

Supporting Information

to accompany

Remote Asymmetric Induction with Vinylketene Silyl *N,O*-acetal

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Experimental Section

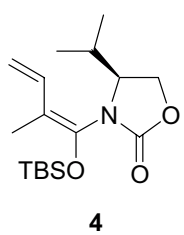
General.

IR spectra were recorded on a JASCO FT/IR-410. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LD400 or JNM-LD500 spectrometer in CDCl_3 or C_6D_6 as a solvent. Tetramethylsilane (TMS) served as internal standard (δ) for ^1H NMR. CDCl_3 (δ 7.0) or C_6D_6 (δ 28.0) were used as internal references for ^{13}C NMR. HPLC was carried out using a GL Science PU614, UV620, CO630N-10 and DG660-2. Optical rotations were recorded on a JASCO P-1030. Flash column chromatography was performed on PSQ 100B (Fuji Silysia Co., Ltd., Japan). Analytical thin-layer chromatography was performed on Silica gel 60 F₂₅₄ plates (Merck). Preparative thin layer chromatography was performed on Wakogel B-5F. Mass Spectra were recorded on a Applied Biosystems mass spectrometer (API QSTAR pulsar i) under conditions as high resolution, using poly(ethylene glycol) as internal standard. Melting points were recorded on Yanaco MP-3S. All air and water sensitive reactions were performed in flame-dried glassware.

General Procedure A for preparation of vinylketene silyl *N,O*-acetal.

To a solution of imide (14.2 mmol) in THF (150 ml) was added NaHMDS (21.1 ml of a 1.01 M solution in THF, 21.3 mmol) at $^{-78}$ °C. After the mixture had been stirred for 90 min at $^{-78}$ °C, a solution of TBSCl (6.42 g, 42.6 mmol) in THF (30 ml) was added at $^{-78}$ °C. Stirring was continued for 30 min at $^{-78}$ °C, then the reaction was quenched with a saturated aq. NH_4Cl , and extracted with ethyl acetate. The extract was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 5 / 1) to give the vinylketene silyl *N,O*-acetal.

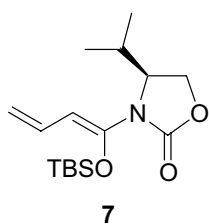
(4*S*)-3-[(*E*)-1-(*tert*-Butyldimethylsilyloxy)-2-methylbuta-1,3-dienyl]-4-isopropylloxazolidin-2-one



The title compound was prepared according to the General Procedure A and isolated by column chromatography as a colorless solid (85%): m.p. 48.7 °C, IR (neat) 3509, 2957, 2859, 1763, 1648, 1472, 1255, 784 cm^{-1} ; ^1H NMR (400 MHz) δ 0.14-0.18 (3H, br s), 0.20 (3H, s), 0.93 (6H, d, $J=6.8\text{Hz}$), 0.99 (9H, s), 1.80 (3H, s), 1.95 (1H, sept d, $J=6.8, 2.2\text{Hz}$), 3.97-4.07 (1H, m), 4.12 (1H, dd, $J=8.3, 8.8\text{Hz}$), 4.32 (1H, t, $J=8.8\text{Hz}$), 5.04 (1H, d, $J=10.7\text{Hz}$), 5.15 (1H, d, $J=17.1\text{Hz}$), 6.54 (1H, dd, $J=10.7, 17.1\text{Hz}$); ^{13}C NMR (100 MHz) δ 4.7, 7.2, 11.7,

16.4, 18.2, 18.4, 25.8, 29.5, 59.5, 64.6, 112.5, 115.3, 134.0, 136.7, 155.9; $[\alpha]_{\text{D}}^{25} = -65.7$ (c 0.87, CHCl_3); HRMS calcd for $\text{C}_{17}\text{H}_{31}\text{NO}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$). 348.1970. found 348.1966.

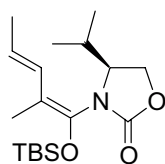
(4*S*)-3-[(*Z*)-1-(*tert*-Butyldimethylsilyloxy) buta-1,3-dienyl]-4-isopropylloxazolidin-2-one



The title compound was prepared according to the General Procedure A and isolated by column chromatography as a colorless oil (63%): IR (neat) 3506, 2959, 2932, 2896, 2860, 1761, 1657, 1472, 1256, 784 cm^{-1} ; ^1H NMR (400 MHz) δ 0.17 (3H, s), 0.21 (3H, s), 0.90 (6H, d, $J=7.1\text{Hz}$), 0.99 (9H, s), 2.07 (1H, sept d, $J=7.1, 3.7\text{Hz}$), 4.00 (1H, ddd, $J=3.7, 4.9, 8.8\text{Hz}$), 4.11 (1H, dd, $J=4.9, 9.0\text{Hz}$), 4.25 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.98 (1H, dd, $J=1.5, 10.7\text{Hz}$), 5.16 (1H, dd, $J=1.5, 17.3\text{Hz}$), 5.65 (1H, d, $J=10.5\text{Hz}$), 6.49 (1H, ddd,

$J=10.5, 10.7, 17.3\text{Hz}$); $^{13}\text{C NMR}$ (100 MHz) δ 4.7, 7.6, 15.1, 17.6, 18.1, 25.5, 29.0, 59.1, 63.1, 108.8, 114.9, 130.4, 139.1, 155.1; $[\alpha]_{\text{D}}^{25} = +4.5$ (c 1.17, CHCl_3); HRMS calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_3$ ($[\text{M}]^+$). 311.1917. found 311.1921.

(4*S*)-3-[(1*E*,3*E*)-1-(*tert*-Butyldimethylsilyloxy)-2-methylpenta-1,3-dienyl]-4-isopropylloxazolidin-2-one **10**.



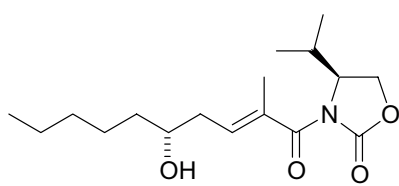
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The title compound was prepared according to the General Procedure A and isolated by column chromatography as a colorless oil (90%).: IR (neat) 3503, 2958, 2931, 2858, 1762, 1652, 1631, 1472, 1286, 784 cm^{-1} ; $^1\text{H NMR}$ (400 MHz) δ 0.14 (3H, s), 0.19 (3H, s), 0.93 (6H, d, $J=7.1\text{Hz}$), 0.98 (9H, s), 1.75-1.82 (3H, m), 1.78 (3H, d, $J=6.6\text{Hz}$), 1.88-2.04 (1H, m), 3.95-4.04 (1H, m), 4.13 (1H, dd, $J=8.3, 8.6\text{Hz}$), 4.32 (1H, dd, $J=8.6, 8.8\text{Hz}$), 5.63 (1H, qd, $J=6.6, 15.4\text{Hz}$), 6.21 (1H, d, $J=15.4\text{Hz}$); $^{13}\text{C NMR}$ (100 MHz) δ 4.9, 7.3, 12.3, 16.3, 18.0, 18.3, 18.8, 25.6, 29.3, 59.4, 64.4, 115.0, 124.4, 128.1, 134.6, 155.9; $[\alpha]_{\text{D}}^{25} = +0.4$ (c 0.84, CHCl_3); HRMS calcd for $\text{C}_{18}\text{H}_{33}\text{NO}_3$ Na ($[\text{M}+\text{Na}]^+$). 362.2127. found 362.2129.

General Procedure B for Vinylogous Mukaiyama aldol reaction of with vinylketene silyl *N,O*-acetal **4** with aldehyde.

To a solution of aldehyde (2.46 mmol) in CH_2Cl_2 (6.0 ml) was added TiCl_4 (1.23 ml of a 1.0 M solution in CH_2Cl_2 , 1.23 mmol) and a solution of **4** (400 mg, 1.23 mmol) in CH_2Cl_2 (6.0 ml) at -78°C . After stirring for 6 hr at -78°C , the reaction was quenched with pyridine. After a saturated aq. Rochelle Salt and a saturated aq. NaHCO_3 were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved, and extracted with ethyl acetate. The extract was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 5 / 1) to give the aldol adducts.

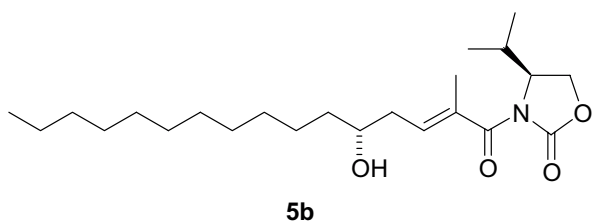
(4*S*)-3-[(2*E*,5*R*)-5-Hydroxy-2-methyldec-2-enoyl]-4-isopropylloxazolidin-2-one **5a**.



5a

The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (97 %).: IR (neat) 3524, 2961, 2930, 2860, 1779, 1685, 1466, 1296, 1209, 1119, 755 cm^{-1} ; $^1\text{H NMR}$ (400 MHz) δ 0.89 (3H, t, $J=6.6\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 0.94 (3H, d, $J=6.8\text{Hz}$), 1.24-1.56 (8H, m), 1.95 (3H, d, $J=1.5\text{Hz}$), 2.23-2.44 (3H, m), 2.85 (1H, d, $J=3.4\text{Hz}$), 3.66-3.77 (1H, m), 4.19 (1H, dd, $J=5.6, 9.0\text{Hz}$), 4.34 (1H, t, $J=9.0\text{Hz}$), 4.56 (1H, ddd, $J=4.4, 5.6, 9.0\text{Hz}$), 6.03 (1H, qt, $J=1.5, 7.8\text{Hz}$); $^{13}\text{C NMR}$ (100 MHz) δ 3.7, 14.0, 15.1, 17.8, 22.6, 25.6, 28.4, 31.8, 36.8, 36.9, 58.1, 63.4, 70.6, 133.0, 135.3, 154.6, 171.6; $[\alpha]_{\text{D}}^{24} = +3.3$ (c 0.97, CHCl_3); HRMS calcd for $\text{C}_{17}\text{H}_{29}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 334.1994. found 334.1990. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 0.3 ml/min, 151 MPa, 254 nm), major diastereomer = 64.5 min, minor diastereomer = 73.4 min; d.s. = 42 : 1.

(4*S*)-3-[(2*E*,5*R*)-5-Hydroxy-2-methylhexadec-2-enoyl]-4-isopropylloxazolidin-2-one **5b**.

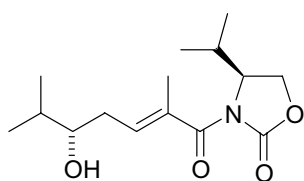


5b

The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (92%); IR (neat) 3526, 2925, 2854, 1780, 1685, 1466, 1297, 1210, 1119, 756 cm^{-1} ; ^1H NMR (400 MHz) δ 0.88 (3H, t, $J=6.6\text{Hz}$), 0.93 (3H, d, $J=6.8\text{Hz}$), 0.94 (3H, d, $J=6.6\text{Hz}$), 1.24-1.35 (18H, m), 1.40-1.50 (2H,

m), 1.95 (3H, d, $J=1.5\text{Hz}$), 2.26-2.42 (3H, m), 2.85 (1H, br s), 3.67-3.76 (1H, m), 4.19 (1H, dd, $J=5.4, 9.0\text{Hz}$), 4.34 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.54-4.59 (1H, m), 6.03 (1H, qt, $J=1.5, 8.0\text{Hz}$); ^{13}C NMR (100 MHz, C_6D_6) δ 3.9, 14.3, 14.9, 17.4, 23.1, 26.4, 28.5, 29.8, 30.1 (3 carbons), 30.2 (2 carbons), 32.2, 37.3, 37.5, 57.9, 63.0, 70.6, 133.2, 135.7, 154.3, 171.3; $[\alpha]_{\text{D}}^{23} = +11.9$ (c 1.02, CHCl_3); HRMS calcd for $\text{C}_{23}\text{H}_{41}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 418.2936. found 418.2933. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 0.3 ml/min, 162 MPa, 254 nm), major diastereomer = 63.6 min, minor diastereomer = 73.1 min; d.s. = 94 : 1.

(4*S*)-3-[(2*E*,5*S*)-5-Hydroxy-2,6-dimethylhept-2-enoyl]-4-isopropylloxazolidin-2-one **5c**.

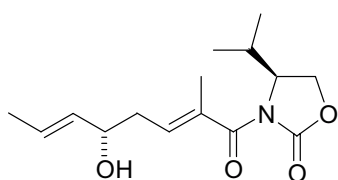


5c

The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (78%); IR (neat) 3524, 2963, 2931, 2876, 1778, 1685, 1468, 1297, 1210, 1119, 754 cm^{-1} ; ^1H NMR (400 MHz) δ 0.93 (3H, t, $J=6.6\text{Hz}$), 0.95 (3H, d, $J=7.1\text{Hz}$), 0.96 (3H, d, $J=6.8\text{Hz}$), 1.00 (3H, d, $J=6.8\text{Hz}$), 1.74 (1H, qqd, $J=6.6, 6.8, 7.1\text{Hz}$), 1.95 (3H, d, $J=1.4\text{Hz}$), 2.26-2.43 (3H, m), 2.88 (1H, br s), 3.41-3.51 (1H, m), 4.19 (1H, dd, $J=5.4, 9.0\text{Hz}$), 4.34 (1H, t,

$J=9.0\text{Hz}$), 4.50-4.59 (1H, m), 6.04 (1H, qt, $J=1.4, 7.6\text{Hz}$); ^{13}C NMR (100 MHz) δ 3.7, 15.1, 17.8, 18.3, 18.8, 28.4, 33.5, 33.7, 58.1, 63.4, 75.4, 132.9, 135.8, 154.3, 171.6; $[\alpha]_{\text{D}}^{24} = +87.4$ (c 1.01, CHCl_3); HRMS calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 306.1681. found 306.1677. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 1.0 ml/min, 17 MPa, 254 nm), major diastereomer = 21.6 min, minor diastereomer = 25.1 min; d.s. = 40 : 1.

(4*S*)-3-[(2*E*,5*S*,6*E*)-5-Hydroxy-2-methylocta-2,6-dienoyl]-4-isopropylloxazolidin-2-one **5d**.

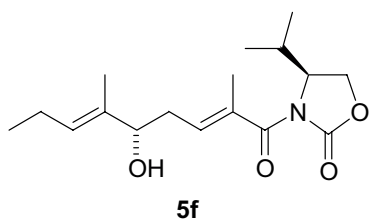


5d

The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (54% (conversion yield 87%)); IR (neat) 3423, 2965, 1781, 1682, 1298, 1210, 1118, 774 cm^{-1} ; ^1H NMR (400 MHz) δ 0.93 (6H, t, $J=6.8\text{Hz}$), 1.70 (3H, dd, $J=1.2, 6.3\text{Hz}$), 1.95 (3H, d, $J=1.4\text{Hz}$), 2.32-2.54 (3H, m), 2.70 (1H, d, $J=3.9\text{Hz}$), 4.16-4.26 (1H, m) 4.20 (1H, dd, $J=5.4, 9.0\text{Hz}$), 4.34 (1H, t, $J=9.0\text{Hz}$), 4.52-4.58 (1H, m), 5.55 (1H, qdd, $J=6.3,$

1.7, 15.3Hz), 5.72 (1H, qd, $J=1.2, 15.3\text{Hz}$), 6.02 (1H, qdd, $J=1.4, 6.6, 9.3\text{Hz}$); ^{13}C NMR (100 MHz) δ 3.9, 15.1, 17.7, 17.9, 28.4, 36.8, 58.2, 63.5, 71.3, 126.8, 132.8, 133.4, 134.3, 154.1, 171.6; $[\alpha]_{\text{D}}^{25} = +21.2$ (c 1.01, CHCl_3); HRMS calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 304.1514. found 304.1524. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 0.3 ml/min, 161 MPa, 254 nm), major diastereomer = 170.6 min, minor diastereomer = 190.3 min; d.s. = 20 : 1.

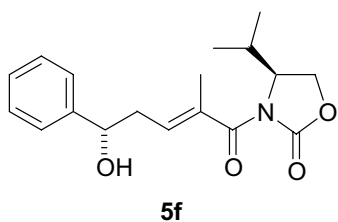
(4*S*)-3-[(2*E*,5*S*,6*E*)-5-Hydroxy-2,6-dimethylnona-2,6-dienoyl]-4-isopropylloxazolidin-2-one **5e**.



The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (55% (conversion yield 65%)); IR (neat) 3511, 2965, 2931, 2874, 1772, 1686, 1301, 1211, 1119, 755 cm^{-1} ; ^1H NMR (400 MHz) δ 0.91 (3H, t, $J=6.8\text{Hz}$), 0.93 (3H, t, $J=6.8\text{Hz}$), 0.96 (3H, t, $J=7.6\text{Hz}$), 1.65 (3H, s), 1.95 (3H, d, $J=1.4\text{Hz}$), 2.04 (2H, qd, $J=7.6, 7.1\text{Hz}$), 2.30-2.41 (2H, m), 2.54 (1H, m), 2.66 (1H, d, $J=4.6\text{Hz}$), 4.13

(1H, dd, $J=4.6, 8.5\text{Hz}$), 4.19 (1H, dd, $J=5.4, 9.0\text{Hz}$), 4.33 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.51-4.59 (1H, m), 5.45 (1H, t, $J=7.1\text{Hz}$), 6.00 (1H, qdd, $J=1.4, 6.3, 8.8\text{Hz}$); ^{13}C NMR (100 MHz) δ 1.9, 13.8, 14.1, 15.0, 17.8, 20.8, 28.4, 34.9, 58.1, 63.4, 75.6, 128.1, 133.0, 134.9, 135.3, 154.0, 171.6; $[\alpha]_{\text{D}}^{25} = +4.3$ (c 0.34, CHCl_3); HRMS calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 332.1837. found 332.1838. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 0.3 ml/min, 161 hMPa, 254 nm), major diastereomer = 170.6 min, minor diastereomer = 190.3 min; d.s. = 20 : 1.

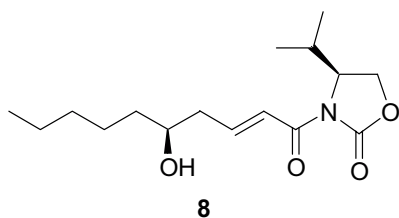
(4*S*)-3-[(2*E*,5*S*)-5-Hydroxy-2-methyl-5-phenylpent-2-enoyl]-4-isopropylloxazolidin-2-one **5f**.



The title compound was prepared according to the General Procedure B and isolated by column chromatography as a colorless oil (94%); IR (neat) 3505, 2964, 2926, 2875, 1778, 1684, 1298, 1211, 1119, 756 cm^{-1} ; ^1H NMR (400 MHz) δ 0.93 (3H, d, $J=6.8\text{Hz}$), 0.94 (3H, d, $J=6.8\text{Hz}$), 1.98 (3H, d, $J=1.4\text{Hz}$), 2.37 (1H, sept d, $J=6.8, 4.4\text{Hz}$), 2.54-2.68 (2H, m), 3.27 (1H, br s), 4.21 (1H, dd, $J=5.1, 9.0\text{Hz}$), 4.35 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.52-4.59 (1H, m), 4.85 (1H, dd, $J=3.7, 8.8\text{Hz}$),

6.04 (1H, qdd, $J=1.4, 6.3, 9.5\text{Hz}$), 7.24-7.43 (5H, m); ^{13}C NMR (100 MHz) δ 3.8, 15.1, 17.8, 28.4, 38.9, 58.3, 63.5, 72.6, 125.6, 127.4, 128.4, 133.2, 133.9, 143.5, 154.3, 171.4; $[\alpha]_{\text{D}}^{23} = +5.7$ (c 1.08, CHCl_3); HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 340.1548. found 340.1541. Diastereoselectivity was determined by HPLC analysis with Mightysil Si-60 (hexane / isopropanol = 60 / 1, 1.0 ml/min, 17 MPa, 254 nm), major diastereomer = 32.7min, minor diastereomer = 35.0 min; d.s. = 86 : 1.

(4*S*)-3-[(2*E*,5*S*)-5-Hydroxydec-2-enoyl]-4-isopropylloxazolidin-2-one **8**.



To a solution of hexanal 0.15 ml (1.28 mmol) in CH_2Cl_2 (3.0 ml) was added TiCl_4 (0.64 ml of a 1.0 M solution in CH_2Cl_2 , 0.64 mmol) and a solution of **7** (200 mg, 0.64 mmol) in CH_2Cl_2 (3.0 ml) at -78°C . After stirring for 6.0 hr at -78°C , the reaction was quenched with pyridine. After a saturated aq. Rochelle Salt and saturated aq. NaHCO_3 were added, the mixture was warmed to room temperature and stirred vigorously until the resulting

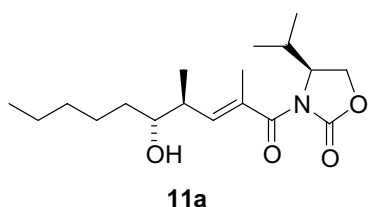
white slurry was completely dissolved, and extracted with ethyl acetate. The extract was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 5 / 1) to give 73 mg (38%) of **8** as a colorless oil. IR (neat) 3486, 3093, 2959, 2930, 1779, 1685, 1634, 1206, 1121, 755 cm^{-1} ; ^1H NMR (400 MHz) δ 0.87 (3H, t, $J=6.8\text{Hz}$), 0.89 (3H, d, $J=6.8\text{Hz}$), 0.91 (3H, d, $J=6.8\text{Hz}$), 1.22-1.36 (6H, m), 1.40-1.54 (3H, m), 2.34-2.52 (3H, m), 3.73-3.83 (1H, m), 4.11 (1H, dd, $J=3.6, 8.4\text{Hz}$), 4.26 (1H, dd, $J=8.4, 9.2\text{Hz}$), 4.50-4.54 (1H,

m), 7.09-7.18 (1H, m), 7.31 (1H, ddd, $J=1.2, 15.2\text{Hz}$); ^{13}C NMR (100 MHz) δ 4.0, 14.7, 18.0, 22.5, 25.2, 28.5, 31.7, 37.2, 40.5, 58.5, 63.4, 70.7, 122.8, 147.2, 154.0, 164.7; HRMS calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 320.1837. found 320.1834.

General Procedure C for Vinylogous Mukaiyama aldol reaction of with vinylketene silyl *N,O*-acetal **10** with aldehyde.

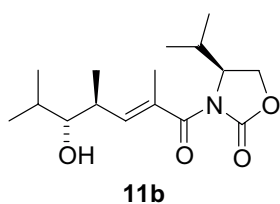
To a solution of aldehyde (1.17 mmol) in CH_2Cl_2 (3.0 ml) was added TiCl_4 (0.59 ml of a 1.0 M solution in CH_2Cl_2 , 0.59 mmol) and a solution of **10** (200 mg, 0.59 mmol) in CH_2Cl_2 (3.0 ml) at -78°C . After stirring for 19 hr, the reaction was quenched with pyridine. After a saturated aq. Rochelle Salt and a saturated aq. NaHCO_3 were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved, and extracted with ethyl acetate. The extract was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 5 / 1) to give the aldol adducts.

(4*S*)-3-[(2*E*,4*S*,5*R*)-5-Hydroxy-2,4-dimethyldec-2-enoyl]-4-isopropylloxazolidin-2-one **11a**.



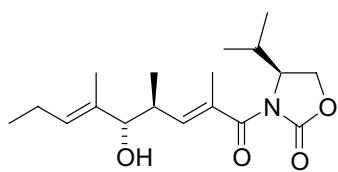
The title compound was prepared according to the General Procedure C, the reaction mixture was stirred at -78°C , and isolated by column chromatography as a colorless oil (92%); IR (neat) 3521, 2961, 2930, 2872, 1771, 1685, 1300, 1211, 755 cm^{-1} ; ^1H NMR (500 MHz) δ 0.89 (3H, t, $J=6.8\text{Hz}$), 0.93 (3H, d, $J=6.1\text{Hz}$), 0.98 (3H, d, $J=6.8\text{Hz}$), 1.22-1.46 (8H, m), 1.61 (3H, d, $J=7.4\text{Hz}$), 1.94 (3H, s), 2.34 (1H, qd, $J=6.8, 11.6\text{Hz}$), 2.56 (1H, m), 3.02-3.17 (1H, br s), 3.34 (1H, m), 4.19 (1H, dd, $J=5.8, 8.9\text{Hz}$), 4.34 (1H, dd, $J=8.9, 9.2\text{Hz}$), 4.56-4.62 (1H, m), 5.82 (1H, qd, $J=1.3, 10.4\text{Hz}$); ^{13}C NMR (100 MHz) δ 3.9, 14.1, 15.2, 16.1, 17.8, 22.7, 25.3, 28.4, 32.0, 33.8, 40.1, 58.1, 63.4, 75.3, 131.0, 142.4, 154.5, 171.6; $[\alpha]_{\text{D}}^{24} = +21.6$ (c 0.86, CHCl_3); HRMS calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 348.2150. found 348.2135.

(4*S*)-3-[(2*E*,4*S*,5*R*)-5-Hydroxy-2,4,6-trimethylhept-2-enoyl]-4-isopropylloxazolidin-2-one **11b**.



The title compound was prepared according to the General Procedure C, the reaction mixture was stirred at -78°C , and isolated by column chromatography as a colorless oil (99%); IR (neat) 3528, 2965, 2933, 2875, 1772, 1686, 1300, 1210, 1119, 755 cm^{-1} ; ^1H NMR (400 MHz) 0.90-0.97 (12H, m), 1.04 (3H, t, $J=6.8\text{Hz}$), 1.82-1.91 (1H, m), 1.95 (3H, d, $J=1.5\text{Hz}$), 2.35 (1H, sept d, $J=6.8, 4.4\text{Hz}$), 2.64-2.76 (1H, m), 2.96 (1H, d, $J=2.7\text{Hz}$), 3.18 (1H, td, $J=2.7, 8.3\text{Hz}$), 4.19 (1H, dd, $J=5.9, 9.0\text{Hz}$), 4.34 (1H, t, $J=9.0\text{Hz}$), 4.54-4.59 (1H, m), 5.82 (1H, qd, $J=1.5, 10.4\text{Hz}$); ^{13}C NMR (100 MHz) δ 3.9, 14.7, 15.2, 15.8, 17.8, 120.6, 28.4, 29.2, 37.4, 58.1, 63.4, 79.1, 131.0, 142.4, 154.5, 171.7; $[\alpha]_{\text{D}}^{23} = +6.7$ (c 2.00, CHCl_3); HRMS calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$). 320.1837. found 320.1823.

(4*S*)-3-[(2*E*,4*S*,5*S*,6*E*)-5-Hydroxy-2,4,6-trimethylnona-2,6-dienyl]-4-isopropylloxazolidin-2-one **11c**.

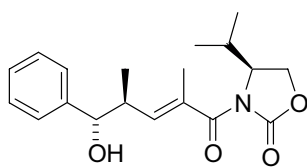


11c

The title compound was prepared according to the General Procedure C, the reaction mixture was stirred at 40 °C, and isolated by column chromatography as a colorless oil (67% (conversion yield 81%)); IR (neat) 3510, 2965, 2931, 2874, 1772, 1686, 1301, 1211, 1119, 756 cm⁻¹; ¹H NMR (400 MHz) δ 0.83 (3H, d, *J*=6.8Hz), 0.90-1.00 (9H, m), 1.67 (3H, s), 1.98 (3H, d, *J*=1.6Hz), 2.07 (2H, quint, *J*=6.8Hz), 2.35 (1H, sept d, *J*=6.8, 4.4Hz), 2.69-2.81 (1H, m), 3.36

(1H, br s), 3.65 (1H, d, *J*=9.2Hz), 4.20 (1H, dd, *J*=5.6, 9.2Hz), 4.35 (1H, t, *J*=9.2Hz), 4.55-4.62 (1H, m), 5.39 (1H, t, *J*=6.8Hz), 5.79 (1H, qd, *J*=1.6, 10.4Hz); ¹³C NMR (100 MHz) δ 0.5, 13.9, 13.9, 15.2, 16.2, 17.8, 20.8, 28.4, 29.7, 37.8, 58.0, 63.4, 82.2, 131.4, 131.7, 133.3, 141.9, 154.4, 171.5; [α]_D²⁵ = -8.30 (*c* 1.33, CHCl₃); HRMS calcd for C₁₈H₂₉NO₄Na ([M+Na]⁺). 346.1994. found 346.1992.

(4*S*)-3-[(2*E*,4*S*,5*S*)-5-Hydroxy-2,4-dimethyl-5-phenylpent-2-enyl]-4-isopropylloxazolidin-2-one **11d**.



11d

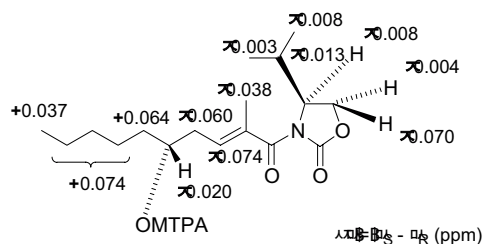
The title compound was prepared according to the General Procedure C, the reaction mixture was stirred at 30 °C, and isolated by column chromatography as a colorless oil (91%); IR (neat) 3503, 2966, 2931, 2875, 1771, 1686, 1301, 1211, 757 cm⁻¹; ¹H NMR (400 MHz) δ 0.79 (3H, d, *J*=6.8Hz), 0.95 (6H, d, *J*=6.8Hz), 2.02 (3H, d, *J*=1.5Hz), 2.37 (1H, sept d, *J*=6.8, 4.4Hz), 2.80-2.90 (1H, m), 3.74 (1H, br s) 4.22 (1H, dd, *J*=5.9, 9.0Hz), 4.32 (1H, t, *J*=9.0Hz), 4.37 (1H, d, *J*=9.0Hz), 4.57-4.65

(1H, m), 5.89 (1H, qd, *J*=1.5, 10.2Hz), 7.27-7.41 (5H, m); ¹³C NMR (100 MHz) δ 4.1, 15.2, 16.2, 17.9, 28.5, 42.4, 58.1, 63.5, 78.7, 127.2, 127.7, 128.3, 132.2, 141.4, 141.8, 154.6, 171.5; [α]_D²⁵ = -5.4 (*c* 0.87, CHCl₃); HRMS calcd for C₁₉H₂₅NO₄Na ([M+Na]⁺). 354.1681. found 354.1683.

Stereochemical Proofs

Aldol adduct **5a** was transformed to 1,3-diacetoxyoctane by ozonolysis, reduction and acetylation, and the sign of its optical rotation compared to the literature value ([α]_D²⁴ = +45.2 (*c* 1.7, CHCl₃)).¹ The absolute configuration of aldol adducts **5a-e** was determined by the modified Mosher's method.

Mosher Ester Analysis for **5a**.



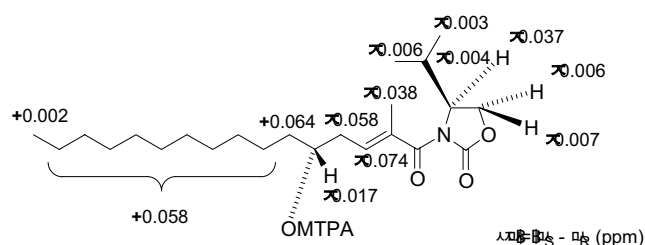
(S)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.87 (3H, t, $J=7.2\text{Hz}$), 0.87 (3H, d, $J=6.8\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 1.20-1.43 (6H, m), 1.60-1.75 (2H, m), 1.88 (3H, d, $J=1.5\text{Hz}$), 2.35 (1H, sept d, $J=6.8, 4.2\text{Hz}$), 2.40-2.57 (2H, m), 3.54 (3H, s), 4.18 (1H, dd, $J=5.1, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.46-4.51 (1H, m), 5.17 (1H, tt, $J=5.6, 6.8\text{Hz}$), 5.91 (1H, qt, $J=1.5, 4.9\text{Hz}$), 7.37-7.43 (3H, m), 7.47-7.58 (2H, m).

(R)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.83 (3H, t, $J=6.8\text{Hz}$), 0.88 (3H, d, $J=7.1\text{Hz}$), 0.92 (3H, d, $J=7.1\text{Hz}$), 1.10-1.30 (6H, m), 1.57-1.68 (2H, m), 1.91 (3H, d, $J=1.5\text{Hz}$), 2.36 (1H, sept d, $J=6.8, 4.2\text{Hz}$), 2.47-2.64 (2H, m), 3.55 (3H, s), 4.18 (1H, dd, $J=5.1, 9.0\text{Hz}$), 4.32 (1H, t, $J=9.0\text{Hz}$), 4.46-4.52 (1H, m), 5.19 (1H, tt, $J=5.6, 7.1\text{Hz}$), 5.98 (1H, qt, $J=1.5, 7.1\text{Hz}$), 7.37-7.43 (3H, m), 7.50-7.53 (2H, m).

Mosher Ester Analysis for 5b.



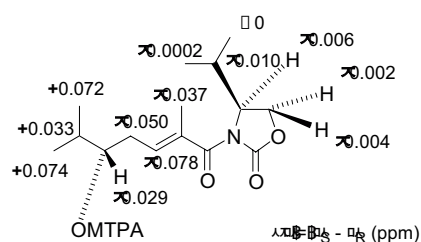
(S)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.87 (3H, d, $J=6.8\text{Hz}$), 0.90 (3H, t, $J=6.8\text{Hz}$), 0.91 (3H, d, $J=6.8\text{Hz}$), 1.22-1.36 (18H, m), 1.55-1.74 (2H, m), 1.87 (3H, d, $J=1.5\text{Hz}$), 2.36 (1H, sept d, $J=6.8, 2.8\text{Hz}$), 2.40-2.57 (2H, m), 3.54 (3H, s), 4.17 (1H, dd, $J=5.1, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.45-4.51 (1H, m), 5.17 (1H, tt, $J=5.9, 7.1\text{Hz}$), 5.91 (1H, qt, $J=1.5, 7.6\text{Hz}$), 7.37-7.41 (3H, m), 7.50-7.54 (2H, m).

(R)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.88 (3H, d, $J=6.8\text{Hz}$), 0.90 (3H, t, $J=6.8\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 1.14-1.37 (18H, m), 1.55-1.72 (2H, m), 1.91 (3H, d, $J=1.2\text{Hz}$), 2.36 (1H, sept d, $J=6.8, 4.4\text{Hz}$), 2.47-2.61 (2H, m), 3.54 (3H, s), 4.18 (1H, dd, $J=5.1, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.46-4.52 (1H, m), 5.19 (1H, tt, $J=6.1, 6.4\text{Hz}$), 5.98 (1H, qt, $J=1.2, 7.3\text{Hz}$), 7.36-7.41 (3H, m), 7.50-7.55 (2H, m).

Mosher Ester Analysis for 5c.



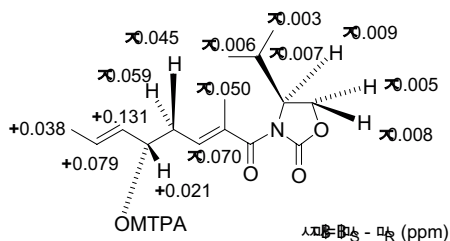
(S)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.87 (3H, d, $J=7.1\text{Hz}$), 0.92 (3H, d, $J=7.1\text{Hz}$), 0.93 (3H, d, $J=6.6\text{Hz}$), 0.95 (3H, d, $J=6.6\text{Hz}$), 1.88 (3H, d, $J=1.0\text{Hz}$), 2.00 (1H, sept d, $J=6.6, 5.3\text{Hz}$), 2.35 (1H, sept d, $J=7.1, 4.4\text{Hz}$), 2.43-2.59 (2H, m), 3.52 (3H, s), 4.18 (1H, dd, $J=5.2, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.45-4.51 (1H, m), 5.03 (1H, td, $J=5.3, 5.8\text{Hz}$), 5.90 (1H, qt, $J=1.0, 7.1\text{Hz}$), 7.37-7.42 (3H, m), 7.50-7.54 (2H, m).

(R)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.86 (3H, d, $J=6.8\text{Hz}$), 0.87 (6H, d, $J=6.8\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 1.92 (3H, d, $J=1.2\text{Hz}$), 1.97 (1H, sept d, $J=6.8, 5.4\text{Hz}$), 2.36 (1H, sept d, $J=6.8, 4.2\text{Hz}$), 2.47-2.63 (2H, m), 3.54 (3H, s), 4.18 (1H, dd, $J=4.9, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.46-4.53 (1H, m), 5.06 (1H, td, $J=5.4, 6.6\text{Hz}$), 5.98 (1H, qt, $J=1.2, 7.1\text{Hz}$), 7.37-7.42 (3H, m), 7.51-7.55 (2H, m).

Mosher Ester Analysis for 5d.



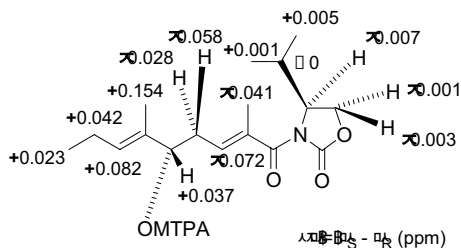
(S)-~~B~~MTPA ester

^1H NMR (400 MHz) δ 0.86 (3H, d, $J=6.8\text{Hz}$), 0.91 (3H, d, $J=6.8\text{Hz}$), 1.72 (3H, dd, $J=1.7, 6.6\text{Hz}$), 1.85 (3H, d, $J=1.4\text{Hz}$), 2.34 (1H, sept d, $J=7.1, 4.4\text{Hz}$), 2.44-2.54 (1H, m), 2.52-2.61 (1H, m), 3.53 (3H, s), 4.17 (1H, dd, $J=5.2, 8.8\text{Hz}$), 4.31 (1H, t, $J=8.8\text{Hz}$), 4.47-4.51 (1H, m), 5.55 (1H, qdd, $J=1.7, 8.0, 13.9\text{Hz}$), 5.50-5.57 (1H, m), 5.89 (1H, qd, $J=6.6, 14.4\text{Hz}$), 5.90 (1H, qt, $J=1.4, 7.3\text{Hz}$), 7.35-7.43 (3H, m), 7.47-7.53 (2H, m).

(R)-~~B~~MTPA ester

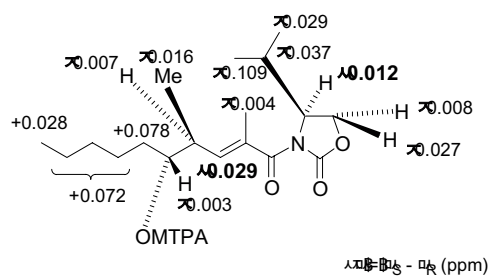
^1H NMR (400 MHz) δ 0.87 (3H, d, $J=6.8\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 1.68 (3H, dd, $J=1.7, 6.6\text{Hz}$), 1.90 (3H, d, $J=1.5\text{Hz}$), 2.35 (1H, sept d, $J=6.8, 4.2\text{Hz}$), 2.54 (1H, ddd, $J=7.1, 7.3, 15.4\text{Hz}$), 2.64 (1H, ddd, $J=6.6, 7.3, 15.4\text{Hz}$), 3.53 (3H, s), 4.18 (1H, dd, $J=5.1, 9.0\text{Hz}$), 4.31 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.47-4.53 (1H, m), 5.42 (1H, qdd, $J=1.7, 6.8, 15.1\text{Hz}$), 5.52 (1H, ddd, $J=6.6, 6.8, 7.1\text{Hz}$), 5.82 (1H, qd, $J=6.6, 15.1\text{Hz}$), 5.97 (1H, qt, $J=1.5, 7.3\text{Hz}$), 7.36-7.43 (3H, m), 7.46-7.52 (2H, m).

Mosher Ester Analysis for 5e.



Aldol adduct **11a** was transformed to methyl ester by three-steps sequence ((i) O₃ then Me₂S; (ii) NaClO₂, NaH₂PO₄; (iii) TMSCHN₂, MeOH), and the sign of its optical rotation compared to the literature value ($[\alpha]_D^{24} = -3.7$ (*c* 2.03, CHCl₃).³ The absolute configuration of aldol adduct **11a** was checked by the modified Mosher's method.

Mosher Ester Analysis for **11a**.



(*S*)-OMTPA ester

¹H NMR (400 MHz) δ 0.85 (3H, t, *J*=6.8Hz), 0.86 (3H, d, *J*=6.8Hz), 0.90 (3H, d, *J*=7.1Hz), 0.93 (3H, d, *J*=6.8Hz), 1.24-1.34 (6H, m), 1.59-1.79 (2H, m), 1.94 (3H, d, *J*=1.4Hz), 2.33 (1H, sept d, *J*=6.8, 4.4Hz), 2.83-2.92 (1H, m), 3.56 (3H, s), 4.15 (1H, dd, *J*=5.4, 9.0Hz), 4.30 (1H, dd, *J*=8.8, 9.0Hz), 4.46-4.52 (1H, m), 5.06-5.12 (1H, m), 5.87 (1H, qd, *J*=1.4, 10.0Hz), 7.37-7.42 (3H, m), 7.52-7.57 (2H, m).

(*R*)-OMTPA ester

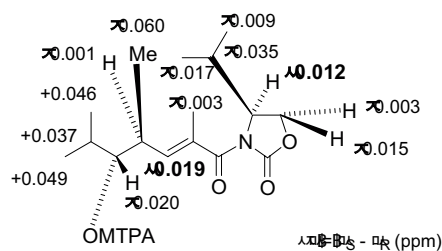
¹H NMR (400 MHz) δ 0.84 (3H, t, *J*=6.8Hz), 0.88 (3H, d, *J*=6.8Hz), 0.92 (3H, d, *J*=7.1Hz), 1.03 (3H, d, *J*=6.8Hz), 1.13-1.30 (6H, m), 1.50-1.70 (2H, m), 1.94 (3H, d, *J*=1.5Hz), 2.37 (1H, sept d, *J*=6.8, 4.4Hz), 2.83-2.96 (1H, m), 3.53 (3H, s), 4.17 (1H, dd, *J*=5.1, 9.0Hz), 4.31 (1H, t, *J*=9.0Hz), 4.46-4.53 (1H, m), 5.06-5.13 (1H, m), 5.84 (1H, qd, *J*=1.5, 9.8Hz), 7.36-7.43 (3H, m), 7.52-7.57 (2H, m).

Aldol adduct **11b** was transformed to acetal by ozonolysis and literature procedure, and the ¹H NMR spectrum was identical to that reported.⁴ The absolute configuration of aldol adduct **11b** was determined by the modified Mosher's method.

(3) Watabu, H.; Ohkubo, M.; Matsubara, H.; Sakai, T.; Tsuboi, S.; Utaka, M. *Chem. Lett.* **1989**, *12*, 2183.

(4) Harada, T.; Egusa, T.; Igarashi, Y.; Kinugasa, M.; Oku, A. *J. Org. Chem.* **2002**, *67*, 7080.

Mosher Ester Analysis for 11b.



(*S*)-OMTPA ester

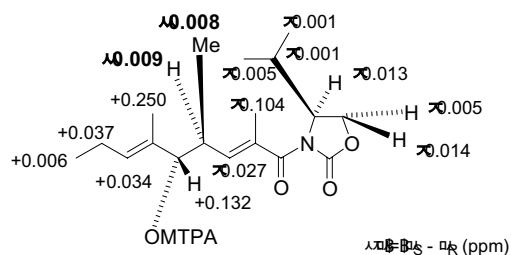
^1H NMR (400 MHz) δ 0.87 (3H, d, $J=7.1\text{Hz}$), 0.88 (3H, d, $J=7.1\text{Hz}$), 0.91 (3H, d, $J=7.1\text{Hz}$), 0.94 (3H, d, $J=7.1\text{Hz}$), 0.94 (3H, d, $J=6.8\text{Hz}$), 1.91 (3H, d, $J=1.0\text{Hz}$), 1.97-2.08 (1H, m), 2.35 (1H, sept d, $J=7.1, 4.4\text{Hz}$), 2.89-2.98 (1H, m), 3.54 (3H, s), 4.17 (1H, dd, $J=5.4, 8.8\text{Hz}$), 4.31 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.46-4.54 (1H, m), 4.95 (1H, dd, $J=3.2, 8.3\text{Hz}$), 5.96 (1H, qd, $J=1.0, 10.0\text{Hz}$), 7.35-7.42 (3H, m), 7.56-7.62 (2H, m).

(*R*)-OMTPA ester

^1H NMR (400 MHz) δ 0.83 (3H, d, $J=6.6\text{Hz}$), 0.89 (3H, d, $J=7.1\text{Hz}$), 0.90 (3H, d, $J=6.6\text{Hz}$), 0.92 (3H, d, $J=7.1\text{Hz}$), 1.00 (3H, d, $J=6.8\text{Hz}$), 1.91 (3H, d, $J=1.4\text{Hz}$), 1.90-2.04 (1H, m), 2.39 (1H, sept d, $J=7.1, 4.4\text{Hz}$), 2.90-3.00 (1H, m), 3.51 (3H, s), 4.18 (1H, dd, $J=5.1, 9.0\text{Hz}$), 4.31 (1H, dd, $J=8.5, 9.0\text{Hz}$), 4.45-4.52 (1H, m), 4.97 (1H, dd, $J=4.2, 7.6$), 5.94 (1H, qd, $J=1.4, 10.0\text{Hz}$), 7.37-7.42 (3H, m), 7.54-7.59 (2H, m).

Aldol adduct **11c** was transformed to ketone by ozonolysis and literature procedure, and the ^1H NMR spectrum was identical to that reported.⁵ The absolute configuration of aldol adduct **11c** was determined by the modified Mosher's method.

Mosher Ester Analysis for 11c.



(*S*)-OMTPA ester

^1H NMR (400 MHz) δ 0.89 (3H, d, $J=6.8\text{Hz}$), 0.92 (3H, d, $J=6.8\text{Hz}$), 0.93 (3H, d, $J=7.1\text{Hz}$), 0.97 (3H, t, $J=7.6\text{Hz}$), 1.65 (3H, d, $J=1.2\text{Hz}$), 1.77 (3H, d, $J=1.4\text{Hz}$), 2.01-2.11 (2H, m), 2.39 (1H, sept d, $J=6.8, 4.4\text{Hz}$), 2.86-2.96 (1H, m), 3.52 (3H, s), 4.18 (1H, dd, $J=4.6, 9.0\text{Hz}$), 4.30 (1H, dd, $J=8.8, 9.0\text{Hz}$), 4.43-4.49 (1H, m), 5.31 (1H, d, $J=8.5\text{Hz}$), 5.61 (1H, qt, $J=1.2, 7.0\text{Hz}$), 5.76 (1H, qd, $J=1.4, 9.8\text{Hz}$), 7.32-7.36 (3H, m), 7.46-7.50 (2H, m).

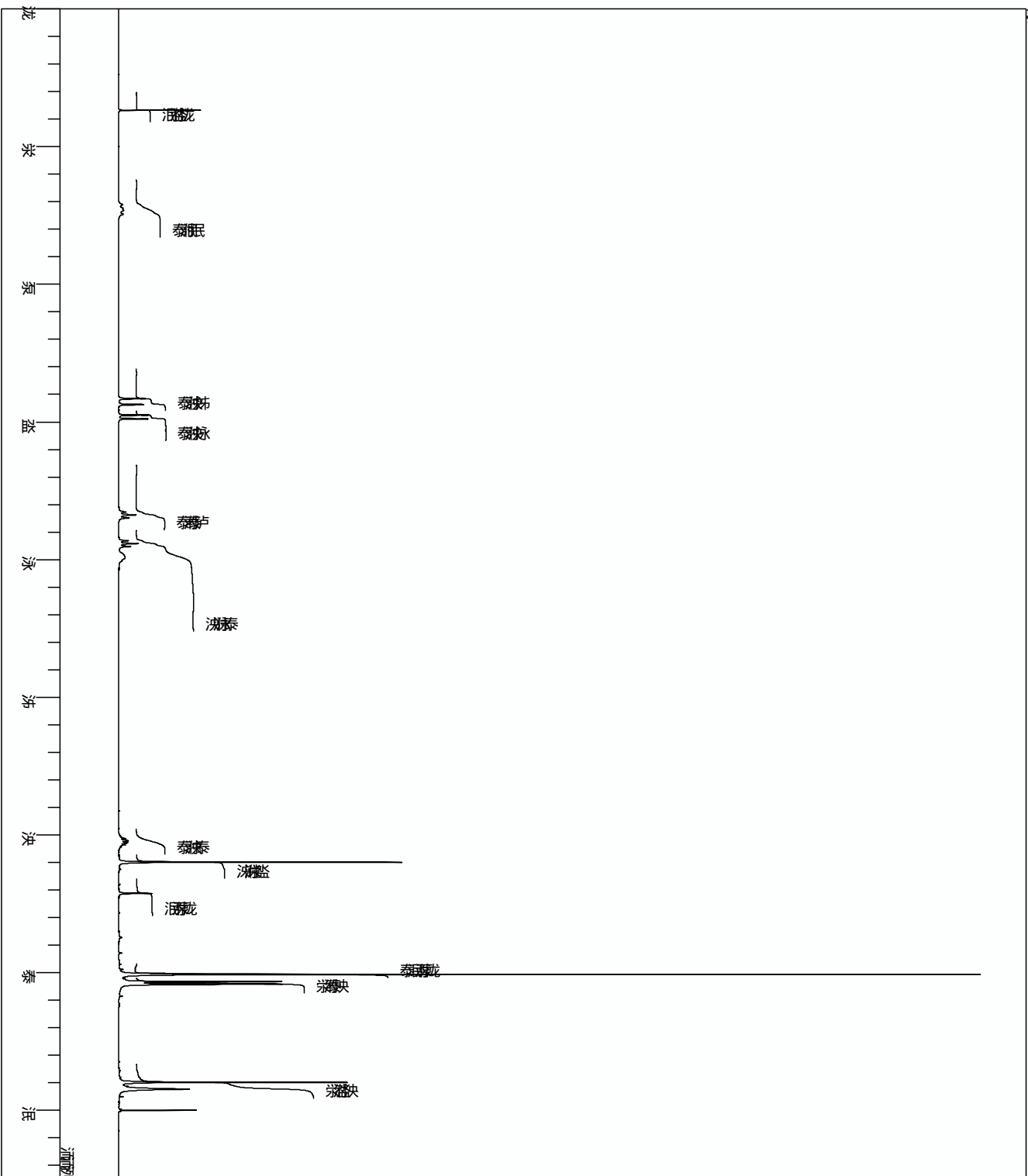
(5) Toshima, K.; Jyojima, T.; Yamaguchi, H.; Noguchi, Y.; Yoshida, T.; Murase, H.; Nakata, M.; Matsumura, *J. Org. Chem.* **1997**, *62*, 3271.

(*R*)-**11b**MTPA ester

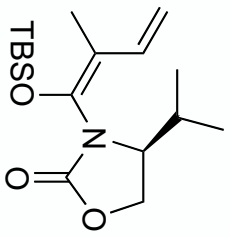
¹H NMR (400 MHz) δ 0.89 (3H, d, $J=7.1$ Hz), 0.91 (3H, d, $J=7.8$ Hz), 0.93 (3H, d, $J=7.1$ Hz), 0.96 (3H, t, $J=7.6$ Hz), 1.40 (3H, d, $J=1.2$ Hz), 1.88 (3H, d, $J=1.5$ Hz), 1.98-2.09 (2H, m), 2.39 (1H, sept d, $J=7.1, 4.2$ Hz), 2.84-2.92 (1H, m), 3.52 (3H, s), 4.19 (1H, dd, $J=4.6, 9.0$ Hz), 4.31 (1H, dd, $J=8.8, 9.0$ Hz), 4.44-4.50 (1H, m), 5.17 (1H, d, $J=9.2$ Hz), 5.58 (1H, qt, $J=1.2, 7.3$ Hz), 5.79 (1H, qd, $J=1.5, 10.0$ Hz), 7.34-7.38 (3H, m), 7.45-7.50 (2H, m).

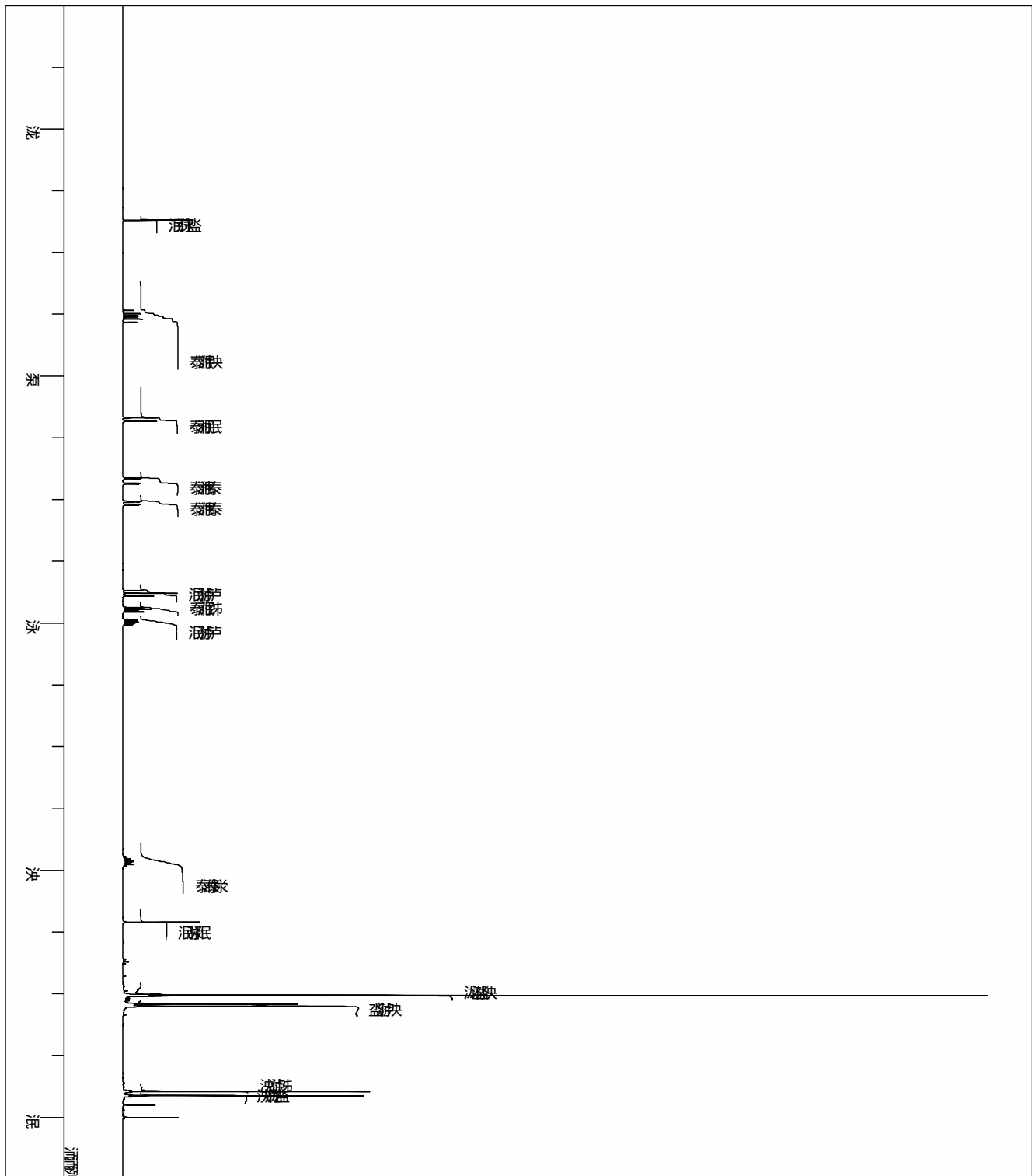
Aldol adduct **11d** was transformed to diol by two-steps sequence ((i) O₃ then Me₂S; (ii) NaBH₄), and the sign of its optical rotation compared to the literature value ($[\alpha]_D^{25} = +40.8$ (c 1.04, CHCl₃).⁶

(6) Abiko, A.; Liu, J.; Masamune, S. *J. Am. Chem. Soc.* **1997**, *119*, 2586.

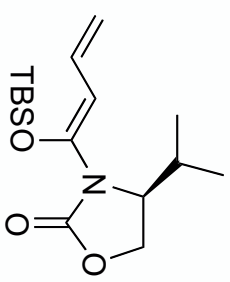


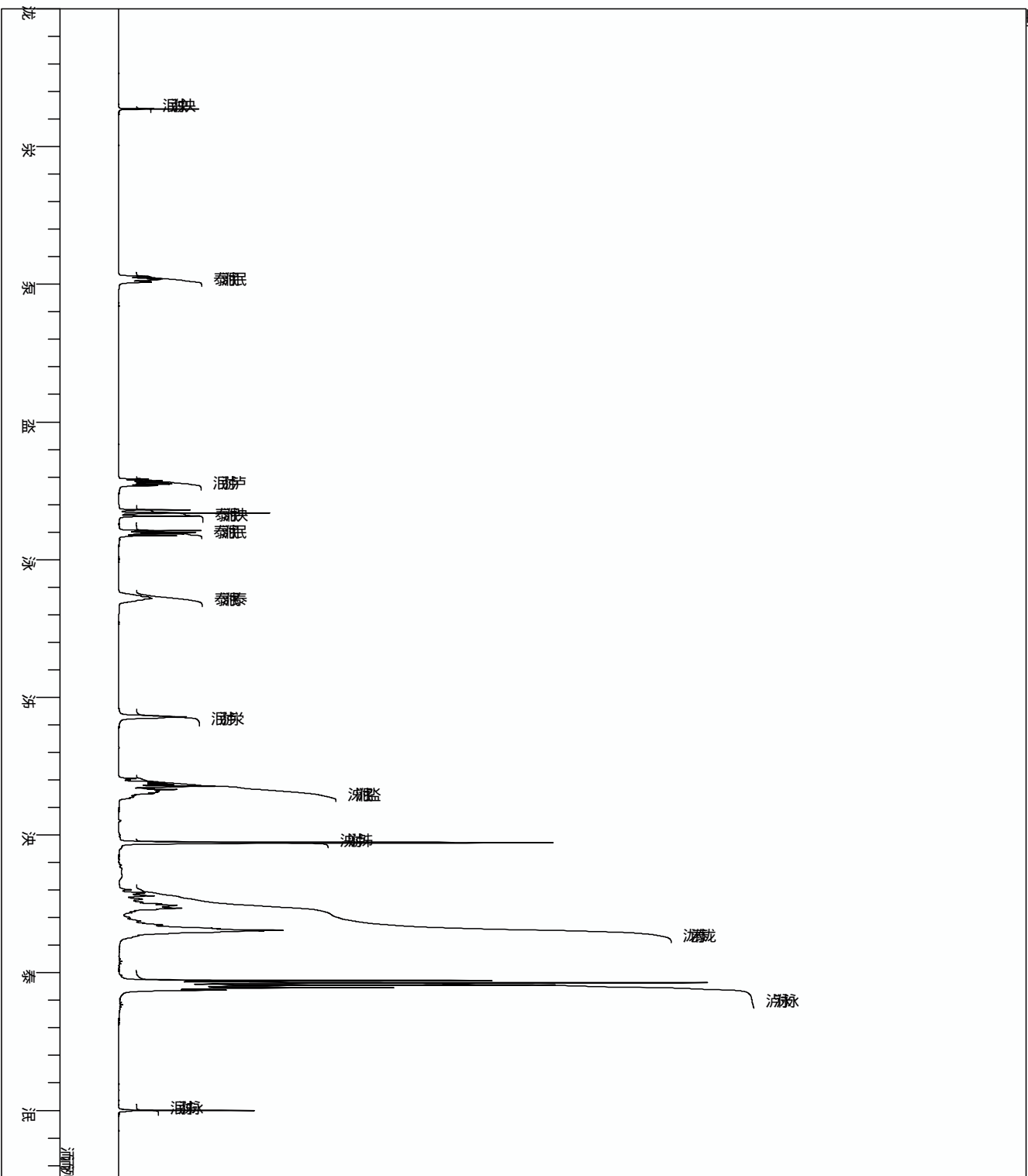
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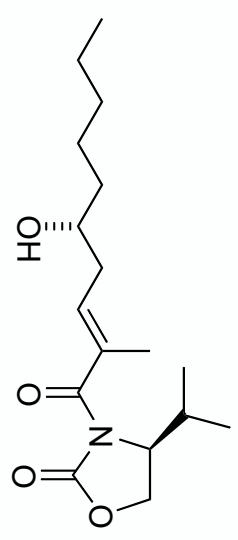


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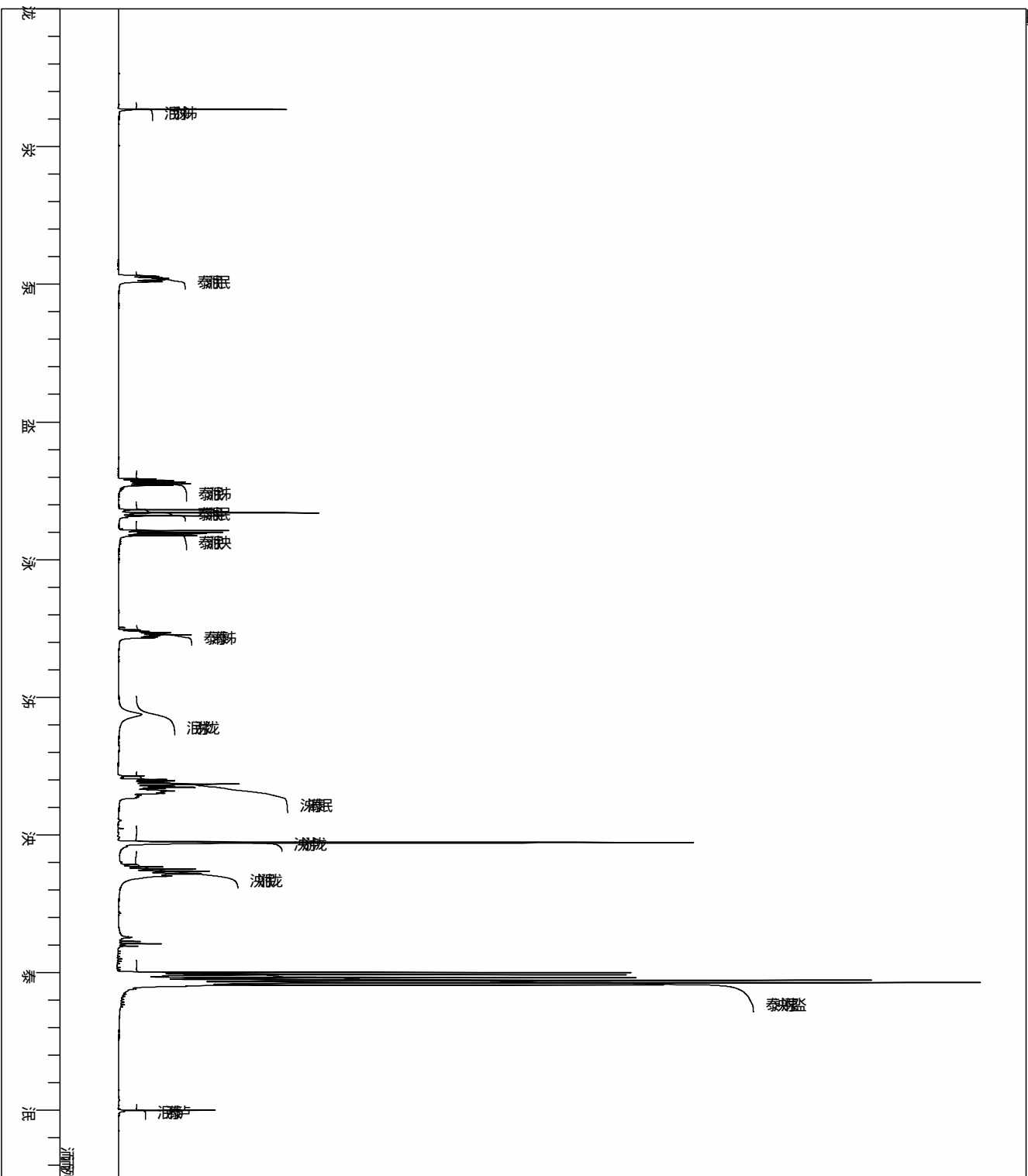




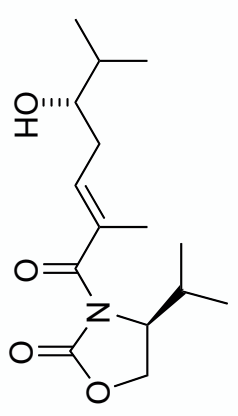
1H NMR spectrum of compound 5a. The x-axis is labeled with chemical shifts in ppm: 10, 9, 8, 7, 6, 5, 4, 3, 2, 1. The spectrum shows several peaks: a small peak at ~10.1 ppm (labeled '溶剂'), a multiplet at ~7.2 ppm (labeled '溶剂'), a multiplet at ~6.8 ppm (labeled '溶剂'), a multiplet at ~6.4 ppm (labeled '溶剂'), a multiplet at ~5.8 ppm (labeled '溶剂'), a multiplet at ~5.2 ppm (labeled '溶剂'), a multiplet at ~4.8 ppm (labeled '溶剂'), a multiplet at ~4.2 ppm (labeled '溶剂'), a multiplet at ~3.8 ppm (labeled '溶剂'), a multiplet at ~3.2 ppm (labeled '溶剂'), a multiplet at ~2.8 ppm (labeled '溶剂'), a multiplet at ~2.4 ppm (labeled '溶剂'), a multiplet at ~2.0 ppm (labeled '溶剂'), a multiplet at ~1.6 ppm (labeled '溶剂'), a multiplet at ~1.2 ppm (labeled '溶剂'), and a multiplet at ~0.8 ppm (labeled '溶剂').



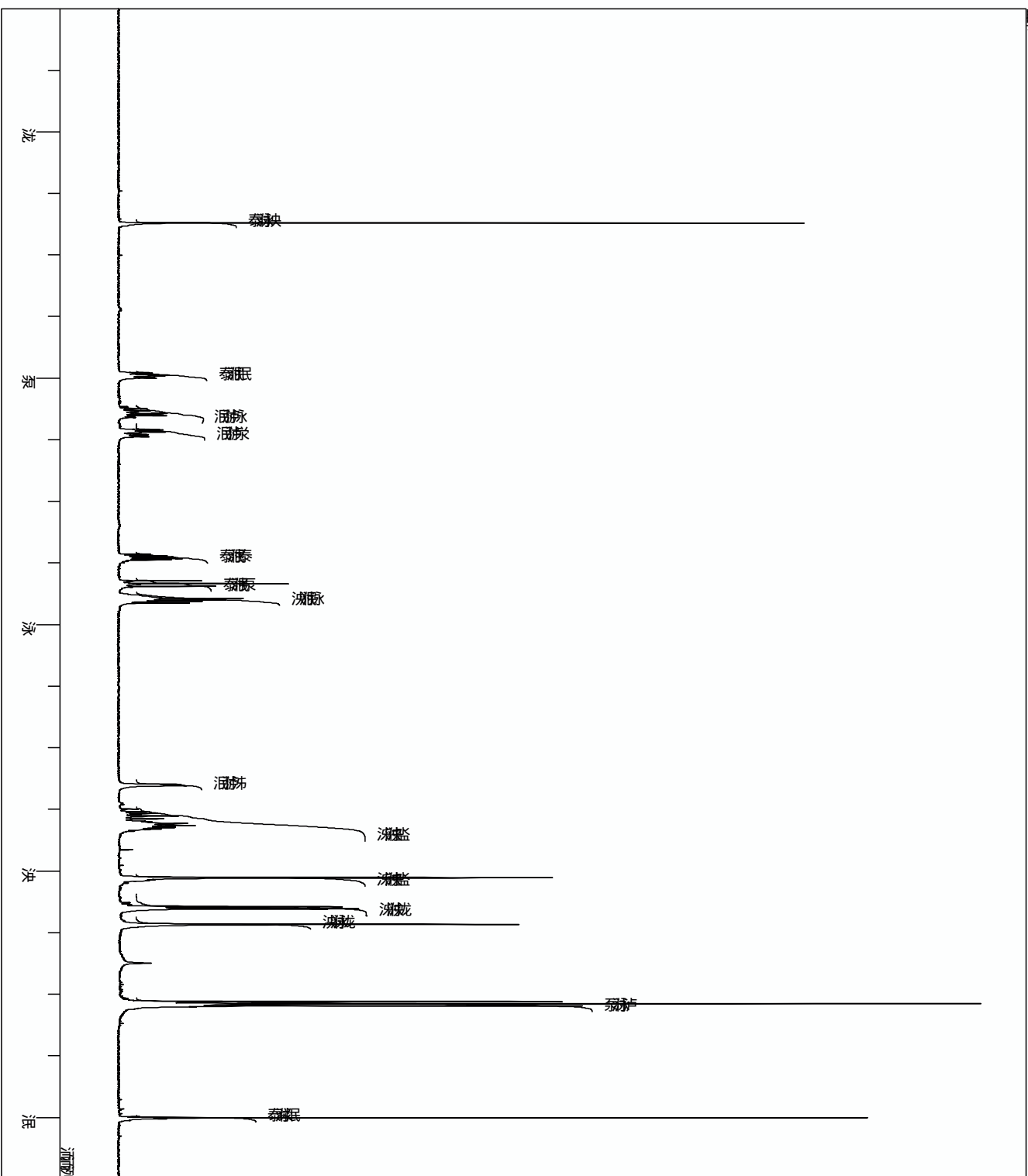
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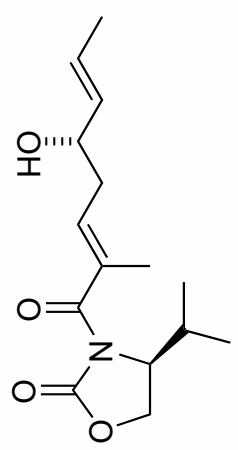
1H NMR spectrum of compound 5c. The x-axis is labeled with chemical shifts in ppm: 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0. The spectrum shows several peaks with corresponding integrations. Key peaks are labeled with their chemical shifts: 10.00 (s, 1H), 7.20 (s, 1H), 6.80 (s, 1H), 6.50 (s, 1H), 6.20 (s, 1H), 5.80 (s, 1H), 5.50 (s, 1H), 5.20 (s, 1H), 4.80 (s, 1H), 4.50 (s, 1H), 4.20 (s, 1H), 3.80 (s, 1H), 3.50 (s, 1H), 3.20 (s, 1H), 2.80 (s, 1H), 2.50 (s, 1H), 2.20 (s, 1H), 1.80 (s, 1H), 1.50 (s, 1H), 1.20 (s, 1H), 0.80 (s, 1H), 0.50 (s, 1H).



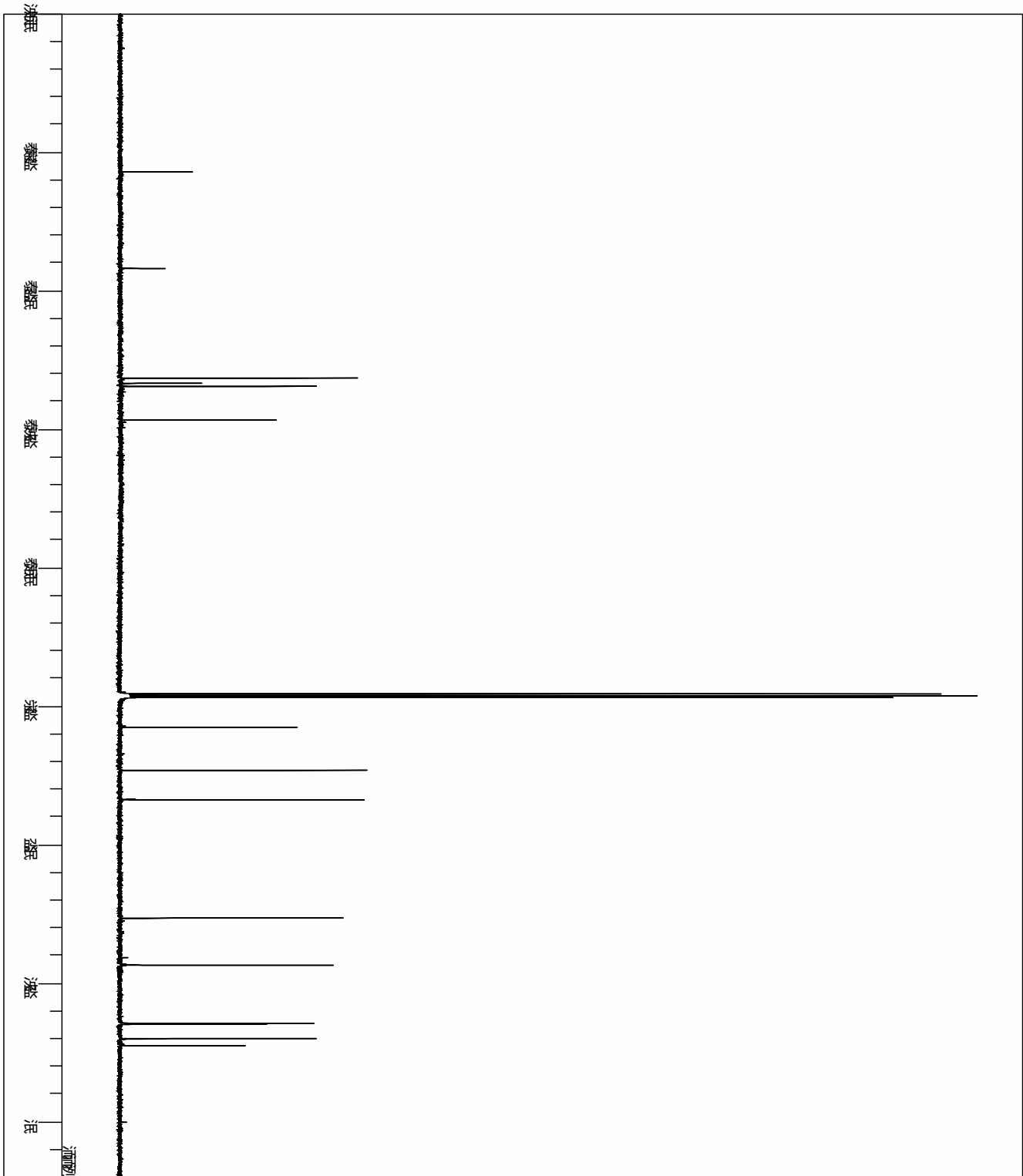
5c



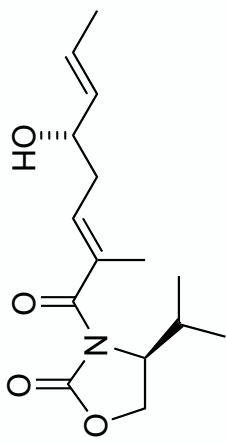
1H NMR (400 MHz, CDCl₃) δ: 10.0 (s, 1H, COOH), 7.5 (m, 1H, COOH), 7.2 (m, 1H, COOH), 6.8 (m, 1H, COOH), 6.5 (m, 1H, COOH), 6.2 (m, 1H, COOH), 5.8 (m, 1H, COOH), 5.5 (m, 1H, COOH), 5.2 (m, 1H, COOH), 4.8 (m, 1H, COOH), 4.5 (m, 1H, COOH), 4.2 (m, 1H, COOH), 4.0 (m, 1H, COOH), 3.8 (m, 1H, COOH), 3.5 (m, 1H, COOH), 3.2 (m, 1H, COOH), 3.0 (m, 1H, COOH), 2.8 (m, 1H, COOH), 2.5 (m, 1H, COOH), 2.2 (m, 1H, COOH), 2.0 (m, 1H, COOH), 1.8 (m, 1H, COOH), 1.5 (m, 1H, COOH), 1.2 (m, 1H, COOH), 1.0 (m, 1H, COOH), 0.8 (m, 1H, COOH), 0.5 (m, 1H, COOH), 0.2 (m, 1H, COOH).



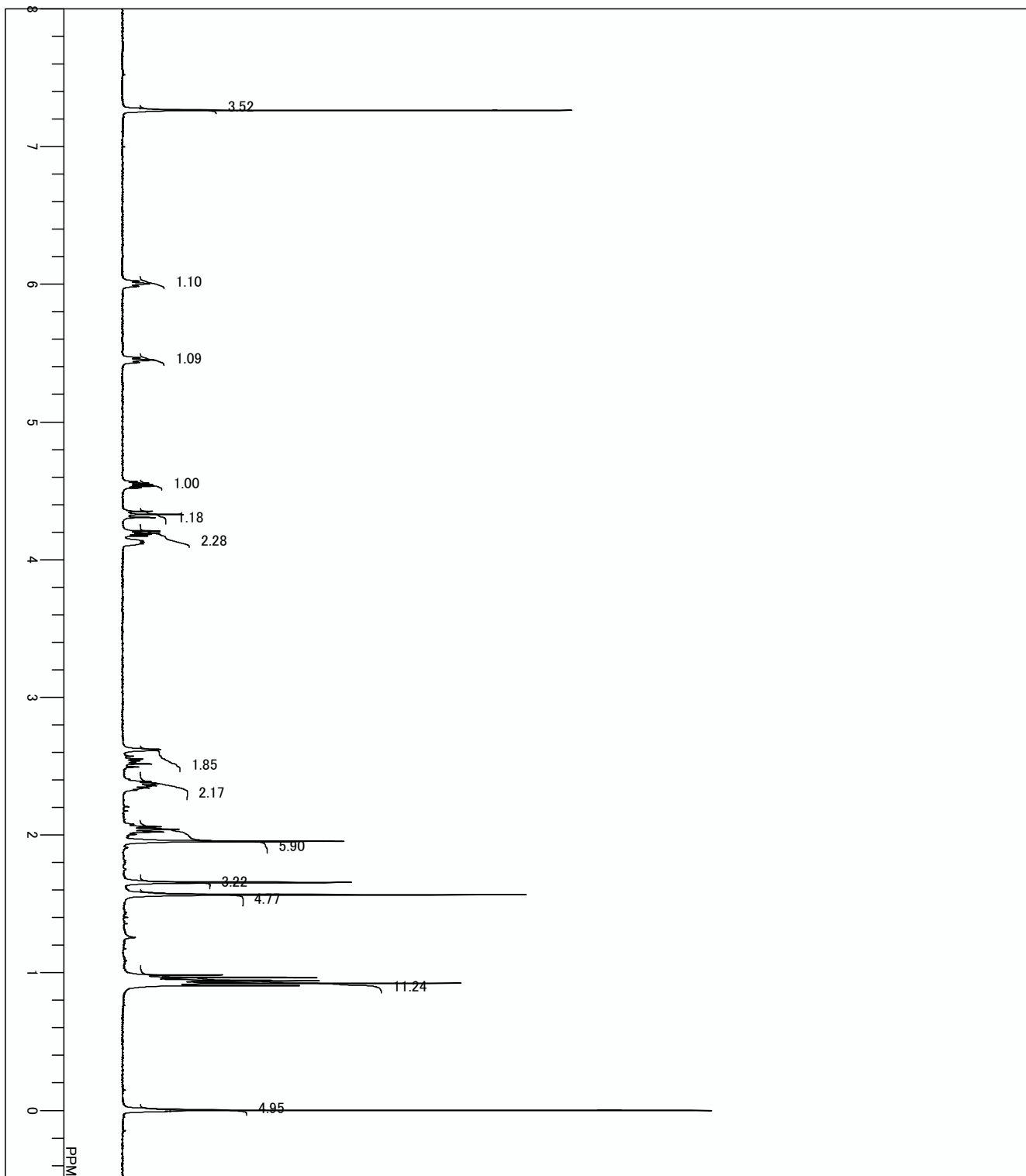
5d



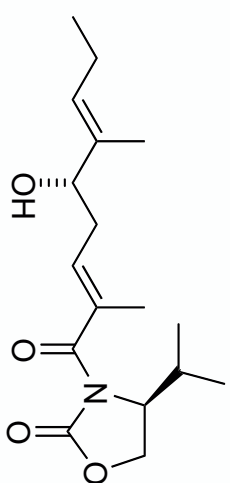
1H NMR (400 MHz, CDCl₃) δ: 7.20 (m, 1H), 6.80 (m, 1H), 6.40 (m, 1H), 5.80 (m, 1H), 5.20 (m, 1H), 4.80 (m, 1H), 4.20 (m, 1H), 3.80 (m, 1H), 3.20 (m, 1H), 2.80 (m, 1H), 2.40 (m, 1H), 2.00 (m, 1H), 1.60 (m, 1H), 1.20 (m, 1H), 0.80 (m, 1H), 0.40 (m, 1H).



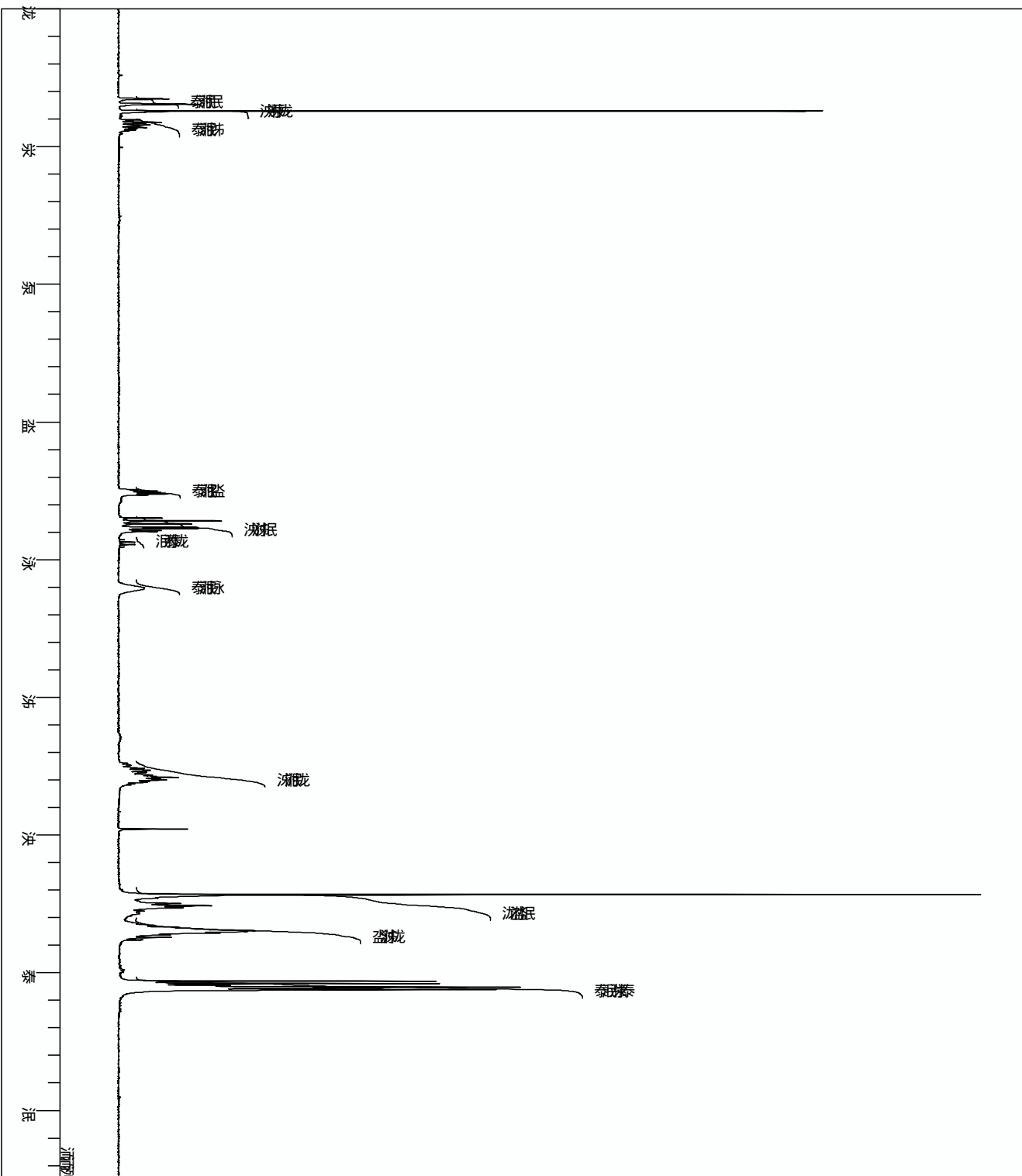
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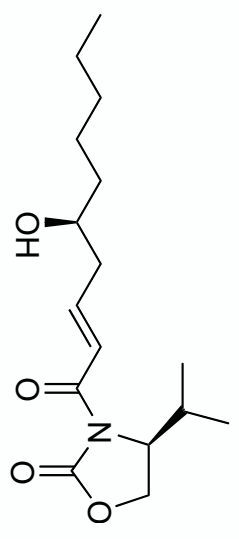
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5e



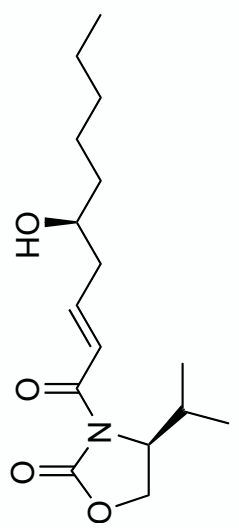
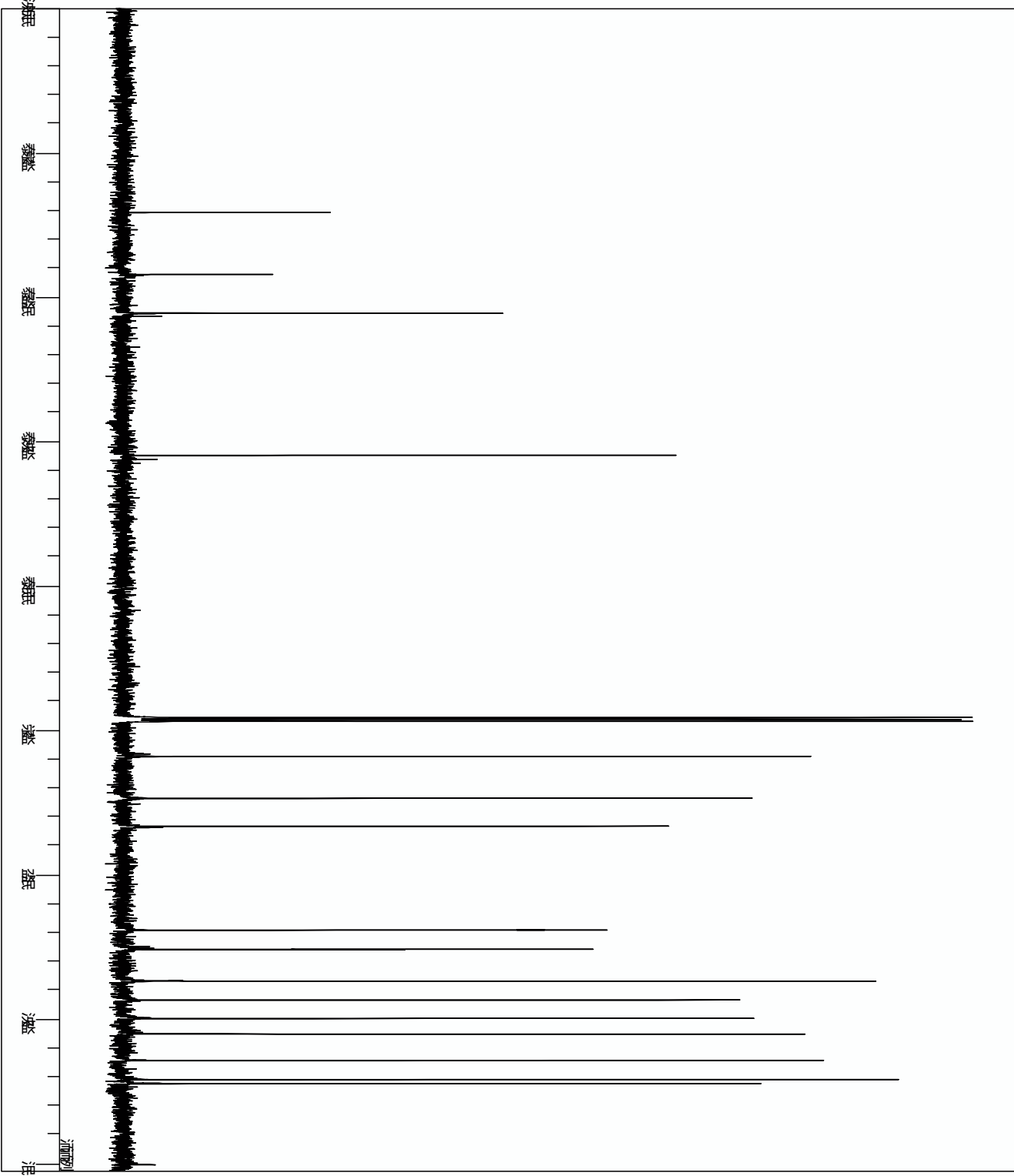
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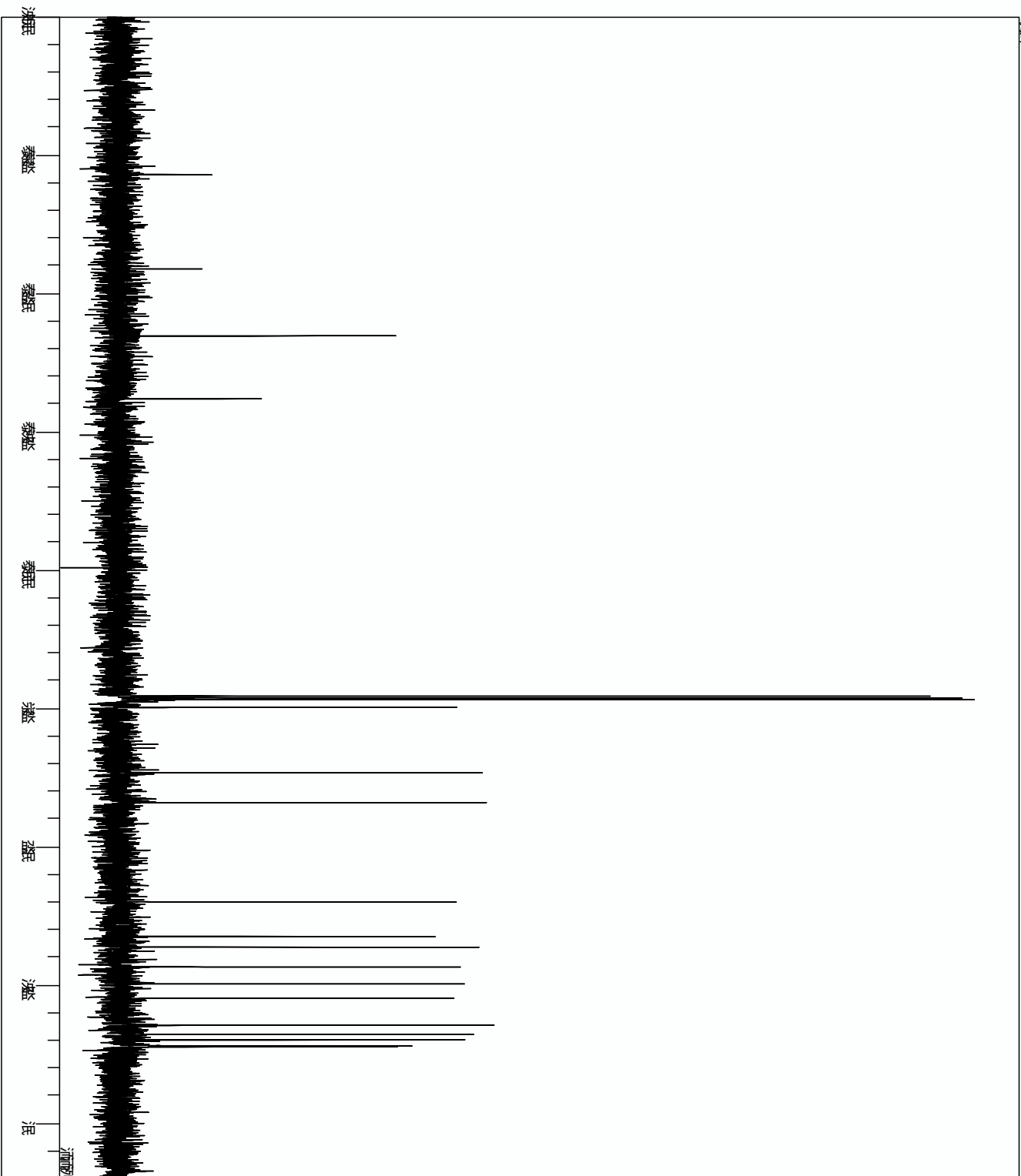
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2. 检测峰列表

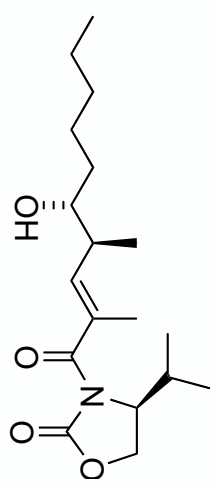
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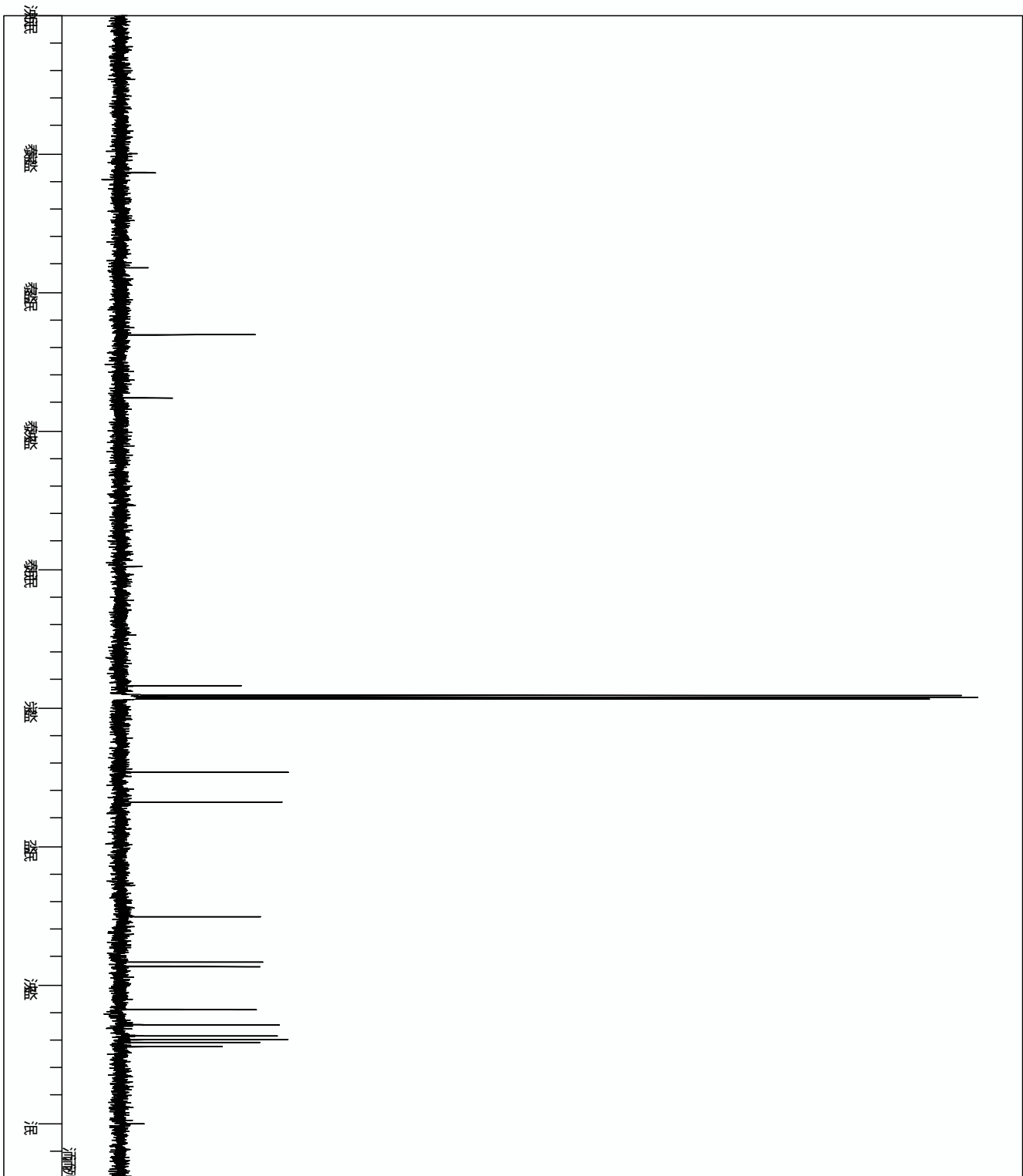


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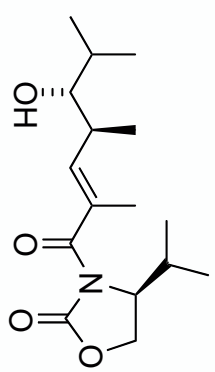


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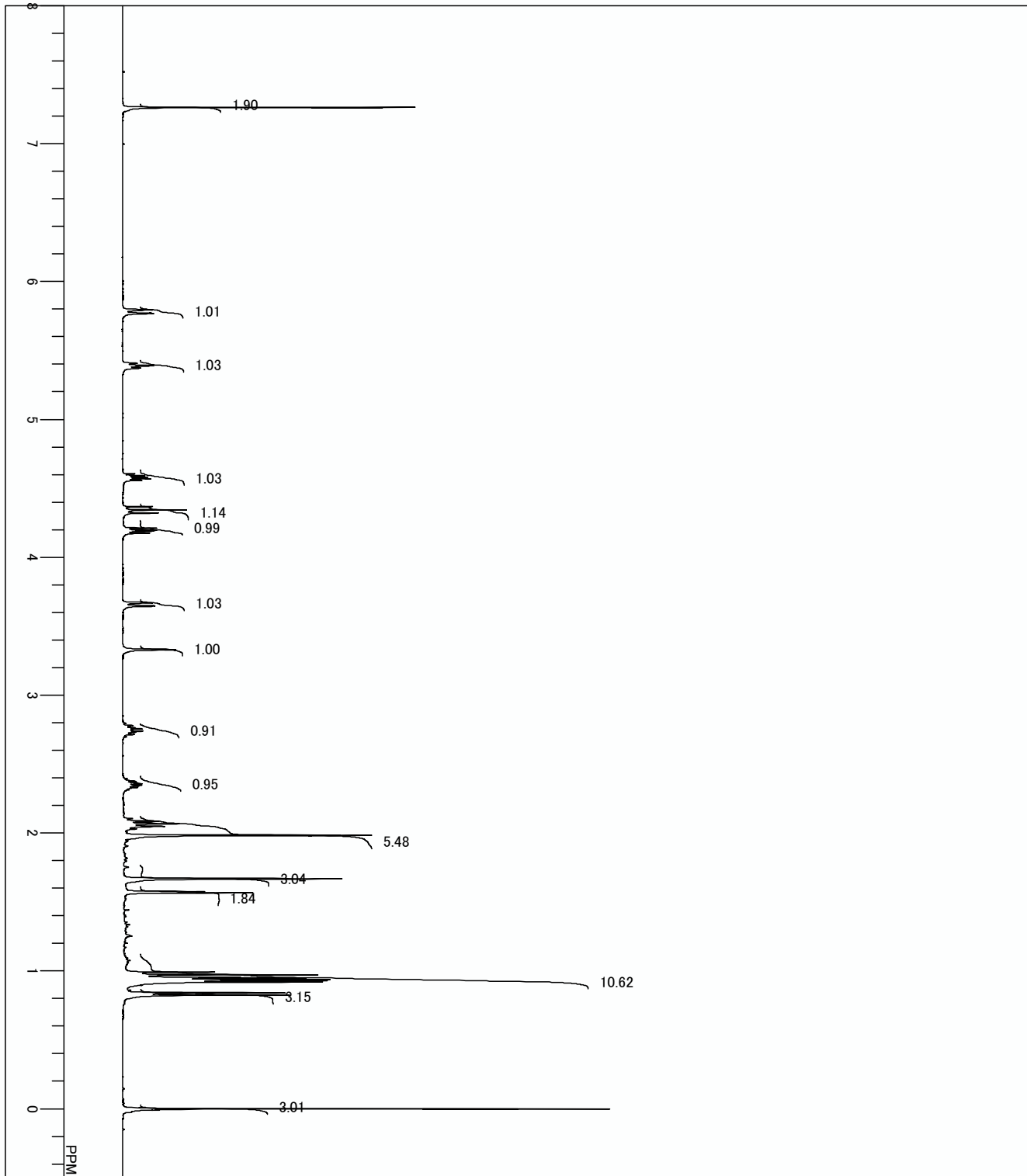


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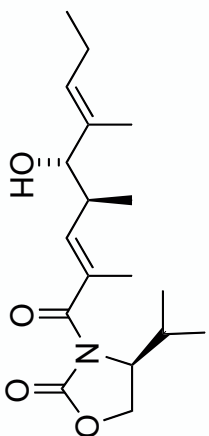


11b

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11c

