

**Ethyl(methyl)dioxirane as an Efficient Reagent for the Oxidation of Nucleoside
Phosphites into Phosphates under Anhydrous Conditions**

**Masanori Kataoka, Akira Hattori, Shinya Okino, Mamoru Hyodo, Mitsue Asano,
Rie Kawai, and Yoshihiro Hayakawa***

Supplemental Information

General. ^{31}P -NMR spectra were obtained in CDCl_3 on a JEOL α -400 instrument. The solid-phase synthesis was conducted on an Applied Biosystems Model 392 DNA/RNA synthesizer. Capillary gel electrophoresis was carried out on an Otsuka Electronics Photal CAPI-3200 instrument. MALDI-TOF mass analysis was done on a PerSeptive Biosystems Voyager-DE RP Biospectrometry Workstation. Acetonitrile and dichloromethane were distilled from CaH_2 . Other organic solvents were used after simple distillation of the commercially supplied ones.

Materials. A solution of ethyl methyl dioxirane (2-butanone peroxide) in dimethyl phthalate was purchased from Kishida. The following compounds are commercially available or literature known. Commercially available compounds: **3**, **5**, **7**, **10**, **11**, and **13** (Glen Research); **16** (Pharmacia Biotech). Literature-known compounds (see references cited below): **1**,¹ **2**,² **4**,¹ **6**,² **8**,¹ **9**,³ **12**,² **14**,⁴ **15**,⁵ **17**,¹ **18**,³ **20**,¹ **22**,³ **24**,¹ **25**,³ **28**,³ and **29**.⁴ The compounds, **19**, **21**, **23**, **26**, and **27**, are unknown. For the characterization of these new compounds, MALDI-TOF mass spectral data, except **23** which gave no molecular peak, are listed below. For **23**, the ^1H -NMR and ^{31}P -NMR spectral charts are attached. A CGE chart and the MALDI-TOF mass spectrum of the crude product of **33** prepared by the method employing TBHP oxidation is attached.

MALDI-TOF Mass Spectral Data.

19. Calcd for $\text{C}_{57}\text{H}_{65}\text{N}_8\text{O}_{13}\text{PSi}$: m/z 1128.42. Found: m/z 1128.35.

21. Calcd for $\text{C}_{51}\text{H}_{63}\text{N}_6\text{O}_{14}\text{PSi}$: m/z 1042.39. Found: m/z 1042.22.

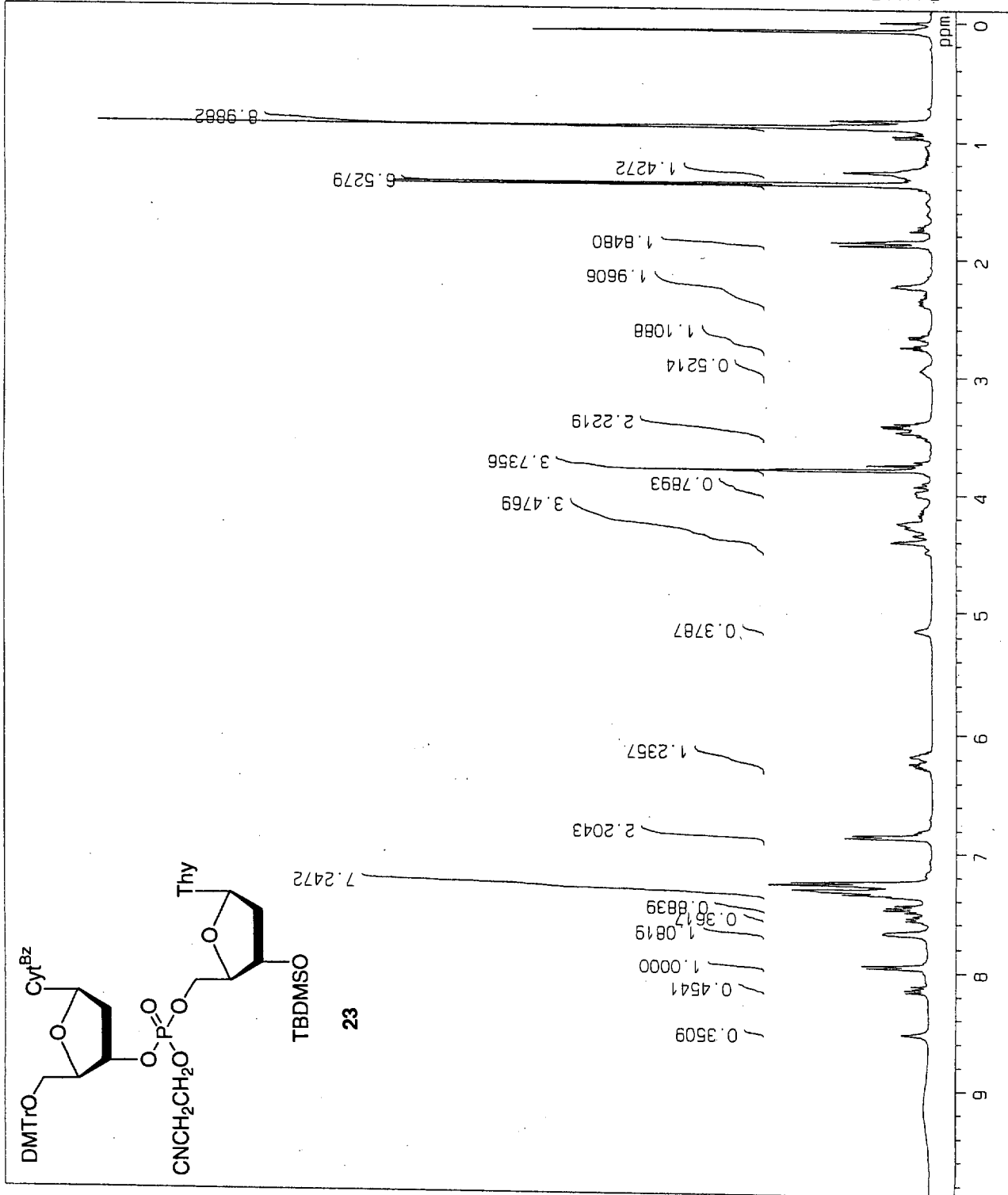
26. Calcd for $\text{C}_{53}\text{H}_{66}\text{N}_9\text{O}_{13}\text{PSi}$: m/z 1095.43. Found: m/z 1095.50.

27. Calcd for $\text{C}_{54}\text{H}_{67}\text{N}_8\text{O}_{14}\text{PSi}$: m/z 1110.43. Found: m/z 1110.53.

References

- (1) Hayakawa, Y.; Kataoka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12395–12401.
- (2) Hayakawa, Y.; Wakabayashi, S.; Kato, H.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 1691–1696.
- (3) Hayakawa, Y.; Kataoka, M. *J. Am. Chem. Soc.* **1997**, *119*, 11758–11762.
- (4) Hayakawa, Y.; Kataoka, M.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 7996–7997.
- (5) Ogilvie, K. K. *Can. J. Chem.* **1973**, *51*, 3799–3807.

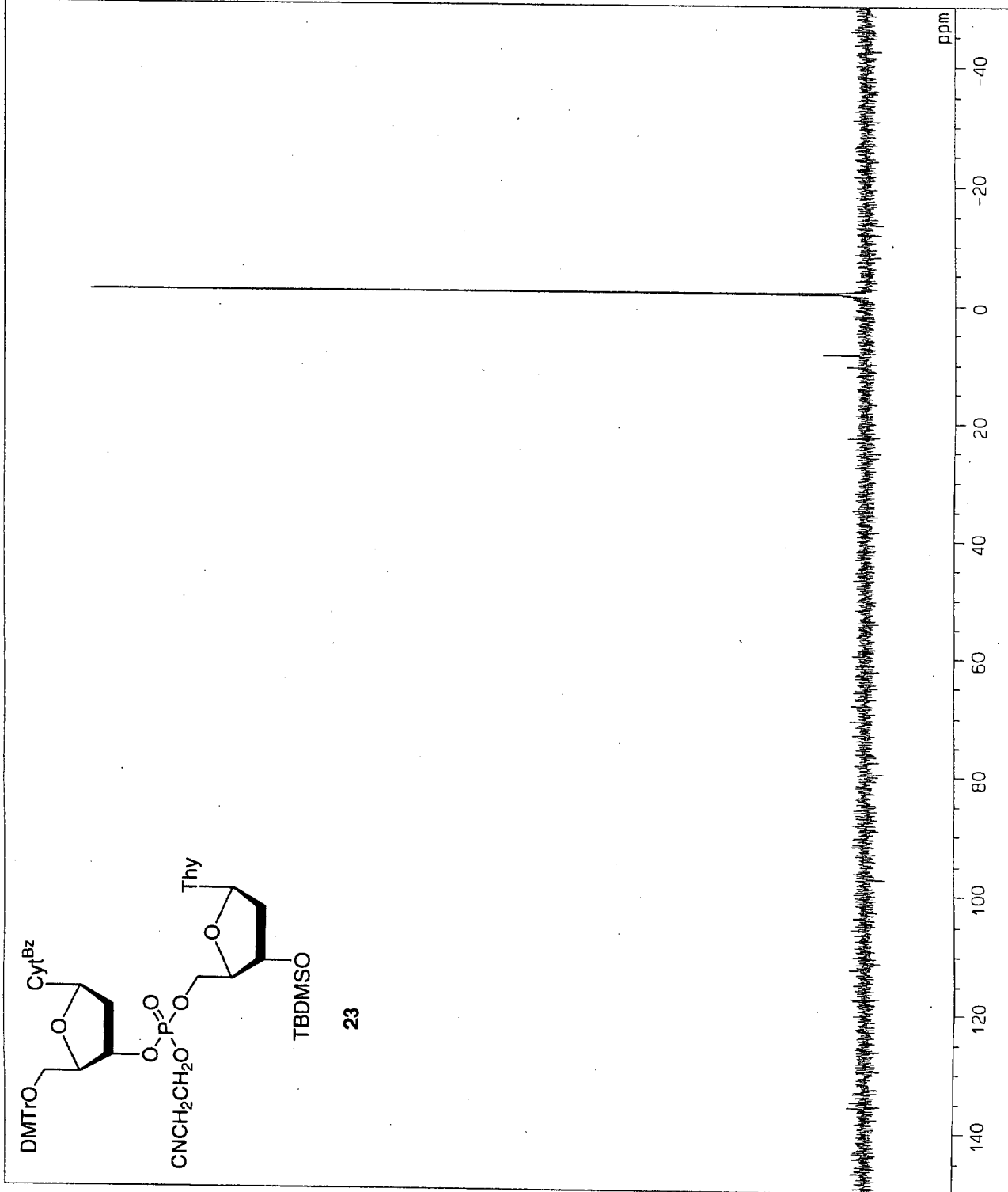
24-NOV-2000 17:53:34.73
 OFILE : ALPHA
 SFIL : 1HSTD
 COMNT :
 EXMOD : SINGL
 IRMOD : NON
 POINT : 16384
 FREQ : 7993.61 Hz
 SCANS : 16
 DUMMY : 4
 ACQTM : 2.0496 sec
 PD : 4.0000 sec
 RGAIN : 18
 PW1 : 5.10 usec
 OBNUC : 1H
 OBFRQ : 399.65 MHz
 OBSET : 134500.00 Hz
 IRNUC : 1H
 IRFRQ : 399.65 MHz
 IRSET : 134300.00 Hz
 IRATN : 511
 IRAPW : 45.0 usec
 IRBP1 : 26
 IRBP2 : 6
 IRBP3 : 0
 ADBIT : 16
 CTEMP : 25.9 C
 CSPED : 14 Hz
 SLVNT : COCL3
 RESOL : 0.49 Hz
 BF : 0.20 Hz
 T1 : 0.00 %
 T2 : 0.00 %
 T3 : 90.00 %
 T4 : 100.00 %
 REFVL : 0.00 ppm
 XE : 3997.29 Hz
 XS : 36.84 Hz
 operator



24-NOV-2000 17:33:12.51

DFILE : ALPHA
SFIL : 31PSTDCOMNT :
EXMOD : SINGL
IRMOD : BCM
POINT : 16384
FREQ : 97087.38 Hz
SCANS : 64
DUMMY : 4
ACQTM : 0.1688 sec
PD : 2.0000 sec
RGAIN : 23

PW1 : 5.30 usec

OBNUC : 31P
OBFRQ : 161.70 MHz
OBSET : 135320.00 HzIRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 45.0 usec
IRBP1 : 26
IRBP2 : 6
IRANS : 0ADBIT : 16
CTEMP : 25.8 c
CSPED : 4 Hz
SLVNT : CDCL3RESOL : 5.93 Hz
BF : 0.20 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 32360.48 Hz
XS : -7581.99 Hz
operator

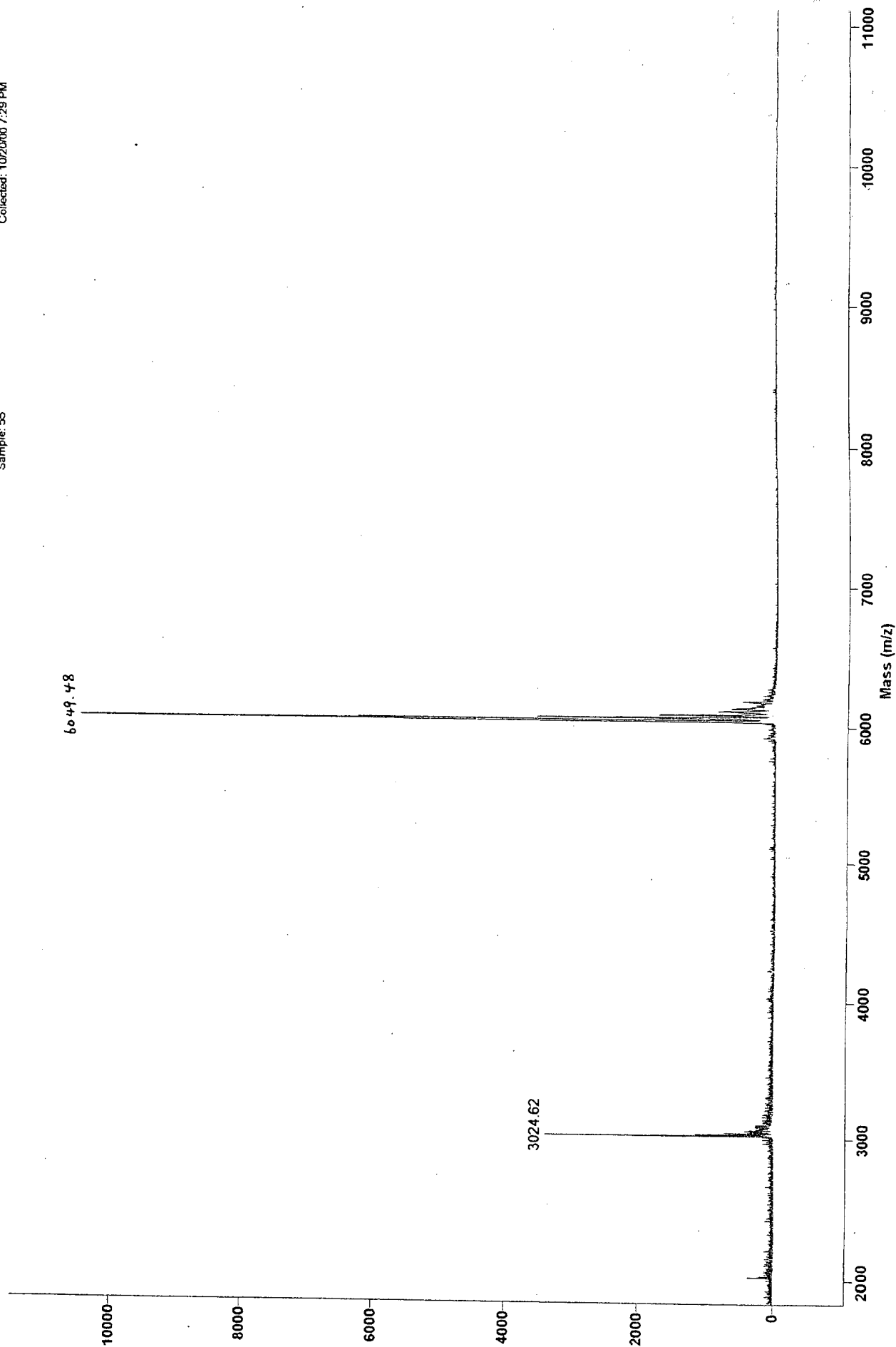
PerSeptive Biosystems

File # 2 = D:\HAYAKAWA\KAWA\10208-DNA.MS
 Method: RIKOX20 DNA 20mer 0.1M BIT washing 2 times

Method: HCD1002
 Mode: Linear
 Accelerating Voltage: 20000
 Grid Voltage: 95.000 %
 Guide Wire Voltage: 0.050 %
 Delay: 875 ON
 Sample: 55

Laser: 2500
 Scans Averaged: 256
 Pressure: 4.12e-07
 Low Mass Gate: 500.0
 Timed Ion Selector: 24.9 OFF
 Negative Ions: ON
 Collected: 10/20/00 7:29 PM

33



解析フェログラム解析レポート

CAP I - 3 2 0 0

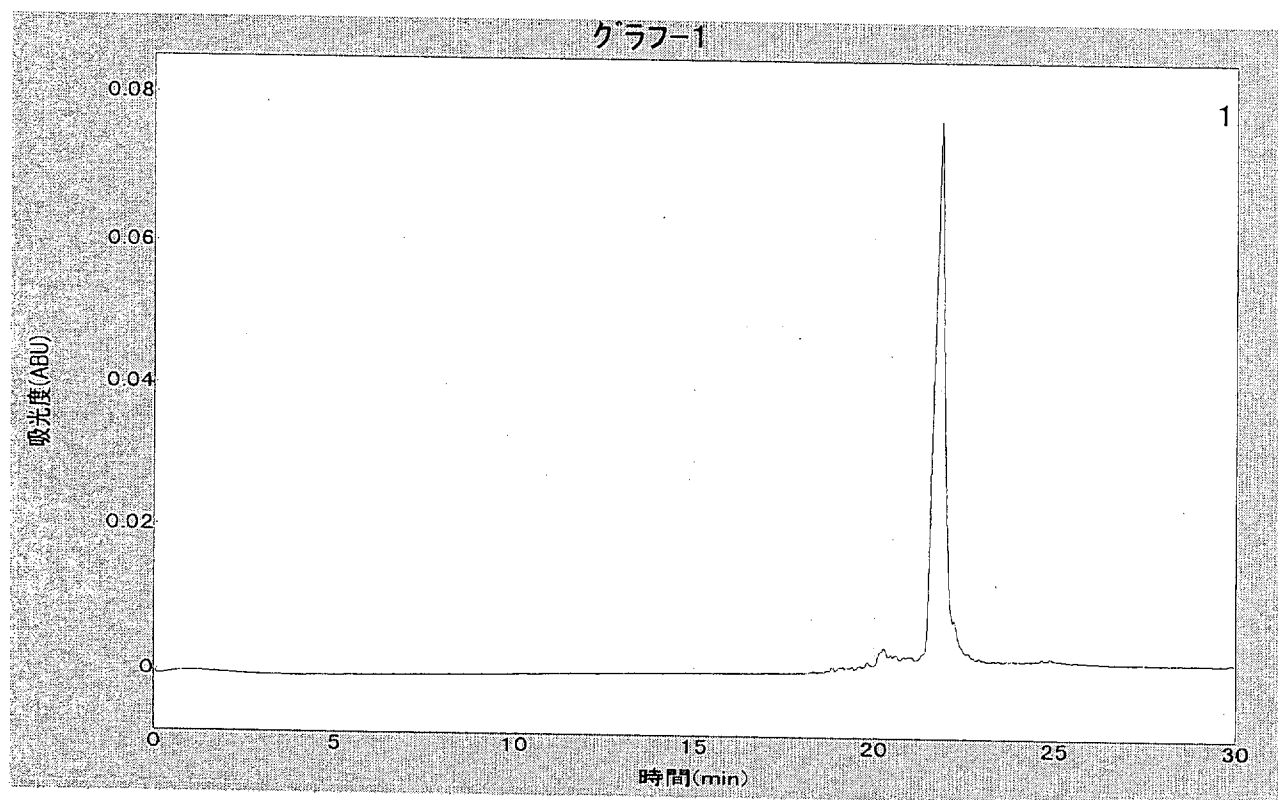
ユーザーID : RIK
 シーズ名 : 簡単測定
 分析名 : 0X20 BIT 2 times
 解析日付 : 2000/12/27 11:11:46.00
 測定日付 : 2000/10/20 23:10:45.00
 印刷日付 : 2000/12/27 11:11:46.00
 サンプルファイル番号(コメント) : 26()
 泳動ファイル番号(コメント) : 46()

分析ID : RIK20001020231041
 解析ID :

設定電圧(電流) 初期値 : -12.5 k V
 温度設定 : 25.0°C
 終了値 : -12.5 k V

データ範囲 開始 : 0.00min
 データ間隔 : 0.47sec
 終了 : 30.00min

符号反転 : 無
 ベースライン補正 : 無



No.	グラフNo.	ピーク	純度	名前	波長	元データ名	種別
1	1	非表示	非表示	260 nm	260.00nm		RAW

CGE profile of 33