Supporting Information

Absolute Asymmetric Synthesis by Nucleophilic Carbonyl Addition using Chiral Crystals of Achiral Amides

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Figure S1. X-Ray Crystallographic Data of N, N-Dimethyl-2-benzoylbenzamide 1a

Crystal data of 1a: C_{16}H_{15}NO_2, \( M = 253.301 \), orthorhombic, \( a = 10.420(2) \) Å, \( b = 17.208(4) \) Å, \( c = 7.519(2) \) Å, \( U = 1348.3(6) \) Å\(^3\), \( T = 293 \) K, space group \( P2_12_12_1 \) (no. 19), \( Z = 4 \), \( \mu (\text{Cu-K}\alpha) = 0.66 \) mm\(^{-1}\), 1511 reflections measured, 1326 unique (\( R_{\text{int}} = 0.046 \)) which were used in all calculations. The final \( wR \) (\( F^2 \)) was 0.151 (all data). The crystallographic data will be sent on quoting the CCDC number CCDC 215659 (e-mail: deposit@ccdc.cam.ac.uk).
Crystal data of 1b: C_{18}H_{19}NO_{2}, M = 281.355, orthorhombic, a = 10.937(5) Å, b = 13.987(5) Å, c = 9.896(4) Å, U = 1513.8(10) Å^{3}, T = 293 K, space group P2_{1}2_{1}2_{1} (no. 19), Z = 4, μ (Cu-Kα) = 0.64 mm^{-1}, 1655 reflections measured, 1616 unique (R_{int} = 0.059) which were used in all calculations. The final wR (F^2) was 0.346 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC 215660.
Crystal data of 1c: C_{23}H_{21}NO_{2}, M = 343.426, orthorhombic, \( a = 14.384(4) \, \text{Å} \), \( b = 16.234(5) \, \text{Å} \), \( c = 8.049(4) \, \text{Å} \), \( U = 1879.6(12) \, \text{Å}^3 \), \( T = 293 \, \text{K} \), space group \( P2_12_12_1 \) (no. 19), \( Z = 4 \), \( \mu (\text{Cu-K}\alpha) = 0.61 \, \text{mm}^{-1} \), 2086 reflections measured, 1810 unique (\( R_{int} = 0.037 \)) which were used in all calculations. The final \( wR(\text{F}^2) \) was 0.094 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC 215661.
Crystal data of 1d: C$_{28}$H$_{23}$NO$_2$, $M = 405.497$, orthorhombic, $a = 19.753(5)$ Å, $b = 22.214(7)$ Å, $c = 9.936(3)$ Å, $U = 1513.8(10)$ Å$^3$, $T = 293$ K, space group $P2_12_12_1$ (no. 61), $Z = 8$, $\mu$(Cu-K$\alpha$) = 0.61 mm$^{-1}$, 4437 reflections measured, 2926 unique ($R_{int} = 0.050$) which were used in all calculations. The final $wR(F^2)$ was 0.217 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC 215662.
Determination of enantiomeric excesses.
Chemical yields were isolated yields. Enantiomeric excesses were determined on the basis of HPLC analysis using chiralcel-OD column. The traces were shown below.

Figure S5. Traces of optically active 2b (84% ee) obtained by the reaction of 1b with n-butyllithium at –80°C. (a) Detector: UV-2075 (JASCO), wave-length: 254 nm; column: CHIRALCEL-OD (DAICEL); eluent: hexane: EtOH = 98 : 2; flow rate: 0.3 ml min⁻¹; column temp.: 32.5°C. (b) Detector: CD-2095 (JASCO)
Figure S6. Traces of optically active 3 (67% ee) obtained by the reaction of 1e with n-butyllithium at -60°C. (a) Detector: UV-2075 (JASCO), wave-length: 254 nm; column: CHIRALCEL-OD (DAICEL); eluent: hexane: EtOH = 98 : 2; flow rate: 0.3 ml min⁻¹; column temp.: 30.0°C. (b) Detector: CD-2095 (JASCO)