

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Title: Hydrogenation of titanocene and zirconocene bis(trimethylsilyl)acetylene complexes

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- Cartesian coordinates and energy data for calculated structures **5D-syn** and **5D-anti**.

Table S1 Crystallographic Data, Data Collection and Structure Refinement for **3A** and **2F**

	3A	2F
formula	C ₂₂ H ₃₃ Ti	C ₃₀ H ₄₀ Ti ₂
mol wt	345.38	496.4251
cryst syst	tetragonal	orthorhombic
space group	<i>P4</i> ₁ (No. 76)	<i>Pbcn</i> (No. 60)
<i>a</i> (Å)	15.558(3)	19.4349(5)
<i>b</i> (Å)	15.558(3)	9.0565(2)
<i>c</i> (Å)	31.543(7)	14.4674(4)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
<i>V</i> (Å ³)	7635(3)	2546.44(11)
<i>Z</i>	16	4
<i>D</i> _{calcd} (g cm ⁻³)	1.202	1.295
μ (mm ⁻¹)	0.447	0.642
color	purple	green
cryst size (mm ³)	not recorded	1.03×0.30×0.17
<i>T</i> (K)	150(2)	150(2)
$\vartheta_{\min}$; $\vartheta_{\max}$ (deg)	1.31; 26.00	2.10; 27.50
range of <i>h</i>	−19/11	−25/25
range of <i>k</i>	−12/13	−11/10
range of <i>l</i>	−8/38	−18/18
no. of diffns collected	16673	17676
no. of unique diffns	8956	2927
<i>F</i> (000)	2992	1056
no. of params	866	154
<i>R</i> (<i>F</i>); <i>wR</i> (<i>F</i> ²) all data (%)	13.07; 17.74	3.80; 8.18
GooF (<i>F</i> ²), all data	1.013	1.028
<i>R</i> (<i>F</i>); <i>wR</i> (<i>F</i> ²) [<i>I</i> > 2σ(<i>I</i>)]	7.13; 14.71	2.98; 7.60
$\Delta\rho$ (e Å ⁻³)	0.466; −0.427	0.437; −0.269

^1H and ^{13}C NMR spectra of $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}\{\eta^2\text{-(SiMe}_3\text{)C}\equiv\text{C(SiMe}_3\text{)}\}]$ (1F**)**

^1H NMR (toluene- d_8): 0.22 (s, 18H, SiMe₃); 1.48 (s, 15H, C₅Me₅); 6.18 (s, 5H, C₅H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8): 2.08 (SiMe₃); 12.42 (C₅Me₅); 116.18 (C₅H₅); 122.56 (C₅Me₅); 245.34 ($\equiv\text{C(SiMe}_3\text{)}$).

^1H NMR spectra of hydrogenation products **2A-2D, **2F** and **5D****

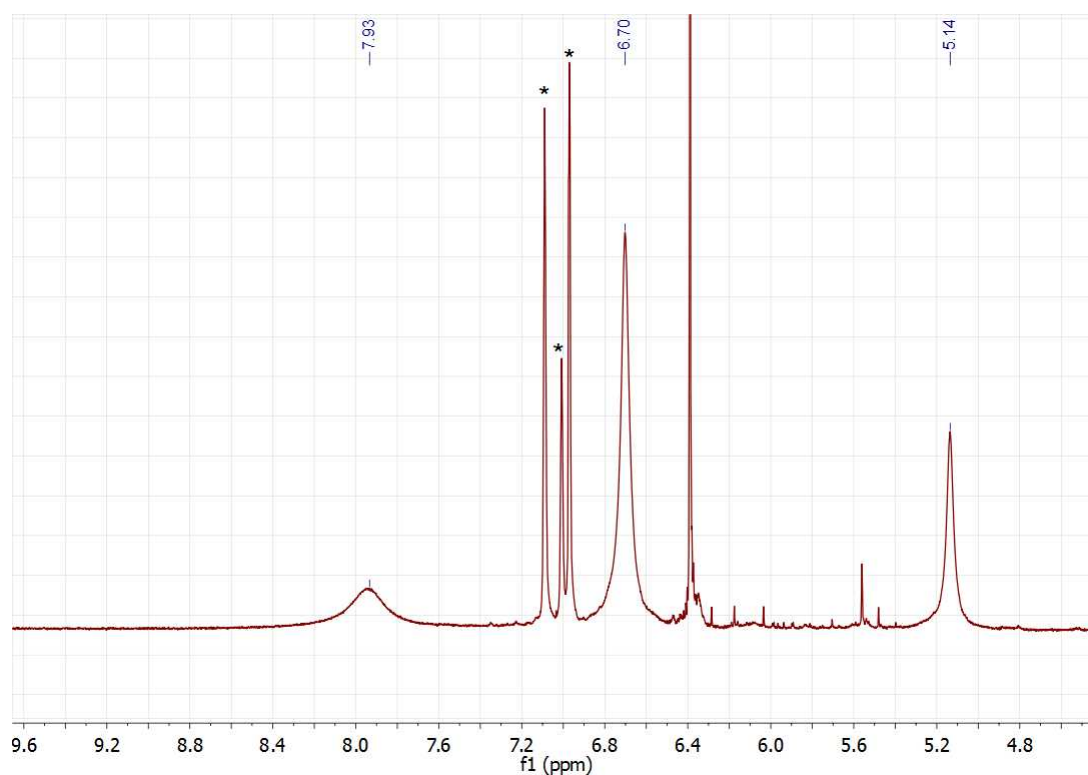


Fig. S1: ^1H NMR spectrum of **2A** in toluene- d_8

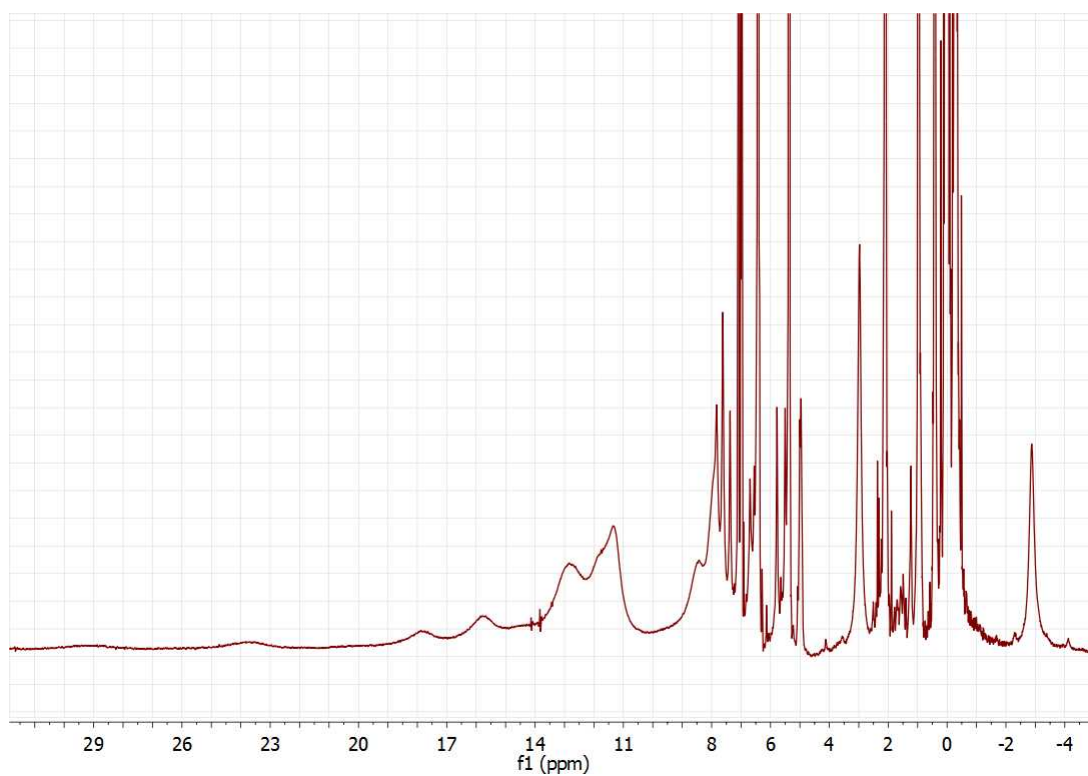


Fig. S2: ^1H NMR spectrum of **2B** in $\text{toluene-}d_8$

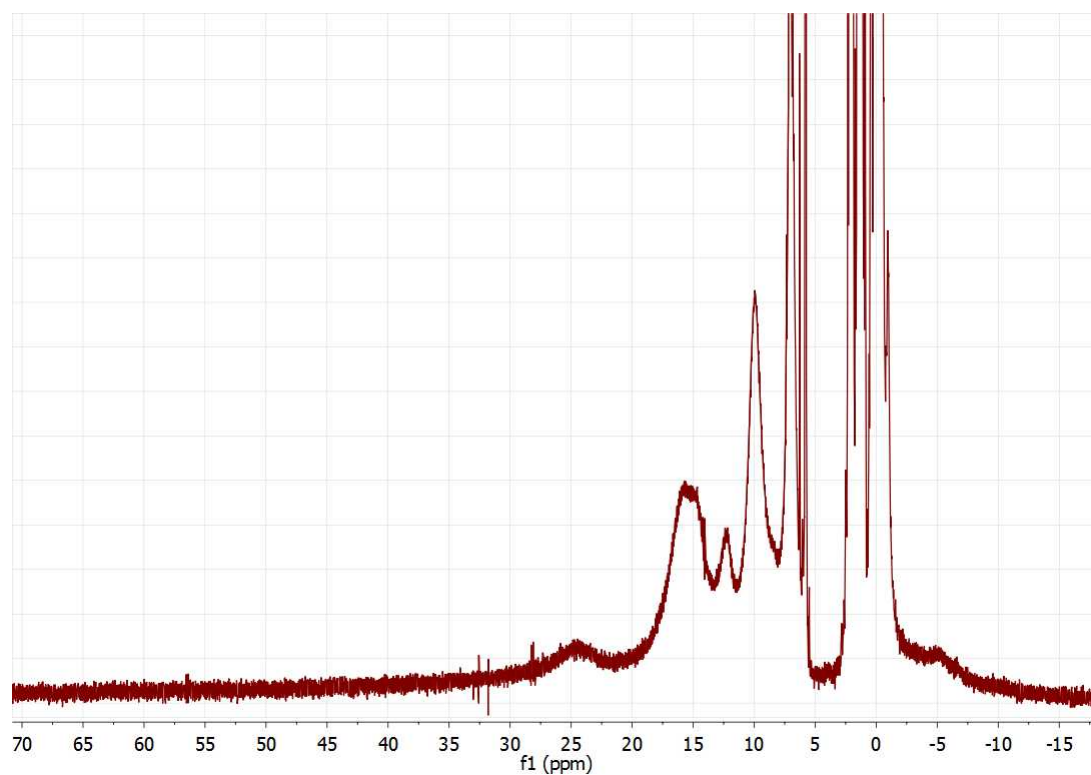


Fig. S3: ^1H NMR spectrum of **2C** in $\text{toluene-}d_8$

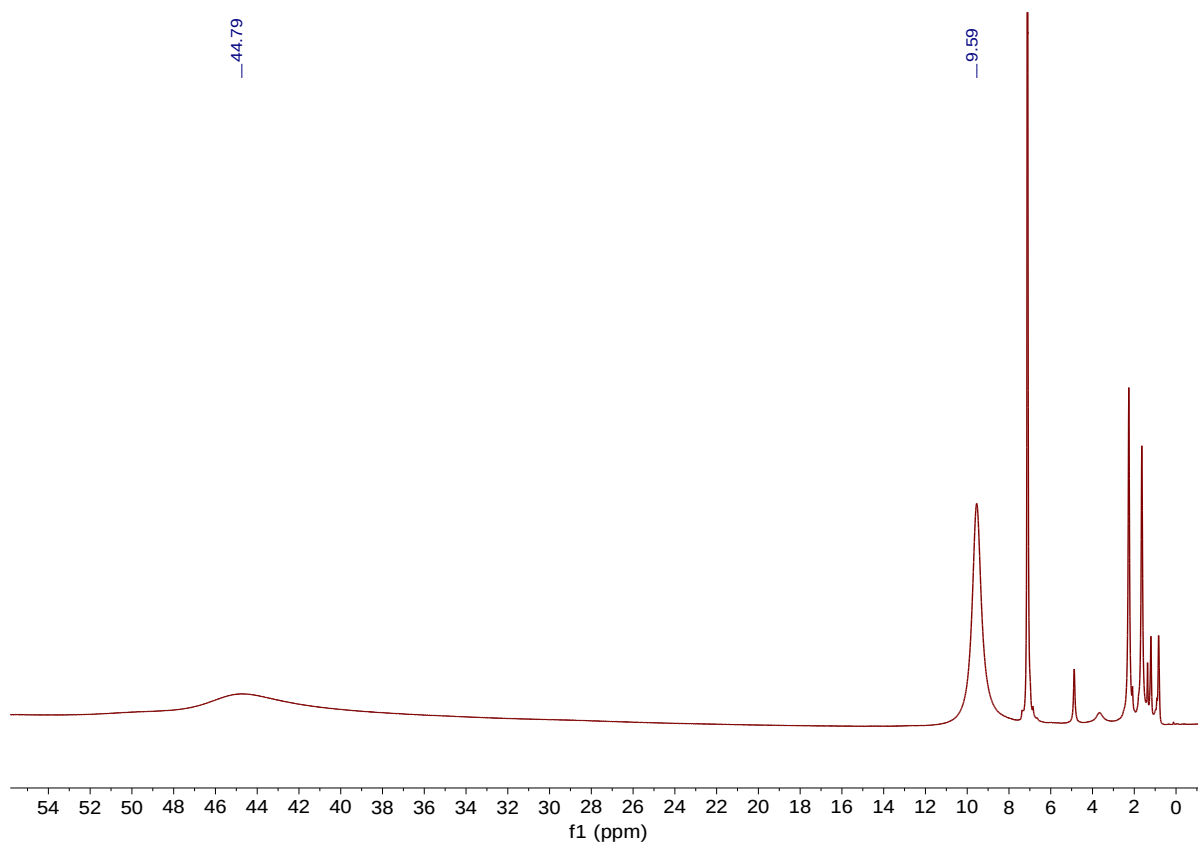


Fig. S4: ¹H NMR spectrum of **2D** in C₆D₆.

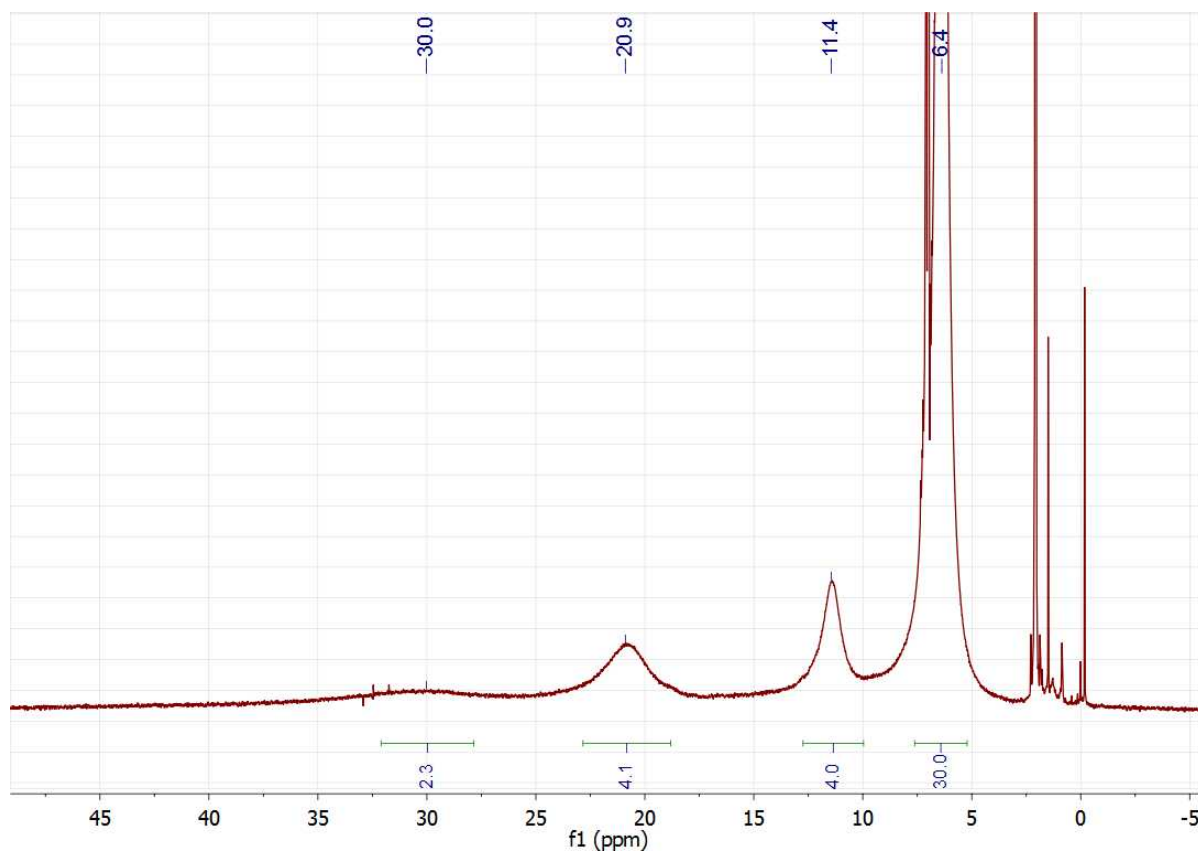


Fig. S5: ¹H NMR spectrum of **2F** in toluene-*d*₈.

$^{13}\text{C}\{^1\text{H}\}$ and ^{13}C NMR spectra of **5D**.

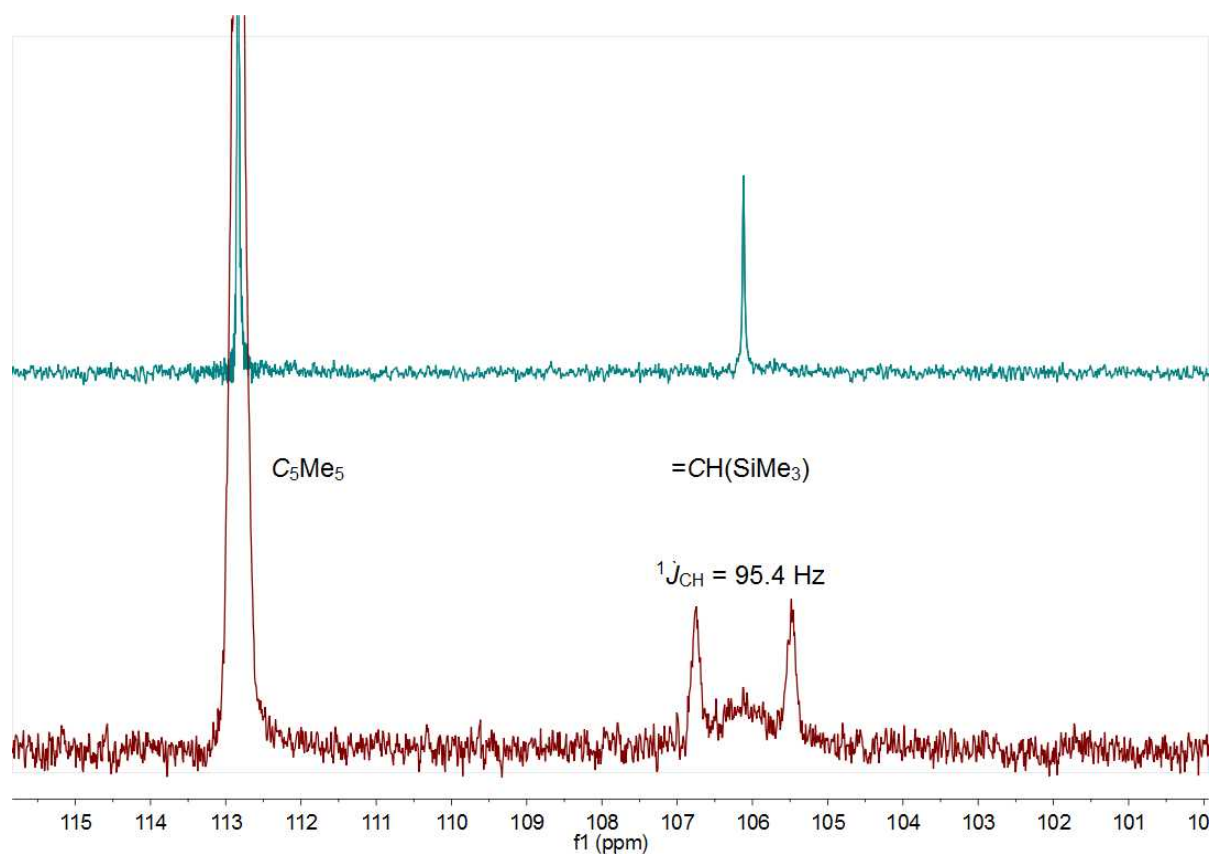
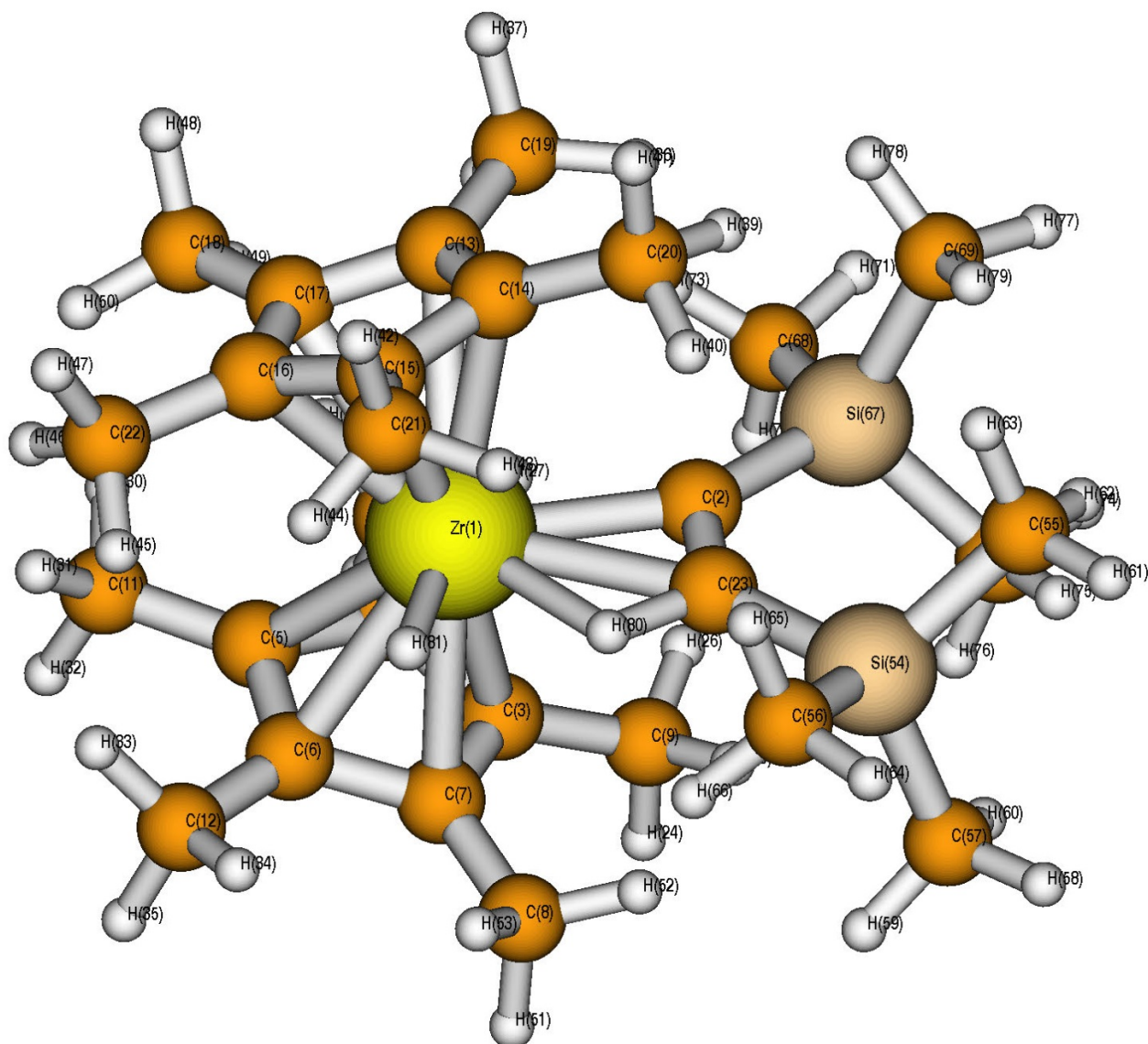


Fig. S6: An expanded region of $^{13}\text{C}\{^1\text{H}\}$ (top) and ^{13}C NMR (bottom) spectra of **5D** measured in toluene- d_8 at -45°C . The coupling constant $^1J_{\text{HH}} = 95.4 \text{ Hz}$ of olefinic proton $=\text{C}_\beta\text{H}$ showed the persistence of β -agostic interaction in solution.

Cartesian coordinates and energy data for calculated structures 5D-syn and 5D-anti.

5D-syn



$E_{\text{TOT}} = -1722.906240$

Zr	0.844276	0.209202	0.159051
C	-1.284654	-0.457165	-0.325037
C	0.520355	1.096306	-2.249231
C	1.659037	0.234235	-2.278861
C	2.701547	0.863893	-1.518738
C	2.188215	2.078632	-0.981334
C	0.833406	2.214218	-1.421807
C	-0.085757	3.365750	-1.126703
C	-0.741608	0.949374	-3.045416
C	1.811293	-1.001805	-3.122447
C	4.152919	0.475137	-1.535688
C	2.976879	3.099095	-0.211568
C	1.156879	-2.176493	1.072053
C	0.464839	-1.460628	2.096736

C	1.334082	-0.448574	2.595314
C	2.577150	-0.544322	1.893546
C	2.471832	-1.622241	0.960346
C	3.592489	-2.264184	0.190899
C	0.692784	-3.420894	0.371703
C	-0.904923	-1.758695	2.632508
C	1.041275	0.467114	3.750998
C	3.794277	0.280321	2.205818
C	-1.639037	0.598132	0.424488
H	-0.692261	1.567215	-3.957493
H	-1.615212	1.273066	-2.467628
H	-0.902377	-0.088238	-3.354121
H	0.854647	-1.520382	-3.248437
H	2.523133	-1.707982	-2.675658
H	2.190671	-0.750019	-4.127229
H	4.287492	-0.581934	-1.784194
H	4.647830	0.674397	-0.577803
H	4.682370	1.064728	-2.302653
H	3.751637	2.623163	0.402495
H	2.325151	3.678434	0.453281
H	3.481272	3.801104	-0.897425
H	-0.397952	-3.453533	0.292744
H	1.016506	-4.322691	0.919077
H	1.109951	-3.487655	-0.641553
H	-1.498557	-2.330399	1.914273
H	-1.454632	-0.834206	2.854095
H	-0.837422	-2.341454	3.566061
H	1.270373	-0.030004	4.709340
H	-0.017173	0.756701	3.770342
H	1.640302	1.382813	3.686623
H	3.547979	1.349905	2.251636
H	4.580092	0.140128	1.454911
H	4.217185	-0.003428	3.183343
H	3.880498	-3.210883	0.676758
H	3.305539	-2.507832	-0.840754
H	4.479193	-1.624338	0.157580
H	-0.017943	4.142686	-1.906499
H	-1.129643	3.029745	-1.085309
H	0.163924	3.827751	-0.163252
Si	-3.243409	1.415667	1.012804
C	-4.544387	0.137613	1.539994
C	-2.771948	2.483542	2.511177
C	-3.958958	2.533708	-0.349286
H	-4.921903	2.961335	-0.028193
H	-3.278678	3.368697	-0.571654
H	-4.127907	1.976825	-1.281030
H	-5.423258	0.653627	1.957285
H	-4.886575	-0.483927	0.702629
H	-4.144980	-0.531556	2.315770
H	-3.630157	3.070545	2.871845
H	-2.413721	1.862107	3.345885
H	-1.965212	3.185715	2.251501
Si	-2.408675	-1.668977	-1.205004
C	-1.479569	-2.722874	-2.490540

C	1.545434	1.855713	1.724557
C	2.629214	0.927948	1.633586
C	2.167690	-0.342416	2.109185
C	0.797334	-0.196119	2.481493
C	-0.052024	-1.253573	3.129613
C	-0.905768	1.772543	2.629415
C	1.635931	3.334598	1.474191
C	4.039415	1.300394	1.267852
C	2.999149	-1.561107	2.399938
C	1.236424	-0.025375	-2.601648
C	0.516571	-1.193144	-2.228499
C	1.359558	-1.982119	-1.374182
C	2.624333	-1.316929	-1.278904
C	2.536631	-0.093497	-2.004842
C	3.645174	0.895012	-2.234362
C	0.770305	1.042523	-3.547660
C	-0.846481	-1.585042	-2.721387
C	1.042297	-3.351974	-0.835081
C	3.883249	-1.927987	-0.734495
C	-1.584426	-0.669349	0.220514
H	-0.905144	2.080676	3.688434
H	-1.727001	1.061617	2.483205
H	-1.118061	2.660668	2.022798
H	0.677291	3.737309	1.129232
H	2.389120	3.559315	0.709470
H	1.919643	3.866547	2.398804
H	4.065327	1.978646	0.405540
H	4.643850	0.418370	1.027280
H	4.532778	1.817771	2.107207
H	3.989475	-1.491341	1.940150
H	2.522563	-2.485353	2.043135
H	3.140836	-1.668992	3.487659
H	-0.318532	1.155908	-3.508180
H	1.044681	0.791185	-4.586439
H	1.222627	2.009131	-3.297153
H	-1.474072	-0.705199	-2.901692
H	-1.367576	-2.216029	-1.991056
H	-0.768280	-2.154227	-3.662634
H	1.362431	-4.142231	-1.534776
H	-0.035378	-3.474642	-0.670569
H	1.552367	-3.535169	0.120838
H	3.673028	-2.671403	0.041006
H	4.564971	-1.176775	-0.319784
H	4.422144	-2.442601	-1.547342
H	4.094546	0.758833	-3.232088
H	3.269587	1.925761	-2.175902
H	4.442875	0.778769	-1.491713
H	0.047750	-1.219980	4.227438
H	-1.111834	-1.106081	2.891265
H	0.239077	-2.260927	2.802262
Si	-3.136580	-1.682749	0.609251
C	-4.376019	-1.540215	-0.820401
C	-2.609195	-3.497424	0.812959
C	-3.949983	-1.086610	2.220814

H	-4.900434	-1.618343	2.385551
H	-3.306289	-1.275891	3.092066
H	-4.165249	-0.010464	2.184507
H	-5.267434	-2.153423	-0.616203
H	-4.706507	-0.504273	-0.970836
H	-3.928891	-1.890035	-1.761897
H	-3.461109	-4.122949	1.120039
H	-2.215372	-3.910753	-0.127697
H	-1.825687	-3.598971	1.578954
Si	-2.511084	1.933734	-0.778567
C	-1.577759	3.585485	-0.790078
C	-3.156122	1.608324	-2.545224
C	-4.021024	2.132430	0.373714
H	-2.151625	4.356689	-1.327511
H	-1.396200	3.953835	0.230383
H	-0.598899	3.457693	-1.272608
H	-4.611105	3.012801	0.072847
H	-4.687511	1.259535	0.348545
H	-3.702716	2.282828	1.415543
H	-3.906693	2.369194	-2.812066
H	-2.349710	1.666511	-3.289600
H	-3.627717	0.619991	-2.631878