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The one-pot halomethylation of 5-substituted salicylaldehydes as convenient precursors for the preparation of heteroditopic ligands for the binding of metal salts

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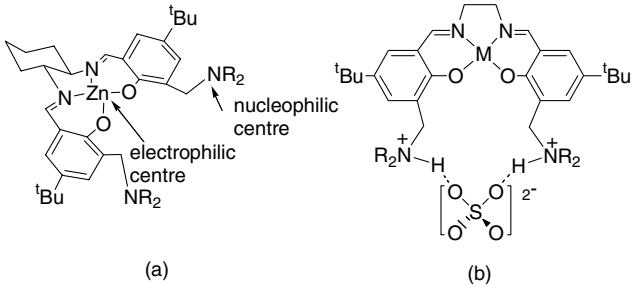
Abstract—The one-pot bromo- and chloro-methylation of various 5-substituted salicylaldehydes with paraformaldehyde and hydrobromic or hydrochloric acid has been achieved. This approach establishes a convenient and flexible method to attach functional arms to salicylaldehydes for further applications in organic and coordination chemistry. Examples are described using 3-bromomethyl-5-*t*-butylsalicylaldehyde in the synthesis of piperazine-containing heteroditopic ligands as receptors for metal salts.

Salicylaldehyde and its derivatives have been widely used both in the industry and academia. They have been used widely in synthetic co-ordination chemistry, particularly to synthesise the salen family of ligands for catalytic applications.[1] For example, several asymmetric diiron complexes have been synthesized[2] from 5-methylsalicylaldehyde, and these complexes mimic the spectroscopic properties of purple acid phosphatase enzymes. The use of bifunctional ligand systems is an attractive method of emulating the reactivity of natural enzymes.[3] DiMauro and Kozlowski have developed[4] powerful catalysts using 5-*t*-butylsalicylaldehyde to prepare a set of bifunctional salen complexes containing Zn(II) as a Lewis acid, with the pendant amine arms acting as Lewis base activating groups. These acid and basic groups can be altered independently to control the nucleophilic and electrophilic activations of the reacting substrates (Scheme 1a). Similar bifunctional acyclic and macrocyclic systems have also been used successfully by Tasker et al. as ditopic ligands for the simultaneous extraction of both anionic and cationic moieties of transition metal salts[5] (Scheme 1b). The zwitterionic form of the ligand generated by transfer of the phenolic protons from the metal binding site to the pendant tertiary amine groups creates a dipositive cavity wherein the anion is bound by a combination of both electrostatic and hydrogen bonding interactions. Additionally, piperazine rings have been appended to salicylaldehydes and used in the synthesis of unsymmetrical imino-macrocyclic complexes with the vanadium complexes showing activity as insulin mimetics.[6]



Scheme 1. Examples showing some bifunctional systems.

The introduction of halomethyl substituents at C3 of the 5-substituted salicylaldehyde has been used as a general approach to precursors to bifunctional ligands.[2,4,7] Indeed, halomethyl-substituted aromatics are versatile synthons in organic synthesis as the halide functionality acts as a synthetic handle for the attachment of further

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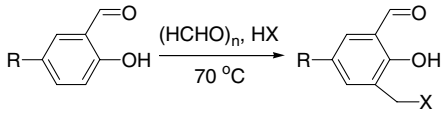
components.[8,9] The preparation of halomethyl-substituted aromatics has been well documented,[10] with the chloromethylation of aromatic compounds having been much more widely studied[9] compared to the bromomethylation, despite the fact that the resulting benzyl bromides are more reactive in subsequent nucleophilic displacement reactions.[11] Surprisingly, the only example of direct halomethylation of salicylaldehyde derivatives is the synthesis of 3-chloromethyl-5-methylsalicylaldehyde via the reaction of 5-methylsalicylaldehyde and formaldehyde in hydrochloric acid.[12] There appears to be no direct bromomethylation procedure reported in the literature. The preparation of 3-bromomethyl-5-*t*-butylsalicylaldehyde has recently been reported via a five-step procedure,[4] and a similar approach has also been reported for the preparation of 3-chloromethyl-5-methylsalicylaldehyde using concentrated hydrochloric acid in the last step.[13] Given the increasing interest in bifunctional ligand systems,[2,4,5] the development of an economical and straightforward synthetic route to halomethyl derivatives of 5-substituted salicylaldehydes is highly desirable; we report herein such a route.

The present study has developed a one-pot synthetic method that affords bromomethyl or chloromethyl derivatives of 5-substituted salicylaldehydes in high purity and in synthetically useful quantities (Scheme 2). 3-Bromomethyl-5-*t*-butylsalicylaldehyde **1**[14] was synthesized by heating a mixture containing 5-*t*-butylsalicylaldehyde,[15] paraformaldehyde and 48% HBr in aqueous solution at 70 °C with concentrated H_2SO_4 as a catalyst.[16] The reaction could be readily monitored by ^{1}H NMR spectroscopy, which showed that a reaction time of 20 h was optimum to furnish a pale yellow solid in a yield of 98%.

Compounds **2**–**6** were synthesized according to a similar procedure as for **1** with different reaction times as shown in Table 1.[17] The advantage of bromomethylation over chloromethylation is apparent. The choice of group at C-5 of the benzene ring clearly affects the rate of the halomethylation of the salicylaldehydes. Modifying the R-group from methyl, *t*-butyl, bromo to *n*-nonyl increases the reaction time for bromomethylation at the *meta*-position from 2 to 20 to 66 h and further to 9 days, respectively. Fuson and McKeever also found that the presence of a halogen atom inhibits the chloromethylation of aromatic compounds.[10] Therefore, the difference in the reaction time is probably due to a combined effect of both steric and electronic properties of the R-group.



R:	X=Br	X=Cl
t-butyl	**1**	**5**
methyl	**2**	**6**
n-nonyl	**3**	**7**
Br	**4**	**8**

Scheme 2. Halomethylation reactions studied in this work.

Table 1. Synthesis of halomethylated salicylaldehydes

Product	Reaction time	Yield (%)
1	20 h	98
2	2 h	95
3	9 days	93
4	66 h	85
5	45 h	93
6	4 h	97
7	10 days	~50
8	6.5 days	~40

The experimental results in Table 1 confirm that the bromomethylation reaction is faster than the corresponding chloromethylation, an observation which can be rationalized by the greater acidity of hydrobromic acid. According to the ^{1}H NMR spectra of the crude reaction mixtures, compounds **7** and **8** were produced in yields of approximately 50% and 40%, respectively, after reaction for 10 and 6.5 days and, therefore, further detailed studies for these two very slow reactions were not pursued. The bromo-analogues **3** and **4** can, however, be prepared in yields of 93% and 85% after reaction for 9 days and 66 h, respectively. The experimental results also show that relatively long reaction times help to generate the desired products in high yields.

For the three compounds **2**, **4** and **6**, single crystals suitable for study by X-ray crystallography were obtained and their structures are shown in Figure 1.[18] In each case, an intramolecular O–H···O hydrogen bond is formed between the phenolic hydrogen and the carbonyl oxygen, with H···O distances of around 1.95 Å in each case. As a result of this hydrogen bond, the OH moiety and the atoms O1, C2, C1, C8 and O8 are co-planar. Additionally, within the solid-state structure, molecules are linked into pairs by longer intermolecular hydrogen bonds between the phenolic hydrogen and the carbonyl oxygen of an adjacent molecule. Here the H···O distances are 2.31, 2.31 and 2.29 Å for compounds **2**, **4** and **6**, respectively, and the resulting motif has the graph set notation $R^2_2(4)$.

Initially, the use of 3-bromomethyl-5-*t*-butylsalicylaldehyde **1** in the synthesis of heteroditopic ligands was investigated by the synthetic sequence shown in Scheme 3. 3-Bromomethyl-5-*t*-butylsalicylaldehyde **1** was treated with excess piperazine in CH_2Cl_2 in the presence of triethylamine to give the monoaldehyde **9** as a minor product and the dialdehyde **10** as the major product. Consequently, 3-bromomethyl-5-*t*-butylsalicylaldehyde **1** was reacted with half an equivalent of piperazine in MeCN in the presence of Et_3N to yield solely the dialdehyde **10**.[19] Subsequently, the dialdehyde **10** underwent a Schiff-base condensation with ethane-1,2-diamine to yield a mixture of the symmetric macrocyclic ligands $\mathbf{L^1H_2}$ and $\mathbf{L^2H_4}$, as identified by mass spectrometry and ^{1}H NMR spectroscopy.[20] Unfortunately, we were unable to separate these two products effectively.

The dialkylation of piperazine is not surprising, as it has been reported that the direct alkylation of piperazine produces a mixture of substitution products from which

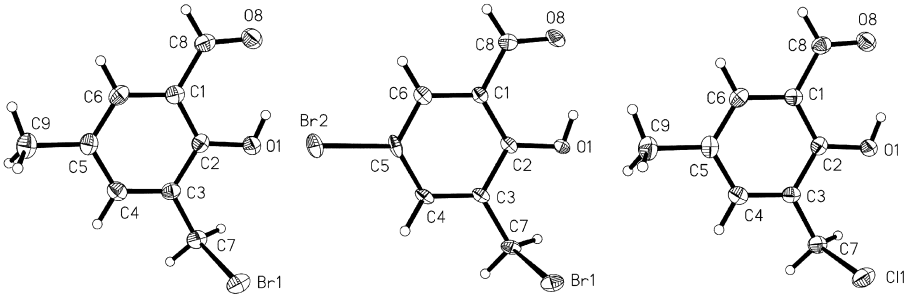
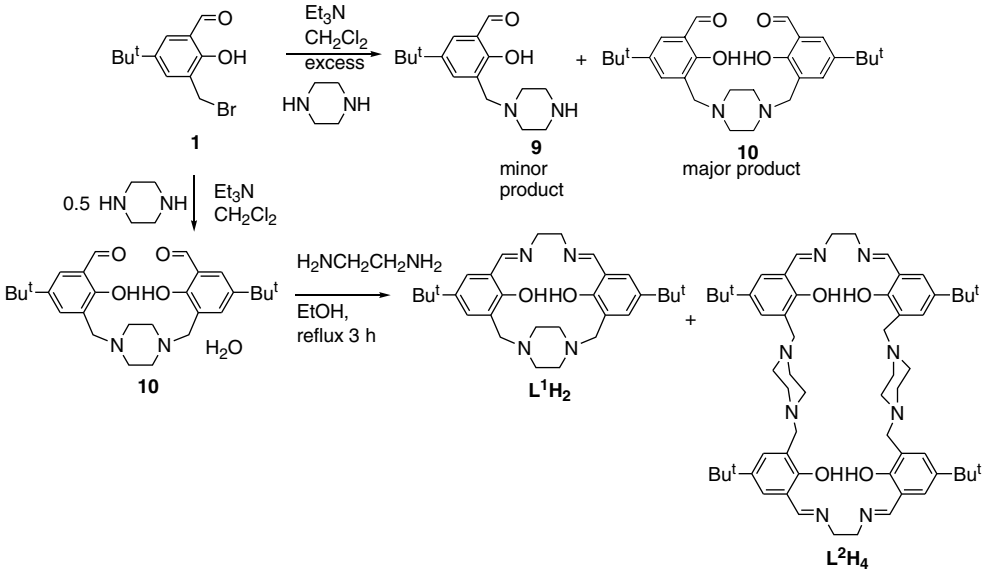
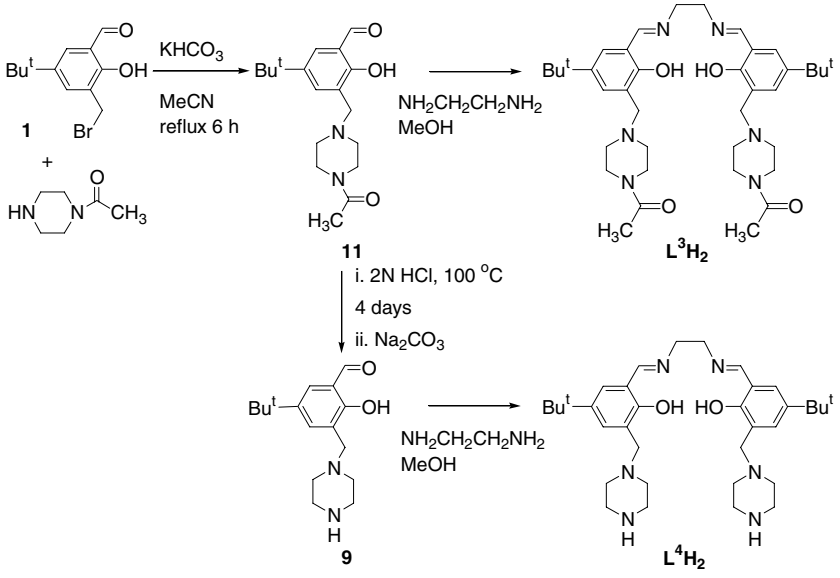


Figure 1. Views of the single crystal X-ray structures for **2**, **4** and **6**. Displacement ellipsoids are drawn at the 50% probability level.



Scheme 3. Synthesis of heteroditopic macrocyclic ligands L^1H_2 and L^2H_4.



Scheme 4. Synthesis of heteroditopic ligands L^3H_2 and L^4H_2.

the isolation of monosubstituted compounds is difficult and very low yielding.[21] However, a better yield can be achieved by the reaction of an alkyl halide with 1-carbethoxypiperazine followed by hydrolysis of the resulting product.[22] Therefore, the synthetic sequence shown in Scheme 4 was performed. 3-Bromomethyl-5-*t*-butyl-

salicylaldehyde **1** was reacted with 1-acetylpiperazine in MeCN in the presence of $KHCO_3$ to yield the aldehyde **11**. Compound **11** underwent a Schiff-base condensation with ethane-1,2-diamine to yield $\mathbf{L^3H_2}$.[23] Alternatively, compound **11** could be deprotected by hydrolysis of the acetyl group to yield the monoaldehyde **9** which then similarly reacted with ethane-1,2-diamine to give ligand $\mathbf{L^4H_2}$.[24]

In conclusion, we have described herein the direct and convenient one-pot synthesis of bromo- and chloromethylated salicylaldehydes. The rate of reaction is strongly influenced by both the electronic and steric configurations of the R-group at the C5 position; furthermore, the bromomethylation is faster than the chloromethylation reaction. This convenient synthesis of bromomethylated salicylaldehydes provides a versatile methodology for attaching a functional arm to salicylaldehydes. We have also prepared a range of heteroditopic ligands for use in the extraction of metal salts via the reactions of the 3-bromomethyl-5-*t*-butylsalicylaldehyde with secondary amines followed by Schiff-base condensation reactions. Their coordination chemistry is currently being studied with a variety of metal salts.

Acknowledgements

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14. *Typical procedure for the synthesis of* **1** *(3-bromomethyl-5-t-butylsalicylaldehyde)*: To a mixture of 5-*t*-butylsalicylaldehyde (2.00 g, 10.90 mmol) and paraformaldehyde (0.49 g, 16.4 mmol) was added 48% HBr (13.68 g, 81.07 mmol) and several drops of concentrated H_2SO_4. The mixture was stirred at 70 °C for 20 h before it was allowed to cool to room temperature. Water (20 cm^3) was added to the mixture and the product was extracted into CH_2Cl_2 (20 cm^3), and the organic phase was dried over anhydrous Na_2SO_4. The $CH_2Cl_2$was then removed under reduced pressure to afford the product as a thick yellow oil, which solidified upon standing.
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17. All compounds were fully characterized by spectroscopic and elemental analysis; **2**, **4** and **6** were also characterized by crystal structure determinations on single crystals grown from CH_2Cl_2/*n*-hexane.
Compound **1**: A pale yellow solid. Mp 42–43.5 °C. IR (KBr) *v* 1654 (vs, C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{15}BrO_2$: C, 53.15; H, 5.58. Found: C, 53.02; H, 5.54. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.35 (1H, s, C*H*O), 9.92 (1H, s, O*H*), 7.66 (1H, d, $J = 2.5$ Hz, Ph–*H*), 7.53 (1H, d, $J = 2.5$ Hz, Ph–*H*), 4.61 (2H, s, CH_2Br), 1.36 (9H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 196.4, 157.4, 142.5, 135.5, 130.3, 125.5, 120.5, 34.2, 31.3, 27.2 ppm. ES^+-MS (*m*/*z*) 191 $[M-Br]^+$.
Compound **2**: A white solid. Mp 115.9–117.2 °C. IR (KBr) *v* 1662 (vs, C=O) cm^{-1}. Anal. Calcd for $C_9H_9BrO_2$: C, 47.16; H, 3.93. Found: C, 47.24; H, 3.95. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.31 (1H, s, C*H*O), 9.87 (1H, s, OH), 7.45 (1H, s, Ph–*H*), 7.35 (1H, s, Ph–*H*), 4.57 (2H, s, CH_2Br), 2.36 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 195.4, 156.4, 137.8, 133.2, 128.3, 125.0, 119.5, 25.7, 19.2 ppm. ES^+-MS (*m*/*z*) 230 $[M]^+$.
Compound **3**: A viscous yellow oil. IR (neat) *v* 1656 (vs, C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.82; H, 7.33. Found: C, 60.12; H, 7.51. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.35 (1H, s, C*H*O), 9.91 (1H, s, O*H*), 7.35–7.70 (2H, m, Ph–*H*), 4.61 (2H, s, CH_2Br), 0.61–1.80 (19H, m, nonyl-*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 196.9, 157.3, 142.7, 142.5, 139.9, 139.8, 13.0, 136.9, 136.6 (m), 132.4 (m), 125.7, 120.2, 51.6–8.7 (m) ppm. ES^+-MS (*m*/*z*) 261 $[M-Br]^+$.
Compound **4**: A white solid. Mp 134.9–136.4 °C. IR (KBr) *v* 1667 (vs) cm^{-1}. Anal. Calcd for $C_8H_6Br_2O_2$: C, 32.65; H, 2.04. Found C, 32.98; H, 1.92. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.44 (1H, s, C*H*O), 9.87 (1H, s, O*H*), 7.73 (1H, d, $J = 2.4$ Hz, Ph–*H*), 7.68 (1H, d, $J = 2.4$ Hz, Ph–*H*), 4.53 (2H, s, CH_2Br) ppm. ^{13}C NMR($CDCl_3$, 75.42 MHz): δ 195.4, 158.5, 140.4, 136.1, 128.9, 121.8, 111.3, 25.4 ppm. ES-MS (*m*/*z*) 215 $[M-Br+H]^+$, 294 $[M]^+$.

Compound **5**: A yellow oil. IR (neat) ν 1657 (vs, C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{15}ClO_2$: C, 63.58; H, 6.62. Found C, 63.75; H, 6.74. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.30 (1H, s, C*H*O), 9.92 (1H, s, O*H*), 7.68 (1H, d, $J = 2.5$ Hz, Ph–*H*), 7.54 (1H, d, $J = 2.5$ Hz, Ph–*H*), 4.72 (2H, s, CH_2Cl), 1.36 (9H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 196.8, 157.4, 142.9, 135.4, 130.6, 125.5, 120.2, 40.3, 34.3, 31.3 ppm. ES^+-MS (*m*/*z*) 191 $[M-Cl]^+$.
Compound **6**: White solid. Mp 96.9–97.6 °C. IR (KBr) ν 1663 (vs, C=O) cm^{-1}. Anal. Calcd for $C_9H_9ClO_2$: C, 58.54; H, 4.88. Found C, 58.31; H, 4.80. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 11.26 (1H, s, C*H*O), 9.88 (1H, s, O*H*), 7.48 (1H, d, $J = 1.98$ Hz, Ph–*H*), 7.36 (1H, d, $J = 1.98$ Hz, Ph–*H*), 4.68 (2H, s, CH_2Cl), 2.37 (3H, s, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 196.5, 157.4, 138.7, 134.1, 129.3, 125.8, 120.5, 39.9, 20.3 ppm. ES^+-MS (*m*/*z*) 186 $[M]^+$.

18. CCDC 239620 (**2**), 239621 (**4**) and 239622 (**6**) contain the supplementary data for this paper and they can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.
19. The synthesis of **10**: To a solution of Et_3N (1.11 g, 11.0 mmol) in CH_2Cl_2 (20 cm^3) were added over 6 h solutions of **1** (1.50 g, 5.54 mmol) and piperazine (0.24 g, 2.77 mmol) each dissolved in dry CH_2Cl_2 (15 cm^3). The yellow solution was stirred for a further 24 h at room temperature. The solution was washed with water (3×70 cm^3) and the organic phase dried over anhydrous Na_2SO_4. Removal of the solvent afforded a yellow solid, which was recrystallised by adding EtOH to a concentrated solution of the compound in $CHCl_3$ to afford a pale yellow powder. Yield = 46%. Mp 169–171 °C. Anal. Calcd for $C_{28}H_{38}N_2O_4{\cdot}H_2O$: C, 69.39; H, 8.32; N, 5.78. Found, C, 69.69; H, 8.16; N, 5.62. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.23 (s, 18H, CH_3), 2.56 (br, 8H, CH_2), 3.67 (s, 4H, Ph–CH_2N), 7.30 (d, $J = 2.43$ Hz, 2H, Ph–*H*), 7.53 (d, $J = 2.45$ Hz, 2H, Ph–*H*), 10.18 (s, 2H, C*H*O). ES^+-MS (*m*/*z*) 467 $[M+1]^+$.
20. Synthesis of $\mathbf{L^1H_2}$ and $\mathbf{L^2H_4}$: Dialdehyde **10** (0.3 g, 0.64 mmol) was suspended in dry EtOH (20 cm^3) and to it was added a solution of ethane-1,2-diamine (0.038 g, 0.64 mmol). The mixture was refluxed for 3 h, and after cooling to room temperature the solvent was removed under reduced pressure to give a yellow solid. Yield = 95%. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.29 (s, 9H, CH_3), 2.60 (s, 4H, CH_2), 3.64 (s, 2H, Ph–CH_2N), 3.91 (s, 2H, CH_2C=N), 7.17 (s, 1H, Ph–*H*), 7.37 (s, 1H, Ph–*H*), 8.39 (s, 1H, C*H*=N). ES^+-MS (*m*/*z*) 491 $[\mathbf{L^1H_2}+1]^+$ and 981 $[\mathbf{L^2H_4}+1]^+$.
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23. The synthesis of aldehyde **11**: 1-Acetylpiperazine (0.47 g, 3.69 mmol) was dissolved in dry MeCN (40 cm^3) and to it was added 3-bromomethyl-5-*t*-butyl-salicylaldehyde **1** (1.00 g, 3.69 mmol) and $KHCO_3$ (0.56 g, 5.60 mmol). The mixture was heated to reflux under N_2 for 6 h and then allowed to cool to room temperature. The resulting yellow solution was filtered and after removal of the solvent under reduced pressure a yellow solid was obtained. The solid was re-dissolved in CH_2Cl_2, and the yellow solution filtered. Removal of the CH_2Cl_2 from the filtrate afforded a bright yellow solid which was purified by chromatography upon silica gel with CH_2Cl_2–MeOH (95:5) as eluent and the first band was collected. Removal of the solvent afforded **11** as an off-white solid. Yield 1.0 g (85%). Mp 90–92 °C. Anal. Calcd for $C_{18}H_{26}N_2O_3$: C, 67.90; H, 8.23; N, 8.80. Found: C, 67.45; H, 8.22; N, 8.65. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.32 (s, 9H, CH_3), 2.11 (s, 3H, CH_3CO), 2.56 (m, 4H, CH_2CH$_2$), 3.51 (s, 2H, Ph–CH_2N), 3.69 (br, 4H, CH_2CH$_2$), 7.48 (s, 1H, Ph–*H*), 7.59 (d, 1H, $J = 2.52$ Hz, Ph–*H*), 10.17 (s, 1H, C*H*O); ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 193.9 (*C*HO), 169.0 (*C*O), 158.7, 142.2, 134.3, 126.9, 123.7, 121.4, 58.2, 52.9, 52.5, 46.2, 41.3, 34.2, 31.4, 21.4 ppm. ES^+-MS (*m*/*z*) 319 $[M+1]^+$.
Synthesis of $\mathbf{L^3H_2}$: To a solution of compound **11** (0.46 g, 1.44 mmol) with $MgSO_4$ (0.27 g, 2.25 mmol) and molecular sieve 4 Å (1 g) in dry MeOH (20 cm^3) was added a solution of ethane-1,2-diamine (0.043 g, 0.72 mmol) in dry MeOH (3 cm^3). The resulting mixture was stirred at room temperature under N_2 overnight. After filtration, the mixture was crystallized from $CHCl_3$–Et_2O to afford a yellow powder. Yield = 84%. Mp 100–103 °C. IR (KBr)ν 1636 (νC=N) cm^{-1}. Anal. Calcd for $C_{38}H_{56}N_6O_4$, C, 69.06; H, 8.54; N, 12.72. Found: C, 69.14; H, 8.47; N, 12.69. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 8.41 (s, 2H, HC=N), 7.47 (s, aromatic, 2H), 7.19 (s, aromatic, 2H), 3.94 (s, 4H, CH_2N=), 3.64 (s, 8H, CH_2), 3.47 (s, 4H, CH_2), 2.51 (s, 8H CH_2), 2.09 (s, 6H, CH_3), 1.31 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$,75.42 MHz): δ 169.0 (*C*=N), 166.8 (*C*=N), 157.4, 157.0, 140.9, 131.3, 127.2, 124.1, 117.9, 59.9, 56.2, 53.2, 52.8, 46.4, 41.5, 34.0, 31.5, 21.5 ppm. MS (LR-ES), (*m*/*z*) 661 $[M+H]^+$.
24. 5-*t*-Butyl-2-hydroxy-3-(piperazinomethyl)benzaldehyde **9**. A solution of compound **11** (549 mg, 1.72 mmol) in 2 M HCl (15 cm^3) was heated under reflux for 4 days. After cooling to room temperature, the mixture was brought to pH ~ 7 with saturated Na_2CO_3 solution. The aqueous layer was then extracted with $CHCl_3$ and the organic layer dried over anhydrous Na_2SO_4 and concentrated to yield compound **9** as a yellow solid. Yield = 83%. Mp 220–225 °C (dec.). IR (KBr)ν 3433 (br, NH), 1679 (s, C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{24}N_2O_2{\cdot}0.15CH_2Cl_2$: C, 67.09; H, 8.47; N, 9.69. Found, C, 67.11; H, 8.43; N, 9.30. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.31 (s, 9H, CH_3), 2.61 (br, 4H, CH_2NH), 2.99 (t, 4H, $J = 4.80$ Hz, CH$_2$CH_2N), 3.74 (s, 2H, Ph–CH_2N), 7.33 (d, $J = 2.53$ Hz, 1H, Ph–*H*), 7.61 (d, $J = 2.51$ Hz, 1H, Ph–*H*), 10.25 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 192.0, 159.3, 141.9, 133.1, 125.0, 122.8, 122.1, 60.6, 53.7, 45.9, 34.2, 31.4 ppm. ES^+-MS (*m*/*z*) 277 $[M+1]^+$.
Synthesis of $\mathbf{L^4H_2}$: To a solution of **9** (0.17 g, 0.62 mmol) in dry MeOH (10 cm^3) was added a solution of ethane-1,2-diamine (0.019 g, 0.31 mmol) in dry MeOH (3 cm^3). The solution was stirred for 3 days and removal of the MeOH under reduced pressure afforded a yellow solid. Yield = 95%. Mp 134–137 °C. IR (KBr)ν: 1632 (vs, C=N) cm^{-1}. Anal. Calcd for $C_{34}H_{52}N_6O_2{\cdot}2CH_3OH{\cdot}0.5H_2O$: C, 66.53; H, 9.46; N, 12.93. Found, C, 66.57; H, 8.99; N, 12.92. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.32 (s, 18H, CH_3), 2.57 (br, 8H, CH_2NH), 2.99 (t, 8H, $J = 4.75$ Hz, CH$_2$CH_2N), 3.63 (s, 4H, Ph–CH_2N), 3.93 (s, 4H, CH_2N=C), 7.18 (d, $J = 2.45$ Hz, 2H, Ph–*H*), 7.38 (d, $J = 2.45$ Hz, 2H, Ph–*H*), 8.41 (s, 2H, C*H*=N); ^{13}C NMR ($CDCl_3$, 75.42 MHz): δ 167.3 (H*C*=N), 157.7, 141.1, 132.0, 127.5, 124.4, 118.0, 61.0, 59.0, 57.2, 53.8, 45.9, 34.4, 31.8, 19.0. ES^+-MS (*m*/*z*) 577 $[M+1]^+$.