Solvent-free synthesis of some N_4O_2, N_4S_2 and N_6 Schiff base ligands assisted by microwave irradiation

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Abstract

A microwave-assisted solvent-free condensation of various aldehydes with two different piperazine-based amines efficiently afforded a series of bis-imine ligands in high yields. All products were characterized by their melting point, elemental analysis, IR, EI mass, ^{1}H and ^{13}C NMR spectra. This method is fast, involves no solvent and has easy work-up and high yields of the desired products.

Keywords: Schiff base, solvent-free, microwave irradiation, piperazine

Introduction

Schiff-bases are widely studied and used in the fields of organic synthesis and metal ion complexation[1,2] for a number of reasons: their physiological and pharmacological activities;[3-5] their use in ion-selective electrodes,[6-11] in the determination of heavy metal ions in environmental samples,[12] and in the extraction of metal ions;[13] and their many catalytic applications (e.g. for epoxidation of olefins,[14] alkene cyclopropanation,[15] trimethylsilylcyanation of ketones,[16] asymmetric oxidation of methyl phenyl sulfide,[17] enantioselective epoxidation of silylenol,[18] and ring-opening polymerization of lactide[19]). Though their synthesis has been extensively investigated,[20-25] many procedures suffer from drawbacks that can include low yield, long reaction times, the need for large amounts of solvent that then have to be removed, and difficult work-up. For example, as regards the compounds synthesized in the work described in this paper, or close analogues, L^4 (*N,N′*-bis((pyridin-2-ylmethyleneamino)ethyl)piperazine) was quite recently prepared by Ghosh *et al.* by refluxing in dry alcohol for 10 h[26] and *N,N′*-bis(3-(thiophen-2-ylmethyleneamino)propyl)piperazine (the propyl analogue of L^5) was prepared by Ibers and co-workers by refluxing thiophene-2-carbaldehyde and *N,N′*-bis(3-aminopropyl)piperazine in methanol for 3h.[27] L^1, L^6, L^7 and L^9 were prepared in methanol or ethanol in the range 0.5-3 h[28-30].

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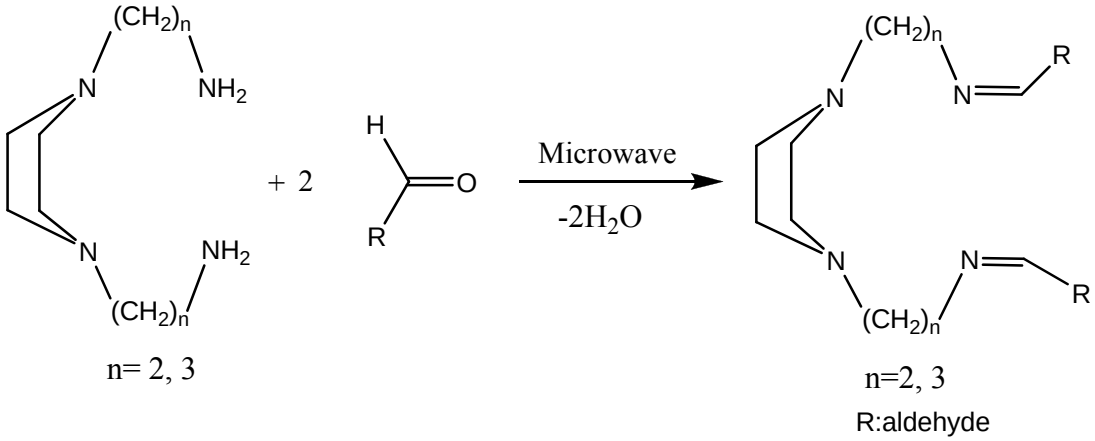
Solvent-free reactions are of interest not only from an ecological point of view, but in many cases also offer considerable advantages in terms of yield, selectivity and simplicity. Under gentle warming,[31] or by grinding at room temperature,[32] aromatic aldehydes and aromatic amines react quite readily in the solid state to give Schiff bases, but these reactions can be relatively slow, making it preferable to use a suspension in water.

Alternatively, heterocyclic and aryl amines have been condensed efficiently with salicylaldehyde and heterocyclic aldehydes by microwaving,[33,34] a technique that has become a powerful tool in organic synthesis.[35]

In this paper we report the fast, clean, solvent-free, microwave-assisted synthesis of ten Schiff base ligands (L^1-L^{10}) in which a piperazine-based amine (*N,N′*-bis(3-aminopropyl)piperazine or *N,N′*-bis(2-aminoethyl)piperazine) is condensed with an aromatic aldehyde (salicylaldehyde, 5-bromosalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde, 2-hydroxy-1-naphthaldehyde, pyridine-2-carbaldehyde or thiophene-2-carbaldehyde) (Scheme 1).

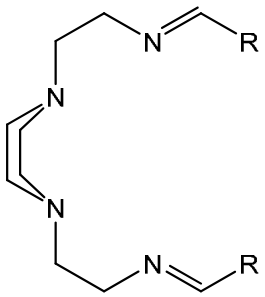
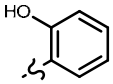
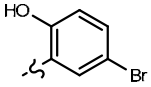
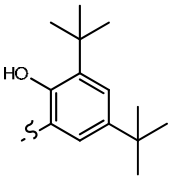
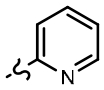
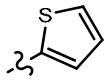
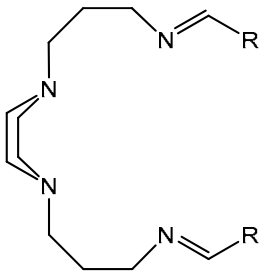
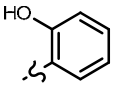
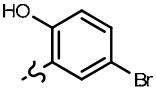
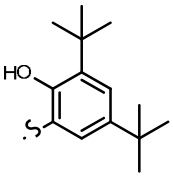
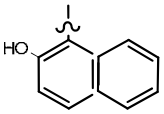


Scheme 1

Result and Discussion

All the new, potentially hexadentate Schiff base ligands were cleanly synthesized in 1-1.5 minutes and >80% yield according to elemental analyses and ^{1}H and ^{13}C NMR analyses of the bulk products after recrystallization from ethanol (Table 1). Their structures are supported by the absence from their IR spectra of the carbonyl and primary amine bands of the reagents, and the presence of a Schiff base ν(C=N) band in the 1631-1652 cm^{-1} region; the alkyl C–H stretching vibrations appear in the 2800–2900 cm^{-1} region. In the ^{1}H NMR spectra, the azomethine protons appear at δ= 8.22–8.73 ppm and the aromatic ring protons at δ = 6.5-8.4 ppm. In the ^{13}C NMR spectra, the imine carbon appears at 158.2-166.8 ppm.

Table 1. Synthesis of L^1-L^{10} under microwave irradiation

Structure	Ligand	R	Time (min)	Yield (%)
	L^1		1	90
	L^2		1	88
	L^3		1.5	85
	L^4		1	80
	L^5		1	84
	L^6		1	84
	L^7		1.5	88
	L^8		1	90
	L^9		1.5	85
	L^{10}		1	86

Conclusions

In this work, we report a rapid, highly efficient microwave-based synthesis of ten potentially hexadentate Schiff base ligands. The advantages of the method employed include a simple reaction set-up, high product yields, short reaction times, and the absence of solvents.

Experimental Section

General Procedures. Reactions were performed in a CEM Discover microwave oven. Melting points were measured in an SMPI apparatus. Elemental analyses for C, H and N were performed using Perkin-Elmer 2400 and Carlo-Erba elemental analysers. Infrared spectra were recorded from liquid films between NaCl plates in a Perkin–Elmer FT-IR Spectrum GX spectrophotometer (4000–500 cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 ºC on 90 MHz Jeol and 400 MHz Bruker spectrometers. EI mass spectra were obtained at 70 eV in a Shimadzu QP-1100EX GC–MS apparatus.

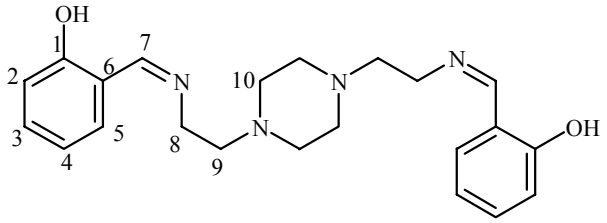
Chemical and starting materials

Salicylaldehyde, 5-bromosalicylaldehyde, 2-hydroxy-1-naphthaldehyde, pyridine-2-carbaldehyde and thiophene-2-carbaldehyde (all from Merck) and *N,N′*-bis(3-aminopropyl)piperazine (from Aldrich) were used as supplied, without further purification. 3,5-Di-*tert*-butylsalicylaldehyde was prepared as described in the literature,[36] as was *N,N′*-bis(2-aminoethyl)piperazine.[26]

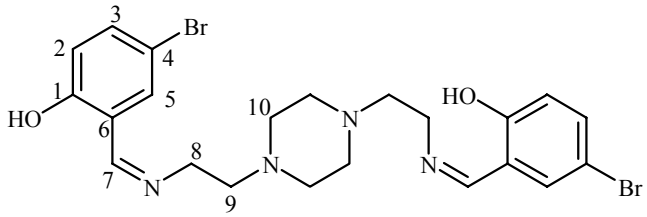
General procedure for synthesis of Schiff base ligands

The aldehyde (1 mmol), the amine (0.5 mmol) and silica gel (0.5 g) were mixed together in a tube and irradiated in a microwave oven. The progress of the reaction was monitored by gas chromatography. Upon completion of the reaction, the crude product was re-crystallized from ethanol and then dried over sodium sulphate. The solvent was evaporated and the product was washed with diethyl ether and dried. All the products were identified by melting point, mass spectrum, elemental analysis, and IR and ^{1}H and ^{13}C NMR spectra.

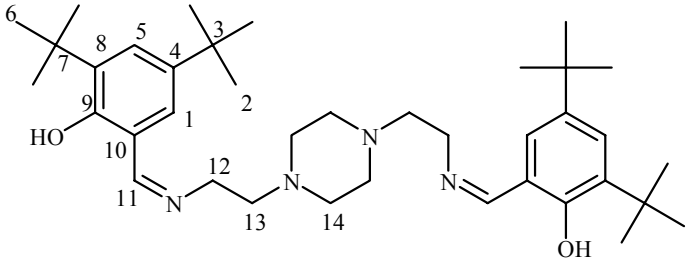
2-((*Z*)-(2-(4-(2-((*Z*)-2-Hydroxybenzylideneamino)ethyl)piperazin-1-yl)ethylimino) methyl) phenol (L^1). Salicylaldehyde (1 mmol, 0.122 g), *N,N′*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{22}H_{28}N_4O_2$ (MW: 380.22): C, 69.45; H, 7.42; N, 14.73. Found: C, 69.60; H, 7.34; N, 14.91%. Yield: 0.17 g (90%). mp. 149.0-151.0 °C. IR (Nujol, cm^{-1}): 1634 [υ(C=N)], 1160(s) [υ(C-O)]. MS (EI): m/z =380 $[L^1]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H : 2.71-2.78 (m, 12H, 9-H and 10-H), 3.78 (t (^{3}J=8.0 Hz), 4H, 8-H), 6.85-7.33 (m, 8H, aromatic ring), 8.35 (s, 2H, 7-H, -C=N), 13.42 (b s, 2H, -OH) . ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C: 53.1 (t, C-10), 56.8 (t, C-9), 58.5 (t, C-8), 118.6 (s, C-6), 117.0, 118.7, 131.3, 132.3(d, C-2–C-5), 161.1(s, C-1) (aromatic ring), 165.8 (d,C-7)**.**



2-((*Z*)-(2-(4-(2-((*Z*)-5-bromo-2-hydroxybenzylideneamino)ethyl)piperazin-1-yl) ethylimino)methyl)-4-bromophenol (L^2). 5-Bromosalicylaldehyde (1 mmol, 0.201 g), *N,N′*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{22}H_{26}Br_2N_4O_2$(MW: 538): C, 49.09; H, 4.87; N, 10.41. Found: C, 49.40; H, 5.0; N, 10.32%. Yield: 0.23 g (88%). mp. 187.0-189.0 °C. IR (Nujol, cm^{-1}): 1634 (s) [υ(C=N)]; 1162 (s) [υ(C-O)]. MS (EI): m/z =538 $[L^2]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 2.58-2.70 (m, 12H, 9-H and 10-H), 3.71 (t (^{3}J=8.0 Hz), 4H, 8-H), 6.82-7.27 (m, 6H, aromatic ring), 8.26 (s, 2H, 7-H, -C=N), 13.32 (b ,2H, -OH). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C: 53.3 (t, C-10), 56.8 (t, C-9) 58.4 (t, C-8), 109.9(s, C-6)), 119.1(d, C-5), 120.1(s, C-4), 133.3(d, C-2 or C-3), 134.9(d, C-2 or C-3), 160.4(s, C-1)(aromatic ring), 164.4 (d, C-7)

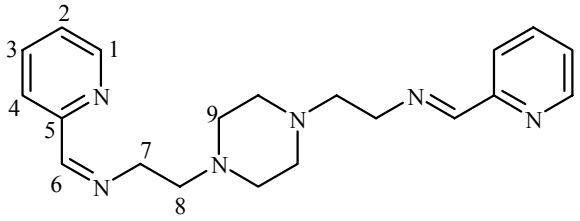


2-((*Z*)-(2-(4-(2-((*Z*)-3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)ethyl)piperazin-1-yl) ethylimino)methyl)-4,6-di-*tert*-butylphenol (L^3). 3,5-Di-*tert*-butylsalicylaldehyde (1 mmol, 0.234 g), *N,N′*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{34}H_{60}N_4O_2$(MW: 604): C, 75.45; H, 10.00; N, 9.26. Found: C, 76.02; H, 9.80; N, 9.76%. Yield: 0.26 g (85%). mp. 166.0-168.0 °C. IR (Nujol, cm^{-1}) 1633 (s) [υ(C=N)]; 1161(s) [υ(C-O)]. MS (EI): m/z =604 $[L^3]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 1.30 (s, 18H, 3-H), 1.44 (s, 18H, 7-H), 2.61 (m, 12H,13-H and 14-H), 3.74 (b, 4H, 12-H), 7.06 -7.38 (m, 4H, 1-H and 5-H), 8.36 (s, 2H, 11-H, -C=N), 13.72 (b s, 2H, -OH). ^{13}C NMR (90 MHz, $CDCl_3$, ppm) δ_C: 29.5 (q, C-2), 31.6(q, C-6), 34.2(s, C-3), 35.1(s, C-7), 53.5 (t, C-14), 57.1 (t, C-13), 59.0(t, C-12), 118.0(s, C-10), 125.9, 126.9 (d, C-1 or C-5) 136.8, 140.1 (s, C-4 or C-8), 158.2(s, C-9) (aromatic ring), 166.8(d, C-11).

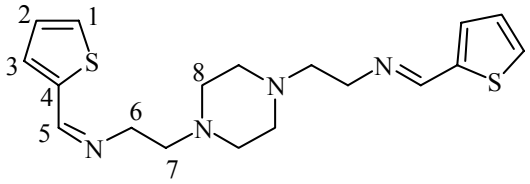


(*E*)-*N*-(Pyridin-2-ylmethylene)-2-(4-(2-((*Z*)-pyridin-2-ylmethyleneamino)ethyl) piperazin-1-yl)ethanamine (L^4). 2-Pyridinecarbaldehyde (1 mmol, 0.107 g), *N,N′*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{20}H_{27}N_6O_{0.5}$(MW: 359.23): C, 66.82; H, 7.57; N, 23.38. Found: C, 67.23; H, 7.46; N, 23.50%. Yield: 0.14 g (80%). mp. 101.0-103.0 °C. IR (Nujol, cm^{-1}): 1647 [υ(C=N)], 1587, 1567 [$\upsilon(C=N)_{py}$ and υ(C=C)]. MS (EI): m/z =350 $[L^4]^+$. ^{1}H NMR (400MHz,

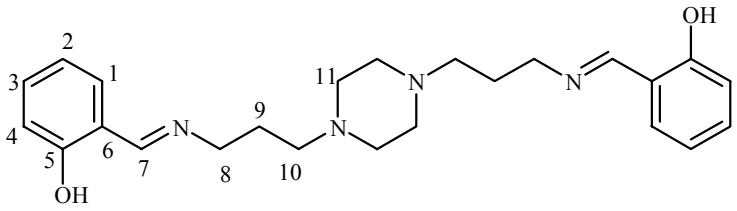
$CDCl_3$, ppm) δ_H: 2.56 (b, 8H, 9-H), 2.68 (t (^3J=8.0 Hz), 4H, 8-H), 3.78 (t(^3J=8.0 Hz), 4H, 7-H), 7.27 -7.90, (m, 8H, aromatic ring), 8.34 (s, 2H, 6-H-C=N), 8.58 (d(^3J=8.0 Hz 2H,), aromatic ring). ^{13}C NMR (90 MHz, DMSO, ppm): 52.8(t, C-9), 57.7(t, C-8), 58.0(t, C-7), 120.7(s, C-1), 125.1(d, C-3), 136.9(d, C-2), 149.3(d, C-4), 153.9(d, C-6, -C=N), 162.4(s, C-5).



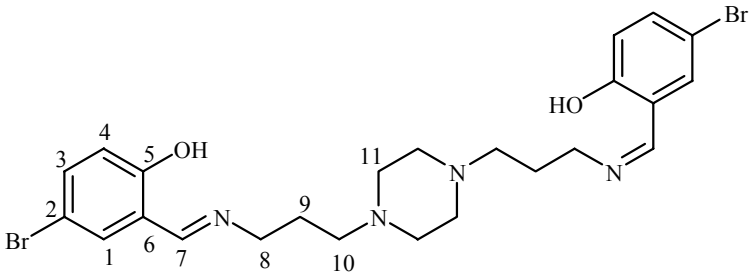
(*Z*)-*N*-(Thiophen-2-ylmethylene)-2-(4-(2-(thiophen-2-ylmethyleneamino)ethyl)piperazin-1-yl)ethanamine (L^5). 2-Thiophenecarbaldehyde (1 mmol, 0.112 g), *N,N′*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{18}H_{24}N_4S_2$(MW: 360.14): C, 59.96; H, 6.71; N, 15.54. Found: C, 61.30; H, 6.58; N, 15.80%. Yield: 0.15 g (84%). m.p. 96.0-98.0 °C. IR (Nujol, cm^{-1}): 1633 [υ(C=N)], 732 (s), υ (thiophene ring). MS (EI): m/z =360 $[L^5]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 2.53 (b, 8H, 8-H), 2.63 (t(^3J=8.0 Hz), 4H, H-7), 3.66 (t(^3J=8.0 Hz), 4H, H-6), 6.99-7.33(m ,6H, aromatic ring), 8.32 (s, 2H, 5-H, -C=N). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C: 53.7(t, C-8), 58.8(t, C-7), 58.8 (t, C-6), 127.8, 128.8, 130.6(d, C-1-C-3), 142.4(s, C-4)(aromatic ring), 155.2(d, C-5, -C=N).



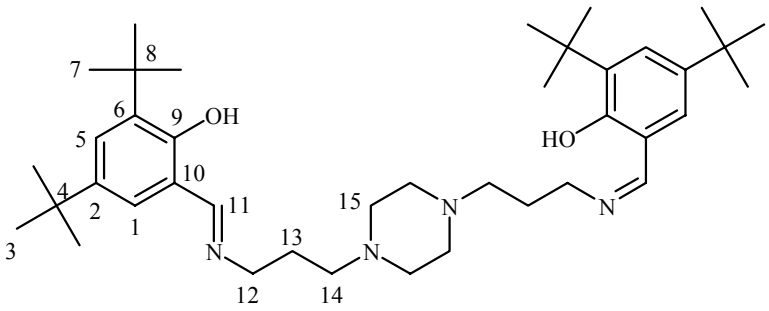
(*Z*)-2-((3-(4-(3-(2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propylimino)methyl) phenol (L^6). Salicylaldehyde (1 mmol, 0.122 g), *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{24}H_{32}N_4O_2$(MW: 408.25): C, 70.56; H, 7.90; N, 13.71. Found: C, 71.48; H, 8.02; N, 13.89%. Yield: 0.17 g (84%). m.p. 77.0-79.0 °C (lit [29]= 76 °C). IR (Nujol, cm^{-1}): 1634 [υ(C=N)], 1163(s) [υ(C-O)]. MS (EI): m/z =408 $[L^6]^+$.^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 1.87 (m, 4H, 9-H), 2.47 (m, 12H,10-H and 11-H), 3.58 (t(^3J=8.0 Hz), 4H, 8-H), 6.79-7.31 (m, 8H,aromatic ring), 8.33 (s, 2H, 7-H), 13.51 (b s, 2H, -OH). ^{13}C NMR (90 MHz, $CDCl_3$, ppm) 27.8(t, C-9), 53.1(t, C-11), 55.7(t, C-10), 57.3(t, C-8), 118.8 (s, C-6),116.9, 118.3, 131.0, 132.0 (d, C-1-C-4), 161.3(s, C-5)(aromatic ring), 164.9(d, C-7, -C=N).



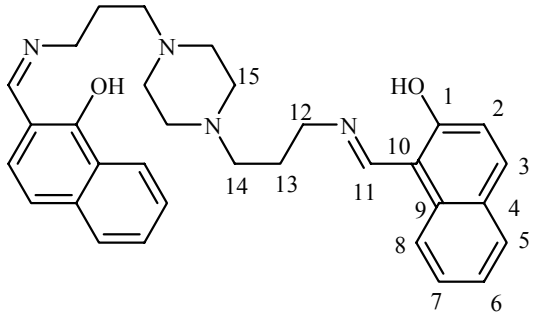
(*Z*)-2-((3-(4-(3-(5-Bromo-2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propylimino)methyl)-4-bromophenol (L^7). 5-Bromosalicylaldehyde (1 mmol, 0.201 g), *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{24}H_{30}Br_2N_4O_2$(MW: 566.33): C, 50.90; H, 5.34; N, 9.89. Found: C, 50.92; H, 5.30; N, 9.90%. Yield: 0.25 g (88%). m.p. 107.0-109.0 °C (lit [29]= 113 °C). IR (Nujol, cm^{-1}): 1635 [υ(C=N)], 1163(s) [υ(C-O)]. MS (EI): m/z =566 $[L^7]^+$.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 1.81 (m, 4H, 9-H), 2.33-2.40 (m, 12H, 10-H and 11-H), 3.58 (t(^{3}J=8.0 Hz), 4H, 8-H), 6.79-7.31 (m, 6H, aromatic ring), 8.20 (s, 2H, 7-H, -C=N), 13.49 (b s, 2H,-OH). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C: 27.8(t, C-9), 53.2(t, C-11), 55.8(t, C-10), 57.4(t, C-8), 109.8 (s, C-6), 119.1(d, C-5), 120.1 (s, C-2), 153.2, 154.8 (d, C-3 or C-4)160.5 (s,C-5)(aromatic ring), 163.8(d, C-7, -C=N).



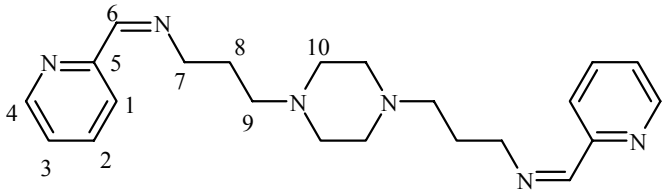
(*Z*)-2-((3-(4-(3-(3,5-Di-*tert*-butyl-2-hydroxybenzylideneamino)propyl)piperazin-1-yl) propylimino)methyl)-4,6-di-*tert*-butylphenol (L^8). 3,5-Di-*tert*-butylsalicylaldehyde (1 mmol, 0.234 g), *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{40}H_{64}N_4O_2 \cdot 0.5H_2O$(MW: 632.5): C, 74.27; H, 10.77; N, 8.66. Found: C, 74.18; H, 11.10; N, 8.50%. Yield: 0.28 g (90%). m.p. 124.0-126.0 °C. IR (Nujol, cm^{-1}): 1631 [υ(C=N)], 1162(s) [υ(C-O)]. MS (EI): m/z =632 $[L^8]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 1.33 (s, 18H, H-3), 1.47 (s, 18H,7-H), 1.90 (b m, 4H,13-H), 2.51 (b m, 12H, 14-H and 15-H), 3.64 (t(^{3}J=8.0 Hz), 4H, 12-H), 7.10-7.39 (m, 4H, 1-H and 5-H), 8.37(b s, 2H, -C=N), 13.89(s, 2H,-OH). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C: 28.1 (t, C-13), 29.4(q, C-3), 31.5(q, C-7), 34.1(s, C-4), 35.0(s, C-8), 53.3(t, C-15), 56.1(t, C-14), 57.6(t, C-12), 117.8 (s, C-10), 125.7, 126.8 (d, C-1, C-5), 136.7, 139.9 (s, C-2 , C-6), 158.2 (s, C-9) (aromatic ring), 166.0(d, C-11, -C=N)



(*Z*)-1-((3-(4-(3-((1-hydroxynaphthalen-2-yl)methyleneamino)propyl)piperazin-1-yl)propylimino)methyl)naphthalen-2-ol (L^9). 2-Hydroxy-1-naphthaldehyde (1 mmol, 0.172 g), *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{32}H_{36}N_4O_2 \cdot 0.5CH_3CH_2OH$(MW: 531.3): C, 74.55; H, 7.39; N, 10.54. Found: C, 74.55; H, 7.60; N, 10.53%. Yield: 0.22 g (85%). m.p. 167.0-169.0 °C (lit [30]= 160 °C). IR (Nujol, cm^{-1}): 1633 [υ(C=N)], 1163(s) [υ(C-O)]. MS (EI): m/z =508 $[L^9]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 1.81 (m, 2H,13-H), 2.41 (m, 12H, 14-H and 15-H), 3.58 (b, 2H, 12-H), 6.80-7.80 (m 12H, aromatic ring), 8.64 (s, 2H, 11-H, -C=N), 14.23 (b s, 2H, -OH). ^{13}C NMR (90 MHz, $CDCl_3$, ppm) δ_C: 27.4(t, C-13), 50.7(t, C-14), 53.0(t, C-15), 54.8 (t, C-12), 106.5 (s, C-10), 117.7 (d, C-2), 122.6 (d, C-8), 125.2 (d, C-6), 126.2 (s, C-4), 127.9(d, C-5), 129.3(d, C-7), 134.0 (s, C-9), 137.3(d, C-3), 158.2(d, C-11, -C=N), 176.9 (s, C-1).



(*Z*)-*N*-(Pyridin-2-ylmethylene)-3-(4-(3-((*Z*)-pyridin-2-ylmethyleneamino)propyl) piperazin-1-yl)propan-1-amine (L^{10}). Pyridine-2-carbaldehyde (1 mmol, 0.107 g), *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $C_{22}H_{32}N_6$·(MW: 378.25): C, 69.44; H, 8.48; N, 22.09. Found: C, 70.25; H, 8.02; N, 22.09%. Yield: 0.15 g (80%). IR (Nujol, cm^{-1}): 1650 [υ(C=N)], 1587, 1567 [$\upsilon(C=N)_{py}$ and υ(C=C)]. MS (EI): m/z =378 $[L^{10}]^+$. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ_H: 1.75 (m, 4H, 8-H), 2.33 (m, 12H, 9 and 10-H), 3.54 (b, 4H, 7-H), 7.13 (t(^{3}J=8.0 Hz), 2H, 2-H), 7.56 (t(^{3}J=8.0 Hz), 2H, 3-H), 7.78 (d(^{3}J=8.0 Hz), 2H,1-H), 8.22 (s, 2H, 6-H, -C=N), 8.47 (d(^{3}J=8.0 Hz), 2H, 4-H). ^{13}C NMR (90 MHz, $CDCl_3$, ppm) δ_C: 27.0(t, C-8), 52.3(t, C-10), 55.2 (t, C-9), 58.4(t, C-7), 120.2(d, C-1), 123.7(d, C-3), 135.5(d, C-2), 148.4 (d, C-4), 153.7 (d, C-6, -C=N), 161.1 (s, C-5).



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