(1*R*,5*R*)-(+)-1,5-Diphenyl-3-methylenepentan-1,5-diol (1a).[2a] From (*S*,*S*)-**3** and benzaldehyde. Colorless oil (55% as an inseparable 21 : 4 mixture of diastereoisomers): TLC R_f 0.3 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ +57.0° (*c* 4.6, $CHCl_3$); IR (film) 3459, 3282, 3064, 3030, 2943, 1644 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.43-7.27 (m, 10H), 5.16 (s, 2H), 4.86 (t, 2H, *J* = 8.0 Hz), 3.0-2.8 (br s, 2H), 2.53 (d, 4H,*J* = 8.0 Hz) (also present from minor diastereoisomer, 5.08 (s, 2H)); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.1, 143.0, 128.5, 127.6, 125.8, 116.5, 72.3, 46.1 (also present from minor diastereoisomer 144.2, 143.3, 116.3, 72.9, 46.5); MS (CI, NH_3) *m/z* 286 $(M+NH_4)^+$, 269 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{18}H_{24}NO_2$ $(M+NH_4)^+$ 286.1807, found $(M+NH_4)^+$ 286.1807. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.39; H, 7.61.

(3*R*,7*R*)-(+)-2,8-Dimethyl-5-methylenenonane-3,7-diol (1b).[2e] From (*S*,*S*)-**3** and isobutyraldehyde. Colorless oil (41% as an inseparable 93 : 7 mixture of diastereoisomers): TLC R_f 0.11 (1 : 4 EtOAc/hexanes); $[\alpha]_D^{23}$ +32.8° (*c* 1.4, $CHCl_3$); IR (film) 3369, 2957, 2875, 1641 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.02 (s, 2H), 3.53-3.47 (m, 2H), 2.33-2.28 (m, 2H), 2.19 (br s, 2H), 2.05 (dd, 2H *J* = 14.1, 10.5 Hz), 1.80-1.66 (m, 2H), 0.95 (t, 12H, *J* = 6.4 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.7, 115.5, 73.8, 40.4, 33.7, 18.6, 17.9 (also present from minor diastereoisomer 74.5, 41.4, 18.7, 17.4); MS (CI, NH_3) *m/z* 218 $(M+NH_4)^+$, 201 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{12}H_{25}O_2$ $(M+H)^+$ 201.1854, found $(M+H)^+$ 201.1851. The enantiomeric diol (3*S*,7*S*)-**1b** was obtained as a clear oil (38% as an inseparable 91 : 9 mixture of diastereoisomers) using (*R*,*R*)-**3**: $[\alpha]_D^{23}$ -26.0° (*c* 1.2, $CHCl_3$).

(3*S*,7*S*)-(+)-5-Methylenenonane-3,7-diol (1c).[2b,f] From (*S*,*S*)-**3** and propanal. Colorless oil (45% as an inseparable 93 : 7 mixture of diastereoisomers): TLC R_f 0.04 (1 : 4 EtOAc/hexanes); $[\alpha]_D^{23}$ +17.2° (*c* 1.1, $CHCl_3$); IR (film) 3368, 3074, 2929, 1643 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.03 (s, 2H), 3.74-3.65 (m, 2H), 2.34-2.29 (m, 2H), 2.30-2.10 (br s, 2H), 2.08 (dd, 2H, *J* = 14.1, 9.9 Hz), 1.58-1.48 (m, 4H), 0.98 (t, 6H, *J* = 7.5 Hz) (also present from minor diastereoisomer 5.00 (s, 2H)); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.1, 115.5, 70.6, 43.5, 30.1, 10.0 (also present

from minor diastereoisomer 44.2, 30.3); MS (CI, NH_3) *m/z* 190 $(M+NH_4)^+$, 173 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{10}H_{21}O_2$ $(M+H)^+$ 173.1542, found $(M+H)^+$ 173.1542.

(4*S*,8*S*)-(–)-2,10-Dimethyl-6-methyleneundecane-4,8-diol (1d).[2d] From (*S*,*S*)-**3** and isovaleraldehyde. Colorless oil (53% as an inseparable 93 : 7 mixture of diastereoisomers): TLC R_f 0.38 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ -4.3° (*c* 1.7, $CHCl_3$); IR (film) 3369, 3076, 2930, 1642 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 5.01 (s, 2H), 3.86-3.80 (m, 2H), 2.30-2.24 (m, 4H), 2.06 (dd, 2H, *J* = 14.1, 9.7 Hz), 1.82-1.75 (m, 2H), 1.50-1.41 (m, 2H), 1.30-1.20 (m, 2H), 0.93 (d, 12H, *J* = 6.7 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.0, 115.5, 67.3, 46.5, 44.5, 24.7, 23.3, 22.2 (also present from minor diastereoisomer 144.3, 115.1, 68.1, 45.2, 23.4, 22.1); MS (CI, NH_3) *m/z* 246 $(M+NH_4)^+$, 229 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{14}H_{29}O_2$ $(M+H)^+$ 229.2168, found $(M+H)^+$ 229.2176.

(6*S*,10*S*)-(+)-8-Methylenepentadecane-6,10-diol (1e). From (*S*,*S*)-**3** and hexenal. Colorless oil (43% as an inseparable 23 : 2 mixture of diastereoisomers): TLC R_f 0.14 (1 : 4 EtOAc/hexanes); $[\alpha]_D^{23}$ +8.6° (*c* 12.3, $CHCl_3$); IR (film) 3350, 3073, 2955, 2927, 2859, 1642 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 4.95 (s, 2H), 3.74-3.70 (m, 2H), 2.71 (br s, 2H), 2.21-2.26 (dd, 2H, *J* = 7.5, 2.7 Hz), 2.09-2.00 (m, 2H), 1.60-1.20 (m, 16H), 0.86 (t, 6H, *J* = 6.7 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.1, 115.1, 69.4, 43.9, 37.3, 31.9, 25.4, 22.6, 14.0 (also present from minor diastereoisomer 144.5, 114.9, 70.2, 44.6); MS (CI, NH_3) *m/z* 274 $(M+NH_4)^+$, 257 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{16}H_{36}NO_2$ $(M+NH_4)^+$ 274.2746, found $(M+NH_4)^+$ 274.2734. Anal. Calcd for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 75.09; H, 12.72.

(1*R*,5*R*)-(+)-1,5-Di-(4-nitrophenyl)-3-methylenepentane-1,5-diol (1f). From (*S*,*S*)-**3** and 4-nitrobenzaldehyde. Pale yellow crystals (51% as an inseparable 19 : 1 mixture of diastereoisomers): m.p. 112-115°C ($CHCl_3$-hexanes); TLC R_f 0.08 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ +50.6° (*c* 1.8, $CHCl_3$); IR ($CHCl_3$) 3591, 3062, 2926, 2857, 1524, 1348 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 8.23 (d, 4H, *J* = 8.6 Hz),

7.58 (d, 4H, J = 8.6 Hz), 5.16 (2H, s), 5.06 (dd, 2H, J = 9.6, 3.3 Hz), 2.79 (br s, 2H), 2.62-2.41 (m, 4H); ^{1}H NMR (300 MHz; CD_3OD) δ 8.18 (d, 4H, J = 8.7 Hz), 7.61 (d, 4H, J = 8.7 Hz), 5.01 (t, 2H, J = 6.7 Hz), 4.89 (2H, s), 2.79 (br s, 2H), 2.50 (d, 4H J = 6.7 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ 151.1, 147.4, 141.4, 126.5, 123.8, 118.0, 71.5, 46.0; ^{13}C NMR (75 MHz; CD_3OD) d 152.7, 147.1, 141.7, 126.7, 123.0, 115.6, 71.4, 45.5 (also present from minor diastereoisomer 115.4, 71.7); MS (CI, NH_3) *m/z* 376 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{18}H_{22}N_3O_6$ $(M+NH_4)^+$ 376.1509, found $(M+NH_4)^+$ 376.1513. Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.31; H, 4.93; N, 7.80.

(1*R*,5*R*)-(+)-1,5-Di-(4-methoxyphenyl)-3-methylenepentane-1,5-diol (1g). From (*S*,*S*)-**3** and 4-methoxybenzaldehyde. White solid (55% as an inseparable 19 : 1 mixture of diastereoisomers): m.p. 55-57 °C (^{i}Pr$_2$O); TLC R_f 0.14 (EtOAc/hexane, 3 : 2); $[a]_D^{27}$ +64.6° (*c* 9.6, $CHCl_3$); IR (film) 3391, 3064, 2998, 2961, 2920, 2835, 1611 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.27 (d, 4H, J = 8.6 Hz), 6.88 (d, 4H, J = 8.6 Hz), 5.06 (s, 2H), 4.78 (dd, 2H, J = 8.5, 4.9 Hz), 3.80 (s, 6H), 3.4-3.2 (br s, 2H), 2.42 (m, 4H) (also present from minor diastereoisomer, 5.00 (s, 2H)); ^{13}C NMR (75 MHz $CDCl_3$) δ 159.0, 143.2, 136.4, 127.1, 116.1, 113.8, 71.9, 55.3, 46.1 (also present from minor diastereoisomer 72.4, 46.4); MS (CI, NH_3) *m/z* 346 $(M+NH_4)^+$, 329 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{20}H_{28}NO_4$ $(M+NH_4)^+$ 346.2018, found $(M+NH_4)^+$ 346.1998. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.04; H, 7.45.

(1*R*,5*R*)-(+)-1,5-Di-(3-nitrophenyl)-3-methylenepentane-1,5-diol (1h). From (*S*,*S*)-**3** and 3-nitrobenzaldehyde. Pale yellow oil (47% as an inseparable 47 : 3 mixture of diastereoisomers): TLC R_f 0.12 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ +44.1° (*c* 6.9, $CHCl_3$); IR (film) 3376, 3069, 2931, 1644, 1537, 1348 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.19 (s, 2H), 8.07 (m, 2H), 7.68 (d, 2H, J = 7.9 Hz), 7.49 (t, 2H, J = 7.9 Hz), 5.12 (2H, s), 5.00 (dd, 2H, J = 9.5, 3.6 Hz), 3.73 (br. s, 2H), 2.56-2.39 (m, 4H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 148.3, 146.1, 141.5, 132.0, 129.5, 122.5, 120.7, 117.6, 71.4, 45.9 (also present from minor diastereoisomer 146.3, 142.0, 72.3, 46.3);

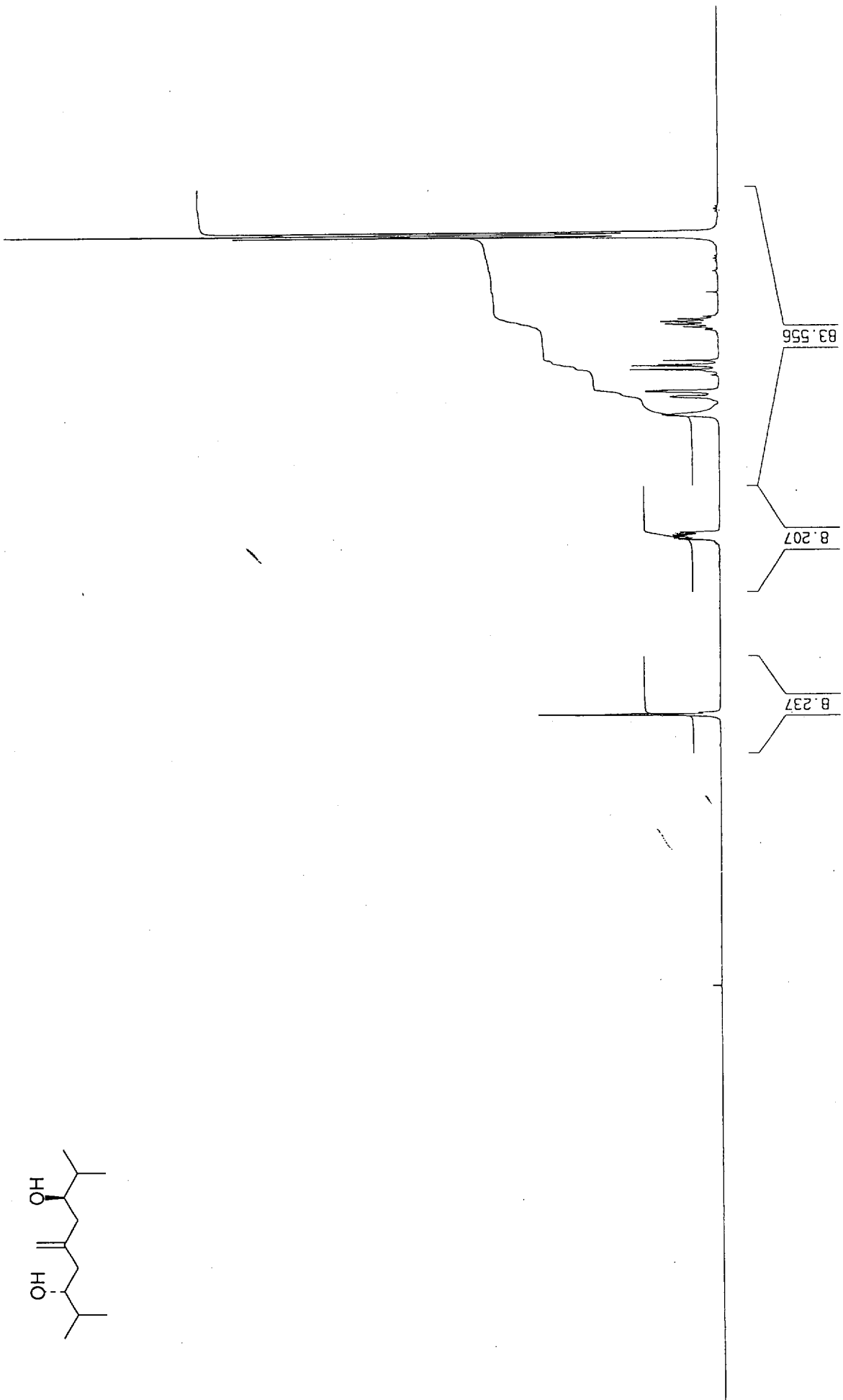
MS (CI, NH_3) *m/z* 376 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{18}H_{22}N_3O_6$ $(M+NH_4)^+$ 376.1509, found $(M+NH_4)^+$ 376.1518. Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.59; H, 5.15; N, 7.67.

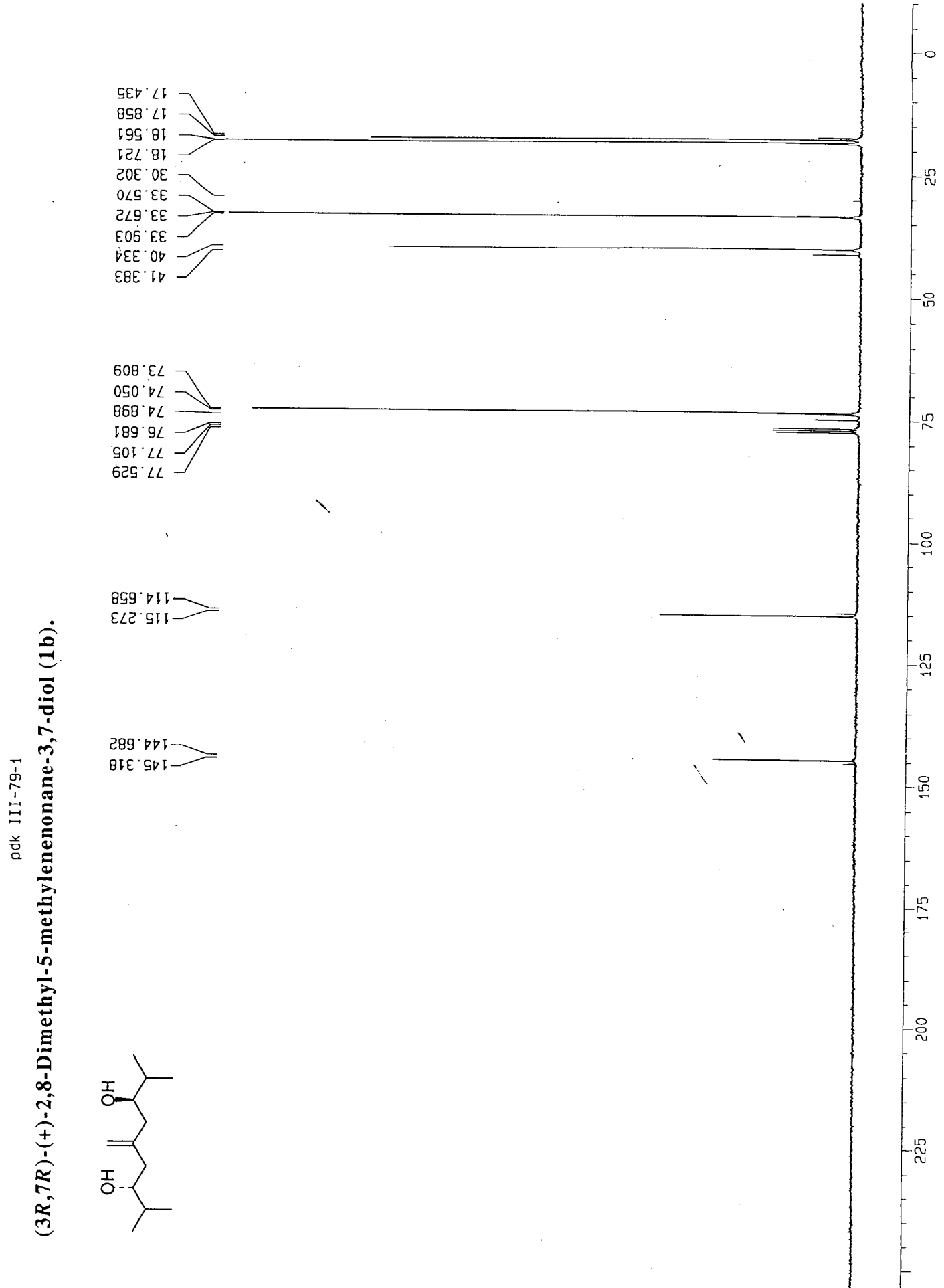
(1*R*,5*R*)-(+)-1,5-Di-[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylenepentan-1,5-diol (1i). From (*S*,*S*)-**3** and 2,3-*O*-isopropylidene-D-glyceraldehyde. Colorless oil (38% as an inseparable 66 : 14.5 : 1 mixture of diastereoisomers): TLC R_f 0.08 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ +17.4° (*c* 7.7, $CHCl_3$); IR (film) 3431, 3075, 2934, 2893, 1644 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) major diastereoisomer δ 4.99 (s, 2H), 4.03-3.97 (m, 4H), 3.77-3.70 (m, 4H), 2.84 (br s, 2H), 2.19 (d, 4h, *J* = 6.5 Hz), 1.41 (s, 6H), 1.34 (s, 6H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 141.9, 115.7, 109.3, 78.5, 70.4, 65.8, 39.8, 26.5, 25.2 (also present from minor diastereoisomers 142.5, 115.5, 109.0, 78.7, 71.0, 65.5, 37.7); MS (CI, NH_3) *m/z* 334 $(M+NH_4)^+$, 317 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{16}H_{29}O_6$ $(M+H)^+$ 317.1964, found $(M+H)^+$ 317.1965. Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92. Found: C, 60.76; H, 8.81.

(1*S*,5*S*)-(+)-1,5-Di-[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylenepentan-1,5-diol (1j). From (*R*,*R*)-**3** and 2,3-*O*-isopropylidene-D-glyceraldehyde. Colorless oil (50% as an inseparable 160 : 22 : 1 mixture of diastereoisomers): TLC R_f 0.08 (2 : 3 EtOAc/hexanes); $[\alpha]_D^{23}$ +5.2° (*c* 2.5, $CHCl_3$); IR (film) 3431, 3075, 2985, 2934, 2893, 1644 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) major diastereoisomer δ 5.06 (s, 2H), 4.08-3.94 (m, 6H), 3.88-3.83 (m, 2H), 2.45-2.40 (m, 4H), 2.09 (dd, 2H, *J* = 14.4, 10.1 Hz), 1.43 (s, 6H), 1.37 (s, 6H) (also present from minor diastereoisomers 5.03 (s, 2H)); ^{13}C NMR (75 MHz; $CDCl_3$) δ 142.3, 116.0, 109.2, 78.4, 69.8, 65.6, 39.6, 26.6, 25.2 (also present from minor diastereoisomers 71.1, 66.4, 37.7); MS (CI, NH_3) *m/z* 334 $(M+NH_4)^+$, 317 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{16}H_{29}O_6$ $(M+H)^+$ 317.1964, found $(M+H)^+$ 317.1958. Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92. Found: C, 60.59; H, 8.95.

(6*S*,8*R*,12*R*,14*S*)-(+)-10-Methylene-2,6,14,18-tetramethylnonadeca-2,17-diene-8,14-diol (1k). From (*R*,*R*)-**3** and (*S*)-

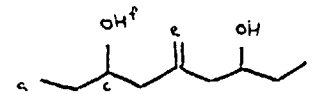
citronellal. Colorless oil (57% as an inseparable 46 : 6 : 1 mixture of diastereoisomers): TLC R_f 0.04 (1 : 9 EtOAc/hexanes); $[\alpha]_D^{23}$ +4.1° (*c* 3.9, $CHCl_3$); IR (film) 3368, 3072, 2962, 2925, 2855, 1642 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) major diastereoisomer δ 5.13-5.08 (m, 2H), 5.00 (s, 2H), 3.90-3.82 (m, 2H), 2.25 (dd, 2H *J* = 14.0, 2.9 Hz), 2.16-1.96 (m, 8H), 1.67 (s, 6H), 1.61 (s, 6H), 1.70-1.15 (m, 10H), 0.93 (d, 6H, *J* = 6.6 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.0, 131.2, 124.8, 115.4, 67.0, 44.8, 44.8, 37.9, 29.0, 25.7, 25.5, 19.2, 17.7 (also present from minor diastereoisomers 144.4, 115.1, 68.2, 67.8, 45.5, 36.8, 29.7, 29.3, 20.2); MS (CI, NH_3) *m/z* 382 $(M+NH_4)^+$, 365 $(M+H)^+$; HRMS (CI, NH_3) calcd for $C_{24}H_{45}O_2$ $(M+H)^+$ 365.3420, found $(M+H)^+$ 365.3429. Anal. Calcd for $C_{24}H_{44}O_2$: C, 79.06; H, 12.16. Found: C, 78.84; H, 12.23.


pdk III-79-1
(3R,7R)-(+)-2,8-Dimethyl-5-methylenenonane-3,7-diol (1b).
OH
OH
83.556
8.207
8.237
0
1
2
3
4
5
6
7
8
9
10



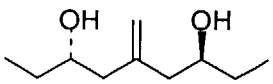
pdk III-79-1

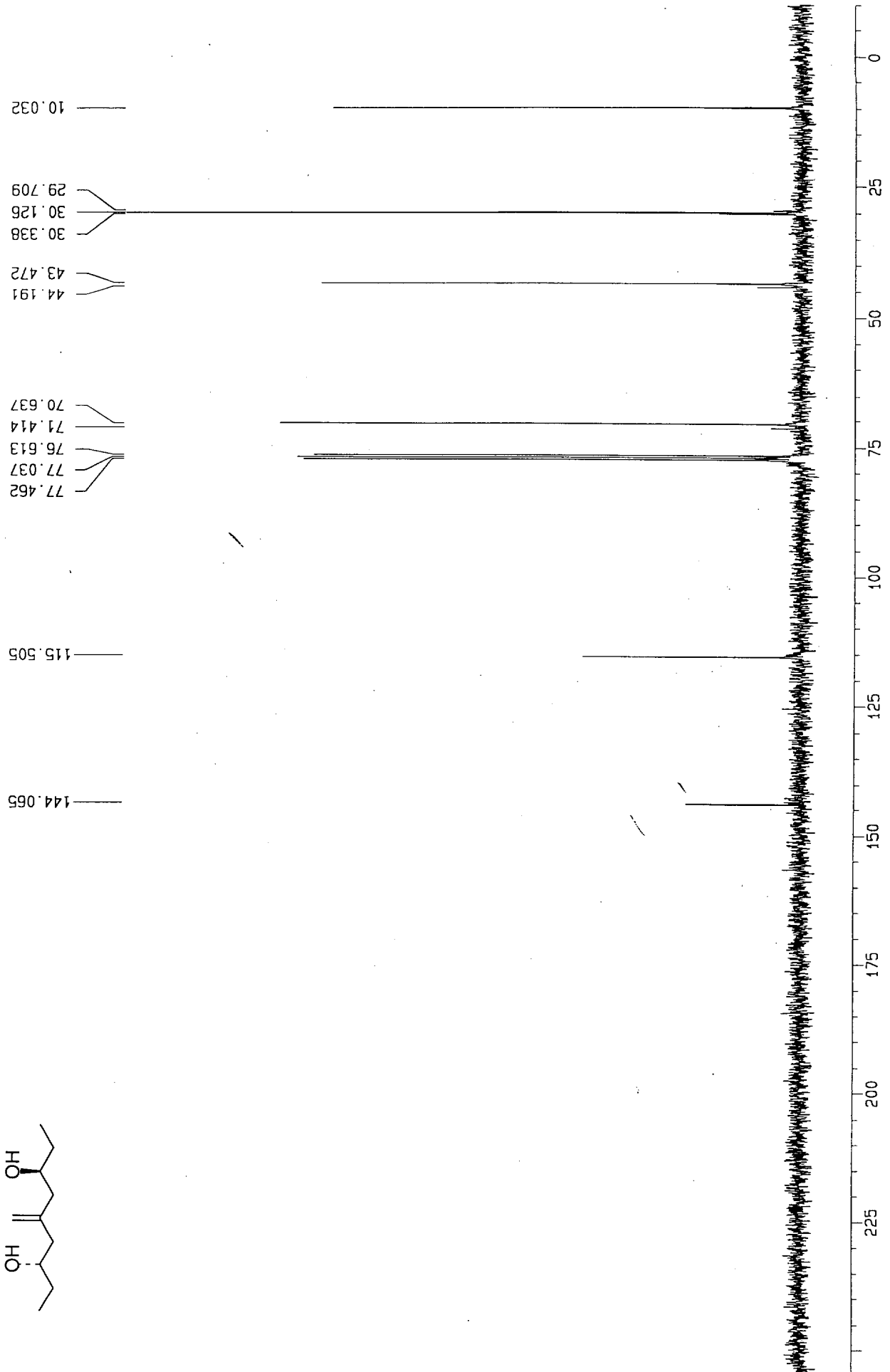
(3*R*,7*R*)-(+)-2,8-Dimethyl-5-methylenenonane-3,7-diol (1b).



pdk II-73-2 (rechrom)

(3*S*,7*S*)-(+)-5-Methylenenonane-3,7-diol (1c).



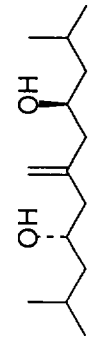


pdk II-73-2 (longer time)

(3*S*,7*S*)-(+)-5-Methylenenonane-3,7-diol (1c).

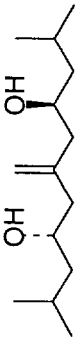
(4*S*,8*S*)-(−)-2,10-Dimethyl-6-methyleneundecane-4,8-diol (1d).

pdk II-113-1



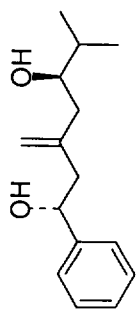
(4*S*,8*S*)-(−)-2,10-Dimethyl-6-methyleneundecane-4,8-diol (1d).

pdk II-113-1

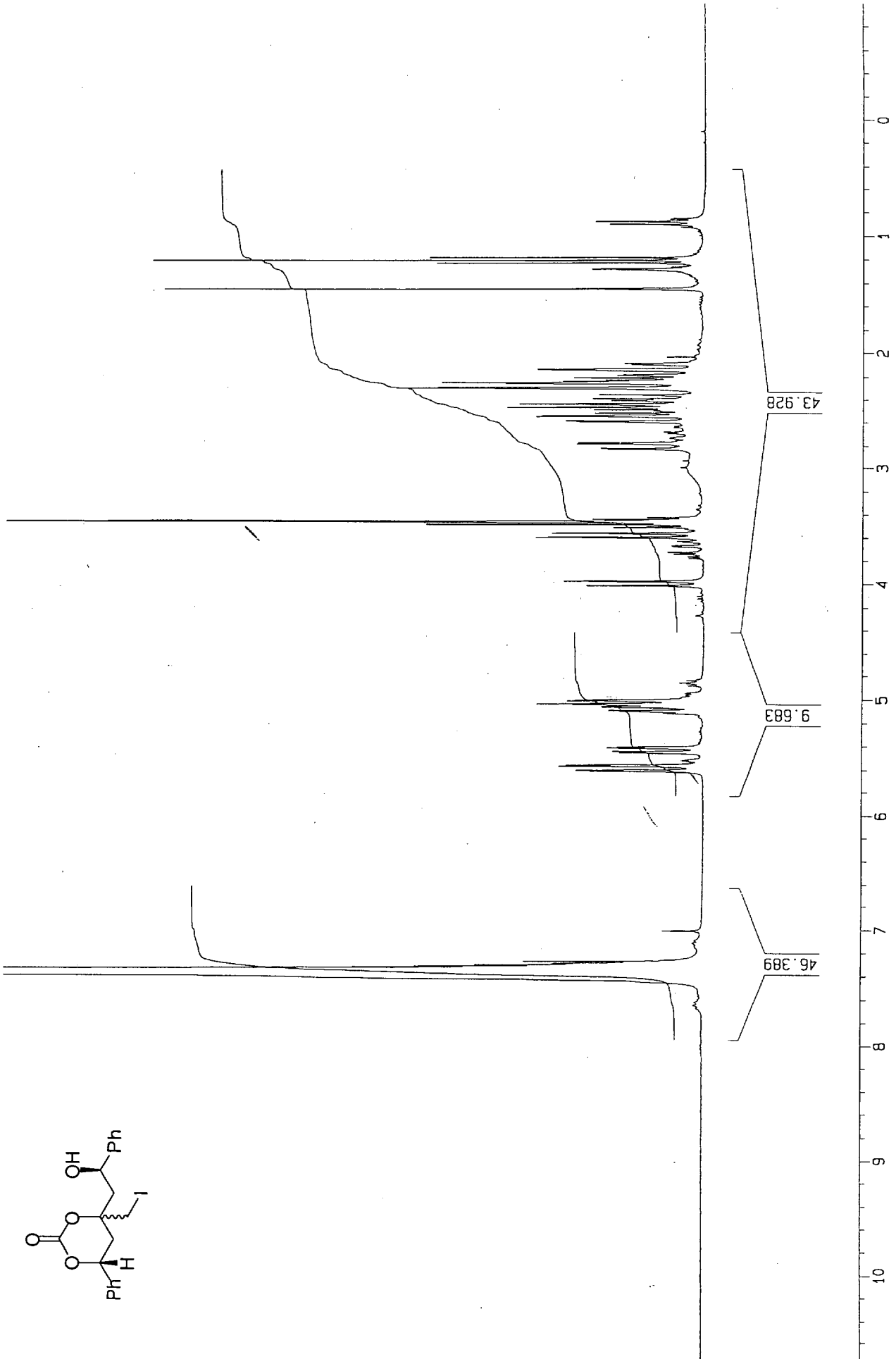


(1*R*,5*R*)-6-methyl-1-phenyl-3-methyleneheptan-1,5-diol (9).

pdk II-43-mixed

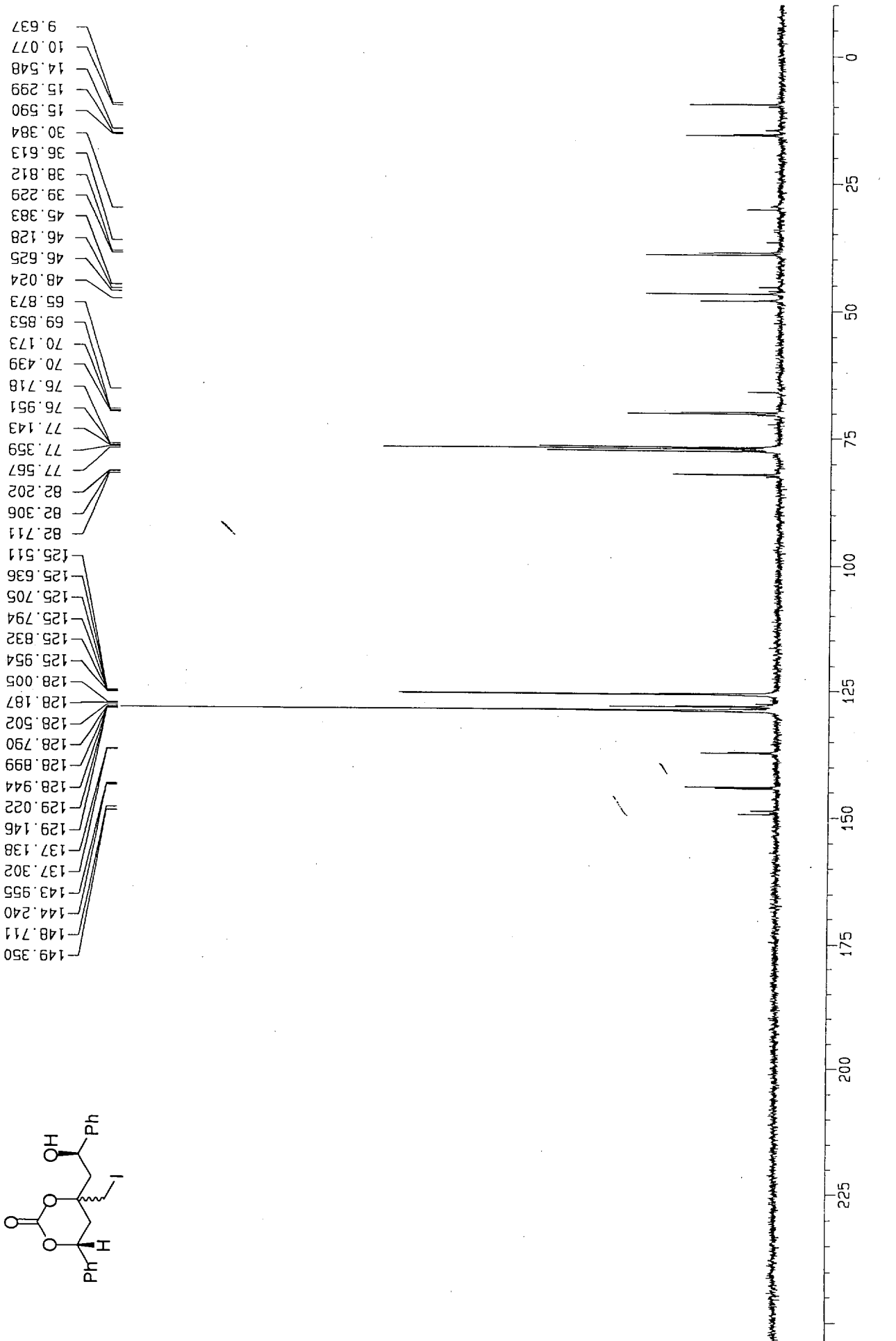


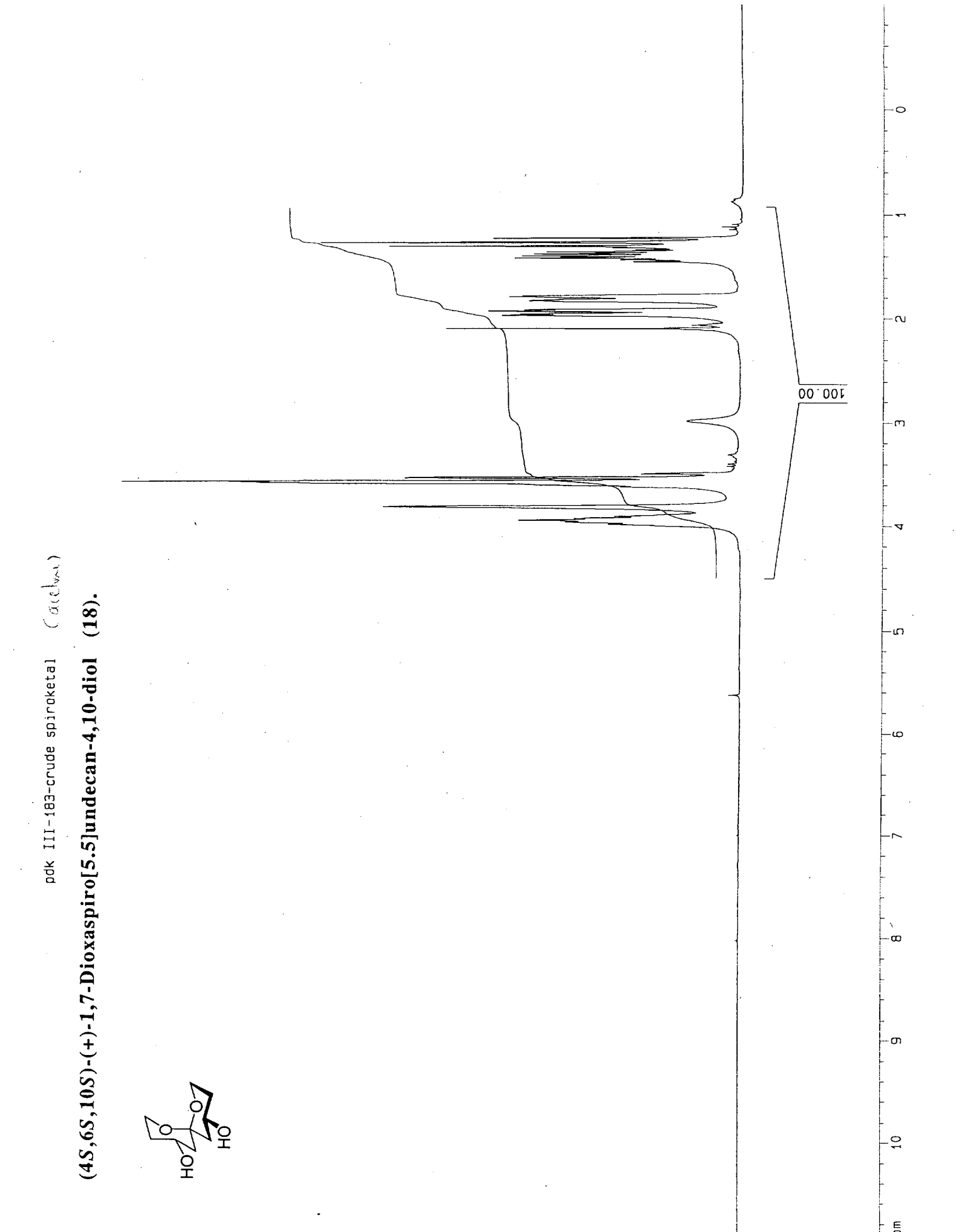
(6*R*)-4-(2-Hydroxy-2*R*-phenylethyl)-4-iodomethyl-6-phenyl-1,3-dioxan-2-one (11).



(6*R*)-4-(2-Hydroxy-2*R*-phenylethyl)-4-iodomethyl-6-phenyl-1,3-dioxan-2-one (11).

pdk II-211-1 (dried? and a mixture)

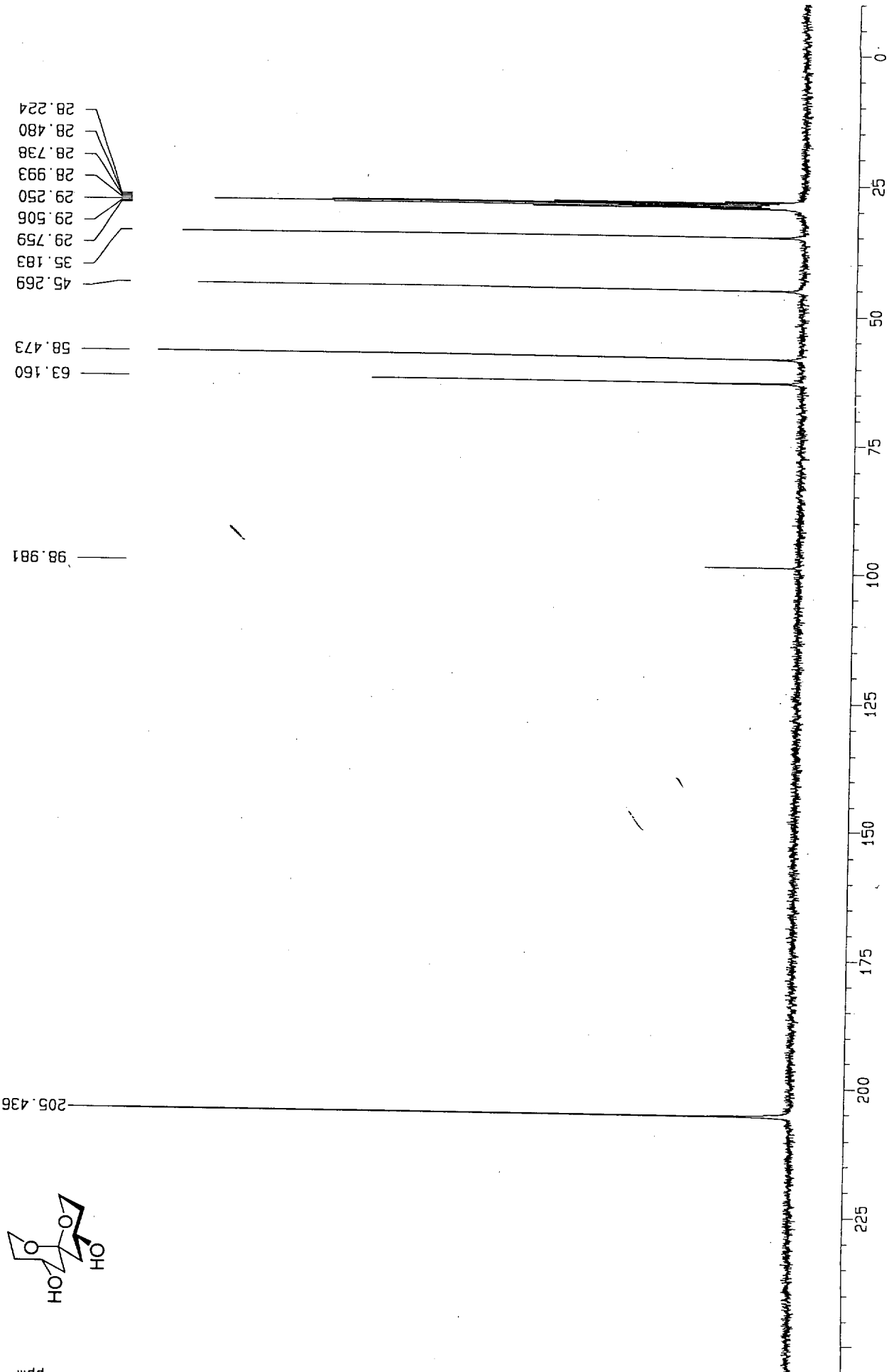




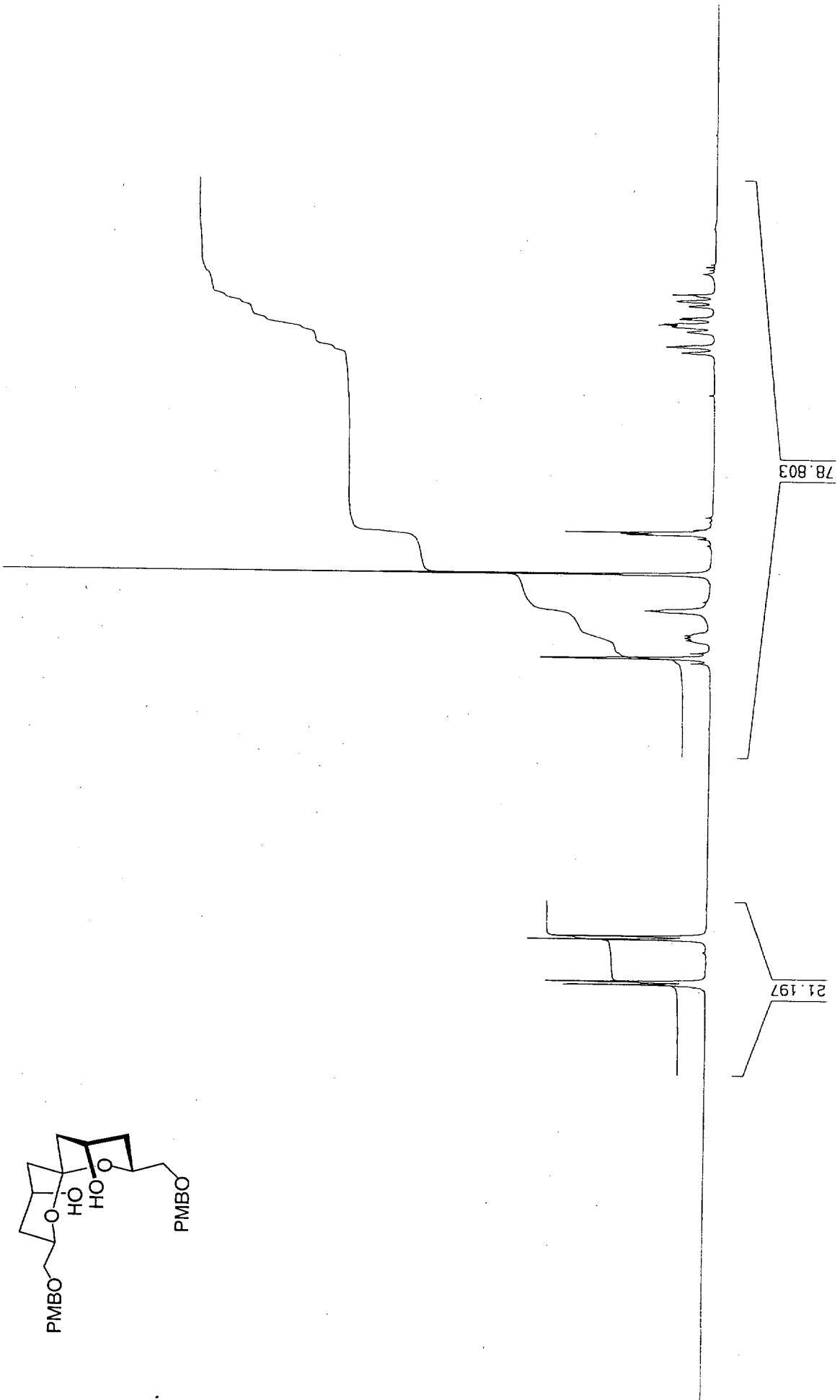
(4*S*,6*S*,10*S*)-(+)-1,7-Dioxaspiro[5.5]undecan-4,10-diol (18).

(4*S*,6*S*,10*S*)-(+)-1,7-Dioxaspiro[5.5]undecan-4,10-diol (18).

pdk III-183-crude spiroketal (active)

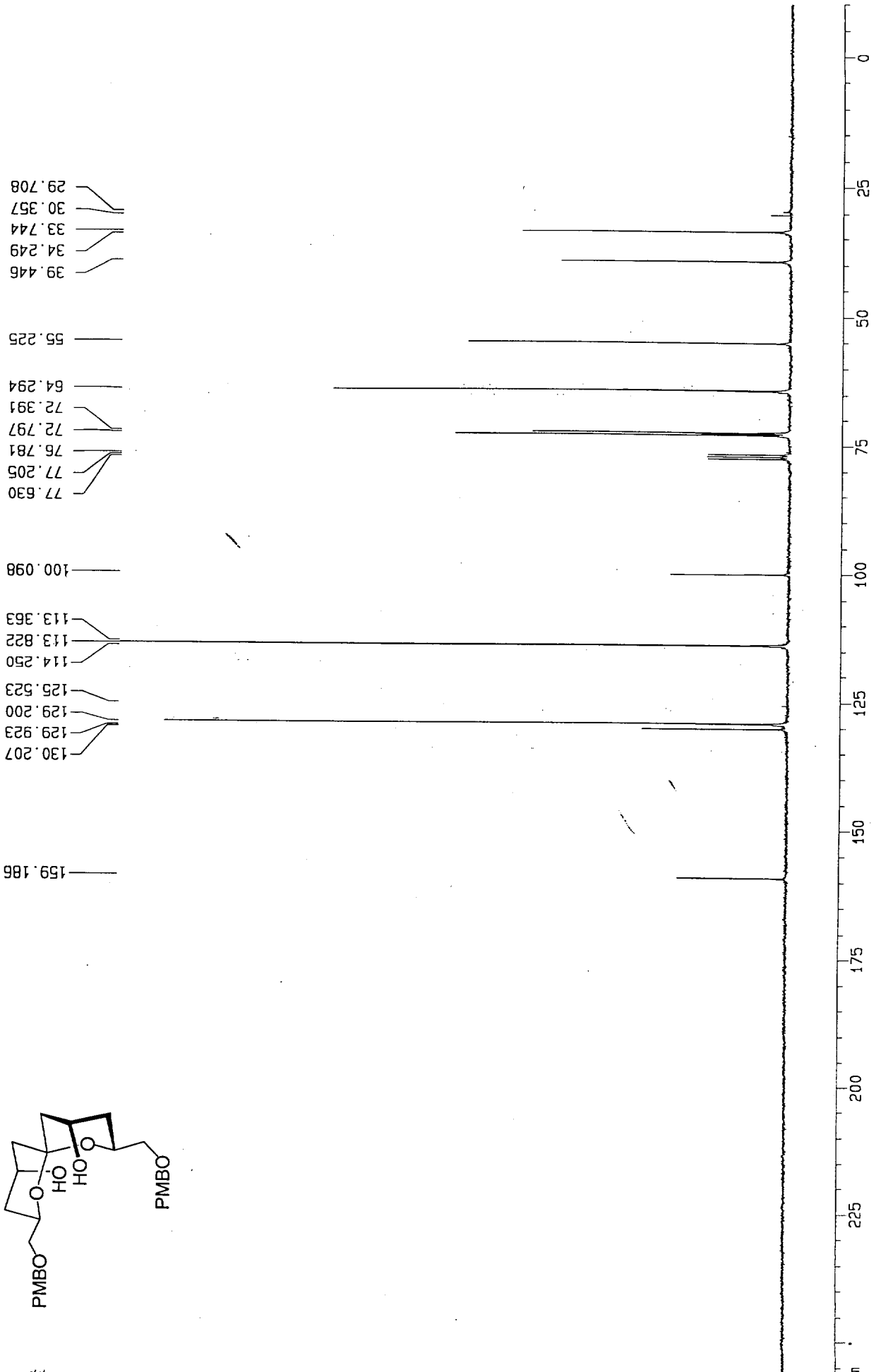


(2*R*,4*S*,6*R*,8*R*,10*S*)-2,8-Di-(4-methoxybenzyloxymethyl)-1,7-dioxaspiro[5.5]undecan-4,10-diol (25).



(2*R*,4*S*,6*R*,8*R*,10*S*)-2,8-Di-(4-methoxybenzyloxymethyl)-1,7-dioxaspiro[5.5]undecan-4,10-diol (25).

pdk III-185-3



Determination of the diastereomeric and enantiomeric excesses. The diols **1a-h** were converted to their bis-(*S*)-Mosher's esters and compared with the bis-(*S*)-Mosher's esters derived from the 1:1 mixture of diols *rac*-**1a-h** : *meso*-**2** prepared by condensation of 1,3-dilithio-3-methylenepropane with the appropriate aldehyde. The diastereomeric ratio and enantiomeric excess were determined by integration of the signals for the olefinic protons. In these spectra excellent separation of the signals for the methylene protons were observed, with those corresponding to the enantiomeric pair (**1**) appearing as singlets generally 0.2-0.3 ppm apart ($\delta \approx 5$ ppm) The signals corresponding to the *meso*-**2** compound appeared as a singlet or two (slightly broadened) singlets roughly in the middle of the two former singlets. The following procedure for the formation of **6g** is representative: A sample of **1g** (10 mg), DMAP (cat.), pyridine (40 μL; 0.5 mmol) and (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher chloride) (22 μL; 0.12 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and stirred at ambient temperature until the reaction was complete (TLC monitoring, *ca.* 3h). If necessary, a further aliquot of the acid chloride (22 μl) was added. Saturated aqueous $NaHCO_3$ (5 mL) was added and the mixture was extracted with Et_2O (2 x 10 mL). The combined organic phase was washed with H_2O, saturated $CuSO_4$ solution and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was filtered through a small column of silica gel, eluting with Et_2O. The solvent was evaporated and the crude *bis*-Mosher ester **6g** was then analyzed by ^1H NMR spectroscopy.

The following data is given for the mosher's esters derived from the *rac*-**1**/*meso*-**2** mixtures:

bis-Mosher ester ex-**1a/2a**: TLC R_f 0.46 (1:4 EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.63-7.20 (m, 60H), 6.16-6.03 (m, 6H), 5.02 (s, =C*H*$_2$, *R,R*, 2H), 4.87 (s, =C*H*$_2$, *meso*, 1H), 4.86 (s, =C*H*$_2$, *meso*, 1H), 4.77 (s, =C*H*$_2$, *S,S*, 2H), 3.52 (s, 6H), 3.49 (s, 6H), 3.45 (s, 6H), 2.78-2.37 (m, 12H); ^1H NMR (300 MHz, C_6D_6) (1:2:1 mixture of diastereomers) δ 7.76-7.10 (m, 60H), 6.30-6.16 (m, 6H), 4.92 (s, =C*H*$_2$, *R,R*, 2H), 4.81 (s, =C*H*$_2$, *meso*, 1H), 4.78

(s, =CH_2, *meso*, 1H), 4.74 (s, =CH_2, *S,S*, 2H), 3.49 (s, 6H), 3.47 (s, 6H), 3.40 (s, 6H), 2.74-2.31 (m, 12H); MS (CI, NH_3) *m/z* 718 $(M+NH_4)^+$.

bis-Mosher ester ex-**1b/2b**: TLC R_f 0.52 (1:4 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.56-7.36 (m, 30H), 5.36-5.28 (m, 6H), 4.89 (s, =CH_2, *R,R*, 2H), 4.83 (s, =CH_2, *meso*, 1H), 4.81 (s, =CH_2, *meso*, 1H), 4.65 (s, =CH_2, *S,S*, 2H), 3.57-3.44 (m, 18H), 2.47-2.24 (m, 12H), 1.99-1.86 (m, 6H), 0.98-0.81 (m, 36H); MS (CI, NH_3) *m/z* 650 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{32}H_{42}F_6NO_6$ $(M+NH_4)^+$ 650.2916, found $(M+NH_4)^+$ 650.2916.

bis-Mosher ester ex-**1c/2c**: TLC R_f 0.4 (1:4 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.56-7.37 (m, 30H), 5.25-5.14 (m, 6H), 4.92 (s, =CH_2, *S,S*, 2H), 4.82 (s, =CH_2, *meso*, 2H), 4.68 (s, =CH_2, *R,R*, 2H), 3.56-3.42 (m, 18H), 2.42-2.26 (m, 12H), 1.73-1.59 (m, 12H), 0.98-0.80 (m, 18H); MS (CI, NH_3) *m/z* 622 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{30}H_{38}F_6NO_6$ $(M+NH_4)^+$ 622.2603, found $(M+NH_4)^+$ 622.2604.

bis-Mosher ester ex-**1d/2d**: TLC R_f 0.6 (1:4 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.56-7.36 (m, 30H), 5.36-5.28 (m, 6H), 4.92 (s, =CH_2, *S,S*, 2H), 4.81 (s, =CH_2, *meso*, 2H), 4.67 (s, =CH_2, *R,R*, 2H), 3.56-3.46 (m, 18H), 2.44-2.23 (m, 12H), 1.67-1.21 (m, 12H), 0.94-0.84 (m, 36H); MS (CI, NH_3) *m/z* 678 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{34}H_{46}F_6NO_6$ $(M+NH_4)^+$ 678.3229, found $(M+NH_4)^+$ 678.3232.

bis-Mosher ester ex-**1e/2e**: TLC R_f 0.6 (1:4 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.56-7.36 (m, 30H), 5.30-5.19 (m, 6H), 4.91 (s, =CH_2, *S,S*, 2H), 4.82 (s, =CH_2, *meso*, 2H), 4.67 (s, =CH_2, *R,R*, 2H), 3.54-3.44 (m, 18H), 2.40-0.80 (m, 78H); MS (CI, NH_3) *m/z* 706 $(M+NH_4)^+$; HRMS (CI, NH_3) calcd for $C_{36}H_{50}F_6NO_6$ $(M+NH_4)^+$ 706.3542, found $(M+NH_4)^+$ 706.3553.

bis-Mosher ester ex-**1f/2f**: TLC R_f 0.23 (1:4 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 8.24-8.14 (m, 12H), 7.48-7.30 (m, 42H), 6.10-6.05 (m, 6H), 4.96 (s, =CH_2, *R,R*, 2H), 4.87 (s, =CH_2, *meso*, 1H), 4.86

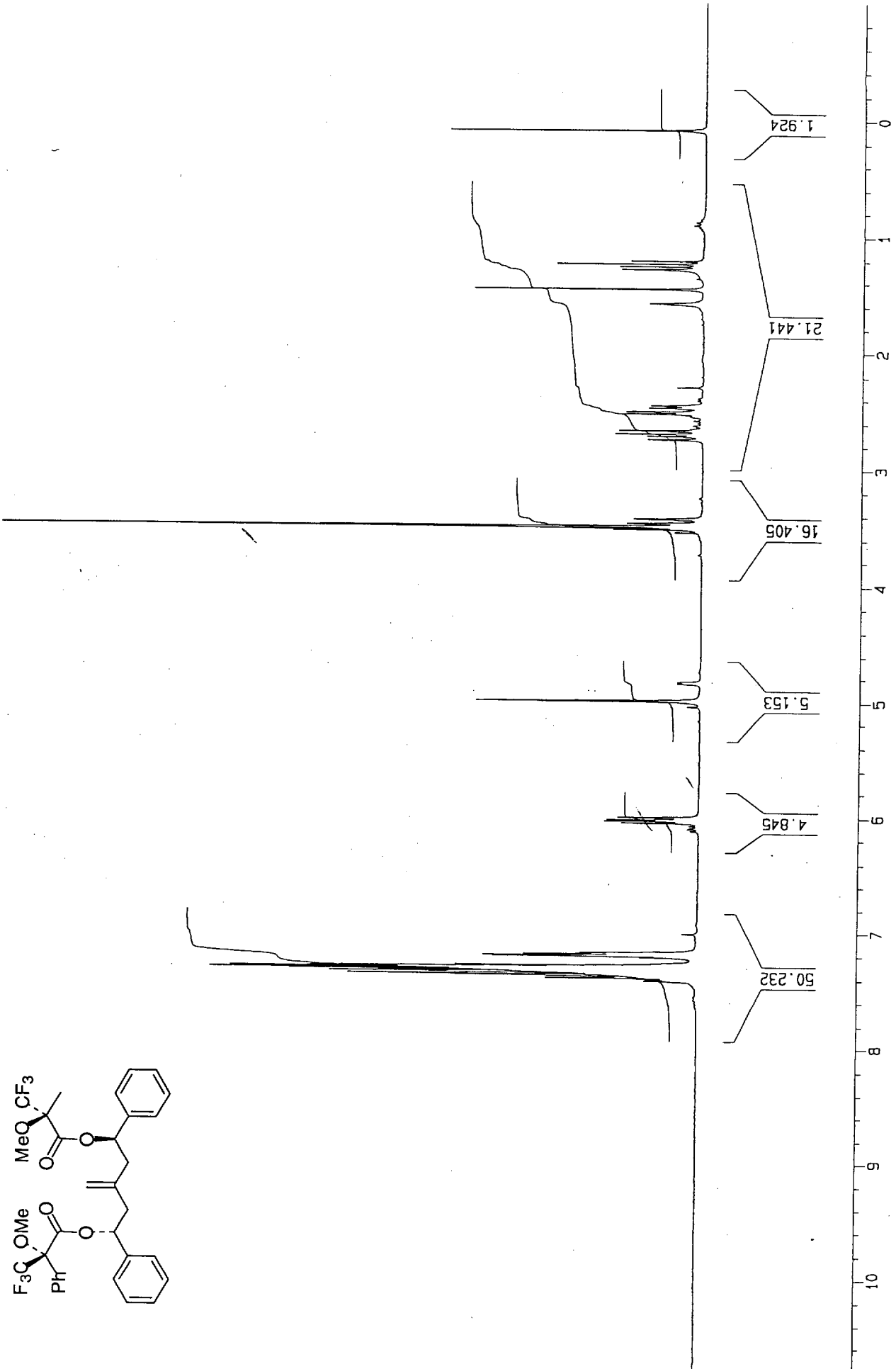
(s, =CH_2, *meso*, 1H), 4.77 (s, =CH_2, *S,S*, 2H), 3.53-3.42 (m, 18H), 2.55-2.29 (m, 12H); MS (CI, NH_3) *m/z* 808 $(M+NH_4)^+$.

bis-Mosher ester ex-**1g/2g**: TLC R_f 0.2 (1:4 EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 7.38-6.80 (m, 54H), 6.06-5.95 (m, 6H), 4.97 (s, =CH_2, *R,R*, 2H), 4.82 (s, =CH_2, *meso*, 1H), 4.81 (s, =CH_2, *meso*, 1H), 4.72 (s, =CH_2, *S,S*, 2H), 3.83-3.81 (m, 18H), 3.49-3.40 (m, 18H), 2.62-2.37 (m, 12H); MS (CI, NH_3) *m/z* 778 $(M+NH_4)^+$.

bis-Mosher ester ex-**1h/2h**: TLC R_f 0.16 (1:4 EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) (1:2:1 mixture of diastereomers) δ 8.24-8.14 (m, 12H), 7.48-7.30 (m, 42H), 6.10-6.05 (m, 6H), 4.98 (s, =CH_2, *R,R*, 2H), 4.88 (s, =CH_2, *meso*, 2H), 4.76 (s, =CH_2, *S,S*, 2H), 3.56-3.44 (m, 18H), 2.80-2.35 (m, 12H); MS (CI, NH_3) *m/z* 808 $(M+NH_4)^+$.

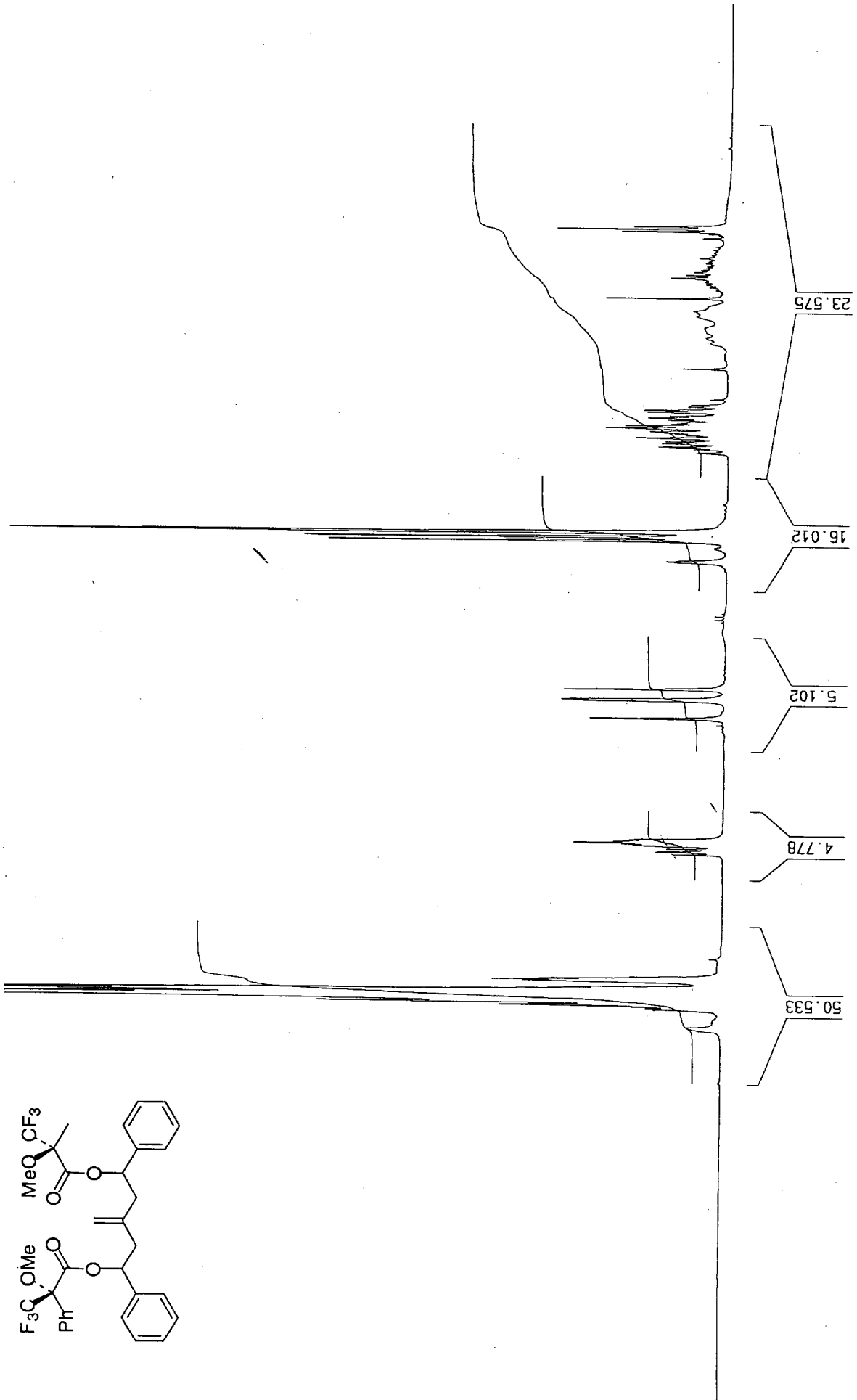
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (1*R*,5*R*)-1a.

pdk II-125-1

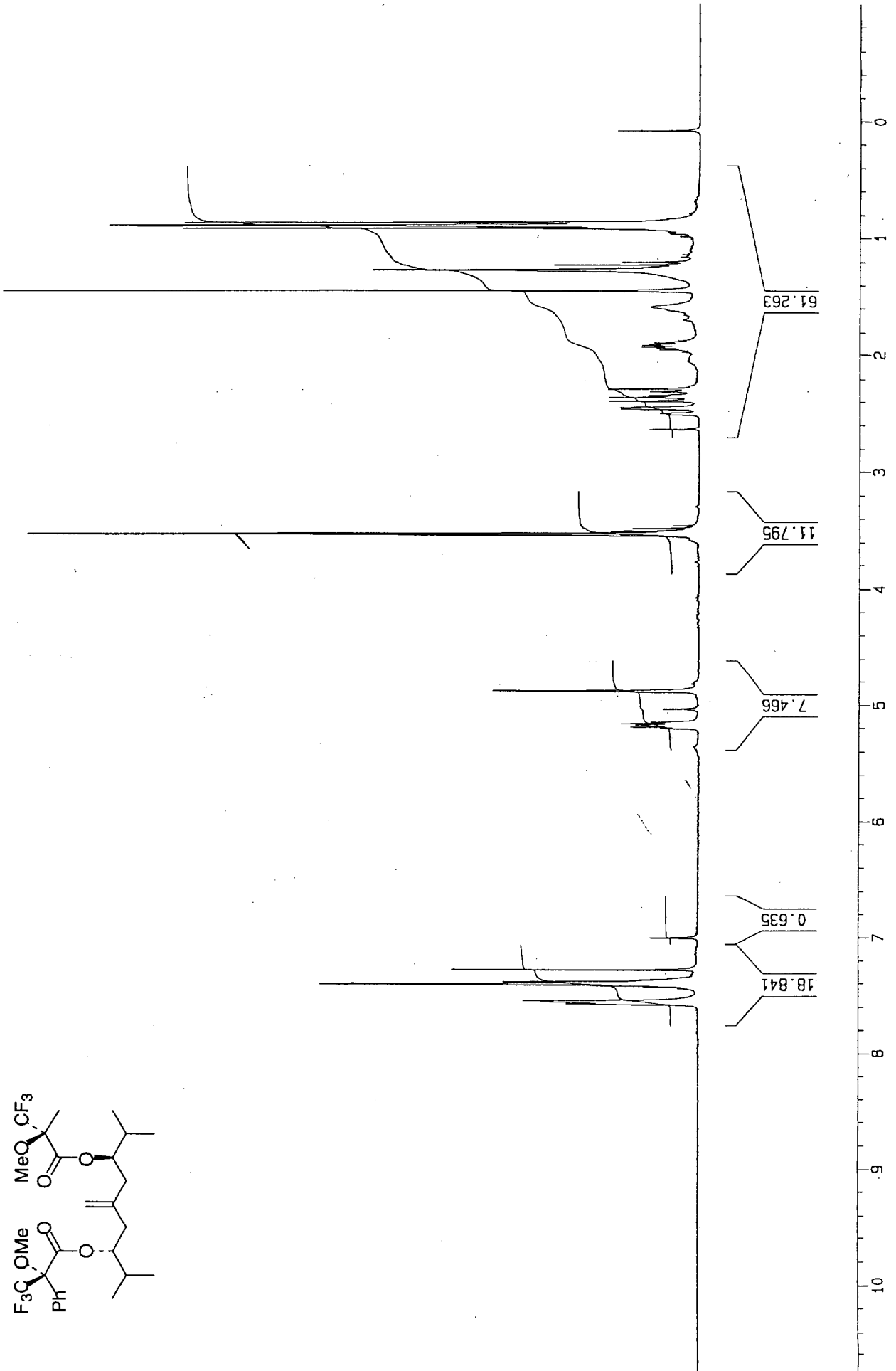


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1a and meso-1a.

pdk II-71-1 (rechram)

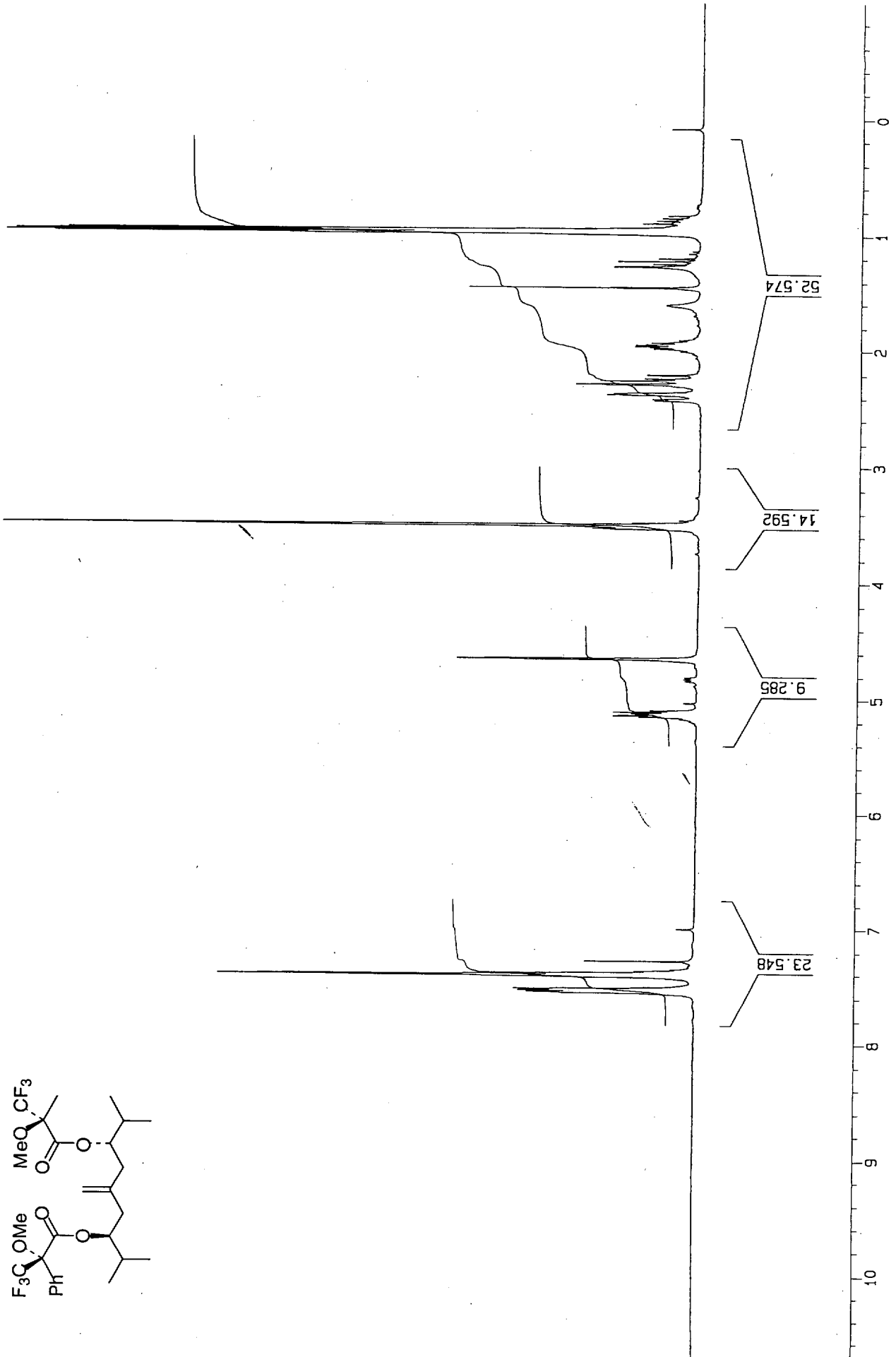


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (3*R*,7*R*)-1b.

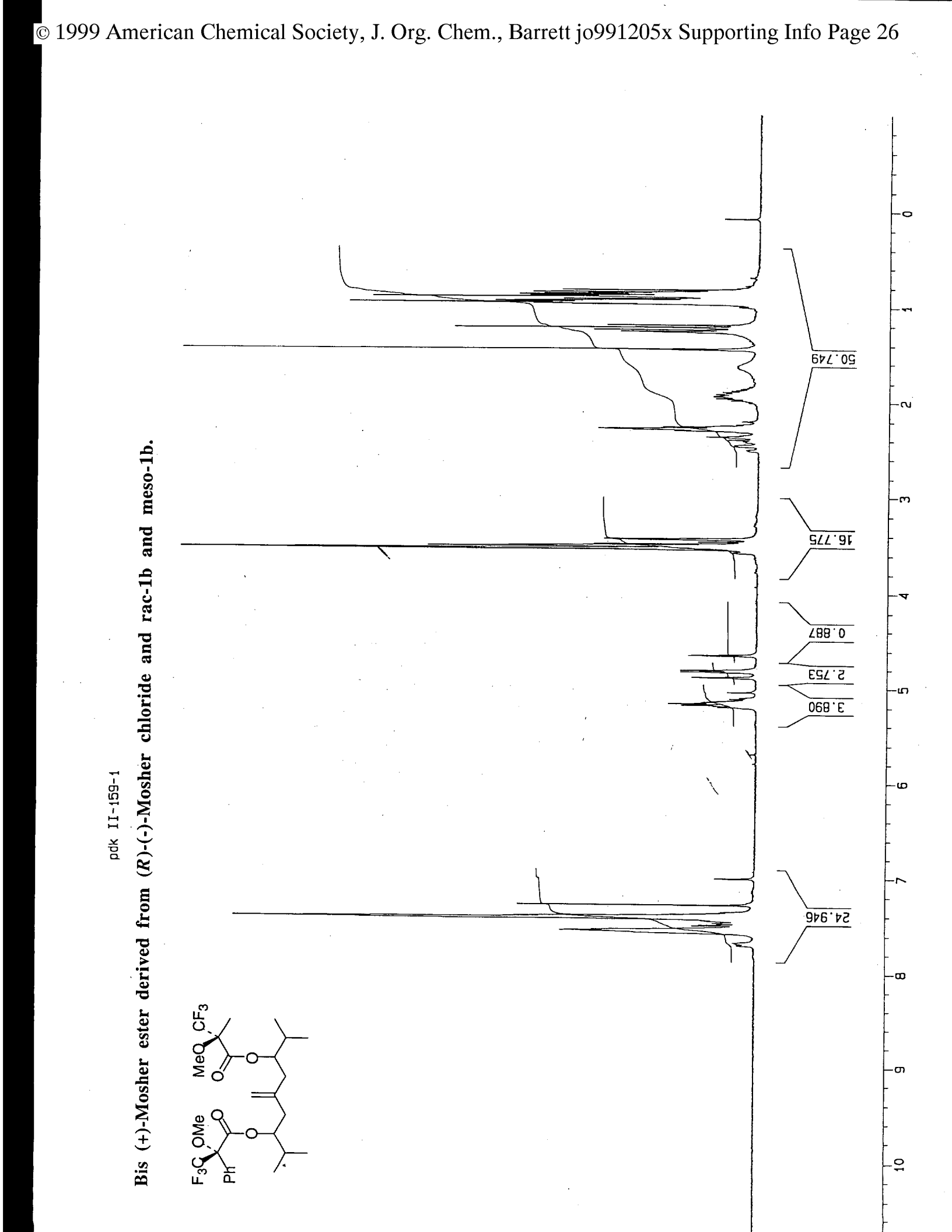


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (1*S*,5*S*)-1b.

pdk II-137-1

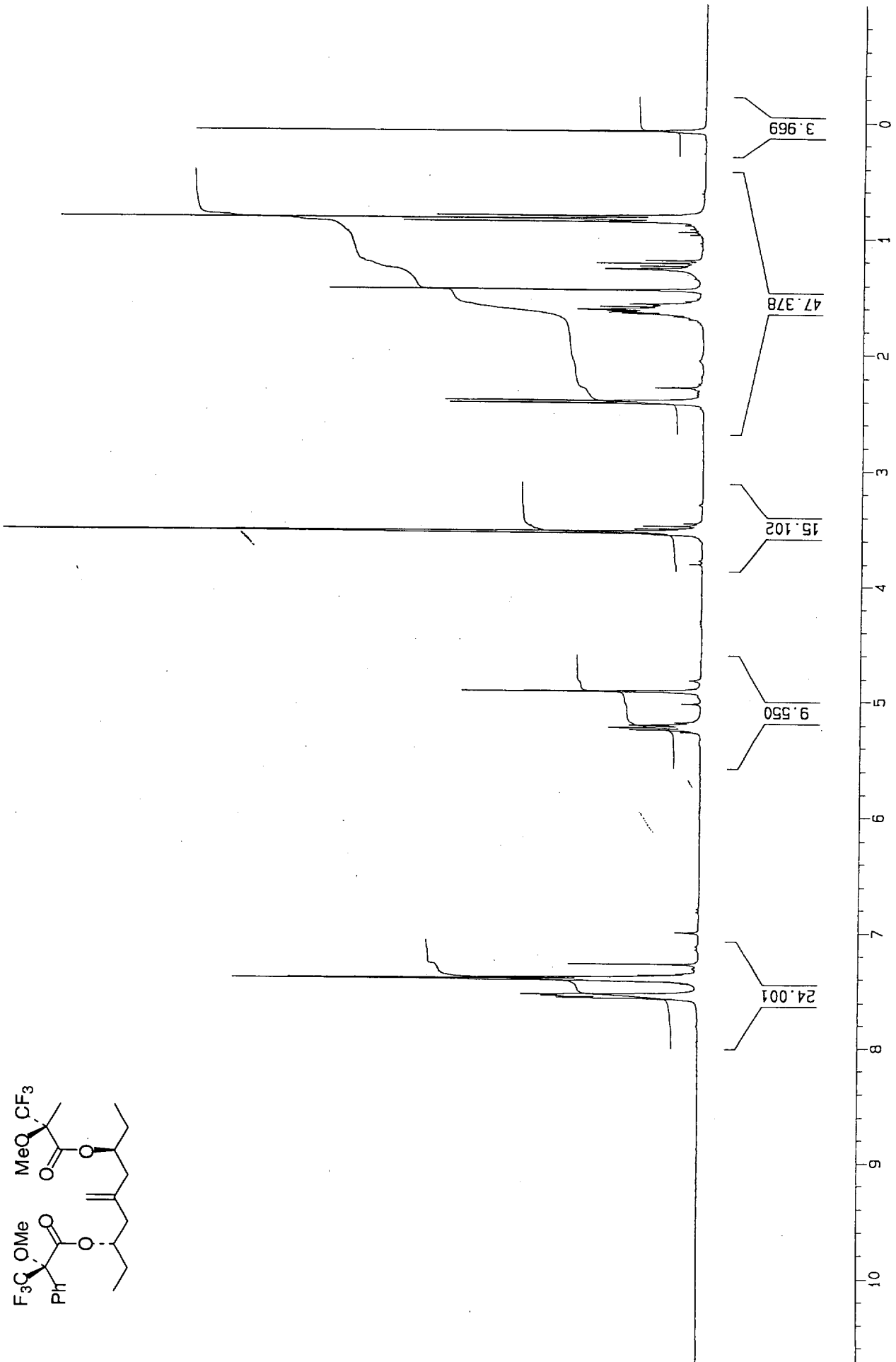


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1b and meso-1b.



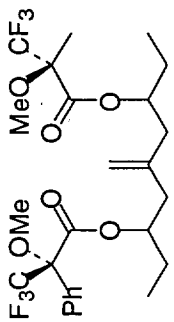
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (3*S*,7*S*)-1c.

pdk II-131-1



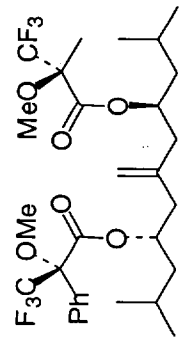
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1c and meso-1c.

pdk II-153-1



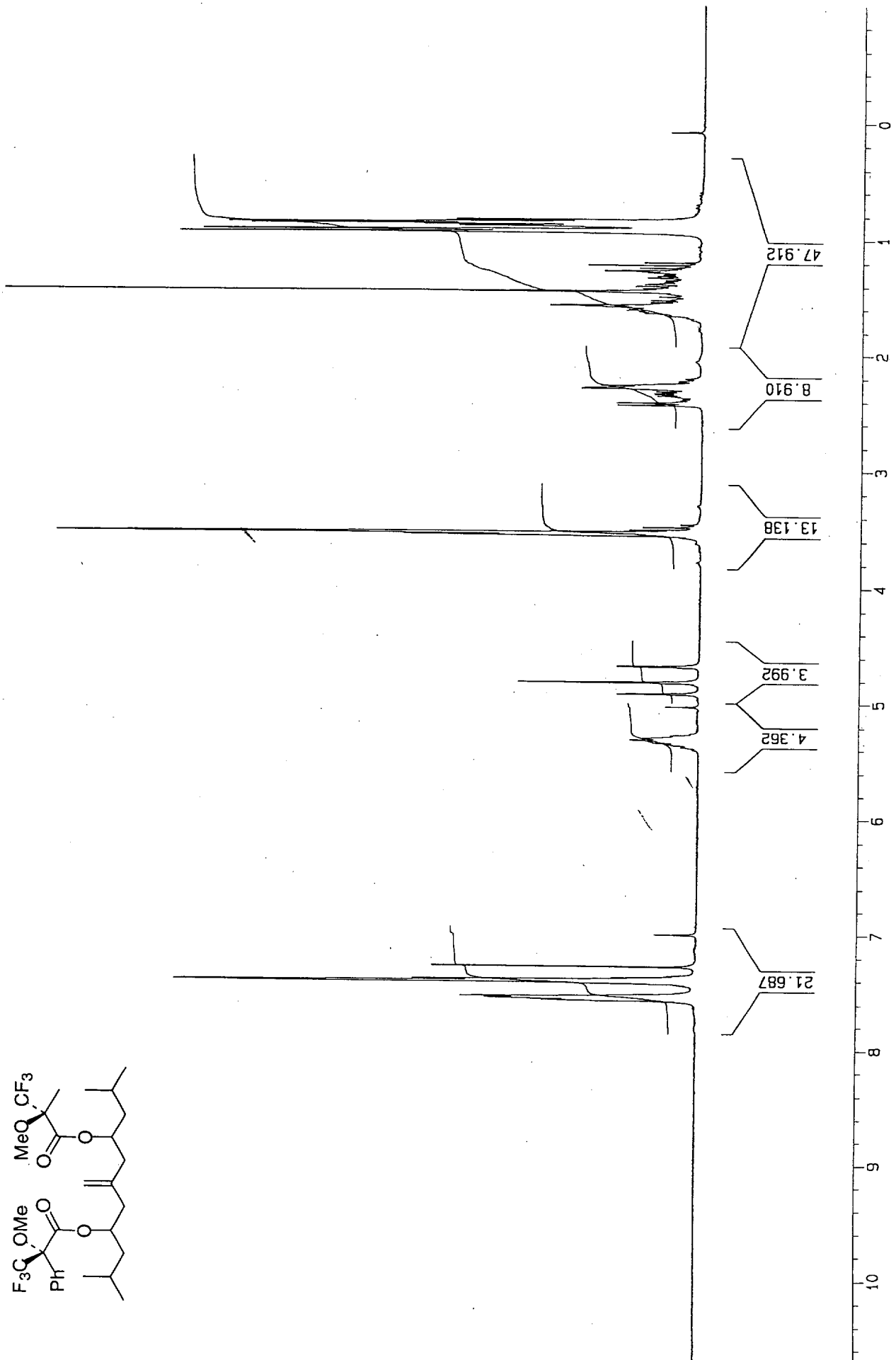
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (4*S*,8*S*)-1d.

pdk II-129-1

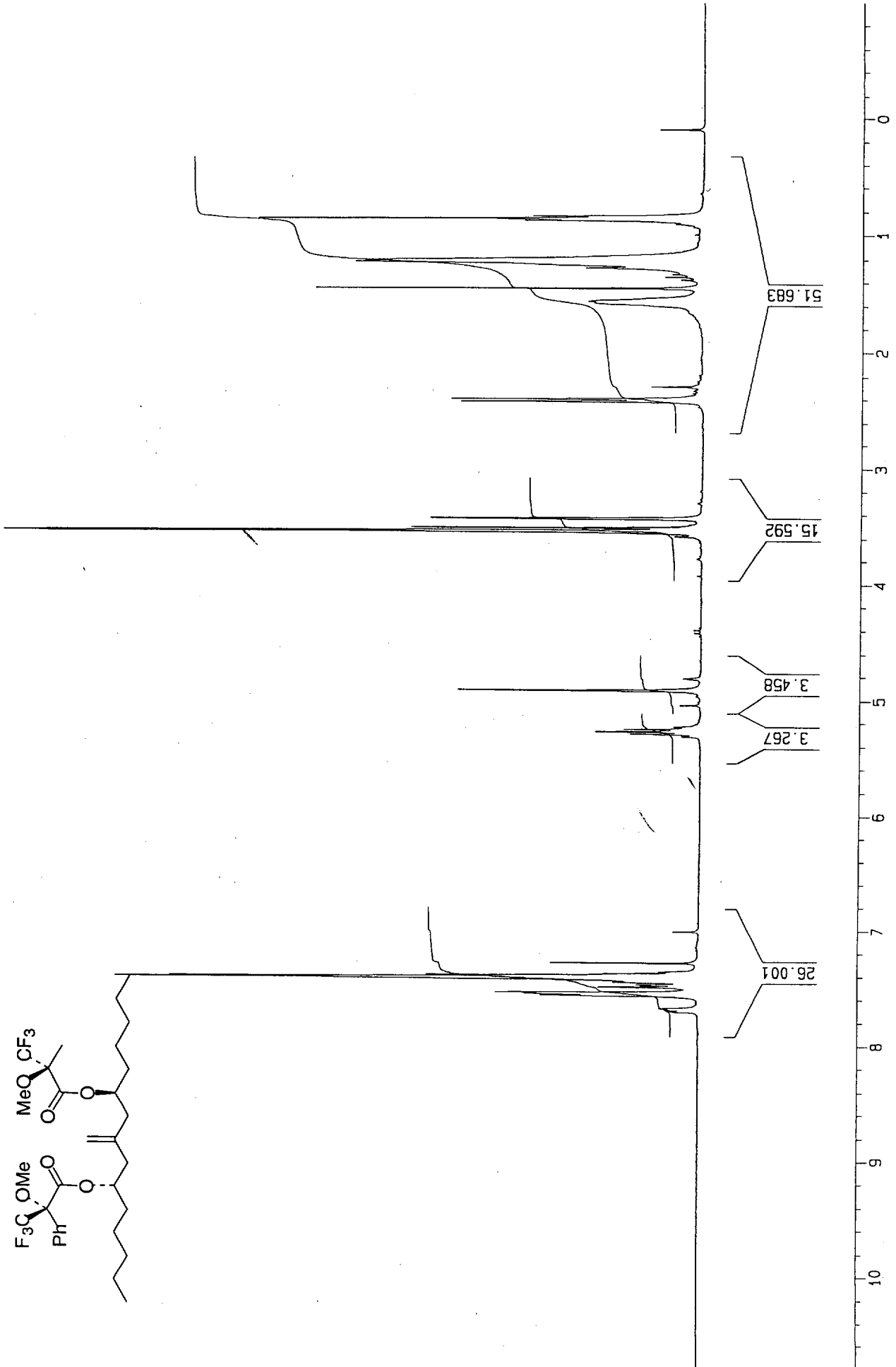


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1d and meso-1d.

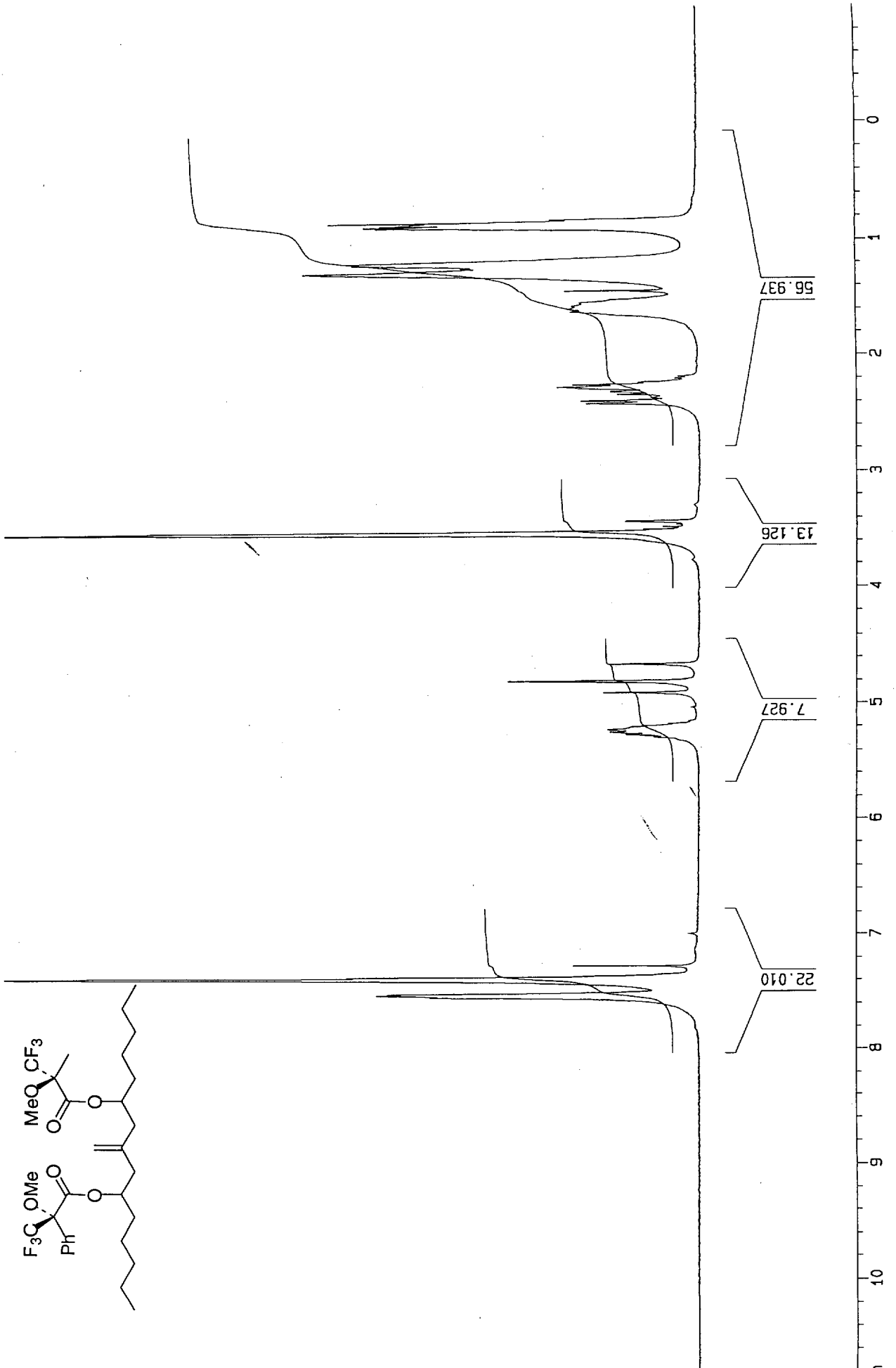
pdk II-155-1



Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (6*S*,10*S*)-1e.

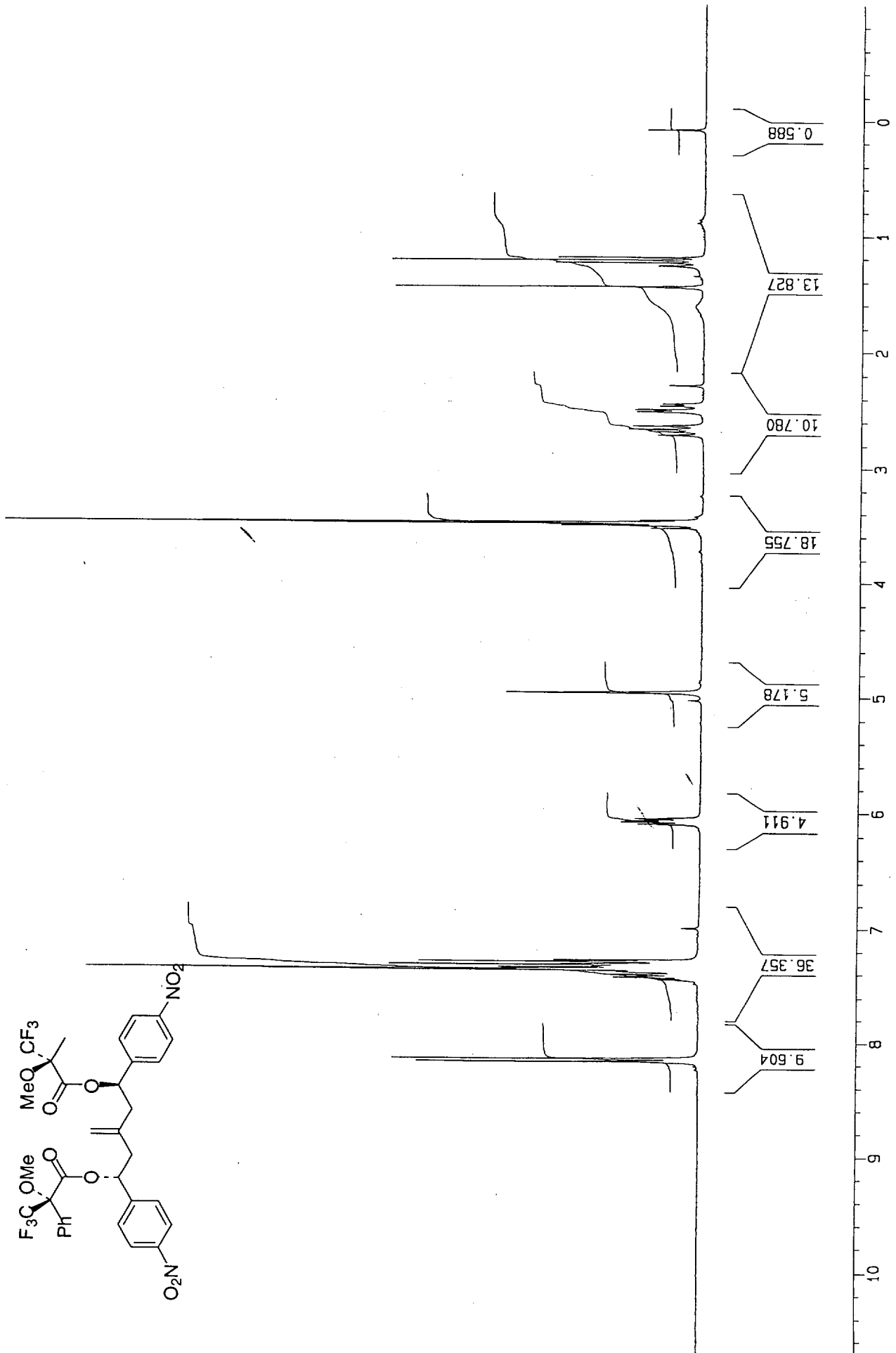


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1e and meso-1e.

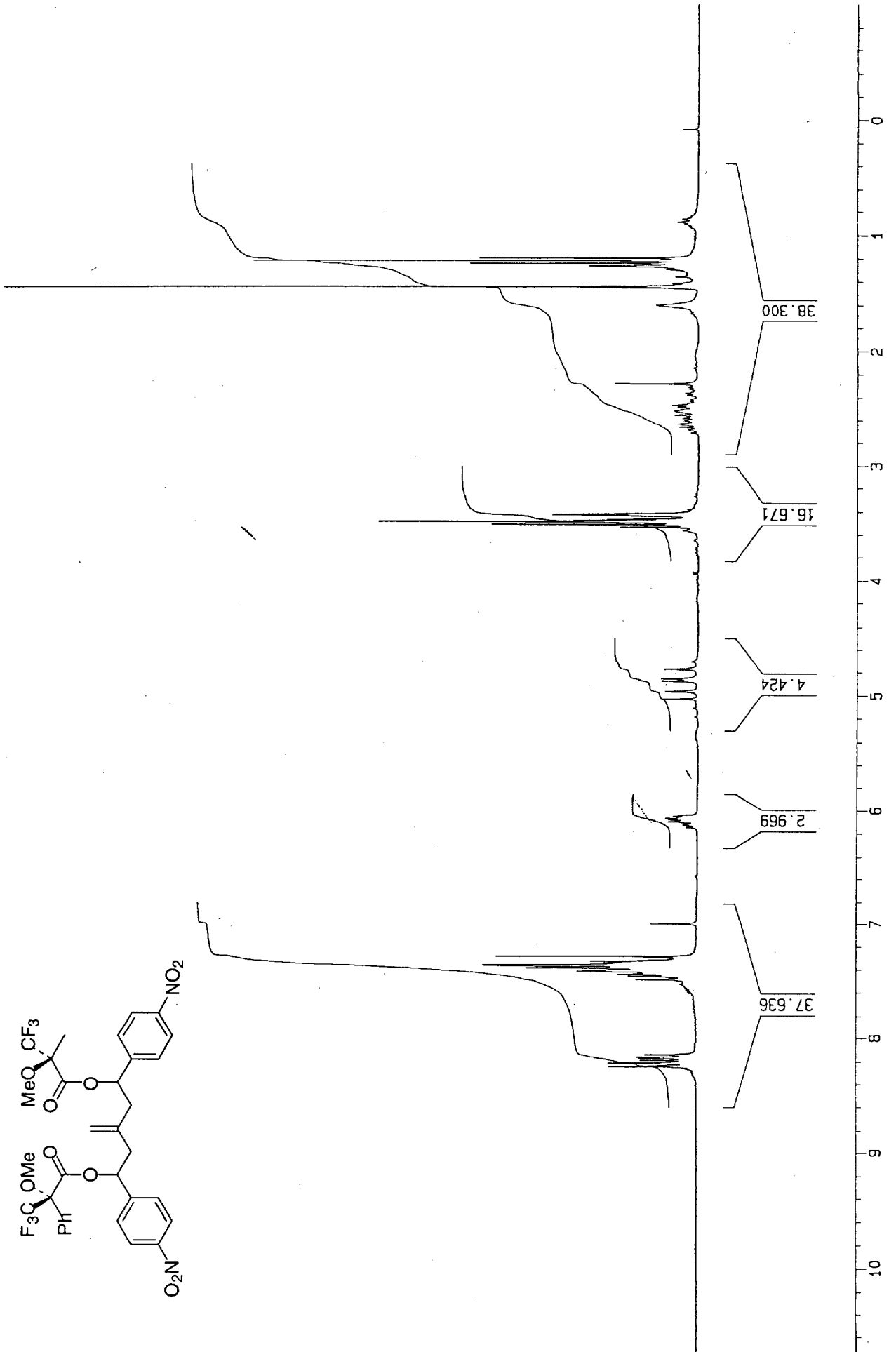


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (1*R*,5*R*)-1f.

pdk II-133-1

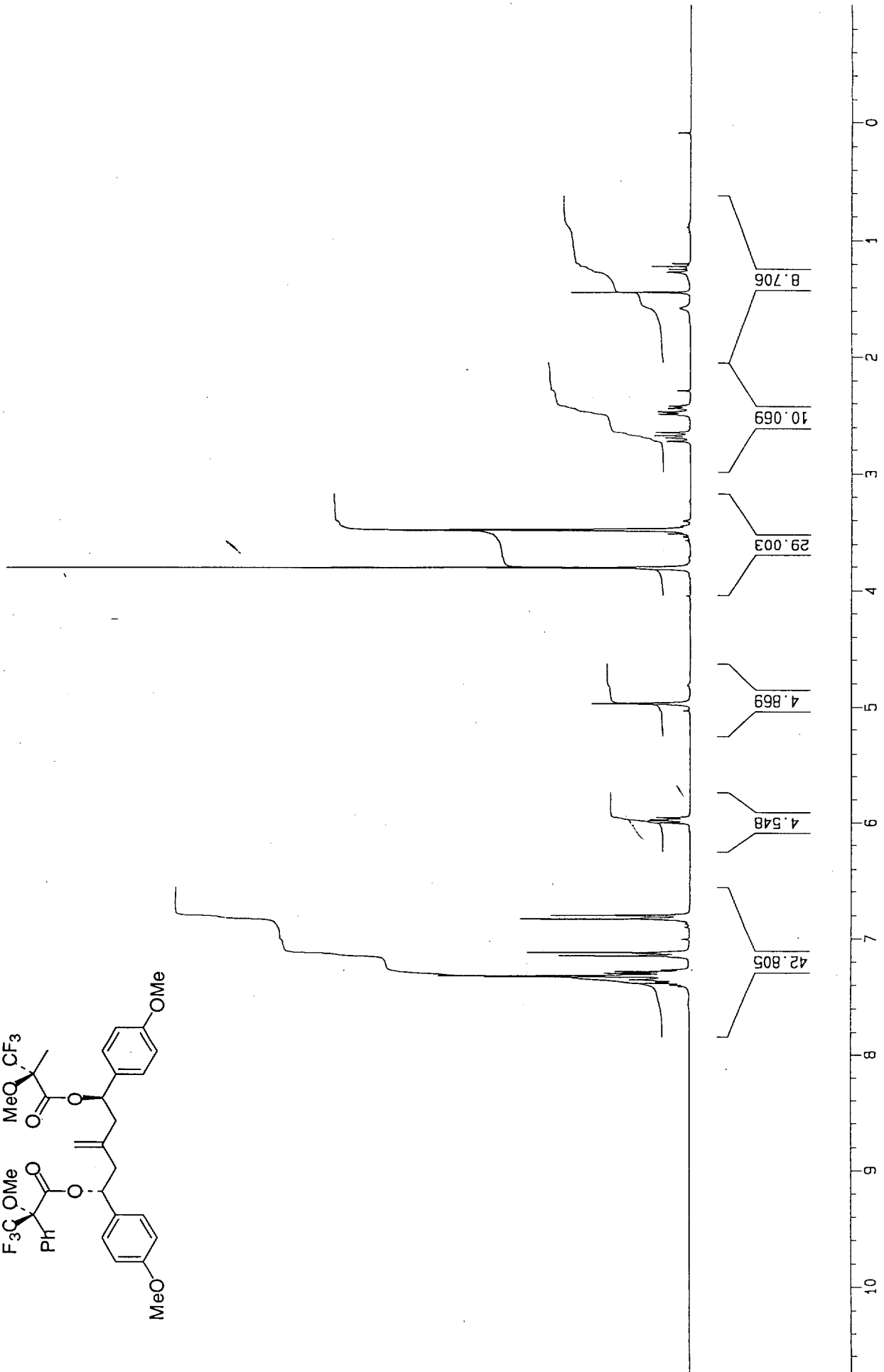


Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1f and meso-1f.



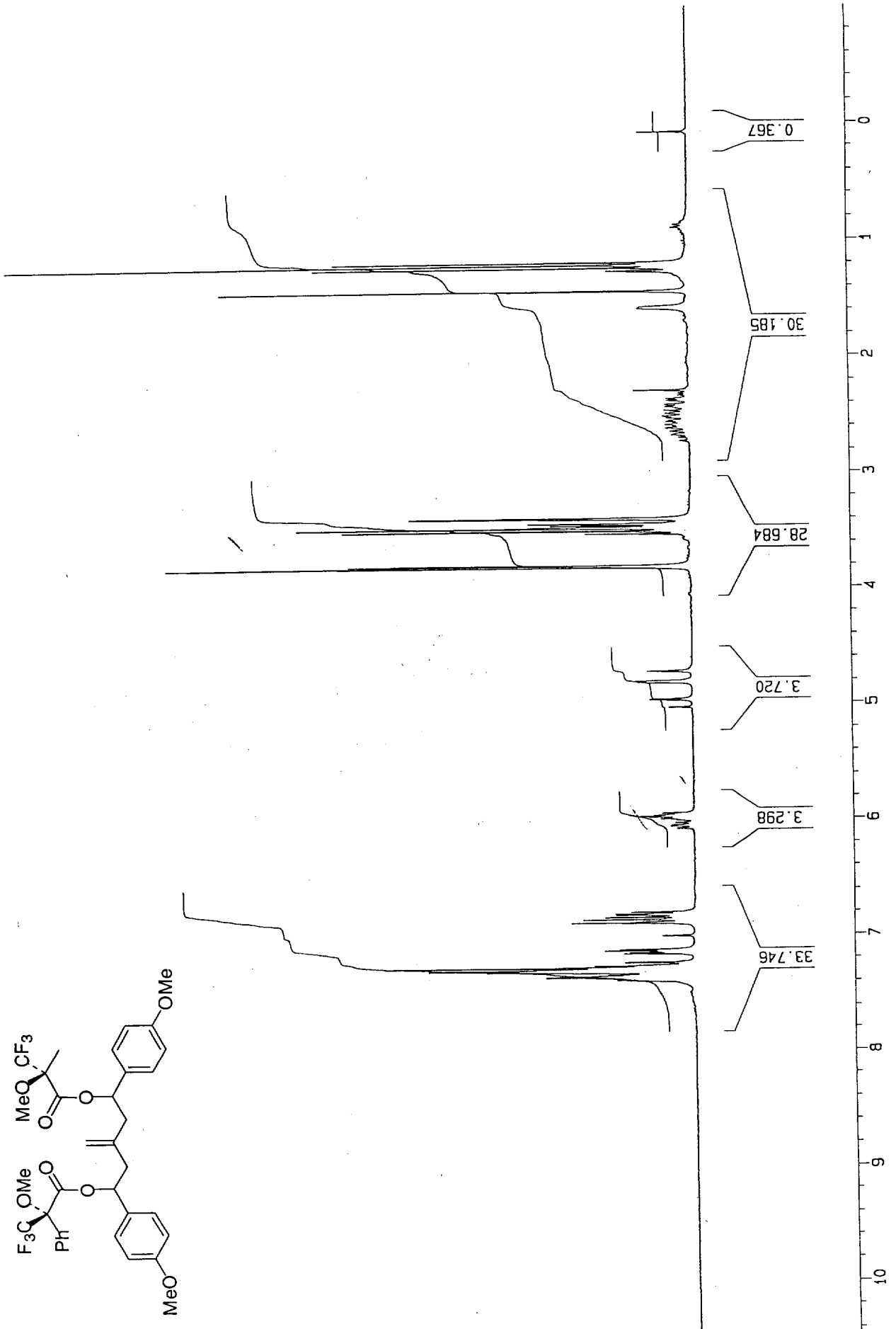
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (1*R*,5*R*)-1g.

pdk II-127-1



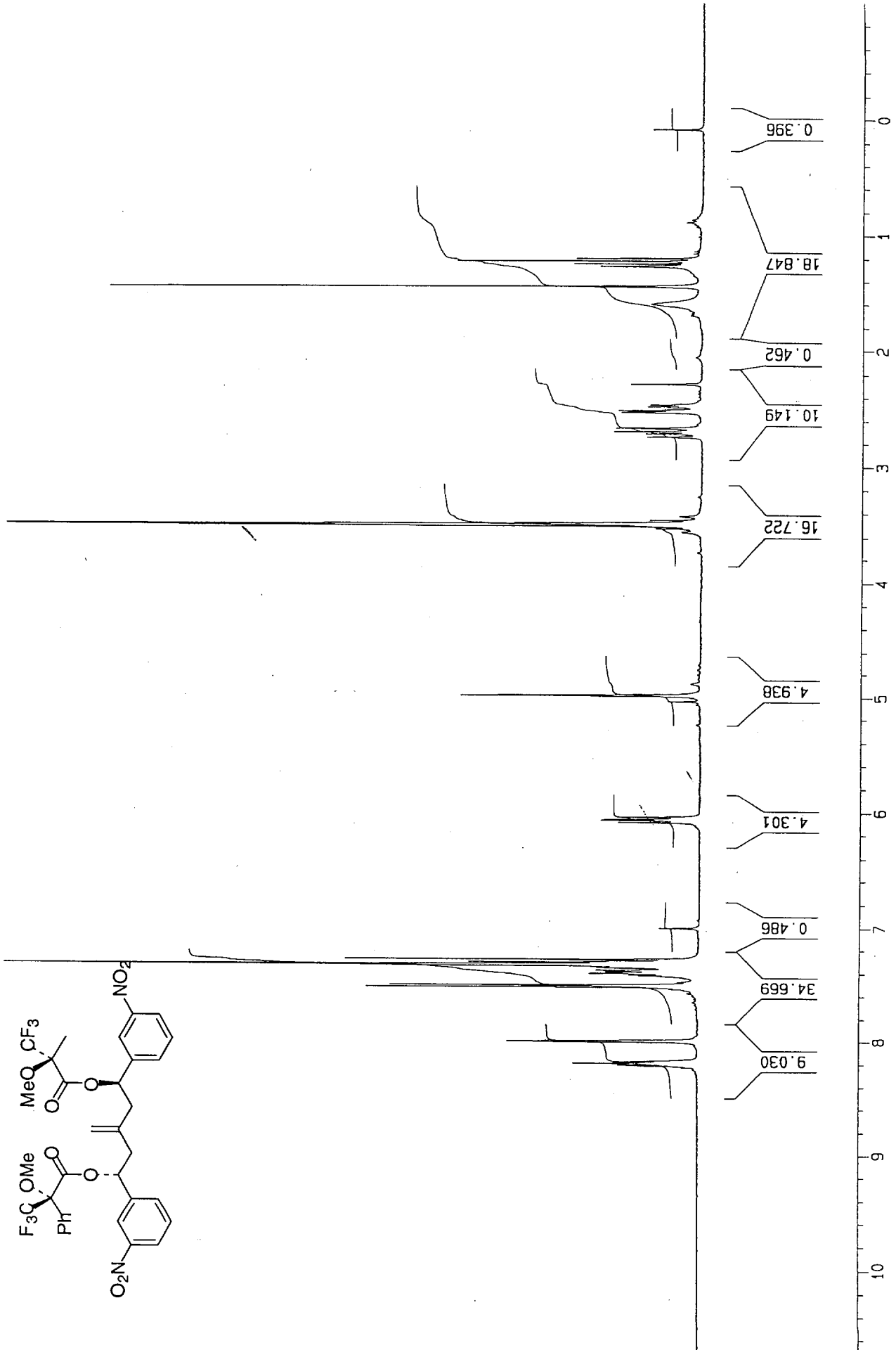
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and rac-1g and meso-1g.

pdk II-157-1



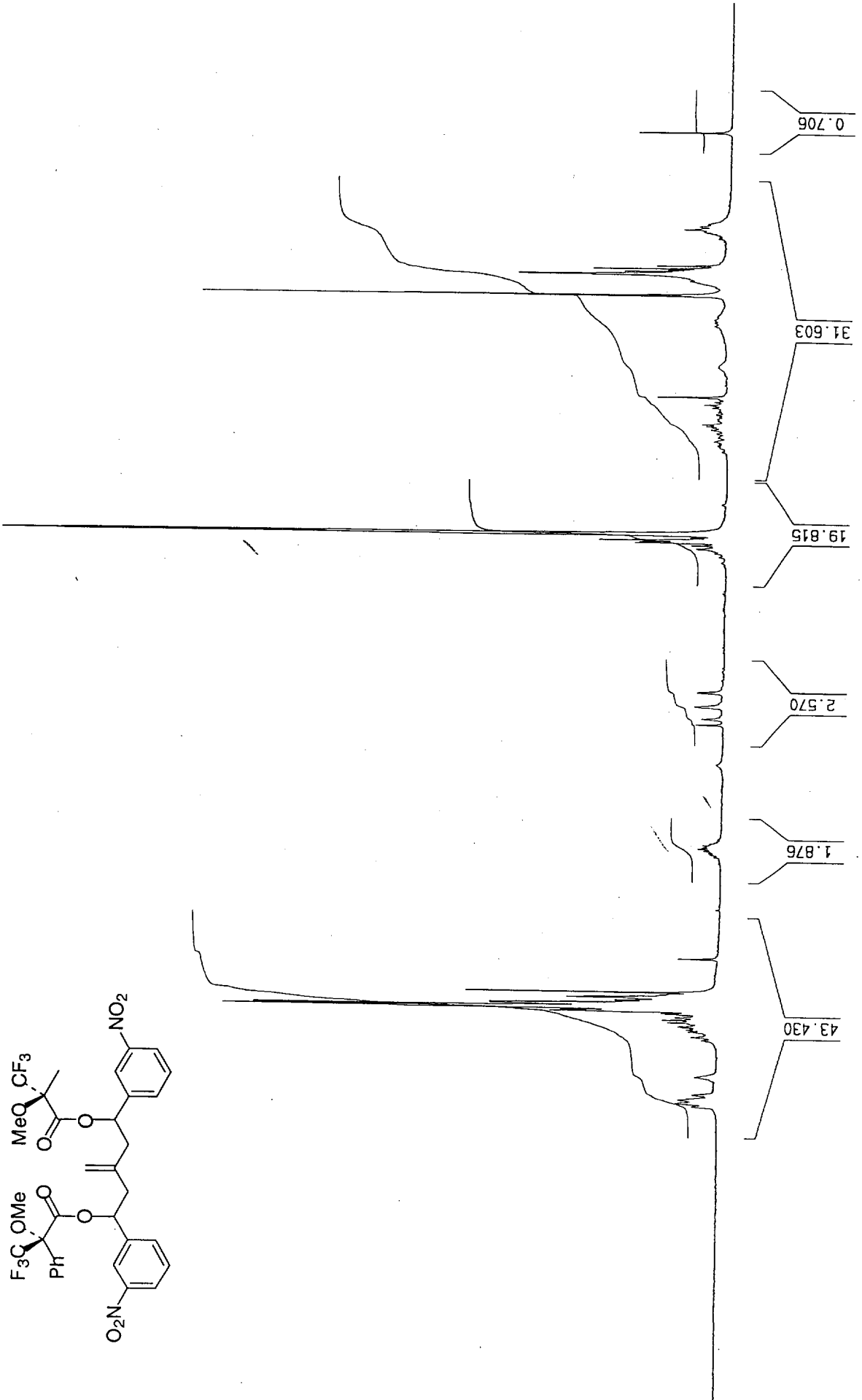
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and (1*R*,5*R*)-1h.

pdk II-139-1



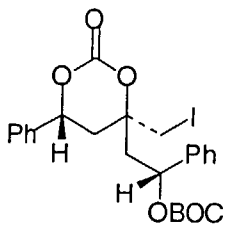
Bis (+)-Mosher ester derived from (*R*)-(-)-Mosher chloride and and rac-1g and meso-1g.

pdk II-163-1

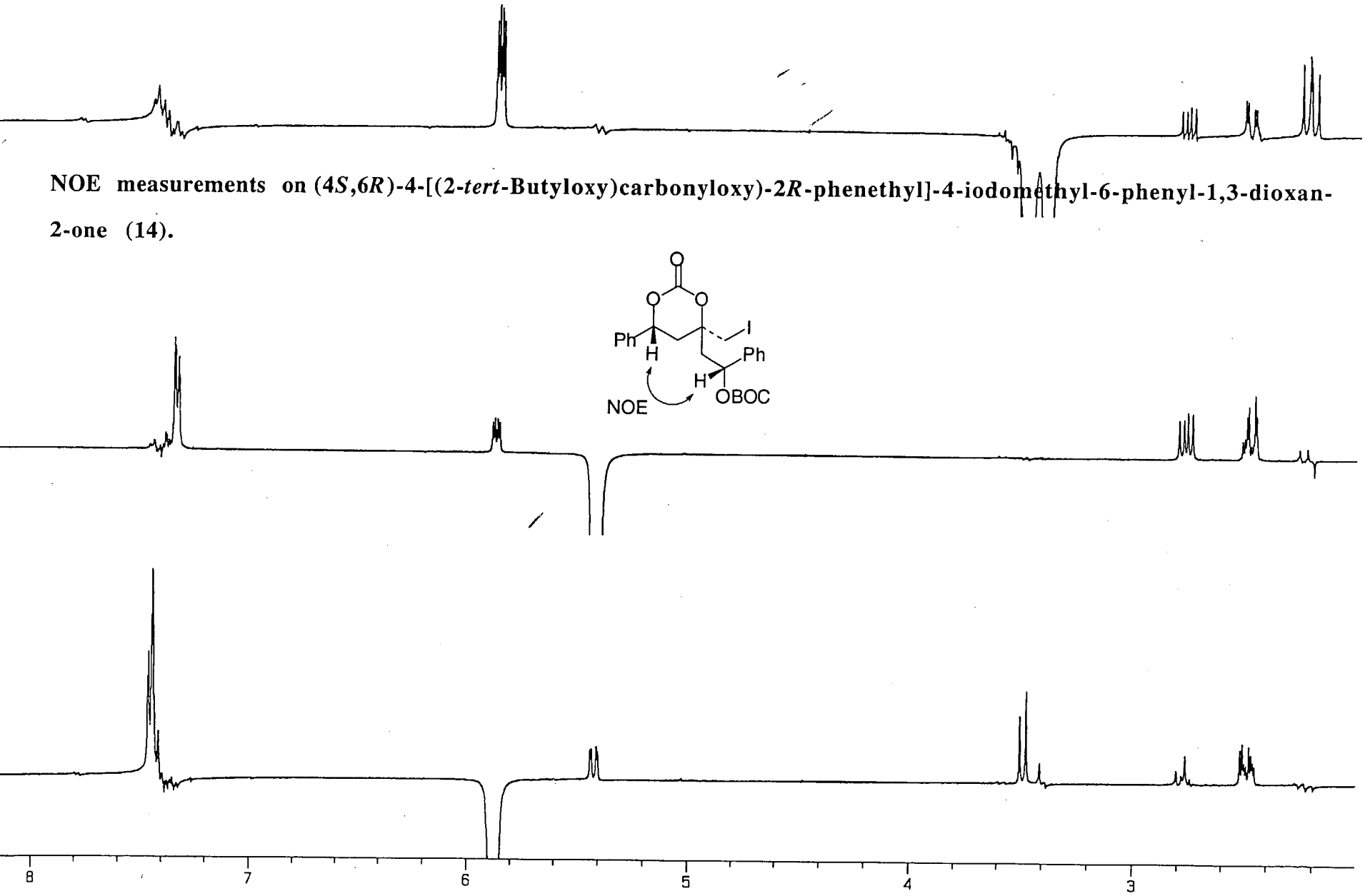


pdk IV-1-1

(4*S*,6*R*)-4-[(2-*tert*-Butyloxy)carbonyloxy)-2*R*-phenethyl]-4-iodomethyl-6-phenyl-1,3-dioxan-2-one (14).



PIETER DE KONING III-157-1: NOE difference plots, scale factor 10.



NOE measurements on (4*S*,6*R*)-4-[(2-*tert*-Butyloxy)carbonyloxy)-2*R*-phenethyl]-4-iodomethyl-6-phenyl-1,3-dioxan-2-one (14).