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Supporting Information

69451 Weinheim, Germany

Diphenylprolinol silyl ether as an efficient organocatalyst for the asymmetric Michael reaction of aldehydes and nitroalkenes

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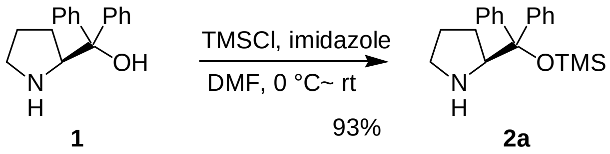
Experimental Section

General Remarks. All reactions were carried out under argon atmosphere and monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plates (0.25 mm thickness). Specific optical rotations were measured using a JASCO P-1020 polarimeter. FT-IR spectra were recorded on a Horiba FT-720 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AM400 (400 MHz) instrument. High-resolution mass spectral analyses (HRMS) were carried out using JEOL JMS-SX 102A. Preparative thin layer chromatography was performed using Wakogel B-5F purchased from Wako Pure Chemical Industries, Tokyo, Japan. Flash chromatography was performed using silica gel 60N of Kanto Chemical Co. Int., Tokyo, Japan.

Procesures for preparation of diphenylprolinol silyl ether organocatalysts.

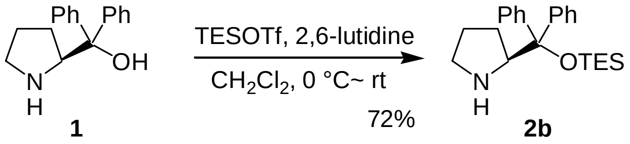
(*S*)-(Diphenyltrimethylsiloxymethyl)-pyrrolidine (2a)



To a DMF (13.9 ml) solution of diphenylprolinol **1** (3.5 g, 13.9 mmol) and imidazole (3.8 g, 55.5 mmol) was added TMSCl (5.1 ml, 41.7 mmol) at 0 °C. The reaction mixture was stirred for 17 h at room temperature and quenched with pH 7.0 phosphate buffer at 0 °C. The organic materials were extracted with ethyl acetate three times and the combined organic phases were washed with brine three times. The organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. Purification by flash column chromatography (ethyl acetate:hexane = 1:7 ~ 1:3) gave **2a** in 93% yield.

^{1}H NMR ($CDCl_3$) δ -0.13 (9H, s), 1.28-1.41 (1H, m), 1.47-1.61 (3H, m), 2.71-2.88 (2H, m), 4.01 (1H, d, *J*=7.0 Hz), 7.14-7.28 (6H, m), 7.29-7.35 (2H, d), 7.39-7.45 (2H, m);
^{13}C NMR ($CDCl_3$) δ 2.1, 25.0, 27.4, 47.1, 65.3, 83.1, 126.7, 126.9, 127.5, 128.4, 145.7, 146.7;
IR (neat) ν 2954, 1491, 1446, 1250, 1072, 879, 839 cm^{-1};
HRMS (FAB) $[M+H]^+$ calculated for $C_{20}H_{28}ONSi$: 326.1940, found: 326.1967;
$[\alpha]_D^{33}$ -52.4 (*c*=1.04, $CHCl_3$).

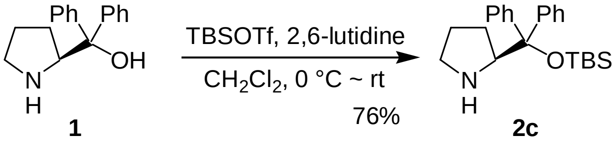
(*S*)-(Diphenyltriethylsiloxymethyl)-pyrrolidine (2b)



To a CH_2Cl_2 (1.2 ml) solution of diphenylprolinol **1** (300 mg, 1.2 mmol) was added 2,6-lutidine (1.2 ml, 8.3 mmol) and TESOTf (1.3 ml, 5.9 mmol) at 0 °C. The reaction mixture was stirred for 8 h at room temperature and quenched with aq. NH_4Cl and the organic materials were extracted with ethyl acetate. The organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. To the organic materials was added MeOH and aq. $NaHCO_3$ at room temperature, and the mixture was stirred at that temperature. The organic materials were extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo after filtration. Purification by silica gel column chromatography (ethyl acetate:hexane=1:100 ~ 1:3) gave **2b** in 72% yield.

^{1}H NMR ($CDCl_3$) δ 0.33 (6H, q, *J*=7.9 Hz), 0.83 (9H, t, *J*=7.9 Hz), 1.16-1.28 (1H, m), 1.43-1.60 (3H, m), 2.62-2.71 (1H, m), 2.79 (1H, dt, *J*d=9.9 Hz, *J*t=6.1 Hz), 4.00 (1H, t, *J*=7.2 Hz), 7.16-7.28 (6H, m), 7.30-7.37 (2H, m), 7.42-7.49 (2H, m);
^{13}C NMR ($CDCl_3$) δ 6.5, 7.2, 25.1, 27.7, 47.2, 65.6, 82.9, 126.88, 126.92, 127.3,127.5, 128.0, 128.8, 145.5, 146.6;
IR (neat) ν 2954, 2875, 1491, 1446, 1238, 1070, 740, 725, 701 cm^{-1};
HRMS (FAB) $[M+H]^+$ calculated for $C_{23}H_{34}ONSi$: 368.2410, found: 368.2415;
$[\alpha]_D^{30}$ -48.4 (*c*=0.097, $CHCl_3$).

(*S*)-[(*tert*-Butyldimethylsiloxy)-diphenylmethyl]-pyrrolidine (2c)



To a CH_2Cl_2 (1.2 ml) solution of diphenylprolinol **1** (300 mg, 1.2 mmol) was added 2,6-lutidine (1.2 ml, 8.3 mmol) and TBSOTf (1.4 ml, 5.9 mmol) at 0 °C. The reaction mixture was stirred for 8 h at room temperature and quenched with aq. NH_4Cl. The organic materials were extracted with ethyl acetate and the organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. Then to the organic materials was added MeOH and aq. $NaHCO_3$ at room temperature, and the mixture was stirred at that temperature. The organic materials were extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo after filtration. Purification by silica gel column chromatography (ethyl acetate:hexane=1:100 ~ 1:3) gave **2c** in 76% yield.

^{1}H NMR ($CDCl_3$) δ -0.47 (3H, s), -0.24 (3H, s), 0.93 (9H, s), 1.12-1.28 (1H, m), 1.43-1.61 (3H, m), 2.62-2.72 (1H, m), 2.79 (1H, dt, *J*d=10.1, *J*t=6.6), 3.99 (1H, t, *J*=7.3 Hz), 7.17-7.38 (6H, m), 7.31-7.36 (2H, m), 7.47-7.53 (2H, m);

^{13}C NMR ($CDCl_3$) δ −3.3, −2.7, 19.0, 25.0, 26.3, 27.8, 47.1, 65.6, 83.0, 127.0, 127.2, 127.6, 128.3, 129.2, 145.2, 146.4;

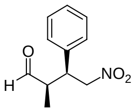
IR (neat) ν 2954, 2927, 2856, 1493, 1471, 1446, 1252, 1066, 835, 775, 702 cm^{-1};

HRMS (FAB) $[M+H]^+$ calculated for $C_{23}H_{34}ONSi$: 368.2410, found: 368.2415;

$[\alpha]_D^{32}$ -34.4 (*c*=0.198, $CHCl_3$).

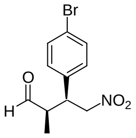
General procedure **(Typical procedure for a Michael reaction):** To a hexane solution of the nitroolefin (1.0 mmol) and **2a** (34 mg, 0.1 mmol) was added an aldehyde (10 mmol) at the temperature indicated in Table 2. After stirring the reaction mixture at that temperature, the reaction was quenched by the addition of aq. 1N HCl. Organic materials were extracted with ethyl acetate three times. The combined organic phases were dried over Na_2SO_4, filtered, concentrated and purified by preparative TLC (chloroform) to afford the Michael adduct.

(2*R*, 3*S*)-2-Methyl-4-nitro-3-phenylbutanal



Title compound was prepared from (*E*)-β-nitrostyrene and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a OD-H column at 237 nm (2-propanol:hexane = 1:10), 1.0 mL/min; major enantiomer tr = 18.5 min, minor enantiomer tr = 14.3 min. Spectroscopic data are in agreement with the published data.[1,2,4)]

(2*R*, 3*S*)-(4-Bromophenyl)-2-methyl-4-nitrobutyraldehyde



Title compound was prepared from 1-bromo-4-(2-nitrovinyl)-benzene and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a AD-H column at 240 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 9.6 min, minor enantiomer tr = 12.6 min.

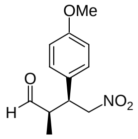
Since the diastereomixture was difficult to separate, *syn:anti* ratio (95:5) was determined by 400 MHz ^{1}H-NMR.

Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, d, *J*=7.3 Hz), 2.67-2.81 (1H, m), 3.71-3.81 (1H, m), 4.57-4.80 (2H, m), 7.03 (1H, d, *J*=8.4 Hz), 7.45 (1H, d, *J*=8.4 Hz), 9.67 (1H, d, *J*=1.1 Hz); ^{13}C NMR ($CDCl_3$) δ 12.2, 43.5, 48.2, 122.2, 129.7, 129.8, 132.3, 135.6, 201.8.

Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ 1.19 (3H, d, *J*=7.3 Hz), 2.67-2.81 (1H, m), 3.71-3.82 (1H, m), 4.57-4.80 (2H, m), 7.07 (1H, d, *J*=8.4 Hz), 7.44 (1H, d, *J*=8.4 Hz), 9.51 (1H, d, *J*=1.2 Hz);

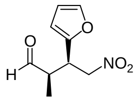
HRMS (FAB) $[M+H]^+$ calculated for $C_{11}H_{13}O_3N_1Br_1$: 286.0079, found: 286.0093

(2*R*, 3*S*)-2-methyl-4-nitro-3-(4-methoxyphenyl)-butanal



Title compound was prepared from 1-methoxy-4-(2-nitrovinyl)-benzene and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a AS-H column at 241 nm (2-propanol:hexane = 1:20), 1.0 mL/min, major enantiomer tr = 21.7 min, minor enantiomer tr = 15.8 min. Spectroscopic data are in agreement with the published data.4)

(2*R*, 3*S*)-3-Furyl-2-methyl-4-nitrobutanal



Title compound was prepared from 2-(2-nitrovinyl)-furan and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a IA column at 265 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 14.4 min, minor enantiomer tr = 15.8 min.

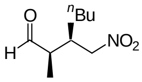
Since the diastereomeric mixture was difficult to separate, *syn:anti* ratio (94:6) was determined by 400 MHz ^{1}H-NMR.

Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 1.30 (3H, d, *J*=7.2 Hz), 2.97-3.11 (1H, m), 4.31 (1H, m), 4.88-5.02 (2H, m), 6.37-6.45 (1H, m), 6.51-6.56 (1H, m), 7.58 (1H, d, *J*=1.7 Hz), 9.93 (1H, d, *J*=1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 11.0, 37.6, 47.0, 75.8, 108.8, 110.4, 142.7, 149.8, 201.6;

Minor diastereomer: 1.45 (1H, d, *J*=7.4 Hz), 4.19-4.26 (1H, m), 4.88-5.02 (2H, m), 6.37-6.45 (1H, m), 6.51-6.56 (1H, m), 7.48 (1H, d, *J*=2.0 Hz), 9.86 (1H, d, *J*=1.4 Hz);

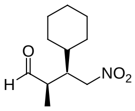
HRMS (FAB) $[M+H]^+$ calculated for $C_9H_{12}O_4N$: 198.0766, found: 198.0765

(2*R*, 3*R*)-2-Methyl-3-nitromethylheptanal



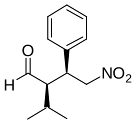
Title compound was prepared from 1-nitrohex-1-ene and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a IA column at 210 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 7.2 min, minor enantiomer tr = 7.5 min. Spectroscopic data are in agreement with the published data.4)

(2*R*, 3*R*)-3-Cyclohexyl-2-methyl-4-nitro-butanal



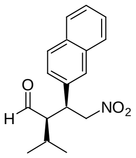
Title compound was prepared from (2-nitrovinyl)-cyclohexane and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a AS-H column at 210 nm (2-propanol:hexane = 1:40), 1.0 mL/min; major enantiomer tr = 6.7 min, minor enantiomer tr = 6.4 min. Spectroscopic data are in agreement with the published data.4)

(2*R*, 3*S*)-2-(methylethyl)-4-nitro-3-phenylbutanal



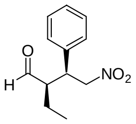
Title compound was prepared from (*E*)-β-nitrostyrene and isovaleraldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with a AD-H column at 281 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 5.9 min, minor enantiomer tr = 6.4 min. Spectroscopic data are in agreement with the published data.1,2,4)

(2*R*,3*S*)-2-(methylethyl)-3-naphthalen-2-yl-4-nitrobutanal



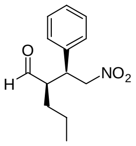
Title compound was prepared from 2-(2-nitrovinyl)-naphthalene and propanal according to General Procedure. The enantiomeric excess was determined by HPLC with a OD-H column at 292 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 22.9 min, minor enantiomer tr = 13.7 min. Spectroscopic data are in agreement with the published data.1)

(2*R*, 3*S*)-2-Ethyl-4-nitro-3-phenylbutanal



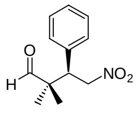
Title compound was prepared from (*E*)-β-nitrostyrene and butanal according to General Procedure. The enantiomeric excess was determined by HPLC with a OD-H column at 221 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 14.9 min, minor enantiomer tr = 12.0 min. Spectroscopic data are in agreement with the published data.1,2,4)

(2*R*)-((*S*)-2-nitro-1-phenylethyl)-pentanal



Title compound was prepared from (*E*)-β-nitrostyrene and hexanal according to General Procedure. The enantiomeric excess was determined by HPLC with a OD-H column at 220 nm (2-propanol:hexane = 1:20), 1.0 mL/min; major enantiomer tr = 14.0 min, minor enantiomer tr = 10.7 min. Spectroscopic data are in agreement with the published data.2,4,5)

(*R*)-2,2-Dimethyl-4-nitrophenylbutanal

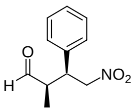


Title compound was prepared from (*E*)-β-nitrostyrene and isobutyraldehyde according to General Procedure. The enantiomeric excess was determined by HPLC with a AS-H column at 220 nm (2-propanol:hexane = 1:10), 1.0 mL/min; major enantiomer tr = 6.6 min, minor enantiomer tr = 6.2 min. Spectroscopic data are in agreement with the published data.[3,4,5)]

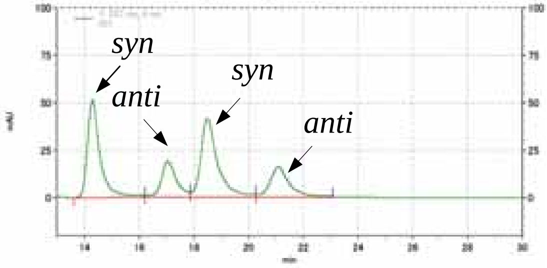
Procedure for a Michael reaction with methylvinylketone: To **2a** (24.9 mg, 0.077 mmol) was added methylvinylketone (207 μl, 2.55 mmol) and 3-phenylpropanal (33.5 μl, 0.26 mmol) at 0 °C. After stirring the reaction mixture for 72 h at room temperature, excess methylvinylketone was azeotropically removed with toluene from the reaction mixture. To the residue was added $NaBH_4$ (48.2 mg, 1.275 mmol) and MeOH (1.0 ml) at 0 °C and the mixture was stirred for 1 h at room temperature. The reaction was quenched with aq. 1N HCl. The organic materials were salted out with ethyl acetate five times. The combined organic phases were dried over Na_2SO_4, filtered, concentrated and purified by preparative TLC (ethyl acetate:hexane=3:1) to afford the reduced Michael adducts as a colorless oil (52%, 97% *ee*). The enantiomeric excess was determined by HPLC with a IA column at 220 nm (2-propanol:hexane = 1:40), 0.5 mL/min; major enantiomer tr = 85.9, 89.7 min, minor enantiomer tr = 94.9, 100.4 min.

1) J. M. Betancort, C. F. Barbas, III, *Org. Let.* **2001**, *3,* 3737.
2) A. Alexakis, O. Andrey, *Org. Lett.* **2002**, *4,* 3611.
3) N. Mase, R. Thayumanavan, F. Tanaka, C. F. Barbas, III, *Org. Lett.* **2004**, *6,* 2527.
4) O. Andrey, A. Alexakis, A. Tomassini, G. Bernardinelli, *Adv. Synth. Catal.* **2004**, *346*, 1147.
5)W. Wang, J. Wang, H. Li, *Angew. Chem.* **2005**, *117*, 1393**;** *Angew***.** *Chem***.** *Int. Ed.* **2005**, *44*, 1369.

HPLC-chromatograms

Entry 1 

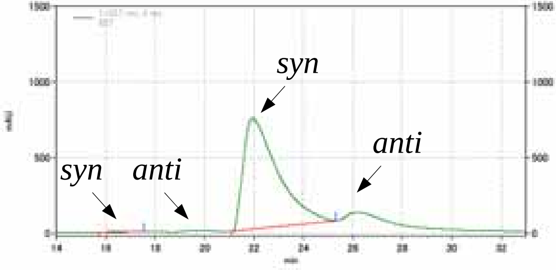
Racemate



1: 237 nm, 4 nm結果

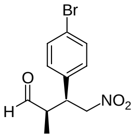
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		14.29	6513385	33.768	BV
2		17.05	2848229	14.767	VV
3		18.49	6942271	35.992	VV
4		21.08	2984557	15.473	VB
トータル			19288442	100.000	

Chiral compound



1: 227 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		16.75	1018118	0.358	BB
2		21.95	283547974	99.642	BB
トータル			284566092	100.000	

Entry 2 

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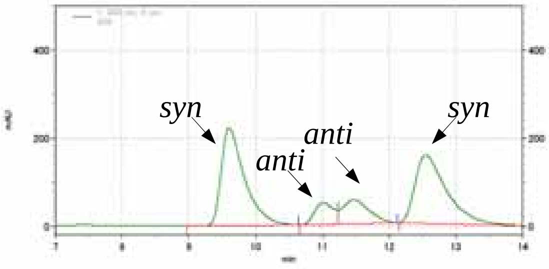
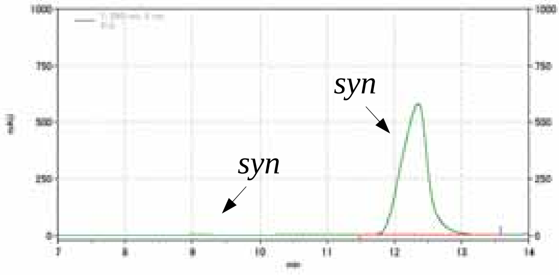


1: 240 nm, 4 nm結果

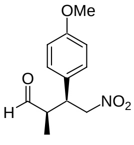
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		9.60	21463110	41.460	MM
2		11.01	3969589	7.668	[illegible]
3		11.47	5972112	11.536	[illegible]
4		12.55	20363649	39.336	MM
トータル			51768460	100.000	

Chiral compound

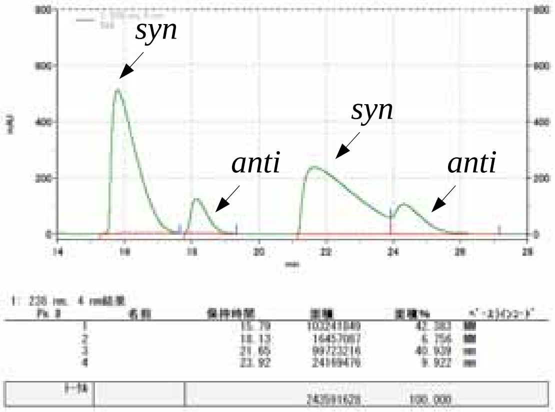


1: 260 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		12.36	63017705	100.000	MM
トータル			63017705	100.000	

Entry 3 

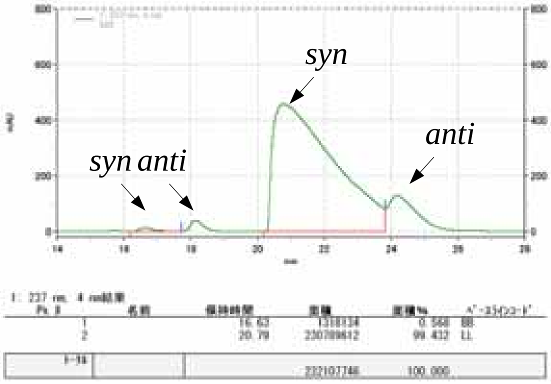
Racemate



1: 228 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		15.79	103241049	42.383	MM
2		18.13	16457067	6.756	MM
3		21.65	99723216	40.939	mm
4		23.92	24169476	9.922	mm
トータル			243591628	100.000	

Chiral compound



1: 237 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
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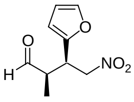
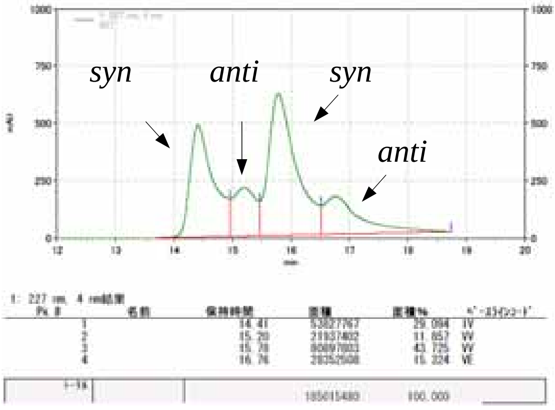
トータル			232107746	100.000	

Entry 4 

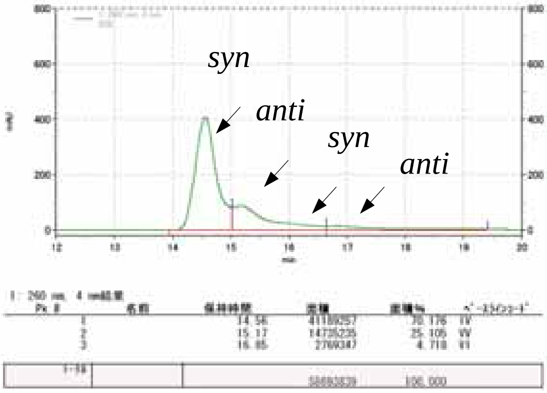
Racemate



1: 227 nm, 4 nm結果

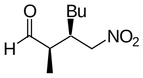
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		14.41	53827767	29.094	IV
2		15.20	21937402	11.857	VV
3		15.78	80897803	43.725	VV
4		16.76	28352508	15.324	VE
トータル			185015480	100.000	

Chiral compound

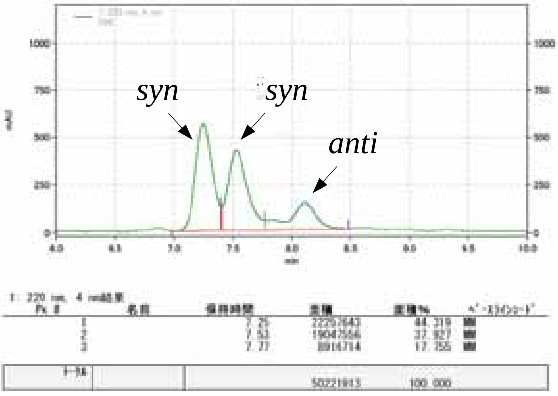


1: 260 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		14.56	41189257	70.176	IV
2		15.17	14735235	25.105	VV
3		16.65	2769347	4.718	VI
トータル			58693839	100.000	

Entry 5 

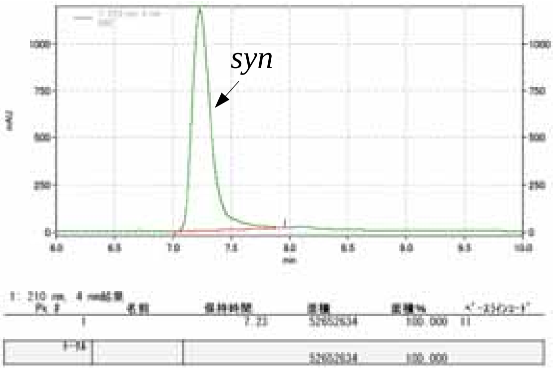
Racemate



1: 220 nm, 4 nm結果

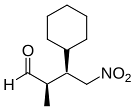
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		7.25	22257643	44.319	MM
2		7.53	19047556	37.927	MM
3		7.77	8916714	17.755	MM
トータル			50221913	100.000	

Chiral compound

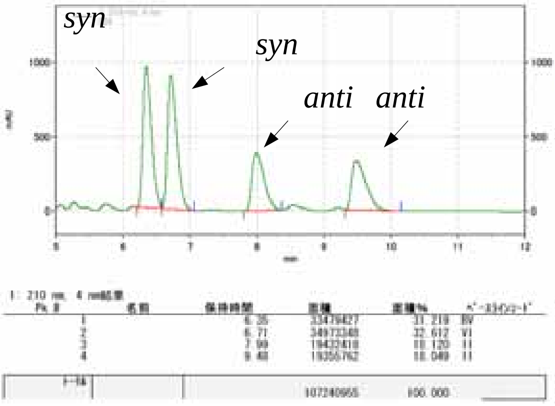


1: 210 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		7.23	52652634	100.000	11
トータル			52652634	100.000	

Entry 6 

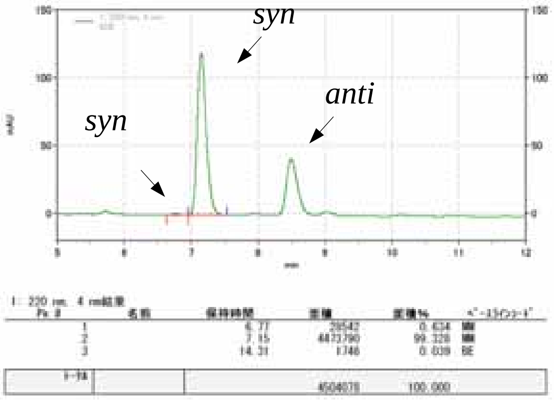
Racemate



1: 210 nm, 4 nm結果

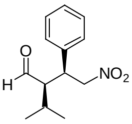
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		6.35	33479427	31.219	BV
2		6.71	34973340	32.612	VV
3		7.99	19432418	18.120	11
4		9.48	19355762	18.049	11
トータル			107240965	100.000	

Chiral compound

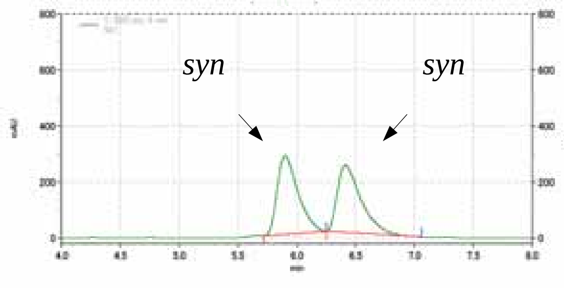


1: 220 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		6.77	28542	0.634	MM
2		7.15	4473790	99.328	MM
3		14.31	1746	0.039	BE
トータル			4504078	100.000	

Entry 7 

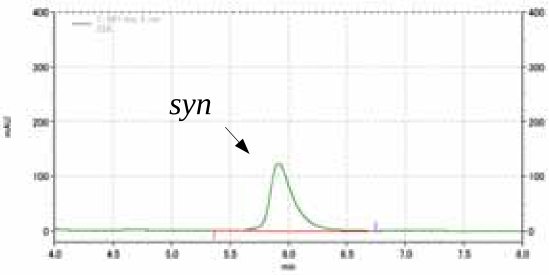
Racemate



1: 250 nm, 4 nm結果

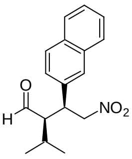
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		5.89	13792340	50.723	MM
2		6.41	13398908	49.277	MM
トータル			27191248	100.000	

Chiral compound

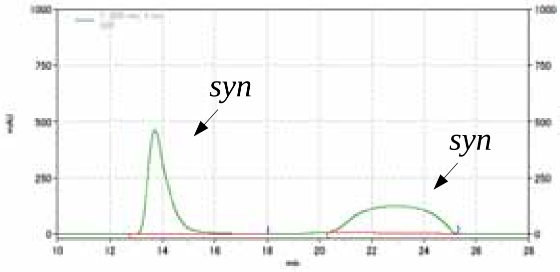


1: 201 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		5.92	7028454	100.000	BB
トータル			7028454	100.000	

Entry 8 

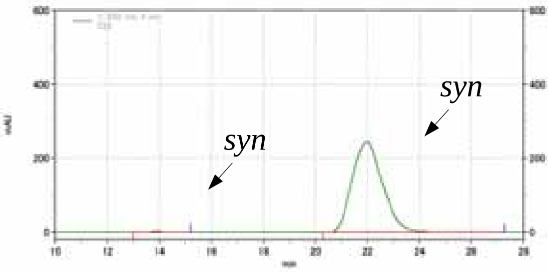
Racemate



1: 300 nm, 4 nm結果

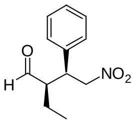
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		13.72	95354598	50.431	BB
2		22.91	93726335	49.569	MM
トータル			189080933	100.000	

Chiral compound

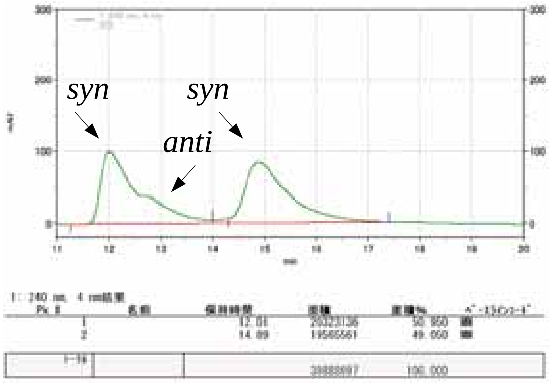


1: 292 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		13.85	494610	0.617	BB
2		21.99	79617268	99.383	mm
トータル			80111878	100.000	

Entry 9 

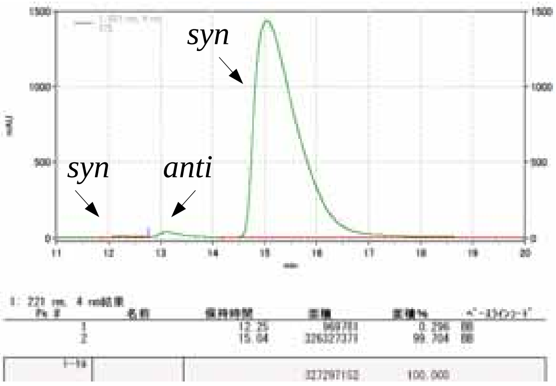
Racemate



1: 240 nm, 4 nm結果

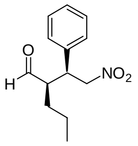
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		12.01	20323136	50.950	[illegible]
2		14.89	19565561	49.050	[illegible]
トータル			39888697	100.000	

Chiral compound

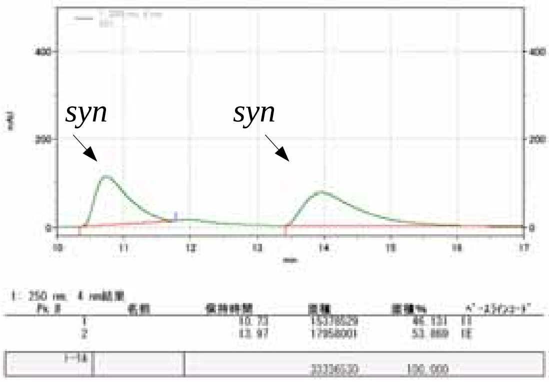


1: 221 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		12.25	969781	0.296	BB
2		15.04	326327371	99.704	BB
トータル			327297152	100.000	

Entry 10 

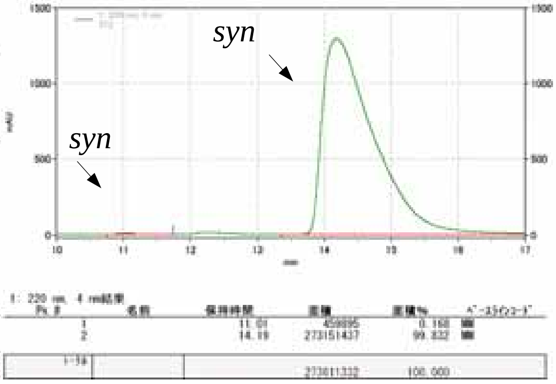
Racemate



1: 250 nm, 4 nm結果

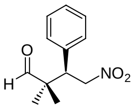
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		10.73	15378529	46.131	[illegible]
2		13.97	17958001	53.869	[illegible]
トータル			33336530	100.000	

Chiral compound

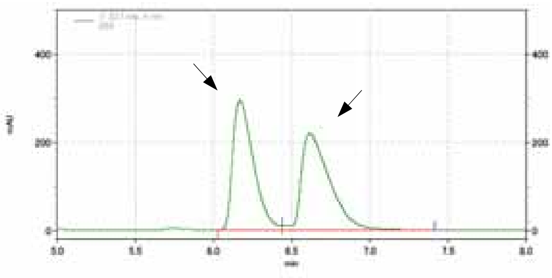


1: 220 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		11.01	459895	0.168	[illegible]
2		14.19	273151437	99.832	[illegible]
トータル			273611332	100.000	

Entry 11 

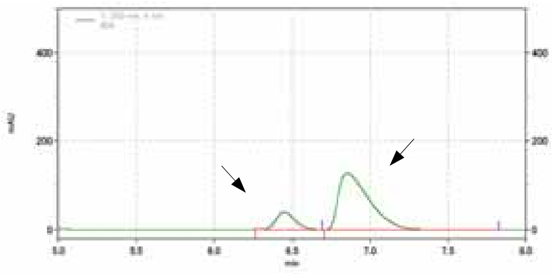
Racemate



1: 237 nm, 4 nm結果

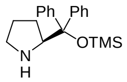
Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		6.17	10825670	49.545	BV
2		6.61	11024407	50.455	VB
トータル			21850077	100.000	

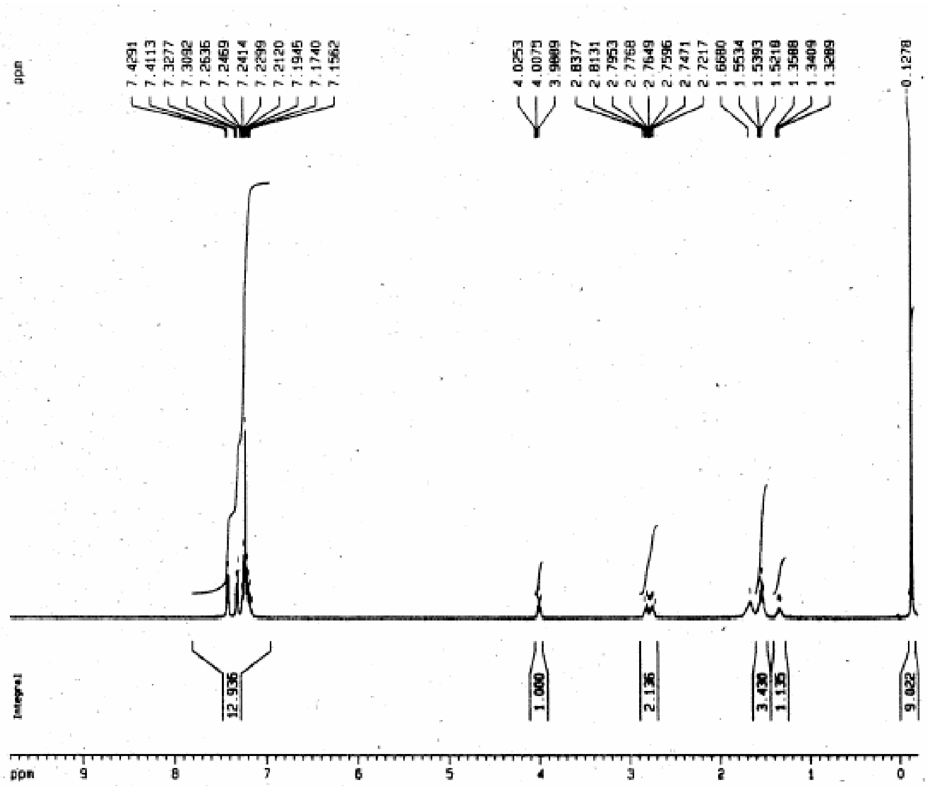
Chiral compound



1: 250 nm, 4 nm結果

Pk #	名前	保持時間	面積	面積%	ベースラインコード
1		6.45	1316252	15.877	MM
2		6.85	6974273	84.123	MM
トータル			8290525	100.000	





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Current Data Parameters
NAME     Dec04-2004-hays
EXPNO                 82
PROCNO                 1

F2 - Acquisition Parameters
Date_           20041204
Time               15.22
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/29
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                 683.2 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.90 usec
PL1                 3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300217 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           200.06502 Hz/cm
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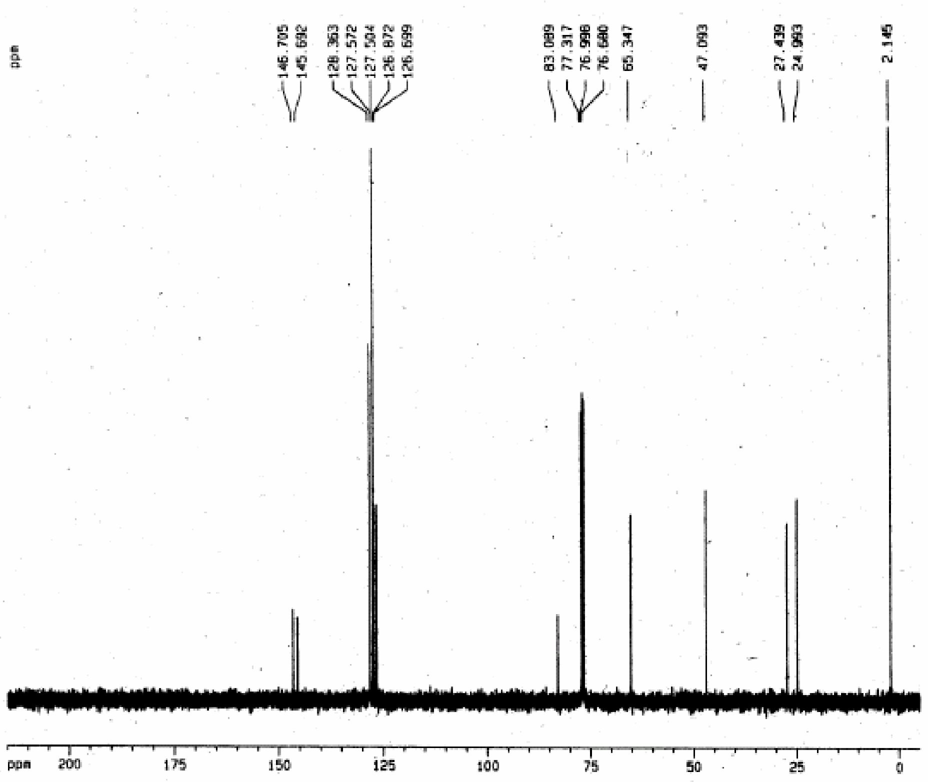

```
Current Data Parameters
NAME     Dec04-2004-hays
EXPNO                 91
PROCNO                 1

F2 - Acquisition Parameters
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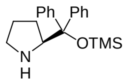
Time               16.56
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/29
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   104
DS                     2
SWH            31847.133 Hz
FIDRES          0.485949 Hz
AQ             1.0289652 sec
RG                1824.6
DW                15.700 usec
DE                  6.00 usec
TE                 683.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

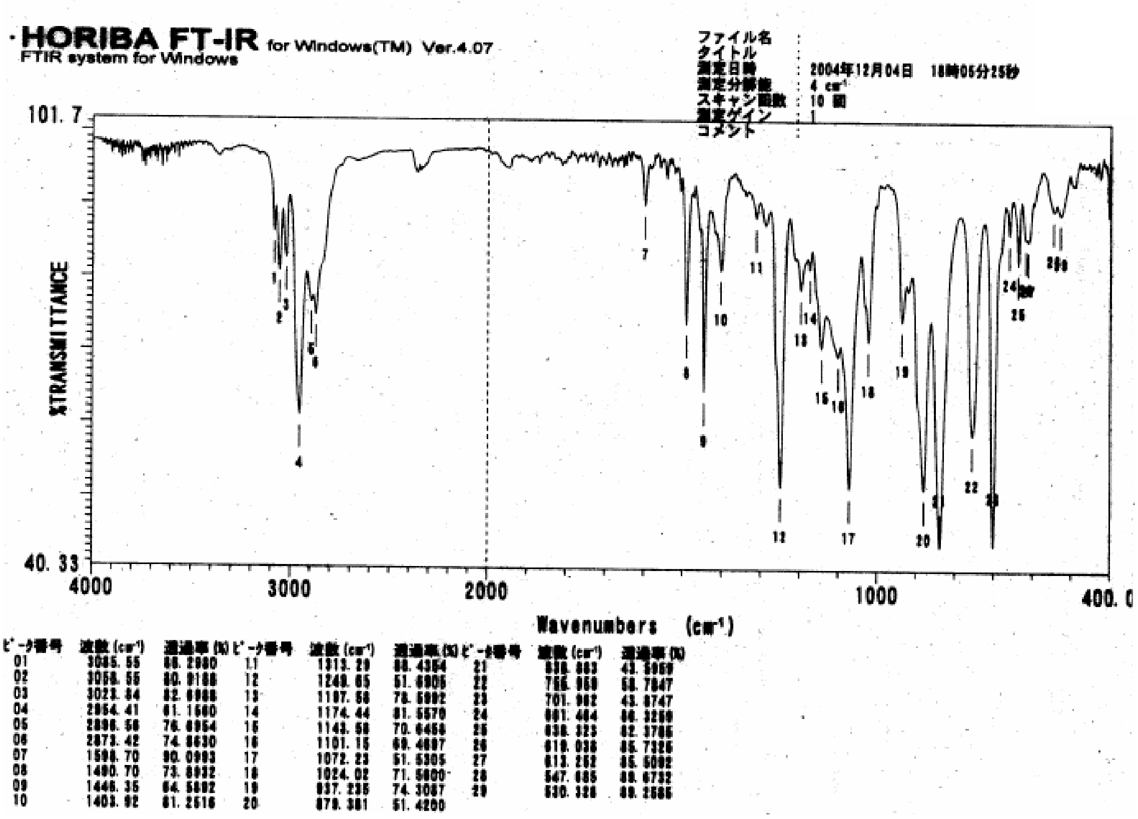
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.30 usec
PL1                 3.00 dB
SFO1         100.6254358 MHz

======== 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           100.6127756 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              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
```

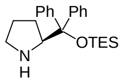


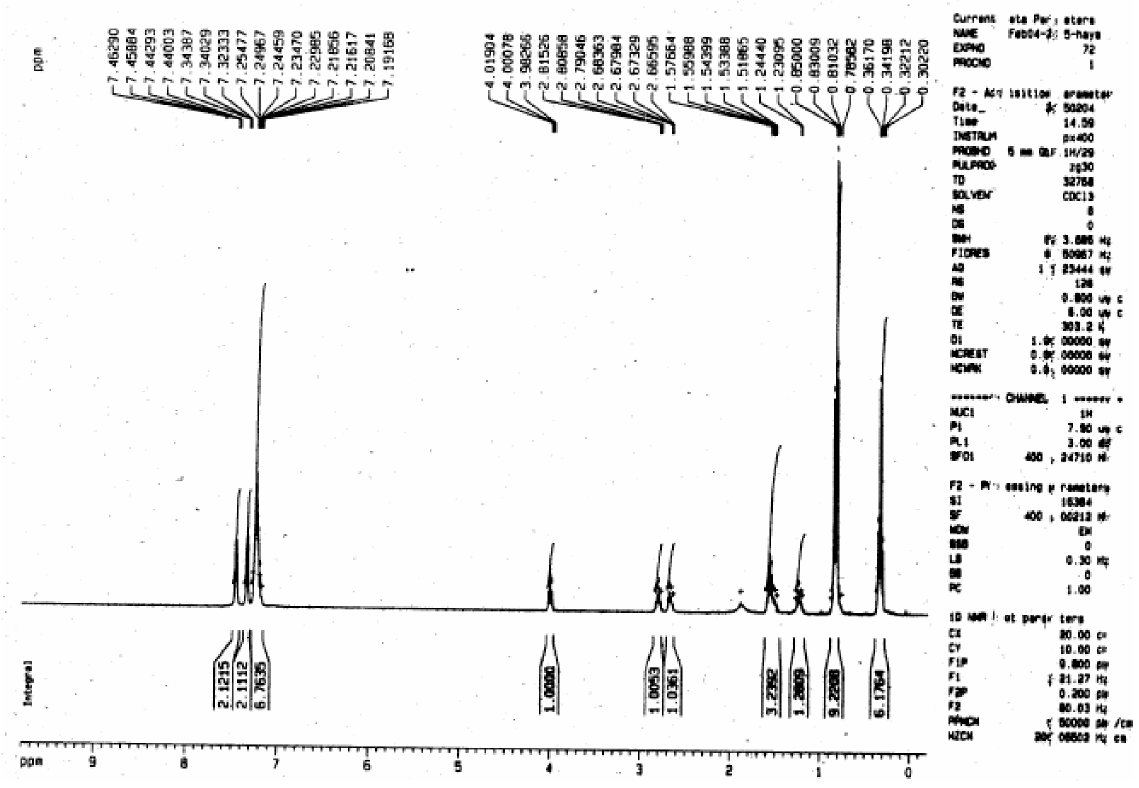


· HORIBA FT-IR for Windows(TM) Ver.4.07
FTIR system for Windows

ファイル名 :
タイトル :
測定日時 : 2004年12月04日 18時05分25秒
測定分解能 : 4 cm^{-1}
スキャン回数 : 10 回
測定ゲイン : 1
コメント :

ピーク番号	波数 (cm^{-1})	透過率 (%)	ピーク番号	波数 (cm^{-1})	透過率 (%)	ピーク番号	波数 (cm^{-1})	透過率 (%)
01	3085. 55	88. 2980	11	1313. 29	88. 4354	21	838. 863	43. 5959
02	3058. 55	80. 0186	12	1249. 65	51. 6905	22	756. 959	58. 7847
03	3023. 84	82. 6986	13	1197. 56	78. 5092	23	701. 902	43. 8747
04	2954. 41	61. 1660	14	1174. 44	81. 5570	24	661. 484	86. 3250
05	2896. 58	76. 6954	15	1143. 58	70. 6456	25	638. 323	82. 3705
06	2873. 42	74. 8630	16	1101. 15	69. 4607	26	619. 036	85. 7326
07	1598. 70	90. 0993	17	1072. 23	51. 5305	27	613. 252	85. 5092
08	1490. 70	73. 8032	18	1024. 02	71. 5600	28	547. 685	88. 6732
09	1446. 35	64. 5602	19	937. 235	74. 3087	29	530. 326	88. 2585
10	1403. 92	81. 2516	20	879. 381	51. 4200			


Ph
Ph
OTES
N
H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7.44003
7.34387
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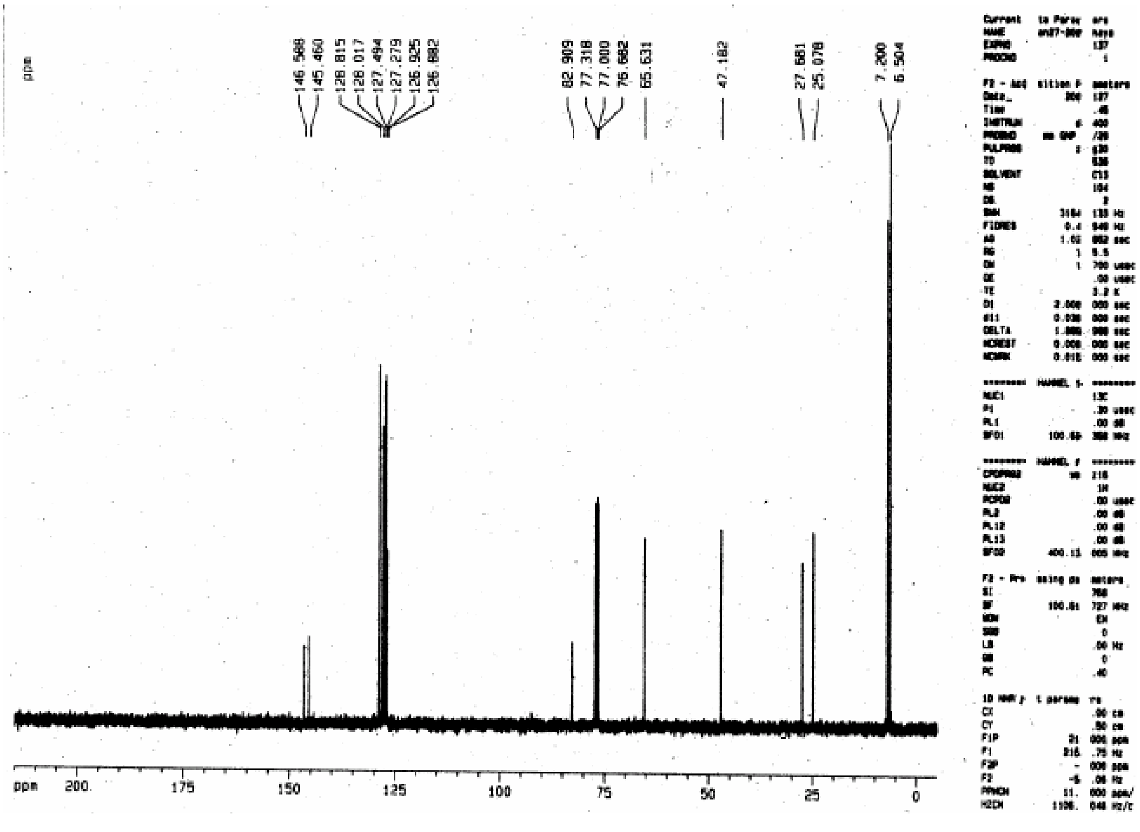
7.32333
7.25477
7.24967
7.24459
7.23470
7.22985
7.21856
7.21617
7.20841
7.19168
4.01904
4.00078
3.98266
2.81526
2.80858
2.79046
2.68363
2.67984
2.67329
2.66595
1.57664
1.55988
1.54399
1.53388
1.51865
1.24440
1.23095
0.85000
0.83009
0.81032
0.78582
0.36170
0.34198
0.32212
0.30220
Integral
2.1215
2.1112
6.7635
1.0000
1.0053
1.0361
3.2392
1.2809
9.2208
6.1764
ppm
9
8
7
6
5
4
3
2
1
0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82.909
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47.182
27.681
25.078
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6.504
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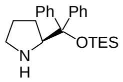
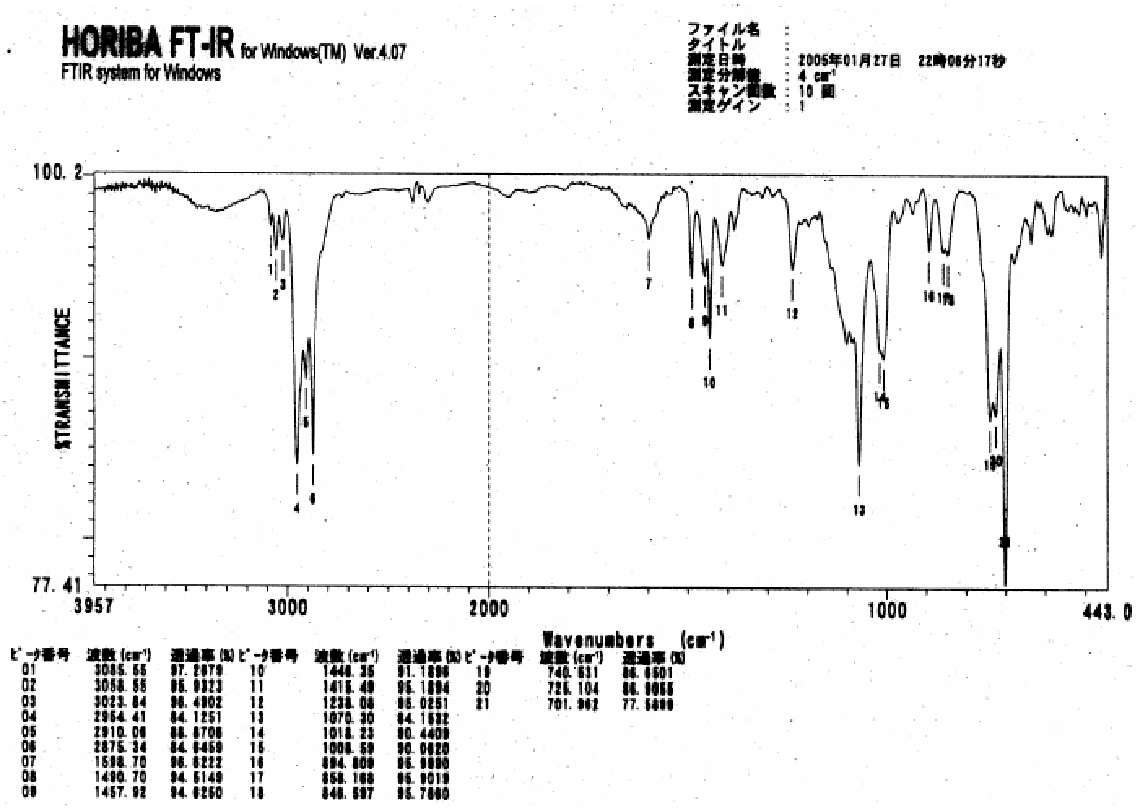
175
150
125
100
75
50
25
0

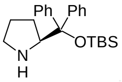


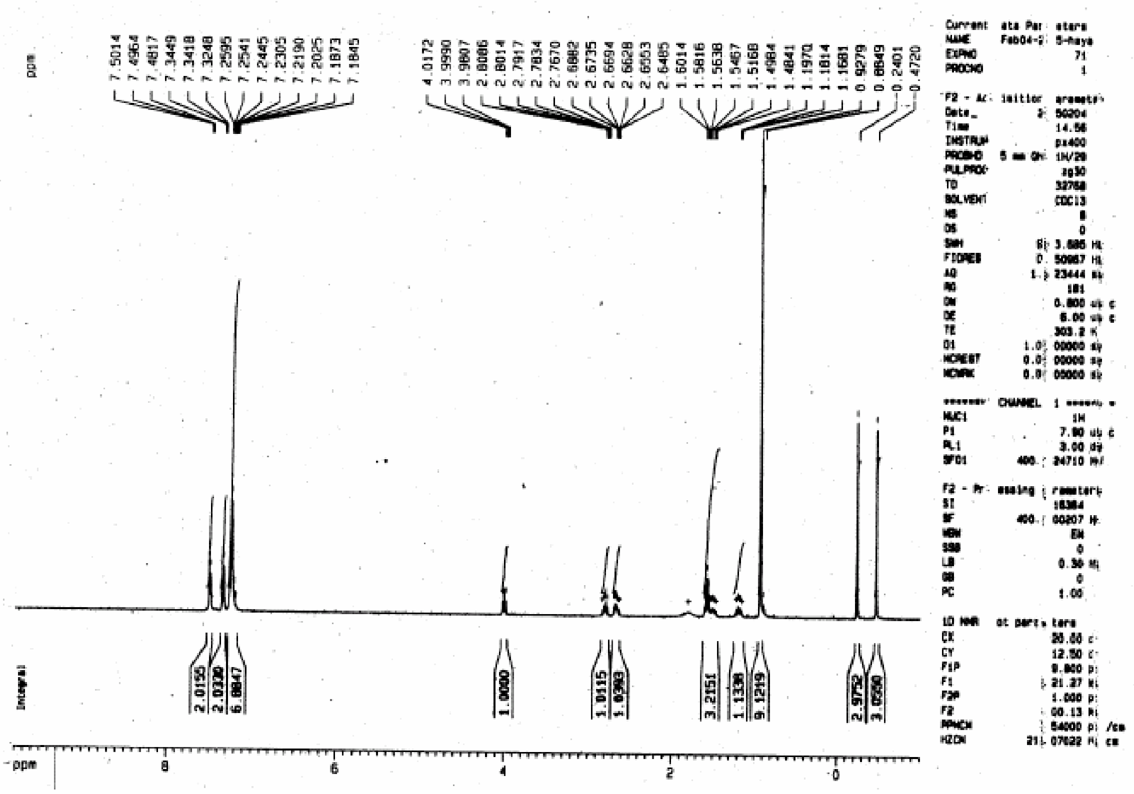


HORIBA FT-IR for Windows(TM) Ver.4.07
FTIR system for Windows

ファイル名 :
タイトル :
測定日時 : 2005年01月27日 22時08分17秒
測定分解能 : 4 cm⁻¹
スキャン回数 : 10 回
測定ゲイン : 1

ピーク番号	波数 (cm⁻¹)	透過率 (%)	ピーク番号	波数 (cm⁻¹)	透過率 (%)	ピーク番号	波数 (cm⁻¹)	透過率 (%)
01	3085. 55	97. 2879	10	1446. 35	91. 1896	19	740. 531	86. 8501
02	3058. 55	95. 9323	11	1415. 49	95. 1894	20	725. 104	86. 9055
03	3023. 84	96. 4802	12	1238. 06	95. 0251	21	701. 962	77. 5888
04	2954. 41	84. 1251	13	1070. 30	84. 1532			
05	2910. 06	88. 8708	14	1018. 23	90. 4409			
06	2875. 34	84. 8459	15	1008. 59	90. 0620			
07	1598. 70	96. 6222	16	894. 809	95. 9990			
08	1490. 70	94. 5149	17	858. 168	95. 9019			
09	1457. 92	94. 6250	18	846. 597	95. 7860			





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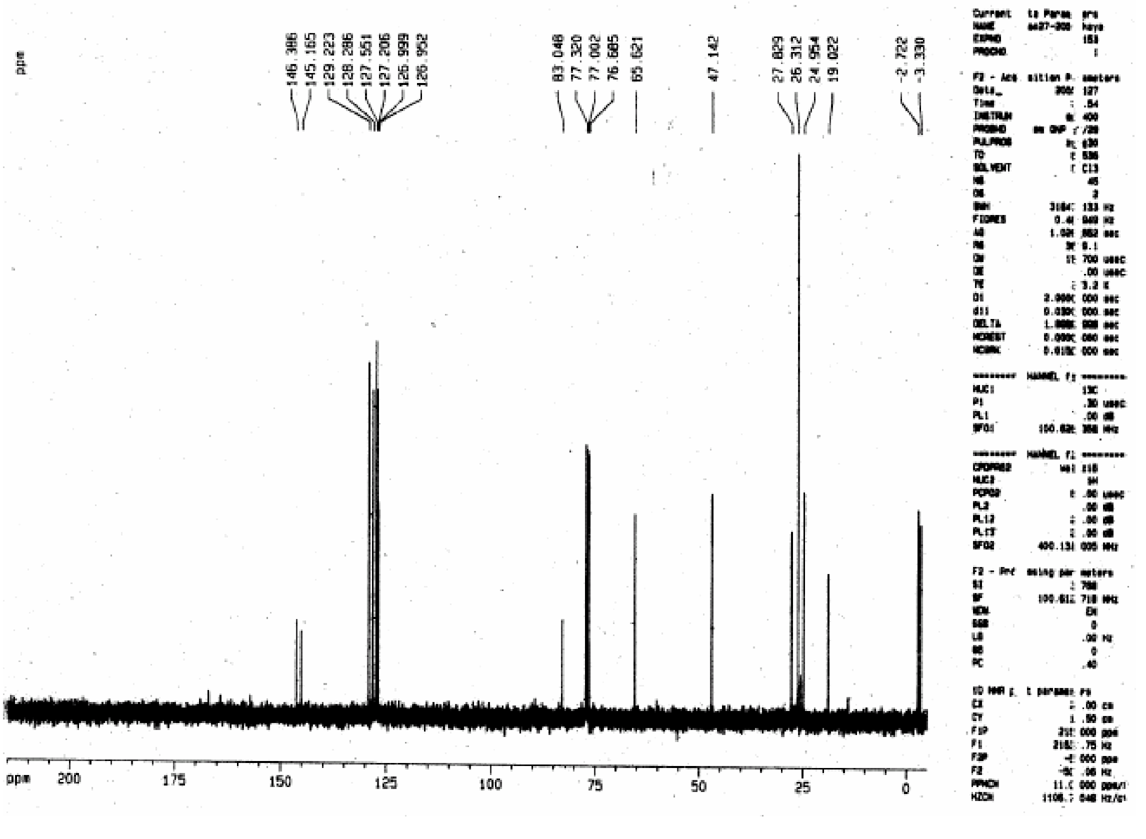
Current  ata Par  aters
NAME     Feb04-2  5-haya
EXPNO               71
PROCNO               1

F2 - Ac  isitior  arameters
Date_          2  50204
Time              14.56
INSTRUM           px400
PROBHD   5 mm Qh  1H/29
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8  3.686 Hz
FIDRES         0. 50967 Hz
AQ             1. 23444 se
RG                  181
DW              0.800 us c
DE               6.00 us c
TE              303.2 K
D1           1.0  00000 se
MCREST       0.0  00000 se
MCWRK        0.0  00000 se

=======  CHANNEL  1 =======
NUC1                 1H
P1               7.80 us c
PL1              3.00 dB
SFO1         400. 24710 MH

F2 - Pr  essing   rameters
SI                16384
SF           400. 00207 MH
WDW                  EM
SSB                   0
LB               0.30 Hz
GB                    0
PC                 1.00

1D NMR   ot paramters
CX              20.00 c
CY              12.50 c
F1P             9.800 p
F1            . 21.27 H
F2P             1.000 p
F2            . 00.13 H
PPMCM         . 54000 p  /cm
HZCM         21 07622 H  cm
```



```
Current   ta Param  ers
NAME      ae27-200  haya
EXPNO               153
PROCNO                1

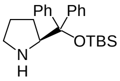
F2 - Acq  sition P  ameters
Date_         200  127
Time            :  .54
INSTRUM         a  400
PROBHD   mm QNP  r /28
PULPROG         g  g30
TD              6  536
SOLVENT         C  Cl3
NS                  45
DS                   2
SWH         3164:  133 Hz
FIDRES       0.4   040 Hz
AQ          1.036  852 sec
RG              3  0.1
DW              15 700 usec
DE                 .00 usec
TE              :  3.2 K
D1          2.000  000 sec
d11         0.030  000 sec
DELTA       1.800  000 sec
MCREST      0.000  000 sec
MCWRK       0.015  000 sec

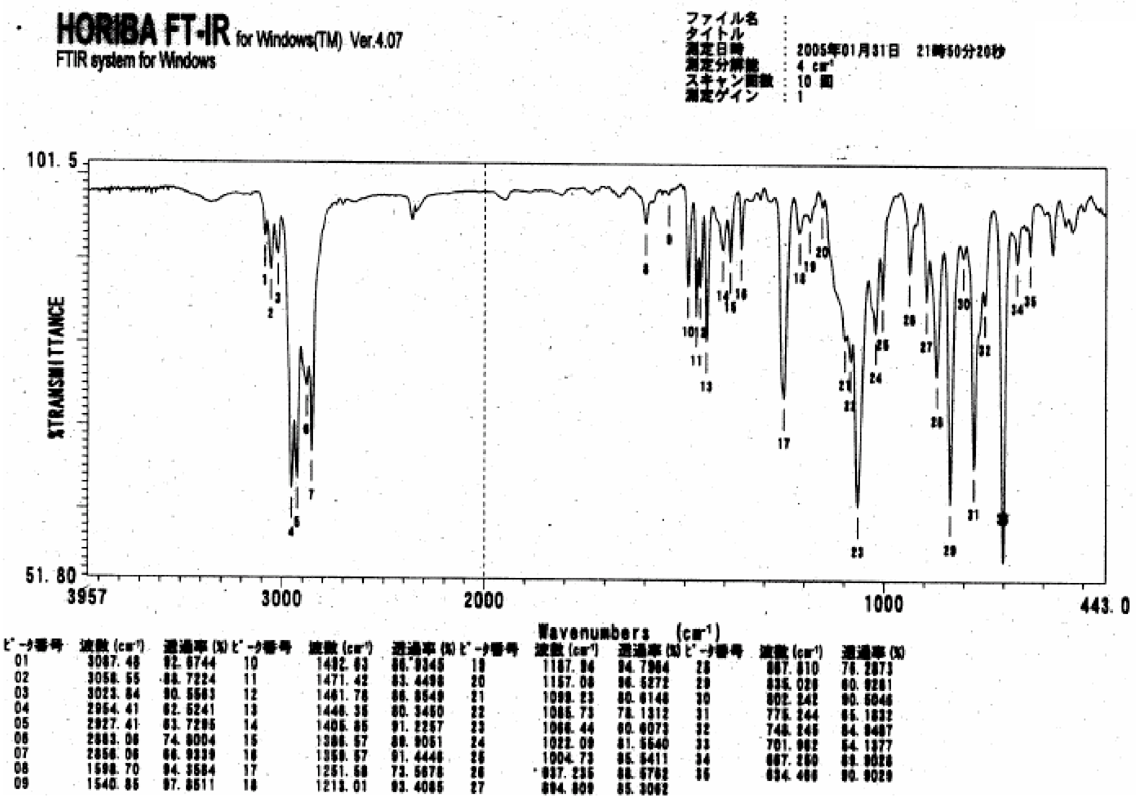
========  HANNEL f1 ========
NUC1               13C
P1                 .30 usec
PL1                .00 dB
SFO1       100.626 358 MHz

========  HANNEL f2 ========
CPDPRG2        wal  z16
NUC2                1H
PCPD2            8 .00 usec
PL2                .00 dB
PL12             1 .00 dB
PL13             1 .00 dB
SFO2       400.131 005 MHz

F2 - Pro  ssing par meters
SI               3 768
SF         100.612 718 MHz
WDW                 EM
SSB                  0
LB                 .00 Hz
GB                   0
PC                 .40

1D NMR p  t paramet rs
CX               2 .00 cm
CY               1 .50 cm
F1P            210 000 ppm
F1            2112 .75 Hz
F2P             -5 000 ppm
F2             -50 .06 Hz
PPMCM          11.0 000 ppm/c
HZCM         1106.7 048 Hz/cm
```

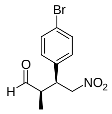


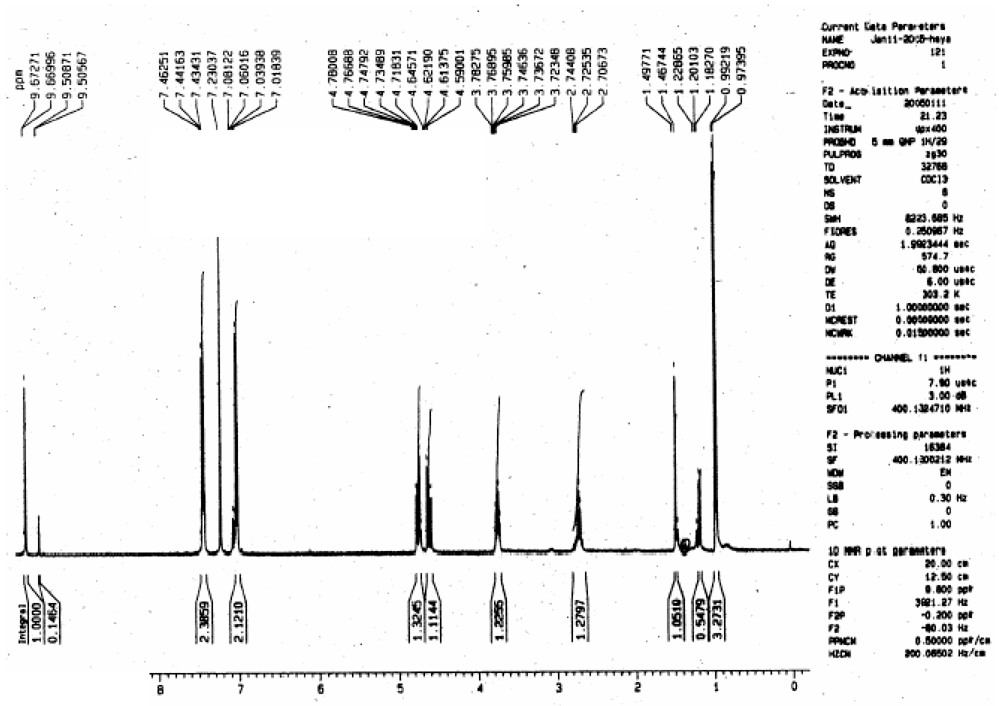


HORIBA FT-IR for Windows(TM) Ver.4.07
FTIR system for Windows

ファイル名 :
タイトル :
測定日時 : 2005年01月31日 21時50分20秒
測定分解能 : 4 cm⁻¹
スキャン回数 : 10 回
測定ゲイン : 1

ピーク番号	波数 (cm⁻¹)	透過率 (%)	ピーク番号	波数 (cm⁻¹)	透過率 (%)	ピーク番号	波数 (cm⁻¹)	透過率 (%)	ピーク番号	波数 (cm⁻¹)	透過率 (%)
01	3087. 48	92. 6744	10	1492. 63	86. 9345	19	1187. 94	94. 7964	28	887. 810	76. 2873
02	3058. 55	88. 7224	11	1471. 42	83. 4498	20	1157. 08	96. 5272	29	835. 028	60. 9281
03	3023. 84	90. 5583	12	1461. 78	86. 8549	21	1099. 23	80. 6146	30	802. 242	90. 5046
04	2954. 41	62. 5241	13	1446. 35	80. 3450	22	1085. 73	78. 1312	31	775. 244	65. 1832
05	2927. 41	63. 7295	14	1405. 85	91. 2257	23	1066. 44	60. 6073	32	748. 245	84. 9487
06	2883. 06	74. 8004	15	1388. 57	88. 9061	24	1022. 09	81. 5540	33	701. 962	54. 1377
07	2856. 06	66. 9339	16	1359. 57	91. 4446	25	1004. 73	85. 5411	34	667. 250	89. 8028
08	1598. 70	94. 3584	17	1251. 58	73. 5678	26	937. 235	88. 5762	35	634. 466	90. 9029
09	1540. 85	97. 8511	18	1213. 01	93. 4085	27	894. 809	85. 3062			





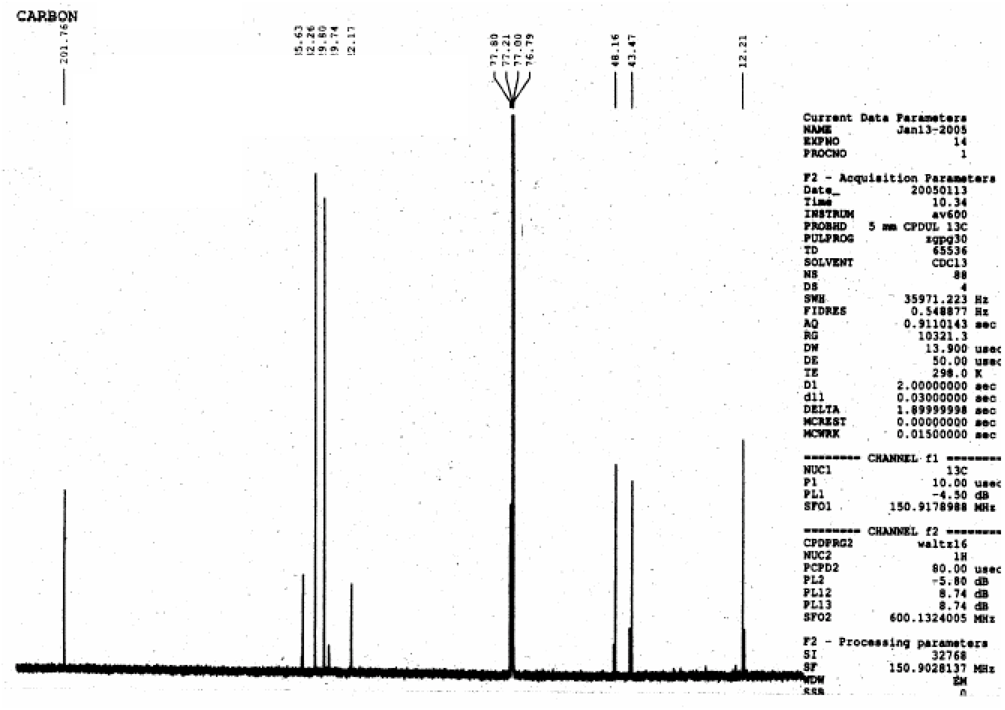
```
Current Data Parameters
NAME        Jan11-2005-heya
EXPNO                   121
PROCNO                    1

F2 - Acquisition Parameters
Date_              20050111
Time                  21.23
INSTRUM              dpx400
PROBHD   5 mm QNP 1H/29
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        0
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ             1.9923444 sec
RG                    574.7
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                 7.80 usec
PL1                 3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                    16384
SF           400.1300212 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               8.800 ppm
F1               3521.27 Hz
F2P              -0.200 ppm
F2               -80.03 Hz
PPMCM          0.50000 ppm/cm
HZCM         200.06502 Hz/cm
```



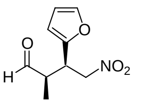
```
Current Data Parameters
NAME            Jan13-2005
EXPNO                   14
PROCNO                   1

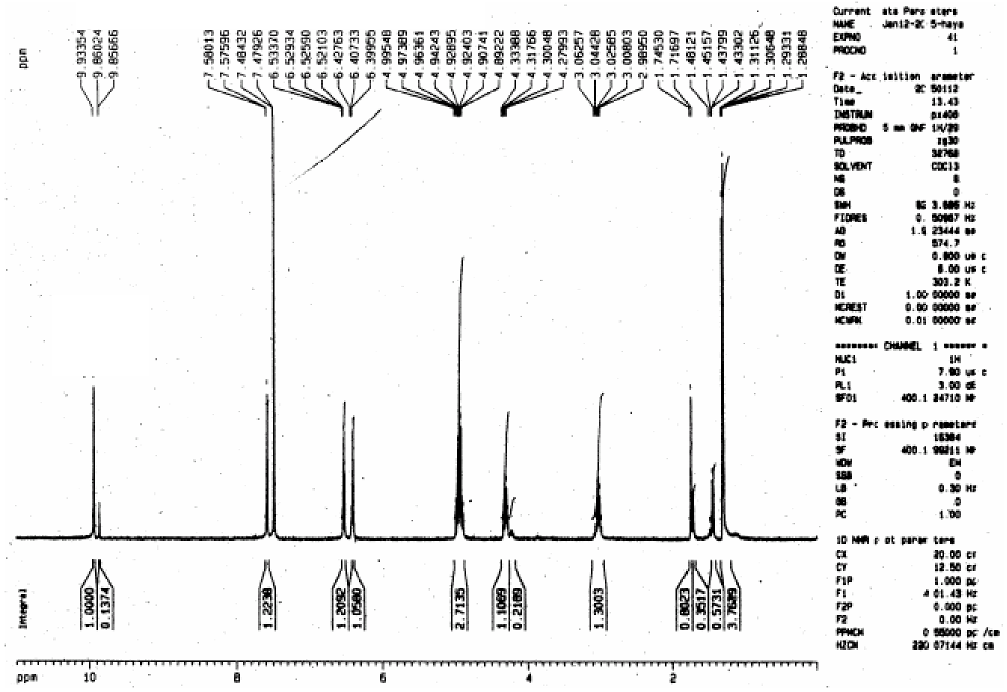
F2 - Acquisition Parameters
Date_             20050113
Time                 10.34
INSTRUM              av600
PROBHD   5 mm CPDUL 13C
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      88
DS                       4
SWH           35971.223 Hz
FIDRES         0.548877 Hz
AQ            0.9110143 sec
RG                 10321.3
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

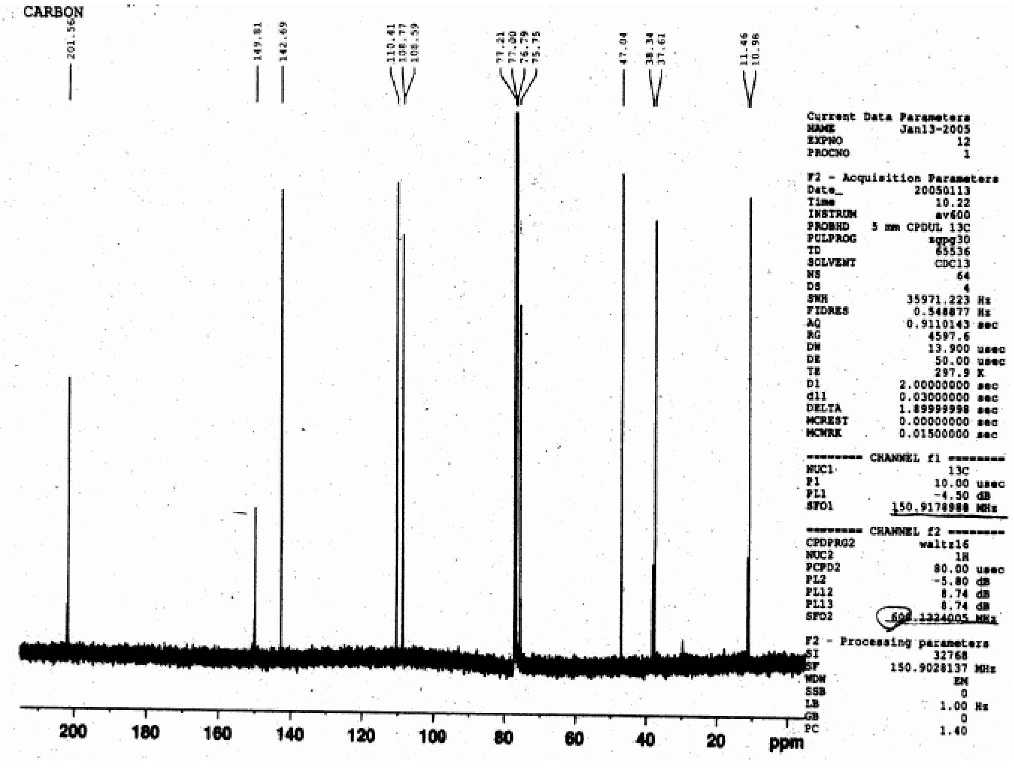
======== CHANNEL f1 ========
NUC1                   13C
P1               10.00 usec
PL1                -4.50 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            80.00 usec
PL2                -5.80 dB
PL12                8.74 dB
PL13                8.74 dB
SFO2        600.1324005 MHz

F2 - Processing parameters
SI                   32768
SF          150.9028137 MHz
WDW                     EM
SSB                      0
```


O
H
O
NO2


ppm
9.93354
9.86024
9.85666
7.58013
7.57596
7.48432
7.47926
6.53370
6.52934
6.52590
6.52103
6.42763
6.40733
6.39955
4.99548
4.97389
4.96361
4.94243
4.92895
4.92403
4.90741
4.89222
4.33988
4.31766
4.30048
4.27993
3.06257
3.04428
3.02585
3.00803
2.98950
1.74530
1.71697
1.48121
1.45157
1.43799
1.43302
1.31126
1.30648
1.29331
1.28848
Integral
1.0000
0.1374
1.2238
1.2092
1.0580
2.7135
1.1069
0.2189
1.3003
0.8023
0.3517
0.5731
3.7639
ppm 10 8 6 4 2
Current Data Parameters
NAME Jan12-2005-maya
EXPNO 41
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050112
Time 13.43
INSTRUM px400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.886 Hz
FIDRES 0.50987 Hz
AQ 1.9923444 sec
RG 574.7
DW 0.800 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 7.90 usec
PL1 3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300211 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 1.000 ppm
F1 4001.43 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07144 Hz/cm


CARBON
201.56
149.81
142.69
110.41
108.77
108.59
77.21
77.00
76.79
75.75
47.04
38.34
37.61
11.46
10.98
200 180 160 140 120 100 80 60 40 20 ppm
Current Data Parameters
NAME Jan13-2005
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050113
Time 10.22
INSTRUM av600
PROBHD 5 mm CPDUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 4597.6
DW 13.900 usec
DE 50.00 usec
TE 297.9 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 -4.50 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.80 dB
PL12 8.74 dB
PL13 8.74 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 1.40