Supporting Information
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Organocatalytic Asymmetric Conjugate Additions of Oxindoles and Benzofuranones to Cyclic Enones

Fabio Pesciaioli, [a] Xu Tian, [b] Giorgio Bencivenni, [a] Giuseppe Bartoli, [a] and Paolo Melchiorre*[b,c]

[a] Dipartimento di Chimica Organica “A. Mangini”, Università di Bologna, Viale Risorgimento 4 - 40136 Bologna, Italy
[b] ICIQ - Institute of Chemical Research of Catalonia, Av. Països Catalans 16 - 43007 Tarragona, Spain
[c] ICREA - Institució Catalana de Recerca i Estudis Avançats, Pg. Lluís Companys 23 - 08010 Barcelona, Spain

e-mail: pmelchiorre@iciq.es

Supplementary Information

[Diagram showing the reaction of 9-amino(9-deoxy)epi cinchona alkaloids with enones, leading to products with dr up to 6:1 and ee up to 98%.]
**General Methods.** The $^1$H and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts ($\delta$) for $^1$H and $^{13}$C are given in ppm relative to residual signals of the solvents (CHCl$_3$ @ 7.26 ppm $^1$H NMR, 77.0 ppm $^{13}$C NMR). Coupling constants are given in Hz. Carbon types were determined from DEPT $^{13}$C NMR experiments. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (230-400 mesh) according to the method of Still.\(^1\) For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF$_{254}$, 0.25 mm) were used, using UV light as the visualizing agent and an acidic mixture of ceric ammonium molybdate or basic aqueous potassium permanganate (KMnO$_4$), and heat as developing agents. High-resolution mass spectra (HRMS) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on Waters GCT gas chromatograph coupled time-of-flight mass spectrometer (GC/MS-TOF) with electron ionisation (EI). X-ray data were obtained from the ICIQ X-Ray Unit using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations are reported as follows: $[\alpha]$\(^D\) (c in g per 100 mL, solvent). All reactions were set up in the air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted.

**Materials.** Commercial grade reagents and solvents were used without further purification; otherwise, where necessary, they were purified as recommended.\(^2\) Chiral primary amine catalysts, 9-Amino(9-deoxy)epi-hydroquinine A, its pseudo-enantiomer 9-Amino(9-deoxy)epi-hydroquinidine B and 6’-hydroxy-9-amin-9-deoxyepiqunine C and were prepared from commercially available hydroquinine, hydroquinidine and quinine, respectively, following the literature procedure.\(^3\) 2-Cyclohexen-1-one 2a, 5,5-dimethyl-2-cyclohexen-1-one, 2-Cyclopenten-1-one, 2-Cyclohepten-1-one, 3-Methyl-2-oxindole, 6-Chloro-2-oxindole, were purchased from Aldrich or Alfa Aesar and used as received. N-Boc-Oxindole 1 derivatives\(^4\) and 3-benzyl benzofuranone 5\(^5\) have been prepared according to the previously reported literature procedure.

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Determination of Diastereomeric Ratios
The diastereomeric ratio was determined by $^1$H NMR analysis of the crude reaction mixture, and confirmed by HPLC analysis on chiral stationary phases columns. The diasteromeric ratio for compound 3e was further confirmed by GC-MS analysis of the crude mixture, since the NMR spectra did not show easily recognizable diagnostic peaks.

Determination of Enantiomeric Purity. HPLC analysis on chiral stationary phase was performed on an Agilent 1100-series instrumentation. Daicel Chiralpak AD-H, AS-H, IA or IC columns and Daicel Chiralcel OD-H with i-PrOH/hexane as the eluent were used. HPLC traces were compared to racemic samples prepared by carrying out the reactions in the presence of 1.5 equivalents of $\text{K}_2\text{CO}_3$ in THF as the solvent (RT, 48 hours reaction time).

General Procedure for the Organocatalytic Asymmetric Conjugate Additions of Oxindoles and Benzofuranones to Cyclic Enones

All the reactions were carried out with no precautions to exclude moisture in undistilled toluene. In an ordinary vial equipped with a magnetic stir bar, amine A or B (0.02 mmol, 6.5 mg, 10 mol%) and benzoic acid (0.04 mmol, 4.9 mg, 20 mol%) were dissolved in 1 mL of toluene. After stirring at r.t. for 10 minutes, the cyclic enones 2 (0.2 mmol) was added, followed by the addition of N-Boc oxindole 1 or benzofuranone 5 (0.24 mmol, 1.2 equiv). The vial was sealed, and the mixture stirred for the indicated time at r.t. The crude mixture was diluted with CH$_2$Cl$_2$ and flushed through a short plug of silica, using dichloromethane/ethyl acetate 1:1 as the eluent. Solvent was removed in vacuo and the Michael adduct 3 or 6 was purified by flash column chromatography (silica gel, hexane-EtOAc).
(R)-tert-butyl 3-benzyl-2-oxo-3-((S)-3-oxocyclohexyl)indoline-1-carboxylate (Table 2, entry 1).

![Chemical Structure]

The reaction was carried out following the general procedure to furnish the crude product: (d.r. 5:1 determined by integration of $^1$H-NMR signal: $\delta_{major}$ 3.04 ppm. d, $\delta_{minor}$ 3.05 ppm. d.). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/acetone = 90/10) in 80% yield 96% ee (major diastereoisomer) and 90% ee (minor diastereoisomer). HPLC analysis on a Daicel Chiralpak AD-H column: 98/2 hexane/i-PrOH, flow rate 0.50 mL/min, $\lambda = 214, 254$ nm: major diastereoisomer $\tau_{major} = 34.1$ min, $\tau_{minor} = 41.7$ min; minor diastereoisomer $\tau_{major} = 43.5$ min, $\tau_{minor} = 32.9$ min; HRMS calcd for (C$_{26}$H$_{29}$NO$_4$): 419.2096, found 419.2092. $[\alpha]_D^\infty = -17.37$ (c = 0.98, CHCl$_3$, d.r. = 5:1, 96% ee).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.47-1.64 (m, 2H), 1.55 (s, 9H), 1.70-1.81 (m, 1H), 1.97-2.12 (m, 1H), 2.15-2.32 (m, 1H), 2.32-2.50 (m, 2H), 2.55-2.61 (m, 2H), [CH$_2$ A-B type spectrum (3.04, d, 1H, $J_{gem} = $ -12.8 Hz), (3.30, d, 1H, $J_{gem} = $ -12.8 Hz)], 6.72-6.77 (m 2H), 6.93-7.06 (m, 3H), 7.13-7.31 (m, 3H), 7.52-7.57 (m, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 25.1 (CH$_2$), 26.4 (CH$_2$), 28.3 3X(CH$_3$), 41.4 (CH$_2$), 42.2 (CH$_2$), 43.0 (CH$_2$), 46.2 (CH), 57.4 (C), 84.3 (C), 115.0 (CH), 123.6 (CH), 124.4 (CH), 126.9 (CH), 127.9 (CH), 128.6 (CH), 129.3 (C), 130.0 (CH), 135.1 (C), 140.3 (C), 148.8 (C), 177.2 (C), 210.6 (C).

(S)-tert-butyl 3-benzyl-2-oxo-3-((R)-3-oxocyclohexyl)indoline-1-carboxylate (Table 2, entry 2).

![Chemical Structure]

The reaction was carried out following the general procedure to furnish the crude product: (d.r. 5:1 determined by integration of $^1$H-NMR signal: $\delta_{major}$ 3.04 ppm. d, $\delta_{minor}$ 3.05 ppm. d.). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/acetone = 90/10) in 94% yield 96% ee (major diastereoisomer) and 90% ee (minor diastereoisomer). HPLC analysis on a Daicel Chiralpak AD-H column: 98/2 hexane/i-PrOH, flow rate 0.50 mL/min, $\lambda = 214, 254$ nm: major diastereoisomer $\tau_{major} = 41.7$ min, $\tau_{minor} = 34.1$ min; minor diastereoisomer $\tau_{major} = 32.9$ min, $\tau_{minor} = 43.5$ min; $[\alpha]_D^\infty = +16.9$ (c = 0.98, CHCl$_3$, dr = 5.2:1, 98% ee).
(R)-tert-butyl 3-benzyl-3-\((S)\)-3,3-dimethyl-5-oxocyclohexyl\)-2-oxoindoline-1-carboxylate (Table 2, entry 3).

![Chemical structure](image)

The reaction was carried out following the general procedure to furnish the crude product: (d.r. 5.7:1 determined by integration of \(^1\)H-NMR signal: \(\delta_{\text{major}} 0.86 \text{ ppm. } \delta_{\text{minor}} 0.95 \text{ ppm. } \)). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/acetone = 90/10) in 30% yield and 92% ee, (major diastereoisomer) and 88% ee (minor diastereoisomer), d.r. 5.7:1. HPLC analysis on a Daicel Chiralpak AD-H column: 98/2 hexane/i-PrOH, flow rate 0.550 mL/min, \(\lambda = 214, 254 \text{ nm: major diastereoisomer } \tau_{\text{major}} = 17.67 \text{ min, } \tau_{\text{minor}} = 20.39 \text{ min; minor diastereoisomer } \tau_{\text{major}} = 28.40 \text{ min, } \tau_{\text{minor}} = 20.70 \text{ min; } [\alpha]_\text{rt}^D = +1.4 \text{ (c } = 0.87, \text{ CHCl}_3, 92\% \text{ ee, d.r. } = 5.7:1).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 0.86 \text{ (s, 3H), 1.00 (s, 3H), 1.33-1.39 (m, 1H), 1.43-1.52 (m, 2H), 1.55 (s, 9H), 2.09 (m, 1H), 2.18 (m, 2H), 2.54-2.66 (m, 3H), [CH}_2\text{ A-B type spectrum (3.01, d, 1H, J}_\text{gem}= -12.8 \text{ Hz), (3.30, d, 1H, J}_\text{gem}= -12.8 \text{ Hz)}, 6.71-6.76 (m, 2H), 6.94-7.00 (m, 2H), 7.01-7.05 (m, 1H), 7.17-7.24 (m, 2H), 7.25-7.28 (m, 1H), 7.51-7.56 (m, 1H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 25.4(\text{CH}_3), 28.0 \text{ (3 CH}_3), 31.9 \text{ (CH}_3), 34.3 \text{ (C), 39.3 (CH}_2), 41.6 \text{ (CH}_2), 41.7 \text{ (CH}_2), 42.4 \text{ (CH}_2), 54.2 \text{ (CH}_2), 56.9 \text{ (C), 84.1 (C), 114.8 (CH), 123.0 (CH), 124.2 (CH), 126.6 (CH), 127.6 (CH), 128.3 (CH), 129.2 (C), 129.7 (CH), 134.7 (C), 140.0 (C), 148.5 (C), 177.1 (C), 210.6 (C).

(R)-tert-butyl 3-benzyl-2-oxo-3-\((S)\)-3-oxocyclopentyl\)indoline-1-carboxylate (Table 2, entry 4).

![Chemical structure](image)

The reaction was carried out following the general procedure to furnish the crude product: (d.r. 5.5:1 determined by integration of \(^1\)H-NMR signal: \(\delta_{\text{major}} 3.10 \text{ ppm. } \delta_{\text{minor}} 3.06 \text{ ppm. } \)). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/ethyl acetate =85/15 to 70/30) in 55% yield and 46% ee. HPLC analysis on a Daicel Chiralcel OD-H column: 85/15 hexane/i-PrOH, flow rate 0.75 mL/min, \(\lambda = 214, 254 \text{ nm: major diastereoisomer } \tau_{\text{major}} = 11.8 \text{ min, } \tau_{\text{minor}} = 14.2 \text{ min; } [\alpha]_\text{rt}^D = -14.1.0 \text{ (c } = 1.00, \text{ CHCl}_3, 46\% \text{ ee).}

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 1.54 \text{ (s, 9H), 1.57-1.69 (m, 1H), 1.87-1.98 (m, 1H), 2.02-2.18 (m 1H), 2.28 (dd, 1H, } J^\text{1}= 19.3 \text{ Hz, } J^\text{2}= 8.9 \text{ Hz), 2.42 (dd, 1H, } J^\text{1}= 18.6 \text{ Hz, } J^\text{2}= 7.4 \text{ Hz), 2.53 (dd, 1H, } J^\text{1}=18.6 \text{ Hz, } J^\text{2}= 12.0 \text{ Hz), 2.77-2.90 (m,1H), [CH}_2\text{ A-B type spectrum (3.10, d, 1H, J}_\text{gem}= -14.1 \text{ Hz), (3.31, d, 1H, J}_\text{gem}= -14.1 \text{ Hz)}, 6.76-6.82 (m, 2H), 6.95-7.07 (m, 3H), 7.14-7.29 (m, 3H), 7.57 (d, 1H, 8.07 Hz).
\(^{13}\text{C} \text{NMR}\) (150 MHz, CDCl\(_3\)): \(\delta\) 25.1 (CH\(_2\)), 28.3 (3 CH\(_3\)), 38.6 (CH\(_2\)), 39.9 (CH\(_2\)), 43.1 (CH\(_2\)), 45.0 (CH), 56.1 (C), 84.5 (C), 115.1 (CH), 123.8 (CH), 124.4 (CH), 127.0 (CH), 128.0 (CH), 130.0 (CH), 130.5 (C), 135.1 (C), 140.1 (C), 148.8 (C), 177.2 (C), 217.1 (C).

\((R)\)-\textit{tert}-butyl 3-benzyl-2-oxo-3-\((\text{S})\)-3-oxocycloheptylindoline-1-carboxylate (Table 2, entry 5).

The reaction was carried out following the general procedure using catalyst A to furnish the crude product: (d.r. 2.8:1 determined by integration of \(^1\text{H}-\text{NMR} \) signal: \(\delta\)\(_{\text{major}}\) 6.72-6.75 ppm. m, \(\delta\)\(_{\text{minor}}\) 6.69-6.71 ppm. m). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/acetone = 90/10 to 85/15) in 62% yield and 98% ee. HPLC analysis on a Daicel Chiralcel OJ-H column: 98/2 hexane/i-PrOH, flow rate 0.75 mL/min, \(\lambda\) = 214, 254 nm: major diastereoisomer \(\tau\)\(_{\text{major}}\) = 23.7 min, \(\tau\)\(_{\text{minor}}\) = 19.5 min; \([\alpha]_D^\circ\) = -29.9 (c = 1.10, CHCl\(_3\), \(\scriptstyle{\text{d}}\) = 2.8:1, 98% ee).

\(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 1.30-1.46 (m, 2H), 1.53 (s, 9H), 1.64-1.82 (m, 1H), 1.83-2.09 (m, 3H), 2.43-2.66 (m, 4H), 2.66-2.76 (m, 1H), 3.04-3.35 (m, 2H), 6.67-6.75 (m, 2H), 6.93-7.07 (m, 3H), 7.09-7.32 (m, 3H), 7.48-7.55 (m, 1H).

\(^{13}\text{C} \text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) 24.9 (CH\(_2\)), 28.3 (3 CH\(_3\)), 29.6 (CH\(_2\)), 31.5 (CH\(_2\)), 43.3 (CH\(_2\)), 43.4 (CH\(_2\)), 43.47 (CH), 43.7 (CH\(_2\)), 45.6 (C), 58.15 (C), 84.2 (C), 115.1 (CH), 123.7 (CH), 124.4 (CH), 126.9 (CH), 127.8 (C), 128.6 (CH), 128.8 (C), 130.0 (CH), 135.0 (C), 140.3 (C), 148.8 (C), 177.6 (C), 213.5

\((R)\)-\textit{tert}-butyl 3-methyl-2-oxo-3-\((\text{S})\)-3-oxocyclohexylindoline-1-carboxylate (3e) (Table 2, entry 6).

The reaction was carried out at room temperature over 24 hours following the general procedure to furnish the crude product as a 4/1 mixture of diastereoisomers (d.r. 4:1 determined by HPLC and GC-MS analysis of the crude mixture). The title compound was isolated as a white solid by column chromatography (hexane/AcOEt = 90/10) in 94% yield (as a 4:1 mixture of diastereoisomers) and 95% ee. HPLC analysis on a Daicel Chiralpak IC column: 8/2 hexane/i-PrOH, flow rate 1.0 mL/min, \(\lambda\) = 254 nm: Major diastereomer (95% ee): \(\tau\)\(_{\text{minor}}\) = 17.7 min, \(\tau\)\(_{\text{major}}\) = 25.5 min; Minor diastereomer (85% ee): \(\tau\)\(_{\text{major}}\) = 11.2 min, \(\tau\)\(_{\text{minor}}\) = 19.3 min.
HRMS calcd for (C_{20}H_{25}NO_{4}+Na): 366.1681, found 366.1670. [\alpha]_{rt}D = -36.9 (c = 0.63, CHCl_{3}, dr 4:1, 95% ee_{major}, 85% ee_{minor}).

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers 1.5:1): $\delta$ 1.34 - 1.57 (m, 5H), 1.64 (s, 10H), 1.97 - 2.04 (m, 1H), 2.13 - 2.23 (m, 2H), 2.31 - 2.41 (m, 2H), 2.45 - 2.51 (m, 1H), 7.14 - 7.19 (m, 2H), 7.28 - 7.33 (m, 1H), 7.84 (d, $J = 8.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 22.0, 25.1, 25.9, 28.1, 41.2, 42.6, 46.9, 51.0, 84.8, 115.2, 122.9, 124.8, 128.6, 132.1 (CH), 139.4 (C), 149.2, 178.2 (C), 210.8.

(R)-tert-butyl-3-methyl-2-oxo-3-((S)-3-oxocycloheptyl)indoline-1-carboxylate (3f) (Table 2, entry 8).

The reaction was carried out at room temperature over 48 hours following the general procedure and using 20 mol% of catalyst A to furnish the crude product as a 2.5/1 mixture of diastereoisomers (d.r. 2.5:1 determined by integration of $^1$H-NMR signal: $\delta_{major}$ 1.46 s, $\delta_{minor}$ 1.44 ppm. s). The title compound was isolated as a colorless oil by column chromatography (hexane/AcOEt = 90/10) in 70% yield (as a 2.5:1 mixture of diastereoisomers) and 95% ee. HPLC analysis on a Daicel Chiralpak IC column: 9/1 hexane/i-PrOH, flow rate 1.0 mL/min, $\lambda = 254$ nm: Major diastereomer (95% ee): $\tau_{minor}$ = 30.3 min, $\tau_{major}$ = 58.5 min; Minor diastereomer (93% ee): $\tau_{major}$ = 18.9 min, $\tau_{minor}$ = 33.9 min. HRMS calcd for (C$_{21}$H$_{27}$NO$_{4}$+Na): 380.1838, found 380.1833. [\alpha]_{rt}D = -61.7 (c = 0.72, CHCl$_3$, dr 2.5:1, 95% ee$_{major}$, 93% ee$_{minor}$).

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers 2.5:1): $\delta$ 1.19 - 1.35 (m, 2H), 1.44 (s, 3H, minor), 1.46 (s, 3H, major), 1.48 - 1.56 (m, 1H), 1.64 (s, 9H, major), 1.64 (s, 9H, minor), 1.84 - 1.98 (m, 3H), 2.16 - 2.14 (m, 1H), 2.36 - 2.57 (m, 4H), 7.12 - 7.18 (m, 2H), 7.27 - 7.32 (m, 1H), 7.81 - 7.84 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.2, 24.1, 24.8, 28.3, 28.8, 29.4, 31.0, 32.0, 43.6, 44.1, 44.3, 44.8, 45.1, 51.5, 51.8, 84.7, 115.2, 122.8, 123.1, 124.7, 128.4, 131.4, 131.8, 139.4, 149.2, 178.6, 178.8, 213.2, 215.5.
(S)-tert-butyl 2-oxo-3-((S)-3-oxocyclohexyl)-3-phenylindoline-1-carboxylate (3g) (Table 2, entry 9).

The reaction was carried out at 0°C over 18 hours following the general procedure to furnish the crude product as a 1.5/1 mixture of diastereoisomers (d.r. 1.5:1 determined by integration of $^1$H-NMR signal: $\delta_{\text{major}}$ 7.98 d, $\delta_{\text{minor}}$ 7.95 ppm. d). The title compound was isolated as a white solid by column chromatography (hexane/AcOEt = 85/15) in 95% yield (as a 1.5:1 mixture of diastereoisomers) and 98% ee. HPLC analysis on a Daicel Chiralpak IC column: 8/2 hexane/i-PrOH, flow rate 1.0 mL/min, $\lambda$ = 254 nm:

- Major diastereomer (98% ee): $\tau_{\text{minor}}$ = 9.8 min, $\tau_{\text{major}}$ = 12.5 min; Minor diastereomer (88% ee): $\tau_{\text{minor}}$ = 14.7 min, $\tau_{\text{major}}$ = 32.2 min. HRMS calcd for (C$_{25}$H$_{27}$NO$_4$+Na): 428.1838, found 428.1847. $[\alpha]_\text{D}^2$ = +26.2 (c = 0.65, CHCl$_3$, dr 1.5:1, 98% ee$_{\text{major}}$, 88% ee$_{\text{minor}}$).

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereomers 1.5:1): $\delta$ 1.61 (m, 9H), 1.54-1.76 (m, 3H), 1.92-2.05 (m, 2H), 2.09-2.20 (m, 1H), 2.25-2.39 (m, 2H), 2.95-3.05 (m, 1H), 7.23-7.46 (m, 9H), 7.95 (d, $J$ = 7.8, 1H, minor), 7.98 (d, $J$ = 8.3, 1H, major). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 24.5 (CH$_2$), 24.7 (CH$_2$), 25.7 (CH$_2$), 26.5 (CH$_2$), 28.0 (CH$_3$), 40.9 (CH$_2$), 41.1 (CH$_2$), 42.6 (CH$_2$), 43.1 (CH$_2$), 46.5 (CH), 46.6 (CH), 59.8 (C), 59.9 (C), 84.7 (CH), 115.4 (CH), 115.5 (CH), 124.2 (CH), 124.3 (CH), 125.59 (CH), 125.63 (CH), 127.3 (CH), 127.4 (CH), 127.7 (CH), 127.8 (CH), 127.91 (CH), 127.99 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 136.6 (C), 137.4 (C), 140.2, 148.9 (C), 149.0 (C), 175.5 (C), 175.9 (C), 209.8 (C), 209.9 (C).

(R)-tert-butyl 3-(3-chlorobenzyl)-6-chloro-2-oxo-3-((S)-3-oxocyclohexyl)indoline-1-carboxylate (Table 2, entry 10).

The reaction was carried out following the general procedure to furnish the crude product: (d.r. 4:1 determined by integration of $^1$H-NMR signal: $\delta_{\text{major}}$ 6.76 ppm. m, $\delta_{\text{minor}}$ 6.82 ppm. m.). The title compound was isolated as a mixture of diastereoisomers by column chromatography (hexane/acetone = 85/15) in 85% yield and 94% ee (major diastereoisomer) and 94% ee (minor diastereoisomer). HPLC analysis on a Daicel Chiralcel OD-H column: 95/5 hexane/i-PrOH, flow rate 0.600 mL/min, $\lambda$ = 214, 254 nm: major diastereoisomer $\tau_{\text{major}}$ = 25.2 min, $\tau_{\text{minor}}$ = 40.7 min; minor diastereoisomer $\tau_{\text{major}}$ = 31.1 min, $\tau_{\text{minor}}$ = 34.7 min.
Compound 3h (0.18 mmol, 1 equiv.) was dissolved in 360 µL of dichloromethane then TFA was slowly added at room temperature. The resulting mixture was stirred at room temperature for 6 hours then it was diluted with ethyl acetate and a saturated solution of NaHCO₃ was added at 0°C. The organic phase was separated and water was extracted 3 times with ethyl acetate. Organic phase was anhydrided with MgSO₄ filtered and the solvent removed under reduced pressure. The crude mixture (d.r. 4:1 determined by integration of ¹H-NMR signal: δ_major 8.02 ppm. bs, δ_minor 8.12 ppm. bs.) was purified by flash column chromatography using dichloromethane/ethyl acetate 95:5 as the eluent mixture. (R)-3-(3-chlorobenzyl)-6-chloro-3-((5)-3-oxocyclohexyl)indolin-2-one was obtained as single diastereomers in 40% and 94% ee. HPLC analysis on a Daicel Chiralcel OD-H column: 90/10 hexane/i-PrOH, flow rate 0.650 mL/min, λ = 214, 254 nm: τ_major = 30.4 min, τ_minor = 33.9 min.

¹H NMR (600 MHz, CDCl₃): δ 1.48-1.62 (m, 2H), 1.82-1.89 (m, 1H), 2.05-2.12 (m, 1H), 2.16-2.27 (m, 1H), 2.32-2.43 (m, 3H), 2.49-2.56 (m, 1H), [CH₂ A-B type spectrum (3.04, d, 1H, J_gem= -12.9 Hz), (3.22, d, 1H, J_gem= -12.9 Hz)], 6.66-6.74 (m, 2H), 6.83 (bs, 1H), 6.96 (t, J = 7.9 Hz, 1H), 7.03-7.06 (m, 1H), 7.08 (dd, J₁ = 7.9 Hz, J₂ = 1.9 Hz, 1H), 7.20 (d, J = 8.1 Hz), 7.42 (bs, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 24.7 (CH₂), 25.9 (CH₂), 40.1 (CH₂), 41.0 (CH₂), 42.5 (CH₂), 45.4 (CH), 57.2 (C), 110.4 (CH), 122.4 (CH), 125.0 (CH), 126.9 (CH), 127.9 (CH), 128.2 (C), 129.0 (CH), 129.9 (CH), 133.5 (C), 134.1 (C), 137.2 (C), 142.1 (C), 179.5 (C), 210.1 (C).
(R)-3-benzyl-3-((S)-3-oxocyclohexyl)benzofuran-2(3H)-one (6) (Scheme 2).
The reaction was carried out at room temperature over 72 hours following
the general procedure to furnish the crude product as a 2/1 mixture of
diastereoisomers (d.r. 2:1 determined by HPLC of the crude mixture). The
title compound was isolated as a white solid by column chromatography (hexane/AcOEt = 90/10)
in 61% yield (as a 2:1 mixture of diastereoisomers) and 94% ee. HPLC analysis on a Daicel Chiralpak
IA column: 97/3 hexane/i-PrOH, flow rate 1.0 mL/min, λ = 254 nm: Major diastereomer (94% ee):
τ_major = 26.1 min, τ_minor = 30.4 min; Minor diastereomer (95% ee): τ_minor = 19.34 min, τ_major = 24.43
min. [α]D = 6.3 (c = 0.51, CHCl₃, dr 4:1, 95% ee_major, 95% ee_minor).

H NMR (400 MHz, CDCl₃, mixture of diastereomers 1.5:1): δ 1.45 - 1.67 (m, 3H), 2.05 - 2.11 (m,
1H), 2.17-2.33 (m, 1H), 2.37 -2.63 (m, 4H), 3.13-3.17(m,1H), 3.26-3.32(m,1H), 6.78 - 6.89 (m, 3H),
7.01-7.09 (m, 3H), 7.16 - 7.3 (m, 3H)

13C NMR (100 MHz, CDCl₃): δ 22.6, 24.6, 26.2, 41.1, 42.7, 45.7, 57.2, 110.7, 124.0, 127.0, 127.5,
128.1, 129.1, 129.2, 134.5, 153.2, 177.6, 209.5.

Organocatalytic Conjugate Additions of Oxindoles to linear trans-4-phenyl-3-buten-2-one

The reactions was carried out with no precautions to exclude moisture in undistilled toluene. In an
ordinary vial equipped with a magnetic stir bar, amine A (0.04 mmol, 13 mg, 20 mol%) and benzoic
acid (0.08 mmol, 9.6 mg, 40 mol%) were dissolved in 0.5 mL of toluene. After stirring at 0°C for 10
minutes, the cyclic enones 2 (0.2 mmol) was added, followed by the addition of N-Boc 3-methyl-
oxindole (0.24 mmol, 1.2 equiv) in toluene (0.5 mL). The vial was sealed, and the mixture stirred
for 24 hours at 0°C. The crude mixture was diluted with CH₂Cl₂ and flushed through a short plug of
silica, using dichloromethane/ethyl acetate 1:1 as the eluent. Solvent was removed in vacuo to
furnish the crude product as a 1.4/1 mixture of diastereoisomers (d.r. 1.4:1 determined by
integration of ¹H-NMR signal: δ_major 2.41 s, δ_minor 2.37 ppm. s). The title compound was isolated as
a colorless oil by column chromatography (hexane/AcOEt = 90/10) in 72% yield (as a 1.5:1 mixture of diastereoisomers) and 95% ee. HPLC analysis on a Daicel Chiralpak IC column: 9/1 hexane/i-PrOH, flow rate 1.0 mL/min, λ = 254 nm: Major diastereomer (95% ee): τ_major = 11.9 min, τ_minor = 16.3 min; Minor diastereomer (94% ee): τ_minor = 14.5 min, τ_major = 19.0 min. HRMS calcld for (C_{24}H_{27}NO_{4}+Na): 416.1838, found 416.1829. [α]_D^25 = +6.3 (c = 0.53, CHCl_3, dr 1.4:1, 95% ee_major, 94% ee_minor).

{\textsuperscript{1}}H NMR (400 MHz, CDCl_3, mixture of diastereomers 1.5:1): δ 1.43 (s, 3H, minor), 1.46 (s, 3H,major), 1.52(s,9H,major), 1.61(s,9H,minor), 1.97(s,3H,major), 2.02(s, 3H,minor), 3.61-3.64 (m, 4H), 3.60-3.72 (m, 2H), 6.79-6.83 (m, 2H), 6.92-6.96 (m, 2H), 7.05-7.19 (m, 10H), 7.26-7.31 (m, 1H),7.53 (d J = 8.8Hz 1H), 7.63 (d J = 7.6Hz 1H)

{\textsuperscript{13}}C NMR (100 MHz, CDCl_3): δ 21.1, 22.5, 28.2, 30.6, 43.4, 43.7, 48.9, 51.5, 51.8, 83.9, 84.2, 114.7, 114.9, 123.6, 123.7, 124.0, 124.2, 127.2, 127.4, 127.7, 127.8, 128.1 128.6, 128.8, 128.9, 130.7, 131.8, 137.9, 138.5, 138.7, 139.6, 148.7, 148.9, 178.1, 178.7, 206.4, 207.0
Absolute and Relative Configuration Determination

X-Ray Structure Analysis.

The absolute and relative configurations of compound 4 (Scheme 1) were assigned by X-ray crystallographic analysis. CCDC 771490 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Synthesis of N-Tos derivative 4 (Scheme 1)\textsuperscript{6}

\[
\begin{align*}
\text{3e or 4:1, 95\%ee} & \quad \text{i) TFA/DCM} \\
\text{Boc} & \quad \text{ii) NaH/TosCl} \\
\text{4} & \quad \text{70\% yield over two steps} \\
\end{align*}
\]

Compound 3e (0.2 mmol) was dissolved in DCM (5 mL) and TFA (3 equiv) was added at room temperature. After 16 h, the reaction was diluted with DCM (5 mL), washed successively with saturated Na\textsubscript{2}CO\textsubscript{3} and brine. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. Then the product was purified by chromatography to yield the pure N-H free oxindole derivative as a white solid. NaH (2 equiv) was suspended in THF (3 mL), and a solution of the above compound (0.15 mmol) in THF (2 mL) was slowly added at 0 °C. Then TosCl (1.3 equiv) was added. After 6 h, the reaction was quenched with water (0.5 mL). The mixture was diluted with EtOAc (5 mL), washed with brine. The organic layer was dried (Na\textsubscript{2}SO\textsubscript{4}), and concentrate in vacuo. The crude product was purified by flash chromatography PE/EA (10:1) to afford 4 as a white solid (0.14 mmol, 70\% overall yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, mixture of diastereomers 4:1): \(\delta\) 1.28 (s, 3H), 1.32-1.45 (m, 2H), 1.83-1.91 (m, 1H), 2.01-2.28 (m, 2H), 2.39 (s, 3H, minor), 2.43 (s, 3H, major), 2.02(s, 3H, minor), 7.07-7.22 (m, 2H), 7.29-7.37 (m, 4H), 7.93-7.99 (m, 4H). HPLC analysis on a Daicel Chiralpak IA column: 85/15 hexane/i-PrOH, flow rate 1.0 mL/min, \(\lambda = 254\) nm: Major diastereomer (95\% ee): \(\tau_{\text{major}} = 32.4\) min, \(\tau_{\text{minor}} = 37.9\) min; Minor diastereomer: \(\tau_{\text{minor}} = 34.1\) min, \(\tau_{\text{major}} = 39.4\) min. HPLC analysis on a crystal morphologically similar to the one used for X-ray

analysis demonstrated the presence of single enantiomer of the major diastereoisomer ($\tau_{major} = 32.4$ min, single pick).

**Single Crystal X-ray Diffraction Data:**

X-ray structure determinations: Crystals of compound 4 were obtained by slow evaporation in a mixture of Hexane and Diethyl-ether in a 1:1 portion at room temperature. The measured crystals were stable under atmosphere conditions; nevertheless they were prepared under inert conditions immersed in perfluoropoly-ether as protecting oil for manipulation.

*Data Collection.* Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK$_x$ radiation, Montel mirrors and a Kryoflex low temperature device ($T = -173 \, ^\circ \text{C}$). Full-sphere data collection was used with $\omega$ and $\varphi$ scans.


*Structure Solution.* SHELXTL Version 6.10 (Sheldrick, 2000) was used.\(^7\)

*Structure Refinement.* SHELXTL-97-UNIX VERSION.

(1) Crystal data for TX1 at 100 K: C$_{22}$ H$_{23}$ N$_1$ O$_4$ S$_1$ 397.47 gmol$^{-1}$, orthorhombic, $P2_12_12_1$, $a = 11.0798(8)$ Å, $b = 11.7870(6)$ Å, $c = 14.9095(7)$ Å, $V = 1947.14(19)$ Å$^3$, $Z = 4$, $\rho_{\text{calc}} = 1.356$ Mg/m$^3$, $R_1 = 0.0373$ (0.0418), $wR_2 = 0.1039$ (0.1096), for 6622 reflections with $I>2\sigma(I)$ (for 7224 reflections [$R_{\text{int}}$: 0.0189] with a total measured of 13438 reflections), 255 parameters, goodness-of-fit on $F^2 = 0.875$, largest diff. peak (hole) = 0.629 (-0.214) e Å$^{-3}$. Absolute structure Flack Parameter: 0.07(4)

CCDC 771490

---

NMR spectra

3a

Boc
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 C, Sig=214,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
--- ------- ------ ----- ------- -----
1 32.935 VV 0.5882 264.75842 6.71223 8.0663
2 34.074 VB 0.6860 1384.74915 31.18521 42.1888
3 41.683 BV 0.8454 1362.56604 24.93976 41.5130
4 43.637 VP 0.7959 270.19366 4.92629 8.2319

Totals : 3282.26727 67.76348

Results obtained with enhanced integrator!

*** End of Report ***
C6 one NBoc Bn Oxi att final
AD-H 98:2 0.500 mL/min

Injection Date : 28/01/02 5.18.02
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOL0.M
Last changed : 28/01/02 4:10.03 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOL0.M
Last changed : 31/01/02 22.58.29 by giorgio
(modified after loading)

--- Area Percent Report ---

Signal 1: DAD1 C, Sig=214.8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

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Totals : 5976.51597 133.19250

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 2 31/01/02 22.58.50 giorgio
5,5-dimethylcyclohexenone, benzilossindolo, racemo
AD-H 98:2 0.550 mL/min

Injection Date : 01/01/02 6.36.52
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPChem2\METHODS\PAOLO.M
Last changed : 01/01/02 6.24.50 by giorgio
(modified after loading)
Analysis Method : D:\HPChem2\METHODS\PAOLO.M
Last changed : 02/01/02 0.31.09 by giorgio
(modified after loading)

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Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 C, Sig=214,8 Ref=360,100

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Totals : 1.55318e4 563.74141

Results obtained with enhanced integrator!

*** End of Report ***
5,5-dimethylcyclohexanone, benzilossindolo, attivo
AD-H 98:2 0.550 mL/min

---

Injection Date : 01/01/02 7.09.14
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 01/01/02 6.24.50 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 02/01/02 0.31.09 by giorgio
(modified after loading)

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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 C, Sig=214,8 Ref=360,100

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Totals : 6253.04858 259.81287

Results obtained with enhanced integrator!

---

*** End of Report ***

Instrument 2 02/01/02 0.35.13 giorgio
Injection Date: 02-Jan-02, 03:13:07
Sample Name: Location: Vial 1
Acq. Operator: giorgio
Acq. Method: PACLQ.M
Analysis Method: D:\HPCHEM\2\METHODS\PAOLO.M
Last changed: 02/01/02 3:38.37 by giorgio
(modified after loading)

DAD1 A, Sig=254,100 Ref=360,100 (SNAPSHOT.D)

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Area Percent Report
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Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: DAD1 A, Sig-254,100 Ref-360,100

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<td>0.5386</td>
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Totals: 1478.11945 47.66967

Results obtained with enhanced integrator!

*** End of Report ***
CS, benzilossindolo, att -10 °C
AD-H 85:15 0.750 ml/min

Injection Date : 02/01/02 2.46.27
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 02/01/02 2.26.26 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 02/01/02 3.16.55 by giorgio
(modified after loading)

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**Area Percent Report**

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**Sorted By** : Signal
**Multiplier** : 1.0000
**Dilution** : 1.0000

**Signal 1: DAD1 A, Sig=254,100 Ref=360,100**

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**Totals :**
6159.60376 209.72848

Results obtained with enhanced integrator!
---

**End of Report**
---
C7 one Bn Boc Oxindolo rac p19
OJ-H 98:2 0.750 mL/min

Injection Date : 27/01/02 8.02.20
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 27/01/02 5.59.52 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 29/01/02 0.51.43 by giorgio
(modified after loading)

DAD1 C, Sig=214.8 Ref=360,100 (FABIO/FP583P.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 C, Sig=214.8 Ref=360,100

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<td>2 23.596 FM</td>
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Totals : 2.89754e4 199.18880

Results obtained with enhanced integrator!

*** End of Report ***
Data File D:\HPChem\2\DATA\FABIO\FP585B.D

C7 one Bn Boc Oxindolo att
OJ-H 98:2 0.750 mL/min

Injection Date: 27/01/02 8.58.52
Sample Name: Location: Vial 1
Acq. Operator: giorgio
Acq. Method: D:\HPChem\2\METHODS\PAOLO.M
Last changed: 27/01/02 5.59.52 by giorgio
(modified after loading)
Analysis Method: D:\HPChem\2\METHODS\PAOLO.M
Last changed: 28/01/02 0.55.30 by giorgio
(modified after loading)

DAD1 C, Sig=214.8 Ref=360.100 (FABIO\FP585B.D)

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: DAD1 C, Sig=214.8 Ref=360.100

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Results obtained with enhanced integrator!

*** End of Report ***
dichloro oxindole, racemo miscela diasteri
OD-H 95:5 0.600 mL/min

Injection Date : 26/01/02 4.31.24
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 26/01/02 5.19.00 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 02/01/02 8.23.02 by giorgio
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 C, Sig=214,8 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*] [mAU] 
----|--------|------|-------|-------|-----|
1  25.798 BB 1.0153 1.18242e4 178.85802 45.7342
2  31.210 PV 1.4463 1649.67810 14.91599 6.3807
3  34.541 VB 1.2130 1067.84680 12.39656 4.1303
4  40.432 BB 1.5448 1.13124e4 114.08656 43.7548

Totals : 2.58541e4 320.25713

Results obtained with enhanced integrator!

*** End of Report ***
Data File D:\HPCHEM\2\DATA\GIORGIO\8381718.D

dichloro oxindole, attivo miscela diasteri
OD-H 95:5 0.600 mL/min

Injection Date : 26/01/02 5.22.19
Sample Name : Location : Vial 1
Acq. Operator : giorgio
Acq. Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 26/01/02 5.19.00 by giorgio
(modified after loading)
Analysis Method : D:\HPCHEM\2\METHODS\PAOLO.M
Last changed : 02/01/02 5.14.35 by giorgio
(modified after loading)

DAD1 C, Sig=214,8 Ref=360,100 (GIORGIO\8381718.D)

Area Percent Report

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Signal 1: DAD1 C, Sig=214,8 Ref=360,100

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| 1      | 25.214 | VB 1.2190   1.45381e5 | 1829.60474 | 97.2066 |
| 2      | 40.738 | MM 1.5819 4177.71777 | 44.01633 | 2.7934 |

Totals : 1.49559e5 1873.62106

Results obtained with enhanced integrator!

*** End of Report ***
### Table 1

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**Totals:**

- Total Area: 7193.97583
- Total Area [%]: 232.16528

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### Peak RetTime Type Width Area Height Area %

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**Totals:**

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### Peak RetTime Type Width Area Height Area %

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**Totals:**

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**Totals:**

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