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A Widely Applicable Method of Resolution of Binaphthyls: Preparation of Enantiomerically Pure 1,1′-Binaphthalene-2,2′-diol, 1,1′-Binaphthalene-2,2′-dithiol, 2′-Mercapto-1,1′-binaphthalen-2-ol, and 1,1′-Binaphthalene-8,8′-diol

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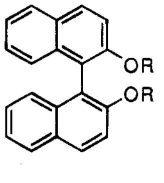
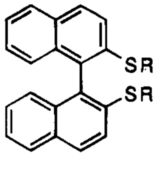
"Man-made" chiral auxiliaries are becoming increasingly popular over the classic auxiliaries derived from the natural chiral pool. From a practical point of view, a requisite that should be fulfilled to make a "man-made" auxiliary directly comparable to a "natural" one is that the ease of resolution matches the ease of extraction and of the further manipulations that are ordinarily required to a natural compound to make it suitable for asymmetric synthesis. When this is accomplished, one can make use of reagents to meet all needs and to incorporate a number of features that are otherwise not possible with natural substances. Among the many virtues of man-made auxiliaries we can cite the high-symmetry chirality, the high crystallinity, the simple spectra, the accessibility to both enantiomers, and the virtual accessibility to any functional group. Among the most well-known examples of man-made auxiliaries are 1,1′-binaphthalene-2,2′-diol (**1a**) and -dithiol (**2a**).[1]



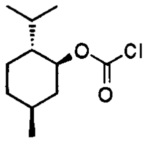
1a (R = H)
1b (R = CO$_2$Menthyl)



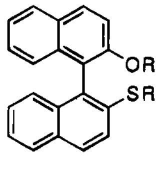
2a (R = H)
2b (R = CO$_2$Menthyl)

The need for new and improved methods of resolution for both **1a**[2] and **2a**[3] is witnessed by the number of groups that in recent times have faced this research problem and by the number of publications that have appeared in the literature.

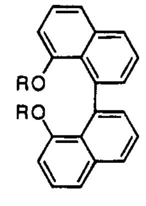
Here, we present a new method of resolution of **1a** and **2a** based on the facile separation of the pair of diastereoisomers **1b** and **2b** derived from the reaction of either **1a** or **2a** with 2 mol of (−)-menthyl chloroformate (**3**). The method appears to be generally applicable to the binaphthyl systems, in as much it was proved possible to prepare and separate with ease the diastereoisomers derived from the reaction of **3** with many other derivatives such as the mixed system **4a** and 1,1′-binaphthalene-8,8′-diol (**5a**).



3



4a (R = H)
4b (R = CO$_2$Menthyl)



5a (R = H)
5b (R = CO$_2$Menthyl)

(−)-(1*R*)-Menthyl chloroformate is commercially available, and the reaction is rapidly accomplished in benzene (or toluene) in the presence of triethylamine. The pair of diastereoisomers (denoted by suffixes **b′** and **b″**) is readily separated by fractional crystallization. The high difference in crystallinity between the stereoisomers allows for the obtainment of the pure diastereoisomers in a single operation. The final deprotection of the hydroxy or thiol groups can be performed with LiAlH$_4$, but other hydrolytic systems are probably effective as well.

The present procedure not only presents advantages that make it amongst the most practical, reliable, and inexpensive method available for the resolution of both **1a** and **2a**, but it is the only method so far reported for the resolution of the mixed system **4a**[4] and of the 8,8′-binaphthol **5a**. The chemistry of the latter enantiomerically pure compounds is presently under investigation.

Experimental Section

Resolution of 1,1′-Binaphthalene-2,2′-diol (1a). A solution of racemic **1a** (2.0 g, 6.98 mmol) and triethylamine (4 mL) in benzene (10 mL) was added dropwise with stirring to a solution of (−)-menthyl chloroformate (**3**) (3.05 g, 13.96 mmol) in benzene (10 mL) at room temperature, under nitrogen. The solution was stirred at room temperature for 1 h, washed with 10% HCl (50 mL) and water (2 × 100 mL), and dried over Na$_2$SO$_4$. After removal of the solvent, a 1:1 diastereomeric mixture of **1b** was obtained as a colorless, crystalline solid (4.23 g, 97% yield). Anal. Calcd for C$_{42}$H$_{50}$O$_6$: C, 77.5; H, 7.7. Found: C, 77.5; H, 7.9.

The 1:1 diastereomeric mixture of **1b** (2 g) was dissolved in refluxing hexane (60 mL) and set aside at room temperature. After 72 h, the solution was filtered to give the diastereoisomer **1b′** of (*R*)-binaphthol as large colorless prisms as a single, pure diastereoisomer (0.95 g, 95% yield): mp 186−188 °C; $[\alpha]^{25}_{D}$ −134.9 (c = 1.1, CHCl$_3$). ^{1}H-NMR (CDCl$_3$) δ 0.15 (d, J = 6.9 Hz, 6H), 0.53 (d, J = 6.9 Hz, 6H), 0.84 (d, J = 6.9 Hz, 6H), 0.70−1.90 (series of m, 18H), 4.20 (td, J = 10.8 and 4.5 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.27 (t, J = 8.7 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H). ^{13}C-NMR (CDCl$_3$) δ 15.79, 20.25, 21.89, 23.27,

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25.75, 31.23, 33.90, 40.30, 46.63, 78.82, 121.40, 123.35, 125.71, 126.34, 126.75, 127.90, 129.80, 131.70, 133.12, 146.88, 152.86. IR (KBr pellet) ν 2960 (w), 2945 (m), 1700 (s), 1150 (s), 1100 (s), 905 (s). The solution was rotoevaporated to dryness to obtain the diastereoisomer of (*S*)-binaphthol **1b″** (95:5 diastereomeric ratio) (1.05 g, quant): mp 60–65 °C; $[\alpha]^{25}_{D}$ −19.1 (*c* = 0.95, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.64 (d, *J* = 6.9 Hz, 6H), 0.76 (d, *J* = 6.9 Hz, 12H), 0.40–1.80 (series of m, 18H), 4.18 (td, *J* = 10.8 and 4.2 Hz, 2H), 7.20–7.50 (series of m, 6H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ 15.96, 20.34, 21.55, 22.92, 25.58, 30.79, 33.67, 39.29, 46.13, 78.70, 121.23, 123.18, 125.50, 126.16, 126.53, 127.70, 129.63, 131.48, 132.92, 146.80, 152.45. IR (KBr pellet) ν 2960 (w), 2955 (m), 1705 (s), 1610 (m), 1585 (m), 1150 (s), 1110 (s), 900 (s).

Diastereomerically pure **1b′** (1.0 g. 1.59 mmol) in anhydrous THF (30 mL) was cooled at 0 °C under argon, and $LiAlH_4$ (0.40 g, 10.60 mmol) was added in portions with vigorous magnetic stirring. After 2 h, water (50 mL) and 10% HCl were cautiously added. The acidic solution was extracted with dichloromethane (2 × 80 mL), dried over Na_2SO_4, and rotoevaporated to afford a colorless solid that was purified by flash chromatography (silica gel, CH_2Cl_2) to give enantiomerically pure (*R*)-binaphthol **1a** (0.44 g, 98% yield): mp 209–210 °C; $[\alpha]^{25}_{D}$ +34.0 (*c* = 1.0, THF) and enantiomerically pure (−)-menthol (0.48 g, 98% yield).

Similar treatment of **1b″** (95:5 diastereomeric ratio) gave (*S*)-binaphthol **1a** (0.45 g, 98.5% yield): mp 209–210 °C; $[\alpha]^{25}_{D}$ −30.6 (*c* = 1.0, THF) of 90% ee and enantiomerically pure (−)-menthol.

Resolution of 1,1′-Binaphthalene-2,2′-dithiol (2a). A solution of racemic 1,1′-binaphthalene-2,2′-dithiol **2a** (2.0 g, 6.98 mmol) and triethylamine (4 mL) in benzene (10 mL) was added dropwise with stirring to a solution of (−)-menthyl chloroformate (**3**) (2.75 g, 12.57 mmol) in benzene (10 mL) at room temperature under nitrogen. The solution was stirred at room temperature for 1 h, diluted with dichloromethane (50 mL), washed with 10% hydrochloric acid (50 mL) and water (2 × 100 mL), extracted with dichloromethane (2 × 100 mL), and dried over Na_2SO_4. After removal of the solvent a colorless crystalline solid composed of a 1:1 mixture of diastereomers **2b** (4.06 g, 98% yield) was obtained. Anal. Calcd for $C_{42}H_{50}O_4S_2$: C, 73.9; H, 7.4. Found: C, 73.8; H, 7.5.

The 1:1 diastereomeric mixture of **2b** (2 g) was dissolved in refluxing hexane (60 mL). After 72 h at 25 °C, the solution was filtered to obtain the diastereoisomer **2b′** formed by (*R*)-dithiol as large colorless crystals (single stereoisomer) (0.98 g, 98% yield): mp 170–172 °C; $[\alpha]^{25}_{D}$ −98.5 (*c* = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.51 (d, *J* = 6.9 Hz, 6H), 0.66 (d, *J* = 6.9 Hz, 6H), 0.87 (d, *J* = 6.9 Hz, 6H), 0.60–2.00 (series of m, 18H), 4.62 (td, *J* = 10.8 and 4.2 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.23 (td, *J* = 6.9 and 1.5 Hz, 2H), 7.47 (td, *J* = 6.9 and 1.5 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ 15.96, 20.23, 21.70, 23.17, 25.74, 31.20, 33.73, 40.51, 46.73, 78.12, 126.50, 126.58, 126.71, 126.89, 127.70, 128.60, 132.01, 132.70, 133.25, 140.51, 168.17. IR (KBr pellet) ν 2970 (w), 2945 (m), 1720 (s), 1600 (w), 1450 (w), 1110 (s), 1100 (s), 905 (s).

The solution was rotoevaporated to dryness to obtain (*S*)-**2b″** (98:2 diastereomeric ratio) (1.05 g, quant): mp 70–72 °C; $[\alpha]^{25}_{D}$ −13.0 (*c* = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.75 (d, *J* = 6.9 Hz, 6H), 0.83 (d, *J* = 6.9 Hz, 12H), 0.60–1.80 (series of m, 18H) 4.63 (td, *J* = 10.8 and 4.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.26 (td, *J* = 8.7 and 1.2 Hz, 2H), 7.48 (td, *J* = 8.1 and 1.2 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ 16.17, 20.40, 21.66, 23.21, 25.93, 31.10, 33.75, 40.14, 46.65, 78.34, 126.54, 126.61, 126.75, 127.05, 127.76, 128.61, 131.98, 132.75, 133.26, 140.47, 168.19. IR (KBr pellet) ν 2970 (w), 2940 (m), 1720 (s), 1155 (s), 1100 (s), 905 (s).

$LiAlH_4$ (0.40 g, 10.60 mmol) was added in portions at 0 °C with vigorous magnetic stirring to a solution of diasteromerically pure **2b′** (1.0 g, 1.51 mmol) in anhydrous THF (30 mL) under argon. After 2 h, water (50 mL) and 10% HCl was added until neutralization. The solution was extracted with dichloromethane (2 × 80 mL), dried over Na_2SO_4, and rotoevaporated to a colorless solid that was purified by flash chromatography (silica gel, CH_2Cl_2) to obtain (*R*)-(−)-1,1′-binaphthalene-2,2′-dithiol (**2a**) (0.46 g, 96% yield): mp 150–151 °C; $[\alpha]^{25}_{D}$ −31.1 (*c* = 1, $CHCl_3$) of 100% ee and enantiomerically pure (−)-menthol (0.45 g, 94% yield).

Similar treatment of **2b″** (98:2 diastereomeric ratio, 1.0 g, 1.51 mmol) gave (*S*)-(+)-1,1′-binaphthalene-2,2′-dithiol (**2a**) (0.46 g, 96% yield): mp 150–151 °C; $[\alpha]^{25}_{D}$ +29.8 (*c* = 1.0, $CHCl_3$) of 96% ee and enantiomerically pure (−)-menthol (0.45 g, 94% yield).

The enantiomeric purity of (*R*)-(−)-**2a** was confirmed by HPLC on Chiracel of the dimethylated derivative as reported elsewhere.[3c]

Resolution of 2′-Mercapto-1,1′-binaphthalen-2-ol (4a). A solution of racemic 2′-mercapto-1,1′-binaphthalen-2-ol (**4a**) (2.0 g, 6.56 mmol) and triethylamine (4 mL) in benzene (10 mL) was added dropwise with stirring to a solution of (−)-menthyl chloroformate (**3**) (2.88 g, 13.12 mmol) in benzene (10 mL) at room temperature under nitrogen. After 1 h, the reaction mixture was diluted with dichloromethane (50 mL), washed with 10% hydrochloric acid (50 mL) and water (2 × 100 mL), extracted with dichloromethane (2 × 100 mL), and dried over Na_2SO_4. After removal of the solvent, a colorless crystalline solid was obtained composed of a 1:1 diastereomeric mixture of **4b′** and **4b″** (3.90 g, 92% yield). Anal. Calcd for $C_{42}H_{50}O_5S$: C, 75.6; H, 7.6. Found: C, 75.8 ; H, 7.8.

The 1:1 diastereomeric mixture of **4b** (2 g) was dissolved in refluxing hexane (60 mL). After 72 h at 25 °C, the solution was filtered to obtain **4b′** as large colorless crystals (single diastereoisomer) (0.89 g, 89% yield): mp 145–146 °C; $[\alpha]^{25}_{D}$ −112.5 (*c* = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.30 (d, *J* = 8.1 Hz, 3H), 0.48 (d, *J* = 8.1 Hz, 3H), 0.57 (d, *J* = 8.1 Hz, 3H), 0.63 (d, *J* = 8.1 Hz, 3H), 0.84 (d, *J* = 8.1 Hz, 3H), 0.86 (d, *J* = 8.1 Hz, 3H), 0.63–2.00 (series of m, 18H), 4.23 (td, *J* = 10.5 and 4.2 Hz, 1H), 4.60 (td, *J* = 10.8 and 4.5 Hz, 1H), 7.13 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.21–7.35 (m, 3H), 7.43 (td, *J* = 6.6 and 1.2 Hz, 1H), 7.48 (td, *J* = 6.6 and 1.5 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ (aliphatic only) 15.85, 16.04, 20.10, 20.29, 21.63, 21.71, 23.13, 23.28, 25.70, 25.94, 31.05, 31.25, 33.71, 33.80, 40.09, 40.60, 46.41, 46.74, 77.95, 78.78. IR (KBr pellet) ν 2995 (m), 2990 (m), 1750 (s), 1720 (s), 1250 (s), 1220 (s), 1130 (s), 950 (s).

The solution was rotoevaporated to dryness to obtain **4b″** (9:1 diastereomeric ratio) (1.11 g, quant): mp *ca.* 40–2 °C; $[\alpha]^{25}_{D}$ −27.1 (*c* = 1.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.61 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 7.2 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 6H), 0.55–1.80 (series of m, 18H), 4.24 (td, *J* = 11.1 and 4.8 Hz, 1H), 4.62 (td, *J* = 10.8, 4.5 Hz, 1H), 7.21–7.35 (series of m, 4H), 7.43–7.55 (series of m, 3H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ (aliphatic only) 16.21, 16.22, 20.30, 20.43, 21.63, 21.71, 23.12, 23.28, 25.72, 25.95, 30.89, 31.05, 33.71, 33.80, 39.57, 40.09, 46.26, 46.56, 78.29, 78.79. IR (KBr pellet) ν 2995 (m), 2990 (m), 1750 (s), 1720 (s), 1250 (s), 1220 (s), 1130 (s), 950 (s).

Diastereomerically pure **4b′** (1.0 g, 1.49 mmol) in anhydrous THF (30 mL) was cooled to 0 °C under Ar, and $LiAlH_4$ (0.40 g, 10.6 mmol) was added in portions while vigorously stirring. After 2 h, water (50 mL) and 10% HCl were added up to neutralization. The solution was extracted with dichloromethane (2 × 80 mL), dried over Na_2SO_4, and rotoevaporated to give a colorless solid that was purified by flash-chromatography on silica gel (CH_2Cl_2) to obtain (−)-**4a** (0.43 g, 95% yield): $[\alpha]^{25}_{D}$ −27.9 (*c* = 1, EtOH) identical to an authentic sample and enantiomerically pure (−)-menthol (0.42 g, 90% yield).

Resolution of 1,1′-Binaphthalene-8,8′-diol (5a). A solution of racemic 8,8′-dihydroxy-1,1′-binaphthalene (**5a**) (2.0 g, 6.98 mmol) and triethylamine (4 mL) in benzene (10 mL) was added dropwise with stirring to a solution of (−)-menthyl chloroformate (**3**) (3.05 g, 13.96 mmol) in benzene (10 mL) at room temperature under nitrogen. The solution was stirred at room temperature for 1 h, diluted with dichloromethane (50 mL), washed with 10% hydrochloric acid (50 mL) and water (2 × 100 mL), extracted with dichloromethane (2 × 100 mL), and dried over Na_2SO_4. After removal of the solvent, a colorless crystalline solid consisting of a 1:1 diastereomeric mixture of **5b′** and **5b″** was obtained (4.20 g, 96% yield). Anal. Calcd for $C_{42}H_{50}O_6$: C, 77.5; H, 7.7. Found: C, 77.7; H, 7.8.

The 1:1 diastereomeric mixture of **5b** (2 g) was dissolved in refluxing hexane (60 mL). After 72 h at 25 °C, the solution was filtered to obtain **5b′** as colorless crystals (single diastereoisomer) (0.85 g, 85% yield): mp 134 °C; $[\alpha]^{25}_{D}$ −248.0 (*c* = 1.0, $CHCl_3$).

^{1}H-NMR ($CDCl_3$) δ 0.41 (m, 2H), 0.63 (d, J = 6.9 Hz, 6H), 0.82 (d, J = 6.6 Hz, 12H), 0.71−1.56 (series of m, 16H), 4.04 (td, J = 10.2 and 3.9 Hz, 2H), 7.16 (dd, J = 7.8 and 1.2 Hz, 2H), 7.24 (dd, J = 6.9 and 1.2 Hz, 2H), 7.41−7.49 (series of m, 4H), 7.80 (dd, J = 8.1 and 0.9 Hz, 2H), 7.86 (dd, J = 8.1 and 0.9 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ 15.70, 20.69, 21.73, 22.50, 24.88, 30.88, 33.72, 39.41, 46.25, 78.37, 118.88, 124.81, 125.04, 126.11, 127.21, 128.68, 129.50, 135.15, 138.02, 147.63, 152.13. IR (KBr pellet) ν 2950 (w), 2940 (m), 1700 (s); 1150 (s), 1105 (s), 905 (s).

The solution was rotoevaporated to dryness to obtain **5b″** (87:13 diastereomeric ratio) (1.15 g, quant): mp 52−4 °C; $[\alpha]^{25}_D$ +229.8 (c = 2.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 0.54 (m, 2H), 0.63 (d, J = 6.6 Hz, 6H), 0.78 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 6.6 Hz, 6H), 0.77−1.70 (series of m, 16H), 4.12 (td, J = 10.2 and 4.2 Hz, 2H), 7.17 (dd, J = 7.8 and 1.2 Hz, 2H), 7.21 (dd, J = 7.2 and 0.9 Hz, 2H), 7.43 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ 15.89, 20.48, 21.85, 22.85, 25.47, 30.96, 33.80, 39.90, 46.53, 78.23, 119.23, 125.01, 125.17, 126.20, 127.57, 128.56, 135.09, 138.34, 147.47, 152.56. IR (KBr pellet) ν 2965 (w), 2945 (m), 1710 (s), 1150 (s), 1005 (s), 910 (s).

Diasteromerically pure **5b′** (1.0 g, 1.59 mmol) in anhydrous THF was cooled to 0 °C under Ar, and $LiAlH_4$ (0.40 g, 10.6 mmol) was added in portions while vigorously stirring. After 2 h, water (50 mL) and 10% HCl were added up to neutralization. The neutral solution was extracted with dichloromethane (2 × 80 mL) and made basic with 100 mL of a 10 M solution of NaOH. The organic layer was dried over Na_2SO_4 and rotoevaporated to obtain enantiomerically pure (−)-menthol (0.48 g, 98% yield). The aqueous solution was acidified with 10% HCl and extracted with dichloromethane (2 × 50 mL). The organic phase was dried (Na_2SO_4) and rotoevaporated to obtain (+)-**5a** as a colorless solid (0.44 g, 98%): mp 116−8 °C (lit.[5] 117−9 °C); $[\alpha]^{25}_D$ +16.5 (c = 1.0, $CHCl_3$).

A sample of **5b″** (87:13 diastereomeric ratio) (1.0 g, 1.59 mmol) was processed in the same way to obtain 0.4 g (88% yield) of the (−)-enantiomer: $[\alpha]^{25}_D$ −12.2 (c = 1.0, $CHCl_3$) corresponding to an enantiomeric purity of 74%.

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