EXPERIMENTAL PROCEDURE

Materials and Methods

NMR spectra were recorded on a Varian XL 200 MHz Gemini Spectrometer. IR spectra were done in $CHCl_3$, using a Shimadzu IR 470 spectrometer. Manganese acetate dihydrate was purchased by Fluka Aldrich and used without further purification.

General procedure for the cyclization of enamides 3: to a solution of enamide **3** (1 mmol) in glacial acetic acid (5 ml), $Mn(OAc)_3$ dihydrate was added (536 mg, 2 mmoles) under an argon athmosphere. The reaction mixture was stirred at 70 °C until the brown colour disappeared; then it was cooled at room temperature and poured into water (50 ml). The resulting mixture was then extracted with CH_2Cl_2, the organic phase was washed with a saturated $NaHCO_3$ solution, then with water, and finally dried over Na_2SO_4. Removal of the solvent under reduced pressure and chromatographic separation on a silica gel column (light petroleum ether/Et_2O) afforded pure β-lactam **6**.

SUPPLEMENTARY MATERIAL

Compound 3a (3b) - oil

^{1}H NMR ($CDCl_3$) δ 1.61 (3 H, t, *J* = 7.2 Hz), 3.12 (1 H, d, *J* = 15.8 Hz), 3.26 (1 H, d, *J* = 15.8 Hz), 3.67 (3 H, s), 6.04 (1 H, q, *J* = 7.2 Hz), 6.21 (1 H, s), 6.90-7.50 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 17.09, 42.18, 52.08, 53.96, 122.85, 127.67-129.13, 137.43, 139.67, 140.63, 142.12, 165.71, 168.06.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3064, 2960, 1734, 1650, 1440, 1421, 1288, 1151, 1023.

Compound 3c - oil

^{1}H NMR ($CDCl_3$) δ 0.80-1.40 (5 H, m); 1.15 (3 H, d, *J* = 7.0 Hz, overlapped), 1.50-1.97 (6 H, m), 3.06 (1 H, d, *J* = 15.6 Hz), 3.39 (1 H, d, *J* = 15.6 Hz), 3.67 (3 H, s), 4.12 (1 H, quintuplet, *J* = 7.2 Hz), 6.38 (1 H, s), 7.15-7.50 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 16.02, 25.93, 26.131, 25.93, 26.131, 29.92, 30.07, 40.19, 42.48, 52.00, 58.98, 125.28, 128.00-129.40, 137.68, 140.65, 140.74, 165.86, 168.09.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3455, 3020, 2855, 1736, 1652, 1619, 1451, 1424, 1348, 1262, 1151, 704.

Compound 3d - oil

^{1}H NMR ($CDCl_3$) δ 1.65 (3 H, d, *J* = 7.0 Hz), 3.33 (2 H, s), 3.69 (3 H, s), 6.06 (1 H, s), 6.80-6.95 (5 H, m), 7.05-7.65 (10 H, m), 7.85 (2 H, m), 8.17-8.25 (1 H, m).

^{13}C NMR ($CDCl_3$) δ 16.96, 42.17, 50.36, 52.12, 122.60, 123.98, 124.81, 125, 18, 125.78, 126.49, 128.05-129.07, 132.01, 133.65, 134.88, 137.17, 140.45, 142.86, 165.89, 167.94.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3465, 3025, 1736, 1650, 1419, 1348, 1151.

Compound 3e - oil

^{1}H NMR ($CDCl_3$) δ 1.36 (3 H, d, *J* = 7.2 Hz), 3.24 (1 H, d, *J* = 15.6 Hz), 3.42 (1 H, d, *J* = 15.6 Hz), 3.68 (3 H, s), 3.70 (3 H, s), 4.56 (1 H, q, *J* = 7.4 Hz), 6.56 (1 H, s), 7.20-7.45 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 14.64, 41.83, 52.13, 56.27, 124.76, 127.79-129.49, 137.08, 139.93, 141.76, 166.84, 167.40, 171.37.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3430, 3030, 1739, 1664, 1621, 1447, 1415, 1344, 1109.

Compound 3f - oil

^{1}H NMR ($CDCl_3$) δ 3.15-3.40 (2 H, m), 3.22 (1 H, d, *J* = 15.6 Hz, overlapped), 3.46 (1 H, d, *J* = 15.6 Hz), 3.62 (3 H, s), 3.72 (3 H, s), 4.40 (1 H, dd, J_1 = 9.6 Hz, J_2 = 5.8 Hz), 6.08 (1 H, s), 6.70-6.83 (2 H, m), 7.10-7.42 (13 H, m).

^{13}C NMR ($CDCl_3$) δ 35.26, 41.86, 51.92, 52.30, 62.99, 125.59, 126.70-129.88, 136.75, 137.82, 138.40, 140.29, 166.64, 167.33, 169.70.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3410, 3030, 1739, 1668, 1446, 1413, 1345, 1167, 1028.

Compound 3g -oil

^{1}H NMR ($CDCl_3$) δ 3.30 (1 H, d, *J* = 15.8 Hz), 3.46 (1 H, d, *J* = 15.8 Hz), 3.70 (3 H, s), 3.71 (3 H, s), 5.99 (1 H, s), 6.54 (1 H, s), 6.76-6.80 (2 H, m), 7.05-7.40 (13 H, m).

^{13}C NMR ($CDCl_3$) δ 41.92, 52.26, 52.42, 63.05, 123.44, 127.50-130.15, 133.01, 136.76, 140.13, 143.42, 167.04, 167.44, 170.17.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3435, 3070, 1740, 1661, 1446, 1216, 1169.

Compound 3h -oil

^{1}H NMR ($CDCl_3$) δ 0.99 (3 H, d, *J* = 6.2 Hz), 1.02 (3 H, d, *J* = 6.2 Hz), 1.25 (3 H, t, *J* = 7.2 Hz), 2.41 (1 H, o, *J* = 9.4 Hz), 3.03 (1 H, d, *J* = 15.8 Hz), 3.36 (1 H, d, *J* = 15.8 Hz), 3.64 (3 H, s), 4.15 (2 H, qq, J_1 = 16.0 Hz, J_2 = 7.2 Hz), 4.75 (1 H, d, *J* = 9.4 Hz), 6.43 (1 H, s), 7.15-7.45 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 13.99, 18.94, 19.75, 27.57, 41.76, 52.00, 60.75, 64.39, 123.78, 126.44-129.25, 137.19, 140.37, 140.65, 166.19, 167.63, 169.54.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3430, 3025, 1734, 1659, 1450, 1418, 1348, 1208 1041.

Compound 3i – oil

^{1}H NMR ($CDCl_3$) δ 1.15 (9 H, s), 3.12, (1 H, d, *J* = 16.0 Hz), 3.41 (1 H, d, *J* = 16.0 Hz), 3.58 (3 H, s), 3.68 (3 H, s), 4.84 (1 H, s), 6.65 (1 H, s), 7.10- 7.35 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 27.94, 36.80, 42.27, 51.24, 52.12, 65.87, 126.44, 128.08- 129.55, 137.24, 138.84, 141.05, 166.60, 167.84, 169.04.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3460, 3025, 1739, 1663, 1446, 1418, 1346, 1251, 1154.

Compound 6a (oil, inseparable mixture)

6"a (6'b): ^{1}H NMR ($CDCl_3$) δ 1.64 (3 H, d, *J* = 7.0 Hz), 2.04 (3 H, s), 3.77 (1 H, d, *J* = 2.4 Hz), 3.82 (3H, s), 4.13 (1 H, q, *J* = 7.2 Hz), 5.47 (1 H, d, *J* = 2.4 Hz), 6.93-7.42 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 21.10, 21.96, 52.83, 57.10, 57.97, 59.93, 86.80, 126.05-129.46, 138.76, 139.83, 141.87, 162.53, 167.58, 168.36.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3070, 1756, 1740, 1499, 1456, 1377, 1316, 1251, 1014.

6'a (6''b): ^{1}H NMR ($CDCl_3$) δ 1.64 (3 H, d, *J* = 7.0 Hz), 2.11 (3 H, s), 3.68 (3 H, s), 3.87 (1 H, d, *J* = 2.4 Hz), 4.23 (1 H, q, *J* = 7.2 Hz), 5.11 (1 H, d, *J* = 2.4 Hz), 6.93-7.42 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 21.10, 22.33, 52.54, 56.44, 57.58, 58.17, 86.35, 126.05-129.46, 139.42, 140.14, 141.53, 162.48, 167.35, 169.19.

Compound 6c (oil, inseparable mixture)

6"c: ^{1}H NMR ($CDCl_3$) δ 1.15 (3 H, d, *J* = 6.6 Hz, overlapped), 0.65-1.38 (5 H, m), 1.58-1.92 (6 H, m), 2.13 (3 H, s), 2.59 (1 H, quintuplet, *J* = 6.6 Hz), 3.79 (3 H, s), 3.92 (1 H, d, *J* = 2.6 Hz), 5.35 (1 H, d, *J* = 2.6 Hz), 7.19-7.38 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 15.53, 22.09, 25.95, 26.22, 28.33, 29.83, 31.46, 40.92, 52.67, 56.93, 57.91, 58.69, 86.64, 127.27-129.59, 139.45, 140.37, 161.78, 167.66, 168.90.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3455, 3025, 2855, 1750, 1735, 1455, 1217.

6'c: ^{1}H NMR ($CDCl_3$) δ 1.28 (3 H, d, *J* = 7.2 Hz, overlapped), 0.65-1.38 (5 H, m), 1.58-1.92 (6 H, m), 2.15 (3 H, s), 2.81 (1 H, quintuplet, *J* = 7.2 Hz) 3.78 (3 H, s), 3.86 (1 H, d, *J* = 2.4 Hz), 5.41 (1 H, d, *J* = 2.4 Hz), 7.19-7.38 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 14.86, 22.09, 25.95, 26.22, 28.33, 29.83, 31.46, 42.19, 53.27, 56.68, 56.93, 59.03, 87.12, 127.27-129.59, 139.45, 139.99, 162.35, 167.66, 168.69.

Compound 6d (both oils, pure diastereomers)

6"d: ^{1}H NMR ($CDCl_3$) δ 1.81 (3 H, d, *J* = 7.0 Hz), 1.83 (3 H, s), 3.86 (3 H, s), 4.00 (1 H, d, *J* = 2.6 Hz), 5.05 (1 H, q, *J* = 7.0 Hz), 5.53 (1 H, d, *J* = 2.6 Hz), 6.91-7.98 (17 H, m).

^{13}C NMR ($CDCl_3$) δ 20.76, 22.28, 52.89, 54.48, 57.20, 60.92, 86.65, 122.33-128.99, 129.56, 133.47, 137.22, 138.73, 140.22, 163.34, 167.51, 169.44.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3415, 3065, 1757, 1651, 1454, 1379, 1322, 1014.

6'd: ^{1}H NMR ($CDCl_3$) δ 1.79 (3 H, d, *J* = 7.0 Hz), 2.00 (3 H, s), 3.76 (3 H, s), 3.99 (1 H, d, *J* = 2.6 Hz), 5.24 (1 H, d, *J* = 2.6 Hz), 5.31 (1 H, q, *J* = 7.0 Hz), 7.08-7.98 (17 H, m).

^{13}C NMR ($CDCl_3$) δ 20.87, 21.84, 52.67, 54.20, 56.36, 57.53, 86.23, 122.31-129.06, 129.84, 134.01, 136.61, 139.51, 140.31, 163.18, 167.53, 168.39.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3405, 3065, 2875, 1757, 1454, 1379, 1332, 1213, 1105.

Compound 6e (oil, inseparable mixture)

6"e: ^{1}H NMR ($CDCl_3$) δ 1.44 (3 H, d, *J* = 7.4 Hz), 2.16 (3 H, s), 3.47 (1 H, q, *J* = 7.0 Hz),3.72 (3 H, s), 3.75 (3 H, s), 3.94 (1 H, d, *J* = 2.8 Hz), 5.37 (1 H, d, *J* = 2.8 Hz), 7.15-7.38 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 15.81, 52.36, 52.89, 56.85, 58.90, 60.04, 86.04, 124.47-128.36, 139.38, 139.73, 166.93, 168.62, 169.77, 171.02.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3420, 3030, 1770, 1739, 1499, 1455, 1378, 1251, 1215, 1162, 1064, 1016.

6'e: ^{1}H NMR ($CDCl_3$) δ 1.58 (3 H, d, *J* = 7.4Hz), 2.13 (3 H, s), 3.67 (1 H, q, overlapped), 3.72 (3 H, s), 3.78 (3 H, s), 3.88 (1 H, d, *J* = 2.9 Hz), 5.47 (1 H, d, *J* = 2.9 Hz), 7.15-7.38 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 15.46, 52.61, 52.75, 54.86, 57.84, 60.04, 86.10, 124.47-128.36, 139.68, 139.73, 166.93, 169.09, 169.77, 171.02.

Compound 6f (both oils, pure diastereomers)

6"f: ^{1}H NMR ($CDCl_3$) δ 2.05 (3 H, s), 3.12-3.72 (3 H, m), 3.78 (3 H, s), 3.79 (3 H, s), 3.88 (1 H, d, *J* = 3.0 Hz), 5.27 (1 H, d, *J* = 3.0 Hz), 6.83-7.42 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 21.74, 35.77, 52.34, 52.67, 57.12, 57.79, 59.80, 62.05, 85.79, 127.01-129.97, 137.21, 138.70, 139.41, 164.63, 166.18, 168.93, 169.84.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3400, 3070, 2955, 1769, 1738, 1667, 1500, 1455, 1282, 1215, 1027.

6'f: ^{1}H NMR ($CDCl_3$) δ 2.16 (3 H, s), 3.13-3.54 (3 H, m), 3.66 (3 H, s), 3.73 (3 H, s), 4.10 (1 H, d, *J* = 2.8 Hz), 4.59 (1 H, d, *J* = 2.8 Hz), 7.13-7.42 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 21.96, 35.86, 52.42, 52.50, 57.13, 60.06, 61.87, 85.00, 126.16-129.39, 136.78, 139.89, 140.15, 161.87, 166.26, 168.95, 169.08.

IR($CHCl_3$) ν_{max} (cm^{-1}) 3400, 3070, 2960, 1762, 1738, 1499, 1454, 1378, 1277, 1251, 1215, 1173 1023.

Compound 6g (oil, inseparable mixture)

6"g: ^{1}H NMR ($CDCl_3$) δ 2.15 (3 H, s), 3.67 (3 H, s), 3.70 (3 H, s), 4.07 (1 H, d, *J* = 2.8 Hz), 4.58 (1 H, s), 5.15 (1 H, d, *J* = 2.8 Hz), 7.10-7.50 (15 H, m).

^{13}C NMR ($CDCl_3$) δ 21.94, 52.80, 57.29, 59.67, 62.00, 63.66, 85.54, 126.28-128.98, 134.31, 139.25, 139.98, 161.65, 166.82, 167.80, 168.62.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3450, 3070, 2960, 1772, 1741, 1500, 1456, 1377, 1311, 1251, 1216, 1011.

6'g: ^{1}H NMR ($CDCl_3$) δ 2.10 (3 H, d, *J* = 7.4 Hz), 3.75 (3 H, s), 3.88 (3 H, s), 3.90 (1 H, d, *J* = 3.0 Hz), 4.55 (1 H, s), 5.60 (1 H, d, *J* = 3.0 Hz), 7.28-7.36 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 21.94, 52.71, 57.27, 59.64, 60.61, 63.61, 86.55, 126.28-128.98, 133.77, 138.99, 139.45, 161.65, 166.82, 167.80, 168.62.

Compound 6h (oil, inseparable mixture)

6"h: ^{1}H NMR ($CDCl_3$) δ 0.89 (3 H, d, *J* = 6.6 Hz), 0.99 (3 H, d, *J* = 6.6 Hz), 1.32 (3 H, t, *J* = 7.2 Hz), 2.13 (3 H, s), 2.76 (1 H, m, overlapped), 3.30 (1 H, d, *J* = 9.8 Hz), 3.78 (3 H, s), 3.84 (1 H, d, *J* = 3.0 Hz), 4.25 (2 H, m), 5.37 (1 H, d, *J* = 3.0 Hz), 7.19-7.63 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 14.02, 19.79, 21.35, 28.81, 52.71, 56.87. 57.74, 61.48, 66.68, 68.63, 87.03, 124.59.-129.00, 139.18, 140.11, 164.13, 165.78, 168.79, 169.70.

IR ($CHCl_3$) ν_{max} (cm^{-1}) 3445, 3030, 1771, 1736, 1499, 1472, 1397, 1278, 1251, 1213, 1159, 1042.

6'h: ^{1}H NMR ($CDCl_3$) δ 0.92 (3 H, d, *J* = 6.6 Hz), 1.08 (3 H, d, *J* = 6.6 Hz), 1.30 (3 H, t, *J* = 7.2 Hz), 2.19 (3 H, s), 2.76 (1 H, m, overlapped), 3.11 (1 H, d, *J* = 9.8 Hz), 3.88 (3 H, s), 3.92 (1 H, d, *J* = 2.6 Hz), 4.25 (2 H, m), 5.43 (1 H, d, *J* = 2.6 Hz), 7.19-7.63 (10 H, m).

Compound 6i (oil, pure diastereomers)

6"i: ^{1}H NMR ($CDCl_3$) δ 1.05 (9 H, s), 2.15 (3 H, s), 3.11 (1 H, s), 3.74 (3 H, s), 3.80 (3 H, s), 4.10 (1 H, d, *J* = 3.0 Hz), 5.12 (1 H, d, *J* = 3.0 Hz), 7.26-7.35 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 22.10, 28.28, 34.07, 52.07, 52.74, 56.48, 59.29, 70.81, 86.44, 126.73-128.55, 139.60, 140.05, 162.69, 166.51, 168.88, 169.52.

6'i: ^{1}H NMR ($CDCl_3$) δ 1.06 (9 H, s), 2.18 (3 H, s), 3.18 (1 H, s), 3.60 (3 H, s), 3.79 (3 H, s), 4.11 (1 H, d, *J* = 2.6 Hz), 5.29 (1 H, d, *J* = 2.6 Hz), 7.19-7.34 (10 H, m).

^{13}C NMR ($CDCl_3$) δ 22.12, 28.03, 37.53, 51.78, 52.81, 57.13, 62.23, 68.68, 86.43, 126.62-128.50, 139.65, 140.44, 158.05, 167.79, 168.93, 169.02.

SEMIEMPIRICAL CALCULATIONS

Semiempirical molecular calculations were done in order to estimate the energy differences between the two cyclized radicals (**5'** and **5"**) and, especially, the two transition states leading to those diastereomeric intermediates. Indeed, the cyclization of radicals **4** is more likely to be under kinetic rather than thermodynamic control and therefore more reliable data on the product distribution can be obtained by calculating the activation energies of the two possible ring closures.

Semiempirical calculations on radicals **4a-b,f-h**, **5'a-b,f-h**, **5"a-b,f-h**, as well as the search for the reaction paths connecting **4** – **5'** and **4** – **5"**, were carried out with the *PC SPARTAN PRO V1.0.1* package. After a careful Montecarlo conformational search — many hundreds or even thousands of conformers were tested, for each structure, by MMFF94 molecular mechanics —, the geometries of the open-shell intermediates were fully optimized following the PM3

parameterization. A rough estimate of the transition-state geometries was then located by determining the maxima of the energy profiles for the ring opening of radicals **5'** and **5"**. The transition state geometries and energies were finally refined starting from the structures resultant from the previous step. Each transition state was characterized by a single imaginary vibrational frequency resulting from a negative force constant in the diagonal form of the Hessian; all of the transition states collapsed to the starting radicals when used as a starting point for equilibrium geometry optimization. Taking into account the very high number of degrees of freedom possessed by this kind of molecules — and thence the uncertainty of the calculated parameters — the energy values were rounded to integer numbers: indeed, the calculations reported here only aim at giving a qualitative indication of the preferred stereochemistry.

Table 1 reports the heath of formation for radicals **4a-b,f-h**, **5'a-b,f-h**, **5"a-b,f-h**, and for the respective transition states, together with their imaginary vibrational frequencies. Figure 1 shows the energy profile for ring closure of radical **4g** to **5'g** and **5"g**, with the geometries of the intermediates and the transition state.

First, we calculated the energies and geometries of the intermediates and transition states for cyclization of radicals **4a-b** to confirm that the configuration of the pre-existing chiral center has a fundamental influence upon the product diastereomeric ratio. As a matter of fact, the calculation fully reflected the enantiomeric relationship between the radical pairs **5'a**,**5"b** and **5'b**,**5"a**, yielding two energy profiles with identical shapes but opposite as far as the favored diastereoisomer is concerned. Although the calculated differences between the two diastereomeric intermediates **5'**,**5"** (ca. 2 kcal/mol) and the two corresponding transition states (ca. 2 kcal/mol) are large compared with the observed stereoselectivity, these data suggest an identical preference (both kinetic and thermodynamic) for radicals **5"a** and **5'b** for the cyclizations of **4a** and **4b**, respectively. They are therefore consistent with an identical but inverted diastereomeric ratio for products **6a** and **6b**, being **6"** the major isomer with **4a** and **6'** the favored diastereoisomer with **4b**. The calculated activation barriers confirm that the cyclization is not likely to be reversible, since the energy barrier for the reverse ring opening is quite large (22 kcal/mol *Vs ca.* 8 kcal/mol for the cyclization). However, the transition state geometries indicate that the reaction proceeds through a fairly late transition state, so that the stability of the cyclized radicals **5'** and **5"** substantially reflects the kinetically preferred pathway as well.

When the same calculations were performed on reaction **g** we obtained practically identical energies for the diastereomeric radicals **5'g** and **5"g** but a difference of about 1 kcal/mol between the two activation barriers. Interestingly, the kinetically-favored cyclized radical (**5"g**) is analogous to that arising from the predicted more favorable cyclization pathway of reaction **a** (with methyl

replaced by the ester moiety). By estimating the product distribution on the basis of the energy gap between the two transition states, we obtained a predicted **6”g**/**6’g** ratio of about 4, which is impressively totally consistent with the experimental datum.

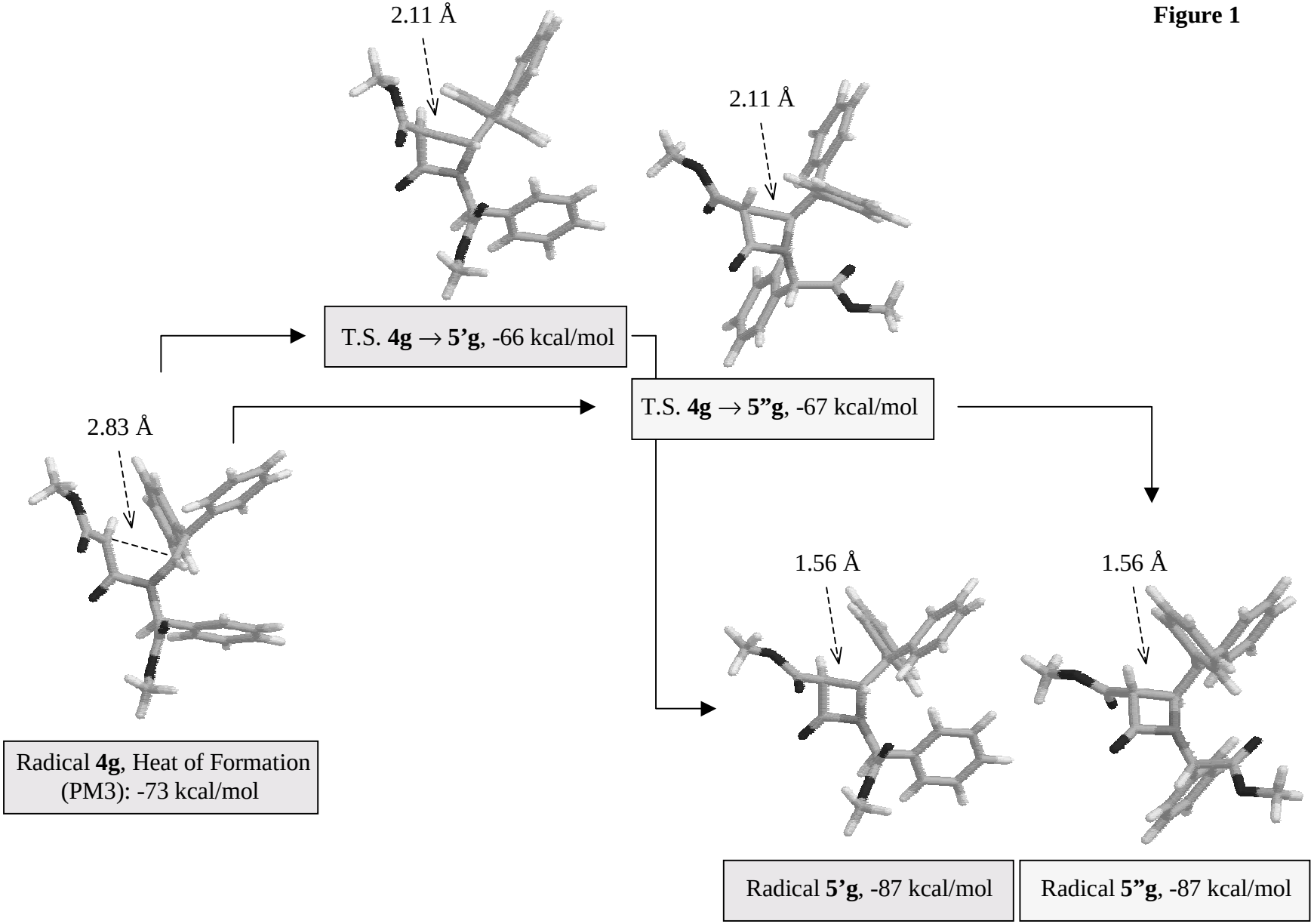
Analogous calculations for reactions **f** and **h** — whose intermediates are however more difficult to minimize due to very high number of degrees of freedom — led to less convincing results. For both reactions the pathway leading to radical **5”** was predicted to be the more favorable, either from a thermodynamic (**h**) or kinetic (**f**, **h**) point of view. Nevertheless, the barrier gap obtained for reaction **f** (3 kcal/mol) is not consistent with the observed absence of stereoselectivity, as well as that calculated for reaction **h** (4 kcal/mol) is too large compared to the experimental product ratio.

However, all of the calculations performed on analogous substrates (reactions **a**, **f**-**h**) clearly indicate that the preferred cyclization pathway is that leading to the *3R*,*4S*-radical (**5”**). Therefore, when a stereoselection is observed, the prevalent compound is suggested to be the diastereoisomer **6”**. With radical **4g**, whose structure is the easiest to minimize in the ester series (reaction **f**-**h**), a very good agreement with the experimental data was obtained.

Table 1

entry	**4** (Kcal/mol)	**5** (Kcal/mol)		TS **4** → **5** (Kcal/mol)	E_A (Kcal/mol)	ν (cm^{-1})
a	-2	**5'**	-15	7	9	615
		5"	-17	5	7	588
b	-2	**5'**	-17	5	7	589
		5"	-15	7	9	616
f	-76	**5'**	-89	-66	10	557
		5"	-89	-69	7	577
g	-73	**5'**	-87	-66	7	586
		5"	-87	-67	6	567
h	-121	**5'**	-133	-111	10	577
		5"	-137	-115	6	558

Figure 1


2.11 Å
2.11 Å
T.S. **4g** → **5'g**, -66 kcal/mol
T.S. **4g** → **5"g**, -67 kcal/mol
2.83 Å
1.56 Å
1.56 Å
Radical **4g**, Heat of Formation (PM3): -73 kcal/mol
Radical **5'g**, -87 kcal/mol
Radical **5"g**, -87 kcal/mol