An Enantioselective Synthetic Route towards Second-Generation Light-Driven Rotary Molecular Motors

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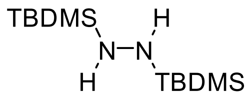
General Experimental

Chemical shifts are denoted in δ-unit (ppm) relative to $CDCl_3$ (7.26), CD_2Cl_2 (5.30), or toluene-d_8 (2.09) for ^1H NMR and relative to $CDCl_3$ (77.16), CD_2Cl_2 (53.52), or toluene-d_8 (20.40) for ^{13}C NMR. The splitting parameters for ^1H NMR are denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), m (multiplet), and b (broad). For ^{13}C NMR, the carbon atoms are assigned as q (primary carbon), t (secondary carbon), d (tertiary carbon), and s (quaternary carbon). Column chromatography was performed on silica gel as described by Still and co-workers.[1] Reactions were performed under a nitrogen atmosphere unless stated otherwise.

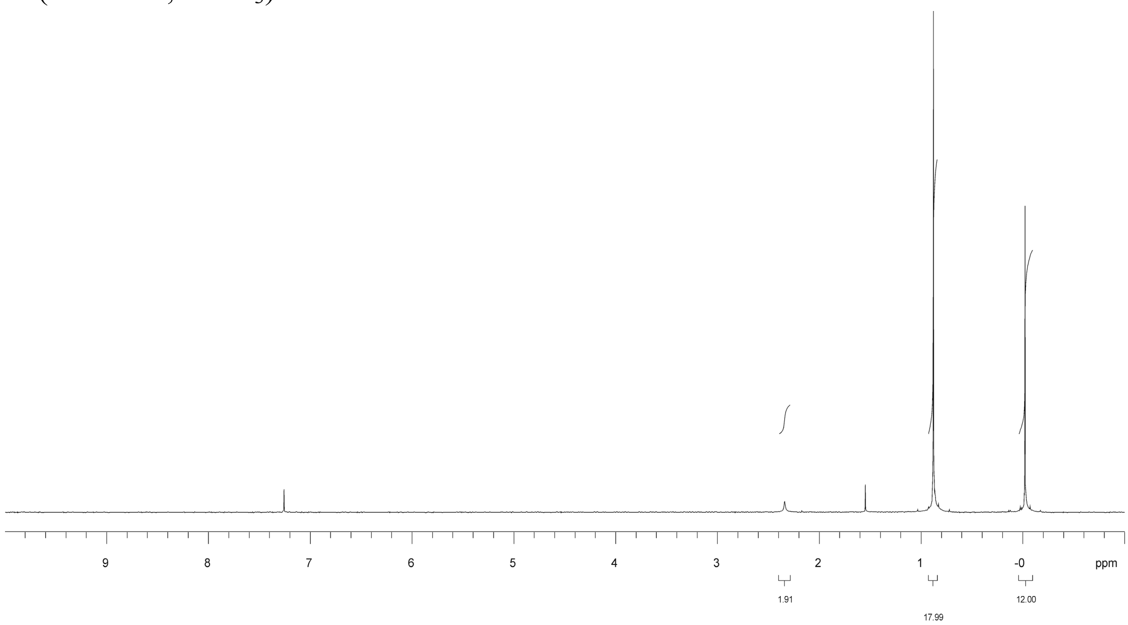
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

^{1}H NMR, ^{13}C NMR, and IR Spectra

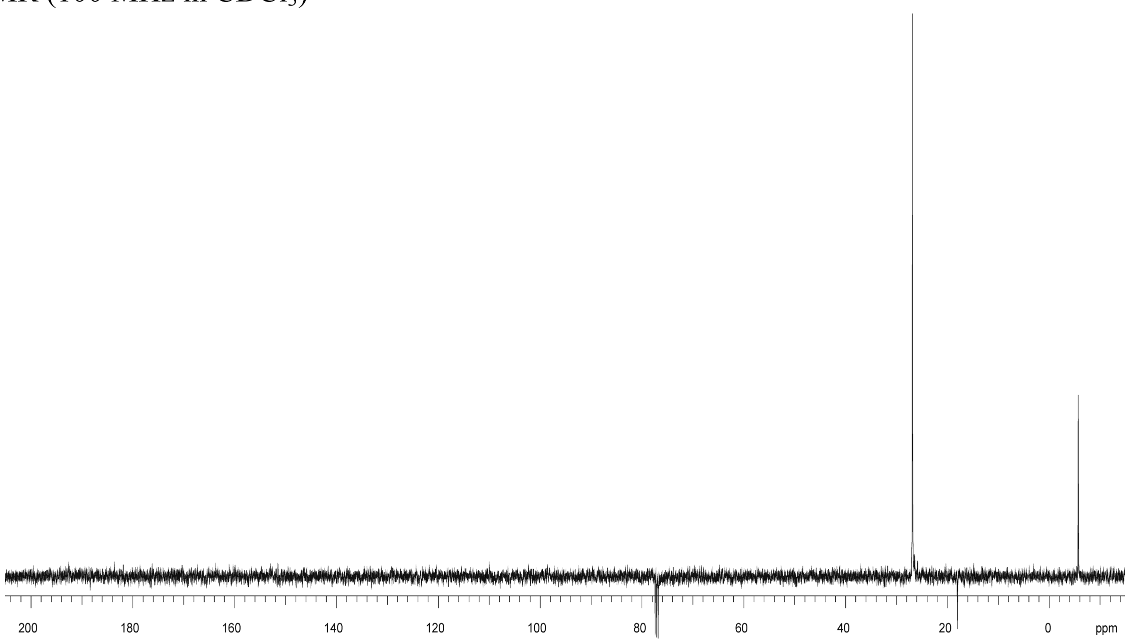
1,2-Bis(*tert*-butyldimethylsilyl)hydrazine



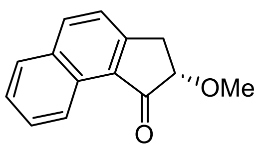
^{1}H NMR (400 MHz, $CDCl_3$)



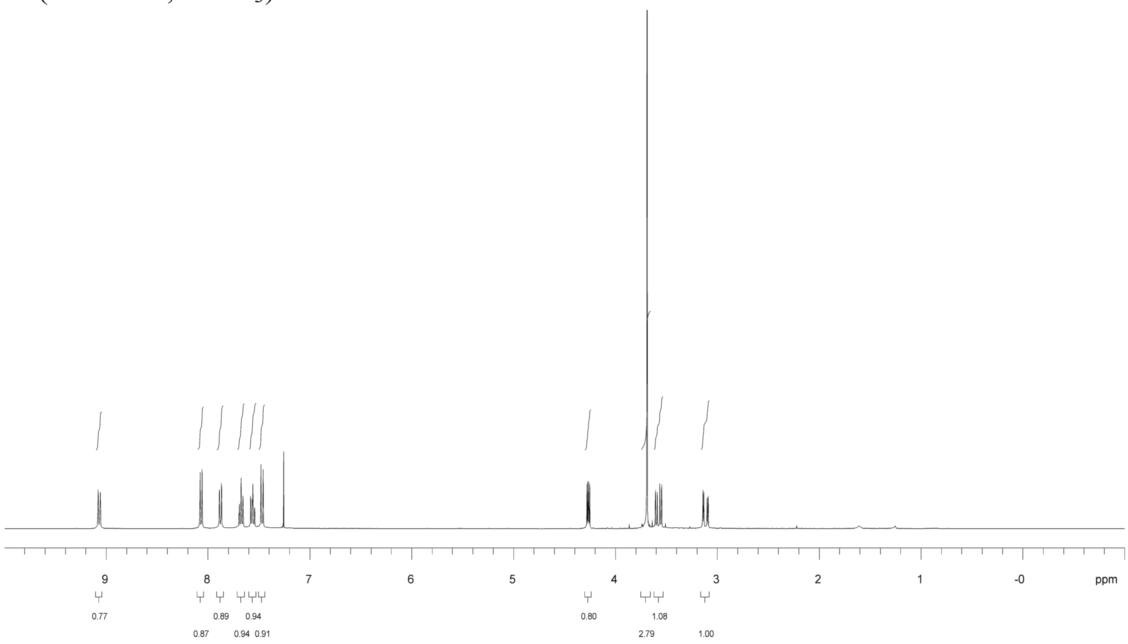
^{13}C NMR (100 MHz in $CDCl_3$)



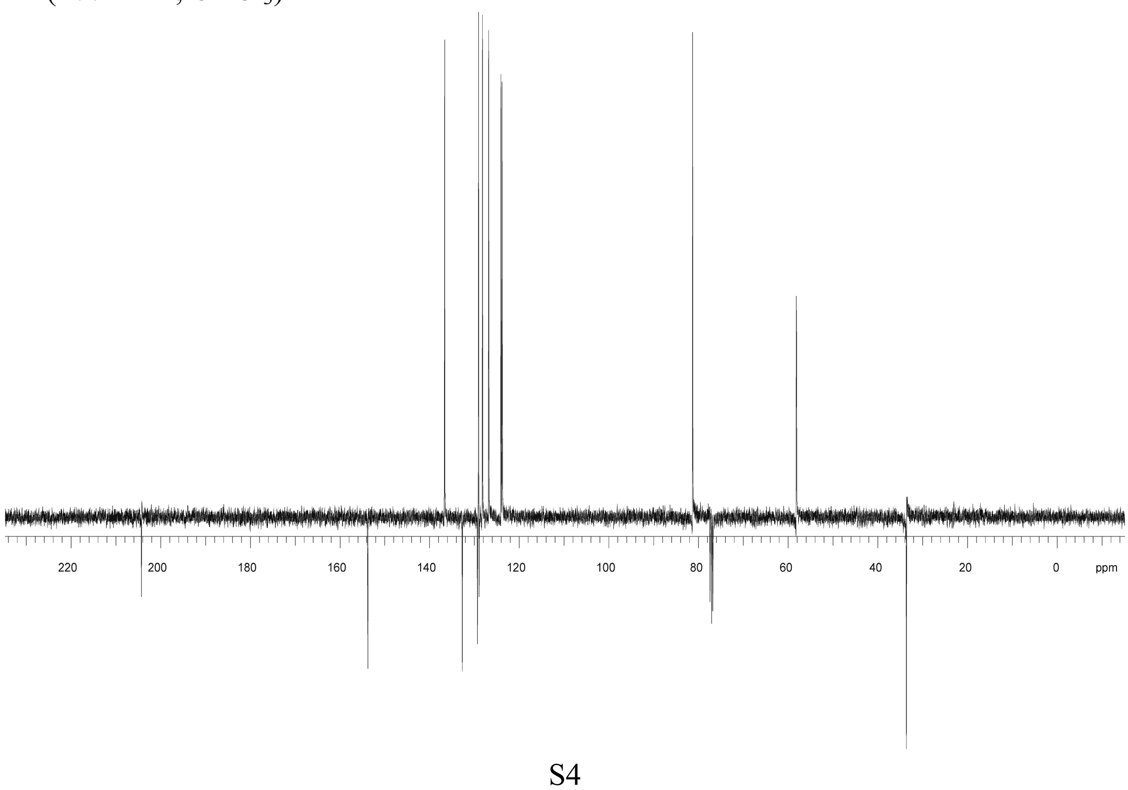
(*S*)-2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (4)



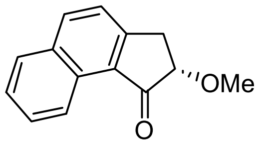
^{1}H NMR (400 MHz, $CDCl_3$)



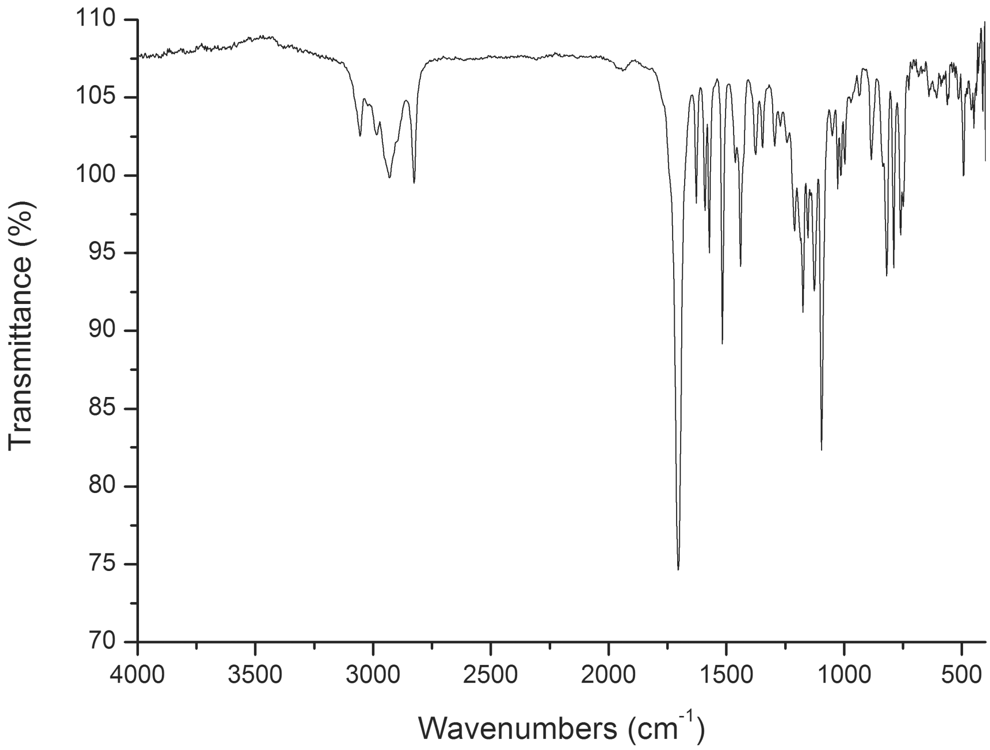
^{13}C NMR (100 MHz, $CDCl_3$)



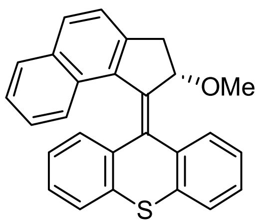
(*S*)-2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (4)



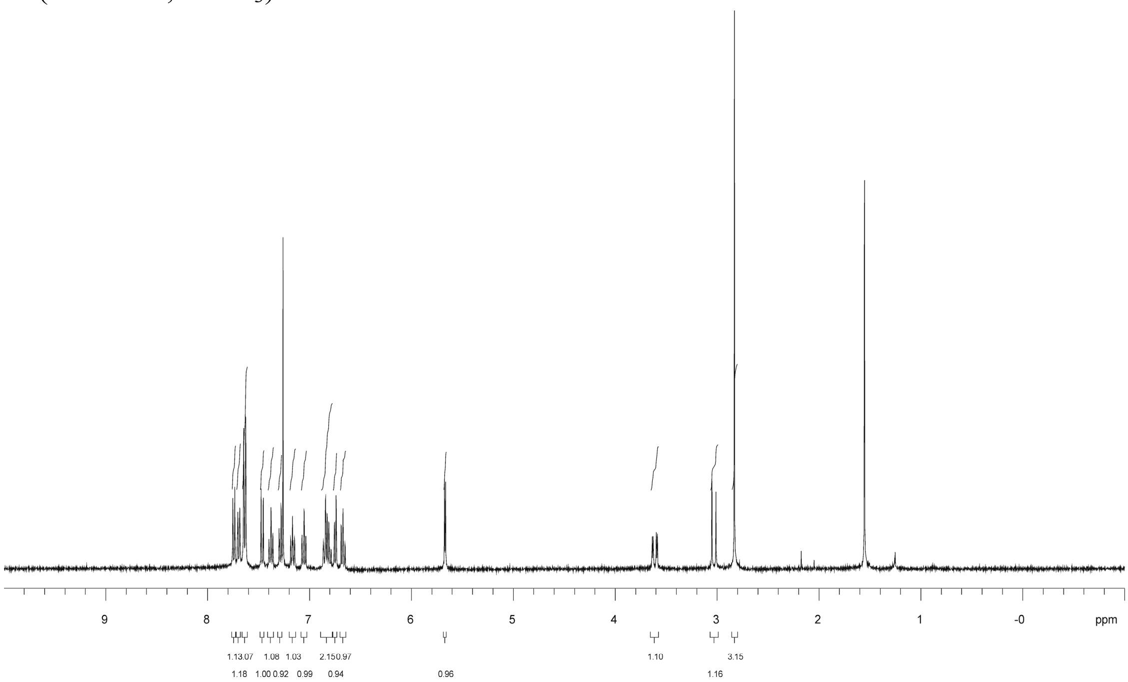
IR (KBr)



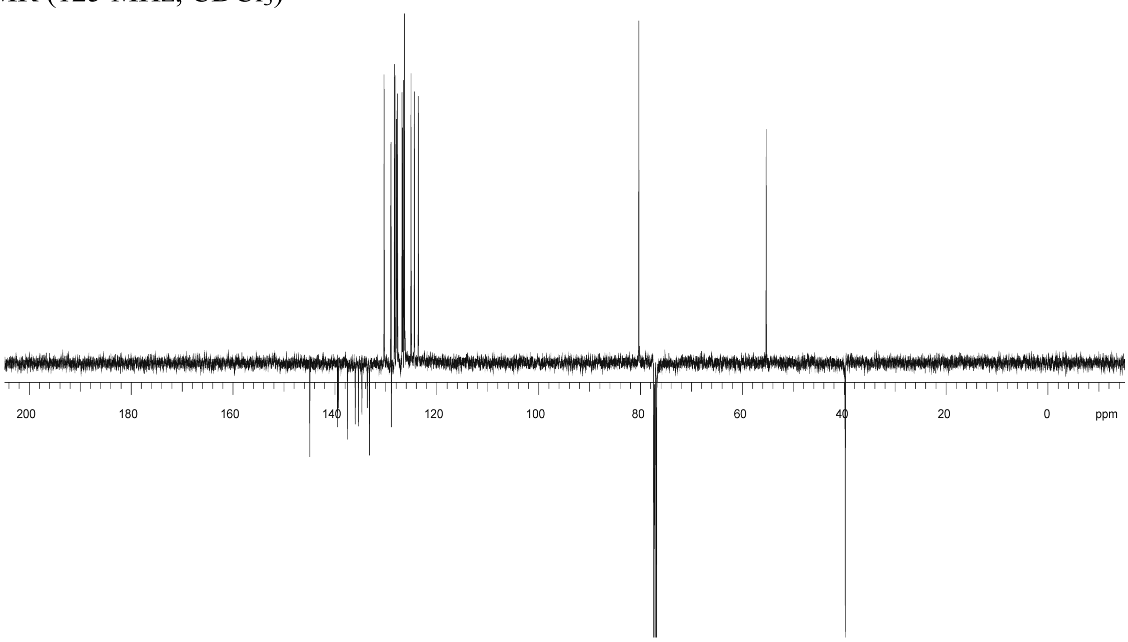
(*S*)-9-(2'-Methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-thioxanthene (5)



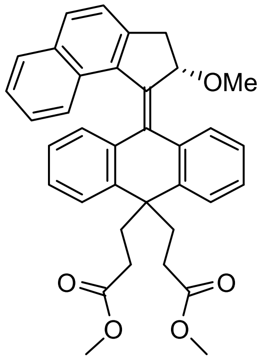
^{1}H NMR (400 MHz, $CDCl_3$)



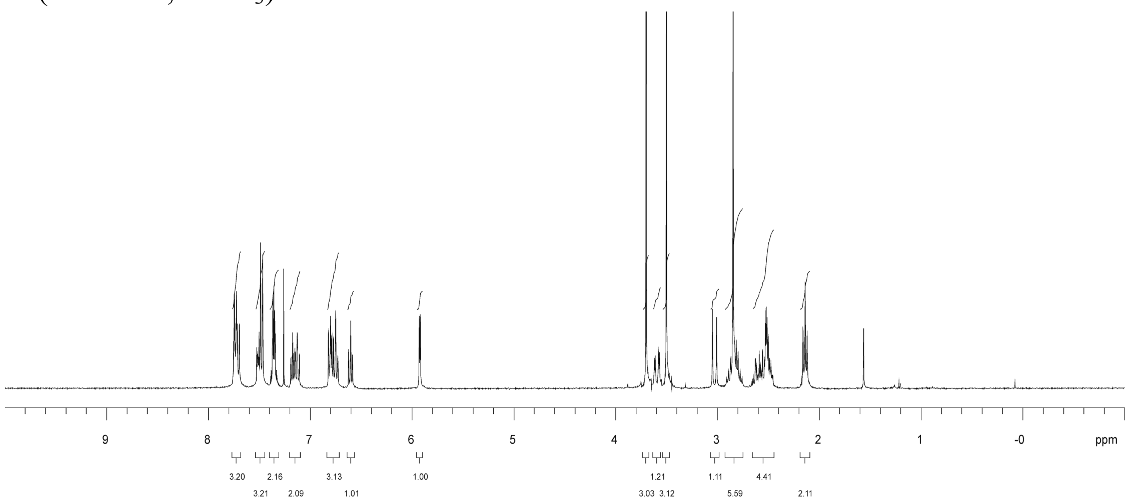
^{13}C NMR (125 MHz, $CDCl_3$)



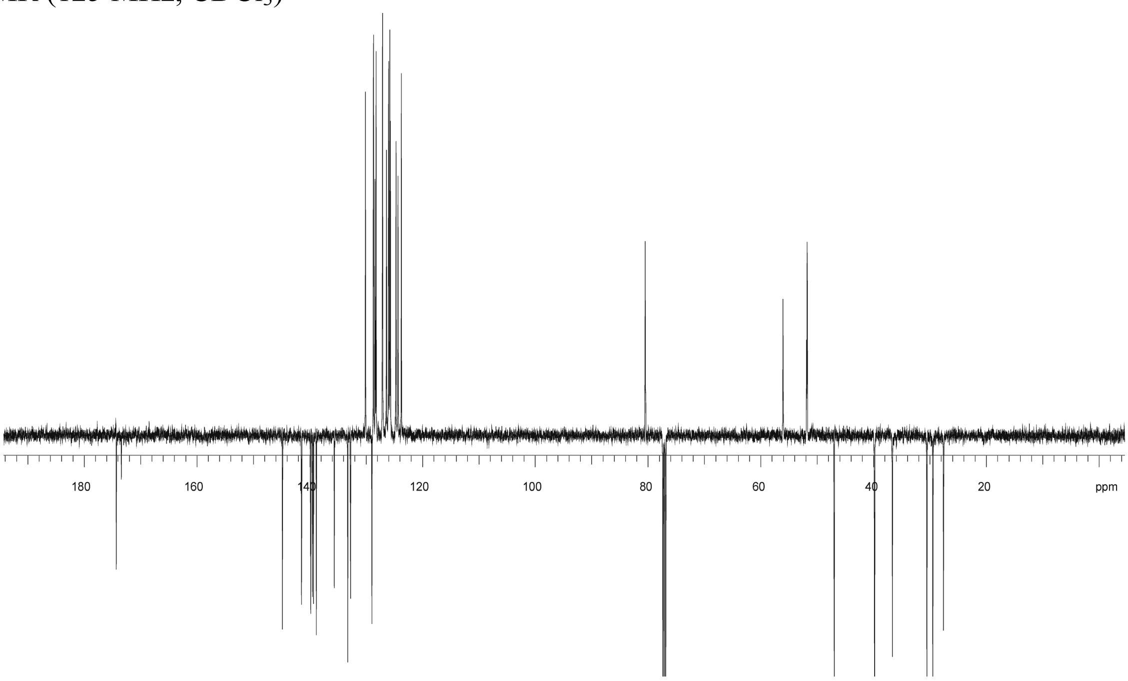
(*S*)-Dimethyl 3,3'-(10-(2'-methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropanoate (6)



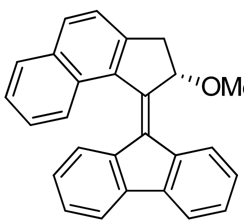
^{1}H NMR (400 MHz, $CDCl_3$)



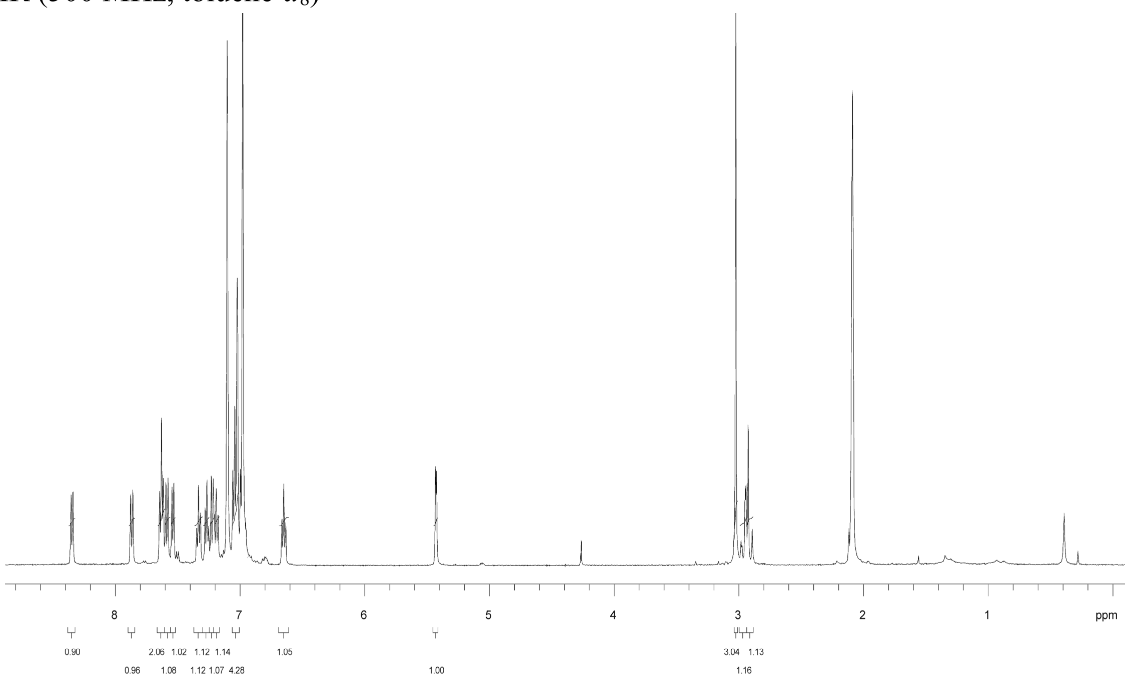
^{13}C NMR (125 MHz, $CDCl_3$)



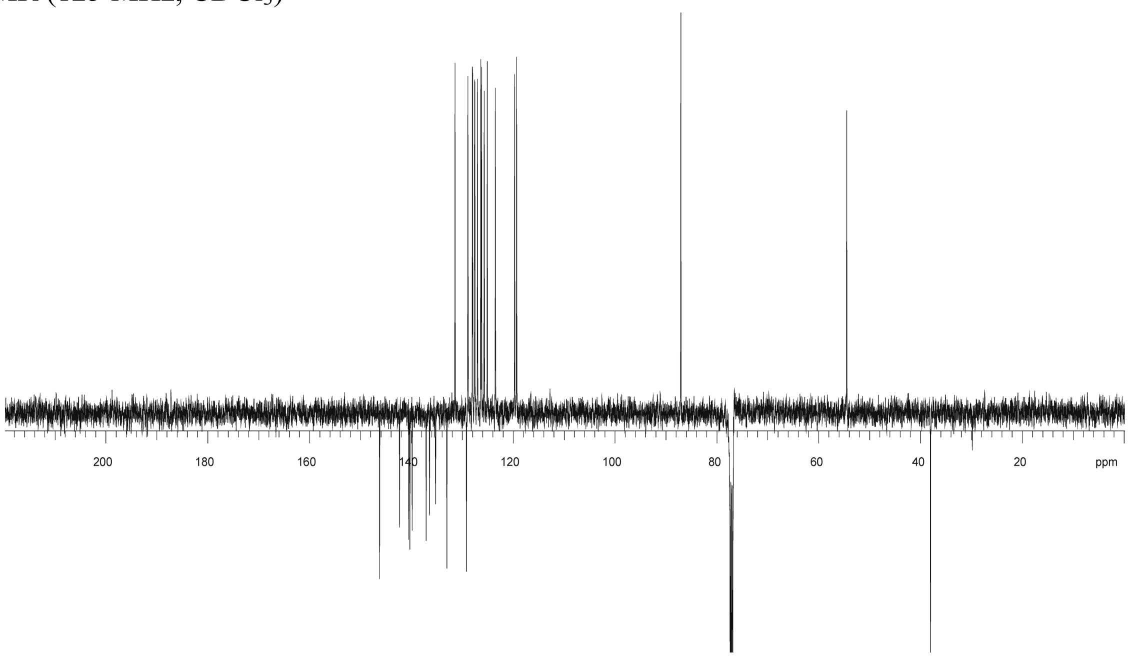
(*S*)-9-(2'-Methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (7)



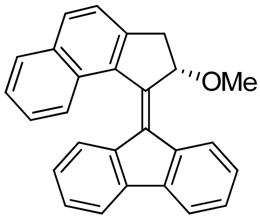
^{1}H NMR (500 MHz, toluene-d_8)



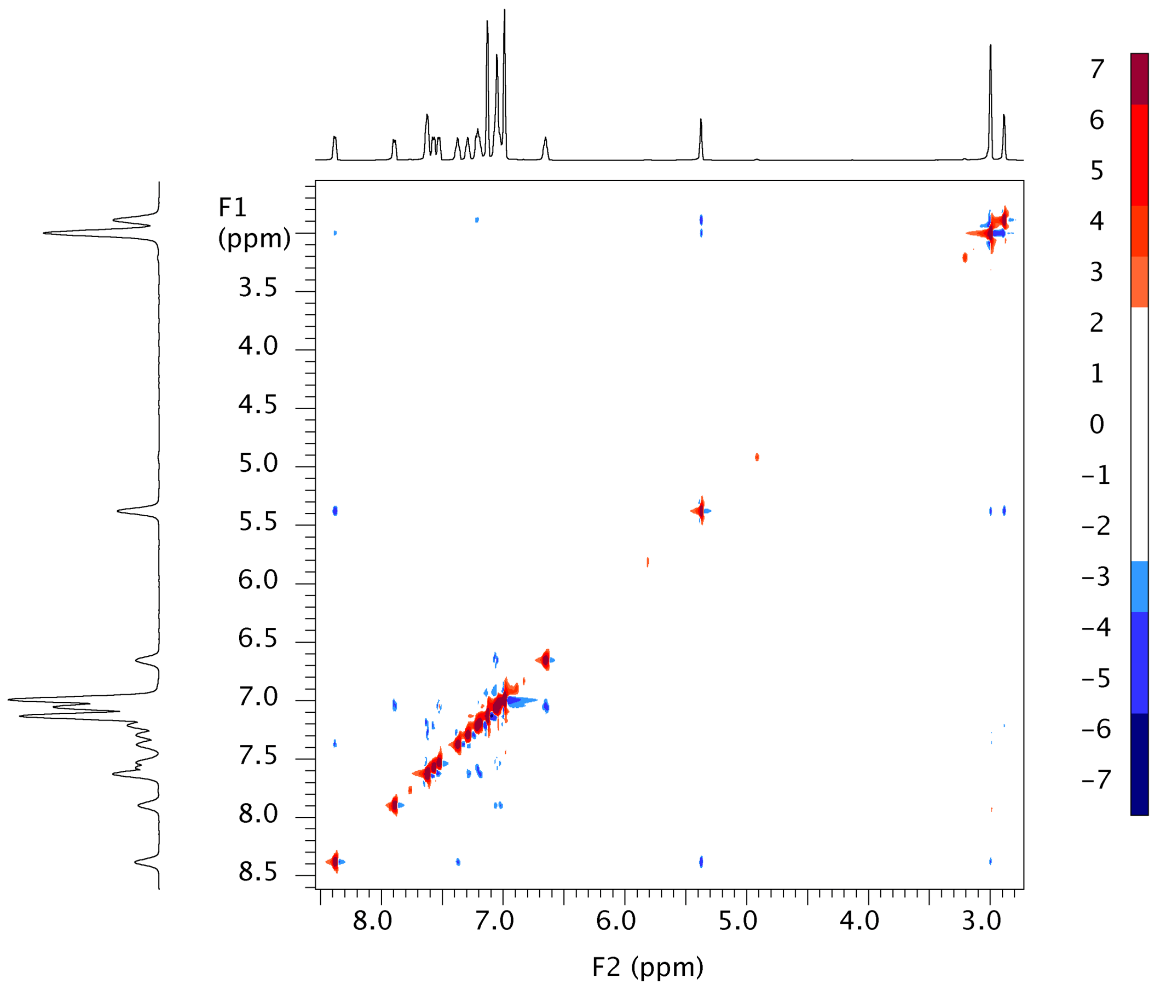
^{13}C NMR (125 MHz, $CDCl_3$)



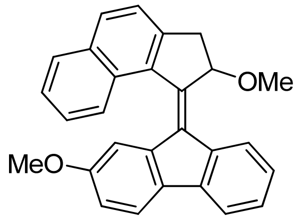
(*S*)-9-(2'-Methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (7)



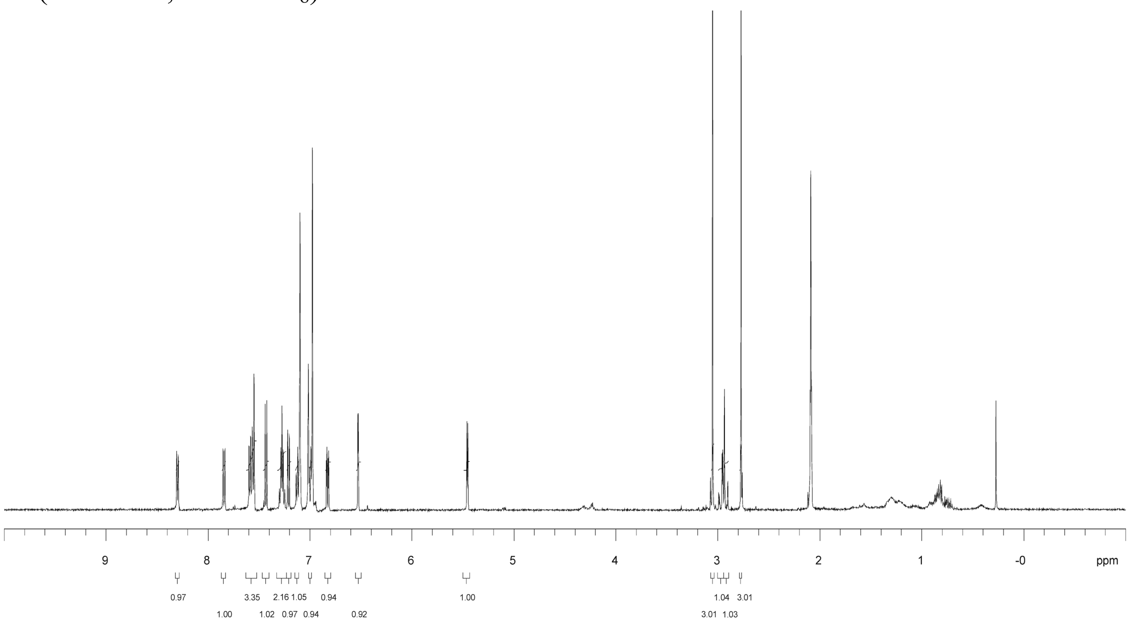
2D NOESY spectrum (500 MHz, toluene-d_8, –20 °C)



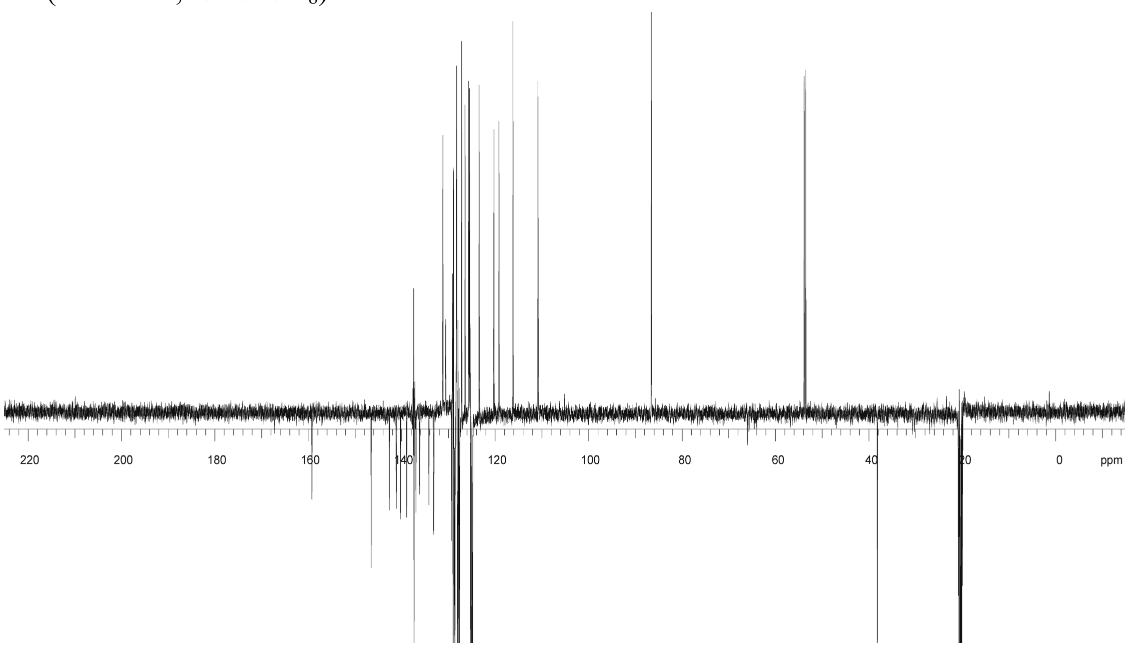
(±)-(*E*)-2-Methoxy-9-(2'-methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (8)



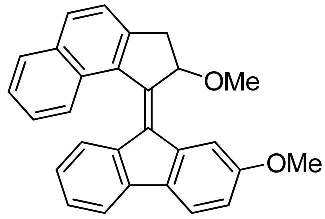
^{1}H NMR (500 MHz, toluene-d_8)



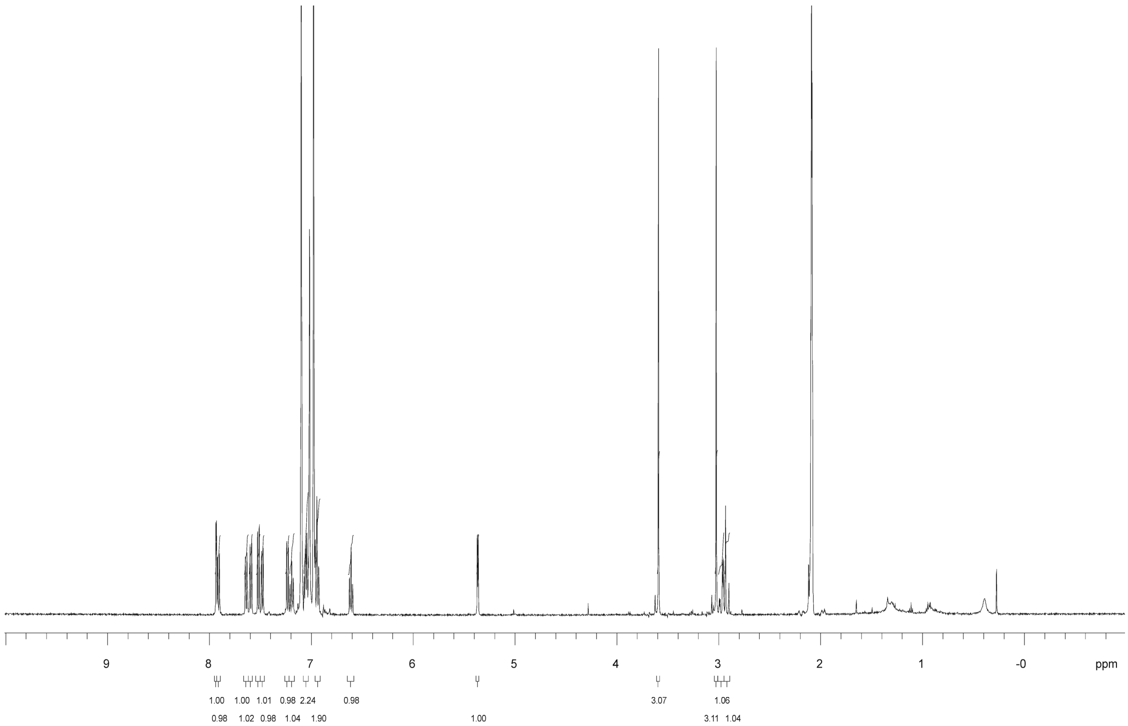
^{13}C NMR (125 MHz, toluene-d_8)



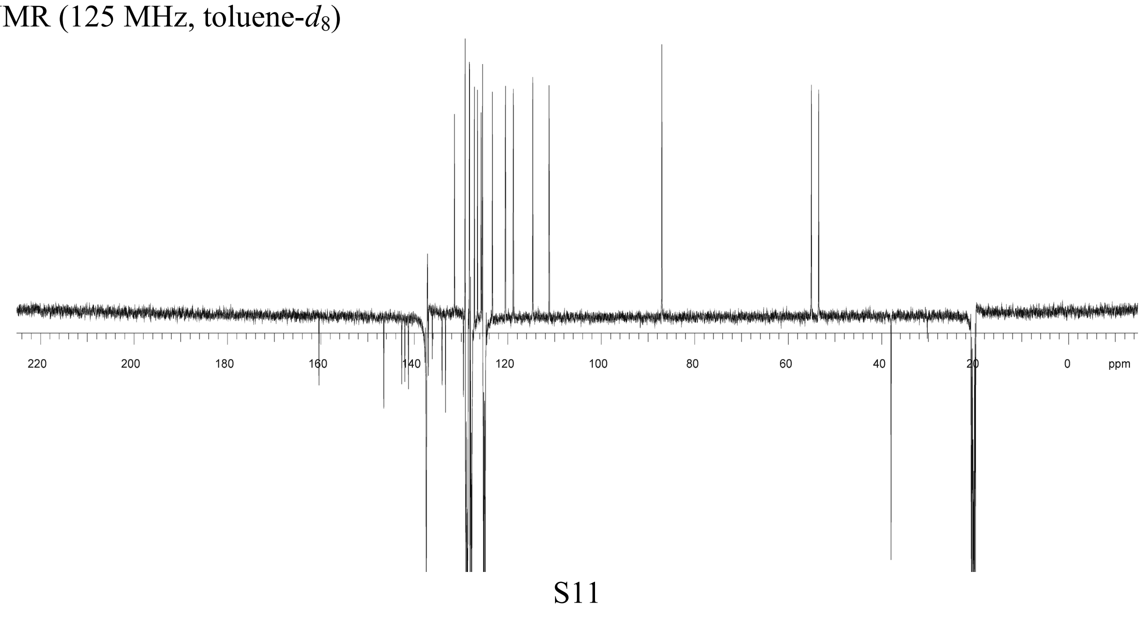
(±)-(*Z*)-2-Methoxy-9-(2'-methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (8)



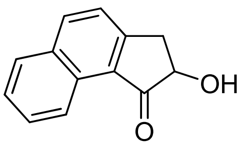
^{1}H NMR (500 MHz, toluene-d_8)



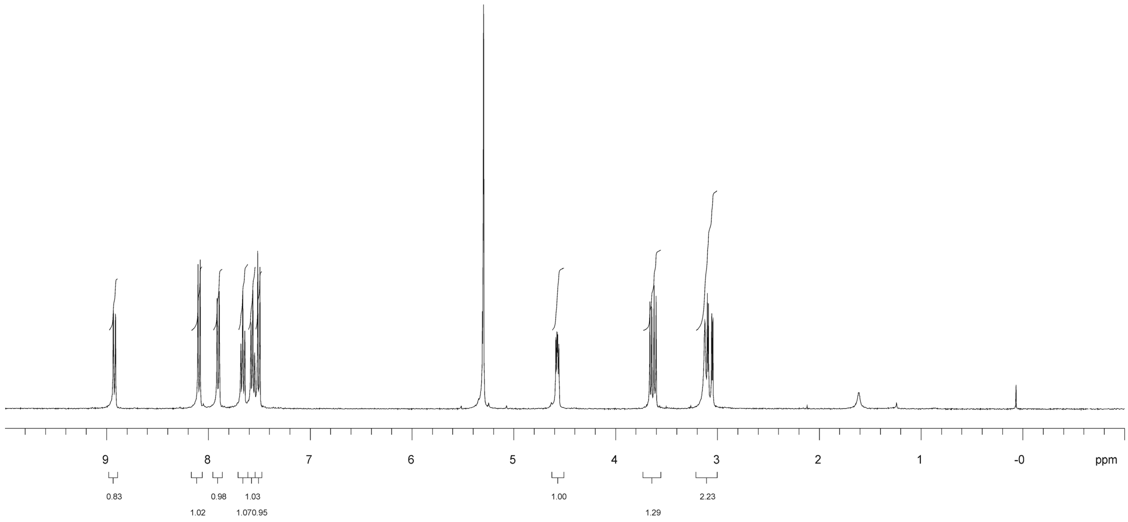
^{13}C NMR (125 MHz, toluene-d_8)



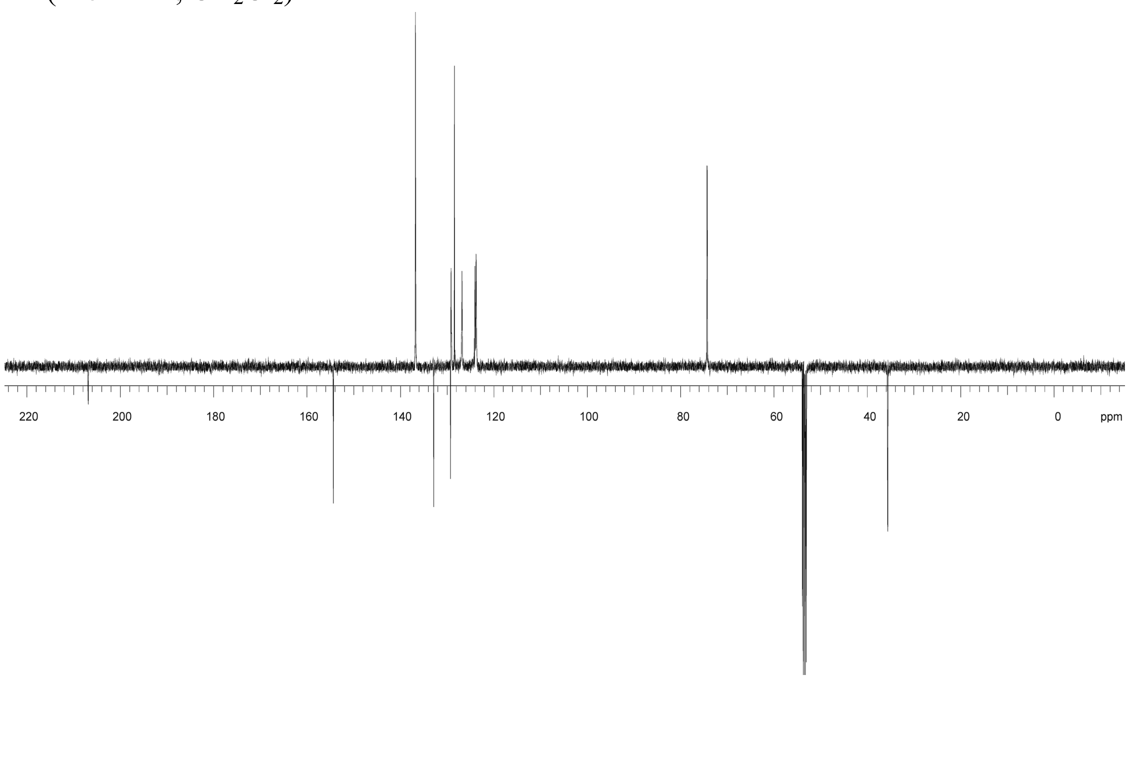
(±)-2-Hydroxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (10)



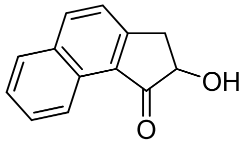
^{1}H NMR (400 MHz, CD_2Cl_2)



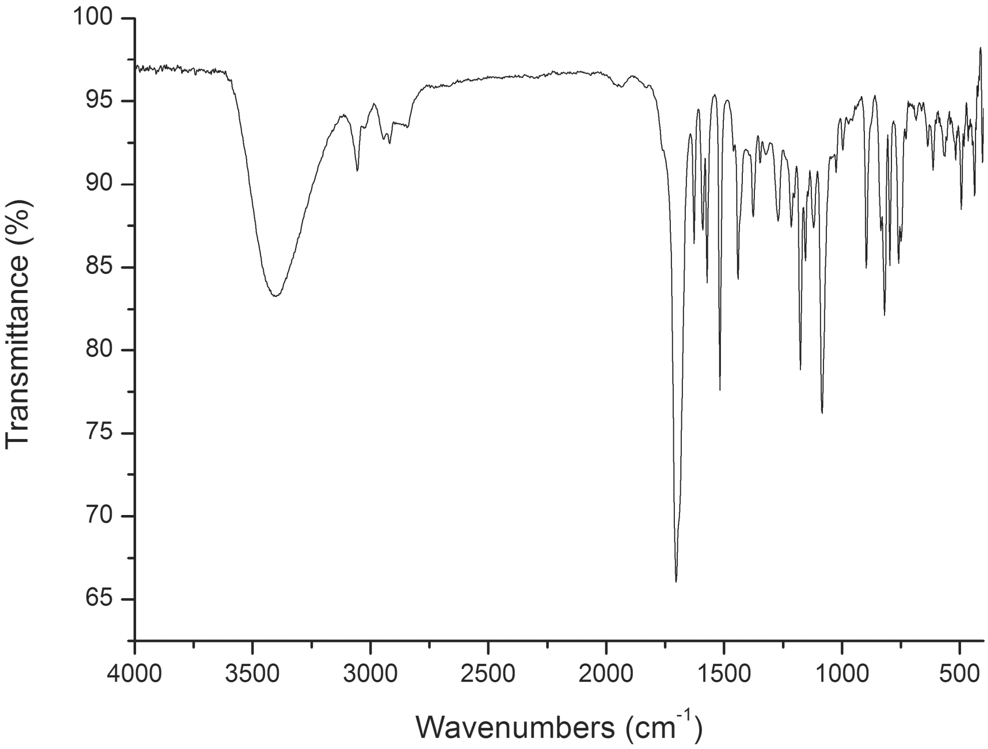
^{13}C NMR (125 MHz, CD_2Cl_2)



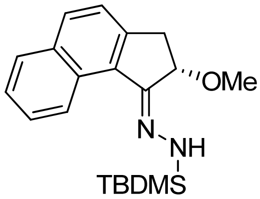
(±)-2-Hydroxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (10)



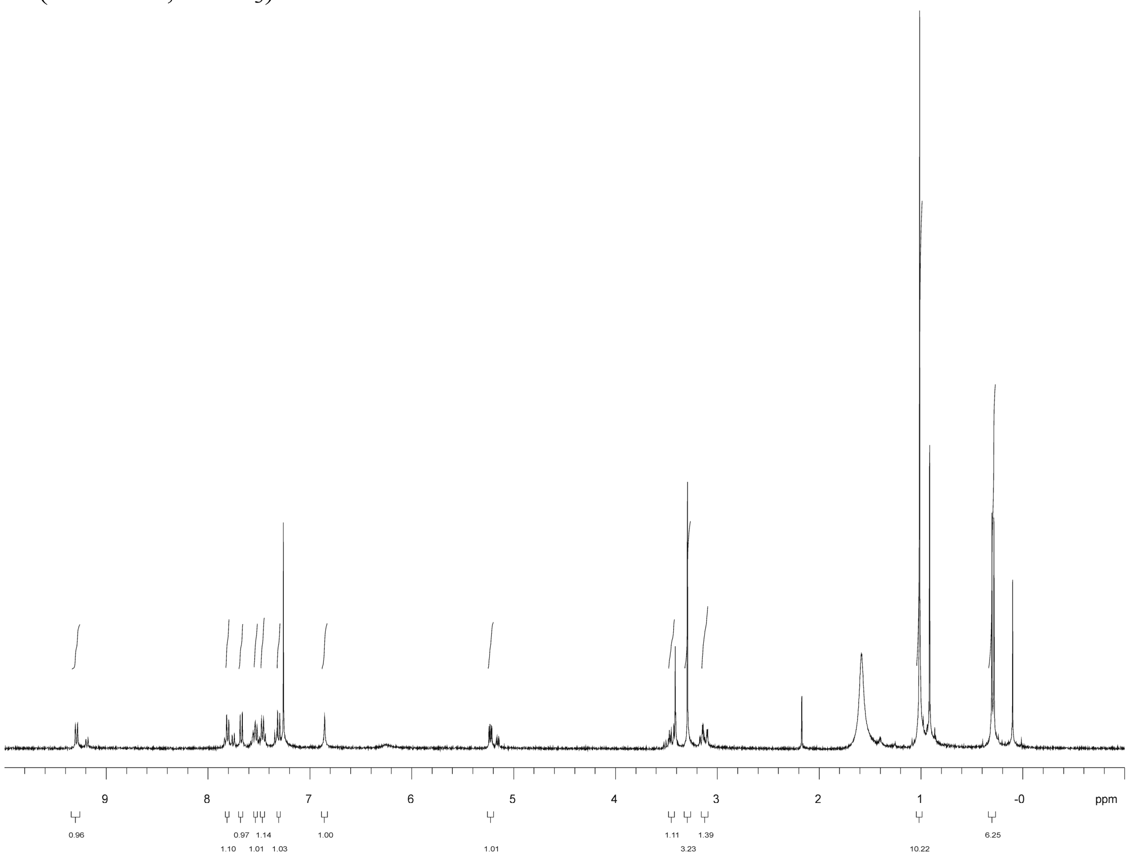
IR (KBr)



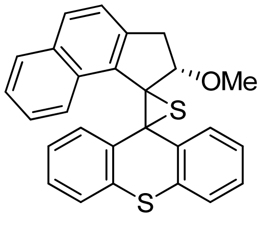
(*S*)-1-(*tert*-Butyldimethylsilyl)-2-(2-methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (11)



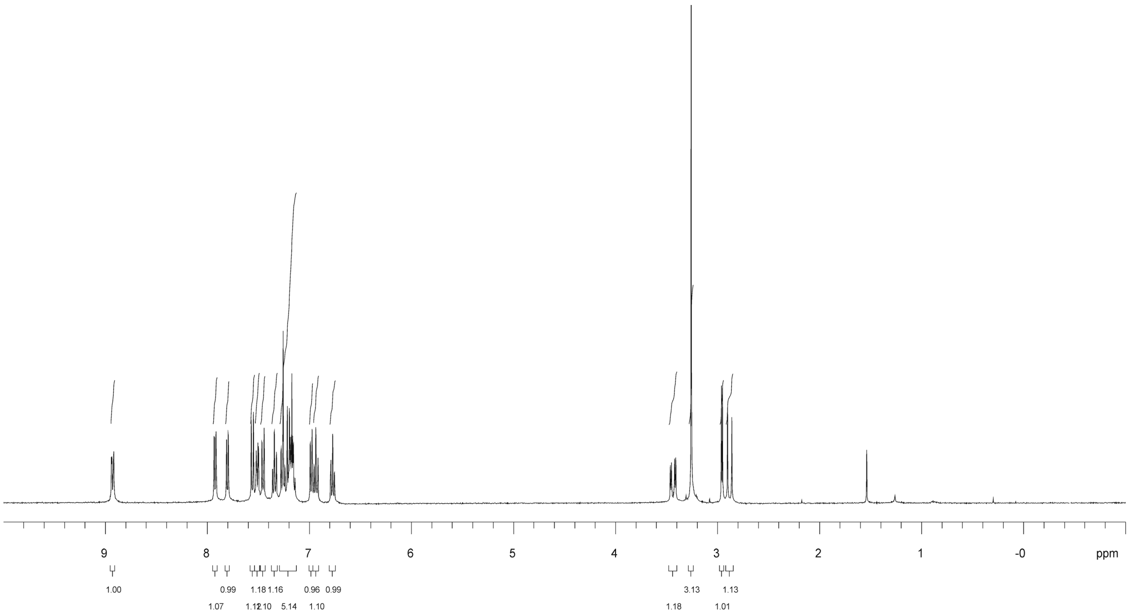
^{1}H NMR (400 MHz, $CDCl_3$)



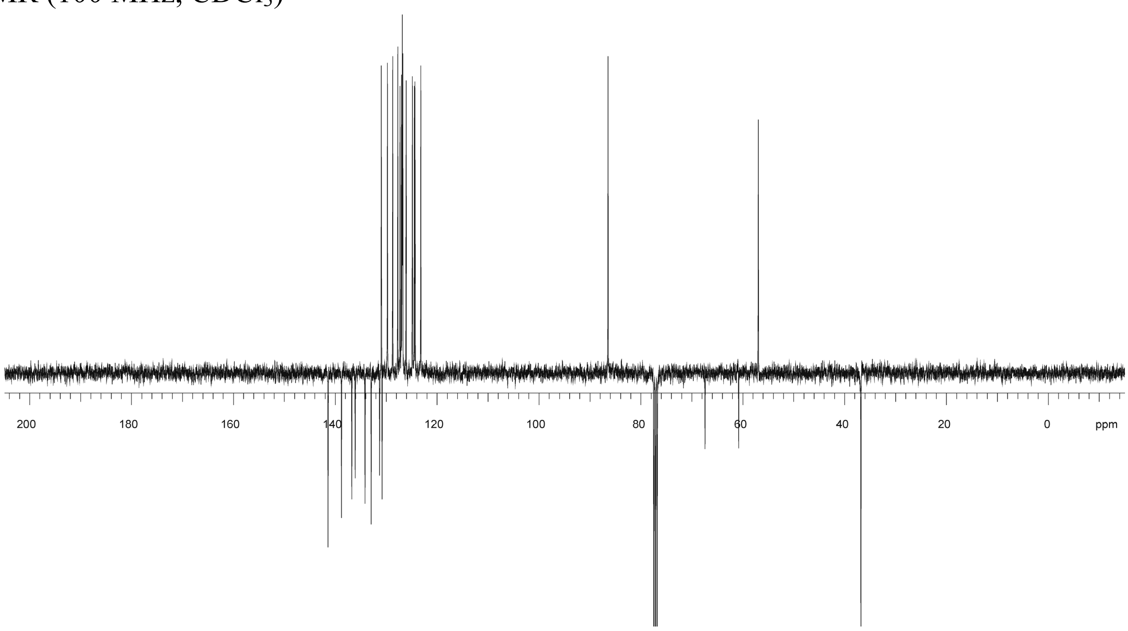
(*S*)-Dispiro[2-methoxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-1,2'-thiirane-3',9''-thioxanthene] (13)



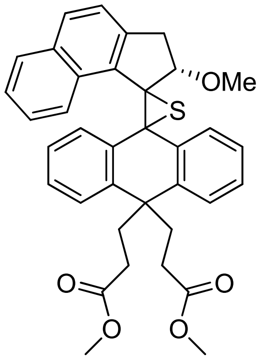
^{1}H NMR (400 MHz, $CDCl_3$)



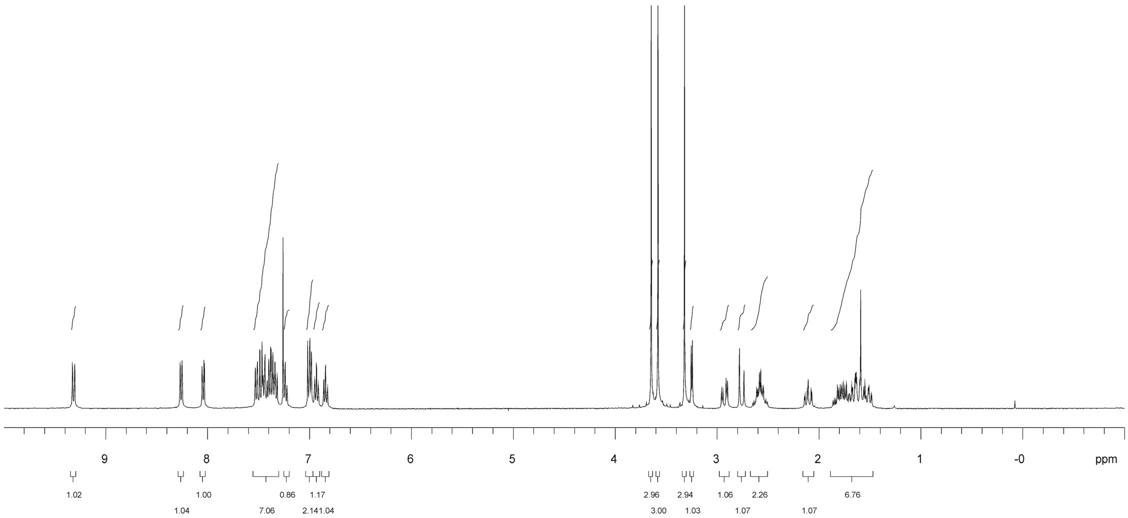
^{13}C NMR (100 MHz, $CDCl_3$)



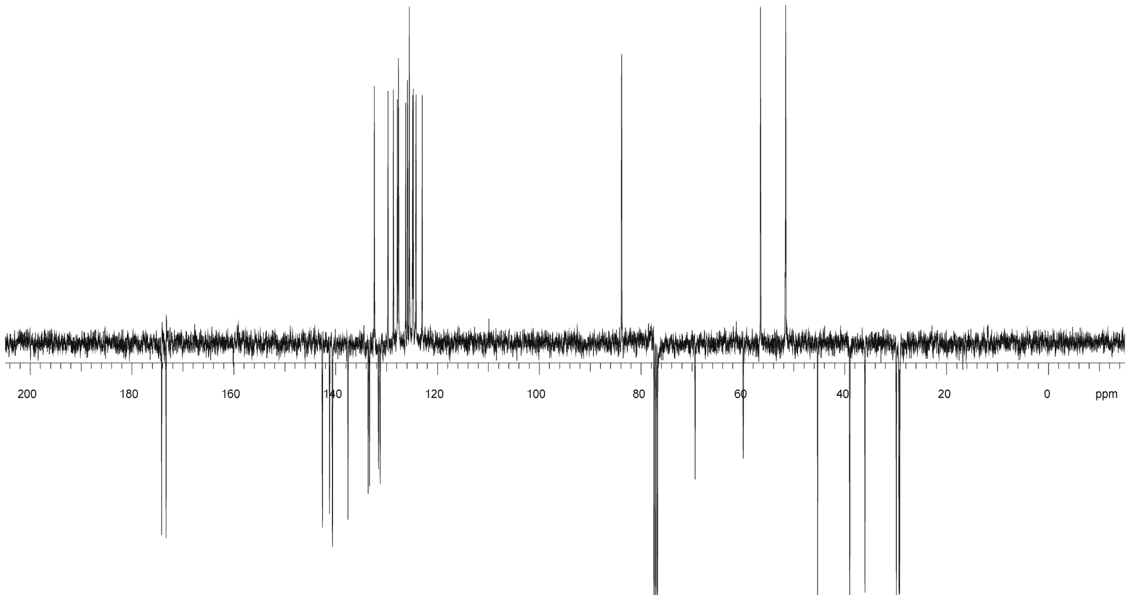
(*S*)-Dispiro[dimethyl 3,3'-(2-methoxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1,2'-thiirane-3',9''-(9'',10''-dihydroanthracene-9'',9''-diyl)dipropanoate)] (15)



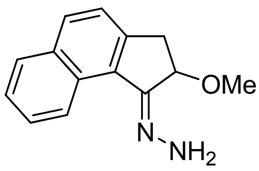
^{1}H NMR (400 MHz, $CDCl_3$)



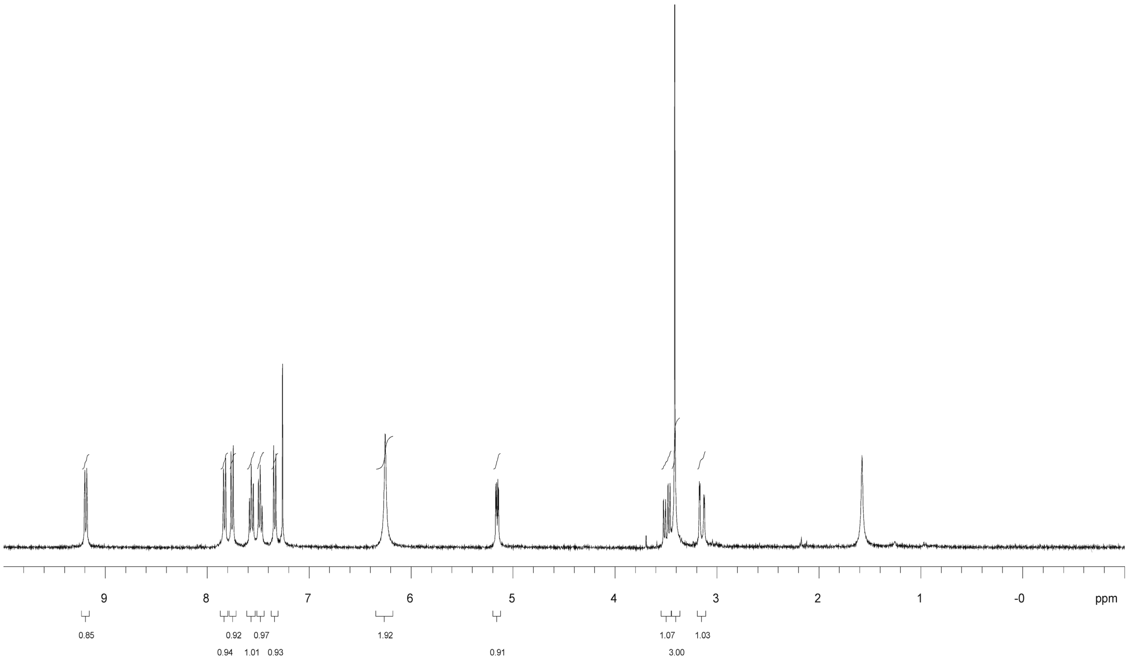
^{13}C NMR (100 MHz, $CDCl_3$)



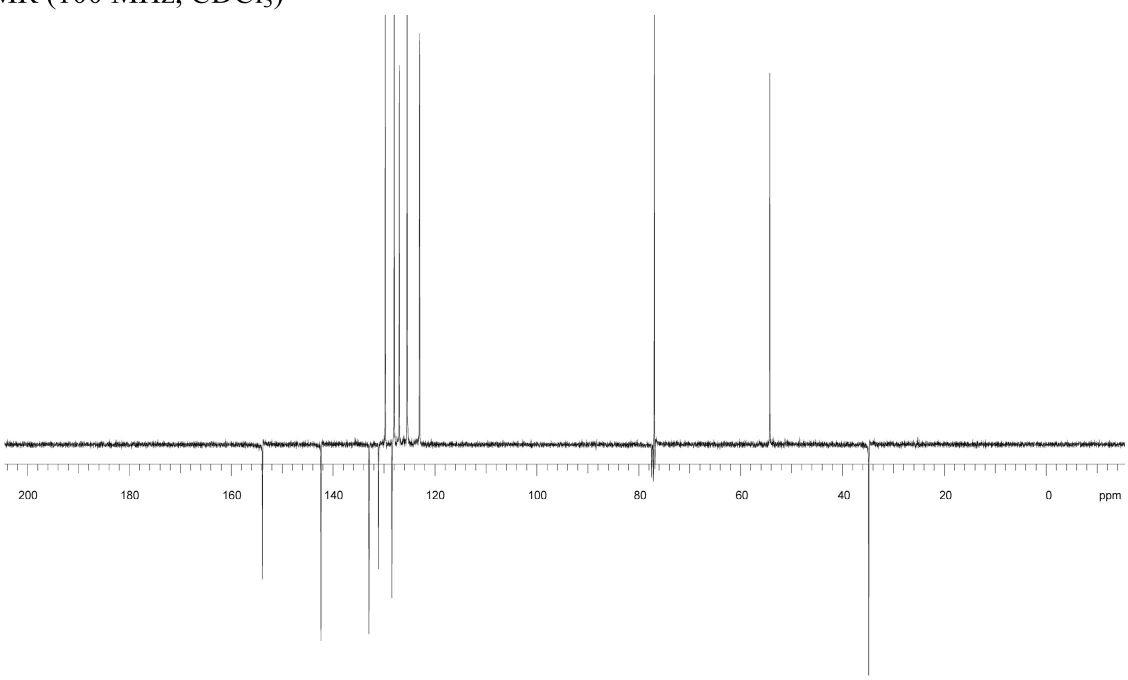
(±)-(2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (18)



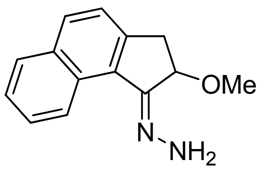
^{1}H NMR (400 MHz, $CDCl_3$)



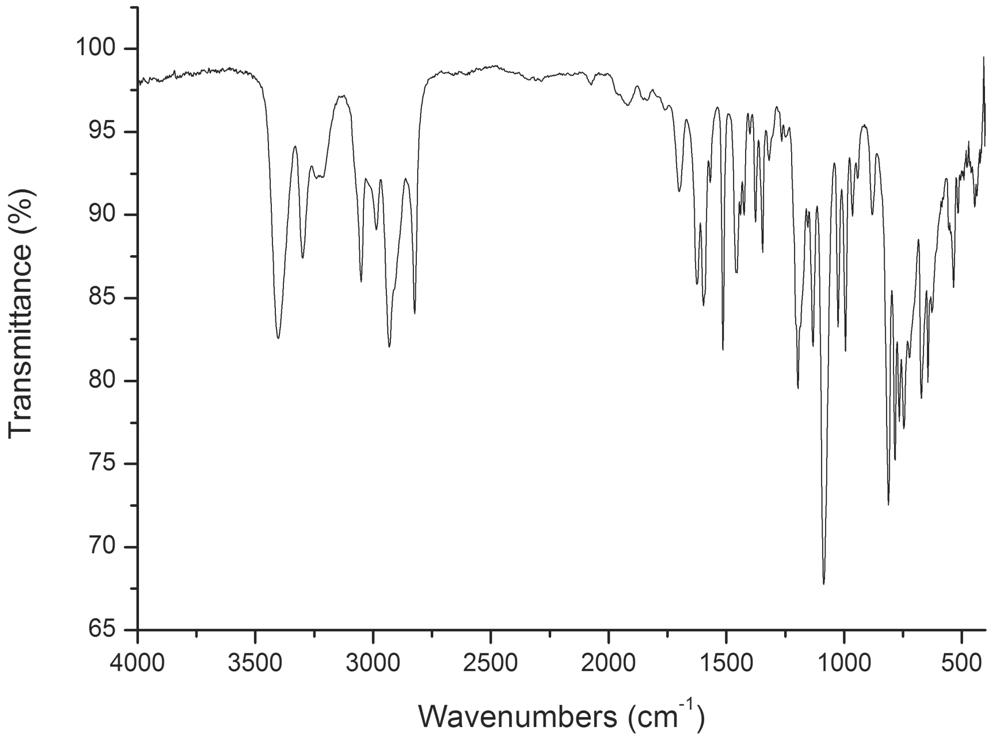
^{13}C NMR (100 MHz, $CDCl_3$)



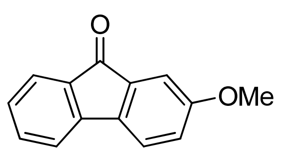
(±)-(2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (18)



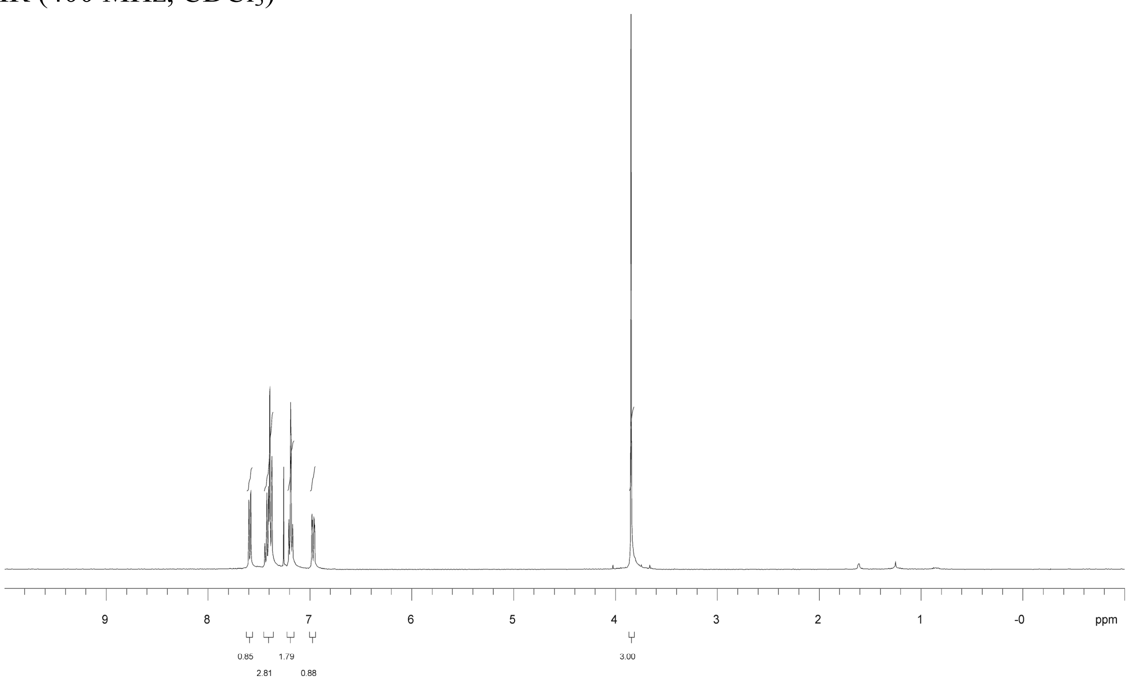
IR (KBr)



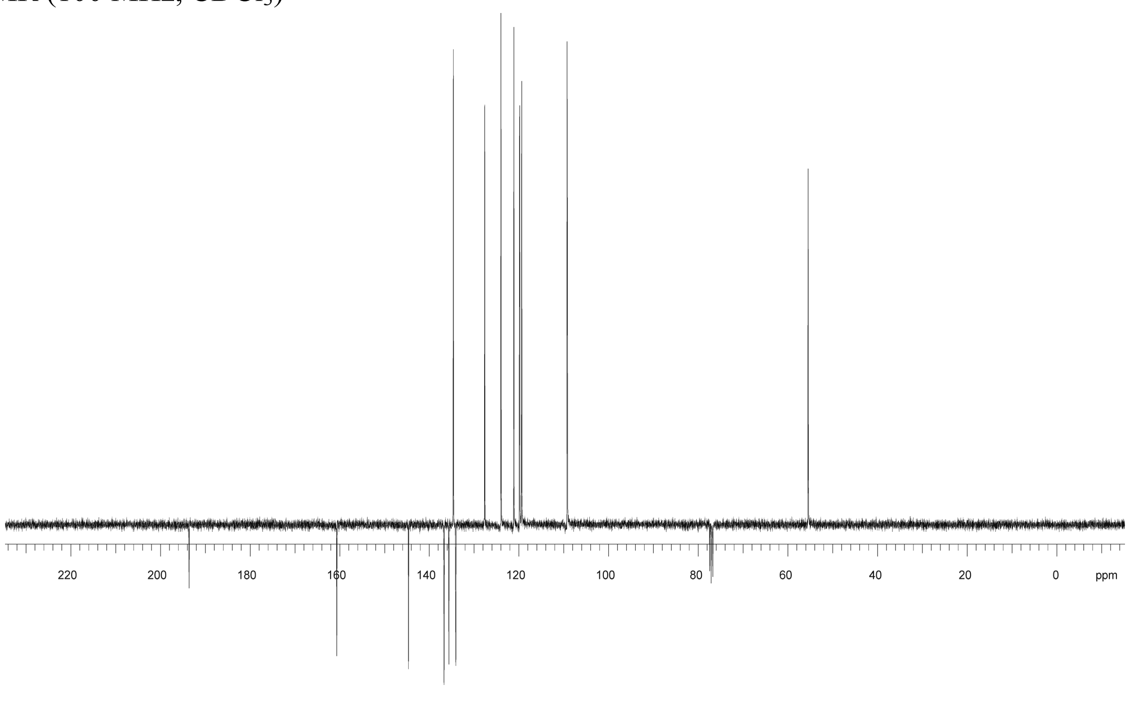
2-Methoxyfluoren-9-one (19)



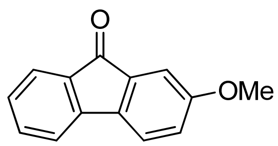
^{1}H NMR (400 MHz, $CDCl_3$)



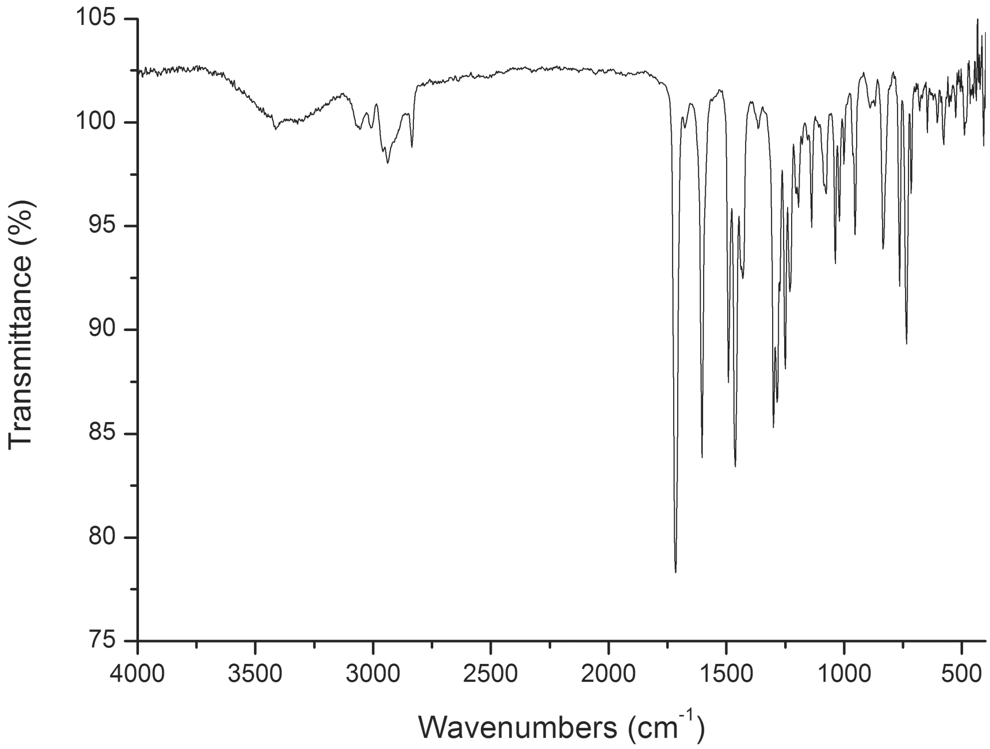
^{13}C NMR (100 MHz, $CDCl_3$)



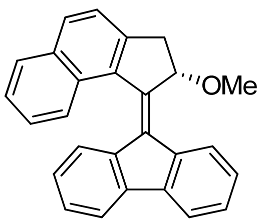
2-Methoxyfluoren-9-one (19)



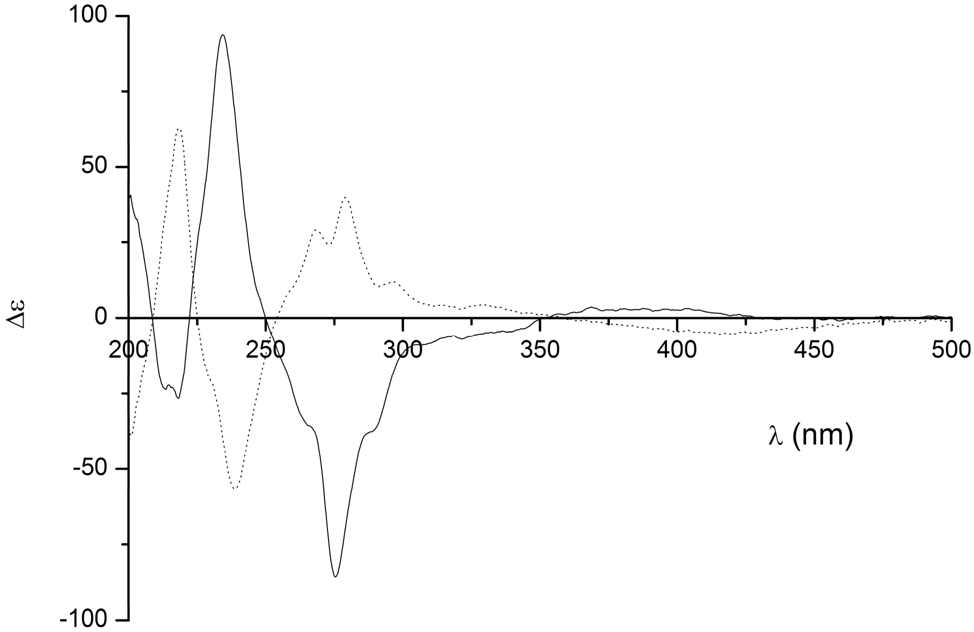
IR (KBr)

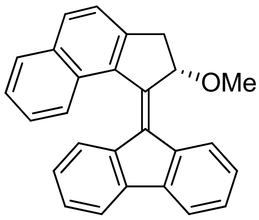


CD, UV/Vis, and ¹H NMR Spectra of Irradiation Experiments

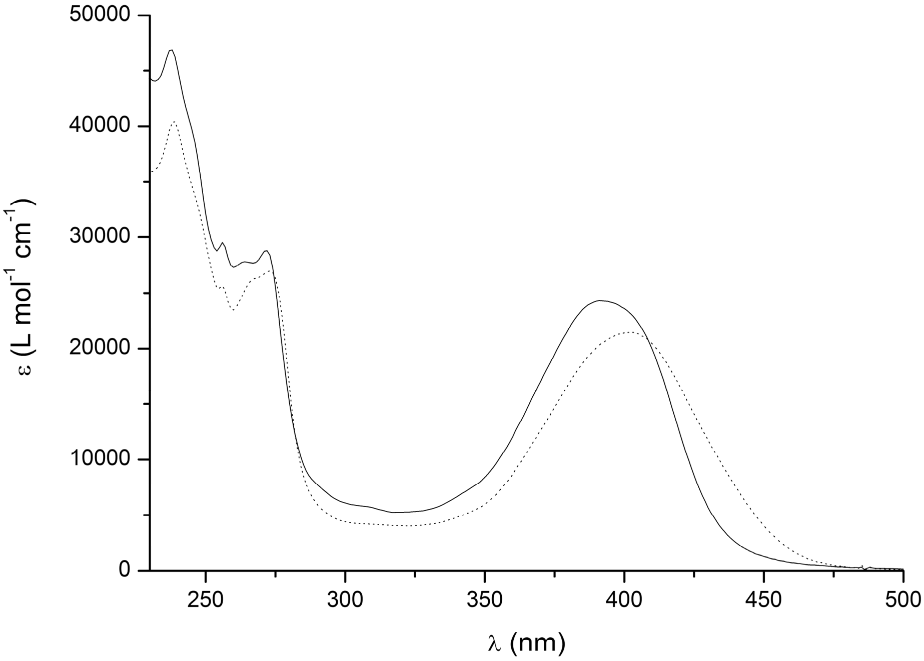


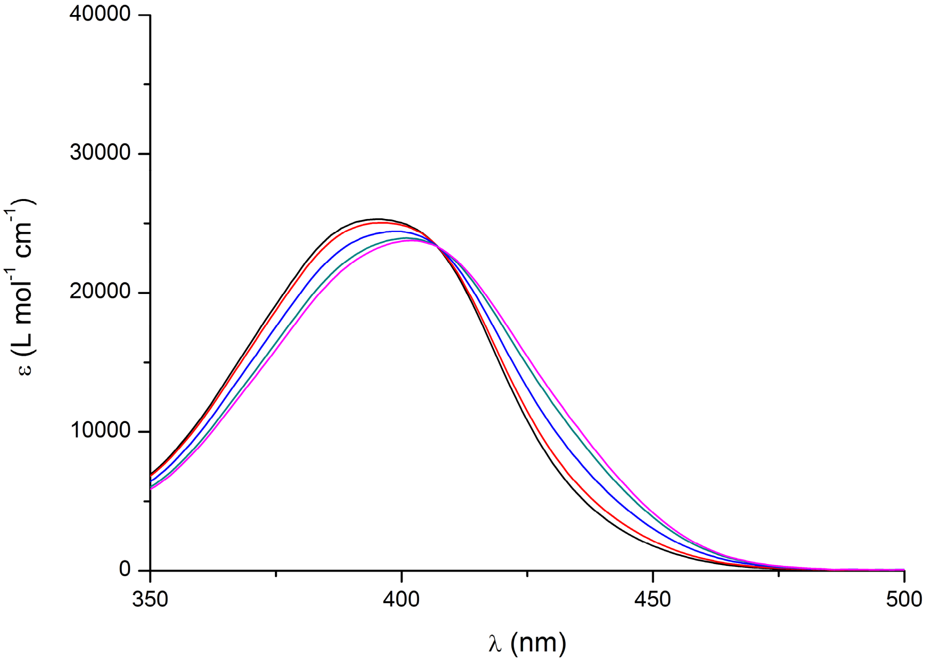
CD spectra of alkene (*S*)-**7** in *n*-hexane at –10 ºC before (solid) and after (dashed) irradiation at 365 nm.



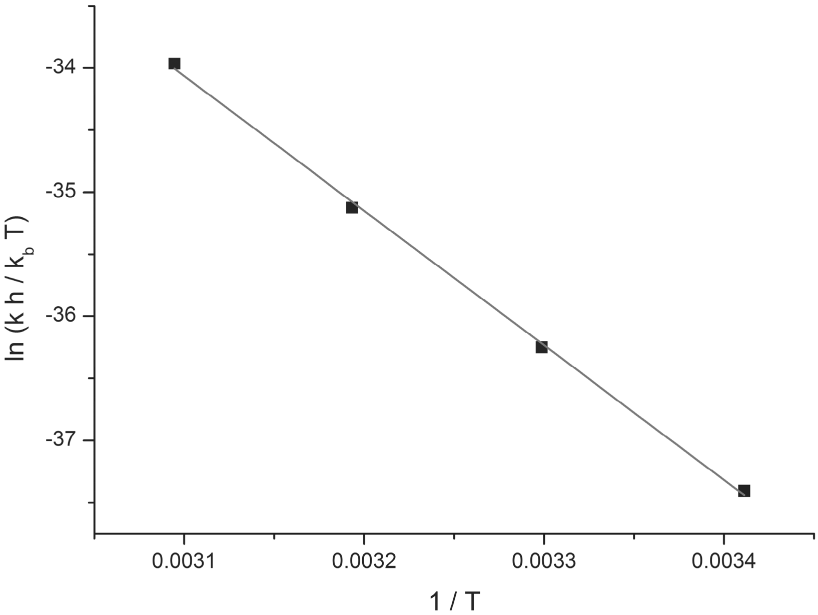


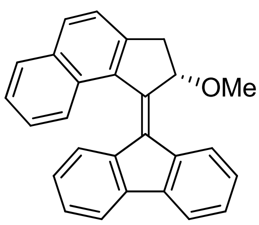
UV/Vis spectra of alkene (*S*)-**7** in *n*-hexane at –20 ºC before (solid) and after (dashed) irradiation at 365 nm.



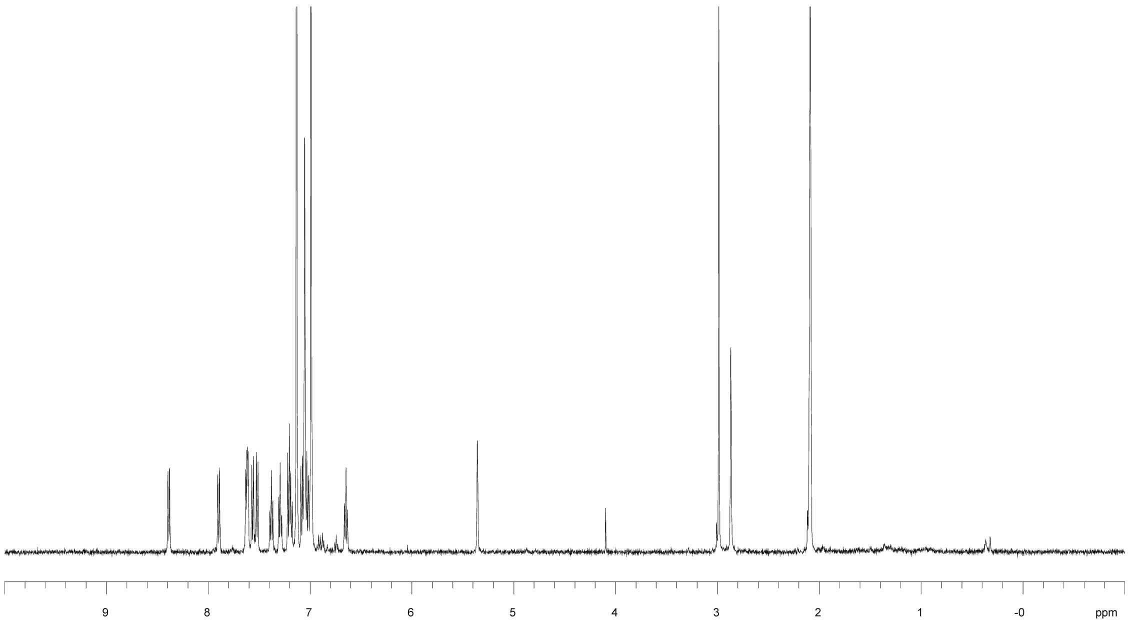


The Eyring Plot used for the determination of the kinetic parameters of the thermal helix inversion of (*S*)-**7**:

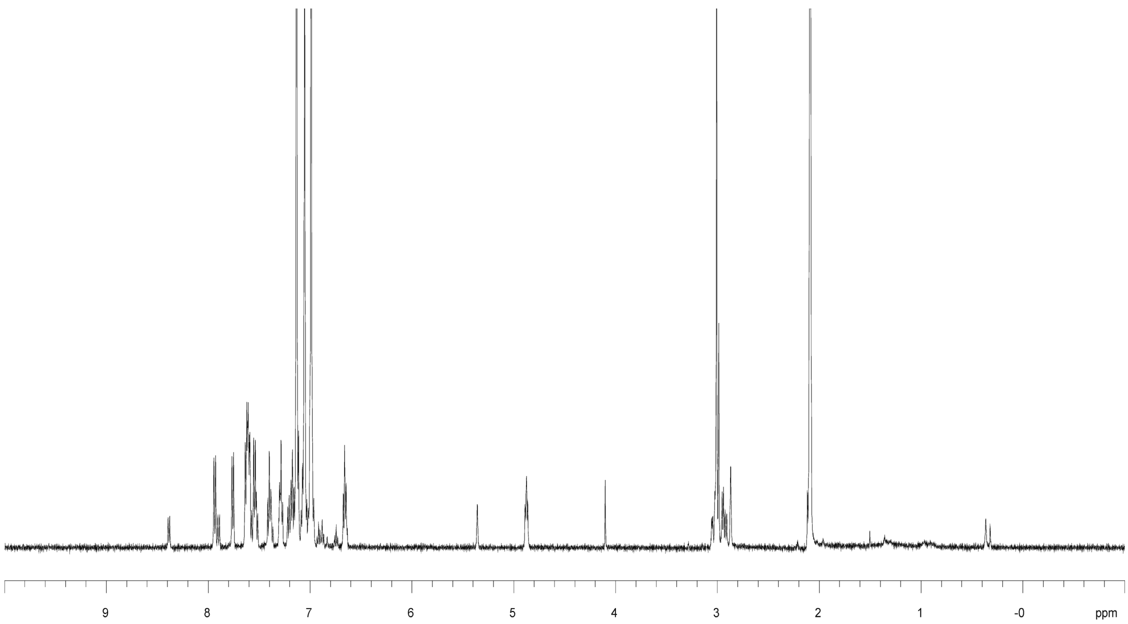




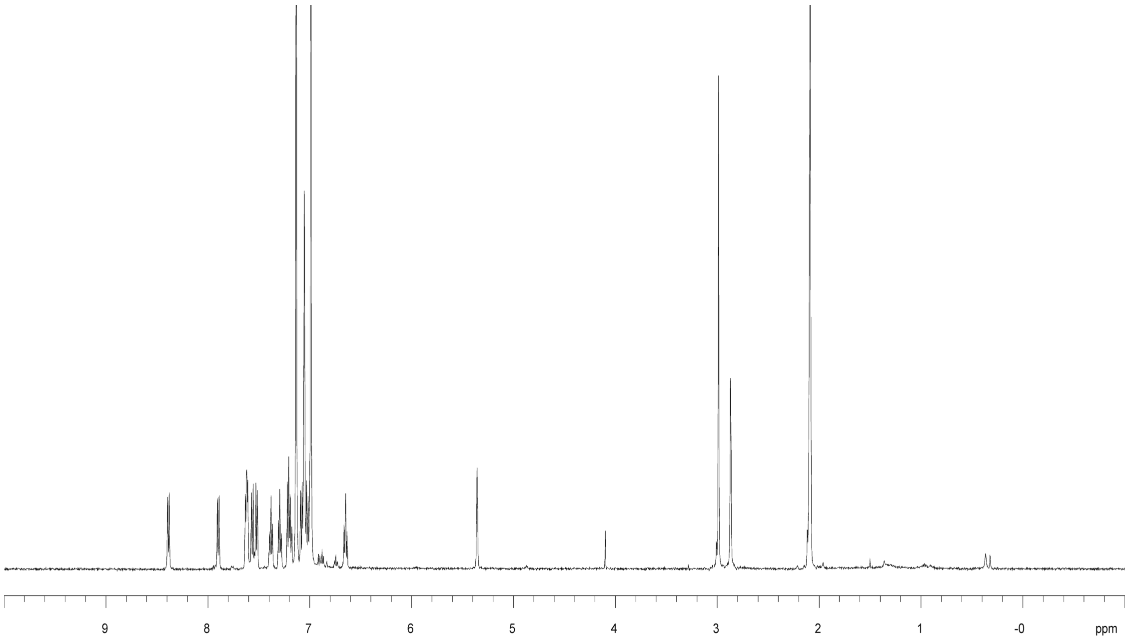
^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*S*)-**7** before irradiation:

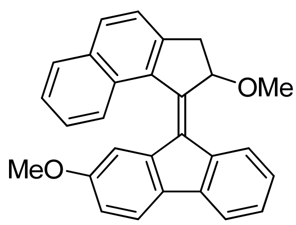


^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*S*)-**7** after irradiation:

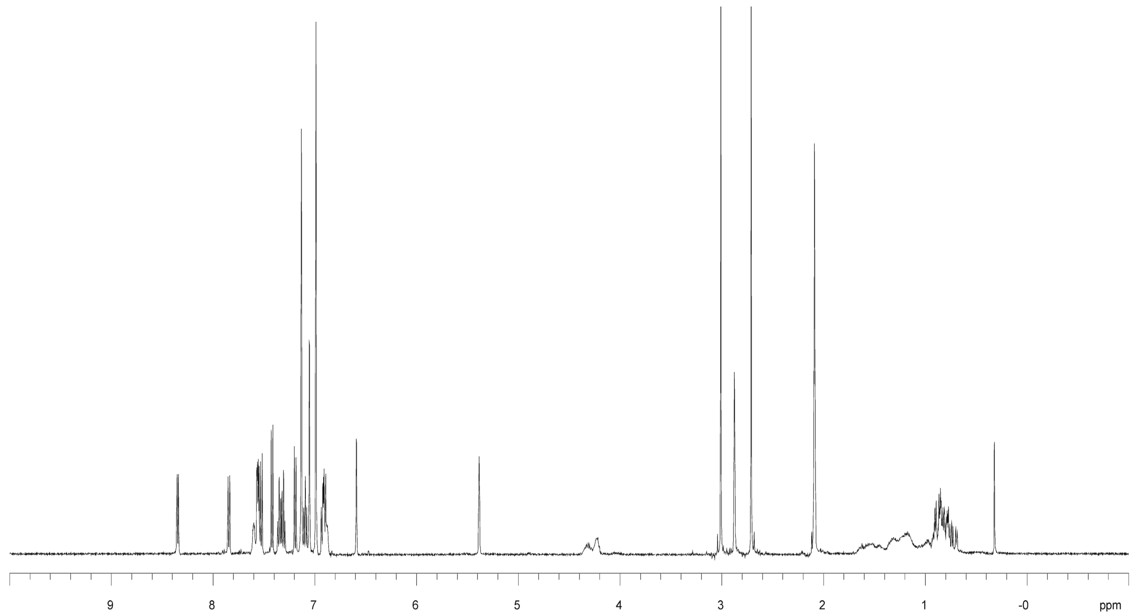


^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (S)-**7** after subsequent heating:

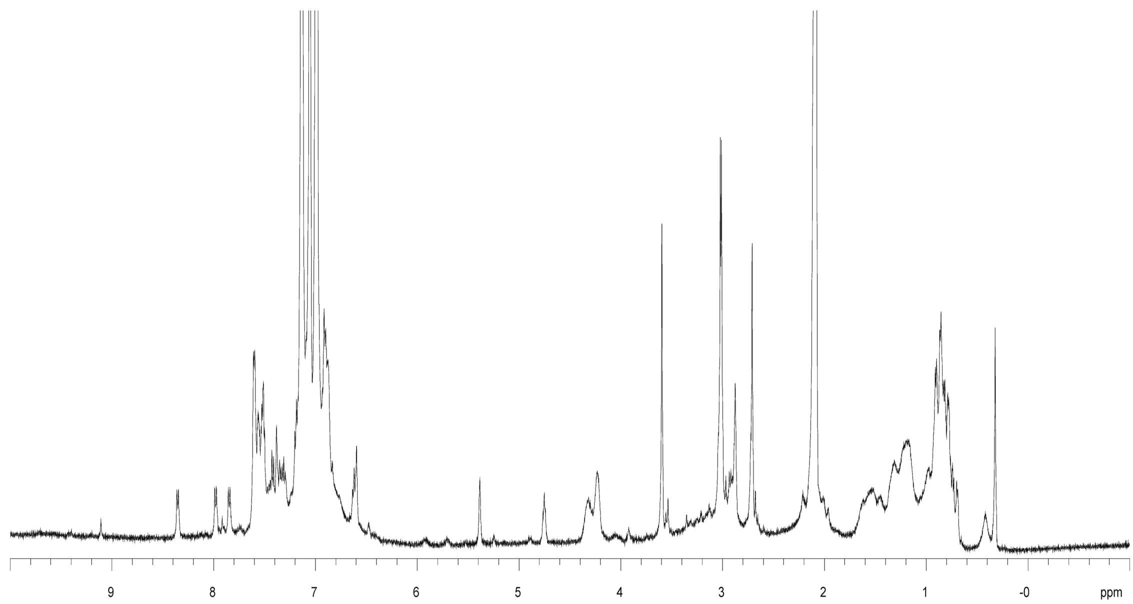




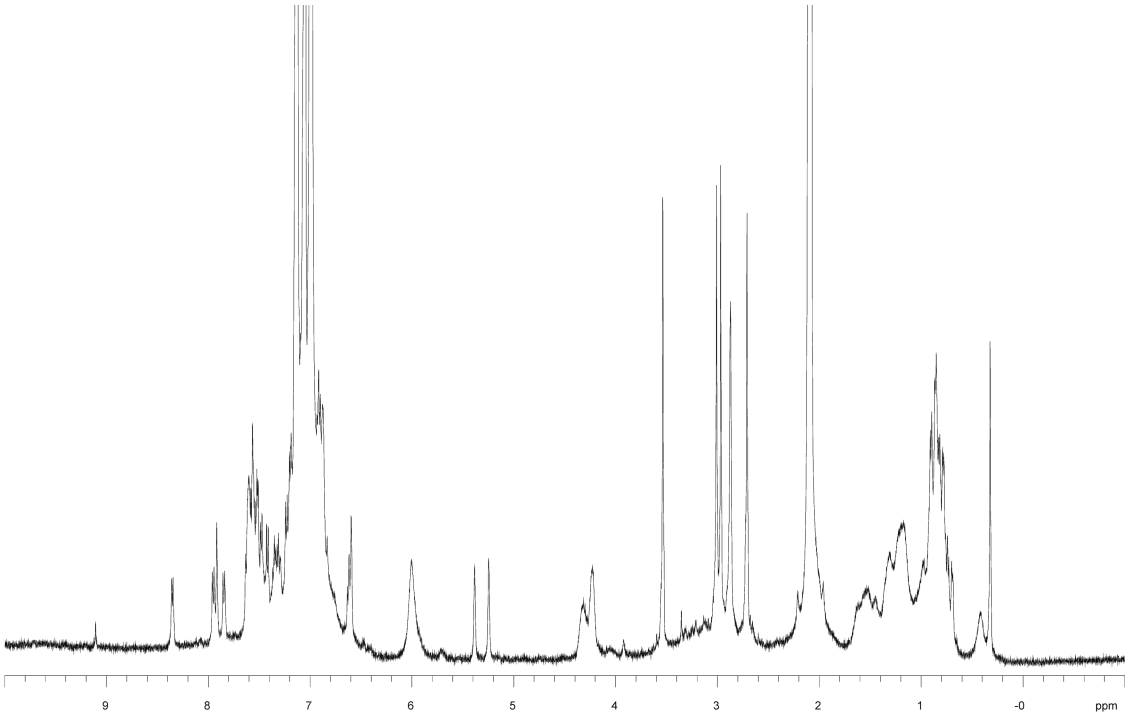
^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*E*)-**8** before irradiation:

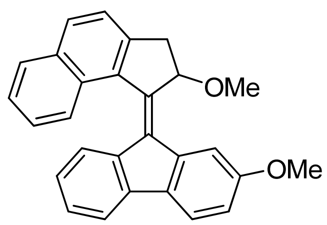


^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*E*)-**8** after irradiation:

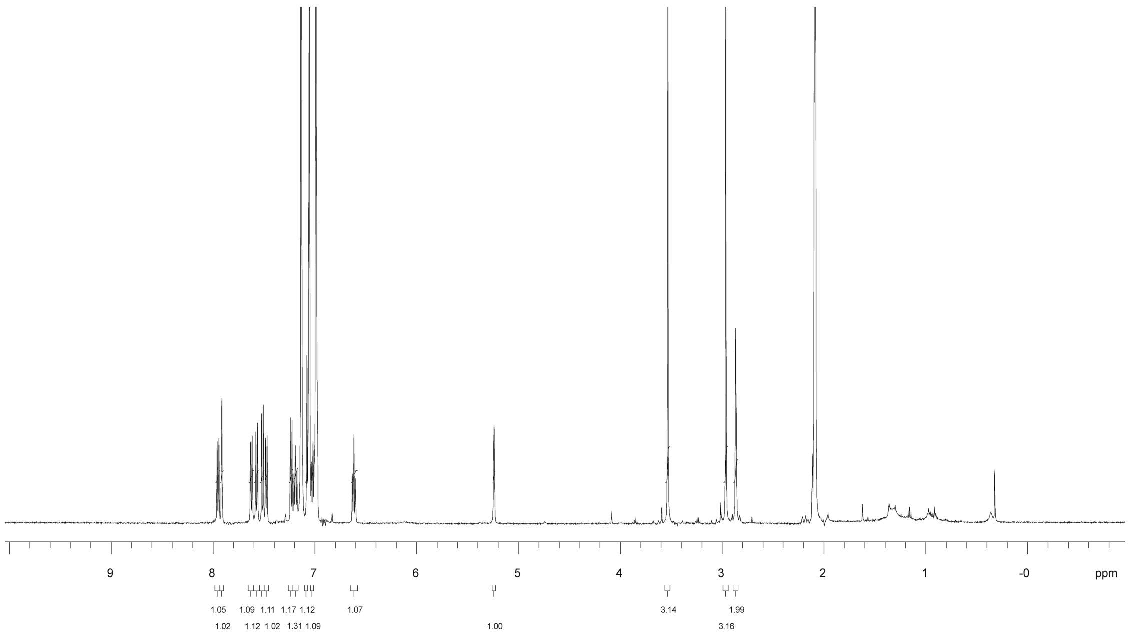


[1]H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*E*)-**8** after subsequent heating:

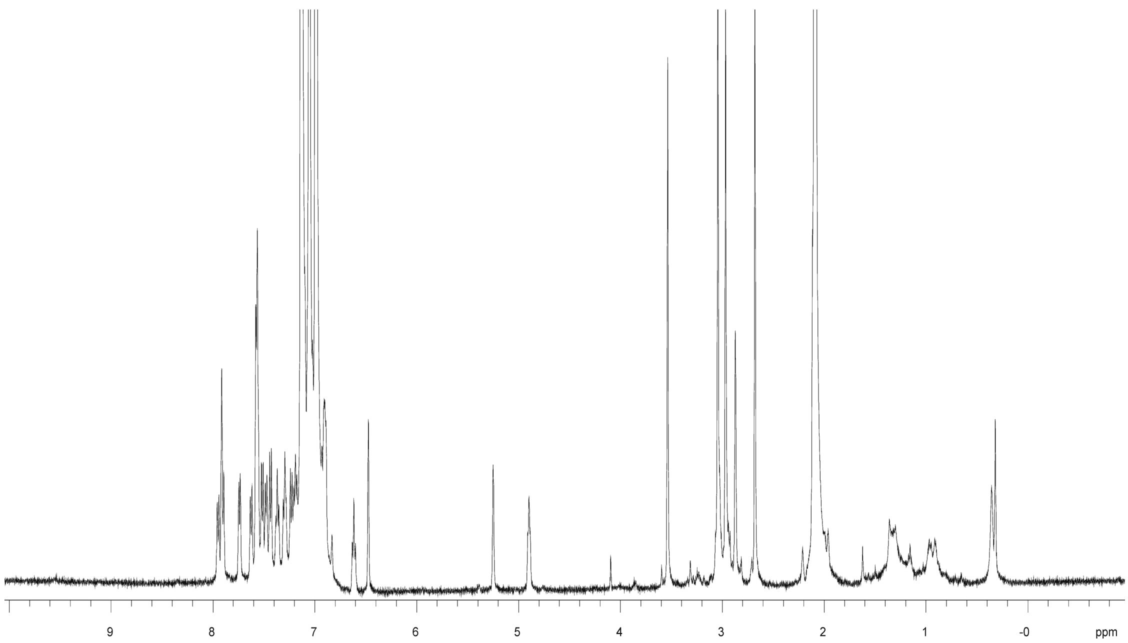




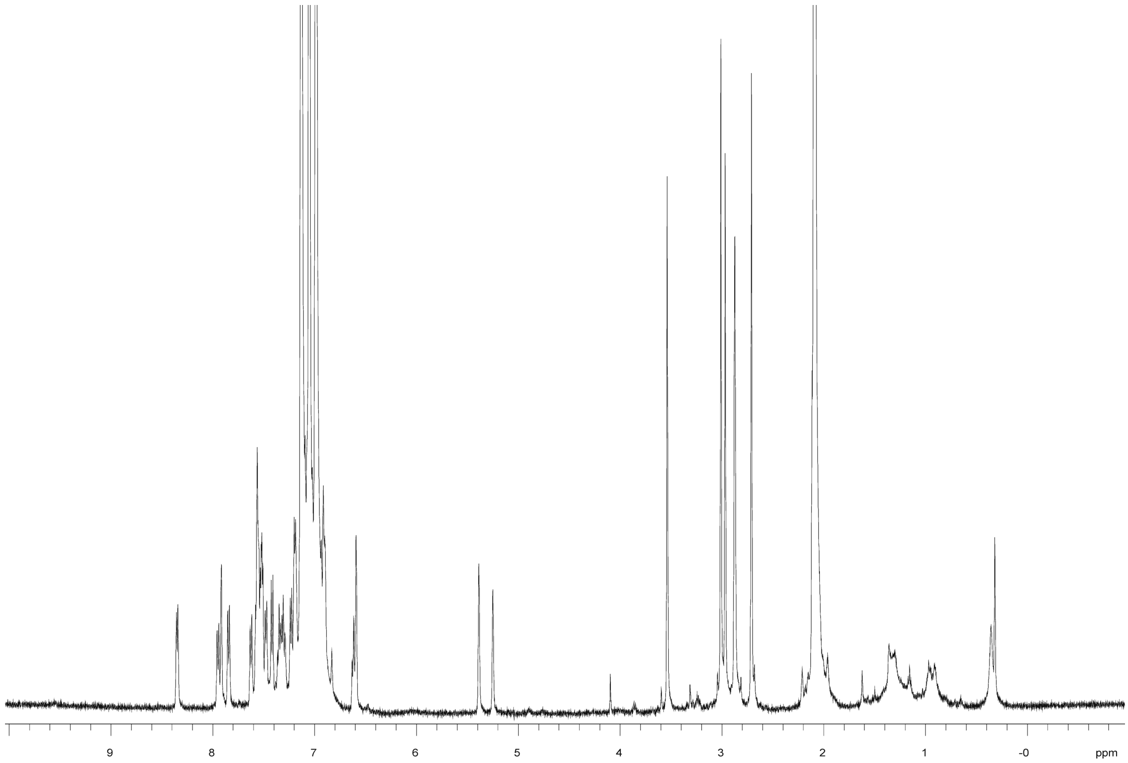
^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*Z*)-**8** before irradiation:



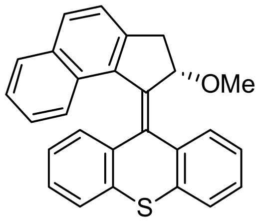
^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*Z*)-**8** after irradiation:



^{1}H NMR spectrum (500 MHz, toluene-d_8, –30 ºC) of (*Z*)-**8** after subsequent heating:



X-ray Crystallographic Analysis of (*S*)-5



At rt, alkene (*S*)-**5** (3.0 mg) was dissolved in a minimal amount of a 1:1 mixture of diethyl ether and pentane. The resulting solution was placed into a small glass vial, after which the vial was placed in a larger glass beaker containing pentane. The beaker was covered and left to stand for several days, during which slow diffusion of the solvents allowed the formation of crystals of (*S*)-**5**. The crystal used in the X-ray diffraction experiment was a small cut fragment which was cleaved from a large coagulated and in different directions grown crystal chunk. This crystal diffracted weakly, so a 30.0 second exposure time for each image was used.

A. Crystal data and details of the structure determination of alkene (*S*)-**5**.

Moiety_Formula	$C_{27}H_{20}OS$
Formula_Weight, g.mol^{-1}	392.52
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	7.7954(15)
b, Å	14.349(3)
c, Å	17.845(4)
V, Å	1996.1(7)
Θ range unit cell: min.-max., deg; reflections	2.69 - 27.54 ; 2645
Formula_*Z*	4
SpaceGroup_*Z*	4
Z' (= Formula_*Z* / SpaceGroup_*Z*)	1
ρ_{calc}, g.cm^{-3}	1.306
F(000), electrons	824
μ(Mo $K\bar{\alpha}$), cm^{-1}	1.78
Color, habit	colorless, cut fragment
Approx. crystal dimension, mm	0.29 x 0.15 x 0.11

B. Data collection

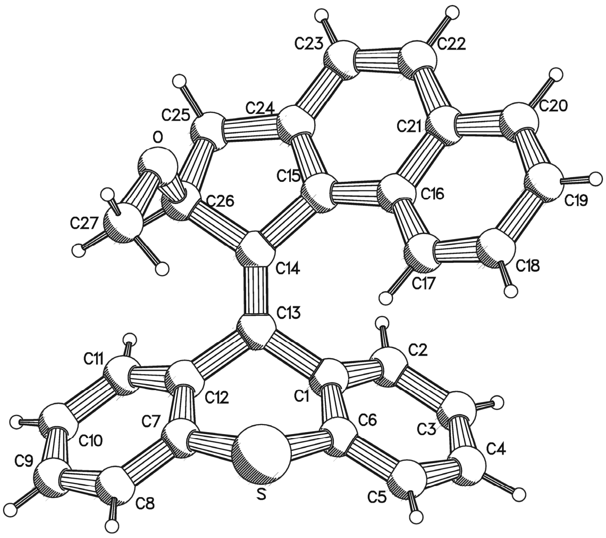
Radiation type; λ, Å	Mo $K\bar{\alpha}$, 0.71073

Monochromator	Graphite
Measurement device type	Bruker SMART APEX *CCD* area-detector diffractometer
Detector Area resolution (pixels / mm)	4096 x 4096 / 62 x 62 (binned 512)
Temperature, K	100(1)
Measurement method	φ- and ω-scans
θ range; min. max., deg	2.69, 25.02
Index ranges	h: –9→9; k: –17→16; l: –21→21
Min.- Max. absorption transmission factor	0.9397 - 0.9806
Frames	1800
X-ray exposure time, h	17.9 (30.0 sec / frame)
Total data	14068
Unique data	3526
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	2696
$R_{int} = \Sigma\ [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \Sigma\ [F_o^2]$	0.0725
$R_{sig} = \Sigma\ \sigma(F_o^2) / \Sigma\ [F_o^2]$	0.0742

C. Refinement

Number of reflections	3526
Number of refined parameters	342
Final agreement factors:	
$wR(F^2) = [\Sigma\ [w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^2)^2]]^{1/2}$	0.0832
Weighting scheme: *a*, *b*	0.0391, 0.0
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
And $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma\ (\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert) / \Sigma\ \lvert F_o\rvert$	0.0429
For $F_o > 4.0\ \sigma\ (F_o)$	
Absolute-Structure parameter Flack's **x**	0.02(9)
GooF = S = $[\Sigma\ [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	0.971
n = number of reflections	
p = number of parameters refined	
Residual electron density in final Difference Fourier map, e/Å^3	–0.33, 0.26(5)
Max. (shift/σ) final cycle	0.001
Average (shift/σ) final cycle	<0.001

Perspective *PLUTO* drawing of (*S*)-**5**, showing the configuration of the asymmetric unit:



Perspective *ORTEP* drawing of (*S*)-**5**. All atoms are represented by their displacement ellipsoids drawn at the 50% probability level; hydrogen atoms have been omitted to improve clarity: