A diastereoselective Ru-catalyzed cross-metathesis dihydroxylation sequence – an efficient approach toward enantiomerically enriched *syn*-diols

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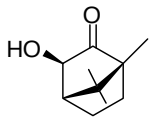
I. General Remarks

All reactions were performed under a N2-atmosphere in dry solvents. CH_2Cl_2 was destilled from CaH_2, MeOH was destilled from Mg turnings. THF, toluene and diethyl ether were destilled from sodium. Ethyl acetate was destilled prior to its use in the dihydroxylation reaction.

II. Preparation of auxiliaries

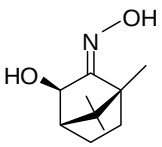
II-I Preparation of camphor oxazolidinone (*exo*-29).

exo-3-Hydroxy-camphor (*exo*-26)[1]:



A solution of D-(+)-camphor (5.0 g, 30.4 mmol) in THF (100 mL) was cooled to -78°C. A solution of KHMDS (73.7 mL, 36.9 mmol, 0.5 M in toluene) was added via cannula. The resulting soultion was stirred for 15 minutes at this temperature and warmed up to 0°C. After 1h at this temperature the solution was again cooled to -78°C and a solution of 1-phenyl-N-(toluylsulfonyl)oxaziridine (9.24 g, 33.6 mmol) in THF (75 mL) was added dropwise. Stirring was continued at this temperature until TLC showed complete conversion (3h). The reaction mixture was warmed to 0°C and hydrolyzed with sat. aq. NH_4Cl-solution. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2x50 mL). The combined organic phases were washed with brine prior to drying with Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (gradient elution from 10:1 to 3:1 petroleum ether/ethyl acetate) to yield *exo*-**26** as an colorless oil: 4.86 g (70%). R_f 0.35 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 101.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 1H), 2.64 (bs, 1H), 2.09 (d, *J* = 4.5 Hz, 1H), 1.96-2.04 (m, 1H), 1.61-1.69 (m, 1H), 1.41-1.48 (m, 1H), 1.33-1.40 (m, 1H), 0.99 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 219.9, 77.5, 57.1, 49.2, 46.8, 28.5, 25.2, 21.0, 20.1, 9.0 ppm; IR (KBr) ν 3448 (s), 2959 (s), 1739 (s), 1454 (w), 1106 (w), 1013 (m), 832 (w), 735 (w), 1041 (s), 918 (m), 735 (s) cm^{-1}.

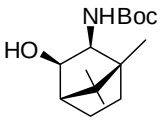
exo-3-Hydroxy-camphoroxime[2] (*exo*-27) :



In a 500mL two-neck-round bottom flask *exo*-3-hydroxy-camphor *exo*-**26** (6.8 g, 40.5 mmol) was dissolved in ethanol (250 mL) at room temperature. NaOAc (4.14 g, 50.5 mmol) and hydroxylamine

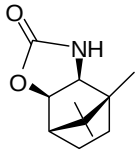
hydrochloride (3.6 g, 51 mmol) which were dissolved in a minimum amount of water were added to this solution. The reaction mixture was heated to reflux for 5h. After cooling to room temperature the solvent was evaporated. The resulting slurry was taken up in diethyl ether (200 mL) and extracted with water (2x20 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash chromatography to yield the oxime *exo*-**27** as a colorless solid: 6.45 g (87%). mp. 149°C; R_f 0.30 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -118.7 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 1H), 1.96 (d, *J* = 4.8 Hz, 1H), 1.82-1.91 (m, 1H), 1.61-1.69 (m, 1H), 1.35-1.44 (m, 1H), 1.18-1.26 (m, 1H), 1.10 (s, 3H), 1.01 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 74.7, 51.9, 49.8, 48.7, 32.0, 24.7, 20.9, 19.6, 10.8 ppm; IR (KBr) ν 3271 (s), 2958 (m), 1680 (w), 1452 (m), 1391 (w), 1321 (m), 1265 (s), 1041 (s), 918 (m), 735 (s) cm^{-1}.

N-boc protected aminoalcohol[3] (*exo*-28):



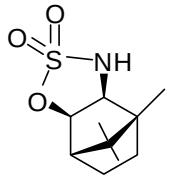
To a -78°C cold and mechanically stirred solution of *exo*-3-hydroxy-camphoroxime *exo*-**27** (2.0g, 10.8 mmol) and $NiCl_2$*$6H_2O$ (6.26 g, 22 mmol) in methanol (100 mL) was added $NaBH_4$ (3.78 g, 100 mmol) within 1 h (caution: gas evolution!). After complete addition the resulting black slurry was allowed to warm up to -30°C and stirred at this temperature until no more starting material was detected (3-5 h). Then the reaction mixture was warmed to 0°C and Boc_2O (3.54 g, 16.2 mmol) was added. Stirring was continued overnight while warming up to room temperature. The reaction was hydrolyzed by slow additon of brine (25 mL) at 0°C (caution: gas evolution!). Methanol was evaporated; the resulting black slurry was taken up in diethyl ether (100 mL). The organic layer was separated and the aqueous phase was extracted with diethyl ether (2x50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography to yield the protected aminoalcohol *exo*-**28** as a colorless oil: 1.86 g (63%). R_f 0.72 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 33.9 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (d, *J* = 7.5 Hz, 1H), 3.98 (d, *J* = 7.5 Hz, 1H), 3.65 (dd, *J* = 7.8, 7.5 Hz, 1H), 2.07 (bs,1H), 1.76 (d, *J* = 5.1 Hz, 1H), 1.63-1.75 (m, 1H), 1.44-1.55 (m, 1H), 1.44 (s, 9H), 1.12-1.25 (m, 1H), 0.99-1.08 (m, 1H), 1.04 (s, 3H), 0.86 (s, 3H), 0.78 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 79.2, 76.1, 74.0, 62.3, 51.4, 46.9, 44.5, 35.0, 38.3, 24.0, 21.4, 20.8, 11.2 ppm; IR (KBr) ν 3418 (m), 3369 (m), 2928 (m), 1684 (s), 1493 (s), 1364 (w), 1164 (m), 1044 (w) 1019 (w) cm^{-1} , HRMS (FAB^+HR) calcd. for $C_{15}H_{28}NO_3$: 270.2069, found: 270.2076.

Camphoroxazolidinone[1,4] **(*exo*-29) :**



To a 0°C cold solution of the protected aminoalcohol *exo*-**28** (8.4 g, 31.4 mmol) in dry THF (200mL) was added NaH (1.9 g. 47 mmol, 60% in mineral oil) portionwise. After complete addition the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. After TLC showed complete conversion the reaction was hydrolyzed by addition of a sat. aq. NH_4Cl-solution (20 mL) at 0°C. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2x50 mL). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography to yield the oxazolidinone *exo*-**29** as a colorless solid: 5.98 g (98%). m.p. 195°C; R_f 0.15 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 1.2 (c 0.9, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.4 (bs, 1H) 4.59 (d, *J* = 8 Hz, 1H), 3.59 (dd, *J* = 8.0, 1.1 Hz, 1H), 2.12 (d, *J* = 5.1 Hz, 1H), 1.69-1.82 (m, 1H), 1.42-1.55 (m, 1H), 1.08 (s, 3H), 0.95-1.02 (m, 1H), 0.92 (s, 3H), 0.89 (s, 3H), 0.86-0.94 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 84.4, 65.6, 48.3, 47.7, 46.5, 33.0, 23.6, 23.1, 19.3, 10.9 ppm; IR (KBr) ν 3286 (s), 2928 (m), 1756 (s), 1494 (m), 1360 (w), 1042 (w) 1019 (w) cm^{-1}.

II-II Synthesis of camphor based sulfamidate (*exo*-31) :



To a cooled (iced bath) solution of *exo,exo*-2-amino-3-hydroxy-camphor *exo*-**30** (5.0 mmol), imidazole (1.36 g, 20.0 mmol) and triethylamine (1.53 mL, 11.0 mmol) in CH_2Cl_2 (60 mL) was added dropwise, a solution of thionyl chloride (0.41 mL, 5.65 mmol) in CH_2Cl_2 (15 mL). The mixture was then stirred at 0°C for one hour before being quenched by the addition of water (50 mL). The phases were separated and the aqueous phase extracted with CH_2Cl_2. The combined organic portions were then washed with water, dried (Na_2SO_4) and concentrated *in vacuo* to afford crude sulfamidite which was used without further purification in the next step. To a cooled (ice bath) solution of crude sulfamidite (ca. 5 mmol) in

MeCN (40 mL) was added ruthenium (III) chloride (10mg), followed by $NaIO_4$ (1.60 g, 7.50 mmol) and then water (30 mL). The mixture was stirred at 0°C for 6 hourd, then diluted with ether and the phases separated. The aqueous phase was extracted with ether. The combined organic portions were washed with $NaHCO_3$ solution, and then brine. The solution was dried ($NaSO_4$) and concentrated *in vacuo*. Purification by column chromatography (petrol-ethyl acetate 4:1) afforded camphorsulfamidate *exo*-**31** as a colorless solid: 810 mg (over two steps 75%). m.p. 187°C; R_f 0.55 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -8.6 (c 4.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (d, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 5.4 Hz, 1H), 3.71 (t, *J* = 6.5 Hz, 1H), 2.22 (d, *J* = 5.2 Hz, 1H), 1.82-1.92 (m, 1H), 1.54-1.68 (m, 1H), 1.23 (s, 3H), 1.03-1.16 (m, 2H), 0.97 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 84.2, 64.5, 45.4, 42.7, 42.6, 31.6, 21.2, 19.7, 17.5, 9.1 ppm; IR (KBr) ν 3250 (s), 2962 (m), 1350 (s), 1120 (s), 1098 (m), 992 (m) 820 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{10}H_{18}NO_3S$: 232.1002, found: 232.1013

III. Preparation of starting materials

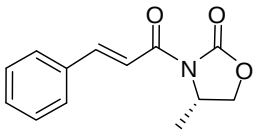
General procedure for the preparation of substituted oxazolidinones (GP-I): In a 250-mL round-bottomed flask NaH (375 mg, 15 mmol, 60% in mineral oil) and 18-crown-6 (264 mg, 1 mmol) were suspended at room temperature under an argon atmosphere in THF (100 mL). The auxiliary (10 mmol) was added and the suspension was heated to reflux for 45 min. After cooling to 0°C a solution of the acid chloride (10 mmol) in THF (10 mL) was added dropwise. After stirring overnight at room temperature TLC showed complete conversion. Sat. NH_4Cl-solution (10 mL) was added. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3x15 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated in vacuum and purified by column chromatography.

General procedure for the preparation of oxazolidinyl substituted α,β-unsaturated carboxylic acid amides (GP-II): In a 100-mL Schlenk-flask the appropiate auxiliary (3 mmol) was dissolved in toluene (50 mL) and NaH (180 mg, 4.5 mmol, 60% suspension in mineral oil) was added. After stirring for 5 minutes the suspension was heated to 60°C and for further 45 minutes. The reaction mixture was cooled down to 0°C and CuCl (15 mg, 0.15 mmol) was added. After stirring for 5 minutes acryloyl chloride (357 µl, 4.4 mmol) was added dropwise. Stirring was conitnued until TLC showed complete conversion. The reaction mixture was cooled down to 0°C and water (5mL) was added dropwise. The

organic layer was separated and the aqueous phase was extracted with ethyl acetate (2x25 mL). The combined organic layers were dried over Na_2SO_4 and filtered. Then BHT (5 mg) was added to prevent polymerization during evaporation of the solvent. The crude product was puriefied by column chromatography or recrystallization from methanol.

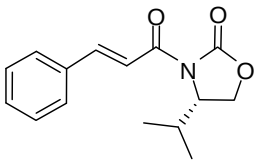
General procedure for the preparation of α,β-unsaturated carboxylic acid derived sultames and sulfamidates (GP-III): In a 50-mL two neck round-bottomed flask camphorsultame (700 mg, 3.25 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled down to 0°C. At this temperature dicyclohexylcarbodiimide (805 mg, 3.9 mmol), N,N-dimethylamino pyridine (122 mg, 1 mmol) and the unsatured carboxylic acid (3.25 mmol) were added. The solution was allowed to warm to room temparture within 2h and stirring was continued overnight. When all of the staring material was consummed (TLC-control) the suspension was diluted with diethyl ether (20 mL) and all solids were filtered off through a plug of silica. The solvent was removed in vacuum and the resulting crude product purified by column chromatography.

(4*S*)-4-Methyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (1) [5]



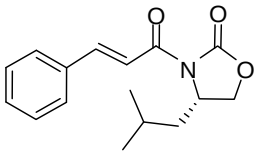
Oxazolidinone 1 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound I as a white solid (2.06 g, 89%). mp. 62°C; R_f 0.45 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 71.3 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.56-7.66 (m, 2H), 7.36-7.42 (m, 3H), 4.61-4.76 (m, 1H), 4.47 (t, *J* = 8.6, Hz, 1H), 4.03 (dd, *J* = 8.4, 3.2 Hz, 1H), 1.43 (d, *J* = 6.3, Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 153.6, 146.1, 134.6, 130.6, 128.9, 128.6, 117.2, 69.1, 50.7, 19.4 ppm ; IR (KBr) ν 2958 (m), 1776 (s), 1674 (s), 1616 (s), 1395 (m), 1338 (s), 1217 (s), 1038 (m), 767 (m), 718 (m) cm^{-1}.

(4*S*)-4-isopropyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (3) [6]



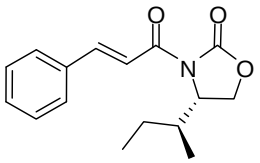
Oxazolidinone 3 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **II** as a colorless solid (2.2 g, 85%). mp.63°C; R_f 0.39 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 94.3 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 16 Hz, 1H), 7.85 (d, *J* = 16 Hz, 1H),7.61-7.63 (m, 2H), 7.38-7.41 (m, 3H), 4.56 (ddd, *J* = 9.0, 4.0, 3.5 Hz, 1H), 4.32 (dd, *J* = 9.0 Hz, 1H), 4.25 (dd, *J* = 9.0, 3.5 Hz, 1H), 2.45 (dq, *J* = 7.0, 4.5 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 1H), 0.91 (d, *J* = 7.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 146.2, 134.6, 130.6, 128.9, 117.1, 63.4, 58.7, 28.5, 18.0, 14.7 ppm; IR (KBr) ν 2952 (m), 1781 (s), 1680 (s), 1616 (s), 1393 (m), 1367 (m), 1337 (s), 767 (m), cm^{-1}.

(4*S*)-4-iso-Butyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (5) [7]



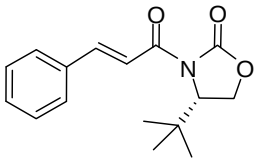
Oxazolidinone 5 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **III** as a colorless solid (2.29 g, 84%). mp. 65°C; R_f 0.42 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 86.8 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 (d, *J* = 16.0 Hz, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.58-7.64 (m, 2H), 7.36-7.42 (m, 3H), 4.61 (dddd, *J* = 7.5, 4.5, 3.0, 2.5 Hz, 1H), 4.43 (dd, *J* = 8.5, 7.5 Hz, 1H), 4.14 (dd, *J* = 8.0, 2.5 Hz, 1H), 1.87 (ddd, *J* = 10.0, 6.5, 3.0 Hz, 1H), 1.6-1.71 (m, 1H), 1.54 (ddd, *J* = 10.0, 5.0, 4.5 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 153.7, 146.1, 134.6, 130.6, 128.9, 128.6, 117.2, 67.7, 53.3,41.6, 24.9, 23.4, 21.6 ppm; IR (KBr) ν 2958 (s), 1774 (s), 1673 (s), 1614 (s), 1449 (m), 1339 (s), 1216 (s), 1048 (m), 764 (m) cm^{-1}.

(4*S*)-4-*sec*-Butyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (7)



Oxazolidinone 7 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **IV** as a colorless solid (2.07 g, 76%). mp. 68°C; R_f 0.42 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 88.1 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16 Hz, 1H), 7.84 (d, *J* = 16 Hz, 1H), 7.62 (m, 2H), 7.4 (m, 3H), 4.66 (ddd, *J* = 8.5, 7.0, 3.3 Hz, 1H), 4.32 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.24 (dd, *J* = 9.0, 3.3 Hz, 1H), 2.25 (m, 1H), 1.29-1.42 (m, 1H), 1.14-1.28 (m, 1H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 154.1, 146.0, 134.5, 130.5, 128.8, 128.5, 117.1, 63.2, 57.6, 34.9, 25.4, 11.7, 11.6 ppm; IR (KBr) ν 3089 (w), 2958 (s), 2925 (s), 1774 (s), 1673 (s), 1614 (s), 1448 (w), 1398 (m), 1339 (s), 1216 (s), 1109 (m), 1048 (m), 764 (m) 713 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{16}H_{20}NO_3$: 274.1443, found: 274.1428.

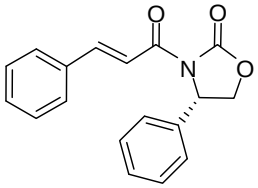
(4*S*)-4-*tert*-Butyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (9) [8]



Oxazolidinone 9 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **V** as a colorless solid (2.13 g, 78%). mp. 99°C; R_f 0.46 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 115.2 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 16 Hz, 1H) 7.85 (d, *J* = 16 Hz, 1H), 7.6-7.66 (m, 2H), 7.36-7.42 (m, 3H), 4.59 (dd, *J* = 7.0, 2.0 Hz, 1H), 4.33 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.28 (dd, *J* = 9.0, 7.0 Hz, 1H), 0.98 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 146.4, 134.6, 130.6, 128.9, 128.5, 117.1, 65.3, 61.0, 36.0,

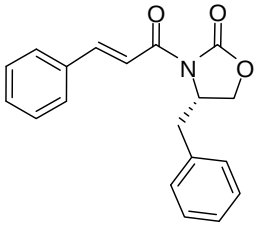
25.7 ppm; IR (KBr) ν 2962 (m), 1777 (s), 1677 (s), 1624 (s), 1401 (m), 1225 (s), 1183 (s), 1111 (m), 767 (s) 705 (m) cm^{-1}; HRMS ($FAB^{+}HR$) calcd. for $C_{16}H_{20}NO_3$: 274.1443, found: 274.1409.

(4*S*)-4-Phenyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (11) [9]



Oxazolidinone 11 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **VI** as a colorless solid (2.4 g, 83%). mp. 169°C; R_f 0.44 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 10.6 (c 0.63, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 16.0 Hz, 1H), 7.91 (d, *J* = 16.0 Hz, 1H) 7.61-7.68 (m, 2H), 7.39-7.43 (m, 3H), 7.21-7.39 (m, 5H), 5.56 (dd, *J* = 8.7, 3.8, Hz, 1H), 4.74 (dd, *J* = 8.7, 1H), 4.32 (dd, *J* = 8.7, 3.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 154.0, 146.9, 139.2, 134.7, 130.9, 129.4, 129.1, 128.9, 128.8, 126.2, 117.1, 70.2, 58.1 ppm; IR (KBr) ν 1775 (s), 1680 (s), 1625 (s), 1330 (s), 1210 (s), 760 (m), 710 (m) cm^{-1}.

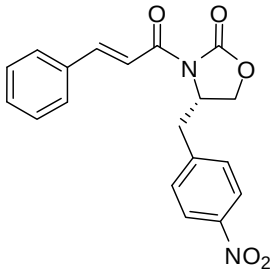
(4*S*)-4-Benzyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (13) [8]



Oxazolidinone 13 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **VII** as a colorless solid (2.06 g, 67%). mp. 122°C; R_f 0.41 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{25}$ 44.2 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 15.7 Hz, 1H), 7.78 (d, *J* = 15.7 Hz, 1H) 7.57-7.61 (m, 2H), 7.37-7.42 (m, 5H), 7.32-7.37 (m, 3H), 4.81 (ddd, *J* = 9.5, 7,5, 3.0 Hz, 1H), 4.18-4.28 (m, 2H), 3.38 (dd, *J* = 13.5,

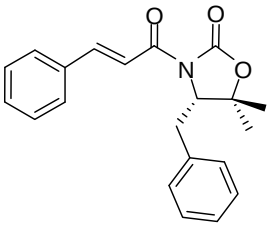
3.0 Hz, 1H), 2.86 (dd, *J* = 13.5, 9.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 154.5, 146.5, 135.3, 134.5, 130.72, 129.5, 128.9, 128.8, 128.7, 128.6, 127.3, 116.9, 66.1, 55.4, 37.9 ppm; IR (KBr) ν 1779 (s), 1673 (s), 1618 (m), 1392 (m), 1351 (s), 1214 (s), 1121 (w), 1082 (w), 1042 (w), 1012 (m), 982 (m), 764 (s), 714 (m) cm^{-1}.

(4*S*)-4-(4-Nitrobenzyl)-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (15)



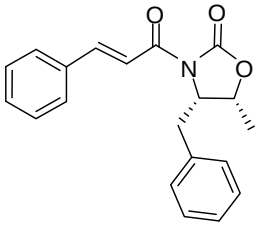
Oxazolidinone 15 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:1) yielded compound **VIII** as a yellow solid (1.58 g, 45%). mp. 142°C; R_f 0.38 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 39.4 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 15.7 Hz, 1H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.3-7.6 (m, 8H), 5.07 (dddd, *J* = 7.7, 7.1, 5.7, 2.5 Hz, 1H), 4.39 (dd, *J* = 9.1, 7.7 Hz, 1H), 4.33 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.48 (dd, *J* = 13.7, 5.7 Hz, 1H), 3.40 (dd, *J* = 13.7, 7.1 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 148.8, 148.6, 139.2, 135.9, 132.9, 130.8, 128.9, 128.7, 128.5, 126.9, 116.7, 68.1, 54.3, 39.4 ppm; IR (KBr) ν 1770 (s), 1681 (m), 1615 (s), 1524 (s), 1449 (m), 1384 (s), 1347 (s), 1180 (m), 103 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{19}H_{17}N_2O_5$: 353.1137, found: [M+H] 353.1169.

(4*S*)-4-Benzyl-5,5-dimethyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (17) [10]



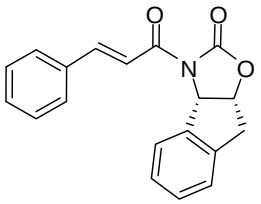
Oxazolidinone 17 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **IX** as a colorless solid (2.85 g, 85%). mp. 134°C; R_f 0.43 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{25}$ -63.0 (c 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 16.0 Hz, 1H), 7.87 (d, *J* = 16.0 Hz, 1H), 7.6-7.65 (m, 2H), 7.38-7.42 (m, 3H), 7.3-7.35 (m, 4H), 7.2-7.3 (m, 1H), 4.63 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.28 (dd, *J* = 14.2, 3.5 Hz, 1H), 2.93 (dd, *J* = 14.2, 9.7 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 152.8, 146.1, 137.1, 134.6, 130.6, 129.1, 128.9, 128.7, 128.6, 126.8, 117.4, 82.3, 63.9, 35.4, 28.6, 22.3 ppm; IR (KBr) ν 1772 (s), 1677 (m), 1621 (m), 1356 (s) 1277 (w), 1232 (w), 1102 (w), 1032 (w) cm^{-1}.

(4*S*,5*R*)-4-Benzyl-5-methyl-3-[(2*E*)-3-phenylprop-2-enoyl]-1,3-oxazolidin-2-one (19)



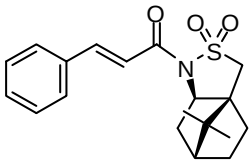
Oxazolidinone 19 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **X** as a colorless solid (2.70 g, 84%). Colorless solid. mp. 127°C; R_f 0.42 (4:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.0 Hz, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.6-7.64 (m, 2H), 7.39-7.44 (m, 3H), 7.3-7.37 (m, 4H), 7.2-7.28 (m, 1H), 4.91 (ddd, *J* = 9.0, 7.0, 3.0 Hz, 1H), 4.76 (dq, *J* = 7.0, 6.5 Hz, 1H), 3.18 (dd, *J* = 14.0, 3.0 Hz, 1H), 3.01 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 148.4, 146.2, 130.7, 129.3, 128.9, 128.7, 128.6, 126.7, 117.2, 75.2, 58.9, 33.9, 15.1 ppm; IR (KBr) ν 1767 (s), 1669 (m), 1614 (m), 1378 (m), 1356 (s), 1213 (m), 1031 (w), 764 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{20}NO_3$: 322.1443, found [M+H]: 322.1490.

(3a*S*,8a*R*)-3-[(2*E*)-3-phenylprop-2-enoyl]-3,3a,8,8a-tetrahydro-2*H*-indeno[1,2-*d*][1,3]oxazol-2-one 21



Oxazolidinone 21[9] was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **XI** as a colorless solid (2.53 g, 83%). mp. 179°C; R_f 0.48 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 279.1 (c 0.54, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 15.7 Hz, 1H), 7.92 (d, *J* = 15.7 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.61-7.64 (m, 2H), 7.27-7.41 (m, 6H), 6.07 (d, *J* = 6.9 Hz, 1H), 5.31-5.35 (m, 1H), 3.42 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 153.1, 146.5, 139.5, 139.2, 134.6, 130.7, 129.9, 128.9, 128.7, 128.2, 127.5, 125.2, 117.0, 78.1, 63.4, 38.0 ppm; IR (KBr) ν 2960 (s), 1770 (s), 1682 (s), 1621 (s), 1341 (s), 1193 (s), 1043 (s), 765 (m), 724 (m) 706 (w) cm^{-1}.

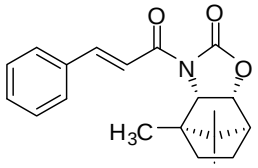
(3a*S*,6*R*,7a*R*)-8,8-dimethyl-1-[(2*E*)-3-phenylprop-2-enoyl]hexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (23) [11]



Sultame 23 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 2:1) yielded compound **23** as a colorless solid (2.9 g, 84%). mp. 189°C; R_f 0.48 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{25}$ -95.0 (c 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.56-7.61 (m, 2H), 7.36-7.41 (m, 3H), 7.17 (d, *J* = 16.0 Hz, 1H), 4.00 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 1H), 2.1- 2.24 (m, 2H), 1.86-1.98 (m, 3H), 1.34-1.5 (m, 2H), 1.21 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$)

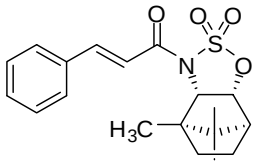
δ 164.3, 145.6, 134.3, 130.7, 128.9, 128.6, 117.4, 65.2, 53.2, 48.6, 47.8, 44.7, 38.5, 32.9, 26.6, 20.9, 19.9 ppm; IR (KBr) ν 2962 (m), 1776 (m), 1677 (s), 1625 (s), 1331 (s), 1207 (s), 1131 (m), 992 (w), 754 (m) 537 (s) cm^{-1}.

(3a*S*,4*R*,7*S*,7a*R*)-4,8,8-trimethyl-3-[(2*E*)-3-phenylprop-2-enoyl]hexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (32)



Oxazolidinone 32[3] was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **32** as a colorless solid (2.73 g, 84%).mp. 142°C; R_f 0.45 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 149.3 (c 0.9 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.6 Hz, 1H), 7.82 (d, *J* = 15.6, 1H), 7.60-7.65 (m, 2H), 7.36-7.42 (m, 3H), 4.55 (s, 2H), 2.19 (d, *J* = 5.0 Hz, 1H), 1.79-1.89(m, 1H), 1.54-1.63 (m, 1H), 1.24-1.33 (m, 1H), 1.04-1.11 (m, 1H), 1.06 (s, 3H), 0.98 (s, 3H) 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.9, 162.6, 146.0, 130.6, 128.8, 128.6, 117.6, 99.0, 81.4, 66.0, 50.3, 33.3, 22.9, 22.8, 19.7, 12.1 ppm; IR (KBr) ν 2956 (s), 1766 (s), 1678 (s), 1618 (s), 1574 (m), 1487 (m), 1445 (m), 1336 (m), 1226 (m) 1085 (m), 768 (s), 720 (s), 552 (w), 505 (w) cm^{-1}.

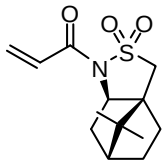
(3a*S*,4*R*,7*S*,7a*R*)-4,8,8-trimethyl-3-[(2*E*)-3-phenylprop-2-enoyl]hexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (34)



Sulfamidate 34 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 5:1) yielded compound **34** as a colorless solid (997

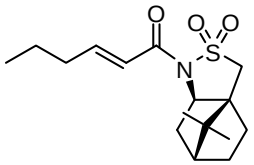
mg, 85%). mp. 169°C; R_f 0.39 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{25}$ -14.8 (c 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 15.3 Hz, 1H), 7.44-7.60 (m, 2H), 7.25-7.39 (m, 3H), 7.19 (d, *J* = 15.3 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 1H), 4.45 (d, *J* = 7.3 Hz, 1H), 2.17 (d, *J* = 4.8 Hz, 1H), 1.76- 1.9 (m, 1H), 1.45-1.62 (m, 1H), 1.16-1.3 (m, 1H), 1.14 (s, 3H), 0.96-1.04 (m, 1H), 0.90 (s, 3H), 0.84 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 147.4, 134.0, 131.1, 129.0, 128.8, 115.5, 84.1, 67.2, 50.8, 47.7, 47.6, 33.3, 26.9, 22.5, 22.3, 19.6, 11.7 ppm; IR (KBr) ν 2961 (m), 1693 (s), 1624 (s), 1370 (s), 1335 (m), 1222 (s), 1161 (m), 981 (w), 850 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{19}H_{24}NO_4S$: 362.1421, found: 362.1527

(3a*S*,6*R*,7a*R*)-1-acryloyl-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (36)
[12]



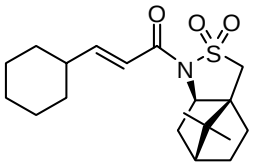
Sultame 36 was obtained according to **GP-II**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **36** as a colorless solid (716 mg, 88%). mp. 190°C; R_f 0.60 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -98.3 (c 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 16.6, 10.3 Hz, 1H), 6.50 (dd, *J* = 16.6, 1.3 Hz, 1H), 5.86 (dd, *J* = 10.3 Hz, *J* = 1.3 Hz, 1H), 3.94 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 13.8 Hz, 1H), 2.14 (m, 2H), 1.9 (m, 3H), 1.39 (s, 2H), 1.17 (m, 3H), 0.98 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 131.3, 127.8, 65.1, 53.1, 48.6, 47.8, 44.7, 38.4, 32.8, 26.5, 20.8, 19.9 ppm; IR (KBr) ν 2963 (s), 1674 (s), 1329 (s) 1273 (m), 1238 (m), cm^{-1}.

(3a*S*,6*R*,7a*R*)-1-[(2*E*)-hex-2-enoyl]-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (38)



Sultame 38 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **38** as a colorless solid (919 mg, 91%). mp. 95-98°C; R_f 0.59 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -93.9 (c 4.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dt, *J* = 15.1, 7.0 Hz, 1H), 6.55 (t, *J* = 15.1 Hz, 1H), 3.93 (dd, *J* = 7.5, 5 Hz, 1H), 3.51 (d, *J* = 13.8 Hz, 1H), 3.44 (d, *J* = 13.8 Hz, 1H), 2.06-2.28 (m, 3H), 1.84-2.0 (m, 3H), 1.34-1.56 (m, 4H), 1.18 (s, 3H), 0.97 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 150.7, 121.0, 65.2, 53.2, 48.5, 47.7, 44.7, 38.7 ppm; IR (KBr) ν 2964 (s), 1675 (s), 1637 (m), 1332 (s) 1236 (w), 1207 (w), 1133 (w), 1056 (w), 991 (w), 535 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{16}H_{26}NO_3S$: 312.1633, found : 312.1615.

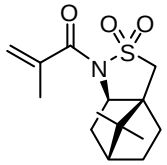
(3a*S*,6*R*,7a*R*)-1-[(2*E*)-3-cyclohexylprop-2-enoyl]-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (40)



Sultame 40 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **40** as a colorless solid (981 mg, 86%). mp. 131°C; R_f 0.61 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -56.26 (c 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 15.1, 7.3 Hz, 1H), 6.49 (dd, *J* = 15.1, 1.3 Hz, 1H), 3.92 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.50 (d, *J* = 13.6 Hz, 1H), 3.43 (d, *J* = 13.6 Hz, 1H), 2.04-2.22 (m, 2H), 1.84-1.96 (m, 3H), 1.7-1.82 (m, 4H), 1.62-1.7 (m, 1H), 1.12-1.46 (m, 8H), 1.17 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 155.7, 118.6, 65.4, 53.2, 48.5, 47.8, 44.8, 40.8, 38.7, 32.9, 31.7, 31.6, 36.5, 25.9,

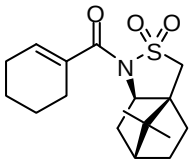
25.6, 20.9, 19.9 ppm; IR (KBr) ν 2927 (s), 1672 (s), 1631 (s), 1332 (s) 1235 (m), 1132 (m), 1059 (m), 991 (w), 760 (w), 543 (s) cm^{-1}; HRMS ($FAB^{+}HR$) calcd. for $C_{19}H_{29}NNaO_3S$: 374.1766, found : 374.1760.

(3a*S*,6*R*,7a*R*)-1-[(2*E*)-but-2-enoyl]-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (42) [13]



Sultame 42 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **42** as a colorless solid (2.43 g, 86%). mp. 145°C; R_f 0.62 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -95.6 (c 1.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 5.68-5.71 (m, 1H), 5.64-5.67 (m, 1H), 4.03 (dd, *J* = 7.5, 4.8 Hz, 1H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.39 (d, *J* = 13.6 Hz, 1H), 1.82-2.08 (m, 7H), 1.32-1.44 (m, 2H), 1.23 (s, 3H), 0.99 (s, 3H), ppm ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 139.1, 124.5, 65.5, 53.7, 48.3, 47.7, 38.5, 33.4, 26.6, 21.5, 20.0, 18.7 ppm; IR (KBr) ν 2959 (s), 1672 (s), 1633 (w), 1333 (s) 1194 (m), 1130 (m), 1115 (w), 1066 (w), 531 (m) cm^{-1}.

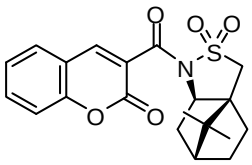
(3a*S*,6*R*,7a*R*)-1-(cyclohex-1-en-1-ylcarbonyl)-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (44)



Sultame 44 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **44** as a colorless solid (892 mg, 85%). mp. 129-130 °C; R_f 0.60 (3:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -44.3 (c 0.31, CH_2Cl_2); ^1H

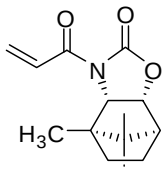
NMR (400 MHz, $CDCl_3$) δ 6.53-6.59 (m, 1H), 4.04 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.38 (d, *J* = 13.7 Hz, 1H), 2.42-2.50 (m, 1H), 2.22-2.30 (m, 1H), 2.08-2.20 (m, 2H), 2.03 (dd, *J* = 13.5, 7.7, 1H), 1.84-1.96 (m, 4H), 1.68-1.78 (m, 1H), 1.58-1.68 (m, 3H), 1.32-1.44 (m, 2H), 1.22 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 139.8, 133.3, 65.3, 53.6, 47.9, 47.7, 45.2, 38.3, 33.3, 26.5, 25.2, 24.3, 21.8, 21.4, 21.2, 19.9 ppm; IR (KBr) ν 2934 (s), 1669 (s), 1645 (m), 1455 (w), 1336 (s), 1165 (w), 1138 (m), 1052 (m), 925 (w), 767 (w), 532 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{17}H_{26}NO_3S$: 324.1633, found : 324.1613.

3-{[(3a*S*,6*R*,7a*R*)-8,8-dimethyl-2,2-dioxidotetrahydro-3a,6-methano-2,1-benzisothiazol-1(4*H*)-yl]carbonyl}-2*H*-chromen-2-one (46)



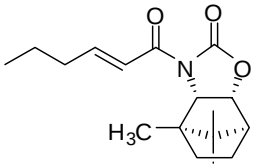
Sultame 46 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 2:1) yielded compound **46** as a colorless solid (943 mg, 75%). mp. 205°C; R_f 0.68 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -89.5 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.54-7.61 (m, 2H), 7.29-7.36 (m, 2H), 4.06 (dd, 6.53-6.59 (m, 1H), 4.04 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.49 (d, *J* = 14.0 Hz, 1H), 3.42 (d, *J* = 14.0 Hz, 1H), 2.15-2.23 (m, 1H), 2.14 (dd, *J* = 14.0, 7.7Hz, 1H), 1.88-1.98 (m, 3H), 1.36-1.45 (m, 2H), 1.29 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6, 164.2, 159.6, 146.2, 145.1, 134.8, 130.6, 126.3, 119.5, 66.3, 54.4, 46.2, 39.3, 34.3, 28.1, 22.2, 21.4 ppm; IR (KBr) ν 2958 (w), 1736 (s), 1682 (m), 1608 (w) 1334 (m), 1274 (w), 1244 (w), 1137 (w), 1074 (w), 762 (w), 535 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{22}NO_5S$: 388.1219, found : 388.1199.

(3a*S*,4*R*,7*S*,7a*R*)-3-acryloyl-4,8,8-trimethylhexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (48)



Oxazolidinone 48[3] was obtained according to **GP-II**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **48** as a colorless solid (665 mg, 89%). mp. 94°C; R_f 0.34 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 82.4 (c 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 17.0, 10.4 Hz, 1H), 6.48 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.84 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.5 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 2.14 (d, *J* = 5.1 Hz, 1H), 1.71-1.87 (m, 1H), 1.48-1.60 (m, 1H), 1.15-1.29 (m, 1H), 0.94-1.08 (m, 1H), 0.99 (s, 3H), 0.91 (s, 3H), 0.87 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 154.8, 131.7, 127.7, 81.3, 69.7, 50.0, 47.5, 46.3, 33.1, 22.2, 19.5, 11.9 ppm; IR (KBr) ν 1787 (m), 1758 (s), 1695 (s), 1616 (w) cm^{-1}

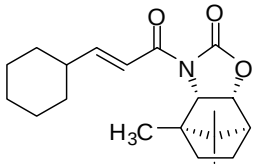
(3a*S*,4*R*,7*S*,7a*R*)-3-[(2*E*)-hex-2-enoyl]-4,8,8-trimethylhexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (50)



Oxazolidinone 50 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 5:1) yielded compound **50** as a colorless oil (2.36 g, 81%). R_f 0.44 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 45.0 (c 0.3, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 15.3 Hz, 1H), 7.11 (dt, *J* = 15.3, 6.8 Hz, 1H), 4.50 (d, *J* = 8 Hz, 1H), 4.47 (d, *J* = 8 Hz, 1H), 2.21-2.28 (m, 2H), 2.16 (d, *J* = 5.3 Hz, 1H), 1.76-1.87 (m, 1H), 1.46-1.64 (m, 3H), 1.20-1.29 (m, 1H), 0.99-1.09 (m, 1H), 1.03 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.94 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 155.0, 151.1, 120.8, 81.2, 65.7, 50.1, 47.6, 46.4, 34.6, 33.2, 22.8, 22.7, 21.3, 19.6, 13.7, 12.1 ppm; IR (KBr) ν 2960 (m), 1775 (s), 1687 (m), 1635 (s) 1384 (w), 1193 (m), 1056 (w)

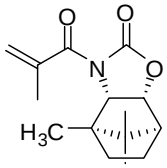
cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{17}H_{29}NO_3$: 292.1913, found: 292.1930.

(3a*S*,4*R*,7*S*,7a*R*)-3-[(2*E*)-3-cyclohexylprop-2-enoyl]-4,8,8-trimethylhexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (52)



Oxazolidinone 52 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 5:1) yielded compound **52** as a colorless solid (2.71 g, 82%). mp. 45°C; R_f 0.46 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 35.0 (c 0.81, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 15.6 Hz 1H), 7.05 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.5 (d, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 8.0 Hz, 1H), 2.18-2.26 (m, 1H), 2.16 (d *J* = 5 Hz, 1H), 1.72-1.86 (m, 5H), 1.62-1.7 (m, 1H), 1.52-1.61 (m, 3H), 1.12-1.34 (m, 7H), 0.98-1.07 (m, 1H), 1.03 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 156.0, 155.0, 151.0, 121.3, 118.5, 81.2, 65.8, 47.7, 40.9, 33.3, 31.7, 26.0, 25.6, 21.5, 21.4, 12.1 ppm; IR (KBr) ν 2929 (s), 2852 (m), 1779 (s), 1688 (s), 1632 (s), 1449 (m), 1339 (m), 1279 (m), 1194 (m), 1057 (m), 762 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{30}NO_3$: 332.2226, found: 332.2241.

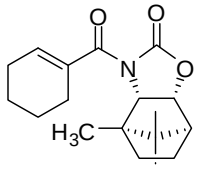
(3a*S*,4*R*,7*S*,7a*R*)-3-methacryloyl-4,8,8-trimethylhexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (54)



Oxazolidinone 54 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **54** as a colorless solid (1.99 g, 76%). mp. 99°C; R_f 0.34 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 29.2 (c 0.75, $CHCl_3$); ^{1}H NMR (400

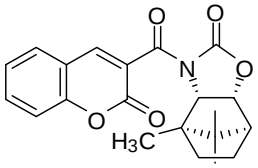
MHz, $CDCl_3$) δ 5.44 (bs, 2H), 4.53 (d, *J* = 8.3 Hz, 1H), 4.51 (d, *J* = 8.3 Hz, 1H), 2.19 (d, *J* = 5 Hz, 1H), 2.03 (s, 3H), 1.77-1.87 (m, 1H), 1.52-1.62 (m, 1H), 1.2-1.29 (m, 1H), 1.01-1.10 (m, 1H), 1.08 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 154.1, 139.9, 120.6, 81.5, 64.9, 49.7, 47.6, 46.5, 33.0, 22.7, 22.6 19.6, 18.8, 11.5 ppm; IR (KBr) ν 2953 (w), 1769 (s), 1689 (s), 1386 (w) 1319 (w), 1198 (m), 1055 (w), 1022 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{15}H_{22}NO_3$: 264.1600, found: 264.1609.

(3a*S*,4*R*,7*S*,7a*R*)-3-(cyclohex-1-en-1-ylcarbonyl)-4,8,8-trimethylhexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (56)



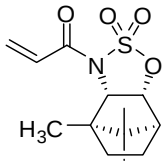
Oxazolidinone 56 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 5:1) yielded compound **56** as a colorless solid (2.39 g, 79%). mp. 57.5°C ; R_f 0.43 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 21.5 (c = 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.32-6.36 (m, 1H), 4.56 (d, *J* = 8.3 Hz, 1H), 4.49 (d, *J* = 8.3 Hz, 1H), 2.52 (d, *J* = 15.1 Hz, 1H), 2.18-2.26 (m, 2H), 2.17 (d, *J* = 5.3 Hz, 1H), 2.02-2.11 (m, 1H), 1.76-1.87 (m, 1H), 1.62-1.76 (m, 4H), 1.5-1.6 (m, 1H), 1.18-1.28 (m, 1H), 1.08 (s, 3H), 1.0 (m, 1H), 0.9 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 154.4, 136.5, 133.6, 81.4, 65.0, 49.6, 47.7, 46.6, 33.0, 25.4, 24.8, 22.9, 22.7, 21.8, 21.4, 19.4, 11.6 ppm; IR (KBr) ν 3417 (s), 2959 (w), 1774 (s), 1686 (m), 1384 (w), 1281 (m), 1195 (m), 1051 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{18}H_{25}NO_3$: 303.1834, found: 303.1824.

(3a*S*,4*R*,7*S*,7a*R*)-4,8,8-trimethyl-3-[(2-oxo-2*H*-chromen-3-yl)carbonyl]hexahydro-4,7-methano-1,3-benzoxazol-2(3*H*)-one (58)



Oxazolidinone 58 was obtained according to **GP-I**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 3:1) yielded compound **58** as a colorless solid (2.31 g, 63%). mp. 178.3°C; R_f 0.25 (4:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 35.2 (c 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.56-7.61 (m, 1H), 7.53 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.28-7.32 (m, 1H), 4.6 (d *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 7.5 Hz, 1H), 2.21 (d, *J* = 5 Hz, 1H), 1.82-1.92 (m, 1H), 1.58-1.67 (m, 1H), 1.24-1.32 (m, 1H), 1.17 (s, 3H), 1.10 (s, 3H), 1.03-1.10 (m, 1H), 0.94 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 163.8, 161.3, 155.3, 149.3, 134.5, 133.1, 129.6, 124.9, 118.1, 117.0, 77.2, 60.4, 53.2, 53.0, 52.1, 26.9, 22.7, 21.1, 14.2, 10.6 ppm; IR (KBr) ν 2956 (w), 2926 (w), 1728 (s), 1699 (s), 1609 (s), 1566 (m), 1244 (m), 1004 (w), 756 (s) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{21}H_{22}NO_5$: 368.1498, found : 368.1460.

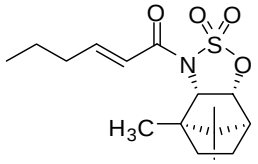
(3a*S*,4*R*,7*S*,7a*R*)-3-acryloyl-4,8,8-trimethylhexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (60)



Sulfamidate 60 was obtained according to **GP-II**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) yielded compound **60** as a colorless solid (735 mg, 86%). mp. 67°C; R_f 0.38 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -8.0 (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 16.8, 10.4 Hz, 1H), 6.58 (dd, *J* = 16.8, 1.4 Hz, 1H), 5.97 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 1H), 4.47 (d, *J* = 7.2 Hz, 1H), 2.22 (d, *J* = 5.3 Hz, 1H), 1.85-1.99 (m, 1H), 1.56-1.69 (m, 1H), 1.23-1.36 (m, 1H), 1.19 (s, 3H), 0.95-1.05 (m, 1H), 0.95 (s, 3H), 0.92 (s, 3H) ppm;

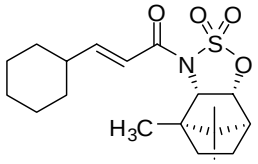
^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 133.2, 126.1, 84.2, 67.3, 50.8, 47.7, 47.6, 33.3, 22.5, 22.3, 19.6, 11.6 ppm; IR (KBr) ν 2969 (m), 1699 (s), 1364 (s), 1317 (s), 1232 (s) 1161 (s), 859 (w) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{13}H_{20}NO_4S$: 286.1108, found: 286.1114

(3a*S*,4*R*,7*S*,7a*R*)-3-[(2*E*)-hex-2-enoyl]-4,8,8-trimethylhexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (62)



Sulfamidate 62 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 8:1) yielded compound **62** as a colorless oil (946 mg, 89%). R_f 0.44 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 14.75 (c 0.6, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (dt, *J* = 15.2, 6.9 Hz, 1H), 6.65 (dt, *J* = 15.2, 1.5 Hz, 1H), 4.76 (d, *J* = 7.3 Hz, 1H), 4.46 (d, *J* = 7.3 Hz, 1H), 2.2-2.45 (m, 3H), 1.84-1.98 (m, 1H), 1.46-1.68 (m, 3H), 1.22-1.35 (m, 1H), 1.19 (s, 3H), 1.04-1.15 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.94 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 153.8, 119.2, 83.9, 67.1, 50.6, 47.6, 47.5, 34.6, 33.3, 22.5, 22.3, 21.6, 19.6, 13.7, 11.6 ppm; IR (KBr) ν 2962 (m), 1700 (s), 1372 (s), 1290 (s) 1165 (m), 981 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{16}H_{26}NO_4S$: 328.1577, found: 328.1569

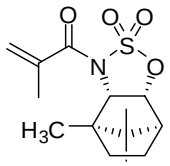
(3a*S*,4*R*,7*S*,7a*R*)-3-[(2*E*)-3-cyclohexylprop-2-enoyl]-4,8,8-trimethylhexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (64)



Sulfamidate 64 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 8:1) yielded compound **64** as a colorless solid (1.09

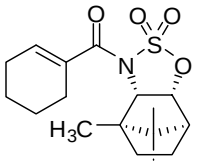
g, 91%). mp. 132°C; R_f 0.47 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 14.3 (c 1.2, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 15.1, 6.9 Hz, 1H), 6.90 (dd, *J* = 15.1, 1.3 Hz 1H), 4.76 (d, *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 7.5 Hz, 1H), 2.15-2.29 (m, 1H), 2.22 (d *J* = 5.3 Hz, 1H), 1.5-1.98 (m, 7H), 1.04-1.84 (m, 7H), 1.19 (s, 3H), 1.52-1.61 (m, 3H), 0.93 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 157.6, 116.8, 83.9, 67.2, 50.7, 47.6, 47.5, 40.9, 33.3, 31.5, 31.4, 25.8, 25.6, 22.5, 22.3, 19.6, 11.6 ppm; IR (KBr) ν 2926 (s), 1699 (s), 1635 (s), 1369 (s), 1260 (s), 1162 (s), 853 (s) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{19}H_{30}NO_4S$: 368.1690, found: 368.1698

(3a*S*,4*R*,7*S*,7a*R*)-3-methacryloyl-4,8,8-trimethylhexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (66)



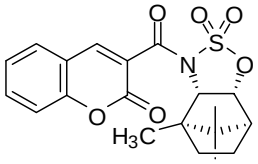
Sulfamidate 66 was obtained according to **GP-II**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 8:1) yielded compound **66** as a colorless solid (2.57 g, 86%). mp. 153°C; R_f 0.39 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -21.4 (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, *J* = 17.4 Hz, 2H), 4.65 (d, *J* = 7.4 Hz, 1H), 4.53 (d, *J* = 7.4 Hz, 1H), 2.16 (d, *J* = 5.4 Hz, 1H), 1.94 (s, 3H), 1.77-1.90 (m, 1H), 1.49-1.61 (m, 1H), 1.17-1.26 (m, 1H), 1.15 (s, 3H), 0.98-1.1 (m, 1H), 0.85 (s, 3H), 0.81 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 136.7, 126.2, 83.1, 66.7, 50.1, 47.8, 47.5, 33.1, 22.6, 22.3 19.3, 18.8, 10.9 ppm; IR (KBr) ν 2959 (w), 1749 (s), 1369 (s), 1202 (s) 1146 (w), 971 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{14}H_{22}NO_4S$: 300.1264, found: 300.1270

(3a*S*,4*R*,7*S*,7a*R*)-3-(cyclohex-1-en-1-ylcarbonyl)-4,8,8-trimethylhexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazole 2,2-dioxide (68)



Sulfamidate 68 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 5:1) yielded compound **68** as a colorless solid (926 mg, 84%). mp. 87°C ; R_f 0.41 (8:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 35.8 (c = 1.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (bs, 1H), 4.69 (d, *J* = 7.5 Hz, 1H), 4.61 (d, *J* = 7.5 Hz, 1H), 2.5 (d, *J* = 16 Hz, 1H), 2.02-2.40 (m, 3H), 2.21 (d, *J* = 5.2 Hz, 1H), 1.82-1.97 (m, 1H), 1.55-1.8 (m, 5H), 1.2-1.34 (m, 1H), 1.23 (s, 3H), 1.04-1.16 (m, 1H), 0.92 (s, 3H), 0.87 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 142.1, 130.9, 82.9, 66.3, 49.9, 47.8, 47.5, 33.1, 25.4, 24.4, 22.7, 22.3, 21.7, 21.2, 19.3, 10.9 ppm; IR (KBr) ν 2958 (m), 1696 (s), 1373 (s), 1238 (m), 1179 (m), 971 (m), 844 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{17}H_{26}NO_4S$: 340.1577, found: 340.1563

3-{[(3a*S*,4*R*,7*S*,7a*R*)-4,8,8-trimethyl-2,2-dioxidohexahydro-3*H*-4,7-methano-1,2,3-benzoxathiazol-3-yl]carbonyl}-2*H*-chromen-2-one (70)

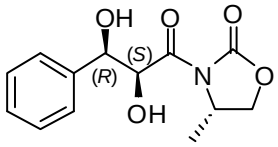


Sulfamidate 70 was obtained according to **GP-III**. Purification of the crude product by column chromatography (SiO_2, petroleum ether/ethyl acetate 3:1) yielded compound **70** as a colorless solid (1.06 g, 81%). mp. 193°C; R_f 0.45 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 69.7 (c 0.59, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 7.90 (s, 1H), 7.47-7.60 (m, 2H), 7.21-7.34 (m, 2H), 4.74 (d *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 7.5 Hz, 1H), 2.19 (d, *J* = 5.2 Hz, 1H), 1.8-1.96 (m, 1H), 1.53-1.67 (m, 1H), 1.15-1.3 (m, 1H), 1.21 (s, 3H), 1.0-1.13 (m, 1H) 1.01 (s, 3H), 0.88 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 161.3, 152.5, 142.7, 131.7, 127.1, 122.7, 119.0, 115.2, 114.9, 82.1, 64.7, 48.8, 45.5, 45.4, 31.0, 20.4, 20.1, 17.3, 9.4

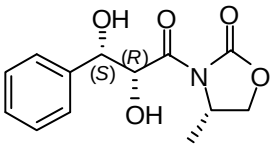
ppm; IR (KBr) ν 2964 (w), 1737 (s), 1706 (s), 1373 (s), 1266 (m), 1242 (m), 1185 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{20}H_{22}NO_6S$: 404.1162, found: 404.1174

IV Dihydroxylation

General Procedure for Dihydroxylations (GP-IV). In a 50-mL round-bottomed flask equipped with magnetic stirring bar and overpressure valve $NaIO_4$ (642 mg, 3 mmol) and $CeCl_3 \cdot 7H_2O$ (149.2 mg. 0.4 mmol, 20 mol%) were stirred in H_2O (0.8 mL) and gently heated until a bright yellow suspension was formed. After cooling to 0°C acetonitrile (6 mL) was added and the suspension was stirred for 2 min. A 0.1 M aqueous solution of $RuCl_3$ (200 µL, 0.02 mmol) was added and the mixture was stirred for 2 min. The olefin (2 mmol) was added in one portion and the resulting slurry was stirred until all starting material was consumed. Solid Na_2SO_4 (2 g) was added followed by ethyl acetate (12 mL). The solids were filtered off and the filtercake was washed several times with ethyl acetate. The filtrate was washed with sat. Na_2SO_3-solution (6 mL), the organic layer was dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash-chromatography. A separation of the diastereomers was done using preparative HPLC (Nucleosil 100-10) under the given conditions.



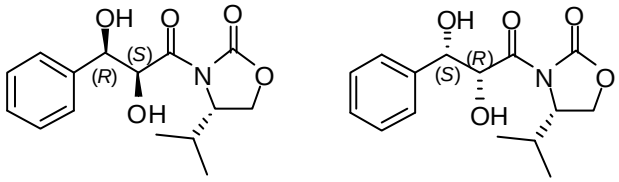
2-A



2-B

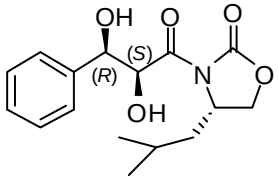
Diol 2-A and 2-B. Olefin **1** was oxidized according to **GP-IV** to give the desired diol as a mixture of two diastereomers **2-A : 2-B** (1.6 : 1.0, ^{1}H NMR integration, combined yield 472 mg, 89%), that were separated by HPLC. **2-B**. colorless oil; R_f 0.50 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.53 (m, 2H), 7.25-7.42 (m, 3H), 5.38 (dd, *J* = 7.1, 2.1 Hz, 1H), 5.17 (dd, *J* = 7.3, 1.7 Hz, 1H), 4.49-4.63 (m, 1H), 4.44 (dd, *J* = 8.5, 7.7 Hz, 1H), 4.07 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.63 (d, *J* = 7.3 Hz, 1H), 2.77 (d, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 6.3 Hz, 3H) ppm. **2-A**. colorless oil; R_f 0.49 (1:1 *iso*-

hexanes/ethyl acetate); $[\alpha]_D^{20}$ 62.6 (c 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.52 (m, 2H), 7.26-7.42 (m, 3H), 5.35 (dd, *J* = 7.2, 2.7 Hz, 1H), 5.07 (dd, *J* = 7.2, 2.2 Hz, 1H), 4.6-4.75 (m, 1H), 4.58 (dd, *J* = 8.4 Hz, 1H), 4.08 (dd, *J* = 8.4, 4.3 Hz, 1H), 3.53 (d, *J* = 7.2 Hz, 1H), 2.67 (d, *J* = 7.6 Hz, 1H), 1.47 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 153.4, 140.1, 128.4, 127.9, 126.1, 74.3, 73.7, 69.9, 50.6, 19.0 ppm; IR (KBr) ν 3462 (s), 1773 (s), 1697 (m), 1389 (m), 1340 (m), 1207 (m), 1130 (m), 701 (w) cm^{-1}; HRMS (ESI-HR) calcd. for $C_{13}H_{15}NNaO_5$: 288.0848, found: 288.0842.

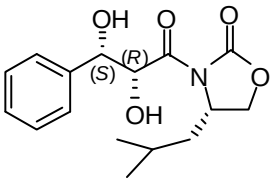


4-A **4-B**

Diol 4-A and 4-B. Olefin **3** was oxidized according to **GP-IV** to give the desired diol as a mixture of two diastereomers **4-A : 4-B** (2.6 : 1.0, ^1H NMR integration, combined yield 440 mg, 75%), that were separated by HPLC. **4-B**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 5.41 (d, *J* = 1.8 Hz, 1H), 5.23 (d, *J* = 2.3 Hz, 1H), 4.56 (ddd, *J* = 8.5, 4.0, 1H), 4.44 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.34 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.37 (dqq, *J* = 7.0, 4.0 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H) ppm ppm. **4-A**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 63.3 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 5.37 (d, *J* = 3.0 Hz, 1H), 5.07 (d, *J* = 3.0 Hz, 1H), 4.40 (ddd, *J* = 6.5, 4.0, 1H), 4.24 (m, 2H), 2.48 (dqq, *J* = 7.0, 4.0 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 153.9, 139.8, 128.9, 128.3, 126.3, 74.2, 73.7, 64.3, 59.2, 28.1, 18.0, 14.5 ppm; IR (KBr) ν 3477 (s), 2966 (w), 1777 (s), 1697 (m), 1385 (s), 1207 (m), 1114 (m), 1051 (m), 711 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{15}H_{19}NO_5$: 293.1263, found: 293.1246.

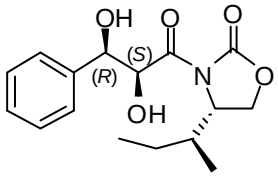


6-A

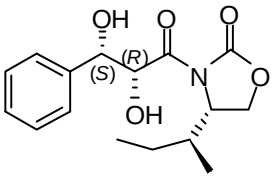


6-B

Diol 6-A and 6-B. Olefin **5** was oxidized according to **GP-IV** to give the desired diol as a mixture of two diastereomers **6-A : 6-B** (2.0 : 1.0, ^{1}H NMR integration, combined isolated yield 504 mg, 82%), that were separated by HPLC. **6-B**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 2H) 7.37 (dd, *J* = 7.7, 7.2 Hz, 2H), 7.3 (dd, *J* = 7.5, 7.2 Hz, 1H), 5.37 (dd, *J* = 6.7, 1.7 Hz, 1H), 5.18 (d, *J* = 5.7 Hz, 1H), 4.61 (m, 1H), 4.54 (dd, *J* = 8.7, 8.2 Hz, 1H), 4.22 (dd, *J* = 8.7, 3.7 Hz, 1H), 3.53 (d, *J* = 7 Hz, 1H), 2.63 (d, *J* = 7.7 Hz, 1H), 1.84 (m, 1H), 1.64 (m, 1H), 1.52 (ddd, *J* = 10.0, 5.0, 3.5 Hz, 1H), 0.99 (d, *J* = 6.5 Hz, 6H) ppm. **6-A**. colorless oil; R_f 0.57 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 19.3 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 5.33 (dd, *J* = 6.5, 2.5 Hz, 1H), 5.06 (bs, 1H), 4.44-4.51 (m, 1H), 4.38 (dd, *J* = 8.5, 7.5 Hz, 1H), 4.2 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.64 (d, *J* = 7.0 Hz, 1H), 2.76 (s, 1H), 1.84 (ddq, *J* = 9.0, 6.5, 3.0 Hz, 1H), 1.5-1.7 (m, 2H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 153.5, 140.3, 128.4, 127.8, 126.1, 74.3, 73.6, 68.8, 53.1, 41.7, 24.8, 23.3, 21.5 ppm; IR (KBr) ν 3442 (s), 2961 (m), 1778 (s), 1620 (m), 1384 (s), 1180 (s), 1031 (s) cm^{-1}; HRMS (FAB^{+}HR) calcd. for $C_{16}H_{21}NO_5$: 307.1420, found: 307.1403.

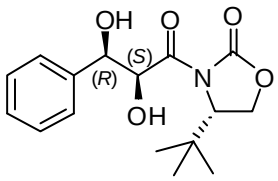


8-A

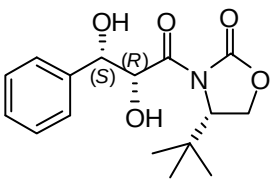


8-B

Diol 8-A and 8-B. Olefin **7** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **8-A : 8-B** (2.6 : 1.0, ^{1}H NMR integration, combined isolated yield 375 mg, 61%), that were separated by HPLC. **8-B**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H) 7.37 (dd, *J* = 7.7, 7.2 Hz, 2H), 7.31 (dd, *J* = 7.5, 7.2 Hz, 1H), 5.4 (s, 1H), 5.2 (s, 1H), 4.51 (ddd, *J* = 8.5, 3.5, 3.2 Hz, 1H), 4.27 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.21 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.50 (s, 1H), 2.6 (s, 1H), 2.27 (m, 1H), 1.15-1.4 (m, 2H) 0.98 (t, 3H), 0.88 (d, 3H) ppm. **8-A**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 61.0 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.7, 7.2 Hz, 2H), 7.31 (dd, *J* = 7.5, 7.2 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 1H), 5.08 (d, *J* = 2.5 Hz, 1H), 4.51 (ddd, *J* = 8.5, 3.5, 3.2 Hz, 1H), 4.27 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.21 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.69 (s, 1H), 2.80 (s, 1H), 2.27 (dddq, *J* = 7.0, 5.5, 3.5, 1.8 Hz, 1H), 1.32 (ddq, *J* = 13.3, 7.5, 5.5 Hz, 1H), 1.23 (ddq, *J* = 13.3, 7.2, 1.8 Hz, 1H,), 0.98 (t, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 153.9, 139.9, 128.3, 128.0, 126.3, 74.2, 73.6, 64.2, 58.2, 34.5, 25.5, 11.7, 11.6, ppm; IR (KBr) ν 3495 (s), 2950 (m), 1788 (s), 1764 (s), 1697 (s), 1385 (s), 1365 (w), 1218 (m), 1112 (m), 1014 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{16}H_{21}NO_5$: 307.1420, found: 307.1452.



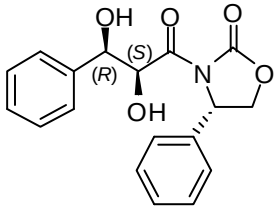
10-A



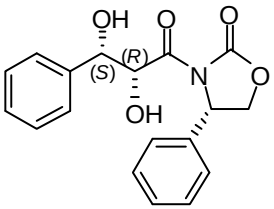
10-B

Diol 10-A and 10-B. Olefin **9** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **10-A : 10-B** (3.7 : 1.0, ^{1}H NMR integration, combined isolated yield 375 mg, 61%), that were separated by HPLC. **10-B**. colorless oil; R_f 0.59 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 7.5, 7.2 Hz,

1H), 5.38 (dd, *J* = 6.5, 1.5 Hz, 1H), 5.32 (d, *J* = 8.7 Hz, 1H), 4.57 (dd, *J* = 7.3, 2.7 Hz, 1H), 4.37-4.44 (m, 2H), 3.56 (d, *J* = 6.5 Hz, 1H), 2.62 (d, *J* = 8.7 Hz, 1H), 1.0 (s, 9H) ppm; **10-A**. colorless oil; R_f 0.61 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -13.0 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* =7.5 Hz, 2H), 7.31 (dd, *J* = 7.5, 7.2 Hz, 1H), 5.39 (dd, *J* = 7.0, 3.0 Hz, 1H), 5.08 (bs, 1H), 4.51 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.25 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.95 (dd, *J* = 14.5, 9.5 Hz, 1H), 2.69 (s, 1H), 1.39 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 147.3, 135.5, 128.4, 127.8, 125.9, 74.6, 73.9, 66.3, 61.3, 29.7, 25.4 ppm; IR (KBr) ν 3441 (s), 2989 (w), 1778 (s), 1633 (s), 1385 (s), 1193 (m), 1031 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{16}H_{21}NO_5$: 307.1420, found: 307.1500.



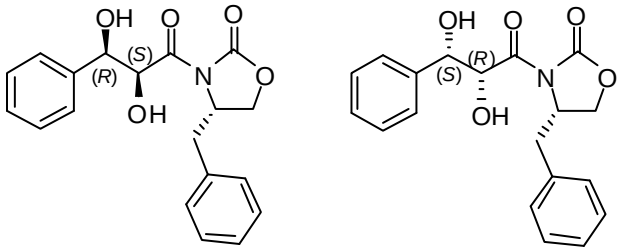
12-A



12-B

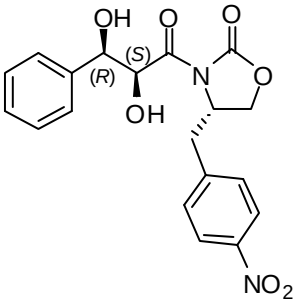
Diol 12-A and 12-B. Olefin **11** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **12-A : 12-B** (2.3 : 1.0, ^{1}H NMR integration, combined isolated yield 425 mg, 65%), that were separated by HPLC. **12-B.** colorless oil; R_f 0.58 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.47 (m, 10H), 5.26 (bs, 1H), 5.23 (dd, *J* = 10.5, 5.3 Hz, 1H), 4.89 (d, *J* = 2.0 Hz, 1H), 4.66 (dd, *J* = 12.0, 10.5 Hz, 1H), 4.02 (dd, *J* = 12.0, 5.3 Hz, 1H) ppm. **12-A.** colorless solid mp. 170°C; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 20.0 (c 0.12, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.46 (m, 10H), 5.56 (dd, *J* = 8.8, 5.3 Hz, 1H), 5.44 (dd, *J* = 7.3, 2.0 Hz, 1H), 5.25 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.85 (dd, *J* = 9.3, 8.8 Hz, 1H), 4.39 (dd, *J* = 9.0, 5.3 Hz, 1H), 3.40 (d, *J* = 7.5 Hz, 1H), 2.45 (d, *J* = 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 156.3, 129.4, 129.1, 128.3, 127.9, 126.1, 125.9, 82.3, 74.4, 73.7, 70.9 ppm; IR (KBr) ν 3143 (m), 2974 (m), 1670 (s), 1611

(s), 1554 (m), 1404 (s), 1288 (m), 1191 (w), 985 (w), 875 (w) cm^{-1}; HRMS ($FAB^{+}HR$) calcd. for $C_{18}H_{16}NO_4$: 310.1074, found: 310.1077.

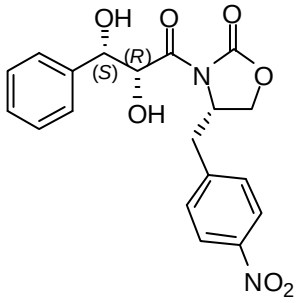


14-A **14-B**

Diol 14-A and 14-B. Olefin **13** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **14-A : 14-B** (1.6 : 1.0, ^1H NMR integration, combined isolated yield 457 mg, 67%), that were separated by HPLC. **14-B.** colorless oil; R_f 0.60 (1:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.52 (m, 2H), 7.24-7.4 (m, 6H), 7.16-7.22 (m, 2H), 5.37 (s, 1H), 5.22 (s, 1H), 4.84 (m, 1H), 4.38 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.31 (dd, *J* = 9.0, 4 Hz, 1H), 3.26 (dd, *J* = 14.0, 3.0 Hz, 1H), 2.92 (dd, *J* = 14.0, 9.0 Hz, 1H) ppm. **14-A**. colorless oil; R_f 0.61 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 85.8 (c 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.52 (m, 2H), 7.24-7.4 (m, 6H), 7.16-7.22 (m, 2H), 5.37 (s, 1H), 5.09 (d, *J* =1,8 Hz, 1H), 4.62-4.71 (m, 1H), 4.20-4.28 (m, 2H), 3.70 (s, 1H), 3.36 (dd, *J* = 13.3, 2.7 Hz, 1H), 2.85 (dd, *J* = 13.3, 9.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 153.4, 140.3, 134.6, 129.7, 129.2, 128.5, 128.0, 127.7, 126.3, 74.5, 73.4, 67.3, 55.0, 37.9 ppm; IR (KBr) ν 3528 (s), 3476 (s), 1799 (s), 1685 (s), 1384 (s), 1198 (m), 1123 (m), 706 (m) cm^{-1}; HRMS (ESI-HR) calcd. for $C_{19}H_{20}NO_5$: 342.1341, found : 342.1336.

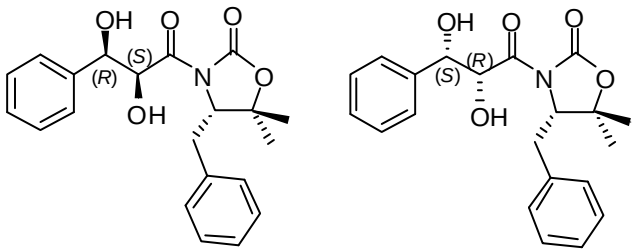


16-A



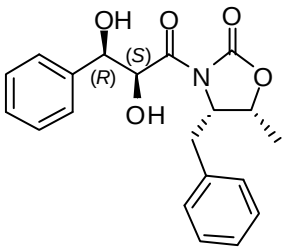
16-B

Diol 16-A and 16-B. Olefin **15** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **16-A : 16-B** (2.1 : 1.0, ^{1}H NMR integration, combined isolated yield 409 mg, 53%), that were separated by HPLC. **16-B**. colorless oil; R_f 0.30 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H) 7.52 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.4 (dd, *J* = 7.7, 7.5 Hz, 2H), 7.32 (dd, *J* = 7.5, 7.0 Hz, 1H), 5.36 (bs, 1H), 5.22 (s, 1H), 4.89 (m, 1H), 4.45 (dd, *J* = 9.0, 8.7 Hz, 1H), 4.25 (dd, *J* = 9.0, 3.7 Hz, 1H), 3.53 (d, *J* = 6 Hz, 1H), 3.32 (dd, *J* = 14.0, 3.5 Hz, 1H), 3.12 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.71 (bs, 1H) ppm. **16-A**. colorless oil; R_f 0.31 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 81.4 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.4 (dd, *J* = 7.7, 7.5 Hz, 2H), 7.32 (dd, *J* = 7.5, 7.0 Hz, 1H), 5.37 (dd, *J* = 6.7, 3.2 Hz, 1H), 5.09 (d, *J* = 2.2 Hz, 1H), 4.71 (dddd, *J* = 9.2, 7.5, 3.2, 2.2 Hz, 1H), 4.29 (dd, *J* = 9.2, 7.5 Hz, 1H), 4.21 (dd, *J* = 9.2, 2.2 Hz, 1H), 3.65 (d, *J* = 7.0 Hz, 1H), 3.45 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.03 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.79 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 139.6, 136.8, 135.5, 130.2, 128.4, 128.1, 126.3, 124.2, 122.8, 74.3, 73.9, 66.9, 55.3, 37.1 ppm; IR (KBr) ν 3427, (s), 1778 (s), 1685 (m), 1624 (m), 1515 (s), 1384 (s), 1351 (s), 1218 (m), 1109 (m) cm^{-1}; HRMS (FAB^{+}HR) calcd. for $C_{19}H_{16}N_2O_6$: 368.0961, found: 367.9921.

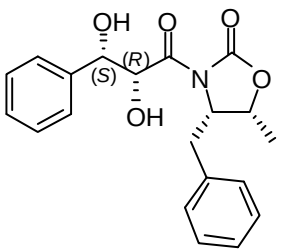


18-A **18-B**

Diol 18-A and 18-B. Olefin **17** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **18-A : 18-B** (1.0 : 1.0, ^{1}H NMR integration, combined isolated yield 576 mg, 78%), that were separated by HPLC. **18-B**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.2 -7.4 (m, 8H), 5.39 (dd, *J* = 7.0, 2.5 Hz, 1H), 5.08 (dd, *J* = 7.0, 2.0 Hz, 1H), 4.51 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.63 (d, *J* = 7.5 Hz, 1H), 3.24 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.95 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.75 (d, *J* = 7.0 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 152.6,139.9, 136.7, 129.1, 128.9, 128.5, 128.1, 127.1, 126.4, 84.1, 74.3, 73.8, 64.4, 35.1, 28.5, 22.3 ppm. **18-A**. colorless oil; R_f 0.63 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –17.0 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.25-7.4 (m, 8H), 5.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 4.65 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.47 (d, *J* = 8.0 Hz, 1H), 3.19 (dd, *J* = 14.5, 4.5 Hz, 1H), 2.94 (dd, *J* = 14.5, 9 Hz, 1H), 2.3 (d, *J* = 7.0 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 152.4, 140.1, 136.3, 129.1, 128.7, 128.3, 127.8, 127.0, 126.0, 83.9, 74.5, 73.4, 63.4, 35.3, 28.6, 22.4 ppm; IR (KBr) ν 3493 (s), 1789 (s), 1687 (m), 1385 (s), 1357 (m), 1219 (m), 1128 (m), 730 (m), 698 (m) cm^{-1}; HRMS (FAB^{+}HR) calcd. for $C_{21}H_{23}NO_5$: 369.1576, found: 369.1583.

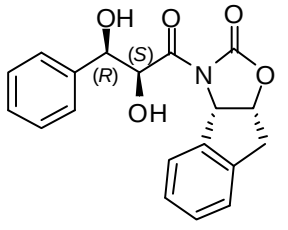


20-A

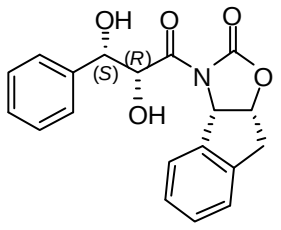


20-B

Diol 20-A and 20-B. Olefin **19** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **20-A : 20-B** (1.6 : 1.0, ^{1}H NMR integration, combined isolated yield 575 mg, 81%), that were separated by HPLC. **20-B**. colorless oil; R_f 0.63 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 2H) 7.25-7.4 (m, 8H), 5.30 (d, *J* = 3.2 Hz, 1H), 5.12 (bs, 1H), 4.95 (ddd, *J* = 8.7, 6.7, 5.0 Hz, 1H), 4.85 (m, 1H), 3.42 (d, *J* = 7.2 Hz, 1H), 3.1 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.03 (dd, *J* = 14.5, 8.7 Hz, 1H), 2.22 (s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H) ppm. **20-A**. colorless oil; R_f 0.64 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –17.0 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.2-7.4 (m, 8H), 5.3 (dd, *J* = 8.2, 1.7 Hz, 1H), 5.12 (d, *J* = 5.2 Hz, 1H), 4.94 (ddd, *J* = 8.7, 6.7, 5.0 Hz, 1H), 4.84 (dq, *J* = 6.7, 6.5 Hz, 1H), 3.46 (d, *J* = 8.2 Hz, 1H), 3.09 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.02 (dd, *J* = 14.5, 8.7 Hz, 1H), 2.39 (d, *J* = 6.7 Hz, 1H), 1.43 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 152.9, 140.1, 136.0, 128.7, 128.3, 127.8, 127.1, 126.1, 76.3, 74.2, 73.1, 58.2, 33.9, 15.0 ppm; IR (KBr) ν 3258 (s), 2912 (w), 1778 (s), 1609 (m), 1536 (m), 1346 (s), 1251 (m), 1010 (m), 770 (m), 703 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{21}NO_5$: 355.1497, found: 355.1430.

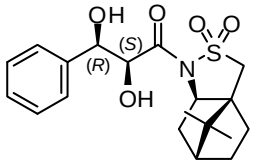


22-A

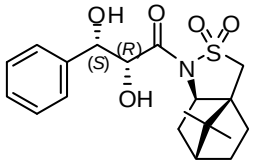


22-B

Diol 22-A and 22-B. Olefin **21** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **22-A : 22-B** (2.3 : 1.0, ^{1}H NMR integration, combined isolated yield 386 mg, 57%), that were separated by HPLC. **22-B**. colorless solid; R_f 0.46 (1:1 *iso*-hexanes/ethyl acetate); δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.24-7.41 (m, 6H), 6.07 (d, *J* = 7.3 Hz, 1H), 5.41-5.46 (m, 1H), 5.37 (dd, *J* = 7.3, 2.0, 1H), 5.07 (dd, *J* = 6.3, 1.3 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 1H), 3.42-3.51 (m, 2H), 2.54 (d, *J* = 6.8 Hz, 1H) ppm. **22-A**. colorless solid mp. 185°C; R_f 0.43 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 63.5 (c 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.3Hz, 1H), 7.26-7.41 (m, 6H), 5.91 (d, *J* = 6.5 Hz, 1H), 5.37 (dd, *J* = 7.3, 2.5 Hz, 1H), 5.26-5.31 (m, 1H), 5.14 (dd, *J* = 6.8, 2.3 Hz, 1H), 3.73 (d, *J* = 7.5 Hz, 1H), 3.39 (dd, *J* = 18.5, 16.3 Hz, 2H), 2.94 (d, *J* = 7.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 152.7, 139.9, 139.4, 138.1, 130.2, 128.3, 127.9, 127.6, 126.2, 125.3, 79.6, 74.4, 73.8, 63.8, 37.7 ppm; IR (KBr) ν 3426 (s), 1777 (w), 1633 (s), 1451 (m), 1336 (w), 1033 (m), 698 (m) cm^{-1}; HRMS (FAB$^+$HR) calcd. for $C_{19}H_{18}NO_5$: 340.1185, found 340.1167.



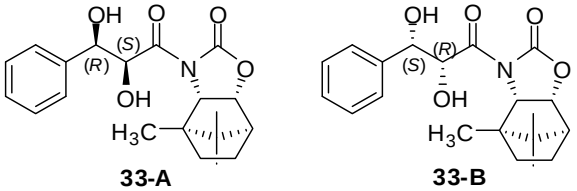
24-A



24-B

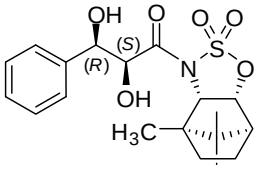
Diol 24-A and 24-B. Olefin **23** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **24-A : 24-B** (1.0 : 4.6, ^{1}H NMR integration, combined isolated 629 mg, yield 83%), that were separated by HPLC. **24-A**. colorless oil; R_f 0.56 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H) 7.36 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.29 (dd, *J* = 7.4, 7.2 Hz, 1H), 5.21 (d, *J* = 3.0 Hz, 1H), 4.93 (s, 1H), 3.94 (bs, 1H), 3.42-3.55 (m, 2H), 3.17 (dd, *J* = 15.0, 7.5 Hz, 1H), 1.85-2.1 (m, 5H), 1.3-1.45 (m, 2H), 1.08 (s, 3H), 0.97 (s, 3H) ppm. **24-B**. colorless solid; mp. 199-202°C; R_f 0.57 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –89.9 (c 0.74, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.36 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.29 (dd, *J* = 7.4, 7.2 Hz, 1H), 5.25 (d, *J* = 3.0 Hz, 1H), 4.79 (s, 1H), 3.93 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.54 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 3.01 (s, 1H), 2.19-2.26 (m, 1H), 2.09 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.85-1.95 (m, 3H), 1.3-1.45 (m, 2H), 1.16 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 133.9, 128.5, 128.0, 126.7, 73.7, 72.2, 65.4, 52.9, 38.5, 32.9, 26.4, 20.8, 19.8 ppm; IR (KBr) ν 3444 (s), 2965 (m), 1644 (s), 1384 (m), 1320 (s), 1217 (m), 1172 (s), 1135 (s), 809 (m), 528 (m) cm^{-1}.

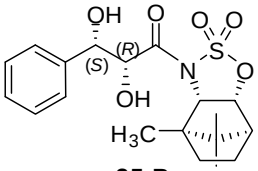


33-A **33-B**

Diol 33-A and 33-B. Olefin **32** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **33-A : 33-B** (4.1 : 1.0, ^{1}H NMR integration, combined isolated yield 610 mg, 85%), that were separated by HPLC. **33-B**. colorless solid; R_f 0.71 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5-7.54 (m, 2H), 7.35-7.4 (m, 2H), 7.24-7.3 (m, 1H), 5.42 (s, 1H), 5.2 (s, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.5 (d, *J* = 8.0 Hz, 1H), 3.6 (bs, 1H), 2.7 (bs, 1H), 2.23 (d, *J* = 5.0 Hz, 1H), 1.8-1.9 (m, 1H), 1.56-1.64 (m, 1H), 1.24-1.31 (m, 1H), 1.06-1.14 (m, 1H), 1.06 (s, 3H), 0.99 (s, 3H), 0.92 (s, 3H) ppm. **33-A**. colorless solid. mp. 184°C; R_f 0.71 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –64.7 (c 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.32-7.38 (m, 2H), 7.24-7.3 (m, 1H), 5.28 (d, *J* = 3.1 Hz, 1H), 5.08 (d, *J* =3.1 Hz, 1H), 4.53 (d, *J* = 7.9 Hz, 1H), 4.34 (d, *J* = 7.9 Hz, 1H), 3.8 (bs, 1H), 3.0 (bs, 1H), 2.18 (d, *J* = 5.1 Hz, 1H), 1.8-1.88 (m, 1H), 1.54-1.62 (m, 1H), 1.2-1.28 (m, 1H), 1.0-1.06 (m, 1H), 1.0 (s, 3H), 0.97 (s, 3H), 0.9 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 155.0, 140.0, 128.3, 127.9, 126.5, 82.6, 74.1, 73.0, 66.7, 50.4, 47.6, 46.5, 33.4, 22.8, 22.6, 19.7, 12.3 ppm; IR (KBr) ν 3448 (s), 2962 (w), 1780 (s), 1701 (s), 1387 (m), 1323 (m), 1299 (s), 1199 (m), 1051 (m), 763 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{26}NO_5$: 360.1811 , found: 360.1779.

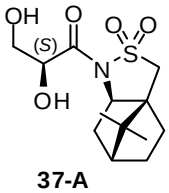


35-A

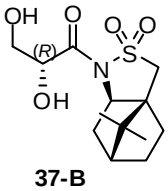


35-B

Diol 35-A and 35-B. Olefin **34** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **35-A : 35-B** (12.0 : 1.0, ^{1}H NMR integration, combined isolated yield 687 mg, 87%), that were separated by HPLC. **35-B**. colorless solid; R_f 0.65 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.52 (m, 2H), 7.28-7.42 (m, 3H), 5.3 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.05 (dd , *J* = 6.8, 1.7 Hz, 1H), 4.87 (d, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 7.5 Hz, 1H), 3.28 (d, *J* = 6.8 Hz, 1H), 2.47 (d, *J* = 7.8 Hz, 1H), 2.28 (d, *J* = 5.6 Hz, 1H), 1.87-2.0 (m, 1H), 1.59-1.70 (m, 1H), 1.05-1.35 (m, 2H), 1.17 (s, 3H), 0.95 (s, 3H), 0.93 (s, 3H) ppm. **35-A**. colorless solid. mp. 198°C; R_f 0.63 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 3.5 (c 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.49 (m, 2H), 7.27-7.41 (m, 3H), 5.23 (t, *J* = 3.3 Hz, 1H), 4.9 (dd, *J* = 8.3, 3.1 Hz, 1H), 4.83 (d, *J* = 7.5 Hz, 1H), 4.43 (d, *J* = 7.5 Hz, 1H), 3.47 (d, *J* = 8.3 Hz, 1H), 2.93 (d, *J* = 3.3 Hz, 1H), 2.26 (d, *J* = 5.6 Hz, 1H), 1.86-2.0 (m, 1H), 1.56-1.68 (m, 1H), 1.2-1.32 (m, 1H), 1.17 (s, 3H), 1.02-1.14 (m, 1H), 0.96 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 137.8, 127.1, 126.8, 125.3, 83.7, 71.8, 71.0, 66.1, 49.8, 46.4, 46.2, 32.0, 21.0, 20.9, 18.3, 10.4 ppm; IR (KBr) ν 3440 (s), 2964 (s), 2840 (m), 1650 (s), 1520 (s), 1382 (m), 1287 (s), 1002 (m), 850 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{19}H_{26}NO_6S$: 396.1481, found:396.1489

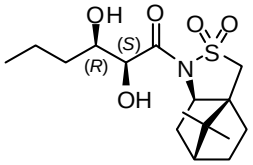


37-A

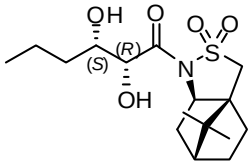


37-B

Diol 37-A and 37-B. Olefin **36** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **37-A : 37-B** (1.0 : 3.8, ^{1}H NMR integration, combined siolated yield 503 mg, 83%), that were separated by HPLC. **37-A**. colorless solid R_f 0.29 1:1 (*iso*-hexanes/ethyl acetate) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.8 (bs, 1H), 3.85-3.96 (m, 3H), 3.40-3.56 (m, 4H), 2.04-2.10 (m, 2H), 1.86-1.98 (m, 4H), 1.32-1.48 (m, 3H), 1.14 (s, 3H), 0.98 (s, 3H) ppm. **37-B**. colorless solid, mp. 196.4°C; R_f 0.28 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –67.3 (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64-4.69 (m, 1H), 3.90-4.0 (m, 3H), 3.56 (d, *J* = 14.1 Hz, 1H), 3.53 (d, *J* = 6.3 Hz, 1H), 3.47 (d, *J* = 14.1 Hz, 1H), 2.16-2.28 (m, 2H), 2.08 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.86-1.96 (m, 3H), 1.32-1.48 (m, 2H), 1.16 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 70.8, 65.1, 62.9, 52.7, 49.3, 47.9, 44.4, 37.9, 32.7, 26.4, 20.7, 19.9 ppm; IR (KBr) ν 3505 (s), 2961 (m), 1689 (s), 1331 (s), 1256 (s), 1167 (w), 1136 (m), 1061 (w), 734 (s) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{13}H_{22}NO_5S$: 304.1219, found : 304.1201.



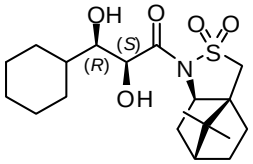
39-A



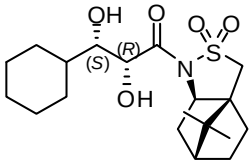
39-B

Diol 39-A and 39-B. Olefin **38** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **39-A : 39-B** (1.0 : 6.3, ^{1}H NMR integration, combined isolated yield 587 mg, 85%), that were separated by HPLC. **39-A**. colorless oil; R_f 0.49 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (dd, *J* = 6.2, 1.5 Hz, 1H), 4.04 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.94 (t, *J* = 6 Hz, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 6.3 Hz, 1H), 2.04-2-12 (m, 1H), 1.84-2.0 (m, 3H), 1.32-1.72 (m, 7H), 1.15 (s, 3H), 0.97 (m, 3H) ppm; IR (KBr) ν 3459 (s), 2959 (w), 1694 (s), 1456 (w), 1332 (s), 1274 (w), 1137 (s), 1060 (m), 538 (m), 703 (m) cm^{-1}. **39-B**. colorless oil; R_f 0.53 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –70.59 (c 0.45, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$)

δ 4.46 (dd, *J* = 8.5, 2.2 Hz, 1H), 4.04-4.11 (m, 1H), 3.93 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.53 (d, *J* = 13.8 Hz, 1H), 3.47 (d, *J* = 8.5 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 2.58 (bs, 1H), 2.16-2.24 (m, 1H), 2.03-2.11 (m, 1H), 1.84-1.96 (m, 3H), 1.32-1.64 (m, 6H), 1.16 (s, 3H), 0.97 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 71.9, 70.2, 65.2, 52.8, 49.1, 47.8, 44.5, 38.0, 34.8, 32.8, 26.3, 19.8, 18.6, 13.9 ppm; IR (KBr) ν 3493 (s), 2959 (w), 1688 (s), 1412 (w), 1331 (s), 1237 (m), 1218 (m), 1136 (s), 1060 (m), 536 (w) cm^{-1}; HRMS (FAB$^+$HR) calcd. for $C_{16}H_{28}NO_5S$: 346.1688, found : 346.1658.



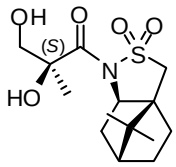
41-A



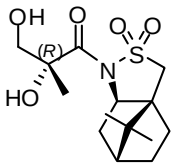
41-B

Diol 41-A and 41-B. Olefin **40** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **41-A : 41-B** (1.0 : 9.0, ^{1}H NMR integration, combined isolated yield 678 mg, 88%), that were separated by HPLC. **41-A**. colorless solid. R_f 0.46 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.95 (t, *J* = 6.3 Hz, 1H), 3.69 (dd, *J* = 9.0, 8.8 Hz, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 3.44 (d, *J* = 13.8 Hz, 1H), 3.35 (d, *J* = 6.0 Hz, 1H), 2.04-2.13 (m, 2H), 1.96-2.04 (m, 1H), 1.85-1.96 (m, 3H), 1.72-1.84 (m, 3H), 1.52-1.70 (m, 3H), 1.32-1.52 (m, 2H), 1.12-1.32 (m, 4H), 1.15 (s, 3H), 0.96-1.08 (m, 1H), 0.97 (m, 3H) ppm. **41-B**. colorless solid; mp. 158°C; R_f 0.55 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 49.28 (c 0.19, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (dd, *J* = 9.0, 1.5 Hz, 1H), 3.92 (dd, *J* = 7.7, 5.0 Hz, 1H), 3.74-3.79 (m, 1H), 3.52 (d, *J* = 13.8 Hz, 1H), 3.51 (d, *J* = 9 Hz, 1H), 3.44 (d, *J* = 13.8 Hz, 1H), 2.61 (d, *J* = 4.5 Hz, 1H), 2.16-2.24 (m, 1H), 2.04-2.10 (m, 1H), 1.94-2.02 (m, 1H), 1.84-1.94 (m, 3H), 1.68-1.80 (m, 3H), 1.30-1.45 (m, 2H), 1.16-1.29 (m, 4H), 1.14 (s, 3H), 0.99-1.16 (m, 1H), 0.96 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 74.6, 69.8, 65.4, 53.0, 49.2, 48.0, 44.6, 39.7, 38.2, 32.9, 29.1, 29.0, 26.5, 26.4, 26.1, 26.0, 20.9, 19.9

ppm; IR (KBr) ν 3499 (s), 2926 (s), 1687 (s), 1450 (w), 1329 (s), 1237 (m), 1221 (m), 1136 (s), 1063 (m), 732 (w), 537 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{19}H_{32}NO_5S$: 386.2001, found : 386.1966.

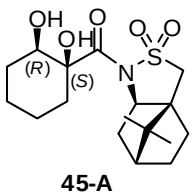


43-A

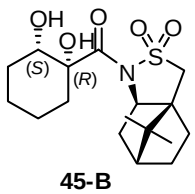


43-B

Diol 43-A and 43-B. Olefin **42** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **43-A : 43-B** (1.0 : 1.4, ^1H NMR integration, combined isolated yield 552 mg, 87%), that could not be separated separated by HPLC. **43-A**. colorless oil; R_f 0.46 (1:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 4.02-4.12 (m, 2H), 3.82 (bs, 1H), 3.54 (dd, *J* = 13.8, 13.0 Hz, 3H), 2.24 (bs, 1H), 2.05 (dd, *J* = 14, 7.8 Hz, 1H), 1.84-2.0 (m, 4H), 1.49 (s, 3H), 1.32-1.46 (m, 2H), 1.18 (s, 3H), 0.97 (s, 3H) ppm. **43-B**. colorless oil; R_f 0.47 (1:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 3.99-4.08 (m, 2H), 3.84 (bs, 1H), 3.54 (dd, *J* = 13.8, 13.0 Hz, 3H), 3.43-3.58 (m, 3H), 2.38 (bs, 1H), 2.06 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.82-1.99 (m, 4H), 1.44 (s, 3H), 1.30-1.44 (m, 2H), 1.19 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 78.1, 68.4, 67.5, 54.2, 48.6, 44.5, 38.7, 33.0, 26.6, 22.4, 21.5, 20.8, 20.0 ppm; IR (KBr) ν 3523 (s), 2937 (s), 1670 (s), 1340 (m), 1329 (m), 1146 (m), 1111 (s), 1033 (s), 766 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{14}H_{22}NO_4S$: 300.11264, found : 300.1274.



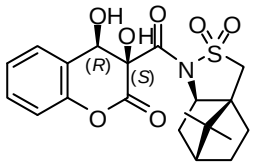
45-A



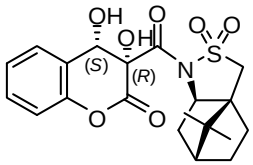
45-B

Diol 45-A and 45-B. Olefin **44** was oxidized according to **GP-IV** to give the desired glycol as a mixture

of two diastereomers **45-A : 45-B** (1.0 : 1.4, ^{1}H NMR integration, combined isolated yield 643 mg, 90%), that were separated by HPLC. **45-A**. colorless solid; R_f 0.44 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04-4.10 (m, 2H), 3.57 (d, *J* = 13.8 Hz, 1H), 3.40-3.45 (m, 2H), 2.10-2.18 (m, 1H), 1.80-2.08 (m, 5H), 1.68-1.80 (m, 2H), 1.44-1.68 (m, 4H), 1.28-1.44 (m, 3H), 1.21 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 79.7, 79.2, 68.0, 54.4, 48.3, 47.7, 45.5, 39.2, 33.6, 32.6, 30.0, 26.3, 23.8, 21.7, 20.0, 19.6 ppm; IR (KBr) ν 3499 (s), 2938 (s), 1674 (s), 1449 (m), 1333 (s), 1283 (m), 1240 (w), 1166 (s), 1134 (m), 1008 (w), 555 (w) cm^{-1}. **45-B**. colorless solid; mp.178°C; R_f 0.51 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ –76.6 (c 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14-4.22 (m, 1H), 4.08 (dd, *J* = 7.3, 4.8 Hz, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.48 (d, *J* = 13.5 Hz, 2H), 2.25 (d, *J* = 6.5 Hz, 1H), 1.77-2.08 (m, 7H), 1.45-1.77 (m, 5H), 1.22-1.44 (m, 3H), 1.17 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 79.7, 71.8, 67.7, 54.5, 48.4, 47.7, 44.8, 39.1, 34.2, 33.2, 29.4, 26.5, 23.8, 21.2, 19.9, 19.8 ppm; IR (KBr) ν 3476 (s), 2937 (s), 1648 (s), 1337 (s), 1294 (m), 1167 (m), 1072 (w), 1006 (w), 550 (w), cm^{-1}; HRMS (ESI-HR) calcd. for $C_{17}H_{28}NO_5S$: 358.1688, found : 358.1683.



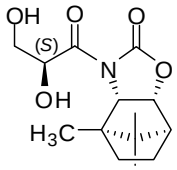
47-A



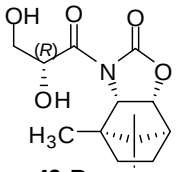
47-B

Diol 47-A and 47-B. Olefin **46** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **47-A : 47-B** (10.2 : 1.0, ^{1}H NMR integration, combined isolated yield 742 mg, 86%), that were separated by HPLC. **47-A.** colorless solid; R_f 0.75 (1:3 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.42 (m, 2H), 7.1-7.21 (m, 2H), 5.43 (bs, 1H), 4.75 (s, 1H), 3.90 (dd, *J* = 6.9, 6 Hz, 1H), 3.51 (d, *J* = 13.5 Hz, 1H), 3.41 (d, *J* = 13.5 Hz, 1H), 1.80-2.0 (m, 5H), 1.36-1.4 (m, 2H), 1.15 (s, 3H), 0.95 (s, 3H) ppm. **47-B.** colorless solid; mp. 235°C; R_f 0.75 (1:3 *iso*-hexanes/ethyl

acetate); $[\alpha]_D^{20}$ -64.5 (c 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 9.3, 8.0, 1.5 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.8, 6.7 Hz, 2H), 5.37 (s, 1H), 4.76 (s, 1H), 3.83 (dd, *J* = 7.5, 3.8 Hz, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.51 (d, *J* = 13.8 Hz, 1H), 3.29 (bs, 1H), 1.9 (dd, *J* = 11.8, 4.5 Hz, 1H), 1.6-1.84 (m, 4H), 1.38-1.45 (m, 1H), 1.12-1.26 (m, 1H), 1.05 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.1, 130.9, 126.5, 118.9, 70.3, 67.8, 55.5, 45.3, 39.3, 34.0, 27.9, 21.8, 21.3 ppm; IR (KBr) ν 2958 (w), 1736 (s), 1682 (m), 1608 (w) 1334 (m), 1274 (w), 1244 (w), 1137 (w), 1074 (w), 762 (w), 535 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{23}NO_7S$: 421.1195, found : 421.1177.



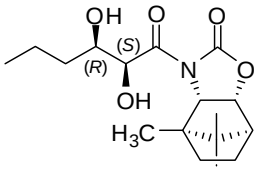
49-A



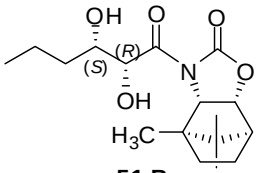
49-B

Diol 49-A and 49-B. Olefin **48** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **49-A : 49-B** (5.0 : 1.0, ^{1}H NMR integration, combined isolated yield 487 mg, 86%), that were separated by HPLC. **49-B**. colorless oil; R_f 0.22 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19-5.24 (m, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 3.9 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.96 (m, 2H), 3.85 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.18 (d, *J* = 5 Hz, 1H), 2.04 (bs, 1H), 1.78-1.87 (m, 1H), 1.52- 1.62 (m, 1H), 1.19-1.28 (m, 1H), 0.99- 1.09 (m, 1H), 1.0 (s, 3H), 0.94 (s, 3H), 0.90 (s, 3H) ppm. **49-A**. colorless solid. mp. 165°C; R_f 0.21 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 52.4 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (t, *J* = 4.5 Hz, 1H), 4.60 (d, *J* = 7.9 Hz, 1H), 4.38 (d, *J* = 7.9 Hz, 1H), 3.9-3.96 (m, 2H), 3.62 (d, *J* = 6.2 Hz, 1H), 2.18 (d, *J* = 5 Hz, 1H), 2.04 (bs, 1H), 1.75-1.87 (m, 1H), 1.50- 1.67 (m, 1H), 1.15-1.27 (m, 2H), 1.00 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 155.4, 82.8, 71.1, 66.3, 63.3, 50.3, 47.6, 46.6, 33.3, 22.8, 22.7, 19.6, 12.1 ppm; IR (KBr) ν 3427 (s), 2961 (m), 1777 (s), 1708 (s), 1377 (m), 1198 (s), 1055

(s) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{17}H_{27}NO_5$: 283.14197, found: 283.1458.

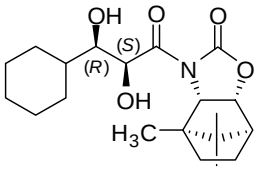


51-A

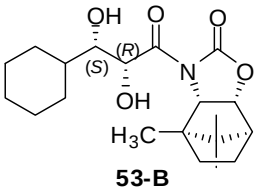


51-B

Diol 51-A and 51-B. Olefin **50** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **51-A : 51-B** (6.1 : 1.0, ^1H NMR integration, combined isolated 553 mg, yield 85%), that were separated by HPLC. **51-B**. colorless oil; R_f 0.45 (2:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (d, *J* = 4.8 Hz, 1H), 4.61 (d, *J* = 8 Hz, 1H), 4.46 (d, *J* = 8 Hz, 1H), 3.96 (dd, *J* = 6.5 Hz, 1H), 3.53 (d, *J* = 5.5 Hz, 1H), 2.20 (d, *J* = 5 Hz, 1H), 2.02 (d, *J* = 13.1 Hz), 1.78-1.88 (m, 1H), 1.75 (bs, 1H), 1.36- 1.72 (m, 5H), 1.18-1.28 (m, 1H), 0.99-1.09 (m, 1H), 1.03 (s, 3H), 0.95 (s, 3H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.90 (s, 3H) ppm. **51-A**. colorless solid. mp. 117°C; R_f 0.44 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 48.2 (c 0.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (d, *J* = 6.0 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 7.8 Hz, 1H), 3.91 (dd, *J* = 6.3 Hz, 1H), 3.75 (d, *J* = 7.5 Hz, 1H), 2.18 (d, *J* = 5 Hz, 1H), 2.08 (bs, 1H), 1.78-1.88 (m, 1H), 1.34- 1.67 (m, 5H), 1.18-1.27 (m, 1H), 0.99-1.08 (m, 1H), 0.99 (s, 3H), 0.97 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 154.9, 82.6, 72.6, 71.0, 66.6, 50.4, 47.5, 46.5, 36.1, 33.4, 22.7, 22.6, 19.7, 18.8, 13.9, 12.3 ppm; IR (KBr) ν 3424 (s), 2959 (m), 1781 (s), 1698 (w), 1446 (s), 1140 (m), 1053 (s) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{17}H_{28}NO_5$: 326.1967, found: 326.1982.

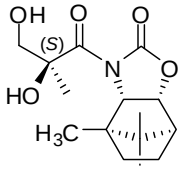


53-A

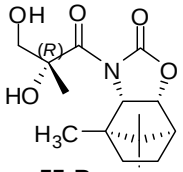


53-B

Diol 53-A and 53-B. Olefin **52** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **53-A : 53-B** (7.3 : 1.0, ^{1}H NMR integration, combined isolated 643 mg, yield 88%), that were separated by HPLC. **53-B**. colorless oil; mp. 152°C; R_f 0.49 (2:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 8 Hz, 1H), 4.47 (d, *J* = 8 Hz, 1H), 3.6 (d, *J* = 8.5 Hz, 1H), 3.54 (bs, 1H), 2.19 (d, *J* = 5 Hz, 1H), 2.02 (d, *J* = 13.1 Hz, 1H), 1.92 (bs, 1H), 1.72-1.88 (m, 4H), 1.53- 1.67 (m, 4H), 1.1-1.28 (m, 5H), 0.98-1.08 (m, 1H), 1.0 (s, 3H), 0.98 (s, 3H), 0.90 (s, 3H) ppm. **53-A**. colorless solid. mp. 152°C; R_f 0.46 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 58.0 (c 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (d, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 8 Hz, 1H), 4.35 (d, *J* = 8 Hz, 1H), 3.70 (d, *J* = 7.3 Hz, 1H), 3.57 (d, *J* = 8.3 Hz, 1H), 2.19 (d, *J* = 5 Hz, 1H), 2.0 (d, *J* = 13.1 Hz), 1.92 (bs, 1H), 1.72-1.88 (m, 4H), 1.53- 1.67 (m, 4H), 1.1-1.28 (m, 5H), 0.98-1.08 (m, 1H), 1.0 (s, 3H), 0.98 (s, 3H), 0.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 154.8, 82.6, 75.4, 70.8, 66.8, 47.6, 40.8, 33.4, 29.2, 28.8, 26.3, 25.9, 22.8, 22.7, 19.7, 12.4ppm; IR (KBr) ν 3414 (s), 2928 (m), 1781 (s), 1694 (s), 1385 (w,), 1320 (w), 1193 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{20}H_{32}NO_5$: 366.2280, found: 366.2263.



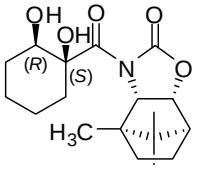
55-A



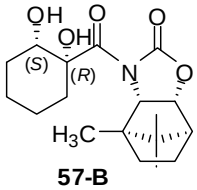
55-B

Diol 55-A and 55-B. Olefin **54** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **55-A : 55-B** (8.1 : 1.0, ^{1}H NMR integration, combined isolated yield 517 mg, 87%), that were separated by HPLC. **55-B**. colorless oil; R_f 0.57 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (bs, 1H), 4.63 (d, *J* = 8 Hz, 1H), 4.53 (d, *J* = 8 Hz, 1H), 3.84 (d, *J* = 11.5 Hz, 1H), 3.74 (d, *J* = 11.5 Hz, 1H), 2.3 (bs, 1H), 2.21 (d, *J* = 5.0 Hz, 1H), 1.79-1.88 (m, 1H), 1.53-1.62 (m, 1H), 1.56 (s, 3H), 1.19-1.28 (m, 1H), 1.01-1.09 (m, 1H), 1.04 (s, 3H), 0.91 (s, 3H), 0.89

(s, 3H) ppm. **55-A**. colorless solid. mp. 85°C; R_f 0.57 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 29.1 (c 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (bs, 1H), 4.63 (d, *J* = 8 Hz, 1H), 4.55 (d, *J* = 8 Hz, 1H), 3.84-3.91 (m, 1H), 3.67 (dd, *J* = 11.0, 5.0 Hz, 1H), 2.49 (bs, 1H), 2.19 (d, *J* = 5 Hz, 1H), 1.76-1.86 (m, 1H), 1.52-1.61 (m, 1H), 1.46 (s, 3H), 1.16-1.25 (m, 1H), 0.99-1.07 (m, 1H), 1.04 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 156.7, 83.1, 77.4, 69.3, 66.5, 49.9, 47.8, 46.5, 33.0, 22.8, 22.7, 21.2, 19.4, 11.8 ppm; IR (KBr) ν 3501 (s), 3368 (s), 2980 (m), 2940 (m), 2886 (m), 1746 (s), 1690 (s), 1395 (m,), 1318 (w), 1220 (s), 1198 (m), 1060 (m), 772 (w) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{15}H_{24}NO_5$: 298.1654, found: 298.1670.



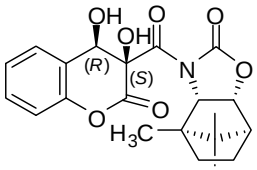
57-A



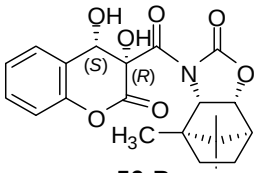
57-B

Diol 57-A and 57-B. Olefin **56** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **57-A : 57-B** (3.2 : 1.0, ^1H NMR integration, combined isolated yield 607 mg, 90%), that were separated by HPLC. **57-B**. colorless oil; R_f 0.45 (2:1 *iso*-hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (bs, 1H), 4.61 (d, *J* = 8 Hz, 1H), 4.56 (d, *J* = 8 Hz, 1H), 4.09 (dd, *J* = 10.8, 4.0 Hz, 1H), 2.3 (bs, 1H), 2.19 (d, *J* = 5.0 Hz, 1H), 1.99-2.07 (m, 1H), 1.44-1.88 (m, 9H), 1.18-1.40 (m, 2H), 0.99-1.08 (m, 1H), 1.03 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H) ppm. **57-A**. colorless solid. mp. 184°C; R_f 0.41 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -1.4 (c 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (bs, 1H), 4.61 (s, 2H), 4.1 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.19 (d, *J* = 5.0 Hz, 1H), 2.15-2.21 (m, 1H), 1.16-1-90 (m, 10H), 1.06 (s, 3H), 0.99-1.06 (m, 1H), 0.92 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 154.1, 86.6, 81.4, 74.5, 68.2, 51.3, 49.3, 48.0, 36.6, 36.5, 31.7, 25.4, 24.3, 24.2, 20.9, 20.8, 13.3 ppm; IR (KBr) ν 3562 (s), 3414 (s), 2940 (m), 1748 (s), 1639 (s), 1398 (m,), 1273

(m), 1200 (m), 1151 (m), 1054 (w), 691 (w) cm^{-1}. HRMS ($FAB^{+}HR$) calcd. for $C_{18}H_{28}NO_5$: 338.1967, found: 338.1993.

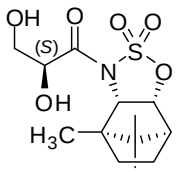


59-A

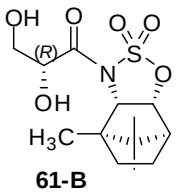


59-B

Diol 59-A and 59-B. Olefin **58** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **59-A : 59-B** (1.0 : <10, ^{1}H NMR integration, combined isolated yield 602 mg, 75%), that were separated by HPLC **59-A**. colorless solid. mp. 195.4°C; R_f 0.44 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 22.5 (c 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.34 (dt, *J* = 7.8, 0.8, Hz, 1H), 7.21 (dt, *J* = 7.8, 0.8 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 5.51 (d, *J* = 10.3 Hz, 1H), 5.2 (bs, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 2.84 (d, *J* = 11.8 Hz, 1H), 2.21 (d, *J* = 5.3 Hz, 1H), 1.83-1.91 (m, 1H), 1.58-1.66 (m, 2H), 1.24-1.31 (m, 1H), 1.02-1.1 (m, 1H), 1.07 (s, 3H), 1.05 (s, 3H), 0.93 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 163.2, 155.2, 148.4, 130.9, 126.8, 125.1, 122.8, 116.8, 83.4, 67.8, 67.1, 51.0, 47.5, 46.5, 33.3, 22.7, 22.3, 19.6, 12.3 ppm; IR (KBr) ν 3512 (m), 2965 (m), 1762 (s), 1745 (m), 1714 (s) 1377 (m), 1307 (w), 1195 (s), 1044 (m), 760 (m) cm^{-1}; HRMS (ESI-HR) calcd. for $C_{21}H_{24}NO_7$: 402.1553, found: 402.1547.



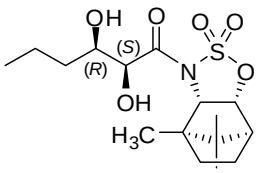
61-A



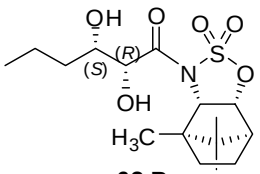
61-B

Diol 61-A and Diol 61-B. Olefin **60** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **61-A : 61-B** (10.1 : 1.0, ^{1}H NMR integration, combined isolated yield 529

mg, 83%), that were separated by HPLC. **61-B**. colorless oil; R_f 0.42 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75-4.82 (m, 1H), 4.70 (d, *J* = 7.5 Hz, 1H), 4.51 (s, 1H), 4.42 (d, *J* = 7.5 Hz, 1H), 3.67-3.73 (m, 2H), 3.36 (d, *J* = 6.4 Hz, 1H), 2.46 (d, *J* = 1.8 Hz, 1H), 2.24 (d, *J* = 5 Hz, 1H), 1.79-1.94 (m, 1H), 1.50- 1.62 (m, 1H), 1.18-1.25 (m, 1H), 1.23 (s, 3H), 0.98-1.16 (m, 1H), 0.97 (s, 3H), 0.91 (s, 3H); ppm. **61-A**. colorless solid. mp. 159°C; R_f 0.21 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 2.4 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 7.5 Hz, 1H), 4.73-4.82 (m, 1H), 4.43 (d, *J* = 7.5 Hz, 1H), 3.90-4.01 (m, 2H), 3.43 (d, *J* = 6.2 Hz, 1H), 2.27 (d, *J* = 5.2 Hz, 1H), 2.16 (bs, 1H), 1.86-2.01 (m, 1H), 1.57- 1.69 (m, 1H), 1.25-1.32 (m, 1H), 1.26 (s, 3H), 1.05-1.23 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 81.9, 73.9, 69.3, 66.3, 50.1, 46.7, 44.2, 32.1, 24.2, 21.4, 18.6, 10.7 ppm; IR (KBr) ν 3420 (s), 2968 (m), 1698 (s), 1384 (s), 1254 (m), 1143 (s), 980 (m), 794 (s) cm^{-1} HRMS (ESI-HR) calcd. for $C_{13}H_{22}NO_6S$: 320.1162, found:320.1154



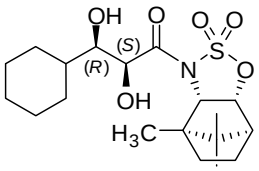
63-A



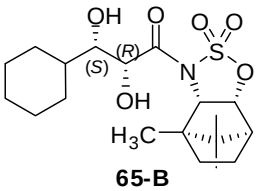
63-B

Diol 63-A and Diol 63-B. Olefin **62** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **63-A : 63-B** (12.2 : 1.0, ^{1}H NMR integration, combined isolated 657 mg, yield 91%), that were separated by HPLC **63-B**. colorless solid. mp. 144°C; R_f 0.40 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 9.3 (c 1.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (d, *J* = 7.2 Hz, 1H), 4.74 (dd, *J* = 6.6, 1.4 Hz, 1H), 4.50 (d, *J* = 7.2 Hz, 1H), 4.03-4.14 (m, 1H), 3.25 (d, *J* = 6.6 Hz, 1H), 2.26 (d, *J* = 5.4 Hz, 1H), 2.03 (bs, 1H), 1.86-1.99 (m, 1H), 1.36- 1.72 (m, 5H), 1.22-1.35 (m, 1H), 1.18 (s, 3H), 1.04-1.14 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.92 (s, 3H), 0.91 (s, 3H) ppm. **63-A**. colorless oil; R_f 0.39 (2:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (d, *J* = 7.5 Hz, 1H), 4.52 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.37 (d, *J* = 7.5 Hz, 1H), 3.97-4.05 (m, 1H), 3.39 (d, *J* = 8.9 Hz, 1H), 2.41 (d,

J = 4 Hz, 1H), 2.18 (d, *J* = 5.2 Hz), 1.80-1.92 (m, 1H), 1.38- 1.62 (m, 5H), 1.14-1.26 (m, 1H), 1.1 (s, 3H), 0.98-1.08 (m, 1H), 0.88 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.85 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 82.5, 69.0, 67.9, 65.0, 48.7, 45.3, 45.1, 32.5, 30.9, 20.0, 19.9, 17.3, 16.3, 11.5, 9.4 ppm; IR (KBr) ν 3470 (s), 2961 (m), 1711 (s), 1371 (m), 1227 (s), 1172 (s), 971 (m), 858 (m), 776(s) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{16}H_{28}NO_6S$: 362.1632, found:362.1625

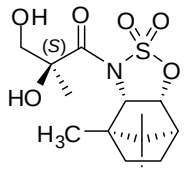


65-A

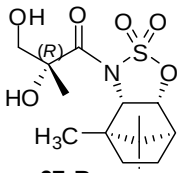


65-B

Diol 65-A and 65-B. Olefin **64** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **65-A : 65-B** (11.8 : 1.0, ^{1}H NMR integration, combined isolated 722 mg, yield 90%), that were separated by HPLC. **65-B**. colorless oil; mp. 147°C; R_f 0.46 (2:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (dd, *J* = 6.3, 1.2 Hz, 1H), 4.71 (d, *J* = 7.5 Hz, 1H), 4.51 (d, *J* = 7.5 Hz, 1H), 3.67-3.75 (m, 1H), 3.31 (d, *J* = 6.3 Hz, 1H), 2.31 (d, *J* = 5.3 Hz, 1H), 2.22 (d, *J* = 5.7 Hz), 1.84-2.04 (m, 2H), 1.56- 1.82 (m, 6H), 1.0-1.34 (m, 8H), 1.17 (s, 3H), 0.97 (s, 3H), 0.92 (s, 3H) ppm. **65-A**. colorless solid. mp. 152°C; R_f 0.44 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 16.5 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (dd, *J* = 9.3, 1.9 Hz, 1H), 4.83 (d, *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 7.5 Hz, 1H), 3.77 (ddd, *J* = 6.3, 4.6, 1.9 Hz, 1H), 3.5 (d, *J* = 9.3 Hz, 1H), 2.56 (d, *J* = 4.6 Hz, 1H), 2.25 (d, *J* = 5.2 Hz), 1.84-2.04 (m, 2H), 1.56- 1.82 (m, 6H), 1.0-1.34 (m, 8H), 1.17 (s, 3H), 0.95 (s, 3H), 0.92 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 83.2, 73.0, 67.6, 65.9, 58.3, 49.6, 46.1, 45.9, 31.8, 27.3, 24.7, 24.4, 24.3, 19.5, 18.1, 12.6, 10.2 ppm; IR (KBr) ν 3507 (s), 2926 (m), 1705 (s), 1449 (s), 1226 (s), 1171 (s), 969 (s), 905 (m), 856 (s), 728 (s) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{19}H_{32}NO_6S$: 402.1950, found:402.1951

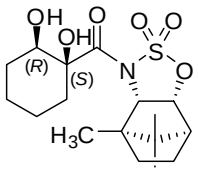


67-A

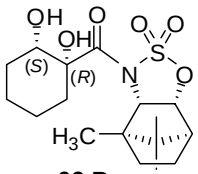


67-B

Diol 67-A and 67-B. Olefin **66** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **67-A : 67-B** (2.2 : 1.0, ^{1}H NMR integration, combined isolated yield 566 mg, 885%), that were separated by HPLC. **67-B**. colorless oil; R_f 0.55 (1:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (d, *J* = 7.5 Hz, 1H), 4.58 (d, *J* = 7.5 Hz, 1H), 4.13 (dd, *J* = 11.3, 7 Hz, 1H), 3.63 (s, 1H), 3.55 (dd, *J* = 11.3, 7 Hz, 1H), 2.23 (d, *J* = 5.8 Hz, 1H), 2.15 (d, *J* = 7 Hz, 1H), 1.76-1.92 (m, 1H), 1.56-1.66 (m, 1H), 1.56 (s, 3H), 1.19-1.28 (m, 1H), 1.2 (s, 3H), 1.01-1.09 (m, 1H), 0.91 (s, 3H), 0.87 (s, 3H) ppm; **67-A**. colorless solid. mp. 115°C; R_f 0.53 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -31.0 (c 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.8 (d, *J* = 7.5 Hz, 1H), 4.65 (d, *J* = 7.5 Hz, 1H), 4.08 (dd, *J* = 11.2, 6 Hz, 1H), 3.83 (s, 1H), 3.63 (dd, *J* = 11.2, 6 Hz, 1H), 2.23 (d, *J* = 5.2 Hz, 1H), 2.19 (d, *J* = 6 Hz, 1H), 1.85-198 (m, 1H), 1.56-1.64 (m, 1H), 1.52 (s, 3H), 1.22-1.30 (m, 1H), 1.2 (s, 3H), 1.04-1.16 (m, 1H), 0.91 (s, 3H), 0.86 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 82.4, 77.3, 67.8, 67.3, 49.1, 46.0, 45.9, 31.6, 20.9, 20.7, 20.3, 17.9, 9.8 ppm; IR (KBr) ν 3514 (s), 2962 (m), 1702 (s), 1369 (s), 1180 (m,), 1033 (m), 976 (s) cm^{-1};. HRMS (ESI-HR) calcd. for $C_{14}H_{24}NO_6S$: 334.1324, found:334.1329



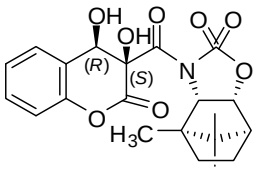
69-A



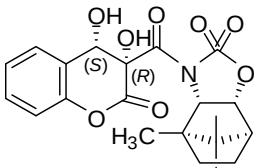
69-B

Diol 69-A and 69-B. Olefin **68**was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **69-A : 69-B** (2.7 : 1.0, ^{1}H NMR integration, combined isolated yield 671 mg,

90%), that were separated by HPLC. **69-B**. colorless oil; R_f 0.47 (2:1 *iso*-hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (d, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 7.5 Hz, 1H), 4.12 (dt, *J* = 10.8, 5.3 Hz, 1H), 3.47 (d, *J* = 1.5 Hz), 2.3 (bs, 1H), 2.21 (d, *J* = 5.6 Hz, 1H), 2.1-2.2 (m, 1H), 1.44-1.88 (m, 9H), 1.18-1.40 (m, 2H), 1.2 (s, 3H), 0.99-1.08 (m, 1H), 0.9 (s, 3H), 0.87 (s, 3H) ppm. **69-A**. colorless solid. mp. 143°C; R_f 0.46 (2:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ -11.3 (c 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (d, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 7.5 Hz, 1H), 4.24 (dt, *J* = 11.2, 5 Hz, 1H), 3.34 (d, *J* = 1.5 Hz), 2.25-2.35 (m, 1H), 2.19 (d, *J* = 5.6 Hz, 1H), 1.25-1-90 (m, 10H), 1.18 (s, 3H), 1.02-1.16 (m, 1H), 0.90 (s, 3H), 0.85 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 82.9, 80.6, 69.2, 66.8, 52.1, 45.3, 44.7, 37.8, 36.2, 31.6, 31.4, 24.4, 21.5, 20.3, 20.4, 17.6 ppm; IR (KBr) ν 3512 (s), 2937 (m), 1698 (s), 1377 (s), 1239 (m), 1150 (m), 1010 (m), 907 (m), 731 (w) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{17}H_{28}NO_6S$: 374.1632, found:374.1621



71-A



71-B

Diol 71-A. Olefin **70** was oxidized according to **GP-IV** to give the desired glycol as a mixture of two diastereomers **71-A : 71-B** (>19.0 : 1.0 ^{1}H NMR integration, combined isolated yield 690 mg, 79%), that were separated by HPLC **71-A**. colorless solid. mp. 206°C; R_f 0.42 (1:1 *iso*-hexanes/ethyl acetate); $[\alpha]_D^{20}$ 22.9 (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.66 (m, 1H), 7.3-7.46 (m, 2H), 7.14-7.26 (m, 1H), 5.44 (d, *J* = 1.5 Hz, 1H), 4.74 (d, *J* = 7.5 Hz, 1H), 4.7 /s, 1H), 4.31 (d, *J* = 7.5 Hz, 1H), 3.3 (d, *J* = 1.9 Hz, 1H), 2.26 (d, *J* = 5.6 Hz, 1H), 1.76-1.88 (m, 1H), 1.60-1.70 (m, 2H), 1.30-1.44 (m, 1H), 1.28 (s, 3H), 1.02-1.18 (m, 1H), 0.78 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.3, 151.1, 132.4, 130.2, 125.3, 119.8, 116.9, 83.5, 68.4, 68.0, 60.3, 51.0, 47.7, 33.2, 21.8, 19.6, 14.1, 10.2

ppm; IR (KBr) ν 3476 (m), 2964 (m), 1736 (s), 1699 (s), 1377 (s) 1182 (m), 857 (m) cm^{-1}. HRMS (ESI-HR) calcd. for $C_{20}H_{24}NO_8S$: 438.1223, found:438.1231

V Cross metathesis-dihydroxylation

General procedure for the tandem cross-metathesis dihydroxylation methanolysis (GP-V): In a 10-mL round-bottomed flask catalyst **75** (21 mg, 0.025 mmol, 2.5 mol%) was dissolved in ethyl acetate (1.5 mL) under an argon atmosphere. CuCl (2.5 mg, 0.025 mmol, 2.5 mol%) and *o*-(*i*-propyloxy) styrene (4 mg, 0.025 mmol, 2.5 mol%) were added. The reaction mixture was stirred at 50°C for 1h until the solution turned deeply green. The olefin **36** or **60** (1 mmol) was added. The dilution flask was installed and filled with a solution of the electron-rich olefin (1.2 mmol) in ethyl acetate (10 mL). The mixture was heated to reflux and stirred until no more starting material could be detected (TLC-control). After complete conversion the slurry was cooled to room temperature and the dilution bulb was removed. Bu_4NIO_4 (10.8 mg, 0.025 mmol, 2.5 mol%) and acetonitrile (1.5 mL) were added and stirring was continued for 5 min. Meanwhile, $NaIO_4$ (427.8 mg, 2 mmol) and $CeCl_3$ (74.5 mg, 0.2 mmol) were stirred in water (0.5 mL) in a 10 mL round-bottomed flask until the color of the suspension turned bride yellow. After cooling down to 0°C acetone (1.5 mL) and the metathesis reaction mixture were added. The resulting slurry was stirred at 0°C until the oxidation was complete (10-30 min.). Solid Na_2SO_4 and ethyl acetate were and the mixture was filtered through a plug of silica into a saturated aq. Na_2SO_3-solution. The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum. The crude diol was then subjected to the standard methanolysis conditions: To a stirred solution of the diastereomeric diols (0.5 mmol) in a 1:1 mixture of CH_2Cl_2/MeOH (2 mL) was added a solution of MeMgBr (1.5 mmol, 500 µl, 3 M in THF) in 1mL MeOH (prepared at 0°C prior to use). After the additon stirring was contiunued for 5-10 min at 0°C. The reaction mixture was hydrolyzed by addition of a satured aq. $NaHSO_4$–solution (1 mL). The organic phase was separated and the aqueous layer extracted with CH_2Cl_2 (2x5 mL). The combined organic phases were dried over Na_2SO_4 and

concentrated in vacuum. The crude diol was purified by column chromatography.

Methyl 3-cyclohexyl-2,3-dihydroxypropanoate (80)[14b]**. (2*S*,3*R*)-80** was obtained in 63 % yield (127 mg) according to **GP-V** starting from sulfamidate **60** and vinyl cyclohexene. $[\alpha]_D^{20}$ 5.7 (c 0.1, CH_2Cl_2). **(2*R*,3*S*)-80** was obtained in 75 % yield (151 mg) according to GP-II starting from sultame **36** and vinyl cyclohexene. $[\alpha]_D^{20}$ –5.8 (c 0.1, CH_2Cl_2); colorless solid; mp. 82°C; R_f 0.79 (1:1 *iso*-hexanes/ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel AD, heptane/2-propanol (90:10), flow: 2mL/min, 215 nm), t_R(2S,3R) = 6.59, t_R(2R,3S) = 9.80; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 1H), 3.82 (s, 3H), 3.55 (d, *J* = 8.7 Hz, 1H), 2.01-2.09 (m, 1H), 1.64-1.82 (m, 2H), 1.54-1.63 (m, 2H), 1.18-1.40 (m, 4H), 0.96-1.16 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 71.1, 52.9, 40.5, 33.9, 29.5, 29.2, 26.4, 26.0, 25.9 ppm; IR (KBr) ν 3330 (s), 2927 (s), 2851 (m), 1733 (s), 1628 (s), 1576 (m), 1446 (m), 1246 (m), 1115 (m), 1039 (m) cm^{-1}.

Methyl 2,3-dihydroxyhexanoate (81). **(2*S*,3*R*)-81** was obtained 61 % yield (99 mg) according to **GP-V** starting from sulfamidate **60** and 1-pentene. $[\alpha]_D^{20}$ 16.8 (c 0.5, CH_2Cl_2); **(2*R*,3*S*)-81** was obtained in 69 % yield (112 mg) acc to the general procedure from sultame **36** and 1-pentene. $[\alpha]_D^{20}$ –20.0 (c 0.48, CH_2Cl_2); colorless oil; R_f 0.20 (1:1 *iso*-hexanes/ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel AD, heptane/2-propanol (90:10), flow: 1.5mL/min, 215 nm), t_R(2*S*,3*R*) = 7.43, t_R(2*R*,3*S*) = 8.87; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (dd, *J* = 7.3, 5.3 Hz, 1H), 3.93 (dd, *J* = 9.0,7.3 Hz, 1H), 3.84 (s, 3H), 3.0 (d, *J* = 5.3 Hz, 1H), 1.83 (d, *J* = 9.0 Hz, 1H), 1.36-1.64 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 73.1, 72.3, 53.0, 35.9, 18.9, 14.1 ppm; IR (KBr) ν 3392 (s), 2958 (m), 1742 (s), 1440 (w), 1219 (m), 1140 (m), 1087 (m) cm^{-1}; HRMS (ESI-HR) calcd. for $C_7H_{14}NaO_4$: 185.0790, found:185.0784.

Methyl 2,3-dihydroxynonanoate (82). **(2*S*,3*R*)-82** was obtained in 55 % yield (112 mg) according to **GP-V** starting from sulfamidate **60** and 1-octene. $[\alpha]_D^{20}$ 20.1 (c 0.4, $CHCl_3$). **(2*R*,3*S*)-82** was obtained in 53 % yield (108 mg) according to the general procedure from sultame **36** and 1-octene. $[\alpha]_D^{20}$ –20.0

(c 0.44, $CHCl_3$); colorless solid; mp. 48°C; R_f 0.52 (1:1 *iso*-hexanes/ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel AD, heptane/2-propanol (90:10), flow: 1mL/min, 215 nm), t_R(2S,3R) = 9.60, t_R(2R,3S) = 11.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (d, *J* = 3.5 Hz, 1H) 3.8-3.91 (m, 1H), 3.84 (s, 3H), 3.05 (d, *J* = 5.3 Hz, 1H), 1.91 (d, *J* = 8.0 Hz, 1H), 1.56-1.66 (m, 3H), 1.24-1-52 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 73.0, 72.4, 52.9, 33.7, 31.7, 29.1, 25.6, 22.5, 14.1 ppm IR (KBr) ν 3396 (s), 2927 (s), 1742 (s), 1440 (m), 1220 (w), 1139 (m) cm^{-1}; HRMS (ESI$^+$HR) calcd. for $C_{10}H_{20}NaO_4$: 227.1259, found: 227.1254.

Methyl 2,3-dihydroxy-3-phenylpropanoate (83). (2*S*,3*R*)-83[14,15] was obtained in 63 % yield (123 mg) according to **GP-V** starting from sulfamidate **60** and styrene. $[\alpha]_D^{20}$ 12.5 (c 1.0, $CHCl_3$). **(2*R*,3*S*)-83** was obtained in 66 % yield (129 mg) according to the general procedure starting from sultame **36** and styrene. $[\alpha]_D^{20}$ –12.1 (c 1.0, $CHCl_3$). White solid; m.p. 79 °C; R_f 0.30 (1:1 *iso*- hexanes / ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel OD, heptane/2-propanol (95:5), flow: 2mL/min, 210 nm) t_R(2*R*,3*S*) = 14.51, t_R(2*S*,3*R*) = 16.18; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H), 5.01 (dd, *J* = 6.5, 2.8 Hz, 1H), 4.36 (dd, *J* = 5.5, 2.8 Hz, 1H), 3.80 (s, 3H), 3.10 (d, *J* = 5.5 Hz, 1H), 2.74 (d, *J* = 6.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 140.0, 128.4, 128.2, 126.3, 75.0, 74.5, 52.7 ppm; IR (KBr) *ν* 3495 (s), 3378 (s), 3086 (m), 3062 (m), 3038 (m), 3007 (m), 2954 (s), 2931 (m), 1732 (s), 1493 (s), 1458 (s), 1324 (s), 1308 (s), 1104 (s), 1083 (s) cm^{-1}.

Methyl 7-(benzyloxy)-2,3-dihydroxyheptanoate (84). **(2*S*,3*R*)-84** was obtained in 55 % yield (155 mg) according to **GP-V** starting from sulfamidate **60** and 1-benzyloxyhex-5-ene. $[\alpha]_D^{20}$ 7.9 (c 0.3, $CHCl_3$). (2*R*,3*S*)-**84** was obtained in 63 % yield (180 mg) according to the general procedure starting from sultame **36** and 1-benzyloxyhex-5-ene. $[\alpha]_D^{20}$ –8.2 (c 0.28, $CHCl_3$); colorless oil; R_f 0.46 (1:1 *iso*-hexanes/ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel AD, heptane/2-propanol (90:10), flow: 2mL/min, 210 nm), t_R(2S,3R) = 10.11, t_R(2R,3S) = 12.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.36 (m, 5H), 4.49 (s, 2H), 4.08 (dd, *J* = 5.8, 2.0 Hz, 1H), 3.88 (bs, 1H), 3.8 (s, 3H), 3.48

(t, J = 6.5 Hz, 2H), 3.29 (d, J = 6.0 Hz, 1H), 2.38 (d, J = 8.0 Hz, 1H), 1.4-1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 138.6, 128.4, 127.7, 127.6, 73.1, 73.0, 72.4, 70.1, 52.9, 33.5, 29.5, 22.5 ppm; IR (KBr) ν 3396 (s), 2927 (s), 1742 (s), 1440 (m), 1220 (w,), 1139 (m) cm^{-1}; HRMS (FAB^+HR) calcd. for $C_{15}H_{23}O_5$: 283.1545, found : 283.1511.

Methyl hydroxy(1-hydroxycyclohexyl)acetate (85). (2*S*)-85 was obtained in 29 % yield (55 mg) according to **GP-V** starting from sulfamidate **60** and methylenecyclohexane. $[\alpha]_D^{20}$ 6.4 (c 0.2, $CHCl_3$). **(2*R*)-85** was obtained in 34 % yield (64 mg) according to the general procedure starting from sultame **36** and methylenecyclohexane. $[\alpha]_D^{20}$ –7.1 (c 0.2, $CHCl_3$); colorless oil; R_f 0.46 (1:1 *iso*-hexanes/ethyl acetate); enantiomeric excess was determined by chiral HPLC (Chiralcel OD, heptane/2-propanol (90:10), flow: 1mL/min, 220 nm), t_R(2S,3R) = 7.11, t_R(2R,3S) = 7.86; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (d, J = 8 Hz, 1H), 3.76 (s, 3H), 3.51 (d, J = 8 Hz, 1H), 2.59 (s, 1H), 1.44-1.66 (m, 8H), 1.34-1.44 (m, 1H), 1.16-1.24 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 76.7, 73.0, 52.2, 33.5, 33.1, 25.5, 21.4, 21.3 ppm; IR (KBr) ν 3448 (s), 2931 (s), 1730 (s), 1440 (w), 1267 (m), 1207 (m), 1087 (m), 979 (m) cm^{-1}; HRMS (ESI-HR) calcd. for $C_9H_{17}O_4$: 189.1127, found:189.1120.

VI Pseudo-Dilution Glas Apparatus

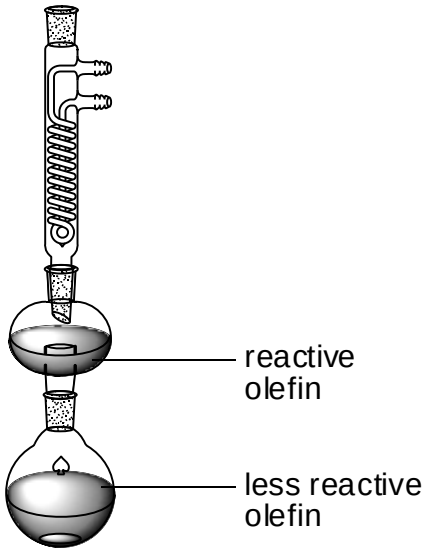


Figure 1. Pseudo-dilution glas apparatus used for the selective cross-metathesis reactions.

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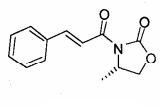
VIII ^{1}H NMR spectra



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4.033
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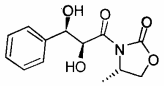

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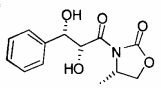

2B

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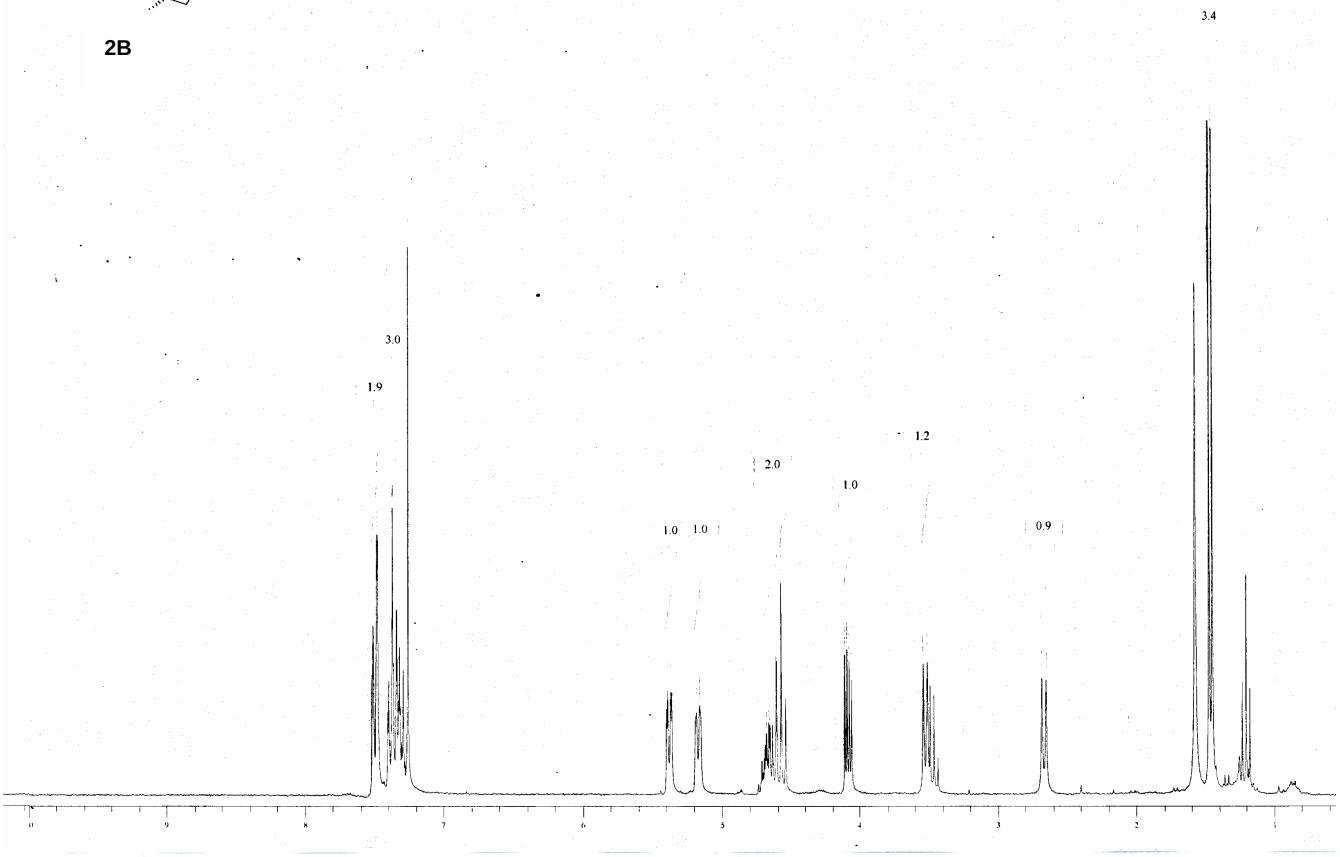

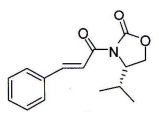

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7.259

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4.344
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4.301
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4.261
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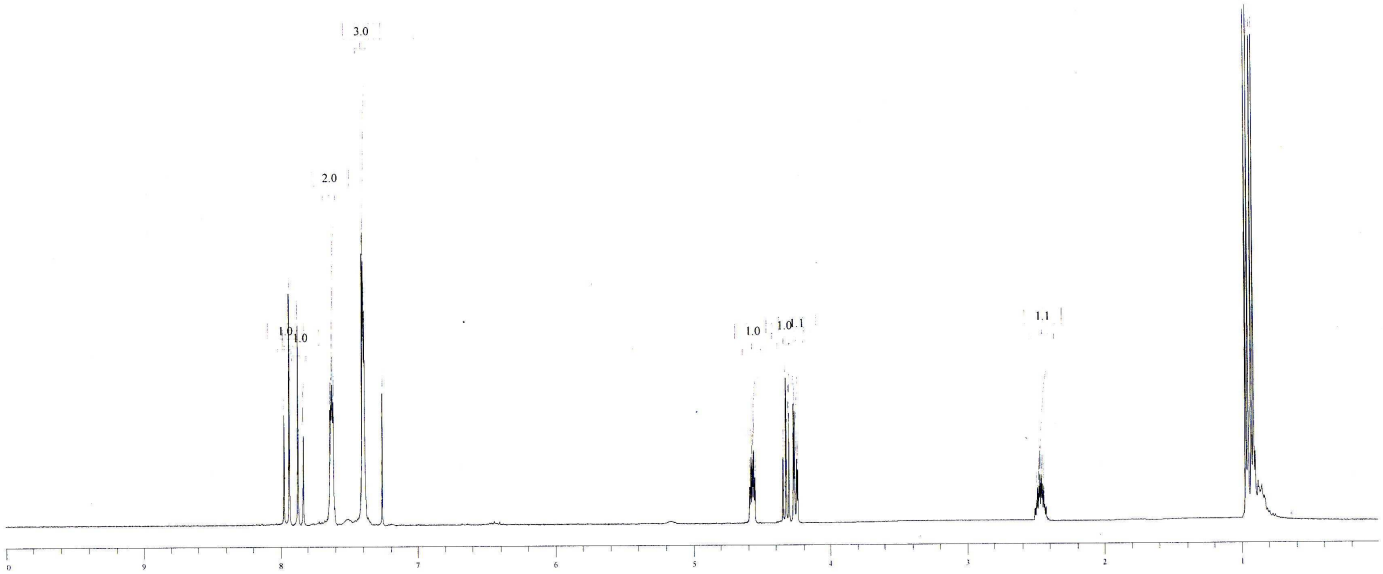

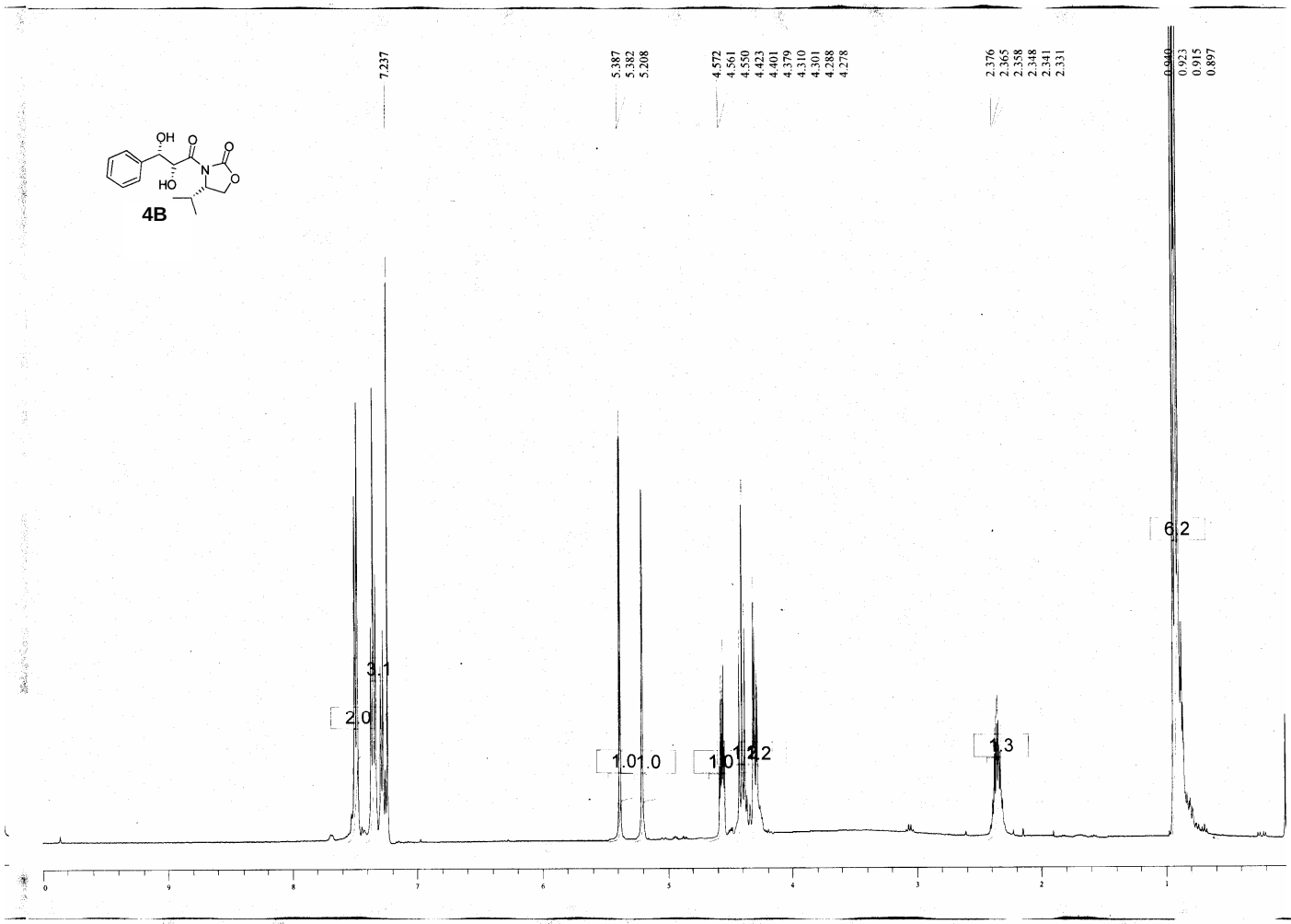
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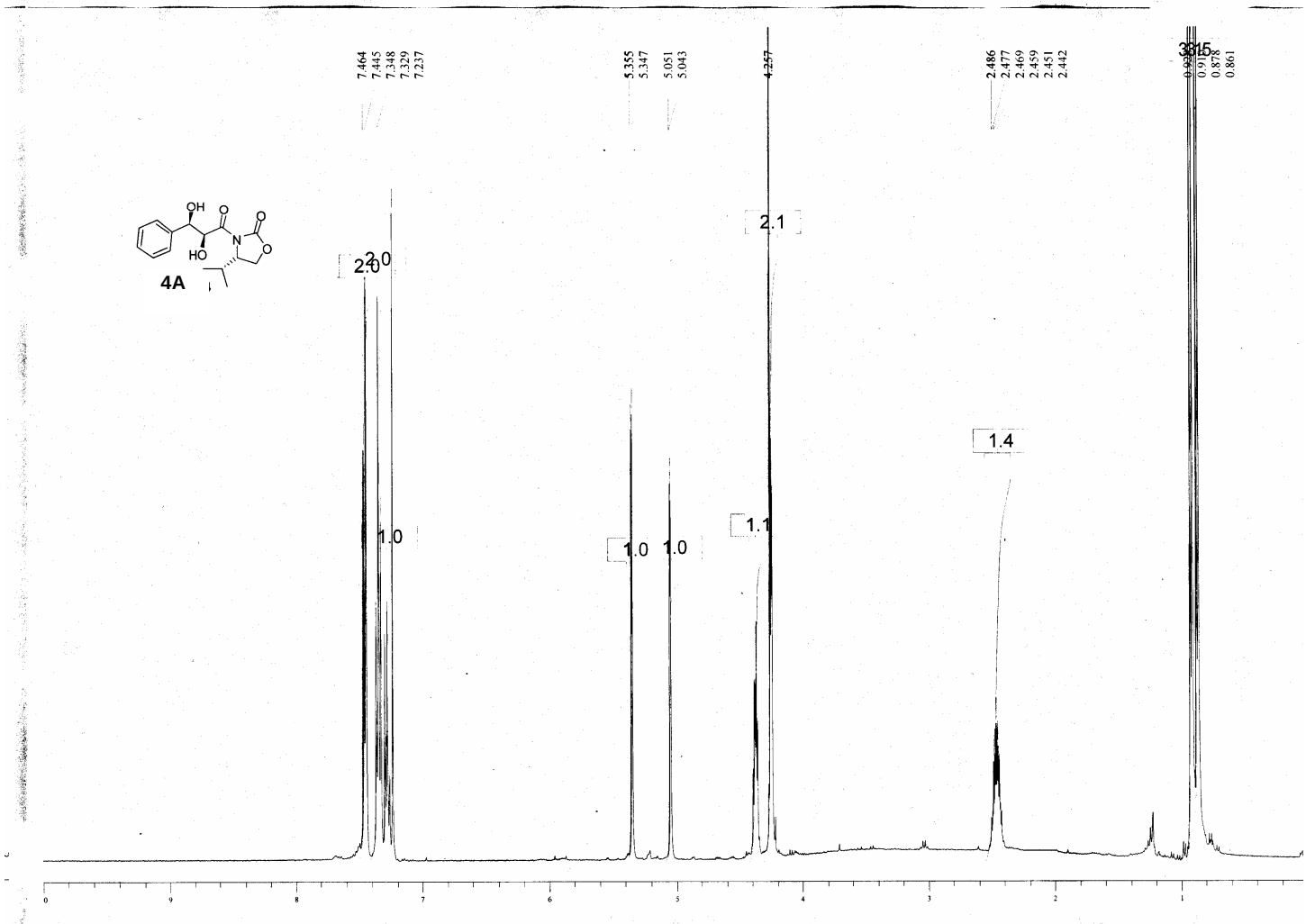
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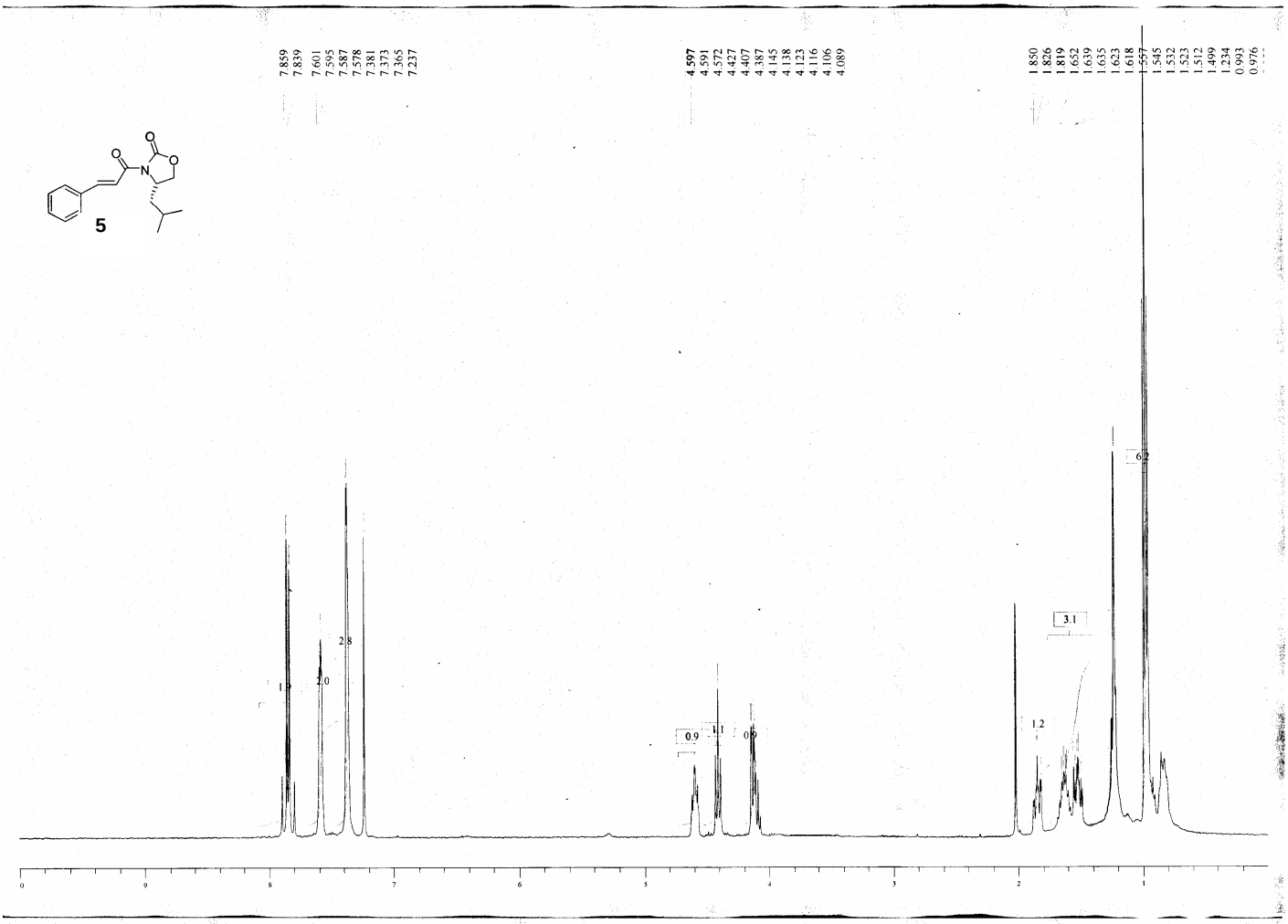
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4.106
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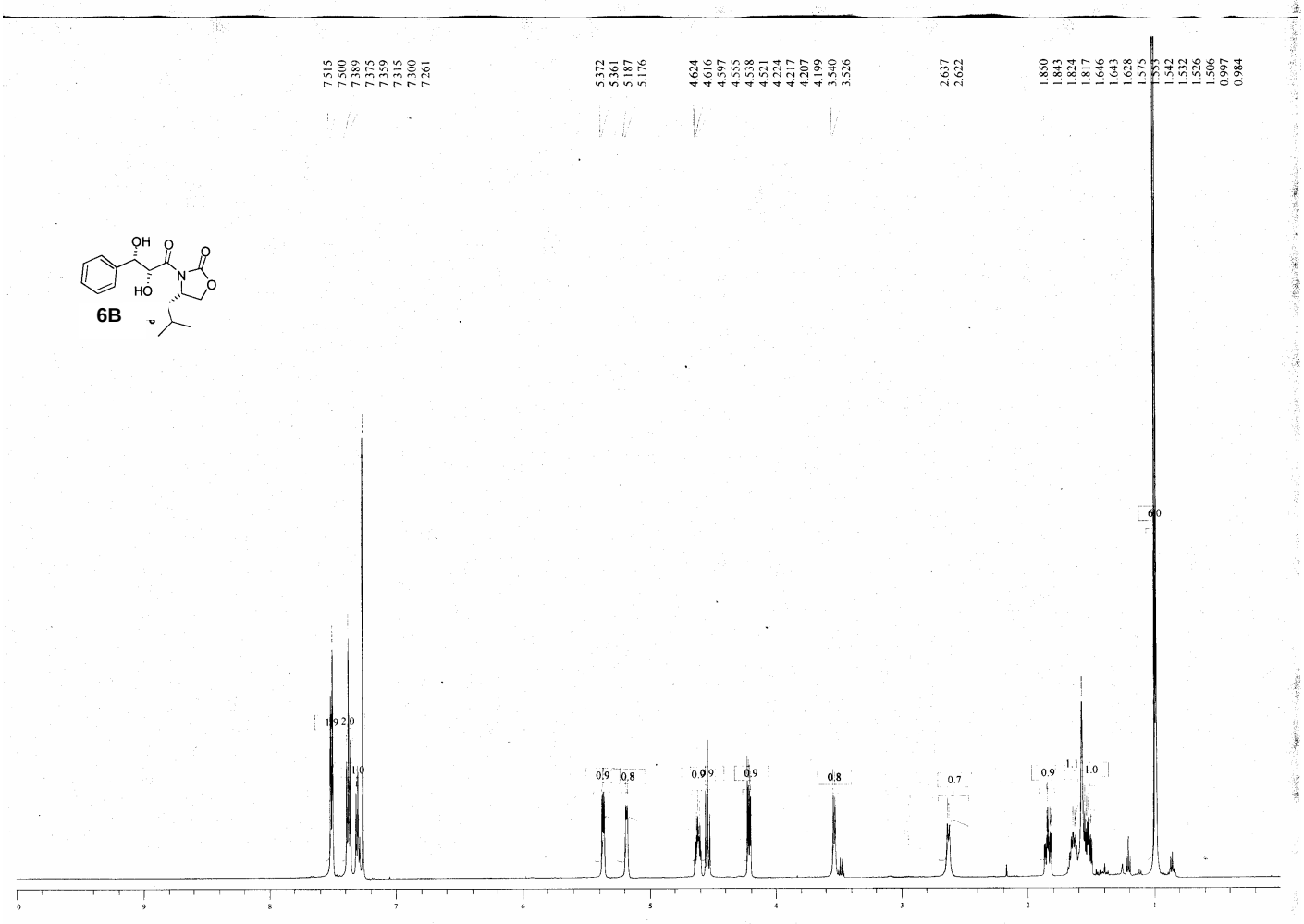
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4.217
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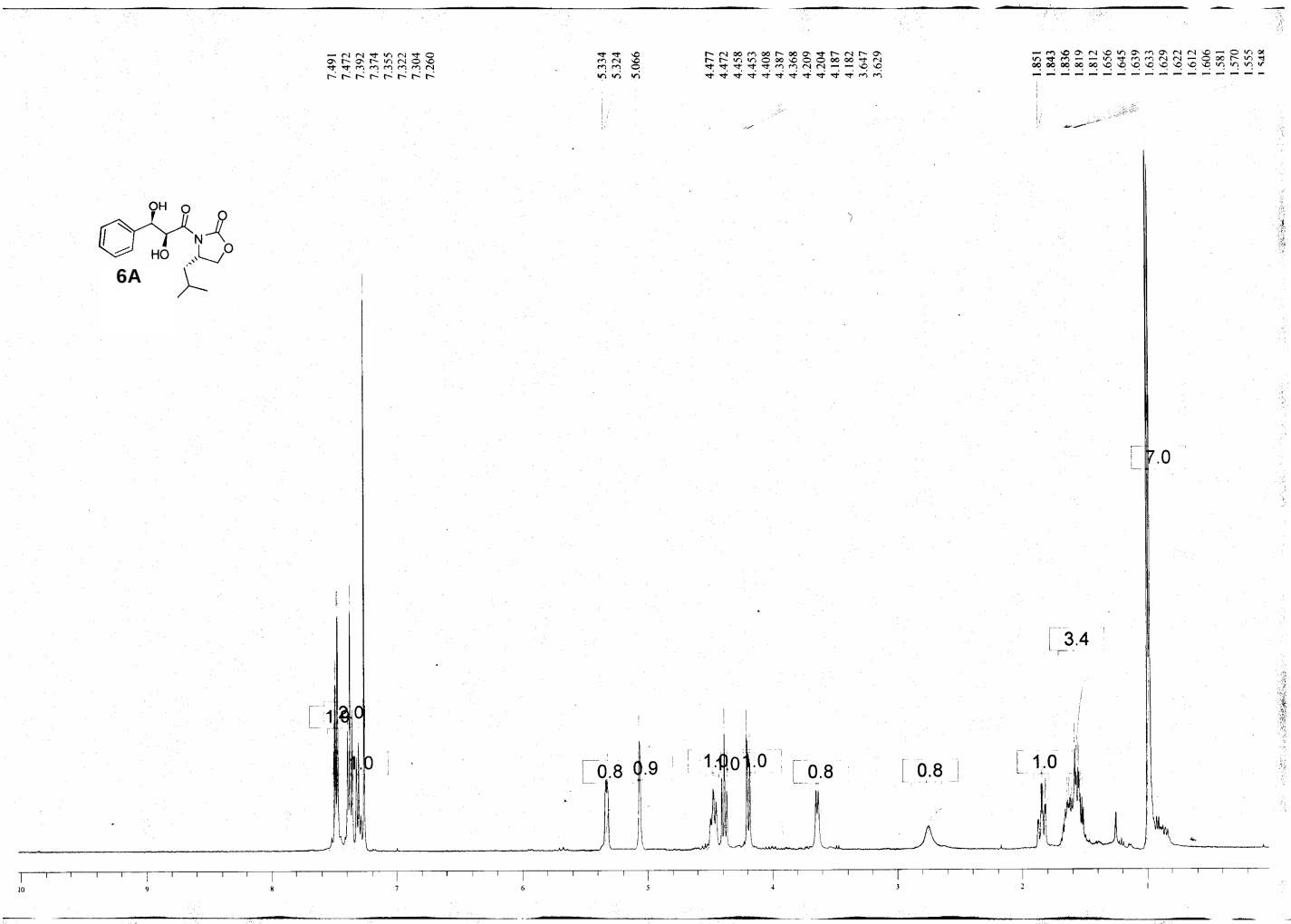
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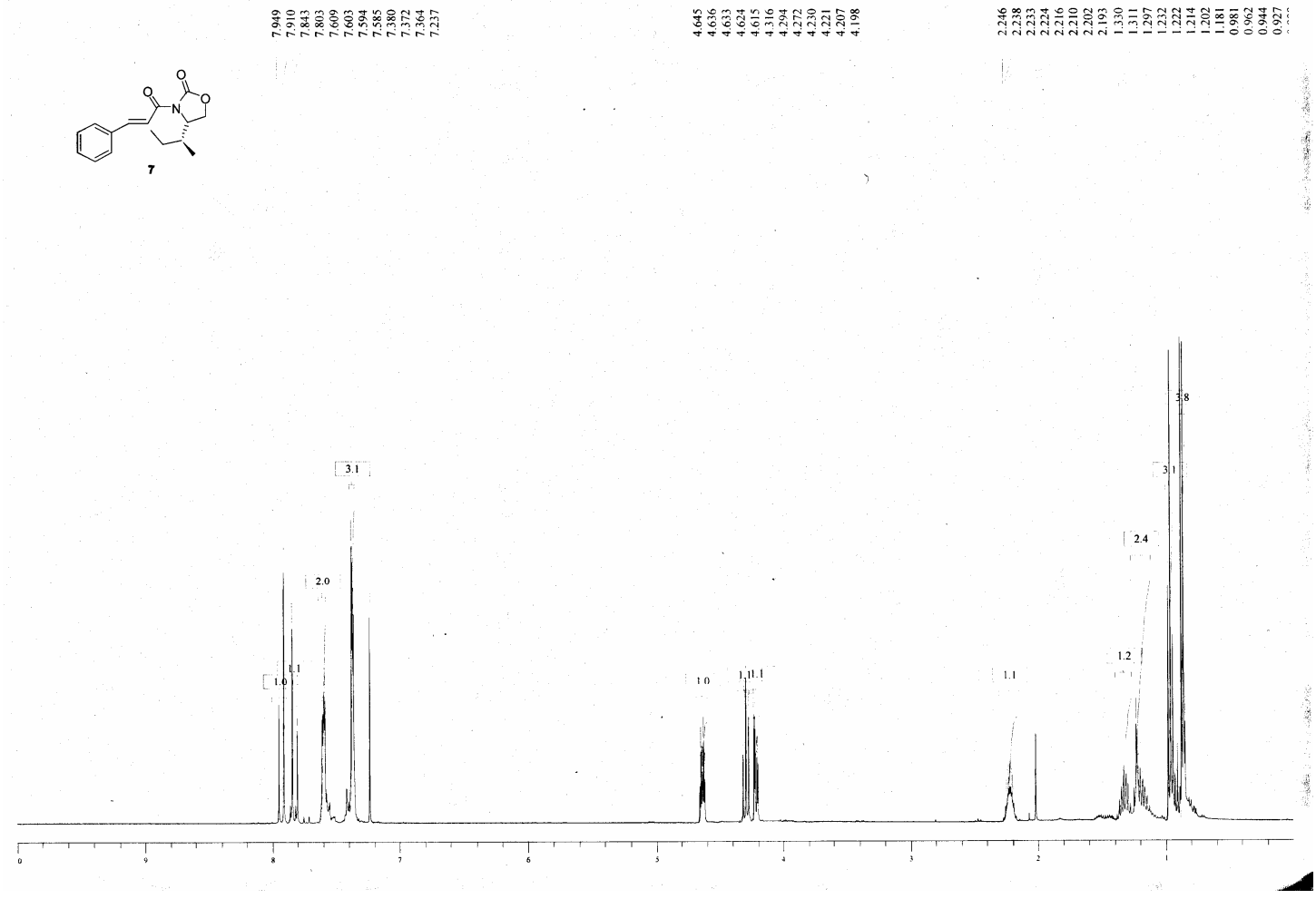
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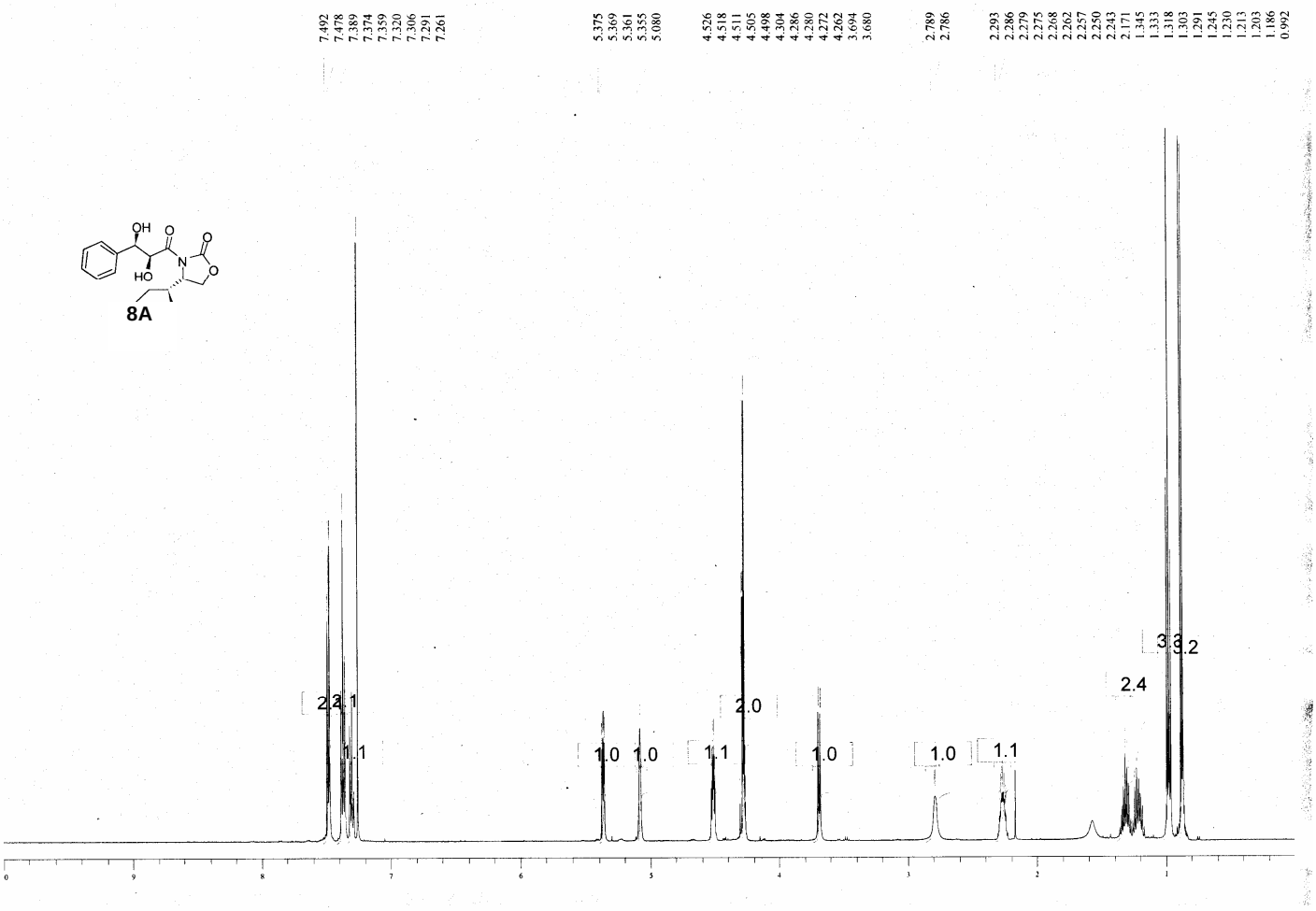
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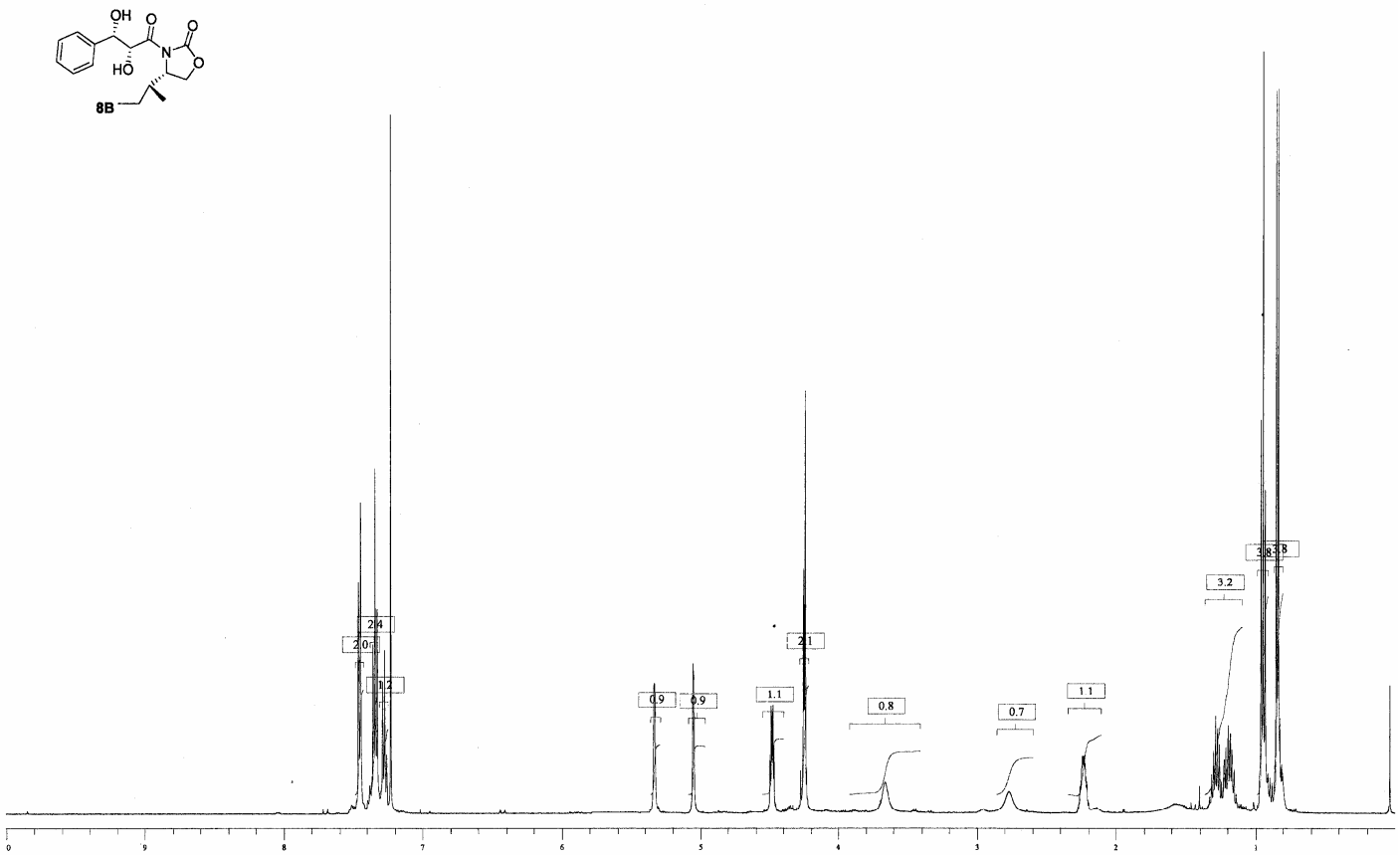
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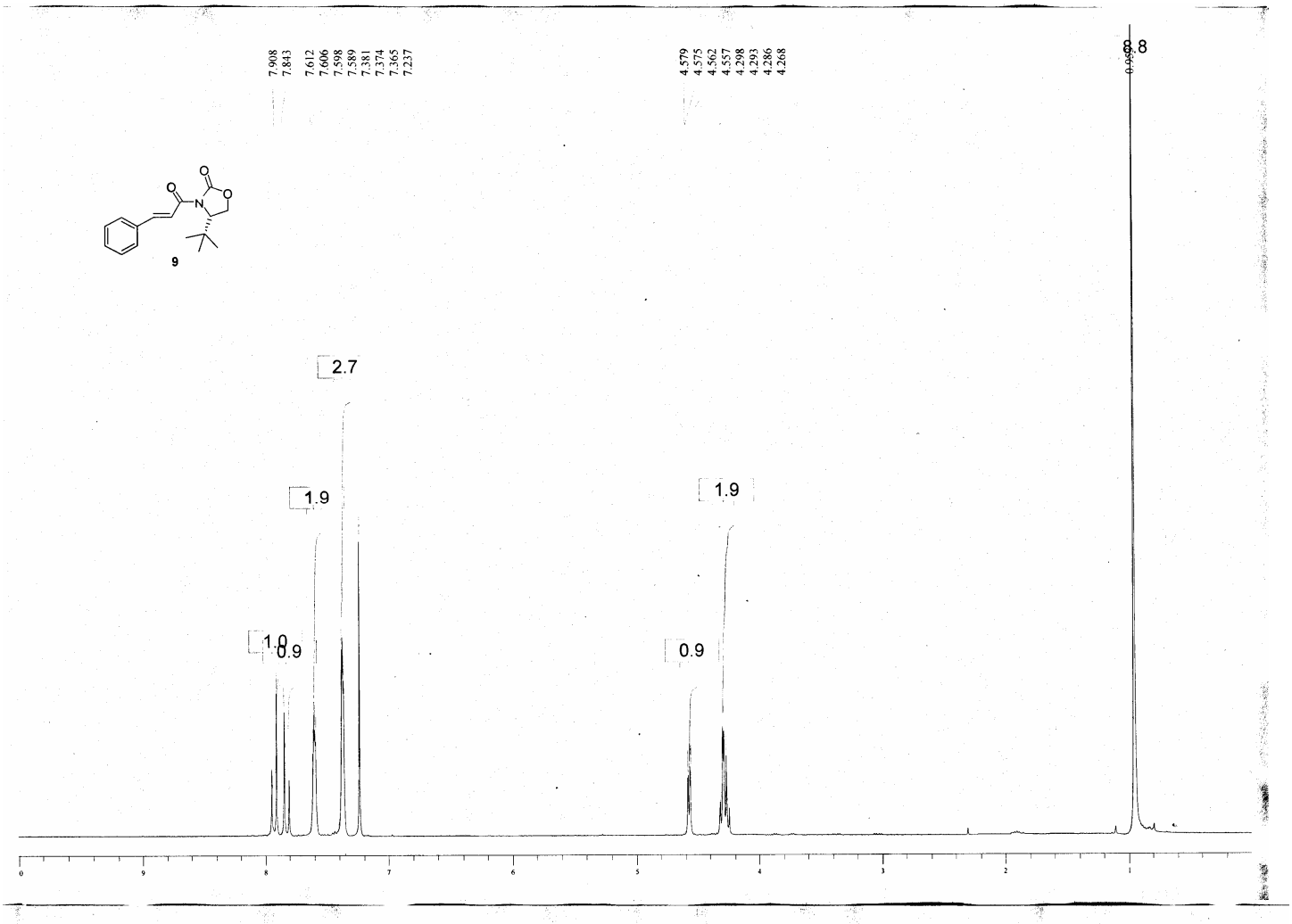
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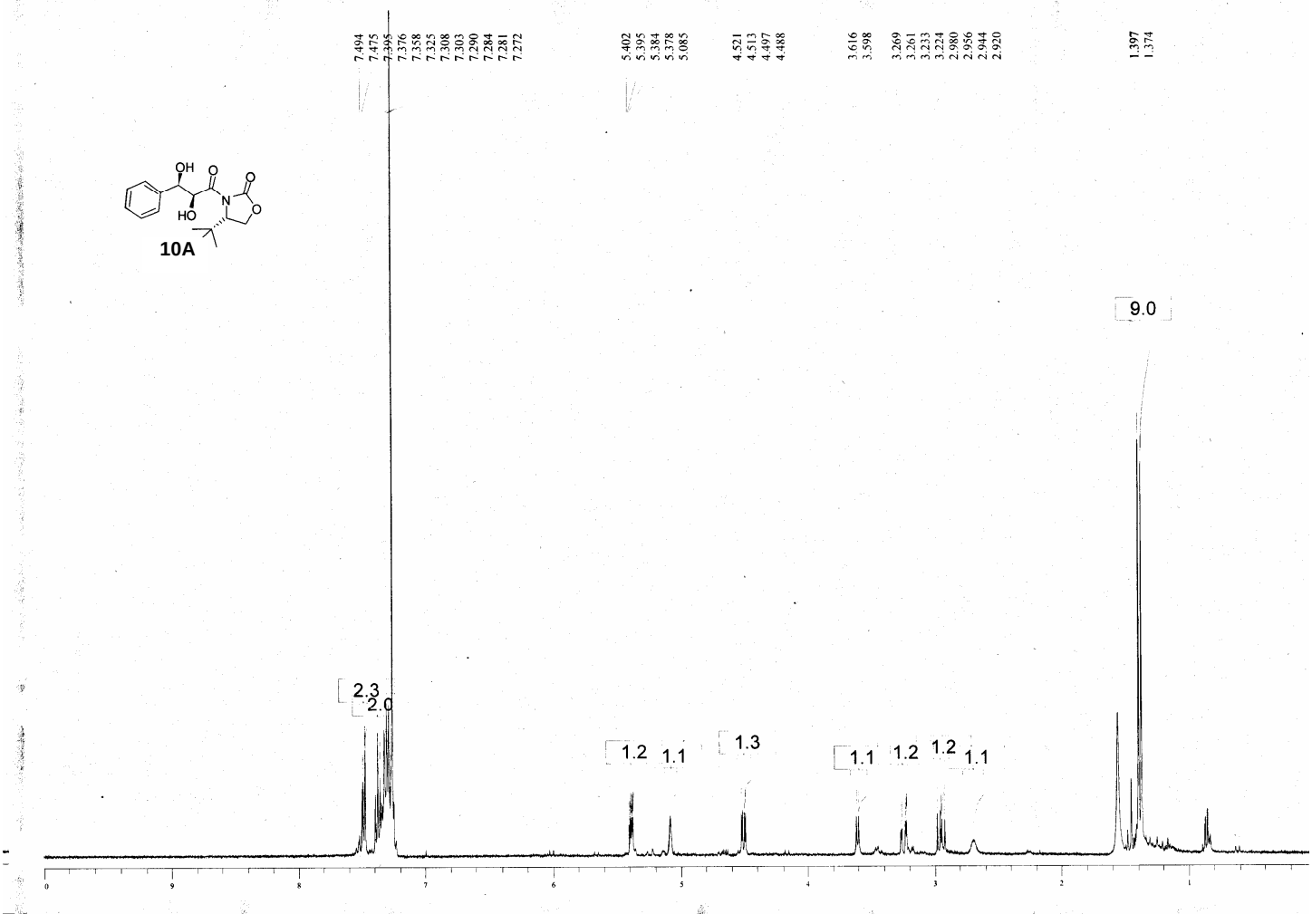
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3.261
3.233
3.224
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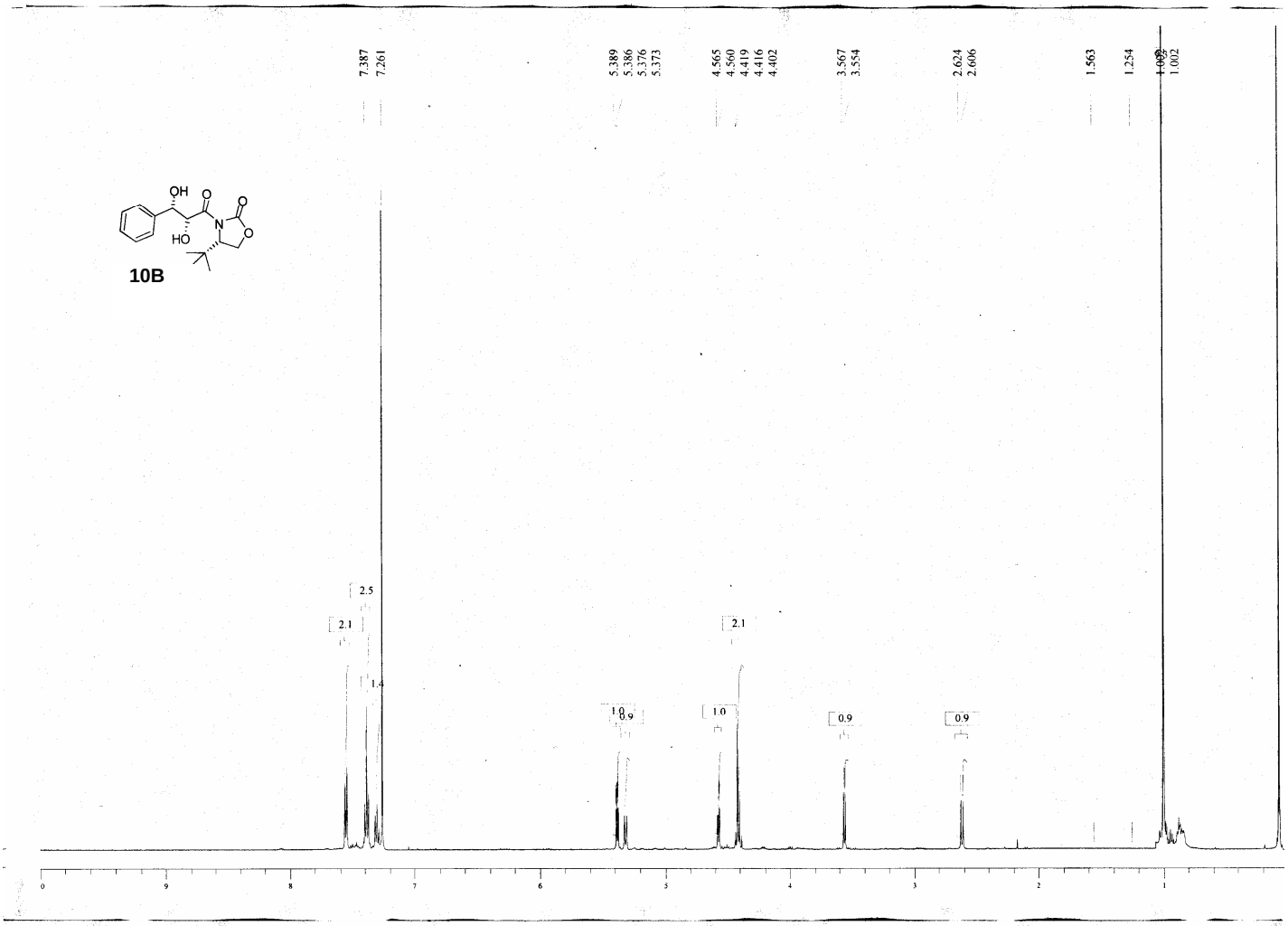
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1.002
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HO
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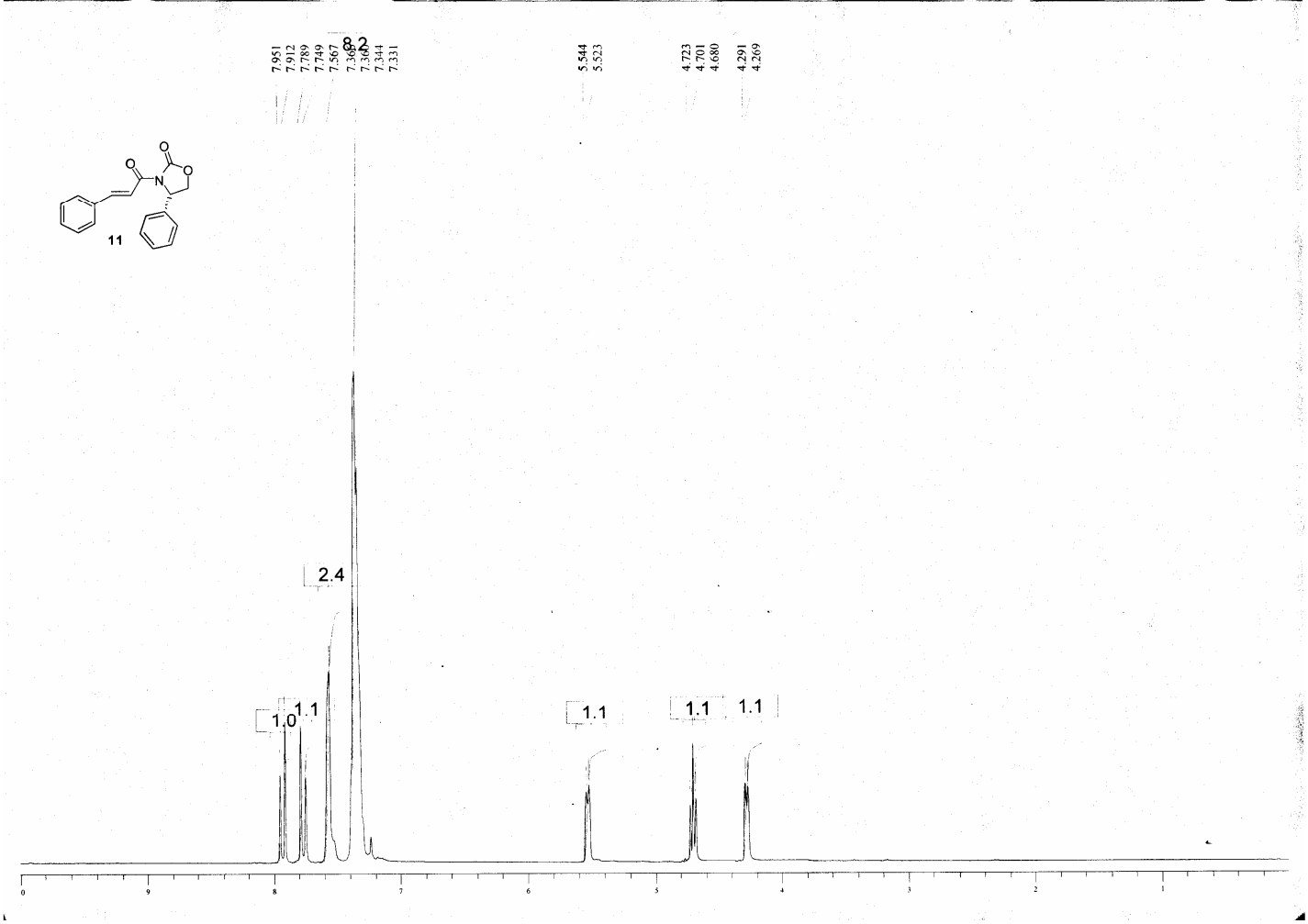
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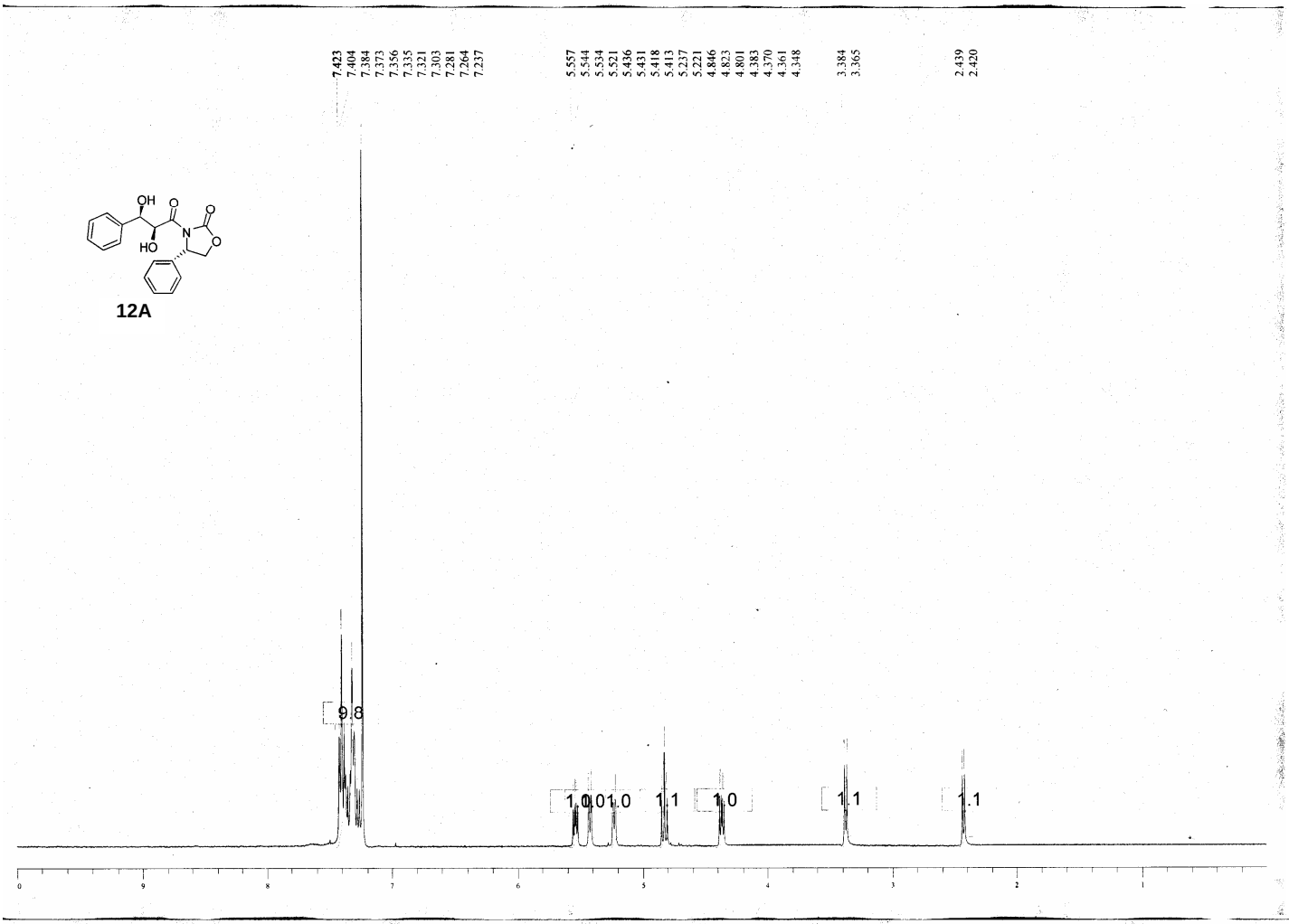
1.1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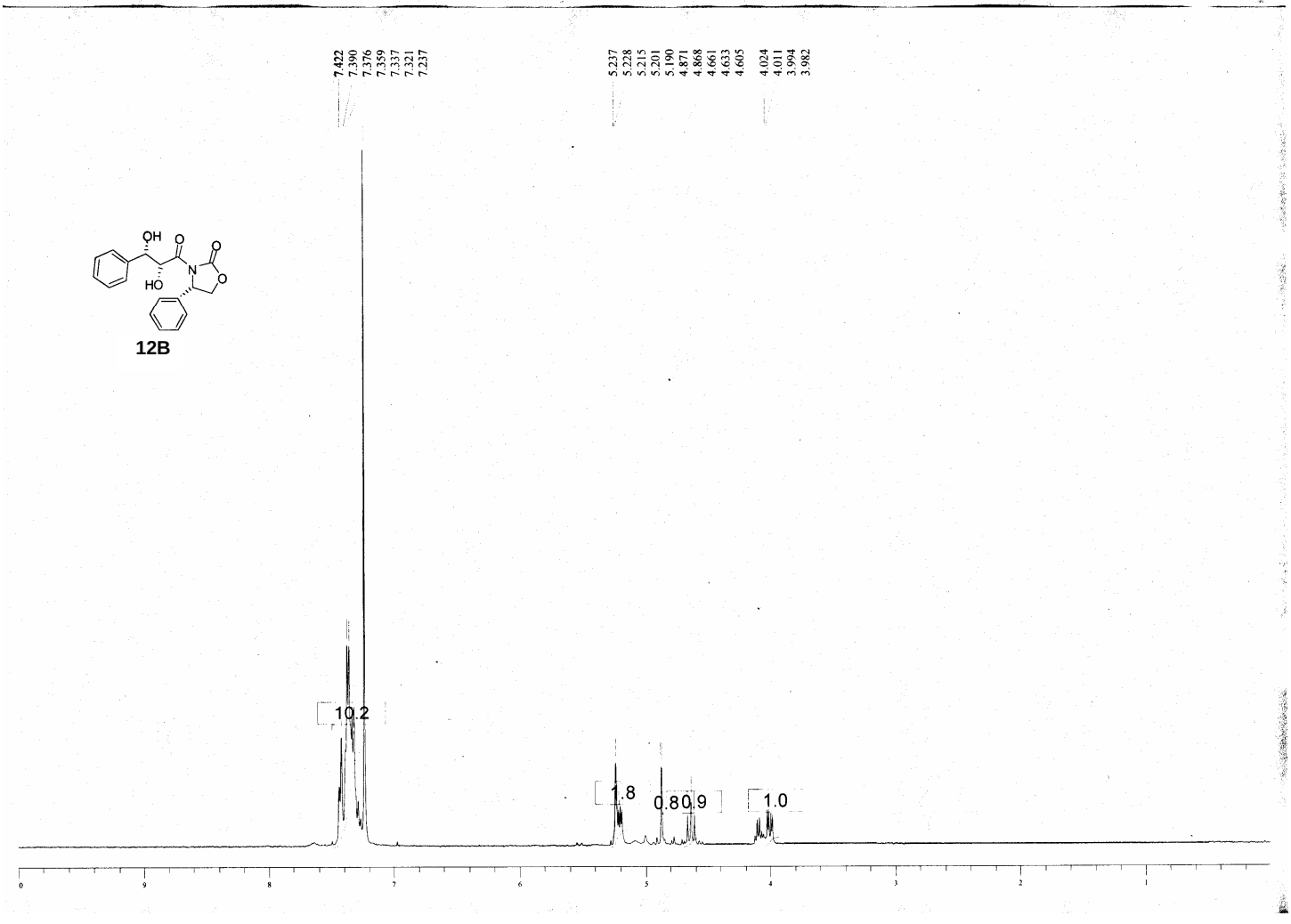
12A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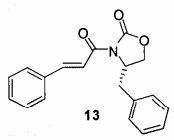
12B



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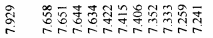
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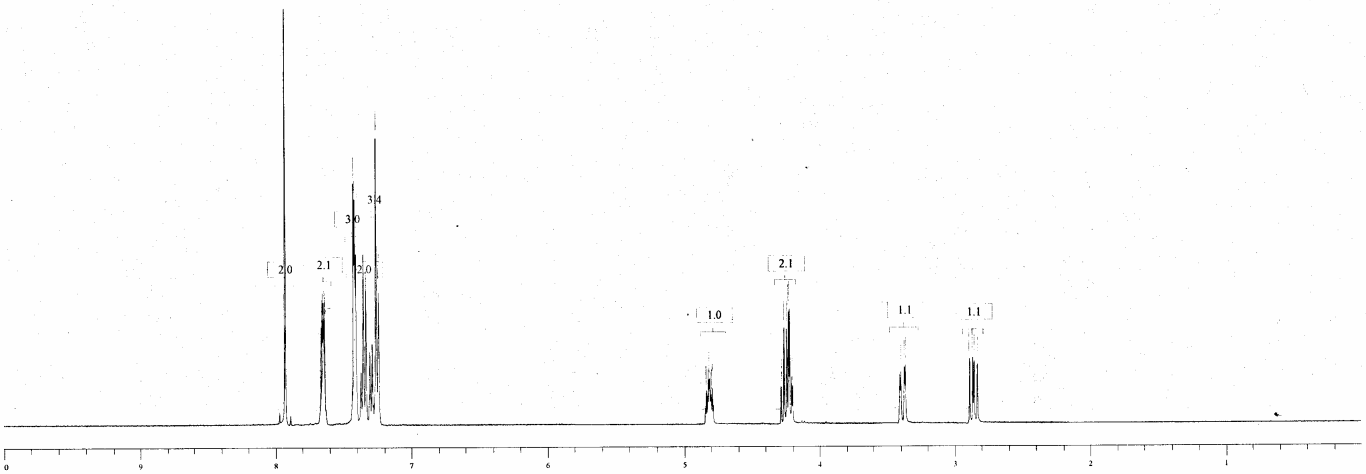
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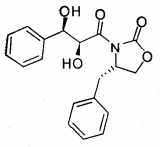

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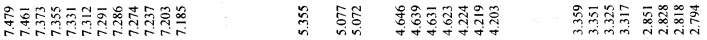
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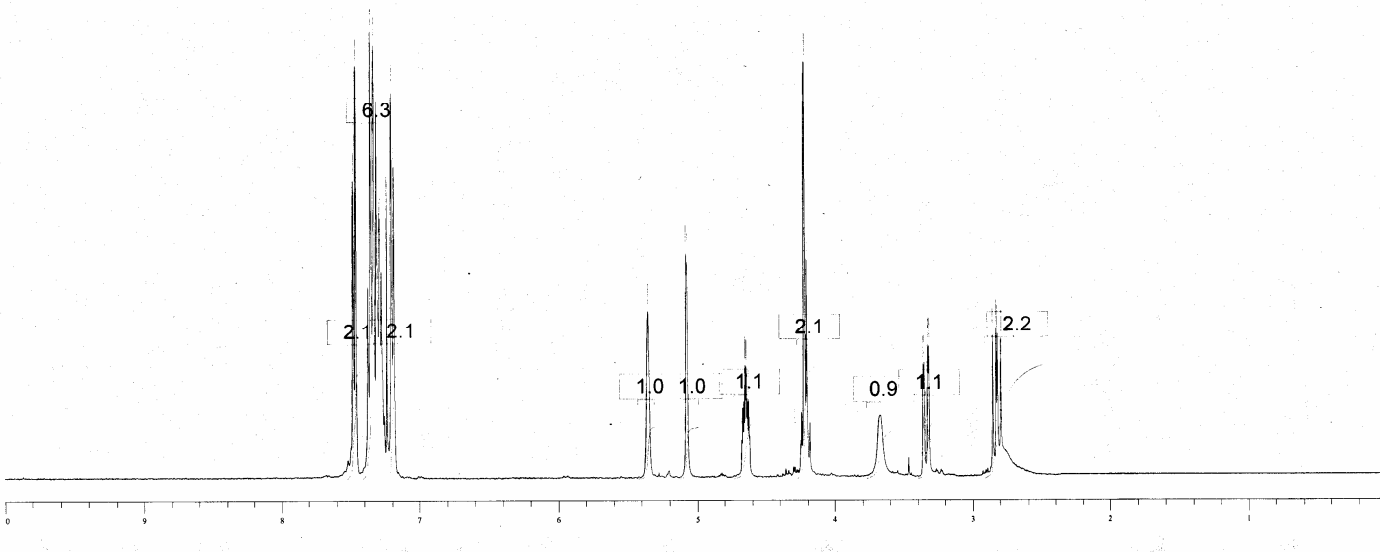
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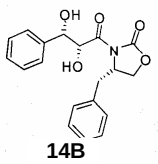
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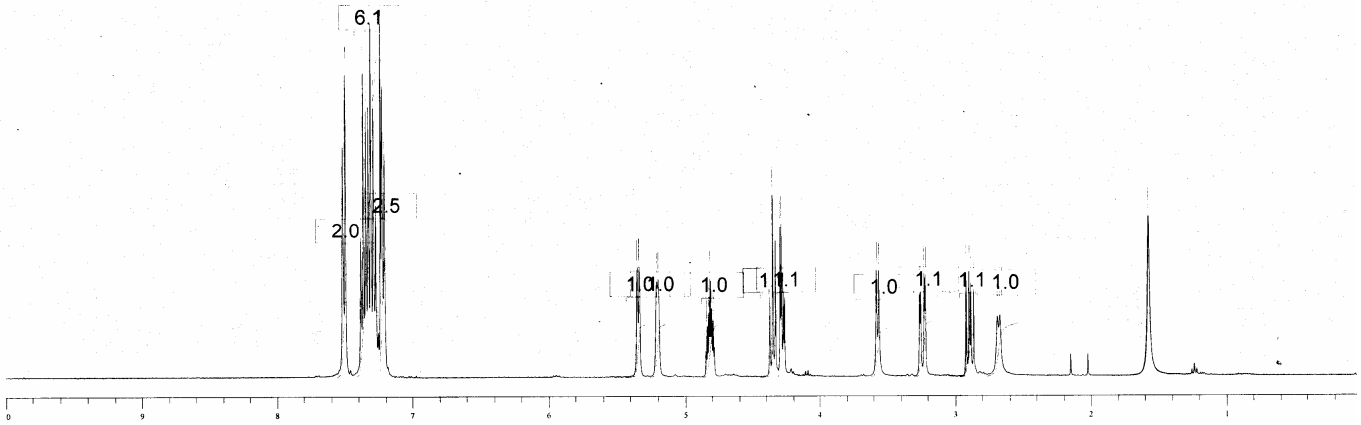
14B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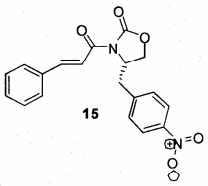
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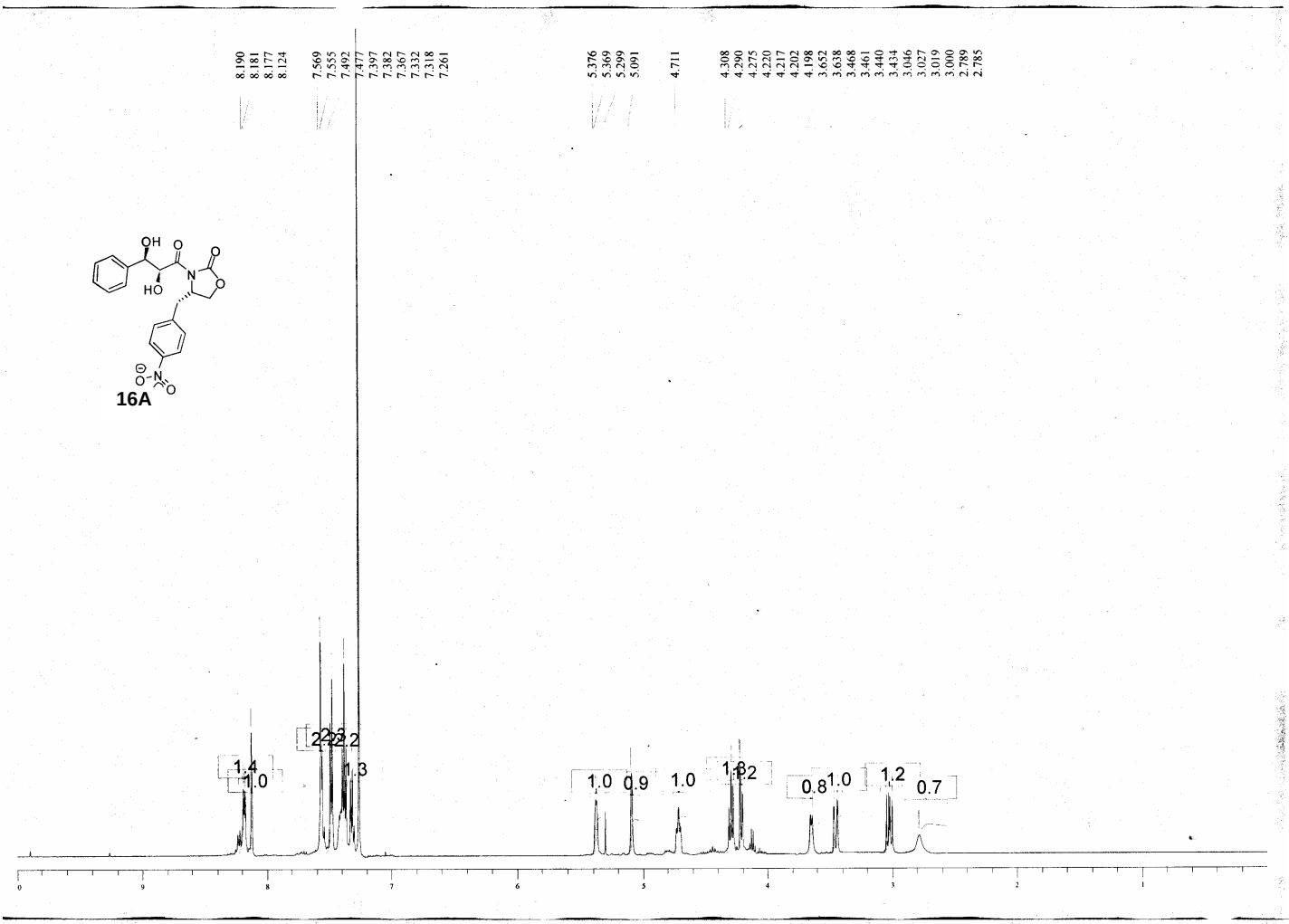
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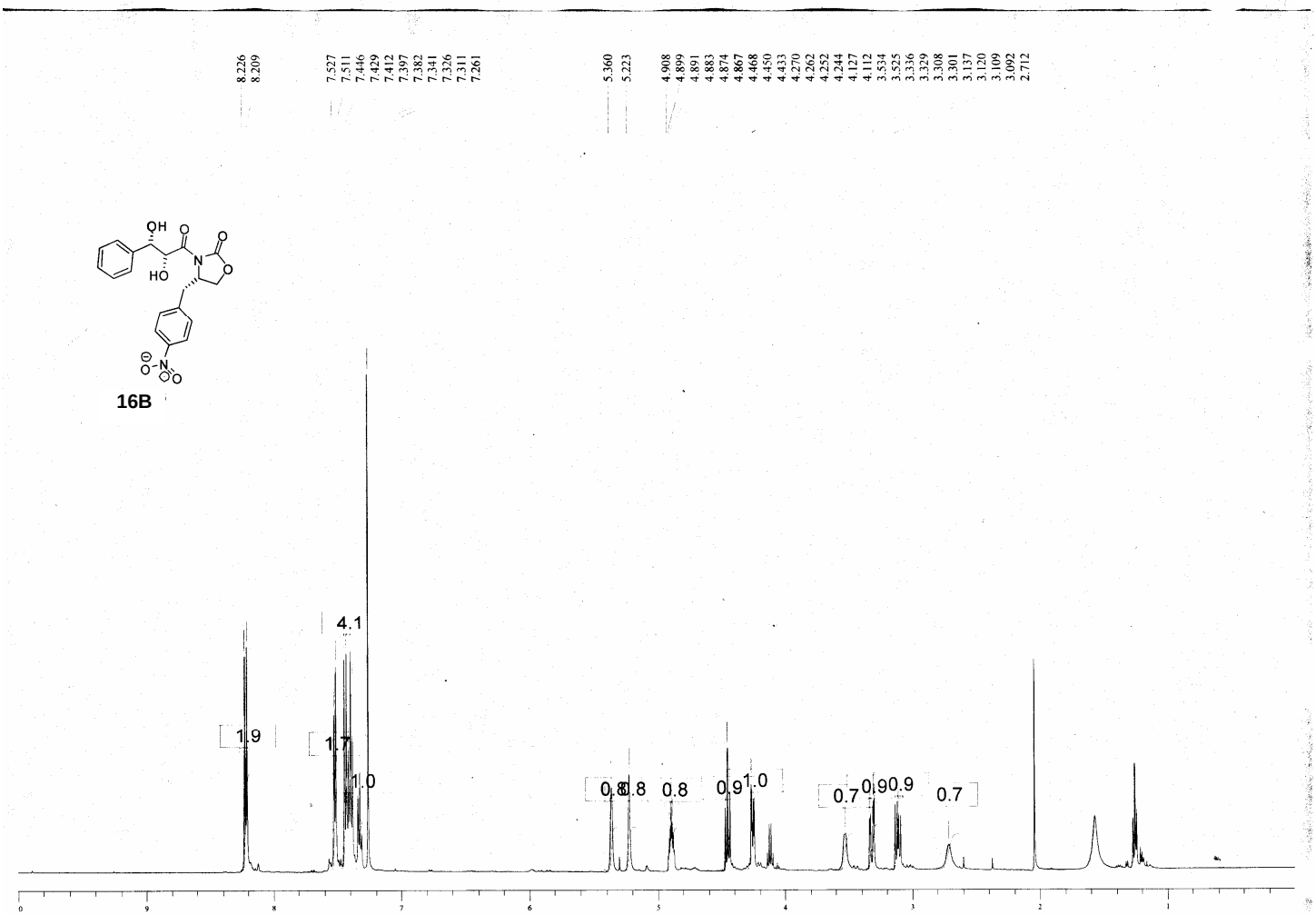
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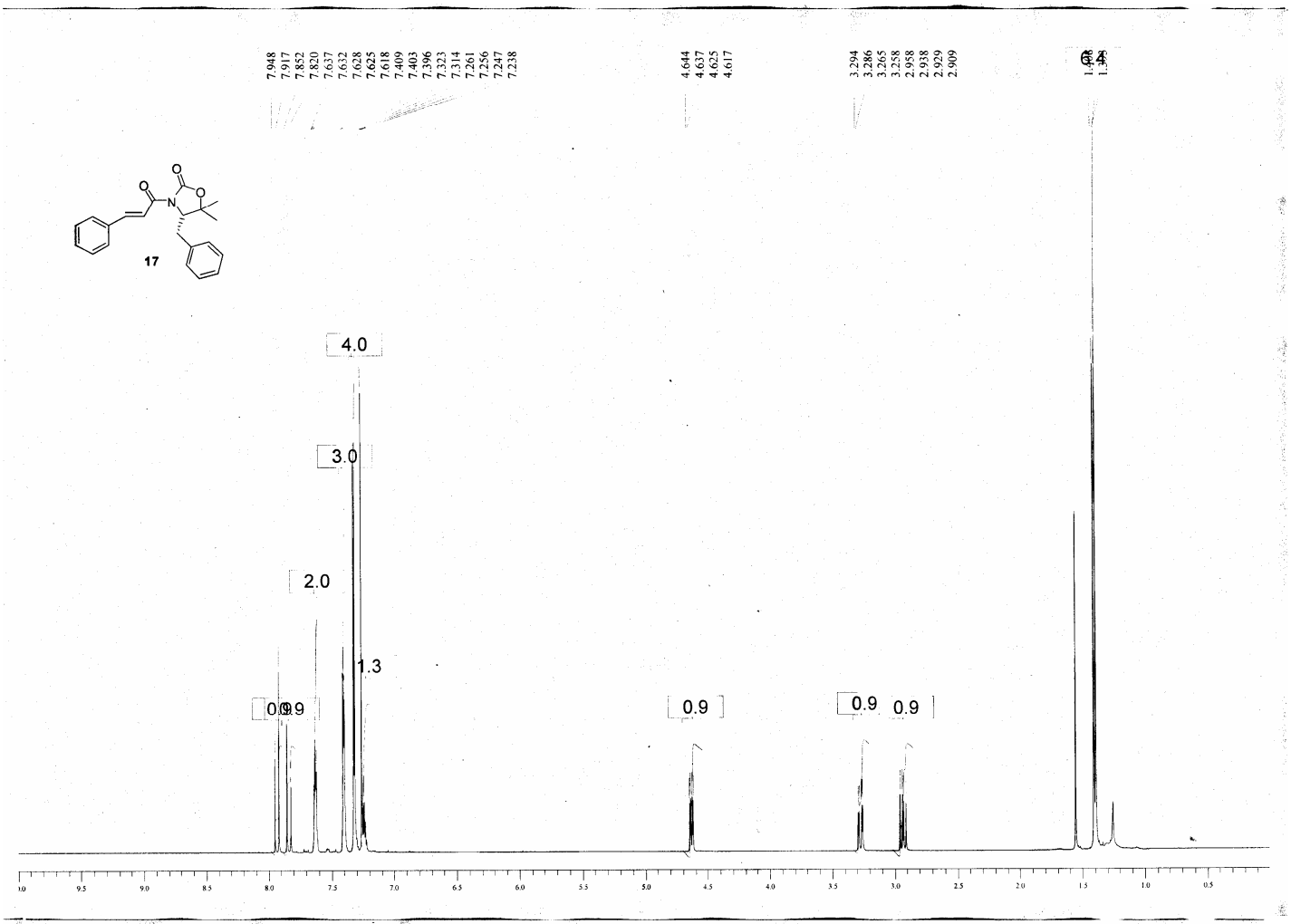
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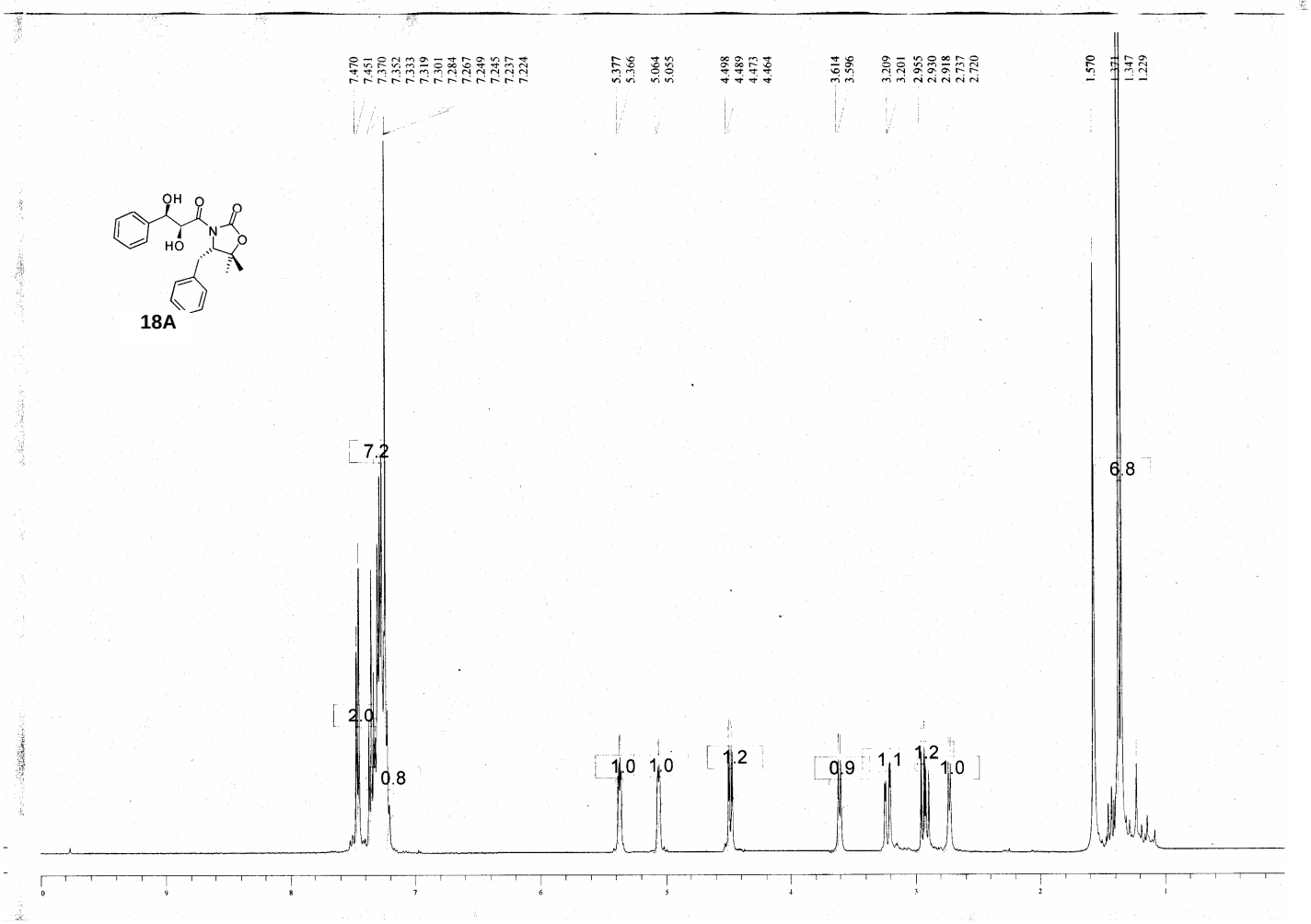
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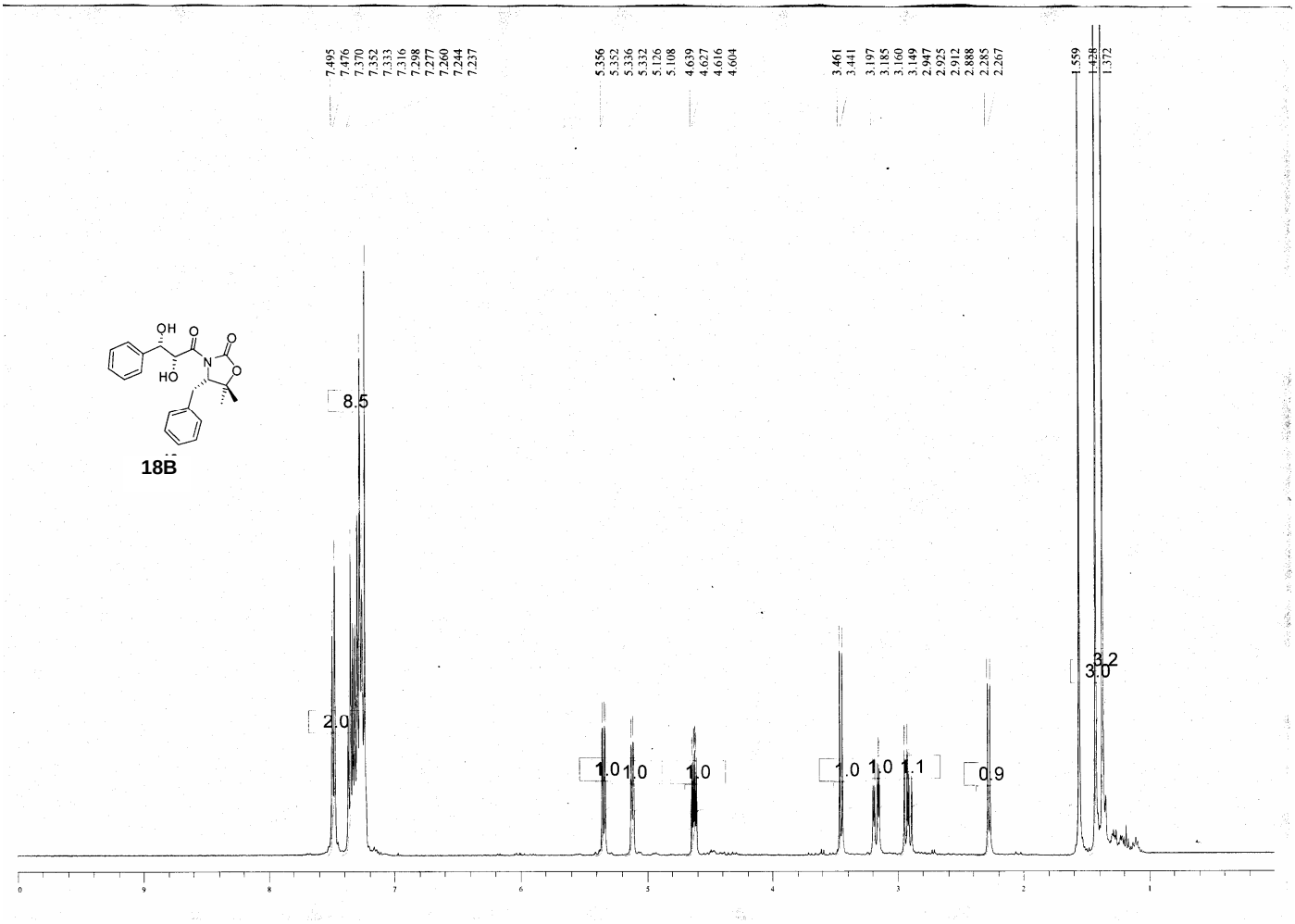
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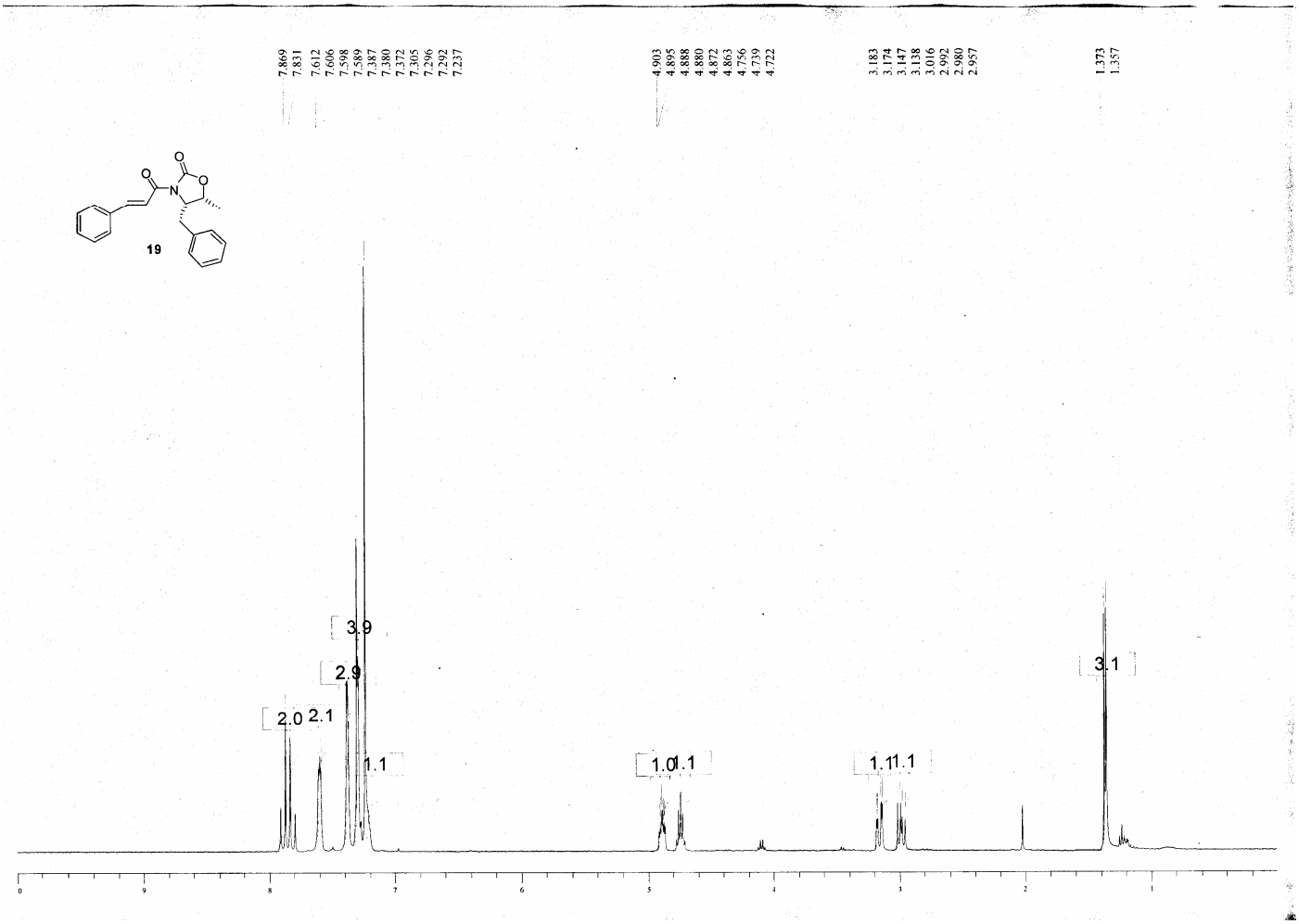
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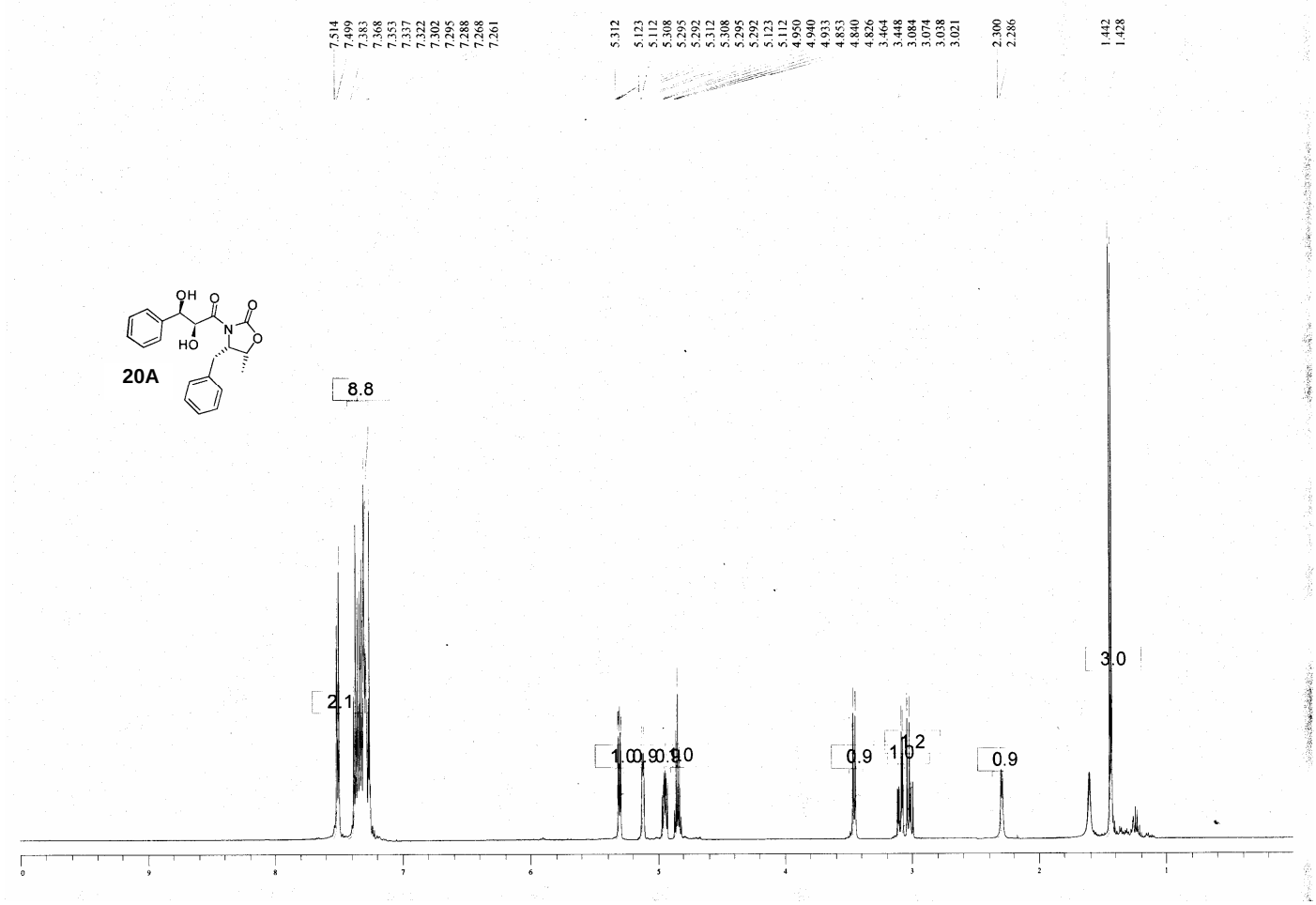
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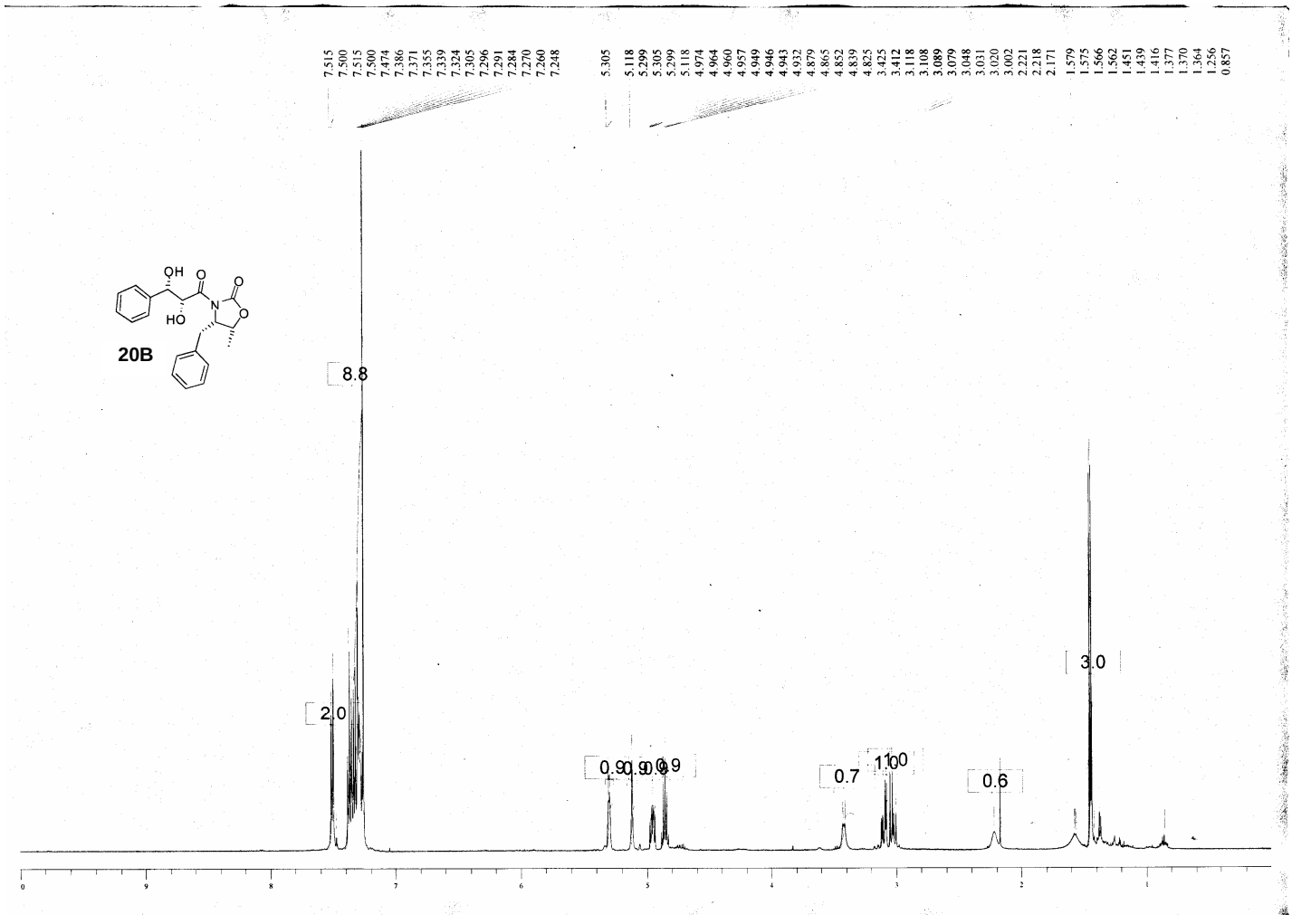
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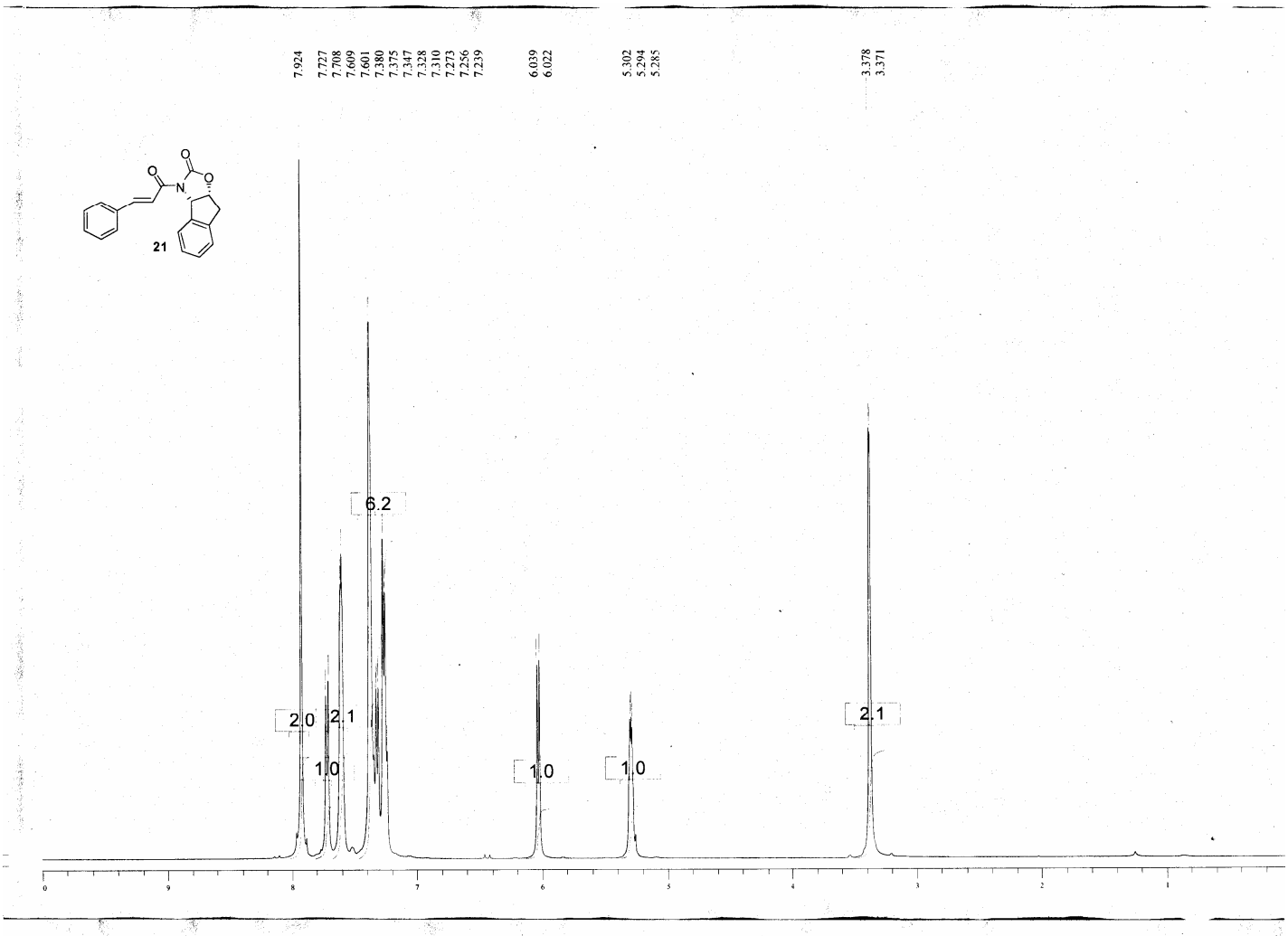
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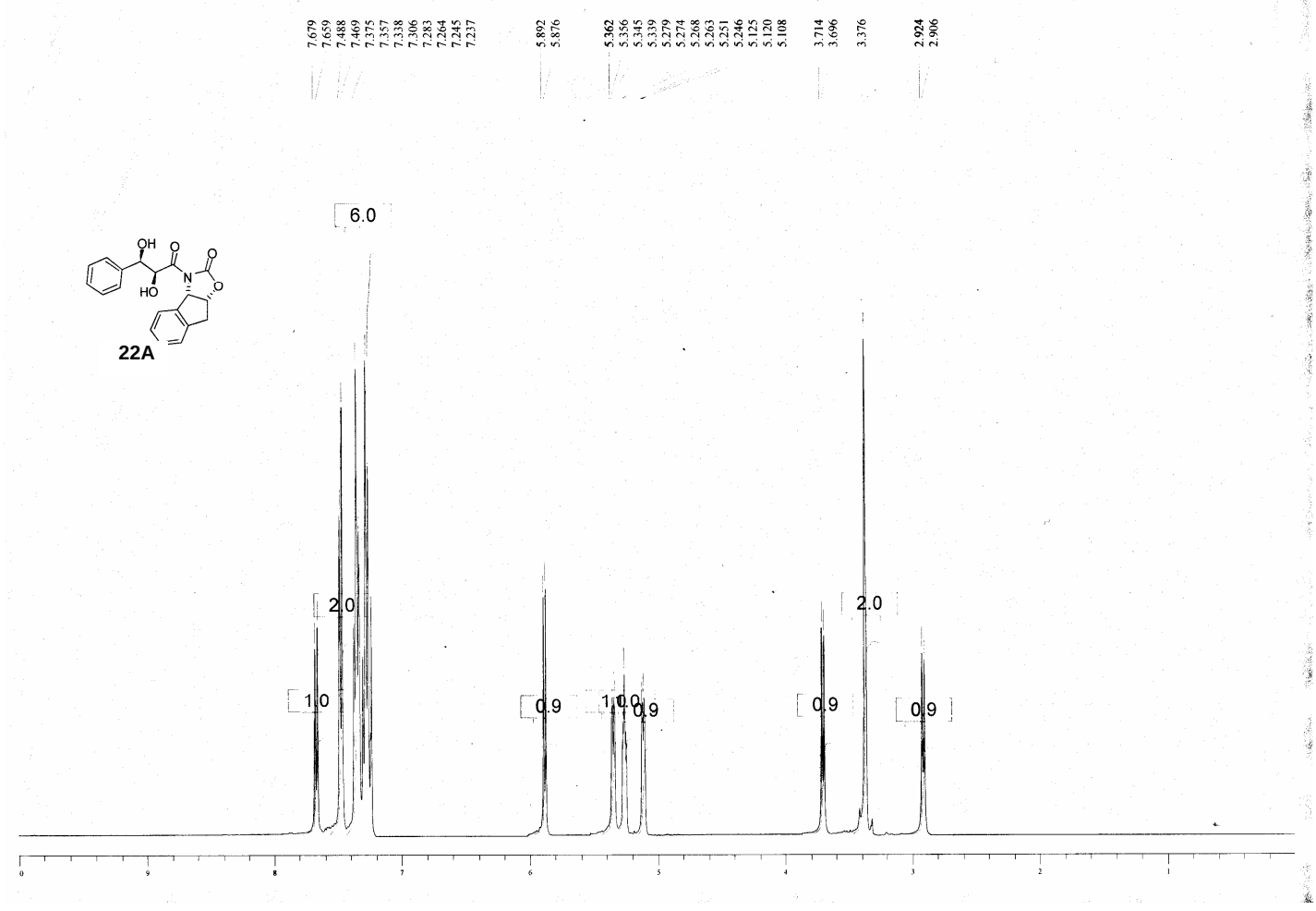
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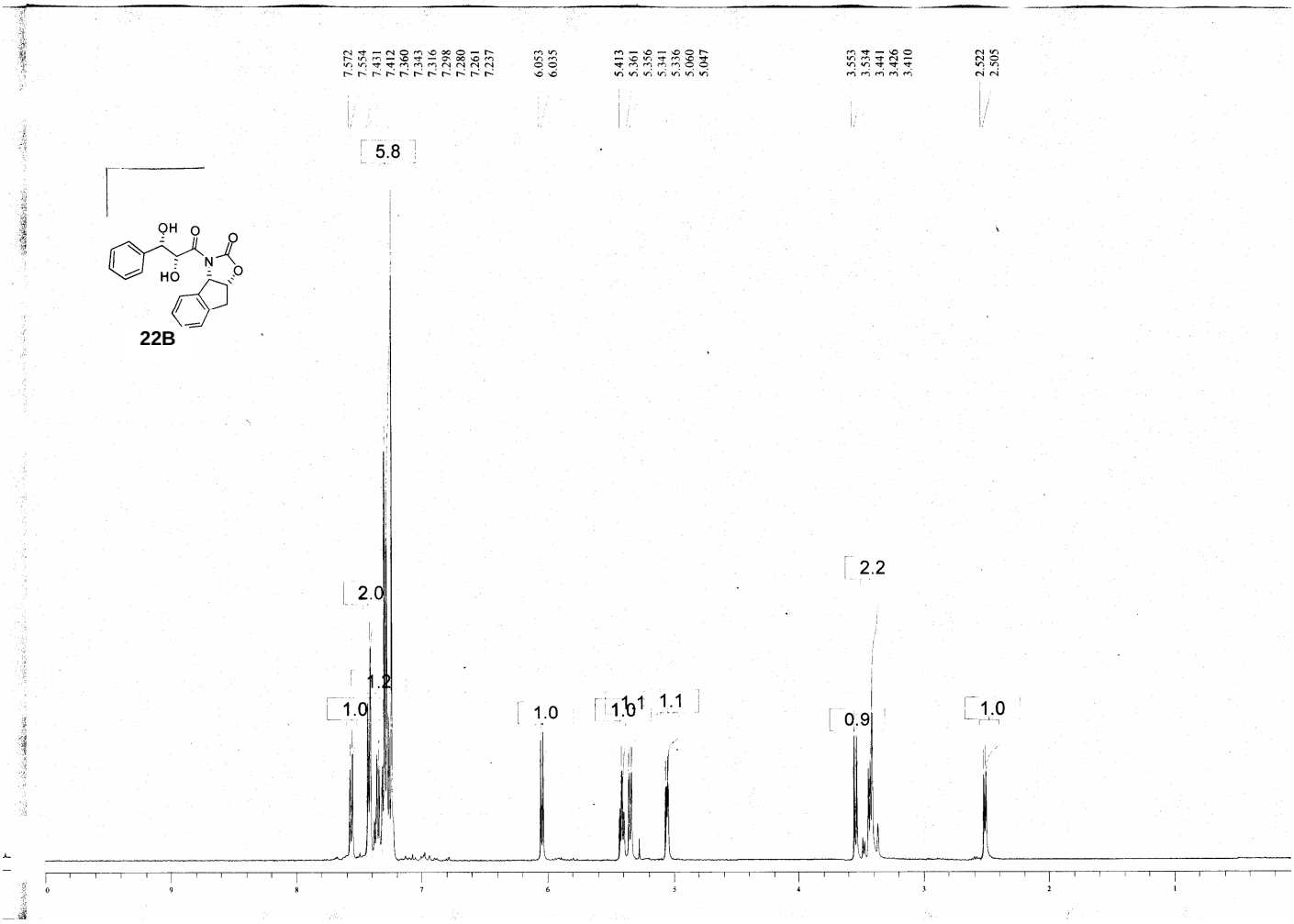
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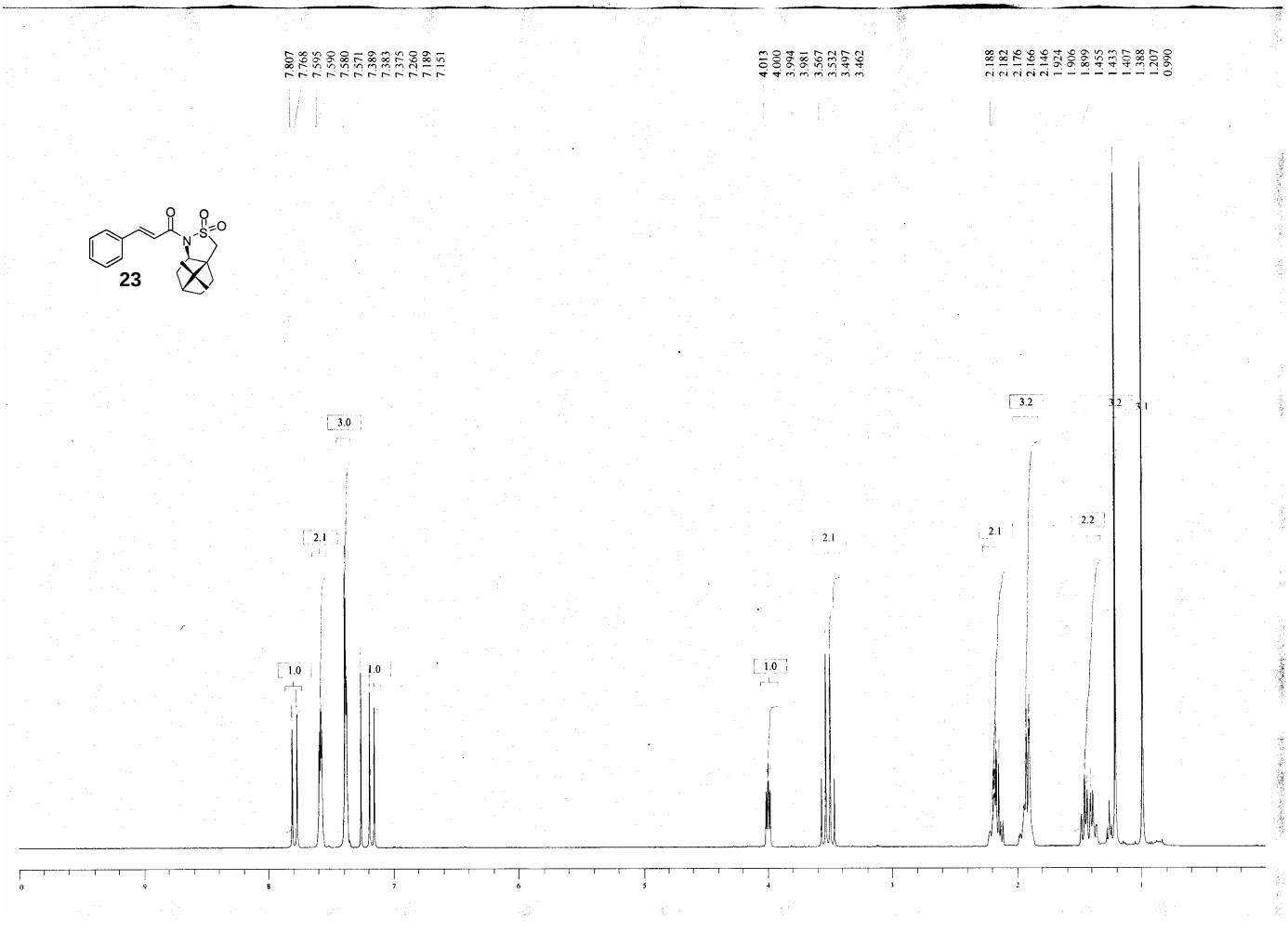
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O
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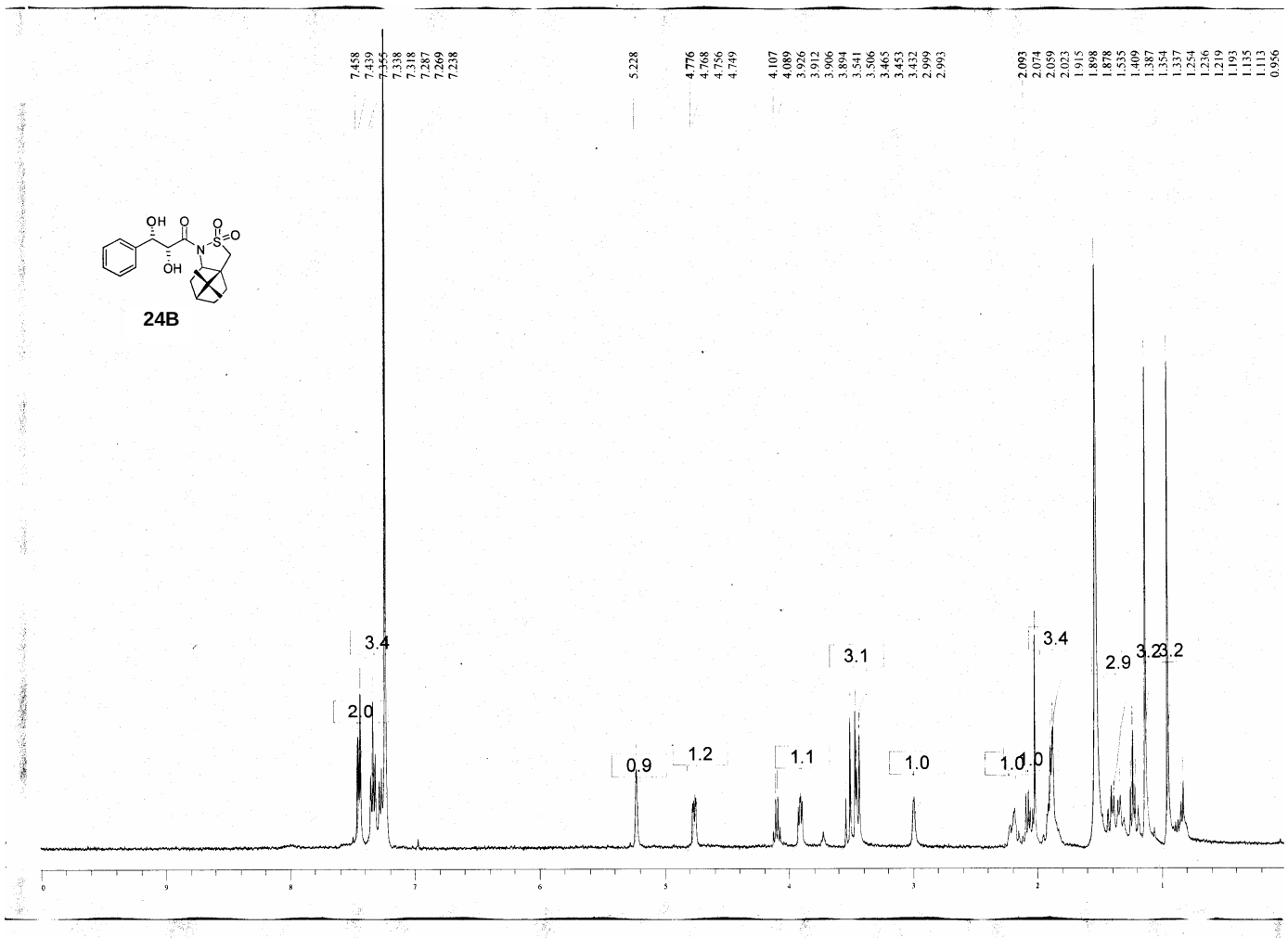
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OH
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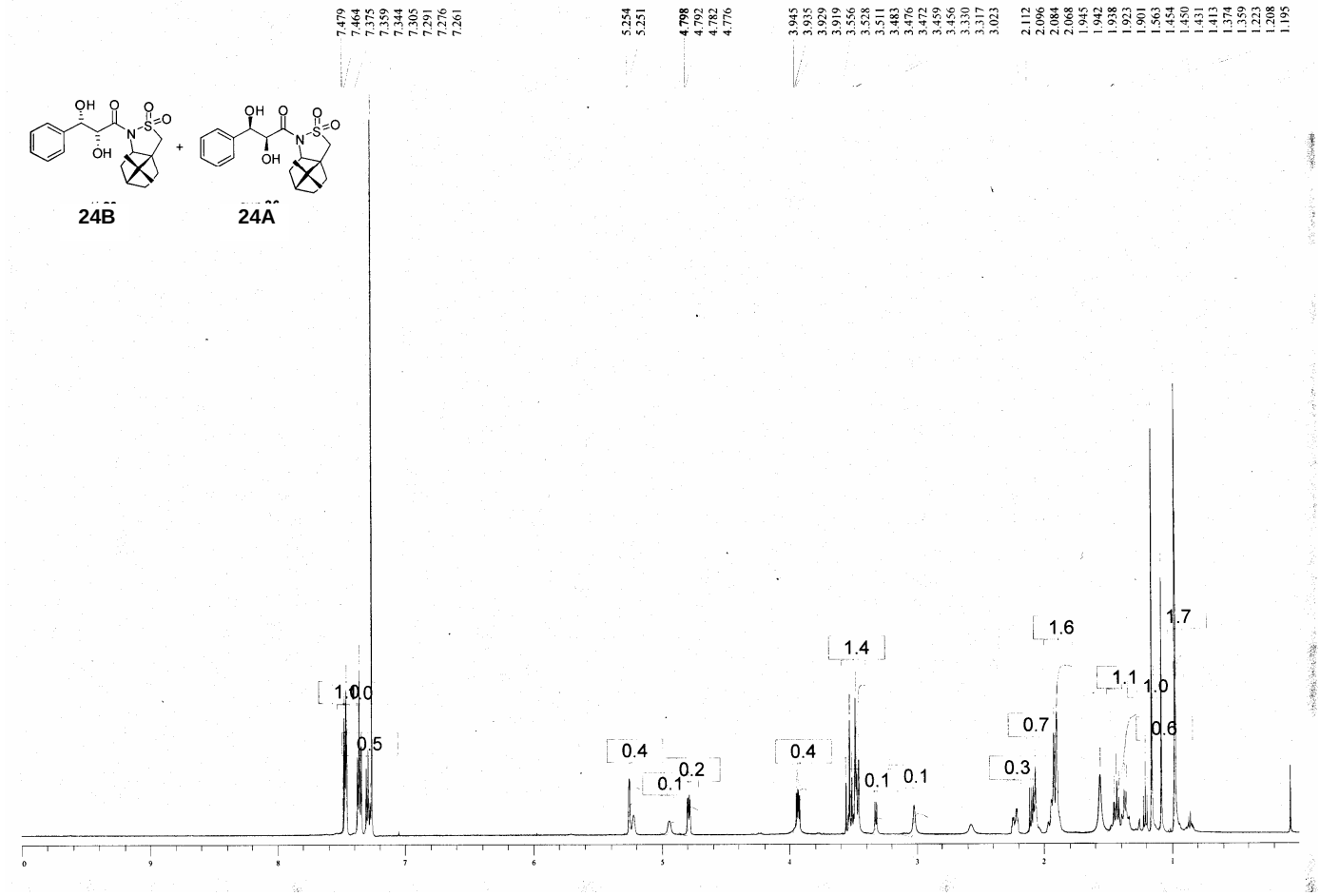
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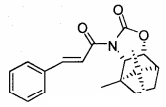

32

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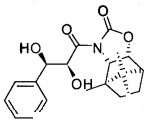

33A

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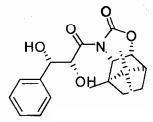

33B

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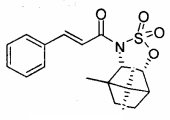

34

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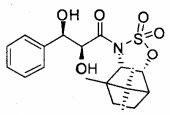

35A

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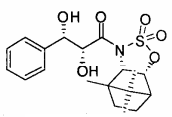

35B

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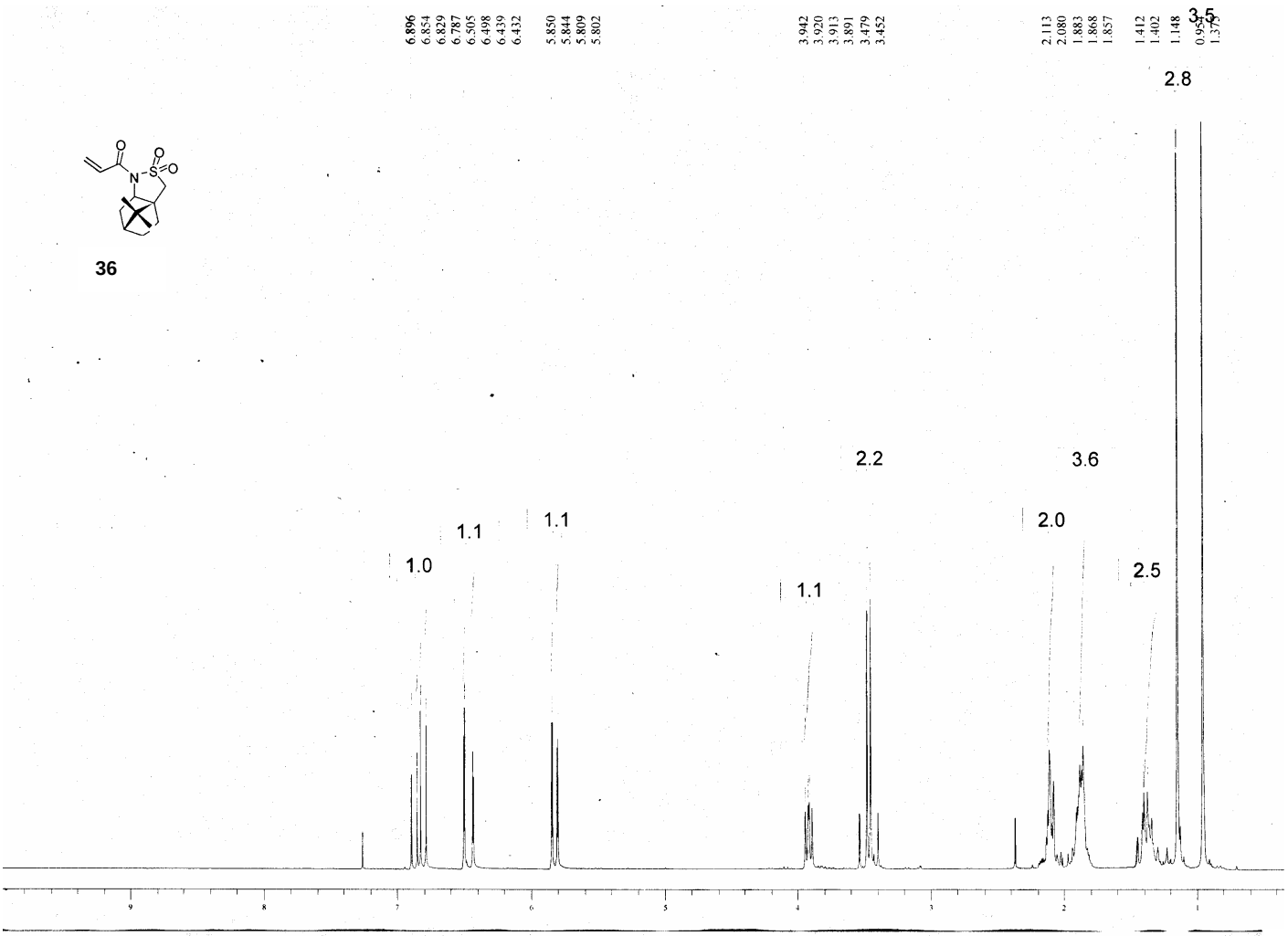
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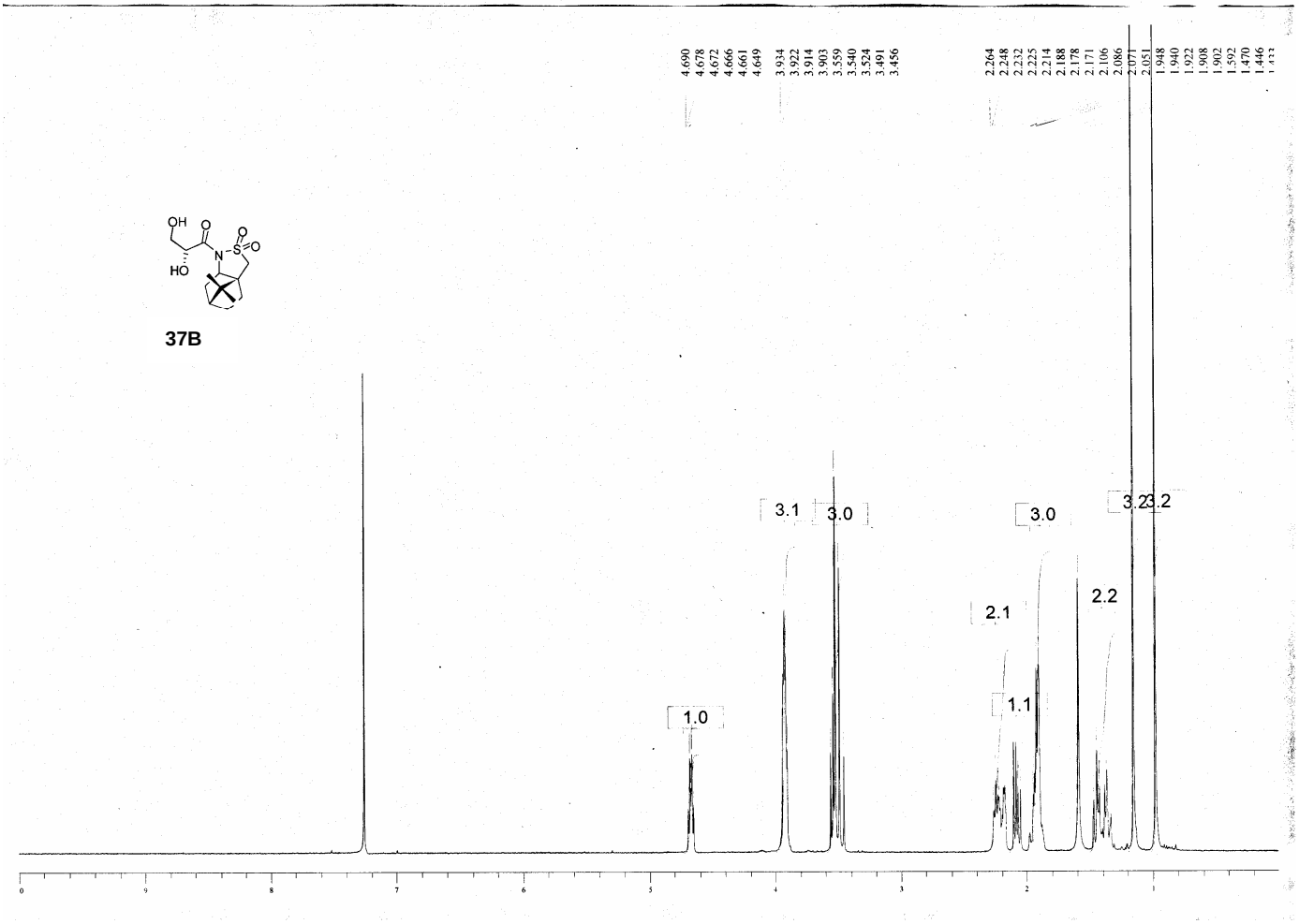
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37B
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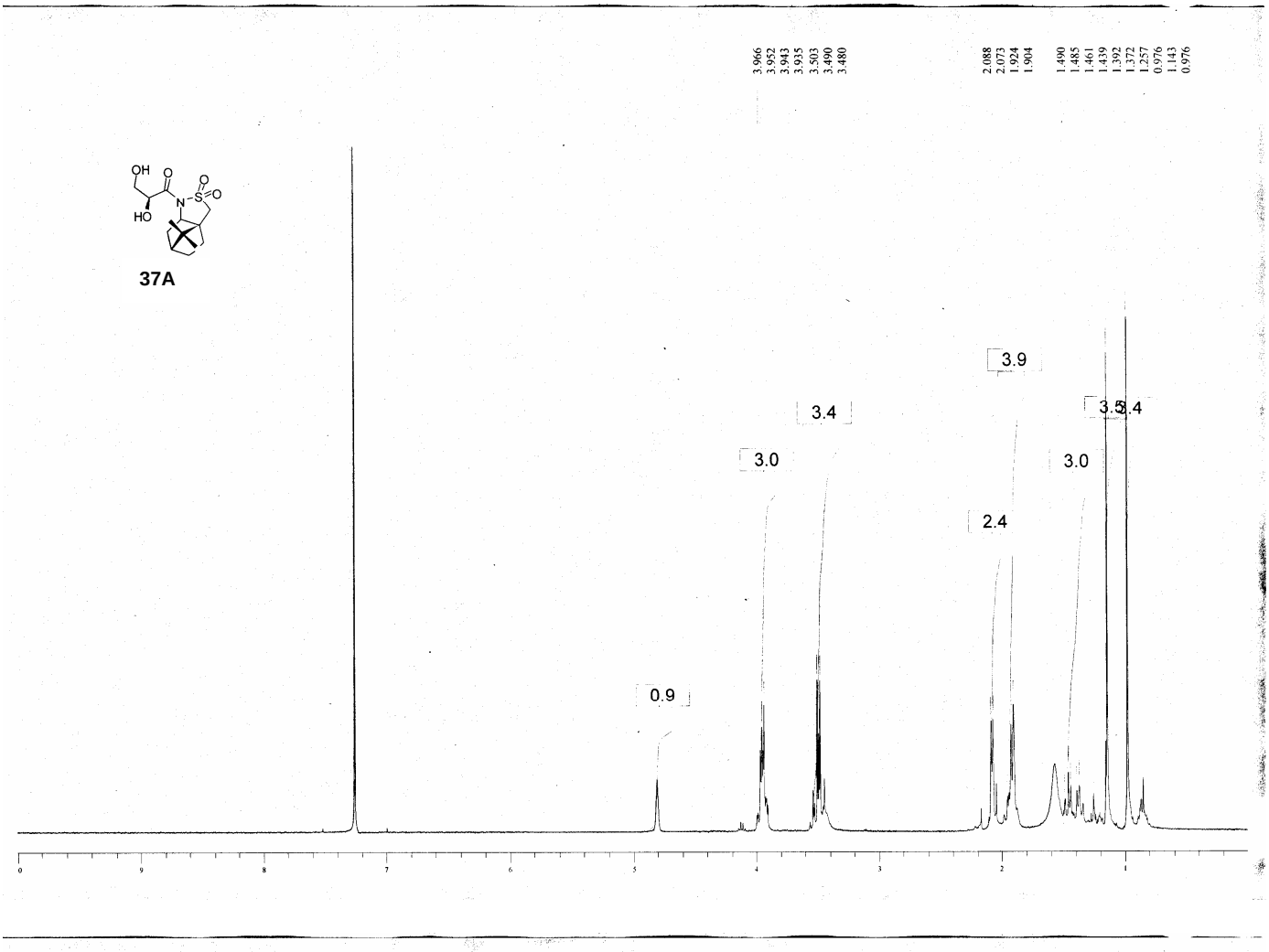
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OH
HO
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N
S
O
O
37A
3.9
3.4
3.5
3.4
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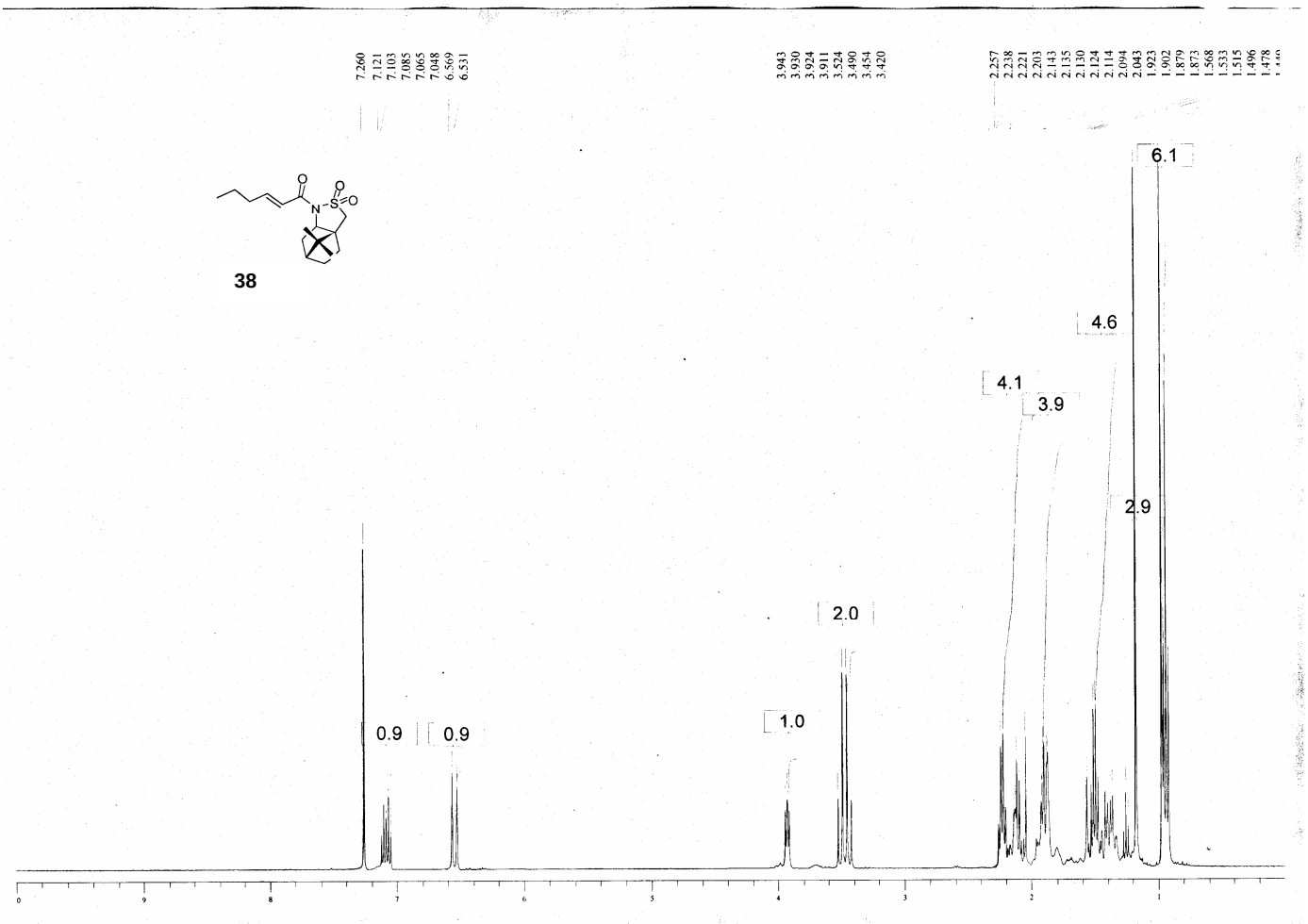
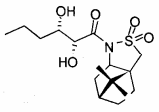
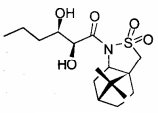
3.0
2.4
0.9


7.260
7.121
7.103
7.085
7.065
7.048
6.569
6.531
3.943
3.930
3.924
3.911
3.524
3.490
3.454
3.420
2.257
2.238
2.221
2.203
2.143
2.135
2.130
2.124
2.114
2.094
2.043
1.923
1.902
1.879
1.873
1.568
1.533
1.515
1.496
1.478
O
N
S
O
O
38
6.1
4.6
4.1
3.9
2.9
2.0
1.0
0.9
0.9



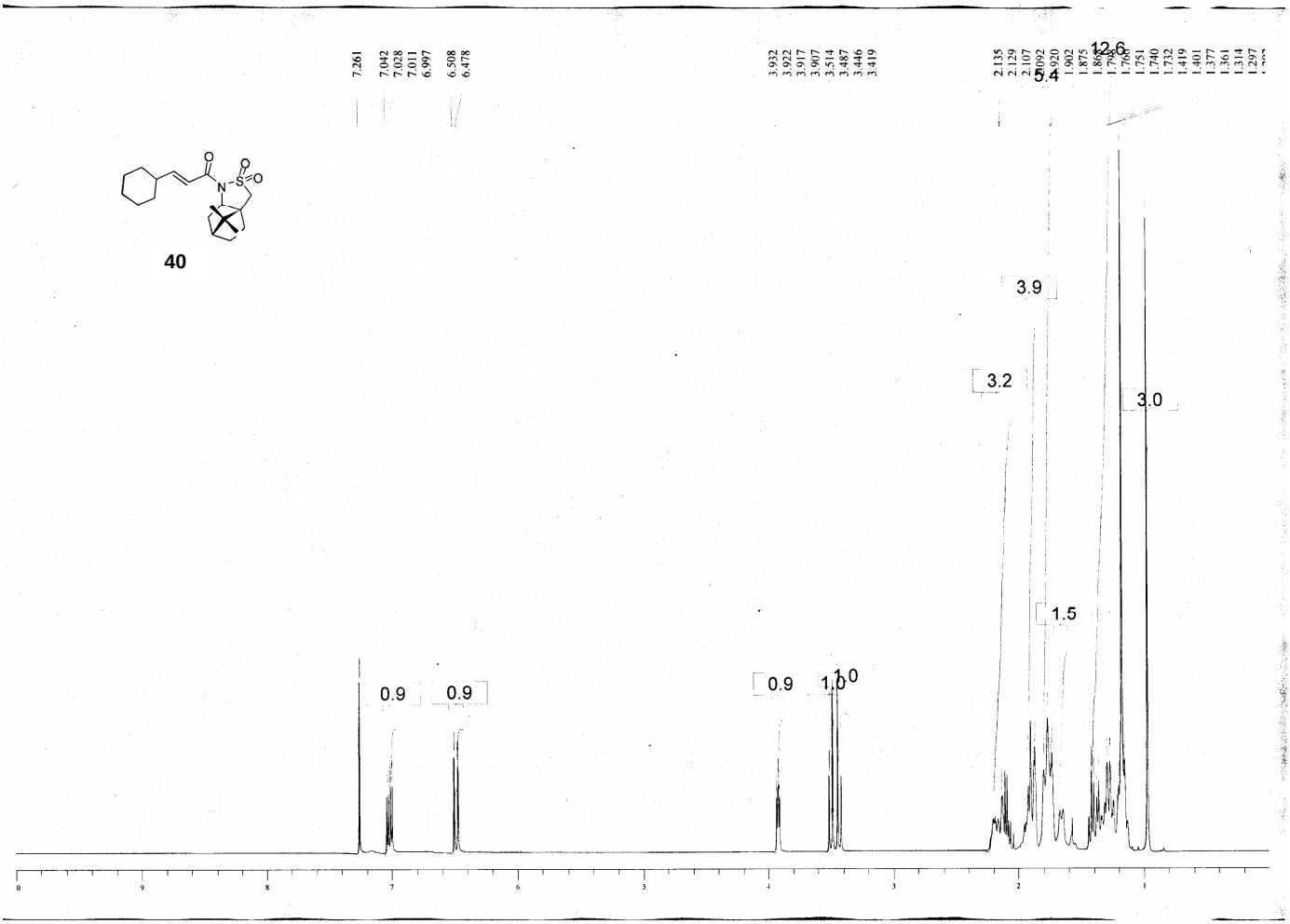
39B

4.451
4.446
4.430
4.424
4.098
4.079
4.062
3.918
3.905
3.898
3.886
3.524
3.489
3.455
3.448
3.434
3.414
2.553
2.208
2.196
2.187
2.181
2.173
2.162
2.153
2.075
2.055
2.040
2.020
2.015
1.914
1.907
1.888
1.872
1.865
1.604
1.593
1.584
6.3
6.2
3.0
3.1
3.1
1.0
1.0
1.0
0.9
1.1
0.8

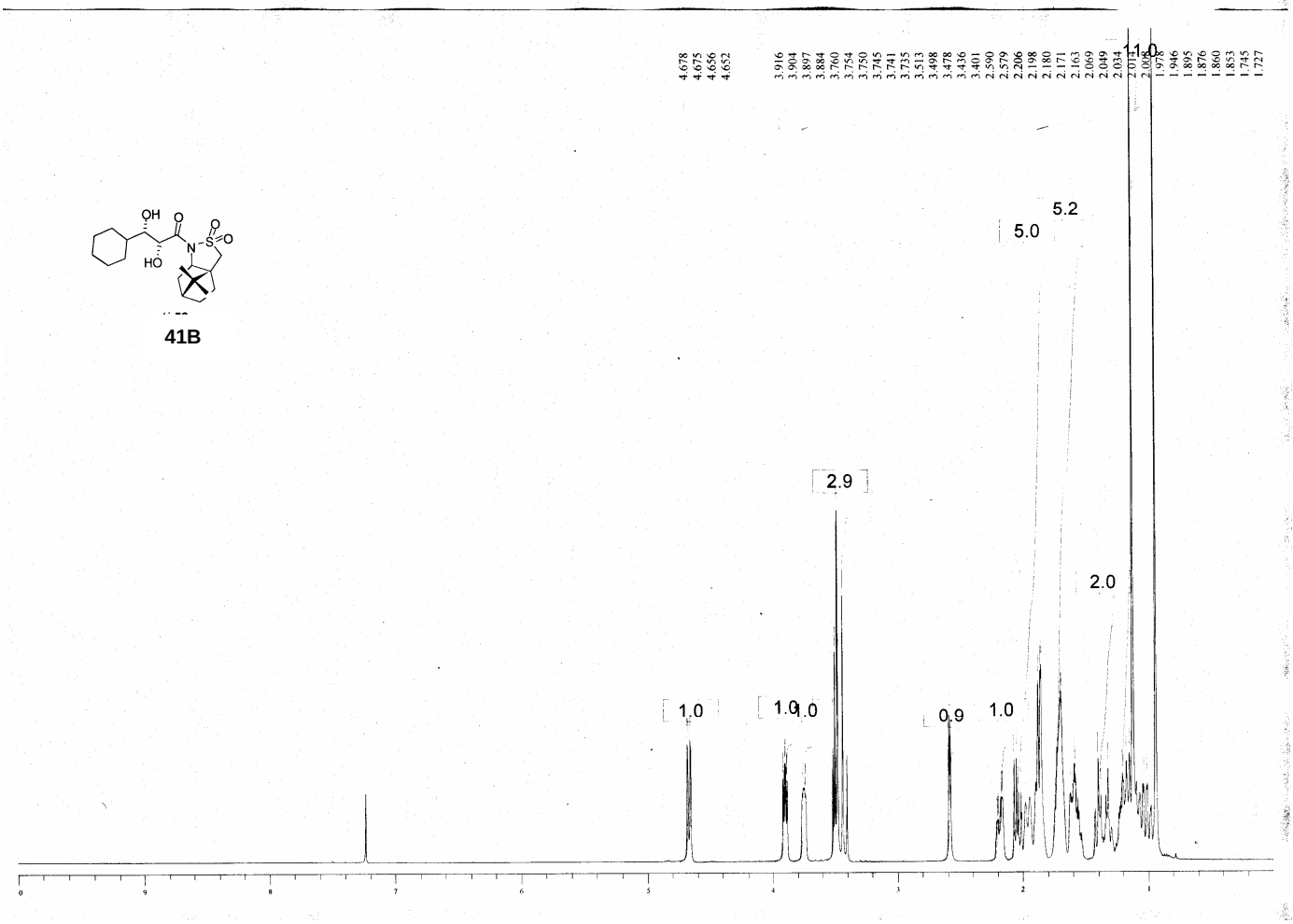


39A

4.632
4.629
4.616
4.613
4.024
4.005
3.938
3.923
3.907
3.460
3.447
3.310
3.294
2.060
2.045
2.022
1.895
1.875
1.611
1.594
1.555
1.436
1.416
1.128
0.950
0.923
5.3
4.0
3.3
2.5
2.1
1.0
1.1
1.0


7.261
7.042
7.028
7.011
6.997
6.508
6.478
3.932
3.922
3.917
3.907
3.514
3.487
3.446
3.419
2.135
2.129
2.107
2.092
2.020
1.902
1.875
1.751
1.740
1.732
1.419
1.401
1.377
1.361
1.314
1.297
12.6
5.4
3.9
3.2
3.0
1.5
0.9
0.9
0.9
1.0
1.0

40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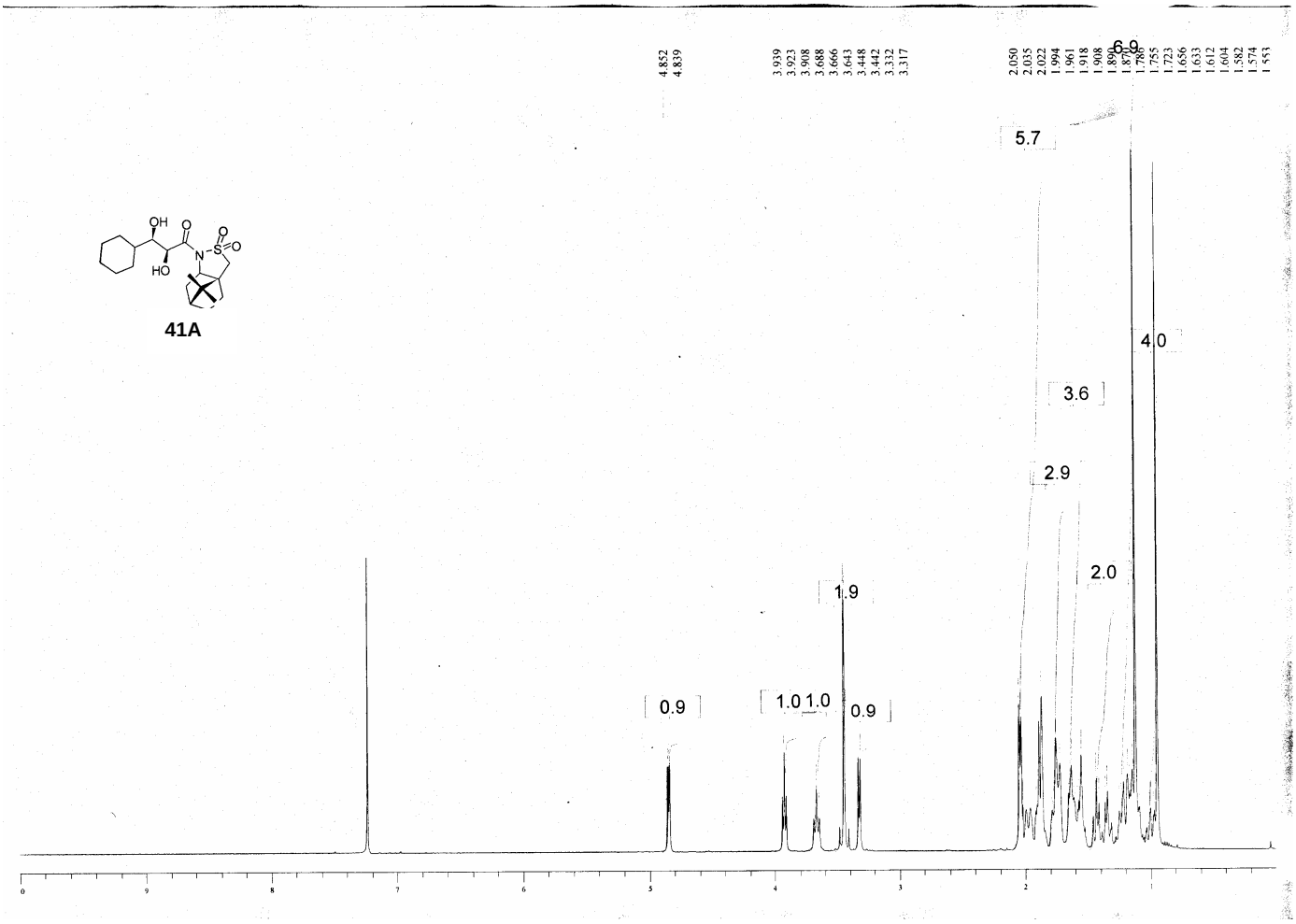
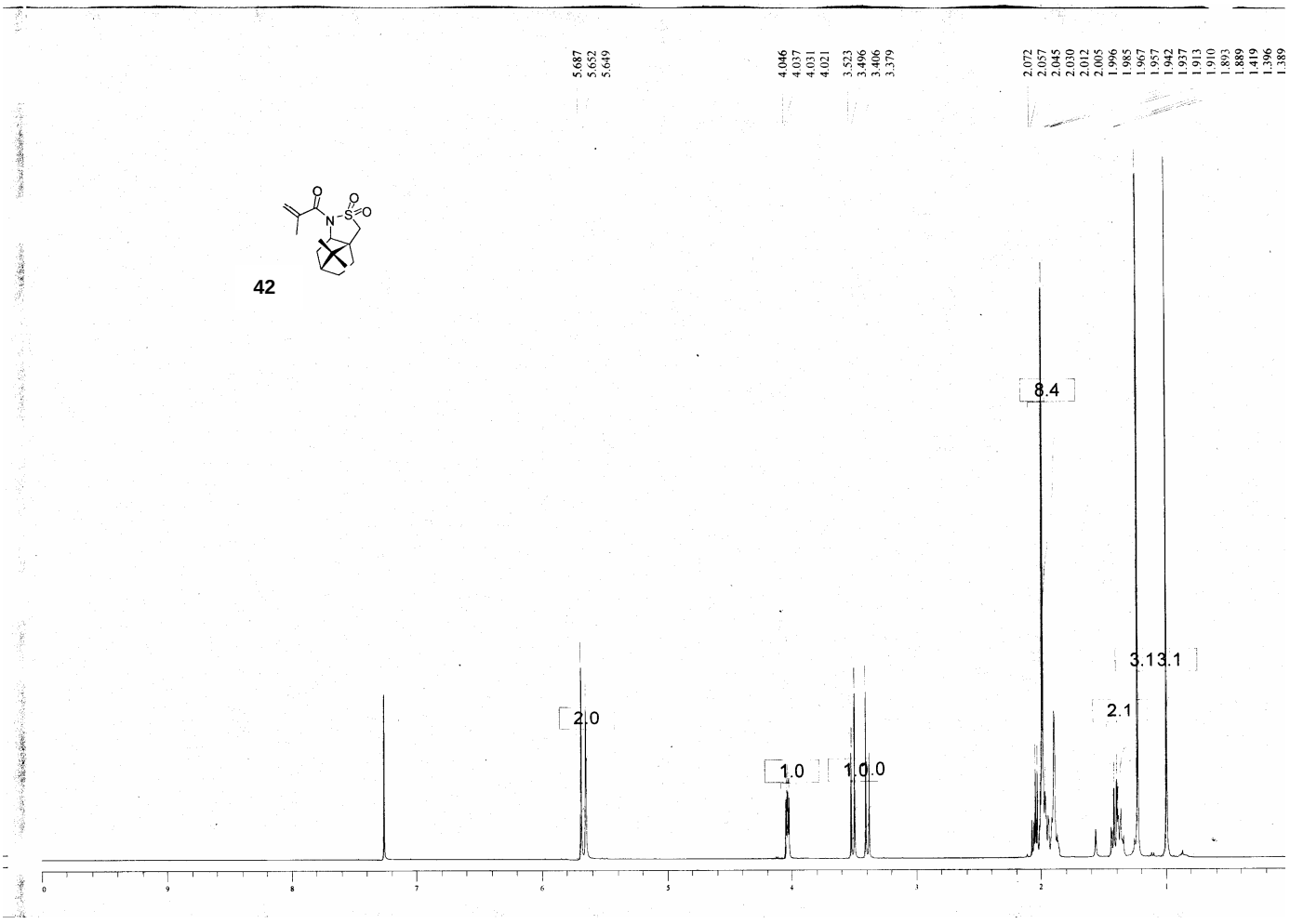
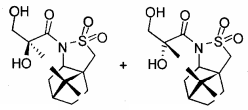
4.656
4.652
3.916
3.904
3.897
3.884
3.760
3.754
3.750
3.745
3.741
3.735
3.513
3.498
3.478
3.436
3.401
2.590
2.579
2.206
2.198
2.180
2.171
2.163
2.069
2.049
2.034
11.0
5.2
5.0
2.9
2.0
1.0
1.0
1.0
0.9
1.0

41B


4.852
4.839
3.939
3.923
3.908
3.688
3.666
3.643
3.448
3.442
3.332
3.317
2.050
2.035
2.022
1.994
1.961
1.918
1.908
1.890
1.878
1.788
1.755
1.723
1.656
1.633
1.612
1.604
1.582
1.574
1.553
OH
HO
O
N
S
O
O
41A
5.7
6.9
4.0
3.6
2.9
2.0
1.9
0.9
1.0
1.0
0.9


5.687
5.652
5.649
4.046
4.037
4.031
4.021
3.523
3.496
3.406
3.379
2.072
2.057
2.045
2.030
2.012
2.005
1.996
1.985
1.967
1.957
1.942
1.937
1.913
1.910
1.893
1.889
1.419
1.396
1.389
O
N
S
O
O
42
8.4
3.1
3.1
2.1
2.0
1.0
1.0
1.0



43A + 43B

4.066
4.046
4.037
4.027
4.010
3.982
3.559
3.526
3.522
3.485
3.451
3.418
2.047
2.031
2.018
2.012
2.000
1.948
1.936
1.929
1.905
1.882
1.836
1.829
1.463
1.430
1.404
1.385
1.361
1.347
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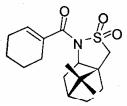
1.3
5.0
2.3
6.8
8.3
5.0
5.0



44

6.569
6.565
6.562
6.559
6.554
4.049
4.040
4.034
4.024
3.489
3.462
3.390
3.363
2.476
2.457
2.452
2.442
2.298
2.292
2.264
2.258
2.253
2.166
2.161
2.159
2.154
2.144
2.127
2.107
2.096
2.045
2.030
2.018
2.003
1.972
1.964
0.9
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1.0
1.0
0.9
1.0
1.0
4.1
4.2
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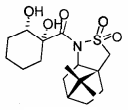
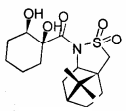
2.0
3.1
3.0



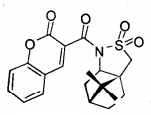
45B

4.167
4.153
4.139
4.063
4.051
4.044
4.032
3.557
3.523
3.477
3.444
2.236
2.220
2.010
1.992
1.927
1.899
1.873
1.862
1.810
1.674
1.663
1.631
1.561
1.381
1.357
1.311
1.282
1.151
0.946
7.0
8.7
3.0
3.0
1.9
1.0
1.0
1.0
0.9



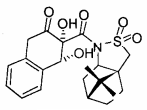
45A

4.081
4.064
4.052
4.044
4.032
3.560
3.526
3.420
3.391
2.118
2.092
2.048
2.030
2.016
1.995
1.947
1.934
1.919
1.901
1.835
1.828
1.806
1.798
1.732
1.715
1.683
1.677
1.646
6.7
7.0
5.0
3.0
2.1
1.9
1.9
1.0
1.0



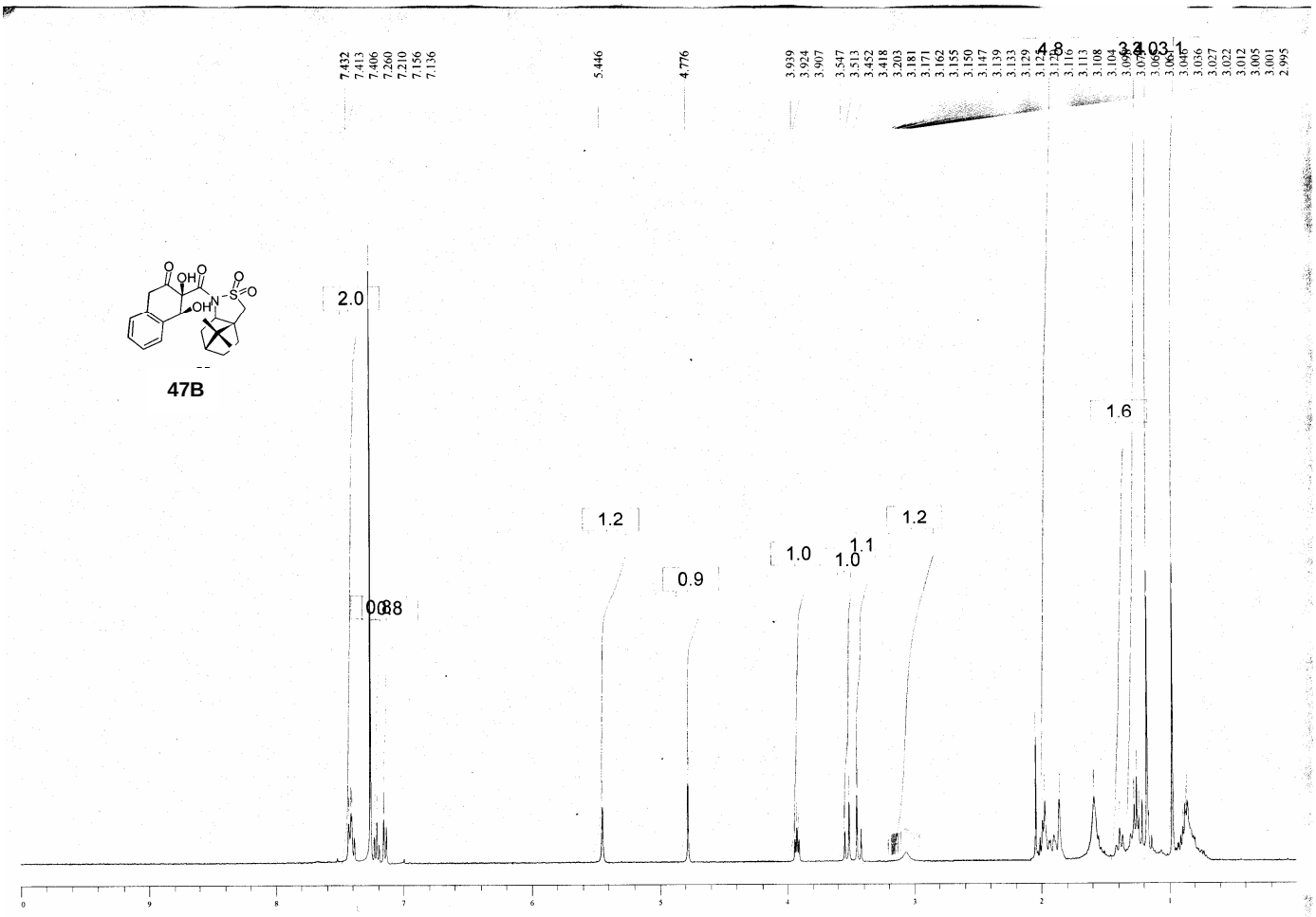
46

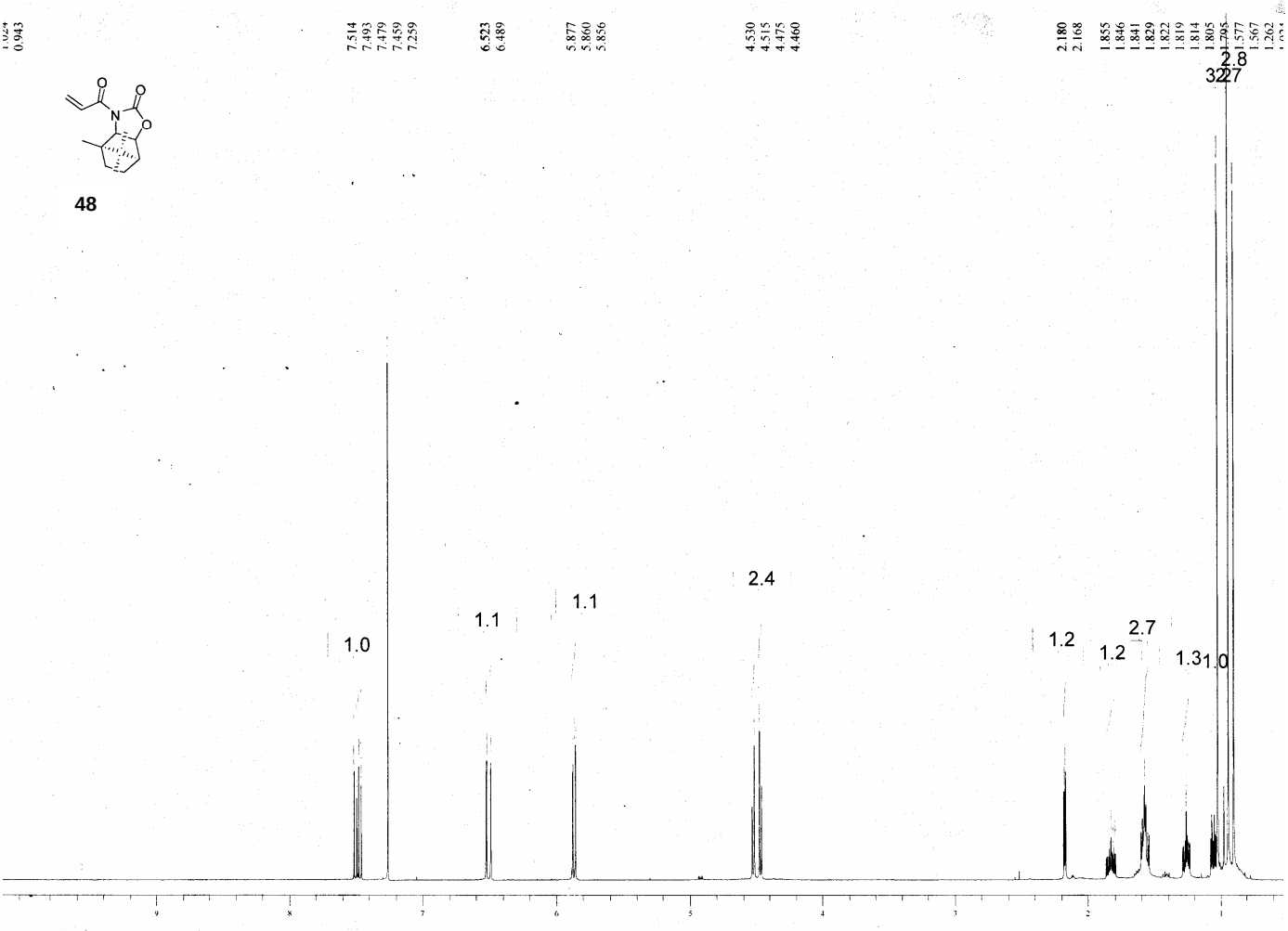
2.0
2.0
1.1
1.1
1.0
1.0
3.2
3.3
2.3
2.9

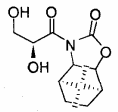


47A

7.441
7.437
7.421
7.402
7.399
7.311
7.294
7.260
7.188
7.171
7.151
5.364
4.761
3.844
3.832
3.825
3.813
3.571
3.537
3.528
3.493
3.288
1.880
1.869
1.844
1.813
1.803
1.764
1.744
1.728
1.708
1.702
1.691
1.682
1.656
1.442
1.436
1.413
1.389
1.8
1.0
1.0
0.9
1.0
1.9
0.8
4.9
5.0
3.7
2.9
1.2

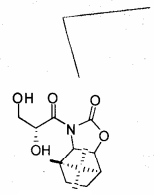

47B
2.0
0.88
1.2
0.9
1.0
1.0
1.1
1.2
4.8
1.6


48
1.0
1.1
1.1
2.4
1.2
1.2
2.7
1.3
1.0
2.8
3.2



49A

4.966
4.623
4.600
4.400
4.375
3.919
3.902
3.893
3.878
2.211
2.194
1.905
1.891
1.887
1.875
1.866
1.861
1.847
1.835
1.821
1.807
1.789
1.634
0.8
0.8
0.9
0.6
2.3
1.2
1.4
1.3
1.3
4.0
3.0
3.0



49B

5.246
5.239
5.232
4.626
4.605
4.479
4.459
3.971
3.970
3.656
3.640
2.213
2.201
2.173
2.046
1.842
1.811
1.625
1.613
1.594
1.581
1.559
1.528
1.285
1.275
1.261
1.251
1.240
1.228
1.219
1.208
1.0
1.1
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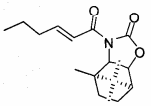
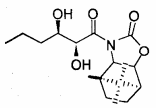
1.0
1.1
1.1
1.4
1.4
1.6
1.4
3.2
3.1
2.8



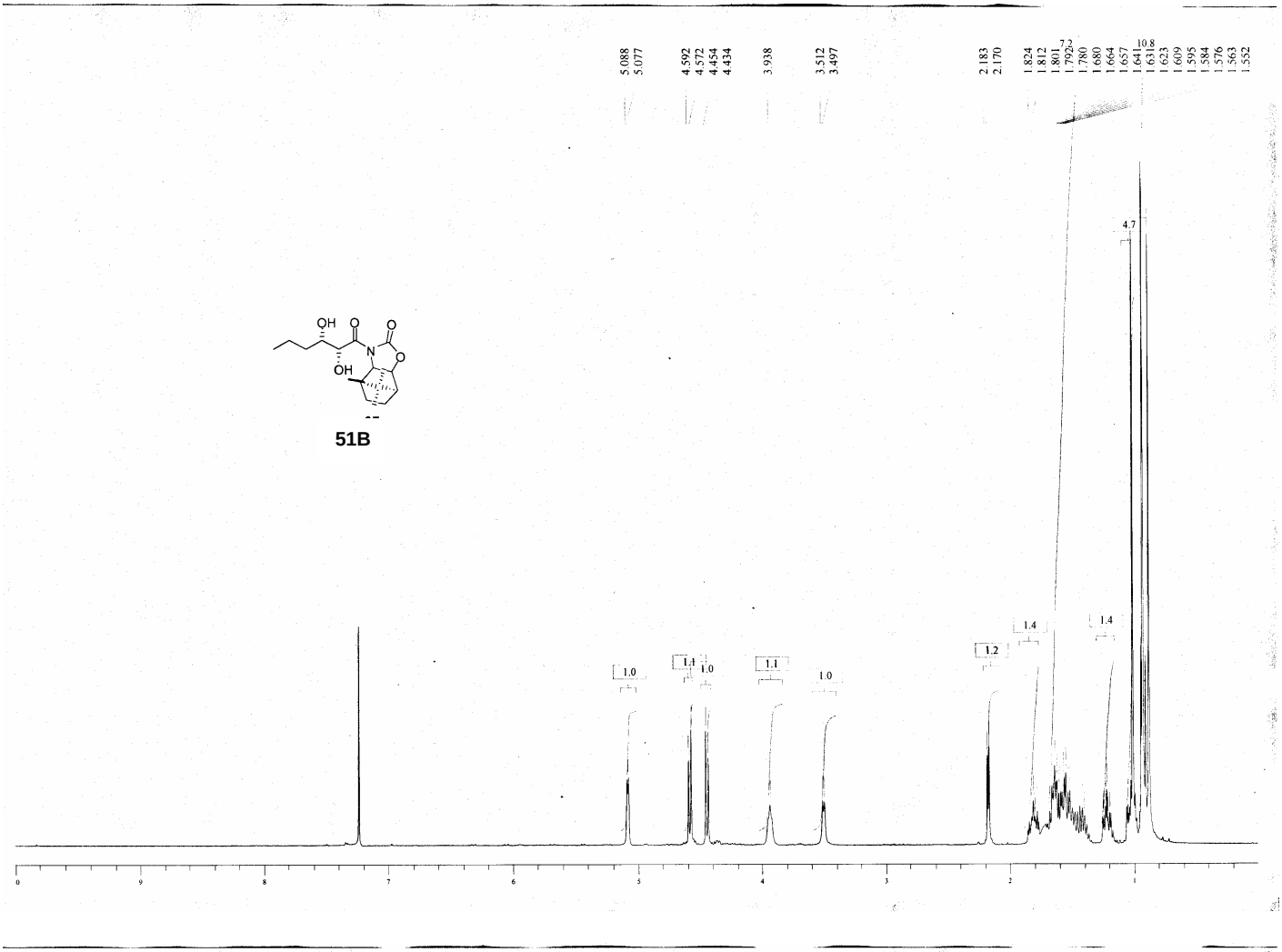
50

7.260
7.242
7.204
7.147
7.130
7.113
7.092
4.489
4.471
2.275
2.257
2.238
2.221
2.166
2.153
1.848
1.829
1.816
1.806
1.796
14.4
1.1
1.0
2.0
2.2
1.0
1.1
3.6
1.2



51A

4.947
4.932
4.569
4.549
4.353
4.333
3.887
3.738
3.719
2.165
2.152
1.806
1.619
1.599
1.581
1.564
1.548
14.3
1.459
1.406
1.387
1.206
1.047
1.036
1.023
5.4
1.4
1.2
1.0
1.1
1.1
1.0
0.9
1.1
0.9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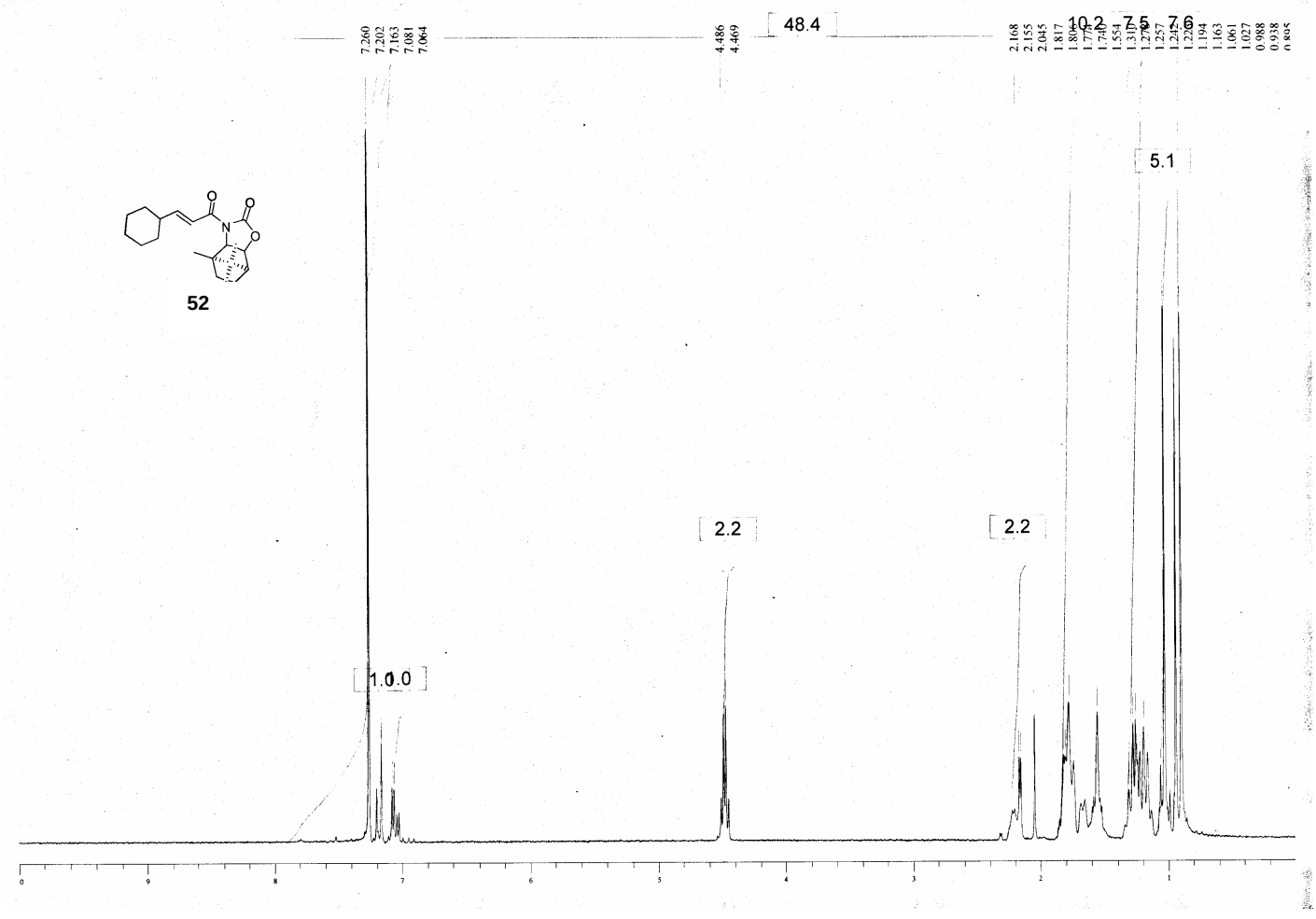
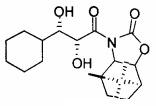
5.077
4.592
4.572
4.454
4.434
3.938
3.512
3.497
2.183
2.170
1.824
1.812
1.801
1.792
1.780
1.680
1.664
1.657
1.641
1.631
1.623
1.609
1.595
1.584
1.576
1.563
1.552
OH
O
N
O
O
OH
51B
1.0
1.1
1.0
1.1
1.0
1.2
1.4
1.4
4.7


7.260
7.202
7.165
7.081
7.064
4.486
4.469
48.4
2.168
2.155
2.045
1.817
1.554
1.318
1.257
1.245
1.226
1.194
1.163
1.061
1.027
0.988
0.938
O
N
O
O
52
1.0.0
2.2
2.2
10.2
7.5
7.6
5.1



53B

5.323
4.609
4.589
4.478
4.458
3.608
3.586
2.202
2.190
2.172
2.045
1.831
1.782
1.757
1.666
1.658
1.636
1.629
1.614
1.603
1.582
1.571
1.551
1.499
1.275
1.257
1.251
12.7
6.6
5.4
5.1
3.4
1.8
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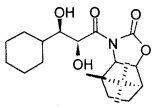
1.0
1.0



53A

5.230
5.213
4.592
4.572
4.364
4.345
3.703
3.685
3.586
3.565
2.193
2.181
2.040
2.016
1.985
1.841
1.831
1.818
1.812
1.800
1.657
1.648
1.627
1.620
1.607
1.596
1.575
1.563
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3.4
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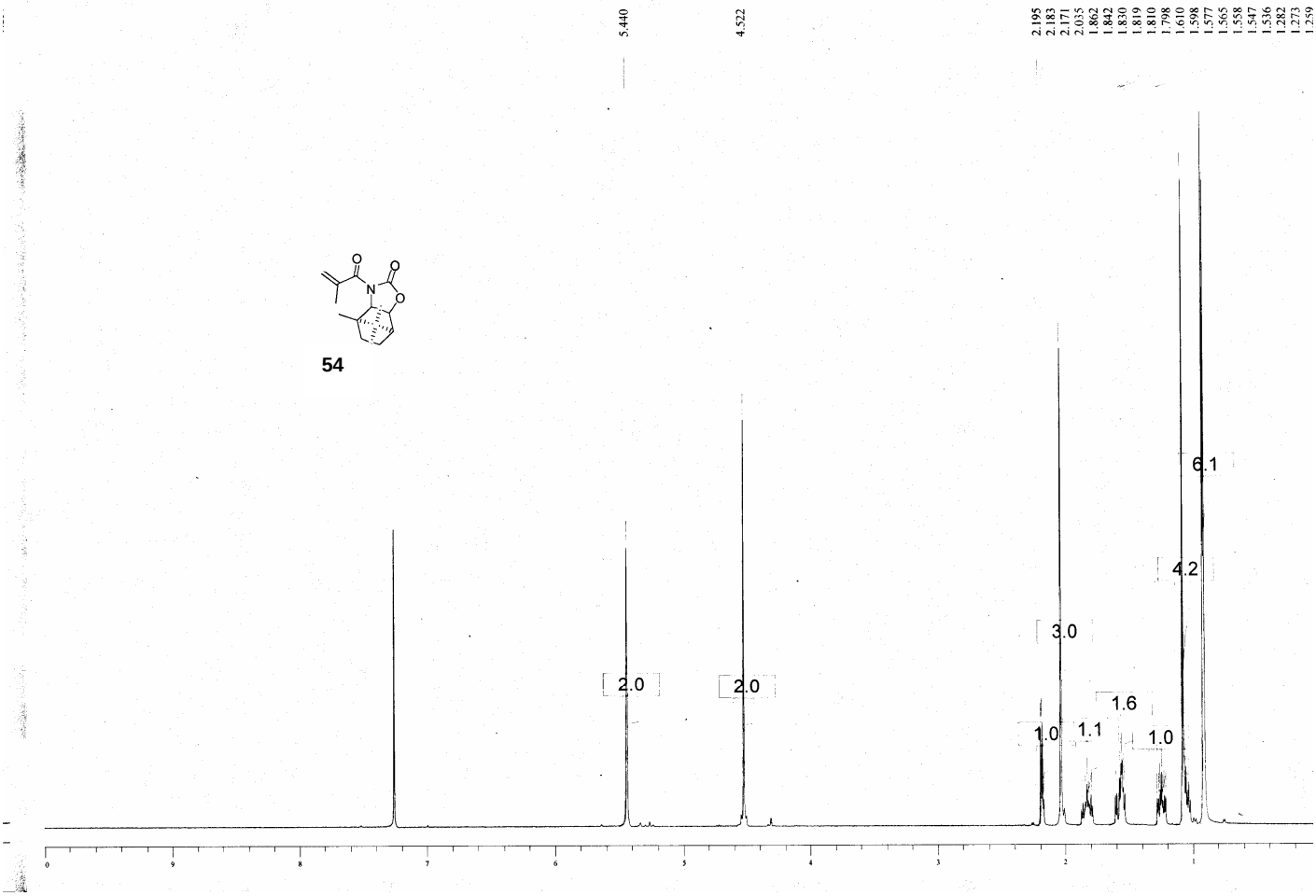
1.0
1.1
1.0
1.0
1.1
1.2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1.810
1.798
1.610
1.598
1.577
1.565
1.558
1.547
1.536
1.282
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54
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2.0
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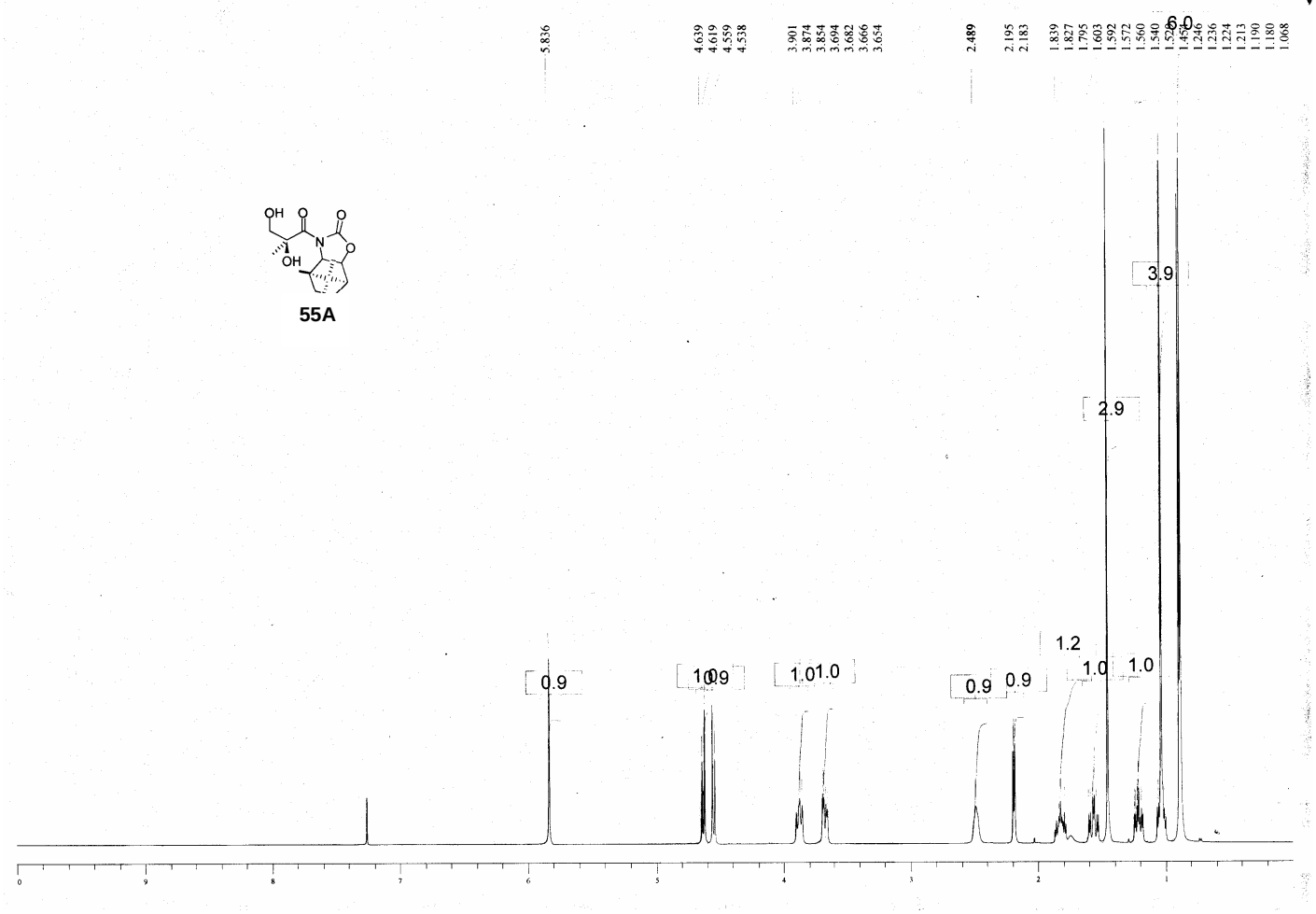
3.0
1.1
1.6
1.0
4.2
6.1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3.666
3.654
2.489
2.195
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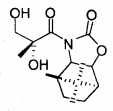
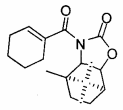
1.827
1.795
1.603
1.592
1.572
1.560
1.540
1.526
1.452
1.246
1.236
1.224
1.213
1.190
1.180
1.068
55A
0.9
1.0
0.9
1.0
1.0
0.9
0.9
1.2
1.0
1.0
2.9
3.9
6.0



55B

5.731
4.624
4.604
4.512
4.492
3.830
3.802
3.737
3.709
2.192
2.178
1.819
1.788
1.590
1.578
1.557
1.535
1.515
1.229
1.219
1.195
1.062
1.050
1.038
1.019
1.006
0.889

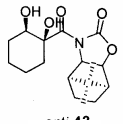
6.4
4.1
1.0
1.0
1.0
1.2
1.2
1.2



56

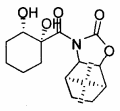
6.335
4.564
4.543
4.504
4.483
2.534
2.529
2.514
2.507
2.492
2.487
2.220
2.205
2.195
2.177
2.164
2.087
2.082
2.066
2.060
2.043
1.844
1.825
1.813
1.802
1.793
1.781
1.769

6.6
4.7
4.6
3.3
1.7
1.0
1.0
1.0
1.2
1.2
1.1



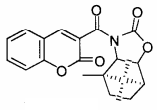
57A

5.757
4.596
4.576
4.550
4.530
4.078
4.070
4.053
2.171
2.159
2.026
1.992
1.836
1.823
1.813
1.803
1.792
1.783
1.772
1.720
1.711
1.701
1.686
1.658
1.649
4.4
2.4
2.1
1.3
1.2
1.2
1.0
0.9



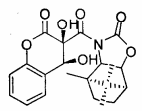
57B

5.772
4.594
4.102
4.090
4.073
4.062
2.170
2.158
2.141
2.136
2.022
1.862
1.852
1.843
1.833
1.821
1.814
1.802
1.791
1.782
1.770
1.758
1.730
1.723
1.716
1.705
4.3
2.5
2.1
1.1
1.0



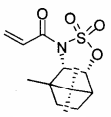
58

7.794
7.559
7.538
7.515
7.496
7.345
7.324
7.296
7.276
7.257
7.237
4.589
4.569
4.533
4.513
2.186
2.174
2.150
1.895
1.885
1.883
1.872
1.865
1.862
1.851
1.838
1.831
1.820
1.808
1.644
1.633
1.612
1.600
1.581
1.569
1.0
1.1
1.1
1.1
1.1
1.0
0.9
1.1
0.8
1.3
2.7
3.5
4.2



59B

7.561
7.542
7.360
7.341
7.322
7.260
7.231
7.213
7.195
7.103
7.082
5.522
5.496
4.699
4.680
4.514
4.494
2.829
2.800
2.223
2.210
1.884
1.881
1.871
1.861
1.840
1.653
1.641
1.620
1.608
1.589
1.577
1.306
1.296
1.283
1.273
1.263
1.250
1.0
1.0
1.0
1.0
0.9
1.0
0.8
1.0
1.0
0.9
1.0
1.0
1.8
1.1
6.9
3.1

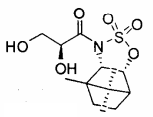


60

6.953 6.919 6.605 6.600 6.550 6.545 5.985 5.980 5.951 5.946 4.792 4.768 4.477 4.453 2.243 2.226 1.934 1.915 1.910 1.903 1.889 1.875 1.870 1.669 1.652 1.624 1.608 1.593 1.585 1.567 1.178

1.0 1.0 1.1 1.0 1.0 1.0 1.0 1.3 1.0 4.4 6.5

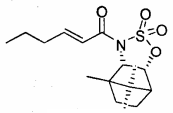
7.260 4.861 4.838 4.778 4.438 4.416 3.950 3.437 3.420 2.274 2.258 2.172 1.938 1.895 1.253 1.175 0.939 0.922 1.253 1.175 0.939 0.922



61A

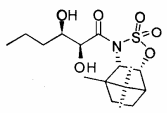
14.5 12.6

2.2 1.1 2.2 1.0 2.4 1.5 1.8



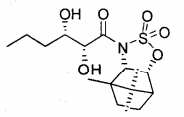
62

7.260
7.209
7.187
7.163
7.136
7.113
6.672
6.667
6.622
6.617
4.769
4.745
4.468
4.444
2.276
2.271
2.252
2.228
2.212
1.950
1.564
1.538
1.515
1.490
1.183
0.978
0.935
0.930
0.907
1.933
1.924
4.4
3.3
3.2
1.0
1.0
1.0
1.0
1.0
1.1



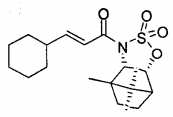
63A

7.260
4.840
4.813
4.603
4.594
4.573
4.565
4.443
4.419
4.103
4.096
4.087
4.073
4.061
3.463
3.434
2.484
2.470
2.260
2.241
1.972
1.966
1.953
1.944
1.939
1.927
1.914
1.899
1.886
1.652
1.646
1.628
10.5
4.7
5.5
1.7
1.0
1.0
1.0
1.0
0.9
0.9
1.0
1.0



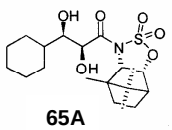
63B

7.260
4.855
4.831
4.744
4.726
4.509
4.485
4.097
4.066
3.256
3.235
2.265
2.247
1.925
1.673
1.553
1.553
1.179
0.922
0.912
10.0
6.8
4.5
1.4
1.2
1.0
1.0
1.0
1.0
0.9

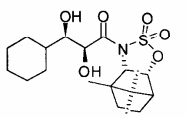


64

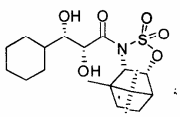
7.259
7.120
7.097
7.069
7.047
6.605
6.600
6.555
4.753
4.729
4.449
4.425
2.212
2.194
1.887
1.811
1.776
1.736
1.727
1.638
1.621
1.596
1.579
1.505
1.291
1.274
1.260
7.9
11.5
7.1
1.9
1.0
0.9
1.0
0.9



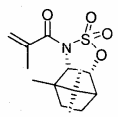
65A



65A



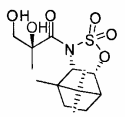
65B



66

5.811
5.754
4.722
4.698
4.602
4.577
2.234
2.216
2.005
1.961
1.948
1.930
1.921
1.916
1.903
1.890
1.876
1.862
1.845
1.662
1.647
1.619

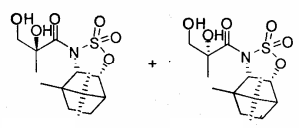
2.0
1.0
1.0
1.1
5.0
1.3
5.0
1.5
1.3
7.2



67A

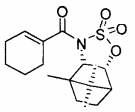
7.260
4.812
4.787
4.654
4.630
4.106
4.100
4.079
4.063
4.040
3.829
3.654
3.637
3.618
3.600
2.235
2.217
2.202
2.171
2.044
1.658
1.618
1.602
1.514
1.296
1.281
1.268
1.257
1.194
1.095
1.074
0.907

1.0
1.0
1.5
1.1
1.1
1.7
1.4
1.8
3.4
3.2
2.5
2.2
7.5



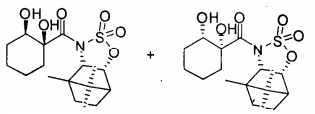
67A + 67B

7.260
7.9
7.8
3.6
3.1
2.3
2.1
1.6
1.7
1.0
0.5
0.6



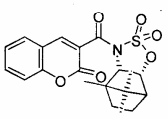
68

6.709
4.697
4.672
4.622
4.597
2.456
2.265
2.220
2.203
2.129
1.894
1.734
1.711
1.649
1.607
1.593
1.566
1.550
1.283
1.271
1.225
1.137
1.122
1.107
6.7
5.8
4.5
4.5
2.1
1.4
1.2
1.0
1.0



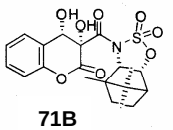
69A + 69B

7.260
4.764
4.749
4.739
4.728
4.686
4.662
4.584
4.560
4.273
4.257
4.236
4.218
4.201
3.474
3.338
2.192
1.560
1.197
1.182
0.880
0.869
0.855
1.0
0.6
0.7
0.4
0.3
0.6
0.6
2.0
4.5
6.5
5.8
1.6
6.8
7.967
7.618
7.589
7.563
7.368
7.342
7.319
7.260
4.821
4.797
4.613
4.589
2.263
2.246
2.036
1.944
1.692
1.666
1.650
1.625
1.608
1.272
1.080
0.946



70

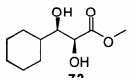
6.9
6.6
5.5
2.3
2.1
1.0
1.0
0.8
1.1
1.3
1.6



71B

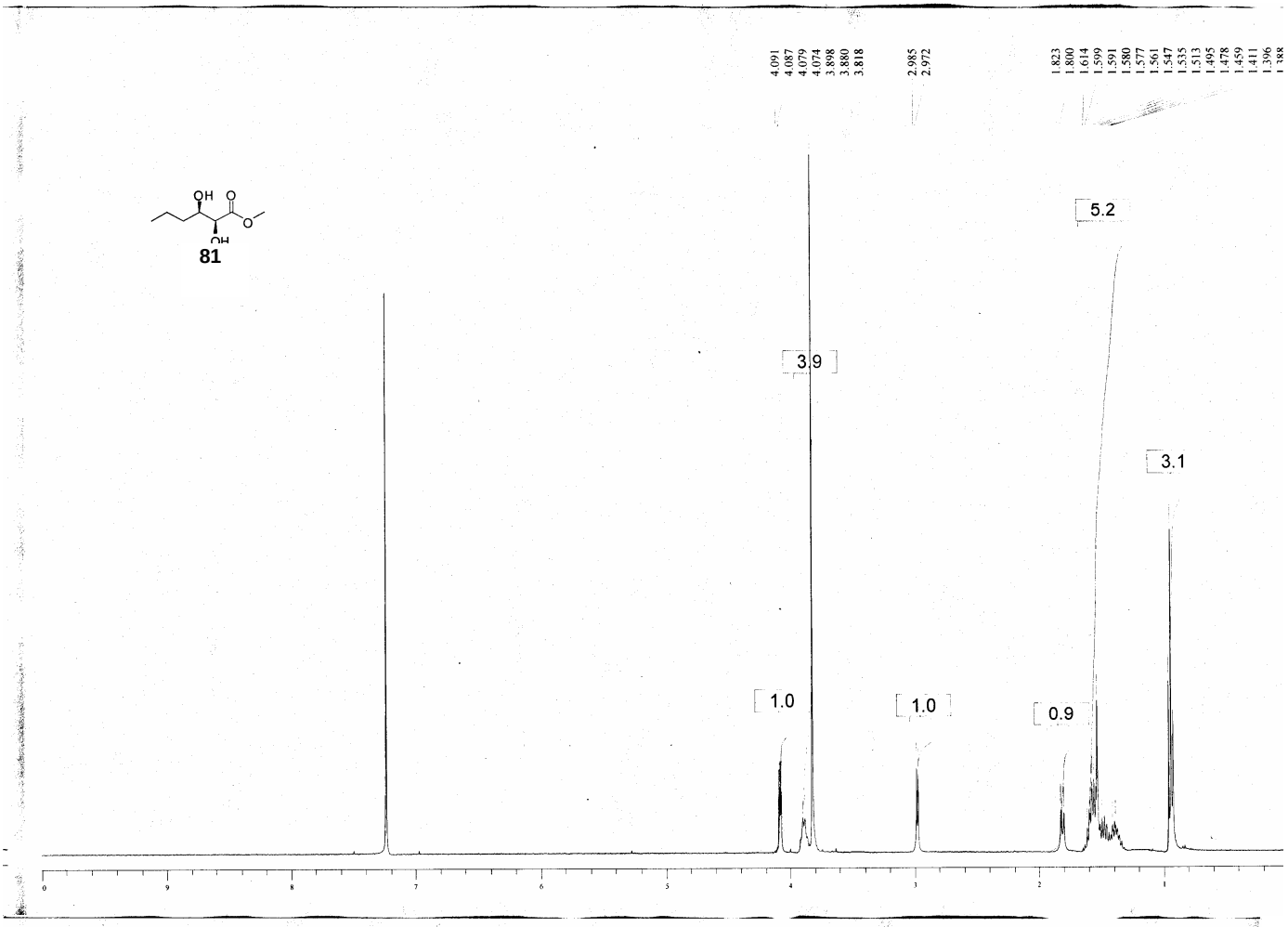
7.437 7.411 7.389 7.260 7.228 7.187 7.160 5.439 4.749 4.725 4.672 4.325 4.301 3.246 2.172 1.579 1.071 0.785

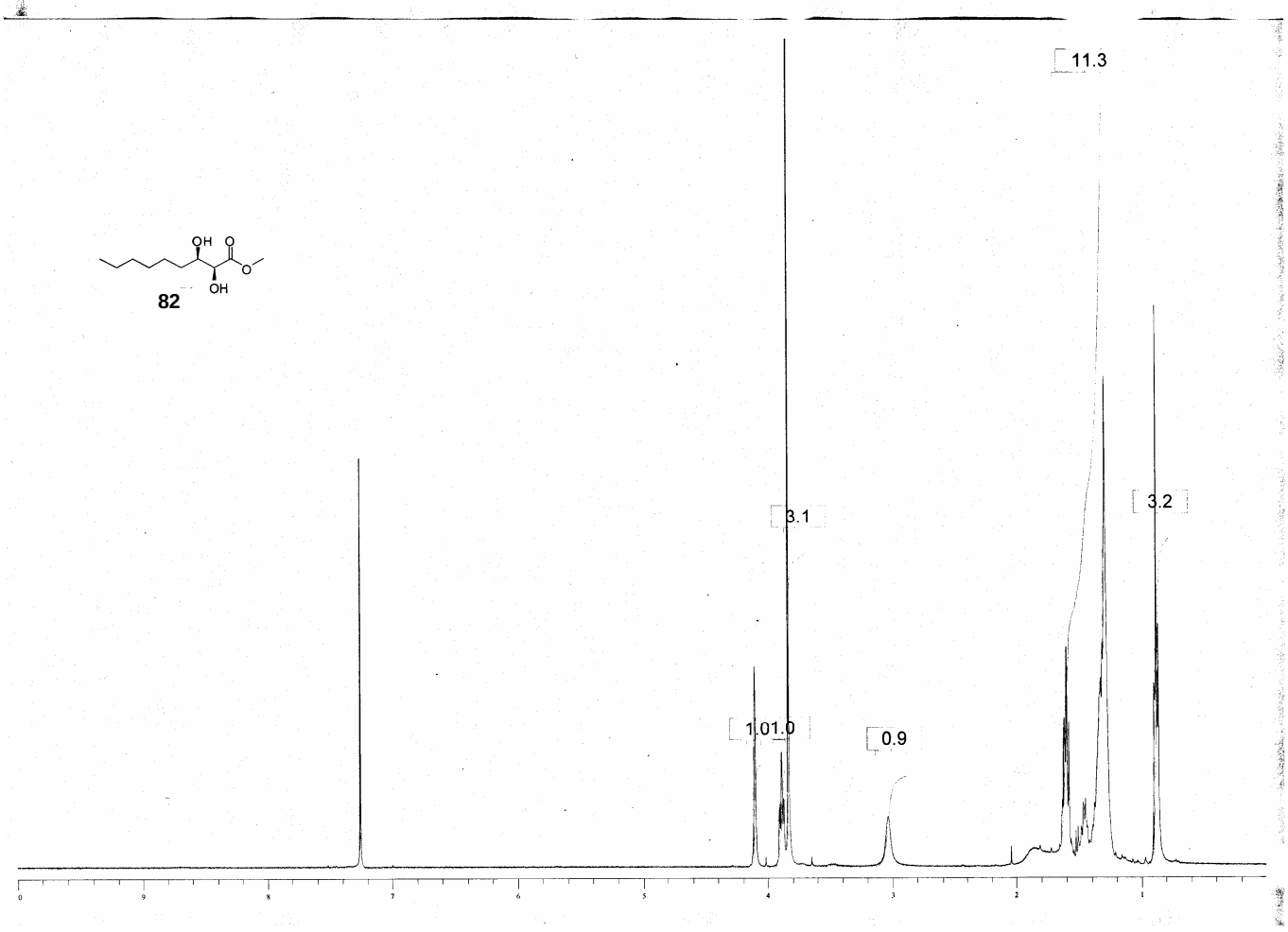
2.2 2.4 1.0 1.1 0.9 1.0 0.9 0.8 1.2 3.2 1.1 0.9 6.4 3.3

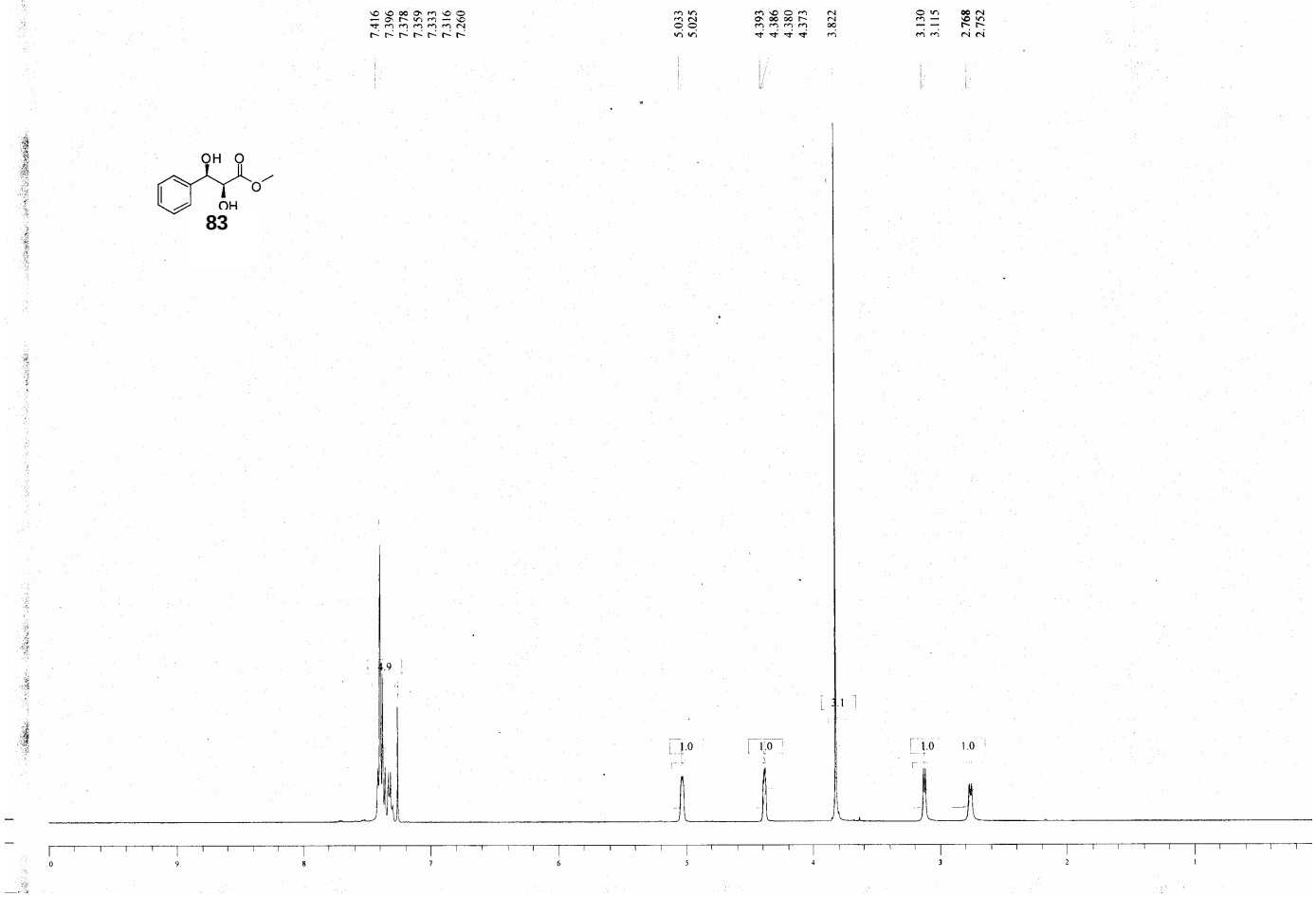


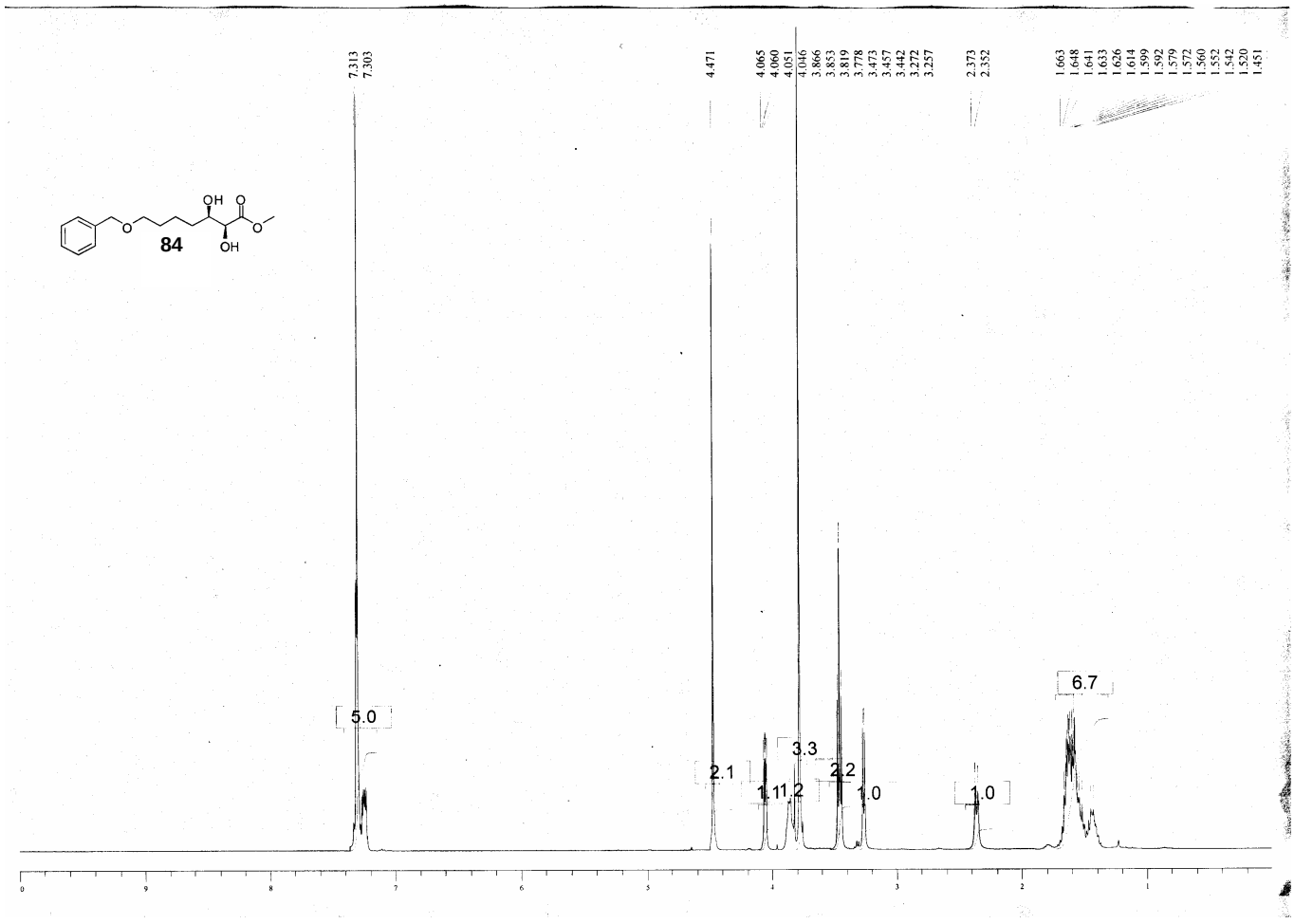
80

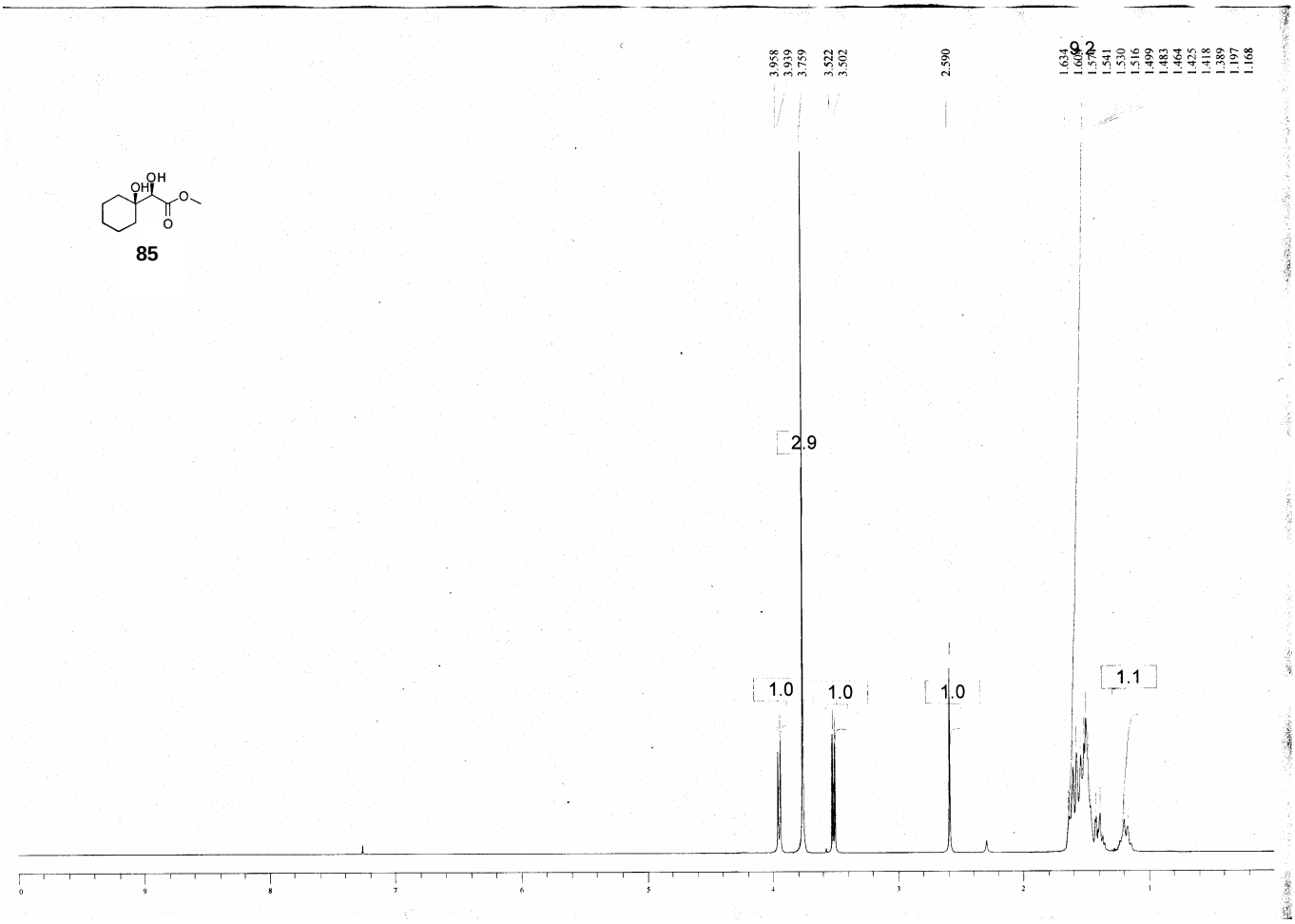
5.9 2.9 3.2 2.2 1.0 1.0 0.9 1.0 0.9

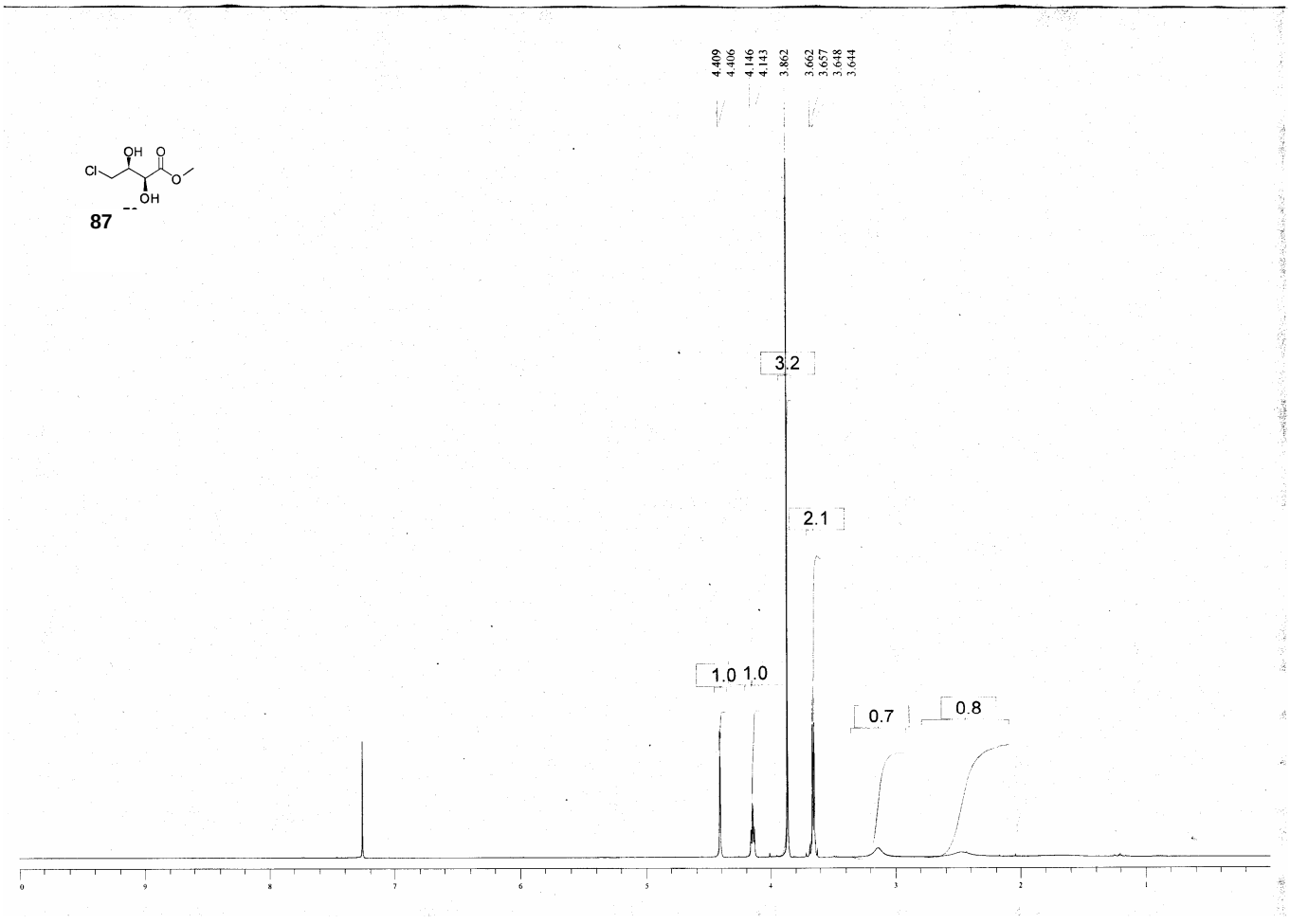

4.091
4.087
4.079
4.074
3.898
3.880
3.818
2.985
2.972
1.823
1.800
1.614
1.599
1.591
1.580
1.577
1.561
1.547
1.535
1.513
1.495
1.478
1.459
1.411
1.396
OH
O
O
OH
81
5.2
3.9
3.1
1.0
1.0
0.9

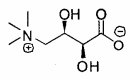

11.3
OH
O
O
OH
82
3.1
3.2
1.01.0
0.9


7.416
7.396
7.378
7.359
7.333
7.316
7.260
5.033
5.025
4.393
4.386
4.380
4.373
3.822
3.130
3.115
2.768
2.752
OH
O
O
OH
83
4.9
1.0
1.0
3.1
1.0
1.0


7.313
7.303
4.471
4.065
4.060
4.051
4.046
3.866
3.853
3.819
3.778
3.473
3.457
3.442
3.272
3.257
2.373
2.352
1.663
1.648
1.641
1.633
1.626
1.614
1.599
1.592
1.579
1.572
1.560
1.552
1.542
1.520
1.451
OH
O
O
OH
84
5.0
2.1
1.1
1.2
3.3
2.2
1.0
1.0
6.7


OH
OH
O
O
85
3.958
3.939
3.759
3.522
3.502
2.590
1.634
1.608
1.574
1.541
1.530
1.516
1.499
1.483
1.464
1.425
1.418
1.389
1.197
1.168
9.2
2.9
1.0
1.0
1.0
1.1


OH
O
Cl
O
OH
87
4.409
4.406
4.146
4.143
3.862
3.662
3.657
3.648
3.644
3.2
2.1
1.0
1.0
0.7
0.8

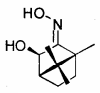


88

4.243
3.727
3.716
3.475
3.435
3.362
3.330
3.122
9.3
1.0
1.0
0.9

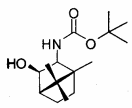
exo-**26**

3.735
2.643
2.095
2.086
2.057
2.027
2.018
2.013
2.003
1.993
1.988
1.978
1.968
1.686
1.678
1.658
1.651
1.634
1.627
1.475
1.465
3.2
3.0
1.0
0.9
1.0
1.1
1.3
1.1
1.2



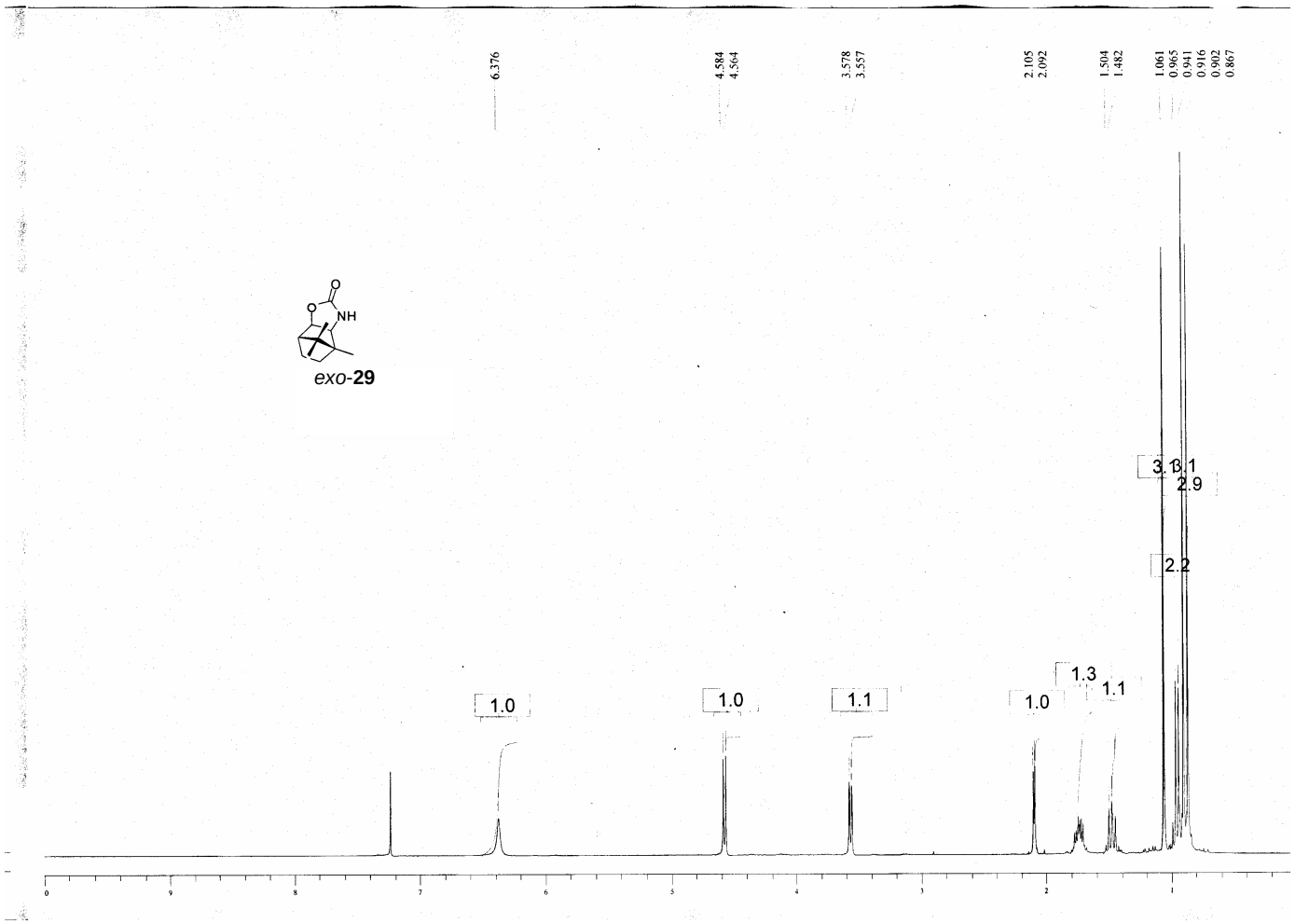
exo-**27**

4.505
3.413
1.963
1.953
1.892
1.878
1.868
1.852
1.843
1.683
1.674
1.656
1.649
1.632
1.625
3.3
3.3
3.1
1.0
2.1
1.1
1.3
1.3
1.3
0.6

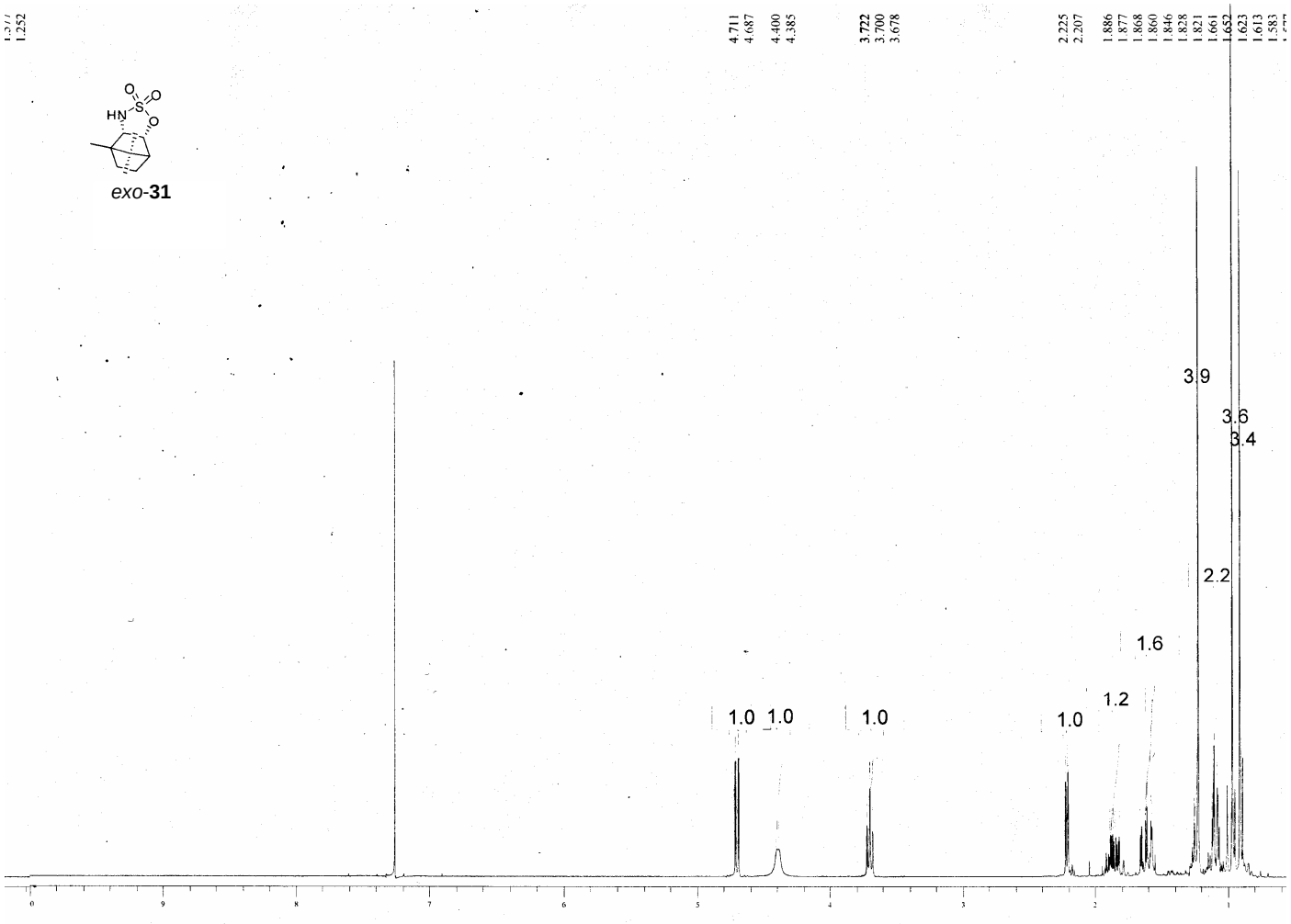


exo-**28**

4.900
3.958
3.940
3.629
2.047
2.037
2.033
2.024
2.013
1.963
1.629
1.515
1.503
1.483
1.473
1.453
1.442
10.0
4.0
3.1
3.0
1.2
1.1
1.0
0.9
0.9
0.8
0.8


6.376
4.584
4.564
3.578
3.557
2.105
2.092
1.504
1.482
1.061
0.965
0.941
0.916
0.902
0.867
NH
O
O
O
1.0
1.0
1.1
1.0
1.3
1.1
3.1
2.9
2.2

exo-**29**


4.711
4.687
4.400
4.385
3.722
3.700
3.678
2.225
2.207
1.886
1.877
1.868
1.860
1.846
1.828
1.821
1.661
1.652
1.623
1.613
1.583
HN
S
O
O
O
O
1.0
1.0
1.0
1.0
1.2
1.6
2.2
3.9
3.6
3.4

exo-**31**