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Supporting Information

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Asymmetric Counteranion Directed Catalysis for the Organocatalytic Epoxidation of Enals: A New Mode of Enamine Catalysis

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General Information: Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.25 mm thickness, 60F-254, E. Merck). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using 2, 4-dinitrophenylhydrazine (2,4-DNP, for epoxides **2a, 2e-m**) or *p*-anisaldehyde (for epoxides **2n-r**) stains. Flash column chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm) from Merck.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise noted) on Bruker DPX-300 and AV-400 spectrometers. Chemical shifts (δ ppm) are relative to tetramethylsilane (TMS) with the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR and $CDCl_3$, δ 77.0 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (*J*) and assignment. The IR spectra of samples were collected on a Magna-IR 750 Nicolet FTIR spectrometer using an ATR cell.

Mass spectra were measured on a Finnigan MAT 8200 (70 eV) and an Agilent 5973 (70 eV) by electron ionization, chemical ionization, of fast atom/ion bombardment techniques. Accurate mass determinations were obtained on a Bruker APEX III FT-MS (7 T magnet). Gas chromatography (GC) was performed on Hewlett-Packard 6890 and 5890 Series gas chromatographs equipped with a split-mode capillary injection system and flame ionization detectors using chiral stationary columns[1] specified in the individual experiments.

Optical rotations were measured on a PerkinElmer 343 polarimeter, and $[\alpha]_D$ values are reported in 10^{-1} dg cm^2 g^{-1}; concentration (c) is in g/100 ml.

Racemic epoxides described in this paper were prepared by epoxidation of the corresponding α,β-unsaturated aldehydes with H_2O_2 according to the reported procedure[2] or through direct catalysis by the dibenzylammonium salts of diphenyl phosphate. The enantiomeric ratios (*er*) of epoxides **2a-r** were determined by GC analysis specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures. The absolute configurations of **2a** and **2o** were determined by measuring its optical rotation and comparison with the literature.[8, 9] All other absolute configurations were assigned by analogy.

Preparation of Catalysts

All the chiral binaphthol derived phosphoric acids **a-m** (table **5**) were prepared according or in analogy to the procedures reported by Terada, Akiyama and our group.[3, 4, 5] Morpholine, pyrrolidine, benzyl-methyl-amine, dibenzyl-amine were

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[1] Hydrodex-β-TBDAC (25 m x 0.25 mm) stationary phase: heptakis (2, 3-di-*o*-acetyl-6-t-butyldimethylsilyl)-β- cyclodextrin; Ivadex-1 (25 m x 0.25 mm) stationary phase: dimethylpentyl-β-cyclodextrin; Ivadex-7 (25 m x 0.25 mm) stationary phase: diethyl-tert-butyl-dimethyl-β-cyclodextrin; G-TA (30 m x 0.25 mm) stationary phase: gamma-cyclodextrin trifluoracetyl; BGB 176 (29.5 m x 0.25 mm) stationary phase: 6-tert-butyl-dimethylsilyl-β-cyclodextrin.

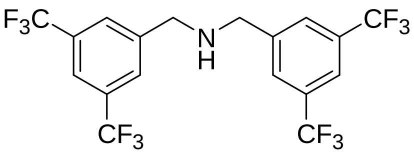
[2] a) G. B. Payne, *J. Org. Chem.* **1960**, *25*, 275-276; b) I. F. Revinskii, I. G. Tishchenko, V. N. burd', O. N. Bubel, *J. Org. Chem. USSR (Engl. transl.) EN*, **1985**, *21*, 637-641; c) Y. Hu, A. Harada, S. Takahashi, Synthetic Communications **1988**, *18*, 1607-1610.

[3] a) T. Akiyama, J. Itoh, K. Yokota, K, Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566-1568; b) T. Akiyama, H. Morita, J. Itoh, K. Fuchibe, *Org. Lett.* **2005**, *7*, 2583-2585; c) T. Akiyama, Y. Saitoh, H. Morita, K. Fuchibe, *Adv. Synth. Cat.* **2005**, *347*, 1523-1526.

[4] a) D. Uraguchi, M. Terada, *J. Am. Chem. Soc.* **2004**, *126*, 5356-5357; b) D. Uraguchi, K. Sorimachi, M. Terada, *J. Am.Chem. Soc.* **2004**, *126*, 11804-11805; c) D. Uraguchi, K. Sorimachi, M. Terada, *J. Am. Chem. Soc.* **2005**, *127*, 9360-9361; also see: d) M.

purchased from Aldrich. All the dibenzyl amine derivatives were prepared according to the following procedures **A** and **B**.

Bis-(3,5-bis-trifluoromethyl-benzyl)-amine



Procedure **A**[6]: Under Ar, a solution of 3,5-bis(trifluoromethyl)benzylamine (1.21 g, 5.0 mmol) and 3,5-bis(trifluoromethyl)benzaldehyde (1.22 g, 5.0 mmol) in dry toluene (75 mL) was heated under reflux with stirring for 15 hours. The water generated during the reaction was collected in a Dean-stark trap. After the solvent was removed under vacuum, the schiff's base was dissolved in anhydrous MeOH (50 mL) and stirred vigorously under Ar while $NaBH_4$ (0.4 g, 10.5 mmol) was added carefully in portions. The resulting solution was stirred at ambient temperature for 3 hours. Aqueous HCl (2.0 M) was added until the suspension became slightly acidic, and then methanol was evaporated in vacuum. CH_2Cl_2 (50 mL) was added to the mixture, and the aqueous layer was separated and extracted again with CH_2Cl_2 (30 mL). The combined organic extracts were washed with aqueous NaOH (1 M, 50 mL), dried over anhydrous Na_2SO_4, filtered, and the solvents were evaporated off to afford the crude product, which was subjected to silica gel column chromatography (5% EtOAc in hexane) to give pure product as the white solid (93% yield).

Procedure **B**[7]: A solution of 3,5-bis(trifluoromethyl)benzylamine (2.42 g, 10.0 mmol) and 3,5-bis(trifluoromethyl)benzaldehyde (2.48 g, 10.2 mmol) in anhydrous acetonitrile (100 mL) was stirred under Ar for 1.5 hours at room temperature. $NaBH_3CN$ (1.88 g, 30 mmol, 3 equiv.) was then added, followed 20 minutes later by acetic acid (3.0 g, 2.86 mL, 50 mmol, 5 equiv.). After stirring 18 hours at room

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Terada, D. Uraguchi, K. Sorimachi, H. Shimizu, PCT Int. Appl. WO2005070875, **2005**.

[5] J. Seayad, A. M. Seayad, B. List, *J. Am. Chem. Soc.* **2006**, *128*, 1086-1087.

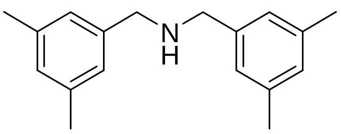
[6] a) M. Horn, J. Ihringer, P. T. Glink, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 4046-4054; b) A. R. Williams, B. H. Northrop, K. N. Houk, J. F. Stoddart, D. J. Williams, *Chem. Eur. J.* **2004**, *10*, 5406-5421.

[7] a) J. M. Mitchell, N. S. Finney, *Tetrahedron Lett.* **2000**, *41*, 8431-8434; b) A. Berkessel, S. Mukherjee, T. N. Müller, F. Cleemann, K. Roland, M. Branderburg, J. M. Neudörfl, J. Lex, *Org. Biomol. Chem.* **2006**, *4*, 4319-4330.

temperature, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with aqueous NaOH (1.0 M, 2×50 mL). The aqueous layer was re-extracted with CH_2Cl_2 (3×50 mL), then the combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuum to obtain the solid residue, which was purified by silica gel column chromatography (3% EtOAc in hexane) to provide pure product (72% yield).

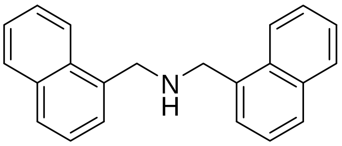
Mp: 37.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 4H), 7.77 (s, 2H), 3.96 (s, 4H), 1.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 132.3, 132.0, 131.7, 131.3, 128.1, 127.4, 124.7, 122.0, 121.3, 119.3, 52.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ 63.2; FTIR: ν = 3320, 2965, 2837, 1618, 1444, 1442, 1383, 1280, 1160,1115, 894, 841, 702, 685 cm^{-1}; MS (EI) (*m*/*z*): 469.15; HRMS (ESI) calcd for $C_{18}H_{12}NF_{12}$ [M^++H]: 470.077010, found 470.077269.

Bis-(3,5-dimethyl-benzyl)-amine



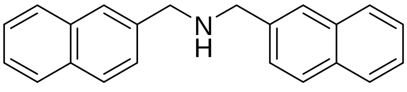
The title compound was isolated with 65% yield as pale yellow solid after silica gel column chromatography (2% EtOAc in hexane) according to procedure **A**. Mp: 26.5°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 4H), 6.80 (s, 2H), 3.65 (s, 4H), 2.22 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 138.2, 128.9, 126.4, 53.7, 21.6; FTIR: ν = 3302, 3016, 2917, 2864, 2724, 1608, 1462, 1376, 1157, 1120, 1037, 845, 765, 695 cm^{-1}; MS (EI) (*m*/*z*): 253.39; HRMS (ESI) calcd for $C_{18}H_{23}NNa$ [M^++Na]: 276.172484, found 276.172270.

Bis-naphthalen-1-ylmethyl-amine



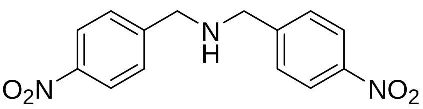
The title compound was isolated with 84% yield as white solid after silica gel column chromatography (25% EtOAc in hexane) according to procedure **A**. Mp: 62.5°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 - 8.01 (m, 2H), 7.67 - 7.79 (m, 4H), 7.31 - 7.44 (m, 8H), 4.26 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 134.3, 132.3, 129.0, 128.2, 126.6, 126.4, 126.0, 125.7, 124.2, 51.8; FTIR: ν = 3322, 2791, 1595, 1509, 1366, 1163, 1107, 967, 795, 765, 678, 649 cm^{-1}; MS (EI) (*m*/*z*): 297.40; HRMS (ESI) calcd for $C_{22}H_{19}NNa$ [M$^+$+Na]: 320.140928, found 320.140966.

Bis-naphthalen-2-ylmethyl-amine



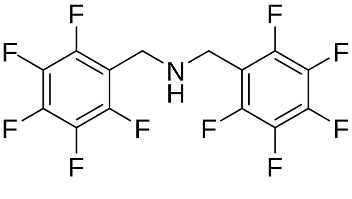
The title compound was isolated with 90% yield as white solid after silica gel column chromatography (25% EtOAc in hexane) according to procedure **A**. Mp: 84.0°C. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ = 7.86 - 7.92 (m, 8H), 7.56 - 7.60 (m, 2H), 7.45 - 7.54 (m, 4H), 3.91 (s, 4H), 2.87 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 138.8, 133.3, 132.5, 127.9, 127.8, 127.7, 127.1, 126.3, 126.2, 125.7, 52.6; FTIR: ν = 3310, 3050, 2771, 1602, 1509, 1432, 1359, 1309, 1177, 1100, 957, 901, 861, 815, 745 cm^{-1}; MS (EI) (*m*/*z*): 297.40; HRMS (ESI) calcd for $C_{22}H_{19}NNa$ [M$^+$+Na]: 320.140928, found 320.140966.

Bis-(4-nitro-benzyl)-amine



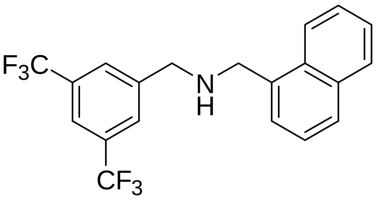
The title compound was isolated with 69% yield as white solid after silica gel column chromatography (30% EtOAc in hexane) according to procedure **B**. Mp: 90.0°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.09 - 8.14 (m, 4H), 7.44 - 7.48 (m, 4H), 3.86 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 147.8, 147.6, 129.0, 124.1, 52.8; FTIR: ν = 3360, 3113, 3030, 2847, 1592, 1509, 1339, 1104, 851, 742, 730, 682 cm^{-1}; MS (EI) (*m*/*z*): 287.27; HRMS (ESI) calcd for $C_{14}H_{13}N_3O_4Na$ [M$^+$+Na]: 310.080049, found 310.079828.

Bis-pentafluorophenylmethyl-amine



The title compound was isolated with 76% yield as colorless oil after silica gel column chromatography (3.3% EtOAc in hexane) according to procedure **B**. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.96 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 146.9, 146.8, 146.7, 146.7, 146.6, 144.4, 144.3 (2), 144.2 (2), 142.4, 139.6, 139.1, 139.0, 138.9, 138.8, 138.7, 136.6, 136.5, 136.4, 136.3, 113.1, 112.9, 112.7, 40.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.6 (t), -155.3 (t), -162.1 (t); FTIR: ν = 3365, 3020, 2862, 1655, 1519, 1497, 1429, 1371, 1339, 1302, 1213, 1127, 1089, 1023, 971, 941, 930, 900, 778, 851, 713 cm^{-1}; MS (EI) (*m*/*z*): 377.08; HRMS (ESI) calcd for $C_{14}H_6NF_{10}$ [M^++H]: 378.033416, found 378.033508.

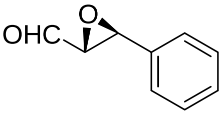
(3,5-Bis-trifluoromethyl-benzyl)-naphthalen-1-ylmethyl-amine



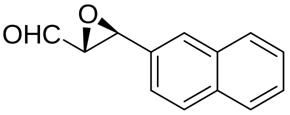
The title compound was isolated with 82% yield as white solid after silica gel column chromatography (33% EtOAc in hexane) according to procedure **A**. Mp: 50.5°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 - 8.02 (m, 1H), 7.68 - 7.80 (m, 5H), 7.33 - 7.45 (m, 4H), 4.17 (s, 2H), 3.92 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 135.4, 134.3, 132.5, 132.1, 131.7, 131.2, 129.1, 128.6, 126.8, 126.6, 126.2, 125.7, 125.6, 123.9, 122.0, 121.5, 121.4, 121.3, 121.2, 52.9, 51.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ 63.0, 63.1; FTIR: ν = 3292, 3050, 2824, 1625, 1595, 1512, 1456, 1379, 1283, 1163, 1123, 961, 918, 884, 849, 818, 788, 768, 702, 678 cm^{-1}; MS (EI) (*m*/*z*): 383.28; HRMS (ESI) calcd for $C_{20}H_{16}NF_6$ [M^++H]: 384.117741, found 384.118145.

General experimental procedure for the Organocatalytic Enantioselective Epoxidation of Enals

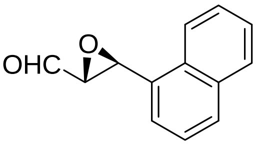
ACDC salt **3m** was prepared in situ by stirring (R)-TRIP (37.6 mg, 0.05 mmol, 10 mol%) and bis-(3,5-bis-trifluoromethyl-benzyl)-amine (23.4 mg, 0.05 mmol, 10 mol%) in dioxane (2 mL) or TBME (2 mL) for 20 minutes. Then, α,β-unsaturated aldehydes (**1a-r**, 0.5 mmol) and tert-butyl hydroperoxide (1.1 equiv. 0.55 mmol, 5.5 M, in decane) were added at room temperature. After stirring for 24 - 72 h at 0-35°C, the reaction mixture was cooled to room temperature, and a 10% aqueous solution of $NaHSO_3$ (5 mL) was added. Then the reaction mixture was diluted with diethyl ether (10 mL), and the aqueous phase was extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtration and evaporation of the solvents furnished the oils or solids. The residue was purified by flash chromatography (SiO_2, diethyl ether in pentane or EtOAc in hexane) to provide α,β-epoxy aldehydes (**2a-r**).



3-Phenyl-oxirane-2-carbaldehyde (**2a**) Compound **2a** was isolated with 75% yield after silica gel column chromatography (25% diethyl ether in pentane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.18 (d, *J* = 6.0 Hz, 1H), 7.24 - 7.35 (m, 5H), 4.15 (d, *J* = 1.8 Hz, 1H), 3.43 (dd, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 133.4, 129.2, 128.6, 125.7, 62.8, 56.6. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 220 °C, 5 min at 220 °C, 0.5 bar H_2). Major enantiomer: t_R = 26.01 min, minor enantiomer: t_R = 25.57 min. The absolute configuration [*2R, 3S*] of **2a** was determined by measuring its optical rotation and comparison with literature values, $[\alpha]^{20}_D$ = +12.8 (c 0.5, $CHCl_3$), 91.0%ee, [Lit. $[\alpha]_D^{23}$ = +14.3 (c 0.48, $CHCl_3$), 94%ee].[8]



3-(2-Naphthyl)-oxirane-2-carbaldehyde (**2b**) Compound **2b** was isolated with 76% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.16 (d, *J* = 6.0 Hz, 1H), 7.17 - 7.78 (m, 4H), 7.39 - 7.44 (m, 3H), 4.23 (d, *J* = 1.8 Hz, 1H), 3.46 (dd, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 134.9, 133.4, 131.9, 129.9, 128.9, 128.2, 127.4, 127.1, 123.1, 122.6, 63.3, 57.3. The enantiomers were analyzed by GC using a chiral BGB 176 column (80 °C, 1.2 °C/min, until 220 °C, 10 min at 220 °C, 0.6 bar H_2). Major enantiomer: t_R = 76.50 min, minor enantiomer: t_R = 77.15 min.



3-(1-Naphthyl)-oxirane-2-carbaldehyde (**2c**) Compound **2c**

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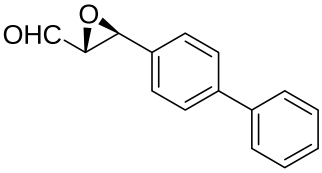
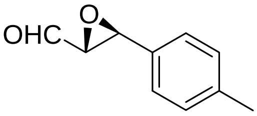
[8] a) T. Nemoto, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2001**, *123,* 9474-9475; b) M. Marigo, J. Franzén, T. B. Poulsen, W. Zhuang, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127,* 6964-6965.

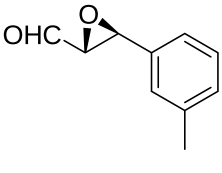
was isolated with 70% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.37 (d, *J* = 6.0 Hz, 1H), 7.84 - 7.89 (m, 3H), 7.41 - 7.57 (m, 4H), 4.80 (d, *J* = 1.8 Hz, 1H), 3.47 (dd, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 133.3, 131.0, 130.1, 129.2, 128.9, 128.6, 126.9, 125.4, 122.8, 122.3, 61.9, 55.1. The enantiomers were analyzed by GC using a chiral Ivadex-7 column (100 °C, 0.8 °C/min, until 160 °C, 18 °C/min, until 220 °C, 5 min at 220 °C, 0.5 bar H_2). Major enantiomer: t_R = 65.48 min, minor enantiomer: t_R = 67.01 min.



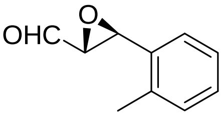
3-(4-Biphthyl)-oxirane-2-carbaldehyde (**2d**) Compound **2d** was isolated with 78% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.13 (d, *J* = 6.0 Hz, 1H), 7.48 - 7.53 (m, 4H), 7.34 - 7.36 (m, 2H), 7.26 - 7.30 (m, 3H), 4.12 (d, *J* = 1.8 Hz, 1H), 3.40 (dd, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 142.6, 140.6, 133.5, 129.2, 128.0, 127.9, 127.4, 126.6, 63.3, 56.9. The enantiomers were analyzed by GC using a chiral Ivadex-7 column (160 °C, 60 min, 5.0 °C/min, until 210 °C, 10 min at 220 °C, 0.6 bar H_2). Major enantiomer: t_R = 44.17 min, minor enantiomer: t_R = 45.23 min.



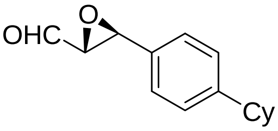
3-(4-tolyl)-oxirane-2-carbaldehyde (**2e**) Compound **2e** was isolated with 65% yield after silica gel column chromatography (5% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.18 (d, *J* = 6.0 Hz, 1H), 7.13 - 7.23 (m, 4H), 4.13 (d, *J* = 1.8 Hz, 1H), 3.42 (dd, *J* = 6.0 Hz, 1H), 2.36(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 129.5, 129.3, 125.8, 125.7, 62.9, 56.6, 21.2. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 8.0 °C/min, until 240 °C, 10 min at 240 °C, 0.5 bar H_2). Major enantiomer: t_R = 43.00 min, minor enantiomer: t_R = 42.42 min.



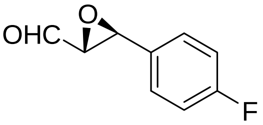
3-(3-tolyl)-oxirane-2-carbaldehyde (**2f**) Compound **2f** was isolated with 68% yield after silica gel column chromatography (5% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.10 (d, *J* = 6.0 Hz, 1H), 7.17 - 7.21 (m, 1H), 7.00 - 7.10 (m, 3H), 4.05 (d, *J* = 1.8 Hz, 1H), 3.35 (dd, *J* = 6.0 Hz, 1H) , 2.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 197.3, 139.0, 134.5, 129.7, 128.9, 126.6, 123.2, 63.2, 57.0, 21.7. The enantiomers were analyzed by GC using a chiral Ivadex-1 column (80 °C, 1.2 °C/min, until 135 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.5 bar H$_2$). Major enantiomer: t$_R$ = 41.72 min, minor enantiomer: t$_R$ = 42.68 min.



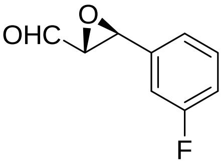
3-(2-tolyl)-oxirane-2-carbaldehyde (**2g**) Compound **2g** was isolated with 62% yield after silica gel column chromatography (3% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.15 (d, *J* = 6.0 Hz, 1H), 7.08 - 7.19 (m, 4H), 4.22 (d, *J* = 1.8 Hz, 1H), 3.24 (dd, *J* = 6.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 197.5, 136.6, 132.9, 130.5, 128.9, 126.7, 124.6, 62.3, 55.2, 19.0. The enantiomers were analyzed by GC using a chiral Ivadex-1 column (80 °C, 1.2 °C/min, until 160 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.5 bar H$_2$). Major enantiomer: t$_R$ = 38.30 min, minor enantiomer: t$_R$ = 38.03 min.



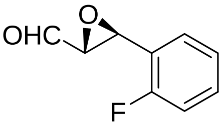
3-(4-Cyclohexyl-phenyl)-oxirane-2-carbaldehyde (**2h**) Compound **2h** was isolated with 60% yield after silica gel column chromatography (5% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.20 (d, *J* = 6.0 Hz, 1H), 7.17 - 7.28 (m, 4H), 4.16 (d, *J* = 1.8 Hz, 1H), 3.47 (dd, *J* = 6.0 Hz, 1H), 2.48 - 2.55 (m, 1H), 1.79 - 1.86 (m, 4H) , 1.30 - 1.45 (m, 6H); MS (EI) (*m*/*z*): 230, 202, 187, 173, 161, 147, 131, 115, 91. The enantiomers were analyzed by GC using a chiral Ivadex-7 column (150 °C, 60 °C/min, until 210 °C, 5.0 °C/min, until 220 °C, 10 min at 220 °C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 48.97 min, minor enantiomer: t$_R$ = 50.15 min.



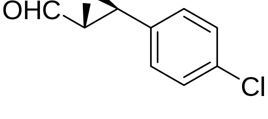
3-(4-Fluoro-phenyl)-oxirane-2-carbaldehyde (**2i**) Compound **2i** was isolated with 78% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.20 (d, *J* = 6.0 Hz, 1H), 7.24 - 7.31 (m, 2H), 7.03 - 7.11 (m, 2H), 4.17 (d, *J* = 1.8 Hz, 1H), 3.28 (dd, *J* = 6.0 Hz, 1H). The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 160 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.5 bar H$_2$). Major enantiomer: t$_R$ = 48.61 min, minor enantiomer: t$_R$ = 47.37 min.



3-(3-Fluoro-phenyl)-oxirane-2-carbaldehyde (**2j**) Compound **2j** was isolated with 82% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.10 (d, *J* = 6.0 Hz, 1H), 7.18 - 7.26 (m, 1H), 6.88 - 7.03 (m, 3H), 4.09 (d, *J* = 1.8 Hz, 1H), 3.33 (dd, *J* = 6.0 Hz, 1H). The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 180 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 43.33 min, minor enantiomer: t$_R$ = 42.39 min.

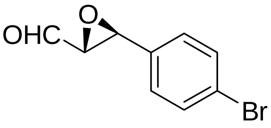


3-(2-Fluoro-phenyl)-oxirane-2-carbaldehyde (**2k**) Compound **2k** was isolated with 69% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 9.21 (d, *J* = 6.0 Hz, 1H), 7.26 - 7.28 (m, 1H), 7.14 - 7.19 (m, 2H), 7.04 - 7.13 (m, 1H), 4.12 (d, *J* = 1.8 Hz, 1H), 3.45 (dd, *J* = 6.0 Hz, 1H). The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 160 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.5 bar H$_2$). Major enantiomer: t$_R$ = 30.63 min, minor enantiomer: t$_R$ = 29.56 min.

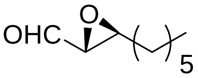


3-(4-Chloro-phenyl)-oxirane-2-carbaldehyde (**2l**) Compound **2l** was isolated with 84% yield after silica gel column chromatography (5% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.19 (d, *J* = 6.0 Hz, 1H), 7.30 - 7.38 (m, 2H), 7.19 - 7.26 (m, 2H), 4.15 (d,

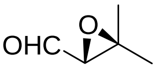
J = 1.8 Hz, 1H), 3.40 (dd, J = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 196.4, 135.1, 132.7, 128.7, 127.1, 62.8, 56.0. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 180 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 59.37 min, minor enantiomer: t$_R$ = 58.32 min.



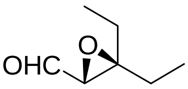
3-(4-Bromo-phenyl)-oxirane-2-carbaldehyde (2m) Compound **2m** was isolated with 80% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.11 (d, J = 6.0 Hz, 1H), 7.38 - 7.45 (m, 2H), 7.06 - 7.11 (m, 2H), 4.06 (d, J = 1.7 Hz, 1H), 3.33 (dd, J = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 196.7, 133.6, 132.2, 128.2, 127.7, 63.1, 56.7. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (80 °C, 1.5 °C/min, until 170 °C, 20 °C/min, until 220 °C, 10 min at 220 °C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 65.97 min, minor enantiomer: t$_R$ = 65.26 min.



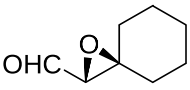
3-Hexyl-oxirane-2-carbaldehyde (2n) Compound **2n** was isolated with 67% yield after silica gel column chromatography (10% EtOAc in hexane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.94 (d, J = 6.2 Hz, 1H), 3.13 - 3.18 (m, 1H), 3.06 (dd, J = 6.2 Hz, 1H), 1.19 - 1.59 (m, 10H), 0.83 (t, J = 5.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.8, 59.5, 57.1, 32.0, 31.5, 29.3, 26.7, 22.9, 14.4; MS (EI) (m/z): 156, 138, 127, 109, 97, 97, 94, 85, 81. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (60 °C, 2.0 °C/min, until 220 °C, 3 min at 220 °C, 0.6 bar H$_2$). Major diastereoisomer: t$_R$ = 25.11 min (major enantiomer), t$_R$ = 24.65 min (minor enantiomer); minor diastereoisomer: t$_R$ = 24.95 min (major enantiomer), t$_R$ = 25.92 min (minor enantiomer).



3,3-Dimethyl-oxirane-2-carbaldehyde[9] (**2o**) Compound **2o** was isolated with 83% yield after silica gel column chromatography (3.3% diethyl ether in pentane). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.38 (d, *J* = 5.0 Hz, 1H), 3.11 (d, *J* = 5.0 Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H); MS (EI)) (*m*/*z*): 100, 94, 85, 81. The enantiomers were analyzed by GC using a chiral G-TA column (50 °C, 1.0 °C/min, until 75 °C, 18 °C/min, until 180 °C, 15 min at 220°C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 8.68 min, minor enantiomer: t$_R$ = 10.63 min. The absolute configuration [2*R*] of **2o** was determined by measuring its optical rotation and comparison with literature values, $[\alpha]^{20}_D$ = -40.6 (c 0.5, CHCl$_3$), 94.0%ee, [Lit. $[\alpha]_D^{25}$ = +6.6 (c 0.48 CHCl$_3$), 75%ee].[8b, 9b]



3,3-Diethyl-oxirane-2-carbaldehyde (**2p**) 85% yield was determined by GC with internal standard. For the volatile compound **2p**, after the reaction completed, the reaction mixture was directly subjected to flash chromatography for removing the salt catalyst. The yield and selectivity were determined with the concentrated eluates by gas chromatography. MS (EI)) (*m*/*z*): 128, 111, 100, 85, 81. The enantiomers were analyzed by GC using a chiral G-TA column (60 °C, 1.0 °C/min, until 180 °C, 15 min at 220 °C, 0.6 bar H$_2$). Major enantiomer: t$_R$ = 19.52 min, minor enantiomer: t$_R$ = 18.68 min.



1-Oxa-spiro[2,5]octane-2-carbaldehyde (**2q**) Compound **2q** was isolated with 75% yield after silica gel column chromatography (2.0% diethyl ether in pentane). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ = 9.38 (d, *J* = 4.8 Hz, 1H), 3.05 (d, *J* = 4.8 Hz, 1H), 1.41 - 1.64 (m, 10H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ 200.0, 67.6, 65.3, 35.9, 30.4, 25.8, 25.5; MS (EI) (*m*/*z*): 140, 122, 112, 97, 94, 91, 83, 81. The enantiomers were analyzed by GC using a chiral BGB 176 column (80 °C,

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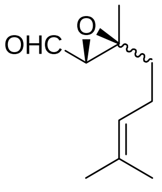
[9] a) D. A. Evans, J. M. Williams, *Tetrahedron Lett.* **1988**, *29*, 5065-5068; b) Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, K. B. Sharpless, *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780; c) A. Krief, W. Dumont, D. Baillieul, *Synthesis* **2002**, *14*, 2019-2022; d) Y. Zou, M. Lobera, B. M. Snider, *J. Org. Chem.* **2005**, *70*, 1761-1770; e) E. L. Clennan, D. Zhang, J. Singleton, *Photochemistry and Photobiology*, **2006**, *82*, 1226-1232.

1.2 °C/min, until 180 °C, 18 °C/min, until 220 °C, 10 min at 220 °C, 0.5 bar H_2). Major enantiomer: t_R = 19.67 min, minor enantiomer: t_R = 18.91 min. $[\alpha]^{20}_D$ = -34.0 (c 0.65, $CHCl_3$).

3-Methyl-3-(4-methyl-pent-3-enyl)-oxirane-2-carbaldehyde[10] (**2r**)



Compound **2r** was isolated with 95% yield after silica gel column chromatography (20% diethyl ether in pentane). 1H NMR (400 MHz, $CDCl_3$, for major isomer) δ = 9.45 (d, *J* = 5.0 Hz, 1H), 5.08 (t, *J* = 1.7 Hz, *J* = 7.2 Hz, 1H), 3.19 (d, *J* = 5.0 Hz, 1H), 2.09 (q, *J* = 7.6 Hz, 2H), 1.66 (s, 3H), 1.55 - 1.69 (m, 2H), 1.60 (s, 3H), 1.45 (s, 3H); MS (EI) (*m/z*): 168, 150, 135, 121, 109, 95. The enantiomers were analyzed by GC using a chiral Hydrodex β TBDAC column (60 °C, 2.0 °C/min, until 220 °C, 3 min at 220 °C, 0.6 bar H_2). Major diastereoisomer: t_R = 25.85 min (major enantiomer), t_R = 24.20 min (minor enantiomer); minor diastereoisomer: t_R = 18.34 min (major enantiomer), t_R = 19.35 min (minor enantiomer).

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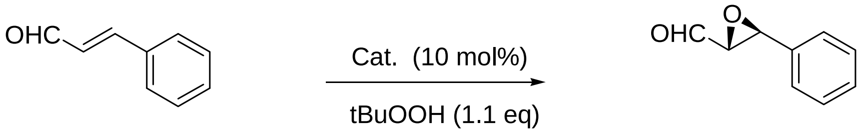
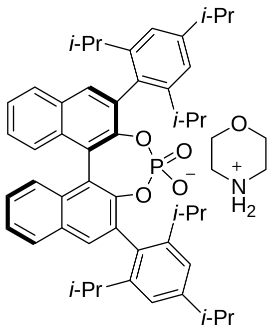
[10] a) C. Dupuy, J. L. Luche, *Tetrahedron* **1989**, *45*, 3437-3444; b) K. Nacro, M. Baltas, J. Escudier, L. Gorrichon, *Tetrahedron* **1996**, *52*, 9047-905.

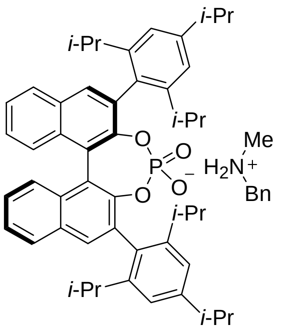
Table 4. Screening Different Oxidants with ACDC-Salt Catalysts for the Epoxidation of Cinnamaldehyde.[a]



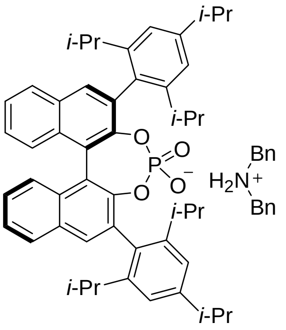
1a **2a**



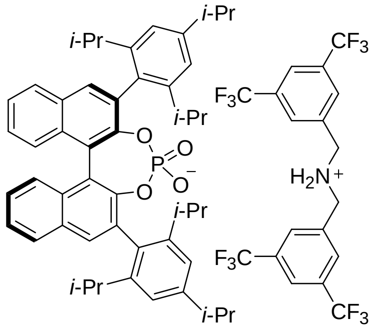
3a



3c



3d

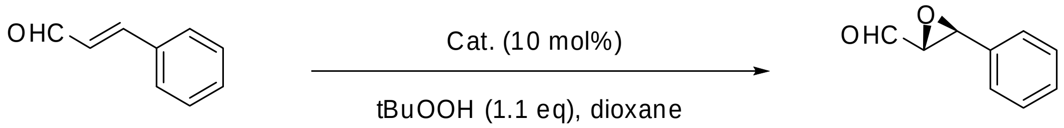


3m

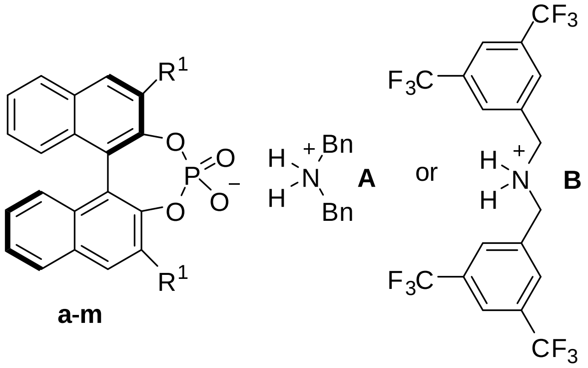
Entry	Catalyst	Oxidant	T(℃)	Yield[%] [b]	dr [c]	er [d]
1	**3a**	*m*CPBA	rt	--	--	--
2	**3a**	H_2O_2	rt	--	--	--
3	**3a**	CMHP	rt	46	80 : 20	52 : 48
5	**3a**	TBHP	rt	24	90 : 10	59 : 41
6	**3a**	TBHP	50	40	93 : 7	77 : 23
7	**3c**	TBHP	50	58	89 : 11	75 : 25
8	**3d**	CMHP	50	90	95 : 5	69 : 31
9	**3d**	TBHP	50	95	98 : 2	83 : 17
10	**3m**	TBHP	50	71	>99 : 1	95 : 5[e]

[a] Reaction performed on a 0.5 mmol scale of cinnamaldehyde **1a** in 2 mL of dioxane at 50°C for 24 hours. [b] Isolated yield. [c] Determined by chiral GC. [d] Determined by chiral GC. [e] Absolute configuration [*2R, 3S*] of **2a** was determined by comparison of its optical rotation with that reported in the literatures.[8]

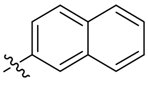
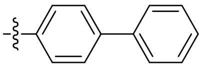
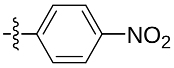
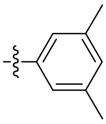
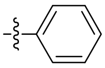
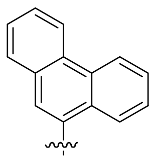
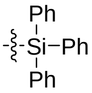
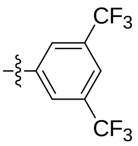
Table 5. Screening Different Counteranions with Amines **A** and **B** for the Epoxidation of Cinnamaldehyde.[a]

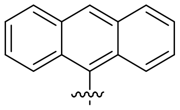
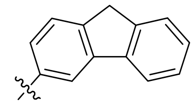
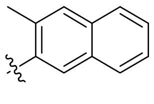
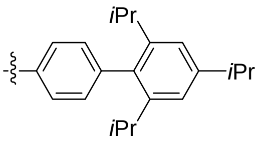
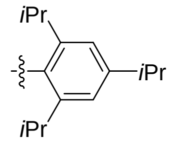
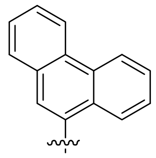
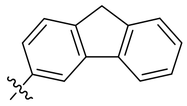
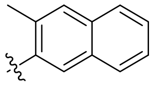
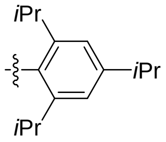


1a **2a**



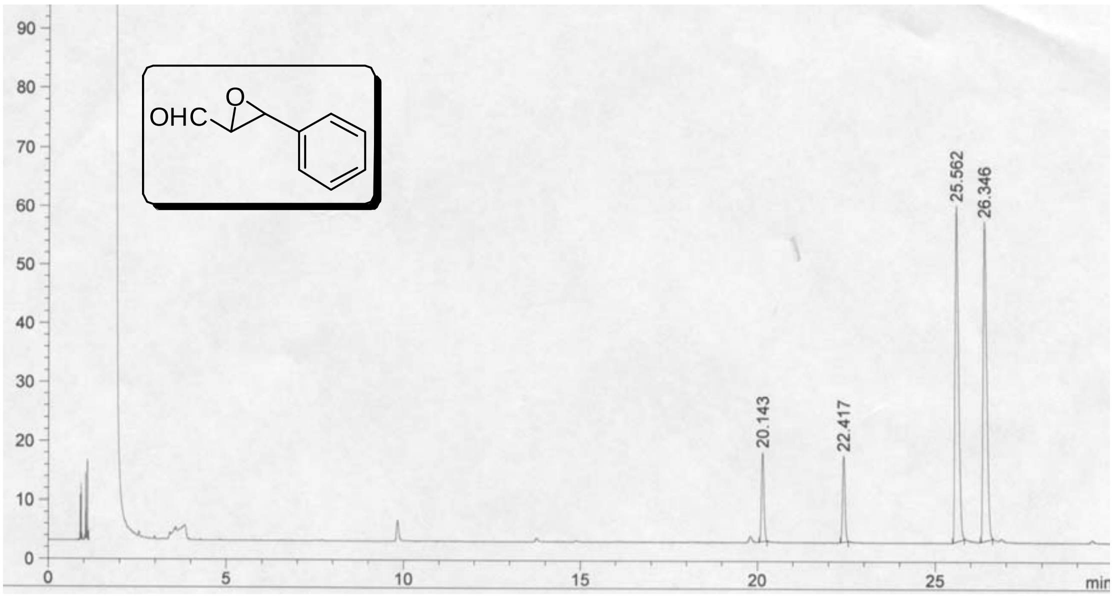
a-m

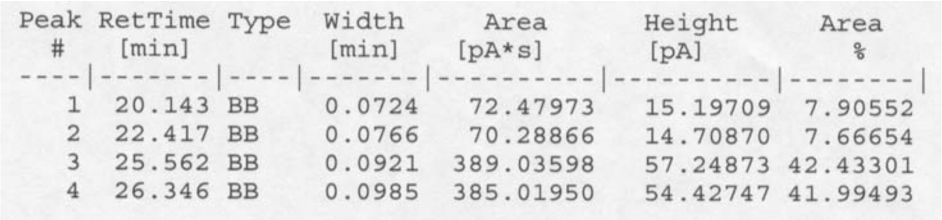
Entry	R^1		Amine	Yield (%) [b]	dr [c]	er [d]
1		**a**	**A**	67	98 : 2	60 : 40
2		**b**	**A**	70	98 : 2	65 : 35
3		**c**	**A**	54	96 : 4	58 : 42
4		**d**	**A**	62	93 : 7	62 : 38
5		**e**	**A**	75	98 : 2	68 : 32
6		**f**	**A**	95	98 : 2	69 : 31
7	 $-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{Ph}$	**g**	**A**	89	97 : 3	60 : 40
8		**h**	**A**	55	98 : 2	61 : 39

9		**i**	**A**	75	98 : 2	63 : 37
10		**j**	**A**	75	>99 : 1	76 : 24
11		**k**	**A**	54	>99 : 1	65 : 35
12		**l**	**A**	73	90 : 10	55 : 45
13		**m**	**A**	95	98 : 2	83 : 17
14		**f**	**B**	81	99 : 1	81 : 19
15		**j**	**B**	89	>99 : 1	76 : 24
16		**k**	**B**	55	>99 : 1	65 : 35
17		**m**	**B**	75	>99 : 1	95.5 : 4.5[e]

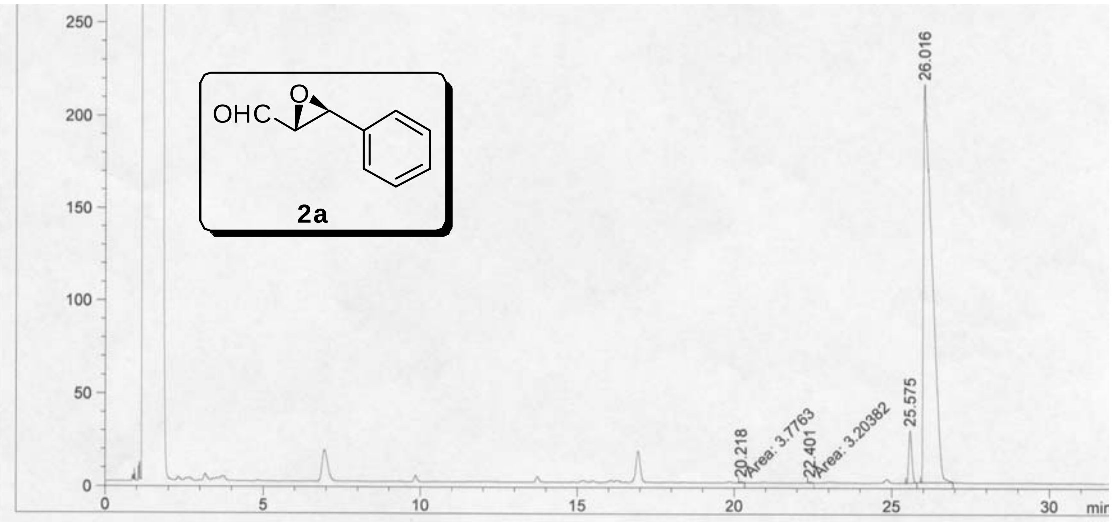
[a] Reaction performed on a 0.5 mmol scale of cinnamaldehyde **1a** in 2 mL of dioxane at 35°C for72 hours. [b] Isolated yield. [c] Determined by chiral GC. [d] Determined by chiral GC. [e] Absolute configuration [*2R*, *3S*] of **2a** was determined by comparison of its optical rotation with that reported in the literatures.[8]

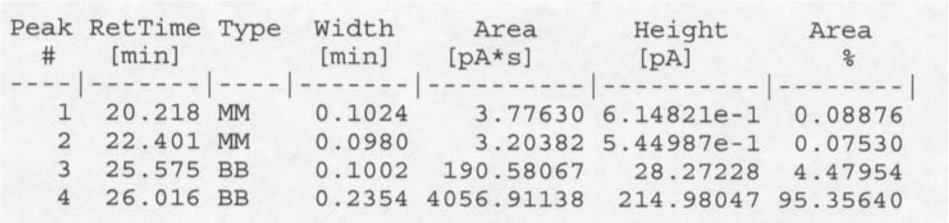
GC traces of the Products 2a-r:



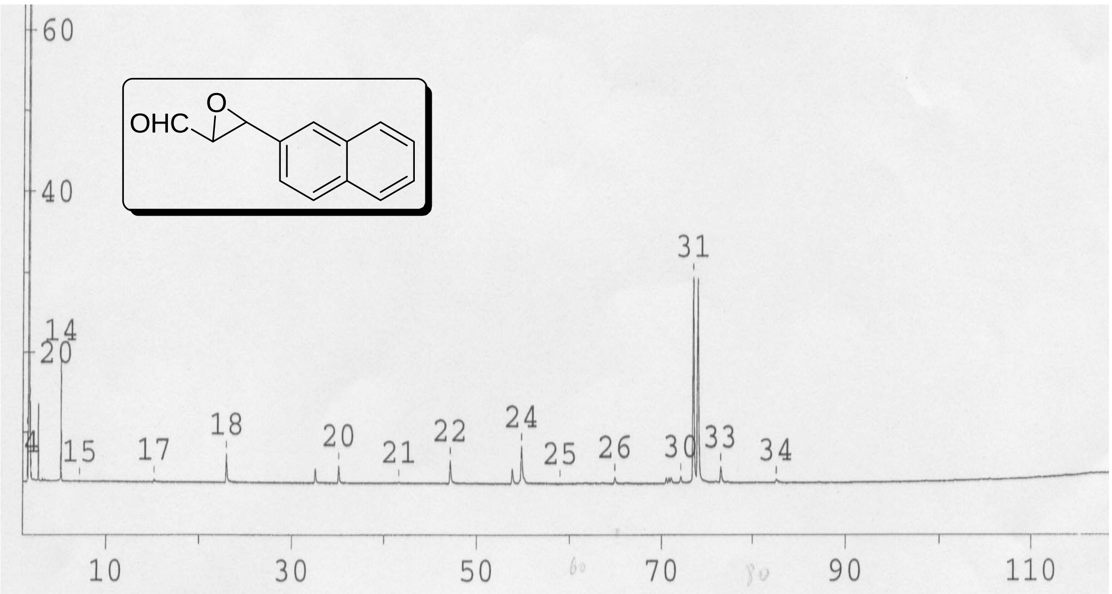


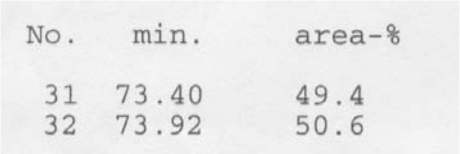
```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  20.143 BB    0.0724   72.47973   15.19709  7.90552
  2  22.417 BB    0.0766   70.28866   14.70870  7.66654
  3  25.562 BB    0.0921  389.03598   57.24873 42.43301
  4  26.346 BB    0.0985  385.01950   54.42747 41.99493
```



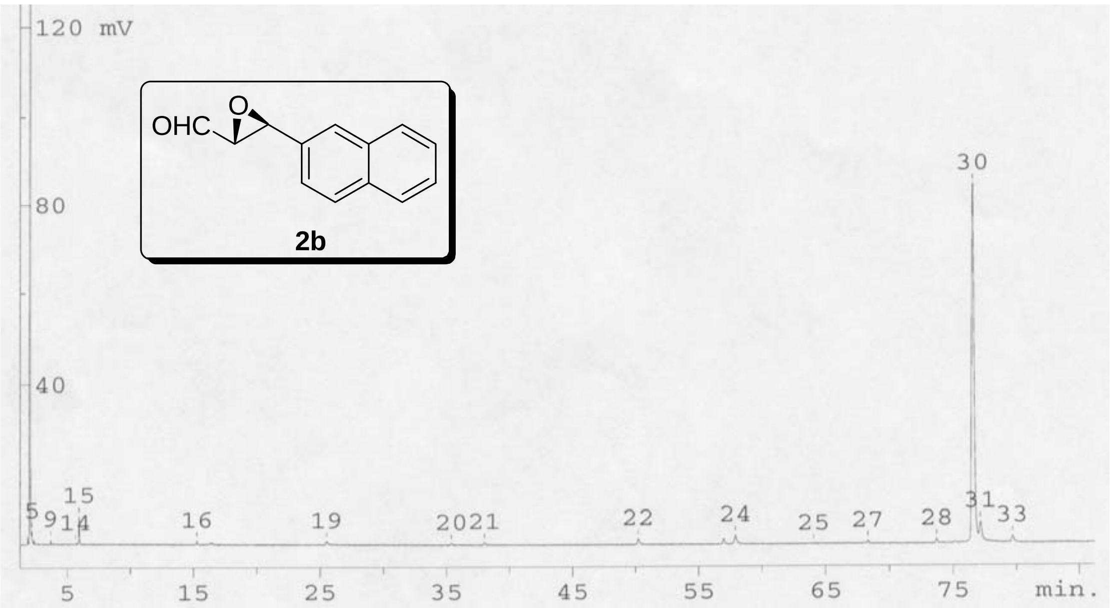


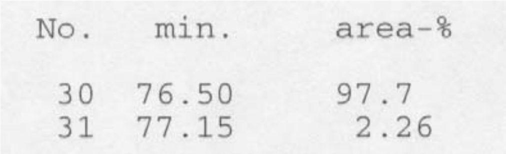
```
Peak RetTime Type  Width      Area      Height       Area
  #   [min]        [min]    [pA*s]       [pA]          %
----|-------|----|-------|----------|----------|--------|
  1  20.218 MM    0.1024    3.77630 6.14821e-1  0.08876
  2  22.401 MM    0.0980    3.20382 5.44987e-1  0.07530
  3  25.575 BB    0.1002  190.58067   28.27228  4.47954
  4  26.016 BB    0.2354 4056.91138  214.98047 95.35640
```



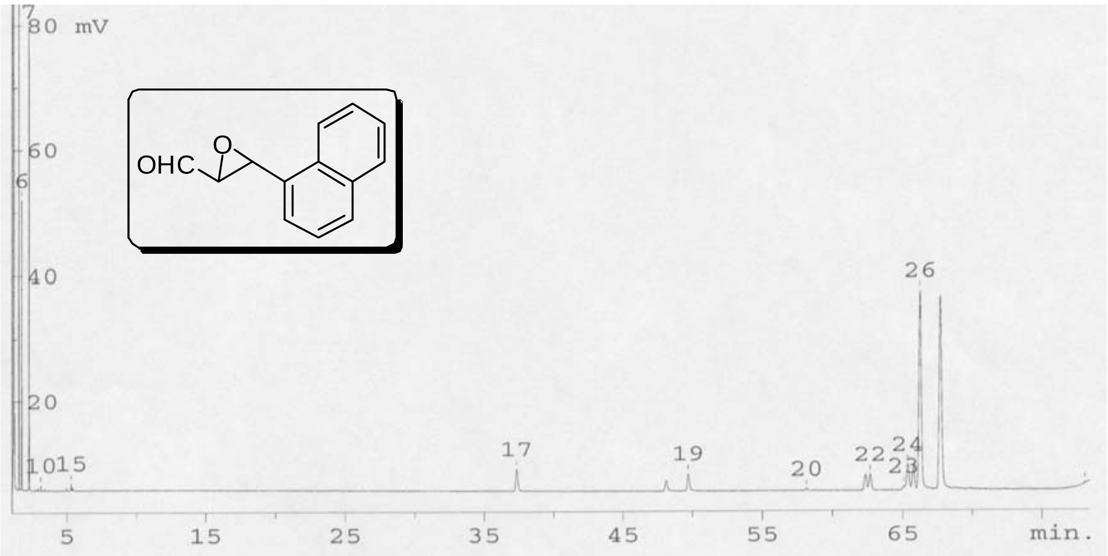


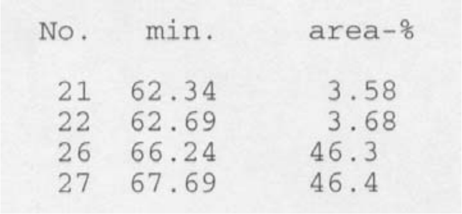
No.	min.	area-%
31	73.40	49.4
32	73.92	50.6



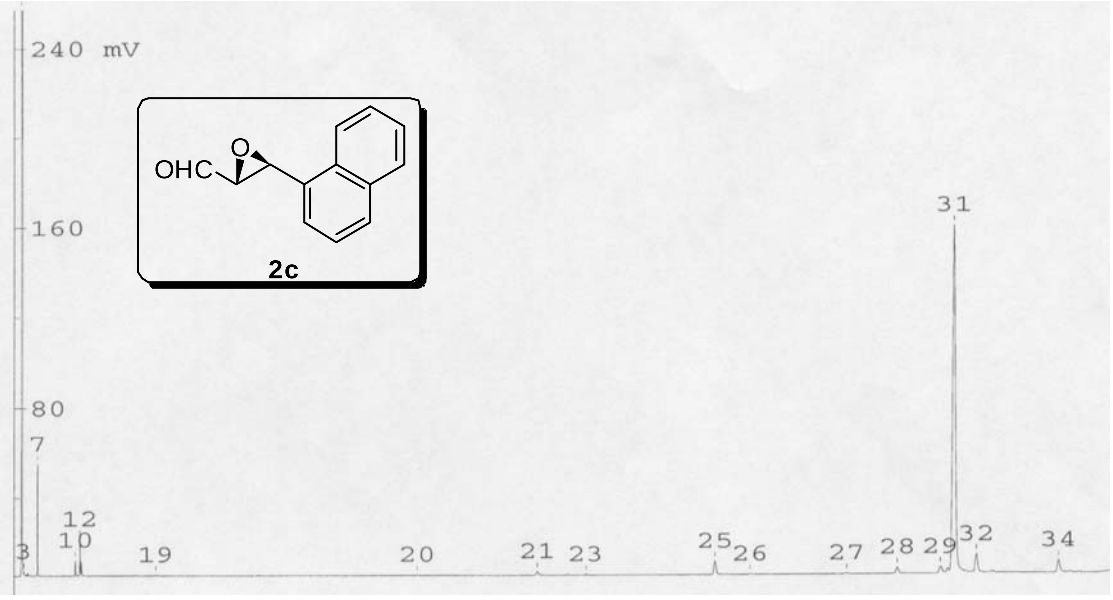


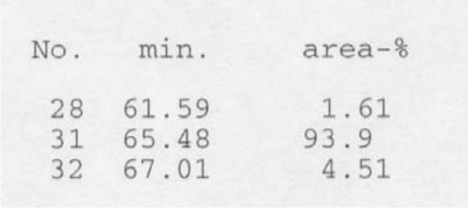
No.	min.	area-%
30	76.50	97.7
31	77.15	2.26



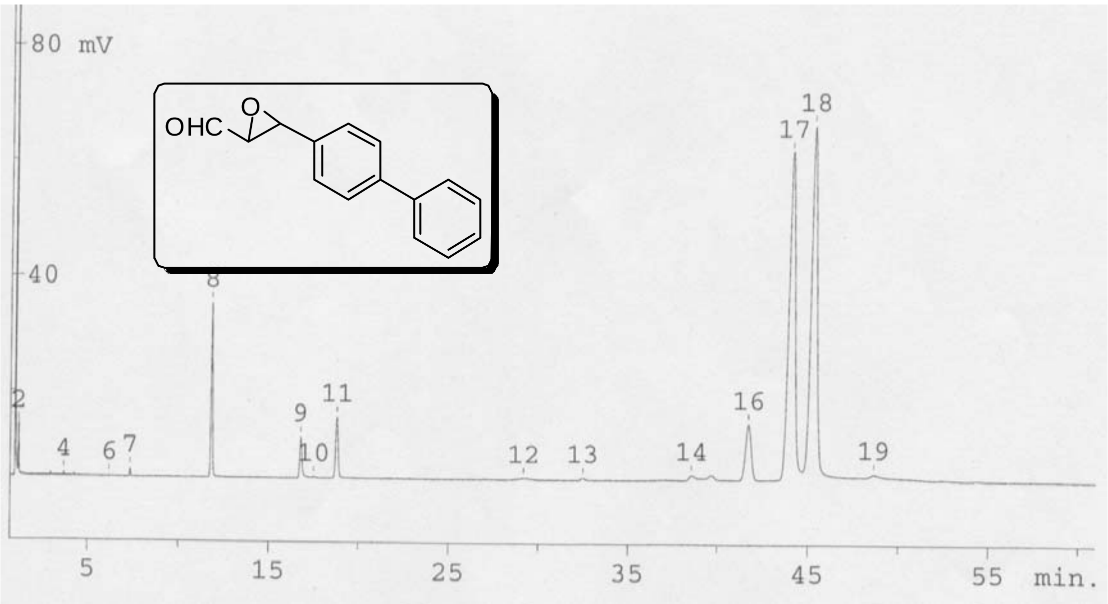


No.	min.	area-%
21	62.34	3.58
22	62.69	3.68
26	66.24	46.3
27	67.69	46.4

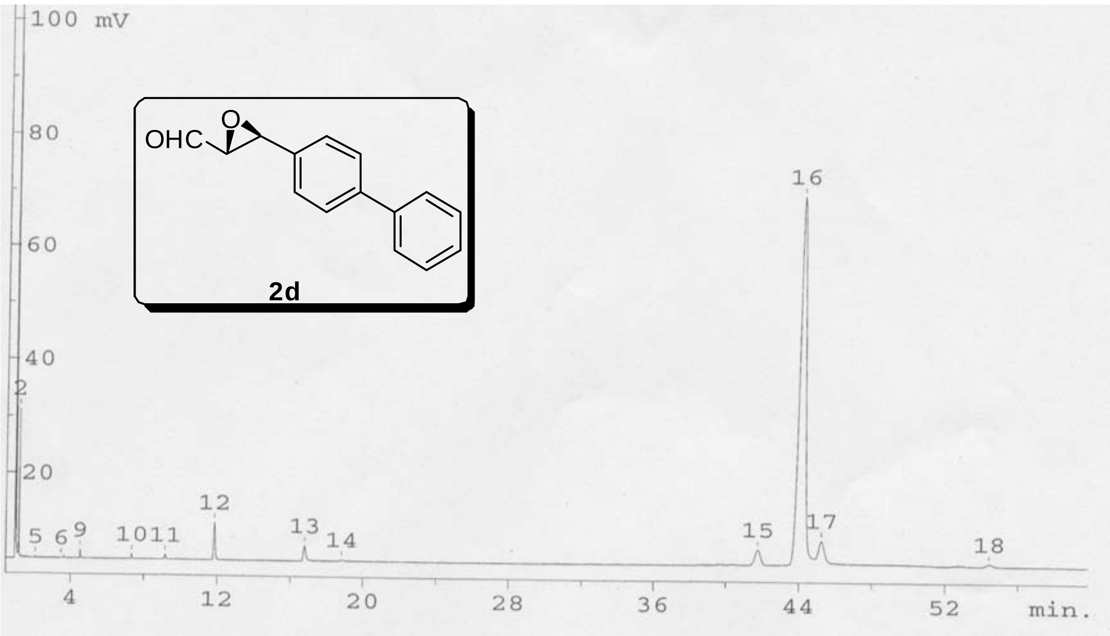




No.	min.	area-%
28	61.59	1.61
31	65.48	93.9
32	67.01	4.51

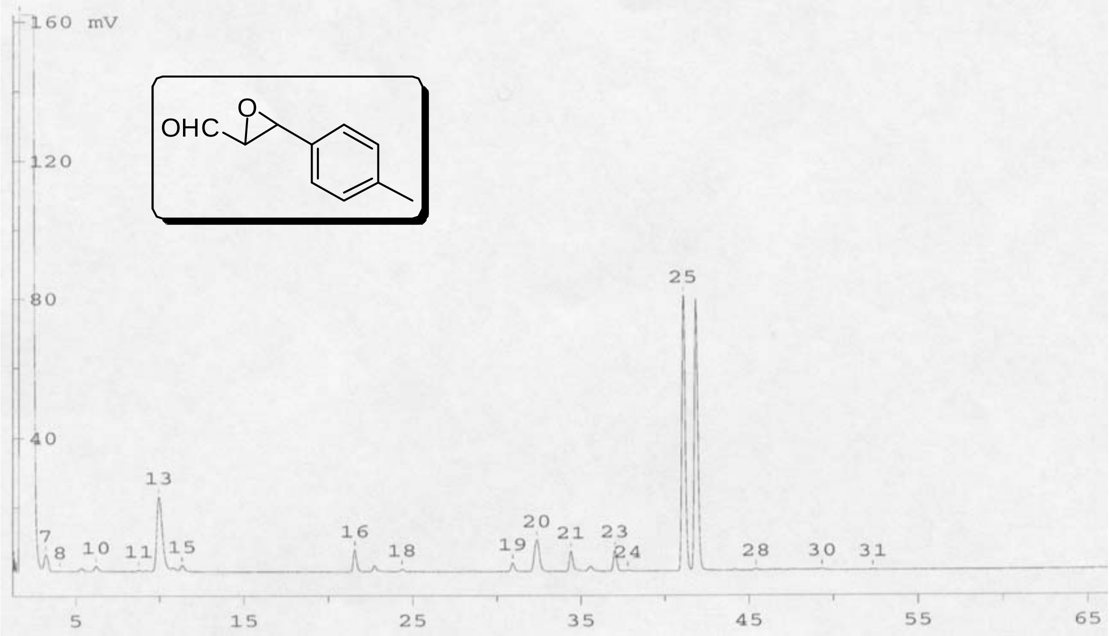


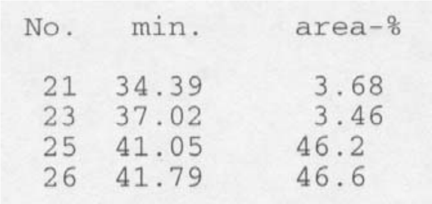
No.	min.	area-%
17	44.10	49.4
18	45.33	50.6



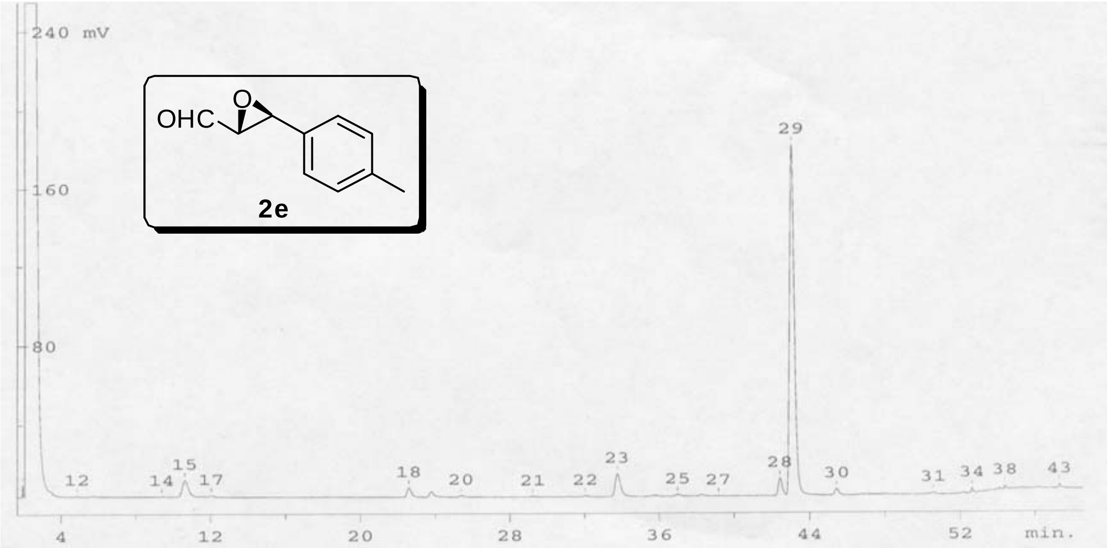
2d

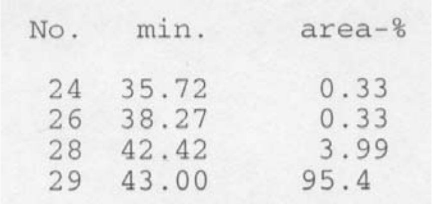
No.	min.	area-%
16	44.17	95.5
17	45.23	4.48



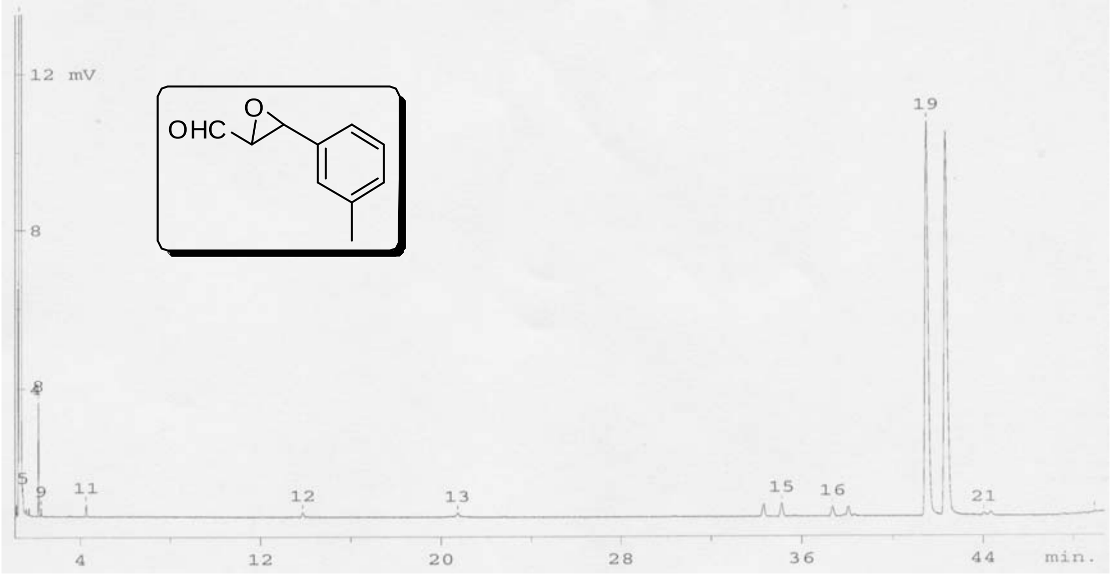


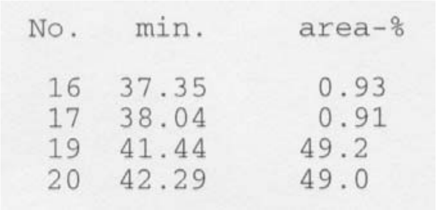
No.	min.	area-%
21	34.39	3.68
23	37.02	3.46
25	41.05	46.2
26	41.79	46.6



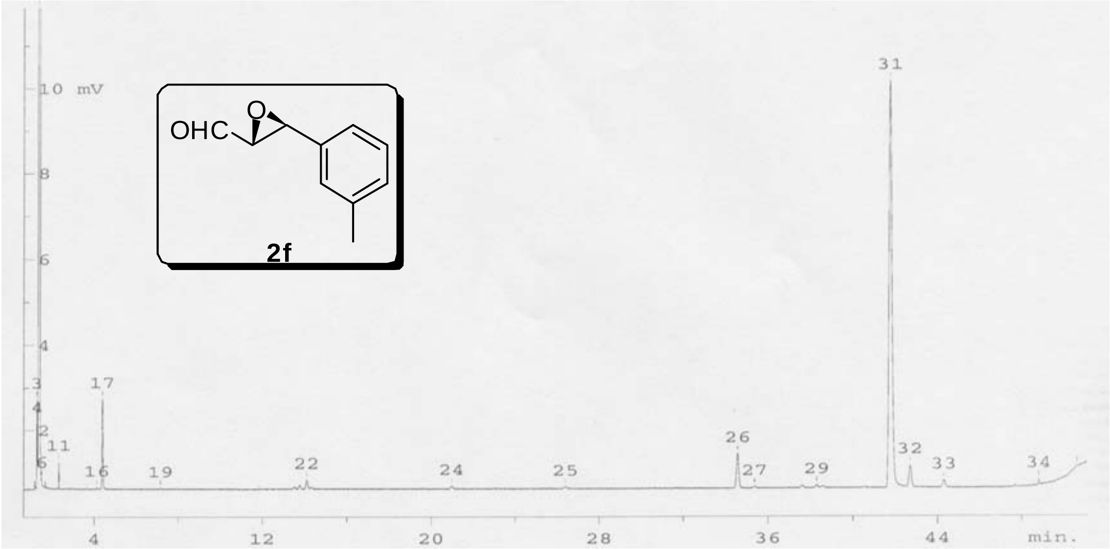


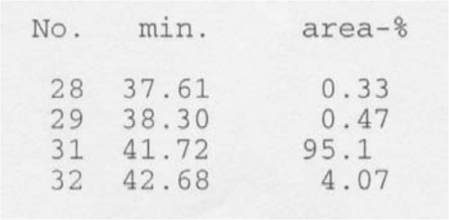
No.	min.	area-%
24	35.72	0.33
26	38.27	0.33
28	42.42	3.99
29	43.00	95.4



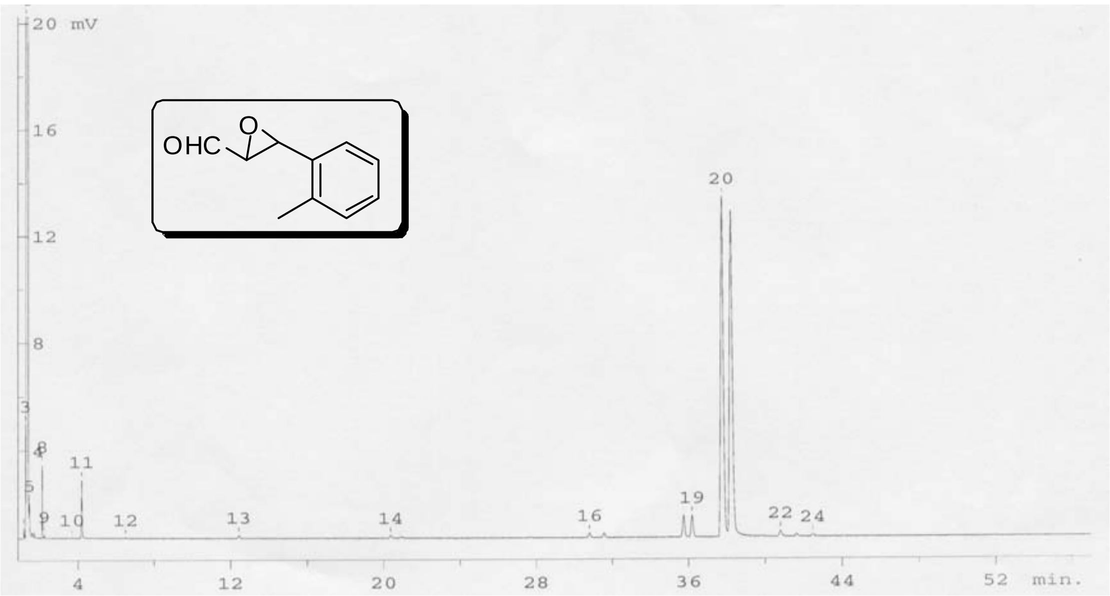


No.	min.	area-%
16	37.35	0.93
17	38.04	0.91
19	41.44	49.2
20	42.29	49.0

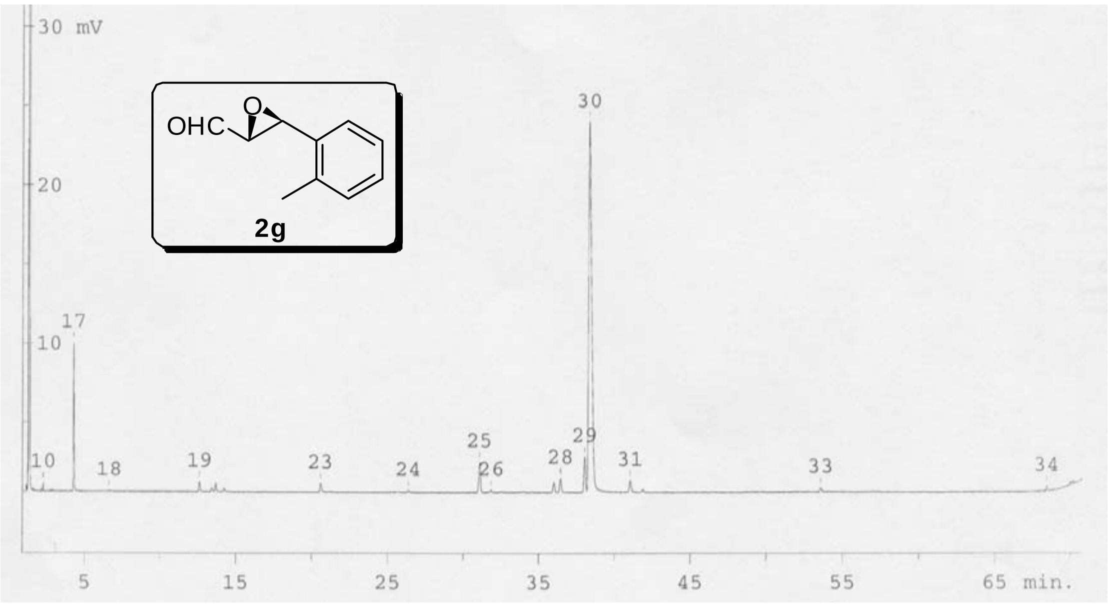

2f



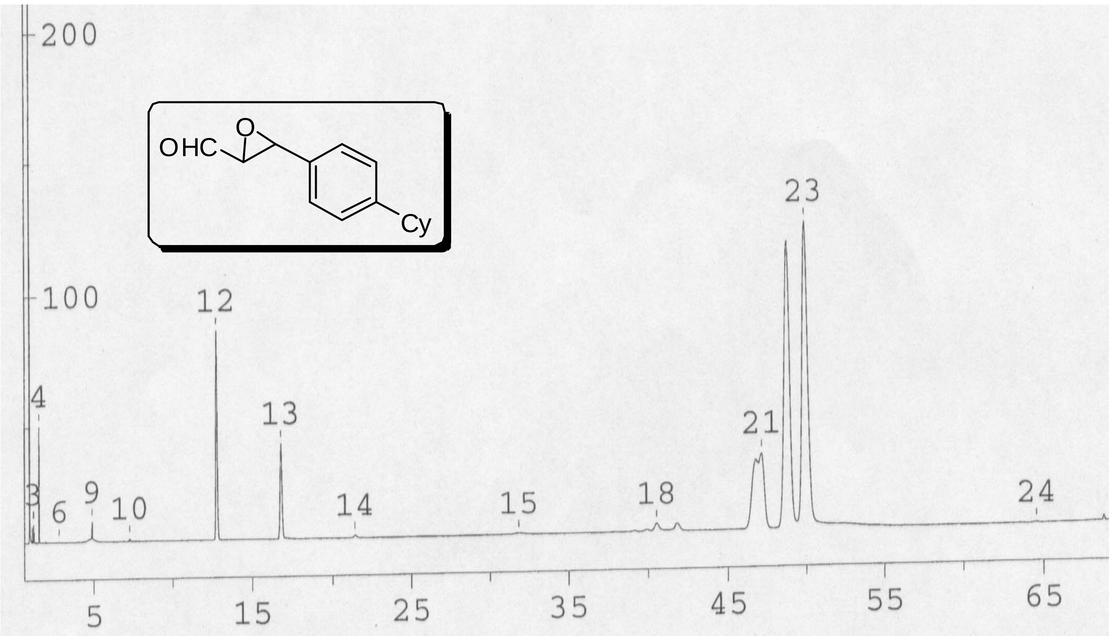
No.	min.	area-%
28	37.61	0.33
29	38.30	0.47
31	41.72	95.1
32	42.68	4.07

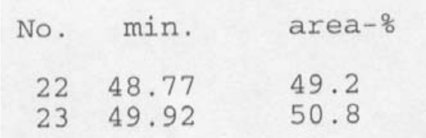


No.	min.	area-%
18	35.74	2.23
19	36.18	2.25
20	37.70	47.2
21	38.17	48.3

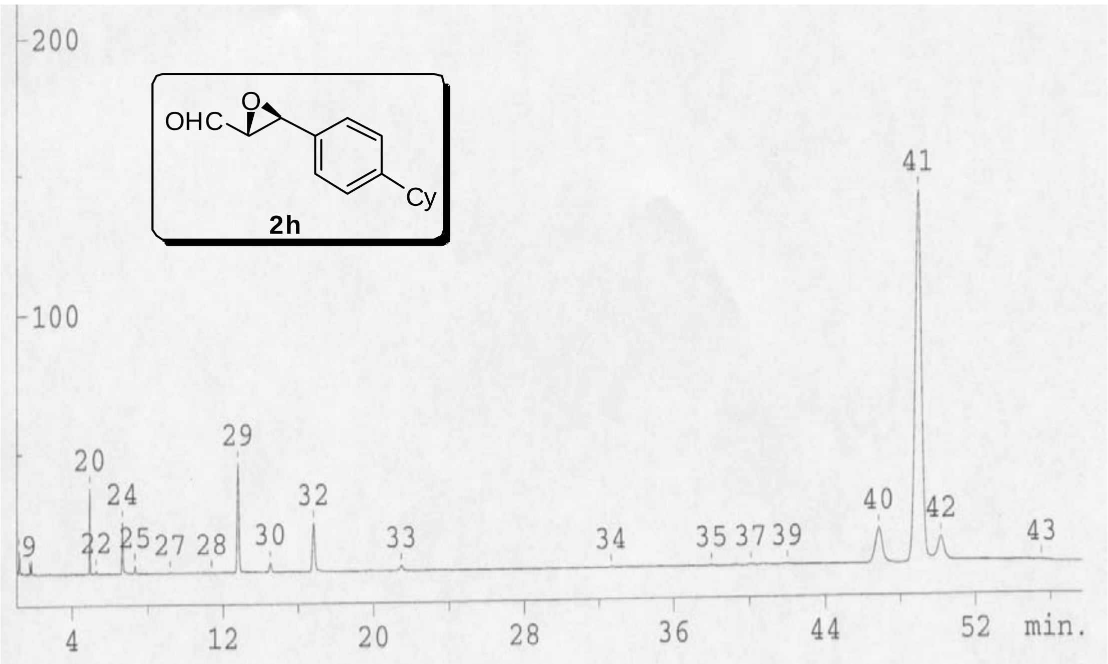


No.	min.	area-%
27	35.99	1.34
28	36.43	1.92
29	38.03	4.67
30	38.30	92.1

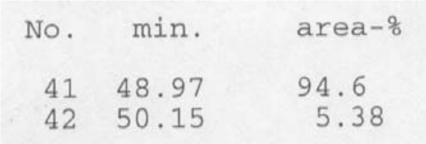




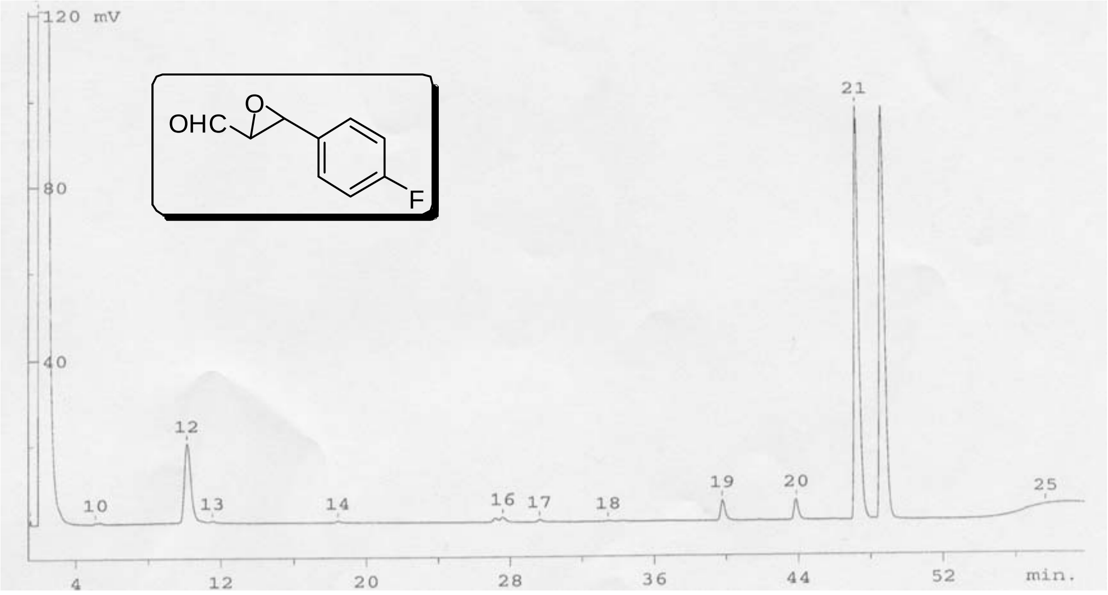
No.	min.	area-%
22	48.77	49.2
23	49.92	50.8



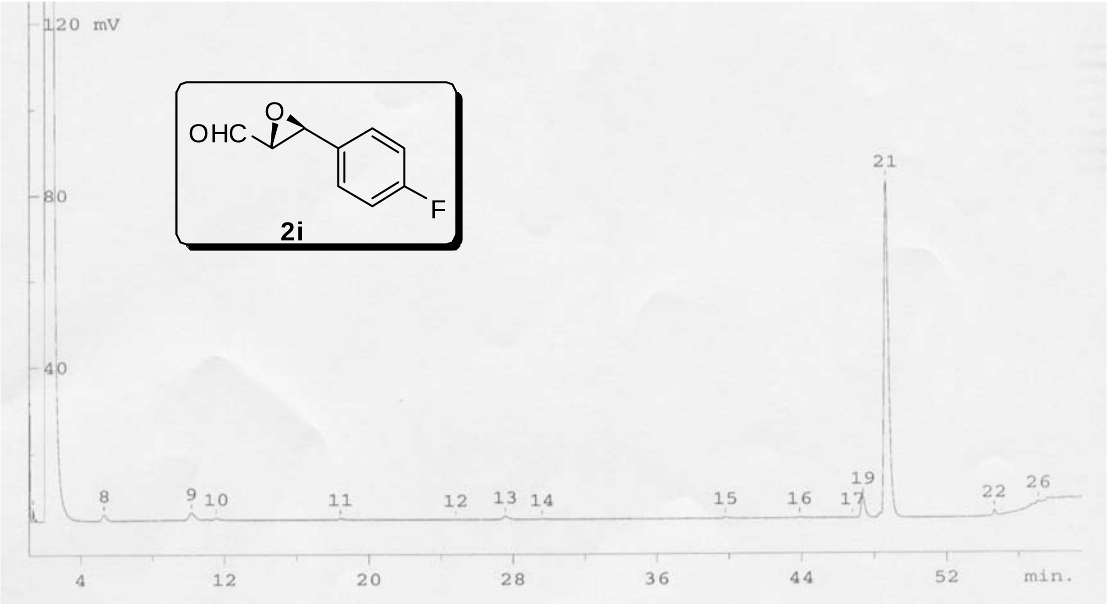
2h



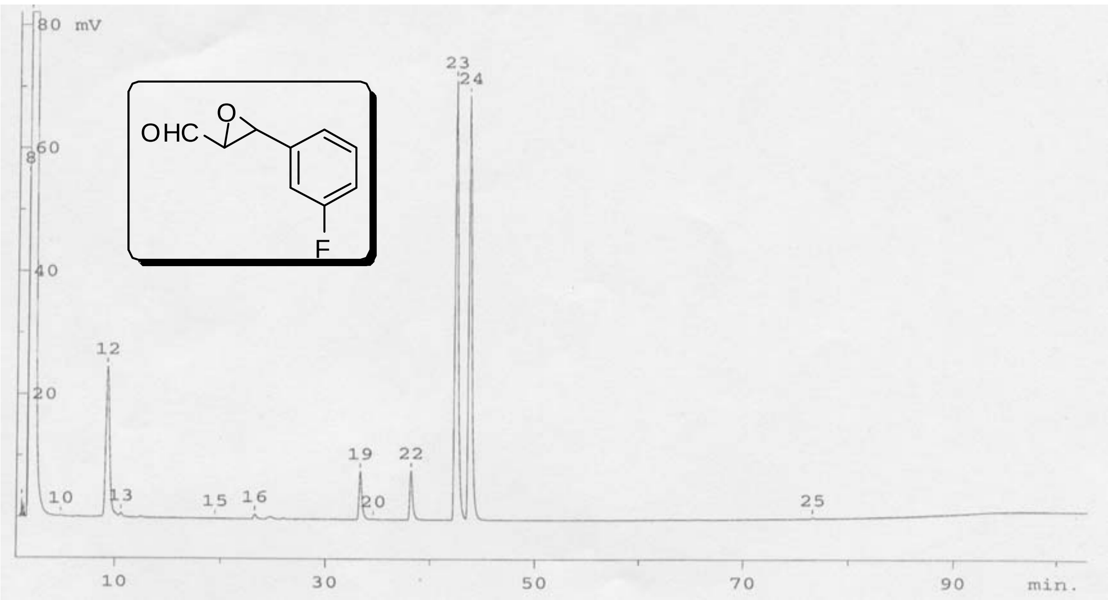
No.	min.	area-%
41	48.97	94.6
42	50.15	5.38



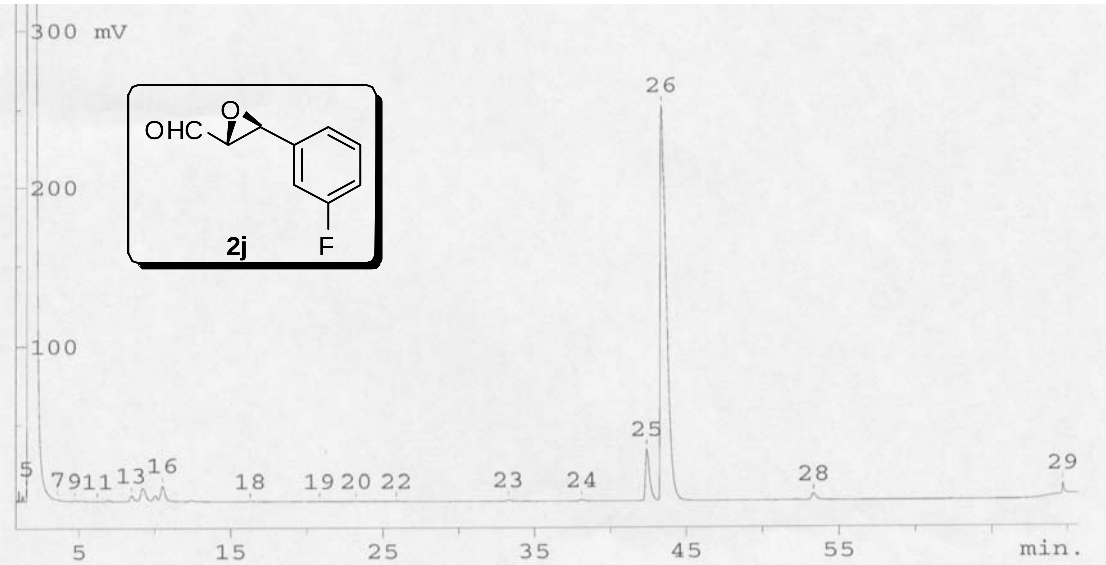
No.-no.	min. -min.	area-%
19	39.79	2.26
20	43.88	2.25
21- 22	47.15- 47.21	47.7
23	48.58	47.8



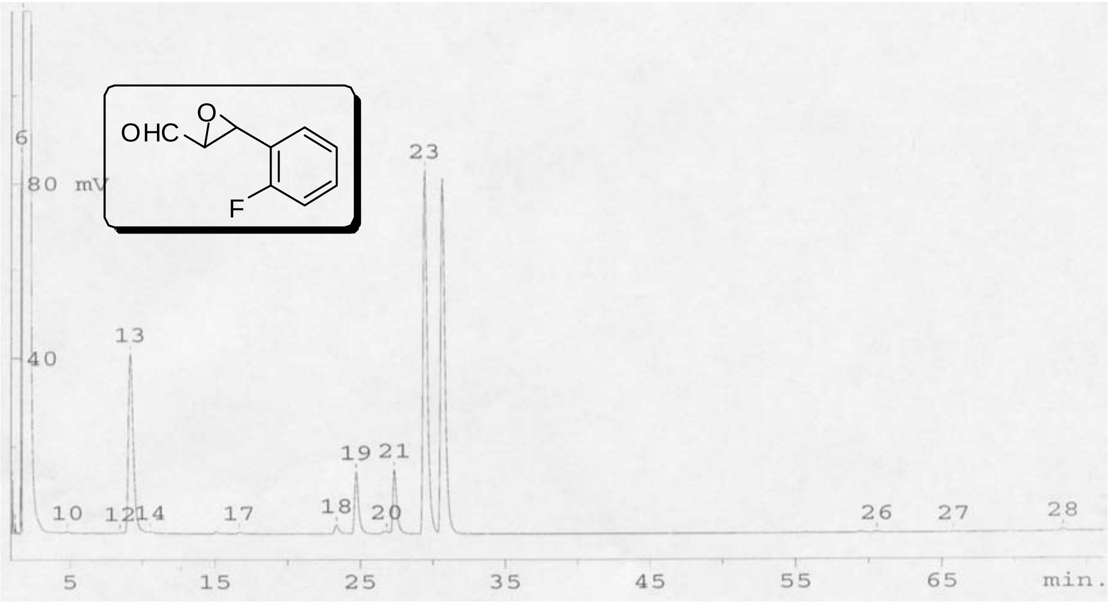
No.	min.	area-%
15	39.80	0.42
16	43.88	0.32
19	47.37	3.28
21	48.61	96.0

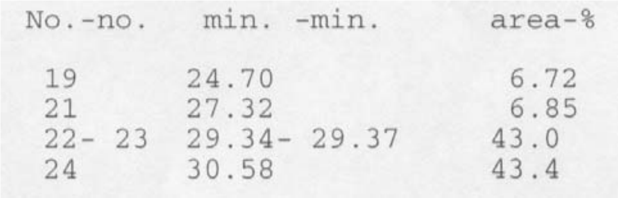


No.	min.	area-%
19	33.30	4.58
22	38.16	2.96
23	42.32	46.1
24	43.63	46.3

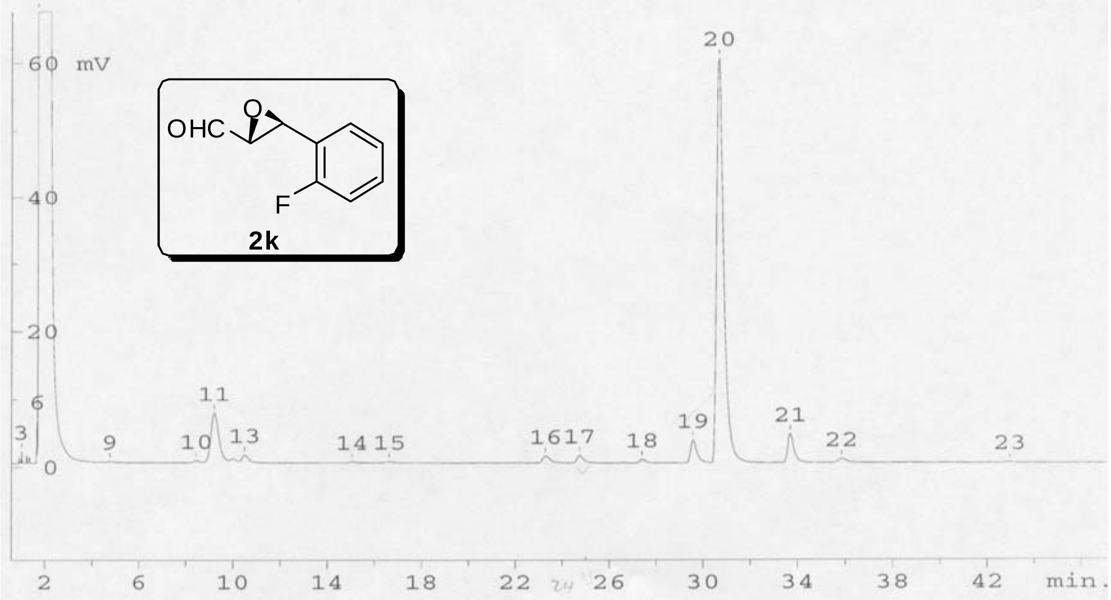


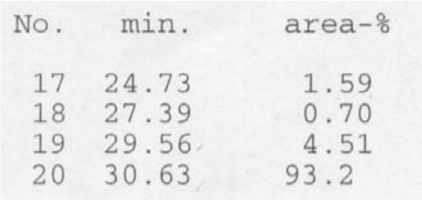
No.	min.	area-%
23	33.29	0.25
24	38.12	0.27
25	42.39	7.98
26	43.33	91.5



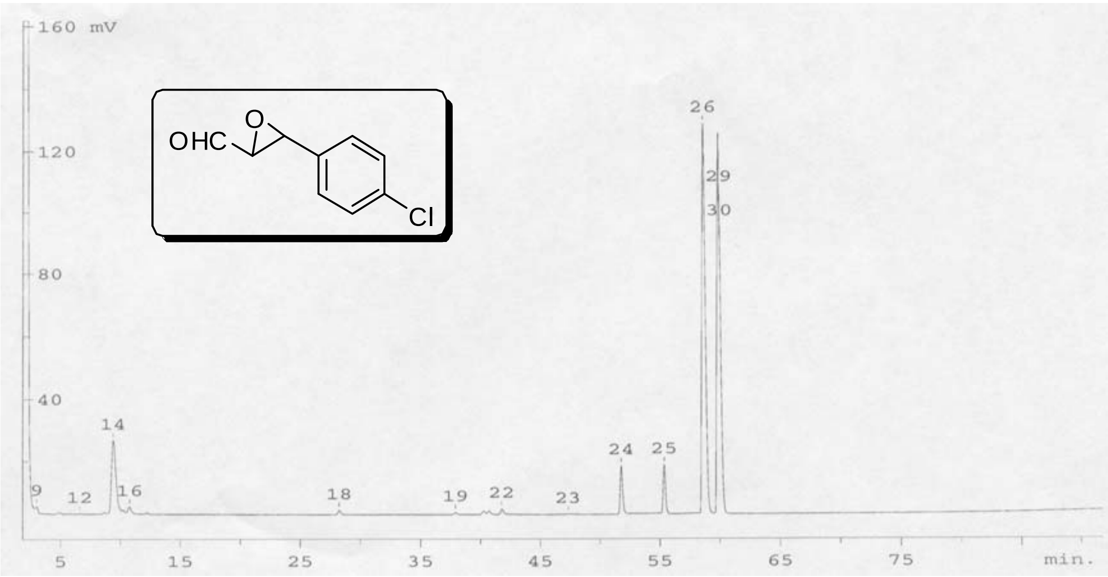


No.-no.	min. -min.	area-%
19	24.70	6.72
21	27.32	6.85
22- 23	29.34- 29.37	43.0
24	30.58	43.4

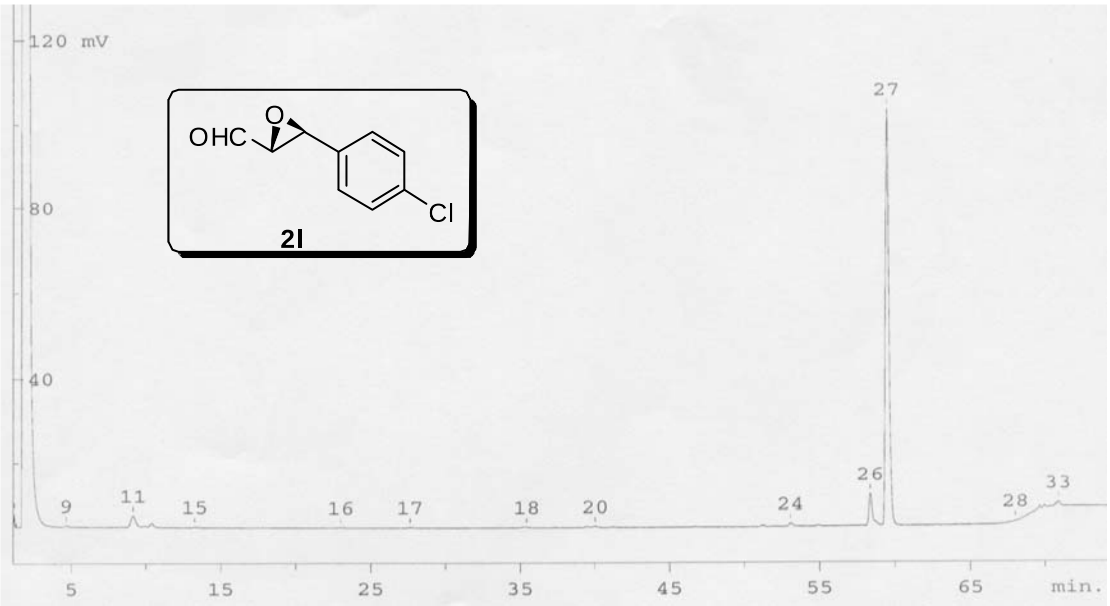




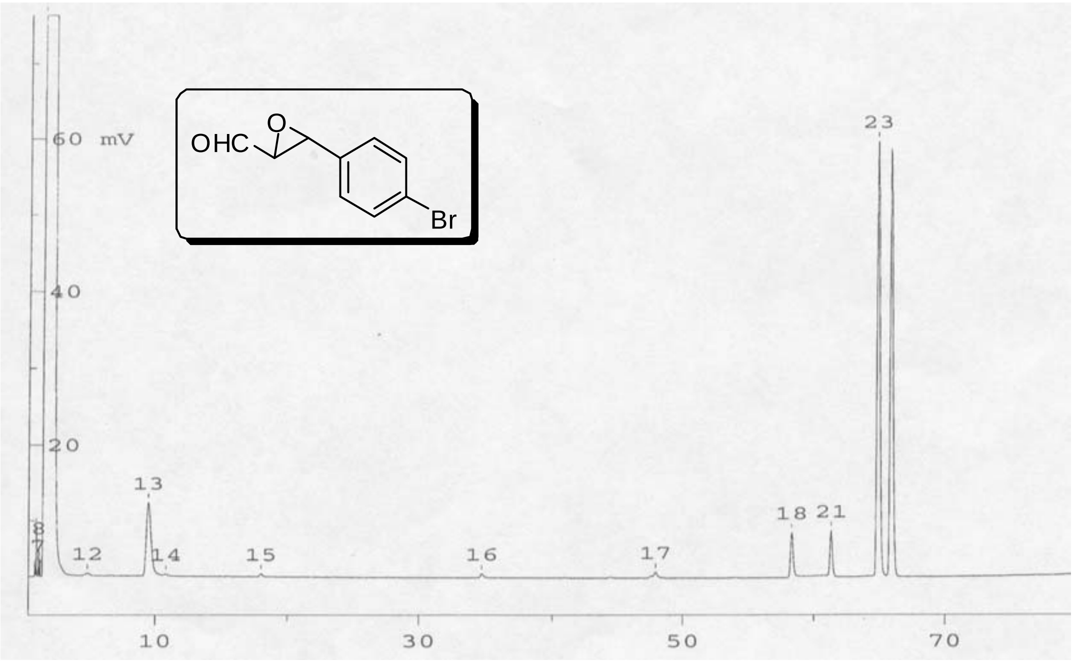
No.	min.	area-%
17	24.73	1.59
18	27.39	0.70
19	29.56	4.51
20	30.63	93.2



No.-no.	min. -min.	area-%
24	51.75	4.27
25	55.33	4.14
26- 27	58.48- 58.50	46.4
28- 30	59.73- 59.88	45.2

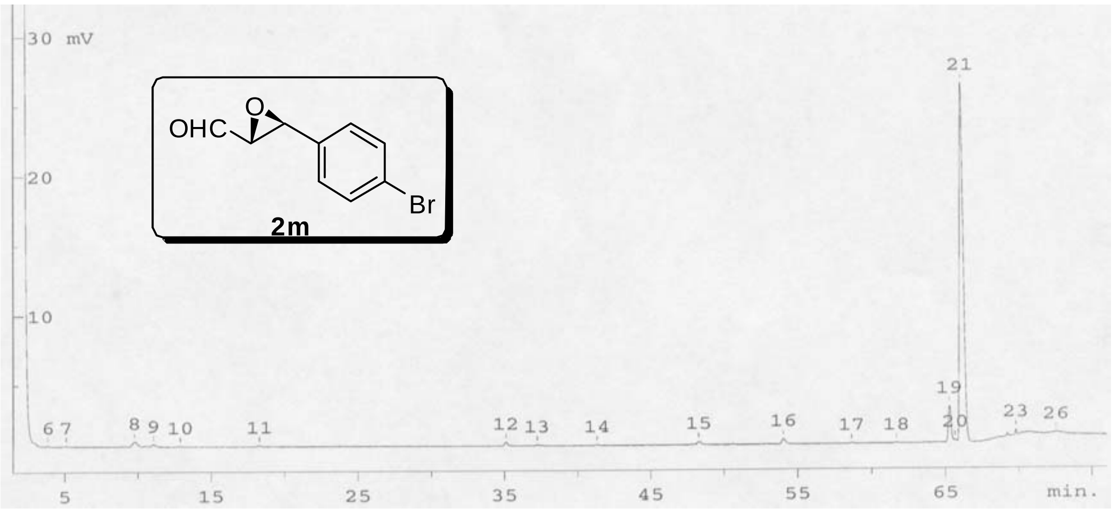


No.	min.	area-%
22	51.20	0.31
25	54.84	0.24
26	58.32	6.63
27	59.37	92.8



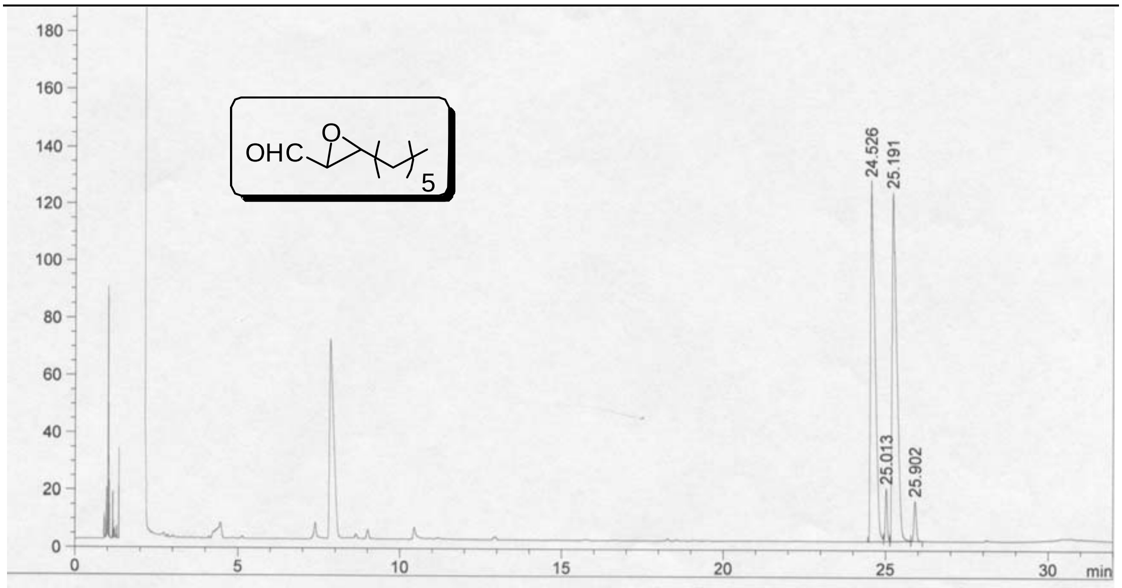
```
No.-no.    min.  -min.        area-%

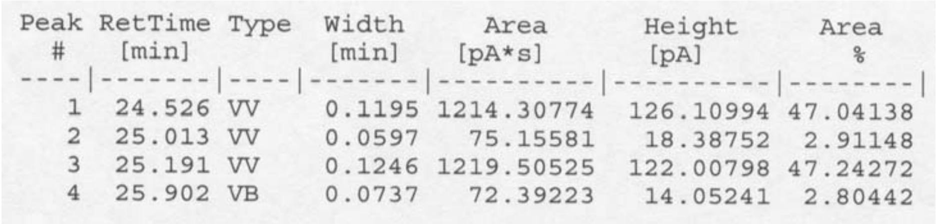
 18        58.28               1.91
 21        61.32               2.37
 22- 23    64.86- 64.88       47.9
 24        65.84              47.8
```



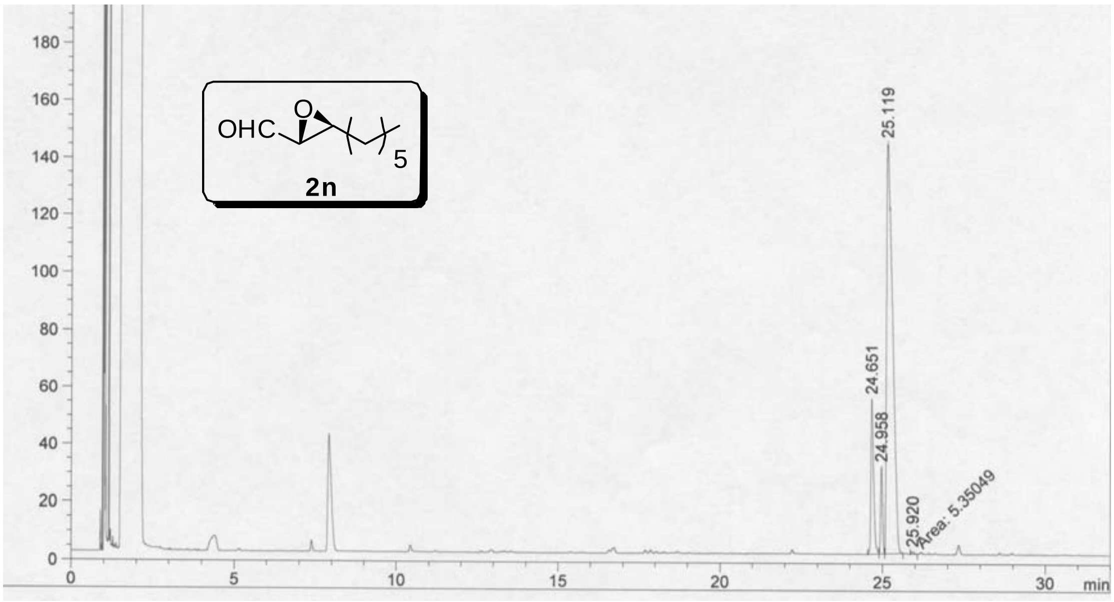
```
No.    min.        area-%

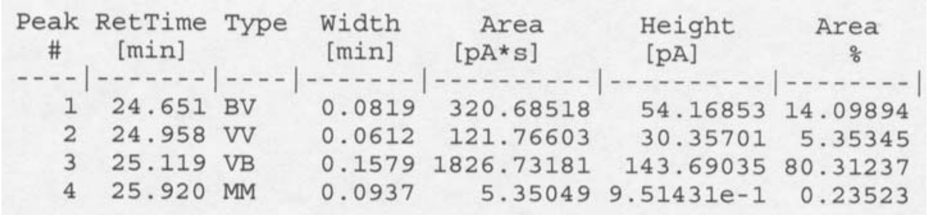
 17   58.64         0.12
 18   61.66         0.11
 19   65.26         6.58
 21   65.97        93.2
```





```
Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  24.526 VV    0.1195 1214.30774  126.10994 47.04138
  2  25.013 VV    0.0597   75.15581   18.38752  2.91148
  3  25.191 VV    0.1246 1219.50525  122.00798 47.24272
  4  25.902 VB    0.0737   72.39223   14.05241  2.80442
```





```
Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  24.651 BV    0.0819  320.68518   54.16853 14.09894
  2  24.958 VV    0.0612  121.76603   30.35701  5.35345
  3  25.119 VB    0.1579 1826.73181  143.69035 80.31237
  4  25.920 MM    0.0937    5.35049 9.51431e-1  0.23523
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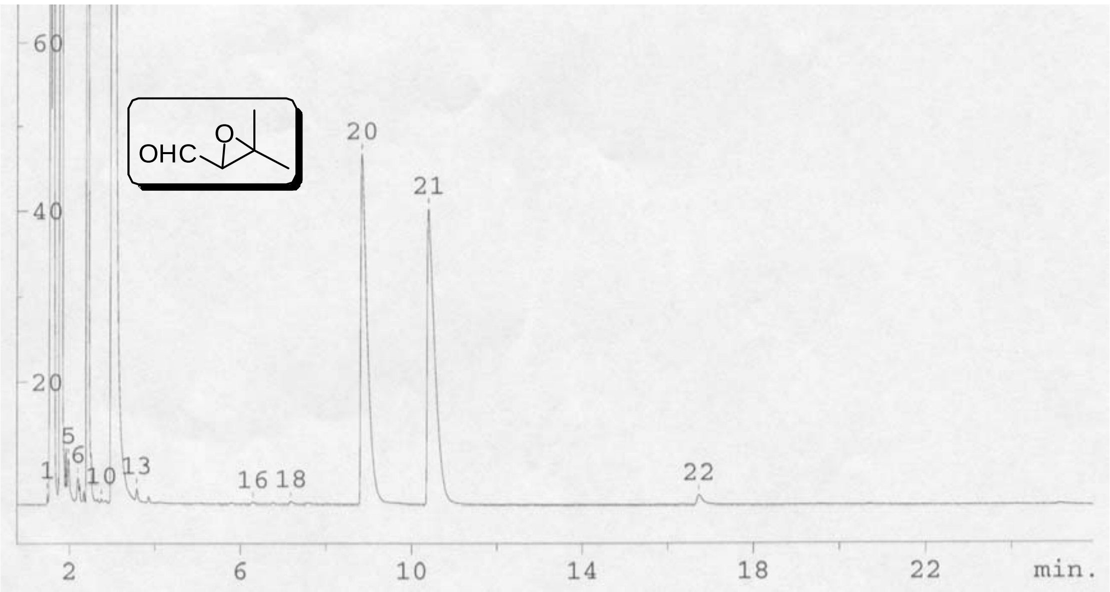
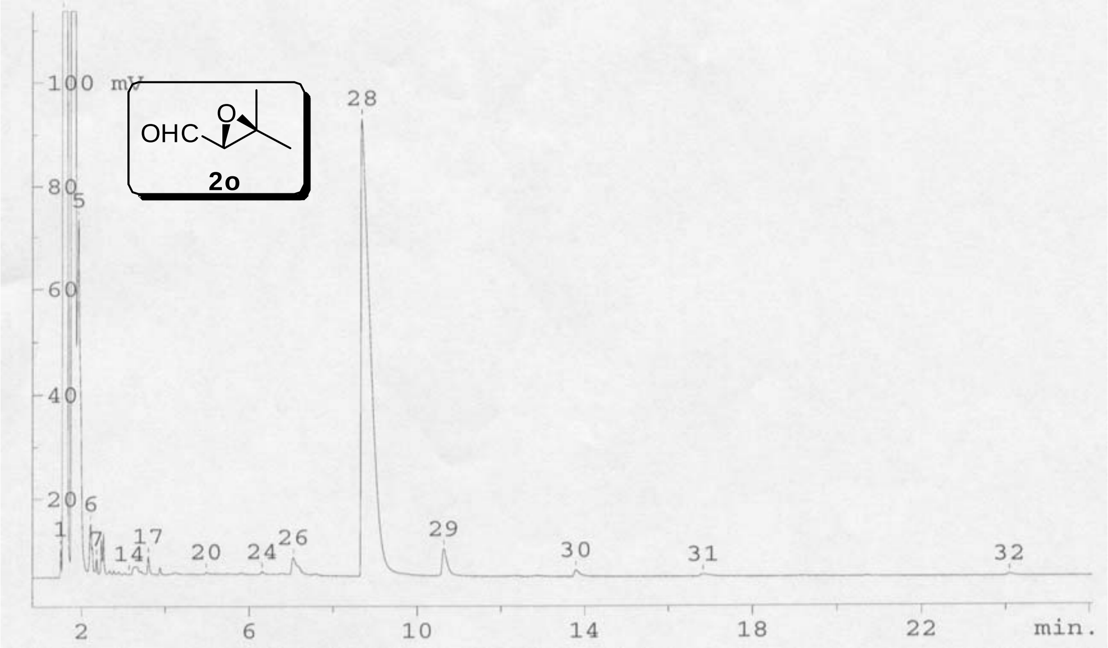
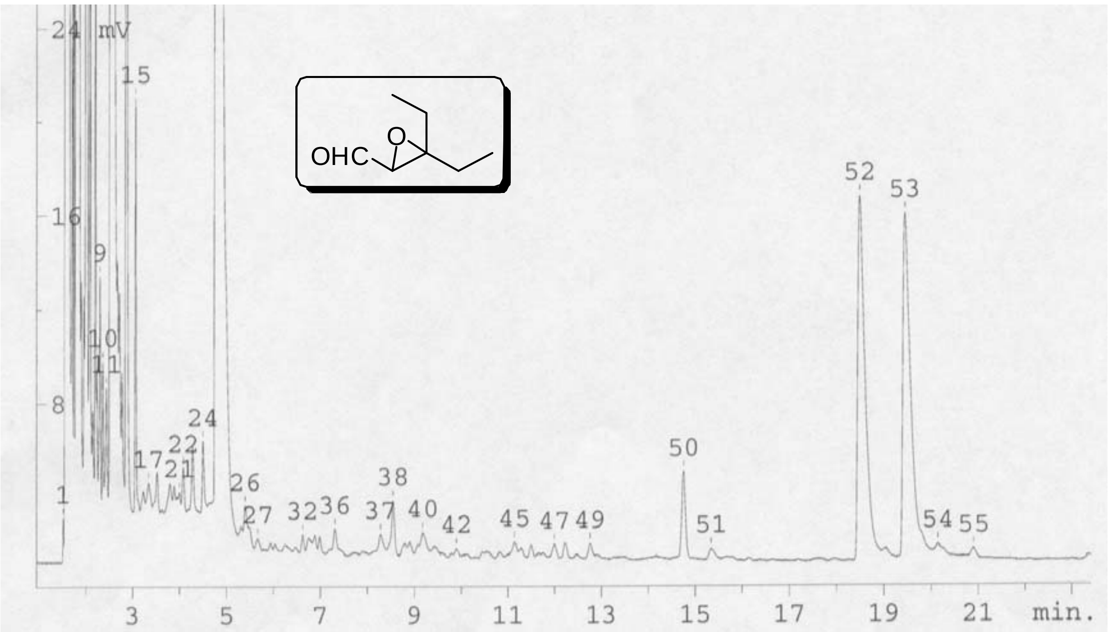
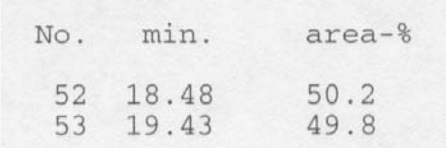


No.	min.	area-%
20	8.83	50.0
21	10.39	50.0

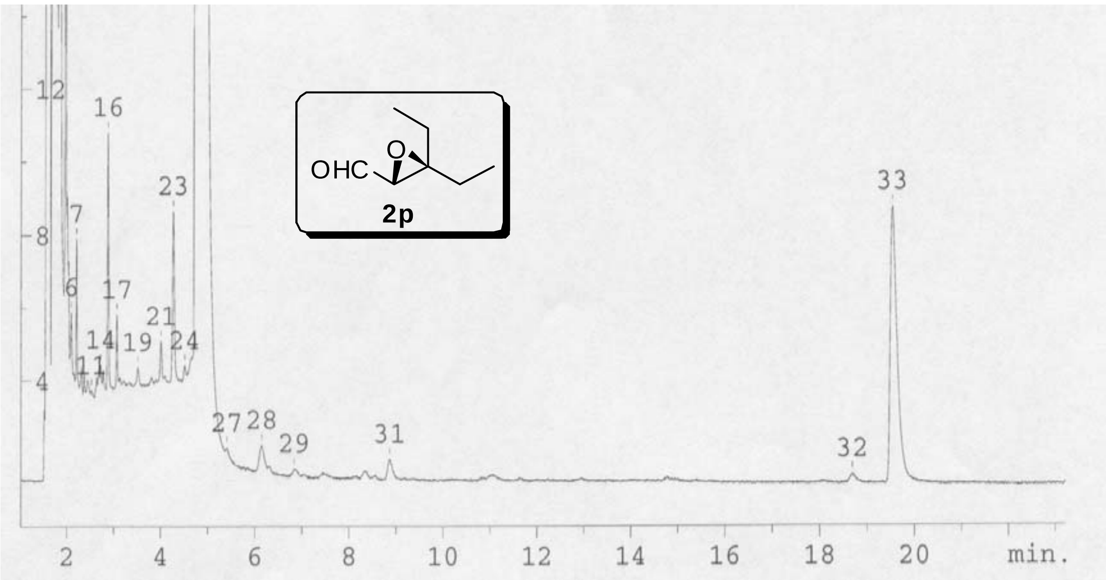


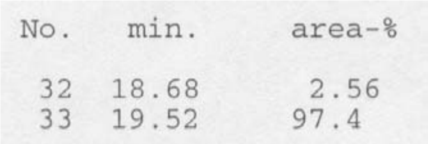
No.	min.	area-%
28	8.68	96.6
29	10.63	3.36



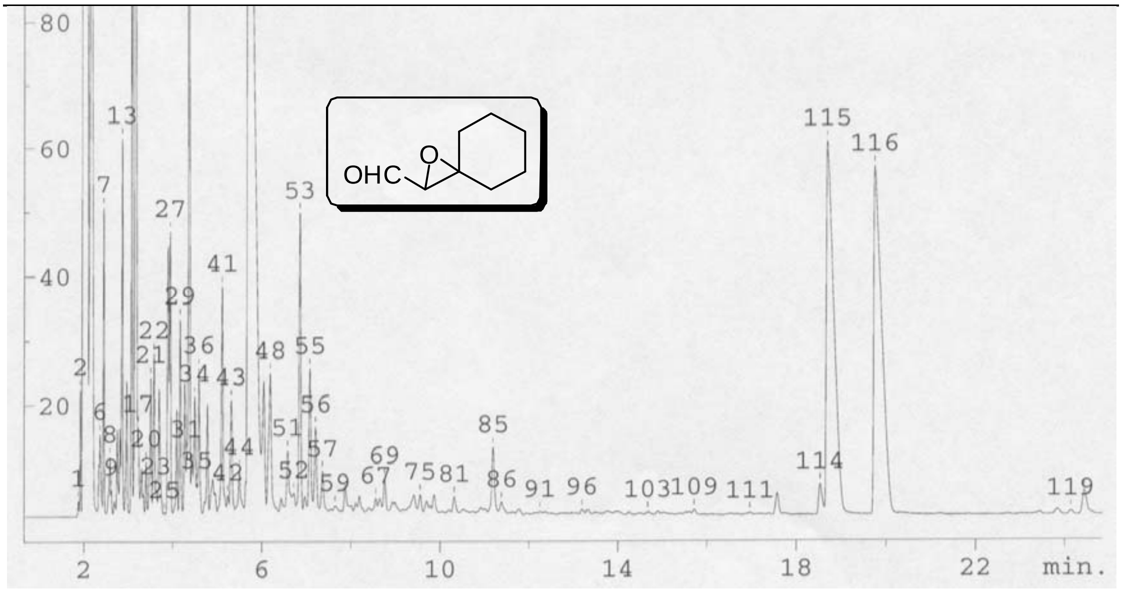


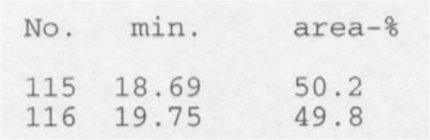
No.	min.	area-%
52	18.48	50.2
53	19.43	49.8



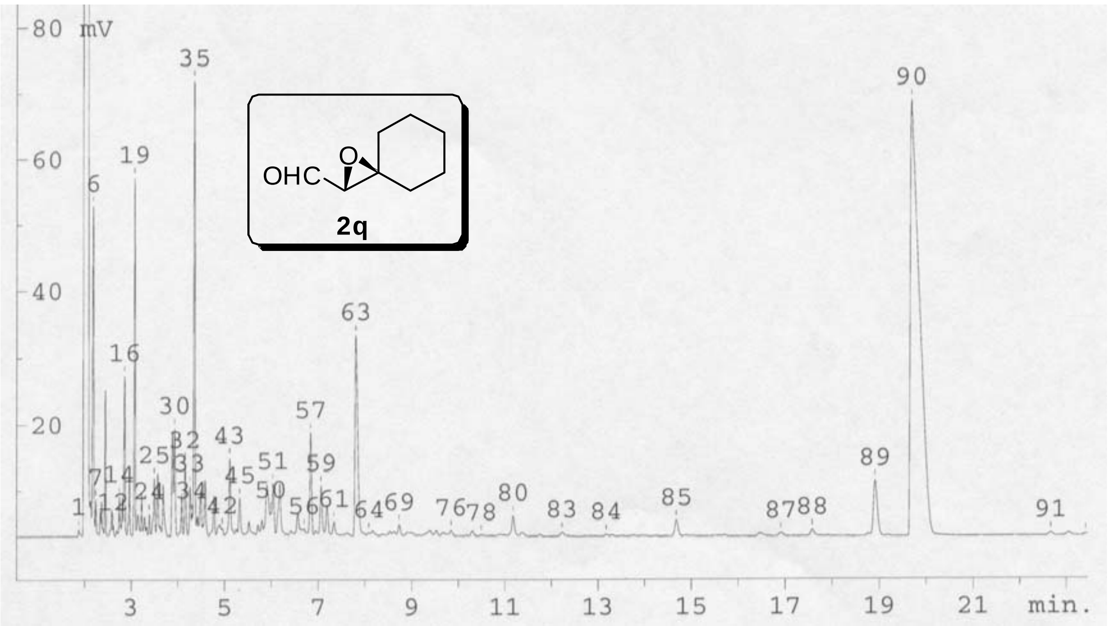


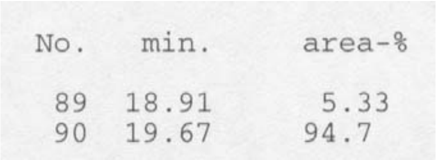
No.	min.	area-%
32	18.68	2.56
33	19.52	97.4



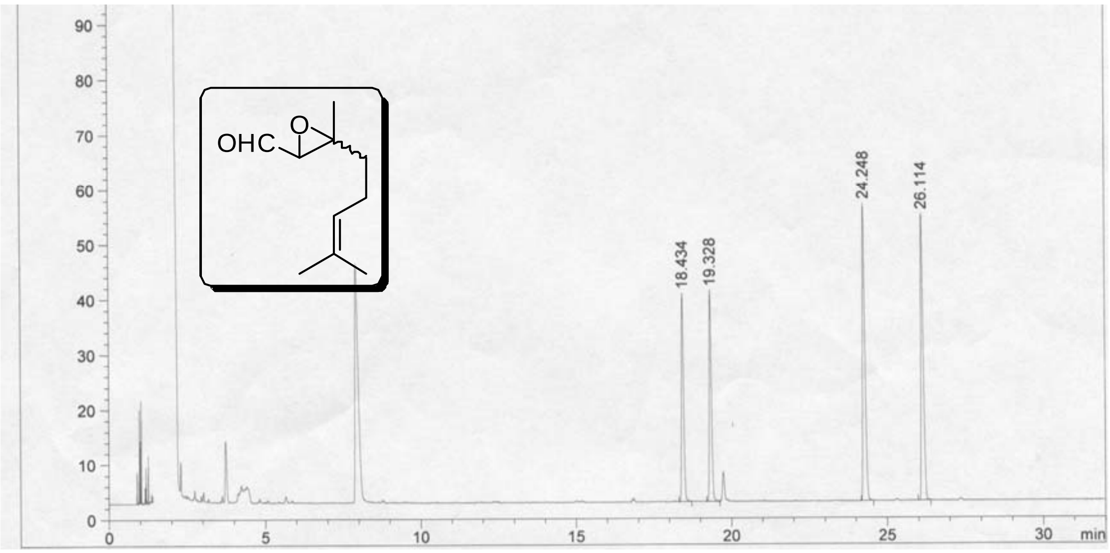


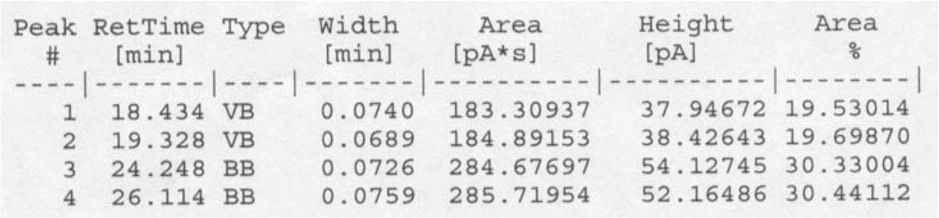
No.	min.	area-%
115	18.69	50.2
116	19.75	49.8



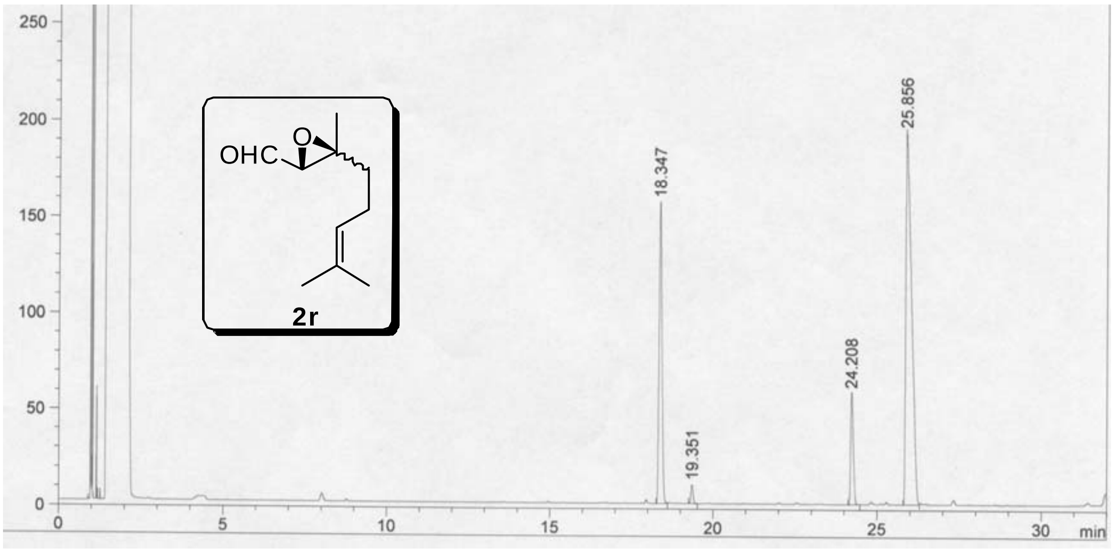


No.	min.	area-%
89	18.91	5.33
90	19.67	94.7





Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.434	VB	0.0740	183.30937	37.94672	19.53014
2	19.328	VB	0.0689	184.89153	38.42643	19.69870
3	24.248	BB	0.0726	284.67697	54.12745	30.33004
4	26.114	BB	0.0759	285.71954	52.16486	30.44112



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.347	BV	0.0922	979.67468	156.65112	26.48430
2	19.351	BB	0.0737	45.71507	9.93837	1.23585
3	24.208	BB	0.0784	327.63480	58.24188	8.85720
4	25.856	BV	0.1501	2346.05273	193.73680	63.42265