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Synthesis of new aza crowns bearing 1-naphthol and 2-naphthol with palmitoyl and octanoyl chains as pendant arms

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ABSTRACT

New aza crowns (lariats) bearing palmitoyl, octanoyl and acetyl side chains were prepared from the reaction of corresponding aza crowns and palmitoyl chloride (or octanoyl chloride or acetyl chloride) in excellent yield. Dinaphthosulfideaza crown of 2-naphthol were prepared from the reaction of diester and diethylenetriamine. Diester was prepared from the reaction of 1,1'-thiobis (2-hydroxy naphthalene) and methylchloroacetate. Diester of 1-naphthol was prepared from the reaction of 2,2'-thiobis (1-hydroxy naphthalene) and methylchloroacetate. The reaction of resulting diester and diethylenetriamine afforded aza crown of 1-naphthol derivative. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Aza crown;
Lariat;
Naphthol;
Dinaphthosulfide;
Palmitoyl chloride;
Octanoyl chloride;
Synthesis.

INTRODUCTION

Since the pioneering work of Pedersen in 1967^[1], crown ethers and aza crowns have gained significant interest in a series of applications such as sensors, biological model systems, host-guest chemistry and supramolecular chemistry^[2]. Crown ethers are compounds that are cyclic oligomers of ethylene oxide. The essential repeating unit of any simple crown ether is ethyleneoxy, i.e., $-\text{CH}_2\text{CH}_2\text{O}-$, which repeats six times in 18-crown-6. Pedersen examined dibenzo-18-crown-6 and similar crown ethers and showed that the receptor and guest ion can interact and form stable complexes.

The crown ethers are known for their ability to strongly enhance cation solubility in organic solvents. The oxygen atoms are ideally situated (normally at the ionic bond distance) to coordinate with a cation inside the ring, whereas the outside of the ring is hydrophobic.

The result of this hydrophilic heart-hydrophobic shell is that the complexed cation is soluble in nonpolar solvents thanks to the hydrophobic shell. The size of the inner ring of the crown ether determines the size of the cation it can solvate^[2].

A large number of research groups developed the new crown ethers and azacrowns^[3]. Introduction of other elements such as N and S improve the complexation ability of crown ethers^[4]. In recent years crown ether and aza crown chemistry led to a large number of receptors such as cyclic peptides^[5], calixarenes^[6], cryptands^[7], lariat ethers^[8] and cyclic polymers^[9].

A large number of lariat ethers with various functional groups as side arms were prepared. The nature of side chain changes the stability of complexes and their applications. Carboxylic acids^[10], phosphoryl^[11], hydroxyl^[12], amide, urea and thiourea^[13] and aliphatic chains^[10] are the common functional groups in lariats.

In polymers with macrocycles as side groups the new properties combined of polymer and macrocycle is appeared. In these compounds the polymer chain is similar to the side group of lariat ether and enhances the properties of macrocycle. The lariat ethers with long aliphatic chains are important candidates for interface applications and micelles^[14].

In continuation of our researches on the synthesis of aza crowns and their applications^[15], new aza crowns containing aliphatic side chains were prepared. The study of these compounds in various systems is underway.

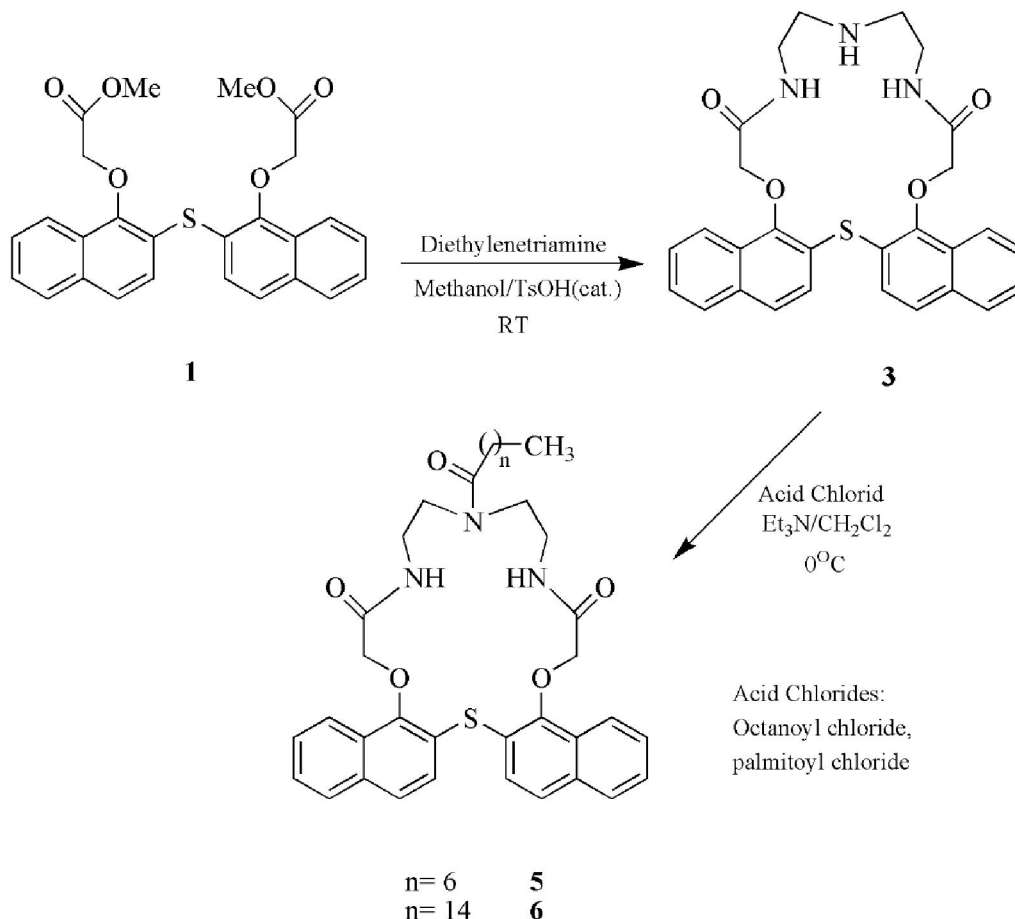
RESULTS AND DISCUSSION

Dinaphthosulfide diester (**1**) was prepared according to the published procedure^[16]. Aza crown (**3**) was synthesized from the reaction of diester (**1**) and diethylenetriamine in methanol in the presence of *p*-toluenesulfonic acid at room temperature in good yield. Lariats of aza crown (**3**) were prepared from the reaction of (**3**) and palmitoyl and octanoyl chlorides in

dichloromethane in the presence of triethylamine.

Sulfide diester (**2**) and aza crown (**4**) were prepared based on the reported procedure^[13]. Reaction of aza crown (**4**) and palmitoyl chloride (or octanoyl or acetyl chloride) in dichloromethane in the presence of triethylamine afforded the corresponding lariats in excellent yields.

P-Toluenesulfonic acid protonate the ester carbonyls and create a high density of positive charge on carbon. The reaction of amine and carbonyl group facilitate the formation of amide bonds and the synthesis of aza crowns were performed conveniently in these conditions. On the other hand, the macrocyclization process and finally the aza crown yield are related to several factors such as the structure of diester, concentration and hydrogen bonding. Near to each other esters and the reaction at lower concentration (for example high dilution conditions) afforded higher yields of aza crowns. Intramolecular hydrogen bonding raise the yield of aza crowns, but the intermolecular hydrogen bondings lower the yields of these macrocycles.



Scheme 1 : Synthesis of 1-naphthol containing lariats (5 and 6).

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EXPERIMENTAL

The reactions were carried out in an efficient hood. All the materials were purchased from Merck, Fluka and Aldrich chemical companies. Acetonitrile and methanol were distilled and stored over molecular sieves. DMF was distilled over molecular sieves under reduced pressure and stored over them. 1^[13], 2^[16] and 4^[13] were reported previously. Merck silica gel 60 F254 TLC plates were used for thin layer chromatography (TLC). The melting points (uncorrected) were measured with an Electrothermal engineering LTD 9100 apparatus. Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer. IR spectra were measured on Perkin-Elmer model 543 and BRUKER FT-IR spectrometers; the ¹H NMR and ¹³C NMR spectra were obtained using BRUKER AVANCE DRX 500 MHz apparatus. The mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

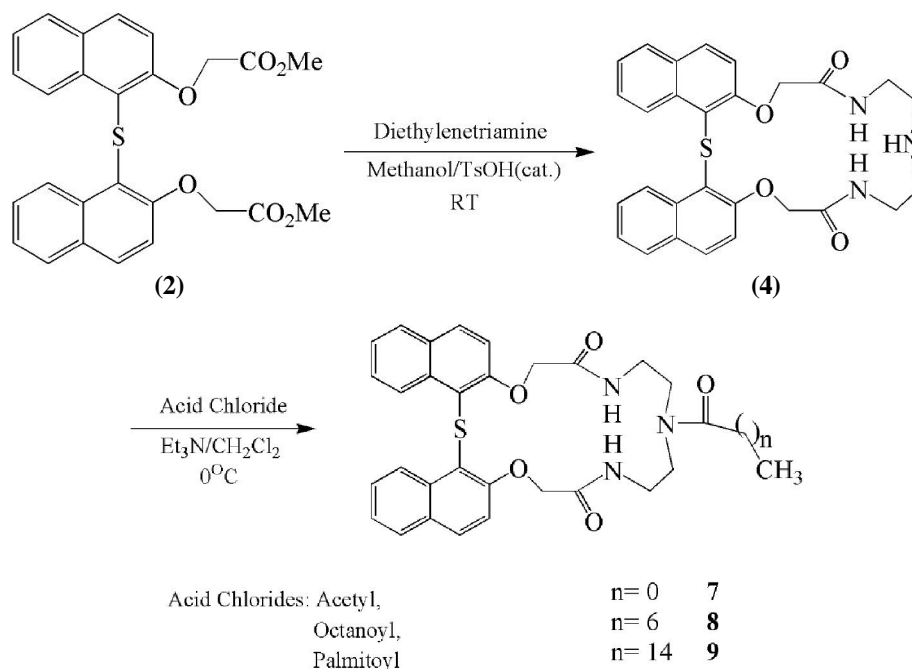
Synthesis of 7,10,13-triaza-1-thia-4,16-dioxa-6,14-dioxo-2,3;17,18-dinaphtho-cyclooctadecane (3)

To diester (1) in dry methanol were added diethylenetriamine and p-toluenesulfonic acid (p-TsOH) (catalytic). The clear solution was refluxed for 48h. After completion of reaction (monitored by TLC), water was added to the reaction mixture and extracted with chloro-

form (3×50mL). The combined chloroform layers were dried (Na₂SO₄) and evaporated under reduced pressure to afford crude product. This product was purified by column chromatography using chloroform/methanol (4:1) as eluent to obtain macrocycle (3) in 76% yield and melting point of 231-232°C; IR (KBr): 3390, 3256, 2987, 1681, 1667, 1610, 1503, 1412, 1266, 1066, 747cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 2.47-2.50 (b, 4H, CH₂), 3.11 (s, 4H, CH₂), 4.58 (s, 4H, CH₂), 7.32-7.42 (m, 8H), 7.85-7.93 (m, 4H), 8.34-8.36 (b, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆): δ 171.1 (carbonyl), 169.7, 158.8, 136.9, 131.8, 130.6, 128.4, 128.7, 126.3, 125.5, 119.4, 115.2, 68.7, 39.6, 38.7, 28.5, 25.3ppm; MS (electron impact) m/z (relative intensity %): 501 [M]⁺ (molecular ion, 12), 483 (12), 300 (41), 287 (21), 187 (38), 144 (100), 128 (27), 115 (56), 56 (31), 44 (12); Anal. calcd. for C₂₈H₂₇N₃O₄S: C, 67.05; H, 5.43; N, 8.38. Found: C, 67.03; H, 5.44; N, 8.40.

General procedure for the synthesis of lariats (5-9)

To aza crown ((3) or (4), 1mmol) in dry dichloromethane (40mL) under N₂ were added acid chloride (palmitoyl or octanoyl or acetyl, 1mmol), and triethyl amine (1mmol). The mixtures were stirred at room temperature for 48h. After completion of the reaction (monitored by TLC), water was added and ex-



Scheme 2 : Synthesis of 2-naphthol containing lariats (7, 8 and 9).

tracted with chloroform (3×50mL) and washed with water and HCl (10%), respectively. The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to afford crude product which was purified by column chromatography on silica gel using appropriate solvents as eluent.

Synthesis of 7,10,13-triaza-1-thia-4,16-dioxo-6,14-dioxo-2,3;17,18-dinaphtho-13-(1-oxo-octyl)-cyclooctadecane (5)

According to the general procedure this aza crown was prepared from the reaction of (3) and octanoyl chloride and purified by column chromatography using chloroform/methanol (4:1) as eluent to afford (5) in 90% yield and melting point 193-194°C; IR (KBr): 3534, 3498, 3406, 2941, 1689, 1532, 1433, 1270, 1057, 819 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6): δ 0.72 (t, J= 8Hz, 2H), 0.83 (t, J= 5.4Hz, 4H), 0.89-0.94 (b, 2H), 1.12-1.18 (b, 4H), 1.37-1.41 (m, 2H), 2.12 (t, J= 7.5Hz, 2H), 2.26 (t, J=7Hz, 4H), 3.31-3.37 (m, 4H), 4.39 (s, 2H), 4.56 (s, 2H), 7.19-7.21 (b, 1H), 7.26-7.29 (b, 2H), 7.33-7.35 (m, 1H), 7.37-7.39 (m, 2H), 7.49-7.51 (m, 1H), 7.73-7.75 (b, 2H), 7.86-7.90 (m, 3H), 7.96-7.99 (b, 1H), 8.35-8.37 (b, 1H)ppm; ^{13}C NMR (125MHz, DMSO-d_6) δ : 175.24, 173.19, 173.06, 171.78, 171.34, 144.77, 144.12, 141.35, 141.14, 139.68, 139.53, 137.81, 135.47, 135.23, 128.91, 128.73, 128.62, 128.25, 119.31, 116.38, 116.13, 68.79, 68.17, 48.93, 47.32, 39.16, 38.23, 23.14, 22.83, 22.55, 21.17, 20.35, 18.76, 17.43 cm^{-1} ; MS (electron impact) m/z (relative intensity %): 627 $[\text{M}]^+$ (6), 542 (12), 493 (11), 453 (100), 397 (17), 281 (100), 255 (27), 144 (23), 71(49); Anal. calcd. for $\text{C}_{36}\text{H}_{14}\text{N}_3\text{O}_5\text{S}$: C, 71.99; H, 2.35; N, 7.00. Found: C, 71.96; H, 2.36; N, 7.03.

Synthesis of 7,10,13-triaza-1-thia-4,16-dioxo-6,14-dioxo-2,3;17,18-dinaphtho-13-(1-oxo-hexadecyl)-cyclooctadecane (6)

Based on the general procedure this aza crown was prepared from the reaction of (3) and palmitoyl chloride and purified by column chromatography using chloroform/methanol (5:1) as eluent to afford (6) in 89% yield and melting point of 186-187°C; IR (KBr): 3518, 3478, 3405, 2971, 1693, 1594, 1328, 1069, 815 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6): δ 0.84-0.91 (b, 7H), 0.99-1.02 (b, 4H), 1.17-1.29 (b, 18H), 1.47-1.49 (b,

2H), 2.01-2.03 (m, 2H), 2.17-2.19 (m, 2H), 3.33-3.35 (b, 4H), 4.43 (s, 2H), 4.62 (s, 2H), 7.24-7.25 (b, 1H), 7.31-7.32 (b, 2H), 7.36-7.38 (m, 1H), 7.41-7.43 (m, 2H), 7.52-7.54 (m, 1H), 7.76-7.77 (b, 2H), 7.90-7.93 (m, 3H), 8.04-8.06 (b, 1H), 8.47-8.48 (b, 1H)ppm; ^{13}C NMR (125MHz, DMSO-d_6) δ : 174.12, 173.96, 173.79, 167.75, 167.41, 143.60, 143.52, 139.43, 139.28, 132.97, 132.63, 130.71, 128.54, 128.19, 126.83, 126.34, 125.12, 116.73, 69.35, 69.08, 49.17, 48.93, 37.42, 37.16, 22.54, 21.73, 21.13, 19.57, 19.36, 19.22, 18.47, 18.09, 17.92, 16.31, 16.12, 15.63, 15.35, 15.14, 14.72ppm; MS (electron impact) m/z (relative intensity %): 740 $[\text{M}]^+$ (5), 688 (12), 451 (7), 281 (9), 268 (13), 239 (100), 144 (28), 115 (17), 96 (27), 71 (53); Anal. calcd. for $\text{C}_{44}\text{H}_{30}\text{N}_3\text{O}_5\text{S}$: C, 74.14; H, 4.24; N, 5.90. Found: C, 74.15; H, 4.23; N, 5.93.

Synthesis of 7,10,13-triaza-1-thia-4,16-dioxo-6,14-dioxo-2,3;17,18-dinaphtho-13-(1-oxo-ethyl)-cyclooctadecane (7)

According to the general procedure this aza crown was prepared from the reaction of (4) and acetyl chloride and purified by column chromatography using chloroform/methanol (4:1) as eluent to afford (7) in 96% yield and melting point of 202-203°C; IR (KBr): 3529, 3492, 3402, 2943, 1682, 1507, 1419, 1269, 1083, 813 cm^{-1} ; ^1H NMR (500 MHz, DMSO-d_6): δ 1.75 (s, 3H), 3.28-3.37 (m, 8H), 4.39 (s, 2H), 4.56 (s, 2H), 7.27-7.33 (m, 3H), 7.37 (d, J= 6Hz, 1H), 7.41 (d, J= 10Hz, 1H), 7.49 (dd, J= 12,13Hz, 1H), 7.75 (t, J= 8.5Hz, 1H), 7.85-7.92 (m, 5H), 8.10-8.13 (m, 1H), 8.43 (d, J= 14Hz, 1H)ppm; ^{13}C NMR (125MHz, DMSO-d_6) δ : 170.82, 167.97, 167.89, 155.72, 155.56, 133.80, 13370, 130.31, 130.07, 129.66, 129.50, 128.71, 127.53, 127.22, 124.35, 124.22, 124.06, 124.02, 117.07, 115.30, 115.08, 68.78, 68.41, 49.59, 47.08, 38.45, 37.55, 21.66ppm; MS (electron impact) m/z (relative intensity %): 543 $[\text{M}]^+$ (7), 493 (16), 452 (100), 397 (18), 309 (56), 28 (100), 278 (58), 239 (100), 144 (41), 115 (10), 96 (32), 71 (61); Anal. calcd. for $\text{C}_{30}\text{H}_{29}\text{N}_3\text{O}_5\text{S}$: C, 66.28; H, 5.38; N, 7.73. Found: C, 66.26; H, 5.39; N, 7.75.

Synthesis of 7,10,13-triaza-1-thia-4,16-dioxo-6,14-dioxo-2,3;17,18-dinaphtho-13-(1-oxo-octyl)-cyclooctadecane (8)

According to the general procedure this aza crown

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was prepared from the reaction of (4) and octanoyl chloride and purified by column chromatography using chloroform/methanol (5:1) as eluent to afford (8) in 92% yield and melting point of 208-209°C; IR (KBr): 3531, 3482, 2937, 1695, 1463, 1248, 1045, 763cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): 0.79 (t, J= 8Hz, 2H), 0.85 (t, J= 5.4Hz, 4H), 0.90-0.93 (b, 2H), 1.19-1.25 (b, 4H), 1.43-1.47 (m, 2H), 2.02 (t, J= 7.5Hz, 2H), 2.37 (t, J=7Hz, 4H), 3.40-3.45 (m, 4H), 4.45 (s, 2H), 4.63 (s, 2H), 7.31-7.33 (b, 2H), 7.37-7.39 (b, 1H), 7.43-7.45 (m, 1H), 7.51-7.54 (m, 1H), 7.78-7.80 (b, 3H), 7.86-7.88 (m, 1H), 7.91-7.94 (b, 3H), 8.05-8.07 (b, 1H), 8.43-8.46 (b, 1H)ppm; ¹³C NMR (125MHz, DMSO-d₆) δ: 171.24, 170.93, 170.52, 165.34, 165.18, 143.83, 143.72, 134.33, 134.25, 131.65, 131.49, 129.73, 127.56, 127.23, 124.86, 124.79, 124.56, 124.29, 118.11, 114.31, 114.19, 67.73, 67.64, 49.51, 46.13, 39.21, 37.58, 21.65, 20.12, 19.83, 19.46, 19.27, 18.12, 17.74cm⁻¹; MS (electron impact) m/z (relative intensity %): 627 [M]⁺ (8), 541 (47), 450 (100), 309 (51), 281 (100), 239 (100), 144 (24), 71 (51); Anal. calcd. for C₃₆H₁₄N₃O₅S: C, 71.99; H, 2.35; N, 7.00. Found: C, 71.97; H, 2.36; N, 7.04.

Synthesis of 7,10,13-triaza-1-thia-4,16-dioxo-6,14-dioxo-2,3;17,18-dinaphtho-13-(1-oxo-hexadecyl)-cyclooctadecane (9)

Similar to general procedure this aza crown was prepared from the reaction of (4) and palmitoyl chloride and purified by column chromatography using chloroform/methanol (4:1) as eluent to afford (9) in 91% yield and melting point of 195-196°C; IR (KBr): 3523, 3498, 3411, 2956, 1687, 1354, 1287, 1030, 823cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 0.84-0.90 (m, 11H), 1.02-1.24 (m, 18H), 2.02 (t, J= 5Hz, 2H), 3.35-3.44 (m, 8H), 4.44 (s, 2H), 4.62 (s, 2H), 7.25-7.28 (m, 1H), 7.31-7.33 (m, 1H), 7.37-7.39 (m, 1H), 7.41-7.45 (b, 2H), 7.51-7.55 (b, 1H), 7.76-7.78 (b, 2H), 7.86-7.89 (b, 1H), 7.90-7.94 (b, 3H), 8.05 (d, J= 10Hz, 1H), 8.49 (d, J= 6.5Hz, 1H)ppm; ¹³C NMR (125MHz, DMSO-d₆) δ: 172.67, 171.85, 171.54, 163.45, 163.24, 145.82, 145.71, 132.14, 132.07, 131.67, 131.43, 129.61, 128.75, 128.16, 125.84, 125.53, 125.38, 125.12, 118.13, 116.93, 116.19, 68.73, 68.39, 49.56, 47.11, 38.43, 37.51, 21.74, 21.43, 21.19, 20.83, 20.56, 18.71, 18.39, 17.98,

17.46, 16.87, 16.67, 16.42, 15.84, 15.38, 14.73ppm; MS (electron impact) m/z (relative intensity %): 740 [M]⁺ (4), 688 (5), 670 (3), 452 (23), 239 (100), 144 (28), 71 (53); Anal. calcd. for C₄₄H₃₀N₃O₅S: C, 74.14; H, 4.24; N, 5.90. Found: C, 74.11; H, 4.23; N, 5.92.

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REFERENCES

- [1] C.J.Pedersen; J.Am.Chem.Soc., **89**, 7017 (1967).
- [2] G.W.Gokel, W.M.Leevy, M.E.Weber; Chem.Rev., **104**, 2723 (2004).
- [3] F.Faridbod, M.R.Ganjali, R.Dinarvand, P.Norouzi, S.Riahi; Sensors, **8**, 1645 (2008).
- [4] (a) K.Dürr, B.P.Macpherson, R.Warratz, F.Hampel, F.Tuczek, M.Helmreich, N.Jux, I.Ivanović-Burmazović; J.Am.Chem.Soc., **129**, 4217 (2007); (b) J.F.Zhang, Y.Zhou, J.Yoon, J.S.Kim; Chem.Soc.Rev., **40**, 3416 (2011).
- [5] J.N.Lambert, J.P.Mitchell, K.D.Roberts; J.Chem.Soc., Perkin Trans., **1**, 471 (2001).
- [6] G.Uysal, S.Memon, M.Yilmaz; Reac.Func.Polym., **50**, 77 (2001).
- [7] B.Tiimmler, G.Maass, E.Weber, W.Weher, F.Vogtle; J.Am.Chem.Soc., **99**, 4683 (1977).
- [8] D.T.McQuade, A.E.Pullen, T.M.Swager; Chem.Rev., **100**, 2537 (2000).
- [9] C.-U.Lee, T.P.Smart, L.Guo, T.H.Epps, D.Zhang; Macromolecules, **44**, 9574 (2011).
- [10] M.-R.Huang, G.-L.Gu, F.-Y.Shi, X.-G.Li; Chin.J.Anal.Chem., **40**, 50 (2012).
- [11] A.N.Turanov, V.K.Karandashev, V.E.Baulin; Russ.J.Inorg.Chem., **57**, 292 (2012).
- [12] S.Bozkurt, M.Yilmaz, A.Sirit; Chirality, **24**, 129 (2012).
- [13] (a) E.Rostami, A.Zare; E-J.Chem., **8**, S7-S12 (2011); (b) A.Shockravi, S.M.Ataei, E.Rostami; J.Chem., **9**, (In press).
- [14] A.Khalfallah, A.Ayari, B.Boughariou, A.Hedhli; J.Inclu.Phen.Macro.Chem., **67**, 1 (2010).
- [15] E.Rostami; Organic Chemistry: An Indian Journal, (In press).
- [16] E.Rostami; Phosphorus, Sulfur, and Silicon, **186**, 1694 (2011).