Synergistic Stereoselective Organocatalysis with Indium(III) Salts

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**General Methods.** $^1$H NMR spectra were recorded on Varian Gemini 200 and Varian Mercury 400 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: $\delta = 7.27$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, dt = double triplet, bs = broad signal, pd = pseudo duplet, pt = pseudo triplet, m = multiplet), coupling constants (Hz). If rotamers are present, the chemical shift of the less abundant rotamer is reported between brackets. $^{13}$C NMR spectra were recorded on Varian Gemini 200, Varian MR400 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: $\delta = 77.0$ ppm). GC-MS spectra were taken by El ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. They are reported as: m/z (rel. intense). Chromatographic purification was done with 240-400 mesh silica gel. Determination of diastereomeric ratio and of enantiomeric excess was performed on Agilent Technologies 1200 instrument equipped with a variable wave-length UV detector (reference 420 nm), using Daicel Chiralpak® columns (0.46 cm I.D. x 25 cm), columns and HPLC grade isopropanol and n-hexane as eluting solvents.

Compounds 5a-c were prepared according to the reported procedure.$^1$ All spectra proprieties are according to the literature.$^1$

(6b): Prepared according to the general procedure A. The residue was purified by flash chromatography (SiO$_2$, cyclohexane:Et$_2$O, 7:3) afforded 6b as a yellow oil (53% yield). D.r. 2:1(syn:anti); Diastereoisomer anti ee = 69%; Diastereoisomer syn ee = 85%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IC: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, $\lambda = 210, 254$ nm: Diastereoisomer anti $\tau_{major} = 9.4$ min, $\tau_{minor} = 8.8$ min.; Diastereoisomer syn $\tau_{minor} = 12.7$ min., $\tau_{major} = 9.1$ min; $^1$H NMR (200 MHz, CDCl$_3$) $\delta_{anti+syn} = 0.89$ (t, $J = 3.8$ Hz, 6H), 1.13-1.28 (m, 16H), 1.59 (m, 4H), 2.29 (s, 6H), 2.33 (s, 6H), 2.69 (m, 2H), 3.60-3.70 (m, 2H), 6.23 (d, $J = 11.0$ Hz, 1H, anti), 6.25 (d, $J = 10.6$ Hz, 1H, syn), 6.79-7.10 (m, 6H), 7.12-7.4 (m, 20H), 9.31 (d, $J = 4.2$ Hz, syn), 9.40 (c, $J = 4.6$ Hz, anti); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta_{anti+syn} = 14.0$ (2C), 21.4 (4C), 22.5, 26.9, 27.1 (2C), 27.4, 27.6 (2C), 29.3 (2C), 31.6, 45.8 (syn), 45.9 (anti), 57.7 (syn), 58.5 (anti), 125.0, 125.6 (2C), 125.7, 127.3 (2C), 127.3 (3C), 127.4, 127.6, 127.9, 128.0, 128.1 (2C), 128.2 (3C), 128.3, 128.4 (2C), 129.0, 129.2, 129.4, 129.5, 129.8 (2C),
(6c): Prepared according to the general procedure A. The residue was purified by flash chromatography (SiO$_2$, cyclohexane:Et$_2$O, 7:3) afforded 6c as a yellow oil (71% yield). D.r. 3:1 (syn:anti); Diasteroisomer anti ee = 68%; Diasteroisomer syn ee = 91%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IC: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, λ = 210, 254 nm: Diasteroisomer anti $\tau_{\text{major}} = 15.8$ min, $\tau_{\text{minor}} = 13.9$ min., Diasteroisomer syn $\tau_{\text{minor}} = 14.9$ min., $\tau_{\text{major}} = 17.7$ min; $^1$H NMR (200 MHz, CDCl$_3$) $\delta_{\text{syn}} = 0.91$ (t, $J = 6.4$ Hz, 3H), 1.29 (m, 8H), 1.72-1.76 (m, 2H), 3.30-3.32 (m, 1H), 4.00 (bs, 3H), 4.60-4.62 (m, 1H), 6.92 (d, $J = 9.4$ Hz, 2H), 7.02 (d, $J = 5.4$ Hz, 2H), 7.22-7.28 (m, 10H), 7.34 (d, $J = 7.0$ Hz, 2H), 7.75 (d, $J = 9.2$ Hz, 2H), 9.17 (d, $J = 4.4$ Hz, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta_{\text{syn}} = 14.1$, 22.6, 27.2, 29.0, 29.4, 31.6, 56.0, 99.8, 121.9, 123.2 (2C), 126.3, 127.0 (4C), 128.1 (4C), 128.4, 128.5, 129.2, 129.3, 129.5 (2C), 130.1 (2CH), 132.0, 139.8 (2C), 142.2, 204.4; HRMS m/z [M]$^+$ calcd for C$_{31}$H$_{36}$O: 424.27661; found: 424.27695.

(8): Prepared according to the general procedure A. The crude was diluted with THF (5 mL) at -78 °C for 5 minutes and 2 eq. of DIBALH was slowly added. The reaction was quenched with water (5 mL) and concentrated under reduce pressure. The crude solution was extracted with EtOAc (2 x mL). The collect organic layers were dried over Na$_2$SO$_4$ and concentrated under reduce pressure to give 8 a yellow oil. The residue was purified by flash chromatography (SiO$_2$, cyclohexane:Et$_2$O, 7:3) afforded 8 as a yellow oil (70% yield). D.r. 1:1(syn:anti), Diasteroisomer syn ee = 80%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IC: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, λ = 210, 254 nm: Diasteroisomer anti $\tau_{\text{major}} = 31.3$ min, $\tau_{\text{minor}} = 38.8$ min.; Diasteroisomer syn $\tau_{\text{minor}} = 21.0$ min., $\tau_{\text{major}} = 26.0$ min; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_{\text{anti+syn}} = 0.83-0.89$ (m, 6H), 1.05-1.18 (m, 16H), 1.41-1.59 (m, 4H), 1.85-1.98 (m, 2H), 3.43-3.59 (m, 4H), 3.65-3.76 (m, 2H), 6.41-6.47 (m, 4H), 7.19-7.37 (m, 20H); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta_{\text{anti+syn}} =14.0$ (2C), 22.6, 26.9, 27.2, 28.2, 28.5, 29.4, 29.6, 29.7, 31.8 (2C), 45.4, 45.6, 51.1, 51.8, 62.8, 63.0, 126.2 (4C), 126.3, 126.3, 127.1, 127.2, 127.8 (2C), 128.0 (2C), 128.3, 128.4 (2C), 128.5, 128.6 (2C), 128.7 (2C), 130.3, 131.0, 132.1, 132.7, 137.3, 143.3, 143.6 (2C).

Benzylic alcohols 9a-g were prepared according to the reported procedure. All spectra proprieties are according to the literature.
(9a): A vial equipped with a magnetic stir bar under inert atmosphere was charged with p-bromoanisole (1 mmol, 125 μL), in 0.5 mL THF at -78°C. The mixture was stirred and a solution of n-BuLi (2.5 M in THF, 0.500 mL) was slowly added. The yellow solution was slowly warmed at r.t and stirring for 1 hour at the same temperature. After that the solution was cooled at 0 °C and p-NMe2-benzaldehyde (1 mmol, 149 mg) was added. The solution was warmed at r.t and stirring until no further conversion take place (controlled by TLC). The reaction was worked up with aqueous solution of NH4Cl (10 mL). The organic layer was separated and washed several times with acid water and the aqueous layer was extracted with EtOAc (2 x 25 mL). The collect organic layers were dried over Na2SO4 and concentrated under reduce pressure obtain an orange oil. The residue was purified by flash chromatography (SiO2, cyclohexane:Et2O, 7:3) to give 9a as a white solid (70% yield); 1H NMR (400 MHz, CDCl3) δ = 1.56 (s, 1H), 2.94 (s, 6H), 3.80 (s, 3H), 5.75 (m, 1H), 6.70 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ = 40.7 (2C), 55.2, 75.6, 112.5 (2C), 113.5(2C), 127.6 (3C), 127.5 (3C), 136.6, 158.8.

(9b): A vial equipped with magnetic stir bar and under inert atmosphere was charged with phenylmagnesium bromide (1.0 M in THF, 0.2 mL) in anhydrous THF (0.1 M). The solution was stirred during 5 minutes at 0 °C, and p-NMe2-benzaldehyde (0.2 mmol, 30 mg) was added at the same temperature. The mixture was warmed at r.t and stirring until no further conversion took place (checked by TLC). The reaction was worked up with H2O (10 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 25 mL). The collect organic layers were dried over Na2SO4 and concentrated under reduce pressure obtain a yellow oil. The residue was purified by flash chromatography (SiO2, cyclohexane:Et2O, 7:3) give 9b as yellow oil (yield 90%); 1H NMR (400 MHz, CDCl3) δ = 2.00 (s, 1H), 2.92 (s, 6H), 5.76 (s, 1H), 6.68 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.23 (m, 1H), 7.31 (t, J = 7.2 Hz, 2H), 7.38 (d, J = 6.4 Hz, 2H); 13C NMR (100MHz, CDCl3) δ= 40.4; 40.5, 75.8, 112.4 (2C), 126.2, 126.9 (2C), 127.6 (2C), 128.1 (2C), 131.8, 144.0, 150.0.

(9c): A vial equipped with magnetic stir bar and under inert atmosphere was charged with 3-bromothiophene (1 mmol, 163 mg) and anhydrous THF (1 M). The solution was stirred at -78°C for 5 minutes, and a solution of n-BuLi (2.5 M in hexane, 0.500 mL) was slowly added. The mixture was stirred during 1 hours at the same temperature. After p-NMe2-benzaldehyde (1 mmol, 149 mg) was slowly added at the same temperature and the solution was warmed at 0 °C and stirring until no further conversion took place (controlled by TLC). The reaction was worked up with saturated solution of NH4Cl (10 mL). The organic layer was separated, and the aqueous layer
was extracted with EtOAc (2 x 25 mL). The collect organic layers were dried over Na₂SO₄ and concentrated under reduce pressure obtain yellow oil. The residue was purified by flash chromatography (SiO₂, cyclohexane: Et₂O, 7:3) obtain 8c as an orange solid (60% yield); ¹H NMR (400 MHz, CDCl₃) δ = 2.44 (bs, 1H), 2.94 (s, 6H), 5.94 (s, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.8 (d, J = 3.4 Hz, 1H), 6.90 (t, J = 4.0 Hz, 1H), 7.20-7.24 (m, 1H), 7.28 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 40.6 (2C). 72.3, 112.3 (2C), 124.3, 124.8, 126.5, 127.4 (2C), 131.2, 148.8, 150.3.

(9e): A vial equipped with magnetic stir bar and under inert atmosphere was charged with 2-iodothiophene (4.4 mmol, 487 µl) and anhydrous THF (5 mL). The solution was stirred at -78º C for 5 minutes, and a solution of n-BuLi (2.5 M in hexane, 1.9 mL) was slowly added. The mixture was stirred during 1 hours at the same temperature. After p-OMe-benzaldehyde (3.67 mmol, 500 mg) was slowly added at the same temperature and the solution was warmed at 0 ºC and stirring until no further conversion took place (controlled by TLC). The reaction was worked up with saturated solution of NH₄Cl (10 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 25mL). The collect organic layers were dried over Na₂SO₄ and concentrated under reduce pressure obtain yellow oil. The residue was purified by flash chromatography (SiO₂, cyclohexane:EtOAc, 8:2) obtain 9e as an white solid (60% yield); ¹H NMR (400 MHz, CDCl₃) δ = 2.38 (d, J = 3.9 Hz, 1H), 3.82 (s, 3H), 6.03 (d, J = 3.5 Hz, 1H), 6.89 (m, 1H), 6.91 (d, J = 8.7 Hz, 1H), 6.95 (dd, J = 3.5 Hz, J = 5.1 Hz, 1H), 7.26 (dd, J = 4.7 Hz, J = 5.9 Hz, 1H), 7.38 (d, J = 8.7 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ = 55.1 (2C), 71.8, 113.7 (2C), 124.5, 125.0, 126.5, 127.6 (2C), 135.4, 148.4, 159.1; ESI-MS: m/z = 203.1 [M - H₂O]+ (100), 243.1 [M + Na]+ (23).

(9f): ¹H NMR (400 MHz, CDCl₃, 25°C): δ = -0.08 (s, 6H), 0.92 (s, 9H), 1.83-1.91 (m, 1H), 1.91-2.02 (m, 1H), 2.92 (s, 6H), 3.40 (bs, 1H), 3. 82 (m, 2H), 4.84 (dd, J = 3.5 Hz, J = 8.3 Hz, 1H), 6.72 (d, J = 8.7 Hz, 2H), 7.23 (d, J= 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = -5.5 (2C), 18.1, 25.9 (3C), 40.7 (2C), 62.1, 73.4, 112.5 (2C), 126.6 (2C), 132.6, 150; ESI-MS: m/z = 292.3 [M - OH]+ (100), 310.3 [M + H]+ (67), 332.1 [M + Na]+ (20), 641.3 [2M + Na]+ (11).

(9g): ¹H NMR (400 MHz, CDCl₃): δ = 1.42 (s, 9H), 1.50-1.61 (m, 1H), 1.61-1.76 (m, 2H), 1.76-1.85 (m, 1H), 2.95 (s, 6H), 3.57-3.77 (m, 2H), 4.58 (dd, J = 5.5 Hz, J = 7.5 Hz, 1H), 6.71 (d, J = 9.1 Hz, 2H), 7.12 (m, 3H), 7.19 (d, J= 8.7 Hz, 2H); 7.32 (t, J = 7.9 Hz, 2H) ¹³C NMR (100 MHz, CDCl₃, 25°C): δ = 25.0, 28.3 (3C), 35.6, 40.7 (2C), 49.7, 74.0, 80.0, 112.6 (2C), 125.9 (2C), 126.8
(2C), 127.1, 128.7 (2C), 132.6, 142.4, 150.2, 154.8; ESI-MS: \( m/z = 367.3 \ [M - OH]^+ \), 407.1 \([M + Na]^+ \) (100), 791.3 \([2M + Na]^+ \) (34).

All spectra proprieties for \( 10a,g \), and \( 12 \) are according to the literature.2

(10a): Prepared according to the general procedure B. The crude was diluted with MeOH (15 mL) at 0 ºC for 5 minutes and 2 eq. of NaBH₄ was slowly added. The reaction was quenched with water (5 mL) and concentrated under reduce pressure. The crude solution was extracted with EtOAc (2 x mL). The collect organic layers were dried over Na₂SO₄ and concentrated under reduce pressure to give \( 10a \) a yellow oil. The residue was purified by flash chromatography (SiO₂, cyclohexane:Et₂O, 7:3) afforded \( 10a \) as a yellow oil (84% yield). D.r. 2:1 \((anti: syn)\); Diasteroisomer \( anti \) ee = 95%; Diasteroisomer \( syn \) ee = 92%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IC: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, \( \lambda = 210, 254 \) nm: Diasteroisomer \( anti \) \( \tau_{major} = 39.2 \) min, \( \tau_{minor} = 40.3 \) min.; Diasteroisomer \( syn \) \( \tau_{minor} = 42.3 \) min., \( \tau_{major} = 43.0 \) min; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta = 0.93 \) \((d, J = 6.7 \) Hz, 3H), 0.96 \((d, J = 6.6 \) Hz, 3H), 1.58 \((s, 2H), 2.87 \((s, 6H, anti), 2.89 \((s, 6H, syn), 3.44-3.37 \((m, 2H), 3.55 \((d, J = 11.2 \) Hz, 1H), 3.57 \((d, J = 10.8 \) Hz, 1H), 3.61-3.53 \((m, 2H), 3.75 \((s, 3H, syn), 3.76 \((s, 3H, anti), 6.66 \((d, J = 8.8 \) Hz, 2H), 6.67 \((d, J = 8.7 \) Hz, 2H), 6.80 \((d, J = 8.6 \) Hz, 2H), 6.81 \((d, J = 8.4 \) Hz, 2H), 7.14 \((d, J = 8.6 \) Hz, 2H), 7.15 \((d, J = 8.6 \) Hz, 2H), 7.20 \((d, J = 8.6 \) Hz, 2H), 7.21 \((d, J = 8.6 \) Hz, 2H); \(^{13}\)C NMR (50 MHz, CDCl₃) \( \delta = 16.3 \) \( (2C), 39.5, 40.6, 53.8, 55.1, 67.0 \((2C), 112.8, 113.0, 113.8, 114.0, 128.3, 128.5 \((2C), 128.6 \((2C), 132.2, 136.8, 149.1, 157.8; \) ESI-MS: \( m/z = 300.1 \ [M + H]^+ \) (100), 322.2 \([M + Na]^+ \) (16).

(10b): Prepared according to the general procedure B. The residue was purified by flash chromatography (SiO₂, cyclohexane:Et₂O, 9:1) affording \( 10b \) as a colourless oil (80% yield); D.r. 2:1 \((anti: syn)\); Diasteroisomer \( anti \) ee = 98%; Diasteroisomer \( syn \) ee = 96%; Ees were determined by chiral HPLC with a Daicel Chiralcel column OD-H: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, \( \lambda = 210, 254 \) nm: Diasteroisomer \( anti \) \( \tau_{major} = 16.3 \) min, \( \tau_{minor} = 15.5 \) min.; Diasteroisomer \( syn \) \( \tau_{minor} = 24.1 \) min., \( \tau_{major} = 18.2 \) min; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta_{syn+anti} = 1.02 \) \((d, J = 6.65 \) Hz, 3H, \( anti), 1.06 \( (d, J = 6.9 \) Hz, \( syn), 2.89 \((s, 6H, anti), 2.91 \((s, 6H, syn), 3.19-3.29 \((m, 2H), 3.98 \((d, J = 11.1 \) Hz, \( anti), 3.99 \((d, J = 10.9 \) Hz, \( syn), 6.66 \((t, J = 8.9 \) Hz, 4H), 7.19-7.10 \((m, 6H), 7.30-7.23 \((m, 8H), 9.58 \((d, J = 3.3 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl₃) \( \delta = 13.5 \) \( (syn), 13.7 \((anti), 29.6 \((2), 40.5 \((2), 50.2 \((2C), 52.6 \((2C), 112.8 \((2C), 112.8 \((2C), 126.3, 126.4, 127.9 \((2C), 128.0 \((4C), 128.6, 128.61 \((4C), 128.7, 129.8 \((2C), 142.9 \((2C), 149.3 \((2C), 204.7 \((2C); \) ESI-MS: \( m/z = 268.3 \ [M + H]^+ \) (100), 290.2 \([M + Na]^+ \) (22).
(12): Prepared according to the general procedure B. The crude was diluted with MeOH (15 mL) at 0 °C for 5 minutes and 2 eq. of NaBH₄ was slowly added. The reaction was quenched with water (5 mL) and concentrated under reduce pressure. The crude solution was extracted with EtOAc (2 x mL). The collect organic layers were dried over Na₂SO₄ and concentrated under reduce pressure to give 12 a yellow oil. The residue was purified by flash chromatography (SiO₂, cyclohexane: EtOAc, 9:1) affording 12 as a colorless oil (88% yield); D.r. 1.1:1 (anti:syn) determined by integration of ArCH ¹H NMR (400 MHz, CDCl₃) signals: δanti = 9.70 (d, J = 3.0 Hz, 1H), δsyn = 9.57 (d, J = 3.0 Hz, 1H); Diasteroisomer anti ee = 88%; Diasteroisomer syn ee = 86%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IB: n-hexane/i-PrOH from 99:1 to 90:10 in 30 min, flow 0.50 mL/min, 30°C, λ = 210, 254 nm: Diasteroisomer anti τmajor = 26.8 min, τminor = 30.0 min.; Diasteroisomer syn τminor = 31.6 min, τmajor = 28.5 min; ¹H NMR (400 MHz, CDCl₃) δanti = 0.92 (d, J = 6.7 Hz, 3H), 2.30-2.46 (m, 1H), 3.79 (s, 3H), 3.51 (dd, J = 5.9 Hz, J = 11.0 Hz, 1H), 3.61 (dd, J = 4.3 Hz, J = 10.6 Hz, 1H), 4.07 (d, J = 9.8 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.89-6.92 (m, 2H), 7.12-7.15 (m, 1H), 7.24 (d, J = 8.7 Hz, 2H); δsyn = 1.05 (d, J = 6.7 Hz, 3H), 2.30-2.46 (m, 1H), 3.37 (dd, J = 5.9 Hz, J = 11.0 Hz, 1H), 3.53 (dd, J = 5.9 Hz, J = 11.0 Hz, 1H), 3.78 (s, 3H), 4.03 (d, J = 10.2 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.89-6.92 (m, 2H), 7.12-7.15 (m, 1H), 7.24 (d, J = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, 25°C): δanti = 15.6, 41.6, 49.7, 55.2, 66.4, 114.5 (2C), 123.5, 124.0, 126.6, 128.8 (2C), 135.5, 148.4, 158.2; δsyn = 16.1, 41.5, 48.9, 55.2, 66.2, 113.9 (2C), 123.5, 124.2, 126.5, 129.2 (2C), 135.5, 148.1, 158.2; ESI-MS: m/z = 263.1 [M + H]+ (100), 285.2 [M + Na]+ (13).

(10f): Prepared according to the general procedure B. The residue was purified by flash chromatography (SiO₂, cyclohexane:E₂O, 9:1) affording 10f as a colourless oil (85%, yield); D.r. 6:1 (anti:syn) determined by integration of ArCH ¹H NMR (400 MHz, CDCl₃) signals: δanti = 9.65 (d, J = 3.5 Hz, 1H), δsyn = 9.56 (d, J = 2.4 Hz, 1H); Diasteroisomer anti ee = 99%; Diasteroisomer syn ee = 86%; Ees were determined by chiral HPLC with a Daicel Chiralcel column IC: n-hexane/i-PrOH 98:2, flow 0.50 mL/min, 30°C, λ = 210, 254 nm: Diasteroisomer anti τmajor = 12.6 min, τminor = 12.3 min.; Diasteroisomer syn τmajor = 20.9 min., τminor = 15.3 min; ¹H NMR (400 MHz, CDCl₃, 25°C): δanti = -0.03 (s, 6H), 0.87 (s, 9H), 0.89 (d, J = 7.8 Hz, 3H), 1.77-1.93 (m, 2H), 2.48-2.61 (m, 1H), 2.94 (s, 6H), 3.00-3.06 (m, 1H), 3.33-3.42 (m, 1H), 3.45-3.55 (m, 1H), 6.69 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 9.65 (d, J = 3.5 Hz, 1H); δsyn = -0.02 (s, 6H), 0.87 (s, 9H), 1.10 (d, J = 7.1 Hz, 3H), 1.77-1.93 (m, 2H), 2.48-2.61 (m, 1H), 2.93 (s, 6H), 3.00-3.06 (m, 1H), 3.33-3.42 (m, 1H), 3.45-3.55 (m, 1H), 6.69 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 9.56 (d, J = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, 25°C): δanti = -5.4 (2C), 12.0, 25.3 (3C), 29.7, 37.2, 40.7 (2C), 41.7, 52.1, 60.7, 112.7 (2C), 128.9, 129.0 (2C), 149.6, 205.5; δsyn = -5.4 (2C), 12.0, 25.9 (3C), 29.7, 37.2,
40.7 (2C), 41.7, 52.1, 60.7, 112.7 (2C), 128.9, 129.0 (2C), 149.6, 205.5; ESI-MS: \( m/z = 350.3 \) [M+H]\(^+\), 372.2 [M+Na]\(^+\), 721.3 [2M+Na]\(^+\).

The propargylic alcohols 13a, b were prepared according to the reported procedure.\(^3\) All spectra proprieties are according to the literature.\(^3\)

\textbf{(13a):} yellow oil; 95%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 0.07 \) (s, 6H), 0.96 (s, 9H), 2.48 (dt, \( J = 2 \) Hz, \( J = 7.2 \) Hz, 2H), 2.91 (s, 6H), 3.74 (t, \( J = 7.2 \) Hz, 2H), 5.32 (s, 1H), 6.69 (d, \( J = 6.8 \) Hz, 2H), 7.37 (d, \( J = 6.8 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = -5.43 \) (2C), 18.1, 23.1, 25.7 (3C), 40.4 (2C), 61.7, 64.2, 81.5, 83.1, 112.3 (2C), 127.5 (2C), 129.3, 150.4; ESI-MS: \( m/z = 316.1 \) [M - OH]\(^+\) (100), 334.1 [M + H]\(^+\) (83), 356.1 [M + Na]\(^+\) (12).

\textbf{(13b):} dark red oil; 96%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.24 \) (t, \( J = 3.2 \) Hz, 6H), 2.94 (s, 6H), 3.21 (bs, 1H), 3.59-3.64 (m, 2H), 3.74-3.78 (m, 2H), 5.35 (d, \( J = 0.8 \) Hz, 1H), 5.42 (bs, 1H), 6.71 (d, \( J = 6.8 \) Hz, 2H), 7.38 (d, \( J = 6.8 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 14.7 \) (2C), 40.2 (2C), 60.5 (2C), 63.7, 77.3, 85.7, 91.0, 112.1 (2C), 127.5 (2C), 128.1, 150.3; ESI-MS: \( m/z = 260.1 \) [M - OH]\(^+\), 278.1 [M + H]\(^+\), 300.0 [M + Na]\(^+\).

References


\[
\text{HO} - \text{MeO}_2 \text{NMe}_2 10a \text{ reduced}
\]
14a reduced
14b
HPLC Traces

H
Ph
Ph
CHO
nC6H13

Racemic

Enantioselective
Racemic

Enantioselective
Racemic

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