

## Modified BINOL Podands: Synthesis of Dinaphthosulfide Podands and Their Application in Spectrophotometric Determination of Toxic Metals

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*New dinaphthosulfide podands [3(a, b, and c)] were synthesized. The structures of these compounds were confirmed by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and Mass spectra. A simple, efficient, and sensitive procedure is described for the spectrophotometric determination of a trace amount of  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  cations in the presence of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  cations using the podand (3a). Formation constants of 1:1 complexes were determined from the absorbance-mole ratio data and found to vary in the order  $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+} > \text{Cr}^{3+} > \text{Ag}^+$ .*

**Keywords** BINOL; chromium; diamide; dinaphthosulfide; lead; Podand; spectrophotometry; sulfide

## INTRODUCTION

The design of a chemosensor for a cation or anion requires a receptor unit or ligand that selectively interacts with the cation or anion, and a method to read-out the binding using a change in a physical signal is a very attractive subject in chemistry.<sup>1</sup> This is due to the special structure of their flexible donor atom containing chain and podand receptor sites which can form complexes with many cations ranging from alkali and alkaline earth metals to transition metals. By chemical modification of

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the arms (e.g., changing the chain length or the donor atom) and under certain experimental conditions, podand receptors can selectively form complexes with metal ions.<sup>2</sup>

As a recognition motif, podand based receptors have been reported to be used successfully as recognition components in electrochemical sensors<sup>3,4</sup> and optical sensors.<sup>5-7</sup> In order to construct ionophore model systems, various macrocyclic compounds, such as crown ethers, cryptands, and calixarenes, have been synthesized and structurally characterized. In addition to these macrocyclic compounds, podands have been employed as noncyclic ionophore models.<sup>8</sup>

BINOL ((1, 1'-di (2-hydroxy naphthalene)) derivatives) are an important group of compounds which have been studied by many researchers including our group.<sup>9</sup> In continuation of our previous studies on the synthesis of new dibenzosulfide and dibenzosulfoxide monomers and macrocyclic compounds,<sup>10</sup> we now wish to report new interesting dinaphthosulfide podands (**3(a, b and c)**) as modified BINOL podands and the podand (**3a**) was used in the determination of  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  cations.

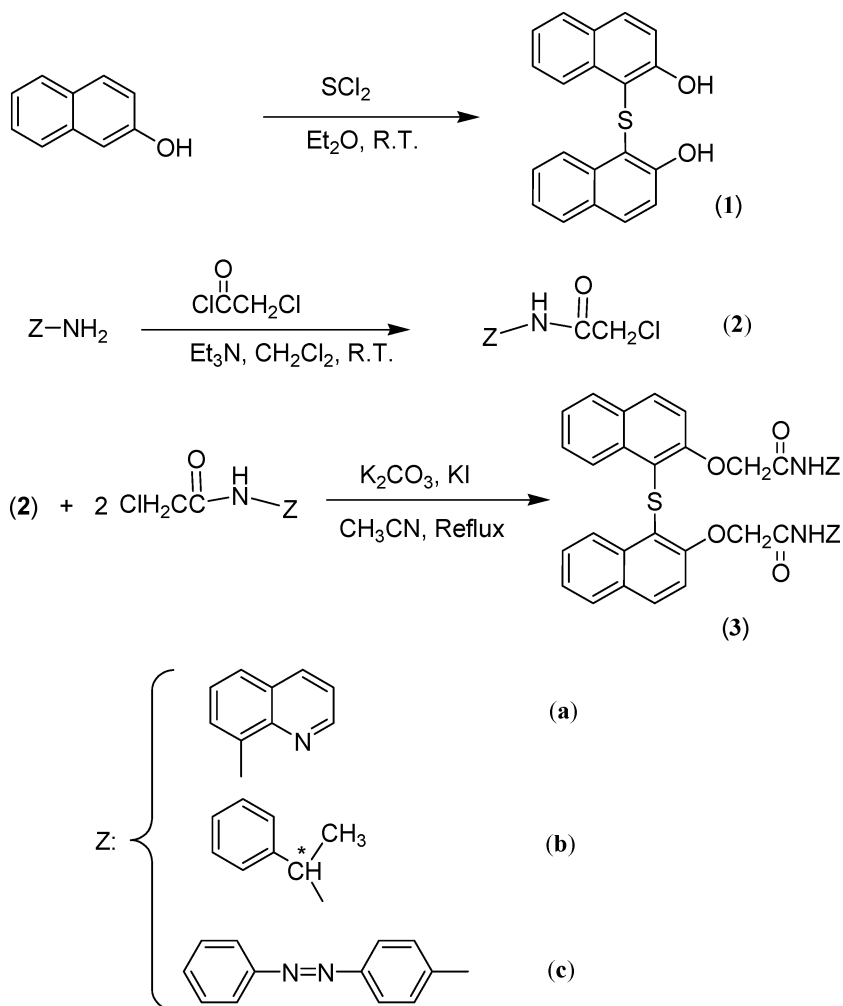
The dinaphthosulfide (**1**) was synthesized from 2-naphthol in a 76% yield.<sup>11</sup> The treatment of (**1**) with the  $\alpha$ -chloroamides (**2 (a, b and c)**) in the presence of  $\text{K}_2\text{CO}_3$  at reflux acetonitrile gave (**3(a, b and c)**) in 93%, 88% and 83% yields respectively (Scheme 1).  $\alpha$ -Chloroamides were synthesized from the reaction of various amines with chloroacetyl chloride.

## RESULTS AND DISCUSSION

In this work, the synthesis of some new podands (**3(a, b and c)**) by the reaction of some  $\alpha$ -chloroamides with (**1**) are described. Our motive behind the synthesis of this type of ligands was to examine their possible application in the cation recognition processes.

The electronic absorption spectra of the ligand (**3a**) with various concentrations are represented in (Figure 1). An examination of (Figure 1) indicates that the electronic spectra of this ligand are largely dependent on the concentration. Increasing the compound concentration results in increasing the absorbance of both bands at 260.2 and 308.2 nm, where beyond a certain concentration of the compound a very broad band is observed. This behavior can be ascribed to the association of molecule through intermolecular hydrogen bonding.

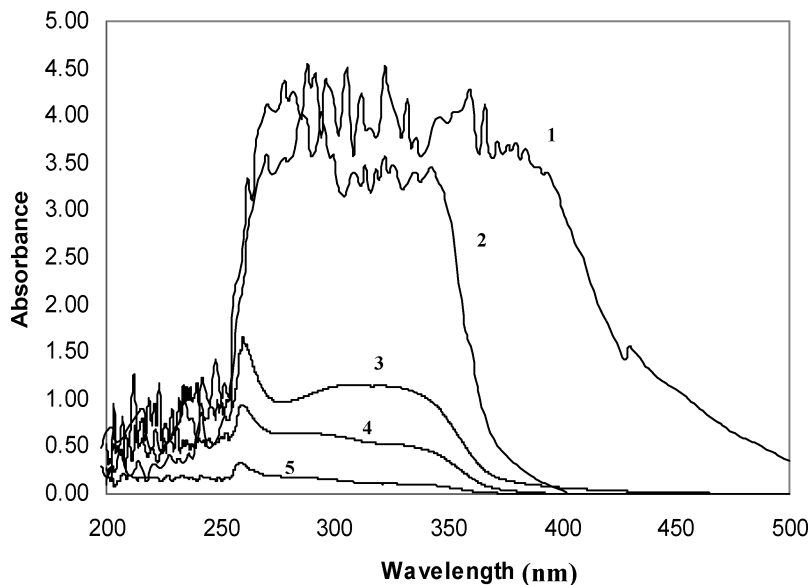
The electronic absorption spectra of the ligand and the complexes with  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in the same concentration of cations are shown in (Figure 2). Under identical experimental conditions, the absorption characteristics of the complexes



SCHEME 1

in solution are listed in (Table 1). As can be noticed, the electronic spectra of the ligand-Co, Mn and ligand-Cd does not show absorptions. Therefore, there are no interferences from  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Mn}^{2+}$  in the determination of  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  with this ligand.

For evaluation of the formation constants from the absorbance vs  $C_M/C_L$  mole ratio data, a non-linear, least-squares, curve fitting program KINFIT was used.<sup>12</sup> The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique<sup>13</sup> or the Powell procedure.<sup>14</sup>



**Figure 1** Electronic spectra of the **3a** ligand in DMSO at **1**)  $5 \times 10^{-3}$  M, **2**)  $5 \times 10^{-4}$  M, **3**)  $1 \times 10^{-4}$  M, **4**)  $5 \times 10^{-5}$  M, **5**)  $1 \times 10^{-6}$  M.

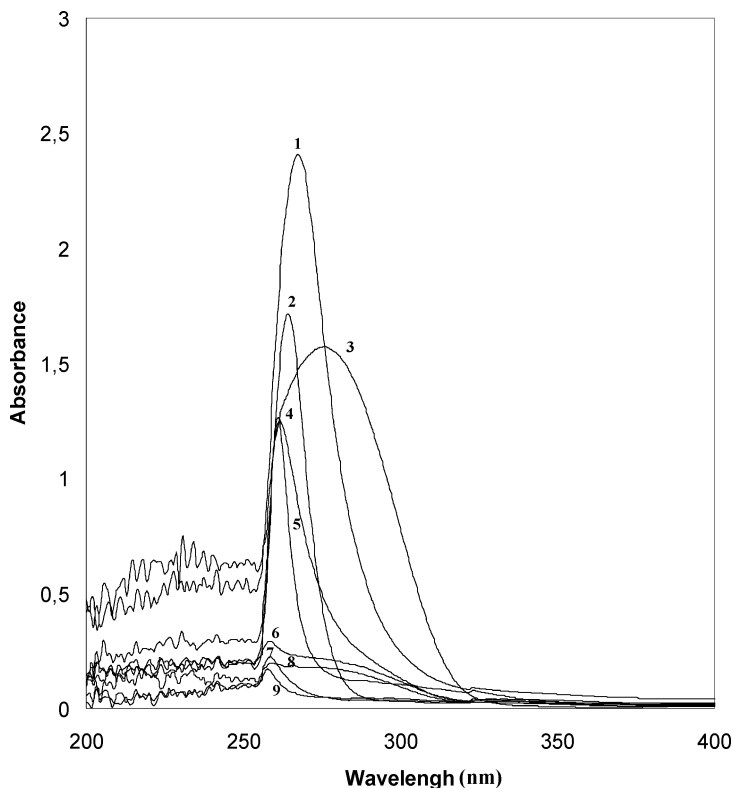
One of the typical fitting curves of podand (**3a**) with cations using the above software are illustrated in (Figure 3), which clearly shows that a 1:1  $\text{Pb}^{2+}$  to (**3a**) complex is formed in solution. The results of formation constants are shown in (Table 1). As is evident from (Table 1), the complexes stabilities of these cations with (**3a**) decrease in the order of  $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+} > \text{Cr}^{3+} > \text{Ag}^{+}$ .

## EXPERIMENTAL

All the experiments for the synthesis of podands were performed in an efficient fume hood cupboard. All the materials were analytical reagent-grade chemicals and pure solvents were purchased from Merck, Aldrich, and Fluka chemical companies. Doubly distilled water was used for the preparation of aqueous solutions. The podands were synthesized and purified as described herein.

For spectrophotometric experiments, reagent grade nitrate salts of lead, nickel, silver, mercury, cobalt, manganese, cadmium, and chromium were available in highest purity and used without any further purification.

UV-Vis absorption spectrophotometry was used for quantification of complexation process. A set of solutions containing (**3a**) ( $1 \times 10^{-6}$  M)



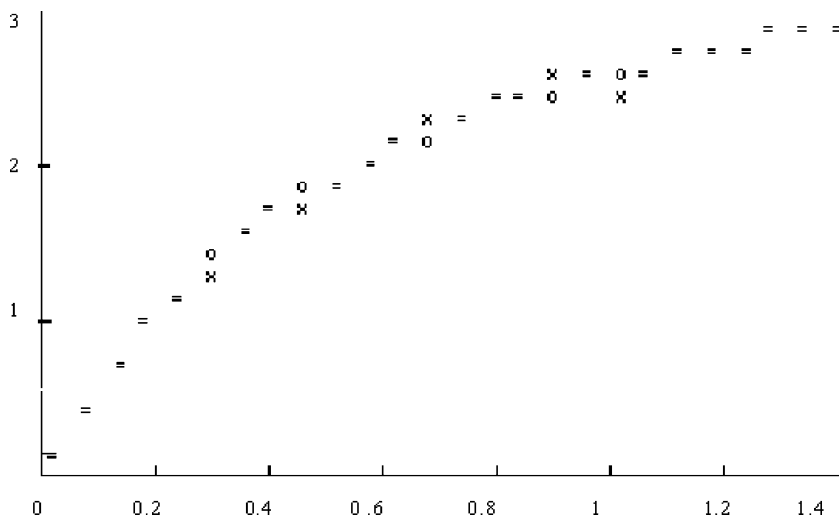
**Figure 2** Electronic spectra of complexes of **3a** with **1**) Cr<sup>2+</sup>, **2**) Pb<sup>2+</sup>, **3**) Ni<sup>2+</sup>, **4**) Ag<sup>+</sup>, **5**) Hg<sup>2+</sup>, **6**) Co<sup>2+</sup>, **7**) **3a**, **8**) Mn<sup>2+</sup>, **9**) Cd<sup>2+</sup> in DMSO.

**TABLE I** Formation Constants and Maximum Wavelengths of M<sup>n+</sup> with Podand (**3a**) (in DMSO, at 23±1 C)

	Pb (II)	Hg (II)	Ni (II)	Cr (III)	Ag (I)	Mn (II)	Cd (II)	Co (II)	L*
$\lambda_{\max}$ (nm)	264.4	261.2	276	267.6	261	258	257.8	259	260.2
LogK <sub>f</sub>	4.81 ± 0.04	1.23 ± 0.03	2.12 ± 0.19	0.8 ± 0.06	0.45 ± 0.25	—	—	—	—

\*L: Ligand.

with 100 ppm concentration of cations were placed in a UV cell of 1cm path length in order to perform the spectrophotometric analysis. All experiments were carried out at conditioned room temperature (23 ± 1°C).



**Figure 3** Computer fit of absorbance vs  $\text{Pb}^{+2}/(3\mathbf{a})$  mole ratio plot at  $23 \pm 1$  °C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

## Apparatus

The melting points (uncorrected) were measured on an electrothermal engineering LTD9100 apparatus. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. IR spectra were measured on a Perkin-Elmer model 543;  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using Bruker Avance DRX 300 MHz apparatus. Absorption measurements were recorded on a Philips UV-Vis spectrophotometer (Pu8750) model.

## Ligand Synthesis and Procedures—General Procedure for the Preparation of $\alpha$ -Chloroamides

To a vigorously stirred solution of amine (0.002 mol (**a** 0.29 g, **b** 0.24 g and **c** 0.39 g)) and triethylamine (0.002 mol,  $d = 0.73$  g/ml, 0.15 ml) in an appropriate dried solvent (50 ml,  $\text{CH}_2\text{Cl}_2$ ) was added a solution of chloroacetyl chloride (0.002 mol,  $d = 1.42$  g/ml, 0.32 ml) in the same solvent (50 ml) at 0 °C. The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with distilled water and then was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 50$  ml). The combined organic layer was washed with 10% aqueous HCl solution (50 ml) and water (50 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to afford solid

products which were purified by recrystallization from the appropriate solvent.

### Synthesis of (2a)

This compound was purified by recrystallization from ethanol to afford brown crystals in 92% yield, mp 125–128°C; IR (KBr): 3337, 3029, 2975, 1683, 1598, 1551, 1490, 1471, 1430, 1395, 1334, 1279, 833, 769  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.32 (s, 2H), 7.46–7.50 (dd,  $J = 4.2$  Hz, 1H), 7.55–7.59 (m, 2H), 8.17, 8.20 (d,  $J = 9$  Hz, 1H), 8.73–8.79 (m, 1H) 8.86, 8.86 (d,  $J = 3$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.36, 116.82, 121.72, 122.56, 127.23, 127.97, 133.50, 136.48, 138.56, 148.55, 164.41 ppm.

### Synthesis of (2b)

This compound was purified by recrystallization from ethanol to afford white crystals in 81% yield, m.p. 99–101°C; IR (KBr): 3264, 3059, 2978, 1658, 1601, 1546, 1489, 1443, 1418, 1368, 1342, 1231, 1198, 1104, 927, 784  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.53, 1.56 (d,  $J = 9$  Hz, 3H), 4.00–4.11 (dd,  $J = 15$  Hz, 2H), 5.10–5.19 (m, 1H), 6.82 (b, 1H), 7.26–7.38 (m, 5H) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.64, 42.62, 49.22, 126.05, 127.61, 128.77, 142.28, 164.91 ppm.

### Synthesis of (2c)

This compound was purified by recrystallization from ethanol to afford white crystals in 86% yield, m.p. 150–153°C; IR (KBr): 3341, 1667, 1598, 1535, 1504, 1442, 1410, 1315, 1252, 1158, 850, 787  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.24(s, 2H), 7.45–7, 7.56 (m, 3H), 7.72–7.76 (m, 2H), 7.89–7.99 (m, 4H), 8.40 (broad, 1H) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  42.89, 120.08, 122.81, 124.05, 129.10, 130.97, 139.06, 149.60, 152.59, 163.83 ppm.

Following the published procedures<sup>11</sup> to a solution of 2-naphthol (10 mmol, 1.44 g) in diethyl ether (50 ml) at room temperature a solution of  $\text{SCl}_2$  (5.5 mmol, 0.92 ml,  $d = 1.62$  g/ml) in diethyl ether (50 ml) was added dropwise over a period of 1 h. After stirring for 2 h at room temperature, the resulting precipitate was filtered and washed with diethyl ether ( $2 \times 30$  ml), and then it was recrystallized from ethanol to afford the product in 76% yield as white needles, m.p. = 212–214°C.

### General Procedure for the Preparation of Diamide Podands

To a mixture of (1) (1 mmol, 0.32 g) and potassium carbonate (2 mmol, 0.28 g) in  $\text{CH}_3\text{CN}$  (50 ml) was added  $\alpha$ -chloroamides (2 mmol) (2a 0.44 g,

**2b** 0.40 g and **2c** 0.55g)), and the suspension mixture was allowed to cool to room temperature and subsequently poured into 700 ml of distilled water. The precipitate was filtered and recrystallized from appropriate solvents.

### **Synthesis of 1,1'-thiobis[2-(quinolin-8"-acetamide-2"-oxy] naphthalene (3a)**

This compound was purified by recrystallization from ethanol to afford brown crystals in 93% yield, m.p. 190–193°C; IR (KBr): 3348, 3059, 1687, 1616, 1592, 1536, 1500, 1483, 1459, 1383, 1327, 1261, 1204, 1148, 1077, 800, 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.69 (s, 2H), 7.32–7.34 (t, 1H), 7.39–7.44 (m, 2H), 7.52–7.58 (m, 3H), 7.77, 7.80 (d,  $J = 9$  Hz, 1H), 8.10, 8.12 (d,  $J = 6$  Hz, 1H), 8.39, 8.42 (d,  $J = 9$  Hz, 1H), 8.52, 8.53 (d,  $J = 3$  Hz, 1H), 8.73–8.76 (d,  $J = 9$  Hz, 1H), 8.89, 8.92 (d,  $J = 9$  Hz, 1H), 10.89 (s, 1H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.47, 115.21, 117.24, 119.59, 122.33, 123.64, 124.09, 124.85, 127.22, 128.42, 129.39, 129.52, 130.22, 131.08, 133.18, 134.37, 141.35, 147.76, 151.98, 156.41, 166.76 ppm; MS: 115(35%), 116(40%), 143(100%), 170(60%), 187(40%), 257(10%), 316(15%), 358(20%).

### **Synthesis of 1,1'-thiobis[2-(phenyl ethyl amine-N-acetamide- $\alpha$ -oxy)] naphthalene (3b)**

This compound was purified by recrystallization from ethanol to afford white crystals in 88% yield, mp 160–163°C; IR (KBr): 3342, 3058, 3033 2978, 1652, 1589, 1526, 1501, 1458, 1279, 1211, 1070, 808, 693  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.19, 1.22 (d,  $J = 9$  Hz, 3H), 4.31–4.42 (dd,  $J = 16$  Hz, 2H), 5.02–5.07 (m, 1H), 6.83–6.86 (d,  $J = 9$  Hz, 1H), 6.96–7.10 (m, 6H) 7.36–7.46 (m, 2H), 7.68–7.76 (dd,  $J = 9$  Hz, 2H), 8.49, 8.52 (d,  $J = 8$  Hz, 1H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.47, 115.21, 117.24, 119.59, 122.33, 123.64, 124.09, 124.85, 127.22, 128.42, 129.39, 129.52, 130.22, 131.08, 133.15, 134.37, 141.35, 147.76, 151.98, 156.41, 166.76 ppm; MS: 98(42%), 109(38%), 130(25%), 145(35%), 158(100%), 161(38%), 215(40%), 298(18%).

### **Synthesis of 1, 1'-thiobis[2-(azobenzene-4"-acetamide- $\alpha$ -oxy)] naphthalene (3c)**

This compound was purified by recrystallization from ethanol to afford yellow crystals in 83% yield, mp 259–262°C; IR (KBr): 3313, 3056, 1682, 1598, 1533, 1505, 1412, 1304, 1262, 1240, 1090, 809, 684  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.84 (s, 2H), 7.32–7.34 (t,  $J = 3$  Hz, 1H), 7.39–7.44 (m, 2H), 7.52–7.58 (m, 3H), 7.78–7.90 (m, 8H), 8.52–8.55 (d,  $J = 9$  Hz, 1H), 10.36 (s, 1H) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.47, 115.21, 117.24, 119.59, 122.33, 123.64, 124.09,



124.85, 127.22, 128.42, 129.39, 129.52, 130.22, 131.08, 134.37, 141.35, 147.76, 151.98, 156.41, 166.76 ppm; MS: 73(30%), 74(60%), 77(60%), 87(45%), 93(35%), 115(50%), 120(70%), 144(100%), 149(40%), 160(38%), 225(20%), 246(18%), 275(23%), 299(38%).

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