Pergamon

Tetrahedron Letters 42 (2001) 1221–1225

TETRAHEDRON LETTERS

Unsymmetrical salen-type ligands: high yield synthesis of salen-type Schiff bases containing two different benzaldehyde moieties

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Received 14 November 2000; revised 30 November 2000; accepted 5 December 2000

Abstract—Salen-type Schiff base ligands incorporating two different benzylidene moieties and a diamine backbone were synthesized in high yield (80–90%) under mild conditions via a stepwise approach. In the first step, anhydrous hydrochloric acid was used to selectively protect one amino group of the vicinal diamine backbone. The resulting ammonium salt was added to a substituted benzaldehyde providing access to a mono-imine product. This compound reacted with an equivalent of a different benzaldehyde in the presence of triethylamine to afford an unsymmetrical salen-type ligand. This synthetic method allows facile access to a plethora of salen-type Schiff base ligands with easily tunable steric and electronic properties. © 2001 Elsevier Science Ltd. All rights reserved.

Salen-type ligands, one of the oldest classes of ligands in coordination chemistry, have been used extensively to complex transition and main group metals.[1] Since the spectacular success of the Jacobsen–Katsuki asymmetric epoxidation of unfunctionalized olefins using chiral salen-type manganese(III) Schiff base catalysts in the early 1990s,[2,3] there has been a resurgence of interest in chiral salen-type ligands as a scaffold for asymmetric catalysis.[4–6]

It is well-known in homogeneous asymmetric catalysis that stereochemical communication between the ligand environment of the catalyst and the substrate is essential for obtaining high enantioselectivities.[7] Although sterics plays a major role in the asymmetric induction mechanism, electronic effects have also been shown to be quite important.[8–11] Of the many effective chiral ligands, only a few are synthetically or structurally well-suited to electronic tuning. Therefore the ability to easily synthesize a series of structurally similar ligands with subtle variations in steric and electronic configuration is essential to optimize and fully understand a catalyst system. As a class, salen-type ligands consist of a flexible and kinetically nonlabile ligand template wherein both steric and electronic properties of the metal center may be tuned in a synthetically straightforward manner.[8] Despite the wide range of synthetic and mechanistic possibilities with salen-type ligands, electronic tuning has been almost exclusively limited to symmetrical cases.[8,12] Until recently, there has not been any practical high-yield synthesis of unsymmetrical salen ligands, in which both sterics and electronics can be manipulated in the same ligand environment. Of the three reported solution syntheses of unsymmetrical salen-type ligands, two gave the desired product in low yield only after painstaking chromatography.[13,14] Although the third study claims to have produced unsymmetrical salen-type ligands in high yield,[15] workers from another laboratory,[13] in addition to us, were unable to reproduce this result. As unsymmetrical salen-type ligands become more prevalent in asymmetric catalysis, an inexpensive, large-scale production of these materials would be highly desirable. Herein we report the first general method for synthesizing unsymmetrical salen-type ligands in high yield from a cyclohexyldiamine backbone and several benzaldehydes.

We recognized early on in the synthesis of the unsymmetrical salen-type ligands that a stepwise, straight condensation methodology, similar to that employed for the synthesis of the symmetrical ligand, was not feasible due to the preferential formation of the bis-imine products compared to the desired mono-imine intermediate.[13] Daly et al. reported that even a 1:2 mixture of aldehyde to diamine, under a variety of

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PII: S0040-4039(00)02226-7

reaction conditions, yielded a mixture that contained only small amounts of mono condensation product.[13] We also had similar results.

To circumvent this bias, we decided to protect one amino group of the diamine backbone prior to condensation with the first benzaldehyde. We theorized that condensation of this partially protected diamine with one equivalent of the first benzaldehyde should yield the imine/protected amine species. Simultaneous deprotection of this complex in the presence of one equivalent of a second benzaldehyde would then afford unsymmetrical salen-type ligands in high yield.

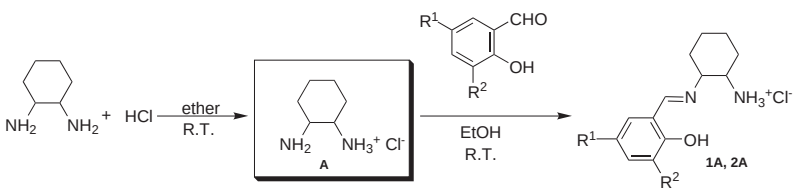
Taking advantage of the well-known insolubility of ammonium salts in ether, we isolated the mono-ammonium salts of diamines by treating them with anhydrous hydrochloric acid in ether.[16] The precipitated mono-ammonium salts were isolated and added to one equivalent of benzaldehyde, producing the mono-imine products in high yield (Eq. (1) and Table 1).[17] Che and co-workers have synthesized the mono-imine derivative of 1,1′-binaphthyl-2,2′-diamine (BINAM) in 63% yield using a stoichiometric mixture of BINAM and salicylaldehyde in ether.[18] Interestingly, the anisaldehyde **3** (Table 2) does not condense with the ammonium salt under our reaction conditions.

The mono-imino ammonium salts can then be added to an equivalent of a second benzaldehyde in the presence of triethylamine to produce the desired unsymmetrical salen-type ligands in high yield after 36–48 hours at room temperature (Eq. (2) and Table 2).[20]

Our synthetic scheme for unsymmetrical salen-type ligands has several advantages over existing methods for synthesizing this class of ligands. The reaction methodology is amenable to large-scale synthesis and conserves expensive chiral diamine starting materials by using these reagents only in a stoichiometric ratio with the aldehydes. Furthermore, the reaction yields mostly a single product, thus eliminating the need for time-consuming chromatography and tedious recrystallization of product mixtures (containing statistical distributions of symmetrical and unsymmetrical salen-type ligands). We have demonstrated the generality of this methodology by showing the variety of potentially useful unsymmetrical salen-type complexes that we could synthesize. This synthetic flexibility allows the facile tuning of both steric and electronic properties of salen-type ligands and greatly enriches the potential of this class of ligand. In particular, our facile synthesis of mono-phenoxy mono-phenoxyether salen type ligands such as **1A3** where two different oxygen binding sites can exist in the same ligand can allow for new coordination environments, and hence new reactivity patterns, for many metal centers.

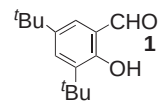
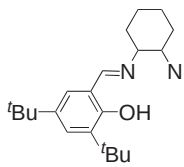
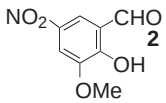
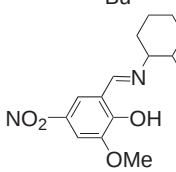
Acknowledgements

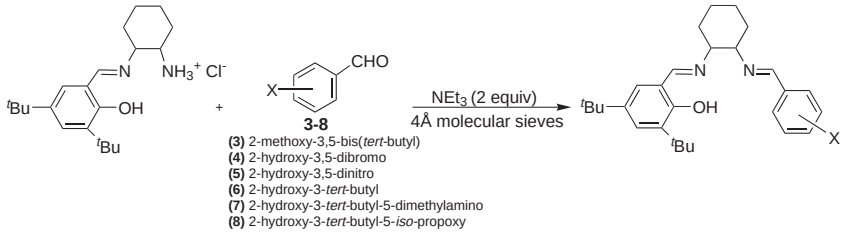
Support from the Dupont company and the Beckman, Dreyfus, and Packard Foundations are gratefully acknowledged. E.J.C. acknowledges the GEM and IMGIP fellowship programs for financial support. We thank the NIH for their support in the purchase of the Micromass Quatro II triple quadrupole electrospray mass spectrometer (grant S10 RR11320). We thank Mark Staples and Dr. Hongying Zhou for their helpful discussion and Brian Kane for his technical help.



(1)

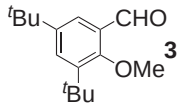
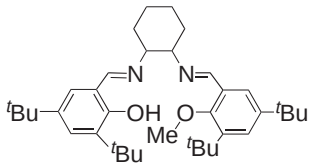
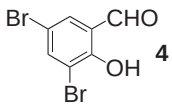
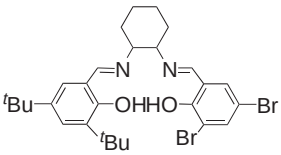
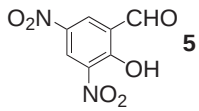
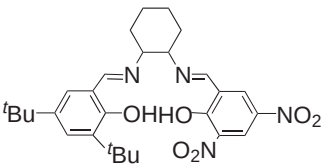
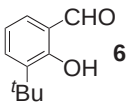
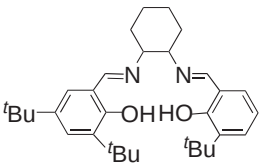
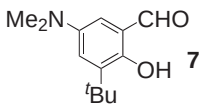
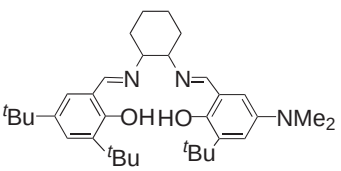
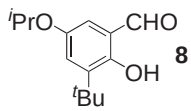
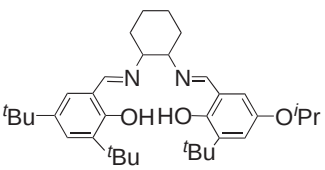
Table 1. Mono-imine ammonium salts

aldehyde	time (h)	*mono*-imine (yield)[17]	analytical data
 **1**	24	 **1A** (85%)	^{1}H NMR (300 MHz, DMSO-d_6): δ 8.68 (b, 1H, O*H*), 8.58 (s, 1H, N=C*H*), 8.14 (b, 3H, N$^+$*H*$_3$), 7.32 (s, 1H, C$_o$*H*), 7.24 (s, 1H, C$_p$*H*), 3.35 (b, 1H, -CH$_2$C*H*-N$^+$H$_3$), 3.21 (m, 1H, -CH$_2$C*H*-N=C), 2.20-1.50 (8H, cyclohexyl), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.26 (s, 9H, C(C*H*$_3$)$_3$). ESI-MS: m/z (%) 331 (M, 100).
 **2**	24	 **2A** (80%)	^{1}H NMR (300 MHz, DMSO-d_6): δ 13.52 (b, 1H, O*H*), 8.78 (s, 1H, N=C*H*), 8.57 (b, 3H, N$^+$*H*$_3$), 7.99 (s, 1H, C$_o$*H*), 7.32 (b, 1H, C$_p$*H*), 3.81 (s, 3H, OC*H*$_3$), 3.62 (b, 1H, -CH$_2$C*H*-N$^+$H$_3$), 3.08 (b, 1H, -CH$_2$C*H*-N=C), 2.20-1.20 (8H, cyclohexyl). Anal. Calcd. for C$_{14}$H$_{21}$ClN$_3$O$_4$·2H$_2$O: C, 45.84; H, 6.87; N, 11.46. Found: C, 45.83; H, 6.76; N, 11.40. ESI-MS m/z (%) 294 (M, 100), 249 (70)



(2)

Table 2. Unsymmetric salen-type compounds and their synthetic conditions

Aldehyde	Rxn time (h)	Solvent	Yield (%)[a,20]	Product
 **3**	48	EtOH	60[b]	**1A3** 
 **4**	36	EtOH	87	**1A4** 
 **5**	48 48	EtOH CH_2Cl_2	No product 80[19]	**1A5** 
 **6**	48	EtOH	70[b]	**1A6** 
 **7**	36	EtOH	80[b]	**1A7** 
 **8**	36	EtOH	86[b]	**1A8** 

[a] Isolated yield from the mono-imine intermediate.
[b] Recrystallized from cold acetonitrile.

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16. Compound **A**. *trans*-1,2-Cyclohexyldiamine (2.13 g, 14.2 mmol) was dissolved in ether (50 mL). The solution was stirred vigorously while anhydrous HCl (1.42 g, 14.2 mmol, 36% in ether) was added dropwise over 15 min. An exothermic reaction was observed upon the addition of the acid, and a precipitate was formed. After complete addition of the acid, the mixture was allowed to stir at room temperature for 10 h. The precipitate was collected by vacuum filtration, washed with excess ether and dried in vacuo. Yield = 85%. ^{1}H NMR (500 MHz, D_2O): δ 2.83 (m, 2H, -CH_2CH-(NH_2)), 1.89 (d, 2H, -CH_2CH-N^+H_3), 1.59 (d, 2H, -CH_2CH-(NH_2)), 1.20 (m, 4H, -CH_2CH_2CH-(NH_2)). ^{13}C NMR (500 MHz, D_2O): δ 53.74 (-CH_2CH-(NH_2)), 30.95 (-CH_2CH-(NH_2)), 23.58 (-CH_2CH_2CH-(NH_2)). ESI-MS: m/z (%) 115 (100), 98 (40).
17. Compound **1A**. Compound **A** (0.90 g, 6.0 mmol) was slurried in a mixture of methanol and ethanol (50/50 v/v, 40 mL). 3,5-Di-*tert*-butylsalicylaldehyde (1.40 g, 6.0 mmol) was added to the reaction, and the mixture was stirred at room temperature. After 24 h the solvent was removed under reduced pressure. The resulting product was washed with water (20 mL) and ether (30 mL) and dried in vacuo to give a white solid. Compound **2A**. Compound **A** (0.90 g, 6.0 mmol) was slurried in a mixture of methanol and ethanol (50/50 v/v, 60 mL). 3-Methoxy-5-nitrosalicylaldehyde (1.18 g, 6.0 mmol) was added to the reaction, and the mixture was stirred at room temperature slowly producing a precipitate. After 24 h the precipitate was collected by vacuum filtration, washed with water (20 mL) and ether (30 mL), and dried in vacuo to give a solid.
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19. Compound **1A** (198 mg, 0.42 mmol) was dissolved in dichloromethane (10 mL) and stirred over 4Å molecular sieves. A solution of the 3,5-dinitrosalicylaldehyde (89 mg, 0.42 mmol) and triethylamine (117 mL, 0.84 mmol) in dry dichloromethane (15 mL) was added, and the reaction was stirred at room temperature. After 36 h the reaction was gravity filtered, and the solvent was removed under reduced pressure. The resulting solid was washed successively with ether (25 mL), 1N HCl (30 mL), H_2O (20 mL), and ether (25 mL). The solid was dried in vacuo.
20. General procedure: Compound **1A** (0.42 mmol) was dissolved in absolute ethanol and stirred over 4Å molecular sieves. A solution of the benzaldehyde (0.42 mmol) and triethylamine (117 mL, 0.84 mmol) in absolute ethanol was added, and the reaction was stirred at room temperature. After 36–48 h the reaction was gravity filtered, and the solvent was removed from the filtrate under reduced pressure. The resulting solid was taken up in dry ether (20 mL) and gravity filtered. The ether was removed under reduced pressure to give a solid. Analytical data for compounds **1A3**–**1A8** are as follows: Compound **1A3**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.46 (s, 1H, Ar**1**-C*H*=N), 8.31 (d, 1H, Ar**3**C$_o$*H*), 7.61 (s, 1H, Ar**3**C*H*=N), 7.33 (s, 1H, Ar**3**C$_p$*H*), 7.28 (d, 1H, Ar**1**C$_o$*H*), 6.98 (d, 1H, Ar**1**C$_p$*H*), 3.46 (s, 3H, O*CH*$_3$), 3.35 (m, 2H, -CHC*H*-N=C-Ar), 2.00–1.20 (8H, cyclohexyl), 1.38 (s, 9H, C(*CH*$_3$)$_3$), 1.32 (s, 9H, C(*CH*$_3$)$_3$), 1.26 (s, 9H C(*CH*$_3$)$_3$), 1.21 (s, 9H, C(*CH*$_3$)$_3$). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 165.89 (Ar**3**-*C*=N), 158.91 (Ar**1**-*C*=N), 145.80 (Ar**3***C*$_2$-OMe), 141.97 (Ar**1***C*$_2$-OH), 140.13 (Ar**3***C*$_5$), 136.40 (Ar**1***C*$_5$), 129.14 (Ar**1***C*$_3$), 126.99 (Ar**3***C*$_3$), 126.82 (Ar**3***C*$_1$), 126.68 (Ar**1***C*$_6$), 126.24 (Ar**3***C*$_5$), 126.06 (Ar**3***C*$_6$), 123.03 (Ar**1***C*$_4$), 118.10 (Ar**1***C*$_1$), 75.32 (-CH_2*C*H-N=C-Ar**1**), 72.88 (-CH_2*C*H-N=C-Ar**3**), 64.13 (O*C*H$_3$), 35.20 (*C*(CH$_3$)$_3$), 34.03 (*C*(CH$_3$)$_3$), 33.44 (-*C*H$_2$CH-N=C-Ar), 33.12 (-*C*H$_2$CH-N=C-Ar), 31.41 (C(*CH*$_3$)$_3$), 31.39 (C(*CH*$_3$)$_3$), 31.81 (C(*CH*$_3$)$_3$), 29.40 (C(*CH*$_3$)$_3$), 24.74 (-*C*H$_2$CH$_2$CH-N=C-Ar), 24.61 (-*C*H$_2$CH$_2$CH-N=C-Ar). HREIMS: calcd for $C_{37}H_{56}N_2O_2$: 560.4341. Found: 560.4343. Compound **1A4**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.18 (s, 1H, Ar**1**-C*H*=N), 8.09 (s, 1H, Ar**4**-C*H*=N), 7.53 (d, 1H, Ar**4**C$_o$*H*), 7.25 (d, 1H, Ar**1**C$_o$*H*), 7.15 (d, 1H, Ar**4**C$_p$*H*), 6.92 (d, 1H, Ar**1**C$_p$*H*), 4.77 (b, 2H, O*H*), 3.38 (m, 1H, -CH_2C*H*-N=C-Ar**4**), 3.27 (m, 1H, -CH_2C*H*-N=C-Ar**1**), 2.00–1.20 (8H, cyclohexyl), 1.32 (s, 9H, C(*CH*$_3$)$_3$), 1.16 (s, 9H, C(*CH*$_3$)$_3$). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 166.53 (Ar**4**-*C*=N), 166.43 (Ar**1**-*C*=N), 158.81 (Ar**4***C*$_2$-OH), 157.98 (Ar**1***C*$_2$-OH), 140.49 (Ar**1***C*$_5$), 137.61 (Ar**4***C*$_4$), 136.52 (Ar**1***C*$_3$), 133.13 (Ar**4***C*$_6$), 127.28 (Ar**1***C*$_6$), 126.40 (Ar**4***C*$_1$), 120.00 (Ar**1***C*$_4$), 117.97 (Ar**1***C*$_1$), 112.11 (Ar**4***C*$_3$), 109.09 (Ar**4***C*$_5$), 72.38 (-CH_2CH-N=*C*-Ar**4**), 72.16 (-CH_2*C*H-N=C-Ar**1**), 35.36 (-*C*H$_2$CH-N=C-Ar), 32.77 (-*C*H$_2$CH-N=C-Ar), 31.38 (C(*C*H$_3$)$_3$), 29.36 (C(*C*H$_3$)$_3$), 24.41 (-*C*H$_2$CH$_2$CH-N=C-Ar), 24.38 (-*C*H$_2$CH$_2$CH-N=C-Ar). HREIMS: calcd for $C_{28}H_{36}N_2O_2Br_2$: 592.1126. Found: 592.1134. Anal. calcd for $C_{28}H_{36}Br_2N_3O_2 \cdot H_2O$: C, 55.09; H, 6.27; N, 4.59. Found: C, 55.39; H, 5.93; N, 4.13. Compound **1A5**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (s, 1H, Ar**5**C$_o$*H*), 8.31 (s, 1H, Ar**1**-C*H*=N), 8.21 (s, 1H, Ar**5**C*H*=N), 7.37 (s, 1H, Ar**5**C$_p$*H*), 7.26 (s, 1H, Ar**1**C$_o$*H*), 6.98 (s, 1H, Ar**1**C$_p$*H*), 3.74 (m, 2H, -CHC*H*-N=C-Ar**5**), 3.23 (m, 2H, -CHC*H*-N=C-Ar**1**), 2.40–1.20 (8H, cyclohexyl), 1.41 (s, 9H, C(*CH*$_3$)$_3$), 1.22 (s, 9H, C(*CH*$_3$)$_3$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 170.75 (Ar**5**-*C*=N), 168.26 (Ar**1**-*C*=N), 165.82 (Ar**5***C*$_2$-OH), 157.71 (Ar**1***C*$_2$-OH), 141.25 (Ar**5***C*$_5$), 140.37 (Ar**1***C*$_5$), 137.21 (Ar**1***C*$_3$), 135.99 (Ar**5***C*$_4$), 132.41 (Ar**5***C*$_6$), 131.42 (Ar**5***C*$_3$), 128.89 (Ar**1***C*$_6$), 126.55 (Ar**1***C*$_4$), 117.38

(Ar**5**C_1), 116.50 (Ar**1**C_1), 71.38 (-CH_2*C*H-N=C-Ar**5**), 67.92 (-CH*C*H-N=C-Ar**1**), 35.41 (-*C*H_2CH-N=C-Ar), 34.52 (C(*C*H_3)$_3$), 33.74 (C(*C*H_3)$_3$), 31.73 (*C*(CH_3)$_3$), 29.70 (*C*(CH_3)$_3$), 24.47 (-*C*$H_2$$CH_2$CH-N=C-Ar**5**), 24.15 (-*C*H_2-CH_2CH-N=C-Ar**1**). HREIMS: calcd for $C_{28}H_{36}N_4O_6$: 524.2635. Found: 524.2634. Anal. calcd for $C_{28}H_{36}N_4$-O_6·0.5H_2O: C, 63.02; H, 6.93; N, 10.49. Found: C, 63.04; H, 6.99; N, 10.46. Compound **1A6**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 13.90 (br, 2H, Ar-O*H*), 8.33 (s, 2H, Ar-C*H*=N), 7.33 (s, 1H, Ar**1**C_o*H*), 7.27 (s, 1H, Ar**6**C_o*H*), 7.03 (t, 2H, Ar**1**C_p*H*+Ar**6**C_p*H*), 6.74 (t, 1H, Ar**6**C_m*H*), 3.38 (b, 2H, -CHC*H*-N=C-Ar), 2.00–1.20 (8H, cyclohexyl), 1.42 (s, 18H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 166.62 (Ar**6**-*C*=N), 166.22 (Ar**1**-*C*=N), 160.88 (Ar**6**C_2-OH), 158.47 (Ar**1**C_2-OH), 140.66 (Ar**1**C_5), 137.58 (Ar**6**C_3), 136.82 (Ar**1**C_3), 130.34 (Ar**6**C_6), 129.84 (Ar**1**C_6), 127.39 (Ar**1**C_4), 126.62 (Ar**6**C_4), 119.22 (Ar**6**C_5), 118.34 (Ar**1**C_1), 118.27 (Ar**6**C_1), 73.08 (-CH_2*C*H-N=C-Ar), 72.96 (-CH_2*C*H-N=C-Ar), 35.46 (*C*(CH_3)$_3$), 35.25 (*C*(CH_3)$_3$), 34.54 (*C*(CH_3)$_3$), 33.74 (-*C*H_2CH-N=C-Ar), 31.77 (C(*C*H_3)$_3$), 29.77 (C(*C*H_3)$_3$), 29.55 (C(*C*H_3)$_3$), 24.94 (-*C*$H_2$$CH_2$CH-N=C-Ar). HREIMS: calcd for $C_{32}H_{46}N_2O_2$: 490.3558. Found: 490.3559. Anal. calcd for $C_{32}H_{46}N_2O_2$·0.5H_2O: C, 76.91; H, 9.41; N, 5.60. Found: C, 76.60; H, 9.45; N, 5.91. Compound **1A7**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, 1H, Ar**7**C_o*H*), 8.29 (s, 1H, Ar**1**-C*H*=N), 7.33 (d, 1H, Ar**1**C_o*H*), 7.00 (m, 1H, Ar**1**C_p*H*), 6.94 (b, 1H, Ar**7**C*H*=N), 6.49 (d, 1H, Ar**7**C_p*H*), 3.35 (m, 2H, -CHC*H*-N=C-Ar), 2.80 (s, 6H, N(CH_3)$_2$), 2.00–1.20 (8H, cyclohexyl), 1.44 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$). HREIMS: calcd for $C_{34}H_{51}N_3O_2$: 533.3982. Found: 533.3985. Anal. calcd for $C_{34}H_{51}N_3O_2$·0.5H_2O: C, 75.23; H, 9.58; N, 7.73. Found: C, 75.32; H, 9.36; N, 7.57. Compound **1A8**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, 1H, Ar**8**C_o*H*), 8.24 (s, 1H, Ar**1**-C*H*=N), 7.32 (s, 1H, Ar**1**C_o*H*), 7.01 (s, 1H, Ar**1**C_p*H*), 6.89 (s, 1H, Ar**8**C*H*=N), 6.52 (s, 1H, Ar**8**C_p*H*), 4.37 (m, 1H, -OC*H*(CH_3)$_2$), 3.38 (m, 2H, -CHC*H*-N=C-Ar), 2.00–1.20 (8H, cyclohexyl), 1.42 (s, 9H, C(CH_3)$_3$), 1.40 (s, 6H, -OCH(CH_3)$_2$), 1.25 (s, 9H, C(CH_3)$_3$). HREIMS: calcd for $C_{35}H_{52}N_2O_3$: 548.3977. Found: 548.3976. Anal. calcd for $C_{35}H_{52}N_2$-O_3·0.5H_2O: C, 75.35; H, 9.50; N, 5.02. Found: C, 75.84; H, 9.41; N, 4.80.