Synthesis of new aza- and thia-crown ethers and their metal ion templates synthesis as model case study

Mahmood Kamali, Abbas Shockravi,* Reza Mohtasham, and Somayeh Pahlavan Moghanlo

Faculty of Chemistry, Kharazmi University, Mofatteh Ave., No.49, 15614 Tehran, Iran
E-mail: Abbas_shockravi@yahoo.co.uk, shockravi@khu.ac.ir

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Abstract

Four new thia- and four new aza- crown ethers were synthesized using the reaction of ethylene glycols ditosylated with 1,1´-(2,2´-dihydroxynaphthyl)sulfide (**DNS**) and 2,6-bis(3-hydroxyphenyl)-4-phenylpyridine in acetonitrile as solvent in the presence of bases (LiOH, NaOH, KOH and Cs_2CO_3). In the synthesis of macrocycles based on **DNS**, the template effects of alkaline metal ions; Li^+, Na^+, K^+ and Cs^+ on the reaction yields were investigated. Sodium template generally was more effective for the synthesis of all four macrocycles. Relatively, good yields of 15- and 18-membered macrocycles were obtained in the presence of all kinds of applied cations. K^+ Cation was more effective template ion than Na^+ in the formation of 18-membered macrocycles due to their larger cavity size compared to the 15-membered cycles. The structures of macrocycles were confirmed by CHN/O analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry.

Keywords: Aza-crown ether, thia-crown ether, template effect, dinaphthylsulfide, 2,4,6-triarylpyridine, naphthalene, pyridine

Introduction

Crown ethers were the first synthetic structures contributing to the vastly increasing field of Host-Guest and molecular recognition chemistry.[1-3] Due to their unique ability to complex particularly alkali and alkaline earth metal ions, they find wide applications in many fields of synthetic, analytical, and physical organic chemistry.[4] Although molecular recognition is now verified by highly diversified and tailor-made structural component,[5-6] simple crown compounds are still attractive, for instance due to their generally good solubility in many solvents. The remarkably easy formation of large crown ether rings from noncyclic precursors using metal

template-directed cyclizations by various modifications of the Williamson ether synthesis guarantees a general and usually high-yield access.[7]

There are number of reports, which suggest that in the case of condensation between dihydroxy aromatics and activated polyethylene glycols, the nature of the template influences the size and extent to the rate of macrocyclization.[8-15]

Diastereotopic character was found in some of dibenzosulfoxide and sulfide crown ethers synthesized in [1:1] and [2:2] macrocycles respectively.[16-19] This character is due to transoid conformation which was found when X-ray crystallography was taken. It is interesting that Mague and his co-workers have observed a cisoid conformation of 1,1'-thiobis(2-naphthol) after X-ray analysis.[20-22] Related binaphthyl sulfide based macrocycles have been synthesized in our research group and used in conductance study of complexation with several different metal ions.[23-25] All these observations in these series of macrocycles proved that the presence of sulfide atom play an important role in Host-Guest chemistry.

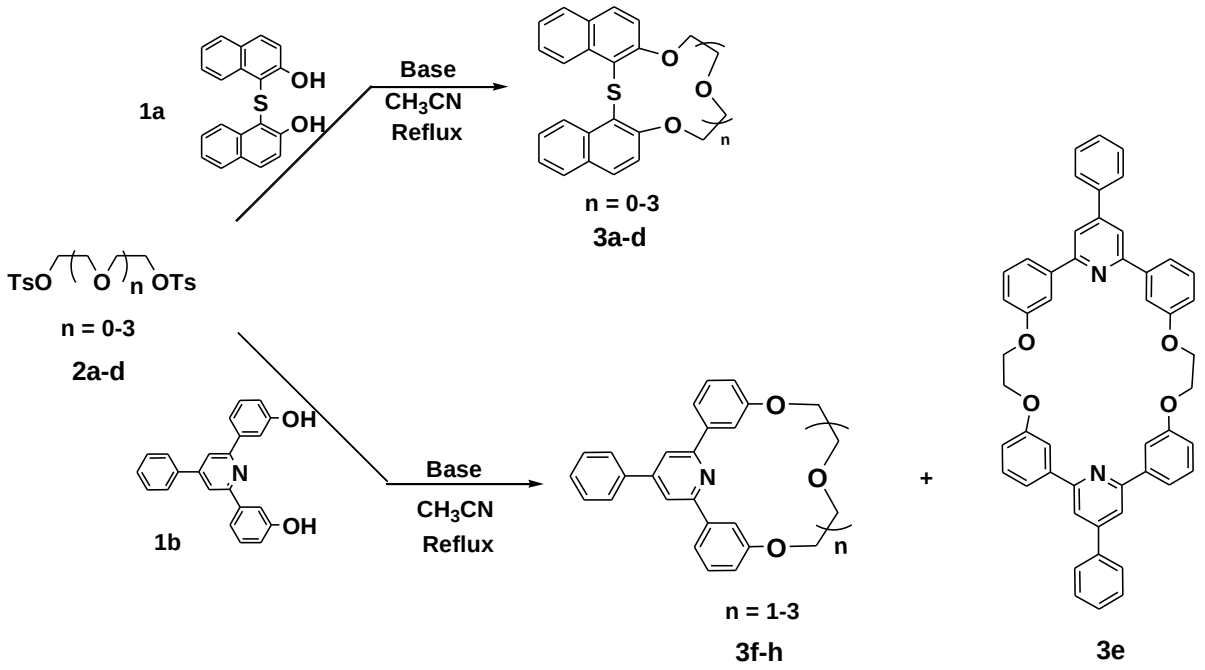
Also variety of macrocycles containing pyridine such as dimethyl-2,6-pyridine dicarboxylates and polyamine fragments have attracted much interest of many research groups during last decade.[26-31] In fact, introduction of a pyridine moiety, strongly influences the thermodynamic properties and complexation kinetics by increasing the conformational rigidity of the macrocycles basicity modifications.[32]

The effects of numbers of factors (nature, number, relative structural and spatial placement of various ligating units, binding forces, etc.) have been studied in this trend in Host-Guest recognitions.[33-35] We have also examined such factors in **DNS** and pyridine based systems and studied them as host molecules in the presence of different metal cations in which the best selectivity and stability was found for Hg^{2+} and Cu^{2+} complexes.[24, 36, 37]

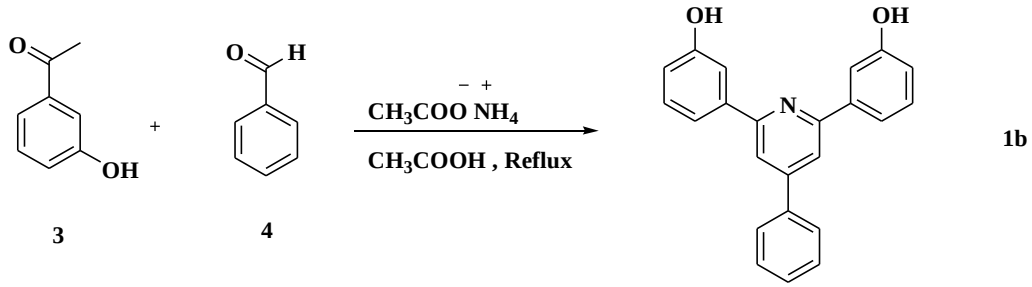
In this work, we wish to report the effect of alkaline metal cations (Li^+, Na^+, K^+, and Cs^+) anchors in the chemical template processes.

Results and Discussion

The synthesis of new thia crown ethers **3a-d** and aza crown ethers **3e-f** were performed by the reaction of ditosylated glycols **2a-d** with **DNS** (**1a**) and 2,6-bis(3-hydroxyphenyl)-4-phenyl pyridine **1b** (Scheme 1). The **DNS** (**1a)** was synthesized using 2-naphthol in 76% yield [38] and 2,6-bis(3-hydroxyphenyl)-4-phenylpyridine **1b** was synthesized by using m-hydroxyacetophenone and bezaldehyde in manner of modified Chichibabin reaction in the yield of 73% (Scheme 2). Treatment of **1a, b** with ditosylated compounds (**2a-d**) in the presence of base (LiOH, NaOH, KOH and Cs_2CO_3) and in refluxing acetonitrile for one day gave the macrocycles **3a-h**.



Scheme 1. Synthesis of crown ethers



Scheme 2. Synthesis of 2,4,6-triarylpyridine via modified Chichibain reaction.

Table 1. Synthesized 9-18 membered aza- or thia-crown ethers

n	Ditosylated glycols	Macrocycle	Macrocycle series	Mp °C
0	**2a**	**3a**, 9-membered	Dinaphthylsulfide based	170-172
1	**2b**	**3b**, 12-membered		191-194
2	**2c**	**3c**, 15-membered		156-158
3	**2d**	**3d**, 18-membered		125-127
0	**2a**	**3e**, 26-membered	Pyridine based	>300
1	**2b**	**3f**, 16-membered		199-201
2	**2c**	**3g**, 19-membered		146-150
3	**2d**	**3h**, 22-membered		141-144

Based on the template effect studies in the presence of alkaline metal ions shown in Table 2, it seems that macrocyclic effect is more enhanced in the presence of Na^+ compared to Li^+ and K^+ ions. This must be the result of ion-macrocycle interactions and preorganization of the macrocyclic ligands toward Na^+ ion. It is interesting that 15-membered ligand **3c** does not have different behavior in the presence of Li^+ ion. This is not only because of preorganization of the macroring, but also may be due to HSAB conditions in which Li^+ ion behaves as hard acid.

The yields in Table 2 show that the template properties of the Na^+ is generally more effective for the synthesis of macrocycles **3a**, **3c** and **3d** (Entry 1, 3 and 4). The macrorings **3c** and **3d** are generally synthesized in the presence of all kinds of applied cations in comparably higher yields. Relatively good yields in the template synthesis of larger ligands **3c** and **3d** (Entry 3, 4) in the presence of all four kinds of ions display that these two polyether rings are able to wrap themselves around the metal ions in a folded conformations which can promote the construction of systems of size exceeding the geometrical parameters of the matrix. There is generally strong relation between template ion size and the yield of the required macrocycle; we have observed this trend mostly for K^+ and Cs^+ ions. It seems that in these two cases the sizes of the template and macrocyclic compounds assembled are matched.

Due to "cesium effect" which is generally observed in the most macrocyclization processes, we expected to observe the highest yields in the presence of Cs^+ ion, but this trend was not completely expressed. This might be because of limitation of solubility of some of the compounds containing the template specially Cs_2CO_3 which determines the concentration of the template ion in the reaction mixture.

Table 2. Template effects of alkaline metal ions in the synthesis of macrocycles **3a-d**

Entry	Macrocycle	Yield%			
		Li^+	Na^+	K^+	Cs^+
1	**3a**	50	60	45	40
2	**3b**	25	30	28	15
3	**3c**	***65***	***70***	***55***	***50***
4	**3d**	***45***	***60***	***70***	***55***

Experimental Section

General. All reactions were carried out on an efficient hood. The starting materials were purchased from Merck and Fluka chemical companies. Melting points were determined with a Branstead Electrothermal model 9200 apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer RX 1 Fourier transform infrared spectrometer. The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ on Bruker Avance 300 MHz spectrometers. Elemental

analyses were carried out by a Perkin Elmer 2400 series II CHN/O analyzer. Mass spectra were obtained by the Fisons Trio 1000 (70ev).

1,1´-(2,2´-Dihydroxynaphthyl)sulfide (1a). This compound was synthesized based on reported procedures.[38]

2,6-Bis(3-hydroxyphenyl)-4-phenylpyridine (1b). In a round-bottomed flask (50 mL) equipped with a reflux condenser, a mixture of benzaldehyde (0.612 mL, 6 mmol), 3-hydroxyacetophenone (1.633 g, 1.2 mmol), ammonium acetate (6 g), and glacial acetic acid (15 ml) was refluxed for 3 h. Then solvent was removed with vacuum evaporator. The resulting oil dissolved in diethyl ether and extracted with water (10 mL, 3 times), organic phase removed, crude product recrystallized from diethylether/petroleum ether (1:1), and then dried at 30 °C. Yield 73%, mp 242-246 °C; IR (KBr): 1203, 1403, 1494, 1550,1583, 1666, 3339 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.94 (m, 2H), 7.35 (t, *J* 7.9 Hz, 2H), 7.49 (m, 3H), 7.76 (m, 2H), 7.87 (t, *J* 1.99 Hz, 2H), 7.96 (m, 2H), 8.08 (s, 2H), 8.51 (s, 2H, exchanged with D_2O) ppm; ^{13}CNMR (75 MHz, DMSO-d_6): δ 114.7, 116.9, 117.4, 117.5, 119.0, 128.1, 129.9, 130.5, 139.5, 141.8, 150.9, 157.8, 158.7 ppm; Anal. Calcd. For $C_{23}H_{17}NO_2$: C, 81.04; H, 5.05; N, 4.05 Found: C, 80.74; H, 5.0; N, 3.88.

General procedure for the synthesis of macrocycles

The ditosylated derivative (**2a-d**) (1 mmol) was dropwisly added into solution of dinaphthylsulfide **1a** (1 mmol) or 2,6-bis(3-hydroxyphenyl)-4-phenylpyridine **1b** (1 mmol) with a base (LiOH, NaOH, KOH, Cs_2CO_3 in the case of 1b only KOH was used) (2.1mmol) in acetonitrile (150 mL) and refluxed for one days. On completion of the reaction (TLC), the solvent removed to obtain the crude product; these macrocycles purified by recrystallization or flash chromatography.

1-Thia-4,7-dioxa-2,3;8,9-dinaphthyl-cyclononane (3a). Purified by recrystallization from ethanol, Yield 60% ; mp 170-172 °C; IR (KBr): 756, 809, 1060, 1224, 1501, 1588, 2959, 3053 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 4.45 (s, 4H), 7.24 (d, *J* 12.0 Hz, 2H), 7.41 (t, *J* 7.2 Hz , 2H), 7.451 (t, *J* 5.7 Hz, 2H), 7.86 (d, *J* 8.7 Hz, 4H), 8.52 (d, *J* 8.4 Hz, 2H) ppm; ^{13}CNMR (75 MHz, DMSO-d_6) δ: 73.4, 121.6, 122.6, 124.5, 125.1, 127.5, 128.6, 130.7, 130.9, 134.0, 159.7 ppm; MS (EI) *m/z* (%): (M^+, molecular ion) 45 (13), 115 (25), 141 (78), 170 (100), 187 (28), 258 (17), 287 (24), 344 (76). Elemental analysis Calcd. For $C_{22}H_{16}O_2S$: C, 76.72; H, 4.68; S, 9.31 Found: C, 76.87; H, 4.79; S, 9.14.

1-Thia-4,7,10-trioxa-2,3;11,12-dinaphthyl-cyclododecane (3b). Purified by recrystallization from ethanol, Yield 30% ; mp 191-194 °C; IR (KBr): 801, 1077, 1148, 1267, 1502, 1589, 2865, 3043 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.74-3.77 (m, 4H), 4.21-4.24 (m, 4H), 7.29-7.39 (m, 4H), 7.41 (d, *J* 9 Hz, 2H), 7.85 (d, *J* 8.4 Hz, 4H), 8.33 (d, *J* 7.8 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 70.0, 70.5, 116.6, 117.6, 124.9, 125.5, 127.9, 129.5, 130.5, 130.7, 235.6, 158.5 ppm; MS (EI) *m/z* (%):43 (29), 115 (22), 144 (100), 170 (31), 187 (56), 214 (24), 388

(69). Elemental analysis Calcd. For $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.25 Found: C, 74.35; H, 5.31; S, 8.08.

1-Thia-4,7,10,13-tetraoxa-2,3;14,15-dinaphthyl-cyclopentadecane (3c). Purified by recrystallization from ethanol, Yield 70% ; mp 156-158 ºC; IR (KBr): 756, 806, 1073, 1226, 1475, 1502, 1587, 1857, 2883, 2964, 3057 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.33-3.36 (m, 4H), 3.55 (s, 4H), 4.08-4.10 (m, 4H), 7.24 (d, *J* 9.0 Hz, 2H), 7.32 (t, *J* 8.1 Hz, 2H), 7.39 (t, *J* 6.9 Hz, 2H), 7.71 (d, *J* 9.0 Hz, 2H), 7.75 (d, *J* 7.5 Hz, 2H), 8.50 (d, *J* 8.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 68.2, 70.7, 71.1, 114.9, 118.3, 123.5, 125.1, 126.6, 128.1, 128.5, 129.3, 134.8, 156.5 ppm; MS (EI) *m/z* (%): 45 (61), 73 (54), 115 (46), 144 (100), 170 (32), 187 (43), 432 (65). Elemental analysis Calcd. For $C_{26}H_{24}O_4S$: C, 72.20; H, 5.59; S, 7.41 Found: C, 72.32; H, 5.73; S, 7.30.

1-Thia-4,7,10,13,16-pentaoxa-2,3;17,18-dinaphthyl-cyclooctadecane (3d). Purified by recrystallization from ethanol, Yield 70% ; mp 125-127 ºC; IR (KBr): 748, 803, 1068, 1124, 1267, 1503, 1589, 2880, 3058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.24 (t, *J* 5.1 Hz, 4H), 3.34 (m, 4H), 3.45 (m, 4H), 4.06 (t, *J* 10.8 Hz, 4H), 7.25 (d, *J* 7.8 Hz, 2H), 7.33 (t, *J* 7.2 Hz, 2H), 7.44 (t, *J* 6.9 Hz, 2H), 7.75 (d, *J* 14.4 Hz, 4H), 8.61 (d, *J* 8.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 68.6, 69.8, 70.7, 71.0, 115.2, 118.7, 123.6, 125.5, 126.6, 128.0, 128.9, 129.4, 135.0, 156.7 ppm; MS (EI) *m/z* (%): 45 (78), 73 (59), 115 (21), 144 (100), 170 (30), 187 (36), 214 (15), 300 (13), 476 (79). Elemental analysis Calcd. For $C_{28}H_{28}O_5S$: C, 70.56; H, 5.92; S, 6.73 Found: C, 70.71; H, 6.03; S, 6.65.

1,14-Diaza-6,9,19,22-tetraoxa-3,5;10,13;16,18;22,25;-tetraphenylene-2,26;13,15-di(*p*-phenyl pyridine)-cyclohexacosane (3e). Purified by recrystallization from chloroform/diethyl ether (1:1), Yield 48%; mp >300 ºC; IR (KBr): 1255, 1497- 1584, 2883-2938, 3056 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 4.50 (s, 8H), 7.03-7.06 (m, 5H), 7.36 -7.54 (m, 10H), 7.80- 8.18 (m, 15H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 66.5, 113.0, 113.6, 115.3, 116.9, 119.5, 127.4, 128.9, 129.1, 129.7, 137.6, 140.2, 155.9, 158.7 ppm ; MS (EI) *m/z* (%): 43 (13), 77 (22), 102 (11), 152 (19), 189 (34), 280 (87), 292 (72), 312 (38), 336 (37), 367 (32), 393 (27), 457 (31), 702 (47), 731 (100). Elemental analysis Calcd. For $C_{50}H_{38}N_2O_4$: C, 82.17; H, 5.24; N, 3.83 Found: C, 82.09; H, 5.09; N, 3.98.

1-Aza-6,9,12-trioxa-3,5;13,15-diphenylene-2,16-(*p*-phenyl pyridine)-cyclohexadecane (3f). Purified by flash chromatography (ethyl acetate/n-hexane (1:9), Yield 45%; mp 199-201 ºC; IR (KBr): 1269, 1489, 1587, 2890, 2964, 1489, 1587, 3066 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 3.91 (t, *J* 5.7 Hz, 4H), 4.41 (t, *J* 5.7 Hz, 4H), 6.96 (d, *J* 8.0 Hz, 2H), 7.36-7.41 (m, 2H), 7.48-7.59 (m, 3H), 7.87 (d, *J* 7.6 Hz, 2H), 8.04 (d, *J* 7.0 Hz, 2H), 8.24 (s, 2H), 8.6 (s, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 67.3, 68.6, 111.7, 115.7, 118.5, 118.7, 127.3, 129.1, 129.3, 129.8, 137.7, 139.8, 150.0, 154.6, 159.0 ppm; MS (EI) *m/z* (%): 43 (100), 57 (56), 77 (42), 85 (11), 102 (9), 149 (9), 228 (10), 291 (8), 364 (8), 378 (9), 409 (7). Elemental analysis Calcd. For $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42 Found: C, 78.87; H, 5.66; N, 3.40

1-Aza-6,9,12,15-tetraoxa-3,5;16,18-diphenylene-2,19-(*p*-phenyl pyridine)-cyclononadecane (3g). Purified by recrystallization from DMF/ethanol (1:2), Yield 53%; mp 146-150 ºC; IR

(KBr): 1126, 1262, 1494, 1589, 2947-2857, 3058 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 3.69 (s, 4H), 3.83 (t, *J* 5.9 Hz, 4H), 4.29 (t, *J* 5.9 Hz, 4H), 7.02- 7.05 (dd, 2H), 7.43 (t, *J* 7.9 Hz, 2H), 7.49-7.60 (m, 3H), 7.82 (d, *J* 7.75 Hz, 2H), 8.04 (d, *J* 6.78 Hz, 2H), 8.24 (s, 2H), 8.28 (s, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 67.6, 68.5, 70.8, 112.3, 116.3, 117.8, 119.4, 127.4, 129.1, 129.4, 129.9, 137.7, 139.9, 149.9, 155.2, 159.1 ppm; MS (EI) *m/z* (%): 43 (100), 77 (64), 139 (18), 189 (29), 228 (32), 265 (13), 291 (28), 311 (16), 339 (37), 365 (22), 422 (8), 454 (7). Elemental analysis Calcd. For $C_{29}H_{27}NO_4$: C, 76.80; H, 6.00; N, 3.09 Found: C, 75.87; H, 5.62; N, 3.22

1-Aza-6,9,12,15,18-pentaoxa-3,5;19,21-diphenylene-2,22-(*p*-phenyl pyridine)-cyclodocosane (3h). Purified by flash chromatography (ethyl acetate/n-hexane (1: 9),Yield 40%; mp 141-144 ºC; IR (KBr): 1132, 1275, 1490, 1589, 2847, 2928, 3053 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 3.57-3.58 (m, 4H), 3.63-3.64 (m, 4H), 3.79 (t, *J* 4.47 Hz, 4H), 4.19 (t, *J* 4.47 Hz, 4H), 7.05-7.08 (dd, 2H), 7.44 (t, *J* 7.9 Hz, 2H), 7.53-7.59 (m, 3H), 7.85 (d, *J* 7.85 Hz, 2H), 8.03 (d, *J* 7.3 Hz, 2H), 8.09 (s, 2H), 8.22 (s, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 67.0, 68.6, 70.0, 70.2, 113.5, 114.7, 116.5, 118.9, 127.3, 129.1, 129.3, 129.4, 137.4, 139.9, 149.8, 155.4, 158.8; MS (EI) *m/z* (%): 43 (89), 71 (51), 91 (42), 147 (27), 199 (36), 227 (100), 278 (32), 292 (23), 339 (18), 378 (8), 496 (3). Elemental analysis Calcd. For $C_{31}H_{31}NO_5$: C, 74.83; H, 6.28; N, 2.81 Found: C, 74.76; H, 5.25; N, 2.40.

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