Supporting Information

for

Asymmetric Michael addition reactions catalyzed by calix[4]thiourea cyclohexanediamine derivatives

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General

All chemicals were used as received without special purification unless stated otherwise. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 300 and 75 MHz NMR spectrometer using TMS as the internal standard. Melting points (mp) are determined with a MPA 100 apparatus and are not corrected. The ee values of products were determined by chiral-phase HPLC analysis. (1R, 2R)-N,N'-dimethylcyclohexane-1,2-diamine, (1R,2R)-N-Boc-cyclohexanediamine, 5a and 5b were prepared according to literature procedures [1,2].

2. Synthesis of catalysts and characterization data

2.1 Synthesis of isothiocyanato-calix[4]arenes

To a solution of 5a or 5b (1 equiv) in 20 mL DCM, NaOH (3 equiv or 6 equiv, respectively) was added and the resulting mixture was stirred at room temperature for 15 min. Next, phenyl chlorothionocarbonate (1 equiv or 2 equiv respectively) was added slowly in 5 min. After the reaction was complete, the reaction mixture washed with 10% HCl and deionized water. The aqueous layer was extracted with DCM, the combined organic phase was dried over MgSO4 and concentrated to give the crude product, which was purified by flash chromatography on silica gel (eluent with ethyl acetate/hexane 1:100) to afford product 6a or 6b.

Compound 6a. White solid; 71% yield; mp: 116-117 °C; $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) = 0.95-1.02 (m, 12H, CH$_3$), 1.25-1.39 (m, 5H, CH$_2$), 1.47-1.59 (m, 3H, CH$_2$), 1.79-1.92 (m, 8H, CH$_2$), 3.08 (d, J = 13.5 Hz, 2H, ArCH$_2$Ar), 3.17 (d, J = 13.5 Hz, 2H, ArCH$_2$Ar), 3.75-3.80 (m, 4H, ArOCCH$_2$), 3.87-4.03 (m, 4H, ArOCCH$_2$), 4.39 (d, J = 9.0 Hz, 2H, ArCH$_2$Ar), 4.44 (d, J = 9.0 Hz, 2H, ArCH$_2$Ar), 6.19 (s, 2H, ArH), 6.42 (d, J = 7.5 Hz, 2H, ArH), 6.46-6.52 (m, 1H, ArH), 6.78-6.95 (m, 6H, ArH). $^{13}$C NMR (75
MHz, CDCl$_3$): $\delta$ (ppm) = 13.9, 14.0, 14.1, 19.1, 19.4, 19.5, 30.8, 31.0, 32.1, 32.3, 32.4, 74.8, 74.9, 75.0, 77.2, 122.0, 122.2, 124.1, 124.9, 127.7, 128.4, 129.1, 134.0, 135.3, 136.0, 136.5, 155.4, 155.8, 157.3.

Compound 6b. White solid; 75% yield; mp: 123–126 ºC; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 0.95-1.02 (m, 12H, CH$_3$), 1.34-1.41 (m, 4H, CH$_2$), 1.47-1.54 (m, 4H, CH$_2$), 1.81-1.92 (m, 8H, CH$_2$), 3.11 (d, $J$= 13.5 Hz, 4H, ArCH$_2$Ar), 3.79-3.93 (m, 8H, ArOC$_2$H$_2$), 4.40 (d, $J$= 13.2 Hz, 4H, ArCH$_2$Ar), 6.38 (s, 4H, ArH), 6.72-6.80 (m, 6H, ArH). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 14.0, 14.1, 19.2, 19.4, 26.9, 29.7, 30.9, 32.1, 32.3, 75.0, 75.2, 77.2, 122.7, 124.7, 125.1, 128.7, 133.3, 134.8, 136.3, 155.6, 156.6.

2.2 Synthesis of catalyst 1

To a solution of chiral (1$R$,2$R$)-N-Boc-cyclohexanediamine (0.21 mmol) in DCM (15 mL) was added 6a (0.21 mmol). The reaction mixture was stirred for 0.5 h at room temperature. After removal of the solvent, the crude product was purified by flash chromatography on silica gel (eluent with ethyl acetate/hexane 1:4) to give Boc-protected product. Subsequently, CF$_3$COOH (1 mL) and DCM (30 mL) were added, and the mixture was stirred at room temperature for 3 h. After the reaction was complete, the solvent was distilled off. Then, DCM (30 mL) and H$_2$O (30 mL) were successively added, and 2.0 mol/L NaOH solution was added dropwise to adjust the pH to 8–9. The aqueous layer was extracted with DCM (3 × 20 mL), the combined organic phase was dried over MgSO$_4$ and concentrated to give the catalyst 1.

Compound 1. White solid; 89% yield; mp: 134-135 ºC; $[\alpha]_D^{20}$ -37.5° (C = 1.0, in CHCl$_3$); $^1$H NMR (300MHz, DMSO-d$_6$): $\delta$ = 0.95-1.01 (m, 12H, CH$_3$), 1.22-1.53 (m, 14H, CH$_2$ + CHHCH$_2$CH$_2$CHH), 1.65-1.75 (m, 2H, CHHCH$_2$CH$_2$CHH), 1.82-2.02 (m, 10H, CH$_2$ + CHNH$_2$ + CHNH), 3.11-3.19 (m, 4H, ArCH$_2$Ar), 3.79-3.88 (m, 8H, ArOCH$_2$), 4.33-4.37 (m, 4H, ArCH$_2$Ar), 6.27-6.80 (m, 11H, ArH), 7.56 (d, 1H, $J$ = 8.4 Hz, NH), 7.88 (s, 2H, NH$_2$), 9.25 (s, 1H, NH). $^{13}$C NMR (75MHz, DMSO-d$_6$): $\delta$ (ppm) = 14.3, 14.4, 19.3, 19.4, 23.7, 24.5, 29.9, 30.7, 31.4, 32.3, 53.5, 55.4, 74.8, 74.9, 75.0,
2.3 Synthesis of catalyst 2 and 3

To a solution of chiral (1R,2R)-N,N'-dimethylcyclohexane-1,2-diamine (1.0 mmol) in DCM (15 mL) was added 6a or 6b (0.5 mmol). The reaction mixture was stirred for 0.5 h at room temperature. After removal of the solvent, the crude product was purified by flash chromatography on silica gel (eluent with CH₃OH/CH₂Cl₂ 1:25) to afford product 2 or 3.

Compound 2. White solid; 81% yield; mp: 92–93 °C; [α]D²⁰ -38.5° (C = 1.0, in CHCl₃); ¹H NMR (300MHz, DMSO-d₆): δ (ppm) = 0.95-0.99 (m, 12H, C₂H₃), 1.15-1.23 (m, 4H, CH₂CH₂CH₂CH₂), 1.34-1.73 (m, 12H, CH₂ + CH₂CH₂CH₂CH₂), 1.80-1.93 (m, 10H, CH₂ + CHN(CH₃)₂ + CHNH), 2.18 (s, 6H, N(CH₃)₂), 3.09-3.19 (m, 4H, ArCH₂Ar), 3.75-3.90 (m, 8H, ArOC₂H₂), 4.29-4.36 (m, 4H, ArCH₂Ar), 6.44-6.82 (m, 11H, ArH), 7.13 (d, 1H, J = 6.6 Hz, NH), 9.11 (s, 1H, NH). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm) = 14.3, 14.4, 19.3, 19.4, 21.8, 24.9, 25.1, 30.6, 32.2, 32.3, 32.8, 55.3, 65.8, 74.7, 74.8, 74.9, 122.3, 123.1, 123.4, 128.1, 128.2, 128.3, 128.6, 128.7, 134.3, 134.6, 134.7, 135.4, 135.5, 153.6, 156.2, 156.8, 174.9. HR-ESI-MS (C₅₃H₈₃N₃O₄S): m/z calcd for [M + H]⁺ = 847.5322, found = 847.5320.

Compound 3. White solid; 55% yield; mp: 142–144 °C; [α]D²⁰ -36.5° (C = 1.0, in CHCl₃); ¹H NMR (300 MHz, DMSO-d₆) δ (ppm) = 0.95-1.40 (m, 28H, CH₃ + CH₂CH₂CH₂CH₂), 1.48-1.97 (m, 18H, CH₂ + CHN(CH₃)₂), 2.22 (s, 12H, N(CH₃)₂), 3.12 (d, 4H, J = 12.6 Hz, ArCH₂Ar), 3.70-3.97 (m, 10H, CHNH + ArOCH₂), 4.32 (d, 4H, J = 13.5 Hz, ArCH₂Ar), 6.36 (s 5H, ArH), 7.00-7.23 (m, 5H, ArH), 9.32 (s, 2H, NH). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 14.0, 14.1, 19.2, 19.5, 22.0, 24.6, 25.1, 29.7, 31.0, 31.1, 32.1, 32.4, 32.8, 40.2, 55.9, 66.7, 74.9, 75.0, 77.2, 122.3, 124.1, 128.8, 128.9, 135.1, 135.2, 135.8, 153.9, 157.3, 179.8. HR-ESI-MS (C₆₂H₉₀N₆O₄S₂): m/z calcd for [M + H]⁺ = 1046.6465, found = 1046.6459.
2.4 Synthesis of catalyst 4

To a solution of 4-butoxyaniline (1.0 mmol) in 20 mL DCM, was added NaOH (4.5 mmol) and the resulting mixture was stirred at room temperature for 15 min. Next, phenyl chlorothionocarbonate was added slowly over 5 min. After the reaction was complete, the reaction mixture washed with 10% HCl (2 × 20 mL) and deionized water (2 × 20 mL). The aqueous layer was extracted with DCM (3 × 20 mL), the combined organic phase was dried over MgSO4 and concentrated to give the crude product, which was purified by flash chromatography on silica gel (eluent with ethyl acetate/hexane 1:100) to afford 1-butoxy-4-isothiocyanatobenzene. Then, 1-butoxy-4-isothiocyanatobenzene (0.5 mmol) was added to a solution of chiral (1R,2R)-N,N'-dimethylcyclohexane-1,2-diamine (1.0 mmol) in DCM (15 mL). The reaction mixture was stirred for 0.5 h at room temperature. After removal of the solvent, the crude product was purified by flash chromatography on silica gel (eluent with CH3OH/CH2Cl2 1:2) to afford catalyst 4.

Compound 4. Yellow solid; 82% yield; [α]D 20°-27.6 (C = 1.0, in CHCl3); 1H NMR (300 MHz, DMSO-d6): δ (ppm) = 0.93 (t, J = 7.5 Hz, 3H, CH3), 1.04-1.24 (m, 4H, CH2CH2CH2CH2), 1.37-1.49 (m, 2H, CH2), 1.55-1.78 (m, 5H, CH2 + CH2CH2CH2CHH), 2.21-2.31 (m, 7H, N(CH3)2 + CH3CH2CH2CHH), 2.42-2.50 (m, 1H, CHN(CH3)2), 3.91-4.05 (m, 3H, ArOCH2 + CHNH), 6.85-6.89 (m, 2H, ArH), 7.21 (d, 1H, J = 6.9 Hz, NH), 7.26-7.29 (m, 2H, ArH), 9.35 (s, 1H, NH). 13C NMR (75 MHz, DMSO-d6): δ (ppm) = 14.2, 19.2, 22.0, 25.0, 25.2, 31.3, 31.7, 32.7, 40.2, 55.3, 65.7, 67.7, 114.8, 125.4, 132.3, 156.0, 179.8. HR-ESI-MS (C19H31N3OS): m/z calcd for [M + H]+ = 349.2188, found = 349.2193.

3. Synthesis of substrates and characterization data

General procedure: To a stirred solution of the nitroalkene (0.5 mmol) and catalyst 2 (0.025 mmol, 5 mol %) in the mixed solvent of toluene (0.32 mL) and water (0.16 mL) was added acetylacetone (1 mmol). After the reaction was completed (monitored by TLC), the resulting mixture was concentrated and the residue was purified by flash
chromatography on silica gel (eluent with ethyl acetate/hexane 1:5 to 1:2) to afford the product. All products had NMR spectra in agreement with published data.

![Chemical Structure](image)

**Compound 9a [3]: (R)-3-(2-Nitro-1-phenylethyl)-pentane-2,4-dione**

White solid; yield 99%; 94% ee determined by HPLC analysis (Daicel Chiralpak AS-H column, hexane/2-propanol = 85/15, flow rate: 1.0 mL/min, wavelength = 210 nm: t<sub>R</sub> (minor) = 16.1 min, t<sub>R</sub> (major) = 25.3 min). \(^1\)H NMR (300 MHz, CDCl<sub>3</sub>) \(\delta\) (ppm) = 7.35-7.27 (m, 3H, CH), 7.20-7.17 (m, 2H, CH), 4.67-4.60 (m, 2H, CH<sub>2</sub>), 4.37 (d, \(J = 10.8\) Hz, 1H, CH), 4.28-4.20 (m, 1H, CH), 2.28 (s, 3H, CH<sub>3</sub>), 1.94 (s, 3H, CH<sub>3</sub>). \(^13\)C NMR (75 MHz, CDCl<sub>3</sub>) \(\delta\) (ppm) = 29.7, 30.5, 42.8, 70.6, 78.2, 128.0, 128.5, 129.3, 136.0, 201.1, 201.8.

![Chemical Structure](image)

**Compound 9b [3]: (R)-3-(2-Nitro-1-(p-tolyl)ethyl)pentane-2,4-dione**

White solid; yield 96%; 72% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 90/10, flow rate: 1.0 mL/min, wavelength = 210 nm: t<sub>R</sub> (minor) = 10.9 min, t<sub>R</sub> (major) = 17.3 min). \(^1\)H NMR (300 MHz, CDCl<sub>3</sub>): 7.14-7.05 (m, 4H, CH), 4.66-4.57 (m, 2H, CH<sub>2</sub>), 4.36 (d, \(J = 10.8\) Hz, 1H, CH), 4.24-4.14 (m, 1H, CH), 2.29 (s, 6H, CH<sub>3</sub>), 1.94 (s, 3H, CH<sub>3</sub>) ppm. \(^13\)C NMR (75 MHz, CDCl<sub>3</sub>) \(\delta\) (ppm) = 201.9, 201.2, 138.4, 132.8, 130.0, 127.8, 78.4, 70.8, 42.5, 30.5, 29.5, 21.1.
Compound 9c [3]: (R)-3-[1-(4-Methoxyphenyl)-2-nitroethyl]pentane-2,4-dione

White solid; yield 97%; 46% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 90/10, flow rate: 1.0 mL/min, wavelength = 210 nm: \( t_R \) (minor) = 14.6 min, \( t_R \) (major) = 22.1 min). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.10 (d, \( J = 8.7 \) Hz, 2H, \( CH \)), 6.85 (d, \( J = 8.7 \) Hz, 2H, \( CH \)), 4.60-4.58 (m, 2H, \( CH_2 \)), 4.33 (d, \( J = 11.1 \) Hz, 1H, \( CH \)), 4.23-4.15 (m, 1H, \( CH \)), 3.78 (s, 3H, OCH\(_3\)), 2.29 (s, 3H, \( CH_3 \)), 1.94 (s, 3H, \( CH_3 \)) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 201.9, 201.2, 159.5, 129.1, 127.6, 114.7, 77.4, 71.0, 55.2, 42.1, 30.4, 29.4.

Compound 9d [3]: (R)-3-[1-(3-Methoxyphenyl)-2-nitroethyl]pentane-2,4-dione

White solid; yield 99%; 63% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol =85/15, flow rate: 1.0 mL/min, wavelength = 210 nm: \( t_R \) (minor) = 9.6 min, \( t_R \) (major) = 12.3 min). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.23 (d, \( J = 8.1 \) Hz, 1H, \( CH \)), 6.83-6.71 (m, 3H, \( CH \)), 4.64-4.61 (m, 2H, \( CH_2 \)), 4.37 (d, \( J = 10.8 \) Hz, 1H, \( CH \)), 4.25-4.20 (m, 1H, \( CH \)) 3.78 (s, 3H, OCH\(_3\)), 2.30 (s, 3H, \( CH_3 \)), 1.97 (s, 3H, \( CH_3 \)) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 201.8, 201.0, 160.1, 137.6, 130.4, 119.9, 114.2, 113.6, 78.2, 70.6, 55.3, 42.8, 30.5, 29.6.
Compound 9e[4]: (R)-3-[1-(4-Trifluoromethylphenyl)-2-nitroethyl]pentane-2,4-dione
Colorless oil; yield 99%; 76% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 90/10, flow rate: 1.0 mL/min, wavelength = 210 nm: $t_R$ (minor) = 9.1 min, $t_R$ (major) = 49.9 min). $^1$H NMR (300 MHz, CDCl$_3$): 7.61 (d, $J = 8.1$ Hz, 2H, CH), 7.34 (d, $J = 8.1$ Hz, 2H, CH), 4.72-4.61 (m, 2H, CH$_2$), 4.41-4.29 (m, 1H, CH), 2.32 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 201.2, 200.4, 140.3, 131.0, 130.6, 128.5, 126.3, 77.7, 70.3, 42.4, 30.5, 29.8.

Compound 9f [5]: (R)-3-[1-(4-Bromophenyl)-2-nitroethyl]pentane-2,4-dione
White solid; yield 93%; 64% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 85/15, flow rate: 0.7 mL/min, wavelength = 210 nm: $t_R$ (minor) = 17.5 min, $t_R$ (major) = 54.3 min). $^1$H NMR (300 MHz, CDCl$_3$): 7.47 (d, $J = 8.4$ Hz, 2H, CH), 7.08 (d, $J = 8.4$ Hz, 2H, CH), 4.67-4.60 (m, 2H, CH$_2$), 4.33 (d, $J = 10.8$ Hz, 1H, CH), 4.26-4.18 (m, 1H, CH), 2.30 (s, 3H, CH$_3$), 1.98 (s, 3H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 201.4, 200.6, 135.1, 132.5, 129.7, 122.7, 77.9, 70.4, 42.2, 30.5, 29.7.
Compound 9g [5]: (R)-3-[1-(2-Bromophenyl)-2-nitroethyl]pentane-2,4-dione

Orange solid; yield 95%; 70% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 98/2, flow rate: 0.7 mL/min, wavelength = 210 nm: $t_R$ (minor) = 43.7 min, $t_R$ (major) = 46.2 min). $^1$H NMR (300 MHz, CDCl$_3$): 7.63 (d, $J$ = 7.8 Hz, 1H, CH), 7.31-7.26 (m, 1H, CH), 7.20-7.13 (m, 2H, CH), 4.87-4.81 (m, 1H, CH), 4.78-4.66 (m, 2H, CH$_2$), 4.60 (d, $J$ = 9.3 Hz, 1H, CH), 2.28 (s, 3H, CH$_3$), 2.05 (s, 3H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 202.0, 200.9, 135.1, 134.0, 130.0, 128.3, 77.5, 69.1, 41.1, 31.0, 28.5.

Compound 9h [5]: (R)-3-[1-(4-Fluorophenyl)-2-nitroethyl]pentane-2,4-dione

Colorless oil; yield 90%; 68% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol = 90/10, flow rate: 0.7 mL/min, wavelength = 210 nm: $t_R$ (minor) = 13.8 min, $t_R$ (major) = 26.5 min). $^1$H NMR (300 MHz, CDCl$_3$): 7.20-7.15 (m, 2H, CH), 7.06-6.99 (m, 2H, CH), 4.62-4.60 (m, 2H, CH$_2$), 4.36-4.20 (m, 2H, CH), 2.28 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 201.5, 200.8, 164.2, 160.9, 131.8, 130.0, 129.5, 116.5, 116.3, 78.2, 70.7, 42.0, 30.5, 29.6.

Compound 9i [3]: (R)-3-[1-(2-Fluorophenyl)-2-nitroethyl]pentane-2,4-dione

Colorless oil; yield 91%; 59% ee determined by HPLC analysis (Daicel Chiralpak
AD-H column, hexane/2-propanol = 90/10, flow rate: 1.0 mL/min, wavelength = 210 nm: \( t_R \) (minor) = 10.5 min, \( t_R \) (major) = 12.0 min. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.33-7.26 (m, 1H, CH), 7.21-7.04 (m, 3H, CH), 4.80-4.61 (m, 2H, CH\(_2\)), 4.53-4.43 (m, 2H, CH), 2.29 (s, 3H, CH\(_3\)), 2.02 (s, 3H, CH\(_3\)) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 201.9, 200.9, 133.8, 133.5, 130.7, 129.7, 129.0, 127.7, 77.5, 68.9, 38.9, 30.9, 28.6.

![Chemical structure](image)

**Compound 9j [5]:** (R)-3-[1-(4-Chlorophenyl)-2-nitroethyl]pentane-2,4-dione

White solid; yield 92%; 70% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol =85/15, flow rate: 0.7 mL/min, wavelength = 210 nm: \( t_R \) (minor) = 16.4 min, \( t_R \) (major) = 42.0 min. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.31 (d, \( J = 8.4 \) Hz, 2H, CH), 7.14 (d, \( J = 8.4 \) Hz, 2H, CH), 4.63-4.60 (m, 2H, CH\(_2\)), 4.34 (d, \( J = 10.5 \) Hz, 1H, CH), 4.27-4.19 (m, 1H, CH), 2.30 (s, 3H, CH\(_3\)), 1.98 (s, 3H, CH\(_3\)) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 201.4, 200.6, 134.6, 129.6, 129.3, 77.9, 70.5, 42.1, 30.5, 29.7.

![Chemical structure](image)

**Compound 9k [5]:** (R)-3-[1-(2-Chlorophenyl)-2-nitroethyl]pentane-2,4-dione

White solid; yield 90%; 72% ee determined by HPLC analysis (Daicel Chiralpak AD-H column, hexane/2-propanol =98/2, flow rate: 0.7 mL/min, wavelength = 210 nm: \( t_R \) (minor) = 30.3 min, \( t_R \) (major) = 32.8 min. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.45-7.40 (m, 1H, CH), 7.26-7.21 (m, 2H, CH), 7.19-7.15 (m, 1H, CH), 4.87-4.58 (m, 4H, CH + CH\(_2\)), 2.28 (s, 3H, CH\(_3\)), 2.04 (s, 3H, CH\(_3\)) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 201.9, 200.9, 133.8, 133.5, 130.7, 129.7, 129.0, 127.7, 77.5, 68.9, 38.9, 30.9, 28.6.
4. NMR spectra for catalysts and intermediates

$^1$H NMR spectrum of 6a

$^{13}$C NMR spectrum of 6a
$^1$H NMR spectrum of 6b

$^{13}$C NMR spectrum of 6b
\(^1\)H NMR spectrum of catalyst 1

\(^{13}\)C NMR spectrum of catalyst 1
$^1$H NMR spectrum of catalyst 2

$^{13}$C NMR spectrum of catalyst 2
$^1$H NMR spectrum of catalyst 3

$^{13}$C NMR spectrum of catalyst 3
$^1$H NMR spectrum of catalyst 4

$^{13}$C NMR spectrum of catalyst 4
5. NMR spectra for products

$^1$H NMR spectrum of 9a

$^{13}$C NMR spectrum of 9a
$^1$H NMR spectrum of 9b

$^{13}$C NMR spectrum of 9b
$^1$H NMR spectrum of 9c

$^{13}$C NMR spectrum of 9c
$^1$H NMR spectrum of 9d

$^{13}$C NMR spectrum of 9d
\(^1\)H NMR spectrum of 9e

\(^{13}\)C NMR spectrum of 9e
$^1$H NMR spectrum of $9f$

$^{13}$C NMR spectrum of $9f$
$^1$H NMR spectrum of $9g$

$^{13}$C NMR spectrum of $9g$
$^1$H NMR spectrum of 9h

$^{13}$C NMR spectrum of 9h
$^1$H NMR spectrum of 9i

$^{13}$C NMR spectrum of 9i
$^1$H NMR spectrum of $9j$

$^{13}$C NMR spectrum of $9j$
$^1$H NMR spectrum of 9k

$^{13}$C NMR spectrum of 9k
6. HPLC chromatograms

![HPLC Chromatograms](image)

(Racemic)

![HPLC Chromatograms](image)

(Chiral)

| 峰号 | 保留时间 | 面积   | 高度   | 面积 % | 高度 % |
|------|----------|--------|--------|--------|--------|
| 1    | 16.134   | 728965 | 27922  | 2.393  | 5.401  |
| 2    | 28.259   | 28982071 | 489071 | 97.197 | 94.599 |
| 总计 |          | 26011834 | 316993 | 100.0000 | 100.0000 |
(Racemic)

(Chiral)

| 峰号 | 保留时间 | 面积 | 高度 | 面积 % | 高度 % |
|------|-----------|------|------|--------|--------|
| 1    | 16.914    | 600672 | 31266 | 15.878 | 20.716 |
| 2    | 17.311    | 3207000 | 125528 | 88.122 | 79.284 |
| 总计 | 3807770   | 153344 | 100.000 | 100.000 |

(Racemic)

(Racemic)

(Chiral)

(Chiral)
(Racemic)

(Chiral)

| 峰号 | 保留时间 | 面积  | 面积 % | 高度  | 面积 % |
|------|---------|------|--------|-------|--------|
| 1    | 9.615   | 4735510 | 320163 | 15.679 | 22.867 |
| 2    | 12.264  | 20668532 | 1079926 | 81.321 | 77.133 |
| 总计 |         | 25355242 | 1400089 | 100.000 | 100.000 |
(Racemic)

(Chiral)

S32
(Racemic)

(Chiral)

| 峰号 | 保留时间 | 面积   | 高度 | 面积 % | 高度 % |
|------|----------|-------|------|-------|-------|
| 1    | 17.500   | 10770979 | 420431 | 17.834 | 39.571 |
| 2    | 54.399   | 19624933 | 6420411 | 82.166 | 60.129 |
| 总计 |          | 60396572 | 10624720 | 100.000 | 100.000 |
(Racemic)

(Chiral)

| 峰号 | 保留时间 | 面积    | 高度 (abs) | 面积 %  | 高度 %  |
|------|-----------|---------|-----------|---------|---------|
| 1    | 43.689    | 2648925 | 47438     | 14.857  | 18.354  |
| 2    | 46.184    | 15174497| 244416    | 85.143  | 83.746  |
| 总计 | 17823023  | 2918547 | 100.000   | 100.000 | 100.000 |
(Racemic)

(Chiral)

| 峰表 | PDA Ch1 210nm 4nm | 保留时间 | 面积 | 面积 % | 高度 | 面积 % | 高度 % |
|------|------------------|----------|------|--------|------|--------|--------|
| 1    | 13.799           | 2401325  | 166232 | 15.999 | 55.237 |
| 2    | 26.477           | 12068996 | 509763 | 84.001 | 74.463 |
| 总计 |                  | 1509422  | 415985 | 100.000 | 100.000 |
(Racemic)

(Chiral)
(Racemic)

(Chiral)

| 峰号 | 保留时间 | 面积   | 高度 | 面积% | 高度% |
|------|----------|-------|------|-------|-------|
| 1    | 30.283   | 1879169 | 46314 | 18.942 | 18.340 |
| 2    | 35.785   | 11999093 | 255600 | 86.058 | 84.660 |
| 总计 |          | 13478202 | 301911 | 100.000 | 100.000 |
7. References

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