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Synthesis of (*R*)-tembamide and (*R*)-aegeline via asymmetric transfer hydrogenation in water

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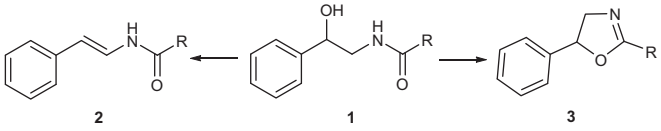
ABSTRACT

The synthesis of (*R*)-tembamide and (*R*)-aegeline via asymmetric transfer hydrogenation involving enantioenriched monosulfonamide–RhCp* complex in aqueous sodium formate as hydride donor is described.

1. Introduction

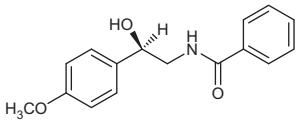
The β-aminoalcohol functionality is a rich resource in organic and medicinal chemistry[1–15] This functional group is often found not only in the structural unit of many building blocks, chiral auxiliaries, and ligands in organic transformations, but also in the structural motif of many biologically active compounds. Optically active β-aminoalcohols are important structural elements in chiral drugs, such as α- or β-adrenergic blockers and agonists in the treatment of cardiovascular disease, cardiac failure, asthma, antidepressant, and glaucoma.[1–15] We have developed a simple and efficient route to various chiral β-aminoalcohols involving the enantioselective addition of trimethylsilylcyanide to prochiral aryl aldehydes catalyzed by chiral Schiff base-titanium complexes to give enantiomerically pure cyanohydrins in good yields and enantioselectivities.[16–19] The trimethylsilylcyanohydrins can subsequently be reduced to give enantiopure β-aminoalcohols in good yields using diborane. Using this technique, we synthesized and reported X-ray structures of the naturally occurring (*R*)-(−)-tembamide and (*R*)-(−)-aegeline, isolated form *Fagara hyemalis* (St. Hill) Engler and *Aegele marmelos* (Correa), respectively, belonging to the family Rutaceae.[20]

β-Hydroxyamides **1** are important biosynthetic intermediates in plants; they are also used in traditional Indian medicine and have been shown to have good hypoglycemic activity. We have discussed a possible biosynthetic pathway to enamides **2** and oxazolines **3**[20–22] (Scheme 1).

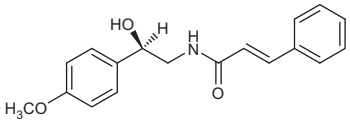


Scheme 1. Pathway to enamides and oxazolines.

Following our work, various other methods leading to the synthesis of optically active (*R*)-(−)-tembamide and (*R*)-(−)-aegeline have been reported. Kumar et al. reported on a synthesis employing the Sharpless asymmetric dihydroxylation as the source of chirality.[23] Lainé et al. reported the synthesis of (*R*)-tembamide, (*R*)-aegeline, and (*R*)-pronethalol via the diastereoselective oxy-Michael addition of delta lactol anions to nitro olefins as the key step.[24] Kamal et al. enantioselectively reduced and resolved the β-azido alcohol from ketoazides using $NaBH_4$/lipase enzymes, and subsequent reduction and coupling led to the desired chiral tembamide and aegeline.[25] Here we report another route to



(*R*)-(-)-tembamide



(*R*)-(-)-aegeline

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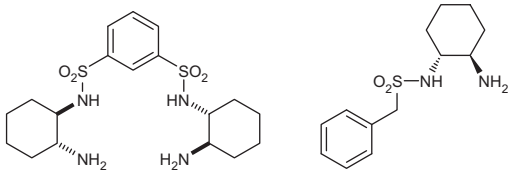
enantiomerically pure (*R*)-(−)-tembamide and (*R*)-(−)-aegeline using the asymmetric transfer hydrogenation technique (ATH) in water.

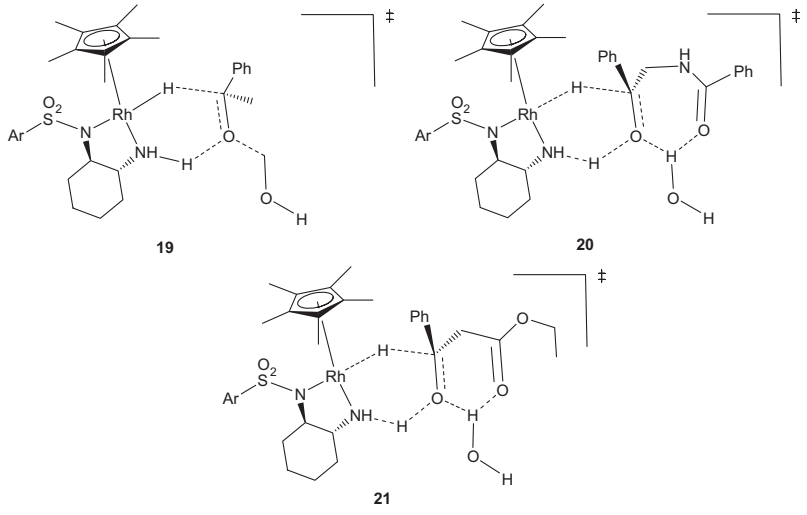
2. Results and discussion

Asymmetric transfer hydrogenation (ATH) offers operational simplicity, since the reaction does not involve molecular hydrogen and is insensitive to air oxidation.[26–31] A wide range of functionalized aromatic ketones were subjected to transfer hydrogenation to produce enantiopure alcohols. In most cases, the ATH reactions with the metal-ligand were performed in situ by reacting the chiral ligand and metal complex. Typical examples involve $[RuCl_2(p\text{-cymene})]_2$ and $[MCp^*Cl_2]_2$ (M = Rh, Ir) in reaction with enantioenriched monosulfonamide ligand derived from cyclohexane-1,2-diamine, using isopropyl alcohol or aqueous sodium formate as the hydride source and solvent.[32–37] Many efficient asymmetric catalysts containing monosulfonamide-type ligands have been developed for this reaction and performed in water. Recently we reported on the use of C_2-symmetric bis(sulfonamide)-cyclohexane-1,2-diamine **4**–RhCp* complex, which gave high enantioselectivities involving conversion in the ATH of ketones in aqueous sodium formate.[38–45] Ligands **4** and **5** with RhCp* gave the best results in the ATH of a variety of ketones.



4 **5**

When the catalyst was changed to RhCp*–**4** and aqueous sodium formate was used as the hydride source the reaction was completed in 4 h with similar enantioselectivities (>99%) and improved yields (95–100%) (Table 2). Using this technique, (*R*)-tembamide **13** and (*R*)-aegeline **14** were obtained in >99% enantioselectivity and 95% yield, respectively. This rate difference observed with Ru(arene)-5 and RhCp*–**4** is in agreement with our theoretical calculations comparing the transition state energies involving Ru(arene)cyclohexane-1,2-diamine and RhCp*-cyclohexane-1,2-diamine in the ATH of acetophenone, which indicated the latter was preferred.[49] Aqueous sodium formate is known to accelerate the rate of ATH for ketones.[38–45] Xiao et al. showed through extensive experimental and theoretical calculations that a water molecule binding to a ketone oxygen in the transition state **19**, lowers the energy substantially, thus enhancing the rate of the reaction and enantioselectivity.[50] Using the same reasoning, we believe that the amide, ester, and amine functionality in our molecules offer an excellent binding site for the water molecule (transition state **20**), thus lowering the transition state energy even further and enhancing the enantioselectivity, which is in accordance with the observation of Marcus[51] on 'the theory of organic catalysis in water'. A similar transition state could also be envisaged for ketoester **12** and ketoamines **10** and **11** (transition state **21**). To test the scope of the reduction using RhCp*–**4** and aqueous sodium formate, we reduced ketoamines **10**, **11**, and ketoester **12** to the corresponding alcohols in excellent enantioselectivities and good yields. The results are shown in Table 2.



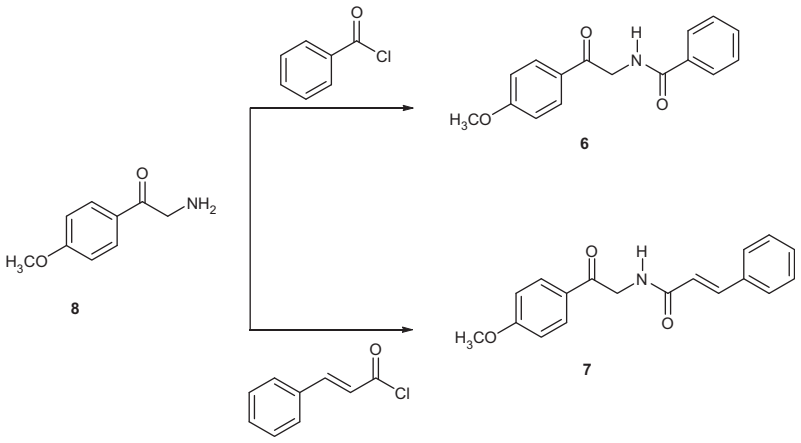
19 **20** **21**

Ketoamides **6** and **7** were synthesized from commercially available 2-amino-1-(4-methoxyphenyl)ethanone **8** in good yields (Scheme 2). Ketones **9**–**12** were purchased from Aldrich Chemical (Fig. 1). Herein we report the synthesis of (*R*)-tembamide, (*R*)-aegeline and other alcohols (Fig. 2) by ATH using $Rh^{III}Cp^*$- or Ru^{II}(arene) complexed with ligands **4** and **5**.

Using Ru(arene)-**5** as the catalyst and isopropanol/KOH as the hydride source in the ATH of ketoamides **6**, **7**, and **9**, gave the corresponding β-hydroxyamides in good yields (85–95%) and enantioselectivities (>99%) in a reaction time of 16 h (Table 1).

3. Conclusion

Herein we have reported the synthesis of enantiomerically pure tembamide **13** and aegeline **14**, two naturally occurring β-hydroxy amides via ATH of the corresponding ketoamides and extended this technique to other ketoamides, ketoamines, and ketoester. The ATH of ketoamides to β-hydroxyamides with the RhCp*–**4** complex as the catalyst in aqueous sodium formate gave excellent yields and enantioselectivities, probably due to the strong hydrogen bonding in the transition state, thus providing a potentially



Scheme 2. Synthesis of ketones.

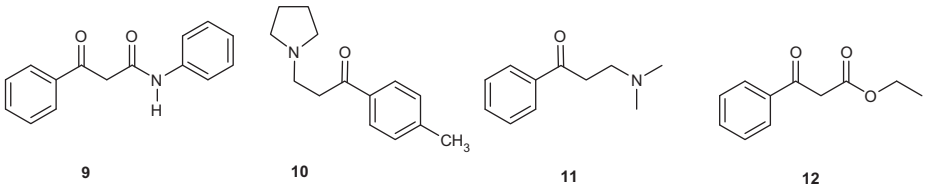


Figure 1. Ketones tested in the ATH.

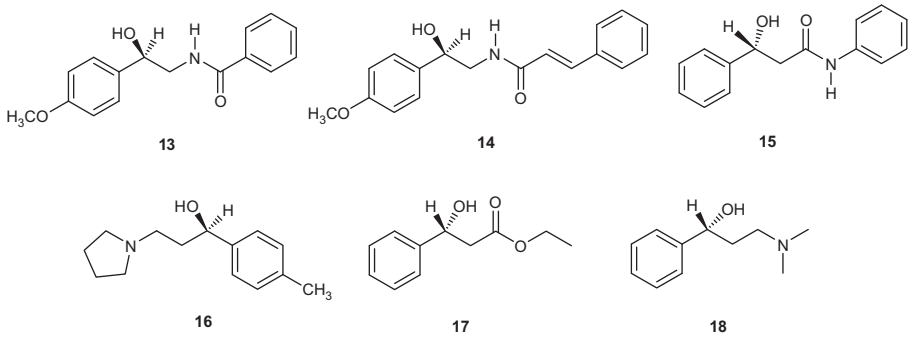


Figure 2. Chiral secondary alcohols.

useful and environmentally safe synthetic technique to biologically active building blocks.

4. Experimental

4.1. General

NMR spectra were recorded at 200 and 500 MHz for ^{1}H and 50 MHz for ^{13}C. Chemicals were purchased from the Aldrich Chemical Company. Chiral monosulfonamide ligands **6** and **7** were synthesized by previously reported methods.[38–41] Ee% values were determined by HPLC with a 25 cm Whelk-01 chiral column. Absolute configurations were determined by comparison with known specific rotation values.

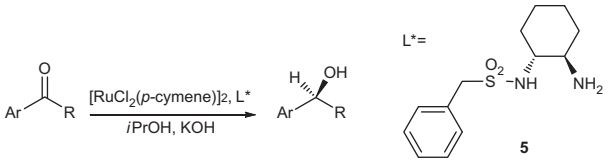
4.2. General procedure for the preparation of ketones 6 and 7

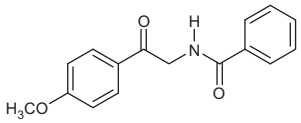
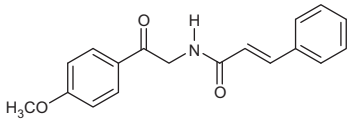
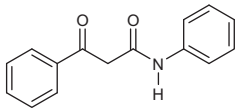
To a solution of 2-amino-1-(4-methoxyphenyl)ethanone **8** (0.5 g, 3.03 mmol) in CH_2Cl_2 (20 mL), a solution of NaOH (0.24 g, 3.0 mmol) in water (3 mL) was added at ice bath temperature and the mixture was stirred vigorously for 10 min. Benzoyl chloride (1.2 mmol, 1 mL) was added dropwise to the reaction mixture, with vigorously stirring. After the addition was complete, the reaction mixture was stirred for a further 1 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was separated and washed with brine and the solvent was removed to give ketoamide **6**.

4.3. *N*-[2-(4-Methoxyphenyl)-2-ketoethyl]benzamide 6

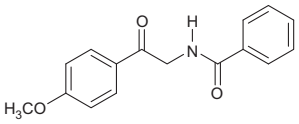
White solid; (0.35 g, 90%); mp 108–110 °C; IR (KBr) 3359, 3056, 2927, 2822, 1668, 1623, 1587, 1510, 1348, 1296, 1223, 1153, 1012 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.0 (d, J = 8.4 Hz, 2H), 7.91–7.87 (m, 2H), 7.54–7.43 (m, 3H), 7.0 (d, J = 8.8 Hz, 2H), 4.91 (d, J = 4.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.62, 167.4, 164.4, 134.1, 131.7, 130.4, 128.7, 127.5, 127.2, 114.2, 55.61, 46.5. EIMS m/z (rel intensity) 269 $[M]^+$ (8), 252 (1), 241 (1), 224 (1), 211 (1), 181 (1), 164 (1), 148 (1), 135 (100), 105 (33), 92 (18), 77 (50), 51 (15). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61. Found: C, 71.40; H, 5.65.

Table 1
Asymmetric transfer hydrogenation of ketones with Ru(arene)-**5**[a]



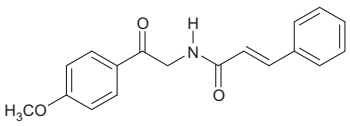
Ketone	*t* (h)	ee[b] (%)	Yield (%)	Abs. Conf.[c]
	16	>99	95	(*R*)[20]
	16	>99	90	(*R*)[20]
	16	>99	85	ND

[a] 25 °C using a mixture of isopropanol/KOH.
[b] Measured by HPLC analysis of the alcohol with chiral capillary column Whelk-01, (250 mm × 4.6 mm × 5 μm).
[c] Absolute configurations were assigned by comparing the specific rotations with the literature values.



4.4. *N*-[2-(4-Methoxyphenyl)-2-keto-ethyl)]-cinnamamide 7

White solid; (0.40 g, 85%); mp 141–143 °C. IR (KBr) 3326, 3052, 2928, 2832, 1657, 1613, 1514, 1363, 1242, 1173, 1027 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 8.0 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 16.0 Hz, 1H), 7.56–7.51 (m, 1H), 7.39–7.36 (m, 3H), 6.97 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 14.2 Hz, 1H), 4.85 (d, J = 4.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.6, 165.9, 164.4, 141.5, 134.8, 130.4, 129.8, 128.6, 127.9, 127.4, 120.3, 114.2, 55.6, 46.3. EIMS m/z (rel intensity) 295 $[M]^+$ (11), 278 (1), 267 (1), 250 (1), 223 (1), 207(1), 192 (1), 164 (1), 146 (5), 135 (100), 107 (12), 103 (22), 77 (34), 51 (5). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80. Found: C, 73.25; H, 5.81.



4.5. General procedure for the ATH

A mixture of the metal precursor $[(arene)RuCl_2]_2$ (0.0039 mmol) and the chiral ligand (0.0075 mmol) in freshly distilled 2-propanol was stirred at 80 °C for 30 min under an argon atmosphere. A solution of potassium hydroxide in 2-propanol was then stirred at 50 °C for 30 min. Next, the prochiral ketone in 2-propanol was added to the catalyst solution followed by KOH solution and stirred at room temperature for the time indicated in Table 1 for each individual reaction. Water was then added to the reaction mixture and extracted with dichloromethane (3 × 10 mL). The dichloromethane layers were combined, dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and then passed through a short silica gel path. The residue containing the alcohol was acetylated using acetic anhydride.

For the ATH of ketones in water, a mixture of the metal precursor $[RhCl_2(Cp^*)]_2$ (0.0039 mmol) and the chiral ligand (0.00075 mmol) was heated in water (2mL) at 40 °C for 1 h in air. HCOONa (5.7 mmol) and the substrate were subsequently added (1.14 mmol). The reaction mixture was stirred at 40 °C in air for the time indicated in Table 2 for each individual reaction. The reaction mixture was extracted with ether (3 × 10 mL). The ether layers were combined, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue containing the alcohol was acetylated using acetic anhydride.

4.6. Tembamide. (*R*)-(-)-*N*-(2-Hydroxy-2-(4-methoxyphenyl) ethyl) benzamide 13

White crystals; mp 155–157 °C; $[\alpha]_D^{20} = -58.4$ (c 0.5, CH_3Cl). IR (KBr) 3365, 3064, 2935, 2848, 1636, 1600, 1525, 1364, 1254, 1159, 1092 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.64 (sa, 1H), 4.86 (dd, J = 3.3 and J = 7.2 Hz, 1H), 3.9–3.82 (m, 1H), 3.8 (s, 3H), 3.56–3.44 (m, 1H), 3.28 (d, J = 3.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 159.4, 134.2, 134.0, 131.2, 128.6, 127.1, 127.0, 114.0, 77.3, 55.3, 47.8. EIMS m/z (rel intensity) 269 $[M]^+$ (11), 252 (1), 241 (1), 224 (1), 211 (1), 181 (1), 164 (1), 148 (1), 105 (28), 92 (13), 77 (41), 51 (11). Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.88; H, 6.37.

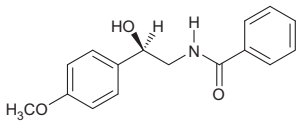
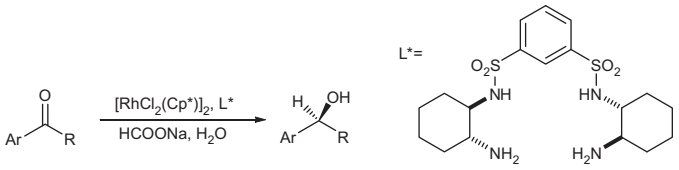
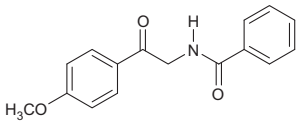
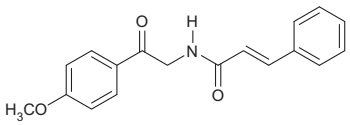
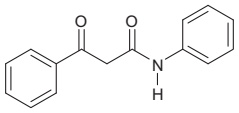
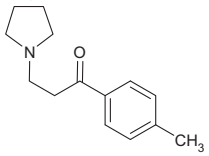
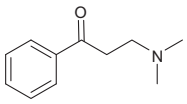
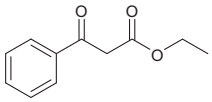


Table 2
Asymmetric transfer hydrogenation of ketones with Rh-**4** by HCOONa in water[a]



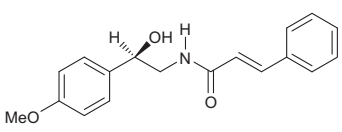
4

Ketone	t (h)	ee[b] (%)	Yield (%)	Abs. Conf.[c]
	6	>99	95	(*R*)
	6	>99	95	(*R*)
	16	>99	95	ND
	6	>99	95	(*R*)[46]
	6	>99	95	(*R*)[47]
	4	>99	100	(*R*)[48]

[a] 40 °C using a mixture of water/sodium formate.
[b] Measured by HPLC analysis of the alcohol with chiral capillary column Whelk-01, (250 mm × 4.6 mm × 5 μm).
[c] Absolute configurations were assigned by comparing the specific rotations with the literature values.

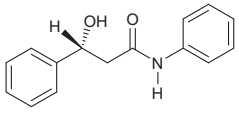
4.7. Aegeline. (*R*)-(−)-*N*-(2-Hydroxy-2-(4-methoxyphenyl) ethyl) cinnamamide 14

White crystal; mp 193–195 °C; $[\alpha]_D^{20} = -39.3$ (*c* 0.4, $CHCl_3$). IR (KBr) 3326, 3052, 2928, 2832, 1657, 1603, 15414, 1363, 1242, 1173, 1027 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 15.6 Hz, 1H), 7.5 (d, *J* = 8.0 Hz, 2H), 7.43 (ta, 1H), 7.36–7.35 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 15.62 Hz, 1H), 5.08 (sa, 3H), 4.79 (dd, *J* = 3.39 and *J* = 8.19 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 3.5 and *J* = 6.9 Hz, 1H), 3.35 (dd, *J* = 4.6 and *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 158.4, 139.7, 134.5, 128.9, 127.2, 126.8, 120.8. EIMS *m*/*z* (rel intensity) 297 $[M]^+$ (7), 279 (6), 267 (3), 219 (3), 161 (100), 150 (48), 131 (50), 109 (21), 103 (27), 77 (31), 57 (10). Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44. Found: C, 72.74; H, 6.45.



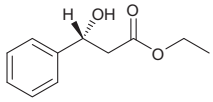
4.8. (*R*)-3-Hydroxy-*N*-3-diphenylpropanamide 15

White crystals; mp 178–180 °C; $[\alpha]_D^{20} = +25$ (*c* 0.4, MeOH). IR (KBr) 3250, 2916, 1662, 1604, 1548, 1441, 1051 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.59 (d, 7.57 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.30 (m, 2H), 7.27–7.22 (m, 3H), 7.04–7.01 (m, 1H), 5.14 (dd, *J* = 3.9 and *J* = 9.0 Hz, 1H), 3.69 (sa, 1H), 2.76 (dd, *J* = 9.2 and *J* = 14.5 Hz, 1H), 2.65 (dd, *J* = 3.9 and *J* = 14.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 144.7, 138.9, 128.5, 128.1, 127.0, 125.6, 123.3, 119.6, 70.2, 46.61, 40.44, 40.3, 39.44. EIMS *m*/*z* (rel intensity) 241 $[M]^+$ (53), 223 (2), 196 (1), 183 (1), 168 (1), 149 (1), 135 (7), 120 (3), 104 (17), 93 (100), 77 (48), 51 (18). Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27. Found: C, 74.71; H, 6.33.



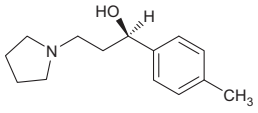
4.9. (*R*)-(+)-Ethyl-3-hydroxy-3-phenylpropanoate 16

Yellow oil; $[\alpha]_D^{20} = +76$ (*c* 0.4, CH_2Cl_2). IR (film) 3367, 3056, 2978, 2935, 1726, 1608, 1436, 1389, 1307, 1247, 1178, 1123, 1062, 1010 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5H), 5.16 (dd, *J* = 3.5 and *J* = 8.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.30 (br s, 1H), 2.75 (dd, *J* = 8.06 and *J* = 16.24 Hz, 1H), 2.71 (dd, *J* = 4.1 and *J* = 16.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.04; H, 7.30.



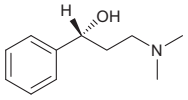
4.10. (*R*)-(+)-3-(Pyrrolidin-1-yl)-1-*p*-tolylpropan-1-ol 17

$[\alpha]_D^{20} = +18$ (*c* 0.3, $CHCl_3$). IR (film) 3380, 3012, 2960, 2803, 1601, 1508, 1444, 1198, 1126, 1073, 816 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.89 (dd, *J* = 5.0 Hz, 1H), 2.97–2.84 (m, 2H), 2.73–.55 (m, 4H), 2.33 (s, 3H), 1.89–1.77 (m, 6H). Calcd for $C_{14}H_{21}NO$: C, 76.67; H,9.65. Found: C, 76.72; H, 9.69.



4.11. (*R*)-(+)-3-(Dimethylamino)-1-phenylpropan-1-ol (18)

$[\alpha]_D^{20} = +24.0$ (*c* 0.5, $CHCl_3$). IR (film) 3386, 3012, 2968, 2803,1601 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 4.92 (dd, *J* = 5 Hz, 1H), 2.73–2.44 (m, 2H), 2.31 (s, 6H), 1.88–1.78 (m, 2H). Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.75; H, 6.60.



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