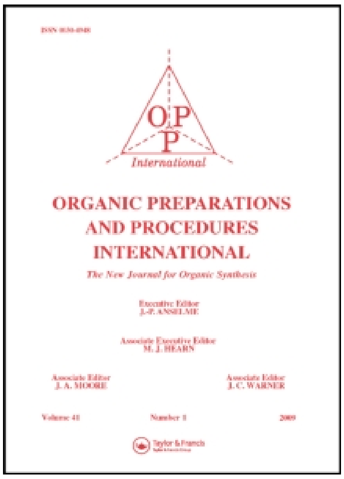

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OPPI BRIEFS

SYNTHESIS AND EXTRACTION STUDIES OF A NOVEL TETRA-CALIX[4]ARENE

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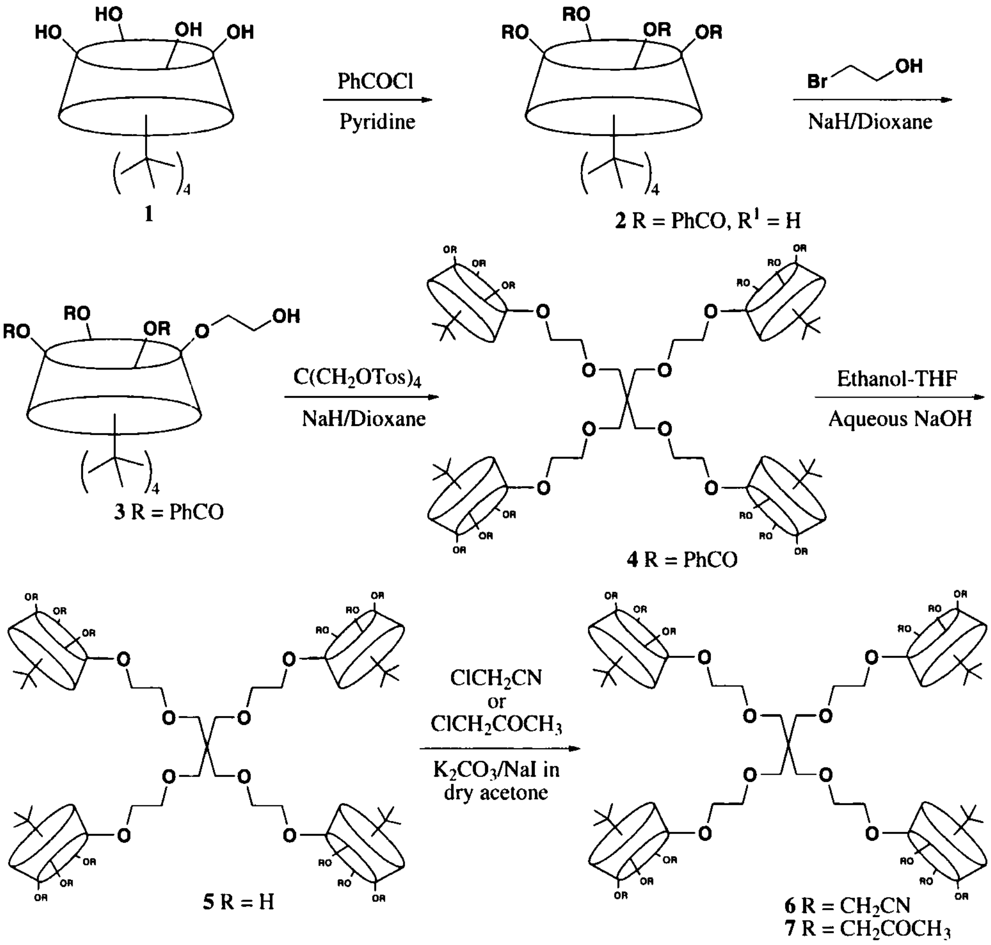
Much attention has been paid in recent years to chemical separation techniques and the design and synthesis of new extraction reagents for metal ions. This attention results in part from environmental concerns, efforts to save energy and recycling at the industrial level. Therefore, search for new synthetic hosts having the ability to form selective inclusion complexes with ions and neutral molecules is very active. The design and synthesis of calixarenes, an important class of building blocks, is very well documented in supramolecular chemistry.[1-5]

The highly ordered structure of calixarenes offers not only boundless possibilities for chemical modifications, but also makes them extremely useful in the study of molecular recognition and supramolecular processes. Numerous studies have been carried out to synthesize new complexants for alkali and alkaline earth metals, transition metals and lanthanides.[1-41] In the past decade several double (or multiple) calixarenes have been prepared as examples of higher order molecular architectures.[17,18]. In these compounds, two or more calixarene units are linked at their upper or lower rims through one or more spacer elements.[19,20] Various structural motifs have been used as spacers, including alkyl, alkenyl, and alkynyl chains, diesters, diamines, metallocenes, polyethers, sulfides and diimines.[21-41] We have chosen the calix[4]arene skeleton as a vehicle for modeling such phenomena. Research in our group has explored a unique dimeric and also polymeric binding mode for the calix[4]arene frame work, which provides for the complexation of metal ions.[31,38,42,44,47-49] Herein we report the synthesis of a novel tetra-calix[4]arene (**5**) and its derivatives (**6-7**), in which calix units are attached around the periphery through the oxygen of the lower rim. Their extraction ability in two-phase extraction systems has also been examined. All of the new compounds have been verified by ^{1}H NMR, IR, elemental analysis and vapor phase osmometric molecular weight determinations. The syntheses of compounds **1** and **2** were based on the previously published methods,[50,51] while the reaction steps leading from **2** to **7** (*Scheme 1*) are reported here. Refluxing a mixture of the tribenzoate derivative of *p-tert-* butylcalix[4]arene **2** and 2-bromoethanol in dioxane in the presence of NaH afforded a 68% yield of **3**, mp. 232°, which upon treatment with pentaerythritol tetratosylate gave, after column chromatography, a periphery type tetrameric compound **4** in 62% yield: mp.127°; MW = 4100 (calcd: 4080) by vapor phase osmometer. From the ^{1}HNMR spectral data of compounds **3** and **4** it has been revealed that the calixarene moieties of these compounds have cone conformations at ordinary temperature as indicated by the typical signals of the *tert*-butyl groups, bridging methylene groups and aromatic protons of the calixarene moiety.[14,50]



Hydrolysis of the compound **4** with 15% aqueous NaOH solution in ethanol/THF (1:1) removes the benzoyl groups. This is verified by IR spectroscopy, which shows the disappearance of the carbonyl band of the benzoyl groups (1739 cm^{-1}) and appearance of new band (3223 cm^{-1}) for the phenolic OH groups. Compound **5** was obtained in 73% yield, mp.210°; MW = 2850 (calcd: 2836). It has been recognized that the calix moieties of the compound **5** also exist in the cone conformation, as inferred from the ^{1}HNMR spectra which exhibit a characteristic pair of doublets at 3.40 and 4.30 ppm (J = 13 Hz) a single AB system for the bridging methylene groups of the calixarene moiety[14,50].

Two different derivatives of compound **5** with moderate molecular weight and good solubility in organic solvents such as $CHCl_3$ and CH_2Cl_2 at room temperature were synthesized for host-guest studies. Thus, compound **5** was treated with chloro derivatives of acetonitrile and acetone in the presence of K_2CO_3 and NaI in dry acetone. The NaI was used to facilitate the reaction by halogen exchange. Compound **6** was obtained in 63% yield, mp.206°; MW = 3325 (calcd: 3304) and the compound **7** was obtained in 65% yield, mp. 140-142°; MW = 3500 (calcd: 3508). From the ^{1}H NMR spectra of **6** and **7**, it has been deduced that the calixarene moieties exist in different conformations. The ^{1}H NMR spectra of **6** and **7** exhibited rather broad signals for all protons, with multiplets for the *tert*-butyl groups, bridging methylene groups and the aromatic protons of the calixarene moieties. It is not a surprising result, because in these compounds (**6** and **7**), the introduction of bulky functional groups at the phenolic oxygens can change the cone conformation of the starting tetra-calix **5** into the various other conformations.

Solvent extraction experiments were performed to ascertain the effectiveness of the ionophores **5-7** in transferring the selected alkali and transition metal cations such as Li^+, Na^+, K^+, Cs^+, Ni^+, Cu^{2+}, Co^{2+}, Cd^{2+} and Hg^{2+} from aqueous into organic phase (dichloromethane). The results of two phase extraction experiment of metal picrates with ionophores (**5-7**) are summarized in Table 1. These data were obtained by using dichloromethane solution of these ligands to extract metal picrates from aqueous phase. The equilibrium concentration of picrates in the aqueous phase was determined spectrophotometrically. The data in Table 1 show that neither alkali nor transition metal ions were extracted significantly by the starting ionophore **1** and its tetrameric derivative **5** from aqueous to organic phase. The introduction of nitrile and ketonic groups to the narrow rim of compound **5** gives more or less similar results but with a higher affinity towards Hg^{2+}.

Table 1. Extraction of Metal Picrates with Ligands[(a)]

	Picrate Salt Extracted (%)								
Ligand	Li+	Na^+	K^+	Cs^+	Ni^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Hg^{2+}
1	18.9	8.9	3.4	2.8	6.3	9.9	7.9	9.4	15.5
5	<1.0	<1.0	<1.0	<1.0	3.7	<1.0	<1.0	3.5	24.6
6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	42.5
7	<1.0	<1.0	2.3	2.9	6.7	5.04	2.2	1.0	32.5

a) Aqueous phase, [metal nitrate] = 1 x 10^{-2} M; [picric acid] = 2.5 x 10^{-5} M ; organic phase, dichloromethane, [ligand] = 1 x 10^{-3} M; at 25°, for 1 h.

In our previous studies it was observed that the triketone derivative of calix[4]arene appended in a polymeric matrix extracts Li^+ selectively from aqueous to the organic phase. In the present case however, it has been concluded that the ketonic groups in **7** are not so effective for the extraction of alkali metals as had been expected, probably due to the steric hindrance exhibited by the calixarene moieties and the flexible structure of the compound. Thus, it can be said that these ionophores (**5-7**) do not provide an appropriate environment for the inclusion of alkali metal cations.

EXPERIMENTAL SECTION

All reactions were carried out under an inert atmosphere (nitrogen). Analytical TLC were performed on precoated silica gel plates (SiO_2 , Merck 60 F_{254}), while silica gel 60 (Merck, particle size 0.040-0.063mm, 230-240 mesh) was used for preparative column chromatography. NaH was used as a 60% dispersion in oil and washed twice with n-hexane before use. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8-12 mesh). Tetrahydrofuran and toluene (BDH) were dried by refluxing over sodium/benzophenone, then fractionally distilled and stored over molecular sieves(4 Å). CH_2Cl_2 was distilled from $CaCl_2$, MeOH was distilled over Mg and stored over molecular sieves (4 Å)All other chemicals were analytically pure and were used without further purification. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification method. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy. Melting points were determined on a Gallenkamp apparatus in sealed capillary tubes and are uncorrected. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as internal standard. In ^1H NMR spectra the chemical shifts (δ) are expressed in ppm. IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis. spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer. Osmometric molecular weight determinations were carried out on a Knauer vapor pressure osmometer at concentrations of ca. 10^{-3} mol/L in $CHCl_3$, operated at 25°. The calibration standard, polystyrene, Mn = 4400, MW/Mn = 1.07 was obtained from Fluka. Compounds **1** and **2** were synthesized according to previously published methods[50,51]. 5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(benzoyloxy)-28-(2-hydroxy)ethoxycalix[4]arene **3** and other compounds illustrated in Schemes 1 and 2 were synthesized as described below.

5,11,17,23-Tetra-(tert-butyl)-25,26,27-tris(benzoyloxy)-28-(2-hydroxy)ethoxycalix[4]arene-(3).- To a solution of compound **2** (19.2 g, 20 mmol) in 200 mL of dioxane was added 5 g of NaH slowly in about half an hour. The mixture was stirred for 30 minutes at room temperature. Then 2-bromoethanol (5 mL) was added dropwise, and the reaction mixture was refluxed with continuous stirring under nitrogen atmosphere for 15 hours. Most of the solvent was evaporated under reduced pressure, the remaining concentrated product was precipitated by addition of ice cold 500 mL distilled water dropwise with vigorous stirring and neutralized by 0.1 M HCl. The precipitated solid material was filtered, washed with distilled water and dried in an oven. Recrystallization of the product from $CHCl_3$-methanol furnished compound **3** as a white semi crystalline solid. (13.6 g, 68%), mp. 232°.

IR(KBr): 3450 cm^{-1} (OH), 1739 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ: 0.85 (s, 9H, Bu^t), 1.15 (s, 27 H, Bu^t), 3.35-3.55 (m, 8H, Ar-CH_{eq}-Ar, CH_2O), 4.35 (d, J =13Hz, 4H, Ar-CH_{ax}-Ar); 4.75 (s, 1H, OH), 6.85-7.25 (m, 23H, ArH).

Anal. Calcd for $C_{67}H_{72}O_8 \cdot CH_3OH$: C,78.73; H,7.38. Found: C,78.50; H,7.45

Reaction of 3 with Pentaerythritol Tetratosylate (4).- To a solution of compound **3** (16 g, 16.0 mmol) in 200 mL of dioxane was added 5 g of NaH slowly in about half an hour. The mixture was stirred for 30 minutes at room temperature. Then pentaerythritol tetratosylate (3.0 g, 4.0 mmol) was added, and the reaction mixture was refluxed with continuous stirring under nitrogen atmosphere for several days. The crude product was purified by passage through a silica gel gravity column using 50% CH_2Cl_2 in n-hexane as eluent. Compound **4** was obtained as a white powder (10.1g, 62%), mp. 127°.

Osmometric MW ($CHCl_3$, 37°): 4100, (Calcd: 4080). IR (KBr): 1739 cm^{-1} (C=O).

^{1}H NMR($CDCl_3$): δ: 0.90 (s, 36H, Bu^t), 1.20 (s, 108H, Bu^t), 3.45-4.30(m, 56H, Ar-CH_2-Ar, OCH_2C, OCH_2CH_2O), 6.80-7.25 (m, 92H, ArH).

Anal. Calcd for $C_{273}H_{292}O_{32}$•H_2O: C, 79.91; H,7.22. Found: C,80.05; H,7.55

Hydrolysis of Compound 4 with Aqueous NaOH in Ethanol-THF (5).- A mixture of compound **4** (10 g, 2.45 mmol.) and 50 mL of 15% aqueous NaOH solution in 500 mL of ethanol-THF (1:1) was stirred and refluxed up to the disappearance of the carbonyl bands in the IR-spectrum of the compound, after which most of the solvent was distilled off. The residue was diluted with hot distilled water(500 mL) and neutralized with 1M HCl. The solid material was then filtered, washed several times with hot distilled water and dried in oven. Recrystallization of the product from ethanol-acetone furnished compound **5** as a semi-crystalline solid (5.1g, 73%), mp. 210°.

Osmometric MW ($CHCl_3$, 37°): 2850 (Calcd: 2836). IR (KBr): 3223 cm^{-1} (OH).

^{1}H NMR($CDCl_3$): δ: 1.20 (bs, 144H, Bu^t), 3.40 (d, J =13 Hz, 16H, Ar-CH_{eq}-Ar), 3.70 (s, 8H,OCH_2C), 3.75-3.90 (bt, 16H,OCH_2CH_2O), 4.30 (d, J = 13 Hz, 16H, Ar-CH_{ax}-Ar), 7.10 (bs, 32 H, ArH),7.25(s,12H, ArOH).

Anal. Calcd for $C_{189}H_{244}O_{20}$•$2H_2O$: C,79.04; H,8.70. Found: C,79.24; H,8.38

Reaction of 5 with Chloroacetonitrile (6).- A mixture of compound **5** (2.5 g, 0.88 mmol) K_2CO_3 (5.95 g), NaI (1.87 g) and chloroacetonitrile (1 mL) was treated according to the previously described method.[31,42] Compound **6** was obtained as an off-white solid (1.84 g, 63%), mp. 206°. Osmometric MW ($CHCl_3$, 37°): 3325, (Calcd: 3304). IR(KBr): 2028 cm^{-1} (CN).

^{1}H NMR($CDCl_3$): δ 1.10 (s, 72 H, Bu^t), 1.25 (s, 72 H, Bu^t), 3.65-4.50 (m, 80H, $ArCH_2Ar$, OCH_2C, OCH_2CH_2O, OCH_2CN), 6.80-7.40 (m, 32H, ArH).

*Anal.*Calcd for $C_{213}H_{256}O_{20}N_{12}$•$2H_2O$: C,76.95; H,7.88; N,5.05. Found: C,76.82; H,7.92; N,5.22

Reaction of 5 with Chloroacetone (7).- A mixture of compound **5** (2.5 g, 0.88 mmol) K_2CO_3 (5.95 g), NaI (1.87 g) and chloroacetone (1 mL) was treated according to the previously described method.[31,42] Compound **7** was obtained as an off-white solid (2.0 g, 65%), mp. 140-142° .Osmometric MW ($CHCl_3$, 37°): 3500, (Calcd: 3508). IR(KBr): 1722 cm^{-1}. (C = O). ^{1}H NMR($CDCl_3$): δ 0.80-1.30 (m, 180 H, Bu^t and $COCH_3$), 3.15-4.65 (m, 80H, $ArCH_2Ar$, OCH_2C, OCH_2CH_2O, OCH_2CO), 6.50-7.40 (m, 32 H, ArH).

Anal. Calcd for $C_{225}H_{292}O_{32}$•H_2O: C, 76.62; H,8.40. Found: C,76.75; H,8.50.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure.[45] Ten mL of a 2.5 x 10^{-5} M aqueous picrate solution and 10 mL of 1 x 10^{-3} M solution of calixarene in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min then magnetically stirred in a thermostated water-bath at 25° for 1 h , and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described.[32] Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The extractability was determined based on the absorbance of picrate ion in the aqueous solution by means of the following equation :

$$\text{Extractability } (\%) = [(Ao-A)/Ao] \times 100$$

Where Ao is the absorbance in the absence of ligand.

The alkali picrates were prepared as described elsewhere[46] by stepwise addition of a 2.0×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried *in vacuo* for 24 h. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25° for 1h.

REFERENCES

1. T. E. Clevenger, *Water, Air, Soil Pollut.*, **50**, 241 (1990).
2. C. D. Gutsche, *Calixarenes*. Royal Society of Chemistry, Cambridge, 1989; *idem.*, *Calixarenes Revisited, ibid* 1998.
3. J. Vicens, V. Böhmer, *Calixarenes: A Versatile Class of Macrocyclic Compounds*. Kluver Academic, Boston, 1991.
4. M. Yilmaz, *Solution State Metal Complexes of Calixarenes and Polymeric Calixarenes: Handbook of Engineering Polymeric Materials* (N. P. Cheremisinoff, Eds.), pp. 339-350. Marcel Dekker, Inc. New York, 1997.
5. F. Arnaud-Neu, S. Barboso, F. Berny, A. Casnati, N. Muzet, A. Pinalli, R. Ungaro, M. J. Schwing-Weill and G. Wipff, *J. Chem. Soc. Perkin Trans.* 2,1727(**1999**).
6. Y. Okada, F. Ishii, Y. Kasai, J. Nishimura, *Tetrahedron Lett.*, **34**, 1971 (1993).
7. K. Araki, A. Yanagi, S. Shinkai, T*etrahedron*, **49**, 7663 (1993).
8. H. Matsumato, S. Shinkai, *Tetrahedron Lett.*, **37**, 77 (1996).
9. F. Arnaud-Neu, Z. Asfari, B. Souley, J. Vicens, *New J. Chem.*, **20**, 453 (1996).
10. H. Deligöz, M. Yilmaz, *J. Polym. Sci., Part A; Polym. Chem.*, **33**, 2851 (1995).
11. M. Yilmaz, *Reactive and Functional Polym.*, **40**, 129 (1999).
12. J. W. Steed, C. P. Johnson, C. L. Barnes, R. K. Juneja, J. L. Atwood, S. Reilly, R. L. Hollis, P. H. Smith, D. L. Clark, *J. Am. Chem. Soc.*, **117**, 11426 (1995).

13. N. T. K. Dung and R. Ludwig, *New J. Chem.*, 23,603(1999).

14. W. P. Van Hoorn, W. J. Briels, J. P. M. Van Duynhoven, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Org. Chem.*, **63**, 1299 (1998).

15. R. Seangprasertkij, Z. Asfari, F. Arnaud, J. Vicens, *J. Org. Chem.*, **59**, 1741 (1994).

16. J. Shen, H. F. Koch and D. M. Roundhill, *J. Inc. Phenom. and Macrocyclic Chem.*, **38**, 57 (2000)

17. V. Böhmer, *Angew. Chem. Int. Ed. Engl.*, **107,** 785 (1995).

18. Z. Asfari, J. Weiss, J. Vicens, *Synlett.*, 719 (**1993**).

19. O. Aleksiuk, S. E. Biali, *J. Org. Chem.*, **61**, 5670 (1996).

20. V. Böhmer, R. Dörrendacher, M. Frings, M. Heydenreich, D. Paoli, W. Vogt, G. Ferguson, I. Thondorf, *J. Org. Chem.*, **61**, 549 (1996).

21. O. Struck, V R. J. Chrisstoffels, V. Lugtenberg, W. Verboom, G. J. van Hummel, S. Harkema, D. N. Reinhoudt, *J. Org. Chem.*, **62**, 2487 (1997).

22. J. A. Perez-Adelmar, H. Abraham, C. Sanchez, K. Rissanen, P. Prados, J. de. Mendoza, *Angew. Chem. Int. Ed. Engl.*, **108**, 1088 (1996).

23. M. A. McKervey, M. Pitarch, *J. Chem. Soc.*, 1689 (**1996**).

24. A. Siepen, A. Zett, F. Vögtle, *Ann.*, 757 (**1996**).

25. J. S. Li, Y. Y. Chen and X. R. Lu, *Eur. J. Org. Chem.*, 485 (**2000**).

26. P. D.Beer and J. B.Cooper, *Chem.Commun.*, 129 (**1998**).

27. S.K. Sharma and C.D. Gutsche, *J. Org. Chem.*, **64**, 998 (1999).

28. F. Ohseto, S. Shinkai, J. Chem. Soc. Perkin Trans. 2, 1103 (**1995**).

29. W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 3037 (**1998**).

30. G. Arena. R. P. Bonomo, A. Contino, F. G. Gulino, A. Magri and D. Sciotto, *J. Inc. Phenom. and Mol. Recogn. in Chem.*, **29**, 347 (1997).

31. S. Memon, M. Yilmaz, *Separation Sci. and Tech.*, **35**, 457 (2000).

32. H. Deligöz, M. Yilmaz, *Solvent Extr. Ion. Exch.*, **13**, 19 (1995) .

33. M. Yilmaz, H. Deligöz, *Separation Sci. and Tech.*, **31**, 2395 (1996).

34. A. T. Yordanov, O. M. Falana, H. F. Koch, D. M.Roundhill, *Inorg. Chem.*, **36**, 6468 (1997).

35. N. Pelizzi, A. Casnati, A. Friggeri and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2,* 1307 (**1998**)

36. D. M. Roundhill, *Progr. Inorg. Chem.*, **43**, 533 (1995).

37. N. Iki, N. Morohashi, F. Narumi, T. Fujimoto, T. Suzuki and S. Miyano, *Tetrahedron Lett.*, **40**, 7337 (1999).

38. M. Yilmaz, *Reactive and Functional Polym.*, **40,** 129 (1999).

39. D. Xie and C. D. Gutsche, *J. Org. Chem.*, **63**, 9270 (1998).

40. A. T. Yordanov, J. T. Mague, D. M. Roundhill, *Inorg. Chim. Acta.*, **240**, 441 (1995).

41. D. M. Rudkevich, *Chem. Eur. J.*, 6 2679 (**2000**).

42. S. Memon, G. Uysal, M. Yilmaz, *Separation Sci. and Tech.*, **35**, 1247 (2000).

43. E. M. Collins, M. A. McKervey, E. Madigan, M. B. Moran, M. Owens, G. Ferguson, S. J. Harris, *J. Chem. Soc., Perkin Trans.*, 1, 3137 (**1991**).

44. S. Memon, M. Yilmaz, *Separation Sci. and Tech.*, **36**, 2785 (2001).

45. C. J. Pedersen, *Fed. Proc. Fed. Am. Soc. Expl. Biol.*, **27**, 1305 (1968).

46. F. Arnaud-Neu, M. J. Schwing-Weill, K. Ziat, S. Cremin, S. J. Harris, M. A. McKervey, *New J. Chem.*, **15**, 33 (1991).

47. S. Memon, M. Yilmaz, *Reactive and Functional Polym.*, 44, 227 (2000).

48. A. Yilmaz, S. Memon, M. Yilmaz, *J. Polym. Sci., Part A; Polym. Chem.*, **37,** 4351 (1999).

49. S. Memon, A. Yilmaz, M. Yilmaz, *J. Macromol. Sci. Part A, Pure and Appl. Chem.*, **37,** 865 (2000).

50. C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No, L. J. Bauer, *Tetrahedron,* **39**, 409 (1983).

51. S. Berthalon, J-B. R. de Vains, R. Lamartine, *Synth. Commun.*, **26**, 3103 (1996).

52. R. G. Pearson, T. L. Ho, *Chem. Rev.*, **75** (1975).