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# Synthesis of aza oxa thia receptors bearing naphthalene

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## ABSTRACT

New aza oxa thia podands bearing 1-naphthol and 2-naphthol were prepared. At first, naphthol sulfides were prepared and then the chloroamide derivatives were reacted with these sulfides to afford corresponding podands.

## KEYWORDS

Receptor;
Aza oxa thia podand;
Dinaphthosulfide;
1-Naphthol;
2-Naphthol.

## INTRODUCTION

Crown ethers and aza crowns are an important class of host molecules[1]. After synthesis and complexation studies of crown ethers by pedersen[2], macrocycles contaning aza, thia, and other functional groups were prepared and their applications were studied[3]. Their complexaton studies toward metal ions and related guests were performed and they showed strong interaction between macrocycles and these species[4]. Acyclic receptors were prepared and similar to crown ethers and aza crowns their applications were studied. Aza podands and related receptors such as aza oxa and aza oxa thia podands are another group of receptors which can be used as important hosts in host-guest chemistry[5]. They have been used as building blocks for the construction of a large number of supramolecular systems[6].

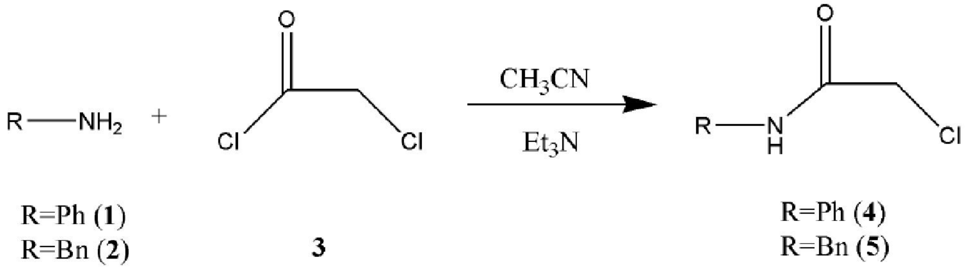
A series of podands with various complexation groups were studied in the design of new organic-inorganic nano frameworks. In these studies the selectivity and stability of complex between podands and metal ions are the key role in the synthesis of this structures[7].

In this research work new aza thia podands bearing dinaphthosulfide were prepared via two reaction routes. Studies on these receptors are underway.

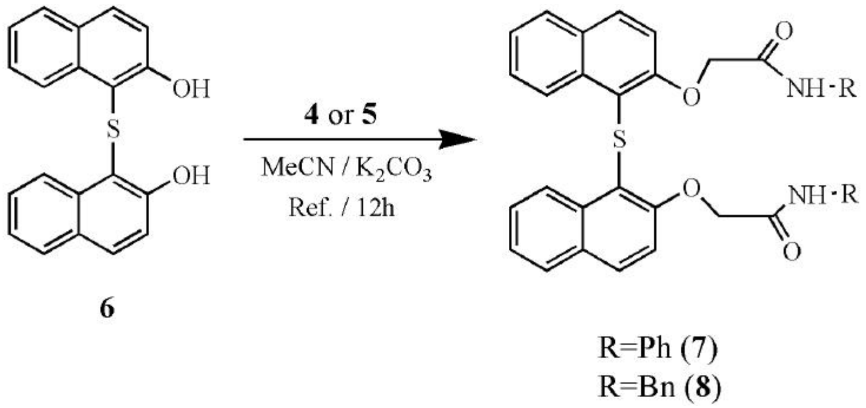
## RESULTS AND DISCUSSION

In this research work, the synthesis of some new podands 7, 8, 10 and 11, by the two synthetic routes are described (Schemes 2-5). In the first route α-chloroamides (4 and 5) were prepared from the reaction of amines (1 and 2) and chloroacetyl chloride (3) in the presence of $Et_3N$ in $CH_2Cl_2$ (Scheme 1). Podands were prepared in good yields from the reaction of α-chloroamides and 6 (or 9) in the presence of $K_2CO_3$ in refluxing MeCN (Schemes 2,3). The resulting podands were purified by recrystallization in ethanol.

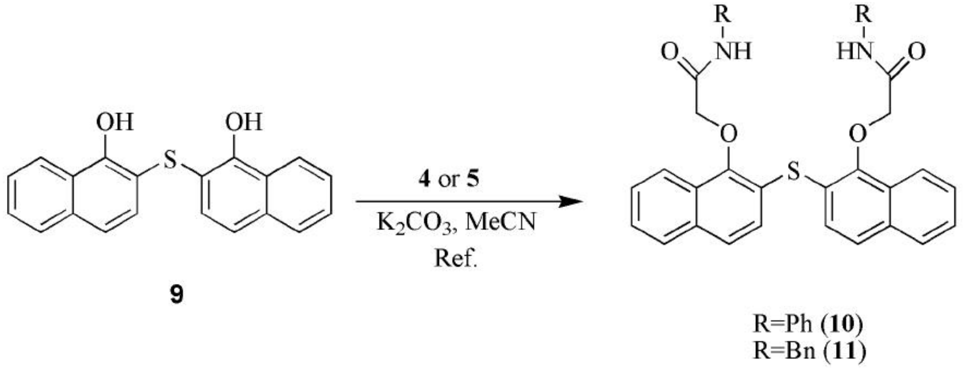
The second route is based on the reaction of amines and acid chlorides. Diesters (12, 15) were hydrolyzed to diacids (13, 16) and then the resulting diacids were converted to acid chlorides (14, 17) by the reaction with oxallyl chloride in the presence of DMF (one drop) at room temperature (Schemes 4, 5). The reaction of acid chlorides (14, 17) and diamines (1, 2) afforded



**Scheme 1 : Synthesis of chloroamides.**



**Scheme 2 : Synthesis of 2-naphthol podands via chloroamides.**



**Scheme 3 : Synthesis of 1-naphthol podands via chloroamide.**

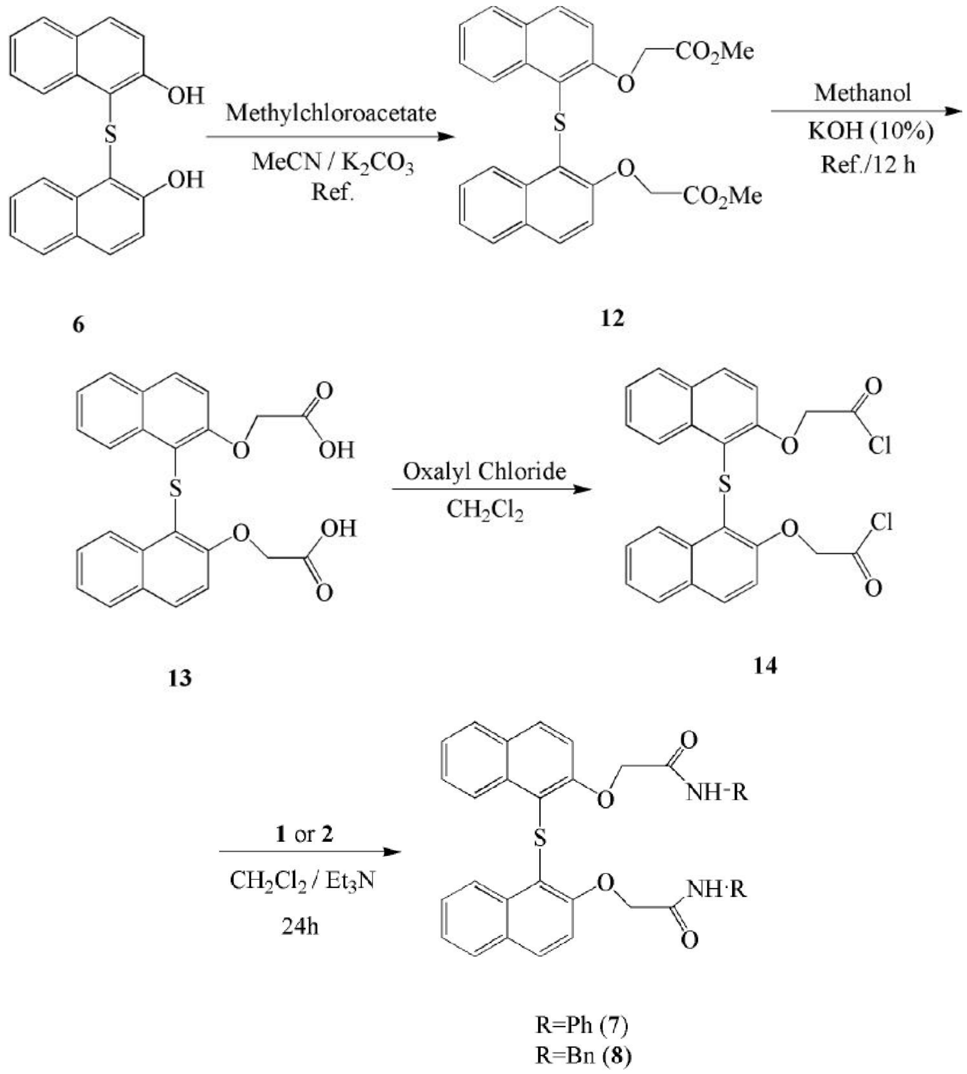
podands (7, 8, 10 and 11) in good yields.

## EXPERIMENTAL

The reactions were carried out in an efficient hood. All the materials were purchased from Merck, Fluka and Aldrich chemical companies. 4,[8] 5,[8] 6,[9] 9,[9] 12,[9,10] 13,[9,11] 15[12,13] and 16[12,13] were reported previously. The melting points (uncorrected) were measured with an Electrothermal engineering LTD 9100 apparatus. Elemental analysis was performed by a CHN-O- Rapid Heraeus elemental analyzer. IR spectra were measured on a Perkin-Elmer model 543, the $^1$H NMR and $^{13}$C NMR spectra were obtained using BRUKER AVANCE DRX 500 and BRUKER AVANCE DPX 300 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

### General procedure 1, for the synthesis of podands via chloroamide route

To a mixture of 6 or 9 (1 mmol) and potassium carbonate (2 mmol) in $CH_3CN$ (50 ml) was added α-chloroamides 4 or 5 (2 mmol), and this mixture was refluxed for 24h, after completion of the reacton (monitored by TLC), the resulting suspension mixture was allowed to cool to room temperature and subsequently poured into 700 ml of distilled water. The precipitate was filtered and recrystalized from ethanol to afford



**Scheme 4 : Synthesis of 2-naphthol podands via diacid chloride route.**

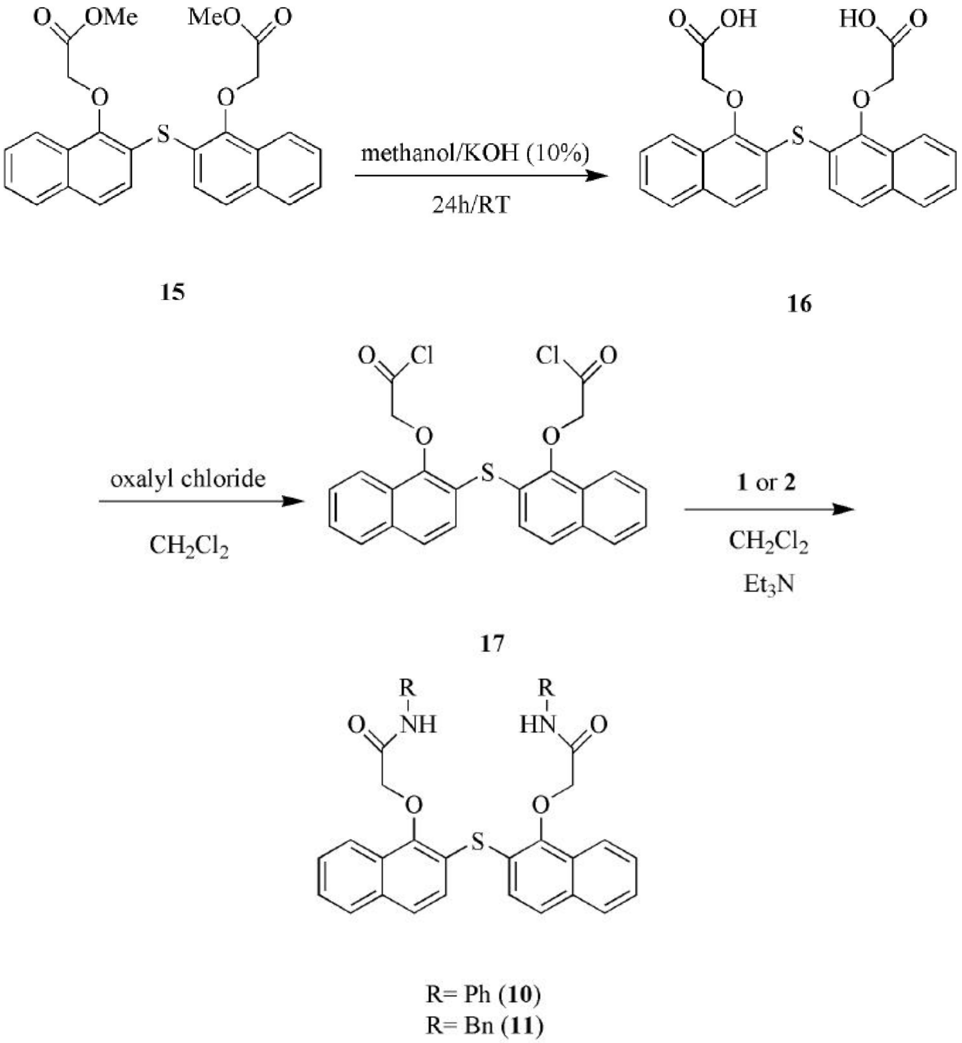
corresponding products.

## General procedure 2, for the synthesis of dinaphthosulfide diaza podands via diacid chloride route

diacid (1 mmol), oxalyl chloride (2 mmol) and catalytic amounts of dimethyl formamide (DMF) in dichloromethane (dry) were stirred at room temperature overnight, after appearance of a clear yellow solution the reaction mixture was filtered and the solvent was evaporatrd to afford a yellow solid. This product was used in another step without further purification. To a reaction mixture of amine (2 mmol), triethyl amine (2 mmol) in CH$_2$Cl$_2$ was added dropwise the above diacid chloride in CH$_2$Cl$_2$ (20 ml), after stirring overnight water was added and the mixture was extracted with CH$_2$Cl$_2$ (3×50) and washed with HCl (10%, 3×50 ml), the combined organic layer were dried and evaporated to afford a white solid which was purified by column chromatography on silica gel using useful solvent mixtures as eluent to obtain pure macrocycles.

### Synthesis of 1,1'-thiobis (4-aza-1-oxa-3-oxo-4-phenyl-butyl)naphthalene (7)

This compound was prepared as white crystals based on the general procedures 1 and 2 in 89% and 71% yields, respectively. mp 225-226 $^{o}$C; IR (KBr): 3338 (broad), 2944, 2866, 1690, 1665, 1656, 1642, 1631, 1624, 1585, 1575, 1565, 1557, 1480, 1463, 1442, 1256, 1218, 1083 cm$^{-1}$; $^{1}$H NMR (300 MHz, DMSO - d6) δ: 4.22 - 4.24 (d, 2H, J = 6Hz), 4.56 (s, 2H), 7.14 - 7.25 (m, 15H), 7.29 - 7.36 (q, 2H), 7.40 - 7.45 (t, 3H, J = 6, 9 Hz), 7.82 - 7.87 (t, 2H, J = 6, 9 Hz), 8.06 - 8.10 (t, 1H, J = 6 Hz), 8.45 - 8.48 (d, 1H,



**Scheme 5 : Synthesis of 1-naphthol podands via diacid chloride.**

J = 9 Hz) ppm; $^{13}$C NMR (75 MHz, DMSO - d6) δ: 167.5, 156.3, 138.8, 134.2, 130.1, 129.4, 128.9, 128.6, 128.4, 127.3, 126.1, 120.1, 127.2, 127.0, 126.7, 124.6, 124.1, 117.2, 115.2, 68.3, 41.7 ppm; MS (electron impact) m/z (relative intensity): 614 (2%), 613 (3%), 612 (4%) [M]$^+$, 554 (2%), 465 (3%), 413 (3%), 412 (2%), 323 (2%), 320 (1%), 316 (1%), 290 (23%), 144 (7%), 115 (14%), 105 (2%), 91 (100%), 65 (10%); Anal. calcd. for $C_{36}H_{28}N_2O_4S$: C, 73.95; H, 4.83; N, 4.79. Found: C, 73.92; H, 4.81; N, 4.82.

### Synthesis of 1,1'-thiobis (4-aza-1-oxa-3-oxo-5-phenyl-pentyl)naphthalene (8)

This compound was prepared via general procedures 1 and 2 as white crystals in 87% and 66% respectively and melting point of 251-252 °C; IR [KBr]: 3301, 3131, 3072, 3048, 1679, 1601, 1540, 1501, 1447, 1315, 1269, 1239, 1090, 809, 759, 688, 504 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO - d6) δ: 3.35 (s, 4H), 4.78 (s, 4H), 7.03 - 7.08 (t, 2H, J = 7.3 Hz), 7.26 - 7.44 (m, 10H), 7.54 - 7.57 (d, 4H, J = 7.8 Hz), 7.78 - 7.81 (d, 2H, J = 7.8 Hz), 7.85 - 7.88 (d, 2H, J = 9 Hz), 8.49 - 8.52 (d, 2H, J = 8.4 Hz), 9.95 (s, 2H) ppm; $^{13}$C NMR (75 MHz, DMSO - d6) δ: 166.25, 156.44, 138.25, 134.37, 130.25, 129.50, 128.78, 128.41, 127.22, 124.83, 124.06, 123.66, 119.36, 117.15, 115.15, 130.25 ppm; MS (electron impact) m/z (relative intensity): 640 (8%) [M]$^+$, 465 (23%), 414 (12%), 323 (2%), 316 (35%), 291 (28%), 144 (19%), 115 (26%), 108 (21%), 91 (100%), 65 (12%); Anal. calcd. for $C_{38}H_{32}N_2O_4S$: C, 74.49; H, 5.26; N, 4.57. Found: C, 74.46; H, 5.24; N, 4.60.

### Synthesis of Synthesis of 1,1'-thiobis (4-aza-1-oxa-3-oxo-5-phenyl-pentyl)naphthalene (10)

This compound was prepared via general procedures 1 and 2 as white crystals in 91% and 73% respectively and melting point of 221-222 °C; IR (KBr): 3390, 3256, 2987, 1681, 1667, 1610, 1503, 1412, 1266, 1066, 747cm-1; $^1$H NMR (500 MHz, DMSO-d$_6$): δ 4.55 (s, 4H, CH$_2$), 7.30-7.37 (m, 13H), 7.86-7.94 (m, 4H), 8.35-8.37 (b, 2H) ppm; $^{13}$C NMR (125 MHz, DMSO-d$_6$): δ 170.2 (carbonyl), 168.4, 158.2, 136.8, 130.9, 130.5, 128.8, 128.4, 126.1, 125.7, 117.1, 114.9, 68.1ppm; MS (electron impact) m/z (relative intensity %): 612 (10%) [M]$^+$, 467 (8%), 413 (9%), 412 (33%), 323 (11%), 316 (23%), 290 (26%), 144 (21%), 115 (12%), 105 (7%), 91 (100%), 65 (15%); Anal. calcd. for $C_{36}H_{28}N_2O_4S$: C, 73.95; H, 4.83; N, 4.79. Found: C, 73.93; H, 4.84; N, 4.81.

### Synthesis of Synthesis of 2,2'-thiobis (4-aza-1-oxa-3-oxo-5-phenyl-pentyl)naphthalene (11)

This compound was prepared via general procedures 1 and 2 as white crystals in 84% and 68% respectively and melting point of 246-247 °C; IR (KBr): 3391, 3257, 2982, 1688, 1669, 1614, 1503, 1415, 1266, 1065, 741cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$): δ 3.31 (s, 4H), 4.55 (s, 4H, CH$_2$), 7.31-7.39 (m, 18H), 7.82-7.87 (m, 4H), 8.32-8.36 (b, 2H) ppm; $^{13}$C NMR (125 MHz, DMSO-d$_6$): δ 172.3 (carbonyl), 168.9, 158.4, 136.6, 130.7, 130.5, 130.1,129.8, 129.6,129.4, 129.2, 128.9, 128.8, 128.6, 128.3, 127.9, 127.7, 127.3, 126.8, 126.1, 125.8, 125.6, 125.2, 119.8, 115.5, 68.2, 45.1 ppm; MS (electron impact) m/z (relative intensity): 640 (9%) [M]$^+$, 465 (22%), 414 (16%), 316 (31%), 291 (22%), 144 (12%), 115 (21%), 108 (32%), 91 (100%), 65 (18%); Anal. calcd. for $C_{38}H_{32}N_2O_4S$: C, 74.49; H, 5.26; N, 4.57. Found: C, 74.47; H, 5.25; N, 4.59.

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