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A synthesis of unsymmetrical chiral salen ligands derived from 2-hydroxynaphthaldehyde and substituted salicylaldehydes

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Abstract—Novel unsymmetrical chiral salen Schiff base ligands have been synthesised via a stepwise approach. A special feature of these ligands is that they possess two different units: a 2-hydroxynaphthaldehyde moiety on one side and a substituted salicylaldehyde on the other.

Salen-type ligands are amongst the oldest ligands in coordination chemistry and have received considerable interest since Jacobsen and Katsuki first reported their significant success using chiral manganese(III) salen Schiff base catalysts in the asymmetric epoxidation of unfunctionalised olefins.[1,2] Over the last 15 years, salen ligands have been widely used as scaffolds in asymmetric catalysis,[3–6] including the enantioselective cyclopropanation of styrenes,[7] the asymmetric aziridination of olefins,[8] asymmetric Diels–Alder cycloaddition reactions,[9] and asymmetric epoxide ring-opening reactions.[10] Furthermore, salen ligands of this type have been used in the synthesis of chiral oligomeric diimines[11] and diimides,[12] and for the controlled formation of hybrid organic–inorganic structures with helical morphology.[13,14]

It is well known in the arena of homogeneous asymmetric catalysis that stereochemical communication between the ligand environment of the catalyst and the substrate is essential for obtaining high enantioselectivity.[15] Although steric factors play a major role in the asymmetric induction mechanism, electronic effects are also important.[16–22] The facile synthesis of a series of structurally similar ligands which incorporate subtle variations in their steric and electronic configuration is highly desirable to optimise and fully understand a catalyst system.

The majority of salen ligands reported in the literature are symmetric and available as their N,N′-disubstituted derivatives.[6] There are only a few procedures which proceed via the mono-imine which would allow alternative functionalisation to be incorporated within the ligand structure and these methods either suffer from low yields after chromatographic separation[23] or have proven difficult to replicate by workers from other laboratories, in addition to us.[24] Other groups have successfully synthesised unsymmetrical salen ligands, however, only via mono-protection of the diamine.[25,26]

Since the use of salen ligands in asymmetric catalysis is on the increase, an inexpensive, easy and large-scale production of these materials was sought within our laboratory. Herein, we report a straightforward and efficient synthesis of unsymmetrical salen Schiff base ligands that possess both a 2-hydroxynaphthaldehyde moiety and variously substituted salicylaldehyde derivatives (Scheme 1)—a combination that allows for tuning of electronic and steric factors simultaneously.

Initial investigations seeking a one-pot condensation procedure for the introduction of two different aldehyde derivatives proved unsuccessful as the reaction mixtures were contaminated with bis-imine products under a variety of conditions. Even a 1:1 mixture of salicylaldehyde to diamine gave a mixture of products from which only small amounts of the mono-condensation product could be isolated.

Keywords: Unsymmetrical salen-type ligands; Schiff base; Asymmetric catalysis.
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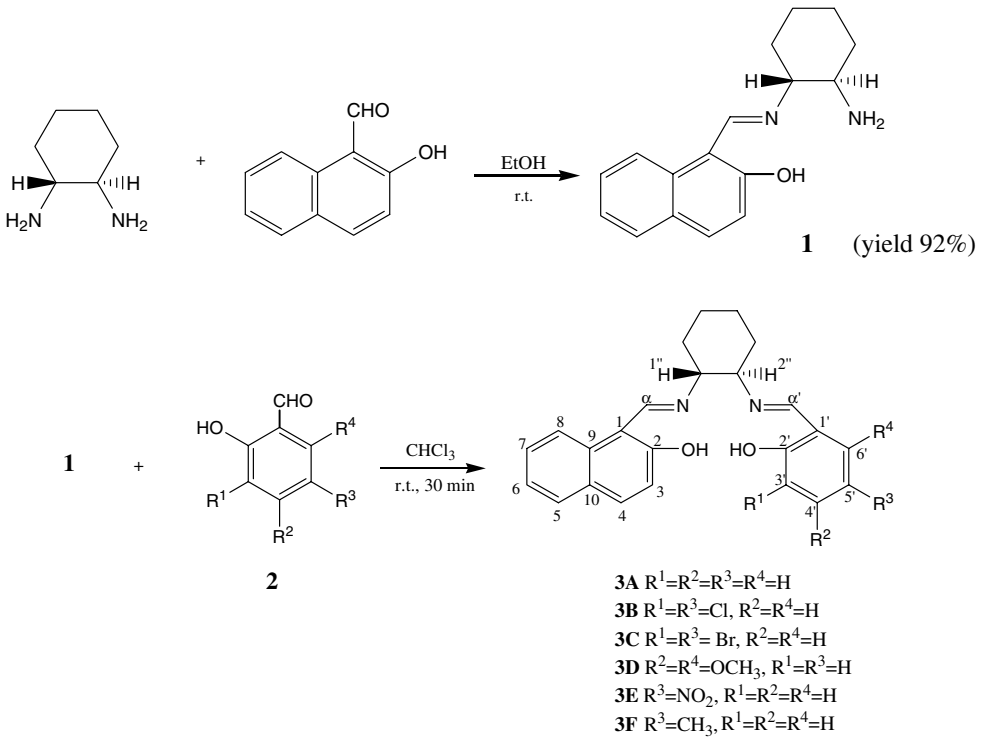


Scheme 1. Preparation of the chiral half unit **1** from (1*R*,2*R*)-(−)-1,2-diaminocyclohexane and 2-hydroxynaphthaldehyde and subsequent reaction with various substituted salicylaldehydes for the preparation of unsymmetrical chiral salen Schiff base ligands.

Instead, a two-pot approach was required and after unsuccessful examination of a wide range of salicylaldehyde derivatives for the first step, 2-hydroxynaphthaldehyde proved to be suitable for obtaining pure mono-imine. The facile procedure involved the addition of (1*R*,2*R*)-1,2-diaminocyclohexane in a dropwise manner to an ethanolic solution of 2-hydroxynaphthaldehyde at room temperature, maintaining the molar ratio of amine to aldehyde between 1:1 and 1.5:1.[27] A yellow precipitate was isolated and washed with a small amount of cold diethyl ether (excess diethyl ether led to a reduced yield of mono-imine) and determined to

Table 1. A list of the unsymmetrical salen Schiff base ligands prepared and the associated product yields

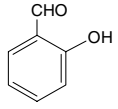
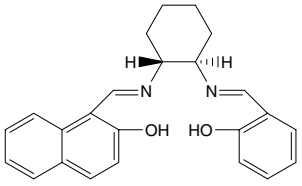
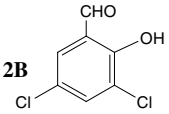
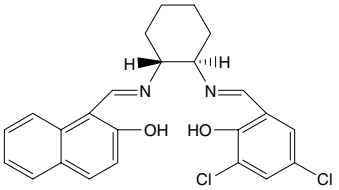
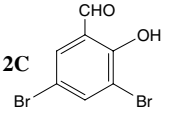
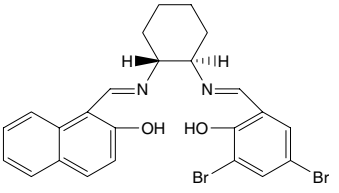
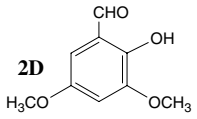
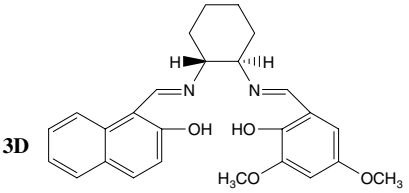
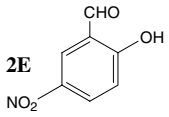
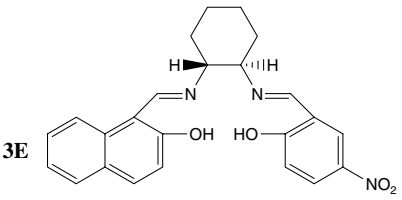
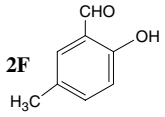
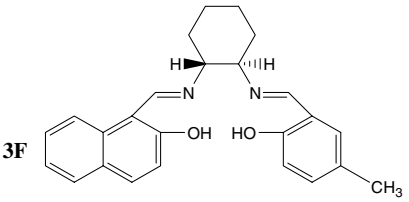
Aldehyde	Product	Yield[a] (%)
2A 	**3A** 	69
2B 	**3B** 	72
2C 	**3C** 	72

Table 1 (*continued*)

Aldehyde	Product	Yield[a] (%)
 **2D**	 **3D**	65
 **2E**	 **3E**	63
 **2F**	 **3F**	42

[a] Isolated yield from imine intermediate **1**.

be the chiral half unit **1** isolated in excellent yield.[28] The mono-imine was very stable and could be stored at room temperature for months without decomposition. Fortunately, the mono-imine was pure enough to use in the next step without further purification, however, as any attempts to crystallise the mono-imine in hot solutions or purify it by column chromatography led to a mixture of mono-imine and bis-imine derivatives. Next, the mono-imine was dissolved in chloroform at room temperature followed by addition of salicylaldehyde in a 1:1 molar ratio. After 30 min, the solvent was evaporated to give the desired unsymmetrical salen ligand in good yield.[29]

The results summarised in Table 1 demonstrate the versatility of our procedure for salicylaldehydes containing one electron-donating substituent (OCH_3, **2D** and Me, **2F**), one electron-withdrawing group (NO_2, **2E**), two more bulky electron withdrawing substituents (Cl, **2B** and Br, **2C**); however, we were unable to obtain pure unsymmetrical ligands using 3,5-di-*tert*-butylsalicylaldehyde as a substrate.

The synthesis of various Co(II), Co(III), Cr(III), Ru(II) and Mo(VI) chiral complexes derived from **3** is in progress and the application of these catalysts is currently being evaluated in several reactions.

In conclusion, this stepwise approach has resulted in a new class of novel unsymmetrical chiral salen Schiff base ligands involving the preparation of a chiral mono-imine in the first instance—the kinetic product of the reaction of 2-hydroxynaphthaldehyde with 1,2-diaminocyclohexane. The mono-imine intermediate has then been converted to various unsymmetrical ligands containing a functionalised salicylaldehyde. This synthetic scheme offers two advantages over existing methods; (i) the sequence does not require a laborious protection, de-protection strategy, and (ii) upon work-up of the crude reaction mixture, the products obtained are pure enough to avoid further time-consuming and potentially inefficient purification steps. The ability to introduce various substituted salicylaldehydes allows for the tuning of both steric and electronic properties of the salen-type ligands and greatly enriches the potential of this class of ligand.

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27. Compound **1**. 2-Hydroxynaphthaldehyde (1.25 g, 10.9 mmol) was dissolved in hot ethanol (30 mL) and the solution was cooled to room temperature. A solution of (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (1.24 g, 10.9 mol) in ethanol (15 mL) was added dropwise. The mixture was allowed to stir at room temperature for 1 h. The solvent was removed by vacuum evaporation at room temperature and the resulting yellow solid was washed with diethyl ether and dried in vacuo. Yield 92%, mp 126–128 °C; $[\alpha]_D^{20}$ −94.0 (CH_2Cl_2, *c* 0.2); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.57 (s, 1H), 8.88 (s, 1H), 7.89–6.95 (m, 6H), 3.00 (m, 1H), 2.83 (m, 1H), 2.18–1.25 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 175.2, 157.5, 136.9, 133.7, 129.2, 127.9, 126.3, 124.4, 122.7, 118.0, 106.6, 71.0, 54.7, 34.1, 32.8, 24.8, 24.6; Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.31; H, 7.42; N, 10.23.
28. On one occasion evaporation of ethanol at room temperature was required to form the precipitate which was then washed with a small quantity of cold ether.
29. Compounds **3A**–**F**. General procedure: *trans*-1-*N*-(2-hydroxynaphthylidene)-2-*N*′-aminocyclohexane **1** (0.134 g, 0.5 mmol) was dissolved in 25 mL of chloroform. The resulting solution was added dropwise to a solution of appropriate salicylaldehyde (0.5 mmol) in 10 mL of chloroform and the mixture was stirred at room temperature for 30 min. The solvent was removed by vacuum evaporation and the resulting precipitate was washed with diethyl ether and dried in vacuo.
Analytical data for compounds **3A**–**F** *are as follows*:
Compound **3A**: mp 172–174 °C; $[\alpha]_D^{20}$ −418.18 (CH_2Cl_2, *c* 0.22); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.51 (s, 1H, ArO*H*); 13.24 (s, 1H, Ar′O*H*); 8.65 (s, 1H, C*H*$^{\alpha}$); 8.27 (s, 1H, C*H*$^{\alpha'}$); 7.74 (d, $J = 9.2$ Hz, 1H, C*H*^{8}); 7.61 (d, $J = 9.2$ Hz, 1H, C*H*^{4}); 7.52 (d, $J = 8$ Hz, 1H, C*H*^{5}); 7.31 (t, $J = 4.2$ Hz, 1H, C*H*^{7}); 7.18 (t, $J = 4.2$ Hz, 1H, C*H*$^{4'}$); ~7.16 (overlapped, 2H, C*H*^{6}, C*H*^{3}); 7.08 (d, $J = 7.6$ Hz, 1H, C*H*$^{6'}$); 6.87 (d, $J = 8.2$ Hz, 1H, C*H*$^{3'}$); 6.72 (t, 1H, C*H*$^{5'}$); 3.47 (m, 1H, C*H*$^{1''}$); 3.24 (m, 1H, C*H*$^{2''}$); 2.20–1.46 (m, 8H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 174.12 (C^2), 160.83 ($C^{2'}$), 165.68 ($C^{\alpha'}$), 158.12 (C^{α}), 136.74 (C^4), 133.53 (C^9), 132.42 ($C^{4'}$), 131.55 ($C^{6'}$), 128.92 (C^5), 127.87 (C^7), 126.32 (C^{10}), 123.78 (C^3), 122.70 (C^6), 118.75 ($C^{5'}$), 118.42 ($C^{1'}$), 118.20 (C^8), 116.76 ($C^{3'}$), 106.73 (C^1), 72.99 ($C^{2''}$), 67.69 ($C^{1''}$), 33.29, 32.35, 24.39, 23.94 (cyclohexyl); Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.58; H, 6.54; N, 7.60.
Compound **3B**: mp 177–179 °C; $[\alpha]_D^{20}$ −332.59 (CH_2Cl_2, *c* 0.135); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.62 (s, 1H, ArO*H*); 14.41 (s, 1H, Ar′O*H*); 8.60 (s, 1H, C*H*$^{\alpha}$); 8.16 (s, 1H, C*H*$^{\alpha'}$); 7.75(d, $J = 7.7$ Hz, 1H, C*H*^{8}); 7.67 (d, $J = 9.2$ Hz, 1H, C*H*^{4}); 7.57 (d, $J = 7.7$ Hz, 1H, C*H*^{5}); 7.41 (t, $J = 7.5$ Hz, 1H, C*H*^{7}); 7.26 (s, 1H, C*H*$^{4'}$); 7.22 (t, $J = 7.5$ Hz, 1H, C*H*^{6}); 6.97 (s, 1H, C*H*$^{6'}$); 6.88 (d, $J = 8.8$ Hz, 1H, C*H*^{3}); 3.46 (m, 1H, C*H*$^{1''}$); 3.30 (m, 1H, C*H*$^{2''}$); 2.20–1.46 (m, 8H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.44 (C^2), 164.10 ($C^{\alpha'}$), 158.77 (C^{α}), 156.43 ($C^{2'}$), 136.66 (C^4), 133.23 (C^9), 132.27 ($C^{4'}$), 129.11 ($C^{6'}$), 129.00 (C^5), 127.97 (C^7), 126.54 (C^{10}), 123.01 (C^3, C^6), 122.73 ($C^{5'}$), 122.60 ($C^{3'}$), 118.42 ($C^{1'}$), 118.33 (C^8), 107.02 (C^1), 72.58 ($C^{2''}$), 68.45 ($C^{1''}$), 32.92, 32.39, 24.28, 23.85 (cyclohexyl); Anal. Calcd for $C_{24}H_{22}N_2O_2Cl_2$: C, 65.31; H, 5.02; N, 6.35. Found: C, 65.12; H, 4.95; N, 6.29.
Compound **3C**: mp 185–187 °C; $[\alpha]_D^{20}$ −397.00 (CH_2Cl_2, *c* 1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.58 (s, 1H, ArO*H*), 14.47 (s, 1H, Ar′O*H*), 8.70 (d, $J = 4.87$ Hz, 1H, C*H*$^{\alpha}$), 8.12 (s, 1H, C*H*$^{\alpha'}$), 7.76 (d, $J = 8.53$ Hz, 1H, C*H*^{8}), 7.67 (d, $J = 9.14$ Hz, 1H, C*H*^{4}), 7.58 (d, $J = 7.92$ Hz, 1H, C*H*^{5}), 7.53 (d, $J = 2.44$ Hz, 1H, C*H*$^{4'}$) 7.40 (t, $J = 7.61$ Hz, 1H, C*H*^{7}), 7.21 (t, $J = 7.61$ Hz, 1H, C*H*^{6}), 7.11 (d, $J = 2.44$ Hz, 1H, C*H*$^{6'}$), 6.92 (d, $J = 9.14$ Hz, 1H, C*H*^{3}), 3.44 (m, 1H, C*H*$^{1''}$), 3.33 (m, 1H, C*H*$^{2''}$), 2.19–1.46 (m, 8H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.34 (C^2), 163.94 ($C^{\alpha'}$), 158.84 (C^{α}), 157.95 ($C^{2'}$), 137.72 ($C^{4'}$), 136.68 (C^4), 133.22 (C^9), 132.81($C^{6'}$), 129.01 (C^5), 128.02 (C^7), 126.56 (C^{10}), 123.03 (C^6), 122.94 (C^3), 119.46 ($C^{1'}$), 118.36 (C^8), 112.19 ($C^{3'}$), 109.59 ($C^{5'}$), 107.05 (C^1), 74.43 ($C^{2''}$), 68.51 ($C^{1''}$), 32.92, 32.40, 24.29, 23.87 (cyclohexyl); Anal. Calcd for $C_{24}H_{22}N_2O_2Br_2$: C, 54.36; H, 4.18; N, 5.28. Found: C, 54.11; H, 4.10; N, 5.25.
Compound **3D**: mp 159–160 °C; $[\alpha]_D^{20}$ −184.32 (CH_2Cl_2, *c* 0.37); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.45 (s, 2H, ArO*H*, Ar′O*H*); 8.63 (s, 1H, C*H*$^{\alpha}$); 8.34 (s, 1H, C*H*$^{\alpha'}$); 7.71 (d, $J = 8.3$ Hz, 1H, C*H*^{8}); 7.63 (d, $J = 9.2$ Hz, 1H, C*H*^{4}); 7.53 (d, $J = 7.8$ Hz, 1H, C*H*^{5}); 7.29 (t, overlapped, 1H, C*H*^{6}); 7.17 (t, $J = 7.4$ Hz, 1H, C*H*^{7}); 6.88 (d, $J = 9.2$ Hz, 1H, C*H*^{3}); 5.86 (s, 1H, C*H*$^{3'}$); 5.48 (s, 1H, C*H*$^{5'}$); 3.70 (s, 3H, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.41 (m, 1H, C*H*$^{1''}$); 3.33 (m, 1H, C*H*$^{2''}$); 2.30–1.46 (m, 8H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 174.12 (C^2), 170.53 ($C^{2'}$), 165.79 ($C^{4'}$), 160.60 ($C^{6'}$), 159.84 ($C^{\alpha'}$), 158.62 (C^{α}), 136.70 (C^4), 133.62 (C^9), 128.80 (C^5), 127.86 (C^7), 126.32 (C^{10}), 123.72 (C^3), 122.65 (C^6), 118.38 (C^8), 106.81 (C^1), 102.18 ($C^{1'}$), 94.25 ($C^{3'}$), 88.64 ($C^{5'}$), 69.89 ($C^{2''}$), 67.98 ($C^{1''}$), 55.28 (O*C*H$_3$), 55.22 (O*C*H$_3$) 33.02, 32.29, 24.32, 24.18 (cyclohexyl); Anal. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.53; N, 6.48. Found: C, 72.01; H, 6.59; N, 6.42.
Compound **3E**: mp 145–148 °C; $[\alpha]_D^{20}$ −154.60 (CH_2Cl_2, *c* 0.13); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.55 (s, 1H,

ArO*H*); 14.46 (s, 1H, Ar′O*H*); 8.72 (s, 1H, C*H*$^{\alpha}$); 8.27 (s, 1H, C*H*$^{\alpha'}$); 8.04 (d,$J = 2.7$ Hz, 1H, C*H*$^{4'}$); 8.02 (s, 1H, C*H*$^{6'}$); 7.76 (d, $J = 8.4$ Hz, 1H, C*H*^{8}); 7.65 (d, $J = 9.2$ Hz, 1H, C*H*^{4}); 7.56 (d, $J = 7.8$ Hz, 1H, C*H*^{5}); 7.35 (t, $J = 7.3$ Hz, 1H, C*H*^{7}); 7.20 (t, $J = 7.3$ Hz, 1H, C*H*^{6}); 6.94 (d, $J = 8.8$ Hz, 1H, C*H*^{3}); 6.86 (d, $J = 9.0$ Hz, 1H, C*H*$^{3'}$); 3.48 (m, 1H, C*H*$^{1''}$); 3.38 (m, 1H, C*H*$^{2''}$); 2.05–1.52 (8H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 171.50 (C^{2}), 167.71 (C$^{2'}$), 164.42 (C$^{\alpha'}$), 158.88 (C$^{\alpha}$), 139.25 (C$^{5'}$), 136.44 (C^{4}), 133.10 (C^{9}), 129.18 (C^{5}), 128.02 (C$^{4'}$, C$^{6'}$), 127.86 (C^{7}), 126.70 (C^{10}), 123.01 (C^{3}), 122.78 (C^{6}), 118.27 (C$^{3'}$), 118.19 (C^{8}), 116.89 (C$^{1'}$), 107.13 (C^{1}), 72.42 (C$^{2''}$), 68.88 (C$^{1''}$), 32.81, 32.55, 24.29, 23.91 (cyclohexyl). Anal. Calcd for $C_{24}H_{23}N_3O_4$: C, 69.05; H, 5.55; N, 10.07. Found: C, 68.87; H, 5.38; N, 9.85.

Compound **3F**: mp 128–131 °C; $[\alpha]_D^{20}$ −401.97 (CH_2Cl_2, *c* 0.305); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 14.47 (s, 1H, ArO*H*); 12.99 (s, 1H, Ar′O*H*); 8.66 (s, 1H, C*H*$^{\alpha}$); 8.18 (s, 1H, C*H*$^{\alpha'}$); 7.72 (d, $J = 8.2$ Hz, 1H, C*H*^{8}); 7.61 (d, $J = 9.2$ Hz, 1H, C*H*$^{4'}$); 7.52 (d, $J = 7.7$ Hz, 1H, C*H*^{5}); 7.31 (t, $J = 7.2$ Hz, 1H, C*H*^{7}); 7.16 (t, $J = 7.3$ Hz, 1H, C*H*^{6}); 6.98 (d, $J = 7.6$ Hz, 1H, C*H*$^{4'}$); ~6.87 (overlapped, 1H, C*H*^{3}); ~6.84 (overlapped, 1H, C*H*$^{6'}$); 6.77 (d, $J = 8.23$ Hz, 1H, C*H*$^{3'}$); 3.47 (m, 1H, C*H*$^{1''}$); 3.23 (m. 1H, C*H*$^{2''}$); 2.18 (m, 1H, cyclohexyl); 2.12 (s, 3H, C*H*$_3$); ~1.92 (m, 3H, cyclohexyl); 1.72 (m, 2H, cyclohexyl); 1.48 (m, 2H, cyclohexyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 174.48 (C^{2}), 165.74 (C$^{\alpha'}$), 158.55 (C$^{2'}$), 158.08 (C$^{\alpha}$), 136.80 (C^{4}), 133.60 (C^{9}), 133.23 (C$^{4'}$), 131.58 (C$^{6'}$), 128.86 (C^{5}), 127.89 (C^{7}), 127.79 (C$^{5'}$), 126.27 (C^{10}), 123.90 (C^{3}), 122.66 (C^{6}), 118.47 (C$^{1'}$), 118.04 (C^{8}), 116.47 (C$^{3'}$), 106.68 (C^{1}), 73.06 (C$^{2''}$), 67.54 (C$^{1''}$), 33.28, 32.30, 24.40, 23.94 (cyclohexyl), 22.16 (*C*H$_3$); Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.74; H, 7.05; N, 7.52.