A CONVENIENT SYNTHESIS OF MACROCYCLIC DIAMIDES

H. Sharghi* and H. Eshghi

Department of Chemistry, Shiraz University, Shiraz 71454, Islamic Republic of Iran

Abstract

Some new macrocyclic dibenzotrioxadiamides, dibenzotetraoxadiamide, dibenzopentaoxadiamide, dibenzothiatrioxadiamide, tribenzotrioxadiamides and tetrabenzohexaoxadiamide (14-21), (26) and (27) have been prepared. These compounds were obtained in the macrocyclization step by reacting the diamine (4) with appropriate dicarboxylic acid dichlorides (5-13) and (24). The cyclization does not require high dilution techniques or template effect and provides the expected dilactams in high yields ranging from 70% to 95%.

Introduction

Many investigations have been carried out into macrocyclic polyethers [1-8], however, the literature on the synthesis and complexes of macrocyclic dilactam is less extensive. Vogtle et al. [9-12] have synthesized some mixed-heteroatom macrocyclic and macrobicyclic molecules and prepared their complexes with various cations. Many macrocyclic azacrown ethers and their corresponding amides find wide application in chemistry, biology, microanalysis, metal separation and molecular recognition [13-16]. However, they are very expensive owing to their difficult preparations, tedious purifications and, in most cases, very low yields [17].

One of the most common and conventional methods of constructing macrocyclic lactams is to utilize the reaction of dicarboxylic acid chlorides with diamines. This route is indeed effective, especially with simple acyl chlorides that are readily purified and in cases of less reactive amines. Adverse factors, however, arise in the generally low yields and difficulty in purifying larger acyl chlorides. Furthermore, high-dilution techniques [18-19] are necessary in most cases to perform such reactions, in order to obtain reasonable yields because of a tendency to form linear polyamides. Although a variety of methods of preparing amides by activating carboxylic acids to combine with amines are known, especially in the synthesis of peptides, examples using such techniques to synthesize macrocyclic lactams are relatively rare. One example was highlighted by Cazaux et al. [20] who employed 2-mercaptothiazoline and 1,3-dicyclohexylcarbodiimide (DCC) to activated esters of such difunctional molecules, and the yields are not high.

Due to the great interest in nitrogen-containing macrocyclic ligands, an impressive array of synthetic methods have been developed for their syntheses. We have now studied the synthesis of macrocyclic diamides (14-21) (Scheme 1).

Diethylene glycol dibromide (2) was reacted with o-nitrophenol (1) in dimethylformamide to give 1,5-bis(o-nitrophenoxy)-3-oxapentane (3) in 80% yield. The dinitro (3) was reduced in a stirred refluxing solution of tin(II) chloride dihydrate in concentrated hydrochloric acid to diamine (4) in 90% yield.

The cyclization between diamine 4 and dicarboxylic acid dichlorides (5-13) was performed without the use of high-dilution techniques. Macrocyclic diamides [21-25]

Keywords: Macrocyclic diamides; Synthesis

*To whom all correspondence should be addressed
were selected as the targets of the present synthetic investigations. In addition, cyclization was carried out with fast addition of a mixture of diamine (2 mmole) and triethylamine (4 mmole) in solvent (10 ml) into a solution of dicarboxylic acid dichloride (2 mmole) in solvent (10 ml) over 5 sec with vigorous stirring at 0°C. The mixture was then stirred at room temperature for 10 min to give dilactams in high yields. So, in a preliminary study, the effect of solvents on the yield of the macrocyclization reactions was investigated with the formation of dilactams, 14, 18 and 19 (Table 1). Table 1 clearly indicates that acetonitrile, benzene, and acetone are suitable general solvents for these macrocyclization reactions. In each case, a properly selected solvent plays an important role.

<table>
<thead>
<tr>
<th>Dilactam</th>
<th>CH₂Cl₂</th>
<th>CH₃CN</th>
<th>CHCl₃</th>
<th>CH₂COCH₃</th>
<th>C₆H₆</th>
<th>(CHCl₃)₂</th>
<th>DMF</th>
<th>THF</th>
<th>(High dilution technique) (solvent) [ref.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>80</td>
<td>95</td>
<td>60</td>
<td>95</td>
<td>80</td>
<td>50</td>
<td>60</td>
<td>40</td>
<td>54 (benzene) [23]</td>
</tr>
<tr>
<td>18</td>
<td>69</td>
<td>85</td>
<td>60</td>
<td>40</td>
<td>55</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>40 (benzene) [23]</td>
</tr>
<tr>
<td>19</td>
<td>85</td>
<td>25</td>
<td>80</td>
<td>80</td>
<td>50</td>
<td>70</td>
<td>95</td>
<td>50</td>
<td>18 (pyridine) [24]</td>
</tr>
</tbody>
</table>
For example, compound 18 was obtained in moderate yield in most solvents, but in high yield in CH$_2$Cl$_2$ and CH$_3$CN. High-dilution techniques applied by Markovich et al. [22] and Biernat et al. [23] for this macrocyclization gave 40% and 41% yields in benzene and pyridine. Also, in the cases of dilactam 14 and 19, high-dilution techniques as presented in literature [23,24] gave 54% and 18% yields respectively. By our procedure, however, dilactam 14 and 19 were obtained in 95% and 85% yields in CH$_2$CN and CH$_2$Cl$_2$ respectively.

Compounds 14-21 were readily obtained in high yields in suitable solvents by the reaction of diamine 4 with the corresponding dicarboxylic acid dichloride (5-12) (Table 2). Dilactam 22 was not obtained under these conditions. The reaction of o-phthaloyl dichloride 13 with diamine 4 in various solvents gave a mixture of products and unreacted starting material 4. Column chromatography of products gave compound 23 in 50% yield.

Also, for comparison of the conformational effect, we reacted dicarboxylic acid dichloride (24) [21] with two diamines (4) and (25) (Scheme 2). Reaction of (24) with diamine 4 in CH$_2$Cl$_2$ gave tetrabenzohexahexadiamid (26) with 26 ring atoms in 80% yield. DibenzopentaheXadiamid (27) was also obtained from the reaction of 24 and 25 by the same method in 88% yield with 23 ring atoms. The structures proposed for the macrocyclic compounds are consistent with data derived from infrared and proton nuclear magnetic resonance spectra in addition to satisfactory combustion analysis and molecular weights determined by mass spectrometric analysis.

These results clearly indicate that the cyclization of different dicarboxylic acid dichlorides with diamines does not need high-dilution method. The question arises as to whether vigorous stirring and fast addition of reactant are indispensable for enforcing the cyclization of these substrates. To check this assumption, it was resolved to perform under normal stirring and/or low addition of reactants the same reactions decreased in macrocyclization reaction yield. All the presented cyclization reactions proceed efficiently under vigorous stirring conditions as well as fast addition of reactants, in a properly selected solvent. The course of the reaction is assumed to depend on the occurrence of self-assembly phenomena [25] which are probably stimulated by a properly selected solvent and the yields are improved by application of high speed stirring and fast addition of reactions.

Also, these products are potential precursors which yield by reduction many useful known, as well as new, azacrown ethers [17,22-24,26].

Experimental Section

Solvents, reagents, and chemical materials were obtained from Merck chemical company (West Germany) and Fluka (Switzerland). Melting points were determined in open capillary tubes in a Buchi 510 circulating oil
Table 2. Cyclization yields and physical properties of macrocyclic dilactams

<table>
<thead>
<tr>
<th>Dilactam</th>
<th>Starting materials</th>
<th>Solvent</th>
<th>Yield%</th>
<th>Melting point(^\circ\text{C}) (recrystallization solvents)</th>
<th>(^1\text{H}) NMR spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>4,5</td>
<td>CH(_3)CN</td>
<td>95</td>
<td>171-173 (\text{CH}_2\text{Cl}_2/\text{C}<em>6\text{H}</em>{12})</td>
<td>3.75(t, 4H, J=4.5 Hz), 4.1(t, 4H, J=4.5 Hz), 6.5-8.1(m, 8H), 8.25(b, 2H)</td>
</tr>
<tr>
<td>15</td>
<td>4,6</td>
<td>CH(_2)Cl(_2)</td>
<td>70</td>
<td>274-275 (\text{CH}_2\text{Cl}_2/\text{C}<em>6\text{H}</em>{12})</td>
<td>3.7(s, 2H), 3.85(t, 4H, J=4.5 Hz), 4.2(t, 4H, J=4.5 Hz), 6.85-8.1(m, 8H), 9.3(b, 2H)</td>
</tr>
<tr>
<td>16</td>
<td>4,7</td>
<td>CH(_2)Cl(_2)</td>
<td>70</td>
<td>214-215 (\text{CH}_2\text{Cl}_2/\text{C}<em>6\text{H}</em>{12})</td>
<td>3.2(s, 4H), 3.6(t, 4H, J=4.5 Hz), 3.9 (t, 4H, J=4.5 Hz), 6.6-7.1(m, 6H), 7.5(dd, 2H, J=8, 2 Hz), 8.7 (b, 2H)</td>
</tr>
<tr>
<td>17</td>
<td>4,8</td>
<td>CH(_3)COCH(_3)</td>
<td>95</td>
<td>228-230 (\text{CH}_2\text{Cl}_2)</td>
<td>1.85(t, 4H, J=4.8 Hz), 2.35(t, 4H, J=4.8 Hz), 3.9(t, 4H, J=4.5 Hz), 4.2(t, 4H, J=4.5 Hz), 6.7-7.7(m, 6H, 8.15(dd, 2H, J=8, 2 Hz), 8.25(b, 2H))</td>
</tr>
<tr>
<td>18</td>
<td>4,9</td>
<td>CH(_2)Cl(_2)</td>
<td>85</td>
<td>172-174 (\text{CH}_2\text{Cl}_2/\text{C}<em>6\text{H}</em>{12})</td>
<td>3.7(s, 4H), 3.9(t, 4H, J=4.5 Hz), 4.1(t, 4H, J=4.5 Hz), 6.6-7.1(m, 6H), 7.9(dd, 2H, J=8, 2 Hz), 9.0(b, 2H)</td>
</tr>
<tr>
<td>19</td>
<td>4,10</td>
<td>CH(_2)Cl(_2)</td>
<td>85</td>
<td>250-252 (\text{CH}_2\text{Cl}_2/\text{C}<em>6\text{H}</em>{12})</td>
<td>3.5(s, 4H), 3.9(t, 4H, J=4.5 Hz), 4.1(t, 4H, J=4.5 Hz), 6.6-7.7(m, 6H), 7.9(dd, 2H, J=8, 2 Hz), 9.0(b, 2H)</td>
</tr>
<tr>
<td>20</td>
<td>4,11</td>
<td>CH(_3)CN</td>
<td>90</td>
<td>256-257 (\text{CH}_2\text{Cl}_2)</td>
<td>3.8(t, 4H, J=4.5 Hz), 4.0(t, 4H, J=4.5 Hz), 6.5-7.2(m, 7H), 7.5-8.5(m, 5H), 8.7(b, 2H)</td>
</tr>
<tr>
<td>21</td>
<td>4,12</td>
<td>CH(_2)Cl(_2)</td>
<td>95</td>
<td>305-307 (\text{CH}_2\text{Cl}_2)</td>
<td>3.4(t, 4H, J=4.5 Hz), 3.55(t, 4H, J=4.5 Hz), 6.7-7.1(m, 6H), 7.4(s, 4H, 7.5(dd, 2H, J=7, 2 Hz), 9.15(b, 2H)</td>
</tr>
<tr>
<td>26</td>
<td>4,24</td>
<td>CH(_2)Cl(_2)</td>
<td>80</td>
<td>165-167 (\text{CH}_2\text{Cl}_2)</td>
<td>3.5-4.0(m, 8H), 4.05-4.4(m, 8H), 6.5-7.5(m, 12H), 8.15(dd, 2H, J=8, 2 Hz), 8.4(dd, 2H, J=8, 2 Hz), 10.1(b, 2H)</td>
</tr>
<tr>
<td>27</td>
<td>24,25</td>
<td>CH(_2)Cl(_2)</td>
<td>88</td>
<td>150-152 (\text{CH}_2\text{OH})</td>
<td>3.45(s, 4H), 3.48-3.7(m, 8H), 4.15(t, 4H, J=4.5 Hz), 4.25(t, 4H, J=4.5 Hz), 7.65-7.8 (m, 6H), 8.1(dd, 2H, J=8, 2 Hz), 8.4(b, 2H)</td>
</tr>
</tbody>
</table>
melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. 1H NMR spectra were obtained on a Jeol EX 90 Q for solutions in CDCl3 with tetramethylsilane as internal standard. Mass spectra (MS) were performed with a GCMS-QP 1000 EX spectrometer at 70 eV. UV spectra were recorded on a UV/VIS spectrometer PU 8750. Satisfactory microanalyses were obtained for compounds 16, 17, 26, 27: C±0.3, H±0.21, N±0.28; compounds 20, 21: C±0.19, H±0.22, N±0.27.

1,5-Bis(o-nitrophenoxy)-3-oxapentane(3)

Diethylene glycol dibromide (11.6 g, 0.05 mol) was treated with o-nitrophenol (14 g, 0.1 mol) in dimethylformamide (100 ml) containing potassium carbonate (14 g) at reflux for 24 h. After cooling, the mixture was poured into cold water and the white precipitate filtered off. The precipitate was washed with distilled water, and was then recrystallized from methanol to give compound (3) in 80% yield (13.9 g); m.p.= 67-69°C (lit. 67-69°C; 28, 29); rf= 0.79 (CH2Cl2-CH2OH/94-6); IR (KBr): 3070 (w), 1610 (s), 1590 (s), cm-1; m/z: 349 (M+1)^+, 241, 349 (M+3, 3.5), 122 (base peak), UV(CH2OH); \( \lambda_{max} (e_{max}) = 224(21000), 260(23340), 324 \text{ nm (17430)}. \)

1,5-Bis(o-aminophenoxo)-3-oxapentane(4)

The dinitro compound (3) (3.5 g, 0.01 mol) was reduced in a stirred refluxing solution of tin(II) chloride dihydrate (15 g, 0.65 mol) in concentrated hydrochloric acid (50 ml). After 7 h, the reaction mixture was cooled and the precipitate filtered off. A solution of sodium hydrosyde (5N, 200 ml) was added to the filtrate and extracted with CH2Cl2 (3x250 ml). The organic layer was washed with water (2x200 ml), dried with sodium sulphate and evaporated. The oil residue was crystallized from ethanol to give diamine 4 as a pale yellow solid in 90% (2.6 g) yield: m.p.= 65-66°C (lit. 65°C, 65°C; 28), 65°C; rf= 0.52 (CH2Cl2-CH2OH/94-6); IR (neat): 3450(b), 1605(s), 1510(s), cm-1; m/z: 292 (M+2H)^+, 3.2, 289(M+H)^+, 10.8, 288(M^+, 22.8, 80(C6H5N, base peak); UV(CH2OH); \( \lambda_{max} (e_{max}) = 224(21200), 270(9870), 276 \text{ nm (9500)}. \)

Preparation of Macrocyclic Diamides 14-21 and 26-27

General procedure

A solution of diamine (0.002 mol) and triethylamine (0.004 mol) in appropriate solvent (50 ml) was added quickly (5 sec.) to a vigorously stirred solution of diacid chloride (0.002 mol) in solvent (50 ml) at 0°C. The reaction mixture was stirred at room temperature for 30 min. The precipitate was filtered off and the filtrate washed with water (2x50 ml), 10% aqueous NaOH solution (50 ml) and then again with water (100 ml). The organic layer was dried over Na2SO4 and the solvent was evaporated to give a solid product.

1,4-Di-aza, 5,6 ; 14,15-di-benzo, 7,10,13- trioxacyclopentadecane, 2,3-dione(14)

14 was obtained from 4 and 5 following the general procedure in 95% yield in CH2CN as solvent: white solids; m.p. = 171-173°C (lit. 23, 23°C); rf = 0.25(CH2Cl2-CH2OH/96-4); IR(neat): 3340(b), 1770(m), 1690(s), 1600(s), 1530(s), cm-1; m/z: 343 [M+H]^+, 7.9, 342(M^+, 120(C6H5NO, base peak); UV(dioxane) \( \lambda_{max} (e_{max}) = 240(4300), 279(9050), 299 \text{ nm (9260)}. \)

1,5-Di-aza, 6,7 ; 15,16-di-benzo, 8,11,14- trioxacyclohexadecane, 2,4-dione(15)

15 was obtained from 4 and 6 following the general procedure in 70% yield in CH2Cl2 as solvent: white solids; m.p. = 274-275°C (lit. 25, 273-275°C; rf = 0.6 [CH2Cl2-CH2OH/94-6]; IR(neat): 3300(b), 1675(s), 1600(s), ms: m/z = 356 (M+^+, C15H5N024.1), 80 (base peak), UV(dioxane); \( \lambda_{max} (e_{max}) = 257(9400), 278.5 \text{ nm (9100)}. \)

1,6-Di-aza, 7,8 ; 16,17-di-benzo, 9,12,15- trioxacycloheptadecane, 2,5-dione(16)

16 was obtained from 4 and 7 following the general procedure in 70% yield in CH2Cl2 as solvent: white solids; m.p. = 214-215°C; rf = 0.26(CH2Cl2-CH2OH/96-4); IR(neat): 3300(b), 2930(w), 1675(s), 1600(s), 1530(s), 1495(s), 1450(s), 1290(m), 1260(s), 1220(m), 1165(m), 1120(s), 1070(m), 1010(s), 940(m), 750(s), 670(s) cm-1; ms/m/z = 372(M+2H)^+, 3.9, 371(M+H)^+, 20.6, 370(M^+, C17H5N2O4, 48.5), 55(C6H5O, base peak); UV(dioxane); \( \lambda_{max} (e_{max}) = 236(2800), 253(8900), 282 \text{ nm (4400)}. \)

1,8-Diaza, 9,10 ; 18,19-di-benzo, 11,14,17- trioxacyclononadecane, 2,7-dione (17)

17 was obtained from 4 and 8 following the general procedure in 95% yield in acetone as solvent: white solids; m.p. = 228-230°C, rf = 0.46(CH2Cl2-CH2OH/96-4); IR(neat): 3420(b), 3300(b), 2940(m), 1670(s), 1600(s), 1530(s), 1450(s), 1290(s), 1260(s), 1120(s), 1050(m), cm-1; ms/m/z = 400(M+2H)^+, 2.2, 399(M+H)^+, 11.6, 398(M^+, C19H5N2O4, 31.9), 55(C6H5O, base peak); UV(dioxane); \( \lambda_{max} (e_{max}) = 260(21000), 277 \text{ nm (27000)}. \)

1,7-Diaza, 8,9 ; 17,18-di-benzo, 4,10,13,16- tetraoxacyclododecane, 2,6-dione (18)

18 was obtained from 4 and 9 following the general procedure in 85% yield in CH2CN as solvent: pale brown solids; m.p. = 170-172°C (lit. 23,30, 172-174°C; rf = 0.62 (CH2Cl2-CH2OH/96-4); IR(neat): 3400(b), 1675(s),
1600 (s), cm⁻¹; m/z = 386 (M⁺, C₂₄H₂₂N₂O₆, 6.6); 86 (C₅H₄NO₂, base peak); UV(dioxane): λₑ_(max): 235(2700), 252(3000), 284 nm (4100).

1,7-Diaza,8,9; 17,18-dibenzo, 10,13,16-trioxa, 4-thiacyclooctadecane, 2,6-dione (19)

19 was obtained from 4 and 10 following the general procedure in 85% yield in CH₂Cl₂ as solvent: white solids; m.p. = 250-252°C (lit. 249-250°C); r.f = 0.61 (CH₂Cl₂-CH₂OH/96-4); Ir(neat): 3400(b), 1680(s), 1600(s), cm⁻¹; m/z = 402 M⁺, C₂₆H₃₂N₂SO₄, 2.5; 45 (C₅H₄O₂, base peak); UV(dioxane): λₑ_(max): 234(3400), 250(9600), 284 nm (4900).

1,13-Diaza-2,3; 11,12; 15,17-tribenzo-4,7,10-thiacyclooctadecane-14,18-dione (20)

20 was obtained from 4 and 11 following the general procedure in 90% yield in CH₂CN as solvent: white solids; m.p. = 256-257°C; r.f = 0.8 (CH₂Cl₂-C₂H₅OH/94-6); Ir(neat): 3300(b), 2960(w), 2880(w), 1670(s), 1600(s), 1540(s), 1490(s), 1455(s), 1340(s), 1290(s), 1260(s), 1220(s), 1140(s), 1120(s), 1070(s), 950(s), 750(s), 720(s), 670(s), cm⁻¹; m/z = 420 [M+2H]⁺, 322, 319 [M+H]⁺, 171, 418 M⁺, C₂₆H₃₂N₂O₄, 47.6, 104 (C₅H₄O₂, base peak); UV(dioxane): λₑ_(max): 235(2700), 255(10500), 294.5 nm (14700).

1,13-Diaza-2,3; 11,12; 15,18-tribenzo-4,7,10-thiacyclononaocatane-14,19-dione (21)

21 was obtained from 4 and 12 following the general procedure in 95% yield in CH₂Cl₂ as solvent: white solids; m.p. = 305-307°C; r.f = 0.27 (CH₂Cl₂-C₂H₅OH/96-4); Ir(neat): 3340(b), 3070(w), 2940(m), 2880(w), 1665(s), 1600(s), 1530(s), 1505(s), 1485(m), 1450(s), 1420(m), 1340(m), 1260(s), 1220(m), 1125(s), 1050(s), 1020(m), 860(m), 750(s), cm⁻¹; m/z = 420 (M+H)⁺, 1.5; 419 (M+H)⁺, 12.4; 418 M⁺, C₂₆H₂₂N₂O₄, 41.3; 104 (C₅H₄O₂, base peak); UV(dioxane): λₑ_(max): 255(20500), 280.5 nm (25000).

11,23-Diaza-8,9; 12,13; 21,22; 25,26; tetranbenzo, 1,4,7,10-hexaoxycyclonoxacoseno-10,24-dione (26)

26 was obtained from 4 and 24 following the general procedure in 80% yield in CH₂Cl₂ as solvent: pale brown solids; m.p. = 165-167°C; r.f = 0.46 (CH₂Cl₂-C₂H₅OH/96-4); Ir(KBr): 3345(s), 3070(w), 2920(m), 2880(m), 1660(s), 1600(s), 1530(s), 1480(s), 1450(s), 1410(m), 1330(m), 1290(s), 1230(s), 1160(m), 1130(s), 1090(s), 1045(s), 950(s), 750(s), 660(m), cm⁻¹; m/z = 599 [(M+H)⁺, 2.4]; 598 (M⁺, C₂₆H₂₂N₂O₄, 6.2); 121 (C₅H₄O₂, base peak); UV(CH₃OH): λₑ_(max): 224(13900), 298 nm (10800).

1,15-Diaza-3,4; 12,13-dibenzo-5,8,11,18,21-pentaoxacyclorosane-2,14-dione (27)

27 was obtained from 24 and 25 following the general procedure in 88% yield in CH₂Cl₂ as solvent: white solids; m.p. = 150°C; r.f = 0.45 (CH₂Cl₂-C₂H₅OH/96-4); Ir(neat): 3400(b), 3070(w), 2920(s), 1660(s), 1600(s), 1530(s), 1485(s), 1450(s), 1350(s), 1300(s), 1240(s), 1160(s), 1130(s), 1045(s), 960(s), 920(s), 870(s), 830(m), 760(s), 735(m), 700(m), 665(s), cm⁻¹; m/z = 460 (M+2H)⁺, 11.9; 459 (M+H)⁺, 37.3; 458 (M⁺, 3.4; 441 (C₂₆H₂₂N₂O₄, 2.4); 121 (C₅H₄O₂, base peak); UV(dioxane): λₑ_(max): 254(9800), 283 nm (12500).

Compound 23

23 was obtained from 4 and 13 following the general procedure in 50% yield in CH₂Cl₂ as solvent: yellow solids; m.p. = 125-127°C; r.f = 0.25 (CH₂Cl₂-C₂H₅OH/96-4); Ir(neat): 3480(b), 3300(b), 3070(w), 2960(w), 2880(w), 1720(s), 1600(s), 1510(s), 1460(s), 1390(s), 1290(s), 1260(s), 1130(s), 1050(s), 890(s), 750(s), 750(s), cm⁻¹; m/z = 419 (M+H)⁺, 28.7; 418 (M⁺, C₂₆H₂₂N₂O₄, 55.7); 45 (C₅H₄O₂, base peak); UV(dioxane): λₑ_(max): 285 nm (8500).

Acknowledgements

We are grateful to the Shiraz University Research Council for their financial support.

References