molecules

MDPI

Supporting Information

Ti group metallocene-catalyzed synthesis of 1-hexene dimers and tetramers

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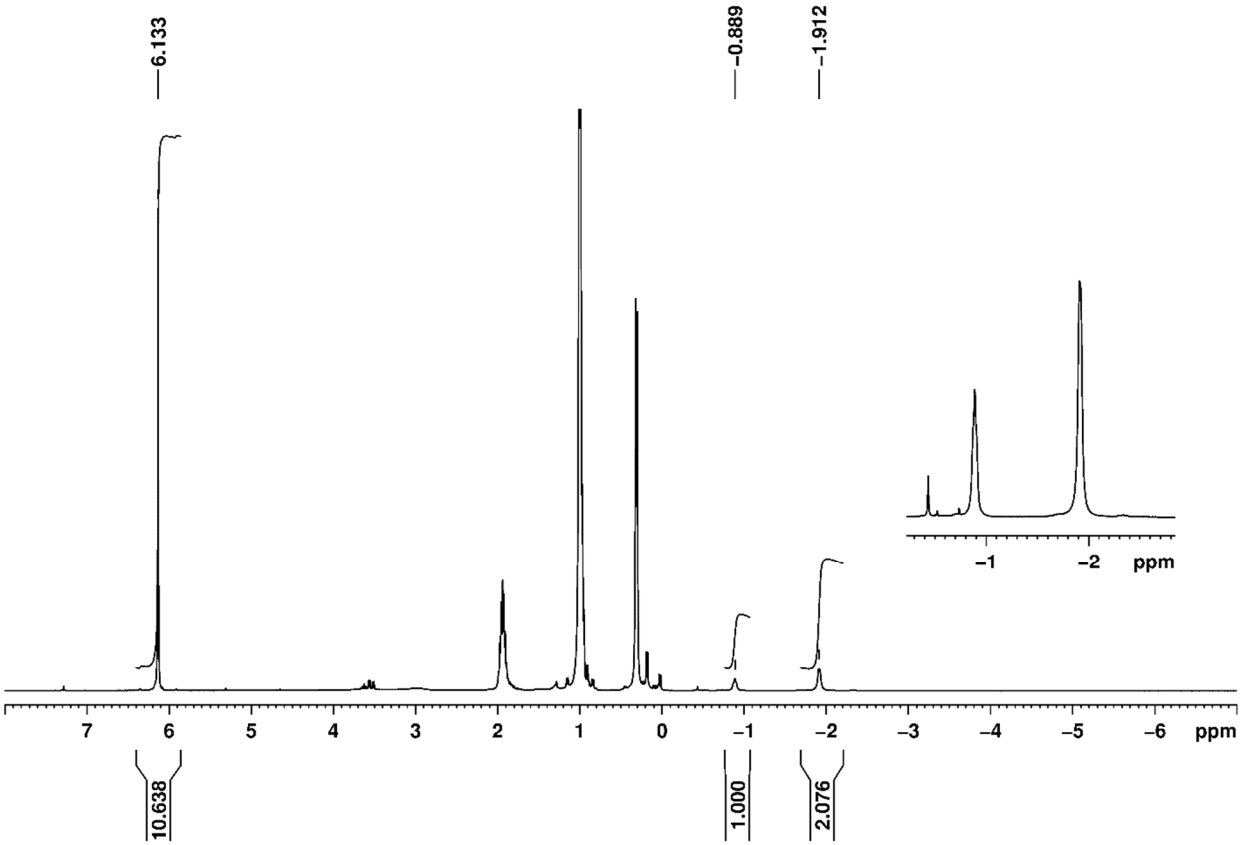


Figure S2. ^{13}C NMR of system Cp_2ZrCl_2−$HAlBu^{i}_2$ (1:4) in $CDCl_3$ (T= 299 K).

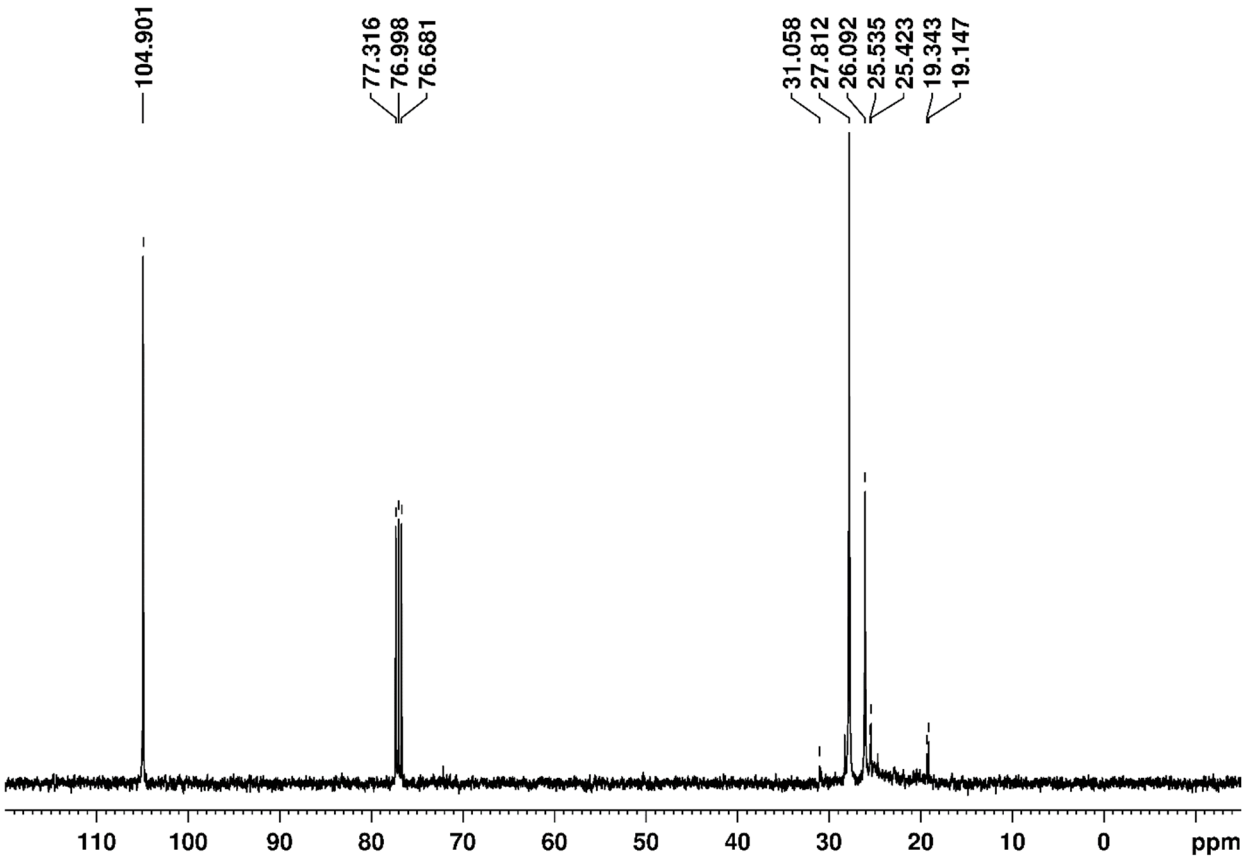
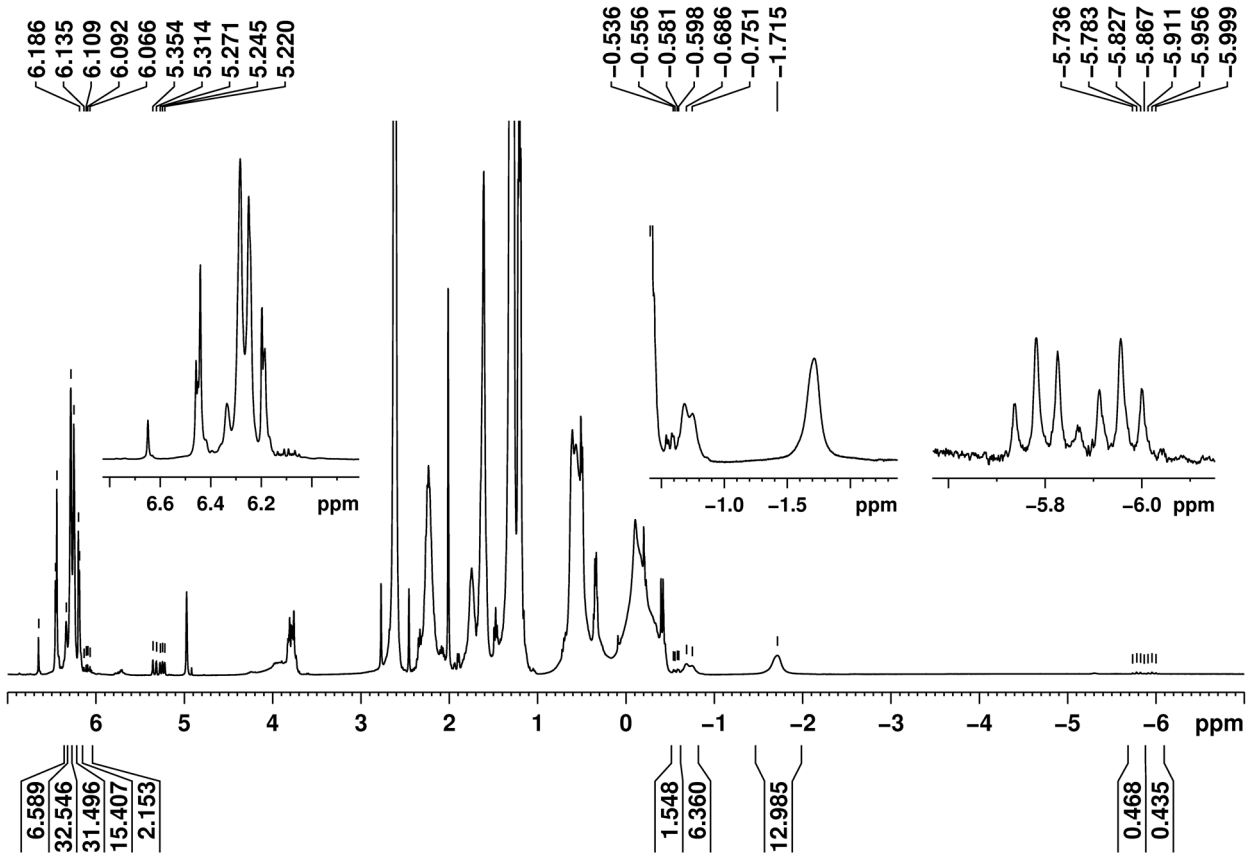


Figure S3. ^{1}H NMR of system Cp_2ZrCl_2−$HAlBu^{i}_2$–MMAO-12– 1-hexene (1:4:8:0.1) in $CDCl_3$ (T= 299 K).



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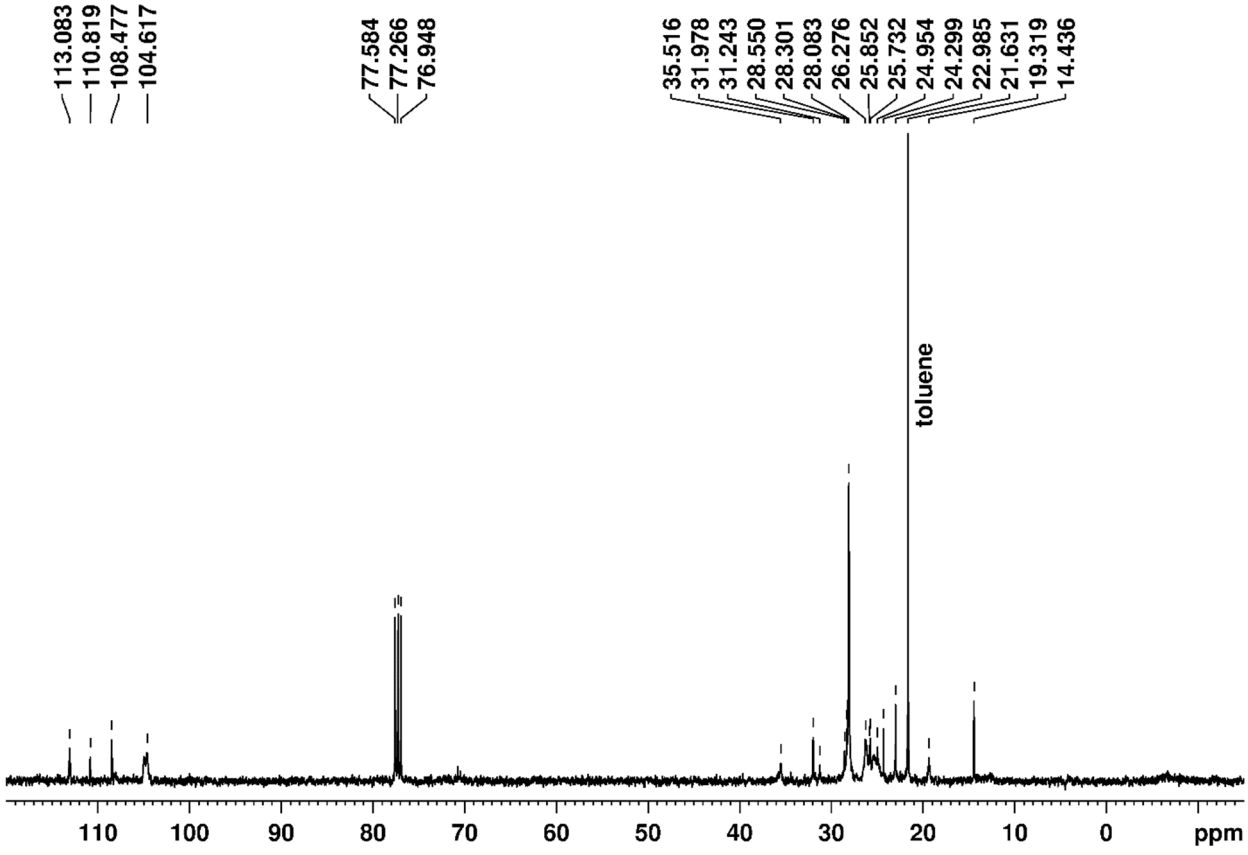
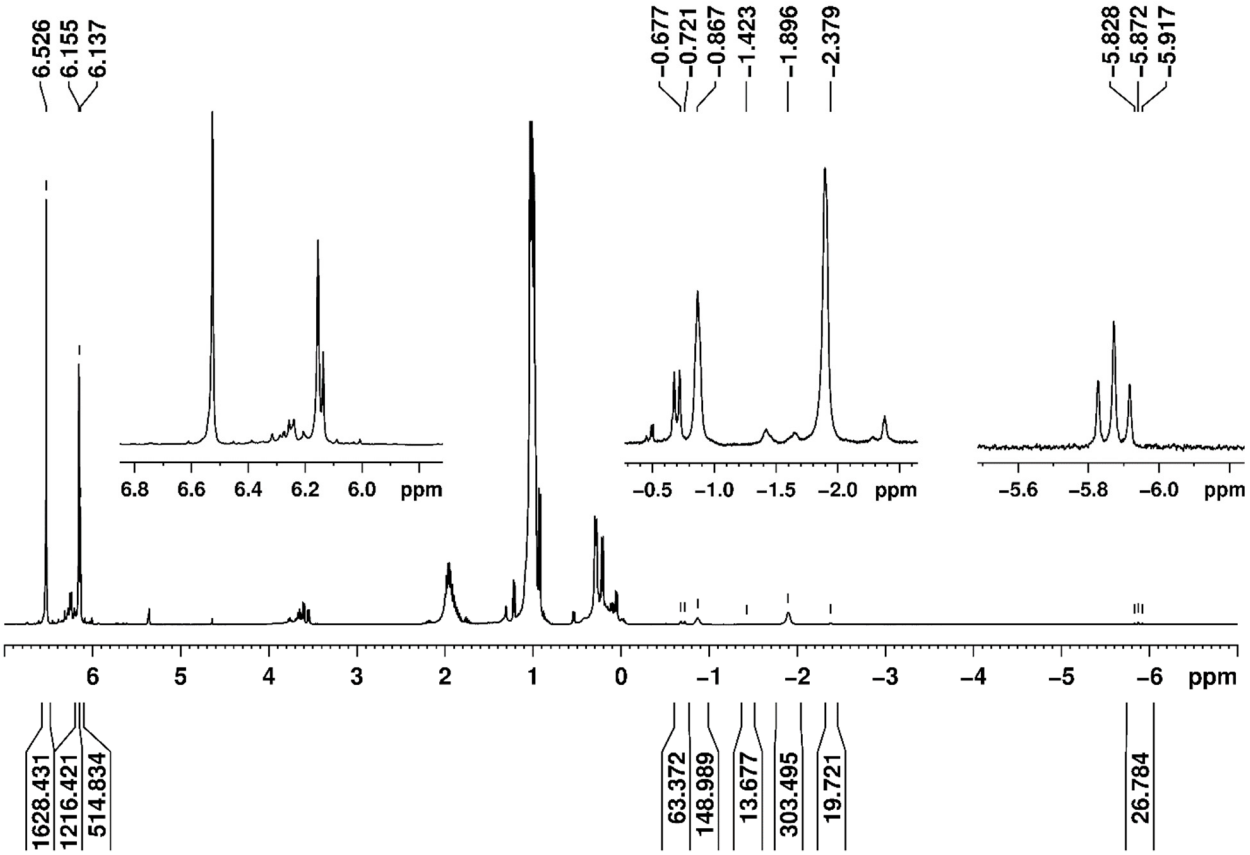


Figure S5. ^{1}H NMR of system Cp_2ZrCl_2−$HAlBu^{i}_2$ (1:2) in CD_2Cl_2 (T= 298.6 K).



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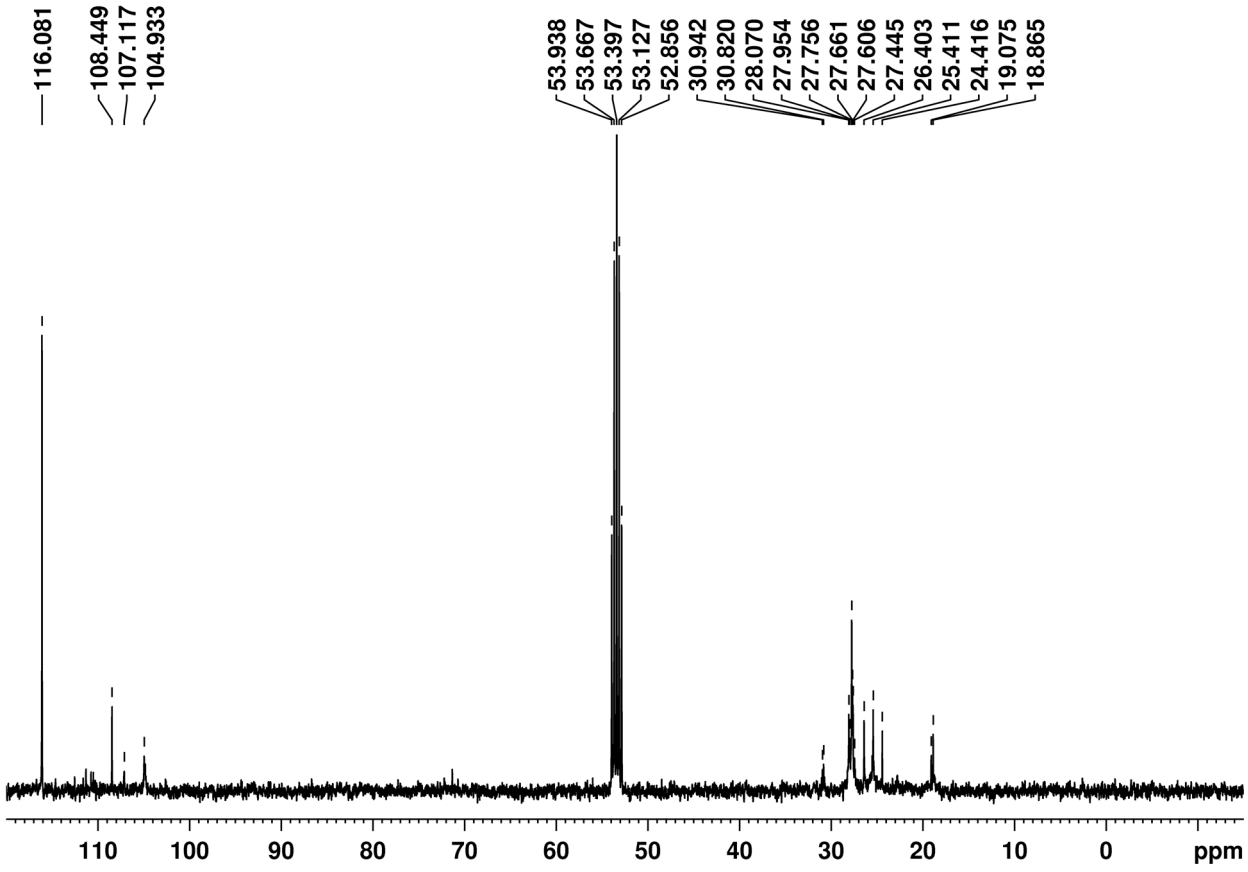


Figure S7. ^{1}H NMR of system Cp_2ZrCl_2−$HAlBu^{i}_2$–MMAO-12 (1:2:5) in CD_2Cl_2 (T= 298.6 K).

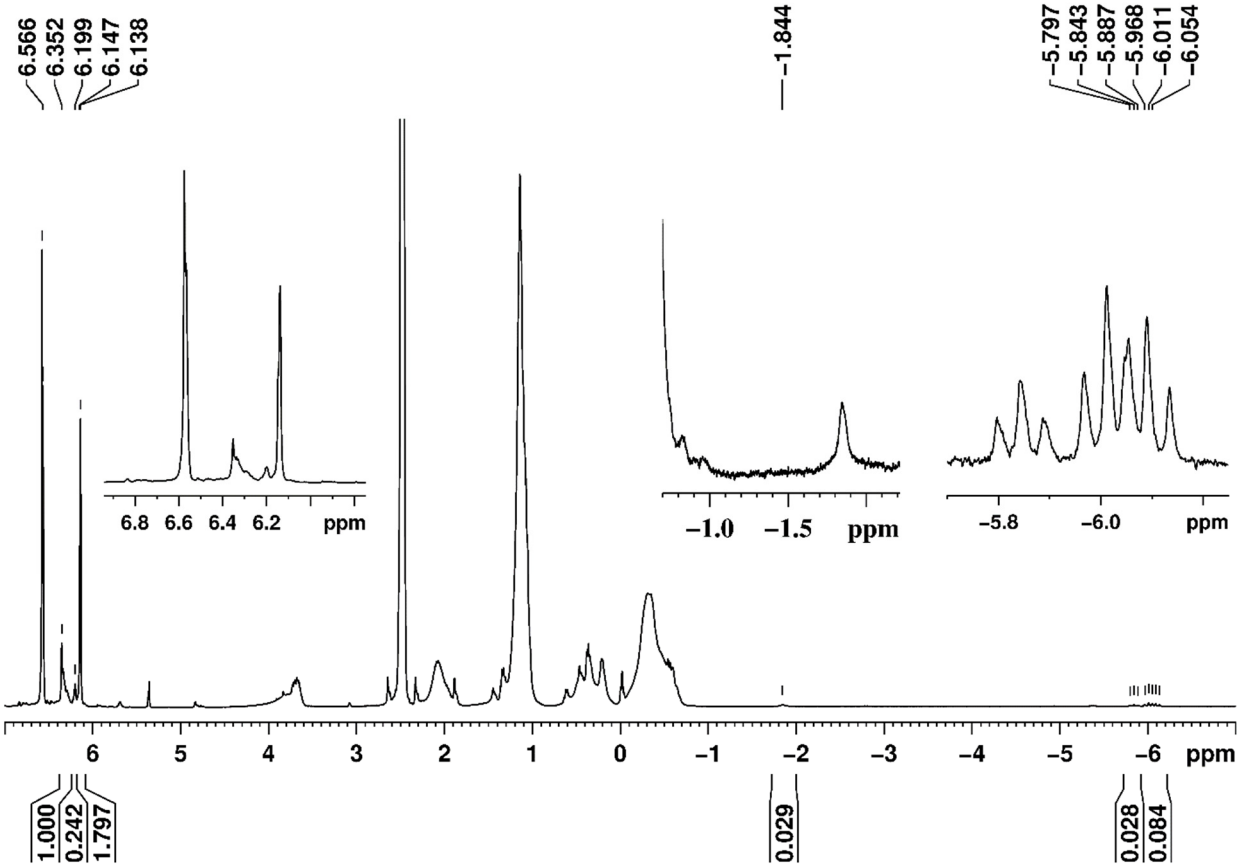
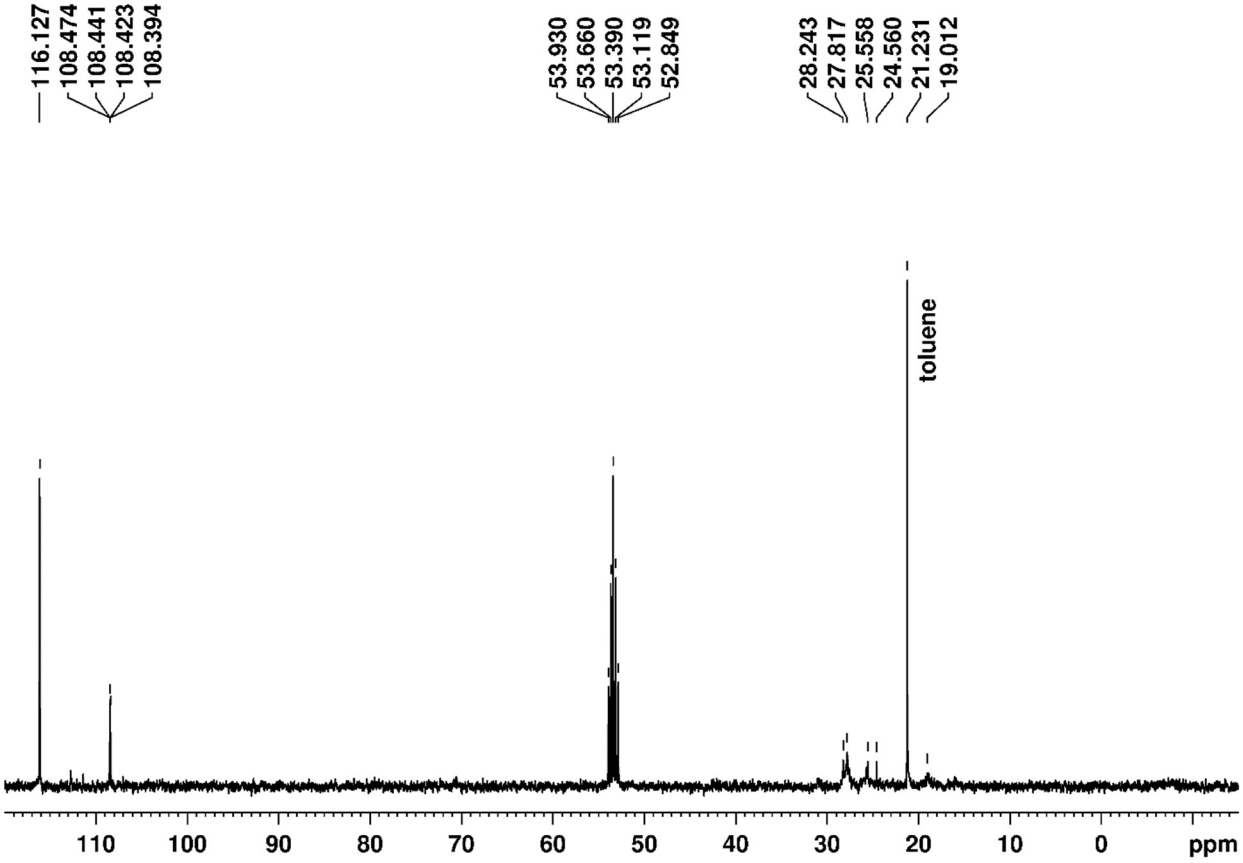


Figure S8. ^{13}C NMR of system Cp_2ZrCl_2−$HAlBu^i_2$–MMAO-12 (1:2:5) in CD_2Cl_2 (T= 299.3 K).



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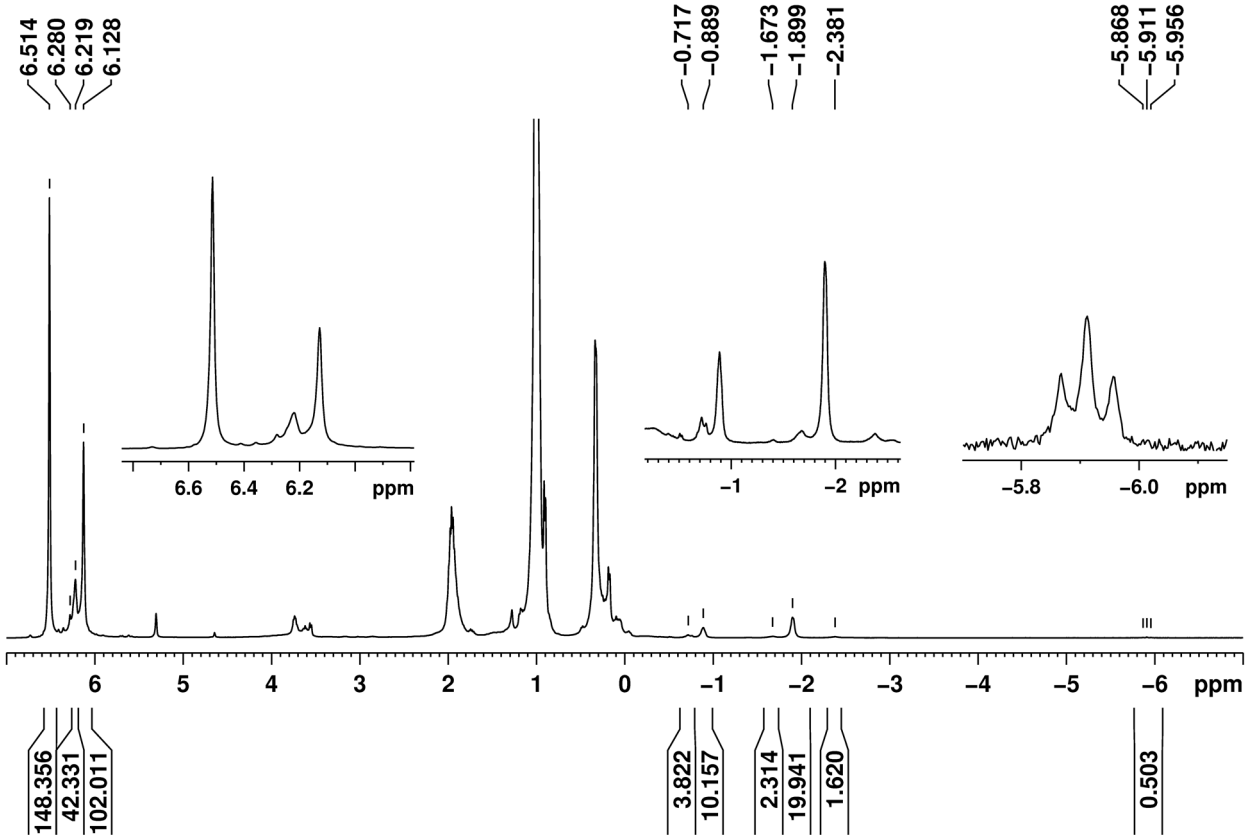

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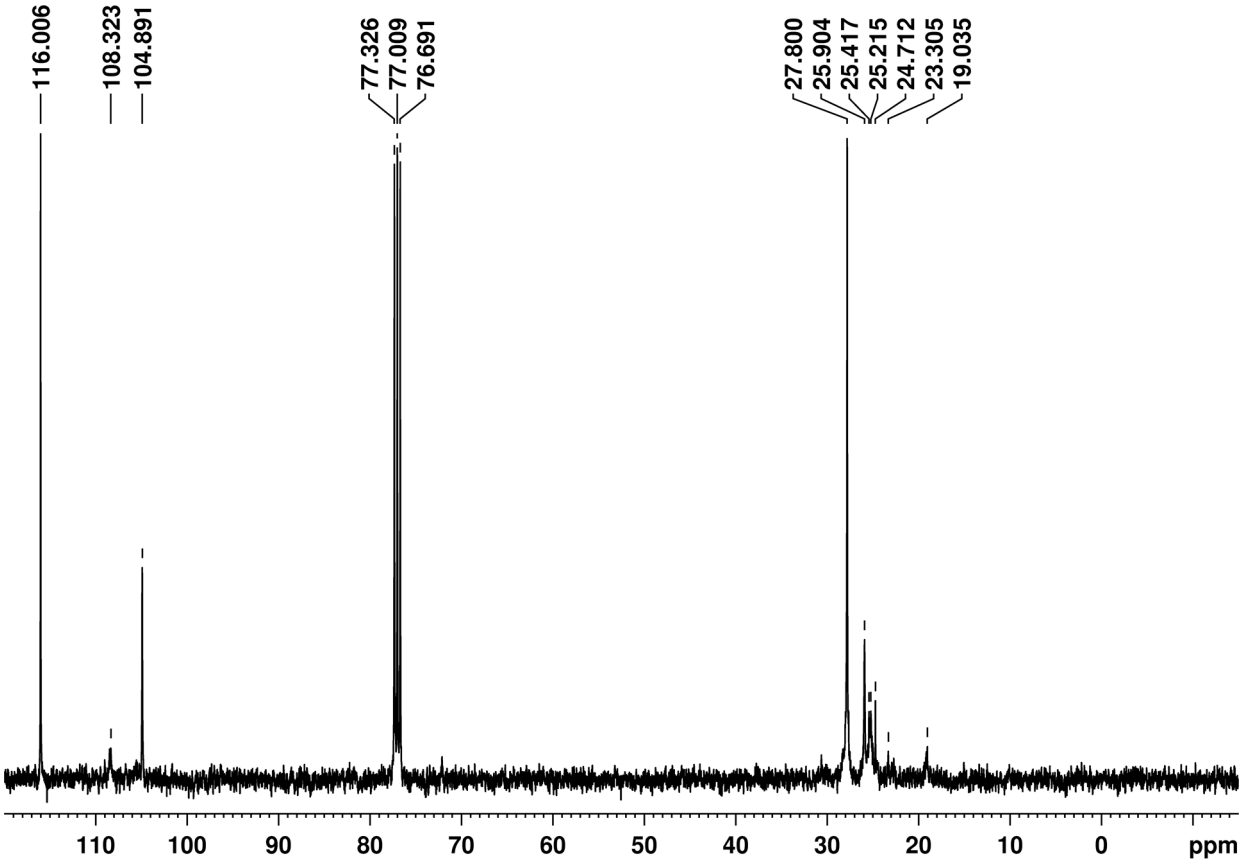

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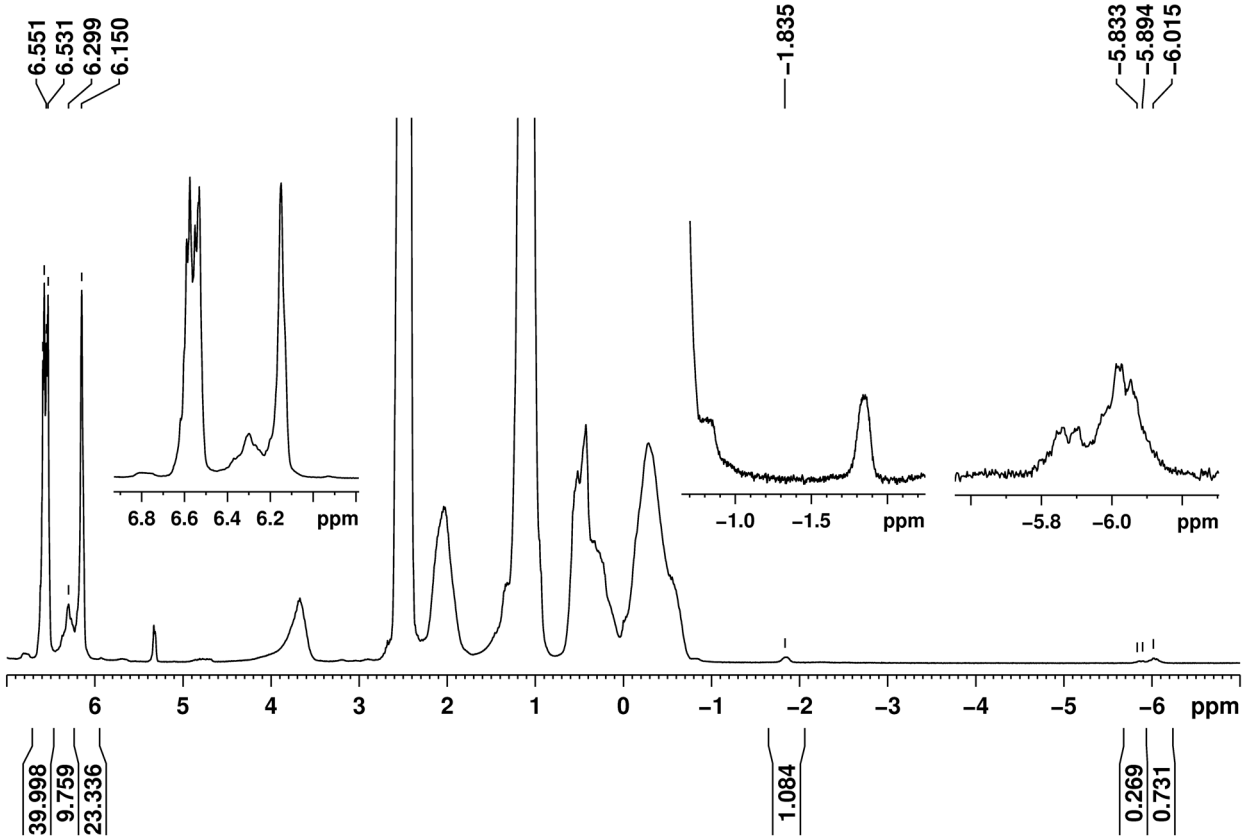

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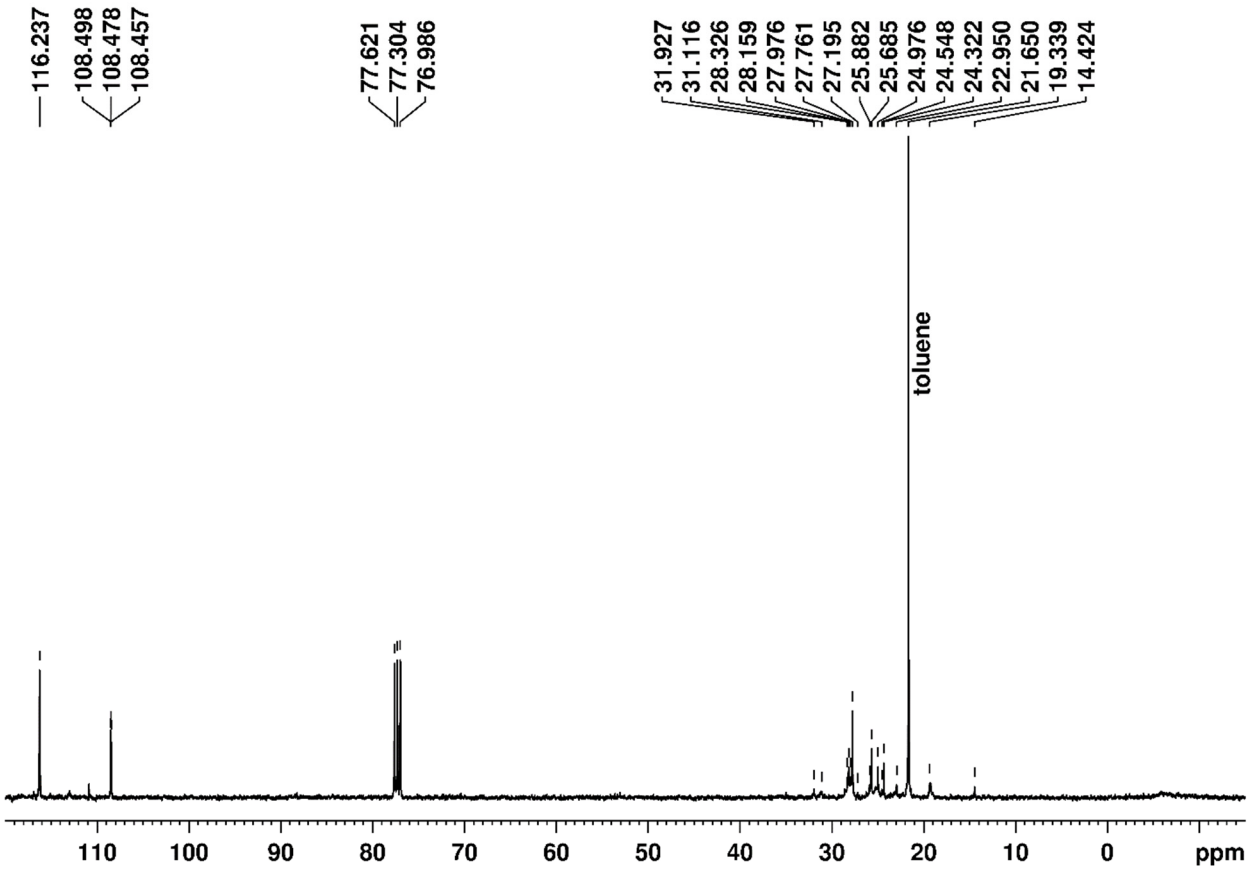

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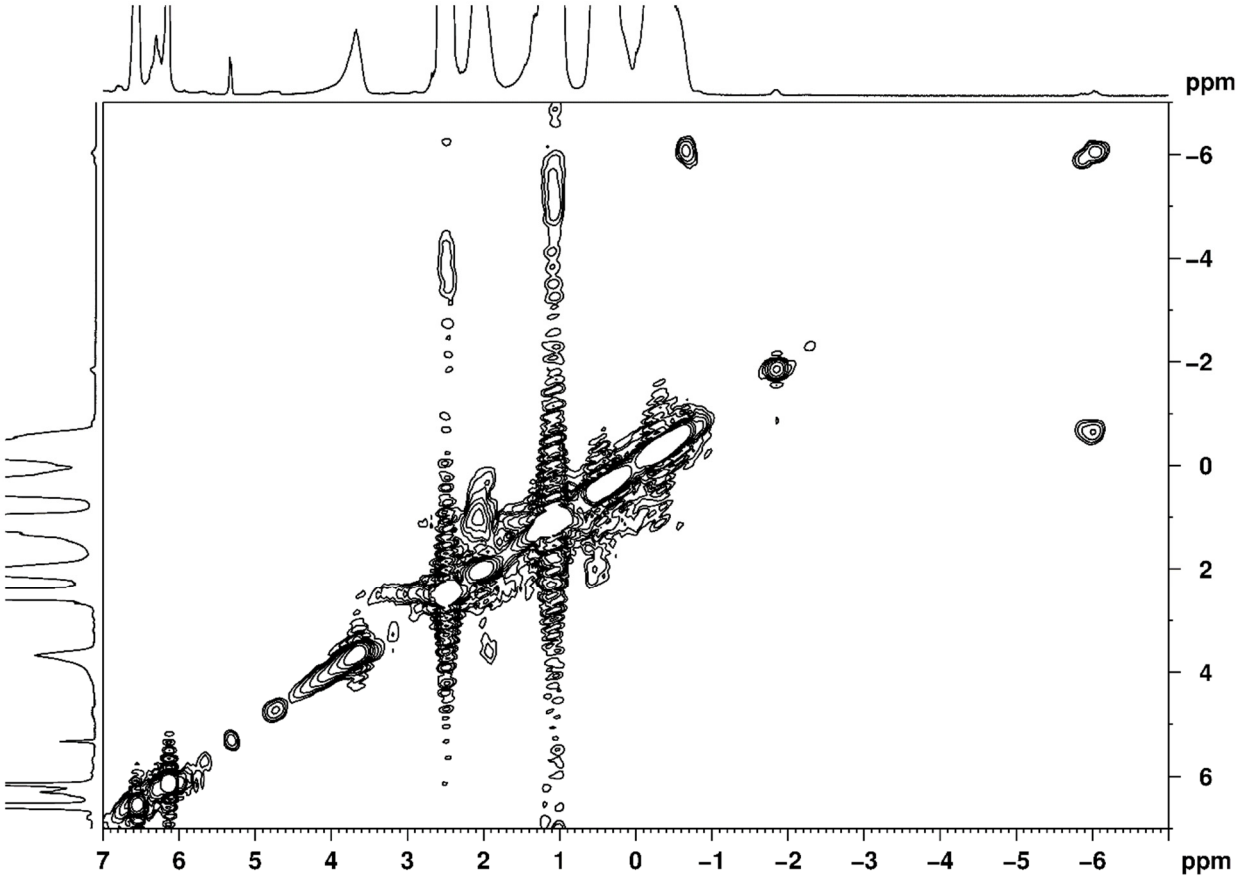

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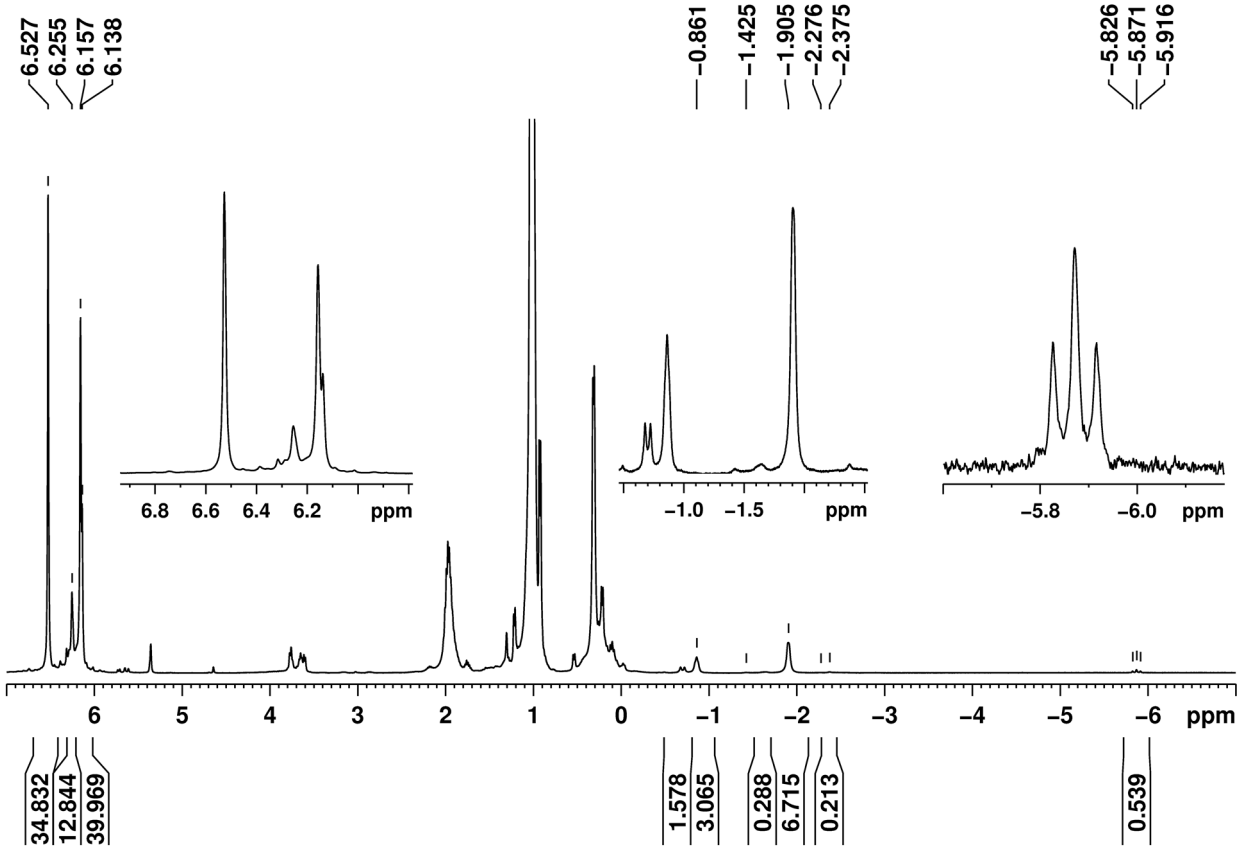

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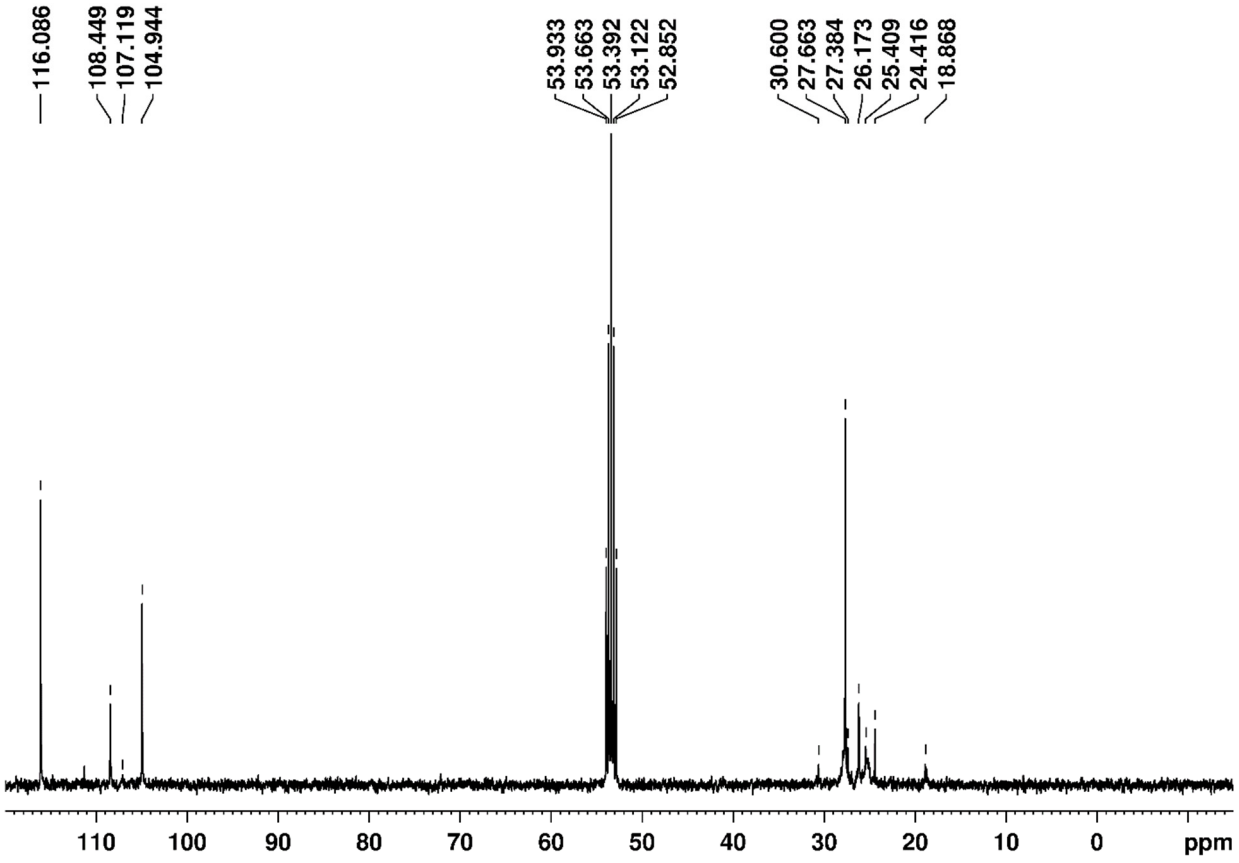

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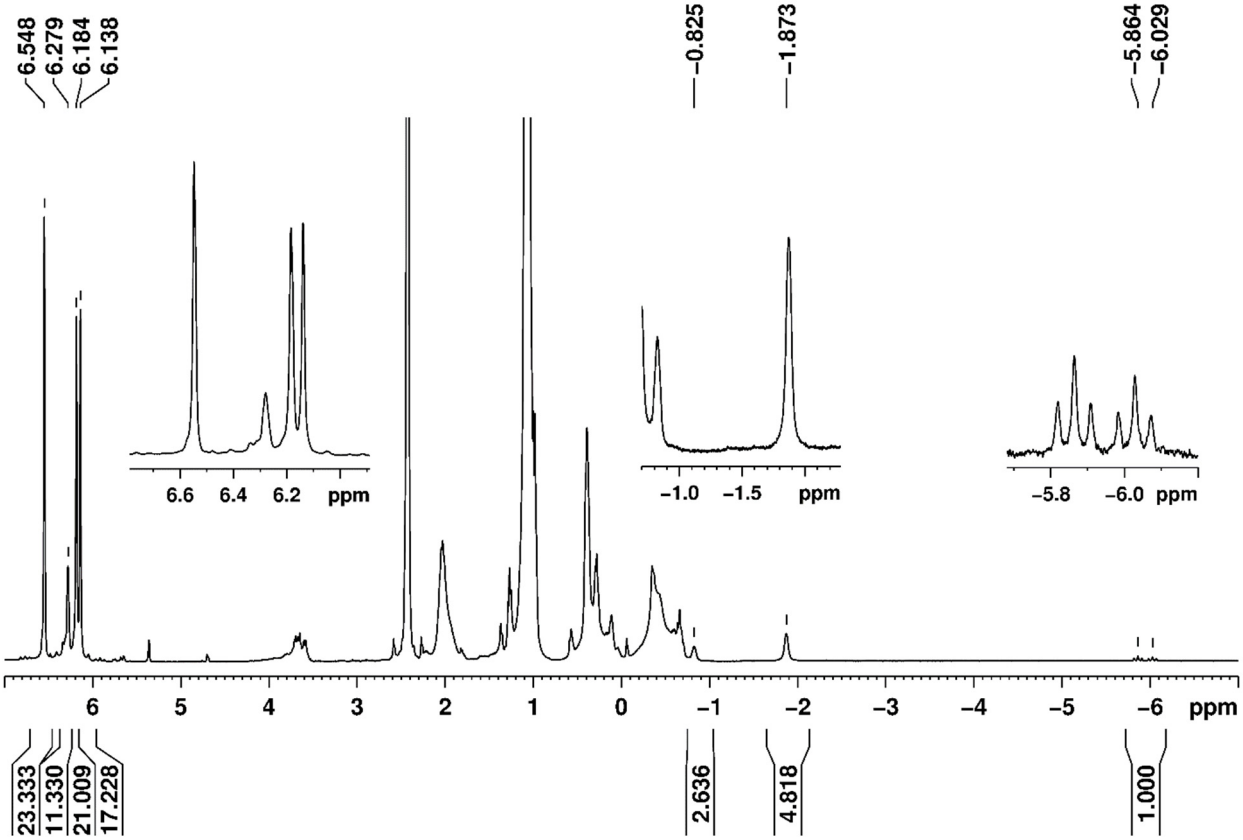

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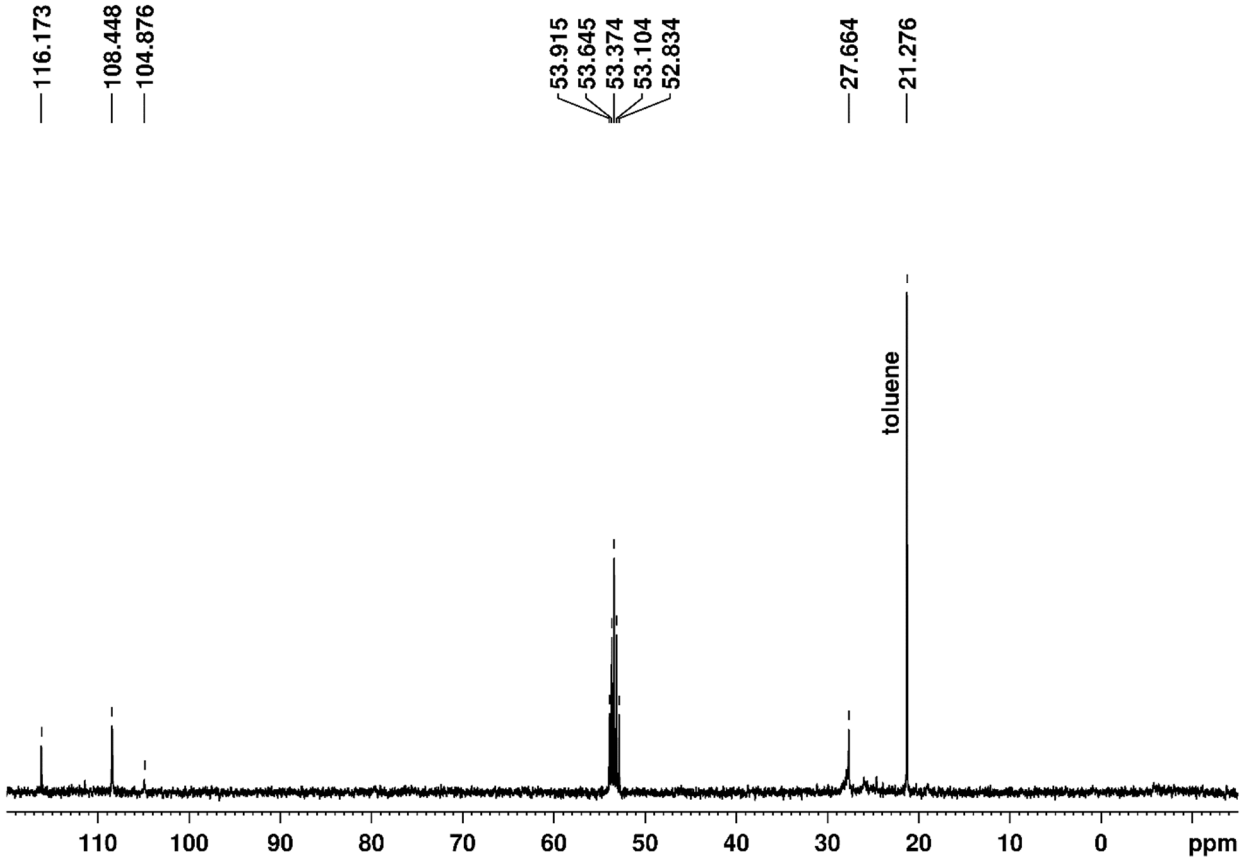
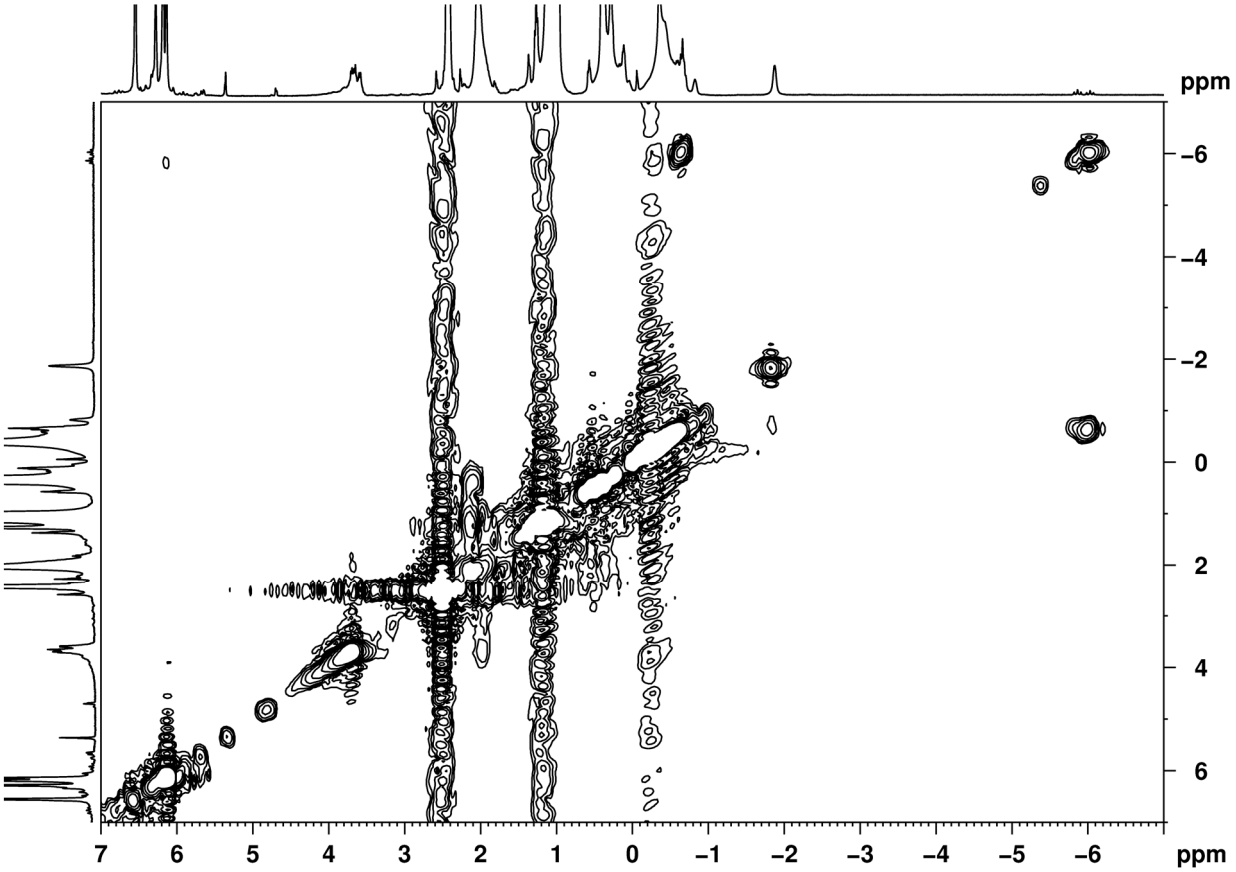


Figure S18. COSY HH NMR of system $[Cp_2ZrH_2]_2$−$ClAlBu^i_2$–MMAO-12 (1:2:5) in CD_2Cl_2 (T= 298.7 K).



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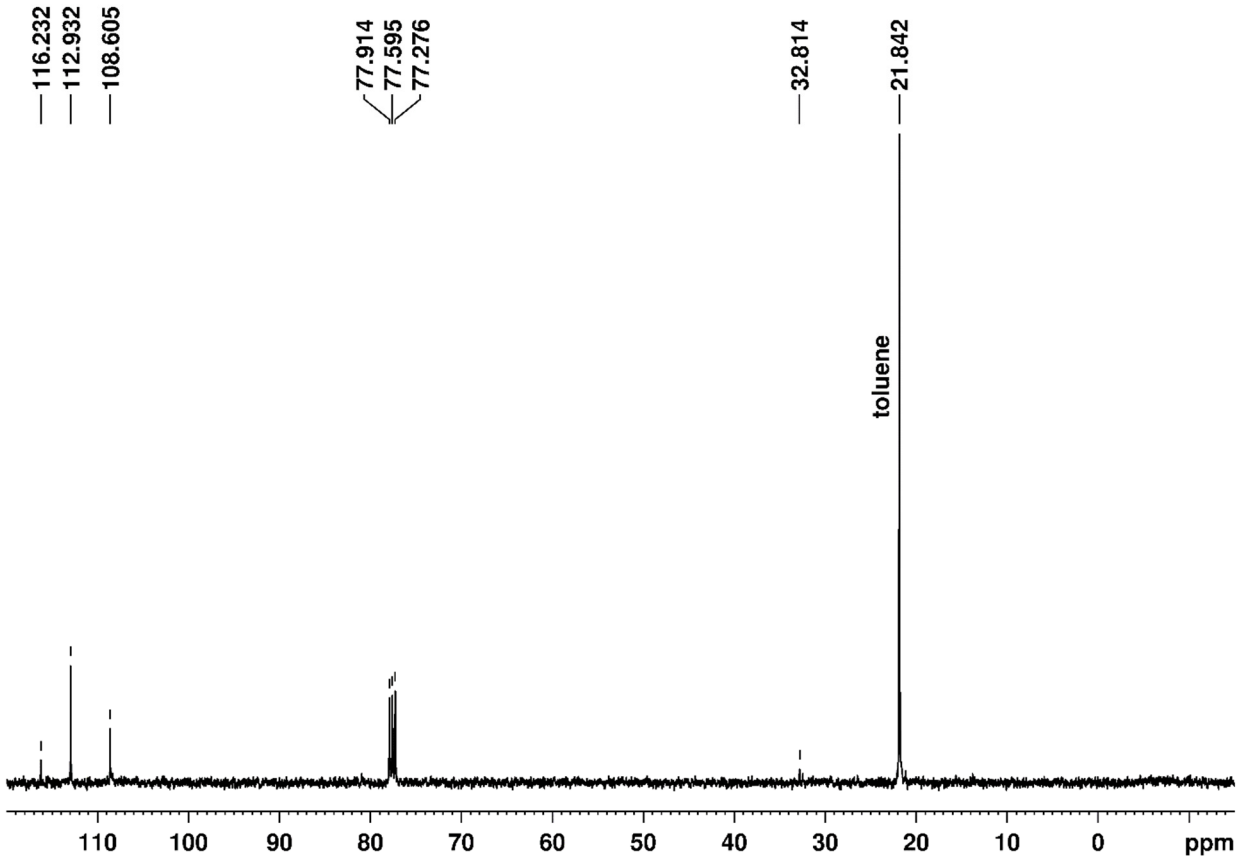

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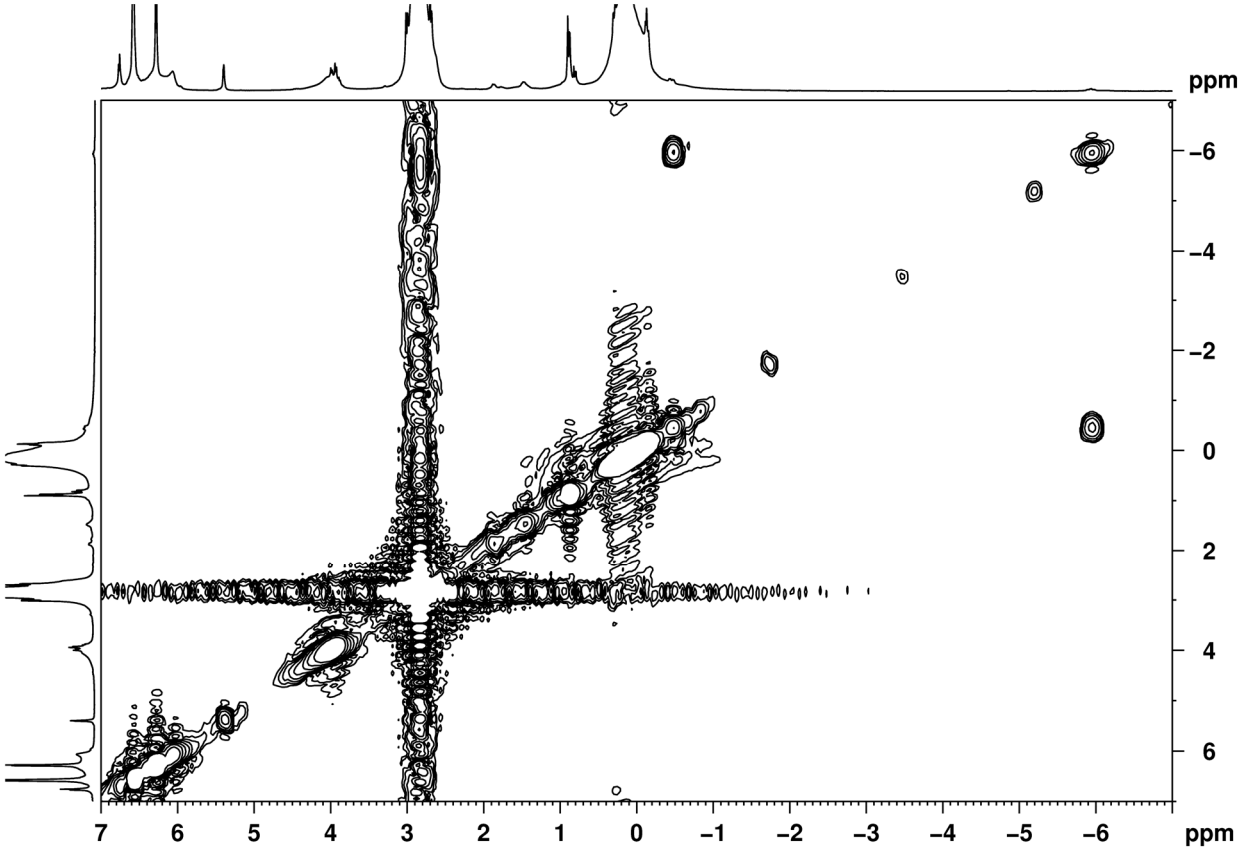

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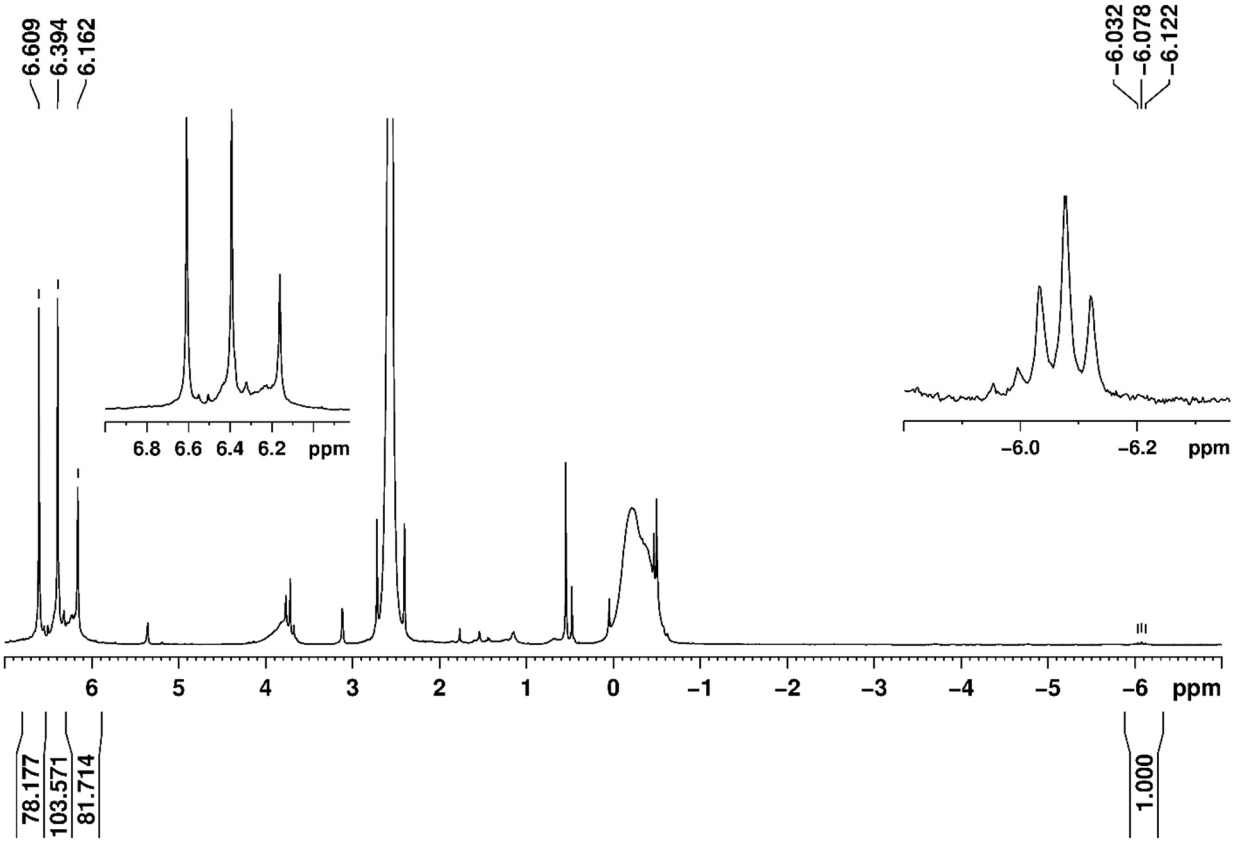


Figure S22. ^{13}C NMR of system $[Cp_2ZrH_2]_2$ – MMAO-12 (1:7) in CD_2Cl_2 (T= 296.6 K).

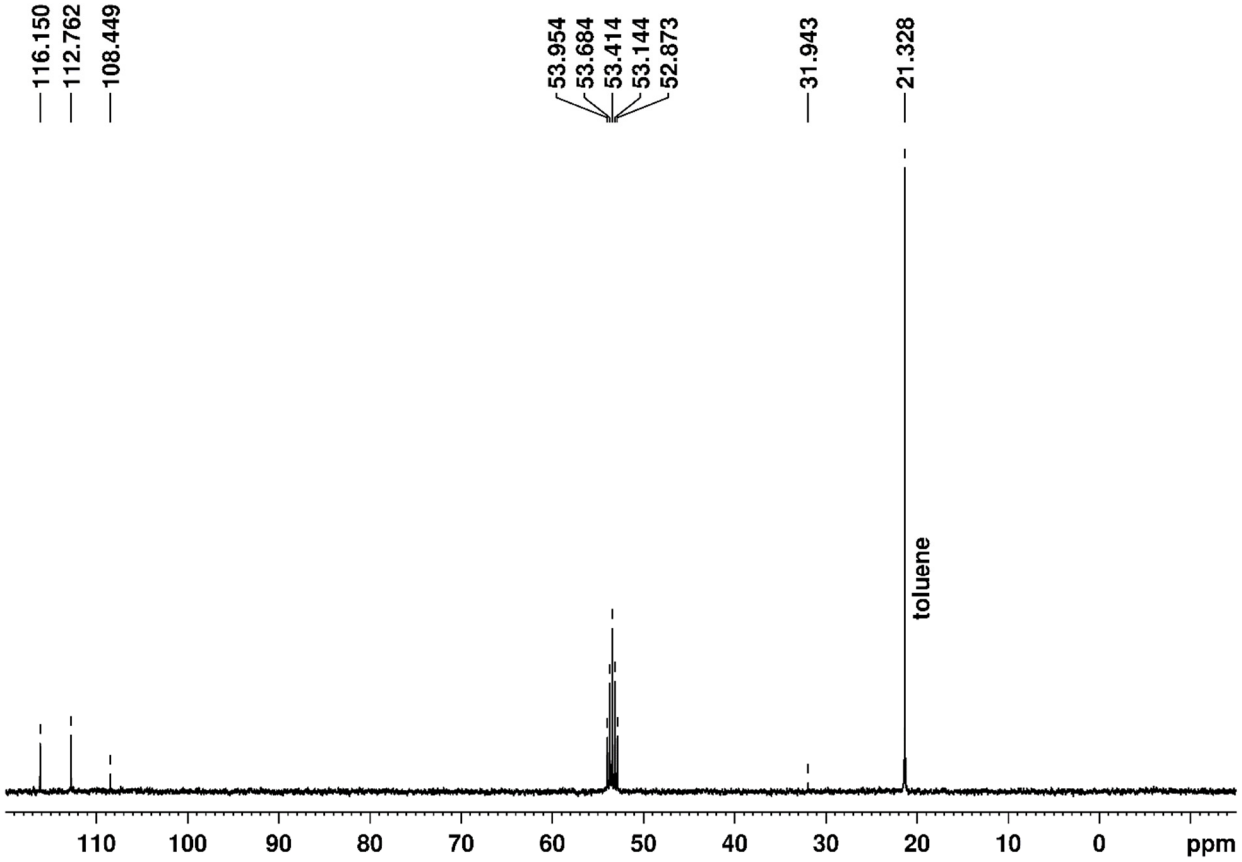
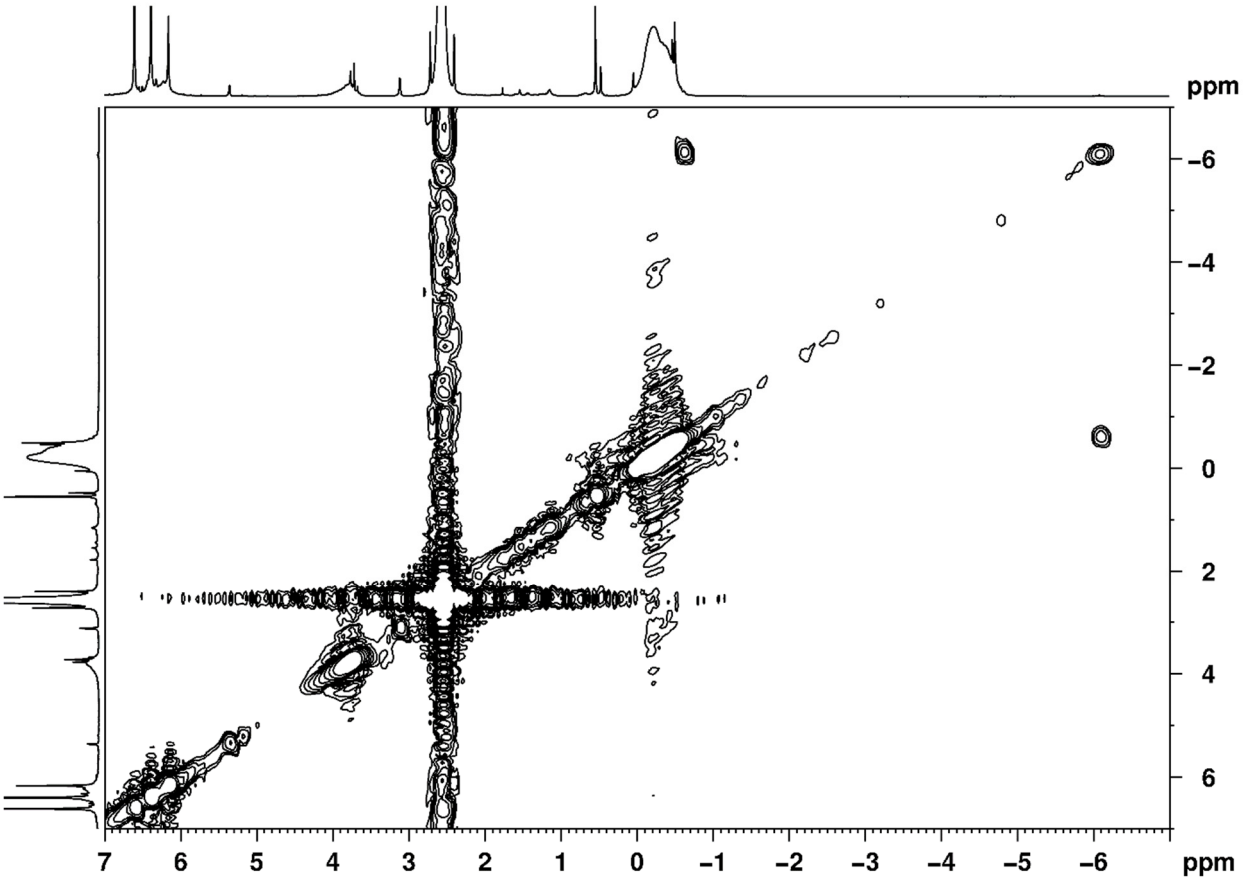


Figure S23. COSY HH of system $[Cp_2ZrH_2]_2$ – MMAO-12 (1:7) in CD_2Cl_2 (T= 296 K)



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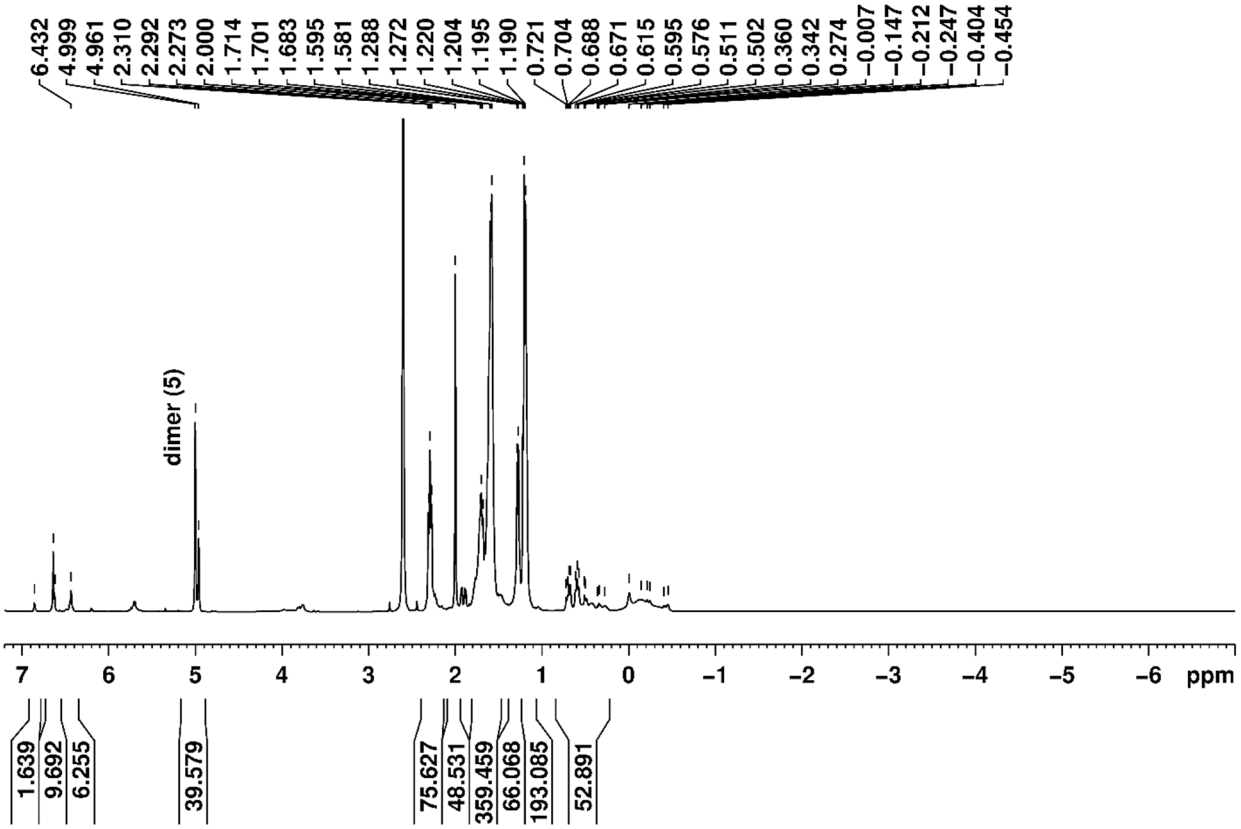

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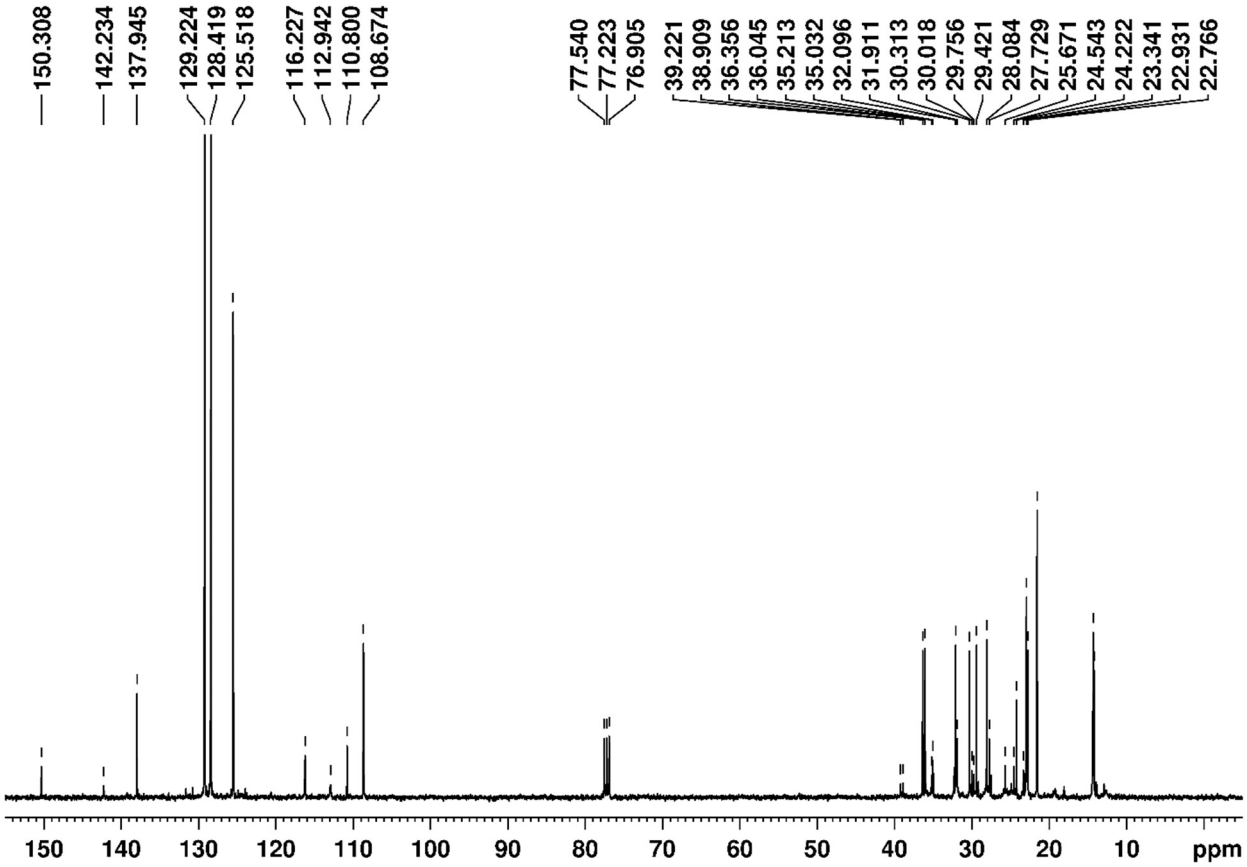

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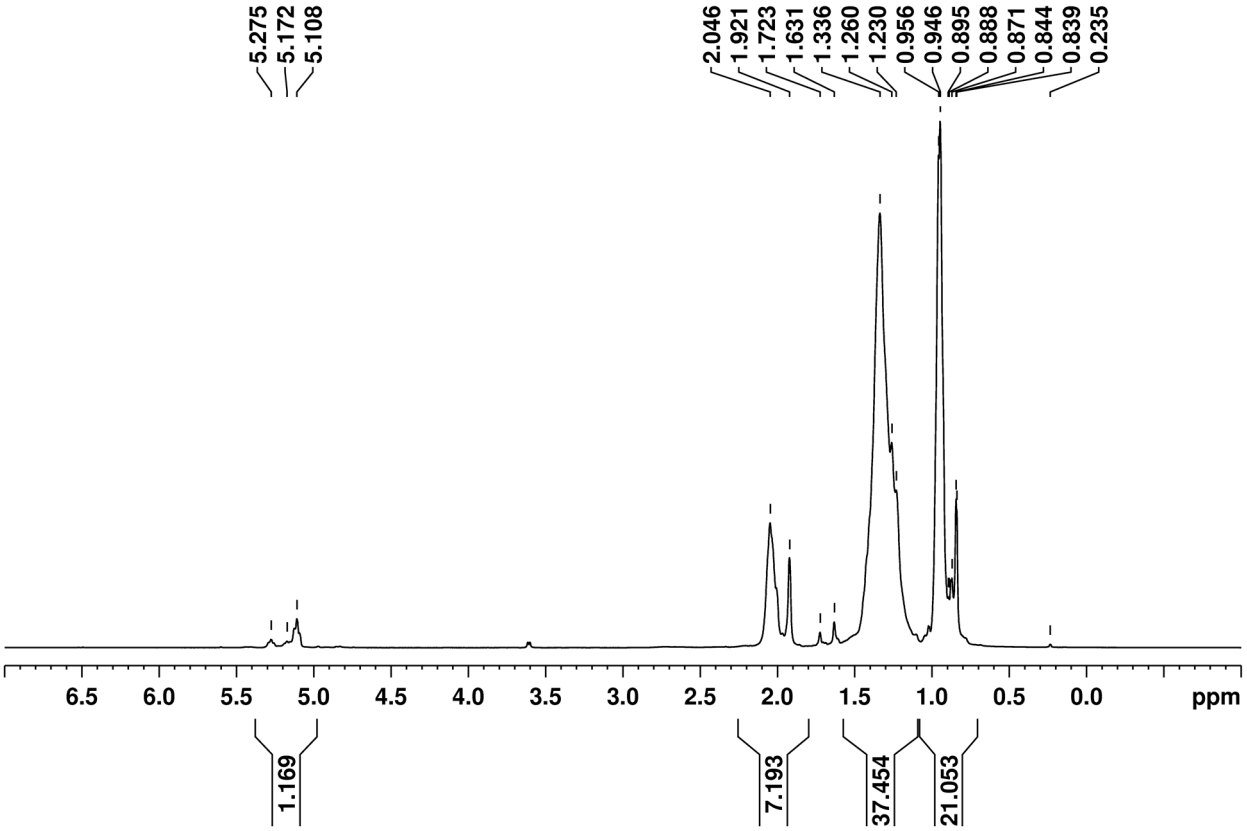

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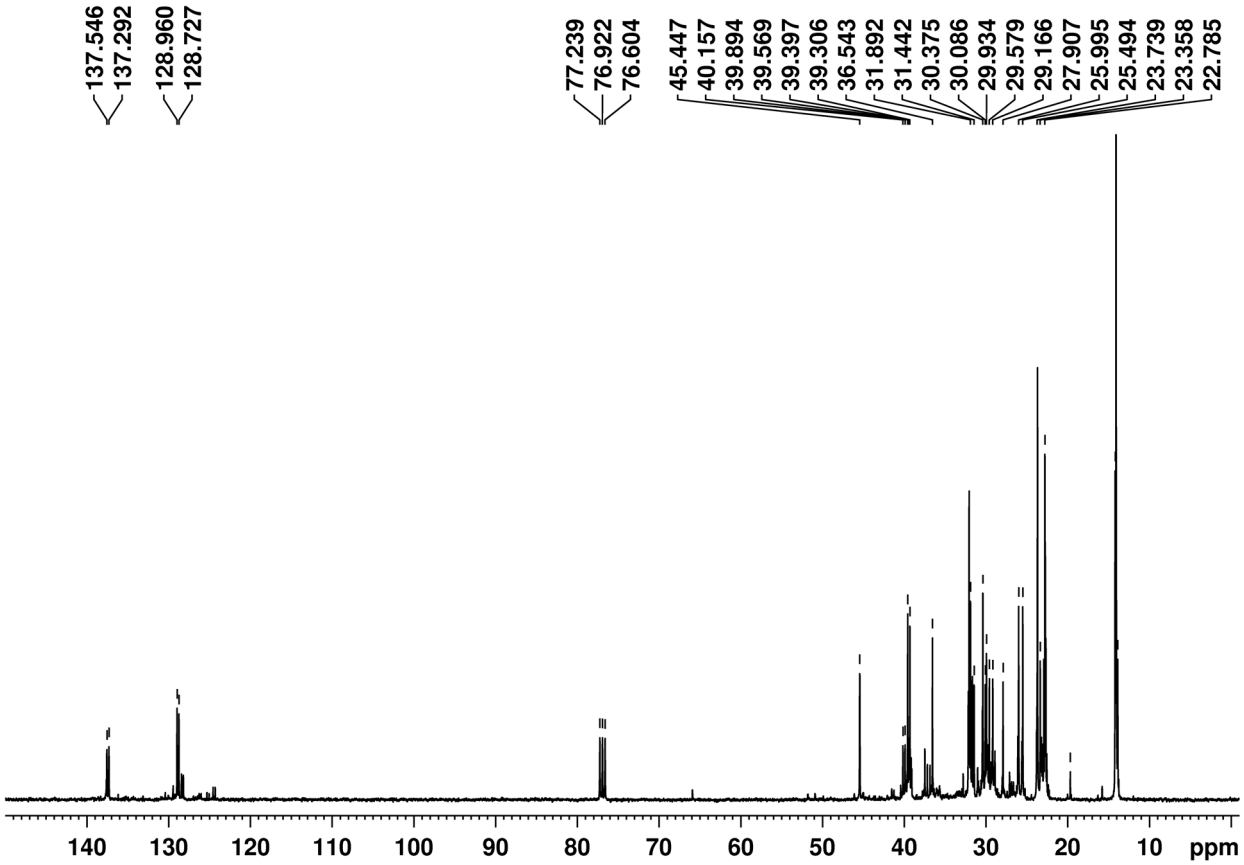
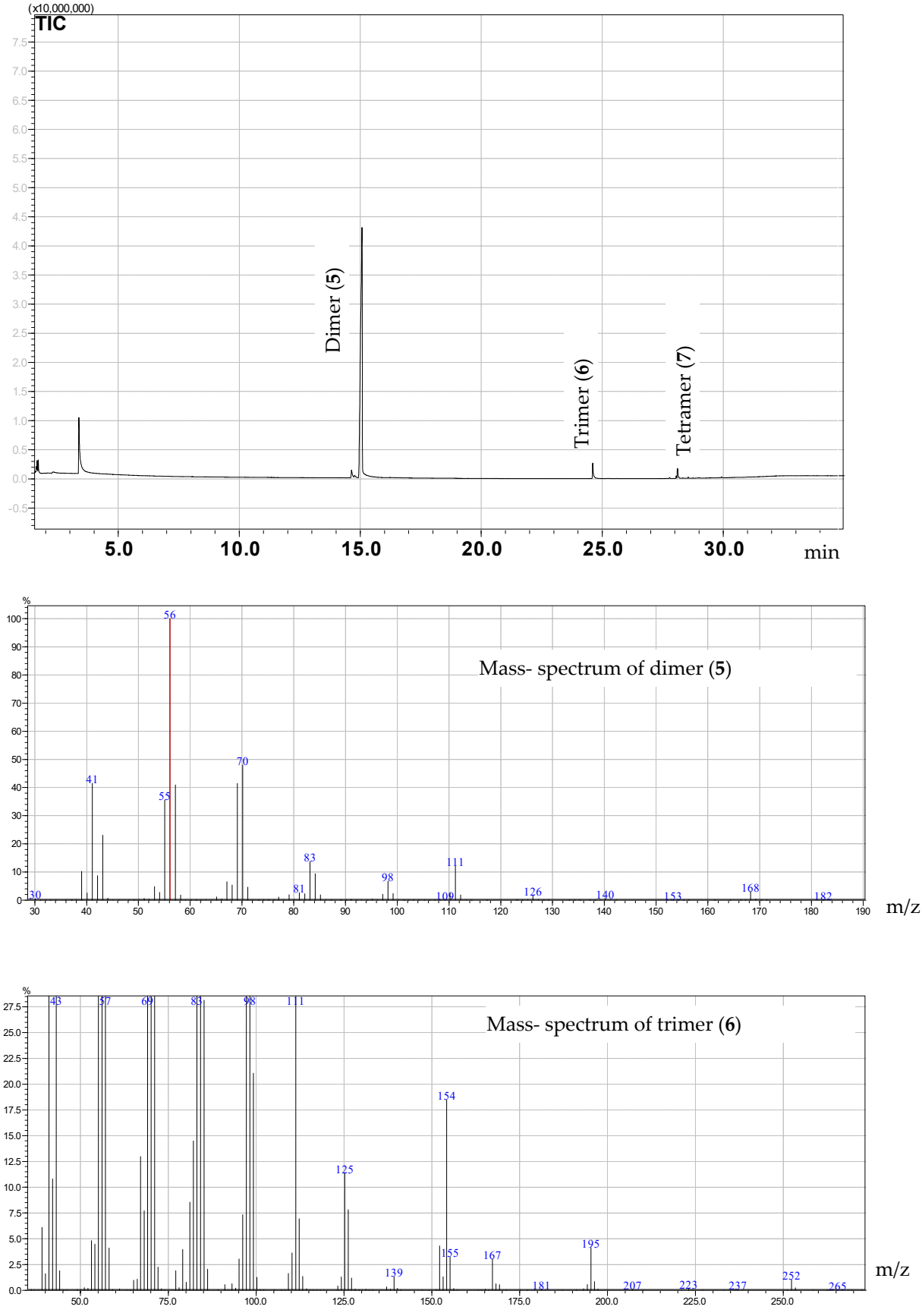


GC-MS analysis of products

Before each series of mass spectral analysis, calibration was performed using 1-hexene – dimer – tetramer mixtures with various mass fractions to determine response factors (RF). Response factors of dimers or tetramers were calculated as RF(dimer or tetramer) = Slope(1-hexene)/Slope(dimer or tetramer), where Slope(1-hexene) was found from the dependence Peak area (1-hexene) – Concentration (1-hexene), and Slope(dimer or tetramer) from the dependence Peak area (dimer or tetramer) – Concentration (dimer or tetramer). 1-Hexene was used as a standard with RF=1. RFs were found for dimer and tetramer as 1.1 and 1.2, correspondingly. Thus, product composition was determined via peak areas multiplied by response factors.

Figure S28. Example of GC-MS analysis of dimers and oligomers obtained in the system $[Cp_2ZrH_2]_2$–$ClAlBu^i_2$–MMAO-12, [Zr]:[Al]:[MMAO-12]:[1-alkene]= 1:3:30:1000, CH_2Cl_2, 40°C, 16 h.



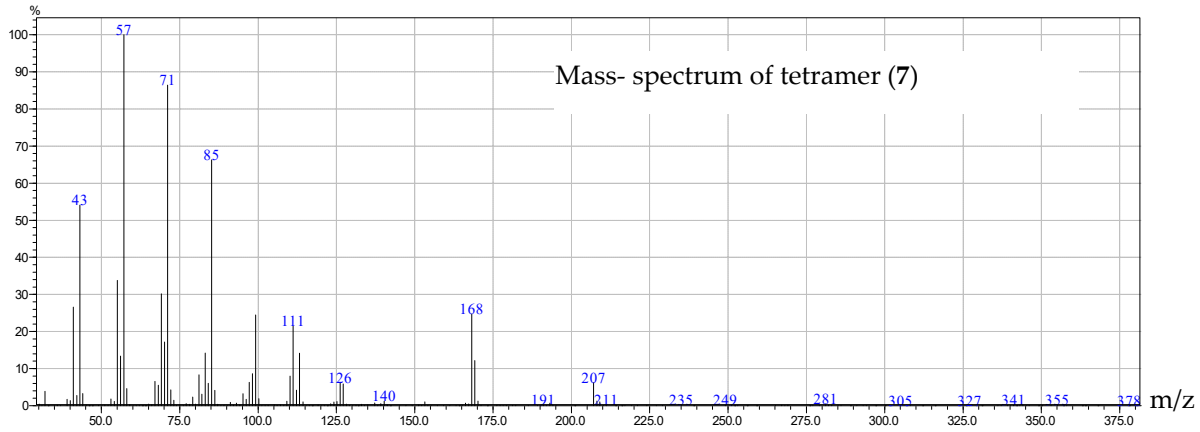
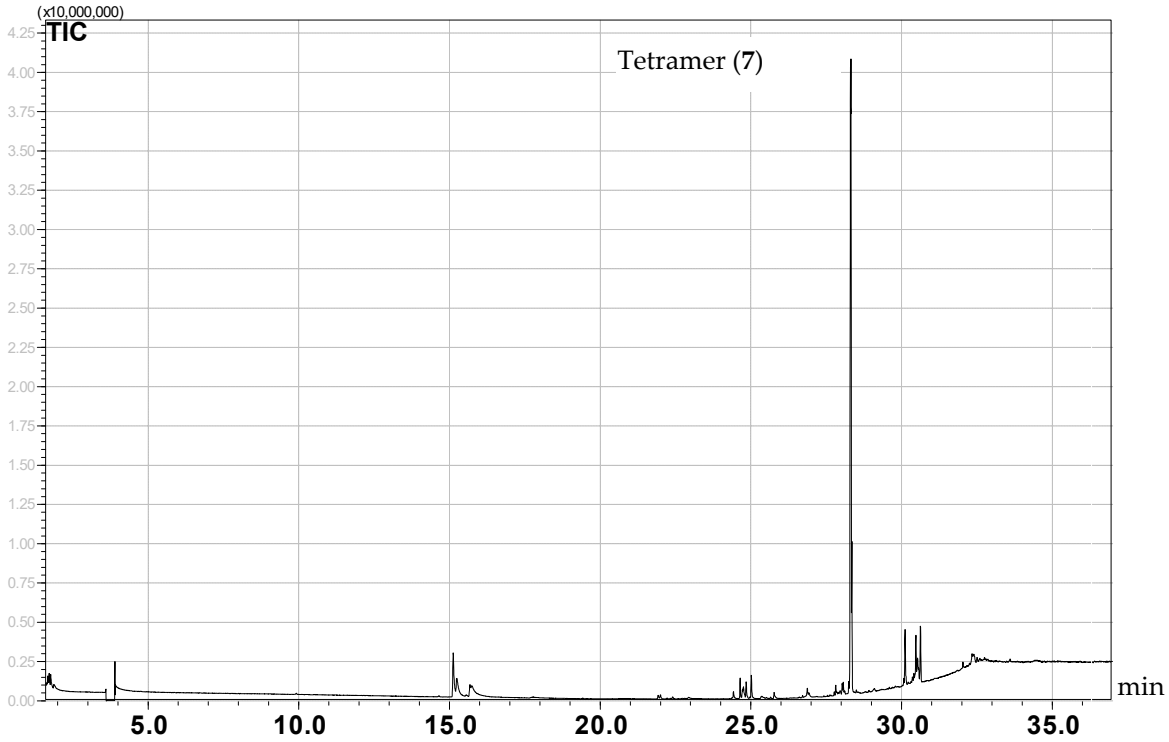


Figure S29. Example of GC-MS analysis of dimers and oligomers obtained in the system Cp_2ZrCl_2–$HAlBu^i_2$–$(Ph_3C)[B(C_6F_5)_4]$, [Zr]:[Al]:[B]:[1-alkene]= 4:16:1:1000, $CHCl_3$, 40°C, 16 h.



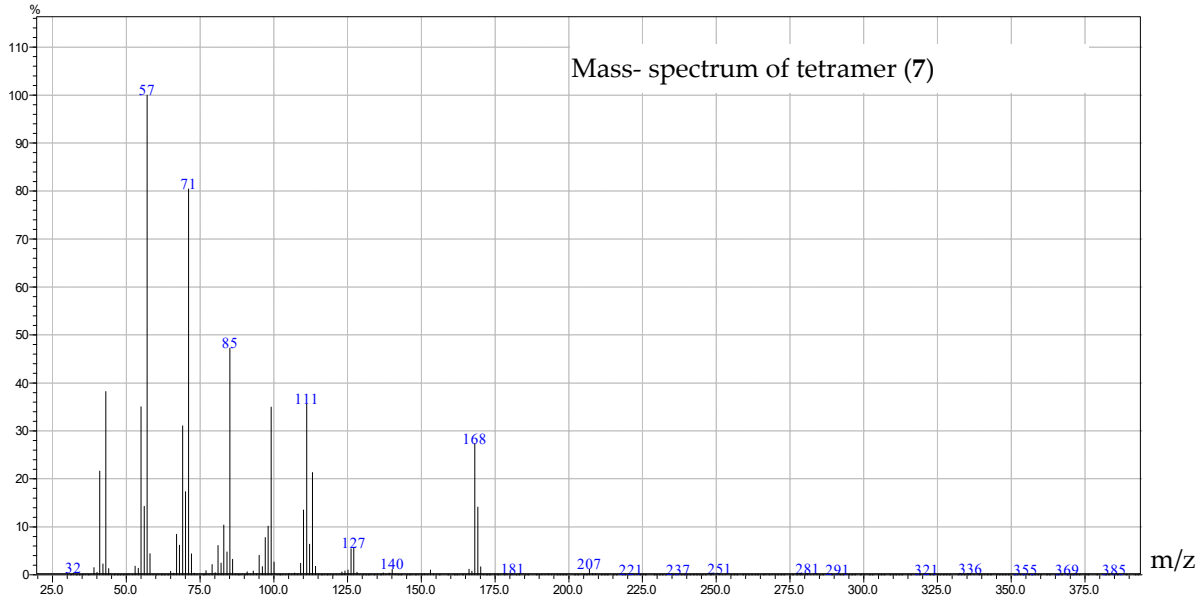

Mass- spectrum of tetramer (7)
%
110
100
90
80
70
60
50
40
30
20
10
0
57
71
85
111
168
127
140
32
181
207
221
237
251
281
291
321
336
355
369
385
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
m/z

Table S1. The energy at 0K, the ZPVE correction, the enthalpy, the Gibbs free energy in gas, the temperature multiplied by the entropy for complexes **9a-e**, calculated at PBE/3ζ level (298.15 K).

Complex	E, Hartree	ZPVE, Hartree	H, kcal/mol	G, kcal/mol	T*S, cal/mol
9a	-9177.483313	0.479046	-5758635.6	-5758702.0	66417.6
9b	-9177.470210	0.478892	-5758627.4	-5758692.4	65081.6
9c	-9177.480291	0.479422	-5758633.2	-5758698.7	65459.5
9d	-9177.461167	0.480010	-5758621.2	-5758685.2	63942.4
9e	-10038.215279	0.607638	-6298665.2	-6298747.2	81996.9

Table S2. Relative thermodynamic parameters of isomeric complexes **9a-d**, calculated at PBE0/def2TZVP level (298.15 K).

Complex	ΔE, Hartree	ΔE_{ZPVE}, Hartree	ΔH, kcal/mol	ΔG, kcal/mol	TΔS, cal/mol
9a	0.001420	0.000052	0.0	0.0	2362.8
9b	0.011620	0.010971	6.8	8.4	796.1
9c	0.000000	0.000000	0.0	1.2	1132.1
9d	0.020137	0.020704	12.7	15.1	0.0

Table S3. Relative thermodynamic parameters of isomeric complexes **9a-d**, calculated at PBE0-GD3/def2TZVP level (298.15 K).

Complex	ΔE, Hartree	ΔE_{ZPVE}, Hartree	ΔH, kcal/mol	ΔG, kcal/mol	TΔS, cal/mol
9a	0.001174	0.000050	0.0	0.0	941.6
9b	0.010265	0.009999	6.3	6.5	686.6
9c	0.000000	0.000000	0.1	0.2	898.6
9d	0.020161	0.020487	12.8	13.7	0.0

Table S4. Relative thermodynamic parameters isomeric complexes **9a-d** in $CHCl_3$ solution, calculated at PBE0/def2TZVP level (298.15 K).

Complex	ΔE, Hartree	ΔE_{ZPVE}, Hartree	ΔH, kcal/mol	ΔG, kcal/mol	TΔS, cal/mol
9a	0.000000	0.000000	0.0	0.0	2322.0
9b	0.004409	0.005690	3.6	4.8	1062.3
9c	0.002469	0.002932	2.1	2.3	2049.2
9d	0.021519	0.023216	14.3	16.6	0.0

Table S5. Relative thermodynamic parameters of isomeric complexes **9a-d** in CH_2Cl_2 solution, calculated at PBE0/def2TZVP level (298.15 K).

Complex	ΔE, Hartree	ΔE_{ZPVE}, Hartree	ΔH, kcal/mol	ΔG, kcal/mol	TΔS, cal/mol
9a	0.000000	0.000000	0.0	0.0	2337.8
9b	0.002884	0.004539	2.8	4.2	906.4
9c	0.003194	0.003504	2.5	2.6	2158.6

9d	0.022043	0.023679	14.6	17.0	0.0

Atomic coordinates of the complexes **9a-e**

9a

C	3.579096680	-1.182145120	2.772116080
C	2.692045280	-0.086220410	2.960824760
C	3.172921060	1.011578820	2.194632780
C	4.590397310	-0.764442430	1.865318010
C	4.338653910	0.593690410	1.508025440
H	3.513442520	-2.147786050	3.258561900
H	1.811129990	-0.092078430	3.595230600
H	2.712778870	1.990377220	2.127821760
H	5.432051580	-1.365961360	1.539545320
H	4.950478160	1.204947060	0.851304440
Zr	2.462548190	-0.792445320	0.540541630
C	4.139309800	-1.673368520	-1.095318320
C	3.068528890	-2.607475830	-1.100619470
C	1.930701140	-1.951407000	-1.649648020
C	3.662198400	-0.442176090	-1.635319280
C	2.298908610	-0.626303840	-1.991142190
H	5.155272930	-1.873424780	-0.772142620
H	3.116113600	-3.642189800	-0.782739350
H	0.943935190	-2.385835160	-1.769440610
H	4.257567880	0.450215750	-1.802894530
H	1.631910700	0.114671980	-2.416832500
Zr	0.111573650	2.615502270	-0.003216450
H	1.198262360	0.846776720	0.248584470
C	-0.430856440	1.923371560	2.382266270
C	0.181485240	3.203883800	2.437103460
C	-0.701726880	4.133904760	1.812510580
C	-1.670094420	2.057116370	1.707607220
C	-1.847457190	3.425843890	1.359338570
H	-0.023583150	0.991215290	2.756498100
H	1.120841600	3.449678460	2.923135770
H	-0.543793250	5.204137880	1.732225500
H	-2.360003790	1.250456950	1.483885180
H	-2.717353220	3.852942090	0.874816760
C	1.488323490	3.061391500	-2.079418210
C	2.420674990	3.007018930	-1.006043320
C	2.156111090	4.092703050	-0.136521610
C	0.659096420	4.201474080	-1.890339800
C	1.064639800	4.831501140	-0.682535970
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H	2.702929040	4.336398020	0.769474130
H	-0.118847430	4.544174980	-2.561736180
H	0.641724300	5.743131690	-0.274502250
H	2.333515050	-2.492526630	1.206988070
H	-1.319248370	3.189002650	-0.991650570
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C	-3.516230950	-1.038975000	0.618643650
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C	-4.587644550	-0.193351680	-0.097418660
H	-4.854604110	-0.621888330	-1.075550840
C	-1.775467240	-2.778490710	-1.751039880
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H	-2.319615410	-4.462596020	-0.445331180
H	-1.586663380	-4.968124690	-1.975392870
H	-0.580929420	-4.286745600	-0.681262100
H	-4.236751930	0.831486800	-0.292381350
H	-5.519448880	-0.117079440	0.485913200
Cl	-0.145739730	-1.590898090	1.157978190
Cl	-1.161426150	0.603831900	-1.467065940

9b

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C	3.338791260	1.066695630	2.090939860
C	4.407401560	-0.960629800	2.242415530
C	4.462717720	0.334401370	1.647112290
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H	1.679023630	0.503046940	3.501396750
H	3.103071630	2.087905120	1.818190020
H	5.122251750	-1.765793730	2.102229640
H	5.235494190	0.699934770	0.977702220
Zr	2.435628620	-0.849392570	0.634973800
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C	2.214337580	-2.070553090	-1.602420490
C	3.550352470	-0.203212160	-1.540685340
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Zr	0.092466200	2.630544300	-0.157089440
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C	0.362138450	2.988213050	2.330558530
C	-0.293709810	4.150521280	1.837380160
C	-1.734612630	2.378917870	1.617166270
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H	-2.599869750	1.783585700	1.348781350
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C	2.024020600	4.302268290	-0.279339080
C	0.867735450	3.967881460	-2.236862510
C	0.985641570	4.819373670	-1.109517420
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H	2.384139790	4.741770430	0.645951390
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C	-1.257218310	-1.713885360	-1.994721740
H	-2.130258870	-1.221364440	-2.460044320
H	-0.434624740	-1.551509520	-2.708704120
C	-1.543779770	-3.221639010	-1.844013400
H	-2.415533400	-3.404452580	-1.197900910
H	-1.753259530	-3.705878470	-2.811657020
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H	-4.018965800	0.276312900	0.244693700
H	-4.649644010	-1.012860610	1.287296930
H	0.453452120	-1.011227640	0.585168260

H	-0.614857110	0.849874560	-0.692421670
Cl	-1.960871720	2.959401590	-1.623916490
Cl	1.774391860	-3.154065270	1.486592000

9c

C	1.955884260	-2.435907860	1.283024320
C	1.939686710	-1.309157740	2.132779030
C	3.213285760	-0.679038880	2.045135630
C	3.256805420	-2.542286060	0.706967450
C	4.035219070	-1.473874390	1.195919030
H	1.126879300	-3.114283010	1.109592410
H	1.101789480	-0.981130650	2.734467350
H	3.536409250	0.203175410	2.589958260
H	3.579422690	-3.316170710	0.017158420
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Zr	2.138212940	-0.341510100	-0.273776410
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C	3.117699910	-1.018482900	-2.630722400
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H	3.328347570	2.212132740	-1.795964130
Zr	0.184707130	2.116141470	0.461459830
H	2.091634580	1.492611190	0.544371710
C	0.694260520	1.828025700	2.969235190
C	0.590243470	3.243172800	2.820668270
C	-0.766269520	3.557021650	2.571800420
C	-0.590345360	1.273123930	2.771074170
C	-1.488797590	2.344656600	2.493516010
H	1.601281240	1.286959560	3.210855580
H	1.408465150	3.949395760	2.928714830
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H	-2.550318910	2.242804600	2.288130860
C	0.743191650	3.311708990	-1.783534890
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C	0.536968520	4.709560180	0.033979610
C	-0.629453610	3.558455990	-1.569235190

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H	-1.693483380	4.807131350	-0.045051330
Al	-1.932656930	-1.427888800	-0.570454440
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H	-2.908638240	-1.405687870	-2.937190650
C	-3.314042350	-3.442368630	-2.270364540
H	-3.638991650	-3.987298270	-1.370685890
C	-2.033332540	-2.203806950	1.253121820
H	-1.913731760	-3.297047900	1.146222330
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H	-4.225262240	-2.259636610	1.425889250
H	-3.394919510	-2.377858680	2.985149100
H	-3.495053020	-0.821052660	2.144076100
H	-2.348913810	-3.875186010	-2.574845020
H	-4.037972040	-3.676054750	-3.067322290
H	0.863815650	1.001652410	-1.005008800
Cl	0.176692580	-1.792489120	-1.440712820
Cl	-2.039213920	0.879305830	-0.466328200

9d

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C	3.368721440	-2.547207280	0.918468400
C	4.193596820	-1.450912360	1.278909730
H	1.220334600	-2.983965860	1.367179210
H	1.282944760	-0.665646600	2.714415560
H	3.764436180	0.383505450	2.468795230
H	3.665541260	-3.415031810	0.340107040
H	5.240586140	-1.317112710	1.028166870
Zr	2.431852200	-0.515144780	-0.353428080
C	4.414490910	-1.659887300	-1.689979290
C	3.200605070	-2.113719040	-2.262301770
C	2.584873140	-1.004221990	-2.911624820
C	4.510488820	-0.264709340	-1.904584970

C	3.389213130	0.132976250	-2.689940690
H	5.131337000	-2.268843330	-1.151715080
H	2.827464090	-3.133873470	-2.260310910
H	1.642293700	-1.028539080	-3.446677090
H	5.317802460	0.382705940	-1.572822230
H	3.170693080	1.143304250	-3.015539430
Zr	0.155983490	2.450917210	0.500237510
H	0.717868140	0.334256410	0.572670530
C	0.928703400	1.978249010	2.918470390
C	0.701216530	3.383823300	2.847036550
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C	-0.313629440	1.325965380	2.784119790
C	-1.319533850	2.322916460	2.626443040
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C	0.693022500	4.667141800	-0.826318230
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C	-1.449694680	4.367470760	-0.058474880
H	0.410984210	3.474765730	-2.685753120
H	1.729377750	4.984230070	-0.898938120
H	0.020650270	5.633233070	1.066682210
H	-2.090148660	3.077962910	-1.777234820
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H	-1.286006800	1.206750360	0.165549290
Al	-0.787973780	-0.571485790	-0.216872810
C	-2.029383550	-0.964176970	-1.755242800
H	-1.692026850	-0.470887340	-2.677055650
H	-1.966049960	-2.050252010	-1.947272890
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H	-3.604682890	0.506067250	-1.329563410
C	-1.423675400	-1.640543050	1.386079370
H	-0.697555010	-1.687631430	2.214369020
H	-2.308298150	-1.126586390	1.805380160
C	-1.825559160	-3.081133540	1.008403070
H	-0.981504880	-3.644405450	0.577218690
H	-2.192944640	-3.659652000	1.872073360

H	-2.622247820	-3.094280710	0.250197300
H	-3.865427380	-1.050347090	-0.536353310
H	-4.176714880	-0.882023760	-2.271443780
Cl	0.583984120	1.030112750	-1.885778890
Cl	2.810437230	2.096560320	0.236026810

9e

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