Supporting Information for In Search of High Stereocontrol for the Construction of *cis*-Disubstituted Cyclopropane Compounds. Total Synthesis of a Cyclopropane-Configured Urea-PETT Analog That is a HIV-1 Reverse Transcriptase Inhibitor

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1*S*,2*R*,5*S*-Menthyl 2-Oxaazetidine-4(*S*)-carboxylate. A flask was charged with (*S*)-2-oxaazetidine-4-carboxylic acid (1.10 g, 9.56 mmole), 1*S*,2*R*,5*S*-(+)-menthol (1.50 g, 9.6 mmole), and 4-dimethylaminopyridine (0.23 g, 1.9 mmole) and purged with argon. Both dichloromethane (20 mL) and acetonitrile (20 mL) were added, and the mixture was cooled to 0 °C. A solution of dicyclohexyl-carbodiimide (2.18 g, 10.6 mmole) in dichloromethane (5 mL) was added to the reaction mixture over a period of 30 min. A white solid precipitated, and the reaction mixture was stirred overnight at room temperature. The white solid was removed by filtration. The solution was evaporated to dryness under reduced pressure, and the solid was dissolved in an excess of ethyl acetate and then washed with 1 M HCl, 5% NaHCO₃, and water. The ethyl acetate solution was then dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (ethyl acetate:hexanes = 2:1) to yield a white solid (0.67 g, 2.64 mmole, 28% yield): ¹H NMR (200 MHz, CDCl₃) δ 6.04 (br s, 1 H), 4.77 (dt, *J* = 10.9, 4.2 Hz, 1 H), 4.16 (dd, *J* = 5.9, 2.6 Hz, 1 H), 3.35 (ddd, *J* = 15.1, 5.9, 1.4 Hz, 1 H), 3.04 (ddd, *J* = 14.6, 4.7, 2.6 Hz, 1 H), 2.05-0.74 (comp, 18 H); ¹³C NMR (75 MHz, CDCl₃) δ 75.9, 47.5, 46.9, 43.5, 40.7, 34.1, 31.4, 26.4, 23.3, 21.9, 20.7, 16.22; [α]_D²⁵ = +35.4 (*c* = 0.33, CH₂Cl₂); mp = 133-134 °C. Anal. Calcd for C₁₄H₂₄NO₃: C, 66.40; H, 9.09; N, 5.53. Found: C, 66.63; H, 9.46; N, 5.61.

Dirhodium(II) Tetrakis[1*S*,2*R*,5*S*-menthyl 2-oxaazetidine-4(*S*)-carboxylate], Rh₂(*S*,*S*-Menth-AZ)₄ (3b**).** The standard procedure was followed using ligand (0.67 g, 2.64 mmole) and Rh₂(OAc)₄ (0.146 g, 0.33 mmole) in about 10 mL of anhydrous chlorobenzene. Product formation was followed by HPLC (Licrosorb-CN column) during 3 h of heating at reflux. The solvent was removed under reduced pressure, and the solid was purified on reverse phase (C8) silica in methanol. Yield 3.65 g of a blue solid (91% yield): ¹H NMR (300 MHz, CDCl₃) δ 4.78-4.62 (comp, 4 H), 4.23-4.16 (comp, 2 H), 4.01-3.95 (comp, 2 H), 3.39-3.14 (comp, 8 H), 2.23-0.64 (comp, 72 H); ¹³C NMR (75 MHz, CDCl₃) δ 172.4, 136.7, 133.1, 132.7, 129.1, 75.7, 75.1, 74.4, 52.8, 51.8, 47.0, 46.7, 40.9, 34.2, 31.4, 26.2, 25.5, 23.0, 21.9, 21.0, 20.7, 16.2, 15.9; [α]_D^{25.5} = -116.1 (*c* = 0.071, CH₂Cl₂); MS (FAB+): [*M*⁺] = 1214.6. Crystallization from a solution containing benzonitrile formed the bis-benzonitrile complex that was somewhat unstable to dissociation of benzonitrile during elemental analysis. Anal. Calcd for C₅₆H₉₂N₄O₁₂Rh₂•(PhCN)₂: C, 59.15; H, 7.18; N, 5.92. Found: C, 58.77; H, 7.28; N, 5.61.

1*R*,2*S*,5*R*-Menthyl 2-oxaazetidine-4(*S*)-carboxylate. A flask was charged with (*I*)-2-oxaazetidine-4-carboxylic acid (1.10 g, 9.56 mmole), 1*R*,2*S*,5*R*-(-)-menthol (1.50 g, 9.56 mmole), and 4-dimethylaminopyridine (0.29 g, 2.4 mmole) and purged with argon. Both dichloromethane (20 mL) and acetonitrile (20 mL) were added, and the mixture was cooled to 0 °C. A solution of dicyclohexyl-carbodiimide (2.47 g, 12.0 mmole) in dichloromethane (5

mL) was added to the reaction mixture over a period of 30 min. A white solid precipitated, and the reaction mixture was stirred overnight at room temperature. The white solid was removed by filtration. The solution was evaporated to dryness under reduced pressure, and the solid was dissolved in an excess of ethyl acetate and then washed with 1 M HCl, 5% NaHCO₃, and water. The ethyl acetate solution was then dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (ethyl acetate:hexanes = 2:1) to yield a white solid (0.98 g, 3.87 mmole, 40% yield): ¹H NMR (300 MHz, CDCl₃) δ 6.09 (s, 1 H), 4.77 (dt, *J* = 10.8, 4.4 Hz, 1 H), 4.16 (dd, *J* = 5.9, 2.7 Hz, 1 H), 3.34 (ddd, *J* = 14.9, 5.9, 1.5 Hz, 1 H), 3.03 (ddd, *J* = 14.9, 2.7, 2.2 Hz, 1 H), 2.02-1.94 (m, 1 H), 1.82 (dq, *J* = 7.1, 2.7 Hz, 1 H), 1.74-1.63 (comp, 3 H), 1.52-1.36 (comp, 2 H), 1.12-0.97 (comp, 2 H), 0.90 (dd, *J* = 6.6, 5.1 Hz, 6 H), 0.76 (d, *J* = 7.1 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 75.9, 47.4, 46.9, 43.6, 40.7, 34.1, 31.4, 26.3, 23.3, 21.9, 20.7, 16.3.

Dirhodium(II) Tetrakis[1*R*,2*S*,5*R*-menthyl 2-oxazetidine-4(*S*)-carboxylate], Rh₂(*S*,*R*-Menth-AZ)₄ (3c). A standard procedure was followed using ligand (0.98 g, 3.87 mmole) and Rh₂(OAc)₄ (0.21 g, 0.48 mmole) in about 10 mL of anhydrous chlorobenzene. Product formation was followed by HPLC during 3 h of heating at reflux. The solvent was removed under reduced pressure and the solid was purified on reverse phase (C8) silica in methanol. Yield 0.43 g of a blue solid (74 % yield): ¹H NMR (300 MHz, CDCl₃) δ 4.84-4.68 (comp, 4 H), 4.12-3.96 (comp, 4 H), 3.44-3.20 (comp, 4 H), 3.07 (br s, 4 H), 2.12-1.79 (comp, 8 H), 1.74-1.62 (comp, 12 H), 1.56-1.32 (comp, 8 H), 1.14-0.71 (comp, 44 H); ¹³C NMR (75 MHz, CDCl₃): δ 75.0, 52.6, 51.5, 47.0, 40.8, 40.5, 34.2, 34.1, 31.4, 26.2, 26.1, 23.4, 23.3, 22.1, 22.0, 20.9, 20.7, 16.4, 16.2. $[\alpha]_D^{29.6} = -184(4)$ (*c* = 0.1, CHCl₃); MS (FAB+): $[M]^+ = 1214.5$. Anal. Calcd for C₅₆H₉₂N₄O₁₂Rh₂: C, 55.35; H, 7.58; N, 4.61. Found: C, 55.52; H, 7.79; N, 4.57.

Standard Procedure for the Decomposition of Diazoacetates by Rh₂(MenthAZ)₄ Catalysts. A round bottom flask containing a stir bar was fitted with a reflux condenser and purged with N₂. The catalyst was added as a solid, then dissolved in 5 mL of anhydrous dichloromethane and heated to 40 °C. The diazoacetate was dissolved in 2 mL of dichloromethane under N₂ and added to the catalyst solution via syringe pump. After the addition was complete, the reaction mixture was allowed to heat at reflux for an additional 30 min. After cooling the solution was forced through a short silica plug with either dichloromethane or 4:1 hexanes:ethyl acetate solution to remove the catalyst. The solvent was

removed under reduced pressure, and the products were analyzed by ¹H NMR and gas chromatography.

***t*-Butyl 2-(*p*-Methylphenyl)cyclopropanecarboxylate (4, Z = *p*-Me, R = *t*-Bu).** For cis isomer: ¹H NMR (600 MHz, CDCl₃) δ 7.14 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 2.47 (dt, *J* = 9.6, 7.8 Hz, 1H), 2.27 (s, 3H), 1.94 (ddd, *J* = 9.6, 7.8, 5.4 Hz, 1H), 1.59 (dt, *J* = 7.8, 5.4 Hz, 1H), 1.20 (td, *J* = 7.8, 5.4 Hz, 1H), 1.16 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 170.2, 135.9, 133.7, 129.3, 128.5, 79.9, 27.8, 24.7, 22.6, 21.0, 10.6. GC on SPB-5 column: *t*_R 14.43 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-DM column: *t*_R 71.3 min and 72.4 min (flow rate: 1 mL/min, oven temp: 90 °C for 20 min then 1 °C/min to 140 °C); for trans isomer: ¹H NMR (600 MHz, CDCl₃) δ 7.06 (d, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 2.40 (ddd, *J* = 9.6, 6.6, 4.2 Hz, 1H), 2.30 (s, 3H), 1.78 (ddd, *J* = 9.6, 5.4, 4.2 Hz, 1H), 1.49 (dt, *J* = 9.6, 4.2 Hz, 1H), 1.46 (s, 9H), 1.19 (ddd, *J* = 9.6, 6.6, 5.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.6, 135.8, 129.0, 126.0, 80.4, 28.2, 25.4, 25.1, 20.9, 16.8. GC on SPB-5 column: *t*_R 15.23 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C). Anal. Calcd for C₁₅H₂₀O₂ (cis and trans mixture): C, 77.55; H, 8.68 Found: C, 76.70; H, 8.80.

***t*-Butyl 2-(*p*-Trifluoromethylphenyl)cyclopropanecarboxylate (4, Z = *p*-CF₃, R = *t*-Bu).** For cis isomer: ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.54 (dt, *J* = 9.6, 7.8 Hz, 1H), 2.05 (ddd, *J* = 9.6, 7.8, 5.4 Hz, 1H), 1.67 (dt, *J* = 7.8, 5.4 Hz, 1H), 1.31 (td, *J* = 7.8, 5.4 Hz, 1H), 1.15 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 169.7, 141.2, 129.8, 128.8 (q, *J*_{F-C} = 36.7 Hz), 124.7 (q, *J*_{F-C} = 3.8 Hz), 124.2 (q, *J*_{F-C} = 270 Hz), 80.4, 27.8, 24.7, 23.0, 10.8. GC on SPB-5 column: *t*_R 13.09 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-DM column: *t*_R 65.6 min and 67.7 min (flow rate: 1 mL/min, oven temp: 90 °C for 20 min then 1 °C/min to 120 °C); for trans isomer: ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.48 (ddd, *J* = 10.2, 6.0, 4.2 Hz, 1H), 1.87 (ddd, *J* = 8.4, 4.8, 4.2 Hz, 1H), 1.59 (dt, *J* = 10.2, 4.8 Hz, 1H), 1.48 (s, 9H), 1.26 (ddd, *J* = 8.4, 6.0, 4.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.0, 144.8, 128.6 (q, *J*_{F-C} = 32.4 Hz), 126.3, 125.3 (q, *J*_{F-C} = 3.5 Hz), 124.2 (q, *J*_{F-C} = 270 Hz), 80.9, 28.1, 25.6, 25.3, 17.2. GC on SPB-5 column: *t*_R 13.89 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-DM column: *t*_R 93.7 min and 95.2 min (flow rate: 1 mL/min, oven temp: 90 °C for 20 min then 1 °C/min to 120 °C). Anal. Calcd for C₁₅H₁₇F₃O₂ (cis and trans mixture): C, 62.93; H, 5.99. Found: C, 62.61; H, 6.01.

***t*-Butyl 2-(*o*-Chlorophenyl)cyclopropanecarboxylate (4, Z = *o*-Cl, R = *t*-Bu).** For cis isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.31 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.27 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.20-7.13 (comp, 2H), 2.48 (q, $J = 8.4$ Hz, 1H), 2.12 (td, $J = 8.4, 5.4$ Hz, 1H), 1.62 (dt, $J = 8.4, 5.4$ Hz, 1H), 1.32 (td, $J = 8.4, 5.4$ Hz, 1H), 1.16 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.1, 136.1, 130.6, 129.4, 128.7, 127.8, 126.1, 80.0, 27.7, 23.9, 22.5, 11.2. GC on SPB-5 column: t_R 15.40 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex G-TA column: t_R 53.4 min and 55.5 min (flow rate: 1 mL/min, oven temp: 120 °C); for trans isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.36 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.20-7.12 (comp, 2H), 6.99 (dd, $J = 7.8, 1.8$ Hz, 1H), 2.67 (ddd, $J = 9.0, 6.6, 4.2$ Hz, 1H), 1.71 (dt, $J = 8.4, 4.8$ Hz, 1H), 1.55 (ddd, $J = 9.0, 4.8, 4.2$ Hz, 1H), 1.25 (ddd, $J = 8.4, 6.6, 4.8$ Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.4, 137.8, 131.0, 129.3, 127.7, 127.0, 126.7, 80.5, 28.1, 24.0, 22.5, 15.0. GC on SPB-5 column: t_R 16.18 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{ClO}_2$ (cis and trans mixture): C, 66.53; H, 6.78. Found: C, 66.07; H, 6.81.

***t*-Butyl-2-(2,6-Dichlorophenyl)cyclopropanecarboxylate (4, Z = 2,6-Cl₂, R = *t*-Bu).** For cis isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.26 (d, $J = 7.8$ Hz, 2H), 7.08 (t, $J = 7.8$ Hz, 1H), 2.22 (q, $J = 8.4$ Hz, 1H), 2.07 (td, $J = 8.4, 5.4$ Hz, 1H), 1.74 (dt, $J = 8.4, 5.4$ Hz, 1H), 1.62 (td, $J = 8.4, 5.4$ Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.9, 135.0, 129.7, 128.4, 128.1, 80.8, 27.7, 23.4, 22.6, 16.9. GC on SPB-5 column: t_R 17.42 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-DM column: t_R 45.0 min and 45.9 min (flow rate: 1 mL/min, oven temp: 150 °C); for trans isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 2.31 (q, $J = 9.0, 8.4, 4.8$ Hz, 1H), 1.80 (dt, $J = 8.4, 4.8$ Hz, 1H), 1.70 (dt, $J = 8.4, 4.8$ Hz, 1H), 1.36 (ddd, $J = 9.0, 8.4, 4.8$ Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.8, 137.4, 133.6, 128.4, 128.3, 80.5, 28.2, 25.0, 23.1, 17.6. GC on SPB-5 column: t_R 18.04 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{O}_2$ (cis and trans mixture): C, 58.50; H, 5.62. Found: C, 58.49; H, 5.75.

***t*-Butyl 2-(2,4,6-Trimethylphenyl)cyclopropanecarboxylate (4, Z = 2,4,6-Me₃, R = *t*-Bu).** For cis isomer: ^1H NMR (500 MHz, CDCl_3) δ 6.77 (s, 2H), 2.33 (s, 6H), 2.24 (s, 3H), 2.23-2.17 (comp, 1H), 2.05-1.98 (comp, 1H), 1.61-1.56 (comp, 1H), 1.48-1.42 (comp, 1H), 1.14 (s, 9H); ^{13}C

NMR (125 MHz, CDCl_3) δ 171.3, 138.3, 135.6, 130.9, 128.8, 79.7, 27.6, 22.5, 22.1, 20.8, 20.4, 15.6. GC on SPB-5 column: t_R 16.49 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-TA column: t_R 38.3 min and 40.6 min (flow rate: 0.7 mL/min, oven temp: 140 °C); for trans isomer: ^1H NMR (500 MHz, CDCl_3) δ 6.81 (s, 2H), 2.33 (s, 6H), 2.22 (s, 3H), 2.24-2.21 (comp, 1H), 1.63-1.56 (comp, 2H), 1.49 (s, 9H), 1.10-1.03 (comp, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 138.3, 136.2, 133.3, 128.8, 80.3, 28.2, 24.2, 22.9, 20.8, 20.4, 17.0. GC on SPB-5 column: t_R 17.56 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-TA column: t_R 60.5 min and 63.7 min (flow rate: 0.7 mL/min, oven temp: 140 °C). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{O}_2$ (cis and trans mixture): C, 78.42; H, 9.29. Found: C, 78.52; H, 9.72.

4-Chloro-1-ethoxy-2-fluorobenzene (6). ^1H NMR (250 MHz, CDCl_3) δ 7.10 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.04-6.98 (comp, 1H), 6.85 (t, $J = 8.8$ Hz, 1H), 4.06 (q, $J = 7.0$ Hz, 2H), 1.43 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 152.4 (d, $J_{\text{FC}} = 247.9$ Hz), 145.8 (d, $J_{\text{FC}} = 10.0$ Hz), 125.1 (d, $J_{\text{FC}} = 8.8$ Hz), 124.1 (d, $J_{\text{FC}} = 3.6$ Hz), 116.8 (d, $J_{\text{FC}} = 21.2$ Hz), 115.3 (d, $J_{\text{FC}} = 2.6$ Hz), 65.1, 14.6.

6-Chloro-3-ethoxy-2-fluorobenzaldehyde (7). ^1H NMR (250 MHz, CDCl_3) δ 10.43 (s, 1H), 7.18 (dd, $J = 8.9, 1.3$ Hz, 1H), 7.10 (t, $J = 8.9$ Hz, 1H), 4.12 (q, $J = 7.0$ Hz, 2H), 1.46 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 187.2 (d, $J_{\text{FC}} = 3.8$ Hz), 153.5 (d, $J_{\text{FC}} = 266.0$ Hz), 146.6 (d, $J_{\text{FC}} = 10.1$ Hz), 126.3, 125.9 (d, $J_{\text{FC}} = 18.3$ Hz), 121.9, 119.7 (d, $J_{\text{FC}} = 3.8$ Hz), 65.7, 14.6.

1-Chloro-4-ethoxy-3-fluoro-2-vinylbenzene (8). ^1H NMR (500 MHz, CDCl_3) δ 7.09 (dd, $J = 9.0, 1.0$ Hz, 1H), 6.76 (t, $J = 9.0$ Hz, 1H), 6.75 (dd, $J = 18.0, 12.0$ Hz, 1H), 5.98 (dt, $J = 18.0, 1.5$ Hz, 1H), 5.65 (dt, $J = 12.0, 1.5$ Hz, 1H), 4.05 (q, $J = 7.0$ Hz, 2H), 1.43 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.3 (d, $J_{\text{FC}} = 251.0$ Hz), 146.2 (d, $J_{\text{FC}} = 5.8$ Hz), 127.7, 125.0 (d, $J_{\text{FC}} = 4.4$ Hz), 124.6 (d, $J_{\text{FC}} = 12.5$ Hz), 124.3 (d, $J_{\text{FC}} = 4.3$ Hz), 122.3 (d, $J_{\text{FC}} = 11.8$ Hz), 113.5, 65.1, 14.7.

Ethyl (1*S*,2*R*)-cis-2-(6-chloro-3-ethoxy-2-fluorophenyl)-cyclopropanecarboxylate (9c, R = Et). $[\alpha]_{\text{D}}^{28} = +11.5$ ($c = 1.9, \text{CH}_2\text{Cl}_2$) for 86% ee (1*R*, 2*S*); ^1H NMR (500 MHz, CDCl_3) δ 7.02 (dd, $J = 8.5, 2.0$ Hz, 1H), 6.77 (t, $J = 8.5$ Hz, 1H), 4.05 (q, $J = 7.0$ Hz, 2H), 3.99 (q, $J = 7.0$ Hz, 2H), 2.25-2.18 (comp, 1H), 1.75-1.69 (comp, 1H), 1.61-1.55 (comp, 2H), 1.42 (t, $J = 7.0$ Hz, 3H); 1.10 (t, $J = 7.0$ Hz, 3H); GC on SPB-5 column: t_R 17.94 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on Chiraldex B-DM column:

t_R 71.5 min (minor) and 73.6 min (major) (flow rate: 1 mL/min, oven temp: 150 °C).

***tert*-Butyl (1*S*,2*R*)-cis-2-(6-chloro-3-ethoxy-2-fluorophenyl)cyclopropanecarboxylate (9c, R = *t*-Bu).** $[\alpha]_D^{25} = +18.8$ ($c = 1.2$, CH_2Cl_2) for 97% ee (1*S*,2*R*); ^1H NMR (600 MHz, CDCl_3) δ 7.02 (dd, $J = 8.4, 1.8$ Hz, 1H), 6.77 (t, $J = 8.4$ Hz, 1H), 4.05 (q, $J = 7.2$ Hz, 2H), 2.16 (q, $J = 8.4$ Hz, 1H); 2.12-2.07 (comp, 1H), 1.70-1.67 (comp, 1H), 1.51 (td, $J = 8.4, 4.8$ Hz, 1H), 1.41 (t, $J = 7.2$ Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.8, 152.9 (d, $J_{\text{FC}} = 249.6$ Hz), 145.9 (d, $J_{\text{FC}} = 11.9$ Hz), 128.0 (d, $J_{\text{FC}} = 4.2$ Hz), 124.3 (d, $J_{\text{FC}} = 13.0$ Hz), 123.7 (d, $J_{\text{FC}} = 4.4$ Hz), 113.3 (d, $J_{\text{FC}} = 2.6$ Hz), 80.0, 65.1, 27.7, 21.4 (d, $J_{\text{FC}} = 1.7$ Hz), 18.6, 14.7, 14.2 (d, $J_{\text{FC}} = 6.9$ Hz). GC on SPB-5 column: t_R 18.65 min (flow rate: 1 mL/min, oven temp: 100 °C for 2 min then 10 °C/min to 275 °C), GC on ChiralDEX B-DM column: t_R 83.2 min (minor) and 84.3 min (major) (flow rate: 1 mL/min, oven temp: 150 °C).

(1*S*,2*R*)-cis-2-(6-Chloro-3-ethoxy-2-fluorophenyl)cyclopropanecarboxylic acid (11). ^1H NMR (600 MHz, CDCl_3) δ 7.03 (d, $J = 8.4$ Hz, 1H), 6.77 (t, $J = 8.4$ Hz, 1H), 4.04 (q, $J = 7.2$ Hz, 2H), 2.27 (q, $J = 8.4$ Hz, 1H); 2.18-2.12 (comp, 1H), 1.72-1.66 (comp, 1H), 1.61 (td, $J = 8.4, 6.6$ Hz, 1H), 1.42 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 178.1, 152.8 (d, $J_{\text{FC}} = 248.0$ Hz), 145.8 (d, $J_{\text{FC}} = 11.9$ Hz), 127.7 (d, $J_{\text{FC}} = 3.5$ Hz), 123.9 (d, $J_{\text{FC}} = 4.2$ Hz), 123.2 (d, $J_{\text{FC}} = 12.6$ Hz), 113.8, 65.2, 19.9, 19.7, 15.4 (d, $J_{\text{FC}} = 6.6$ Hz), 14.7.

(1*S*,2*R*)-1-[cis-2-(6-Chloro-3-ethoxy-2-fluorophenyl)-cyclopropyl]-3*N*-(5-chloropyridin-2-yl)urea (12).⁶ $[\alpha]_D^{27} = -3.9$ ($c = 0.8$, CH_2Cl_2) for 86% ee; ^1H NMR (600 MHz, CDCl_3) δ 9.19 (br s, 1H), 8.44 (br s, 1H), 7.83 (br s, 1H), 7.46 (dd, $J = 9.0, 2.5$ Hz, 1H), 7.26 (s, 1H), 7.14 (dd, $J = 9.0, 1.2$ Hz), 6.81 (t, $J = 9.0$ Hz, 1H), 6.75-6.73 (comp, 1H), 4.09-4.03 (comp, 2H), 3.35-3.28 (comp, 1H), 2.09 (q, $J = 7.8$ Hz, 1H), 1.68-1.61 (comp, 1H), 1.45 (t, $J = 7.2$ Hz, 3H); 1.33 (q, $J = 6.0$ Hz, 1H); HPLC on Chiralpak OD column: t_R 21.47 min (major) and 25.31 min (minor) (flow rate: 1 mL/min, hexanes : isopropanol = 95:5).