Experimental

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded on a Shimadzu FTIR-8100 spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on VARIAN VXR-200, JEOL JNM-EX 270, JEOL JNM-AL 300 and JEOL JNM-LA 500 spectrometers with TMS or $CHCl_3$ as the internal standard. E. Merck silica gel 60 (70-230 mesh ASTM) and Fuji Silysia Chemical silica gel BW-300 were used for column chromatography and flash column chromatography. Anhydrous CH_2Cl_2 was distilled from P_2O_5. Anhydrous THF was distilled from sodium/benzophenone under nitrogen. The assignment of stereochemistry of the cyclization product was based on NOE difference. Cis-trans (or exo-endo) ratios were determined from the integration in the ^1H NMR spectra of the diastereomeric mixture.

General procedure for the preparation of allyl ether 1a-I and allyl amine 1k-l:

Under nitrogen atmosphere, the allyl alcohol or amine (7.52 mmol) was added to a solution of the olefin (3.76 mmol) in dry CH_2Cl_2 (25 ml) at room temperature. After 5 min, the reaction mixture was cooled to –78°C, added N-iodosuccinimide (5.64 mmol) and allowed to reach 0°C in about 1-6 h. To the reaction mixture, a saturated aqueous solution of $Na_2S_2O_3$ was added, and stirred vigorously for 5 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silicagel using hexane/Et_2O (20:1-1:1) to give the products **1a-i, k and l**.

2-iodo-1-(4-methoxyphenyl)-1-prop-2-enyloxyethane (1a)

Obtained in 98% as colorless oil: ^1H NMR ($CDCl_3$) δ: 3.27-3.41 (m, 2H), 3.81 (s, 3H), 3.81 (dd, 1H, J = 12.5, 5.0 Hz), 3.98 (dd, 1H, J = 12.5, 5.0 Hz), 4.43 (dd, 1H, J = 8.0, 5.0 Hz), 5.18 (dd, 1H, J = 10.0, 1.0 Hz), 5.27 (dd, 1H, J = 17.0, 1.0 Hz), 5.85-5.98 (m, 1H), 6.89 (d, 2H, J = 9.0 Hz), 7.24 (d, 2H, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 10.9, 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 134.4, 159.6. HRMS (EI) Calcd for $C_{12}H_{15}O_2I$ (M^+): 318.0117. Found: 318.0113. Anal. Calcd for $C_{12}H_{15}O_2I$: C, 45.30; H, 4.75; I, 39.89.

Found: C, 45.50; H, 4.74; I, 39.73.

1-but-2-enyloxy-2-iodo-1-(4-methoxyphenyl)ethane (1b)

Obtained in 86% as colorless oil: ^{1}H NMR ($CDCl_3$) δ: 1.70 (d, 3H, J = 6.0 Hz), 3.26-3.40 (m, 2H), 3.82 (s, 3H), 3.72-3.98 (m, 2H), 4.41 (dd, 1H, J = 8.0, 5.0 Hz), 5.53-5.71 (m, 2H), 6.85-6.92 (m, 2H), 7.22-7.25 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.1, 17.8, 55.2, 69.7, 80.3, 114.0, 127.2, 127.9, 129.9, 132.1, 159.5. HRMS (EI) Calcd for $C_{13}H_{17}O_2I$ (M^+): 332.0273. Found: 332.0268.

2-iodo-1-(3-methylbut-2-enyloxy)1-(4-methoxyphenyl)ethane (1c)

Obtained in 99% as colorless oil: ^{1}H NMR ($CDCl_3$) δ: 1.57 (s, 3H), 1.74 (s, 3H), 3.25-3.39 (m, 2H), 3.81 (s, 3H), 3.87 (t, 2H, J = 8.5 Hz), 4.40 (dd, 1H, J = 8.0, 5.0 Hz), 5.38 (t, 1H, J = 6.0 Hz), 6.89 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 11.2, 18.1, 25.8, 55.3, 65.5, 80.5, 114.0, 120.6, 127.9, 132.3, 137.9, 159.6. HRMS (EI) Calcd for $C_{14}H_{19}O_2I$ (M^+): 346.0430. Found: 346.0432.

2-iodo-1-(4-methoxyphenyl)-1-(2-methylprop-2-enyloxy)ethane (1d)

Obtained in 70% as colorless oil: ^{1}H NMR ($CDCl_3$) δ: 1.79 (s, 3H), 3.27-3.42 (m, 2H), 3.69 (d, 1H, J = 12.5 Hz), 3.82 (s, 3H), 3.86 (d, 1H, J = 12.5 Hz), 4.40 (dd, 1H, J = 8.5, 4.5 Hz), 4.90 (s, 1H), 4.95 (s, 1H), 6.90 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 10.8, 19.9, 55.3, 72.9, 80.3, 112.9, 114.0, 127.9, 132.0, 141.8, 159.6. HRMS (EI) Calcd for $C_{13}H_{17}O_2I$ (M^+): 332.0273. Found: 332.0292.

1-cyclohex-2-enyloxy-2-iodo-1-(4-methoxyphenyl)ethane (1e)

Obtained in 75% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) δ: 1.39-1.75 (m, 3H), 1.87-2.13 (m, 3H), 3.25-3.35 (m, 2H), 3.81 (s, 3H), 3.68-3.76, 3.82-3.93 (each m, total 1H), 4.52-4.57 (m, 1H), 5.56-5.59, 5.84-5.87 (each m, total 1H), 5.87-5.89 (m, 1H), 6.89 (d, 2H, J = 8.5 Hz), 7.28 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 11.7. 12.0, 18.8, 19.3, 25.2, 27.2, 29.6, 55.3, 70.4, 72.5, 79.5, 79.9, 113.9, 114.0, 127.2, 127.6, 127.7, 127.8, 131.0, 131.5, 133.1, 133.4, 159.4. HRMS (EI) Calcd for $C_{15}H_{19}O_2I$ (M^+): 358.0430. Found: 358.0436.

ethyl 4-[2-iodo-1-(4-methoxyphenyl)ethoxy]but-2-enoate (1f)

Obtained in 56% as colorless oil: IR (KBr) cm^{-1}: 1717. ^1H NMR ($CDCl_3$) δ: 1.30 (t, 3H, *J* = 7.0 Hz), 3.31 (dd, 1H, *J* = 10.0, 5.0 Hz), 3.39 (dd, 1H, *J* = 10.0, 8.5 Hz), 3.82 (s, 3H), 3.96-4.12 (m, 2H), 4.21 (q, 2H, *J* = 7.0 Hz), 4.43 (dd, 1H, *J* = 8.5, 4.5 Hz), 6.19 (td, 1H, *J* = 15.5, 2.0 Hz), 6.90 (d, 2H, *J* = 8.5 Hz), 6.92 (td, 1H, *J* = 15.5, 4.0 Hz), 7.23 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 10.3, 14.3, 55.3, 60.4, 67.5, 81.5, 114.2, 121.5, 127.8, 131.3, 143.8, 159.8, 166.3. HRMS (EI) Calcd for $C_{15}H_{19}O_4I$ (M^+): 390.0328. Found: 390.0323.

2-iodo-1-phenyl-1-prop-2-enyloxyethane (1g)[1]

Obtained in 14% as colorless oil: ^1H NMR ($CDCl_3$) δ: 3.30-3.42 (m, 2H), 3.85 (dd, 1H, *J* = 12.5, 6.0 Hz), 3.99 (dd, 1H, *J* = 12.5, 5.5 Hz), 4.48 (dd, 1H, *J* = 8.0, 5.0 Hz), 5.20 (dd, 1H, *J* = 10.0, 1.5 Hz), 5.29 (dd, 1H, *J* = 17.0, 1.5 Hz), 5.88-5.94 (m, 1H), 7.30-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 10.6, 70.1, 80.9, 117.5, 126.6, 128.4, 128.7, 134.3, 140.0.

6-hex-2-enyloxy-5-iodooxane (1h)

Obtained in 98% as colorless oil: ^1H NMR ($CDCl_3$) δ: 0.91 (t, 3H, *J* = 7.0 Hz), 1.35-1.48 (m, 2H), 1.52-1.64 (m, 1H), 1.71-1.83 (m, 1H), 1.96-2.08 (m, 3H), 2.33-2.43 (m, 1H), 3.58 (ddd, 1H, *J* = 11.0, 7.0, 3.5 Hz), 3.95-4.03 (m, 2H), 4.08-4.14 (m, 1H), 4.20 (dd, 1H, *J* = 12.0, 5.5 Hz), 4.68 (d, 1H, *J* = 5.5 Hz), 5.52-5.61 (m, 1H), 5.69-5.78 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 13.7, 22.1, 25.5, 29.5, 32.7, 34.3, 63.4, 68.9, 101.2, 125.4, 135.3. HRMS (FAB) Calcd for $C_{11}H_{19}O_2NaI$ (M^++Na): 333.0327. Found: 333.0329.

1-butoxy-1-hex-2-enyloxy-2-iodoethane (1i)

Obtained in 99% as colorless oil: ^1H NMR ($CDCl_3$) δ: 0.91 (t, 3H, *J* = 7.5 Hz), 0.93 (t, 3H, *J* = 7.5 Hz), 1.35-1.47 (m, 4H), 1.53-1.63 (m, 2H), 2.03 (td, 2H, *J* = 7.0, 6.5 Hz), 3.23 (d, 2H, *J* = 5.5 Hz), 3.48 (td, 1H, *J* = 9.0, 6.5 Hz), 3.60 (td, 1H, *J* = 9.0, 6.5 Hz), 4.00 (ddd, 1H, *J* = 11.5, 6.5, 2.0 Hz), 4.10 (ddd, 1H, *J* = 11.5, 6.5, 2.0 Hz), 4.64 (t, 1H, *J* = 5.5 Hz), 5.53-5.60 (m, 1H), 5.68-5.75 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 5.5, 13.7, 13.9, 19.3, 22.2, 31.7, 34.3, 66.2, 67.4, 101.0, 125.7, 135.2. HRMS (FAB) Calcd for $C_{12}H_{23}O_2NaI$ (M^++Na): 349.0640. Found: 349.0648.

1-but-2-enyloxy-2-iodobenzene (1j)

Under nitrogen atmosphere, DEAD (40% solution in toluene, 2.16 ml, 4.77 mmol) was added to a mixture of 2-iodophenol (500 mg, 2.27 mmol), triphenylphosphine (1.25 g, 4.77 mmol) and crotyl alcohol (0.407 ml, 4.77 mmol) in dry THF (20 ml) and stirred at room temperature for 3 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography on silicagel using hexane/AcOEt (20:1) to give **1j** (615 mg, 99%) as colorless oil: ^1H NMR ($CDCl_3$) δ: 1.76 (d, 3H, J = 5.0 Hz), 4.52 (d, 2H, J = 4.0 Hz), 5.70-5.94 (m, 2H), 6.71 (d, 1H, J = 8.0 Hz), 6.87 (d, 1H, J = 8.0 Hz), 7.24-7.30 (m, 1H), 7.77 (d, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 17.9, 69.8, 86.8, 112.6, 122.5, 125.5, 129.3, 130.1, 139.5, 157.3. HRMS (EI) Calcd for $C_{10}H_{11}OI$ (M^+): 273.9855. Found: 273.9830.

[2-iodo-1-(4-methoxyphenyl)ethyl](methylsulfonyl)prop-2-enylamine (1k)

Obtained in 34% as colorless oil: IR (KBr) cm^{-1}: 1329, 1150. ^1H NMR ($CDCl_3$) δ: 2.79 (s, 3H), 3.64 (dd, 1H, J = 16.0, 7.0 Hz), 3.72-3.89 (m, 3H), 3.83 (s, 3H), 5.11 (t, 1H, J = 8.0 Hz), 5.18-5.28 (m, 2H), 5.72-5.85 (m, 1H), 6.92 (d, 2H, J = 8.5 Hz), 7.29 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 6.1, 41.1, 48.0, 55.3, 62.9, 114.1, 118.9, 127.8, 129.7, 134.7, 159.7. HRMS (EI) Calcd for $C_{13}H_{18}NO_3SI$ (M^+): 395.0052. Found: 395.0066. Anal. Calcd for $C_{13}H_{18}NO_3SI$: C, 39.50; H, 4.59; N, 3.54. Found: C, 39.62; H, 4.54; N, 3.51.

[2-iodo-1-(4-methoxyphenyl)ethyl][(4-methylphenyl)sulfonyl]prop-2-enylamine (1l)

Obtained in 30% as colorless columnar crystals: mp 104-105°C: IR (KBr) cm^{-1}: 1336, 1159. ^1H NMR ($CDCl_3$) δ: 2.44 (s, 3H), 3.35 (dd, 1H, J = 16.5, 8.0 Hz), 3.59-3.71 (m, 2H), 3.79 (s, 3H), 3.89 (dd, 1H, J = 16.5, 4.0 Hz), 5.05 (d, 2H, J = 12.0 Hz), 5.14 (dd, 1H, J = 10.5, 5.5 Hz), 5.58-5.72 (m, 1H), 6.80 (d, 2H, J = 8.5 Hz), 6.97 (d, 2H, J = 8.5 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.70 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 5.1, 21.6, 47.1, 55.2, 62.0, 113.8, 117.7, 126.8, 127.2, 129.7, 130.0, 135.8, 137.7, 143.5, 159.5.

HRMS (EI) Calcd for $C_{19}H_{22}NO_3SI$ (M^+): 471.0365. Found: 471.0377. Anal. Calcd for $C_{19}H_{22}NO_3SI$: C, 48.41; H, 4.70; N, 2.97. Found: C, 48.32; H, 4.69; N, 2.95.

General procedure for the preparation of tetrahydrofuran 2a-g, j-l and pyrrolidine 2h, i using VA-061:

VA-061 (37.6 mg, 0.15 mmol) was added to a solution of **1a-l** (0.30 mmol), CTAB (21.9 mg, 0.060 mmol) and aqueous EPHP (538 mg, 3.0 mmol; H_2O solution, 3 ml) in H_2O (3 ml) at room temperature. The reaction mixture was then stirred and heated to 80°C. The progress of the reaction was monitored by TLC. An additional amount of the initiator VA-061 (37.6 mg, 0.15 mmol) was added to the reaction mixture, when the reaction showed slow conversion. The reaction mixture was then extracted with AcOEt, and the organic layer was dried using Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silicagel using hexane/Et_2O (20:1-1:1) to give the products **2a-l** (64-99%).

1- methoxy-4-(4-methyl-2-oxolanyl)benzene (2a)

Obtained in 98% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *trans*-**2a** δ: 1.09 (d, 3H, J = 6.5 Hz), 1.86-2.01 (m, 2H), 2.37-2.54 (m, 1H), 3.44 (dd, 1H, J = 8.0, 7.0 Hz), 3.79 (s, 3H), 4.20 (dd, 1H, J = 8.0, 7.0 Hz), 4.97 (t, 1H, J = 7.0 Hz), 6.86 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2a** δ: 17.8, 33.3, 42.6, 55.3, 75.6, 79.8, 113.6, 126.8, 135.8, 158.7. ^{1}H NMR ($CDCl_3$) *cis*-**2a** δ: 1.10 (d, 3H, J = 6.5 Hz), 1.38-1.49 (m, 1H), 2.37-2.54 (m, 2H), 3.56 (t, 1H, J = 8.0 Hz), 3.79 (s, 3H), 4.06 (t, 1H, J = 8.0 Hz), 4.85 (dd, 1H, J = 10.0, 5.5 Hz), 6.86 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2a** δ: 17.5, 34.9, 43.8, 55.3, 75.3, 81.4, 113.7, 127.0, 135.3, 158.8. HRMS (EI) Calcd for $C_{12}H_{16}O_2$ (M^+): 192.1150. Found: 192.1166.

4-(4-ethyl-2-oxolanyl)-1-methoxybenzene (2b)

Obtained in 88% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *trans*-**2b** δ: 0.93 (t, 3H, J = 7.5 Hz), 1.40-1.50 (m, 2H),

1.93-1.99 (m, 2H), 2.19-2.47 (m, 1H), 3.50 (t, 1H, J = 8.0 Hz), 3.79 (s, 3H), 4.21 (dd, 1H, J = 8.0, 7.0 Hz), 4.93 (t, 1H, J = 7.0 Hz), 6.86 (d, 2H, J = 8.5 Hz), 7.27 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2b** δ: 12.8, 26.4, 40.5, 40.8, 55.2, 73.9, 79.8, 113.6, 126.8, 135.9, 158.7. ^{1}H NMR ($CDCl_3$) *cis*-**2b** δ: 0.93 (t, 3H, J = 7.5 Hz), 1.40-1.50 (m, 3H), 2.19-2.47 (m, 2H), 3.64 (t, 1H, J = 7.5 Hz), 3.79 (s, 3H), 4.07 (t, 1H, J = 8.0 Hz), 4.83 (dd, 1H, J = 10.5, 5.5 Hz), 6.86 (d, 2H, J = 8.5 Hz), 7.27 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2b** δ: 12.9, 26.1, 41.7, 42.2, 55.2, 73.7, 81.2, 113.7, 127.0, 135.1, 158.8. HRMS (EI) Calcd for $C_{13}H_{18}O_2$ (M^+): 206.1307. Found: 206.1309.

1-methoxy-4-[4-(methylethyl)-2-oxolanyl]benzene (2c)

Obtained in 94% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *trans*-**2c** δ: 0.89-0.96 (m, 6H), 1.41-1.60 (m, 1H), 1.93-2.20 (m, 3H), 3.52 (t, 1H, J = 8.5 Hz), 3.80 (s, 3H), 4.21 (t, 1H, J = 7.0 Hz), 4.96 (t, 1H, J = 6.0 Hz), 6.87 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2c** δ: 21.6, 31.7, 39.1, 46.3, 55.2, 73.0, 80.2, 113.6, 126.7, 136.1, 158.6. ^{1}H NMR ($CDCl_3$) *cis*-**2c** δ: 0.89-0.96 (m, 6H), 1.41-1.60 (m, 2H), 1.93-2.20 (m, 1H), 2.31-2.40 (m, 1H), 3.71 (t, 1H, J = 8.5 Hz), 3.80 (s, 3H), 4.08 (t, 1H, J = 8.0 Hz), 4.84 (dd, 1H, J = 10.5, 5.5 Hz), 6.87 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2c** δ: 21.5, 32.1, 40.6, 48.1, 55.2, 72.7, 81.5, 113.7, 126.9, 135.1, 158.8. HRMS (EI) Calcd for $C_{14}H_{20}O_2$ (M^+): 220.1463. Found: 220.1463.

1-methoxy-4-(4,4-dimethyl-2-oxolanyl)benzene (2d)

Obtained in 86% as colorless oil: ^{1}H NMR ($CDCl_3$) δ: 1.14 (s, 3H), 1.19 (s, 3H), 1.67 (dd, 1H, J = 12.5, 9.5 Hz), 2.07 (dd, 1H, J = 12.5, 6.5 Hz), 3.63 (d, 1H, J = 8.0 Hz), 3.74 (d, 1H, J = 8.0 Hz), 3.79 (s, 3H), 4.98 (dd, 1H, J = 9.5, 6.5 Hz), 6.87 (d, 2H, J = 7.0 Hz), 7.27 (d, 2H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.5, 26.7, 40.1, 49.7, 55.2, 80.5, 80.8, 113.7, 126.9, 135.6, 158.7. HRMS (EI) Calcd for $C_{13}H_{18}O_2$ (M^+): 206.1307. Found: 206.1316.

1-methoxy-4-(7-oxabicyclo[4.3.0.]non-8-yl)benzene (2e)

Obtained in 94% as diastereomeric mixture. Further purification of the diastereomers

using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *endo*-**2e** δ: 1.22-1.79 (m, 7H), 1.86-2.30 (m, 4H), 3.80 (s, 3H), 4.23 (d, 1H, J = 3.5 Hz), 5.13 (t, 1H, J = 7.5 Hz), 6.84-6.89 (m, 2H), 7.24-7.33 (m, 2H). ^{1}H NMR ($CDCl_3$) *exo*-**2e** δ: 1.22-1.79 (m, 8H), 1.86-2.30 (m, 2H), 2.33-2.42 (m, 1H), 3.80 (s, 3H), 3.99 (d, 1H, J = 5.0 Hz), 4.90 (t, 1H, J = 7.5 Hz), 6.84-6.89 (m, 2H), 7.24-7.33 (m, 2H). ^{13}C NMR ($CDCl_3$) *endo+exo*-**2e** δ: 20.5, 21.5, 23.8, 24.1, 27.3, 28.5, 28.6, 28.9, 38.1, 38.7, 40.4, 41.9, 55.2, 77.8, 78.5, 79.3, 113.6, 113.7, 126.7, 126.9, 136.3, 137.3, 158.5, 158.6. HRMS (EI) Calcd for $C_{15}H_{20}O_2$ (M^+): 232.1463. Found: 232.1465.

ethyl 2-[4-(4-methoxyphenyl)-3-oxolanyl]acetate (2f)

Obtained in 96% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: IR (KBr) cm^{-1}: 1732. ^{1}H NMR ($CDCl_3$) *trans*-**2f** δ: 1.26 (t, 3H, J = 7.0 Hz), 1.97-2.12 (m, 2H), 2.45-2.56 (m, 2H), 2.72-2.85 (m, 1H), 3.55 (dd, 1H, J = 8.5, 7.0 Hz), 3.79 (s, 3H), 4.28 (dd, 1H, J = 8.5, 7.0 Hz), 4.94 (t, 1H, J = 7.0 Hz), 6.87 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2f** δ: 14.2, 35.4, 37.8, 40.2, 55.2, 60.5, 73.5, 79.6, 113.7, 126.8, 135.0, 158.8, 172.3. ^{1}H NMR ($CDCl_3$) *cis*-**2f** δ: 1.26 (t, 3H, J = 7.0 Hz), 1.43-1.55 (m, 1H), 2.45-2.56 (m, 3H), 2.72-2.85 (m, 1H), 3.68-3.74 (m, 1H), 3.79 (s, 3H), 4.10-4.18 (m, 1H), 4.84 (dd, 1H, J = 6.5, 6.0 Hz), 6.87 (d, 2H, J = 8.5 Hz), 7.24 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2f** δ: 14.2, 36.4, 38.1, 41.3, 55.2, 60.5, 73.1, 80.9, 113.7, 127.0, 135.0, 158.8, 172.3. HRMS (EI) Calcd for $C_{15}H_{20}O_4$ (M^+): 264.1361. Found: 264.1368.

3-methyl-5-phenyloxolane (2g)[2]

Obtained in 87% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *trans*-**2g** δ: 1.09 (d, 3H, J = 7.0 Hz), 1.90-2.05 (m, 2H), 2.37-2.49 (m, 1H), 3.47 (dd, 1H, J = 8.0, 7.0 Hz), 4.22 (dd, 1H, J = 8.0, 7.0 Hz), 5.03 (t, 1H, J = 7.0 Hz), 7.20-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$) *trans*-**2g** δ: 17.7, 33.2, 42.6, 75.7, 80.0, 125.5, 127.0, 128.2, 154.1. ^{1}H NMR ($CDCl_3$) *cis*-**2g** δ: 1.09 (d, 3H, J = 7.0 Hz), 1.45 (dd, 1H, J = 9.5, 2.0 Hz), 2.40-2.55 (m, 2H), 3.58 (t, 1H, J = 8.0 Hz), 4.09

(t, 1H, J = 8.0 Hz), 4.92 (dd, 1H, J = 9.5, 6.0 Hz), 7.20-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$) *cis*-**2g** δ: 17.3, 35.0, 43.9, 75.4, 81.6, 125.9, 127.0, 128.3, 154.1.

7-butyl-2,9-dioxabicyclo[4.3.0]nonane (2h)

Obtained in 98% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *endo*-**2h** δ: 0.90 (t, 3H, J = 7.0 Hz), 1.10-1.50 (m, 6H), 1.50-1.99 (m, 5H), 2.20-2.39 (m, 1H), 3.38-3.56 (m, 1H), 3.57-3.79 (m, 2H), 3.94 (t, 1H, J = 8.0 Hz), 5.28 (d, 1H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$) *endo*-**2h** δ: 14.0, 19.2, 22.9, 23.3, 26.7, 30.5, 36.5, 41.0, 61.0, 70.2, 102.1. ^{1}H NMR ($CDCl_3$) *exo*-**2h** δ: 0.90 (t, 3H, J = 7.0 Hz), 1.10-1.50 (m, 6H), 1.50-1.99 (m, 5H), 2.20-2.39 (m, 1H), 3.38-3.56 (m, 1H), 3.57-3.79 (m, 1H), 3.82-3.92 (m, 1H), 4.28 (t, 1H, J = 8.0 Hz), 4.99 (d, 1H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$) *exo*-**2h** δ: 14.0, 20.8, 22.4, 22.9, 30.8, 32.4, 37.8, 44.2, 64.5, 74.3, 102.2. HRMS (FAB) Calcd for $C_{14}H_{20}O_2$ (M^++H): 185.1542. Found: 185.1525.

3-butyl-5-butoxyoxolane (2i)[3]

Obtained in 99% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless oil: ^{1}H NMR ($CDCl_3$) *trans*-**2i** δ: 0.89 (t, 3H, J = 7.5 Hz), 0.92 (t, 3H, J = 7.5 Hz), 1.21-1.60 (m, 11H), 1.98-2.45 (m, 2H), 3.31-3.47 (m, 2H), 3.62-3.71 (m, 1H), 3.94 (t, 1H, J = 7.5 Hz), 5.10 (dd, 1H, J = 5.5, 3.0 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2i** δ: 13.9, 14.0, 19.4, 22.8, 30.9, 31.9, 32.8, 38.6, 39.1, 67.5, 71.9, 104.5. ^{1}H NMR ($CDCl_3$) *cis*-**2i** δ: 0.89 (t, 3H, J = 7.5 Hz), 0.92 (t, 3H, J = 7.5 Hz), 1.21-1.60 (m, 11H), 1.98-2.45 (m, 2H), 3.31-3.47 (m, 2H), 3.62-3.71 (m, 1H), 4.04 (t, 1H, J = 8.0 Hz), 5.10 (dd, 1H, J = 5.5, 3.0 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2i** δ: 13.9, 14.0, 19.4, 22.8, 30.7, 31.8, 33.7, 37.0, 39.3, 67.0, 72.6, 104.1.

3-ethyloxaindane (2j)[4]

Obtained in 64% as colorless oil: ^{1}H NMR ($CDCl_3$) δ: 0.99 (t, 3H, J = 7.5 Hz), 1.56-1.69 (m, 1H), 1.75-1.86 (m, 1H), 3.33-3.43 (m, 1H), 4.23 (dd, 1H, J = 9.0, 6.5 Hz), 4.64 (t, 1H, J = 9.0 Hz), 6.78-6.89 (m, 2H), 7.10-7.19 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.4, 27.6, 43.3, 76.5, 109.4, 120.2, 124.3, 128.0, 130.9, 159.9.

1-(methylsulfonyl)-4-methyl-2-(4-methoxyphenyl)pyrrolidine (2k)

Obtained in 98% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless needles: mp 105-106°C: IR (KBr) cm^{-1}: 1337, 1149. ^1H NMR ($CDCl_3$) *cis*-**2k** δ: 1.08 (d, 3H, *J* = 6.5 Hz), 1.55-1.67 (m, 1H), 2.24-2.38 (m, 1H), 2.44-2.58 (m, 1H), 2.54 (s, 3H), 3.04 (t, 1H, *J* = 10.5 Hz), 3.80 (s, 3H), 3.97 (dd, 1H, *J* = 10.5, 8.5 Hz), 4.77 (dd, 1H, *J* = 10.0, 7.0 Hz), 6.88 (d, 2H, *J* = 8.5 Hz), 7.28 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2k** δ: 16.4, 33.8, 39.2, 45.7, 55.2, 55.8, 63.9, 114.0, 128.0, 134.2, 159.0. ^1H NMR ($CDCl_3$) *trans*-**2k** δ: 1.09 (d, 3H, *J* = 6.5 Hz), 1.96-2.05 (m, 2H), 2.44-2.58 (m, 1H), 2.67 (s, 3H), 3.15 (t, 1H, *J* = 9.0 Hz), 3.70 (dd, 1H, *J* = 9.0, 6.5 Hz), 3.80 (s, 3H), 4.90 (dd, 1H, *J* = 6.5, 4.5 Hz), 6.88 (d, 2H, *J* = 8.5 Hz), 7.28 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2k** δ: 17.1, 31.7, 38.1, 43.8, 55.2, 55.5, 62.3, 113.9, 127.4, 134.9, 158.8. HRMS (EI) Calcd for $C_{13}H_{19}NO_3S$ (M^+): 269.1085. Found: 269.1091. Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.90. Found: C, 57.74; H, 6.96; N, 5.14; S, 11.80.

4-methyl-1-[(4-methylphenyl)sulfonyl]-2-(4-methoxyphenyl)pyrrolidine (2l)

Obtained in 88% as diastereomeric mixture. Further purification of the diastereomers using column chromatography was unsuccessful.

colorless needles: mp 103-104°C: IR (KBr) cm^{-1}: 1346, 1159. ^1H NMR ($CDCl_3$) *cis*-**2l** δ: 0.95 (d, 3H, *J* = 6.5 Hz), 1.41-1.52 (m, 1H), 1.77-1.87 (m, 1H), 2.29-2.36 (m, 1H), 2.41 (s, 3H), 3.07 (t, 1H, *J* = 11.0 Hz), 3.78-3.84 (m, 1H), 3.79 (s, 3H), 4.58 (dd, 1H, *J* = 9.5, 7.0 Hz), 6.81 (d, 2H, *J* = 8.0 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 7.59 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$) *cis*-**2l** δ: 16.5, 21.5, 33.2, 45.6, 55.3, 56.6, 64.2, 113.7, 127.4, 127.5, 129.5, 135.0, 135.7, 143.1, 158.7. ^1H NMR ($CDCl_3$) *trans*-**2l** δ: 0.87 (d, 3H, *J* = 6.5 Hz), 1.48-1.60 (m, 1H), 1.77-1.87 (m, 1H), 2.29-2.36 (m, 1H), 2.42 (s, 3H), 2.85 (t, 1H, *J* = 9.0 Hz), 3.72 (dd, 1H, *J* = 9.0, 7.0 Hz), 3.79 (s, 3H), 4.79 (dd, 1H, *J* = 8.0, 2.5 Hz), 6.83 (d, 2H, *J* = 8.0 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.66 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$) *trans*-**2l** δ: 16.9, 21.5, 31.3, 43.5, 55.3, 55.8, 62.7, 113.6, 127.2, 127.5, 129.5, 135.0, 135.5, 143.2, 158.6. HRMS (EI) Calcd for $C_{19}H_{23}NO_3S$ (M^+): 345.1398. Found: 345.1396. Anal. Calcd for

$C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05; S, 9.28. Found: C, 66.06; H, 6.72; N, 4.00; S, 9.21.

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