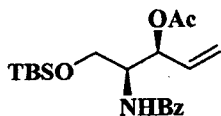


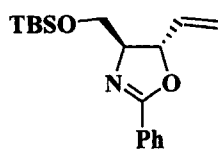
Revised

Supporting Information

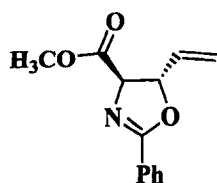


Compound 10 : To a stirred solution of **9** (3.10 g, 10.02 mmol) in 20 mL of CH_2Cl_2 at 0 °C under argon was added Dess-Martin periodinane (6.32g, 15.03mmol), and stirring was allowed to continue for 2 h.. Dilution with Et_2O (100 mL) followed by washing with saturated aqueous NaHCO_3 solution (20 mL \times 2), brine (20 mL \times 2), dried with MgSO_4 , and evaporated in *vacuo*. The crude aldehyde was immediately employed in the next step without further purification. To a stirred solution of crude aldehyde (1.0 mmol) in THF (50 mL) at -78°C , added with a double-tipped needle to a room temperature solution (50.1 mL, 1.0 M, 50.1 mmol) of vinylmagnesium bromide in THF. After being stirred for 1 h, the reaction mixture was washed with saturated aqueous NH_4Cl (20 mL \times 2), brine (20 mL \times 2), dried with Na_2SO_4 , and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/10) gave allyl alcohol (2.52g, 95.7%); To a stirred solution of allyl alcohol (350 mg, 1.04 mmol) in CH_2Cl_2 (4 mL) was added acetic anhydride (0.11 mL, 1.42 mmol), pyridine (0.093 mL, 1.42 mmol), and stirring was allowed to continue for 12 h. The reaction mixture was washed with 1N-HCl (20 mL \times 2), saturated aqueous NaHCO_3 solution (20 mL \times 2), brine (20 mL \times 2), dried with Na_2SO_4 , and evaporated in *vacuo*. Purification by silica gel chromatography (ethyl acetate/hexane = 1/15) gave **3** (389 mg, 99 %); colorless oil; $[\alpha]_D^{24} +8.43$ (c 1.0, CHCl_3); IR (neat) 3322, 2931, 2857, 1745, 1646 cm^{-1} ; ^1H NMR (500 MHz) δ 0.036 - 0.060 (dd, 6H), 0.91 (s, 9H), 1.58 (s, 3H), 3.69 (dd, $J = 3.0$ Hz, 1H), 3.82 (dd, $J = 5.5$ Hz, 1H), 4.39 (m, $J = 5.5, 6.5, 9.5$ Hz, 1H), 5.31 (dd, $J = 11.0$ Hz, 1H), 5.37 (dd, $J =$

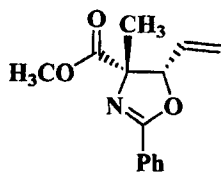
17.5 Hz, 1H), 5.67 (m, $J = 6.5$ Hz, 1H), 5.88 (ddd, $J = 6.5, 11.0, 17.5$ Hz, 1H), 6.49 (d, $J = 9.5$ Hz, 1H), 7.43 - 7.52 (m, 3H), 7.74 - 7.75 (m, 2H); ^{13}C NMR (125MHz) δ -5.35, 18.42, 21.34, 26.03, 53.55, 62.00, 73.86, 119.41, 127.07, 128.93, 131.85, 133.71, 134.61, 167.25, 170.63; HRMS(EI, 70eV) calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_4\text{Si}$ 377.2022 found 377.2027.



Compound 8 : To a stirred solution of **3** (400 mg, 1.06 mmol) and K_2CO_3 (439 mg, 3.178 mmol) in CH_3CN (20 mL) was added (6.12 mg, 0.053 mmol) of $\text{Pd}(\text{PPh}_3)_4$ under N_2 . The resulting mixture was refluxed for 24 h, whereupon it was allowed to cool to room temperature and was filtered through a pad of silica, which was then evaporated under reduced pressure to give crude product. Purification by silica gel chromatography (ethyl acetate/hexane = 1/20) gave **4** (252 mg, 75 %); colorless oil; $[\alpha]_D^{25}$ -3.66 (c 1.0, CHCl_3); IR (neat) 2930, 2857, 1650 cm^{-1} ; ^1H NMR (500 MHz) δ 0.04 - 0.076 (dd, 6H), 0.86 (s, 9H), 3.69 (dd, $J = 7.0$ Hz, 1H), 3.94 (dd, $J = 4.0$ Hz, 1H), 4.06 (ddd, $J = 4.0, 5.5, 7.0$ Hz, 1H), 5.02 (dd, $J = 5.5, 6.5$ Hz, 1H), 5.21 (dt, $J = 1.5, 10.5$ Hz, 1H), 5.36 - 5.40 (dt, $J = 1.5, 17.0$ Hz, 1H), 5.96 (m, $J = 6.5, 10.5, 17.0$ Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ^{13}C NMR (125MHz) δ -5.08, 26.04, 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11; HRMS m/e calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{Si}$ 318.1889 found 318.1880.

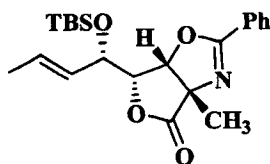


Compound 7 : To a solution of alcohol(617mg, 4.0mmol) in 1M-potassium hydroxide (50ml), potassium persulphate (2.7g, 10mmol) followed by $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (48mg, 0.2mmol) was added with vigorous stirring. The progress of reaction was followed by t.l.c. of acidified aliquots of ether. After 7 hrs, an optimal yield of product was observed. The reaction was acidified to pH 9 with 1N HCl and extracted with ether (50ml). Evaporation of the ether extract after passage through a Celite pad gave corresponding acid, which was treated with diazomethane in ether. Purification by silica gel chromatography (ethyl acetate/hexane = 1/10) gave **7** (252 mg, 75 %).%; colorless oil; $[\alpha]_D^{25} -10.6$ (c 1.0, CHCl_3); IR (neat) 2930, 2857, 1650 cm^{-1} ; ^1H NMR (500 MHz) δ 3.83 (s, 3H), 4.06 (ddd, $J = 4.0, 5.5, 7.0$ Hz, 1H), 5.02 (dd, $J = 5.5, 6.5$ Hz, 1H), 5.21 (dt, $J = 1.5, 10.5$ Hz, 1H), 5.36 - 5.40 (dt, $J = 1.5, 17.0$ Hz, 1H), 5.96 (m, $J = 6.5, 10.5, 17.0$ Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ^{13}C NMR (100MHz) δ 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11, 185.88; HRMS m/e calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$ 231.2521 found 231.2525.



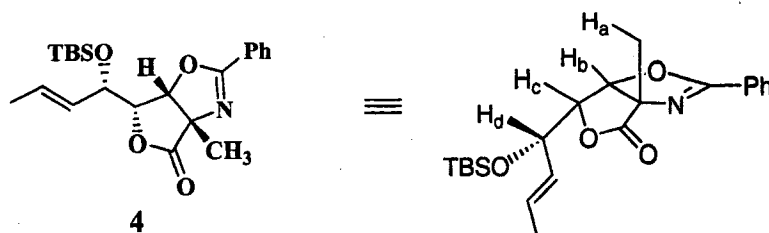
Compound 6 : To a solution of KHMDS (7.0mL, 0.5 M in toluene) and HMPA (3.0mL) in THF (3.0mL) at -78°C was added **7** (1.20g, 3.20 mmol) in THF(10mL) at -78°C via cannula. The resulting deep orange/red solution was stirred for 20 min at -78°C

followed by the addition of methyl iodide (0.45mL, 3.80mmol). After stirring for 3 h, the reaction mixture was poured into ether (15mL) and NH₄Cl (aqueous, 15mL). Following further extraction with EtOAc (3 × 15mL), the combined organics were dried (MgSO₄), filtered, evaporated, and chromatographed (10% EtOAc/hexanes) to give **6** (1.34g, 73). colorless oil; $[\alpha]_D^{25}$ -9.5 (c 1.0, CHCl₃); IR (neat) 2930, 2857, 1650 cm⁻¹; ¹H NMR (500 MHz) δ 1.67 (s, 3H), 3.83 (s, 3H), 4.80 (d, J = 7.0 Hz, 1H), 5.21 (dt, J = 1.5, 10.5 Hz, 1H), 5.36 - 5.40 (dt, J = 1.5, 17.0 Hz, 1H), 5.96 (m, J = 6.5, 10.5, 17.0 Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ¹³C NMR (100MHz) δ 18.1, 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11, 180.885 HRMS m/e calcd for C₁₄H₁₅NO₃ 245.2722 found 247.2725.

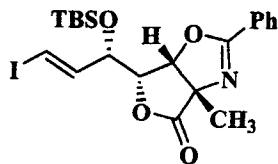


Compound 4 : A slurry of MgBr₂·Et₂O (6.5g, 25.2mmol, 2.0 equiv) in CH₂Cl₂ (24mL) under nitrogen was cooled to -20 °C and a solution of aldehyde (7.2g, 27.8mmol) in CH₂Cl₂ (53mL) was added dropwise via syringe. The reaction mixture was stirred at -20 °C for 30 min. A solution of racemic stannane **6** (31g, 0.65mmol, 1.5 equiv of (S)-enantiomer) in CH₂Cl₂ (3mL) was added dropwise via syringe over a 30 min period at -20 °C and the reaction mixture was allowed to warm to 25 °C over a 3 h period. The reaction mixture was quenched by the addition of saturated aqueous NaHCO₃ (100mL) and was diluted with Et₂O (200mL). The aqueous layer was extracted with Et₂O (3×100mL) and the combined organic extracts were washed with saturated aqueous NaCl (2×150mL), and were dried (MgSO₄) and concentrated in vacuo to give a pale

yellow oil. Purification by flash chromatography (10% EtOAc/hexanes) afforded **4** (10.0g, 78%) as a colorless oil. $[\alpha]_D^{25} + 20.5$ (c 1.0, CHCl_3); IR (neat) 2930, 2857, 1650 cm^{-1} ; ^1H NMR (500 MHz) δ 0.04 - 0.076 (dd, 6H), 0.86 (s, 9H), 1.67 (s, 3H), 1.78 (m, 3H), 4.39 (m, 2H), 4.82 (d, $J = 4.0$ Hz, 1H), 5.64 (dt, $J = 1.5, 15.0$ Hz, 1H), 6.0 (dq, $J = 1.5, 15.0$ Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ^{13}C NMR (125MHz) δ - 5.08, 26.04, 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11, 180.11; HRMS m/e calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_4\text{Si}$ 401.5752 found 401.5751.

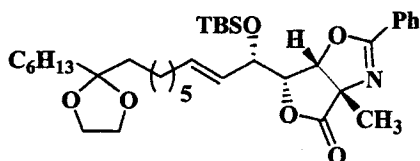


To determine the relative stereochemistry, an NOE study on **4** was conducted. Irradiation of H_b at δ 4.82 (d, $J = 4.0$ Hz) induced an enhancement of the intensity of the H_c and H_d at δ 4.39 (m, 2H) and H_a signal at δ 1.67 (s, 3H) by 18% and 4%, respectively. Based on these observation, the *syn* relationship among carbon-oxygen bonds was reasonably established.



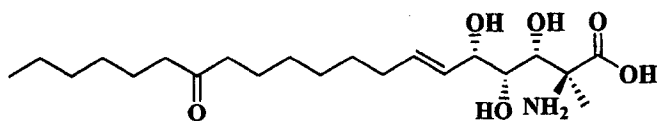
Compound 2 : To a solution of anhydrous NaHCO_3 (1.05g, 2.40mmol) in CH_2Cl_2 (5.0mL) was added Dess-Martin periodinane (1.05g, 2.49mmol) followed by alcohol **11a** (0.374g, 0.829mmol) in CH_2Cl_2 (1mL). After 3 h, the excess periodinane was

quenched by the addition of a saturated aqueous solution of sodium thiosulfate (5.0mL). The mixture was diluted with hexanes (50mL) and washed with saturated aqueous NaHCO_3 (50mL). The organic layer was dried over MgSO_4 , filtered, and concentrated in vacuo. The crude aldehyde was used without further purification. To suspension of flame dried CrCl_2 (611mg, 4.97mmol) in THF (11.1mL) was added a solution of aldehyde and CHI_3 (653mg, 1.66mmol) in THF (22.2mL). After 30 min, the reaction mixture was poured into brine (300mL), and the mixture was extracted with Et_2O (4×100mL). The combined organic layers were washed with brine (200mL), dried over MgSO_4 , filtered, and concentrated in vacuo. Purification of the residue via flash chromatography (24g of SiO_2 , 4% EtOAc /hexanes) afforded 367mg (63%) of **2** as a clear, yellow oil. $[\alpha]_D^{25} + 20.5$ (c 1.0, CHCl_3); IR (neat) 2930, 2857, 1650 cm^{-1} ; ^1H NMR (500 MHz) δ 0.04 - 0.076 (dd, 6H), 0.86 (s, 9H), 1.67 (s, 3H), 4.39 (m, 2H), 4.82 (d, $J = 4.0$ Hz, 1H), 5.64 (dt, $J = 1.5, 15.0$ Hz, 1H), 6.0 (dq, $J = 1.5, 15.0$ Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ^{13}C NMR (125MHz) δ -5.08, 26.04, 64.95, 74.33, 83.31, 116.62, 128.02, 128.54, 131.59, 137.00, 164.11, 180.11; HRMS m/e calcd for $\text{C}_{21}\text{H}_{28}\text{INO}_4\text{Si}$ 513.4425 found 513.4421.



Compound 11 : tert-Butyllithium (5.00mL of a 1.7 M solution in pentane, 8.50mmol) was added dropwise to THF(10mL) at -78°C . Iodide **3** (1.31g, 3.86mmol) in THF (10mL) was added dropwise to the tert-butyllithium solution, allowing the drops to run down the inside of the flask to cool. After the solution of lithium reagent had stirred for

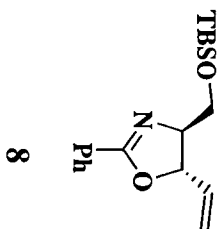
15 min, a freshly prepared solution of fused ZnCl_2 in THF (6.43mL of a 1.0 M solution, 6.43mmol) was added dropwise, and the reaction was allowed to warm to room temperature over 30 min. The zinc reagent was added to a mixture of vinyl iodide **2** (1.57g, 2.57mmol) and $(\text{Ph}_3\text{P})_2\text{Pd}$ (0.148g, 0.129mmol) which had been evacuated and backfilled with argon 3 times. After 3 h, the reaction mixture was diluted with Et_2O (75mL) and washed with saturated aqueous NH_4Cl (75mL). The Et_2O layer was dried over MgSO_4 , filtered, and concentrated in vacuo. Flash chromatography of the residue (140g of SiO_2 , 2% EtOAc /hexanes) provided 1.50 g (80%) of **11** as a clear, yellow oil. $[\alpha]_D^{25} + 16.8$ (c 1.0, CHCl_3); IR (neat) 2930, 2857, 1650 cm^{-1} ; ^1H NMR (500 MHz) δ 0.04 - 0.076 (dd, 6H), 0.86 (s, 9H), 0.87 (t, $J = 6.5$ Hz), 1.27-1.47 (m, 16H), 1.54-1.62 (m, 4H), 1.67 (s, 3H), 4.39 (m, 2H), 4.82 (d, $J = 4.0$ Hz, 1H), 5.64 (dt, $J = 1.5, 15.0$ Hz, 1H), 6.0 (dq, $J = 1.5, 15.0$ Hz, 1H), 7.39 - 7.48 (m, 3H), 7.95 - 7.97 (m, 2H); ^{13}C NMR (125MHz) δ -5.08, 13.0, 20.3, 20.5, 23.7, 26.04, 28.9, 29.1, 29.5, 29.6, 30.2, 31.5, 32.4, 37.1, 55.0, 64.9, 74.3, 83.3, 116.6, 128.0, 128.5, 131.5, 137.0, 164.1, 175.3.



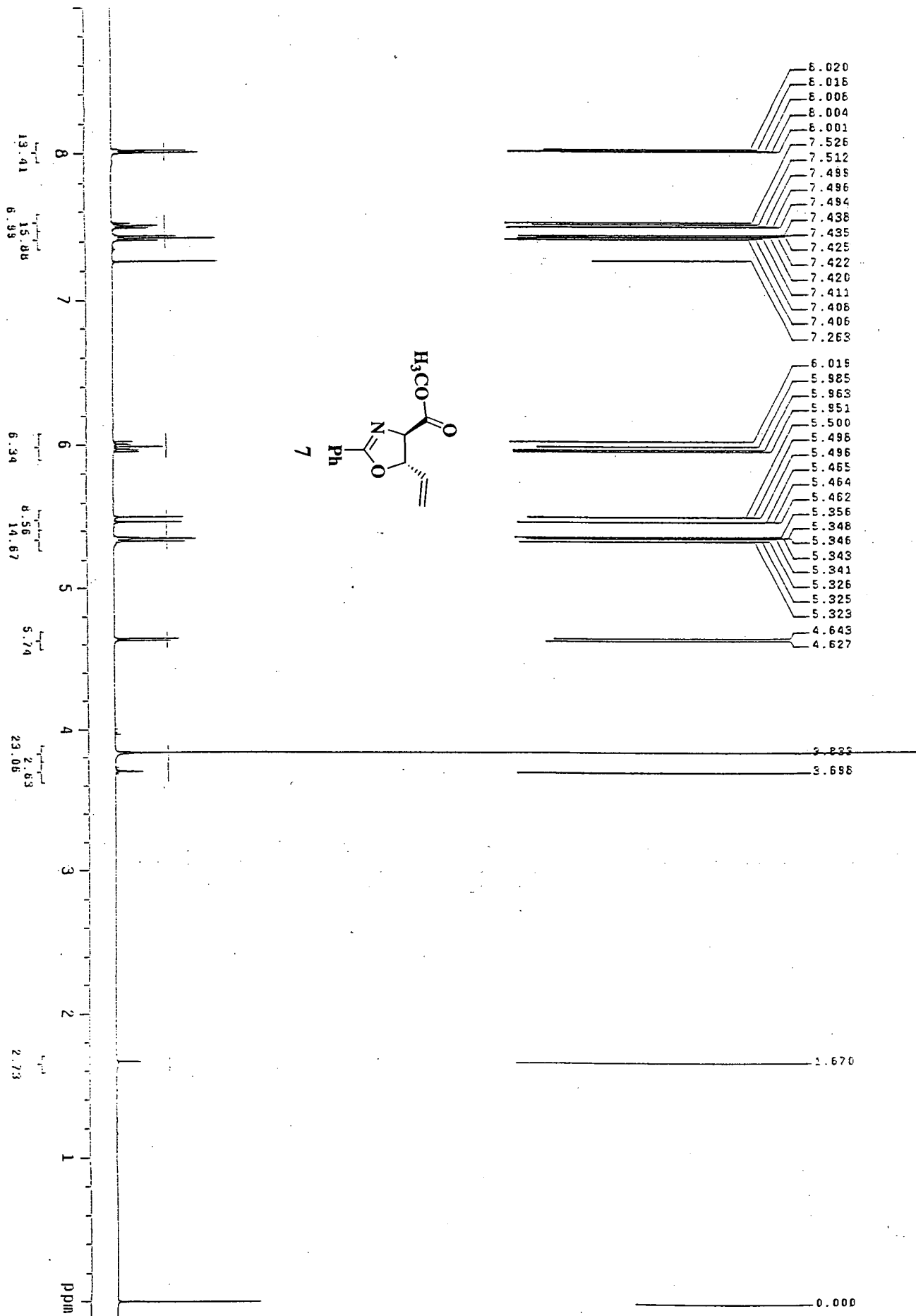
Compound 1 : To a solution of **11** (12 mg, 0.02mmol) in THF-2N-HCl (2mL, 1:1) was added at room temperature. The mixture was stirred for 24h and solution of saturated sodium bicarbonate (4mL) was added. The reaction mixture became turbid and was stirred for 12h. Extraction with ethyl acetate (5mL \times 3), drying over anhydrous magnesium sulfate, evaporation in vacuo and a column chromatography (petroleum

ether:ethyl acetate = 3:1) yielded 8.2 mg of the benzamidolactone as a clear sticky oil. The mixture of the benzamidolactone and 1N NaOH(1mL) was heated under reflux for 8h. The reaction mixture was cooled to room temperature, and Amberlite IRC-76 resin (pre-treated and washed with 2N HCl and deionized water) was added until the pH of the solution reached approximately 7. The resin was filtered off and the filtrate was concentrated in vacuo to give a white solid. The white solid was dissolved in a minimal amount of methanol-water and chromatographed on a silica gel column (SiO₂, 2.5g; CHCl₃-CH₃OH-H₂O = 20:5:1) to yield 7.2 mg of pure sphingofungin F(1) as a white solid (79%).

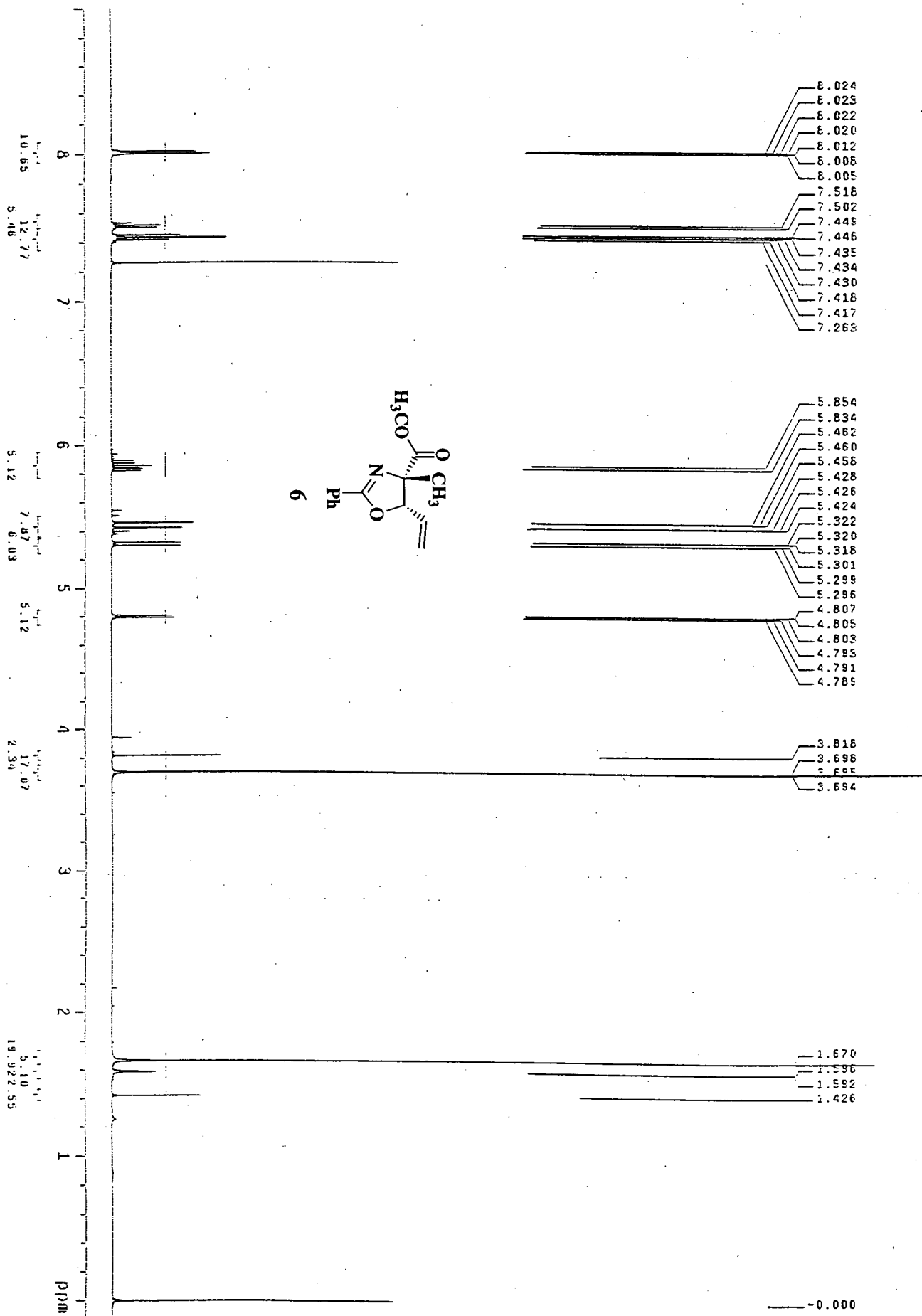
Mp 143~145° (CH₃OH-H₂O) [α]_D +0.80 (c 0.25, CH₃OH) IR(KBr): 3423, 1718, 1629, 1459, 1408, 1113, 790 cm⁻¹. ¹H NMR (400MHz, CD₃OD): δ 5.77 (dt, J = 15.4 6.8Hz, 1H), 5.45 (dd, J = 15.5, 7.8Hz, 1H), 4.10 (t, J = 7.5Hz, 1H), 3.86 (d, J = 0.7Hz, 1H), 3.67 (d, J = 7.3Hz, 1H), 2.44 (t, J = 7.3Hz, 2H), 2.44 (t, J = 7.5Hz, 2H), 2.06 (q, J = 6.8Hz, 2H), 1.57~1.50 (m, 4H), 1.48 (s, 3H), 1.42~1.38 (m, 2H), 1.36~1.23 (m, 10H), 0.90 (t, J = 7.0Hz, 3H). ¹³C NMR (100MHz, CD₃OD): δ 214.4, 175.2, 135.7, 130.2, 76.2, 75.7, 72.4, 66.7, 43.5(2), 33.5(2), 32.8, 30.2(2), 30.0(2), 24.9(2), 23.6, 21.8, 14.4. HRMS (M+Na⁺) 423.3247 Calcd for C₂₁H₃₉NNaO₆ Found: 423.3239.



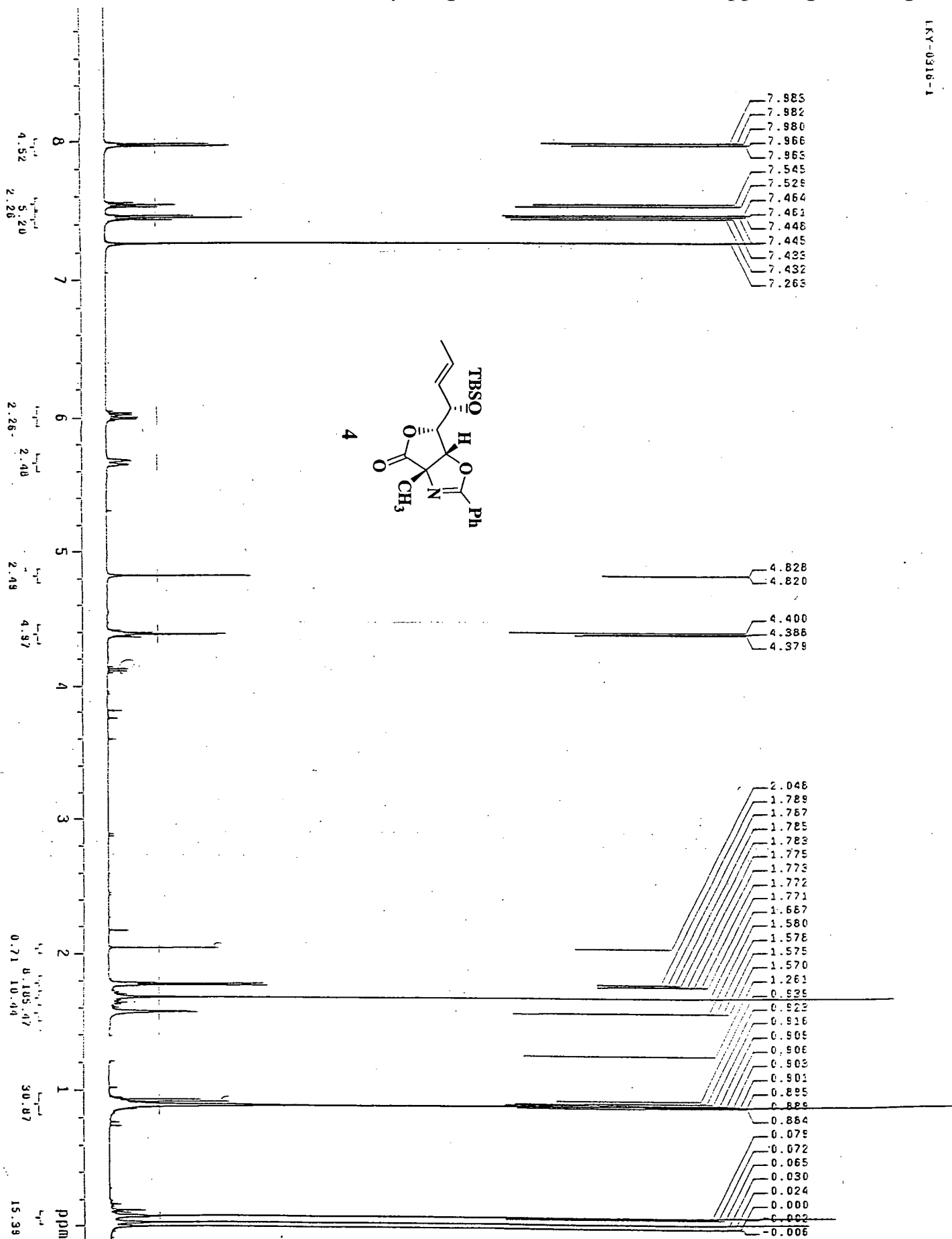
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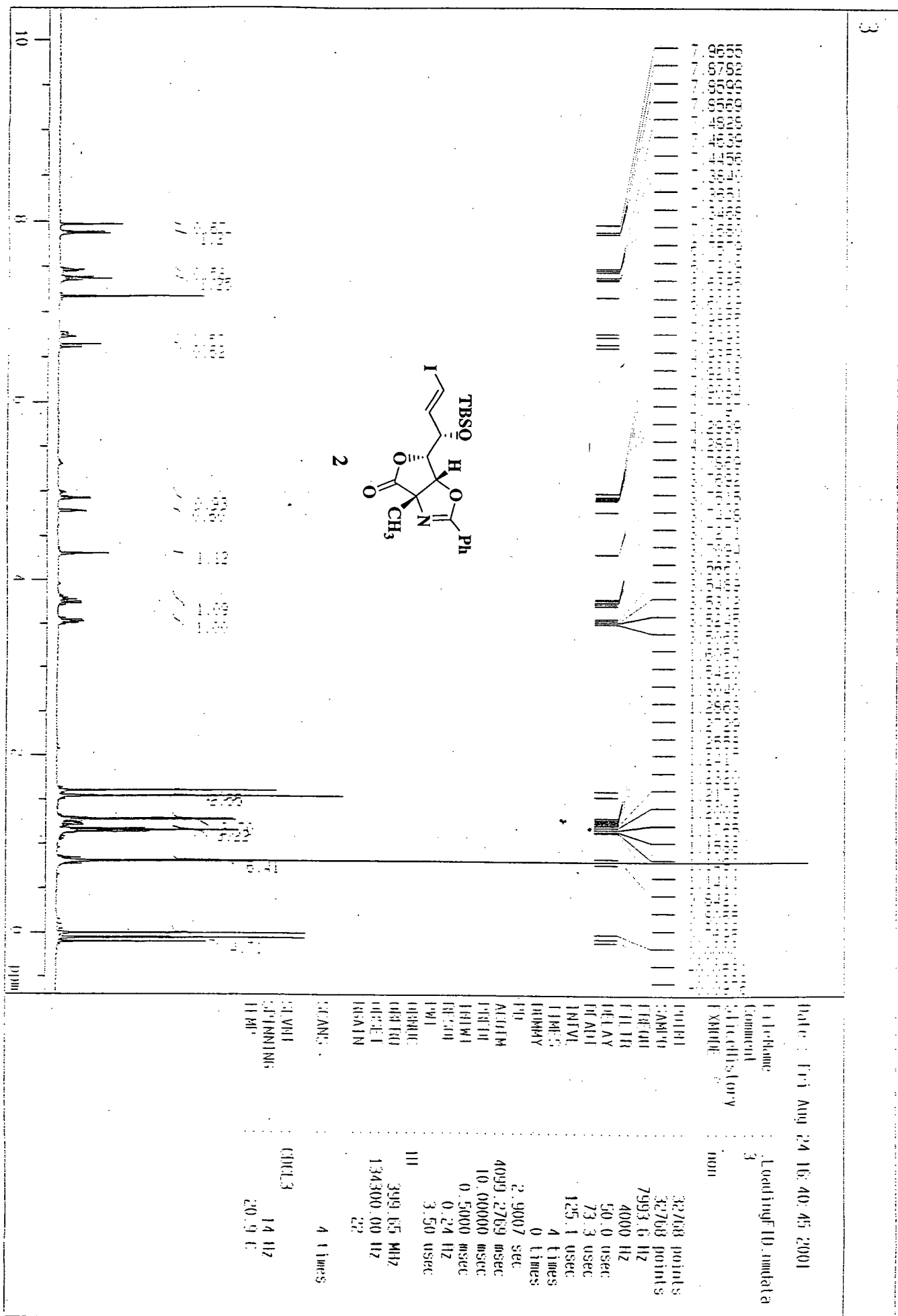


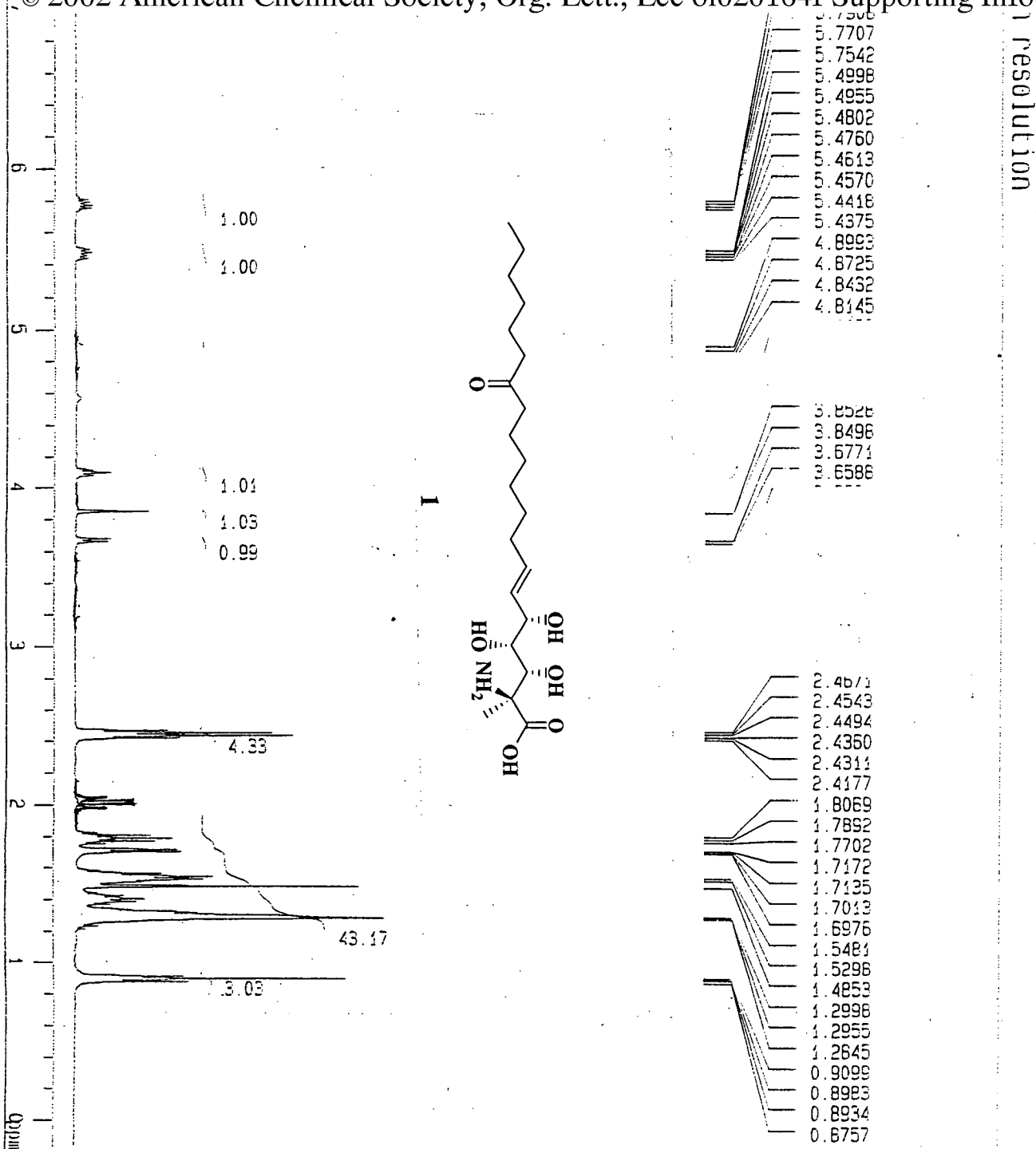
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LKY-0316-1







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מדינת ישראל : משרד המשפטים