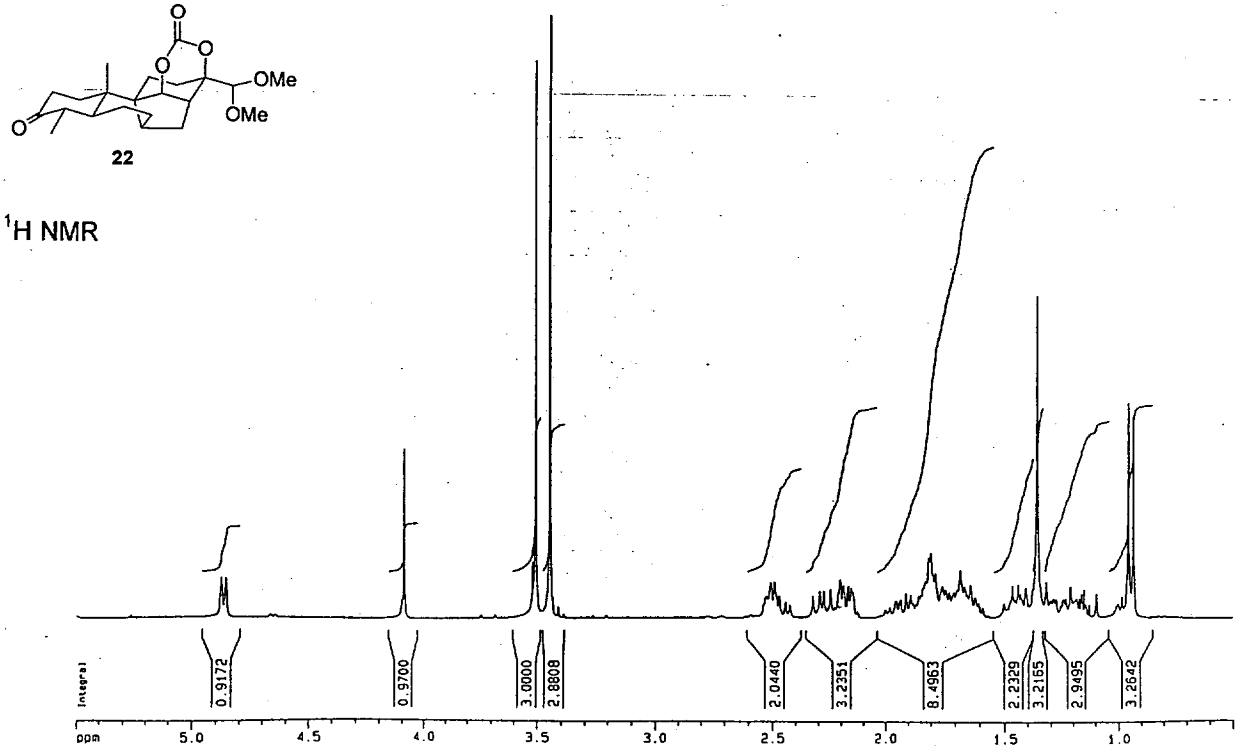


^{13}C NMR

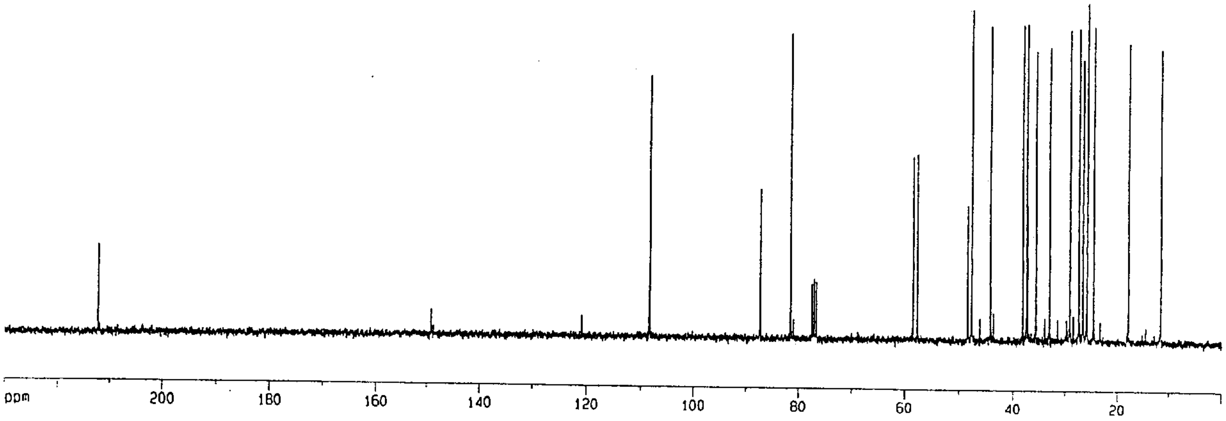


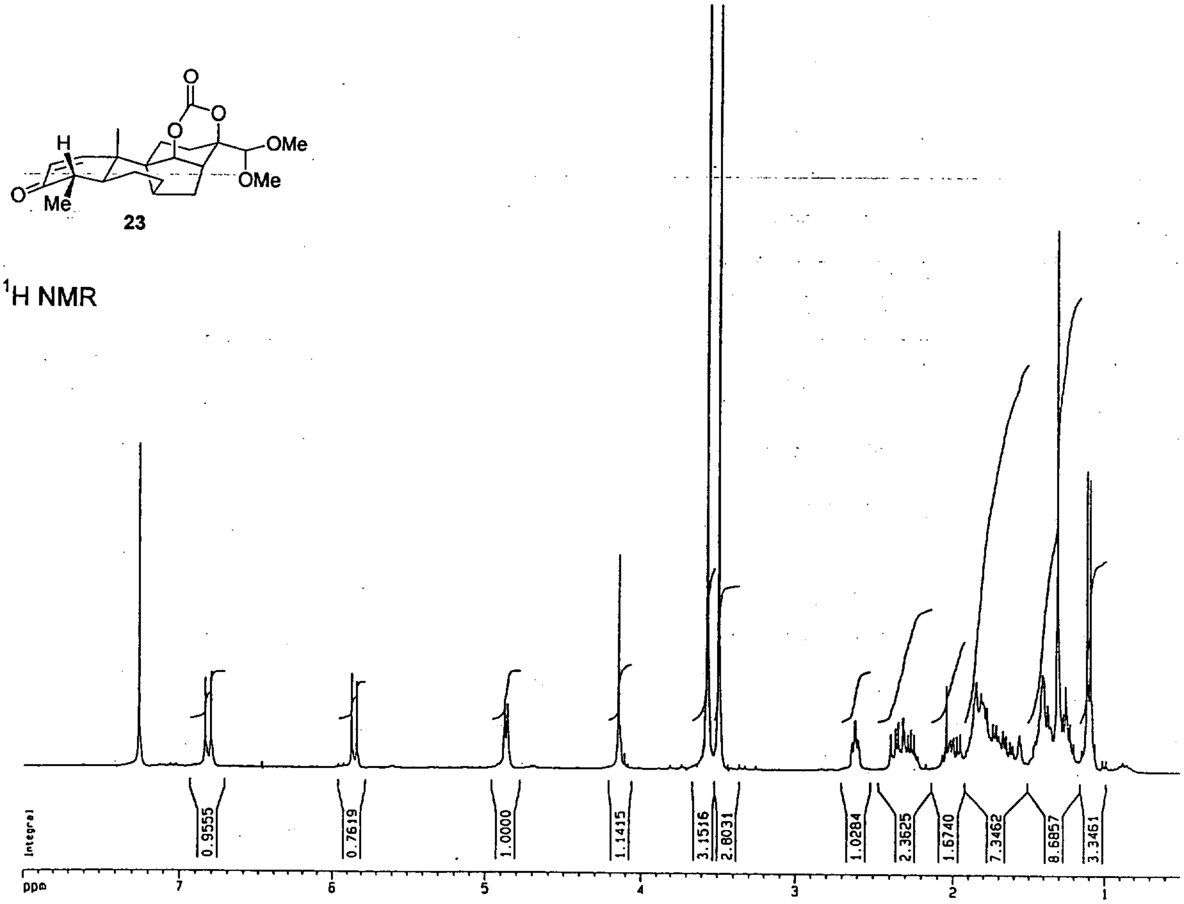
22

^{1}H NMR



^{13}C NMR

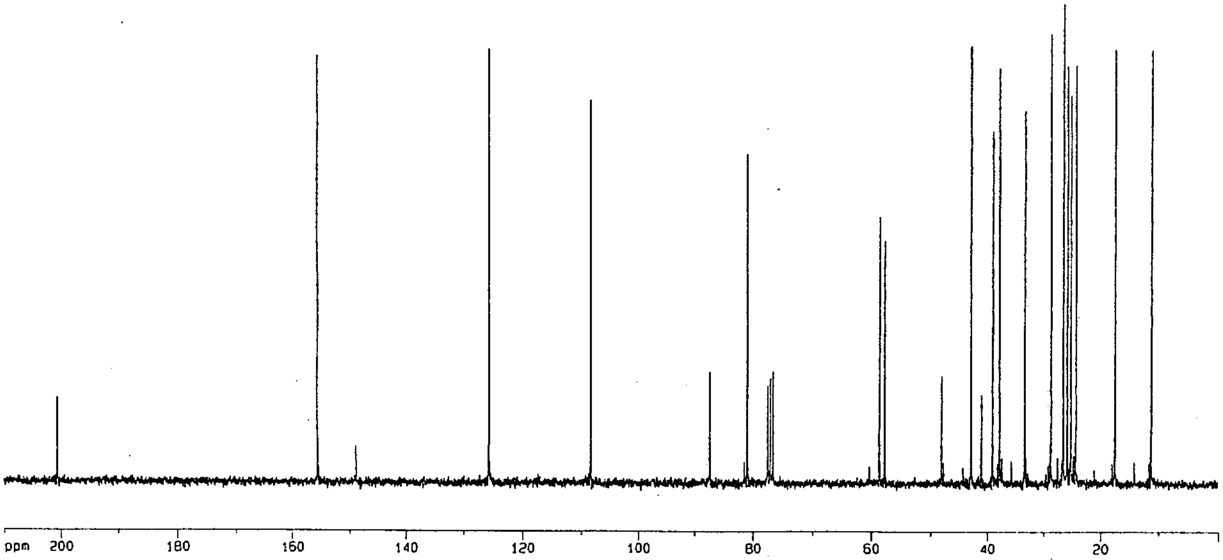




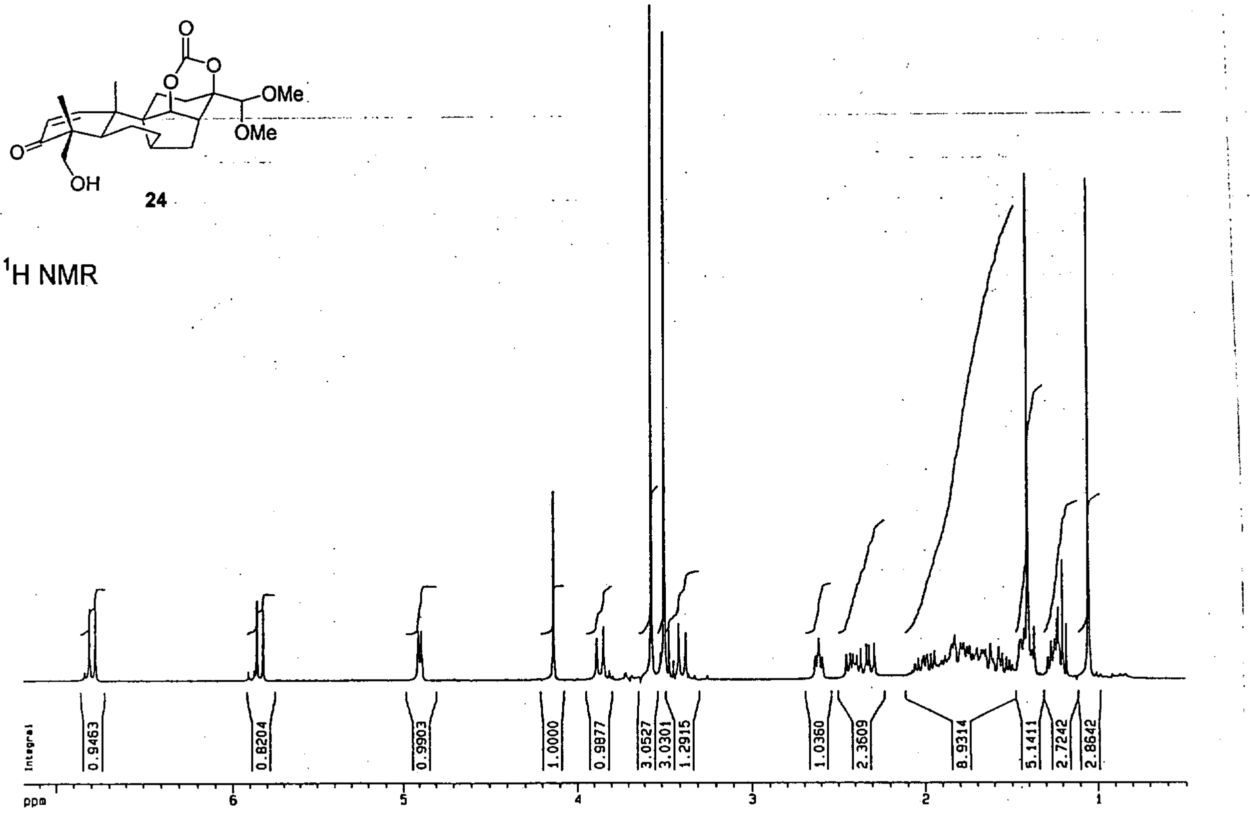
23

^{1}H NMR

^{13}C NMR



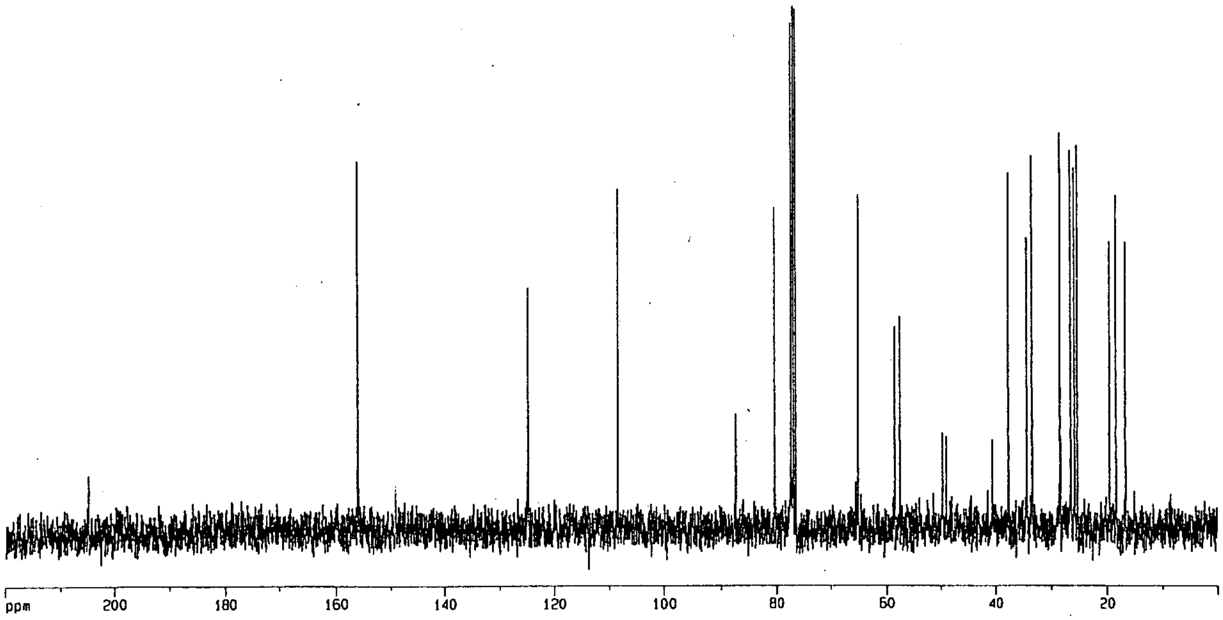
19

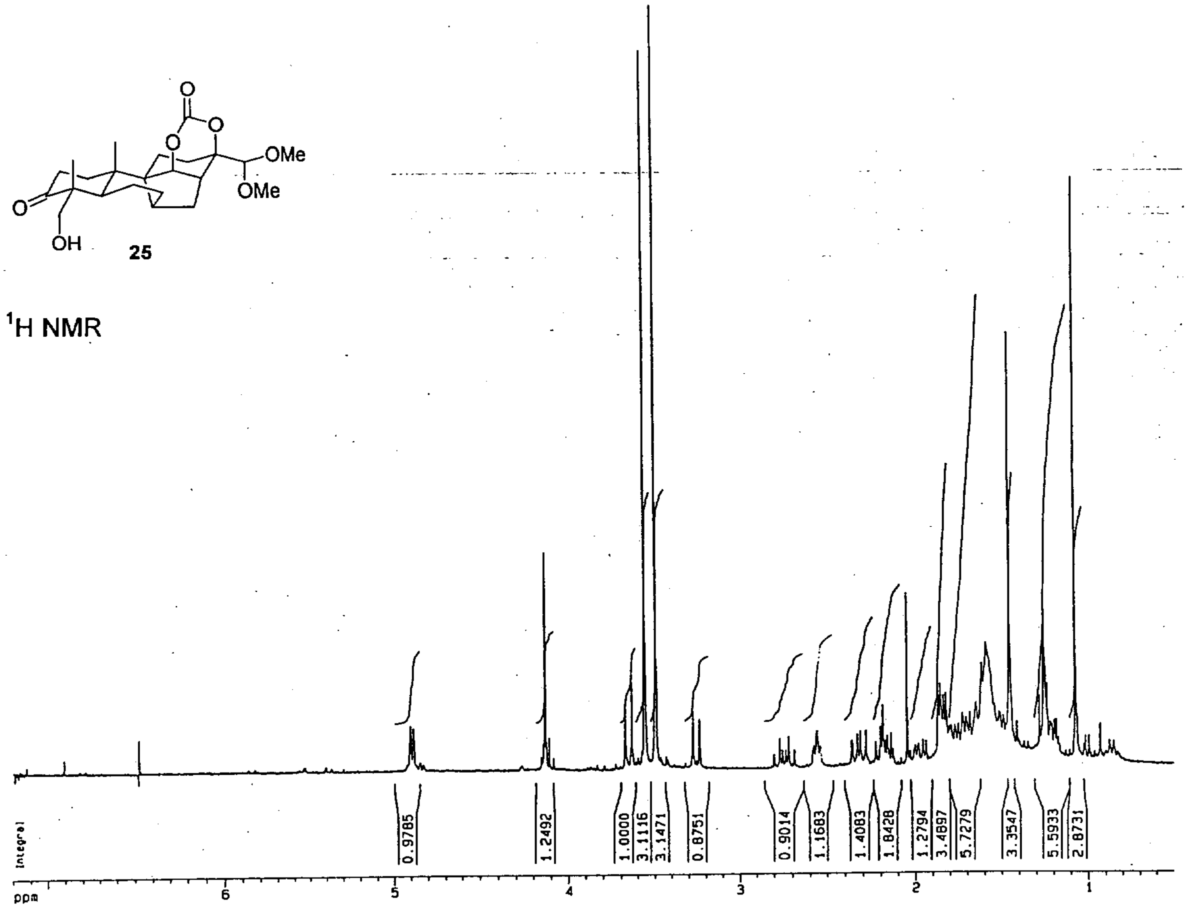


24

^{1}H NMR

^{13}C NMR




O
O
O
OMe
OMe
O
OH
25
¹H NMR
Integral
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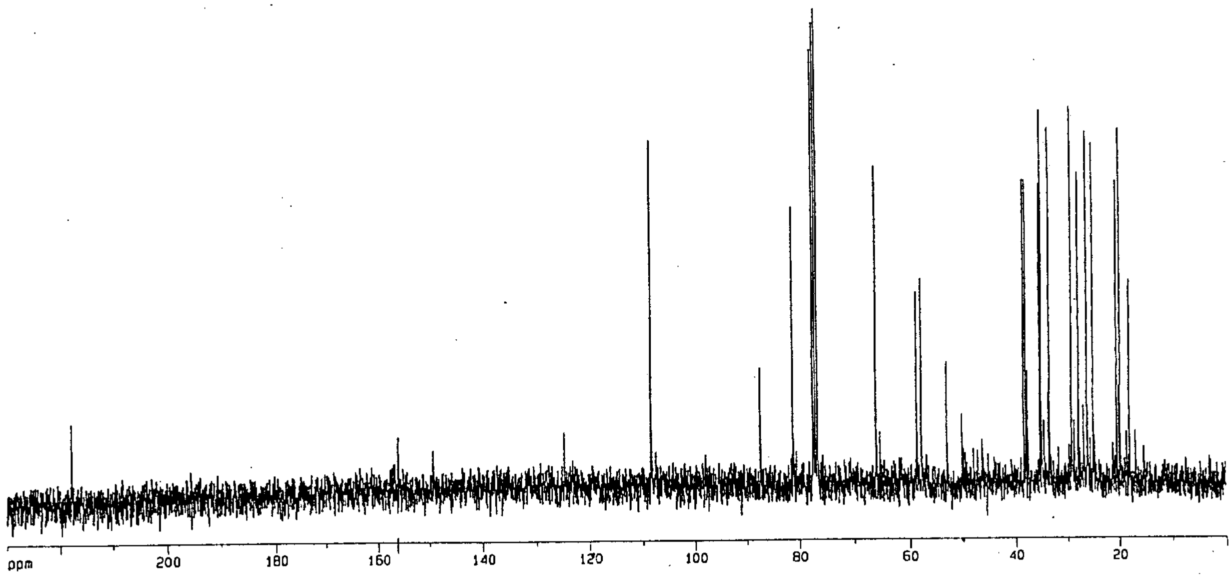
1.0000
3.1116
3.1471
0.8751
0.9014
1.1683
1.4083
1.8428
1.2794
3.4897
5.7279
3.3547
5.5933
2.8731
ppm
6
5
4
3
2
1

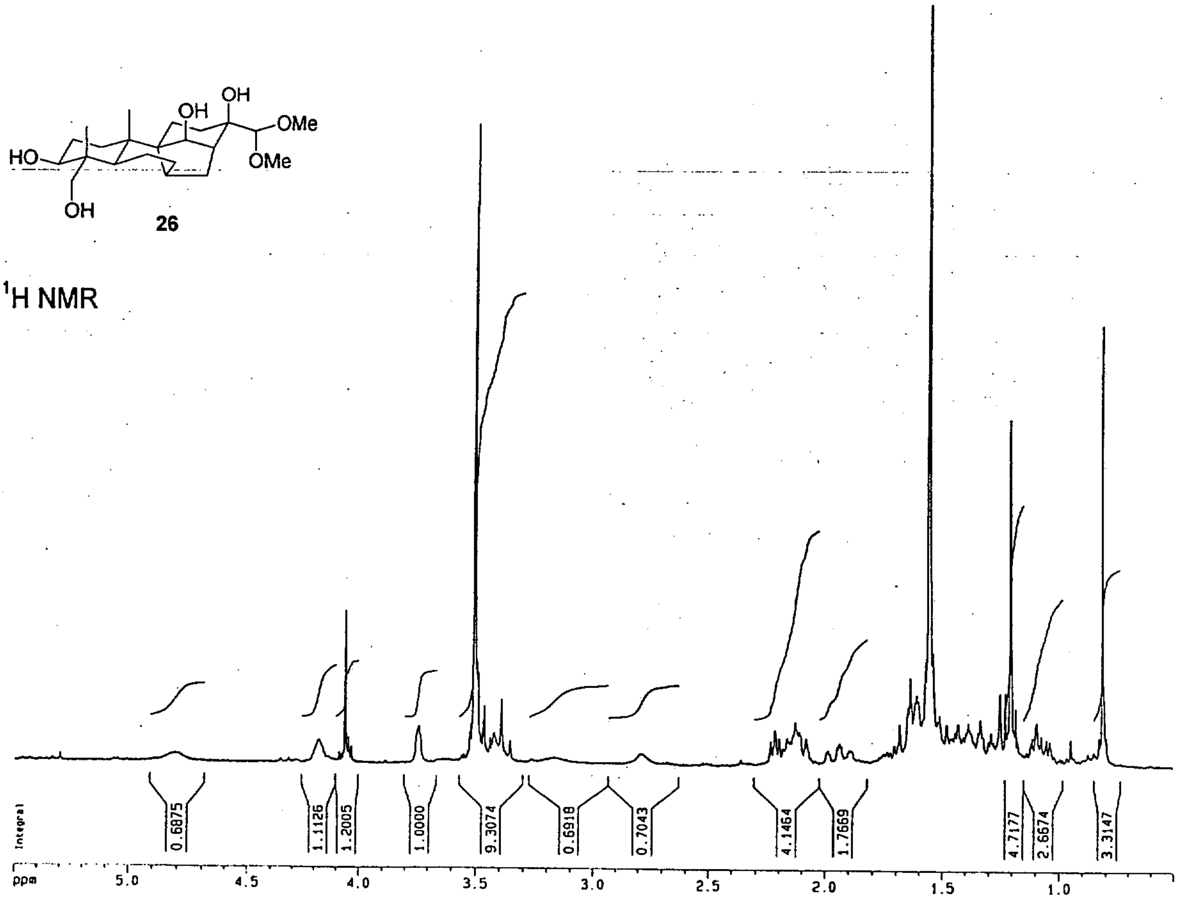
^{13}C NMR


ppm
200
180
160
140
120
100
80
60
40
20

OH
OH
OMe
OMe
HO
OH

26

¹H NMR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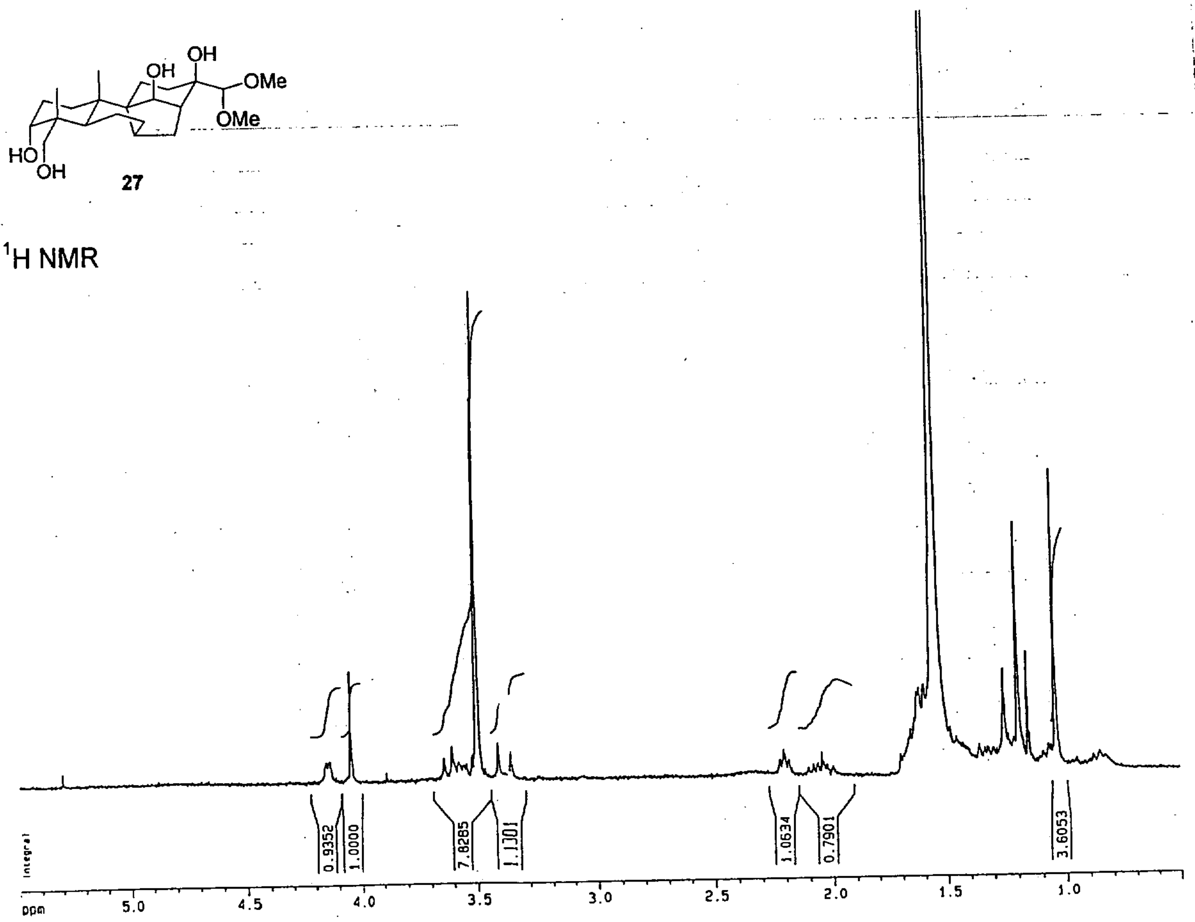
1.2005
1.0000
9.3074
0.6918
0.7043
4.1464
1.7669
4.7177
2.6674
3.1147
Integral
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

OH
OH
OMe
OMe
HO
OH

27

^{1}H NMR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1.0000
7.8285
1.1301
1.0634
0.7901
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Integral
ppm
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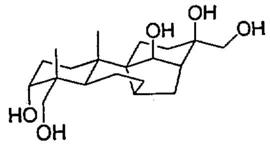
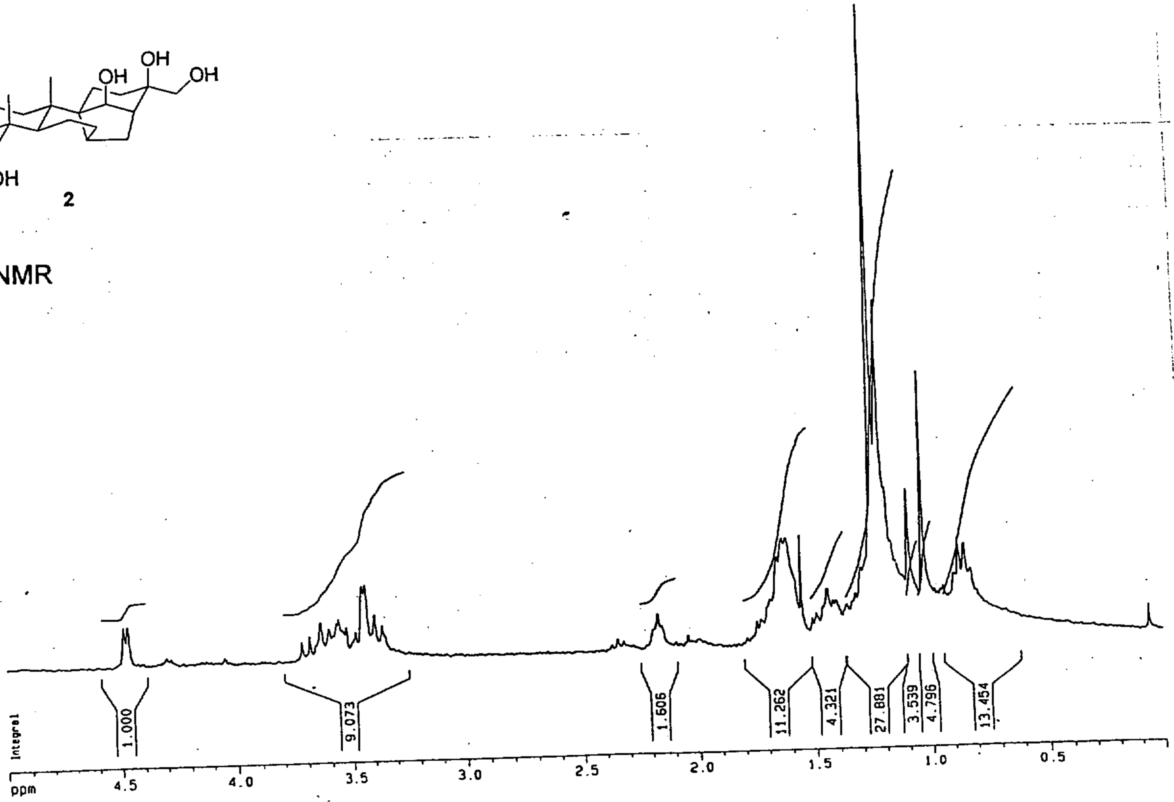
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


OH
OH
OH
HO
OH

2

^{1}H NMR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1.606
11.262
4.321
27.881
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Integral
ppm
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4.0
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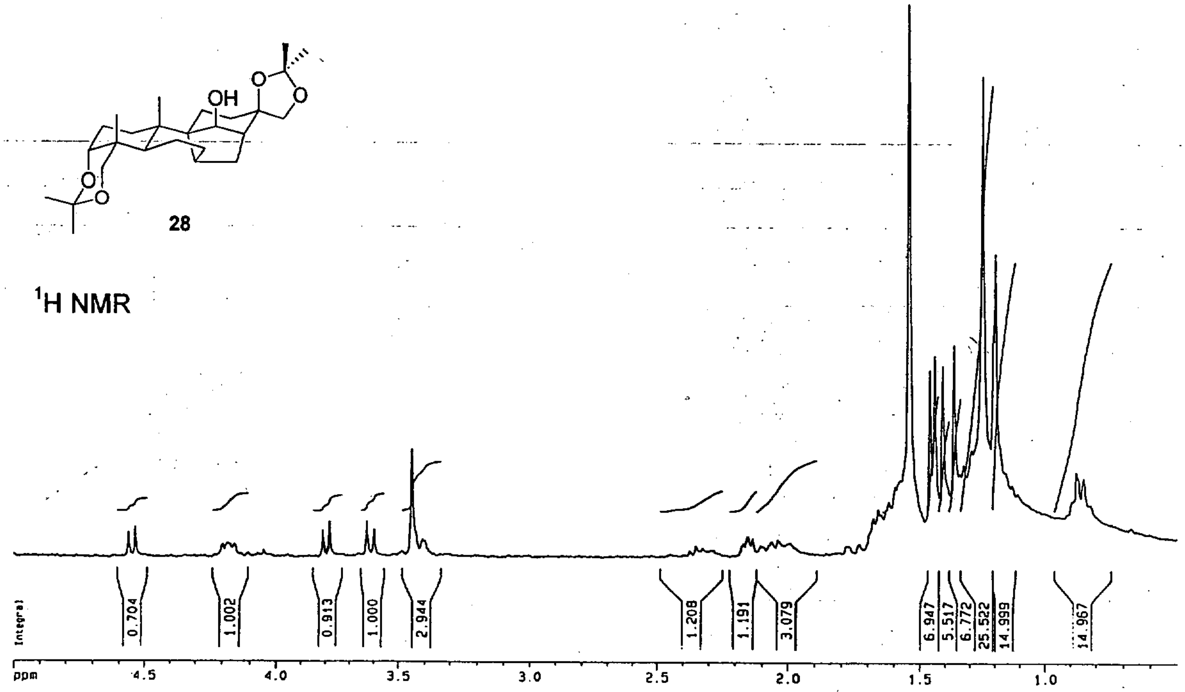
2.5
2.0
1.5
1.0
0.5



28

^{1}H NMR

COSY