Supporting Information

Dry and Wet Prolines for Asymmetric Organic-Solvent-Free Aldehyde-Aldehyde and Aldehyde-Ketone Aldol Reactions

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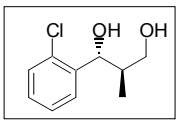
Typical procedure for the solvent-free cross-aldol reaction between two aldehydes catalyzed by proline

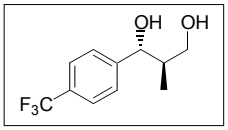
To a mixture of *o*-chlorobenzaldehyde (45 μL, 0.4 mmol) and L-proline (5 mg, 0.04 mmol) was added propanal (144 μL, 2.0 mmol) successively at 0 °C. After stirring the reaction mixture for 48 hours at that temperature, the reaction mixture was cooled at 0 °C and MeOH (1 mL) and $NaBH_4$ (76 mg, 2.0 mmol) was added. The reaction mixture was stirred for 1 hour at 0 °C. The reaction was quenched with pH 7.0 phosphate buffer solution and the organic materials were extracted with ethyl acetate three times and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. Purification by preparative thin layer chromatography (ethyl acetate) gave (1*R*, 2*R*)-1-(*o*-chlorophenyl)-2-methylpropane-1,3 -diol (72 mg, 0.36 mmol) in 90% yield as the diastereomeric mixture (*anti* : *syn* = 12.9 : 1). Enantiometric excess of *anti* aldol was 96%ee.

(1*R*, 2*R*)-1-(*o*-Chlorophenyl)-2-methylpropane-1,3-diol (1)



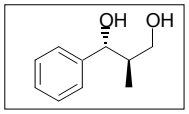
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (3H, t, *J*= 7.2 Hz), 2.02-2.05 (1H, m), 2.80 (1H, br s), 3.30 (1H, br s), 3.61-3.70 (2H, m), 5.05 (1H, d, *J*= 6.8 Hz), 7.14 (1H, t, *J*= 7.6 Hz), 7.22-7.27 (2H, m), 7.50 (1H, d, *J*= 7.6 Hz);
^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 40.7, 67.1, 76.1, 127.2, 128.1, 128.7, 129.4, 132.5, 140.9;
IR (neat): ν 3357, 2966, 2932, 1572, 1471, 1438, 1034, 754, 703 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_{10}H_{13}ClO_2Na$]: 223.0504, found: 223.0496;
Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (100:1 hexane:2-propanol, λ=254 nm), 1.2 mL/min; major enantiomer tr = 15.2 min, minor enantiomer tr = 17.2 min, after conversion to the monobenzoyl ester.

(1*R*, 2*R*)-1-(*p*-Trifluoromethylphenyl)-2-methylpropane-1,3-diol (2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71 (3H, d, *J*= 7.2 Hz), 1.95-2.06 (1H, m), 2.15-2.32 (2H, m), 4.59 (1H, d, *J*= 7.6 Hz), 7.43 (2H, d, *J*= 8.0 Hz), 7.59 (2H, d, *J*= 8.0 Hz);
^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 41.6, 67.6, 79.8, 125.3, 127.0, 130.2, 147.3;
IR (neat): ν 3349, 2884, 1619, 1419, 1326, 1164, 1126, 1068, 1017, 841 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_{11}H_{13}F_3O_2Na$]: 257.0760, found: 257.0764;
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (80:1 hexane:2-propanol, λ= 254 nm), 1.0 mL/min; major enantiomer tr = 39.2 min, minor enantiomer tr = 52.8 min, after conversion to the monobenzoyl ester.

(1*R*, 2*R*)-1-Phenyl-2-methylpropane-1,3-diol[1] (3)

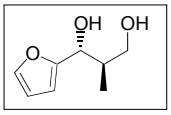


was known compound.
Enantiometric excess was determined by HPLC with a Chiralpak AD-H column (30:1 hexane:2-propanol, λ= 230 nm), 1.0 mL/min; major enantiomer tr = 27.2 min, minor enantiomer tr = 38.6 min, after conversion to the monobenzoyl ester.

The absolute stereochemistry of the aldol **3** was determined by the chiral HPLC analysis by comparing the retention time of the present aldol product with that synthesized by L-proline in DMF by MacMillan's

procedure[1].

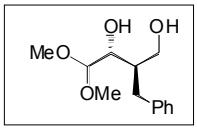
(1*R*,2*R*)-1-(Furan-2-yl)-2-methylpropane-1,3-diol[2] (4)



was known compound.
Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (100:1 hexane:2-propanol), 0.5 mL/min; major enantiomer tr = 42.4 min, minor enantiomer tr = 47.8 min, after conversion to the monobenzoyl ester.

The absolute stereochemistry of the aldols **1**, **2**, **4** were assumed by the chiral HPLC analysis by comparing the retention time of the present aldol product with that synthesized by L-proline in DMF by MacMillan's procedure[1].

4,4-Dimethoxy-2-benzylbutane-1,3-diol (diastereomeric mixture (*anti* : *syn* = 3.3 : 1)) (5)

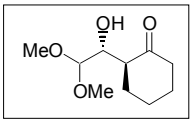


^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07-2.17 (0.77H, m), 2.45-2.48 (0.23H, m), 2.67 (0.23H, d, *J*= 2.4 Hz), 2.72 (0.77H, d, *J*= 3.2 Hz), 2.80-2.92 (3H, m), 3.34 (2.31H, s), 3.40 (0.69H, s), 3.45 (2.31H, s), 3.49 (0.69H, s), 3.62-3.73 (2H, m), 3.90 (0.77H, dt, *J*= 11.6, 3.2 Hz), 3.95 (0.23H, dt, *J*= 2.4, 6.8 Hz), 4.41 (0.23H, d, *J*= 6.8 Hz), 4.49 (0.77H, d, *J*= 6.8 Hz), 7.22-7.36 (5H, m);
^{13}C NMR (100 MHz, $CDCl_3$): δ 31.7, 35.6, 42.6, 43.6, 54.8, 55.1, 55.3, 55.5, 62.8, 64.3, 73.4, 73.7, 105.2, 105.6, 126.4, 126.5, 128.8, 129.6, 140.6, 141.1;
IR (neat): ν 3423, 3061, 3027, 2936, 2832, 2360, 1496, 1454, 1193, 1133, 1064, 971, 746, 701 cm^{-1};
HRMS (FAB): [M+Na] calcd for [$C_{13}H_{20}O_4Na$]: 263.1254, found: 263.1248;
Enantiomeric excess of major *anti* isomer was determined by HPLC with a Chiralpak IA column (50:1 hexane:2-propanol, λ= 254 nm), 1.0 mL/min; major enantiomer tr = 21.2 min, minor enantiomer tr = 19.6 min after conversion to the monobenzoyl ester.

Typical procedure of cross-aldol reaction between dimethoxyacetaldehyde and another aldehyde catalyzed by proline in the presence of water

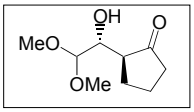
To a mixture of 60 wt% aqueous solution of dimethoxyacetaldehyde (60 μL, 0.4 mmol), L-proline (9 mg, 0.08 mmol) and was added 2,2-dimethyl-1,3-dioxan-5-one (238 μL, 2.0 mmol) successively at room temperature. After stirring the reaction mixture for 16 hours at that temperature. The reaction was quenched with pH 7.0 phosphate buffer solution and the organic materials were extracted with ethyl acetate three times and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. Purification by silicagel column chromatography (ethyl acetate:hexane=1:5 ~ 1:1) gave (4*R*, 1'*R*)-4-(1'-hydroxy-2',2'-dimethoxyethyl)-2,2-dimethyl-1,3-dioxan-5-one (44 mg, 0.19 mmol) in 47% yield.

(2*R*, 1'*R*)-2-(1'-Hydroxy-2',2'-dimethoxyethyl)-cyclohexan-1-one (6)



^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61-1.82 (3H, m), 1.85-1.91 (1H, m), 2.03-2.12 (2H, m), 2.28-2.39 (2H, m), 2.65-2.70 (1H, m), 3.17 (1H, d, *J*= 7.6 Hz), 3.39 (3H, s), 3.43 (3H, s), 3.58-3.62 (1H, m), 4.47 (1H, d, *J*= 5.6 Hz);
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 27.8, 31.4, 42.9, 51.4, 54.4, 55.6, 73.0, 105.5, 214.8;
IR (neat): ν 3499, 2937, 2864, 2833, 1704, 1450, 1191, 1123, 1078, 972 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_{10}H_{18}O_4Na$]: 225.1097, found: 225.1089;
Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (100:1 hexane:2-propanol, λ= 254 nm), 1.0 mL/min; major enantiomer tr = 7.3 min, minor enantiomer tr = 6.8 min, after conversion to the monobenzoyl ester.

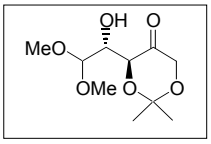
(2*R*, 1'*R*)-2-(1'-Hydroxy-2',2'-dimethoxyethyl)-cyclopentan-1-one (7)



^{1}H NMR (600 MHz, $CDCl_3$): δ 1.73-1.81 (1H, m), 1.87-1.94 (1H, m), 2.01-2.09 (1H, m), 2.11-2.22 (2H, m), 2.28-2.36 (1H, m), 2.40-2.44 (1H, m), 3.02 (1H, d, *J*= 1.6 Hz), 3.46 (3H, s), 3.47 (3H, s), 3.76-3.78 (1H, m), 4.61 (1H, d, *J*= 4.4 Hz);

^{13}C NMR (150 MHz, $CDCl_3$): δ 21.1, 26.9, 39.2, 49.2, 54.9, 56.1, 72.9, 105.0, 221.3;
IR (neat): ν 3460, 2960, 2833, 1734, 1454, 1404, 1193, 1127, 1060, 969 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_9H_{16}O_4Na$]: 211.0941, found: 211.0932;
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (30:1 hexane:2-propanol, λ=240 nm), 1.0 mL/min; major enantiomer tr = 15.4 min, minor enantiomer tr = 17.8 min.

(4*R*, 1'*R*)-4-(1'-Hydroxy-2',2'-dimethoxyethyl)-2,2-dimethyl-1,3-dioxan-5-one[3] (8)



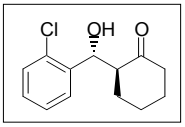
was known compound.
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (30:1 hexane:2-propanol), 1 mL/min; major enantiomer tr = 19.3 min, minor enantiomer tr = 27.5 min, after conversion to the 3,5-dinitrobenzoyl ester.
The absolute stereochemistry of the aldol **8** was determined by the chiral HPLC analysis by comparing the retention time of the 3,5-dinitrobenzoyl ester of the present aldol product with that synthesized by L-proline in DMF by Barbas's procedure[3].

The absolute stereochemistry of the aldols **5**, **6**, **7** were assumed by the chiral HPLC analysis by comparing the retention time of the 3,5-dinitrobenzoyl ester of the present aldols product with that synthesized by L-proline in DMF by Barbas's procedure[3].

Typical procedure of cross-aldol reaction between aldehyde and ketone catalyzed by proline in the presence of water

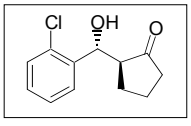
To a mixture of *o*-chlorobenzaldehyde (45 μL, 0.4 mmol), L-proline (14 mg, 0.12 mmol) and water (22 μL, 1.2 mmol) was added cyclohexanone (123 μL, 1.2 mmol) successively at room temperature. After stirring the reaction mixture for 72 hours at that temperature, the reaction was quenched with pH 7.0 phosphate buffer solution and the organic materials were extracted with ethyl acetate three times and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. Purification by preparative thin layer chromatography (ethyl acetate) gave (2*S*, 1'*R*)-2-(hydroxy-*o*-chlorophenylmethyl) cyclohexan-1-one (67 mg, 0.28 mmol) in 70% yield as the diastereomeric mixture (*anti* : *syn* = 12.5 : 1). Enantiometric excess of *anti* aldol was 97%ee.

(2*S*, 1'*R*)-2-(Hydroxy-*o*-chlorophenylmethyl)cyclohexan-1-one[4]



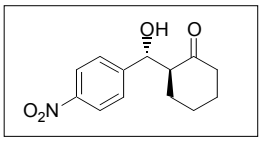
was known compound.
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (100:1 hexane:2-propanol, λ= 220 nm), 1.0 mL/min; major enantiomer tr = 14.2 min, minor enantiomer tr = 16.5 min.

(2*S*, 1'*R*)-2-(Hydroxy-*o*-chlorophenylmethyl)cyclopentan-1-one



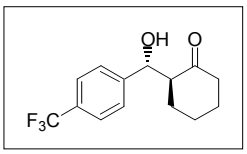
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64-1.78 (3H, m), 1.93-2.07 (1H, m), 2.22-2.35 (1H, m), 2.36-2.52 (2H, m), 4.47 (1H, d, *J*= 1.2 Hz), 5.29 (1H, br d, *J*= 9.3 Hz), 7.15-7.23 (1H, m), 7.26-7.36 (2H, m), 7.52 (1H, m);
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 26.4, 38.7, 55.6, 70.4, 127.4, 128.4, 128.9, 129.3, 132.5, 139.2, 222.8;
IR (neat): ν 3447, 2965, 1735, 1695, 1440, 1402, 1156, 1024, 749 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_{12}H_{13}ClO_2Na$]: 247.0604, found: 247.0506;
Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (100:1 hexane:2-propanol, λ= 220 nm), 1.0 mL/min; major enantiomer tr = 28.2 min, minor enantiomer tr = 37.8 min.

(2*S*, 1'*R*)-2-(Hydroxy-*p*-nitrophenylmethyl)cyclohexan-1-one[5]



was known compound.
Melting point: 98.0-98.5 ^{O}C;
Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (10:1 hexane:2-propanol, λ= 254 nm), 1.0 mL/min; major enantiomer tr = 10.3 min, minor enantiomer tr = 12.3 min.

(2*S*, 1'*R*)-2-(Hydroxy-*p*-trifluoromethylphenylmethyl)cyclohexan-1-one[6]



^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24-1.37 (1H, m), 1.48-1.70 (3H, m), 1.77-1.82 (1H, m), 2.09 (1H, ddd, *J*= 3.2, 6.0, 12.8 Hz), 2.34 (1H, ddt, *J*= 0.8, 6.0, 13.6 Hz), 2.44-2.50 (1H, m), 2.54-2.61 (1H, m), 3.99 (1H, br s), 4.83 (1H, d, *J*= 8.8 Hz), 7.42 (2H, d, *J*= 8.0 Hz), 7.59 (2H, d, *J*= 8.0 Hz);
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 27.7, 30.7, 42.7, 57.2, 74.3, 123.2, 125.3, 127.4, 130.1, 144.9, 215.2;
IR (KBr): ν 3752, 3361, 2948, 2910, 1700, 1328, 1170, 1138, 1109, 845 cm^{-1};
HRMS(FAB): [M+Na] calcd for [$C_{14}H_{15}F_3O_2Na$]: 295.0916, found: 295.0907;
$[\alpha]_D^{22}$ –35.2 (*c* 1.00, MeOH), >99% ee for *anti*;
Melting point: 86.5-87.0 ^{O}C;
Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (10:1 hexane:2-propanol, λ=254 nm), 1.0 mL/min; major enantiomer tr = 12.9 min, minor enantiomer tr = 9.5 min.

The absolute stereochemistry of the aldols **9**, **10**, **11**, **12** were assumed by the chiral HPLC analysis by comparing the retention time of the present aldol products with that synthesized by Barbas's procedure[7].

Procedure of cross-aldol reaction catalyzed by proline in the presence of water without using any organic solvent (in the case of aldol product was oil)

To a mixture of *o*-chlorobenzaldehyde (7.9 mL, 70 mmol), L-proline (2.42 g, 21 mmol) and water (3.8 mL) was added cyclopentanone (30.9 mL, 350 mmol) successively at room temperature. After stirring the reaction mixture for 25 hours at that temperature, water (40 mL) and brine (20 mL) were added to the reaction mixture, which was sirred for 10 minutes. After removal of aqueous phase, bulb to bulb distillation of the organic residue at 140 ºC under 0.8 mmHg gave (2*S*, 1'*R*)-2-(hydroxy-*o*-chlorophenylmethyl)cyclopentan-1-one (11.7 g, 52.1 mmol) in 75% yield as the diastereomeric mixture (*anti* : *syn* = 1.7 : 1). Enantiomeric excess of *anti* aldol was >99%ee.

Procedure of cross-aldol reaction catalyzed by proline in the presence of water without using any organic solvent (in the case of aldol product was crystal)

To a mixture of *p*-trifluoromethylbenzaldehyde (8.6 mL, 57.4 mmol), L-proline (1.98 g, 17.2 mmol) and water (3.1 mL) was added cyclohexanone (29.6 mL, 287 mmol) successively at room temperature. After stirring the reaction mixture for 96 hours at that temperature, organic phase was washed with water (50 mL) three times to remove proline and the organic phase was concentrated in vacuo. Purification by recrystallization from cyclohexane (57.6 mL) gave (2*S*, 1'*R*)-2-[hydroxy-(*p*-trifluoromethylphenyl)methyl]cyclohexan-1-one (11.4 g, 41.8 mmol) in 73% yield (*anti* : *syn* = >20 : 1). Enantiomeric excess of *anti* aldol was >99%ee.

References

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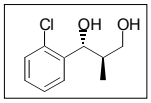

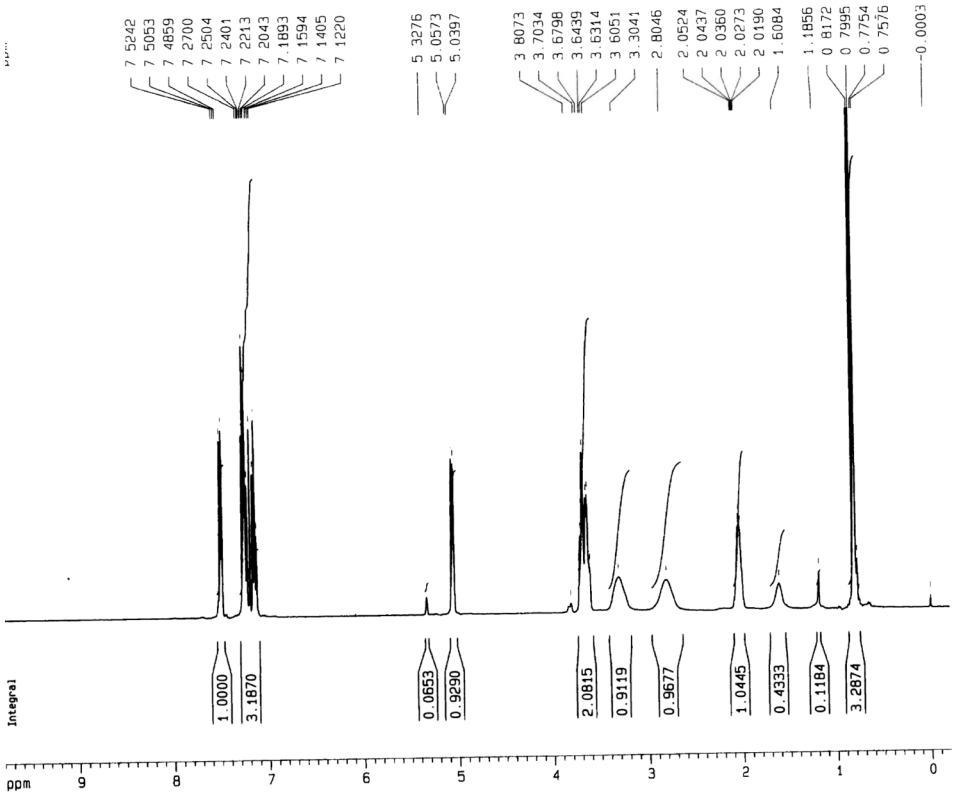


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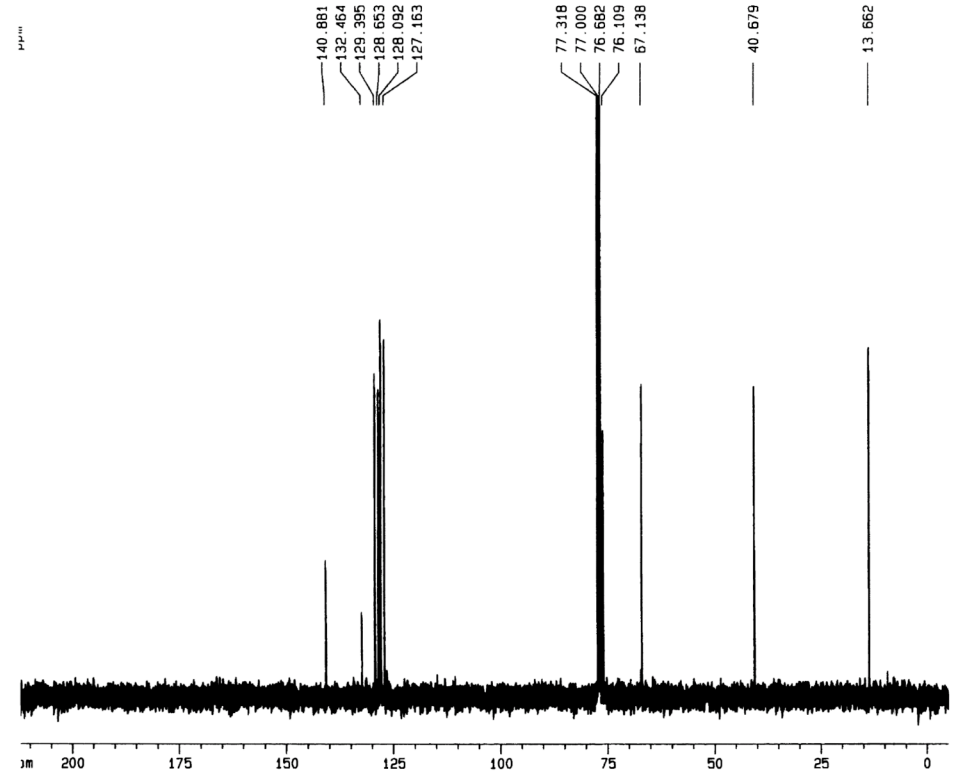


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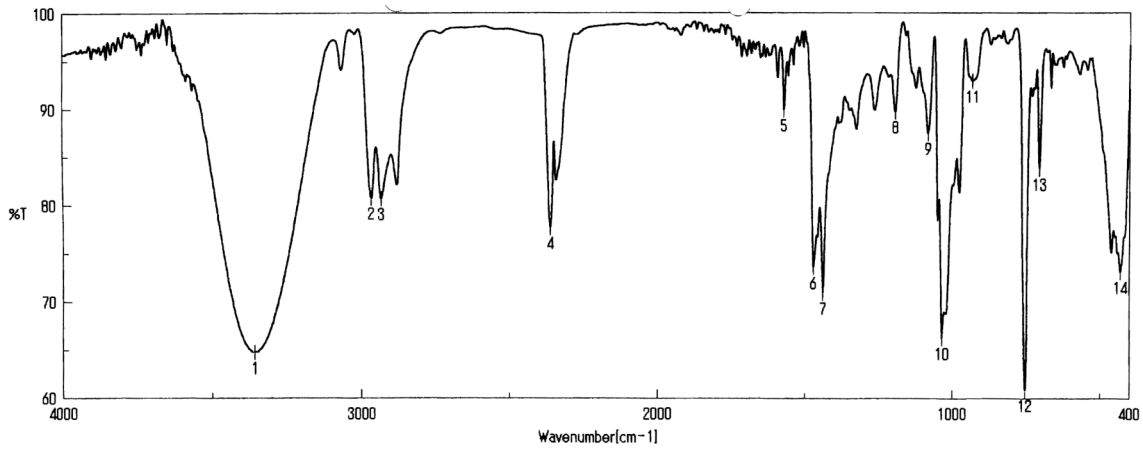
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.30 usec
PL1                3.00 dB
SFO1          100.6254358 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2                3.00 dB
PL12              22.00 dB
PL13              22.00 dB
SFO2          400.1316005 MHz

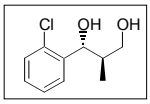
F2 - Processing parameters
SI                 32768
SF            100.6127698 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40

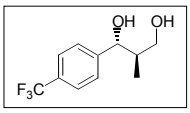
1D NMR plot parameters
CX                20.00 cm
CY                 8.00 cm
F1P             215.000 ppm
F1              21631.75 Hz
F2P              -5.000 ppm
F2              -503.06 Hz
PPMCM          11.00000 ppm/cm
HZCM          1106.74048 Hz/cm
```

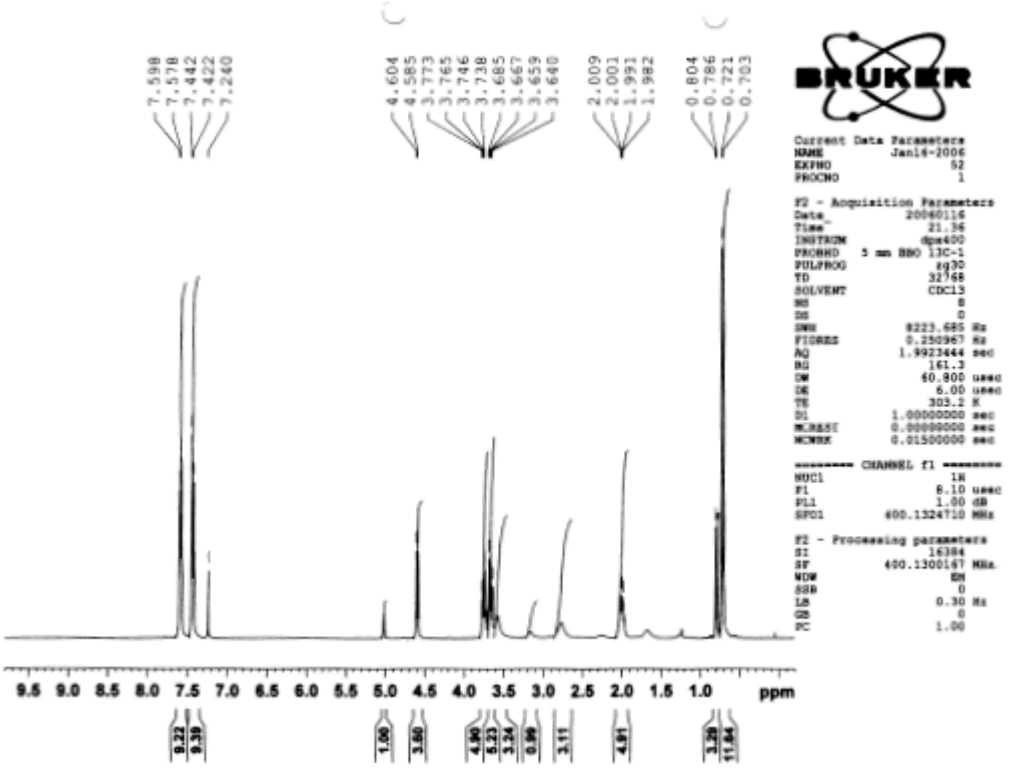


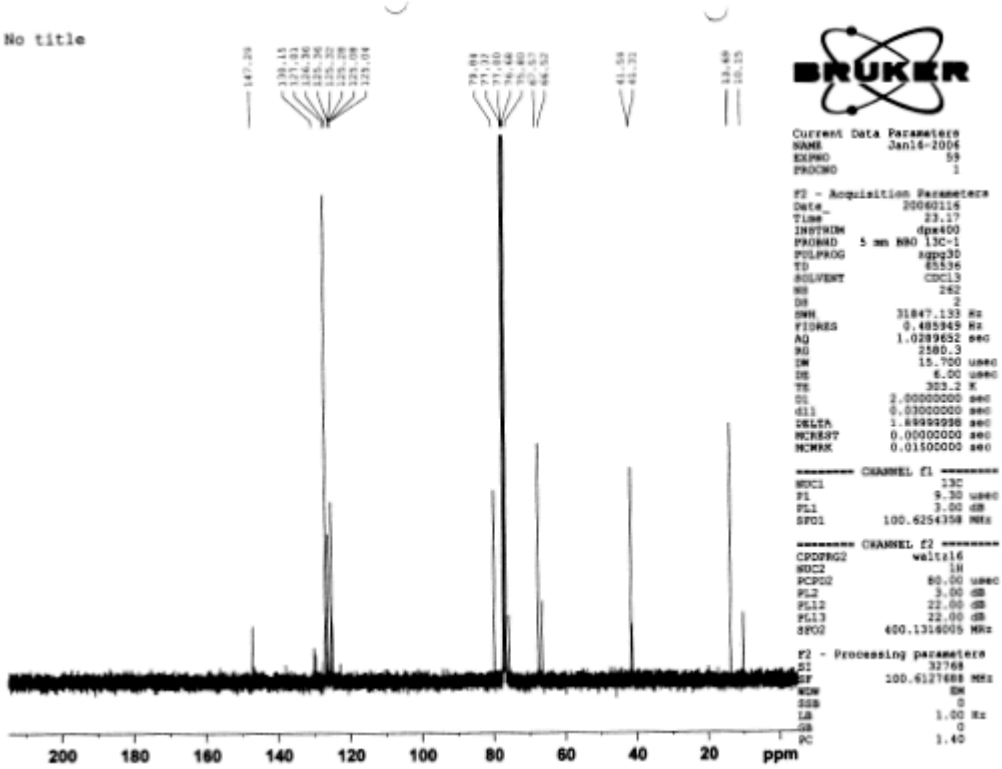
積算回数	16	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/01/25 21:13		
測定者			
ファイル名	Memory#6		
サンプル名			
コメント	コメント		

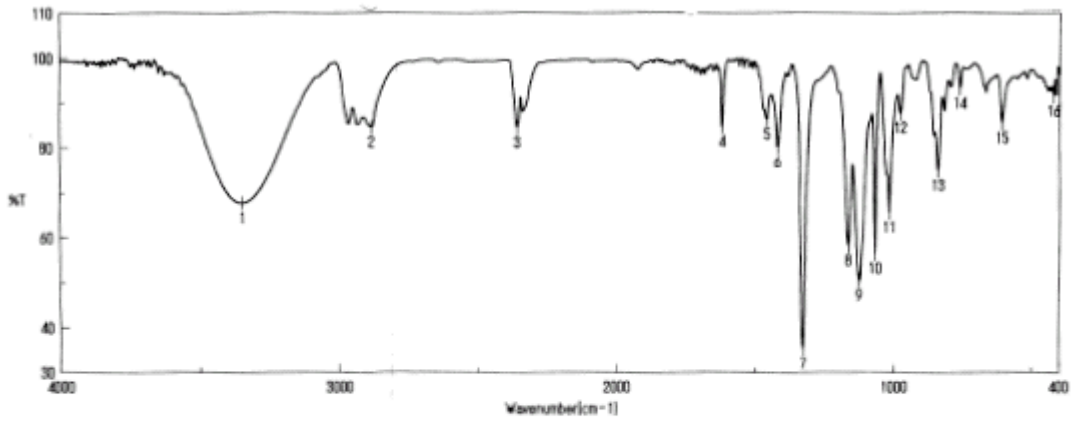
1:	3357.46,	64.7432	2:	2965.98,	80.7845	3:	2932.23,	80.7236	4:	2360.44,	77.7355
5:	1572.66,	89.9476	6:	1471.42,	73.6355	7:	1438.64,	70.9591	8:	1194.69,	89.7558
9:	1082.83,	87.5273	10:	1034.62,	66.2728	11:	934.34,	92.9301	12:	754.03,	60.8449
13:	705.82,	83.8262	14:	431.01,	73.1540						




OH
OH
F3C

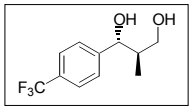

7.598
7.578
7.442
7.422
7.240
4.604
4.585
3.773
3.765
3.746
3.738
3.685
3.667
3.659
3.640
2.009
2.001
1.991
1.982
0.804
0.786
0.721
0.703
BRUKER
Current Data Parameters
NAME Jan16-2006
EXPNO 52
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060116
Time 21.36
INSTRUM dpx400
PROBHD 5 mm BBO 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 161.3
DW 60.800 usec
DE 6.00 usec
TE 303.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 8.10 usec
PL1 1.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
9.22
9.30
1.00
3.60
4.90
4.23
3.24
0.99
3.11
4.91
3.29
11.84

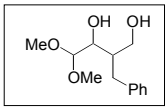

No title
147.29
130.15
127.03
126.36
125.32
125.28
125.24
123.04
79.84
77.32
77.00
76.68
70.53
64.52
41.56
41.31
13.49
10.35
BRUKER
Current Data Parameters
NAME Jan16-2006
EXPNO 59
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060116
Time 23.17
INSTRUM dpx400
PROBHD 5 mm BBO 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 262
DS 2
SWH 31847.133 Hz
FIDRES 0.485949 Hz
AQ 1.0289652 sec
RG 2580.3
DW 15.700 usec
DE 6.00 usec
TE 303.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.88999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 9.30 usec
PL1 3.00 dB
SFO1 100.6254358 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 22.00 dB
PL13 22.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127688 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20
ppm

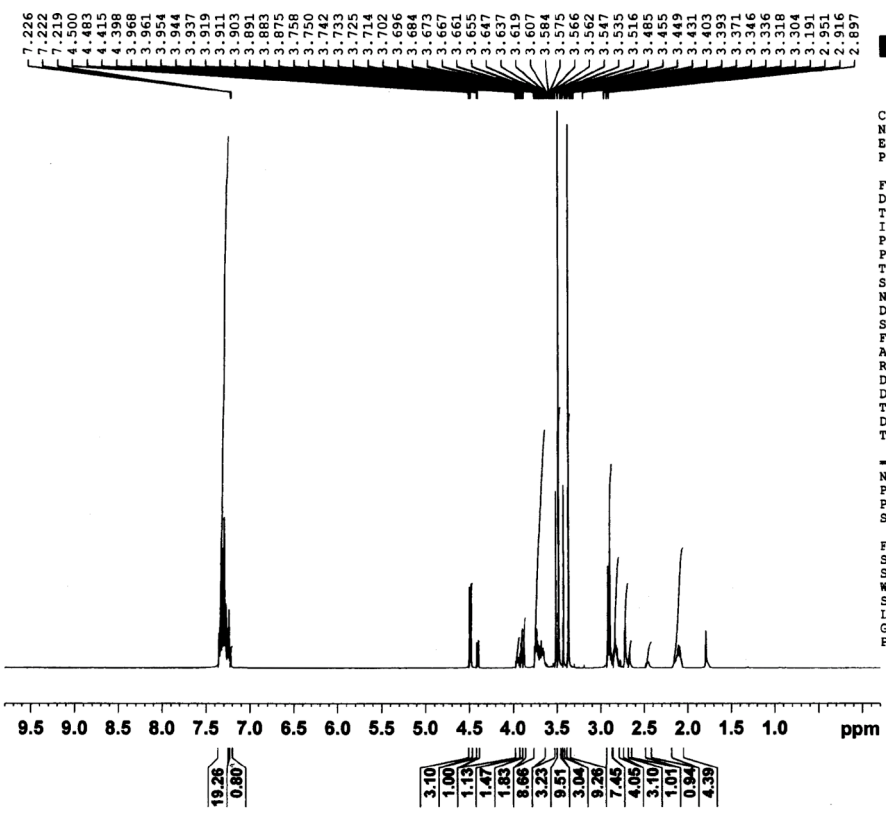


積算回数	16	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/01/25 21:07		
測定者			
ファイル名	Mercury64		
サンプル名			
コメント	コメント		

1:	3346.78,	67.5849	2:	2884.02,	84.5052	3:	2360.44,	84.4507	4:	1619.91,	84.7104
5:	1457.92,	66.3330	6:	1419.35,	80.1194	7:	1326.79,	35.3028	8:	1164.19,	58.2467
9:	1126.22,	50.4584	10:	1066.37,	56.4829	11:	1017.27,	65.6149	12:	977.73,	87.7752
13:	840.81,	74.9422	14:	762.71,	93.2935	15:	609.40,	85.5953	16:	421.37,	91.4970





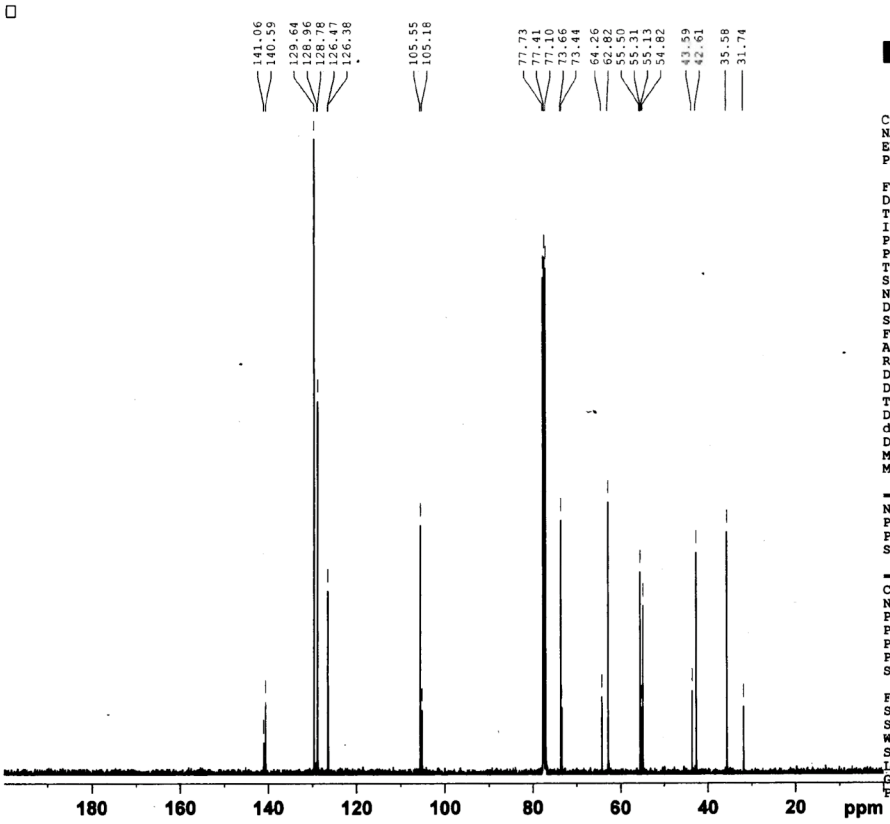


Current Data Parameters
NAME Feb23-2006-hayashi
EXPNO 41
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060223
Time 23.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 101
DW 60.800 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 400.1824713 MHz

F2 - Processing parameters
SI 32768
SF 400.1799873 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



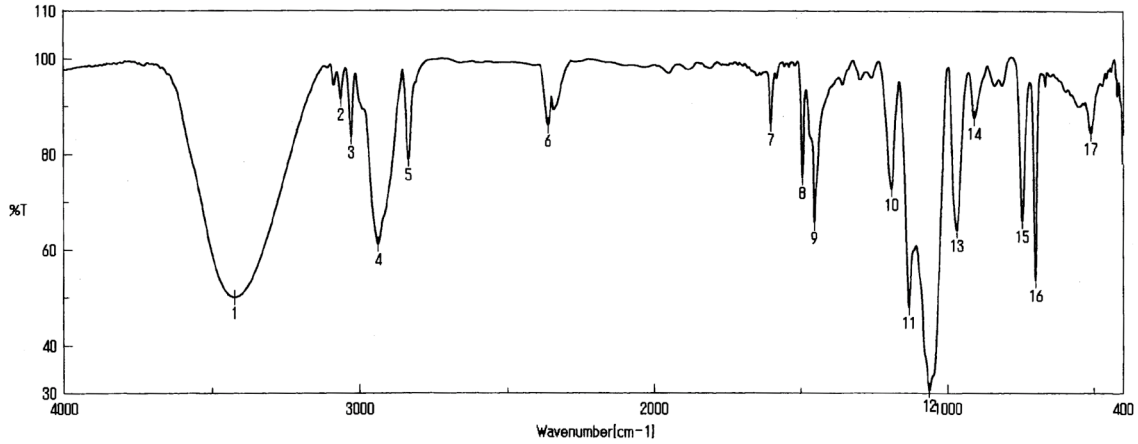
Current Data Parameters
NAME Feb24-2006
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060224
Time 19.18
INSTRUM dpx400
PROBHD 5 mm BBO 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 555
DS 2
SWH 31847.133 Hz
FIDRES 0.485949 Hz
AQ 1.0289652 sec
RG 3251
DW 15.700 usec
DE 6.00 usec
TE 303.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 2.20 dB
SFO1 100.6254358 MHz

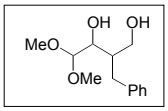
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 20.00 dB
PL13 22.00 dB
SFO2 400.1316005 MHz

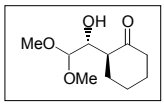
F2 - Processing parameters
SI 32768
SF 100.6127290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

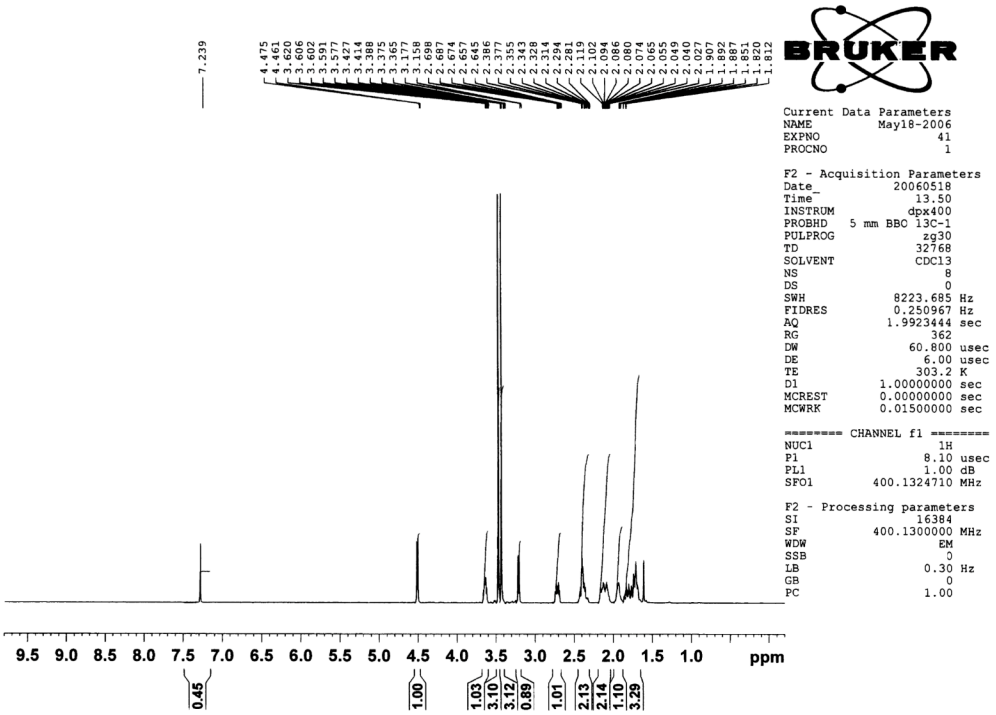


積算回数	16	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/02/24 19:21		
測定者			
ファイル名	Memory#3		
サンプル名			
コメント	コメント		

1:	3423.03,	50.0156	2:	3061.44,	91.4794	3:	3026.73,	83.6091	4:	2936.09,	61.1712
5:	2831.95,	78.9846	6:	2360.44,	85.9987	7:	1602.56,	86.3100	8:	1495.53,	75.1662
9:	1454.06,	65.7203	10:	1192.76,	72.7447	11:	1132.97,	48.0437	12:	1063.55,	30.7035
13:	970.98,	64.1610	14:	911.20,	87.6000	15:	746.32,	66.1189	16:	701.00,	53.7279
17:	511.04,	84.5132									







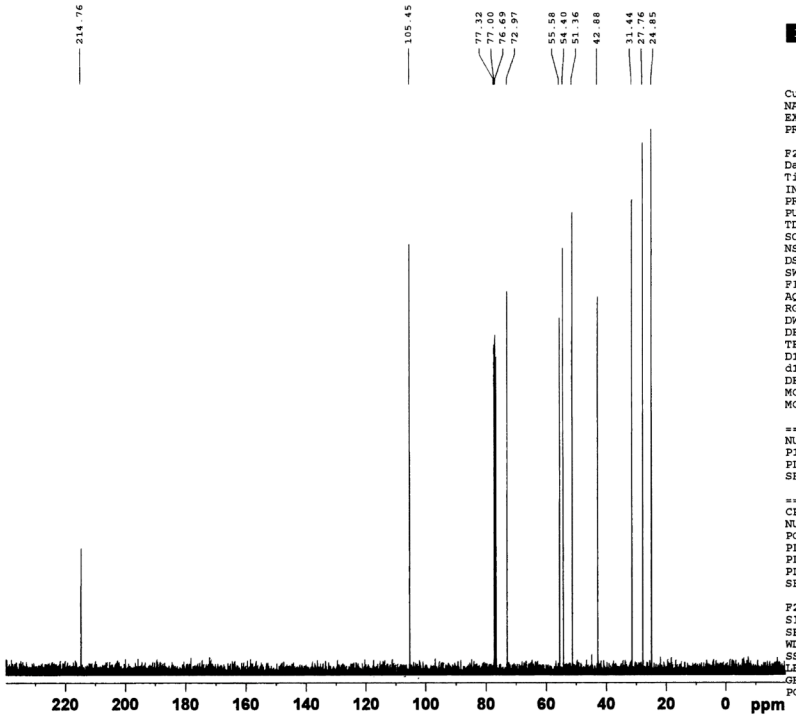
BRUKER

```
Current Data Parameters
NAME                  May18-2006
EXPNO                         41
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20060518
Time                       13.50
INSTRUM                   dpx400
PROBHD   5 mm BBO 13C-1
PULPROG                    zg30
TD                        32768
SOLVENT                   CDCl3
NS                             8
DS                             0
SWH                    8223.685 Hz
FIDRES                 0.250967 Hz
AQ                     1.9923444 sec
RG                           362
DW                        60.800 usec
DE                         6.00 usec
TE                        303.2 K
D1                    1.00000000 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                          1H
P1                         8.10 usec
PL1                        1.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        16384
SF                  400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



BRUKER

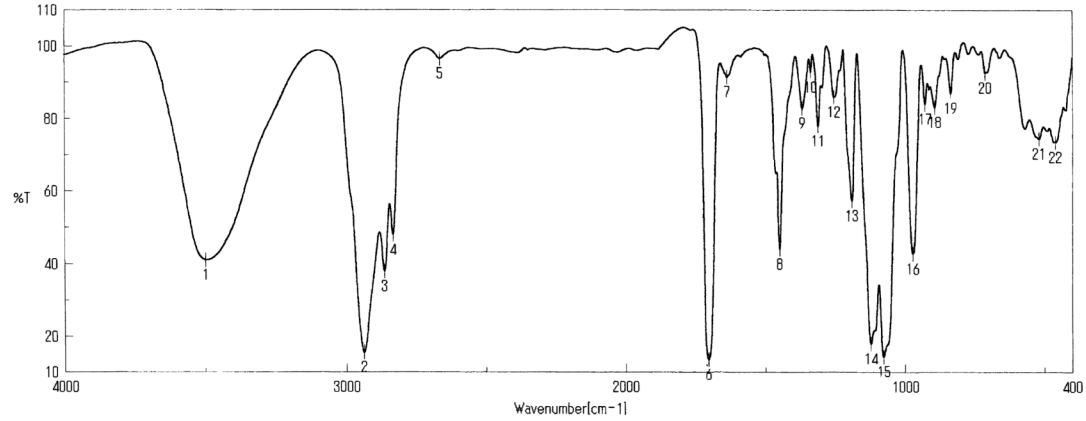
```
Current Data Parameters
NAME                  May18-2006
EXPNO                         52
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20060518
Time                       15.32
INSTRUM                   dpx400
PROBHD   5 mm BBO 13C-1
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          277
DS                            2
SWH                31847.133 Hz
FIDRES             0.485949 Hz
AQ                 1.0289652 sec
RG                      5160.6
DW                      15.700 usec
DE                         6.00 usec
TE                        303.2 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                         13C
P1                        10.00 usec
PL1                        2.20 dB
SFO1               100.6254358 MHz

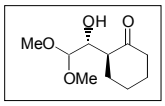
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                          1H
PCPD2                     80.00 usec
PL2                        3.00 dB
PL12                      20.00 dB
PL13                      22.00 dB
SFO2               400.1316005 MHz

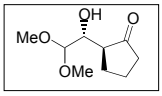
F2 - Processing parameters
SI                        32768
SF                 100.6127727 MHz
WDW                          no
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.40
```



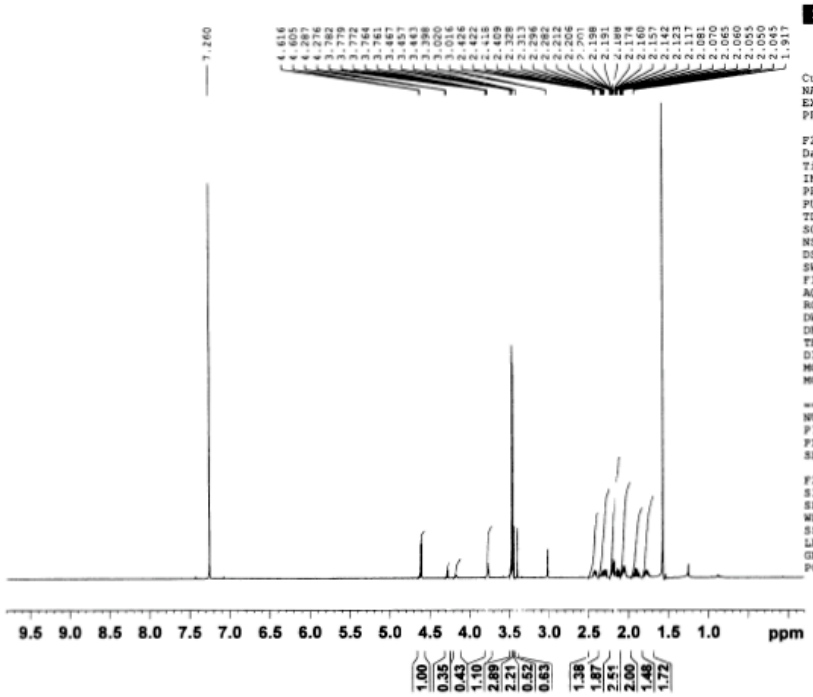
積算回数	64	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/05/29 21:30		
測定者			
ファイル名	Memory#3		
サンプル名			
コメント	コメント		

1:	3499.20,	41.0771	2:	2937.06,	15.5381	3:	2864.74,	37.9466	4:	2833.88,	47.9944
5:	2666.11,	96.5365	6:	1704.76,	13.4889	7:	1638.23,	91.4756	8:	1450.21,	44.0295
9:	1369.21,	82.8205	10:	1338.36,	92.8116	11:	1313.29,	78.0197	12:	1256.40,	86.0258
13:	1191.79,	57.3338	14:	1123.33,	17.8419	15:	1078.01,	14.2854	16:	972.91,	42.7452
17:	928.56,	83.9779	18:	893.84,	83.1425	19:	836.95,	87.0591	20:	712.57,	92.5984





No title



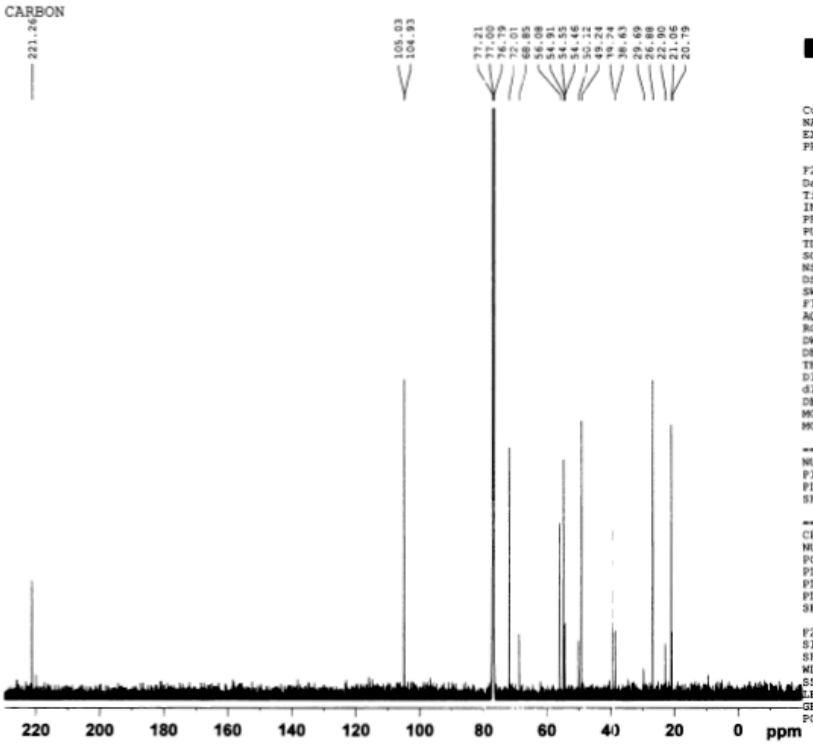

```
Current Data Parameters
NAME                  May27-2006
EXPNO                         15
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20060527
Time                       18.25
INSTRUM                     av600
PROBHD    5 mm CPDUL 13C
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                   12376.237 Hz
FIDRES                 0.188846 Hz
AQ                    2.6477449 sec
RG                         25.4
DW                       40.400 usec
DE                        6.00 usec
TE                       298.0 K
D1                    1.00000000 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        14.40 usec
PL1                       -5.80 dB
SFO1                600.1337060 MHz

F2 - Processing parameters
SI                         32768
SF                  600.1297098 MHz
WDW                           no
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00
```

CARBON



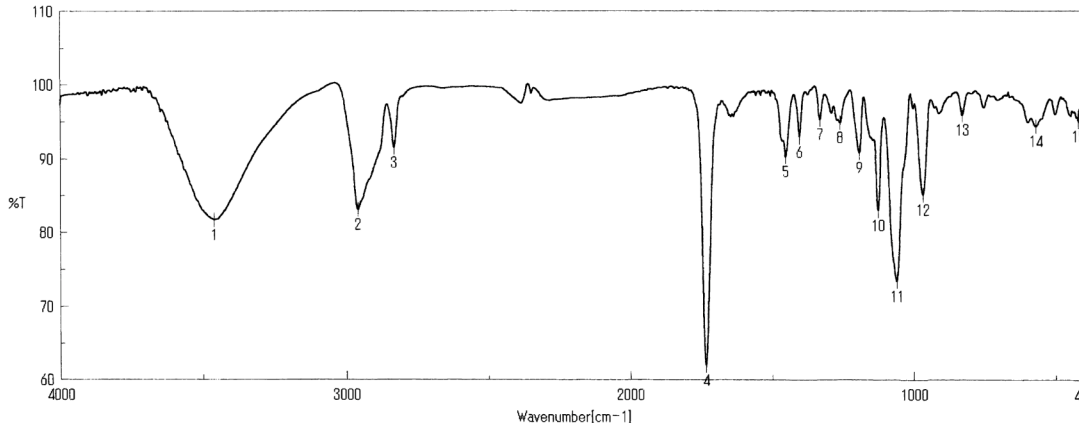

```
Current Data Parameters
NAME                  May27-2006
EXPNO                         16
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20060527
Time                       18.42
INSTRUM                     av600
PROBHD    5 mm CPDUL 13C
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                           414
DS                             4
SWH                   39370.078 Hz
FIDRES                 0.600740 Hz
AQ                    0.8323699 sec
RG                         13004
DW                       12.700 usec
DE                        50.00 usec
TE                       298.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
MCREST                0.00000000 sec
MCWRK                 0.01500000 sec

======== CHANNEL f1 ========
NUC1                         13C
P1                        10.00 usec
PL1                       -4.90 dB
SFO1                150.9178988 MHz

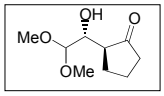
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    100.00 usec
PL2                       -5.80 dB
PL12                       8.00 dB
PL13                       8.00 dB
SFO2                600.1324005 MHz

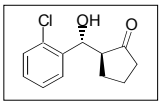
F2 - Processing parameters
SI                         32768
SF                  150.9027373 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

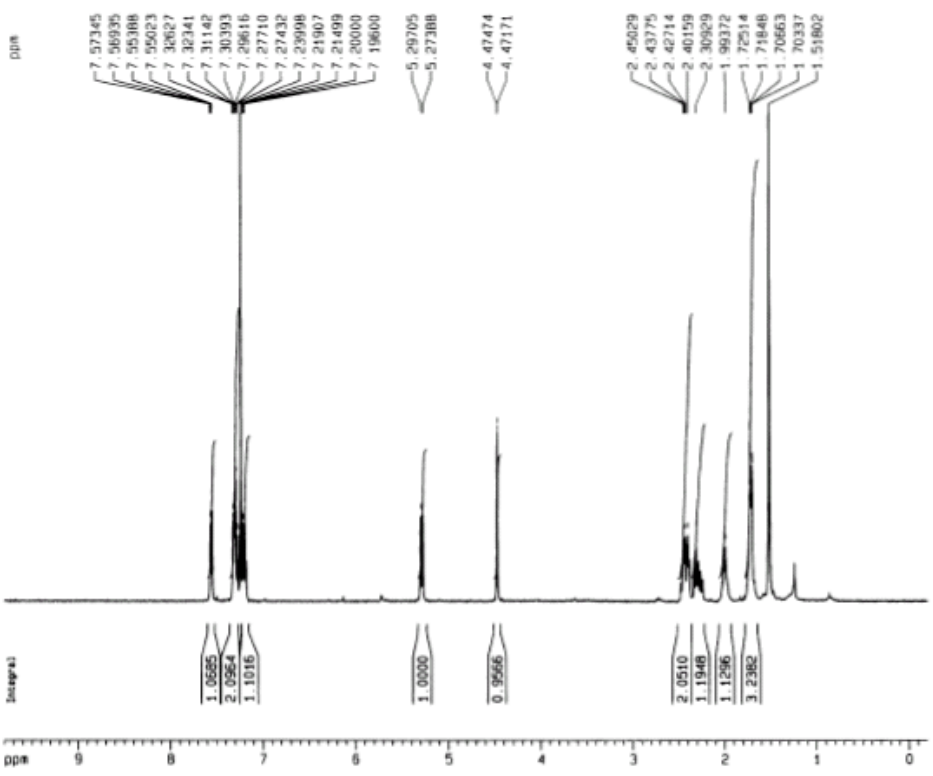


積算回数	64	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/05/29 21:40		
測定者			
ファイル名	Memory#3		
サンプル名			
コメント	コメント		

1:	3460.63,	81.7020	2:	2960.20,	83.0975	3:	2833.88,	91.5482	4:	1734.66,	61.9678
5:	1454.06,	90.3252	6:	1404.89,	92.9734	7:	1332.57,	95.3790	8:	1262.18,	94.9252
9:	1193.72,	90.8441	10:	1127.19,	82.9879	11:	1060.66,	73.4402	12	969.05,	85.0852
13	829.24,	95.9570	14:	570.83,	94.4109	15:	420.41,	95.0951			








```
Current Data Parameters
NAME            Jan25-2006
EXPNO                   31
PROCNO                   1

F2 - Acquisition Parameters
Date_         20060125
Time               12.24
INSTRUM           dpx400
PROBHD  5 mm BBO 13C-1
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ              1.9923444 sec
RG                 456.1
DW                60.800 usec
DE                 6.00 usec
TE                303.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  8.10 usec
PL1                 1.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                     16384
SF            400.1300172 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                  12.50 cm
F1P                 9.800 ppm
F1                3921.27 Hz
F2P                -0.200 ppm
F2                 -80.03 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.06500 Hz/cm
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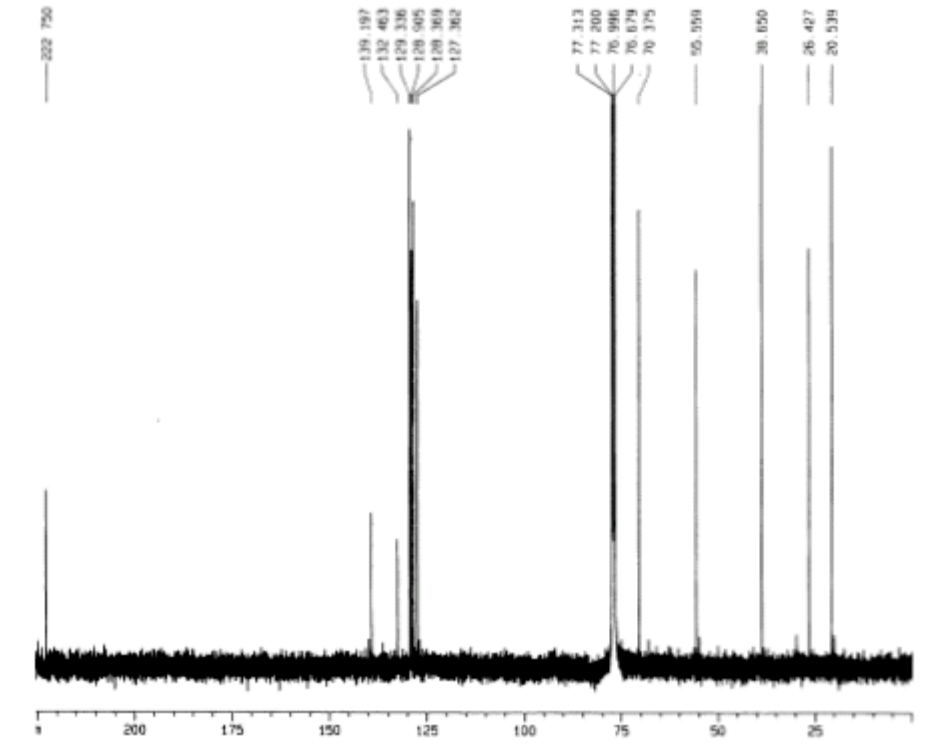


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Current Data Parameters
NAME            Jan26-2006
EXPNO                  136
PROCNO                   1

F2 - Acquisition Parameters
Date_         20060126
Time               23.34
INSTRUM           dpx400
PROBHD  5 mm BBO 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT             CDCl3
NS                  8236
DS                      2
SWH             30847.133 Hz
FIDRES          0.485649 Hz
AQ              1.0289852 sec
RG                 1824.0
DW                15.700 usec
DE                 6.00 usec
TE                303.2 K
D1              3.00000000 sec
D11             0.03000000 sec
DELTA           2.90000010 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  9.30 usec
PL1                 3.00 dB
SFO1          100.6254056 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2          400.1315005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127688 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
CY                  12.50 cm
F1P               230.000 ppm
F1              23146.64 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM            11.50000 ppm/cm
HZCM          1157.64688 Hz/cm
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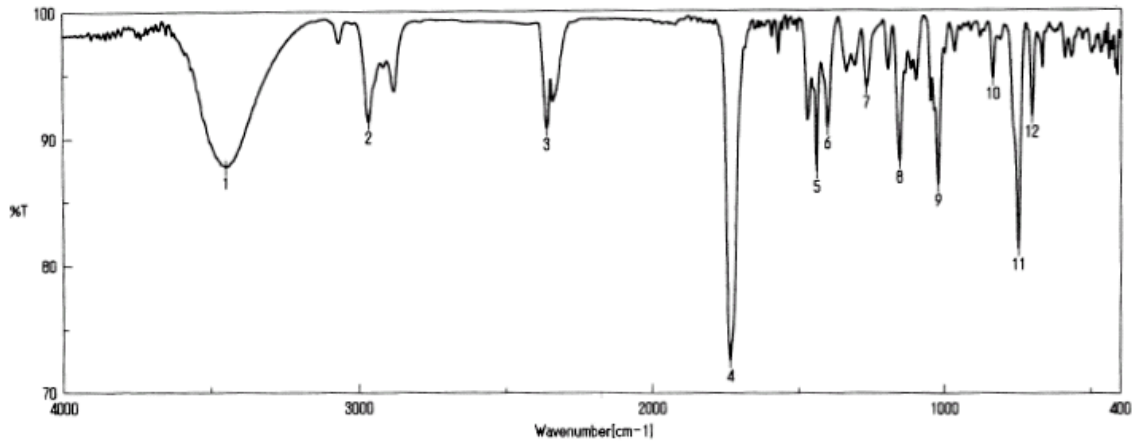
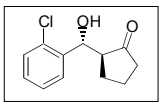
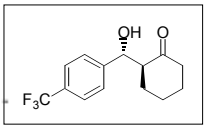
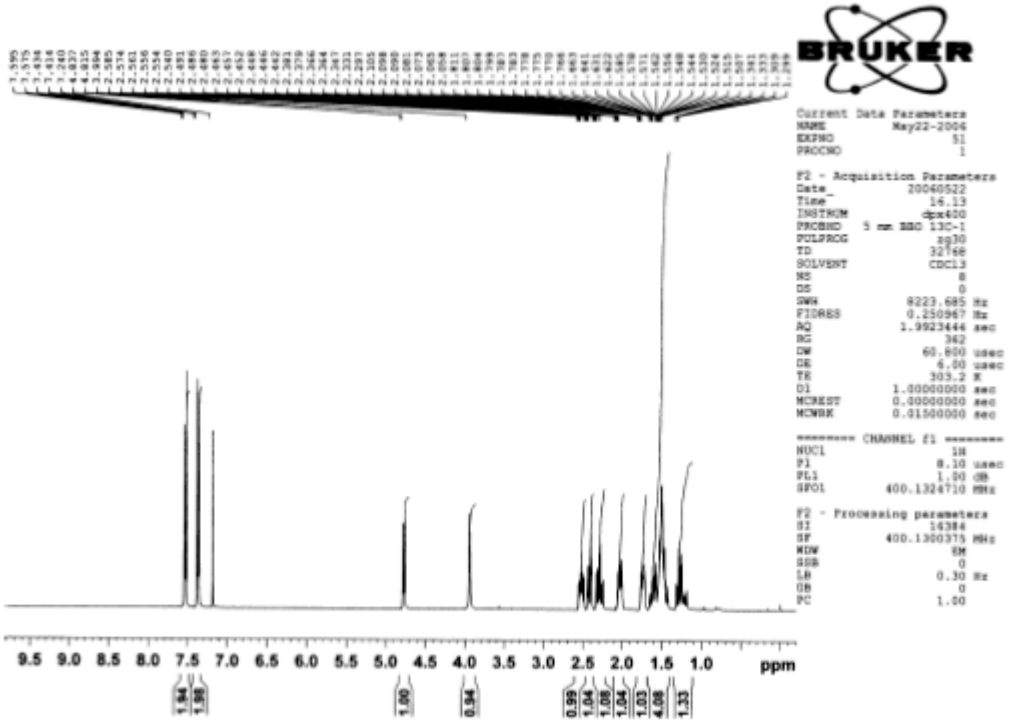


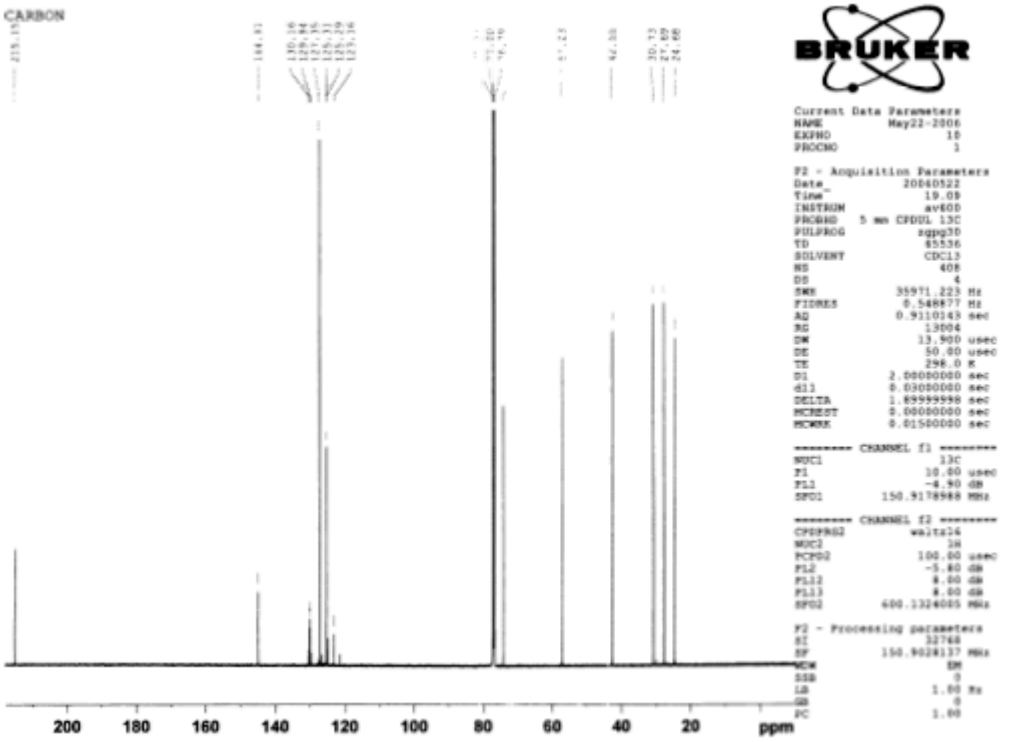
積算回数	16	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	1	スキャンスピード	2 mm/sec
日時	106/01/25 20:58		
測定者			
ファイル名	Memory#3		
サンプル名			
コメント	コメント		

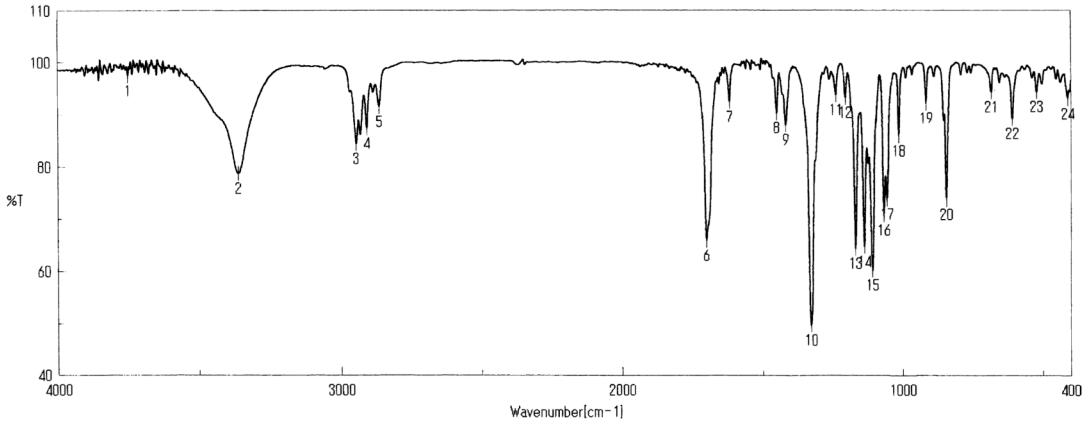
1:	3447.13,	87.7456	2:	2965.02,	91.2738	3:	2360.44,	90.7449	4:	1734.66,	72.5640
5:	1439.60,	87.4352	6:	1402.00,	90.8397	7:	1269.90,	94.0409	8:	1156.12,	88.1940
9:	1024.02,	86.3197	10:	838.88,	94.6881	11:	749.21,	81.3388	12:	704.85,	91.6975




OH
O
F3C


BRUKER
Current Data Parameters
NAME May22-2006
EXPNO 51
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060522
Time 14.13
INSTRUM dpx400
PROBHD 5 mm BBO 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 9223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 362
DW 60.800 usec
DE 6.00 usec
TE 303.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.10 usec
PL1 1.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300375 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
1.94
1.98
1.00
0.94
0.99
1.04
1.08
1.04
1.03
4.08
1.33


CARBON
BRUKER
Current Data Parameters
NAME May22-2006
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060522
Time 19.09
INSTRUM av600
PROBHD 5 mm CPDUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 408
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 13004
DW 13.900 usec
DE 50.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.80 usec
PL1 -4.90 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.80 dB
PL12 8.00 dB
PL13 8.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9028137 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
200 180 160 140 120 100 80 60 40 20
ppm



積算回数	64	分解	4 cm-1
ゼロフィリング	ON	アポダイゼーション	Cosine
ゲイン	2	スキャンスピード	2 mm/sec
日時	106/05/29 21:17		
測定者			
ファイル名	Memory#3		
サンプル名			
コメント	コメント		

1:	3751.83,	97.4254	2:	3361.32,	78.7848	3:	2947.66,	84.4286	4:	2910.06,	87.3490
5:	2865.70,	91.5038	6	1699.94,	65.8844	7:	1617.98,	92.4863	8:	1450.21,	90.3235
9:	1417.42,	88.0405	10:	1327.75,	49.7135	11.	1239.04,	93.8274	12.	1205.29,	93.3165
13:	1169.62,	64.4192	14:	1137.80,	64.7555	15:	1108.87,	60.2842	16:	1067.41,	70.7612
17:	1056.80,	73.8871	18	1014.37,	85.9426	19:	916.99,	92.1844	20:	844.67,	73.8058