Organocatalytic Asymmetric Michael Addition of α-Aryl Cyclopentanones to Nitroolefins for Construction of Adjacent Quaternary and Tertiary Stereocenters

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1. General Remarks

$^1$H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). $^{13}$C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude $^1$H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralpak AS-H column, a chiralpak AD-H column with hexane and i-PrOH as solvents.

Catalyst I-VII were prepared according to literature report.$^{[1]}$ α-Aryl Cyclopentanones were prepared according to the literature procedure.$^{[2]}$ The racemic adducts were attained by using DABCO (1.2 eq.) as the base. The absolute (2S,3S)-configuration of 3ad and (2S,3S,4S)-7 were determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

2. General procedure for asymmetric Michael Addition Reaction of α-substituted cyclopentanones to Nitroolefins catalyzed by organocatalysts (I-d)

The catalyst I-d (13.5 mg, 0.02 mmol) was added to a vial containing α-substituted cyclopentanone (0.2 mmol) and nitroolefins (0.21 mmol) in CH$_2$Cl$_2$ (0.45 mL) at the indicated temperature, TLC analysis indicated completion of the reaction after about 12-20h. Then the reaction mixture was concentrated in vacuo to obtain the crude product. The crude product was purified by flash silica gel chromatography to afford the product.
(2S, 3S)-2-(2-Nitro-1-phenyl-ethyl)-2-phenyl-cyclopentanone (table 2, entry 1):
The title compound was prepared according to the general procedure as described above in 90% yield. $[\alpha]^{25}_D +65.8$ (c 1.24, CHCl$_3$); m.p 106.5 $^\circ$C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) \( \delta \) 1.55-1.68 (m, 1H), 1.75-1.84 (m, 1H), 1.96-2.14 (m, 2H), 2.19-2.36 (m, 2H), 4.19-4.23 (dd, \( J = 3.0 \) and 12.3 Hz, 1H), 4.48-4.56 (t, \( J = 12.9 \) Hz, 1H), 4.86-4.92 (dd, \( J = 4.3 \) and 12.9 Hz, 1H), 7.09 (brs, 2H), 7.17-7.26 (m, 3H), 7.31-7.39 (m, 5H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) \( \delta \) 18.4, 31.5, 37.6, 49.5, 58.9, 76.5, 128.1, 128.6, 129.4, 129.9, 134.6, 135.9, 217.1; IR (KBr) v: 3019, 2972, 2894, 2400, 1732, 1555, 1515, 1437, 1378, 1216, 1046, 928, 757 cm$^{-1}$; HRMS Calcd. for C$_{19}$H$_{19}$NO$_3$: 309.1365, found: 309.1363; dr > 99:1, determined by the crude $^1$HNMR; 92% ee, determined by chiral HPLC analysis (Chiralcel AD-H, i-propanol/hexane = 1/99, flow rate 0.25 mL/min, \( \lambda = 254 \) nm): \( t_{\text{minor}} = 78.7 \) min, \( t_{\text{major}} = 86.3 \) min. Enantioenriched compounds (>99% ee) can be easily obtained by direct crystallization of the crude products from methanol.

(2S, 3S)-2-[1-(4-chloro-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 2):
The title compound was prepared according to the general procedure as described above in 88% yield. $[\alpha]^{25}_D +76.5$ (c 1.02, CHCl$_3$); m.p 86 $^\circ$C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) \( \delta \) 1.58-1.64 (m, 1H), 1.78-1.88 (m, 1H), 1.99-2.06 (m, 2H), 2.23-2.32 (m, 2H), 4.12-4.17 (dd, \( J = 3.9 \) and 12.6 Hz, 1H), 4.40-4.48 (t, \( J = 12.6 \) Hz, 1H), 4.88-4.94 (dd, \( J = 3.9 \) and 12.9 Hz, 1H), 6.97-7.00 (m, 2H), 7.24-7.26 (m, 3H), 7.32-7.42 (m, 4H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) \( \delta \) 17.9, 31.3, 37.1, 48.6, 58.4,
75.9, 127.6, 128.3, 128.4, 129.1, 130.8, 133.7, 134.0, 216.5; IR (KBr) ν: 3015, 2972, 2887, 2396, 1739, 1591, 1556, 1420, 1395, 1210, 1042, 933, 754 cm⁻¹; HRMS Calcd. for C₁₉H₁₈ClNO₃: 343.0975, found: 343.0973; dr > 99:1, determined by the crude ¹HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): t_minor = 38.7 min, t_major = 30.5 min.

(2S, 3S)-2-[1-(2-chloro-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 3):

The title compound was prepared according to the general procedure as described above in 92% yield. [α]25 D +108.8 (c 1.28, CHCl₃); m.p 76 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.52-1.60 (m, 1H), 1.82-1.92 (m, 1H), 2.23-2.36 (m, 4H), 4.28-4.32 (t, J = 12.6 Hz, 1H), 4.66-4.70 (m, 1H), 5.66-5.69 (m, 1H), 6.42-6.44 (m, 1H), 7.03-7.08 (m, 1H), 7.18 (m, 3H), 7.39 (m, 4H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 17.9, 33.6, 37.5, 42.8, 58.7, 76.9, 126.6, 128.7, 128.8, 129.1, 129.4, 130.4, 133.3, 134.4, 135.7, 218.0; IR (KBr) ν: 3019, 2976, 2894, 2396, 1727, 1555, 1524, 1478, 1377, 1213, 1050, 933, 754 cm⁻¹; HRMS Calcd. for C₁₉H₁₈ClNO₃: 343.0975, found: 343.0974; dr > 99:1, determined by the crude ¹HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): t_minor = 19.1 min, t_major = 22.8 min.

(2S, 3S)-2-[1-(4-Bromo-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 4):
The title compound was prepared according to the general procedure as described above in 94% yield. \([\alpha]_{D}^{25} +95.7 \, (c \, 1.02, \, \text{CHCl}_3)\); m.p 108 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 1.57-1.63 (m, 1H), 1.81-1.83 (m, 1H), 2.00-2.09 (m, 2H), 2.22-2.35 (m, 2H), 4.10-4.15 (dd, \(J = 3.9\) and 11.7 Hz, 1H), 4.38-4.47 (t, \(J = 12.6\) Hz, 1H), 4.87-4.93 (dd, \(J = 3.9\) and 13.8 Hz, 1H), 6.90-6.93 (d, \(J = 8.7\) Hz, 2H), 7.25 (s, 2H), 7.31-7.41 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 75 MHz) \(\delta\) 17.9, 31.3, 37.1, 48.7, 58.3, 75.9, 122.0, 127.7, 128.3, 129.1, 131.2, 131.4, 133.7, 134.5, 216.5; IR (KBr) \(\nu\): 3015, 2976, 2439, 1739, 1556, 1493, 1373, 1213, 929, 762 cm\(^{-1}\); HRMS Calcd. for C\(_{19}\)H\(_{18}\)BrNO\(_3\): 387.0470, found: 387.0471; dr > 99:1, determined by the crude \(^1\)HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \(\lambda = 210\) nm): \(t_{\text{minor}} = 41.5\) min, \(t_{\text{major}} = 32.3\) min. Enantioenriched compounds (>99% ee) can be easily obtained by direct crystallization of the crude products from methanol.

(2S, 3S)-2-[1-(4-Fluoro-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 5):

The title compound was prepared according to the general procedure as described above in 83% yield. \([\alpha]_{D}^{25} +62.2 \, (c \, 0.85, \, \text{CHCl}_3)\); m.p 86 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 1.58-1.64 (m, 1H), 1.83-1.90 (m, 1H), 2.01-2.13 (m, 2H), 2.24-2.38 (m, 2H), 4.16-4.21 (dd, \(J = 3.0\) and 11.7 Hz, 1H), 4.42-4.51 (t, \(J = 12.9\) Hz, 1H), 4.89-4.94 (dd, \(J = 2.7\) and 12.6 Hz, 1H), 6.96-7.07 (m, 4H), 7.28-7.43 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 75 MHz) \(\delta\) 18.3, 31.6, 37.5, 48.8, 58.5, 76.5, 115.4, 115.6, 128.0, 128.6, 129.4, 131.4, 131.5, 134.2, 216.9; IR (KBr) \(\nu\): 3016, 2973, 2883, 1736, 1599, 1556, 1478, 1420, 1210, 1046, 929, 761 cm\(^{-1}\); HRMS Calcd. for C\(_{19}\)H\(_{18}\)FNO\(_3\): 327.1259, found: 327.1265; dr > 99:1, determined by the crude \(^1\)HNMR; 95% ee, determined by chiral HPLC analysis (Chiralcel AS-H,
\( i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \( \lambda = 210\text{ nm} \): \( t_{\text{minor}} = 37.4\text{ min} \), \( t_{\text{major}} = 30.5\text{ min} \).

(2S, 3S)-2-(2-Nitro-1-p-tolyl-ethyl)-2-phenyl-cyclopentanone (table 2, entry 6):
The title compound was prepared according to the general procedure as described above in 90% yield. \([\alpha]_{D}^{25} +65.0 \text{ (c 1.15, CHCl}_3)\); m.p 82 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \( \delta \) 1.50-1.68 (m, 1H), 1.75-1.86 (m, 1H), 1.98-2.15 (m, 2H), 2.21-2.28 (m, 2H), 2.30 (s, 3H), 4.12-4.18 (dd, \( J = 3.9 \) and 12.6 Hz, 1H), 4.43-4.51 (t, \( J = 12.9 \) Hz, 1H), 4.81-4.87 (dd, \( J = 4.2 \) and 13.2 Hz, 1H), 6.92-6.95 (d, \( J = 8.1 \) Hz, 2H), 7.06-7.08 (d, \( J = 7.5 \) Hz, 2H), 7.38 (brs, 5H); \(^13\)C NMR (CDCl\(_3\), TMS, 75 MHz) \( \delta \) 18.4, 21.3, 31.6, 37.6, 49.1, 58.9, 76.5, 128.1, 128.4, 129.3, 129.7, 132.6, 134.7, 137.8, 217.2; IR (KBr) \( \nu \) : 3013, 2969, 2899, 2393, 1741, 1558, 1509, 1439, 1383, 1211, 1038, 931, 758 cm\(^{-1}\); dr > 99:1, determined by the crude \(^1\)HNMR; 95% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \( i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \( \lambda = 210\text{ nm} \)): \( t_{\text{minor}} = 44.7\text{ min} \), \( t_{\text{major}} = 25.0\text{ min} \).

(2S, 3S)-2-[1-(4-Methoxy-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 7):
The title compound was prepared according to the general procedure as described above in 87% yield. \([\alpha]_{D}^{25} +76.5 \text{ (c 1.15, CHCl}_3)\); m.p 140 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \( \delta \) 1.55-1.68 (m, 1H), 1.82-1.86 (m, 1H), 2.01-2.18 (m, 2H), 2.25-2.41 (m, 2H), 3.82 (s, 3H), 4.15-4.21 (dd, \( J = 3.9 \) and 12.0 Hz, 1H), 4.44-4.53 (t, \( J = 12.6 \) Hz, 1H), 4.84-4.90 (dd, \( J = 4.2 \) and 13.2 Hz, 1H), 6.82-6.85 (d, \( J = 8.7 \) Hz,
2H), 7.00-7.03 (d, J = 9.0 Hz, 2H), 7.42 (brs, 5H); 13C NMR (CDCl₃, TMS, 75 MHz) δ 18.6, 31.7, 37.8, 49.0, 55.6, 59.2, 76.8, 114.1, 127.8, 128.2, 128.6, 129.5, 131.1, 134.9, 159.5, 217.4; IR (KBr) ν: 3015, 2976, 2400, 1739, 1552, 1513, 1423, 1375, 1252, 1220, 1036, 929, 754 cm⁻¹; HRMS Calcd. for C₂₀H₂₁NO₄: 339.1471, found: 339.1468; dr > 99:1, determined by the crude ¹H NMR; 95% ee, determined by chiral HPLC analysis (Chiralcel AD-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): tminor = 21.3 min, tmajor = 25.8 min.

![Chemical structure](image)

(3ah)

(2S, 3S)-2-[1-(3-Methoxy-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 8):

The title compound was prepared according to the general procedure as described above in 93% yield. [α]²⁵D +42.5 (c 0.85, CHCl₃); m.p 58 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.50-1.60 (m, 1H), 1.72-1.75 (m, 1H), 1.93-2.08 (m, 2H), 2.14-2.32 (m, 2H), 3.67 (s, 3H), 4.05-4.11 (dd, J = 3.6 and 12.3 Hz, 1H), 4.35-4.44 (t, J = 12.9 Hz, 1H), 4.78-4.84 (dd, J = 4.5 and 13.5 Hz, 1H), 6.50 (brs, 1H), 6.56-6.59 (d, J = 7.8 Hz, 1H), 6.70-6.74 (dd, J = 2.1 and 8.1 Hz, 1H), 7.08-7.14 (t, J = 7.8 Hz, 1H), 7.31 (m, 5H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 18.4, 31.8, 37.6, 49.3, 55.4, 58.7, 76.4, 113.5, 115.7, 122.1, 128.1, 128.5, 129.3, 129.5, 134.5, 137.3, 159.5, 217.1; IR (KBr) ν: 3015, 2970, 2934, 2887, 2400, 1735, 1603, 1554, 1517, 1498, 1424, 1389, 1220, 1038, 925, 767 cm⁻¹; HRMS Calcd. for C₂₀H₂₁NO₄: 339.1471, found: 339.1472; dr > 99:1, determined by the crude ¹H NMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AD-H, i-propanol/hexane = 10/90, flow rate 0.4 mL/min, λ = 210 nm): tminor = 24.7 min, tmajor = 27.9 min.

![Chemical structure](image)

(3ai)
(2S, 3S)-2-[1-(2-Methoxy-phenyl)-2-Nitro-ethyl]-2-phenyl-cyclopentanone (table 2, entry 9):
The title compound was prepared according to the general procedure as described above in 85% yield. $[\alpha]^{25}_D +135.8$ (c 0.59, CHCl$_3$); m.p 85 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 1.46-1.53 (m, 1H), 1.62-1.90 (m, 1H), 2.03-2.13 (m, 2H), 2.15-2.30 (m, 2H), 3.75 (s, 3H), 4.36-4.44 (t, $J = 12.9$ Hz, 1H), 4.50-4.55 (dd, $J = 3.3$ and 11.7 Hz, 1H), 5.13-5.17 (m, 1H), 6.49-6.52 (d, $J = 7.2$ Hz, 1H), 6.68-6.73 (t, $J = 7.8$ Hz, 1H), 6.78-6.81 (d, $J = 8.1$ Hz, 1H), 7.11-7.19 (m, 3H), 7.27 (brs, 3H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 17.8, 29.6, 32.7, 37.4, 41.1, 55.6, 58.6, 76.3, 111.1, 120.1, 124.4, 127.9, 128.2, 128.6, 128.8, 130.1, 134.3, 157.9, 217.9; IR (KBr) ν: 3014, 2985, 2404, 1727, 1552, 1521, 1490, 1420, 1377, 1212, 1054, 1027, 929, 758 cm$^{-1}$; dr > 99:1, determined by the crude $^1$HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): $t_{\text{minor}} = 19.6$ min, $t_{\text{major}} = 22.3$ min.

(3aj)

(2S, 3S)-2-(1-Naphthalen-1-yl-2-Nitro-ethyl)-2-phenyl-cyclopentanone (table 2, entry 10):
The title compound was prepared according to the general procedure as described above in 89% yield. $[\alpha]^{25}_D +42.2$ (c 1.49, CHCl$_3$); m.p 40 °C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 1.40-1.53 (m, 1H), 1.62-1.80 (m, 1H), 1.90-2.05 (m, 2H), 2.10-2.35 (m, 2H), 4.42-4.51 (t, $J = 12.3$ Hz, 1H), 5.00-5.05 (dd, $J = 3.3$ and 12.0 Hz, 1H), 5.59-5.65 (dd, $J = 3.9$ and 12.9 Hz, 1H), 6.65-6.67 (d, $J = 7.2$ Hz, 1H), 7.21-7.30 (m, 3H), 7.40 (brs, 3H), 7.49-7.52 (t, $J = 7.8$ Hz, 1H), 7.57-7.60 (t, $J = 7.8$ Hz, 1H), 7.74-7.77 (d, $J = 8.1$ Hz, 1H), 7.83-7.85 (d, $J = 8.1$ Hz, 1H), 8.34-8.37 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 17.6, 29.6, 33.7, 36.9, 40.7, 53.4, 58.3, 77.4, 123.3, 124.3, 125.6, 125.8, 126.4, 128.3, 128.4, 128.8, 132.5, 132.7, 133.1, 133.9, 217.9; IR (KBr) ν: 3011, 2976, 2397, 1727, 1556, 1513, 1424, 1213, 1040,
925, 754 cm\(^{-1}\); dr > 99:1, determined by the crude \(^1\)HNMR; 96% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \(\lambda = 210\) nm): \(t_{\text{minor}} = 32.8\) min, \(t_{\text{major}} = 41.9\) min.

(25, 35)-2-(1-Naphthalen-2-yl-2-Nitro-ethyl)-2-phenyl-cyclopentanone (table 2, entry 11):

The title compound was prepared according to the general procedure as described above in 95% yield. [\(\alpha\)]\(^{25}\)\(_D\) +78.6 (c 1.08, CHCl\(_3\)); m.p 105 °C; \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 1.50-1.59 (m, 1H), 1.72-1.84 (m, 1H), 2.01-2.16 (m, 2H), 2.18-2.38 (m, 2H), 4.32-4.37 (dd, \(J = 3.6\) and 12.0 Hz, 1H), 4.58-4.67 (t, \(J = 12.9\) Hz, 1H), 4.96-5.02 (dd, \(J = 3.9\) and 12.9 Hz, 1H), 7.17-7.20 (d, \(J = 8.1\) Hz, 1H), 7.40 (brs, 5H), 7.48 (brs, 3H), 7.74-7.80 (m, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 75 MHz) \(\delta\) 18.0, 31.5, 37.2, 49.2, 58.7, 76.2, 126.2, 127.4, 127.5, 127.8, 127.9, 128.2, 128.7, 129.0, 132.7, 132.8, 133.1, 134.2, 216.8; IR (KBr) v: 3015, 2980, 2891, 2435, 2400, 1727, 1603, 1552, 1521, 1485, 1424, 1381, 1210, 1046, 925, 762 cm\(^{-1}\); HRMS Calcd. for C\(_{23}\)H\(_{21}\)NO\(_3\): 359.1521, found: 359.1524; dr > 99:1, determined by the crude \(^1\)HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 1 mL/min, \(\lambda = 210\) nm): \(t_{\text{minor}} = 38.7\) min, \(t_{\text{major}} = 22.1\) min.

(25, 35)-2-(1-Furan-2-yl-2-Nitro-ethyl)-2-phenyl-cyclopentanone (table 2, entry 12):

The title compound was prepared according to the general procedure as described above in 93% yield. [\(\alpha\)]\(^{25}\)\(_D\) +10.6 (c 0.99, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 1.50-1.60 (m, 1H), 1.73-1.80 (m, 1H), 1.89-2.02 (m, 2H), 2.14-2.24 (m, 1H),
2.41-2.46 (m, 1H), 4.27-4.50 (m, 3H), 6.06 (s, 1H), 6.23 (s, 1H), 7.20-7.38 (m, 6H);

$^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 18.3, 30.2, 36.9, 43.9, 58.8, 74.2, 109.6, 110.6, 127.1, 128.2, 129.2, 134.4, 142.1, 150.2, 216.3; IR (KBr) v: 3019, 2973, 2400, 1731, 1560, 1427, 1377, 1217, 1046, 929, 754 cm$^{-1}$; HRMS Calcd. for C$_{17}$H$_{17}$NO$_4$: 299.1158, found: 299.1161; dr = 98:2 , determined by the crude $^1$HNMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, $i$-propanol/hexane = 10/90, flow rate 0.5 mL/min, $\lambda$ = 210 nm): $t_{\text{minor}}$ = 34.1 min, $t_{\text{major}}$ = 24.7 min.

![Chemical structure](3am)

**(2S, 3S)-2-(1-Nitromethyl-3-phenyl-allyl)-2-phenyl-cyclopentanone** (table 2, entry 13):

The title compound was prepared according to the general procedure as described above in 89% yield. [α]$^2$$_D$ +41.7 (c 1.01, CHCl$_3$); m.p 80 \degree C; $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 1.62-1.78 (m, 1H), 1.82-1.96 (m, 1H), 2.15-2.38 (m, 3H), 2.56-2.62 (m, 1H), 3.63-3.69 (t, $J$ = 8.4 Hz, 1H), 4.02-4.10 (t, $J$ = 11.4 Hz, 1H), 4.63-4.68 (dd, $J$ = 3.3 and 12.0 Hz, 1H), 5.93-6.01 (dd, $J$ = 9.0 and 15.6 Hz, 1H), 6.52-6.57 (d, $J$ = 15.6 Hz, 1H), 7.26-7.48 (m, 10H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 18.5, 31.4, 37.5, 48.0, 58.2, 76.7, 123.6, 126.7, 127.4, 128.1, 128.2, 128.7, 129.4, 134.9, 135.9, 136.3, 217.0; IR (KBr) v: 3015, 2980, 2895, 2400, 1735, 1556, 1521, 1474, 1424, 1213, 1042, 929, 770 cm$^{-1}$; dr > 99:1, determined by the crude $^1$HNMR; 96% ee, determined by chiral HPLC analysis (Chiralcel AS-H, $i$-propanol/hexane = 10/90, flow rate 0.5 mL/min, $\lambda$ = 210 nm): $t_{\text{minor}}$ = 52.0 min, $t_{\text{major}}$ = 41.0 min.
(S)-2-((S)-1-nitropentan-2-yl)-2-phenylcyclohexanone

The catalyst I-d (13.5 mg, 0.02 mmol) was added to a vial containing α-phenyl cyclopentanone (0.2 mmol) and aliphatic nitroolefin (0.21 mmol) in CH₂Cl₂ (0.45 mL) at room temperature about 30 h. Then the reaction mixture was concentrated in vacuo to obtain the crude product. The crude product was purified by flash silica gel chromatography in 50% yield. [α]²⁵⁺D = +30.6 (c 0.2, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.12-1.38 (m, 5H), 1.66-1.71 (m, 2H), 1.91-2.04 (m, 3H), 2.09-2.20 (m, 1H), 2.12-2.26 (m, 1H), 2.53-2.56 (m, 1H), 2.91 (brs, 1H), 3.83-3.89 (dd, J = 7.2 and 12.6 Hz, 1H), 4.13-4.18 (m, 1H), 7.20-7.32 (m, 3H), 7.38-7.41 (m, 2H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 14.4, 18.5, 21.5, 28.3, 29.5, 33.6, 37.4, 44.5, 59.9, 127.5, 128.2, 129.3, 135.8, 217.8; IR (KBr) ν: 3059, 2961, 2926, 2874, 1732, 1544, 1495, 1462, 1382, 1260, 1151, 1083, 1024, 799, 753 cm⁻¹; dr > 99:1, determined by the crude ¹HNMR; 80% ee, determined by chiral HPLC analysis (Chiralcel OD-H, i-propanol/hexane = 5/95, flow rate 0.5 mL/min, λ = 210 nm): t_minor = 17.3 min, t_major = 16.1 min.

(2S, 3S)-2-(2-Nitro-1-phenyl-ethyl)-2-p-tolyl-cyclopentanone (table 2, entry 14):

The title compound was prepared according to the general procedure as described above in 88% yield. [α]²⁵⁺D = +65.2 (c 1.24, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.42-1.62 (m, 1H), 1.65-1.78 (m, 1H), 1.85-2.04 (m, 2H), 2.12-2.27 (m, 2H), 2.29 (s, 3H), 4.06-4.11 (m, 1H), 4.37-4.46 (m, 1H), 4.80-4.85 (m, 1H), 7.00 (brs, 2H), 7.11-7.18 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 18.0, 20.9, 31.4, 37.1, 49.1, 58.2, 76.2, 127.7, 127.8,
128.2, 129.5, 129.7, 130.9, 135.6, 138.1, 216.9; IR (KBr) ν: 3015, 2969, 2891, 2432, 2397, 1727, 1552, 1513, 1427, 1381, 1217, 1042, 925, 754 cm⁻¹; HRMS Calcd. for C₂₀H₂₁NO₃: 323.1521, found: 323.1524; dr > 99:1, determined by the crude ¹H NMR; 91% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): tminor = 43.1 min, t_major = 22.1 min.

(3ca)

(2S, 3S)-2-(2-Nitro-1-phenyl-ethyl)-2-m-tolyl-cyclopentanone (table 2, entry 15):
The title compound was prepared according to the general procedure as described above in 91% yield. [α]²⁵_D +100.1 (c 0.50, CHCl₃); m.p 70 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.57-1.75 (m, 1H), 1.77-1.82 (m, 1H), 1.95-2.12 (m, 2H), 2.21-2.30 (m, 2H), 2.37 (s, 3H), 4.15-4.20 (dd, J = 3.3 and 12 Hz, 1H), 4.45-4.54 (t, J = 12.6 Hz, 1H), 4.83-4.89 (dd, J = 3.9 and 13.8 Hz, 1H), 7.05-7.07 (m, 2H), 7.13-7.16 (m, 3H), 7.26-7.30(m, 4H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 18.1, 21.6, 31.3, 37.2, 49.1, 58.5, 76.1, 124.7, 127.8, 128.2, 128.4, 128.8, 128.9, 129.6, 134.1, 135.5, 138.7, 216.8; IR (KBr) ν: 3023, 2972, 2891, 2432, 2404, 1731, 1559, 1521, 1478, 1424, 1381, 1210, 1046, 925, 762 cm⁻¹; HRMS Calcd. for C₂₀H₂₁NO₃: 323.1521, found: 323.1520; dr > 99:1, determined by the crude ¹H NMR; 90% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): tminor = 32.4 min, t_major = 21.9 min.

(3da)

(2S, 3S)-2-(4-Methoxy-phenyl)-2-(2-Nitro-1-phenyl-ethyl)-cyclopentanone (table 2, entry 16)
The title compound was prepared according to the general procedure as described above in 93% yield. \([\alpha]_{D}^{25}+86.9 (c 0.82, \text{CHCl}_3); ^1\text{H NMR (CDCl}_3, \text{TMS, 300 MHz)}\)

\(^1\text{H NMR (CDCl}_3, \text{TMS, 300 MHz)}\) \(\delta\) 1.42-1.60 (m, 1H), 1.62-1.69 (m, 1H), 1.90-2.02 (m, 2H), 2.10-2.21 (m, 2H), 3.76 (s, 3H), 4.04-4.08 (m, 1H), 4.38-4.46 (t, J = 12.3 Hz, 1H), 4.83-4.87 (m, 1H), 6.83-6.86 (t, J = 9 Hz, 2H), 6.96-6.99 (m, 2H), 7.18-7.20 (m, 5H); \(^{13}\text{C NMR (CDCl}_3, \text{TMS, 75 MHz)}\) \(\delta\) 18.3, 31.9, 37.4, 49.4, 55.5, 58.1, 76.5, 114.6, 125.9, 128.0, 128.5, 129.3, 129.8, 135.9, 159.6, 217.2; IR (KBr) \(\nu\): 3018, 2972, 2891, 2397, 1731, 1602, 1559, 1511, 1479, 1421, 1213, 1042, 929, 758 cm\(^{-1}\); HRMS Calcd. for C\(_{20}\)H\(_{21}\)NO\(_4\): 339.1471, found: 339.1469; \(\text{dr > 99:1, determined by the crude } ^1\text{HNMR; 90% ee, determined by chiral HPLC analysis (Chiralcel AS-H, } i\text{-propanol/hexane = 10/90, flow rate 1.0 mL/min, } \lambda = 210 \text{ nm)}: t_{\text{minor}} = 30.0 \text{ min, } t_{\text{major}} = 19.2 \text{ min.}\)

\((2S, 3S)-2-(3\text{-Methoxy-phenyl})-2-(2\text{-Nitro-1-phenyl-ethyl})-\text{cyclopentanone}\) (table 2, entry 17):

The title compound was prepared according to the general procedure as described above in 90% yield. \([\alpha]_{D}^{25}+85.9 (c 0.71, \text{CHCl}_3); \text{m.p 85 }^\circ\text{C; } ^1\text{H NMR (CDCl}_3, \text{TMS, 300 MHz)}\) \(\delta\) 1.56-1.72 (m, 1H), 1.76-1.82 (m, 1H), 1.96-2.15 (m, 2H), 2.21-2.35 (m, 2H), 3.81 (s, 3H), 4.16-4.21 (dd, J = 4.2 and 12.6 Hz, 1H), 4.48-4.57 (t, J = 12.3 Hz, 1H), 4.83-4.89 (dd, J = 4.2 and 13.2 Hz, 1H), 6.88-6.96 (m, 3H), 7.08-7.10 (m, 2H), 7.26-7.35 (m, 4H); \(^{13}\text{C NMR (CDCl}_3, \text{TMS, 75 MHz)}\) \(\delta\) 18.2, 31.4, 37.2, 49.1, 55.3, 58.6, 76.1, 113.1, 114.0, 119.3, 127.9, 128.2, 129.6, 129.9, 135.5, 135.9, 159.9, 216.7; IR (KBr) \(\nu\): 3019, 2972, 2895, 2397, 1735, 1600, 1556, 1521, 1424, 1217, 1046, 929, 754 cm\(^{-1}\); HRMS Calcd. for C\(_{20}\)H\(_{21}\)NO\(_4\): 339.1471, found: 339.1475; \(\text{dr > 99:1, determined by the crude } ^1\text{HNMR; 91% ee, determined by chiral HPLC analysis (Chiralcel AS-H, } i\text{-propanol/hexane = 10/90, flow rate 1.0 mL/min, } \lambda = 210 \text{ nm)}: t_{\text{minor}} = 27.3 \text{ min, } t_{\text{major}} = 19.3 \text{ min.}\)
(2S, 3S)-2-(4-Chloro-phenyl)-2-(2-Nitro-1-phenyl-ethyl)-cyclopentanone (table 2, entry 18):

The title compound was prepared according to the general procedure as described above in 89% yield. \([\alpha]^{25}_{D} +73.1\) (c 1.01, CHCl_3); \(^1^H\) NMR (CDCl_3, TMS, 300 MHz) \(\delta\) 1.56-1.66 (m, 1H), 1.79-1.88 (m, 1H), 2.01-2.17 (m, 2H), 2.22-2.35 (m, 2H), 4.11-4.16 (dd, J = 4.2 and 12.3 Hz, 1H), 4.45-4.53 (t, J = 12.3 Hz, 1H), 4.88-4.94 (dd, J = 4.5 and 13.5 Hz, 1H), 7.01-7.04 (m, 2H), 7.26-7.31 (m, 5H), 7.36-7.39 (m, 2H); \(^1^C\) NMR (CDCl_3, TMS, 75 MHz) \(\delta\) 18.2, 31.9, 37.5, 49.1, 58.1, 76.0, 128.2, 128.5, 129.3, 129.4, 129.6, 133.2, 134.5, 135.2, 216.8; IR (KBr) v: 3019, 2976, 2891, 2439, 2400, 1731, 1599, 1556, 1525, 1424, 1377, 1217, 1046, 929, 762 cm\(^{-1}\); HRMS Calcd. for C_{19}H_{18}ClNO_3: 343.0970, found: 343.0969; dr > 99:1, determined by the crude \(^1^H\)NMR; 91% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \(\lambda\) = 210 nm): t\(_{\text{minor}}\) = 35.6 min, t\(_{\text{major}}\) = 28.4 min.

(3ga)

(2S, 3S)-2-(3-Chloro-phenyl)-2-(2-Nitro-1-phenyl-ethyl)-cyclopentanone (table 2, entry 19):

The title compound was prepared according to the general procedure as described above in 95% yield. \([\alpha]^{25}_{D} +54.5\) (c 1.09, CHCl_3); m.p 107.6 °C; \(^1^H\) NMR (CDCl_3, TMS, 300 MHz) \(\delta\) 1.56-1.68 (m, 1H), 1.80-1.88 (m, 1H), 2.01-2.18 (m, 2H), 2.24-2.33 (m, 2H), 4.13-4.18 (dd, J = 4.2 and 12.3 Hz, 1H), 4.47-4.55 (t, J = 12.6 Hz, 1H), 4.85-4.91 (dd, J = 3.9 and 13.2 Hz, 1H), 7.03-7.06 (m, 2H), 7.26-7.36 (m, 7H); \(^1^C\) NMR (CDCl_3, TMS, 75 MHz) \(\delta\) 18.1, 31.5, 37.4, 48.9, 58.2, 75.8, 126.0, 127.9,
128.1, 128.3, 128.4, 129.5, 130.2, 134.9, 135.0, 136.8, 216.3; IR (KBr) v: 3019, 2973, 2890, 2432, 2398, 1735, 1556, 1521, 1424, 1213, 1046, 925, 758 cm⁻¹; dr > 99:1, determined by the crude ¹H NMR; 94% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): t_{minor} = 45.8 min, t_{major} = 33.5 min.

(2S, 3S)-2-(2-Nitro-1-phenyl-ethyl)-2-(4-trifluoromethyl-phenyl)-cyclopentanone (table 2, entry 20):

The title compound was prepared according to the general procedure as described above in 90% yield. [α]₂⁵^D +35.3 (c 1.16, CHCl₃); m.p 65.5 °C; ¹H NMR (CDCl₃, TMS, 300 MHz) δ 1.50-1.63 (m, 1H), 1.70-1.82 (m, 1H), 2.03-2.36 (m, 4H), 4.09-4.15 (dd, J = 3.9 and 12.0 Hz, 1H), 4.38-4.47 (t, J = 12.3 Hz, 1H), 4.78-4.84 (dd, J = 4.5 and 13.5 Hz, 1H), 6.95-6.97 (m, 2H), 7.19-7.21 (m, 3H), 7.44-7.46 (d, J = 8.1 Hz, 2H), 7.58-7.61 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 18.3, 31.8, 37.6, 49.1, 58.5, 75.8, 125.93, 125.98, 128.3, 128.5, 128.6, 129.6, 134.9, 139.1, 216.5; IR (KBr) v: 3018, 2976, 2891, 2428, 2400, 1736, 1556, 1525, 1420, 1324, 1213, 1170, 1131, 1069, 1050, 925, 758 cm⁻¹; dr > 99:1, determined by the crude ¹H NMR; 95% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm): t_{minor} = 29.9 min, t_{major} = 20.9 min.
The catalyst I-d (13.5 mg, 0.02 mmol) was added to a vial containing α-phenyl cyclohexanone (0.2 mmol) and nitroolefin (0.21 mmol) in CHCl₃ (0.45 mL) at 50°C about 30 h. Then the reaction mixture was concentrated in vacuo to obtain the crude product. The crude product was purified by flash silica gel chromatography in 20% yield. \([\alpha]_{D}^{25} +25.2 (c 0.34, \text{CHCl}_3); \) \(^1\)H NMR (CDCl₃, TMS, 300 MHz) δ 1.50-1.63 (m, 2H), 1.70-1.95 (m, 3H), 2.05-2.15 (m, 1H), 2.20-2.30 (m, 1H), 2.35-2.50 (m, 1H), 4.02-4.20 (m, 2H), 5.08-5.11 (d, \(J = 10.8\) Hz, 1H), 6.70-6.73 (d, \(J = 6.6\) Hz, 1H), 6.79-6.81 (d, \(J = 4.8\) Hz, 2H), 7.08-7.18 (m, 3H), 7.24-7.31 (m, 3H); \(^1\)^3\)C NMR (CDCl₃, TMS, 75 MHz) δ 21.3, 29.1, 29.9, 37.5, 40.4, 49.4, 59.6, 127.98, 128.1, 128.6, 128.8, 129.1, 130.3, 135.8, 136.0, 213.4; IR (KBr) ν: 3060, 3029, 2925, 2855, 1703, 1551, 1469, 1449, 1377, 1308, 1278, 1119, 1086, 802, 759 cm⁻¹; The dr was > 99:1, determined by the crude \(^1\)HNMR; 84% ee, determined by chiral HPLC analysis (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 0.5 mL/min, \(\lambda = 210\) nm): \(t_{\text{minor}} = 26.6\) min, \(t_{\text{major}} = 28.2\) min.

3. Synthetic Transformation of the Michael adduct 3aa

Conditions: i) Zn/HCl, 40 °C, 78% yield; ii) Pd/C, \(H_2\) (20 atm), 50°C, 10 h, 60% yield; iii) Pd/C, \(H_2\) (40 atm), 80°C, 30 h, 63% yield; iv) TsCl/Et₃N/DCM, 91% yield.
3,3a-Diphenyl-2,3,3a,4,5,6-hexahydro-cyclopenta[b]pyrrole: A 100mL round bottom flask with well-stirring was filled with Zinc powder 945 mg (15 mmol, 15eq.), and optical pure 3aa 309.4 mg (1.0 mmol), then EtOH (9.5 mL) was added. After the mixture was kept at 40 °C for 10 min, 6.4 mL 4 M HCl aq. was added dropwise over 2 h. The contents were stirred at 40 °C for 24 h. To maintain the pH value of the mixture between 0-1, additional 4N HCl aq. was added. After the reaction was completed to afford the final product (monitored by TLC), EtOH was removed under reduced pressure, 3N NaOH aq. (20 mL) was added, and then the solution was stirred for 5 min. After diluted with 15 mL CH₂Cl₂, the mixture was filtrated through a plug of Celite. The layers were separated. The acquired aqueous layer was extracted with CH₂Cl₂, and then the combined organic layers were washed with brine and dried over anhydrous MgSO₄ and concentrated. The crude oil was purified by flash chromatography on silica gel to afford the product 4 (204.4 mg, 78% yield). \([\alpha]_D^{25} +369.8 (c 0.44, \text{CHCl}_3); ^1\text{H NMR (CDCl}_3, \text{TMS, 300 MHz)} \delta 1.83-2.01 (m, 2H), 2.13-2.18 (m, 1H), 2.45-2.51 (m, 1H), 2.59 (brs, 2H), 3.67-3.73 (m, 1H), 4.24-4.32 (m, 1H), 4.38-4.45 (m, 1H), 6.67-6.76 (m, 4H), 7.03-7.15 (m, 5H); ^13\text{C NMR (CDCl}_3, \text{TMS, 75 MHz)} \delta 25.3, 25.6, 37.6, 59.3, 69.0, 69.3, 126.8, 126.9, 127.8, 127.9, 128.4, 128.6, 137.6, 138.2, 192.2; IR (KBr) ν: 3019, 2973, 2899, 2428, 2400, 1667, 1601, 1522, 1497, 1422, 1216, 1047, 928, 758 cm⁻¹; HRMS Calcd. for C₁₉H₁₅N: 261.1517, found: 261.1521; >99% ee, determined by chiral HPLC analysis (Chiralcel AD-H, i-propanol/hexane = 10/90, flow rate 0.25 mL/min, \(\lambda = 210\) nm): \(t_{\text{major}} = 21.7\) min.

3,3a-Diphenyl-2,3,3a,4,5,6-hexahydro-cyclopenta[b]pyrrole 1-oxide:
A suspension of Pd/C (20 mg) and 3aa (200 mg) in MeOH (5 mL) was stirred at 50°C under 20 atm hydrogen atmosphere. After being stirred for 10 h, the mixture was filtrated through a pad of Celite and the filtration was concentrated in vacuo, the residue was purified by column chromatography on silica gel to afford the desired product 5 (178 mg, 60% yield). [α]$_{25}^D$ +10.5 (c 1.0, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 1.80-1.86 (m, 1H), 1.96-2.08 (m, 1H), 2.13-2.22 (m, 1H), 2.43-2.54 (m, 2H), 2.73-2.82 (m, 1H), 4.02-4.09 (dd, $J$ = 8.1 and 11.4 Hz, 1H), 4.23-4.30 (dd, $J$ = 8.1 and 12.3 Hz, 1H), 4.74-4.82 (t, $J$ = 12.3 Hz, 1H), 6.68-6.77 (m, 4H), 7.07-7.15 (m, 5H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 22.5, 26.4, 38.9, 55.1, 65.9, 70.7, 127.5, 127.7, 128.4, 128.6, 135.3, 137.7, 158.6; IR (KBr) v: 3019, 2976, 2891, 2430, 2400, 1521, 1477, 1423, 1216, 1046, 928, 904, 758 cm$^{-1}$; HRMS Calcd. for C$_{19}$H$_{19}$NO: 277.1467, found: 277.1468.

3,3a-Diphenyl-2,3,3a,4,5,6-hexahydro-cyclopenta[b]pyrrole: A suspension of Pd/C (30 mg) and 3aa (300 mg) in MeOH (6 mL) was stirred at 80°C under 40 atm hydrogen atmosphere. After being stirred for 30 h, the mixture was filtrated through a pad of Celite and the filtration was concentrated in vacuo, the residue was purified by column chromatography on silica gel to afford the desired product 6 (255 mg, 63% yield, d.r. > 99:1). [α]$_{25}^D$ +65.4 (c 0.44, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 1.75-2.04 (m, 4H), 2.12-2.16 (m, 1H), 2.40-2.45 (m, 1H), 3.23-3.29 (m, 1H), 3.36-3.39 (m, 2H), 4.45 (brs, 1H), 4.57 (m, 1H), 6.59-6.62 (d, $J$ = 7.2 Hz, 2H), 6.96-7.08 (m, 7H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 23.7, 34.1, 38.7, 50.3, 56.1, 63.6, 68.7, 126.3, 126.8, 127.8, 128.1, 128.5, 128.6, 137.4, 144.5; IR (KBr) v: 3450, 3019, 2976, 2891, 2426, 2400, 1521, 1477, 1423, 1216, 1046, 929, 758 cm$^{-1}$; HRMS Calcd. for C$_{19}$H$_{21}$N: 263.1674, found: 263.1744.
3,3a-Diphenyl-1-(toluene-4-sulfonyl)-octahydro-cyclopenta[b]pyrrole: To a magnetically stirred solution of 6 (263 mg, 1 mmol) in dry DCM (5 ml), Et₃N (0.42 ml, 3 mmol) was added, then TsCl (285 mg, 1.5 mmol) in 1 mL DCM was added slowly. After the reaction was completed to afford the final product (monitored by TLC), DCM was removed in vacuo, the residue was purified by column chromatography on silica gel to afford the desired product 7 (431 mg, 91% yield). 

$\left[\alpha\right]_{D}^{25} +60.9$ (c 1.48, CHCl₃); m.p. 216.5 °C; $^1$H NMR (CDCl₃, TMS, 300 MHz) δ 1.61-1.64 (m, 1H), 1.80-1.89 (m, 1H), 1.90-2.02 (m, 1H), 2.04-2.20 (m, 1H), 2.29-2.35 (m, 2H), 2.58 (s, 3H), 3.30-3.34 (m, 1H), 3.39-3.41 (m, 1H), 3.71-3.76 (dd, J = 6.3 and 8.1 Hz, 1H), 4.21-4.23 (d, J = 7.2 Hz, 1H), 5.96-5.98 (d, J = 7.5 Hz, 2H), 6.41-6.44 (d, J = 7.8 Hz, 2H), 6.70-6.75 (t, J = 7.8 Hz, 2H), 6.93-6.98 (t, J = 7.8 Hz, 3H), 7.03-7.08 (d, J = 7.2 Hz, 1H), 7.49-7.52 (d, J = 7.8 Hz, 2H), 7.91-7.94 (d, J = 8.1 Hz, 2H); $^{13}$C NMR (CDCl₃, TMS, 75 MHz) δ 21.9, 23.5, 35.3, 37.3, 52.3, 52.5, 63.6, 70.3, 126.3, 127.2, 127.6, 127.8, 128.4, 128.7, 130.3, 133.6, 136.0, 143.8, 144.2; IR (KBr) ν: 3019, 2976, 2895, 2428, 2400, 1599, 1520, 1475, 1423, 1374, 1213, 1162, 1047, 928, 877, 769, 669 cm⁻¹; HRMS Calcd. for C₂₆H₂₇NO₂S: 417.1762, found: 417.1844; 99% ee, determined by chiral HPLC analysis (Chiralcel AS-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 210 nm): $t_{major} = 36.9$ min.
4. The absolute configuration of (2S,3S)-3ad and (2S,3S,4S)-7 were determined by X-ray diffraction analysis.

Crystal data for (2S,3S)-3ad: C_{19}H_{18}BrNO_{3}, \( M_r = 388.25 \), \( T = 293 \) K, Orthorhombic, space group \( P2_12_12_1 \), \( a = 8.367(4) \), \( b = 13.132(6) \), \( c = 16.078(8) \) Å, \( V = 1766.6(15) \) Å\(^3\), \( Z = 4 \), 3435 unique reflections, final \( R_1 = 0.0354 \) and \( wR_2 = 0.0922 \) for 2914 observed \([I>2\sigma(I)]\) reflections. CCDC 768128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
Crystal data for (2S,3S,4S)-7: C_{26}H_{27}NO_2S, \( M_r = 417.55 \), \( T = 293 \) K, Orthorhombic, space group \( P2_12_12_1 \), \( a = 7.4773(6) \) Å, \( b = 11.8993(9) \) Å, \( c = 25.2455(19) \) Å, \( V = 2246.2(3) \) Å\(^3\), \( Z = 4 \), 4657 unique reflections, final \( R_1 = 0.0364 \) and \( wR_2 = 0.0787 \) for 3641 observed \([I>2\sigma(I)]\) reflections. CCDC 768129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

5. Proposed transition-state models through synergistic dual activation

Based on the absolute configuration of (2S,3S)-3ad and previous studies\(^6\), a plausible dual activation model accounting for the observed selectivity of the addition of \( \alpha \)-phenyl cyclopentanones to nitroolefins in the presence of I-d as a catalyst is shown in Figure 2, in which the thiourea and sulfonamide moiety interact through hydrogen bonding with a nitro group of the nitroolefins and enhances their electrophilicity while the neighboring tertiary amine deprotonates the \( \alpha \)-proton of \( \alpha \)-phenyl cyclopentanones.
and enhances their nucleophilicity simultaneously. Compared with the extremely slow reaction rate exhibited in the single base-catalyzed racemic version of this Michael addition, the synergistic activation of both nitroolefins and α-phenyl cyclopentanones through the bifunctional catalyst I-d might be responsible for the significantly enhanced reactivity. To avoid the highly steric congestion imposed by the aryl ring of I-d and the phenyl group of 1, the Michael addition would proceed predominantly via the favored transition state A giving the adduct 3aa in (2S,3S)-configuration, which is compatible with the experimental results. Nevertheless, the real catalytic mechanism still needs further investigation.

![Diagram](image-url)
References


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Data File D:\LC\EXQ\DATA\EXQ-6-10\EXQ-6-10K 2009-11-19 15:50-30\SIG1000031.D
Sample Name: dqg-6-10k

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Injection Volume : 5 µl
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Last changed : 11/11/2009 11:12:52 AM by dqg
Last changed : 3/6/2010 4:10:08 PM by zh
(modified after loading)

Area Percent Report

Signal 1: UV1 A, Wavelength=210 nm
Peak Name Type Width Area Height Area
# [mU] [mU] mAU % [mAU] %
1 19.148 88 0.504 5 138.11832 4.77254 3.0275
2 22.836 88 0.300 5 308.68571 145.39640 96.2753
Totals : 322.90533 159.59495

Instrument 1 3/6/2010 4:10:08 PM by zh
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

Data File D:\LC\MQ2\DATA\MQ2-6-201309-6-03\MEL-0-30428\10-23210080001.D
Sample Name: dqg-0-MeCrystal-0

Acq. Operator : dqg  Seq. Line : 1
Acq. Instrument : Instrument 1 Location: Vial 2
Injection Date : 12/15/2009 4:25:54 PM Inj : 1
Injection Volume : 5 μl
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Last changed : 11/17/2009 11:13:52 AM by dqg
Analysis Method : D:\LC\MQ2\DATA\MQ2-6-201309-6-03\MEL-0-30428\10-23210080001.D
Last changed : 3/15/2010 2:45:57 PM by LTL
(modified after loading)

Area Percent Report

Spots By : Signal
Multiplier : 1.0000
Integration : 1.0000
Use Multiplier & Integration with ESDs

Signal 1: V001 A, Wavelength=210 nm

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Totals : 4417.78392 70.39272

**End of Report**

Instrument 1 3/15/2010 3:47:02 PM LTL

Page 1 of 1
Supplementary Material (ESI) for Chemical Communications
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Data File D:\DATA\0Q-6-7778\0Q-6-7778 2010-01-21 21-27-37\0Q-6-7778.D
Sample Name: 0Q-6-7778

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### Area Percent Report

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**Signal 1: VWD1 A, Wavelength=210 nm**

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**Totals:** 9.441706 1796.28065


Page 1 of 1
Data File D:\ICP\DMQ\DATA\DMQ-5-31C\2009-12-07 21-01-40\Q\QI0001.D
Sample Name: dqg-5-12

In Instrument 1 Location: Viol 76
Injection Date: 12/7/2009 9:03:10 PM
Injection Volume: 5 μL
Inj.: 1

Acq. Method: D:\ICP\DMQ\DATA\DMQ-5-31C\2009-12-07 21-01-40\Q\QI0001.D

Analysis Method: D:\ICP\DMQ\DATA\DMQ-5-31C\2009-12-07 21-01-40\Q\QI0001.D

modified after loading

试探图

Area Percent Report

Signal 1: WDL A, Wavelength=310 nm

Peak Height Type Width Area Height Area
# [μM] [μM] ΔμM % [μM] %
1 28.419 88 0.8867 1.8786e+05 338.8298 95.3019
2 35.572 88 1.0358 926.59991 13.06383 4.5981

Totals: 1.97279e+06 341.88569

Instrument 1 3/6/2010 7:58:02 PM by zzh
Data File D:\LC\Data\09-08-2009\5-57\DQ\2009-12-09 10-57-22\SIG100021.D
Sample Name: dqg-0-35a

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Injection Date : 12/9/2009 10:56:59 AM Rinj: 1
Injection Volume : 5 µl
Acq. Method : D:\LC\Data\09-08-2009\5-57\DQ\2009-12-09 10-57-22\SIG100021.D\DQ.D
Last changed : 11/5/2009 2:15:10 PM by DQ
Analysis Method : D:\LC\Data\09-08-2009\5-57\DQ\2009-12-09 10-57-22\SIG100021.D\DQ.D (A31-904-109006=21000.M)
Last changed : 3/6/2010 7:47:47 PM by zh
(modified after loading)

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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Injection : 1.0000
Use Multiplier & Injection Factor with ESTDs
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Signal at 210 A, Wavelength=210 nm

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Page 1 of 1

90