

Solvent-free synthesis of some N₄O₂, N₄S₂ and N₆ 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, ¹H and ¹³C 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

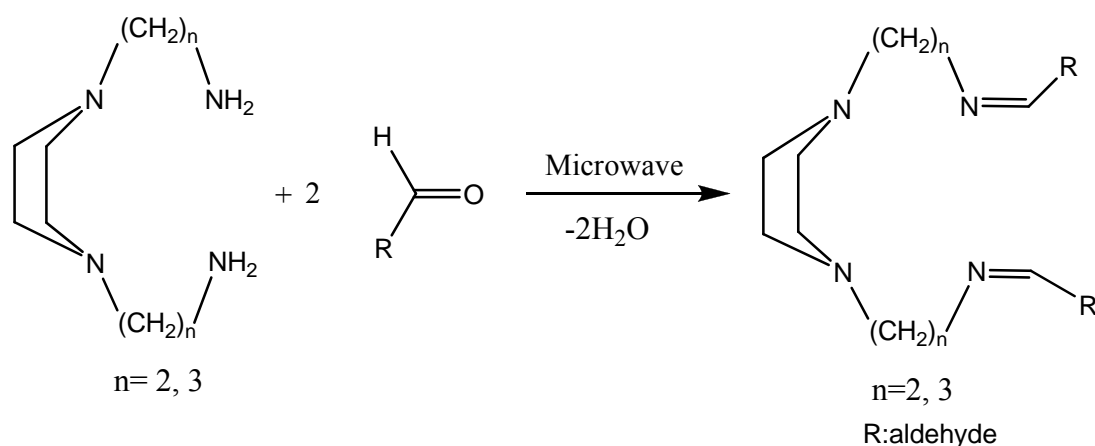
Introduction

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 lactide¹⁹). 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, L⁴ (*N,N'*-bis((pyridin-2-ylmethyleneamino)ethyl)piperazine) was quite recently prepared by Ghosh *et al.* by refluxing in dry alcohol for 10 h²⁶ and *N,N'*-bis(3-(thiophen-2-ylmethyleneamino)propyl)piperazine (the propyl analogue of L⁵) was prepared by Ibers and co-workers by refluxing thiophene-2-carbaldehyde and *N,N'*-bis(3-aminopropyl)piperazine in methanol for 3h.²⁷ L¹, L⁶, L⁷ and L⁹ were prepared in methanol or ethanol in the range 0.5-3 h²⁸⁻³⁰.

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).

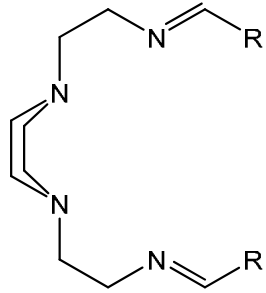
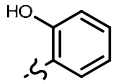
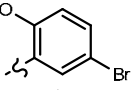
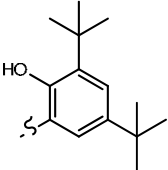


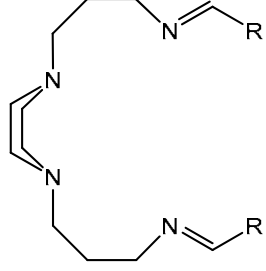
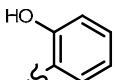
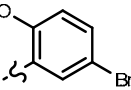
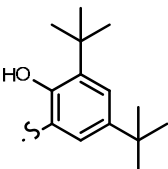
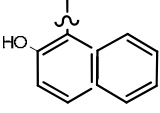



Scheme 1

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 ^1H 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 $\nu(\text{C}=\text{N})$ band in the 1631-1652 cm^{-1} region; the alkyl C-H stretching vibrations appear in the 2800-2900 cm^{-1} region. In the ^1H NMR spectra, the azomethine protons appear at $\delta = 8.22$ -8.73 ppm and the aromatic ring protons at $\delta = 6.5$ -8.4 ppm. In the ^{13}C NMR spectra, the imine carbon appears at 158.2-166.8 ppm.

Table 1. Synthesis of L¹-L¹⁰ 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}). ^1H and ^{13}C NMR spectra were recorded in CDCl_3 at 25 °C 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.

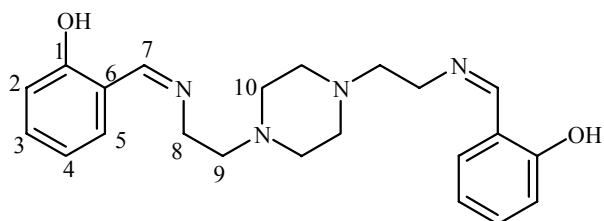
Chemical and starting materials

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

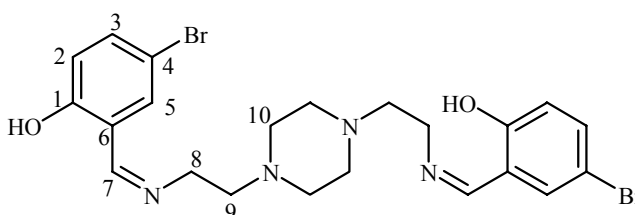
General procedure for synthesis of Schiff base ligands

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 ^1H and ^{13}C NMR spectra.

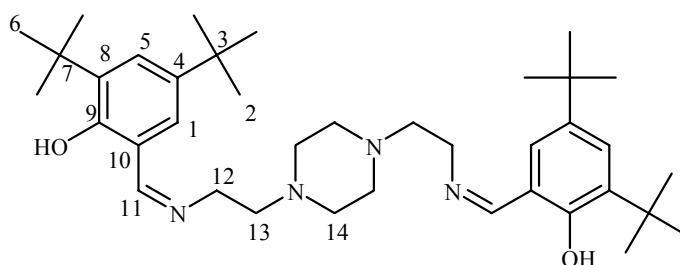
2-((*Z*)-(2-(4-(2-((*Z*)-2-Hydroxybenzylideneamino)ethyl)piperazin-1-yl)ethylimino)methyl) phenol (L**¹).** Salicylaldehyde (1 mmol, 0.122 g), *N,N'*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{N}_4\text{O}_2$ (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 [$\nu(\text{C}=\text{N})$], 1160(s) [$\nu(\text{C}-\text{O})$]. MS (EI): $m/z = 380$ [L^1]⁺. ^1H NMR (90 MHz, CDCl_3 , ppm) δ_{H} : 2.71-2.78 (m, 12H, 9-H and 10-H), 3.78 (t ($^3J=8.0$ 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 (L²). 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 C₂₂H₂₆Br₂N₄O₂(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) [ν(C=N)]; 1162 (s) [ν(C-O)]. MS (EI): m/z =538 [L²]⁺. ¹H NMR (90 MHz, CDCl₃, ppm) δ_H: 2.58-2.70 (m, 12H, 9-H and 10-H), 3.71 (t (³J=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). ¹³C NMR (400 MHz, CDCl₃, 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)

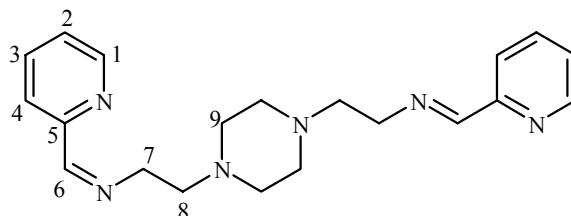


2-((Z)-(2-(4-(2-((Z)-3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)ethyl)piperazin-1-yl)ethylimino)methyl)-4,6-di-*tert*-butylphenol (L³). 3,5-Di-*tert*-butylsalicylaldehyde (1 mmol, 0.234 g), *N,N'*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for C₃₄H₆₀N₄O₂(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) [ν(C=N)]; 1161(s) [ν(C-O)]. MS (EI): m/z =604 [L³]⁺. ¹H NMR (90 MHz, CDCl₃, 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). ¹³C NMR (90 MHz, CDCl₃, 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).

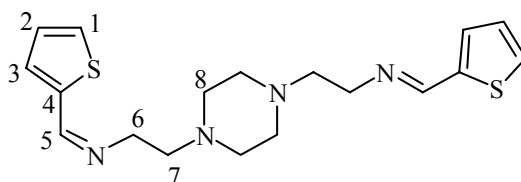


(*E*)-*N*-(Pyridin-2-ylmethylene)-2-(4-(2-((Z)-pyridin-2-ylmethyleneamino)ethyl)piperazin-1-yl)ethanamine (L⁴). 2-Pyridinecarbaldehyde (1 mmol, 0.107 g), *N,N'*-bis(2-aminoethyl)piperazine (0.5 mmol, 0.086 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for C₂₀H₂₇N₆O_{0.5}(MW: 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 [ν(C=N)], 1587, 1567 [ν(C=N)_{py} and ν(C=C)]. MS (EI): m/z =350 [L⁴]⁺. ¹H NMR (400MHz,

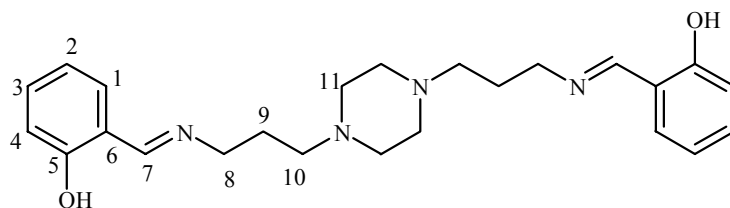
CDCl₃, ppm) δ_{H} : 2.56 (b, 8H, 9-H), 2.68 (t (³J=8.0 Hz), 4H, 8-H), 3.78 (t (³J=8.0 Hz), 4H, 7-H), 7.27 -7.90, (m, 8H, aromatic ring), 8.34 (s, 2H, 6-H-C=N), 8.58 (d (³J=8.0 Hz 2H), aromatic ring). ¹³C NMR (90 MHz, DMSO, ppm): 52.8(t, C-9), 57.7(t, C-8), 58.0(t, C-7), 120.7 (s, C-1), 125.1(d, C-3), 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 (L⁵). 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 C₁₈H₂₄N₄S₂(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 [ν (C=N)], 732 (s), ν (thiophene ring). MS (EI): m/z =360 [L⁵]⁺. ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (400 MHz, CDCl₃, 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).

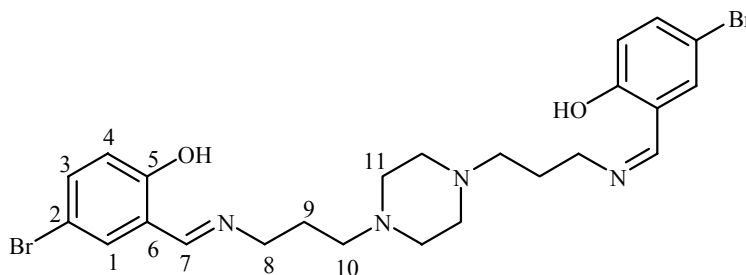


(Z)-2-((3-(4-(3-(2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propylimino)methyl)phenol (L⁶). Salicylaldehyde (1 mmol, 0.122 g), *N,N'*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for C₂₄H₃₂N₄O₂(MW: 408.25): C, 70.56; H, 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 [ν (C=N)], 1163(s) [ν (C-O)]. MS (EI): m/z =408 [L⁶]⁺. ¹H NMR (90 MHz, CDCl₃, 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). ¹³C NMR (90 MHz, CDCl₃, 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).



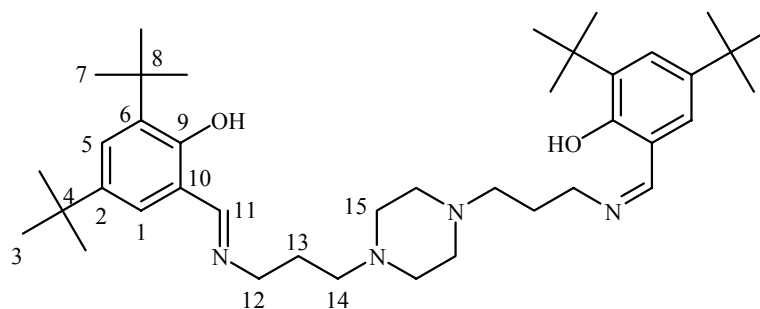
(Z)-2-((3-(4-(3-(5-Bromo-2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propyl)imino)methyl)-4-bromophenol (L⁷).

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 C₂₄H₃₀Br₂N₄O₂ (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 [ν(C=N)], 1163(s) [ν(C-O)]. MS (EI): m/z =566 [L⁷]⁺. ¹H NMR (400 MHz, CDCl₃, ppm) δ_H: 1.81 (m, 4H, 9-H), 2.33-2.40 (m, 12H, 10-H and 11-H), 3.58 (t³J=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). ¹³C NMR (400 MHz, CDCl₃, 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).

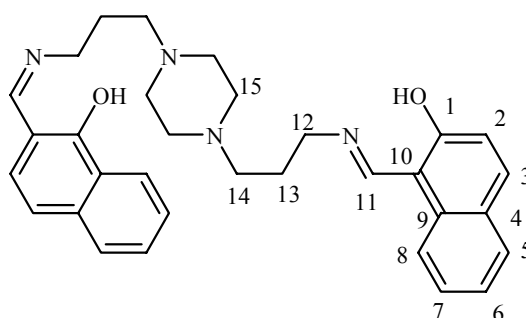


(Z)-2-((3-(4-(3-(3,5-Di-*tert*-butyl-2-hydroxybenzylideneamino)propyl)piperazin-1-yl)propyl)imino)methyl)-4,6-di-*tert*-butylphenol (L⁸).

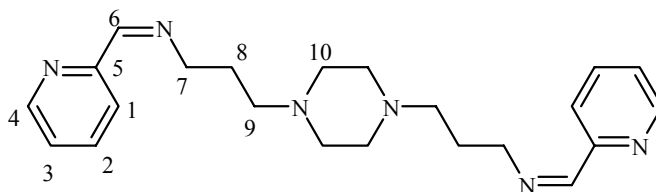
3,5-Di-*tert*-butylsalicylaldehyde (1 mmol, 0.234 g), *N,N'*-bis(3-aminopropyl)piperazine (0.5 mmol, 0.1 g) and silica gel (0.5 g) were subjected to the general procedure. Anal. Calc. for C₄₀H₆₄N₄O₂·0.5H₂O (MW: 632.5): C, 74.27; H, 10.77; N, 8.66. Found: C, 74.18; H, 11.10; N, 8.50%. Yield: 0.28 g (90%). m.p. 124.0-126.0 °C. IR (Nujol, cm⁻¹): 1631 [ν(C=N)], 1162(s) [ν(C-O)]. MS (EI): m/z =632 [L⁸]⁺. ¹H NMR (90 MHz, CDCl₃, 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 (t³J=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). ¹³C NMR (400 MHz, CDCl₃, 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 (L⁹). 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 C₃₂H₃₆N₄O₂·0.5CH₃CH₂OH(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 [ν(C=N)], 1163(s) [ν(C-O)]. MS (EI): m/z =508 [L⁹]⁺. ¹H NMR (90 MHz, CDCl₃, 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). ¹³C NMR (90 MHz, CDCl₃, 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 (L¹⁰). 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 C₂₂H₃₂N₆(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 [ν(C=N)], 1587, 1567 [ν(C=N)_{py} and ν(C=C)]. MS (EI): m/z =378 [L¹⁰]⁺. ¹H NMR (90 MHz, CDCl₃, 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(³J=8.0 Hz), 2H, 2-H), 7.56 (t(³J=8.0 Hz), 2H, 3-H), 7.78 (d(³J=8.0 Hz), 2H,1-H), 8.22 (s, 2H, 6-H, -C=N), 8.47 (d(³J=8.0 Hz), 2H, 4-H). ¹³C NMR (90 MHz, CDCl₃, 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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