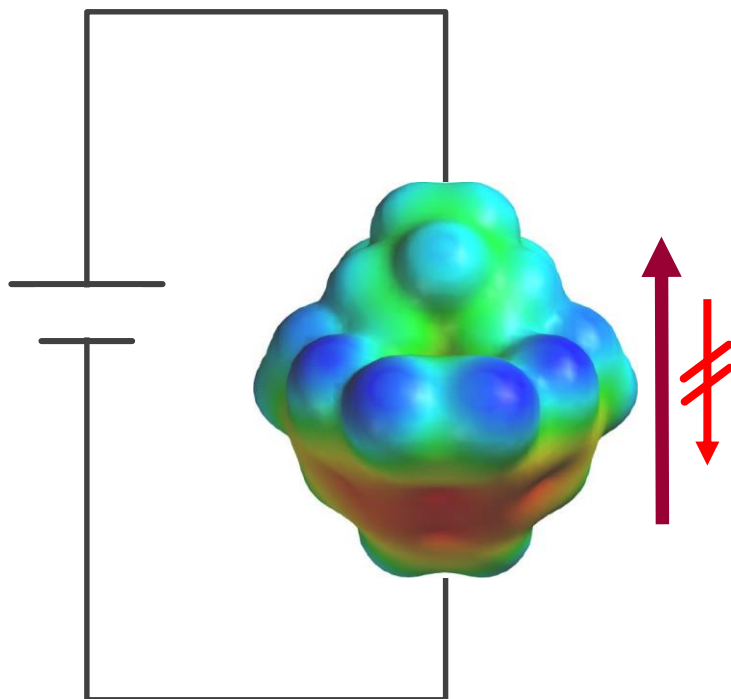


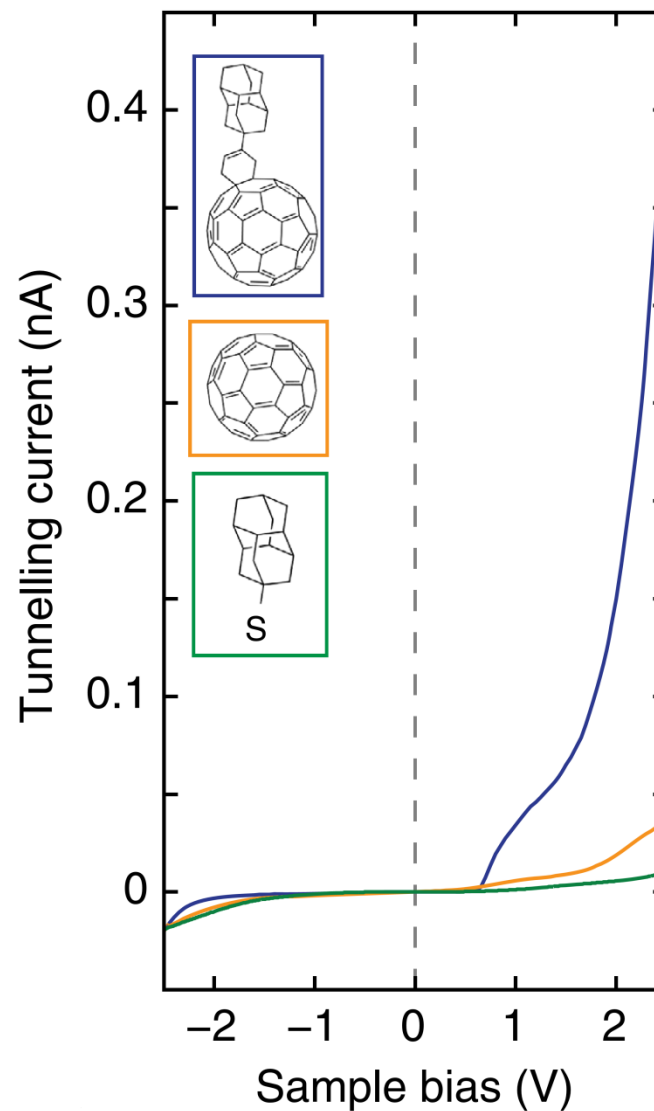
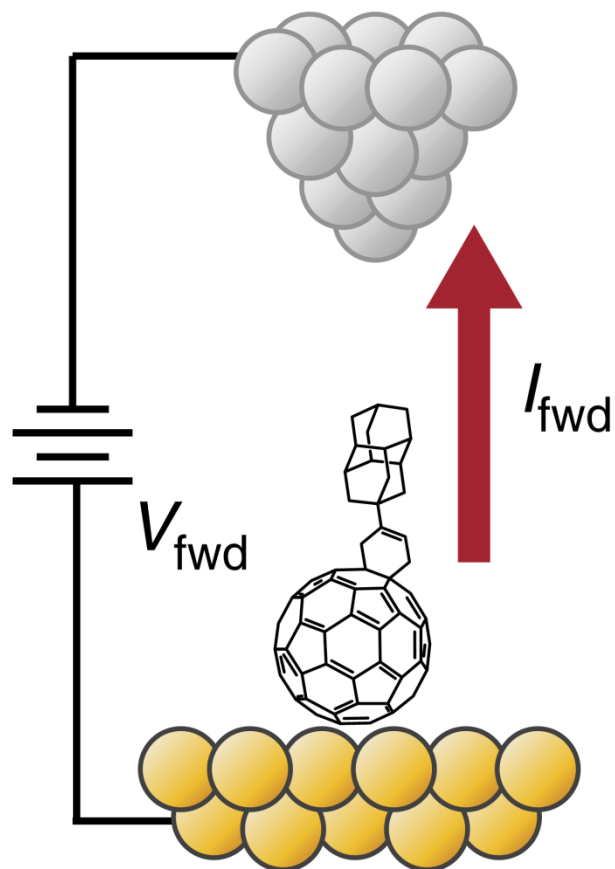
The Next Generation Diode



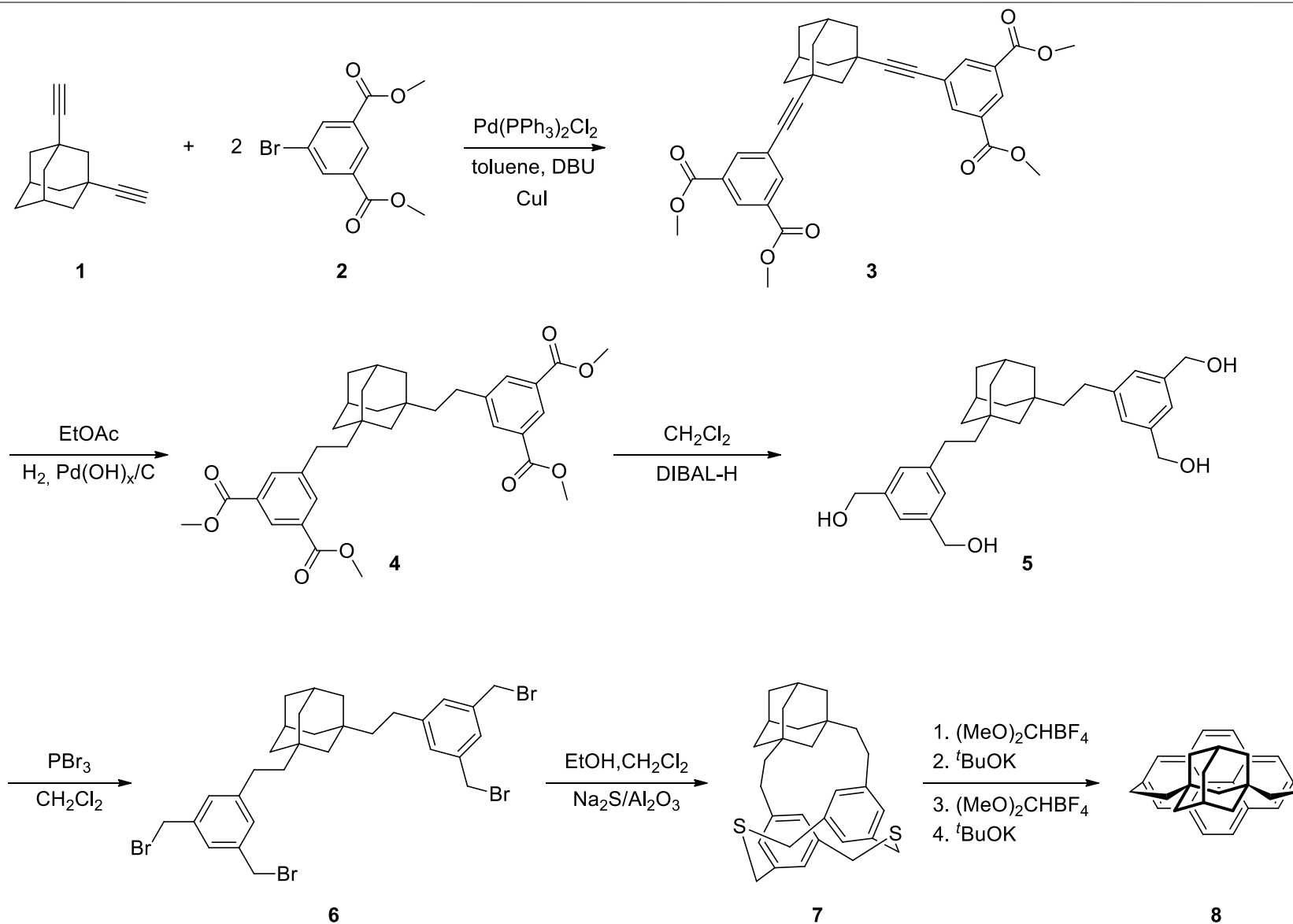
12 October 2015

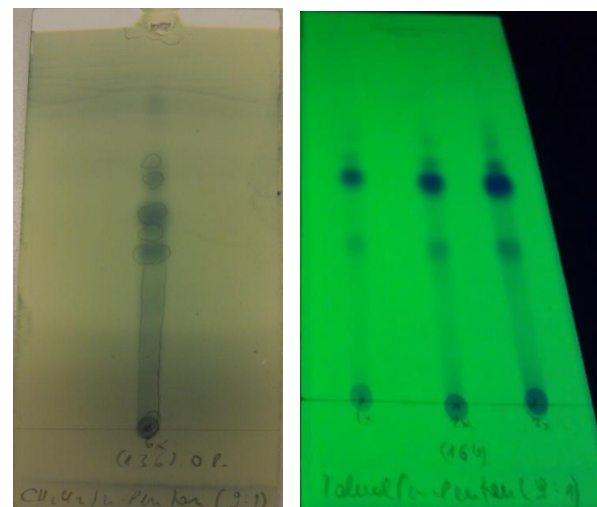
Paul Kahl

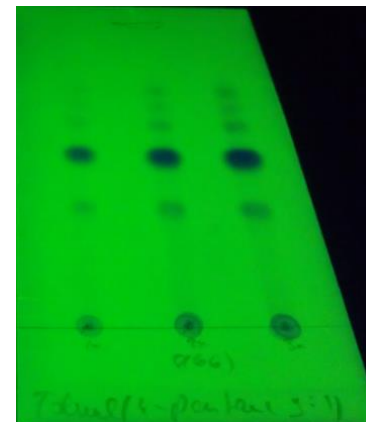
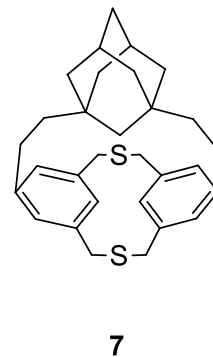
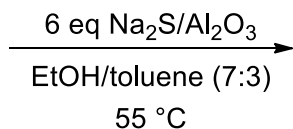
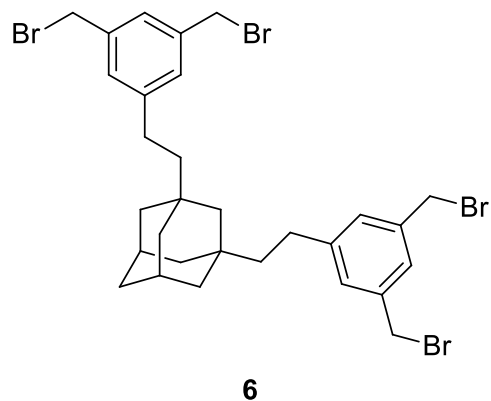
*Institut für Organische Chemie
Justus-Liebig-Universität
35435 Giessen, Germany*



[2](1,3)Adamantano[2](2,7)pyrenophane

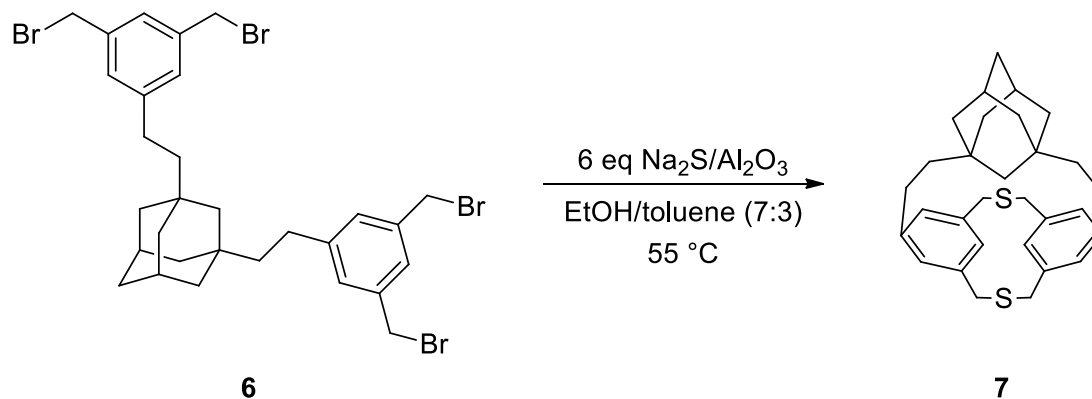


^a25 mg scale; ^b addition through dropping funnel



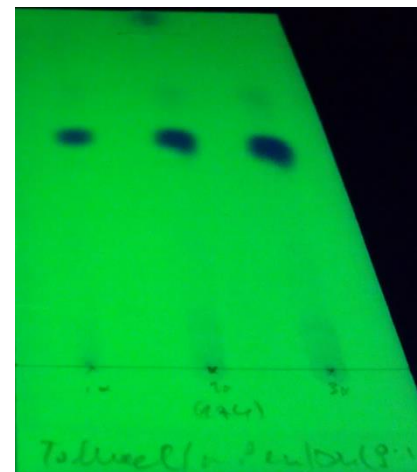
# ^a	Na ₂ S/Al ₂ O ₃ / mmol/g	solvent	mL	t / h	Detection of conversion with TLC and ¹ H-NMR	7 / %
1	1.7 + 3.7	EtOH/toluene (1:9)	120	4	conversion not complete; TLC much better, no singlets in ¹ H-NMR	
2	3.7	- „ - (1:9)	60 ^b + 60	0.5 + 5	Same as #1	
3	- „ -	- „ - (1:9)	180	7	Higher conversion than #2, but same ratios	
4	- „ -	- „ - (2:8)	180	4	Same as #3	
5	- „ -	- „ - (7:3)	135	2	Higher conversion than #4	
6	- „ -	- „ - (7:3)	45 ^b + 45	1.5 + 2.5	less side products	113 raw
7	- „ -	- „ - (7:3)	10 ^b + 85	0.5 + 2.5	even less side products	109 raw

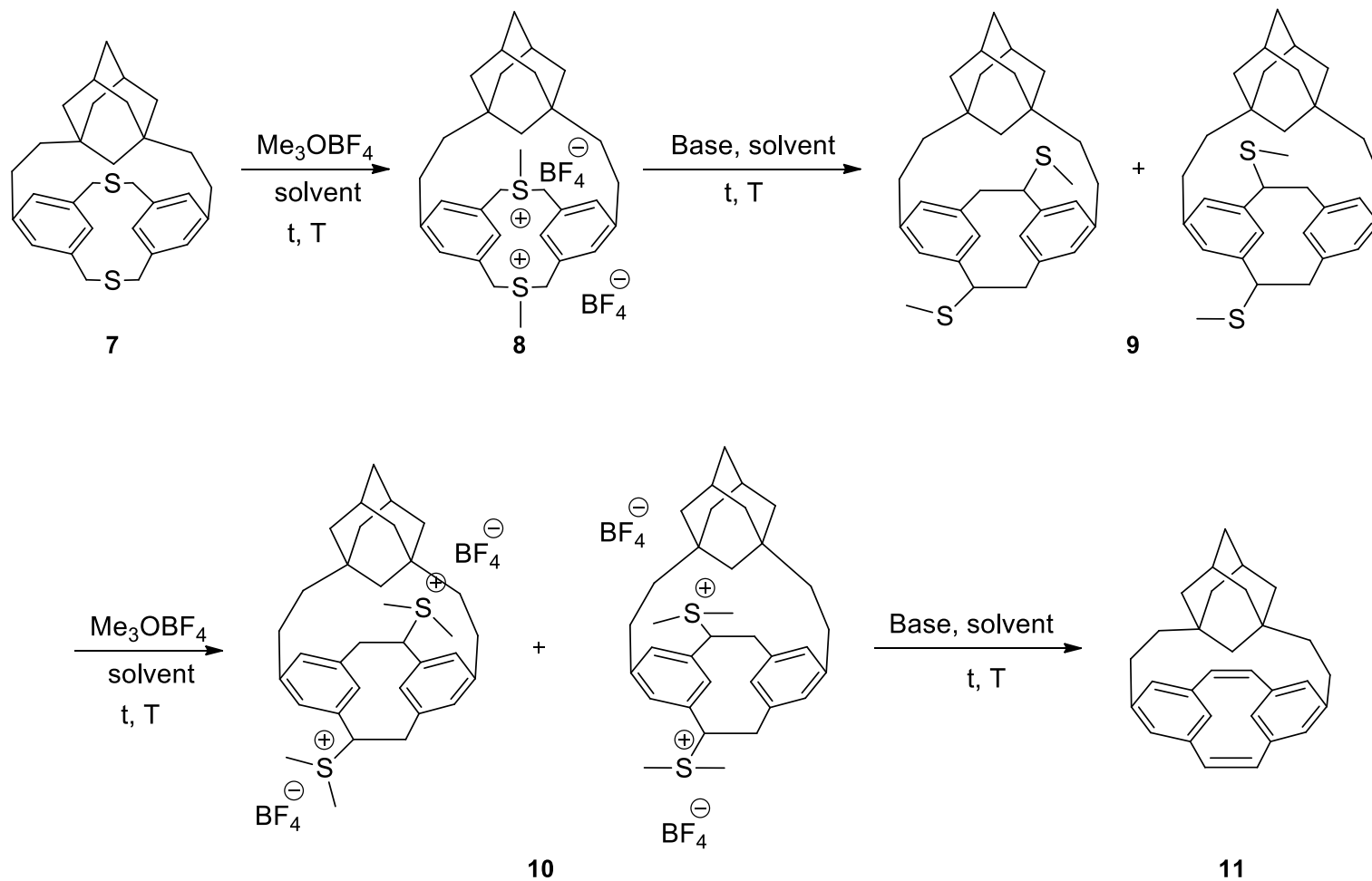
^a 25 mg scale; ^b addition through dropping funnel

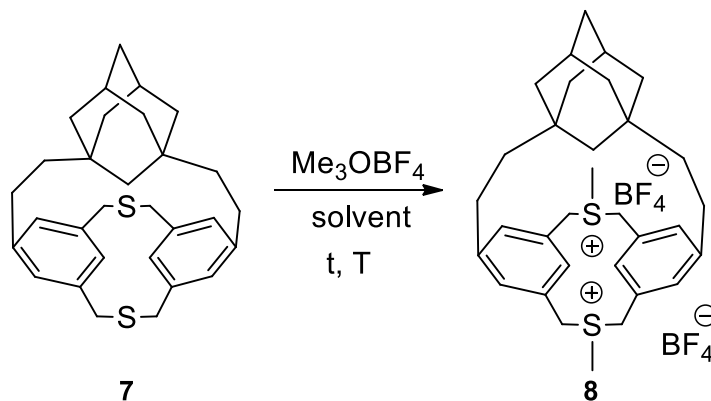


# ^a	<i>EtOH</i> / <i>toluene</i> (7:3) / mL	<i>t</i> / h	7 / %
1	100 ^b + 850	2.5	115 crude
2	50 ^b + 900	1.5	114 crude
3	80 ^b + 880	2	94
4	100 ^b + 850	1.5	86
5	100 ^b + 900	3	88

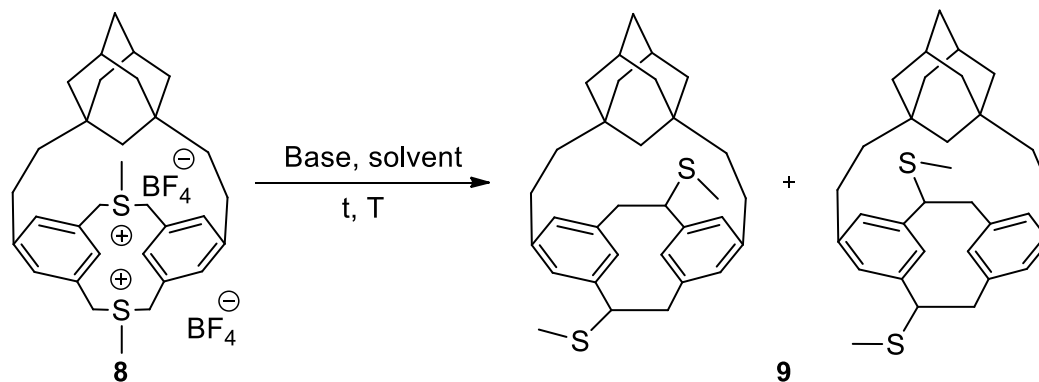
^a 250 mg scale; ^b addition through dropping funnel



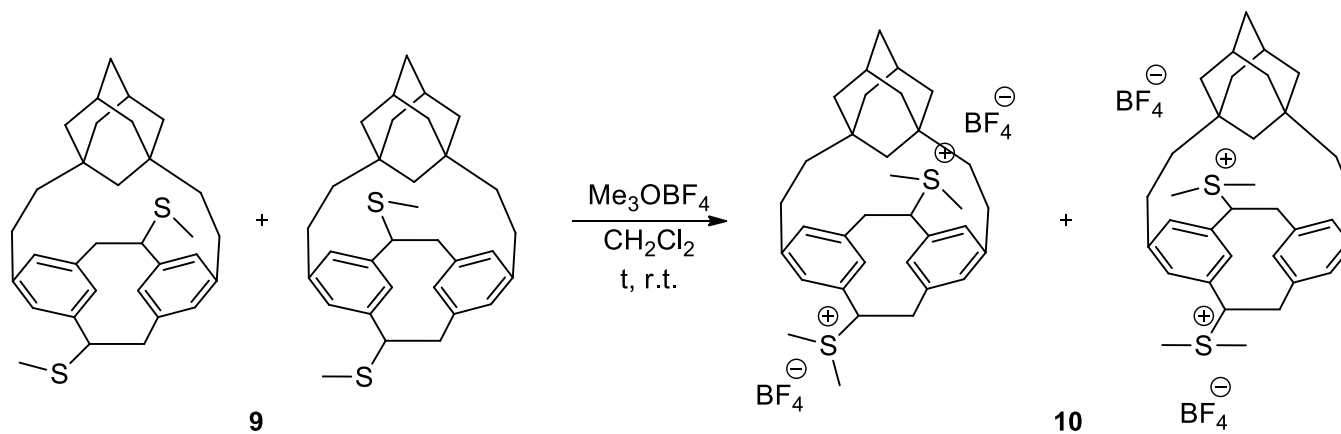




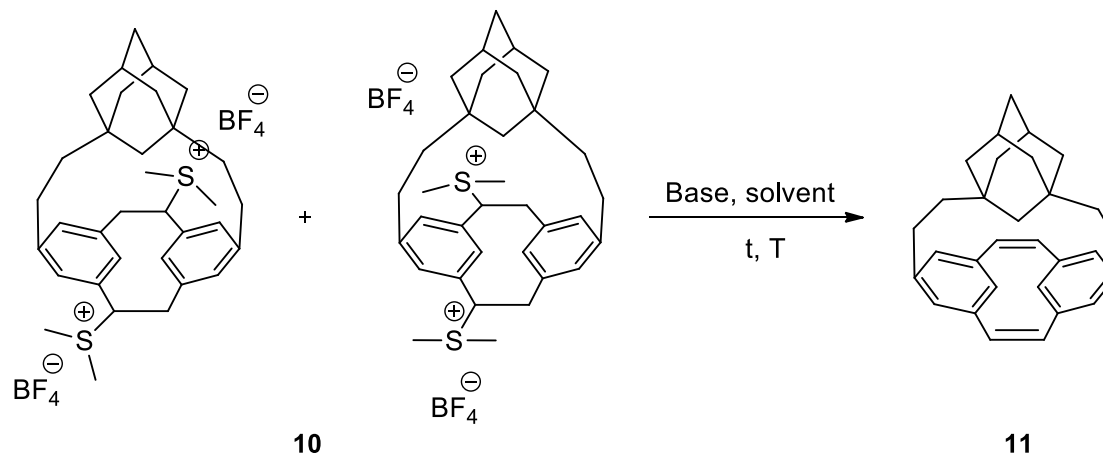
#	Me_3OBF_4 / eq	solvent	t / h	Conversion detection with TLC and $^1\text{H-NMR}$	8 / %
1	3	CH_2Cl_2	0.5	Same as #1	101
2	3	CH_2Cl_2	1	Same as #1	106
3	4	dry CH_2Cl_2	2	Same as #1	-
4	8	CH_2Cl_2	4	Same as #1 + dirt	203
5	3	dry toluene	4.5	No reaction	-
6	3	CHCl_3	6	Very slow conversion	-



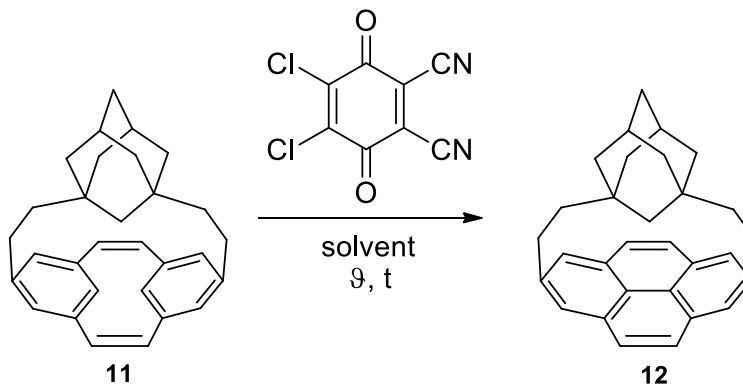
#	<i>KO^tBu</i> / eq	dry solvent / mL	<i>t</i> / h	<i>T</i> / °C	9 / %
1	8	THF / 15	2	r.t.	63 raw
2	4	Et ₂ O / 15	4	r.t. → 50 → r.t.	76 raw
3	NaO ^t Bu / 6	THF / 15	21.5	r.t.	61 raw
4	4	THF / 15	21.5	r.t.	50
5	4	THF / 25	2	r.t.	48
6	3	THF / 25	1	r.t.	22
7	4	DMF / 10	2	r.t.	49
8	7	DMF / 10	4	r.t.	27
9	3	DMF / 10	2	r.t.	21



#	$\text{Me}_3\text{OBF}_4/\text{eq}$	t/h	$\vartheta/^\circ\text{C}$	10 / %
1	2	1.25	r.t.	94
2	4	2	r.t.	103
3	4	3.5	r.t.	137
4	3	1	r.t.	105
5	6	2	r.t.	107
6	3	1	60	109

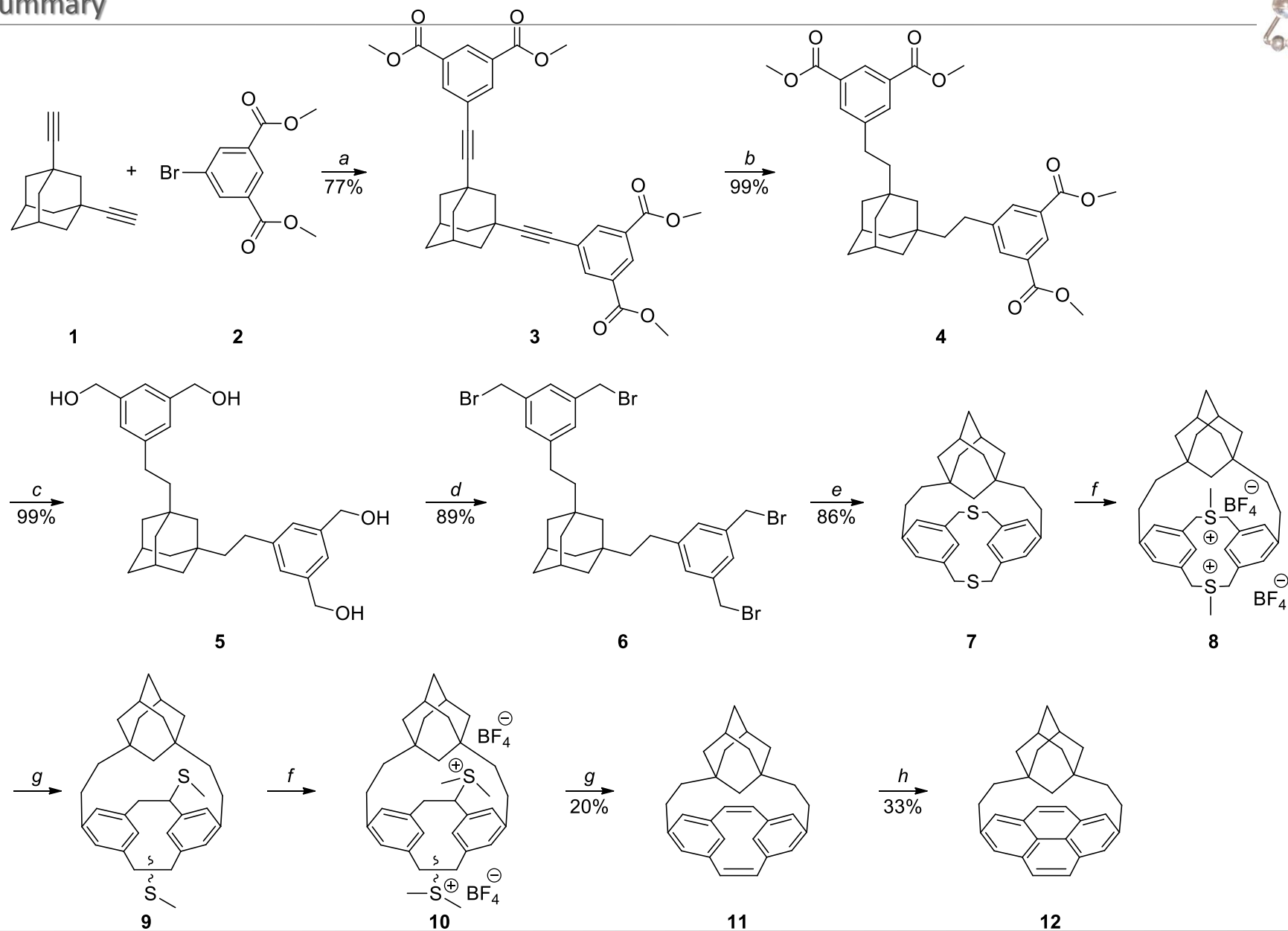


#	$\text{KO}^t\text{Bu} / \text{eq}$	$\text{dry solvent} / \text{mL}$	t / h	$\vartheta / ^\circ\text{C}$	$\text{11} / \%$
1	5	THF / 15	3	r.t. $\rightarrow$ 90	42 raw
2	$\text{NaO}^t\text{Bu} / 4$	THF / 15	20	r.t.	48
3	4	THF / 15	2	r.t.	70 raw
4	4	THF / 25	2	r.t.	40
5	5	DMF/THF (1:1) / 15	2	r.t.	53
6	5	DMF / 15	2	r.t.	47
7	6	DMF / 10	2	r.t.	23

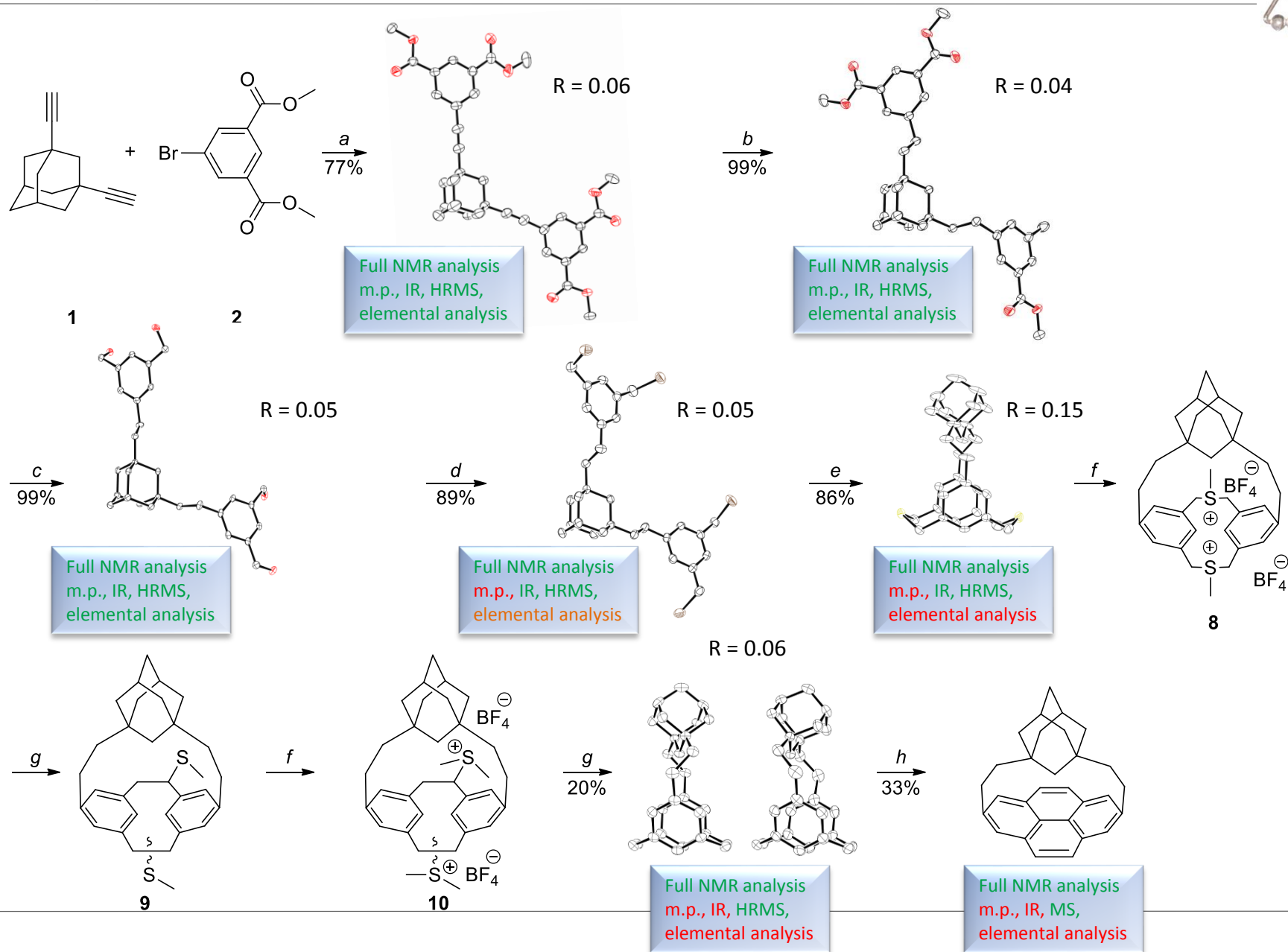


#	solvent	$\vartheta / ^\circ\text{C}$	t / h	purification	conversion	12 / %
1	toluene	120	2.5	CC(SiO ₂)	¹ H-NMR: ~1:4 product : starting material	-
2	toluene	140	10	-	wild mix, almost no product	-
3	dry toluene	40 -> 80	20	-	Less, but still wild mix, more product	-
4	dry CH ₂ Cl ₂	r.t.	4	VFC(ALOX N)	good	33

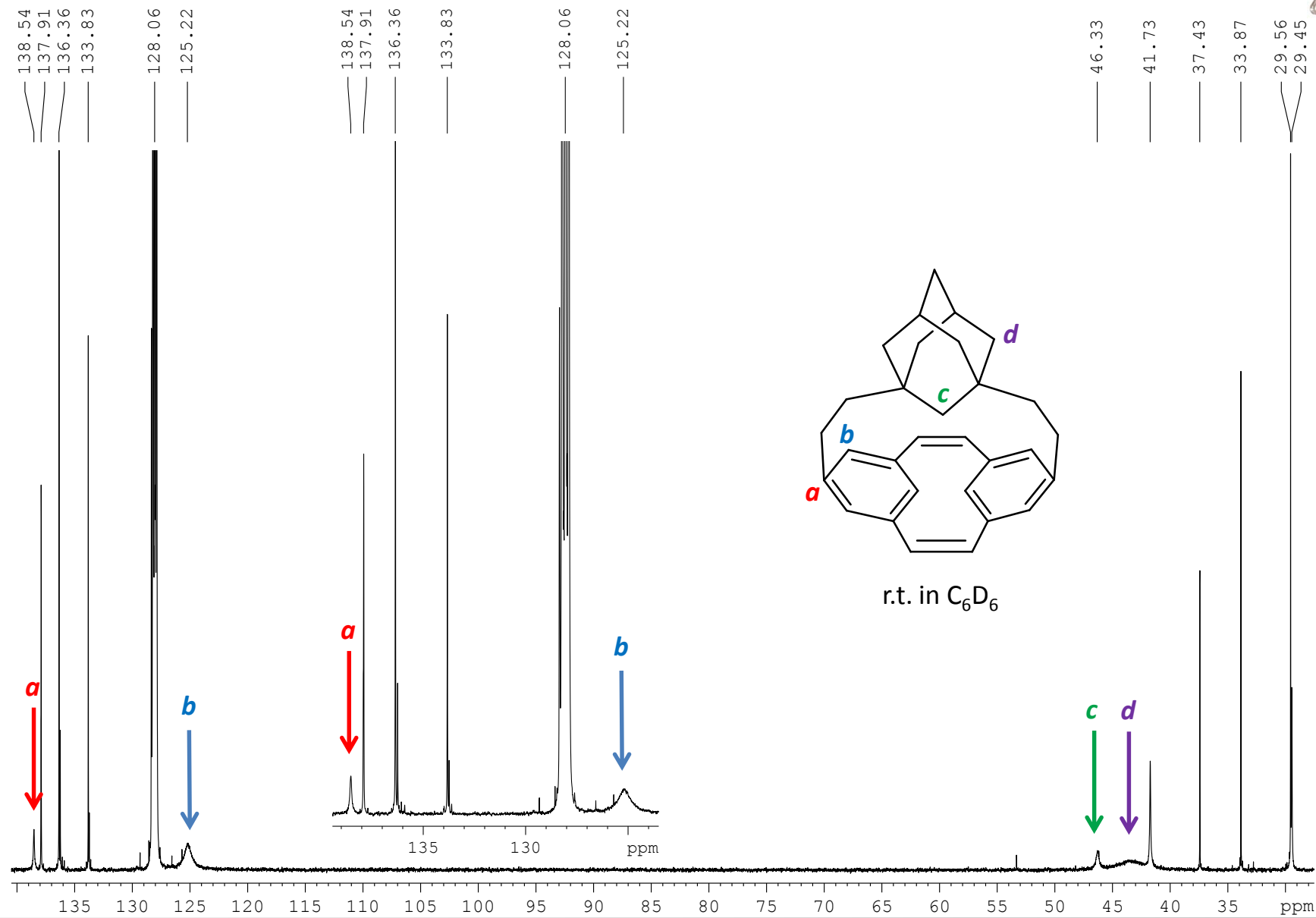
CC = column chromatography; VFC = vacuum filtration chromatography



^a Pd(PPh₃)₂Cl₂, CuI, *n*-DBU, toluene, r.t. 22 h; ^b 10 mol% Pd/C, CH₂Cl₂, 6 h r.t.; ^c LiAlH₄, THF, 2 h 95 °C; ^d 33 wt.% HBr/HOAc, 60 °C 1 h; ^e Na₂S/Al₂O₃, toluene/EtOH (3:7), 55 °C, 2 h; ^f CH₂Cl₂, Me₃OBF₄, r.t. 1 h; ^g KO^tBu, DMF, r.t. 2 h; ^h DDQ, CH₂Cl₂, r.t. 4 h;

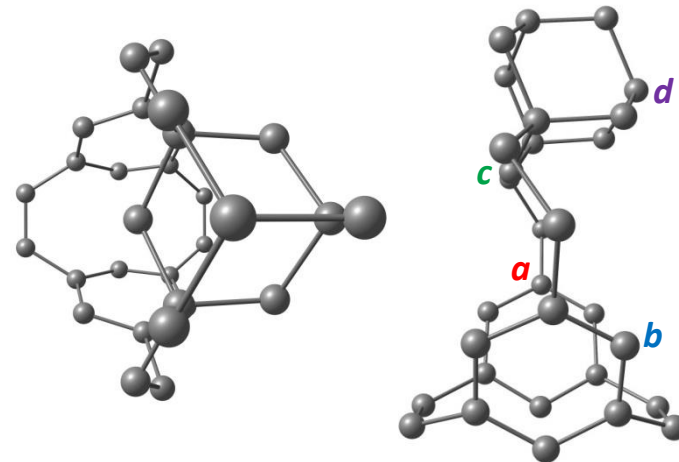
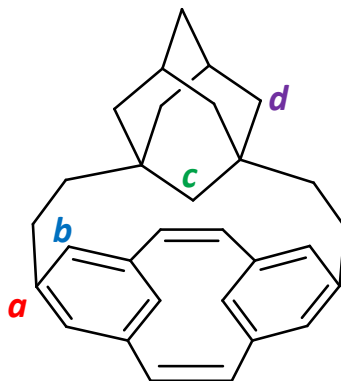
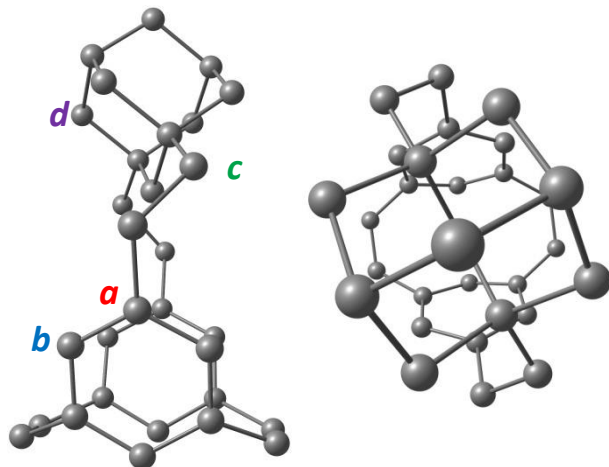


Strained dynamics in NMR





M06-2X/6-31G**



C₂ symmetry δ / ppm

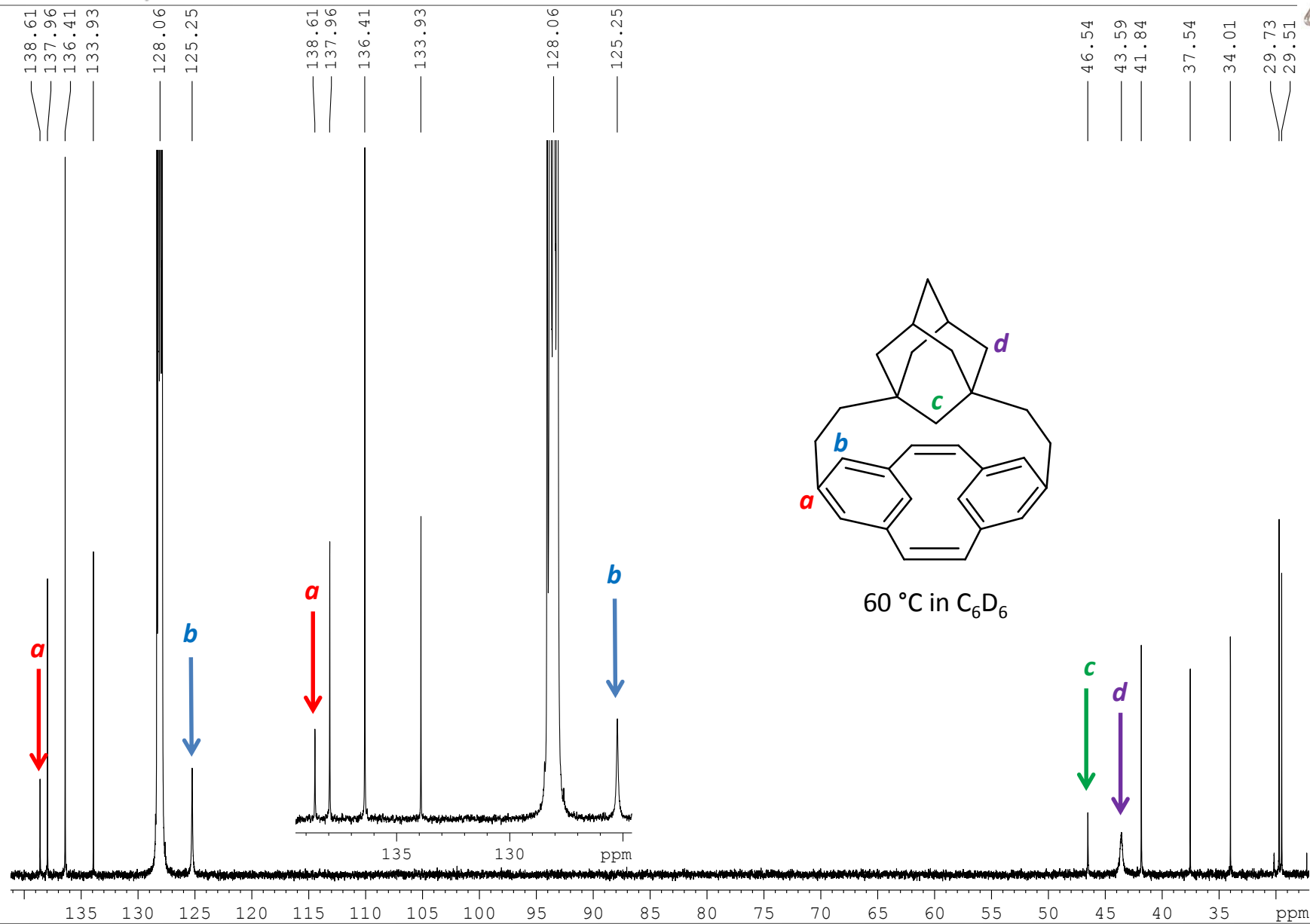
<i>d</i>	44,18
<i>d</i>	49,91
<i>c</i>	50,62
<i>b</i>	142,46
<i>b</i>	145,84
<i>a</i>	160,04

M06-2X/6-311G** NMR=csgt
in relation to TMS

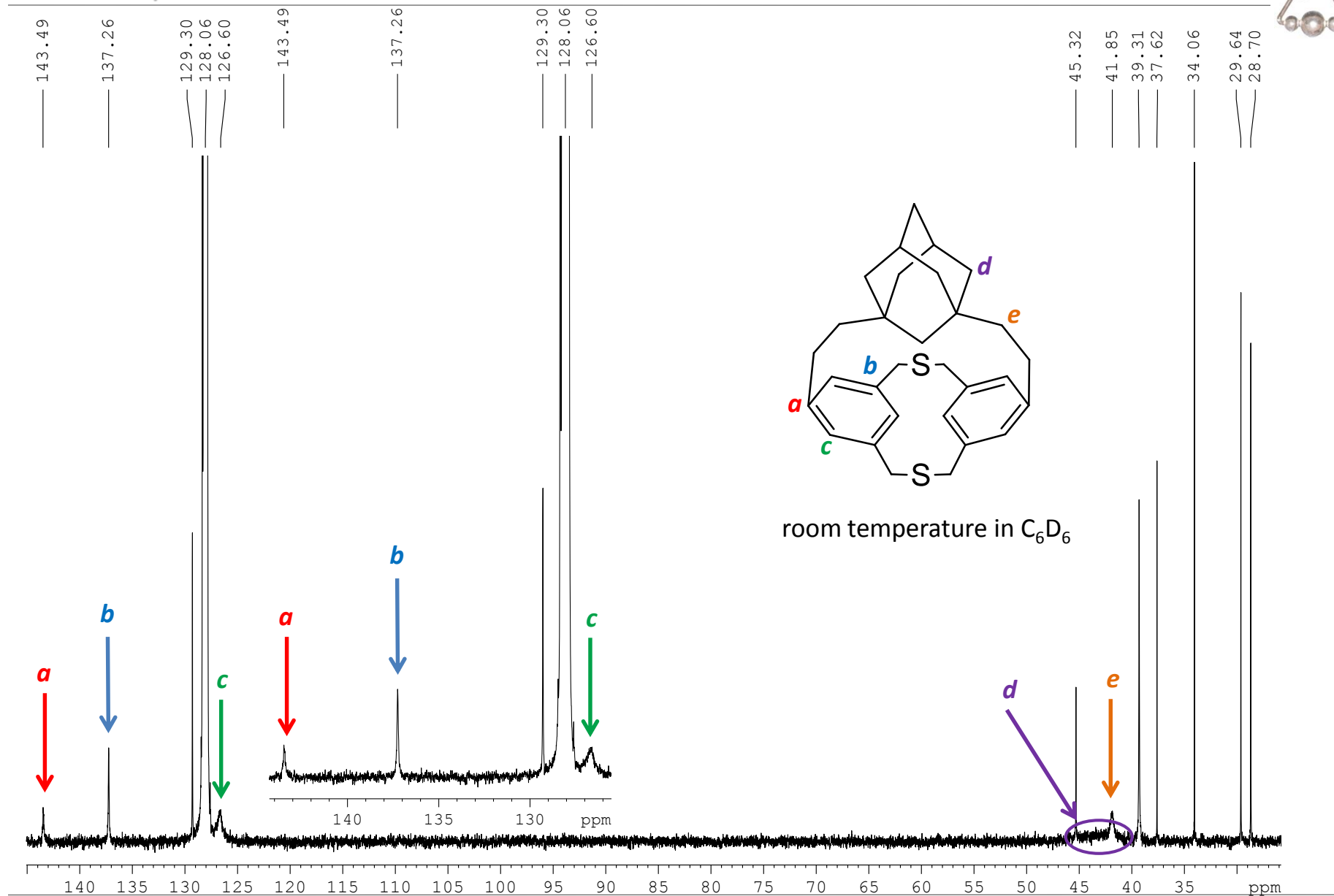
C_s symmetry δ / ppm

<i>d</i>	42,96
<i>d</i>	50,76
<i>c</i>	54,00
<i>b</i>	143,00
<i>b</i>	144,60
<i>a</i>	158,21

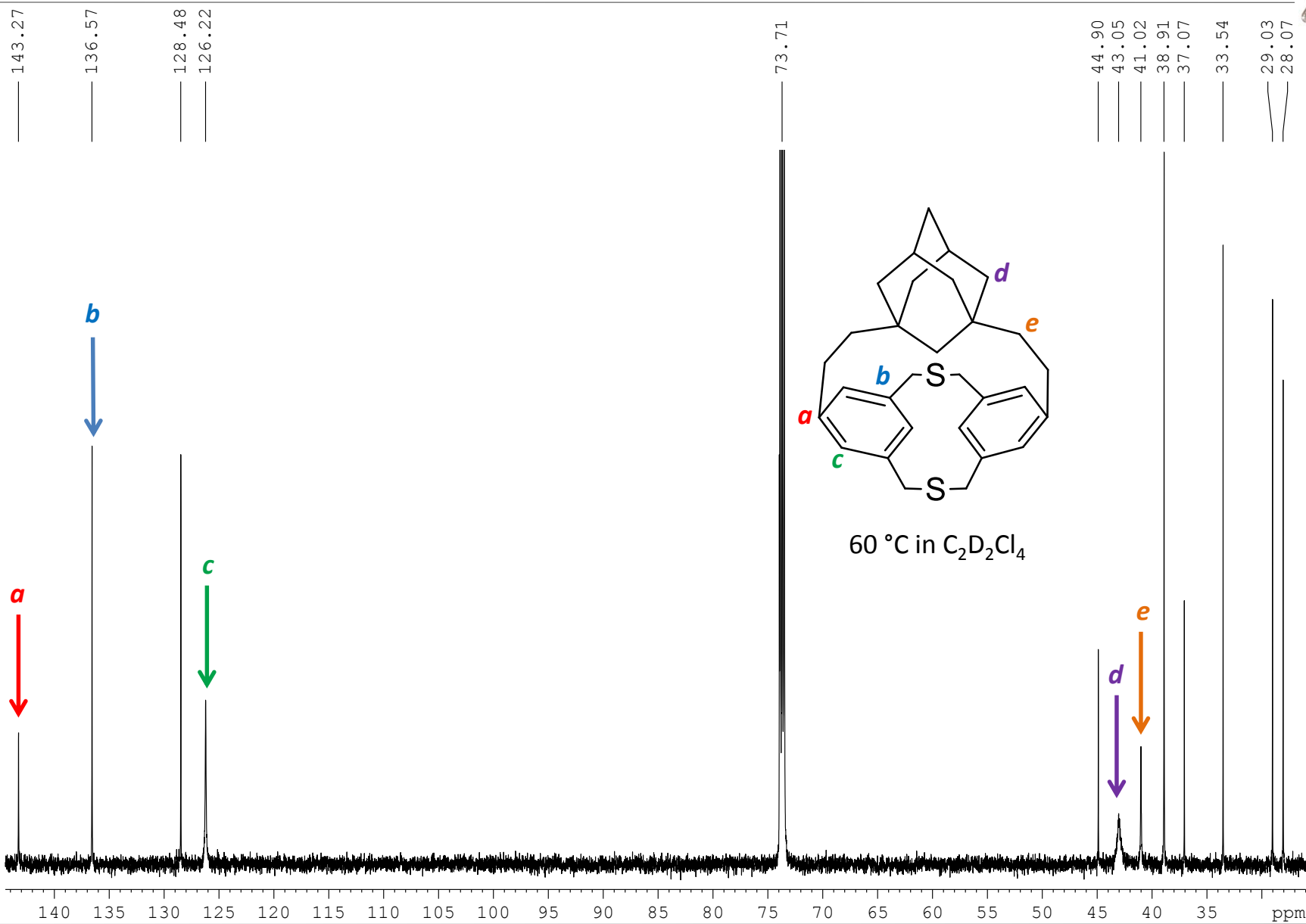
Strained dynamics in NMR

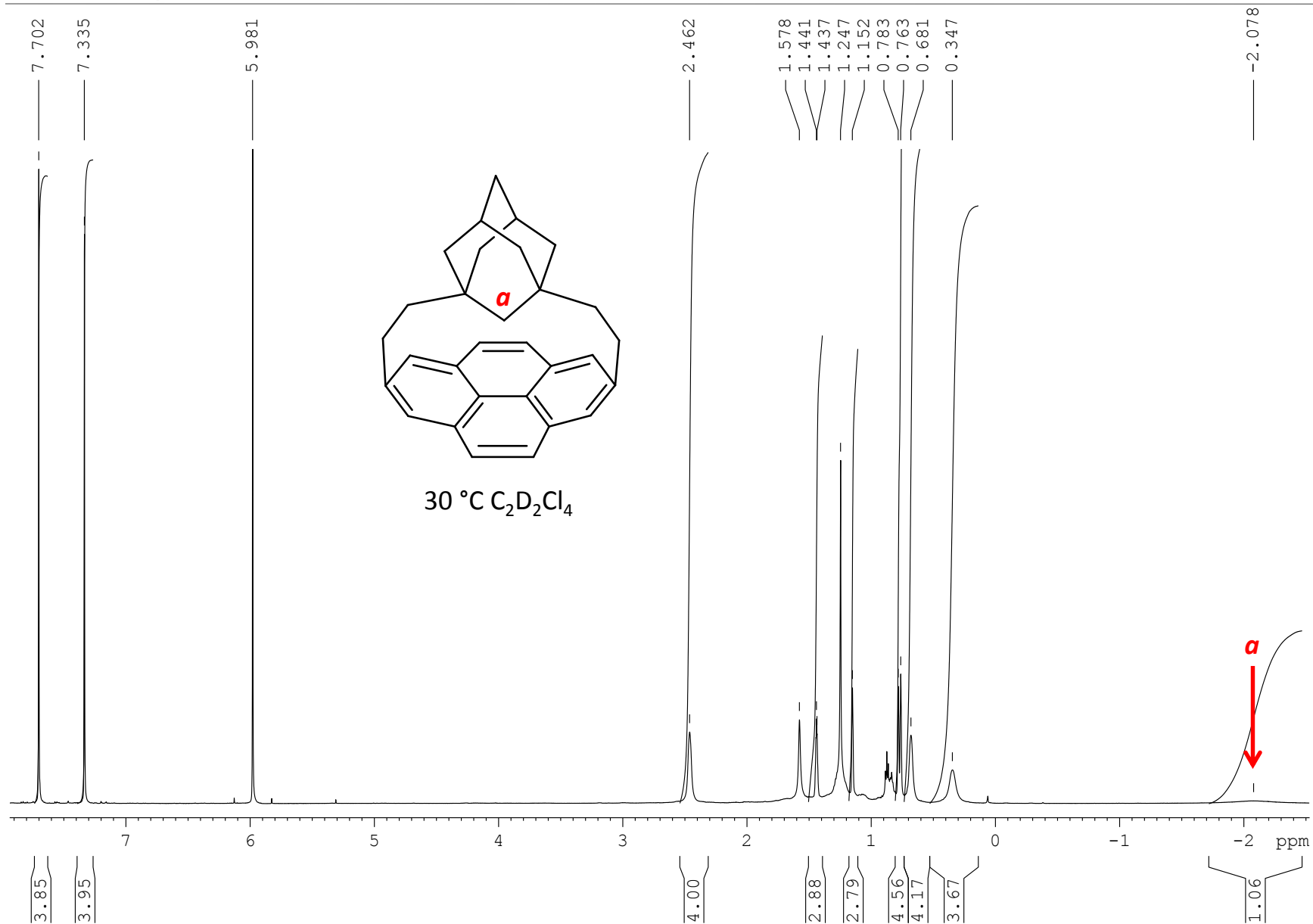


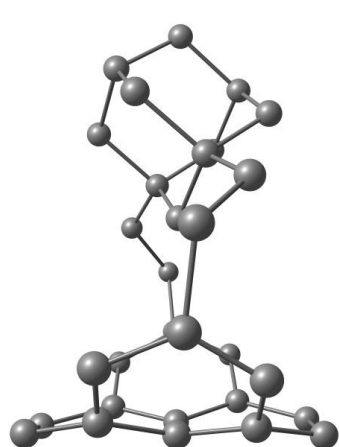
Strained dynamics in NMR



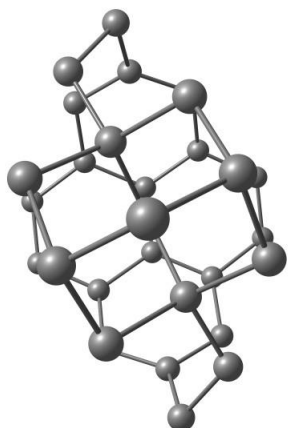
Strained dynamics in NMR



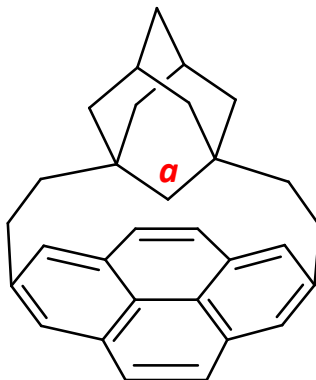




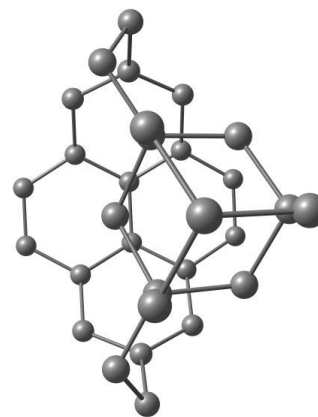
C₂ symmetry δ / ppm
a -2,35



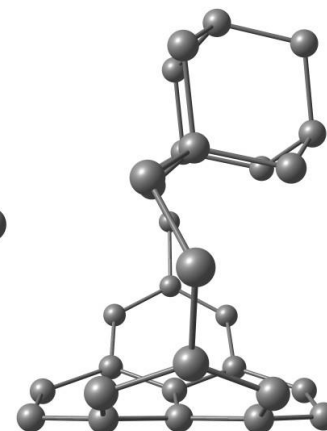
M06-2X/6-31G**



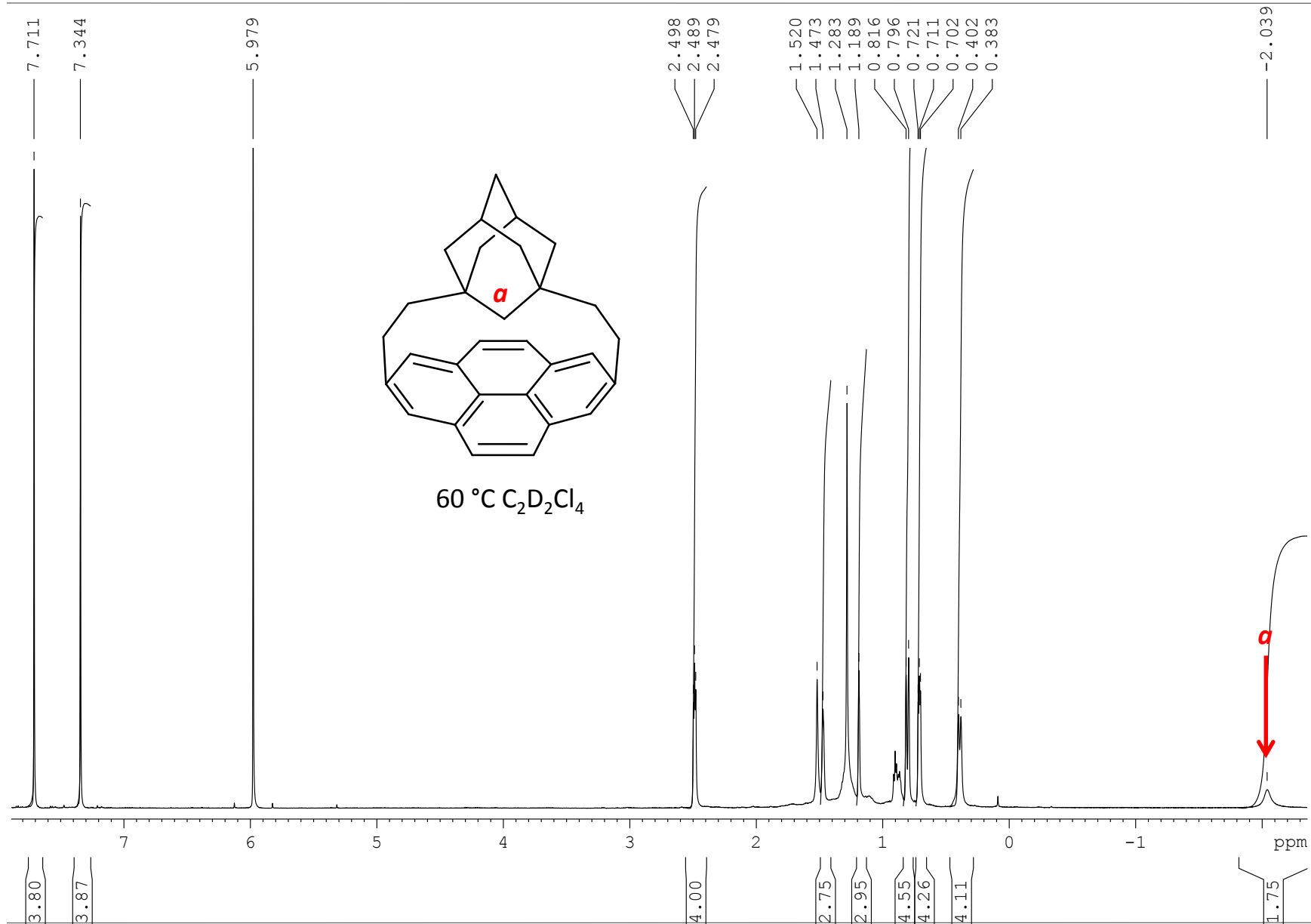
M06-2X/6-311G** NMR=csgt
 in relation to TMS



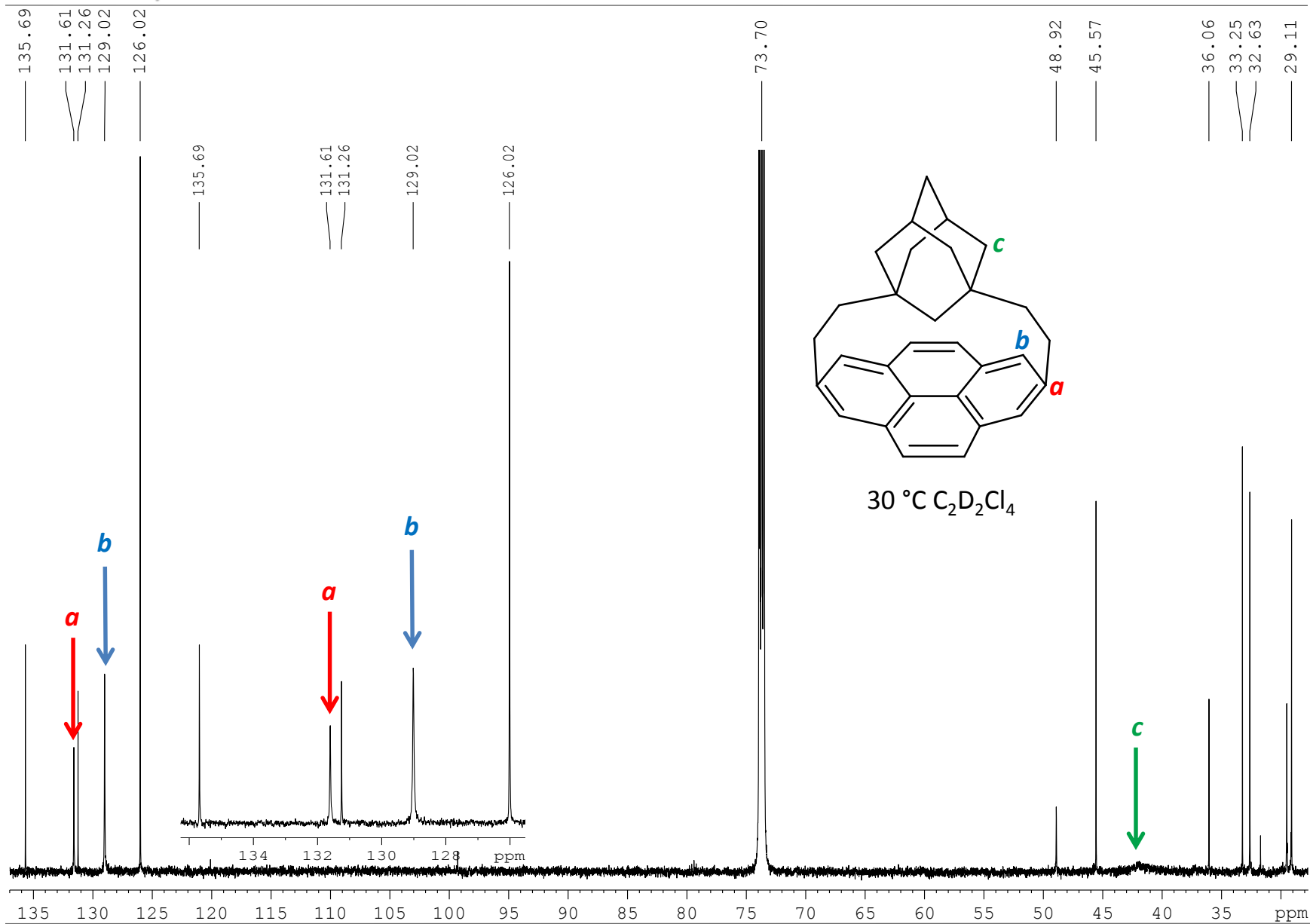
C_s symmetry δ / ppm
a -3,19
a -1,03



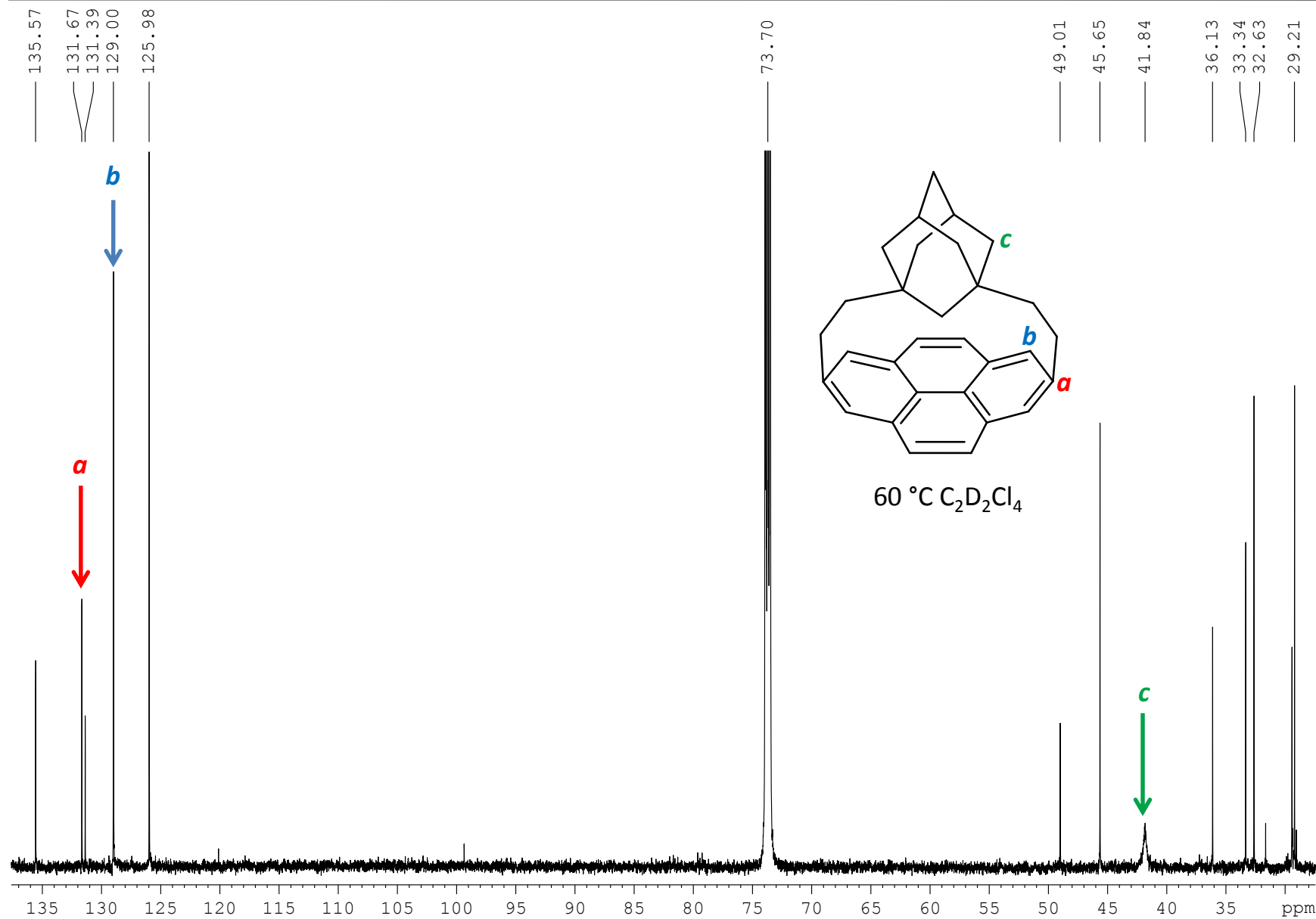
Strained dynamics in NMR

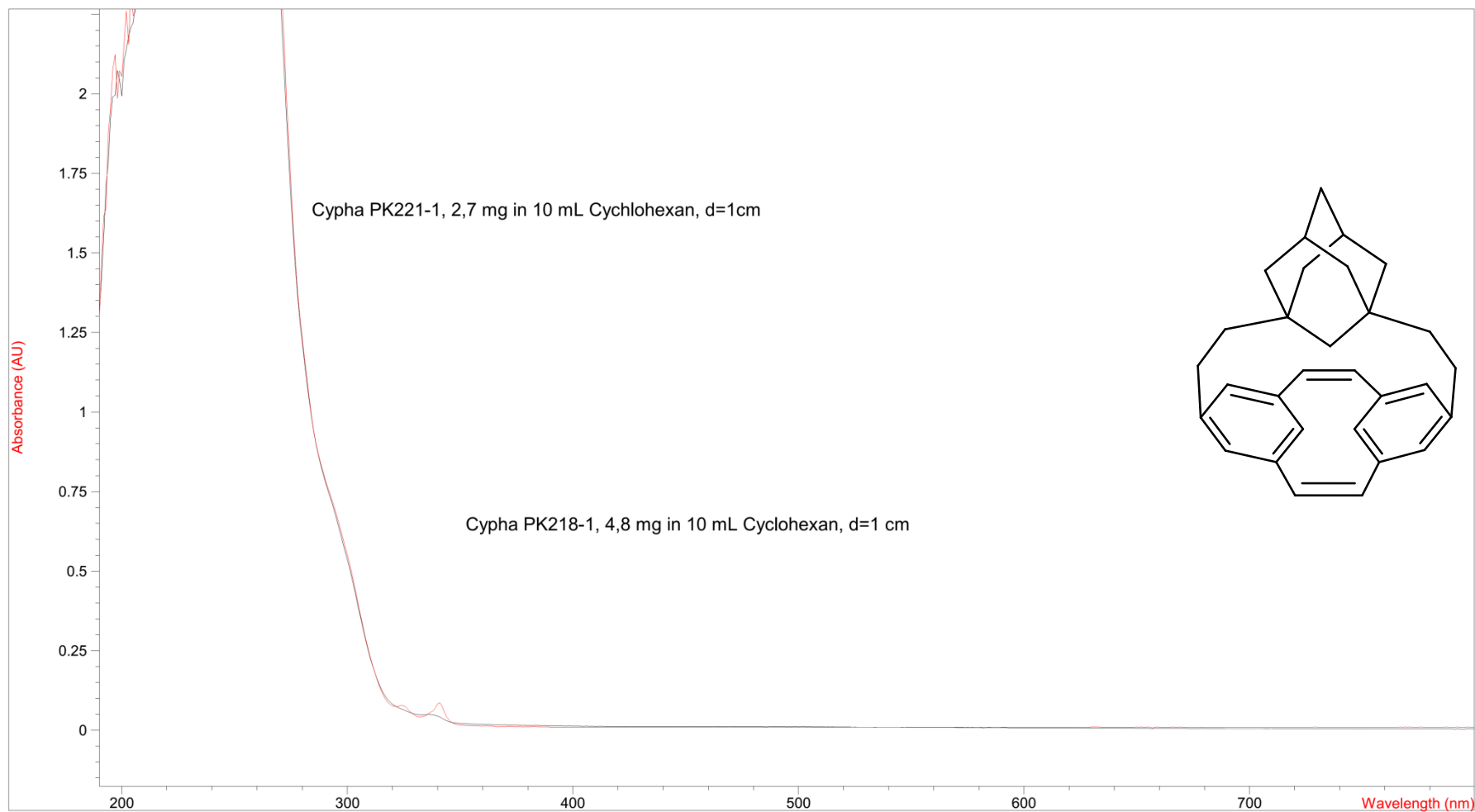


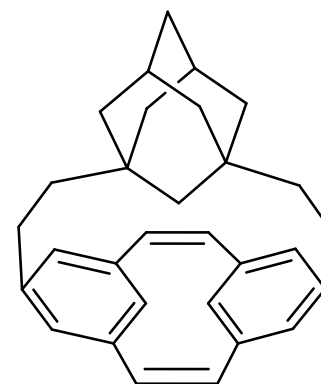
Strained dynamics in NMR

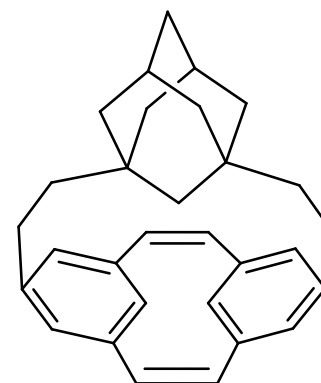


Strained dynamics in NMR

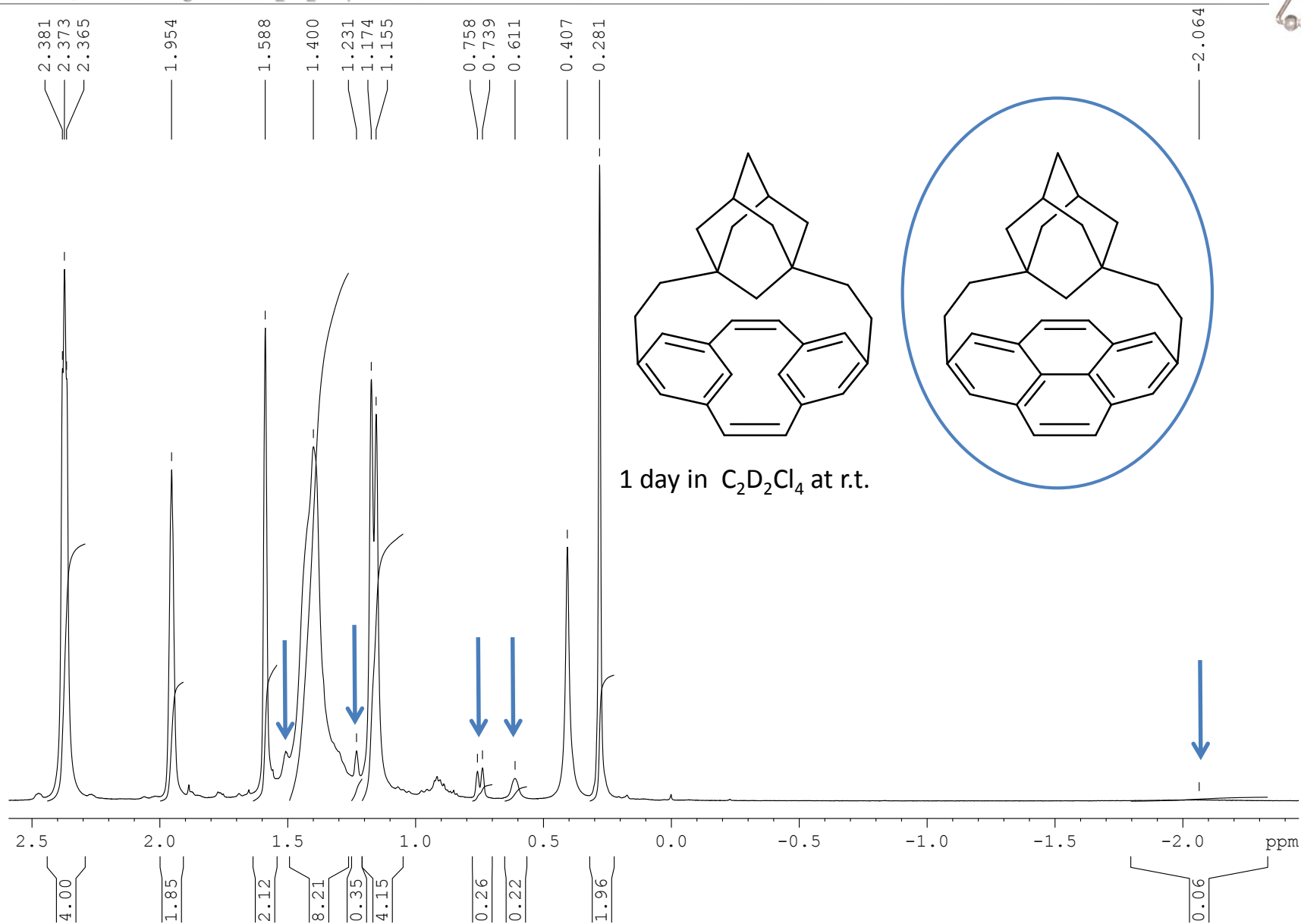




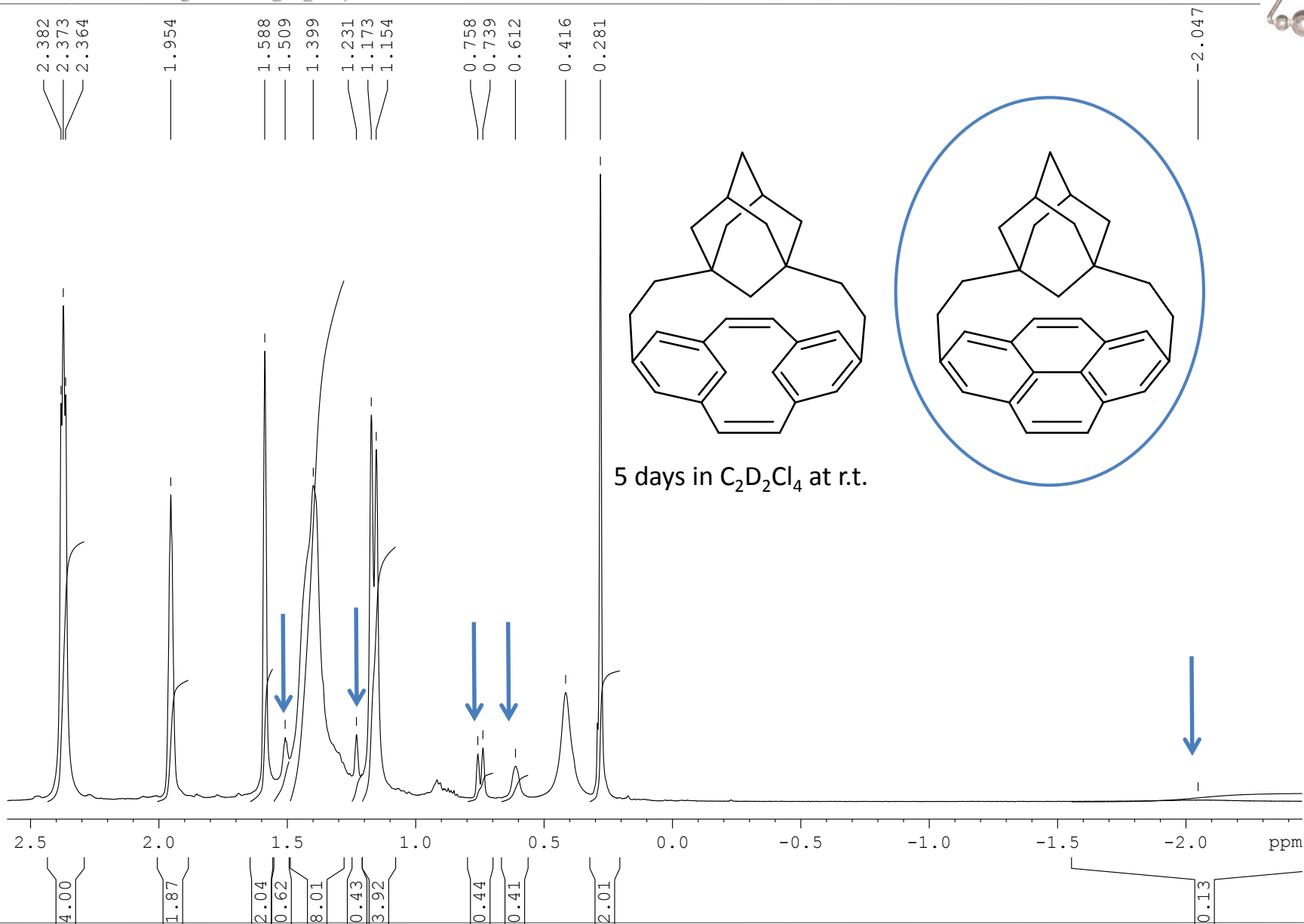




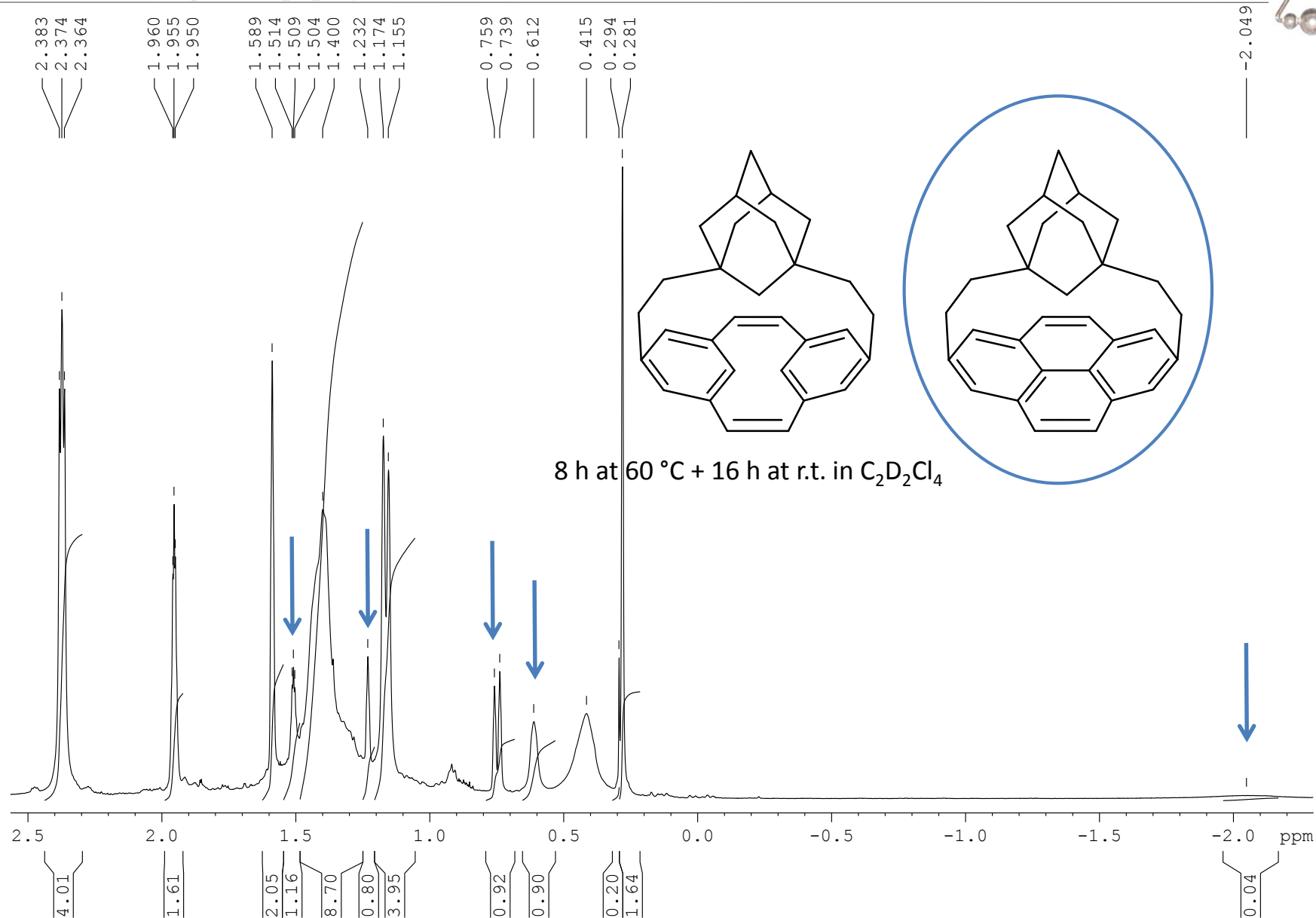
Coloring in CDCl_3 and $\text{C}_2\text{D}_2\text{Cl}_4$



Coloring in CDCl_3 and $\text{C}_2\text{D}_2\text{Cl}_4$



Coloring in CDCl_3 and $\text{C}_2\text{D}_2\text{Cl}_4$





Low temperature NMR

STM

Acknowledgement



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Thank you for your attention!
