Supporting Information

Iridium(I)-Catalyzed Regio- and Enantioselective Decarboxylative Allylic Amidation of Substituted Allyl Benzyl Imidodicarbonates

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General

Melting points were recorded on MEL-TEMP melting point apparatus in open capillaries and uncorrected. ^1H - and ^{13}C -NMR spectra were recorded on Advanced Varian-500 (500 MHz) and GE-300 (300 MHz) instruments using residual solvent as internal standard. The following abbreviations were used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The NMR signals of a major rotamer were presented with *, and those of a minor rotamer with **. Optical rotations were measured in a 10 cm cell (concentration c given in g/100 mL). Enantiomeric excesses were determined by Shimadzu HPLC LC-8A using Diode array detector SPD-10A, Chiracel OD-H column (250x4.6 mm) and hexane-isopropanol as mobile phase. TLC was performed with silica gel GF₂₅₄ precoated aluminum plates, and spots were visualized with UV and/or by staining with KMnO_4 . Flash column chromatography was performed on silica gel, unless otherwise stated. $[\text{Ir}(\text{COD})\text{Cl}]_2$, O,O' -(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-phenylethylphosphoramidite (**L1**) and proton sponge (1,8-bis-dimethylaminonaphthalene) were purchased from Strem Chemicals. O,O' -(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-(1-naphthyl)ethylphosphoramidite (**L2**)¹, O,O' -(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-(2-methoxyphenyl)-ethylphosphoramidite (**L3**)² and benzyloxycarbonyl isocyanate³ were synthesized by literature procedures. THF was distilled from benzophenone and sodium metal, while CH_2Cl_2 from CaH_2 . All other solvents and reagents were purchased as reagent-grade and were used without further purification.

Synthesis of substituted allyl benzyl imidodicarbonates

General Procedure: To a solution of a substituted allylic alcohol (1 mmol) in CH_2Cl_2 (10 mL) was added benzyloxycarbonyl isocyanate³ (230 mg, 1.3 mmol). The reaction mixture was stirred at room temperature for 3 h. All volatiles were distilled off by rotary evaporator, and the residue was purified by flash chromatography on silica gel to afford a substituted allyl benzyl imidodicarbonate in almost quantitative yield. The following substituted allyl benzyl imidodicarbonates were synthesized:

Benzyl *trans*-pent-2-enyl imidodicarbonate: Benzyl *trans*-pent-2-enyl imidodicarbonate was synthesized from *trans* 2-pentenol (172 mg, 2 mmol) and benzyloxycarbonyl isocyanate (460 mg, 2.6 mmol) as described above in 98% yield (515 mg) as white crystalline solid: m.p.= 59 °C; ¹H-NMR (500 MHz, CDCl_3) δ 7.38-7.32 (m, 5H), 7.30 (brs, 1H), 5.84 (ttd, 1H, J = 1.1, 6.3 & 15.4 Hz), 5.55 (ttd, 1H, J = 1.6, 6.6 & 15.4 Hz), 5.18 (s, 2H), 4.59 (dd, 2H, J = 1.1 & 6.6 Hz), 2.09-2.02 (m, 2H), 0.99 (t, 3H, J = 7.4 Hz); ¹³C-NMR (75 MHz, CDCl_3) δ 150.35, 150.29, 139.10, 134.86, 128.48, 128.42, 128.31, 121.81, 67.80, 67.00, 25.28, 13.05.

Methyl *trans*-pent-2-enyl imidodicarbonate: Methyl *trans*-pent-2-enyl imidodicarbonate was synthesized from *trans* 2-pentenol (86 mg, 1 mmol) and methoxycarbonyl isocyanate (130 mg, 1.3 mmol) as described above in 96% yield (180 mg) as white crystalline solid: m.p.= 55 °C; ¹H-NMR (500 MHz, CDCl_3) δ 7.45 (brs, 1H), 5.82 (dt, 1H, J = 6.5 & 15.4 Hz), 5.52 (dt, 1H, J = 6.5 & 15.6 Hz), 4.56 (d, 2H, J = 6.6 Hz), 3.74 (s, 3H), 2.06-1.99 (m, 2H), 0.95 (t, 3H, J = 7.0 Hz); ¹³C-NMR (75 MHz, CDCl_3) δ 151.30, 150.53, 138.85, 121.78, 66.84, 52.99, 25.16, 12.95.

Benzyl *trans*-hexa-2-enyl imidodicarbonate: Benzyl *trans*-hexa-2-enyl imidodicarbonate was synthesized from *trans* 2-hexenol (100 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 98% yield (271 mg) as white crystalline solid: m.p.= 48-49 °C; ¹H-NMR (500 MHz, CDCl₃) δ 7.39-7.31 (m, 5H), 7.11 (brs, 1H), 5.80 (dt, 1H, *J* = 6.6 & 15.4 Hz), 5.59-5.53 (m, 1H), 5.19 (s, 2H), 4.60 (d, 2H, *J* = 6.6 Hz), 2.02 (q, 2H, *J* = 7.0 Hz), 1.43-1.36 (m, 2H), 0.89 (t, 3H, *J* = 7.4 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 150.61, 150.53, 137.45, 134.99, 128.52, 128.47, 128.33, 123.01, 67.69, 66.90, 34.17, 21.87, 13.53.

Benzyl *trans,trans*-hexa-2,4-dienyl imidodicarbonate: Benzyl *trans, trans*-hexa-2,4-dienyl imidodicarbonate was synthesized from *trans, trans* hexa-2,4-dienol (98 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 97% yield (267 mg) as white crystalline solid: m.p.= 80-81 °C; ¹H-NMR (500 MHz, CDCl₃) δ 7.38-7.31 (m 5H), 7.14 (brs, 1H), 6.27 (dd, 1H, *J* = 10.4 & 15.6 Hz), 6.04 (dd, 1H, *J* = 10.5 & 15.6 Hz), 5.80-5.73 (m, 1H), 5.61 (dt, 1H, *J* = 6.8 & 15.4 Hz), 5.19 (s, 2H), 4.66 (d, 2H, *J* = 6.5 Hz), 1.76 (d, 3H, *J* = 6.5 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 150.41, 150.35, 135.74, 134.84, 131.80, 130.04, 128.44, 128.41, 128.27, 122.42, 67.77, 66.64, 18.18.

Benzyl *trans*-4-methylpent-2-enyl imidodicarbonate: Benzyl *trans*-4-methylpent-2-enyl imidodicarbonate was synthesized from *trans* 4-methylpent-2-enol (100 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 98% yield (271 mg) as

white crystalline solid: m.p.= 41-42 °C; ^1H -NMR (500 MHz, CDCl_3) δ 7.41-7.29 (m, 6H), 5.76 (ddd, 1H, J = 0.8, 6.6 & 15.4 Hz), 5.50 (dt, 1H, J = 6.6 & 15.4 Hz), 5.17 (s, 2H), 4.58 (d, 2H, J = 6.6 Hz), 2.32-2.26 (m, 1H), 0.98 (d, 6H, J = 6.6 Hz); ^{13}C -NMR (125 MHz, CDCl_3) δ 150.61, 150.53, 144.26, 134.99, 128.50, 128.41, 128.36, 120.05, 67.72, 67.04, 30.67, 21.83.

Benzyl *trans*-3-cyclopentylprop-2-enyl imidodicarbonate: Benzyl *trans*-3-cyclopentylprop-2-enyl imidodicarbonate was synthesized from *trans* 3-cyclopentylprop-2-enol (126 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 96% yield (291 mg) as white crystalline solid: m.p.= 74-75 °C; ^1H -NMR (500 MHz, CDCl_3) δ 7.38-7.31 (m, 5H), 7.21 (brs, 1H), 5.78 (dd, 1H, J = 6.6 & 15.4 Hz), 5.54 (dt, 1H, J = 6.6 & 15.4 Hz), 5.18 (s, 2H), 4.59 (d, 2H, J = 6.6 Hz), 2.47-2.39 (m, 1H), 1.80-1.74 (m, 2H), 1.68-1.60 (m, 2H), 1.59-1.52 (m, 2H), 1.32-1.24 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3) δ 150.38, 150.32, 142.00 134.86, 128.45, 128.39, 128.27, 120.86, 67.73, 67.03, 42.85, 32.72, 25.13.

Benzyl cinnamyl imidodicarbonate: Benzyl cinnamyl imidodicarbonate was synthesized from *trans* cinnamyl alcohol (134 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 98% yield (304 mg) as white crystalline solid: m.p.= 107-108 °C; ^1H -NMR (500 MHz, CDCl_3) δ 7.41 (m, 11H), 6.68 (d, 1H, J = 15.9 Hz), 6.27 (dt, 1H, J = 6.6 & 15.9 Hz), 5.20 (s, 2H), 4.82 (dd, 2H, J = 1.4 & 6.6 Hz); ^{13}C -NMR (75 MHz, CDCl_3) δ 150.42, 150.41, 135.71, 135.01, 134.81, 128.45 (for three carbons), 128.30, 128.10, 126.52, 121.97, 67.84, 66.71.

Benzyl 3-(furan-2-yl)-prop-2-enyl imidodicarbonate: Benzyl 3-(furan-2-yl)-prop-2-enyl imidodicarbonate was synthesized from *trans* 3-(furan-2-yl)-prop-2-enol (124 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 96% yield (289 mg) as off-white crystalline solid: m.p.= 72-73 °C; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.38-7.31 (m, 6H), 7.23 (brs, 1H), 6.48 (d, 1H, J = 16.0 Hz), 6.37 (dd, 1H, J = 2.0 & 3.5 Hz), 6.28 (d, 1H, J = 3.2 Hz), 6.18 (dt, 1H, J = 6.5 & 16.0 Hz), 5.19 (s, 2H), 4.78 (dd, 2H, J = 1.3 & 6.5 Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 151.58, 150.52, 150.45, 142.57, 134.97, 128.63 (for 2 carbons), 128.47, 123.12, 120.49, 111.37, 109.33, 67.91, 66.33.

Benzyl 6-*t*-butyldiphenylsilyloxyhex-2-enyl imidodicarbonate: Benzyl 4-*t*-butyldiphenylsilyloxyhex-2-enyl imidodicarbonate was synthesized from *trans* 4-*t*-butyldiphenylsilyloxyhex-2-enol (177 mg, 0.5 mmol) and benzyloxycarbonyl isocyanate (115 mg, 0.65 mmol) as described above in 95% yield (252 mg) as colorless thick oil: $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.69-7.64 (d, 4H, J = 8.6 Hz), 7.43-7.34 (m, 11H), 7.12 (brs 1H), 5.79 (dt, 1H, J = 6.6 & 15.4 Hz), 5.56 (dt, 1H, J = 6.6 & 15.4Hz), 5.21 (s, 2H), 4.58 (d, 2H, J = 6.6 Hz), 3.67 (t, 2H, J = 6.5 Hz), 2.20-2.14 (q, 2H, J = 6.7 Hz), 1.69-1.59 (m, 2H), 1.05 (s, 9H).

Benzyl 7-*t*-butyldiphenylsilyloxyhept-2-enyl imidodicarbonate: Benzyl 4-*t*-butyldiphenylsilyloxyhept-2-enyl imidodicarbonate was synthesized from *trans* 4-*t*-butyldiphenylsilyloxyhept-2-enol (184 mg, 0.5 mmol) and benzyloxycarbonyl isocyanate (115 mg, 0.65 mmol) as described above in 95% yield (258 mg) as colorless thick oil: $^1\text{H-NMR}$ (500

MHz, CDCl₃) δ 7.70-7.67 (d, 4H, J = 8.6 Hz), 7.45-7.34 (m, 11H), 7.22 (brs, 1H), 5.80 (dt, 1H, J = 6.6 & 15.5 Hz), 5.56 (dt, 1H, J = 6.6 & 15.4 Hz), 5.21 (s, 2H), 4.61 (d, 2H, J = 6.6 Hz), 3.68 (t, 2H, J = 6.4 Hz), 2.08-2.02 (q, 2H, J = 6.7 Hz), 1.61-1.55 (m, 2H), 1.51-1.44 (m, 2H), 1.07 (m, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.38, 150.29, 137.36, 135.35, 134.83, 133.82, 129.34, 128.42 (for 2 carbons), 128.27, 127.42, 122.91, 67.73, 66.88, 63.56, 31.96, 31.86, 26.87, 25.01, 19.21.

Benzyl *trans*-hepta-2,6-dienyl imidodicarbonate: Benzyl hepta-2,6-dienyl imidodicarbonate was synthesized from *trans* hepta-2,6-dienol (112 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 96% yield (277 mg) as white crystalline solid: m.p.= 41-42 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.39-7.31 (m, 6H), 5.85-5.72 (m, 2H), 5.58 (dt, 1H, J = 6.5 & 18.0 Hz), 5.17 (s, 2H), 5.02-4.93 (m, 2H), 4.59 (d, 2H, J = 7.5 Hz), 2.13 (m, 4H); ¹³C-NMR (75 MHz, CDCl₃) δ 150.51, 150.42, 137.52, 136.34, 135.04, 128.43, 128.37, 128.20, 123.47, 114.89, 67.37, 66.72, 32.87, 31.49.

Benzyl *trans*-octa-2,7-dienyl imidodicarbonate: Benzyl octa-2,6-dienyl imidodicarbonate was synthesized from *trans* octa-2,6-dienol (126 mg, 1 mmol) and benzyloxycarbonyl isocyanate (230 mg, 1.3 mmol) as described above in 96% yield (290 mg) as white crystalline solid: m.p.= 37-38 °C; ¹H-NMR (500 MHz, CDCl₃) δ 7.36 (m, 5H), 7.18 (brs, 1H), 5.85-5.73 (m, 2H), 5.62-5.63 (m, 1H), 5.19 (s, 2H), 5.05-4.93 (m, 2H), 4.60 (d, 2H, J = 6.2 Hz), 2.11-2.00 (m, 4H), 1.51-1.44 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃) δ 150.44, 150.40, 138.18, 137.10, 134.84, 128.44, 128.41, 128.26, 123.10, 114.59, 67.75, 66.87, 33.12, 31.57, 27.92.

Iridium(I)-catalyzed decarboxylative allylic amidation of benzyl allyl imidodicarbonates

Reaction condition A: A flame dried 5-mL spherical flask was cooled to room temperature under vacuum and flushed with N₂. To this flask were added [Ir(cod)Cl]₂ (2.7 mg, 0.004 mmol, 2 mol %), posphoramidite ligand **L3** [*O,O'*-(*S*)-1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-1-(2-methoxyphenyl)ethylphosphoramidite] (5 mg, 0.008 mmol, 4 mol %) and THF (0.5 mL) under N₂. The resulting mixture was stirred to obtain a homogenous orange solution. Upon addition of DBU (30 μ L, 0.2 mmol, 100 mol %), the color of the solution changed from orange to light yellow. To this yellow solution were added a substituted allyl benzyl imidodicarbonate (0.2 mmol) and proton sponge (0.2 mmol, 100 mol %). The homogenous solution was stirred at room temperature for 1-12 h depending upon a substrate (for details, see Table 2). After complete reaction, the mixture was transferred to a separatory funnel with help of CHCl₃ (4x5 mL). The combined organic solvents were washed with 1 N HCl (10 mL), water (10 mL), and saturated sodium bicarbonate solution (10 mL), and finally dried over Na₂SO₄. All volatiles were distilled off by rotary evaporator, and the residue was purified by flash column chromatography.

Reaction condition B: The reaction condition B is the same as the condition A except 4 mol % [Ir(COD)Cl]₂, 8 mol % **L3**, and 55 °C were used for the reaction.

(R)-(-)-3-Benzylaminopent-1-ene (Entry 1, Table 2): Colorless oil (40 mg, 92%); $[\alpha]_D^{25} = -12.8$ (c, 1.25, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.36-7.30 (m, 5H), 5.75 (ddd, 1H, *J* = 5.5, 10.5 & 17.0 Hz), 5.15 (d, 1H, *J* = 17.5 Hz), 5.11 (m, 3H), 4.72 (brs, 1H), 4.11 (m, 1H), 1.63-1.47 (m, 2H), 0.92 (t, 3H, *J* = 7.5 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 155.64, 138.21, 136.38, 128.33, 127.92 (for 2 carbons), 114.68, 66.62, 54.64, 28.00, 10.08.; IR (thin film) 3318, 1681 cm⁻¹. Enantiomeric excess was determined after converting this compound to the known compound, (*R*)-(+)-2-benzylaminobutyric acid as follows:

Synthesis of (R)-(+)-2-Benzylloxycarbonylaminobutyric acid: To a round-bottom flask (25 mL) were added CCl₄ (1 mL), MeCN (1 mL), water (1.5 mL), (R)-(-)-3-benzylloxycarbonylaminopent-1-ene (110 mg, 0.5 mmol) and sodium metaperiodate (439 mg, 2.05 mmol), and the resulting mixture was stirred at room temperature until a clear biphasic solution was obtained. This biphasic solution was cooled to 0 °C, and ruthenium trichloride dihydrate (2.5 mg, 2.2 mol %) was added. The reaction mixture was stirred at 0 °C for 1 h and then overnight at room temperature. The reaction mixture was diluted with CH₂Cl₂ (50 mL), and washed with water (20 mL). The organic phase was filtered through celite, and concentrated by rotary evaporator. The residue was dissolved in sodium bicarbonate solution (20 mL), and extracted with ether (2x 20 mL). The aqueous phase was acidified with 1N HCl, and extracted with ether (2x 30 mL). The combined organic layers were dried over Na₂SO₄. The solvents were removed, and the residue was triturated with hexane to afford (R)-(+)-2-benzylloxycarbonylaminobutyric acid as white solid (77 mg, 65%): m.p.= 78-79 °C (Lit.⁴ m.p.= 78-79 °C); [α]_D²⁵ = +8.9 (c, 1.0, EtOH), [Lit.⁵ [α]_D²⁶ = +9.3 (c, 2.0, absolute EtOH)]; ¹H-NMR (500 MHz, CDCl₃) δ 7.37-7.30 (m, 6H), 6.19-6.06* (m, 1H), 5.27** (brs, 1H), 51.2 (s, 2H), 4.39** (m, 1H), 4.25* (brs, 1H), 1.99-1.87 (m, 1H), 1.81-1.72 (m, 1H), 0.98 (t, 3H, *J* = 7.3 Hz). The enantiomeric excess was determined to be 94% by HPLC analysis (Chiralcel OD-H, 15% *i*-PrOH and 0.1% TFA in hexane, 208 nm): *t*_R 6.30 min (minor) and *t*_R 13.38 min (major).

(R)-(-)-3-Benzylloxycarbonylaminohepta-1-ene (Entry 2, Table 2): White crystalline solid (42 mg, 90%): m.p.= 60 °C; [α]_D²⁵ = -18.0 (c, 1.05, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.36-7.30 (m, 5H), 5.75 (ddd, 1H, *J* = 5.5, 10.5, 17.0 Hz), 5.16 (d, 1H, *J* = 17.2 Hz), 5.10-5.08 (m, 3H), 4.68 (brs, 1H), 4.18 (brs, 1H), 1.55-1.32 (m, 4H), 0.92 (t, 3H, *J* = 7.5 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 155.61, 138.58, 136.40, 128.36, 127.89 (for 2 carbons), 114.47, 66.65, 53.11, 37.28, 18.94, 13.91;⁹ IR (thin film) 3315, 1681 cm⁻¹. The enantiomeric excess was determined to be 96% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): *t*_R 11.61 min (major) and *t*_R 12.64 min (minor).

(R)-(-)-3-Benzyloxycarbonylamino-4-methylpent-1-ene (Entry 3, Table 2): White crystalline solid (40 mg, 85%): m.p.= 47-48 °C; $[\alpha]_D^{25} = -25.0$ (c, 1.3, CHCl₃) [Lit.⁶ $[\alpha]_D^{25} = +19.6$ (c, 1.3, CHCl₃) at 67 % *ee* of *S*-enantiomer]; ¹H-NMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 5.75 (ddd, 1H, *J* = 5.9, 10.3 & 16.6 Hz), 5.18-5.12 (m, 4H), 4.79 (brs, 1H), 4.07 (m, 1H), 1.86-1.77 (m, 1H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.90 (d, 3H, *J* = 6.8 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 155.96, 136.87, 136.53, 128.49, 128.07 (for 2 carbons), 115.44, 66.68, 58.58, 32.14, 18.61, 17.94; IR (thin film) 3303, 1683 cm⁻¹. The enantiomeric excess was determined to be 96% by HPLC analysis (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 208 nm): *t*_R 11.90 min (major) and *t*_R 11.20 min (minor).

(R)-(-)-1-benzyloxycarbonylamino-1-cyclopentylprop-2-ene (Entry 4, Table 2): White crystalline solid (44 mg, 85%): m.p.= 85 °C; $[\alpha]_D^{25} = -22.8$ (c, 1.1, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 5.77 (ddd, 1H, *J* = 6.1, 10.4 & 16.7 Hz), 5.17 (d, 1H, *J* = 17.2 Hz), 5.11-5.09 (m, 3H), 4.78 (brs, 1H), 4.06 (m, 1H), 1.99-1.96 (m, 1H), 1.76-1.66 (m, 2H), 1.65-1.58 (m, 2H), 1.57-1.49 (m, 2H), 1.33-1.25 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 155.73, 137.76, 136.42, 128.36, 127.95 (for 2 carbons), 114.87, 66.68, 57.55, 44.36, 29.28, 29.11, 25.59, 25.37; IR (thin film) 3316, 1682 cm⁻¹. The enantiomeric excess was determined to be 96% by HPLC analysis (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 208 nm): *t*_R 13.02 min (major) and *t*_R 13.90 min (minor).

(S)-(-)-3-Benzylloxycarbonylaminohepta-1,4-diene (Entry 5, Table 2): White crystalline solid (37 mg, 80%): m.p.= 69 °C; $[\alpha]_D^{25} = -32.1$ (c, 0.8, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.36-7.30 (m, 5H), 5.82 (ddd, 1H, $J = 4.8, 10.0$ & 17.2 Hz), 5.69-5.62 (m, 1H), 5.43 (dd, 1H, $J = 4.8$ & 15.8 Hz), 5.19 (d, 1H, $J = 17.6$ Hz), 5.14 (d, 1H, $J = 10.6$ Hz), 5.11 (s, 2H), 4.72 (brs, 2H), 1.70 (d, 3H, $J = 6.5$ Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 155.48, 137.51, 136.47, 129.59, 128.42, 128.03 (for 2 carbons), 127.50, 115.06, 66.68, 54.55, 17.67;⁹ IR (thin film) 3303, 1682 cm⁻¹. The enantiomeric excess was determined to be 92% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): t_R 12.52 min (major) and t_R 14.12 min (minor).

(S)-(-)-1-Phenyl-1-benzylloxycarbonylamino-2-propene (Entry 6, Table 2): Colorless needles (48 mg, 90%): m.p.= 67-68 °C; $[\alpha]_D^{25} = -58.3$ (c, 1.0, CHCl₃); [Lit.² $[\alpha]_D^{25} = -14.1$ (c, 1.0, CHCl₃) at 24% *ee*]; ¹H-NMR (500 MHz, CDCl₃) δ 7.36-7.28 (m, 10 H), 6.01 (ddd, 1H, $J = 5.4, 10.5$ & 17.0 Hz), 5.37 (m, 1H), 5.27-5.22 (m, 2H), 5.15-5.09 (m, 3H). The enantiomeric excess was determined to be >99% by HPLC analysis (Chiralcel OD-H, 7.5% *i*-PrOH in hexane, 208 nm): t_R 12.15 min (major) and t_R 14.96 min (minor).

(S)-(-)-1-(2-Furyl)-1-benzylloxycarbonylamino-2-propene (Entry 7, Table 2): White crystalline solid (36 mg, 70%): m.p.= 82 °C; $[\alpha]_D^{25} = -88.5$ (c, 0.45, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.39-7.31 (m, 6H), 6.32 (dd, 1H, $J = 2.0$ & 3.5 Hz), 6.21 (d, 1H, $J = 3.2$ Hz), 6.01 (ddd, 1H, $J = 4.8, 10.5$ & 17.0 Hz), 5.46 (m, 1H), 5.30-5.25 (m, 2H), 5.14 (brs, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 155.29, 152.69, 142.24, 136.13, 134.89, 128.41, 128.06 (for 2 carbons), 116.36, 110.20, 106.77, 67.03, 51.17; IR (thin film) 3288, 1686 cm⁻¹. The

enantiomeric excess was determined to be 94% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): t_R 10.57 min (major) and t_R 12.13 min (minor).

(R)-(-)-3-Benzyloxycarbonylamino-6-*t*-butyldiphenylsilyloxyhex-1-ene (Entry 8, Table 2):

Colorless oil (78 mg, 80%): $[\alpha]_D^{25} = -9.64$ (c, 1.4, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.67-7.65 (d, 4H, $J = 8.6$ Hz), 7.44-7.31 (m, 11H), 5.75 (ddd, 1H, $J = 5.2, 10.0$ & 17.2 Hz), 5.22-5.10 (m, 4H), 4.77 (d, 1H, $J = 7.0$ Hz), 4.22-4.14 (m 1H), 3.67 (t, 2H, $J = 6.5$ Hz), 1.70-1.53 (m, 4H), 1.09 (s, 9H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.75, 138.57, 136.53, 135.52, 133.81, 129.57, 128.49, 128.07 (for 2 carbons), 127.62, 114.77, 66.71, 63.42, 53.15, 31.32, 28.59, 26.85, 19.19; IR (thin film) 3304, 1696 cm^{-1} . The enantiomeric excess was determined to be 98% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): t_R 11.78 min (major) and t_R 11.19 min (minor).

(R)-(-)-3-Benzyloxycarbonylamino-7-*t*-butyldiphenylsilyloxyhept-1-ene (Entry 9, Table 2):

Colorless oil (78 mg, 78%): $[\alpha]_D^{25} = -8.94$ (c, 1.6, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.67-7.65 (d, 4H, $J = 8.6$ Hz), 7.44-7.31 (m, 11H), 5.75 (ddd, 1H, $J = 5.6, 10.3$ & 16.5 Hz), 5.17 (d, 1H, $J = 17.0$ Hz), 5.13-5.10 (m, 3H), 4.77 (d, 1H, $J = 7.0$ Hz), 4.22-4.16 (m, 1H), 3.67 (t, 2H, $J = 6.5$ Hz), 1.70-1.55 (m, 6H), 1.05 (s, 9H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.73, 138.57, 136.53, 135.53, 133.98, 129.51, 128.47, 128.06 (for 2 carbons), 127.57, 114.69, 66.65, 63.57, 53.30, 34.73, 32.19, 26.85, 21.94, 19.16; IR (thin film) 3324, 1695 cm^{-1} . The enantiomeric excess was determined to be 99% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): t_R 12.98 min (major) and t_R 12.15 min (minor).

(R)-(-)-3-Benzyloxycarbonylaminohept-1,6-diene (Entry 10, Table 2): White crystalline solid (42 mg, 86%): m.p.= 40 °C; $[\alpha]_D^{25} = -10.8$ (c, 0.9, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.39-7.31 (m, 5H), 5.85-5.72 (m, 2H), 5.18 (d, 1H, *J* = 17.0 Hz), 5.13-5.11 (m, 3H), 5.02 (d, 1H, *J* = 17.2 Hz), 4.98 (d, 1H, *J* = 10.2 Hz), 4.71 (brs, 1H), 4.21 (brm, 1H), 2.11 (q, 2H, *J* = 7.2 Hz), 1.68-1.55 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 155.56, 138.21, 137.47, 136.37, 128.39, 127.99 (for 2 carbons), 115.15, 114.88, 66.72, 52.96, 34.27, 29.95;⁹ IR (thin film) 3314, 1680 cm⁻¹. The enantiomeric excess was determined to be 96% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): *t*_R 12.65 min (major) and *t*_R 14.29 min (minor).

(R)-(-)-3-Benzyloxycarbonylamino-octa-1,7-diene (Entry 11, Table 2): White crystalline solid (44 mg, 85%): m.p.= 38 °C; $[\alpha]_D^{25} = -14.7$ (c, 1.0, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.38-7.29 (m, 5H), 5.70-5.82 (m, 2H), 4.97-5.18 (m, 6H), 4.52 (brs, 1H), 4.08-4.10 (m, 1H), 2.02-2.10 (m, 2H), 1.40-1.58 (m, 4H); ¹³C-NMR (125 MHz, CDCl₃) δ 155.73, 138.54, 138.23, 136.50, 128.44, 128.03 (for 2 carbons), 114.80, 114.69, 66.62, 53.18, 34.42, 33.33, 24.85;⁹ IR (thin film) 3311, 1686 cm⁻¹. The enantiomeric excess was determined to be 95% by HPLC analysis (Chiralcel OD-H, 2.5% *i*-PrOH in hexane, 208 nm): *t*_R 12.30 min (major) and *t*_R 14.20 min (minor).

Crossover Experiment: An oven dried 5-mL round-bottom flask was cooled to room temperature under vacuum and flushed with N₂. To this flask were added [Ir(cod)Cl]₂ (5.4 mg, 0.008 mmol, 4 mol %), phosphoramidite ligand **L3**, [*O,O'*-(*S*)-1,1'-dinaphthyl-2,2'-diyl]-*N,N'*-di-(*S,S*)-1-(2-methoxyphenyl)-ethylphosphoramidite] (10 mg, 0.016 mmol, 8 mol %), and THF (1 mL) under N₂. The resulting mixture was stirred to obtain an orange solution. Upon addition of DBU (60 μL, 0.4 mmol, 100 mol %), the color of the solution changed from orange to light yellow. To this yellow solution were added methyl *trans*-pent-2-enyl imidodicarbonate (37.4 mg, 0.2 mmol) and benzyl *trans,trans*-hex-2,4-dienyl imidodicarbonate (55 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 1 h. After complete reaction, the mixture was transferred to a separatory funnel with help of CHCl₃ (4x5 mL). The combined organic solvents were washed by water (2x10 mL) and dried over Na₂SO₄. All volatiles were distilled off by rotary evaporator, and the residue was purified by flash column chromatography using an ethyl acetate: hexane mixture to afford two fractions. The first fraction (36 mg, 40%) contained an inseparable ~1:1 mixture of 3-benzyloxycarbonylamino-hexa-1,4-diene (**6**) and 3-benzyloxycarbonylamino-pent-1-ene (**7**) based on ¹H-NMR, whereas the second fraction (27 mg; 46%) an ~1:1 mixture of 3-methoxycarbonylamino-hexa-1,4-diene (**8**) and 3-methoxycarbonylamino-pent-1-ene (**9**) based on ¹H-NMR.

Synthesis of (S)-(-)-N-Allyl-1-phenyl-1-benzyloxycarbonylaminoprop-2-ene (11): To a solution of (S)-(-)-1-phenyl-1-benzyloxycarbonylaminoprop-2-ene (134 mg, 0.5 mmol) in dry THF (10 mL) under nitrogen atmosphere was added KH (30%, 120 mg, 1 mmol). The suspension was stirred at room temperature for 30 min. Allyl bromide (100 μ L, 1 mmol) was added dropwise, and the mixture was stirred for additional 2 h. After complete reaction as judged by TLC, the mixture was neutralized with saturated NH_4Cl solution and extracted with CH_2Cl_2 (2 x 25 mL). The organic layers were washed with water (2 x 20 mL) and dried over Na_2SO_4 . All volatiles were distilled off, and the residue was purified by flash column chromatography on silica gel using an ethyl acetate: hexane mixture (4:96) as eluent to afford (S)-(-)-N-allyl-1-phenyl-1-benzyloxycarbonylaminoprop-2-ene as colorless oil (149 mg, 98%): $[\alpha]_{\text{D}}^{25} = -59.03$ (c, 1.65, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.41-7.24 (m, 10H), 6.16 (ddd, 1H, $J = 5.4, 10.5 \text{ \& } 17.0$ Hz), 5.85 (brm, 1H), 5.63 (m, 1H), 5.35 (d, 1H, $J = 10.5$ Hz), 5.24 (d, 1H, $J = 17.0$ Hz), 5.18 (s, 2H), 4.98 (m, 2H), 3.98-3.76 (m, 2H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 156.14, 139.39, 136.70, 135.42, 134.82, 128.29, 127.83, 127.75, 127.69, 127.36, 118.06, 116.23, 67.30, 62.41, 47.80.

(S)-(-)-N-Benzyloxycarbonyl-2-phenyl-2,5-dihydropyrrole (12): To a solution of (S)-(-)-N-allyl-1-phenyl-1-benzyloxycarbonylaminoprop-2-ene (102 mg, 0.33 mmol) in CH_2Cl_2 (30 mL) was added Grubbs 2nd catalyst (0.017 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 4 h. After complete reaction, all volatiles were removed, and the remaining residue was purified by flash column chromatography using an ethyl acetate: hexane mixture (5:95) as eluent to afford (S)-(-)-N-benzyloxycarbonyl-2-phenyl-2,5-dihydropyrrole as white crystalline solid (90 mg, 97%): m.p. = 61-62 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = -237.3$ (c, 1.1, CHCl_3), [Lit.⁷ $[\alpha]_{\text{D}}^{25} = -120$ (CHCl_3)]; $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.38-7.20 (m, 9H), 6.94 (brd, 1H), 5.92 (m, 1H), 5.81** (m, 1H), 5.76* (m, 1H), 5.60** (brs, 1H), 5.52* (brs, 1H), 5.21** (d, 1H, $J = 12.4$ Hz), 5.08-5.03 (m, 1H), 4.98* (d, 1H, $J = 12.4$ Hz), 4.47-4.34 (m, 2H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 154.43**, 154.20*, 141.70**, 140.88*, 136.84*, 136.50**.

131.02, 128.31, 128.03, 127.74, 127.35, 126.78*, 126.37**, 124.53*, 124.37**, 68.34*, 68.04**, 66.72, 54.28**, 53.75*

Synthesis of *cis*-(2*R*,6*S*)-(+)-(N-Benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide (14):⁸ To a solution of (*R*)-3-benzyloxycarbonylamino-1,7-octadiene (129 mg; 0.5 mmol) in nitromethane (12 mL) was added mercury(II) trifluoroacetate (256 mg; 0.6 mmol) at room temperature, and the reaction mixture was stirred for additional 1 h. The reaction mixture was quenched by adding saturated potassium bromide solution (3 mL), and further stirred for 1 h. After water (50 mL) was added, the resulting mixture was extracted with ethyl acetate (2x25 mL). The combined organic phases were washed with water (2x25 mL) and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was purified by flash column chromatography on silica gel using an ethyl acetate: hexane mixture (05:95) as eluent to *cis*-(2*R*,6*S*)-(N-benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide as colorless thick oil (175 mg, 65%): $[\alpha]_D^{25} = +38.2$ (c, 1.1, CHCl₃); ¹H-NMR (500 MHz, CDCl₃) δ 7.40-7.29 (m, 5H), 5.95 (ddd, 1H, *J* = 6.0, 10.5 & 16.5 Hz), 5.25 (d, 1H, *J* = 12.0 Hz), 5.17-5.10 (m, 3H), 4.81-4.78 (m, 1H), 4.6-4.55 (m, 1H), 2.30 (dd, 1H, *J* = 11.0 & 12.0 Hz), 1.92-1.88 (m, 2H), 1.82-1.73 (m, 2H), 1.68-1.61 (m, 2 H), 1.54-1.40 (m, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 155.42, 139.57, 136.23, 128.40, 128.16, 127.97, 116.05, 67.45, 51.44, 50.65, 40.08, 32.03, 27.24, 13.92.

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- 9 ^{13}C -NMR of the product is matching with that of the authentic sample that was prepared by an alternative route using Overman rearrangement (see below), indicating that a broader signal at 127.89 ppm for Entry 2, 128.03 ppm for Entry 5, 127.99 ppm for Entry 10, or 128.03 ppm for Entry 11 is for the 2 CH carbons in the benzene ring of the Cbz-protection group.

S-31

S-36

Synthesized by an alternate route using Overman rearrangement

S-46

Synthesized by using Iridium(I)-catalyst

Synthesized by using Iridium(I)-catalyst

S-53

Synthesized by an alternate route using Overman rearrangement

Synthesized by using Iridium(I)-catalyst

Synthesized by an alternate route using Overman rearrangement

Synthesized by using Iridium(I)-catalyst

S-58

S-62

Synthesized by an alternate route using Overman rearrangement

S-65

Synthesized by using Iridium(I)-catalyst

Synthesized by an alternate route using Overman rearrangement

Synthesized by using Iridium(I)-catalyst

Synthesized by an alternate route using Overman rearrangement

Synthesized by using Iridium(I)-catalyst

Synthesized by an alternate route using Overman rearrangement

Synthesized by using Iridium(I)-catalyst