Stereospecific Construction of β-Isopropenyl Alcohol Moiety at the C(2) and (3) of Kallolide A and Pinnatin A Using [2,3] Wittig Rearrangement of Cyclic Furfuryl Ethers

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Supporting Information

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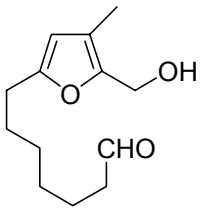
General Information. All reactions were performed under argon atmosphere unless otherwise indicated. Analytical thin-layer chromatography was performed on glass plates bearing 0.25 mm layer of silica gel 60 F_{254}. All chromatographic purifications were performed on silica gel 60 (230-400 mesh) using the indicating solvent systems. IR spectra were obtained on a FT/IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz or 500 and 125 MHz, respectively. Chemical shifts are reported on the δ scale from internal TMS. Mass spectra were measured with a mass spectrometer. Optical rotations were taken with a polarimeter. HPLC was taken with a UV detector, pump, column oven and integrator.

Materials. Commercial grade reagents were used as received except as indicated below. Bromofuran was prepared according to the literature procedure. Chiral bis(oxazoline)s **11** and **13** were prepared according to the literature procedure.[1] Other chiral bis(oxazoline)s **12** and **14** were purchased and used without further purification.

Methyl 5-(6'-cyanohexyl)-3-methyl-2-furoate 2

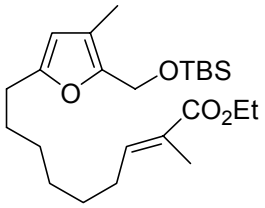
To a solution of bromofuran **1**[2] (9.12 g, 41.6 mmol) and $Pd(Ph_3P)_4$ (2.40 g, 2.08 mmol) in THF (94.6 mL) was added 6-cyanohexylzinc bromide (0.5 M in THF, 100 mL, 50.0 mmol) at room temperature. After stirring for 1 hr, the reaction mixture was quenched with sat. NH_4Cl aq., the precipitate was filtered and the filtrate was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (8:2, v/v) as eluent to give compound **2** (8.7 g, 84%) as a yellow oil. IR ν max 1712 and 2245 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 1.24-1.54 (4H, m, 2×CH_2), 1.60-1.74 (4H, m, 2×CH_2), 2.31 (3H, s, 3-CCH_3), 2.34 (2H, t, *J*=6.9 Hz, 6'-CH_2), 2.64 (2H, t, *J*=7.4 Hz, 1'-CH_2), 3.87 (3H, s, OCH_3), 6.00 (1H, s, 4-H); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 11.6, 17.0, 25.1, 27.3, 27.9, 28.1, 28.2, 51.3, 111.1, 119.6, 132.5, 138.5, 159.2, 159.9; MS (EI): 249 (M^+); HRMS (EI): calcd for $C_{14}H_{19}NO_3$: 249.1365. Found; 249.1363.



5-(6'-Formylhexyl)-2-hydroxymethyl-3-methylfuran 3

To a solution of compound **2** (1.07 g, 4.3 mmol) in CH_2Cl_2 (20 mL) was added dropwise DIBAL (0.93 M in hexane, 18.9 mL, 17.6 mmol) at -78 °C. After stirring for 1 hr at the same temperature, the reaction mixture was quenched with sat. potassium sodium tartrate aq. and stirred for 2 hr at room temperature. The precipitate was filtered

and extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using CH_2Cl_2-EtOAc (7:3, v/v) as eluent to give compound **3** (767.6 mg, 80%) as a colorless oil. IR ν max 1720 and 3400 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 1.32-1.42 (4H, m, 2×CH_2), 1.56-1.74 (4H, m, 2×CH_2), 1.56-1.74 (1H, br s, OH), 2.00 (3H, s, 3-CH_3), 2.42 (2H, dt, *J*=1.8 and 5.6 Hz, 6'-CH_2), 2.55 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.53 (2H, s, CH_2OH), 5.81 (1H, s, 4-H), 9.76 (1H, t, *J*=1.8 Hz, CHO); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 9.8, 21.9, 27.7, 27.8, 28.8(2), 43.8, 55.3, 108.3, 118.3, 147.4, 155.4, 202.9; MS (EI): 224 (M^+); HRMS (EI): calcd for $C_{13}H_{20}O_3$: 224.1412. Found; 224.1382.

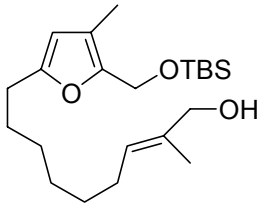


2-*tert*-Butyldimethylsiloxymethyl-5-[(7'*E*)-8'-ethoxycarbonyl-7'-nonenyl]-3-methyl-furan (*E*)-**4**

To a solution of compound **3** (657.3 mg, 2.9 mmol) in CH_3CN (12 mL) was added $Ph_3PCH(CH_3)CO_2Et$ (1.05 g, 2.9 mmol) at 0 °C. After stirring for 13 hr at room temperature, the solvent was removed under vacuum. The precipitate was dissolved Et_2O-pentane (1:1) and filtered. Evaporation of the filtrate gave an oil (803 mg). For the analysis a small amount of the crude product was purified by silica gel chromatography using hexane-EtOAc (93:7, v/v) as eluent to give 5-[(7'*E*)-8'-ethoxycarbonyl-7'-nonenyl]-2-hydroxymethyl-3-methylfuran as a colorless oil. IR ν max 1710 and 3440 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 1.29 (3H, t, *J*=7.3 Hz, $CO_2CH_2CH_3$), 1.33-1.49 (6H, m, 3×CH_2), 1.61 (2H, quintet, *J*=7.3 Hz, 2'-CH_2), 1.82 (3H, d, *J*=1.5 Hz, 9'-CH_3), 2.00 (3H, s, 3-CH_3), 2.16 (2H, q, *J*=7.4 Hz, 6'-CH_2), 2.55 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.18 (2H, q, J=7.3 Hz, OCH_2CH_3), 4.52 (2H, s, CH_2OH), 5.81 (1H, s, 4-CH), 6.80 (1H, tq, *J*=1.5 and 7.4 Hz, 7'-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 9.7, 12.2, 14.2, 27.7, 27.9, 28.3, 28.5, 28.9, 29.0, 55.1, 60.3, 108.2, 118.1, 127.6, 142.2, 147.3, 155.4, 168.3; MS (CI): 308 (M+1); HRMS (CI): calcd for $C_{18}H_{27}O_4$+H : 308.1987. Found; 308.2004. The crude product was used for the next reaction due to its instability.

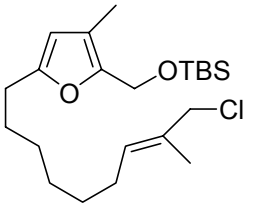
To a solution of the above product in CH_2Cl_2 (25 mL) were added γ-collidine (1.2 mL, 9.1 mmol) and TBSOTf (0.99 mL, 4.3 mmol) at -78 °C. After stirring for 1 hr at same temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. and allowed to warm to room temperature and then extracted with Et_2O-pentane (1:1). The extract was washed with brine, sat. $NaHSO_3$ aq. and brine, dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (92.5:7.5, v/v) as eluent to give compound (*E*)-**4** (1.015 g, 82% in two steps) as a colorless oil. IR ν max 1070 and 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.04 (6H, s, 2×$SiCH_3$), 0.87 (9H, s, $C(CH_3)_3$), 1.28 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 1.24-1.48 (6H, m, 3×CH_2), 1.59 (2H, quintet, *J*=7.3 Hz, 2'-CH_2), 1.80 (3H, d, *J*=1.3 Hz,

9'-CH_3), 1.96 (3H, s, 3-CCH_3), 2.14 (2H, q, *J*=6.9 Hz, 6'-CH_2), 2.52 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.17 (2H, q, *J*=7.1 Hz, OCH_2CH_3), 4.54 (2H, s, CH_2OTBS), 5.75 (1H, s, 4-H), 6.73 (1H, tq, *J*=1.3 and 6.1 Hz, 7'-H); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 12.3, 14.2, 18.4, 25.9 (3), 27.9 (2), 28.4, 28.6, 28.9, 29.1, 56.0, 60.3, 108.1, 117.5, 127.7, 142.2, 147.3, 154.9, 168.2 ; MS (EI): 422 (M^+); HRMS (EI): calcd for $C_{24}H_{42}O_4Si$: 422.2852. Found; 422.2824.



2-*tert*-Butyldimethylsiloxymethyl-5-[(7'*E*)-9'-hydroxy-8'-methyl-7'-nonenyl]-3-methylfuran (*E*)-**5**

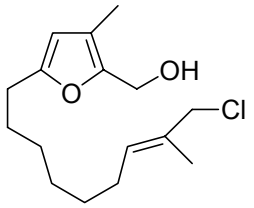
To a solution of compound (*E*)-**4** (1.45 g, 3.4 mmol) in CH_2Cl_2 (13 mL) was added dropwise DIBAL (0.95 M in hexane, 7.95 mL, 7.6 mmol) at -78 °C. After stirring for 1 hr, the reaction mixture was quenched with sat. potassium sodium tartrate aq. and stirred for 2 hr at room temperature. The precipitate was filtered and extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (9:1, v/v) as eluent to give compound (*E*)-**5** (1.15 g, 89%) as a colorless oil. IR ν max 3340 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.05 (6H, s, 2×$SiCH_3$), 0.88 (9H, s, $C(CH_3)_3$), 1.31 (6H, br s, 3×CH_2), 1.31 (1H, br s, OH), 1.59 (2H, quintet, *J*=7.3 Hz, 2'-CH_2), 1.65 (3H, s, 8'-CCH_3), 1.96 (3H, s, 3-CCH_3), 2.00 (2H, q, *J*=6.9 Hz, 6'-CH_2), 2.50 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.00 (2H, s, 9'-CH_2), 4.50 (2H, s, CH_2OTBS), 5.40 (1H, t, *J*=6.9 Hz, 7'-H), 5.80 (1H, s, 4-H); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 13.6, 18.5, 25.9 (3), 27.5, 28.0 (2), 29.0 (2), 29.4, 56.0, 69.0, 108.1, 117.5, 126.5, 134.6, 147.3, 155.1; MS (EI): 380 (M^+); HRMS (EI): calcd for $C_{22}H_{40}O_3Si$: 380.2747. Found; 380.2727.



2-*tert*-Butyldimethylsiloxymethyl-5-[(7'*E*)-9'-chloro-8'-methyl-7'-nonenyl]-3-methyl furan (*E*)-**6**

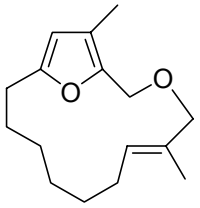
To a suspension of compound (*E*)-**5** (1.01 g, 2.65 mmol), LiCl (280.3 mg, 6.67 mmol), and 2,6-lutidine (0.84 mL, 7.22 mol) in DMF (20 mL) was added dropwise MsCl (0.53 mL, 6.84 mmol) at -5 °C. After stirring for 2 hr at the same temperature, the reaction mixture was quenched with water and extracted with Et_2O-pentane (1:1). The extract was washed with brine, brine/water (1:1), and brine, and then dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography

using hexane-EtOAc (95:5, v/v) as eluent to give compound (*E*)-**6** (990.4 mg, 93%) as a colorless oil. IR ν max 1065 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.05 (3H, s, $SiCH_3$), 0.06 (3H, s, $SiCH_3$), 0.89 (9H, s, $C(CH_3)_3$), 1.25-1.40 (6H, m, 3×CH_2), 1.60 (2H, quintet, *J*=7.1 Hz, 2'-CH_2), 1.72 (3H, s, 8'-CCH_3), 1.97 (3H, s, 3-CCH_3), 2.02 (2H, q, *J*=6.8 Hz, 6'-CH_2), 2.54 (2H, t, *J*=7.1 Hz, 1'-CH_2),4.01 (2H, s, 9'-CH_2), 4.55 (2H, s, CH_2OTBS), 5.52 (1H, t, *J*=6.8 Hz, 7'-H), 5.77 (1H, s, 4-H) ; ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 14.1, 18.4, 25.9 (3), 27.9 (3), 28.9 (2), 29.0, 52.6, 56.0, 108.1, 117.5, 131.1, 131.5, 147.3, 155.0 ; MS (EI): 398 (M+); HRMS (EI) calcd for $C_{22}H_{40}ClO_2Si$+H : 399.2486. Found; 399.2467.



5-[(7'*E*)-9'-Chloro-8'-methyl-7'-nonenyl]-2-hydroxymethyl-3-methylfuran (*E*)-**7**

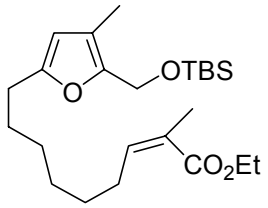
To a solution of compound (*E*)-**6** (396.5 mg, 0.99 mmol) in THF (4 mL) was added TBAF (1 M in THF, 1.15 mL, 1.09 mmol) at 0 °C. After stirring for 3 hr at room temperature, the reaction mixture was quenched with brine and extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (8:2, v/v) as eluent to give compound (*E*)-**7** (277.9 mg, 98%) as a colorless oil. IR ν max 3350 cm^{-1}; ^{1}H-NMR ($CDCl_3$; $CDCl_3$; $CDCl_3$; 270 MHz) δ 1.28-1.42 (6H, m, 3×CH_2), 1.61 (2H, quintet, *J*=7.6 Hz, 2'-CH_2), 1.72 (3H, s, 8'-CCH_3), 1.99 (3H, s, 3-CCH_3), 2.03 (2H, q, *J*=6.9 Hz, 6'-CH_2), 2.54 (2H, t, *J*=7.6 Hz, 1'-CH_2), 4.02 (2H, s, 9'-CH_2), 4.51(2H, s, CH_2OH), 5.52 (1H, t, *J*=7.3 Hz, 7'-H), 5.81 (1H, s, 4-H); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 9.7, 14.0, 27.8, 27.9 (2), 28.8, 28.9, 29.0, 52.5, 55.2, 108.2, 118.2, 131.0, 131.5, 147.3, 155.5 ; MS (EI): 284 (M^+); HRMS (EI): calcd for $C_{16}H_{25}ClO_2$: 284.1543. Found; 284.1546.



(5*E*)-5,15-Dimethyl-3,16-dioxabicyclo[11.2.1]hexadeca-1(15),5,13-triene *(E)*-**8**

To a solution of 18-crown-6 (1.65 g, 6.43mmol), 60% NaH (250 mg, 6.25 mmol) in benzene (93 mL) was added dropwise a solution of compound (*E*)-**7** (252.5 mg, 0.89 mmol) in benzene (40 mL) over 4 hr at reflux. After stirring for 30 min at the same temperature, the reaction mixture was quenched with sat. NH_4Cl aq. and the precipitate was filtered, extracted with Et_2O-pentane (1:1). The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica

gel chromatography using hexane-Et_2O (98:2, v/v) as eluent to give compound (*E*)-**8** (202.7 mg, 92%) as a colorless oil. IR ν max 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 1.22-1.27 (4H, m, 2×CH_2), 1.37-1.44 (2H, m, CH_2), 1.47 (3H, br s, 5-CCH_3), 1.58-1.65 (2H, m, 11-CH_2), 1.97 (2H, q, *J*=5.8 Hz, 7-CH_2), 2.01 (3H, s, 15-CCH_3), 2.58 (2H, t, *J*=6.1 Hz, 12-CH_2), 3.91 (2H, br s, 4-CH_2), 4.44 (2H, s, 2-CH_2), 5.24 (1H, dt, *J*=1.5 Hz, 7.0 Hz, 6-H), 5.78 (1H, s, 14-H); ^{13}C-NMR ($CDCl_3$; 125 MHz) δ 9.9, 13.6, 26.4, 26.7, 26.8, 27.0, 27.1, 27.2, 63.4, 75.8, 108.7, 119.5, 125.8, 132.7, 145.7, 155.0; MS (EI): 248 (M^+); HRMS (EI): calcd for $C_{16}H_{24}O_2$: 248.1776. Found; 248.1774.

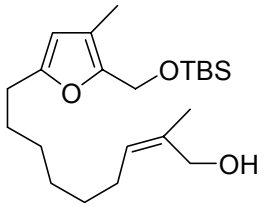


5-[(7'*Z*)-8'-Ethoxycarbonyl-7'-nonenyl]-2-*tert*-butyldimethylsiloxymethyl-3-methyl-furan (*Z*)-**4**

To a solution of $(PhO)_2P(O)CH(CH_3)CO_2Et$[3] (4.78 g, 0.01 mmol) in THF (68 mL) was added 60% NaH (690 mg, 0.03 mmol) at 0 °C and stirred 15 min at the same temperature. The mixture was added dropwise to a solution of compound **3** (2.91 g, 0.01 mmol) in THF (12 mL) at -78 °C and stirring was continued for 1 hr at the same temperature. The reaction mixture was allowed to warm to 0 °C over 1 hr and quenched with sat. aq. NH_4Cl and extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (8:2, v/v) as eluent to give an inseparable mixture of geometrical isomers *(Z)*- and *(E)*-5-[(7'*Z*)-8'-ethoxycarbonyl-7'-nonenyl]-2-hydroxymethyl-3-methylfuran (2.54 g, 69%) as a colorless oil. The ^{1}H NMR spectrum of the mixture showed the ratio of *(Z)*- and *(E)*-unsaturated ester to be 10:1. IR ν max 1715 and 3420 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 1.29 (3H, t, *J*=7.1 Hz, $CO_2CH_2C\mathit{H}_3$), 1.20-1.42 (6H, m, 3×CH_2), 1.60 (2H, quintet, *J*=7.4 Hz, 2'-CH_2), 1.88(3H, s, 3-CH_3), 1.98(3H, d, *J*=1.6 Hz, 9'-CH_3), 2.14-2.29 (1H, br s, OH), 2.43 (2H, q, *J*=7.4 Hz, 6'-CH_2), 2.54 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.18 (2H, q, *J*=7.1 Hz, $OC\mathit{H}_2CH_3$), 4.50 (2H, s, CH_2OH), 5.79 (1H, s, 4-CH), 5.91 (1H, tq, *J*=1.5 and 7.4 Hz, 7'-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 9.6, 14.1, 20.5, 27.7, 27.8, 28.8, 28.9, 29.2, 29.4, 55.0, 59.9, 108.1, 118.0, 127.0, 142.9, 147.3, 155.4, 168.1 ; MS (EI): 307 (M^+); HRMS (EI): calcd for $C_{18}H_{27}O_4$: 307.1909. Found; 307.1891.

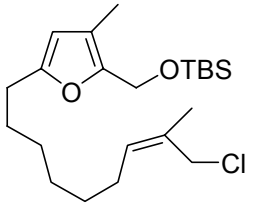
To a solution of the above alcohol (2.10 g, 7.5 mmol) in CH_2Cl_2 (147 mL) were added γ-collidine (3.1 mL, 22.5 mmol) and TBSOTf (2.6 mL, 11.2 mmol) at -78 °C. After stirring for 30 min at the same temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. and warm to room temperature and then extracted with Et_2O-pentane (1:1). The extract was washed with brine, sat. $KHSO_3$ aq. and brine, dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography

using hexane-EtOAc (95:5, v/v) as eluent to give an inseparable mixture (*Z*/*E*=10:1) of geometrical isomers **4** (2.74 g, 87%) as a colorless oil. IR ν max 1070 and 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.04 (6H, s, 2×$SiCH_3$), 0.88 (9H, s, $C(CH_3)_3$), 1.28 (3H, t, *J*=7.3 Hz, $CO_2CH_2CH_3$), 1.26-1.44 (6H, m, 3×CH_2), 1.59(2H, quintet, *J*=7.3 Hz, 2'-CH_2), 1.87 (3H, d, *J*=1.5 Hz, 9'-CH_3), 1.96 (3H, s, 3-CH_3), 2.42(2H, q, *J*=7.4 Hz, 6'-CH_2), 2.52 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.18(2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 4.54 (2H, s, CH_2OTBS), 5.75 (1H, s, 4-CH), 5.90 (1H, tq, *J*=1.5 and 7.4 Hz, 7'-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 14.3, 18.4, 20.6, 25.9 (3), 27.9 (2), 29.0, 29.1, 29.3, 29.5, 56.0, 60.0, 108.1, 117.5, 127.1, 143.0, 147.3, 155.0, 168.2 ; MS (EI): 422 (M^+); HRMS (EI): calcd for $C_{24}H_{42}O_4Si$: 422.2852. Found; 422.2859.



2-*tert*-Butyldimethylsiloxymethyl-5-[(7'*Z*)-9'-hydroxy-8'-methyl-7'-nonenyl]-3-methylfuran (*Z*)-**5**

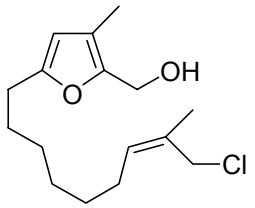
To a solution of compound (*Z*)-**4** (1.21 g, 2.86 mmol) in CH_2Cl_2 (12 mL) was added dropwise DIBAL (0.93 M in hexane, 6.8 mL, 6.3 mmol) at -78 °C. After stirring for 1 hr at the same temperature, the reaction mixture was quenched with sat. potassium sodium tartrate aq. and stirred for 2 hr at room temperature. The precipitate was filtered and extract with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (8:2, v/v) as eluent to give an inseparable mixture (*Z*/*E*=10:1) of geometrical isomers **5** (960.2 mg, 88%) as a colorless oil. IR ν max 3340 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.05 (6H, s, 2×$Si(CH_3)_2$), 0.88 (9H, s, $C(CH_3)_3$), 1.20-1.40 (7H, m, 3×CH_2 and OH), 1.58 (2H, quintet, *J*=7.4 Hz, 2'-CH_2), 1.78 (3H, s, 8'-CCH_3), 1.96 (3H, s, 3-CCH_3), 2.02 (2H, q, *J*=6.6 Hz, 6'-CH_2), 2.52 (2H, t, *J*=7.3 Hz, 1'-CH_2), 4.10 (2H, s, 9'-CH_2), 4.54 (2H, s, CH_2OTBS), 5.28 (1H, tq, *J*=1.2 and 7.4 Hz, 7'-CH), 5.76 (1H, s, 4-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 18.5, 21.2, 25.9 (3), 27.5, 27.9 (2), 28.9, 29.0, 29.9, 56.0, 61.6, 108.1, 117.5, 128.7, 134.1, 147.3, 155.0; MS (EI): 380 (M^+); HRMS (EI): calcd for $C_{22}H_{40}O_3Si$: 380.2747. Found; 380.2767.



2-*tert*-Butyldimethylsiloxymethyl-5-[(7'*Z*)-9'-chloro-8'-methyl-7'-nonenyl]-3-methyl furan (*Z*)-**6**

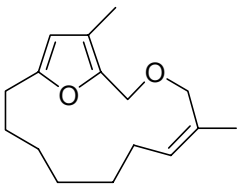
To a suspension of compound **5** (1.0 g, 2.6 mmol), LiCl (276.3 mg, 2.6 mmol),

and 2,6-lutidine (0.84 mL, 6.6 mol) in DMF (20 mL) was dropwise MsCl (0.84 mL, 7.2 mmol) at -5 °C. After stirring for 5 hr, the reaction mixture was quenched with water and extracted with Et_2O-pentane (1:1). The extract was washed with water, brine/water (1:1) (×3) and brine, dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (95:5, v/v) as eluent to give an inseparable mixture (*Z/E*=10:1) of geometrical isomers **6** (990.2 mg, 94%) as a colorless oil. IR ν max 1000 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 0.05 (6H, s, 2×$SiCH_3$), 0.89 (9H, s, $C(CH_3)_3$), 1.25-1.40 (6H, m, 3×CH_2), 1.60 (2H, quintet, *J*=7.4 Hz, 2'-CH_2), 1.81 (3H, d, *J*=1.3 Hz, 8'-CCH_3), 1.97 (3H, s, 3-CCH_3), 2.05 (2H, q, *J*=7.5 Hz, 6'-CH_2), 2.53(2H, t, *J*=7.4 Hz, 1'-CH_2), 4.05 (2H, s, 9'-CH_2), 4.55 (2H, s, CH_2OTBS), 5.37 (1H, tq, *J*=1.3 and 7.5 Hz, 7'-CH), 5.76 (1H, s, 4-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ -5.2 (2), 9.9, 18.5, 21.5, 25.9 (3), 27.8, 27.9 (2), 28.9, 29.0, 29.4, 43.7, 56.0, 108.1, 117.5, 131.1, 131.4, 147.3, 155.0 ; MS (CI): 399 (M+1); HRMS (CI): calcd for $C_{22}H_{40}ClO_2Si$+H : 399.2486. Found; 399.2503.



5-[(7'*Z*)-9'-Chloro-8'-methyl-7'-nonenyl]-2-hydroxymethyl-3-methylfuran (*Z*)-**7**

To a solution of compound **6** (990.2 mg, 2.5 mmol) in THF (8.8 mL) was added TBAF (1 M in THF, 2.7 mL, 2.7 mmol) at 0 °C. After stirring for 3.5 hr, the reaction mixture was washed with brine and extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-EtOAc (9:1, v/v) as eluent to give an inseparable mixture (*Z/E*=10:1) of geometrical isomers **7** (655.4 mg, 93%) as a colorless oil. IR ν max 3340 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 270 MHz) δ 1.23-1.42 (6H, m, 3×CH_2), 1.60 (2H, quintet, *J*=7.4 Hz, 2'-CH_2), 1.82 (1H, br s, OH), 1.82 (3H, d, *J*=1.0 Hz, 8'-CCH_3), 1.99 (3H, s, 3-CH_3), 1.99-2.12 (2H, m, 6'-CH_2), 2.55 (2H, t, *J*=7.4 Hz, 1'-CH_2), 4.06 (2H, s, 9'-CH_2), 4.51 (2H, s, CH_2OH), 5.37 (1H, dt, *J*=1.2 and 7.4 Hz, 7'-CH), 5.81 (1H, s, 4-CH); ^{13}C-NMR ($CDCl_3$; 67.8 MHz) δ 9.7, 21.5, 27.7, 27.8, 27.9, 28.9, 29.4, 43.7, 55.2, 108.2, 118.3, 131.1, 131.3, 131.4, 147.3, 155.6; MS (CI): 283 (M+1); HRMS (CI): calcd for $C_{16}H_{16}O_2Cl$+H : 283.1465. Found; 283.1472.

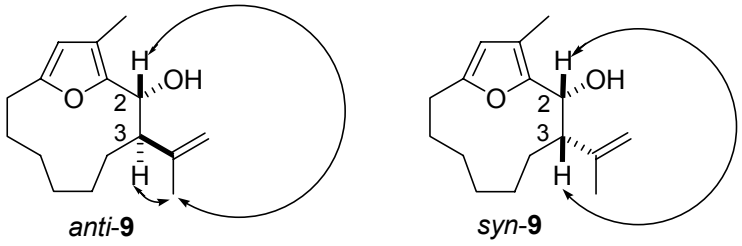


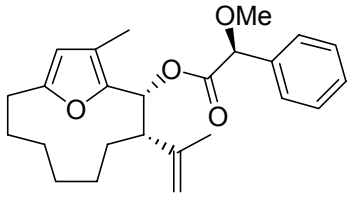
(5*Z*)-5,15-Dimethyl-3,16-dioxabicyclo[11.2.1]hexadeca-1(15),5,13-triene (*Z*)-**8**

To a solution of 18-crown-6 (4.3 g, 16.3 mmol) and 60% NaH (670.2 mg, 16.8

mmol) in benzene (221 mL) was added dropwise a solution of compound **7** (655.4 mg, 2.3 mmol) in benzene (95 mL) over 4 hr at reflux and stirred for 30 min at the same temperature. The reaction mixture was quenched with sat. NH_4Cl aq. and the precipitate was filtered and extracted with Et_2O-pentane (1:1). The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by silica gel chromatography using hexane-Et_2O (97:3, v/v) as eluent to give an inseparable mixture (*Z*/*E*=10:1) of geometrical isomers **8** (461.8 mg, 81%) as a yellow oil. IR ν max 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 1.15-1.30 (6H, m, 3×CH_2), 1.65-1.70 (4H, m, 7- and 11-CH_2), 1.79 (3H, d, *J*=1.2 Hz, 5-CCH_3), 1.99 (3H, s, 15-CCH_3), 2.57 (2H, t, *J*=5.8 Hz, 12-CH_2), 3.76 (2H, s, 4-CH_2), 4.41 (2H, s, 2-CH_2), 5.33 (1H, dt, *J*=1.2 Hz, 7.6 Hz, 6-H), 5.83 (1H, s, 14-H); ^{13}C-NMR ($CDCl_3$; 125 MHz) δ 9.8, 22.3, 24.7, 24.9, 26.2, 27.0, 27.2, 27.7, 61.4, 65.7, 109.6, 119.8, 130.1, 131.9, 145.3, 154.8; MS (EI): 248 (M^+); HRMS (EI): calcd for $C_{16}H_{24}O_2$: 248.1776. Found; 248.1768.

2D NOESY spectra of *anti*- and *syn*-**9** show the correlations between H(2) and H(3) as follows.

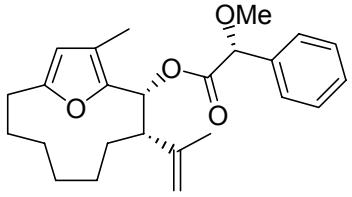




(2*R*',2*R*,3*S*)-3-Isopropenyl-2-[2'-methoxyphenylacetoxy]-12-methyl-13-oxabicyclo[8.2.1]trideca-1(12),10-diene

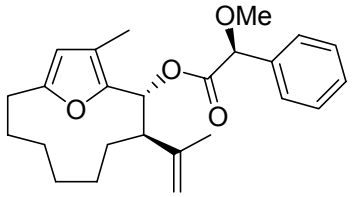
To a solution of *syn*-**9** (5.5 mg, 0.02 mmol) in CH_2Cl_2 (2 mL) was added portionwise (*R*)–2-methoxyphenylacetic acid [(*R*)-MPA] (18.4 mg, 0.1 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC) (34 mg, 0.2 mmol) and DMAP (13.5 mg, 0.1 mmol) at 0 °C. After stirring for 1 hr at the room temperature, the reaction mixture was quenched with brine and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified with silica gel chromatography by using hexane-NEt_3 (95:5, v/v) as eluent to give compound the corresponding (*R*)-MPA ester (7.8 mg, 89%) as a colorless oil. IR ν max 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 0.50-0.68 (1H, m, 7-CH*H*), 1.04-1.15 (1H, m, 8-CH*H*), 1.18-1.30 (2H, m, 5-CH_2), 1.54 (2H, dt, *J*=7.0 and 11.9 Hz,

6-CH_2), 1.38 (1H, ddd, *J*=4.6, 10.4 and 14.0 Hz, 4-CH*H*), 1.62-1.77 (1H, m, 7-CH*H*), 1.72 (3H, s, 3'-CH_3), 1.88-1.94 (1H, m, 8-C*H*H), 1.93 (3H, s, 12-CCH_3), 2.04 (1H, dt, *J*=1.2 and 4.6 Hz, 3-CH), 2.29 (1H, dt, *J*=4.0 and 14.3 Hz, 9-CH*H*), 2.38 (1H, ddd, *J*=4.6, 10.4 and 14.0 Hz, 4CH*H*), 2.50 (1H, dt, *J*=4.0 and 14.3 Hz, 9-C*H*H), 3.44 (3H, s, OCH_3), 4.69 (1H, s, 1'-CH*H*), 4.71 (1H, s, 1'-CH*H*), 4.79 (1H, s, 2"-CH), 5.66 (1H, s, 11-CH), 5.78 (1H, d, *J*=1.2 Hz, 2-CH), 7.24-7.47 (5H, m, Ar); ^{13}C-NMR ($CDCl_3$: 125 MHz) δ 9.4, 21.5, 24.3, 25.1, 27.2, 27.5, 27.7, 29.0, 52.2, 57.5, 69.3, 82.4, 107.5, 111.2, 117.3, 127.1, 128.2 (2), 128.3 (2), 136.3, 145.7, 147.7, 155.6, 170.1 ; MS (EI): 396 (M^+); HRMS (EI): calcd for $C_{25}H_{32}O_4$: 396.2300. Found; 396.2319.



(2*S'*,2*R*,3*S*)-3-Isopropenyl-2-[2'-methoxyphenylacetoxy]-12-methyl-13-oxabicyclo[8.2.1]trideca-1(12),10-diene

Esterification was performed as described above by treatment of *syn*-**9**, (*S*)-MPA, WSC, and DMAP in CH_2Cl_2 to afford (*S*)-MPA ester (91%) as a colorless oil. IR ν max 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 0.82-1.01 (2H, m, 4-CH*H*, 6-CH*H*), 1.10-1.45 (1H, m, 8-CH*H*), 1.18-1.30 (2H, m, 5-CH_2), 1.54 (1H, dt, *J*=7.0 and 11.9 Hz, 6-CH_2), 1.38 (1H, ddd, *J*=4.6, 10.4 and 14.0 Hz, 4-CH*H*), 1.62-1.77 (1H, m, 7-CH*H*), 1.72 (3H, s, 3'-CH_3), 1.88-1.94 (1H, m, 8-C*H*H), 1.93 (3H, s, 12-CCH_3), 2.04 (1H, dt, *J*=1.2 and 4.6 Hz, 3-CH), 2.29 (1H, dt, *J*=4.0 and 14.3 Hz, 9-CH*H*), 2.38 (1H, ddd, *J*=4.6, 10.4 and 14.0 Hz, 4-CH*H*), 2.50 (1H, dt, *J*=4.0 and 14.3 Hz, 9-C*H*H), 3.44 (3H, s, OCH_3), 4.69 (1H, s, 1'-CH*H*), 4.71 (1H, s, 1'-CH*H*), 4.79 (1H, s, 2"-CH), 5.66 (1H, s, 11-CH), 5.78 (1H, d, *J*=1.2 Hz, 2-CH), 7.25-8.0 (5H, m, Ar); ^{13}C-NMR ($CDCl_3$: 125 MHz) δ 9.4, 21.5, 24.3, 25.1, 27.2, 27.5, 27.7, 29.0, 52.2, 57.5, 69.3, 82.4, 107.5, 111.2, 117.3, 127.1, 128.2 (2), 128.3 (2), 136.3, 145.7, 147.7, 155.6, 170.1 ; MS (EI): 396 (M^+); HRMS (EI): calcd for $C_{25}H_{32}O_4$: 396.2300. Found; 396.2319.



(2*R'*,2*R*,3*R*)-3-Isopropenyl-2-[2'-methoxyphenylacetoxy]-12-methyl-13-oxabicyclo[8.2.1]trideca-1(12),10-diene

Esterification was performed as described above by treatment of *anti*-**9**, (*R*)-MPA, WSC, and DMAP in CH_2Cl_2 to afford (*R*)-MPA ester (73%) as a colorless oil. IR ν max 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 1.05-1.20 (4H, m, 4-CH_2, 5-CH*H*), 1.25-1.40 (2H, m, 7-CH_2), 1.50-1.75 (4H, m, 6-CH_2, 8-CH_2), 1.60 (3H, s, 3-CH_3), 1.75-1.88 (1H, m, 5-C*H*H), 1.95 (3H, s, 12-CCH_3), 2.59 (1H, m, 9-CH*H*), 2.69 (1H, m, 9-C*H*H), 3.00 (1H,

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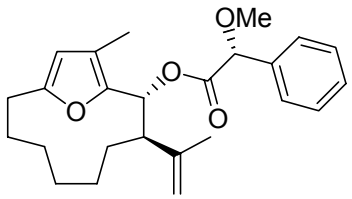
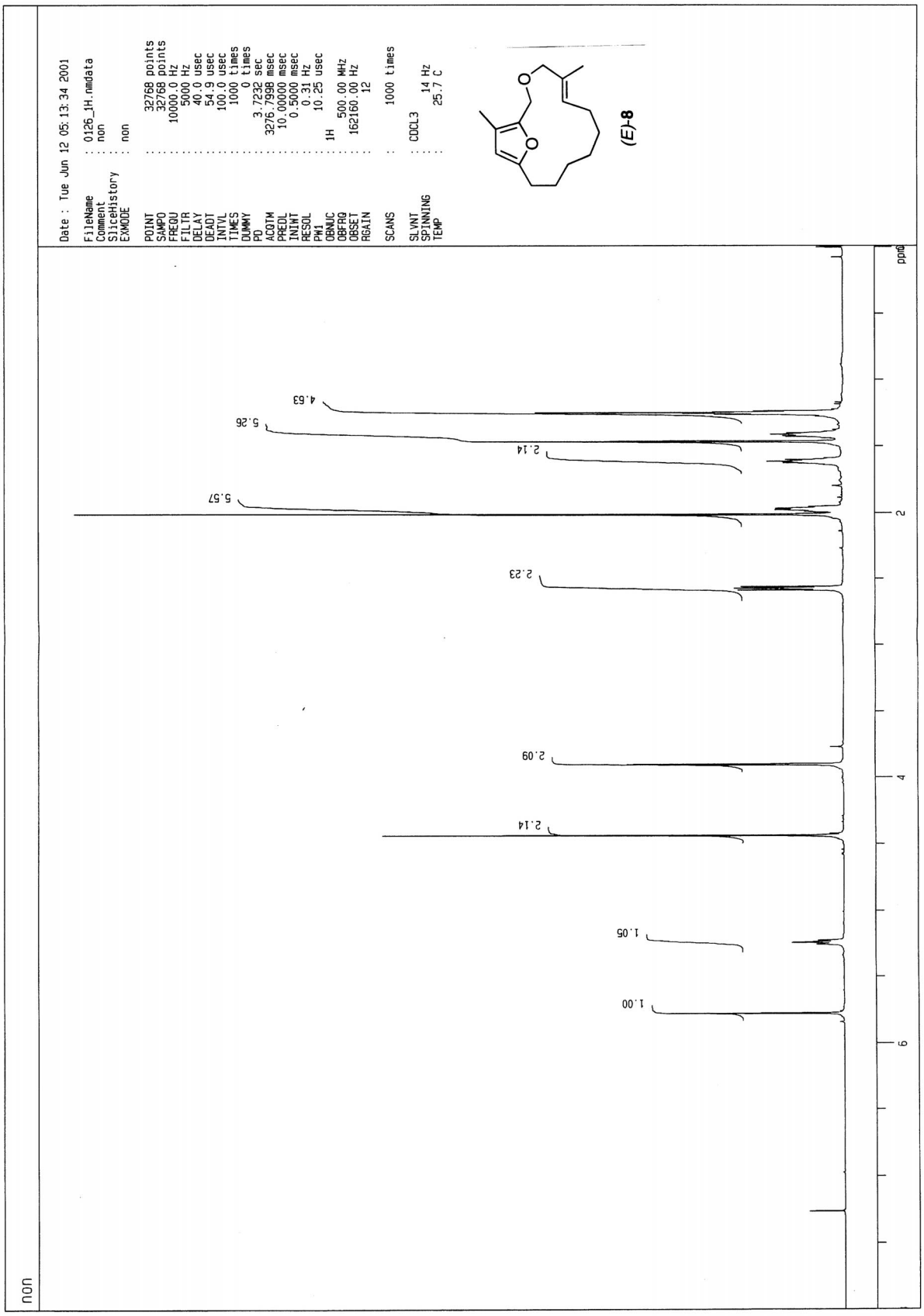


(2*S’*,2*R*,3*R*)-3-Isopropenyl-2-[2’-methoxyphenylacetoxy]-12-methyl-13-oxabicyclo[8.2.1]trideca-1(12),10-diene

Esterification was performed as described above by treatment of *anti*-**9**, (*S*)-MPA, WSC, and DMAP in CH_2Cl_2 to afford (*S*)-MPA ester (54%) as a colorless oil. IR ν max 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 500 MHz) δ 0.58-0.69 (1H, m, 6-CH*H*), 0.80-0.88 (1H, m, 4-CH*H*), 0.89-1.00 (1H, m, 5-CH*H*), 1.00-1.09 (1H, m, 4-C*H*H), 1.10-1.20 (2H, m, 6-C*H*H, 7-CH*H*), 1.24 (3H, s, 3’-CH_3), 1.28-1.39 (1H, m, 5-C*H*H), 1.55-1.74 (2H, m, 8-CH_2), 1.75-1.84 (1H, m, 7-C*H*H), 2.09 (3H, s, 12-CCH_3), 2.65 (1H, ddd, *J*=4.3, 7.0 and 15.0 Hz, 9-CH*H*), 2.75 (1H, ddd, *J*=6.7, 9.2 and 15.0 Hz, 9-C*H*H), 2.91 (1H, ddd, *J*=2.4, 6.7 and 11.5 Hz, 3-CH), 3.33 (3H, s, OCH_3), 4.34 (1H, s, 1’-CH*H*), 4.57 (1H, s, 1’-C*H*H), 4.69 (1H, s, 2”-CH), 5.65 (1H, d, *J*=11.5 Hz, 2-CH), 5.84 (1H, s, 11-CH), 7.30-7.42 (5H, m, Ar); ^{13}C-NMR ($CDCl_3$: 125 MHz) δ 9.8, 17.9, 22.8, 23.4, 25.1, 25.2, 25.5, 27.1, 48.1, 57.1, 68.5, 82.2, 109.5, 113.2, 122.6, 127.4 (2), 128.3 (2), 128.5, 136.3, 144.1, 144.7, 155.4, 170.1 ; MS (EI): 396 (M^+); HRMS (EI): calcd for $C_{25}H_{32}O_4$: 396.2300. Found; 396.2294.

References

1. Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C.; Faucher, A.-M.; Edwards, J.-P. *J. Org. Chem*. **1995**, *60*, 4884-4892.
2. (a) Knight, D. W.; Rustidge, D. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 679-683. (b) Grigg, R.; Knight, J. A.; Sargent, M. V. *J. Chem. Soc*. **1966**, 976-981.
3. Ando, K. *J. Org. Chem*. **1998**, 63, 8411-8416.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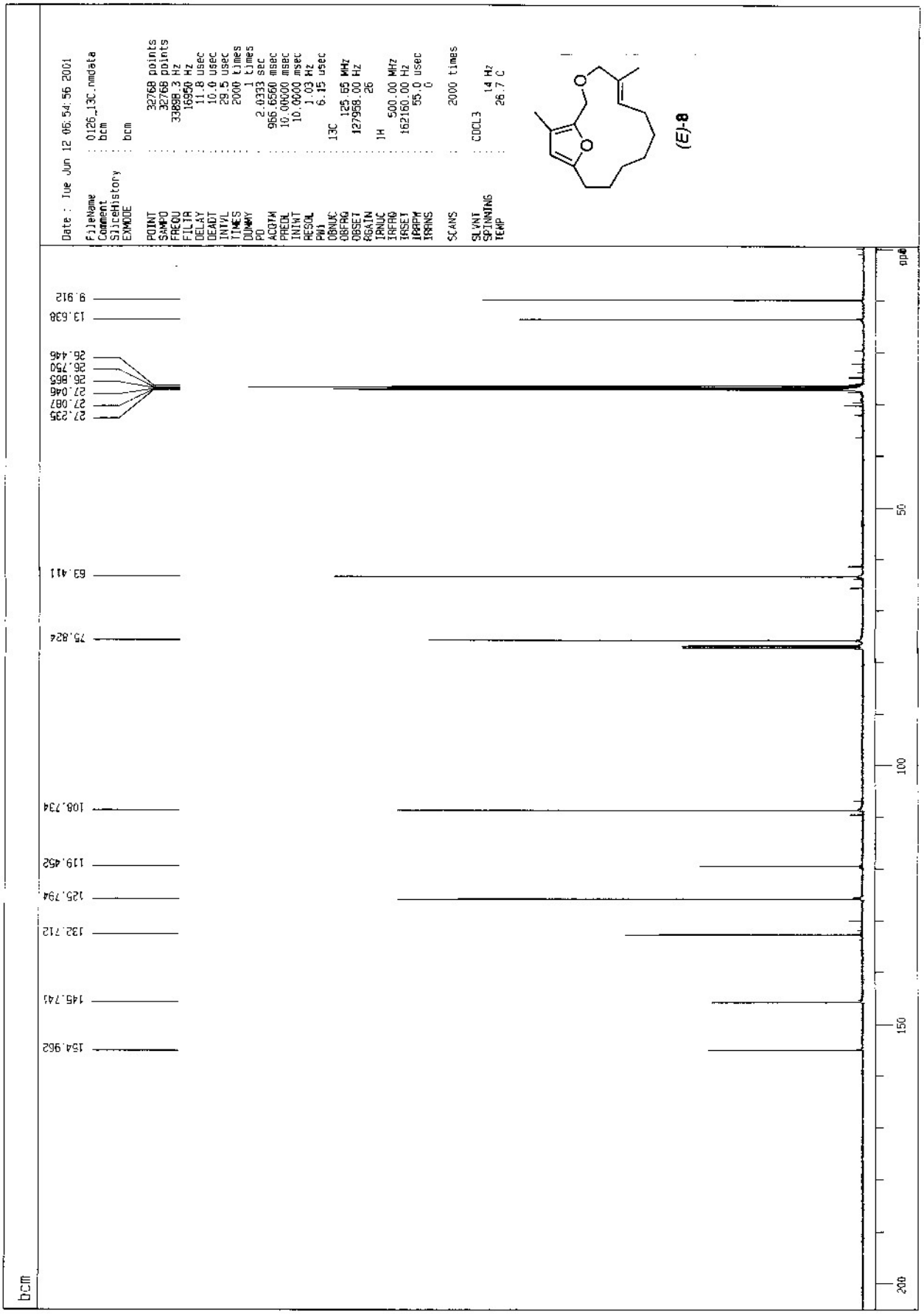
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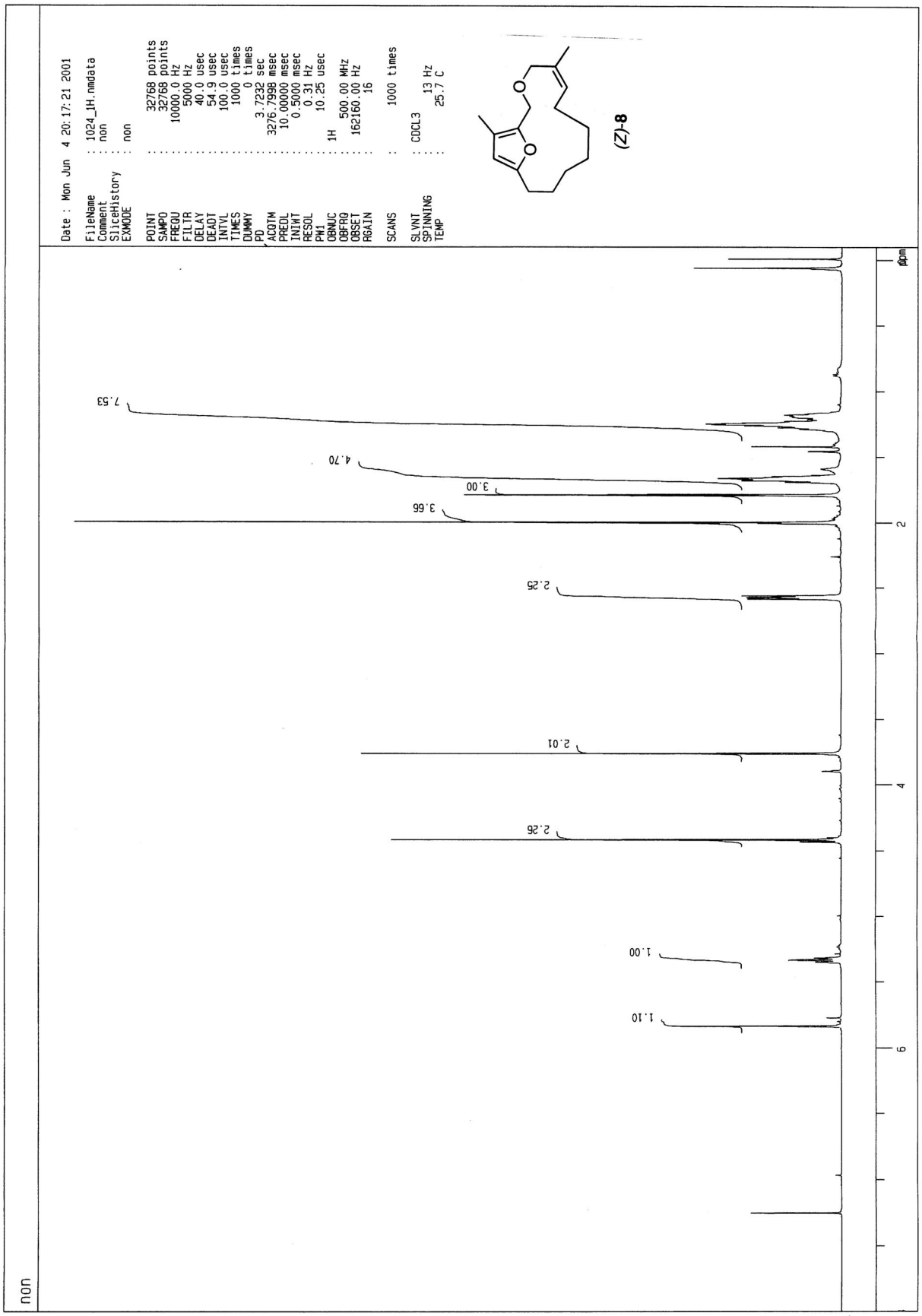
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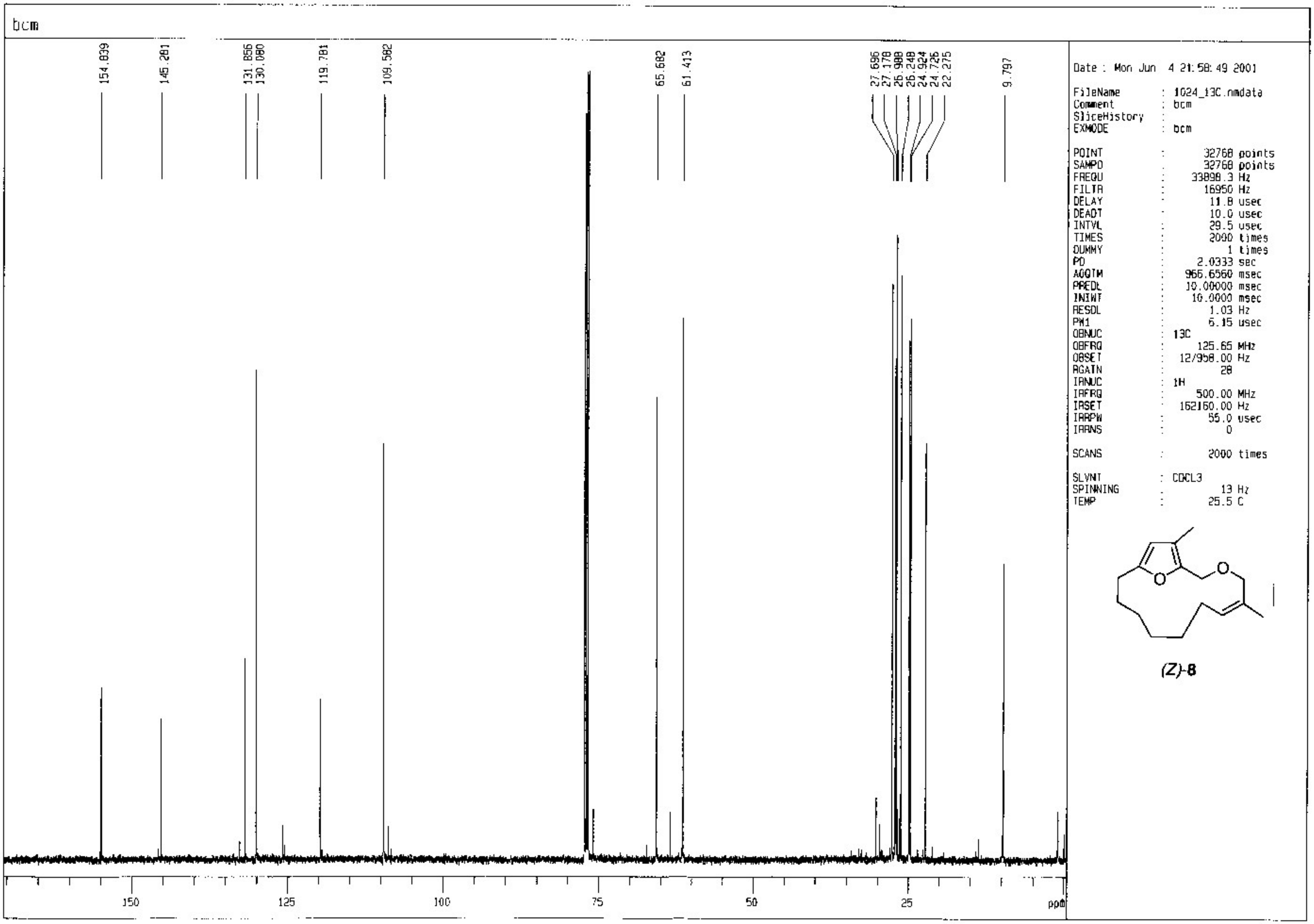
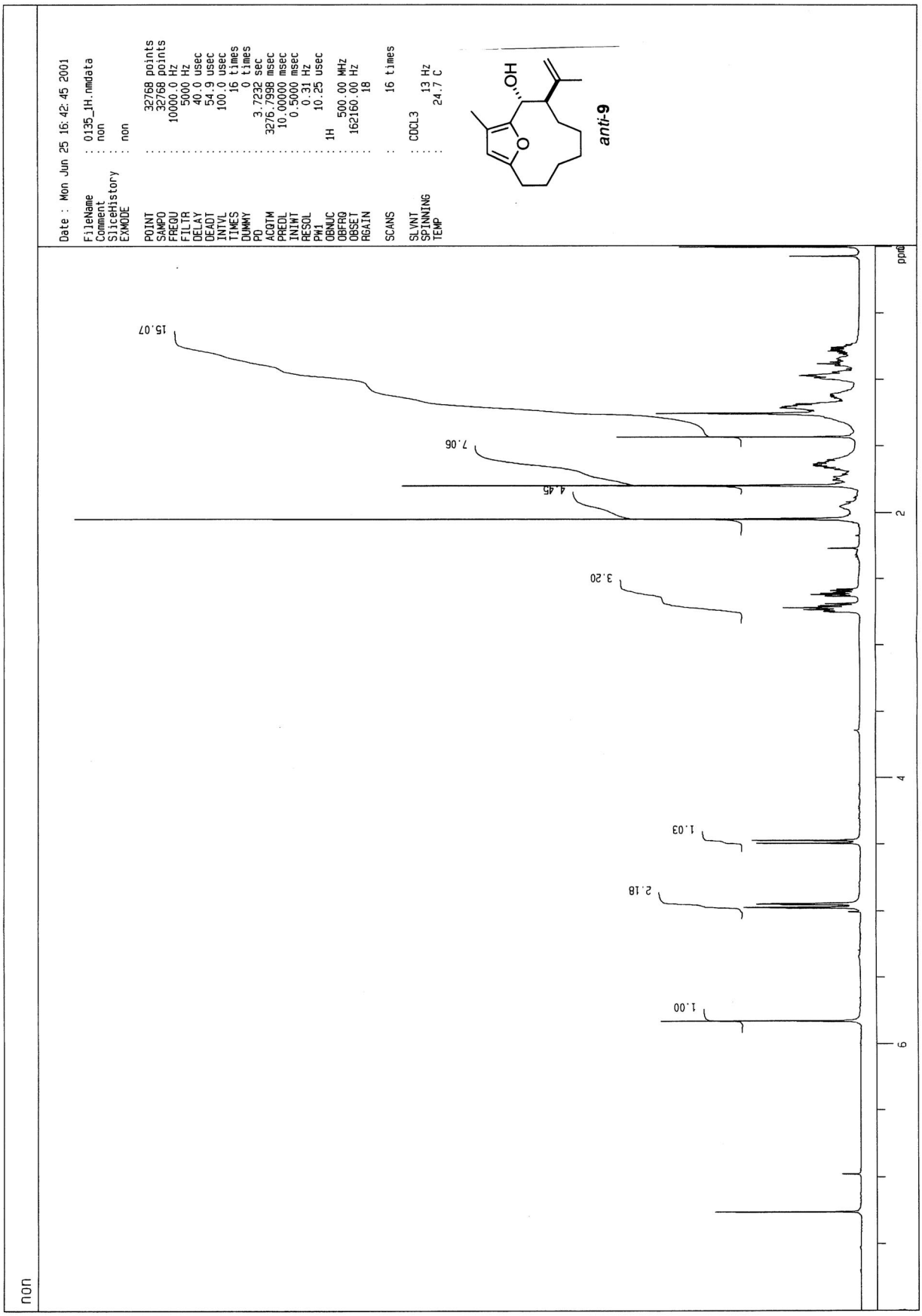
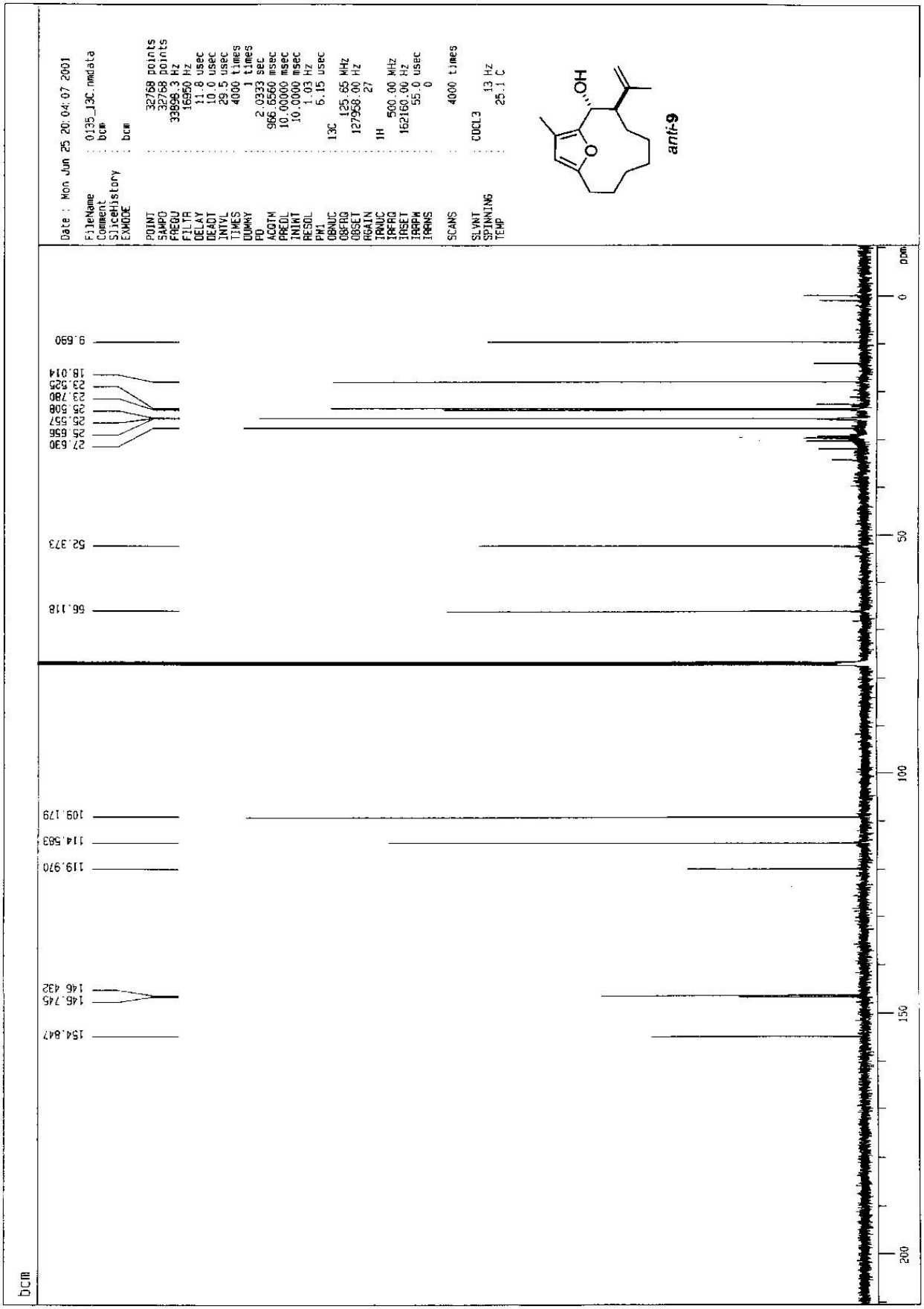
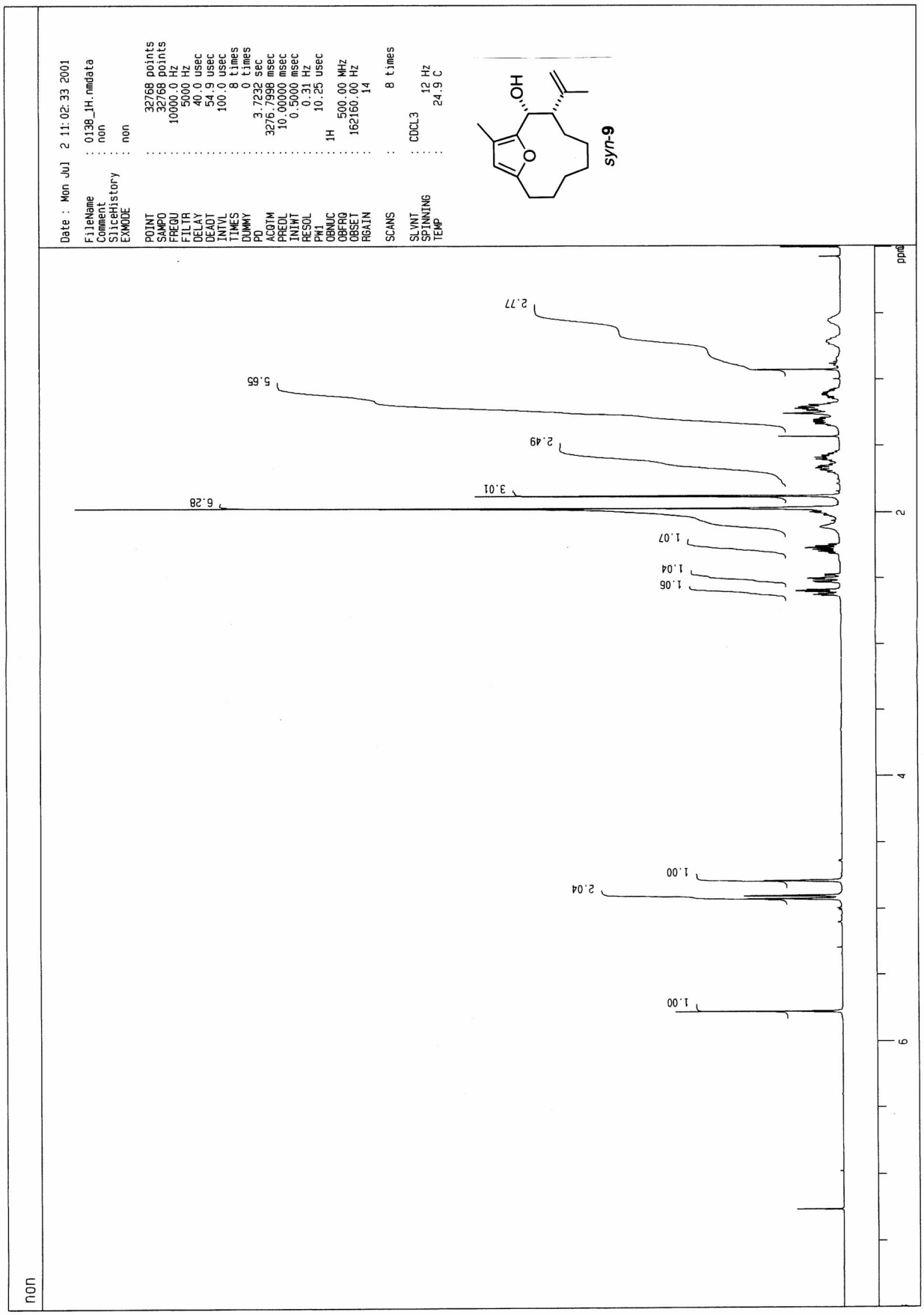
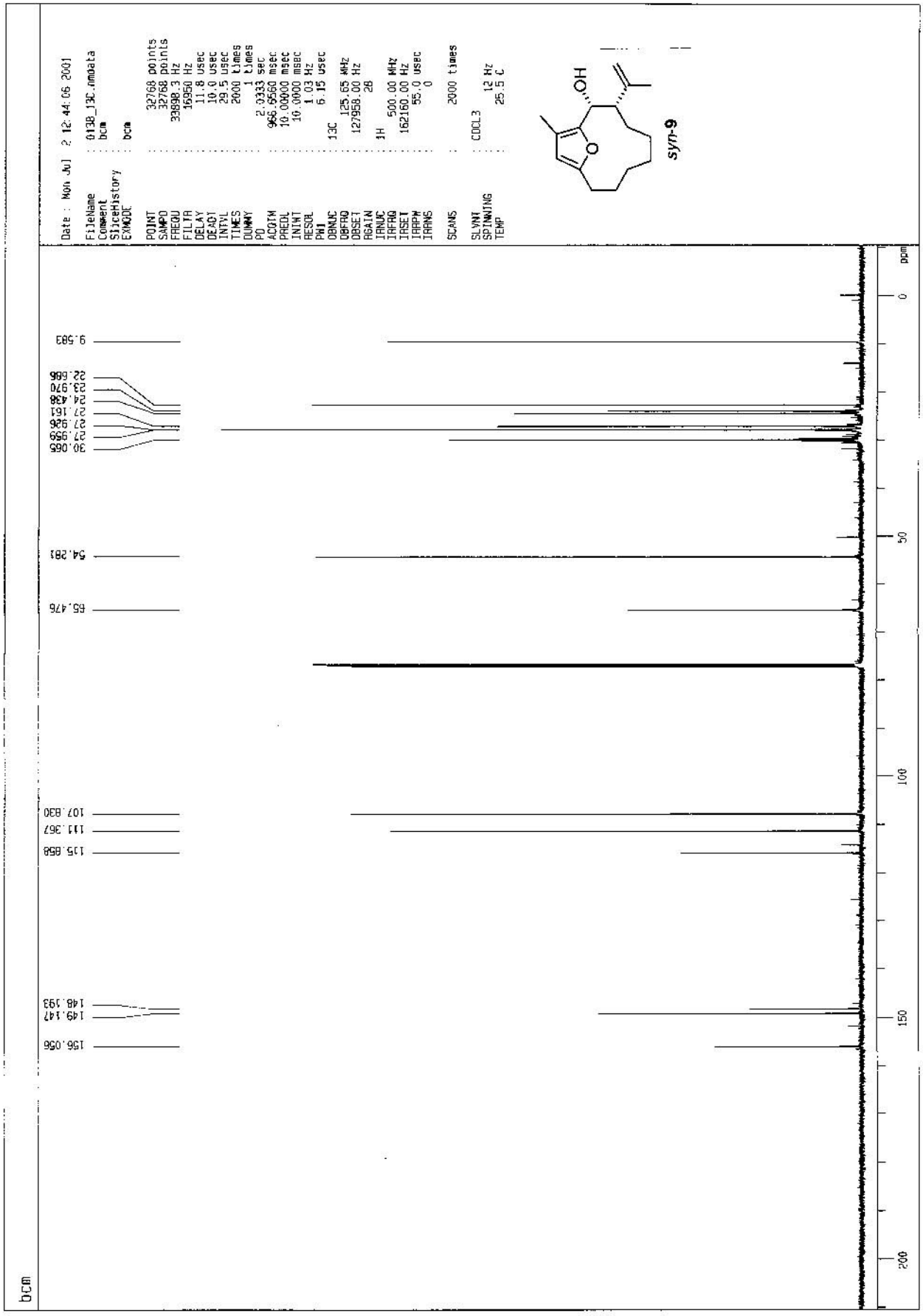
1.10
ppm


bcm
154.839
145.281
131.856
130.080
119.781
109.582
65.682
61.413
27.696
27.178
26.988
26.248
24.924
24.726
22.275
9.797
150
125
100
75
50
25
ppm
Date : Mon Jun 4 21:58:49 2001
FileName : 1024_13C.nmdata
Comment : bcm
SliceHistory :
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 10.0 usec
INTVL : 29.5 usec
TIMES : 2000 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 6.15 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 12/958.00 Hz
RGAIN : 28
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRRPW : 55.0 usec
IRRNS : 0
SCANS : 2000 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 25.5 C
(Z)-8


Date : Mon Jun 25 16:42:45 2001
FileName : 0135_1H.nmrdata
Comment : non
SliceHistory : non
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 54.9 usec
INTVL : 100.0 usec
TIMES : 16 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
ININT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 10.25 usec
OBNUC : 1H 500.00 MHz
OBFRQ : 162160.00 Hz
OBSET : 18
RGAIN :
SCANS : 16 times
SLVNT : CDCL3 13 Hz
SPINNING : 24.7 C
TEMP :
OH
anti-9
15.07
7.06
4.45
3.20
1.03
2.18
1.00
ppm
2
4
6


Date : Mon Jun 25 20:04:07 2001
FileName 0135_13C.nmrdata
Comment bcm
SliceHistory
EXMODE bcm
POINT 32768 points
SAMPD 32768 points
FREQU 33898.3 Hz
FILTR 16950 Hz
DELAY 11.8 usec
DEADT 10.0 usec
INTVL 29.5 usec
TIMES 4000 times
DUMMY 1 times
PD 2.0333 sec
ACQTM 966.6560 msec
PREDL 10.00000 msec
INIWT 10.0000 msec
RESOL 1.03 Hz
PW1 6.15 usec
OBNUC 13C
OBFRQ 125.65 MHz
OBSET 127958.00 Hz
AGAIN 27
IRNUC 1H
IRFRQ 500.00 MHz
IRSET 162160.00 Hz
IRAPW 55.0 usec
IRANS 0
SCANS 4000 times
SLVNT CDCL3
SPINNING 13 Hz
TEMP 25.1 C
anti-9
9.690
18.014
23.525
23.780
25.508
25.557
25.656
27.630
52.373
66.118
109.179
114.583
119.970
146.432
146.745
154.847
ppm
0
50
100
150
200
bcm


Date : Mon Jul 2 11:02:33 2001
FileName : 0138_1H.nmdata
Comment : non
SliceHistory : non
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 54.9 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 10.25 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 14
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 24.9 C
OH
syn-9
2.77
5.65
2.49
3.01
6.28
1.07
1.04
1.06
1.00
2.04
1.00
ppm
2
4
6
non


Date : Mon Jul 2 12:44:06 2001
FileName : 0130_13C.nmdata
Comment : bcm
SliceHistory : bcm
EXMODE : bcm
POINT 32768 points
SAMPO 32768 points
FREQU 33898.3 Hz
FILTR 16950 Hz
DELAY 11.8 usec
DEADI 10.0 usec
INTVL 29.5 usec
TIMES 2000 times
DUMMY 1 times
PD 2.0333 sec
ACQTM 966.9560 msec
PREDL 10.00000 msec
ININT 10.0000 msec
RESOL 1.03 Hz
PW1 6.15 usec
OBNUC 13C
OBFRQ 125.65 MHz
OBSET 127958.00 Hz
AGAIN 28
1H
IRNUC 500.00 MHz
IRFRQ 162160.00 Hz
IRSET 55.0 usec
IRPPM 0
IRAMS
SCANS 2000 times
SLVNT CDCL3
SPINNING 12 Hz
TEMP 25.5 C
OH
O
syn-9
9.583
22.686
23.970
24.438
27.161
27.926
27.999
30.065
54.281
65.476
107.830
111.367
135.858
148.393
149.147
156.056
bcm
ppm
0
50
100
150
200