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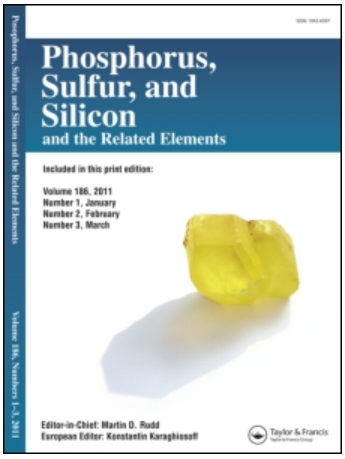

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BINOL Aza Macrocycle Derivatives: Synthesis of Dinaphthosulfone Aza Macrocycles Using p-Toluenesulfonic Acid (p-TsOH) in Methanol as an Efficient Route and Evaluation of Their ^{1}H NMR Spectra

Esmael Rostami[a]; Abbas Shockravi[b]; Hanif Fattahi[b]; Davood Heydarian[b]; Shima Shahbanzadeh Minaee[b]; Shaghayegh Naghdi[b]; Ebrahim Abouzari Lotf[b]; Mahdieh Sadeghpour[b]; Hamideh Hosseini[b]; Zahra Taheri[b]; Shahla Ghorbani[b]; Ali Javadi[b]; Shahram Mehdipoure Ataei[c]
[a] Faculty of Science, Department of Chemistry, Payame Noor University (PNU), Bushehr, Iran [b] Faculty of Chemistry, Tarbiat Moallem University (Teacher Training University), Tehran, Iran [c] Iran Polymer and Petrochemical Institute, Tehran, Iran

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BINOL Aza Macrocycle Derivatives: Synthesis of Dinaphthosulfone Aza Macrocycles Using p-Toluenesulfonic Acid (p-TsOH) in Methanol as an Efficient Route and Evaluation of Their ^{1}H NMR Spectra

Esmael Rostami,[1] Abbas Shockravi,[2] Hanif Fattahi,[2] Davood Heydarian,[2] Shima Shahbanzadeh Minaee,[2] Shaghayegh Naghdi,[2] Ebrahim Abouzari Lotf,[2] Mahdieh Sadeghpour,[2] Hamideh Hosseini,[2] Zahra Taheri,[2] Shahla Ghorbani,[2] Ali Javadi,[2] and Shahram Mehdipoure Ataei[3]
[1]Faculty of Science, Department of Chemistry, Payame Noor University (PNU), Bushehr, Iran
[2]Faculty of Chemistry, Tarbiat Moallem University (Teacher Training University), Tehran, Iran
[3]Iran Polymer and Petrochemical Institute, Tehran, Iran

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Dinaphthosulfone aza macrocycles were synthesized from the reaction of diamines and dinaphthosulfone diester (1,1′-sulfoxobis-(2-naphthoxy(2-methyl acetate))) in methanol in the presence of catalytic amounts of para toluenesulfonic acid (p-TsOH). Dinaphthosulfone diester (1,1′-sulfoxobis-(2-naphthoxy(2-methyl acetate))) was synthesized from the corresponding dinaphthosulfide diester and hydrogen peroxide in formic acid at room temperature. Dinaphthosulfide diester was prepared from initial dinaphtholsulfide diol (1,1′-thio bis(2-hydroxy naphthalene)) and methylchloroacetate. ^{1}H NMR spectroscopy showed the unusual splittings for these dinaphthosulfone aza macrocycles, and this finding could be proposed as the role of tetrahedral structure of sulfone functional group, hydrogen bonding in the cavity and size of macrocycle.

Keywords Aza thia macrocycle; BINOL; dinaphthosulfone; ^{1}H NMR; synthesis

INTRODUCTION

Since their accidental discovery by Pedersen in 1967,[1,2] the crown ethers have proved to be enormously popular, and extremely useful ligands (hosts) for a startling range of metal ions and neutral or ionic

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Address correspondence to Esmael Rostami, Faculty of Science, Department of Chemistry, Bushehr Payamenoor University, P.O. Box 1698, Bushehr, Iran; Payame Noor University (PNU), Iran. E-mail: Esmaelrostami@gmail.com

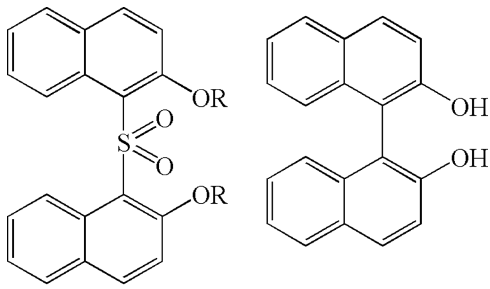

FIGURE 1 The structure of dinaphthosulfones and **BINOL**.

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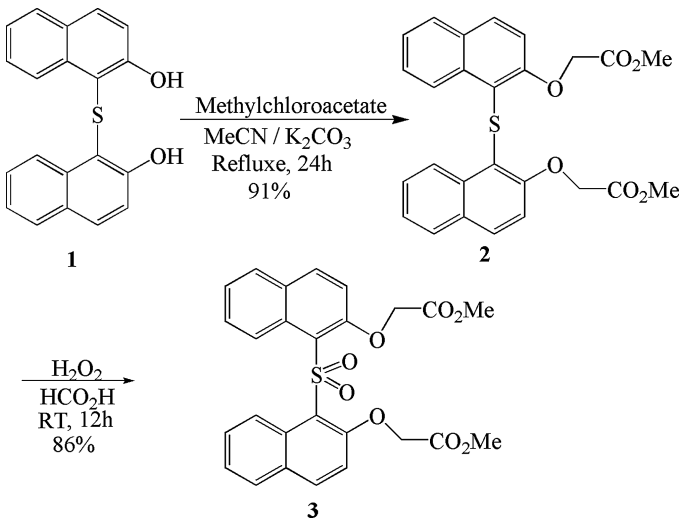
organic species.[3] Indeed, it seems as if they bind the majority of the elements of the periodic table. One of the facets that has made crown ether chemistry so popular is the notion that these ligands may select the metal cations that they "choose" to bind on the basis of size fit within the interior of the macrocycle. The versatile solubility and transport capabilities of the crown ethers make them highly suited to applications as ionophores (phase transfer catalysis)[4] or in sensing and signaling applications,[5] often as a binding site in chemical devices.[6–8]

Some of the crown ether derivatives have several potential applications, including their use as contrast agent for magnetic resonance imaging[9–11] and in the analytical separation of metal cations.[12,13]

Dinaphthosulfone macrocycles are derivatives of BINOL (Figure 1),[14] They have not been reported previously. The sulfone functional group has tetrahedral structure,[15] and the synthesis of macrocycles via this route is an inefficient process. In this research work, we synthesized dinaphthosulfone aza macrocycles (**4–7**) from their diester derivative (**3**) in the presence of para toluene sulfonic acid (p-TsOH, catalytic) in refluxing methanol in low to moderate yields. The synthesis of macrocycles in methanol is a standard procedure.[16]

RESULTS AND DISCUSSION

Dinaphthol (**1**) was synthesized from the reaction of 2-hydroxy naphthalene and sulfur dichloride based on the reported procedure.[17] The corresponding diester (**2**) was reported previously[17c] and was synthesized from the reaction of **1** and methylchloroacetate in high yields.[18] Sulfone diester (**3**) was prepared from the reaction of sulfide diester (**2**) and hydrogen peroxide in formic acid at room temperature in good to



SCHEME 1

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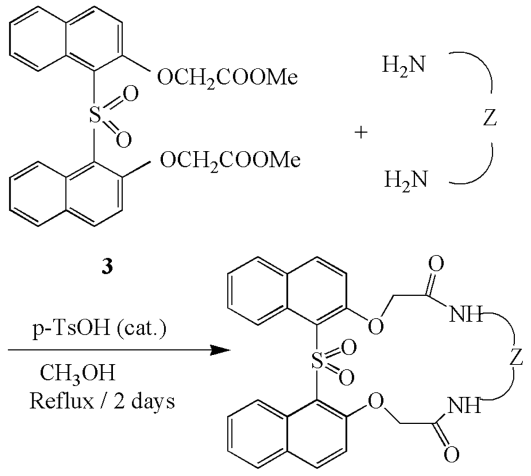
excellent yields (Scheme 1).[19] Macrocycles were synthesized from the reaction of sulfone diester (**3**) and diamines in the presence of *para* toluene sulfonic acid (*p*-TsOH, catalytic) in refluxing methanol for two days (Scheme 2). The optimization of the macrocyclization reaction was carried out using K_2CO_3, $Cu(OAc)_2$, *p*-TsOH, and acetic acid as catalysts. The best results were observed when p-TsOH was used as a macrocyclization catalyst. ^{1}H NMR spectroscopy (Figures 2, 3, 4, and 5) shows that from **4** to **7** the flexibility of macrocycles increased but the methylene hydrogens of these macrocycles (**4–7**) have different splitting patterns. For **5**, in comparison with **4**, **6**, and **7**, no splitting was observed. These findings could be explained based on the role of internal hydrogen bonding and the tetrahedral structure of sulfone functional group. **4** has a small size and its protons are diastereotopic because of the presence of sulfone, **5** has no hydrogen bonding between NH and O in the cavity, but in **6** and **7**, hydrogen bonding between NH and O may be formed and their protons split.

Based on the ^{1}H and ^{13}C NMR spectroscopies and elemental analysis (CHN) (Figures 6 and 7), the proportion of macrocycle (**7**) and chloroform is 1:1. In ^{1}H NMR the integral of chloroform show the integral for one proton, and in elemental analysis, the 1:1 proportion of **7** and $CHCl_3$ is the correct formula and $CHCl_3$ may be trapped inside the macrocycle cavity.



Z (Macrocycle): $CH_2CH_2CH_2$ (**4**) $CH_2CH_2CH_2CH_2$ (**5**)
$CH_2CH_2NHCH_2CH2$ (**6**) $CH_2CH_2OCH_2CH_2OCH_2CH_2$ (**7**)

SCHEME 2

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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. Methanol was distilled and stored under a Lind 4 Å molecular sieve. Compound **1** was synthesized based on the reported procedures.[17] **2** was prepared based on the published procedure.[17c,19] 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 a Bruker Avance DPX 300 MHz apparatus, and mass spectra were obtained with a Shimadzu GC-MS-QP 1100 EX model.

Synthesis of 1,1′-Sulfoxobis-(2-naphthoxy (2-methyl acetate)) (3)

To a mixture of **2** (2 mmol, 0.92 g) and formic acid (50 mL) at 0°C, hydrogen peroxide (4 mmol, 0.44 mL) was added and stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), water was added, and the resulting mixture was filtered, washed

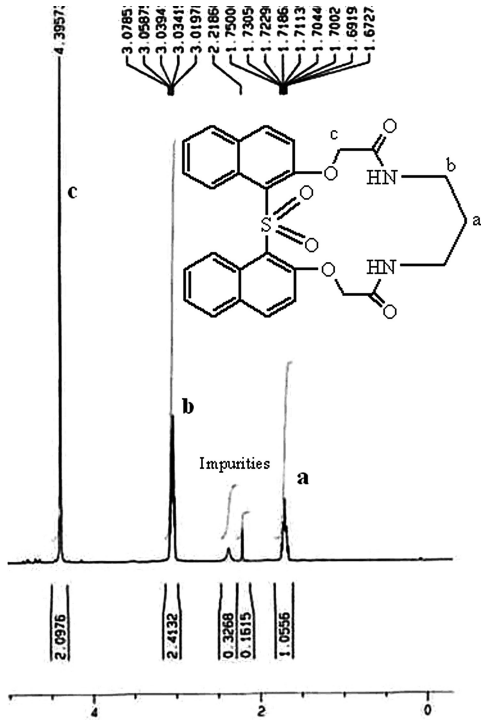

FIGURE 2 Methylene region of 300 MHz ^{1}H NMR spectrum of **4** (impurities are H_2O and methanol).

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with water, dried (Na_2SO_4), and recrystallized in ethanol/THF to afford a white powder (**3**) in 86% yield, with a melting point of 207–208°C; IR (KBr): 3132, 3083, 2954, 2936, 2855, 1754, 1623, 1598, 1565, 1513, 1468, 1436, 1381, 1340, 1287, 1248, 1212, 1148, 1130, 1092, 1038, 1000, 972, 819, 762, 595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.43$ (s, 6H, CH_3), 4.25 (s, 4H, CH_2), 7.03 (d, J = 9.3 Hz, 2H, Ar), 7.46 (ddd, J = 0.9, 7.2, 7.3 Hz, 2H, Ar), 7.65 (ddd, J = 1.5, 8.1, 8.2 Hz, 2H, Ar), 7.78 (d, J = 13.5 Hz, 2H, Ar), 7.93 (d, J = 9 Hz, 2H, Ar), 9.61 (dd, J = 0.6, 9 Hz, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.29$, 156.14, 135.39, 131.29, 129.59, 128.58, 128.45, 127.05, 124.78, 124.28, 114.57, 66.72, 52.00 ppm; MS (EI): m/z (%) = 494 $[M]^+$ (2), 462 (45), 316 (4), 300 (32), 283 (15), 268 (8), 248 (17), 216 (73), 187 (49), 144 (28), 127 (45), 115 (100), 102 (17), 99 (12), 69 (9), 63 (18), 45 (71); Anal. Calcd. for $C_{26}H_{22}O_8S$ (494.1): C, 63.15; H, 4.48. Found: C, 63.19; H, 4.44.

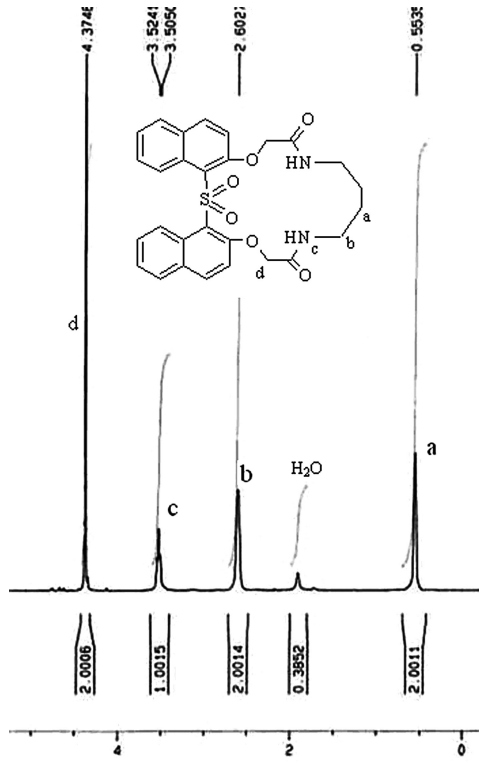

FIGURE 3 Methylene region of 300 MHz ^{1}H NMR spectrum of **5**.

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General Procedure for the Synthesis of Dinaphthosulfone Aza Macrocycles (4–7)

To a mixture of sulfone diester (**3**) (2 mmol, 0.98 g) in dry methanol (100 mL), catalytic amounts of *p*-toluene sulfonic acid (p-TsOH) and appropriate diamine (5 mmol, excess) were added. This mixture was refluxed for 48 h. After completion of the reaction (monitored by TLC), water was added to the reaction mixture and extracted with CH_2Cl_2 (3 $\times$ 50 mL). The combined organic layers were dried with Na_2SO_4 and evaporated to afford the crude product, which was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (4:1) as an eluent to obtain the macrocycles in pure form.

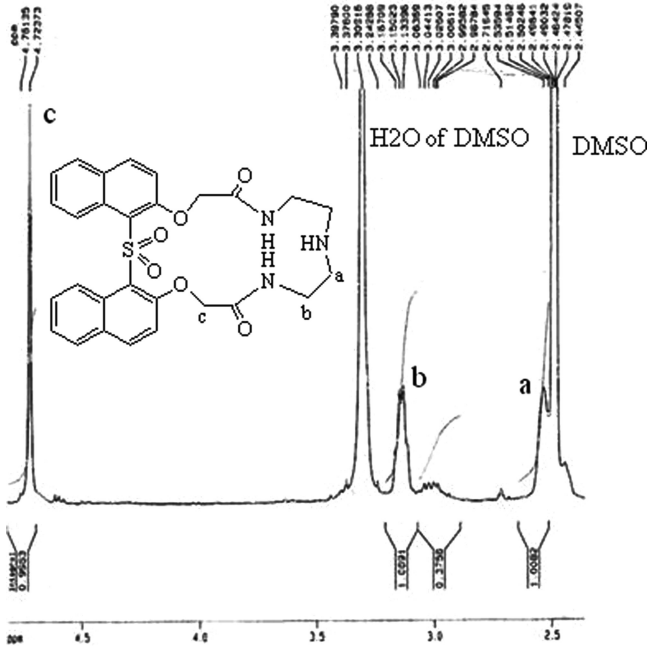

FIGURE 4 Methylene region of 300 MHz ^{1}H NMR spectrum of **6** (peaks in 3.0 and 4.6 ppm are impurities).

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Synthesis of 7,11-Diaza-1-sulfoxo-4,14-dioxa-6,12-dioxo-2,3;15,16-dinaphtho-cyclohexadecane (4)

According to the general procedure, this macrocycle (**4**) was synthesized in 34% yield with a melting point of 266–267°C; IR (KBr): 3411, 3335, 3063, 2915, 1695, 1638, 1596, 1543, 1510, 1452, 1350, 1275, 1236, 1149, 1066, 1023, 816, 743, 497 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67–1.75 (m, 2H), 3.01–3.07 (m, 4H), 4.39 (s, 4H), 5.77 (t, J = 5.4 Hz, 2H), 7.09 (d, J = 9 Hz, 2H), 7.44 (ddd, J = 0.9, 7.2, 7.3 Hz, 2H), 7.56 (ddd, J = 1.4, 7.8, 7.9 Hz, 2H), 7.81 (dd, J = 2.7, 13.5 Hz, 4H), 8.75 (dd, J = 0.6, 8.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.93, 154.93, 135.21, 130.80, 129.85, 128.51, 127.84, 125.41, 124.88, 117.77, 112.70, 67.79, 38.05, 29.53 ppm; MS (EI) m/z (%) = 330 (31), 329 (22), 300 (9), 299 (19), 283 (100), 257 (59), 211 (12), 141 (5), 137 (18), 126 (8), 99 (11); Anal. Calcd. for $C_{27}H_{24}N_2O_6S$ (504.14): C, 64.27; H, 4.79; N, 5.55 Found: C, 64.22; H, 4.74; N, 5.66.

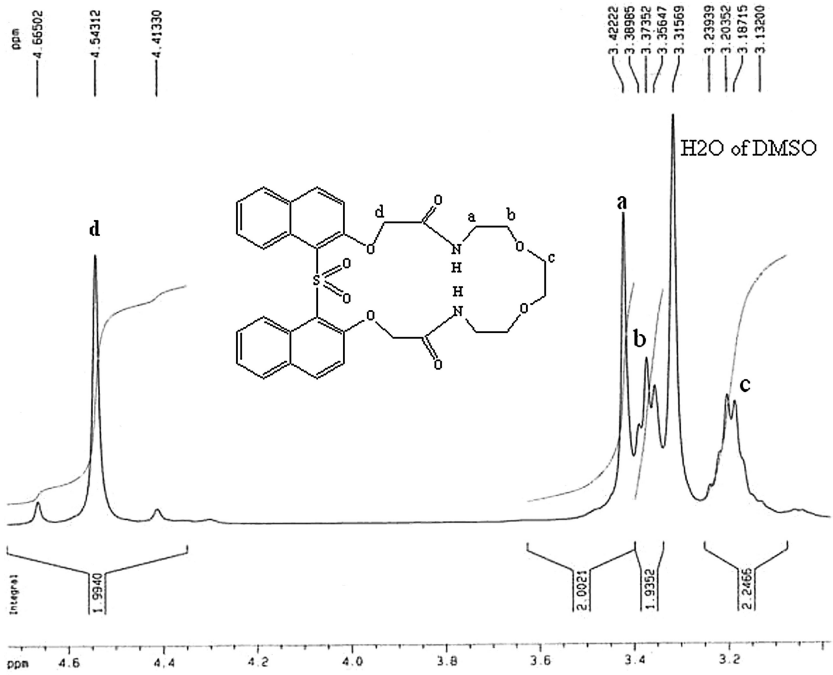

FIGURE 5 Methylene region of 300 MHz ^{1}H NMR spectrum of **7**.

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Synthesis of 7,12-Diaza-1-sulfoxo-4,15-dioxa-6,13-dioxo-2,3;13,14-dinaphtho-cycloheptadecane (5)

Based on the general procedure, **5** was synthesized in 38% yield with a melting point of 255–256°C; IR (KBr): 3356, 3076, 2929, 2891, 1695, 1678, 1636, 1595, 1556, 1510, 1473, 1436, 1342, 1281, 1161, 1123, 1123, 1074, 1023, 976, 811, 751, 599, 496 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.55$ (m, 4H), 2.60 (m, 4H), 3.50–3.52 (broad, 2H), 4.37 (m, 4H), 7.05 (d, J = 9Hz, 2H), 7.46 (ddd, J = 0.9, 7.2, 7.4 Hz, 2H), 7.69 (ddd, J = 1.2, 7.8, 7.9 Hz, 2H), 7.80 (t, J = 9.3 Hz, 4H,), 9.16 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.11$, 155.38, 135.97, 130.55, 129.09, 127.89, 127.69, 126.40, 125.00, 117.90, 112.14, 67.06, 36.49, 24.09 ppm; MS (EI): m/z (%) = 484 (3), 483 (5), 456 (3), 318 (1), 299 (7), 297 (21), 271 (21), 254 (9), 210 (7), 145 (5), 70 (9), 58 (12), 56 (37), 55 (59), 43 (100); Anal. Calcd. for $C_{28}H_{26}N_2O_6S$ (518.15): C, 64.85; H, 5.05; N, 5.40 Found: C, 64.89; H, 5.01; N, 5.32.

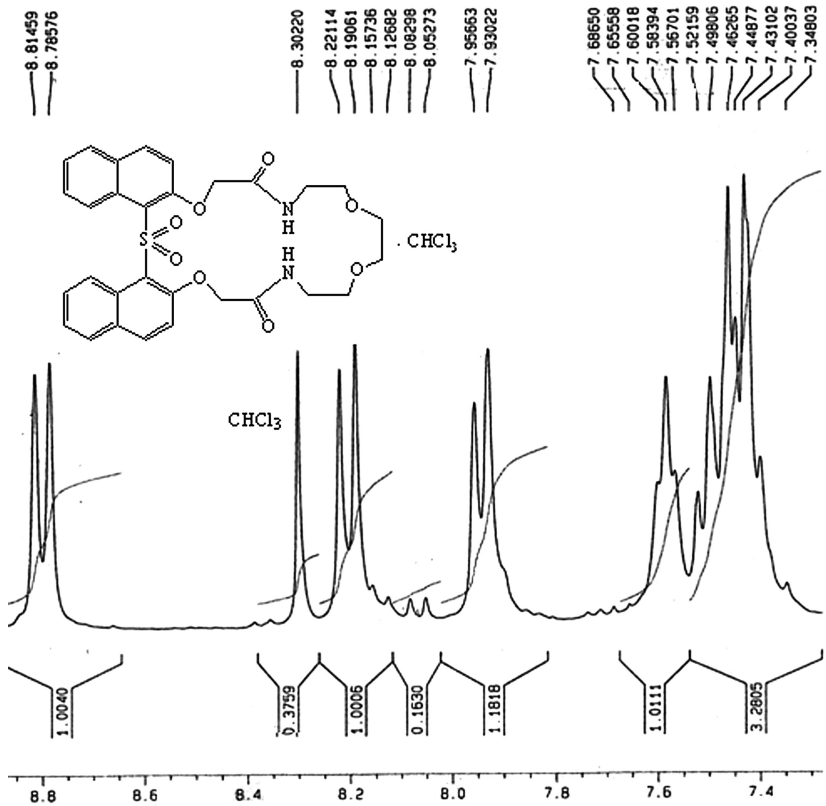

FIGURE 6 Aromatic region of 300 MHz ^{1}H NMR spectrum of **7** and chloroform.

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

According to the general procedure, this macrocycle (**6**) was synthesized in 45% yield with a melting point of 247–248°C; IR (KBr): 3367, 3073, 2940, 1684, 1516, 1466, 1435, 1340, 1281, 1133, 1083, 819 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.53 (broad, 4H), 3.13–3.16 (m, 4H), 4.72–4.76 (m, 4H), 7.39–7.49 (m, 8H), 7.90 (t, J = 5.7 Hz, 2H), 7.95 (dd, J = 1.2, 8.4 Hz, 2H), 8.22 (d, J = 9 Hz, 2H), 8.83 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 167.12, 166.94, 155.51, 136.77, 129.81, 129.40, 128.87, 128.62, 124.52, 122.20, 114.03, 67.60, 45.59, 37.53 ppm; Anal. Calcd. for $C_{28}H_{27}N_3O_6S$ (533.16): C, 63.03; H, 5.10; N, 7.87. Found: C, 62.84; H, 5.08; N, 7.74.

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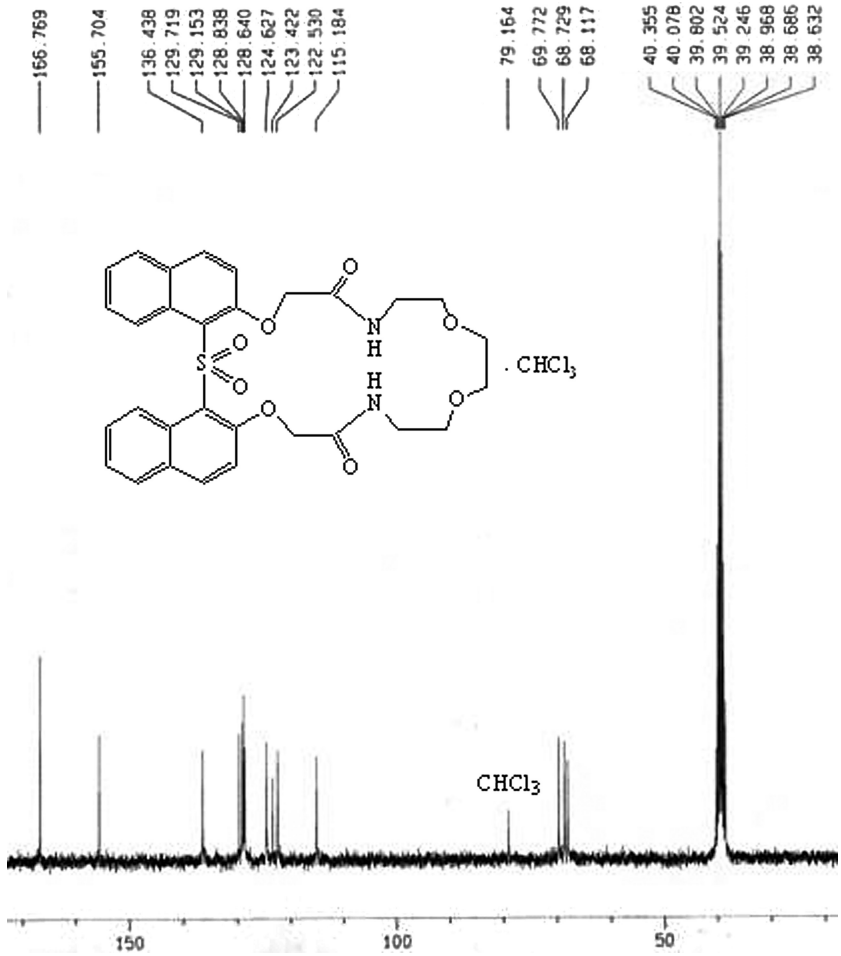

FIGURE 7 Aromatic region of 75 MHz ^{13}C NMR spectrum of **7** and chloroform.

Synthesis of 7,16-Diaza-1-sulfoxo-4,10,13,19-tetraoxa-6,7-dioxo-2,3;20,21-dinaphtho-yclouneicosane (7)

Based on the general procedure, **7** was synthesized in 43% yield with a melting point of 235–236°C; IR (KBr): 3364, 3088, 3016, 2942, 2903, 2881, 1691, 1681, 1627, 1600, 1567, 1559, 1551, 1515, 1471, 1434, 1338, 1280, 1254, 1162, 1149, 1130, 1103, 1079, 995, 828, 813, 757, 663, 490 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 3.13–3.23 (m, 4H), 3.35–3.38 (m, 4H), 3.42 (broad, 4H), 4.45 (d, J = 39 Hz, 2H), 4.60 (d, J = 36.6 Hz, 2H), 7.34–7.52 (m, 6H), 7.58 (t, J = 5.1 Hz, 2H), 7.93 (d, J =

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7.8 Hz, 2H), 8.20 (d, J = 9.3 Hz, 2H), 8.30 (s, 1H, $CHCl_3$), 8.80 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 166.76, 155.70, 136.43, 129.71, 129.15, 128.83, 128.64, 124.62, 123.42, 122.53, 115.18, 79.16 ($CHCl_3$), 69.77, 68.72, 68.11, 38.68 (masked by DMSO); Anal. Calcd. for $C_{31}H_{31}Cl_3N_2O_8S$ (Macrocycle and Chloroform) (696.09): C, 53.34; H, 4.48; N, 4.01. Found: C, 53.16; H, 4.36; N, 3.91.

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[18] Synthesis of 1,1′-thiobis-(2-naphthoxy(2-methyl acetate)) (2): To a mixture of **1** (6.04 g, 19 mmol), potassium carbonate (5.24 g, 38 mmol), and potassium iodide (catalytic) in acetonitrile (100 mL) at room temperature, methylchloroacetate (3.35 mL, 38 mmol) was added. Then the reaction mixture was refluxed for 24 h. After completion of the reaction (TLC), the mixture was cooled to room temperature, water was added and extracted with chloroform (3 × 50 mL). The mixture was washed

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with sodium hydroxide solution (10%), dried, and evaporated to afford a precipitate that recrystallized from ethanol, to give pure **2** in 91% yield. Mp 126.5–127°C; IR (KBr): 3040, 3000, 2970, 1750, 1595, 1500, 1450, 1300, 1250,1200, 1090, 1040, 810, 750 cm^{-1};^{1}H NMR (300 MHz, acetone-d_6)): δ = 3.65 (s, 6H, CH_3), 4.65 (s, 4H, CH_2), 7.09 (ddd, J = 1.32, 6.94, 8.46 Hz, 2H, Ar), 7.26 (d, J = 9.05 Hz, 2H, Ar), 7.35 (ddd, J = 1.11, 6.84, 7.98 Hz, 2H, Ar), 7.81 (d, J = 7.91 Hz, 2H, Ar), 7.83 (d, 2H, J = 9.02 Hz, Ar), 8.69 (d, 2H, J = 8.59 Hz, Ar) ppm; MS (EI) m/z (%) = 462 (43), 316 (4), 300 (36), 283 (12), 268 (7), 248 (11), 216 (63), 187 (44), 144 (23), 127 (40), 115 (100), 102 (14), 99 (18), 69 (5), 63 (19), 45 (73); Anal. Calcd. for $C_{26}H_{22}O_6S$ (462.11): C, 67.52; H, 4.79. Found: C, 67.45; H, 4.67.

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