CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Stereoselective Synthesis of Cyclopropanes Based on a 1,2–Chirality Transfer

Olaf Muehling,[b] Pablo Wessig*[a]

[a] Humboldt University Berlin
Department of Chemistry
Brook–Taylor–Str. 2
D–12489 Berlin

[b] Fraunhofer Institute of Applied Polymer Science (IAP)
Volmerstr. 7B
D–12489 Berlin

1 Experimental Procedures – Product Characterization

1.1 General

THF and Et_2O were dried over Na metal in the presence of benzophenone as an indicator of dryness and distilled at atmospheric pressure. CH_2Cl_2 was dried by heating under reflux over P_2O_5 and distilled at atmospheric pressure. All moisture sensitive reagents were transferred *via* syringe under N_2 or Ar atmosphere; moisture–sensitive reactions were carried out under N_2 or Ar atmosphere. Flash column chromatography (FCC): silica gel (230 – 400 mesh, FLUKA), petroleum ether/ethyl acetate mixtures as mobile phase, "? " indicates a concentration gradient. Filter agents: Florisil (60 – 100 mesh magnesium silicate, ALDRICH), Celite (545, Kieselgur, ALDRICH). Analytical TLC: precoated MERCK silica gel 60 F_{254} plates; detection by UV light. Mp: BUECHI 530, uncorrected. NMR: $CDCl_3$ solutions; BRUKER DPX300 equipment; chemical shifts δ in ppm; calibration: ^{1}H: 0.00 ppm = Me_4Si or 7.24 ppm = C*H*Cl_3, ^{13}C: 77.0 ppm; abbreviations: cProp = cyclopropyl, cHex = cyclohexyl, Ts = toluene–4–sulfonyl, TsPip = 1–(toluene–4–sulfonyl)–piperidin–4–yl, *t*Bu = *tert*–butyl, Boc = *tert*–butyloxycarbonyl, BocPip = 1–(*tert*–butyloxycarbonyl)–piperidin–4–yl, THP = tetrahydro–*2H*–pyran–4–yl, 2–Ind = 2,3–dihydro–*1H*–indene–2–yl (indan-2-yl), br = broad, Cq = quaternary C–atom, ar = aromatic, ax = axial or pseudo axial, eq = equatorial or pseudo equatorial. 2D–NMR: H,H–Cosy – H,H–*Co*rrelated *S*pectroscop*y*, HSQC – *H*eteronuclear *S*ingle *Q*uantum *C*oherence. IR: PERKIN–ELMER–881, solids as KBr pastilles, liquids and oils on NaCl crystals as film, ν in cm^{-1}. MS(EI): HEWLETT–PACKARD 5995 A, 70 eV at 293 – 593 K, *m*/*z* (%). HRMS (EI): MSI CONCEPT 1H. HRMS (ESI): THERMO FINNEGAN LTQ FT. Elemental analyses (EA) were carried out by the Analytical Laboratory of the Department Of Chemistry, Humboldt University Berlin.

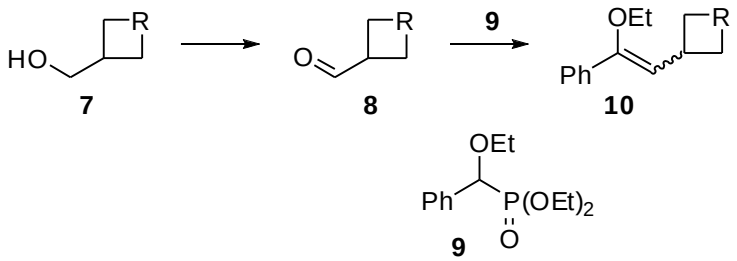
1.2 Commercially Available Compounds

The following compounds are commercially available and were used without further purification: (*N*–Boc–piperidin–4–yl)methanol (**7e**, ALDRICH); Methanesulfonamide ($MeSO_2NH_2$, LANCASTER); $(DHQD)_2$–PHAL (for AD–Mix–β, FLUKA); Potassium osmate(VI) dihydrate [$K_2OsO_2(OH)_4$, RIEDEL–DE HAEN].

1.3 Published Syntheses

The following compounds were prepared according to literature procedures: *trans*–(4–*tert*–butyl–cyclohexyl)–methanol (**7a**);[1] *cis*–(4–*tert*–butyl–cyclohexyl)–methanol (**7b**);[1,2] (tetrahydro–pyran–4–yl)–methanol (**7c**);[1] [1–(toluene–4–sulfonyl)–piperidin–4–yl]–methanol (**7d**);[1] indan–2–yl–methanol (**7f**);[1] 1,1,1–triacetoxy–1,1–dihydro–1,2–benziodoxol–3(1*H*)–one (Dess–Martin–periodinane);[3] pyridinium chlorochromate;[4] (Ethoxy–phenyl–methyl)–phosphonic acid diethyl ester (**9**);[5] toluene–4–sulfonic anhydride (Ts_2O).[6]

1.4 Preparation of Enol Ethers 10



7a–c,e,f ? **8a–c,e,f**: To an ice–cooled and magnetically stirred mixture of Dess–Martin–periodinane (1,1,1–Triacetoxy–1,1–dihydro–1,2–benziodoxol–3(1*H*)–one, 2.33 g, 5.5 mmol) and anhydrous CH_2Cl_2 (30 mL) was added the respective alcohol **7** (5.0 mmol) in anhydrous CH_2Cl_2 (5 mL). The ice–bath was removed after 5 min, and the reaction was allowed to stir at ambient temperature until TLC indicated complete conversion of the alcohol **7** (1 – 4 h). The reaction mixture was washed with an aqueous $NaHCO_3/Na_2S_2O_3$ solution[7] (approx. 5 x 20 mL) until all iodine–containing compounds were removed (TLC). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The aldehyde **8** was used immediately for the next reaction (**8** ? **10**) without further purification.

7d ? **8d**: Alcohol **7d** (20.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was added in one portion to an ice–cooled and magnetically stirred suspension of PCC (6.47 g, 30.0 mmol) in anhydrous CH_2Cl_2 (50 mL). The ice–bath was removed after 5 min, and the reaction was allowed to stir

---

[1] Wessig, P.; Muehling, O. *Helv. Chim. Acta* **2003**, *86*, 865–893.

[2] Spectroscopic data (^1H, ^{13}C, MS, IR): (a) Hiroya, K.; Hasegawa, J.; Watanabe, T.; Ogasawara, K. *Synthesis* **1995**, 379-381. (b) Gansaeuer, A.; Barchuk, A.; Fielenbach, D. *Synthesis* **2004**, 2567-2573.

[3] Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.

[4] Corey, E. J.; Suggs, W. J. *Tetrahedron Lett.* **1975**, 2647–2650.

[5] Burkhouse, D.; Zimmer, H. *Synthesis* **1984**, 330–332.

[6] Peterli-Roth, P.; Maguire, M. P.; León, E.; Rapoport, H. *J. Org. Chem.* **1994**, *59*, 4186-4193.

[7] 25 g $Na_2S_2O_3$ in 100 mL saturated aqueous $NaHCO_3$ solution.

at ambient temperature. After TLC indicated disappearance of the alcohol (1.5 – 4 h) the supernatant liquid was decanted from the black gum. The insoluble residue was extracted with Et_2O (5 x 25 mL). The combined organic layers were passed through a short column of Florisil, Celite and silica gel (volume ratio: Florisil/Celite/silica gel ˜ 1/1/4, silica gel as bottom layer) and the solvent was removed under reduced pressure. The aldehyde **8d** was used immediately for the next reaction (**8d** ? **10d**) without further purification.

8 ? **10**: A magnetically stirred mixture of phosphonate **9** (5.0 mmol) and anhydrous THF (10 mL) was cooled to = – 70 °C (cooling bath temperature). Under N_2 or Ar atmosphere *n*BuLi (3.2 mL, 5.12 mmol, 1.6 M in hexane) was added dropwise. After stirring for 30 – 45 min at = – 70 °C, the respective aldehyde **8** (5.0 mmol) in anhydrous THF (5 mL) was added, the cooling bath was removed, and the reaction was allowed to stir at ambient temperature until TLC analysis (petroleum ether/ethyl acetate = 10:1) indicated complete conversion (16 – 24 h). After addition of H_2O (20 mL) the reaction mixture was extracted with pentane (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. Purification of the residue by FCC (petroleum ether/ethyl acetate = 100:1 – 10:1) gave the enol ether **10** as a colorless liquid. The enol ether either was used immediately for the next reaction or was stored at – 20 °C for no longer than one week before use.

1.4.1 Analytical Data of Enol Ethers 10, Determination of *E*/*Z* Ratio

Spectral and structural assignments were made by additional 2D NMR experiments (H,H–Cosy [^{1}H/^{1}H], HSQC [^{1}H/^{13}C]). The NMR data of the minor isomer are given in curly brackets.

The *E*/*Z* ratio was determined by ^{1}H NMR integration of the olefinic protons. The olefinic protons were assigned by using the additive increment method of Matter. [8] According to this estimation method, the *Z*–olefinic proton (δ_Z = 4.85 ppm) [9] are about 0.3 ppm downfield to the *E*–olefinic proton (δ_E = 4.56 ppm) [10] for all enol ethers of type **10**.

10a FCC (petroleum ether/ethyl acetate = 100:1 ? 100:2); colorless liquid (69%, *E*/*Z* = 25:75).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.41-7.14 (m, 5 H, H_{ar}), 5.06 {4.47} (d, ^3J = 9.4 {10.2}, 1

[8] (a) Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 691-697. (b) Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 2023-2034.

[9] δ_Z [ppm] = 5.25 + I_{gem} + I_z + I_E = 5.25 + 0.45 + 0.36 (R_Z = aryl) - 1.21 (R_E = OAlkyl) = 4.85

[10] δ_E [ppm] = 5.25 + I_{gem} + I_z + I_E = 5.25 + 0.45 - 1.07 (R_Z = OAlkyl) - 0.07 (R_E = aryl) = 4.56

H, C=C*H*), {3.70} 3.62 (q, ^3J = 7.0, 2 H, OCH_2CH$_3$), 2.56-2.37 {2.00-1.81} [br m, 1 H, CHC*H* (cHex)], 1.82-1.58 [br m, 4 eq H, CH_2 (cHex)], 1.29-0.66 [br m, 4 ax H, CH_2 (cHex), 1 H, C*H*(*t*Bu)], {1.24} 1.20 (t, ^3J = 7.0, 3 H, OCH$_2$CH_3), 0.79 {0.73} (s, 9 H, *t*Bu).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = {153.3} 151.9 [Ph(OEt)*C*=CH], {137.0} 136.7 (C_{ar}), {128.5} 128.2 (2 x C_{ar}H), 127.9 {127.8} (C_{ar}H), {127.5} 125.9 (2 x C_{ar}H), 121.6 {108.6} (C=*C*H), 66.1 {62.9} (O*C*H_2CH$_3$), 47.7 {47.6} [*C*H(*t*Bu)], {36.5} 35.2 [CH*C*H (cHex)], {35.3} 34.0 [CH_2CH*C*H_2 (cHex)], 32.5 {32.4} [*C*(CH_3)$_3$], 27.6 {27.5} [C(*C*H$_3$)$_3$], 27.0 {26.9} [*C*H_2CH(*t*Bu)*C*H_2 (cHex)], 15.4 {14.8} (OCH$_2$*C*H$_3$).

10b FCC (petroleum ether/ethyl acetate = 100:1 ? 100:2); colorless liquid (79%, *E/Z* = 25:75).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50-7.23 (m, 5 H, H_{ar}), 5.59 {5.16} (d, ^3J = 9.4 {10.6}, 1 H, C=C*H*), {3.80} 3.68 (q, ^3J = 7.0, 2 H, OCH_2CH$_3$), 3.12-3.01 {2.60-2.50} [br m, 1 H, CHC*H* (cHex)], 1.82-1.58 [br m, 4 eq H, CH_2 (cHex)], 1.29-0.66 [br m, 4 ax H, CH_2 (cHex), 1 H, C*H*(*t*Bu)], {1.34} 1.26 (t, ^3J = 7.0, 3 H, OCH$_2$CH_3), {0.87} 0.86 (s, 9 H, *t*Bu).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = {153.3} 152.1 [Ph(OEt)*C*=CH], {136.9} 136.8 (C_{ar}), {128.7} 128.3 (2 x C_{ar}H), 127.9 {127.8} (C_{ar}H), {127.5} 126.2 (2 x C_{ar}H), 117.7 {104.1} (C=*C*H), 65.8 {63.0} (O*C*H_2CH$_3$), 48.4 {48.3} [*C*H(*t*Bu)], {32.9} 32.1 [*C*H_2CH*C*H_2 (cHex)], 32.6 [*C*(CH_3)$_3$], {30.5} 29.5 [CH*C*H (cHex)], 27.5 [C(*C*H$_3$)$_3$], 22.5 {22.1} [*C*H_2CH(*t*Bu)*C*H_2 (cHex)], 15.4 {14.8} (OCH$_2$*C*H$_3$).

10c FCC (petroleum ether/ethyl acetate = 100:3 ? 10:1); colorless liquid (64%, *E/Z* = 37:63).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46-7.24 (m, 5 H, H_{ar}), 5.12 {4.56} (d, ^3J = 9.3 {10.0}, 1 H, C=C*H*), 3.97 {3.89} [ddd, ^2J = 11.5, $^3J_{eq,eq}$ = 4.0, $^3J_{eq,ax}$ = 2.1, 2 eq H, CH_2OCH_2 (THP)], {3.79} 3.70 (q, ^3J = 7.0, 2 H, OCH_2CH$_3$), 3.49 {3.29} [dt, ^2J = $^3J_{ax,ax}$ = 11.5, $^3J_{ax,eq}$ = 2.1, 2 ax H, CH_2OCH_2 (THP)], 2.95-2.83 {2.35-2.21} [m, 1 H, C*H* (THP)], 1.68-1.44 [m, 4 H, CH_2CHCH_2 (THP)], {1.33} 1.27 (t, ^3J = 7.0, 3 H, OCH$_2$CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = {154.4} 152.8 [Ph(OEt)*C*=CH], {136.6} 136.2 (C_{ar}), {128.4} 128.3 (2 x C_{ar}H), {128.1} 128.0 (C_{ar}H), {127.8} 126.0 (2 x C_{ar}H), 119.2 {106.3} (C=*C*H), 67.7 {67.6} [*C*H_2O*C*H_2 (THP)], 66.0 {63.0} (O*C*H_2CH$_3$), {34.3} 33.0 [*C*H_2CH*C*H_2 (THP)], {33.7} 33.1 [*C*H (THP)], 15.3 {14.7}

(OCH_2CH_3).

10d FCC (petroleum ether/ethyl acetate = 100:5 ? 10:1); colorless liquid (61%, *E/Z* = 53:47).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = {7.59} 7.52 (d, 2 H, ^3J = 8.3, H_{ar}), 7.34-7.15 (m, 7 H, H_{ar}), 4.95 {4.41} (d, ^3J = 9.8 {9.0}, 1 H, C=C*H*), 3.76-3.59 [m, 2 eq H, CH_2N(Ts)CH_2 (TsPip)], 3.69 {3.55} (q, ^3J = 7.0, 2 H, OCH_2CH$_3$), {2.59-2.39} 1.93-1.76 [m, 1 H, C*H* (TsPip)], {2.37} 2.33 [s, 3 H, CH_3 (Ts)], {2.27} 2.02 [dt, $^2J = {}^3J_{ax,ax}$ = 12.0, $^3J_{ax,eq}$ = 2.8, 2 ax H, CH_2N(Ts)CH_2 (TsPip)], 1.74-1.34 [m, 4 H, CH_2CHCH_2 (TsPip)], 1.24 {1.11} (t, ^3J = 7.0, 3 H, OCH_2CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.9 {153.4} [Ph(OEt)*C*=CH], 143.3 ($C_{ar}CH_3$), 136.5 {135.9} (C_{ar}), 133.1 {132.9} (C_{ar}), {129.6} 129.5 (2 x C_{ar}H), 128.4 {128.3} (2 x C_{ar}H), 128.1 {128.0} (C_{ar}H), {128.0} 127.7 (2 x C_{ar}H), 127.6 {126.1} (2 x C_{ar}H), {118.0} 105.0 (C=*C*H), {65.8} 63.1 (O*C*H_2CH_3), {46.2} 46.1 [*C*H_2N(Ts)*C*H_2 (TsPip)], 33.9 {32.2} [*C*H (TsPip)], 33.0 {31.7} [*C*H_2CH*C*H_2 (TsPip)], 21.5 {21.4} (*C*H_3, Ts), {15.2} 14.6 (OCH_2CH_3).

10e FCC (petroleum ether/ethyl acetate = 100:5 ? 10:1); colorless liquid (72%, *E/Z* = 22:78).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45-7.24 (m, 5 H, H_{ar}), 5.10 {4.53} (d, ^3J = 9.0 {10.0}, 1 H, C=C*H*), 4.25-3.92 [m, 2 H, CH_2N(Boc)CH_2 (BocPip)], {3.78} 3.70 (q, 2 H, ^3J = 7.0, OCH_2CH$_3$), {3.43-3.25} 2.91-2.72 [m, 2 H, CH_2N(Boc)CH_2 (BocPip)], 1.91-1.15 [m, 5 H, (BocPip)] 1.47 {1.45} (s, 9 H, *t*Bu); 1.27 {1.19} (t, 3 H, ^3J = 7.0, OCH_2CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.9 [Ph(OEt)*C*=CH], 152.9 [C=O (Boc)], 136.2 (C_{ar}), {128.5} 128.3 (2 x C_{ar}H), {128.1} 127.9 (C_{ar}H), {127.9} 126.1 (2 x C_{ar}H), {126.7} 119.0 (C=*C*H), 79.2 [Cq (*t*Bu)], 66.0 {63.0} (O*C*H_2CH_3), 46-41 [br, *C*H_2N(Boc)*C*H_2 (BocPip)], {34.7} 33.1 [*C*H (BocPip)], {33.6} 32.2 [br, *C*H_2CH*C*H_2 (BocPip)], 28.5 {28.4} [C(*C*H_3)$_3$], 15.3 {14.7} (OCH_2CH_3). [11]

10f FCC (petroleum ether/ethyl acetate = 100:2 ? 100:4); colorless liquid (75%, *E/Z* = 31:69).

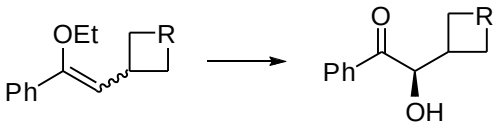
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52-7.06 (m, 9 H, H_{ar}), 5.46 {4.88} (dd, ^3J = 9.4 {9.8}, ^5J = 2.6 {2.2}, 1 H, C=C*H*), {3.80} 3.73 (dq, ^3J_q = 7.0, J_d = 2.6 {2.2}, 2 H, OCH_2CH$_3$), 3.16 {3.03} [ddd, ^2J = 15.5 {15.8}, ^3J = 9.4 {9.8}, ^4J = 1.7, 2 H,

[11] The quaternary C atoms of the minor isomer are not visible.

C*H*$_2$CHC*H*$_2$ (2-Ind)], 3.82-3.70 {3.22-3.10} [m, 1 H, CH$_2$C*H*CH$_2$ (2-Ind)], 2.78 {2.82-2.70} [ddd {m}, ^2J = 15.5, ^3J = 9.4, ^4J = 1.7, 2 H, C*H*$_2$CHC*H*$_2$ (2-Ind)], {1.33} 1.28 (dt, ^3J_t = 7.0, J_d = 2.6 {2.2}, 3 H, OCH$_2$C*H*$_3$).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = {154.8} 153.2 [Ph(OEt)*C*=CH], 143.3 {142.2} [2 x C_{ar} (2-Ind)], {136.6} 136.2 (C_{ar}), {128.6} 128.3 (2 x C_{ar}H), {128.1} 128.0 (C_{ar}H), {127.8} 125.9 (2 x C_{ar}H), 126.2 {126.1} [2 x C_{ar}H (2-Ind)], 124.3 {124.2} [2 x C_{ar}H (2-Ind)], 119.3 {105.7} (C=*C*H), 66.2 {63.1} (O*C*H$_2$CH$_3$), {41.4} 40.2 [*C*H$_2$CH*C*H$_2$ (2-Ind)], {38.9} 36.8 [CH$_2$*C*HCH$_2$ (2-Ind)], 15.3 {14.7} (OCH$_2$*C*H$_3$).

1.5 Preparation of *R*–configured 2–Hydroxy Ketones *R*–11



10 ***R*-11**

To a vigorously stirred mixture of AD–mix–β[12] (2.8 g), $MeSO_2NH_2$ (0.19 g, 2 mmol) and *t*BuOH/H_2O (1:1, 15 mL) was added the respective enol ether **10** (2 mmol) in *t*BuOH/H_2O (1:1, 5 mL). The reaction mixture was stirred at ambient temperature until TLC analysis indicated complete conversion (6 – 24 h). After addition of solid sodium sulfite (2 g) the mixture was stirred for an additional hour. CH_2Cl_2 (40 mL) and H_2O (20 mL) was added to the reaction mixture and after phase separation, the aqueous layer was further extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by FCC (petroleum ether/ethyl acetate = 10:1 – 10:4) gave the respective *R*–configured 2–hydroxy ketone ***R*–11**.

1.5.1 Analytical Data of *R*–11

Analytical data (^{1}H, ^{13}C, IR, EI–MS, HRMS, Mp.) of 2–hydroxy ketones **11a,c–f** are given in reference 1. For determination of *ee* by HPLC see chapter 2.2.

***R*–11a** FCC (petroleum ether/ethyl acetate = 10:1); colorless solid (81%, 95% *ee*).

---

[12] 1.4 g AD–Mix–ß (for 1 mmol substrate contains 0.980 g $K_3Fe(CN)_6$, 0.410 g K_2CO_3, 0.0078g (1 mol%) $(DHQD)_2$–Phal and $K_2OsO_2(OH)_4$ (0.2 mol%).

***R*–11b** FCC (petroleum ether/ethyl acetate = 10:1); colorless solid (86%, 55% *ee*).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96-7.89 (m, 2 H, H_{ar}), 7.65-7.57 (m, 1 H, H_{ar}), 7.54-7.45 (m, 2 H, H_{ar}), 5.13 [dd, 1 H, ^3J = 7.9, ^3J = 6.4, C*H*(OH)], 3.30 (d, ^3J = 7.9, 1 H, O*H*), 1.99-1.81 [m, 1 H, CH(OH)C*H*, (cHex), 1 eq H, CH_2CHCH_2 (cHex)], 1.73-1.61 [m, 1 eq H, CH_2CHCH_2 (cHex)], 1.57-1.16 [m, 2 ax H, CH_2CHCH_2 (cHex), 4 H, CH_2CH(*t*Bu)CH_2 (cHex)], 1.06-0.93 [m, 1 H, C*H*(*t*Bu) (cHex)], 0.84 [s, 9 H, C(CH_3)$_3$].

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 203.8 (C=O), 135.3 (C_{ar}), 133.7 (C_{ar}H), 128.8 (2 x C_{ar}H), 128.5 (2 x C_{ar}H), 75.3 [*C*H(OH)], 46.8 [*C*H(*t*Bu) (cHex)], 37.6 [CH(OH)*C*H (cHex)], 32.6 [*C*(CH_3)$_3$], 28.8 [CH_2CH*C*H$_2$ (cHex)], 27.5 [C(*C*H$_3$)$_3$], 25.7 [*C*H$_2$CHCH$_2$ (cHex)], 22.9 [*C*H$_2$CH(*t*Bu)CH$_2$ (cHex)], 22.8 [CH$_2$CH(*t*Bu)*C*H$_2$ (cHex)].

2D-NMR H,H-Cosy (^{1}H/^{1}H), HSQC (^{1}H/^{13}C).

IR (KBr) ν = 3455, 2940, 2865, 1676, 1596, 1578, 1447, 1263, 1208, 1098, 982.

MS (EI) *m*/*z* (%): 274 (1, M^+), 169 (9, [M - PhCO]$^+$), 151 (11), 139 (5, [cHex(*t*Bu)]$^+$), 136 (30, [MH - cHex(*t*Bu)]$^+$), 122 (31), 105 (78, [PhCO]$^+$), 95 (30), 81 (26), 77 (50, Ph$^+$), 57 (100, *t*Bu$^+$), 41 (38).

Mp. 62 – 64 °C.

EA $C_{18}H_{26}O_2$ (274.40); calculated: C: 78.79, H: 9.55; found: C: 77.97, H: 9.68.

TLC R_f = 0.57 (petroleum ether/ethyl acetate = 10:2).

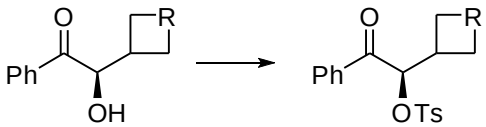
***R*–11c** FCC (petroleum ether/ethyl acetate = 10:1 ? 10:2); colorless solid (92%, 91% *ee*).

***R*–11d** FCC (petroleum ether/ethyl acetate = 10:4); colorless solid (87%, 99% *ee*).

***R*–11e** FCC (petroleum ether/ethyl acetate = 10:4); colorless solid (91%, 93% *ee*).

***R*–11f** FCC (petroleum ether/ethyl acetate = 10:1 ? 10:2); colorless solid (98%, 97% *ee*).

1.6 Preparation of *R*–configured 2–Tosyloxy Ketones *R*–12



***R*-11** ***R*-12**

To a magnetically stirred solution of the respective 2–hydroxy ketone ***R*–11** (15.0 mmol) and anhydrous CH_2Cl_2 (30 mL) was added at 0 °C (ice–bath) pyridine (1.19 g, 15.0 mmol),

toluene–4–sulfonic anhydride (Ts_2O) (4.90 g, 15.0 mmol) and a small amount of 4–dimethylaminopyridine (DMAP). The ice–bath was removed, and the reaction was allowed to stir at ambient temperature until TLC indicated completion of the reaction (0.5 – 6 h). The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with 2 M HCl (20 mL) and saturated aqueous $NaHCO_3$ solution (3 x 20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. Purification of the residue by FCC (petroleum ether/ethyl acetate = 10:1 – 10:3) gave the respective *R*–configured 2–tosyloxy ketones ***R*–12**.

1.6.1 Analytical Data of *R*–12

Analytical data (^1H, ^{13}C, IR, EI–MS, HRMS, Mp.) of 2–tosyloxy ketones **12a,c–f** are given in reference 1.

***R*–12a** FCC (petroleum ether/ethyl acetate = 10:1 ? 10:2); colorless solid (87%).

***R*–12b** FCC (petroleum ether/ethyl acetate = 10:1 ? 10:2); colorless solid (75%).

^1H-NMR (300 MHz, $CDCl_3$): δ = 7.91-7.85 (m, 2 H, H_{ar}), 7.63 [d, ^3J = 8.3, 2 H, H_{ar} (Ts)], 7.54-7.46 (m, 1 H, H_{ar}), 7.40-7.32 (m, 2 H, H_{ar}), 7.15 [d, ^3J = 8.3, 2 H, H_{ar} (Ts)], 5.23 [d, ^3J = 10.8, 1 H, C*H*(OTs)], 2.31 [s, 3 H, CH_3 (Ts)], 2.32-2.22 [m, 1 H, CH(OTs)C*H*, (cHex)], 1.96 [br d, ^2J = 13.5, 1 eq H, CH_2CHCH_2 (cHex)], 1.40-1.26 [m, 1 ax H, CH_2CHCH_2 (cHex), 2 H, CH_2CHCH_2 (cHex), 2 eq H, CH_2CH(*t*Bu)CH_2 (cHex)], 1.06-0.52 [m, 2 ax H, CH_2CH(*t*Bu)CH_2 (cHex), 1 H, C*H*(*t*Bu) (cHex)], 0.70 [s, 9 H, C(CH_3)$_3$].

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 196.2 (C=O), 145.1 (SO_2C_{ar}), 134.5 (C_{ar}), 133.6 ($C_{ar}H$), 132.4 (C_{ar}), 129.7 (2 x $C_{ar}H$), 129.2 (2 x $C_{ar}H$), 128.5 (2 x $C_{ar}H$), 128.3 (2 x $C_{ar}H$), 82.3 [*C*H(OTs)], 47.5 [*C*H(*t*Bu) (cHex)], 35.8 [CH(OTs)*C*H (cHex)], 32.4 [*C*(CH$_3$)$_3$], 27.3 [C(*C*H$_3$)$_3$], 26.7 [CH$_2$CH*C*H$_2$ (cHex)], 26.6 [*C*H$_2$CHCH$_2$ (cHex)], 21.7 [*C*H$_2$CH(*t*Bu)CH$_2$ (cHex)], 21.6 [CH$_3$ (Ts)], 21.0 [CH$_2$CH(*t*Bu)*C*H$_2$ (cHex)].

2D-NMR H,H-Cosy ($^1H/^1H$), HSQC ($^1H/^{13}C$).

IR (KBr) ν = 2935, 2867, 1681, 1597, 1446, 1365, 1176, 941.

MS *m*/*z* (%): 428 (1, M^+), 323 (3, [M - PhCO]$^+$), 290 (12, [PhC=OCH$_2$OTs]$^+$), 256 (3, [M - TsOH]$^+$), 155 (16, Ts$^+$), 151 (23), 105 (100, [PhCO]$^+$), 91 (23), 77 (21, Ph$^+$), 57 (24, *t*Bu$^+$), 41 (11).

HRMS (ESI) [$C_{25}H_{32}O_4S$ + ^{23}Na], calculated: 451.1914, found: 451.1921.

Mp. 121 – 123 °C

TLC R_f = 0.48 (petroleum ether/ethyl acetate = 10:2).

***R*–12c** FCC (petroleum ether/ethyl acetate = 10:3); colorless solid (84%).

***R*–12d** FCC (petroleum ether/ethyl acetate = 10:3); colorless solid (81%).

***R*–12e** FCC (petroleum ether/ethyl acetate = 10:2 ? 10:3); colorless solid (87%).

***R*–12f** FCC (petroleum ether/ethyl acetate = 10:1 ? 10:2); colorless solid (82%).

1.7 Photochemistry

1.7.1 Preparative Photolyses – Preparation of Cyclopropanes 13

Experimental procedures and the analytical data (^{1}H, ^{13}C, IR, EI–MS, HRMS, Mp.) of cyclopropanes **13a,c–f** are given in reference 1.

Irradiation of 2–tosyloxy ketone ***R*–12b** was performed in CH_2Cl_2 (400 mL) at a concentration of 0.01 mol L^{-1} (1.72 g) in the presence of *N*–methylimidazole (0.66 g). The reaction mixture was degassed with N_2 for 15 min and irradiated using a high pressure mercury arc lamp (150 W). Light of wavelength below 300 nm was absorbed using a Pyrex^{TM} glass jacket between the lamp and the reaction vessel. The reaction was monitored by TLC and aborted when ***R*–12b** had completely disappeared (40 min). The solution was washed with H_2O (2 x 100 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to 10% of the original volume. To the solution was added silica gel, and the remaining solvent was removed under reduced pressure. The residue was purified immediately by FCC (petroleum ether/ethyl acetate = 100:5) to give ***exo*–13b** as a colorless oil (0.74 g, 72%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92-7.86 (m, 2 H, H_{ar}), 7.52-7.45 (m, 1 H, H_{ar}), 7.44-7.36 (m, 2 H, H_{ar}), 2.33 [t, 1 H, ^3J = 4.1, (C=O)C*H* (cProp)], 2.18-1.97 [m, 1 H, CH_2 (cHex), 1 H, CH_2 (cHex)], 1.93-1.70 [m, 1 H, C*H* (cProp), 1 H, CH_2 (cHex)], 1.60-1.49 [m, 1 H, CH_2 (cHex)], 1.32-1.15 [m, 1 H, CH_2 (cHex), 1 H, C*H* (cProp)], 1.02-0.90 [m, 1 H, C*H*(*t*Bu) (cHex)], 0.77 [s, 9 H, C(CH_3)$_3$], 0.78-0.65 [m, 1 H, CH_2 (cHex)].

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 200.4 (C=O), 138.4 (C_{ar}), 132.4 (C_{ar}H), 128.4 (2 x C_{ar}H), 127.9 (2 x C_{ar}H), 44.1 [*C*H(*t*Bu) (cHex)], 32.2 [*C*(CH_3)$_3$], 31.1 [(C=O)*C*H (cProp)], 27.8 [*C*H (cProp)], 27.1 [C(*C*H_3)$_3$], 26.7 [*C*H (cProp)], 25.1 [*C*H_2 (cHex)], 24.5 [*C*H_2 (cHex)], 21.3 [*C*H_2 (cHex)].

2D-NMR H,H-Cosy (^{1}H/^{1}H), HSQC (^{1}H/^{13}C).

IR (film) ν = 2865, 1661, 1446, 1414, 1363, 1321, 1288, 1219, 1039, 1023, 693.

MS (EI) *m*/*z* (%): 256 (23, M^+), 199 (23, [M - *t*Bu]$^+$), 157 (34), 136 (40), 121 (33), 105 (100, [PhCO]$^+$), 77 (48, Ph^+), 57 (35, *t*Bu^+), 41 (23).

HRMS (EI) $C_{18}H_{24}O$, calculated: 256.18272, found: 256.18273.

TLC R_f = 0.59 (petroleum ether/ethyl acetate = 10:1).

1.7.2 Temperature–dependent Photolyses

For temperature–dependent irradiations in analytical scale a stock solution was prepared from *R*–configured 2–tosyloxy ketone ***R*–12** (0.10 mmol), dissolved in dichloromethane and methanol (100 mL), respectively. In the case of dichloromethane as solvent, *N*–methylimidazole (16.5 mg, 0.20 mmol) was added as an acid scavenger. The solutions were degassed at ambient temperature with N_2 for 15 min. 10 mL of the stock solution was placed in a quartz round–bottomed flask equipped with a magnetic stir bar and a temperature sensor (Pt 100) of an electronic digital thermometer (AMA–DIGIT AD 170th). The reaction mixture was cooled by means of an external cooling bath (Table 1). For irradiations at the boiling point of the solvent (dichloromethane: 40 °C, methanol: 64 °C) the quartz flask was equipped with a reflux condenser and the reaction mixture was carefully heated to reflux with a heat gun. After reaching the desired internal temperature, the reaction mixture was irradiated (500 W high pressure Hg–arc lamp [OSRAM HBO–500], filter [WG 295, SCHOTT]) over a defined period of time: $T > 0$ °C ? 3 min, $T = 0 – (– 40)$ °C ? 5 min, $T = (– 41) – (– 70)$ °C ? 10 min. Small variations of temperature during the irradiation process have been considered by calculating the arithmetic mean. After irradiation, the reaction mixture was allowed to come to room temperature, silica gel (1 g) was added, and the solvent was removed carefully under reduced pressure. The residue was purified immediately by FCC (petroleum ether/ethyl acetate = 100:5 – 10:2) and the enantiomeric purity was determined by HPLC.

Table 1.

ΔT [°C] [a]	Cooling Bath
20 – 30	H_2O
0 – 10	ice water
0 – (– 15)	3 parts ice, 1 part NaCl
– 15 – (– 50)	*i*PrOH/dry ice + H_2O [b]
– 50 – (– 60)	*i*PrOH/dry ice
– 60 – (– 70)	acetone/dry ice

[a]: Internal temperature range of the reaction mixture. [b]: To an *i*PrOH/dry ice mixture were added small amounts of H_2O until the desired temperature was reached.

2 Determination of the Enantiomeric Excess (*ee*) by HPLC

2.1 General

Equipment: HPLC pump *64* (KNAUER), photo diode array detector *996* (WATERS), injection valve (10 µL, KNAUER), Software *Empower* (WATERS).

Analytical chiral columns: Chiralcel®–OD (Cellulose tris–3,5–dimethylphenylcarbamate, normal phase, internal diameter: 4.6 mm, column length: 250 mm, particule size: 10 µm, DAICEL) or Chiralpak®–AD–H (Amylose tris–3,5–dimethylphenylcarbamate, normal phase, internal diameter: 4.6 mm, column length: 250 mm, particule size: 5 µm, DAICEL).

Mobile phase: *n*–hexane/*i*PrOH mixtures (HPLC grade, J.T. BAKER, ACROS).

2.2 2–Hydroxy Ketones *R*–11

The optimized measurement conditions are summarized in Table 2. Enantiomers were identified by means of their same UV spectra. The *ee* values were determined from the peak areas *I* according to *ee* [%] = $(I_A - I_B)/(I_A + I_B)\cdot 100$, where I_A is the peak area of the major enantiomer and I_B the peak area of the minor enantiomer.

Table 2.

11	column	hexane/*i*PrOH	flow rate [mL min^{-1}]	λ [nm] [a]	R_t [min] ***R*–11**	R_t [min] ***S*–11**
11a	OD	98:2	1.0	242.3	13.12	7.87
11b	OD	98:2	1.0	242.3	10.75	8.64
11b	AD–H	98:2	1.0	242.3	19.40	17.12
11c	AD–H	95:5	1.0	229.7	31.80	29.22
11d	OD	80:20	1.0	232.8	24.07	18.56
11e	AD–H	90:10	1.0	242.3	17.75	26.98
11f	OD	90:10	0.5	240.0	13.24	9.36

[a]: detection wavelength.

2.3 Cyclopropanes 13

The optimized measurement conditions are summarized in Table 3. Enantiomers were identified by means of their same UV spectra. The *ee* values were determined from the peak areas *I* according to *ee* [%] = $(I_A - I_B)/(I_A + I_B)\cdot 100$, where I_A is the peak area of the major enantiomer and I_B the peak area of the minor enantiomer.

Table 3.

13	column	hexane/*i*PrOH	flow rate [mL min^{-1}]	λ [nm] [a]	R_t [min] [b]
***exo*–13a**	AD–H	98:2	1.0	238.7	*7.34*, 9.82
***exo*–13b**	AD–H	98:2	0.5	238.7	*11.69*, 17.57
***exo*–13c**	AD–H	99:1	0.6	238.7	38.78, *44.60*
***exo*–13d**	AD–H	90:10	1.0	236.4	27.90, *29.54*
***exo*–13e**	AD–H	98:2	1.0	239.9	*14.17*, 18.55
***exo*–13f**	AD–H	90:10	1.0	240.0	*5.57*, 6.44
***endo*–13f**	OD	90:10	0.5	240.0	14.96, *21.03*

[a]: detection wavelength. [b]: The retention time R_t of the excess enantiomer (dichloromethane, 25 °C) is given in italic letters.

3 Eyring Plots, Calculation of Activation Parameters, Calculation of Errors

The *ee* values determined by HPLC were converted to *CT* values according to *CT* = (*ee*[**13**]/*ee*[**12**])*100. The Eyring plots were obtained after plotting ln(A/B) against 1/*T* [10^{-3} K^{-1}], where A/B is the enantiomeric ratio corresponding to A/B = k_A/k_B = (1 + *CT*)/(1 – *CT*). After linear regression[13] (y = mx + b) $\Delta\Delta H^{\#}$, $\Delta\Delta S^{\#}$, $\Delta\Delta G^{\#}$ and T_0 were calculated using the following equations: $\Delta\Delta H^{\#}$ [kcal mol^{-1}] = – m·*R*/4.1868/1000 (*R* = 8.314472 [J mol^{-1} K^{-1}]), $\Delta\Delta S^{\#}$ [cal mol^{-1} K^{-1}] = b·*R*/4.1868, $\Delta\Delta G^{\#}$ (25 °C) [kcal mol^{-1}] = $\Delta\Delta H^{\#}$ – 298·($\Delta\Delta S^{\#}$/1000), T_0 [°C] = $\Delta\Delta H^{\#}$/($\Delta\Delta S^{\#}$/1000) – 273.

The errors (Δm, Δb) resulting from the linear regression analysis[13] were used as the starting point for the calculation of errors. Δ($\Delta\Delta H^{\#}$) and Δ($\Delta\Delta S^{\#}$), respectively were calculated according to Δ($\Delta\Delta H^{\#}$) = Δm/m·$\Delta\Delta H^{\#}$ and Δ($\Delta\Delta S^{\#}$) = Δb/b·$\Delta\Delta S^{\#}$ while for Δ($\Delta\Delta G^{\#}$) and ΔT_0 the Gauss' error propagation laws were used:

[13] Software *OriginLab* 7.5

$$\Delta z = \sqrt{(\Delta x)^2 + (\Delta y)^2} \;\Rightarrow \Delta(\Delta\Delta G^{\#}) = \sqrt{\left(\Delta(\Delta\Delta H^{\#})\right)^2 + \left(\Delta(\Delta\Delta S^{\#})\right)^2}$$

$$\Delta z = z \cdot \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2} \;\Rightarrow \Delta T_0 = T_0 \cdot \sqrt{\left(\frac{\Delta(\Delta\Delta H^{\#})}{\Delta\Delta H^{\#}}\right)^2 + \left(\frac{\Delta(\Delta\Delta S^{\#})}{\Delta\Delta S^{\#}}\right)^2}$$

4 Vibrational Circular Dichroism (VCD)

4.1 Measurements

Equipment: *IFS 66n/S* vacuum FT–IR spectrometer (BRUKER OPTICS) in combination with an external VCD module *PMA 37* (BRUKER OPTICS); liquid cell A145 (CaF_2 window, layer thickness 50 µm, BRUKER OPTICS).

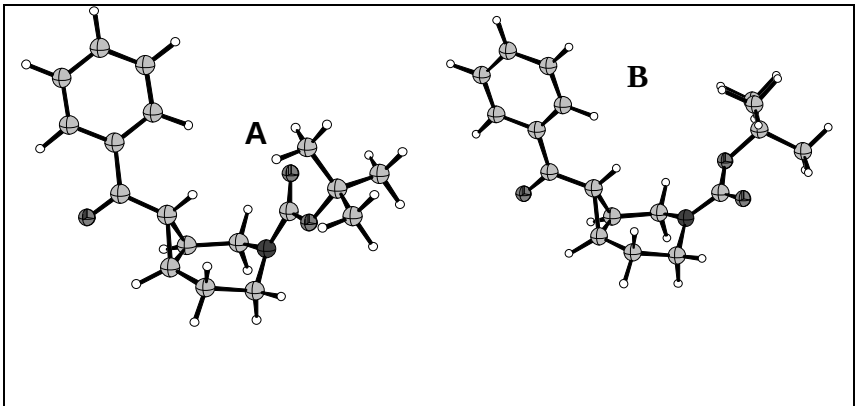
Conditions: Samples (5 – 15 mg) were dissolved in 150 µL $CDCl_3$; wave number range: 1800 – 1000 cm^{-1}; spectral resolution: 6 cm^{-1}; measurement period: 75 – 90 min. All spectra were presented in molar absorptivity Δε (L mol^{-1} cm^{-1}), and corrected by a solvent spectrum obtained at the same experimental conditions.

All measurements were carried out at BRUKER OPTICS (Ettlingen, H.–H. Drews).

4.2 Results of *exo*–13e

Table 4. Relative Energies and Fractional Boltzmann Populations for Conformers of ***exo–R–*13e** (B3LYP/6–311++G**//B3LYP/6–31G*).

Conformer	E_{rel} [kcal·mol^{-1}]	P(25 °C) [%]
***exo–R–*13e–A**	0.0	49.3
***exo–R–*13e–B**	0.1	41.6
***exo–R–*13e–C**	2.1	1.4
***exo–R–*13e–D**	1.1	7.7



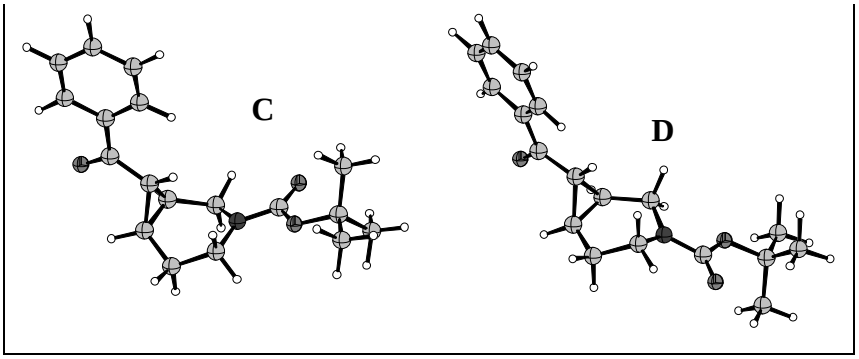


Figure 1. Optimized geometries of ***exo–R–*13e** (B3LYP/6–311++G**//B3LYP/6–31G*).

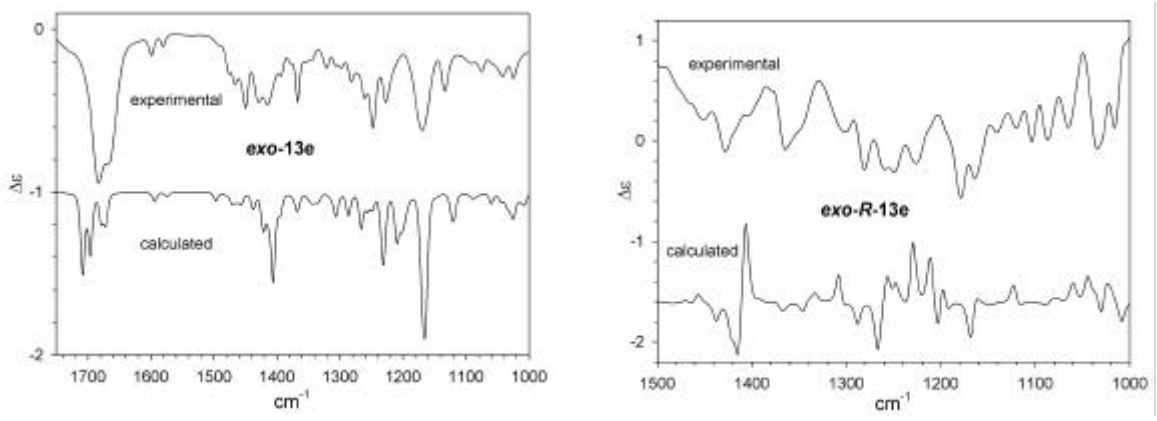


Figure 2. Comparison of experimental and calculated IR and VCD spectra of ***exo–R–*13e**.

4.3 Quantum Chemical Calculations

All IR/VCD calculations were carried out at the DFT level with the Gaussian 98 program package[14] using the hybrid functional B3LYP[15] and the 6–31G* basis set. At the same level of theory, frequency calculations were carried out to characterize each structure as minimum and to obtain the zero-point vibrational energies. Based on the optimized geometries single point calculations were accomplished with the same DFT method and a higher 6–311++G** basis

[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, Jr., 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.; Rega, N.; Salvador, P.; Dannenberg, J. J.; 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 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

[15] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* B **1988**, *37*, 785–789.

set. The output includes additionally the dipole and rotational strengths (input “Freq = VCD” required) for each mode that are proportional to the integrated IR and VCD intensities. For comparison with experimental spectra, the calculated frequencies were uniformly scaled with 0.9614 and the IR and VCD intensities were represented as Pseudo–Voigt bands with 8 cm^{-1} half width (c = 0.5):

$$y = a\left[c\left(\frac{1}{1+\left(\frac{x-x_0}{b}\right)^2}\right)+(1-c)e^{-0.5\left(\frac{x-x_0}{b}\right)^2}\right]$$

4.3.1 Electronic Energy, Zero–point Vibrational Energy, Cartesian Coordinates

structure: ***exo–S–13c–A***

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 654.2237878

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 153.10253

cartesian coordinates:

C	-1.892069	.608873	.873252
C	-1.939040	.877772	-.596453
C	-2.943479	.101765	-1.447428
O	-3.989929	-.500625	-.694824
C	-3.493229	-1.284686	.378082
C	-2.868203	-.395883	1.460591
H	-1.644119	1.460464	1.502439
H	-1.720581	1.895867	-.907400
H	-3.441419	.783072	-2.143079
H	-2.429770	-.670095	-2.046288
H	-2.765488	-2.026977	.004178
H	-3.675229	.161462	1.952488
H	-2.386735	-1.015199	2.229356
C	-.732142	.145367	-.005030
C	.540039	.916283	.099218
H	-.672677	-.916695	-.219334
O	.503891	2.134731	.251567
C	1.862057	.209081	.017324
C	3.020092	1.004720	.004453
C	4.280997	.422089	-.066894
C	4.406389	-.969440	-.120729
C	3.264390	-1.771136	-.102144
C	1.999449	-1.186445	-.035639
H	2.899134	2.081795	.051578
H	5.168101	1.049592	-.079686
H	5.390913	-1.426511	-.175470
H	3.356913	-2.853158	-.138906
H	1.126600	-1.830354	-.014369

H	-4.348843	-1.836258	.778948

structure: ***exo–S*–13c–B**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 654.2269012

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 153.18845

cartesian coordinates:

C	-1.943563	.873291	.643760
C	-1.912267	.670590	-.839179
C	-2.857620	-.347409	-1.446909
C	-2.915321	.054160	1.491912
H	-1.710611	1.877324	.987918
H	-1.692291	1.543364	-1.449877
H	-3.733878	.177022	-1.867210
H	-2.377518	-.906067	-2.257585
H	-3.461703	.718579	2.172556
H	-2.364339	-.655849	2.121137
C	-.746836	.166351	.001859
C	.528468	.933648	-.075304
H	-.709083	-.906950	.151040
O	.500723	2.156846	-.190216
C	1.845657	.215737	-.010357
C	3.010191	1.001864	.002582
C	4.266689	.408324	.059500
C	4.380776	-.984719	.099608
C	3.232053	-1.776750	.082383
C	1.971400	-1.181333	.029555
H	2.897591	2.080316	-.032801
H	5.159131	1.028298	.071915
H	5.361888	-1.450355	.143052
H	3.315708	-2.859776	.109667
H	1.092669	-1.817047	.011775
C	-3.921939	-.702950	.616514
O	-3.286958	-1.317865	-.501015
H	-4.706989	-.016150	.258100
H	-4.406840	-1.509380	1.174601

structure: ***exo–R*–13a–A**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 775.5783707

zero–point vibrational energy (ZPE) [kcal/mol]: 239.40430

cartesian coordinates:

C	.535302	.407257	-1.063325
C	.657840	.741878	.388998
C	1.627175	-.019996	1.297760
C	2.740210	-.807433	.556374

C	2.095713	-1.566791	-.628347
C	1.409110	-.674431	-1.675511
H	.286011	1.241543	-1.715637
H	.479758	1.784649	.639402
H	2.069530	.688455	2.005491
H	1.060342	-.730990	1.913501
C	4.040634	.028582	.258784
H	1.349365	-2.252110	-.199835
H	2.170887	-.186153	-2.295809
H	.818502	-1.296495	-2.362088
C	-.606280	.037665	-.117399
C	-1.847587	.854528	-.206841
H	-.698383	-1.010109	.148696
O	-1.774896	2.058280	-.444212
C	-3.192301	.214589	-.002825
C	-4.313391	1.061239	.013817
C	-5.591879	.544307	.195052
C	-5.772856	-.832535	.357736
C	-4.668351	-1.685037	.337194
C	-3.385555	-1.165570	.160105
H	-4.149131	2.125376	-.118782
H	-6.449484	1.211655	.209133
H	-6.771121	-1.238706	.498507
H	-4.804093	-2.756341	.458599
H	-2.542997	-1.848638	.140270
H	3.078471	-1.591276	1.249368
C	4.978960	-.755766	-.681803
C	3.775272	1.420596	-.352947
C	4.792371	.235995	1.594815
H	2.828953	-2.210631	-1.124894
H	4.567810	-.849375	-1.692921
H	5.174986	-1.766752	-.302374
H	5.944691	-.243391	-.769028
H	3.291481	1.364830	-1.331794
H	4.725601	1.952073	-.488032
H	3.145698	2.039433	.294845
H	5.076499	-.723664	2.044271
H	4.188956	.782137	2.328655
H	5.710516	.813776	1.434328

structure: ***exo–R*–13a–B**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 775.5842223

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 239.14634

cartesian coordinates:

C	.501341	-1.192735	-.869495
C	.321718	-1.897815	.435776
C	1.364944	-1.723146	1.537751
C	2.694684	-1.151708	1.015338
C	2.481163	.105326	.145943

C	1.716882	-.314868	-1.131164
H	.110707	-1.712510	-1.742020
H	-.181967	-2.859772	.384246
H	1.550031	-2.695175	2.010209
H	.973968	-1.071197	2.331168
H	3.201566	-1.919985	.415438
H	1.829397	.789881	.714084
H	2.397201	-.881940	-1.782061
H	1.402966	.564817	-1.705374
C	-.602150	-.728964	.083746
C	-2.003869	-1.056145	-.296458
H	-.424250	.192886	.627003
O	-2.269545	-2.146026	-.797936
C	-3.097812	-.051014	-.069436
C	-4.421765	-.479841	-.260201
C	-5.485538	.397543	-.076761
C	-5.242525	1.724418	.291069
C	-3.931229	2.165416	.473760
C	-2.864962	1.282791	.298633
H	-4.586334	-1.511156	-.554184
H	-6.505287	.051076	-.222036
H	-6.072366	2.411973	.432298
H	-3.736728	3.197671	.752161
H	-1.852764	1.649278	.434376
C	3.789106	.924275	-.137603
C	3.484536	2.100739	-1.089618
C	4.898393	.054463	-.763901
C	4.316327	1.524272	1.184439
H	3.347441	-.939579	1.868851
H	3.229877	1.762446	-2.099220
H	2.651383	2.711141	-.717925
H	4.360317	2.754893	-1.176596
H	5.211897	-.753586	-.093875
H	4.580347	-.397596	-1.710300
H	5.783772	.665989	-.976232
H	3.560182	2.162048	1.659521
H	4.608198	.754717	1.906812
H	5.201327	2.143842	.996228

structure: ***exo*–*S*–13d–A**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 1453.3035059

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 235.32205

cartesian coordinates:

C	-.861045	-2.964035	-.196528
C	-.453117	-2.235056	1.043987
C	.972381	-1.741753	1.202731
C	.161265	-3.203291	-1.306500
H	-1.627788	-3.722129	-.061286
H	-.935050	-2.541582	1.969343

H	1.535106	-2.433675	1.848189
H	.981546	-.758702	1.685762
H	.111047	-4.249989	-1.628752
H	-.080331	-2.591437	-2.183928
C	-1.376093	-1.543562	.047827
C	-2.807153	-1.396635	.438834
H	-.918536	-.773098	-.562147
O	-3.373864	-2.302050	1.045573
C	-3.554278	-.143079	.087373
C	-4.941055	-.131547	.311983
C	-5.698592	.996459	.014743
C	-5.079209	2.137491	-.504330
C	-3.700844	2.141600	-.722304
C	-2.941404	1.007802	-.431890
H	-5.399021	-1.025453	.722197
H	-6.771371	.990297	.187772
H	-5.669258	3.020381	-.735879
H	-3.214805	3.028770	-1.119285
H	-1.869461	1.038401	-.597495
C	1.598565	-2.907151	-.859078
N	1.616636	-1.628505	-.117828
S	3.103740	-.794158	-.102247
O	3.706775	-1.017333	-1.420498
O	3.858833	-1.087927	1.124495
H	1.975078	-3.718862	-.216551
H	2.263354	-2.817893	-1.718720
C	2.548774	.908541	-.001458
C	2.776585	1.640072	1.162008
C	2.367033	2.973816	1.216906
C	1.738167	3.584357	.126008
C	1.532388	2.825019	-1.038812
C	1.933330	1.495377	-1.111512
H	3.278101	1.170744	2.001663
H	2.546217	3.548570	2.122001
C	1.280125	5.021562	.193974
H	1.061580	3.288246	-1.902814
H	1.788208	.919400	-2.019650
H	.189787	5.083245	.306449
H	1.728954	5.545833	1.042937
H	1.541447	5.567559	-.719409

structure: ***exo*–*S*–13d–B**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 1453.3042358

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 235.53976

cartesian coordinates:

C	-1.628920	2.536155	-.369418
C	-1.055347	1.585765	-1.379611
C	.416412	1.206980	-1.329920
C	-.738840	3.103025	.737820

H	-2.424308	3.178096	-.738437
H	-1.474863	1.642887	-2.381845
H	.952144	1.750503	-2.121396
H	.552556	.139102	-1.522475
H	-.931921	4.176764	.849724
H	-.980013	2.638861	1.701638
C	-2.015906	1.062071	-.320689
C	-3.385453	.685424	-.776694
H	-1.566589	.484727	.477875
O	-3.989237	1.396619	-1.576258
C	-4.011640	-.572638	-.253818
C	-5.369135	-.792353	-.541198
C	-6.010542	-1.941851	-.092287
C	-5.299838	-2.896108	.642671
C	-3.948029	-2.693263	.923638
C	-3.304000	-1.536459	.482631
H	-5.897401	-.041751	-1.119961
H	-7.062903	-2.098183	-.314241
H	-5.799182	-3.795752	.993219
H	-3.390856	-3.435646	1.488497
H	-2.249079	-1.406494	.702197
C	.754585	2.903627	.442287
N	1.057963	1.550980	-.052560
S	1.441515	.327056	1.032781
O	.430683	-.743318	.986867
O	1.763206	.994343	2.299152
H	1.078996	3.592734	-.348915
H	1.362280	3.093991	1.327192
C	2.948015	-.369026	.349771
C	4.132006	.373259	.408463
C	5.301296	-.173738	-.106222
C	5.313262	-1.456417	-.680989
C	4.116024	-2.178927	-.720086
C	2.932049	-1.646648	-.205024
H	4.134758	1.359849	.860485
H	6.223978	.399872	-.059340
C	6.594641	-2.034439	-1.232544
H	4.106269	-3.175801	-1.153436
H	2.008166	-2.214374	-.220446
H	7.015066	-1.392946	-2.016621
H	7.357297	-2.125979	-.449436
H	6.434565	-3.027988	-1.661611

structure: ***exo*–*S*–13d–C**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 1453.301997

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 235.39

cartesian coordinates:

C	1.453829	-2.306583	.556102
C	1.015602	-1.810260	-.781847

C	-.420803	-1.344128	-1.007011
N	-1.303069	-1.751829	.102769
C	-.778410	-1.487888	1.449475
C	.445971	-2.379676	1.687536
H	2.208797	-3.089028	.541558
H	1.494966	-2.270933	-1.640987
H	-.811468	-1.806064	-1.914786
H	-.447963	-.250203	-1.147993
H	-.524294	-.420937	1.573327
H	.098936	-3.416305	1.772526
H	.912160	-2.111475	2.644747
C	1.968447	-.957462	.058804
C	3.390565	-.899199	-.388748
H	1.537392	-.070467	.510559
O	3.878846	-1.852102	-.990285
C	4.221091	.319087	-.108401
C	5.503091	.372233	-.681018
C	6.332319	1.467462	-.463715
C	5.896026	2.526933	.337661
C	4.627902	2.482675	.918462
C	3.793577	1.387140	.695224
H	5.822908	-.463712	-1.294063
H	7.319793	1.497827	-.916179
H	6.543385	3.382736	.509877
H	4.286982	3.300988	1.546793
H	2.815677	1.370150	1.164864
H	-1.557764	-1.733061	2.171946
S	-2.959694	-1.533152	-.144007
C	-3.264392	.238479	-.135533
C	-3.536914	.888540	1.071016
C	-3.732351	2.268194	1.073373
C	-3.663593	3.014177	-.112020
C	-3.393973	2.337379	-1.309859
C	-3.196628	.957939	-1.331610
C	-3.911226	4.503839	-.104597
H	-3.619949	.314107	1.987558
H	-3.950819	2.773370	2.011161
H	-3.345833	2.896732	-2.241088
H	-3.017154	.436128	-2.265592
H	-3.349573	5.007821	-.897929
H	-3.628095	4.953208	.852775
H	-4.974258	4.725665	-.267147
O	-3.625771	-2.096397	1.032889
O	-3.232827	-2.014825	-1.499725

structure: ***exo*–*S*–13d–D**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 1453.3015533

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 235.26580

cartesian coordinates:

C	-1.266854	.152850	1.727594
C	-.805722	.730441	.429436
C	.284668	.035468	-.381679
N	1.023336	-.942442	.444939
C	.146454	-1.883260	1.168163
C	-.604820	-1.107171	2.254923
H	-1.579266	.876131	2.477027
H	-.829630	1.814000	.354958
H	1.002014	.785264	-.728744
H	-.134497	-.451716	-1.274313
H	-.553050	-2.380032	.475634
H	.116877	-.816778	3.028251
H	-1.342102	-1.767223	2.730410
C	-2.196469	.096891	.518957
C	-3.361857	1.028712	.522831
H	-2.309277	-.866461	.034192
O	-3.245346	2.143508	1.025831
C	-4.669691	.608400	-.081346
C	-5.722823	1.538382	-.049511
C	-6.964918	1.222923	-.589572
C	-7.176423	-.030660	-1.171797
C	-6.139345	-.963468	-1.209090
C	-4.893186	-.646994	-.667759
H	-5.536031	2.504523	.407122
H	-7.770361	1.951695	-.558566
H	-8.146418	-.278828	-1.594493
H	-6.298778	-1.939008	-1.660098
H	-4.103664	-1.389697	-.708920
H	.770792	-2.657083	1.615735
S	2.345929	-1.657353	-.357561
C	3.539814	-.319981	-.332522
C	3.967101	.238859	-1.534890
C	4.931383	1.248518	-1.509462
C	5.473254	1.702207	-.301902
C	5.028074	1.114367	.894816
C	4.070166	.107218	.888964
C	6.512079	2.797709	-.274002
H	3.552761	-.120578	-2.470724
H	5.267956	1.686706	-2.445588
H	5.443084	1.450246	1.842198
H	3.736107	-.347707	1.815521
H	6.141080	3.682273	.258578
H	6.793757	3.109411	-1.284112
H	7.421503	2.469457	.243461
O	2.022285	-1.936603	-1.765505
O	2.817263	-2.735444	.519169

structure: ***exo*–*R*–13e–A**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 980.2044183

zero–point vibrational energy 241.19366

(ZPE) [kcal mol^{-1}]:

cartesian coordinates:

C	-.443345	2.531473	-.625503
C	-.545485	2.267380	.849283
C	.699912	1.899478	1.640450
C	.915876	2.456157	-1.326757
H	-1.156376	3.250529	-1.019879
H	-1.294079	2.836602	1.396105
H	1.058240	2.785134	2.184687
H	.495506	1.112289	2.367517
H	1.053573	3.345140	-1.953903
H	.949087	1.589817	-1.999405
C	-1.103513	1.248552	-.140096
C	-2.587219	1.128509	-.234413
H	-.523896	.338859	-.254759
O	-3.287711	2.125700	-.382672
C	-3.208675	-.231619	-.123193
C	-4.555905	-.370078	-.493891
C	-5.190653	-1.604558	-.401592
C	-4.490768	-2.715737	.078955
C	-3.156144	-2.584958	.466068
C	-2.513258	-1.351072	.361429
H	-5.082604	.508748	-.851508
H	-6.230997	-1.703701	-.699761
H	-4.986726	-3.679939	.155027
H	-2.613474	-3.443400	.852287
H	-1.480588	-1.264326	.685940
C	2.082647	2.367446	-.326296
N	1.772328	1.438908	.762468
C	2.091014	.102350	.744747
O	1.614690	-.723013	1.514505
O	3.005456	-.162908	-.219901
C	3.560976	-1.515578	-.390065
C	4.536190	-1.326485	-1.555475
C	4.307655	-1.940457	.878586
C	2.450079	-2.500245	-.770758
H	5.304843	-.589311	-1.301486
H	5.030020	-2.275166	-1.790298
H	4.008073	-.980808	-2.450281
H	4.811790	-2.897830	.704717
H	3.621007	-2.051252	1.719088
H	5.069948	-1.197340	1.137647
H	1.907259	-2.138888	-1.651430
H	1.745494	-2.633870	.050976
H	2.890701	-3.472090	-1.020482
H	2.256040	3.349831	.131843
H	3.005069	2.057026	-.814248

structure: ***exo–R*–13e–B**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 980.2040108

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 240.99705

cartesian coordinates:

C	.740697	-2.585342	-.234462
C	.311156	-1.944550	1.048768
C	-1.137003	-1.526260	1.248272
C	-.272921	-2.807425	-1.357597
H	1.540986	-3.315358	-.145107
H	.821586	-2.280224	1.948303
H	-1.632286	-2.273256	1.890192
H	-1.201446	-.562778	1.752615
H	-.156329	-3.821008	-1.758974
H	-.079338	-2.116999	-2.187714
C	1.194354	-1.157832	.090636
C	2.618906	-.969270	.487544
H	.700065	-.371365	-.469537
O	3.185475	-1.829393	1.157671
C	3.359830	.268879	.073125
C	4.655623	.448460	.585981
C	5.404681	1.569690	.245234
C	4.872470	2.529280	-.621412
C	3.589308	2.359357	-1.142806
C	2.835514	1.237695	-.796287
H	5.050270	-.311480	1.252104
H	6.404159	1.698132	.651999
H	5.457028	3.405284	-.890056
H	3.173413	3.099807	-1.820625
H	1.843065	1.123553	-1.219154
C	-1.719503	-2.629423	-.873648
N	-1.843875	-1.445565	-.026668
C	-2.688011	-.430217	-.401958
O	-3.305693	-.418771	-1.457686
O	-2.731651	.542937	.542333
C	-3.553231	1.748238	.348903
C	-3.287631	2.537870	1.633773
C	-3.065759	2.529049	-.876430
C	-5.033818	1.366373	.244826
H	-2.222761	2.773930	1.730632
H	-3.850549	3.477088	1.621145
H	-3.595152	1.961987	2.512780
H	-3.606794	3.479564	-.945664
H	-3.230542	1.961437	-1.793211
H	-1.997242	2.754023	-.783060
H	-5.335809	.776439	1.117396
H	-5.226198	.786087	-.658450
H	-5.646578	2.274680	.220760
H	-2.024907	-3.507031	-.284248
H	-2.410551	-2.519168	-1.708760

structure: ***exo–R*–13e–C**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 980.2007313

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 240.93924

cartesian coordinates:

C	-.904502	-2.467930	.620653
C	-.682425	-2.114762	-.805314
C	.738832	-1.835312	-1.251585
N	1.540441	-1.165798	-.221233
C	1.353382	-1.432638	1.216404
C	.334886	-2.546407	1.490571
H	-1.694533	-3.183892	.832610
H	-1.307344	-2.604635	-1.548267
H	1.206475	-2.790422	-1.539791
H	.760767	-1.195536	-2.135958
H	1.028051	-.508878	1.710943
H	.801950	-3.526835	1.322513
H	.074556	-2.504603	2.555266
C	-1.415344	-1.122347	.099729
C	-2.890462	-1.002783	-.093751
H	-.868682	-.233818	.389904
O	-3.565092	-2.004735	-.316186
C	-3.547989	.343847	-.013422
C	-4.952182	.378635	.012973
C	-5.630106	1.591280	.080038
C	-4.914041	2.791896	.110235
C	-3.519192	2.770876	.072830
C	-2.838737	1.554353	.015656
H	-5.487229	-.564559	-.021281
H	-6.716390	1.604457	.106232
H	-5.442350	3.740399	.159786
H	-2.958985	3.701787	.086650
H	-1.754595	1.561184	-.026977
H	2.316123	-1.697712	1.665067
C	2.490289	-.274819	-.653455
O	2.709575	-.021729	-1.830292
O	3.135824	.277814	.405687
C	4.216591	1.255108	.206340
C	4.638330	1.580396	1.642062
C	5.374249	.612727	-.565750
C	3.673060	2.505638	-.493754
H	4.988668	.679761	2.156872
H	5.450267	2.315166	1.637950
H	3.797912	1.996200	2.207619
H	6.219329	1.309219	-.607374
H	5.074550	.360240	-1.583774
H	5.710019	-.298196	-.057667
H	2.824660	2.915037	.066189
H	3.349462	2.275340	-1.509623
H	4.453935	3.273525	-.534682

structure: ***exo–R*–13e–D**

method: B3LYP/6–311++G**//B3LYP/6–31G*

electronic energy [a.u.]: – 980.2022031

zero–point vibrational energy (ZPE) [kcal mol^{-1}]: 240.84989

cartesian coordinates:

C	.763164	1.181057	-1.365653
C	.344702	-.229438	-1.114824
C	-.901201	-.550609	-.292304
N	-1.660428	.646112	.082709
C	-.910766	1.854431	.410533
C	-.069233	2.309858	-.786145
H	1.229468	1.373054	-2.329352
H	.560725	-.937138	-1.910717
H	-1.557358	-1.186249	-.886586
H	-.627597	-1.127696	.605558
H	-.269718	1.668361	1.287091
H	-.745960	2.678654	-1.567662
H	.570330	3.151611	-.489231
C	1.610397	.304805	-.441975
C	2.911723	-.186249	-.980326
H	1.541350	.501081	.622424
O	2.999257	-.519367	-2.159523
C	4.110947	-.277879	-.082431
C	5.252641	-.919523	-.591048
C	6.402074	-1.040390	.182756
C	6.432760	-.512290	1.477083
C	5.308567	.136077	1.990140
C	4.152982	.250269	1.217013
H	5.208742	-1.315513	-1.600145
H	7.276385	-1.544279	-.220394
H	7.330822	-.604391	2.082206
H	5.330109	.554299	2.992762
H	3.294276	.767908	1.631638
H	-1.634300	2.618554	.692850
C	-3.009420	.623833	.338636
O	-3.647307	1.595106	.722147
O	-3.525221	-.608555	.102216
C	-4.965620	-.868141	.255480
C	-5.076870	-2.346924	-.126517
C	-5.386750	-.652654	1.713169
C	-5.766498	.004326	-.717054
H	-4.465966	-2.965536	.539062
H	-6.117720	-2.678089	-.048912
H	-4.738309	-2.508031	-1.155353
H	-6.432450	-.954530	1.841882
H	-5.283011	.394782	1.999013
H	-4.771714	-1.266346	2.380871
H	-5.409244	-.143144	-1.742391
H	-5.677378	1.060568	-.459581
H	-6.823914	-.281541	-.681920