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Supporting Information

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Dynamic Effects on [3,3] and [1,3] Shifts of 6-Methylenebicyclo[3.2.0]hept-2-ene

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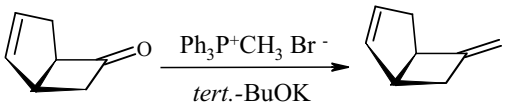
General Experimental Details

Reactions were carried out under Ar. The solvents used were purified by distillation over the appropriate drying agents and were transferred under Ar. Flash chromatography: Merck silica gel 60 (230-400 mesh). Gas chromatography (GC): a) analytical GC (AGC): Siemens Sichromat 2, Siemens Sichromat 3,Varian 3300, Perkin Elmer F22, Perkin Elmer Sigma 2B; integrations by LDC 308 Computing Integrator or by PC with the software Varian System Control V A2 and Chromstar 2.0; all recorders were Siemens-Kompensograph III; Carrier gas: Nitrogen or hydrogen; detector: FID; glass capillary columns were used and are given below; b) Preparative GC (PGC): Varian Aerograph 90-P, Varian Aerograph 920, Siemens RGC 202 Sichromat; recorders: Siemens-Kompensograph III; detector: thermal conductivity detector; carrier gas: Helium; packed glass columns (Chromosorb P 60-80 mesh) were used (n meters x 9 mm in diameter), details are given below; all retention times were measured from the point of injection to the maximum of the signal registered. IR spectra: Perkin Elmer spectrometers 257, 325, and PE 841. MS (EI, 70 eV): Varian Mat CH-5, CH-7. ^{1}H NMR spectra were recorded on: Varian NV 14, Bruker AM 400 (400 MHz); ^{2}H NMR: Bruker AM 400 (61.4 MHz); ^{13}C NMR: Bruker AM 400 (100.6 MHz). All NMR spectra were collected at 25° C, and chemical shifts δ (ppm) were indirectly referenced to residual solvent signals as internal standards. Assignments have been made on the basis of the results of DEPT, HMQC, HMBC, H,H-, and H,C-COSY experiments and by NOE difference spectra. Coupling constants J (Hz) given are absolute values of the apparent couplings. Elemental analyses: Micro analytical Laboratory *Ilse Beetz*, Kronach (Germany).

Preparation of Compounds

6-Methylenebicyclo[3.2.0]hept-2-ene (1) [1, 2]



4 **1**

(a) By *Wittig*-Reaction in Dimethylsulfoxide (DMSO). At a bath temperature of 70-75 °C and stirring for 1 h 12.2 g (0.29 mol) NaH, as a 55-60% suspension in oil, in DMSO (150 mL, distilled from CaH_2) reacted to the DMSO anion with hydrogen evolution. After cooling to room temperature 110.0 g (308 mmol) of methyltriphenylphosphonium bromide [3] in DMSO (300 mL) were injected into the grey-green solution. To the now orange-red solution after 10 min was added a solution of 10.0 g (92 mmol) of bicyclo[3.2.0]hept-2-en-6-one (**4**) [4] in DMSO (10 mL). Stirring was continued for 4.5 h at 70 °C. Then, volatile products were distilled under slight vacuum directly from the reaction flask into a flask kept at –78 °C. To remove co-distilled DMSO, H_2O (50 mL) was added, and the solution was extracted with n-pentane (4 x 30 mL). The combined organic phases were washed with H_2O (2 x 30 mL) and dried (Na_2SO_4). After evaporation of the solvent the residue was distilled in vacuo using a 10-cm-*Vigreux* column. Yield: 6.1 g (61%), b. p. 62-65 °C/ 90 mm.

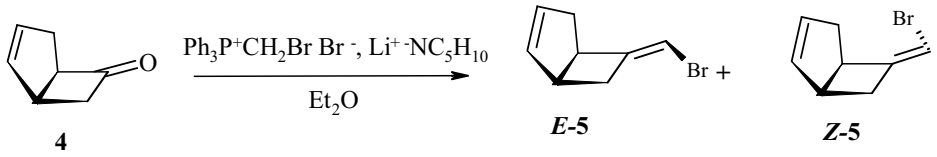
PGC (Carbowax 20 M, 20 % on Chromosorb W, 45-60 mesh, 20' x 3/8'', 90 °C, 65 mL He/ min, t_R (**1**) = 36 min) gave **1** of >99.9 % purity (AGC: capillary-column, OV 101, 50 m x 0.23 mm, 85 °C, t_R (**1**) = 500 s).

(b) By *Wittig*-Reaction in Diethyl ether. To 7.14 g (20.0 mmol) Methyltriphenylphosphonium bromide [3] in dry diethyl ether (25 mL) is added at room temperature with stirring 1.68 g (15.0 mmol) freshly sublimed potassium *tert.*-butanolate. The solution at once turns deep yellow. After 45 min 1.08 g (10.0 mmol) of ketone **4**[4] in diethyl ether (5 mL) is added. After 22 h of further stirring all volatiles are distilled from the reaction flask via a short path. Most of the solvent is distilled via a 10-cm-Vigreux-column, and the product is isolated and purified by PGC (20% OV 17 on Chromosorb P AW 60-80 mesh, 1.4 m x 9 mm, 87 °C, t_R (**1**) = 18 min). Yield: 0.85 g (80.5%) of 99.7% purity by AGC (glass capillary-column, OV 101, 50 m x 0.23 mm, 85 °C, t_R (**1**) = 500 s). IR spectrum: see [2]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.77 (m, 2 H, 2-H, 3-H), 4.88 (q, 1 H, 8*Z*-H, $J_{8Z,7n} \approx J_{8Z,7x} \approx J_{8Z,5} \approx$ 2.4-2.9*), 4.79 (q, 1 H, 8*E*-H, $J_{8E,7n} \approx J_{8E,7x} \approx J_{8E,5} \approx$ 1.7-2.7*), 3.48 (m, 1 H, 5-H), 3.26 (m, 1 H, 1-H), 2.95 (ddt, 1 H, 7x-H, part A of the AB system 7x-H/7n-H, $J_{7x,7n} \approx$ 15.5, $J_{7x,1} \approx$ 8.3, $J_{7x,8Z} \approx J_{7x,8E} \approx$ 2.8), 2.54 (ddq, 1 H, 4x-H, part A of the AB system 4x-H/4n-H, $J_d \approx$ 8.5, $J_q \approx$ 1.7, $J_{4x,4n} \approx$ 16.5), 2.38 [#] (dm, part B of the AB system 4x-H/4n-H, $J_d \approx$ 16.5), and 2.33 [#] (2 H) (dquin, 1 H, 7n-H, part B of the AB system 7x-H/7n-H, $J_{7n,7x} \approx$ 15.5, $J_{quin} \approx$ 2.2-2.9).

* $J_{8E,8Z} \approx 0$, this is seen from the ^{1}H NMR spectra of the isotopomers 8*E*-**1** and 8*Z*-**1**, here the signals of 8*Z*-H and of 8*E*-H are unchanged compared to those in **1**. [#] Signals partially overlap.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 155.53 (C_q, C-6), 133.53 (CH), 131.30 (CH) (C-2, C-3), 107.33 (CH_2, C-8), 45.48 (CH, C-5), 42.45 (CH, C-1), 39.45 (CH_2, C-4), 38.03 (CH_2, C-7).

(*Z*)- and (*E*)-6-Bromomethylenebicyclo[3.2.0]hept-2-ene (*Z*-5, *E*-5)



(a) By *Wittig*-Reaction in Diethyl ether. A lithium piperidide suspension in pentane was generated by slowly adding 22 mmol of n-butyl lithium (15% solution in pentane) to 1.9 g (22 mmol) dry piperidine. This suspension was added in 20 min to a slurry of 10.0 g (23 mmol) bromomethyltriphenylphosphonium bromide[5] in 150 mL diethyl ether (dist. from $LiAlH_4$) at –40 °C. After stirring for 20 min at room temperature, ketone **4**[4] (2.0 g, 18.5 mmol) was added, causing a slight increase in temperature. After 0.5 h of additional stirring the reaction was quenched by pouring it into water (30 mL). This solution was extracted with pentane (4 x 40 mL), and the combined extracts were washed with 40 mL each of 1N HCl, sat. $NaHCO_3$, and water, then dried with $MgSO_4$. After evaporation of the solvents, the residue was distilled via a short path in vacuo (10^{-2} mm) at a bath temperature up to 80 °C. Yield: 1.3 g (38%).

By PGC (Column 1: Carbowax 20 M, 20 % on Chromosorb W, 45-60 mesh, 20' x 3/8'', 130 °C, 65 mL He/min, t_R = 113 min, t_R = 122 min; column 2: Polypropylene glycol, 20 % on Chromosorb P, 60-80 mesh, 2 m x 3/8'', 133 °C, 70 mL He/ min, t_R = 97 min, t_R = 105 min) two fractions in a ratio 2:1 were isolated and identified to be ***Z*-5** and ***E*-5**, respectively.

(*Z*)- 6-Bromomethylenebicyclo[3.2.0]hept-2-ene (*Z*-5):

Diastereomeric purity: 99.9% (AGC: capillary-column, polypropylene glycol, 50 m x 0.25 mm, 120 °C, t_R (***Z*-5**) = 36 min)

IR (neat): 3050 (=CH), 2940, 2910, 2845, 1655 (C=C), 1609 (C=C), 1230, 712 cm^{-1}; MS (EI, 70 eV): *m/z* (%) 186 (6, M^+, ^{81}Br), 184 (6, M^+, ^{79}Br), 171 (3), 169 (3), 105 (100, $C_8H_9^+$), 79 (29),78 (18), 77 (28), 66 (79), 51 (21), 39 (30); ^1H NMR: see below.

(*E*)-6-Bromomethylenebicyclo[3.2.0]hept-2-ene (*E*-5):

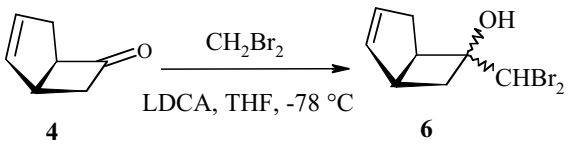
Diastereomeric purity: 99.0% (AGC: capillary-column, polypropylene glycol, 50 m x 0.25 mm, 120 °C, t_R (***E*-5**) = 38 min)

IR (neat): 3050 (=CH), 2945, 2910, 2845, 1660 (C=C), 1610 (C=C), 1250, 712 cm^{-1}; MS (EI, 70 eV): *m/z* (%) 186 (6, M^+, ^{81}Br), 184 (6, M^+, ^{79}Br), 171 (3), 169 (3), 105 (100, $C_8H_9^+$), 79 (27),78 (20), 77 (26), 66 (79), 51 (19), 39 (22); ^1H NMR: see below.

Anal. calcd. for C_8H_9Br: C, 51.90; H, 4.90. Found: C, 51.88; H, 4.86 (For a mixture of diastereomers).

(b) By a two step sequence from 4:

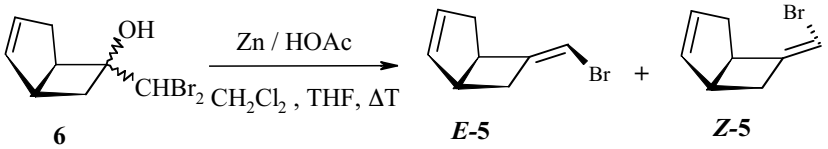
6-Dibromomethyl-bicyclo[3.2.0]hept-2-ene-6-ol (6)



Synthesis of **6** was carried out similar to a method reported previously.[6] Under nitrogen a solution of 4.05 g (37 mmol) ketone **4**[4] and 13.20 g (76 mmol) dibromomethane in 100 mL of dry THF was cooled to -78 °C. With stirring, a solution of lithium dicyclohexylamide, prepared from 13.80 g (75 mmol) dicyclohexylamine and 75 mmol n-butyl lithium (47.1 mL of a 1.6 M solution in hexane), in 100 mL THF was added drop wise. After stirring another h at -78 °C, the reaction mixture was poured into 200 mL 5% HCl, giving a white, voluminous solid. The reaction was extracted several times with Et_2O, and the

combined organic phases were washed with sat. $NaHCO_3$ (3 x 150 mL). The solution was dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. Crude product was chromatographed on silica gel using Et_2O as the eluent. Yield: 9.39 g (90%); m. p. 25-30 °C; purity: 96.1% (AGC: glass capillary, OV17, 17 m x 0.23 mm, 170 °C, t_R = 774 s); IR (neat): 3530 vs (O-H), 3046 s (=CH), 2934 vs, 2843 vs, 1739 w, 1604 w (C=C), 1424 s, 1345 vs, 1212 vs, 1155 vs, 1082 vs, 716 vs, 679 vs cm^{-1}; MS (EI, 70 eV): *m/z* (%) 243/241/239 (0.15/0.30/0.15, $C_5H_5OBr_2^+$), 203/201 (0.45/0.50, $C_8H_{10}OBr^+$), 185/183 (0.7/0.8, $C_8H_8Br^+$), 175/173 (1.1/1.3, $C_6H_6OBr^+$), 121 (12), 104 (5), 93 (6), 79 (11), 66 (100, $C_5H_6^+$), 39 (4); ^{13}C NMR (100.6 MHz, $CDCl_3$): 133.29 (CH, 3-C*), 132.50 (CH, 2-C*), 94.42 (weak, 6-C (?)), 57.98 (CH, 8-C), 44.78 (CH, 1-C or 5-C), 40.26 (CH_2, 7-C), 36.42 (CH, 5-C or 1-C), 32.90 (CH_2, 4-C); ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.83 (m), 5.79 (m), 5.76 (s) (3H, 3-H*, 2-H*, 8-H), 2.96 (m, 2H, 1-H, 5-H), 2.70 (dquin, 1 H, 4x-H, part A of the AB system 4x-H/4n-H, $J_{4x,4n} \approx 17.3$, $J_{quin} \approx 2.2$-2.9), 2.45 (m, 2 H, 4n-H, 7x-H, part B of the AB system 4x-H/4n-H, and part A of the AB system of 7x-H/7n-H), 2.22 (br s, 1 H, -OH), 1.87 (dd, 1 H, 7n-H, part B of the AB system of 7x-H/7n-H, $J_{7n,7x} \approx 13.5$, $J_{7n,1} \approx 2.8$). * interchangeable

b-2) (*Z*)- and (*E*)-6-Bromomethylenebicyclo[3.2.0]hept-2-ene (*Z*-5, *E*-5)



6 ***E*-5** ***Z*-5**

A solution of 8.65 g (30.7 mmol) **6**, 6.90 g (106 mmol) activated zinc dust, and 14.5 g (242 mmol) acetic acid in 180 mL CH_2Cl_2 were heated under reflux for 20 h. After cooling, excess zinc and salts were filtered, and the filtrate was washed with H_2O (150 mL), sat. $NaHCO_3$ solution (2 x 150 mL), and H_2O (150 mL). After drying over $MgSO_4$, evaporation of the solvent in vacuo, the crude product was chromatographed on silica gel using n-pentane as the eluent. Yield: 2.22 g (39 %) of ***Z*-5** and ***E*-5** (1.3:1.0).

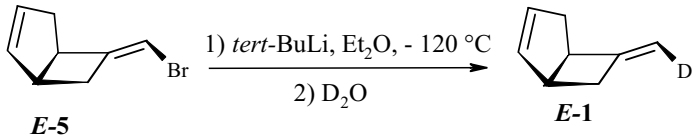
Further purification of the product was achieved by PGC: First, both diastereomers were collected in one fraction (Column: OV 101, 20 % on Chromosorb P, 60/80 mesh, 1.6 m x 9 mm, 110 °C, 65 mL He/min, t_R = 20 min) with a purity of >99.5% (AGC: glass capillary-column, OV 17, 17 m x 0.23 mm, 120 °C, t_R (***Z*-5**) = 512 s, t_R (***E*-5**) = 556 s). Then, separation of diastereomers was performed (Column: Carbowax 20M, 20% + 5% KOH on Chromosorb P, 60/80 mesh, 4 m x 9 mm, 110 °C, 85 mL He/min, t_R (***Z*-5**) = 140 min, t_R (***E*-5**) = 160 min).

***Z*-5**: Diastereomeric purity by AGC (see above): 99.1% (0.9% ***E*-5**); IR (neat): 3050 s (=CH), 2939 vs, 2910, 2848 vs, 1652 m (C=C), 1605 w (C=C), 1262 s, 1232 vs, 928 s, 801 s, 733 s, 714 vs, 687 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.76 (m, 3 H, 2-H, 3-H, 8*E*H), 3.46 (m, 1H, 5-H), 3.32 (m, 1 H, 1-H), 2.85* (ddd, 7x-H, part A of the AB system 7x-H/7n-H, $J_{7x,7n} \approx 15.8$, $J_{7x,1} \approx 8.3$, $J_{7x,8E} \approx 2.2$), and 2.80* (2H) (ddq, 4n-H$^{\#}$, part A of the AB system 4n-H/4x-H, $J_{4n,4x} \approx 17.1$, $J_d \approx 3.5$, $J_q \approx 2.0$), 2.55 (ddq, 4x-H$^{\#}$, part B of the AB system 4n-H/4x-H, $J_{4x,4n} \approx 17.1$, $J_d \approx 9.3$, $J_q \approx 2.1$), 2.30 (ddq, 1 H, 7n-H, part B of the AB system of 7x-H/7n-H, $J_{7n,7x} \approx 15.8$, $J_d \approx 3.4$, $J_q \approx 2.0$). * Signals partially overlap, $^{\#}$ interchangeable.

***E*-5**: Diastereomeric purity by AGC (see above): 98.2% (1.8% ***Z*-5**) ;IR (neat): 3051 s (=CH), 2942 vs, 2913 vs, 2842 s, 1655 s (C=C), 1604 w (C=C), 1440 w, 1413 m, 1346 m, 1248 vs, 1208 s, 971 m, 928 m, 742 s, 709 vs, 685 s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.93 (q, 1 H, 8*Z*-H, $J_{8Z,7n} \approx J_{8Z,7x} \approx J_{8Z,5} \approx 2.5$), 5.77 (dq, 1 H, 2-H$^{\#}$, $J_d \approx 5.6$, $J_q \approx 2.2$), 5.73 (dq, 1 H, 3-H$^{\#}$, $J_d \approx 5.6$, $J_q \approx 1.5$), 3.43 (tm, 1H, 5-H, $J_t \approx 7.7$), 3.28 (m, 1 H, 1-H), 2.80 (ddd, 7x-H, part A of the AB system 7x-H/7n-H, $J_{7x,7n} \approx 16.4$, $J_{7x,1} \approx 8.3$, $J_{7x,8Z} \approx 2.9$), 2.56 (ddq, 4n-H$^{\#\#}$, part A of the AB system 4n-H/4x-H, $J_{4n,4x} \approx 16.9$, $J_d \approx 8.4$, $J_q \approx$ 1.9-2.2), 2.38* (dm, 4x-H$^{\#\#}$, part B of the AB system 4n-H/4x-H, $J_{4x,4n} \approx 16.9$), and 2.32* (dq, 1 H, 7n-H, part B of the AB system of 7x-H/7n-H, $J_{7n,7x} \approx 16.4$, $J_{7n,1} \approx J_{7n,5} \approx J_{7n,8Z} \approx 2.9$). * Signals partially overlap, $^{\#}$ interchangeable,

[##] interchangeable.

8*E*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (*E*-1)



***E*-5** ***E*-1**

In a three-necked flask under argon, diethyl ether (8 mL) and *tert*-butyl lithium (5.1 mmol) (3.4 mL of a 15% solution in hexane) were cooled with stirring to –120 °C (*n*-pentane/liquid nitrogen). Via syringe through a septum 0.25 g (1.4 mmol) (*E*)-6-Bromomethylenebicyclo[3.2.0]hept-2-ene (***E*-5**) was added slowly. After stirring for additional 2 h at –120 °C about 2 mL of D_2O (99.8 atom % D, Janssen, Belgium) was added by syringe. With continued stirring the reaction mixture was slowly warmed to room temperature. The organic phase was separated and dried ($MgSO_4$). This protocol was repeated, and from the combined crude product, ***E*-1** was isolated by PGC (20% OV 17 on Chromosorb P AW 60/80 mesh, 1.4 m x 9 mm, 82 °C, t_R (***E*-1**) = 20 min). Yield: 150 mg (52%) of 98.5% purity by AGC (glass capillary-column, OV 101, 50 m x 0.23 mm, 85 °C, t_R (***E*-1**) = 508 s).

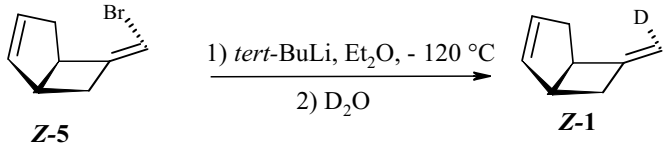
Isotopomeric purity by ^{1}H NMR: 98.2% ***E*-1**, 1.8% ***Z*-1**

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.76 (m, 2H, 2-H, 3-H), 4.87 (q, 0.98$^+$ H, 8*Z*-H, $J_{8Z,7n} \approx J_{8Z,7x} \approx J_{8Z,5} \approx 2.5$), 4.77 (0.02$^+$ H, residual 8*E*-H), 3.48 (m, 1 H, 5-H), 3.25 (m, 1 H, 1-H), 2.95 (ddd, 1 H, 7x-H, part A of the AB system 7x-H/7n-H, $J_{7x,7n} \approx 15.5$, $J_{7x,1} \approx 8.3$, $J_{7x,8Z} \approx$ 2.9), 2.53 (ddm, 1 H, 4n-H*, part A of the AB system 4x-H/4n-H, $J_{4n,4x} \approx 16.5$, $J_d \approx 8.3$, $J_m \approx 1.7$), 2.37 [#] (dm, 4x-H*, part B of the AB system 4x-H/4n-H, $J_d \approx 16.5$), and 2.33 [#] (2 H) (dq, 1 H, 7n-H, part B of the AB system 7x-H/7n-H, $J_{7n,7x} \approx 15.5$, $J_q \approx$ 2.8). * Interchangeable, [#] signals partially overlap.

Exact integration, normalized to (2-H + 3-H) = 2.000, gave: 8*Z*-H = 0.981; 8*E*-H = 0.018; corresponding to a total of 1.001 D/mol at C-8 of **1**.

^{2}H NMR (61.4 MHz, $CHCl_3$): Besides the signal of the solvent only a singlet is observed at δ = 4.84 ppm for 8*E*-D.

8*Z*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (*Z*-1)



***Z*-5** ***Z*-1**

The procedure followed was analogous to the protocol for ***E*-1** given above. The yield after PGC purification from 0.8 g (4.4 mmol) (*Z*)-6-Bromomethylenebicyclo[3.2.0]hept-2-ene (***Z*-5**) was 80 mg (17%) ***Z*-1** of 99.1% purity by AGC (glass capillary-column, OV 101, 50 m x 0.23 mm, 85 °C, t_R (***Z*-1**) = 503 s).

Isotopomeric purity by ^{1}H NMR: 94.0% ***Z*-1**, 6.0% ***E*-1**.

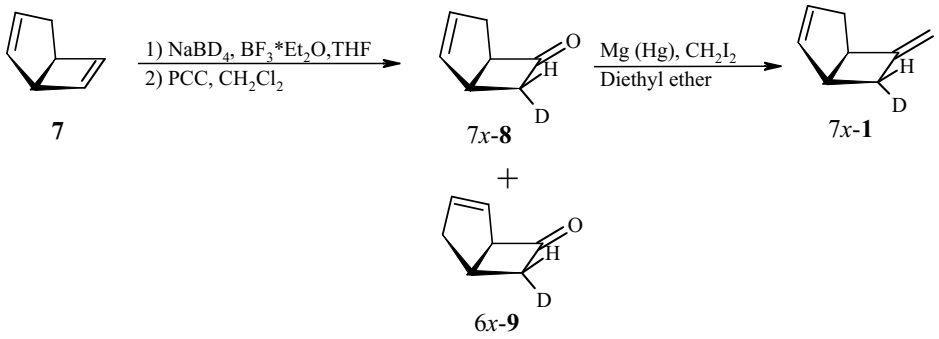
^{2}H NMR (61.4 MHz, $CHCl_3$): Besides the signal of the solvent a singlet is observed at δ = 4.93 ppm for 8*Z*-D with a small residual signal at δ = 4.84 ppm for 8*E*-D.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.76 (m, 2H, 2-H, 3-H), 4.87 (0.06$^+$ H, residual 8*Z*-H), 4.77 (q, 0.94$^+$ H, 8*E*-H, $J_{8E,7n} \approx J_{8E,7x} \approx J_{8E,5} \approx 2.2$), 3.48 (m, 1 H, 5-H), 3.25 (m, 1 H, 1-H), 2.94 (ddd, 1 H, 7x-H, part A of the AB system 7x-H/7n-H, $J_{7x,7n} \approx 15.5$, $J_{7x,1} \approx 8.3$, $J_{7x,8E} \approx$ 2.4), 2.53 (ddm, 1 H, 4n-H*, part A of the AB system 4x-H/4n-H, $J_{4n,4x} \approx 16.5$, $J_d \approx 8.3$, $J_m \approx 1.7$), 2.37 [#] (dm, 4x-H*, part B of the AB system 4x-

H/4n-H, $J_d \approx 16.5$), and 2.33 # (2 H) (dq, 7n-H, part B of the AB system 7x-H/7n-H, $J_{7n,7x} \approx 15.5$, $J_q \approx 2.0$). * Interchangeable, # signals partially overlap.

Exact integration, normalized to (2-H + 3-H) = 2.000, gave: 8*Z*-H = 0.060; 8*E*-H = 0.934; corresponding to a total of 1.006 D/mol at C-8 of **1**.

7*exo*-[$^2H_1$]-6-methylenebicyclo[3.2.0]hept-2-ene (7*x*-1)



7 7*x*-**8** 7*x*-**1**

6*x*-**9**

a) Deuterioboration of Bicyclo[3.2.0]hepta-2, 6-diene (7) followed by oxidation:

7*exo*-[$^2H_1$]-bicyclo[3.2.0]hept-2-en-6-one (7*x*-8) and 6*exo*-[$^2H_1$]-bicyclo[3.2.0]hept-2-en-*6exo*-ol (6*x*-9)

A route first reported by *J. A. Berson* and *G. L. Nelson*[7] was adapted and modified. To a solution of 4.80 g (52.1 mmol) bicyclo[3.2.0]hepta-2, 6-diene (**7**)[8], of >98% purity, in 20 mL THF (freshly distilled from $LiAlH_4$) under Ar at 0 °C was added 0.50 g (11.9 mmol) sodium borodeuteride (98 atom % D, Merck). After 5 min of stirring a solution of 2.64 g (18.6 mmol, 2.33 mL) boron trifluoride etherate (freshly distilled)[9] in 12 mL of THF was added slowly to the above suspension. After continued stirring over night at room temperature most of the solvent was evaporated in vacuo without external warming. The residue was dissolved in 210 mL of CH_2Cl_2, and after cooling to 0 °C in 0.5 h 30.0 g (139.2 mmol) PCC[10] was added in portions. After stirring over night, the reaction mixture was filtered over a short column charged with $MgSO_4$ and neutral Al_2O_3. The solvent was distilled via a short *Vigreux* column. GC analysis of the crude products showed three compounds in the ratio 3:1:1 (**8**:**9**: unknown). For further purification the crude products were chromatographed over silica using n-pentane/diethyl ether (9:1) as the eluent. After evaporation of the solvent, PGC separation (column: 20% QF1 on Chromosorb P 60/80 mesh, 3.6 m x 9 mm, 120°C) of the residue gave one fraction of desired ketone, **7*x*-8**, and another fraction containing **6*x*-9** and the unknown.

Yield: 0.32 g (2.9 mmol) **7*x*-8** of 99.3 % purity (AGC: glass capillary-column, Marlophen 814, 10 m x 0.23 mm, 100 °C, t_R (7*x*-**8**) = 584 s), and 0.23 g (2.1 mmol) 6x-**9** (AGC: t_R (6*x*-**9**) = 662 s) with the unknown (AGC: t_R (unknown) = 601 s).

This reaction was repeated several times. The use of neutral PCC is important.

7*exo*-[$^2H_1$]-bicyclo[3.2.0]hept-2-en-6-one (7*x*-8):

^{1}H NMR (400 MHz, $CDCl_3$)[cf. 5a] : δ (ppm) = 5.82 (dq, 1 H, 2-H*, $J_{2,3} \approx 5.5$, $J_{2,1} \approx J_{2,4x} \approx J_{2,4n} \approx$ 2.0), 5.77 (dq, 1 H, 3-H*, $J_{3,2} \approx 5.5$, $J_{3,1} \approx J_{3,4x} \approx J_{3,4n} \approx$ 2.0), 3.85 (tq, 1 H, 1-H, $J_{1,5} \approx J_{1,7n} \approx 8.8$, $J_{1,2} \approx J_{1,3} \approx J_{1,4x} \approx$ 2.3), 3.46 (m, 1 H, 5-H), 2.72-2.63 (m, 2 H, 4x-H, 7n-H), 2.46 (ddq, 1 H, 4n-H, $J_{4n,4x} \approx 17.3$, $J_{4n,5} \approx 9.9$, $J_{4n,2} \approx J_{4n,3} \approx J_{4n,1} \approx$ 2.0). * Interchangeable.

^{2}H NMR (61.4 MHz, $CHCl_3$): δ(ppm) = 7.24 (solvent), 3.33 (s large, 7x-D), 2.72 (s, small, 7n-D) is observed: 97.7 % 7x-D, 2.3 % 7n-D.

b) 7*exo*-[$^2H_1$]-6-methylenebicyclo[3.2.0]hept-2-ene (7*x*-1) by carbonyl methylenation:

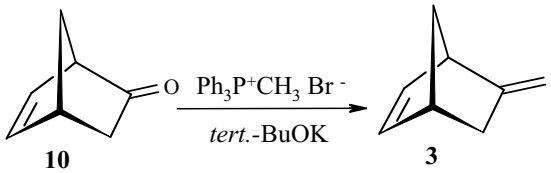
Under Ar, 150.0 g (0.7 mol) mercury and 0.49 g (20.2 mmol) magnesium were reacted to the amalgam with heating and stirring. At room temperature 20 mL diethyl ether was added, then in 45 min a solution of 0.50 g (4.58 mmol) 7x-**8** and 2.35 g (8.77 mmol) CH_2I_2 in 20 mL diethyl ether was added drop wise. This caused a slight temperature increase, and the mixture turned opaque. After 3.5 h of additional stirring, the organic phase was decanted; the amalgamic residue was washed with diethyl ether (4 x 10 mL). The combined organic phases were washed with 10 mL of ice cold saturated NH_4Cl followed by 3 x 10 mL ice water, and dried ($MgSO_4$). Most of the solvent was distilled using a 25 cm glass-bead column, and the residue was distilled via a short path. Then the product was isolated by PGC (column: 20 % OV 101 on chromosorb P 60/80 mesh, 4 m x 9 mm, 120 °C, t_R = 28 min). Yield: 0.25 g (2.33 mmol, 50.9 %) 7x-**1** of 99.9 % purity (AGC: glass capillary-column, OV 1, 29 m x 0.23 mm, 80 °C, t_R (7*x*-**1**) = 415 s).

This reaction was repeated several times with similar results.

7*exo*-[$^2H_1$]-6-methylenebicyclo[3.2.0]hept-2-ene (7*x*-1):

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.76 (m, 2 H, 2-H, 3-H), 4.88 (t, 1 H, 8*Z*-H, $J_{8Z,7n} \approx J_{8Z,5} \approx$ 2.5*), 4.79 (t, 1 H, 8*E*-H, $J_{8E,7n} \approx J_{8E,5} \approx$ 2.3*), 3.47 (m, 1 H, 5-H), 3.25 (m, 1 H, 1-H), (2.95 (ddt, ≈ 0.05 H, residual 7x-H, $J_{7x,7n} \approx$ 15.6, $J_{7x,1} \approx$ 8.2, $J_{7x,8Z} \approx J_{7x,8E} \approx$ 2.8)), 2.54 (ddq, 1 H, 4x-H, $J_{4x,4n} \approx$ 16.5, $J_{4x,5} \approx$ 8.3, $J_q \approx$ 2.3), 2.38 (dm, 4n-H, $J_d \approx$ 16.5), and 2.31 (2 H) ("sept", 1 H, 7n-H, $J_{sept} \approx$ 2.5). * $J_{8E,8Z} \approx 0$.

5-Methylenebicyclo[2.2.1]hept-2-ene (3):



10 **3**

The synthesis of **3** by a *Wittig* olefination in diethyl ether was analogous to that given above for **1**. From 1.08 g (10.0 mmol) bicyclo[2.2.1]hept-5-en-2-one (**10**),[11] 7.16 g (20.0 mmol) methyltriphenylphosphonium bromide[3] , and 1.68 g (15.0 mmol) potassium *tert*-butanolate in diethyl ether (30 mL) the yield of **3** was: 0.72 g (68%).

PGC (20% OV 17 on Chromosorb P AW 60/80 mesh, 1.4 m x 9 mm, 65 °C, t_R (**3**) = 30 min) gave **3** of 99.7 % purity (AGC: capillary-column, OV 101, 50 m x 0.23 mm, 85 °C, t_R (**3**) = 438 s).

IR (neat): 3130 w (=CH), 3066 s (=CH), 2981 vs, 2882 s, 1660 s (C=C), 1564 w (C=C), 1432 m, 1323 s, 898 vs, 836 s, 724 vs, 686 s cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.11 (dd, 1 H, 2-H, $J_{2,3} \approx$ 5.5, $J_d \approx$ 2.9), 6.06 (dd, 1 H, 3-H, $J_{3,2} \approx$ 5.5, $J_d \approx$ 2.9), 4.97 (s br, 1 H, 8*Z*-H), 4.70 (s br, 1 H, 8*E*-H), 3.14 (s br, 1 H, 4-H), 2.95 (s br, 1 H, 1-H), 2.24 (dm, 1 H, 6x-H, part A of the AB system 6x-H/6n-H, $J_{6x,6n} \approx$ 14.8), 1.74 (dm, 1 H, 6n-H, part B of the AB system 6x-H/6n-H, $J_{6n,6x} \approx$ 14.8), 1.57 (dm, 1 H, 7*syn*-H, part A of the AB system *7syn*-H/*7anti*-H, $J_{7s,7a} \approx$ 8.2), 1.40 (dm, 1 H, *7anti*-H, part B of the AB system *7syn*-H/*7anti*-H, $J_{7a,7s} \approx$ 8.2).

These assignments are in good agreement with the recent literature.[12]

Thermolyses

Apparatus

Gas phase thermolyses have been carried out in a 20 L pyrex round bottomed flask at a pressure of about 1 – 3 mbar. This flask was warmed in a well insulated air thermostat by proportional heating regulated by a Pt-100. Temperatures in the flask were measured by a specially calibrated iron/constantan differential-thermocouple which was in a flexible metal encasing. The reference junction was kept at 0 °C. The hot junction of the thermocouple was placed in a glass well, reaching to the center of the flask. Temperature constancy in the flask was better than ± 0.1 °C over extended periods of time (days) for temperatures up to above 300 °C. The emf of the thermocouple was measured with a digital voltmeter type 2501 from Yokogawa Electric Works, Ltd., Tokyo, Japan. The reaction flask was connected to a vacuum line, two 1 L sampling flasks, each connected to a 1 mL cold-finger. The vacuum line was connected to a pump stand including an oil diffusion pump. The hole system could be evacuated to better than 10^{-3} mbar. All connecting stopcocks were greaseless.

Prior to the thermolyses, the walls of the reaction flask were well conditioned by heating cyclopentadiene, bistrimethylsilylamine and/or triethylamine for at least one night at the temperature of the intended thermolyses.

Procedure

For the thermolyses of unlabeled **1** a solution made up from 40 μL **1**, 20 μL ethylbenzene as internal standard and 200 μL of n-hexane was used. The above 1 mL cold- finger of the thermolysis apparatus was charged with 30 μL of this solution. After freezing (N_2, l), the system was evacuated. Then, after warming to room temperature, the sample was condensed to the 1 L flask, and degassed by freeze-thaw cycles. The 1 L sampling flask was disconnected from the pumps, and the sample expended in the 1 L flask at room temperature. Then the sample was introduced into the evacuated 20 L reaction flask. The reaction flask was closed, and the line was evacuated again after recondensing residual material in the line. The pressure in the flask was 1 – 3 mbar. After heating at the respective temperature, samples were taken at different points of time by shortly opening the reaction flask, condensing aliquots in the 1 L flask, then recondensing this sample in the 1 mL cold-finger. The samples, thus obtained, were subjected to AGC (glass capillary, OV 101, 50m x 0.26 mm, 80 °C). With **1** as the educt, the only product formed was 5-methylenebicyclo[2.2.1]hept-2-ene (**3**). The reaction was followed up to about 95% conversion of the educt. A significant mass loss was not observed. Retention times: t_R (**1**) = 706 s, t_R (**3**) = 622 s. The complete kinetics of **1** will be described elsewhere.

For the stereospecifically labeled educts 8*E*-**1**, 8*Z*-**1**, and 7*x*-**1** individual thermolyses were carried out as follows: In each case a solution of 25-40 μL labeled d-**1**, 10-20 μL n-nonane as internal standard, and 30-40 μL n-hexane as the solvent and collision partner was transferred to the reaction flask and thermolysed at a pressure of ≈ 3 mbar. For sampling at each point of time (after 20 to 80 % structural conversion) the whole contents of the 20 L flask was recondensed into the 1 L flask (N_2, l), then condensed to the 1 mL cold-finger. These samples were first analysed by AGC (see above) for the amount of structural isomerization, then the structural isomers d-**1** and d-**3** were separated by PGC (glass column: 20% PPG on Chromosorb P 60/80 mesh, 2.4 m x 9 mm, 90 °C). A fraction containing the d-**1** isotopomers (t_R = 45 min), and a fraction with the d-**3** isotopomers was collected (t_R = 37 min) for each point of time. There was no loss of deuterium, as was shown by MS deuterium analysis for a sample of rearranged d-**3** (210.08 °C / 79.1 % structural conversion).

These samples have been analysed qualitatively and quantitatively by ^{2}H NMR (61.4 MHz) spectroscopy. The *d*-**1** fraction consisted of the four isotopomers 8*Z*-**1** (δ / *ppm* = 4.93), 8*E*-**1** (4.84), 7*x*-**1** (2.97), and 7*n*-**1** (2.37); the d-**3** fraction was a mixture of the four isotopomers 8*Z*-**3** (5.02), 8*E*-**3** (4.74), 6*x*-**3** (2.24), and 6*n*-**3** (1.74). The ratio of isotopomers in 1 and in **3** has been quantified for each sample by

careful integration of the ^{2}H NMR spectra. For each sample of the rearranged product mixture d-**3** at each time point six independent integrations of the ^{2}H NMR spectra have been averaged. Then these means for the different time points have been extrapolated to zero time by linear regression (best estimate), and the sum of the four isotopomeric fractions was normalized to 1.0. In Table 1 the results from the thermolysis of 7*x*-**1** at T = 219.8 °C are given. Table 2 and Table 3 collect the results from the thermolyses of 8*E*-**1** and 8*Z*-**1** at T = 220.0 °C, respectively, in a more condensed version.

Supporting Figures S1 to S12 give the ^{1}H NMR spectra of **1**, 8*E*-**1**, 8*Z*-**1**, 7*x*-**1**, and **3** and ^{2}H NMR spectra of 8*E*-**1**, 8*Z*-**1**, 7*x*-**1**. As examples for the thermolysis results the ^{2}H NMR spectra from the thermolyses of 8*E*-**1** and 7*x*-**1** as a function of time of thermolysis follow.

Table S1. Thermolyses of 7*x*-1 at 219.8 °C. Distribution of isotopomeric 5-methylenebicyclo[2.2.1]hept-2-ene products *d*-**3** at three times of sthermolysis (*t*); best estimates for $t = 0$, and values normalized over the four respected positions to 1.000.

	Experimental Points						Estimate[e]
Thermolysis time (*t*/min)	60		108		188		0
Extent of Reaction **1** → **3**	40.25 %		59.80 %		79.78 %		0 %
6*n*-**3**	0.224884[a] ± 0.003702[b]	0.201665[c]	0.227387 ± 0.003814	0.205882	0.224188 ± 0.000987	0.200930	0.204187
6*x*-**3**	0.352801 ± 0.002688	0.376020	0.345857 ± 0.005089	0.367362	0.352315 ± 0.001144	0.375573	0.3721151
8*E*-**3**	0.212287 ± 0.005703	0.212697	0.212840 ± 0,001918	0.212645	0.209060 ± 0,001293	0.208084	0.215672
8*Z*-**3**	0.210028 ± 0.00654239	0.209618	0.213916 ± 0.000811	0.214111	0.214437 ± 0.001079	0.215413	0.208026
Sum	1.000000	1.0000000	1.000000	1.000000	1.000000	1.000000	1.000000

(a) Means of six independent ^{2}H NMR integrations; values not rounded for calculations.

(b) Errors are standard deviations of the means at the 95 % confidence limit.

(c) Corrected for label distribution in starting 7*x*-**1**.

(d) Rounded values.

(e) Best estimates at $t = 0$ and normalized to sum = 1.

Table S2. Thermolyses of 8*E*-1 at 220.0 °C. Distribution of isotopomeric 5-methylenebicyclo[2.2.1]hept-2-ene products *d*-**3** at different times of thermolysis (*t*); best estimates for *t* = 0, and values normalized over the four respected positions to 1.000.

	Experimental Points				Estimate[(d)]
Thermolysis time (*t*/min)	30	60	108	188	0
Extent of Reaction **1** → **3**[(e)]	24.2 %	42.1 %	62.4 %	81.7 %	0 %
6*n*-**3**	0.234[(a,b,c)]	0.229	0.216	0.230	0.229893
6*x*-**3**	0.138	0.138	0.157	0.155	0.134994
8*E*-**3**	0.628	0.630	0.619	0.605	0.635113
8*Z*-**3**	0.00	0.003	0.008	0.010	0.0
Sum	1.000	1.000	1.000	1.000	1.000000

(a) Means of six independent ^{2}H NMR integrations.

(b) Standard deviations of these means at the 95 % confidence limit are ± 0.001 to ± 0.01.

(c) Corrected for label distribution in starting 8*E*-**1**.

(d) Values are best estimates at t = 0 and normalized to sum = 1.

(e) Values inferred from thermolysis time (*t*) and the experimental rate constant $k_{1\text{-}3}$ (219.8 °C) = (15.005±0.0791) x 10^{-5} s^{-1} (r = -0.99993) with c_0 = 0.993.

Table S3. Thermolyses of 8*Z*-1 at 220.0 °C. Distribution of isotopomeric 5-methylenebicyclo[2.2.1]hept-2-ene products *d*-**3** at different times of thermolysis (*t*); best estimates for *t* = 0, and values normalized over the four respected positions to 1.000.

	Experimental Points		Estimate[(d)]
Thermolysis time (*t*/min)	30	188	0
Extent of Reaction **1** → **3**[(e)]	24.2 %	81.7 %	0 %
6*n*-**3**	0.145[(a,b,c)]	0.167	0.140823
6*x*-**3**	0.240	0.236	0.240759
8*E*-**3**	0.0	0.0	0.0
8*Z*-**3**	0.615	0.599	0.618418
Sum	1.000	1.000	1.000000

(a) Means of six independent ^{2}H NMR integrations.

(b) Standard deviations of these means at the 95 % confidence limit are ± 0.001 to ± 0.01.

(c) Corrected for label distribution in starting 8*Z*-**1**.

(d) Values are best estimates at t = 0 and normalized to sum = 1.

(e) Values inferred from thermolysis time (*t*) and the experimental rate constant $k_{1\text{-}3}$ (219.8 °C) = (15.005±0.0791) x 10^{-5} s^{-1} (r = -0.99993) with c_0 = 0.993.

NMR Data

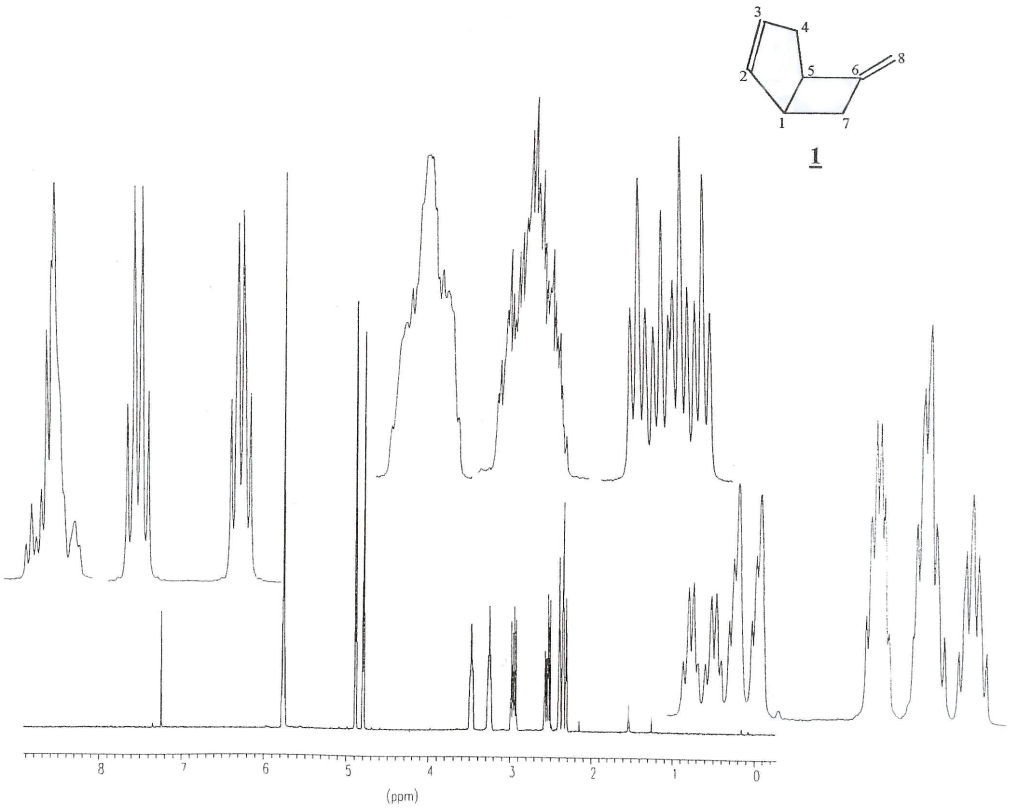


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$): 6-Methylenebicyclo[3.2.0]hept-2-ene (**1**).

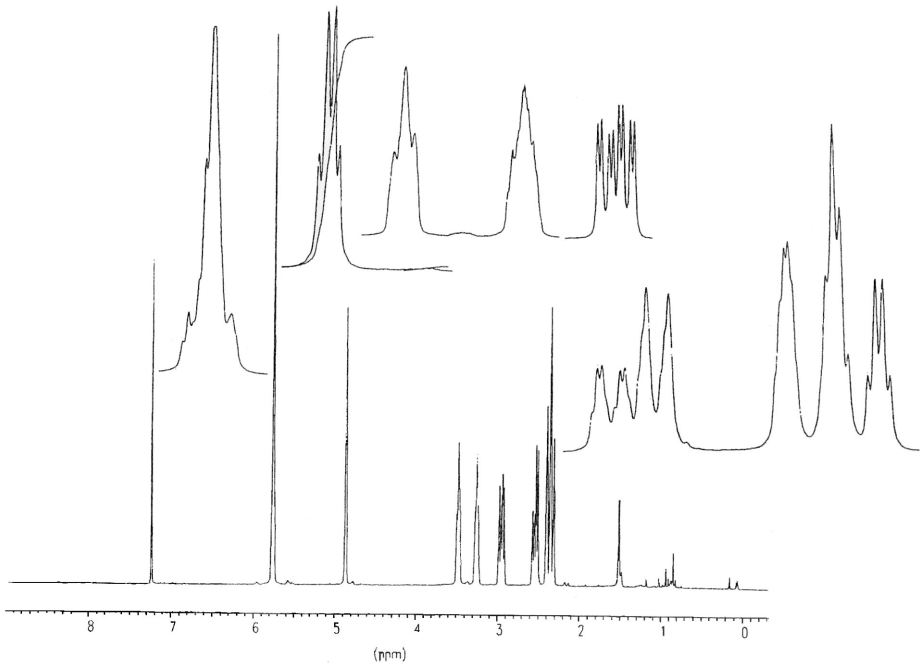


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$): 8*E*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (8*E*-**1**).

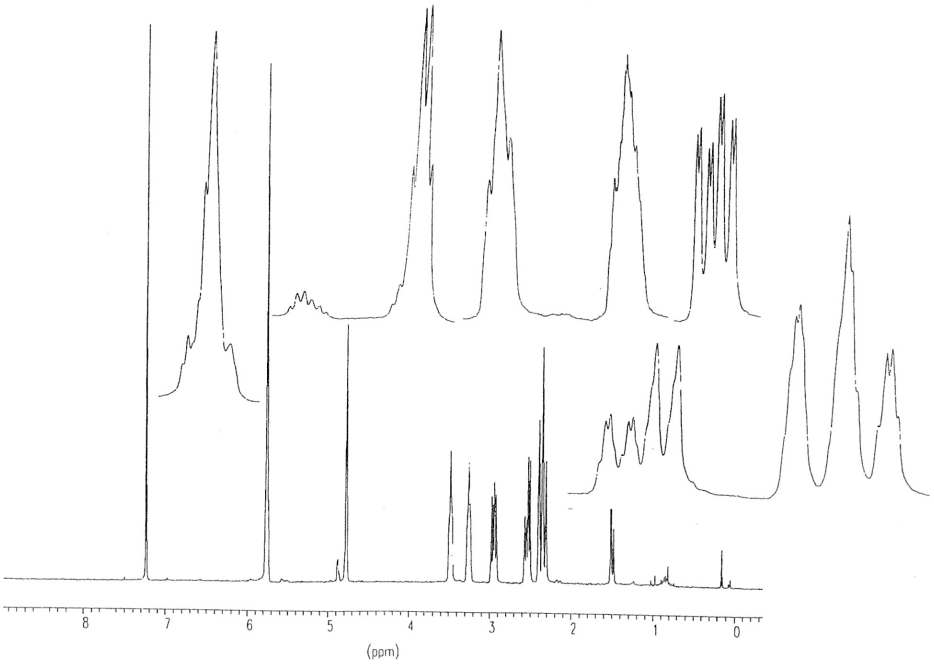


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$): 8*Z*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (*Z*-**1**)

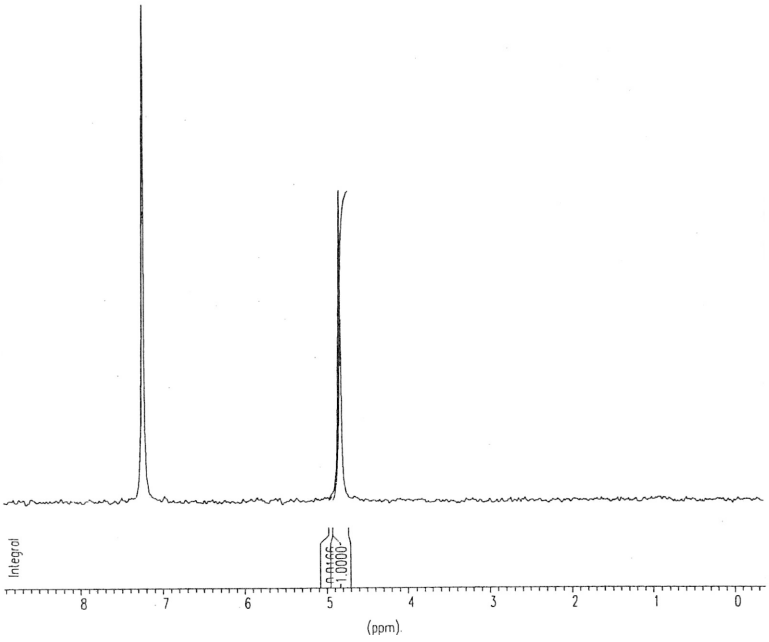


Figure S4. ^{2}H NMR (61.4 MHz, $CHCl_3$): 8*E*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (8*E*-**1**).

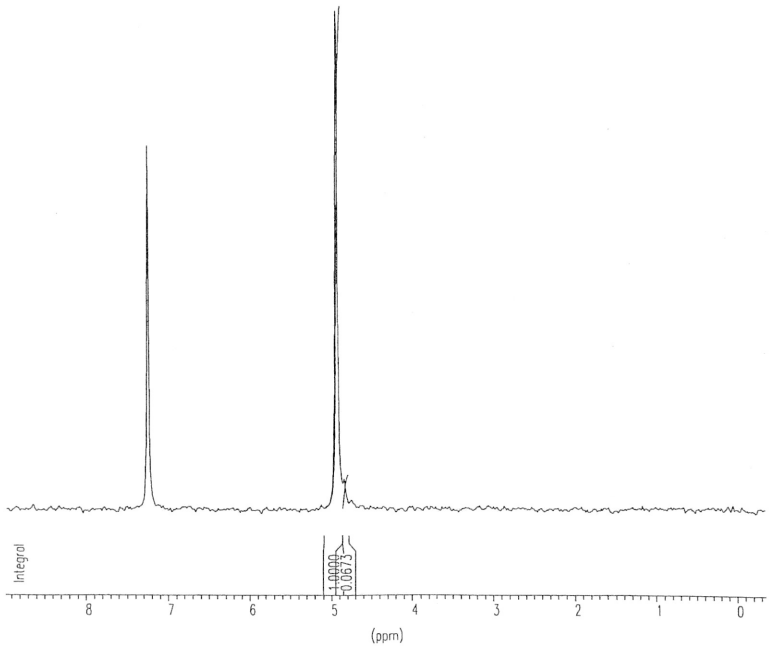


Figure S5. ^{2}H NMR (61.4 MHz, $CHCl_3$): 8*Z*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (**Z-1**)

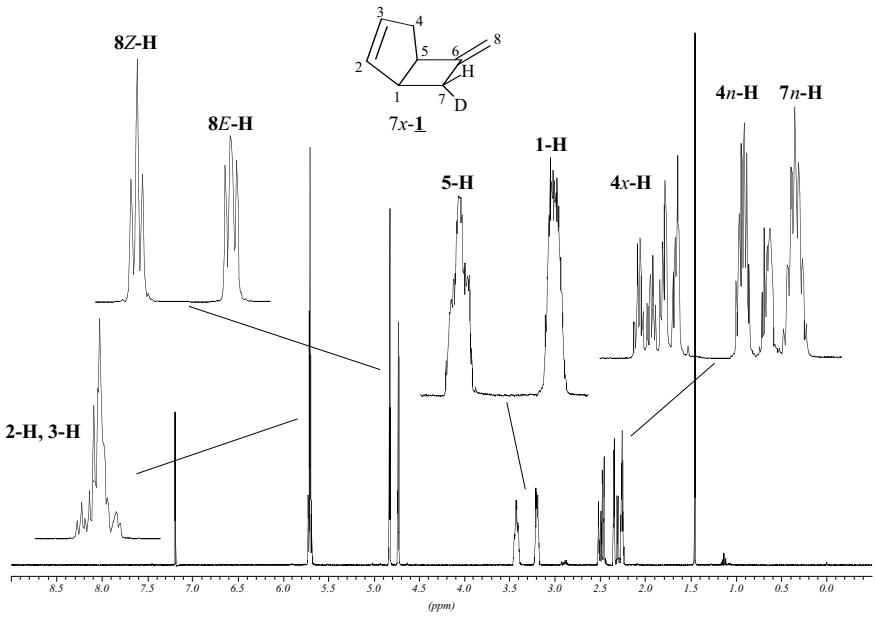


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$): 7*x*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (7***x*-1**)

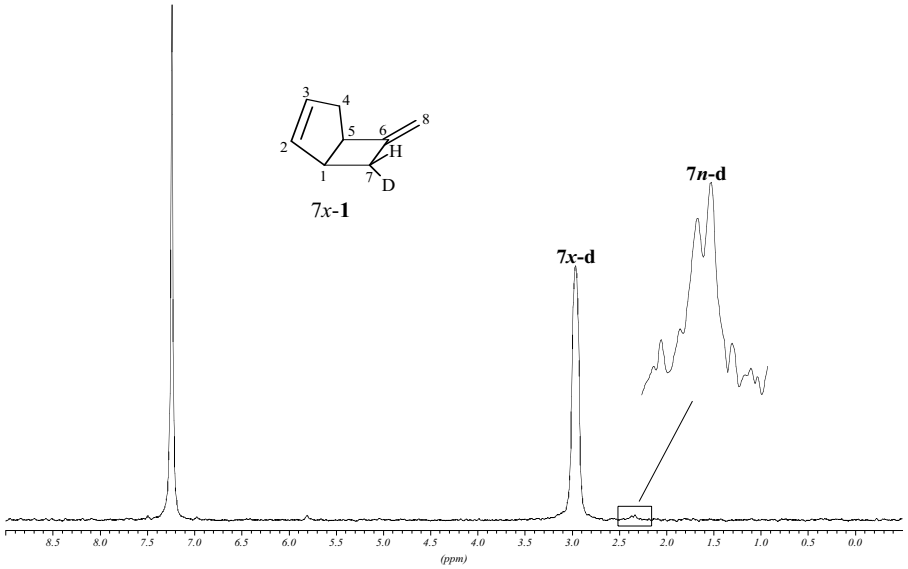


Figure S7. ^{2}H NMR (61.4 MHz, $CHCl_3$): 7*x*-[$^{2}H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (7***x*-1**).

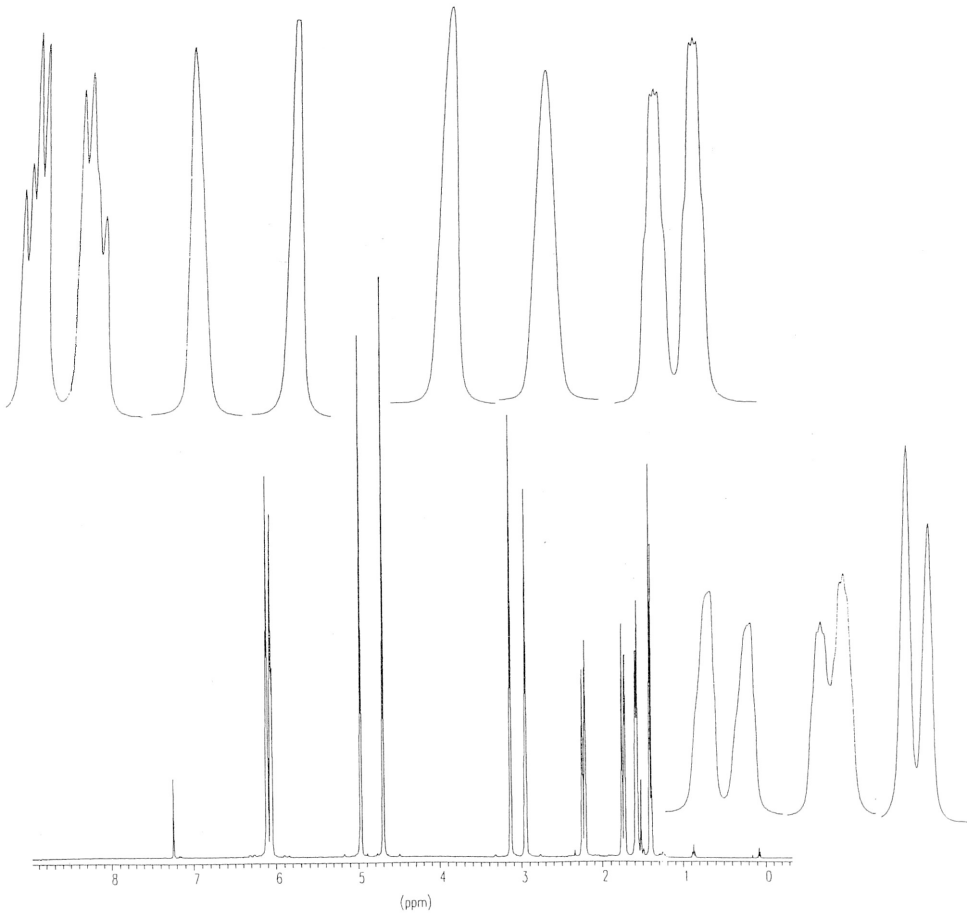


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$): 5-Methylenebicyclo[2.2.1]hept-2-ene (**3**).

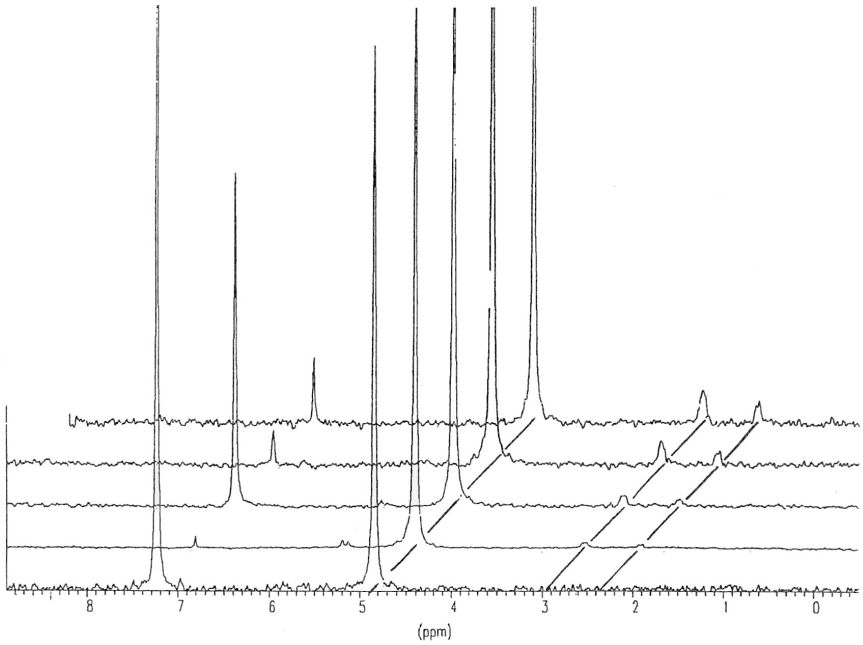


Figure S9. ^{2}H NMR (61.4 MHz, $CHCl_3$): Spectra of the [$^2H_1$]-**1** fractions of the thermolyses of 8*E*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (***E*-1**) at 220 °C at different times of thermolysis. Traces bottom to top: t = 0, 30, 60, 108, 188 min.

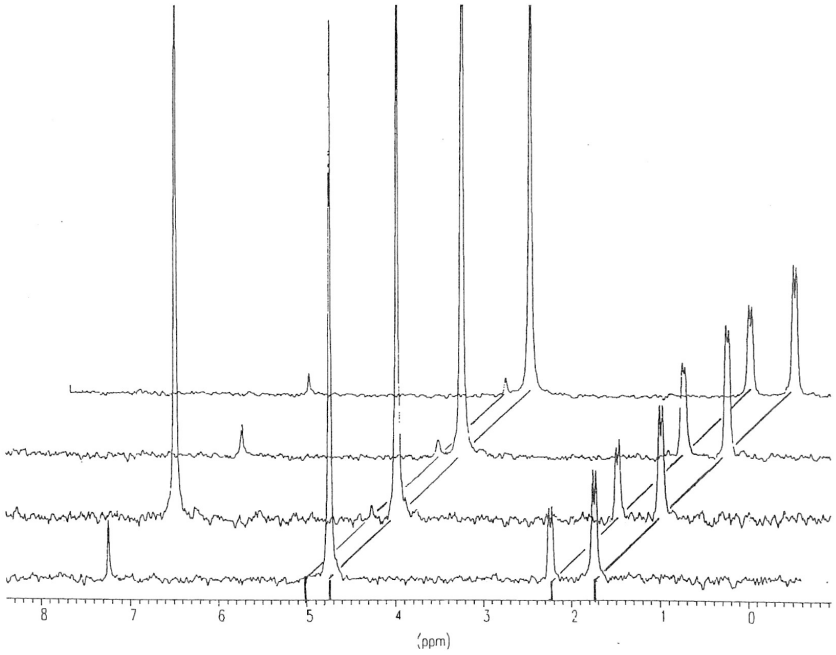


Figure S10. ^{2}H NMR (61.4 MHz, $CHCl_3$): Spectra of the [$^2H_1$]-**3** fractions of the thermolyses of 8*E*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (8*E*-**1**) at 220 °C at different times of thermolysis. Traces bottom to top: t = 30, 60, 108, 188 min.

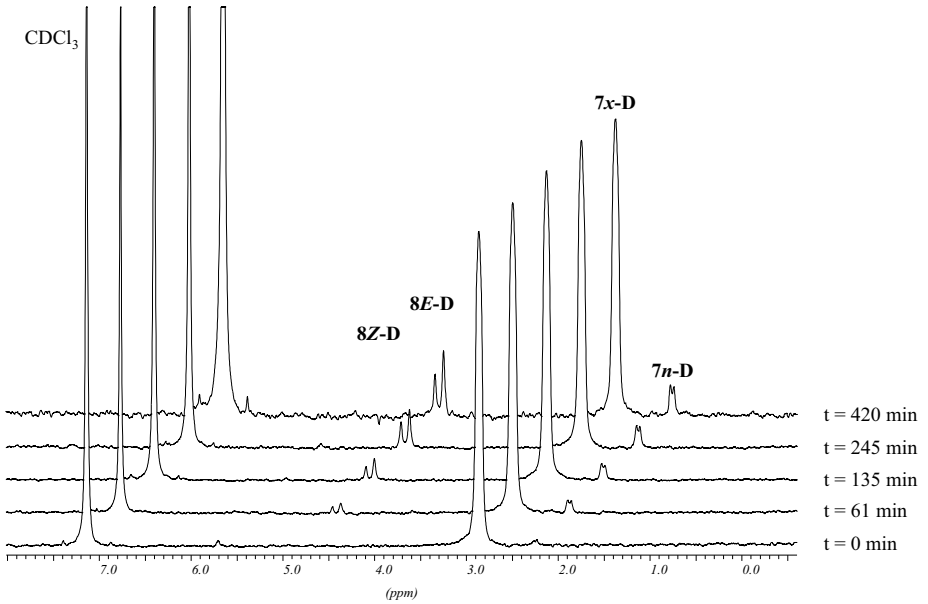


Figure S11. ^{2}H NMR (61.4 MHz, $CHCl_3$): Spectra of the [$^2H_1$]-**1** fractions of the thermolyses of 7*x*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (7*x*-**1**) at 210 °C at different times of thermolysis.

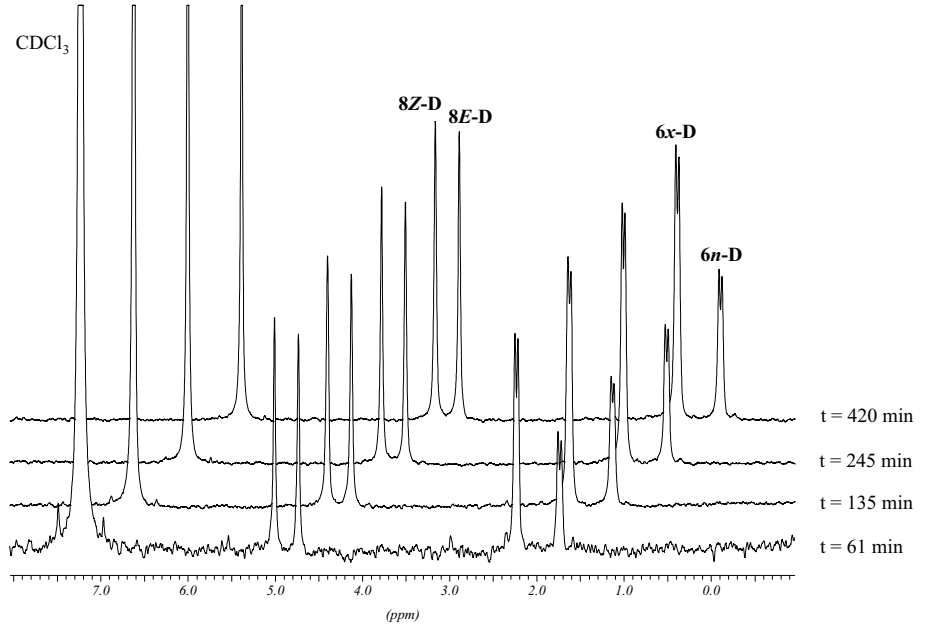


Figure S12. ^{2}H NMR (61.4 MHz, $CHCl_3$): Spectra of the [$^2H_1$]-**3** fractions of the thermolyses of 7*x*-[$^2H_1$]-6-Methylenebicyclo[3.2.0]hept-2-ene (7*x*-**1**) at 210 °C at different times of thermolysis.

Computational Details

(U)B3LYP. (U)B3LYP calculations were performed in Gaussian 98. RB3LYP/6-31G(d) was used for all calculations on **1**, **3**, **TS-1i3s**, and **TS-3s3s**. **2**, **TS-12n**, **TS-12x**, **TS-22**, **TS-23n**, **TS-23x**, **TS-ezP**, and **TS-ezD** were treated with UB3LYP/6-31G(d). With UB3LYP, appropriate steps were taken (Guess=Mix) to ensure that the lowest-energy open-shell wavefunctions were generated. Reported ΔH values include thermal corrections based on (U)B3LYP/6-31G(d) frequency calculations (*v.i.*).

(6,6)CASSCF. All CASSCF calculations were performed with the 6-31G(d) basis set in Gaussian 98. The (6,6) active space used for CAS calculations included the six π and π^* orbitals in **2**, the corresponding π, π^*, σ, and σ^* orbitals in **1** and **3**, and the various corresponding orbitals of transition states. **TS-1i3s** and **TS-3s3s** were not treated with CASSCF.

(6,6)CASPT2. Single point (6,6)CASPT2/6-31G(d) calculations were performed in MOLCAS on the structures which had been optimized using (U)B3LYP in Gaussian 98. The (6,6) active space used was the same as described above for CASSCF. The CASPT2//UB3LYP ΔH values referred to throughout the text include CASPT2 electronic energies plus zero-point and thermal corrections calculated from (U)B3LYP frequencies (*v.i.*).

Geometry optimizations. Minima and saddle points were optimized in Gaussian 98 (keyword Opt for minima **1**, **2**, and **3**; keyword Opt=(TS,CalcFC,noeigentest) for **TS-12n**, **TS-12x**, **TS-22**, **TS-23n**, **TS-23x**, **TS-ezP**, **TS-ezD**, **TS-1i3s**, and **TS-3s3s**). Saddle points were identified on the basis of frequency calculations and potential energy surface analysis.

Potential Energy Surface. UB3LYP constrained optimizations were conducted using the Opt=ModRedundant keyword and an appropriate ModRedundant input section. For some points it was possible to optimize more than one structure which satisfied the bond length constraints; in each such case, the lowest energy UB3LYP-optimized conformation was used. A (6,6)CASPT2/6-31G(d) single-point energy calculation was performed for each lowest-energy UB3LYP-optimized structure. Complete source data for the plot in Figure 4 are listed in Table S5.

Frequencies and thermochemistry. Zero-point energy and thermal corrections to enthalpy were derived for 493 K and 1.0 atm from (U)B3LYP frequencies, scaled by 0.9806, calculated on (U)B3LYP optimized geometries.

See following pages for summaries of calculated data for optimized stationary points. Cartesian coordinates and B3LYP bond lengths (CASSCF bond lengths in parentheses) are listed in angstroms; electronic energies are reported in hartrees.

Software Citations

Gaussian 98, revision A.9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.

Molcas, version 5.0. Andersson, K. ; Barysz, M.; Bernhardsson, A.; Blomberg, M. R. A.; Cooper, D. L.; Fleig, T.; Fülscher, M. P.; de Graaf, C.; Hess, B. A.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. Lund University, Sweden, 2001.

Table S4. Complete table of energies for CASSCF and (U)B3LYP optimized structures. Thermal corrections were calculated for 493 K and 1 atm based on (U)B3LYP frequencies, scaled by 0.9806.[13]

	(6,6)CASSCF	(U)B3LYP	(6,6)CASPT2 // CASSCF	(6,6)CASPT2 // (U)B3LYP			
	E_{ele}	E_{ele}	E_{ele}	E_{ele}	E^{0K}	H^{493K}	G^{493K}
1	-308.769419	-310.799382	-309.731001	-309.731718	-309.578479	-309.558258	-309.638016
TS-12n	-308.705643	-310.733496	-309.666192	-309.668485	-309.519592	-309.498803	-309.579421
TS-12x	-308.700296	-310.729228	-309.662400	-309.665802	-309.516540	-309.495949	-309.575928
2	-308.716421	-310.747370	-309.675315	-309.676099	-309.528302	-309.505688	-309.592223
TS-22	-308.711241	-310.742531	-309.669880	-309.670574	-309.522877	-309.501807	-309.582745
TS-ezP	-308.696358	-310.721068	-309.649611	-309.650346	-309.504242	-309.481977	-309.568412
TS-ezD	-308.695824	-310.721041	-309.649755	-309.650905	-309.504588	-309.482512	-309.567622
TS-23n	-308.703655	-310.733527	-309.669851	-309.672434	-309.522892	-309.502537	-309.581366
TS-23x	-308.700864	-310.732373	-309.668423	-309.671420	-309.522130	-309.501679	-309.580627
3	-308.779615	-310.809428	-309.748443	-309.749175	-309.594506	-309.575024	-309.651844
TS-3s3s		-310.726729					
TS-1i3s		-310.723666					

1 6-Methylenebicyclo[3.2.0]hept-2-ene

RB3LYP/6-31G(d) optimized parameters:

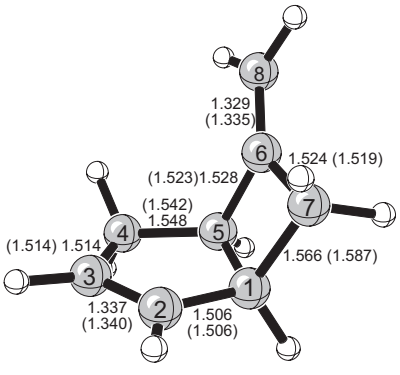
C	1.047881	0.541241	-0.452049
C	0.790065	-0.412324	-1.588351
C	-0.512962	-0.587383	-1.831554
C	-1.402284	0.235152	-0.923112
C	-0.397840	0.842285	0.086787
C	-0.052712	0.008881	1.320200
C	1.412025	-0.120280	0.920070
C	-0.778308	-0.471229	2.325362
H	1.593916	-0.903614	-2.131627
H	1.679906	1.390525	-0.737311
H	-0.608506	1.892418	0.317262
H	2.083966	0.497248	1.530006
H	1.822296	-1.136035	0.878325
H	-2.166713	-0.373833	-0.422630
H	-0.916671	-1.238285	-2.603342
H	-1.940941	1.010285	-1.488188
H	-0.338988	-1.090991	3.103969
H	-1.843455	-0.265775	2.409427

E(RB+HF+LYP) = -310.799382
(6,6)CASPT2/6-31G(d) E = -309.731718

(6,6)CASSCF/6-31G(d) optimized parameters:

C	1.041612	0.547850	-0.456617
C	0.792648	-0.414806	-1.587272
C	-0.513647	-0.593391	-1.828392
C	-1.395928	0.239849	-0.923841
C	-0.392496	0.838061	0.081916
C	-0.053330	0.006221	1.312078
C	1.411826	-0.122982	0.933652
C	-0.784163	-0.468572	2.322884
H	1.588502	-0.905104	-2.119845
H	1.659968	1.392214	-0.741150
H	-0.599759	1.876095	0.317460
H	2.068888	0.492442	1.540609
H	1.815343	-1.128661	0.886316
H	-2.160067	-0.353855	-0.431210
H	-0.914289	-1.239912	-2.588851
H	-1.911655	1.013308	-1.488668
H	-0.347326	-1.073372	3.098746
H	-1.838736	-0.266534	2.400153

E = -308.769419
(6,6)CASPT2/6-31G(d) E = -309.731001



R(1,5) = 1.572 (1.559)
R(3,7) = 3.390 (3.400)
R(1,8) = 3.475 (3.477)
R(3,8) = 4.167 (4.162)
D(1,5,6,7) = +7.8° (+8.2°)
D(1,5,6,8) = -169.3° (-169.9°)

3 5-Methylenenorbornene

RB3LYP/6-31G(d) optimized parameters:

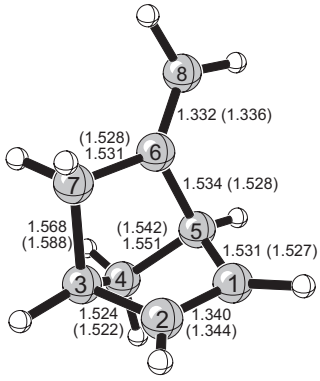
C	-1.279534	-0.578345	0.819229
C	-0.187471	-0.883239	1.533745
C	0.927359	0.057074	1.090233
C	0.102354	1.333636	0.789008
C	-0.914604	0.582570	-0.109332
C	0.038110	-0.030500	-1.144190
C	1.311400	-0.374996	-0.367700
C	-0.198225	-0.201171	-2.443825
H	-2.220932	-1.117098	0.784733
H	-0.058575	-1.720287	2.212797
H	0.669850	2.104216	0.253146
H	-1.746519	1.151109	-0.529871
H	1.777187	0.159650	1.768956
H	-0.360524	1.764006	1.682403
H	1.580864	-1.434329	-0.434546
H	2.164914	0.208839	-0.735604
H	-1.138650	0.104680	-2.896512
H	0.536038	-0.650962	-3.108508

E(RB+HF+LYP) = -310.809428
(6,6)CASPT2/6-31G(d) E = -309.749175

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-1.274888	-0.576593	0.837603
C	-0.173448	-0.873131	1.548522
C	0.929879	0.068403	1.088571
C	0.099858	1.327531	0.778090
C	-0.913437	0.570596	-0.103851
C	0.030048	-0.033272	-1.143133
C	1.311827	-0.378146	-0.386503
C	-0.209837	-0.200592	-2.447055
H	-0.035742	-1.704337	2.215061
H	0.654503	2.088176	0.236645
H	-1.741330	1.134259	-0.512603
H	1.775360	0.181677	1.754155
H	-0.351852	1.765731	1.660380
H	1.568957	-1.429722	-0.444994
H	2.155197	0.197478	-0.756224
H	-1.144912	0.094887	-2.890472
H	0.520662	-0.636967	-3.106506
H	-2.200861	-1.119965	0.811089

E = -308.779615
(6,6)CASPT2/6-31G(d) E = -309.748443



R(3,4) = 1.550 (1.540)
R(1,7) = 2.857 (2.869)
R(1,8) = 3.458 (3.473)
R(3,8) = 3.718 (3.725)
D(1,5,6,7) = -68.1° (-67.9°)
D(1,5,6,8) = +112.8° (+113.2°)

2

UB3LYP/6-31G(d) optimized parameters:

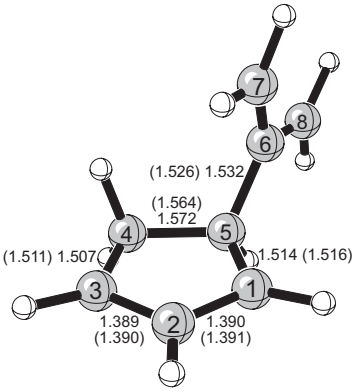
C	-0.806177	-0.919800	-0.815766
C	-0.711077	-0.284630	-2.048209
C	0.424402	0.512704	-2.115767
C	1.193627	0.439493	-0.821373
C	0.360009	-0.547007	0.075263
C	-0.069639	0.043170	1.422306
C	-0.995458	1.085384	1.433251
C	0.468651	-0.468615	2.591837
H	2.218696	0.072238	-0.973058
H	1.292291	1.424556	-0.345343
H	0.964204	-1.440167	0.289395
H	-1.594544	-1.595967	-0.504209
H	-1.431153	-0.399011	-2.853726
H	0.728664	1.113769	-2.965740
H	1.189618	-1.280354	2.580341
H	-1.427669	1.468450	0.514858
H	-1.308192	1.546762	2.365393
H	0.182061	-0.074472	3.562836

E(UB+HF+LYP) = -310.747370; S**2 = 1.0486
(6,6)CASPT2/6-31G(d) E = -309.676119

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-0.809370	-0.914399	-0.817174
C	-0.710802	-0.286659	-2.054750
C	0.424902	0.512462	-2.116173
C	1.190052	0.440442	-0.815777
C	0.359627	-0.542011	0.073285
C	-0.066620	0.038520	1.418316
C	-0.988681	1.092498	1.443452
C	0.465579	-0.479395	2.589327
H	2.200878	0.071576	-0.967384
H	1.283658	1.416842	-0.350709
H	0.954576	-1.428432	0.273995
H	-1.585658	-1.589713	-0.512621
H	-1.419256	-0.402735	-2.854546
H	0.727627	1.109898	-2.954466
H	1.172379	-1.288058	2.578695
H	-1.408124	1.495464	0.541582
H	-1.295011	1.536643	2.372533
H	0.180804	-0.090229	3.549880

E = -308.716421
(6,6)CASPT2/6-31G(d) E = -309.662400



R(6,7) = 1.394 (1.401)
R(6,8) = 1.385 (1.387)
R(1,7) = 3.019 (3.028)
R(3,7) = 3.865 (3.874)
R(1,8) = 3.666 (3.663)
R(3,8) = 4.809 (4.809)
D(1,5,6,7) = -50.4° (-51.0°)
D(1,5,6,8) = +129.7° (+129.2°)

TS-12n

UB3LYP/6-31G(d) optimized parameters:

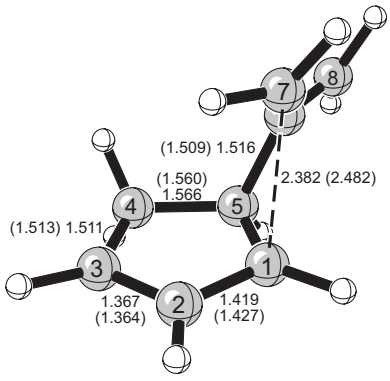
C	-0.763645	0.883521	0.549716
C	-0.797079	0.309548	1.847089
C	0.328086	-0.431081	2.082142
C	1.286276	-0.371181	0.915005
C	0.557329	0.539969	-0.129869
C	0.027415	-0.122380	-1.385799
C	-1.162355	-0.850434	-1.034383
C	0.432788	0.172046	-2.642796
H	2.254316	0.056839	1.211915
H	1.509182	-1.366383	0.507820
H	1.173513	1.415094	-0.366347
H	-1.419838	1.664184	0.184716
H	-1.626679	0.415385	2.540003
H	0.533429	-0.989322	2.990353
H	1.289790	0.812876	-2.829963
H	-1.190338	-1.445049	-0.129032
H	-1.880329	-1.132447	-1.804355
H	-0.095945	-0.211217	-3.511742

E(UB+HF+LYP) = -310.733496; S**2 = 0.5167
(6,6)CASPT2/6-31G(d) E = -309.668482

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-0.789406	0.876291	0.606746
C	-0.763576	0.297411	1.911048
C	0.367737	-0.444157	2.089560
C	1.263794	-0.390307	0.871082
C	0.508313	0.548742	-0.119749
C	0.017633	-0.087467	-1.396915
C	-1.170796	-0.877844	-1.107137
C	0.456925	0.216409	-2.636175
H	2.244659	0.006391	1.117434
H	1.428951	-1.376703	0.447698
H	1.107557	1.430087	-0.324565
H	-1.431648	1.679712	0.301828
H	-1.549269	0.405556	2.636056
H	0.611740	-1.004887	2.972598
H	1.289556	0.879006	-2.791911
H	-1.174040	-1.531175	-0.255841
H	-1.852232	-1.139440	-1.899641
H	-0.019021	-0.183022	-3.514415

E = -308.705643
(6,6)CASPT2/6-31G(d) E = -309.666192



R(1,5) = 1.525 (1.523)
R(6,7) = 1.438 (1.456)
R(6,8) = 1.353 (1.349)
R(3,7) = 3.480 (3.574)
R(1,8) = 3.483 (3.536)
R(3,8) = 4.764 (4.773)
D(1,5,6,7) = -35.7° (-36.2°)
D(1,5,6,8) = +130.9° (+132.8°)

TS-12x

UB3LYP/6-31G(d) optimized parameters:

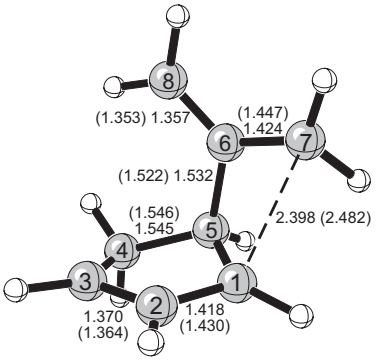
C	-1.275571	0.246723	0.473726
C	-0.895931	-0.733623	1.425183
C	0.424713	-0.595277	1.761833
C	1.004407	0.659309	1.147991
C	0.000928	0.953601	0.011010
C	0.240041	0.125395	-1.255339
C	-1.016399	-0.110487	-1.883163
C	1.378279	-0.553143	-1.548489
H	-2.282107	0.618813	0.333769
H	-1.564154	-1.489653	1.826119
H	0.964500	-1.228811	2.458499
H	-1.783501	0.655000	-1.886518
H	2.310746	-0.399671	-1.018111
H	1.390225	-1.287271	-2.349937
H	-1.117625	-0.878219	-2.649253
H	1.001874	1.477943	1.885927
H	2.037031	0.555436	0.802882
H	-0.119782	2.021438	-0.199887

E(UB+HF+LYP) = -310.729228; S**2 = 0.4469
(6,6)CASPT2/6-31G(d) E = -309.665808

(6,6)CASSCF/6-31G(d) optimized parameters:

C	1.232397	0.295345	-0.601824
C	0.848586	-0.631541	-1.620877
C	-0.495831	-0.573577	-1.844827
C	-1.124360	0.554611	-1.054840
C	-0.044982	0.878827	0.002947
C	-0.157877	0.090232	1.300350
C	1.163569	-0.152853	1.838408
C	-1.270799	-0.494113	1.800266
H	2.197594	0.757628	-0.542431
H	1.532804	-1.281398	-2.134462
H	-1.034753	-1.167488	-2.559097
H	1.900801	0.626335	1.809634
H	-2.246245	-0.354473	1.376092
H	-1.210081	-1.135720	2.661555
H	1.308342	-0.901061	2.599684
H	-1.291961	1.412251	-1.704051
H	-2.083599	0.298509	-0.625448
H	0.022881	1.943828	0.200912

E = -308.700296
(6,6)CASPT2/6-31G(d) E = -309.662400



R(3,4) = 1.512 (1.514)
R(1,5) = 1.531 (1.529)
R(3,7) = 3.949 (4.062)
R(1,8) = 3.431 (3.558)
R(3,8) = 3.445 (3.727)
D(1,5,6,7) = +40.0° (+35.9°)
D(1,5,6,8) = -124.6° (-134.3°)

TS-22

UB3LYP/6-31G(d) optimized parameters:

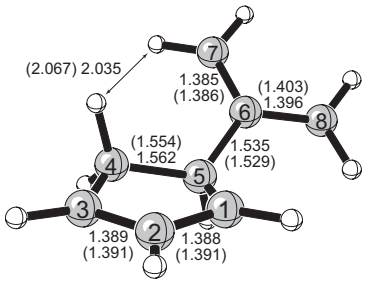
C	-1.205505	-0.102701	0.786576
C	-0.792325	-0.365400	2.085833
C	0.556911	-0.078501	2.247385
C	1.160937	0.319063	0.924479
C	-0.071941	0.512985	-0.014771
C	0.038516	0.022806	-1.465664
C	1.232375	-0.428249	-2.004203
C	-1.105888	0.092626	-2.262584
H	1.788848	1.217118	0.981739
H	1.813227	-0.490076	0.563819
H	-0.268162	1.597640	-0.084228
H	-2.206829	-0.247502	0.398517
H	-1.440483	-0.745996	2.870159
H	1.130458	-0.200963	3.159484
H	-2.049936	0.472929	-1.886231
H	2.157294	-0.470106	-1.442210
H	1.277775	-0.746204	-3.041959
H	-1.080668	-0.222603	-3.301398

E(UB+HF+LYP) = -310.742531; S**2 = 1.0613
(6,6)CASPT2/6-31G(d) E = -309.670574

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-1.188156	-0.186065	0.781750
C	-0.783926	-0.374505	2.099063
C	0.548328	-0.009889	2.259898
C	1.149884	0.335744	0.918144
C	-0.083761	0.490178	-0.013952
C	0.043280	0.022950	-1.464187
C	1.222228	-0.471249	-2.000365
C	-1.087925	0.159211	-2.283453
H	1.761873	1.231750	0.938103
H	1.792031	-0.479490	0.598887
H	-0.325120	1.552282	-0.060543
H	-2.175140	-0.360920	0.400708
H	-1.414896	-0.752137	2.882627
H	1.119501	-0.096274	3.164065
H	-2.007500	0.575337	-1.917135
H	2.128808	-0.568434	-1.438773
H	1.262677	-0.763612	-3.033740
H	-1.061954	-0.136750	-3.315586

E = -308.711241
(6,6)CASPT2/6-31G(d) E = -309.669880



R(3,4) = 1.508 (1.511)
R(1,5) = 1.519 (1.520)
R(1,7) = 3.720 (3.692)
R(3,7) = 4.319 (4.338)
R(1,8) = 3.057 (3.086)
R(3,8) = 4.810 (4.832)
D(1,5,6,7) = -129.8° (-124.6°)
D(1,5,6,8) = +52.7° (+57.8°)

TS-23n

UB3LYP/6-31G(d) optimized parameters:

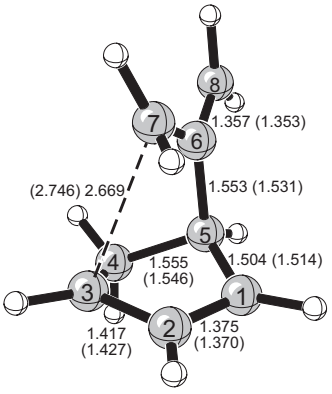
C	-0.439781	-1.212068	0.965057
C	0.371149	-0.522274	1.835239
C	0.384324	0.849820	1.482895
C	-0.819326	1.107439	0.620779
C	-0.909622	-0.264508	-0.104868
C	0.148915	-0.139278	-1.234133
C	1.495103	0.046154	-0.807112
C	-0.270057	-0.043236	-2.520806
H	-1.713676	1.267067	1.245819
H	-0.724993	1.949722	-0.069695
H	-1.890764	-0.493807	-0.528685
H	-0.604799	-2.283693	0.949835
H	0.976817	-0.967977	2.619063
H	0.961124	1.619330	1.983455
H	-1.324378	-0.090039	-2.780872
H	1.939159	-0.561497	-0.034051
H	2.184508	0.572429	-1.463714
H	0.432764	0.056172	-3.343465

E(UB+HF+LYP) = -310.733527; S**2 = 0.4748
(6,6)CASPT2/6-31G(d) E = -309.672434

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-0.401930	1.224736	-0.948863
C	0.378796	0.550434	-1.850533
C	0.375287	-0.841534	-1.534424
C	-0.824328	-1.089679	-0.657172
C	-0.886319	0.252915	0.105914
C	0.122360	0.127733	1.250862
C	1.500438	-0.101580	0.859370
C	-0.295297	0.048537	2.535349
H	-1.716492	-1.223711	-1.267884
H	-0.732417	-1.943550	0.002009
H	-1.869811	0.484455	0.496392
H	-0.527904	2.289179	-0.888949
H	0.968871	1.002605	-2.626540
H	0.873819	-1.601527	-2.105374
H	-1.333718	0.150301	2.796947
H	1.977393	0.524785	0.136568
H	2.150573	-0.614047	1.547296
H	0.395631	-0.097865	3.346513

E = -308.703655
(6,6)CASPT2/6-31G(d) E = -309.669851



R(3,4) = 1.503 (1.506)
R(6,7) = 1.424 (1.451)
R(1,7) = 2.910 (2.941)
R(1,8) = 3.681 (3.069)
R(3,8) = 4.154 (4.220)
D(1,5,6,7) = -46.3° (-49.1X°)
D(1,5,6,8) = +141.9° (+139.9°)

TS-23x

UB3LYP/6-31G(d) optimized parameters:

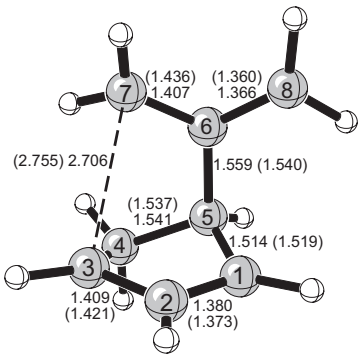
C	-1.402548	-0.061216	0.529270
C	-0.735223	-0.920078	1.377921
C	0.578622	-0.453709	1.580925
C	0.628417	0.986273	1.135108
C	-0.391254	0.923399	-0.019117
C	0.235708	0.122792	-1.200287
C	1.469668	-0.514484	-0.973555
C	-0.561707	-0.107022	-2.284876
H	0.244112	1.645500	1.929113
H	1.614699	1.360070	0.848388
H	-2.418264	-0.161706	0.165854
H	-1.135061	-1.844982	1.781638
H	1.323540	-0.928035	2.210269
H	-1.559665	0.316649	-2.357017
H	2.275453	-0.057527	-0.416724
H	1.733631	-1.392583	-1.557169
H	-0.210243	-0.679713	-3.138880
H	-0.798297	1.886601	-0.337802

E(UB+HF+LYP) = -310.732373; S**2 = 0.4694
(6,6)CASPT2/6-31G(d) E = -309.671412

(6,6)CASSCF/6-31G(d) optimized parameters:

C	-1.391643	-0.107748	0.617202
C	-0.677649	-0.900367	1.482172
C	0.644140	-0.392834	1.607954
C	0.624407	1.022044	1.079449
C	-0.426303	0.869866	-0.031303
C	0.181398	0.110680	-1.225338
C	1.441213	-0.548380	-1.024519
C	-0.577950	-0.096258	-2.334056
H	0.256576	1.702371	1.845529
H	1.578920	1.402128	0.740132
H	-2.389854	-0.285196	0.265596
H	-1.039628	-1.793325	1.956900
H	1.387294	-0.774637	2.282142
H	-1.555382	0.341590	-2.436540
H	2.262106	-0.068494	-0.534983
H	1.689934	-1.395423	-1.638832
H	-0.217938	-0.674790	-3.165882
H	-0.877708	1.803763	-0.343441

E = -308.700864
(6,6)CASPT2/6-31G(d) E = -309.668423



R(3,4) = 1.508 (1.510)
R(1,7) = 3.273 (3.304)
R(1,8) = 2.937 (3.061)
R(3,8) = 4.045 (4.138)
D(1,5,6,7) = -99.0° (-95.4°)
D(1,5,6,8) = +69.4° (+73.9°)

TS-ezP

UB3LYP/6-31G(d) optimized parameters:

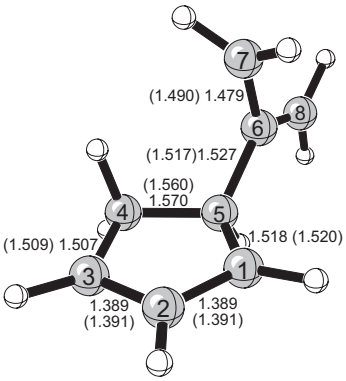
C	-1.032374	-0.650825	-0.791938
C	-0.778779	-0.134853	-2.056321
C	0.525506	0.333228	-2.154789
C	1.233216	0.185760	-0.832948
C	0.215048	-0.596644	0.070669
C	-0.013096	0.019945	1.448990
C	-0.572296	1.388888	1.494968
C	0.265648	-0.662833	2.566800
H	0.975362	0.779701	-3.034906
H	1.470309	1.169785	-0.400840
H	2.190777	-0.345236	-0.916449
H	0.588387	-1.620100	0.231509
H	-1.966949	-1.084917	-0.453622
H	-1.505133	-0.105720	-2.863796
H	-1.645664	1.555803	1.469198
H	0.065948	2.264762	1.412703
H	0.668676	-1.672973	2.530735
H	0.101047	-0.237101	3.552886

E(UB+HF+LYP) = -310.721068; S**2 = 1.0301
(6,6)CASPT2/6-31G(d) E = -309.650346

(6,6)CASSCF/6-31G(d) optimized parameters:

C	0.911785	-0.777338	0.803937
C	0.705277	-0.273978	2.083924
C	-0.509632	0.399836	2.159735
C	-1.161534	0.446471	0.799153
C	-0.307899	-0.529387	-0.067939
C	0.023918	-0.004821	-1.452046
C	0.959856	1.151073	-1.534333
C	-0.496180	-0.554940	-2.560765
H	-2.206844	0.154870	0.819002
H	-1.128550	1.456840	0.396624
H	-0.853813	-1.463973	-0.179823
H	1.748854	-1.371422	0.489834
H	1.391167	-0.389841	2.903096
H	-0.895540	0.901703	3.026073
H	-1.164850	-1.396854	-2.512215
H	2.016666	0.991293	-1.420579
H	0.603524	2.152251	-1.371826
H	-0.264153	-0.176353	-3.540179

E = -308.696358
(6,6)CASPT2/6-31G(d) E = -309.649611



R(6,8) = 1.339 (1.342)
R(1,7) = 3.099 (3.031)
R(3,7) = 3.955 (4.046)
R(1,8) = 3.601 (3.654)
R(3,8) = 4.833 (4.816)
D(1,5,6,7) = -56.8° (-49.3°)
D(1,5,6,8) = +122.3° (+130.5°)

TS-ezD

UB3LYP/6-31G(d) optimized parameters:

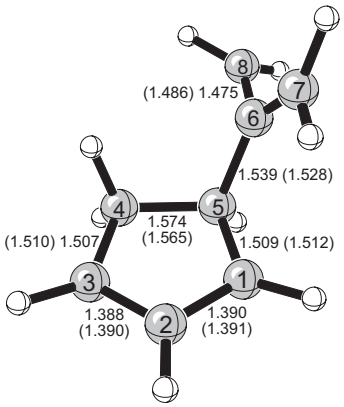
C	0.996253	0.644395	-0.937357
C	0.649842	0.008275	-2.123788
C	-0.647555	-0.482346	-2.070134
C	-1.267144	-0.183384	-0.729562
C	-0.148257	0.608229	0.045019
C	0.170625	-0.009509	1.418465
C	1.296944	-0.695337	1.646647
C	-0.852636	0.179245	2.463339
H	-1.154625	-1.025512	-2.860225
H	-1.541723	-1.106817	-0.200262
H	-2.192660	0.402413	-0.821299
H	-0.502518	1.632831	0.237179
H	1.942593	1.131119	-0.729539
H	1.306942	-0.084447	-2.984076
H	2.041306	-0.837879	0.867182
H	1.502769	-1.139762	2.616465
H	-1.728151	-0.463626	2.517280
H	-0.862368	1.074267	3.081521

E(UB+HF+LYP) = -310.721041; S**2 = 1.0125
(6,6)CASPT2/6-31G(d) E = -309.650906

(6,6)CASSCF/6-31G(d) optimized parameters:

C	1.007330	0.622090	-0.935603
C	0.650436	0.018578	-2.136928
C	-0.651943	-0.462712	-2.082422
C	-1.251799	-0.204119	-0.721347
C	-0.142896	0.591002	0.045329
C	0.170863	-0.005786	1.416387
C	1.296392	-0.686330	1.683332
C	-0.869914	0.182974	2.460057
H	-2.179593	0.357478	-0.785438
H	-1.485722	-1.137870	-0.216969
H	-0.489815	1.608674	0.214006
H	1.944313	1.102131	-0.729322
H	1.293870	-0.058302	-2.994258
H	-1.162266	-0.985494	-2.868210
H	2.056998	-0.843756	0.940606
H	-1.783273	-0.384241	2.412879
H	-0.918415	1.114690	2.996982
H	1.473086	-1.107498	2.656892

E = -308.695824
(6,6)CASPT2/6-31G(d) E = -309.649755



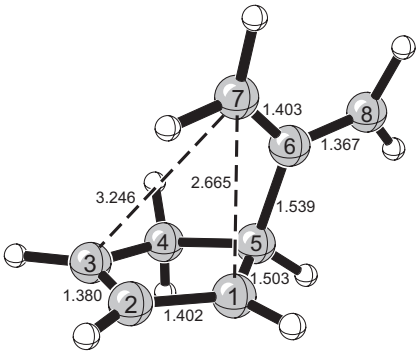
R(6,7) = 1.338 (1.342)
R(1,7) = 2.926 (2.942)
R(3,7) = 4.200 (4.246)
R(1,8) = 3.899 (3.905)
R(3,8) = 4.586 (4.593)
D(1,5,6,7) = -12.2° (-12.0°)
D(1,5,6,8) = +168.9° (+169.3°)

TS-1i3s

RB3LYP/6-31G(d) optimized parameters:

C	-0.516154	1.131464	0.674833
C	-0.721360	0.360623	1.827361
C	0.206932	-0.658283	1.898436
C	1.271405	-0.467806	0.854824
C	0.621100	0.555704	-0.121699
C	-0.073083	-0.104518	-1.325705
C	-1.242620	-0.808366	-1.001815
C	0.374135	0.132755	-2.595551
H	2.176754	-0.032443	1.310146
H	1.584425	-1.391128	0.355461
H	1.343186	1.294567	-0.478265
H	-1.063639	2.020484	0.387379
H	-1.541196	0.504388	2.525048
H	0.228972	-1.437359	2.653070
H	1.308735	0.653221	-2.779416
H	-1.563816	-0.977263	0.011137
H	-1.776943	-1.343145	-1.784883
H	-0.218609	-0.140767	-3.463784

E(RB+HF+LYP) = -310.723666
(6,6)CASPT2/6-31G(d) E = -309.672818



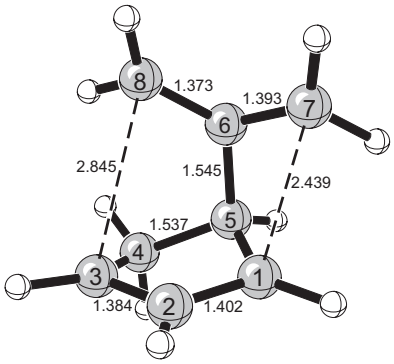
R(3,4) = 1.503
R(4,5) = 1.557
R(1,8) = 3.533
R(3,8) = 4.566
D(1,5,6,7) = -42.0°
D(1,5,6,8) = +131.3°

TS-3s3s

RB3LYP/6-31G(d) optimized parameters:

C	-1.366103	0.115072	0.291884
C	-0.915831	-0.895613	1.153478
C	0.375226	-0.618620	1.567204
C	0.701470	0.825565	1.265117
C	-0.176651	1.029528	0.020526
C	0.372408	0.193443	-1.157612
C	-0.666071	-0.114828	-2.033361
C	1.535047	-0.524526	-1.028572
H	0.364519	1.477985	2.086387
H	1.760820	1.037891	1.097654
H	-2.389408	0.310411	0.001766
H	-1.468612	-1.797927	1.394375
H	0.974915	-1.253210	2.211165
H	-1.525056	0.537081	-2.134669
H	2.358877	-0.201239	-0.407055
H	1.719906	-1.382970	-1.669150
H	-0.537237	-0.854399	-2.822669
H	-0.415703	2.066244	-0.229789

E(RB+HF+LYP) = -310.726729
(6,6)CASPT2/6-31G(d) E = -309.666700



R(3,4) = 1.511
R(1,5) = 1.525
R(1,8) = 3.251
R(3,7) = 3.782
D(1,5,6,7) = +47.7°
D(1,5,6,8) = -109.5°

Table S5. Raw data for (6,6)CASPT2/6-31G(d) // UB3LYP/6-31G(d) potential energy surface plot in Figure 4. Absolute energies are listed in a.u.; relative energies are listed in kcal/mol relative to **1** (E_{ele}(B3LYP) = –310.799382; E_{ele} (CASPT2) = –309.731718).

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.25	2.45	-310.723734	47.470	-309.662346	43.532
2.25	2.50	-310.724268	47.135	-309.662666	43.331
2.25	2.55	-310.724941	46.712	-309.663074	43.074
2.25	2.60	-310.725717	46.226	-309.663575	42.760
2.25	2.65	-310.726556	45.699	-309.664139	42.406
2.25	2.70	-310.727425	45.153	-309.664751	42.022
2.25	2.75	-310.728294	44.608	-309.665379	41.629
2.25	2.80	-310.729143	44.076	-309.666007	41.234
2.25	2.85	-310.729959	43.563	-309.666614	40.853
2.25	2.90	-310.730737	43.075	-309.667183	40.496
2.25	2.95	-310.731470	42.616	-309.667706	40.168
2.25	3.00	-310.732148	42.190	-309.668174	39.875
2.25	3.05	-310.732758	41.807	-309.668585	39.617
2.25	3.10	-310.733295	41.470	-309.668938	39.395
2.25	3.15	-310.733763	41.177	-309.669235	39.208
2.25	3.20	-310.734169	40.922	-309.669478	39.056
2.25	3.25	-310.734517	40.704	-309.669674	38.933
2.25	3.30	-310.734808	40.521	-309.669810	38.848
2.25	3.35	-310.735043	40.374	-309.669899	38.792
2.25	3.40	-310.735222	40.261	-309.669953	38.758
2.25	3.45	-310.735348	40.182	-309.669963	38.752
2.25	3.50	-310.735430	40.131	-309.669933	38.771
2.25	3.55	-310.735473	40.103	-309.669870	38.810
2.25	3.60	-310.735483	40.097	-309.669766	38.875
2.25	3.65	-310.735457	40.114	-309.669629	38.961
2.25	3.70	-310.735389	40.156	-309.669464	39.065
2.25	3.75	-310.735278	40.226	-309.669269	39.187
2.25	3.80	-310.735127	40.320	-309.669044	39.329
2.25	3.85	-310.734947	40.434	-309.668807	39.477
2.25	3.90	-310.734743	40.561	-309.668548	39.640
2.30	2.45	-310.724613	46.918	-309.663423	42.856
2.30	2.50	-310.724774	46.817	-309.663537	42.784
2.30	2.55	-310.725089	46.620	-309.663730	42.663
2.30	2.60	-310.725523	46.347	-309.663989	42.501
2.30	2.65	-310.726042	46.022	-309.664305	42.302
2.30	2.70	-310.726612	45.664	-309.664666	42.076
2.30	2.75	-310.727207	45.291	-309.665060	41.829
2.30	2.80	-310.727804	44.916	-309.665453	41.582
2.30	2.85	-310.728392	44.547	-309.665853	41.331
2.30	2.90	-310.728958	44.192	-309.666224	41.098
2.30	2.95	-310.729496	43.854	-309.666573	40.879
2.30	3.00	-310.729990	43.544	-309.666874	40.690
2.30	3.05	-310.730430	43.268	-309.667137	40.525
2.30	3.10	-310.730807	43.031	-309.667349	40.392
2.30	3.15	-310.731127	42.830	-309.667521	40.284
2.30	3.20	-310.731395	42.663	-309.667638	40.211
2.30	3.25	-310.731615	42.524	-309.667724	40.157
2.30	3.30	-310.731786	42.417	-309.667758	40.135
2.30	3.35	-310.731908	42.340	-309.667748	40.142
2.30	3.40	-310.731979	42.296	-309.667699	40.172
2.30	3.45	-310.732000	42.283	-309.667618	40.223
2.30	3.50	-310.731975	42.298	-309.667493	40.302
2.30	3.55	-310.731916	42.336	-309.667353	40.390
2.30	3.60	-310.731827	42.392	-309.667176	40.501
2.30	3.65	-310.731707	42.466	-309.666955	40.639
2.30	3.70	-310.731554	42.563	-309.666712	40.792
2.30	3.75	-310.731362	42.683	-309.666442	40.961
2.30	3.80	-310.731134	42.827	-309.666140	41.151
2.30	3.85	-310.730872	42.990	-309.665814	41.355
2.30	3.90	-310.730586	43.170	-309.665475	41.568
2.35	2.45	-310.725888	46.118	-309.664727	42.037
2.35	2.50	-310.725723	46.222	-309.664655	42.083
2.35	2.55	-310.725718	46.225	-309.664697	42.056
2.35	2.60	-310.725841	46.147	-309.664796	41.994
2.35	2.65	-310.726062	46.009	-309.664941	41.903
2.35	2.70	-310.726349	45.829	-309.665125	41.788
2.35	2.75	-310.726678	45.622	-309.665335	41.656
2.35	2.80	-310.727030	45.401	-309.665557	41.516
2.35	2.85	-310.727389	45.176	-309.665780	41.377
2.35	2.90	-310.727743	44.954	-309.665990	41.245
2.35	2.95	-310.728081	44.742	-309.666180	41.125
2.35	3.00	-310.728398	44.543	-309.666357	41.015
2.35	3.05	-310.728694	44.358	-309.666508	40.920
2.35	3.10	-310.728957	44.192	-309.666620	40.850
2.35	3.15	-310.729185	44.049	-309.666691	40.805
2.35	3.20	-310.729379	43.927	-309.666720	40.787
2.35	3.25	-310.729541	43.826	-309.666718	40.788
2.35	3.30	-310.729668	43.746	-309.666651	40.830
2.35	3.35	-310.729758	43.690	-309.666564	40.885
2.35	3.40	-310.729807	43.659	-309.666448	40.957
2.35	3.45	-310.729810	43.657	-309.666287	41.059
2.35	3.50	-310.729770	43.682	-309.666086	41.185
2.35	3.55	-310.729694	43.730	-309.665858	41.328
2.35	3.60	-310.729584	43.799	-309.665597	41.492
2.35	3.65	-310.729443	43.887	-309.665312	41.670
2.35	3.70	-310.729270	43.996	-309.664986	41.875
2.35	3.75	-310.729062	44.126	-309.664628	42.100
2.35	3.80	-310.728818	44.280	-309.664231	42.349
2.35	3.85	-310.728539	44.455	-309.663829	42.601
2.35	3.90	-310.728228	44.650	-309.663385	42.880
2.40	2.45	-310.727399	45.170	-309.666140	41.151
2.40	2.50	-310.726955	45.448	-309.665921	41.289
2.40	2.55	-310.726675	45.624	-309.665819	41.352
2.40	2.60	-310.726529	45.716	-309.665796	41.367
2.40	2.65	-310.726487	45.742	-309.665823	41.350
2.40	2.70	-310.726523	45.720	-309.665887	41.310
2.40	2.75	-310.726613	45.663	-309.665977	41.253
2.40	2.80	-310.726739	45.584	-309.666085	41.185
2.40	2.85	-310.726923	45.469	-309.666223	41.099
2.40	2.90	-310.727179	45.308	-309.666351	41.018
2.40	2.95	-310.727473	45.124	-309.666457	40.952
2.40	3.00	-310.727774	44.935	-309.666543	40.898
2.40	3.05	-310.728059	44.756	-309.666592	40.867
2.40	3.10	-310.728317	44.594	-309.666611	40.855
2.40	3.15	-310.728543	44.452	-309.666598	40.863
2.40	3.20	-310.728738	44.330	-309.666543	40.898
2.40	3.25	-310.728904	44.225	-309.666457	40.952
2.40	3.30	-310.729040	44.140	-309.666335	41.028
2.40	3.35	-310.729143	44.076	-309.666180	41.126
2.40	3.40	-310.729207	44.035	-309.665991	41.244
2.40	3.45	-310.729229	44.022	-309.665775	41.380
2.40	3.50	-310.729209	44.034	-309.665522	41.538
2.40	3.55	-310.729151	44.070	-309.665243	41.713
2.40	3.60	-310.729059	44.128	-309.664930	41.910
2.40	3.65	-310.728935	44.206	-309.664584	42.127
2.40	3.70	-310.728781	44.303	-309.664209	42.362
2.40	3.75	-310.728596	44.419	-309.663806	42.615
2.40	3.80	-310.728379	44.555	-309.663375	42.886
2.40	3.85	-310.728127	44.713	-309.662918	43.173
2.40	3.90	-310.727842	44.892	-309.662444	43.470
2.45	2.45	-310.728998	44.167	-309.667626	40.218

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.45	2.50	-310.728320	44.592	-309.667243	40.459
2.45	2.55	-310.727809	44.913	-309.667005	40.608
2.45	2.60	-310.727435	45.147	-309.666867	40.695
2.45	2.65	-310.727172	45.313	-309.666800	40.737
2.45	2.70	-310.726994	45.424	-309.666782	40.748
2.45	2.75	-310.726897	45.485	-309.666805	40.733
2.45	2.80	-310.726958	45.446	-309.666876	40.689
2.45	2.85	-310.727143	45.331	-309.666945	40.646
2.45	2.90	-310.727405	45.166	-309.666997	40.613
2.45	2.95	-310.727711	44.974	-309.667032	40.591
2.45	3.00	-310.728027	44.776	-309.667047	40.582
2.45	3.05	-310.728331	44.585	-309.667039	40.587
2.45	3.10	-310.728609	44.411	-309.667003	40.609
2.45	3.15	-310.728858	44.254	-309.666940	40.649
2.45	3.20	-310.729079	44.116	-309.666843	40.709
2.45	3.25	-310.729268	43.997	-309.666730	40.781
2.45	3.30	-310.729434	43.893	-309.666565	40.884
2.45	3.35	-310.729569	43.809	-309.666382	40.999
2.45	3.40	-310.729668	43.746	-309.666174	41.130
2.45	3.45	-310.729731	43.707	-309.665925	41.286
2.45	3.50	-310.729753	43.693	-309.665661	41.451
2.45	3.55	-310.729736	43.703	-309.665369	41.634
2.45	3.60	-310.729686	43.735	-309.665053	41.833
2.45	3.65	-310.729607	43.784	-309.664700	42.054
2.45	3.70	-310.729500	43.851	-309.664323	42.291
2.45	3.75	-310.729368	43.934	-309.663931	42.537
2.45	3.80	-310.729208	44.035	-309.663510	42.801
2.45	3.85	-310.729018	44.154	-309.663067	43.079
2.45	3.90	-310.728797	44.293	-309.662605	43.369
2.50	2.45	-310.730587	43.170	-309.669088	39.301
2.50	2.50	-310.729708	43.721	-309.668550	39.639
2.50	2.55	-310.729001	44.165	-309.668180	39.871
2.50	2.60	-310.728436	44.519	-309.667936	40.024
2.50	2.65	-310.727987	44.801	-309.667778	40.123
2.50	2.70	-310.727649	45.013	-309.667751	40.140
2.50	2.75	-310.727533	45.086	-309.667754	40.138
2.50	2.80	-310.727607	45.039	-309.667756	40.137
2.50	2.85	-310.727813	44.910	-309.667756	40.137
2.50	2.90	-310.728102	44.729	-309.667754	40.138
2.50	2.95	-310.728439	44.518	-309.667757	40.136
2.50	3.00	-310.728787	44.299	-309.667723	40.157
2.50	3.05	-310.729125	44.087	-309.667684	40.182
2.50	3.10	-310.729441	43.889	-309.667627	40.218
2.50	3.15	-310.729726	43.710	-309.667548	40.268
2.50	3.20	-310.729984	43.548	-309.667434	40.339
2.50	3.25	-310.730213	43.404	-309.667291	40.429
2.50	3.30	-310.730417	43.276	-309.667126	40.532
2.50	3.35	-310.730593	43.166	-309.666953	40.640
2.50	3.40	-310.730735	43.076	-309.666741	40.774
2.50	3.45	-310.730842	43.009	-309.666505	40.922
2.50	3.50	-310.730912	42.965	-309.666252	41.081
2.50	3.55	-310.730947	42.944	-309.665959	41.264
2.50	3.60	-310.730948	42.943	-309.665661	41.451
2.50	3.65	-310.730924	42.958	-309.665358	41.641
2.50	3.70	-310.730874	42.989	-309.665020	41.854
2.50	3.75	-310.730805	43.033	-309.664663	42.078
2.50	3.80	-310.730714	43.090	-309.664286	42.314
2.50	3.85	-310.730601	43.161	-309.663894	42.560
2.50	3.90	-310.730466	43.246	-309.663494	42.811
2.55	2.45	-310.732089	42.227	-309.670485	38.424
2.55	2.50	-310.731036	42.888	-309.669802	38.853
2.55	2.55	-310.730163	43.436	-309.669310	39.162
2.55	2.60	-310.729437	43.891	-309.668965	39.378
2.55	2.65	-310.728835	44.269	-309.668731	39.525

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.55	2.70	-310.728459	44.505	-309.668691	39.550
2.55	2.75	-310.728361	44.566	-309.668647	39.578
2.55	2.80	-310.728463	44.502	-309.668611	39.600
2.55	2.85	-310.728702	44.352	-309.668582	39.619
2.55	2.90	-310.729030	44.146	-309.668549	39.639
2.55	2.95	-310.729406	43.911	-309.668526	39.654
2.55	3.00	-310.729796	43.666	-309.668473	39.687
2.55	3.05	-310.730177	43.427	-309.668419	39.721
2.55	3.10	-310.730535	43.202	-309.668350	39.764
2.55	3.15	-310.730864	42.996	-309.668261	39.820
2.55	3.20	-310.731163	42.808	-309.668150	39.890
2.55	3.25	-310.731433	42.639	-309.668027	39.967
2.55	3.30	-310.731677	42.486	-309.667876	40.062
2.55	3.35	-310.731893	42.350	-309.667703	40.170
2.55	3.40	-310.732079	42.233	-309.667515	40.288
2.55	3.45	-310.732231	42.138	-309.667303	40.421
2.55	3.50	-310.732349	42.064	-309.667080	40.561
2.55	3.55	-310.732432	42.012	-309.666835	40.715
2.55	3.60	-310.732484	41.979	-309.666576	40.877
2.55	3.65	-310.732509	41.963	-309.666300	41.050
2.55	3.70	-310.732513	41.961	-309.666012	41.231
2.55	3.75	-310.732503	41.967	-309.665710	41.421
2.55	3.80	-310.732481	41.981	-309.665397	41.617
2.55	3.85	-310.732446	42.003	-309.665080	41.816
2.55	3.90	-310.732402	42.031	-309.664746	42.026
2.60	2.45	-310.733465	41.364	-309.671733	37.641
2.60	2.50	-310.732258	42.121	-309.670917	38.153
2.60	2.55	-310.731235	42.763	-309.670324	38.525
2.60	2.60	-310.730371	43.305	-309.669895	38.794
2.60	2.65	-310.729672	43.743	-309.669665	38.939
2.60	2.70	-310.729313	43.969	-309.669556	39.008
2.60	2.75	-310.729240	44.015	-309.669467	39.063
2.60	2.80	-310.729375	43.930	-309.669393	39.110
2.60	2.85	-310.729655	43.754	-309.669344	39.140
2.60	2.90	-310.730025	43.522	-309.669279	39.181
2.60	2.95	-310.730445	43.258	-309.669259	39.194
2.60	3.00	-310.730879	42.987	-309.669185	39.240
2.60	3.05	-310.731306	42.719	-309.669136	39.271
2.60	3.10	-310.731710	42.465	-309.669083	39.304
2.60	3.15	-310.732081	42.232	-309.669020	39.344
2.60	3.20	-310.732420	42.019	-309.668912	39.411
2.60	3.25	-310.732731	41.824	-309.668802	39.481
2.60	3.30	-310.733012	41.648	-309.668671	39.563
2.60	3.35	-310.733265	41.489	-309.668522	39.656
2.60	3.40	-310.733488	41.349	-309.668361	39.757
2.60	3.45	-310.733680	41.228	-309.668178	39.872
2.60	3.50	-310.733839	41.129	-309.667983	39.994
2.60	3.55	-310.733965	41.050	-309.667782	40.120
2.60	3.60	-310.734060	40.990	-309.667566	40.256
2.60	3.65	-310.734129	40.947	-309.667328	40.406
2.60	3.70	-310.734178	40.916	-309.667089	40.555
2.60	3.75	-310.734217	40.892	-309.666844	40.709
2.60	3.80	-310.734252	40.870	-309.666598	40.863
2.60	3.85	-310.734284	40.849	-309.666356	41.015
2.60	3.90	-310.734322	40.826	-309.666106	41.172
2.65	2.45	-310.734687	40.597	-309.672847	36.942
2.65	2.50	-310.733338	41.443	-309.671912	37.529
2.65	2.55	-310.732185	42.167	-309.671199	37.976
2.65	2.60	-310.731194	42.788	-309.670673	38.306
2.65	2.65	-310.730463	43.247	-309.670417	38.467
2.65	2.70	-310.730120	43.462	-309.670281	38.552
2.65	2.75	-310.730077	43.489	-309.670163	38.626
2.65	2.80	-310.730250	43.381	-309.670066	38.687
2.65	2.85	-310.730572	43.179	-309.669995	38.732

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.65	2.90	-310.730987	42.919	-309.669935	38.769
2.65	2.95	-310.731451	42.627	-309.669887	38.799
2.65	3.00	-310.731931	42.326	-309.669845	38.826
2.65	3.05	-310.732403	42.030	-309.669801	38.853
2.65	3.10	-310.732852	41.748	-309.669748	38.886
2.65	3.15	-310.733268	41.487	-309.669683	38.928
2.65	3.20	-310.733648	41.248	-309.669602	38.978
2.65	3.25	-310.733991	41.034	-309.669531	39.023
2.65	3.30	-310.734305	40.836	-309.669401	39.104
2.65	3.35	-310.734588	40.659	-309.669291	39.173
2.65	3.40	-310.734840	40.500	-309.669158	39.257
2.65	3.45	-310.735063	40.361	-309.669008	39.351
2.65	3.50	-310.735256	40.240	-309.668867	39.440
2.65	3.55	-310.735417	40.139	-309.668689	39.551
2.65	3.60	-310.735547	40.057	-309.668497	39.672
2.65	3.65	-310.735650	39.992	-309.668304	39.793
2.65	3.70	-310.735732	39.941	-309.668110	39.915
2.65	3.75	-310.735805	39.895	-309.667922	40.032
2.65	3.80	-310.735879	39.849	-309.667727	40.155
2.65	3.85	-310.735959	39.798	-309.667550	40.266
2.65	3.90	-310.736064	39.733	-309.667398	40.361
2.70	2.45	-310.735749	39.930	-309.673781	36.356
2.70	2.50	-310.734269	40.859	-309.672736	37.012
2.70	2.55	-310.732988	41.663	-309.671921	37.523
2.70	2.60	-310.731886	42.355	-309.671357	37.877
2.70	2.65	-310.731155	42.813	-309.671073	38.055
2.70	2.70	-310.730832	43.016	-309.670861	38.189
2.70	2.75	-310.730819	43.024	-309.670716	38.280
2.70	2.80	-310.731030	42.891	-309.670588	38.360
2.70	2.85	-310.731394	42.663	-309.670506	38.411
2.70	2.90	-310.731853	42.375	-309.670445	38.450
2.70	2.95	-310.732362	42.056	-309.670405	38.474
2.70	3.00	-310.732887	41.726	-309.670376	38.493
2.70	3.05	-310.733404	41.402	-309.670344	38.513
2.70	3.10	-310.733897	41.092	-309.670314	38.532
2.70	3.15	-310.734355	40.805	-309.670275	38.556
2.70	3.20	-310.734774	40.542	-309.670216	38.593
2.70	3.25	-310.735151	40.305	-309.670137	38.643
2.70	3.30	-310.735492	40.092	-309.670074	38.682
2.70	3.35	-310.735799	39.899	-309.669982	38.740
2.70	3.40	-310.736073	39.727	-309.669872	38.809
2.70	3.45	-310.736318	39.573	-309.669754	38.883
2.70	3.50	-310.736534	39.438	-309.669626	38.963
2.70	3.55	-310.736719	39.322	-309.669461	39.067
2.70	3.60	-310.736876	39.223	-309.669306	39.164
2.70	3.65	-310.737005	39.142	-309.669146	39.264
2.70	3.70	-310.737111	39.076	-309.668981	39.368
2.70	3.75	-310.737202	39.018	-309.668824	39.467
2.70	3.80	-310.737292	38.962	-309.668678	39.558
2.70	3.85	-310.737394	38.898	-309.668552	39.637
2.70	3.90	-310.737528	38.814	-309.668487	39.678
2.75	2.45	-310.736644	39.369	-309.674582	35.853
2.75	2.50	-310.735036	40.378	-309.673382	36.607
2.75	2.55	-310.733638	41.255	-309.672478	37.174
2.75	2.60	-310.732454	41.998	-309.671863	37.560
2.75	2.65	-310.731725	42.455	-309.671533	37.767
2.75	2.70	-310.731418	42.648	-309.671273	37.930
2.75	2.75	-310.731434	42.638	-309.671106	38.035
2.75	2.80	-310.731683	42.481	-309.670970	38.120
2.75	2.85	-310.732089	42.227	-309.670874	38.180
2.75	2.90	-310.732592	41.911	-309.670796	38.229
2.75	2.95	-310.733146	41.564	-309.670781	38.239
2.75	3.00	-310.733716	41.206	-309.670752	38.257
2.75	3.05	-310.734277	40.854	-309.670752	38.257
2.75	3.10	-310.734813	40.518	-309.670732	38.270
2.75	3.15	-310.735312	40.205	-309.670723	38.275
2.75	3.20	-310.735767	39.919	-309.670683	38.300
2.75	3.25	-310.736178	39.661	-309.670650	38.321
2.75	3.30	-310.736545	39.431	-309.670593	38.357
2.75	3.35	-310.736872	39.226	-309.670520	38.402
2.75	3.40	-310.737162	39.043	-309.670434	38.456
2.75	3.45	-310.737421	38.881	-309.670345	38.512
2.75	3.50	-310.737648	38.738	-309.670218	38.592
2.75	3.55	-310.737849	38.613	-309.670105	38.663
2.75	3.60	-310.738020	38.505	-309.669958	38.755
2.75	3.65	-310.738167	38.413	-309.669818	38.843
2.75	3.70	-310.738289	38.337	-309.669672	38.934
2.75	3.75	-310.738390	38.273	-309.669516	39.032
2.75	3.80	-310.738481	38.216	-309.669379	39.118
2.75	3.85	-310.738576	38.157	-309.669288	39.175
2.75	3.90	-310.738705	38.076	-309.669253	39.197
2.80	2.45	-310.737379	38.907	-309.675180	35.478
2.80	2.50	-310.735649	39.993	-309.673907	36.277
2.80	2.55	-310.734133	40.944	-309.672889	36.915
2.80	2.60	-310.732887	41.726	-309.672246	37.319
2.80	2.65	-310.732156	42.185	-309.671818	37.588
2.80	2.70	-310.731866	42.367	-309.671552	37.754
2.80	2.75	-310.731910	42.339	-309.671332	37.893
2.80	2.80	-310.732198	42.159	-309.671182	37.987
2.80	2.85	-310.732647	41.877	-309.671080	38.051
2.80	2.90	-310.733195	41.533	-309.671018	38.090
2.80	2.95	-310.733794	41.157	-309.670997	38.103
2.80	3.00	-310.734408	40.772	-309.671002	38.100
2.80	3.05	-310.735013	40.392	-309.671011	38.094
2.80	3.10	-310.735590	40.030	-309.671025	38.086
2.80	3.15	-310.736129	39.692	-309.671040	38.076
2.80	3.20	-310.736620	39.384	-309.671034	38.080
2.80	3.25	-310.737062	39.106	-309.671023	38.087
2.80	3.30	-310.737455	38.860	-309.670990	38.108
2.80	3.35	-310.737802	38.642	-309.670935	38.142
2.80	3.40	-310.738106	38.451	-309.670879	38.177
2.80	3.45	-310.738373	38.283	-309.670790	38.233
2.80	3.50	-310.738607	38.137	-309.670696	38.292
2.80	3.55	-310.738812	38.008	-309.670588	38.359
2.80	3.60	-310.738988	37.898	-309.670467	38.436
2.80	3.65	-310.739140	37.802	-309.670330	38.522
2.80	3.70	-310.739269	37.722	-309.670187	38.612
2.80	3.75	-310.739375	37.655	-309.670037	38.705
2.80	3.80	-310.739463	37.600	-309.669898	38.793
2.80	3.85	-310.739538	37.553	-309.669774	38.870
2.80	3.90	-310.739624	37.499	-309.669710	38.910
2.85	2.45	-310.737961	38.542	-309.675679	35.165
2.85	2.50	-310.736106	39.706	-309.674256	36.058
2.85	2.55	-310.734479	40.727	-309.673141	36.758
2.85	2.60	-310.733185	41.539	-309.672452	37.190
2.85	2.65	-310.732449	42.001	-309.671997	37.476
2.85	2.70	-310.732171	42.176	-309.671653	37.691
2.85	2.75	-310.732245	42.129	-309.671404	37.848
2.85	2.80	-310.732572	41.924	-309.671236	37.953
2.85	2.85	-310.733066	41.614	-309.671127	38.022
2.85	2.90	-310.733662	41.240	-309.671076	38.053
2.85	2.95	-310.734308	40.834	-309.671070	38.057
2.85	3.00	-310.734968	40.420	-309.671096	38.041
2.85	3.05	-310.735616	40.014	-309.671136	38.016
2.85	3.10	-310.736234	39.626	-309.671179	37.989
2.85	3.15	-310.736812	39.263	-309.671230	37.957
2.85	3.20	-310.737339	38.933	-309.671253	37.942
2.85	3.25	-310.737812	38.636	-309.671265	37.935

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.85	3.30	-310.738231	38.373	-309.671258	37.939
2.85	3.35	-310.738598	38.143	-309.671232	37.955
2.85	3.40	-310.738916	37.943	-309.671187	37.984
2.85	3.45	-310.739191	37.771	-309.671118	38.027
2.85	3.50	-310.739428	37.621	-309.671046	38.072
2.85	3.55	-310.739632	37.494	-309.670942	38.138
2.85	3.60	-310.739806	37.385	-309.670823	38.212
2.85	3.65	-310.739952	37.293	-309.670682	38.301
2.85	3.70	-310.740076	37.215	-309.670556	38.380
2.85	3.75	-310.740179	37.151	-309.670408	38.473
2.85	3.80	-310.740261	37.099	-309.670252	38.570
2.85	3.85	-310.740324	37.060	-309.670117	38.655
2.85	3.90	-310.740375	37.028	-309.669972	38.746
2.90	2.45	-310.738398	38.268	-309.676043	34.937
2.90	2.50	-310.736425	39.506	-309.674522	35.891
2.90	2.55	-310.734683	40.599	-309.673284	36.668
2.90	2.60	-310.733350	41.436	-309.672512	37.153
2.90	2.65	-310.732605	41.903	-309.671978	37.487
2.90	2.70	-310.732338	42.070	-309.671594	37.729
2.90	2.75	-310.732440	42.007	-309.671322	37.899
2.90	2.80	-310.732809	41.775	-309.671137	38.015
2.90	2.85	-310.733353	41.434	-309.671037	38.078
2.90	2.90	-310.734001	41.027	-309.670988	38.109
2.90	2.95	-310.734699	40.589	-309.671005	38.098
2.90	3.00	-310.735408	40.144	-309.671060	38.063
2.90	3.05	-310.736100	39.710	-309.671143	38.012
2.90	3.10	-310.736760	39.296	-309.671222	37.962
2.90	3.15	-310.737376	38.909	-309.671310	37.907
2.90	3.20	-310.737938	38.557	-309.671373	37.867
2.90	3.25	-310.738442	38.241	-309.671416	37.840
2.90	3.30	-310.738887	37.961	-309.671438	37.826
2.90	3.35	-310.739275	37.718	-309.671437	37.827
2.90	3.40	-310.739608	37.509	-309.671412	37.843
2.90	3.45	-310.739892	37.331	-309.671362	37.874
2.90	3.50	-310.740132	37.180	-309.671289	37.920
2.90	3.55	-310.740334	37.053	-309.671196	37.978
2.90	3.60	-310.740502	36.948	-309.671086	38.047
2.90	3.65	-310.740639	36.862	-309.670950	38.132
2.90	3.70	-310.740752	36.791	-309.670800	38.226
2.90	3.75	-310.740842	36.735	-309.670653	38.319
2.90	3.80	-310.740911	36.691	-309.670492	38.420
2.90	3.85	-310.740961	36.660	-309.670323	38.526
2.90	3.90	-310.740993	36.640	-309.670174	38.619
2.95	2.45	-310.738703	38.077	-309.676292	34.780
2.95	2.50	-310.736611	39.390	-309.674644	35.815
2.95	2.55	-310.734759	40.552	-309.673309	36.652
2.95	2.60	-310.733390	41.411	-309.672447	37.193
2.95	2.65	-310.732630	41.888	-309.671842	37.573
2.95	2.70	-310.732372	42.050	-309.671405	37.847
2.95	2.75	-310.732505	41.966	-309.671088	38.046
2.95	2.80	-310.732919	41.706	-309.670906	38.160
2.95	2.85	-310.733519	41.330	-309.670792	38.232
2.95	2.90	-310.734225	40.886	-309.670770	38.245
2.95	2.95	-310.734980	40.413	-309.670817	38.216
2.95	3.00	-310.735741	39.935	-309.670910	38.158
2.95	3.05	-310.736481	39.471	-309.671033	38.080
2.95	3.10	-310.737185	39.029	-309.671157	38.002
2.95	3.15	-310.737839	38.619	-309.671286	37.922
2.95	3.20	-310.738435	38.245	-309.671393	37.855
2.95	3.25	-310.738970	37.909	-309.671478	37.801
2.95	3.30	-310.739442	37.613	-309.671536	37.765
2.95	3.35	-310.739852	37.356	-309.671564	37.747
2.95	3.40	-310.740202	37.136	-309.671563	37.748
2.95	3.45	-310.740496	36.951	-309.671534	37.766

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
2.95	3.50	-310.740741	36.798	-309.671477	37.802
2.95	3.55	-310.740941	36.672	-309.671410	37.844
2.95	3.60	-310.741104	36.570	-309.671294	37.916
2.95	3.65	-310.741233	36.489	-309.671163	37.999
2.95	3.70	-310.741333	36.426	-309.671021	38.088
2.95	3.75	-310.741409	36.379	-309.670863	38.187
2.95	3.80	-310.741464	36.344	-309.670691	38.295
2.95	3.85	-310.741499	36.322	-309.670514	38.406
2.95	3.90	-310.741517	36.311	-309.670338	38.517
3.00	2.45	-310.738892	37.958	-309.676463	34.673
3.00	2.50	-310.736679	39.347	-309.674676	35.795
3.00	2.55	-310.734722	40.575	-309.673246	36.692
3.00	2.60	-310.733311	41.460	-309.672289	37.292
3.00	2.65	-310.732530	41.950	-309.671581	37.736
3.00	2.70	-310.732278	42.108	-309.671081	38.050
3.00	2.75	-310.732445	42.004	-309.670738	38.266
3.00	2.80	-310.732910	41.712	-309.670521	38.402
3.00	2.85	-310.733574	41.295	-309.670439	38.453
3.00	2.90	-310.734348	40.810	-309.670427	38.461
3.00	2.95	-310.735167	40.296	-309.670516	38.405
3.00	3.00	-310.735986	39.781	-309.670659	38.315
3.00	3.05	-310.736779	39.284	-309.670843	38.200
3.00	3.10	-310.737528	38.814	-309.671021	38.088
3.00	3.15	-310.738222	38.379	-309.671219	37.964
3.00	3.20	-310.738853	37.982	-309.671343	37.886
3.00	3.25	-310.739418	37.628	-309.671494	37.791
3.00	3.30	-310.739916	37.315	-309.671596	37.727
3.00	3.35	-310.740349	37.044	-309.671662	37.686
3.00	3.40	-310.740717	36.813	-309.671692	37.667
3.00	3.45	-310.741025	36.619	-309.671687	37.670
3.00	3.50	-310.741278	36.461	-309.671651	37.693
3.00	3.55	-310.741482	36.333	-309.671585	37.734
3.00	3.60	-310.741642	36.233	-309.671491	37.793
3.00	3.65	-310.741765	36.155	-309.671370	37.869
3.00	3.70	-310.741857	36.098	-309.671237	37.952
3.00	3.75	-310.741923	36.056	-309.671084	38.048
3.00	3.80	-310.741968	36.028	-309.670916	38.154
3.00	3.85	-310.741993	36.012	-309.670746	38.261
3.00	3.90	-310.742003	36.006	-309.670575	38.368
3.05	2.45	-310.738982	37.901	-309.676550	34.619
3.05	2.50	-310.736645	39.368	-309.674626	35.826
3.05	2.55	-310.734584	40.661	-309.673076	36.798
3.05	2.60	-310.733122	41.579	-309.672012	37.466
3.05	2.65	-310.732312	42.087	-309.671207	37.971
3.05	2.70	-310.732064	42.243	-309.670638	38.328
3.05	2.75	-310.732267	42.115	-309.670257	38.567
3.05	2.80	-310.732795	41.784	-309.670032	38.708
3.05	2.85	-310.733530	41.323	-309.669955	38.757
3.05	2.90	-310.734381	40.789	-309.669978	38.743
3.05	2.95	-310.735273	40.229	-309.670118	38.655
3.05	3.00	-310.736161	39.672	-309.670321	38.527
3.05	3.05	-310.737014	39.137	-309.670572	38.370
3.05	3.10	-310.737813	38.635	-309.670820	38.214
3.05	3.15	-310.738550	38.172	-309.671067	38.059
3.05	3.20	-310.739218	37.754	-309.671286	37.922
3.05	3.25	-310.739814	37.380	-309.671475	37.803
3.05	3.30	-310.740338	37.051	-309.671628	37.707
3.05	3.35	-310.740793	36.765	-309.671742	37.636
3.05	3.40	-310.741182	36.521	-309.671812	37.592
3.05	3.45	-310.741506	36.318	-309.671844	37.572
3.05	3.50	-310.741772	36.151	-309.671836	37.576
3.05	3.55	-310.741985	36.017	-309.671795	37.603
3.05	3.60	-310.742151	35.913	-309.671727	37.645
3.05	3.65	-310.742276	35.835	-309.671630	37.706

R(1,7)	R(3,8)	E_{ele} UB3LYP		E_{ele} CASPT2	
		absolute	*rel.*	*absolute*	*rel.*
3.05	3.70	-310.742366	35.778	-309.671508	37.782
3.05	3.75	-310.742428	35.739	-309.671370	37.869
3.05	3.80	-310.742467	35.715	-309.671222	37.962
3.05	3.85	-310.742489	35.701	-309.671067	38.059
3.05	3.90	-310.742497	35.696	-309.670912	38.156
3.10	2.45	-310.738990	37.897	-309.676576	34.602
3.10	2.50	-310.736523	39.445	-309.674517	35.894
3.10	2.55	-310.734357	40.804	-309.672863	36.932
3.10	2.60	-310.732831	41.761	-309.671651	37.692
3.10	2.65	-310.731981	42.295	-309.670736	38.267
3.10	2.70	-310.731732	42.451	-309.670090	38.672
3.10	2.75	-310.731974	42.299	-309.669660	38.942
3.10	2.80	-310.732572	41.924	-309.669401	39.105
3.10	2.85	-310.733394	41.408	-309.669367	39.126
3.10	2.90	-310.734335	40.818	-309.669425	39.090
3.10	2.95	-310.735313	40.204	-309.669645	38.952
3.10	3.00	-310.736280	39.597	-309.669931	38.772
3.10	3.05	-310.737202	39.019	-309.670246	38.574
3.10	3.10	-310.738061	38.479	-309.670599	38.353
3.10	3.15	-310.738848	37.986	-309.670919	38.152
3.10	3.20	-310.739557	37.541	-309.671214	37.967
3.10	3.25	-310.740186	37.146	-309.671477	37.802
3.10	3.30	-310.740738	36.800	-309.671694	37.666
3.10	3.35	-310.741216	36.500	-309.671864	37.559
3.10	3.40	-310.741625	36.243	-309.671985	37.483
3.10	3.45	-310.741968	36.028	-309.672060	37.436
3.10	3.50	-310.742251	35.850	-309.672089	37.418
3.10	3.55	-310.742479	35.707	-309.672082	37.422
3.10	3.60	-310.742658	35.595	-309.672040	37.448
3.10	3.65	-310.742793	35.510	-309.671968	37.494
3.10	3.70	-310.742889	35.450	-309.671872	37.554
3.10	3.75	-310.742953	35.410	-309.671756	37.627
3.10	3.80	-310.742993	35.385	-309.671629	37.706
3.10	3.85	-310.743013	35.372	-309.671489	37.794
3.10	3.90	-310.743019	35.368	-309.671355	37.878
3.15	2.45	-310.738920	37.940	-309.676562	34.611
3.15	2.50	-310.736323	39.570	-309.674367	35.988
3.15	2.55	-310.734048	40.998	-309.672578	37.111
3.15	2.60	-310.732444	42.004	-309.671221	37.963
3.15	2.65	-310.731541	42.571	-309.670173	38.620
3.15	2.70	-310.731284	42.732	-309.669438	39.082
3.15	2.75	-310.731569	42.554	-309.668957	39.383
3.15	2.80	-310.732248	42.127	-309.668704	39.542
3.15	2.85	-310.733172	41.548	-309.668668	39.564
3.15	2.90	-310.734217	40.892	-309.668800	39.481
3.15	2.95	-310.735299	40.213	-309.669105	39.290
3.15	3.00	-310.736358	39.548	-309.669499	39.043
3.15	3.05	-310.737362	38.918	-309.669922	38.778
3.15	3.10	-310.738292	38.335	-309.670374	38.494
3.15	3.15	-310.739138	37.803	-309.670800	38.227
3.15	3.20	-310.739896	37.328	-309.671196	37.978
3.15	3.25	-310.740565	36.908	-309.671540	37.762
3.15	3.30	-310.741147	36.543	-309.671832	37.579
3.15	3.35	-310.741650	36.227	-309.672066	37.433
3.15	3.40	-310.742080	35.958	-309.672243	37.321
3.15	3.45	-310.742441	35.731	-309.672361	37.247
3.15	3.50	-310.742740	35.544	-309.672435	37.201
3.15	3.55	-310.742983	35.391	-309.672461	37.184
3.15	3.60	-310.743175	35.271	-309.672449	37.192
3.15	3.65	-310.743321	35.179	-309.672401	37.222
3.15	3.70	-310.743425	35.114	-309.672332	37.265
3.15	3.75	-310.743497	35.068	-309.672229	37.330
3.15	3.80	-310.743540	35.042	-309.672114	37.402
3.15	3.85	-310.743560	35.029	-309.671989	37.480
3.15	3.90	-310.743562	35.028	-309.671852	37.566
3.20	2.45	-310.738784	38.026	-309.676537	34.626
3.20	2.50	-310.736055	39.738	-309.674204	36.091
3.20	2.55	-310.733664	41.239	-309.672279	37.299
3.20	2.60	-310.731969	42.302	-309.670747	38.260
3.20	2.65	-310.730994	42.914	-309.669537	39.019
3.20	2.70	-310.730719	43.087	-309.668688	39.552
3.20	2.75	-310.731051	42.879	-309.668124	39.906
3.20	2.80	-310.731825	42.393	-309.667876	40.061
3.20	2.85	-310.732870	41.737	-309.667887	40.055
3.20	2.90	-310.734040	41.003	-309.668097	39.923
3.20	2.95	-310.735241	40.249	-309.668526	39.653
3.20	3.00	-310.736408	39.516	-309.669052	39.323
3.20	3.05	-310.737507	38.827	-309.669612	38.972
3.20	3.10	-310.738518	38.193	-309.670206	38.599
3.20	3.15	-310.739434	37.618	-309.670767	38.248
3.20	3.20	-310.740248	37.107	-309.671268	37.933
3.20	3.25	-310.740962	36.659	-309.671711	37.655
3.20	3.30	-310.741581	36.271	-309.672081	37.423
3.20	3.35	-310.742112	35.938	-309.672383	37.233
3.20	3.40	-310.742563	35.655	-309.672613	37.089
3.20	3.45	-310.742941	35.417	-309.672781	36.984
3.20	3.50	-310.743253	35.221	-309.672884	36.919
3.20	3.55	-310.743506	35.063	-309.672935	36.887
3.20	3.60	-310.743706	34.937	-309.672941	36.883
3.20	3.65	-310.743858	34.842	-309.672903	36.907
3.20	3.70	-310.743968	34.773	-309.672837	36.949
3.20	3.75	-310.744042	34.726	-309.672745	37.006
3.20	3.80	-310.744085	34.699	-309.672632	37.077
3.20	3.85	-310.744102	34.688	-309.672506	37.156
3.20	3.90	-310.744098	34.691	-309.672371	37.241

Mathematical Analysis

Relative yield of products at $t = 0$ can be computed based on three independent parameters related to k_{12n} vs. k_{12x}, and k_{23n} vs. k_{23x} vs. k_{22}. These parameters have been designated a, b, and c; they are defined in Equations S1 through S3. Table S6 lists expressions for the fractional yield for each reactant-product pair in terms of a, b, and c.

$$a = k_{12n} / (k_{12n} + k_{12x}) \tag{S1}$$

$$b = (k_{22} + k_{23n} + k_{23x}) / (2k_{22} + k_{23n} + k_{23x}) \tag{S2}$$

$$c = k_{23n} / (k_{23n} + k_{23x}) \tag{S3}$$

Table S6. Experimental fractional product yields (from Table 1) and the corresponding selectivity expressions derived from Scheme 2. Parameters a, b, and c are defined in Equations S1, S2, and S3.

Educt	Product	Kinetic Expression	Experiment	CASPT2[(a)]	Fit[(b)]
7*x*-**1**	6*x*-**3**	$abc + (1-a)(1-b)(1-c)$	0.37	0.39	0.33
	6*n*-**3**	$ab(1-c) + (1-a)(1-b)c$	0.20	0.25	0.28
	8*E*-**3**	$a(1-b)$	0.22	0.26	0.20
	8*Z*-**3**	$(1-a)b$	0.21	0.10	0.19
8*E*-**1**[(c)]	8*E*-**3**	$ab + (1-a)(1-b)$	0.63	0.64	0.62
	6*n*-**3**	$a(1-b)(1-c) + (1-a)b(1-c)$	0.23	0.13	0.17
	6*x*-**3**	$a(1-b)c + (1-a)bc$	0.14	0.23	0.21

(a) $a = 0.861$, $b = 0.692$, $c = 0.634$, based on CASPT2//UB3LYP: $\Delta\Delta H^{\ddagger}$(**TS-12x** – **TS-12n**) = 1.8; $\Delta\Delta H^{\ddagger}$(**TS-22** – **TS-23n**) = 0.4; $\Delta\Delta H^{\ddagger}$(**TS-23x** – **TS-23n**) = 0.5 kcal/mol.

(b) $a = 0.744$, $b = 0.735$, $c = 0.556$, based on best fit to experiment ($R^2 = 0.628$), whence: $\Delta\Delta G^{\ddagger}$(**TS-12x** – **TS-12n**) = 1.0; $\Delta\Delta G^{\ddagger}$(**TS-22** – **TS-23n**) = 0.7; $\Delta\Delta G^{\ddagger}$(**TS-23x** – **TS-23n**) = 0.2 kcal/mol.

(c) The 8*E*-**1** and 8*Z*-**1** experiments are redundant, excluding isotope effects. For this reason, they have been averaged for the purposes of comparison and fit to theory, so as to simplify the analysis and not to assign the two 8-*d*-**1** experiments undue weight as compared to the single 7-*d*-**1** experiment. For example, the entry for "8*E*-**1** → 6*n*-**3**" is actually the average of experimental proportion in which 8*E*-**1** forms 6*n*-**3**, and 8*Z*-**1** forms 6*x*-**3**.

Table S7. Experimental relative product yields (from Table 1) and the corresponding selectivity expressions derived from Scheme 2, plus an additional parameter d which reflects the k_{12x} partitioning represented in Figure 4b.

Educt	Product	Kinetic Expression	Experiment	Fit[(a)]
7*x*-**1**	6*x*-**3**	$abc + (1-a)(1-b)(1-c)(1-d)$	0.37	0.39
	6*n*-**3**	$ab(1-c) + (1-a)(1-b)c(1-d)$	0.20	0.22
	8*E*-**3**	$a(1-b)$	0.22	0.20
	8*Z*-**3**	$(1-a)b(1-d) + (1-a)d$	0.21	0.19
8*E*-**1**[(b)]	8*E*-**3**	$ab + (1-a)(1-b)(1-d)$	0.63	0.61
	6*n*-**3**	$a(1-b)(1-c) + (1-a)b(1-c)(1-d) + (1-a)d$	0.23	0.24
	6*x*-**3**	$a(1-b)c + (1-a)bc(1-d)$	0.14	0.15

(a) $a = 0.797$, $b = 0.748$, $c = 0.643$, $d = 0.808$, based on fit to experiment ($R^2 = 0.969$), whence: $\Delta\Delta G^{\ddagger}$(**TS-12x** – **TS-12n**) = 1.3; $\Delta\Delta G^{\ddagger}$(**TS-22** – **TS-23n**) = 0.9; $\Delta\Delta G^{\ddagger}$(**TS-23x** – **TS-23n**) = 0.6 kcal/mol.

(b) See Note (c) to Table S6.

Kinetic Isotope Effects

Table S8. Calculated kinetic isotope effects for individual reaction steps in the rearrangements of d_1-**1** to d_1-**3** (see Scheme 2), and d_2-**1** to d_2-**3**.

			k_H/k_D		
Rate	From	To	$\Delta\Delta H^{\ddagger}$ [(a)]	$\Delta\Delta G^{\ddagger}$ [(b)]	B-M[14]
k_{12n}	7*x*-**1**	P*e*-**2**	1.12	1.10	1.11
	7*n*-**1**	P*z*-**2**	1.08	1.06	1.06
	8*E*-**1**	D*e*-**2**	1.01	1.01	1.00
	8*Z*-**1**	D*z*-**2**	1.01	1.00	1.00
	7-d_2-**1**	P-d_2-**2**	1.22	1.17	1.18
	8-d_2-**1**	D-d_2-**2**	1.02	1.01	1.01
k_{12x}	7*x*-**1**	D*z*-**2**	1.08	1.04	1.04
	7*n*-**1**	D*e*-**2**	1.11	1.10	1.11
	8*E*-**1**	P*e*-**2**	1.01	1.01	0.99
	8*Z*-**1**	P*z*-**2**	1.00	1.00	1.01
	7-d_2-**1**	D-d_2-**2**	1.20	1.15	1.15
	8-d_2-**1**	P-d_2-**2**	1.02	1.00	1.00
k_{22}	P*e*-**2**	D*e*-**2**	0.99	1.00	1.01
	P*z*-**2**	D*z*-**2**	0.99	1.02	1.03
	D*e*-**2**	P*e*-**2**	0.99	1.01	1.01
	D*z*-**2**	P*z*-**2**	1.00	1.02	1.03
	P-d_2-**2**	D-d_2-**2**	0.98	1.02	1.03
	D-d_2-**2**	P-d_2-**2**	1.00	1.02	1.04
k_{23n}	P*e*-**2**	6*x*-**3**	1.00	1.05	1.06
	P*z*-**2**	6*n*-**3**	0.96	0.98	0.99
	D*e*-**2**	8*E*-**3**	0.96	0.99	0.99
	D*z*-**2**	8*Z*-**3**	0.97	0.98	0.99
	P-d_2-**2**	6-d_2-**3**	0.96	1.03	1.05
	D-d_2-**2**	8-d_2-**3**	0.95	0.97	0.97
k_{23x}	P*e*-**2**	6*n*-**3**	1.00	1.06	1.06
	P*z*-**2**	6*x*-**3**	0.98	0.99	1.00
	D*e*-**2**	8*E*-**3**	0.97	0.99	0.99
	D*z*-**2**	8*Z*-**3**	0.98	0.98	0.99
	P-d_2-**2**	6-d_2-**3**	0.98	1.05	1.06
	D-d_2-**2**	8-d_2-**3**	0.96	0.97	0.98

(a) $k_H/k_D = \exp[-(\Delta H^{\ddagger}_H - \Delta H^{\ddagger}_D)/RT]$.

(b) $k_H/k_D = \exp[-(\Delta G^{\ddagger}_H - \Delta G^{\ddagger}_D)/RT]$.

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