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Supporting Information

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Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

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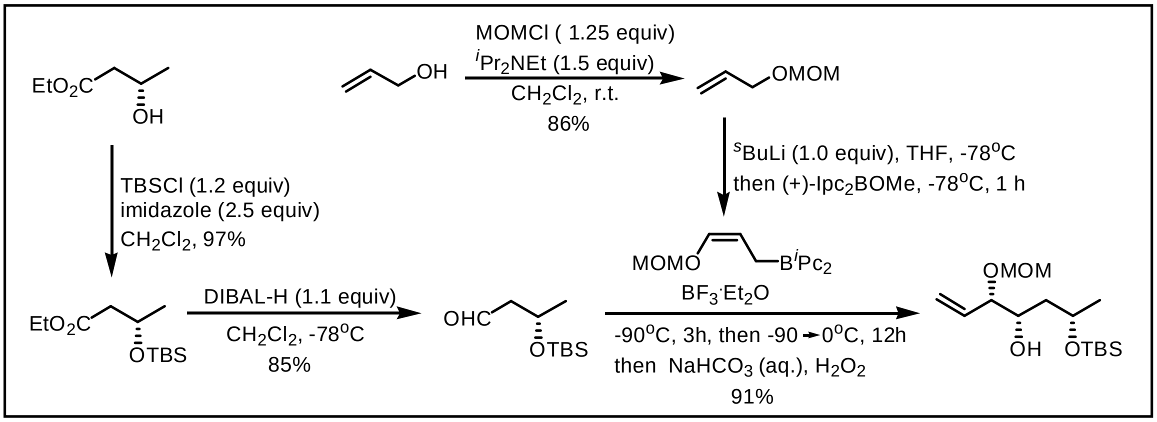
General Procedures. All reactions were run under a dry Ar atmosphere. Reactions were monitored by GC analysis of reaction aliquots. GC analysis was performed on an HP6890 Gas Chromatograph using an HP-5 capillary column (30 m × 0.32 mm, 0.5 µM film) packed with SE-30 on Chromosorb W. Column chromatography was carried out on 230-400 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Inova-300 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL95 mass spectrometers, respectively. Optical rotations were performed on a Autopol III automatic polarimeter. THF was distilled from sodium/benzophenone. $ZnBr_2$ was flame-dried under vacuum. $Cl_2Pd(DPEphos)$[a] and $Pd(tBu_3P)_2$[b] were prepared according to the literature procedure.



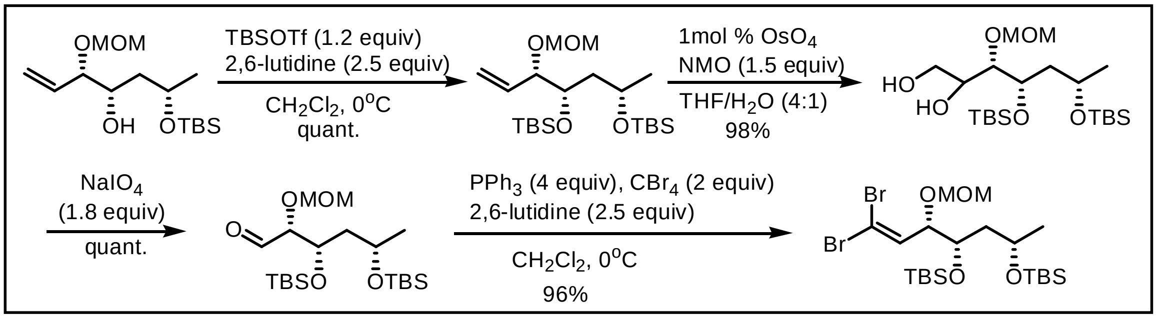
Methoxymethyl allyl ether: To a stirred solution of allyl alcohol (5.45 mL, 80 mmol) and Hünig's base (20.9 mL, 120 mmol) was added chloromethyl methyl ether (7.60 mL, 100 mmol) dropwise at 0°C. The reaction mixture was warmed up to room temperature and stirred for 12 h, then quenched with water and extracted with CH_2Cl_2 (3 × 20 mL).

The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and distilled to afford methoxymethyl allyl ether (7.013 g, 86% yield) as a colorless oil: B.p. 80-81°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 3 H), 4.12 (d, J = 5.7 Hz, 2 H), 4.71 (s, 2 H), 5.25 (d, J = 10.5 Hz, 1 H), 5.36 (d, J = 16.8 Hz, 1 H), 5.9-6.05 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 55.2, 68.2, 95.6, 117.0, 134.3 ppm.

(*S*)-Ethyl 3-(*tert*-Butyldimethylsiloxy)butyrate: To a stirred solution of (*S*)-ethyl 3-hydroxybutyrate (5.91 g, 50 mmol) in DMF (80 mL) were added imidazole (8.6 g, 125 mmol) and TBSCl (9.8 g, 65 mmol) at 0°C. Then the reaction mixture was stirred at 23°C for 12 h, quenched with saturated $NaHCO_3$ (100 mL) and extracted with ether (3 × 50 mL). The combined organic layers were washed with H_2O and brine (50 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (eluent: 3 % EtOAc in hexanes) and to give the silyl ether as a colorless oil (12.008 g, 97% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3 H), 0.05 (s, 3 H), 0.85 (s, 9 H), 1.18 (d, J = 6.6 Hz, 3 H), 1.25 (t, J = 5.6 Hz, 3 H), 2.34 (dd, J = 5.1, 14.4 Hz, 1 H), 2.46 (dd, J = 7.8, 14.4 Hz, 1 H), 4.05-4.15 (m, 2 H), 4.2-4.3 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ -5.11, -4.6, 14.1, 17.9, 23.9, 25.7, 44.9, 60.2, 65.8, 71.6 ppm.

(*S*)-3-(*tert*-Butyldimethylsiloxy)butanal: A stirred solution of (*S*)-ethyl 3-(*tert*-butyldimethylsiloxy)butyrate (11.8 g, 47.9 mmol) in CH_2Cl_2 (480 mL) was cooled to -78°C under argon atmosphere. To this solution was added diisobutylaluminum hydride (52.7 mL, 1.0 M in hexanes, 52.7 mmol) very slowly over 1 h period. After the addition was completed, the reaction mixture was further stirred at -78°C for half an hour. Then methanol (30 mL) was added to the reaction mixture slowly over 15 min. After removing dry ice/acetone bath, the reaction mixture was stirred for another 15 min, then saturated aqueous Rochelle salts (45 mL) was added and the resultant solution was stirred for 2 h. The layers were separated and the aqueous phase was extracted three times with methylene chloride. The combined organic phase was dried with Na_2SO_4 and concentrated. Purification by a flash chromatography (eluent: 3% EtOAc in hexanes) gave (*S*)-3-(*tert*-Butyldimethylsiloxy) butanal (8.217 g, 85% yield) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3 H), 0.08 (s, 3 H), 0.887 (s, 9 H), 1.24 (d, J = 6.3 Hz, 3 H), 2.46 (ddd, *J* = 2.4, 5.4, 15.9 Hz, 1 H), 2.55 (ddd, *J* = 3.0, 7.2, 15.9 Hz, 1 H), 4.3-4.4 (m, 1 H), 9.81-9.80 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ -4.6, -5.1, 17.8, 24.0, 25.5, 52.8, 64.4, 201.6 ppm.

(3*S*,4*S*,6*S*)-3-Methoxymethoxy-6-*tert*-butyldimethylsiloxy-hept-1-en-4-ol: To a stirred solution of methoxymethyl allyl ether (4.39 g, 43.0 mmol) in THF (90 mL) was added *sec*-butyllithium in cyclohexane (1.4 M, 25.6 mL, 35.8 mmol) at -78°C slowly. After the resultant orange yellow solution was stirred at -78°C for 30 min, (+)-B-methoxydiisopinocamphenylborane (11.32 g, 35.8 mmol) in THF (90 mL) was added. After the addition was completed, the mixture was stirred at -78°C for 1 h and boron trifluoride etherate (6 mL, 47.6 mmol) was added dropwisely. Immediately afterwards, (*S*)-3-(*tert*-Butyldimethylsiloxy)-butanal (7.248 g, 35.8 mmol) was added dropwisely, then the mixture was kept at -90°C for 3 h and warmed to room temperature over 12 h. The mixture was cooled to 0°C and saturated $NaHCO_3$ (80 mL) was added followed by 30% H_2O_2 (50 mL) and further stirred for 30 min. Et_2O (80 mL) was added and the organic layer was collected. The aqueous layer was extracted with Et_2O (2 × 30 mL) and the combined organic layers were then dried over $MgSO_4$. Removal of the solvent in vacuo and purification by flash chromatography eluting with a solvent gradient of hexane, then 15% EtOAc/hexane through 20% EtOAc/hexane gave the product (9.898 g, yield 91%, 96/4 diastereoisomer) as a colorless oil: $[\alpha]_D^{25} = 64^o$ (c 3.63, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.08 (s, 6 H), 0.73 (s, 9 H), 1.01 (d, *J* = 6.0 Hz, 3 H), 1.44-1.47 (m, 2 H), 3.09 (s, 1 H), 3.20 (s, 3 H), 3.5-3.6 (m, 1 H), 3.73-3.77 (m, 1 H), 3.9-3.95 (m, 1 H), 4.41 (d, *J* = 7.2 Hz, 1 H), 4.55 (d, *J* = 6.0 Hz, 1 H), 5.10 (s, 1 H), 5.15 (d, *J* = 3.6 Hz, 1 H), 5.64-5.52 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ -5.21, -4.6, 17.5, 23.4, 25.5, 41.5, 55.0, 67.4, 71.5, 80.1, 93.5, 118.8, 134.5 ppm; IR: 3401, 2858, 1463, 1251, 1106, 1006 cm^{-1}; HRMS (CI) *m/z* for M + H^+: 305.2149, calcd. 305.2148.

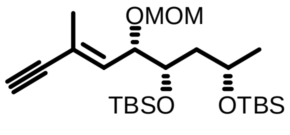


(3*S*,4*S*,6*S*)-3-Methoxymethoxy-4,6-bi(*tert*-butyldimethylsiloxy)-hept-1-en: To a cooled solution of (3*S*,4*S*,6*S*)-3-methoxymethoxy-6-*tert*-butyldimethyl-siloxy-hept-1-en-4-ol (9.48 g, 31.2 mmol) in CH_2Cl_2 (200 mL) were added successively 2,6-lutidine (9.0 mL, 77.8 mmol) and TBSOTf (8.4 mL, 37.4 mmol). The reaction mixture was stirred at 0^oC for 1 h, and then quenched with water and the layers were separated. The aqueous layer was extracted once with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$. The product was obtained after flash chromatography (eluent: 1% EtOAc in hexanes) as a colorless oil (13.07 g, 100% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.07 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 0.90 (s, 9 H), 1.15 (d, *J* = 6.0 Hz, 3 H), 1.55-1.65 (m, 1 H), 1.7-1.8 (m, 1 H), 3.36 (s, 3 H), 3.80-3.85 (m, 1 H), 3.95-4.05 (m, 2 H), 4.58 (d, *J* = 6.6 Hz, 1 H), 4.68 (d, *J* = 6.6 Hz, 1 H), 5.24 (s, 1 H), 5.28 (d, *J* = 3.6 Hz, 1 H), 5.75-5.9 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ -4.3, -4.35, -4.6, -4.7, 18.0, 18.1, 23.7, 25.88, 25.91,42.7, 55.5, 65.5, 71.7, 79.2, 94.4, 117.9, 135.1 ppm.

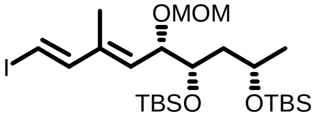
(3*S*,4*S*,6*S*)-3-Methoxymethoxy-4,6-bi(*tert*-butyldimethylsiloxy)-heptane-1,2-diol: A solution of (3*S*,4*S*,6*S*)-3-methoxymethoxy-4,6-bi(*tert*-butyldimethylsiloxy)-hept-1-en (8.2 g, 19.6 mmol) and NMO (50% solution in H_2O, 14 mL, 58.8 mmol) in THF-H_2O (4:1, 150 mL) was treated with OsO_4 (4% solution in H_2O, 1.3 mL, 0.2 mmol) and the resultant reaction mixture was stirred at room temperature for 24 hours. After saturated aqueous $Na_2S_2O_3$ (30 mL) was added, the mixture was extracted with EtOAc (2 × 30 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was simply purified by short silica gel column chromatography (eluent: 40% EtOAc in hexanes) to afford the diol (8.7 g, 98% yield) for the next step use.

(2*R*,3*S*,5*S*)-2-Methoxymethoxy-3,5-bi(*tert*-butyldimethylsiloxy)-hexanal: To the (3*S*,4*S*,6*S*)-3-methoxymethoxy-4,6-bis-triethylsiloxy-heptane-1,2-diol (8.286 g, 18.3 mmol) in THF-H_2O (130 mL, 1:1) was added $NaIO_4$ (7.593 g, 35.5 mmol). The heterogenous reaction mixture was stirred at 23°C for 1 h, and then filtered through Celite and extracted with ether. The combined layers were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was simply purified by a short silica gel column and used immediately for next step without further purification.

(3*S*,4*S*,6*S*)-1,1-dibromo-3-methoxymethoxy-4,6-bi(*tert*-Butyldimethylsiloxy)-hept-1-ene: In a reaction flask under Ar were combined PPh_3 (19.2 g, 73.2 mmol) and CH_2Cl_2 (180 mL). The flask was cooled to 0°C, and the CBr_4 (12.14 g, 36.6 mmol) was added (afforded a yellow solution). The reaction mixture was stirred at 0°C for 15 min, then 2,6-lutidine (4.9 g, 5.33 mL, 45.8 mmol) was added (afforded a dark yellow solution). Then the aldehyde (ca. 18.3 mmol) from above in CH_2Cl_2 (30 mL) was added *via* cannula and the reaction mixture was further stirred for 20 min at 0°C. Then the reaction mixture was poured into hexanes (500 mL) and filtered. The dibromo product was obtained after flash chromatography (2% EtOAc in hexanes) as a colorless oil (10.13 g, 96% yield): $[\alpha]_D^{25}$ = 37° (c 1.48, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.07 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 0.89 (s, 9 H), 1.63 (ddd, *J* = 5.7, 7.5, 15.3Hz, 1 H), 1.14 (d, *J* = 6.0 Hz, 3 H), 1.87 (ddd, *J* = 5.4, 7.2, 15.3Hz, 1 H), 3.34 (s, 3 H), 3.85-3.95 (m, 2 H), 4.26 (dd, *J* = 3.6, 8.7 Hz, 1 H), 4.55 (d, *J* = 6.9 Hz, 1 H), 4.66 (d, *J* = 6.9 Hz, 1 H), 6.48 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ -4.1, -4.6, -4.55, 18.0, 18.1, 24.1, 25.9, 43.5, 55.7,65.4, 70.8, 78.0, 92.1, 94.6, 137.0 ppm; IR 2930, 1472, 1256, 1029 cm^{-1}; HRMS (EI) *m/z* for $[M\text{-}OTBS]^+$: 443.0249, calcd. 443.0253.

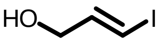


(5*S*,6*S*,8*S*)-6,8-bi(*tert*-Butyldimethylsiloxy)-5-methoxymethoxy-3-methyl-3-nonen-1-yne. To a solution of trimethylsilyl acetylene (200μL, 1.4mmol) in THF (2 mL) was added *n*-BuLi (0.56 mL, 2.5 mL in hexanes, 1.4 mmol) at -78 °C. To this was added *via* cannula a solution of dry $ZnBr_2$ (316mg, 1.4 mmol) in THF (2 mL). The mixture thus obtained was stirred for 15 min at -78 °C and then warmed to 23 °C over 30 min, and added *via* cannula to a mixture of (3*S*,4*S*,6*S*)-1,1-dibromo-4,6-bis-(*tert*-butyl-dimethyl-siloxy)-3-methoxymethoxy-1-heptene (574mg, 1.0 mmol) and Cl_2Pd(DPEphos) (36 mg, 0.01 mmol) in THF (3 mL) *via* cannula at 0 °C. After stirring at 0 °C for 45 min, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was passed through a short (5 cm) column using 1:24 EtOAc/hexanes as eluent. To a mixture of the crude product obtained above and Pd($t$$Bu_3P)_2$ (10 mg, 0.02 mmol) in THF (6 mL) was added Me_2Zn (0.75 mL, 2.0 M solution in toluene, 1.5 mmol) at 23 °C. After stirring at 23 °C for 3 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was dissolved in MeOH (8 mL) followed by addition of K_2CO_3 (28 mg, 0.2 mmol) at 23 °C. After 4 h, the solvent was removed *in vacuo*, and the remaining slurry was chromatographed (silica gel, EtOAc/hexanes 3:200) to afford the title compound (278 mg, 61% over three steps) as oil. $[\alpha]_D^{23}$ +25° (c 3.8, CH_2Cl_2); IR (neat) 3315, 2956, 2888, 2858, 1472, 1463, 1380, 1361, 1255, 1148, 1032, 836, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.055 (s, 3 H) 0.065 (s, 3 H), 0.071 (s, 3 H), 0.086 (s, 3 H), 0.89 (s, 9 H), 0.90 (s, 9 H), 1.15 (d, *J* = 5.8 Hz, 3 H), 1.6-1.85 (m, 2 H), 1.88 (d, *J* = 1.2 Hz, 3 H), 2.85 (s, 1 H), 3.40 (s, 3 H), 3.75-3.85 (m, 1 H), 3.96 (sextet, *J* = 6.5 Hz, 1 H), 4.29 (dd, *J* = 4.7, 10.0 Hz, 1 H), 4.52 (d, *J* =7.1 Hz, 1 H), 4.62 (d, *J* = 6.5 Hz, 1 H), 5.85 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ,-4.55, -4.09, -3.94, 18.13, 18.28, 18.41, 24.23, 26.10, 26.20, 43.89, 55.78, 65.79, 72.07, 73.87, 75.59, 86.11, 94.20, 121.91, 136.17 ppm; HRCI-MS *m/z* ($[M+H]^+$) 457.3174; calcd. 457.3169.

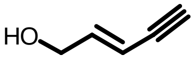


(5*S*,6*S*,8*S*)-6,8-Bi(*tert*-butyldimethylsiloxy)-1-iodo-5-methoxymethoxy-3-methyl-1,3-nonadiene. A flame-dried, round-bottomed flask was charged with HCp_2ZrCl (263mg, 1.03 mmol). To this was added a solution of (5*S*,6*S*,8*S*)-6,8-bi(*tert*-butyldimethylsiloxy)-

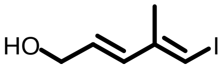
5-methoxymethoxy-3-methyl-3-nonen-1-yne (360 mg, 0.79 mmol) in THF (5 mL) at 23 °C. After stirring for 2 h, a solution of I_2 (401 mg, 1.58 mmol) in THF (3 mL) was added *via* cannula at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h, and then quenched with a mixture of $Na_2S_2O_3$ (sat.) and $NaHCO_3$ (sat.) solution (1:1), extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, EtOAc/hexanes 2:98) afforded the title compound (376 mg, 81%) as oil. $[\alpha]_D^{23}$ +27° (c 3.4, CH_2Cl_2); IR (neat) 2955, 2929, 2857, 1472, 1256, 1098, 1032, 808, 774 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 0.09 (s, 6 H), 0.11 (s, 3 H), 0.13 (s, 3 H), 0.96 (s, 9 H), 0.97 (s, 9 H), 1.15 (d, *J* = 5.9 Hz, 3 H), 1.52 (s, 3 H), 1.75-1.85 (m, *2* H), 3.12 (s, 3 H), 3.8-3.9 (m, 1 H), 4.08 (sextet, *J* = 6.6 Hz, 1 H), 4.33 (d, *J* =6.4 Hz, 1 H), 4.37 (dd, *J* =7.1, 11.2 Hz, 1 H), 4.49 (d, *J* =6.5 Hz, 1 H), 5.22 (d, *J* = 10.0 Hz, 1 H), 5.98 (d, *J* = 14.6 Hz, 1 H), 6.94 (d, *J* = 14.6 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.05, -4.01, -3.67, -3.50, 18.01, 18.66, 18.77, 24.52, 26.53, 26.59, 44.65, 55.69, 66.34, 72.86, 74.69, 77.56, 94.26, 130.85, 139.33, 149.43 ppm; HRESI-MS *m/z* ($[M+Na]^+$) 607.2108; calcd. 607.2112.



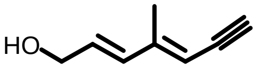
(*E*)-3-Iodo-2-propen-1-ol. To a solution of Cp_2ZrCl_2 (7.0g, 24 mmol) in THF (90 mL) was added DIBAL-H (3.9 mL, neat, 22mmol) at 0 °C with the exclusion of light. This reaction mixture was stirred at 0 °C for 30min. Meanwhile, in another flask, propargyl alcohol (1.16 mL, 20 mmol) was dropped in a solution of DIBAL-H (4.2 mL, neat, 24mmol) in THF at -78 °C. This reaction mixture was stirred at 0 °C for 30 min and transfer to the flask containing *in situ* generated HCp_2ZrCl solution. After stirring at 23 °C for 2 h, a solution of I_2 (7.6 g, 30 mmol) in THF (20 mL) was added *via* cannula at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h, and then quenched with 1 M HCl, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, Et_2O/pentane 1:9-3:7) afforded the title compound (2.71 g, 74%) as liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 3.94 (d, *J* = 5.1 Hz, 2 H), 4.19 (s, 1 H), 6.28 (d, *J* = 15.5 Hz, 1 H), 6.58 (td, *J* = 5.4, 14.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.44, 78.04, 144.35 ppm.



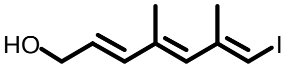
(*E*)-2-Penten-4-yn-1-ol. A flame-dried round-bottomed flask was charged with $ZnBr_2$ (405mg, 1.8 mmol). To this were added sequentially at 0 °C THF (2 mL), and C_2H_5MgBr (3.3 mL, 1.0 M solution in THF, 3.3 mmol). This slurry mixture was stirred at 0 °C for 30 min. A solution of (*E*)-3-iodo-2-propen-1-ol (552 mg, 3 mmol) in THF (1 mL) was dropped in and the reaction mixture was stirred for another 30 min. Meanwhile, another flask was charged with $ZnBr_2$ (472 mg, 2.1 mmol). To this were added sequentially at 0 °C THF (2 mL), and C_2HMgBr (7.8 mL, 0.5 M solution in THF, 3.9 mmol). This reaction mixture was stirred at 0 °C for 30 min and then transferred to the flask containing above obtained alkenylzinc mixture, followed by the introduction of a suspension of $Cl_2Pd(DPEphos)$ (107mg, 0.15 mmol) in DMF(7 mL). After stirring at 23 °C for 4 h, the reaction mixture was quenched with 1 M HCl, extracted with Et_2O, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 1:9 – 1:4 Et_2O/pentane) afforded the title compound (191 mg, 78%) as liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96 (d, *J* =1.8 Hz, 1 H), 3.22 (s, 1 H), 4.22 (s, 1 H), 5.75 (dd, *J* = 1.8, 15.8 Hz, 1 H), 6.58 (td, *J* = 4.7, 16.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.43, 78.10, 81.78, 109.08, 143.94 ppm.



(2*E*,4*E*)-5-Iodo-4-methyl-2,4-pentadien-1-ol. To a solution of Me_3Al (2.0 mL, 21.2 mmol) in CH_2Cl_2 (15 mL) was introduced (*E*)-2-penten-4-yn-1-ol (600 mg, 7.3 mmol) in CH_2Cl_2 (10 mL) with syringe at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h. To this reaction mixture was then added a solution of Cp_2ZrCl_2 (1.06 g, 3.65 mmol) in CH_2Cl_2 (15 mL) via cannula at 0 °C. The reaction mixture was warmed to 23 °C and stirred for 3 h. TLC analysis indicated that the starting material had been completely consumed. To this mixture was added *via* cannula a solution of I_2 (2.41 g, 9.5 mmol) in THF (10 mL) at -78 °C. After stirring at -78 °C for 30 min, the reaction mixture was quenched with 1 M HCl, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 1:9 – 1:4 Et_2O/pentane) afforded the title compound (1.14 g, 70%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3 H), 3.07 (s, br, 1 H), 6.3-6.35 (m, 2 H), 4.14 (d, *J* = 4.3 Hz, 1 H), 5.89 (td, *J* = 5.3, 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.96, 62.71, 83.88, 128.70, 131.45, 144.30 ppm.

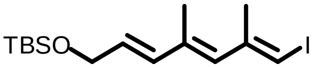


(2*E*,3*E*)-2,3-Heptandien-6-yn-1-ol. A flame-dried round-bottomed flask was charged with $ZnBr_2$ (579mg, 2.6 mmol). To this were added sequentially at 0 °C THF (3 mL), and C_2H_5MgBr (4.72 mL, 1.0 M solution in THF, 4.72 mmol). This slurry mixture was stirred at 0 °C for 30 min. A solution of (2*E*,4*E*)-5-iodo-4-methyl-2,4-pentadien-1-ol (960 mg, 4.3 mmol) in THF (3 mL) was dropped in and the reaction mixture was stirred for another 30 min. Meanwhile, another flask was charged with $ZnBr_2$ (673 mg, 3.0 mmol). To this were added sequentially at 0 °C THF (3 mL), and C_2HMgBr (11.1 mL, 0.5 M solution in THF, 5.55 mmol). This reaction mixture was stirred at 0 °C for 30 min and then transferred to the flask containing above obtained alkenylzinc mixture, followed by the introduction of a suspension of $Cl_2Pd(DPEphos)$ (153 mg, 0.22 mmol) in DMF(9 mL). After stirring at 23 °C for 4 h, the reaction mixture was quenched with 1 M HCl, extracted with Et_2O, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 1:9 – 1:4 Et_2O/pentane) afforded the title compound (466 mg, 89%) as liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 3 H), 2.88 (s, br, 1 H), 3.29 (d, *J* = 1.8 Hz, 1 H), 4.18 (d, *J* = 5.3 Hz, 2 H), 5.42 (s, 1 H), 5.91 (td, *J* = 5.9, 15,8 Hz, 1 H), 6.26 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.29, 63.08, 81.96, 84.25, 109.15, 131.12, 132.86, 148.11 ppm; HREI-MS *m/z* ($[M]^+$) 122.0730; calcd. 122.0732.

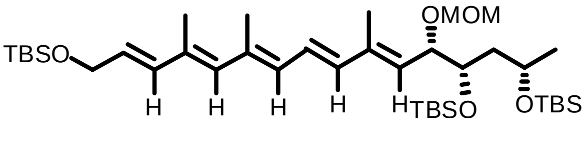


(2*E*,4*E*,6*E*)-4,6-Dimethyl-7-iodo-2,4,6-heptatrien-1-ol. To a solution of Me_3Al (1.7 mL, 17.5 mmol) in CH_2Cl_2 (16 mL) was introduced (2*E*,3*E*)-2,3-heptandien-6-yn-1-ol (820 mg, 6.7 mmol) in CH_2Cl_2 (16 mL) with syringe at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h. To this reaction mixture was then added a solution of

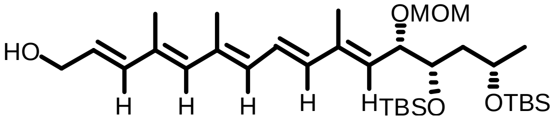
Cp_2ZrCl_2 (392 mg, 1.3 mmol) in CH_2Cl_2 (16 mL) via cannula at 0 °C. The reaction mixture was warmed to 23 °C and stirred for 1 h. TLC analysis indicated that the starting material had been completely consumed. To this mixture was added *via* cannula a solution of I_2 (2.21g, 8.7 mmol) in THF (10 mL) at -78 °C. After stirring at -78 °C for 30 min, the reaction mixture was quenched with a mixture of $Na_2S_2O_3$ (sat.) and $NaHCO_3$ (sat.) solution (1:1), extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, EtOAc/hexanes 1:5 – 1:4) afforded the title compound (1.22 g, 69%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3 H), 1.79 (s, 3 H), 3.19 (s, br, 1 H) 4.05 (d, *J* = 4.7 Hz, 2 H), 5.65-5.70 (m, 2 H), 6.00 (s, 1 H), 6.16 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.55, 25.65, 63.62, 82.06, 129.80, 132.06, 135.49, 135.53, 144.98 ppm; HREI-MS *m/z* ($[M]^+$) 264.0015; calcd. 264.0011.



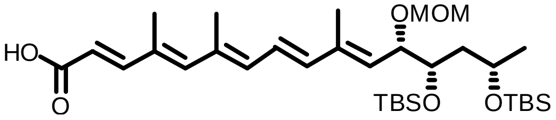
(2*E*,4*E*,6*E*)-1-(*tert*-Butyldimethylsiloxy)-4,6-dimethyl-7-iodo-2,4,6-heptatriene. To a solution of (2*E*,4*E*,6*E*)-4,6-dimethyl-7-iodo-2,4,6-heptatrien-1-ol (330 mg, 1.25 mmol) in DMF (6 mL) was introduced sequentially imidazole (170 mg, 2.50 mmol) and *ter*-butyldimethylsilyl chloride (281 mg, 1.88 mmol). After stirring at 23 °C for 3 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, Et_2O/hexanes 1:24) afforded the title compound (429 mg, 91%) as oil. ^{1}H NMR (300 MHz, benzene-d_6) δ 0.08 (s, 6 H), 0.99 (s, 9 H), 1.62 (s, 3 H), 1.77 (s, 3 H), 4.14 (d, *J* = 4.1 Hz, 2 H), 5.65-5.75 (m, 2 H), 5.95 (s, 1 H), 6.28 (d, *J* = 15.5 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.63, 14.58, 18.92, 25.64, 26.54, 64.30, 81.68, 130.03, 131.66, 134.48, 135.61, 145.00 ppm; HREI-MS *m/z* ($[M]^+$) 378.0881; calcd. 378.0876.



(2*E*,4*E*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-1,13,15-Tri(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaene. To a solution of (2*E*,4*E*,6*E*)-1-(*tert*-butyldimethylsiloxy)-4,6-dimethyl-7-iodo-2,4,6-heptatriene (430 mg, 1.14 mmol) in Et$_2$O (3 mL) was added *t*BuLi (1.33 mL, 1.7 M in pentane, 2.3 mmol) slowly (5 min) at -78 °C. The resultant solution was stirred for 30 min at -78 °C. To this was added *via* cannula a solution of dry ZnBr$_2$ (256 mg, 1.1 mmol) in THF (3mL). The mixture thus obtained was stirred for 15 min at -78 °C and then warmed to 23 °C over 30 min. To this reaction mixture was added a solution of (5S,6S,8S)-6,8-bis-(*tert*-butyldimethylsiloxy)-1-iodo-5-methoxymethoxy-3-methyl-1,3-nonadiene (514 mg, 0.88 mmol) and Cl$_2$Pd(DPEphos) (36 mg, 0.05 mmol) in DMF (3 mL) *via* cannula at 23 °C. After stirring at 23 °C for 8 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over MgSO$_4$, filtered, and concentrated. Flash chromatography (silica gel, pure hexanes–98:2 hexanes/ethyl acetate) afforded the title compound (456 mg, 73%). $[\alpha]_D^{23}$ +32° (c 3.3, CH$_2$Cl$_2$); IR (neat) 2928, 2857, 1472, 1387, 1256, 1032, 961, 834, 774 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d$_6$) δ 0.11 (s, 6 H), 0.15 (s, 3 H), 0.17 (s, 3 H), 0.20 (s, 3 H), 0.24 (s, 3 H), 1.01 (s, 9 H), 1.02 (s, 9 H), 1.05 (s, 9 H), 1.24 (d, *J* = 5.9 Hz, 3 H), 1.92 (s, 3 H), 1.94 (s, 3 H), 1.95-2.1 (m, 2 H), 3.22 (s, 3 H), 4.0-4.05 (m, 1 H), 4.2-4.25 (m, 3 H), 5.80 (td, *J* = 5.2, 15.2 Hz, 1 H), 1.84 (s, 3 H), 4.46 (d, *J* = 7.0 Hz, 1 H), 4.62 (dd, *J* = 5.3, 9.4 Hz, 1 H), 4.72 (d, *J* =6.5 Hz, 1 H), 5.60 (d, *J* = 9.9 Hz, 1 H), 6.05 (s, 1 H), 6.21 (d, *J* = 11.1 Hz, 1 H), 6.36 (d, *J* = 15.2 Hz, 1 H), 6.60 (dd, *J* = 11.1, 14.6 Hz, 1 H), 6.48 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d$_6$) δ -4.60, -3.98, -3.66, -3.43, 13.80, 15.04, 17.96, 18.66, 18.84, 18.96, 24.58, 26.54, 26.64, 44.93, 55.72, 64.62, 66.50, 73.25, 75.14, 94.27, 125.90, 128.59, 129.98, 132.37, 134.48, 135.86, 136.22, 136.34, 137.95, 139.62 ppm; HRESI-MS *m/z* ([M+Na]$^+$) 731.4900; calcd. 731.4898.

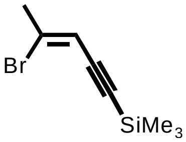


(2*E*,4*E*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-Bi(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaen-1-ol. To a solution of (2*E*,4*E*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-1,13,15-Tri(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaene (270 mg, 0.38 mmol) in THF (7 mL) was added TBAF (0.7 mL, 1M solution in THF, 0.7 mmol) slowly and the reaction was monitored by TLC. After stirring at 23 °C for 2 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 12:1 – 6:1 hexanes/ethyl acetate) afforded the title compound (185 mg, 82%) as oil. $[\alpha]_D^{23}$ +40° (c 1.7, CH_2Cl_2); IR (neat) 3400, 2929, 2857, 1472, 1386, 1255, 1096, 962, 834 cm^{-1};^{1}H NMR (300 MHz, benzene-d_6) δ 0.17 (s, 3 H), 0.19 (s, 3 H), 0.22 (s, 3 H), 0.27 (s, 3 H), 1.04 (s, 9 H), 1.08 (s, 9 H), 1.26 (d, *J* = 5.9 Hz, 3 H), 1.89 (s, 3 H), 1.94 (s, 3 H), 1.96 (s, 3 H), 2.0-2.1 (m, 2 H), 3.25 (s, 3 H), 4.0-4.05 (m, 3 H), 4.22 (sextet, *J* = 6.4 Hz, 1 H), 4.49 (d, *J* = 7.5 Hz, 1 H), 4.64 (dd, *J* = 5.3, 10.0 Hz, 1 H), 4.74 (d, *J* = 7.0 Hz, 1 H), 5.63 (d, *J* = 9.4 Hz, 1 H), 5.73 (td, *J* = 5.9, 15.2 Hz, 1 H), 6.06 (s, 1 H), 6.25 (d, *J* =11.1 Hz, 1 H), 6.33 (d, *J* = 15.8 Hz, 1 H), 6.41 (d, *J* =15.2 Hz, 1 H), 6.64 (dd, *J* = 11.2, 15.3 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.01, -3.67, -3.46, 13.78, 14.97, 17.94, 18.64, 18.81, 24.54, 26.51, 26.61, 44.89, 55.71, 63.98, 66.50, 73.22, 75.14, 94.27, 125.84, 128.69, 130.04, 132.45, 134.37, 135.83, 136.45, 137.13, 137.64, 139.57 ppm; HRESI-MS *m/z* ($[M+Na]^+$) 617.4030; calcd. 617.4034.

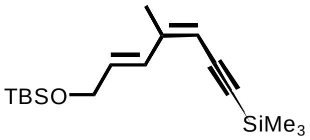


(2*E*,4*E*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-Bi(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaenoic acid. Starting material (2*E*,4*E*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-bi(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaen-1-ol (85 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (5 mL) followed by the introduction of $NaHCO_3$ (120 mg, 1.4 mmol) and Dess-Martin periodinane (130 mg, 0.30 mmol) with exclusion of light. After 20 min, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. This crude product was dissolved in *t*BuOH (3 mL), H_2O (1.5 mL) and 2-methyl-2-butene (1.5 mL) followed by the addition of NaH_2PO_4 (150 mg, 1.3 mmol) and $NaClO_2$ (60 mg, 0.66 mmol) with exclusion of light. After stirring at 23 °C for 6 h, the reaction mixture was quenched with NH_4Cl (sat.), extracted with EtOAc, washed with brine, dried over $MgSO_4$, filtered, and concentrated.

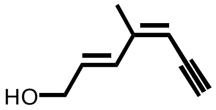
Flash chromatography (silica gel, 2:1–3:2 hexanes/ethyl acetate) afforded the title compound (67 mg, 77% over two steps) as oil. $[\alpha]_D^{23}$ +33° (c 6.6, CH_2Cl_2); IR (neat) 2955, 2930, 2857, 1683, 1609, 1256, 1029, 836, 775 cm^{-1}. ^1H NMR (300 MHz, benzene-d_6) δ 0.17 (s, 3 H), 0.19 (s, 3 H), 0.22 (s, 3 H), 0.26 (s, 3 H), 1.04 (s, 9 H), 1.08 (s, 9 H), 1.26 (d, J = 6.0 Hz, 3 H), 1.67 (s, 3 H), 1.73 (s, 3 H), 1.92 (s, 3 H), 1.9-2.1 (m, 2 H), 3.24 (s, 3 H), 4.05 (q, J = 6.1 Hz, 1 H), 4.22 (sextet, J = 6.0 Hz, 1 H), 4.49 (d, J = 6.6 Hz, 1 H), 4.64 (dd, J = 5.3, 9.8 Hz, 1 H), 4.72 (d, J = 6.6 Hz, 1 H), 5.68 (d, J = 9.8 Hz, 1 H), 6.48 (d, J =15.4 Hz, 1 H), 6.1-6.15 (m, 2 H), 6.40 (d, J =15.2 Hz, 1 H), 6.52 (dd, J = 10.9, 15.1 Hz, 1 H), 7.68 (d, J = 15.4 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.00, -3.66, -3.48, 13.74, 14.29, 17.19, 18.66, 18.82, 24.53, 26.51, 26.59, 44.87, 55.71, 66.49, 73.17, 75.15, 94.37, 116.55, 125.33, 131.46, 133.05, 135.22, 136.09, 139.37, 139.68, 145.06, 153.51, 173.61 ppm; HRMS(ESI) calcd. for $C_{33}H_{60}O_6Si_2Na$ $[M+Na]^+$ 631.3826, found 631.3828.



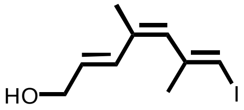
(Z)-1-Trimethylsilyl-4-bromo-3-penten-1-yne. To a mixture of 4-trimethylsilyl-1,1-dibromo-1-buten-3-yne[c] (1.49 g, 5.3 mmol) and $Cl_2Pd(DPEphos)$ (189 mg, 0.26 mmol) in THF (15 mL) and DMF (15 mL) was added Me_2Zn (1.7 mL, 2.0 M in toluene, 3.4 mmol) at 23 °C. The resultant mixture was stirred at 23 °C and monitored by GLC. After 2 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, pure hexanes) afforded the title compound (805 mg, 70%) as liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 2.34 (s, 3 H), 5.89 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.015, 28.87, 99.63, 101.91, 111.44, 134.77 ppm; HREI-MS m/z ($[M]^+$) 215.9968; calcd. 215.9970.



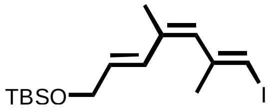
(3*Z*,5*E*)-7-(*tert*-Butyldimethylsiloxy)-1-trimethylsily-3,5-heptadien-1-yne. To a solution of (*E*)-1-(*tert*-butyldimethylsiloxy)-3-iodo-2-propene[d] (2.23g, 7.5 mmol) in Et_2O (7.5 mL) was added *t*BuLi (8.60 mL, 1.7 M in pentane, 14.6 mmol) slowly (~15 min) at -78 °C. The resultant solution was stirred for 30 min at -78 °C. To this was added *via* cannula a solution of dry $ZnBr_2$ (1.69 g, 7.5 mmol) in THF (7.5 mL). The mixture thus obtained was stirred for 15 min at -78 °C and then warmed to 23 °C over 30 min. To this reaction mixture was added a solution of (*Z*)-1-trimethylsilyl-4-bromo-3-penten-1-yne (805 mg, 3.7 mmol) and Cl_2Pd(DPEphos) (134 mg, 0.19 mmol) in DMF (7.5 mL) *via* cannula at 23 °C. The reaction mixture was then warmed to 45 °C. After stirring at 45 °C for 8 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, pure hexanes – 99:1 hexanes/EtOAc) afforded the title compound (941 mg, 82%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6 H), 0.20 (s, 9 H), 0.94 (s, 9 H), 1.89 (s, 3 H), 4.34 (d, *J* = 4.1 Hz, 2 H), 5.40 (s, 1 H), 5.94 (td, *J* = 4.7, 15.2 Hz, 1 H), 6.99 (d, *J* = 15.3 Hz, 1 H); ^{13}C NMR (75MHz, $CDCl_3$) δ -5.00, 0.26, 18.59, 19.59, 26.20, 63.77, 99.58, 102.76, 108.40, 128.12, 132.73, 146.38 ppm; HREI-MS *m/z* ($[M]^+$) 308.1996; calcd. 308.1992.



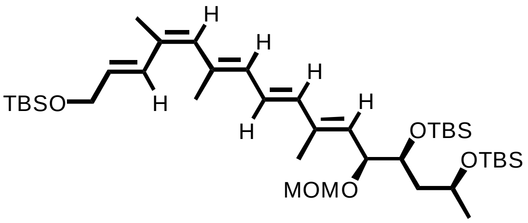
(2*E*,3*Z*)-2,3-Heptandien-6-yn-1-ol. To a solution of (3*Z*, 5*E*)-7-(*tert*-butyldimethylsiloxy)-1-trimethylsily-3,5-heptadien-1-yne (941 mg, 3.1 mmol) in THF (7 mL) was added TBAF (6.20 mL, 1.0 M in THF, 6.2 mmol) at 23 °C. After stirring for 2 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, Et_2O/pentane 1:4 – 1:3) afforded the title compound (305 mg, 81%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (s, 3 H), 3.01 (brs, 1 H), 3.19 (d, *J* = 2.3 Hz, 1 H), 4.23 (d, *J* = 5.3 Hz, 2 H), 5.35 (s, 1 H), 5.97 (td, *J* = 5.9, 15,8 Hz, 1 H), 6.91 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.30, 63.21, 81.06, 82.71, 107.70, 129.11, 132.45, 146.95 ppm; HREI-MS *m/z* ($[M]^+$) 122.0734; calcd. 122.0732.



(2*E*,4*Z*,6*E*)-4,6-Dimethyl-7-iodo-2,4,6-heptatrien-1-ol. To a solution of Me_3Al (0.60 mL, 6.2 mmol) in CH_2Cl_2 (5 mL) was introduced (2*E*, 3*Z*)-2,3-heptandien-6-yn-1-ol (305 mg, 2.5 mmol) in CH_2Cl_2 (5 mL) with syringe at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h. To this reaction mixture was then added a solution of Cp_2ZrCl_2 (213 mg, 0.73 mmol) in CH_2Cl_2 (5 mL) via cannula at 0 °C. The reaction mixture was warmed to 23 °C and stirred for 1 h. TLC analysis indicated that the starting material had been completely consumed. To this mixture was added *via* cannula a solution of I_2 (945 mg, 3.7 mmol) in THF (5 mL) at -78 °C. After stirring at -78 °C for 30 min, the reaction mixture was quenched with a mixture of $Na_2S_2O_3$ (sat.) and $NaHCO_3$ (sat.) solution (1:1), extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, EtOAc/hexanes 1:5–1:4) afforded the title compound (455 mg, 69%) as oil. ^1H NMR (300 MHz, benzene-d_6) δ 0.86 (brs, 1H), 1.69 (s, 3 H), 1.79 (s, 3 H), 3.96 (d, *J* = 5.3 Hz, 2 H), 5.51 (s, 1 H), 5.75 (td, *J* = 5.8, 15.6 Hz, 1 H), 6.08 (s, 1 H), 6.69 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 21.24, 25.60, 63.78, 81.93, 128.93, 130.60, 131.82, 134.77, 144.80 ppm; HREI-MS *m/z* ($[M]^+$) 264.0006; calcd. 264.0011.

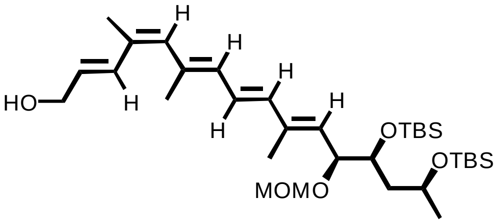


(2*E*,4*Z*,6*E*)-1-(*tert*-Butyldimethylsiloxy)-4,6-dimethyl-7-iodo-2,4,6-heptatriene. To a solution of (2*E*,4*Z*,6*E*)-4,6-dimethyl-7-iodo-2,4,6-heptatrien-1-ol (455 mg, 1.7 mmol) in DMF (13 mL) was introduced imidazole (351 mg, 5.2 mmol) and *ter*-butyldimethylsilyl chloride (517 g, 3.4 mmol). After stirring at 23 °C for 3 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, Et_2O/hexanes 1:24) afforded the title compound (612 mg, 94%) as oil. ^{1}H NMR (300 MHz, benzene-d_6) δ 0.03 (s, 6 H), 0.96 (s, 9 H), 1.69 (s, 3 H), 1.78 (s, 3 H), 4.08 (d, *J* = 4.3 Hz, 2 H), 5.50 (s, 1 H), 5.70 (td, *J* = 4.4, 15.7 Hz, 1 H), 6.04 (s, 1 H), 6.80 (d, *J* = 15.7 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.67, 18.95, 21.23, 25.57, 26.63, 64.01, 81.52, 127.63, 130.12, 131.75, 134.79, 144.82, ppm; HREI-MS *m/z* ($[M]^+$) 378.0870; calcd. 378.0876.

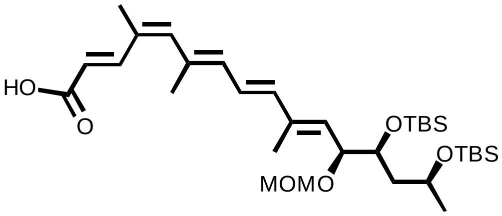


(2*E*,4*Z*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-1,13,15-Tri(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaene. To a solution of (2*E*,4*Z*,6*E*)-1-(*t*-butyldimethylsiloxy)-4,6-dimethyl-7-iodo-2,4,6-heptatriene (250 mg, 0.66 mmol) in Et_2O (2 mL) was added *t*BuLi (0.78 mL, 1.7 M in pentane, 1.3 mmol) slowly (5 min) at -78 °C. The resultant solution was stirred for 30 min at -78 °C. To this was added *via* cannula a solution of dry $ZnBr_2$ (149 mg, 0.66 mmol) in THF (2 mL). The mixture thus obtained was stirred for 15 min at -78 °C and then warmed to 23 °C over 30 min. To this reaction mixture was added a solution of (5S,6S,8S)-6,8-bi(*tert*-butyldimethylsiloxy)-1-iodo-5-methoxymethoxy-3-methyl-1,3-nonadiene (270 mg, 0.46 mmol) and $Cl_2Pd(DPEphos)$ (16 mg, 0.022 mmol) in DMF (2 mL) *via* cannula at 23 °C. After stirring at 23 °C for 8 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, pure hexanes – 98:2 hexanes/ethyl acetate) afforded the title compound (231 mg, 71%) as oil. $[\alpha]_D^{23}$ +35° (c 2.8, CH_2Cl_2); IR (neat) 3045, 2955, 2930, 2857, 1683, 1609, 1256, 1029, 836, 775 cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.07 (s, 6 H), 0.14 (s, 3 H), 0.16 (s, 3 H), 0.19 (s, 3 H), 0.23 (s, 3 H), 1.00 (s, 9 H), 1.01 (s, 9 H), 1.04 (s, 9 H), 1.23 (d, *J* = 5.9 Hz, 3 H), 1.87 (s, 6 H), 1.82 (s, 3 H), 1.95-2.05 (m, 2 H), 3.21 (s, 3 H), 4.0-4.05 (m, 1 H), 4.20-4.25 (m, 3 H), 4.45 (d, *J* = 6.4 Hz, 1 H), 4.61 (dd, *J* = 5.3, 9.4 Hz, 1 H), 4.71 (d, *J* =6.4 Hz, 1 H), 5.55 (d, *J* = 10.0 Hz, 1 H), 5.88 (s, 1 H), 5.80 (td, *J* = 4.7, 15.8 Hz, 1 H), 6.3-6.4 (m, 2 H), 6.61 (dd, *J* = 11.1, 14.6 Hz, 1 H), 7.17

(d, J = 15.8 Hz, 1 H); ^{13}C NMR (75MHz, benzene-d$_6$) δ -4.68, -3.98, -3.66, -3.42, 13.81, 18.22, 18.68, 18.84, 22.16, 24.57, 26.54, 26.66, 44.93, 55.71, 64.30, 66.50, 73.25, 75.10, 94.21, 125.93, 128.63, 129.70, 130.77, 131.97, 133.49, 134.22, 135.56, 137.53, 139.69 ppm; HRESI-MS *m/z* ([M+Na]$^+$) 731.4884; calcd. 731.4898.



(2*E*,4*Z*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-Bi(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaen-1-ol. To a solution of (2*E*,4*Z*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-1,13,15-tri(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaene (110 mg, 0.16 mmol) in THF (3 mL) was added TBAF (0.35 mL, 1 M solution in THF, 0.35 mmol) slowly and the reaction was monitored by TLC. After stirring at 23 °C for 2 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 12:1 – 6:1 hexanes/ethyl acetate) afforded the title compound (84 mg, 88%) as oil. $[\alpha]_D^{23}$ +44° (c 1.2, CH_2Cl_2); IR (neat) 3421, 2954, 2930, 2886, 2857, 1472, 1463, 1361, 1256, 1096, 1031, 940, 836, 775 cm^{-1}; ^{1}H NMR (300MHz, benzene-d$_6$) δ 0.13 (s, 3 H), 0.16 (s, 3 H), 0.18 (s, 3 H), 0.23 (s, 3 H), 1.01 (s, 9 H), 1.04 (s, 9 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.84 (s, 3 H), 1.85 (s, 3 H), 1.91 (s, 3 H), 1.95-2.05 (m, 2 H), 3.20 (s, 3 H), 3.91 (brs, 2 H), 4.00 (q, J = 5.9 Hz, 1 H), 4.19 (hex, J = 6.4 Hz, 1 H), 4.43 (d, J = 7.1 Hz, 1 H), 4.6-4.65 (m, 1 H), 4.68 (d, J = 6.4 Hz, 1 H), 5.53 (d, J = 9.4 Hz, 1 H), 5.72 (td, J = 5.8, 15.9 Hz, 1 H), 5.90 (s, 1 H), 6.26 (d, J =11.2 Hz, 1 H), 6.36 (d, J =15.2 Hz, 1 H), 6.60 (dd, J = 11.1, 14.8 Hz, 1 H), 6.98 (d, J = 15.8 Hz, 1 H); ^{13}C NMR (75MHz, benzene-d$_6$) δ -3.67, -3.46, -4.01, 13.78, 18.18, 18.66, 18.82, 22.14, 24.55, 26.53, 26.62, 44.91, 55.71, 64.04, 66.50, 73.23, 75.13, 94.23, 125.86, 129.81, 129.99, 130.98, 132.13, 133.33, 134.65, 135.56, 137.53, 139.55 ppm; HRESI-MS *m/z* ([M+Na]$^+$) 617.4024; calcd. 617.4034.



(2*E*,4*Z*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-Bi(*tert*-butyl-dimethyl-siloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaenoic acid. Starting material (2*E*,4*Z*,6*E*,8*E*,10*E*,12*S*,13*S*,15*S*)-13,15-bi(*tert*-butyldimethylsiloxy)-12-methoxymethoxy-4,6,10-trimethyl-2,4,6,8,10-hexadecapentaen-1-ol (65 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (3 mL) followed by the introduction of $NaHCO_3$ (88 mg, 1.05 mmol) and Dess-Martin periodinane (89 mg, 0.21 mmol) with exclusion of light. After 20 min, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. This crude product was dissolved in *t*BuOH (2 mL), H_2O (1 mL) and 2-methyl-2-butene (1 mL) followed by the addition of NaH_2PO_4 (60 mg, 0.5 mmol) and $NaClO_2$ (40 mg, 0.44 mmol) with exclusion of light. After stirring at 23 °C for 6 h, the reaction mixture was quenched with NH_4Cl (sat.), extracted with EtOAc, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 2:1 – 3:2 hexanes/ethyl acetate) afforded the title compound (49 mg, 73% over two steps) as oil. $[\alpha]_D^{23}$ +26° (c 3.5, CH_2Cl_2); IR (neat) 2955, 2957, 2887, 1685, 1606, 1255, 1097, 1033, 835, 775 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 0.14 (s, 3 H), 0.17 (s, 3 H), 0.20 (s, 3 H), 0.24 (s, 3 H), 1.01 (s, 9 H), 1.05 (s, 9 H), 1.23 (d, *J* = 6.4 Hz, 3 H), 1.63 (s, 3 H), 1.78 (s, 3 H), 1.87 (s, 3 H), 1.9-2.0 (m, 2 H), 3.32 (s, 3 H), 3.97 (sextet, *J* = 5.9 Hz, 1 H), 4.00 (q, *J* = 6.5 Hz, 1 H), 4.39 (dd, *J* = 4.6, 10.0 Hz, 1 H), 4.49 (d, *J* = 6.5 Hz, 1 H), 4.60 (d, *J* = 7.0 Hz, 1 H), 5.58 (d, *J* = 9.4 Hz, 1 H), 5.95-6.0 (m, 2 H), 6.13 (d, *J* = 10.6 Hz, 1 H), 6.35 (d, *J* = 15.2 Hz, 1 H), 6.47 (dd, *J* = 10.5, 15.2, Hz, 1 H), 8.29 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR (75 MHz, benzene-d_6) δ -4.00, -3.65, -3.48, 13.71, 17.65, 18.68, 18.82, 21.27, 24.61, 26.53, 26.62, 44.96, 55.72, 66.50, 73.20, 75.18, 94.51, 118.71, 125.38, 131.38, 131.66, 135.01, 135.53, 139.30, 139.54, 142.83, 145.25, 173.52 ppm; HRMS(ESI) calcd. for $C_{33}H_{60}O_6Si_2Na$ $[M+Na]^+$ 631.3826, found 631.3848.

References:

[a] X. Zeng, Q. Hu, M. Qian, E.-i. Negishi, *J. Am. Chem. Soc.* **2003**, *125*, 13636-13637.

[b] C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 2719-2724.

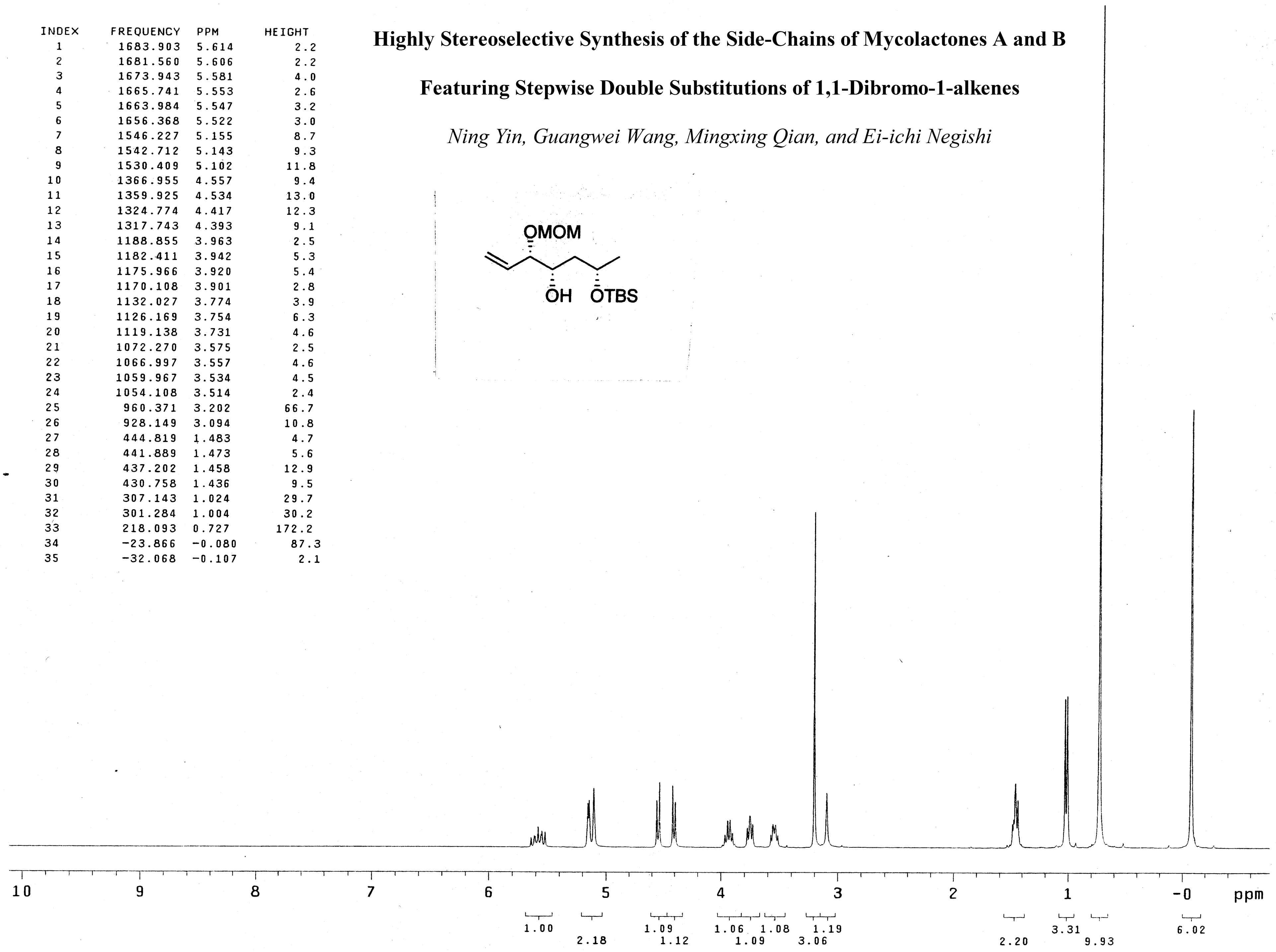
[c] J. Uenishi, R. Kawahama, O. Yonemitsu, J. Tsuji, *J. Org. Chem.* **1996**, *61*, 5716-5717.

[d] C. Xu, E.-i. Negishi, *Tetrahedron Lett.* **1999**, *40*, 431-434.

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

INDEX	FREQUENCY	PPM	HEIGHT
1	1683.903	5.614	2.2
2	1681.560	5.606	2.2
3	1673.943	5.581	4.0
4	1665.741	5.553	2.6
5	1663.984	5.547	3.2
6	1656.368	5.522	3.0
7	1546.227	5.155	8.7
8	1542.712	5.143	9.3
9	1530.409	5.102	11.8
10	1366.955	4.557	9.4
11	1359.925	4.534	13.0
12	1324.774	4.417	12.3
13	1317.743	4.393	9.1
14	1188.855	3.963	2.5
15	1182.411	3.942	5.3
16	1175.966	3.920	5.4
17	1170.108	3.901	2.8
18	1132.027	3.774	3.9
19	1126.169	3.754	6.3
20	1119.138	3.731	4.6
21	1072.270	3.575	2.5
22	1066.997	3.557	4.6
23	1059.967	3.534	4.5
24	1054.108	3.514	2.4
25	960.371	3.202	66.7
26	928.149	3.094	10.8
27	444.819	1.483	4.7
28	441.889	1.473	5.6
29	437.202	1.458	12.9
30	430.758	1.436	9.5
31	307.143	1.024	29.7
32	301.284	1.004	30.2
33	218.093	0.727	172.2
34	-23.866	-0.080	87.3
35	-32.068	-0.107	2.1



INDEX	FREQUENCY	PPM	HEIGHT
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2	8962.479	118.826	43.7
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4	6040.421	80.085	47.0
5	5839.768	77.425	7.5
6	5807.724	77.000	7.7
7	5775.681	76.575	7.3
8	5391.159	71.477	46.9
9	5083.695	67.401	46.6
10	4150.620	55.030	39.6
11	3129.807	41.496	44.2
12	1920.548	25.463	154.0
13	1765.671	23.410	48.6
14	1323.166	17.543	31.2
15	-349.960	-4.640	38.3
16	-389.633	-5.166	37.4

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

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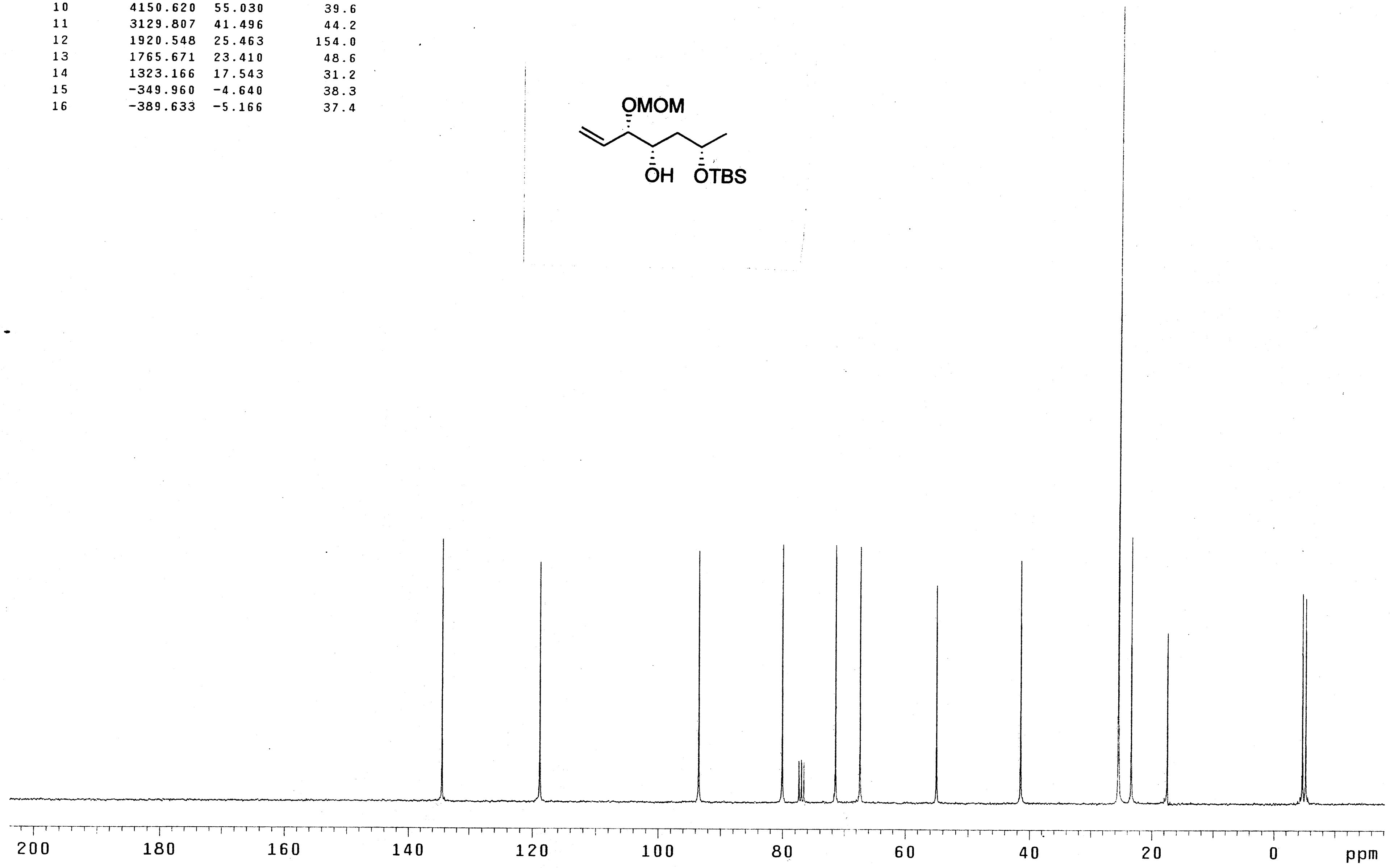

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  4    1394.490   4.649    12.3
  5    1368.127   4.561    11.0
  6    1361.097   4.538     8.1
  7    1283.178   4.278     4.3
  8    1279.663   4.266     4.8
  9    1274.390   4.249     4.4
 10    1270.875   4.237     4.6
 11    1177.138   3.924     2.8
 12    1171.865   3.907     4.0
 13    1168.936   3.897     3.8
 14    1164.835   3.883     4.2
 15    1162.492   3.875     3.6
 16    1159.562   3.866     2.6
 17    1002.553   3.342    63.6
 18     559.646   1.866     3.1
 19     553.788   1.846     2.5
 20     552.030   1.840     2.7
 21     546.757   1.823     2.2
 22     501.647   1.672     2.3
 23     495.788   1.653     2.6
 24     494.030   1.647     2.6
 25     488.172   1.627     4.0
 26     423.142   1.411     3.2
 27     345.809   1.153    24.8
 28     339.950   1.133    24.2
 29     267.890   0.893   147.4
 30     262.618   0.876   151.2
 31      27.104   0.090     2.4
 32      24.174   0.081    54.5
 33      20.073   0.067    58.0
 34      17.730   0.059    86.4
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Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

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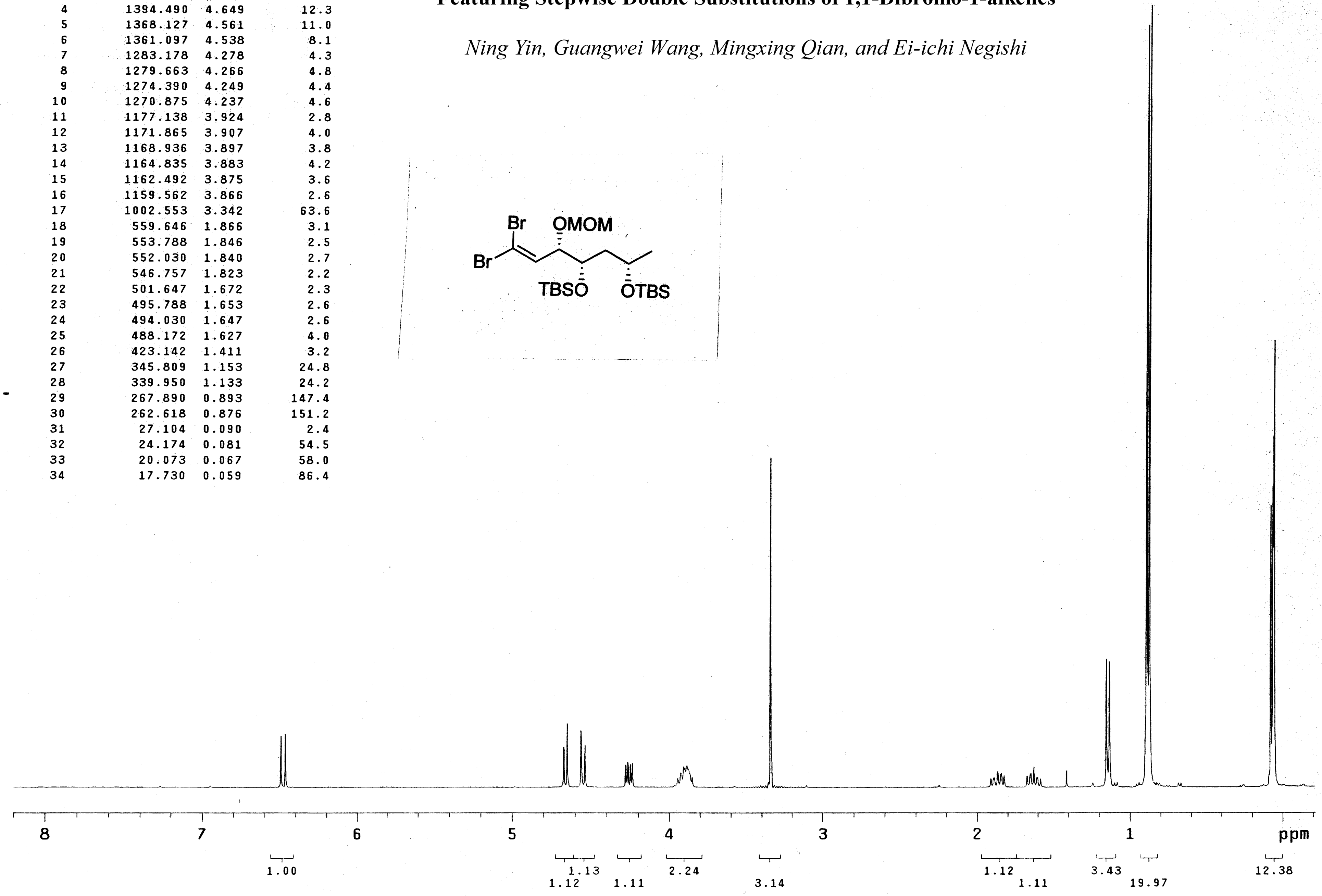

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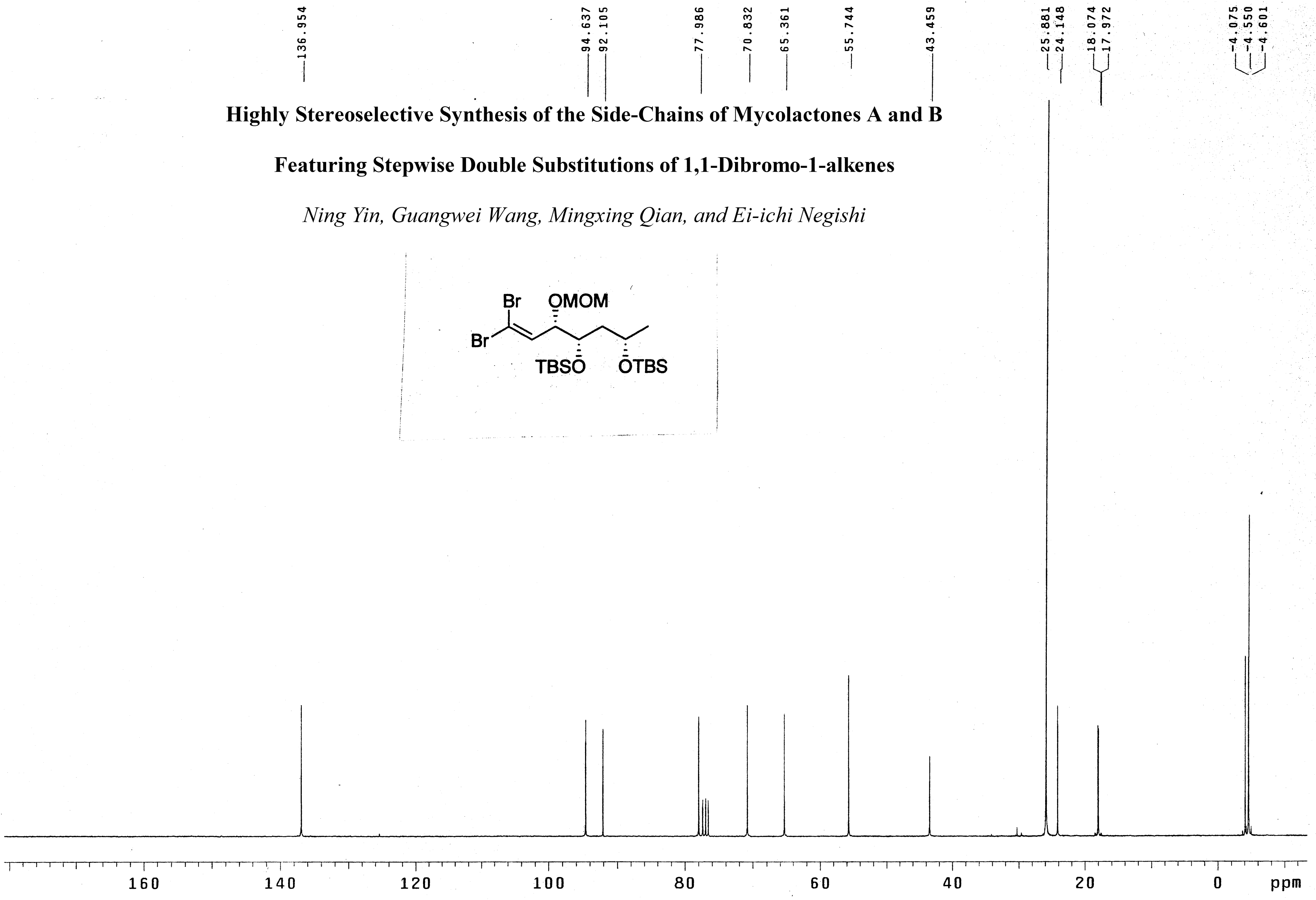

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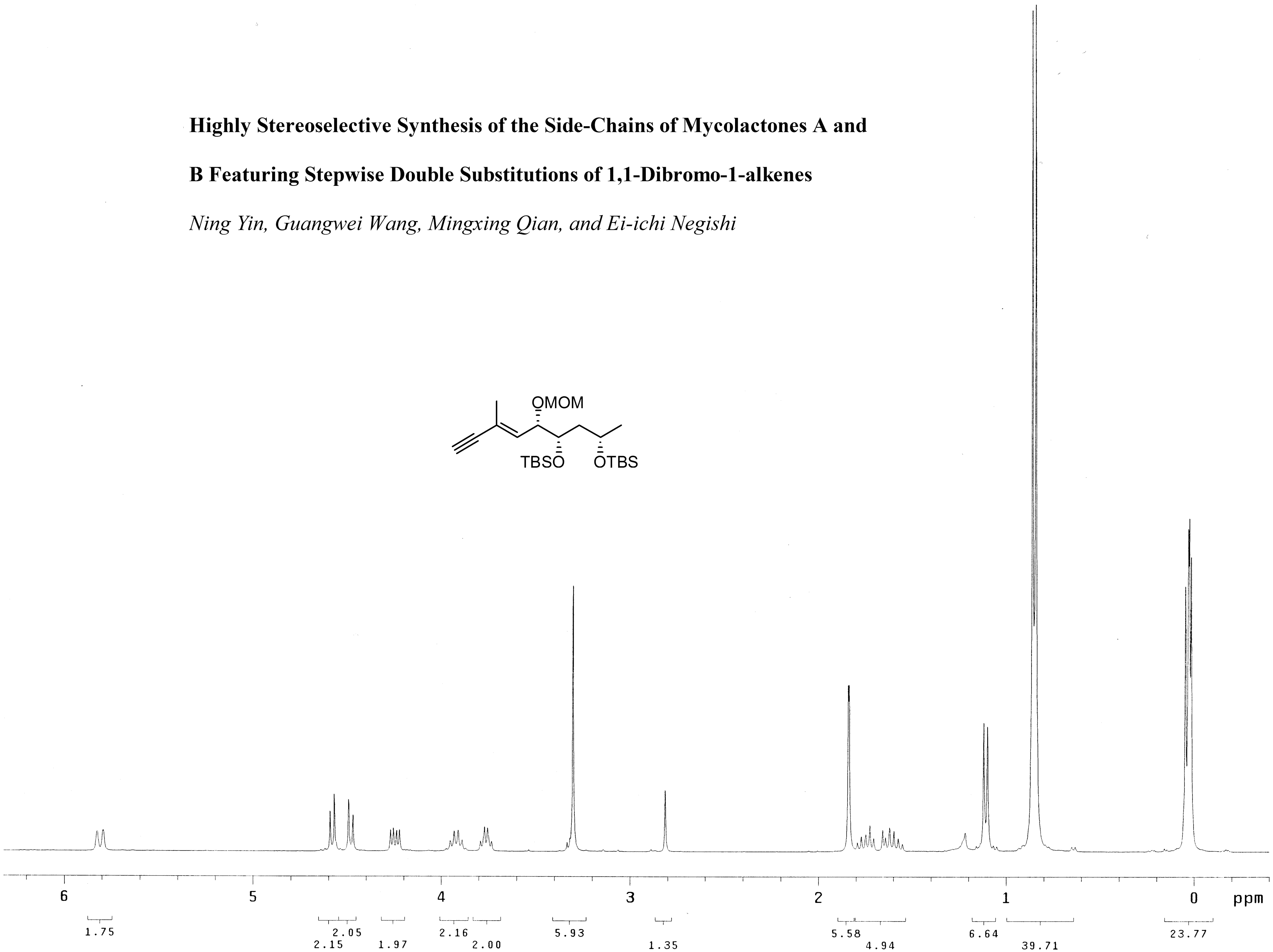

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  3      7105.614    94.208    33.0
  4      6494.831    86.110    14.3
  5      5857.004    77.653    27.5
  6      5825.070    77.230    28.5
  7      5793.135    76.807    27.7
  8      5701.072    75.586    35.1
  9      5571.895    73.873    29.0
 10      5436.102    72.073    33.7
 11      4961.975    65.787    30.7
 12      4207.055    55.778    34.2
 13      3310.300    43.889    31.0
 14      1975.956    26.198   132.0
 15      1968.476    26.098   134.2
 16      1827.216    24.226    38.9
 17      1388.477    18.409    26.4
 18      1378.407    18.275    25.4
 19      1367.763    18.134    31.4
 20      -297.434    -3.943    28.6
 21      -308.079    -4.085    30.4
 22      -335.410    -4.447    44.9
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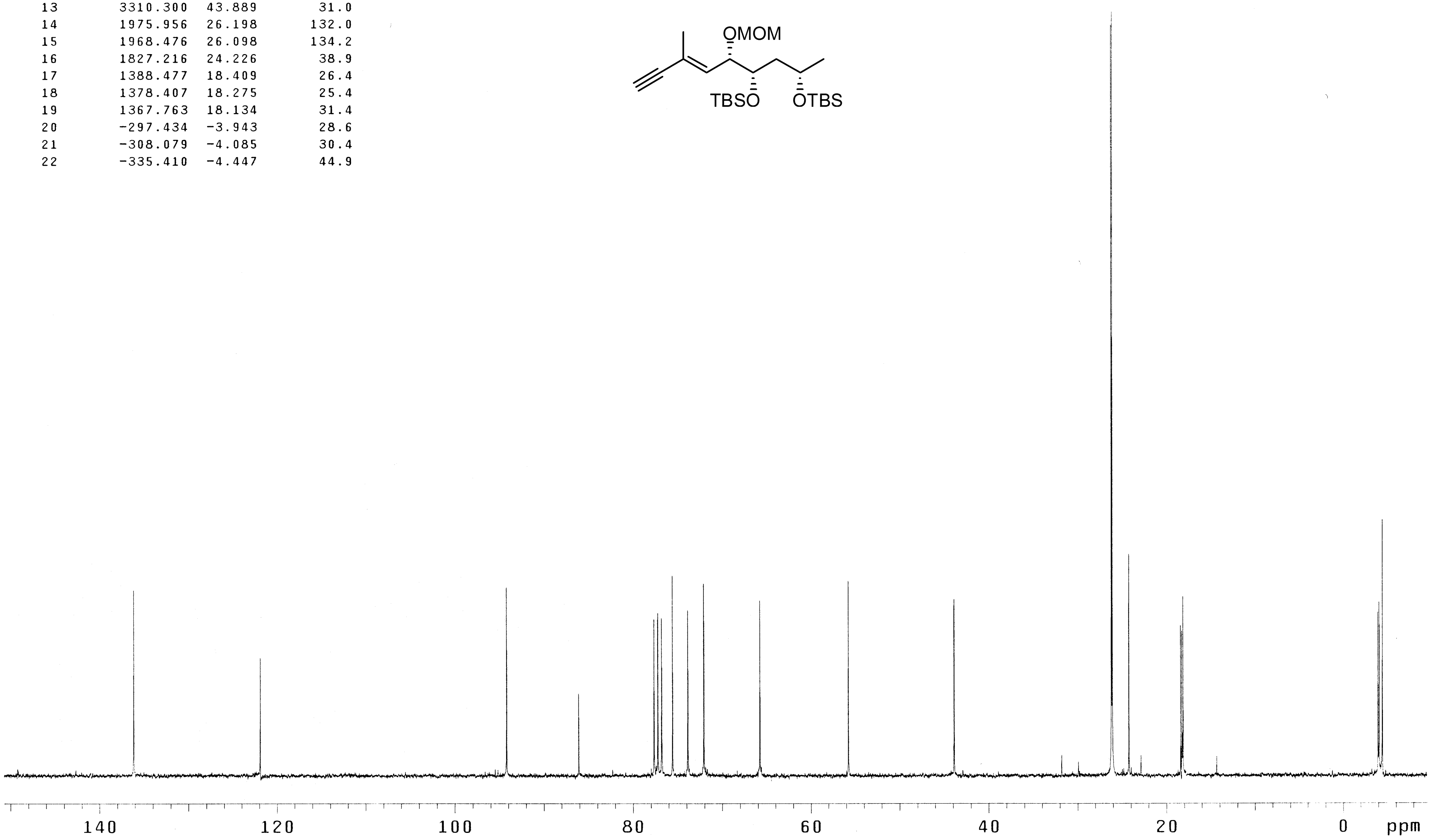

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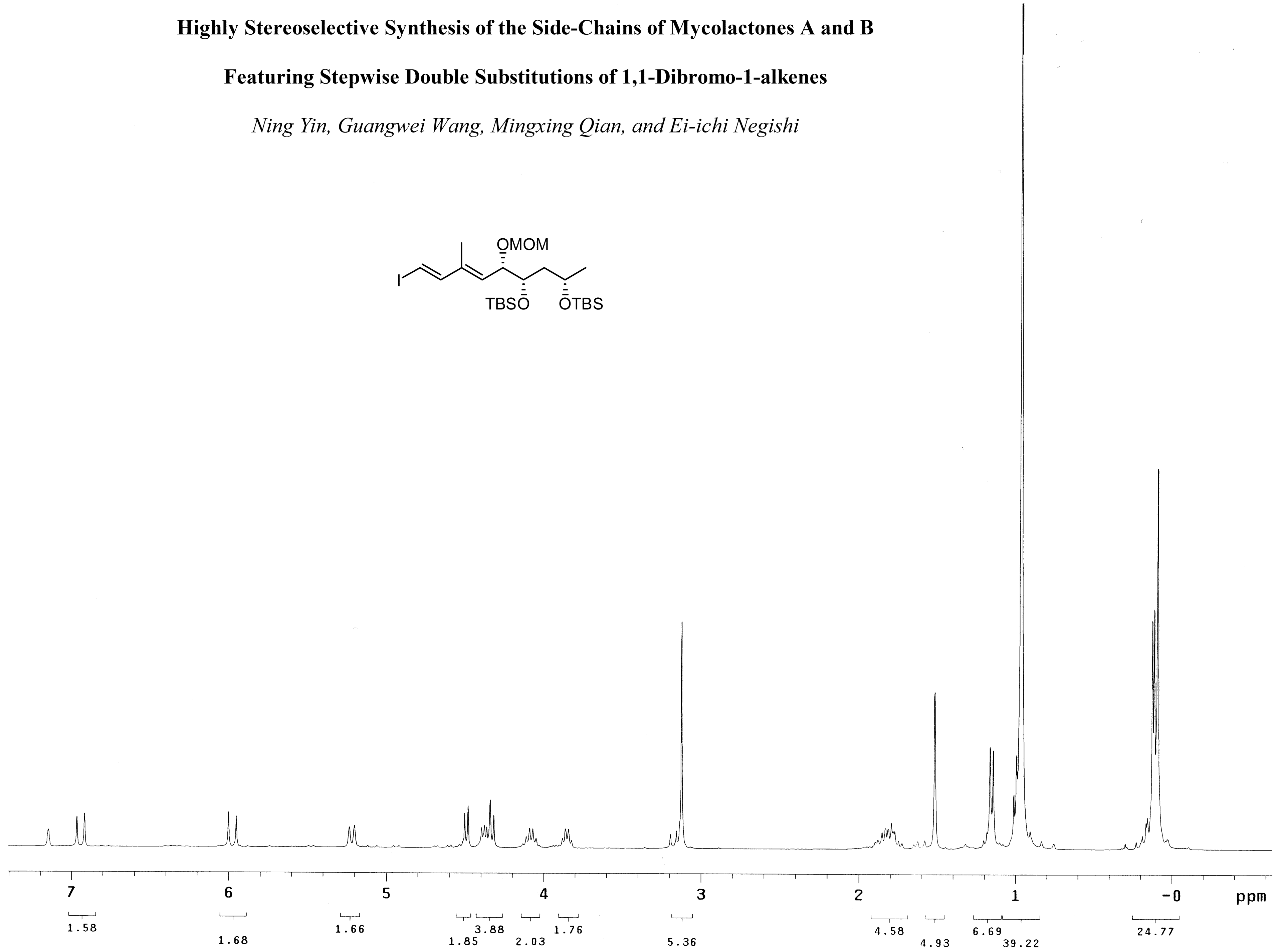

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  4       9707.000   128.698    65.4
  5       9683.806   128.390    64.9
  6       9659.392   128.066    66.7
  7       7109.343    94.257    32.3
  8       5849.578    77.555    28.2
  9       5633.513    74.690    30.0
 10       5495.574    72.862    33.5
 11       5003.630    66.339    30.7
 12       4200.408    55.690    23.8
 13       3367.888    44.652    29.3
 14       2005.584    26.590   104.5
 15       2000.701    26.526   117.9
 16       1849.334    24.519    33.2
 17       1415.984    18.773    17.1
 18       1407.439    18.660    21.7
 19        981.414    13.012    25.5
 20       -263.704    -3.496    20.5
 21       -277.131    -3.674    21.2
 22       -302.766    -4.014    30.9
 23       -305.207    -4.047    28.6
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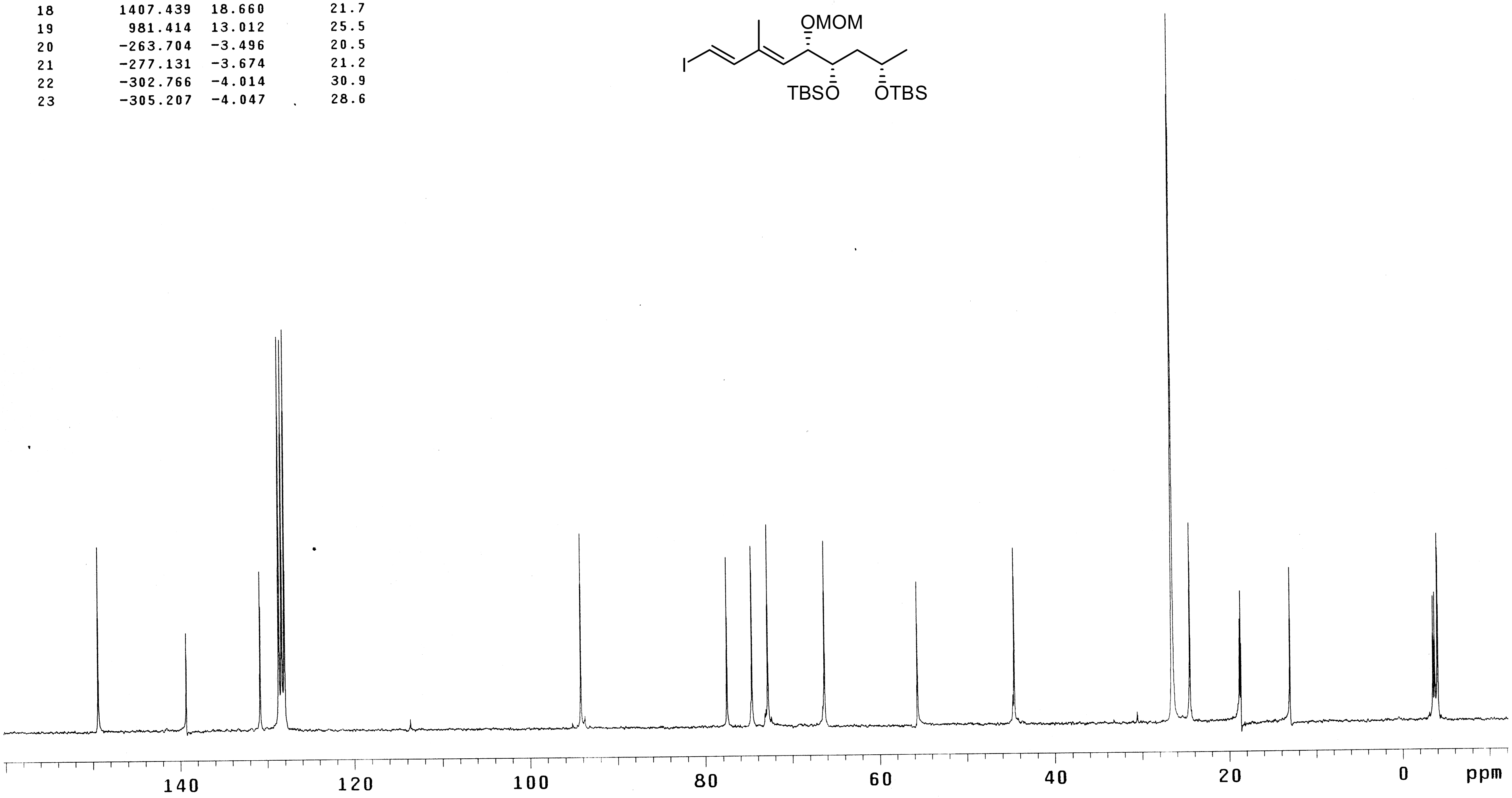
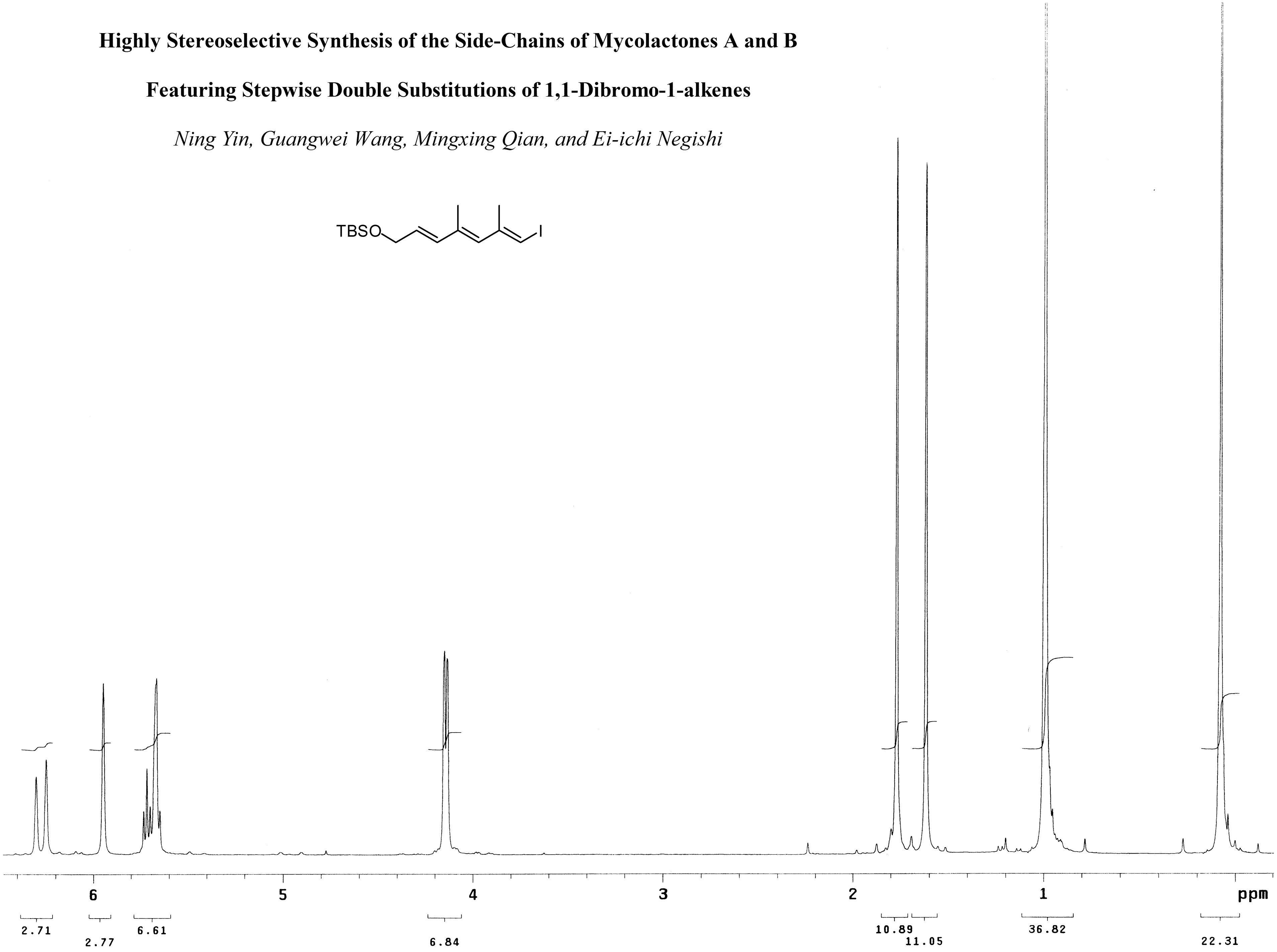


Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

```
INDEX     FREQUENCY   PPM        HEIGHT
  1       10936.248   144.995      17.2
  2       10228.240   135.608      20.8
  3       10142.791   134.475      44.9
  4        9930.388   131.659      38.5
  5        9807.097   130.025      40.7
  6        9707.000   128.698      98.6
  7        9682.586   128.374      98.1
  8        9658.172   128.050      96.8
  9        6160.857   81.682       35.4
 10        4849.822   64.300       46.3
 11        2001.922   26.542      134.7
 12        1933.562   25.636       28.5
 13        1426.970   18.919       21.4
 14        1099.822   14.582       35.1
 15        -349.153   -4.629       50.2
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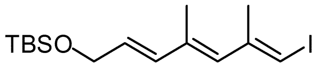

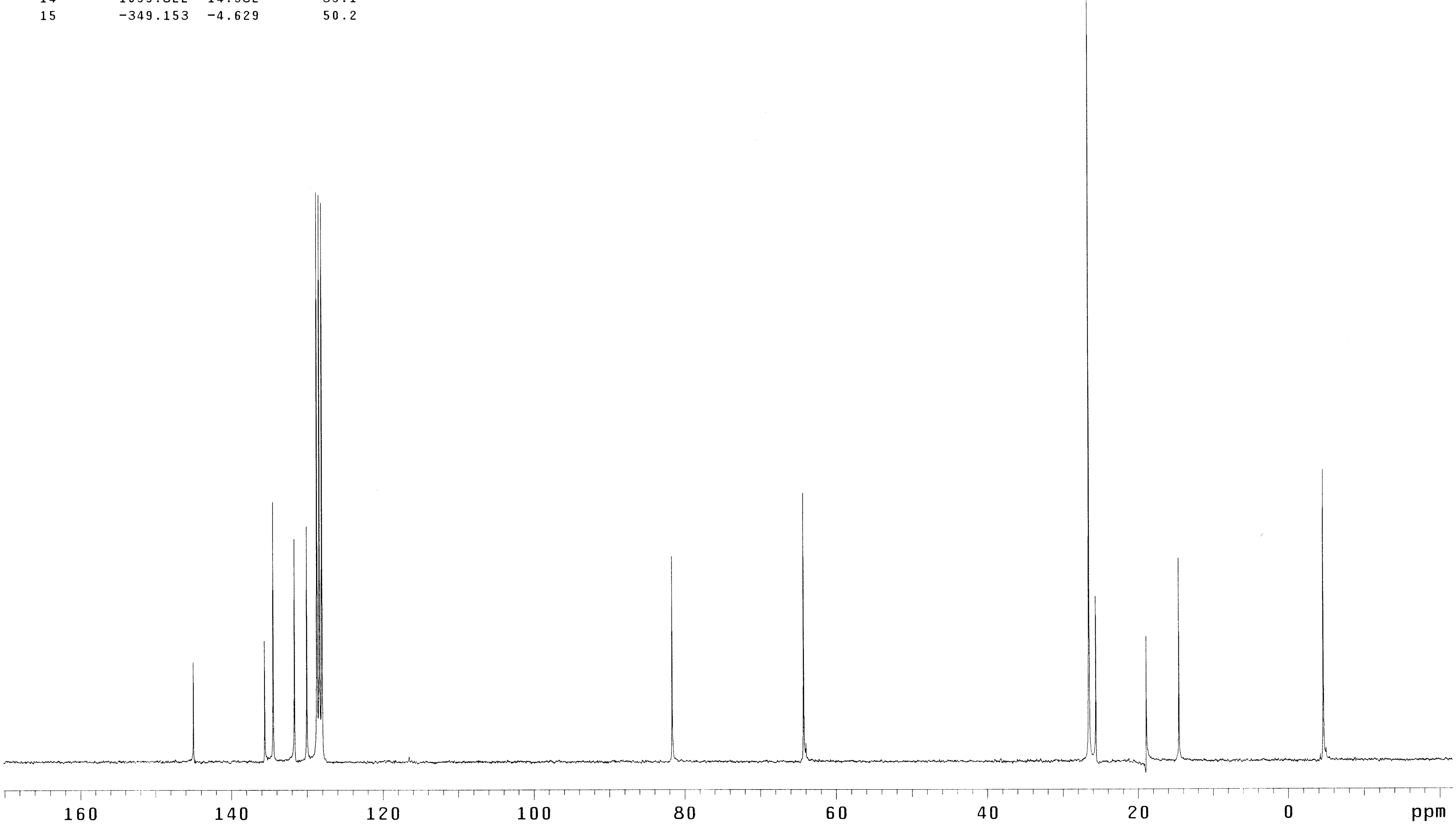

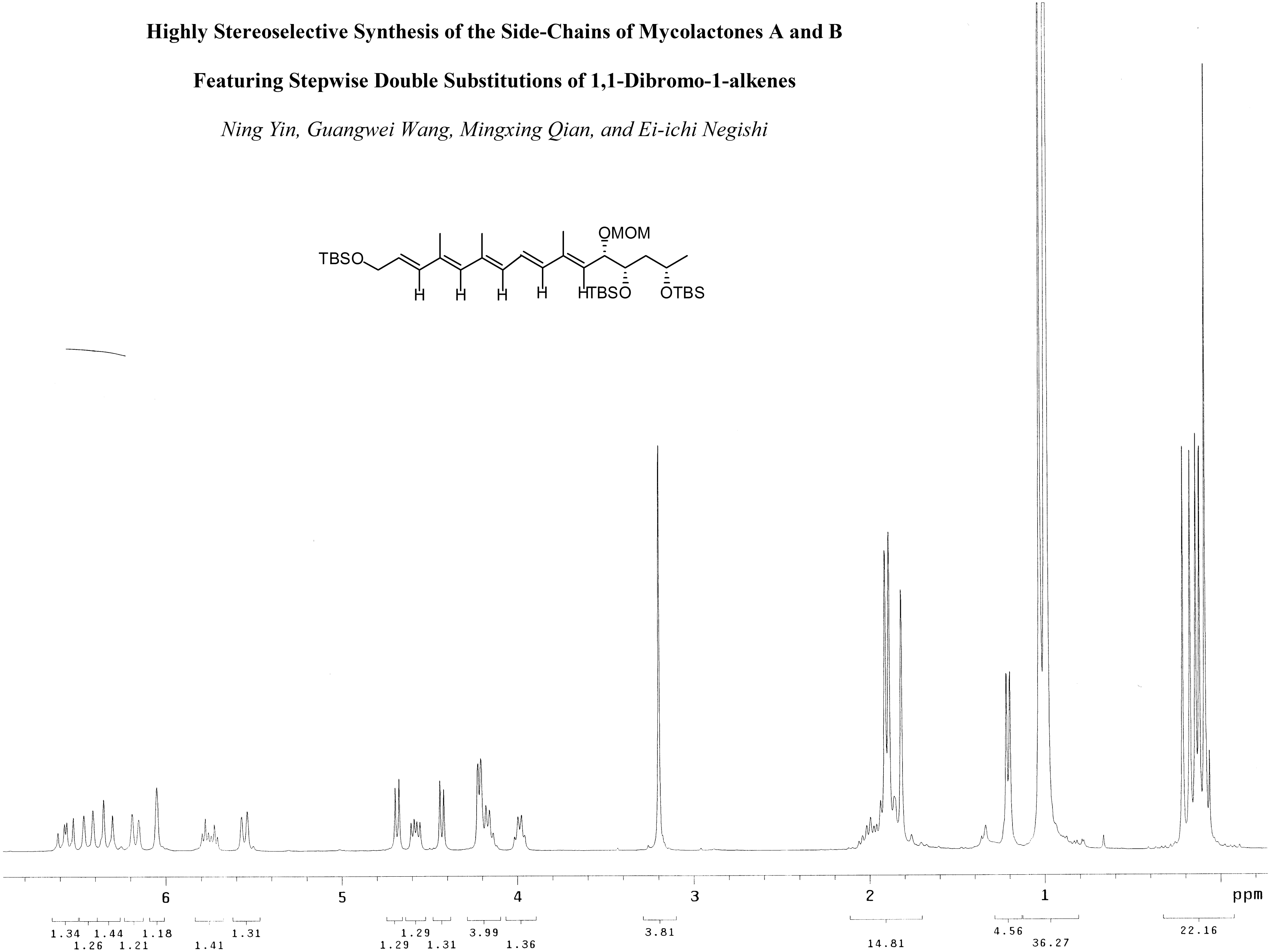
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36.27
22.16

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

```
INDEX     FREQUENCY   PPM       HEIGHT
  1       10530.974   139.622     23.0
  2       10374.724   137.550     39.4
  3       10283.171   136.337     45.3
  4       10274.626   136.223     36.3
  5       10247.771   135.867     23.2
  6       10142.791   134.475     20.3
  7        9984.099   132.371     35.3
  8        9803.435   129.976     32.6
  9        9708.220   128.714    218.8
 10        9683.806   128.390    210.5
 11        9660.613   128.082    207.7
 12        9495.818   125.898     36.7
 13        7110.564   94.273      34.8
 14        5667.693   75.144      37.3
 15        5524.871   73.250      38.5
 16        5015.837   66.501      38.5
 17        4874.236   64.624      40.5
 18        4202.849   55.722      36.2
 19        3388.640   44.927      32.9
 20        2009.246   26.639     128.8
 21        2001.921   26.542     284.1
 22        1854.216   24.584      38.5
 23        1430.632   18.968      24.2
 24        1420.867   18.838      26.2
 25        1407.439   18.660      25.8
 26        1354.949   17.964      31.8
 27        1134.001   15.035      29.4
 28        1041.228   13.805      30.7
 29        -258.821   -3.432      27.8
 30        -275.911   -3.658      25.8
 31        -300.325   -3.982      62.0
 32        -346.711   -4.597      45.0
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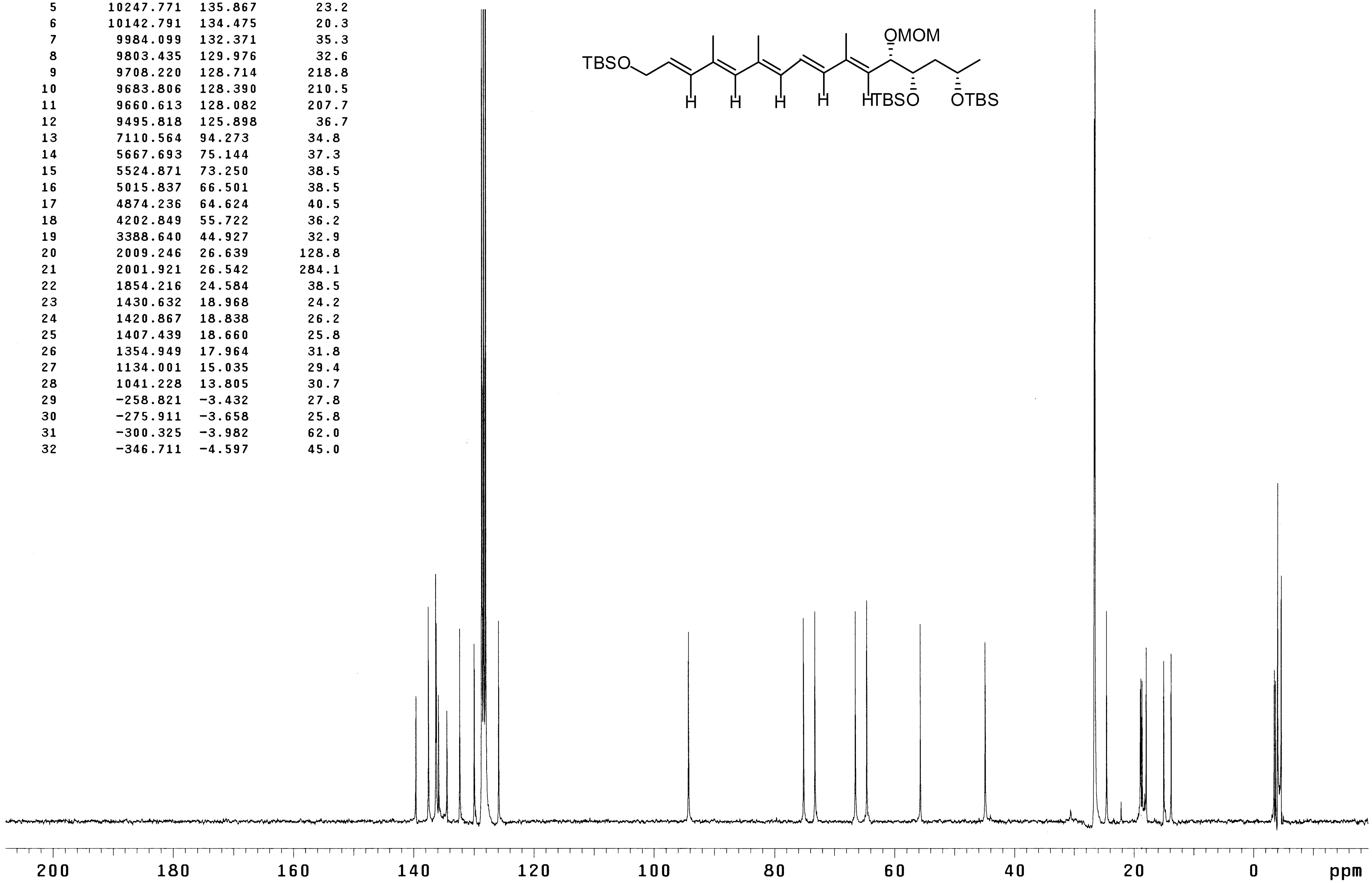
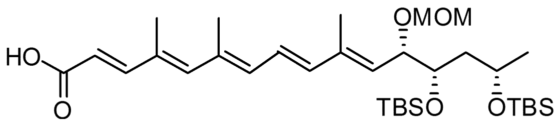
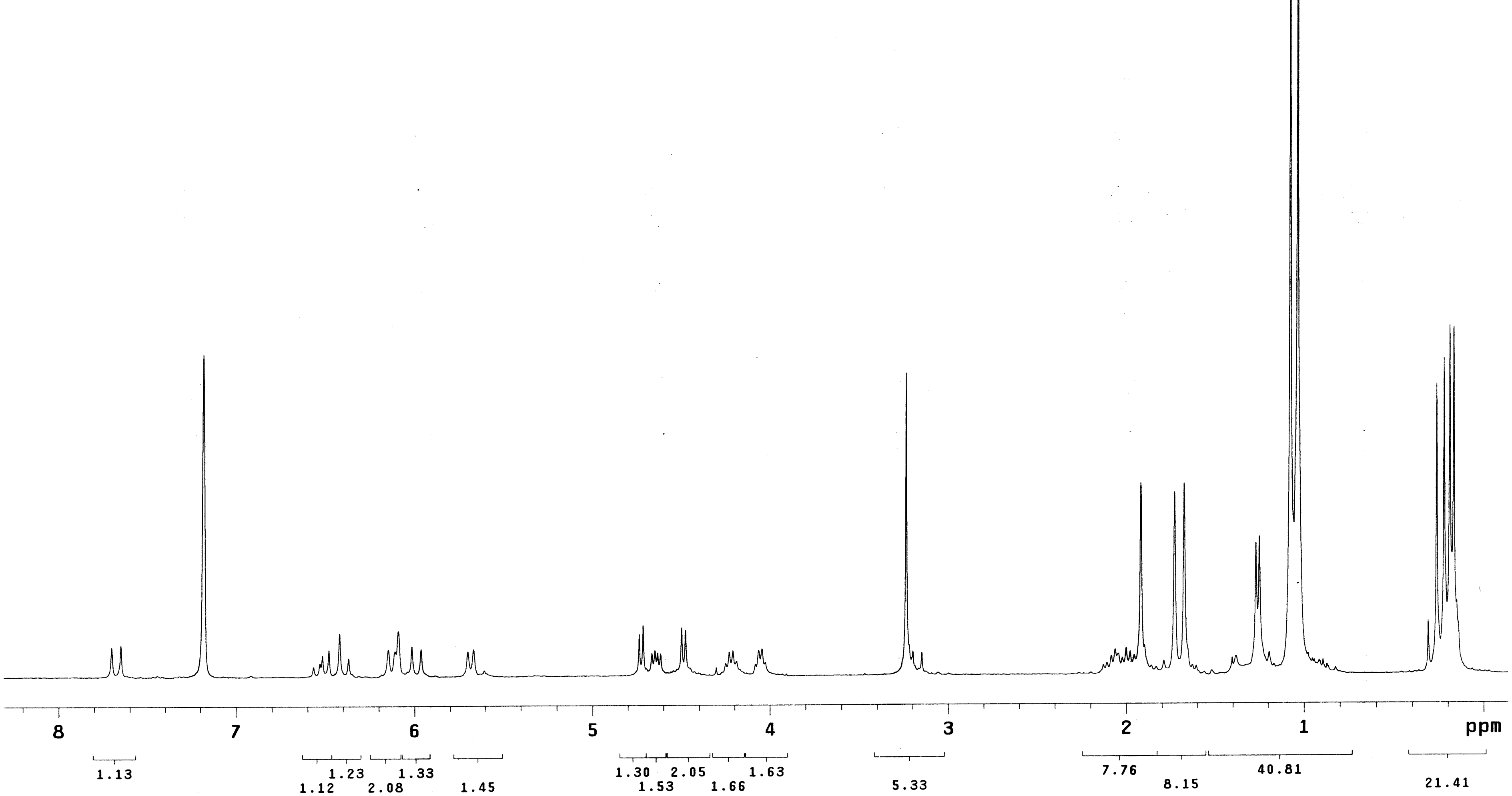


Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi





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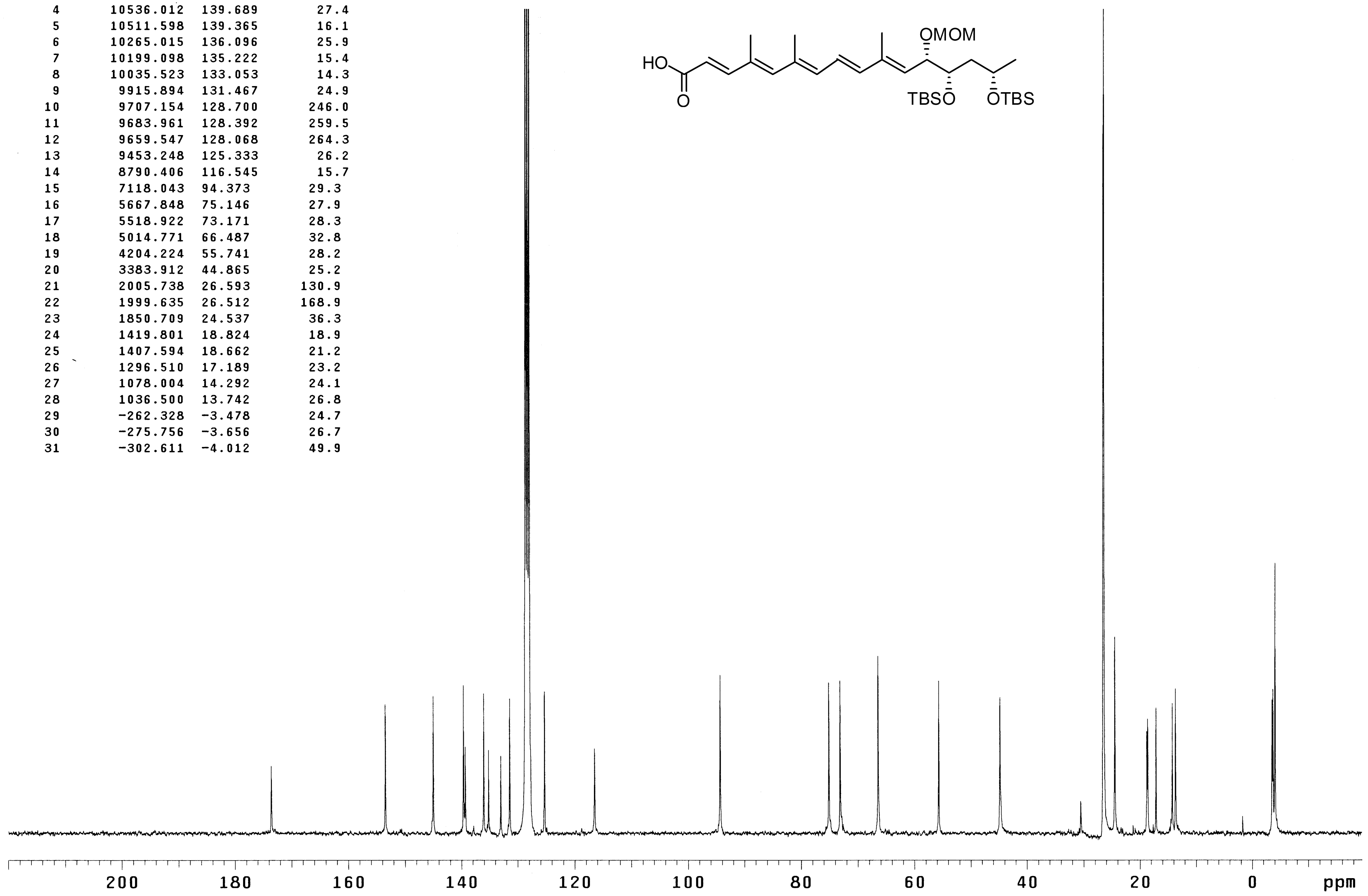
Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

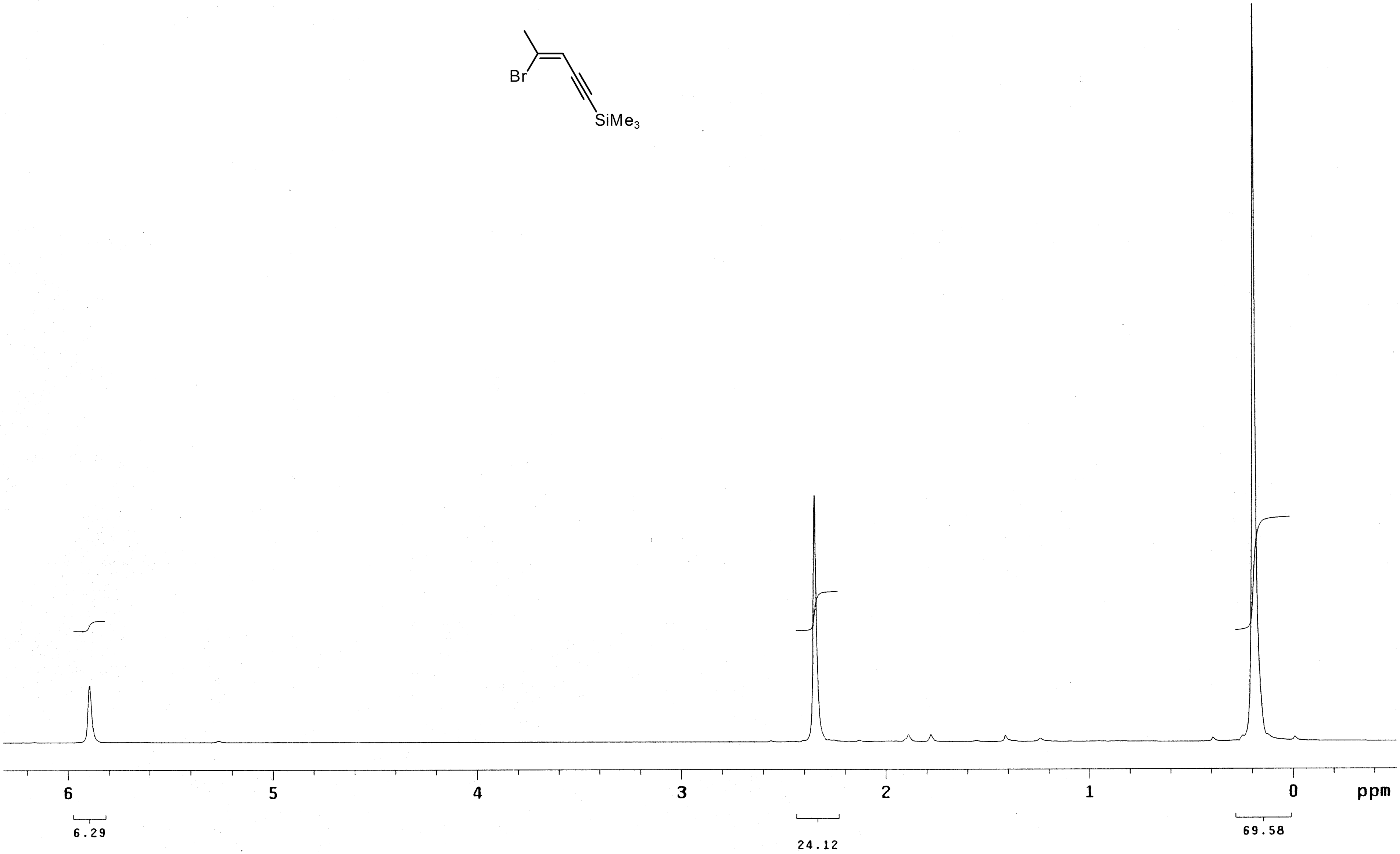
Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

INDEX	FREQUENCY	PPM	HEIGHT
1	13094.605	173.611	12.5
2	11578.492	153.510	23.8
3	10941.285	145.062	25.4
4	10536.012	139.689	27.4
5	10511.598	139.365	16.1
6	10265.015	136.096	25.9
7	10199.098	135.222	15.4
8	10035.523	133.053	14.3
9	9915.894	131.467	24.9
10	9707.154	128.700	246.0
11	9683.961	128.392	259.5
12	9659.547	128.068	264.3
13	9453.248	125.333	26.2
14	8790.406	116.545	15.7
15	7118.043	94.373	29.3
16	5667.848	75.146	27.9
17	5518.922	73.171	28.3
18	5014.771	66.487	32.8
19	4204.224	55.741	28.2
20	3383.912	44.865	25.2
21	2005.738	26.593	130.9
22	1999.635	26.512	168.9
23	1850.709	24.537	36.3
24	1419.801	18.824	18.9
25	1407.594	18.662	21.2
26	1296.510	17.189	23.2
27	1078.004	14.292	24.1
28	1036.500	13.742	26.8
29	-262.328	-3.478	24.7
30	-275.756	-3.656	26.7
31	-302.611	-4.012	49.9



Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



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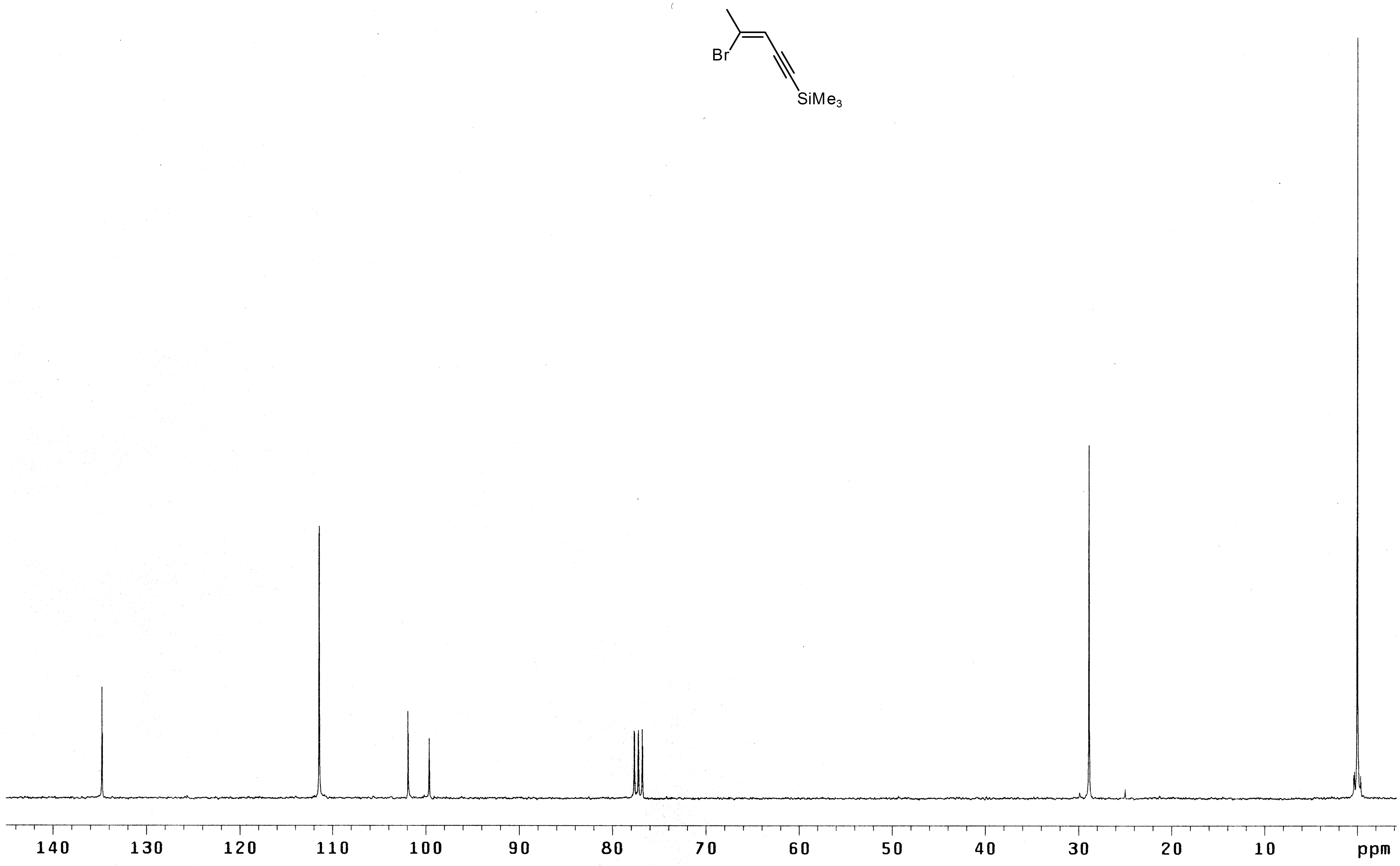
INDEX   FREQUENCY  PPM      HEIGHT
  1     10164.669  134.765    20.0
  2      8405.636  111.444    48.9
  3      7686.642  101.911    15.7
  4      7514.523  99.629     10.7
  5      5858.029  77.667     12.2
  6      5825.070  77.230     12.2
  7      5793.331  76.809     12.4
  8      2177.609  28.871     63.6
  9         1.095  0.015     136.9
```

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

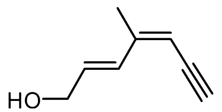
Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

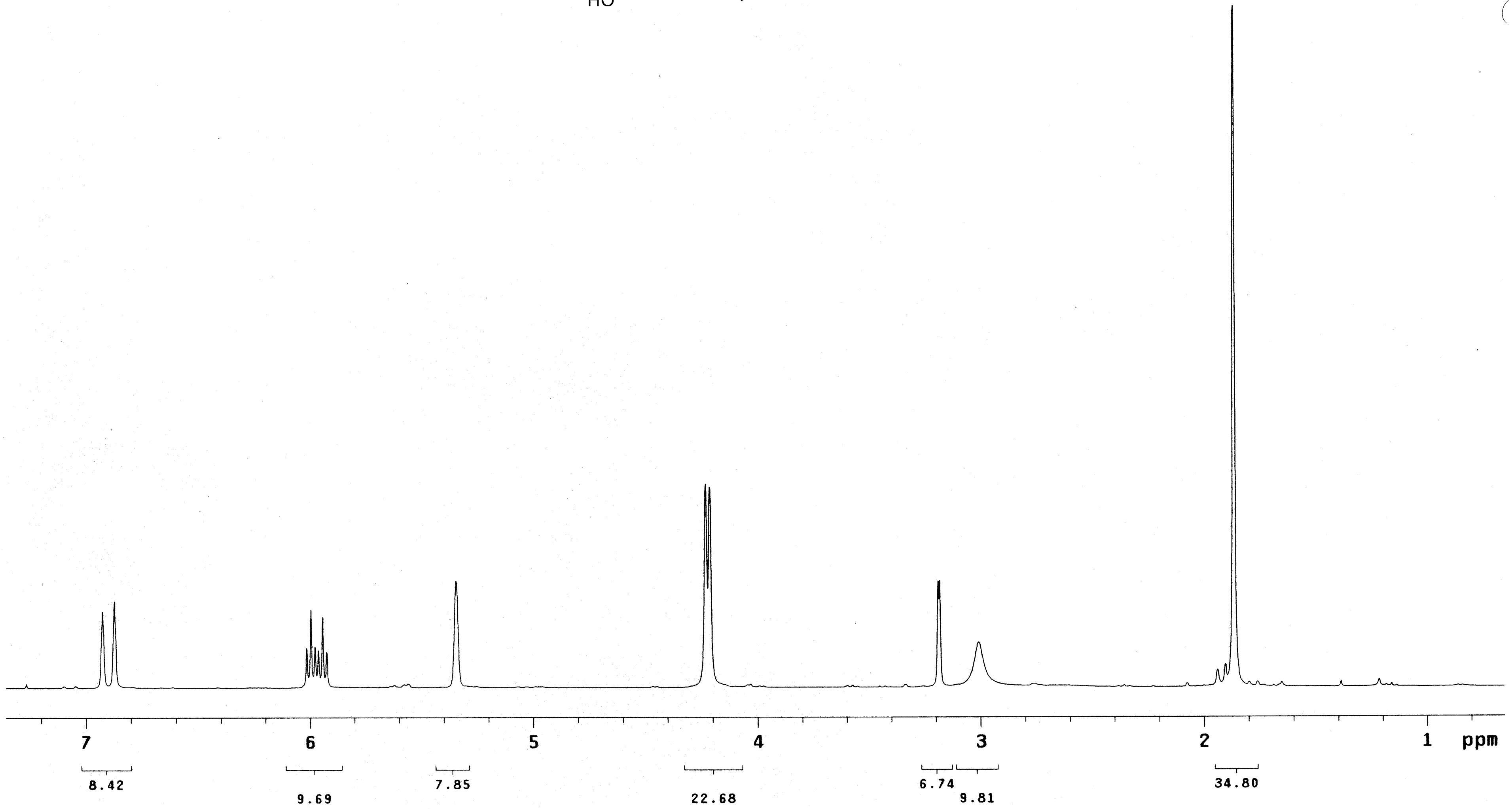


Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi





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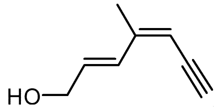
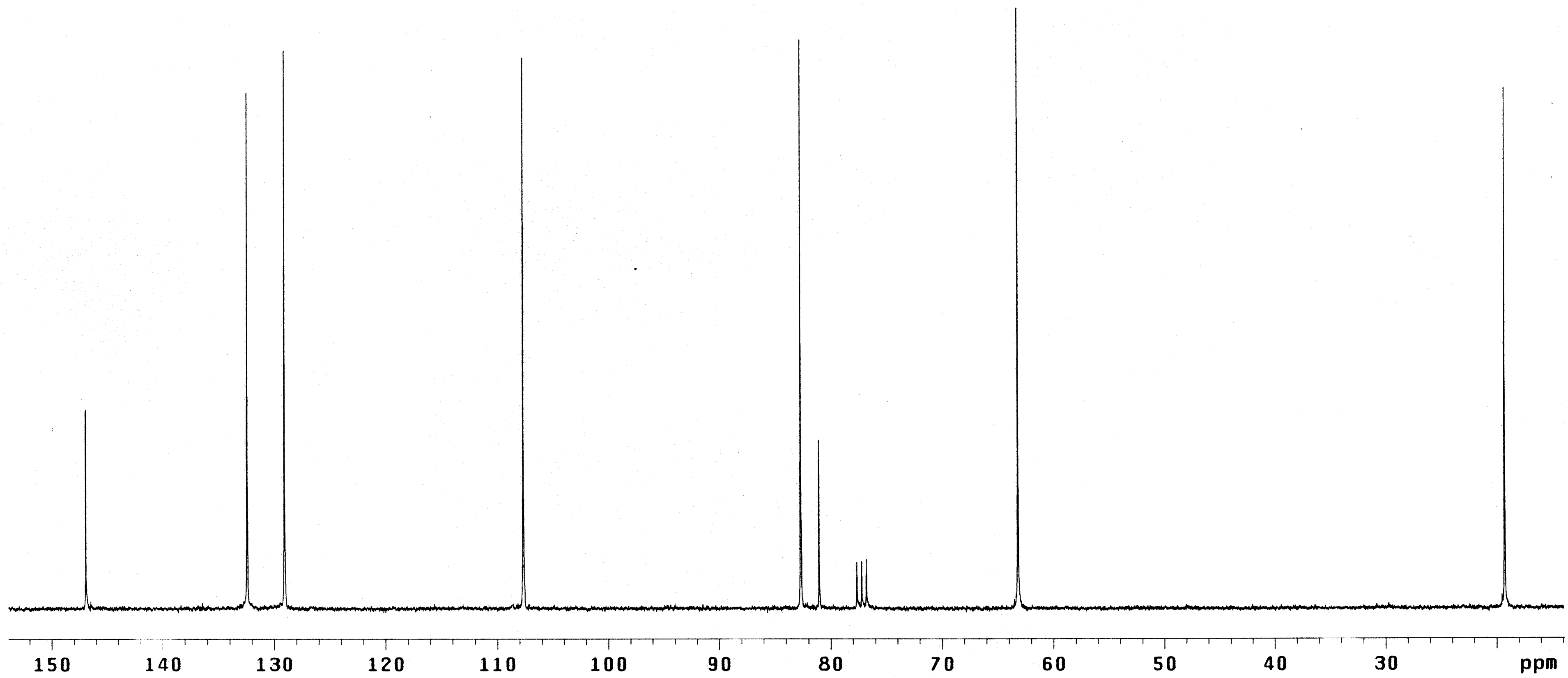
INDEX    FREQUENCY  PPM      HEIGHT
  1      11083.617  146.949     31.9
  2       9990.076  132.451     83.1
  3       9738.052  129.109     89.9
  4       8123.491  107.703     88.8
  5       6238.493  82.711      91.6
  6       6114.207  81.063      27.1
  7       4767.204  63.205      96.8
  8       1457.237  19.320      83.8
```

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

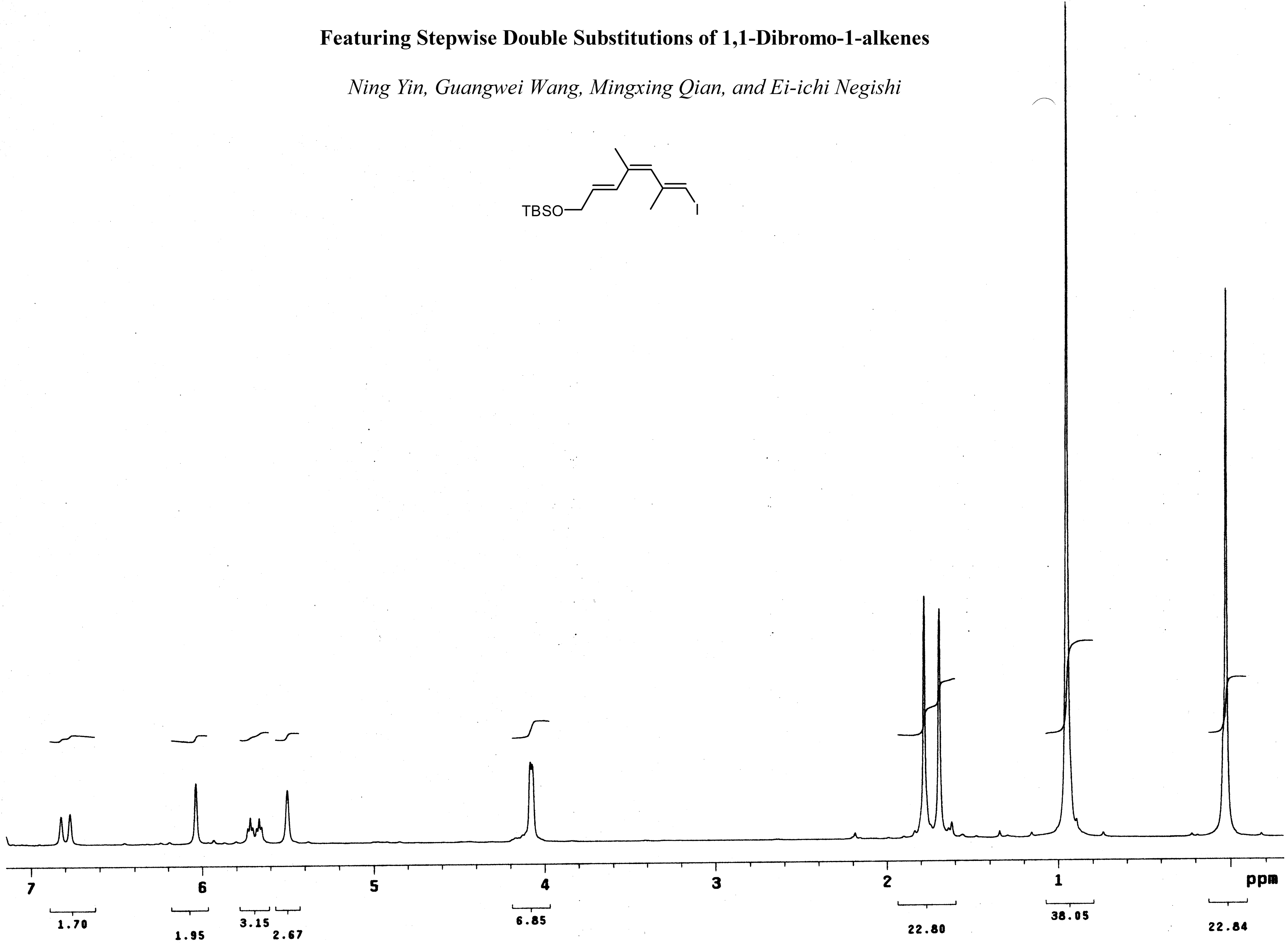




Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



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INDEX    FREQUENCY   PPM      HEIGHT
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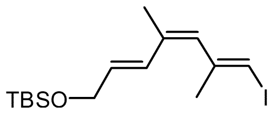
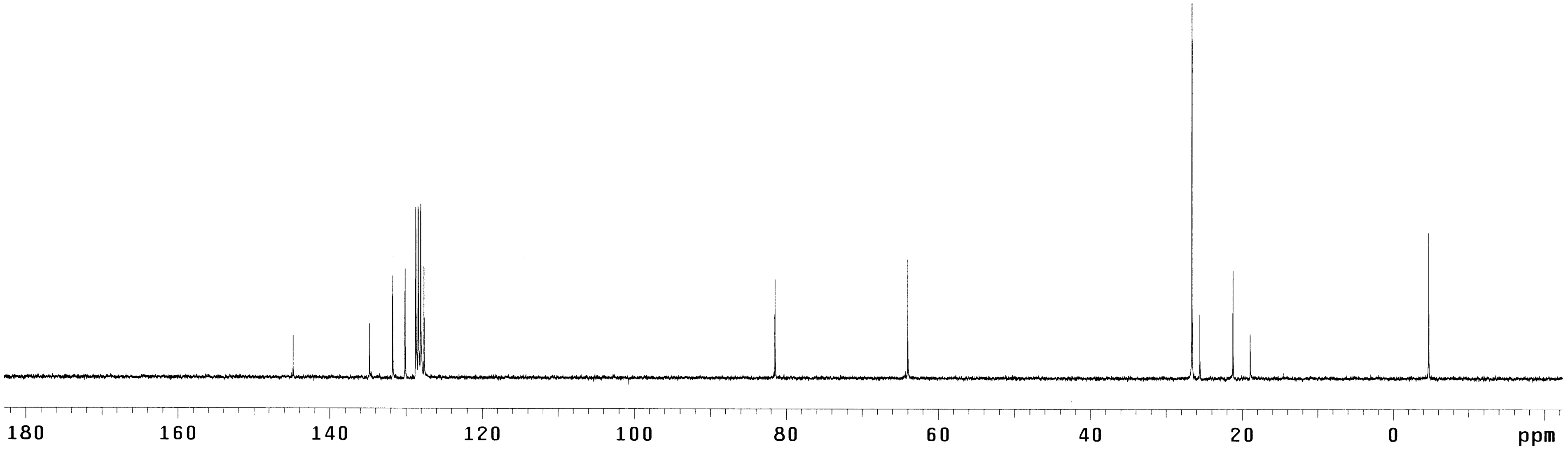
  2      10167.139   134.798     8.7
  3       9938.131   131.762    16.4
  4       9814.709   130.126    17.5
  5       9708.260   128.714    27.3
  6       9683.806   128.390    27.4
  7       9659.639   128.070    27.8
  8       9626.554   127.631    17.9
  9       6148.859   81.523     15.9
 10       4828.325   64.015     19.0
 11       2008.883   26.634     60.2
 12       1928.903   25.574     10.3
 13       1601.503   21.233     17.3
 14       1429.459   18.952      7.1
 15       -351.968   -4.666     23.4
```

Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

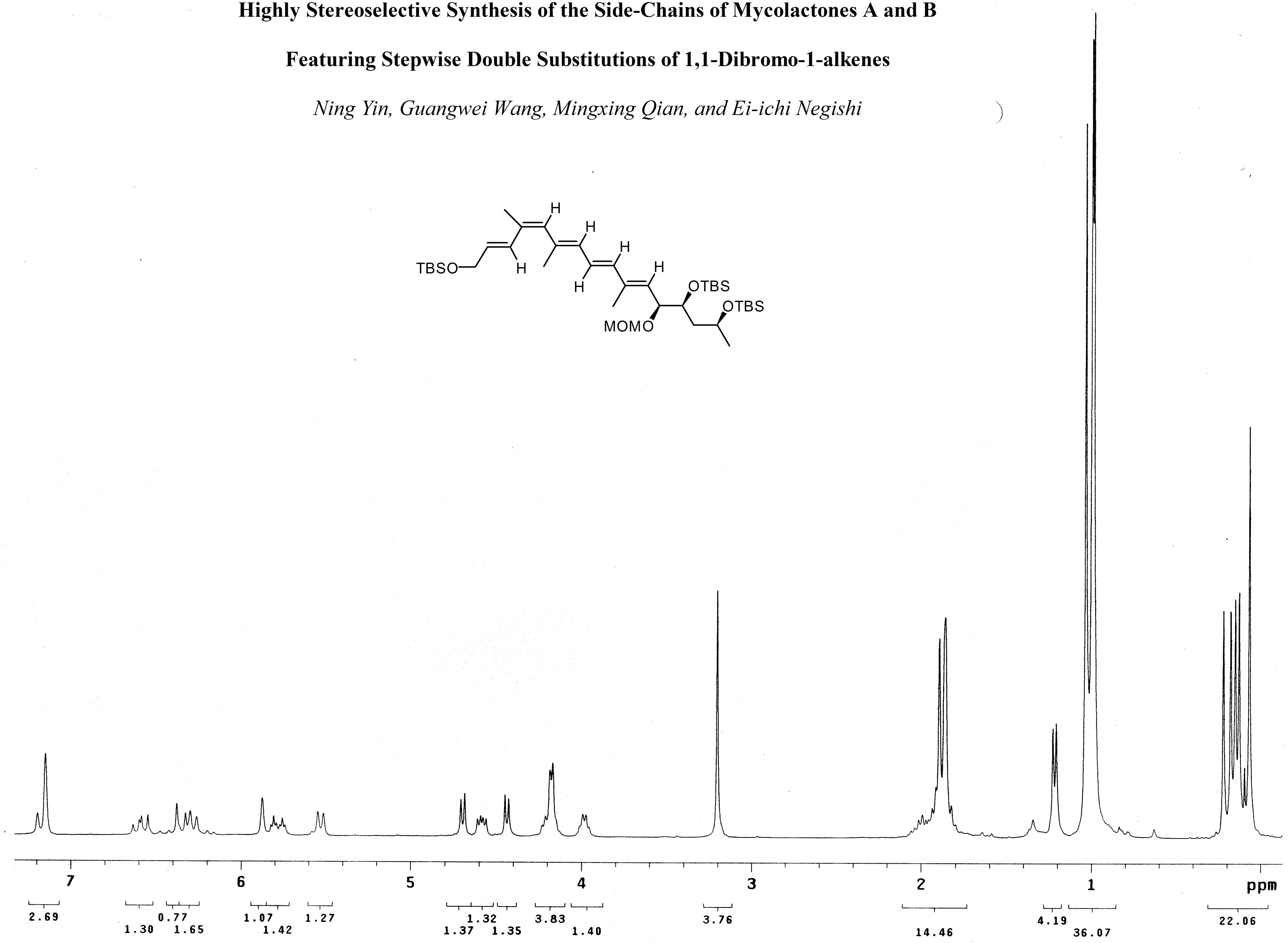




Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



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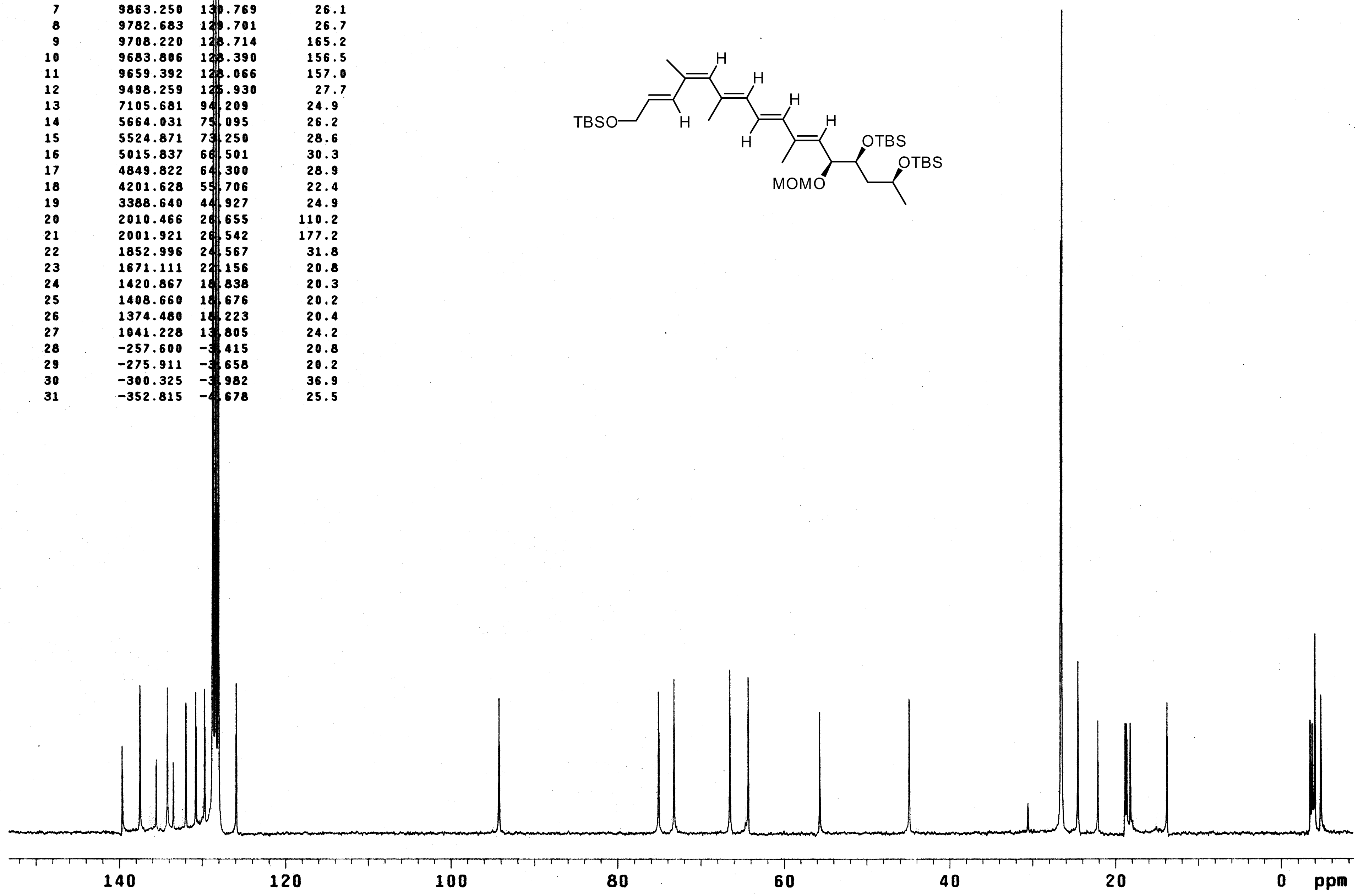
Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

INDEX	FREQUENCY	PPM	HEIGHT
1	10535.857	139.687	16.1
2	10373.503	137.534	27.4
3	10224.578	135.560	13.7
4	10123.259	134.216	26.9
5	10068.328	133.488	13.0
6	9953.582	131.967	24.1
7	9863.250	130.769	26.1
8	9782.683	129.701	26.7
9	9708.220	128.714	165.2
10	9683.806	128.390	156.5
11	9659.392	128.066	157.0
12	9498.259	125.930	27.7
13	7105.681	94.209	24.9
14	5664.031	75.095	26.2
15	5524.871	73.250	28.6
16	5015.837	66.501	30.3
17	4849.822	64.300	28.9
18	4201.628	55.706	22.4
19	3388.640	44.927	24.9
20	2010.466	26.655	110.2
21	2001.921	26.542	177.2
22	1852.996	24.567	31.8
23	1671.111	22.156	20.8
24	1420.867	18.838	20.3
25	1408.660	18.676	20.2
26	1374.480	18.223	20.4
27	1041.228	13.805	24.2
28	-257.600	-3.415	20.8
29	-275.911	-3.658	20.2
30	-300.325	-3.982	36.9
31	-352.815	-4.678	25.5



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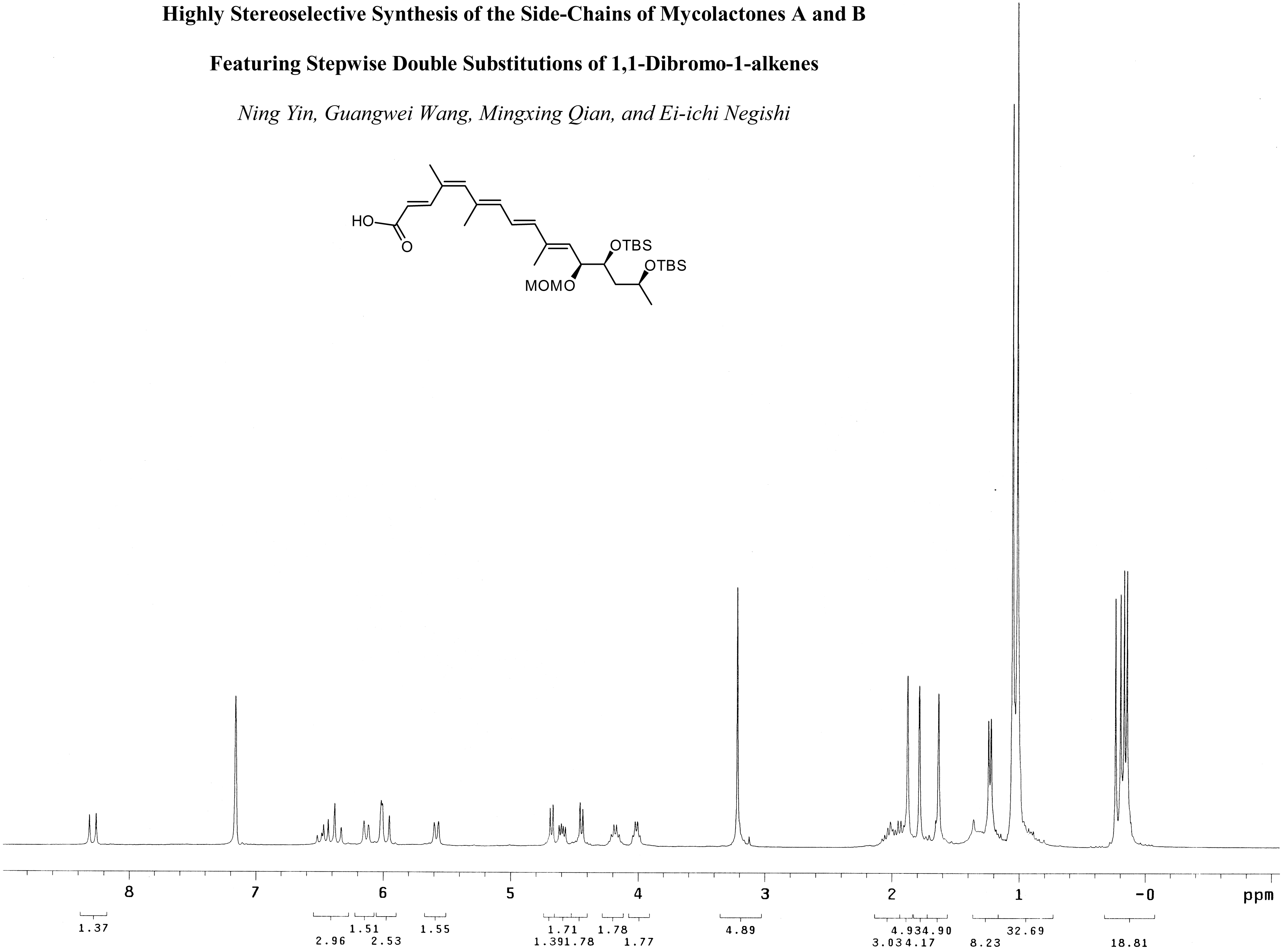
Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



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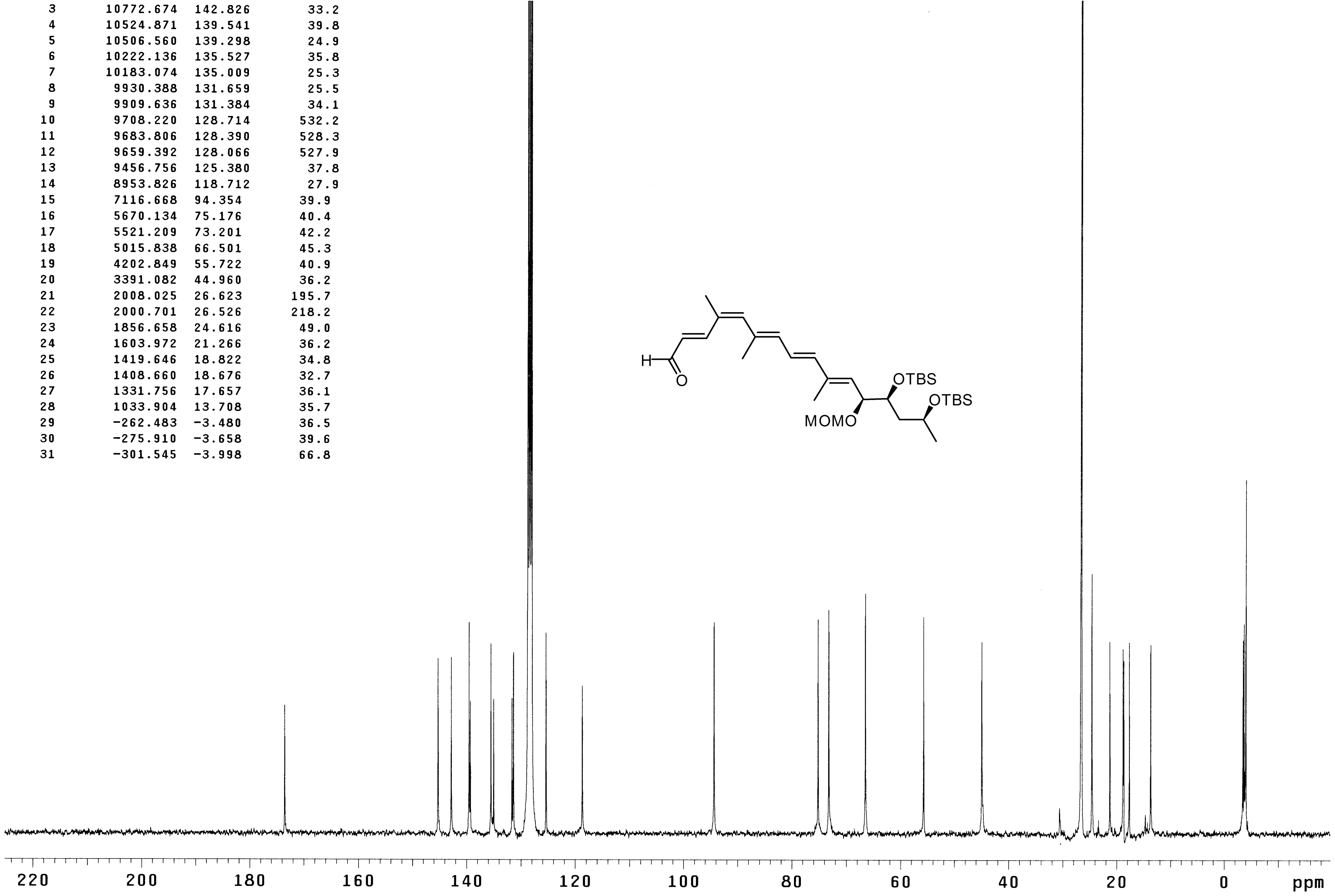
Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi

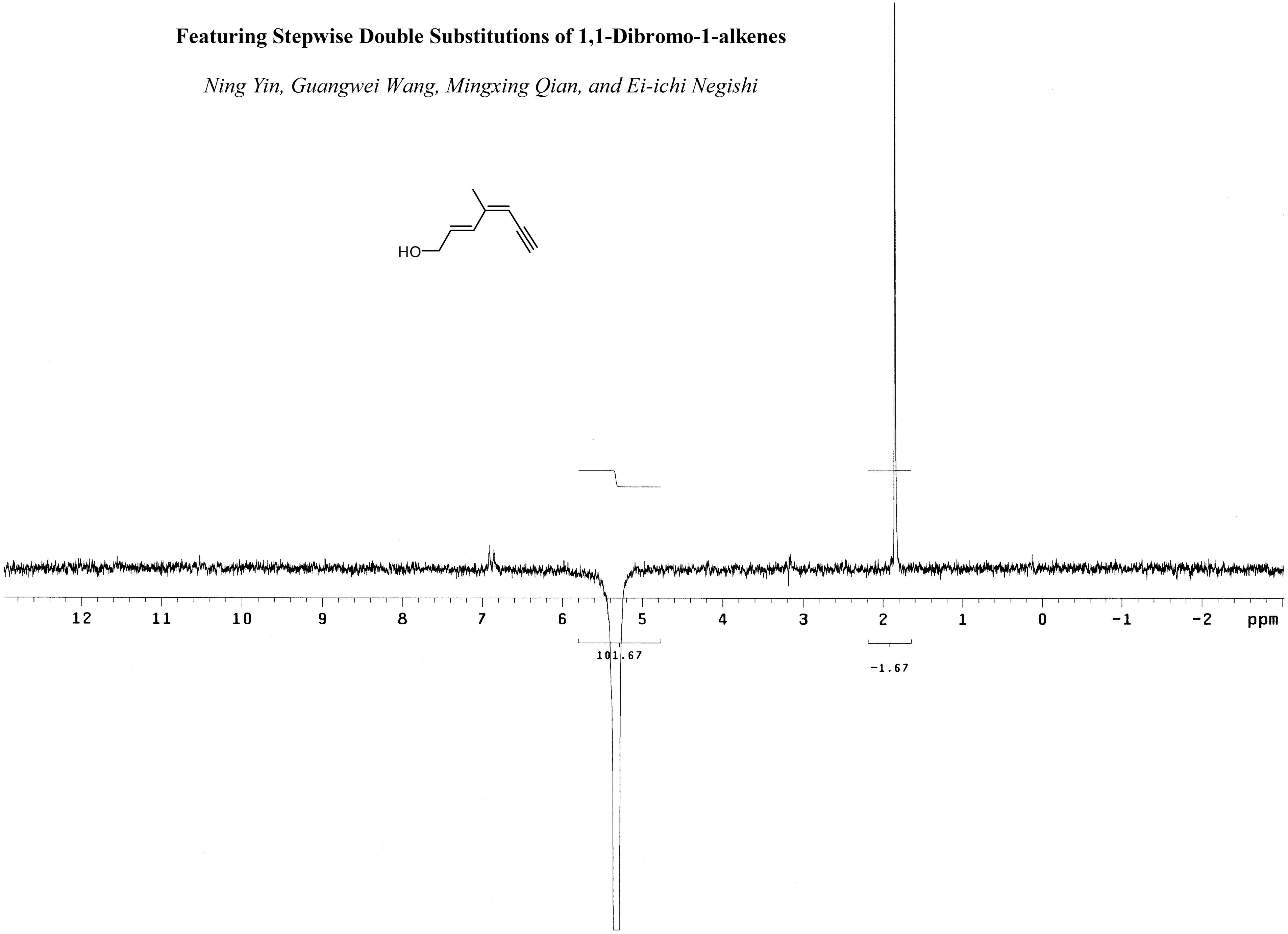
INDEX	FREQUENCY	PPM	HEIGHT
1	13088.347	173.528	24.1
2	10955.779	145.254	33.0
3	10772.674	142.826	33.2
4	10524.871	139.541	39.8
5	10506.560	139.298	24.9
6	10222.136	135.527	35.8
7	10183.074	135.009	25.3
8	9930.388	131.659	25.5
9	9909.636	131.384	34.1
10	9708.220	128.714	532.2
11	9683.806	128.390	528.3
12	9659.392	128.066	527.9
13	9456.756	125.380	37.8
14	8953.826	118.712	27.9
15	7116.668	94.354	39.9
16	5670.134	75.176	40.4
17	5521.209	73.201	42.2
18	5015.838	66.501	45.3
19	4202.849	55.722	40.9
20	3391.082	44.960	36.2
21	2008.025	26.623	195.7
22	2000.701	26.526	218.2
23	1856.658	24.616	49.0
24	1603.972	21.266	36.2
25	1419.646	18.822	34.8
26	1408.660	18.676	32.7
27	1331.756	17.657	36.1
28	1033.904	13.708	35.7
29	-262.483	-3.480	36.5
30	-275.910	-3.658	39.6
31	-301.545	-3.998	66.8



Highly Stereoselective Synthesis of the Side-Chains of Mycolactones A and B

Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

Ning Yin, Guangwei Wang, Mingxing Qian, and Ei-ichi Negishi



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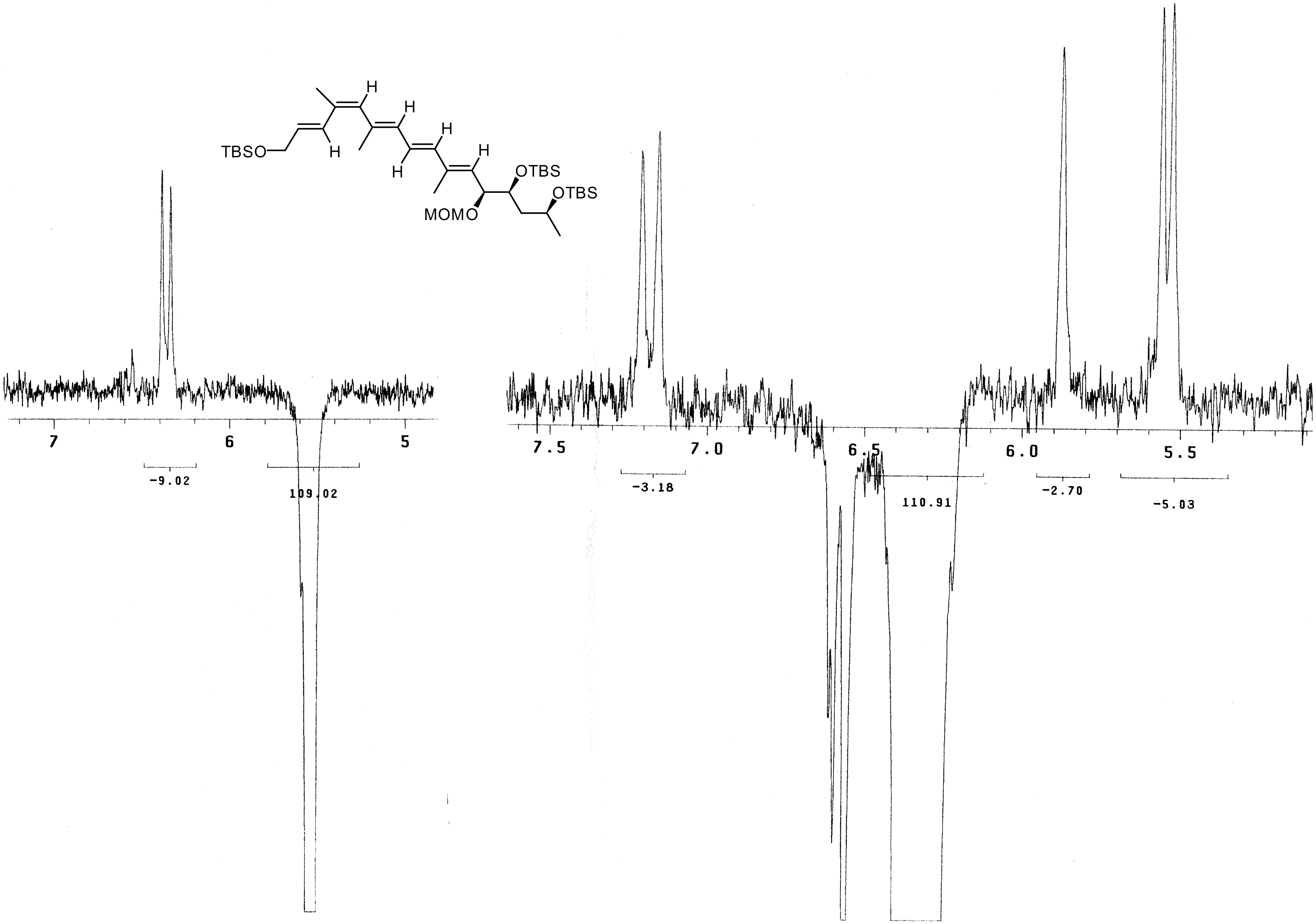

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Featuring Stepwise Double Substitutions of 1,1-Dibromo-1-alkenes

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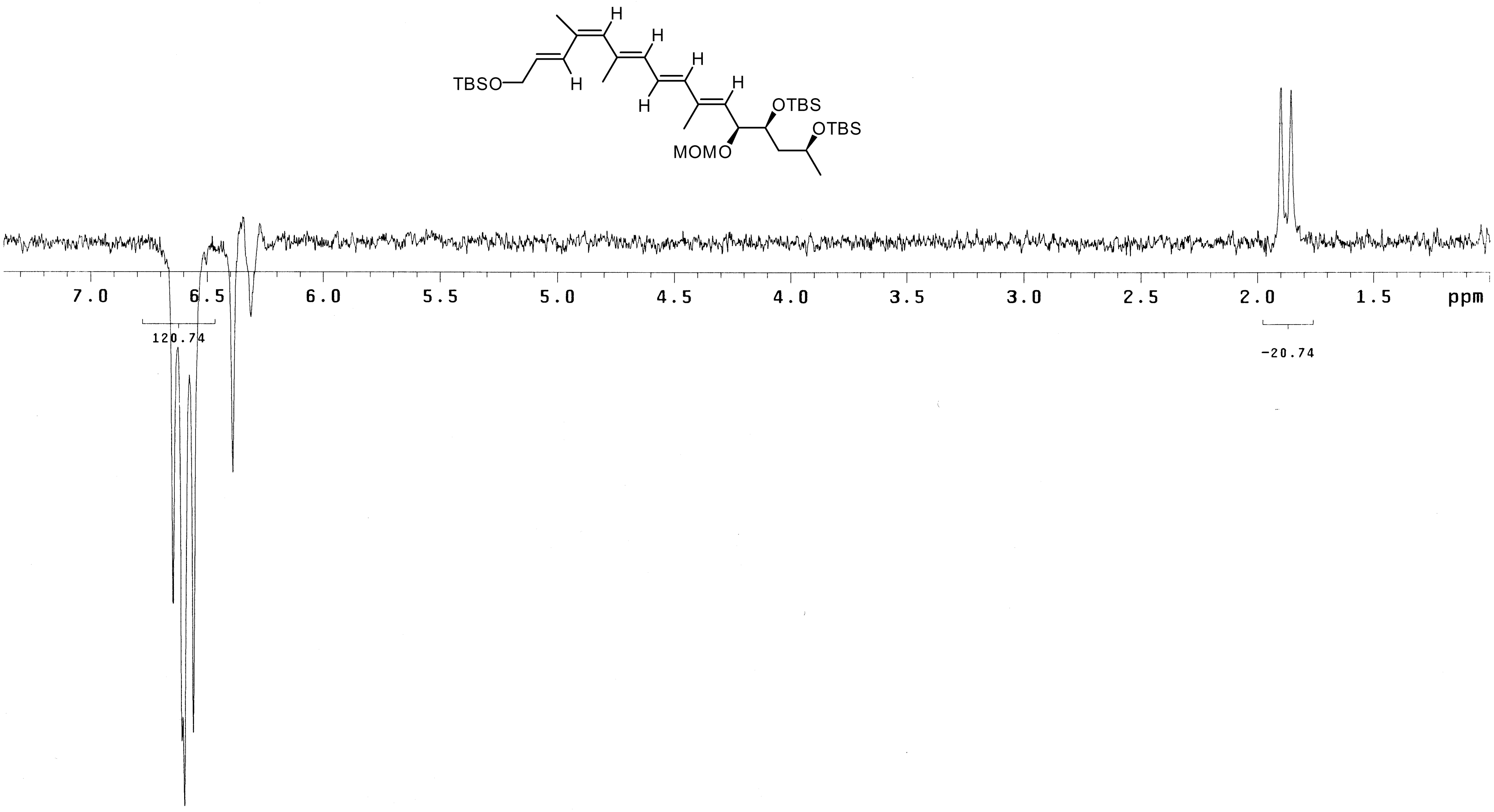

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