

Supporting Information for

Total Synthesis of Four Isomers of the Proposed Structure of Cryptorigidiofoliol K

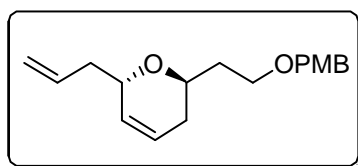
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General method:

All moisture or/and air sensitive experiments were carried out in flame-dried glassware under an inert atmosphere. Anhydrous solvents were freshly distilled prior to use: Tetrahydrofuran (THF) and toluene from sodium and benzophenone, dichloromethane (CH_2Cl_2), DMF, hexane from calcium hydride and MeOH from Mg cake under a nitrogen atmosphere. Commercially available starting materials and reagents were used as received without further purification. Column chromatography on a silica gel (60–120 mesh) furnished the corresponding products. Thin layer chromatography was run on silica gel GF254 (0.25 mm), while monitoring the reactions. Diastereomeric ratio was analyzed by Shimadzu LC-MS-8040 instrument and HPLC was performed on Shimadzu HPLC systems consisting of the following mobile phase, acetonitrile, water, isopropanol and hexane; flow rate, 1 mL/min. Melting points were determined by Stuart SMP3 apparatus. Specific optical rotations $[\alpha]^D$ are mentioned in $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$ and were measured with Anton Paar MCP 200 digital polarimeter at 20 °C. Infrared spectra were recorded in CHCl_3 with Bruker Alpha spectrometer and reported in wave number (cm^{-1}). ^1H NMR spectra were recorded at 300, 400, 500 MHz, and ^{13}C NMR spectra at 75, 100, 125 MHz in deuteriochloroform (CDCl_3). Chemical shifts are reported as ppm downfield from tetramethylsilane relative to the CDCl_3 , 7.26 ppm for ^1H NMR and 77.00 ppm for ^{13}C NMR, respectively and coupling constants (J) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS spectra were recorded by using Waters Q-TOF mass spectrometer.

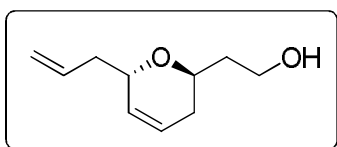
Experimental Section:

(2*R*,6*S*)-6-Allyl-2-(2-((4-methoxybenzyl)oxy)ethyl)-3,6-dihydro-2*H*-pyran (5):



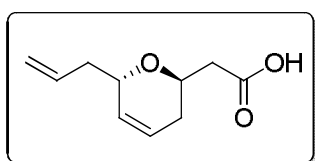
To a stirred solution of δ -hydroxy α, β -unsaturated aldehyde (2.0 g, 7.57 mmol) in THF (30 mL) were sequentially added allyltrimethylsilane (1.8 mL, 11.36 mmol) and iodine (0.29 g, 1.14 mmol) at 0 °C. The reaction mixture was allowed to stir at room temperature for 1 h. After completion of the reaction (monitored by TLC), it was quenched with aqueous saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) and diluted with EtOAc (30 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (2 \times 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (ethyl acetate/hexane = 1:9) to obtain the cyclized product **5** (1.96 g, 90%) as a colourless liquid. $[\alpha]_{\text{D}}^{20} +38.7$ (c 0.7, CHCl_3); IR (CHCl_3) ν_{max} 3032, 2916, 1640, 1612, 1586, 1513, 1436, 1361, 1248, 1178, 1088, 1036, 823, 709 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.90-5.78 (m, 2H), 5.73-5.67 (m, 1H), 5.12-5.03 (m, 2H), 4.43 (s, 2H), 4.22-4.15 (m, 1H), 3.91-3.83 (m, 1H), 3.79 (s, 3H), 3.62-3.52 (m, 2H), 2.43-2.36 (m, 1H), 2.28-2.20 (m, 1H), 2.04-1.92 (m, 2H), 1.82-1.77 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 135.1, 130.5, 129.2, 129.1, 124.3, 116.6, 113.6, 72.6, 72.2, 66.5, 64.7, 55.1, 38.7, 35.5, 30.6 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$: 311.1618, Found: 311.1616.

2-((2R,6S)-6-Allyl-3,6-dihydro-2H-pyran-2-yl)ethanol (10):



To a stirred solution of compound **5** (1.5 g, 5.21 mmol) in CH_2Cl_2 (27 mL) and water (3 mL) was added DDQ (1.77 g, 7.81 mmol) at room temperature and allowed to stir for 2 h at the same temperature. After completion of the reaction (monitored by TLC), it was quenched with saturated NaHCO_3 (30 mL) solution. After stirring for 3 h, the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was washed with brine (2×60 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/ hexane = 3:17) to afford the desired primary alcohol **10** (0.84 g, 96%) as a pale yellow colour liquid. $[\alpha]_{\text{D}}^{20} +71.0$ (c 0.6, CHCl_3); IR (CHCl_3) ν_{max} 3438, 3075, 3034, 2926, 1646, 1431, 1183, 10689, 920, 758, 711 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.91-5.81 (m, 2H), 5.74-5.69 (m, 1H), 5.18-5.10 (m, 2H), 4.26 (br s, 1H), 3.95-3.89 (m, 1H), 3.81-3.76 (m, 2H), 2.48-2.42 (m, 1H), 2.33-2.26 (m, 1H), 2.07-1.95 (m, 2H), 1.82-1.71 (m, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 134.9, 128.8, 124.2, 117.1, 72.4, 67.8, 61.2, 38.7, 37.4, 30.7 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Na}$: 191.1043, Found: 191.1035.

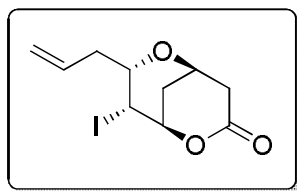
2-((2R,6S)-6-Allyl-3,6-dihydro-2H-pyran-2-yl)acetic acid (4):



To a stirred solution of alcohol **10** (500 mg, 2.98 mmol) in a mixture of CH_2Cl_2 : H_2O (2:1, 15 mL), were added $\text{PhI}(\text{OAc})_2$ (2.40 g, 7.44 mmol) and TEMPO (92 mg, 0.60 mmol) at room temperature. The reaction mixture was allowed to stir at same temperature for 6 h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was separated and the

aqueous layer extracted with CH_2Cl_2 (3×30 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:3) to afford the acid **4** (471 mg, 87%) as a viscous liquid. $[\alpha]_{\text{D}}^{20} +92.3$ (c 0.6, CHCl_3); IR (CHCl_3) ν_{max} 3032, 2922, 1717, 1647, 1428, 1291, 1219, 1076, 919, 753 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.90-5.78 (m, 2H), 5.75-5.69 (m, 1H), 5.15-5.02 (m, 2H), 4.24 (br s, 1H), 4.22-4.16 (m, 1H), 2.61 (dd, $J = 15.6, 8.4$ Hz, 1H), 2.53 (dd, $J = 15.4, 8.2$ Hz, 1H), 2.46-2.39 (m, 1H), 2.33-2.21 (m, 1H), 2.15-2.08 (m, 1H), 2.04-1.94 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 176.8, 134.5, 128.9, 123.4, 117.1, 72.4, 64.8, 40.1, 38.6, 29.8 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{Na}$: 205.0835, Found: 205.0843.

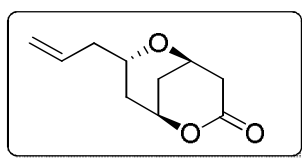
(1*R*,5*R*,7*S*,8*R*)-7-Allyl-8-iodo-2,6-dioxabicyclo[3.3.1]nonan-3-one (11):



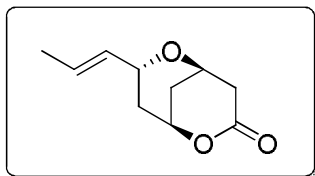
To a stirred solution of acid **4** (400 mg, 2.21 mmol) in MeCN (15 mL), were sequentially added NaHCO_3 (553 mg, 6.60 mmol) and I_2 (315 mg, 1.24 mmol) at -20 °C. After stirring for 2 h, the mixture was allowed to warm to room temperature and stirred for 10 h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) and diluted with EtOAc (25 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (2×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 3:17) obtained the bicyclic lactone **11** (608 mg,

90%, $dr = 98:2$) as a yellow colour liquid. $[\alpha]_D^{20} -46.31$ (c 0.9, CHCl_3); IR (CHCl_3) ν_{max} 3076, 2967, 1740, 1643, 1437, 1342, 1255, 1157, 1060, 923, 814, 658 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.76-5.65 (m, 1H), 5.28-5.19 (m, 1H), 5.17-5.11 (m, 1H), 5.04-4.98 (m, 1H), 4.38-4.30 (m, 2H), 3.03-2.95 (m, 2H), 2.85-2.80 (m, 2H), 2.48-2.40 (m, 1H), 2.24-2.16 (m, 1H), 1.94-1.84 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 131.9, 118.9, 77.1, 66.3, 66.0, 42.4, 36.7, 34.0, 25.3 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{INa}$: 330.9802, Found: 330.9807.

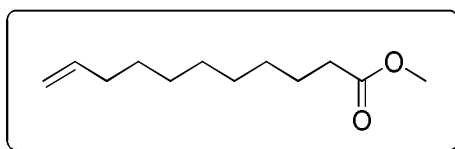
(1*S*,5*R*,7*S*)-7-Allyl-2,6-dioxabicyclo[3.3.1]nonan-3-one (12):



To a stirred solution of iodo-lactone **11** (500 mg, 1.62 mmol) in toluene (20 mL), were added catalytic amount of AIBN (26 mg, 0.16 mmol) followed by *n*-tributyltinhydride (1.3 mL, 4.87 mmol) and refluxed for 30 min. After completion of the reaction (monitored by TLC), toluene was removed under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 3:7) to give compound **12** (283 mg, 96%) as a colorless liquid. $[\alpha]_D^{20} -20.8$ (c 0.9, CHCl_3); IR (CHCl_3) ν_{max} 3076, 2967, 2861, 1731, 1642, 1434, 1350, 1203, 1154, 1074, 996, 921, 793, 754 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.84-5.74 (m, 1H), 5.15-5.06 (m, 2H), 4.93-4.87 (m, 1H), 4.37 (br s, 1H), 3.89-3.80 (m, 1H), 2.90-2.76 (m, 2H), 2.34-2.22 (m, 2H), 2.07-1.99 (m, 2H), 1.96-1.91 (m, 1H), 1.59 (dt, $J = 11.79, 2.13$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.5, 133.4, 117.4, 72.8, 65.7, 65.1, 39.8, 36.2, 36.1, 29.4 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{15}\text{O}_3$: 181.1016, Found: 181.1008.

(1*R*,5*R*,7*R*)-7-((*E*)-Prop-1-en-1-yl)-2,6-dioxabicyclo [3.3.1] nonan-3-one (2):

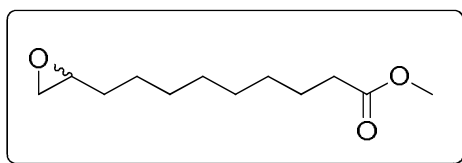
To a stirred solution of alkene **12** (200 mg, 1.10 mmol) in methanol (20 mL) Grubb's second generation catalyst (0.28 g, 0.33 mmol) was added at room temperature. The reaction mixture was then heated at 60 °C. After 20 minutes the suspension was turned to brown colour solution and allowed to stir for 12 h at the same temperature. After completion of the reaction (monitored by TLC), MeOH was evaporated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 3:7) to give internal alkene **2** (163 mg, 82%) as a pale yellow liquid. $[\alpha]_D^{20} -15.7$ (*c* 0.4, CHCl₃); IR (CHCl₃) ν_{\max} 2929, 2861, 1740, 1454, 1350, 1218, 1161, 1079, 989, 761 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.82-5.71 (m, 1H), 5.49-5.41 (m, 1H), 4.93-4.90 (m, 1H), 4.39 (br s, 1H), 4.26-4.18 (m, 1H), 2.95-2.90 (m, 1H), 2.86-2.80 (m, 1H), 2.08-2.02 (m, 2H), 1.95-1.91 (m, 1H), 1.72-1.69 (m, 3H), 1.68-1.65 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 130.0, 129.0, 72.9, 66.8, 65.9, 37.0, 36.4, 29.4, 17.7 ppm HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₁₀H₁₄O₃Na: 205.0841, Found: 205.0840.

Methyl undec-10-enoate (9a):

To a stirred solution of 10-undecenoic acid (10.0 g, 54.35 mmol) in methanol (100 mL), was added concentrated sulphuric acid (2 mL) dropwise with a dropping funnel over 10 min. The

reaction mixture was heated at 65 °C for 13 h. After completion of the reaction (monitored by TLC), MeOH was removed under reduced pressure and the reaction mixture was diluted with EtOAc (100 mL) and saturated aqueous NaHCO₃ solution (50 mL) followed by the addition of brine (50 mL) until the pH of the solution become neutral. The organic layer was separated and the aqueous layer extracted with EtOAc (2 × 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:19) to afford the desired compound **9a** (9.68 g, 90%) as a wine colour liquid. IR (CHCl₃) ν_{max} 3216, 2926, 2861, 1736, 1614, 1454, 1350, 1218, 1161, 1079, 761 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.82-5.74 (m, 1H), 4.98-4.89 (m, 2H), 3.64 (s, 3H), 2.28 (t, *J* = 7.47 Hz, 2H), 2.03-1.99 (m, 2H), 1.62 (quint, *J* = 7.2 Hz, 2H), 1.37-1.33 (m, 2H), 1.31-1.25 (m, 8H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 138.9, 114.0, 51.2, 33.9, 33.6, 29.1, 29.1, 29.0, 28.9, 28.7, 24.8 ppm; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₁₂H₂₂O₂Na: 221.1512, Found: 221.1520.

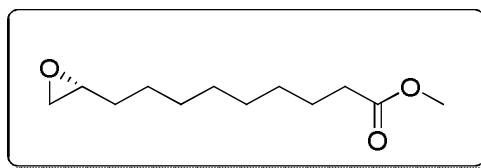
Methyl-9-(oxiran-2-yl)nonanoate (**13**):



To a stirred solution of compound **9a** (9.0 g, 45.45 mmol) in CH₂Cl₂ (150 mL), was added *m*-CPBA (77%, 9.41 g, 54.55 mmol) at 0 °C. The reaction mixture was then allowed to stir at room temperature for 7 h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous Na₂S₂O₃ (70 mL) solution and 10% aqueous solution of NaOH (70 mL) to dissolve the resultant solids and the layers were separated. The aqueous layer was extracted with

CH_2Cl_2 (2×150 mL) and the combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:9) to obtained epoxide **13** (8.27 g, 85%) as a colorless liquid. IR (CHCl_3) ν_{max} 3018, 2931, 2858, 1731, 1448, 1365, 1216, 1047 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 3.63 (s, 3H), 2.88-2.85 (m, 1H), 2.74 (dd, $J = 4.8, 3.9$ Hz, 1H), 2.46 (dd, $J = 5.0, 2.7$ Hz, 1H), 2.27 (t, $J = 7.47$ Hz, 2H), 1.63-1.55 (m, 2H), 1.52-1.47 (m, 2H), 1.45-1.35 (m, 2H), 1.34-1.24 (m, 8H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 52.0, 51.1, 46.7, 33.7, 32.2, 29.1, 28.9, 28.8, 25.7, 24.6 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Na}$: 237.1461, Found: 237.1466.

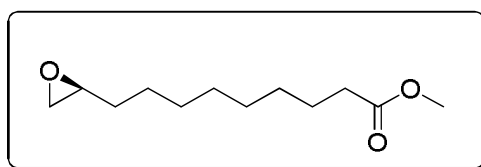
(R)-Methyl-9-(oxiran-2-yl)nonanoate (8a):



To a stirred solution of (*R,R*)-Jacobsen's catalyst ($[(R,R)\text{-}N,N'\text{-bis}(3,5\text{-di-}i\text{-tert-butylsalicylidene})\text{-}1,2\text{-cyclohexanediaminato}(2\text{-})]\text{cobalt(II)}$) (25 mg, 0.3 mol%, 0.04 mmol) in toluene (2 mL), was added acetic acid (3 μL , 0.4 mol%, 0.06 mmol) at room temperature, and allowed to stir in an unsealed flask. After 2 h, toluene and excess acetic acid were removed under reduced pressure and compound **13** (3.0 g, 14.0 mmol) was then added. Water (138 μL , 0.55 eq, 7.71 mmol) was added to the reaction mixture at -10 $^{\circ}\text{C}$. The reaction mixture was allowed to stir for 24 h at room temperature. After completion of the reaction (monitored by TLC), the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:9) to give the chiral (*R*)-epoxide **8a** (1.4 g, 48%) as a colourless liquid. $[\alpha]_{\text{D}}^{20} +8.7$ (c 0.9, CHCl_3); IR (CHCl_3) ν_{max} 3018,

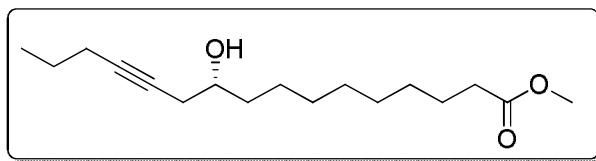
2928, 2857, 1735, 1445, 1361, 1213, 1171, 1011, 837, 747, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.63 (s, 3H), 2.89-2.84 (m, 1H), 2.74 (dd, $J = 5.0, 4.0$ Hz, 1H), 2.46 (dd, $J = 5.1, 2.8$ Hz, 1H), 2.27 (t, $J = 7.45$ Hz, 2H), 1.63-1.54 (m, 2H), 1.53-1.45 (m, 2H), 1.45-1.39 (m, 2H), 1.34-1.24 (m, 8H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 52.0, 51.1, 46.7, 33.8, 32.2, 29.1, 28.9, 28.8, 25.7, 24.7 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Na}$: 237.1461, Found: 237.1477.

(S)-Methyl 9-(oxiran-2-yl)nonanoate (8b):



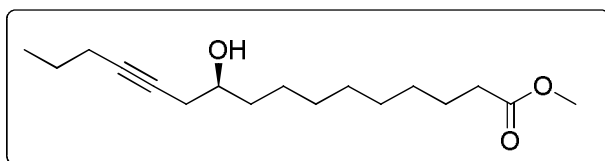
To a stirred solution of (*S,S*)-Jacobsen's catalyst ($[(S,S)\text{-}N,N'\text{-bis}(3,5\text{-di-}i\text{-tert-butylsalicylidene})\text{-}1,2\text{-cyclohexanediaminato}(2-)]\text{cobalt(II)}$) (21 mg, 0.3 mol%, 0.04 mmol) in toluene (1.5 mL) was added acetic acid (2 μL , 0.4 mol%, 0.05 mmol) at room temperature, and allowed to stir in an unsealed flask. After 2 h, toluene and excess acetic acid were removed under vacuo and compound **13** (2.5 g, 11.68 mmol) was then added. Water (115 μL , 0.55 eq, 6.43 mmol) was added to the reaction mixture at -10°C . The reaction mixture was allowed to stir for 24 h. After completion of the reaction (monitored by TLC), the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:9) to give the chiral (*S*)-epoxide **8b** (1.14 g, 46%) as a colourless liquid. $[\alpha]_{\text{D}}^{20} -9.2$ (c 0.8, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Na}$: 237.1467, Found: 237.1464.

(R)-Methyl-10-hydroxyhexadec-12-ynoate (7a):



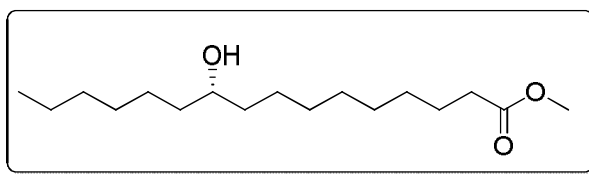
To a stirred solution of 1-pentyne (245 mg, 3.60 mmol) in dry THF (10 mL), was added LiHMDS (4.9 mL, 4.90 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 30 min, epoxide (*R*)-**8a** (700 mg, 3.27 mmol) dissolved in dry THF (20 mL) and boron trifluoride diethyletherate complex (0.5 mL, 3.92 mmol) were sequentially added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and allowed to stir for 2 h at the same temperature. After completion of the reaction (monitored by TLC), it was quenched with a saturated aqueous NH_4Cl (30 mL) solution and diluted with EtOAc (30 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc ($2 \times 40\text{ mL}$). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 3:17) to furnish the alkyne **7a** (756 mg, 82%) as a colourless liquid. $[\alpha]_{\text{D}}^{20} -4.1$ (c 1.0, CHCl_3); IR (CHCl_3) ν_{max} 3455, 2927, 1732, 1447, 1341, 1177, 1099, 1018, 752, 662 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.72-3.68 (m, 1H), 3.67 (s, 3H), 2.43-2.36 (m, 1H), 2.34-2.26 (m, 3H), 2.18-2.12 (m, 2H), 1.99 (br s, 1H), 1.67-1.58 (m, 2H), 1.55-1.48 (m, 4H), 1.47-1.33 (m, 2H), 1.32-1.26 (m, 8H), 0.97 (t, $J = 7.3\text{ Hz}$, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 82.5, 76.2, 69.9, 51.1, 35.9, 33.8, 29.3, 29.1, 28.9, 28.8, 27.5, 25.3, 24.7, 22.2, 20.5, 13.2 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{31}\text{O}_3$: 283.2268, Found: 283.2274.

(S)-Methyl-10-hydroxyhexadec-12-ynoate (7b):



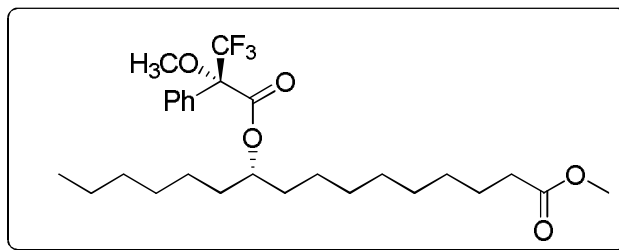
Compound **7b** (671 mg, 85%) was synthesized starting from epoxide (*S*)-**8b** (600 mg, 2.80 mmol) by following the above mentioned procedure. $[\alpha]_D^{20} +5.6$ (*c* 0.9, CHCl₃); HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for C₁₇H₃₁O₃: 283.2273, Found: 283.2272.

(*S*)-Methyl-10-hydroxyhexadecanoate (14a):



To a stirred solution of compound **7a** (600 mg, 2.13 mmol) in EtOAc (5 mL), was added 10% Pd/C (10% wt; 70 mg). The flask was purged with hydrogen gas and stirred for 6 h under hydrogen balloon pressure at room temperature. After completion of the reaction (monitored by TLC), the solution was filtered over a small Celite pad and washed with EtOAc (2 × 5 mL). The solvent was evaporated under reduced pressure and the residue obtained was purified by flash chromatography (ethyl acetate/hexane = 3:17) to give saturated compound **14a** (517 mg, 85%) as a colourless liquid. $[\alpha]_D^{20} +3.4$ (*c* 0.5, CHCl₃).; IR (CHCl₃) ν_{\max} 3326, 2922, 2826, 1737, 1465, 1211, 1120, 1020, 871, 758, 665 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.66 (s, 3H), 3.60-3.54 (m, 1H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.65-1.57 (m, 2H), 1.48-1.37 (m, 8H), 1.32-1.28 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 174.2, 71.7, 51.3, 37.4, 37.3, 33.9, 31.7, 29.5, 29.3, 29.1, 29.0, 25.5, 24.8, 22.5, 13.9 ppm; HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for C₁₇H₃₄O₃Na: 309.2400, Found: 309.2402.

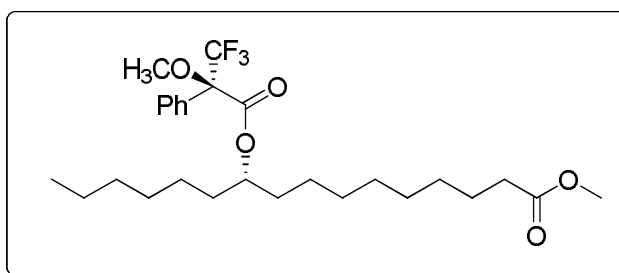
(*S*)-Methyl-10-(((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)hexadecanoate (14ai):



To a stirred solution of alcohol **14a** (20 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) were sequentially added *N,N*-dicycloheptylcarbodiimide (DCC) (22 mg, 0.10 mmol), (*S*)-(-)- α -methoxy- α -(trifluoromethyl)phenylacetic acid (*S*-MTPA) (25 mg, 0.10 mmol) and catalytic amount of DMAP (2mg) and the reaction was allowed to stirred at room temperature for 10h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous NaHCO_3 (3 mL) solution. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2×5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/ hexane = 1:9) to afford (*S*)-MTPA ester **14ai** (28 mg, 80%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.53 (m, 2H), 7.42-7.36 (m, 3H), 5.12-5.05 (m, 1H), 3.67 (s, 3H), 3.57-3.55 (m, 3H), 2.30 (t, $J = 7.58$ Hz, 2H), 1.67-1.55 (m, 6H), 1.32-1.24 (m, 12H), 1.22-1.13 (m, 6H), 0.86 (t, $J = 7.09$ Hz, 3H) ppm.

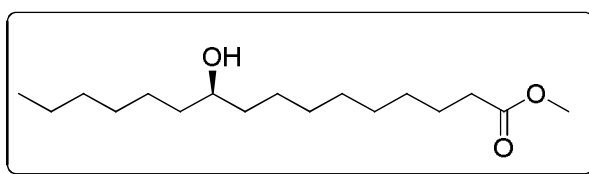
(*S*)-Methyl-10-(((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)hexadecanoate

(14aii):



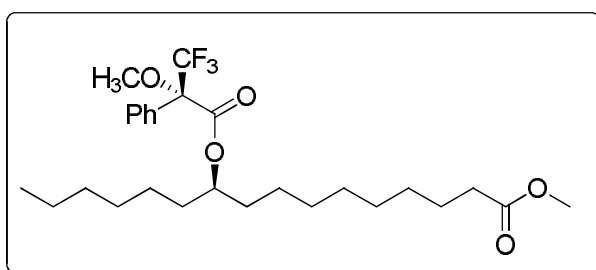
(*R*)-MTPA ester **14aii** was synthesized from the reaction of alcohol **14a** with (*R*)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetic acid (*R*-MTPA) by following the above mentioned procedure. ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.51 (m, 2H), 7.43-7.35 (m, 3H), 5.13-5.04 (m, 1H), 3.67 (s, 3H), 3.60-3.53 (m, 3H), 2.30 (t, $J = 7.43$ Hz, 2H), 1.66-1.53 (m, 6H), 1.34-1.23 (m, 12H), 1.22-1.15 (m, 6H), 0.88 (t, $J = 6.87$ Hz, 3H) ppm.

(*R*)-Methyl-10-hydroxyhexadecanoate (14b):



Compound **14b** (445 mg, 88%) was synthesized starting from alkyne (*S*)-**7b** (500 mg, 1.77 mmol) by following the above mentioned procedure. $[\alpha]_{\text{D}}^{20} -3.9$ (c 1.0, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{34}\text{O}_3\text{Na}$: 309.2406, Found: 309.2412.

(*R*)-Methyl-10-(((*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)hexadecanoate (14bi):

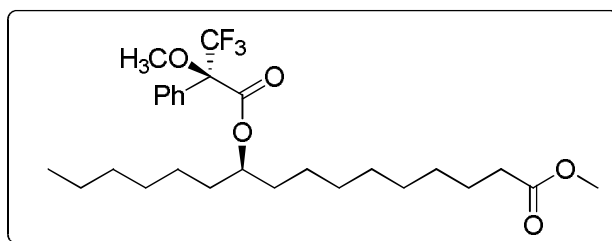


(*S*)-MTPA ester **14bi** was synthesized from the reaction of alcohol **14b** with (*S*)-(-)- α -methoxy- α -(trifluoromethyl)phenylacetic acid (*S*-MTPA) by following procedure described for the synthesis of compound **14ai**. ^1H NMR (500 MHz, CDCl_3) δ 7.57-7.53 (m, 2H), 7.41-7.37 (m,

3H), 5.11-5.05 (m, 1H), 3.67 (s, 3H), 3.57-3.55 (m, 3H), 2.30 (t, $J = 7.47$ Hz, 2H), 1.65-1.55 (m, 6H), 1.32-1.23 (m, 12H), 1.22-1.15 (m, 6H), 0.88 (t, $J = 7.17$ Hz, 3H) ppm.

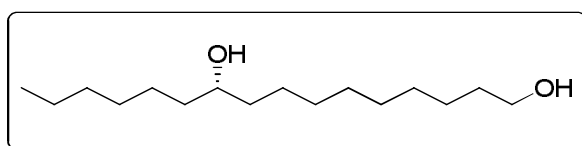
(*R*)-Methyl-10-(((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)hexadecanoate

(14bii):



(*R*)-MTPA ester **14bii** was synthesized from the reaction of alcohol **14b** with (*R*)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetic acid (*R*-MTPA) by following procedure described for the synthesis of compound **14ai**. ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.52 (m, 2H), 7.43-7.37 (m, 3H), 5.13-5.03 (m, 1H), 3.67 (s, 3H), 3.58-3.55 (m, 3H), 2.30 (t, $J = 7.70$ Hz, 2H), 1.64-1.53 (m, 6H), 1.35-1.24 (m, 12H), 1.22-1.15 (m, 6H), 0.86 (t, $J = 6.87$ Hz, 3H) ppm.

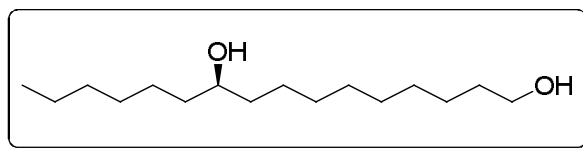
(*S*)-Hexadecane-1,10-diol (15a):



To a stirred solution of compound **14a** (450 mg, 1.58 mmol) in CH_2Cl_2 (25 mL), was added DIBAL-*H* (1.4 M in toluene, 2.8 mL, 3.90 mmol) at -10°C and the reaction mixture was stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous solution of sodium potassium tartrate (20 mL), diluted with CH_2Cl_2 (15 mL) and stirred at room temperature for 4 h. The organic layer was separated and the

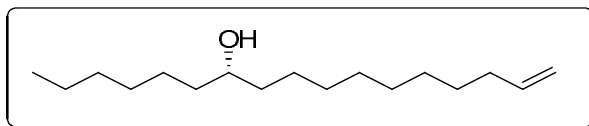
aqueous layer extracted with CH_2Cl_2 (2×30 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:4) to obtain the diol **15a** (365 mg, 90%) as a white amorphous solid. Mp. 62-63 °C; $[\alpha]_{\text{D}}^{20} -5.0$ (c 0.3, CHCl_3); IR (CHCl_3) ν_{max} 3310, 3013, 2924, 2856, 1462, 1216, 1061, 749, 668 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.62 (t, J = 6.6 Hz, 2H), 3.60-3.56 (m, 1H), 1.59-1.51 (m, 2H), 1.49-1.37 (m, 8H), 1.34-1.28 (m, 16H), 0.88 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 71.9, 62.8, 37.4, 32.7, 31.8, 29.6, 29.5, 29.3, 25.7, 25.6, 22.6, 14.0 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Na}$: 281.2451, Found: 281.2451.

(R)-Hexadecane-1,10-diol (15b):



Compound **15b** (331 mg, 92%) was synthesized starting from saturated ester (*R*)-**14b** (400 mg, 1.39 mmol) by following the above mentioned procedure. $[\alpha]_{\text{D}}^{20} +4.8$ (c 0.5, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Na}$: 281.2456, Found: 281.2462.

(S)-Heptadec-16-en-7-ol (3a):



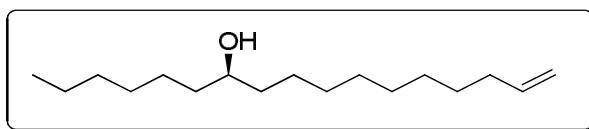
To a stirred solution of diol compound **15a** (250 mg, 0.97 mmol) in CH_2Cl_2 (10 mL), were added bis(acetoxy)iodobenzene (BAIB) (467 mg, 0.467 mmol) and TEMPO (15 mg, 0.096 mmol) to

the reaction mixture at 0 °C and the resultant mixture was warmed to room temperature. After completion of the reaction (monitored by TLC), it was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) solution and diluted with CH_2Cl_2 (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layer was washed with saturated aqueous NaHCO_3 (40 mL) solution and brine (40 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (ethyl acetate/ hexane = 1:9) to furnish the corresponding aldehyde (232 mg) as a white amorphous solid, which was used for the next step without further characterization.

To a stirred solution of triphenylmethylphosphonium bromide (1.7 g, 4.69 mmol) in THF (15 mL), was added NaHMDS (3.1 mL, 3.1 mmol) at -78 °C. After stirring for 30 min at room temperature, the reaction mixture was again cooled to -78 °C and the above mentioned aldehyde (200 mg, 0.78 mmol) in THF (15 mL) was added. The reaction mixture was warmed to room temperature and allowed to stir for 12 h. After completion of the reaction (monitored by TLC), it was quenched with a saturated aqueous NH_4Cl (20 mL) solution and diluted with EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , and evaporated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:19) to afford alkenol **3a** (126 mg, 60% over two steps) as a white amorphous solid. Mp 48 °C; $[\alpha]_{\text{D}}^{20} +7.4$ (c 0.5, CHCl_3); IR (CHCl_3) ν_{max} 3334, 3076, 2920, 2853, 1642, 1458, 1350, 1126, 1033, 909, 722 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.86-5.77 (m, 1H), 5.02-4.91 (m, 2H), 3.61-3.56 (m, 1H), 2.07-2.02 (m, 2H), 1.46-1.39 (m, 6H), 1.34-1.25 (m, 18H),

0.88 (t, $J = 6.71$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 114.1, 72.0, 37.4, 33.8, 31.8, 29.7, 29.5, 29.4, 29.4, 29.1, 28.9, 25.6, 22.6, 14.0 ppm; EIMS: m/z : 254 (M) $^+$.

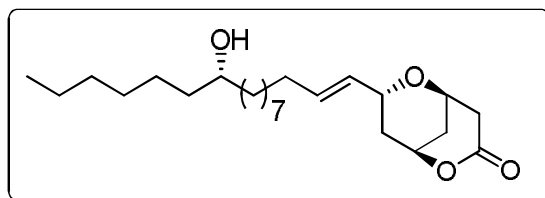
(*R*)-Heptadec-16-en-7-ol (3b):



Compound **3b** (132 mg, 64% over two steps) was synthesized starting from diol (*R*)-**15b** (250 mg, 0.97 mmol) by following the above mentioned procedure. $[\alpha]_{\text{D}}^{20} -6.2$ (c 0.5, CHCl_3); EIMS: m/z : 254 (M) $^+$.

(1*R*,5*R*,7*R*)-7-((*S*,*E*)-11-Hydroxyheptadec-1-en-1-yl)-2,6-dioxabicyclo[3.3.1]nonan-3-one

(1a):

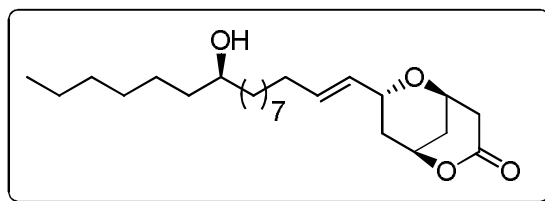


To a stirred solution of bicyclic compound **2** (15 mg, 0.08 mmol) in CH_2Cl_2 (2 mL), were sequentially added alkenol **3a** (31 mg, 0.12 mmol) and Hoveyda-Grubbs' second generation catalyst (3 mg, 10% mol) at room temperature. The reaction mixture was allowed to stir at room temperature for 16 h. After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and the resulting crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 3:7) to yield **1a** (23 mg, 72%) as amorphous solid. Mp. 54 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{21} -8.0$ (c 0.6, MeOH); IR (CHCl_3) ν_{max} 2922, 2855, 1732, 1456, 1379,

1342, 1216, 1155, 1071, 91, 866, 764 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.73 (m, 1H), 5.42 (ddt, $J = 15.4, 6.6, 1.2$ Hz, 1H), 4.91 (m, 1H), 4.40 (br s, 1H), 4.23 (m, 1H), 3.58 (m, 1H), 2.93 (brd, $J = 19.2$ Hz, 1H), 2.79 (dd, $J = 19.2, 5.3$ Hz, 1H), 2.12-1.95 (m, 5H), 1.92 (m, 1H), 1.74-1.63 (m, 2H), 1.45-1.40 (m, 4H), 1.33-1.25 (m, 18H), 0.88 (t, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.71, 134.34, 128.67, 72.96, 71.99, 66.91, 65.93, 37.48, 37.45, 37.17, 36.47, 32.17, 31.82, 29.65, 29.49, 29.47, 29.35, 29.09, 28.86, 25.60, 22.60, 14.07 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{42}\text{O}_4\text{Na}$: 417.2975, Found: 417.2985.

(1*R*,5*R*,7*R*)-7-((*R*,*E*)-11-Hydroxyheptadec-1-en-1-yl)-2,6-dioxabicyclo[3.3.1]nonan-3-one

(1b):

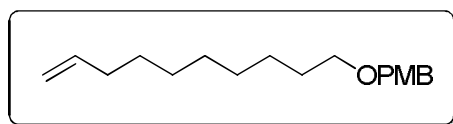


Compound **1b** (24 mg, 74%) was synthesized from coupling of **2** (15 mg, 0.08 mmol) with **3b** (31 mg, 0.12 mmol)

by following the above mentioned procedure. $[\alpha]_{\text{D}}^{21} -12.0$ (c 0.6, MeOH); IR (CHCl_3) ν_{max} 3311, 2919, 2853, 1729, 1459, 1379, 1342, 1265, 1205, 1070, 981, 759 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.73 (m, 1H), 5.41 (ddt, $J = 15.4, 6.5, 1.2$ Hz, 1H), 4.90 (m, 1H), 4.39 (brs, 1H), 4.22 (m, 1H), 3.58 (m, 1H), 2.93 (brd, $J = 19.2$ Hz, 1H), 2.79 (dd, $J = 19.2, 5.3$ Hz, 1H), 2.12-1.96 (m, 5H), 1.92 (m, 1H), 1.73-1.61 (m, 2H), 1.45-1.41 (m, 4H), 1.32-1.25 (m, 18H), 0.88 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.71, 134.34, 128.68, 72.96, 72.00, 66.92, 65.94, 37.49, 37.46, 37.18, 36.49, 32.18, 31.83, 29.66, 29.49, 29.48, 29.36, 29.09, 28.86, 25.61,

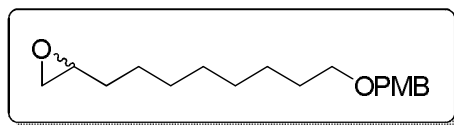
22.61, 14.08 ppm; HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{24}H_{42}O_4Na$: 417.2975, Found: 417.2966.

1-((Dec-9-en-1-yloxy)methyl)-4-methoxybenzene (16a):



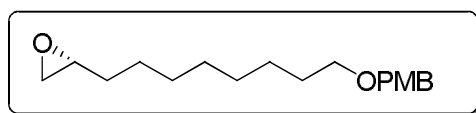
To a stirred solution of 9-decen-1-ol (5.0 g, 32.05 mmol) in THF (100 mL), was added NaH (1.54 g, 64.10 mmol, 60% dispersion in mineral oil) at 0 °C. After stirring for 30 minutes, 4-methoxybenzyl bromide (5.6 mL, 38.46 mmol) was slowly added to the reaction mixture at 0 °C and allowed to stir at room temperature for 5 h. After completion of the reaction (monitored by TLC), it was quenched with ice cold water (70 mL) and dilute with EtOAc (100 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 × 100 mL). The combined organic layers were washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:19) to furnish compound **16a** (7.5 g, 85%) as a colorless oil. IR ($CHCl_3$) ν_{max} 3736, 2925, 2852, 1610, 1512, 1455, 1244, 1097, 910, 818 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.68 Hz, 2H), 6.87 (d, J = 8.68 Hz, 2H), 5.87-5.74 (m, 1H), 5.03-4.89 (m, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.42 (t, J = 6.7 Hz, 2H), 2.07-1.99 (m, 2H), 1.64-1.55 (m, 2H), 1.41-1.24 (m, 10 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 139.0, 130.7, 129.1, 114.0, 113.6, 72.4, 70.1, 55.1, 33.7, 29.7, 29.3, 29.0, 28.8, 26.1 ppm; HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{18}H_{28}O_2Na$: 299.1987, Found: 299.1989.

2-(8-((4-Methoxybenzyl)oxy)octyl)oxirane (17):

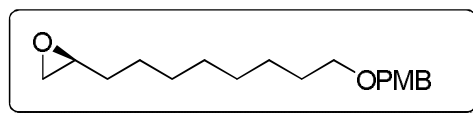


Compound **17** (5.9 g, 80%) was synthesized from **16a** (7.0, 25.36 mmol) by following procedure described for the synthesis of compound **13**. IR (CHCl₃) ν_{\max} 3736, 2927, 2854, 1612, 1513, 1458, 1245, 1095, 1036, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.42 (s, 2H), 3.79 (s, 3H), 3.43 (t, J = 6.6 Hz, 2H), 2.92-2.86 (m, 1H), 2.73 (dd, J = 5.0, 4.0 Hz, 1H), 2.45 (dd, J = 5.0, 2.5 Hz, 1H), 1.64-1.40 (m, 6H), 1.38-1.24 (m, 8H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 130.6, 129.0, 113.6, 72.3, 70.0, 55.1, 52.2, 46.9, 32.3, 29.6, 29.3, 29.2, 26.0, 25.8 ppm; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₈H₂₈O₃Na: 315.1936, Found: 315.1935.

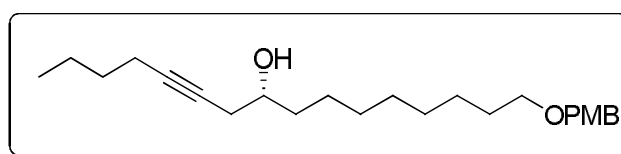
(R)-2-(8-((4-Methoxybenzyl)oxy)octyl)oxirane (8c):



Compound **8c** (0.92 g, 48%) was synthesized from **17** (2.0 g, 6.85 mmol) by following procedure described for the synthesis of compound **8a**. [α]_D²⁰ +8.7 (c 0.8, CHCl₃); IR (CHCl₃) ν_{\max} 3736, 2926, 2853, 1608, 1513, 1458, 1246, 1094, 822, 750 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.43 (t, J = 6.7 Hz, 2H), 2.92-2.87 (m, 1H), 2.74 (dd, J = 5.0, 4.1 Hz, 1H), 2.46 (dd, J = 5.0, 2.7 Hz, 1H), 1.62-1.56 (m, 2H), 1.55-1.49 (m, 2H), 1.48-1.39 (m, 2H), 1.37-1.27 (m, 8H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 159.0, 130.7, 129.1, 113.6, 72.4, 70.1, 55.2, 52.3, 47.0, 32.4, 29.7, 29.4, 29.3, 26.1, 25.9 ppm; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₈H₂₈O₃Na: 315.1936, Found: 315.1953.

(S)-2-(8-((4-Methoxybenzyl)oxy)octyl)oxirane (8d):

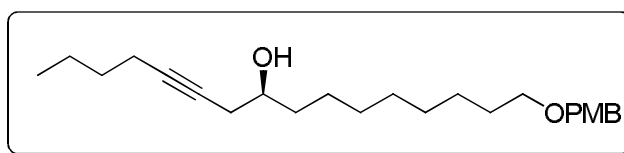
Compound **8d** (0.92 g, 48%) was synthesized from **17** (2.0 g, 6.85 mmol) by following procedure described for the synthesis of compound **8b**. $[\alpha]_D^{20} -7.1$ (*c* 1.2, CHCl₃); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for C₁₈H₂₈O₃Na: 315.1936, Found: 315.1942.

(R)-16-((4-Methoxybenzyl)oxy)hexadec-5-yn-8-ol (7c):

To a stirred solution of 1-hexyne (154 mg, 1.88 mmol) in dry THF (10 mL), was added LiHMDS (2.6 mL, 2.60 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 30 min, (*R*)-epoxide **8c** (500 mg, 1.71 mmol) dissolved in dry THF (15 mL) and boron trifluoride diethyletherate complex (0.25 mL, 2.05 mmol) were added sequentially to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and allowed to stir for 2 h at the same temperature. After completion of the reaction (monitored by TLC), it was quenched with a saturated aqueous NH₄Cl (20 mL) solution and diluted with EtOAc (25 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (2 \times 30 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 3:17) to obtain the alkyne **7c** (563 mg, 88%) as a pale yellow liquid. $[\alpha]_D^{20} -4.1$ (*c* 0.7, CHCl₃); IR (CHCl₃) ν_{max} 3735, 2925, 2855, 1609, 1513, 1456, 1301, 1245, 1092, 820, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H), 3.80 (s,

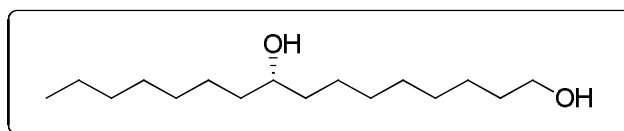
3H), 3.72-3.67(m, 1H), 3.43 (t, $J = 6.6$ Hz, 2H), 2.43-2.35 (m, 1H), 2.30-2.22 (m, 1H), 2.20-2.14 (m, 2H), 2.01(brs, 1H), 1.63-1.55 (m, 2H), 1.53-1.37 (m, 8H), 1.34-1.26 (m, 8H), 0.91 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 130.6, 129.0, 113.6, 82.9, 76.0, 72.3, 70.0, 55.1, 36.1, 30.9, 29.6, 29.4, 29.3, 27.6, 26.0, 25.5, 21.8, 18.3, 13.5 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{38}\text{O}_3\text{Na}$: 397.2719, Found: 397.2713.

(S)-16-((4-Methoxybenzyl)oxy)hexadec-5-yn-8-ol (7d):



Compound **7d** (691 mg, 90%) was synthesized from **8d** (250 mg, 0.97 mmol) by following the above mentioned procedure. $[\alpha]_{\text{D}}^{20} +5.6$ (c 1.0, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{38}\text{O}_3\text{Na}$: 397.2719, Found: 397.2718.

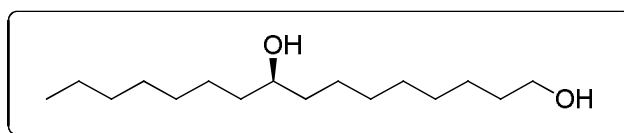
(S)-Hexadecane-1,9-diol (15c):



To a stirred solution of compound **7c** (400 mg, 1.07 mmol) in MeOH (8 mL) was added palladium 10% on carbon (60 mg). The reaction mixture was stirred under H_2 atmosphere for 14 h. After completion of the reaction (monitored by TLC), Pd/C was filtered through a small pad of Celite and the filtrate was concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:4) to afford diol **15c** (256 mg, 93%) as a white amorphous solid. Mp. 70°C ; $[\alpha]_{\text{D}}^{20} +5.3$ (c 0.6, CHCl_3); IR (CHCl_3) ν_{max} 3736,

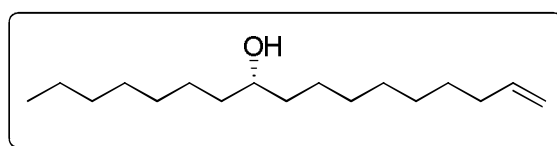
3319, 2922, 2856, 1464, 1216, 1060, 752 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.64 (t, J = 6.6 Hz, 2H), 3.60-3.54 (m, 1H), 1.61-1.52 (m, 2H), 1.47-1.38 (m, 6H), 1.37-1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 71.9, 62.9, 37.4, 37.4, 32.7, 31.8, 29.6, 29.6, 29.5, 29.3, 29.2, 25.7, 25.6, 25.6, 22.6, 14.0 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Na}$: 281.2456, Found: 281.2457.

(R)-Hexadecane-1,9-diol (15d):



Compound **15d** (313 mg, 91%) was synthesized from the alkyne **7d** (250 mg, 0.97 mmol) by following the above mentioned procedure. $[\alpha]_{\text{D}}^{20}$ -4.2 (c 1.1, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Na}$: 281.2456, Found: 281.2464.

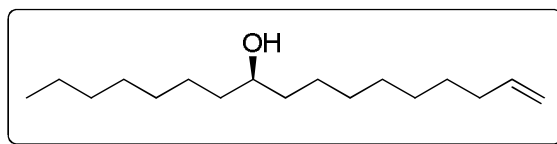
(S)-Heptadec-16-en-8-ol (3c):



Compound **3c** (101 mg, 68% over two steps) was synthesized from **15c** (180 mg, 0.70 mmol) by following procedure described for the synthesis of compound **3a**. Mp. 54 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20}$ $+6.2$ (c 0.4, CHCl_3); IR (CHCl_3) ν_{max} 3735, 2921, 2855, 1645, 1457, 1343, 1249, 1159, 911 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.87-5.75 (m, 1H), 5.02-4.90 (m, 2H), 3.60-3.56 (m, 1H), 2.06-2.00 (m, 2H), 1.48-1.38 (m, 8H), 1.34-1.25 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz,

CDCl_3) δ 139.2, 114.1, 72.0, 37.5, 37.4, 33.8, 31.8, 29.7, 29.6, 29.4, 29.3, 29.0, 28.9, 25.6, 25.6, 22.6, 14.1 ppm; EIMS: m/z : 254 (M)⁺.

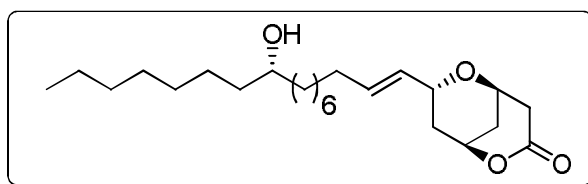
(R)-Heptadec-16-en-8-ol (3d):



Compound **3d** (136 mg, 69% over two steps) was synthesized from **15d** (250 mg, 0.96 mmol) by following procedure described for the synthesis of compound **3a**. $[\alpha]_{\text{D}}^{20} -5.3$ (c 1.0, CHCl_3); EIMS: m/z : 254 (M)⁺.

(1R,5R,7R)-7-((S,E)-10-Hydroxyheptadec-1-en-1-yl)-2,6-dioxabicyclo[3.3.1]nonan-3-one

(1c):

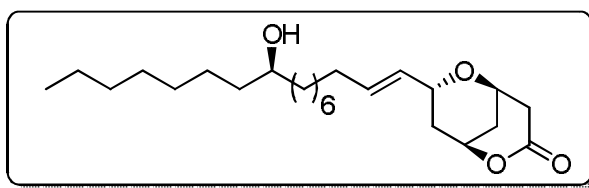


Compound **1c** (15 mg, 70%) was synthesized from coupling of **2** (10 mg, 0.05 mmol) with **3c** (20 mg, 0.08 mmol) by following the procedure described for the synthesis of compound **1a**. $[\alpha]_{\text{D}}^{21} -6.2$ (c 0.6, MeOH); IR (CHCl_3) ν_{max} 3538, 2923, 2855, 1732, 1514, 1456, 1378, 1342, 1265, 1216, 1156, 1071, 980, 869, 766 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.74 (m, 1H), 5.42 (ddt, J = 15.4, 6.5, 1.4 Hz, 1H), 4.91 (m, 1H), 4.40 (brs, 1H), 4.23 (m, 1H), 3.58 (m, 1H), 2.93 (brd, J = 19.2 Hz, 1H), 2.79 (dd, J = 19.2, 5.3 Hz, 1H), 2.10-1.99 (m, 5H), 1.92 (m, 1H), 1.73-1.64 (m, 2H), 1.47-1.38 (m, 6H), 1.31-1.25 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz,

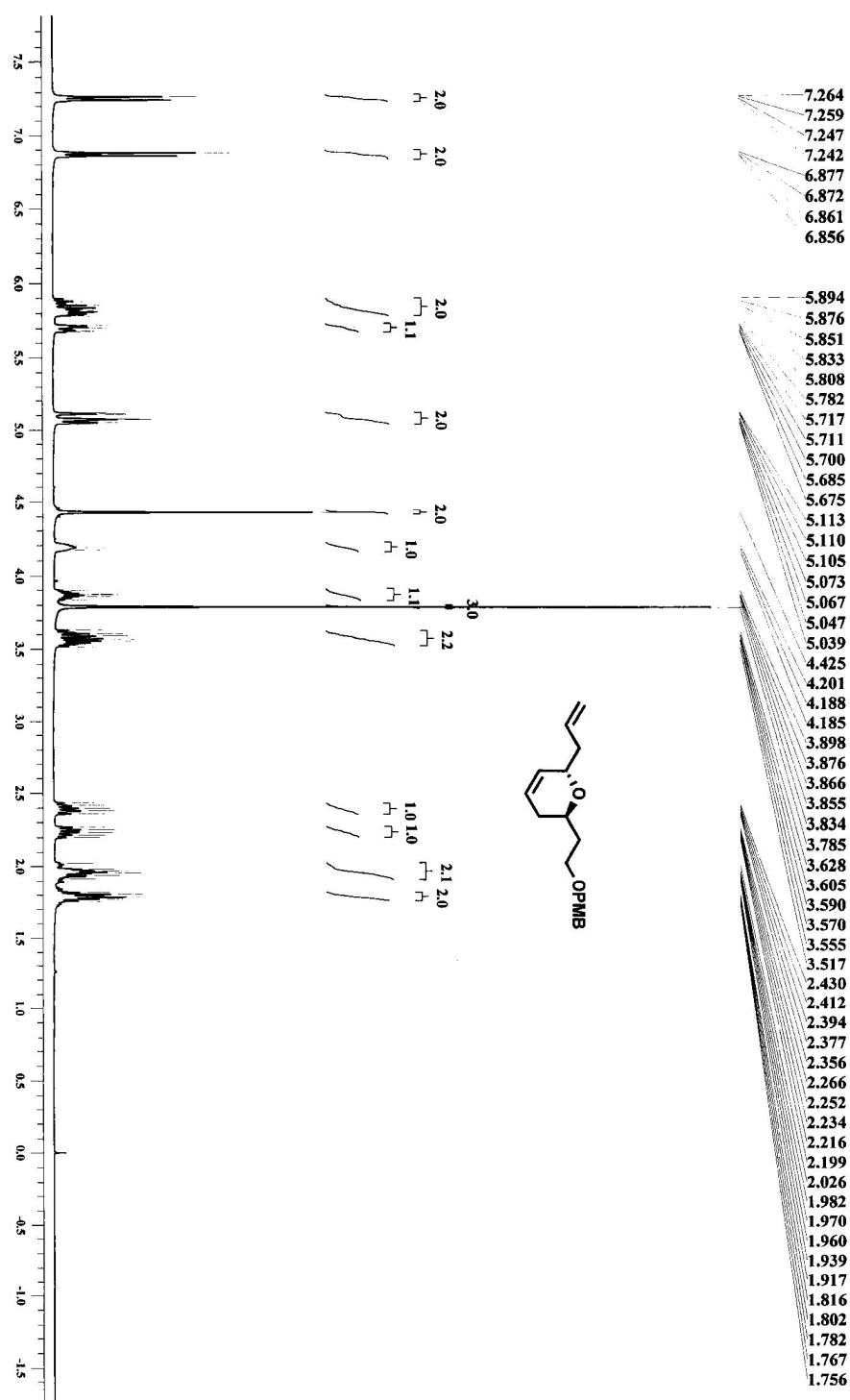
CDCl_3) δ 169.70, 134.31, 128.71, 72.96, 71.99, 66.92, 65.94, 37.49, 37.44, 37.18, 36.49, 32.16, 31.82, 29.66, 29.58, 29.48, 29.36, 29.28, 29.03, 28.84, 25.65, 25.60, 22.64, 14.08 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{42}\text{O}_4\text{Na}$: 417.2981, Found: 417.2982.

(1*R*,5*R*,7*R*)-7-((*R*,*E*)-10-Hydroxyheptadec-1-en-1-yl)-2,6-dioxabicyclo[3.3.1]nonan-3-one

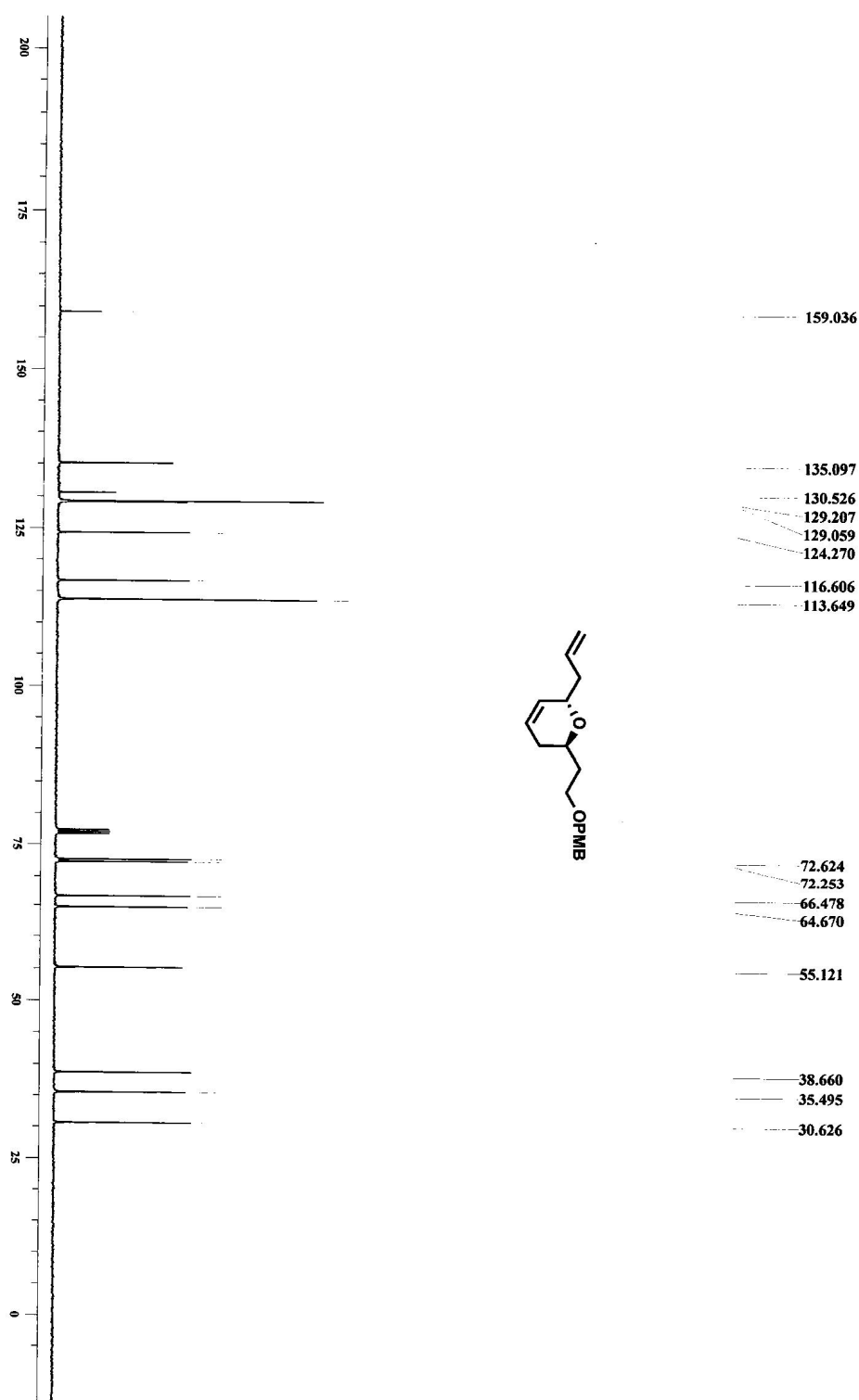
(1d):



Compound **1d** (16 mg, 74%) was synthesized from coupling of **2** (10 mg, 0.05 mmol) with **3d** (20 mg, 0.08 mmol) by following procedure described for the synthesis of compound **1a**. $[\alpha]_{\text{D}}^{21}$ -20.0 (c 0.6, MeOH); IR (CHCl_3) ν_{max} 3307, 2918, 2852, 1728, 1459, 1379, 1342, 1268, 1204, 1152, 1070, 978, 760 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.72 (m, 1H), 5.40 (ddt, $J = 15.4, 6.4, 1.4$ Hz, 1H), 4.89 (m, 1H), 4.38 (brs, 1H), 4.21 (m, 1H), 3.57 (m, 1H), 2.92 (brd, $J = 19.2$ Hz, 1H), 2.78 (dd, $J = 19.2, 5.3$ Hz, 1H), 2.10-1.96 (m, 5H), 1.91 (m, 1H), 1.73-1.61 (m, 2H), 1.45-1.38 (m, 6H), 1.30-1.25 (m, 16H), 0.87 (t, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 169.57, 134.13, 128.80, 72.95, 71.96, 66.86, 65.97, 37.52, 37.46, 37.25, 36.52, 32.14, 31.81, 29.66, 29.58, 29.53, 29.36, 29.26, 29.02, 28.86, 25.63, 25.59, 22.62, 14.03 ppm; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{42}\text{O}_4\text{Na}$: 417.2981, Found: 417.2974.



¹H NMR spectrum of **5** (400 MHz, CDCl₃)



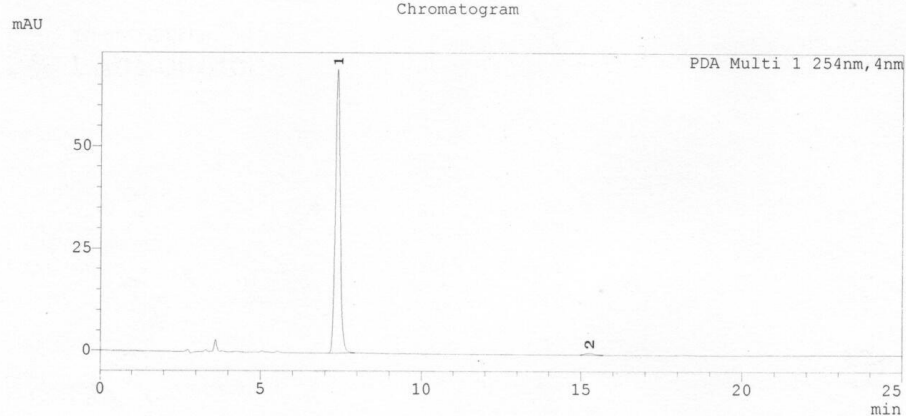
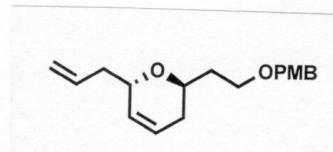
¹³C NMR spectrum of **5** (100 MHz, CDCl₃)



LC-MS DATA REPORT

HCT-DNFC

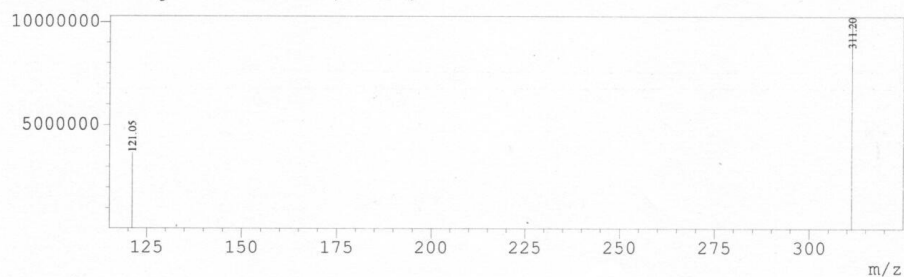
Sample Code : DKM-GSR-CYC-288
Data File : 110417_16.lcd
Method : LC-MS Lab Method_85.lcm
Injection Volume : 10
Date Acquired : 4/11/2017 6:20:17 PM
Report File : LC-MS Data Report.lsr
Chromatographic Conditions : Column : LUNA (250 X 4.6mm, 5u)
Mobile Phase: 80 % MECH IN 0.1 % FA
Flow Rate : 1.0 mL/min



Peak Table

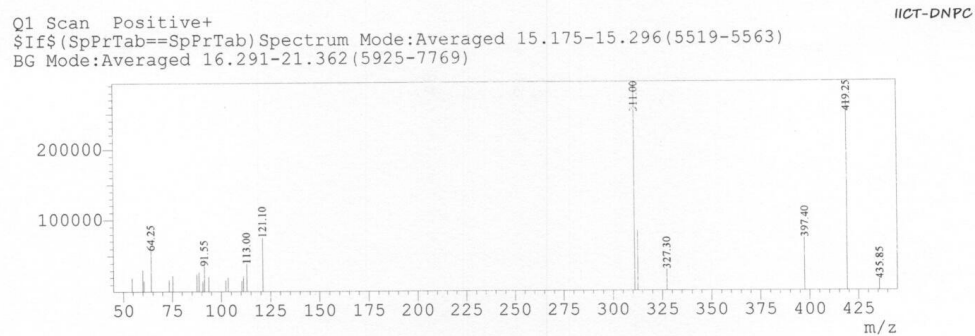
Peak#	Ret. Time	Peak Start	Peak End	Area	Area%
1	7.373	7.061	7.936	735658	98.928
2	15.265	14.912	15.701	7973	1.072
Total				743632	100.000

Q1 Scan Positive+
\$If\$(SpPrTab==SpPrTab) Spectrum Mode:Averaged 7.117-8.267 (2589-3007)
BG Mode:Averaged 0.000-6.578 (1-2393)



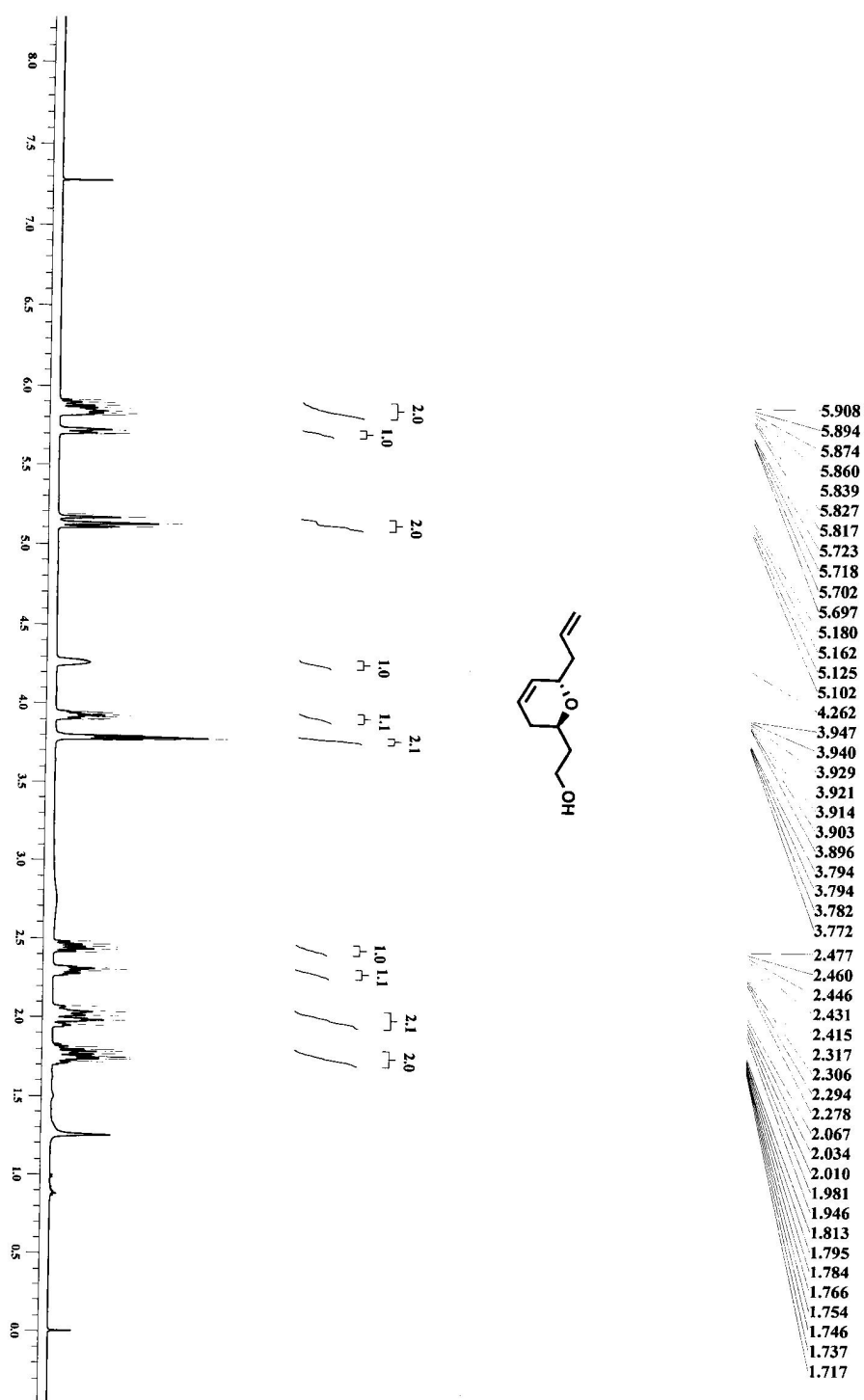
REPORT

HPLC Chromatogram of 5

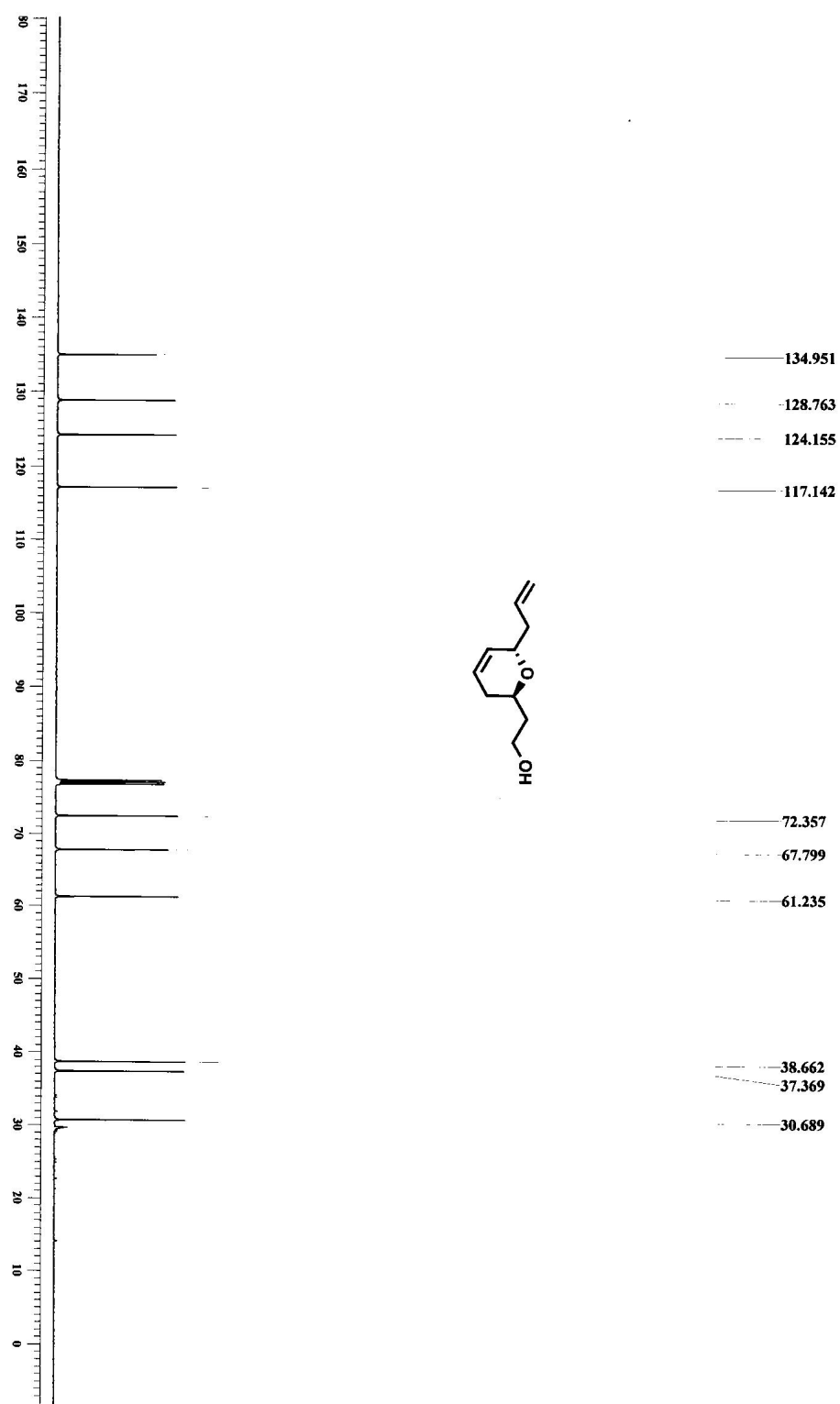


LC-MS REPORT

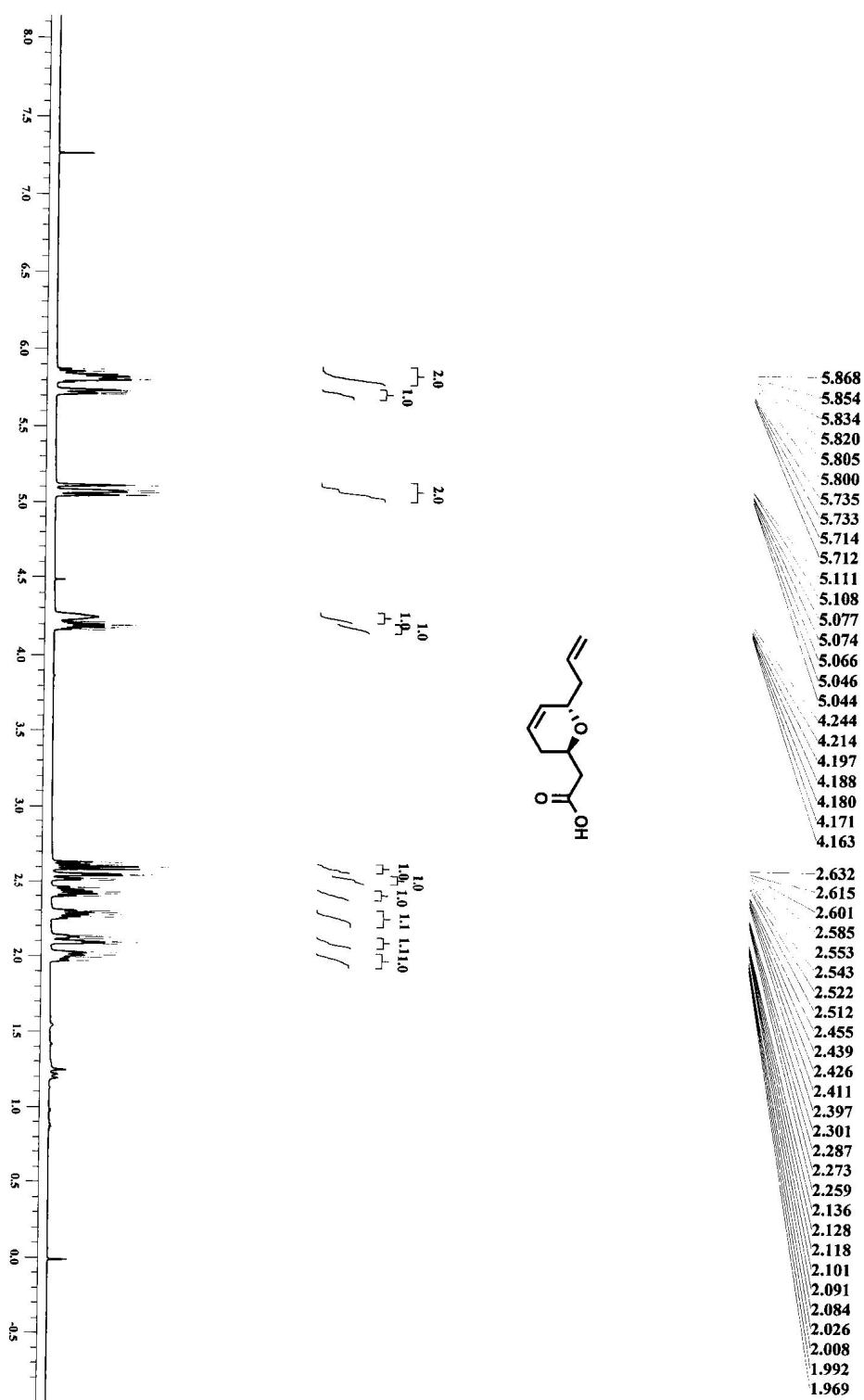
Mass Chromatogram of 5



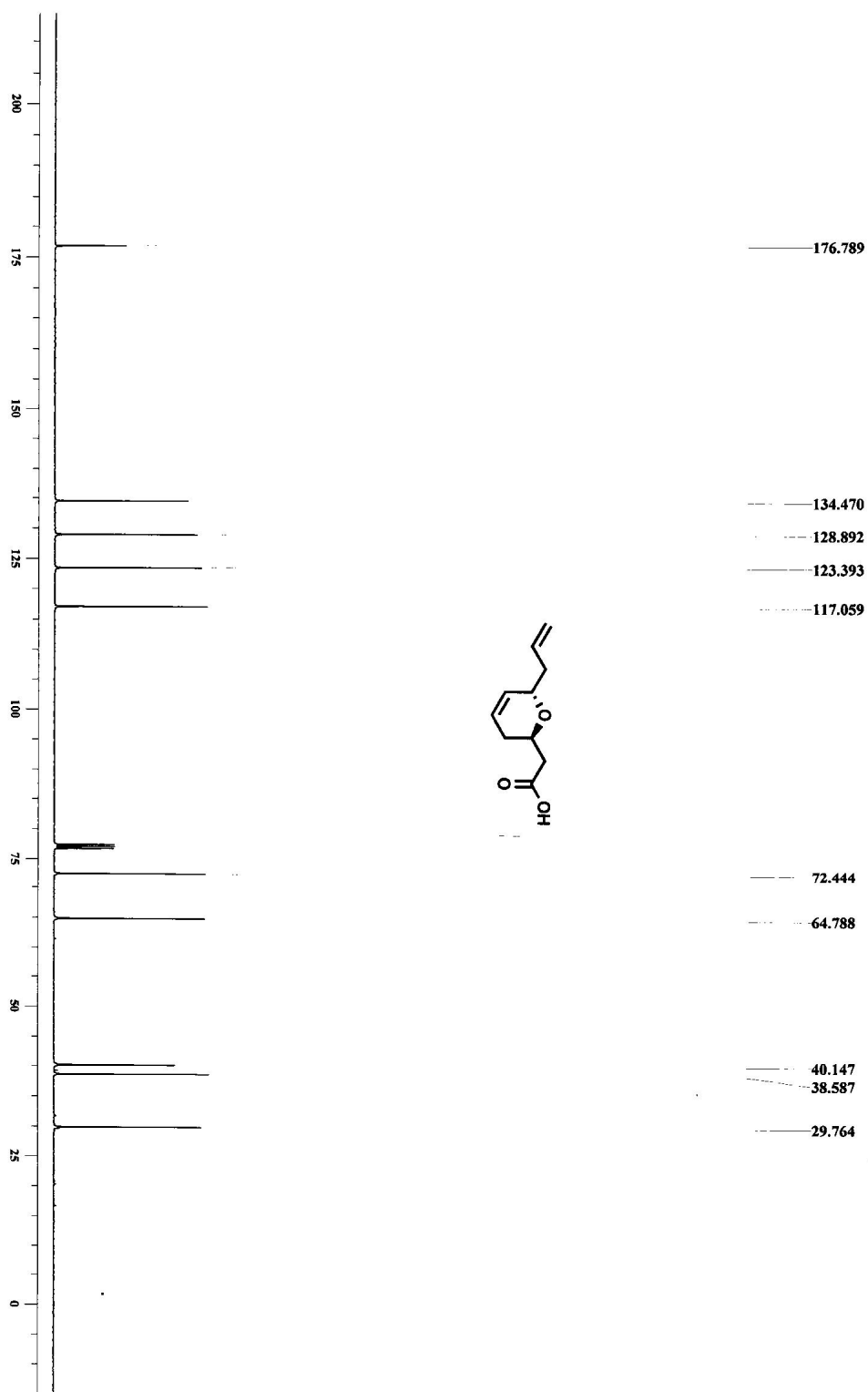
^1H NMR spectrum of **10** (500 MHz, CDCl_3)

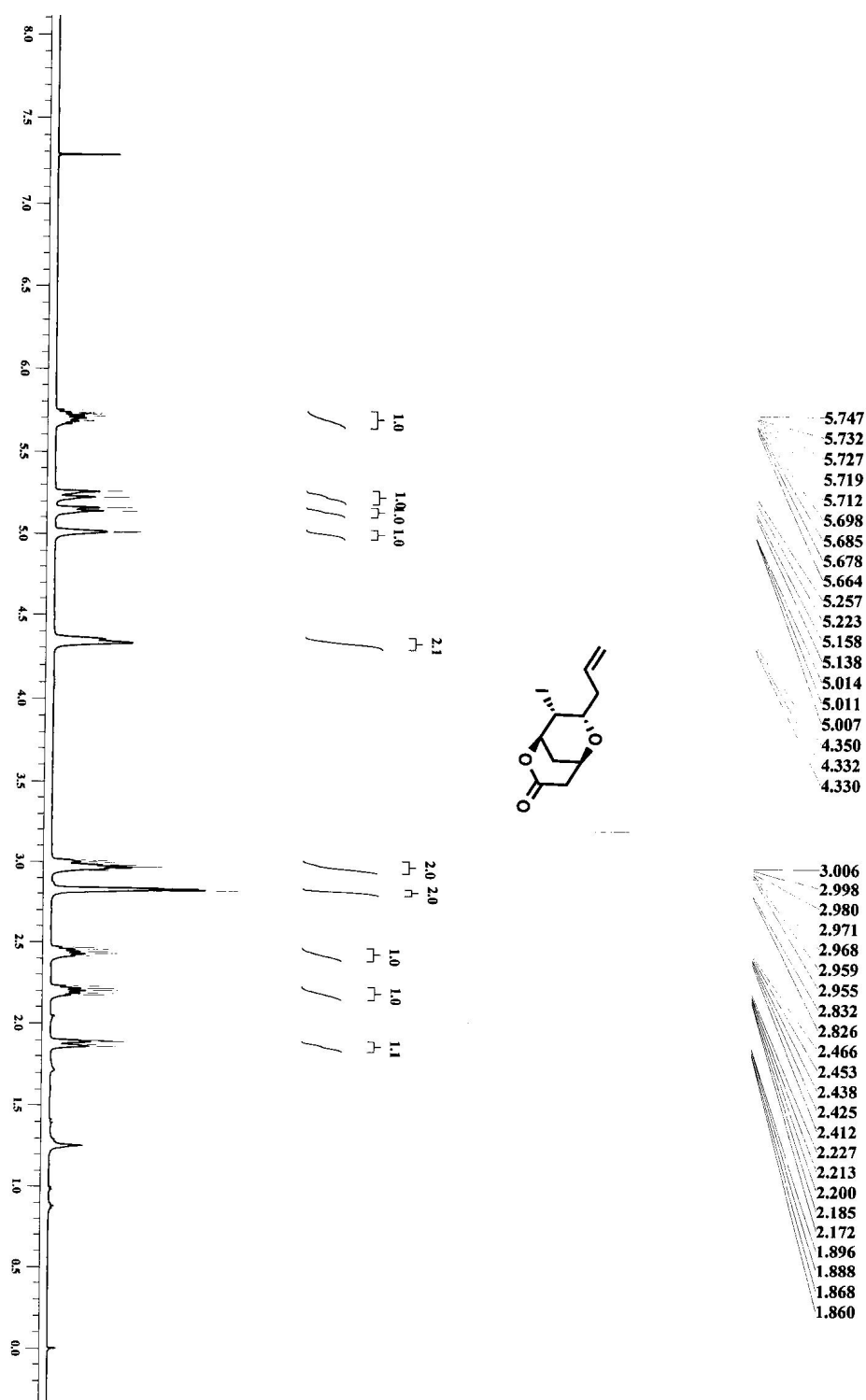


^{13}C NMR spectrum of **10** (125 MHz, CDCl_3)

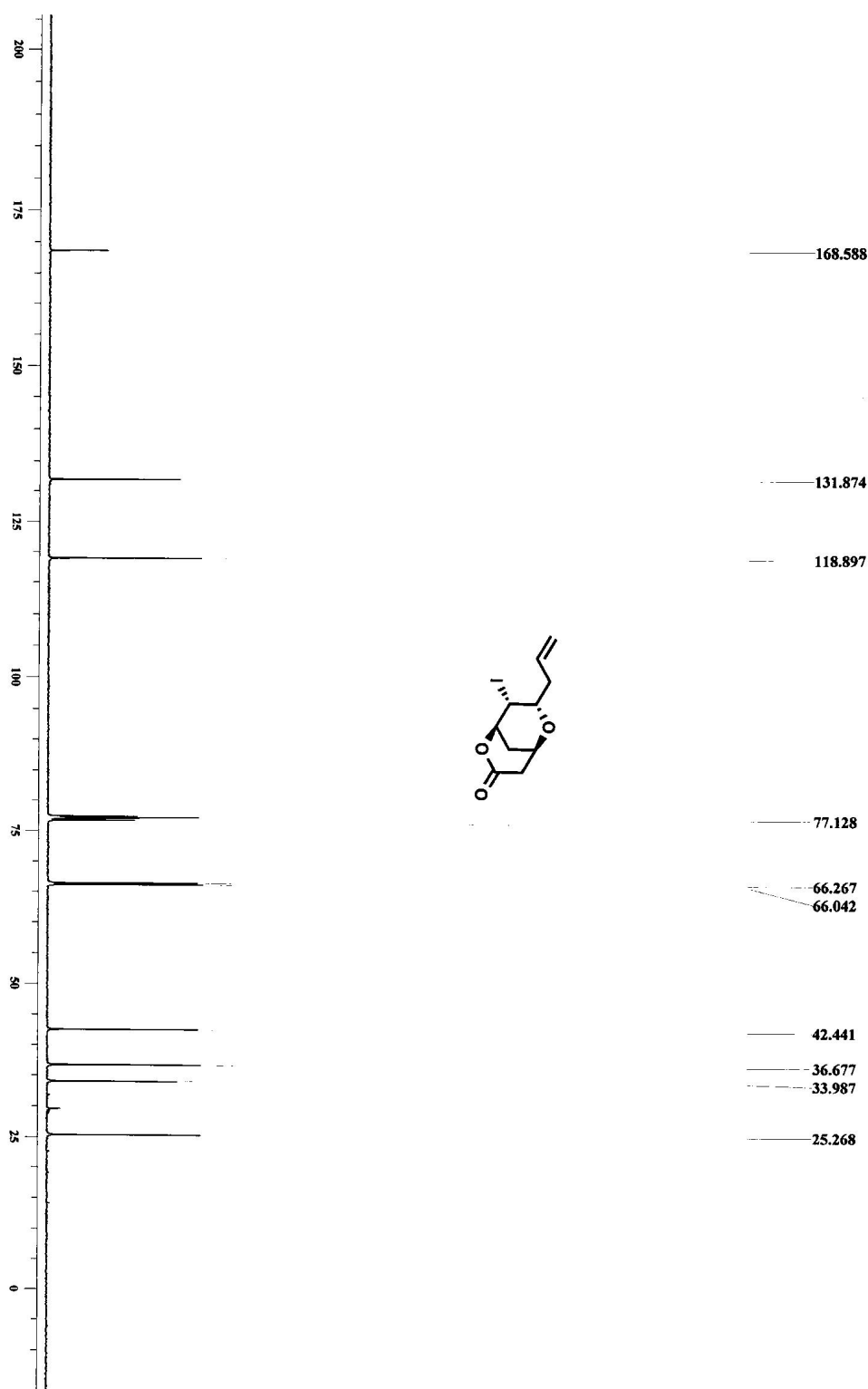


¹H NMR spectrum of **4** (500 MHz, CDCl₃)

 ^{13}C NMR spectrum of **4** (100 MHz, CDCl_3)



^1H NMR spectrum of **11** (500 MHz, CDCl_3)



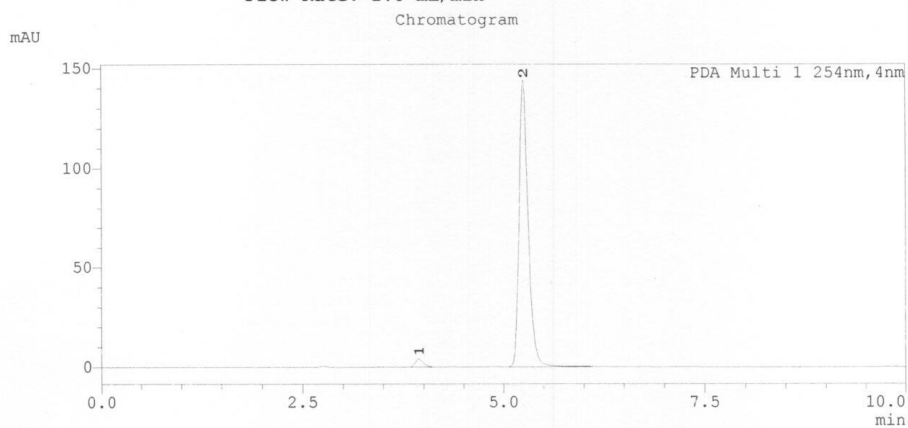
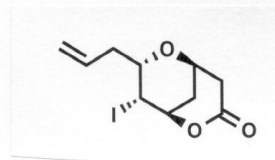
^{13}C NMR spectrum of **11** (100 MHz, CDCl_3)



LC-MS DATA REPORT

IIC-T-DNPC

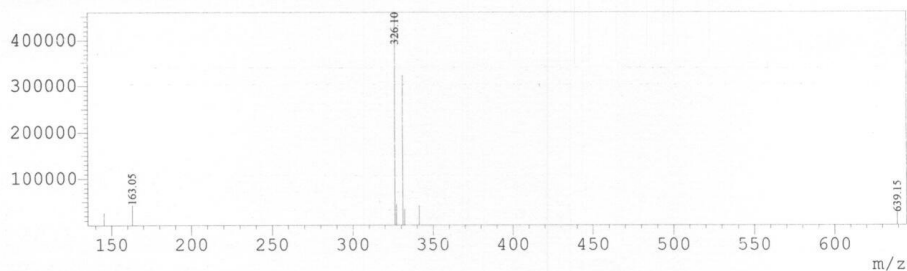
Sample Code : DKM-GSR-I2-308
Data File : 110717.2.lcd
Method : LC_MS_ISO.lcm
Injection Volume : 7
Date Acquired : 7/11/2017 2:52:41 PM
Report File : LC-MS Data Report.lsr
Chromatographic Conditions : Column: LUNA-C8 (250 X 4.6mm, 5.0u)
Mobile Phase: 70% MECH IN 0.1%FA
Flow Rate: 1.0 mL/min



Peak Table

Peak#	Ret. Time	Peak Start	Peak End	Area	Area%
1	3.939	3.840	4.117	24802	2.109
2	5.252	5.013	6.165	1151277	97.891
Total				1176079	100.000

Q1 Scan Positive+
\$If\$(SpPrTab==SpPrTab)Spectrum Mode:Averaged 3.775-4.292(907-1031)
BG Mode:Averaged 0.000-3.442(1-827)

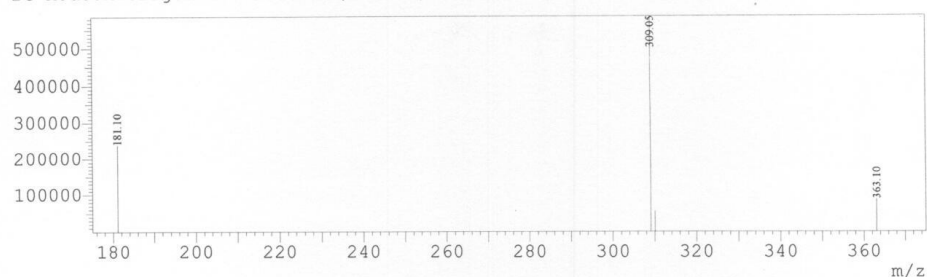


REPORT

HPLC Chromatogram of 11

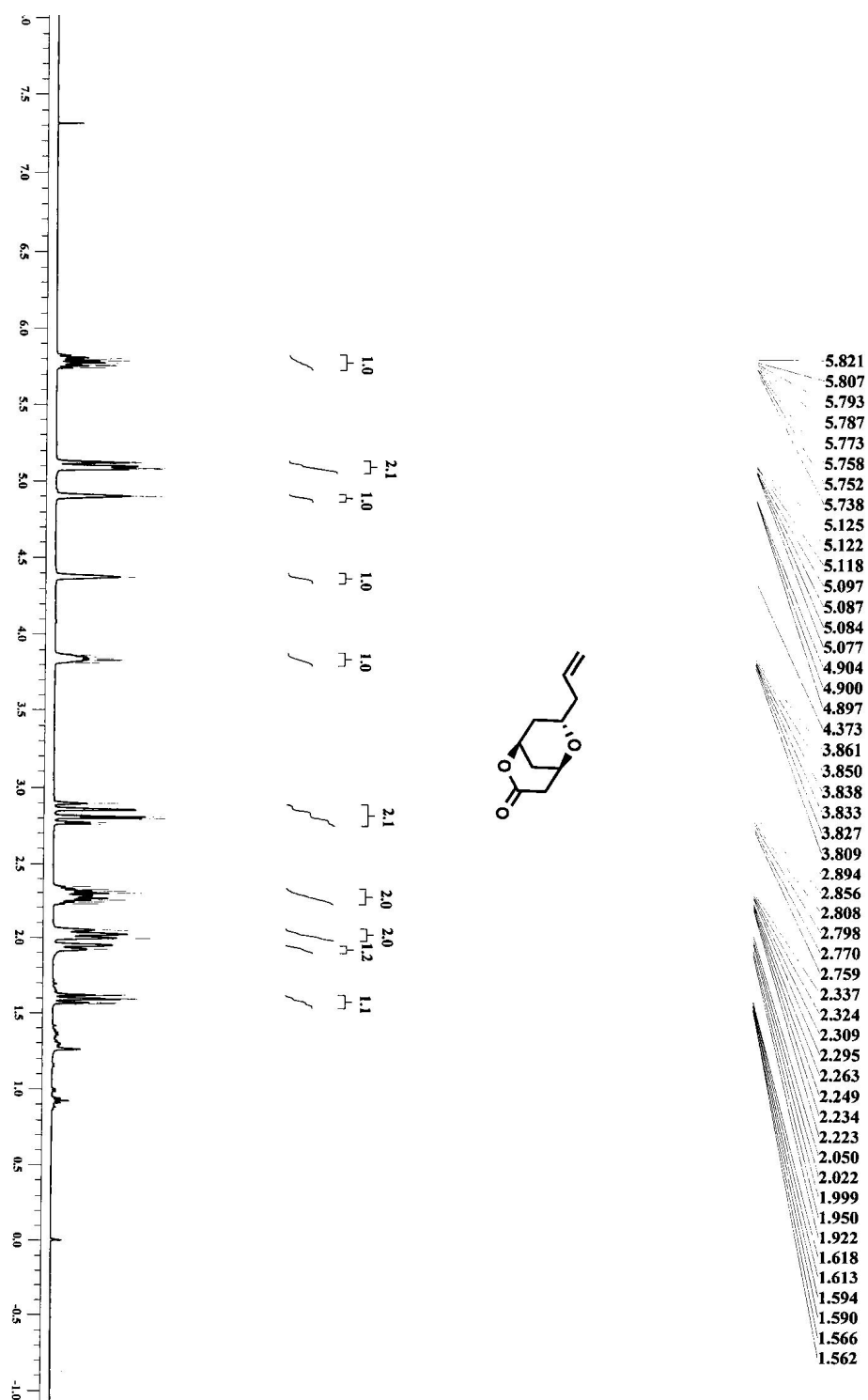
Q1 Scan Positive+
\$If\$(SpPrTab==SpPrTab)Spectrum Mode:Averaged 5.104-5.746(1226-1380)
BG Mode:Averaged 0.000-4.896(1-1176)

ICT-DNPG

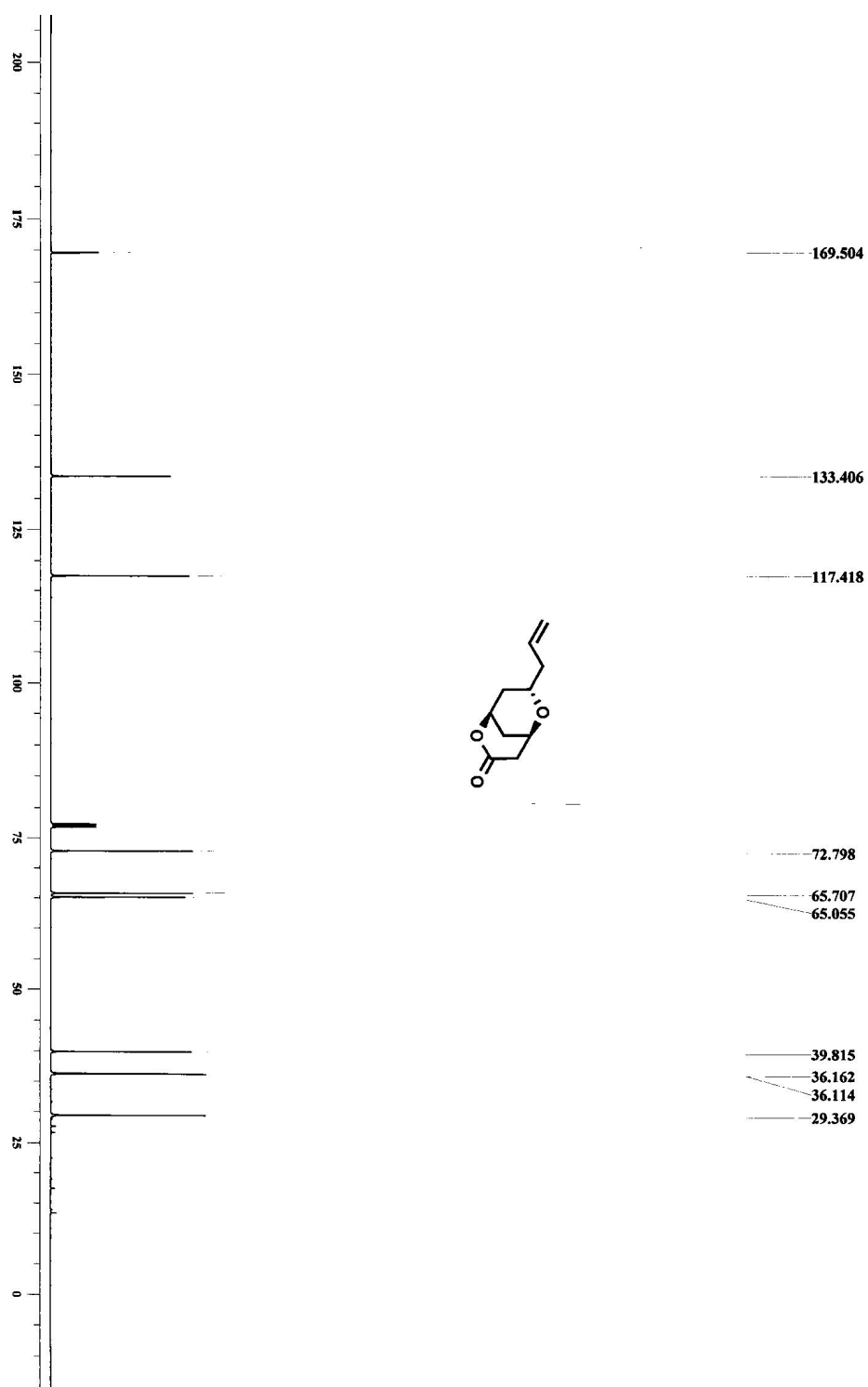


LC-MS REPORT

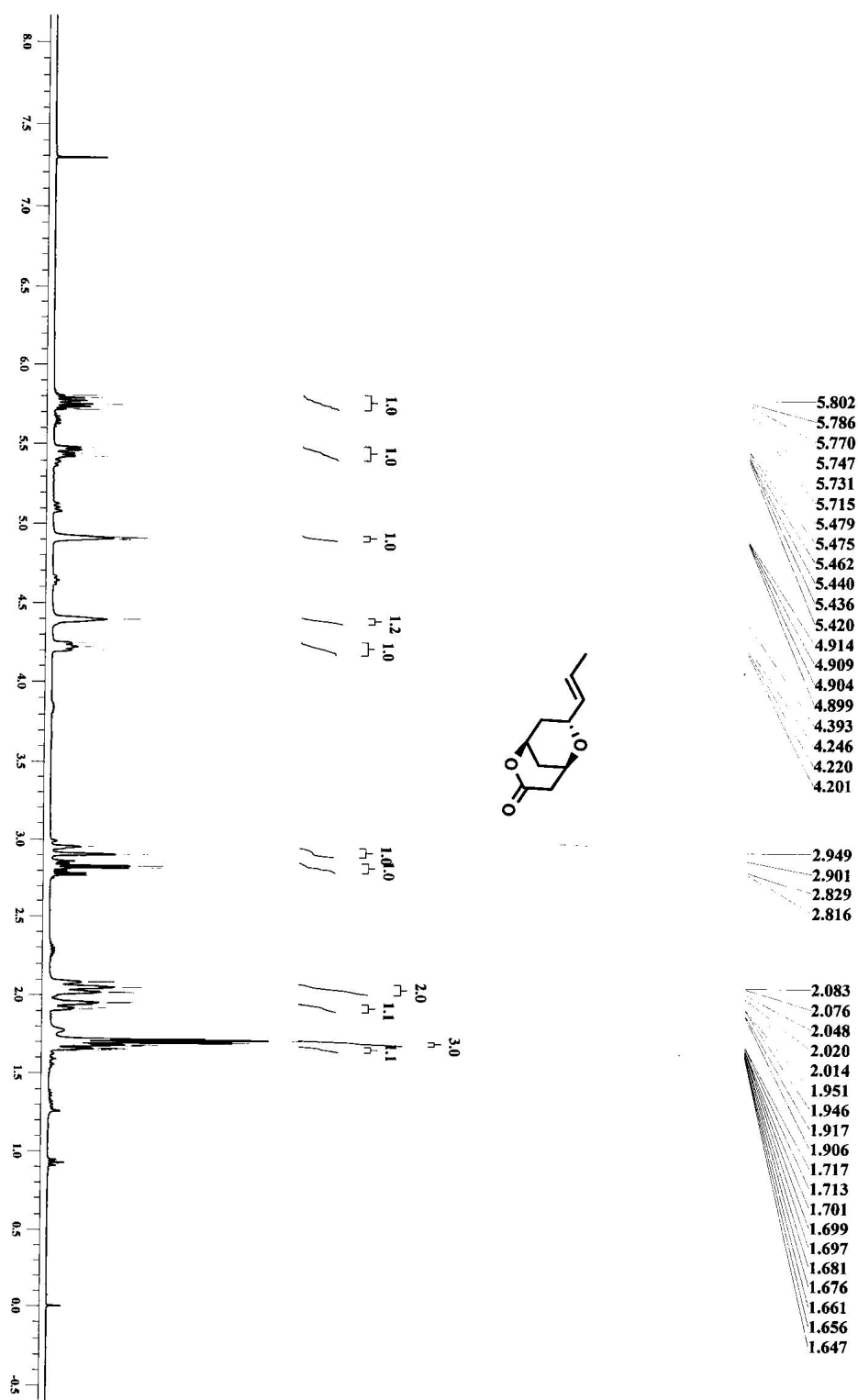
Mass Chromatogram of 11



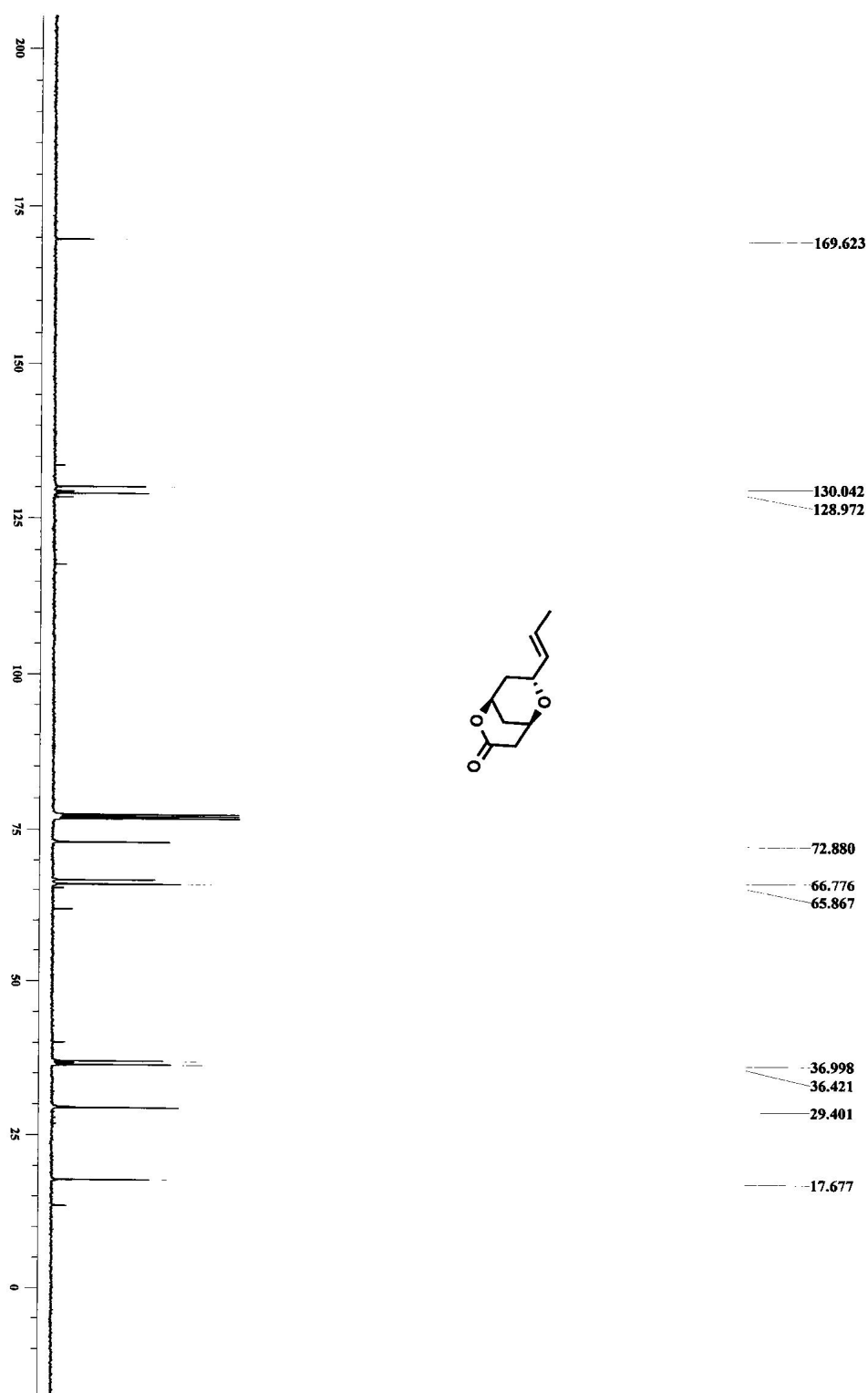
¹H NMR spectrum of **12** (400 MHz, CDCl₃)



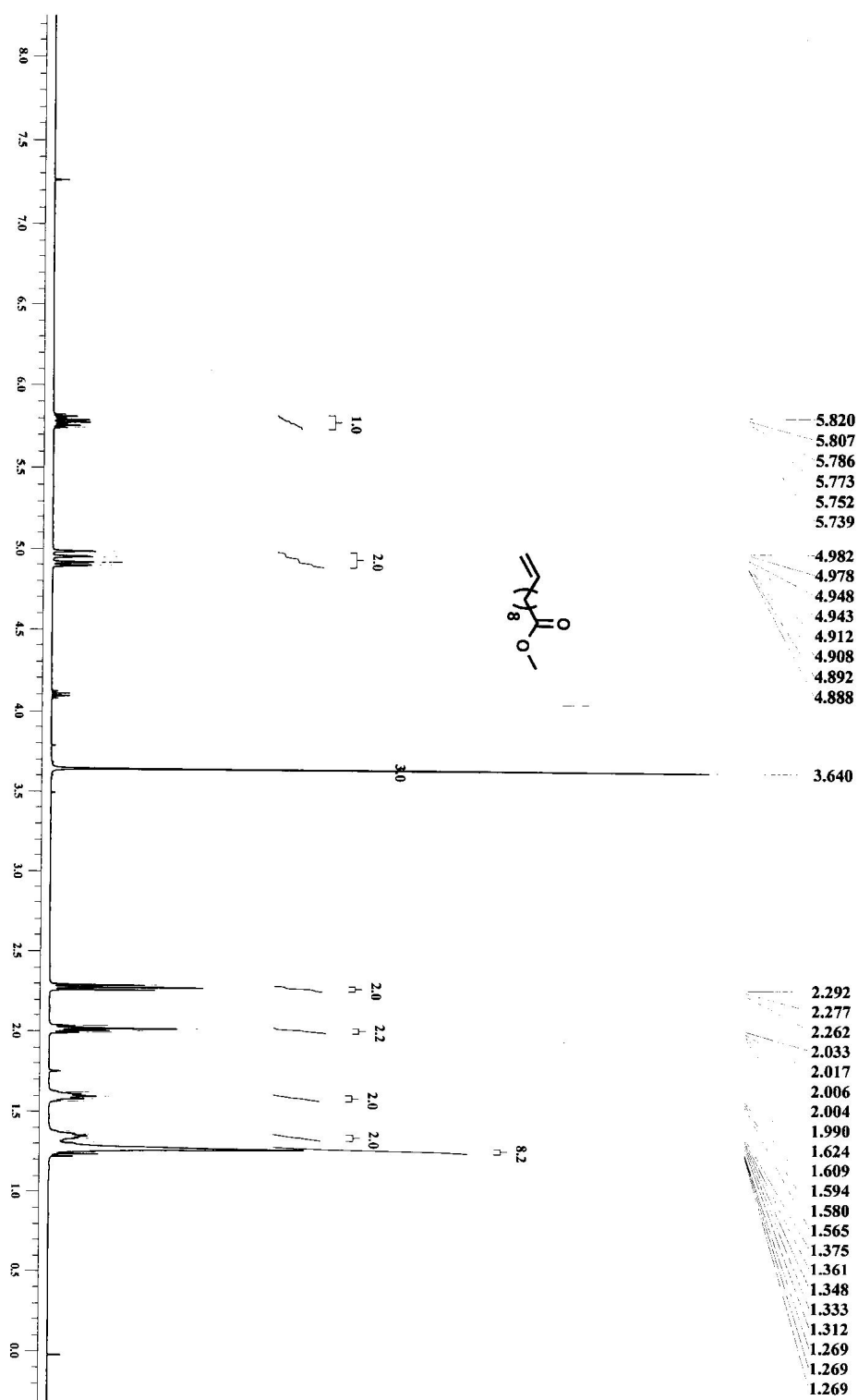
^{13}C NMR spectrum of **12** (125 MHz, CDCl_3)



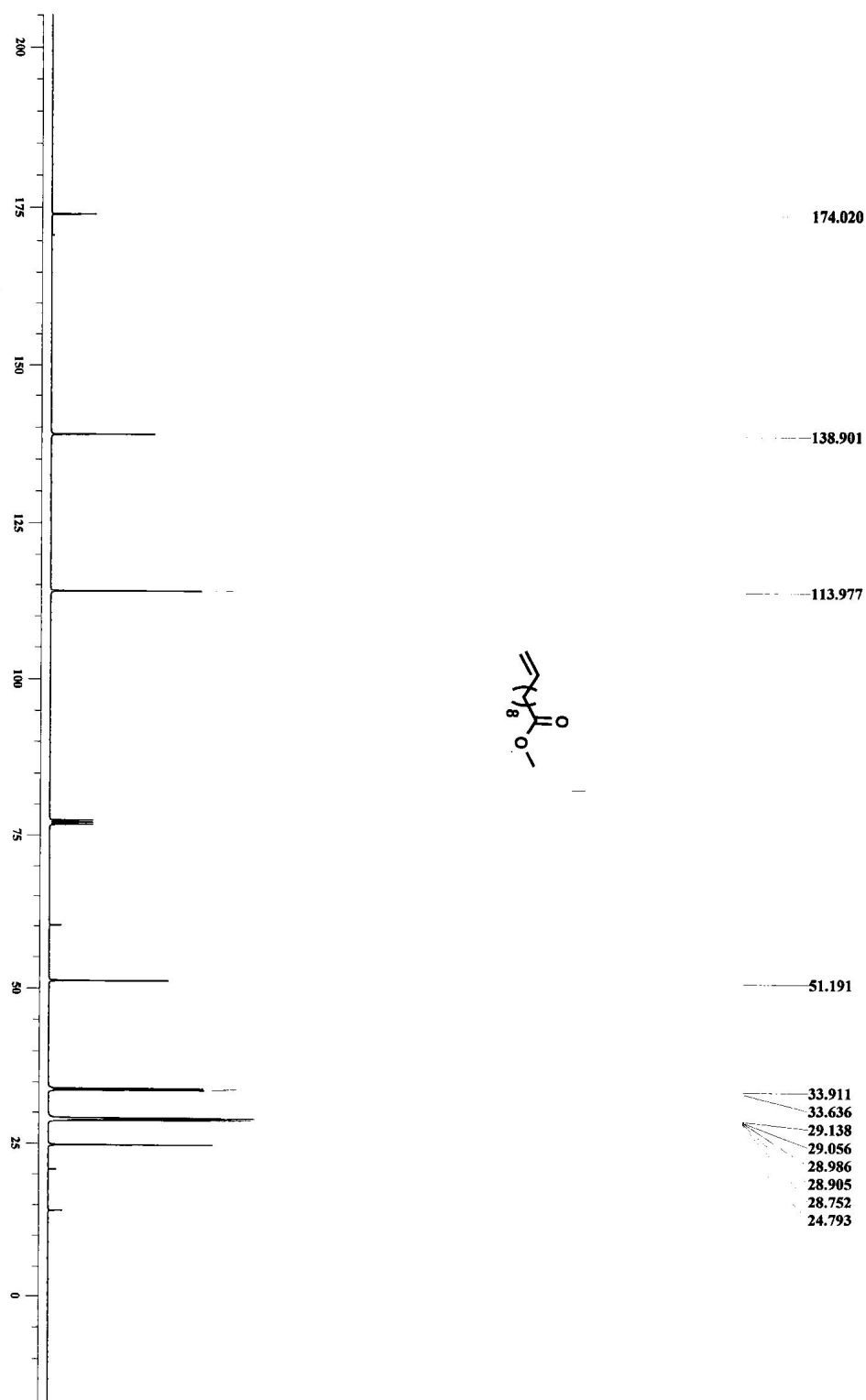
¹H NMR spectrum of **2** (400 MHz, CDCl₃)



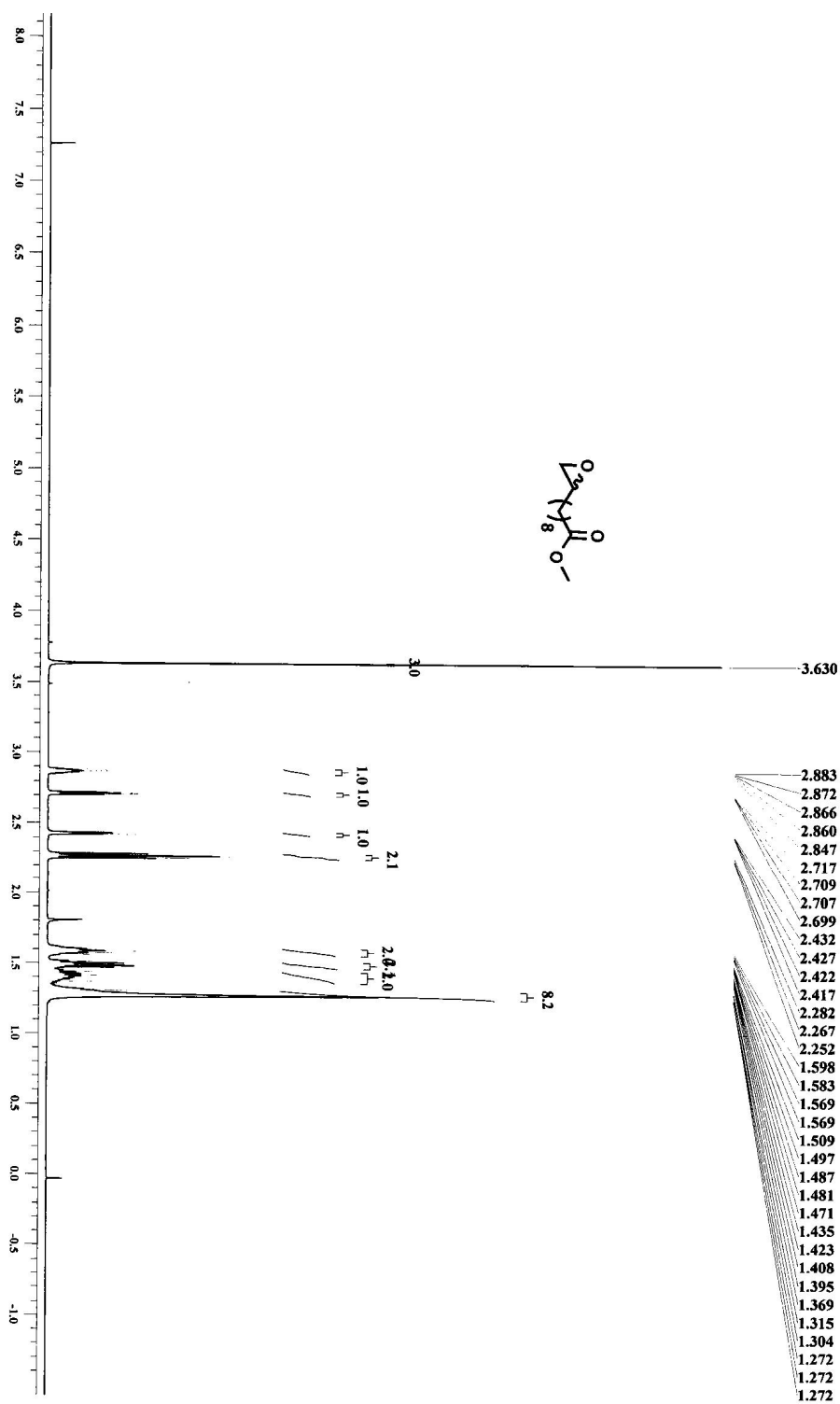
^{13}C NMR spectrum of **2** (125 MHz, CDCl_3)



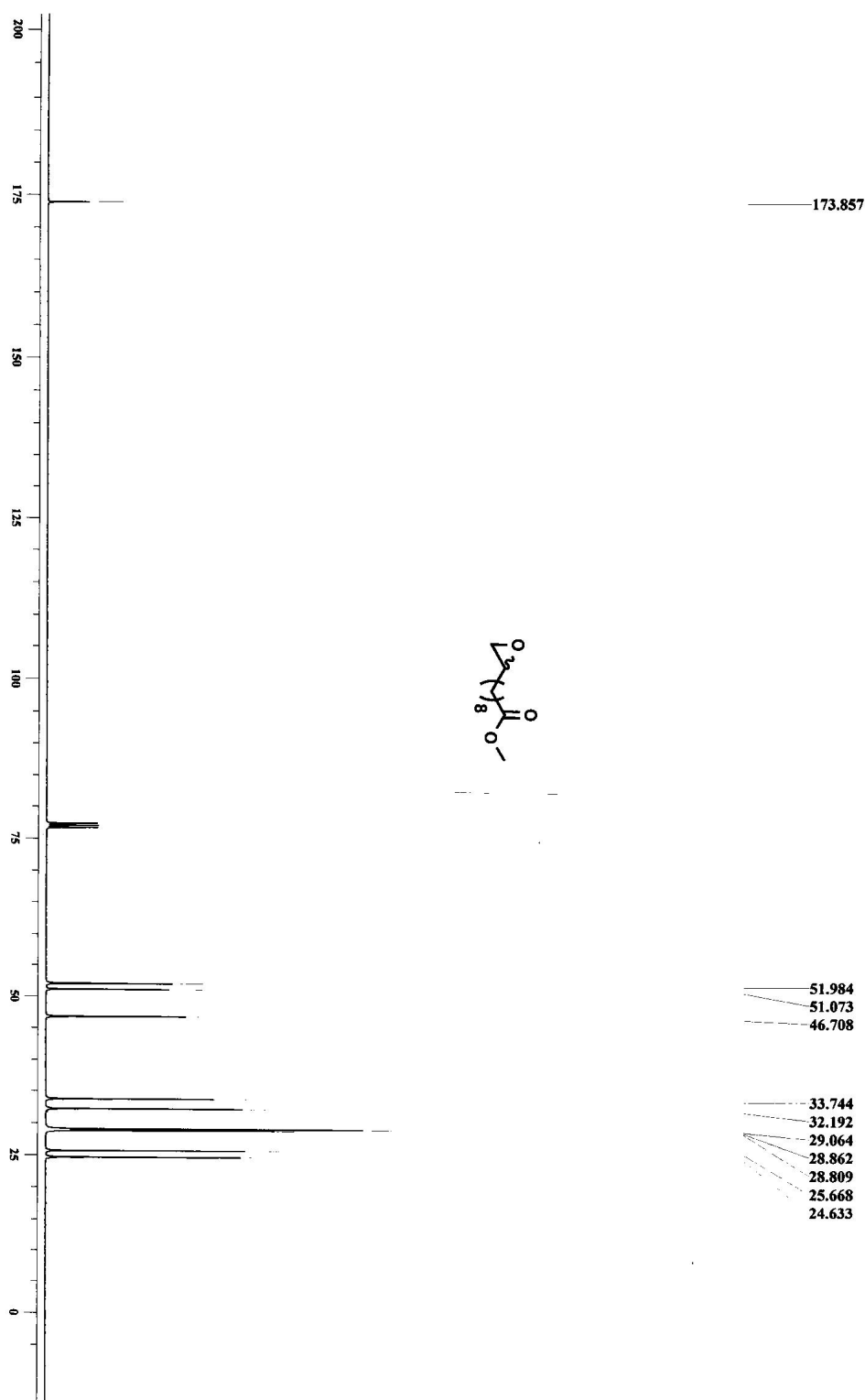
¹H NMR spectrum of **9a** (500 MHz, CDCl₃)



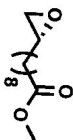
^{13}C NMR spectrum of **9a** (100 MHz, CDCl_3)



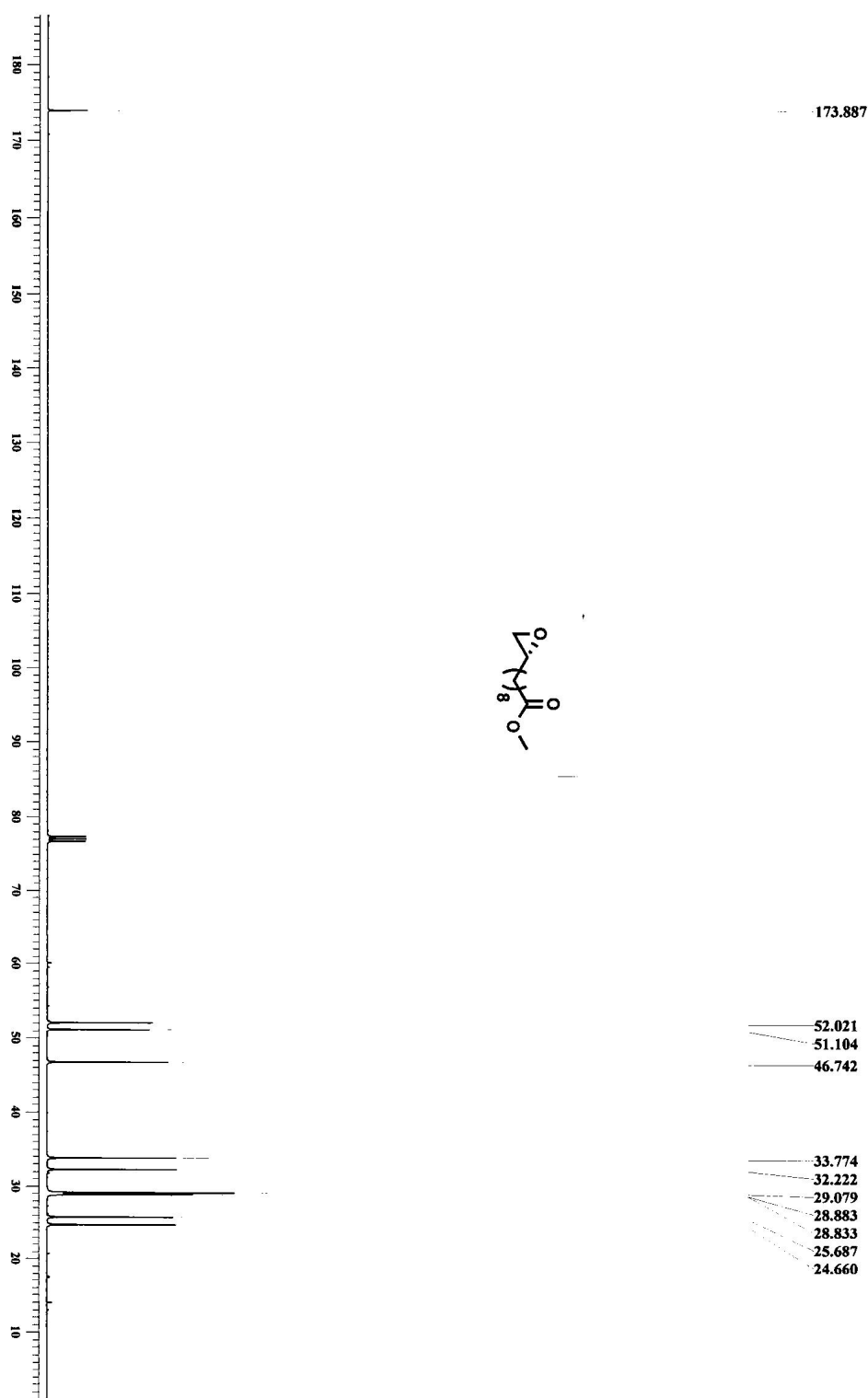
¹H NMR spectrum of **13** (500 MHz, CDCl₃)



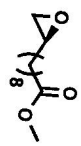
^{13}C NMR spectrum of **13** (100 MHz, CDCl_3)

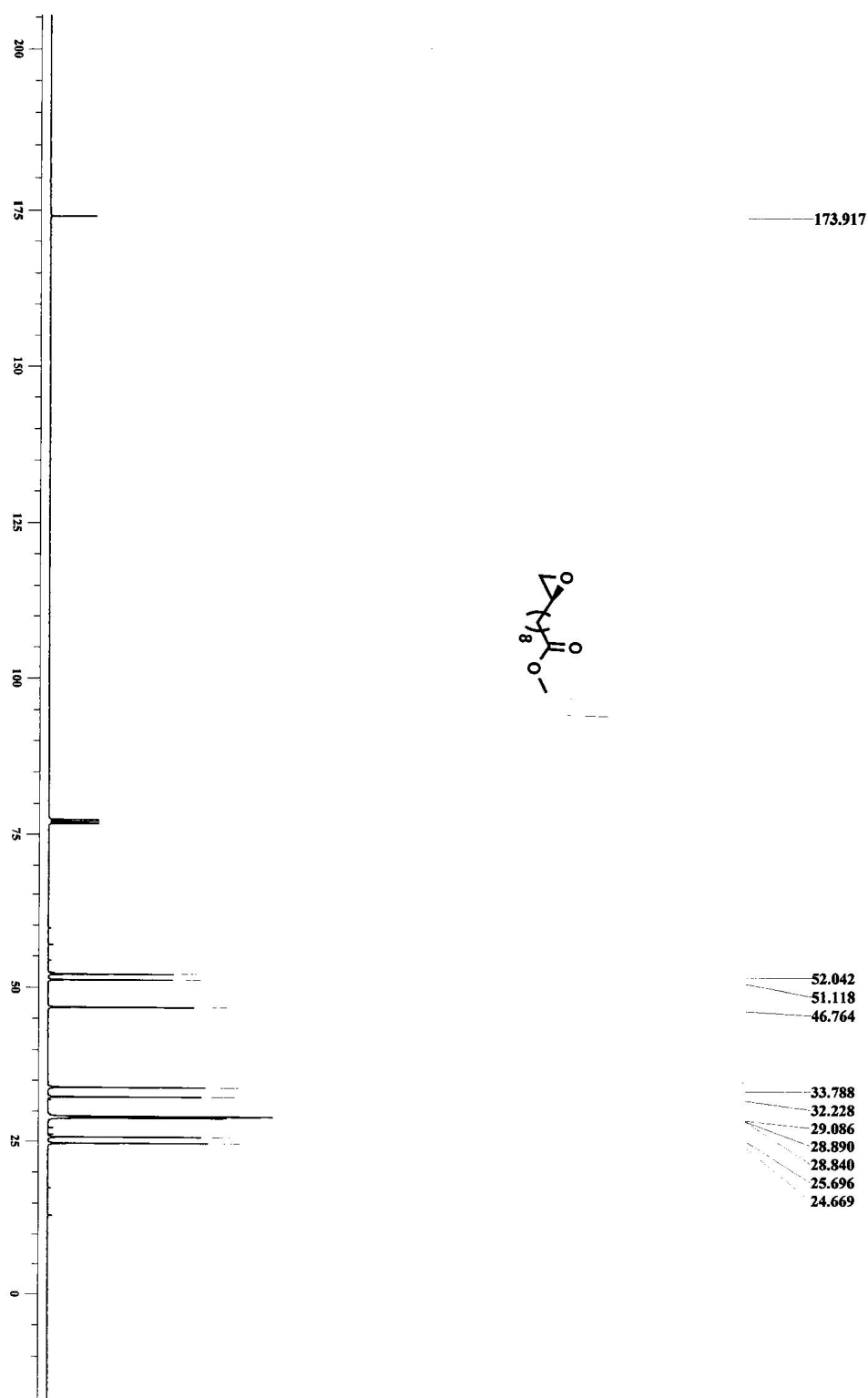


¹H NMR spectrum of **8a** (400 MHz, CDCl₃)

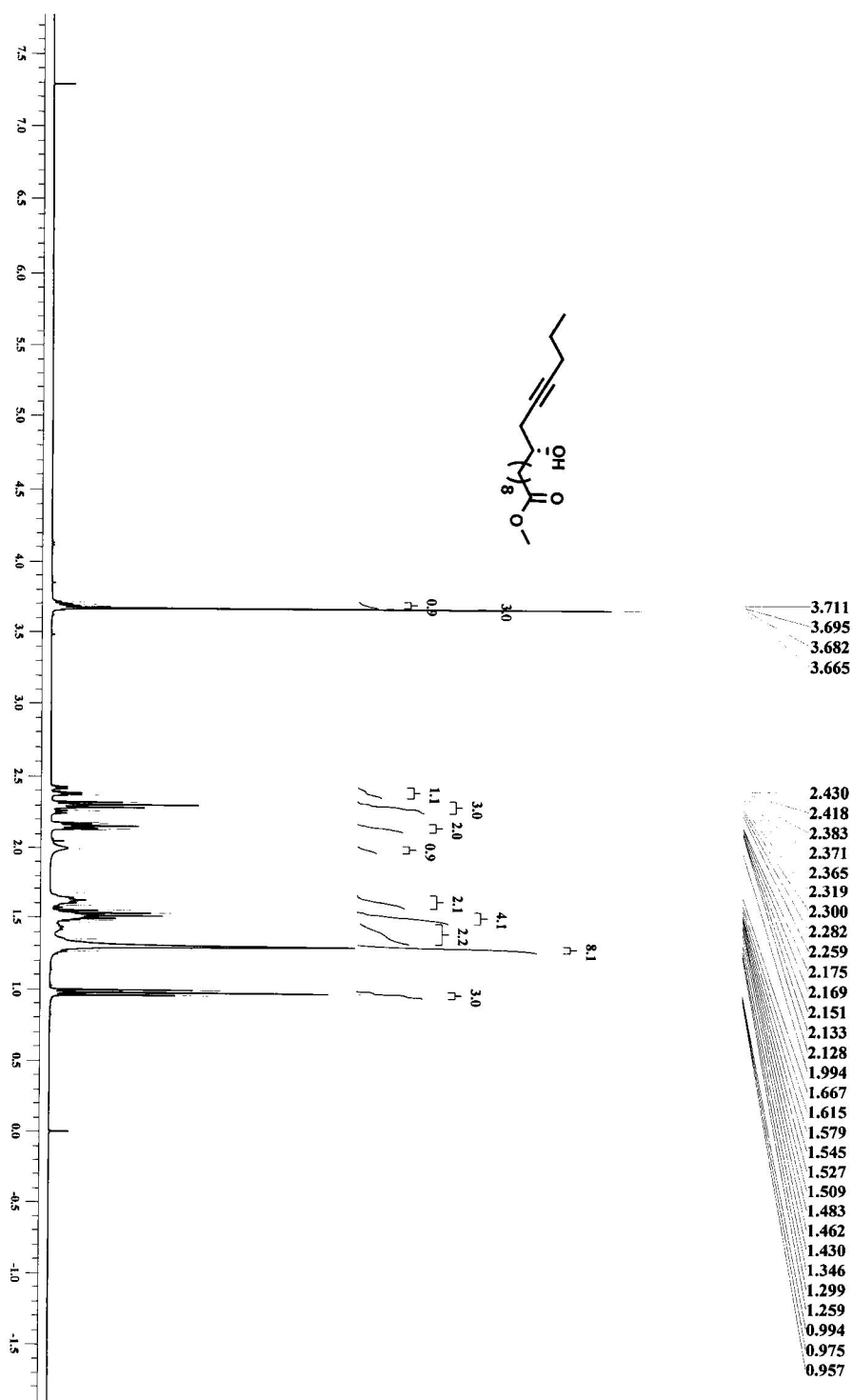


¹³C NMR spectrum of **8a** (100 MHz, CDCl₃)

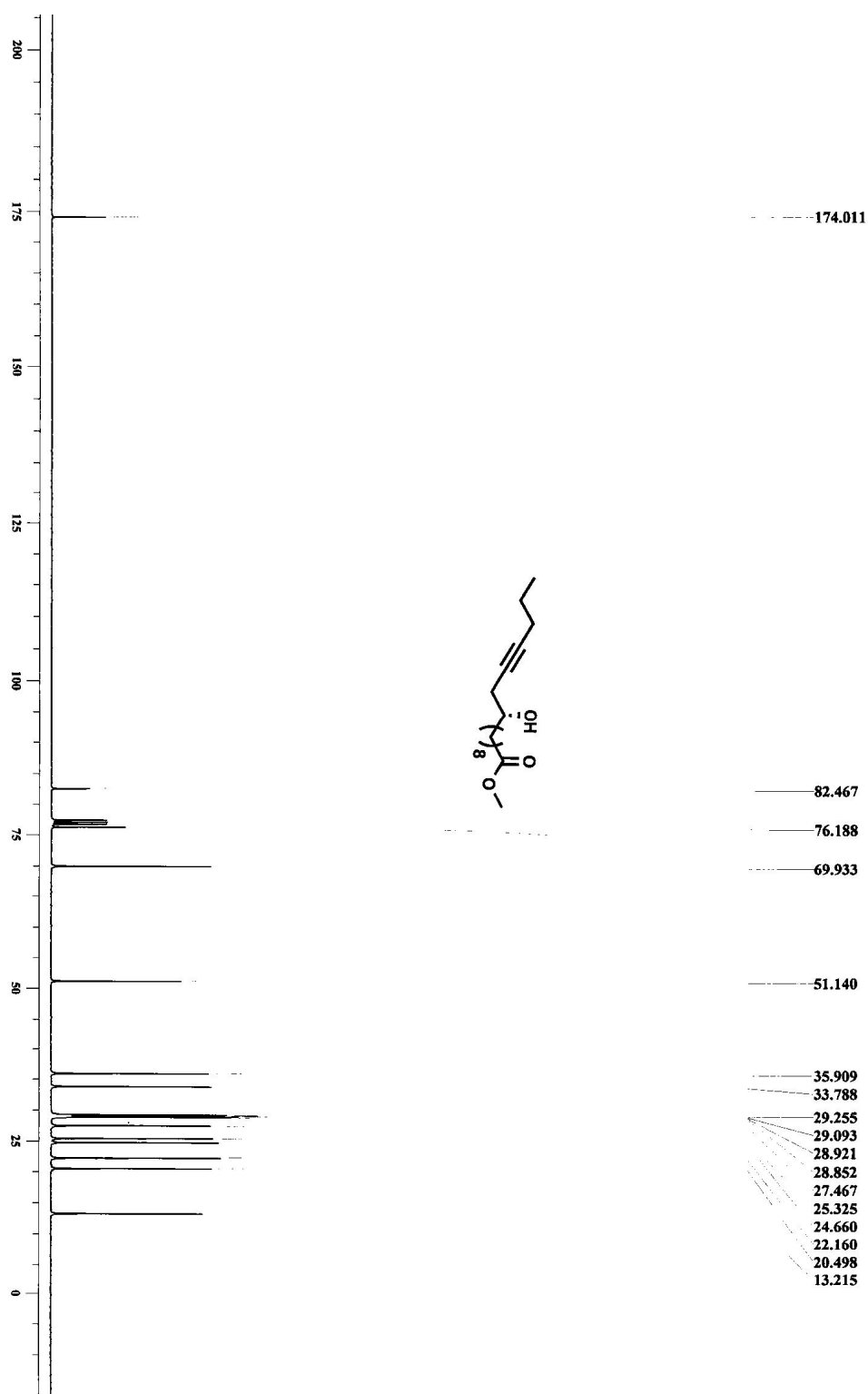
¹H NMR spectrum of **8b** (400 MHz, CDCl₃)



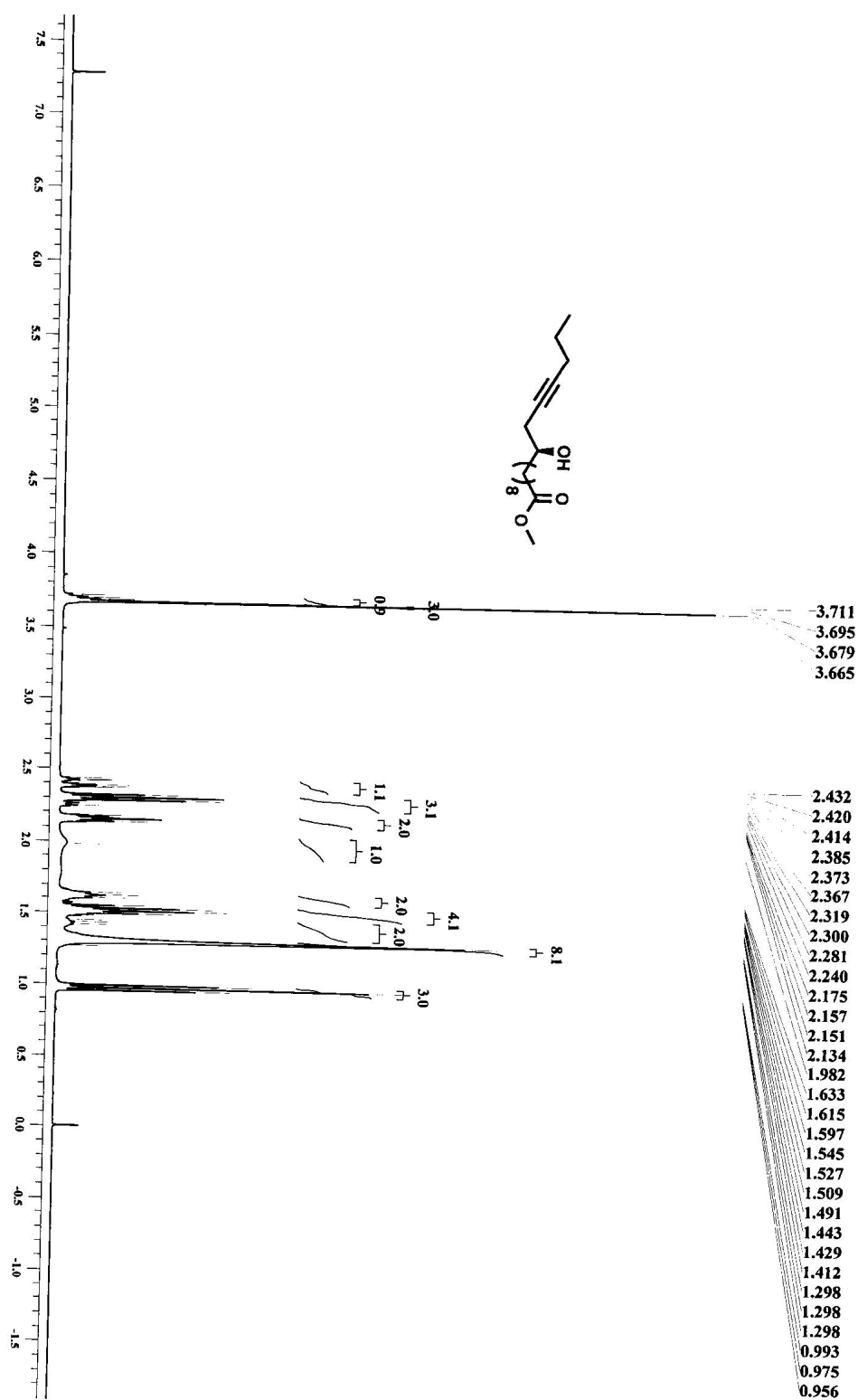
^{13}C NMR spectrum of **8b** (100 MHz, CDCl_3)



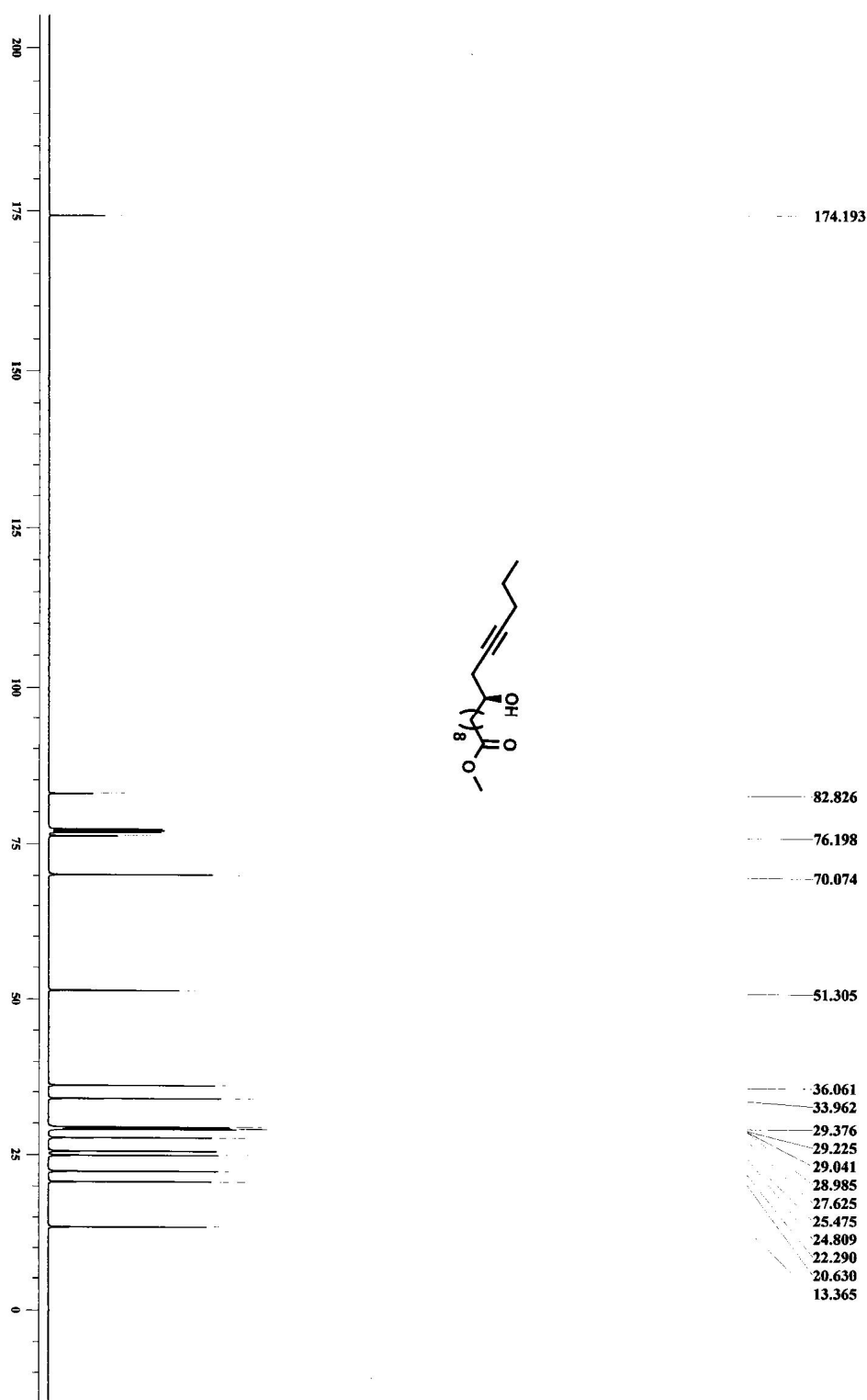
¹H NMR spectrum of **7a** (400 MHz, CDCl₃)



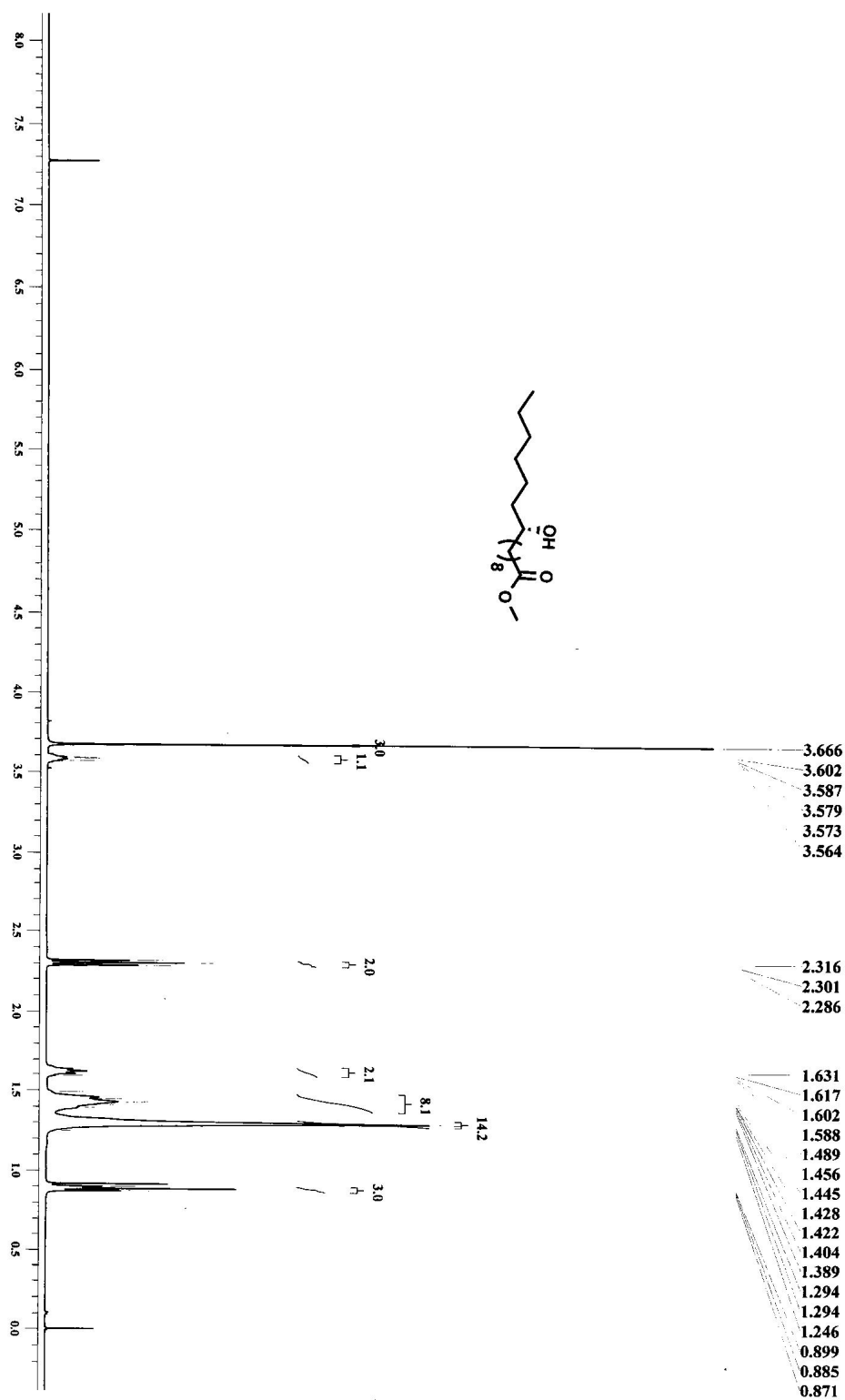
^{13}C NMR spectrum of **7a** (100 MHz, CDCl_3)



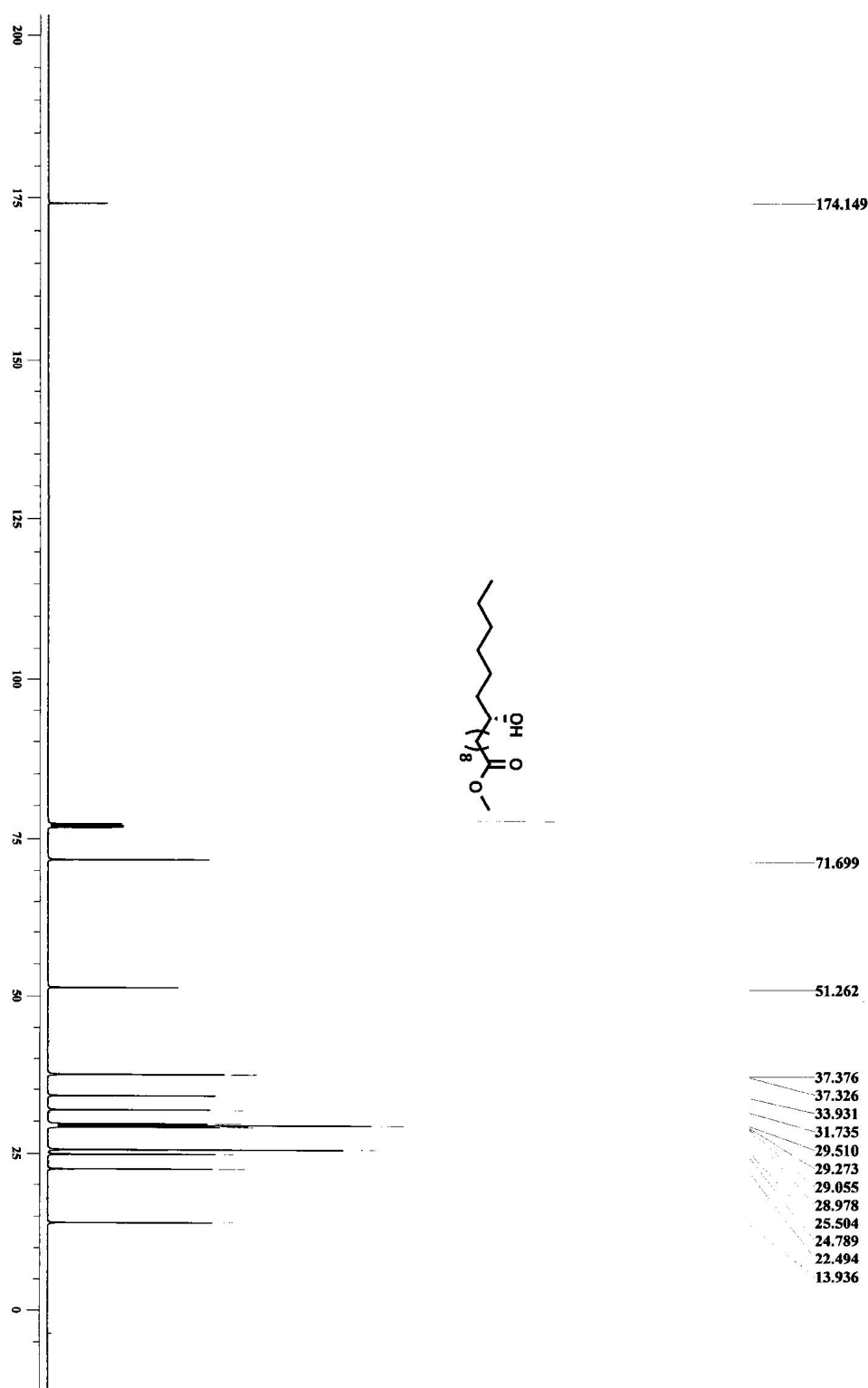
¹H NMR spectrum of **7b** (400 MHz, CDCl₃)



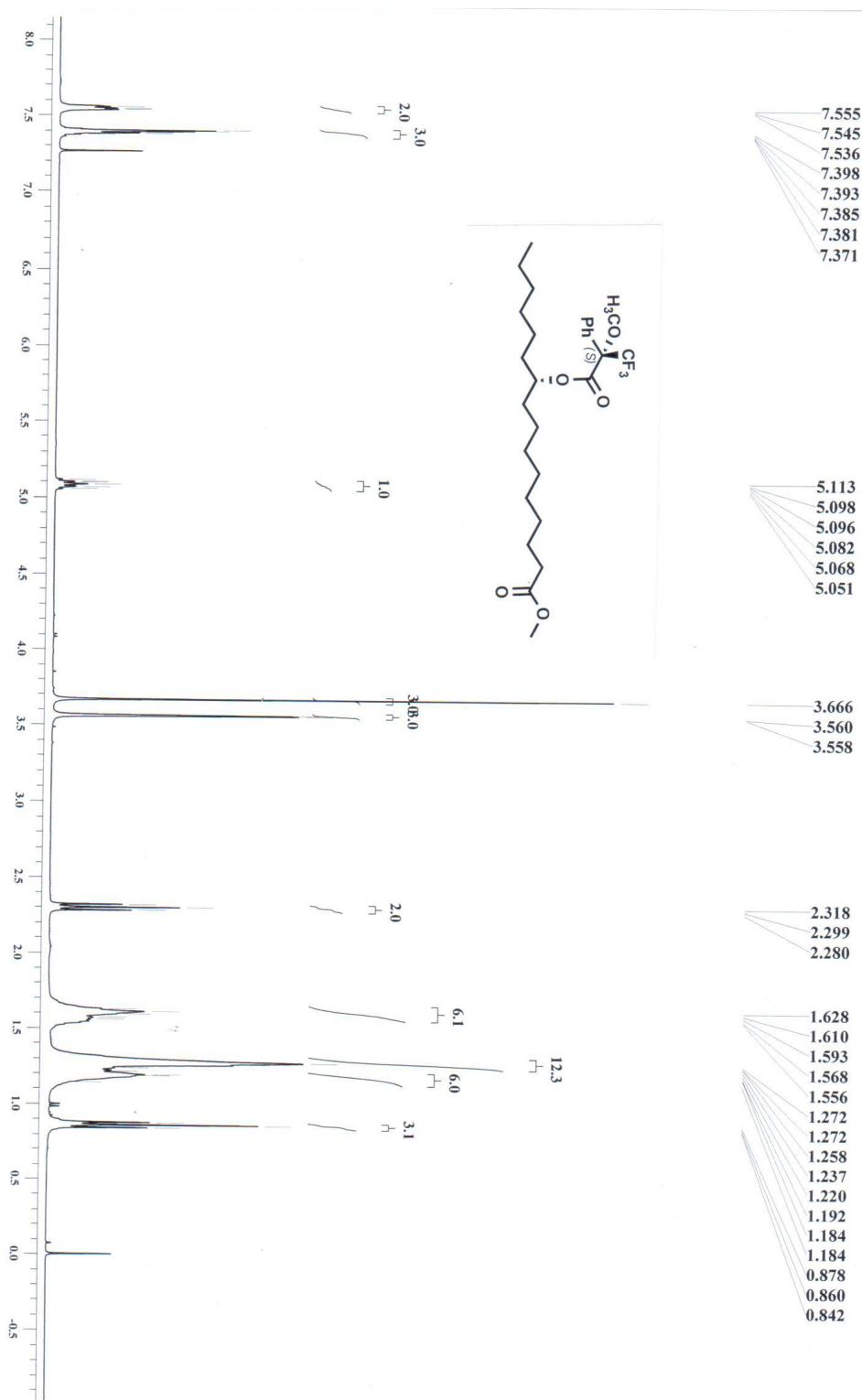
¹³C NMR spectrum of **7b** (125 MHz, CDCl₃)



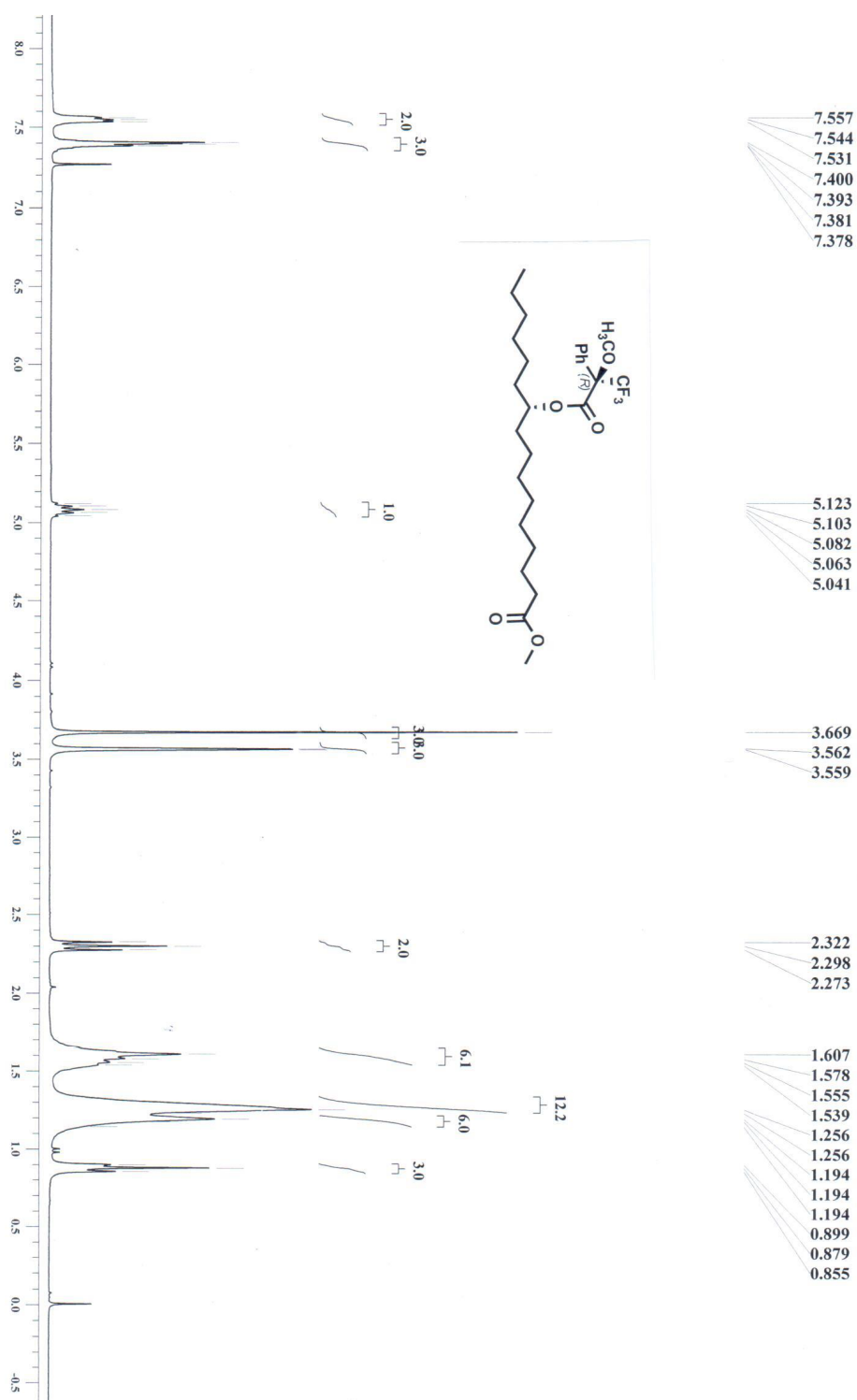
¹H NMR spectrum of **14a** (500 MHz, CDCl₃)



^{13}C NMR spectrum of **14a** (125 MHz, CDCl_3)



¹H NMR spectrum of (S)-MTPA ester **14ai** (400 MHz, CDCl₃)



^1H NMR spectrum of *(R)*-MTPA ester **14a** (300 MHz, CDCl_3)

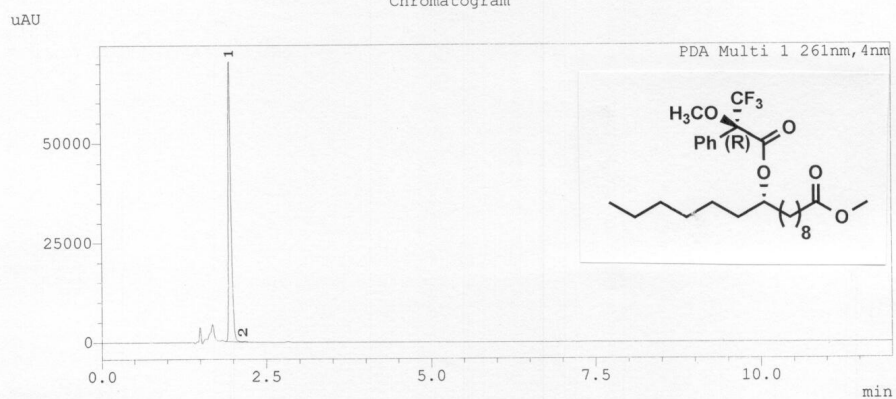


LC-MS DATA REPORT

IICT-DNPG

Sample Code : DKM-GSR-RMRR-502
 Data File : 181117.2.lcd
 Method : LC-MS-ISO.lcm
 Injection Volume : 7
 Date Acquired : 11/18/2017 11:50:40 AM
 Report File : HPLC Report - New.lsr
 Chromatographic Conditions : Column : KINETEX-F5 (150 X 4.6mm, 5.0u)
 Mobile Phase: 95% ACN 0.1% FA
 Flow Rate : 1.0 mL/min

Chromatogram



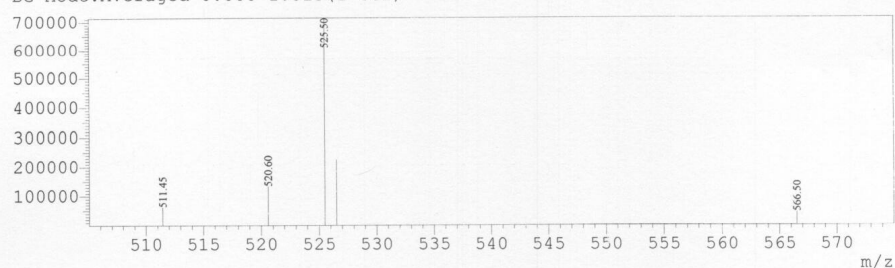
Peak Table

Peak#	Ret. Time	Peak Start	Peak End	Area	Area%
1	1.958	1.877	2.123	204740	99.907
2	2.139	2.123	2.251	192	0.093
Total				204931	100.000

Q1 Scan Positive+

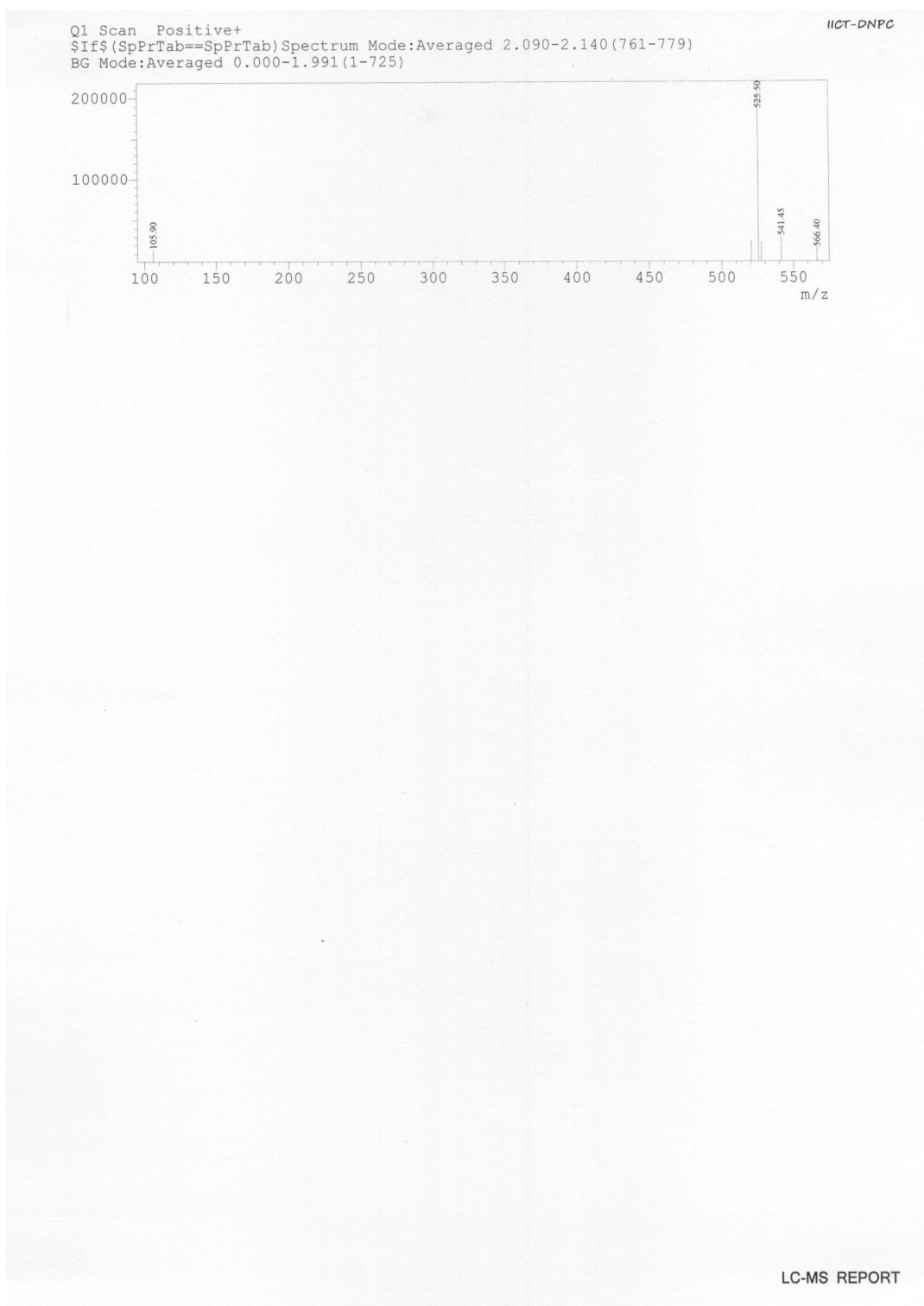
\$If\$(SpPrTab==SpPrTab)Spectrum Mode:Averaged 1.898-1.969(691-717)

BG Mode:Averaged 0.000-1.815(1-661)

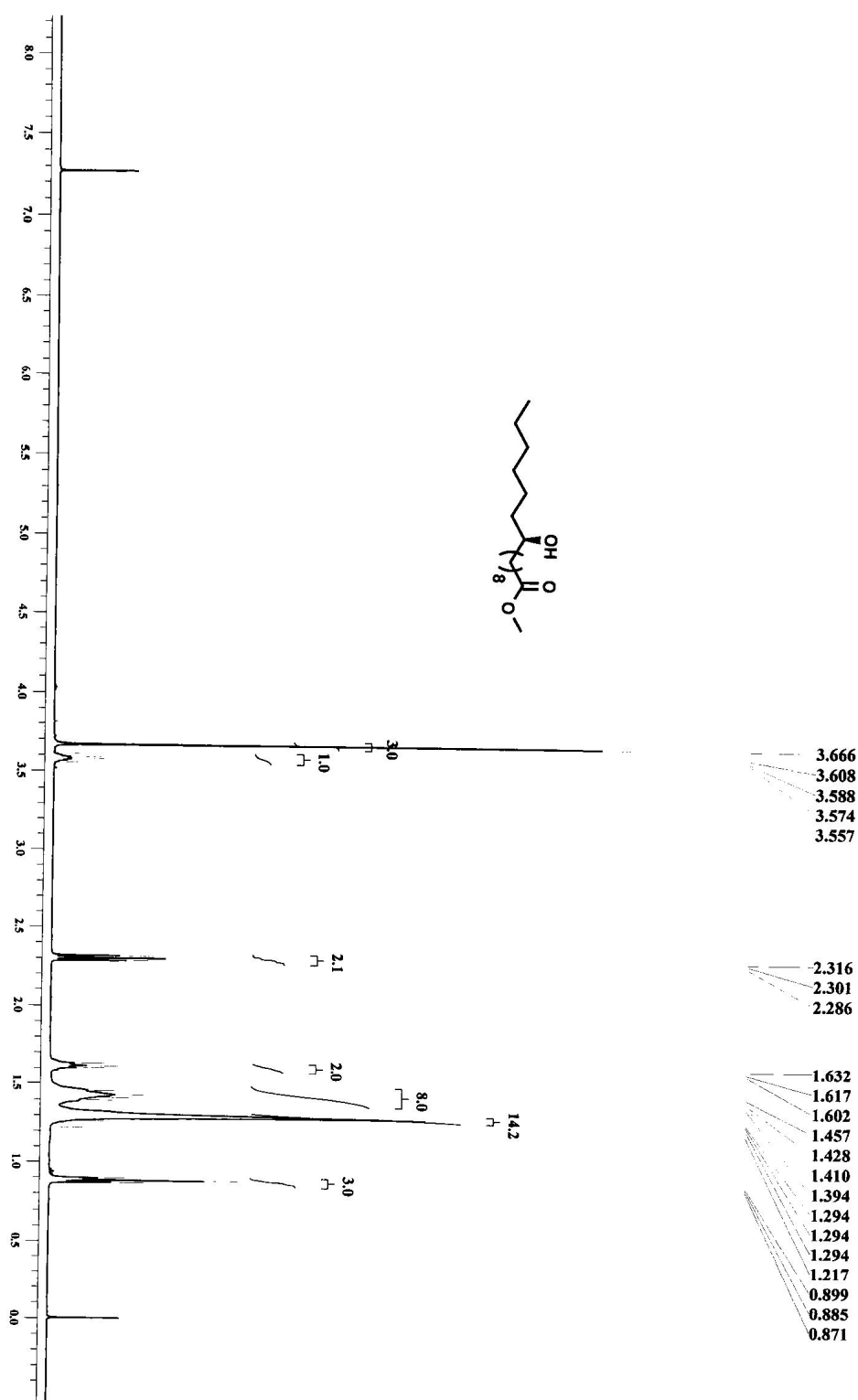


REPORT

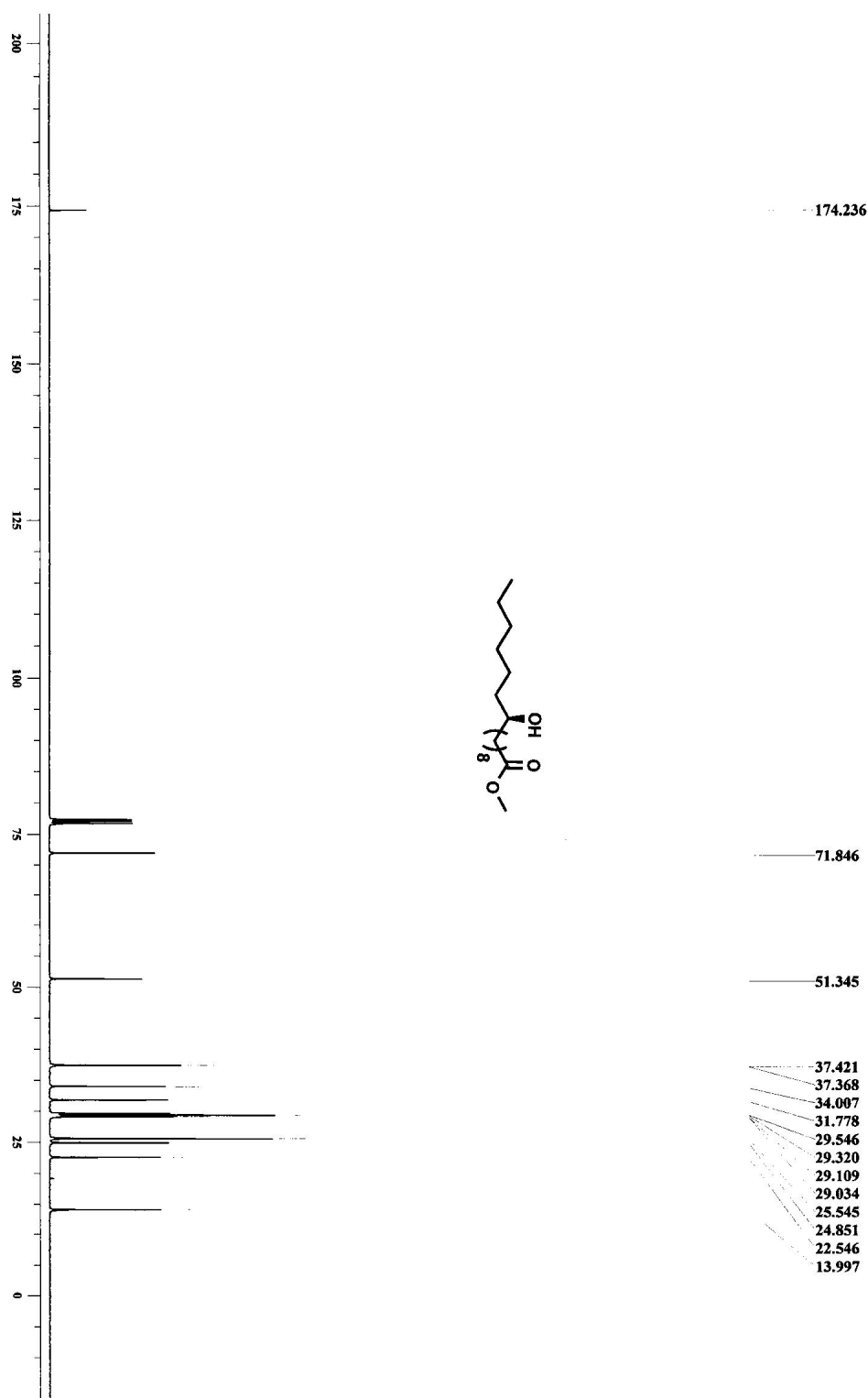
LC-LCMS data of (R)-MTPA ester **14a**

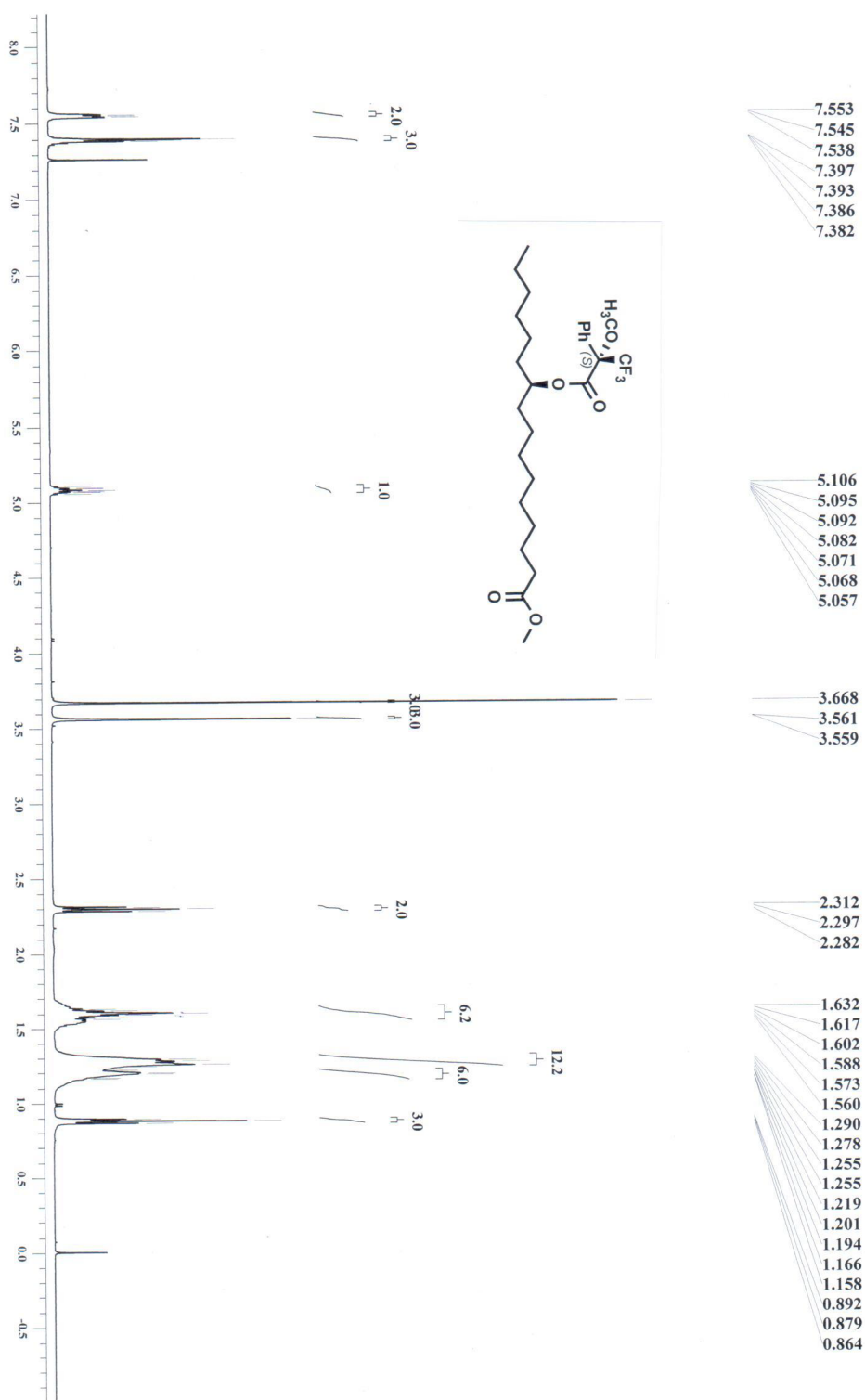


LC-LCMS data of (*R*)-MTPA ester **14a**ii

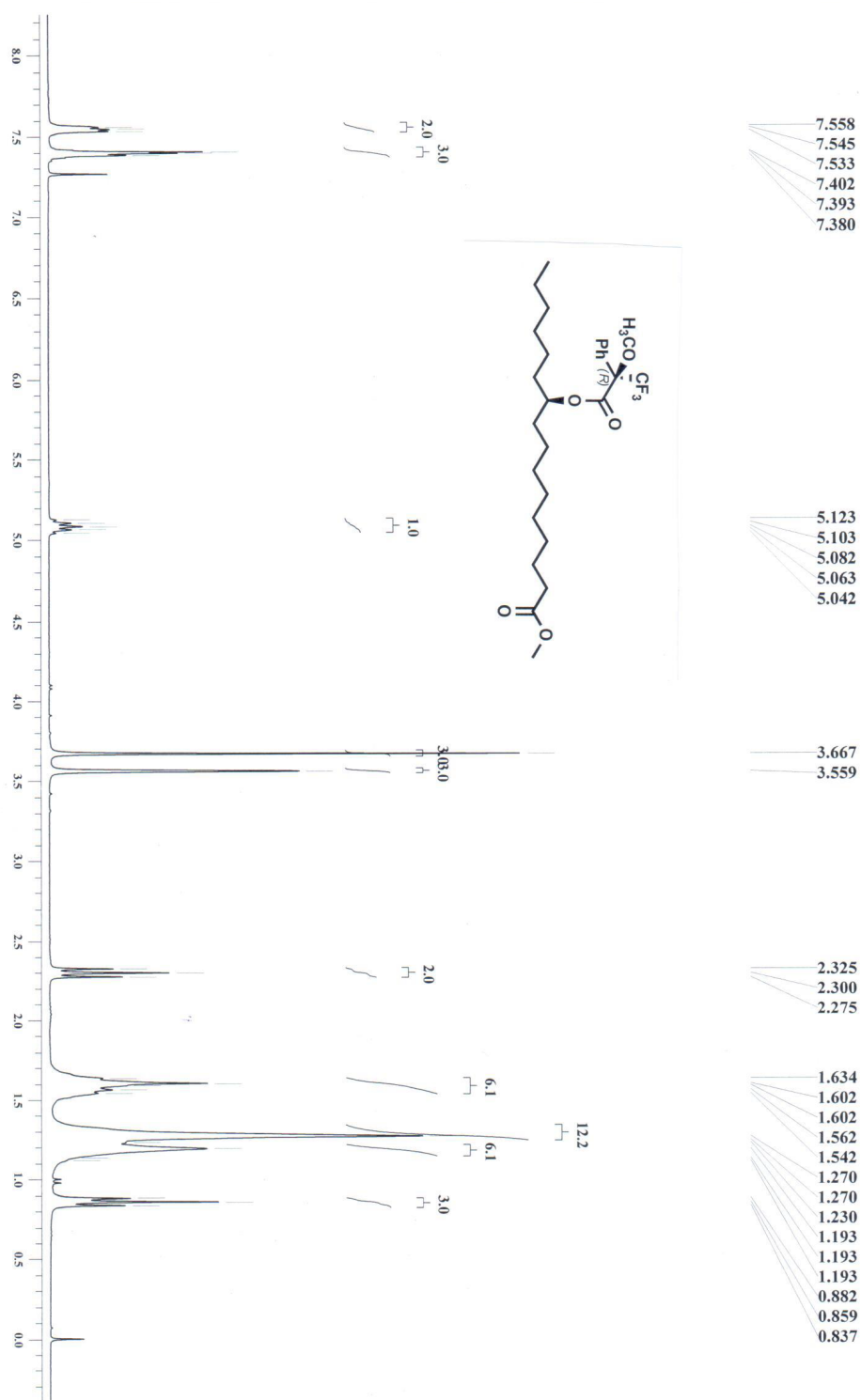


¹H NMR spectrum of **14b** (500 MHz, CDCl₃)

 ^{13}C NMR spectrum of **14b** (100 MHz, CDCl_3)

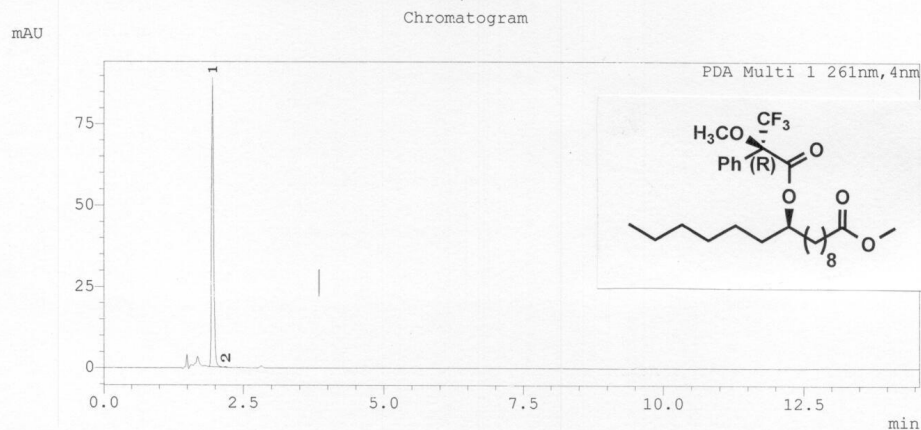


¹H NMR spectrum of (*S*)-MTPA ester **14bi** (500 MHz, CDCl₃)



¹H NMR spectrum of (*R*)-MTPA ester **14bii** (300 MHz, CDCl₃)

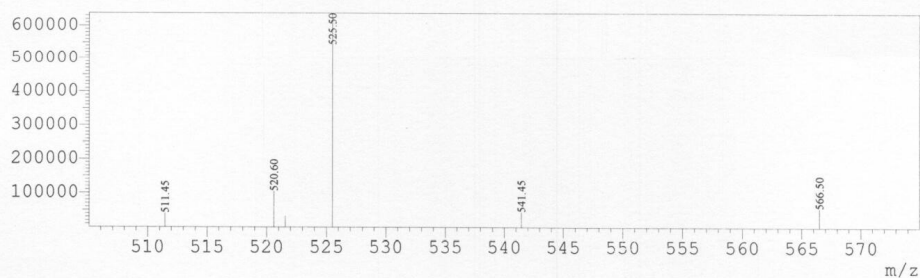
Sample Code : DKM-GSR-RMSS-502
 Data File : 181117.3.1cd
 Method : LC-MS-ISO.1cm
 Injection Volume : 7
 Date Acquired : 11/18/2017 12:07:52 PM
 Report File : HPLC Report - New.1sr
 Chromatographic Conditions : Column : KINETEX-F5 (150 X 4.6mm, 5.0u)
 Mobile Phase: 95% ACN 0.1% FA
 Flow Rate : 1.0 mL/min



Peak Table

Peak#	Ret. Time	Peak Start	Peak End	Area	Area%
1	1.952	1.877	2.123	249273	99.871
2	2.183	2.133	2.240	323	0.129
Total				249595	100.000

Q1 Scan Positive+
 \$If\$(SpPrTab==SpPrTab)Spectrum Mode:Averaged 1.892-1.964(689-715)
 BG Mode:Averaged 0.000-1.771(1-645)

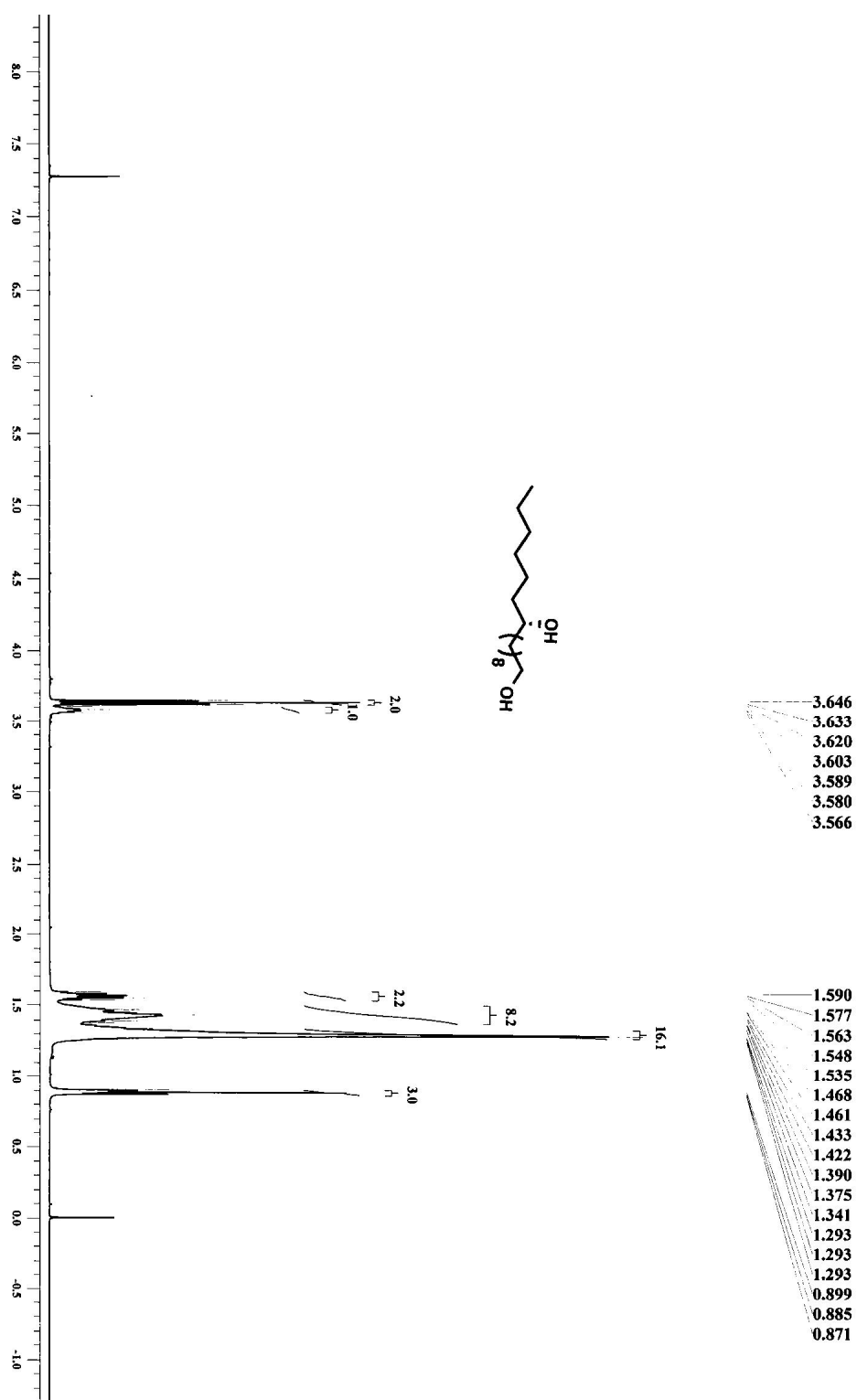


REPORT

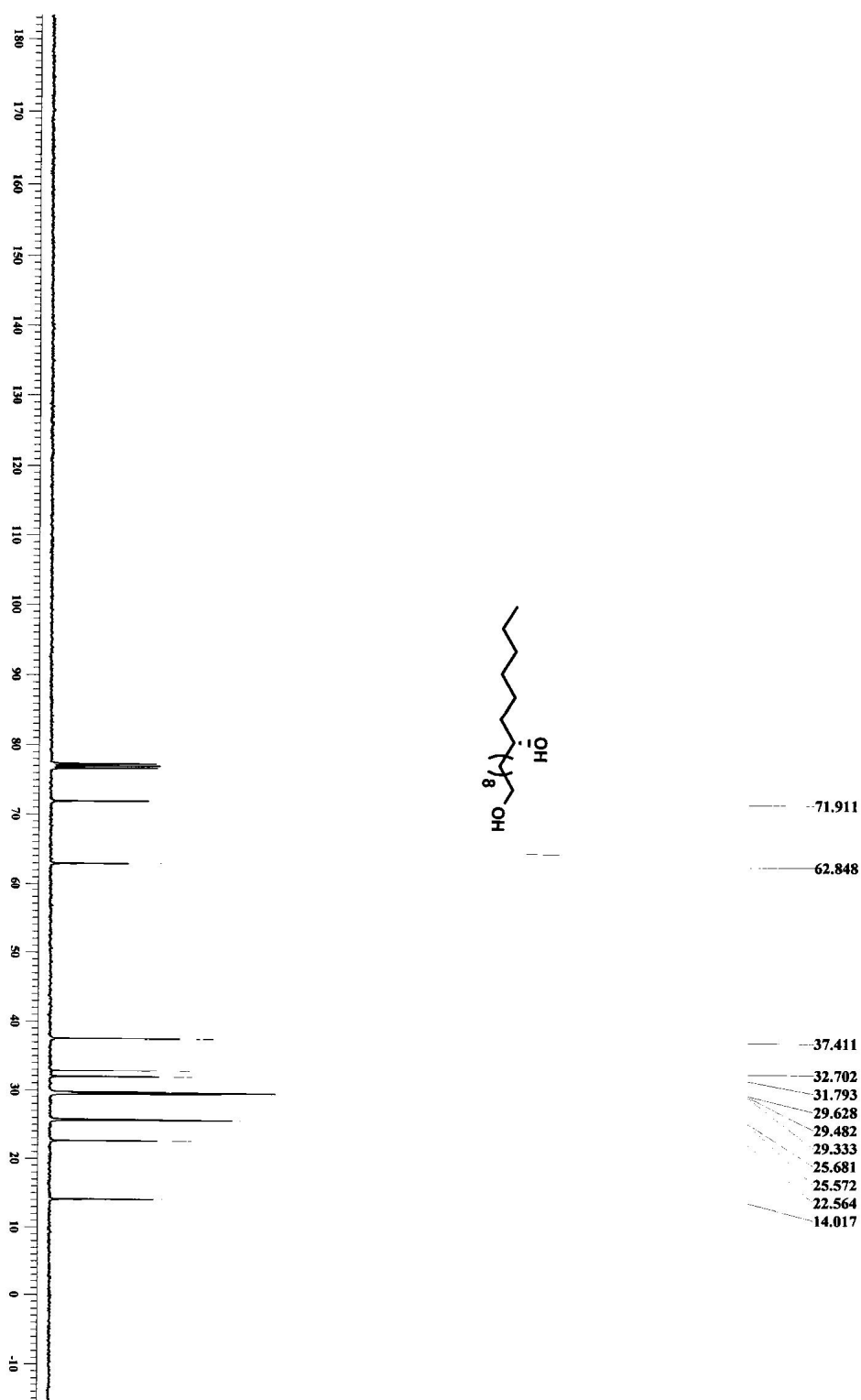
LC-LCMS data of (R)-MTPA ester **14bii**



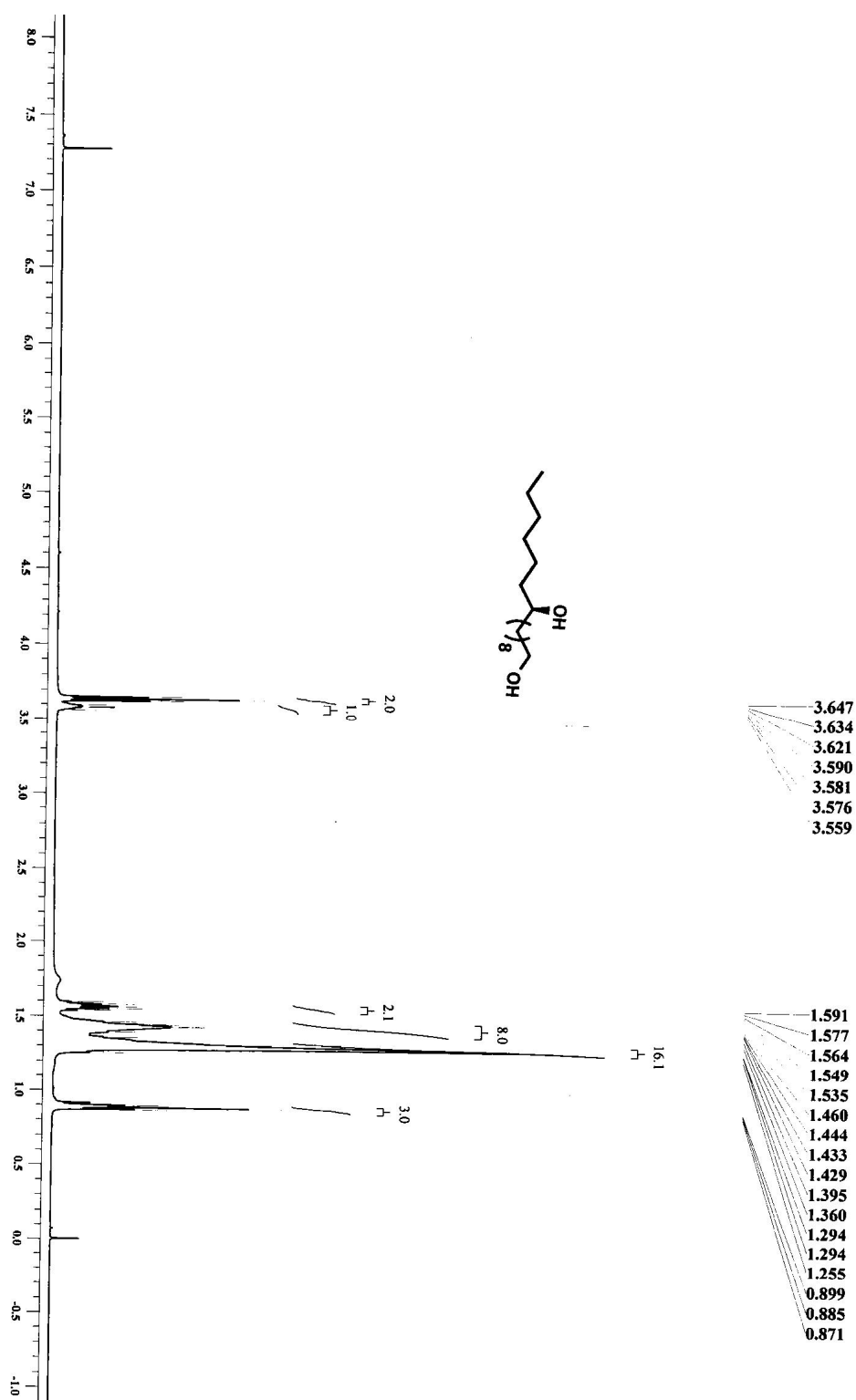
LC-LCMS data of (*R*)-MTPA ester **14bii**



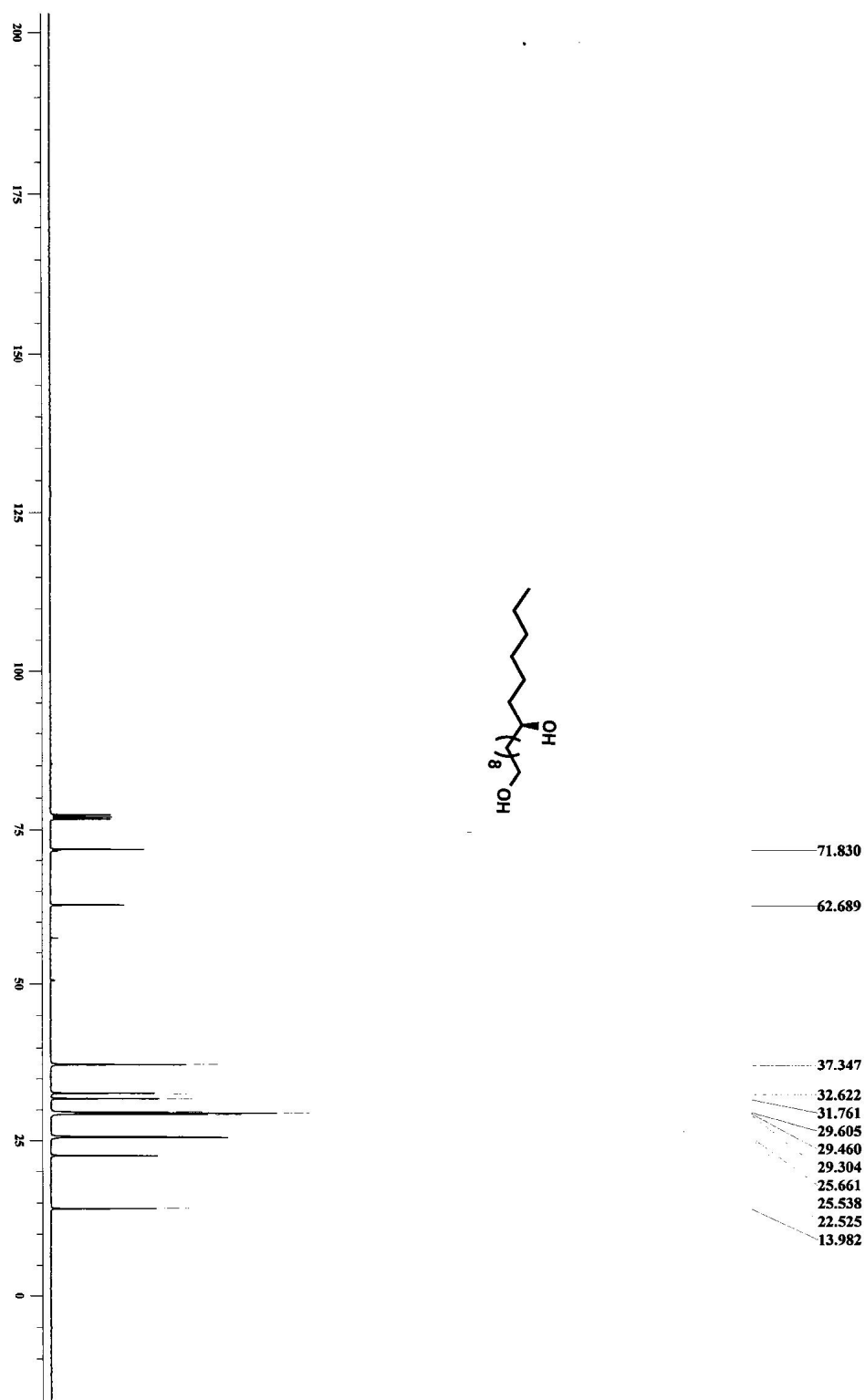
^1H NMR spectrum of **15a** (500 MHz, CDCl_3)



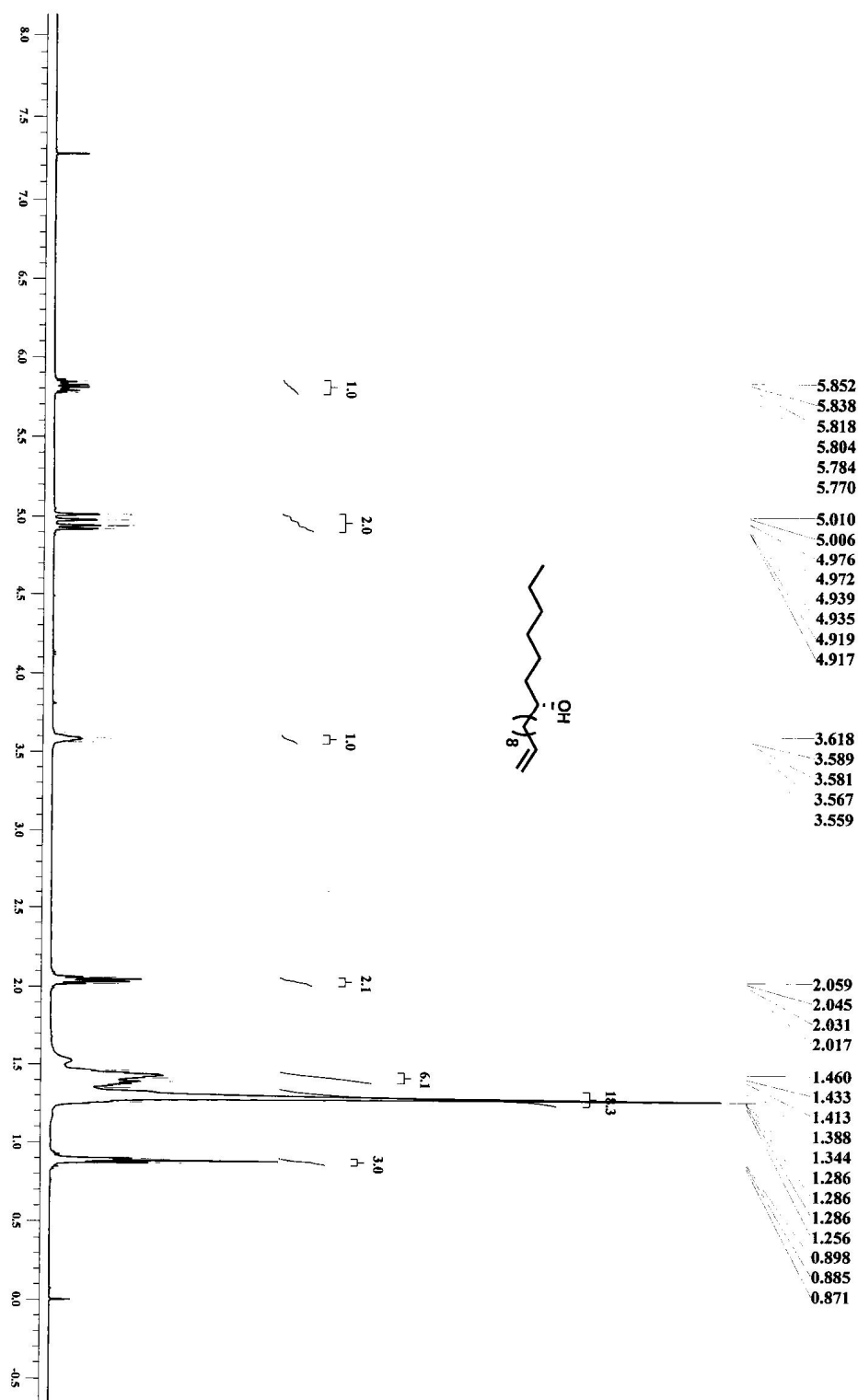
^{13}C NMR spectrum of **15a** (100 MHz, CDCl_3)

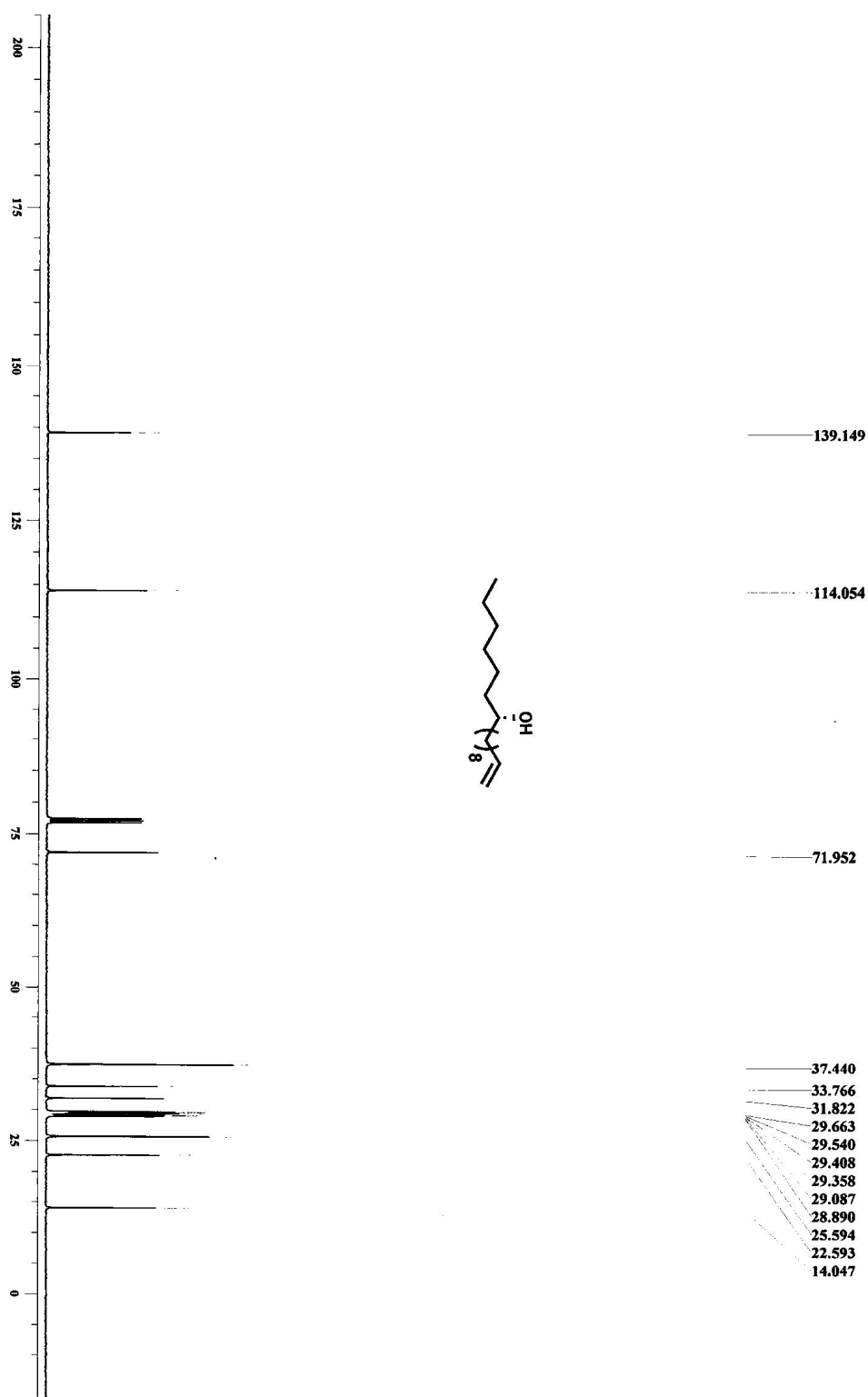


^1H NMR spectrum of **15b** (400 MHz, CDCl_3)

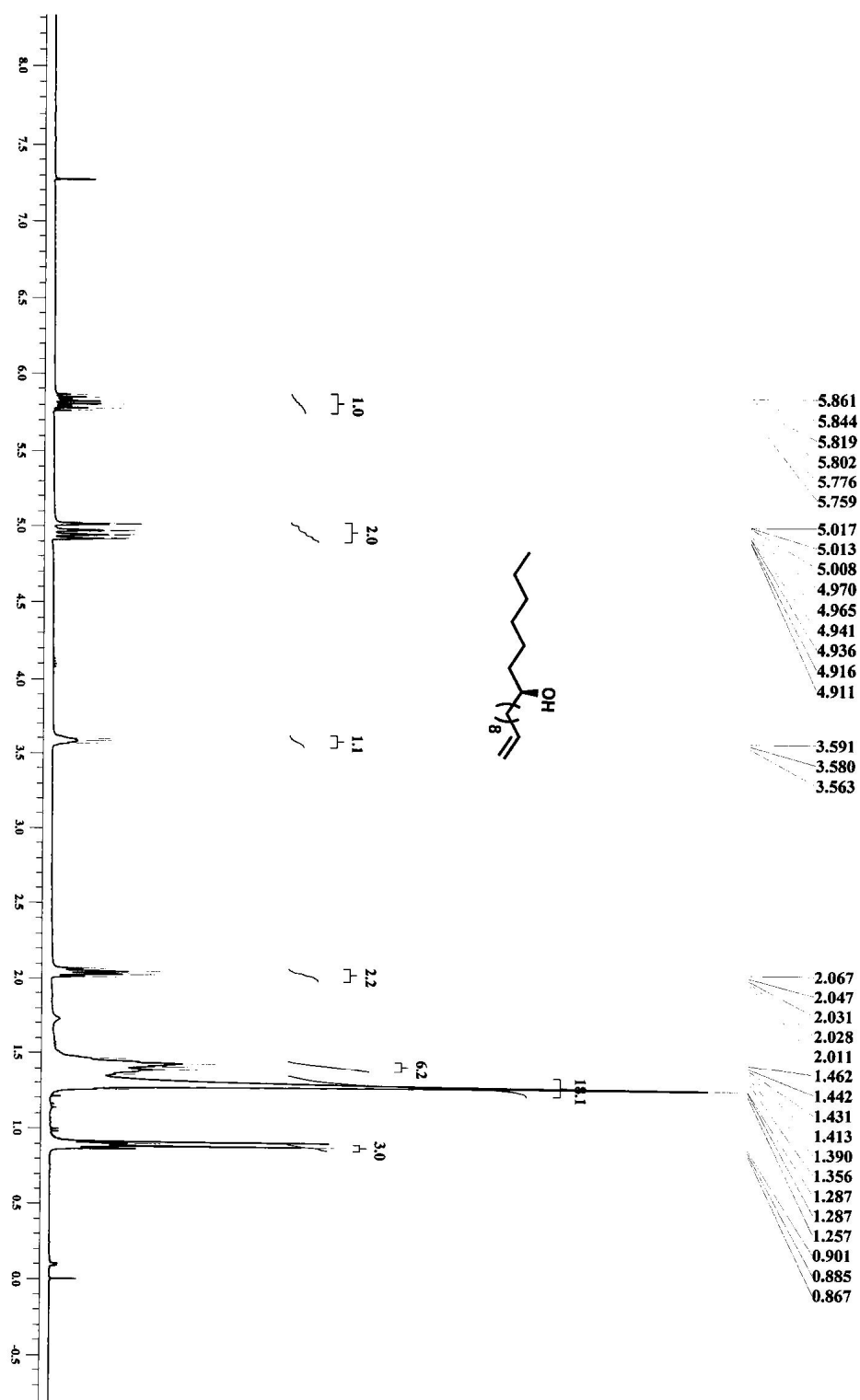


^{13}C NMR spectrum of **15b** (100 MHz, CDCl_3)

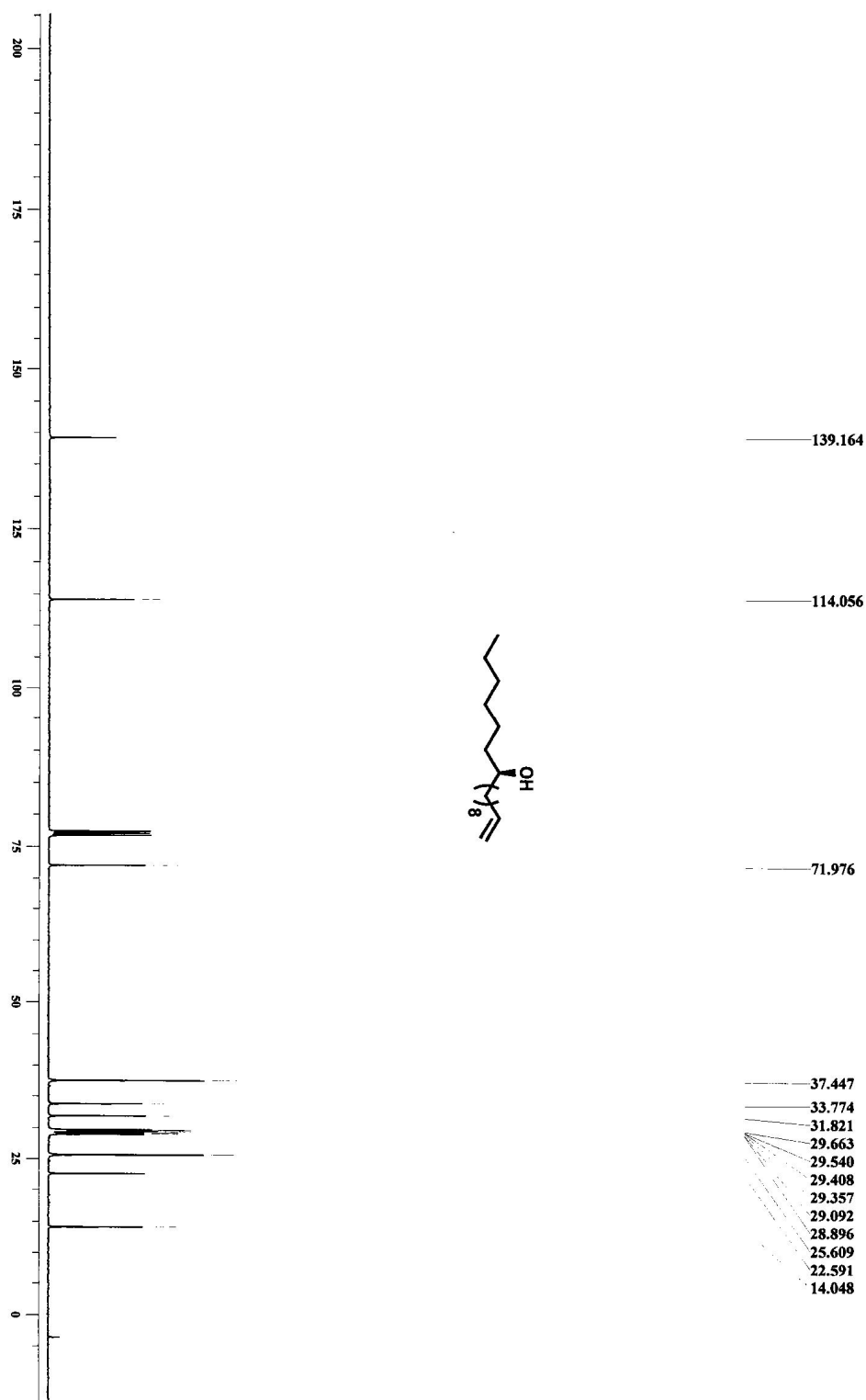
 ^1H NMR spectrum of **3a** (500 MHz, CDCl_3)



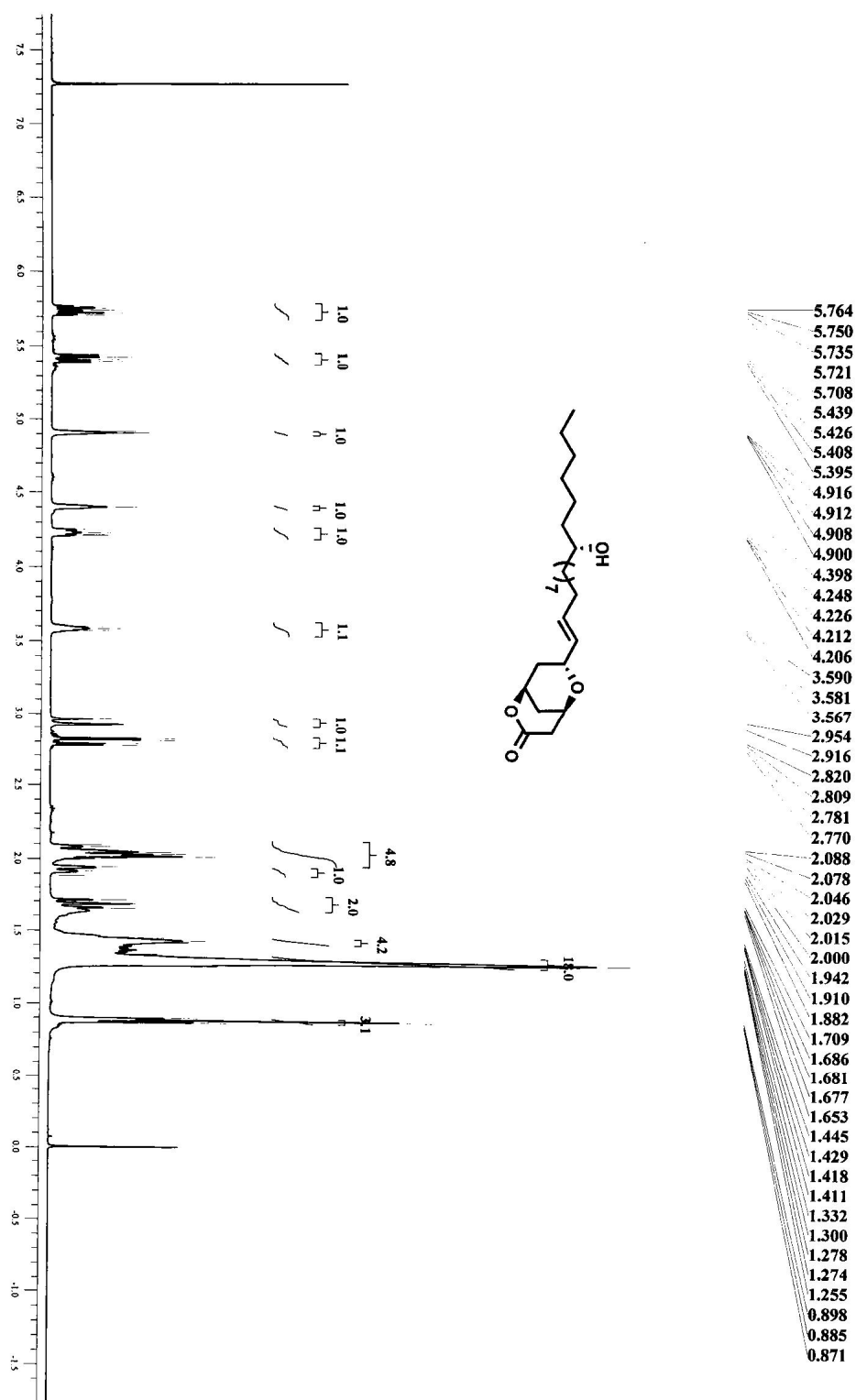
^{13}C NMR spectrum of **3a** (100 MHz, CDCl_3)

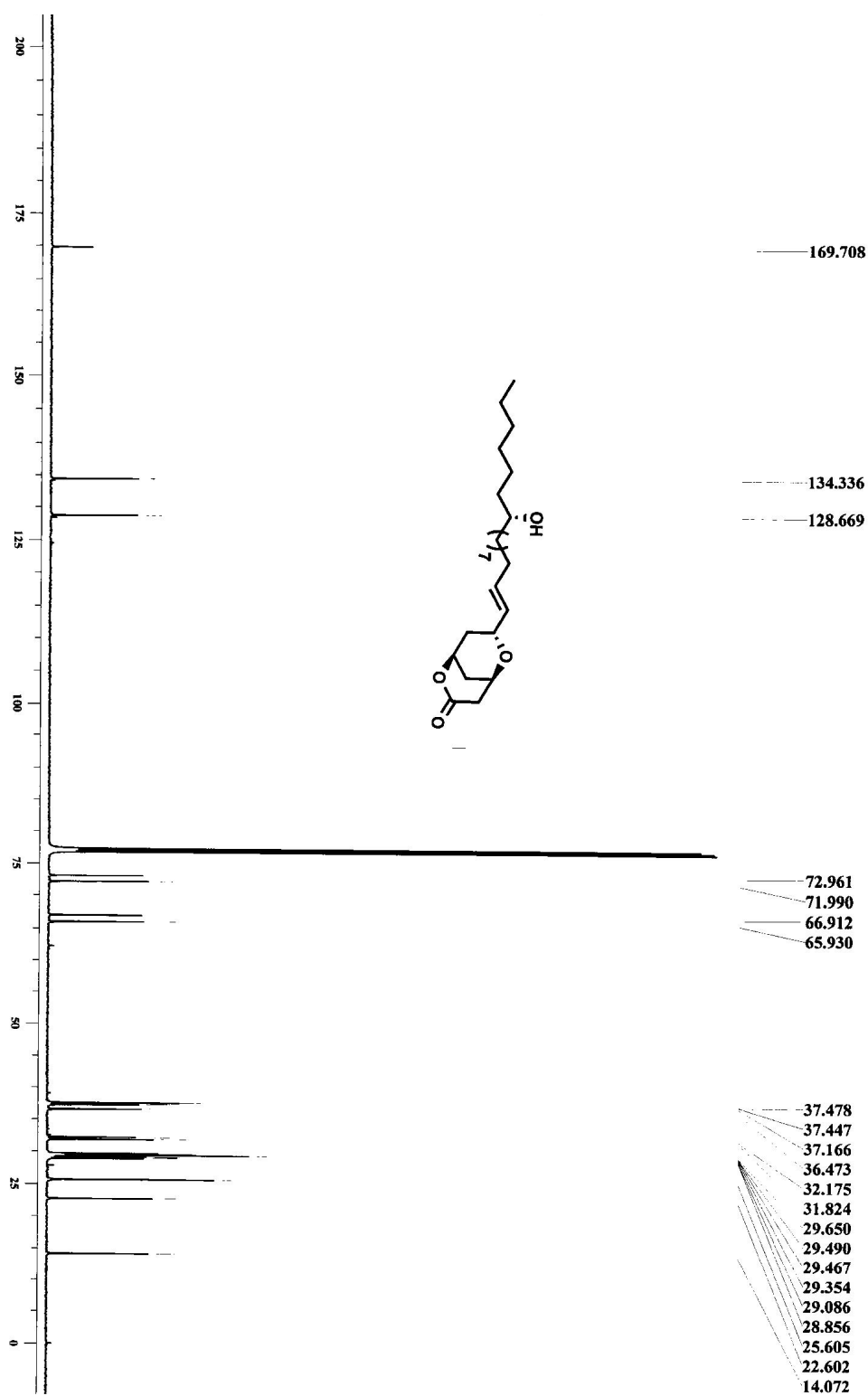


¹H NMR spectrum of **3b** (400 MHz, CDCl₃)



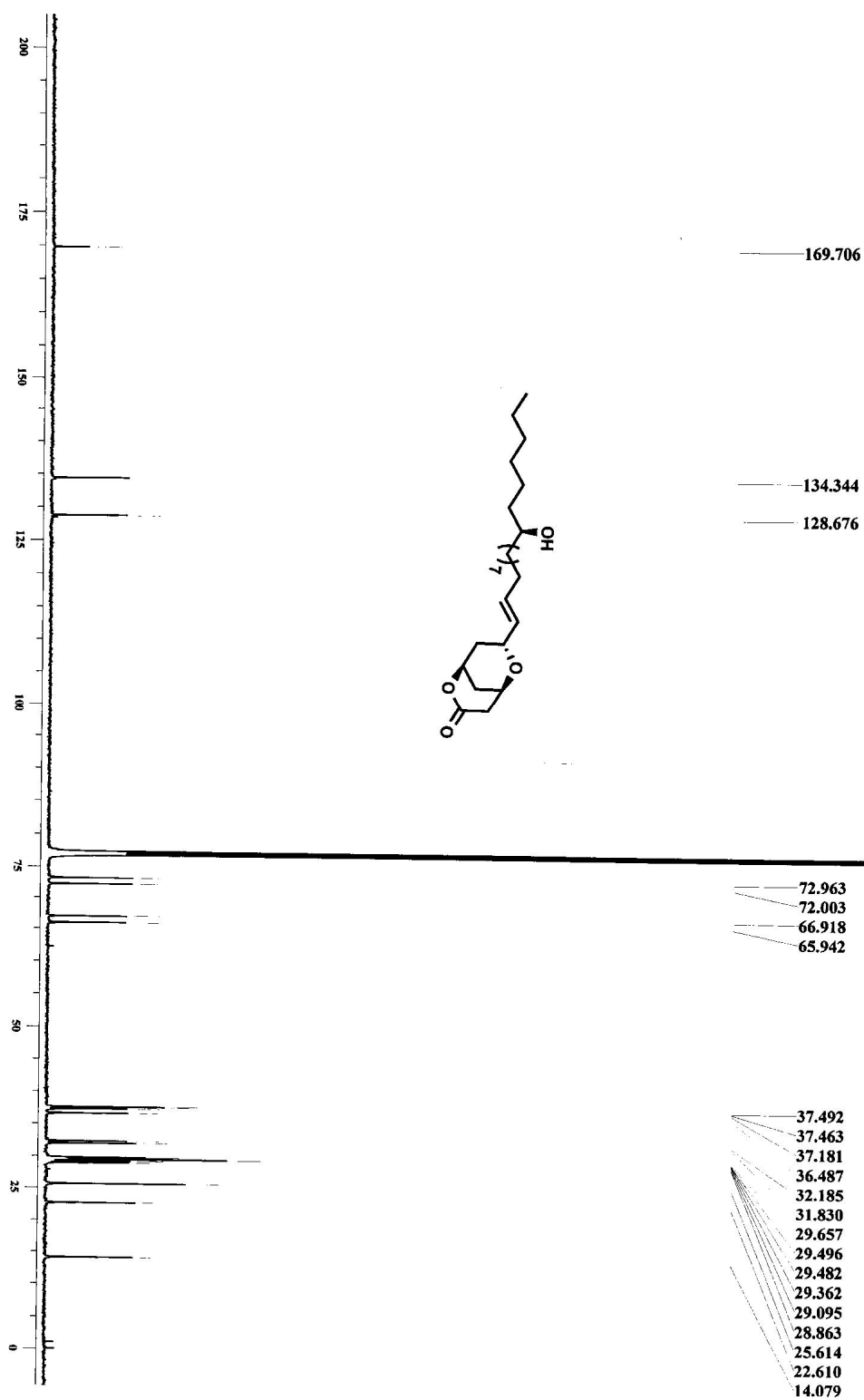
^{13}C NMR spectrum of **3b** (100 MHz, CDCl_3)

¹H NMR spectrum of 1a (500 MHz, CDCl₃)

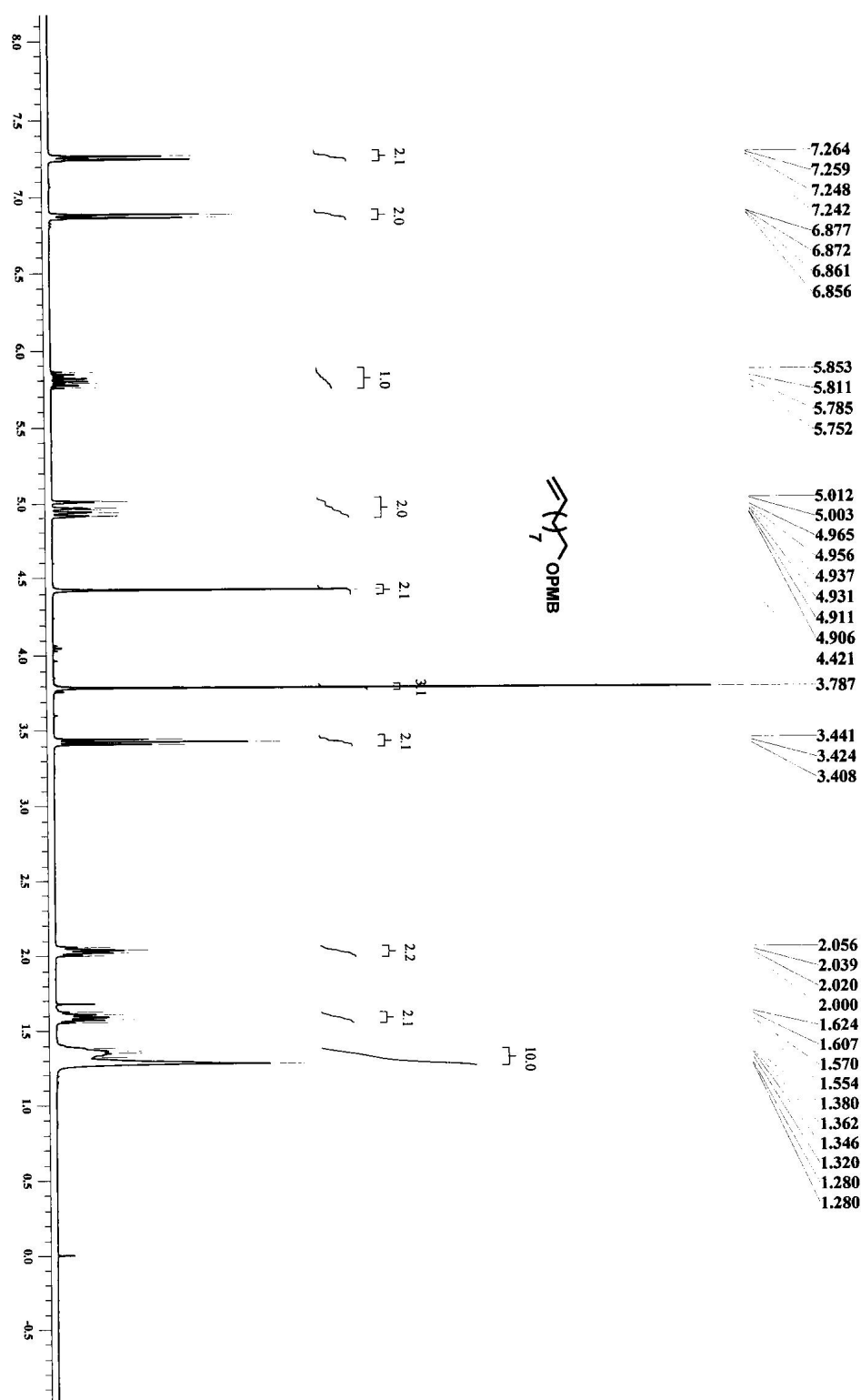


¹³C NMR spectrum of **1a** (125 MHz, CDCl₃)

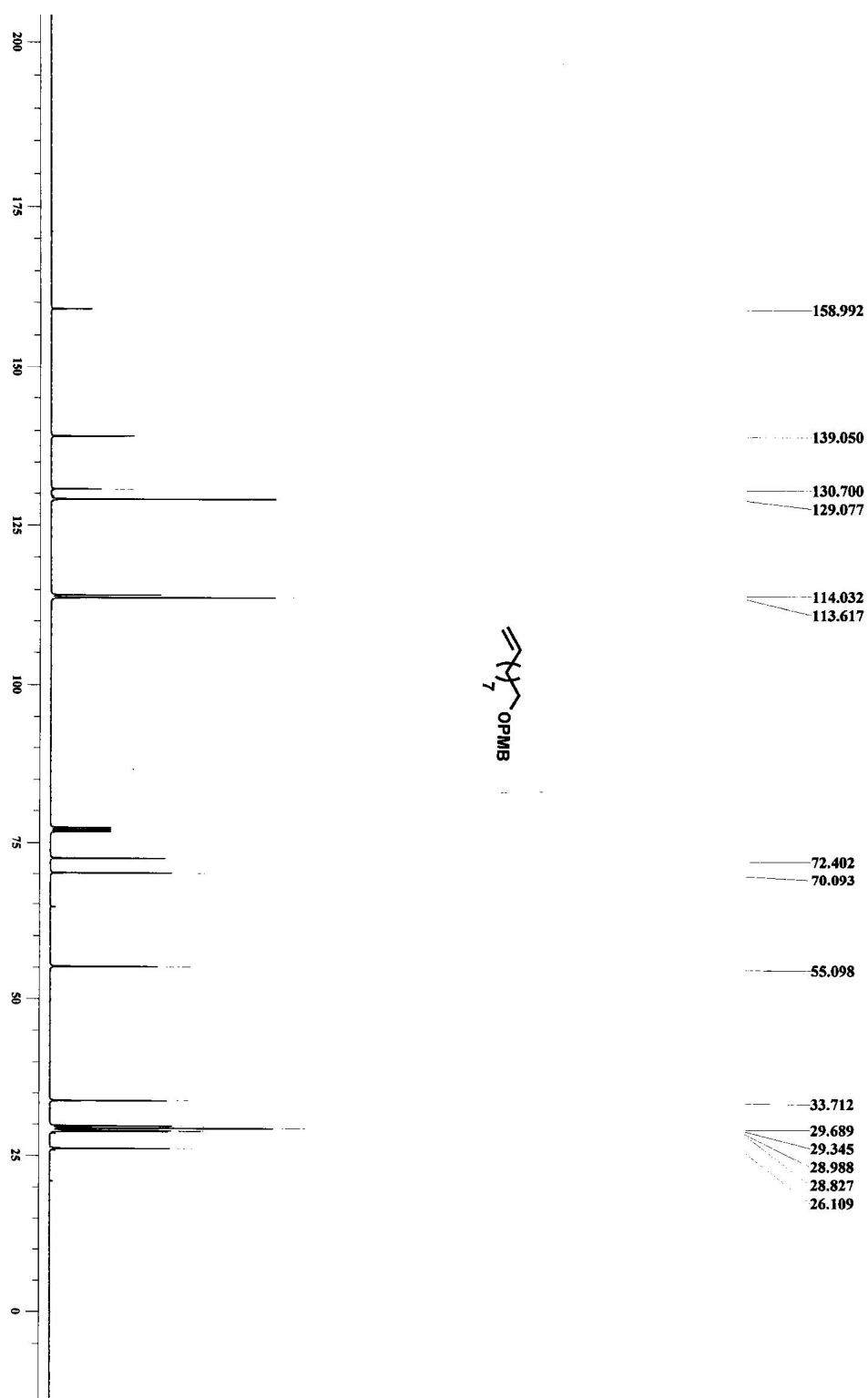
¹H NMR spectrum of **1b** (500 MHz, CDCl₃)



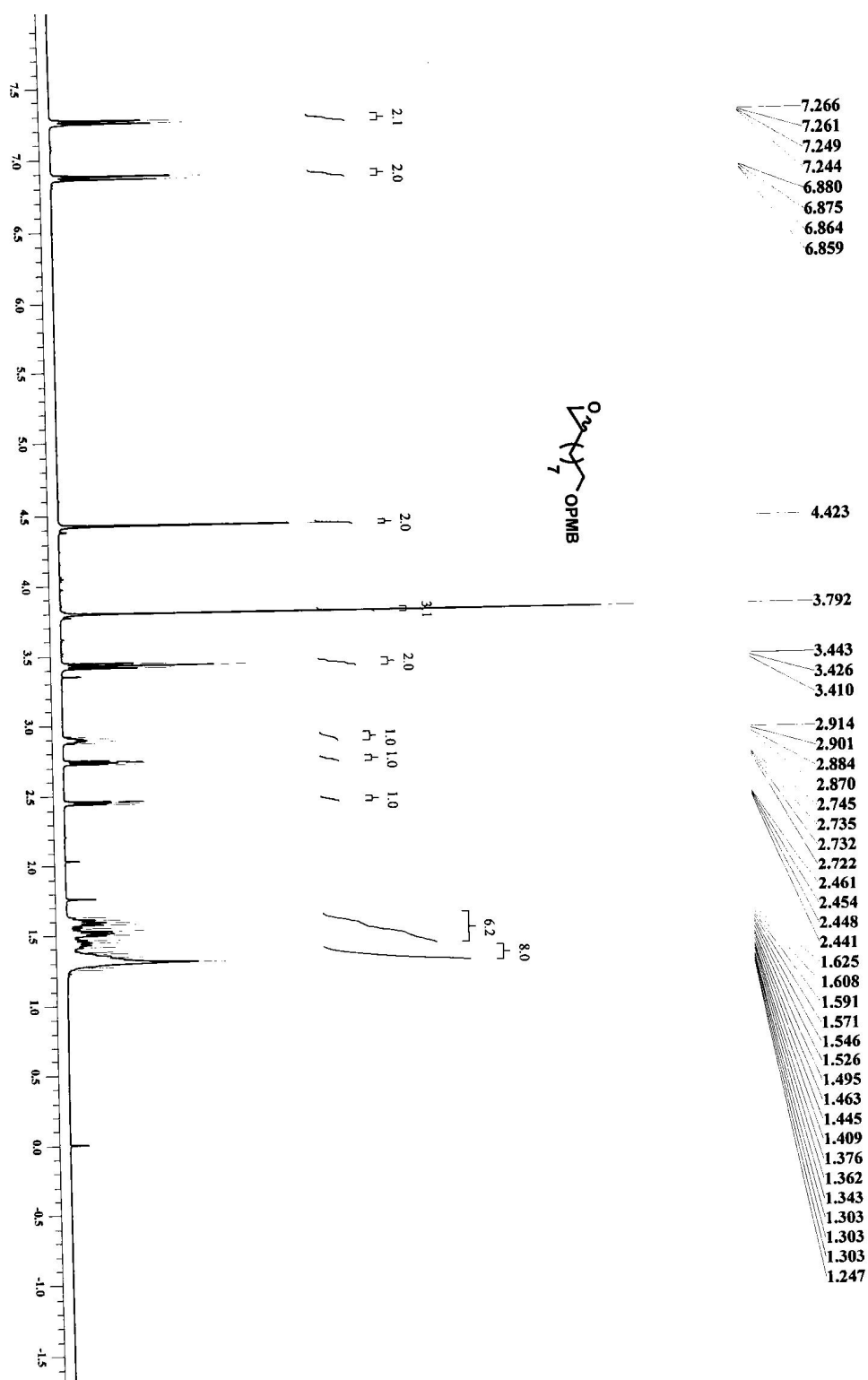
¹³C NMR spectrum of **1b** (125 MHz, CDCl₃)



¹H NMR spectrum of **16a** (400 MHz, CDCl₃)



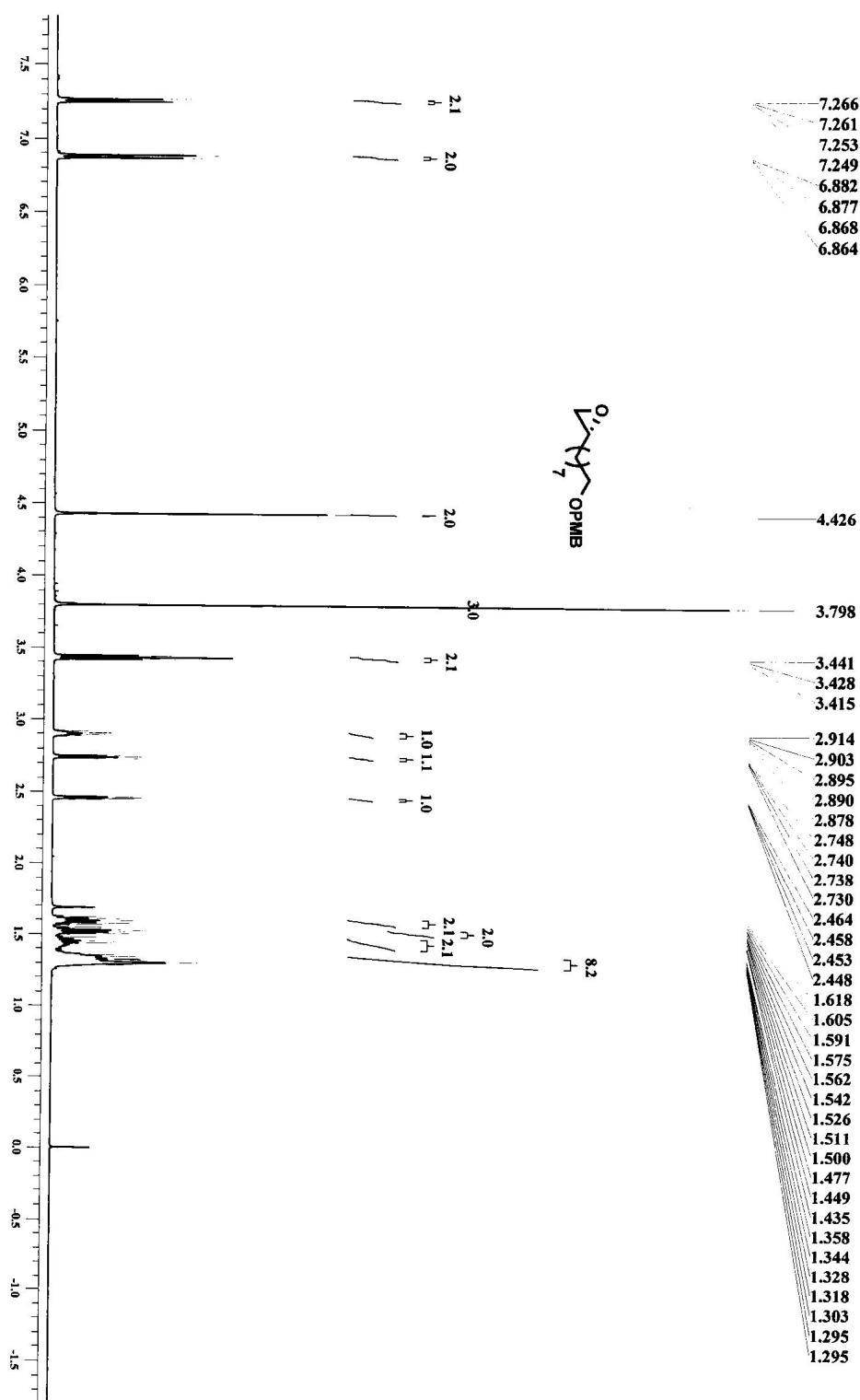
¹³C NMR spectrum of **16a** (100 MHz, CDCl₃)



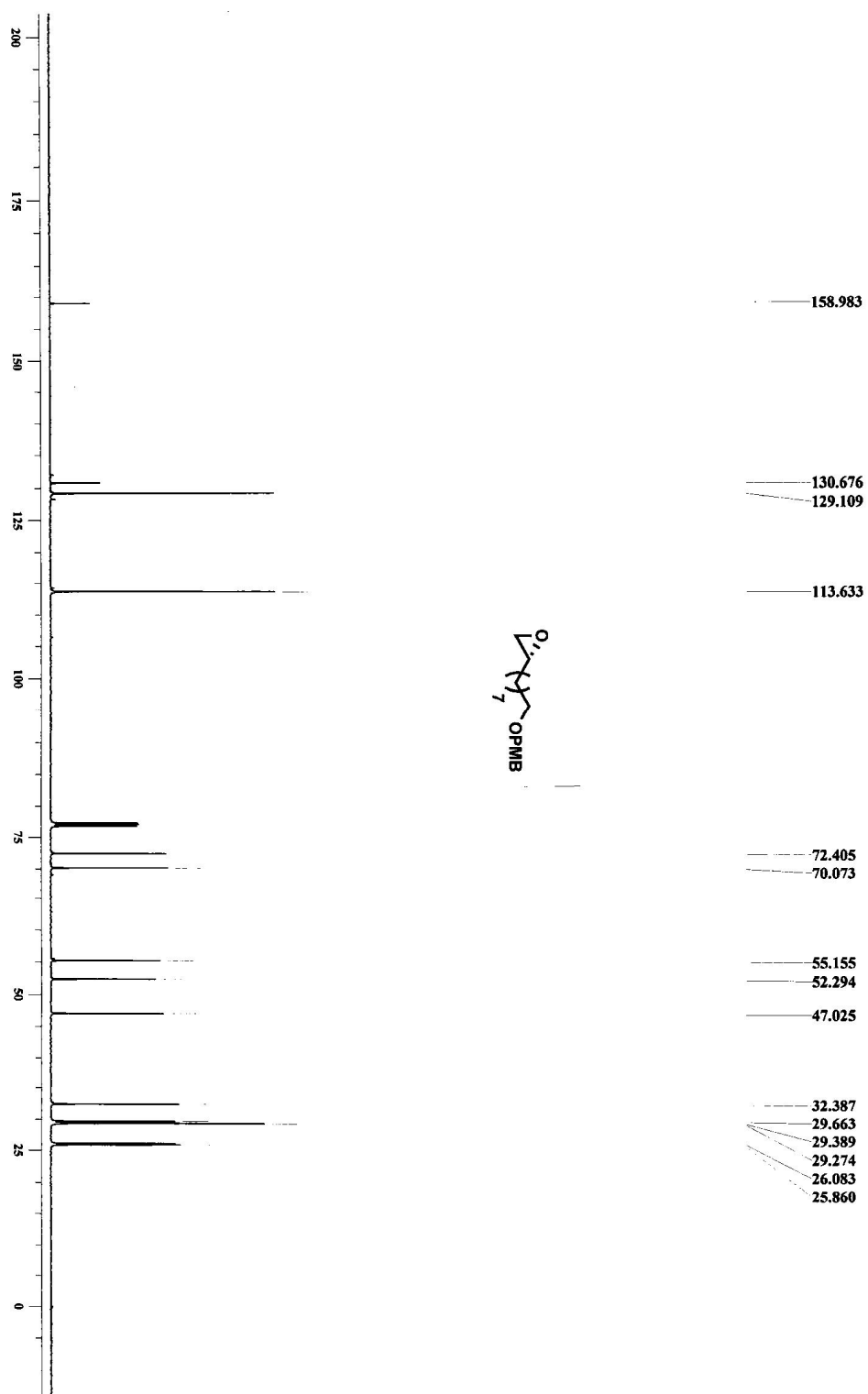
¹H NMR spectrum of **17** (400 MHz, CDCl₃)



^{13}C NMR spectrum of **17** (100 MHz, CDCl_3)

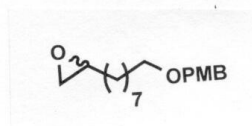


¹H NMR spectrum of **8c** (500 MHz, CDCl₃)

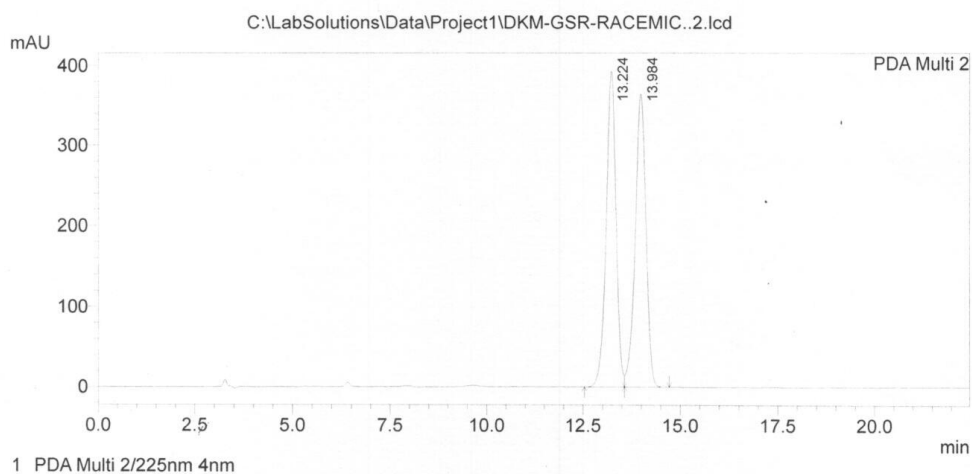
 ^{13}C NMR spectrum of **8c** (125 MHz, CDCl_3)

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\DKM-GSR-RACEMIC..2.lcd
 Acquired by : Manjula
 Sample Name : DKM-GSR-RACEMIC
 Sample ID : DKM-GSR-RACEMIC
 Tray# : 1
 Vial # : 90
 Injection Volume : 20 uL
 Data File Name : DKM-GSR-RACEMIC..2.lcd
 Method File Name : VIKRAM.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Data Acquired : 7/18/2017 11:16:46 AM
 Data Processed : 7/18/2017 11:39:16 AM
 Column: CHIRAL PAK IC 250 X 4.6mm, 5u
 Mobile Phase: 5% IPA IN HEXANE
 Flow Rate: 1 mL/min
 Detection : 240 225nm



<Chromatogram>



1 PDA Multi 2/225nm 4nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.224	7017582	392934	50.102	51.916
2	13.984	6989019	363932	49.898	48.084
Total		14006601	756866	100.000	100.000

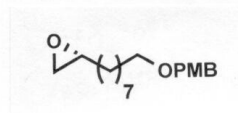
C:\LabSolutions\Data\Project1\DKM-GSR-RACEMIC..2.lcd

HPLC Chromatogram of 17

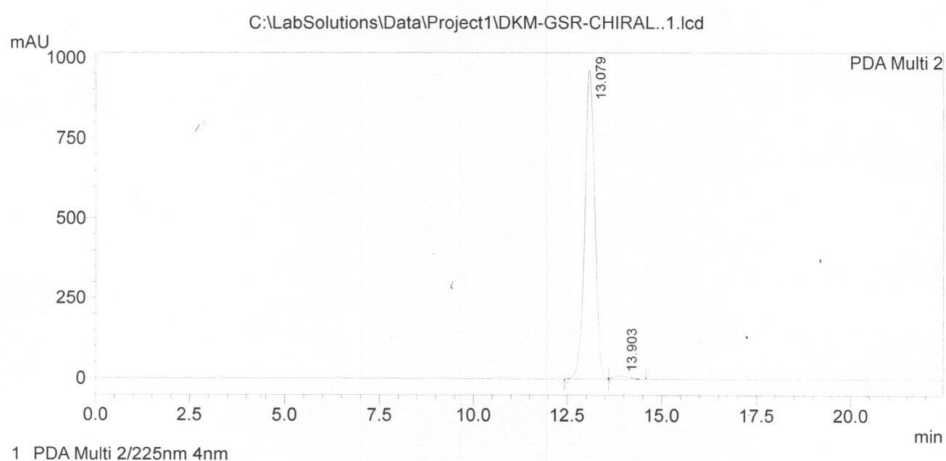
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\DKM-GSR-CHIRAL...1.lcd

Acquired by : Manjula
 Sample Name : DKM-GSR-CHIRAL
 Sample ID : DKM-GSR-CHIRAL
 Tray# : 1
 Vial # : 89
 Injection Volume : 20 uL
 Data File Name : DKM-GSR-CHIRAL...1.lcd
 Method File Name : VIKRAM.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Data Acquired : 7/18/2017 11:41:50 AM
 Data Processed : 7/18/2017 12:04:21 PM
 Column: CHIRAL PAK IC 250 X 4.6mm, 5u
 Mobile Phase: 5% IPA IN HEXANE
 Flow Rate: 1 mL/min
 Detection : 210 225 nm



<Chromatogram>

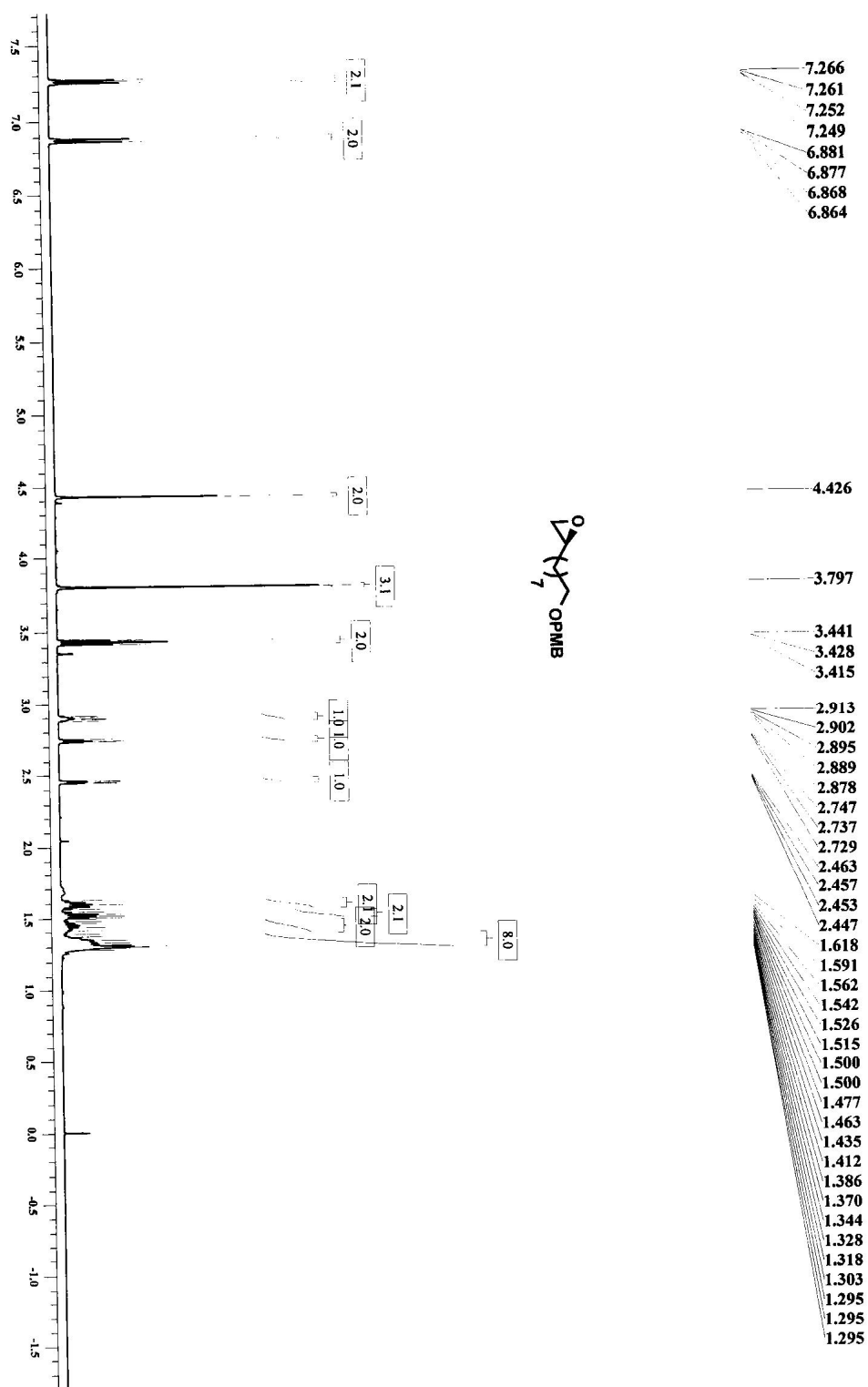


PeakTable

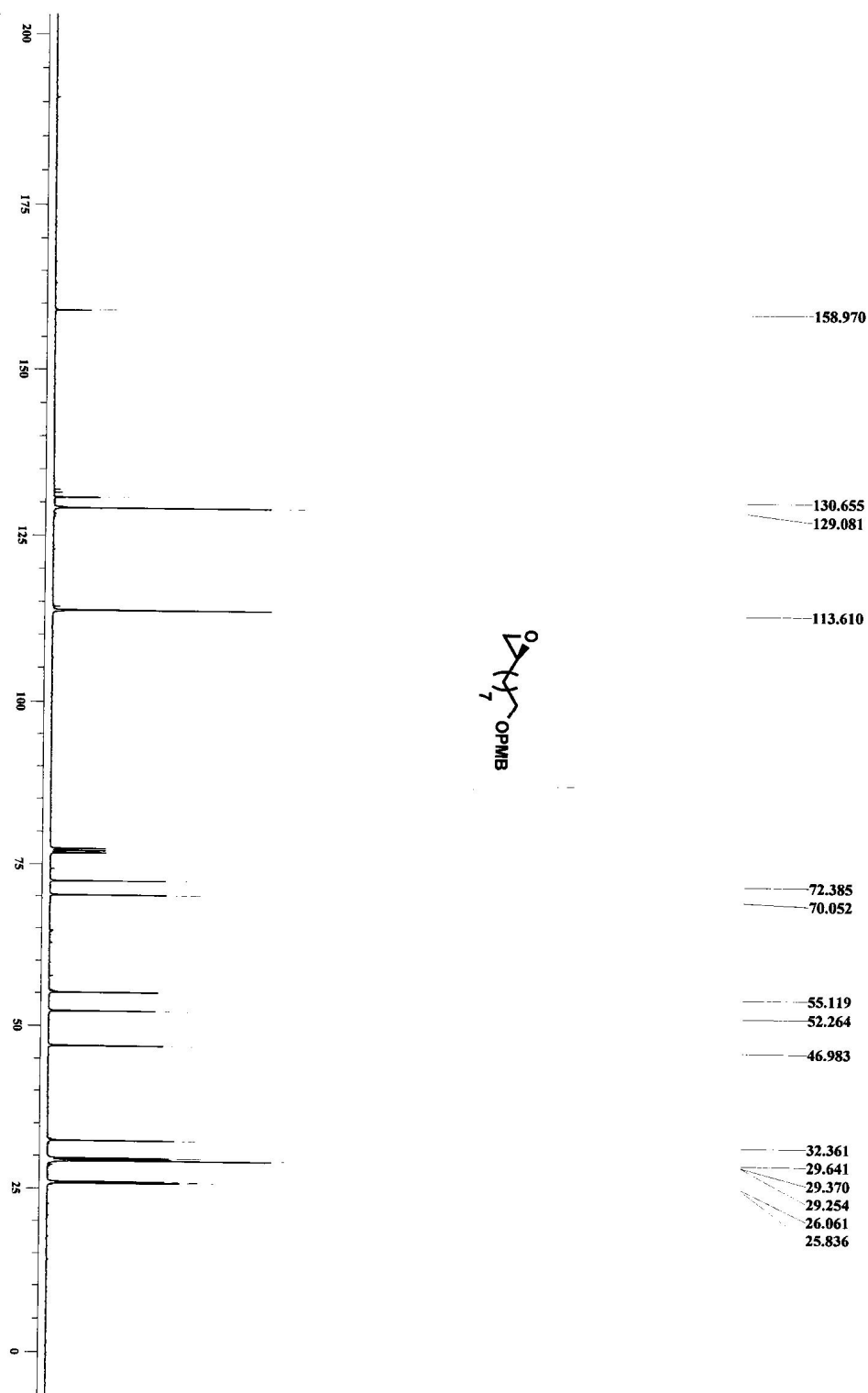
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.079	17698001	962233	98.526	98.964
2	13.903	264766	10072	1.474	1.036
Total		17962767	972305	100.000	100.000

C:\LabSolutions\Data\Project1\DKM-GSR-CHIRAL...1.lcd

HPLC Chromatogram of 8c



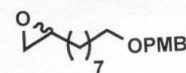
¹H NMR spectrum of **8d** (500 MHz, CDCl₃)



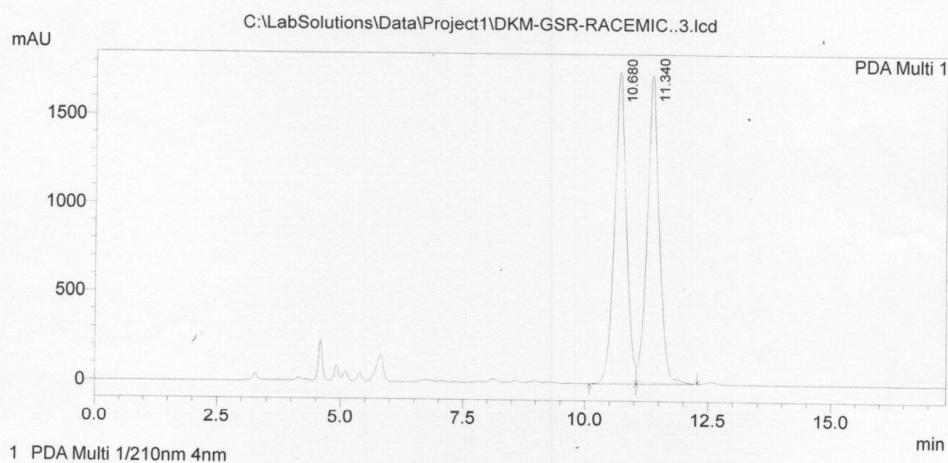
¹³C NMR spectrum of **8d** (100 MHz, CDCl₃)

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\DKM-GSR-RACEMIC...3.lcd
 Acquired by : Manjula
 Sample Name : DKM-GSR-RACEMIC
 Sample ID : DKM-GSR-RACEMIC
 Tray# : 1
 Vial # : 13
 Injection Volume : 20 uL
 Data File Name : DKM-GSR-RACEMIC...3.lcd
 Method File Name : DKM.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Data Acquired : 8/7/2017 4:07:16 PM
 Data Processed : 8/7/2017 4:24:41 PM
 Column: CHIRAL PAK IC 250 X 4.6mm, 5u
 Mobile Phase: 10% IPA IN HEXANE
 Flow Rate: 1 mL/min
 Detection : 210



<Chromatogram>



PDA Ch1 210nm 4nm

PeakTable

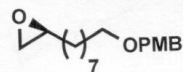
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.680	29394915	1749712	49.833	50.259
2	11.340	29591365	1731711	50.167	49.741
Total		58986280	3481423	100.000	100.000

C:\LabSolutions\Data\Project1\DKM-GSR-RACEMIC...3.lcd

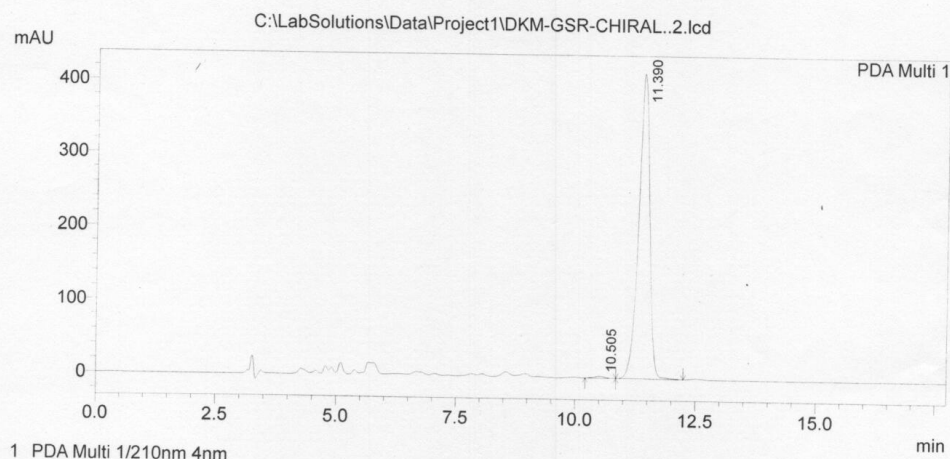
HPLC Chromatogram of 17

==== Shimadzu LCsolution Analysis Report ====

Acquired by : Manjula
 Sample Name : DKM-GSR-CHIRAL
 Sample ID : DKM-GSR-CHIRAL
 Tray# : 1
 Vial # : 14
 Injection Volume : 20 uL
 Data File Name : DKM-GSR-CHIRAL..2.lcd
 Method File Name : DKM.lcm
 Batch File Name :
 Report File Name : Default.lcr
 Data Acquired : 8/7/2017 4:25:37 PM
 Data Processed : 8/7/2017 4:43:25 PM
 Column: CHIRAL PAK IC 250 X 4.6mm, 5u
 Mobile Phase: 10% IPA IN HEXANE
 Flow Rate: 1 mL/min
 Detection : 210



<Chromatogram>

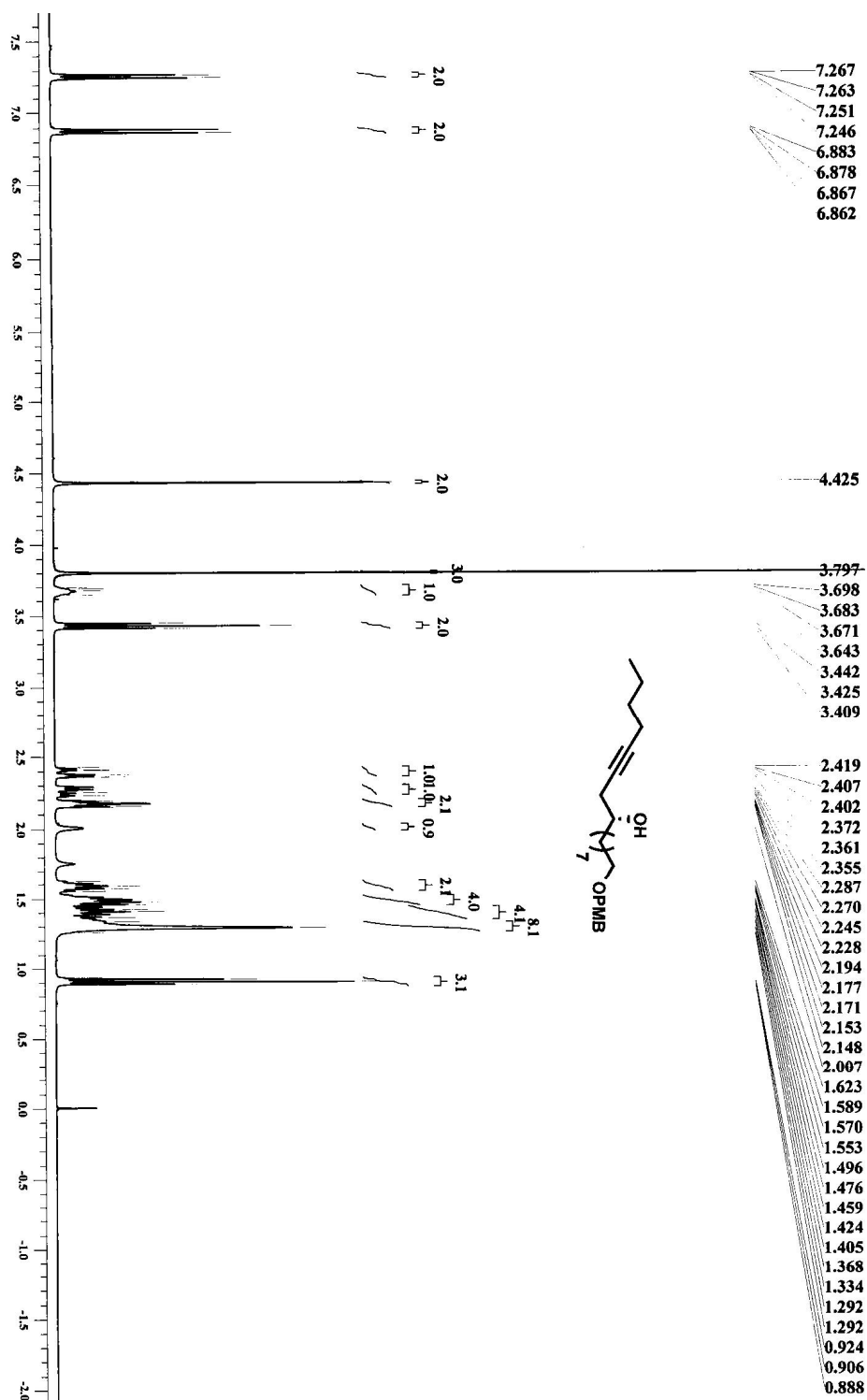


PDA Ch1 210nm 4nm

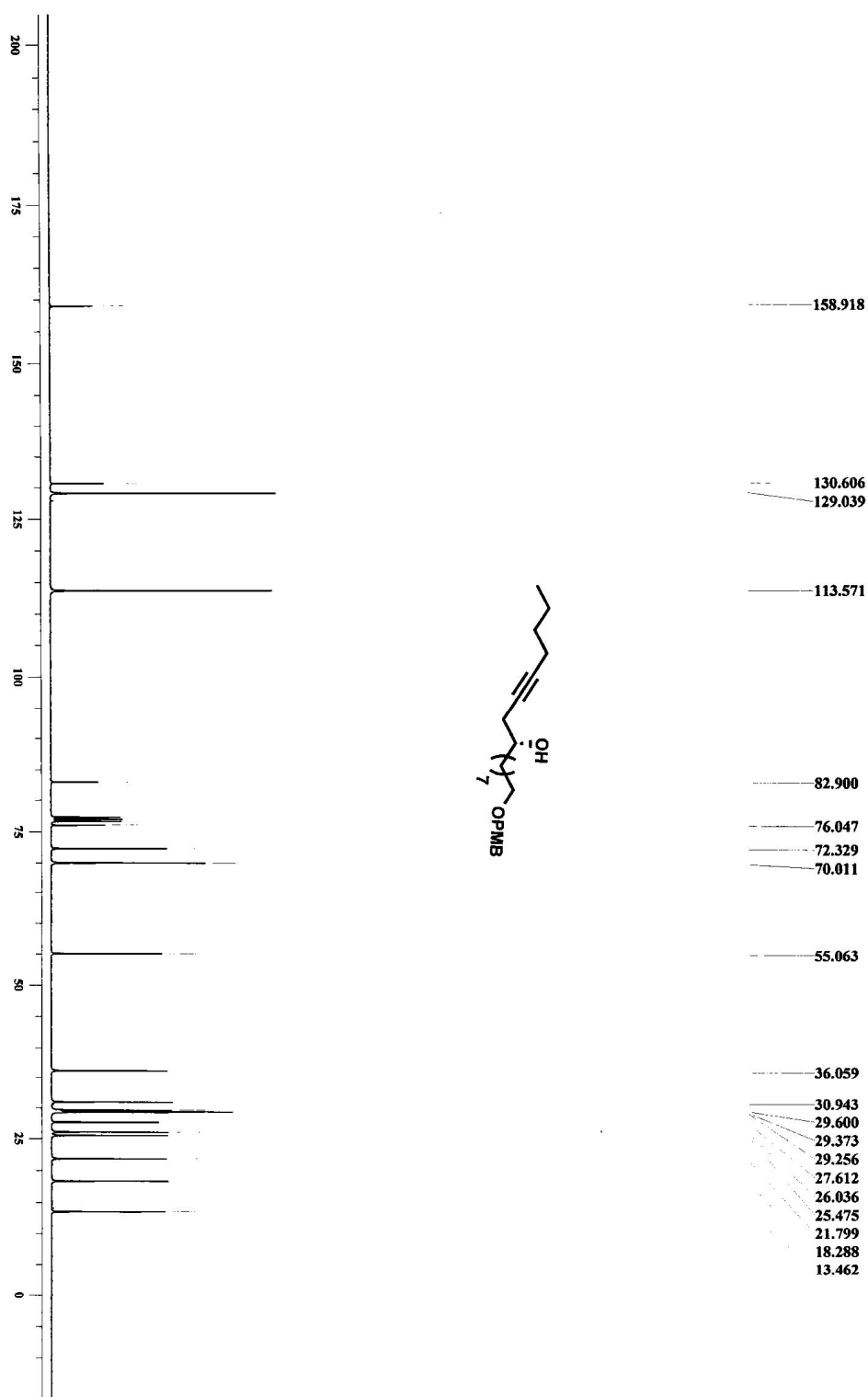
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.505	37895	2732	0.576	0.654
2	11.390	6538787	414859	99.424	99.346
Total		6576682	417591	100.000	100.000

C:\LabSolutions\Data\Project1\DKM-GSR-CHIRAL..2.lcd

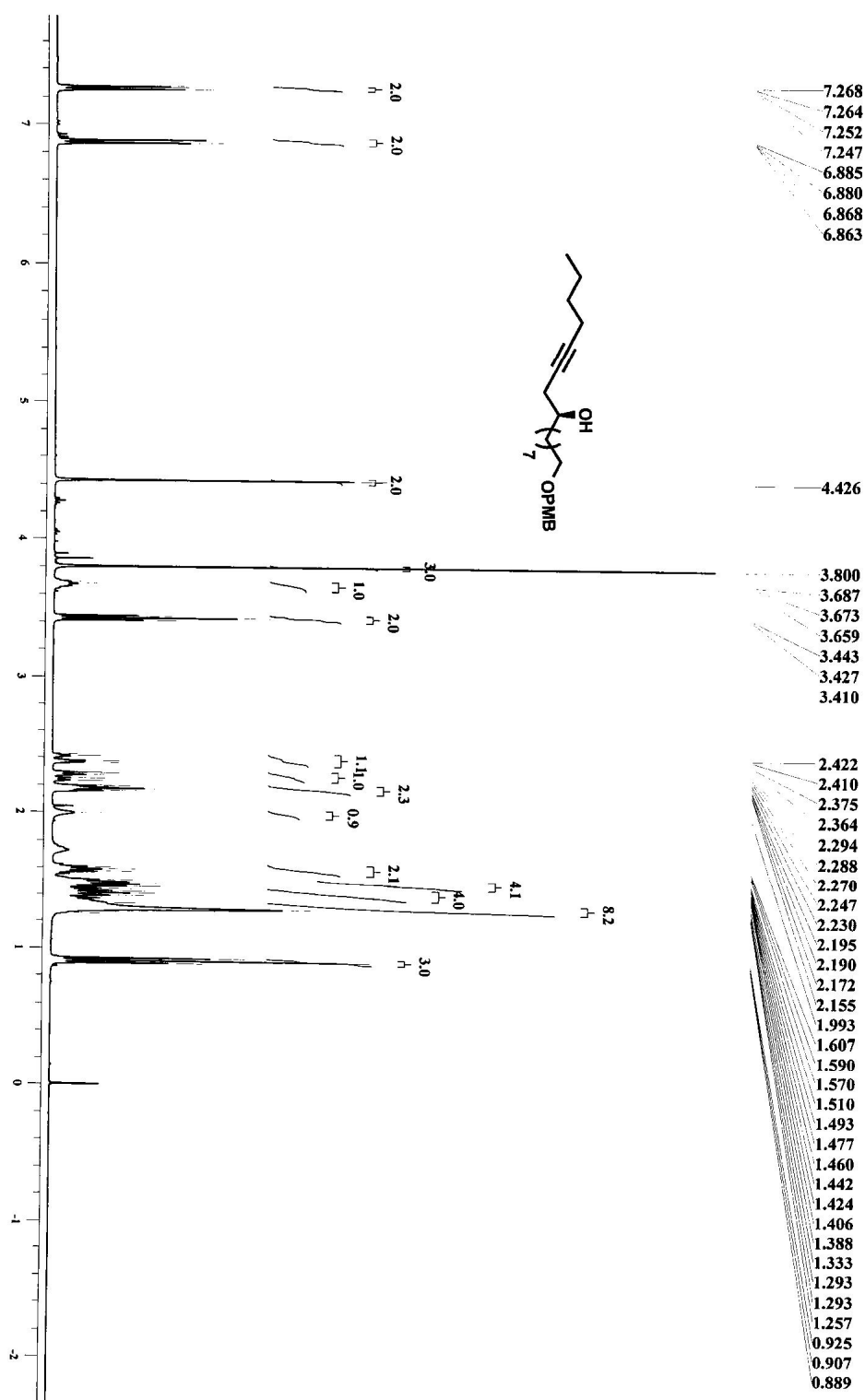
HPLC Chromatogram of **8d**



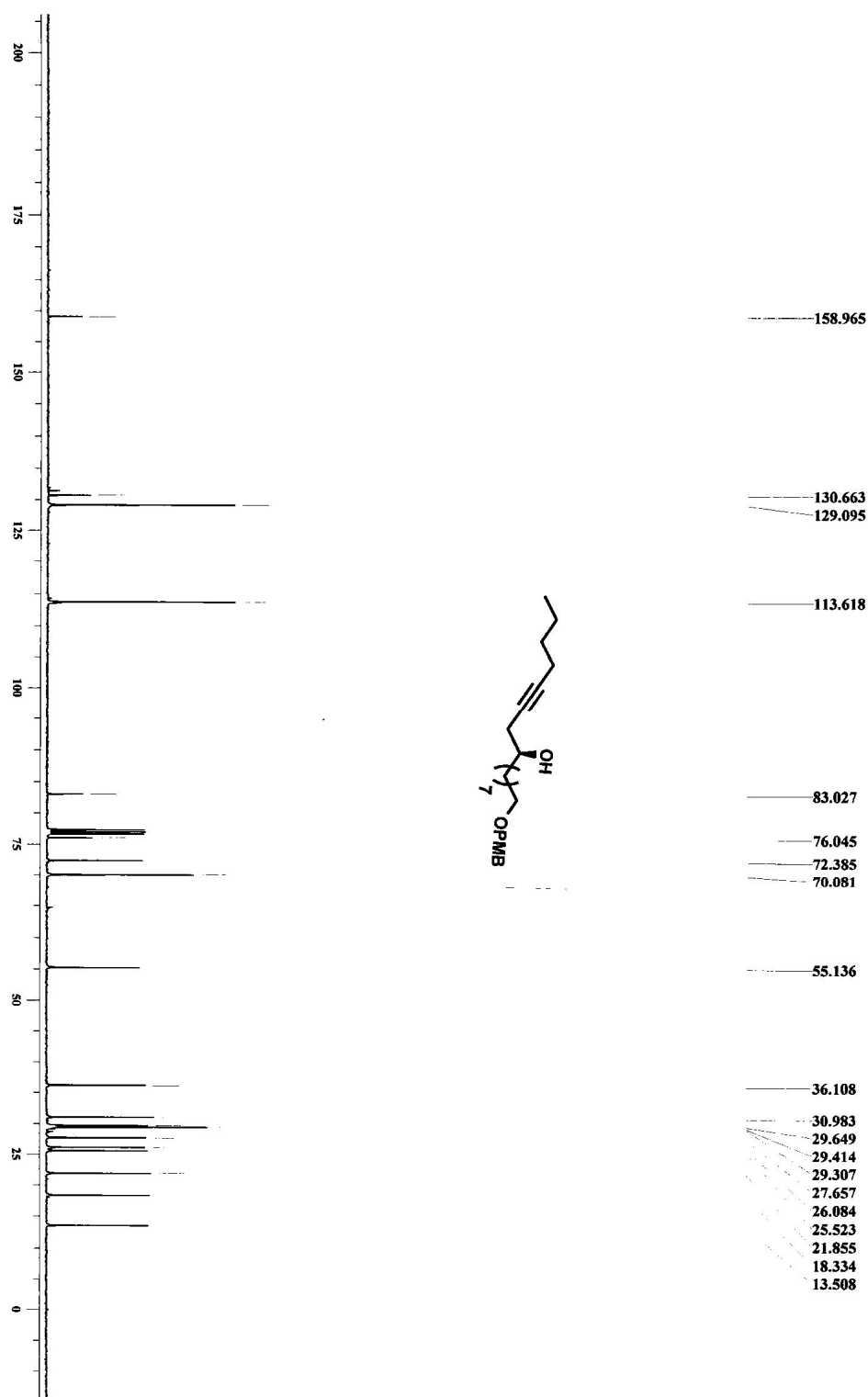
^1H NMR spectrum of **7c** (400 MHz, CDCl_3)



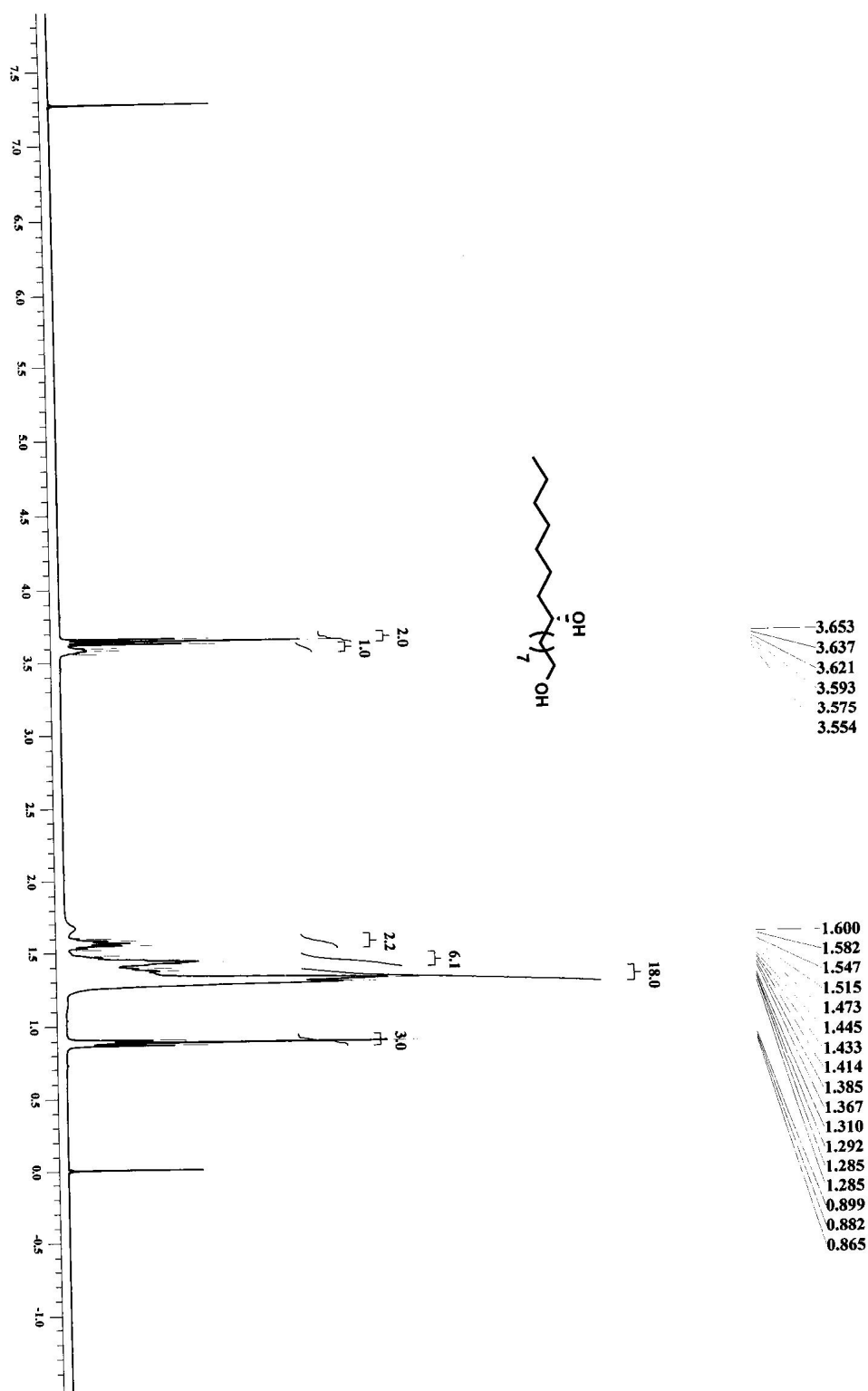
¹³C NMR spectrum of **7c** (100 MHz, CDCl₃)



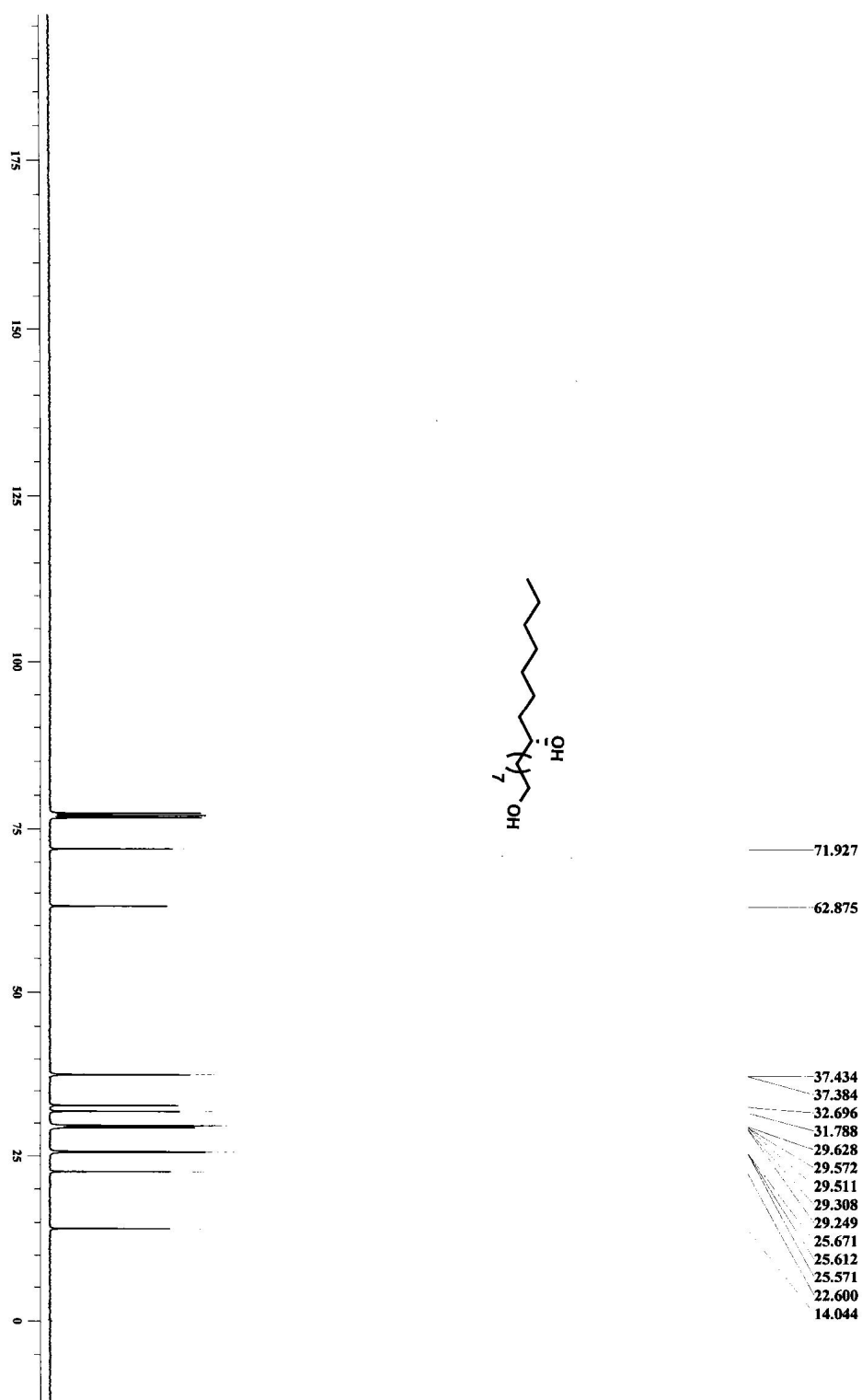
¹H NMR spectrum of **7d** (400 MHz, CDCl₃)

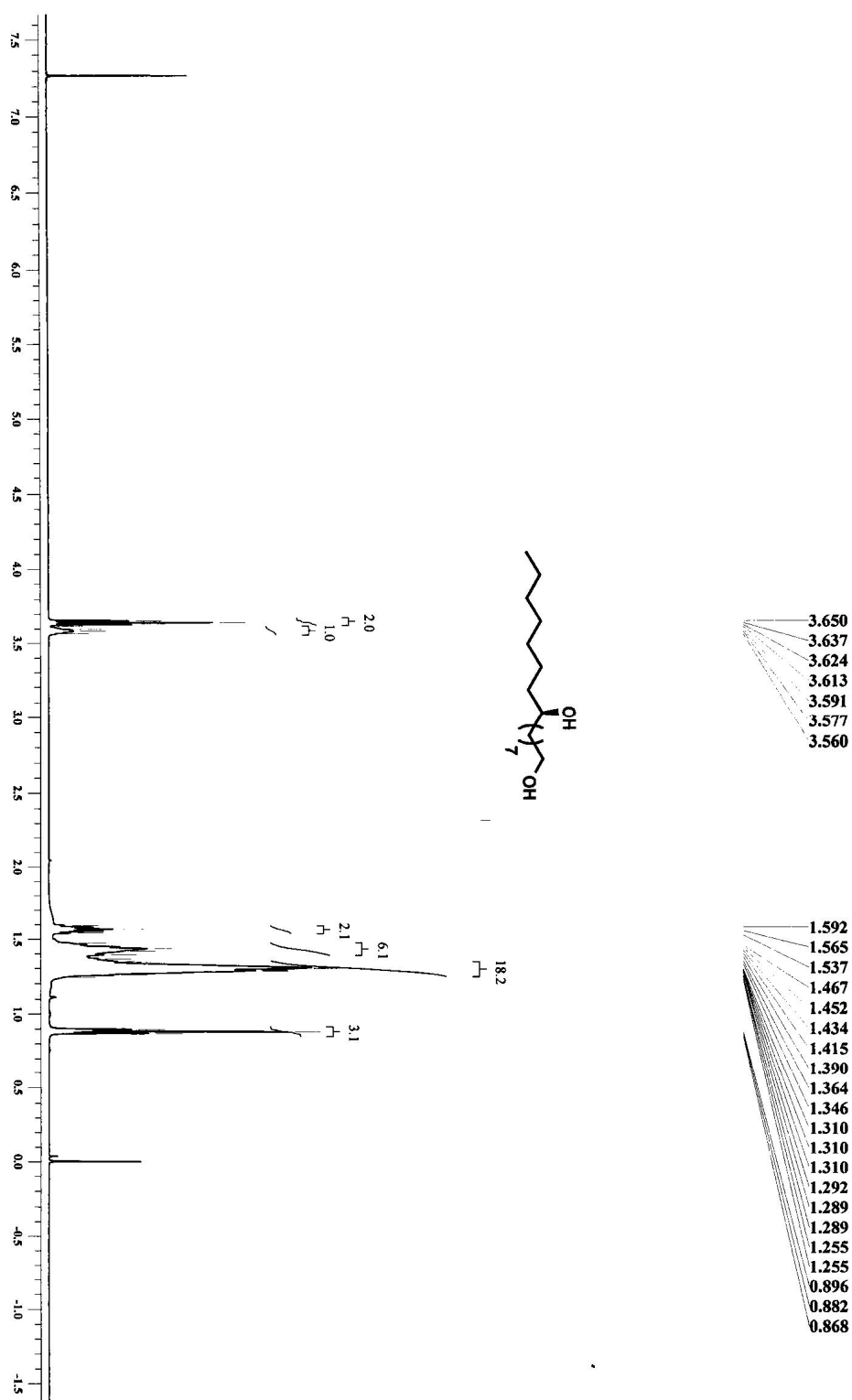


¹³C NMR spectrum of **7d** (100 MHz, CDCl₃)

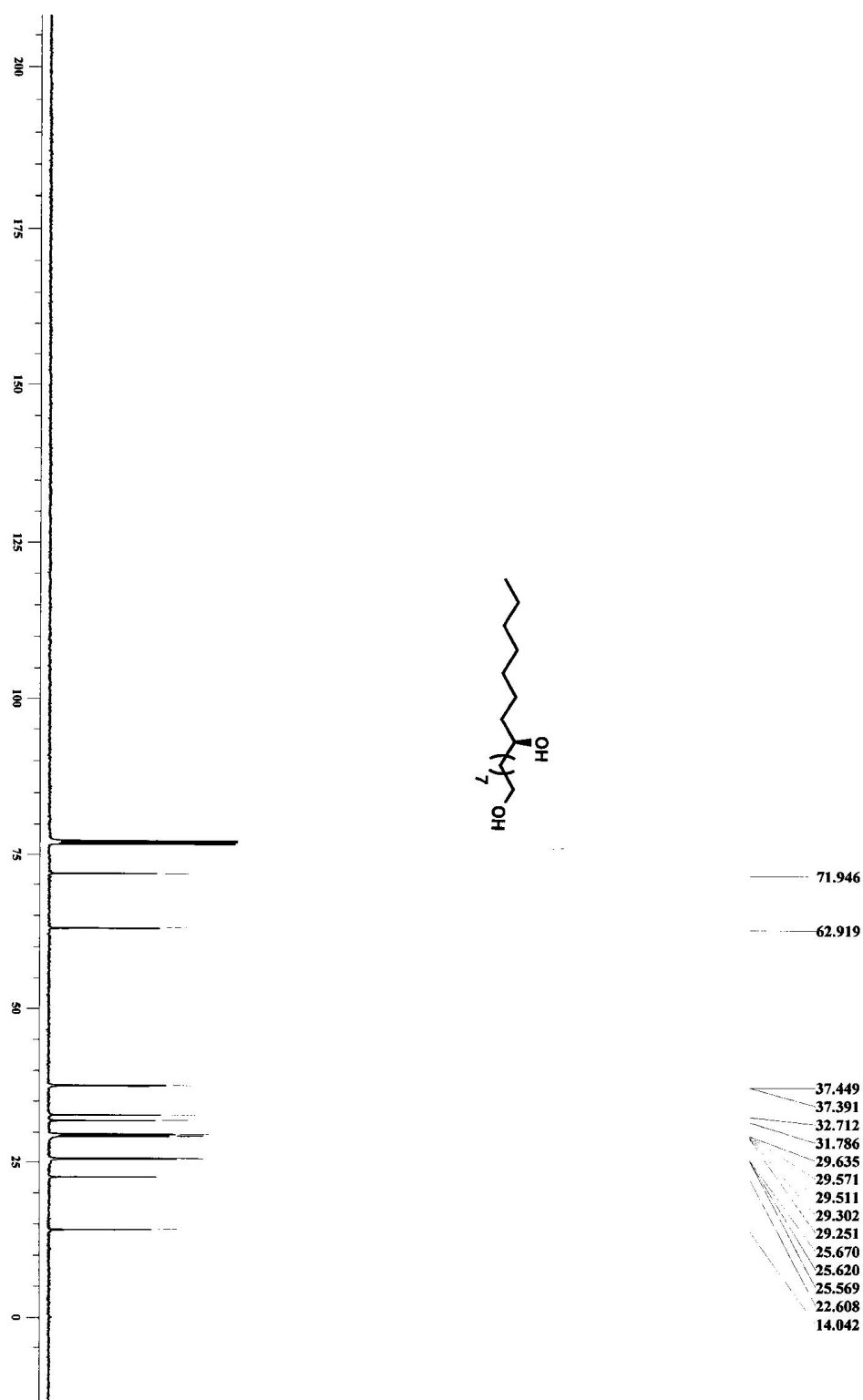


^1H NMR spectrum of **15c** (400 MHz, CDCl_3)

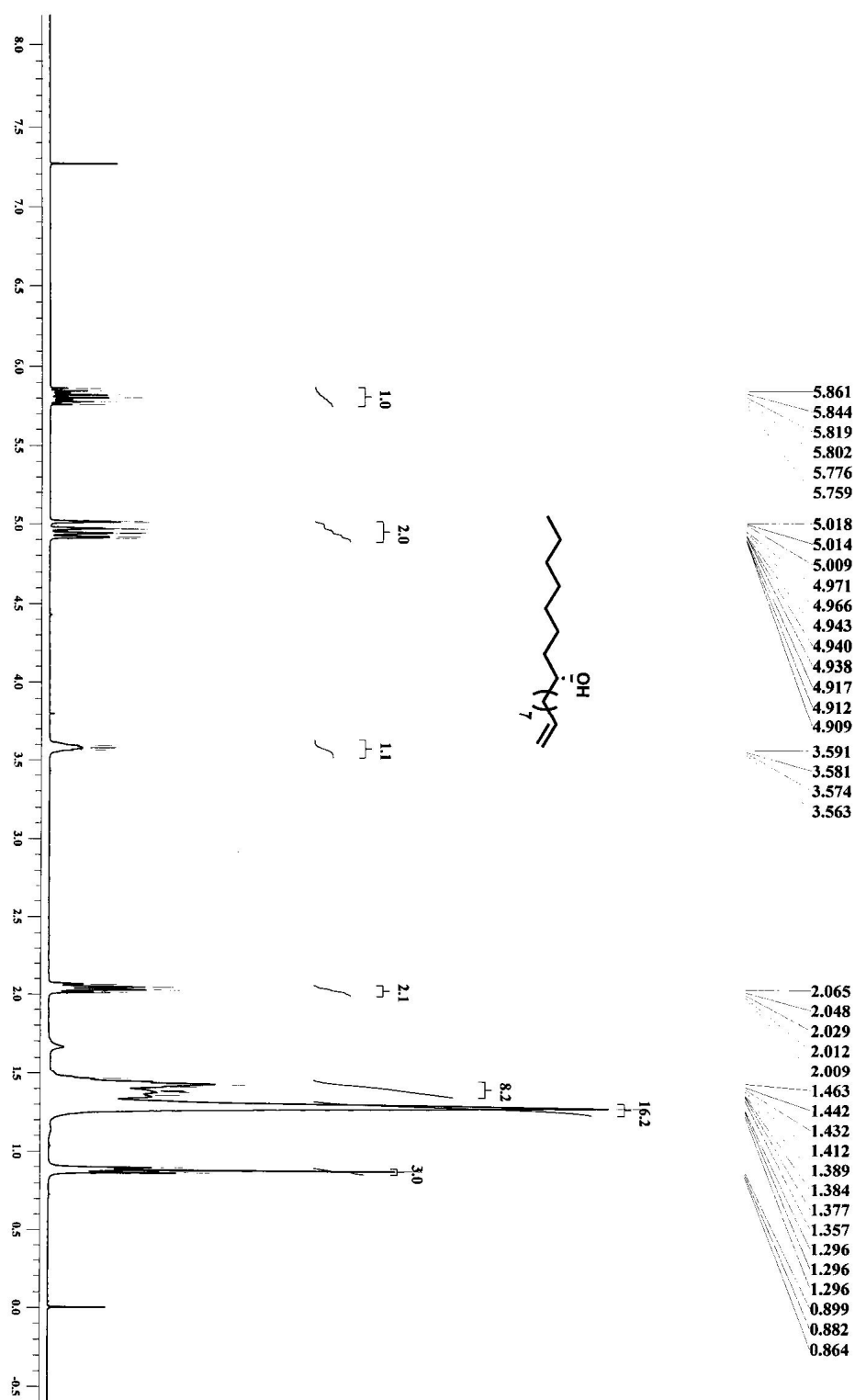
 ^{13}C NMR spectrum of **15c** (100 MHz, CDCl_3)

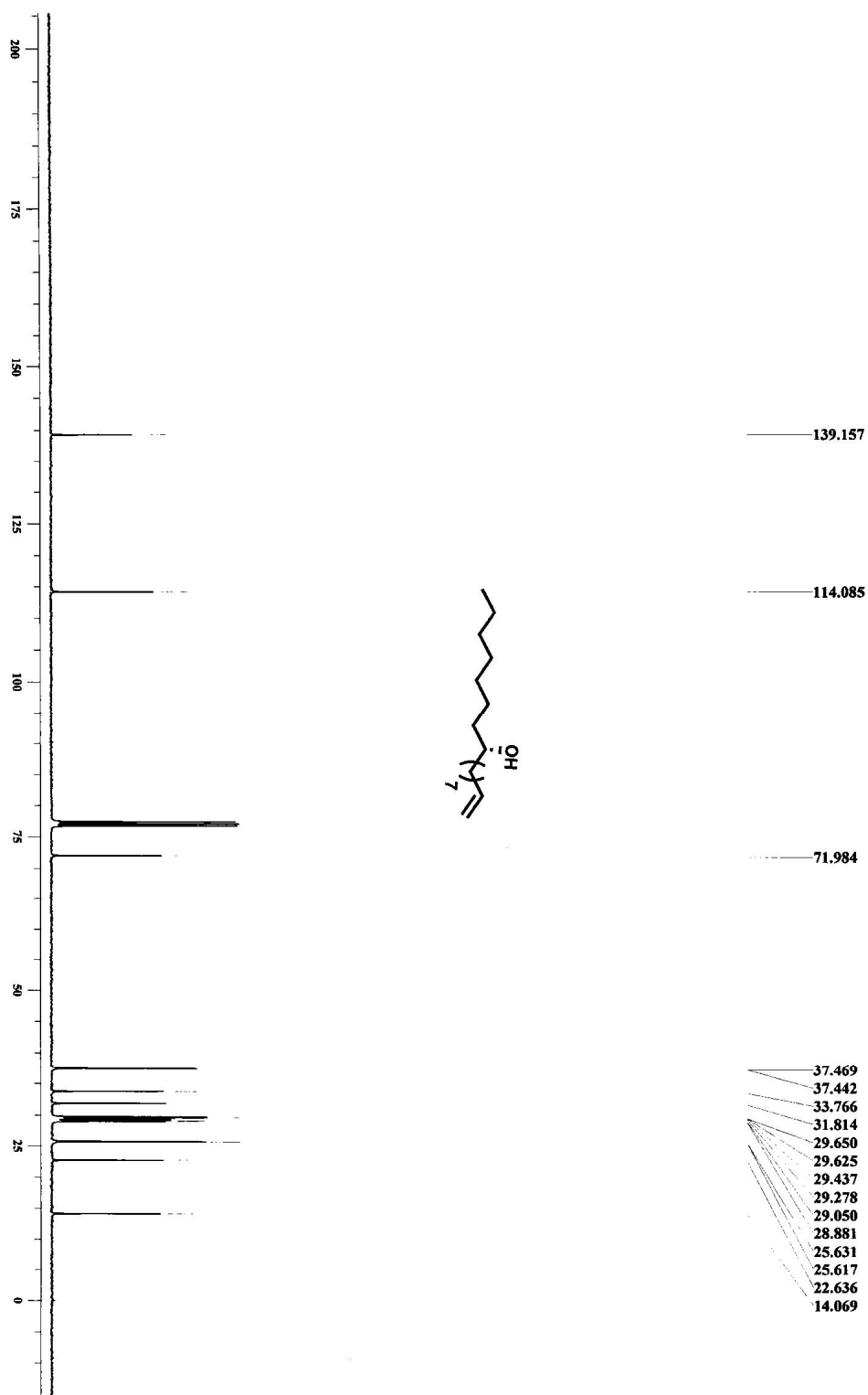


¹H NMR spectrum of **15d** (500 MHz, CDCl₃)

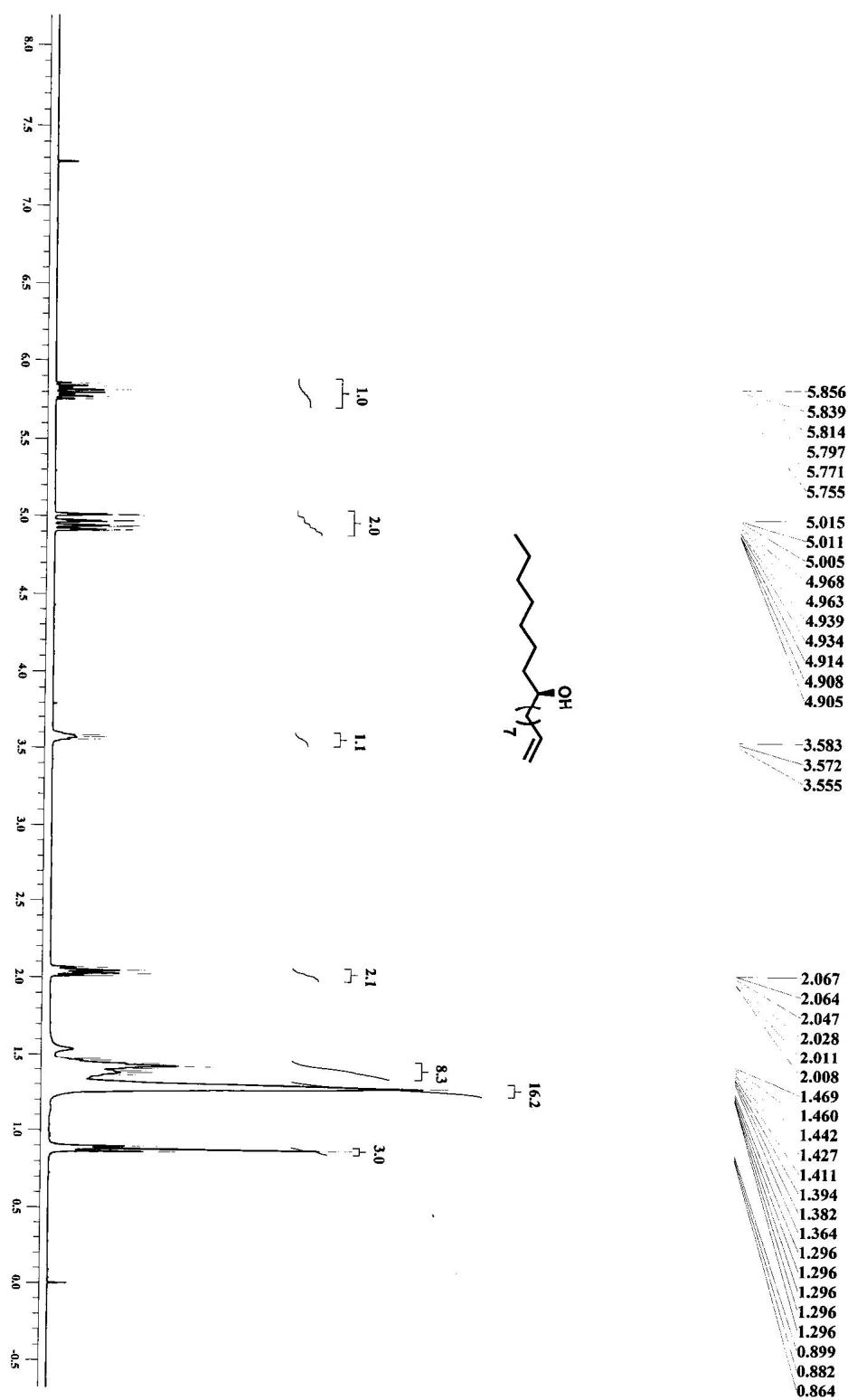


^{13}C NMR spectrum of **15d** (125 MHz, CDCl_3)

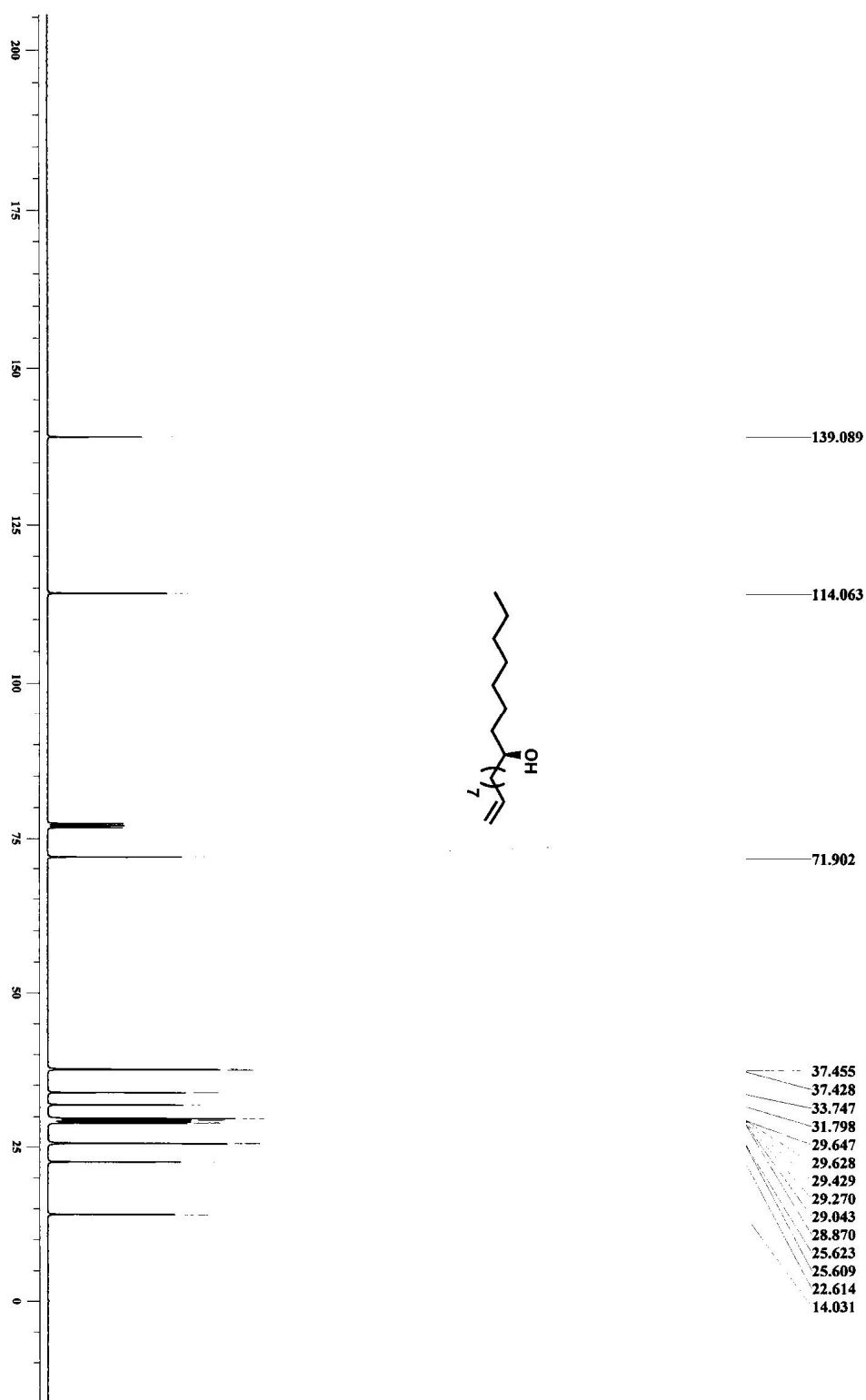
¹H NMR spectrum of **3c** (400 MHz, CDCl₃)



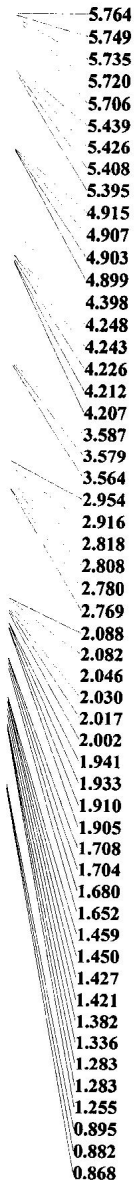
^{13}C NMR spectrum of **3c** (100 MHz, CDCl_3)

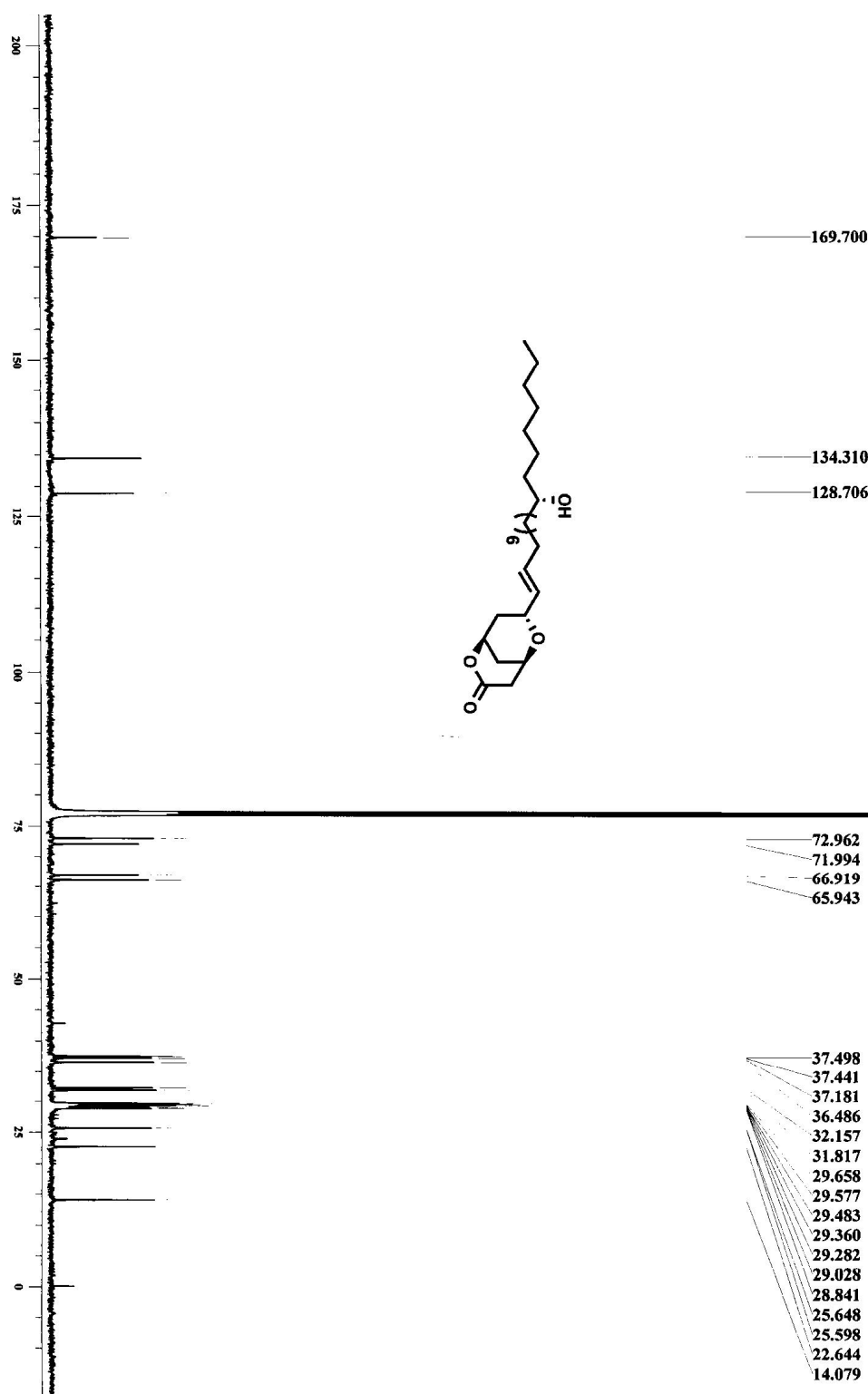


¹H NMR spectrum of **3d** (400 MHz, CDCl₃)

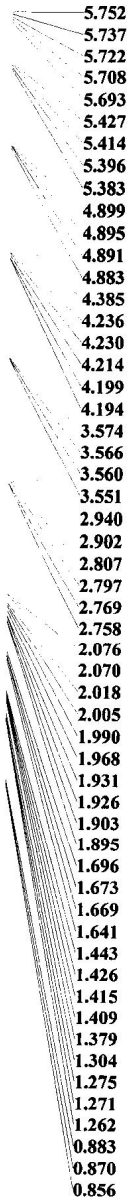


¹³C NMR spectrum of **3d** (100 MHz, CDCl₃)

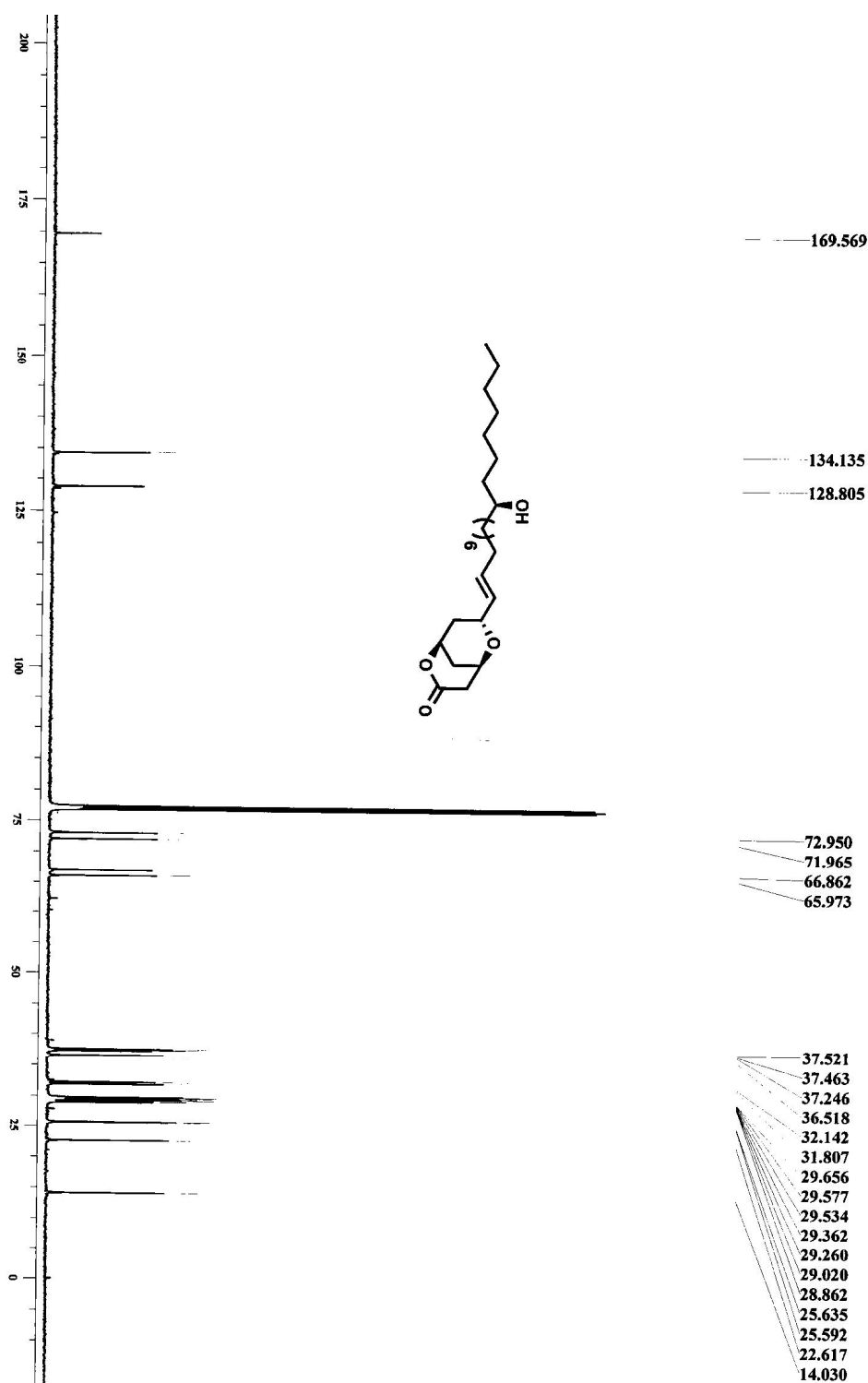
¹H NMR spectrum of **1c** (500 MHz, CDCl₃)



¹³C NMR spectrum of **1c** (125 MHz, CDCl₃)



¹H NMR spectrum of **1d** (500 MHz, CDCl₃)



¹³C NMR spectrum of **1d** (125 MHz, CDCl₃)