

Vanadium-Catalyzed Deoxydehydration of Glycols – Supporting Information

Garry Chapman Jr. and Kenneth M. Nicholas*

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019

General Methods: All glycols were obtained commercially and used without further purification. G.C. analysis was conducted on an OV-12 packed column (40 °C/5 min; 20 deg/min to 250 °C; 5 min @ 250 °C) on an instrument fitted with an FID detector. Product concentrations were calculated from GC calibration curves (lines) of standard alkene/naphthalene solutions. GC-MS analyses were carried out on an instrument with an Econo-Cap-5 capillary column; mass spectra were acquired in the EI mode. Electrospray mass spectra were acquired on a quadrupole TOF mass spectrometer. NMR spectra were obtained at 300 MHz (for ¹H).

Synthesis of [NBu₄][VO₃]: Was prepared by the method of Day, Klemperer, and Yagasake (Chemistry Letters 1990, 1267 – 1270)¹.

Synthesis of [NBu₄][VO₂(CA)₂]: was prepared by the method of Ohde and Limberg (Chem Eur. J. 2010, 16, 6892 – 6899)².

Synthesis of HC(Pz)VO₂BF₄: was prepared by the method of Silva et al (Adv. Synth. Catal. 2010, 352, 171 – 187)³.

Synthesis of TpaVO₂PF₆: was prepared by the method of Tajika, Tsuge and Sasaki (Dalton Trans., 2005, 1438 – 1447)⁴.

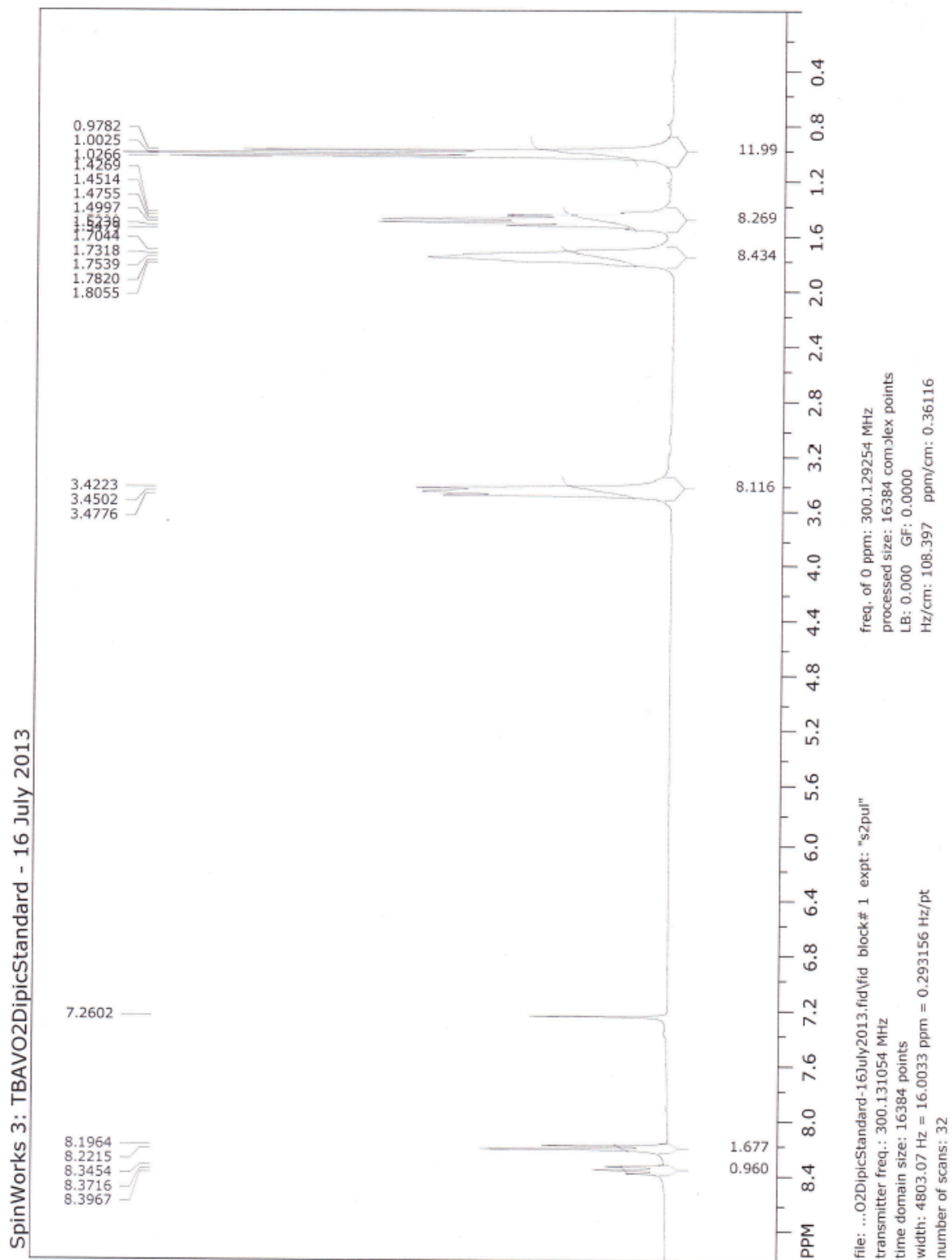
Synthesis of NaVO₂(acac)₂: was prepared by the method of Popova, Bogolitsyn, Gribosh, and Samotus (Russian Journal of General Chemistry (1997), 67(5), 819)⁵.

Preparation of [Bu₄N](dipic)VO₂ (1). [NBu₄][VO₃] (1.00 g, 2.96 mmol; V. W. Day, W. G. Klemperer and A. Yagasaki, *Chem. Lett.* 1990, 1267) was dissolved in CH₂Cl₂ (15 mL) and molecular sieves (3Å, 2.30 g) were added. Then 2,6-pyridinedicarboxylic acid (0.49 g, 2.96 mmol) was added slowly with stirring at rt. After stirring for 25 min the mixture was filtered to remove the sieves. The filtrate was concentrated under reduced pressure to a volume of approximately 5 mL and then Et₂O (25 mL) was added. The mixture was stirred for 30 min at rt and then cooled to 0 °C for 1.5 h. The mixture was filtered, the solid was washed with Et₂O (15 mL), and then dried under high vacuum overnight. This gave [Bu₄N]VO₂(dipic) (1.38 g, 2.81 mmol, 95 %) as a beige powder. Characterizational data for **1**: M. p. 126 – 128 °C; MS – ESI (negative ion, M/z): 247.9531, calcd for C₇H₃NO₆V 247.9400; IR (KBr, cm⁻¹) 1685, 1670, 1342, 948, 920, 747; ¹H NMR (300 MHz, CDCl₃, δ ppm) 0.98 (t, J= 7 Hz, 12H), 1.46 (m, 8H), 1.73 (m, 8H), 3.42 (m, 8H), 8.19 (d, J = 7 Hz, 2H), 8.35 (t, J= 7 Hz, 1H).

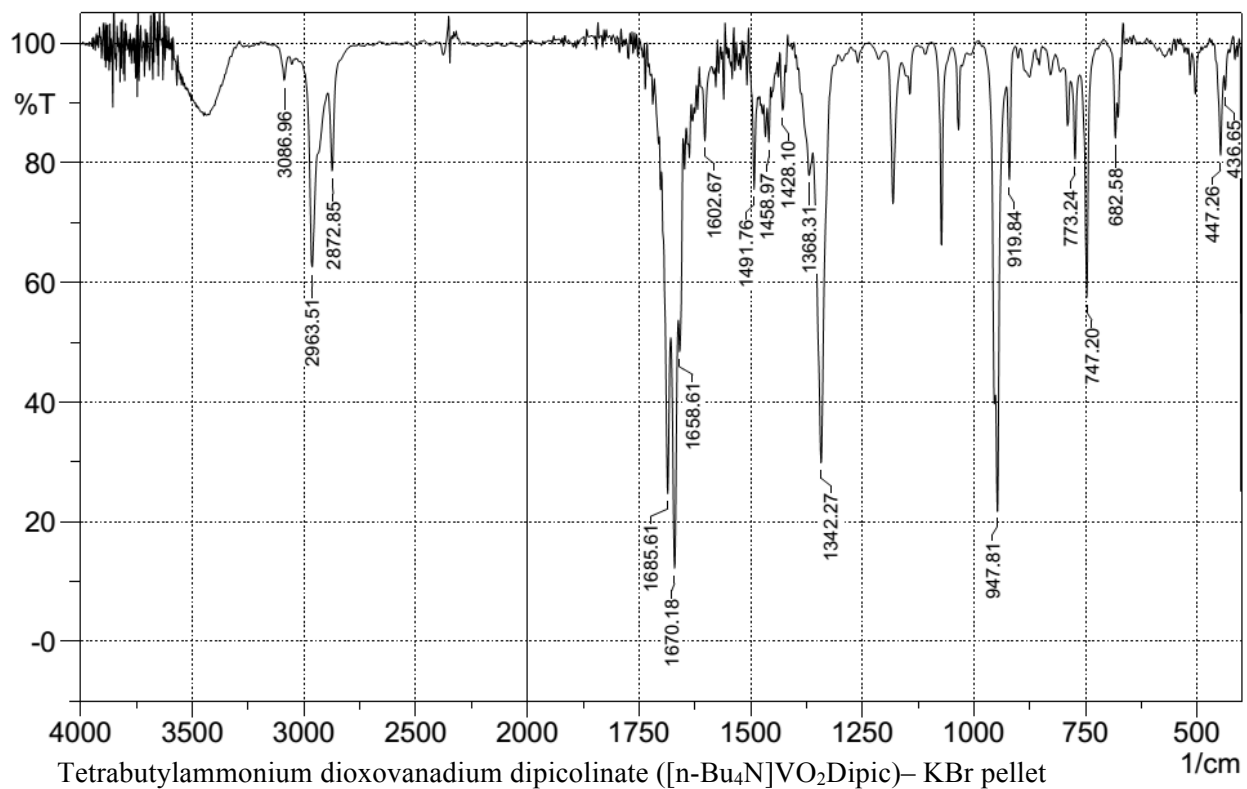
General procedure for the ZVO_{2,3}-mediated deoxydehydration of glycols.

The glycol (1.00 mmol), ZVO_{2,3} (0.099 mmol, 10 mol %), PPh₃ or Na₂SO₃ (1.25 mmol) and naphthalene (0.468 mmol, internal reference) were mixed with 5.0 mL of reagent grade benzene or chlorobenzene in a 15 mL thick-walled glass tube fitted with a teflon screw-cap/plunger (Ace Glass) and a spin bar was added. The reaction mixture was heated at 150 - 170 °C while stirred in a preheated silicone oil bath for the indicated time period. The mixture was cooled to room temperature and an aliquot was removed for analysis by ¹H NMR spectroscopy, gas chromatography and GC-MS. All the olefinic products are known compounds and were identified by GC-MS, and in some cases by ¹H NMR, and compared to the spectra of authentic commercial samples.

H-NMR Spectrum of [NBu₄]VO₂Dipic (**1**)

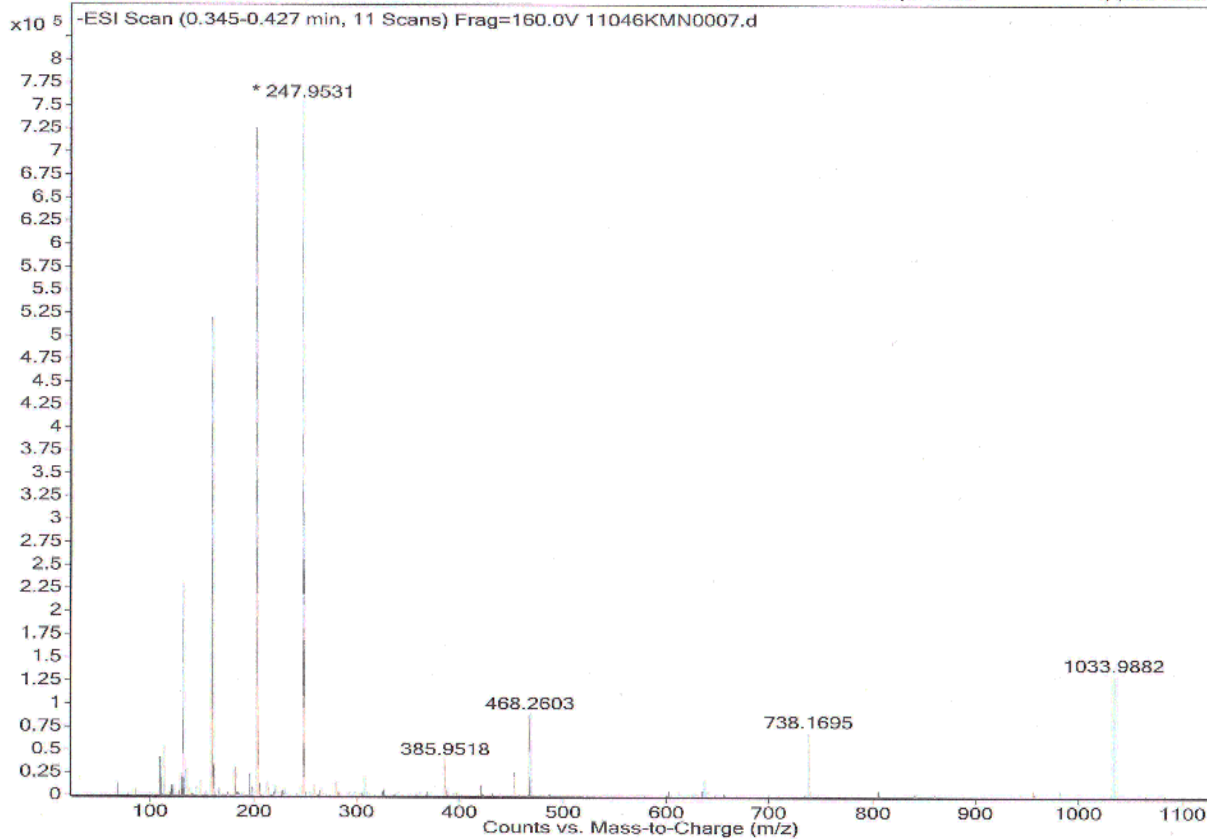


IR Spectrum of [NBu₄]VO₂Dipic:



Mass Spectrum of [NBu₄]VO₂Dipic:

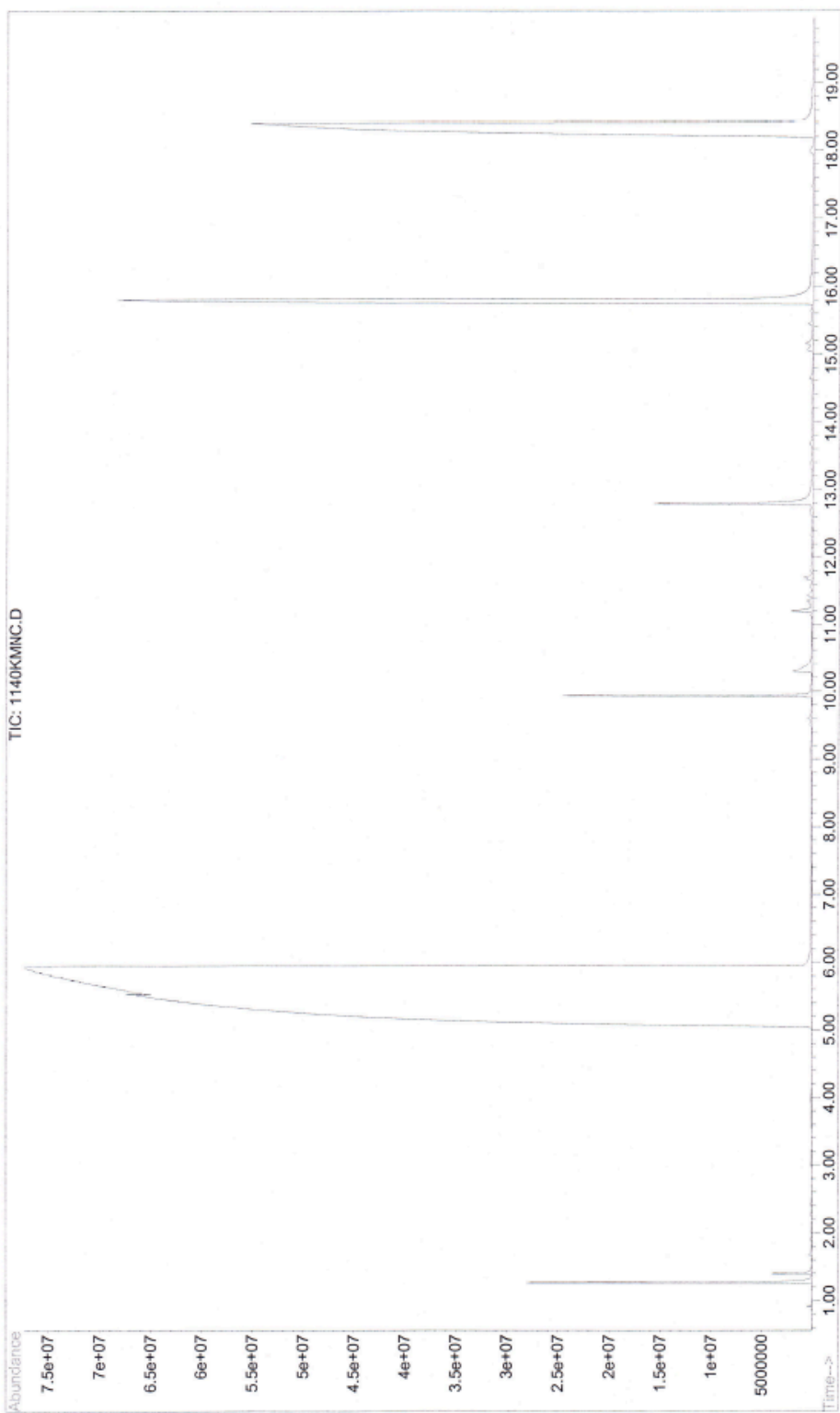
Sample Name	TBAVO2Dipic	Position	P1-D6	Instrument Name	Instrument MS	User Name	Foster
Inj Vol	3	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	11046KMN0007.d	ACQ Method		Comment	wash	Acquired Time	1/4/2013 11:31:33 AM



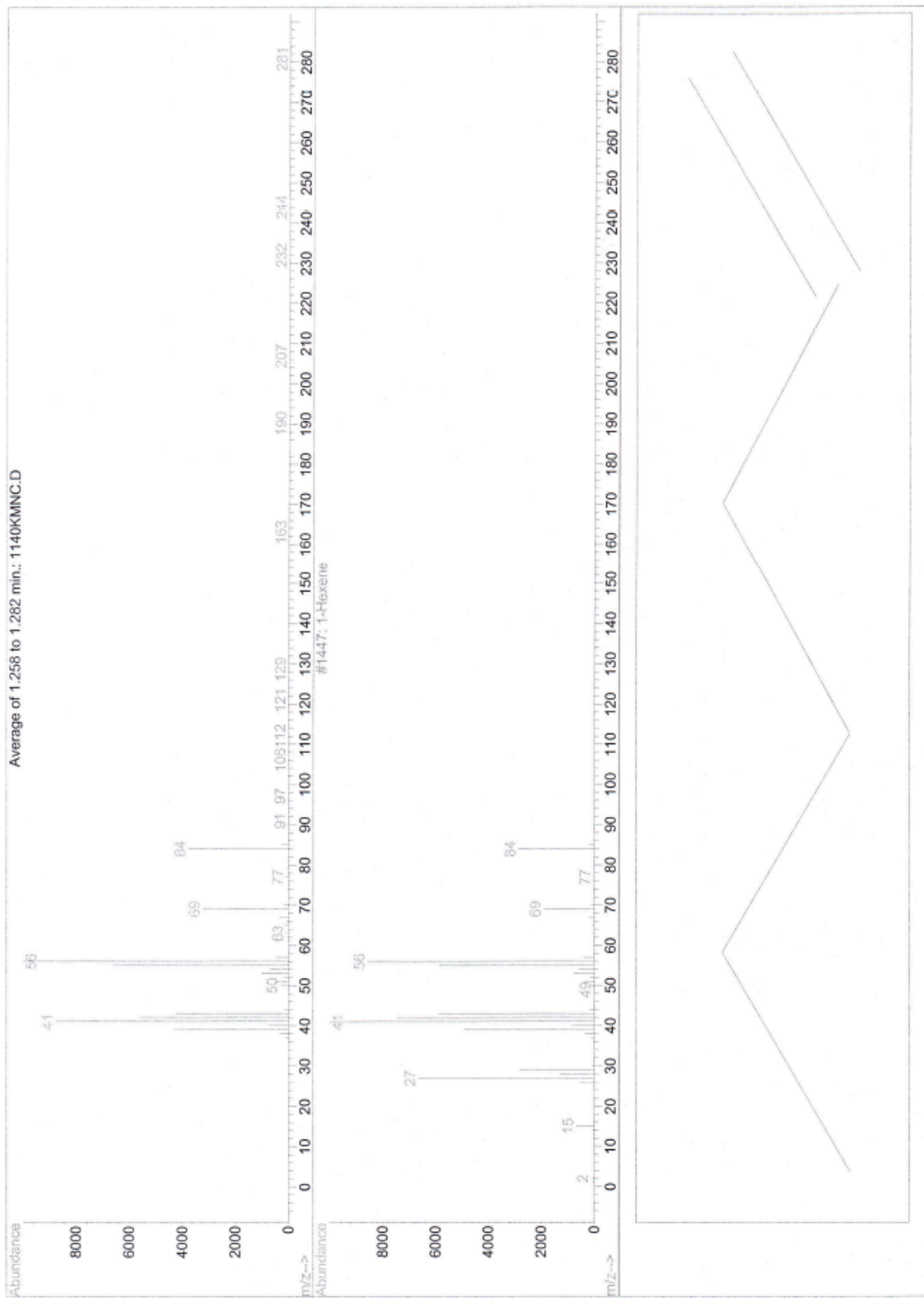
GC-MS of hexanediol DODH reaction with PPh_3 catalyzed by **1** (on following pages)

Mass chromatogram:

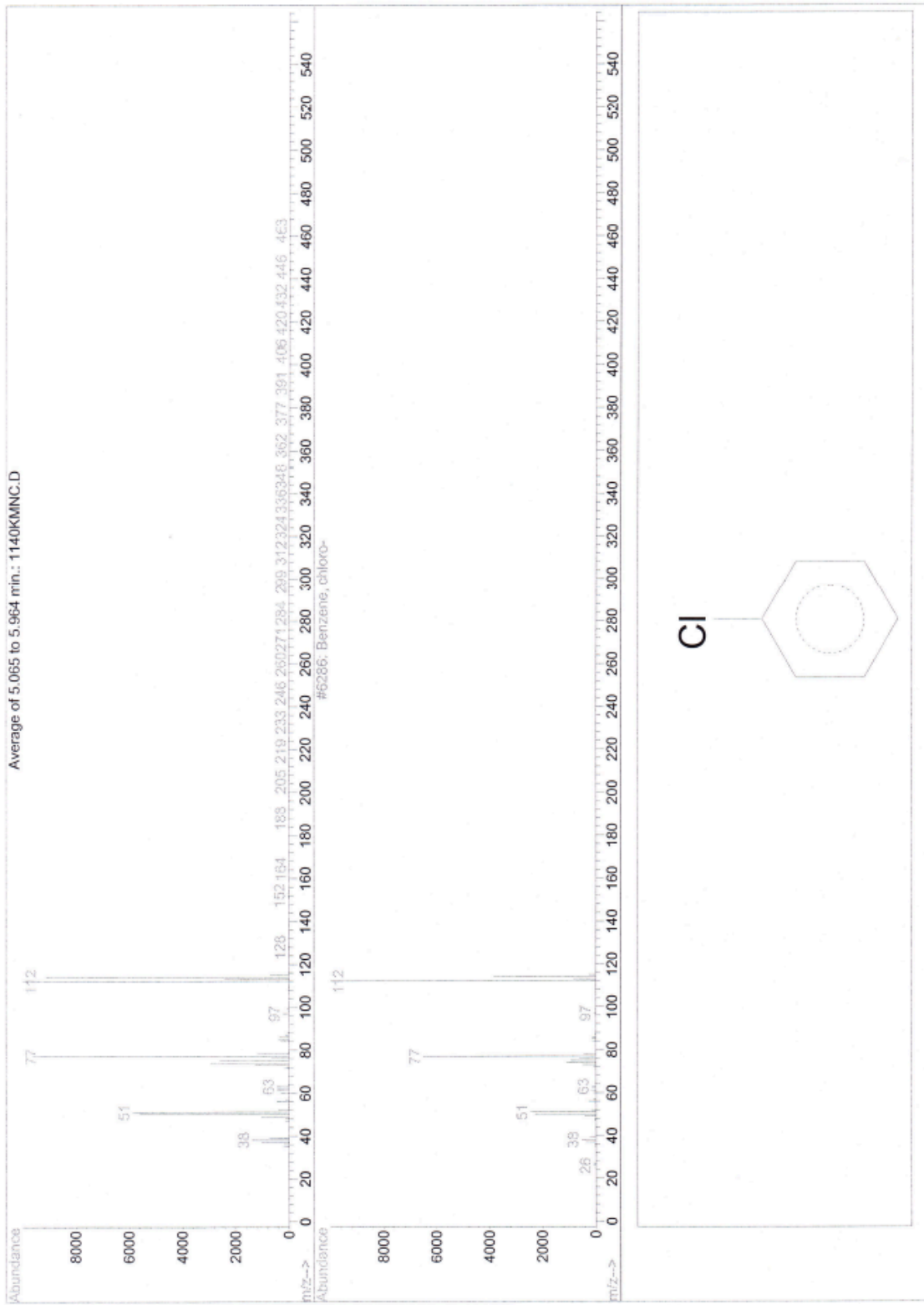
File : C:\HPCHEM\1\DATA\1140KMNC.D
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Instrument : GC/MS Ins
Sample Name: GC_5May
Misc Info : 50:1 split
Vial Number: 1



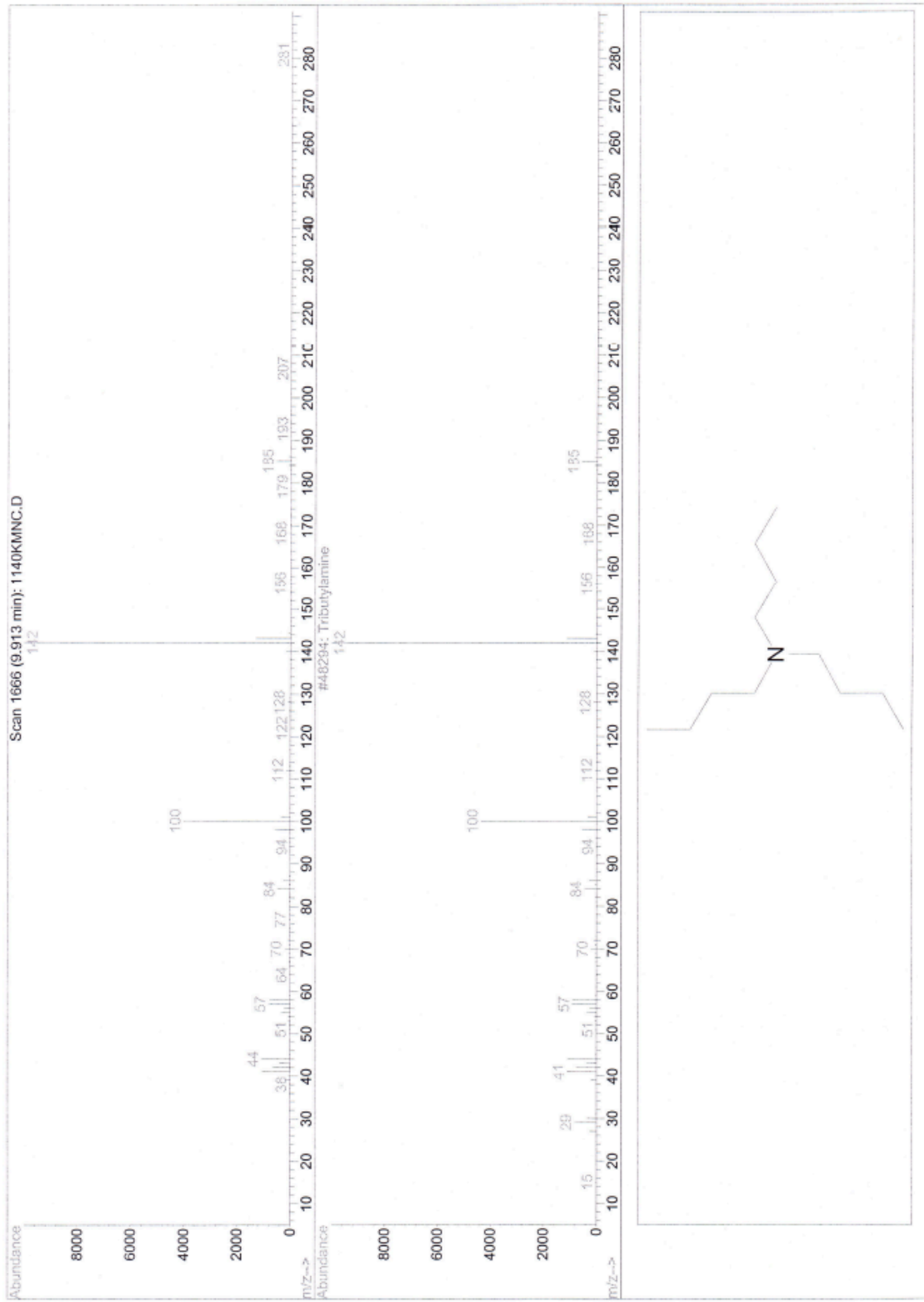
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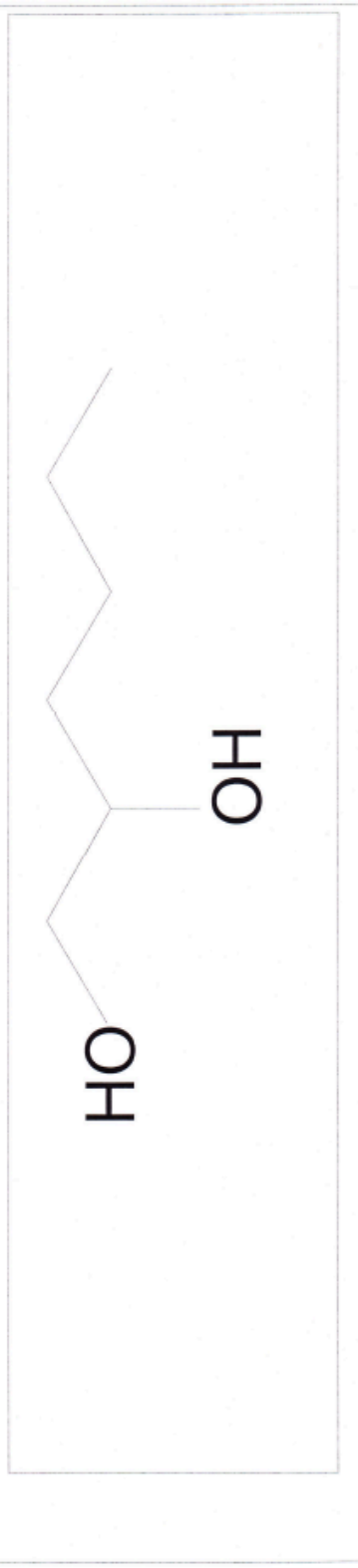
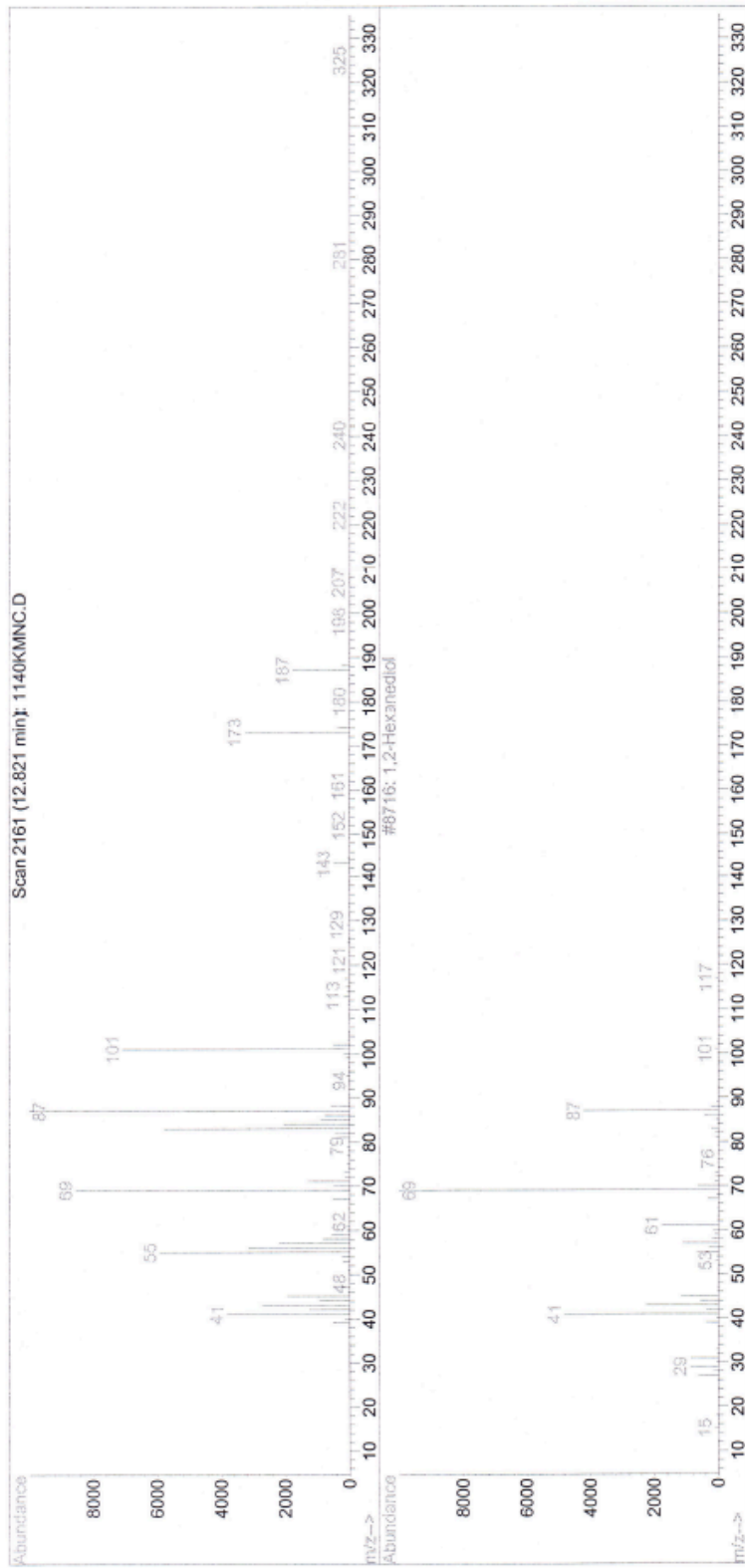
Library Searched : C:\DATABASE\nist08.1
Quality : 87
ID : Benzene, chloro-



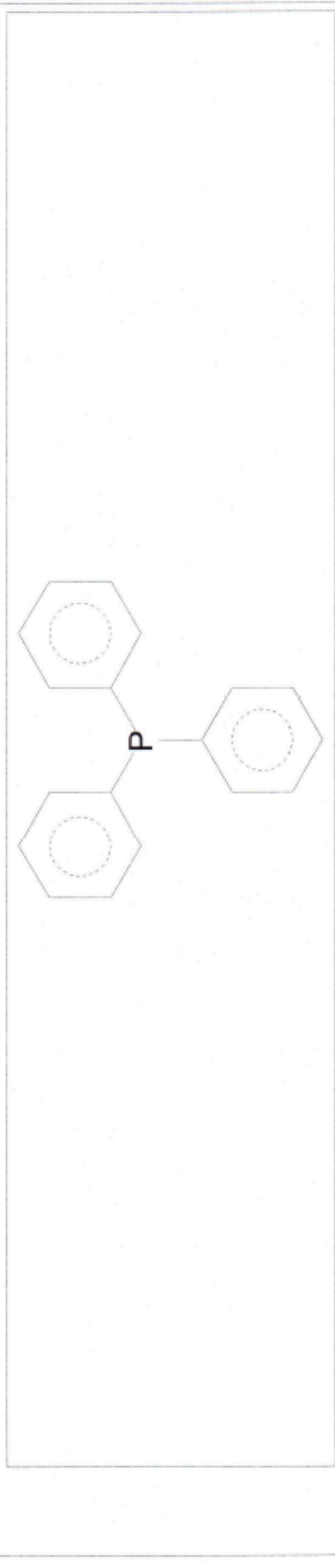
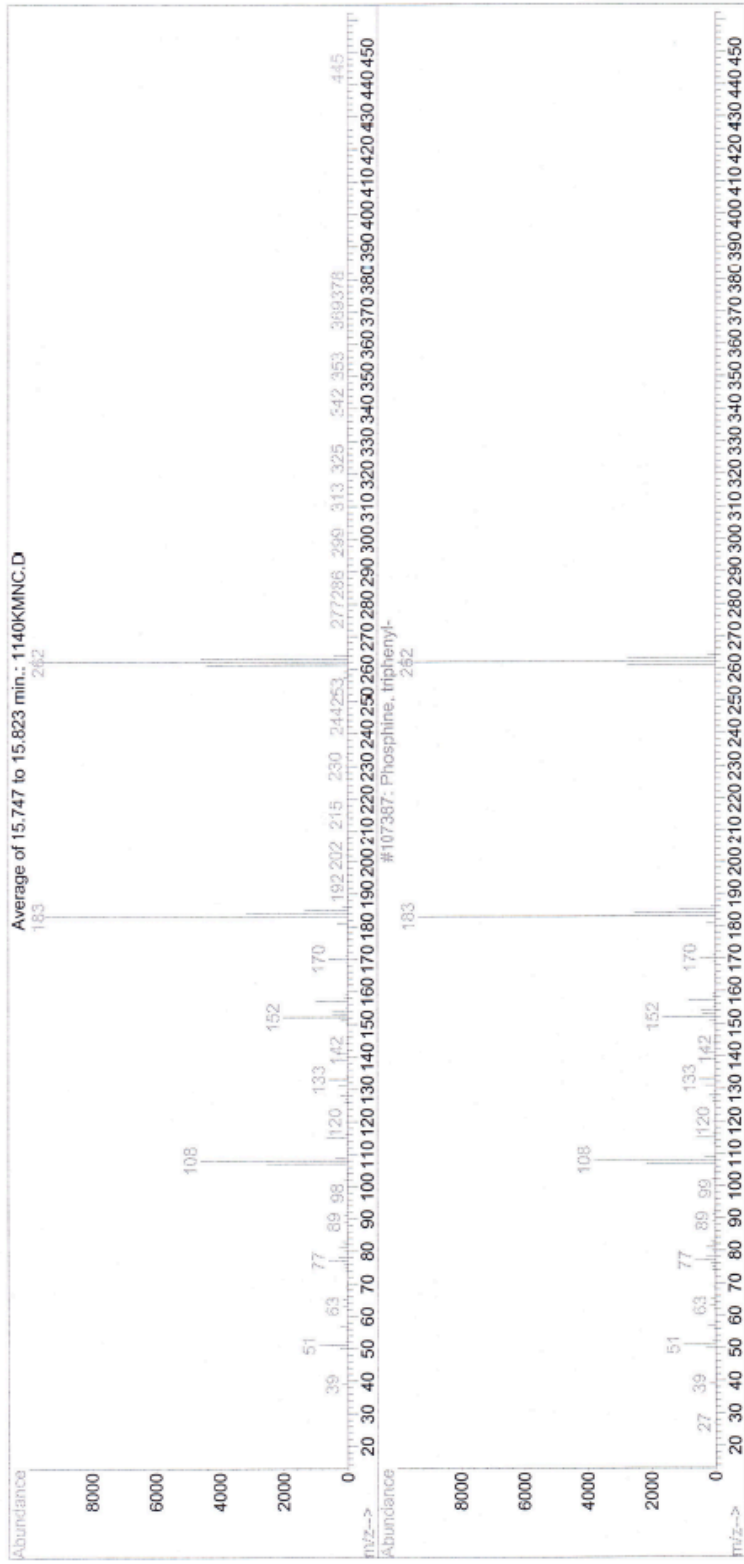
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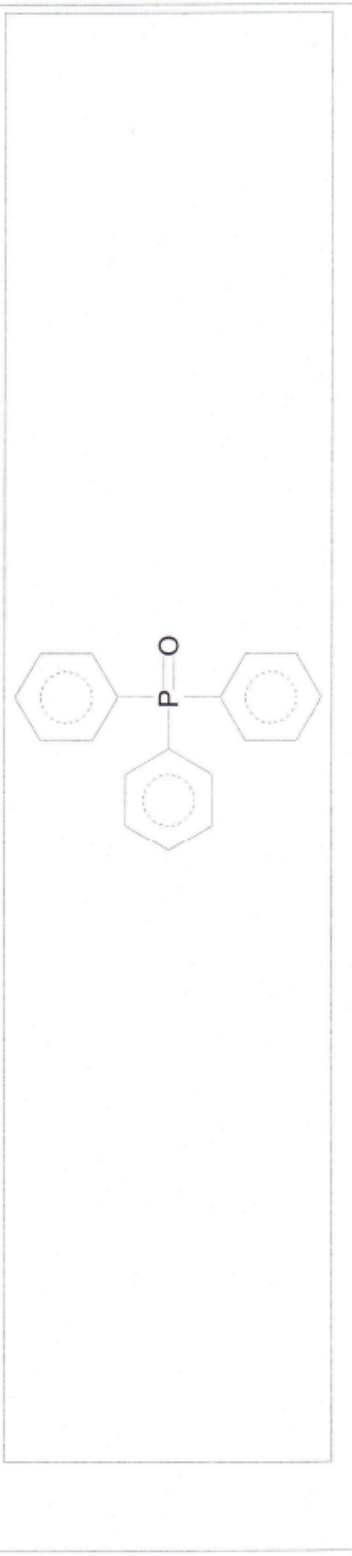
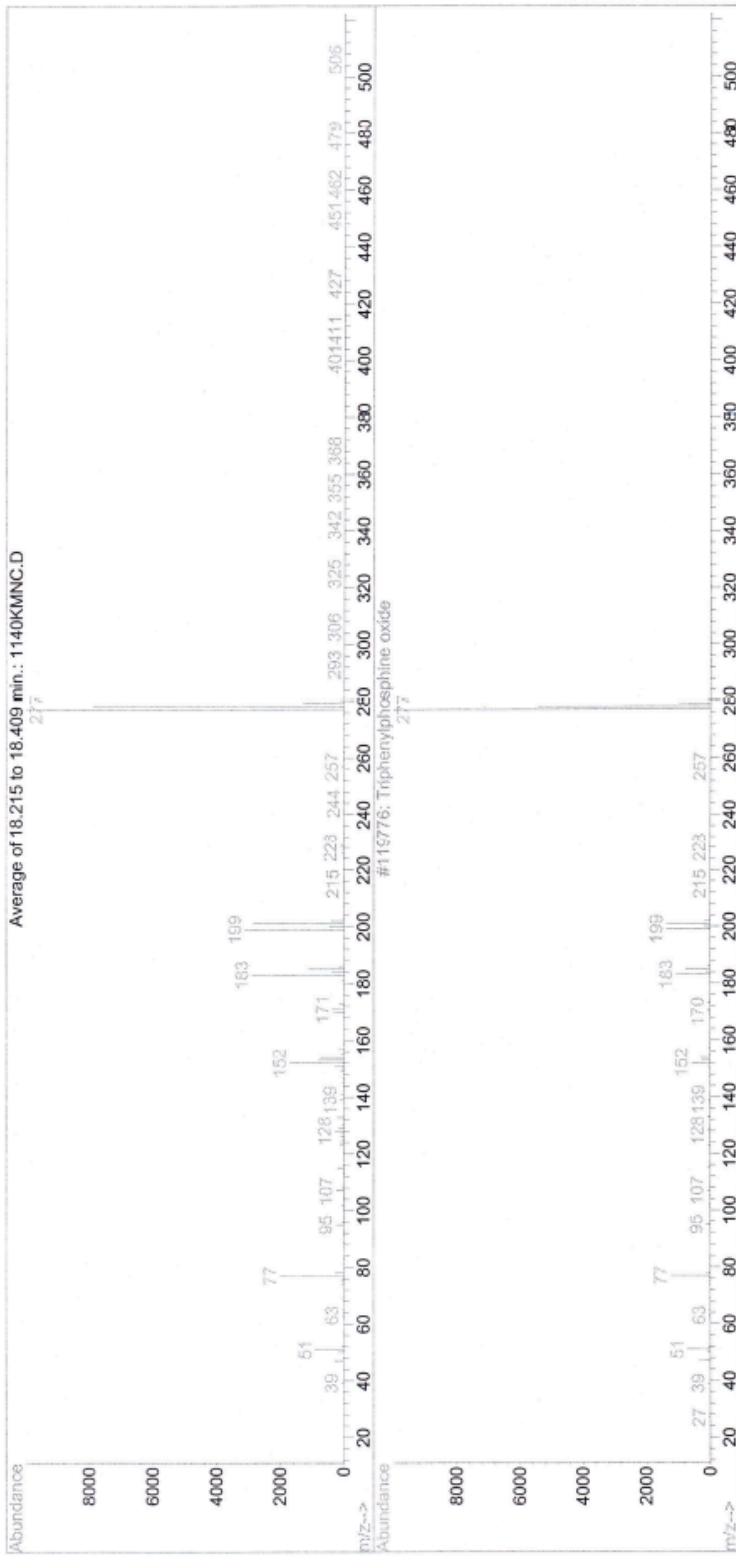
Library Searched : C:\DATABASE\nist08.1
Quality : 35
ID : 1,2-Hexanediol



Library Searched : C:\DATABASE\nist08.1
Quality : 99
ID : Phosphine, triphenyl-



Library Searched : C:\DATABASE\nist08.1
Quality : 94
ID : Triphenylphosphine oxide



References:

1. V. W. Day, W. Klemperer, and A. Yagasaki, *Chemistry Letters* 1990, 1267 – 1270.
2. C. Ohde and C. Limberg, *Chem Eur. J.* 2010, **16**, 6892 – 6899.
3. T. F. S. Silva, K. V. Luzyanin, M. V. Kirillova, M. F. G. de Silva, L. M. D. R. S. Martins, and A. J. L. Pombeiro, *Adv. Synth. Catal.* 2010, **352**, 171 – 187.
4. Y. Tajika, K. Tsuge and Y. Sasaki, *Dalton Trans.*, 2005, 1438 – 1447.
5. N. R. Popova, K. G. Bogolitsyn, R. Gribosh, and A. Samotus, *Russian Journal of General Chemistry* 1997, **67**(5), 819.