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Supporting Information

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Supporting Information

A New Chiral Hypervalent Iodine(III) Reagent for Enantioselective Dearomatization of Phenols

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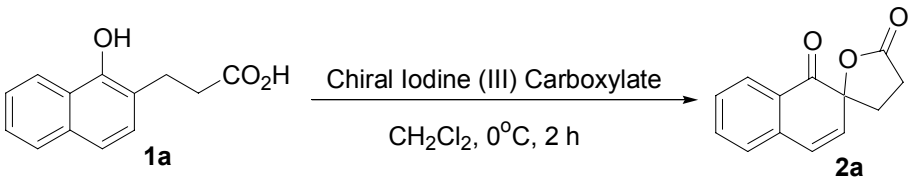
General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JMN-300 or EX-270 spectrometer in $CDCl_3$ with tetramethylsilane (δ 0.00 for ^{1}H and ^{13}C) as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. High resolution mass spectra and elemental analysis were performed by the Elemental Analysis Section of Osaka University. Flash column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh)). HPLC analysis was performed using multiwavelength detector JASCO DM-2010. Chiral columns include Chiralcel OD, Chiralpark AD, and Chiralpark AD-H (Daicel Chemical Industries, Ltd., 0.46 $\phi \times 25$ cm).

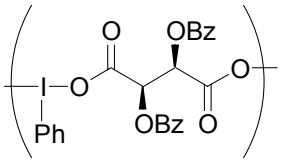
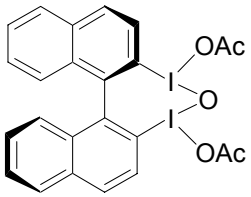
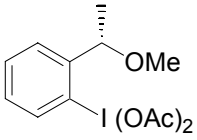
1.Preliminary investigation using the known chiral iodine(III) carboxylates 3-5

Chiral iodine(III) carboxylates **3-5** were prepared according to the procedures of the literatures.[1-3] The reactions were performed with 0.55-1.1 eq. (110 mol% of the iodine(III) atoms) of chiral iodine(III) carboxylates **3-5** at 0.02 M concentration of **1a** in CH_2Cl_2. The reaction mixtures were stirred at 0 ^{o}C for the appropriate times (see, the following table). After the reaction was completed, saturated $NaHCO_3$ aq. was added to the mixtures. The organic layer was separated, and the aqueous phase was extracted

with CH_2Cl_2. The combined extract was dried with anhydrous Na_2SO_4 and evaporated to dryness. The residues were purified by column chromatography on silica-gel (eluent: *n*-hexane/AcOEt) to give pure **2a**. The enantiomeric excesses of the product were measured by HPLC analysis.



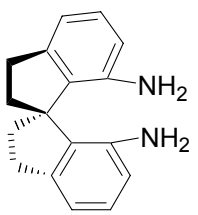
1a **2a**

Chiral Iodine (III) Carboxylate	yield(%)	ee. (%)
1)  **3**	40	3
2)  **4**	47	5
3)  **5**	66	1

2. Synthesis of the New Hypervalent Iodine(III) Reagent (R)-9

2-1. Synthesis of (*R*)-1,1'-Spirobiindane-7,7'-diamine (*R*)-7 [4]

(*R*)-7,7'-Bis(trifluoromethanesulfonyloxy)-1,1'-spirobiindane **(*R*)-6** was prepared according to the procedure of the literature.[5] To a mixture of $Pd(OAc)_2$ (1 g, 4.45 mmol), Cs_2CO_3 (16.4 g, 50.3 mmol), and (±)-BINAP (3.36 g, 5.40 mmol) in toluene (100 mL), benzylamine (20 mL, 183 mmol) and **(*R*)-6** (9.28 g, 18.0 mmol)

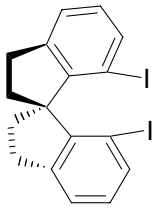


(*R*)-7

were added, and then stirred for 2 h at 100 °C. After cooling the reaction mixture, it was filtrated through celite, and toluene was removed from the filtrate using a rotary evaporator. The residue was subjected to column chromatography on silica-gel (eluent: *n*-hexane/AcOEt 20/1) to give crude (*R*)-7,7'-bis(benzylamino)-1,1'-spirobiindane, which was used without further purification in the next step.

Then, (*R*)-7,7'-bis(benzylamino)-1,1'-spirobiindane was dissolved in a mixed solvent [EtOAc (500 mL) and MeOH (200 mL)]. 10% $Pd(OH)_2/C$ (1 g) was then added, and the resulting suspension was stirred under an atmosphere of hydrogen for 16 h at 40 °C. The reaction mixture was filtrated through celite, and the solvents were removed under vacuum. Pure (*R*)-1,1'-spirobiindane-7,7'-diamine **(*R*)-7** (3.6 g, 14.4 mmol) was obtained in 80% yield after column chromatography on silica-gel (eluent: *n*-hexane/AcOEt 10/1); white powder**,** m.p. 167-168 °C, R_f = 0.17 (hexane/EtOAc = 10/1); ^{1}H-NMR (300 MHz, $CDCl_3$): 2.13-2.28 (m, 4H), 2.88-3.06 (m, 4H), 3.44 (s, 4H), 6.43 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 30.9, 35.2, 58.7, 113.2, 115.0, 128.5, 129.7, 143.2, 144.9.

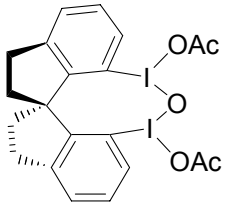
2-2. Synthesis of (*R*)-7,7'-Diiodo-1,1'-spirobiindane (*R*)-8



(*R*)-8

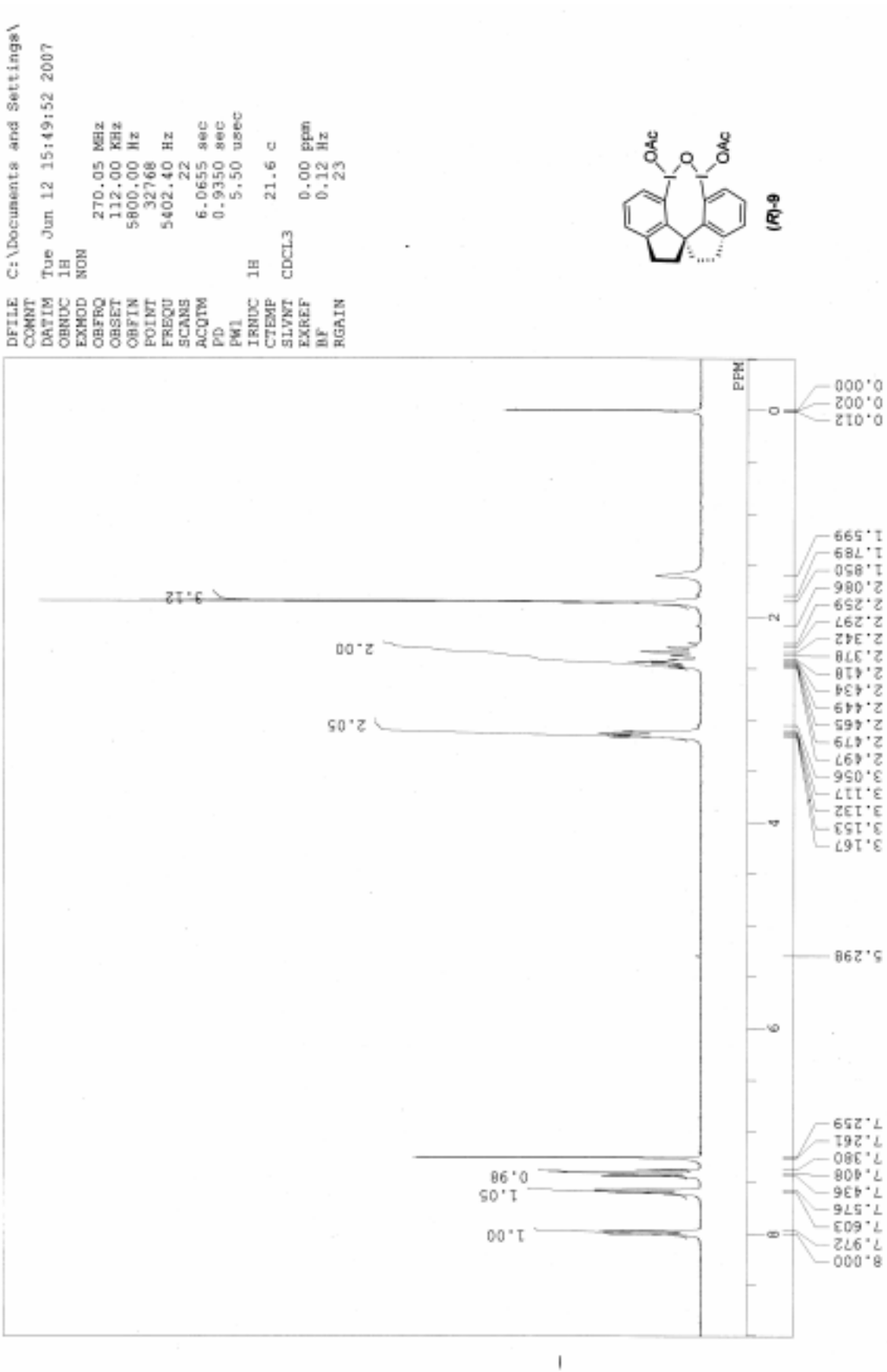
(*R*)-7 (500 mg, 2.0 mmol) was dissolved in 24 mL of trifluoroacetic acid under nitrogen. $NaNO_2$ (552 mg, 8.0 mmol) was added to the solution, and it was stirred for 30 min at 0 °C. The reaction mixture was added to a solution of KI (2.66 g, 16.0 mmol) in H_2O (40 mL) at room temperature, and it was stirred for additional 15 min., and then for 5 h at 40 °C. After cooling, the reaction mixture was extracted with CH_2Cl_2. The organic phase was washed with dilute sodium thiosulfate aq. and sat. NaCl aq., and dried with anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica-gel (eluent: *n*-hexane) to give (*R*)-7,7'-diiodo-1,1'-spirobiindane **(*R*)-8** (474 mg, 1.0 mmol, 50% yield) as white powder.**;** m.p. 105-107 °C, R_f = 0.44 (hexane); $[\alpha]^{25}_D$ +6.3 (c 0.93, $CHCl_3$); IR (KBr, cm^{-1}): 2928s, 2851m, 1556m, 1440s, 1423m, 1317w, 1107m, 866m, 847w, 766s;
^{1}H-NMR (300 MHz, $CDCl_3$): 2.19-2.40 (m, 4H), 3.03-3.09 (m, 4H), 6.91 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.2Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 30.6, 36.9, 66.2, 93.7, 124.6, 128.5, 137.9, 146.7, 148.2; HRMS (FAB) calcd for $C_{17}H_{14}I_2Na$ (M^+ + Na) : 494.9083, found: 494.9090.

2-3. Synthesis of the New Hypervalent Iodine(III) Reagent (R)-9



(*R*)-9

To a solution of ***(R)*-8** (340 mg, 0.72 mmol) in AcOH (7 mL) and CH_3CN (23 mL), Selectfluor^{TM} (1.28 g, 3.61 mmol) was added, and the mixture was stirred for 12 h. CH_3CN was removed, and H_2O was added to the residue. The resulting solution was extracted with CH_2Cl_2, and the organic phase was dried with anhydrous Na_2SO_4. After removal of the solvent, the crude **(*R*)-9** was dissolved in minimal amount of CH_2Cl_2. The CH_2Cl_2 solution including **(*R*)-9** was added dropwise to a stirred hexane. The resulting precipitate was collected and dried in vacuo to give **(*R*)-9** (400 mg, 0.66 mmol, 90% yield) as white powder**;** m.p. 134-136 ^{o}C; $[\alpha]^{25}_{D}$ +21.0 (c 1.09, $CHCl_3$); IR (KBr, cm^{-1}): 2924s, 2851s, 1715m, 1657m, 1587w, 1558m, 1442m, 1219m, 1107m, 868m, 770s, 671w; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.85 (s, 6H), 2.30-2.49 (m, 4H), 3.13-3.16 (m, 4H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 21.4, 30.8, 37.8, 68.3, 116.6, 129.7, 131.6, 135.6, 145.3, 146.0, 177.2; HRMS (FAB) calcd for $C_{21}H_{20}I_2O_5 \cdot H_2O$ ($M^+ + H_2O$): 623.9506, found: 623.9515.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BF 0.12 Hz
RGAIN 23
OAc
OAc
(R)-9
PPM
3.12
2.00
2.05
0.98
1.05
1.00
0.000
0.002
0.012
1.599
1.789
1.850
2.086
2.259
2.297
2.342
2.378
2.418
2.434
2.449
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77.427
116.615
129.695
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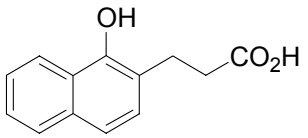
177.177

3. Synthesis of 3-(1-Hydroxy-2-naphthyl)propionic acid derivatives 1

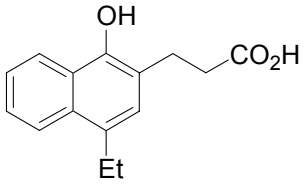
3-(1-Hydroxy-2-naphthyl)propionic acid **1a** was prepared by hydrolysis of 3,4-dihydro-2H-naphtho[1,2-b]pyran-2-one.[6] Other substituted derivatives (**1b**-**1e**) were prepared from the corresponding naphthols according to the procedure of the literature.[7]

3-(1-Hydroxy-2-naphthyl)propionic acid (1a)



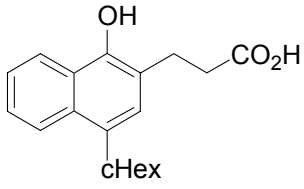
white powder; m.p. 104-107 °C; IR (KBr, cm^{-1}): 3100s, 1681s, 1082m, 808s; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.85-2.89 (m, 2H), 3.01-3.05 (m, 2H), 7.17 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.42-7.47 (m, 2H), 7.71-7.76 (m, 1H), 8.22-8.25 (m, 1H); ^{13}C-NMR (75 MHz, acetone-d_6): 25.7, 35.1, 120.7, 122.1, 122.7, 125.7, 126.3, 126.7, 128.2, 129.4, 134.6, 150.5, 176.8; HRMS (FAB) calcd for $C_{13}H_{12}O_3Na$ (M^+ + Na): 239.0684, found: 239.0686.

3-(4-Ethyl-1-hydroxy-2-naphthyl)propionic acid (1c)



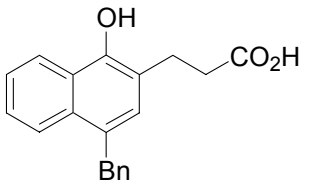
yellow powder; m.p. 130-131 °C; IR (KBr, cm^{-1}): 3100s, 1682s, 1454m, 1392m, 1099m, 883m; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.24 (t, J = 7.5 Hz, 3H), 2.09-2.24 (m, 1H), 2.36-2.45 (m, 1H), 2.53-2.64 (m, 3H), 2.80-2.93 (m, 1H), 6.00 (s, 1H), 7.38-7.48 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H); ^{13}C-NMR (75 MHz, acetone-d_6): 15.7, 25.7, 25.9, 35.3, 121.6, 123.5, 124.3, 125.3, 126.1, 127.3, 128.3, 132.5, 132.7, 149.0, 176.9; HRMS (FAB) calcd for $C_{15}H_{16}O_3$ (M^+): 244.1099, found: 244.1091.

3-(4-Cyclohexyl-1-hydroxy-2-naphthyl)propionic acid (1d)



yellow powder; m.p. 124-125 °C; IR (KBr) cm^{-1}: 3100s, 2925s, 2850s, 1693s, 1392s, 1101m, 760s; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23-1.60 (m, 5H), 1.81-2.05 (m, 5H), 2.84-2.91 (m, 2H), 2.96-3.03 (m, 2H), 3.17-3.23 (m, 1H), 7.04 (s, 1H), 7.41-7.49 (m, 2H), 7.98-8.02 (m, 1H), 8.27-8.30 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): 25.9, 27.2, 27.9, 35.2, 35.3, 39.4, 121.6, 123.6, 123.7, 125.1, 125.8, 126.0, 127.3, 132.2, 136.3, 148.7, 176.8; HRMS (FAB) calcd for $C_{19}H_{22}O_3Na$ (M^+ + Na): 321.1467, found: 321.1479.

3-(4-Benzyl-1-hydroxy-2-naphthyl)propionic acid (1e)



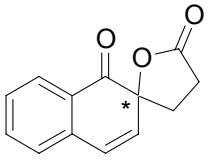
yellow powder; m.p. 131-132 °C; IR (KBr) cm^{-1}: 3026s, 2918m, 1722s, 1390s, 1203s, 1097m, 912m, 760s, 737s, 696m; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.82-2.86 (m, 2H), 2.97-3.02 (m, 2H), 4.33 (s, 2H), 6.98 (s, 1H), 7.15-7.28 (m, 5H), 7.36-7.47 (m, 2H), 7.83-7.86 (m, 1H), 8.27-8.30 (m, 1H); ^{13}C-NMR (75 MHz, acetone-d_6): 25.7, 35.2, 39.1, 121.6, 123.4, 125.1, 125.4, 126.2, 126.6, 127.4, 129.1, 129.28, 129.33, 131.0, 132.9, 142.4, 149.6, 176.8; HRMS (FAB) calcd for $C_{20}H_{18}O_3Na$ (M^+ + Na): 329.1154, found: 329.1138.

***4. General Procedure for Ortho-Spirocyclization by the Chiral Hypervalent Iodine(III) Reagent* (*R*)-9**

In a flame-dried flask, under nitrogen, to a stirred solution of 3-(1-Hydroxy-2-naphthyl)propionic acid **1a** (21.6 mg, 0.10 mmol) in dry $CHCl_3$ (5 mL), the chiral reagent **(*R*)-9** (33.4 mg, 0.055 mmol) was added at -50 °C. After being stirred for 2 h under the same conditions while the reaction progress was evaluated by TLC. After the reaction was completed, saturated $NaHCO_3$ aq. was added to the mixture. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 several times. The combined extract was dried with anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica-gel (eluent: *n*-hexane/AcOEt) to give spiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione **2a** (14.1 mg, 0.066 mmol) in 66% yield. The enantiomeric excess was measured by HPLC analysis.

The use of (*S*)-**9** could afford the opposite enantiomer (-)-**2** in a comparable yield and ee.

Spiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione (2a)

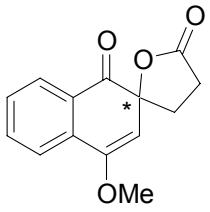


(+) - **2a**

white powder; m.p. 104-105 °C; IR (KBr, cm^{-1}): 1788s, 1693s, 1597s, 1481m, 1454m, 1323m, 1296s, 1178s, 1123m, 1032s, 930s, 787s, 696m; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.13-2.25 (m, 1H), 2.39-2.47 (m, 1H), 2.55-2.65 (m, 1H), 2.85-2.98 (m, 1H), 6.21 (d, J = 9.9 Hz, 1H), 6.66 (d, J = 9.9 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H); ^{13}C-NMR (75 MHz,

$CDCl_3$): 26.4, 31.0, 83.4, 127.1, 127.5, 127.8, 127.9, 128.8, 132.1, 135.6, 136.7, 176.5, 196.5; HRMS (FAB) calcd for $C_{13}H_{11}O_3$ (M^+ + H): 215.0708, found: 215.0694. The enantiomeric excess of 78% was determined by HPLC (OD chiral column, eluent: *n*-Hexane/*i*-PrOH 85/15, flow rate: 1.0 ml/min, 25 °C, λ = 230 nm, t (major) = 16.07 min, t (minor) = 21.37 min).

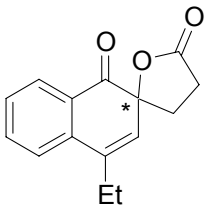
4'-Methoxyspiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione (2b)



(±) - **2b**

yellow oil; IR (KBr) cm^{-1}: 3069, 2940, 2843, 1783, 1693, 1656, 1597, 1573; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.14-2.25 (m, 1H), 2.45-2.53 (m, 1H), 2.57-2.67 (m, 1H), 2.90-3.03 (m, 1H), 3.85 (s, 3H), 5.12 (s, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): 27.7, 33.1, 55.3, 83.9, 100.0, 123.2, 127.2, 127.5, 129.4, 134.6, 125.3, 152.0, 176.6, 195.7; HRMS (FAB) calcd for $C_{14}H_{13}O_4$ (M^+ + H): 245.0814, found: 245.0812.

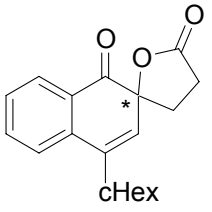
4'-Ethylspiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione (2c)



(+) - **2c**

white powder; m.p. 96-97 °C; IR (KBr, cm^{-1}): 2968m, 2937m, 2878m, 1787s, 1693s, 1597s, 1452m, 1294s, 1211s, 1175s, 1032s, 931s, 849m, 750m, 707m; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26 (t, *J* = 7.2 Hz, 3H), 2.13-2.22 (m, 1H), 2.36-2.45 (m, 1H), 2.54-2.64 (m, 3H), 2.82-2.96 (m, 1H), 6.00 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 8.05 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): 12.2, 24.8, 26.7, 31.4, 83.7, 124.2, 127.0, 127.3, 127.8, 128.4, 135.4, 137.3, 138.1, 176.5, 196.8; HRMS (EI) calcd for $C_{15}H_{14}O_3$ (M^+): 242.0943, found: 242.0941. The enantiomeric excess of 81% was determined by HPLC (AD-H chiral column, eluent: *n*-Hexane/*i*-PrOH 92/08, flow rate: 1.0 ml/min, 25 °C, λ = 230 nm, t (minor) = 19.40 min, t (major) = 21.48 min).

4'-Cyclohexylspiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione (2d)

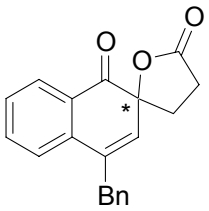


(+) - **2d**

white powder; m.p. 151-152 °C; IR (KBr, cm^{-1}): 2928s, 2853m, 1789s, 1693s, 1593m, 1450m, 1294m, 1175s, 1034m, 935m, 712m; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21-1.51 (m, 5H), 1.75-2.13 (m, 5H), 2.16-2.20 (m, 1H), 2.36-2.44 (m, 1H), 2.53-2.65 (m, 2H), 2.80-2.92 (m, 1H), 5.97 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.67 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 8.04 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): 26.2, 26.7, 31.5, 32.5, 32.8, 38.5,

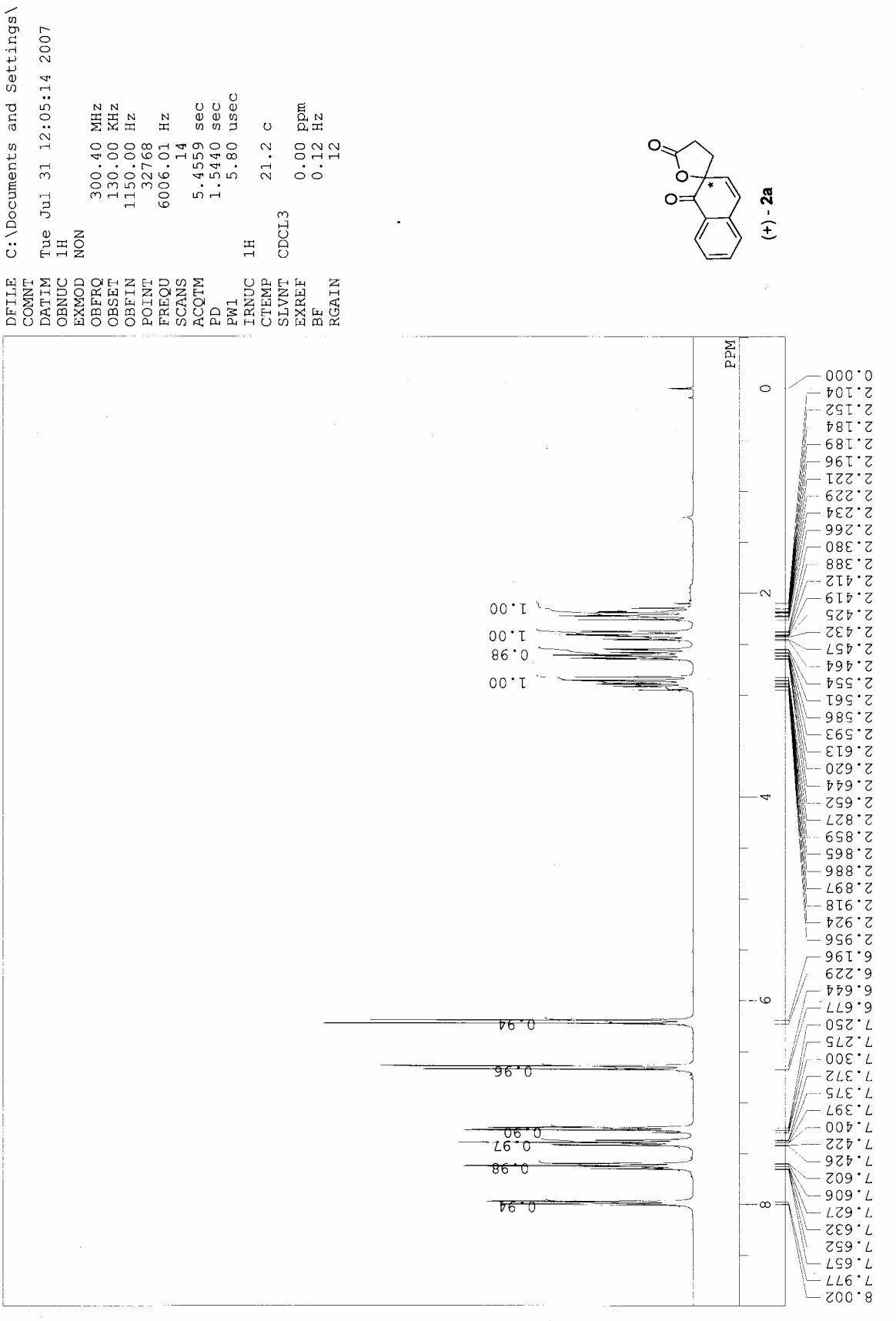
83.9, 124.0, 125.9, 127.7, 128.1, 128.2, 135.3, 137.0, 141.8, 176.5, 196.9; HRMS (FAB) calcd for $C_{19}H_{21}O_3$ (M^+ + H): 297.1412, found: 297.1505. The enantiomeric excess of 81% was determined by HPLC (AD chiral column, eluent: *n*-Hexane/ *i*-PrOH 97/03, flow rate: 0.8 ml/min, 25 °C, λ = 235 nm, t (major) = 33.41 min, t (minor) = 36.68 min).

4'-Benzylspiro[tetrahydrofuran-2,2'-(1'H-naphthalin)]-1',5-dione (2e)



(+) - **2e**

white powder; m.p. 159-160 °C; IR (KBr, cm^{-1}): 3061m, 3028m, 1790s, 1693s, 1597m, 1495m, 1452s, 1294m, 1211m, 1172s, 1032s, 930m, 735s, 700s, 654m; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.11-2.23 (m, 1H), 2.40-2.47 (m, 1H), 2.52-2.62 (m, 1H), 2.82-2.95 (m, 1H), 3.89 (s, 2H), 5.90 (s, 1H), 7.23-7.42 (m, 7H), 7.59 (t, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, d); ^{13}C-NMR (75 MHz, $CDCl_3$): 26.6, 31.4, 38.5, 83.6, 125.0, 126.7, 127.4, 127.9, 128.57, 128.64, 130.7, 135.4, 135.7, 137.0, 137.3, 176.4, 196.5; HRMS (FAB) calcd for $C_{20}H_{17}O_3$ (M^+ + H): 305.1099, found: 305.1168. The enantiomeric excess of 86% was determined by HPLC (OD chiral column, eluent: *n*-Hexane/*i*-PrOH 85/15, flow rate: 1.0 ml/min, 25 °C, λ = 235 nm, t (major) = 22.56 min, t (minor) = 52.23 min).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EXMOD NON
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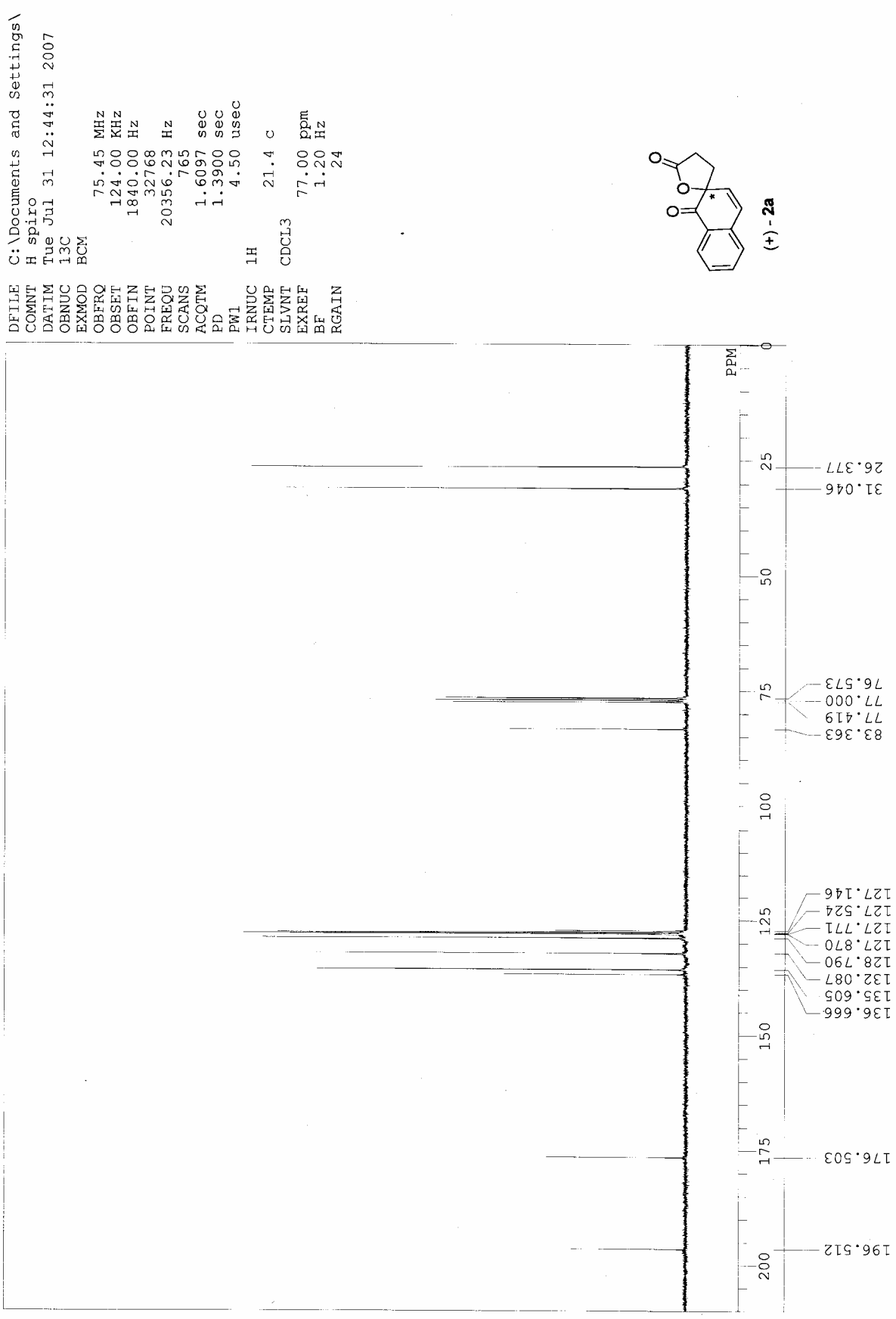
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 14
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
(+) - 2a
PPM
0 2 4 6 8
1.00
1.00
0.98
1.00
0.94
0.96
0.90
0.97
0.98
0.94
0.000
2.104
2.152
2.184
2.189
2.196
2.221
2.229
2.234
2.266
2.380
2.388
2.412
2.419
2.425
2.432
2.457
2.464
2.554
2.561
2.586
2.593
2.613
2.620
2.644
2.652
2.827
2.859
2.865
2.886
2.897
2.918
2.924
2.956
6.196
6.229
6.644
6.677
7.250
7.275
7.300
7.372
7.375
7.397
7.400
7.422
7.426
7.602
7.606
7.627
7.632
7.652
7.657
7.977
8.002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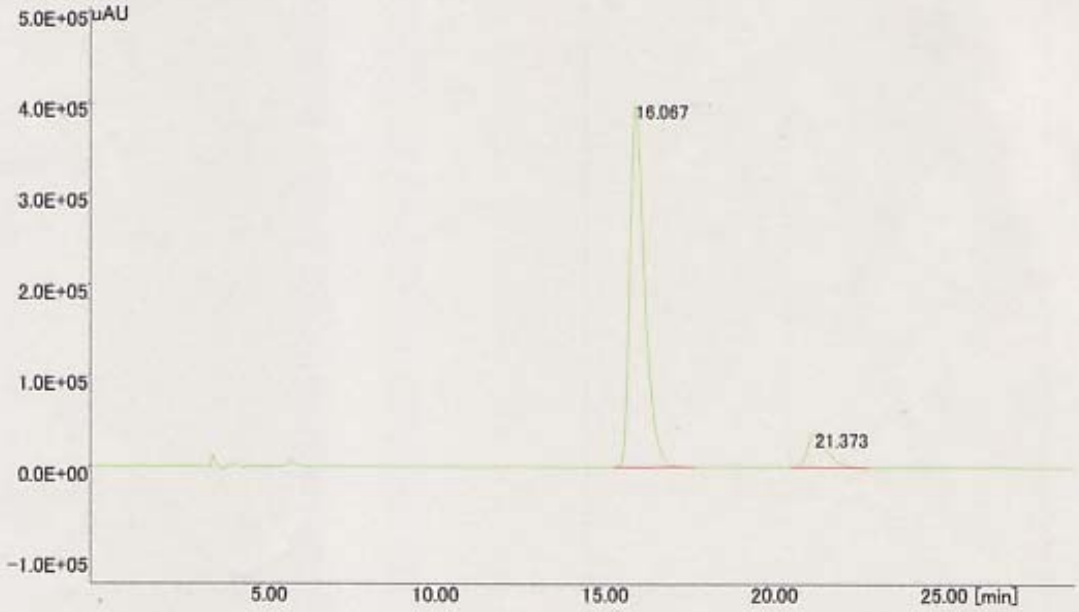
COMNT H spiro
DATIM Tue Jul 31 12:44:31 2007
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFTN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 765
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
(+)-2a
PPM
0
25
50
75
100
125
150
175
200
26.377
31.046
76.573
77.000
77.419
83.363
127.146
127.524
127.771
127.870
128.790
132.087
135.605
136.666
176.503
196.512

Chromatogram



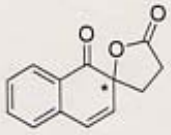
ファイル名: AM890_230.CH1

コメント:
OD
Hex/iPrOH=85/15
1.0ml/min 25C
Wavelength = 230 [nm]
Tacc [Sec] = 0.80 Wacc [nm] = 4.0
Autozero [min] : 0.00

Vial # = 1 Rack # = 0
注入日 : 25-Apr-2007 18:55:04
現在日時: 7-Aug-2007 17:16:44
ユーザー : TANIMOTO
グループ : TANIMOTO
システムプログラム:

#	ピーク名	Rt	高さ[uAU]	面積[uAU.Sec]	面積%
1		16.067	396957	11909025.777	89.01
2		21.373	36655	1470795.222	10.99

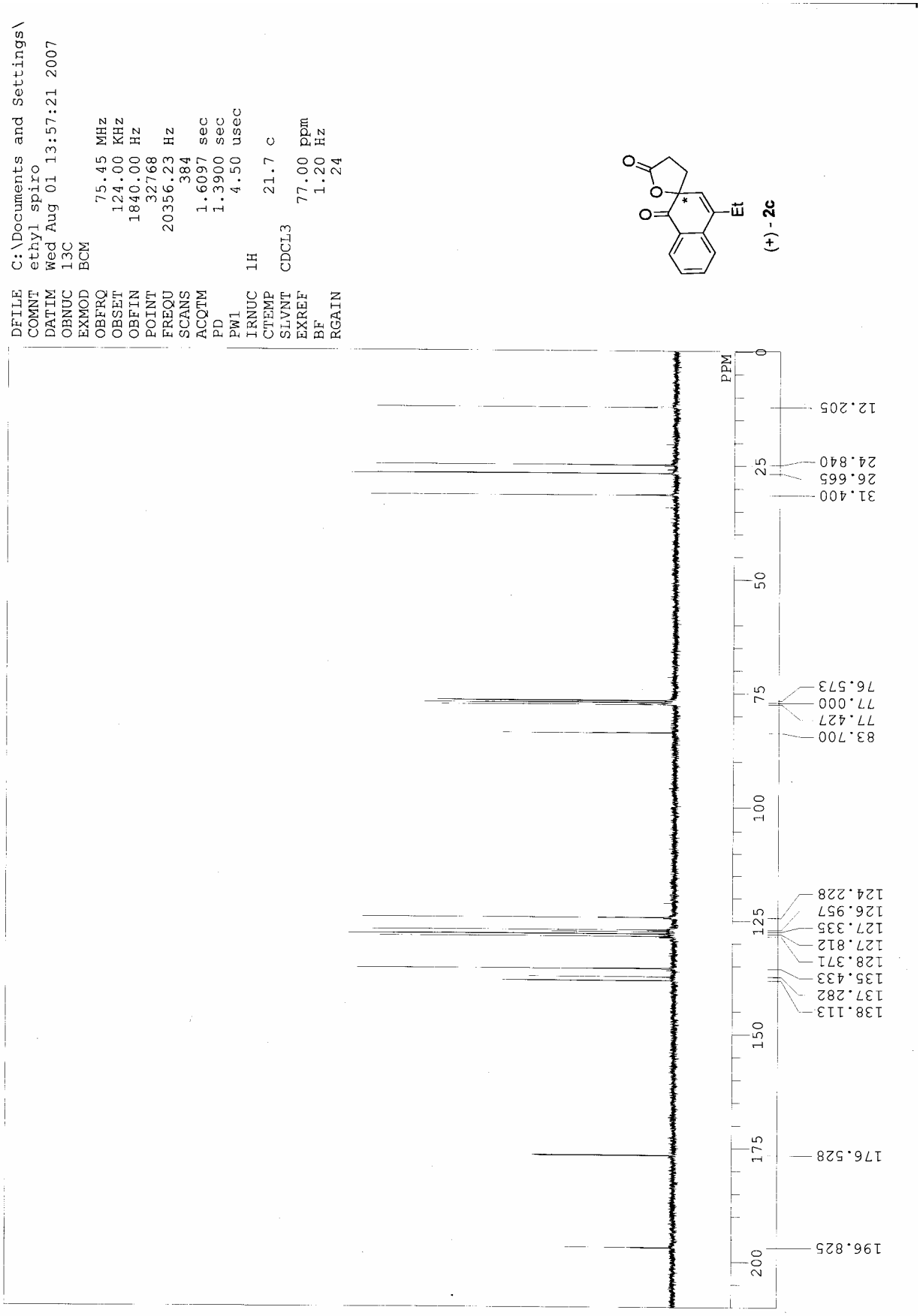
ピーク総面積= 13379820.999 [uAU.Sec]



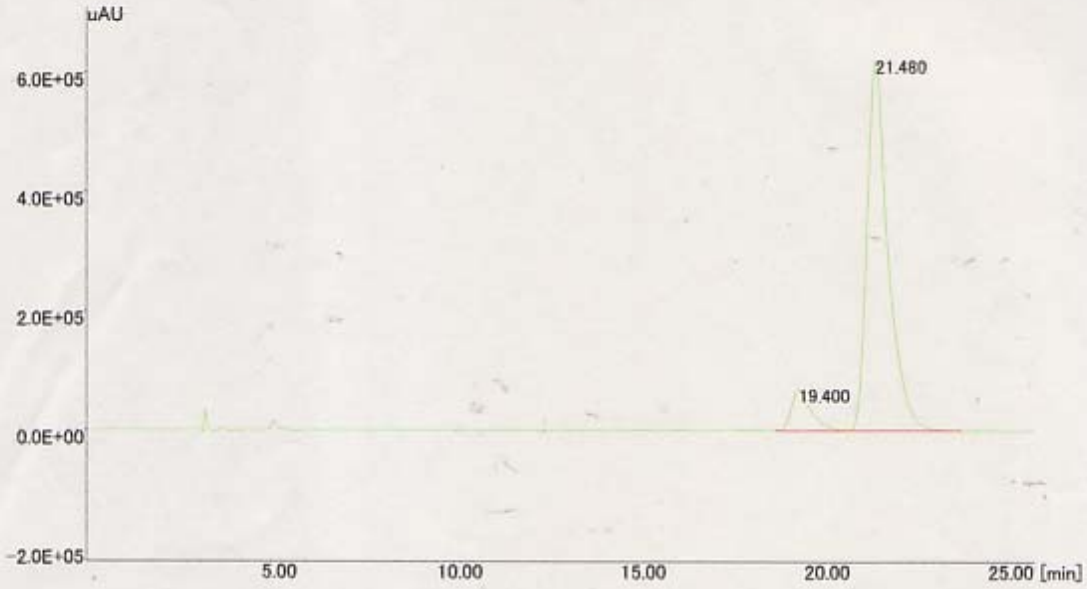
(+) - **2a**

7-Aug-2007 17:16:44,TANIMOTO,Page N- 1/1

DFILE C:\Documents and Settings\
COMNT
DATIM Wed Aug 01 13:37:35 2007
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 10
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
Et
(+) - 2c
PPM
3.12
1.06
0.93
3.00
1.00
0.95
1.97
0.98
0.86


DFILE C:\Documents and Settings\
COMNT ethyl spiro
DATIM Wed Aug 01 13:57:21 2007
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 384
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
Et
(+) - 2c
PPM
0
25
50
75
100
125
150
175
200
12.205
24.840
26.665
31.400
76.573
77.000
77.427
83.700
124.228
126.957
127.335
127.812
128.371
135.433
137.282
138.113
176.528
196.825

Chromatogram



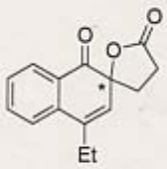
ファイル名: AM930_230.CH1

コメント:
AD-H
Hex/iPrOH=92/08
1.0ml/min 25C
Wavelength = 230 [nm]
Tacc [Sec] = 0.80 Wacc [nm] = 4.0
Autozero [min] : 0.00

Vial # = 1 Rack # = 0
注入日 : 23-May-2007 16:07:36
現在日時: 7-Aug-2007 17:14:18
ユーザー : TANIMOTO
グループ : TANIMOTO
システムプログラム:

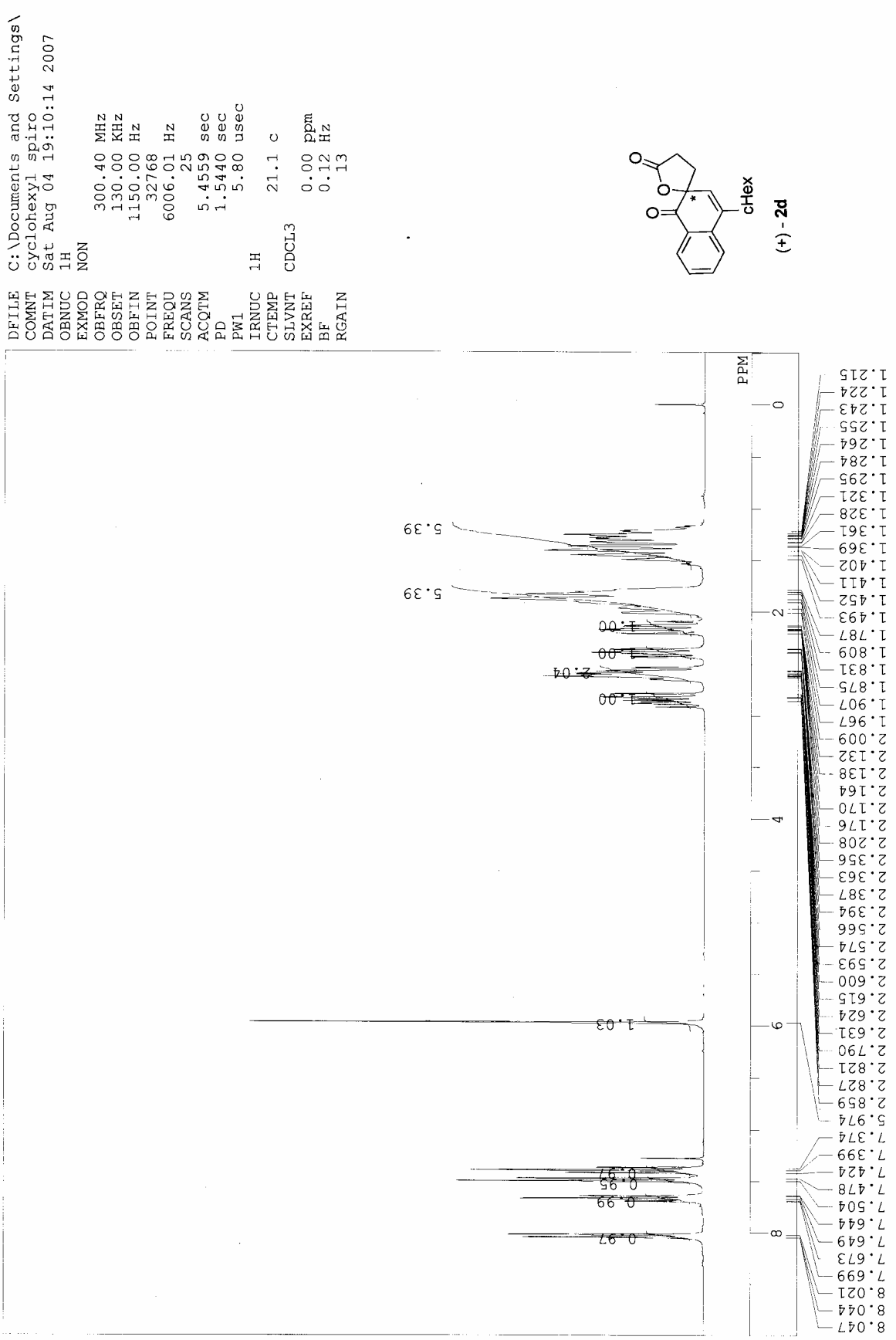
#	ピーク名	Rt	高さ[uAU]	面積[uAU.Sec]	面積%
1	*	19.400	69003	2546532.038	9.34
2		21.480	621402	24729823.569	90.66

ピーク総面積= 27276355.607 [uAU.Sec]



(+) - **2c**

7-Aug-2007 17:14:18,TANIMOTO,Page N- 1/1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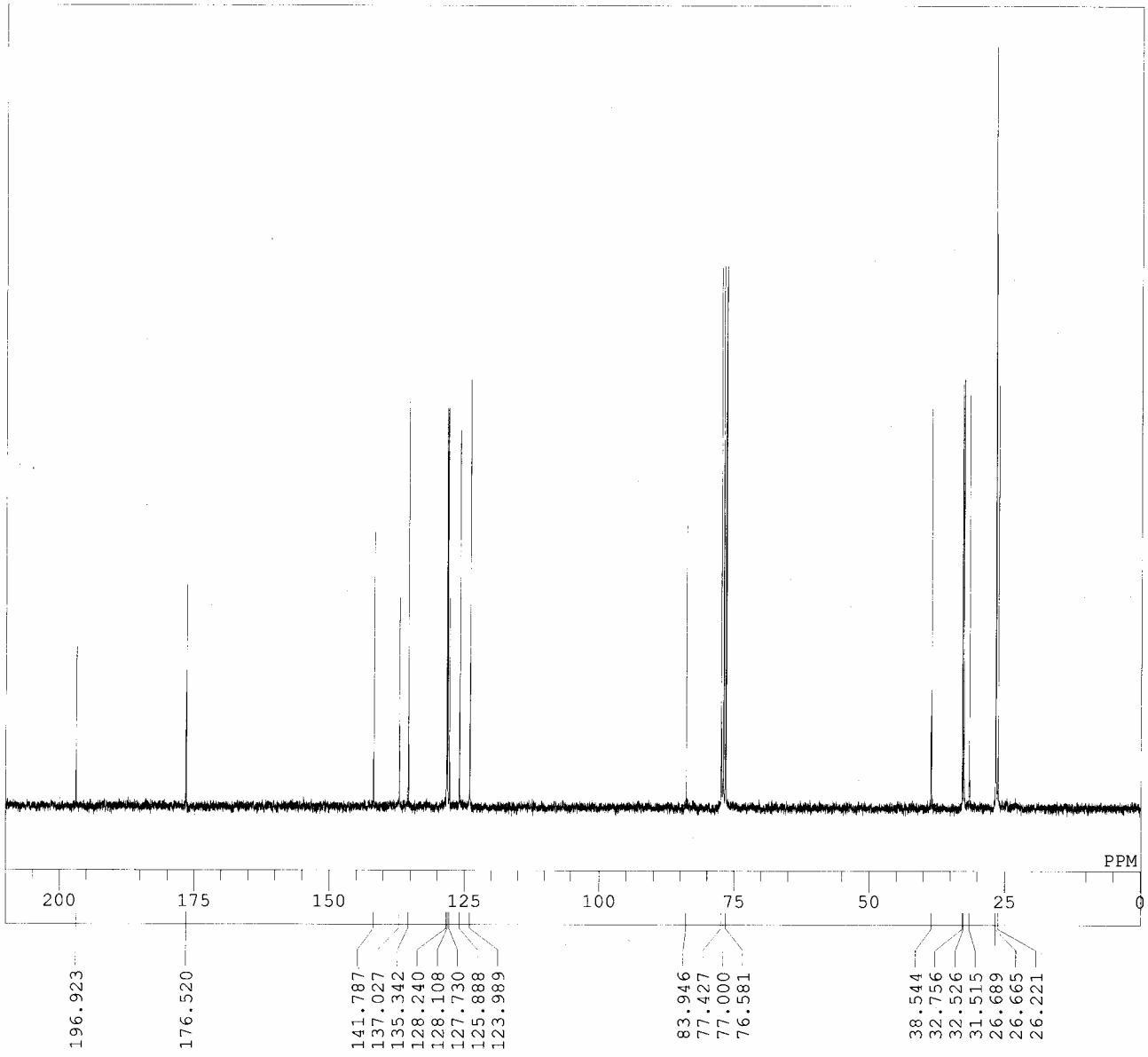
COMNT cyclohexyl spiro
DATIM Sat Aug 04 19:10:14 2007
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 25
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
cHex
(+)-2d
PPM

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DATIM   Sat Aug 04 19:45:28 2007
OBNUC   13C
EXMOD   BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN       1840.00 Hz
POINT         32768
FREQU      20356.23 Hz
SCANS           692
ACQTM         1.6097 sec
PD            1.3900 sec
PW1             4.50 usec
IRNUC   1H
CTEMP           20.9 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               1.20 Hz
RGAIN              24
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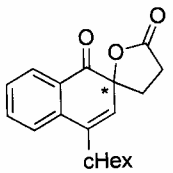
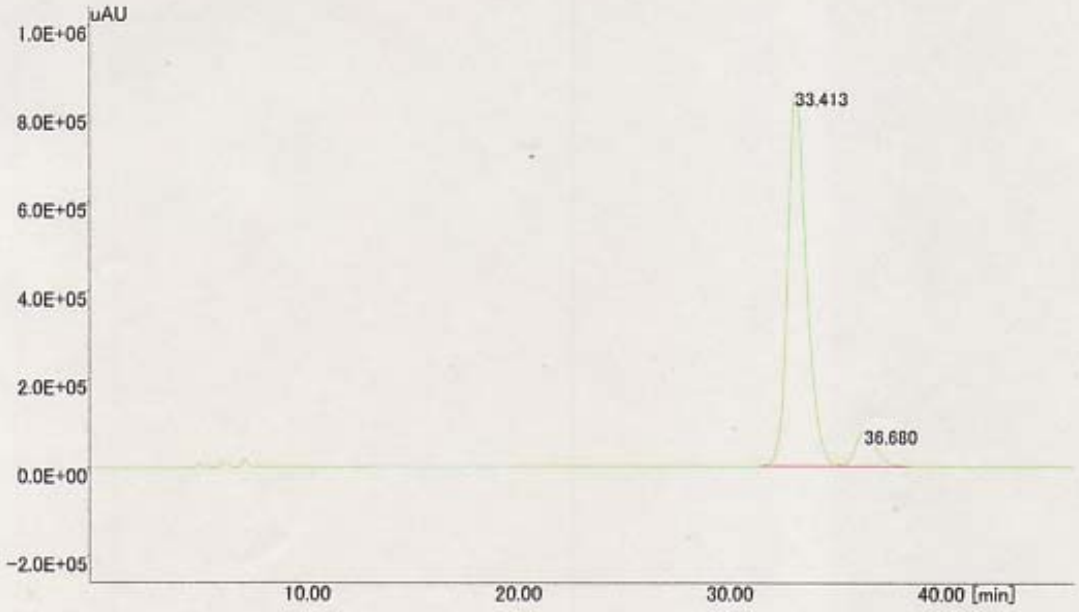


(+) - 2d

Chromatogram



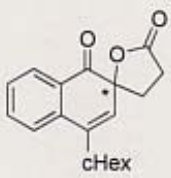
ファイル名: TN-1989_235.CH1

コメント:
AD
Hex/iPrOH=97/03
0.8ml/min 25C
Wavelength = 235 [nm]
Tacc [Sec] = 0.80 Wacc [nm] = 4.0
Autozero [min] : 0.00

Vial # = 1 Rack # = 0
注入日 : 13-Jul-2007 18:07:42
現在日時: 7-Aug-2007 17:07:22
ユーザー : TANIMOTO
グループ : TANIMOTO
システムプログラム:

#	ピーク名	Rt	高さ[uAU]	面積[uAU.Sec]	面積%
1		33.413	844843	51514709.116	90.65
2		36.680	80045	5312456.930	9.35

ピーク総面積= 56827166.047 [uAU.Sec]



(+) - **2d**

7-Aug-2007 17:07:22,TANIMOTO,Page N- 1/1

DFILE C:\Documents and Settings\
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DATIM Wed Aug 01 17:22:14 2007
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 22
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22
Bn
(+) - 2e
PPM
0.92
1.06
1.97
1.00
1.93
0.92
7.58
0.92
0.000
0.010
1.554
1.557
1.584
2.144
2.150
2.157
2.182
2.188
2.194
2.227
2.401
2.407
2.432
2.439
2.445
2.452
2.477
2.483
2.523
2.530
2.555
2.582
2.588
2.613
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2.824
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2.863
2.883
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3.897
5.905
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7.351
7.356
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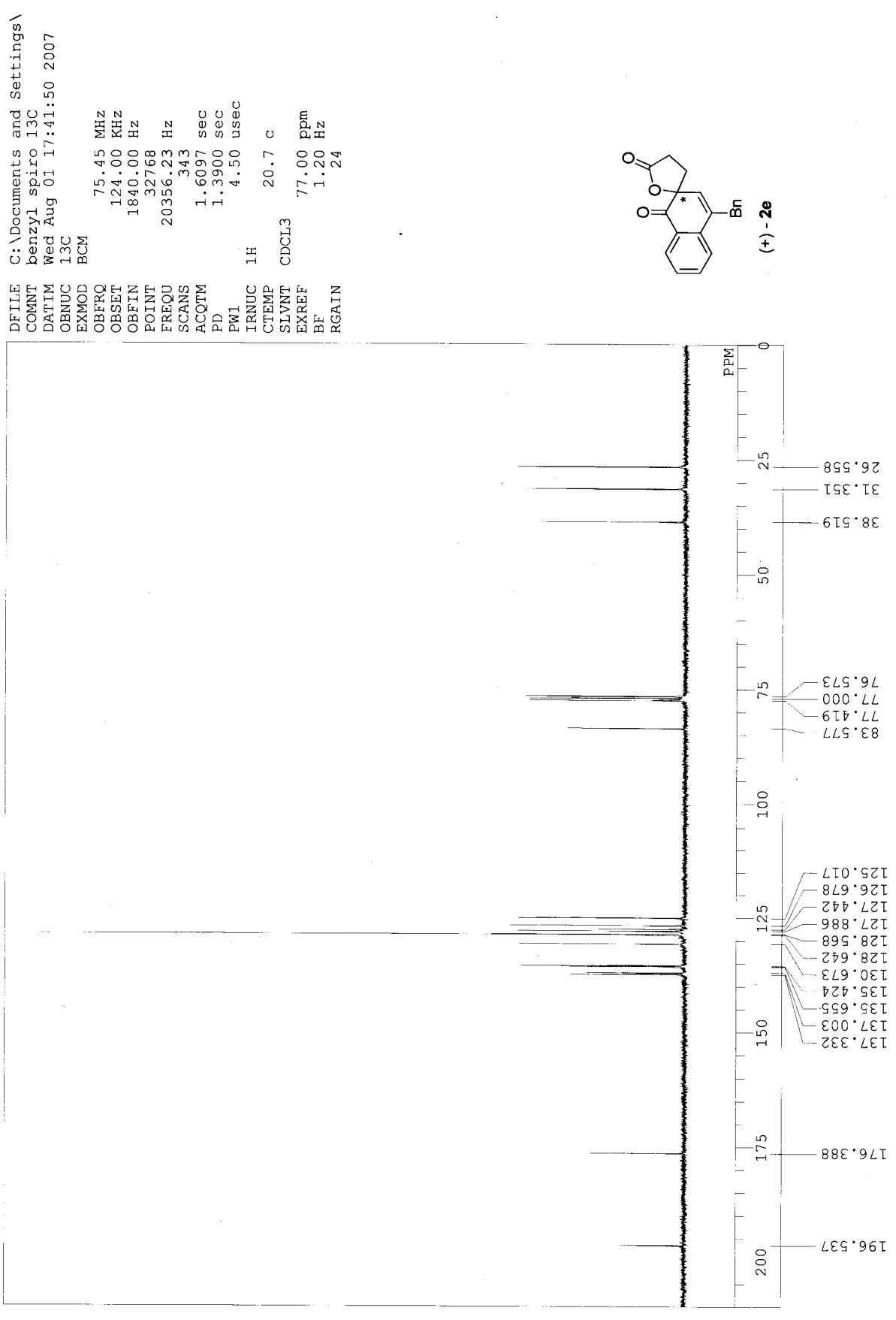
8.063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DATIM Wed Aug 01 17:41:50 2007
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 343
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
Bn
(+)-2e
PPM
0
25
50
75
100
125
150
175
200
26.558
31.351
38.519
76.573
77.000
77.419
83.577
125.017
126.678
127.442
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135.655
137.003
137.332
176.388
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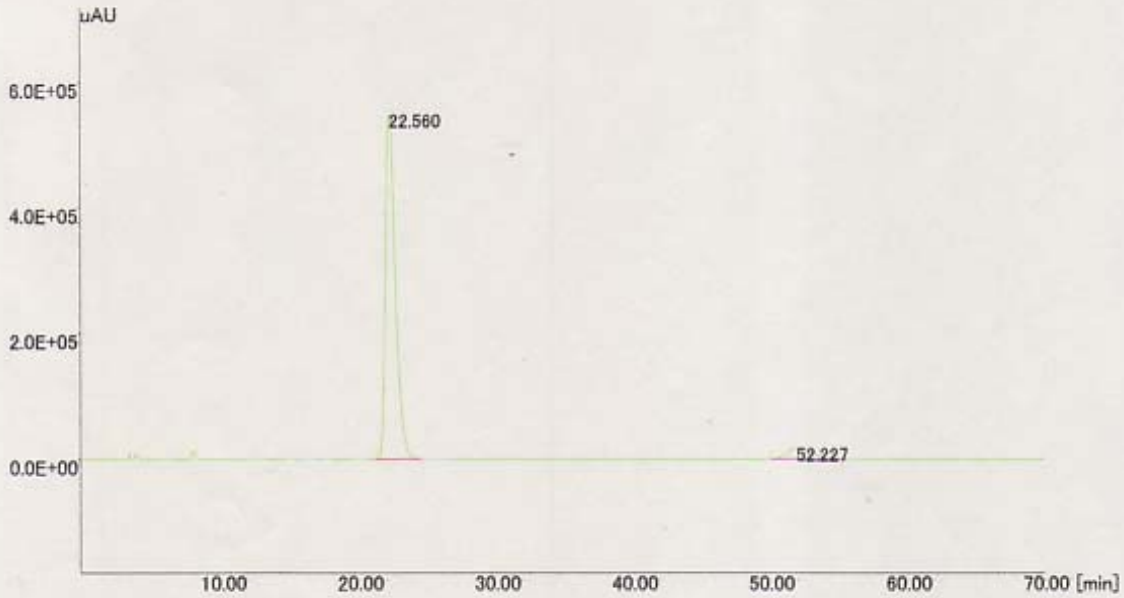
Chromatogram



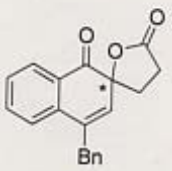
ファイル名: AM987_235.CH1

コメント:
OD
Hex/iPrOH=85/15
1.0ml/min 25C
Wavelength = 235 [nm]
Tacc [Sec] = 0.80 Wacc [nm] = 4.0
Autozero [min] : 0.00

Vial # = 1 Rack # = 0
注入日 : 12-Jul-2007 23:22:38
現在日時: 7-Aug-2007 17:09:28
ユーザー : TANIMOTO
グループ : TANIMOTO
システムプログラム:

#	ピーク名	Rt	高さ[uAU]	面積[uAU.Sec]	面積%
1		22.560	548439	26607103.596	92.79
2		52.227	16690	2068880.831	7.21

ピーク総面積= 28675984.427 [uAU.Sec]



(+) - **2e**

7-Aug-2007 17:09:28,TANIMOTO,Page N- 1/1

References

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2) Ochiai, M.; Kitagawa, Y.; Takayama, N.; Takaoka, Y.; Shiro, M. *J. Am. Chem. Soc.* **1999**, *121*, 9233.

3) Hirt, U. H.; Spingler, B.; Wirth, T. *J. Org. Chem.* **1998**, *63*, 7674.

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5) (a) Birman, V. B.; Rheingold, A. L.; Lam, K. -C. *Tetrahedron Asymmetry* **1999**, *10*, 125. (b) Zhang, J. -H.; Liao, J.; Cui, X.; Yu, K. -B.; Zhu, J.; Deng, J. -G.; Zhu, S. -F.; Wang, L. -X.; Zhou, Q. -L.; Chung, L. W.; Ye, T. *Tetrahedron Asymmetry* **2002**, *13*, 1363. (c) Xie, J. -H.; Wang, L. -X.; Fu, Y.; Zhu, S. -F.; Fang, B. -M.; Duan, H. -F.; Zhou, Q. -L. *J. Am. Chem. Soc.* **2003**, *125*, 4404.

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