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Efficient synthesis of 13- to 20-membered Schiff base macrocycles *via* non-template method

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A set of hitherto unreported 13- to 20-membered Schiff base macrocycles have been synthesized by the reaction of Schiff base with dielectrophiles *via* the intermediacy of remote dianion in non-template method. The structural features of the synthesized macrocycles have been determined by their satisfactory elemental analyses and spectral (IR, ^{1}H, ^{13}C NMR and Mass) studies.

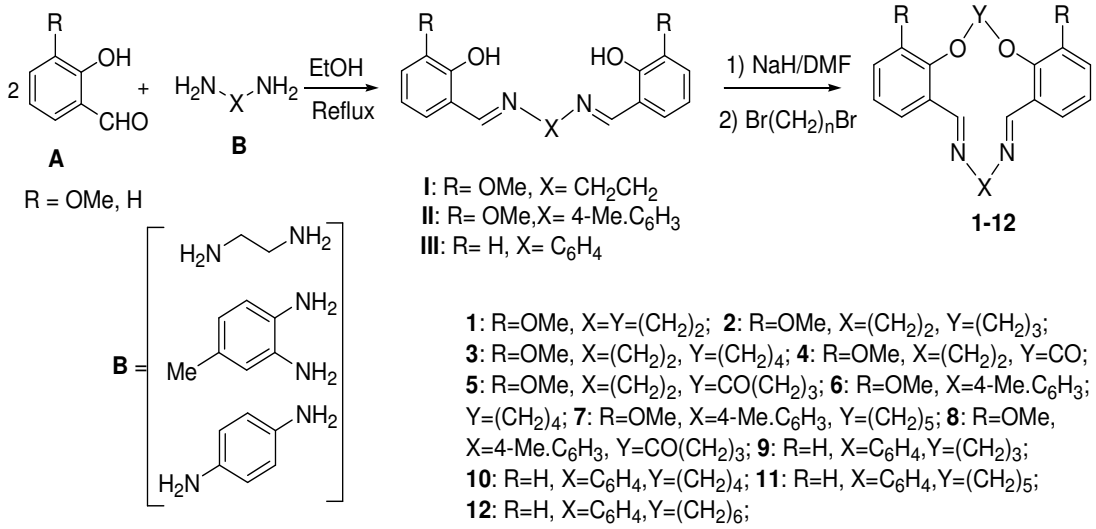
Keywords: Schiff's base, macrocycles, remote dianion, cyclization, non-template method

Schiff base macrocycles having cavities of various sizes incorporating nitrogen and oxygen as part of the skeleton are interesting metal complexing reagents[1]. The design and synthesis of Schiff base macrocycles is of vital importance and developing very rapidly because of their numerous applications[2]. Macrocycles and their complexes exhibit broad spectrum of pharmacological activities such as antibiotic, antiviral, antitumour, antifungal, antibacterial, and anticancer agents due to their specific structures[3-5]. Moreover, they have potential applications in the fields of host-guest chemistry, molecular recognition, and supramolecular chemistry[6]. More importantly, macrocyclic Schiff bases and their relevant metal complexes are of great interest in coordination chemistry, although this subject has been extensively studied[7,8]. They are important to both synthetic as well as medicinal chemists mainly due to their relevance to the bioorganic and bioinorganic chemistry[9]. Further, particular attention has been devoted to their correlation with the active sites of metalloenzymes and metalloproteins[10]. Transition metal complexes with macrocyclic ligands are well known for their enhanced kinetic and thermodynamic stability[11-13]. Recently, the syntheses and photo-chromic studies of macrocyclic Schiff bases have attracted increasing interest[14].

Although template synthesis with metal ions is the common route to get macrocyclic Schiff bases, but it has disadvantage of difficulty to isolate the free ligand by demetallation since metal ion is strongly bound in the macrocyclic cavity. To the best of our knowledge, no work has been reported on the condensation of *o*-vanilline with *o*-/*p*-phenylenediamine followed by treatment with suitable dielectrophiles to provide macrocycles by non-template method. Hence, in continuation of our interest for the development of useful synthetic methodology[15], we report here the non-template synthesis of new macrocyclic compounds (**1-12**) by the reaction of dibasic ligands such as N,N'-bis(*o*-vanillidene) ethylenediamine **I**, N,N'-bis(*o*-vanillidene)-4-methyl-*o*-phenylenediamine **II**, and N,N´-bis(salicylidine)-*p*-phenylenediamine **III** with various dielectrophiles **Y** *via* remote dianion strategy. These compounds may behave as tetradentate ligands by donating four lone pairs of electrons, two each from nitrogen atoms and other two each from oxygen atoms.

Results and Discussion

Owing to the relevance of Schiff base macrocycles in catalysis and in organic synthesis, we explored the possibility for the synthesis of hitherto unreported 13- to 20-membered Schiff base macrocycles *via* non-template method. This synthesis involves the treatment of Schiff base ligands (**I**, **II,** and **III)** with NaH in 1:2 molar ratio in dry dimethyl formamide (DMF) under inert atmosphere generating 1, 12- (from ligands **I**, **II**) or 1, 14- (from ligand **III**) remote dianions, which attacks to various dielectrophiles **Y**



1: R=OMe, X=Y=$(CH_2)_2$; **2**: R=OMe, X=$(CH_2)_2$, Y=$(CH_2)_3$; **3**: R=OMe, X=$(CH_2)_2$, Y=$(CH_2)_4$; **4**: R=OMe, X=$(CH_2)_2$, Y=CO; **5**: R=OMe, X=$(CH_2)_2$, Y=$CO(CH_2)_3$; **6**: R=OMe, X=4-Me.C_6H_3; Y=$(CH_2)_4$; **7**: R=OMe, X=4-Me.C_6H_3, Y=$(CH_2)_5$; **8**: R=OMe, X=4-Me.C_6H_3, Y=$CO(CH_2)_3$; **9**: R=H, X=C_6H_4,Y=$(CH_2)_3$; **10**: R=H, X=C_6H_4,Y=$(CH_2)_4$; **11**: R=H, X=C_6H_4,Y=$(CH_2)_5$; **12**: R=H, X=C_6H_4,Y=$(CH_2)_6$;

Scheme I — Synthesis of ligands **I**, **II, III** and macrocycles **1-12**

giving desired macrocycles in good yields (**Scheme I**). The corresponding dibasic ligands, **I**, **II**, and **III** were synthesized by the condensation of flexible and rigid diamines **B** and *o*-vanillin/salicylaldehyde **A**. The dibasic ligands and the macrocyclic compounds were characterized by their spectral (IR, ^{1}H and ^{13}C NMR, Mass), and analytical studies. The appearance of a strong intensity band in the IR spectra of the Schiff base (**I-III**) in the range of 1622-1608 cm^{-1} attributable to ν(C=N), provides a strong evidence for the condensation[16]. ^{1}H NMR spectra of the ligands exhibit a sharp downfield singlet in the range δ 13.19–13.60 assigned to phenolic -OH groups (D_2O exchangeable), suggests intramolecular hydrogen bonding between azomethine nitrogen and -OH group. Two azomethine protons in ligands **I**, **II**, and **III** appear as a sharp singlet in the range δ 8.30–8.61.

The comparison of the IR spectra of the Schiff bases with those of macrocycles showed the overlapping of the bands in the region 1622-1608 cm^{-1} due to ν(C=N), indicating that the C=N group is an integral part of both the ligand as well as the macrocyclic system. The disappearance of absorption band in IR and signals in ^{1}H NMR spectra corresponding to ν(O–H) (Ref 17) of the macrocycles suggests the cyclization reaction between phenolic groups and dielectrophiles forming carbon–oxygen (C–O) bonds. This fact is further supported by the appearance of new and intense broad band in the region 1260–1160 cm^{-1} of the IR spectra of all macrocycles due to the stretching vibrations of the (C–O) bonds. In ^{1}H NMR spectra of the macrocycles, signals arising from azomethine (CH=N) protons appeared in the range δ 8.41–8.80. The formation of Ar–O–C linkage was further supported by the presence of signals in the range of δ 3.81–3.96 corresponding to methylenic protons adjacent to phenolic oxygen. In ^{13}C NMR spectra, the signals in the range δ 161–166 are due to azomethine carbons and signals in the region δ 114–150 are due to aromatic carbons. The signals in the range of δ 60.0–67.4 due to methylenic carbon adjacent to oxygen atoms indicate the presence of O–CH_2 linkage. All the macrocycles displayed a single peak in ESI-MS suggesting their purity.

Experimental Section

All chemicals were used as received from Merck or Sigma-Aldrich. All solvents (AR or extra pure grade) used for spectroscopic and other physical studies were further purified as described elsewhere[18]. All operations were performed under nitrogen atmosphere using standard glass wares. All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F_{254} UV indicator). IR spectra were recorded as KBr discs on Jasco FT/IR-5300 spectrophotometer. NMR spectra were recorded in $CDCl_3$ (300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively) with TMS as an internal standard on a

Jeol AL 300 FT NMR spectrometer. Chemical shifts were reported in parts per million (δ, ppm). Mass spectra (MS) were recorded at 70 eV ionizing voltage on a Jeol SX-102 (ESI). Melting points were determined using a calibrated thermometer by Büchi B-540 melting point apparatus and are uncorrected.

Synthesis of N, N'-bis(*o*-vanillidene) ethylene diamine I

To a stirred solution of *o*-vanillin (7.6 g, 50 mmol) in ethanol (30 mL), a solution of ethylenediamine (1.5 g, 25 mmol) in ethanol (20 mL) was added. Reaction mixture was stirred at reflux for 4 hr (monitored by TLC). A yellow coloured solid was separated out on cooling, which was filtered, washed with diethyl ether, and recrystallized from ethanol to afford the pure N, N'-bis(*o*-vanillidene) ethylenediamine **I** (Yield 6.2g, 76%); m.p. 145-47°C; IR (KBr): 3450, 1631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 13.6 (s, 2H, ArOH), 8.3 (s, 2H, CH=N), 7.00-6.74 (m, 6H, ArH), 3.96 (s, 6H, OCH_3), 3.89-3.93 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 151.6, 148.4, 123.3, 118.5, 118.1, 114.3, 59.4, 56.1; ESI MS: (*m/z*) 328 (M^+). Anal. Calcd. for $C_{18}H_{20}N_2O_4$ (328.33): C, 65.84; H, 6.14; N, 8.53. Found C, 65.65; H, 6.05; N, 8.01%.

N, N'-bis(*o*-vanillidene)-4-methyl-*o*-phenylenediamine II

Following similar procedure as discussed above using *o*-vanilline (3.04 g, 20 mmol) and 4-methyl-*o*-phenylenediamine (1.22 g, 10 mmol) yielded 2.7 g (68%) of N, N'-bis(*o*-vanillidene)-4-methyl-*o*-phenylenediamine **II**; m.p. 182-83°C; IR (KBr): 3448, 1615, 1464, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 13.26 and 13.19 (s, 2H, ArOH), 8.61 (s, 2H, CH=N), 7.15-6.82 (m, 9H, ArH), 3.89 (s, 6H, OCH_3), 2.41 (s, 3H, $ArCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 163.4, 151.6, 151.5, 148.5, 142.3, 139.7, 137.7, 128.3, 128.1, 123.8, 123.8, 120.9, 119.2, 118.4, 115.0, 114.9, 56.1, 21.0; ESI MS: (*m/z*) 390 (M^+). Anal. Calcd. for $C_{23}H_{22}N_2O_4$ (390.39): C, 70.76; H, 5.68; N, 7.17, Found C, 70.50; H, 5.32; N, 7.38%.

N, N´-bis(salicylidine)-*p*-phenylenediamine III[19]

Following similar procedure as above using *p*-phenylene diamine (10 mmol, 1.08 g) and salicylaldehyde (20 mmol, 2 mL) furnished 3.03 g (96%) of N, N´-bis(salicylidine)-*p*-phenylenediamine[19] **III**; m.p. 196-98°C. IR (KBr): 3451, 1610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 13.20 (s, 2H, OH), 8.60 (s, 2H, CH=N), 7.42-6.81 (m, 12H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 159.9, 146.4, 132.6, 131.9, 121.9, 121.7, 119.1, 118.6, 116.6, 113.9; ESI MS: (*m/z*) 316.34 (M^+). Anal. Calcd. for $C_{20}H_{16}N_2O_2$ (316.35): C, 75.93; H, 5.09; N, 8.85. Found: C, 75.64; H, 5.22; N, 8.36%.

General procedure for the synthesis of macrocycles 1-12

A solution of Schiff base ligand **I**, **II** or **III** (1.0 mmol) in dry DMF (2 mL) was added drop-wise to a stirred suspension of NaH (62 mg, 2.58 mmol) in dry DMF (3 mL) at RT under nitrogen atmosphere. A solution of suitable dielectrophile (1.0 mmol) in dry DMF (1 mL) was added drop-wise at 0°C over a period of 10 min and the content was stirred at RT for 4 hr (monitored by TLC). Water was added to the reaction mixture and extracted with ethyl acetate (2 × 10 mL). The combined organic extract was dried over anhydrous Na_2SO_4. Solvent was evaporated under vacuum to yield the crude product, which was purified by column chromatography using 15% EtOAc in *n*-hexane to yield the desired macrocycle. The spectral and analytical data of the macrocycles are given below:

Compound 1: Brown solid. Yield 0.223 g, 63%. m.p. 131-33°C; IR (KBr): 2934, 2858, 1633, 1251 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 2H, CH=N), 6.92-6.82 (m, 6H, ArH), 3.94 (s, 6H, OCH_3), 3.89-3.81 (m, 4H, OCH_2), 3.63-3.58 (t, *J* = 6.9 Hz, 4H, NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 151.5, 148.5, 123.2, 118.4, 118.1, 114.2, 68.3, 59.5, 56.1; ESI MS: *m/z* 354 (M^+). Anal. Calcd. for $C_{20}H_{22}N_2O_4$ (354.37): C, 67.78; H, 6.25; N, 7.90. Found C, 68.05; H, 6.55; N, 7.52%.

Compound 2: Brown solid. Yield 0.224 g, 61%. m.p. 122-24°C; IR (KBr): 2926, 2853, 1631,1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (s, 2H, CH=N), 6.91-6.77 (m, 6H, ArH), 3.90 (s, 6H, OCH_3), 3.92-3.84 (m, 4H, OCH_2), 3.61-3.54 (m, 4H, NCH_2), 0.92 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 152.0, 149.4, 123.8, 118.9, 118.2, 114.7, 65.2, 59.2, 55.9, 28.1; ESI MS: *m/z* 368 (M^+). Anal. Calcd. for $C_{21}H_{24}N_2O_4$ (368.39): C, 68.46; H, 6.56; N, 7.60. Found C, 67.98; H, 6.29; N, 7.30%.

Compound 3: Light brown solid. Yield 0.255 g, 67%. m.p. 126-27°C; IR (KBr): 2918, 1633, 1261 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (s, 2H, CH=N), 6.91-6.77 (m, 6H, ArH), 3.96 (s, 6H, OCH_3), 3.94-

3.86 (m, 4H, OCH_2), 3.63-3.55 (m, 4H, NCH_2), 1.78-1.69 (m, 4H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 151.4, 149.1, 123.5, 118.1, 118.0, 114.4, 65.3, 59.5, 24.0; ESI MS: *m/z* 382 $(M)^+$. Anal. Calcd. for $C_{22}H_{26}N_2O_4$ (382.42): C, 69.09; H, 6.85; N, 7.32. Found C, 69.75; H, 6.64; N, 7.81%.

Compound 4: Brown solid. Yield 0.208 g, 59%. m.p. 102-04°C; IR (KBr): 2931, 1705, 1631,1268 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 2H, CH=N), 6.93-6.67 (m, 6H, ArH), 3.94 (s, 6H, OCH_3), 3.64-3.56 (m, 4H, NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.29, 166.5, 151.11, 148.72, 122.68, 117.71, 118.42, 113.97, 59.09; ESI MS: *m/z* 354 $(M)^+$. Anal. Calcd. for $C_{19}H_{18}N_2O_5$ (354.316): C, 64.40; H, 5.12; N, 7.90. Found C, 64.24; H, 5.86; N, 7.28%.

Compound 5: Light brown solid. Yield 0.241 g, 61%. m.p. 92-94°C; IR (KBr): 2917, 1716, 1631, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 2H, CH=N), 6.92-6.8 (m, 6H, ArH), 3.92 (s, 6H, OCH_3), 3.88 (t, *J* = 6.0 Hz, 2H, OCH_2), 3.66-3.54 (m, 4H, NCH_2), 2.44 (t, *J* = 6.0 Hz, 2H, $COCH_2$), 2.01 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.1, 165.7, 165.6, 150.7, 150.5, 147.3, 147.2, 123.5, 122.1, 118.5, 117.3, 116.9, 113.0, 58.2, 55.2, 55.0, 28.6; ESI MS: *m/z* 396 $(M)^+$. Anal. Calcd. for $C_{22}H_{24}N_2O_5$ (396.395): C, 66.66; H, 6.10; N, 7.06, Found C, 67.02; H, 6.61; N, 7.38%.

Compound 6: Brown solid. Yield 0.306 g, 69%. m.p. 151-53°C; IR (KBr): 2898, 1615, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 2H, CH=N), 7.05-6.75 (m, 9H, ArH), 3.89 (t, *J* = 6 Hz, 4H, OCH_2), 3.82 (s, 6H, OCH_3), 2.35 (s, 3H, $ArCH_3$), 1.96-1.92 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1, 162.4, 150.5, 150.5, 147.5, 141.2, 138.7, 136.7, 127.1, 122.8, 122.7, 119.9, 118.8, 118.1, 117.3, 117.3, 113.9, 113.7, 75.6, 55.0, 31.2, 20.0; ESI MS: *m/z* 444 $(M)^+$. Anal. Calcd. for $C_{27}H_{28}N_2O_4$ (444.49): C, 72.95; H, 6.34; N, 6.30. Found C, 72.86; H, 6.09; N, 6.99%.

Compound 7: Brown solid. Yield 0.311 g, 68%. m.p. 139-41°C; IR (KBr): 2867, 1615, 1236 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 2H, CH=N), 7.12-6.59 (m, 9H, ArH), 3.82 (s, 6H, OCH_3), 3.94 (t, *J* = 6.6 Hz, 4H, OCH_2), 2.29 (m, 4H, CH_2), 2.26 (s, 3H, $ArCH_3$), 1.21 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.9, 162.3, 151.0, 150.8, 148.2, 141.9, 137.9, 136.3, 127.0, 123.7, 122.5, 119.4, 118.5, 118.3, 117.4, 117.3, 114.0, 113.5, 69.8, 55.3, 28.3, 21.2, 20.1; ESI MS: *m/z* 458 $(M)^+$. Anal. calcd. for $C_{28}H_{30}N_2O_4$ (458.521): C, 73.34; H, 6.59; N, 6.10. Found C, 72.84; H, 6.49; N, 6.22%.

Compound 8: Brown solid. Yield 0.325 g, 71%. m.p. 120-21°C; IR (KBr): 2905, 1720, 1615, 1241 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 2H, CH=N), 7.64-6.94 (m, 9H, ArH), 3.89 (s, 6H, OCH_3), 3.82 (t, *J* = 6.6 Hz, 2H, OCH_2), 2.59-2.25 (m, 4H, CH_2), 2.36 (s, 3H, $ArCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 163.3, 162.0, 151.3, 150.2, 147.6, 141.2, 138.4, 136.7, 127.6, 122.3, 122.0, 119.3, 118.2, 118.0, 117.6, 117.3, 113.8, 113.3, 72.4, 55.1, 29.2, 24.9, 20.0; ESI MS: *m/z* 458 $(M)^+$. Anal. Calcd. for $C_{27}H_{26}N_2O_5$ (458.468): C, 70.73; H, 5.71; N, 6.11. Found C, 70.71; H, 5.67; N, 6.44%.

Compound 9: Yellow solid. Yield 0.217 g, 61%. m.p. 147-49°C. IR (KBr): 1608, 1261 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (s, 2H, CH=N), 7.83-6.97 (m, 12H, ArH), 4.01 (t, *J* = 6.3 Hz, 4H, OCH_2), 2.41-2.23 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 145.7, 131.9, 131.0, 121.5, 121.0, 118.9, 118.5, 116.7, 114.0, 65.0, 28.5; ESI MS: *m/z* 356.406 $[M]^+$. Anal. Calcd. for $C_{23}H_{20}N_2O_2$ (356.406): C, 77.51; H, 5.65; N, 7.85. Found: C, 77.25; H, 5.46; N, 7.52%.

Compound 10: Yellow solid. Yield 0.24 g, 64%. m.p. 138-40°C. IR (KBr): 1608, 1264 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 2H, CH=N), 7.33-6.89 (m, 12H, ArH), 4.10 (t, *J* = 6.0 Hz, 4H, OCH_2), 2.04-2.01 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 145.6, 132.4, 131.1, 122.2, 121.0, 118.9, 118.4, 116.7, 114.7, 69.1, 25.3; ESI MS: *m/z* 370 $(M)^+$. Anal. Calcd. for $C_{24}H_{22}N_2O_2$ (370.43): C, 77.81; H, 5.98; N, 7.56%. Found: C, 77.22; H, 5.25; N, 7.79%.

Compound 11: Yellow solid.Yield 0.23 g, 59%. m.p. 135-36°C. IR (KBr): 1607, 1246 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 2H, CH=N), 7.81-6.67 (m, 12H, ArH), 4.08 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.93-1.70 (m, 4H, CH_2), 1.27-1.21 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 145.8, 131.4, 131.1, 122.3, 121.0, 118.9, 118.4, 116.7, 114.7, 71.0, 29.3, 21.3; ESI MS: *m/z* 384 $(M)^+$. Anal. Calcd. for $C_{25}H_{24}N_2O_2$ (384.46): C, 78.10; H, 6.29; N, 7.28. Found: C, 77.82; H, 6.41; N, 7.48%.

Compound 12: Yellow solid. Yield 0.23 g, 60%. m.p. 126-28°C. IR (KBr): 1608, 1259, 781 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 2H, CH=N), 7.83-6.68 (m, 12H, ArH), 4.04 (t, *J* = 6.3 Hz, 4H, OCH_2), 1.90-1.88 (m, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 145.6, 132.4, 131.4, 122.6, 122.0, 119.5, 119.0, 116.3, 114.7, 69.3, 32.3, 20.9; ESI MS: *m/z* 398 $(M)^+$. Anal. Calcd. for $C_{26}H_{26}N_2O_2$ (398.48): C, 78.36; H, 6.57; N, 7.02. Found: C, 78.11; H, 6.21; N, 7.24%.

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