# New Lariat Ether Carboxylic and Hydroxamic Acids: Synthesis and Lanthanide Ion Complexation

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Twenty-six new lariat ether carboxylic and hydroxamic acids based upon dibenzo-13-crown-4, dibenzo-14-crown-4, dibenzo-16-crown-5 and dibenzo-19-crown-6 ring systems are synthesized and the solid-state structure for a dibenzo-19-crown-6 lariat ether hydroxamic acid is determined. The efficiency and selectivity for lanthanide ion extraction into chloroform by these proton-ionizable lariat ethers is strongly influenced by the crown ether ring size, lipophilic group attachment site and identity of the acidic function. In general, the lariat ether hydroxamic acids were more efficient and selective lanthanide ion extractants than the corresponding lariat ether carboxylic acids. The $^1$H nmr and ir binding studies indicate that both the macrocyclic polyether unit and the proton-ionizable group are involved in lanthanide ion complexation.

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## Introduction.

Host-guest chemistry continues to be an important theme in organic chemistry [1]. Molecules have been designed and constructed which mimic active sites of enzymes [2] and exhibit highly selective complexation for metal ions [3].

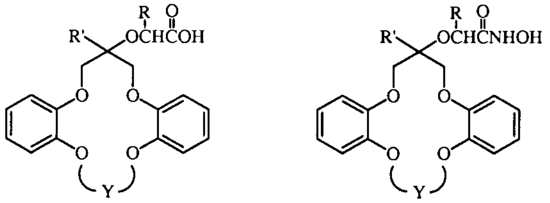
Neutral crown ethers and cryptands are widely used for complexation and selective extraction of alkali metal ions, alkaline earth metal ions and trivalent lanthanide ions [4]. In these systems, the counteranion plays an important role in determining the extraction efficiency. Thus, extractability of a metal ion-crown ether pair into the organic solvent depends strongly on the identity of the counteranion. Elimination of the need to utilize certain, highly extractable counteranion species would represent a significant advance in the area of ion separations.

Lariat ether carboxylic acids are effective chelating agents for alkali metal and alkaline earth metal cations [5]. When such ligands are employed [5a-c], an ionized group on the pendant arm provides the counteranion necessary for the transport of the cation into the organic layer. Therefore, the extraction efficiency is independent of the identity of the aqueous phase anion.

Because the separation of the lanthanide ions is difficult due to the similarities of their reactivities and their ionic radii, we have been interested in the study of host molecules which can selectively complex these ions. Previously we have observed that lanthanide [6] and actinide ions [7] may be selectively extracted into organic media by lariat ether carboxylic acids.

Hydroxamic acid compounds which contain anionic hydroxamates as bidentate groups exhibit a propensity for formation of coordination compounds [8]. Natural and synthetic siderophores with catecholate and hydroxamate chelating groups exhibit high affinites for ferric ion and for other trivalent metal ions [9-17].

These facts led us to synthesize a series of lariat ethers with pendent hydroxamic acid moieties with the goal of enhancing the extraction efficiency and selectivity of trivalent lanthanides. We recently reported that lariat ether hydroxamic acids are effective agents for the separation of $^{90}$Y from $^{90}$Sr by solvent extraction [18]. In this report, we provide full experimental details for the preparation of new lariat ether carboxylic acids **4-10, 12, 13** and **15-17** and lariat ether hydroxamic acids **18-31** (Figure 1). Results from a systematic study of the effect of structural



| Compound | R | R' | Y | Compound |
|---|---|---|---|---|
| **1** | H | H | $CH_2CH_2$ | **18** |
| **2** | H | H | $CH_2CH_2OCH_2CH_2$ | **19** |
| **3** | H | H | $CH_2(CH_2OCH_2)_2CH_2$ | **20** |
| **4** | $C_6H_5$ | H | $CH_2CH_2CH_2$ | |
| **5** | $C_{16}H_{33}$ | H | $CH_2CH_2CH_2$ | **21** |
| **6** | $C_6H_5$ | H | $CH_2CH_2OCH_2CH_2$ | **22** |
| **7** | $C_{10}H_{21}$ | H | $CH_2CH_2OCH_2CH_2$ | **23** |
| **8** | $C_{12}H_{25}$ | H | $CH_2CH_2OCH_2CH_2$ | **24** |
| **9** | $C_{14}H_{29}$ | H | $CH_2CH_2OCH_2CH_2$ | **25** |
| **10** | $C_{16}H_{33}$ | H | $CH_2CH_2OCH_2CH_2$ | **26** |
| **11** | H | $C_3H_7$ | $CH_2CH_2OCH_2CH_2$ | **27** |
| **12** | H | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ | |
| **13** | H | $c$-$C_6H_{11}$ | $CH_2CH_2OCH_2CH_2$ | **28** |
| **14** | H | $C_{10}H_{21}$ | $CH_2CH_2OCH_2CH_2$ | **29** |
| **15** | H | $C_{18}H_{37}$ | $CH_2CH_2OCH_2CH_2$ | **30** |
| **16** | $C_{10}H_{21}$ | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ | **31** |
| **17** | $C_6H_5$ | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ | |

Figure 1. Structures of the lariat ether carboxylic and hydroxamic acids.

variation within such lariat ether carboxylic and hydroxamic acids upon their ability to extract lanthanide ions are also summarized.

## Results and Discussion.

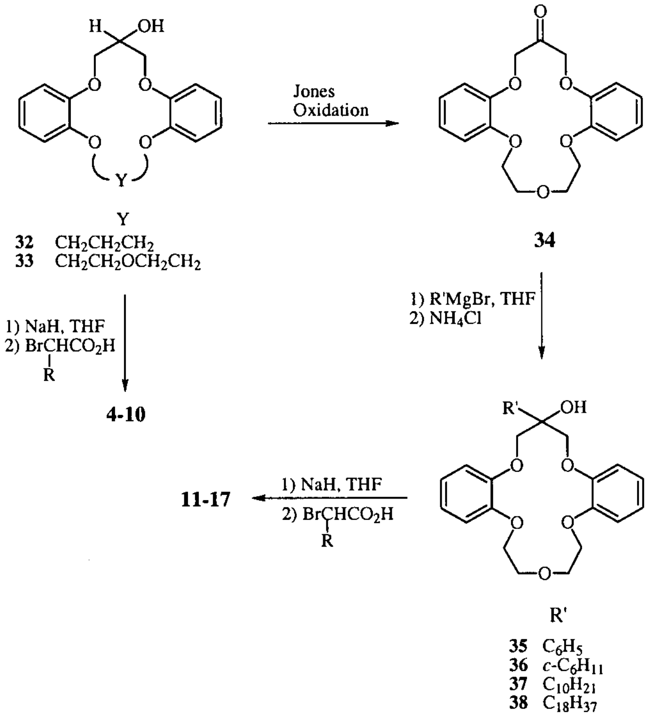
Structures of the lariat ether carboxylic acids **1-17** and hydroxamic acids **18-31** which were utilized in the study of lanthanide ion extraction are presented in Figure 1.

### Synthesis of Lariat Ether Carboxylic Acids.

Known lariat ether carboxylic acids **1-3** and **11** were prepared essentially according to the procedures of Bartsch and coworkers [5f,19]. It was noted previously that proton-ionizable macrocycles **1-3** were of insufficient lipophilicity to remain completely in the organic phase during solvent extractions of alkali metal cations. To avoid ligand loss during the extraction of lanthanide ions, a lipophilic group was attached α to the carboxylic acid group or on the polyether ring carbon geminal to the carboxylic acid-containing side arm or to both positions.

As shown in Scheme I, lariat ether alcohols **32** and **33** [20] were reacted with sodium hydride and the appropriate α-bromocarboxylic acid in tetrahydrofuran to provide lariat ether carboxylic acids **4-10** in which the lipophilic group is incorporated into the side arm. Structurally related dibenzo-16-crown-5 lariat ether carboxylic acids with R = propyl and octyl were prepared previously by Bartsch *et al.* [19] in relatively low yields (23-40%). With modification in the amounts of reactants, reaction conditions, and work-up procedure, we were able to isolate compounds **4-10** in good to excellent yields (60-80%). An important factor is the quantitative conversion of the lariat ether alcohol into the carboxylic acid, which avoids difficulties in isolation and purification of these highly lipophilic macrocyclic compounds.

Scheme I



Jones oxidation of lariat ether alcohol **33** gave the corresponding ketone **34** [21] (Scheme I). Grignard reactions of **34** produced the lipophilic lariat ether tertiary alcohols **35-38** which were transformed into lariat ether carboxylic acids **11-17** by reaction with sodium hydride and the appropriate α-bromocarboxylic acid in tetrahydrofuran at room temperature. For the preparation of lariat ether carboxylic acid **15**, quantitative conversion of the cyclic polyether alcohol **38** into the corresponding carboxylic acid avoided difficulties in the isolation and purification of this highly lipophilic compound. In the preparation of crown ether carboxylic acids **11-14**, the unreacted lipophilic lariat ether alcohols were removed easily by extraction with diethyl ether.

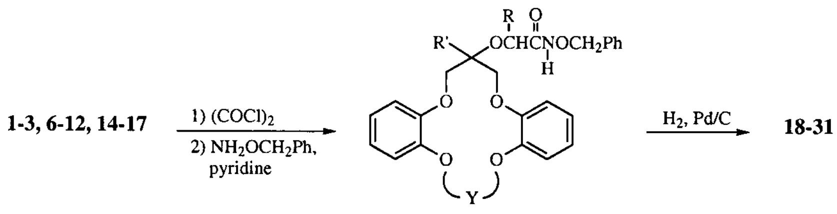
In this series of lariat ether carboxylic acids, the lipophilic group has been incorporated into the functional side arm in **4-10** or is attached to the polyether ring carbon which bears the functional side arm in **11-15**. Lariat ether **16** and **17** bear lipophilic groups on both the functional side arm and the geminal carbon.

### Synthesis of Lariat Ether Hydroxamic Acids.

Lariat ether hydroxamic acids **18-31** were prepared by three-step reactions in very good yields from the corresponding lariat ether carboxylic acids as shown in Scheme II. First, the lariat ether carboxylic acids **1-3**, **6-12** and **14-17** were converted into the corresponding acid chlorides by reaction with oxalyl chloride in benzene at 0° followed by stirring at room temperature and finally at 60-70° [22]. The reaction, as monitored by tlc, was continued until none of the starting carboxylic acid was evident. Reaction of the lariat ether acid chlorides with *O*-benzyl hydroxylamine hydrochloride and pyridine in dry acetonitrile [23] afforded the lariat ether *O*-benzyl hydroxamates **39-52.** The reactants were added at 0° and then the reaction mixture was stirred at room temperature for 24 hours. Finally, the lariat ether *O*-benzyl hydroxamates were subjected to catalytic hydrogenation under one atmosphere of hydrogen over Pd/C catalyst in methanol at room temperature to produce the corresponding lariat ether hydroxamic acids **18-31** in very good yields [23]. All of the hydroxamic acids gave positive Fe(III) tests (purple color).

Identities of the new lariat ether carboxylic acids **4-10**, **12**, **13** and **15-17** and the lariat ether hydroxamic acids **18-31** were confirmed by infrared (ir) and proton magnetic resonance ($^1$H nmr) spectroscopy and by combustion analyses. For the lariat *O*-benzyl hydroxamates **39-52** which are synthetic intermediates for the lariat ether hydroxamic acids **18-31**, spectrosopic structural verification, but no combustion analysis, was performed.

Scheme II



| Compound | R | R' | Y |
|---|---|---|---|
| **39** | H | H | $CH_2CH_2$ |
| **40** | H | H | $CH_2CH_2OCH_2CH_2$ |
| **41** | H | H | $CH_2(CH_2OCH_2)_2CH_2$ |
| **42** | $C_6H_5$ | H | $CH_2CH_2OCH_2CH_2$ |
| **43** | $C_{10}H_{21}$ | H | $CH_2CH_2OCH_2CH_2$ |
| **44** | $C_{12}H_{25}$ | H | $CH_2CH_2OCH_2CH_2$ |
| **45** | $C_{14}H_{29}$ | H | $CH_2CH_2OCH_2CH_2$ |
| **46** | $C_{16}H_{33}$ | H | $CH_2CH_2OCH_2CH_2$ |
| **47** | H | $C_3H_7$ | $CH_2CH_2OCH_2CH_2$ |
| **48** | H | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ |
| **49** | H | $C_{10}H_{21}$ | $CH_2CH_2OCH_2CH_2$ |
| **50** | H | $C_{18}H_{37}$ | $CH_2CH_2OCH_2CH_2$ |
| **51** | $C_{10}H_{21}$ | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ |
| **52** | $C_6H_5$ | $C_6H_5$ | $CH_2CH_2OCH_2CH_2$ |

### Solvent Extraction of Lanthanide Ions from Aqueous Solutions into Chloroform by Lariat Ether Carboxylic and Hydroxamic Acids.

Competitive solvent extraction of lanthanide ions from aqueous solution of lanthanide nitrates into chloroform by lariat ether carboxylic acids **1-17** and hydroxamic acids **18-31** was conducted by the previously described method [6,7]. During the extractions, no loss of the proton-ionizable lariat ether extractants from the chloroform phase to the aqueous phase was detectable. Although the detailed results from the extraction experiments will be published separately, certain trends may be presented at this time.

For lariat ether carboxylic acids **1-17**, extraction efficiencies were high and the selectivity order was Lu(III) > Ho(III) > Eu(III) > Hd(III) > La(III) with Lu(III)/La(III) extraction selectivity ratios of 25-30. Incorporation of lipophilic R and/or R' groups into the dibenzo-16-crown-5 lariat ether carboxylic acid **2** had no significant effect on the lanthanide ion extraction efficiency. On the other hand, a relationship between the ring size in the ligand and the lanthanide ion extraction efficiency was clearly evident.

Dramatic changes in both the lanthanide extraction efficiency and selectivity were observed on going to the crown hydroxamic acids **18-31** which gave Lu(III)/La(III) selectivity ratios 2-3 orders of magnitude greater than those for their carboxylic acid analogues. All of the lariat ether hydroxamic acids with either a lipophilic R or R' group showed very high extraction efficiency; whereas the presence of lipophilic groups at both the R and R' positions generally gave lower extraction efficiency. This could be explained by a preferred conformation in the former which places the hydroxamic acid group over the macrocyclic polyether cavity; whereas in the latter, unfavorable non-bonding interactions between the R and R' groups change the conformational population to an average conformation which has the hydroxamic acid function pointing away from the polyether cavity. Also, the presence of two large lipophilic groups may cause steric hindrance, which prevents the metal cation from approaching the macrocyclic cavity.

Certain of the lariat ether carboxylic and hydroxamic acids described in this paper were found to be very efficient and selective agents for the separation of $Y^{3+}$ from $Sr^{2+}$ [18]. Quantitative separation of $Y^{3+}$ from $Sr^{2+}$ was achieved over a wide *p*H range when lariat ether hydroxamic acids were employed. Alkali metal and alkaline earth metal cations were not efficiently extracted under our standard conditions (*p*H 2-8). On the other hand, both lariat ether carboxylic acid **2** and lariat ether hydroxamic acid **19** are quite efficient extractants for several of the actinide ions [7]. Hence the application of such protonionizable lariat ethers for the cleanup and recovery of hazardous radionuclides is worthy of further investigation.

The present study demonstrates that lariat ether carboxylic acids and hydroxamic acids are effective agents for lanthanide extraction. Further investigations concerning the extraction efficiency of these and related proton-ionizable lariat ether ligands are ongoing in our laboratories and progress will be reported in due course.

### Solid-state Structure of Lariat Ether Hydroxamic Acid **20**.

Suitable crystals of the dibenzo-19-crown-6 hydroxamic acid **20** were obtained and its solid-state structure was determined by X-ray diffraction. An ORTEP drawing for **20** is shown in Figure 2.

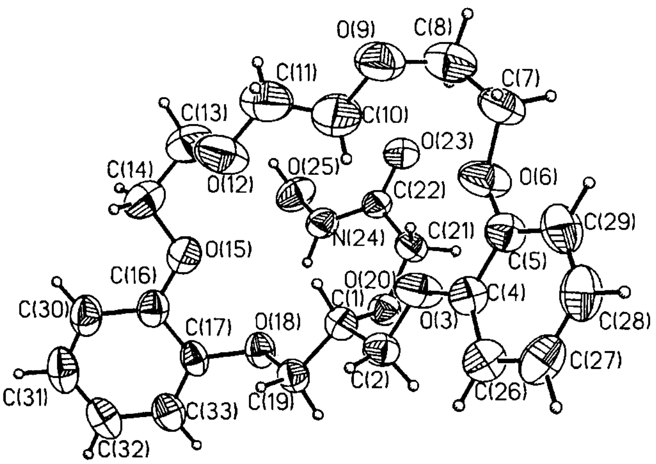


Figure 2. ORTEP drawing with 50% probability ellipsoids for solid-state structure of (*sym*-dibenzo-19-crown-6-oxy)acetylhydroxamic acid (**20**).

Hydroxamic acids can exist in several possible tautomeric forms, as well as in either *Z*- or *E*-conformations [8,24-27]. In the case of lariat ether hydroxamic acid **20**, the hydroxamic acid group appears to be in the *Z*-keto form in the solid state.

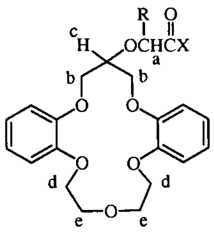
Another notable feature of this structure is the side arm orientation. The side arm in this lariat ether hydroxamic acid is located over the cyclic polyether cavity in **20**.

## Spectroscopic Studies of Lanthanide Ion Complexation by Proton-ionizable Lariat Ethers.

The $^1$H nmr and ir spectroscopies were found to be useful techniques for the study of proton-ionizable lariat ether-lanthanide ion complexes. For the nmr and ir studies, we chose the three representative proton-ionizable lariat ethers of **2**, **6** and **19**, which have the same crown ether ring size but different substituents. Resonances of methylene protons of lariat ethers **2**, **6** and **19** in deuteriochloroform were observed to shift upfield (Table 1) and broaden in the $^1$H nmr spectra of proton-ionizable lariat ether-La(III) and Lu(III) complexes due to contact or pseudo-contact interactions. All of the methylene protons are shifted significantly and broadened for complexes of **2** and **19**. For **6**, the methylene protons converged into two broad upfield resonances.

Table 1

$^1$H NMR Chemical Shifts for Proton-ionizable Lariat Ethers **2**, **6**, **19** and their Lanthanide Ion Complexes



| Compound | R | X |
|---|---|---|
| **2** | H | OH |
| **6** | $C_6H_5$ | OH |
| **19** | H | NHOH |

chemical shift (δ) of proton

| host | guest | a | b,c | d | e |
|---|---|---|---|---|---|
| **2** | none | 4.43 | 4.23 | 4.14 | 3.90 |
| **2** | $La^{3+}$ | 4.23 | 4.11 | 3.97 | 3.77 |
| **2** | $Lu^{3+}$ | 4.10 | 4.10 | 3.91 | 3.74 |
| **6** | none | 5.40 | 4.39 | 4.14 | 3.90 |
| **6** | $Lu^{3+}$ | 4.88 | 3.97 | 3.72 | 3.11 |
| **19** | none | 4.46 | 4.24 | 4.14 | 3.90 |
| **19** | $La^{3+}$ | 3.90 | 3.90 | 3.90 | 3.70 |
| **19** | $Lu^{3+}$ | 3.91 | 3.91 | 3.91 | 3.70 |

Table 2

Crystal and Refinement Data for **20**

| | |
|---|---|
| formula | $C_{23}H_{29}NO_9$ |
| crystal system | triclinic |
| space group | P 1 |
| a, Å | 8.790(4) |
| b, Å | 10.056(5) |
| c, Å | 13.125(7) |
| V Å3 | 1135.3(10) |
| Z | 2 |
| formula weight | 463.5 |
| F(000) | 492 |
| density (calc.), Mg/m$^3$ | 1.356 |
| crystal dim., mm | 0.45 x 0.5 x 0.5 |
| μ, absorption coef., mm$^{-1}$ | 0.838 |
| 2Theta (max), deg. | 110° |
| unique data | 2854 ($R_{int}$ = 1.99%) |
| unique data, $F_o > 3\sigma(F_o)$ | 2658 |
| parameters refined | 298 |
| R (observed) | 7.63 |
| R (all data) | 7.91 |
| GoF | 2.00 |

In the chemical shift data, it is seen that the methylene protons "a" adjacent to the functional groups in **2** and **19** show large chemical shift changes consistent with a closest proximity to the lanthanide ion. Also, protons "b", "c" and "d" are significantly shifted compared to the "e" protons, suggesting that the ethyleneoxy linkage (-Y- in Figure 1) is further away from the lanthanide ion. In the complex of lariat ether **6** with Lu(III), all of the protons on the macrocycle exhibited greater upfield shifts compared with those of **2** and **19**, which suggests stronger lanthanide ion complexation by **6**.

In the case of the complex of lariat ether carboxylic acid **2** and Eu(III), all of the methylene protons significantly shifted and collapsed into a single broad upfield envelope. The aromatic protons were broadened also, but relatively smaller chemical shift changes were noted. Similar nmr shifts and line broadening have been reported for the complexes of lanthanide ions and neutral crown ethers [28].

The ir spectra for the three macrocycles-lanthanide complexes are very similar in appearance. The uncomplexed proton-ionizable lariat ethers have carbonyl group asymmetric stretches at 1762, 1747 and 1678 cm$^{-1}$ for **2**, **6** and **19**, respectively. Upon complexation with La(III) or

Table 3

Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$x$10^3$) for **20**

| | X | Y | Z | U(eq) |
|---|---|---|---|---|
| C(1) | -73(3) | 4635(3) | 7187(2) | 41(1) |
| C(2) | 427(3) | 5285(3) | 8087(2) | 46(1) |
| O(3) | -895(3) | 6174(3) | 8375(2) | 65(1) |
| C(4) | -804(4) | 6998(3) | 9126(2) | 48(1) |
| C(5) | -2185(4) | 7857(3) | 9293(3) | 53(1) |
| O(6) | -3367(3) | 7776(3) | 8647(2) | 75(1) |
| C(7) | -4928(4) | 8296(4) | 8893(3) | 73(2) |
| C(8) | -5954(4) | 7584(5) | 8317(3) | 79(2) |
| O(9) | -5918(3) | 6234(3) | 8722(2) | 80(1) |
| C(10) | -4805(6) | 5256(6) | 8302(5) | 110(2) |
| C(11) | -5119(6) | 3993(6) | 8462(6) | 117(3) |
| O(12) | -3937(3) | 2941(3) | 8196(3) | 89(1) |
| C(13) | -4253(4) | 2315(5) | 7345(3) | 74(2) |
| C(14) | -2969(4) | 1191(4) | 7169(3) | 71(2) |
| O(15) | -1648(3) | 1745(2) | 6846(2) | 65(1) |
| C(16) | -364(4) | 877(3) | 6571(2) | 49(1) |
| C(17) | 848(4) | 1502(3) | 6178(2) | 44(1) |
| O(18) | 641(2) | 2894(2) | 6059(2) | 46(1) |
| C(19) | 1155(3) | 3492(3) | 6907(2) | 45(1) |
| O(20) | -360(2) | 5594(2) | 6297(1) | 43(1) |
| C(21) | -1868(3) | 6394(3) | 6200(2) | 44(1) |
| C(22) | -2930(3) | 5908(3) | 5480(2) | 42(1) |
| O(23) | -4193(2) | 6644(2) | 5224(2) | 60(1) |
| N(24) | -2460(3) | 4702(3) | 5182(2) | 49(1) |
| NH(24) | -1620 | 3961 | 5346 | 80 |
| O(25) | -3227(3) | 4257(3) | 4405(2) | 65(1) |
| OH(25) | -3331 | 3604 | 3932 | 80 |
| C(26) | 489(4) | 7003(4) | 9719(2) | 55(1) |
| C(27) | 397(5) | 7896(4) | 1047](3) | 63(1) |
| C(28) | -937(6) | 8742(4) | 10630(3) | 72(2) |
| C(29) | -2247(5) | 8728(4) | 10044(3) | 67(1) |
| C(30) | -183(5) | -527(3) | 6658(3) | 60(1) |
| C(31) | 1145(5) | -1297(4) | 6334(3) | 68(1) |
| C(32) | 2338(5) | -690(4) | 5943(3) | 65(1) |
| C(33) | 2191(4) | 716(3) | 5875(3) | 56(1) |

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 4

Bond Lengths (Å) and Bond Angles (deg) for **20**

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.511(4) | C(1)-C(19) | 1.501(4) |
| C(1)-O(20) | 1.430(3) | C(2)-O(3) | 1.407(4) |
| O(3)-C(4) | 1.361(4) | C(4)-C(5) | 1.389(4) |
| C(4)-C(26) | 1.383(5) | C(5)-O(6) | 1.365(4) |
| C(5)-C(29) | 1.377(5) | O(6)-C(7) | 1.425(4) |
| C(7)-C(8) | 1.500(7) | C(8)-O(9) | 1.402(6) |
| O(9)-C(10) | 1.409(6) | C(10)-C(11) | 1.343(9) |
| C(11)-O(12) | 1.412(6) | O(12)-C(13) | 1.390(6) |
| C(13)-C(14) | 1.482(6) | C(14)-O(15) | 1.420(5) |
| O(15)-C(16) | 1.367(4) | C(16)-C(17) | 1.401(5) |
| C(16)-C(30) | 1.385(5) | C(17)-O(18) | 1.371(3) |
| C(17)-C(33) | 1.378(4) | O(18)-C(19) | 1.429(4) |
| O(20)-C(21) | 1.421(3) | C(21)-C(22) | 1.508(4) |
| C(22)-O(23) | 1.246(3) | C(22)-N(24) | 1.307(4) |
| N(24)-NH(24) | 0.959 | N(24)-O(25) | 1.380(4) |
| O(25)-OH(25) | 0.964 | C(26)-C(27) | 1.392(5) |
| C(27)-C(28) | 1.348(6) | C(28)-C(29) | 1.392(6) |
| C(30)-C(31) | 1.370(5) | C(31)-C(32) | 1.376(6) |
| C(32)-C(33) | 1.391(5) | | |

Table 4 (continued)

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(19) | 111.5(2) | C(2)-C(1)-O(20) | 111.2(2) |
| C(19)-C(1)-O(20) | 106.8(2) | C(1)-C(2)-O(3) | 105.8(2) |
| C(2)-O(3)-C(4) | 120.5(3) | O(3)-C(4)-C(5) | 113.8(3) |
| O(3)-C(4)-C(26) | 126.0(3) | C(5)-C(4)-C(26) | 120.2(3) |
| C(4)-C(5)-O(6) | 114.6(3) | C(4)-C(5)-C(29) | 119.3(3) |
| O(6)-C(5)-C(29) | 126.0(3) | C(5)-O(6)-C(7) | 120.5(3) |
| O(6)-C(7)-C(8) | 107.7(3) | C(7)-C(8)-O(9) | 112.9(3) |
| C(8)-O(9)-C(10) | 115.6(4) | O(9)-C(10)-C(11) | 113.1(5) |
| C(10)-C(11)-O(12) | 115.7(5) | C(11)-O(12)-C(13) | 115.2(4) |
| O(12)-C(13)-C(14) | 110.5(3) | C(13)-C(14)-O(15) | 109.0(3) |
| C(14)-O(15)-C(16) | 118.2(3) | O(15)-C(16)-C(17) | 115.2(3) |
| O(15)-C(16)-C(30) | 125.6(3) | C(17)-C(16)-C(30) | 119.2(3) |
| C(16)-C(17)-O(18) | 118.9(3) | C(16)-C(17)-C(33) | 119.7(3) |
| O(18)-C(17)-C(33) | 121.3(3) | C(17)-O(18)-C(19) | 115.0(2) |
| C(1)-C(19)-O(18) | 110.0(2) | C(1)-O(20)-C(21) | 116.2(2) |
| O(20)-C(21)-C(22) | 114.4(2) | C(21)-C(22)-O(23) | 119.4(3) |
| C(21)-C(22)-N(24) | 116.5(2) | O(23)-C(22)-N(24) | 124.1(3) |
| C(22)-N(24)-NH(24) | 136.6(3) | C(22)-N(24)-0(25) | 120.6(2) |
| NH(24)-N(24)-O(25) | 102.8(2) | N(24)-O(25)-OH(25) | 152.0(2) |
| C(4)-C(26)-C(27) | 119.3(3) | C(26)-C(27)-C(28) | 120.7(4) |
| C(27)-C(28)-C(29) | 120.1(4) | C(5)-C(29)-C(28) | 120.3(3) |
| C(16)-C(30)-C(31) | 120.5(4) | C(30)-C(31)-C(32) | 120.5(3) |
| C(31)-C(32)-C(33) | 119.6(3) | C(17)-C(33)-C(32) | 120.3(3) |

Lu(III), these stretching frequencies shifted to 1616, 1616 and 1627 cm$^{-1}$, respectively. Smaller changes were observed in the C-O-C stretching absorptions of the polyether rings. A new peak appeared in the complexes near 910 cm$^{-1}$. Bunzli has reported similar observations for complexes of lanthanide ions and neutral crown ethers [29] and attributed them to interactions of the metal ion and macrocyclic polyether unit in the ligand.

## Conclusions.

Two series of new, lipophilic, proton-ionizable lariat ethers with pendant carboxylic or hydroxamic acid groups have been prepared and fully characterized.

Complexation of trivalent lanthanide ions by these proton-ionizable lariat ethers is dependent upon the molecular structure of the complexing agent. Our investigations suggest that the type of acidic functionality on the side arm markedly affects the selectivity and efficiency of solvent extraction of lanthanide ions by proton-ionizable lariat ether compounds. In particular, lariat ether hydroxamic acids exhibit excellent efficiency and selectivity in trivalent lanthanide extractions. Proton nuclear magnetic resonance ($^1$H nmr) and infrared (ir) spectroscopic studies of the proton-ionizable lariat ether-lanthanide ion complexes indicate that both the macrocyclic polyether unit and the carboxylate or hydroxamate group are involved in the metal ion complexation process.

## EXPERIMENTAL

Commercial reagents were obtained from Aldrich Chemical Company and purified by crystallization or distillation before use, as appropriate. Tetrahydrofuran was distilled from sodium and benzophenone. *sym*-Dibenzo-13-crown-4-oxyacetic acid (**1**) [20], *sym*-dibenzo-16-crown-5-oxyacetic acid (**2**) [20], *sym*-dibenzo-19-crown-6-oxyacetic acid (**3**) [20], *sym*-(propyl)dibenzo-16-crown-5-oxyacetic acid (**11**) [5f], *sym*-(hydroxy)dibenzo-13-crown-4 (**32**) [20], *sym*-(hydroxy)dibenzo-16-crown-5 (**33**) [20], *sym*-(keto)dibenzo-16-crown-5 (**34**) [21], and *sym*-(hydroxy)(propyl)dibenzo-16-crown-5 [5f] were prepared by the reported procedures.

The proton nuclear magnetic resonance (nmr) spectra were obtained with a Bruker AF 200 Instrument (200 MHz for $^1H$). Infrared (ir) spectra were measured with a Digilab FTS-80 spectrophotometer and are reported in wave numbers ($cm^{-1}$). Mass spectra (ms) were obtained with a VG Micromass 70/70 HS mass spectrometer. Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. For tlc analysis, Merck precoated tlc plates (silica gel 60 F254) were used. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

### General Procedure for the Preparation of Lariat Ether Alcohols **35-38.**

A 100 ml round bottom flask was charged with 20 mmoles of the appropriate Grignard reagent solution (*ca.* 1-2 *M* in tetrahydrofuran) and a solution of 3.45 g (10 mmoles) of *sym*-(keto)dibenzo-16-crown-5 in 40 ml of tetrahydrofuran was added at room temperature.

The reaction mixture was heated to reflux for 5 hours. (For **36**, the reaction mixture was allowed to stir at room temperature for an additional hour). After cooling to room temperature, 20 ml of 5% ammonium chloride was added and stirring was continued overnight. The tetrahydrofuran was evaporated and the aqueous solution was extracted with diethyl ether (2 x 50 ml). The combined organic layers were dried over sodium sulfate and evaporated *in vacuo*. Although combustion analyses were not obtained for lariat ether alcohols **35-38**, satisfactory combustion analysis results were obtained for each lariat ether carboxylic acid which was prepared from these precursors.

### *sym*-(Hydroxy)(phenyl)dibenzo-16-crown-5 (**35**).

After stirring for 1 hour in pentane, a white solid was obtained in 90% yield with mp 87.5-88.5°; ir (potassium bromide): ν 3456 (OH) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 3.83 (s, 1H), 3.87-4.19 (m, 8H), 4.2-4.48 (q, 4H, J = 9.6 Hz), 6.77-6.91 (m, 8H), 7.31-7.43 (m, 3H), 7.74-7.77 (m, 2H).

### *sym*-(Cyclohexyl)(hydroxy)dibenzo-16-crown-5 (**36**).

After stirring for several hours in pentane, a white solid was obtained in 74% yield with mp 85-87°; ir (potassium bromide): ν 3464 (OH) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 1.05-1.36 (m, 5H), 1.64-1.84 (m, 3H), 2.00-2.30 (m, 3H), 3.22 (s, 1H), 3.82-4.28 (m, 10H), 4.26-4.29 (d, 2H, J = 9 Hz), 6.81-6.98 (m, 8H).

### *sym*-(Decyl)(hydroxy)dibenzo-16-crown-5 (**37**).

After stirring for 1 hour in pentane, a white solid was obtained in 85% yield with mp 87-88° (lit mp [30] 82-83°); ir (potassium bromide): ν 3456 (OH) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.18 (s, 16H), 1.79-1.87 (m, 2H), 3.25 (s, 1H), 3.87-4.37 (m, 12H), 6.81-6.97 (m, 8H).

### *sym*-(Hydroxy)(octadecyl)dibenzo-16-crown-5 (**38**).

After stirring for 1 hour in pentane, a white solid was obtained in 89% yield with mp 68-70°; ir (potassium bromide): ν 3458 (OH) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.23 (s, 32H), 1.78-1.87 (m, 2H), 3.51 (s, 1H), 3.87-4.23 (m, 12H), 6.81-6.97 (m, 8H).

### General Procedure for the Preparation of Lariat Ether Carboxylic Acids **4-17**.

Tetrahydrofuran (50 ml) was added to 2.40 g (100 mmoles) of dry sodium hydride under nitrogen. After the mixture was stirred for 30 minutes at room temperature, the appropriate lariat ether alcohol (10 mmoles) dissolved in 80 ml of tetrahydrofuran was added dropwise over a 1 hour period. The reaction mixture was stirred at room temperature for an additional hour and 15 mmoles of the appropriate 2-bromocarboxylic acid dissolved in 80 ml of tetrahydrofuran was added dropwise over a period of 3-4 hours. The reaction mixture was stirred at room temperature for 12 hours, at which time the reaction was monitored by tlc. If tlc indicated incomplete reaction, additional 2-bromocarboxylic acid dissolved in 20 ml of tetrahydrofuran was added during a 1 hour period and the reaction mixture was stirred for an additional 5.5 hours at room temperature. After the reaction was completed, careful addition of water was followed by evaporation of the tetrahydrofuran *in vacuo*. To the residue, 100 ml of water was added and the aqueous mixture was acidified with aqueous 6 *N* hydrochloric acid and extracted with dichloromethane. The combined organic layers were washed with water, dried over magnesium sulfate, and evaporated *in vacuo*. The residual oil was treated with hexane and cooled to 0°. The resulting solid was purified by recrystallization or column chromatography to give the product.

### α-(*sym*-Dibenzo-14-crown-4-oxy)phenyl acetic acid (**4**).

Recrystallization from hexane gave a 60% yield of a white solid with mp 69-71°; ir (potassium bromide): ν 3410 (br, COOH), 1751, 1724 (C=O) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 4.13-4.54 (m, 11H), 5.26 (s, 1H), 6.80-6.99 (m, 8H), 7.00-7.44 (m, 5H).

*Anal.* Calcd. for $C_{26}H_{26}O_7$: C, 69.32; H, 5.81. Found: C, 69.08; H, 5.72.

### 2-(*sym*-Dibenzo-14-crown-4-oxy)octadecanoic Acid (**5**).

Recrystallization from methanol provided a white solid in 60% yield with mp 66-68°; ir (potassium bromide): ν 3437 (br, COOH), 1728, 1700 (C=O) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 0.82-0.89 (t, 3H, J = 6 Hz), 1.24 (s, 26H), 1.78-1.85 (q, 2H, J = 6 Hz), 2.26-2.31 (m, 2H), 4.18-4.26 (m, 11H), 4.50-4.53 (dd, 1H, J = 3, 12 Hz), 6.82-7.03 (m, 8H).

*Anal.* Calcd. for $C_{36}H_{54}O_7$: C, 72.20; H, 9.08. Found: C, 72.18; H, 8.90.

### α-(*sym*-Dibenzo-16-crown-5-oxy)phenyl acetic Acid (**6**).

Recrystallization from ethyl acetate-hexane gave a white solid in 76% yield with mp 127-128.5°; ir (potassium bromide): ν 3437 (br, COOH), 1762, 1751 (C=O) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 3.87-4.51 (m, 13H), 5.42 (s, 1H), 6.78-7.06 (m, 8H), 7.34-7.36 (m, 3H), 7.48-7.51 (m, 2H).

*Anal.* Calcd. for $C_{27}H_{28}O_8$: C, 67.49; H, 5.87. Found: C, 67.47; H, 5.67.

### 2-(*sym*-Dibenzo-16-crown-5-oxy)dodecanoic Acid (**7**).

Recrystallization from hexane gave an 80% yield of a white solid with mp 69-70°; ir (potassium bromide): ν 3423 (br, OH), 1728, 1697 (C=O) $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 0.84-

0.87 (t, 3H, J = 6 Hz), 1.28 (br s, 14H), 1.48-1.53 (q, 2H, J = 6 Hz), 1.80-1.9 (m, 2H), 3.83-4.30 (m, 13H), 4.53-4.57 (dd, 1H, J = 3, 12 Hz), 6.82-7.07 (m, 8H).

*Anal.* Calcd. for $C_{31}H_{44}O_8 \cdot 0.3H_2O$: C, 67.71; H, 8.11. Found: C, 67.70; H, 8.20.

### 2-(*sym*-Dibenzo-16-crown-5-oxy)tetradecanoic Acid (**8**).

Recrystallization from hexane gave a white solid in 66% yield with mp 78-78.5°; ir (potassium bromide): ν 3429 (COOH), 1726, 1699 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.84-0.86 (t, 3H, J = 6 Hz), 1.23 (br s, 18H), 1.41-1.53 (q, 2H, J = 6 Hz), 1.81-1.90 (m, 2H), 3.87-4.30 (m, 13H), 4.56-4.59 (dd, 1H, J = 3, 12 Hz), 6.80-7.07 (m, 8H).

*Anal.* Calcd. for $C_{33}H_{48}O_8$: C, 69.20; H, 8.44. Found: C, 68.99; H, 8.59.

### 2-(*sym*-Dibenzo-16-crown-5-oxy)hexadecanoic Acid (**9**).

Recrystallization from hexane produce a 70% yield of a white solid with mp 78-80°; ir (potassium bromide): ν 3442 (br, COOH), 1726, 1697 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.84-0.88 (t, 3H, J = 6 Hz), 1.28 (br s, 22H), 1.47-1.82 (q, 2H, J = 6 Hz), 1.83-1.90 (m, 2H), 3.86-4.31 (m, 13H), 4.57-4.61 (dd, 1H, J = 3, 12 Hz), 6.82-7.07 (m, 8H).

*Anal.* Calcd. for $C_{35}H_{52}O_8$: C, 69.97; H, 8.72. Found: C, 70.12; H, 8.70.

### 2-(*sym*-Dibenzo-16-crown-5-oxy)octadecanoic Acid (**10**).

Recrystallization from hexane gave a 64% yield of a white solid with mp 65.5-67°; ir (potassium bromide): ν 3433 (br, COOH), 1728, 1697 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.84-0.88 (t, 3H, J = 6 Hz), 1.23 (br s, 26H), 1.46-1.50 (q, 2H, J = 6 Hz), 1.82-1.90 (m, 2H), 3.87-4.30 (m, 13H), 4.56-4.59 (dd, 1H, J = 3, 12 Hz), 6.83-7.07 (m, 8H).

*Anal.* Calcd. for $C_{37}H_{56}O_8$: C, 70.67; H 8.97. Found: C, 70.82; H, 9.26.

### *sym*-(Phenyl)dibenzo-16-crown-5-oxyacetic Acid (**12**).

Recrystallization from ethyl acetate-hexanes gave a white solid in 71% yield with mp 170.5-172°; ir (potassium bromide): ν 3425 (COOH), 1728 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.82-4.30 (m, 10H), 4.76-4.81 (d, 2H, J = 6 Hz), 4.89 (s, 2H), 6.67-6.97 (m, 8H), 7.37-7.50 (m, 3H), 7.61-7.65 (m, 2H).

*Anal.* Calcd. for $C_{27}H_{28}O_8$: C, 67,49; H, 5.87. Found: C, 67.70; H, 5.79.

### *sym*-(Cyclohexyl)dibenzo-16-crown-5-oxyacetic Acid (**13**).

Recrystallization from ethyl acetate-hexanes gave a white solid in 26% yield with mp 155-157°; ir (potassium bromide): ν 3421 (COOH), 1770, 1728, 1701 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 1.10-1.41 (m, 6H), 1.74-1.98 (m, 3H), 2.04-2.24 (t, 2H, J = 6 Hz), 3.69-4.05 (m, 10H), 4.59-4.64 (d, 2H, J = 10 Hz), 4.85 (s, 2H), 6.77-6.99 (m, 8H).

*Anal.* Calcd. for $C_{27}H_{34}O_8$: C, 66.65; H, 7.04. Found: C, 66.36; H, 6.82.

### *sym*-(Decyl)dibenzo-16-crown-5-oxyacetic Acid (**14**).

The oil was crystallized from hexane by keeping the hexane solution overnight in a refrigerator to give a 78% yield of a white solid with mp 102-103° (lit mp [5e] 102-102.5°); ir (potassium bromide): ν 3417 (COOH), 1732 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.83-0.89 (t, 3H, J = 6 Hz), 1.27 (s, 16H), 1.89-1.94 (m, 2H), 3.79-4.26 (m, 10H), 4.54-4.59 (d, 2H, J = 10 Hz), 4.82 (s, 2H), 6.77-6.98 (m, 8H).

*Anal.* Calcd. for $C_{31}H_{44}O_8$: C, 68.36; H, 8.14. Found: C, 68.30; H, 7.96.

### *sym*-(*n*-Octadecyl)dibenzo-16-crown-5-oxyacetic Acid (**15**).

The yellow-brown oil was dissolved in hexane and the solution was placed in a refrigerator for several hours to produce a white solid in 89% yield with mp 101-103°; ir (potassium bromide): ν 3425 (COOH), 1730 (C=O); $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.23 (s, 32H), 1.80-1.94 (m, 2H), 3.79-4.16 (m, 10H), 4.54-4.60 (d, 2H, J = 10 Hz, 4.82 (s, 2H), 6.78-6.99 (m, 8H).

*Anal.* Calcd. for $C_{39}H_{60}O_8$: C, 71.30; H, 9.20. Found: C, 71.57; H, 9.39.

### α-[*sym*-(Decyl)dibenzo-16-crown-5-oxy]phenylacetic Acid (**16**).

Column chromatography on silica gel with dichloromethane-methanol (9:1) as eluent gave an oil which solidified on standing to provide an 86% yield of a white solid with mp 46-48°; ir (potassium bromide): ν 3346 (COOH), 1762, 1724 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.83-0.90 (t, 3H, J = 6 Hz), 1.25 (s, 16H), 1.89-1.99 (m 2H), 3.82-4.21 (m, 10H), 4.40-4.46 (d, 1H, J = 10 Hz), 4.77-4.82 (d, 1H, J = 10 Hz), 6.12 (s, 1H); 6.62-6.98 (m, 8H), 7.19-7.24 (m, 3H), 7.40-7.45 (m, 2H).

*Anal.* Calcd. for $C_{37}H_{48}O_8$: C, 71.58; H, 7.79. Found: C, 71.84; H, 7.73.

### α-[*sym*-(Phenyl)dibenzo-16-crown-5-oxy]phenylacetic Acid (**17**).

Recrystallization from ethyl acetate-hexane gave a 97% yield of white solid with mp 177-178°; ir (potassium bromide): ν 3383 (COOH), 1759 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.86-4.38 (m, 10H), 4.78-4.87 (t, 2H, J = 6 Hz), 6.15 (s, 1H), 6.56-6.95 (m, 8H), 7.24-7.61 (m, 10H).

*Anal.* Calcd. for $C_{33}H_{32}O_8$: C, 71.21; H, 5.79. Found: C, 71.09; H, 5.78.

### General Procedure for the Preparation of Lariat Ether *O*-Benzyl Hydroxamates **39-52.**

The lariat ether carboxylic acid (5.0 mmoles) was added to dry benzene (10 ml) under nitrogen. After cooling to 0°, oxalyl chloride (2.50 g, 20 mmoles) was added dropwise. The solution was stirred at room temperature for one hour, heated at 60° for one hour, and evaporated *in vacuo* to give the corresponding lariat ether acid chloride which was used immediately in the next step. *O*-Benzyl hydroxylamine hydrochloride (800 mg, 5.0 mmoles) was suspended in dry acetonitrile (10 ml) and pyridine (0.80 ml, 10 mmoles) was added.

The mixture was cooled to 0° and an acetonitrile solution of the lariat ether acid chloride was added dropwise. The mixture was allowed to warm to room temperature and was then stirred at room temperature for 24 hours. The mixture was evaporated *in vacuo* and the residue dissolved in ethyl acetate. The organic solution was washed with 0.6 *N* hydrochloric acid, water, 0.6 *M* aqueous sodium bicarbonate and water, dried over magnesium sulfate, and evaporated *in vacuo* to produce the lariat ether *O*-benzyl hydroxamate. Combustion analyses were not performed for the lariat ether *O*-benzyl hydroxamates, but satisfactory combustion analysis results were obtained for each of the subsequent lariat ether hydroxamic compounds.

*O*-Benzyl *sym*-Dibenzo-13-crown-4-oxyacetohydroxamate (**39**).

This compound was obtained as a white solid with mp 95-97° in 80% yield; ir (deposit from dichloromethane solution on a sodium chloride plate): ν 3279 (NH), 1693 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.81-4.38 (m, 11H), 4.81 (s, 2H), 6.87-7.10 (m, 13H), 9.96 (br s, 1H); ms: (70 eV, electron impact): m/z 465 (5% relative intensity, M$^+$), 359 (21.6, M-PhCHO), 136 (100), 121 (71), 107 (35.6), 91 (69.7), 77 (57), 65 (23.5).

*O*-Benzyl *sym*-Dibenzo-16-crown-5-oxyacetohydroxamate (**40**).

A white solid with mp 112-114° was isolated in 83% yield; ir (potassium bromide): ν 3275 (NH), 1689 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 4.25-4.62 (m, 13H), 4.73 (s, 2H), 5.31 (s, 2H), 7.20-7.42 (m, 8H), 7.62-7.66 (m, 5H), 10.66 (br s, 1H); ms: (70 eV, electron impact): m/z 509 (2% relative intensity, M$^+$), 403 (27.9, M-PhCHO), 360 (10), 175 (21), 149 (34), 136 (100), 107 (49.8), 91 (62).

*O*-Benzyl *sym*-Dibenzo-19-crown-6-oxyacetohydroxamate (**41**).

This compound was obtained in 84% yield as an oil; ir (neat): ν 3296 (NH), 1693 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.66-4.19 (m, 17H), 4.36 (s, 2H), 4.86 (s, 2H), 6.83-6.98 (m, 8H), 7.19-7.30 (m, 5H), 10.15 (br s, 1H); ms: (70 eV, electron impact): m/z 553 (3.7% relative intensity, M$^+$), 447 (29.9, M-PhCHO), 389 (17), 171 (18.6), 136 (100), 121 (88.6), 91 (60.2), 77 (81.4), 65 (28).

*O*-Benzyl α-(*sym*-Dibenzo-16-crown-5-oxy)phenylacetohydroxamate (**42**).

After recrystallization from ethyl acetate-hexane, a white solid with mp 128-130° was obtained in 74% yield; ir (potassium bromide): ν 3262 (NH), 1666 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.93-4.80 (m, 13H), 4.85 (s, 2H), 5.27 (s, 1H), 6.75-7.05 (m, 8H), 7.31-7.50 (m, 10H), 10.63 (br s, 1H).

*O*-Benzyl 2-(*sym*-Dibenzo-16-crown-5-oxy)dodecanohydroxamate (**43**).

After recrystallization form methanol, a 69% yield of white solid with mp 79-81° was obtained; ir (potassium bromide): ν 3275 (NH), 1689 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.24 (s, 14H), 1.42-1.45 (q, 2H, J = 6 Hz), 1.69-1.89 (m, 2H), 3.80-4.16 (m, 13H), 4.59-4.63 (dd, 1H, J = 3, 12 Hz), 4.88 (s, 2H), 6.79-7.02 (m, 8H), 7.22-7.32 (m, 5H), 10.50 (s, 1H).

*O*-Benzyl 2-(*sym*-Dibenzo-16-crown-5-oxy)tetradecanohydroxamate (**44**).

Recrystallization from methanol provided a white solid in 73% yield with mp 77-78°; ir (potassium bromide): ν 3271 (NH), 1685 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.23 (s, 18H), 1.68-1.73 (q, 2H, J = 6 Hz), 1.86 (m, 2H), 3.80-4.16 (m, 13H), 4.59-4.63 (dd, 1H, J = 3, 12 Hz), 4.88 (s, 2H), 6.79-7.03 (m, 8H), 7.05-7.33 (m, 5H), 10.51 (s, 1H).

*O*-Benzyl 2-(*sym*-Dibenzo-16-crown-5-oxy)hexadecanohydroxamate (**45**).

After recrystallization from methanol, a white solid with mp 77-78° was realized in 79% yield; ir (potassium bromide): ν 3266 (NH), 1685 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.23 (s, 22H), 1.62-1.73 (q, 2H, J = 6 Hz), 1.86-1.88 (m, 2H), 3.80-4.17 (m, 13H), 4.59-4.63 (dd, 1H, J = 3, 12 Hz), 4.88 (s, 2H), 6.79-7.03 (m, 8H), 7.22-7.31 (m, 5H), 10.51 (s, 1H).

*O*-Benzyl 2-(*sym*-Dibenzo-16-crown-5-oxy)octadecanohydroxamate (**46**).

Recrystallization from acetonitrile provided a 76% yield of a white solid with mp 75-77°; ir (potassium bromide): ν 3232 (NH), 1654 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.83-0.87 (t, 3H, J = 6 Hz), 1.22 (s, 26H), 1.43-1.48 (q, 2H, J = 6 Hz), 1.86-1.93 (m, 2H), 3.48-4.53 (m, 13H), 4.63-4.87 (dd, 1H, J = 3, 12 Hz), 4.87 (s, 2H), 6.85-7.03 (m, 8H), 7.28- 7.85 (m, 5H), 9.63 (s, 1H).

*O*-Benzyl 2-[*sym*-(Propyl)dibenzo-16-crown-5-oxylacetohydroxamate (**47**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent gave a colorless oil in 66% yield; ir (neat): ν 3155 (NH), 1670 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.95-1.03 (t, 3H, J = 8 Hz), 1.38-1.43 (m, 2H), 1.77-1.86 (m, 2H), 3.61-4.15 (m, 10H), 4.46-4.51 (d, 2H, J = 10 Hz), 4.72 (s, 2H), 4.85 (s, 2H), 6.79-6.97 (m, 8H), 7.28-7.35 (m, 5H), 9.38 (br s, 1H).

*O*-Benzyl 2-[*sym*-(Phenyl)dibenzo-16-crown-5-oxy]acetohydroxamate (**48**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent and recrystallization from ethyl acetate-hexanes gave a 79% yield of a white solid with mp 136-138°; ir (potassium bromide): ν 3402 (NH), 1708 (C=O) cm$^{-1}$: $^1$H nmr (deuteriochloroform): δ 3.83-4.27 (m, 10H), 4.68-4.73 (d, 2H, J = 10 Hz), 4.80 (s, 2H), 4.87 (s, 2H), 6.67-6.92 (m, 8H), 7.30-7.49 (m, 10H), 9.50 (br s, 1H).

*O*-Benzyl [*sym*-(Decyl)dibenzo-16-crown-5-oxy]acetohydroxamate (**49**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent gave a 92% yield of a colorless oil; ir (neat): ν 3163 (NH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.84-0.87 (t, 3H, J = 6 Hz), 1.27 (s, 16H), 1.81-2.02 (m, 2H), 3.83-4.72 (m, 10H), 4.68-4.73 (d, 2H, J = 10 Hz), 4.80 (s, 2H), 4.87 (s, 2H), 6.67-6.92 (m, 8H), 7.30-7.49 (m, 5H), 9.50 (br s, 1H).

*O*-Benzyl [*sym*-(Octadecyl)dibenzo-16-crown-5-oxy]acetohydroxamate (**50**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent provided a colorless oil in 88% yield; ir (neat): ν 3333 (NH), 1697 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.23 (s, 32H), 1.80-1.93 (m, 2H), 3.79-4.21 (m, 10H), 4.44-4.49 (d, 2H, J = 10 Hz), 4.69 (s, 2H), 4.83 (s, 2H), 6.77-6.97 (m, 8H), 7.21-7.32 (m, 5H), 9.36 (br s, 1H).

*O*-Benzyl α-[sym-(Decyl)dibenzo-16-crown-5-oxy]phenylacetohydroxamate (**51**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent gave a colorless oil in 93% yield; ir (neat): ν 3333 (NH), 1697 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.89 (t, 3H, J = 6 Hz), 1.24 (s, 16H), 1.82 (m, 2H), 3.80-4.13 (m, 10H), 4.24-4.29 (d, 1H, J = 10 Hz), 4.61-4.66 (d, 1H, J = 10 Hz), 4.80 (s, 2H), 5.88 (s, 1H), 6.61-6.99 (m, 8H), 7.20-7.42 (m, 10H), 9.95 (br s, 1H).

*O*-Benzyl α-[*sym*-(Phenyl)dibenzo-16-crown-5-oxy]phenylacetohydroxamate (**52**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent and recrystallization from ethyl acetate-hexanes gave a 92% yield of a white solid with mp 84-86°; ir (potassium bromide): ν 3371 (NH), 1697 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.81-4.16 (m, 10H), 4.55-4.58 (d, 1H, J = 9 Hz), 4.81 (s, 2H); 4.84-4.87 (d, 1H, J = 9 Hz), 5.96 (s, 1H), 6.56-6.97 (m, 8H), 7.21-7.57 (m, 15H), 9.98 (br s, 1H).

General Procedure for the Preparation of Lariat Ether Hydroxamic Acids **18-31.**

The lariat ether *O*-benzyl hydroxamate (4.0 mmoles) in methanol (150 ml) was stirred under one atmosphere of hydrogen at room temperature in the presence of 10% Pd/C (200 mg) for 3-10 hours until no starting material was detectable by tlc (longer reduction times were required for hydroxamates with lipophilic R groups). The catalyst was filtered and the methanol was evaporated *in vacuo*. The crude lariat ether hydroxamic acids were purified by recystallization or by column chromatography on silica gel. All of the hydroxamic acids gave positive Fe(III) tests (purple color).

(*sym*-Dibenzo-13-crown-4-oxy)acetylhydroxamic Acid (**18**).

Recrystallization from methanol gave a 72% yield of a white solid with mp 136-137°; ir (potassium bromide): ν 3356, 3244 (NHOH), 1666 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.85-4.38 (m, 11H), 6.88-7.07 (m, 8H), 10.09 (br s, 1H).

*Anal.* Calcd. for $C_{19}H_{21}NO_7$: C, 60.79; H, 5.63; N, 3.73. Found: C, 60.97; H, 5.59; N, 3.60.

(*sym*-Dibenzo-16-crown-5-oxy)acetylhydroxamic Acid (**19**).

Recrystallization from methanol gave an 87% yield of white solid with mp 108-110°; ir (potassium bromide): ν 3433, 3279 (NHOH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.91-4.24 (m, 13H), 4.37 (s, 2H), 6.80-6.98 (m, 8H), 10.51 (br s, 1H).

*Anal.* Calcd. for $C_{21}H_{25}NO_8 \cdot 0.5H_2O$: C, 58.87; H, 6.11; N, 3.27. Found: C, 58.87; H, 5.88; N, 3.56.

(*sym*-Dibenzo-19-crown-6-oxy)acetylhydroxamic Acid (**20**).

Recrystallization from methanol produced a white solid in 88% yield with mp 134-135°; ir (potassium bromide): ν 3402, 3136 (NHOH), 1662 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.46-4.22 (m, 17H), 4.41 (s, 2H), 6.85-7.01 (m, 8H), 10.37 (br s, 1H).

*Anal.* Calcd. for $C_{23}H_{29}NO_9$: C, 59.60; H, 6.30; N, 3.02. Found: C, 59.74; H, 6.34; N, 3.07.

α-(*sym*-Dibenzo-16-crown-5-oxy)phenylacetylhydroxamic Acid (**21**).

A 95% yield of white solid with mp 138-140° was realized after recrystallization from ethyl acetate-hexane; ir (potassium bromide): ν 3433, 3209 (NHOH), 1654 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.88-4.52 (m, 13H), 5.29 (s, 1H), 6.77-6.92 (m, 8H), 7.09-7.34 (m, 3H), 7.43-7.48 (m, 2H), 10.62 (br s, 1H).

*Anal.* Calcd. for $C_{27}H_{29}NO_8$: C, 65.44; H, 5.89; N, 2.82. Found: C, 65.32; H, 6.01; N, 2.84.

2-(*sym*-Dibenzo-16-crown-5-oxy)dodecanoylhydroxamic Acid (**22**).

After recrystallization from methanol, a 75% yield of white solid with mp 64-66° was obtained; ir (potassium bromide): ν 3410, 3309 (NHOH), 1670 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.81-0.89 (t, 3H, J = 6 Hz), 1.22 (br s, 14H), 1.47-1.70 (q, 2H, J = 6 Hz), 1.75-1.89 (m, 2H), 3.87-4.29 (m, 13H), 4.60-4.64 (dd, 1H, J = 3, 12 Hz), 6.81-7.13 (m, 8H), 10.80 (br s, 1H).

*Anal.* Calcd. for $C_{31}H_{45}NO_8$: C, 66.52; H, 8.10; N, 2.50. Found: C, 66.38; H, 8.21; N, 2.49.

2-(*sym*-Dibenzo-16-crown-5-oxy)tetradecanoylhydroxamic Acid (**23**).

Recrystallization from methanol gave a 77% yield of white solid with mp 62-64°; ir (potassium bromide): ν 3390, 3282 (NHOH), 1670 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.22 (br s, 18H), 1.75 (q, 2H, J = 6 Hz), 1.89 (m, 2H), 3.87-4.25 (m, 13H), 4.60-4-64 (dd, 1H, J = 3, 12 Hz), 6.86-7.13 (m, 8H), 10.95 (br s, 1H).

*Anal.* Calcd. for $C_{33}H_{49}NO_8$: C, 67.43; H, 8.40; N, 2.38. Found: C, 67.78; H, 8.38; N, 2.25.

2-(*sym*-Dibenzo-16-crown-5-oxy)hexadecanoylhydroxamic Acid (**24**).

Recrystallization from methanol provided a white solid with mp 74-76° in 79% yield; ir (potassium bromide): ν 3414, 3302 (NHOH),. 1670 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.88 (t, 3H, J = 6 Hz), 1.22 (br s, 22H), 1.70-1.75 (q, 2H, J = 6 Hz), 1.89 (m, 2H), 3.87-4.29 (m, 13H), 4.59-4.63 (dd, 1H, J = 3, 12 Hz), 6.81-7.13 (m, 8H), 10.95 (br s, 1H).

*Anal.* Calcd. for $C_{35}H_{53}NO_8$: C, 68.26; H, 8.67; N, 2.27. Found: C, 68.62; H, 8.69; N, 2.16.

2-(*sym*-Dibenzo-16-crown-5-oxy)octadecanoylhydroxamic Acid (**25**).

A white solid with mp 51-53° was obtained in 74% yield after recrystallization from methanol; ir (potassium bromide): ν 3429, 3266 (NHOH), 1670 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.87 (t, 3H, J = 6 Hz), 1.14 (br s, 26H), 1.45-1.49 (q, 2H, J = 6 Hz), 1.82-1.91 (m, 2H), 3.45-4.24 (m, 13H), 4.50-4.57 (dd, 1H, J = 3, 12 Hz), 6.82-7.04 (m, 8H), 10.72 (br. s, 1H).

*Anal.* Calcd. for $C_{37}H_{57}NO_8$: C, 69.02; H, 8.92; N, 2.17. Found: C, 69.07; H, 8.93; N, 2.31.

α-[*sym*-(Propyl)dibenzo-16-crown-5-oxy]acetylhydroxamic Acid (**26**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent gave an oil which solidified on standing to provide a 93% yield of a white solid with mp 69-71°; ir (potassium bromide): ν 3412 (OH), 3205 (NH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform); δ 1.00-1.07 (t, 3H, J = 8H), 1.38-1.54 (m, 2H), 1.84-2.02 (m, 2H), 3.47-4.26 (m, 10H), 4.50-4.55 (d, 2H, J = 10 Hz), 4.78 (s, 2H), 6.80-7.07 (m, 8H), 9.56 (br s, 1H).

*Anal.* Calcd. for $C_{24}H_{31}NO_8$: C, 62.46; H, 6.77. Found: C, 62.59; H, 6.69.

α-[*sym*-(Phenyl)dibenzo-16-crown-5-oxy]acetylhydroxamic Acid (**27**).

After recrystallization from ethyl acetate-hexanes, an 85% yield of white solid with mp 153-155° was realized; ir (potassium bromide): ν 3410 (OH), 3252 (NH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 3.84-4.20 (m, 10H), 4.71-4.75 (d, 2H, J = 10 Hz), 4.80 (s, 2H), 6.68-6.96 (m, 8H), 7.36-7.41 (m, 3H), 7.45-7.58 (m, 2H), 9.80 (s, 1H).

*Anal.* Calcd. for $C_{27}H_{29}NO_8$: C, 65.44; H, 5.89; N, 2.82. Found: C, 65.47; H, 5.85; N, 2.56.

### α-[sym-(Decyl)dibenzo-16-crown-5-oxy]acetylhydroxamic Acid (**28**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent gave a 73% yield of a colorless oil which solidified upon drying under vacuum to give a white solid with mp 41-42°; ir (potassium bromide): ν 3417 (OH), 3213 (NH), 1678 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.83-0.86 (t, 3H, J = 6 Hz), 1.16 (s, 16H), 1.87-2.09 (m, 2H), 3.78-4.13 (m, 10H), 4.48-4.53 (d, 2H, J = 10 Hz), 4.64 (s, 2H), 6.77-6.96 (m, 8H), 9.52 (s, 1H).

*Anal.* Calcd. for $C_{31}H_{45}NO_8$: C, 66.52; H, 8.10; N, 2.50. Found: C, 66.56; H, 8.02; N, 2.54.

### α-[*sym*-(Octadecyl)dibenzo-16-crown-5-oxy]acetylhydroxamic Acid (**29**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent provided a colorless oil in 73% yield; ir (deposit from dichloromethane solution of a sodium chloride plate): ν 3336 (OH), 3163 (NH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.79-0.88 (t, 3H, J = 6 Hz), 1.24 (s, 32H), 1.87-1.95 (m, 2H), 3.79-4.12 (m, 10H), 4.48-4.53 (d, 2H, J = 10 Hz), 4.65 (s, 2H), 6.78-6.94 (m, 8H), 9.53 (s, 1H).

*Anal.* Calcd. for $C_{39}H_{61}NO_8$: C, 69.71; H, 9.15; N, 2.08. Found: C, 69.62; H, 9.32; N, 1.98.

### α-[*sym*-(Decyl)dibenzo-16-crown-5-oxy]phenylacetylhydroxamic Acid (**30**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent and recrystallization from ethyl acetate-hexanes gave an 87% yield of white solid with mp 56-58°; ir (potassium bromide): ν 3367 (NHOH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): δ 0.82-0.89 (t, 3H, J = 10 Hz), 1.22 (br s, 16H), 1.85 (m, 2H), 3.81-4.07 (m, 10H), 4.48-4.53 (d, 1H, J = 10 Hz), 4.62-4.67 (d, 1H, J = 10 Hz), 6.00 (s, 1H), 6.75-6.91 (m, 8H), 7.20-7.38 (m, 5H), 10.21 (br s, 1H).

*Anal.* Calcd. for $C_{37}H_{49}NO_8$: C, 69.90; H, 7.68; N, 2.17. Found: C, 70.09; H, 7.67; N, 1.99.

### α-[*sym*-(Phenyl)dibenzo-16-crown-5-oxy]phenylacetylhydroxamic Acid (**31**).

Column chromatography on silica gel with dichloromethane-ethyl acetate (9:1) as eluent and recrystallization from ethyl acetate-hexanes provided a 91% yield of white solid with mp 109-110°; ir (potassium bromide): ν 3367 (NHOH), 1674 (C=O) cm$^{-1}$; $^1$H nmr (deuteriochloroform): 3.85-4.41 (m, 10H), 4.60-4.65 (d, 1H, J = 10 Hz), 5.01-5.07 (d, 1H, J = 12 Hz), 6.00 (s, 1H), 6.60-6.90 (m, 8H), 6.91-7.47 (m, 10H), 10.29 (br s, 1H).

*Anal.* Calcd. for $C_{33}H_{33}NO_8$: C, 69.33; H, 5.81; N, 2.45. Found: C, 69.19; H, 5.81; N, 2.24.

### Solvent Extraction of Lanthanide Ions by Proton-Ionizable Lariat Ethers.

The solvent extraction studies were conducted as previously described [6,7]. Rare-earth radioisotopes were used as tracers in the extraction experiments. The radioisotopes were produced in a 1 MW TRIGA nuclear reactor at the DOE shared reactor facility at Washington State University. A weighed amount of the lariat ether carboxylic acid or hydroxamic acid was dissolved in chloroform. This solution was shaken with an aqueous solution of the lanthanide ion on a Burell Model 75 wrist-action shaker for several minutes at room temperature. After phase separation, 5.0 ml aliquots of each phase were removed and subjected to γ counting.

### X-ray Crystal Structure Determination of Lariat Ether Hydroxamic Acid **20**.

Crystals of compound **20** suitable for X-ray investigation were grown from methanol. The data collection was carried out on a Siemens R3m/V system with CuKα radiation and graphite monochromator. The orientation matrix and lattice parameters were optimized from the full-matrix, least-squares refinement data from 2658 observed reflections. The SHELXTL-Plus program package was used for data reduction and refinement [31]. Crystal and refinement date are reported in Table 2. Atomic coordinates are shown in Table 3 and the bond lengths and angles in Table 4.

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