Supporting Information
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Supporting Information for

Towards a series of chiral primary amines bearing α-amino acid and benzo[d]imidazole and their application in asymmetric aldol reactions

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1. $^1$H/$^{13}$C NMR and HR-MALDI-MS spectra of compounds 3, 4, and 5

Figure S1 $^1$H NMR spectrum of compound 3a (400 MHz, DMSO, 25 °C).

Figure S2 $^{13}$C APT NMR spectrum of compound 3a (100 MHz, DMSO, 25 °C).
Figure S3 HR-MALDI-MS spectrum of compound 3a (DHB matrix).

Figure S4 $^1$H NMR spectrum of compound 4a (400 MHz, CDCl$_3$, 25 °C).
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Figure S16 $^1$H NMR spectrum of compound 5b (400 MHz, DMSO, 25°C).
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Figure S32 $^{13}$C APT NMR spectrum of compound 4d (100 MHz, CDCl$_3$, 25°C).
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Figure S34 $^1$H NMR spectrum of compound 5d (500 MHz, DMSO, 25°C).
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Figure S60 HR-MALDI-MS spectrum of compound 4g (DHB matrix).
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Figure S62 $^{13}$C APT NMR spectrum of compound 5g (100 MHz, CDCl$_3$, 25 °C).
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Figure S65 $^{13}$C APT NMR spectrum of compound 3h (125 MHz, DMSO, 25 °C).

Figure S66 HR-MALDI-MS spectrum of compound 3h (DHB matrix).
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Figure S68 $^{13}$C APT NMR spectrum of compound 4h (125 MHz, CDCl$_3$, 25°C).
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Figure S72 HR-MALDI-MS spectrum of compound 5h (DHB matrix).
Figure S73 $^1$H NMR spectrum of compound 12 (400 MHz, DMSO, 25 °C).

Figure S74 $^{13}$C APT NMR spectrum of compound 12 (100 MHz, DMSO, 25 °C).
Figure S75 $^1$H NMR spectrum of compound 13 (500 MHz, DMSO, 25 °C).

Figure S76 $^{13}$C NMR spectrum of compound 13 (100 MHz, DMSO, 25 °C).
2. $^1$H NMR spectra of target catalysts 5a-h measured with Mosher’s acid

**Figure S77** $^1$H NMR spectrum of compound 5a measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).

**Figure S78** $^1$H NMR spectrum of compound 5b measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).
Figure S79 $^1$H NMR spectrum of compound 5c measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).

Figure S80 $^1$H NMR spectrum of compound 5d measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).
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Figure S82 $^1$H NMR spectrum of compound 5f measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).
Figure S83 $^1$H NMR spectrum of compound 5g measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).

Figure S84 $^1$H NMR spectrum of compound 5h measured with Mosher’s acid (400 MHz, CDCl$_3$, 25 °C).
3. Chiral phase HPLC analyses of target catalysts 5a-h

Figure S85 Chiral phase HPLC analysis of 5a (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL min⁻¹, t₁ = 8.08 min, t₂ = 9.65 min). Estimated ee of 0 %.
Figure S86  Chiral phase HPLC analysis of 5b (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL.min⁻¹, tᵣ = 12.9 min, tₓ = 14.8 min). Estimated ee of 94 %.
Figure S87 Chiral phase HPLC analysis of 5c (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL min⁻¹, $t_R = 8.04$ min, $t_R = 9.65$ min). Estimated ee of 99%.
Figure S88 Chiral phase HPLC analysis of 5d (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL/min, t_R = 21.0 min). Estimated ee of 99%.
Figure S89 Chiral phase HPLC analysis of 5e (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL.min⁻¹, tᵣ = 18.5 min). Estimated ee of 99 %.
Figure S90 Chiral phase HPLC analysis of 5f (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL.min⁻¹, $t_R = 23.4$ min). Estimated ee of 99%.
Figure S91 Chiral phase HPLC analysis of 5g (Daicel Chiralcel OD-H, n-hexane/i-PrOH 90:10, flow rate 0.8 mL.min⁻¹, tᵣ₁ = 11.8 min, tᵣ₂ = 14.5 min). Estimated ee of 20%.
Figure S92: Chiral phase HPLC analysis of 5h (Daicel Chiralcel OD-H, n-hexane/i-PrOH 70:30, flow rate 0.8 mL min⁻¹, t_R = 16.7 min). Estimated ee of 99%.
4. Representative chiral phase HPLC analyses for aldol processes

**Figure S93** Chiral phase HPLC analysis of 12 (Daicel Chiralpak OJ-H, n-hexane/i-PrOH 80:20, flow rate 0.8 mL.min$^{-1}$, $\lambda = 254$ nm, $t_R = 22.02$ min, $t_R = 24.62$ min)
Figure S94 Chiral phase HPLC analysis of 13 (Daicel Chiralpak OJ-H, n-hexane/i-PrOH 85:15, flow rate 0.8 mL.min⁻¹, λ = 254 nm, tᵣ(anti) = 16.75, tᵣ(anti) = 18.64, tᵣ(syn) = 21.25 min, tᵣ(syn) = 28.16 min).