Supporting Information

Protolysis of Seven-Membered Zirconacyclocumulene Complexes of Zirconocene

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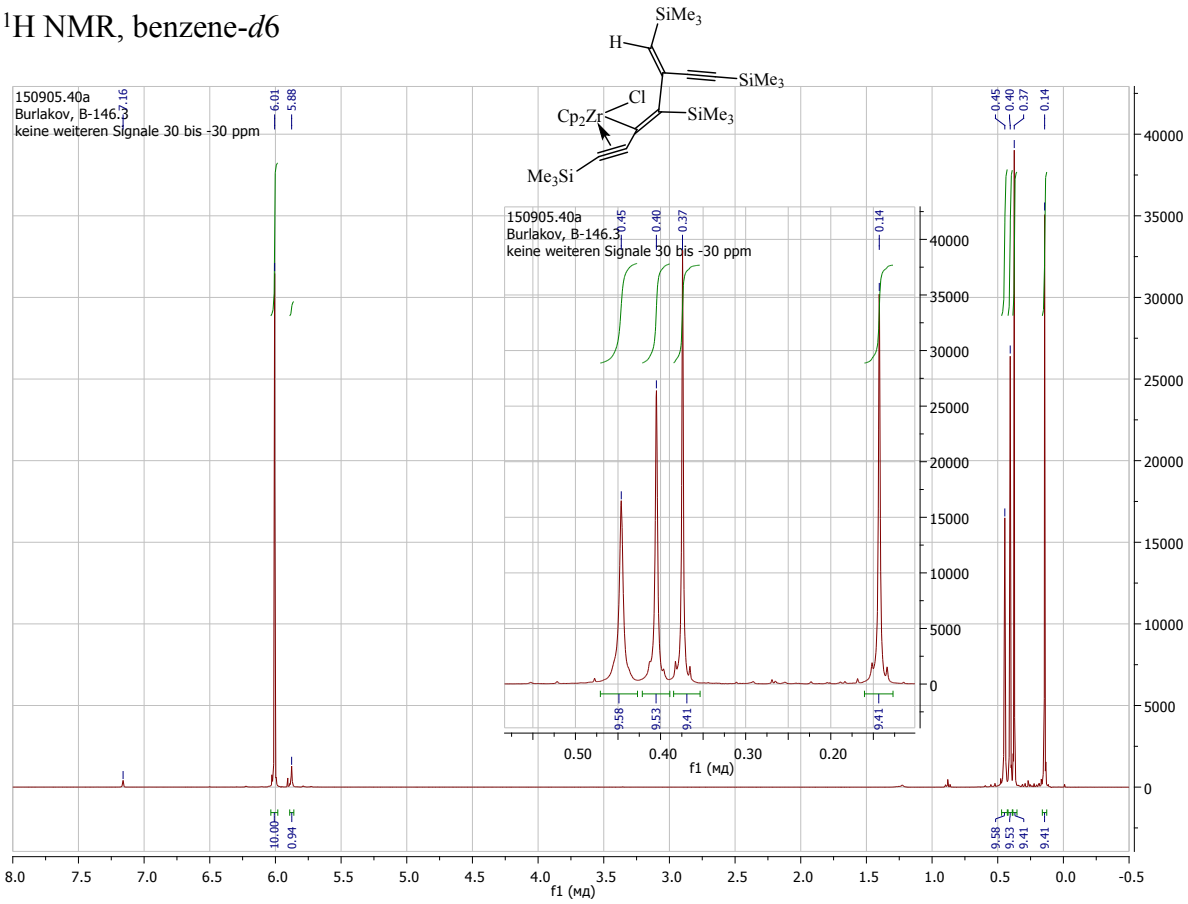
Table S1. Crystal Data and Structure Refinement Parameters for 4, 10, 11

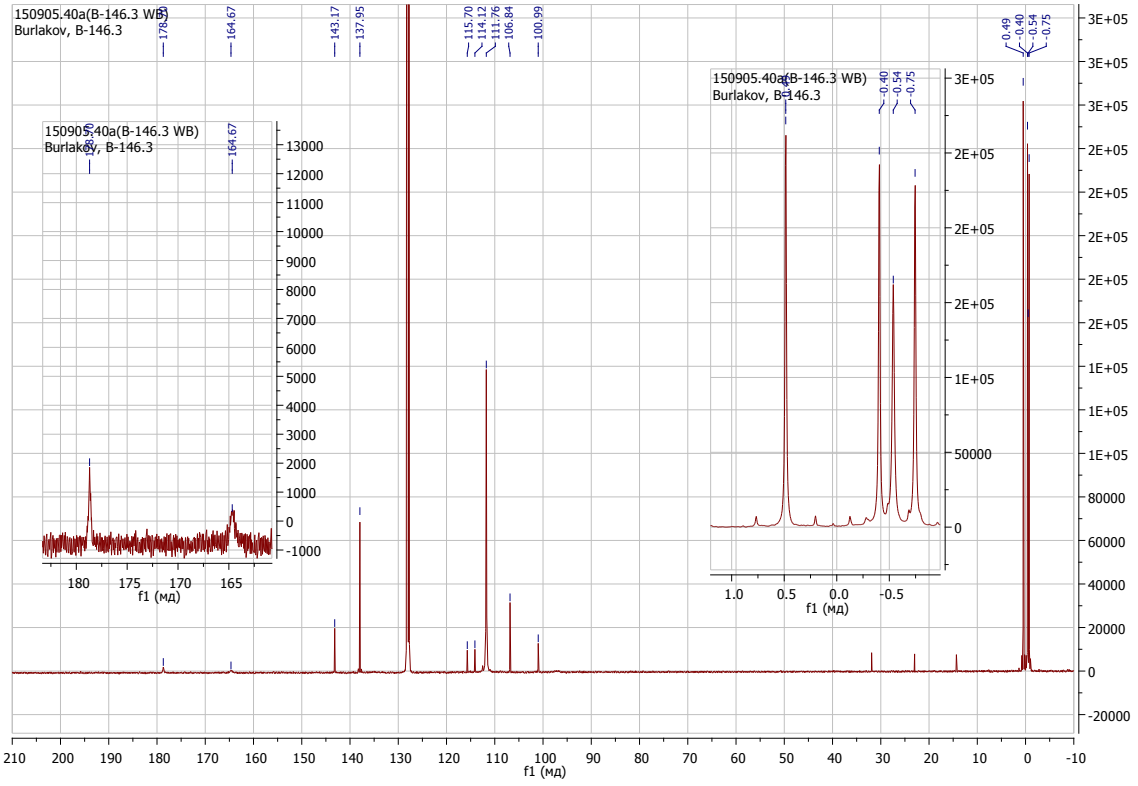
	4	**10**·Et_2O	**11**
formula	$C_{30}H_{47}ClSi_4Zr$	$C_{34}H_{58}OSi_4Zr$	$C_{40}H_{68}Si_4Zr$
molecular wt	646.70	686.38	752.52
T (K)	150(2)	150(2)	150(2)
cryst syst	Triclinic	Monoclinic	Monoclinic
space group	P-1	$P2_1/c$	$C2/c$
Z	4	4	12
a (Å)	12.7748(5)	11.1132(2)	36.1895(5)
b (Å)	16.4250(7)	14.0202(2)	24.7016(4)
c (Å)	17.5631(7)	24.6769(4)	15.3660(2)
α (deg)	105.2479(11)	90	90
β (deg)	90.9179(11)	94.7277(5)	114.8684(6)
γ (deg)	90.5160(11)	90	90
V (Å^3)	3554.7(3)	3831.81(11)	12462.6(3)
D_{calc} (g cm^{-3})	1.208	1.190	1.203
μ (cm^{-1})	5.36	4.35	4.06
T_{min}/T_{max}	0.97/0.94	0.93/0.88	0.91/0.95
F (000)	3264	1464	4848
reflection collected	129047	43717	79292
independent reflections	18003	9687	15033
R_{int}	0.0536	0.0292	0.0392
observed reflections with $I>2\sigma(I)$	13657	8061	12230
no. of params	673	375	642
R_1	0.0312	0.0316	0.0326
wR_2	0.0720	0.0780	0.0847
GOF	1.010	1.016	1.023
largest diff. peak and hole (e·Å^{-3})	0.382/–0.377	0.484/–0.304	0.639/–0.393

Compound **4**

^{1}H NMR, benzene-*d*6

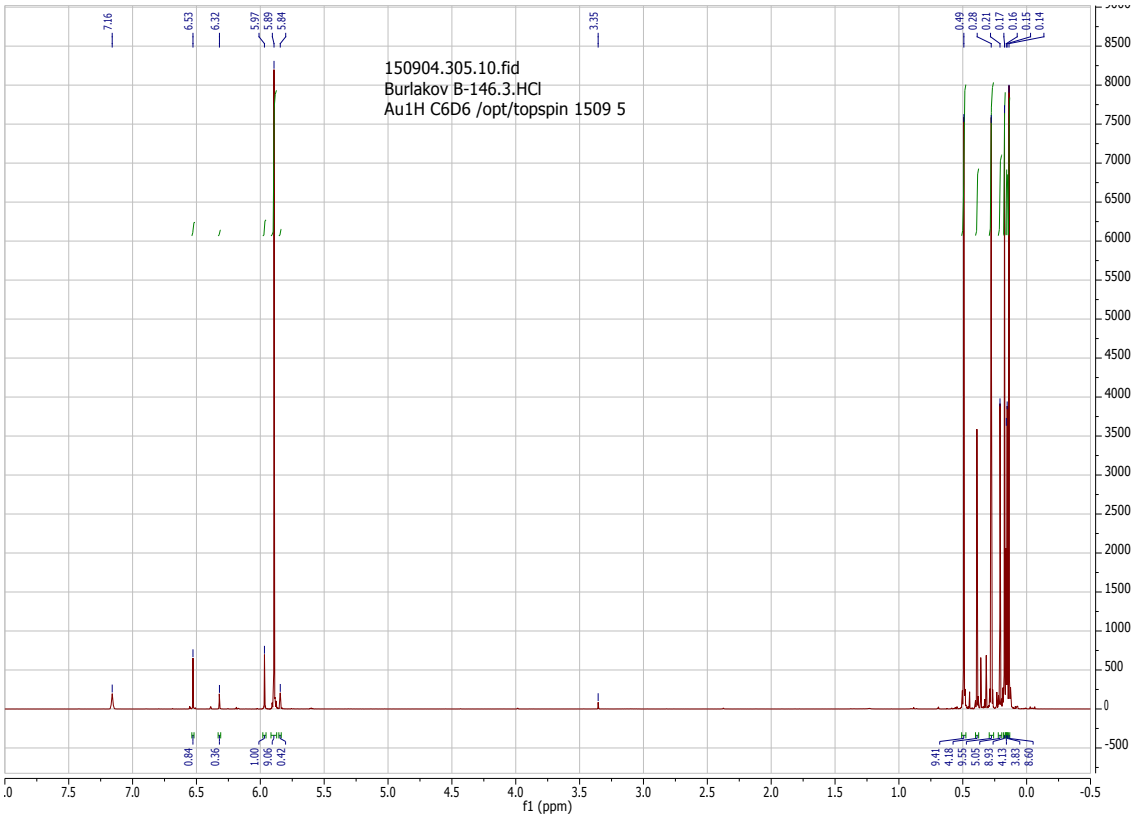


^{13}C NMR, benzene-*d*6

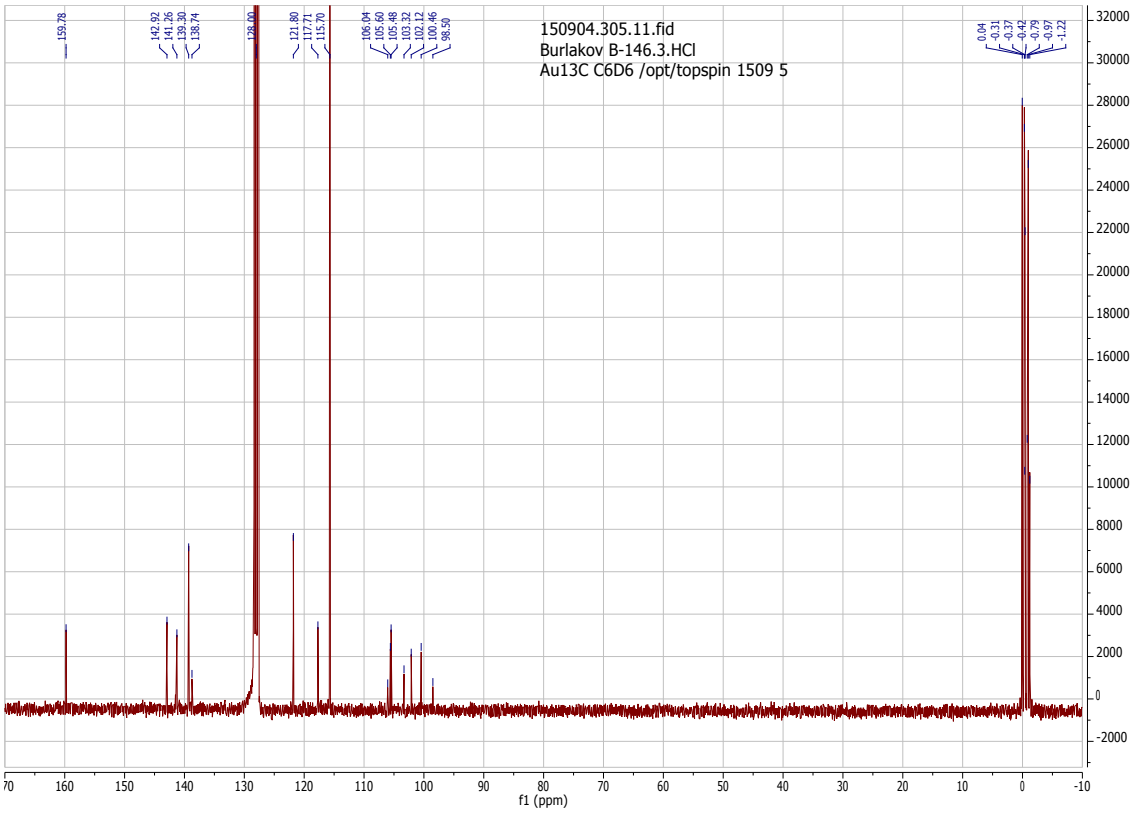


NMR spectra of the mixture of **5** and **6**

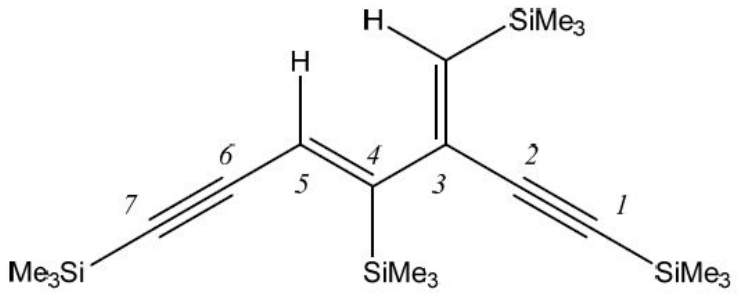
^{1}H NMR, benzene-*d*6



^{13}C NMR, benzene-*d*6



Compound **5**



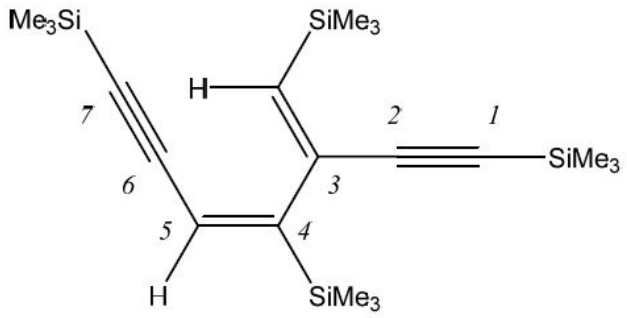
$C_{20}H_{38}Si_4$
M = 390,86 g/mol

Benzene-*d*6

Pos.	^1H	^{13}C [^1J(H,C)]	^{29}Si [^1J(Si,C)]
1		E 100,4$_5$ ppm	
1 ($SiMe_3$)	a 0,14 ppm (s*)	B -0,42 ppm	B -18,4 ppm [56,5]
2		H 105,61 ppm	
3		K 142,95 ppm	
3 (CH)	e 5,95 ppm (s**)	J 139,26 ppm	, [62,9]
3 ($SiMe_3$)	c 0,27 ppm (s*)	A -0,97 ppm	C -8,8 ppm [56,5]
4		L 159,78 ppm	, [59,8]
4 ($SiMe_3$)	d 0,48 ppm (s*)	D 0,03 ppm	D -4,9 ppm [53,0]
5	f 6,50 ppm (s**)	I 121,80 ppm	
6		G 105,48 ppm	
7		F 102,07 ppm	
7 ($SiMe_3$)	b 0,17 ppm (s*)	C -0,31 ppm	A -18,5 ppm [52,8]

* ^2J(Si,H): a-B 7,1 Hz; b-A 7,0 Hz; c-C 6,8 Hz; d-D 6,8 Hz
** J(Si,H): e-C 4,5 Hz; f-D 11,1 Hz; J(H,H) nicht aufgelöst

Compound **6**



$C_{20}H_{38}Si_4$
M = 390,86 g/mol

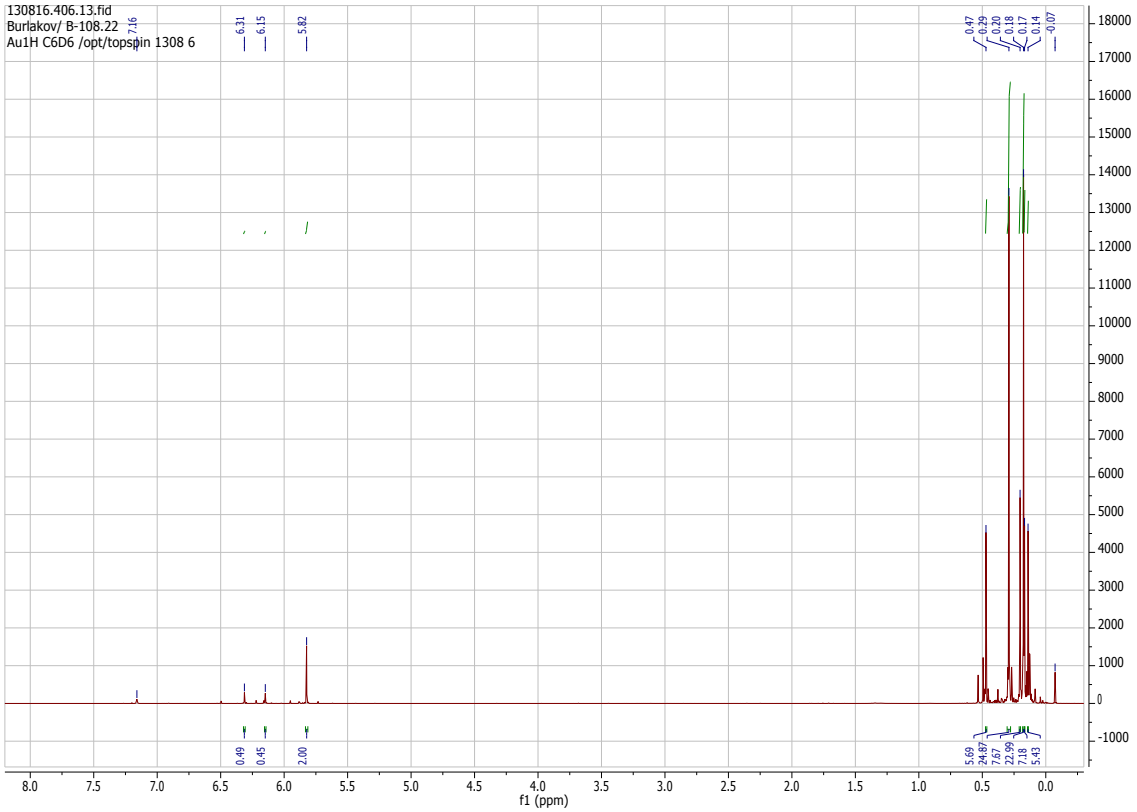
Benzene-d_6

Pos.	^{1}H	^{13}C [^1J(H,C)]	^{29}Si [^1J(Si,C)]
1		E 98,49 ppm	
1 ($SiMe_3$)	a 0,15 ppm (s*)	C -0,37 ppm	B -18,6 ppm []
2		H 106,05 ppm	
3		J 138,77 ppm	
3 (CH)	f 5,83 ppm (d**)	K 141,25 ppm [138]	, []
3 ($SiMe_3$)	d 0,38 ppm (s*)	B -0,79 ppm	C -8,8 ppm []
4		L 159,74 ppm	, []
4 ($SiMe_3$)	b 0,16 ppm (s*)	A -1,22 ppm	D -3,0 ppm []
5	e 6,30 ppm (d**)	I 117,72 ppm [164]	
6		G 103,31 ppm	
7		F 100,52 ppm	
7 ($SiMe_3$)	c 0,21 ppm (s*)	D 0,05 ppm	A -18,6 ppm []

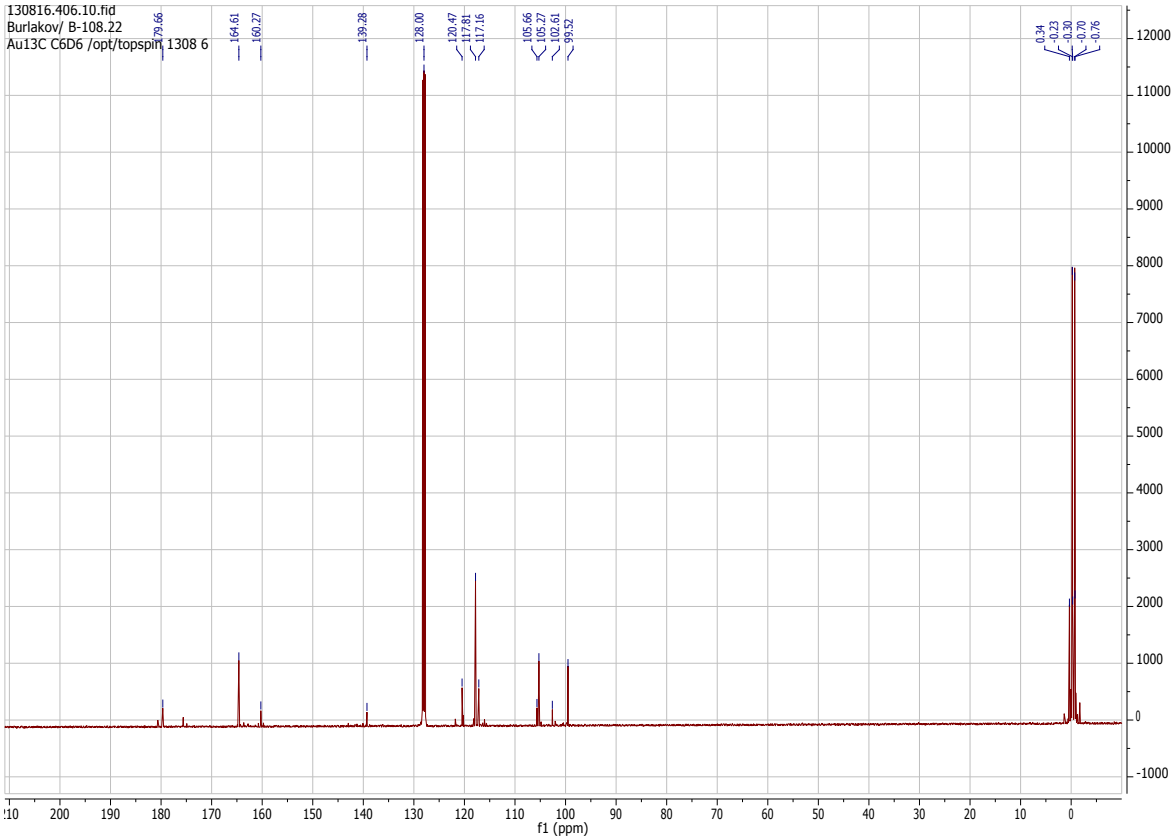
* ^2J(Si,H): a-B / b-D / c-A / d-C alle ca. 7 Hz
** J(Si,H): e-D 6,9 Hz; f-C 4,8 Hz; $J(H_e,H_f)$ 0,4 Hz

NMR spectra of the mixture of **7** and **8**

^{1}H NMR, benzene-*d*6

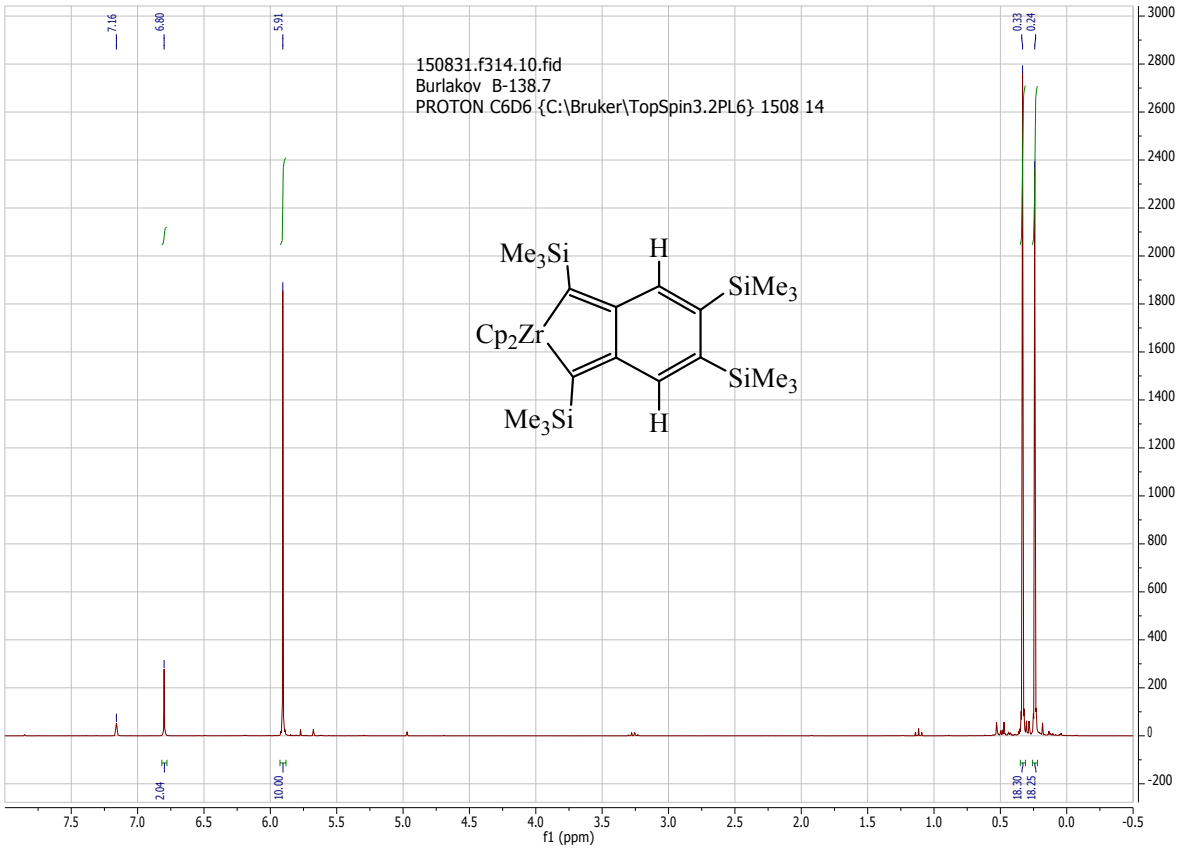


^{13}C NMR, benzene-*d*6

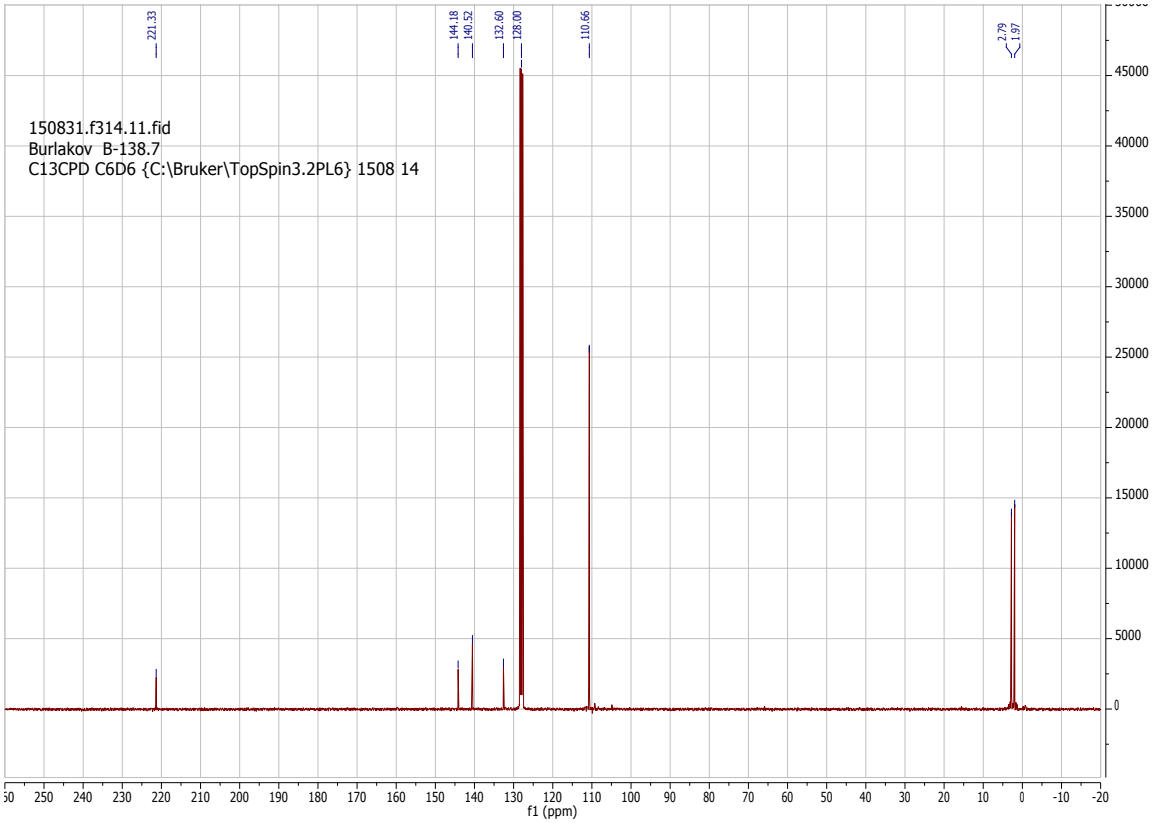


Compound **9**

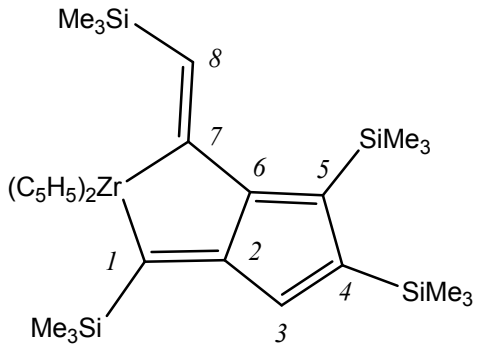
^{1}H NMR, benzene-*d*6



^{13}C NMR, benzene-*d*6



$Cp_2Zr(C_8H_2TMS_4)$ (**10**)



$C_{30}H_{48}Si_4Zr$
M = 612,27 g/mol

Benzene-d_6

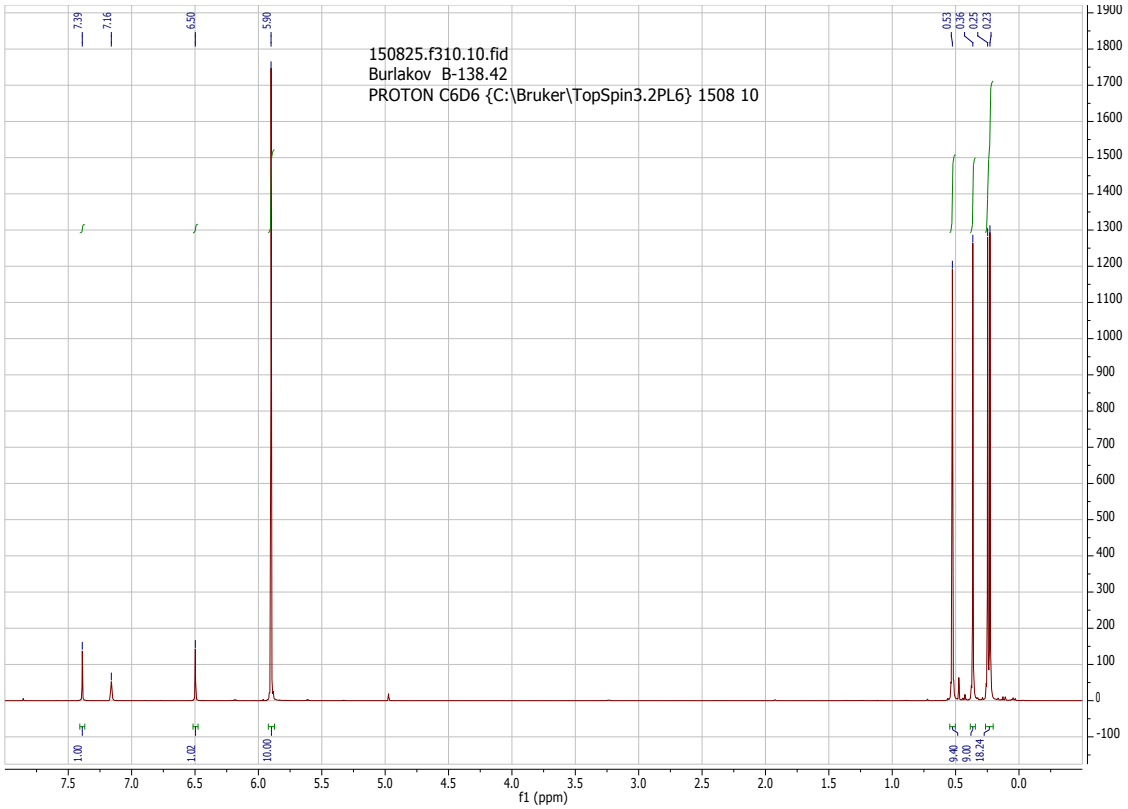
Pos.	^1H	^{13}C	$[^1J_{C,H}]$	$[^1J_{C,Si}]$	^{29}Si
1		M 238,20		[50]	
1-$SiMe_3$	a 0,23	C 2,8$_5$	[119]	[50]	A -12,3
2		K 154,08			
3	f 6,50	F 134,84	[166]	[71]	
4		J 150,13		[68]	
4-$SiMe_3$	c 0,36	B 1,60	[120]	[53]	D -8,1
5		G 139,08		[71]	
5-$SiMe_3$	d 0,53	D 3,08	[119]	[52]	B -10,8
6		H 143,01			
7		L 201,80			
8	g 7,39	I 145,70	[126]	[75]	
8-$SiMe_3$	b 0,2$_5$	A 1,14	[118]	[51]	C -10,6
C_5H_5	e 5,90	E 111,40			

^nJ(H-C or H-Si):

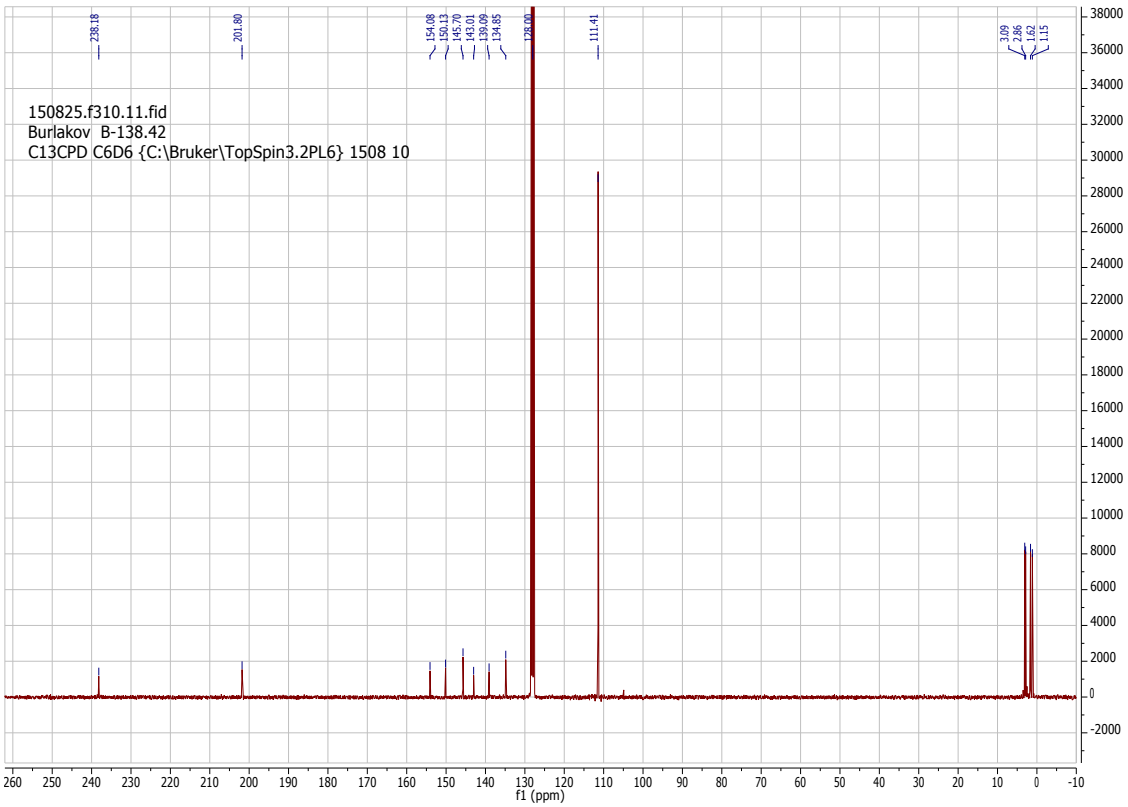
Pos.	Labels	n	J
3-H/C2	f/K	2	10 Hz
3-H/C4	f/J	2	8 Hz
3-H/C5	f/G	3	11 Hz
8-H/C7	g/L	2	12 Hz
8-H/C6	g/H	3	15 Hz
1-Me/1-Si	a/A	2	6,3 Hz
4-Me/4-Si	c/D	2	6,4 Hz
5-Me/5-Si	d/B	2	6,4 Hz
8-Me/8-Si	b/C	2	6,4 Hz
8-H/8-Si	g/C	2	6,0 Hz
3-H/4-Si	f/D	3	4,3 Hz

Stereochemistry: There is a strong NOE contact between 8-$SiMe_3$ (b) and the C_5H_5 ligand (e), also a strong one between 5-$SiMe_3$ (d) and 8-H (g), but no one between e and g.

^{1}H NMR, benzene-*d*6

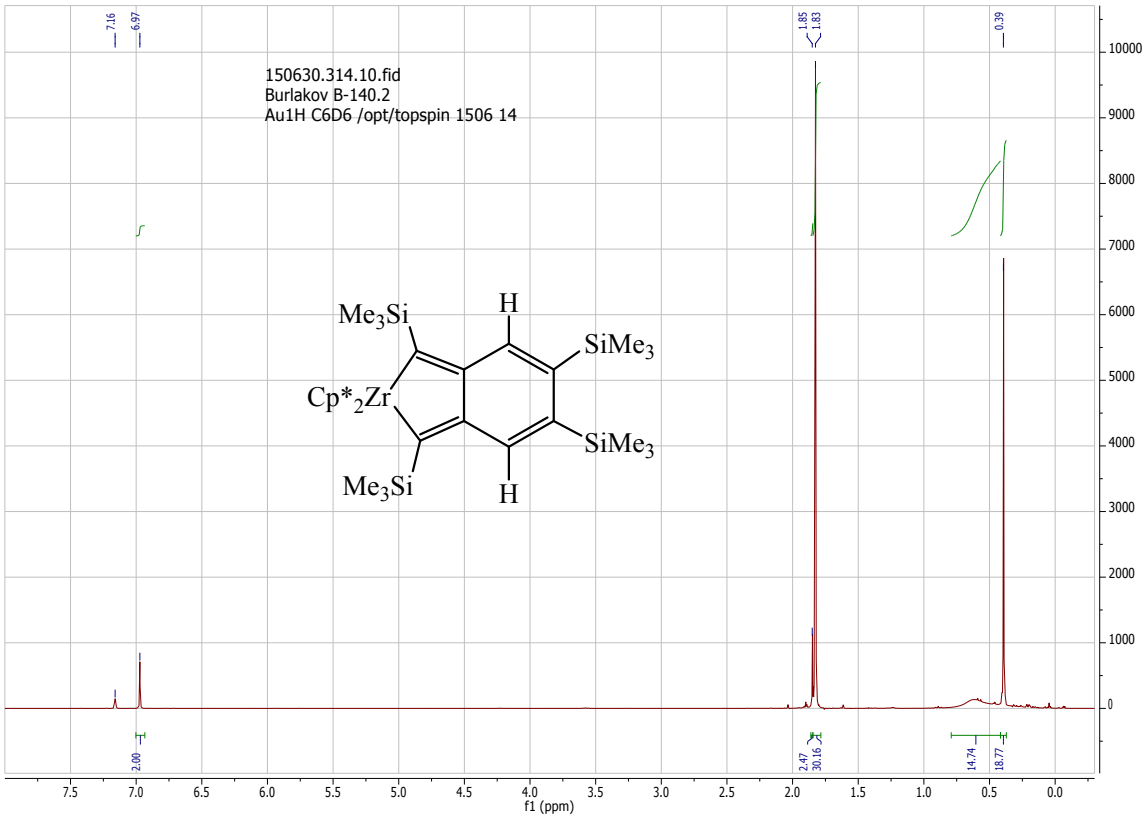


^{13}C NMR, benzene-*d*6



Compound **11**

^{1}H NMR, benzene-*d*6



^{13}C NMR, benzene-*d*6