A Convenient and Efficient Method for the Preparation of Unique Fluorophores of Lariat Naphtho-Aza-Crown Ethers

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New naphtho-aza-crown ethers containing different phenolic side-arms attached through the *ortho*-position of the phenol have been prepared under solvent-free conditions. The starting macrocyclic naphtho-aza-crown ether **2** was obtained by treatment of naphthalene dicarboxylic acid diester **1** with diethylenetriamine in EtOH at room temperature for two days without stirring in 77% yield (*Scheme 1*). Phenolic ligands (**3**–**14**) were synthesized by the *Mannich* reaction of the secondary macrocyclic amine **2** with the substituted phenols using nontoxic and inexpensive $CaCl_2$. This procedure was applied successfully for the synthesis of *Mannich* bases from simple secondary amines. The $CaCl_2$ powder can be reused up to three times after simple washing with dry acetone.

Introduction. – There is a continuing interest in the synthesis of aza-crown ethers [1]. The aza-crown ethers have complexation properties that are in between those of the all-oxa-crown ethers, which strongly complex alkali and alkaline earth metal ions, and those of the all-nitrogen cyclams, which strongly complex heavy-metal cations. The aza-crowns have important uses as synthetic receptors in molecular recognition processes [2]. There are a number of interesting uses of aza-crowns as catalysts in nucleophilic substitution and oxidation reactions [3][4], in the design of chromogenic reagents that are sensitive to alkali and alkaline earth metal cations, and in the chromatographic separation of metal cations [5]. The naphthalene moiety is a well known fluorophore, and its ability to block intersystem crossing in the first excited *singlet* state is remarkable. Also, it is known that the strong fluorescence induced by interaction of crown ether macrocycles with cations plays an important role in determining the nature of excited *singlet* and *triplet* states [6–9].

The term 'lariat ether' refers to a crown ether or a similar macrocyclic derivative with one or more accompanying appendages. They were designed to have the three-dimensionality of cryptands while retaining the faster complexation dynamics of crown ethers [10]. Aza-crown ethers bearing phenolic sidearms are powerful and selective cation binding agents for alkali, alkaline earth, and some heavy metal cations and draw great attention as sensitive reagents for extraction spectrophotometry of these ions [10][11]. In general, the complexing ability and selectivity of these lariat ethers for metal ions can be varied by changing [12] certain parameters such as the acidity of the phenolic OH group, the size of the crown-ether ring, type, number, and position of the complexing crown ether heteroatoms, the stereochemistry imposed by the arms which connect the phenolic group to the macrocyclic ring and the pH of the media [13]. These compounds are usually prepared by alkylation of aza-crown ethers with hydroxybenzyl

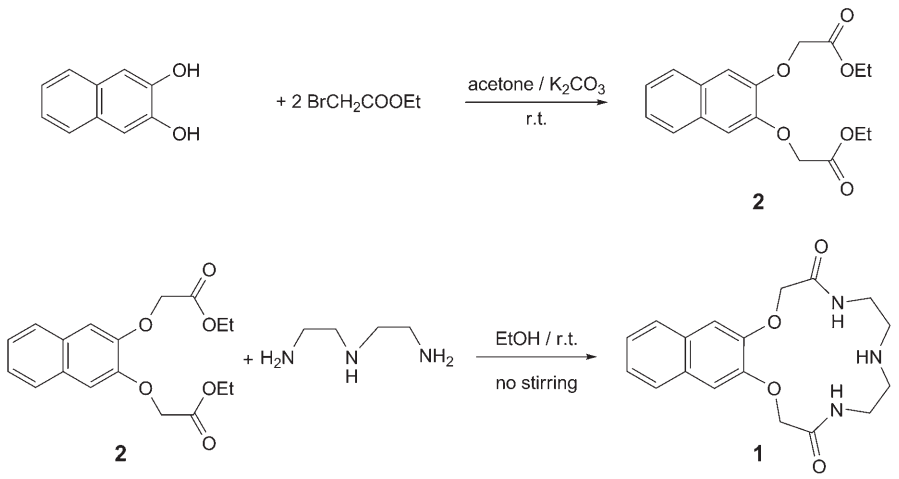
halides [14][15]. In some cases, the preliminary protection of phenol, OH [14] and other functional groups of the substituted hydroxybenzyl halides, which are able to interact alternatively with aza-crown ethers, is necessary. Furthermore, in most cases the substituted hydroxybenzyl halides are not readily available.

The *Mannich* reaction has a wide applicability in organic synthesis, and many reviews have been reported so far [16–20]. Advantages of the *Mannich* reaction in organic synthesis are as follows: *i*) the synthesis operation is simple and *ii*) the desired compounds are generally obtained in high yields. The *Mannich* reaction is suitable for the synthesis of armed macrocyclic ligands containing phenol and hydroxyquinoline as sidearms [21][22], because the aminomethylation occurs in *ortho*-position to the OH group. The *o*-OH group of the resulting armed macrocycle can bind guest cations incorporated into the macrocyclic cavity. The selectivity and complexing ability toward guest cations in these armed ligands are enhanced over that for the parent macrocyclic ligands.

As a part of our continued efforts to utilize surface-mediated reactions for the preparation of new lariat aza-crown ethers, we wish to disclose a very simple, fast, general, and improved one-step synthesis for new lariat aza-crown ethers without any solvent, in the presence of $CaCl_2$, in relatively high yields.

Results and Discussion. – The aza-crown ether **1** has been synthesized *via* the latest method in our laboratory [23] (*Scheme 1*). Each of the starting materials for the two step process is readily available. Naphthalene-2,3-diol was allowed to react with ethyl bromoacetate in the presence of K_2CO_3 as base in dried acetone. The mixture was stirred at room temperature for 24 h, the solid was removed by filtration through a *Celite* pad, the solvent was evaporated, and the yellow solid was recrystallized from warm hexane to give **2** as a white solid in 80% yield. The cyclocondensation was performed by mixing **2** and diethylenetriamine in EtOH as the solvent at room

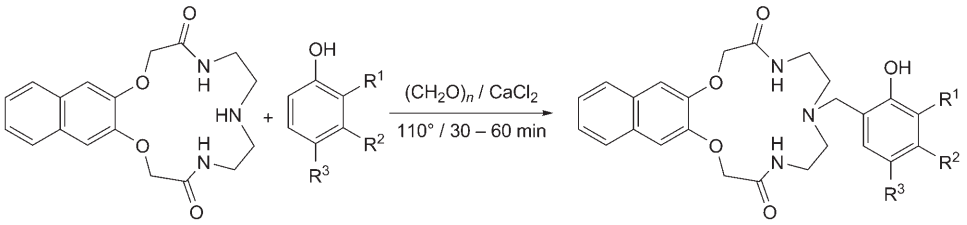
Scheme 1



temperature and keeping the mixture for two days without stirring. Then, the white needles precipitated were filtered to give the aza-crown ether **1** in 77% yield. The successful cyclization appears to be dependent on the ring size of the macrocycle.

During the course of our studies aimed at developing solvent-free procedures [24–26], we have now discovered that $CaCl_2$ alone promotes a very efficient *Mannich* reaction of activated and unactivated phenols with aza-crown ether **1** and paraformaldehyde at 110°, without any of the environmental disadvantages of using toxic solvents (*Scheme 2*). In a typical experiment, $CaCl_2$, **1**, 2,4-dimethylphenol, and paraformaldehyde were mixed thoroughly. The mixture was heated in an oil bath at 110° with stirring until the reaction was completed (30 min). The product **3** was isolated by simple extraction of the solid mass by acetone followed by the usual workup.

Scheme 2[a])



1 **3 – 14**

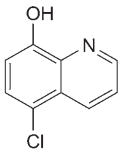
[a]) For R^1–R^3, see *Table 1*.

To establish the generality and applicability of this method, various phenols with both electron-donating and electron-withdrawing substituents were subjected to the same reaction conditions as in the case of **3** to furnish the corresponding new lariat ethers **4**–**14**. The formation of the benzylamines occurred very rapidly (30–60 min) with phenols bearing either electron-donating or electron-withdrawing substituents. The results are collected in *Table 1*. The yields are good for almost all products, although they drop when strong electron-withdrawing substituents are present, as in **6**. The moderate yield of **6** is attributed to the relatively weak nucleophilicity of *p*-nitrophenol and its anion (*Table 1*, *Entry 4*) [27]. Quinolin-8-ol is an analytical reagent containing a phenol-like function wherein ligand fluorescence is moderated upon complexation with certain metal ions [28b]. Therefore, we decided to attach 5-chloroquinolin-8-ol to **1** as a fluorescence side-arm (*Table 1*, *Entry 12*).

Additionally, a variety of secondary amines were examined using 2,4-dimethylphenol as model substrate (*Scheme 3*). Other aliphatic amines were efficiently converted to the desired products in excellent yields (*Table 2*). For example, the reaction between piperazine and two moles of 2,4-dimethylphenol under conventional heating (reflux in MeOH) in 12 h produced product **17** in 51% yield [29], whereas the same reaction gave **17** in excellent yield under the new solvent-less conditions within 30 min (*Table 2*, *Entry 3*).

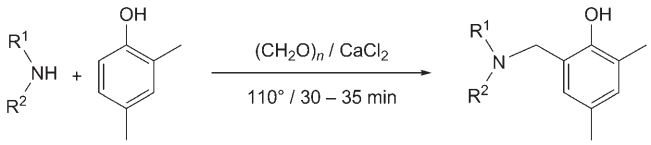
A comparison of the present protocol, using $CaCl_2$, with selected previously known protocols is collected in *Table 3* to demonstrate that the present protocol is indeed superior to several of the other protocols. In the absence of $CaCl_2$ (*Table 3*, *Entry 1*),

Table 1. *Reaction of Aza-Crown* **1** (1 mmol), *a Phenol* (1.2 mmol), *and Paraformaldehyde* (1.2 mmol) *in the Presence of* $CaCl_2$ (1 g) *at 110°*

Entry	R^1	R^2	R^3	Product	Time [min]	Yield [%][a])
1	Me	H	Me	**3**	30	85
2	H	H	Cl	**4**	40	58
3	H	H	Br	**5**	40	55
4	H	H	NO_2	**6**	60	45
5	H	H	Ph	**7**	35	63
6	H	H	Me	**8**	30	69
7	H	H	^{t}Bu	**9**	30	62
8	H	H	MeO	**10**	55	61
9	MeO	H	CH_2=$CHCH_2$	**11**	35	78
10	H	Me	Me	**12**	40	65
11	Cl	H	Cl	**13**	50	53
12				**14**	45	68

[a]) Yield of isolated products.

Scheme 3[a])



15 – 20

[a]) For R^1 and R^2, see *Table 2*.

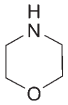
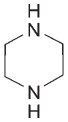
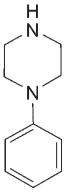
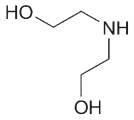
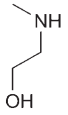
the reaction of **1**, 2,4-dimethylphenol, and paraformaldehyde was conducted at 110° for 2 h, affording the compound **3** in only 20% yield.

Using the present protocol, the reaction is complete in 30 min at 110° leading to **3** in 85% yield. Most of the other protocols listed either need a longer time for completion or use toxic solvents and lead in general to reduced yields.

The *Mannich* reaction of aza-crown ether **1** with 2,4-dimethylphenol on a 30 mmol scale proceeded just as well as the 1 mmol reaction. Furthermore, the reusability of $CaCl_2$ has been examined. As shown in *Table 4*, the yield of **3** in a second and third use of the $CaCl_2$ was almost the same as that in the first use. In each case, $>90\%$ of the $CaCl_2$ was easily recovered from the mixture by simple washing with dry acetone. No attempt has been made to probe the mechanism of the reaction. As for now, we believe that $CaCl_2$ acts as a dehydration reagent for the *Mannich* reaction.

In conclusion, we have described a novel and highly efficient solvent-free protocol for the *Mannich* reaction of phenols by using nontoxic and inexpensive $CaCl_2$. The advantages of this environmentally benign and safe protocol include a simple reaction

Table 2. *Reaction of 2,4-Dimethylphenol* (1.2 mmol), *an Amine* (1 mmol), *and Paraformaldehyde* (1.2 mmol) *in the Presence of* $CaCl_2$ (1 g) *at 110°*

Entry	Amine (R^1R^2NH)	Product	Time [min]	Yield [%][a])
1		**15**	35	81
2		**16**	30	88
3		**17**	30	87
4		**18**	30	90
5		**19**	30	72
6		**20**	30	68

[a]) Yield of isolated products.

setup not requiring specialized equipment, high product yields, short reaction times, and the avoidance of solvents. Furthermore, the $CaCl_2$ could be recovered and reused for the one-pot formation of the *Mannich* reaction products.

Experimental Part

General. Chemical materials were either prepared in our laboratories or were purchased from *Fluka*, *Aldrich*, or *Merck*. Purity determination of the substrates and reaction monitoring: TLC on silica gel *PolyGram SILG/UV 254* plates. Column chromatography (CC): on short columns of silica gel *60* (SiO_2, 70–230 mesh) in glass columns (2–3 cm diameter) using 15–30 g SiO_2 per 1 g of crude mixture. M.p.: open capillary tubes in a *Büchi-535* circulating oil melting point apparatus. IR Spectra: *Shimadzu FT-IR 8300* spectrophotometer. NMR Spectra: *Bruker Avance DPX-250* (^{1}H-NMR 250 MHz and ^{13}C-NMR

Table 3. *Reaction of Aza-Crown Ether* **1** (1 mmol), *2,4-Dimethylphenol* (1.2 mmol), *and Paraformaldehyde* (1.2 mmol) *under Various Conditions*

Entry	Conditions	Time [h]	Yield [%][a])
1	No catalyst/110°	2	20
2	CCl_4/reflux [30]	2	0
3	Toluene/reflux [28]	2	0
4	Benzene/reflux [27]	2	0
5	Toluene/reflux [28]	7 d	50
6	$CaCl_2$/100°	2	50
7	$CaCl_2$/110°	0.5	85
8	$CaCl_2$/130°	0.3	88

[a]) Yield of isolated products.

Table 4. *Reuse of $CaCl_2$*

Number of uses	Recovery of $CaCl_2$	Yield [%][a])
1	95	85
2	92	82
3	91	80

[a]) Yield of isolated products.

62.9 MHz) spectrometer in pure deuterated solvents with Me_4Si as an internal standard. MS: *Shimadzu GCMS-QP 1000 EX* instrument at 70 or 20 eV. Elemental analyses: *Thermofinnigan Flash-Ea 1112 series* apparatus.

Preparation of Diethyl 2,2′-[Naphthalene-2,3-diylbis(oxy)]diacetate (**2**) [31]. To a mixture of K_2CO_3 (8 g) in dried acetone (100 ml) was added naphthalene-2,3-diol (2 g, 12.5 mmol) and ethyl bromoacetate (3.5 ml, 30 mmol). The resulting mixture was stirred at r.t. for 24 h. The mixture was filtered, and the solvent was evaporated under reduced pressure, the resulting yellow solid was recrystallized from warm hexane to give **2** as a white solid. Yield 3.32 g, 80%. M.p. 63–65° ([31]: 62–63°). IR (KBr): 2995*m*, 1758*s*, 1455*m*, 1371*s*, 1213*s*, 864*s*. ^{1}H-NMR ($CDCl_3$): 1.28 (*t*, *J* = 7.1, 6 H); 4.30 (*q*, *J* = 7.1, 4 H); 4.81 (*s*, 4 H); 7.12 (*s*, 2 H); 7.26–7.35 (*m*, 2 H); 7.64–7.69 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 14.2; 61.4; 66.4; 109.8; 124.8; 126.5; 129.5; 147.9; 168.6. MS: 333 (0.3), 332 (13.1, M^+), 257 (11.1), 131 (18.6), 115 (26.0), 59 (100). Anal. calc. for $C_{18}H_{20}O_6$ (332.35): C 65.05, H 6.07; found: C 65.25, H 6.25.

*Preparation of 5,6,7,8,9,10-Hexahydro-*2H*-naphtho[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**1**). To a soln. of **2** (1 g, 3 mmol) in EtOH (100 ml) was added diethylenetriamine (0.3 ml, 3 mmol), and the mixture was left 2 d at r.t. Then, the white solid was collected by filtration. Yield 0.79 g, 77%. M.p. 273–275°. IR (KBr): 3398*m*, 2846*m*, 1679*s*, 1533*m*, 1257*s*, 887*m*. ^{1}H-NMR ($CDCl_3$): 1.00 (*s*, 1 H); 2.95 (*t*, *J* = 5.2, 4 H); 3.49 (*t*, *J* = 5.2, 4 H); 4.58 (*s*, 4 H); 7.07 (*s*, 2 H); 7.36–7.42 (*m*, 2 H); 7.65–7.72 (*m*, 2 H); 7.81 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 38.2; 47.4; 66.9; 107.8; 125.1; 126.1; 129.2; 146.1; 166.9. MS: 344 (0.5), 343 (0.5, M^+), 275 (23.9), 217 (13.1), 200 (32.7), 172 (38.3), 115 (27.1), 85 (34.9), 56 (100). Anal. calc. for $C_{18}H_{21}N_3O_4$ (343.38): C 62.96, H 6.16; found: C 63.09, H 6.29.

General Procedure for the Preparation of Lariat Naphthalene Aza-Crown Ethers **3**–**14**. Crown ether **1** (1 mmol), phenol (1.2 mmol), paraformaldehyde (1.2 mmol), and $CaCl_2$ (1 g) were thoroughly mixed. The resulting fine powder was transferred to a round-bottom flask and stirred in an oil bath at 110° for 30–60 min (see *Table 1*). After cooling, dried acetone (5 × 25 ml) was added to the mixture, and $CaCl_2$ was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude product in 45–85% yield, which was purified by CC (hexane/AcOEt).

General Procedure for the Preparation of Compounds **15**–**20**. Secondary amine (1 mmol), 2,4-dimethylphenol (1.2 mmol), paraformaldehyde (1.2 mmol), and $CaCl_2$ (1 g) were thoroughly mixed. The resulting fine powder was transferred to a round-bottom flask and stirred in an oil bath at 110° for 30–35 min. After cooling, acetone was added to the mixture, and $CaCl_2$ was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude product, which was purified by recrystallization with warm MeOH (**17** and **18**) or prep. TLC (hexane/AcOEt; 10:3) (**15**, **16**, **19**, and **20**).

*5,6,7,8,9,10-Hexahydro-7-[(2-hydroxy-3,5-dimethylphenyl)methyl]-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**3**). White crystals (0.41 g, 85%). M.p. 242–243°. IR (KBr): 3425*s*, 2889*m*, 1693*s*, 1485*s*, 1261*s*, 1176*s*, 856*m*. ^{1}H-NMR ($CDCl_3$): 1.93 (*s*, 3 H); 2.21 (*s*, 3 H); 2.78 (*t*, *J* = 5.0, 4 H); 3.55 (*t*, *J* = 5.0, 4 H); 3.72 (*s*, 2 H); 4.62 (*s*, 4 H); 6.67 (*s*, 1 H); 6.87 (*s*, 1 H); 7.26 (*s*, 2 H); 7.39–7.46 (*m*, 4 H); 7.46–7.74 (*m*, 2 H); 8.17 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 15.2; 20.3; 52.9; 68.0; 108.1; 109.4; 121.0; 124.4; 126.4; 127.0; 127.5; 128.6; 129.2; 147.1; 150.4; 166.9. MS: 479 (0.6), 478 (16.4), 477 (3.2, M^+), 406 (10.6), 344 (9.7), 314 (8.1), 200 (38.0), 91 (80.5), 56 (100). Anal. calc. for $C_{27}H_{31}N_3O_5$ (477.55): C 67.91, H 6.54; found: C 68.15, H 6.67.

*7-[(5-Chloro-2-hydroxyphenyl)methyl]-5,6,7,8,9,10-hexahydro-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**4**). White crystals (0.28 g, 58%). M.p. 266–268°. IR (KBr): 3406*s*, 3253*m*, 2952*m*, 1678*s*, 1485*m*, 1265*s*, 891*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.60 (*t*, *J* = 5.0, 4 H); 3.47 (*s*, 2 H); 4.53 (*s*, 4 H); 6.64 (*d*, *J* = 7.5, 1 H); 6.90 (*d*, *J* = 7.5, 1 H); 7.25–7.30 (*m*, 3 H); 7.38 (*s*, 2 H); 7.67–7.75 (*m*, 2 H); 8.01 (*s*, 2 H); 9.68 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 35.1; 49.3; 52.1; 67.3; 108.4; 116.3; 122.3; 124.4; 126.4; 126.9; 127.1; 129.0; 146.7; 154.2; 166.5. MS: 483 (0.6, M^+), 342 (17.5), 275 (59.5), 217 (18.2), 200 (42.3), 172 (42.2), 113 (29.3), 77 (62.3), 56 (100). Anal. calc. for $C_{25}H_{26}ClN_3O_5$ (483.95): C 62.05, H 5.41; found: C 62.29, H 5.57.

*7-[(5-Bromo-2-hydroxyphenyl)methyl]-5,6,7,8,9,10-hexahydro-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**5**). White crystals (0.29 g, 55%). M.p. 262–263°. IR (KBr): 3406*s*, 3290*m*, 2954*w*, 1677*s*, 1485*s*, 1265*s*, 898*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.61 (*t*, *J* = 5.0, 4 H); 3.47 (*s*, 2 H); 4.51 (*s*, 4 H); 6.61 (*d*, *J* = 7.5, 1 H); 7.02 (*d*, *J* = 8.3, 1 H); 7.28–7.31 (*m*, 5 H); 7.68–7.75 (*m*, 4 H); 9.93 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 24.4; 49.3; 52.7; 67.3; 108.4; 109.9; 116.9; 124.4; 126.4; 126.9; 127.3; 129.0; 130.0; 131.9; 146.7; 154.7; 166.5. MS: 528 (7.5, M^+), 344 (19.3), 276 (73.0), 218 (20.7), 172 (64.3), 113 (37.9), 56 (100). Anal. calc. for $C_{25}H_{26}BrN_3O_5$ (528.40): C 56.83, H 4.96; found: C 56.98, H 5.17.

*5,6,7,8,9,10-Hexahydro-7-[(2-hydroxy-5-nitrophenyl)methyl]-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**6**). Yellow crystals (0.22 g, 45%). M.p. 238–242°. IR (KBr): 3406*s*, 2964*m*, 2842*m*, 1677*s*, 1527*s*, 1485*m*, 1334*s*, 1265*s*, 856*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.64 (*t*, *J* = 5.1, 4 H); 3.57 (*s*, 2 H); 4.46 (*s*, 4 H); 6.81 (*d*, *J* = 7.5, 1 H); 7.27–7.32 (*m*, 3 H); 7.49 (*s*, 2 H); 7.68–7.72 (*m*, 4 H); 7.86 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 35.2; 49.6; 55.7; 67.4; 108.6; 115.1; 124.4; 125.9; 126.4; 128.9; 139.3; 146.7; 162.0; 166.3. MS: 494 (6.8, M^+), 375 (12.0), 185 (10.3), 127 (17.5), 70 (100). Anal. calc. for $C_{25}H_{26}N_4O_7$ (494.50): C 60.72, H 5.30; found: C 60.95, H 5.47.

*5,6,7,8,9,10-Hexahydro-7-[(4-hydroxy[1,1′-biphenyl]-3-yl)methyl]-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**7**). White crystals (0.33 g, 63%). M.p. 257–258°. IR (KBr): 3267*s*, 2819*m*, 1674*s*, 1485*m*, 1265*s*, 763*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.65 (*t*, *J* = 5.2, 4 H); 3.58 (*s*, 2 H); 4.40 (*s*, 4 H); 6.74–6.86 (*m*, 4 H); 7.20 (*d*, *J* = 8.5, 1 H); 7.24–7.32 (*m*, 5 H); 7.41 (*s*, 1 H); 7.69–7.80 (*m*, 4 H); 9.60 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 35.3; 49.8; 52.6; 67.2; 108.5; 115.4; 124.4; 125.6; 125.8; 126.1; 126.4; 128.3; 129.0; 130.9; 146.4; 155.3; 166.4. MS: 527 (4.3), 525 (5.7, M^+), 454 (2.6), 343 (11.8), 276 (68.1), 200 (63.1), 113 (41.6), 56 (100). Anal. calc. for $C_{31}H_{31}N_3O_5$ (525.60): C 70.84, H 5.94; found: C 70.98, H 6.17.

*5,6,7,8,9,10-Hexahydro-7-[(2-hydroxy-5-methylphenyl)methyl]-2*H*-naphtho[2,3-b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione* (**8**). White crystals (0.32 g, 69%). M.p. 253–254°. IR (KBr): 3402*s*, 3244*m*, 2854*m*, 1678*s*, 1485*m*, 1257*s*, 817*m*. ^{1}H-NMR ((D$_6$)DMSO): 1.80 (*s*, 3 H); 2.58 (*t*, *J* = 5.0, 4 H); 3.45 (*s*, 2 H); 4.60 (*s*, 4 H); 6.51 (*d*, *J* = 8.1, 1 H); 6.68 (*d*, *J* = 8.1, 1 H); 6.97 (*s*, 1 H); 7.27–7.30 (*m*, 2 H); 7.38 (*s*, 2 H); 7.67–7.70 (*m*, 4 H); 9.10 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 19.8; 35.1; 49.2; 50.5; 67.3; 108.4; 114.8; 123.5; 124.4; 126.4; 126.9; 128.0; 129.0; 130.6; 146.5; 153.2; 166.4. MS: 463 (57.9, M^+), 275 (46.0), 217 (12.4), 200 (33.2), 172 (32.2), 131 (100), 91 (67.3), 56 (78.2). Anal. calc. for $C_{26}H_{29}N_3O_5$ (463.53): C 67.37, H 6.31; found: C 67.59, H 6.47.

*7-{[5-(1,1-Dimethylethyl)-2-hydroxyphenyl]methyl}-5,6,7,8,9,10-hexahydro-2*H-*naphtho[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**9**). White crystals (0.31 g, 62%). M.p. 240–243°. IR (KBr): 3402*s*, 2954*m*, 1678*s*, 1485*m*, 1261*s*, 829*m*. ^{1}H-NMR ((D$_6$)DMSO): 1.02 (*s*, 9 H); 2.65 (*t*, *J* = 5.0, 4 H); 3.57 (*s*, 2 H); 4.53 (*s*, 4 H); 6.62 (*d*, *J* = 7.5, 1 H); 7.01 (*d*, *J* = 7.5, 1 H); 7.13 (*s*, 1 H); 7.33–7.36 (*m*, 2 H); 7.42 (*s*, 2 H); 7.68–7.75 (*m*, 4 H); 9.23 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 30.9; 33.3; 35.2; 49.8; 52.5; 67.2; 108.4; 114.5; 122.7; 124.4; 126.4; 126.9; 129.0; 140.7; 146.4; 153.2; 166.5. MS: 507 (3.56), 506 (6.8), 505 (5.5, M^+), 344 (19.3), 275 (78.9), 200 (76.6), 172 (68.0), 56 (100). Anal. calc. for $C_{29}H_{35}N_3O_5$ (505.61): C 68.89, H 6.98; found: C 69.05, H 7.17.

*5,6,7,8,9,10-Hexahydro-7-[(2-hydroxy-5-methoxyphenyl)methyl]-2*H-*naphtho[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**10**). White crystals (0.29 g, 61%). M.p. 241–243°. IR (KBr): 3406*s*, 3244*m*, 2831*m*, 1678*s*, 1485*m*, 1265*s*, 891*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.64 (*t*, *J* = 5.0, 4 H); 3.53 (*s*, 2 H); 4.55 (*s*, 4 H); 6.52–6.64 (*m*, 2 H); 6.77 (*s*, 1 H); 7.33–7.39 (*m*, 2 H); 7.43 (*s*, 2 H); 7.73–7.78 (*m*, 4 H); 8.87 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 35.1; 49.6; 52.0; 54.8; 67.3; 108.5; 113.0; 115.5; 124.4; 126.4; 129.0; 146.5; 149.4; 151.8; 166.5. MS: 481 (2.3), 480 (2.4), 479 (3.2, M^+), 438 (3.3), 369 (12.8), 276 (43.5), 200 (39.7), 172 (33.8), 57 (100). Anal. calc. for $C_{26}H_{29}N_3O_6$ (479.53): C 65.12, H 6.10; found: C 65.25, H 6.29.

*5,6,7,8,9,10-Hexahydro-7-{[2-hydroxy-3-methoxy-5-(2-propen-1-yl)phenyl]methyl}-2*H-*naphtho[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**11**). White crystals (0.40 g, 78%). M.p. 235–236°. IR (KBr): 3417*s*, 2854*m*, 1678*s*, 1485*m*, 1261*s*, 1176*m*, 617*w*. ^{1}H-NMR (CDCl$_3$): 2.67 (*t*, *J* = 5.0, 4 H); 3.13 (*d*, *J* = 7.5, 2 H); 3.45 (*t*, *J* = 5.0, 4 H); 3.60 (*s*, 2 H); 3.64 (*s*, 3 H); 4.49 (*s*, 4 H); 4.84–4.92 (*m*, 1 H); 5.76–5.81 (*m*, 1 H); 6.50 (*s*, 1 H); 6.52 (*s*, 1 H); 7.07 (*s*, 2 H); 7.32–7.35 (*m*, 2 H); 7.62–7.68 (*m*, 2 H); 7.80 (*s*, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 35.6; 39.7; 51.0; 52.8; 55.9; 67.5; 108.6; 110.5; 115.7; 123.0; 125.1; 126.6; 129.3; 131.3; 137.5; 146.7; 167.5. MS: 520 (25.3), 519 (2.1, M^+), 343 (13.2), 275 (20.5), 217 (14.9), 172 (40.2), 115 (33.9), 56 (100). Anal. calc. for $C_{29}H_{33}N_3O_6$ (519.59): C 67.04, H 6.40; found: C 67.25, H 6.65.

*5,6,7,8,9,10-Hexahydro-7-[(2-hydroxy-4,5-dimethylphenyl)methyl]-2*H-*naphtho[2,3-*b*][1,4,7,10,13]-dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**12**). White crystals (0.31 g, 65%). M.p. 240–243°. IR (KBr): 3398*s*, 3236*m*, 2854*m*, 1679*s*, 1485*m*, 1261*s*, 856*m*. ^{1}H-NMR ((D$_6$)DMSO): 1.80 (*s*, 3 H); 1.99 (*s*, 3 H); 2.62 (*t*, *J* = 5.0, 4 H); 3.49 (*s*, 2 H); 4.55 (*s*, 4 H); 6.49 (*s*, 1 H); 6.93 (*s*, 1 H); 7.34–7.37 (*m*, 2 H); 7.52 (*s*, 2 H); 7.72–8.06 (*m*, 4 H); 9.05 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 18.0; 19.1; 35.1; 48.7; 51.9; 67.3; 108.4; 116.3; 120.5; 124.5; 125.8; 126.4; 129.0; 131.2; 135.3; 146.5; 153.4; 166.5. MS: 479 (0.8), 478 (14.4), 477 (3.7, M^+), 406 (12.5), 344 (9.3), 314 (11.1), 200 (33.0), 91 (75.5), 56 (100). Anal. calc. for $C_{27}H_{31}N_3O_5$ (477.56): C 67.91, H 6.54; found: C 68.17, H 6.69.

*7-[(3,5-Dichloro-2-hydroxyphenyl)methyl]-5,6,7,8,9,10-hexahydro-2*H-*naphtho[2,3-*b*][1,4,7,10,13]-dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**13**). White crystals (0.27 g, 53%). M.p. 245–247°. IR (KBr): 3417*s*, 2823*m*, 1678*s*, 1442*m*, 1261*s*, 825*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.66 (*t*, *J* = 5.0, 4 H); 3.62 (*s*, 2 H); 4.54 (*s*, 4 H); 7.22 (*s*, 1 H); 7.27 (*s*, 1 H); 7.34–7.37 (*m*, 2 H); 7.47 (*s*, 2 H); 7.73–7.77 (*m*, 2 H); 7.97 (*s*, 2 H); 10.11 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 34.9; 51.3; 51.6; 68.0; 109.4; 120.9; 122.7; 124.4; 126.4; 127.0; 127.5; 128.5; 129.1; 147.0; 150.3; 166.9. MS: 519 (1.1), 518 (2.7, M^+), 344 (14.2), 276 (63.7), 217 (30.0), 172 (66.7), 113 (34.1), 56 (100). Anal. calc. for $C_{25}H_{25}Cl_2N_3O_5$ (518.39): C 57.92, H 4.86; found: C 58.13, H 4.99.

*7-[(5-Chloro-8-hydroxyquinolin-7-yl)methyl]-5,6,7,8,9,10-hexahydro-2*H-*naphtho[2,3-*b*][1,4,7,10,13]-dioxatriazacyclopentadecine-3,11(4*H,*12*H*)-dione* (**14**). White crystals (0.36 g, 68%). M.p. 275–277°. IR (KBr): 3406*s*, 2964*m*, 2842*m*, 1677*s*, 1529*s*, 1485*s*, 1336*s*, 1265*s*, 1176*s*, 856*m*. ^{1}H-NMR ((D$_6$)DMSO): 2.49 (*t*, *J* = 5.0, 4 H); 3.75 (*s*, 2 H); 4.52 (*s*, 4 H); 7.34–7.38 (*m*, 2 H); 7.44 (*s*, 2 H); 7.58–7.63 (*m*, 2 H); 7.74–7.87 (*m*, 3 H); 8.29 (*d*, *J* = 7.5, 1 H); 8.84 (*s*, 2 H); 10.07 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 35.2; 52.1; 67.2; 108.3; 121.9; 122.5; 126.4; 128.3; 129.0; 146.7; 148.7; 166.5. MS: 537 (1.4), 535 (3.2, M^+), 356 (2.0), 276 (62.1), 200 (64.0), 128 (55.3), 56 (100). Anal. calc. for $C_{28}H_{27}ClN_4O_5$ (534.99): C 62.86, H 5.09; found: C 62.98, H 5.26.

2,4-Dimethyl-6-(morpholin-4-ylmethyl)phenol (**15**) [32]. Yellow viscous oil (0.18 g, 81%). IR (neat): 2950*m*, 1485*s*, 1245*m*, 1118*s*, 867*m*. ^{1}H-NMR (CDCl$_3$): 2.20 (*s*, 6 H); 2.44–2.53 (*m*, 4 H); 3.62 (*s*, 2 H); 3.71–3.75 (*m*, 4 H); 6.53 (*s*, 1 H); 6.90 (*s*, 1 H); 10.46 (*s*, 1 H). ^{13}C-NMR (CDCl$_3$): 15.6; 20.4; 52.9; 61.9; 66.8; 119.7; 124.6; 126.9; 127.8; 130.7; 153.2. MS: 223 (5.0), 222 (34.1), 221 (32.9, M^+), 174 (10.1), 134

(40.2), 106 (13.1), 86 (100), 57 (62.6). Anal. calc. for $C_{13}H_{19}NO_2$ (221.29): C 70.56, H 8.65; found: C 70.77, H 8.79.

2,4-Dimethyl-6-(piperidin-1-ylmethyl)phenol (**16**) [33]. Colourless viscous oil (0.19 g, 88%). IR (neat): 2943*s*, 1485*s*, 1245*m*, 864*m*. ^{1}H-NMR ($CDCl_3$): 1.40–1.47 (*m*, 4 H); 2.11 (*s*, 6 H); 2.36–2.39 (*m*, 5 H); 3.50 (*s*, 2 H); 6.50 (*s*, 1 H); 6.80 (*s*, 1 H); 10.40 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 15.7; 20.4; 24.1; 25.9; 53.9; 62.1; 120.6; 124.4; 126.6; 127.3; 131.6; 153.7. MS: 220 (10.8), 219 (11.2, M^+), 135 (6.3), 105 (3.6), 84 (100), 56 (11.6). Anal. calc. for $C_{14}H_{21}NO$ (219.32): C 76.67, H 9.65; found: C 76.79, H 9.79.

2,2′-[Piperazine-1,4-diylbis(methylene)]bis[4,6-dimethylphenol] (**17**) [24]. White crystals (0.31 g, 87%). M.p. 185–188° ([24]: 184°). IR (KBr): 2824*s*, 1485*s*, 1267*s*, 1112*s*, 892*m*. ^{1}H-NMR ($CDCl_3$): 2.11 (*s*, 12 H); 2.37–2.50 (*m*, 8 H); 3.57 (*s*, 4 H); 6.79 (*s*, 2 H); 7.17 (*s*, 2 H); 10.48 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 15.6; 20.4; 52.3; 61.2; 119.8; 124.6; 126.6; 127.8; 130.5; 153.2. MS: 356 (5.6), 355 (17.4), 354 (4.5, M^+), 340 (12.0), 220 (27.4), 178 (19.1), 135 (100), 105 (16.6), 85 (86.8), 56 (52.3). Anal. calc. for $C_{22}H_{30}N_2O_2$ (354.49): C 74.54, H 8.53; found: C 74.79, H 8.76.

2,4-Dimethyl-6-[(4-phenylpiperazin-1-yl)methyl]phenol (**18**). White crystals (0.27 g, 90%). M.p. 168–169°. IR (KBr): 2827*s*, 1596*s*, 1481*s*, 1242*s*, 756*s*. ^{1}H-NMR ($CDCl_3$): 2.14–2.21 (*s*, 6 H); 2.38–2.46 (*m*, 4 H); 3.14–3.21 (*m*, 4 H); 3.61 (*s*, 2 H); 6.57 (*s*, 1 H); 6.73–6.85 (*m*, 4 H); 7.14–7.21 (*m*, 2 H); 10.54 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 15.6; 20.4; 42.9; 52.5; 58.1; 61.5; 116.4; 120.0; 120.2; 124.7; 126.8; 127.8; 129.2; 130.7; 151.0; 153.4. MS: 298 (1.2), 297 (5.6), 296 (4.6, M^+), 149 (32.3), 120 (23.1), 94 (100), 57 (51.0). Anal. calc. for $C_{19}H_{24}N_2O$ (296.41): C 76.99, H 8.16; found: C 77.19, H 8.34.

2-{[Bis(2-hydroxyethyl)amino]methyl}-4,6-dimethylphenol (**19**) [34]. Colorless viscous oil (0.17 g, 72%). ^{1}H-NMR ($CDCl_3$): 2.07 (*s*, 3 H); 2.10 (*s*, 3 H); 2.60 (*t*, $J = 5.0$, 4 H); 3.53–3.65 (*m*, 6 H); 3.72 (*s*, 2 H); 5.98 (*s*, 3 H); 6.58 (*s*, 1 H) 6.74 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 14.7; 19.4; 54.9; 58.1; 58.5; 118.7; 123.7; 125.8; 126.8; 129.6; 151.9. MS: 240 (2.7), 239 (2.2, M^+), 208 (7.3), 176 (1.7), 135 (40.0), 91 (22.5), 74 (100), 56 (22.7). Anal. calc. for $C_{13}H_{21}NO_3$ (239.31): C 65.25, H 8.84; found: C 65.38, H 8.99.

2-{[(2-Hydroxyethyl)methylamino]methyl}-4,6-dimethylphenol (**20**) [35]. Colorless viscous oil (0.14 g, 68%). ^{1}H-NMR ($CDCl_3$): 2.18 (*s*, 6 H); 2.20 (*s*, 3 H); 2.53 (*t*, $J = 6.2$, 2 H); 3.51 (*s*, 2 H); 3.57 (*t*, $J = 6.2$, 2 H); 6.40 (*s*, 1 H); 6.79 (*s*, 1 H); 7.12 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 15.7; 20.5; 41.6; 58.8; 59.4; 61.1; 120.9; 124.8; 125.7; 128.6; 130.1; 153.4. MS: 210 (9.3), 209 (14.1, M^+), 178 (23.1), 135 (100), 91 (35.5). Anal. calc. for $C_{12}H_{19}NO_2$ (209.29): C 68.87, H 9.15; found: C 69.04, H 9.29.

We gratefully acknowledge the support of this work by the Shiraz University Research Council.

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Received January 25, 2008