Supporting Information

Highly Stereoselective Ru(II)-Pheox Catalyzed Asymmetric Cyclopropanation of Terminal Olefins with Succinimidyl Diazoacetate

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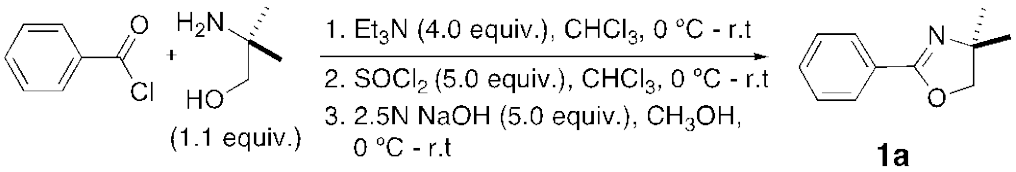
CONTENTS:

General: All reactions were performed under an atmosphere of argon unless otherwise noted. Dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) dehydrated were purchased from Kanto Chemical Co., Inc.. Acetonitrile and diethyl ether dehydrated were purchased from Wako Pure Chemical Industries, Ltd.. All reactions were monitored by thin layer chromatography (TLC), glass plates pre-coated with silica gel Merck KGaA 60 F_{254}, layer thickness 0.2 mm. All the starting materials are commercially available and were used after purification. The products were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid or by treatment with a solution of *p*-anisaldehyde. Flash column chromatography was performed using silica gel (Merck, Art. No. 7734). ^{1}H NMR (400 MHz or 300 MHz) and ^{13}C NMR (100 MHz or 75 MHz) spectra were recorded on Varian Inova-400 or Mercury-300 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane (0.00 ppm) in $CDCl_3$. Melting points were measured on a Yanaco MP-J3 and not corrected. Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Optical rotations were performed with a JASCO P-1030 polarimeter at the sodium D line (1.0 ml sample cell). Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) analyses with a JASCO GULLIVER using Daicel CHIRALPAK or CHIRALCEL columns.

1. Preparation of Ru(II)-phenyloxazoline complexes [2a and 2b].

Synthesis of 4,5-dihydro-4,4-dimethyl-2-phenyloxazole (*dm*-Pheox ligand) [1a].

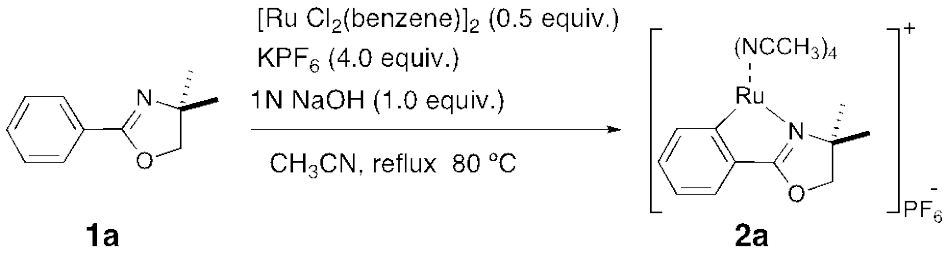


1a

To a mixture of 2-amino-2-methyl-1-propanol (784.4 mg, 8.8 mmol) and triethylamine (4.5 ml, 32 mmol) in dichloromethane (20.0 mL) was added a solution of benzoylchloride (928.6 ml, 8.0 mmol) in dichloromethane (15.0 mL) at 0 °C. After stirring for 10 h at room temperature, the reaction mixture was concentrated under reduce pressure. The residue was dissolved in $CHCl_3$ (20.0 mL) and was treated with $SOCl_2$ (3.0 mL, 40 mmol) at 0 °C. After stirring for 24 h at room temperature, the solvent and $SOCl_2$ were removed under reduce pressure. Saturated $NaHCO_3$ (aqua, 50 mL) was added to the residue with stirring for 5 min. The organic product was extracted with dichloromethane (3x50 mL), dried over anhydrous Na_2SO_4 or $MgSO_4$, filtered, and concentrated under reduced pressure. Subsequently, to a solution of the previous reaction residue in methanol (20.0 mL) was added 2.5N NaOH(aqua) (16.0 mL, 40 mmol, ca. 2.5 M) at 0 °C. After stirring for 12 h at room temperature, the solvent was removed under vacuo, followed by addition of water (30.0 mL) and

dichloromethane (3x25 mL) for extraction. The organic layer dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuo. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 10/1 v/v) to afford 4,5-dihydro-4,4-dimethyl-2-phenyloxazole (*dm*-Pheox) **1a** (1340.7 mg, 1.65 mmol) in 92% yield for 3 steps as a colorless oil. IR (NaCl, cm^{-1}) 3064, 2968, 1650, 1451, 1320, 1061, 967. ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 6H), 4.11 (s, 2H), 7.37-7.47 (m, 3H), 7.91-7.95 (m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 28.5, 67.6, 79.2, 128.1, 128.3, 128.4, 131.2, 162.1. Anal. $C_{11}H_{13}NO{\cdot}0.25H_2O$, Found: C 73.79, H 7.33, N 7.81%; Calcd: C 73.51, H 7.57, N 7.79%.

Synthesis of [4,5-dihydro-4,4-dimethyl-2-phenyloxazole $Ru(CH_3CN)_4]PF_6$ complex (Ru(II)-*dm*-Pheox complex) [2a].



1a **2a**

A two necked round bottom flask (100 mL) fittted with a magnetic stirring bar and a reflux condenser was charged with a mixture of **1a** (52.5 mg, 0.3 mmol), $[RuCl_2(benzene)]_2$ (75.0 mg, 0.15 mmol), and KPF_6 (220.9 mg, 1.2 mmol). The reaction flask was evacuated and backfilled with argon. Through the side arm CH_3CN (5.0 mL, degassed) and NaOH (aqua)(0.3 mL, 0.3 mmol, ca. 1.0 M) was injected. The suspended reaction medium was refluxed for 24 h at 80 ºC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_3CN/CH_2Cl_2 (1/20-1/10 (v/v)) to furnish the desired complex **2a** in 89% yield (155.5 mg, 0.266 mmol) as a yellow solid. Mp 89–90 °C. IR (KBr, cm^{-1}) 3039, 2978, 2936, 2271, 1625, 1452, 843. ^1H NMR(400 MHz, $CDCl_3$) d 1.36 (s, 6H), 2.01 (s, 3H), 2.15 (s, 3H), 2.52 (s, 3H), 2.54 (s, 3H), 4.39 (s, 2H), 6.94 (dd, *J* = 7.3, 7.5 Hz, 1H), 7.16 (dd, *J* = 7.3, 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H). ^1H NMR(400 MHz, CD_3CN) δ 1.40 (s, 6H), 1.98 (s, 3H), 2.12 (s, 3H), 2.19 (s, 3H), 2.52 (s, 3H), 4.46 (s, 2H), 6.91 (dd, *J* = 7.5, 7.6 Hz, 1H), 7.13 (dd, *J* = 7.5, 7.6 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR(100 MHz, CD_3CN) δ 3.7, 4.3, 27.4, 66.8, 82.3, 121.0, 122.5, 123.2, 126.0, 129.6, 136.5, 139.1, 173.0, 186.4. Anal. $C_{19}H_{24}F_6N_5OPRu$, Found: C 39.11, H 4.20, N 11.90%; Calcd: C 39.05, H 4.14, N 11.98%.

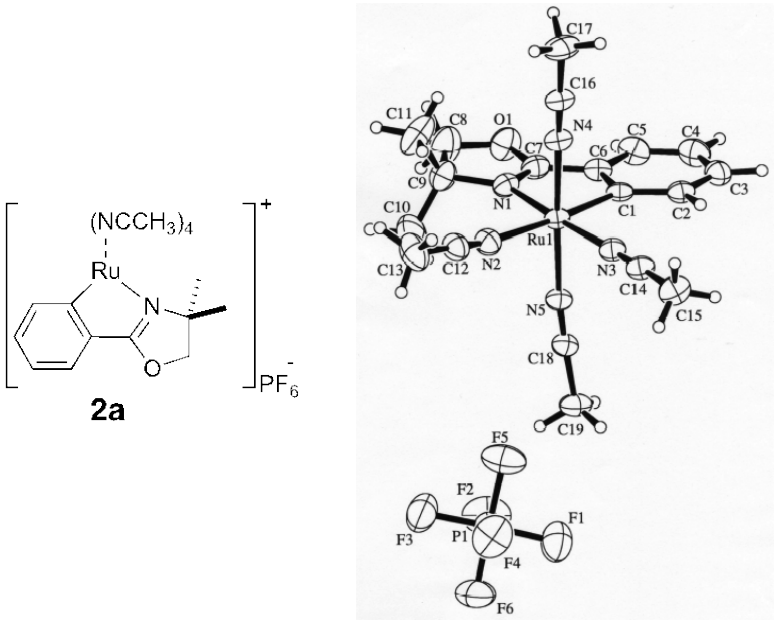
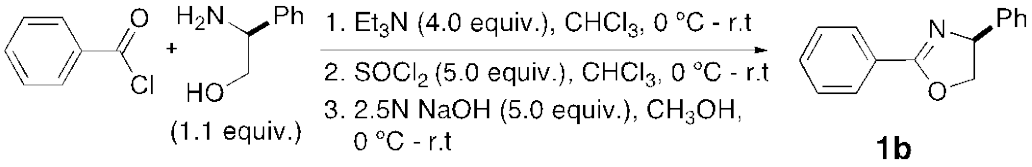


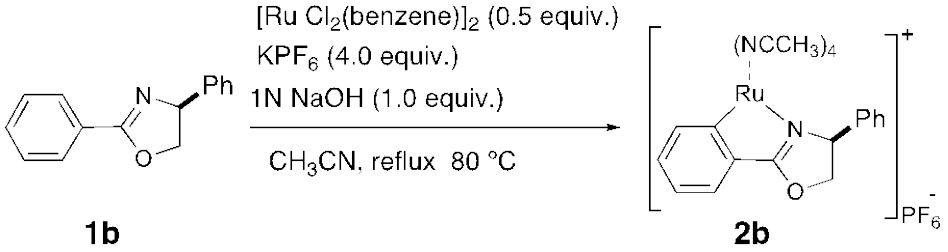
Figure 1. X-ray crystal structure of **2a**. Selected bond lengths (Å) and angles (°): Ru1-N1 = 2.088Å(3); Ru1-N2 = 2.147Å(4); Ru1-N3 = 2.032Å(4); N2-C12 = 1.132Å(4); C12-C13 = 1.446Å(7); N1-Ru1-C1 = 79.4°(2); N2-Ru1-C1 = 176.3°(1); C1-C6-C7 = 112.5°(4); Ru1-C1-C6 = 114.3°(3).

Synthesis of (*S*)-4,5-dihydro-2,4-diphenyloxazole (*Ph*-Pheox ligand) [1b].



Compound **1b** was synthesized from (*S*)-2-amino-2-phenylethanol in 86% yield for 3 steps by the same procedure as that for **1a** and was obtained as a yellow oil; $[\alpha]^{27}_{D} = -37.2°$ (c 1.02, $CHCl_3$ for >99% ee). IR (NaCl, cm^{-1}) 3062, 3030, 2898, 1646, 1495, 1358, 1065, 951. ^{1}H NMR(400 MHz, $CDCl_3$) δ 4.28 (dd, *J* = 8.2, 8.2 Hz, 1H), 4.80 (dd, *J* = 8.2, 10.1 Hz, 1H), 5.39 (dd, *J* = 8.2, 10.1 Hz, 1H), 7.27-7.55 (m, 8H), 8.03-8.08 (m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 70.2, 75.0, 126.8, 127.6, 127.7, 128.4, 128.5, 128.8, 131.6, 142.5, 164.8. Anal. $C_{15}H_{13}NO$, Found: C 80.76, H 6.02, N 6.26%; Calcd: C 80.69, H 5.87, N 6.27%.

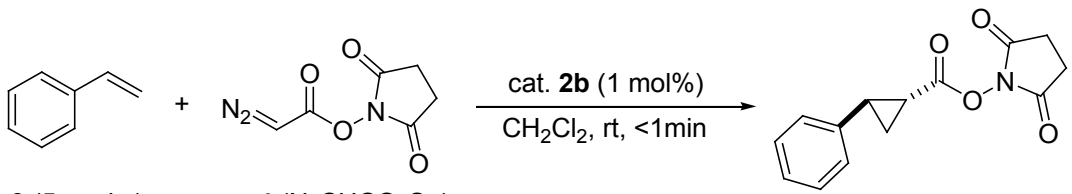
Synthesis of [(*S*)-4,5-dihydro-2,4-diphenyloxazole Ru(CH_3CN)$_4$]PF_6 complex (Ru(II)-*Ph*-Pheox complex) [2b].



1b **2b**

Complex **2b** was synthesized from **1b** in 82% yield by the same procedure as that for **2a** and was obtained as a yellow solid. Mp 92-93 ºC. IR (KBr, cm^{-1}) 3034, 2936, 2272, 1621, 1396, 846. ^{1}H NMR(400 MHz, CDCl3) δ 2.00 (s, 3H), 2.17 (s, 3H), 2.20 (s, 3H), 2.48 (s, 3H), 4.54 (dd, *J* = 7.3, 8.5 Hz, 1H), 5.09 (dd, *J* = 8.7, 9.9 Hz, 1H), 5.24 (dd, *J* = 7.3, 9.9 Hz, 1H), 6.83 (dd, *J* = 7.3, 7.7 Hz, 1H), 7.19 (dd, *J* = 7.3, 7.7 Hz, 1H), 7.28-7.35 (m, 5H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR(100 MHz, CDCl3) δ 2.9, 3.8, 3.9, 4.1, 67.6, 77.9, 120.1, 120.3, 120.4, 121.0, 121.4, 125.9, 127.8, 128.1, 128.2, 129.3, 134.3, 138.0, 141.4, 174.9, 186.0. Anal. $C_{23}H_{24}F_6N_5OPRu\cdot 1.0H_2O$, Found: C 42.20, H 3.95, N 10.42%; Calcd: C 42.47, H 4.03, N 10.77%.

2. General Procedure for 2b catalyzed intermolecular cyclopropanation of styrene with succinimidyl diazoacetate.



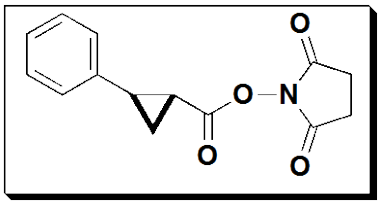
3 (5 equiv.) **4** (N_2CHCO_2Su) **5**

To the solution of succinimidyl diazocetate (36.6 mg, 0.2 mmol) and styrene (114.6 μL, 1 mmol) in CH_2Cl_2 (2.0 mL) was added Ru(II)-Pheox catalyst **2b** (0.002 mmol) at room temperature. After that we checked the TLC in less than 1 min, and we noticed the disapperance of the diazo compound. The residue was purified by column chromatography on silica gel (eluting with hexane/ ethyl acetate = 3/1). The diastereomeric ratio was determined by ^{1}H NMR of the crude product.

Note: Succinimidyl diazoacetate **4** was prepared by using the previously reported literature procedure.[1]

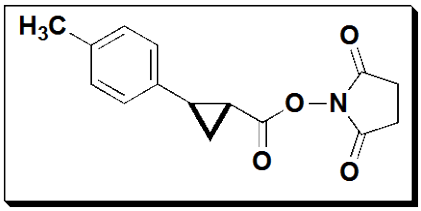
3. Analytical data for cyclopropanation products.

2,5-dioxopyrrolidin-1-yl 2-phenylcyclopropanecarboxylate (5a)[2] was obtained as a white solid



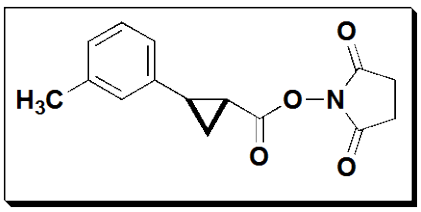
(50.9 mg, 98% yield). *trans/cis* = >99/<1, TLC (R_f) = 0.45 (hexane/ethyl acetate=1/1). $[\alpha]^{27}_D$= -251 (c = 0.62, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.39 (m, 3H), 7.11-7.17 (m, 2H), 2.85 (bs, 4H), 2.69-2.79 (m, 1H), 2.11-2.19 (m, 1H), 1.75-1.83 (m, 1H), 1.55-1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 18.7, 21.2, 25.9, 28.6, 126.7, 127.4, 128.9, 138.6, 169.1, 169.5. IR (NaCl, cm^{-1}) 3031, 2948, 1810, 1787, 1741. Anal. $C_{14}H_{13}NO_4$, Found: C 65.29, H 5.28, N 5.08%; Calcd: C 64.86, H 5.05, N 5.40%.

2,5-dioxopyrrolidin-1-yl 2-*p*-tolylcyclopropanecarboxylate (5b)[2] was obtained as a white solid



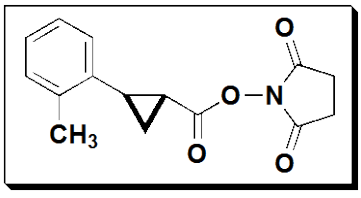
(52.1 mg, 95% yield). *trans/cis* = >99/<1. TLC (R_f) = 0.50 (hexane/ethyl acetate=1/1). $[\alpha]^{27}_D$= -272 (c = 0.47, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ 7.12 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 2.83 (bs, 4H), 2.67-2.76 (m, 1H), 2.33 (s, 3H), 2.07-2.15 (m, 1H), 1.81-1.87 (m, 1H), 1.53-1.62 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 18.61, 21.11, 21.31, 25.86, 28.38, 126.59, 129.58, 135.59, 137.12, 169.13, 169.51. IR (NaCl, cm^{-1}) 2925, 1799, 1753. Anal. $C_{15}H_{15}NO_4$, Found: C 66.32, H 5.83, N 4.83%; Calcd: C 65.92, H 5.53, N 5.13%.

2,5-dioxopyrrolidin-1-yl 2-*m*-tolylcyclopropanecarboxylate (5c) was obtained as a white solid (53



mg, 97% yield). *trans/ci s*=>99/<1. TLC (R_f) = 0.3 (hexane/ethyl acetate=3/1). $[\alpha]^{24}_D$= -251 (c= 0.43, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ 7.20 (t, *J* = 15 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.90-7.01 (m, 2H), 2.84 (bs, 4H), 2.67-2.76 (m, 1H), 2.34 (s, 3H), 2.10-2.18 (m, 1H), 1.73-1.81 (m, 1H), 1.55-1.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 18.67, 21.14, 21.64, 25.85, 28.56, 123.57, 127.12, 128.17, 129.11, 138.59, 169.12, 169.60. IR (NaCl, cm^{-1}) 3076, 3030, 2960, 1799, 1776, 1741. Anal. $C_{15}H_{15}NO_4$, Found: C 65.96, H 5.57, N 4.96%; Calcd: C 65.92, H 5.53, N 5.13%.

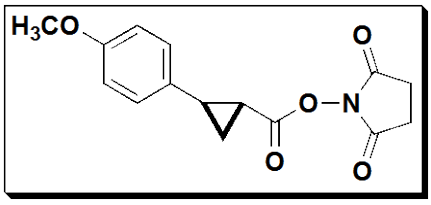
2,5-dioxopyrrolidin-1-yl 2-*o*-tolylcyclopropanecarboxylate (5d) was obtained as a white solid (50.3



mg, 92% yield). *trans/cis* = >99/>1. TLC (R_f) = 0.4 (hexane/ethyl acetate=3/1). $[\alpha]^{25}_D$ = -209 (c = 0.57, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ 7.16-7.25 (m, 3H), 6.94 (d, *J* = 12.5 Hz, 1H), 2.85 (bs, 4H), 2.67-2.76 (m, 1H), 2.34 (s, 3H), 2.10-2.18 (m, 1H), 1.73-1.81 (m, 1H),

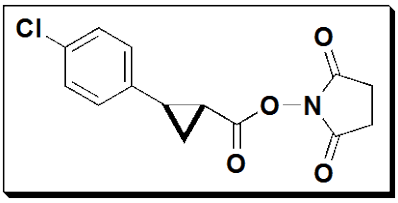
1.55-1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.69, 19.81, 25.88, 27.59, 126.23, 127.66, 130.39, 136.53, 138.78, 169.54. IR (NaCl, cm^{-1}) 3076, 3019, 2972, 1810, 1787, 1753. Anal. $C_{15}H_{15}NO_4$, Found: C 66.32, H 5.54, N 5.07%; Calcd: C 65.92, H 5.53, N 5.13%.

2,5-dioxopyrrolidin-1-yl 2-(4-methoxyphenyl)cyclopropanecarboxylate (5e)[2] was obtained as a



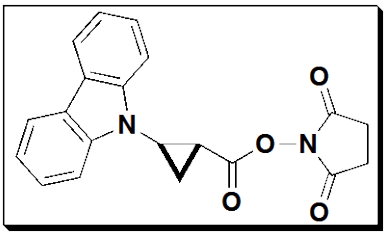
white solid (56.7 mg, 98% yield). *trans*/*cis* = >99/<1. TLC (R_f) = 0.20 (hexane/ethyl acetate=3/1). $[\alpha]^{22}_D$= -260 (c = 0.46, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.83 (bs, 4H), 2.67-2.76 (m, 1H), 2.03-2.10 (m, 1H), 1.70-1.80 (m, 1H), 1.51-1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.34, 20.96, 25.86, 28.09, 55.61, 114.36, 127.92, 130.6, 159.07, 169.12, 169.5. IR (NaCl, cm^{-1}) 3065, 2925, 2844, 1810, 1787, 1741 cm^{-1}. Anal. $C_{15}H_{15}NO_5$, Found: C 62.76, H 5.35, N 4.54%; Calcd: C 62.28, H 5.23, N 4.84%.

2,5-dioxopyrrolidin-1-yl 2-(4-chlorophenyl)cyclopropanecarboxylate (5f)[2] was obtained as a white



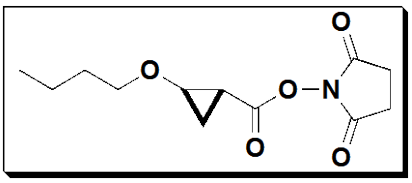
solid (54 mg, 92% yield). *trans*/*cis* = >99/<1. TLC (R_f) = 0.3 (hexane/ethyl acetate=3/1). $[\alpha]^{27}_D$= -210 (c = 0.52, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 2.85 (bs, 4H), 2.67-2.76 (m, 1H), 2.07-2.15 (m, 1H), 1.81-1.87 (m, 1H), 1.53-1.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 21.2, 25.8, 27.8, 128.11, 129.06, 133.19, 137.16, 168.85, 169.47. IR (NaCl, cm^{-1}) 3076, 2995, 2948, 1810, 1787, 1741. Anal. $C_{14}H_{12}ClNO_4$, Found: C 56.96, H 4.28, N 4.45%; Calcd.: C 57.25, H 4.12, N 4.77%.

2,5-dioxopyrrolidin-1-yl 2-(9H-carbazol-9-yl)cyclopropanecarboxylate (5g) was obtained as a

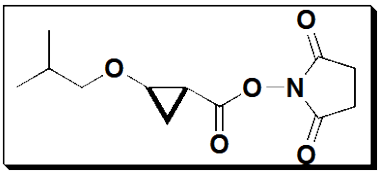


white solid (69 mg, 99% yield). *trans*/*cis* = >99/<1. TLC (R_f) = 0.20 (hexane/ethyl acetate=3/1). $[\alpha]^{24}_D$= -234 (c= 0.89, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 8 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 8.2 Hz, 2H), 3.92-3.99 (m, 1H), 2.91 (bs, 4H), 2.46-2.57 (m, 1H), 2.16-2.25 (m, 1H), 2.02-2.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.79, 20.02, 25.87, 35.07, 110.05, 120.34, 120.66, 123.53, 126.51, 140.78, 167.9, 169.3. IR (NaCl, cm^{-1}) 3066, 2357, 1782, 1743. Anal. $C_{20}H_{16}N_2O_4$, Found: C 68.93, H 4.81, N 7.58%; Calcd: C 68.96, H 4.63, N 8.04%.

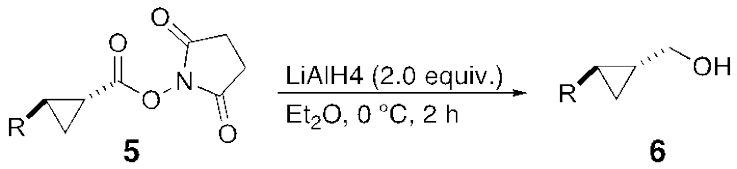
2,5-dioxopyrrolidin-1-yl 2-butoxycyclopropanecarboxylate (5h) was obtained as a colorless oil (48 mg, 94% yield). *trans*/*cis* = >99/<1. TLC (R_f) = 0.4 (hexane/ethyl acetate=3/1). $[\alpha]^{25}_D$= -74 (c = 0.815, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71-3.77 (m, 1H), 3.53-3.66 (m, 2H), 3.79 (s, 3H), 2.82 (bs, 4H), 1.95-2.09 (m, 1H), 1.43-1.61 (m, 4H), 1.28-1.42 (m, 2H), 1.51 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 17.71, 18.64, 19.46, 25.85, 31.6, 62.75, 71.8, 168.18, 169.63. IR (NaCl, cm^{-1}) 2960, 2867, 1787, 1741. Anal. $C_{12}H_{17}NO_5$•0.2CH_2Cl_2, Found: C 55.30, H 6.54, N 5.39%; Calcd: C 55.26, H 6.61, N 5.28%.



2,5-dioxopyrrolidin-1-yl 2-*iso*-butoxycyclopropanecarboxylate (5i) was obtained as a colorless oil (48 mg, 94% yield). *trans*/*cis* = >99/<1. TLC (R_f) = 0.30 (hexane/ethyl acetate=3/1). $[\alpha]^{27}_D$= -75 (c = 0.565, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71-3.78 (m, 1H), 3.28-3.43 (m, 2H), 2.81 (bs, 4H), 1.94-2.02 (m, 1H), 1.77-1.93 (m, 1H), 1.43-1.57 (m, 2H), 1.51 (d, J = 2.5 Hz, 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.86, 18.64, 19.49, 25.86, 28.48, 62.89, 78.66, 168.2, 169.65. IR (NaCl, cm^{-1}) 2960, 2879, 1787, 1741. Anal. $C_{12}H_{17}NO_5$•0.05CH_2Cl_2, Found: C 55.81, H 6.62, N 5.43%; Calcd: C 55.77, H 6.64, N 5.40%.



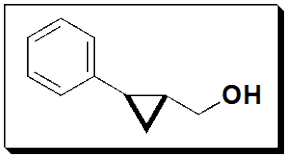
4. General procedure for synthesis of cyclopropylmethanols.



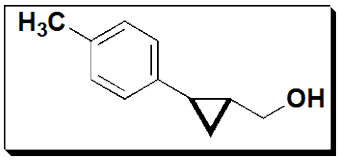
5 **6**

To the solution of succinimidyl cyclopropyl carboxylate derivatives **5** (0.2 mmol) in Et_2O (3.0 mL) was added lithium aluminium hydride (15.2 mg, 0.4 mmol) at 0 ºC. After stirring for 2 h at same temperature, the reaction solution was quenched with water (0.5 mL), filtered, and evaporated under vacuo. The crude cyclopropylmethanol product was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 2/1) to the desired cyclopropylmethanol product. The diastereomeric ratio was determined by ^{1}H NMR of the crude product and the enantiomeric excess of the *trans* product was determined by chiral HPLC analysis.

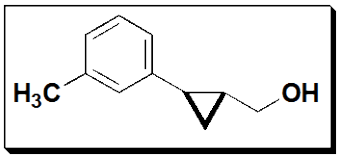
5. Analytical data for cyclopropylmethanol products.

2-phenylcyclopropylmethanol (6a) was obtained as a yellow oil (80% yield). *trans*/*cis* = >99/<1, 

trans ee = 98%. TLC (R_f) = 0.50 (hexane/ethyl acetate=1/1). $[\alpha]^{23}_D$= -82 (c = 0.485, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.57-3.69 (m, 2H), 1.79-1.87 (m, 1H), 1.40-1.53 (m, 2H), 0.89-1.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.18, 21.63, 25.66, 66.95, 126.0, 126.15, 128.69, 142.74. IR (NaCl, cm^{-1}) 3274, 3030, 2925, 1706. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 9/1. Anal. $C_{10}H_{12}O•0.45H_2O$, Found: C 77.97, H 7.84%; Calcd: C 77.61, H 8.04%.

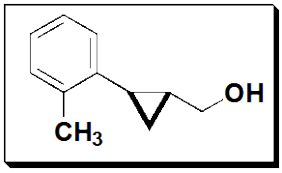
2-*p*-tolylcyclopropylmethanol (6b) was obtained as a colorless oil (81% yield). *trans*/*cis* = >99/<1, 

trans ee = >99%. TLC (R_f) = 0.50 (hexane/ethyl acetate=2/1). $[\alpha]^{23}_D$= -71 (c = 0.41, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 3.55-3.67 (m, 2H), 2.31 (s, 3H), 1.76-1.84 (m, 1H), 1.37-1.49 (m, 2H), 0.86-0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 21.27, 21.29, 25.41, 67.01, 126.10, 129.36, 135.53, 139.61. IR (NaCl, cm^{-1}) 3355, 3019, 2920, 2871, 1729. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 9/1. Anal. $C_{11}H_{14}O•0.1CH_2Cl_2$: Found: C 77.79, H 8.21%; Calcd: C 78.09, H 8.38%.

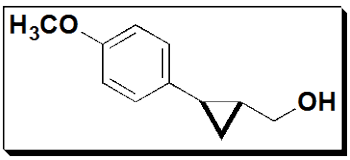
2-*m*-tolylcyclopropylmethanol (6c) was obtained as a colorless oil (87% yield). *trans*/*cis* = >99/<1, 

trans ee = 91%. TLC (R_f) = 0.40 (hexane/ethyl acetate=2/1). $[\alpha]^{23}_D$ = -62 (c = 0.88, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (t, *J* = 14.8 Hz, 1H), 6.97 (d, *J* = 7.1 Hz, 1H), 6.85-6.91 (m, 2H), 3.62 (d, *J* = 6.6 Hz 2H), 2.31 (s, 3H), 1.77-1.83 (m, 1H), 1.40-1.48 (m, 1H), 0.88-1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.07, 21.55, 21.73, 25.52, 66.94, 123.11, 126.76, 126.99, 128.60, 138.26, 142.67. IR (NaCl, cm^{-1}) 3378, 3019, 2925, 2867, 1729 cm^{-1}. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 9/1. Anal. $C_{11}H_{14}O•0.3H_2O$, Found: C 78.76, H 8.55%; Calcd: C 78.81, H 8.78%.

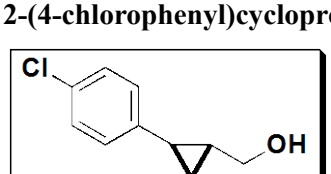
2-*o*-tolylcyclopropylmethanol (6d) was obtained as a colorless oil (73% yield). *trans*/*cis* = >99/<1, *trans* ee = 91%. TLC (R_f): 0.50 (hexane/ethyl acetate=2/1). $[\alpha]^{23}_D$ = -55 (c = 0.77, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08-7.17 (m, 3H), 6.98-7.01 (m, 1H), 3.74 (dd, *J* = 6.7, 11.1 Hz, 1H), 3.63 (dd, *J* = 6.9, 11.3 Hz, 1H), 2.42 (s, 3H), 1.80-1.86 (m, 1H), 1.35-1.45 (m, 1H), 0.86-0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.96, 19.70, 20.04, 23.54, 67.13, 126.03, 126.19, 126.29, 130.02, 137.92, 140.09. IR (NaCl, cm^{-1}) 3355, 3019, 2925, 2867. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 20/1. Anal. $C_{11}H_{14}O$•$0.1CH_2Cl_2$, Found: C 77.85, H 8.38%; Calcd: C 78.09, H 8.38%.



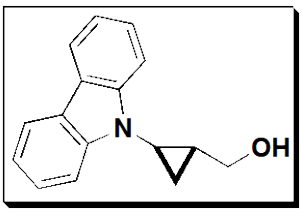
2-(4-methoxyphenyl)cyclopropylmethanol (6e) was obtained as a white solid (81% yield). *trans*/*cis* = >99/<1, *trans* ee = 92%. TLC (R_f) = 0.30 (hexane/ethyl acetate=2/1). $[\alpha]^{23}_D$ = -63 (c = 0.72, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 3H), 3.64 (dd, *J* = 4.6, 8.9 Hz, 1H), 3.58 (dd, *J* = 6.9, 11.3 Hz, 1H), 1.77-1.83 (m, 2H), 1.37-1.48 (m, 1H), 0.87-0.97 (m, 2H). IR (NaCl, cm^{-1}) 3309, 2995, 2925 2832, 1891. ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.67, 20.91, 25.05, 55.65, 67.00, 114.14, 127.30, 134.66, 158.07. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 30/1. Anal. $C_{11}H_{14}O_2$, Found: C 73.67, H 8.0%; Calcd: C 74.13, H 7.92%.



2-(4-chlorophenyl)cyclopropylmethanol (6f) was obtained as a colorless oil (81% yield). *trans*/*cis* = >99/<1, *trans* ee = >99%. TLC (R_f): 0.2 (hexane/ethyl acetate=4/1). $[\alpha]^{20}_D$ = -69 (c= 0.495, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.62 (d, *J* = 6.6 Hz, 2H), 1.76-1.84 (m, 1H), 1.36-1.48 (m, 2H), 0.91-0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.19, 21.09, 25.70, 26.69, 127.54, 128.73, 131.57, 141.30. IR (NaCl, cm^{-1}) 3378, 3007, 2925, 2867, 1787, 1741, 1706. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 0.5 ml/min, Eluent: hexane/2-propanal= 95/5. Anal. $C_{10}H_{11}ClO$•$0.14CH_2Cl_2$, Found: C 62.89, H 5.82%; Calcd: C 62.60, H 5.84%.

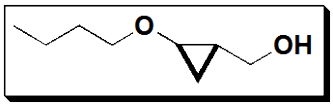


2-(9*H*-carbazol-9-yl)cyclopropylmethanol (6g) was obtained as a white solid (90% yield). *trans*/*cis* = >99/<1, *trans* ee = 98%. TLC (R_f) = 0.3 (hexane/ethyl acetate=4/1). $[\alpha]^{23}_D$ = -62 (c= 0.78, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* =



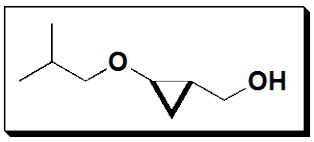
7.4 Hz, 2H), 4.04 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.74 (dd, *J* = 11.5, 7.9 Hz, 1H), 3.19-3.24 (m, 1H), 1.79-1.90 (m, 1H), 1.31-1.37 (m, 1H), 1.22-1.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.02, 22.66, 29.29, 65.01, 110.41, 119.57, 120.49, 123.26, 125.98, 141.52. IR (NaCl, cm^{-1}) 3320, 3052, 2937, 2867, 1729. HPLC condition: Daicel CHIRALPAK OD-H, UV Detector: 254 nm, Flow rate: 1 ml/min, Eluent: hexane/2-propanal = 9/1. Anal. $C_{16}H_{15}NO•0.2H_2O$, Found: C 79.63, H 6.35, N 5.57%; Calcd: C 79.77, H 6.44, N 5.81%.

2-butoxycyclopropylmethanol (6h) was obtained as a colorless oil (70% yield). *trans*/*cis* = >99/<1.



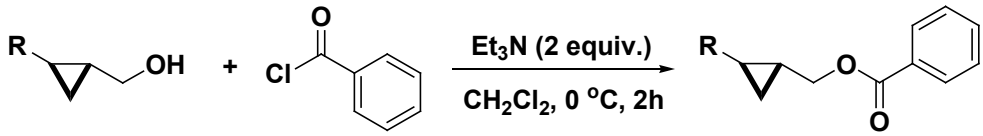
TLC (R_f) = 0.4 (hexane/ethyl acetate=4/1). $[\alpha]^{19}_D$ = -31 (c = 0.53, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.41-3.50 (m, 4H), 3.10-3.14 (m, 1H), 1.80-1.56 (m, 2H), 1.25-1.40 (m, 3H), 0.91 (t, *J*= 7.3 Hz, 3H), 0.77-0.84 (m, 1H), 0.44-0.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.84, 14.20, 19.65, 21.82, 31.95, 57.85, 64.66, 70.95. IR (NaCl, cm^{-1}) 3431, 2959, 2929, 2868, 1732. Anal. $C_8H_{16}O_2•0.48CH_2Cl_2$, Found: C 55.28, H 9.09%; Calcd: C 55.06, H 9.24%.

2-isobutoxycyclopropylmethanol (6i) was obtained as a colorless oil (86% yield). *trans*/*cis* = >99/<1.



TLC (R_f): 0.3 (hexane/ethyl acetate = 2/1). $[\alpha]^{23}_D$= -46(c = 0.17, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37-3.49 (m, 2H), 3.25 (d, *J* = 6.6 Hz, 2H), 3.10-3.14 (m, 1H), 1.82 (sept, 1H), 1.24-1.35 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 6H), 0.78-0.85 (m, 1H), 0.43-0.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.90, 19.72, 21.90, 28.59, 58.00, 64.72, 78.11. IR (NaCl, cm^{-1}) 3401, 2959, 2868. Anal. $C_8H_{16}O_2•0.4CH_2Cl_2$, Found: C 56.48, H 9.34%; Calcd: C 56.62, H 9.5%.

6. General procedure for acylation of cyclopropylmethanol products.



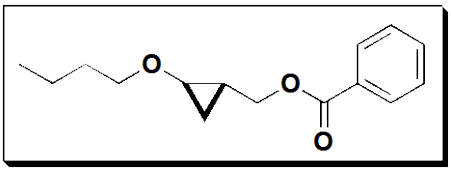
6h; R= *n*-BuO
6i; R= *i*-BuO

(1.2 equiv.)

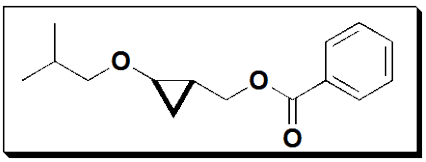
7h; R= *n*-BuO
7i; R= *i*-BuO

To the solution of cyclopropylmethanol **6h** or **6i** (0.1 mmol) and triethylamine (30 μL, 0.2 mmol) in CH_2Cl_2 (1.0 mL) was slowly added benzoyl chloride (0.12 mmol) at 0 ºC. After stirring for 2h at same temperature, the residue was purified by silica gel column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give the desired product.

2-butoxycyclopropylmethyl benzoate (7h) was obtained as a colorless oil (83% yield). *trans*/*cis* = >99/<1, *trans* ee = >99%. TLC (R_f) = 0.4 (hexane/ethyl acetate=10/1). $[\alpha]^{18}_D$ = -8 (c = 0.515, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 4.23 (dd, 11.8 Hz, 6.9 Hz, 1H), 4.05 (dd, 11.3 Hz, 8.3 Hz, 1H), 3.49 (t, *J* = 6.5 Hz, 2H), 3.23-3.30 (m, 1H), 1.24-1.62 (m, 5H), 0.86-0.99 (m, 4H), 0.59-0.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.48, 14.19, 18.33, 19.65, 31.87, 58.13, 66.72, 71.01, 128.70, 129.93, 130.64, 133.29, 167.00. IR (cm^{-1}) 2964, 2936, 2870, 1726. HPLC condition: Daicel CHIRALPAK OK, UV Detector: 254 nm, Flow rate: 0.3 ml/min, Eluent: hexane/2-propanal= 400/1. Anal. $C_{15}H_{20}O_3 \cdot 0.3H_2O$, Found: C 71.24, H 7.88%; Calcd: C 71.01, H 8.18%.



2-isobutoxycyclopropylmethyl benzoate (7i) was obtained as colorless oil (75% yield). *trans*/*cis* = >99/<1, *trans* ee = >99%. TLC (R_f): 0.4 (hexane/ethyl acetate=30/1). $[\alpha]^{19}_D$= -16 (c = 0.26, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 4.22 (dd, 11.8 Hz, 7.1 Hz, 1H), 4.06 (dd, 11.3 Hz, 8.3 Hz, 1H), 3.26 (d, 2H), 1.84 (sept, 1H), 1.39-1.50 (m, 1H), 0.90-0.96. (m, 1H), 0.88 (d, 2.2 Hz, 3H), 0.86 (d, 2.0 Hz, 3H), 0.59-0.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.58, 18.36, 19.68, 28.45, 58.23, 66.72, 78.13, 128.70, 129.93, 130.65, 133.29, 167.00. IR (cm^{-1}) 2964, 2870, 1726. HPLC condition: Daicel CHIRALPAK OK, UV Detector: 254 nm, Flow rate: 0.3 ml/min, Eluent: hexane/2-propanal= 800/1. Anal. $C_{15}H_{20}O_3 \cdot 0.2H_2O$, Found: C 71.20, H 7.85%; Calcd: C 71.51, H 8.16%.



7. Linear effect.

To explore the behavior of Ru(II)-Pheox complex in the catalytic asymmetric cyclopropanation of succinimidyl diazoacetate with olefins, we examined the correlation between the optical purities of the ligand with the optical purities of *trans* product. As a general method, we adjusted the optical purities of the ligand **1b** to be 30% ee, 70% ee, and 100% ee and was then mixed with $[RuCl_2(benzene)]_2$ under basic condition to form Ru(II)-Pheox complexes **2b**. After using these catalysts in the cyclopropanation of *p*-methyl styrene with succinimidyl diazoacetate, we observed the linear correlation between the optical purities of the ligand and the *trans* product as shown in Figure 2. Therefore, the catalyst proceeded by 1:1 with substrate as a molecular catalyst.

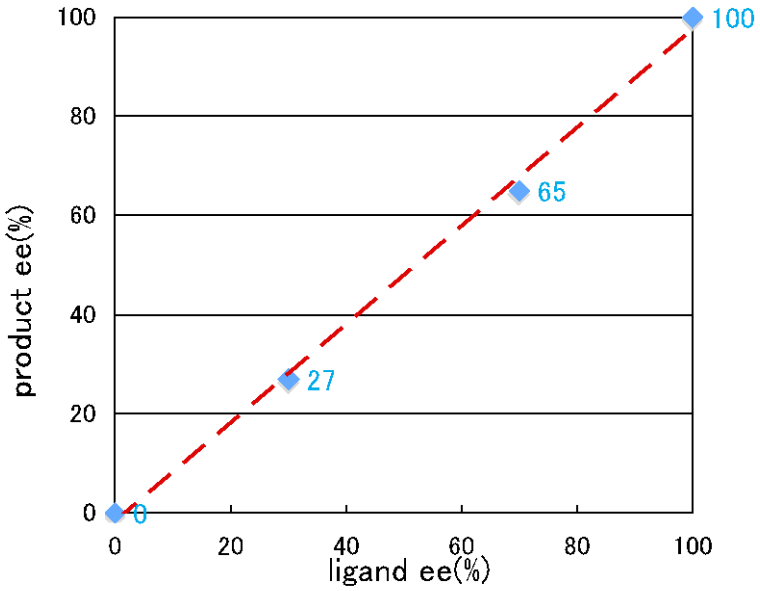
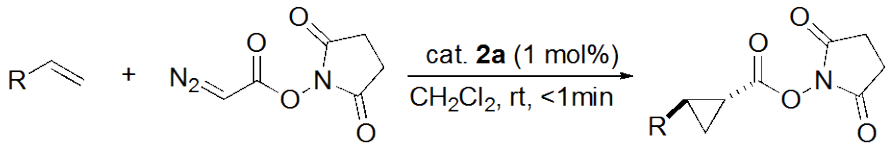
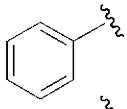
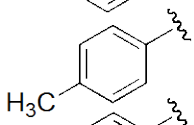
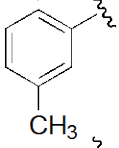
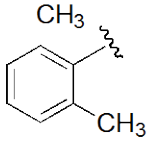
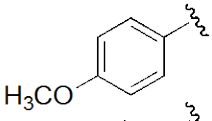
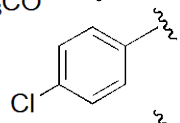
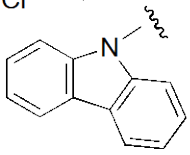
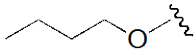
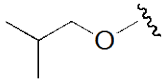


Figure 2. Linear correlation of *Ph*-Pheox ligand ees with *trans*-product ees.

8. Catalytic symmetric cyclopropanation by using 2a.



3 (5 equiv.) **4** (N_2CHCO_2Su)

Entry	R	yield(%)[b]	*trans*:*cis*[c]
1		99	>99:<1
2		90	>99:<1
3		94	>99:<1
4		95	>99:<1
5		84	>99:<1
6		84	>99:<1
7		91	>99:<1
8		91	>99:<1
9		95	>99:<1

[a] Reactions were carried out in CH_2Cl_2 for 1 min on a 0.2 mmol scale with a molar ratio of cat/succinimidyl diazoacetate/styren= 0.01/1/5. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis.

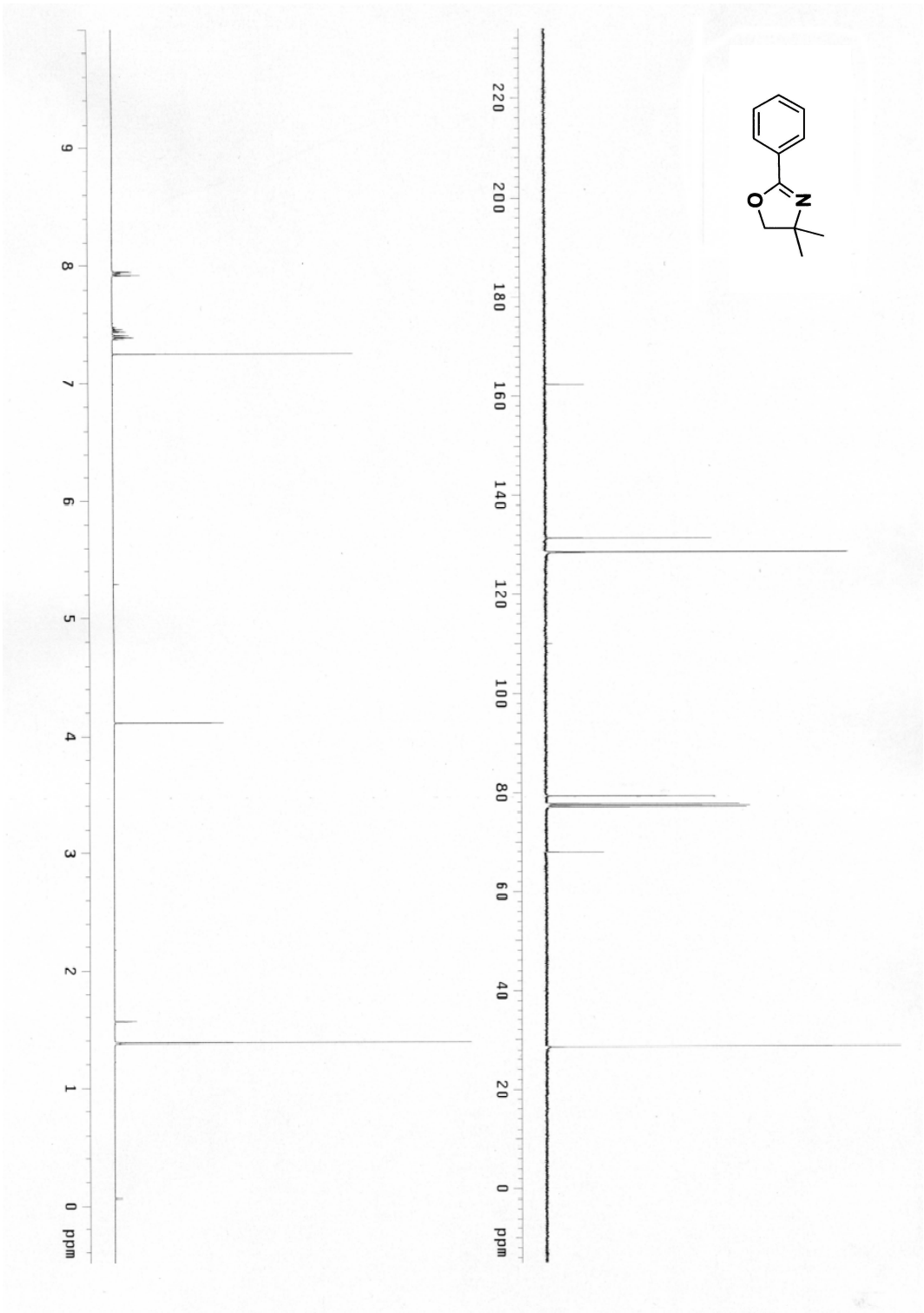
References

1- (a) Ouihia, A.; René, L.; Guilhem, J.; Pascard, C.; Badet, B. *J. Org. Chem*. **1993**, *58*, 1641. (b) Doyle, M. P.; Klinin, A. V. J. Org. Chem. 1996, 61, 2179.

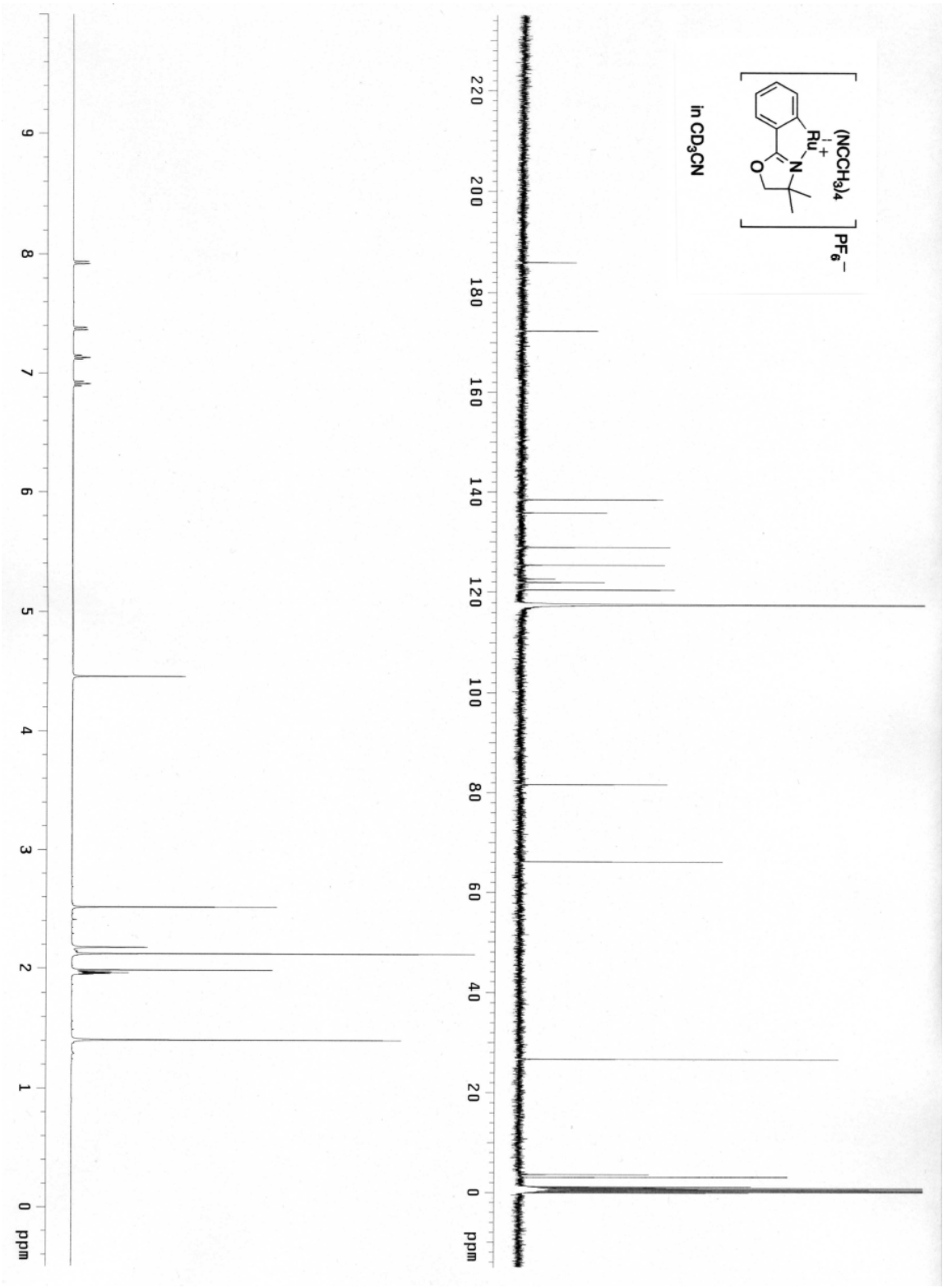
2- Ruppel, J. V.; Gauthier, T. J.; Snyder, N. L.; Perman, J. A.; Zhang, X. P. *Org. Lett.* **2009**, *11*, 2273.

9. NMR and HPLC Spectral data.

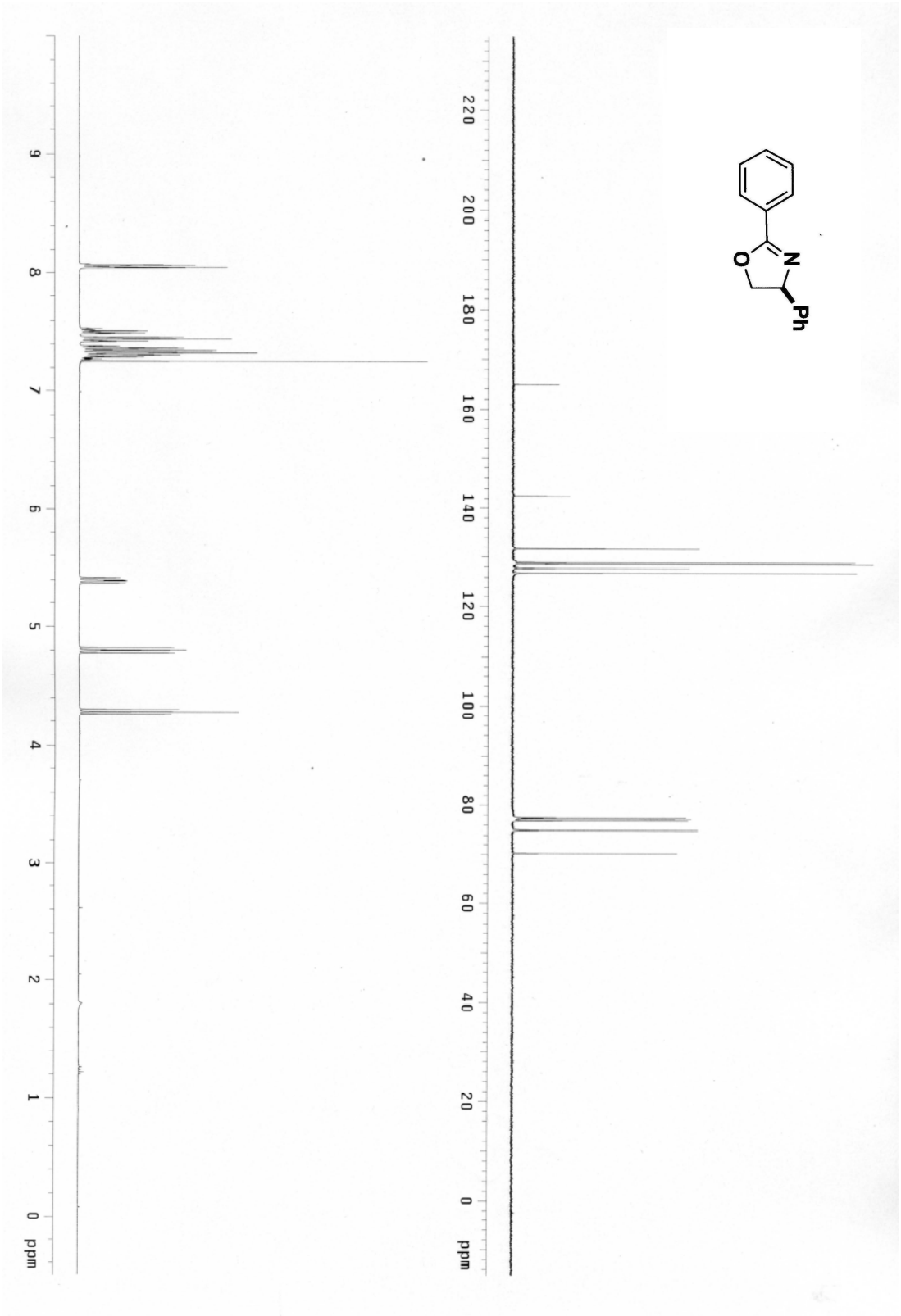
^{1}H NMR and ^{13}C NMR (*dm*-Pheox ligand) **1a**.



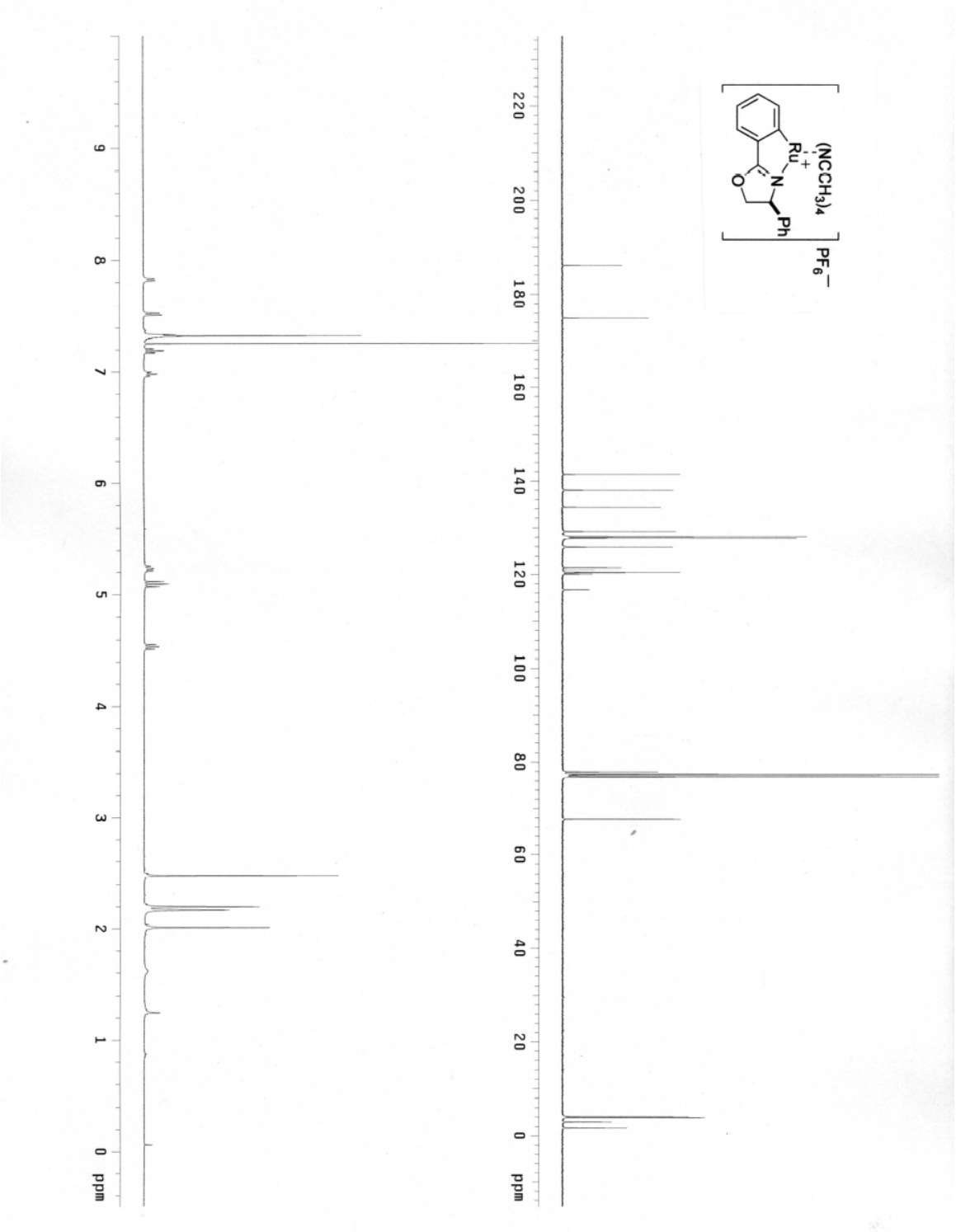
^{1}H NMR and ^{13}C NMR [Ru-*dm*-Pheox$(CH_3CN)_4$]PF_6 **2a**.

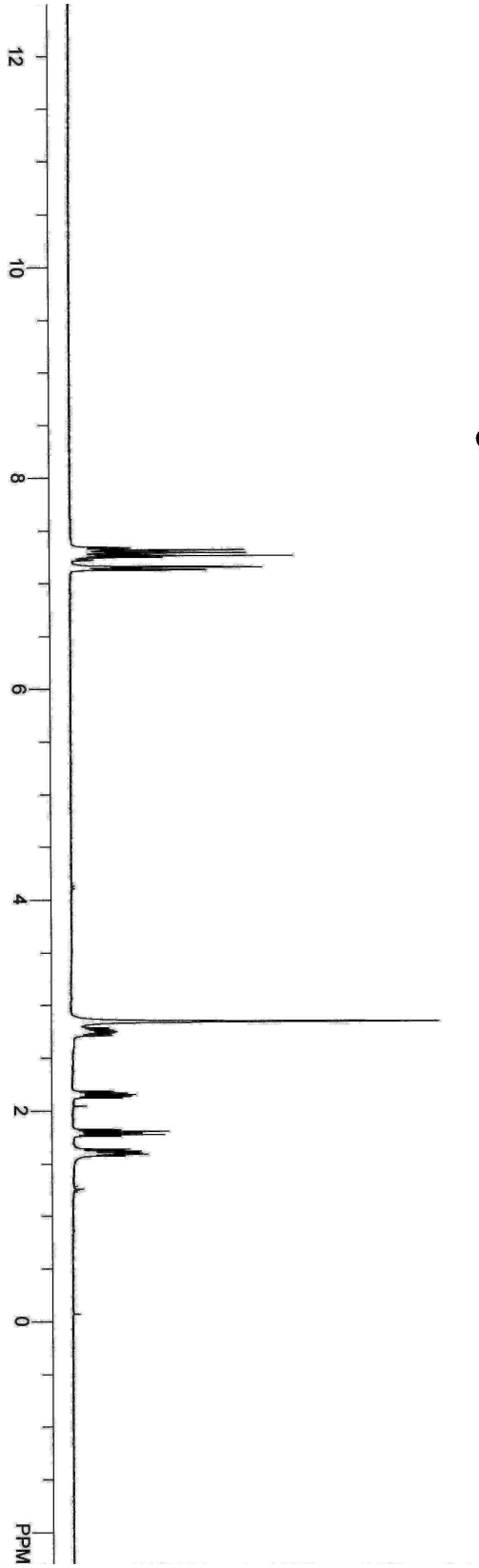


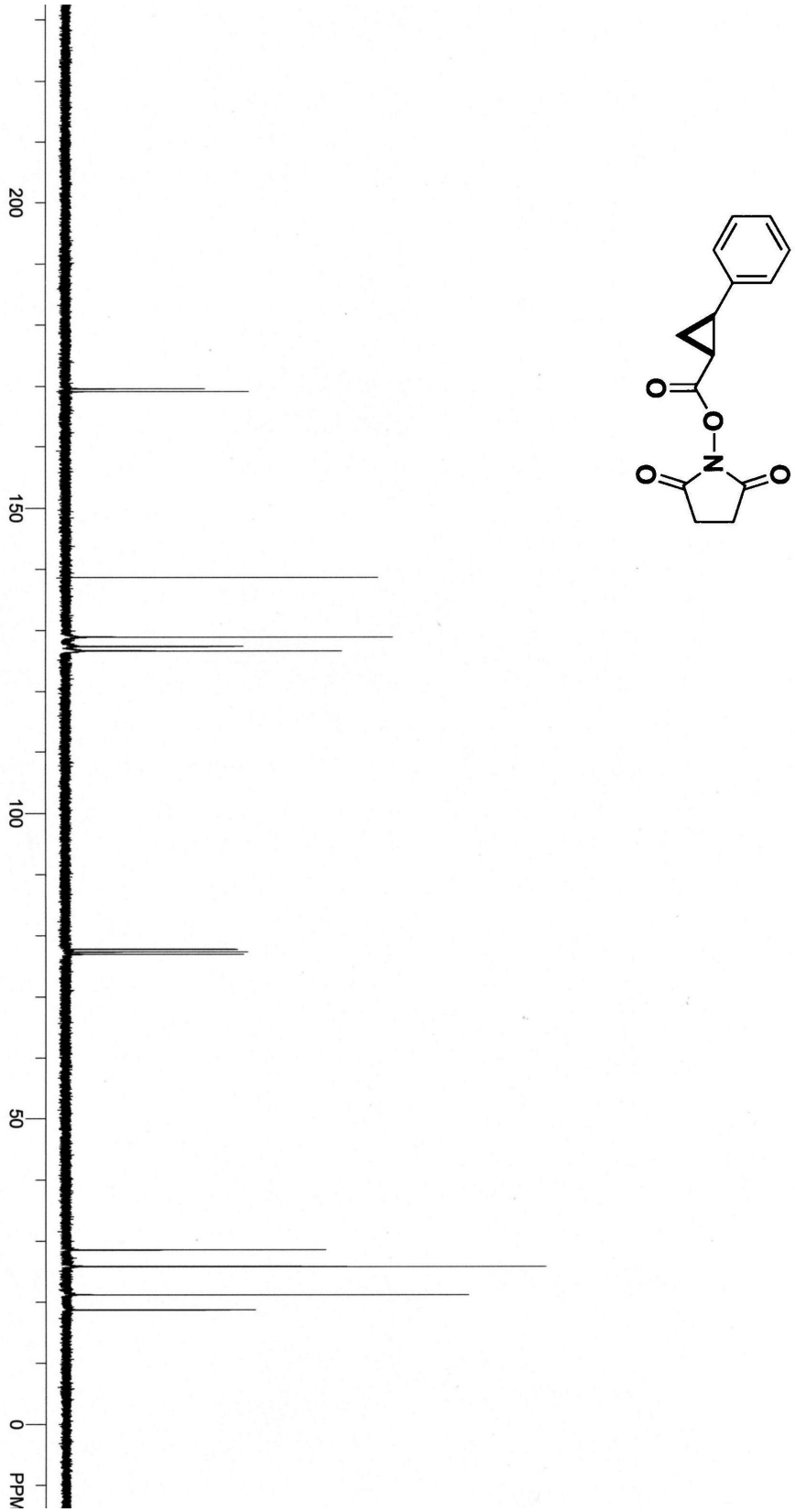
^{1}H NMR and ^{13}C NMR (*Ph*-Pheox ligand) **1b**.

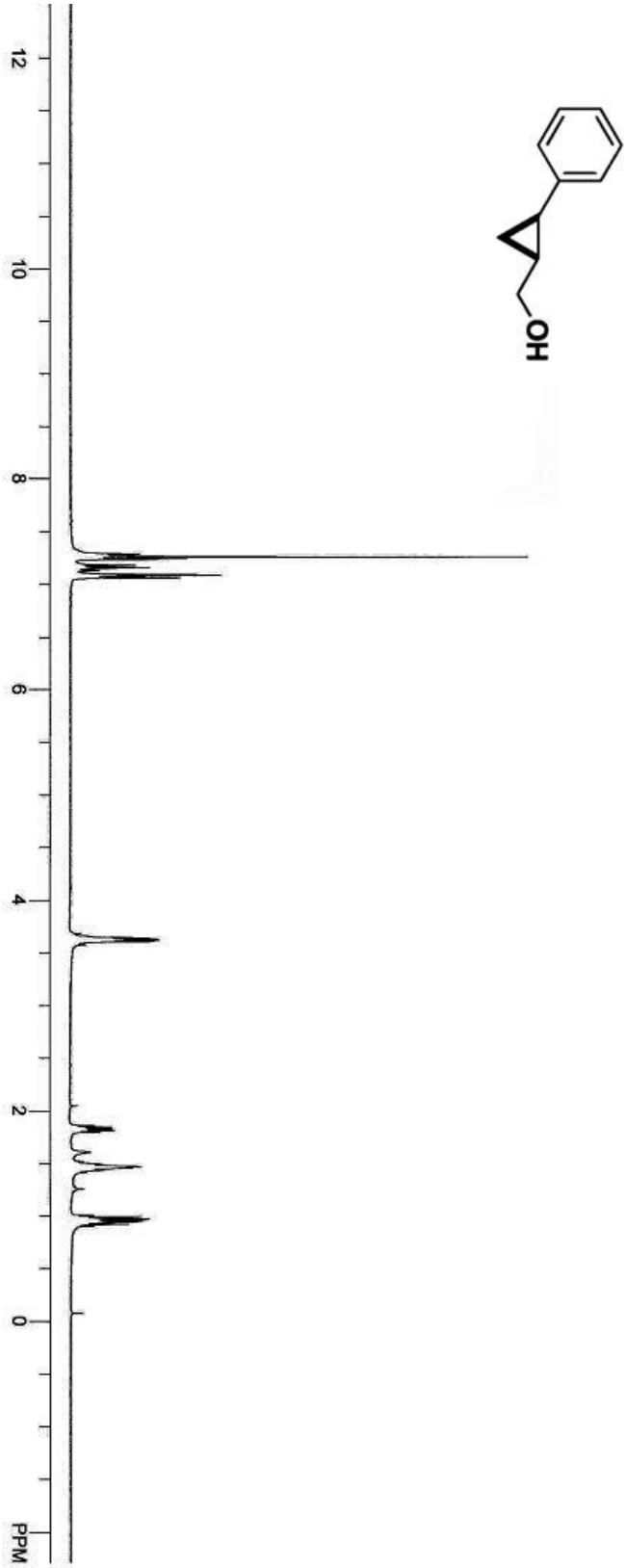


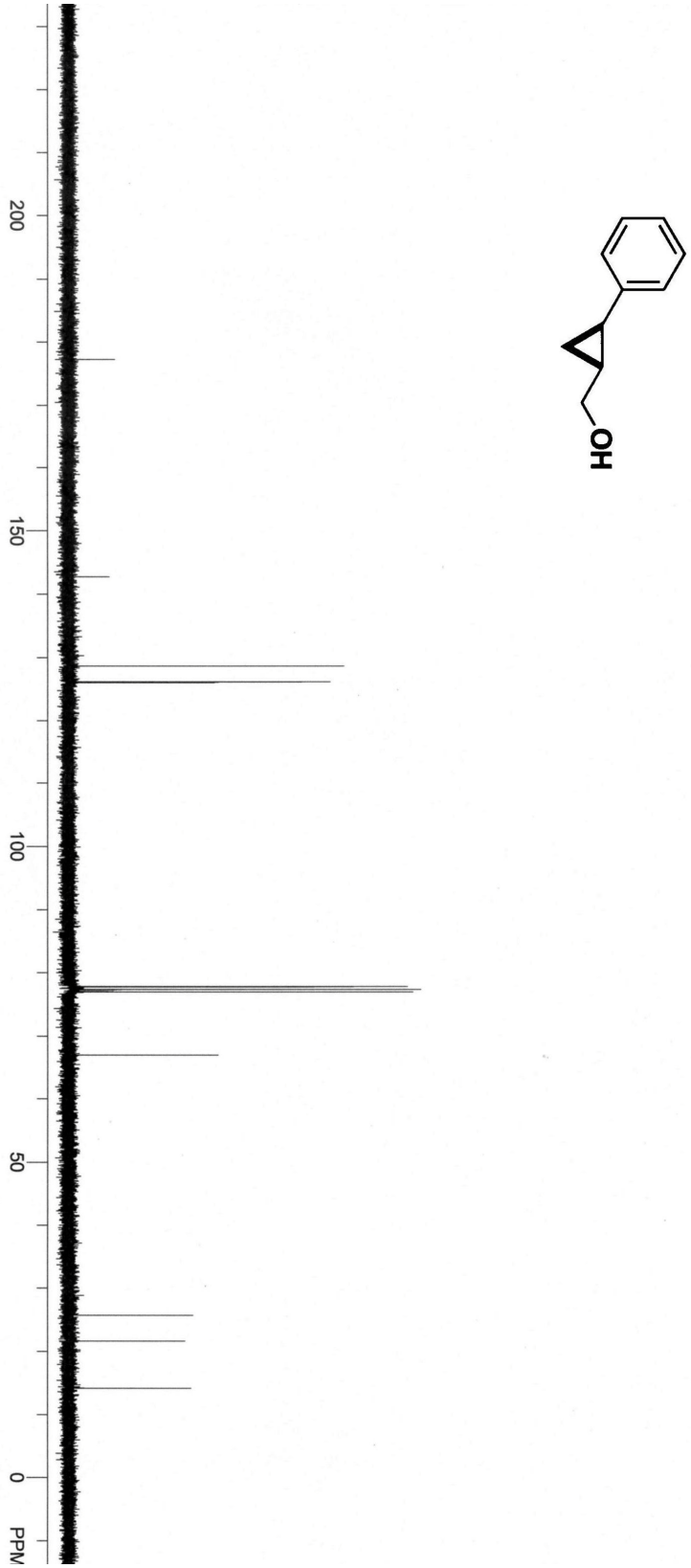
^{1}H NMR and ^{13}C NMR [Ru-*Ph*-Pheox$(CH_3CN)_4$]PF_6 **2b**.




12
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
O
O
N
O
O


12
10
8
6
4
2
0
PPM
OH


200
150
100
50
0
PPM
HO

HPLC of 2-phenylcyclopropylmethanol (Racemic product).

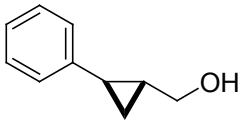
>807-IT PARAM FILE# 1 RUN# 847 STARTED AT 15:36 08/27/'08
CHART SPEED 1 mm/min
START DELAY 0.00 min ATTENUATION 256 mV F.S.

-- % CALCULATION RESULT --

NONAME1 NONAME2

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	15.742	329509	13876		50.5543
2	20.317	322284	10981		49.4457
	TOTAL	651793	24857		100.0000



racemic

HPLC condition

Column: Daicel CHIRALPAK OD-H

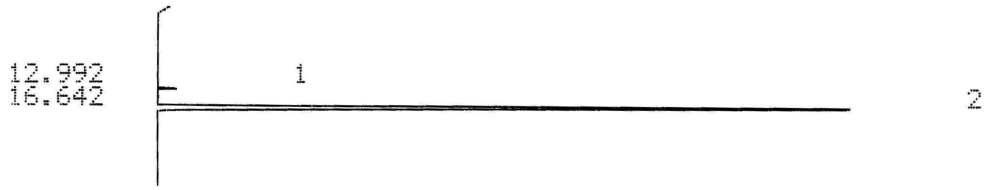
UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 9:1

HPLC of 2-phenylcyclopropylmethanol (Table 1, entry 9 or Table 2, entry 2).

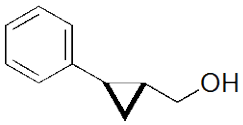
```
>807-IT  PARAM FILE# 0          RUN# 862     CHROMATOGRAM REPLOT
                                             CHART SPEED      1 mm/min
    START DELAY   0.00 min                   ATTENUATION   512 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	12.992	76327	8082	EEE	1.0561
2	16.642	7151023	314889	EEE	98.9439
	TOTAL	7227350	322971		100.0000



trans ee: 98%

HPLC condition

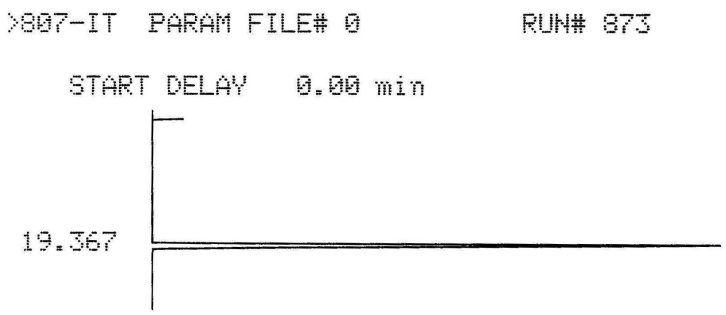
Column: Daicel CHIRALPAK OD-H

UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 9:1

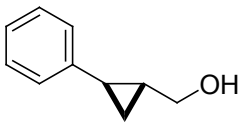
HPLC of 2-phenylcyclopropylmethanol (Table 1, entry 11).



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

ID#	RT(min)	NAME	AREA	HEIGHT	MK	AREA%
1	19.367		1664957	64232	EEE	100.0000
		TOTAL	1664957	64232		100.0000



trans ee: >99%

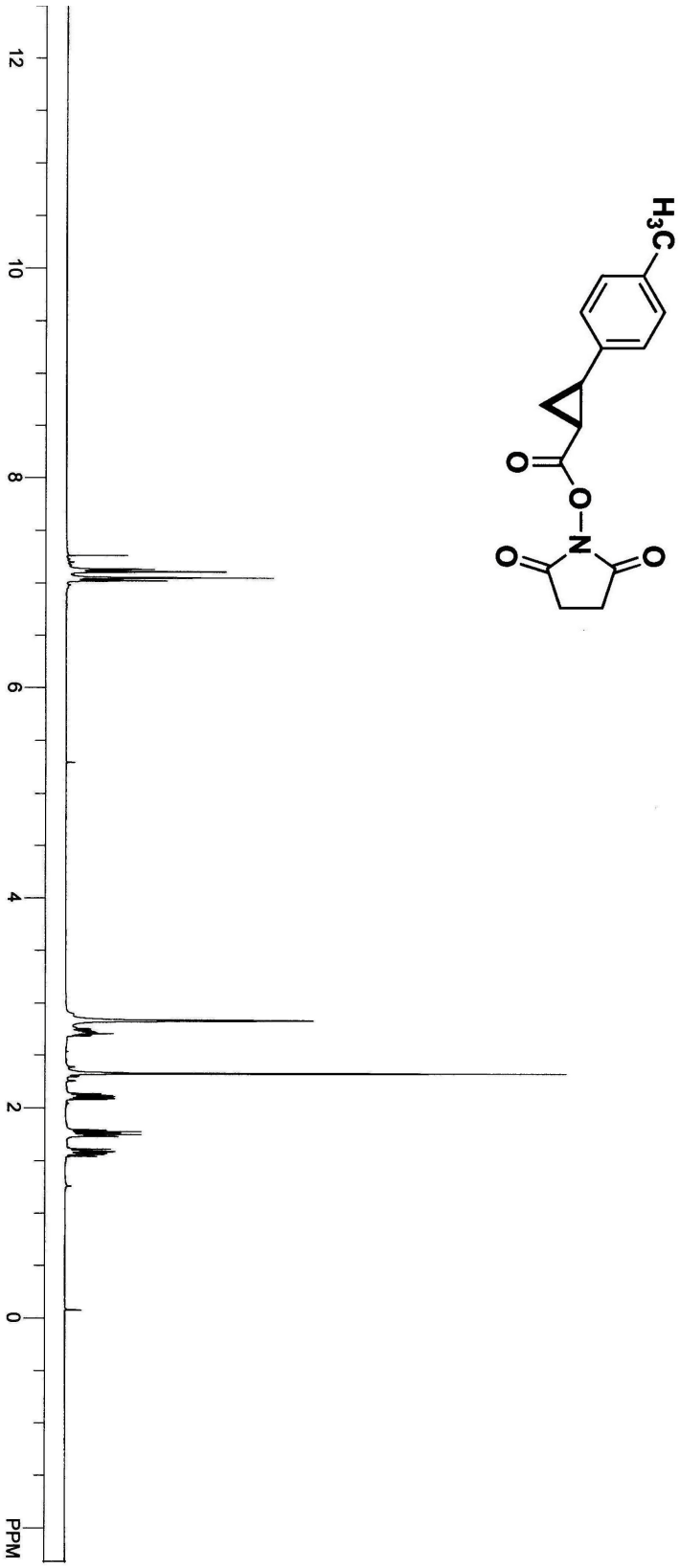
HPLC condition

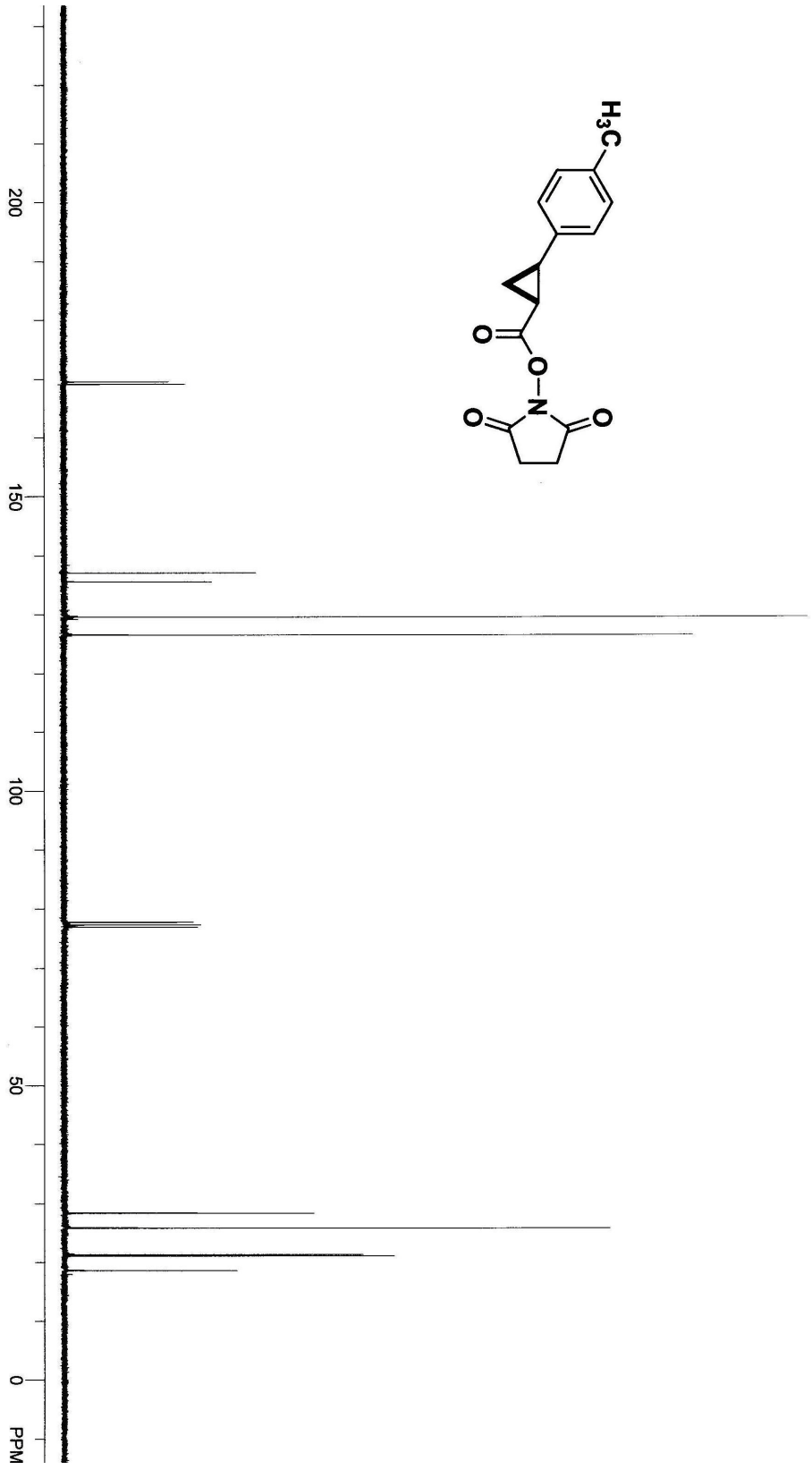
Column: Daicel CHIRALPAK OD-H

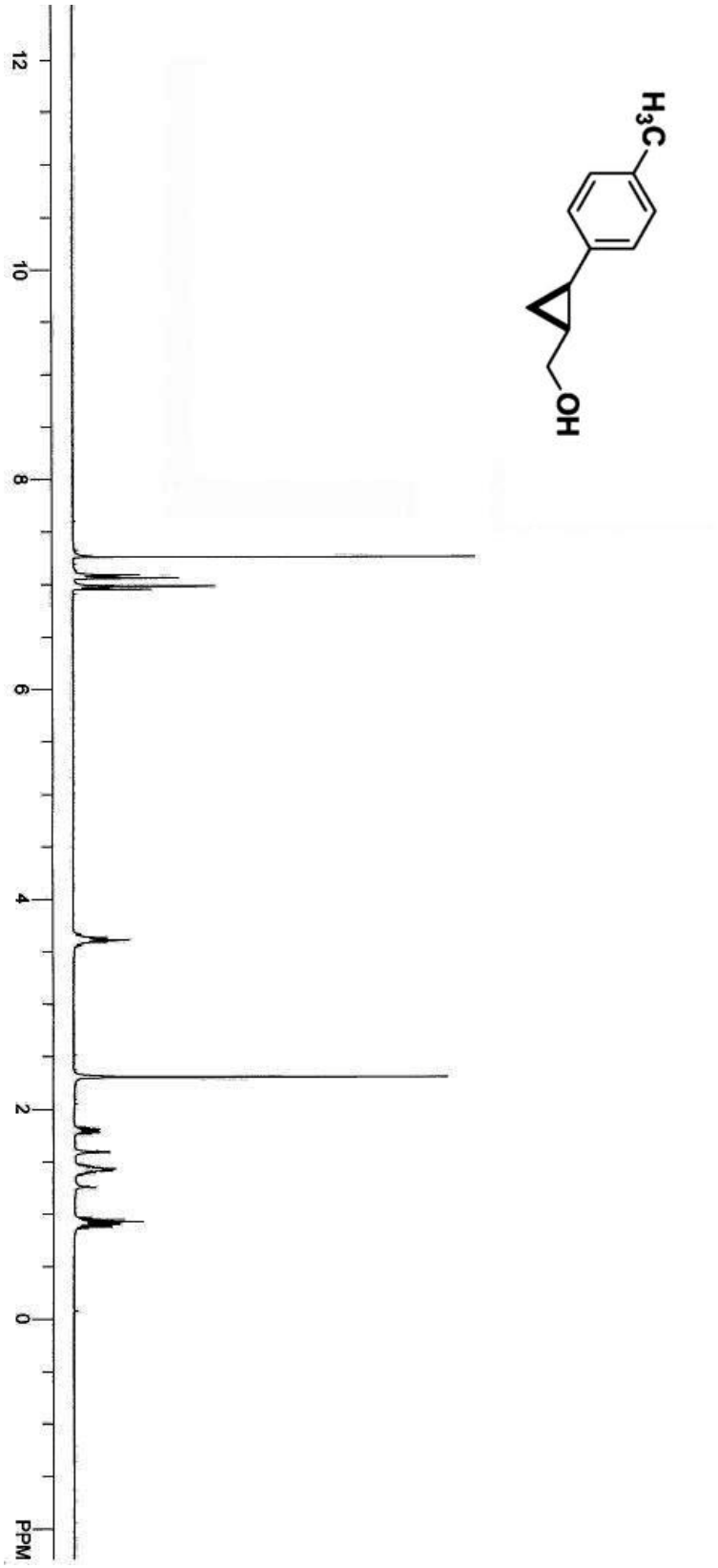
UV Detector: 254 nm

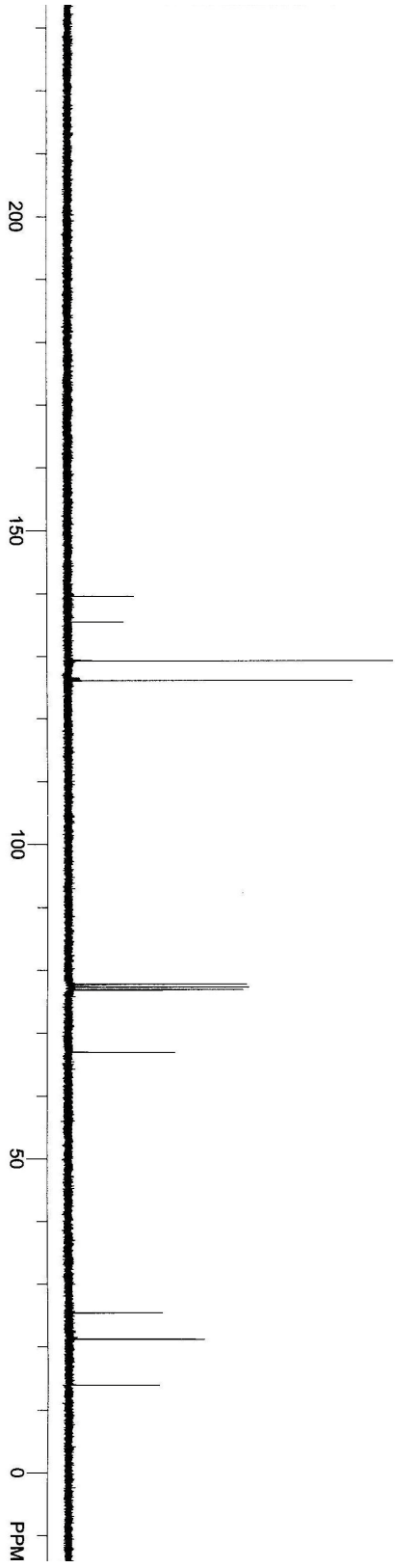
Flow rate: 0.5 ml/min

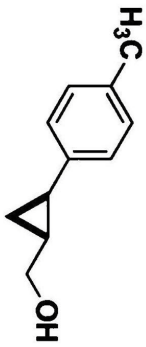
Eluent: hexane:2-propanol= 9:1


12
10
8
6
4
2
0
PPM
H3C
O
O
N
O
O


H3C
O
O
N
O
O
200
150
100
50
0
PPM

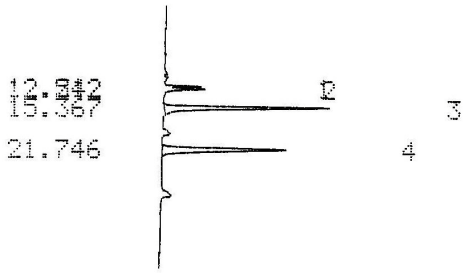

H3C
OH
12
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM


H3C
OH

HPLC of 2-*p*-tolylcyclopropylmethanol (racemic).

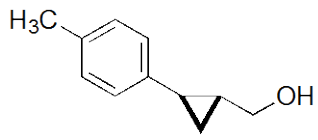
```
>807-IT  PARAM FILE# 0          RUN# 232      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION   256 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	12.212	45327	3844	VV	2.1470
2	12.542	70745	4611	VV	3.3511
3	15.367	1015567	38159	VV	48.1054
4	21.746	979489	28206	VV	46.3965
	TOTAL	2111128	74819		100.0000



racemic

HPLC condition

Column: Daicel CHIRALPAK OD-H

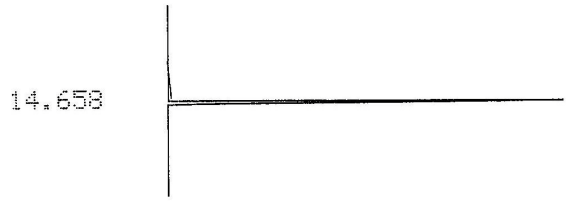
UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 9:1

HPLC of 2-*p*-tolylcyclopropylmethanol (Table 2, entry 4).

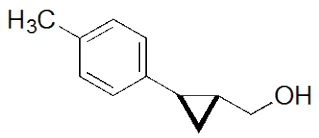
```
>807-IT  PARAM FILE# 0          RUN# 883      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION   512 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

ID#	RT(min)	NAME	AREA	HEIGHT	MK	AREA%
2	14.658		2628790	179038	EEE	100.0000
		TOTAL	2628790	179038		100.0000



trans ee: >99%

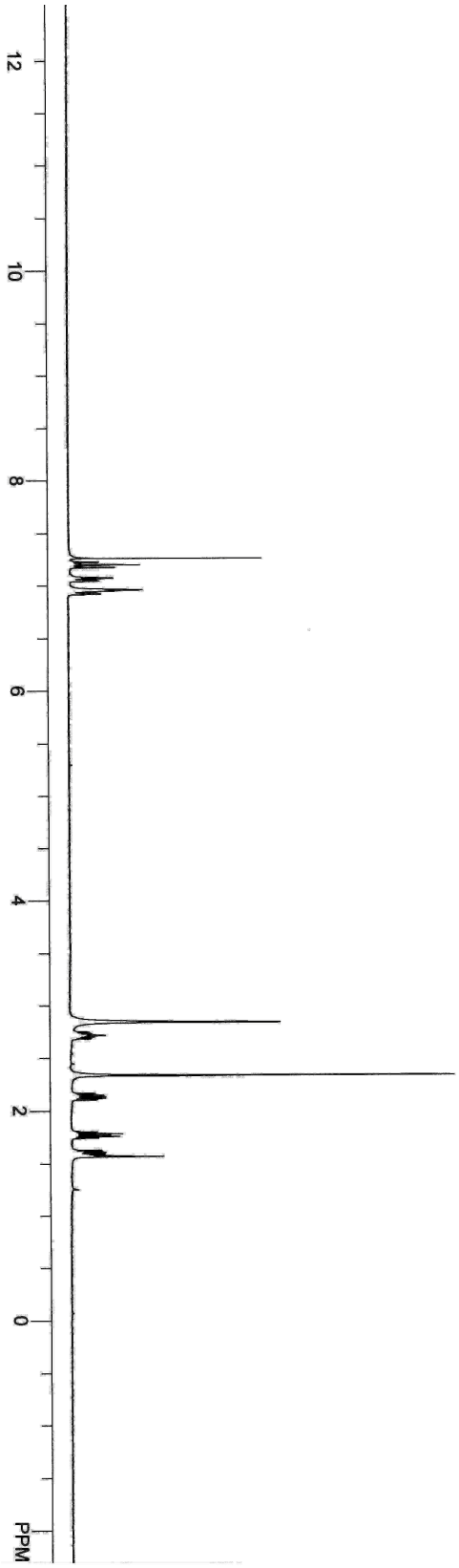
HPLC condition

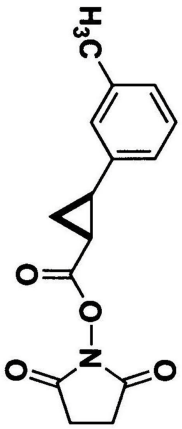
Column: Daicel CHIRALPAK OD-H

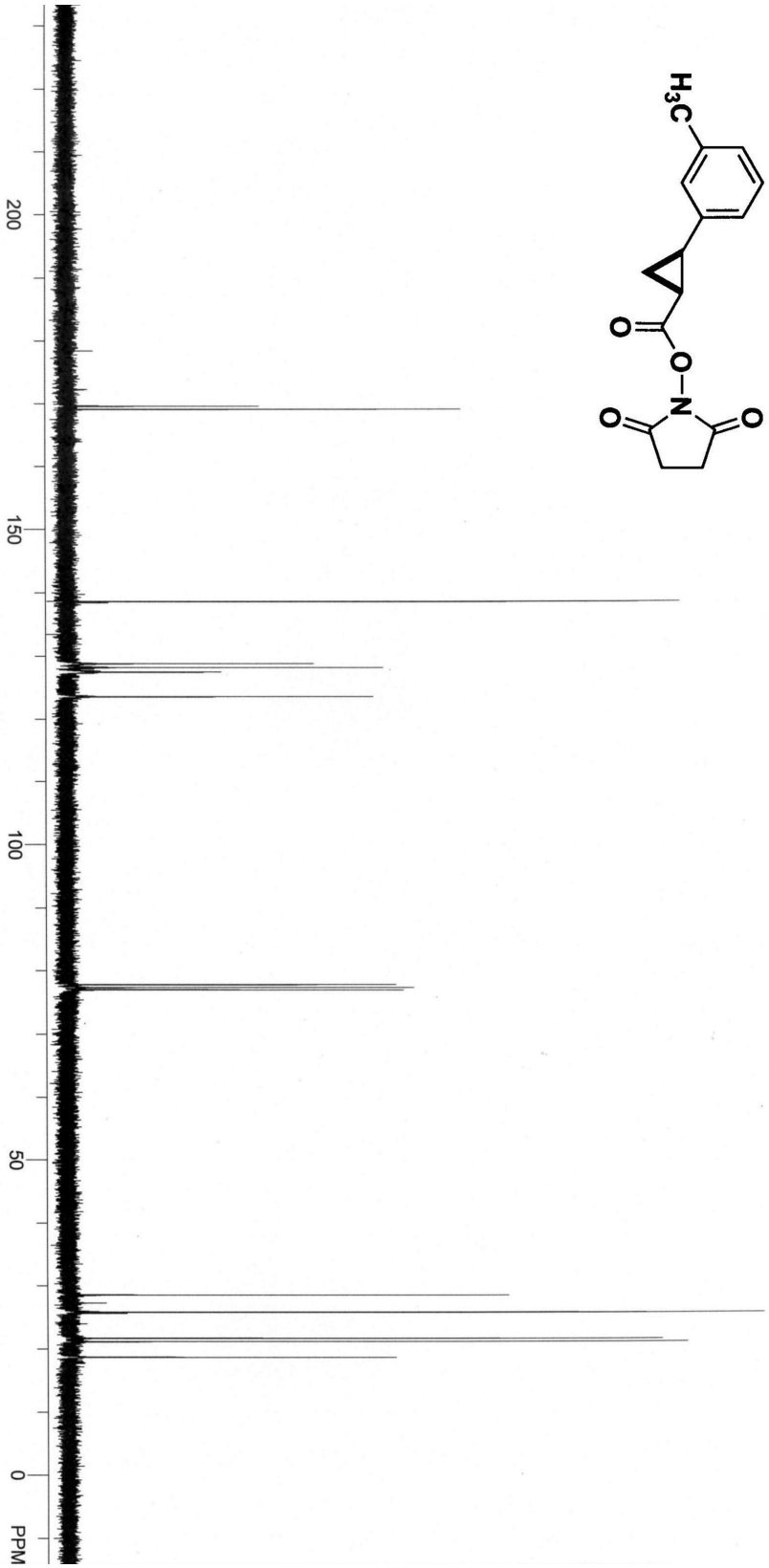
UV Detector: 254 nm

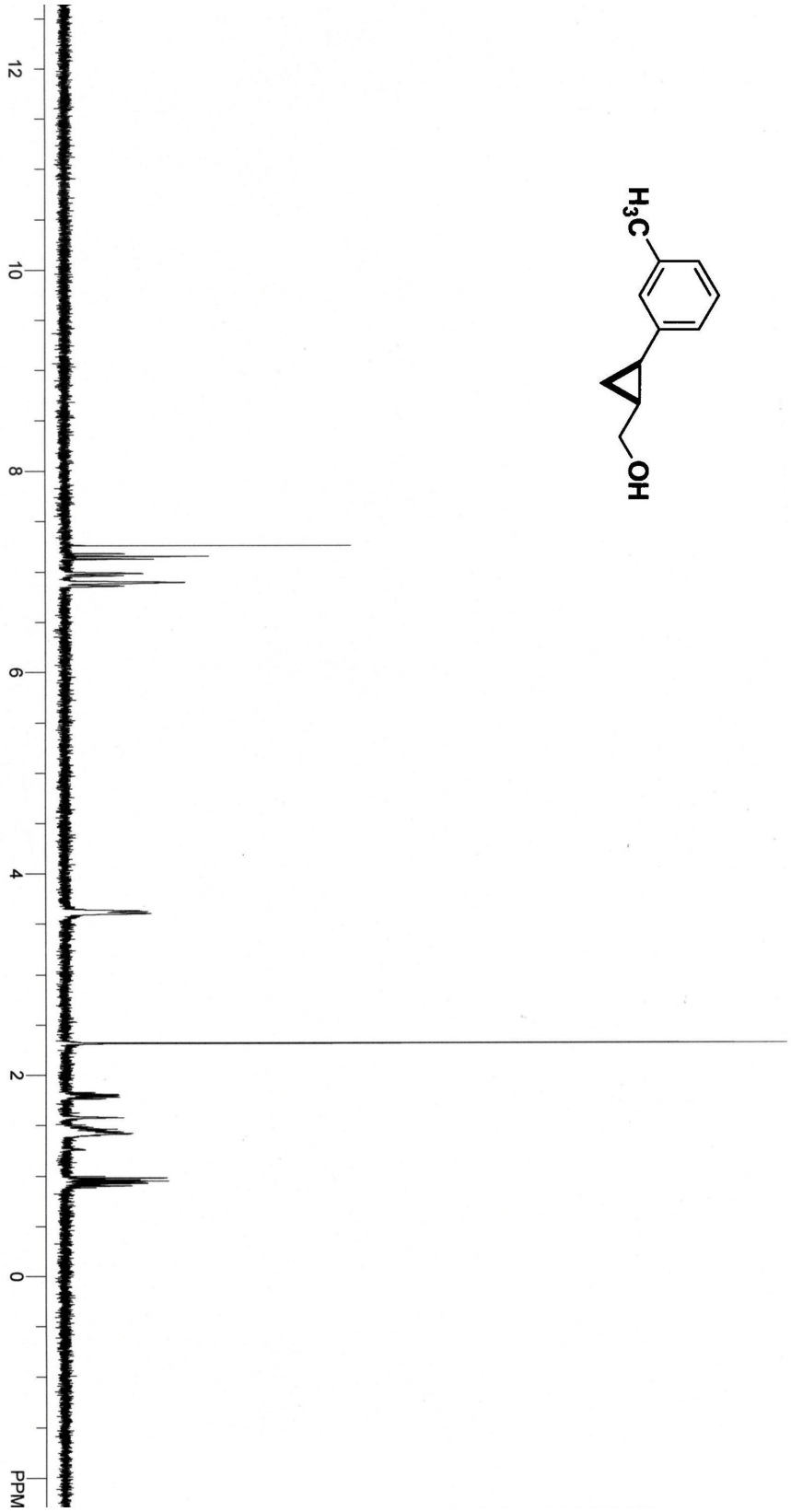
Flow rate: 0.5 ml/min

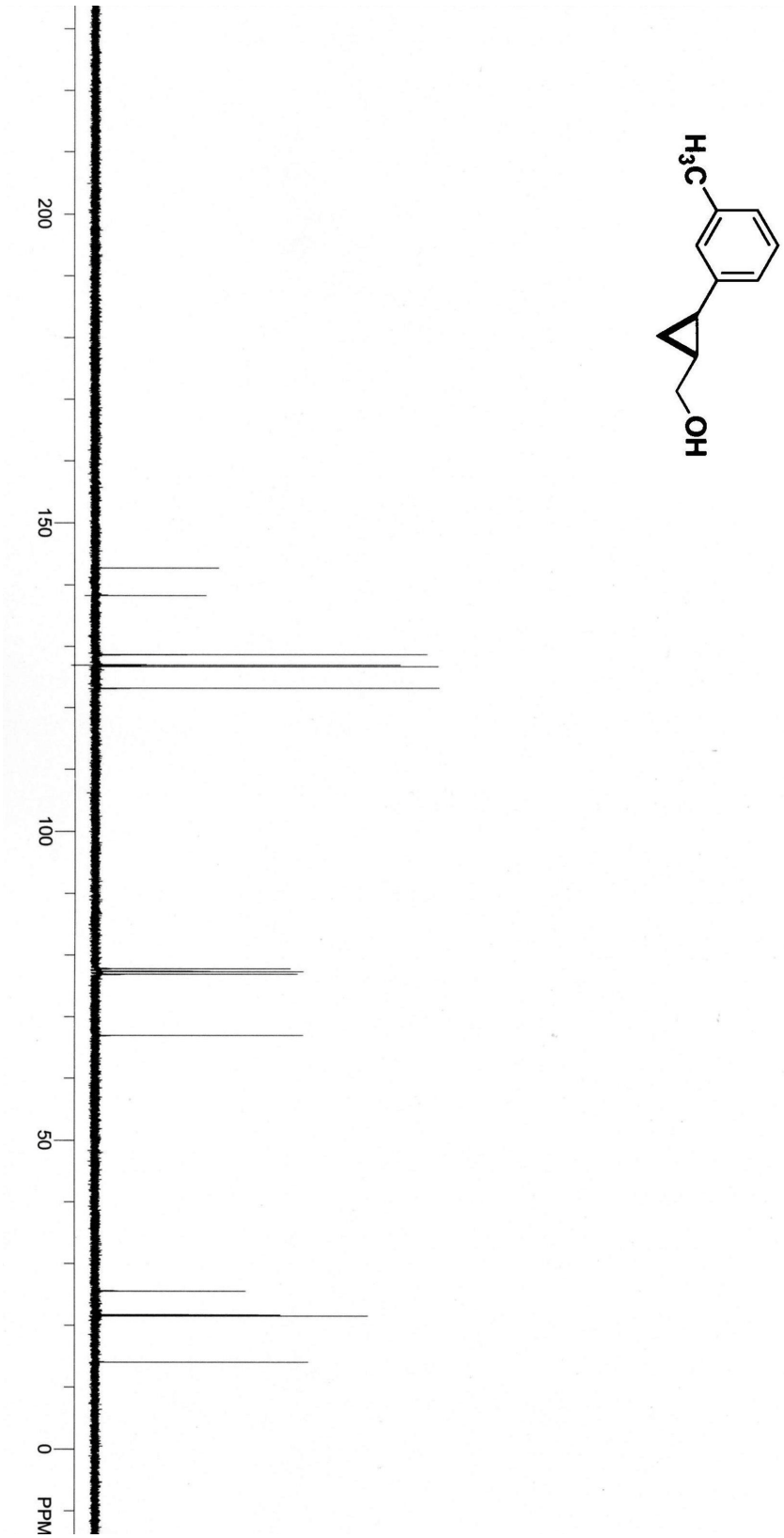
Eluent: hexane:2-propanol= 9:1


12
10
8
6
4
2
0
PPM


H3C
O
O
N
O
O

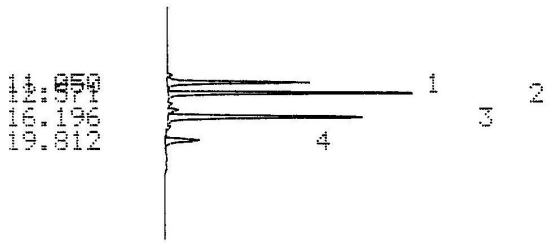





H3C
OH
200
150
100
50
0
PPM

HPLC of 2-*m*-tolylcyclopropylmethanol (Racemic).

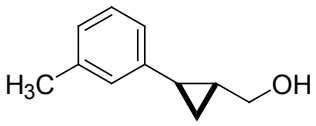
```
>807-IT  PARAM FILE# 0          RUN# 228      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION  1024 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	11.050	2906833	127617	VV	22.1912
2	12.571	4665635	220317	VV	35.6181
3	16.196	4623518	174258	VV	35.2966
4	19.812	903060	29552	VV	6.8941
	TOTAL	13099046	551744		100.0000



racemic

HPLC condition

Column: Daicel CHIRALPAK OD-H

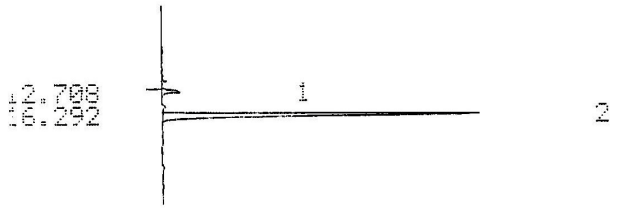
UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 9:1

HPLC of 2-*m*-tolylcyclopropylmethanol (Table 2, entry 6).

```
>007-IT  PARAM FILE# 1          RUN# 790      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION   256 mV F.S.
```

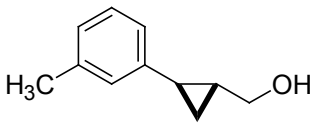


-- % CALCULATION RESULT --

NONAME1 NONAME2

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	12.708	100792	4203	V	4.5488
2	16.292	2114995	73234		95.4512
	TOTAL	2215787	77437		100.0000



trans ee: 91%

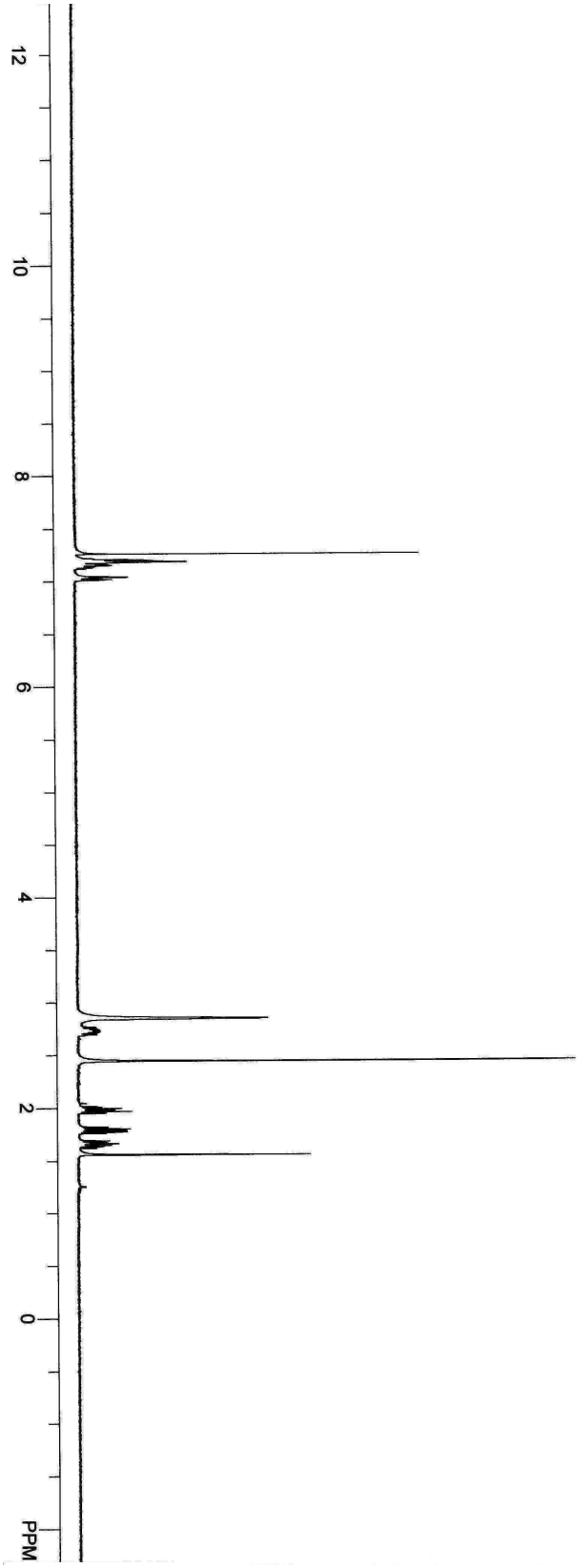
HPLC condition

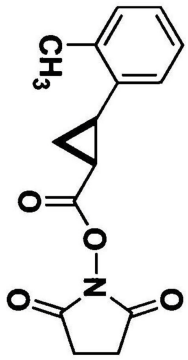
Column: Daicel CHIRALPAK OD-H

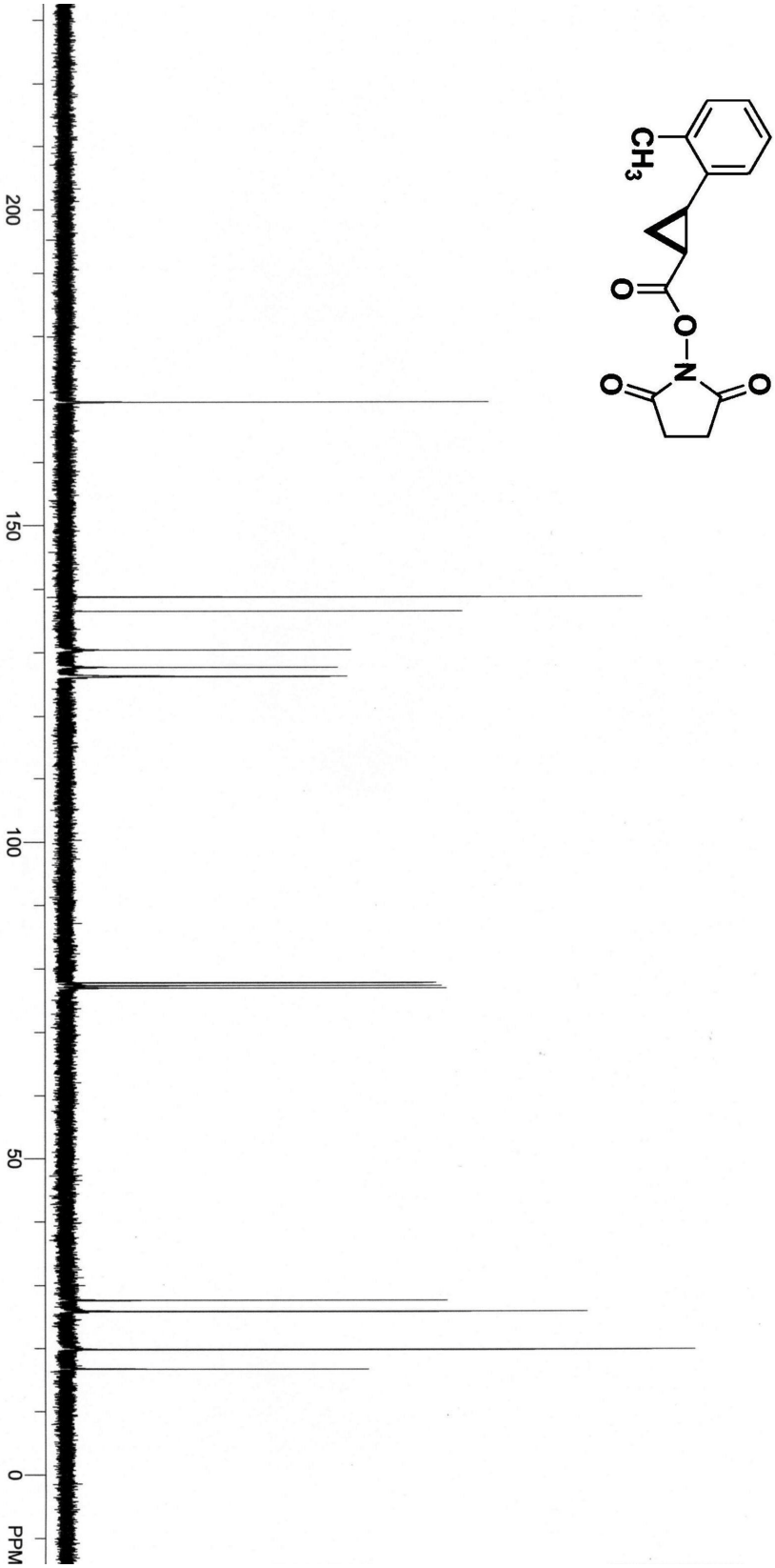
UV Detector: 254 nm

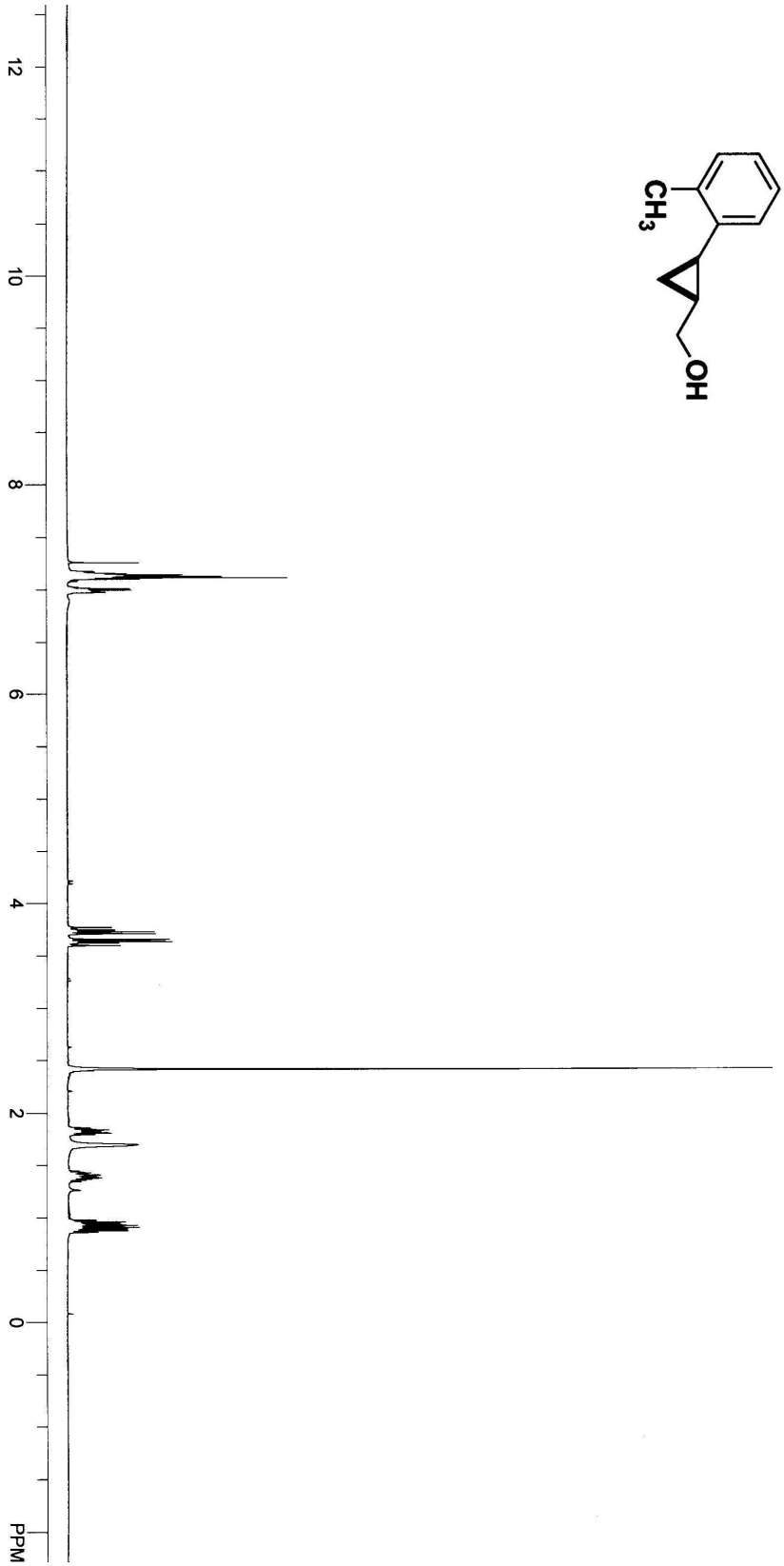
Flow rate: 0.5 ml/min

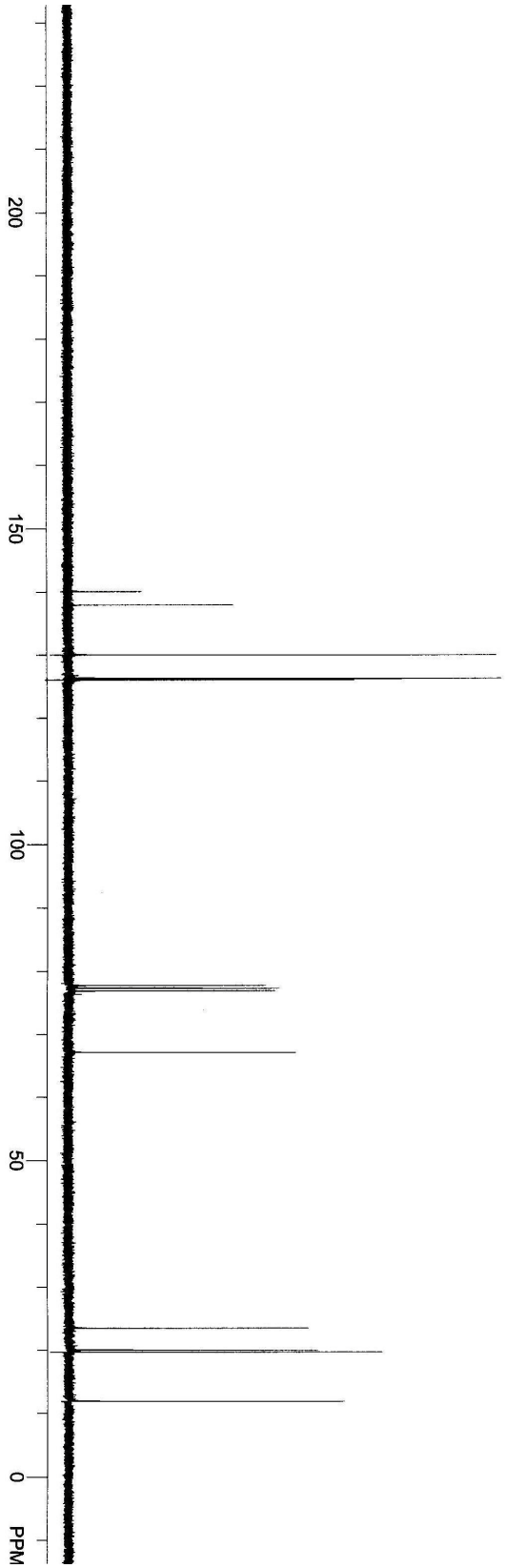
Eluent: hexane:2-propanol= 9:1

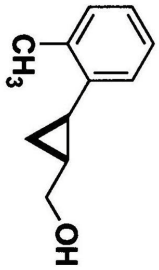





200
150
100
50
0
PPM
CH3
O
O
N
O
O

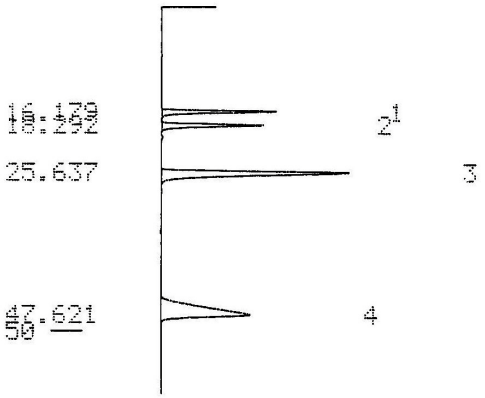

12
10
8
6
4
2
0
PPM
CH3
OH


200
150
100
50
0
PPM


CH3
OH

HPLC of 2-*o*-tolylcyclopropylmethanol (Racemic).

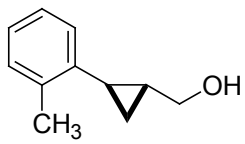
```
>807-IT  PARAM FILE# 0          RUN# 230      STARTED AT 15:52 11/05/'08
                                              CHART SPEED       1 mm/min
    START DELAY   0.00 min                    ATTENUATION    512 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	16.179	1387196	53377	VV	12.8382
2	18.292	1392464	47687	VV	12.8870
3	25.637	4008179	87757		37.0948
4	47.621	4017389	41469		37.1800
	TOTAL	10805229	230291		100.0000



racemic

HPLC condition

Column: Daicel CHIRALPAK OD-H

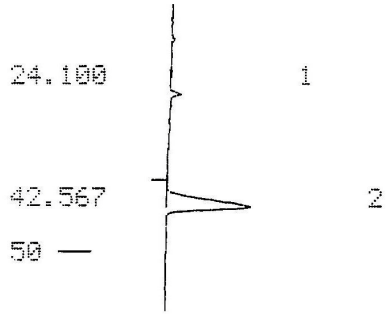
UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 20:1

HPLC of 2-*o*-tolylcyclopropylmethanol (Table 2, entry 8).

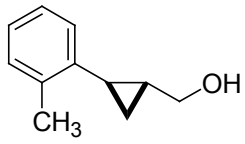
```
>807-IT  PARAM FILE# 0          RUN#  95      CHROMATOGRAM REPLOT
                                               CHART SPEED      1 mm/min
    START DELAY  10.00 min                     ATTENUATION    256 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	24.100	83060	2298		4.3887
2	42.567	1809512	18710	V	95.6113
	TOTAL	1892572	21007		100.0000



trans ee: 91%

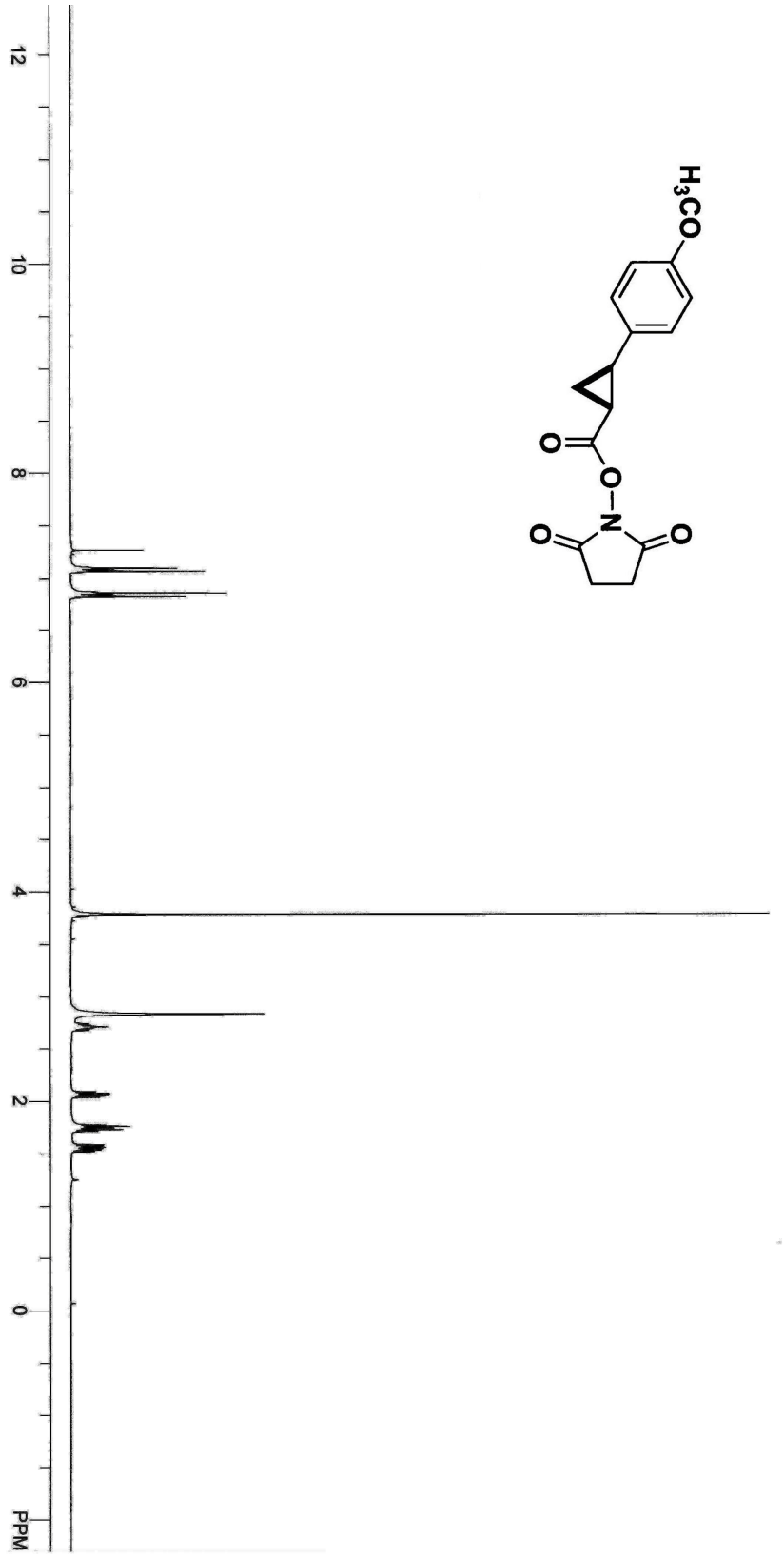
HPLC condition

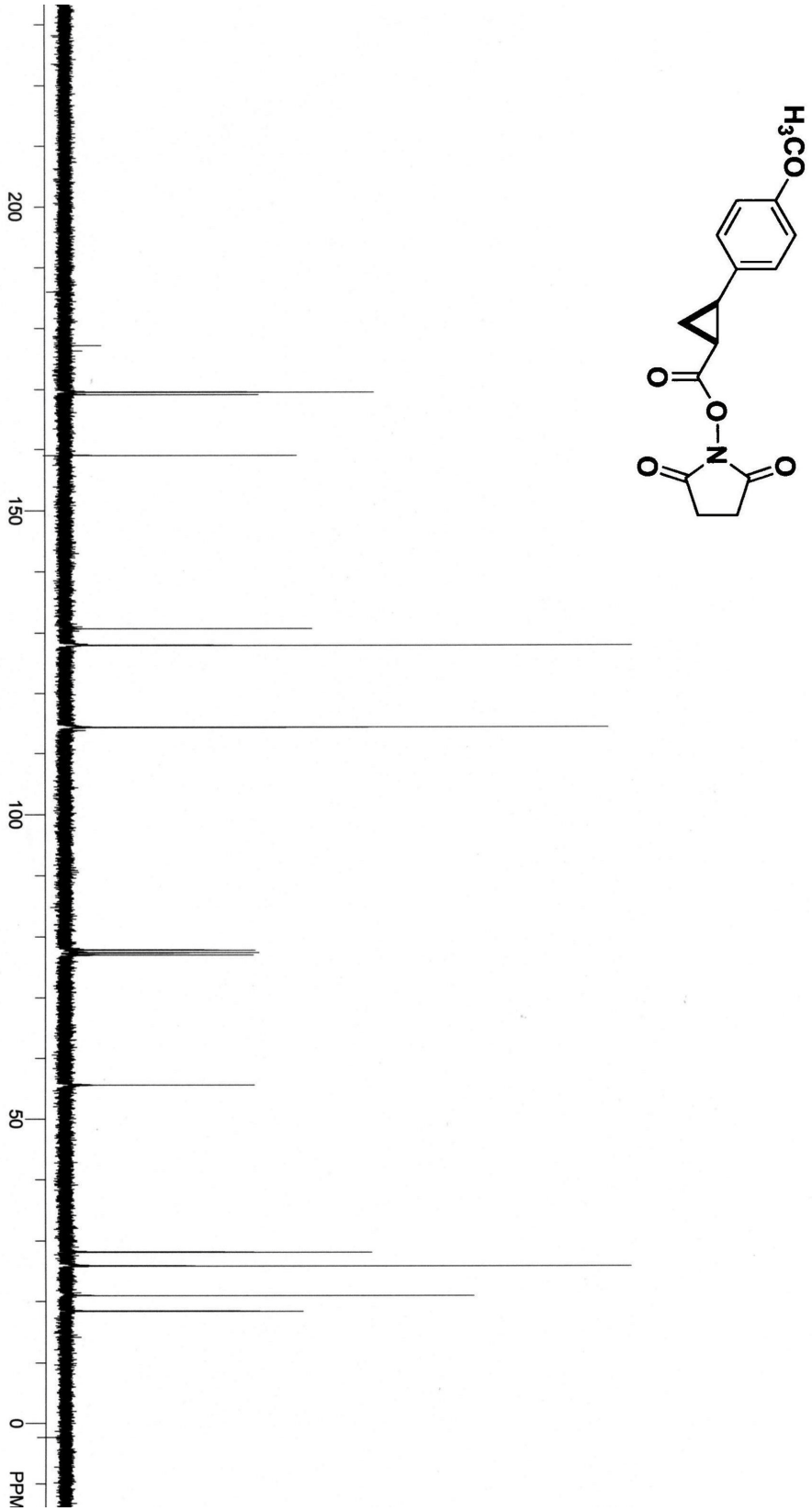
Column: Daicel CHIRALPAK OD-H

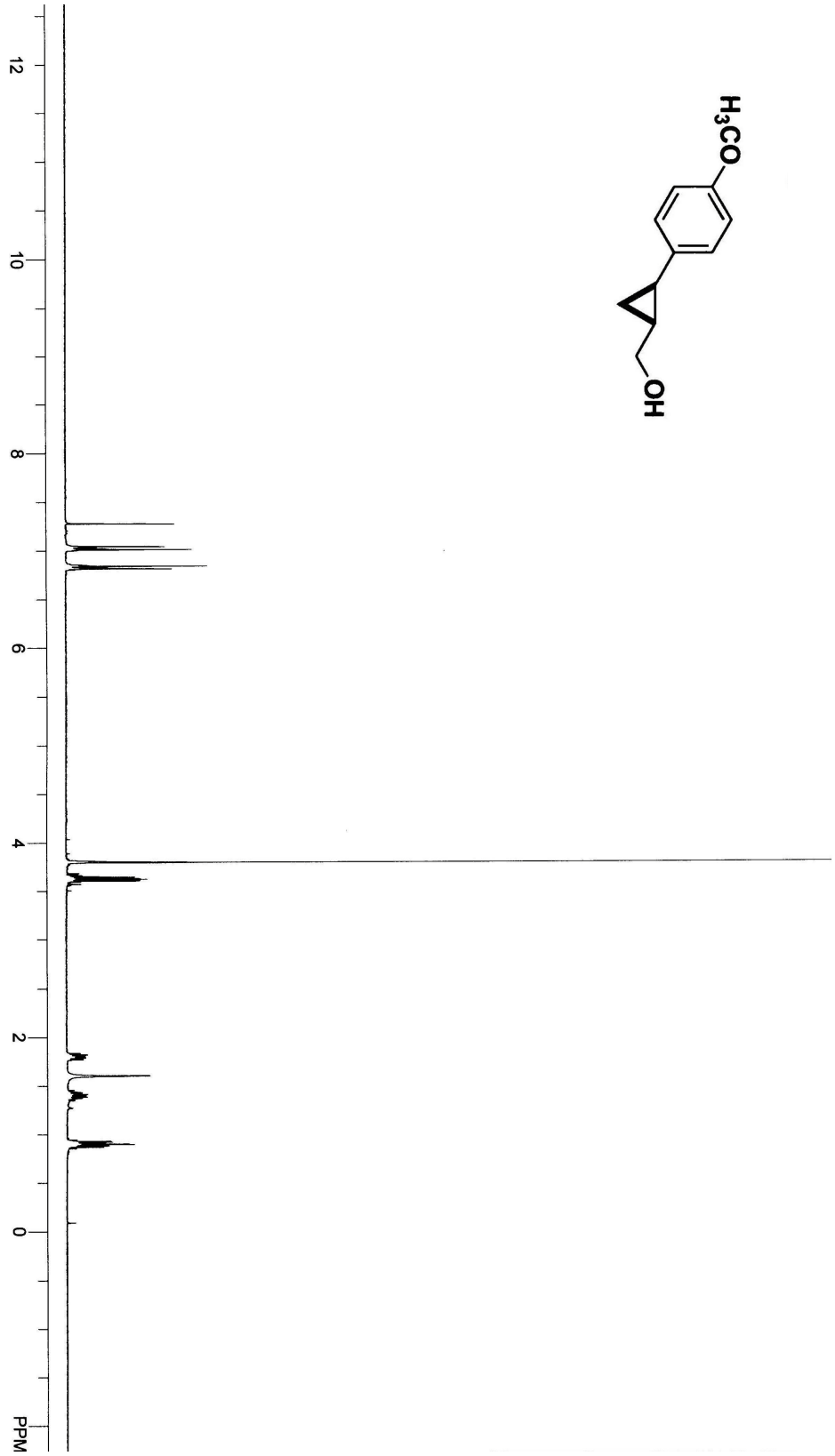
UV Detector: 254 nm

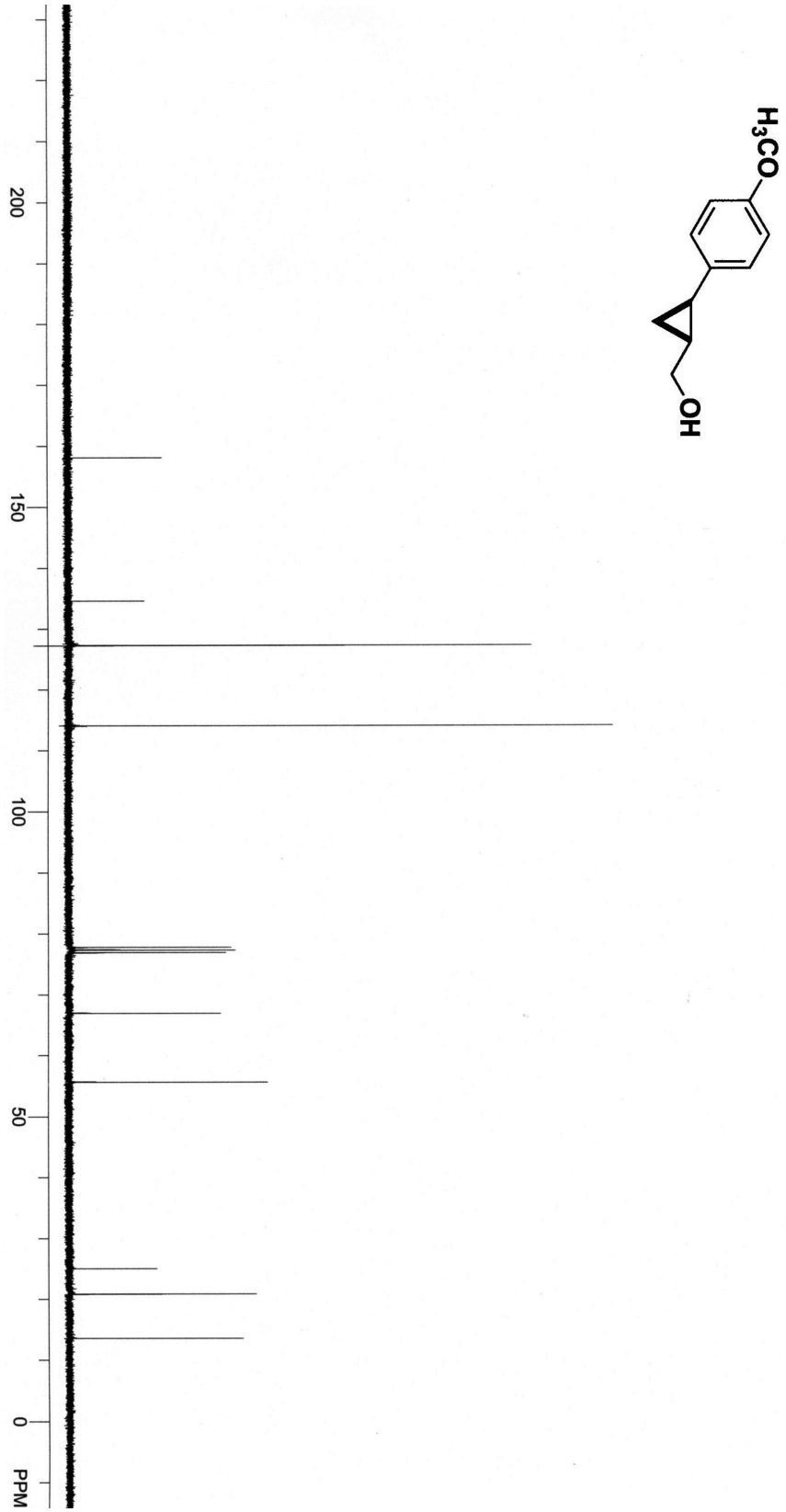
Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 20:1



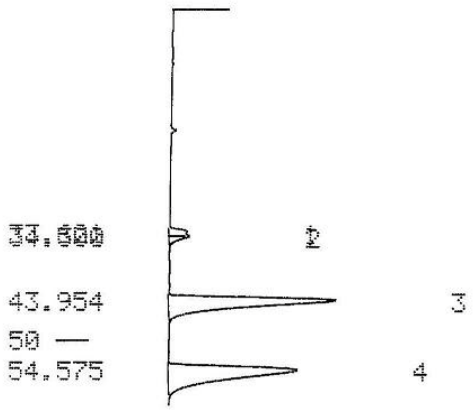

200
150
100
50
0
PPM
H3CO
O
O
N
O
O


12
10
8
6
4
2
0
PPM
H3CO
OH


H3CO
OH
200
150
100
50
0
PPM

HPLC of 2-(4-methoxyphenyl)cyclopropylmethanol (Racemic).

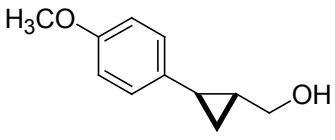
```
>807-IT  PARAM FILE# 0          RUN# 231      STARTED AT 14:33 11/07/'08
                                               CHART SPEED      1 mm/min
    START DELAY   0.00 min                     ATTENUATION    512 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	33.621	296244	7719	V	1.9922
2	34.300	462223	8457	V	3.1084
3	43.954	7054704	75265		47.4426
4	54.575	7056822	57798		47.4568
	TOTAL	14869994	149240		100.0000



racemic

HPLC condition

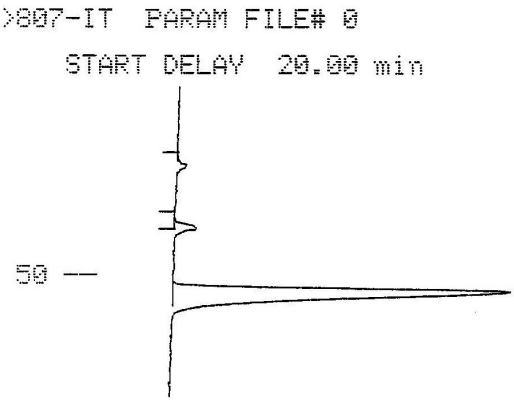
Column: Daicel CHIRALPAK OD-H

UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 30:1

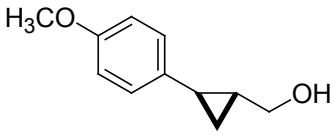
HPLC of 2-(4-methoxyphenyl)cyclopropylmethanol (Table2, entry10).



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	33.958	26475	517	V	1.2696
2	43.000	85018	1246	V	4.0772
3	52.500	1973731	18937		94.6532
	TOTAL	2085224	20700		100.0000



trans ee: 92%

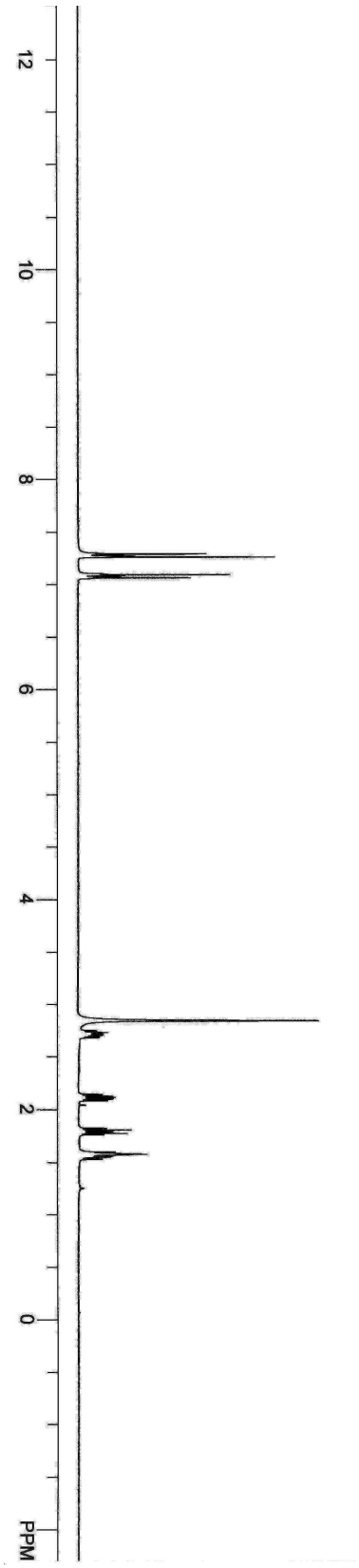
HPLC condition

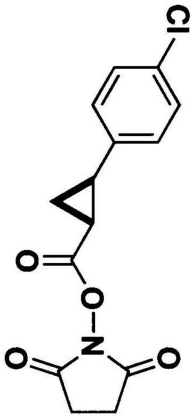
Column: Daicel CHIRALPAK OD-H

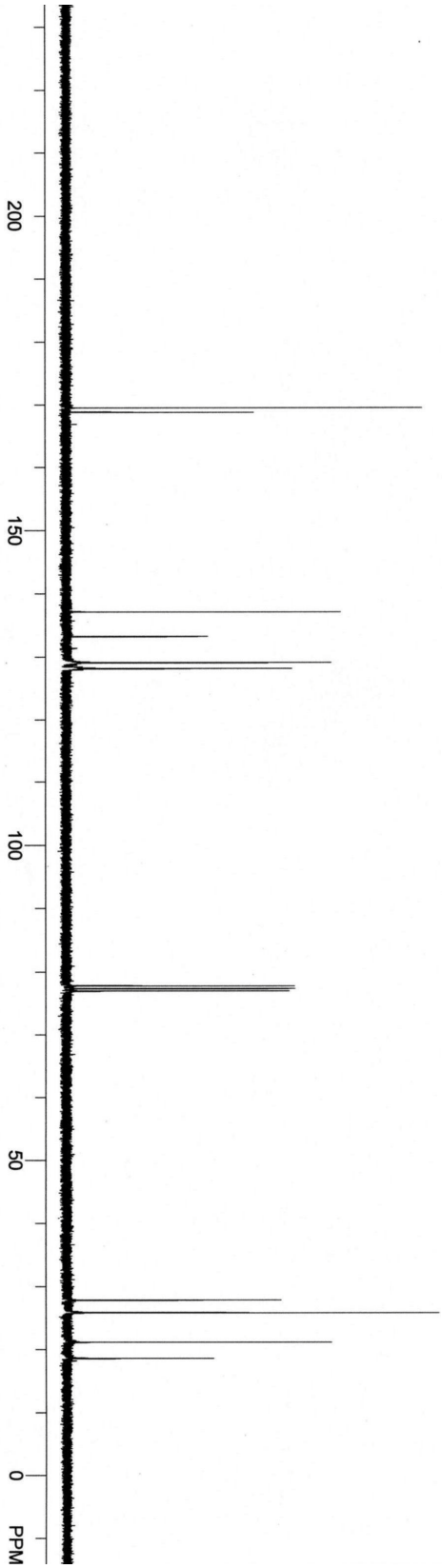
UV Detector: 254 nm

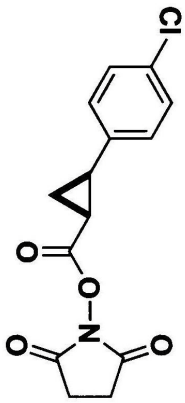
Flow rate: 0.5 ml/min

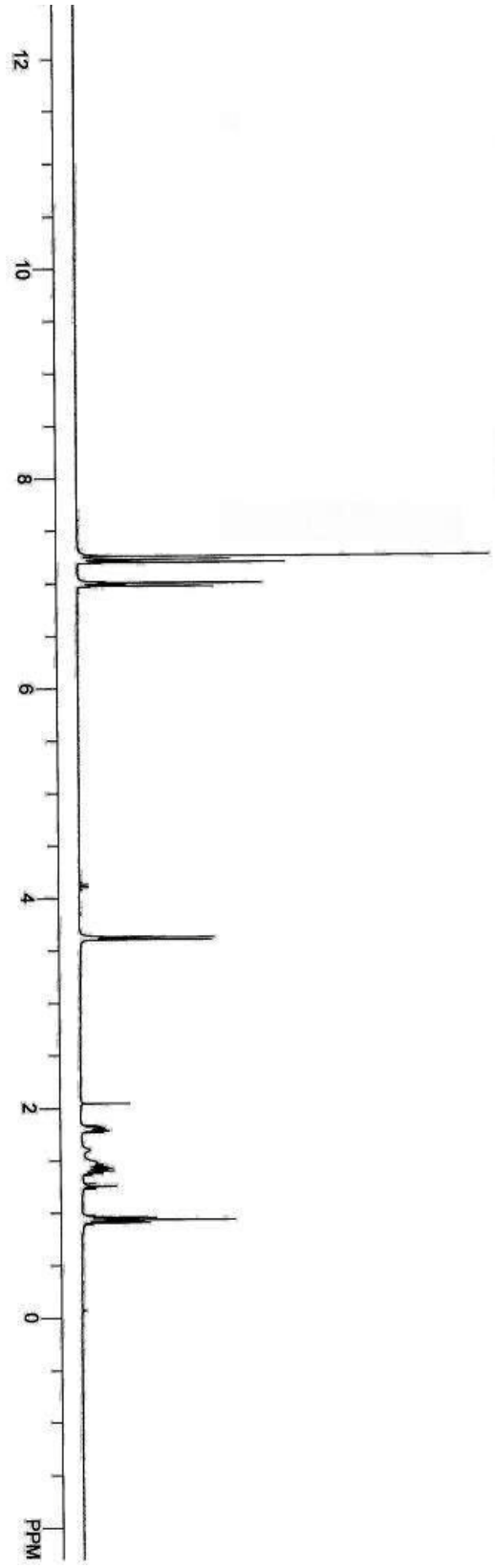
Eluent: hexane:2-propanol= 30:1


12
10
8
6
4
2
0
PPM

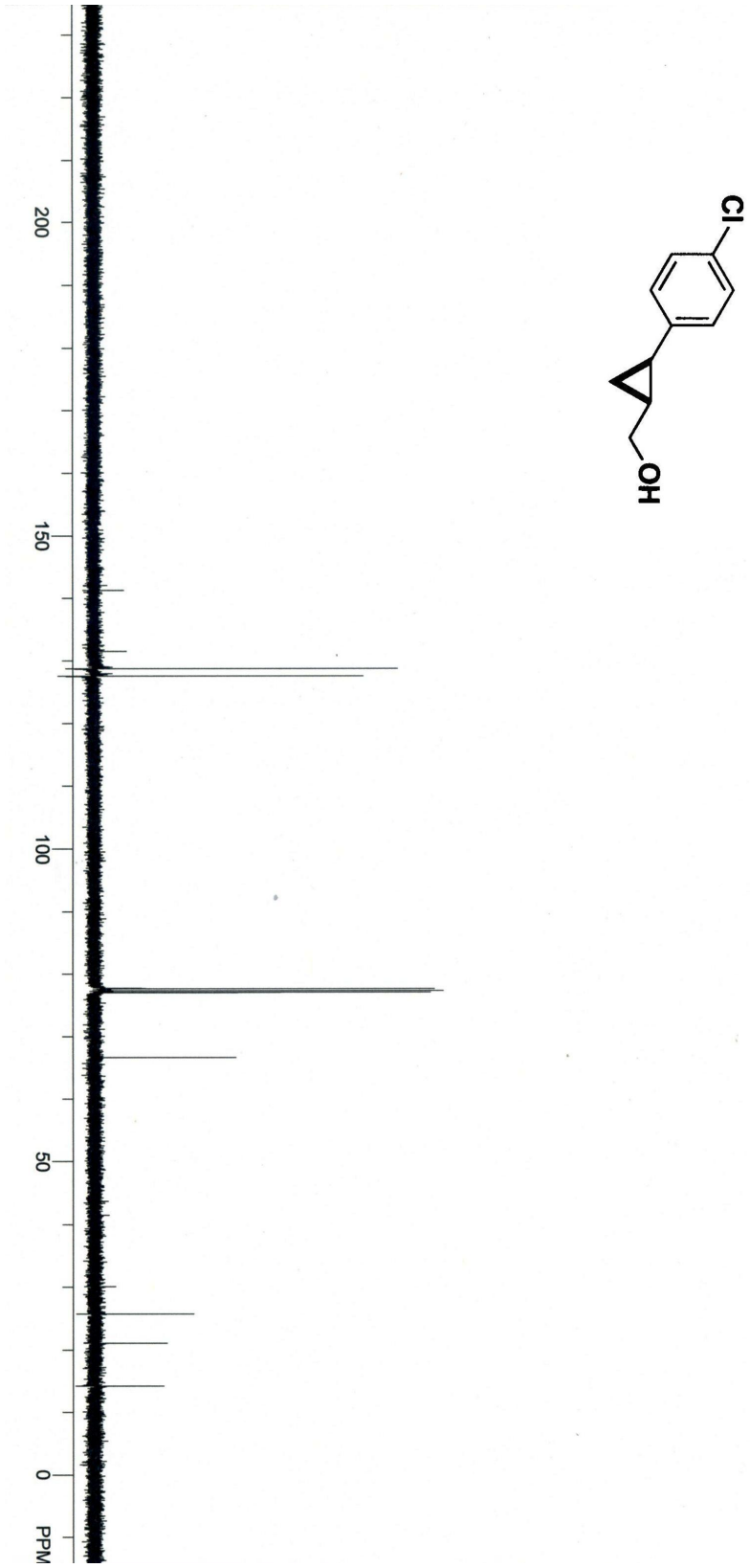

Cl
O
O
N
O
O


200
150
100
50
0
PPM

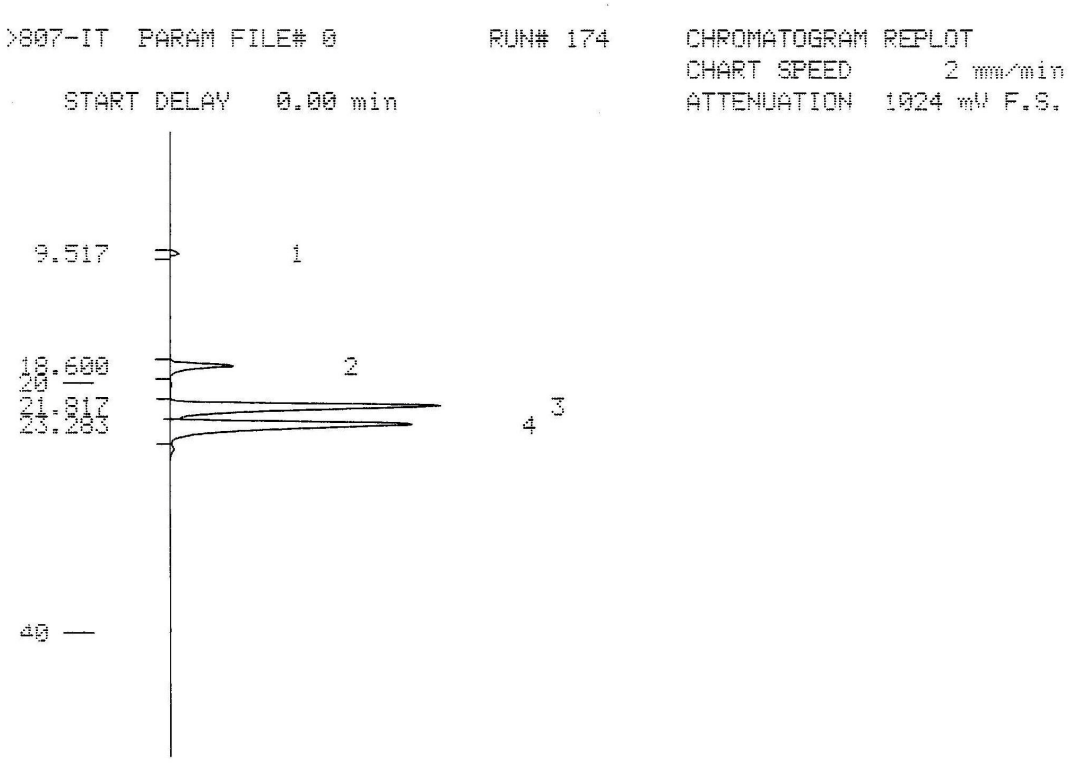

Cl
O
O
N
O
O


12
10
8
6
4
2
0
PPM


Cl
OH


200
150
100
50
0
PPM
Cl
OH

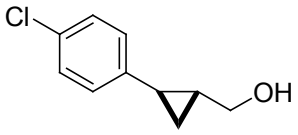
HPLC of 2-(4-chlorophenyl)cyclopropylmethanol (Racemic).



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	9.517	133305	8380	V	0.6543
2	18.600	1668970	60007	V	8.1916
3	21.817	9186874	259621	V	45.0909
4	23.283	9384981	231972	V	46.0632
	TOTAL	20374130	559980		100.0000



racemic

HPLC condition

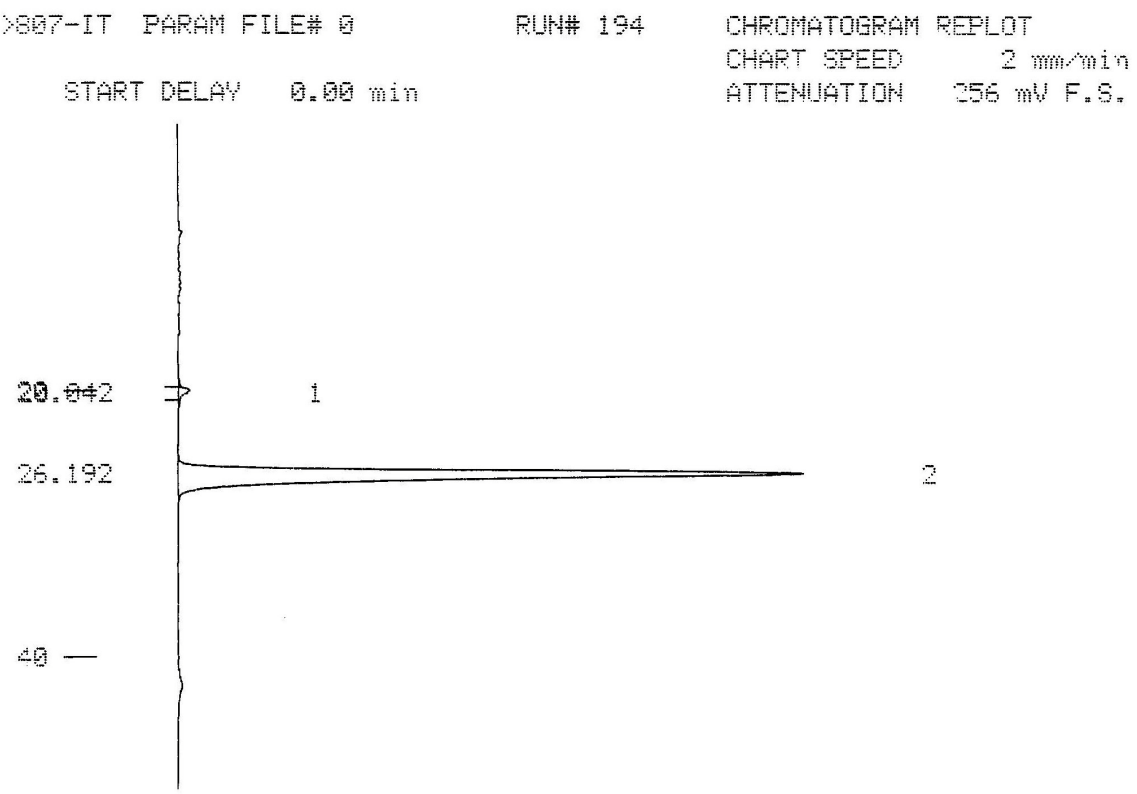
Column: Daicel CHIRALPAK OD

UV Detector: 254 nm

Flow rate: 0.5 ml/min

Eluent: hexane:2-propanol= 95:5

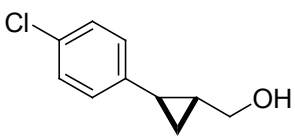
HPLC of 2-(4-chlorophenyl)cyclopropylmethanol (Table 2, entry 12).



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	20.042	84967	2705	V	1.3112
2	26.192	6395281	141602		98.6888
	TOTAL	6480248	144308		100.0000



trans ee: >99%

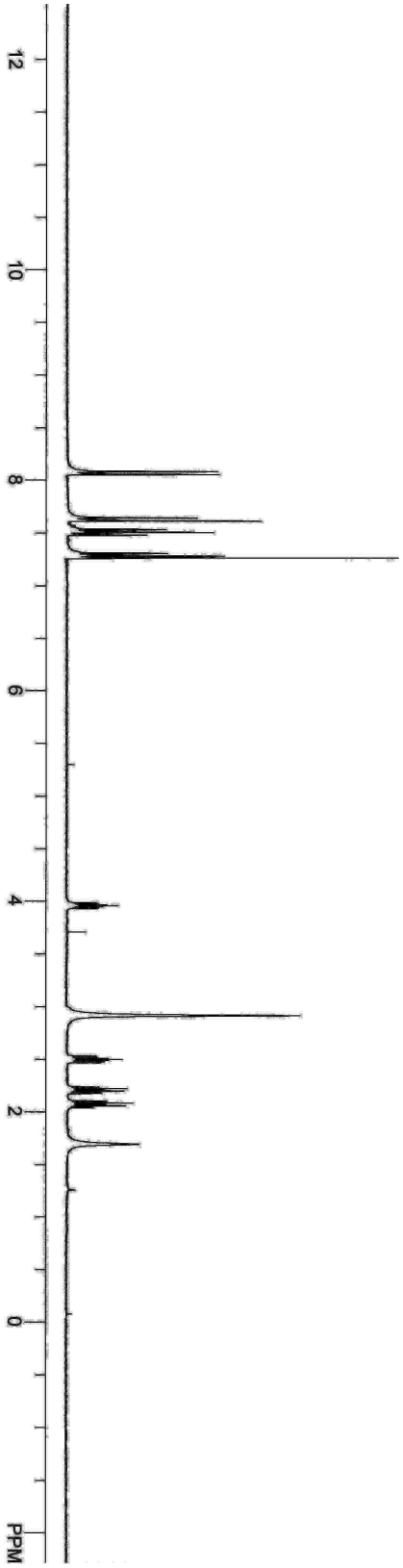
HPLC condition

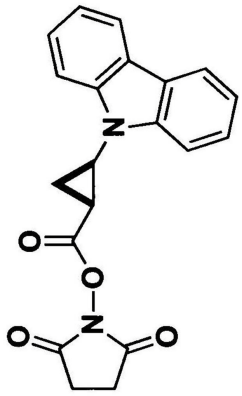
Column: Daicel CHIRALPAK OD

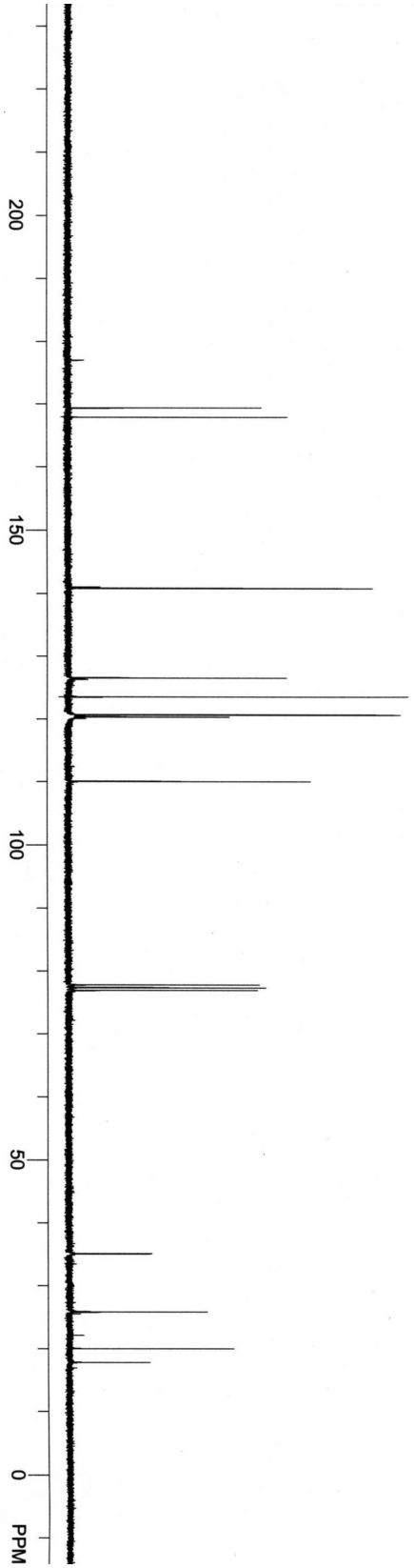
UV Detector: 254 nm

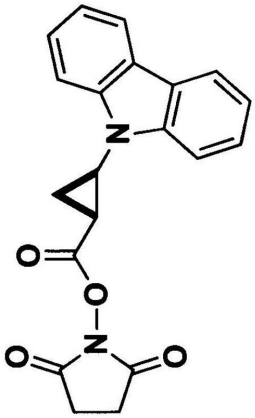
Flow rate: 0.5 ml/min

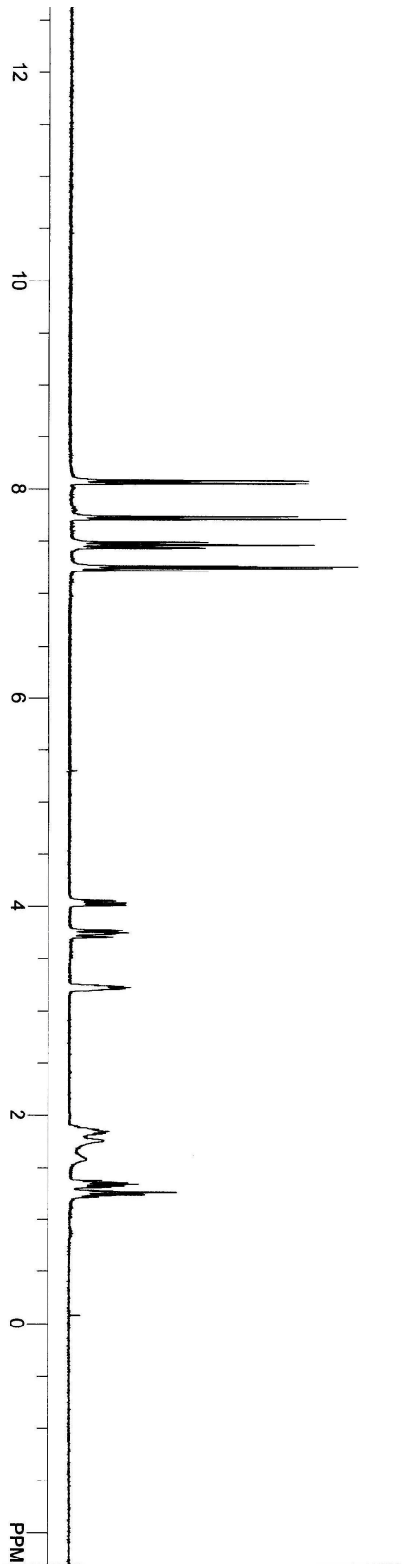
Eluent: hexane:2-propanol= 95:5

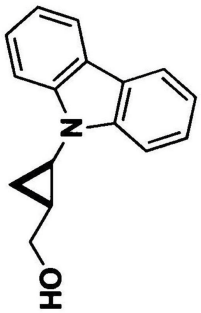

12
10
8
6
4
2
0
PPM

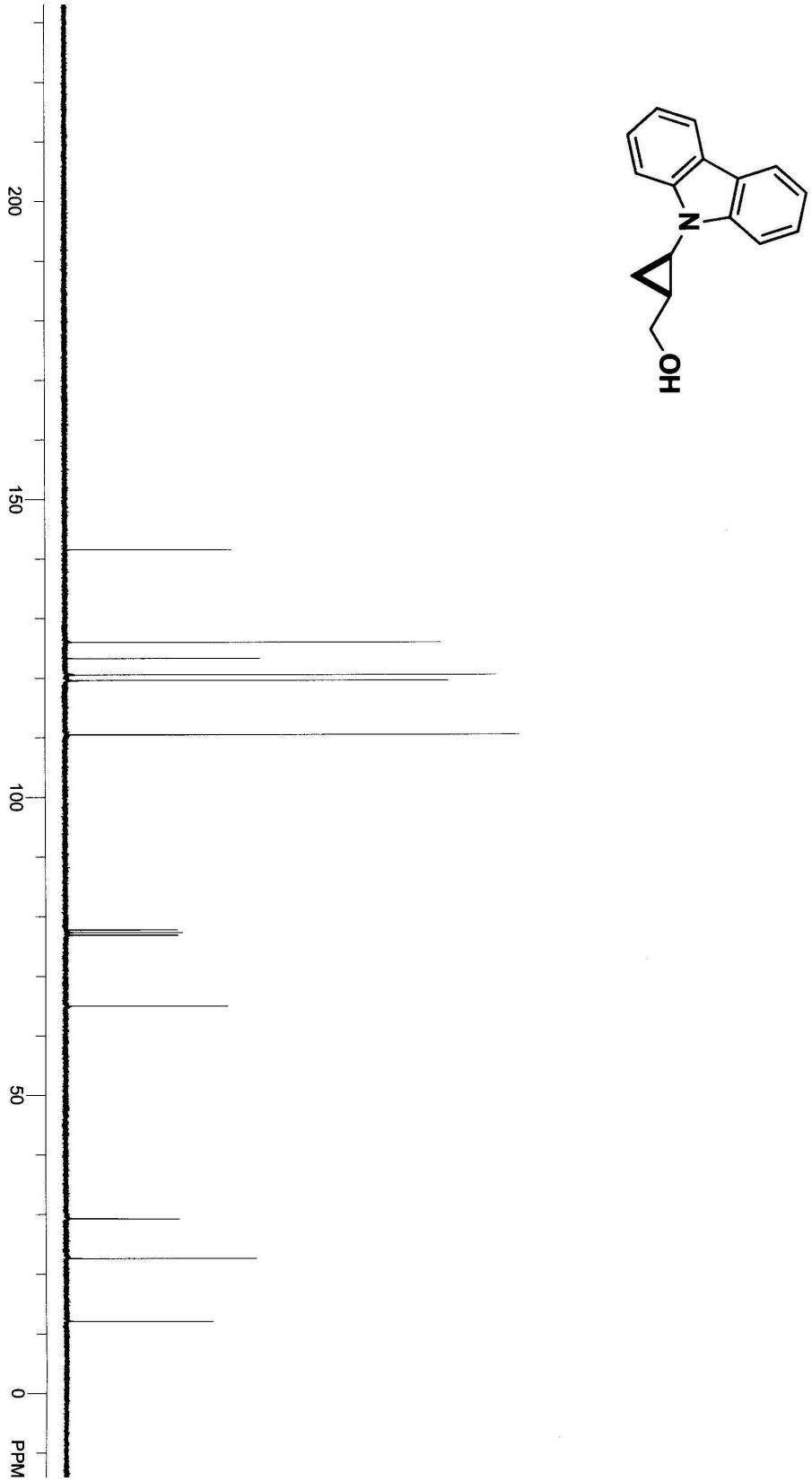

N
O
O
N
O
O


200
150
100
50
0
PPM


N
O
O
N
O
O

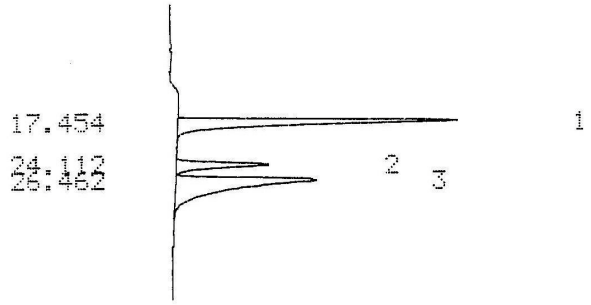

12
10
8
6
4
2
0
PPM


N
OH


200
150
100
50
0
PPM
N
HO

HPLC of 2-(*9H*-carbazol-9-yl)cyclopropylmethanol (Racemic).

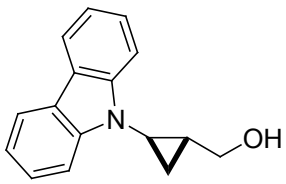
```
>807-IT  PARAM FILE# 0          RUN# 225      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION  1024 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	17.454	14372547	254762	VV	43.2339
2	24.112	4674464	84580	VV	14.0612
3	26.462	14196695	127120		42.7049
	TOTAL	33243706	466462		100.0000



racemic

HPLC condition

Column: Daicel CHIRALPAK OD-H

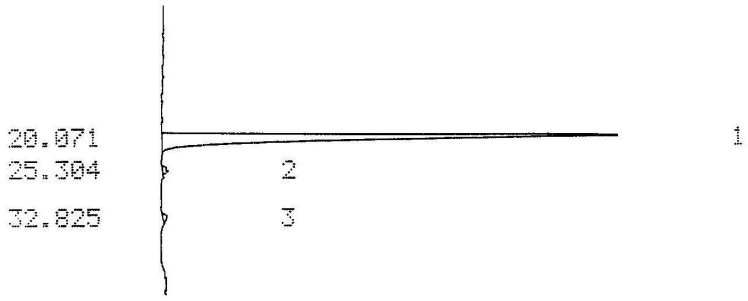
UV Detector: 254 nm

Flow rate: 1 ml/min

Eluent: hexane:2-propanol= 9:1

HPLC of 2-(*9H*-carbazol-9-yl)cyclopropyl methanol (Table 2, entry 14)

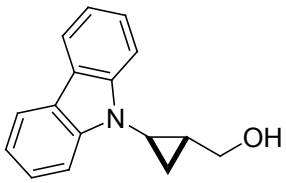
```
>807-IT  PARAM FILE# 0          RUN# 227      CHROMATOGRAM REPLOT
                                              CHART SPEED      1 mm/min
    START DELAY   0.00 min                    ATTENUATION  1024 mV F.S.
```



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	20.071	24100734	425200	VV	98.3400
2	25.304	161267	4917		0.6580
3	32.825	245565	3975		1.0020
	TOTAL	24507565	434092		100.0000



trans ee: 98%

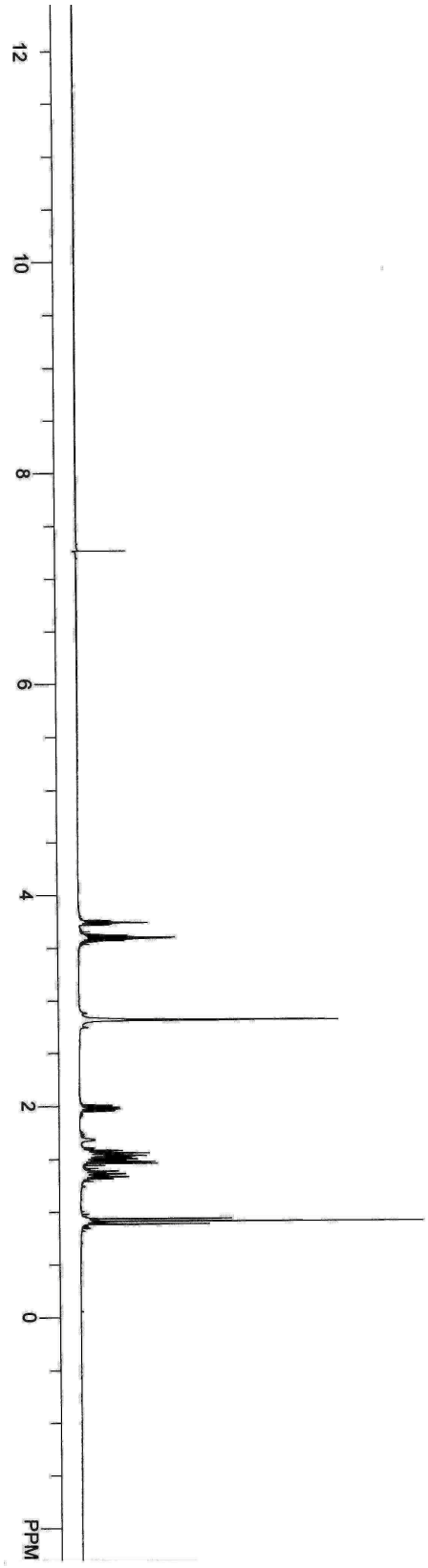
HPLC condition

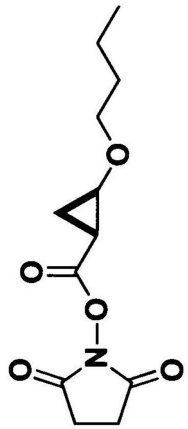
Column: Daicel CHIRALPAK OD-H

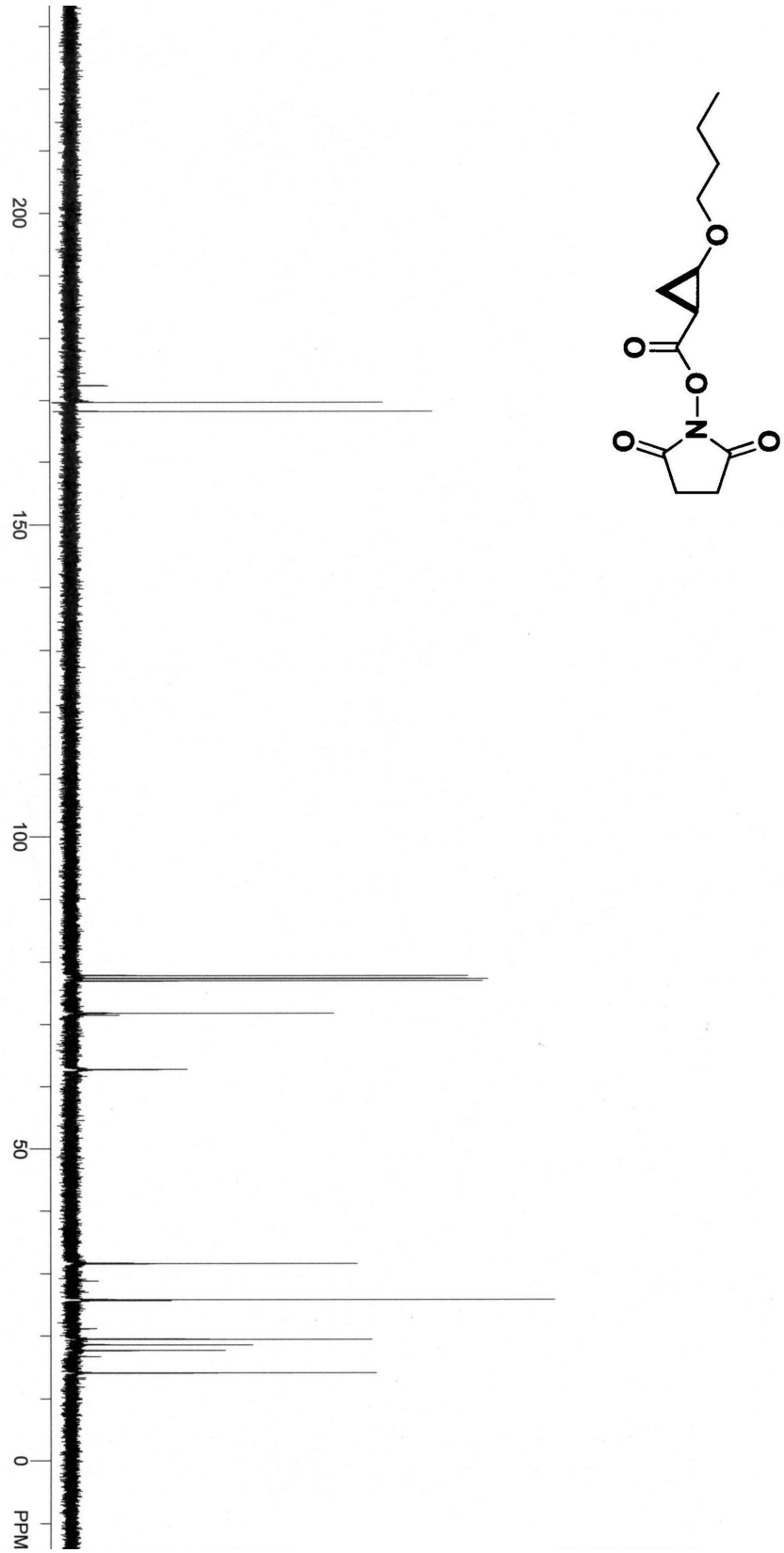
UV Detector: 254 nm

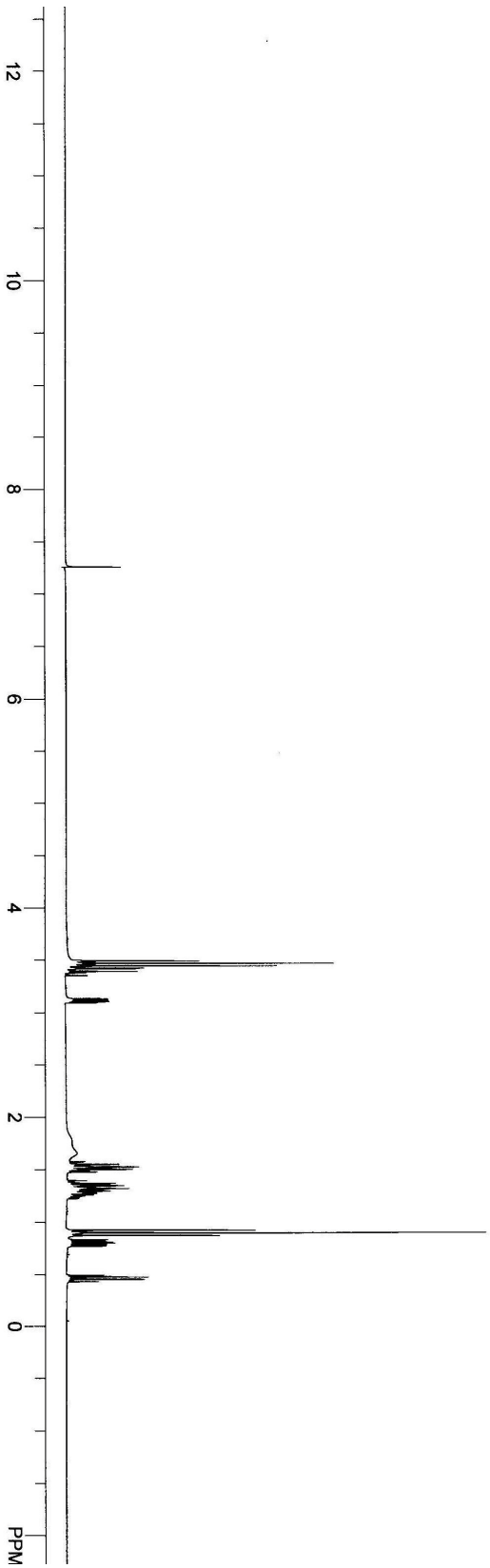
Flow rate: 1 ml/min

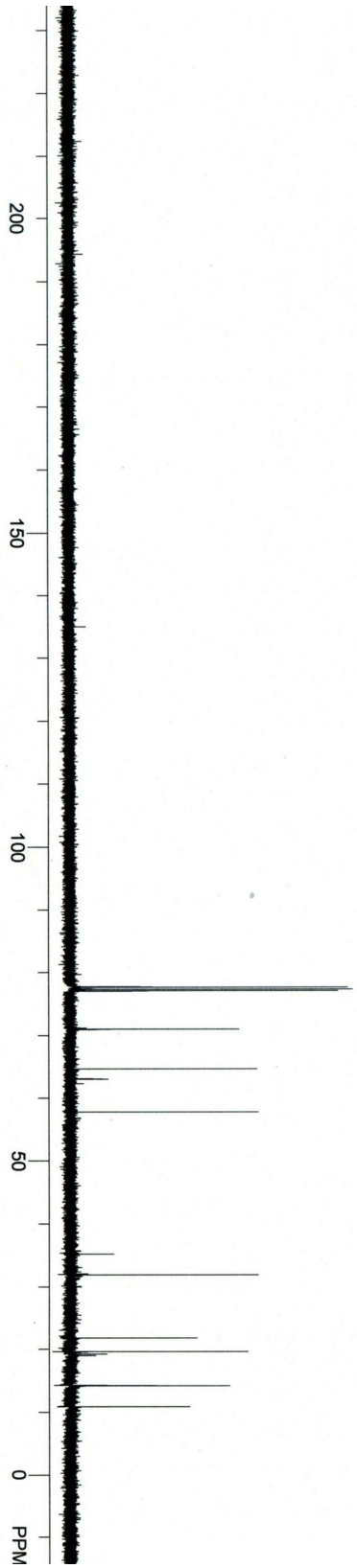
Eluent: hexane:2-propanol= 9:1


12
10
8
6
4
2
0
PPM

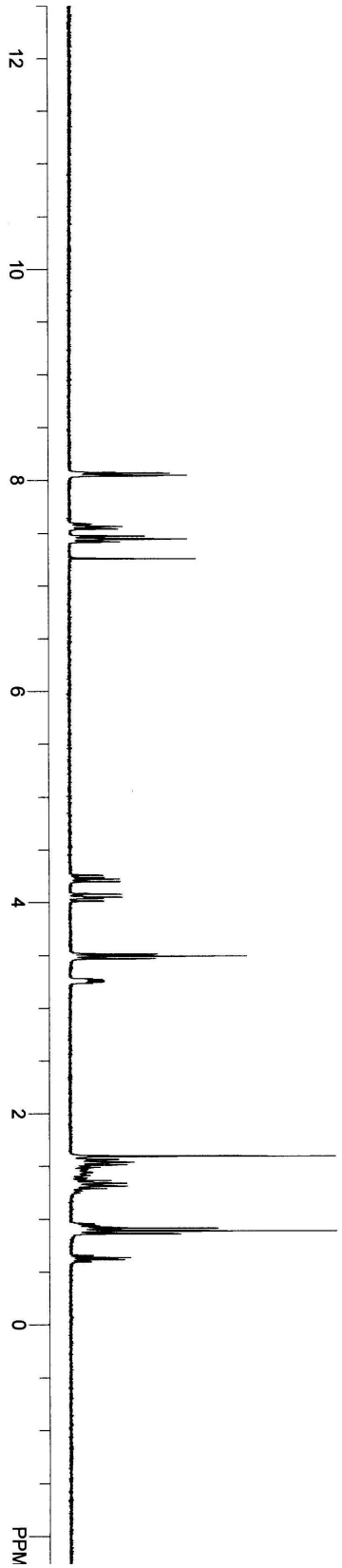

O
O
O
N
O
O

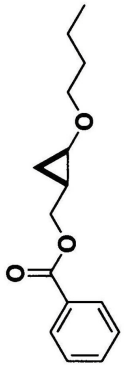

200
150
100
50
0
PPM
O
O
O
O
N
O
O

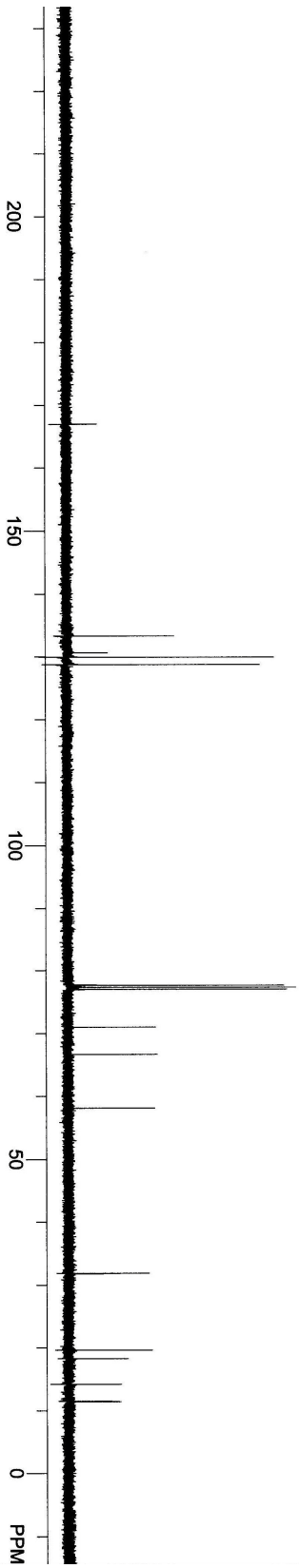

12
10
8
6
4
2
0
PPM
O
OH

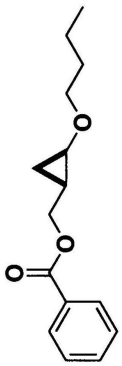

200
150
100
50
0
PPM


O
OH



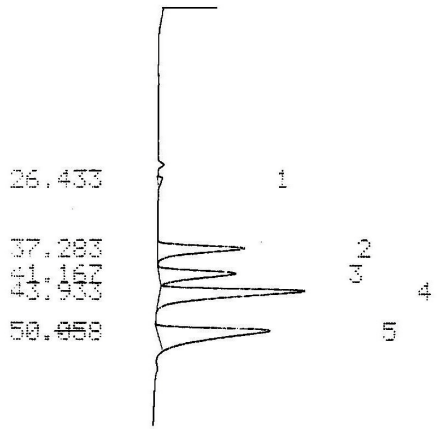



200
150
100
50
0
PPM



HPLC of 2-butoxycyclopropylmethyl benzoate (Racemic).

```
>807-IT  PARAM FILE# 1          RUN# 895      STARTED AT 18:04 12/19/'08
                                               CHART SPEED      1 mm/min
    START DELAY   0.00 min                     ATTENUATION   512 mV F.S.
```

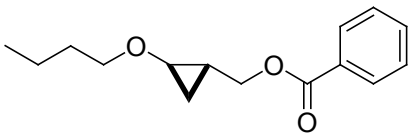



```
    -- % CALCULATION RESULT --

    NONAME1                                NONAME2

       WINDOW =  0 %   SCALE FACTOR =    1.0000     PEAK AREA

     PEAK#  RT(min)       AREA      HEIGHT   MK       AREA%
    ------------------------------------------------------------
         1   26.433       94298        1872  VV        0.5417
         2   37.283     3062230       41198  VV       17.5906
         3   41.167     2810930       36288  VV       16.1471
         4   43.933     5874408       68435  VV       33.7449
         5   50.058     5566425       53068  VV       31.9757
    ------------------------------------------------------------
             TOTAL     17408291      200860           100.0000
```



racemic

HPLC condition

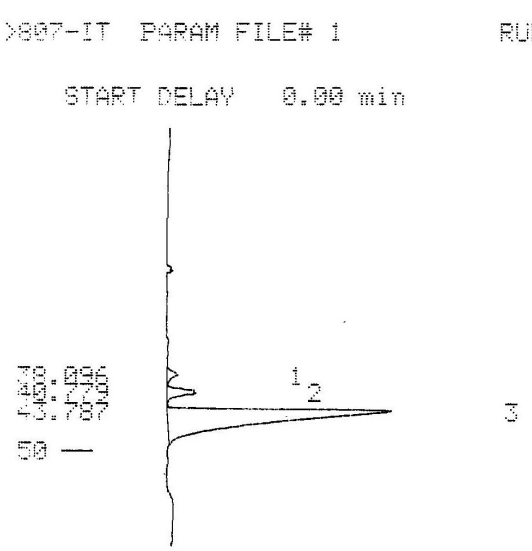
Column: Daicel CHIRALPAK OK

UV Detector: 254 nm

Flow rate: 0.3 ml/min

Eluent: hexane:2-propanol= 400:1

HPLC of 2-butoxycyclopropylmethyl benzoate (Table 2, entry 16).

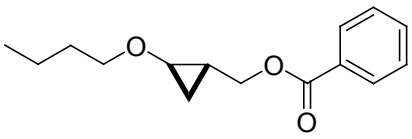


-- % CALCULATION RESULT --

NONAME1 NONAME2

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	38.096	651201	9565	VV	2.1580
2	40.779	1728015	26802	VV	5.7264
3	43.787	27796882	214300	VV	92.1156
	TOTAL	30176098	250667		100.0000



trans ee: >99%

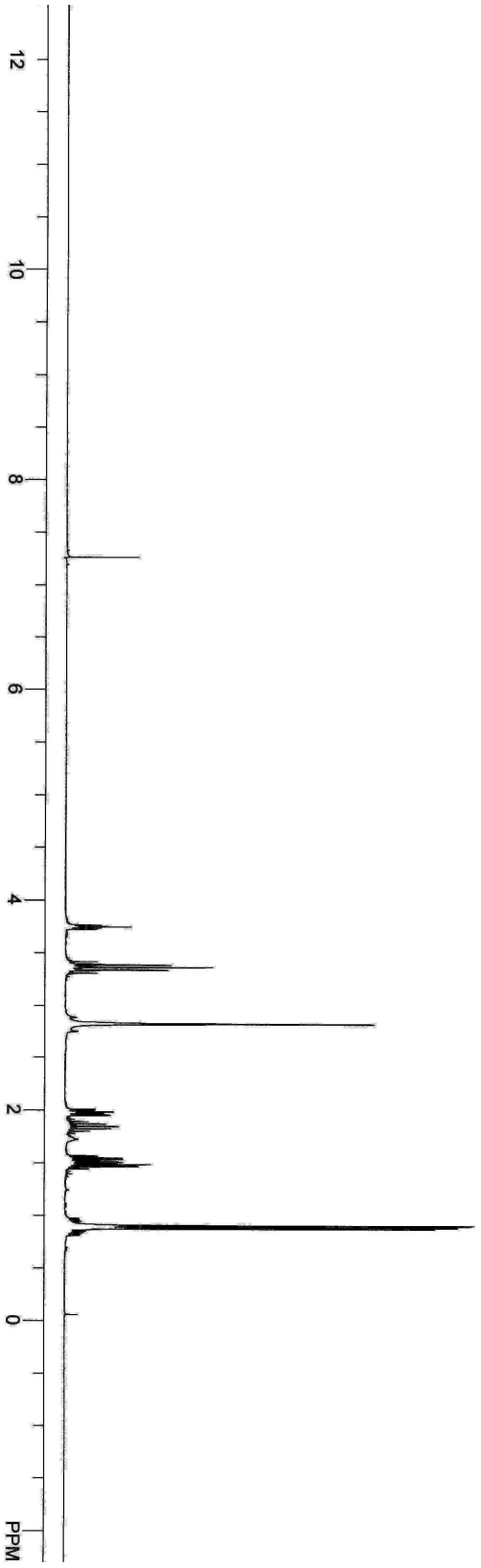
HPLC condition

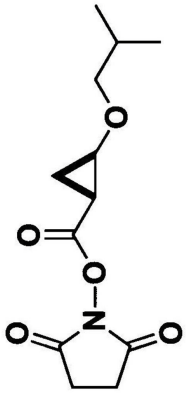
Column: Daicel CHIRALPAK OK

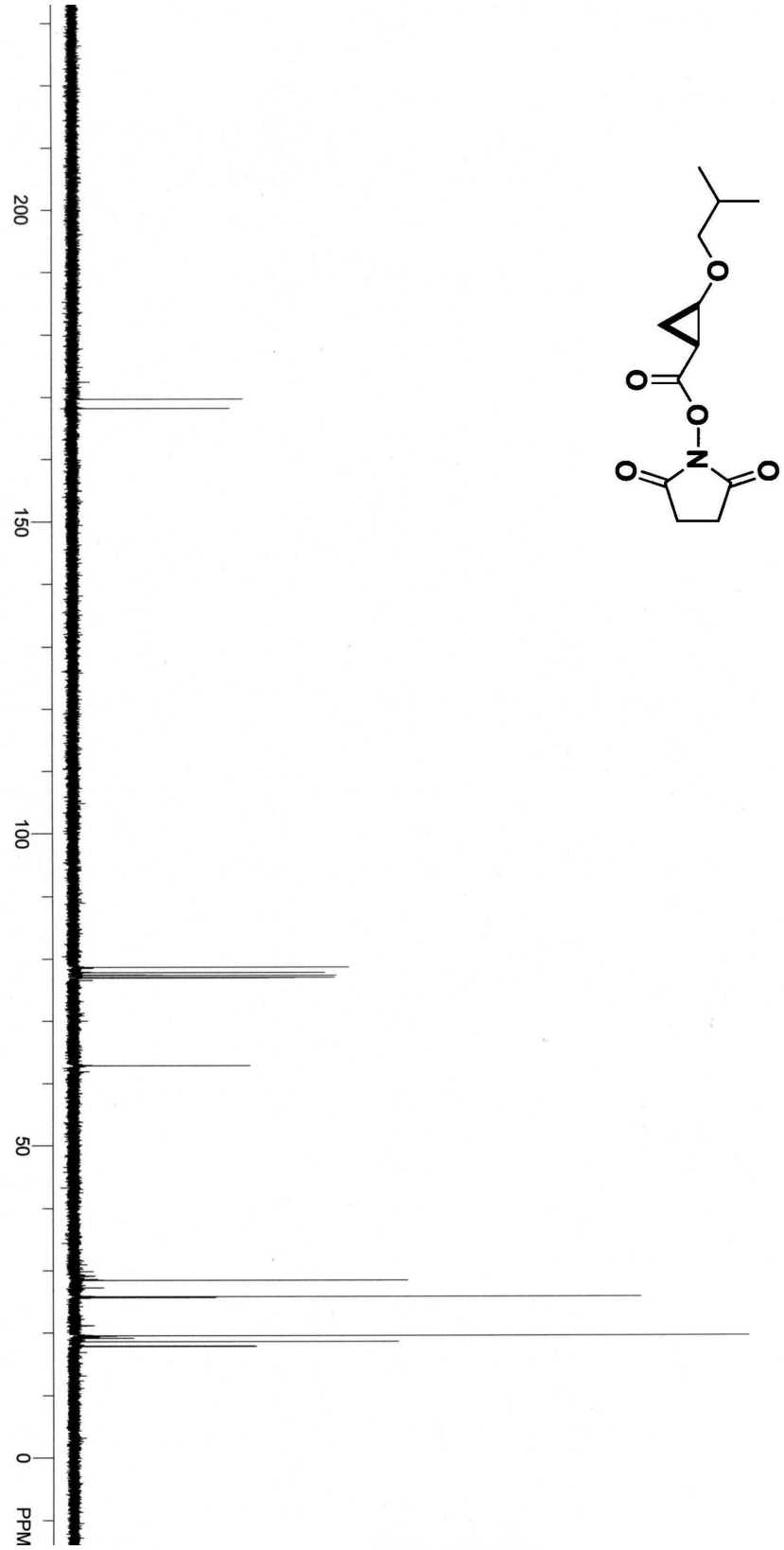
UV Detector: 254 nm

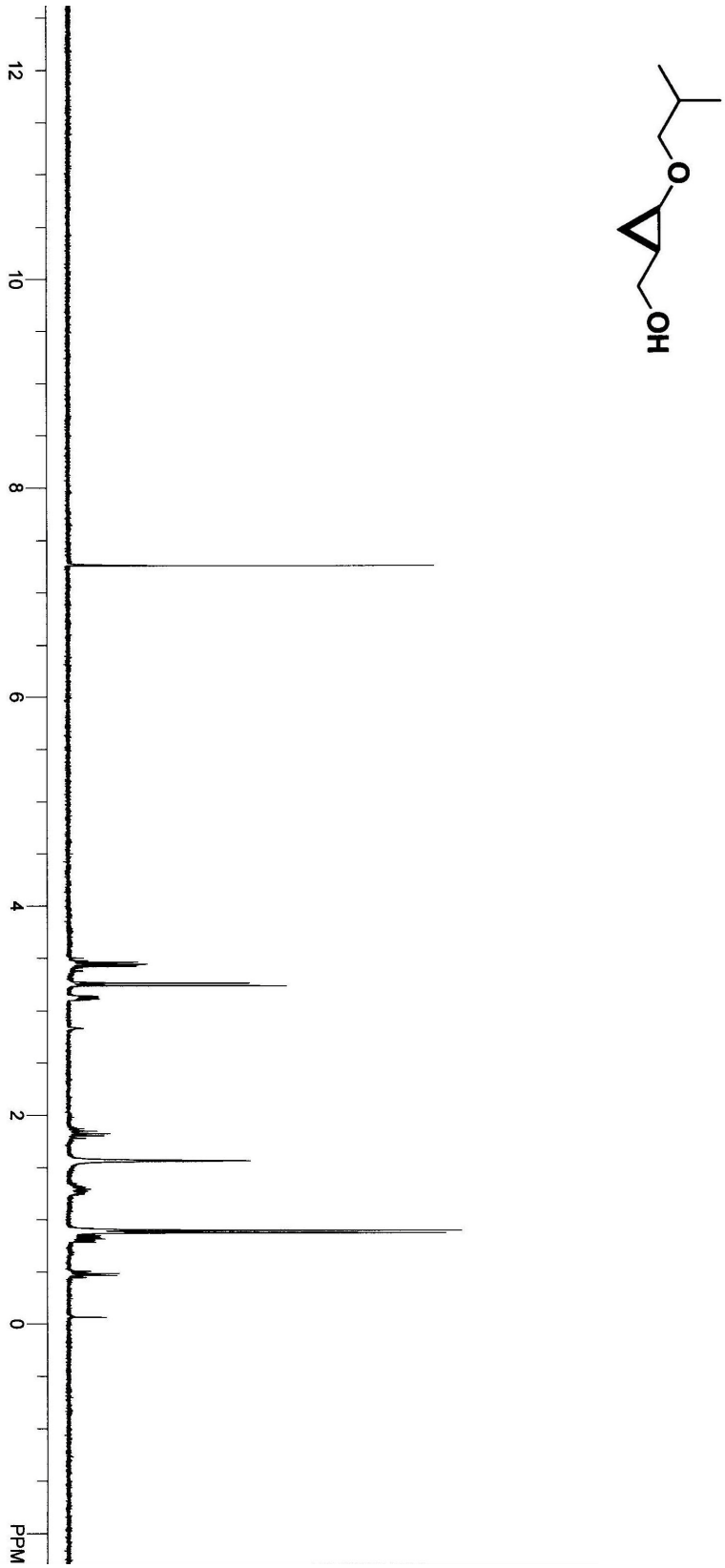
Flow rate: 0.3 ml/min

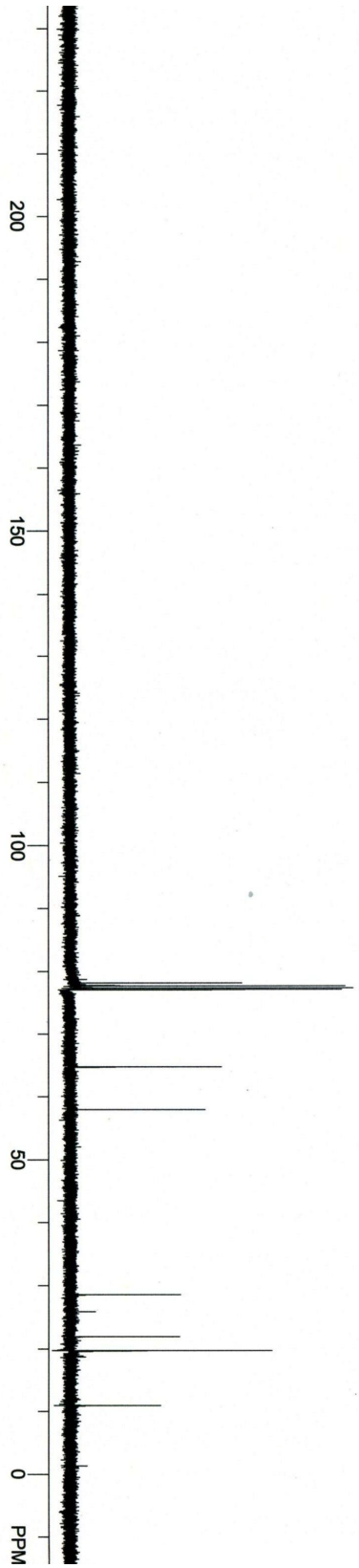
Eluent: hexane:2-propanol= 400:1


12
10
8
6
4
2
0
PPM

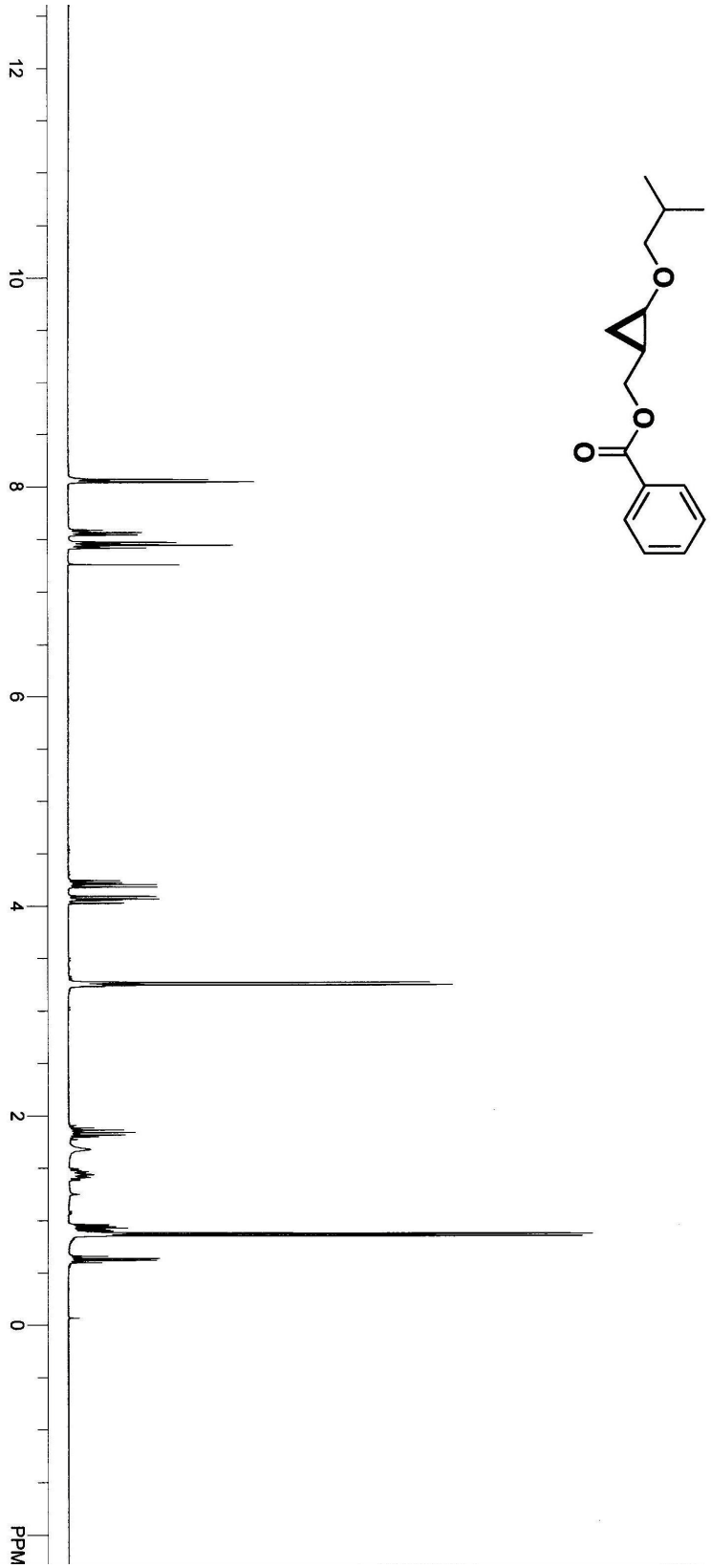


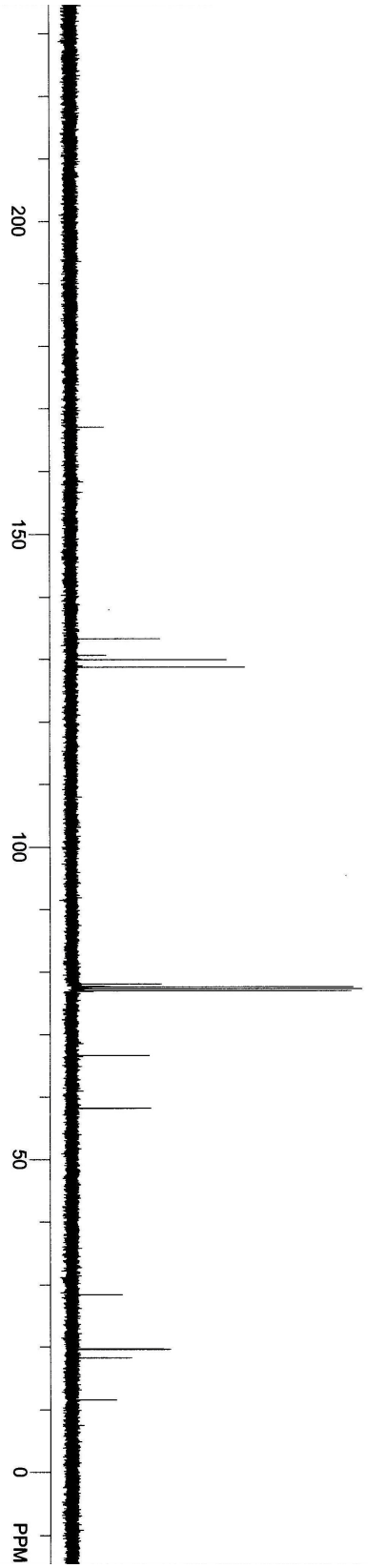

200
150
100
50
0
PPM

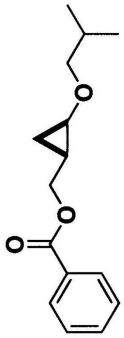



200
150
100
50
0
PPM

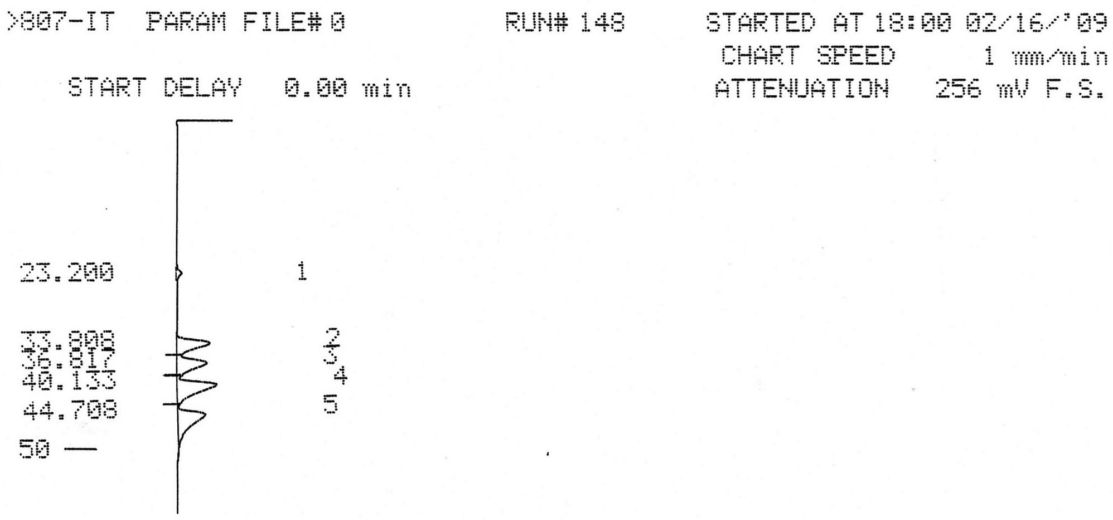

O
HO


12
10
8
6
4
2
0
PPM
O
O
O





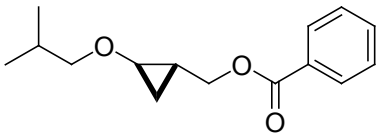
HPLC of 2-isobutoxycyclopropylmethyl benzoate (Racemic).



-- % CALCULATION RESULT --

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	23.200	55557	1014		1.6011
2	33.808	684463	7694	V	19.7252
3	36.817	706399	6819	V	20.3573
4	40.133	1026851	9203	V	29.5923
5	44.708	996726	6457	V	28.7241
	TOTAL	3469996	31188		100.0000



racemic

HPLC condition

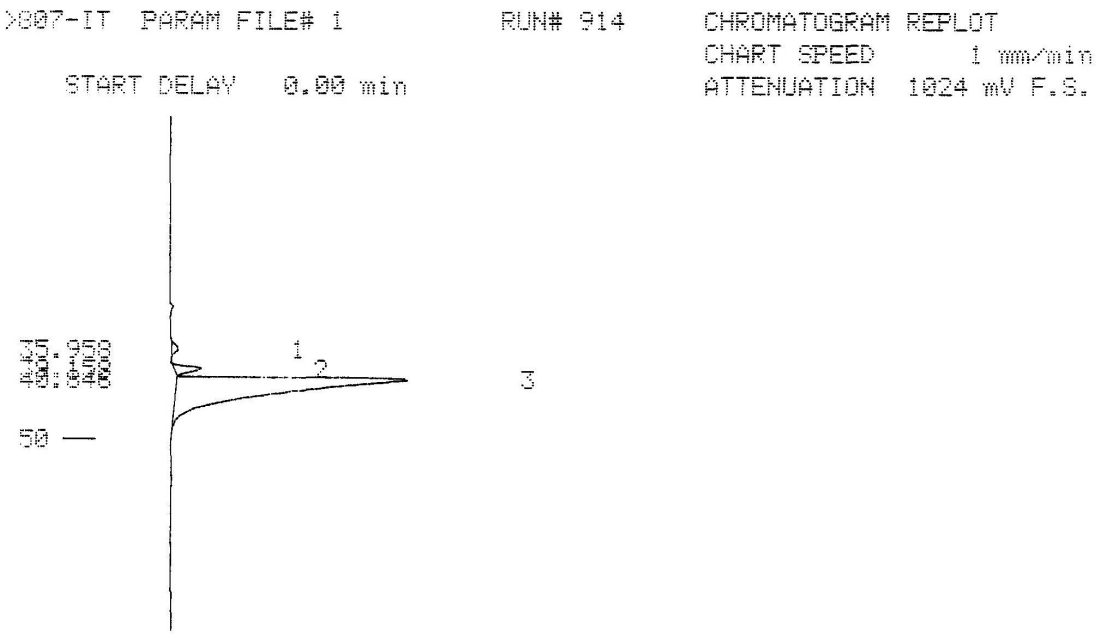
Column: Daicel CHIRALPAK OK

UV Detector: 254 nm

Flow rate: 0.3 ml/min

Eluent: hexane:2-propanol= 800:1

HPLC of 2-isobutoxycyclopropylmethyl benzoate (Table 2, entry 18).

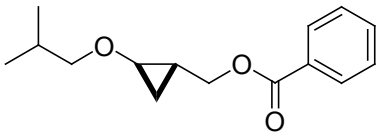


-- % CALCULATION RESULT --

NONAME1 NONAME2

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	35.958	451326	5840	VV	1.2675
2	39.158	1431373	25481	VV	4.0199
3	40.846	33724783	220136	VV	94.7126
	TOTAL	35607482	251457		100.0000



trans ee: >99%

HPLC condition

Column: Daicel CHIRALPAK OK

UV Detector: 254 nm

Flow rate: 0.3 ml/min

Eluent: hexane:2-propanol= 800:1