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

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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 Appliled Biosystems Model 392 DNA/RNA synthesizer. Capillary gel electrophoresis was carried out on an Otsuka Electronics Photal CAPI-3200 insrtument. MALDI-TOF mass analysis was done on a PerSeptive Biosystems Voyager-DE RP Biospectrometory 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 ^{1}H-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 $C_{57}H_{65}N_8O_{13}PSi$: *m/z* 1128.42. Found: *m/z* 1128.35.

21. Calcd for $C_{51}H_{63}N_6O_{14}PSi$: *m/z* 1042.39. Found: *m/z* 1042.22.

26. Calcd for $C_{53}H_{66}N_9O_{13}PSi$: *m/z* 1095.43. Found: *m/z* 1095.50.

27. Calcd for $C_{54}H_{67}N_8O_{14}PSi$: *m/z* 1110.43. Found: *m/z* 1110.53.

References

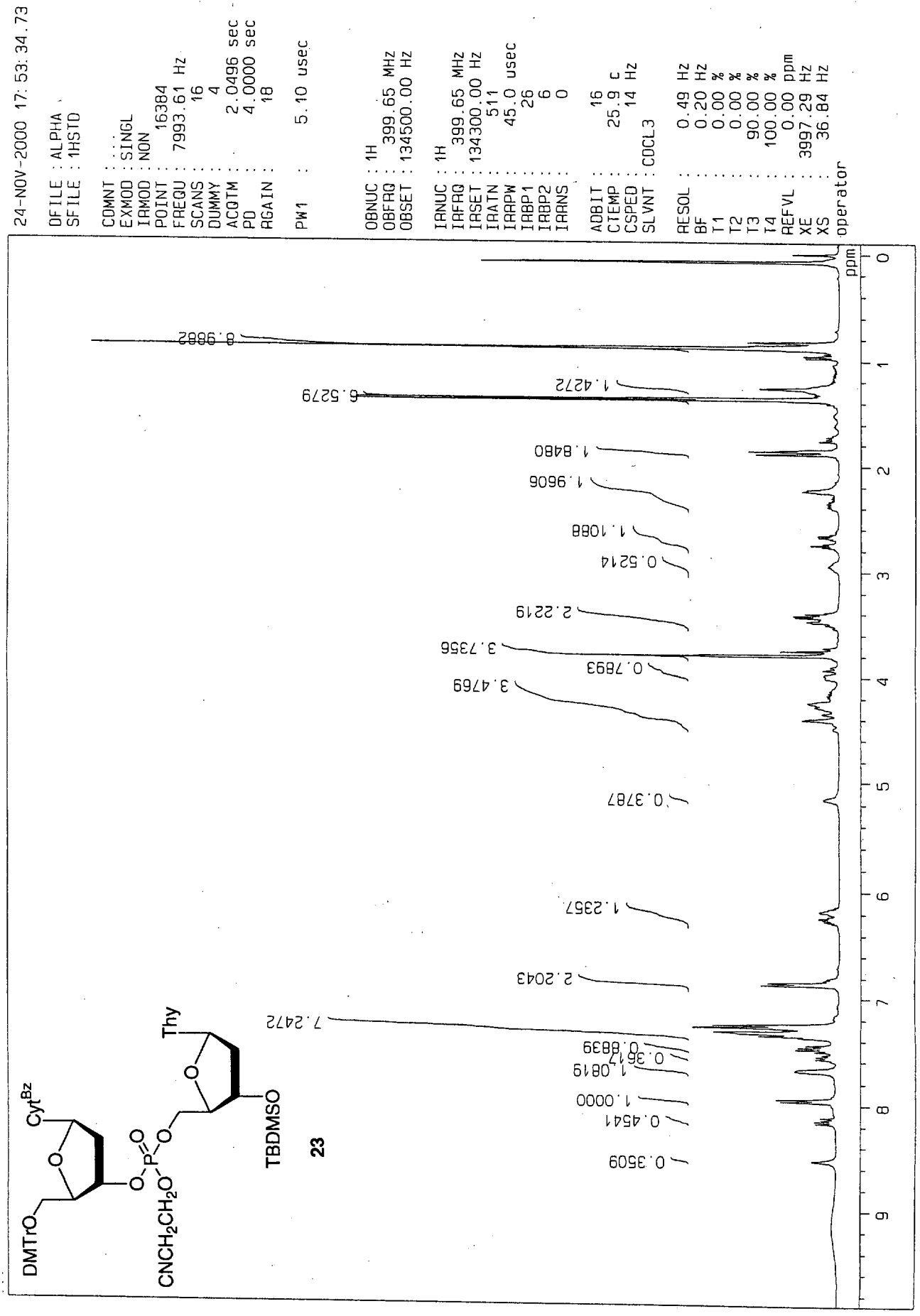
(1) Hayakawa, Y.; Kataoka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12395–12401.

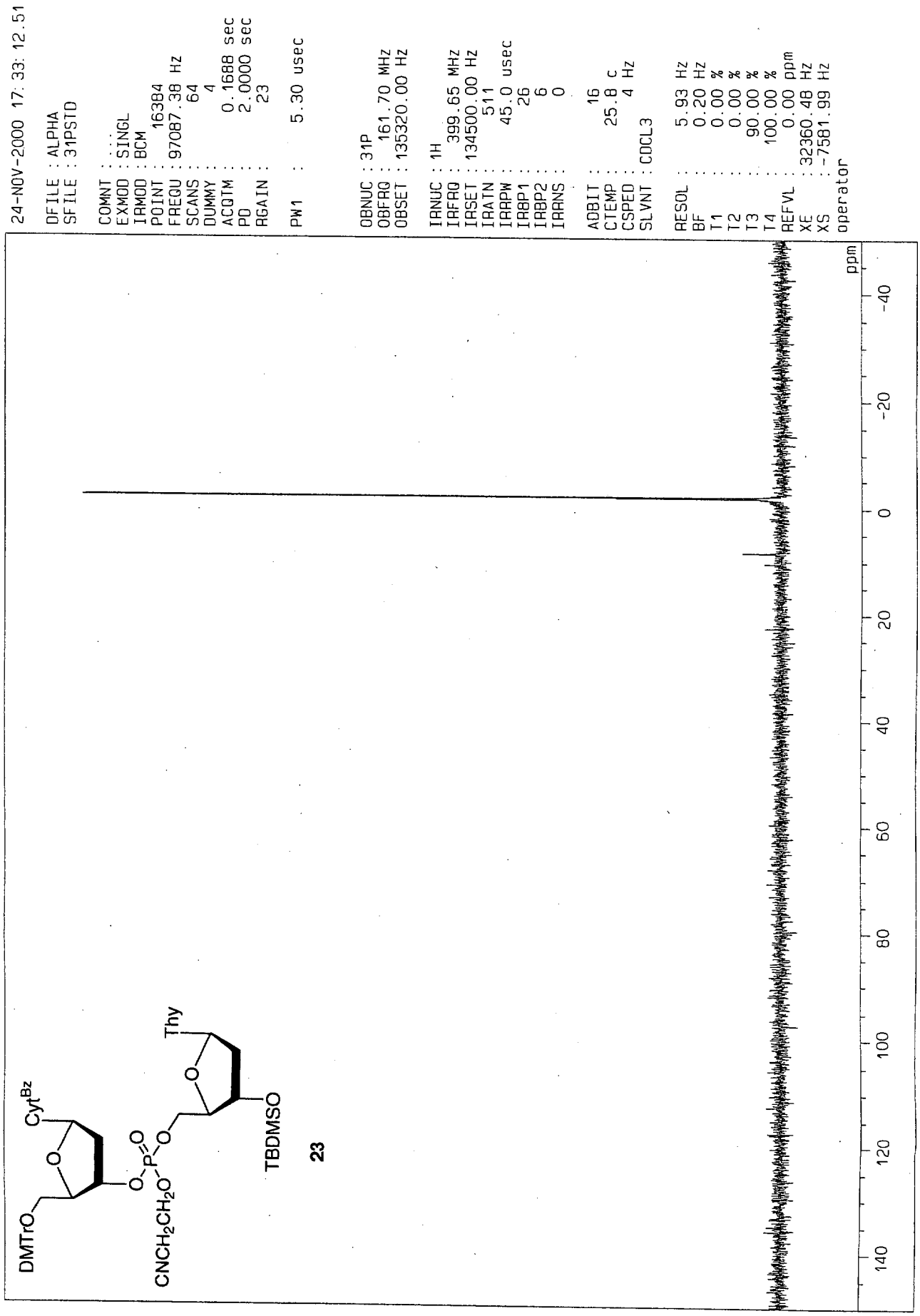
(2) Hayakawa, Y.; Wakabayashi, S.; Kato, H.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 1691–1696.

(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.





PerSeptive Biosystems

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ent: RIK0X20 DNA 20mer 0.1M BIT washing 2 times

33

Method: HCD1002
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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
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Negative Ions: ON
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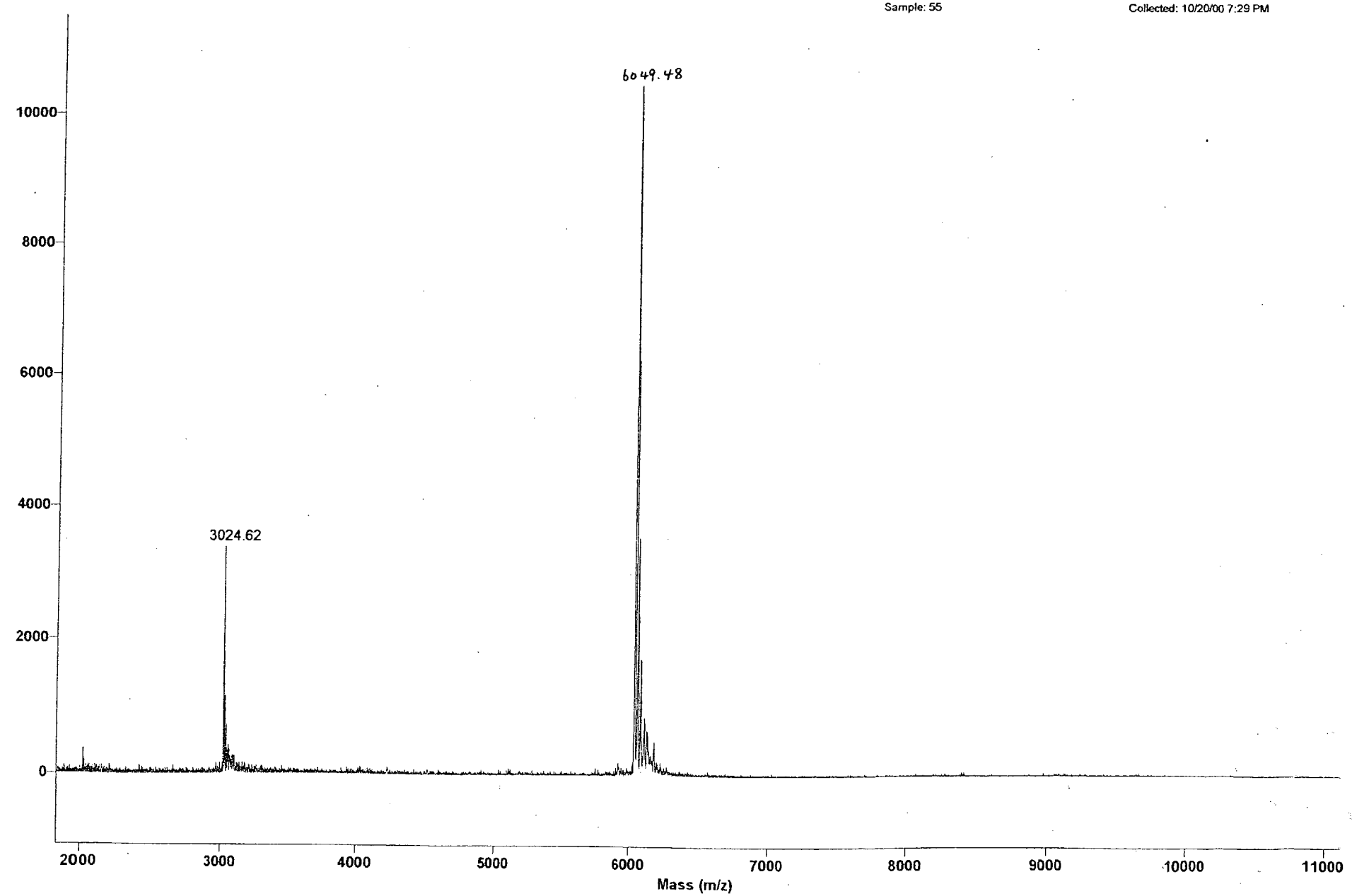

解析フェログラム解析レポート

CAPI-3200

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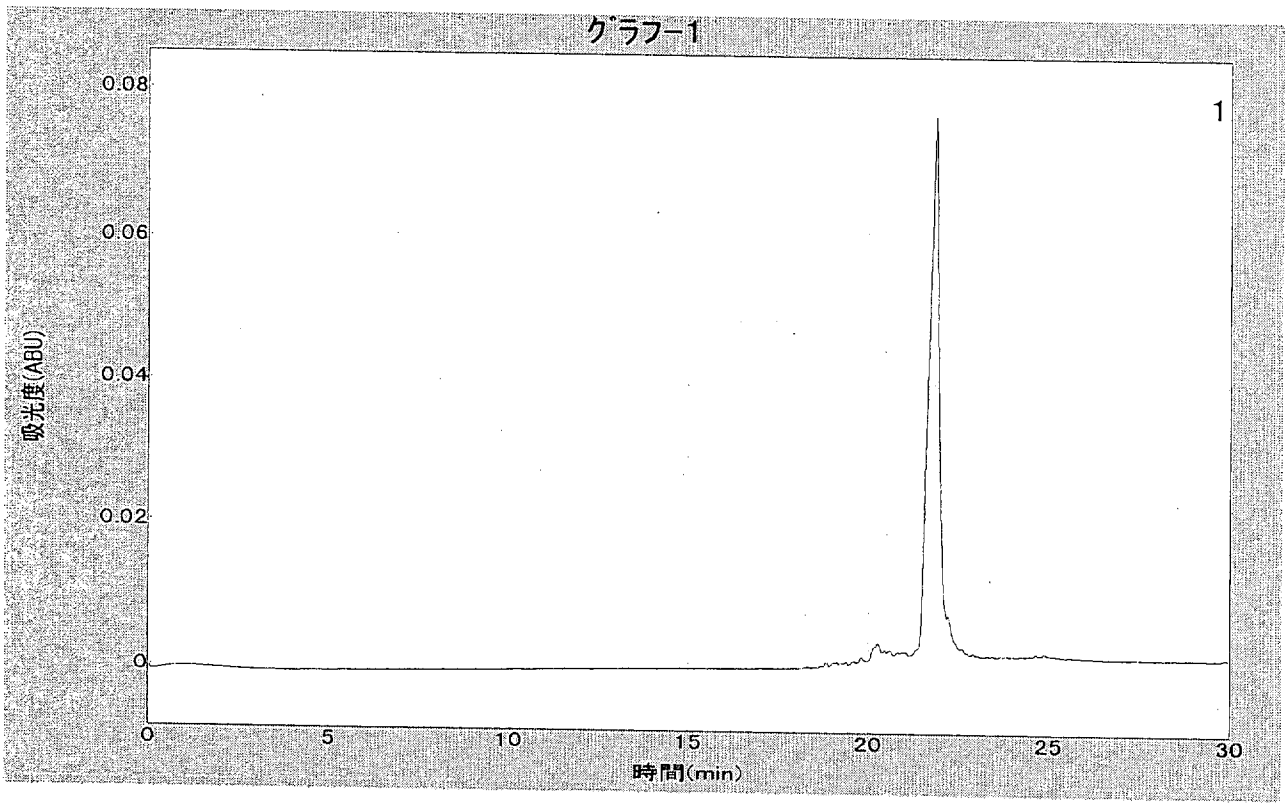

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