Differentiating Catalysis in the Dearomative [4+2]-Cycloaddition Involving Enals and Heteroaromatic Aldehydes

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1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for $^1$H and 176 MHz for $^{13}$C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl$_3$: 7.26 ppm for $^1$H NMR, 77.16 ppm for $^{13}$C NMR). Mass spectra were recorded on a Bruker Maxis Impact quadrupole-time-of-flight spectrometer using electrospray (ES+) ionization (referred to the mass of the charged species). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or Hanessian’s stain. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). The enantiomeric ratio (er) of the products were determined by Ultra Performance Convergence Chromatography (UPC$^2$) using Daicel Chiralpak IA column as chiral stationary phases. Aldehydes 2 were synthesized according to the literature procedure.$^1$ Heteroaromatic aldehydes 1 were prepared from the corresponding starting materials following the literature procedure.$^2$

(1) Daubresse, N.; Francesch, C.; Rolando, C. Phase transfer Wittig reaction with 1,3-dioxolan-2-yl-methyltriphenyl phosphonium salts: An efficient method for vinylogation of aromatic aldehydes. *Tetrahedron* **1998**, *54*, 10761-10770.
(2) Bojanowski, J.; Skrzyńska, A.; Albrecht, A. Dearomatizative and Decarboxylative Reaction Cascade in the Aminocatalytic Synthesis of 3,4-Dihydrocoumarins. *Asian J. Org. Chem.* **2019**, *8*, 844-848.
2. Differentiating catalysis in the [4+2]-cycloaddition – general procedure

In an ordinary 4 mL glass vial equipped with a magnetic stirring bar α,β-unsaturated aldehyde 2 (0.12 mmol, 1.2 equiv.) and heteroaromatic aldehyde 1 (0.1 mmol, 1 equiv.) were dissolved in Et₂O (0.4 mL) and catalyst 4c (4.7 mg, 0.02 mmol, 0.2 equiv.) and benzoic acid (4.9 mg, 0.04 mmol, 0.4 equiv.) were added and the reaction mixture was stirred in room temperature for indicated time. The progress of the reaction was controlled by ¹H NMR spectroscopy. After full conversion of the starting material 1, the reaction mixture was directly subjected to column chromatography on silica gel (hexanes : diethyl ether 85:15) to afford pure products 3a-o.

(6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a

Following the general procedure, using 1a (18.6 mg), product 3a (>20:1 dr in a crude reaction mixture) was isolated in 95% yield (28.5 mg) as light-yellow solid (m.p. = 148 – 150 °C after recrystallization from hexane/diethyl ether mixture). ¹H NMR (700 MHz, CDCl₃) δ 9.54 (s, 1H), 7.46 (s, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.28 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 7.05 – 7.04 (m, 2H), 6.60 (d, J = 2.0 Hz, 1H), 4.44 (s, 1H), 4.34 (s, 1H). ¹³C NMR (176 MHz, CDCl₃) δ 191.3, 157.6, 144.3, 142.6, 141.6, 139.7, 136.5, 129.2 (2C), 129.0 (2C), 127.6, 127.4, 127.0 (2C), 126.8 (2C), 117.6, 108.6, 47.4, 47.1. The er was determined by UPC² using a chiral Chiralpack IA column gradient from 100% CO₂ up to 40%; i-PrOH, flow rate = 2.2 mL/min, l = 295 nm) tR = 3.1 min (major), 2.9 min (minor), (>99:1 er). [α]D²³ = + 625.9 (c = 1.0, CHCl₃). HRMS (ESI) m/z [M+H]+ Calcd. for C₂₁H₁₇O₂+: 301.1224; found: 301.1230.
(6S,7S)-6-(4-Nitrophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3b

Following the general procedure, using 1a (18.6 mg), product 3b (10.5:1 dr in a crude reaction mixture) was isolated in 69% yield (23.8 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) δ 9.56 (s, 1H), 8.15 – 8.13 (m, 2H), 7.55 (s, 1H), 7.47 (d, $J = 2.0$ Hz, 1H), 7.43 (d, $J = 8.6$ Hz, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.06 – 7.04 (m, 2H), 6.65 (d, $J = 2.0$ Hz, 1H), 4.53 (s, 1H), 4.31 (s, 1H). $^{13}$C NMR (176 MHz, CDCl$_3$) δ 190.9, 157.0, 149.7, 147.4, 144.9, 140.7, 135.3, 129.3 (2C), 128.0 (2C), 127.9, 126.7 (2C), 124.3 (2C), 117.7, 108.7, 47.0, 46.9. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; i-PrOH, flow rate = 2.2 mL/min, l = 358 nm) tR = 4.0 min (major), 3.7 min (minor), (97:3 er). [$\alpha$]$_D^{22}$ = +776.8 (c = 1.0, CHCl$_3$). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{21}$H$_{16}$NO$_4$+: 346.1074; found: 346.1085.

(6S,7S)-6-(4-Chlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3c

Following the general procedure, using 1a (18.6 mg), product 3c (>20:1 dr in a crude reaction mixture) was isolated in 71% yield (23.7 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) δ 9.52 (s, 1H), 7.46 (s, 1H), 7.42 (d, $J = 2.0$ Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.19 – 7.17 (m, 2H), 7.04 – 7.01 (m, 2H), 6.60 (d, $J = 2.0$ Hz, 1H), 4.39 (s, 1H), 4.27 (s, 1H). $^{13}$C NMR (176 MHz, CDCl$_3$) δ 191.1, 157.3, 144.5, 141.2, 141.0, 139.8, 136.1, 133.2, 129.2 (2C), 129.1 (2C), 128.4 (2C), 127.7, 126.7 (2C), 117.6, 108.6, 47.3, 46.4. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; i-PrOH, flow rate = 2.2 mL/min, l = 330 nm) tR = 3.6 min (major), 3.2 min (minor), (98:2 er). [$\alpha$]$_D^{23}$ = +753.3 (c = 1.0, CHCl$_3$). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{21}$H$_{16}$ClO$_2$+: 335.0761; found: 335.0769.

(6S,7S)-7-Phenyl-6-(p-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3d

Following the general procedure, using 1a (18.6 mg), product 3d (>20:1 dr in a crude reaction mixture) was isolated in 69% yield (21.7 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) δ 9.53 (s, 1H), 7.43 (s, 1H), 7.41 (d, $J = 2.0$ Hz, 1H), 7.28 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.16 –
7.13 (m, 2H), 7.07 – 7.06 (m, 2H), 7.05 – 7.04 (m, 2H), 6.59 (d, J = 2.0 Hz, 1H), 4.40 (d, J = 1.4 Hz, 1H), 4.32 (s, 1H), 2.30 (s, 3H). 13C NMR (176 MHz, CDCl3) δ 191.3, 157.6, 144.3, 141.6, 139.7, 139.5, 137.0, 136.6, 129.6 (2C), 129.1 (2C), 127.5, 126.9 (2C), 126.8 (2C), 117.6, 108.6, 47.5, 46.7, 21.2. The er was determined by UPC2 using a chiral Chiralpack IA column gradient from 100% CO2 up to 40%; i-PrOH, flow rate = 2.2 mL/min, l = 230 nm) tR = 3.3 min (major), 3.0 min (minor), (98:2 er). [α]D23 = +329.3 (c = 1.0, CHCl3). HRMS (ESI) m/z [M+H]+ Calcd. for C22H19O2+: 315.1380; found: 315.1388.

(6S,7S)-6-(4-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3e

Following the general procedure, using 1a (18.6 mg), product 3e (>20:1 dr in a crude reaction mixture) was isolated in 76% yield (25.1 mg) as light-yellow oil. 1H NMR (700 MHz, CDCl3) δ 9.52 (s, 1H), 7.41 – 7.40 (m, 2H), 7.28 – 7.27 (m, 2H), 7.24 – 7.21 (m, 1H), 7.18 – 7.16 (m, 2H), 7.05 – 7.01 (m, 2H), 6.79 – 6.77 (m, 2H), 6.59 (d, J = 2.1 Hz, 1H), 4.37 (s, 1H), 4.30 (s, 1H), 3.76 (s, 3H). 13C NMR (176 MHz, CDCl3) δ 191.4, 158.9, 157.6, 144.3, 141.6, 139.3, 136.8, 134.8, 129.1 (2C), 128.1 (2C), 127.5, 126.8 (2C), 117.6, 114.3 (2C), 108.6, 55.4, 47.5, 46.3. The er was determined by UPC2 using a chiral Chiralpack IA column gradient from 100% CO2 up to 40%; i-PrOH, flow rate = 2.2 mL/min, l = 215 nm) tR = 3.6 min (major), 3.3 min (minor), (98:2 er). [α]D23 = +593.4 (c = 1.0, CHCl3). HRMS (ESI) m/z [M+H]+ Calcd. for C22H19O3+: 331.1329; found: 331.1337.

(6S,7S)-6-(3-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3f

Following the general procedure, using 1a (18.6 mg), product 3f (>20:1 dr in a crude reaction mixture) was isolated in 68% yield (22.4 mg) as light-yellow oil. 1H NMR (700 MHz, CDCl3) δ 9.53 (s, 1H), 7.45 (s, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.19 – 7.17 (m, 1H), 7.06 – 7.03 (m, 2H), 6.88 – 6.86 (m, 1H), 6.81 (d, J = 2.0 Hz, 1H), 6.78 – 6.76 (m, 1H), 6.58 (d, J = 2.2 Hz, 1H), 4.41 (s, 1H), 4.35 (s, 1H), 3.76 (s, 3H). 13C NMR (176 MHz, CDCl3) δ 191.3, 160.0, 157.6, 144.3, 144.1, 141.6, 139.8, 136.3, 130.0, 129.2 (2C), 127.5, 126.8 (2C), 119.4, 117.5, 113.2, 112.3, 108.6, 55.3, 47.3, 47.0. The er was determined by UPC2 using a chiral Chiralpack IA column gradient from 100% CO2 up to
40%; i-PrOH, flow rate = 2.2 mL/min, λ = 251 nm) tR = 3.2 min (major), 3.1 min (minor), (98:2 er). \([\alpha]_D^{23} = +468.0 \ (c = 1.0, \text{CHCl}_3)\). HRMS (ESI) m/z [M+H]⁺ Calcd. for C₂₂H₁₉O₃⁺ : 331.1329; found: 331.1338.

(6S,7S)-6-(2-methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3g

Following the general procedure, using 1a (18.6 mg), product 3g (>20:1 dr in a crude reaction mixture) was isolated in 57% yield (18.8 mg) as light-yellow oil. \(^1\)H NMR (700 MHz, CDCl₃) δ 9.54 (s, 1H), 7.60 (s, 1H), 7.36 – 7.35 (d, J = 1.8 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 7.20 – 7.19 (m, 1H), 7.10 – 7.06 (m, 2H), 6.95 – 6.94 (m, 1H), 6.88 (d, J = 1.8 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.59 (s, 1H), 4.86 (s, 1H), 4.28 (s, 1H), 4.00 (s, 3H). \(^{13}\)C NMR (176 MHz, CDCl₃) δ 191.3, 158.2, 157.0, 144.1, 141.6, 141.2, 135.4, 128.8 (2C), 128.4, 128.3, 127.2, 127.0 (2C), 126.9, 120.4, 117.7, 111.2, 108.5, 55.6, 45.9, 40.7. The er was determined by UPC² using a chiral Chiralpack IA column gradient from 100% CO₂ up to 40%; i-PrOH, flow rate = 2.2 mL/min, λ = 339 nm) tR = 3.2 min (major), 3.0 min (minor), (>99:1 er). \([\alpha]_D^{23} = +402.2 \ (c = 1.0, \text{CHCl}_3)\). HRMS (ESI) m/z [M+H]⁺ Calcd. for C₂₂H₁₉O₃⁺ : 331.1329; found: 331.1340.

(6R,7S)-6-(2,4-Dichlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3h

Following the general procedure, using 1a (18.6 mg), product 3h (>20:1 dr in a crude reaction mixture) was isolated in 70% yield (25.8 mg) as light-yellow oil. \(^1\)H NMR (700 MHz, CDCl₃) δ 9.57 (s, 1H), 7.43 (s, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.28 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.05 – 7.01 (m, 2H), 6.56 (d, J = 1.9 Hz, 1H), 6.22 (dd, J = 3.2, 1.9 Hz, 1H), 5.96 (d, J = 3.2 Hz, 1H), 4.61 (s, 1H), 4.60 (s, 1H). \(^{13}\)C NMR (176 MHz, CDCl₃) δ 190.8, 157.8, 154.1, 144.2 (2C), 142.0 (2C), 140.5, 140.0, 133.5, 129.1, 127.6 (2C), 126.9 (2C), 117.2, 110.3, 108.7, 105.8, 43.9, 40.5. The er was determined by UPC² using a chiral Chiralpack IA column gradient from 100% CO₂ up to 40%; ACN, flow rate = 2.2 mL/min, λ = 235 nm) tR = 3.0 min (major), 3.4 min (minor), (90:10 er). \([\alpha]_D^{23} = +591.1 \ (c = 1.0, \text{CHCl}_3)\). HRMS (ESI) m/z [M+H]⁺ Calcd. for C₂₁H₁₅Cl₂O₂⁺ : 369.0444; found: 369.0455.
**(6R,7S)-6-(Furan-2-yl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3i**

Following the general procedure, using 1a (18.6 mg), product 3i (>20:1 dr in a crude reaction mixture) was isolated in 64% yield (18.6 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.55 (s, 1H), 7.64 (s, 1H), 7.48 (d, $J$ = 2.0 Hz, 1H), 7.39 (d, $J$ = 2.1 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.14 – 7.12 (m, 2H), 7.05 (dd, $J$ = 8.4, 2.0 Hz, 1H), 6.91 (d, $J$ = 8.4 Hz, 1H), 6.60 (d, $J$ = 2.1 Hz, 1H), 4.88 (s, 1H), 4.20 (s, 1H). $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 190.7, 157.4, 144.6, 141.2, 140.4, 136.5, 135.3, 134.5, 133.7, 130.3, 129.2, 127.7, 127.3, 127.2, 117.6, 108.5, 46.0, 42.8. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; ACN, flow rate = 2.2 mL/min, $l$ = 237 nm) $t$R = 2.5 min (major), 2.7 min (minor), (95:5 er). $[\alpha]_D^{23}$ = + 614.1 (c = 1.0, CHCl$_3$). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{19}$H$_{15}$O$_3$ + : 291.1016; found: 291.1022.

**(6S,7S)-7-(4-Fluorophenyl)-6-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3j**

Following the general procedure, using 1b (20.4 mg), product 3j (>20:1 dr in a crude reaction mixture) was isolated in 90% yield (28.6 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.48 (s, 1H), 7.45 (d, $J$ = 2.1 Hz, 1H), 7.31 – 7.22 (m, 5H), 7.06 – 6.97 (m, 4H), 6.63 (d, $J$ = 2.1 Hz, 1H), 4.41 (s, 1H), 4.35 (s, 1H). $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 191.3, 162.8 (d, $J$ = 246.1 Hz, 2C), 161.5, 157.3, 144.5, 142.3, 139.6, 137.3, 136.3, 129.0, 128.4 (d, $J$ = 8.2 Hz, 2C), 127.5, 127.0, 117.6, 116.0 (d, $J$ = 21.2 Hz, 2C), 108.6, 47.2, 46.5. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; i-PrOH, flow rate = 2.2 mL/min, $l$ = 244 nm) $t$R= 3.0 min (major), 2.7 min (minor), (97:3 er). $[\alpha]_D^{23}$ = + 734.4 (c = 1.0, CHCl$_3$). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{21}$H$_{16}$FO$_2$ + : 319.1129; found: 319.1141.

**(6S,7S)-6-Phenyl-7-(p-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3k**

Following the general procedure, using 1c (20.0 mg), product 3k (15:1 dr in a crude reaction mixture) was isolated in 56% yield (17.6 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.54 (s, 1H), 7.45 (s, 1H), 7.41 (dd, $J$ = 2.0, 0.6 Hz, 1H), 7.27 (s, 4H), 7.25 – 7.21 (m, 1H), 7.11 – 7.08 (m,
Following the general procedure, using 1d (21.6 mg), product 3l (>20:1 dr in a crude reaction mixture) was isolated in 93% yield (30.7 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.54 (s, 1H), 7.45 (s, 1H), 7.42 (d, $J$ = 2.1 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.24 – 7.18 (m, 2H), 6.79 – 6.77 (m, 1H), 6.68 – 6.67 (m, 1H), 6.59 (d, $J$ = 2.1 Hz, 1H), 6.58 – 6.57 (m, 1H), 4.44 (s, 1H), 4.32 (s, 1H), 3.77 (s, 3H). $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 191.3, 160.1, 157.4, 146.9, 144.3, 142.9, 139.5, 139.3, 136.7, 134.9, 131.3, 129.0, 127.4, 127.3, 127.0, 126.6, 126.5, 118.4, 108.5, 85.3, 46.4, 43.1, 27.6. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; $i$-PrOH, flow rate = 2.2 mL/min, l = 230 nm) tR = 3.2 min (major), 3.1 min (minor), (81:19 er). [α]$_D^{23}$ = + 692.2 (c = 1.0, CHCl$_3$). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{22}$H$_{19}$O$_3^+$ : 331.1329; found: 331.1343.

Following the general procedure, using 1e (20.0 mg), product 3m (6:1 dr in a crude reaction mixture) was isolated in 67% yield (21.0 mg) as light-yellow oil. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.51 (s, 1H), 7.44 (d, $J$ = 3.6 Hz, 2H), 7.32 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 7.14 (td, $J$ = 7.6, 1.3 Hz, 1H), 7.05 (td, $J$ = 7.6, 1.3 Hz, 1H), 6.63 (d, $J$ = 2.0 Hz, 1H), 6.60 (dd, $J$ = 7.6, 1.3 Hz, 1H), 4.59 (d, $J$ = 1.3 Hz, 1H), 4.28 (d, $J$ = 1.3 Hz, 1H), 2.51 (s, 3H). $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 191.3, 157.9, 146.9, 144.3, 142.9, 139.5, 139.3, 136.7, 134.9, 131.3, 129.0, 127.4, 127.3, 127.0, 126.6, 126.5, 118.4, 108.5, 85.3, 46.4, 43.1, 27.6. The er was determined by UPC$^2$ using a chiral Chiralpack IA column gradient from 100% CO$_2$ up to 40%; $i$-
PrOH, flow rate = 2.2 mL/min, l = 248 nm) tR = 2.7 min (major), 2.9 min (minor), (>99:1 er). [α]_D^{23} = + 496.5 (c = 1.0, CHCl₃). HRMS (ESI) m/z [M+H]^+ Calcd. for C_{22}H_{16}O₂^+: 315.1380; found: 315.1388.

(6S,7R)-6-Phenyl-7-vinyl-6,7-dihydrobenzofuran-5-carbaldehyde 3n

Following the general procedure, using 1f (13.6 mg), product 3n (>20:1 dr in a crude reaction mixture) was isolated in 91% yield (22.8 mg) as light-yellow oil. \(^1\)H NMR (700 MHz, CDCl₃) δ 9.55 (s, 1H), 7.42 (d, \(J = 2.0\) Hz, 1H), 7.36 (s, 1H), 7.23 – 7.19 (m, 2H), 7.19 – 7.16 (m, 3H), 6.53 (dd, \(J = 2.0, 0.6\) Hz, 1H), 5.85 (ddd, \(J = 17.0, 10.1, 6.7\) Hz, 1H), 5.05 (dt, \(J = 10.1, 1.1\) Hz, 1H), 4.88 (ddd, \(J = 17.0, 1.4, 1.1\) Hz, 1H), 4.28 (d, \(J = 1.1\) Hz, 1H), 3.76 (dd, \(J = 6.8, 1.4\) Hz, 1H). \(^13\)C NMR (176 MHz, CDCl₃) δ 191.5, 157.2, 144.1, 141.5, 139.9, 136.9, 136.2, 128.8 (2C), 127.3, 127.1 (2C), 117.0, 115.7, 108.6, 45.4, 43.7. The er was determined by UPC² using a chiral Chiralpak IA column gradient from 100% CO₂ up to 40%; ACN, flow rate = 2.2 mL/min, l = 228 nm) tR = 2.5 min (major), 2.1 min (minor), (94:6 er). [α]_D^{23} = + 85.6 (c = 1.0, CHCl₃).

HRMS (ESI) m/z [M+H]^+ Calcd. for C_{17}H_{15}O₂^+: 251.1067; found: 251.1074.

(3S,4S)-3,4-Diphenyl-3,4-dihydrodibenzo[b,d]furan-2-carbaldehyde 3o

Following the general procedure, using 1g (23.6 mg), product 3o (>20:1 dr in a crude reaction mixture) was isolated in 86% yield (30.1 mg) as light-yellow oil. \(^1\)H NMR (700 MHz, CDCl₃) \(^1\)H NMR (700 MHz, CDCl₃) δ 9.66 (s, 1H), 7.79 – 7.76 (m, 2H), 7.47 (dt, \(J = 8.1, 0.9\) Hz, 1H), 7.39 (td, \(J = 7.5, 1.1\) Hz, 1H), 7.36 – 7.34 (m, 1H), 7.32 – 7.28 (m, 4H), 7.28 – 7.26 (m, 1H), 7.26 – 7.21 (m, 3H), 7.17 – 7.14 (m, 2H), 4.56 (d, \(J = 1.3\) Hz, 1H), 4.49 (d, \(J = 1.3\) Hz, 1H). \(^13\)C NMR (176 MHz, CDCl₃) δ 191.1, 161.0, 156.3, 142.4, 141.0, 137.4, 136.3, 129.3 (2C), 129.1 (2C), 127.8, 127.5, 127.0 (2C), 126.9 (2C), 125.0, 124.7, 124.1, 119.1, 113.8, 112.2, 47.8, 46.9. The er was determined by UPC² using a chiral Chiralpak IA column gradient from 100% CO₂ up to 40%; i-ProH, flow rate = 2.2 mL/min, l = 216 nm) tR = 3.5 min (major), 3.3 min (minor), (92:8 er). [α]_D^{21} = + 395.5 (c = 1.0, MeOH). HRMS (ESI) m/z [M+H]^+ Calcd. for C_{25}H_{19}O₂^+: 351.1380; found: 351.1389.
3. Selective transformations of the product 3a

3.1. Oxidation of the product 3a to benzofuran-5-carbaldehyde 9

In an ordinary 4 mL glass vial, equipped with a Teflon-coated magnetic stirring bar the aldehyde 3a (30.1 mg, 0.1 mmol, 1 equiv.) was dissolved in CHCl₃ (0.2 mL). Then DDQ (34 mg, 0.15 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at room temperature overnight. After full conversion of the starting material 3a (as confirmed by ¹H NMR spectroscopy), the reaction mixture was directly subjected to column chromatography on silica gel (eluent: hexanes/diethyl ether 4:1) to afford pure product 9 in 80% yield (23.9 mg) as light-yellow oil.

6,7-Diphenylbenzofuran-5-carbaldehyde 9. ¹H NMR (700 MHz, CDCl₃) δ 9.83 (s, 1H), 8.35 (s, 1H), 7.70 (d, J = 2.2 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.19 (m, 2H), 7.16 – 7.13 (m, 2H), 6.96 (d, J = 2.2 Hz, 1H). ¹³C NMR (176 MHz, CDCl₃) δ 192.7, 156.0, 147.7, 141.2, 136.0, 134.1, 131.8 (2C), 131.1, 130.8 (2C), 128.0 (2C), 127.8 (2C), 127.6, 127.5, 127.3, 126.1, 120.6, 107.7. HRMS (ESI) m/z [M+H]⁺ Calcd. for C₂₁H₁₅O₂⁺: 299.1067; found: 299.1074.
3.2. Synthesis of diazepine derivative 8

In an ordinary 8 mL glass vial, equipped with a Teflon-coated magnetic stirring bar the aldehyde 3a (30.1 mg, 0.1 mmol, 1 equiv.) was dissolved in MeOH/CH$_2$Cl$_2$ 3:1 v/v (1 mL). Then o-phenylenediamine (10.8 mg, 0.1 mmol, 1 equiv.) and CeCl$_3$·7H$_2$O (37.2 mg, 0.1 mmol, 1 equiv.) were added and the reaction mixture was stirred at 50 °C for 20 hours. After full conversion of the starting material 3a (as confirmed by TLC analysis), the reaction mixture was diluted with CH$_2$Cl$_2$ (10 mL) and washed with water (2×5 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting solid was subjected to column chromatography on silica gel (eluent: CH$_2$Cl$_2$) to afford pure product 8 (>20:1 dr) in 62% yield (24.0 mg) as light-yellow oil.

(4S,5S)-4,5-Diphenyl-5,12-dihydro-4H-benzo[b]benzofuro[4,5-e][1,4]diazepine 8. $^1$H NMR (700 MHz, DMSO-d$_6$) $\delta$ 12.57 (s, 1H), 7.72 (s, 1H), 7.65 (d, $J = 1.9$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.43 – 7.39 (m, 2H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.25 (t, $J = 7.7$ Hz, 2H), 7.24 – 7.20 (m, 1H), 7.20 – 7.15 (m, 3H), 7.14 – 7.03 (m, 2H), 6.79 – 6.75 (m, 1H), 4.93 (s, 1H), 4.33 (s, 1H). $^{13}$C NMR (176 MHz, DMSO-d$_6$) $\delta$ 152.6, 151.5, 143.9, 143.4, 142.1, 141.6, 134.7, 128.8 (2C), 128.5 (2C), 127.1 (2C), 127.0, 126.8, 126.7 (2C), 124.7, 122.5, 121.6, 121.3, 118.6, 118.0, 110.7, 108.6, 49.8, 47.1. $[\alpha]_D^{23}$ = + 249.9 (c = 1.0, MeOH). HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{27}$H$_{21}$N$_2$O$^+$: 389.1649; found: 389.1644.
3.3. Selective reduction of aldehyde 3a

In an ordinary 4 mL glass vial equipped with a magnetic stirring bar the aldehyde 3a (30.1 mg, 0.1 mmol, 1 equiv.) was dissolved in CH$_2$Cl$_2$ (0.2 mL). Then MeOH (0.1 mL) and NaBH$_4$ (15.2 mg, 0.4 mmol, 4 equiv.) were added and the reaction mixture was stirred in room temperature for 30 min. Then the reaction mixture was directly subjected to column chromatography on silica gel (eluent: hexanes/ethyl acetate 4:1) to afford pure product 7 in 78% yield (23.6 mg) as light-yellow oil.

((6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-yl)methanol 7. $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 7.30 – 7.26 (m, 5H), 7.26 – 7.21 (m, 4H), 7.14 – 7.10 (m, 2H), 6.60 (dt, $J$ = 1.5, 0.8 Hz, 1H), 6.43 (dd, $J$ = 1.9, 0.6 Hz, 1H), 4.18 (d, $J$ = 2.3 Hz, 1H), 4.05 – 4.01 (m, 1H), 3.97 (d, $J$ = 13.9 Hz, 1H), 3.80 (d, $J$ = 2.4 Hz, 1H). $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 151.5, 142.8, 142.7, 142.6, 135.7, 129.1 (2C), 129.0 (2C), 127.5 (2C), 127.3, 127.2, 127.1 (2C), 117.7, 117.2, 108.2, 65.3, 52.8, 48.2. HRMS (ESI) m/z [M+H]$^+$ Calcd. for C$_{21}$H$_{19}$O$_2$: 303.1380; found: 303.1384.
3.3. Enantioselective synthesis of (6S,7S)-6,7-diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a on a 1 mmol scale

In an ordinary 8 mL glass vial equipped with a magnetic stirring bar α,β-unsaturated aldehyde 2a (158.0 mg, 1.2 mmol, 1.2 equiv.) and heteroaromatic aldehyde 1a (186.0 mg, 1.0 mmol, 1.0 equiv.) were dissolved in Et₂O (4 mL) and catalyst 4c (47.0 mg, 0.2 mmol, 0.2 equiv.) and benzoic acid (49.0 mg, 0.4 mmol, 0.4 equiv.) were added and the reaction mixture was stirred in room temperature for indicated time. The progress of the reaction was controlled by ¹H NMR spectroscopy. After full conversion of the starting material 1a, the reaction mixture was directly subjected to column chromatography on silica gel (hexanes : diethyl ether 85:15) to afford pure product 3a as single diastereoisomer in 91% yield (273.0 mg) as light-yellow solid. Spectral data were in accordance with the previously reported on page S3.
4. Crystal and X-ray data for 3a

The crystal structure of the compound (6S,7S)-6,7-diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a, C_{21}H_{16}O_{2}, was established by single-crystal X-ray diffraction at 100 K. The compound crystallizes in the non-centrosymmetric orthorhombic space group P2_{1}2_{1}2_{1} (Z = 4) and the crystal structure consists of one crystallographically independent formula unit in the unit cell (Figure 1).

![Molecular structure of 3a at 100 K](image)

Figure 1. The molecular structure of the compound 3a at 100 K, with the atom labeling scheme, showing 50% probability displacement ellipsoids. Hydrogen atoms are drawn with an arbitrary radius.

Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer with PhotonJet micro-focus X-ray Source Cu-Kα (λ = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software. The crystal structure was solved by using direct methods with the SHELXT 2018/2 program. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic thermal
parameters by using the SHELXL 2018/3 program. All hydrogen atoms were found from the difference Fourier maps and for further calculations they were positioned geometrically in calculated positions (C–H = 0.95–1.00 Å) and constrained to ride on their parent atoms with isotropic displacement parameters set to 1.2 times the Ueq of the parent atom.

(6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a: Formula C21H16O2, orthorhombic, space group P212121, Z = 4, unit cell constants a = 8.12398(4), b = 10.30996(6), c = 17.96578(9) Å, V = 1504.776(14) Å³. The integration of the data yielded a total of 41425 reflections with θ angles in the range of 4.92 to 66.59°, of which 2662 were independent (Rint = 2.92%), and 2642 were greater than 2σ(F²). The final anisotropic full-matrix least-squares refinement on F² with 209 parameters converged at R₁ = 2.34% and wR₂ = 5.92% for all data. The largest peak in the final difference electron density synthesis was 0.162 e Å⁻³ and the largest hole was -0.144 e Å⁻³. The goodness-of-fit was 1.055. The absolute configuration was unambiguously established from anomalous scattering, by calculating the Flack parameter of 0.00(3) using 1099 quotients.

CCDC 2103952 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

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(5) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Cryst. 2015, C71, 3-8.

(6) Parsons, S.; Flack, H. D.; Wagner, T. Use of intensity quotients and differences in absolute structure refinement. Acta Cryst. 2013, B69, 249-259.
5. Non-linear effect study

The experiments for non-linear effect study were carried out according to the procedure of the synthesis of 3a. The catalyst 4c mixtures with different ee values were prepared by mixing (S)-4c and (R)-4c in appropriate ratios (with the (R)-4c being the major). The ee value of product 3a was determined by UPC², which indicated a non-linear relationship between ee values of products 3a and amine catalyst 4c, as shown in the figure below.

![Non-linear effect studies](image)
6. NMR Data

(6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-(4-Nitrophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3b

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-(4-Chlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3c

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-7-Phenyl-6-(p-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3d

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-(4-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3e

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-(3-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3f

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-(2-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3g

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6R,7S)-6-(2,4-Dichlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3h

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6R,7S)-6-(Furan-2-yl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3i

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-7-(4-Fluorophenyl)-6-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3j

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-Phenyl-7-(p-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3k

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-7-(3-Methoxyphenyl)-6-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3l

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7S)-6-Phenyl-7-(o-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3m

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(6S,7R)-6-Phenyl-7-vinyl-6,7-dihydrobenzofuran-5-carbaldehyde 3n

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
(3S,4S)-3,4-Diphenyl-3,4-dihydrodibenzo[b,d]furan-2-carbaldehyde 3o

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
6,7-Diphenylbenzofuran-5-carboxaldehyde 9

\( ^1H \text{ NMR (700 MHz, CDCl}_3 \)\)

\( ^{13}C \text{ NMR (176 MHz, CDCl}_3 \)\)
((6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-yl)methanol 7

${^1}H$ NMR (700 MHz, CDCl$_3$)

${^{13}}C$ NMR (176 MHz, CDCl$_3$)
(4S,5S)-4,5-Diphenyl-5,12-dihydro-4H-benzo[b]benzofuro[4,5-e][1,4]diazepine 8.

$^1$H NMR (700 MHz, CDCl$_3$)

$^{13}$C NMR (176 MHz, CDCl$_3$)
7. UPC² Data

(6S,7S)-6,7-Diphenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3a

Racemic sample

![Racemic sample graph]

| Peak Results |
|--------------|
| RT | % Area |
| 1  | 2.882  | 54.03 |
| 2  | 3.082  | 45.97 |

Enantiomerically enriched sample

![Enantiomerically enriched sample graph]

| Peak Results |
|--------------|
| RT | % Area |
| 1  | 2.881  | 0.44  |
| 2  | 3.070  | 99.56 |
(65,7S)-6-(4-Nitrophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3b

Racemic sample

Enantiomerically enriched sample
(6S,7S)-6-(4-Chlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3c

**Racemic sample**

![Graph of racemic sample]

**Peak Results**

| RT | % Area |
|----|--------|
| 1  | 3.207  | 41.88 |
| 2  | 3.599  | 58.12 |

**EnantiomERICally enriched sample**

![Graph of enantiomERICally enriched sample]

**Peak Results**

| RT  | % Area |
|-----|--------|
| 1   | 3.212  | 2.16  |
| 2   | 3.599  | 97.82 |
(6S,7S)-7-Phenyl-6-(p-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3d

Racemic sample

Peek Results

| RT  | % Area |
|-----|--------|
| 3.052 | 55.83 |
| 3.323 | 44.17 |

Enantiomerically enriched sample

Peek Results

| RT  | % Area |
|-----|--------|
| 3.047 | 98.10 |
| 3.301 | 1.90  |
(6S,7S)-6-(4-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3e

Racemic sample

Enantiomerically enriched sample

Peak Results

| RT | % Area |
|----|--------|
| 1  | 3.271  | 64.19  |
| 2  | 3.592  | 35.81  |

| RT | % Area |
|----|--------|
| 1  | 3.277  | 2.33   |
| 2  | 3.596  | 97.67  |
(6S,7S)-6-(3-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3f

Racemic sample

Enantiomerically enriched sample

Peaks Results

| RT  | % Area |
|-----|--------|
| 3.082 | 56.55  |
| 3.230 | 41.45  |

| RT  | % Area |
|-----|--------|
| 3.082 | 1.72   |
| 3.230 | 98.26  |
(6S,7S)-6-(2-Methoxyphenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3g

**Racemic sample**

**Enantiomerically enriched sample**

**Peak Results**

|     | RT | % Area |
|-----|----|--------|
| 1   | 2.996 | 56.31 |
| 2   | 3.212 | 43.69 |

|     | RT | % Area |
|-----|----|--------|
| 1   | 2.996 | 0.37  |
| 2   | 3.213 | 99.63 |
(6\text{R}, 7\text{S})-6-(2,4-Dichlorophenyl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3h

Racemic sample

![Racemic sample graph]

| RT   | % Area |
|------|--------|
| 2.959| 43.84  |
| 3.423| 56.16  |

Enantiomerically enriched sample

![Enantiomerically enriched sample graph]

| RT   | % Area |
|------|--------|
| 2.951| 90.14  |
| 3.423| 9.88   |
(6R,7S)-6-(Furan-2-yl)-7-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3i

Racemic sample

Enantiomerically enriched sample

Peak Results

| RT | % Area |
|----|--------|
| 1  | 2.505  | 52.87 |
| 2  | 2.646  | 47.13 |

Peak Results

| RT | % Area |
|----|--------|
| 1  | 2.498  | 94.68 |
| 2  | 2.661  | 5.32 |
(6S,7S)-7-(4-Fluorophenyl)-6-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3j

**Racemic sample**

![Racemic sample graph]

**Peak Results**

| RT  | % Area |
|-----|--------|
| 2.734 | 52.50 |
| 2.983 | 47.50 |

**Enantiomerically enriched sample**

![Enantiomerically enriched sample graph]

**Peak Results**

| RT  | % Area |
|-----|--------|
| 2.731 | 3.27  |
| 2.961 | 96.73 |
(6S,7S)-6-Phenyl-7-(p-toly)-6,7-dihydrobenzofuran-5-carbaldehyde 3k

**Racemic sample**

![Racemic sample graph](chart1.png)

**Peak Results**

| RT | % Area |
|----|--------|
| 2.833 | 58.54 |
| 3.016 | 41.46 |

**Enantiomerically enriched sample**

![Enantiomerically enriched sample graph](chart2.png)

**Peak Results**

| RT | % Area |
|----|--------|
| 2.867 | 3.73 |
| 3.054 | 96.27 |
(6S,7S)-7-(3-Methoxyphenyl)-6-phenyl-6,7-dihydrobenzofuran-5-carbaldehyde 3l

Racemic sample

Enantiomerically enriched sample

| Peak Results | RT | % Area |
|--------------|----|--------|
| 1            | 3.005 | 60.42 |
| 2            | 3.238 | 39.58 |

| Peak Results | RT | % Area |
|--------------|----|--------|
| 1            | 3.059 | 18.99 |
| 2            | 3.229 | 81.01 |
(6S,7S)-6-Phenyl-7-(o-tolyl)-6,7-dihydrobenzofuran-5-carbaldehyde 3m

Racemic sample

Enantiomerically enriched sample

Peak Results

| RT  | % Area |
|-----|--------|
| 1   | 2.619  | 38.92 |
| 2   | 2.708  | 60.08 |

| RT  | % Area |
|-----|--------|
| 1   | 2.696  | 99.42 |
| 2   | 2.886  | 0.58  |
(6S,7R)-6-Phenyl-7-vinyl-6,7-dihydrobenzofuran-5-carbaldehyde 3n

**Racemic sample**

![Graph of racemic sample]

**Peak Results**

| RT  | % Area |
|-----|--------|
| 2.081 | 49.25 |
| 2.524 | 50.77 |

**Enantiomerically enriched sample**

![Graph of enriched sample]

**Peak Results**

| RT  | % Area |
|-----|--------|
| 2.092 | 5.66 |
| 2.525 | 94.44 |
(3S,4S)-3,4-Diphenyl-3,4-dihydrodibenzo[b,d]furan-2-carbaldehyde 3o

Racemic sample

Enantiomerically enriched sample

| Peak Results |
|--------------|
| RT | % Area |
| 1  | 3.325 | 57.36 |
| 2  | 3.497 | 42.64 |

| Peak Results |
|--------------|
| RT | % Area |
| 1  | 3.322 | 8.07  |
| 2  | 3.407 | 91.93 |