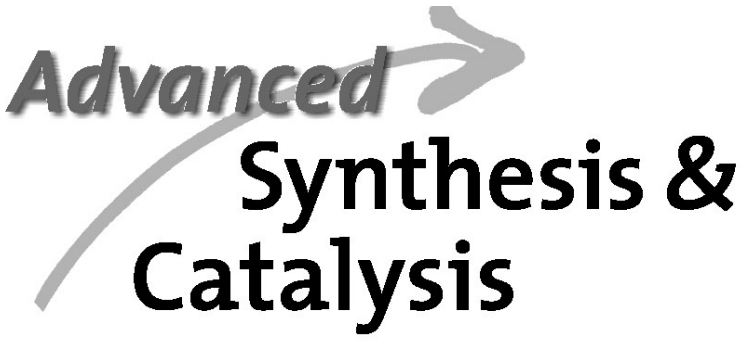

Supporting Information

Supporting Information

New Mono-quarternized Bis-Cinchona Alkaloid Ligands for Asymmetric Dihydroxylation of Olefins in Aqueous Medium: Unprecedented High Enantioselectivity and Recyclability

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Experimental

General: The NMR spectra were recorded on a Varian Unity Inova 500MHZ spectrometer. HPLC (High Performance Liquid Chromatography) for the determination of enantiomeric purity was performed by Varian Prostar 321 UV/VIS apparatus with Daicel Chiralcel OJ-H, OD-H, OB-H chiral column. Optical rotations were obtained on a P-1020 JASCO polarimeter. HRMS were analyzed by JMS-700 JEOL. LC-MS data were acquired using Agilent-Micromass (Agilent 1100 Series-Qutro micro). Osmium concentration was analyzed by ICP-AES (Jobin Yvon-2000). Column chromatography was performed using Kieselgel 60 (230~400 mesh) and TLC was carried out using glass sheets pre-coated with silica gel $60F_{254}$ purchased from Merck.

OsO_4 was purchased from Next Chimica, South Africa. All of olefins, $(DHQ)_2PHAL$, $NMO{\cdot}H_2O$ were purchased from Aldrich. All other solvents and chemicals were obtained from commercial sources, and were used without further purification. The chiral ligand $(QN)_2PHAL$ was synthesized according to our literature procedure.[12]

1) Chracterization Data for Ligands

[$(QD)_2$PHAL-Allyl]Br

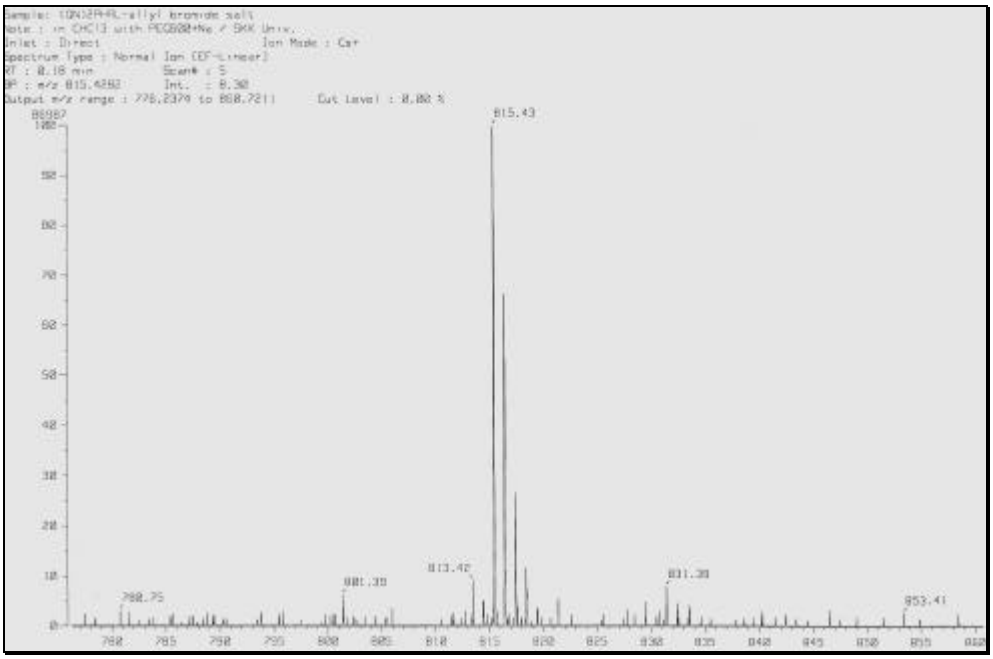
$[\alpha]_D$ -270.06 (c 1, $CHCl_3$). ^{13}C NMR (CD_3OD): δ = 160.00, 159.55, 158.67, 156.76, 148.01, 147.97, 145.93, 145.06, 144.95, 141.18, 141.01, 137.92, 135.02, 131.92, 131.39, 128.82, 128.28, 127.45, 126.52, 124.78, 124.17, 123.89, 123.77, 123.71, 123.35, 120.78, 119.51, 115.86, 102.70, 102.35, 77.40, 71.40, 66.44, 64.74, 60.73, 59.53, 58.78, 56.67, 56.48, 50.86, 50.56, 49.99, 40.07, 38.80, 28.78, 27.79, 26.72, 25.81, 24.69, 23.49, 23.25, HRMS (ESI): calcd for [M($C_{51}H_{55}BrN_6O_4$)-Br^{-1}]: 815.4284, found 815.4276.

[$(QN)_2$PHAL-Allyl]Br

$[\alpha]_D$ +290.55 (c 1, MeOH). ^{13}C NMR (CD_3OD): δ = 160.27, 159.94, 158.46, 157.04, 148.11, 148.00, 145.53, 145.18, 145.09, 141.89, 141.81, 138.46, 135.30, 135.26, 132.15, 131.54, 129.22, 128.24, 127.42, 126.21, 124.44, 124.21, 123.99, 123.94, 123.84, 123.50, 120.80, 119.67, 118.04, 115.85, 102.71, 102.23, 76.84, 70.47, 67.55, 64.96, 63.03, 60.91, 57.35, 56.74, 56.54, 54.34, 44.38, 40.27, 39.33, 29.01, 28.31, 27.86, 26.51, 23.24, 22.87. HRMS (ESI): calcd for [M($C_{51}H_{55}BrN_6O_4$)-Br^{-1}]: 815.4284, found 815.4282.

2) HRMS of Ligands

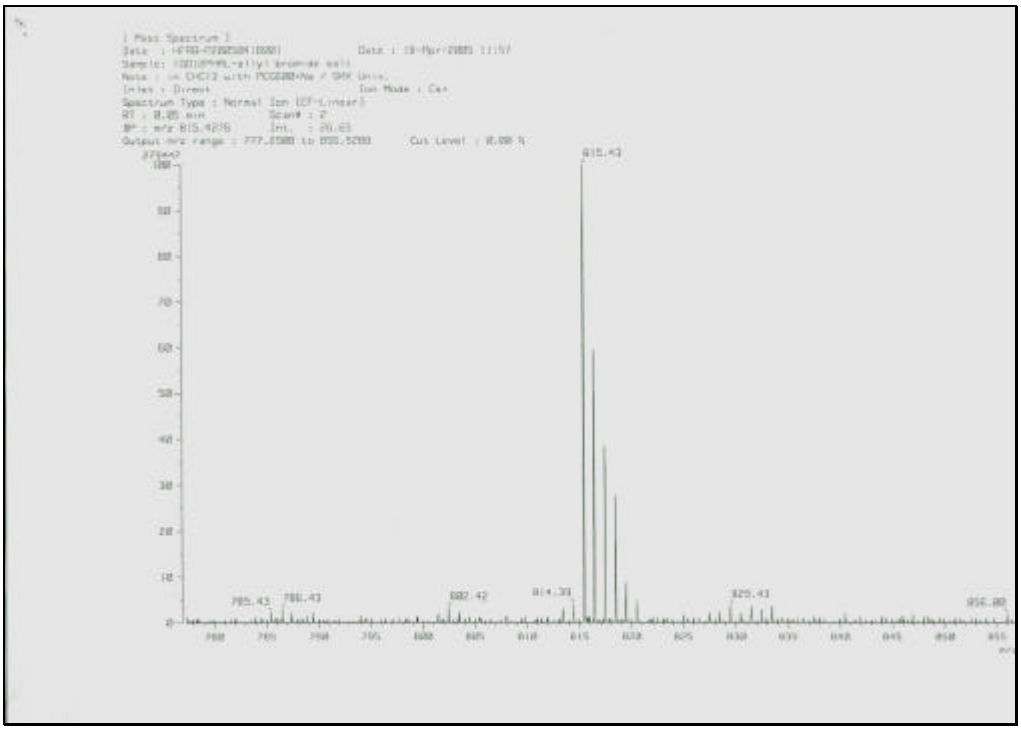
HRMS of [$(QN)_2$PHAL-Allyl]Br




```
[ Elemental Composition ]
Data  : HFAB-P20050418002              Date : 18-Apr-2005 12:07
Sample: (QN)2PHAL-allyl bromide salt
Note : in CHCl3 with PEG600+Na / SKK Univ.
Inlet : Direct                         Ion Mode : Cs+
RT : 0.18 min                          Scan#: 5
Elements : C 51/0, H 55/0, O 4/0, N 6/0
Mass Tolerance      : 5ppm, 10mmu if m/z < 2000, 20mmu if m/z > 4000
Unsaturation (U.S.) : 0.0 - 50.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  815.4282   100.0     -0.3 /  -0.3   27.5  C 51 H 55 O 4 N 6
```

HRMS of [(QD)$_2$PHAL-Allyl]Br



```
[ Elemental Composition ]
Data  : HFAB-P20050418001              Date : 18-Apr-2005 11:57
Sample: (QD)2PHAL-allyl bromide salt
Note : in CHCl3 with PEG600+Na / SKK Univ.
Inlet : Direct                         Ion Mode : Cs+
RT : 0.05 min                          Scan#: 2
Elements : C 51/0, H 55/0, O 4/0, N 6/0
Mass Tolerance      : 5ppm, 10mmu if m/z < 2000, 20mmu if m/z > 4000
Unsaturation (U.S.) : 0.0 - 50.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  815.4276   100.0     -1.1 /  -0.9   27.5  C 51 H 55 O 4 N 6
```

3) Characterization of Products.

The following compounds are known compounds, and their NMR spectra are in accordance with those reported in the literature. The enantiomeric excess of the diols was determined by HPLC analysis with chiral stationary phases.

1-Phenyl-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 0.5 mL min^{-1}): t_R =32.4 min (*R*-isomer), t_R = 37.2 min (*S*-isomer).

1-phenyl-1,2-propanediol. HPLC (Chiralcel AD-H, *i*-PrOH/hexane (v/v = 10:90), flow rate 1.0 mL min^{-1}): t_R = 11.9 min (1*R*, 2*R*-isomer), t_R = 13.3 min (1*S*, 2*S*-isomer).

1-(4-bromophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 0.5 mL min^{-1}): t_R = 38.9 min (*R*-isomer), t_R = 43.9 min (*S*-isomer).

1-(4-chlorophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 1.0 mL min^{-1}): t_R = 17.2 min (*R*-isomer), t_R = 18.8 min (*S*-isomer).

1-(4-flurophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 1.0 mL min^{-1}): t_R = 15.2 min (*R*-isomer), t_R = 17.6 min (*S*-isomer).

1-(3-chlorophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 1.0 mL min^{-1}): t_R = 15.4min (*R*-isomer), t_R = 19 min (*S*-isomer).

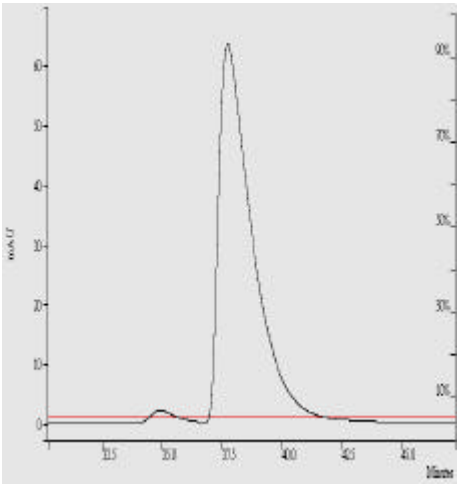
1-(3-fluorophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 1.0 mL min^{-1}): t_R = 15 min (*R*-isomer), t_R = 17.7 min (*S*-isomer).

1-(2-chlorophenyl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 10:90), flow rate 1.0 mL min^{-1}): t_R = 13 min (*R*-isomer), t_R = 18 min (*S*-isomer).

1-(naphthalene-2-yl)-1,2-ethanediol. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 10:90), flow rate 1.0 mL min^{-1}): t_R = 12.7 min (*R*-isomer), t_R = 15.7 min (*S*-isomer).

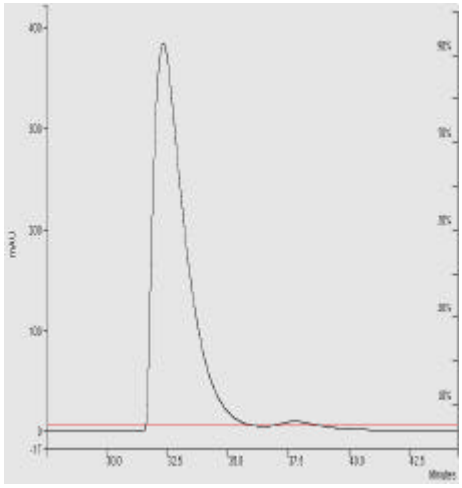
HPLC Spectra (Table 1)

Using [$(QN)_2$PHAL-Allyl]Br (Entry 1)



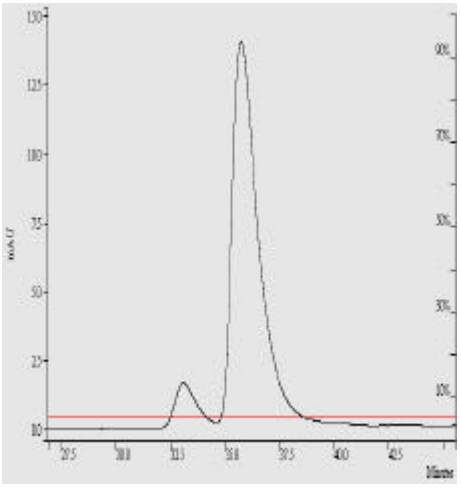
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	2.4642	34.911	1574031	77.2
2	97.5358	37.735	62302280	104.4
	100.0000		**63876312**	

Using [$(QD)_2$PHAL-Allyl]Br (Entry 2)



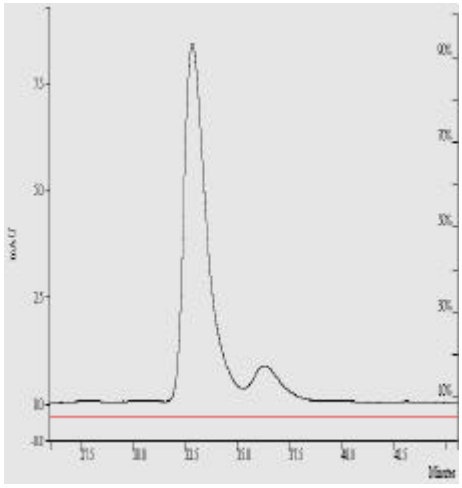
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	98.6757	32.322	352786464	101.0
2	1.3243	37.753	4734702	71.0
	100.0000		**357521152**	

Using [$(QN)_2$PHAL] (Entry 3)



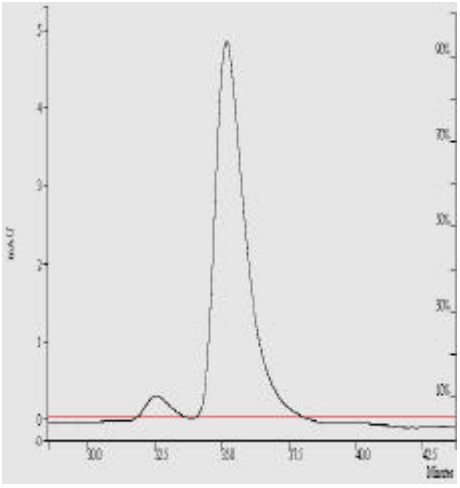
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	8.1321	33.078	1013768	73.2
2	91.8679	35.722	11452443	85.6
	100.0000		**12466211**	

Using [$(QD)_2$PHAL] (Entry 4)



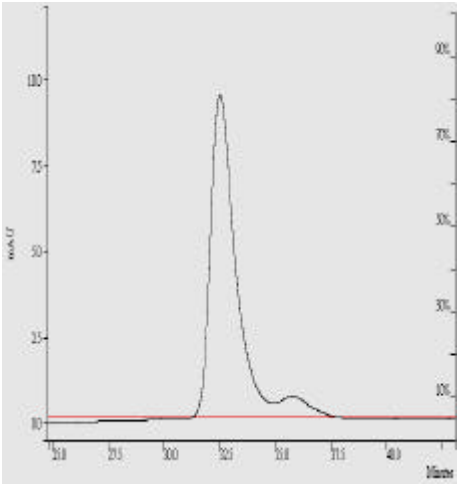
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	95.3611	32.856	5994617	73.8
2	4.6389	36.317	291610	71.4
	100.0000		**6286227**	

Using [$(DHQN)_2PHAL$] (Entry 5)



Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	4.6970	32.535	187027	60.3
2	95.3030	35.171	3794847	69.9
	100.0000		**3981874**	

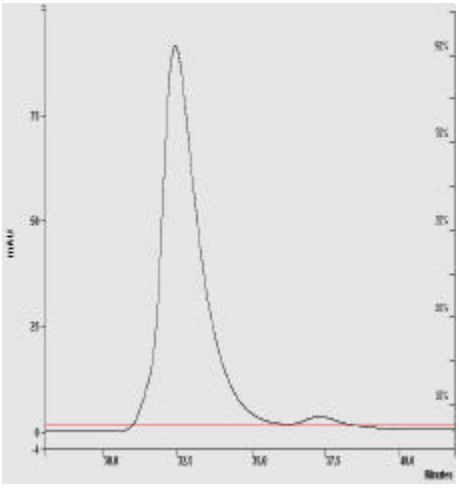
Using [$(DHQD)_2PHAL$] (Entry 6)



Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	96.5679	32.504	6802913	73.9
2	3.4321	35.740	241780	49.7
	100.0000		**7044693**	

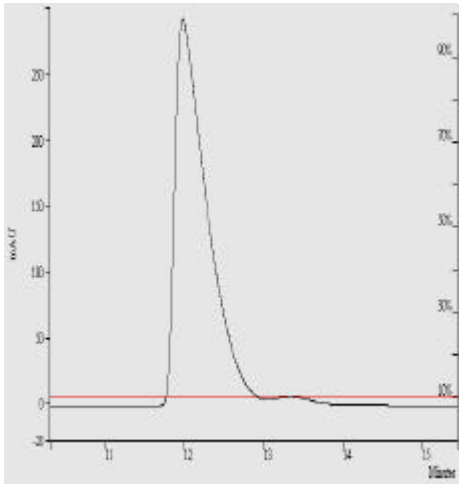
HPLC Spectra (Table 2)

1-Phenyl-1,2-ethanediol (Entry 1)



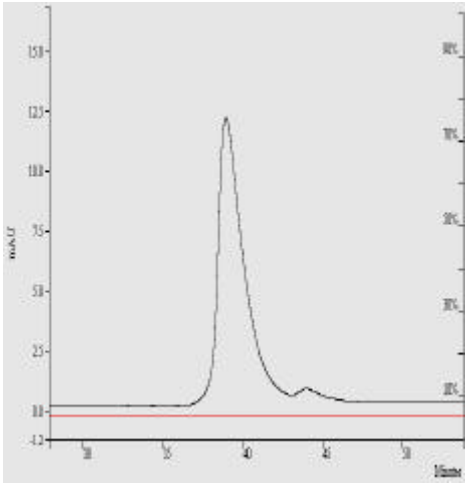
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	98.7338	32.412	80701224	88.1
2	1.2662	37.259	1034975	48.4
	100.0000		**81736200**	

1-phenyl-1,2-propanediol (Entry 2)



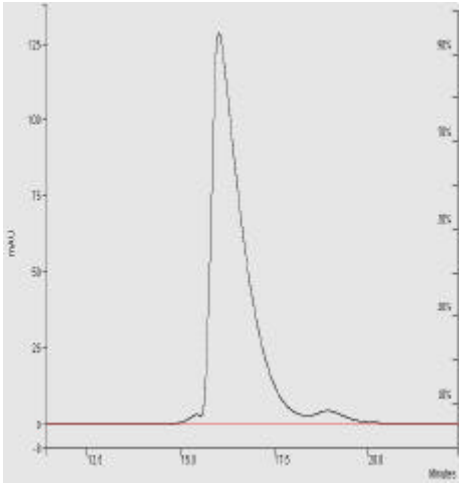
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	98.9856	11.977	81454232	25.6
2	1.0144	13.327	834770	17.6
	100.0000		**82289000**	

1-(4-bromophenyl)-1,2-ethanediol (Entry 3)



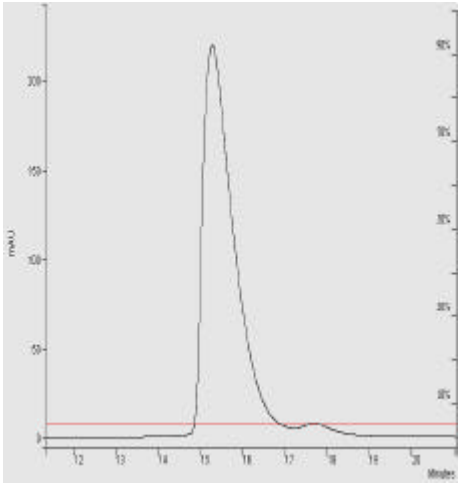
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	98.8971	38.934	12768655	116.7
2	1.1029	43.938	142396	48.0
	100.0000		**12911051**	

1-(4-chlorophenyl)-1,2-ethanediol (Entry 4)



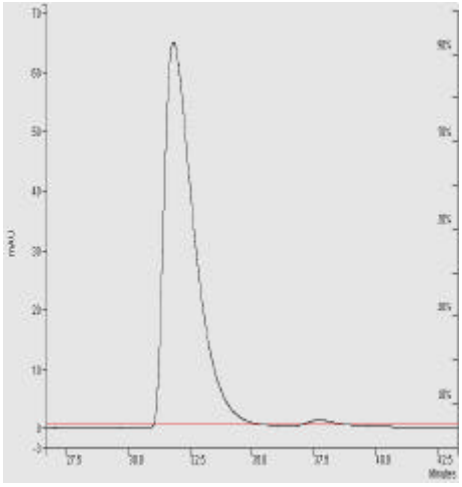
Peak No	Result ()	Ret. Time (min)	Area (counts)	Rel Ret Time	Width 1/2 (sec)
1	98.8955	16.012	69442672	0.00	49.3
2	1.1045	18.909	775538	0.00	27.5
	100.0000		**70218208**		

1-(4-flurophenyl)-1,2-ethanediol (Entry 5)



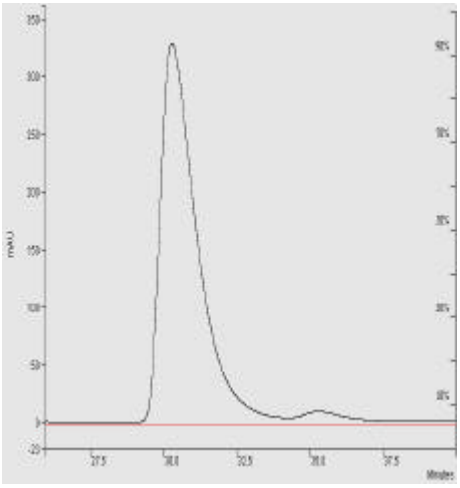
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	98.6475	15.277	109861928	51.9
2	1.3525	17.678	1506205	0.0
	100.0000		**111368136**	

1-(3-chlorophenyl)-1,2-ethanediol (Entry 6)



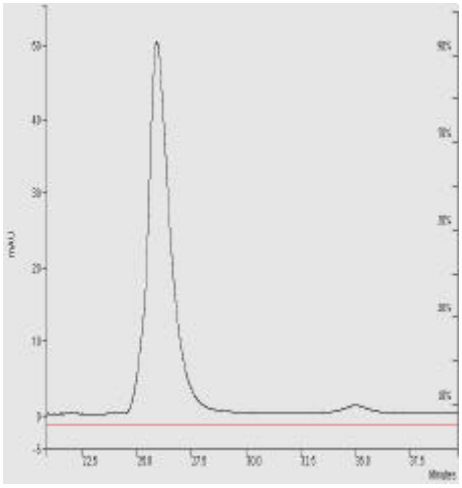
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	98.5046	31.822	54772348	87.9
2	1.4954	37.731	831504	76.2
	100.0000		**55603852**	

1-(3-fluorophenyl)-1,2-ethanediol (Entry 7)



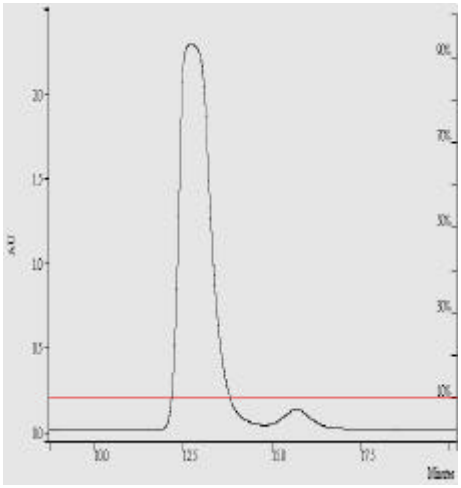
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	98.2279	30.266	279804320	86.9
2	1.7721	35.266	5047755	64.7
	100.0000		**284852064**	

1-(2-chlorophenyl)-1,2-ethanediol (Entry 8)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	98.0127	25.904	36014192	60.1
2	1.9873	35.022	730236	71.1
	100.0000		**36744428**	

1-(naphthalene-2-yl)-1,2-ethanediol (Entry 9)

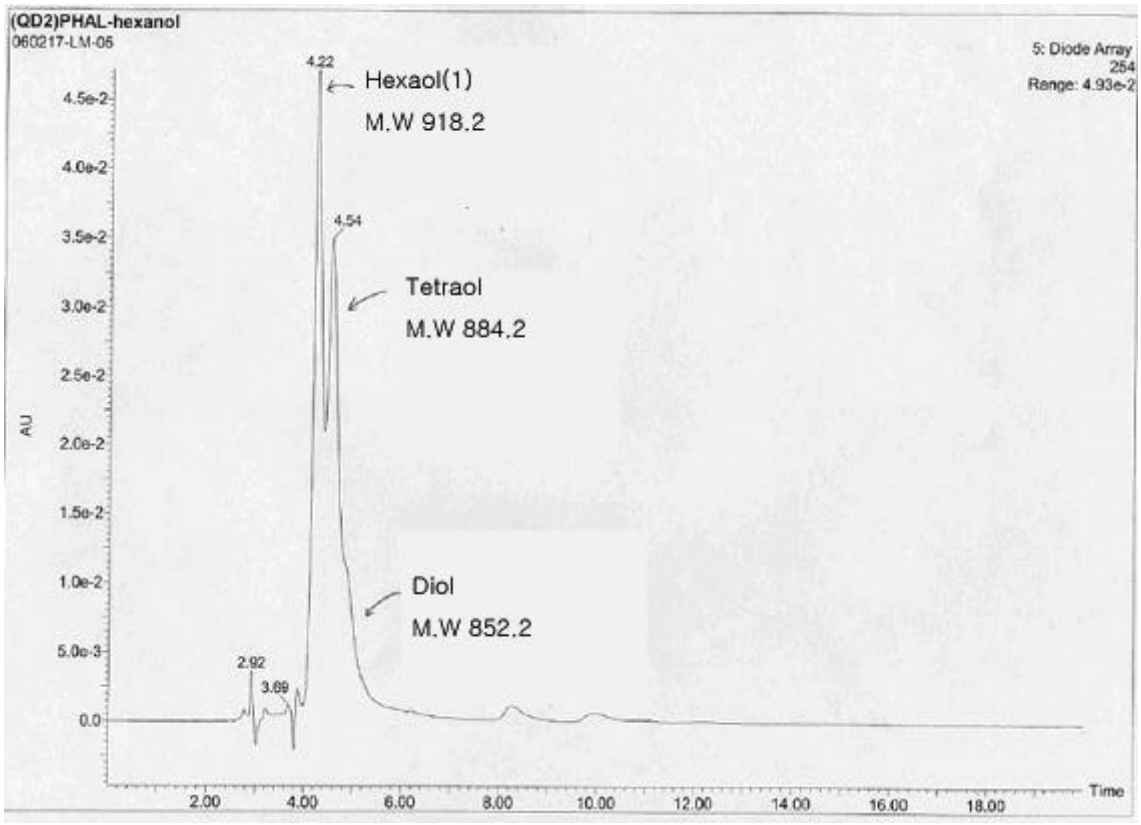


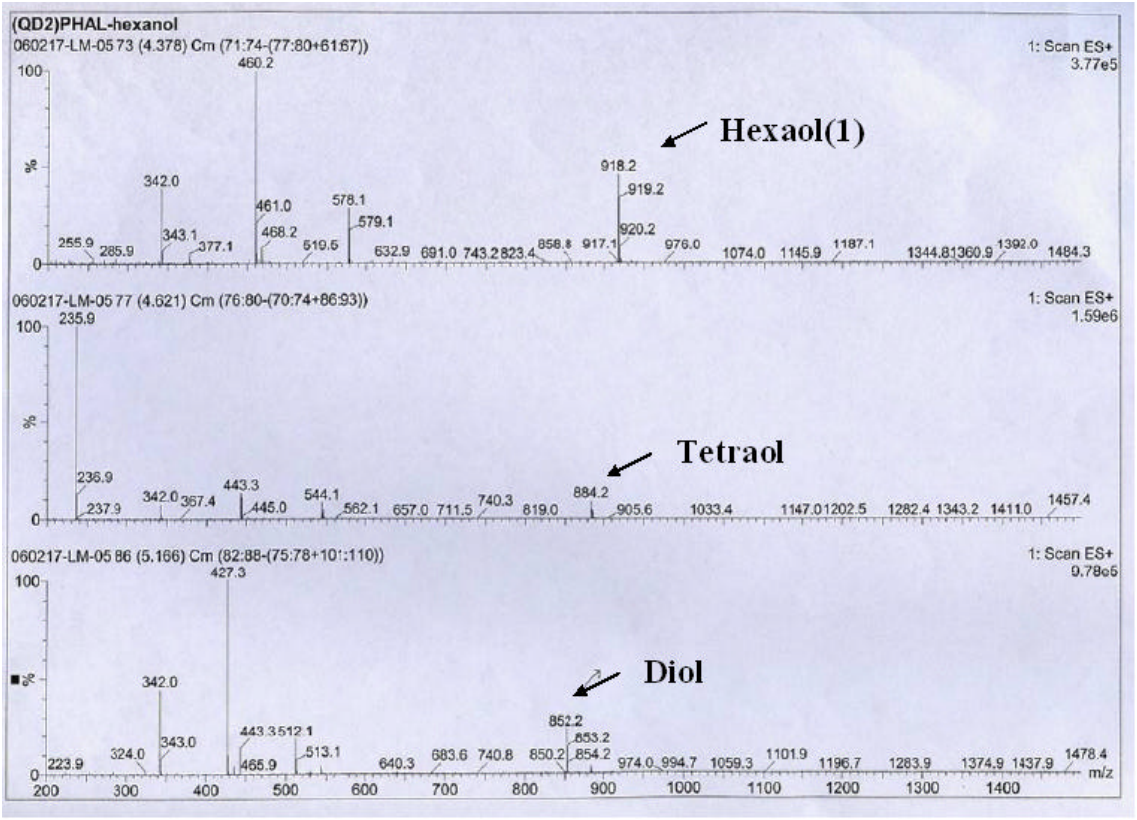
Peak No	Result ()	Ret Time (min)	Peak Area (counts)	Width 1/2 (sec)
1	96.5964	12.719	1398096384	61.0
2	3.4036	15.690	49262556	43.4
	100.0000		**447358976**	

4) LC-MS Analysis

LC-MS conditions; LC condition – Agilent 1100 series, column (XDB-C18, 4.6X150mm, 3.5um), column Oven (40^{o}C), mobile phase (10 mM ammoniumacetate in MeOH/H_2O=85/15, solvent (acetonitrile), mobile phase flow rate (0.8mL/min); MS condition – ion mode (ESI), mass range (500~1000 m/z), capillary voltage (3.20 kV), extractor voltage (2.00 V), RF lens voltage (0.3 V), source temperature (120 ^{o}C), desolvation temperature (300 ^{o}C), cone gas flow (25 L/h), desolvation gas flow (550 L/h).

LC-MS Spectrum of multi-hydroxylated ligands dissolved in the aqueous phase




(QD2)PHAL-hexanol
060217-LM-0573 (4.378) Cm (71:74-(77:80+61:67))
1: Scan ES+
3.77e5
Hexaol(1)
060217-LM-0577 (4.621) Cm (76:80-(70:74+86:93))
1: Scan ES+
1.59e6
Tetraol
060217-LM-0586 (5.166) Cm (82:88-(75:78+101:110))
1: Scan ES+
9.78e5
Diol
m/z

6) ICP-Analysis of Os in the Product

After reaction (entry 1 in Table 2), the amount of Os present in the organic phase was determined by ICP. The Os content in the product diol was 965 ppm which indicates that ca. half amount of Os was leached into the organic phase..

Calibration Curve