HETEROCYCLES, Vol. , No. , , pp. -. © The Japan Institute of Heterocyclic Chemistry
Received, , Accepted, , Published online, .
DOI: 10.3987/COM- (Please do not delete.)

SUPPORTING INFORMATION

SYNTHESIS AND OPTICAL PROPERTIES OF SUBSTITUTED 5,6,7,8-TETRAAZA-AZULENO[1,8-*b*,*c*]FLUORENES, SMALL ORGANIC MOLECULES OF UNUSUAL TOPOLOGY DESIGNED FOR CIRCULARLY POLARIZED LUMINESCENCE.

Tadeusz Lemek,[a]* Krzysztof Danel,[b] Oskar Michalski,[b] and Wojciech Nitek[c]

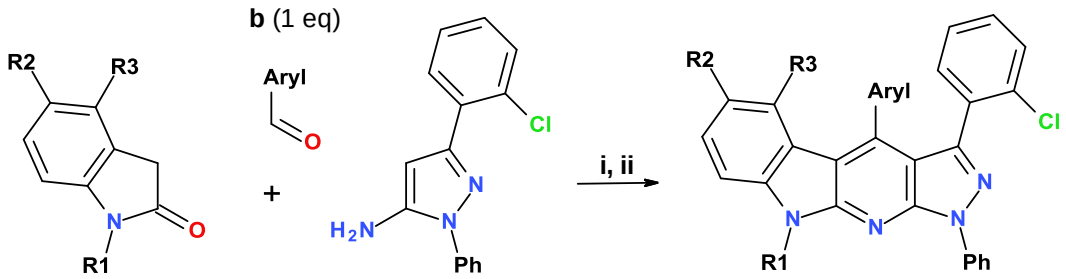
a) Tadeusz Lemek; R&D Institute of Celon Pharma S.A., ul. Marymoncka 15, 05-152 Kazuń Nowy, Poland; E-mail: Tadeusz.Lemek@celonpharma.com; b) Krzysztof Danel, Oskar Michalski; Institute of Chemistry, Faculty of Food Technology, University of Agricultural in Cracow; ul. Balicka 122, 30-149 Cracow, Poland; E-mail: Krzysztof.Danel@urk.edu.pl; Oskar.Michalski@urk.edu.pl. c) Wojciech Nitek; Department of Chemistry, Jagiellonian University of Cracow; ul. Gronostajowa 12, 30-387 Cracow, Poland; E-mail: Wojciech.Nitek@uj.edu.pl

Abstract – Helical photoluminescent substituted 5,6,7,8-tetraazaazuleno[1,8-*b*,*c*]fluorenes were obtained as racemates. The compounds have been designed for circularly polarized luminescence. Some of the compounds were separated on to enantiomers with chiral HPLC column and showed Cottons effects in absorption and emission spectra. The experimental results were compared with DFT calculations, which led us to assess the chirality to structure.

INSTRUMENTS AND MATERIALS. ^{1}H and ^{13}C NMR spectra ware measured on Bruker 600 MHz for ^{1}H and 151 MHz for ^{13}C with TopSpin 3.0 software utilisation. Chemical shifts in ^{1}H and ^{13}C NMR spectra are expressed in ppm and refer to Me_4Si (δH = 0.00 ppm, δC = 0.00 ppm). Coupling constants are in Hz. Mass spectra ware measured in IChO PAN in Warsaw. JASCO J-815 CD spectrometer was used for CD spectra measurement. JASCO P-2000 Polarimeter for optical rotation measurement. Hitachi F-7000 Fluorescence Spectrophotometer for emission spectra measurement. Shimadzu UV-2101 PC UV-Vis Scanning Spectrophotometer for UV-Vis spectra measurement. Melting points are uncorrected.

The yields refer to isolated products without optimization of the procedures. Quinoline and DMF were dried over CaH_2 and distilled under reduced pressure. Compounds **1-5** was prepared according to literature procedures as shown on Scheme 1.[1]

Substrates for **1-5** synthesis ware commercial available or were prepared according to literature procedures. All chemicals were of maximum purity available or were purified according known methods. Aluminium sheets silica gel 60F254 pre-coated layer thickness 0.2 mm ware used for TLC. Al_2O_3 gel 60 mesh was used for column chromatography. HPLC analyses ware performed on HPLC HSM D-6000A system with DAICEL Chiralcel OD-H 4,6 mm x 250 mm chiral column.



Indolinone **a** (1 eq) (1 eq) Precursor **1-5**

a			b	i	Yield	ii	Yield	
R1	R2	R3	Aryl		(%)		(%)	
H	H	H	4-*t*Bu-C_6H_4	EG, PTS (0.3 eq), reflux, 2h	32	Et-I, K_2CO_3, DMF, rt, 1d	78	**1**
Ph	H	H	2-Me-C_6H_4	Br [Bmim], PTS (0.3 eq), 140 °C, 1d	40	-	-	**2**
H	H	H	2-Me-C_6H_4	-‖-	65	Et-I, K_2CO_3, DMF, rt, 1d	83	**3**
Ph	H	H	1-Naphthyl	-‖-	27	-		**4**
Ph	Benzo		1-Naphthyl	-‖-	17			**5**

Scheme 1. Precursor compounds **1-5** synthesis[1]

COMPUTATIONS. All calculations were carried out with the GAUSSIAN 09W rev. A.02 program for M enantiomers.[2] Preliminary geometry optimizations were done semiempirically at AM1 level. Final structure optimizations were accomplished with the use of DFT B3LYP functional and 6-31G(d) basis set including the polarisable continuum model (PCM) for modelling molecules in solution (dichloromethane). In order to eliminate known systematic errors in Gibbs energies a scaling factor (0.9804) was used for zero-point energies calculations.[3] The transition state of racemisation was found by scanning the appropriate dihedral angle (dh1) and forcing a gradual change of configuration. All found transition states were saddle-points of 1st order. Cartesian coordinates of optimized structures are listed at the end of supporting information.

Absorption and CD spectra were calculated by TD DFT method at B3LYP/6-31G(d) level with PCM-LR (linear response solvation model) in dichloromethane. Peak half-width at half height: 0.167 eV

(absorbance spectra) and 0.250 eV (CD spectra). Fluorescence spectra were simulated with use of TD DFT B3LYP/6-31G(d) PCM-SS (state specific solvation model) approach in CH_2Cl_2.

X-RAY DATA COLLECTION AND REDUCTION

Crystal data	**Compound 2a**	**Compound 3a**	**Compound 4a**
CCDC dep. No	2144433	2144434	2144435
Summ. formula	$C_{37}H_{24}N_4$	$C_{33}H_{24}N_4$	$C_{40}H_{24}N_4$
M_r	524.60	476.56	560.63
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*	Triclinic, *P*
Temperature (K)	100	293	100
a, *b*, *c* (Å)	12.5372 (3), 8.8856 (2), 23.4126 (5)	18.4874 (2), 13.0915 (2), 19.9078 (2)	10.6024 (2), 11.5892 (2), 25.3271 (7)
α, β, γ (°)	90, 104.973 (2), 90	90, 90, 90	84.1643 (19), 82.6366 (19), 66.0372 (18)
V (Å^3)	2519.62 (10)	4818.24 (10)	2816.10 (11)
Z	4	8	4
Radiation type	Cu *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	0.64	0.61	0.61
Crystal size (mm)	0.31 × 0.04 × 0.03	0.42 × 0.30 × 0.05	0.16 × 0.13 × 0.07
Data collection			
Diffractometer	XtaLAB Synergy, Dualflex, HyPix	SuperNova, Dual, Cu at zero, Atlas	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian *CrysAlis PRO* 1.171.41.93a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a	Gaussian *CrysAlis PRO* 1.171.38.34a (Rigaku Oxford Diffraction, 2015) Numerical absorption correction based on gaussian integration over a	Multi-scan *CrysAlis PRO* 1.171.41.93a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical

	multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.604, 1.000	0.813, 0.972	0.670, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17536, 5330, 4497	70904, 4683, 3913	13902, 13902, 12978
R_{int}	0.058	0.077	-
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.640	0.615	0.612
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.150, 1.03	0.057, 0.163, 1.07	0.091, 0.250, 1.11
No. of reflections	5330	4683	13902
No. of parameters	371	336	795
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$_{\Delta}\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.41, −0.24	0.36, −0.30	0.46, −0.40

STRUCTURE SOLUTION AND REFINEMENT

The Table above shows technical details of diffraction experiment for compounds **2a**, **3a** and **4a**. The phase problem was solved by direct methods and positions of all of non-hydrogen atoms were determined using Sir2014[4] for compound **3a** and SHELXT[5] for **2a** and **4a**. All non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F^2. Refinement and further calculations were carried out using SHELXL2014.[6] Both Shelx programs are component of the Olex2,[7] integrated system for solution, refinement and structure analysis. Graphics were created by MERCURY.[8]

All hydrogen atoms joined to carbon atoms were positioned with an idealized geometry and refined using a riding model with $U_{iso}(H)$ fixed at 1.2 U_{eq} of C and 1.5 U_{eq} for methyl groups.
Note that in case of **4a** The analysis of the collected data showed the need to refine the structure with twin law [-1, 0, 0; 0, -1, 0; -0.4921, -0.2608, 1]. The refined BASF (Relative batch scale factor) parameter is 0.3154(17).

1a. (*M*)(*P*)(±)15-*tert*-Butyl-8-ethyl-6,8-dihydro-6-phenyl-5,6,7,8-tetraazadibenz[4,5:6,7]azuleno-[1,8-*b*,*c*]fluorene, $C_{36}H_{30}N_4$, yelow solid; m.p. 319-321 °C (546 mg, 73%, $CHCl_3$/MeOH), TLC toluene r.f.= 0.81, toluene/CH_2Cl_2 4/1 r.f.= 0.68 yellow spot; δ_H (300 MHz, $CDCl_3$) 1.42 (9 H, s), 1.54 (3 H, t, *J* 7.17 Hz), 4.59 (2 H, q, *J* 7.18 Hz), 7.18 (1 H, ddd, *J* 8.21 Hz, *J* 6.21 Hz, *J* 2.12 Hz), 7.30 (1 H, m), 7.41 (1 H, dd, *J* 8.42 Hz, *J* 2.14 Hz), 7.45-7.51 (4 H, m), 7.53-7.60 (2 H, m), 7.74 (1 H, d, *J* 2.12 Hz), 7.81-7.87 (1 H, m), 8.31 (1 H, m), 8.38(1 H, ddd, *J* 7.20 Hz, *J* 6.26 Hz, *J* 4.14 Hz), 8.43 (1 H, d, *J* 8.38 Hz), 8.58-8.63 (2 H, m);

2a. (*M*)(*P*)(±)6,8-Dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b*,*c*]-fluorene, $C_{37}H_{24}N_4$, yelow solid; m.p. 270-274 °C (45 mg, 49%, CH_2Cl_2/MeOH), TLC toluene/PE 1/1 r.f.= 0.63 yellow spot; δ_H (600 MHz, $CDCl_3$) 2.05 (s, 3H), 7.18 (dd, *J* 7.90 Hz, *J* 1.00 Hz, 1H), 7.23 (ddd, *J* 7.56, *J* 2.16, *J* 1.08 Hz, 1H), 7.36-7.53 (m, 9 H), 7.61 (dd, *J* 7.88 Hz, *J* 0.53, 1H), 7.63-7.67 (m, *2*H), 7.74 (dd, *J* 7.74, *J* 0.35, 1H), 7.81 (m, *J* 8.49, *J* 1.62 Hz, 2H), 7.95 (dd, *J* 7.79, *J* 1.42 Hz, 1H), 8.33 (dd, *J* 7.75, *J* 1.56 Hz, 1H), 8.52 (m, *J* 3.95, *J* 3.10, *J* 1.61 Hz, 2H);

δ_C (151 MHz, $CDCl_3$) 22.81, 110.20, 114.25, 119.80, 119.85, 120.95, 122.01, 122.62, 124.90, 126.59, 127.13, 127.24, 127.40, 128.08, 128.84, 129.23, 131.53, 131.67, 133.09, 134.13, 134.32, 136.37, 136.56, 138.62, 138.72, 140.33, 140.65, 141.44, 144.13, 149.59, 153.68.

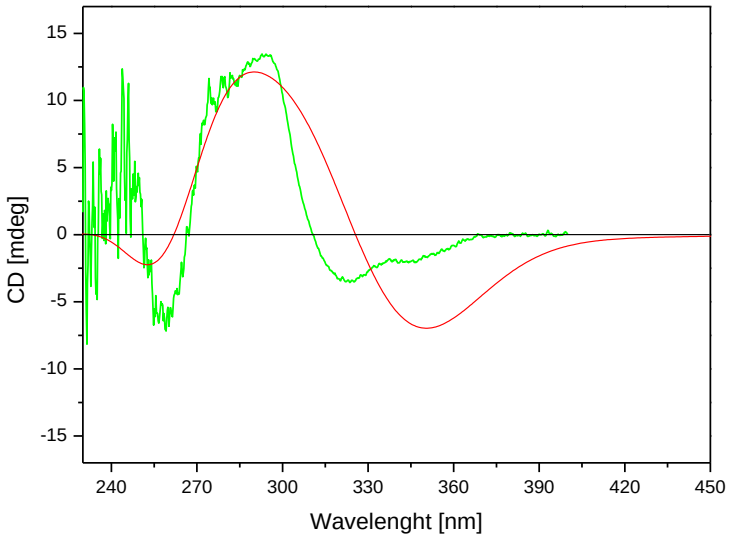


Figure 1. Comparison of the measured CD spectrum of (*P*)(-)6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]-azuleno[1,8-*b*,*c*]fluorene **2a** – (green line, CH_2Cl_2) the second fraction from HPLC with retention time 25,4 min. with calculated CD-spectrum (red line), measured specific optical rotation $[\alpha]_D^{20}$ = -926º (± 187º) (CH_2Cl_2)

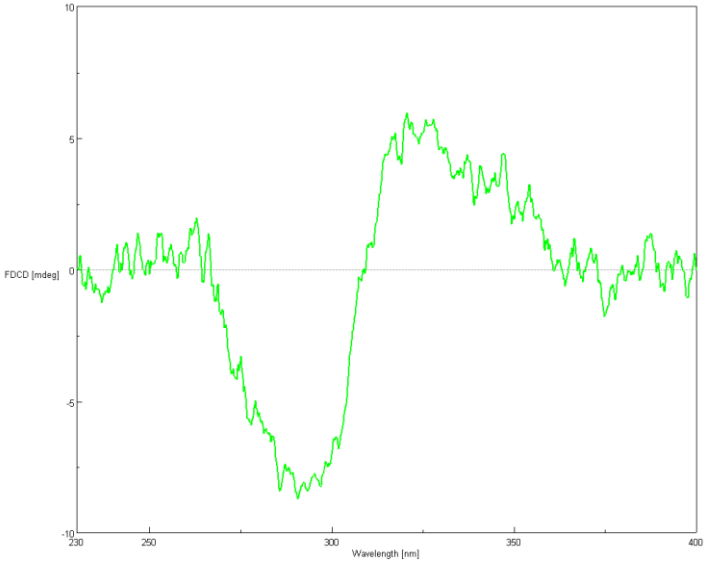


Figure 2. Fluorescence detected circular dichroism (FDCD spectrum) of **2a** fraction 15.6 min. (*M*)(+)6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b*,*c*]fluorene. (CH_2Cl_2, filter L-42)

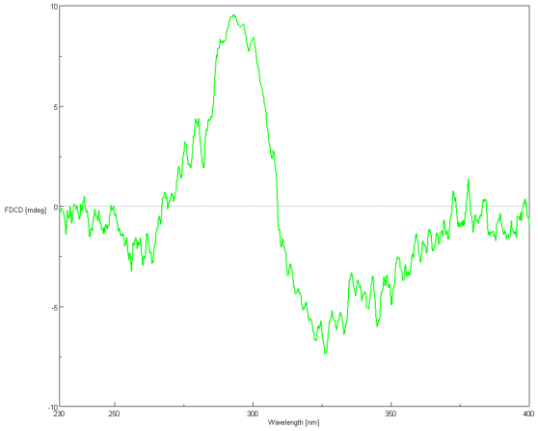


Figure 3. Fluorescence detected circular dichroism (FDCD spectrum) of **2a** fraction 25.4 min. (*P*)(-)6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b*,*c*]fluorene). (CH_2Cl_2, filter L-42)

3a. (*M*)(*P*)(±)8-Ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno-[1,8-*b*,*c*]fluorene, $C_{33}H_{24}N_4$, yelow solid; m.p. 265-269°C (42 mg, 46%, toluene/MeOH), TLC toluene/ethyl acetate 9/1 r.f.= 0.74 yellow spot; δ_H (600 MHz, $CDCl_3$) 1.52 (3 H, t, *J* 7.23 Hz), 1.95 (3 H, s), 4.55 (1 H, dq, *J* 14.36 Hz, *J* 7.19 Hz), 4.62 (1 H dq, *J* 14.49 Hz, *J* 7.26 Hz), 7.12 (1 H, ddd, *J* 8.01 Hz, *J* 7.05 Hz, *J* 1.17 Hz), 7.30 (1 H, dddd, *J* 7.49 Hz, *J* 7.37 Hz, *J* 1.10 Hz, *J* 1.00 Hz), 7.34 (1 H, dd, *J* 7.48 Hz, *J* 0.55 Hz), 7.35-7.47 (5 H, m), 7.55-7.59 (3 H, m, *J* 7.37 Hz, *J* 1.90 Hz,) , 7.69 (1 H, d, *J* 7.69 Hz), 7.92 (1 H, dd, *J* 7.83 Hz, *J* 1.35 Hz), 8.32 (1 H, dd, *J* 7.80 Hz, *J* 1.52 Hz), 8.61 (2 H, m);

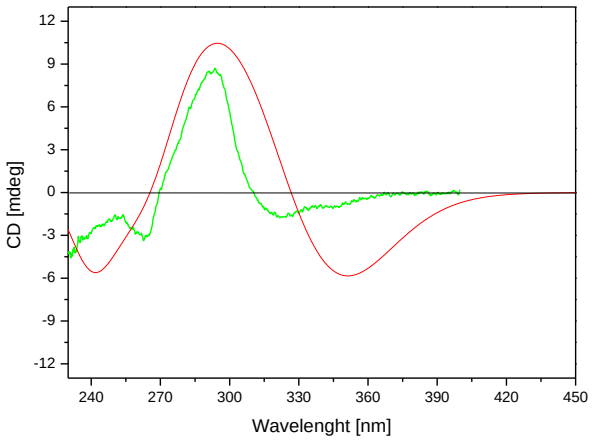


Figure 4. Measured CD spectrum of **3a** (second fraction from HPLC with retention time 10.1 min.) (*P*)(-)-8-ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b*,*c*]fluorene (green line CH_2Cl_2), and calculated CD spectrum (red line), measured specific optical rotation $[\alpha]_D^{20}$ = -773º (±187º) (CH_2Cl_2)

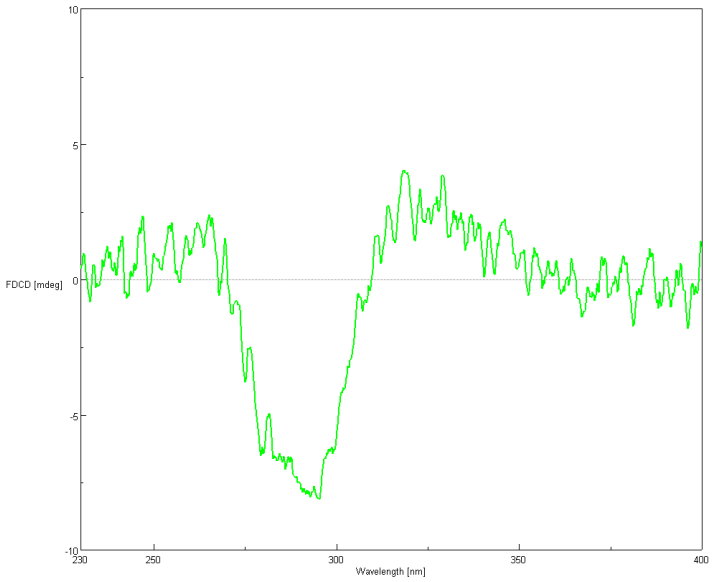


Figure 5. Fluorescence detected circular dichroism - FDCD spectrum of **3a** (fraction from HPLC with retention time 7.64 min.) (*M*)(+) enantiomer. (CH_2Cl_2) filter L-42

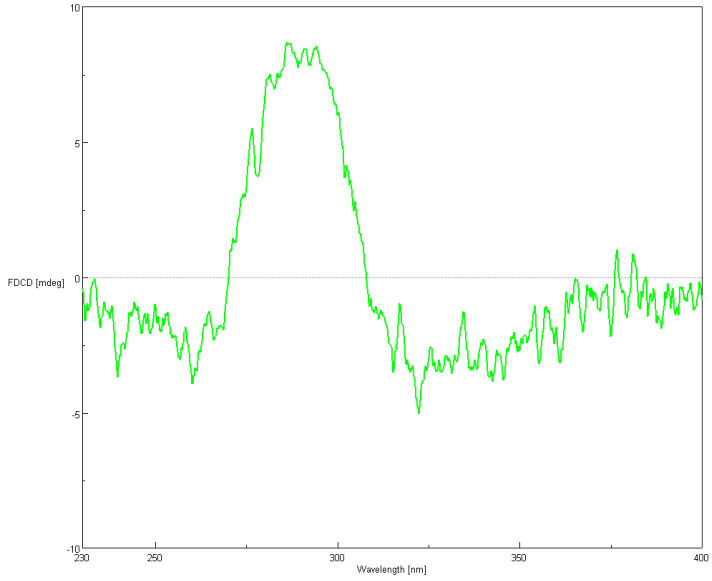


Figure 6. FDCD spectrum of **3a** fraction with retention time of 10.1 min. (*P*)(-) enantiomer. (CH_2Cl_2) filter L-42

4a. (*M*)(*P*)(±)6,8-Dihydro-6,8-diphenyl-5,6,7,8-tetraazabenzo[4,5]naphtho[2',1':6,7]azuleno[1,8-*b*,*c*]-fluorene, $C_{40}H_{24}N_4$, dark yellow solid; m.p. 278-282 °C (200 mg, 48%, CH_2Cl_2/acetone), TLC toluene/CH_2Cl_2 10/1 r.f.= 0.59 yellow spot; δ_H (600 MHz, $CDCl_3$) 6.62 (1 H, d, *J* 7.90 Hz), 6.78 (1 H, ddd, *J* 7.87 Hz, *J* 7.22 Hz, *J* 0.82 Hz), 7.02 (1 H, ddd, *J* 6.81 Hz, *J* 6.80 Hz, *J* 1.28 Hz), 7.21-7.27 (4 H, m), 7.40-7.54 (15 H, m), 7.57 (1 H, ddd, *J* 8.05 Hz, *J* 7.70 Hz, *J* 1.27 Hz), 7.58 (1 H, d, *J* 8.85 Hz),

7.64-7.70 (4 H, m), 7.71 (1 H, dd, *J* 7.80 Hz, *J* 0.52 Hz), 7.79-7.80 (2 H, m), 7.83-7.88 (4 H, m), 7.90-7.93 (3 H, m), 8.07 (1 H, d, *J* 8.79 Hz), 8.10 (1 H, dd, *J* 7.70 Hz, *J* 1.27 Hz), 8.26 (1 H, dd, *J* 7.87 Hz, *J* 1.22 Hz), 8.41 (1 H, dd, *J* 7.52 Hz, *J* 1.80 Hz), 8.46 (1 H, d, *J* 7.90 Hz), 8.49-8.52 (2 H, m), 8.53 (1 H, d, *J* 8.69 Hz), 8.55-8.58 (2 H, m);

δ_C (151 MHz, $CDCl_3$) 109.8, 110.4, 110.4, 114.4, 119.9, 119.9, 119.9, 120.3, 120.6, 120.7, 121.7, 121.8, 123.3, 123.8, 124.9, 125.0, 126.1, 126.1, 126.3, 126.5, 126.7, 126.8, 126.9, 127.0, 127.3, 127.4, 127.4, 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 128.6, 128.7, 128.8, 128.9, 128.9, 129.2, 129.2, 129.3, 130.1, 130.7, 130.8, 131.9, 132.3, 133.1, 133.6, 134.4, 135.0, 135.1, 135.6, 136.4, 136.5, 136.7, 137.7, 138.2, 138.9, 140.3, 140.4, 140.7, 141.2, 144.33, 149.5, 150.1, 153.7, 154.8. MS (m/z (MALDI-TOF/TOF) 560 (M^+, 30), 545 (100), 533 (70), 483 (90), 442 (50), 332 (12), 179 (10);

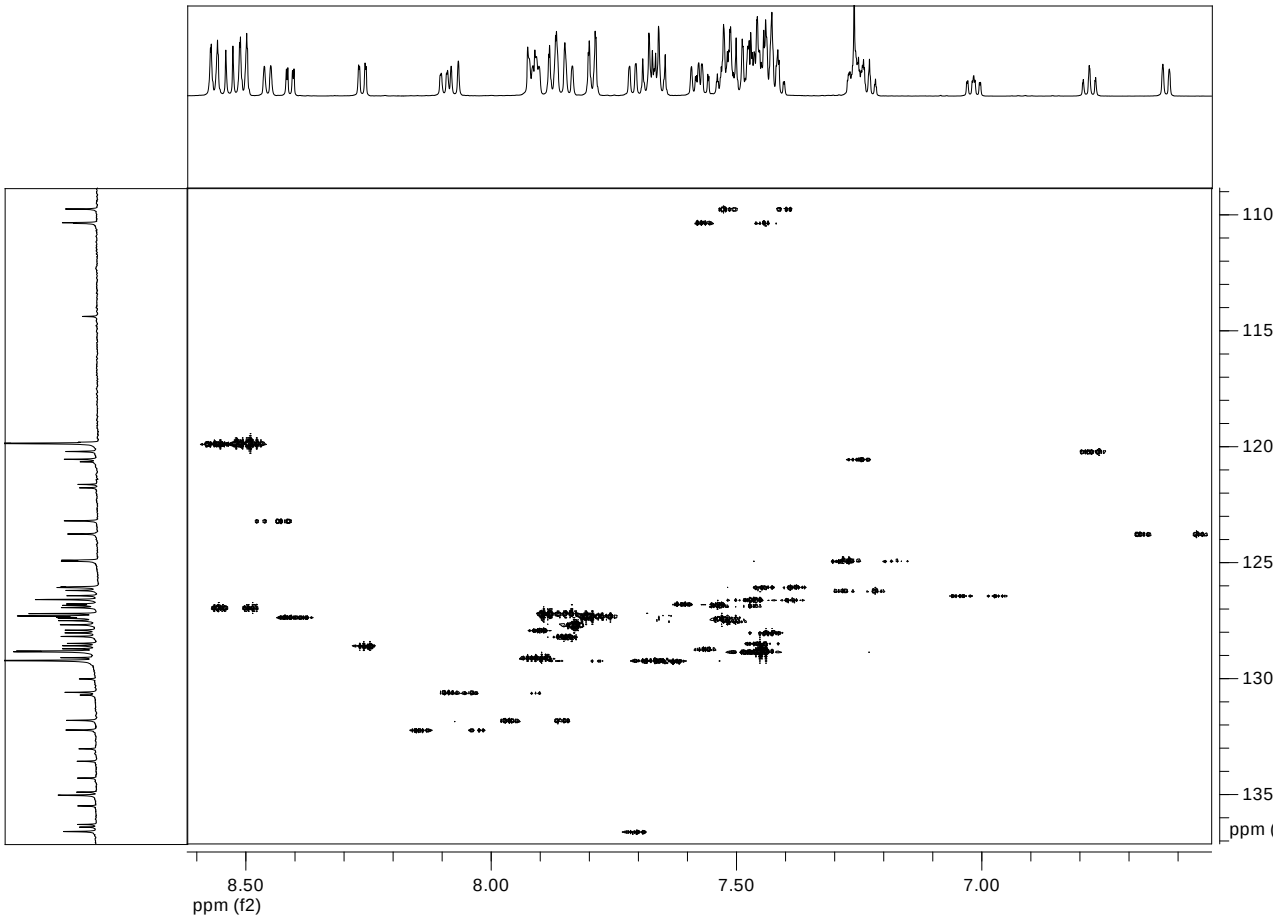


Figure 7. ^1H-^{13}C-NMR correlation spectrum of compound **4a** ($CDCl_3$)

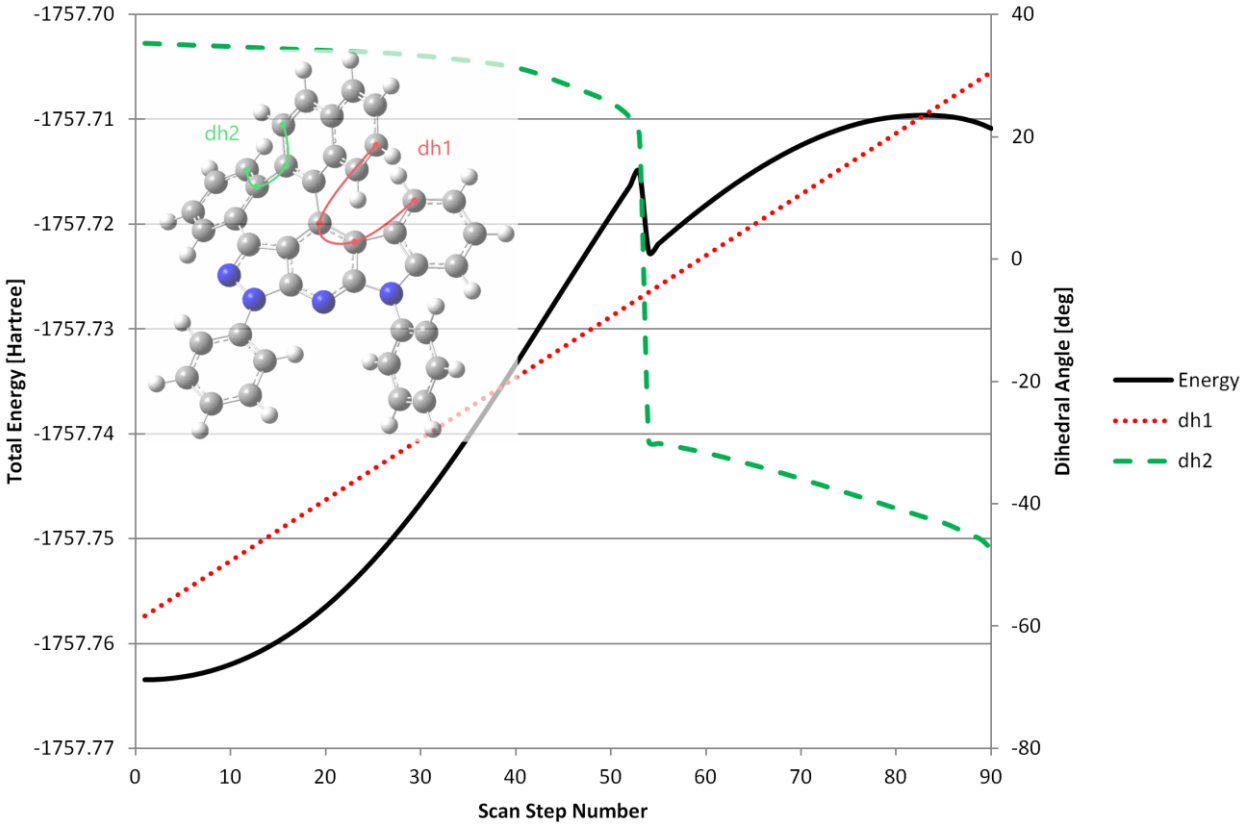


Figure 8. Configuration inversion energetic in molecule **4a**.

See also Movie 1 imagines the calculated inversion

The best inversion model of the configuration molecule **4a** was obtained by scanning the dihedral angle **dh1** (Figure 8). Scanning other dihedral angles resulted in higher energy barriers for configuration inversion. The stepwise increase of the **dh1** angle from the initial value of -58° also forces a sudden change in the value of the dihedral angle **dh2** and, as a result, a complete change of the configuration in the entire molecule. Movie 1 visualizes the whole transformation. Modelling of the conformer structure with opposite sign of the dihedral angle **dh2** showed that the energy barrier between both conformers is relatively low and the "ring flip" is easy.

5a. (*M*)(*P*)(±)6,8-dihydro-6,8-diphenyl-5,6,7,8-tetraazabenzo[*g*]benzo[6,5]naphtho[2',1':6,7]azuleno-[1,8-*b*,*c*]fluorene, orange colour solid; m.p. 303-306 °C (50 mg, 18%, CH_2Cl_2/acetone), TLC toluene/CH_2Cl_2 4/1 r.f.= 0.70 yellow spot; δ_H (600 MHz, $CDCl_3$) 7.22 (1 H, ddd, *J* 7.35 Hz, *J* 7.33 Hz, *J* 1.06 Hz), 7.27 (1 H, ddd, *J* 8.00 Hz, *J* 7.00 Hz, *J* 1.02 Hz), 7.40-7.47 (5 H, m), 7.50-7.54 (3 H, m), 7.57 (1 H, ddd, *J* 8.46 Hz, *J* 7.77 Hz, *J* 1.28 Hz), 7.64-7.67 (2 H, m), 7.71 (1 H, dd, *J* 7.84 Hz, *J* 1.09 Hz), 7.78-7.80 (2 H, m), 7.84-7.87 (2 H, m), 7.91 (1 H, d, *J* 8.70 Hz), 8.25 (1 H, dd, *J* 7.89 Hz, *J* 1.20 Hz), 8.47 (1 H, d, *J* 7.70 Hz), 8.49-8.51 (2 H, m), 8.54 (1 H, d, *J* 8.70 Hz); δ_C (151 MHz, $CDCl_3$) 110.4, 119.8,

119.9, 120.6, 121.7, 123.2, 124.9, 126.07, 126.09, 126.6, 126.9, 127.0, 127.3, 127.5, 127.7, 128.2, 128.6, 128.7, 128.8, 129.1, 129.3, 133.6, 134.3, 134.9, 135.0, 135.5, 136.3, 136.6, 137.7, 138.9, 140.3, 141.1, 144.3, 149.5, 154.8. MS (m/z (EI, 70 eV) 610 (M^+, 5), 574 (6), 560 (100), 280 (20).

REFERENCES

1. a) R. Ghahremanzadeh, S. Ahadi, and A. Bazgir, *Tetrahedron Lett.*, 2009, **50**, 7379; b) H. Yupeng, Q. Wei, G. Dewen, and T. Yao, Wuhan Shengchengyu Tech. LLC., PRC, Faming Zhuanli Shenqing Patent, 2018, CN 109096281, A.
2. Gaussian 09W, rev. A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
3. M.W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
4. Sir2014 - M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone, and G. Polidori, *J. Appl. Cryst.*, 2015, **48**, 306.
5. SHELXT, G.M. Sheldrick, *Acta Crystallographica Section A*, 2015, **A71**, 3.
6. SHELXL 2014, G.M. Sheldrick, *Acta Crystallographica Section C*, 2015, **C71**, 3.
7. OLEX2, O.V. Dolomanov, L. J. Bourhis J., R.J. Gildea, J.A.K. Howard, and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339.
8. MERCURY, C.F. Macrae, I. Sovago, S.J. Cottrell, P.T.A. Galek, P. McCabe, E. Pidcock, M. Platings, G.P. Shields, J.S. Stevens, M. Towler, and P.A. Wood, *J. Appl. Cryst.*, 2020, **53**, 226.

OPTIMIZED STRUCTURES COORDINATES

Compound **1a**

- structure of the basic conformer:

C	-0.44522000	1.73297300	0.18625000
C	-1.86284300	1.79100400	-0.08264700
C	0.18467200	0.47277400	0.16046100
C	-0.03941700	3.11069200	0.43307600
N	-2.68983300	0.77790400	-0.33550000
C	-0.71108900	-0.61334300	0.09003800
C	-1.20248600	3.91311700	0.26922100
N	-2.28027500	3.10284500	-0.07483100
C	1.14878300	3.73076300	0.84926000
C	1.63498700	0.24084200	-0.03222800
C	-2.08192700	-0.40600400	-0.19805300
C	-0.57454400	-2.02644000	0.24461300
C	1.16938900	5.10853600	1.05722000
C	-1.18614900	5.29549900	0.46808000
C	-3.66092900	3.53736900	-0.26659400
C	2.33286100	-0.95166700	0.31654900
C	2.32763900	1.20553400	-0.78524900
H	2.04698200	3.14587800	1.01392100
N	-2.64941100	-1.66197700	-0.29799700
N	-1.72801400	-2.63577900	0.00488500
C	0.01592500	5.88399300	0.85833300
C	0.52918700	-2.71082200	0.92823800
C	1.80823700	-2.11979300	1.09468400
C	3.66967000	-1.07185700	-0.11036200
C	3.65461500	1.05910000	-1.17061400
H	2.09019200	5.58698800	1.37812200
H	-2.08115700	5.89520100	0.33675100
C	-4.44676400	3.64243100	1.04345500
H	-4.13056800	2.81500200	-0.93806400
H	-3.63709700	4.50049100	-0.78575600
C	-3.97020700	-2.04618500	-0.64593200
C	4.36492900	-0.09877500	-0.83829600
C	0.24495000	-3.93695600	1.55963200
C	2.70314700	-2.75395400	1.98278100
H	0.05406300	6.95757100	1.02030000
H	4.18024200	-2.00030500	0.11650900
H	4.11236100	1.84775100	-1.75673500
H	-3.98038700	4.35622000	1.73040600
H	-4.49986100	2.66906500	1.54129600
H	-5.46827800	3.98109700	0.83886400
C	-5.02646500	-1.12378800	-0.61652100
C	-4.21392200	-3.37706500	-1.01825300
C	1.16961400	-4.56779800	2.38070500
C	2.40031700	-3.95215200	2.61989100
H	-0.74042900	-4.36631400	1.41486400
H	3.66022200	-2.28377700	2.18284200

C	-6.31227300	-1.54089100	-0.96317200
C	-5.50560400	-3.77659400	-1.35376700
H	-4.83737000	-0.09784900	-0.33160400
H	-3.39181900	-4.08144500	-1.03893000
H	0.91876300	-5.51007600	2.85953600
H	3.11973000	-4.39844400	3.30056700
C	-6.56307900	-2.86361700	-1.33098200
H	-7.12415400	-0.81899300	-0.93763600
H	-5.68216500	-4.80974600	-1.64047900
H	-7.56768500	-3.17949500	-1.59707900
H	1.79289700	2.08837300	-1.11291200
C	5.82596700	-0.34300800	-1.25337500
C	6.40937800	0.84422400	-2.04279600
H	5.86295000	1.02300300	-2.97582000
H	6.39775800	1.76953900	-1.45560400
H	7.45156300	0.63242500	-2.30601800
C	5.90644900	-1.60467900	-2.14562400
H	6.94546900	-1.78967800	-2.44334100
H	5.54493100	-2.49811400	-1.62592200
H	5.30895800	-1.47915100	-3.05585700
C	6.69140700	-0.55354800	0.01231200
H	6.65942800	0.32909600	0.66151800
H	6.35577800	-1.41545400	0.59883900
H	7.73618900	-0.72928700	-0.27048900

Compound **1a**

- structure of the transition state by racemisation inversion:

C	-0.38970700	1.72639500	-0.37128900
C	-1.84126400	1.74435000	-0.26082300
C	0.22427100	0.41745800	-0.41030900
C	-0.04232000	3.17916500	-0.49275800
N	-2.68344400	0.74177000	-0.05011500
C	-0.68718100	-0.66751800	-0.24198000
C	-1.28367800	3.89290100	-0.51474300
N	-2.33632700	3.01499300	-0.37533300
C	1.10129000	4.01197300	-0.56557100
C	1.68745000	0.12775500	-0.38514500
C	-2.06968800	-0.43387300	-0.02917300
C	-0.58770900	-2.10395800	-0.19467300
C	0.99925300	5.39564100	-0.70053300
C	-1.40114300	5.27819100	-0.65333300
C	-3.75040600	3.36572800	-0.27422200
C	2.33216200	-1.13739500	-0.15102300
C	2.55841900	1.22040900	-0.46170400
H	2.10699800	3.64187700	-0.46198900
N	-2.67765200	-1.65025700	0.17083700
N	-1.76515400	-2.65886100	0.05461700
C	-0.24218000	6.03482600	-0.76050400
C	0.54009200	-2.97306800	-0.51750100
C	1.86754500	-2.50164100	-0.54559600

C	3.64823800	-1.10084700	0.35513200
C	3.89456400	1.20845600	-0.08707600
H	1.91387400	5.97945900	-0.74662800
H	-2.37783800	5.75002900	-0.66758500
C	-4.16462200	3.79015900	1.13745700
H	-4.31510100	2.48702000	-0.59004400
H	-3.94942800	4.16340200	-0.99642400
C	-4.04091400	-1.96476200	0.41041500
C	4.44946800	0.04319500	0.44665400
C	0.26129000	-4.31073100	-0.86209400
C	2.85674600	-3.39611500	-1.02051600
H	-0.30370600	7.11368500	-0.86958600
H	4.07346400	-2.04579300	0.67211200
H	4.47130300	2.12213800	-0.17864200
H	-3.59795900	4.66444000	1.47398000
H	-3.99704500	2.97625100	1.84999400
H	-5.22953600	4.04656000	1.15087300
C	-4.91985300	-1.01632700	0.95241500
C	-4.50025800	-3.25672900	0.11483500
C	1.26137100	-5.18319900	-1.26382600
C	2.57216600	-4.71106700	-1.36570600
H	-0.76971700	-4.64218800	-0.82249000
H	3.87143600	-3.03878200	-1.14974900
C	-6.25135100	-1.36556900	1.18166600
C	-5.83044000	-3.59121000	0.35942500
H	-4.56451900	-0.02159200	1.18409100
H	-3.81202100	-3.98363700	-0.29826600
H	1.01748600	-6.20800400	-1.52913000
H	3.36723400	-5.35618200	-1.72875900
C	-6.71547100	-2.64920700	0.88998600
H	-6.92593600	-0.62420300	1.60126800
H	-6.17596900	-4.59481600	0.12686700
H	-7.75272200	-2.91342100	1.07470900
H	2.15373200	2.11507100	-0.88082200
C	5.86110900	-0.03418100	1.04786000
C	6.55916100	1.33911300	1.05131000
H	6.70255100	1.72646800	0.03615700
H	5.99226000	2.08136900	1.62464600
H	7.54891200	1.24744800	1.51218500
C	6.72910700	-1.01754000	0.22638300
H	7.73999700	-1.06999500	0.64804500
H	6.31454200	-2.03104400	0.23080100
H	6.81272600	-0.69046000	-0.81639500
C	5.76298700	-0.53549800	2.50843000
H	5.16791400	0.15176100	3.12061900
H	5.30015600	-1.52608400	2.56815300
H	6.76392200	-0.60597900	2.95075300

Compound **2a**
- structure of the basic conformer:

C	-0.07811200	-1.42405100	-0.05934200
C	-1.29990700	-0.65609600	-0.05494400
C	1.13044100	-0.75785800	0.20493800
C	-0.46273600	-2.78731300	-0.37440500
N	-1.43858000	0.64689800	0.16823000
C	1.01360600	0.64434900	0.18379100
C	-1.87449500	-2.79828600	-0.50923900
N	-2.37141200	-1.50727500	-0.28179500
C	0.25507200	-3.96439200	-0.62997500
C	2.40136600	-1.37720800	0.66043300
C	-0.25363000	1.26882600	0.23172800
C	1.95416500	1.71074000	0.08104800
C	-0.43568500	-5.11893300	-0.99176600
C	-2.57292400	-3.94973500	-0.87565000
C	3.67419400	-0.88005100	0.24370900
C	2.34653600	-2.39003000	1.66377200
H	1.33762900	-3.97433000	-0.54970500
N	-0.00716700	2.62838200	0.30626700
N	1.33734900	2.88262400	0.16828500
C	-1.83529700	-5.10993900	-1.10970700
C	3.29273300	1.57321700	-0.50874100
C	3.94882700	0.31715900	-0.61903800
C	4.83028400	-1.52113400	0.72890500
C	3.53129300	-2.99797100	2.09398900
H	0.11456800	-6.03444200	-1.18826900
H	-3.65201000	-3.94104000	-0.98491800
C	1.08520800	-2.79300200	2.40242600
C	-0.90422800	3.71779900	0.45875600
C	4.76745500	-2.59138700	1.61085300
C	3.83729600	2.69809700	-1.15713700
C	5.05831800	0.24427500	-1.48771300
H	-2.35602300	-6.01930600	-1.39611500
H	5.80254800	-1.13743900	0.44313500
H	3.47480100	-3.77394900	2.85289900
H	1.35245500	-3.12307900	3.41110100
H	0.55796400	-3.62088400	1.91821200
H	0.37698400	-1.96663700	2.49576300
C	-2.29260700	3.53447500	0.37163400
C	-0.38193600	4.99743600	0.70334100
C	4.97271800	2.60631600	-1.95059300
C	5.56593000	1.35735400	-2.14873800
H	3.31583100	3.64394700	-1.05699500
H	5.53285600	-0.71851900	-1.64629900
H	5.68120000	-3.06060800	1.96442100
C	-3.14034300	4.63192300	0.52897400
C	-1.24472500	6.08074300	0.85293500
H	-2.69699300	2.54845600	0.18688300
H	0.69032800	5.12868900	0.77275900
H	5.36524800	3.49107700	-2.44372400
H	6.41915200	1.24857700	-2.81220300

C	-2.62855900	5.90803800	0.76799400
H	-4.21409500	4.47939300	0.46016700
H	-0.82767100	7.06623600	1.04187500
H	-3.29702700	6.75571100	0.88802200
C	-3.74574200	-1.12431700	-0.32023600
C	-4.66116400	-1.74910000	0.53379000
C	-4.17637700	-0.13592100	-1.21231900
C	-6.00918900	-1.39042300	0.48615700
H	-4.31480600	-2.50340500	1.23355200
C	-5.52258100	0.22856000	-1.24114700
H	-3.45986400	0.33908200	-1.87348600
C	-6.44235600	-0.39936400	-0.39721800
H	-6.71714100	-1.87983900	1.14885200
H	-5.85358800	0.99814300	-1.93264500
H	-7.49077600	-0.11700100	-0.42777300

Compound **2a**

- structure of the transition state by racemisation inversion:

C	0.22590000	-1.51143800	-0.41169400
C	1.33117700	-0.61481500	-0.11026500
C	-1.09821700	-0.93328100	-0.39034500
C	0.90134400	-2.80481600	-0.64579000
N	1.34746200	0.70512000	-0.04389000
C	-1.07290100	0.49928100	-0.36470300
C	2.26317100	-2.65160400	-0.24822200
N	2.49335800	-1.32971400	0.10262500
C	0.61370200	-3.99681200	-1.33687400
C	-2.34474300	-1.62307800	0.10849100
C	0.14419800	1.22265500	-0.27553800
C	-2.06006800	1.53939800	-0.38584800
C	1.55443500	-5.02058100	-1.43294500
C	3.20919900	-3.67568000	-0.30020400
C	-3.35664200	-0.88836200	0.83462500
C	-2.50807900	-3.04034300	0.18802500
H	-0.32523300	-4.13830800	-1.83344500
N	-0.15489900	2.56444800	-0.32873300
N	-1.50884900	2.74328100	-0.39551200
C	2.83314000	-4.88353300	-0.87877300
C	-3.50811400	1.41188600	-0.35193100
C	-4.08332100	0.30625800	0.30063100
C	-3.92143700	-1.48845000	1.97389200
C	-3.09977300	-3.61822000	1.31487000
H	1.28871100	-5.93007600	-1.96412300
H	4.21902300	-3.51065700	0.05967800
C	-2.42748200	-3.89791600	-1.05605700
C	0.69566600	3.69946100	-0.26303800
C	-3.69582100	-2.82516400	2.29098400
C	-4.31600100	2.43458700	-0.87462100
C	-5.49268100	0.26487700	0.38300200
H	3.54923100	-5.69790500	-0.94233300

H	-4.58371700	-0.89256600	2.59374700
H	-3.14433700	-4.70279500	1.38133100
H	-3.46578500	-4.10002000	-1.35306300
H	-1.94885400	-4.86703800	-0.89804700
H	-1.97508100	-3.37664700	-1.90009700
C	2.08058900	3.58496900	-0.45374800
C	0.12556100	4.95827100	-0.01861300
C	-5.70002200	2.37936100	-0.76567200
C	-6.28996200	1.28370800	-0.13057900
H	-3.83249400	3.27490800	-1.36163600
H	-5.97014000	-0.59848400	0.83305100
H	-4.09792600	-3.25683100	3.20266400
C	2.87916600	4.72764600	-0.39070000
C	0.93818500	6.08863000	0.03313400
H	2.52429500	2.61566200	-0.63479300
H	-0.94464100	5.03691200	0.12472900
H	-6.31302900	3.17421900	-1.18083500
H	-7.37091200	1.21024700	-0.05021300
C	2.31922300	5.98312600	-0.15007300
H	3.95122500	4.62767100	-0.53732300
H	0.48467500	7.05769600	0.22305500
H	2.94896900	6.86701200	-0.10521600
C	3.75965800	-0.75282800	0.43382200
C	4.79040100	-0.73814100	-0.51155700
C	3.96043900	-0.21046000	1.70658800
C	6.02751900	-0.18560700	-0.17579900
H	4.61918200	-1.15325300	-1.49995400
C	5.19550900	0.35142500	2.03100300
H	3.15193100	-0.23139400	2.43028500
C	6.23112200	0.36156900	1.09311200
H	6.82821900	-0.17665100	-0.90977000
H	5.34946800	0.77556600	3.01903000
H	7.19347600	0.79490200	1.35029600

Compound **3a**

- structure of the basic conformer:

C	1.20911300	-1.08422200	-0.01363000
C	0.09237700	-2.00207300	-0.00555300
C	0.95678400	0.27504200	0.23109800
C	2.37807200	-1.88992000	-0.31304100
N	-1.19354400	-1.71764200	0.19214000
C	-0.41110900	0.60734500	0.19151500
C	1.92855000	-3.23202900	-0.43796800
N	0.55514200	-3.28381700	-0.20764300
C	3.72846400	-1.59867400	-0.55019400
C	1.94243300	1.28980700	0.68436900
C	-1.40726100	-0.39508600	0.23841700
C	-1.12085900	1.83684500	0.06234300
C	4.60122400	-2.63340000	-0.88234600
C	2.79911900	-4.27333100	-0.76674800

C	-0.29082100	-4.47002500	-0.30380800
C	1.88011700	2.64935900	0.25097000
C	2.87450900	0.92790200	1.70227200
H	4.09038100	-0.57777300	-0.47617200
N	-2.61858800	0.27346900	0.28820700
N	-2.42932100	1.62752600	0.13514300
C	4.14044500	-3.95645000	-0.98277200
C	-0.55774700	3.05437200	-0.53744000
C	0.84268800	3.27799400	-0.63284800
C	2.84932300	3.54819100	0.73667000
C	3.82223700	1.86355900	2.13212700
H	5.64877800	-2.41389300	-1.06687900
H	2.44754000	-5.29566100	-0.86284200
C	-0.74070700	-4.77458000	-1.73538600
H	-1.15516300	-4.29707800	0.34149400
H	0.26890900	-5.31129800	0.11667800
C	2.84744800	-0.38773600	2.45557900
C	-3.93921800	-0.22524400	0.43295400
C	3.83450000	3.15920800	1.63403000
C	-1.44354500	3.91844000	-1.20919000
C	1.27455900	4.29542500	-1.50985300
H	4.83686500	-4.74918400	-1.24130300
H	2.79747800	4.58856800	0.43775200
H	4.53200300	1.57272000	2.90212200
H	0.11801500	-4.94196500	-2.39376000
H	-1.32963900	-3.94537300	-2.13985200
H	-1.36222200	-5.67658200	-1.74675700
H	3.24537600	-0.23077500	3.46296600
H	3.45915700	-1.16068100	1.98011300
H	1.83590900	-0.78885300	2.55199400
C	-4.20906700	-1.60048300	0.36548900
C	-4.98830100	0.68198900	0.64982500
C	-0.98661800	4.95586100	-2.01060200
C	0.38830100	5.12050600	-2.19347000
H	-2.50702300	3.72443800	-1.12058800
H	2.34012600	4.43831000	-1.65649400
H	4.56567900	3.88086400	1.98721400
C	-5.52130200	-2.05143700	0.51451800
C	-6.29203900	0.21256000	0.79155900
H	-3.40079900	-2.29957800	0.20026600
H	-4.77151300	1.74107500	0.70423600
H	-1.69515600	5.60161700	-2.52156000
H	0.77021600	5.88638400	-2.86250500
C	-6.56979400	-1.15520000	0.72610500
H	-5.71907500	-3.11866500	0.46035200
H	-7.09493100	0.92546200	0.95888600
H	-7.58801000	-1.51590200	0.83977000

Compound **3a**
- structure of the transition state by racemisation inversion:

C	-1.59455700	-0.50959400	-0.37820900
C	-0.91887300	-1.75039500	-0.01670600
C	-0.78942100	0.68844800	-0.37715100
C	-2.98979600	-0.94720300	-0.59261100
N	0.37744800	-2.00013300	0.07747400
C	0.61654700	0.40508900	-0.33556100
C	-3.08533000	-2.29405200	-0.12509000
N	-1.83206400	-2.74589900	0.23580200
C	-4.10027100	-0.49116200	-1.32659200
C	-1.24271700	2.05703000	0.07316600
C	1.10393000	-0.91953100	-0.19536200
C	1.82085200	1.18315500	-0.37870900
C	-5.27486200	-1.23858000	-1.39974600
C	-4.26270300	-3.04500200	-0.15714400
C	-1.49750700	-4.09451200	0.68309800
C	-0.33096400	2.95232800	0.75120900
C	-2.60800600	2.47116000	0.15607300
H	-4.06107100	0.42515900	-1.88201600
N	2.47682300	-0.87198200	-0.24101300
N	2.90483400	0.42170200	-0.35055000
C	-5.37579000	-2.49078400	-0.78146400
C	1.95911700	2.62989600	-0.41869500
C	0.97100900	3.42753400	0.18528900
C	-0.80484700	3.66735100	1.86470600
C	-3.05438000	3.20525400	1.25918900
H	-6.11442100	-0.84445900	-1.96523200
H	-4.29418900	-4.04843700	0.25442100
C	-1.72299700	-4.29725700	2.18374400
H	-0.44884500	-4.25828300	0.42964400
H	-2.09582800	-4.80277500	0.09978300
C	-3.49911200	2.47771800	-1.06592300
C	3.42731700	-1.91814900	-0.12242700
C	-2.15559800	3.69740100	2.20027800
C	3.11195100	3.21283200	-0.96919000
C	1.17902000	4.82430400	0.18979200
H	-6.30366900	-3.05361300	-0.83046100
H	-0.09188100	4.24199900	2.44724800
H	-4.11353000	3.44158600	1.33180900
H	-2.76772400	-4.11864000	2.45941400
H	-1.09299900	-3.61621800	2.76482700
H	-1.46733300	-5.32538100	2.46246700
H	-3.56988100	3.52601900	-1.38662300
H	-4.51824600	2.13337900	-0.87737500
H	-3.05972200	1.93904500	-1.90533700
C	3.09753600	-3.23549300	-0.46932200
C	4.72031900	-1.61336200	0.32611900
C	3.30278300	4.58877300	-0.93620000
C	2.32572300	5.39849800	-0.35158600
H	3.85501900	2.56153700	-1.41743000
H	0.41199500	5.47070400	0.60206400

H	-2.49685600	4.21159200	3.09379300
C	4.06017800	-4.23851800	-0.35128900
C	5.67314300	-2.62509500	0.42744800
H	2.10193100	-3.46895300	-0.82279900
H	4.96396700	-0.59023800	0.58525000
H	4.19627100	5.02704200	-1.37164900
H	2.44515900	6.47816500	-0.33168600
C	5.34976800	-3.94292200	0.09447000
H	3.79673700	-5.25754600	-0.62125900
H	6.67263100	-2.37943200	0.77575400
H	6.09444600	-4.72903800	0.17979700

Compound **4a**

- structure of the basic conformer:

C	0.21015600	-1.11713400	-0.39100100
C	-1.20867500	-0.89142400	-0.25781000
C	1.08612300	-0.05707000	-0.09473400
C	0.35806700	-2.49606000	-0.82235500
N	-1.82102000	0.22582500	0.12171100
C	0.43553300	1.18170500	0.05622600
C	-0.94723000	-3.04391300	-0.90924200
N	-1.88494300	-2.06925100	-0.53841400
C	1.45343400	-3.28380600	-1.20275300
C	2.53489600	-0.16118400	0.21540400
C	-0.96655500	1.25215400	0.22338200
C	0.88015200	2.53602500	0.04937600
C	1.23465300	-4.58587100	-1.64737300
C	-1.17446000	-4.34557100	-1.35799400
C	3.46239000	0.81304600	-0.19872300
C	2.97854400	-1.23964700	1.08295300
N	-1.25843700	2.58512900	0.45329600
N	-0.13153900	3.35765000	0.29939000
C	-0.06586800	-5.11019300	-1.72038000
C	2.11556000	2.99339700	-0.59874600
C	3.18758400	2.10943000	-0.90102600
C	4.84411900	0.60133500	0.10562300
C	4.37882500	-1.43171600	1.32206700
H	-2.17930600	-4.74699100	-1.43138100
C	-2.49498100	3.21713900	0.74997600
C	5.29471600	-0.49518000	0.78761000
C	2.13487500	4.30509500	-1.11004500
C	4.15905100	2.56727600	-1.81755200
H	-0.21667800	-6.12690500	-2.07221800
H	5.56124300	1.35553500	-0.19413800
C	-3.67716600	2.47293100	0.88407200
C	-2.52369900	4.61024800	0.92072700
C	3.14419400	4.74654800	-1.95424600
C	4.14434900	3.85314900	-2.34519800
H	1.30551900	4.95876700	-0.86284800

H	4.94629800	1.88832300	-2.12741600
H	6.35692800	-0.62125100	0.98089300
C	-4.87186500	3.13018200	1.18149200
C	-3.72636200	5.24712200	1.21780800
H	-3.65850800	1.39970900	0.75204600
H	-1.60688600	5.17647400	0.82056500
H	3.12747700	5.76268300	-2.33786500
H	4.91063600	4.15464700	-3.05350300
C	-4.90882900	4.51488700	1.35011300
H	-5.78147300	2.54417300	1.28223600
H	-3.73449900	6.32599200	1.34750200
H	-5.84379100	5.01669600	1.58211300
C	-3.29910000	-2.25103800	-0.47986700
C	-4.14682300	-1.42282000	-1.22414700
H	-3.72389700	-0.63966500	-1.84358800
C	-5.52735200	-1.61201500	-1.15986400
H	-6.18286200	-0.96547200	-1.73632800
C	-6.06472300	-2.63278000	-0.37129500
H	-7.14001000	-2.78083700	-0.33016600
C	-5.21464300	-3.46092000	0.36459600
H	-5.62454900	-4.25316500	0.98446200
C	-3.83316200	-3.26740300	0.32036200
H	-3.16948900	-3.89408500	0.90800700
C	2.08828500	-2.09419000	1.79624400
C	2.55043600	-3.10448900	2.61254600
H	1.83680400	-3.72449600	3.14801700
C	4.82999400	-2.50087400	2.14118300
C	3.93562200	-3.33524100	2.76976600
H	4.28592500	-4.14538300	3.40291200
H	5.90073100	-2.62609500	2.28144100
H	1.02149300	-1.93627200	1.72359500
H	2.46025200	-2.88335300	-1.15770100
H	2.07983700	-5.20128000	-1.94153600

Compound **4a**

- structure of the transition state by racemisation inversion:

C	-0.18498400	-1.19851700	-0.54143400
C	1.19996100	-0.93317500	-0.17132400
C	-1.09870300	-0.08453400	-0.40048000
C	-0.17324700	-2.64711000	-0.85485900
N	1.81802700	0.22139700	0.00453200
C	-0.40997800	1.17751000	-0.34594500
C	1.09546700	-3.15823000	-0.45214800
N	1.89580300	-2.11438800	-0.01373700
C	-0.95652400	-3.54232200	-1.61043600
C	-2.52186600	-0.10307300	0.08091500
C	0.99822200	1.24900400	-0.20638700
C	-0.79547600	2.55900100	-0.38809500
C	-0.58457800	-4.87428100	-1.76983700
C	1.47240100	-4.49779500	-0.56616400

C	-3.15053900	1.04515200	0.63709100
C	-3.28476600	-1.32630500	0.30644100
N	1.35932800	2.57595000	-0.21083600
N	0.25185800	3.36786800	-0.33417300
C	0.60205400	-5.36798400	-1.21146100
C	-2.13337000	3.11319500	-0.51821500
C	-3.21654900	2.40115600	0.02214200
C	-3.95992900	0.87882900	1.80481600
C	-4.07845300	-1.48676500	1.48874700
H	2.43634900	-4.83028500	-0.19650300
C	2.63709400	3.17929800	-0.07247800
C	-4.29144000	-0.34952100	2.31185400
C	-2.33140100	4.37349100	-1.10410900
C	-4.49658000	2.98930900	-0.05663200
H	0.86782400	-6.41521100	-1.32393000
H	-4.27970400	1.77965500	2.31871000
C	3.81498900	2.44641000	-0.27788000
C	2.70870500	4.54079400	0.25886400
C	-3.60017700	4.93762700	-1.16789000
C	-4.68963900	4.23731000	-0.64194600
H	-1.47023700	4.89876300	-1.50363900
H	-5.35332500	2.44501700	0.32720300
H	-4.82907800	-0.44559300	3.25092600
C	5.05041400	3.08113700	-0.14341400
C	3.95103300	5.15943400	0.38052400
H	3.76216500	1.39546700	-0.52720000
H	1.79309900	5.09777800	0.41338800
H	-3.74156300	5.91040600	-1.63007800
H	-5.69046400	4.65632700	-0.69528000
C	5.12975500	4.43586700	0.18275600
H	5.95754400	2.50456900	-0.30292800
H	3.99404900	6.21443500	0.63724800
H	6.09610900	4.92177400	0.28235900
C	3.27670300	-2.20919900	0.34832600
C	3.66673600	-1.94154200	1.66362000
H	2.91755700	-1.65880500	2.39622000
C	5.01231000	-2.04118300	2.01858800
H	5.31531400	-1.83034100	3.04012800
C	5.96408400	-2.41718600	1.06725600
H	7.01033000	-2.49878900	1.34789600
C	5.56928200	-2.68706700	-0.24517100
H	6.30606700	-2.97603500	-0.98916400
C	4.22632700	-2.57814900	-0.60997100
H	3.91139400	-2.77515300	-1.63012700
C	-3.45985700	-2.28641500	-0.70864500
C	-4.21431400	-3.42978800	-0.51402700
H	-4.35301600	-4.12957700	-1.33332900
C	-4.76798400	-2.70452500	1.71265500
C	-4.82126200	-3.67600100	0.73334900
H	-5.38438100	-4.59045600	0.89618100

H	-5.32192000	-2.82308900	2.64053800
H	-3.08136300	-2.04470900	-1.69145300
H	-1.83878000	-3.21399800	-2.12759800
H	-1.22259600	-5.53107600	-2.35404900

Compound **5a**
- structure of the basic conformer:

C	0.40347800	-0.68184200	-0.29647200
C	-0.94167500	-1.21081500	-0.19043500
C	0.57693600	0.68660900	0.00858500
C	1.25429800	-1.81876800	-0.61466000
N	-2.06816500	-0.55632400	0.07073500
C	-0.62620900	1.41787600	0.02213300
C	0.42715900	-2.95660400	-0.59533200
N	-0.89169700	-2.58640200	-0.32580300
C	2.62208400	-1.96585200	-1.02333700
C	1.80464400	1.35496600	0.51670600
C	-1.87774700	0.76756800	0.09691900
C	-0.93182400	2.80921600	-0.04867100
C	3.10808800	-3.29722100	-1.26822100
C	0.89740200	-4.26025700	-0.85876200
C	2.15083000	2.66765200	0.14881700
C	2.58971500	0.67164600	1.53243100
N	-2.82713400	1.76927600	0.19773500
N	-2.23951100	3.00449900	0.06239400
C	2.22799300	-4.41473000	-1.16117300
C	-0.03352700	3.81664000	-0.62469000
C	1.36993200	3.61389900	-0.71184400
C	3.36561200	3.21907300	0.66439000
C	3.81659500	1.25324000	1.99265000
H	0.22442100	-5.10970400	-0.82267900
C	-4.23264300	1.68741400	0.37797200
C	4.18988500	2.53043000	1.51114600
C	-0.61564700	4.92316200	-1.27118100
C	2.09786600	4.48489300	-1.54970200
H	2.62522500	-5.40674500	-1.35941800
H	3.62790600	4.23460400	0.39301200
C	-4.90335800	0.45690200	0.30882200
C	-4.95450500	2.86410700	0.63201400
C	0.13927500	5.79909900	-2.03950600
C	1.50398400	5.55429300	-2.21084600
H	-1.68935200	5.05331200	-1.18895700
H	3.16035600	4.31237500	-1.68676900
H	5.11112900	2.98393300	1.86772000
C	-6.28611100	0.41832800	0.49384300
C	-6.33484800	2.80488500	0.80948000
H	-4.34847600	-0.45176100	0.11816100
H	-4.42814000	3.80843800	0.68739400
H	-0.33852800	6.64084200	-2.53264100

H	2.10439700	6.19272700	-2.85253300
C	-7.01140600	1.58424600	0.74280600
H	-6.79612000	-0.53970400	0.43908000
H	-6.88219800	3.72289900	1.00561600
H	-8.08753300	1.54342200	0.88452800
C	-2.01082700	-3.46991600	-0.23251000
C	-3.07246800	-3.35274600	-1.13572500
H	-3.03977500	-2.58944300	-1.90589000
C	-4.16122700	-4.21916800	-1.03563900
H	-4.98625300	-4.12556400	-1.73594800
C	-4.18620100	-5.20912800	-0.04962000
H	-5.03292600	-5.88584100	0.02082100
C	-3.12076900	-5.32591300	0.84554500
H	-3.13605500	-6.09003800	1.61733800
C	-2.03513200	-4.45239700	0.76270800
H	-1.21264800	-4.52305200	1.46791500
C	2.17704400	-0.53288500	2.17195300
C	2.95259400	-1.14730500	3.13219500
H	2.59379000	-2.05827500	3.60323300
C	4.61094200	0.58539500	2.96222500
C	4.19749800	-0.60253300	3.51836800
H	4.80563100	-1.10474000	4.26530900
H	5.54414500	1.04936000	3.27184300
H	1.22092100	-0.97043100	1.92502000
C	3.50813300	-0.88315500	-1.25944800
C	4.45953300	-3.48319300	-1.66035800
C	5.30294400	-2.40934400	-1.84703100
H	6.33320600	-2.56628300	-2.15376700
C	4.81202100	-1.09845000	-1.65952800
H	5.46479200	-0.24790800	-1.83673300
H	3.15096700	0.13167500	-1.14071500
H	4.81450300	-4.49732200	-1.82848100

Compound **5a**
- structure of the transition state by racemisation inversion:

C	-0.54468000	-0.65141300	-0.33111900
C	0.71543800	-1.34685900	-0.09331800
C	-0.44834300	0.79419200	-0.29858600
C	-1.55394800	-1.71643500	-0.17279700
N	1.95277300	-0.92093400	-0.27788900
C	0.89316600	1.27541500	-0.38782900
C	-0.89954700	-2.80116700	0.44864300
N	0.47201600	-2.59477400	0.44229500
C	-2.86745600	-2.03488500	-0.68938100
C	-1.50583000	1.71962200	0.18934300
C	1.98796500	0.38877200	-0.52457500
C	1.51814900	2.56295900	-0.34738700
C	-3.57898700	-3.14714500	-0.11186100
C	-1.57039900	-3.90644700	1.01608600

C	-1.20859400	2.80048600	1.06789700
C	-2.93127500	1.52214100	-0.01518000
N	3.12036800	1.14743700	-0.70477500
N	2.82421600	2.47703100	-0.56936100
C	-2.92260900	-4.01273600	0.81192600
C	0.94242600	3.84478700	0.03812800
C	-0.23399300	3.90458700	0.82323800
C	-2.11261100	2.98005600	2.16932900
C	-3.86771700	1.83198500	1.02307300
H	-1.02168900	-4.63833700	1.59863700
C	4.46604600	0.73883200	-0.88145500
C	-3.35963400	2.41689400	2.21533000
C	1.65340200	5.01758600	-0.26826000
C	-0.63622300	5.18815300	1.26600000
H	-3.48306700	-4.83018000	1.25733300
H	-1.77255300	3.58881300	3.00062000
C	4.77088100	-0.55376800	-1.33188700
C	5.49834400	1.65176900	-0.62031500
C	1.23830600	6.25997000	0.19111000
C	0.08313200	6.34051600	0.97137200
H	2.55196000	4.92587000	-0.86845500
H	-1.56327900	5.29393700	1.81585400
H	-3.99951500	2.54250200	3.08419200
C	6.10467100	-0.92388700	-1.50563200
C	6.82443300	1.26795000	-0.80906800
H	3.97616700	-1.26034100	-1.53164400
H	5.25072800	2.64818500	-0.27632300
H	1.80101400	7.15362700	-0.06284300
H	-0.27505700	7.30071600	1.33159200
C	7.13771800	-0.02056500	-1.24912300
H	6.33181700	-1.92830400	-1.85233000
H	7.61685500	1.98267000	-0.60414700
H	8.17334200	-0.31600700	-1.39055700
C	1.46777500	-3.52643100	0.87028000
C	2.35549900	-3.18011400	1.89423300
H	2.28701800	-2.20064200	2.35502800
C	3.31937400	-4.09811300	2.31044800
H	4.01016800	-3.82702200	3.10359600
C	3.39098800	-5.36200300	1.71855400
H	4.13954300	-6.07615900	2.04961000
C	2.49948800	-5.70480900	0.69985100
H	2.55297900	-6.68397900	0.23275500
C	1.54120000	-4.78664300	0.26741300
H	0.85577600	-5.03901900	-0.53565900
C	-3.44074300	1.31042900	-1.31466600
C	-4.80258600	1.31648900	-1.55959700
H	-5.16493400	1.20577900	-2.57717000
C	-5.25504900	1.70808300	0.77644900
C	-5.71996600	1.45875000	-0.50038400
H	-6.78771300	1.42164100	-0.69703000

H	-5.94938100	1.90227600	1.59022700
H	-2.74130400	1.23656400	-2.14034400
C	-3.39307500	-1.49827800	-1.88765100
C	-4.86722900	-3.48470400	-0.60043400
C	-5.38776300	-2.86928900	-1.71971500
H	-6.35837000	-3.16303100	-2.10943900
C	-4.61009100	-1.90923300	-2.39830800
H	-4.96332600	-1.49424300	-3.33844100
H	-2.78614900	-0.80465700	-2.45224400
H	-5.40698200	-4.29498800	-0.11575700