Half-Sandwich Chiral Rare-Earth Metal Complexes with Linked Tridentate Amido-Indenyl Ligand: Synthesis, Characterization, and Catalytic Properties for Intramolecular Hydroamination

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Determination of the enantiomeric excess (ee) values

The enantiomeric excess values were determined by HPLC analysis of 7 using AS-H, AD-H, or OJ-H column. Typical procedure of derivatization: To a solution of the corresponding cyclized product 6 (0.16 mmol) in CH2Cl2 (5 mL) was added 4-dimethylaminopyridine (DMAP, 4.8 mg, 0.04 mmol), triethylamine (45 μL, 0.3 mmol), and 4-methoxybenzoyl chloride (40 μL, 0.3 mmol) at ambient temperature. After stirring for 2 h, a saturated aqueous solution of ammonium chloride (5 mL) was poured into the reaction mixture and the layers were separated. The aqueous layer was extracted with CH2Cl2 (3×5 mL). The combined organic layers were washed with saturated aqueous solution of ammonium chloride (5 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC (silica gel).

(7a): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 94% yield (87% ee). The ee was determined by HPLC analysis using a Chiralcel OD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 6.2 (minor), 8.1 (major) min). 1H NMR (300 MHz, CDCl3): δ 7.52 (d, J = 8.8 Hz, 2H), 7.36–7.08 (m, 11H), 7.06–6.91 (m, 6H), 4.39–4.25 (m, 2H), 3.87 (s, 3H), 3.57 (d, J = 11.1 Hz, 1H), 3.31 (dd, J = 13.2, 3.0 Hz, 1H), 3.04 (dd, J = 12.9, 8.1 Hz, 1H), 2.74–2.64 (m, 1H), 2.49 (dd, J = 12.6, 10.5 Hz, 1H). 13C NMR (75.5 MHz, CDCl3): δ 169.9, 161.3, 145.2, 144.1, 138.1, 130.0, 129.5, 129.1, 128.6, 128.5, 128.4, 126.7, 126.6, 126.5, 126.4, 113.7, 60.2, 57.3, 55.4, 53.4, 42.0, 38.5. HRMS (ESI) calcd for C31H29NO2Na ([M + Na]+) 470.2096, found 470.2095.

(7b): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 92% yield (68% ee). The ee was determined by HPLC analysis using a Chiralcel OD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 37.9 (major), 11.6 (minor) min). 1H NMR (300 MHz, CDCl3): δ 7.54 (d, J = 8.2 Hz, 2H), 7.33–7.10 (m, 8H), 7.03 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 4.38 (d, J = 11.1 Hz, 1H), 4.17–4.01 (m, 1H), 3.94–3.76 (m, 4H), 2.96–2.81 (m, 1H), 2.36 (t, J = 11.3 Hz, 1H), 1.45 (d, J = 5.8 Hz, 3H). 13C NMR (75.5 MHz, CDCl3): δ 168.8, 160.2, 144.4, 143.3, 128.5, 128.3, 127.6, 127.5, 125.7, 125.6, 125.5, 125.3, 112.6, 58.7, 54.3, 52.6, 51.5, 44.6, 18.8. HRMS (ESI) calcd for C25H26NO2 ([M + H]+) 372.1964,
found 372.1964.

(7c): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 94% yield (45% ee). Mp 187–188 °C. The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 8.2 (major), 20.6 (minor) min). 1H NMR (300 MHz, CDCl3): δ 7.44–7.12 (m, 12H), 6.93–6.83 (m, 2H), 5.41–5.10 (brs, 1H), 4.34–4.07 (brs, 1H), 3.81 (s, 3H), 3.17 (d, J = 13.5 Hz, 1H), 2.66–2.49 (m, 2H), 1.84–1.66 (m, 1H), 1.43 (d, J = 13.5 Hz, 1H), 1.20 (d, J = 6.9 Hz, 3H). 13C NMR (75.5 MHz, CDCl3): δ 171.0, 160.4, 147.4, 143.8, 129.3, 128.5, 128.4, 128.0, 127.7, 126.5, 126.4, 126.1, 113.8, 55.3, 48.4, 47.2, 45.9, 29.5, 26.2, 17.2. HRMS (ESI) calcd for C26H28NO2 ([M + H]+) 386.2120, found 386.2120.

(7d): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a viscous colorless oil in 91% yield (56% ee). The ee was determined by HPLC analysis using a Chiralcel AS-H column (4/1 hexane/i-PrOH; flow rate 0.8 mL/min; λ = 254 nm; tR = 9.03 (minor), 11.2 (major) min). 1H NMR (300 MHz, CDCl3): δ 7.51 (d, J = 8.4 Hz, 2H), 6.96–6.84 (m, 2H), 4.44–4.23 (m, 1H), 3.84 (s, 3H), 3.39–3.25 (m, 1H), 3.24–3.07 (m, 1H), 1.99–1.85 (m, 1H), 1.49–1.25 (m, 4H), 1.06 (s, 3H), 0.90 (s, 3H). 13C NMR (75.5 MHz, CDCl3): δ 169.8, 161.0, 129.6, 113.4, 62.9, 55.3, 53.0, 47.6, 38.3, 25.8, 25.5, 20.3. HRMS (ESI) calcd for C15H21NO2Na ([M + Na]+) 270.1470, found 270.1470.

(7e): Purified by preparative TLC (petroleum ether/ethyl acetate = 6/1) to afford the product as a viscous colorless oil in 90% yield (52% ee). The ee was determined by HPLC analysis using a Chiralcel AS-H column (2/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 9.47 (major), 6.83 (minor) min). 1H NMR (300 MHz, CDCl3): δ 7.56–7.48 (m, 2H), 7.34–7.18 (m, 5H), 6.95–6.87 (m, 2H), 4.65–4.50 (m, 1H), 3.84 (s, 3H), 3.27 (dd, J = 12.9, 2.6 Hz, 1H), 3.13 (d, J = 13.2 Hz, 1H), 3.05–2.88 (m, 2H), 1.70 (ddd, J = 12.6, 7.4, 1.7 Hz, 1H), 1.56 (dd, J = 12.5, 10.0 Hz, 1H), 0.95 (s, 3H), 0.84 (s, 3H). 13C NMR (75.5 MHz, CDCl3): δ 169.9, 161.0, 129.6, 113.4, 62.9, 55.3, 53.0, 47.6, 38.3, 25.8, 25.5. HRMS (ESI) calcd for C21H26NO2 ([M + H]+) 324.1964, found 324.1963.

(7f): Purified by preparative TLC (petroleum ether/ethyl acetate = 5/1) to afford the product as a viscous colorless oil in 93% yield (41% ee). The ee was determined by HPLC analysis using a Chiralcel AS-H column (3/1
hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 10.12 (major), 12.32 (minor) min.  

1H NMR (300 MHz, CDCl3): δ 7.31 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 1H), 4.79–4.27 (brs, 1H), 3.83 (s, 3H), 3.76–3.36 (brs, 1H), 2.79 (d, J = 12.9 Hz, 1H), 2.00–1.83 (m, 1H), 1.65–1.50 (m, 1H), 1.42–1.24 (m, 2H), 1.20 (d, J = 6.9 Hz, 3H), 0.93 (s, 3H), 0.90 (s, 3H). 13C NMR (75.5 MHz, CDCl3): δ 170.9, 160.2, 129.4, 128.3, 113.7, 55.3, 32.4, 31.4, 29.1, 26.1, 23.0, 16.2. HRMS (ESI) calcd for C16H24NO2 ([M + H]+) 262.1807, found 262.1806.

(7g): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a viscous colorless oil in 91% yield (65% ee). The ee was determined by HPLC analysis using a Chiralcel AS-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 12.52 (major), 7.61 (minor) min).  

1H NMR (300 MHz, CDCl3): δ 7.51 (d, J = 8.1 Hz, 2H), 6.95–6.85 (m, 2H), 4.39–4.17 (brs, 1H), 3.84 (s, 3H), 3.36 (d, J = 10.2 Hz, 1H), 3.22 (d, J = 10.5 Hz, 1H), 2.12 (dd, J = 12.3, 7.5 Hz, 1H), 1.60–1.12 (m, 14H). 13C NMR (75.5 MHz, CDCl3): δ 169.9, 160.9, 129.5, 113.4, 60.7, 55.3, 52.1, 44.7, 42.3, 36.3, 33.4, 26.1, 22.5, 20.3. HRMS (ESI) calcd for C18H26NO2 ([M + H]+) 288.1963, found 288.1961.

(7h): Purified by preparative TLC (petroleum ether/ethyl acetate = 5/1) to afford the product as a viscous colorless oil in 89% yield (43% ee). The ee was determined by HPLC analysis using a Chiralcel AS-H column (3/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 13.36 (major), 7.88 (minor) min).  

1H NMR (300 MHz, CDCl3): δ 7.31 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.73–4.31 (brs, 1H), 3.84 (s, 3H), 2.70 (d, J = 12.8 Hz, 1H), 2.00–1.69 (m, 2H), 1.62–1.12 (m, 16H). 13C NMR (75.5 MHz, CDCl3): δ 170.9, 160.9, 129.4, 128.6, 113.7, 55.3, 38.3, 33.8, 30.9, 29.9, 26.5, 25.4, 21.6, 21.4, 16.4. HRMS (ESI) calcd for C19H28NO2 ([M + H]+) 302.2120, found 302.2119.

(7i): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a viscous colorless oil in 90% yield (65% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tR = 25.31 (major), 12.25 (minor) min).  

1H NMR (500 MHz, CDCl3): δ 7.58 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.25–7.02 (m, 10H), 7.01–6.92 (m, 4H), 4.43–4.32 (m, 2H), 3.89 (s, 3H), 3.67 (d, J = 12.1 Hz, 1H), 3.57 (d, J = 13.4 Hz, 1H), 3.28–3.21 (m, 1H), 2.75–2.68 (m, 1H), 2.63–2.55 (m, 1H). 13C NMR (125 MHz, CDCl3): δ 170.2, 161.4, 145.2, 144.0, 138.1, 132.9, 132.0, 129.7, 129.0, 128.65, 128.56, 128.1, 127.4, 126.7, 126.64, 126.55, 126.4, 125.4, 113.8, 60.1, 57.3, 55.4, 53.5, 42.0, 37.8. HRMS (ESI–TOF) m/z [M + H]+ calcd for C31H29BrNO2 526.1382, found 526.1382.
(7j): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 94% yield (80% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t<sub>R</sub> = 32.58 (major), 12.82 (minor) min). ¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.33–7.09 (m, 8H), 7.04 (d, J = 7.9 Hz, 2H), 7.00–6.93 (m, 4H), 4.35 (dd, J = 11.2, 1.5 Hz, 1H), 4.29–4.21 (m, 1H), 3.88 (s, 3H), 3.58 (d, J = 11.2 Hz, 1H), 3.25 (dd, J = 13.2, 2.8 Hz, 1H), 3.02 (dd, J = 13.2, 8.1 Hz, 1H), 2.69 (ddd, J = 12.2, 6.3, 1.5 Hz), 2.43 (dd, J = 12.0, 11.1 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 170.1, 161.5, 145.1, 143.9, 137.1, 131.7, 131.5, 129.5, 128.9, 128.7, 128.6, 126.7, 126.65, 126.60, 126.3, 120.4, 113.8, 60.2, 57.1, 55.4, 53.4, 42.0, 37.9. HRMS (ESI–TOF) m/z [M + H]⁺ calcd for C₃₁H₂₉BrNO₂ 526.1382, found 526.1380.

(7k): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 86% yield (51% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t<sub>R</sub> = 12.01 (major), 8.1 (minor) min). ¹H NMR (500 MHz, CDCl₃): δ 7.56 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 1.9 Hz, 1H), 7.28–7.10 (m, 8H), 7.06 (d, J = 7.4 Hz, 2H), 7.00–6.94 (m, 4H), 4.40 (dd, J = 11.0, 1.2 Hz, 1H), 4.34–4.26 (m, 1H), 3.88 (s, 3H), 3.67 (d, J = 11.2 Hz, 1H), 3.49 (dd, J = 13.5, 3.5 Hz, 1H), 3.19 (dd, J = 13.5, 7.7 Hz, 1H), 2.75–2.68 (m, 1H), 2.49 (dd, J = 12.0, 11.2 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 170.3, 161.5, 145.1, 143.9, 135.3, 135.0, 132.9, 132.8, 129.6, 129.3, 128.8, 128.7, 128.6, 127.1, 126.71, 126.67, 126.6, 126.3, 113.8, 60.1, 57.2, 55.4, 53.5, 42.0, 34.9. HRMS (ESI–TOF) m/z [M + H]⁺ calcd for C₃₁H₂₈Cl₂NO₂ 516.1497, found 516.1492.

(7l): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 92% yield (80% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t<sub>R</sub> = 30.1 (major), 10.6 (minor) min). ¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.25–7.10 (m, 8H), 7.04 (d, J = 7.3 Hz, 2H), 7.00–6.94 (m, 4H), 4.35 (dd, J = 11.2, 1.9 Hz, 1H), 4.30–4.22 (m, 1H), 3.88 (s, 3H), 3.57 (d, J = 11.1 Hz, 1H), 3.26 (dd, J = 13.2, 2.8 Hz, 1H), 3.04 (dd, J = 13.2, 8.1 Hz, 1H), 2.72–2.66 (m, 1H), 2.43 (dd, J = 12.2, 10.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 170.1, 161.4, 145.1, 144.0, 136.6, 132.3, 131.3, 129.5,
128.9, 128.7, 128.6, 128.5, 126.7, 126.65, 126.60, 126.3, 113.8, 60.2, 57.2, 55.4, 53.4, 42.0, 37.8.

HRMS (ESI–TOF) m/z [M + H]+ calcd for C₃₁H₂₉ClNO₂ 482.1887, found 482.1884.

(7m): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 93% yield (67% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tᵣ = 31.03 (major), 14.44 (minor) min).¹H NMR (500 MHz, CDCl₃): δ 7.56–7.50 (m, 2H), 7.24–7.08 (m, 10H), 7.07–7.01 (m, 2H), 7.00–6.92 (m, 4H), 4.36–4.25 (m, 2H), 3.87 (s, 3H), 3.58 (d, J = 11.2 Hz, 1H), 3.26 (dd, J = 13.1, 2.7 Hz, 1H), 3.01 (dd, J = 13.2, 8.1 Hz, 1H), 2.73–2.65 (m, 1H), 2.48 (dd, J = 12.3, 10.7 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 169.9, 161.3, 145.3, 144.2, 135.8, 135.0, 129.9, 129.5, 129.2, 129.0, 128.6, 128.5, 126.7, 126.6, 126.5, 126.4, 113.7, 60.2, 57.4, 55.4, 53.4, 42.0, 38.1, 21.1. HRMS (ESI–TOF) m/z [M + H]+ calcd for C₃₂H₃₂NO₂ 462.2433, found 462.2430.

(7n): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 95% yield (28% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tᵣ = 26.67 (major), 10.33 (minor) min).¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, J = 8.0 Hz, 2H), 7.33–7.09 (m, 9H), 7.07–6.92 (m, 5H), 6.84 (d, J = 7.7 Hz, 2H), 4.37–4.22 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.58–3.50 (m, 1H), 3.24–3.16 (m, 1H), 3.02 (dd, J = 13.2, 8.2 Hz, 1H), 2.74–2.64 (m, 1H), 2.52–2.44 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 169.9, 161.3, 158.3, 145.3, 144.2, 130.9, 130.1, 129.5, 129.2, 128.6, 128.5, 126.7, 126.6, 126.5, 126.4, 113.77, 113.74, 60.2, 57.4, 55.4, 53.4, 41.9, 37.5. HRMS (ESI–TOF) m/z [M + H]+ calcd for C₃₂H₃₂NO₃ 478.2382, found 478.2381.

(7o): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 96% yield (61% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; tᵣ = 38.05 (major), 9.4 (minor) min).¹H NMR (500 MHz, CDCl₃): δ 7.53 (d, J = 8.0 Hz, 2H), 7.32–7.09 (m, 10H), 7.07–6.85 (m, 6H), 4.43–4.27 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.63–3.56 (m, 1H), 3.44–3.35 (m, 1H), 3.14–3.04 (m, 1H), 2.75–2.66 (m, 1H), 2.58–2.48 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 169.9, 161.2, 157.9, 145.4, 144.3, 131.8, 129.6, 129.4, 128.6, 128.4, 127.6, 126.8,
126.7, 126.48, 126.45, 126.42, 120.5, 113.7, 110.5, 60.1, 56.9, 55.43, 55.39, 53.5, 42.0, 32.0.

HRMS (ESI–TOF) m/z [M + H]^+ calcd for C_{32}H_{32}NO_3 478.2382, found 478.2377.

(7p): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 88% yield (83% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 28.67 (major), 16.46 (minor) min). ^1H NMR (500 MHz, CDCl_3): δ 7.54 (d, J = 8.6 Hz, 2H), 7.01–6.94 (m, 4H), 6.87 (d, J = 7.4 Hz, 1H), 6.83–6.76 (m, 2H), 4.38–4.27 (m, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 3.63 (d, J = 11.2 Hz, 1H), 3.33 (dd, J = 13.1, 7.9 Hz, 1H), 2.98 (dd, J = 13.1, 8.4 Hz, 1H), 2.71 (dd, J = 12.6, 6.6, 2.0 Hz, 1H), 2.50 (dd, J = 12.3, 10.7 Hz, 1H). ^13C NMR (125 MHz, CDCl_3): δ 169.9, 161.4, 159.6, 145.3, 144.1, 139.8, 129.6, 129.3, 129.1, 128.6, 128.5, 126.7, 126.6, 126.5, 126.4, 122.4, 115.3, 113.7, 112.1, 60.2, 57.3, 55.4, 55.2, 53.4, 42.1, 38.8. HRMS (ESI–TOF) m/z [M + H]^+ calcd for C_{32}H_{32}NO_3 478.2382, found 478.2379.

(7q): Purified by preparative TLC (petroleum ether/ethyl acetate = 4/1) to afford the product as a white solid in 90% yield (78% ee). The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/i-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 23.73 (major), 18.24 (minor) min). ^1H NMR (500 MHz, CDCl_3): δ 7.85–7.76 (m, 3H), 7.71 (s, 1H), 7.55 (d, J = 8.6 Hz, 2H), 7.22–7.10 (m, 6H), 7.06–6.92 (m, 6H), 4.43–4.31 (m, 2H), 3.89 (s, 3H), 3.56 (d, J = 11.2 Hz, 1H), 3.48 (dd, J = 13.1, 2.9 Hz, 1H), 3.21 (dd, J = 13.2, 8.2 Hz, 1H), 2.75–2.69 (m, 1H), 2.58–2.50 (m, 1H). ^13C NMR (125 MHz, CDCl_3): δ 170.1, 161.4, 145.2, 144.0, 135.7, 133.6, 132.3, 129.6, 129.1, 128.6, 128.5, 128.4, 127.9, 127.7, 127.6, 126.7, 126.6, 126.5, 126.3, 126.0, 125.4, 113.8, 60.2, 57.5, 55.4, 53.4, 42.1, 38.7. HRMS (ESI–TOF) m/z [M + H]^+ calcd for C_{35}H_{32}NO_2 498.2433, found 498.2432.
Copies of $^1$H NMR and $^{13}$C NMR for aminoalkene substrates
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1\text{H NMR}$
300 MHz, CDCl$_3$

$^{13}\text{C NMR}$
75 MHz, CDCl$_3$
$^1$H NMR
500 MHz, CDCl$_3$

$^{13}$C NMR
125 MHz, CDCl$_3$
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
Copies of $^1$H NMR and $^{13}$C NMR for 4-methoxybenzoyl amides
$^1$H NMR 300 MHz, CDCl₃

$^{13}$C NMR 75 MHz, CDCl₃
$^{13}$C NMR
75 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1$H NMR
300 MHz, CDCl$_3$

$^{13}$C NMR
75 MHz, CDCl$_3$
$^1$H NMR
500 MHz, CDCl₃

$^{13}$C NMR
125 MHz, CDCl₃
$^1$H NMR
500 MHz, CDCl$_3$

$^{13}$C NMR
125 MHz, CDCl$_3$
$^1$H NMR
500 MHz, CDCl$_3$

$^{13}$C NMR
125 MHz, CDCl$_3$
$^1$H NMR
500 MHz, CDCl$_3$

$^{13}$C NMR
125 MHz, CDCl$_3$
$^1$H NMR
500 MHz, CDCl$_3$

$^{13}$C NMR
125 MHz, CDCl$_3$
HPLC profile of 4-methoxybenzoyl amides

Racemic

OD-H, hexane/2-propanol=1:1,1mL/min

Table 2 entry 1
Table 3 entry 1

OD-H, hexane/2-propanol=1:1,1mL/min
Table 2 entry 3
Table 4 entry 1
OD-H, hexane/2-propanol=1:1,1mL/min

Racemic

AS-H, hexane/2-propanol=1:1,1mL/min
Table 3 entry 2

<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间</th>
<th>类型</th>
<th>宽度</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.128</td>
<td>1.2854</td>
<td>6625.4333</td>
<td>85.9074</td>
<td>20.2468</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>35.600</td>
<td>6.1738</td>
<td>2.6079e4</td>
<td>70.4530</td>
<td>79.7532</td>
<td></td>
</tr>
</tbody>
</table>

AS-H, hexane/2-propanol=1:1,1mL/min

Table 4 entry 2

<table>
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<th>峰</th>
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<th>宽度</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.589</td>
<td>1.5264</td>
<td>6419.0303</td>
<td>70.0511</td>
<td>16.1119</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>37.570</td>
<td>7.3516</td>
<td>3.3249e4</td>
<td>73.5671</td>
<td>83.8181</td>
<td></td>
</tr>
</tbody>
</table>

AS-H, hexane/2-propanol=1:1,1mL/min
Racemic

<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间 [min]</th>
<th>类型</th>
<th>峰宽 [min]</th>
<th>峰面积 [mAU]</th>
<th>峰高 [mAU]</th>
<th>峰面积 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.555</td>
<td>VPB</td>
<td>0.341</td>
<td>1.4704</td>
<td>663.0571</td>
<td>50.0509</td>
</tr>
<tr>
<td>2</td>
<td>22.600</td>
<td>VPB</td>
<td>1.0039</td>
<td>1.4875</td>
<td>222.0930</td>
<td>16.9461</td>
</tr>
</tbody>
</table>

AD-H, hexane/2-propanol=1:1,1mL/min

--

Table 3 entry 3

<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间 [min]</th>
<th>类型</th>
<th>峰宽 [min]</th>
<th>峰面积 [mAU]</th>
<th>峰高 [mAU]</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.024</td>
<td>VPB</td>
<td>0.2995</td>
<td>4175.9578</td>
<td>206.9127</td>
<td>72.6165</td>
</tr>
<tr>
<td>2</td>
<td>20.578</td>
<td>VPB</td>
<td>0.8786</td>
<td>1574.7436</td>
<td>26.7664</td>
<td>27.3835</td>
</tr>
</tbody>
</table>

AD-H, hexane/2-propanol=1:1,1mL/min
AD-H, hexane/2-propanol=1:1,1mL/min

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.610</td>
<td>MM</td>
<td>0.3911</td>
<td>5088.59180</td>
<td>216.87120</td>
<td>70.8984</td>
</tr>
<tr>
<td>22.663</td>
<td>MM</td>
<td>1.0763</td>
<td>2088.70874</td>
<td>32.34435</td>
<td>29.1016</td>
</tr>
</tbody>
</table>

Racemic

<table>
<thead>
<tr>
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<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.027</td>
<td>VV</td>
<td>0.4571</td>
<td>1.56573×10⁻⁴</td>
<td>527.29132</td>
<td>50.0790</td>
</tr>
</tbody>
</table>
Table 3 entry 4

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.031</td>
<td>VV</td>
<td>0.2908</td>
<td>1515.78555</td>
<td>80.06336</td>
<td>21.8012</td>
</tr>
<tr>
<td>11.151</td>
<td>VB</td>
<td>0.6414</td>
<td>5437.001955</td>
<td>188.44278</td>
<td>79.1998</td>
</tr>
</tbody>
</table>

AD-H, hexane/2-propanol=1:1,1mL/min

Racemic

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.825</td>
<td>VV</td>
<td>0.4259</td>
<td>9541.03027</td>
<td>346.74686</td>
<td>50.0763</td>
</tr>
<tr>
<td>9.436</td>
<td>VB</td>
<td>0.8917</td>
<td>9511.93945</td>
<td>163.52412</td>
<td>49.5237</td>
</tr>
</tbody>
</table>

AS-H, hexane/2-propanol=2:1,1mL/min
Table 3 entry 6

\[
\text{AS-H, hexane/2-propanol=2:1,1mL/min}
\]

---

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.834 min</td>
<td>MM</td>
<td>0.4518</td>
<td>3542.19946</td>
<td>130.65689</td>
<td>24.0490</td>
</tr>
<tr>
<td>9.476 min</td>
<td>VV</td>
<td>0.8794</td>
<td>51186.864</td>
<td>198.32396</td>
<td>75.9510</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.210 min</td>
<td>VV</td>
<td>0.5509</td>
<td>1.02497e4</td>
<td>287.22165</td>
<td>51.0520</td>
</tr>
</tbody>
</table>

---

Racemic

\[
\text{AD-H, hexane/2-propanol=1:1,1mL/min}
\]
Table 3 entry 6

AD-H, hexane/2-propanol=1:1,1mL/min

Racemic

AS-H, hexane/2-propanol=1:1,1mL/min
### Table 3 entry 7

<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.613</td>
<td>BB</td>
<td>0.3987</td>
<td>2844.62207</td>
<td>110.7195</td>
<td>17.4406</td>
</tr>
<tr>
<td>2</td>
<td>12.524</td>
<td>VB</td>
<td>1.2315</td>
<td>1.34657e4</td>
<td>166.05386</td>
<td>82.5594</td>
</tr>
</tbody>
</table>

AS-H, hexane/2-propanol=1:1,1mL/min

### Table 3 entry 8

<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.459</td>
<td>BB</td>
<td>1.1399</td>
<td>1.0927e4</td>
<td>248.16748</td>
<td>50.3524</td>
</tr>
<tr>
<td>2</td>
<td>21.377</td>
<td>BB</td>
<td>2.0271</td>
<td>1.0774e4</td>
<td>80.81483</td>
<td>49.6476</td>
</tr>
</tbody>
</table>

AS-H, hexane/2-propanol=3:1,1mL/min

Racemic
Table 3 entry 8

AS-H, hexane/2-propanol=3:1, 1mL/min

Racemic

AD-H, hexane/2-propanol=1:1, 1mL/min
Table 4 entry 4

AD-H, hexane/2-propanol=1:1, 1mL/min

<table>
<thead>
<tr>
<th>#</th>
<th>retention time (min)</th>
<th>mAU</th>
<th>%</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.55</td>
<td>0.8710</td>
<td>126.08276</td>
<td>17.2156</td>
</tr>
<tr>
<td>2</td>
<td>25.316</td>
<td>1.3499</td>
<td>688.06354</td>
<td>82.7844</td>
</tr>
</tbody>
</table>

Racemic

<table>
<thead>
<tr>
<th>#</th>
<th>retention time (min)</th>
<th>mAU</th>
<th>%</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.955</td>
<td>0.5194</td>
<td>236.60399</td>
<td>49.9170</td>
</tr>
<tr>
<td>2</td>
<td>32.772</td>
<td>1.4272</td>
<td>87.92950</td>
<td>50.0830</td>
</tr>
</tbody>
</table>

AD-H, hexane/2-propanol=1:1, 1mL/min
**Table 4 entry 5**

AD-H, hexane/2-propanol=1:1,1mL/min

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2816</td>
<td>MM</td>
<td>0.5367</td>
<td>2083.51514</td>
<td>65.44341</td>
<td>10.1487</td>
</tr>
<tr>
<td>2.32584</td>
<td>MM</td>
<td>1.6529</td>
<td>1.84463e+4</td>
<td>185.99442</td>
<td>89.8513</td>
</tr>
</tbody>
</table>

**Racemic**

AD-H, hexane/2-propanol=1:1,1mL/min

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.136</td>
<td>BB</td>
<td>0.3756</td>
<td>7534.80518</td>
<td>294.95108</td>
<td>50.3635</td>
</tr>
<tr>
<td>12.075</td>
<td>VV</td>
<td>0.5763</td>
<td>7426.02734</td>
<td>193.29860</td>
<td>49.6365</td>
</tr>
</tbody>
</table>
Table 4 entry 5
AD-H, hexane/2-propanol=1:1,1mL/min

Table 4 entry 6
AD-H, hexane/2-propanol=1:1,1mL/min
Table 4 entry 7

AD-H, hexane/2-propanol=1:1,1mL/min

Racemic

AD-H, hexane/2-propanol=1:1,1mL/min
### Table 4 entry 8

AD-H, hexane/2-propanol=1:1,1mL/min

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention Time [min]</th>
<th>Peak Width [min]</th>
<th>Peak Area [mAU]</th>
<th>Peak Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.443</td>
<td>0.7843</td>
<td>5890.50342</td>
<td>126.17089</td>
<td>16.6107</td>
</tr>
<tr>
<td>2</td>
<td>31.036</td>
<td>1.0851</td>
<td>2.95716×10^4</td>
<td>266.26874</td>
<td>93.3893</td>
</tr>
</tbody>
</table>

### Racemic

AD-H, hexane/2-propanol=1:1,1mL/min

[Diagram of Racemic Structure]
Table 4 entry 9

AD-H, hexane/2-propanol=1:1,1mL/min

Racemic

AD-H, hexane/2-propanol=1:1,1mL/min
### Table 4 entry 10

<table>
<thead>
<tr>
<th>Peak</th>
<th>Retention Time</th>
<th>Width</th>
<th>Area (%)</th>
<th>Height</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.400</td>
<td>0.5499</td>
<td>3332.30444</td>
<td>100.99450</td>
<td>19.4150</td>
</tr>
<tr>
<td>2</td>
<td>38.054</td>
<td>2.1423</td>
<td>1.38304 × 10^4</td>
<td>97.60650</td>
<td>80.5841</td>
</tr>
</tbody>
</table>

**AD-H, hexane/2-propanol=1:1,1 mL/min**

---

### Racemic

<table>
<thead>
<tr>
<th>Peak</th>
<th>Retention Time</th>
<th>Width</th>
<th>Area (%)</th>
<th>Height</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.559</td>
<td>0.7879</td>
<td>1.806944</td>
<td>337.33194</td>
<td>49.7383</td>
</tr>
<tr>
<td>2</td>
<td>28.951</td>
<td>1.4253</td>
<td>1.825954</td>
<td>192.69735</td>
<td>50.2517</td>
</tr>
</tbody>
</table>

**AD-H, hexane/2-propanol=1:1,1 mL/min**
### Table 4 entry 11

AD-H, hexane/2-propanol=1:1 mL/min

<table>
<thead>
<tr>
<th>#</th>
<th>[min]</th>
<th>[min]</th>
<th>mAU</th>
<th>%</th>
<th>[mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.462</td>
<td>0.7975</td>
<td>2761.26758</td>
<td>51.72498</td>
<td>9.6298</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28.676</td>
<td>1.4388</td>
<td>2.92357e4</td>
<td>304.94705</td>
<td>91.3702</td>
<td></td>
</tr>
</tbody>
</table>

---

### Table 4 entry 11

AD-H, hexane/2-propanol=1:1 mL/min

<table>
<thead>
<tr>
<th>#</th>
<th>[min]</th>
<th>[min]</th>
<th>mAU</th>
<th>%</th>
<th>[mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.164</td>
<td>0.9546</td>
<td>7123.69043</td>
<td>113.72398</td>
<td>50.4220</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>23.731</td>
<td>1.1529</td>
<td>7904.43945</td>
<td>91.40789</td>
<td>49.5790</td>
<td></td>
</tr>
</tbody>
</table>

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Racemic
### Table 4 entry 12

<table>
<thead>
<tr>
<th>#</th>
<th>Retention Time (min)</th>
<th>Type</th>
<th>Peak Width (min)</th>
<th>Peak Area (mAU)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.240</td>
<td>MM</td>
<td>1.0552</td>
<td>1664.83801</td>
<td>26.29528</td>
</tr>
<tr>
<td>2</td>
<td>23.727</td>
<td>MM</td>
<td>1.2963</td>
<td>1.39006e+4</td>
<td>176.72612</td>
</tr>
</tbody>
</table>

AD=H, hexane/2-propanol=1:1 mL/min
$^1$H NMR monitoring of reactions in Table 4

Table 4, Entry 1

Table 4, Entry 2
Table 4, Entry 3

Table 4, Entry 4
Table 4, Entry 5

Table 4, Entry 6
Table 4, Entry 9

Table 4, Entry 10
Table 4, Entry 11

$\delta$ (ppm)

$\begin{array}{c}
t = 1 \text{ h} 10 \text{ min} \\
t = 3 \text{ h} 10 \text{ min} \\
t = 4 \text{ h} 20 \text{ min} \\
t = 6 \text{ h} 20 \text{ min}
\end{array}$

Table 4, Entry 12

$\delta$ (ppm)

$\begin{array}{c}
t = 40 \text{ min} \\
t = 1 \text{ h} 55 \text{ min} \\
t = 3 \text{ h} 10 \text{ min} \\
t = 4 \text{ h} 55 \text{ min}
\end{array}$