Supporting Information

Stereoselectivity of Superacid-Catalyzed Pictet-Spengler

Cyclization Reactions

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Experimental Sections

General Methods

Melting points were determined with a Yazawa micro melting point apparatus and uncorrected. ¹H-NMR spectra were recorded on a JEOL GX-400 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, and brs = broad singlet. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-O1SG-2 spectrometer.

Preparation of *N*-Benzyldene-2-Arylethylamines **1**, **5** and **8**

A Typical procedure (**1b**)

To a suspension of MgSO₄ (1.5322 g) in 3 mL of dry benzene was added a solution of 637.6 mg of benzaldehyde (6.01 mmol, 1.0 eq.) in 2 mL of dry benzene, followed by a solution of 812.2 mg of 2-methylphenethylamine (6.01 mmol) in 2 mL of dry benzene. The reaction mixture was stirred at r.t. for 3.5 h. Then, the mixture was filtered and the solvent was evaporated under reduced pressure to give 1.1268 g of *N*-benzyldene-2-methyl-2-phenethylamine **1b** (5.05 mmol, 84% yield).

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.116 (1H, s), 7.676-7.651 (total 2H, m), 7.408-7.175 (total 8H, m), 3.811 (1H, dd, *J* = 6.05, 11.3 Hz), 3.697 (1H, t, *J* = 9.34 Hz), 3.211 (1H, q, *J* = 6.78 Hz), 1.339 (3H, d, *J* = 6.96 Hz). Anal. Calcd. for C₁₆H₁₇N: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.85; H, 7.61; N, 6.24.

N-Benzyldene-2-ethyl-2-phenethylamine (**1c**)

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.089 (1H, s), 7.666 (2H, dd, J = 3.03, 6.50 Hz), 7.415-7.165 (total 8H, m), 3.866-3.754 (total 2H, m), 2.970-2.899 (total 1H, m), 1.935-1.815 (total 1H, m), 1.712-1.599 (total 1H, m), 0.841 (3H, t, J = 7.33 Hz). Anal. Calcd. for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.85; H, 8.10; N, 5.83.

***N*-Benzylidene-2-buthyl-2-phenethylamine (1d)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.064 (1H, s), 7.649-7.640 (total 2H, m), 7.386-7.154 (total 8H, m), 3.836 (total 2H, m), 2.99-2.970 (total 1H, m), 1.858-1.772 (total 1H, m), 1.691-1.633 (total 1H, m), 1.338-1.162 (total 4H, m), 0.823 (3H, t, J = 6.60 Hz). Anal. Calcd. for C₁₉H₂₃N: C, 85.99; H, 8.74; N, 5.28. Found: C, 86.04; H, 8.96; N, 5.27.

***N*-Benzylidene-1-ethyl-2-phenethylamine (1e)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.913 (1H, s), 7.647 (2H, dd, J = 2.01, 5.50 Hz), 7.401-7.344 (total 3H, m), 7.244-7.122 (total 5H, m), 3.247-3.182 (total 1H, m), 2.978-2.866 (total 2H, m), 1.759-1.668 (total 2H, m), 0.855 (3H, t, J = 7.33 Hz). Anal. Calcd. for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.04; H, 8.07; N, 5.69.

***N*-Benzylidene-1-butyl-2-phenethylamine (1f)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.886 (1H, s), 7.650-7.626 (total 2H, m), 7.387-7.364 (total 3H, m), 7.245-7.113 (total 5H, m), 3.328-3.263 (total 1H, m), 2.963-2.858 (total 2H, m), 1.743-1.644 (total 2H, m), 1.354-1.145 (total 4H, m), 0.858 (3H, t, J = 7.14 Hz). Anal. Calcd. for C₁₉H₂₃N: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.74; H, 8.75; N, 5.30.

***N*-Benzylidene-2-methyl-2-(3',4'-dimethoxy)phenylethylamine (5b)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.102 (1H, s), 7.692 (2H, dd, J = 2.02, 5.50 Hz), 7.414-7.377 (total 3H, m), 6.803-6.772 (total 3H, m), 3.850 (3H, s), 3.822 (3H, s), 3.808-3.749 (total 1H, m), 3.705-3.639 (total 1H, m), 3.193-3.107 (total 1H, m), 1.328 (3H, d, J = 6.96 Hz). Anal. Calcd. for C₁₈H₂₁NO₂: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.00; H, 7.57; N, 4.92.

***N*-Benzylidene-2-ethyl-2-(3',4'-dimethoxy)phenylethylamine (5c)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.057 (1H, s), 7.683-7.651 (total 2H, m), 7.417-7.352 (total 3H, m), 6.837-6.713 (total 3H, m), 3.859 (3H, s), 3.808 (3H, s), 3.800-3.718 (total 2H, m), 2.901-2.831 (total 1H, m), 1.909-1.807 (total 1H, m), 1.672-1.577 (total 1H, m), 0.854 (3H, t, J = 7.33 Hz). Anal. Calcd. for C₁₉H₂₃NO₂: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.75; H, 7.94; N, 4.72.

***N*-Benzylidene-2-buthyl-2-(3',4'-dimethoxy)phenylethylamine (5d)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.040 (1H, s), 7.672-7.642 (total 2H, m), 7.412-7.350 (total 3H, m), 6.799-6.710 (total 3H, m), 3.844 (3H, s), 3.804 (3H, s), 3.792-3.662 (total 2H, m), 2.980-2.910 (total 1H, m), 1.840-1.816 (total 1H, m), 1.806-1.581 (total 1H, m), 1.368-1.163 (total 4H, m), 0.842 (3H, t, J = 6.96 Hz). Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.34; H, 8.52; N, 4.23.

***N*-Benzylidene-1-ethyl-2-(3',4'-dimethoxy)phenylethylamine (5e)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.908 (1H, s), 7.670-7.646 (total 2H, m), 7.407-7.344 (total 3H, m), 6.744-6.621 (total 3H, m), 3.821 (3H, s), 3.686 (3H, s), 3.190-3.124 (1H, m), 2.907-2.809 (total 2H, m), 1.768-1.698 (total 2H, m), 0.870 (3H, t, J = 7.33 Hz). Anal. Calcd. for C₁₉H₂₃NO₂: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.45; H, 7.72; N, 4.74.

***N*-Benzylidene-1-buthyl-2-(3',4'-dimethoxy)phenylethylamine (5f)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.855 (1H, s), 7.663-7.626 (total 2H, m), 7.392-7.341 (total 3H, m), 6.741-6.610 (total 3H, m), 3.818 (3H, s), 3.676 (3H, s), 3.272-3.208 (total 1H, m), 2.895-2.800 (total 2H, m), 1.784-1.648 (total 2H, m), 1.367-1.166 (total 4H, m), 0.871 (3H, t, J = 6.96 Hz). Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.23; H, 8.52; N, 4.30.

***N*-(*p*-Chlorobenzylidene)-1-ethyl-2-phenylethylamine (8c)**

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.022 (1H, s), 7.589 (2H, d, J=8.43 Hz), 7.350 (2H, d, J=8.43 Hz), 7.320-7.160 (total 5H, m), 3.825 (1H, ddd, J=11.46, 6.97, 1.19 Hz), 3.752 (1H, ddd, J=11.46, 6.60, 1.10 Hz), 2.950-2.870 (1H, m), 1.920-1.800 (1H, m), 1.720-1.600 (1H, m), 0.871 (3H, t, J = 7.33 Hz). HRMS Calcd for C₁₇H₁₈NCl: 271.1128. Found: 271.1128.

Trifluoromethanesulfonic acid (TFSA)-Catalyzed Cyclization Reaction of *N*-Benzylidene-2-phenethylamines 1b-1f

A Typical Procedure (1b)

To 19.6 mL (220 mmol, 100 eq.) of ice-cooled TFSA was added 492.5 mg (2.2 mmol) of *N*-benzylidene-2-methyl-2-phenethylamine **1b** slowly, and the mixture was heated at 120°C for 19.5 h with stirring. Then, the reaction mixture was poured into 30 mL of ice-water, basified with 5N NaOH, and the whole was extracted with CH₂Cl₂. The organic phase was washed with brine, dried over Na₂SO₄, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica gel (eluent: *n*-hexane:CHCl₃:MeOH=2:1:0.05). Removal of the solvent afforded 4-methyl-1-phenyl-tetrahydroisoquinoline **2b** (a mixture of diastereomers, 375.2 mg, total 76% yield, *trans*:*cis* = 88:12 (evaluated from the ¹H NMR signal integration)). The *trans* isomer could be isolated by repeated recrystallization.

Trans isomer **2b**;

Mp 108.0-109.0 °C (recrystallized from *n*-hexane, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm) : 7.331-7.146 (7H, m, total), 7.031 (1H, d, J = 7.69 Hz), 6.735 (1H, d, J = 7.69 Hz), 5.110 (1H, s), 3.301 (1H, dd, J = 5.40, 12.0 Hz), 3.132-3.081 (1H, m), 2.769 (1H, dd, J = 8.06, 12.1 Hz), 1.329 (3H, d, J = 6.78 Hz). Anal. Calcd. for C₁₆H₁₇N: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.30; H, 7.85; N, 6.24.

NOE:

(and its enantiomer)

Cis isomer **2b'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.331-7.146 (7H, m, total), 7.031 (1H, d, J = 7.69 Hz), 6.735 (1H, d, J = 7.69 Hz), 5.077 (s, 1H), 3.217 (1H, dd, J = 4.40, 12.3 Hz), 2.964 (2H, dd, J = 3.20, 11.9 Hz), 1.435 (3H, d, J = 6.78 Hz).

NOE

(and its enantiomer)

4-Ethyl-1-phenyltetrahydroisoquinoline (**2c**)

The *trans* isomer was isolated by repeated recrystallization.

Trans isomer **2c**;

Mp; 88.0-89.1 °C (recrystallized from *n*-hexane, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.328-7.168 (7H, m), 7.035 (1H, t, J = 7.42 Hz), 6.754 (1H, d, J = 7.69 Hz), 5.095 (1H, s), 3.326-3.270 (1H, m), 2.870-2.833 (2H, m), 1.944-1.828 (1H, m), 1.690-1.634 (1H, m, overlap with H₂O), 1.008 (3H, t, J = 7.51 Hz). Anal. Calcd. for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.01; H, 8.21; N, 5.81.

Cis isomer **2c'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.328-7.168 (7H, m), 7.035 (1H, t, J = 7.42 Hz), 6.754 (1H, d, J = 7.69 Hz), 5.078 (1H, s), 3.175-3.169 (1H, m), 2.632-2.623 (2H, m), 1.944-1.828 (1H, m), 1.690-1.634 (1H, m, overlap with H₂O), 0.915 (3H, t, J = 6.96 Hz).

4-Buthyl-1-phenyltetrahydroisoquinoline (2d)

Trans isomer **2d**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.342-7.129 (7H, m), 7.032 (1H, t, J = 7.33 Hz), 6.741 (1H, d, J = 7.69 Hz), 5.096 (1H, s), 3.288 (1H, dd, J = 4.76, 12.09 Hz), 2.921-2.886 (1H, m), 2.838 (1H, dd, J = 6.41, 11.91 Hz), 1.874-1.825 (1H, m), 1.699-1.643 (1H, m, overlap with H₂O), 1.400-1.385 (4H, m), 0.935 (3H, t, J = 6.96 Hz).

Cis isomer **2d'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.342-7.129 (7H, m), 7.032 (1H, t, J = 7.33 Hz), 6.741 (1H, d, J = 7.69 Hz), 5.069 (1H, s), 3.288 (1H, dd, J = 4.76, 12.09 Hz), 3.163 (2H, d, J = 3.85 Hz), 2.710-2.699 (1H, m), 1.874-1.825 (1H, m), 1.699-1.643 (1H, m, overlap with H₂O), 1.400-1.385 (4H, m), 0.935 (3H, t, J = 6.96 Hz).

3-Ethyl-1-phenyltetrahydroisoquinoline (2e)

The diastereomers could be separated by column chromatography.

Trans isomer **2e**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.308-7.067 (8H, m), 6.912 (1H, d, J = 7.51 Hz), 5.254 (1H, s), 2.951-2.862 (2H, m), 2.618-2.548 (1H, m), 1.864 (1H, s), 1.490-1.418 (2H, m), 0.890 (3H, t, J = 7.51 Hz). MS *m/z*: 237 (M⁺). HRMS Calcd for C₁₇H₁₉N: 237.1517. Found: 237.1478.

NOE

(and its enantiomer)

Cis isomer **2e'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.341-7.262 (5H, m), 7.121-7.110 (2H, m), 7.001-6.971 (1H, m), 6.661 (1H, d, J = 7.51 Hz), 5.097 (1H, s), 3.027-2.959 (1H, m), 2.857 (1H, dd, J = 3.30, 15.8 Hz), 2.725 (1H, dd, J = 11.2, 16.1 Hz), 1.630-1.558 (2H, m), 1.018 (3H, t, J = 7.51 Hz). MS *m/z*: 237 (M⁺). HRMS Calcd for C₁₇H₁₉N: 237.1517. Found: 237.1524.

NOE

(and its enantiomer)

3-Buthyl-1-phenyltetrahydroisoquinoline (2f);

The diastereomers could be separated by column chromatography.

Trans isomer **2f**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.334-7.067 (8H, m), 6.909 (1H, d, J = 13.0 Hz), 5.249 (1H, s), 3.000-2.883 (2H, m), 2.592 (1H, dd, J = 9.34, 16.1 Hz), 1.434-1.378 (2H, m), 1.315-1.202 (4H, m), 0.848 (3H, t, J = 6.78 Hz).

MS *m/z*: 265 (M⁺). HRMS Calcd for C₁₉H₂₃N: 265.1830. Found: 265.1835.

Cis isomer **2f'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.351-7.253 (5H, m), 7.111 (2H, d, J = 3.85 Hz), 7.012-6.961 (1H, m), 6.659 (1H, d, J = 7.51 Hz), 5.094 (1H, s), 3.096-3.027 (1H, m), 2.842 (1H, dd, J = 3.66, 15.9 Hz), 2.735 (1H, dd, J = 10.6, 15.9 Hz), 1.591-1.537 (2H, m), 1.451-1.315 (4H, m), 0.920 (3H, t, J = 7.14 Hz). MS *m/z*: 265 (M⁺). HRMS Calcd for C₁₉H₂₁N: 265.1830. Found: 265.1855. Anal. Calcd. for C₁₉H₂₁N: C, 85.74; H, 8.75; N, 5.30. Found: C, 86.00; H, 8.87; N, 5.18.

4-Methyl-1-(p-chlorophenyl)tetrahydroisoquinoline (9b);

N-Mesylate of *trans* isomer **9b**;

Mp: 193.7-195.9 °C (recrystallized from n-hexane:CH₂Cl₂, colorless plates). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.320-7.223 (6H, m), 7.162 (1H, m), 6.913 (1H, d, J=7.70 Hz), 6.004(1H, s), 3.548 (1H, dd, J=12.46 Hz, 4.03 Hz), 3.445 (1H, dd, J=12.28 Hz, 3.67 Hz), 3.043-2.999 (1H, m), 2.423 (3H, s), 1.394 (3H, d, J=6.97 Hz). Anal. Calcd. for C₁₇H₁₈NO₂SCl: C, 60.80; H, 5.40; N, 4.17. Found: C, 60.72; H, 5.36; N, 4.35. HRMS: Calcd for C₁₇H₁₈NO₂SCl: 336.0825. Found: 36.0835.

N-Mesylate of *cis* isomer **9b'**;

Mp 113.0-117.7 °C (colorless solid). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.421 (1H, d, J=7.88 Hz), 7.341-7.163 (6H, m), 6.967 (1H, d, J=7.25 Hz), 6.039 (1H, s), 3.875-3.819 (1H, m), 3.229-3.184 (1H, m), 2.840 (1H, dd, J=14.30 Hz, 11.55 Hz), 2.635 (3H,s), 1.315 (3H, d, J=6.78 Hz). HRMS: Calcd for C₁₇H₁₈NO₂SCl: 336.0825. Found: 336.0825.

4-Ethyl-1-(p-chlorophenyl)tetrahydroisoquinoline (9c);

N-Mesylate of *trans* isomer **9c**;

Mp: 113.5-115.3 °C (recrystallized from methanol, colorless cubes). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.330-7.240 (6H, m), 7.150-7.110 (1H, m), 6.823 (1H, d, J=7.70 Hz), 6.039 (1H, s), 3.752 (1H, d, J=12.65 Hz), 3.415 (1H, dd, J=12.65 Hz, 3.12 Hz), 2.770-2.710 (1H, m), 2.344 (3H, s), 1.860-1.660 (2H, m), 1.078 (3H, t, J=7.33 Hz). Anal. Calcd. for C₁₈H₂₀NO₂SCl: C, 61.79; H, 5.76; N, 4.00. Found: C, 61.74; H, 5.73; N, 4.16. HRMS Calcd for C₁₇H₁₆NCl (M-SO₂CH₃-H): 269.0971. Found: 269.0970.

N-Mesylate of *cis* isomer **9c'**;

Colorless wax. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.412 (1H, d, J=7.88 Hz), 7.340-

7.270 (3H, m), 7.230-7.160 (3H, m), 7.004 (1H, d, $J=7.52$ Hz), 6.011 (1H, s), 3.902 (1H, dd, $J=14.30$ Hz, 6.78 Hz), 3.160-3.080 (1H, m), 2.918 (1H, dd, $J=14.30$ Hz, 11.36 Hz), 2.634 (3H, s), 2.050-1.950 (1H, m), 1.680-1.500 (2H, m), 0.908 (3H, t, $J=7.52$ Hz). HRMS Calcd for $C_{18}H_{20}NO_2SCl$: 349.0903. Found: 349.0907.

TFA-Catalyzed Cyclization Reaction of *N*-Benzyldene-2-(3',4'-dimethoxy)-phenethylamines **5b-5f**

A Typical procedure (**5b**)

To 7.8 mL (100 mmol, 100 eq.) of ice-cooled TFA was added 299.6 mg of *N*-benzyldene-2-methyl-2-(3',4'-dimethoxy)phenethylamine **5b** slowly and the reaction mixture was heated at reflux for 3 h with stirring. Then, the reaction mixture was poured into 20 mL of ice-water, basified with 5N NaOH, and extracted with CH_2Cl_2 . The organic phase was washed with brine, dried over Na_2SO_4 , and the solvent evaporated under reduced pressure to give a residue, which was column-chromatographed on silica gel (eluent n-hexane: $CHCl_3$:MeOH= 2:1:0.1). Removal of the solvent afforded 4-methyl-1-phenyl-(3',4'-dimethoxy)tetrahydroisoquinoline **6b** (a mixture of diastereomers, 272.1 mg, total 76% yield, *trans*:*cis* = 80:20 (estimated from the 1H NMR signal integration)).

Trans isomer **6b**;

1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.346-7.209 (5H, m), 6.768 (1H, s), 6.227 (1H, s), 5.050 (1H, s), 3.889 (3H, s), 3.628 (3H, s), 3.245 (1H, dd, $J = 5.13$ Hz, 12.3 Hz), 3.035-2.951 (1H, m), 2.713 (1H, dd, $J = 7.33$ Hz, 12.3 Hz), 1.309 (3H, d, $J = 6.96$ Hz).

Cis isomer **6b'**;

1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.346-7.209 (5H, m), 6.693 (1H, s), 5.016 (1H, s), 3.889 (3H, s), 3.628 (3H, s), 3.164 (1H, dd, $J = 7.88$ Hz, 12.3 Hz), 2.926-2.848 (2H, m), 1.399 (3H, d, $J = 6.78$ Hz).

4-Ethyl-1-phenyl-(3',4'-dimethoxy)tetrahydroisoquinoline (**6c**)

Trans isomer **6c**;

1H -NMR (400 MHz, $CDCl_3$) δ (ppm): 7.344-7.182 (5H, m), 6.753 (1H, s), 6.246 (1H, s), 5.030 (1H, s), 3.889 (3H, s), 3.640 (3H, s), 3.212 (1H, dd, $J = 4.95$, 12.5 Hz), 2.815 (1H, dd, $J = 5.86$, 12.5 Hz), 2.755-2.707 (1H, m), 1.909-1.774 (1H, m), 1.696-1.601 (1H, m), 1.011 (3H, t, $J = 7.51$ Hz).

NOE

Cis isomer **6c'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.344-7.182 (5H, m), 6.672 (1H, s), 6.212 (1H, s), 5.013 (1H, s), 3.880 (3H, s), 3.620 (3H, s), 3.127-3.117 (2H, m), 2.568-2.535 (1H, m), 1.909-1.774 (1H, m), 1.696-1.601 (1H, m), 1.407 (3H, t, J = 7.33 Hz).

NOE

4-Buthyl-1-phenyl-(3',4'-dimethoxy)tetrahydroisoquinoline (6d)

Trans isomer **6d**;

Mp 93.0-95.0 °C (recrystallized from *n*-hexane:CH₂Cl₂, colorless plates). ¹H-NMR (400 MHz, CDCl₃) δ (ppm) : 7.325-7.269 (3H, m), 7.188 (2H, d, J = 6.78 Hz), 6.745 (1H, s), 6.246 (1H, s), 5.045 (1H, s), 3.897 (3H, s), 3.643 (3H, s), 3.212-3.195 (1H, m), 2.811-2.787 (2H, m), 1.398-1.385 (4H, m), 0.882 (3H, t, J = 6.78 Hz). Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36; N, 4.30. Found: C, 74.23; H, 8.14; N, 4.40.

Cis isomer **6d'**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm) : 7.36-7.257 (5H, m), 6.659 (1H, s), 6.206 (1H, s), 5.015 (1H, s), 3.844 (3H, s), 3.619 (3H, s), 3.144-3.106 (2H, m), 2.645-2.612 (1H, m), 1.858-1.696 (2H, m), 1.479-1.330 (4H, m), 0.939 (3H, t, J = 6.96 Hz).

3-Ethyl-1-phenyl-(3',4'-dimethoxy)tetrahydroisoquinoline (6e)

The diastereomers could be separated by column chromatography.

Trans isomer **6e**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.343-7.204 (3H, m), 7.162 (2H, d, J = 8.24 Hz), 6.647 (1H, s), 6.382 (1H, s), 5.199 (1H, s), 3.883 (3H, s), 3.709 (3H, s), 2.876-2.816 (2H, m), 2.544 (1H, dd, J = 11.0, 17.0 Hz), 1.464 (2H, t, J = 7.14 Hz), 0.877 (3H, t, J = 7.51 Hz). MS *m/z*: 297 (M⁺). HRMS Calcd for C₁₉H₂₃N₂O₂: 297.1729. Found: 297.1700.

NOE

Cis isomer **6e'**;

Mp 59.0-60.0 °C (recrystallized from *n*-hexane:ether, colorless cubes). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.351-7.271 (5H, m), 6.608 (1H, s), 6.130 (1H, s), 5.071 (1H, s), 3.855 (3H, s), 3.575 (3H, s), 2.990-2.939 (1H, m), 2.803-2.699 (2H, m), 1.667-1.542 (2H, m, overlap with H₂O), 0.980 (3H, t, J = 7.33 Hz). Anal. Calcd. for C₁₉H₂₃NO₂: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.66; H, 7.91; N, 4.66.

NOE

(and its enantiomer)

3-Buthyl-1-phenyl-(3',4'-dimethoxy)tetrahydroisoquinoline (**6f**)

The diastereomers could be separated by column chromatography.

Trans isomer **6f**;

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.337-7.221 (3H, m), 7.158-7.137 (2H, m), 6.639 (1H, s), 6.386 (1H, s), 5.179 (1H, s), 3.883 (3H, s), 3.710 (3H, s), 2.921-2.886 (1H, m), 2.869-2.750 (1H, m), 2.523 (1H, dd, J = 9.53, 15.8 Hz), 1.422-1.209 (6H, m), 0.840 (3H, t, J = 6.96 Hz). MS *m/z*: 325 (M⁺). HRMS Calcd for C₂₁H₂₇NO₂: 325.2041. Found: 325.2027.

Cis isomer **6f'**;

Mp 80.5-81.5 °C (recrystallized from *n*-hexane:ether, colorless needles). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.366-7.264 (5H, m), 6.605 (1H, s), 6.614 (1H, s), 5.033 (1H, s), 3.854 (3H, s), 3.579 (3H, s), 3.055-2.986 (1H, m), 2.747 (1H, dd, J = 3.48, 15.6 Hz), 2.654 (1H, dd, J = 10.3, 15.0 Hz), 1.577-1.525 (2H, m), 1.444-1.312 (4H, m), 0.918 (3H, t, J = 6.96 Hz). Anal. Calcd. for C₂₁H₂₇NO₂·1/8H₂O: C, 76.97; H, 8.38; N, 4.27. Found: C, 76.83; H, 8.36; N, 4.29.

Detection of Acid-catalyzed Isomerization of the Cyclized Products

A Typical Procedure (**2'f**)

To 1.5 mL of ice-cooled TFSA (16.9 mmol, 400 eq.) was added 9.8 mg of **2f** (*trans* isomer, 0.04 mmol). The whole was heated at 120°C for 12h with stirring, and the whole was poured into 10 mL of ice-water, basified with 5N NaOH and extracted with CH₂Cl₂. The organic phase was washed with brine, dried over Na₂SO₄, and the solvent evaporated under reduced pressure to give 8.5 mg of residue which was used for the ¹H NMR measurement. Only the *trans* isomer was observed. See **Table 1S**.

Table 1S Detection of Acid-catalyzed Stereo Isomerizations

	Product				Acid	Conditions	<i>cis: trans</i>	<i>cis: trans</i>
	X ₁	X ₂	R ₂	R ₁			Initial	Final
2'b	H	H	Me	H	TFSA (100 eq)	120 °C, 12 hrs	67 : 33	66 : 34
2f	H	H	H	n-Bu	TFSA (400 eq)	120 °C, 12 hrs	0 : 100	0 : 100
6'd	OMe	OMe	n-Bu	H	TFA (300 eq)	90 °C, 3 hrs	85 : 15	88 : 12
6e	OMe	OMe	H	Et	TFA (300 eq)	90 °C, 3 hrs	12 : 88	12 : 88

Supporting Information

Figure 1S

Calculated Transition Structures of Cationic Cyclization of 2-Ethyl Substituted Imines

Activation barriers (after scaled ZPE corrections) for cyclization were shown in parentheses.

Coordinates of Calculated Structures

3a (*N*-monoprotonated 1a) (reactant)

Total electronic energy (a.u.) =

-631.5985274 (RHF/6-31G* (5d))

-635.7512043 (B3LYP/6-31G* (5d)//RHF/6-31G* (5d))

-635.9234934 (B3LYP/6-311++G** (5d)//RHF/6-31G* (5d))

Zero-point correction (kcal / mol) = 185.02047 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.308713 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 0 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-2.888758	-1.831797	.839888
2	6	0	-3.716237	-1.975774	-.259933
3	6	0	-4.017837	-.870621	-1.043369
4	6	0	-3.489635	.369360	-.729559
5	6	0	-2.652702	.526249	.372820
6	6	0	-2.359915	-.586772	1.153806
7	6	0	1.401830	1.410533	-.109316
8	7	0	.143847	1.216406	-.231529
9	6	0	-.903024	2.253223	-.250769
10	6	0	-2.048248	1.878928	.696211
11	6	0	2.435769	.403596	-.092682
12	6	0	3.753556	.849995	.032098
13	6	0	4.797096	-.056217	.051228
14	6	0	4.524389	-1.409952	-.052665
15	6	0	3.213187	-1.868437	-.175441
16	6	0	2.172672	-.970772	-.196091
17	1	0	-2.664843	-2.679244	1.461849
18	1	0	-4.132921	-2.936419	-.500340
19	1	0	-4.670385	-.973898	-1.890779
20	1	0	-3.745417	1.221648	-1.335666
21	1	0	-1.740784	-.480261	2.028595
22	1	0	1.710206	2.436476	-.009677
23	1	0	-.199353	.278674	-.323175
24	1	0	-1.256126	2.334724	-1.270175

25	1	0	-.445044	3.190796	.032386
26	1	0	-1.685382	1.894484	1.717808
27	1	0	-2.796815	2.659463	.613706
28	1	0	3.960497	1.902189	.112398
29	1	0	5.808972	.288520	.145984
30	1	0	5.332194	-2.117909	-.038019
31	1	0	3.017257	-2.920817	-.253758
32	1	0	1.168155	-1.342516	-.287788

TS1 of 3a

Total Energy (a.u.) =

-631.54632 (RHF/6-31G* (5d))

-635.7162167 (B3LYP/6-31G* (5d)//RHF/6-31G* (5d))

-635.8858349 (B3LYP/6-311++G** (5d)//RHF/6-31G*(5d))

Zero-point correction (kcal/mol) = 184.96093 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.307275 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 1 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.721638	2.055555	.314905
2	6	0	1.511406	2.506010	-.237973
3	6	0	.701459	1.612487	-.873920
4	6	0	1.026075	.222471	-.894099
5	6	0	2.307434	-.187654	-.426084
6	6	0	3.117198	.733358	.222432
7	6	0	.004428	-.588366	.528462
8	7	0	.349202	-1.896120	.524798
9	6	0	1.725066	-2.284613	.697206
10	6	0	2.611468	-1.647534	-.415580
11	6	0	-1.424844	-.258696	.258597
12	6	0	-2.065820	.639508	1.102853
13	6	0	-3.407569	.931888	.919271
14	6	0	-4.110012	.337425	-.115410
15	6	0	-3.471642	-.552124	-.969082

16	6	0	-2.134770	-.849513	-.783882
17	1	0	3.362054	2.759533	.814666
18	1	0	1.250173	3.545436	-.180682
19	1	0	-.215974	1.935715	-1.328203
20	1	0	.564703	-.367847	-1.665349
21	1	0	4.057566	.425257	.640124
22	1	0	.443031	-.022667	1.330542
23	1	0	-.223754	-2.508228	-.014772
24	1	0	1.790737	-3.362115	.665827
25	1	0	2.072911	-1.955504	1.668134
26	1	0	3.654231	-1.836364	-.194938
27	1	0	2.375115	-2.106790	-1.367972
28	1	0	-1.526392	1.102524	1.909752
29	1	0	-3.899766	1.618114	1.582741
30	1	0	-5.149600	.565646	-.259915
31	1	0	-4.014084	-1.009410	-1.775344
32	1	0	-1.654458	-1.531680	-1.464374

4a (reactant)

Total Energy (a.u.) = -631.7575039 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 192.98834 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.321716 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 0 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.747684	-.607883	1.625072
2	6	0	-4.368456	-1.432175	.704008
3	6	0	-4.208668	-1.196693	-.656777
4	6	0	-3.424426	-.144906	-1.094114
5	6	0	-2.793378	.693611	-.174777
6	6	0	-2.962296	.452936	1.187847
7	6	0	1.147679	-.384664	-.427306
8	7	0	.088279	.484333	.000977
9	6	0	-.553383	1.326721	-1.140245
10	6	0	-1.913044	1.831816	-.649816

11	6	0	2.453735	-.273604	-.120066
12	6	0	3.334802	-1.283982	-.681865
13	6	0	4.669539	-1.264281	-.424531
14	6	0	5.182181	-.246797	.393181
15	6	0	4.363000	.764968	.962533
16	6	0	3.035273	.760192	.719233
17	1	0	-3.889201	-.769386	2.677510
18	1	0	-4.988114	-2.242786	1.038943
19	1	0	-4.708520	-1.823083	-1.371950
20	1	0	-3.334446	.045070	-2.150207
21	1	0	-2.536592	1.126355	1.914291
22	1	0	.791844	-1.176097	-1.060786
23	1	0	.367664	1.103913	.747894
24	1	0	-.690782	-.069234	.377786
25	1	0	-.652804	.650873	-1.976064
26	1	0	.154718	2.107613	-1.373747
27	1	0	-1.772125	2.569948	.132899
28	1	0	-2.359109	2.353617	-1.489567
29	1	0	2.914108	-2.052544	-1.304478
30	1	0	5.324379	-2.008524	-.834475
31	1	0	6.237754	-.227832	.599748
32	1	0	4.810425	1.520193	1.579406
33	1	0	2.423612	1.530034	1.151689

TS2 of 4a

Total Energy (a.u.) = -631.7421975 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 193.31348 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.321065 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 1 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.721491	2.060329	-.453085
2	6	0	-1.623721	2.544274	.273864
3	6	0	-.893028	1.680209	1.045425

4	6	0	-1.220755	.305336	1.075562
5	6	0	-2.353667	-.162425	.374263
6	6	0	-3.077760	.720311	-.411757
7	6	0	.163910	-.629937	-.543295
8	7	0	-.283849	-2.019348	-.353138
9	6	0	-1.752805	-2.345159	-.624806
10	6	0	-2.650486	-1.638137	.387095
11	6	0	1.497321	-.288587	-.275306
12	6	0	2.008114	.857370	-.938342
13	6	0	3.319029	1.229341	-.772573
14	6	0	4.137806	.482480	.070888
15	6	0	3.651825	-.642768	.755609
16	6	0	2.350918	-1.024145	.592240
17	1	0	-3.303380	2.741928	-1.045894
18	1	0	-1.384582	3.590473	.246742
19	1	0	-.071527	2.039104	1.637305
20	1	0	-.786425	-.304394	1.850691
21	1	0	-3.933379	.379264	-.965333
22	1	0	-.369843	-.126424	-1.323185
23	1	0	-.042647	-2.344893	.573716
24	1	0	.275137	-2.586839	-.986087
25	1	0	-1.823972	-3.421489	-.563390
26	1	0	-1.945243	-2.031636	-1.640475
27	1	0	-3.676182	-1.839385	.104174
28	1	0	-2.505345	-2.059802	1.376196
29	1	0	1.367858	1.426948	-1.587048
30	1	0	3.711103	2.084217	-1.288916
31	1	0	5.163705	.772836	.204296
32	1	0	4.303018	-1.195041	1.405427
33	1	0	1.997380	-1.880381	1.139054

4a-product (sigma-complex)

Total Energy (a.u.) = -631.7922602 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 195.02915 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.323699 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 0 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.202546	-1.940732	-.158713
2	6	0	1.929091	-2.546145	-.086024
3	6	0	.853133	-1.764726	.142380
4	6	0	.973893	-.297341	.381101
5	6	0	2.357467	.260836	.235924
6	6	0	3.411800	-.551403	-.007599
7	6	0	-.083338	.497884	-.444112
8	7	0	.106769	1.983338	-.177886
9	6	0	1.488720	2.510935	-.433046
10	6	0	2.498256	1.747381	.420881
11	6	0	-1.524273	.130502	-.182335
12	6	0	-2.053414	.139504	1.109807
13	6	0	-3.386731	-.161543	1.313661
14	6	0	-4.200098	-.479371	.232039
15	6	0	-3.679712	-.493811	-1.050804
16	6	0	-2.343080	-.187001	-1.259771
17	1	0	4.058556	-2.566069	-.345547
18	1	0	1.833537	-3.606557	-.218390
19	1	0	-.131608	-2.191349	.198333
20	1	0	.727398	-.181611	1.443198
21	1	0	4.409244	-.162506	-.088286
22	1	0	.141102	.380549	-1.495453
23	1	0	-.184620	2.197489	.767433
24	1	0	-.557985	2.474347	-.764356
25	1	0	1.490425	3.565141	-.197557
26	1	0	1.680109	2.389607	-1.490081
27	1	0	3.495559	2.076083	.161072
28	1	0	2.352321	1.985072	1.472916
29	1	0	-1.443673	.374863	1.967657
30	1	0	-3.791681	-.152012	2.308014
31	1	0	-5.235061	-.715388	.393842
32	1	0	-4.307068	-.740328	-1.886434
33	1	0	-1.949495	-.200514	-2.261494

7a (reactant)

Total Energy (a.u.) = -859.3554607 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 229.15347 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.384197 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 0 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-2.114139	-.566986	.591139
2	6	0	-3.070315	-.312386	-.404383
3	6	0	-3.170496	.969373	-.919976
4	6	0	-2.328096	1.982005	-.475022
5	6	0	-1.375693	1.741756	.497447
6	6	0	-1.295476	.452194	1.029060
7	6	0	2.735481	1.434574	-.050335
8	7	0	1.479776	1.651281	-.152409
9	6	0	.795172	2.947378	-.006493
10	6	0	-.405078	2.817172	.940544
11	6	0	3.402293	.159953	-.173687
12	6	0	4.797950	.164884	-.112163
13	6	0	5.504029	-1.017223	-.229623
14	6	0	4.815450	-2.206847	-.401148
15	6	0	3.422685	-2.225946	-.455825
16	6	0	2.715969	-1.051950	-.344262
17	8	0	-1.936680	-1.808977	1.092856
18	8	0	-3.820497	-1.353686	-.784251
19	6	0	-2.919741	-2.280575	1.996942
20	6	0	-4.807834	-1.189146	-1.771672
21	1	0	-3.898520	1.195100	-1.673884
22	1	0	-2.435654	2.965501	-.898403
23	1	0	-.593169	.218726	1.811152
24	1	0	3.347595	2.297390	.146050
25	1	0	.867127	.879597	-.339315
26	1	0	.472163	3.253241	-.992813
27	1	0	1.516920	3.664019	.360757

28	1	0	-.046018	2.612969	1.943361
29	1	0	-.892852	3.785192	.969380
30	1	0	5.327832	1.090776	.023602
31	1	0	6.576332	-1.011572	-.185737
32	1	0	5.360241	-3.128458	-.489833
33	1	0	2.901617	-3.155785	-.581674
34	1	0	1.642064	-1.089192	-.376806
35	1	0	-3.884664	-2.352854	1.517325
36	1	0	-2.983884	-1.626563	2.859668
37	1	0	-2.595376	-3.260686	2.310748
38	1	0	-4.370925	-.873821	-2.712214
39	1	0	-5.559331	-.473449	-1.459082
40	1	0	-5.265480	-2.157166	-1.897516

TS3 of 7a

Total Energy (a.u.) = -859.312805 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 228.88272 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.382504 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 1 (RHF/6-31G* (5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.554496	-.275962	-.158666
2	6	0	-1.553939	-1.173217	-.668076
3	6	0	-.386351	-.663487	-1.107579
4	6	0	-.077889	.740063	-.994239
5	6	0	-1.130660	1.618248	-.581564
6	6	0	-2.318565	1.103136	-.114095
7	6	0	1.067953	.982426	.540456
8	7	0	1.289828	2.326188	.657593
9	6	0	.165234	3.216062	.768739
10	6	0	-.799418	3.067974	-.445555
11	6	0	2.264803	.117184	.319668
12	6	0	2.443043	-.995558	1.131775
13	6	0	3.561561	-1.799867	.980717
14	6	0	4.503507	-1.500663	.011417

15	6	0	4.327785	-.394415	-.808469
16	6	0	3.214234	.410243	-.656143
17	8	0	-3.652520	-.843496	.240851
18	8	0	-1.850841	-2.478192	-.794953
19	6	0	-4.772585	-.096311	.699552
20	6	0	-1.680178	-3.293666	.349967
21	1	0	.340118	-1.330357	-1.532027
22	1	0	.612738	1.126026	-1.723591
23	1	0	-3.074354	1.763823	.260951
24	1	0	.391010	.599114	1.284796
25	1	0	2.085387	2.682982	.174162
26	1	0	.527067	4.231777	.835744
27	1	0	-.375573	2.996187	1.681437
28	1	0	-1.686368	3.664760	-.274229
29	1	0	-.308592	3.436606	-1.338569
30	1	0	1.719989	-1.228893	1.892975
31	1	0	3.696489	-2.652212	1.620289
32	1	0	5.370110	-2.124092	-.107567
33	1	0	5.055196	-.162375	-1.563936
34	1	0	3.089781	1.256401	-1.309966
35	1	0	-5.117071	.576064	-.073411
36	1	0	-4.519633	.450390	1.597636
37	1	0	-5.532244	-.827313	.915781
38	1	0	-2.319295	-2.966334	1.159632
39	1	0	-.643916	-3.283374	.669502
40	1	0	-1.956967	-4.292125	.052621

7a-product (sigma-complex)

Total Energy (a.u.) = -859.3203136 (RHF/6-31G* (5d))

Zero-point correction (kcal/mol) = 229.73616 (RHF/6-31G* (5d))

Thermal correction to Enthalpy (a.u.) = 0.384099 (RHF/6-31G* (5d))

Number of Imaginary Frequencies = 0 (RHF/6-31G*(5d))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.662393	-.240143	-.176946

2	6	0	-1.625405	-1.211681	-.478729
3	6	0	-.389728	-.773113	-.721097
4	6	0	-.000902	.657751	-.653619
5	6	0	-1.127147	1.595152	-.396457
6	6	0	-2.380606	1.149998	-.140988
7	6	0	1.116356	.916451	.472123
8	7	0	1.443993	2.309305	.582656
9	6	0	.334113	3.205808	.768125
10	6	0	-.758507	3.041685	-.320199
11	8	0	-3.818859	-.735102	.040591
12	6	0	-4.986971	.052787	.310627
13	8	0	-1.983712	-2.499955	-.592078
14	6	0	-1.966251	-3.282154	.591914
15	6	0	2.352395	.072111	.230935
16	6	0	3.083944	.177968	-.948567
17	6	0	4.224411	-.582515	-1.141042
18	6	0	4.647027	-1.462836	-.156557
19	6	0	3.925659	-1.574831	1.019467
20	6	0	2.784515	-.810785	1.210927
21	1	0	.369741	-1.487362	-.978259
22	1	0	.461340	.934024	-1.597935
23	1	0	-3.167675	1.843797	.076244
24	1	0	.663941	.608433	1.407699
25	1	0	2.086539	2.615051	-.118711
26	1	0	.695554	4.224802	.765428
27	1	0	-.106870	3.024097	1.742686
28	1	0	-1.623019	3.655495	-.099436
29	1	0	-.355337	3.358709	-1.277705
30	1	0	-5.782466	-.662499	.419511
31	1	0	-5.184879	.710168	-.522257
32	1	0	-4.851837	.608341	1.226424
33	1	0	-2.265568	-4.275108	.299372
34	1	0	-2.663408	-2.893233	1.323435
35	1	0	-.967697	-3.308740	1.011364
36	1	0	2.778053	.856815	-1.726934
37	1	0	4.781377	-.487712	-2.054991
38	1	0	5.532191	-2.053069	-.305717
39	1	0	4.250472	-2.250180	1.789466

40	1	0	2.239126	-.896430	2.134121
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