Practical, Highly Stereoselective Allyl- and Crotylsilylation of Aldehydes Catalyzed by Readily Available Cinchona Alkaloid Amide

Yuan Huang, Licheng Yang, Panlin Shao and Yu Zhao*

Supplementary Information

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1. General Information

Melting point (MP) was obtained on Buchi B-540. Thin layer chromatography (TLC) was performed on Merck pre-coated TLC plates (Merck 60 F254), and compounds were visualized with a UV light at 254nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform $\delta$ 7.26), carbon (chloroform $\delta$ 77.0) or tetramethylsilane (TMS $\delta$ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity ($s =$ singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were obtained on a Finnigan/MAT 95XL-T spectrometer. Optical rotations were recorded on an mrc AP81 automatic polarimeter. Enantiomeric excesses (ee) were determined by HPLC analysis on Agilent HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OD-H, Chiralpak AS-H, AD-H or IC.

All reactions were carried out under nitrogen atmosphere. Liquid reagents were handled with a micropipette. THF was dried on alumina columns using a solvent dispensing system. All commercially available aldehydes, allyltrichlorosilane and $N,N$-diisopropylethylamine were purchased for Aldrich and used as received for the reactions without any purification. Aldehyde 1d and 1e were prepared based on reported procedure$^{1-2}$. (E)- and (Z)-crotyltrichlorosilanes were synthesized according to literature procedure$^3$. 

2. General procedure for one-pot preparation of the catalysts.

![Chemical structure](image)
Quinine 3 (5 mmol) and triphenylphosphine (1.6 g, 6 mmol) were dissolved in anhydrous THF (25 mL), and the solution was cooled to 0 °C. Diethyl azodicarboxylate (1.0 g, 6 mmol) was subsequently added. To the resulting solution was added dropwise the solution of diphenyl phosphoryl azide (1.3 mL, 6 mmol) in anhydrous THF (10 mL) at 0 °C. The mixture was allowed to warm to ambient temperature. After 24 h, it was heated to 50 °C when more triphenylphosphine (1.7 g, 6.5 mmol) was added, and the mixture was allowed to stir at 50 °C for additional 3 h. After that the solution was cooled to ambient temperature and H₂O (0.5 mL) was added. After the reaction mixture was stirred for another 10 h, 4-(Dimethylamino) acid chloride (1.098 g, 6 mmol) was added in one portion, then the reaction mixture was kept stirring at room temperature for 1 h. Solvents were removed in vacuo, and the residue was dissolved in CH₂Cl₂/10% aqueous HCl (25 mL/25 mL). The aqueous phase was separated and washed with CH₂Cl₂ (25 mL × 4). It was subsequently basified with excess aqueous NH₃, and extracted with CH₂Cl₂ (25 mL × 4). The combined organic layers were dried over Na₂SO₄, and concentrated in vacuo. Purification by flash chromatography using silica gel with EtOAc/hexane (v/v = 1/1) then EtOAc/CH₃OH (v/v = 10/1) as an eluent yielded the corresponding amide containing product 11.

Pale yellow solid, 56% yield. MP: 78.9-79.7 °C. TLC (Methanol: Ethyl acetate, 10:1 v/v): Rf = 0.30. ¹H NMR (300 MHz, CDCl₃) δ 10.13 (s, 1H), 8.87 (s, 1H), 8.12 (ddd, J = 27.4, 17.0, 13.1 Hz, 4H), 7.87 (s, 1H), 7.69 (s, 1H), 7.47 (dd, J = 9.2, 2.6 Hz, 1H), 5.79 (ddd, J = 17.0, 10.4, 6.6 Hz, 1H), 5.39 – 5.09 (m, 2H), 4.45 (s, 1H), 4.09 (s, 3H), 3.92 (d, J = 25.6 Hz, 1H), 3.37 – 2.99 (m, 2H), 2.75 (s, 1H), 2.15 (dd, J = 20.5, 11.2 Hz, 3H), 1.91 (d, J = 13.3 Hz, 1H), 1.32-1.28 (d, J = 1.3 Hz, 2H), 0.89 (d, J = 6.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 165.08, 157.83, 147.64, 141.49, 132.76, 132.12, 131.82, 121.66, 121.53, 121.27, 114.51, 111.54, 56.33, 55.98, 55.56, 41.09, 39.74, 28.05, 27.50, 26.33. HRMS (ESI) m/z Calcd for [C₂₇H₂₈N₄O₄, M+H]⁺: 473.2183; Found: 473.2179.

Optical Rotation: [α]D²⁵ = –55 (c1.0, CH₂Cl₂).

White solid 70% yield. MP: 119.1-120.1 °C. TLC (Methanol: Ethyl acetate, 10:1 v/v): Rf = 0.34. ¹H NMR (500 MHz, CDCl₃): δ 8.72 (dd, J = 9.6, 4.6 Hz, 1H), 8.02 (t, J = 8.7 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.73 (t, J = 7.8 Hz, 1H), 7.60 (s, 1H), 7.45 (dd, J = 8.8, 4.6 Hz, 1H), 7.42 – 7.32 (m, 1H), 6.65 (t, J = 9.3 Hz, 2H), 5.74 (td, J = 17.3, 9.0 Hz, 1H), 5.11 – 4.87 (m, 2H), 3.99 (d, J = 8.0 Hz, 3H), 3.37 – 3.26 (m, 1H), 3.19 (d, J = 8.5 Hz, 2H), 3.00 (d, J = 10.2 Hz, 6H), 2.84 – 2.66 (m, 2H), 2.33 (s, 2H), 2.21 (s, 1H), 1.79 – 1.57 (m, 3H), 1.47 (d, J = 8.0 Hz, 1H), 1.12 – 0.92 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 167.37, 157.70, 152.60, 147.57, 144.78, 141.29, 131.70, 128.69, 121.53, 120.72, 114.61, 111.01, 102.05, 56.06, 55.64, 40.93, 40.09, 39.60, 27.94, 27.41, 26.19. HRMS
(ESI) m/z Calcd for [C_{29}H_{35}N_{4}O_{2}, M+H]^+: 471.2776; Found: 471.2755. Optical Rotation: $[\alpha]_{D}^{23} = -50.3$ (c 1.0, CH$_2$Cl$_2$).

White solid. 68% Yield. MP: 145.5-146.4 °C. 

TLC (Methanol: Ethyl acetate, 10:1 v/v): $R_f = 0.32$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.89 (d, $J = 4.5$ Hz, 1H), 8.53 (d, $J = 8.5$ Hz, 1H), 8.15 (d, $J = 8.5$ Hz, 1H), 7.73 (t, $J = 7.9$ Hz, 4H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.54 (d, $J = 4.6$ Hz, 1H), 6.67 (d, $J = 8.8$ Hz, 2H), 5.73 (ddd, $J = 17.4$, 10.2, 7.6 Hz, 1H), 5.45 (s, 1H), 4.98 (dd, $J = 19.7$, 13.7 Hz, 2H), 3.31 (dd, $J = 13.8$, 10.2 Hz, 1H), 3.23-3.10 (m, 2H), 3.03 (d, $J = 13.2$ Hz, 6H), 2.86-2.63 (m, 2H), 2.33 (s, 1H), 1.76-1.55 (m, 3H), 1.40 (dd, $J = 13.2$, 10.1 Hz, 1H), 1.07 (dd, $J = 13.7$, 6.3 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 167.52, 152.60, 150.08, 148.62, 141.29, 130.43, 128.97, 128.71, 126.57, 123.46, 120.78, 114.60, 111.02, 56.01, 40.84, 40.11, 39.65, 27.85, 27.38, 25.92.

HRMS (ESI) m/z Calcd for [C$_{28}$H$_{32}$N$_{4}$O, M+H]$^+$: 441.2649; Found: 441.2637.

Optical Rotation: $[\alpha]_{D}^{23} = -52.5$ (c 1.0, CH$_2$Cl$_2$).

White solid. 50% yield. MP: 178.1-179.2 °C. TLC (Hexane: Ethyl acetate, 2:1 v/v): $R_f = 0.4$.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.43-8.18 (m, 1H), 8.03-7.80 (m, 2H), 7.78-7.45 (m, 6H), 6.64 (t, $J = 10.6$ Hz, 2H), 6.39 (d, $J = 7.5$ Hz, 1H), 6.16 (dd, $J = 13.6$, 6.8 Hz, 1H), 3.11-2.97 (m, 6H), 1.81 (dd, $J = 13.2$, 6.5 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 152.37, 138.75, 133.90, 131.27, 128.62, 128.39, 128.19, 126.47, 125.74, 125.15, 123.66, 122.60, 110.95, 44.87, 40.01, 20.78.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{22}$N$_{2}$O, M+Na]$^+$: 341.1625; Found: 341.1635.

Optical Rotation: $[\alpha]_{D}^{23} = -10$ (c 1.0, CH$_2$Cl$_2$).

White solid. 63% Yield. MP: 71.4-72.5 °C. TLC (Methanol: Ethyl acetate, 10:1 v/v): $R_f = 0.38$.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.76 (d, $J = 4.6$ Hz, 1H), 8.04 (d, $J = 9.2$ Hz, 2H), 7.93-7.66 (m, 3H), 7.54 (d, $J = 4.6$ Hz, 1H), 7.40 (dd, $J = 9.2$, 2.7 Hz, 1H), 6.72-6.52 (m, 2H), 6.08-5.90 (m, 1H), 5.37-5.16 (m, 2H), 4.04 (s, 3H), 3.43 (d, $J = 8.9$ Hz, 1H), 3.14 (d, $J = 15.7$ Hz, 3H), 3.08-2.96 (m, 6H), 2.44 (s, 1H), 2.05 (d, $J = 16.0$ Hz, 2H), 1.84-1.60 (m, 3H), 1.54-1.41 (m, 1H), 1.19 (d, $J = 8.2$ Hz, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.37, 157.70, 150.76, 147.57, 144.78, 141.29, 131.70, 128.68, 121.53, 120.72, 114.61, 111.06, 102.05, 56.09, 55.68, 40.93, 40.09, 39.64, 27.94, 27.41, 26.18.

HRMS (ESI) m/z Calcd for [C$_{29}$H$_{35}$N$_{4}$O$_{2}$, M+H]$^+$: 471.2749; Found: 471.2771. Optical Rotation: $[\alpha]_{D}^{23} = +53.5$ (c 1.0, CH$_2$Cl$_2$).
3. Representative procedure for allylation reaction.

\[
\begin{align*}
\text{R}^1 \text{H} & \quad \text{R}_1 \text{R}_2 \text{SiCl}_3 \\
1 & \quad \text{R}_1 \text{R}_2 \text{SiCl}_3 \\
2 \text{ or } 16 & \quad \text{R}_1 \text{R}_2 \text{OH}
\end{align*}
\]

To a 4 mL vial equipped with a stir bar was added the catalyst (0.03 mmol, 10 mol%). The vial was taken into glovebox, where anhydrous THF (1 mL), DIPEA (0.45 mmol, 1.5 equiv.) and allyltrichlorosilane (0.75 mmol, 2.5 equiv.) were added. The reaction mixture was taken outside the glovebox and the aldehyde (0.3 mmol) was added using a micropipette (open to air). The reaction mixture changed to bright red in color upon addition of aldehyde. The vial was then sealed and the reaction mixture was allowed to stir at ambient temperature for 24 h. The crude reaction mixture was quenched by pouring into a mixture of dichloromethane (5 mL) and saturated NaHCO₃ solution (5 mL). The resulting mixture was vigorously stirred for 1 h, and then extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL), dried over anhydrous Na₂SO₄ and concentrated. Purification by silica gel chromatography yielded the recovered catalyst in quantitative yield and the desired product that was analyzed for purity by NMR and for enantioenrichment by chiral HPLC (Chiralcel OD-H, Chiralpark IC, AS-H or AD-H).
4. Preliminary kinetic studies of the allylation reaction.

Determination of the dependence of the allylation reaction on catalyst:

To a 25 mL vial equipped with a stir bar was added the catalyst (0.036 mmol). The vial was taken into glovebox, where anhydrous THF (3 mL), DIPEA (0.45 mmol) and allyl trichlorosilane (2.5 mmol) were added. The reaction mixture was taken outside the glovebox, and the aldehyde (0.3 mmol) in 3 mL THF was added using a micropipette. The vial was then sealed and the reaction mixture was allowed to stir at ambient temperature. Real time conversion was determined by NMR (500MHz).

Table S1. Effect of initial catalyst concentration [11] on the rate of allylation reaction.

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Figure S1. First order dependence on catalyst of allylation of aldehydes.
5. Analytical data of allylation and crotylation Reaction products.

(R)-1-(benzylxoy) pent-4-en-2-ol (2a, Entry 1, Table 2).

Colorless oil, 83% yield with catalyst 11, 86% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.63. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.44 – 7.32 (m, 5H), 5.87 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 5.22 – 5.05 (m, 2H), 4.60 (s, 2H), 3.99 – 3.85 (m, 1H), 3.56 (dd, J = 9.5, 3.4 Hz, 1H), 3.42 (dd, J = 9.5, 7.4 Hz, 1H), 2.42 (d, J = 3.6 Hz, 1H), 2.36 – 2.24 (m, 2H). \(^1\)C NMR (75 MHz, CDCl\(_3\)): δ 137.89, 134.15, 128.39, 127.72, 127.66, 117.62, 73.82, 73.31, 69.65, 37.83.

Optical Rotation (from reaction with catalyst 11): \([\alpha]^{25}_D = -6.5\) (0.24, CHCl\(_3\)). The absolute configuration of 2a was assigned by comparing its specific rotation with that of the same compound reported in the literature. 5% 96% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99:1, flow rate = 1.0 ml/min, wavelength = 254nm, t\(_R\) = 24.09 min for major isomer, t\(_R\) = 26.57 min for minor isomer).

### Catalyst 11

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Colorless oil, 89% yield with catalyst 11, 82% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.7. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.45 – 7.26 (m, 5H), 5.95 – 5.79 (m, 1H), 5.24 – 5.08 (m, 2H), 4.55 (s, 2H), 3.97 – 3.84 (m, 1H), 3.83 – 3.64 (m, 2H), 2.93 (s, 1H), 2.28 (t, J = 6.5 Hz, 2H), 1.97 – 1.76 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 137.99, 134.89, 128.47, 127.76, 127.69, 117.58, 73.32, 70.32, 68.91, 41.94, 35.90.

**Optical Rotation** (from reaction with catalyst 11): [α]<sub>D</sub> = -10.75 (0.2, CHCl<sub>3</sub>). The absolute configuration of 2b was assigned by comparing its specific rotation with that of the same compound reported in the literature<sup>6</sup>. 99% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, t<sub>R</sub> = 32.93 min for minor isomer, t<sub>R</sub> = 33.76 min for major isomer).
(R)-3-hydroxyhex-5-en-1-yl benzoate (2c, Entry 3, Table 2).

Colorless oil, 90% yield with catalyst 11, 88% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): Rf = 0.56. ¹H NMR (300 MHz, CHCl₃): δ 8.17 – 8.01 (m, 2H), 7.70 – 7.44 (m, 3H), 6.01 – 5.78 (m, 1H), 5.32 – 5.11 (m, 2H), 4.62 (dd, J = 11.2, 8.5, 5.3 Hz, 1H), 4.47 (dt, J = 11.2, 5.7 Hz, 1H), 3.89 (s, 1H), 2.50 – 2.19 (m, 3H), 2.13 – 1.74 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 166.71, 134.27, 132.93, 129.51, 128.31, 118.31, 67.51, 62.01, 41.89, 35.81. HRMS (ESI) m/z Calcd for [C₁₃H₁₆O₃, M+H]⁺: 221.1123; Found:221.1218.

Optical Rotation (from reaction with catalyst 11): [α]²⁵ D = -8.333 (0.6, CHCl₃). The absolute configuration of 2c was assigned by comparing its specific rotation with analogue, 98% ee. (HPLC condition: Chiralpark IC column, n-hexane/i-PrOH = 97:3, flow rate = 1.0 ml/min, wavelength = 254 nm, tᵣ = 32.81 min for major isomer, tᵣ = 41.08 min for minor isomer).
(R)-1-((tert-butyldimethylsilyl)oxy) pent-4-en-2-ol (2d, Entry 4, Table 2).

Colorless oil, 70% yield with catalyst 11, 73% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.82. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.90 – 5.77 (m, 1H), 5.14 – 5.04 (m, 2H), 3.89 (dt, J = 9.9, 4.9 Hz, 2H), 3.84 – 3.76 (m, 2H), 3.37 (d, J = 2.0 Hz, 1H), 2.33 – 2.14 (m, 2H), 0.90 (d, J = 6.8 Hz, 9H), 0.08 (d, J = 8.5 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 135.01, 117.29, 71.25, 62.58, 41.95, 37.76, 25.85, 25.64, -3.60, -5.58.

**Optical Rotation** (from reaction with catalyst 11): [α]<sub>D</sub> = -6.76 (0.3, CHCl<sub>3</sub>). The absolute configuration of 2d was assigned by comparing its specific rotation with that of the same compound reported in the literature. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 95% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99.5:0.5, flow rate = 0.5 ml/min, wavelength = 254 nm, t<sub>R</sub> = 32.81 min for major isomer, t<sub>R</sub> = 41.08 min for minor isomer).

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**Electronic Supplementary Material (ESI) for Chemical Science**

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(R)-1-(1H-indol-3-yl) pent-4-en-2-ol (2e, Entry 5, Table 2)

Colorless oil, 75% yield with catalyst 11. 80% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): Rf = 0.33. H NMR (300 MHz, CDCl3): δ 8.01 (s, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.48 – 7.35 (m, 1H), 7.33 – 7.12 (m, 2H), 7.07 – 6.98 (m, 1H), 5.88 (ddddd, J = 11.1, 9.3, 7.8, 6.5 Hz, 1H), 5.32 – 5.12 (m, 2H), 3.80 (dd, J = 12.1, 7.7, 4.6 Hz, 1H), 3.10 – 2.82 (m, 2H), 2.50 – 2.33 (m, 1H), 2.33 – 2.16 (m, 1H), 2.00 – 1.88 (m, 2H).

13C NMR (75 MHz, CDCl3): δ 136.40, 134.79, 127.49, 121.98, 121.20, 119.21, 118.94, 118.21, 116.21, 111.10, 70.31, 42.05, 37.10, 21.35. HRMS (ESI) m/z Calcd for [C14H16NO], M+: 215.1237; Found: 215.1230.

Optical Rotation (from reaction with catalyst 11): [α]25D = -3.083(0.6, CH2Cl2). The absolute configuration of 2e was assigned by comparing its specific rotation with analogue. 96% ee. (HPLC condition: Chiralpak IC column, n-hexane/i-PrOH = 95:5 flow rate = 1 ml/min, wavelength = 254 nm, tR = 33.56 min for major isomer, tR = 37.40 min for minor isomer).

Catalyst 11

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(S)-hex-5-en-3-ol (2f, Entry 6, Table 2).

Colorless oil, 80% yield with catalyst 11, 74% yield with catalyst 14. 

**TLC** (Hexane: Ethyl acetate, 5:1 v/v): R\textsubscript{f} = 0.82. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 5.85 (dddd, \(J\) = 11.6, 9.4, 7.8, 6.5 Hz, 1H), 5.19 – 5.12 (m, 2H), 3.67 (s, 1H), 2.39 – 2.28 (m, 1H), 2.22 – 2.14 (m, 1H), 1.68 (s, 2H), 1.38 – 1.26 (m, 10H), 0.90 (t, \(J\) = 6.9 Hz, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 134.94, 118.03, 70.71, 41.94, 36.83, 31.82, 29.62, 29.27, 25.67, 22.65, 14.08.

**Optical Rotation** (from reaction with catalyst 11): \([\alpha]_{D}^{25} = -18\) (0.5, CH\textsubscript{2}Cl\textsubscript{2}). The absolute configuration of 2f was assigned by comparing its specific rotation with that of the same compound reported in the literature\textsuperscript{6}. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 96% ee. (HPLC condition: Chiralpak AD-H column, n-hexane/i-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, \(t\)\textsubscript{R} = 14.34 min for major isomer, \(t\)\textsubscript{R} = 17.27 min for minor isomer).
(S)-tridec-1-en-4-ol (2g, Entry 7, Table 2).

Colorless oil, 78% yield with catalyst 11. 71% yield with catalyst 14. 

**TLC** (Hexane: Ethyl acetate, 5:1 v/v): \( R_f = 0.86 \). 

**\( ^1H \) NMR** (300 MHz, CDCl\(_3\)): \( \delta \) 5.83 (ddddd, \( J = 14.5, 9.5, 7.8, 6.6 \) Hz, 1H), 5.18 – 5.05 (m, 2H), 3.63 (s, 1H), 2.38 – 2.22 (m, 1H), 2.23 – 2.07 (m, 1H), 1.51 – 1.38 (m, 3H), 1.21 (d, \( J = 31.6 \) Hz, 14H), 0.88 (q, \( J = 6.5 \) Hz, 3H).

**\( ^{13}C \) NMR** (75 MHz, CDCl\(_3\)): \( \delta \) 134.85, 117.95, 70.62, 41.84, 36.74, 31.81, 29.61, 29.57, 29.48, 29.23, 25.58, 22.59, 14.02.

**Optical Rotation** (from reaction with catalyst 11): \( [\alpha]^{25}_D = -20.3 \) (0.6, CH\(_2\)Cl\(_2\)). The absolute configuration of 2h was assigned by comparing its specific rotation with that of the same compound reported in the literature\(^6\). The enantiomeric ratio of the compound was determined after converting to the corresponding para-dimethylaminobenzate. 96% ee. 

(HPLC condition: Chiralpak AD-H column, \( n \)-hexane/i-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, \( t_R = 14.34 \) min for minor isomer, \( t_R = 17.27 \) min for major isomer).
(R)-1-phenylpent-4-en-2-ol (2h, Entry 8, Table 2)

Colorless oil, 76% yield with catalyst 11. 71% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R\(_f\) = 0.67. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.47 – 7.18 (m, 5H), 5.87 (dddd, \(J = 16.2, 9.5, 7.8, 6.6\) Hz, 1H), 5.26 – 5.14 (m, 2H), 3.79 – 3.66 (m, 1H), 3.02 – 2.61 (m, 2H), 2.49 – 2.28 (m, 1H), 2.30 – 2.17 (m, 1H), 1.84 (ddd, \(J = 8.9, 7.2, 3.5\) Hz, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ 141.99, 134.54, 128.36, 128.33, 125.75, 118.22, 69.88, 41.98, 38.37, 31.97.

Optical Rotation (from reaction with catalyst 11): \([\alpha]^{25}_D = -3.2\) (0.7, CH\(_2\)Cl\(_2\)). The absolute configuration of 2i was assigned by comparing its specific rotation with that of the same compound reported in the literature\(^6\). 97% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 0.5 ml/min, wavelength = 254 nm, \(t_R = 14.31\) min for major isomer, \(t_R = 20.65\) min for minor isomer).

### Catalyst 11

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EElectronic Supplementary Material (ESI) for Chemical Science
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(S)-tetradeca-1,13-dien-4-ol (2i, Entry 9, Table 2)

Colorless oil, 78% yield with catalyst 11. 85% yield with catalyst 14. 

**TLC** (Hexane: Ethyl acetate, 5:1 v/v): \( R_f = 0.86 \). **\(^1\)H NMR** (500 MHz, CDCl\(_3\)): \( \delta \ 6.15 - 5.59 \) (m, 2H), \( 5.14 \) (dd, \( J = 10.2, 6.5 \) Hz, 2H), \( 5.05 - 4.82 \) (m, 2H), \( 3.63 \) (s, 1H), \( 2.37 - 2.23 \) (m, 1H), \( 2.19 - 2.08 \) (m, 1H), \( 2.03 \) (dd, \( J = 14.4, 6.9 \) Hz, 2H), \( 1.69 - 1.54 \) (m, 1H), \( 1.40 - 1.20 \) (m, 14H). **\(^13\)C NMR** (125 MHz, CDCl\(_3\)): \( \delta \ 139.22, 134.93, 118.03, 114.11, 70.70, 41.94, 36.82, 33.80, 29.63, 29.54, 29.42, 29.11, 28.92, 25.65. **HRMS (ESI)** m/z Calcd for [C\(_{14}H_{26}O\), M+H\(^+\)]: 211.2043; Found:211.2010.

**Optical Rotation** (from reaction with catalyst 11): \([\alpha]^{25}_D = -14.2 \) (0.58, CH\(_2\)Cl\(_2\)). The absolute configuration of \( 2j \) was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 97% ee. (HPLC condition: Chiralpak AS-H column, n-hexane/i-PrOH = 99:1 flow rate = 0.4 ml/min, wavelength = 254 nm, \( t_R \) = 14.38 min for minor isomer, \( t_R \) = 15.16 min for major isomer).
(S, Z)-tetradeca-1, 11-dien-4-ol (2j, Entry 10, Table 2)

Colorless oil, 83% yield with catalyst 11. 80% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): $R_f = 0.86$. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.06 – 5.64 (m, 1H), 5.42 – 5.26 (m, 2H), 5.18 – 5.05 (m, 2H), 3.63 (s, 1H), 2.39 – 2.22 (m, 1H), 2.19 – 2.07 (m, 1H), 2.01 (dd, $J = 13.5, 7.1$ Hz, 3H), 1.32 (dd, $J = 33.5, 27.4$ Hz, 12H), 0.95 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 134.91, 134.59, 129.24, 118.08, 70.69, 41.94, 36.82, 33.80, 29.54, 24.92, 27.06, 25.65, 20.51, 14.39. HRMS (ESI) m/z Calcd for [C$_{14}$H$_{26}$O, M+H]$^+$: 211.2021; Found: 211.2036.

Optical Rotation (from reaction with catalyst 11): $[\alpha]^{25}_D = -11.24$ (0.58, CH$_2$Cl$_2$). The absolute configuration of 2k was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 96% ee. (HPLC condition: Chiralpak AD-H column, n-hexane/i-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_R = 14.38$ min for minor isomer, $t_R = 15.16$ min for major isomer).

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(R)-1-phenylbut-3-en-1-ol (2k, Entry 11, Table 2)

Pale yellow oil, 77% yield with catalyst 11. 75% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.71. 1H NMR (500 MHz, CDCl_3): δ 7.38-7.27 (m, 5H), 5.82 (ddt, J = 17.2, 10.0, 7.2 Hz, 1H), 5.17 (dd, J = 17.2, 1.2 Hz, 1H), 5.15 (dd, J = 10.4, 1.2 Hz, 1H), 4.74 (dt, J = 6.4, 2.4 Hz, 1H), 2.58-2.6 (m, 2H), 2.06 (d, J = 2.8 Hz, 1H). 13C NMR (500 MHz, CDCl_3): δ 143.9, 134.5, 128.5, 127.6, 125.9, 118.5, 73.5, 44.1.

Optical Rotation (from reaction with catalyst 11): [α]_25°D +34.90 (c 0.7, CHCl_3). The absolute configuration of 2l was assigned by comparing its specific rotation with that of the same compound reported in the literature. 90% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 95:5 flow rate = 0.5 ml/min, wavelength = 254 nm, t_R = 16.55 min for major isomer, t_R = 18.61 min for minor isomer).
Yellow oil, 83% yield with catalyst 11. 90% yield with catalyst 14. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R\(_f\) = 0.53. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.23 (d, \(J = 8.7\) Hz, 2H), 7.56 (d, \(J = 8.5\) Hz, 2H), 6.00 – 5.72 (m, 1H), 5.31 – 5.12 (m, 2H), 5.02 – 4.83 (m, 1H), 2.71 – 2.34 (m, 3H). \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 151.05, 133.13, 126.49, 123.54, 119.52, 72.10, 43.80.

**Optical Rotation** (from reaction with catalyst 11): \([\alpha]^{25}_D +56.25\) (c 0.7, CHCl\(_3\)). The absolute configuration of 2m was assigned by comparing its specific rotation with analogue. 92% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, \(t_R = 92.22\) min for major isomer, \(t_R = 96.58\) min for minor isomer).

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**Electronic Supplementary Material (ESI)** for Chemical Science

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(R)-1-(4-bromophenyl) but-3-en-1-ol (2m, Entry 13, Table 2)

Yellow oil, 77% yield with catalyst 11. 80% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): \( R_f = 0.63 \). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta 7.46 \) (d, \( J = 8.3 \) Hz, 2H), 7.21 (d, \( J = 8.3 \) Hz, 2H), 5.85 – 5.65 (m, 1H), 5.22 – 5.09 (m, 2H), 4.76 – 4.61 (m, 1H), 2.57 – 2.36 (m, 2H), 2.30 (d, \( J = 2.7 \) Hz, 1H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta 142.85, 133.96, 131.48, 127.59, 121.26, 118.82, 72.62, 43.78 \).

Optical Rotation (from reaction with catalyst 11): \( [\alpha]_{D}^{25} = +50.25 \) (c 0.5, CHCl\(_3\)). The absolute configuration of 2n was assigned by comparing its specific rotation with that of the same compound reported in the literature. 94% ee (HPLC condition: Chiralpak AS-H column, n-hexane/i-PrOH = 99:1 flow rate = 0.4 ml/min, wavelength = 254 nm, \( t_R = 92.22 \) min for major isomer, \( t_R = 96.58 \) min for minor isomer).

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Catalyst 11

Catalyst 14
White solid, 80% yield with catalyst 11. 89% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): Rf = 0.71.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (dd, $J = 7.1$, 5.6 Hz, 4H), 7.52 (dd, $J = 6.1$, 1.9 Hz, 3H), 5.88 (ddt, $J = 17.1$, 10.1, 7.1 Hz, 1H), 5.29 – 5.16 (m, 2H), 5.03 – 4.87 (m, 1H), 2.65 (dd, $J = 9.0$, 6.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 141.21, 134.31, 133.21, 132.89, 128.14, 127.89, 127.61, 126.06, 125.74, 124.44, 123.95, 118.44, 73.33, 43.67.

Optical Rotation (from reaction with catalyst 11): $[\alpha]_D^{25} = +11.33$ (c = 0.3, CHCl$_3$). The absolute configuration of 2o was assigned by comparing its specific rotation with that of the same compound reported in the literature$. 94% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 95:5 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_R$ = 32.85 min for minor isomer, $t_R = 35.98$ min for major isomer).
(4R, 6S)-6, 10-dimethylundeca-1, 9-dien-4-ol (2o and epi-2o, Scheme 2)

Colorless oil, 88% yield with catalyst 11. 80% yield with catalyst 14. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): Rf = 0.86. **1H NMR** (300 MHz, CDCl₃): δ 5.92 – 5.72 (m, 1H), 5.22 – 5.02 (m, 3H), 3.81 – 3.65 (m, 1H), 2.37 – 2.22 (m, 1H), 2.11 (dd, J = 14.7, 7.0 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.68 (d, J = 0.8 Hz, 3H), 1.60 (s, 3H), 1.47 – 1.32 (m, 3H), 1.25 (s, 1H), 1.20 – 1.02 (m, 2H), 0.92 (d, J = 6.6 Hz, 3H). **13C NMR** (75 MHz, CDCl₃): δ 134.77, 131.17, 124.67, 118.10, 68.64, 44.23, 42.06, 36.63, 29.20, 25.63, 25.26, 20.14, 17.57. **HRMS (ESI)** m/z Calcd for [C₁₃H₂₄O₂, M+H]+: 197.1237; Found: 197.1232.

The absolute configuration of 2n was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding para-dimethylaminobenzate. 96% de. (HPLC condition: Chiralpak AD-H column, n-hexane/i-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, t_R = 16.66 min for minor isomer, t_R = 19.043 min for major isomer).
Colorless oil, 78% yield with catalyst 11. 75% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.67. ^1H NMR (500 MHz, CDCl_3): δ 7.59 – 7.31 (m, 5H), 6.05 – 5.70 (m, 1H), 5.15 – 5.05 (m, 2H), 4.58 (s, 2H), 3.75 – 3.64 (m, 1H), 3.58 (dd, J = 9.8, 3.1 Hz, 2H), 3.45 (dd, J = 9.5, 7.6 Hz, 1H), 2.38 (dt, J = 13.5, 6.8 Hz, 1H), 1.07 (d, J = 6.9 Hz, 3H). ^13C NMR (125 MHz, CDCl_3): δ 140.08, 138.4, 128.63, 128.46, 128.06, 115.59, 73.2, 72.8, 40.83, 16.19.

The absolute configuration of 16a was assigned by comparing its specific rotation with that of the same compound reported in the literature, 97% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, t_R = 17.51 min for minor isomer, t_R = 25.082 min for major isomer).
(2R,3S)-1-(benzoxyl)-3-methylpent-4-en-2-ol (16b, Entry 2, Table 3)

Colorless oil, 78% yield with catalyst 11. 75% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.73. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.44 – 7.32 (m, 5H), 5.79 (ddd, J = 17.4, 10.3, 7.9 Hz, 1H), 5.09 (ddd, J = 9.4, 5.2, 1.3 Hz, 2H), 4.59 (s, 2H), 3.69 (dd, J = 10.7, 3.6 Hz, 1H), 3.61 (dd, J = 9.5, 3.1 Hz, 1H), 3.44 (dd, J = 9.5, 7.7 Hz, 1H), 2.51 (d, J = 3.8 Hz, 1H), 2.38 (dd, J = 14.5, 6.9 Hz, 1H), 1.13 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 140.30, 137.95, 128.38, 127.69, 127.64, 115.01, 73.37, 73.29, 72.70, 41.03, 15.59.

The absolute configuration of 16b was assigned by comparing its specific rotation with that of the same compound reported in the literature<sup>8</sup>. 96% ee. (HPLC condition: Chiralcel OD-H column, n-hexane/i-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, t<sub>R</sub> = 15.99 min for minor isomer, t<sub>R</sub> = 17.897 min for major isomer).
Colorless oil, 74% yield with catalyst 11. 70% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): \( R_f = 0.70 \). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.36 (dd, \( J = 5.8, 2.1 \) Hz, 5H), 5.97 – 5.72 (m, 1H), 5.21 – 5.04 (m, 2H), 4.57 (d, \( J = 2.3 \) Hz, 2H), 3.73 (dt, \( J = 12.6, 5.7 \) Hz, 2H), 2.74 (td, \( J = 6.1, 1.8 \) Hz, 1H), 2.31 – 2.18 (m, 1H), 2.06 (s, 1H), 1.78 (dt, \( J = 7.6, 3.8 \) Hz, 2H), 1.12 – 1.03 (m, 3H). \(^1\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 140.39, 137.94, 128.35, 127.60, 115.42, 74.09, 73.25, 69.10, 43.94, 33.54, 15.75.

The absolute configuration of 16c was assigned by comparing its specific rotation with that of the same compound reported in the literature. 96% ee. (HPLC condition: Chiralpak AS-H column, \( n \)-hexane/i-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, \( t_R = 17.89 \) min for minor isomer, \( t_R = 21.42 \) min for major isomer).

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Catalyst 11

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Catalyst 14
(3S, 4S)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16d, Entry 4, Table 3)

Colorless oil, 72% yield with catalyst 11. 73% yield with catalyst 14. TLC (Hexane: Ethyl acetate, 5:1 v/v): \( R_f = 0.73 \). \( ^1 \)H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.39 – 7.27 (m, 5H), 5.86 – 5.71 (m, 1H), 5.12 – 4.99 (m, 2H), 4.53 (d, \( J = 6.3 \) Hz, 2H), 3.77 – 3.69 (m, 1H), 3.69 – 3.62 (m, 2H), 2.86 (d, \( J = 3.2 \) Hz, 1H), 2.26 (dd, \( J = 13.6 \), 6.8 Hz), 1.87 – 1.81 (m, 1H), 1.75 – 1.65 (m, 1H), 1.05 (d, \( J = 6.8 \) Hz, 3H). \( ^1 \)C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 141.00, 137.94, 128.46, 127.75, 127.70, 114.99, 74.52, 73.37, 69.48, 43.87, 33.53, 15.03.

The absolute configuration of 16d was assigned by comparing its specific rotation with that of the same compound reported in the literature. 95% ee. (HPLC condition: Chiralpak AS-H column, \( n \)-hexane/\( i \)-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, \( t_R = 17.89 \) min for minor isomer, \( t_R = 21.42 \) min for major isomer).
6. NMR Spectra of the Products

(R)-1-(benzylxy) pent-4-en-2-ol (2a, Entry 1, Table 2)
(R)-1-(benzyloxy)hex-5-en-3-ol (2b, Entry 2, Table 2)
(R)-1-((tert-butyldimethylsilyl)oxy)pent-4-en-2-ol (2c, Entry 3, Table 2)
(R)-3-hydroxyhex-5-en-1-yl benzoate (2d, Entry 4, Table 2).
(R)-1-(1H-indol-3-yl) pent-4-en-2-ol (2e, Entry 5, Table 2)
(S)-hex-5-en-3-ol (2f, Entry 6, Table 2).
(R)-tridec-1-en-4-ol (2g, Entry 7, Table 2)
(S)-1-phenylhex-5-en-3-ol (2h, Entry 8, Table 2)
(R)-tetradeca-1,13-dien-4-ol (2i, Entry 9, Table 2)
(S, Z)-tetradeca-1,11-dien-4-ol (2j, Entry 10, Table 2)
(R)-1-phenylbut-3-en-1-ol (2k, Entry 11, Table 2)
(R)-1-(4-nitrophenyl) but-3-en-1-ol (2l, Entry 12, Table 2)
(R)-1-(4-bromophenyl)but-3-en-1-ol (2m, Entry 13, Table 2)
(R)-1-(naphthalen-2-yl) but-3-en-1-ol (2n, Entry 14, Table 2)

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(4R, 6S)-6, 10-dimethylundeca-1, 9-dien-4-ol (2o, Scheme 2)
(2R, 3R)-1-(benzyloxy)-3-methylpent-4-en-2-ol (16a, Entry 1, Table 3)
(2\text{R}, 3\text{S})-1-(benzyloxy)-3-methylpent-4-en-2-ol (16b, Entry 2, Table 3)
(3S, 4R)-1-(benzyl oxy)-4-methylhex-5-en-3-ol (16c, Entry 3, Table 3)
(3S,4S)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16d, Entry 4, Table 3)
$N-((S)-(6$-methoxyquinolin-4-yl)$((1S,2S,4S,5R)-5$-vinylquinuclidin-2-yl)methyl)-4$-nitrobenzamide

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4-(dimethylamino)-N-((S)-(6-methoxyquinolin-4-yl)(1S,2S,4S,5R)-5-vinylquinuclidin-2-yl)methyl)benzamide
4-(dimethylamino)-N-((S)-quinolin-4-yl)((1S,2S,4S,5R)-5-vinylnuclidin-2-yl)methyl)benzamide

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(R)-4-(dimethylamino)-N-(1-(naphthalen-1-yl)ethyl)benzamide
4-(dimethylamino)-N-((R)-(6-methoxyquinolin-4-yl)((1S,2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)benzamide
7. References


2. X. Li, D. Lantrip and P. L. Fuchs, J. Am. Chem. Soc. 2003, 125, 14262.


