Supporting Information

A stable NHC-Coordinated Silagermenylidene Functionalized in Allylic Position and its Behaviour as a Ligand

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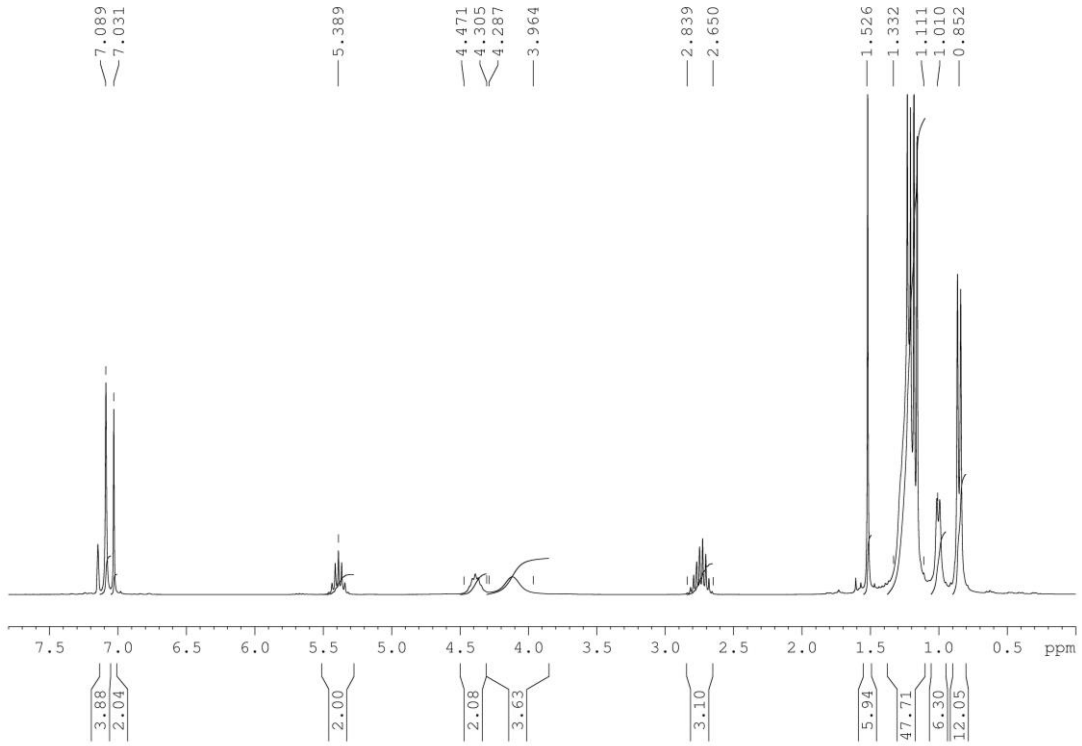


Figure S1: ^{1}H NMR of **4**-*E* in [D_6]-benzene at RT directly after sample preparation.

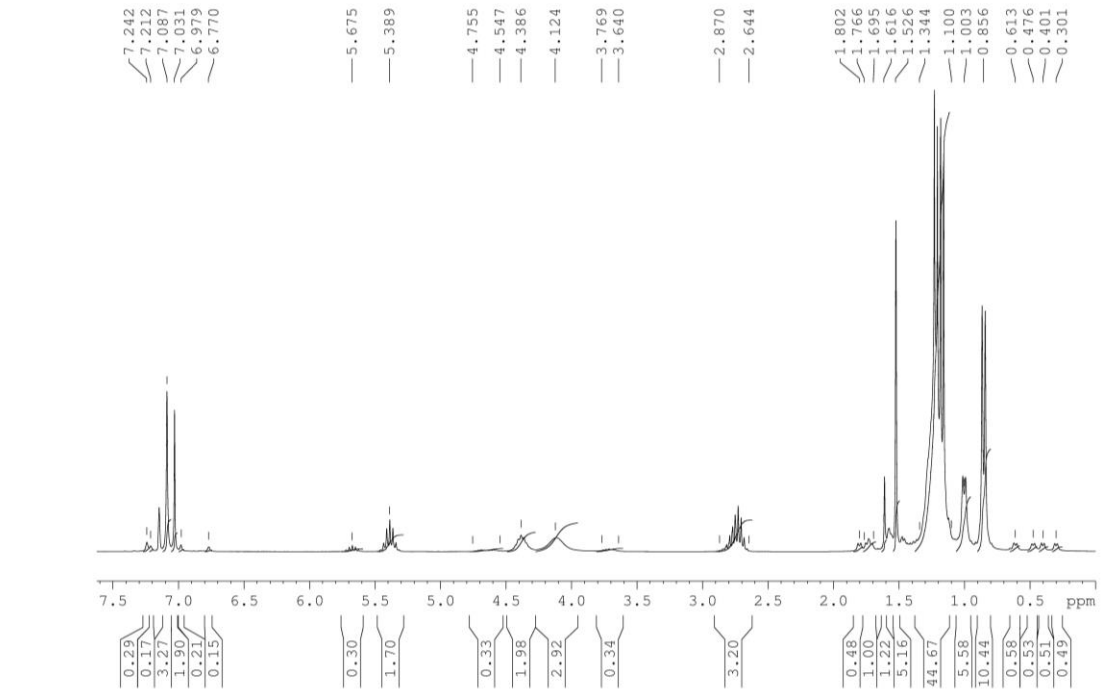


Figure S2: ^{1}H NMR of **4**-*E* and **4**-*Z* in [D_6]-benzene after reaching equilibrium at RT.

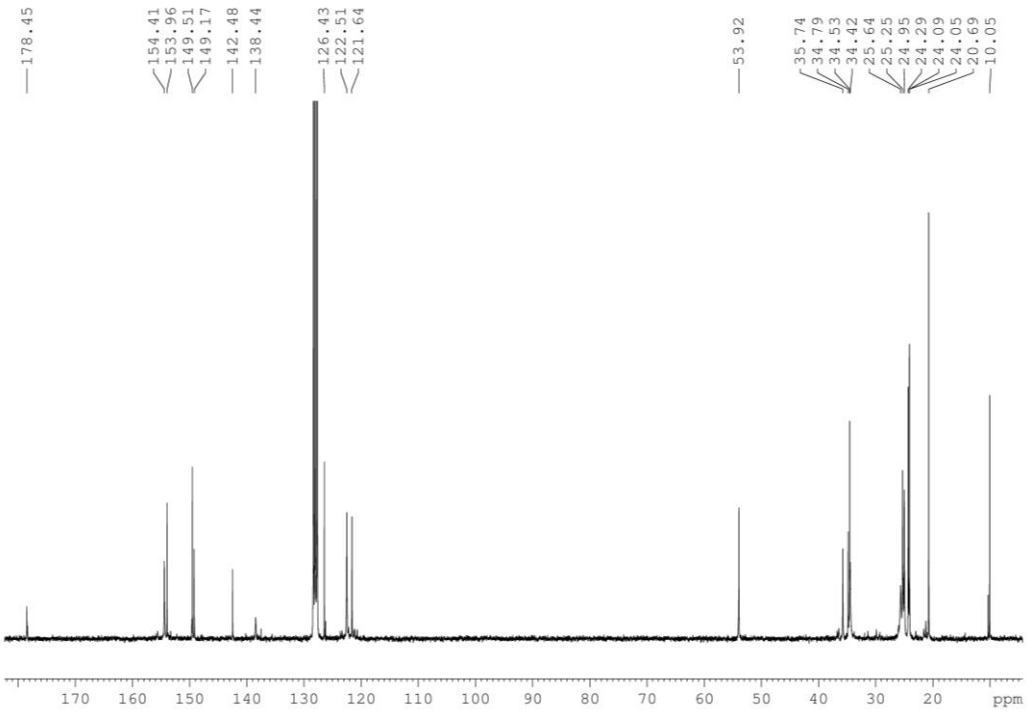


Figure S3: $^{13}C\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in $[D_6]$-benzene after reaching equilibrium at RT.

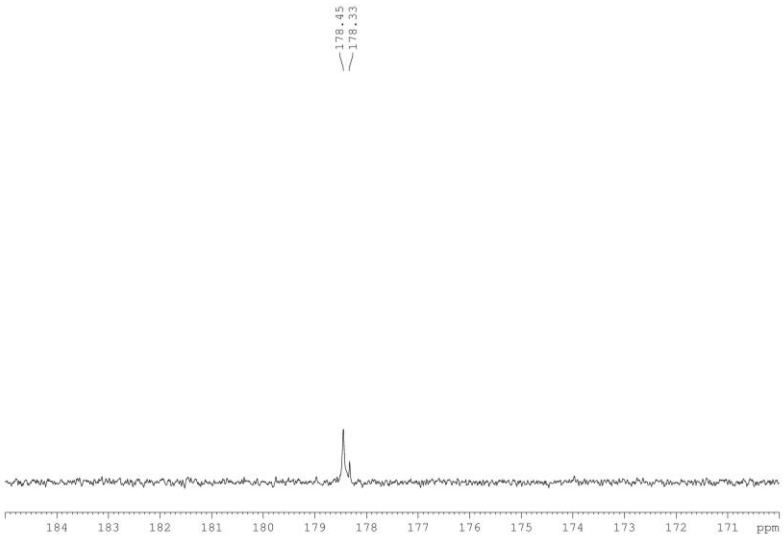


Figure S4: Carbenic region of $^{13}C\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in $[D_6]$-benzene at RT.

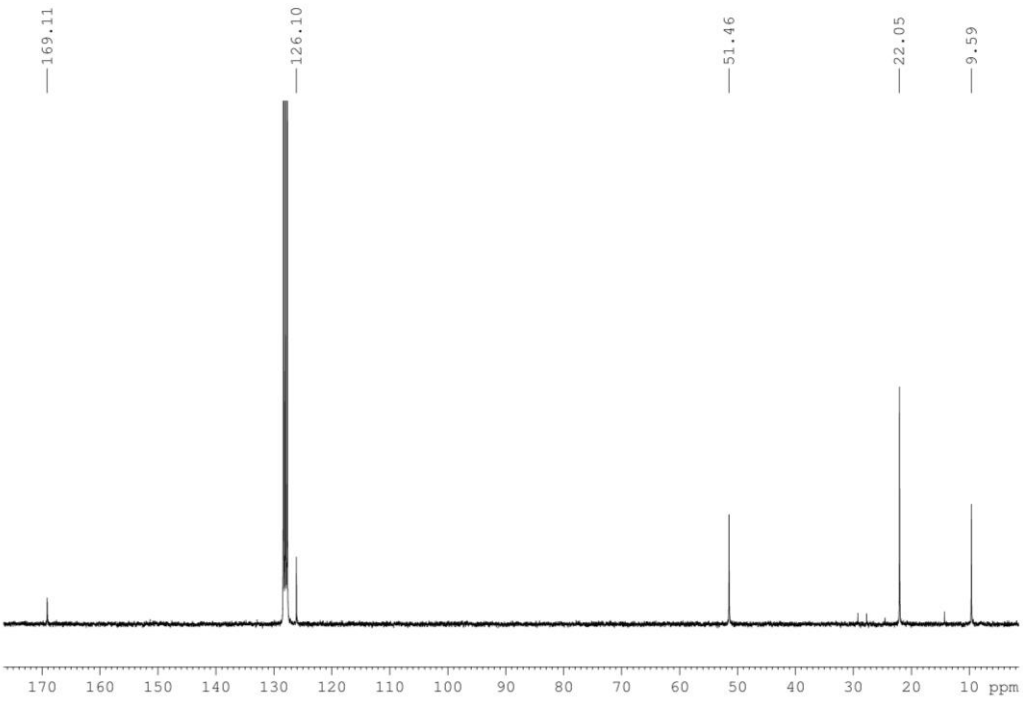


Figure S5: $^{13}C\{^{1}H\}$ NMR of NHC^{iPr2Me2}•$GeCl_2$, **2** in [D_6]-benzene at RT.

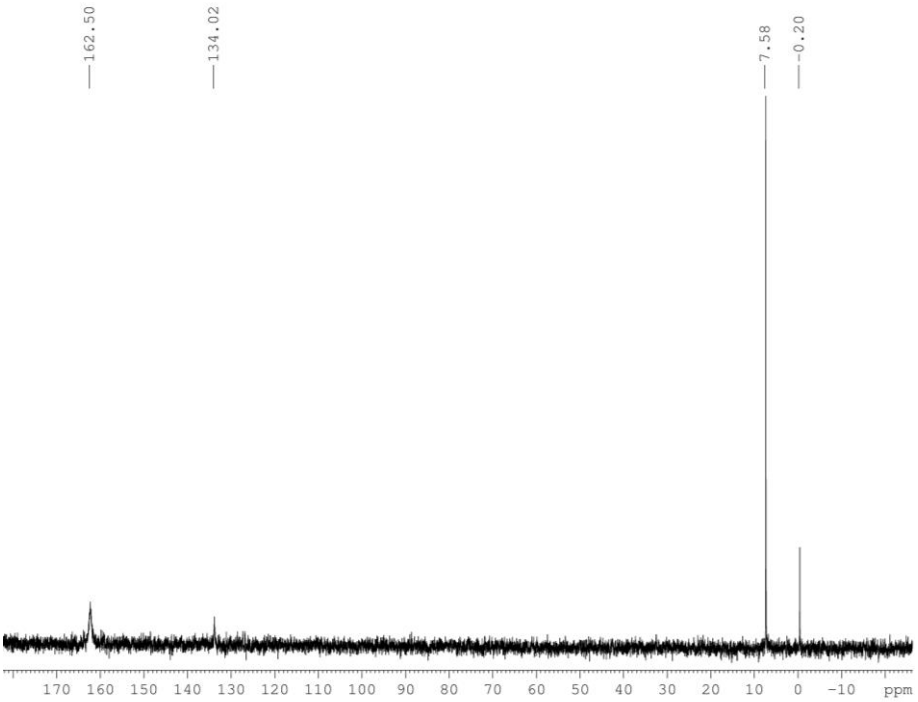


Figure S6: $^{29}Si\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in [D_6]-benzene after reaching equilibrium at RT.

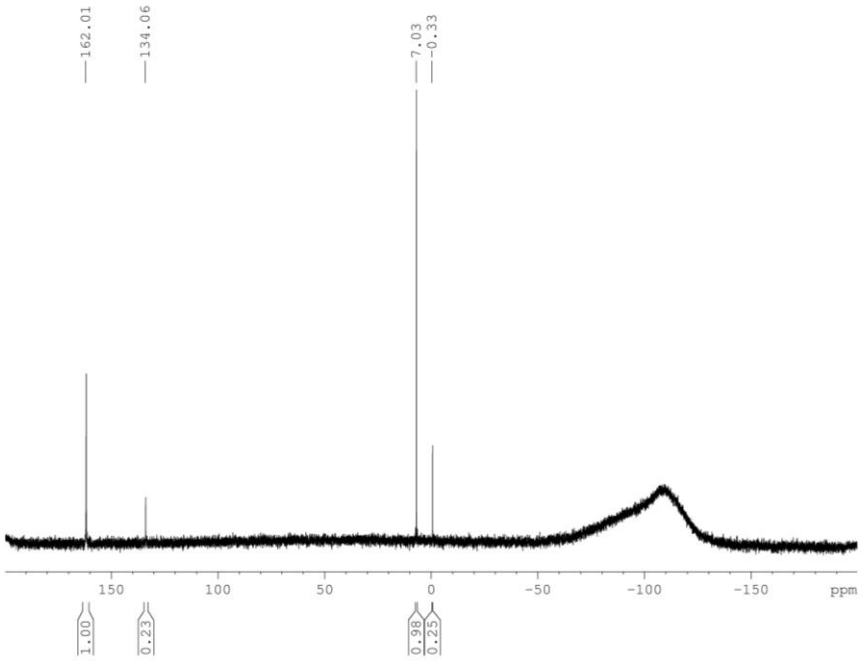


Figure S7: $^{29}Si\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in [D_8]-toluene after reaching equilibrium at 343 K.

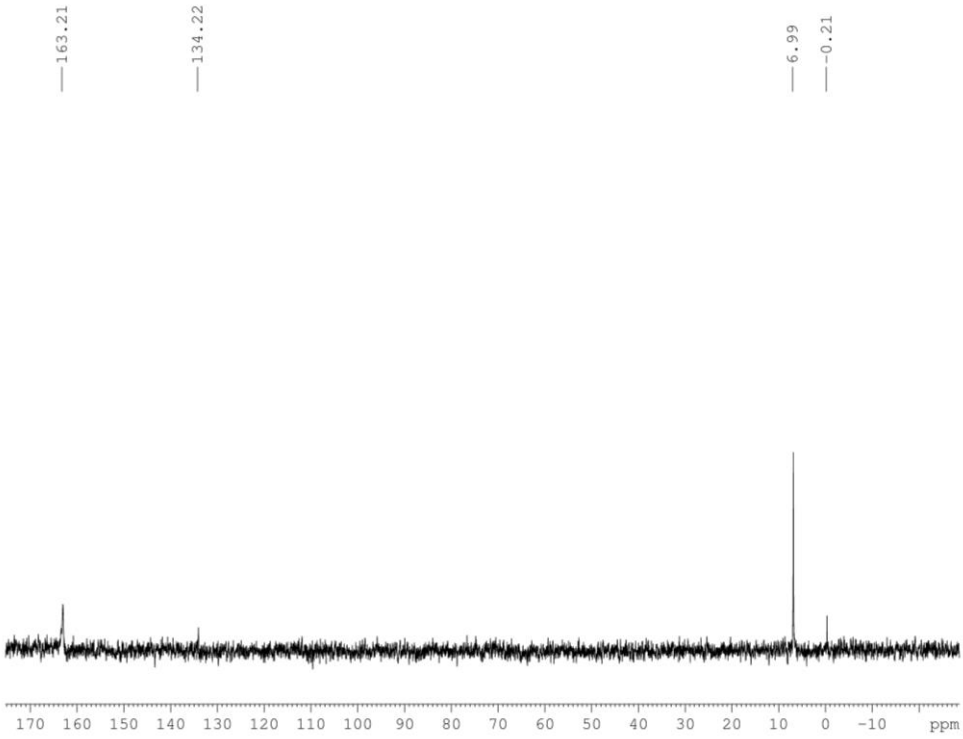


Figure S8: $^{29}Si\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in [D_8]-toluene after reaching equilibrium at 273 K

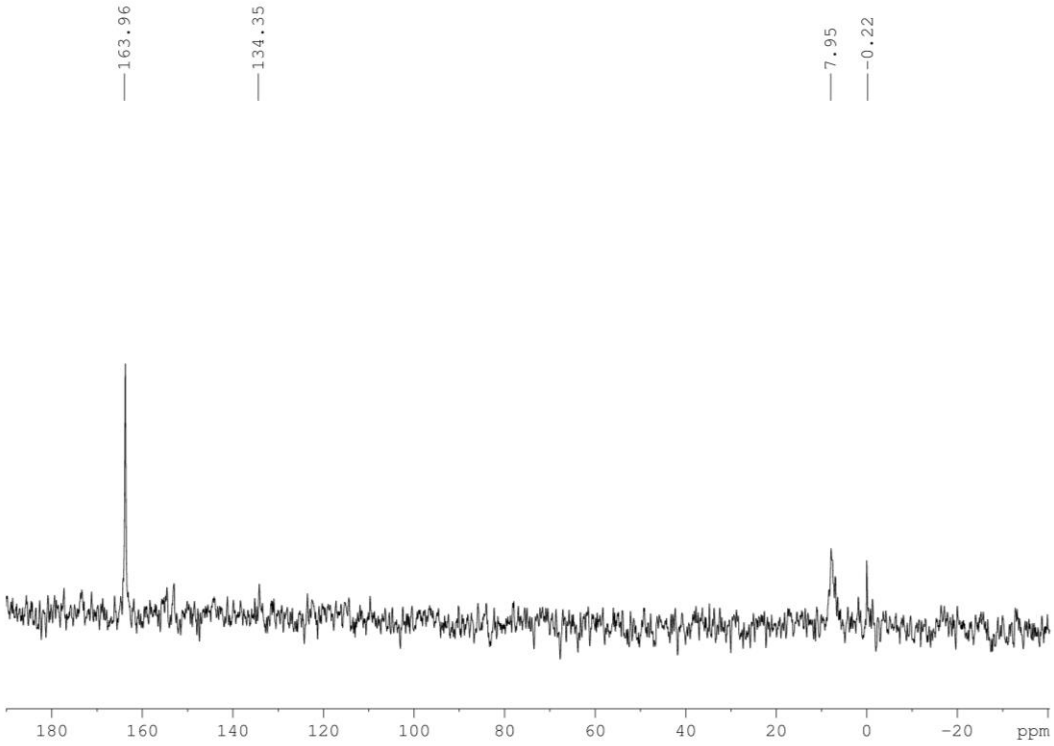


Figure S9: $^{29}Si\{^{1}H\}$ NMR of **4**-*E* and **4**-*Z* in $[D_8]$-toluene after reaching equilibrium at 213 K

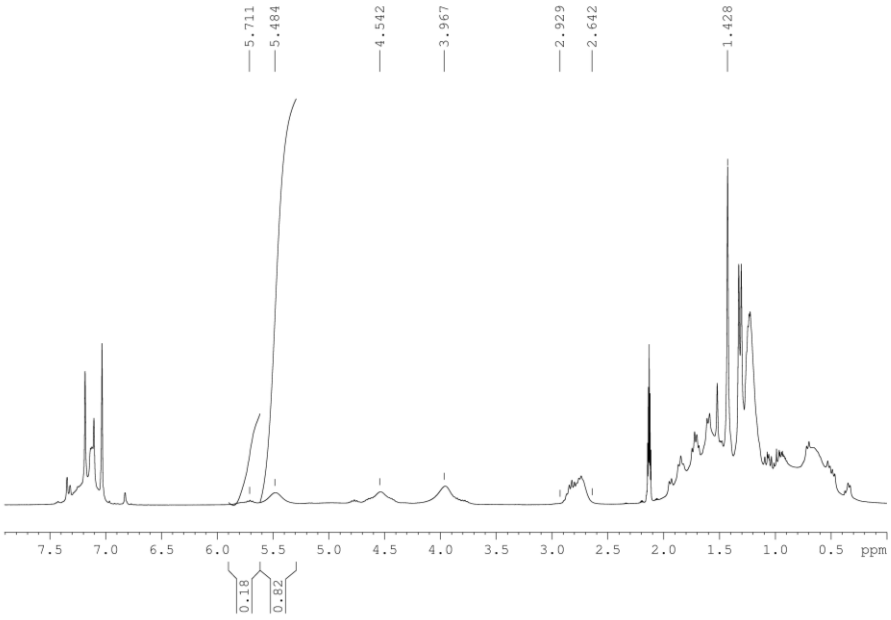


Figure S10: ^{1}H NMR of **4**-*E* and **4**-*Z* in $[D_8]$-toluene at 213 K

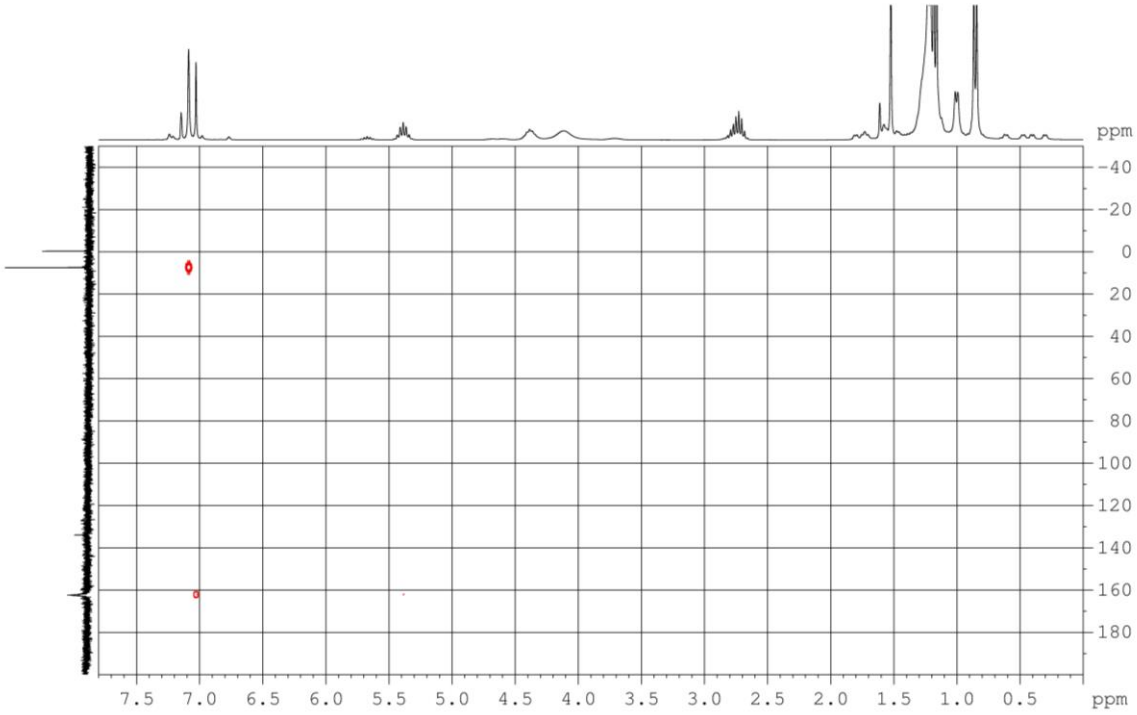


Figure S11: ^{1}H-^{29}Si 2D-NMR of **4**-*E* and **4**-*Z* in [D_6]-benzene after reaching equilibrium at RT.

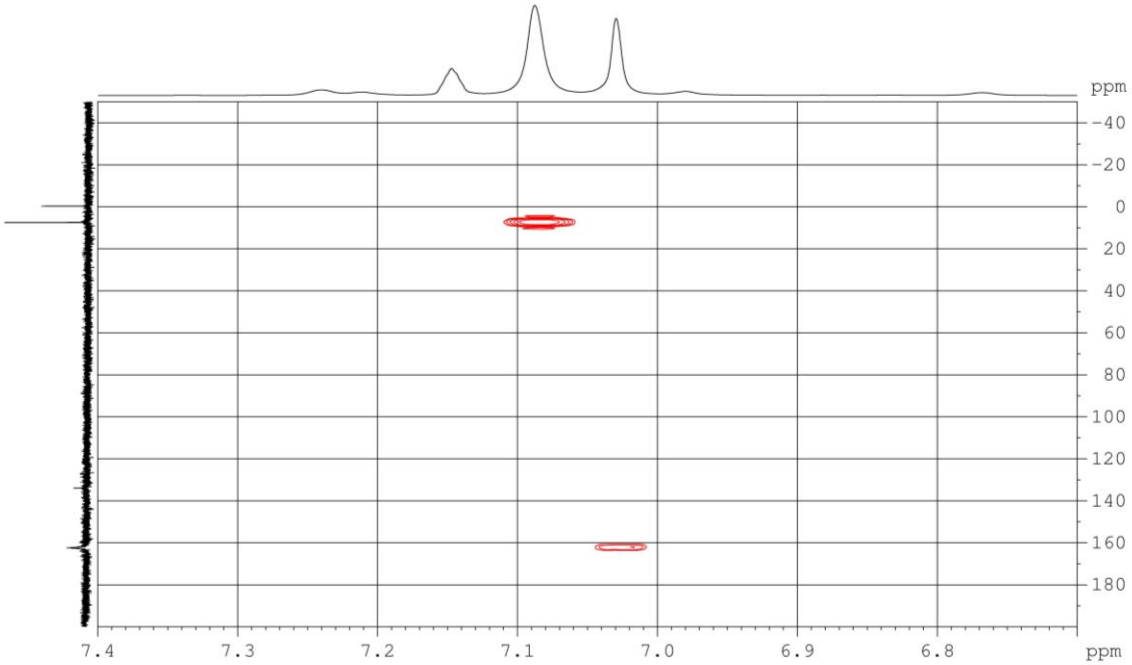


Figure S12: ^{1}H-^{29}Si 2D-NMR(zoom) of **4**-*E* and **4**-*Z* in [D_6]-benzene after reaching equilibrium at RT.

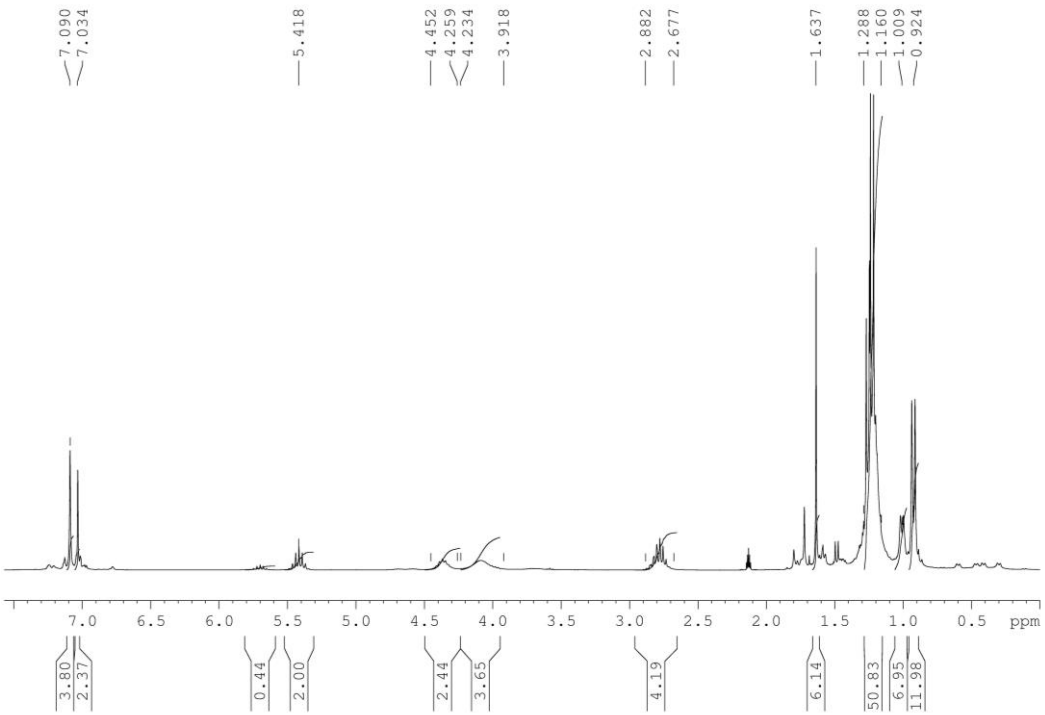


Figure S13: ^{1}H NMR of **4**-*E* and **4**-*Z* in [D_8]-toluene after reaching equilibrium at 343 K.

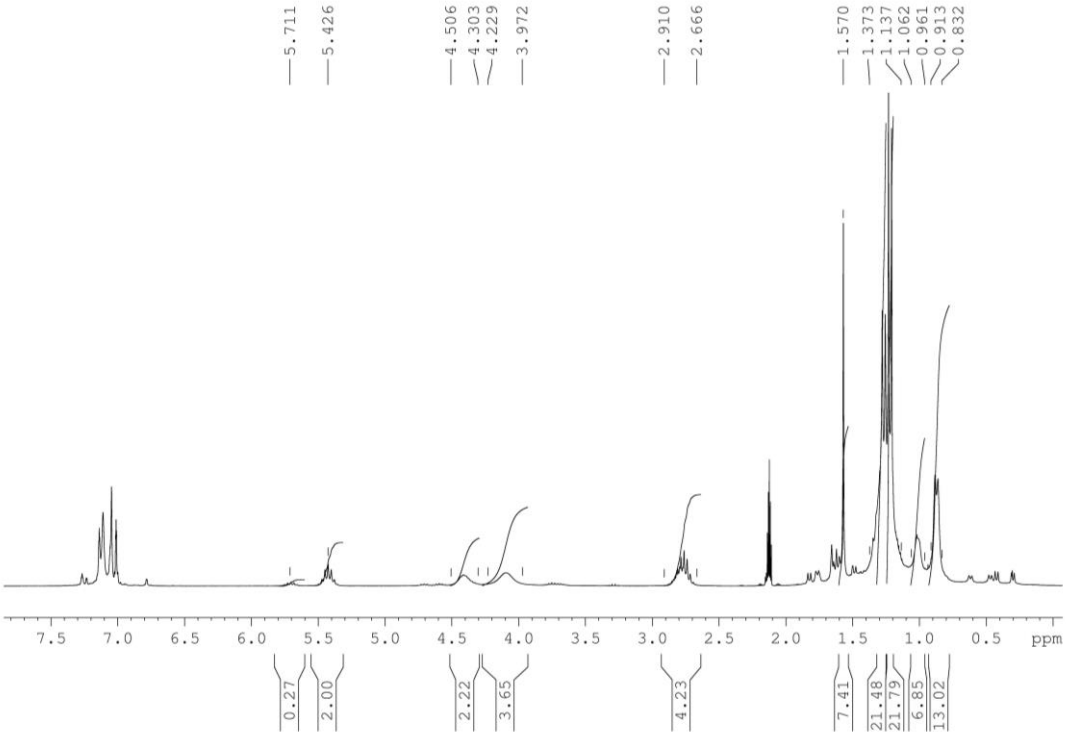


Figure S14: ^{1}H NMR of **4-*E*** and **4-*Z*** in [D_8]-toluene after reaching equilibrium at 273 K.

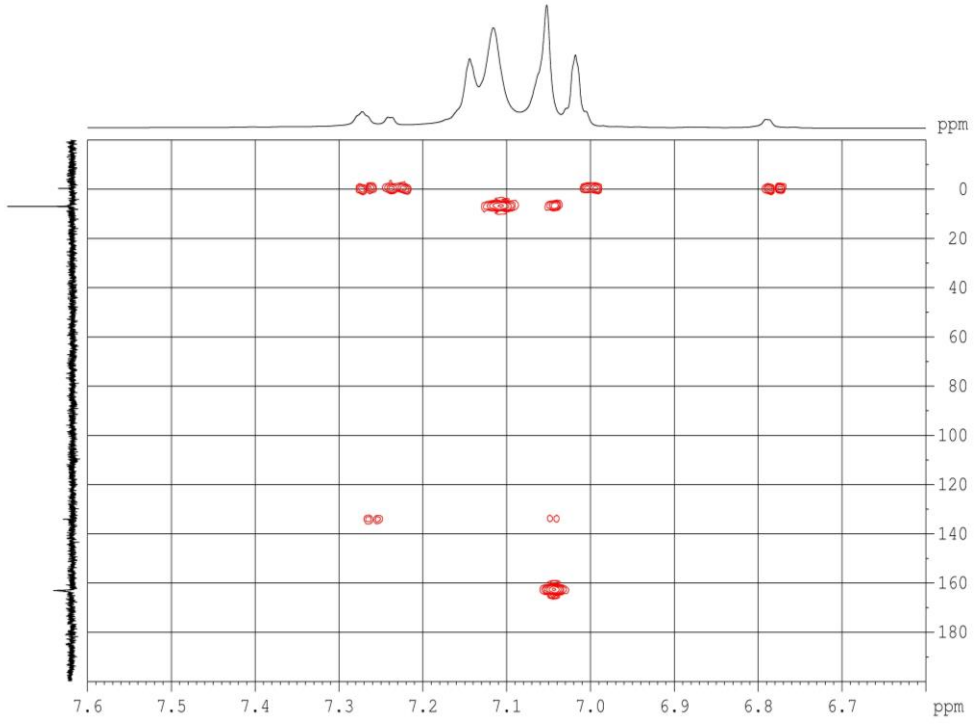


Figure S15: ^{1}H-^{29}Si 2D-NMR (zoom) of **4**-*E* and **4**-*Z* in [D_8]-toluene at 273 K.

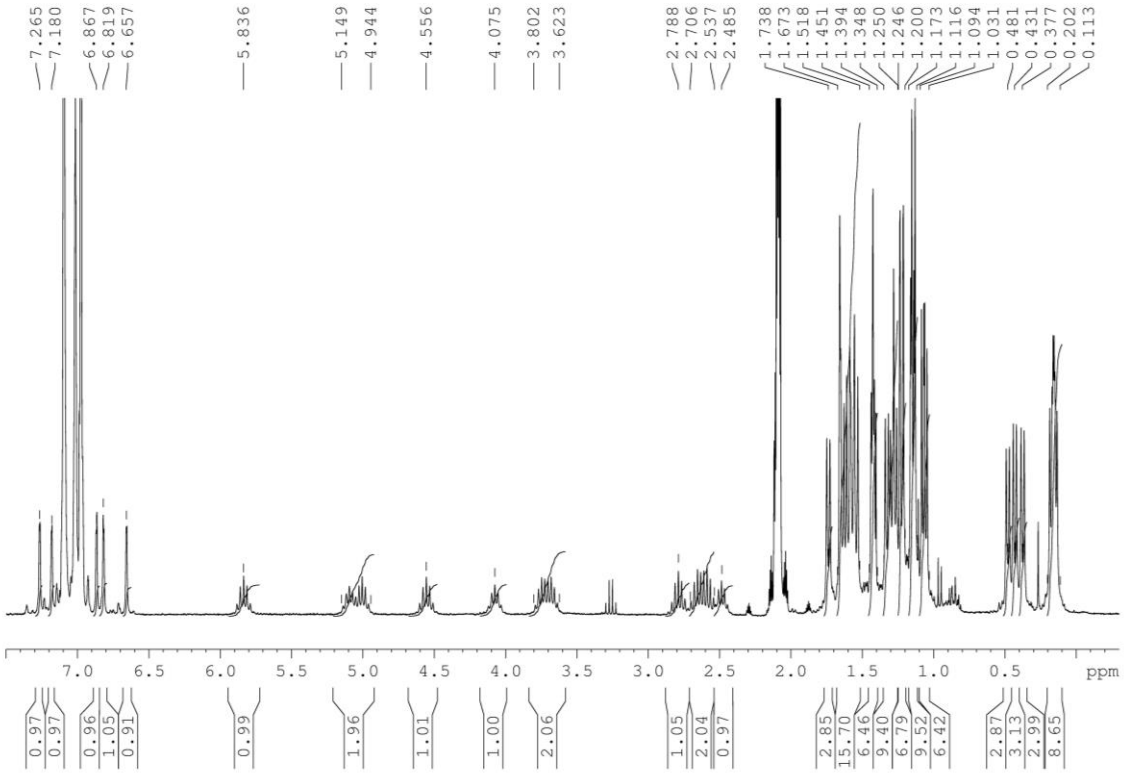


Figure S16: ^{1}H NMR of **5**-*Z* in [D_8]-toluene.

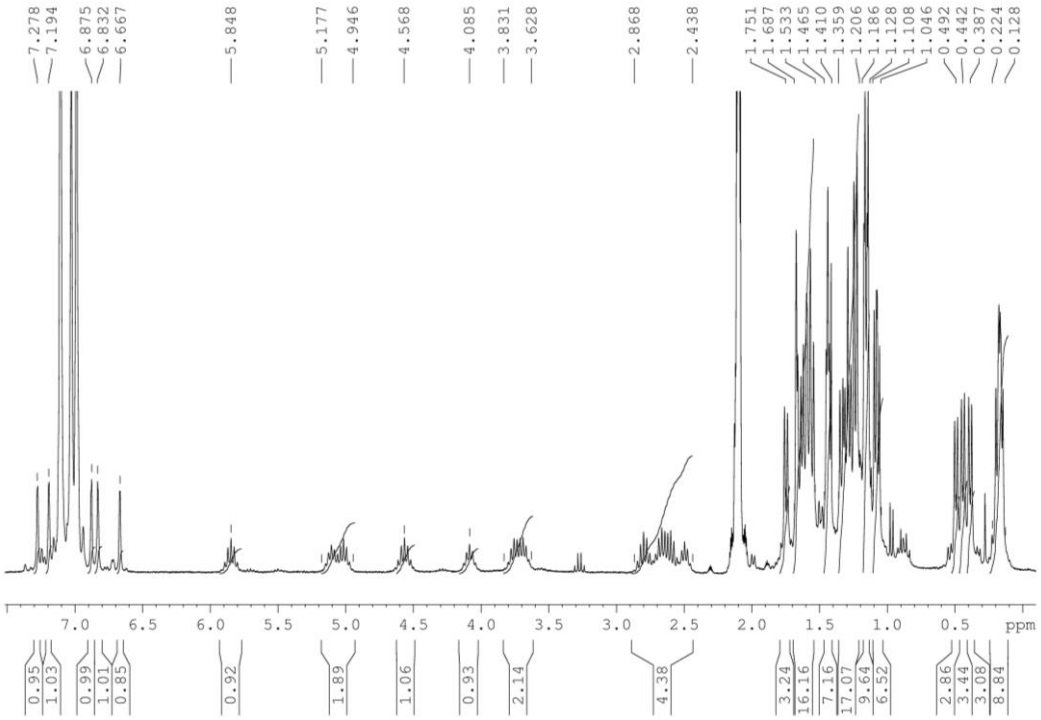


Figure S17: ^{1}H NMR of **5**-*Z* in [D_8]-toluene after 10 days in the solid form.

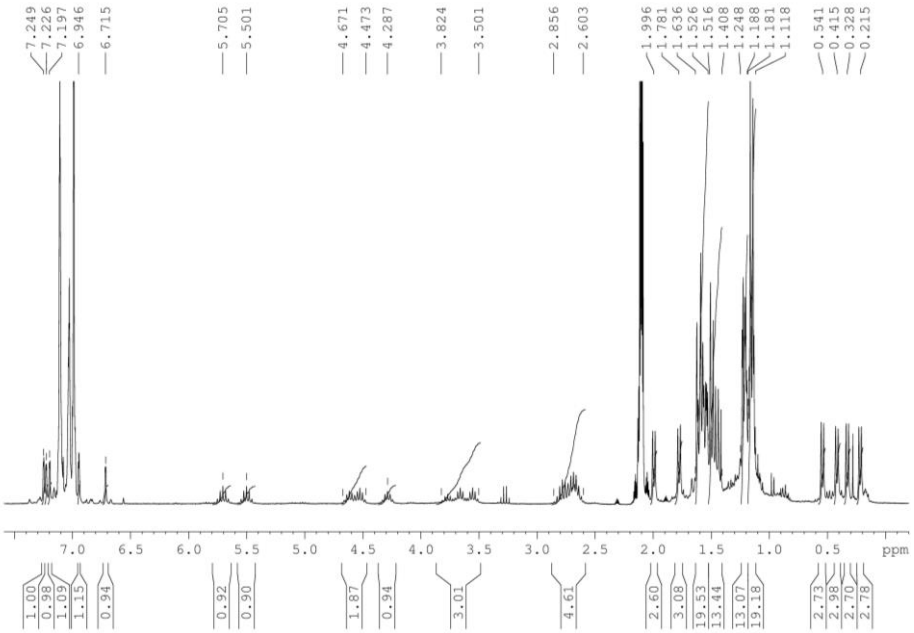


Figure S18: ^{1}H NMR of a sample of **5**-*Z* in [D_8]-toluene after 9 days in solution (complete isomerization of **5**-*Z* to **5**-*E* happened during this time).

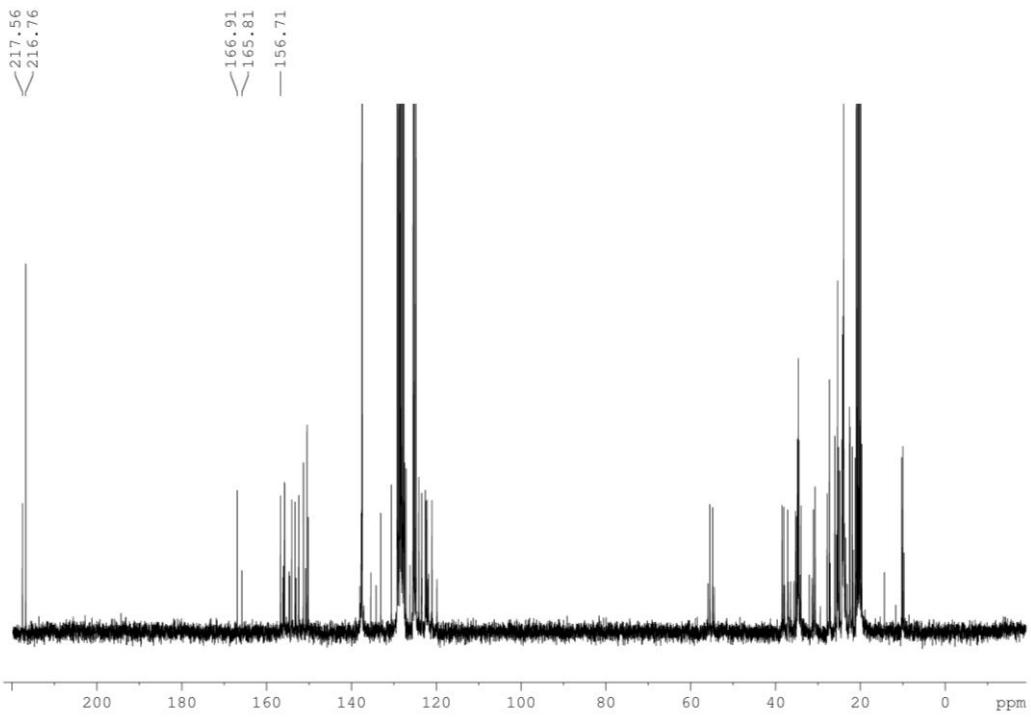


Figure S19: $^{13}C\{^{1}H\}$ NMR of a sample of **5**-*Z* in [D_8]-toluene. Conversion to the **5**-*E* had mostly completed during the acquisition of the spectrum (minor signals correspond to **5**-*Z*).

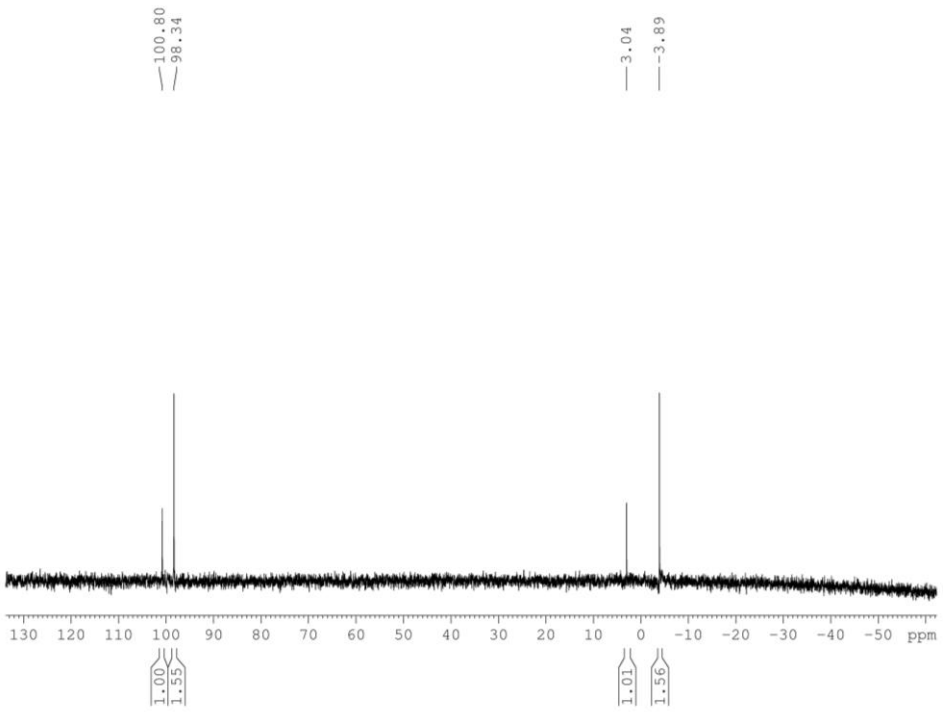


Figure S20: $^{29}Si\{^{1}H\}$ NMR of a sample of **5**-*Z* in [D_8]-toluene. Conversion to the **5**-*E* had mostly completed during the acquisition of the spectrum (minor signals correspond to **5**-*Z*).

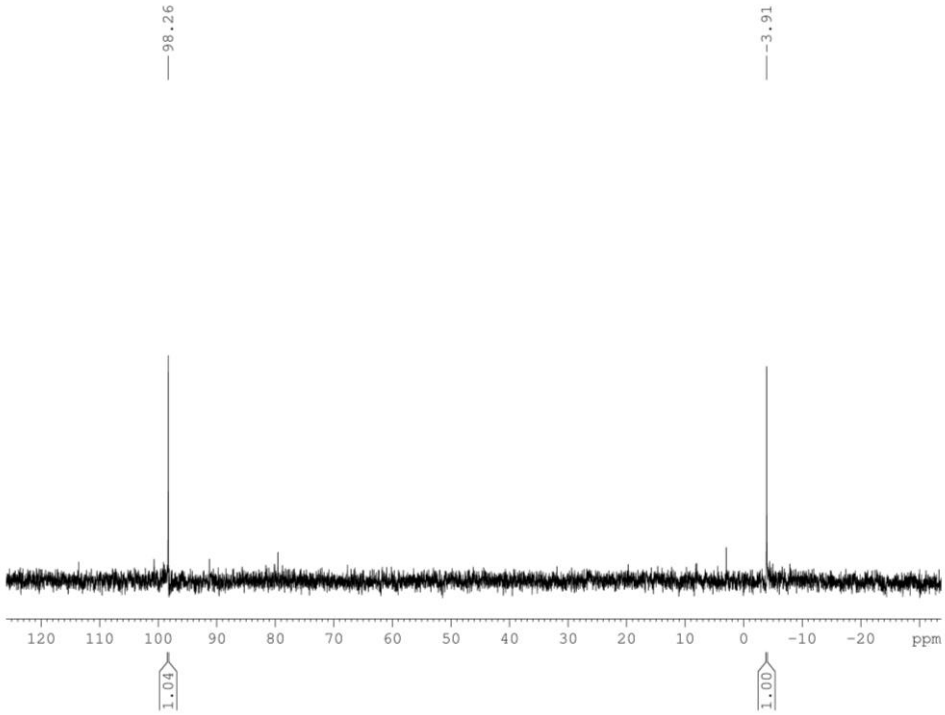


Figure S21: $^{29}Si\{^{1}H\}$ NMR of a sample of **5**-*Z* in [D_8]-toluene after 9 days in solution (complete isomerization of **5**-*Z* to **5**-*E* happened during this time).

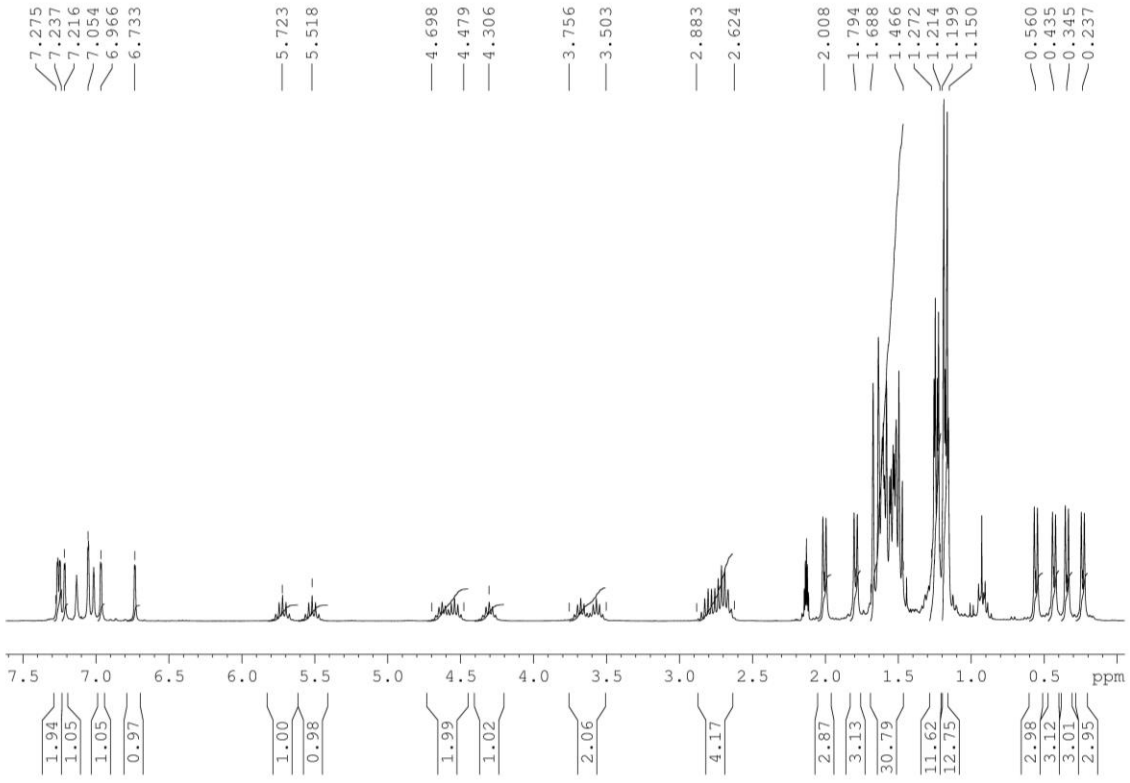


Figure S22: ^{1}H NMR of **5**-*E* in [D_8]-toluene.

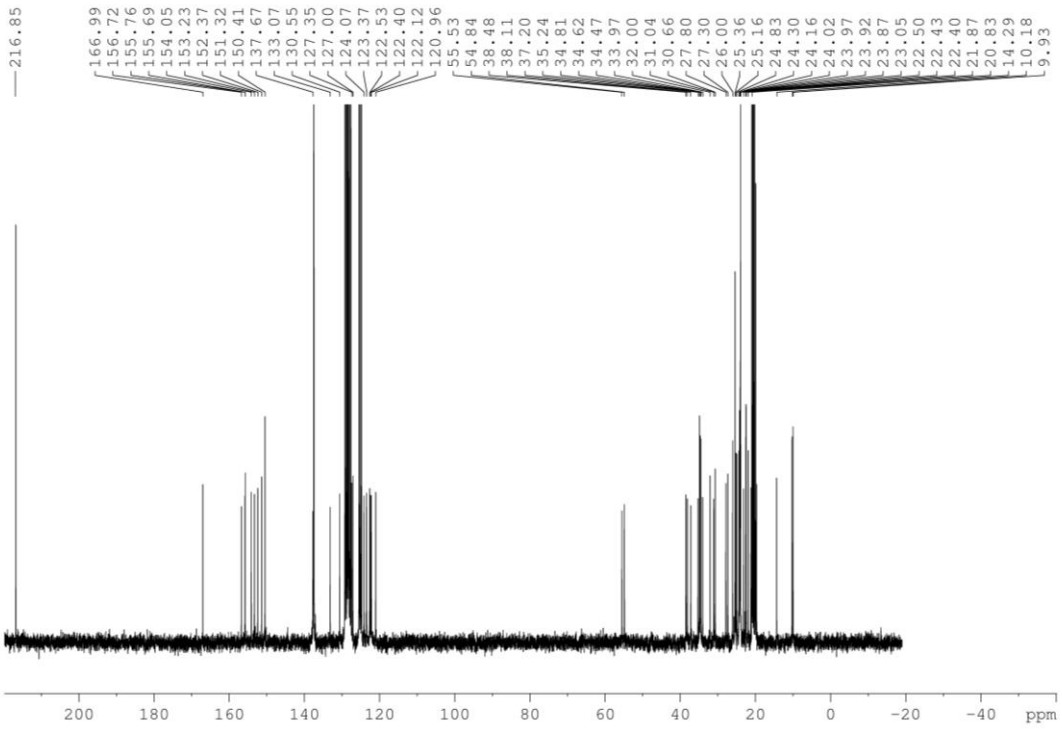


Figure S23: $^{13}C\{^{1}H\}$ NMR of **5**-*E* in $[D_8]$-toluene.

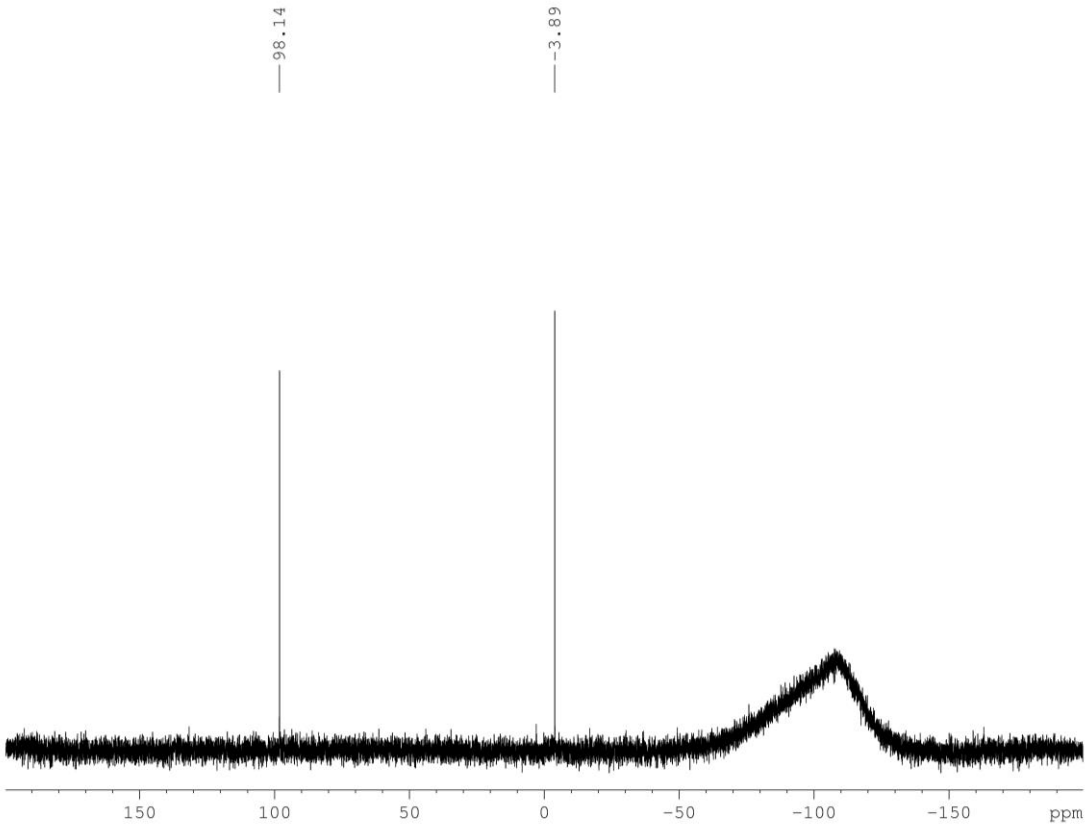


Figure S24: $^{29}Si\{^{1}H\}$ NMR of **5**-*E* in $[D_8]$-toluene.

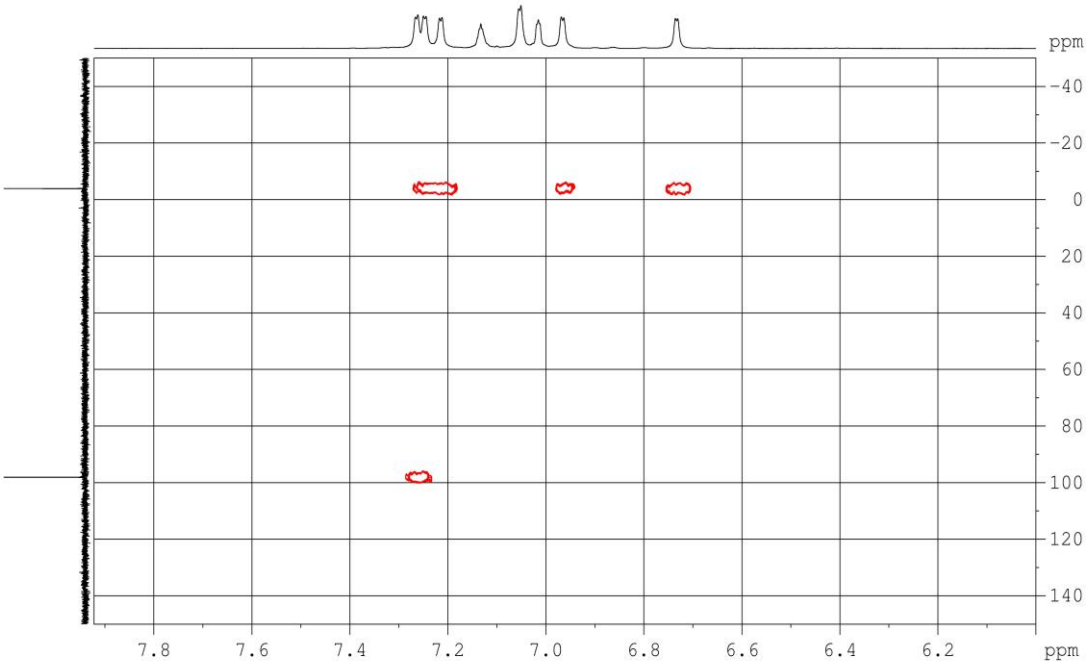


Figure S25: 1H-^{29}Si 2D-NMR(zoom) of **5**-*E* in [D_8]-toluene.

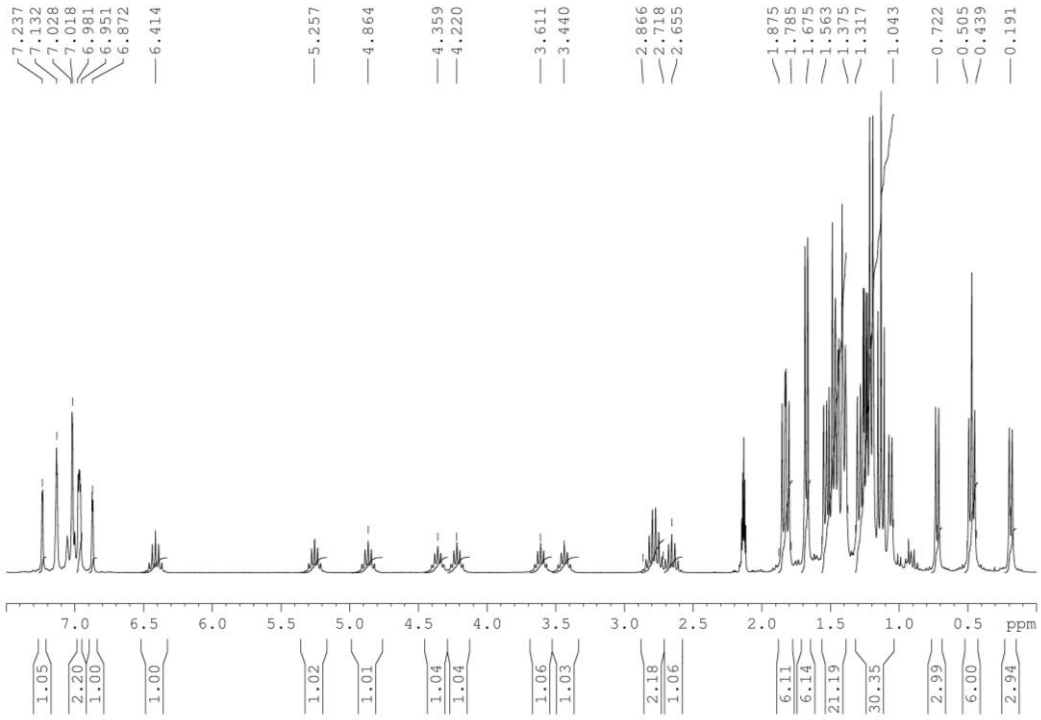


Figure S26: ^{1}H NMR of **6** in [D_8]-toluene.

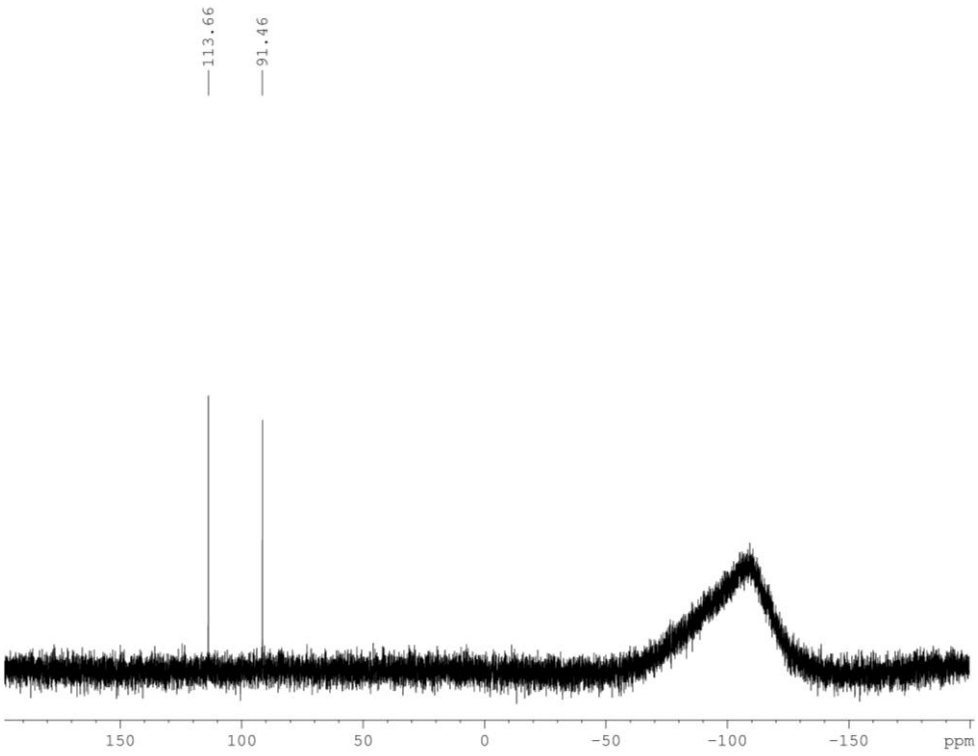


Figure S27: $^{29}Si\{^{1}H\}$ NMR of **6** in [D_8]-toluene.

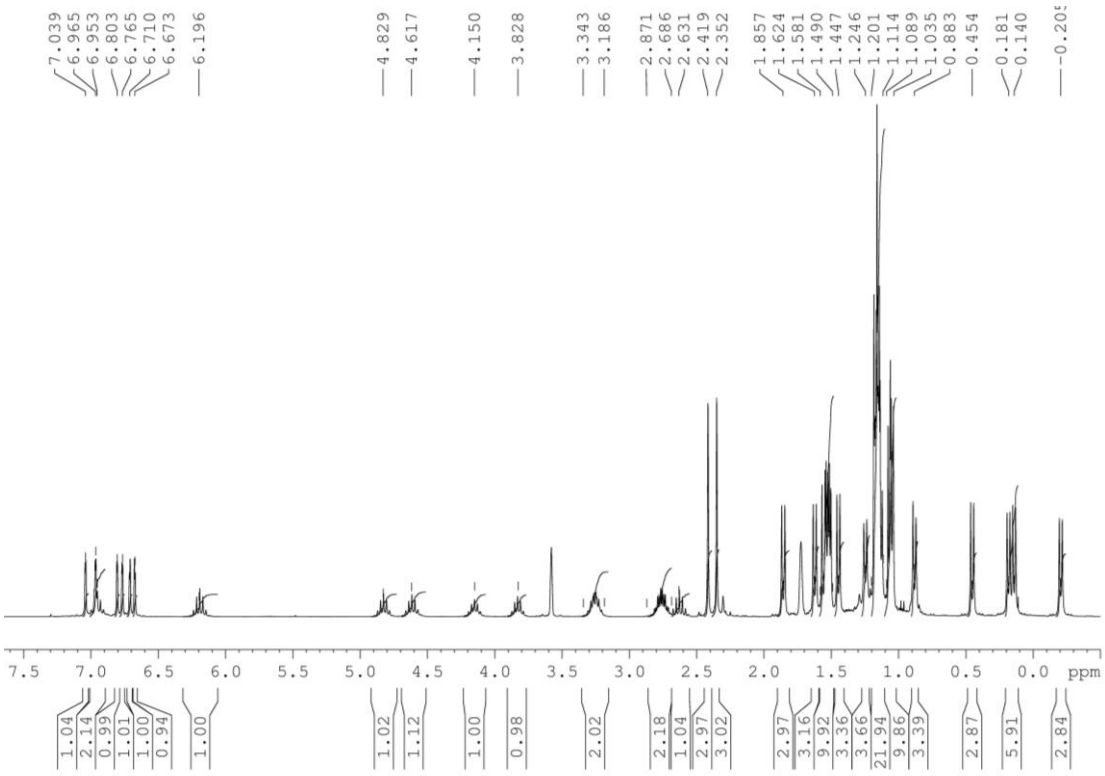


Figure S28: ^{1}H NMR of **6** in [D_8]-THF.

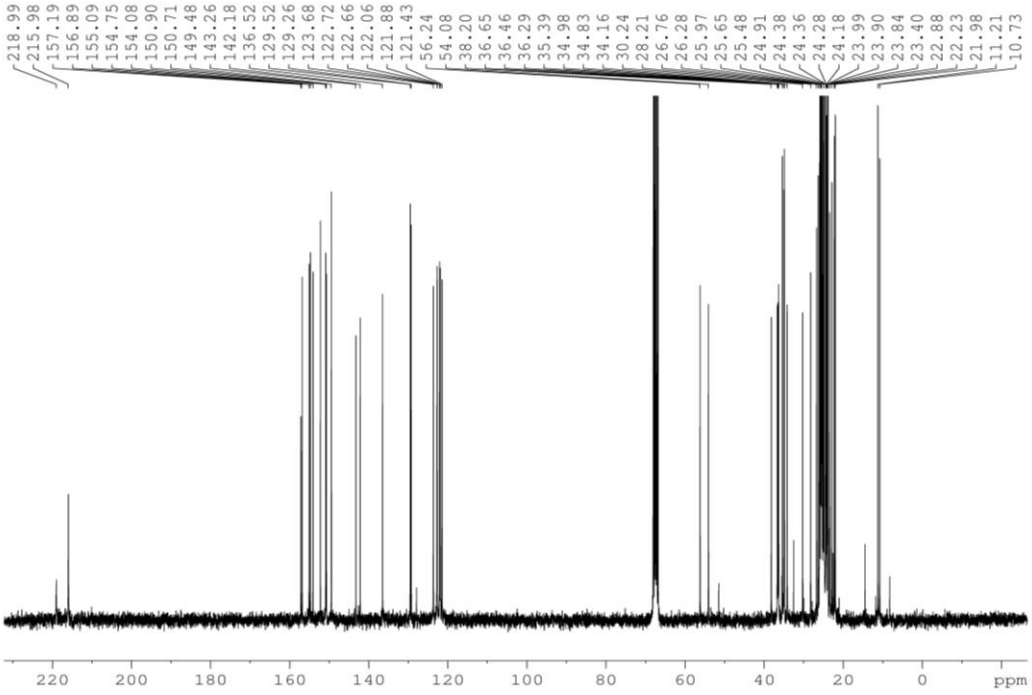


Figure S29: $^{13}C\{^{1}H\}$ NMR of **6** in $[D_8]$-THF.

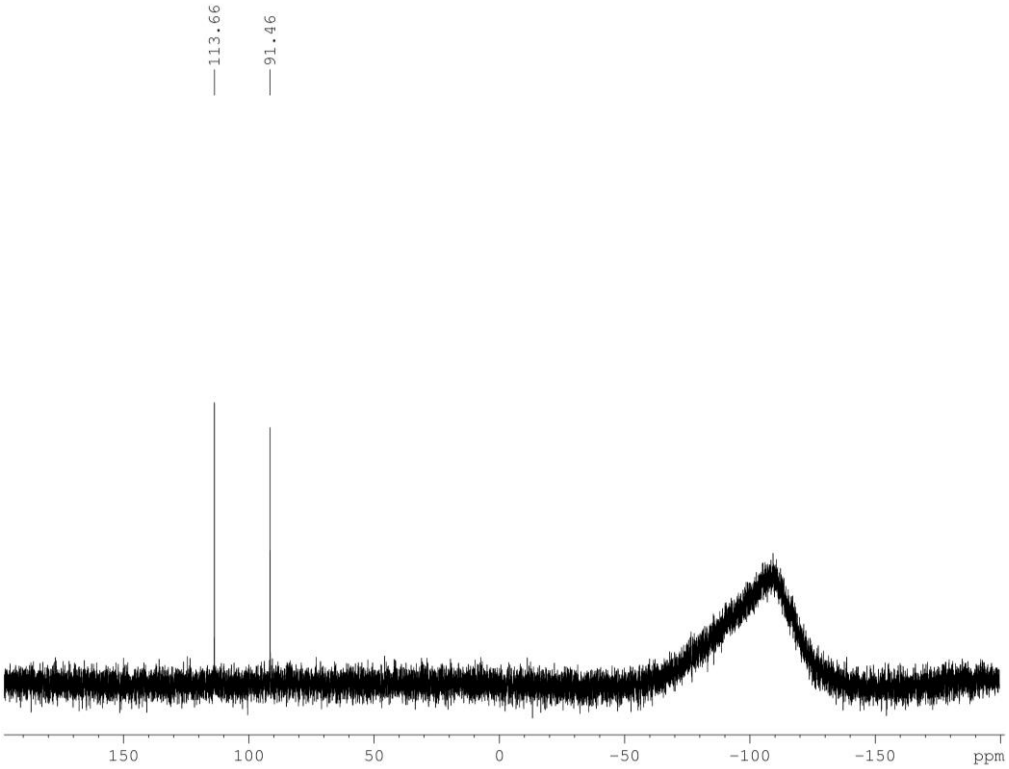


Figure S30: $^{29}Si\{^{1}H\}$ NMR of **6** in $[D_8]$-toluene.

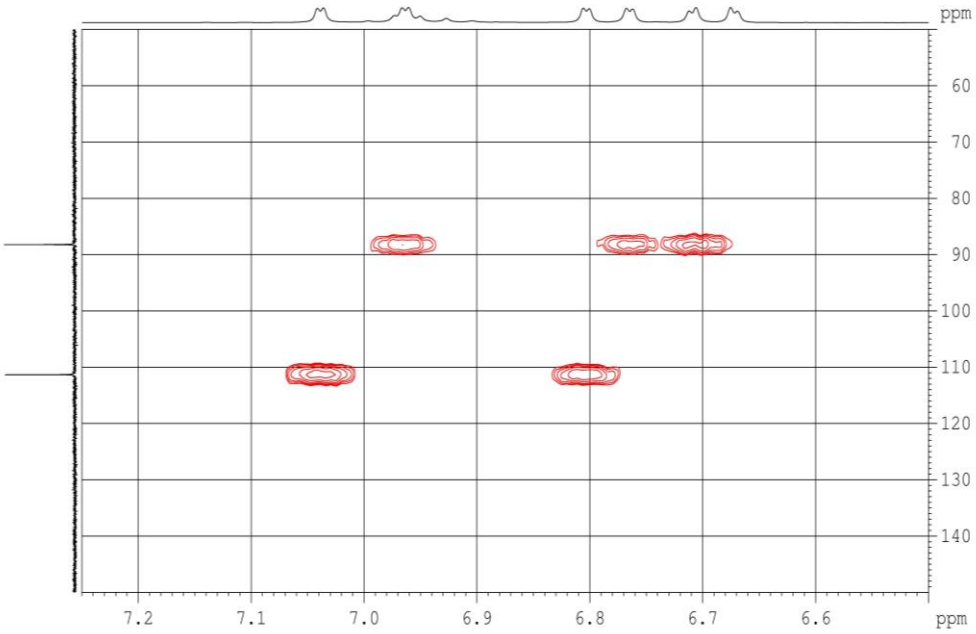


Figure S31: ^{1}H-^{29}Si 2D-NMR(zoom) of **6** in [D_8]-THF.

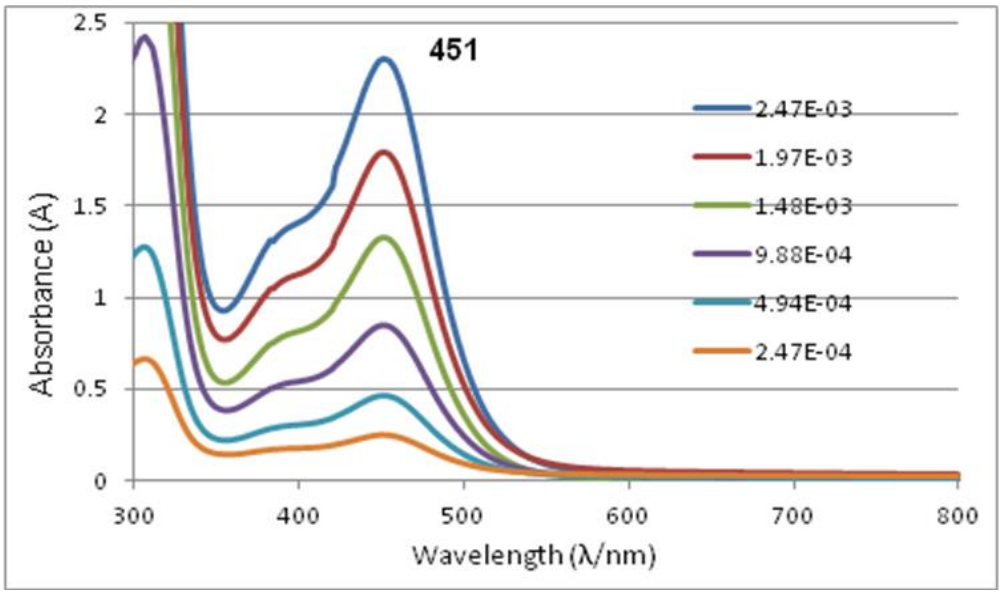


Figure S32: UV/vis spectra of **4**-*E* and **4**-*Z* in hexane at different concentrations.

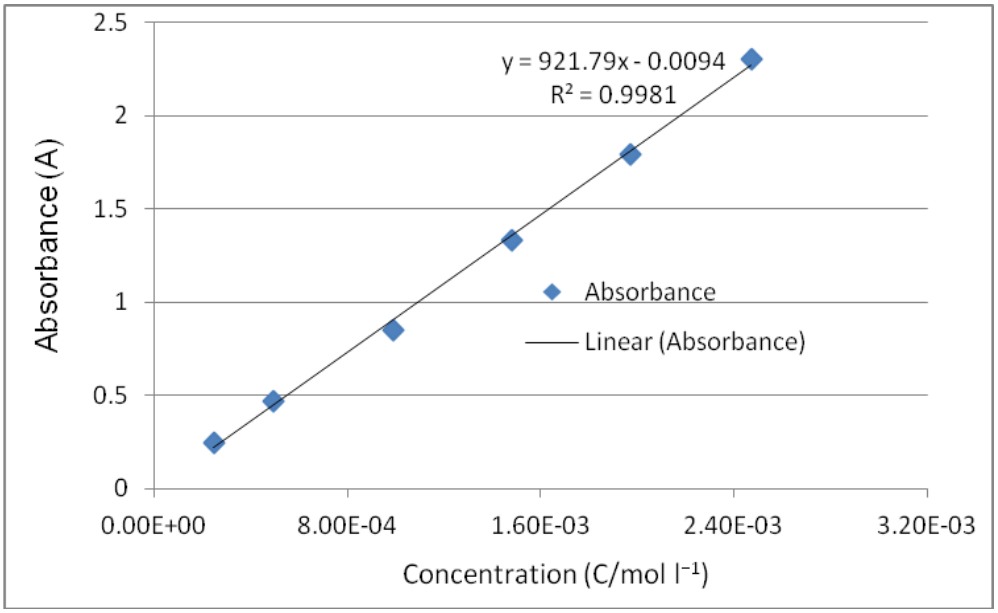


Figure S33: Linear regression of **4**-*E* and **4**-*Z* at 503 nm.

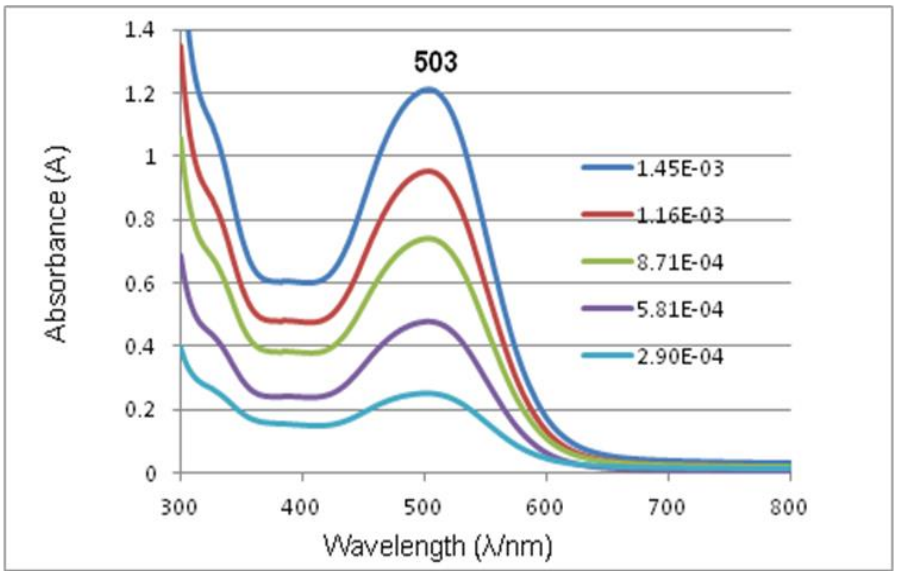


Figure S34: UV/vis spectra of **5**-*Z* in hexane at different concentrations.

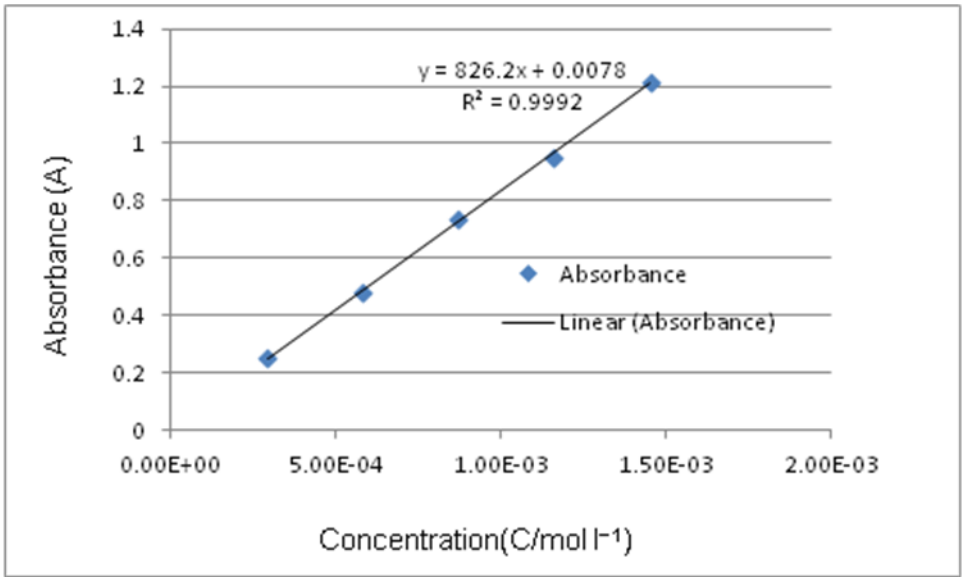


Figure S35: Linear regression of **5**-*Z* at 503 nm.

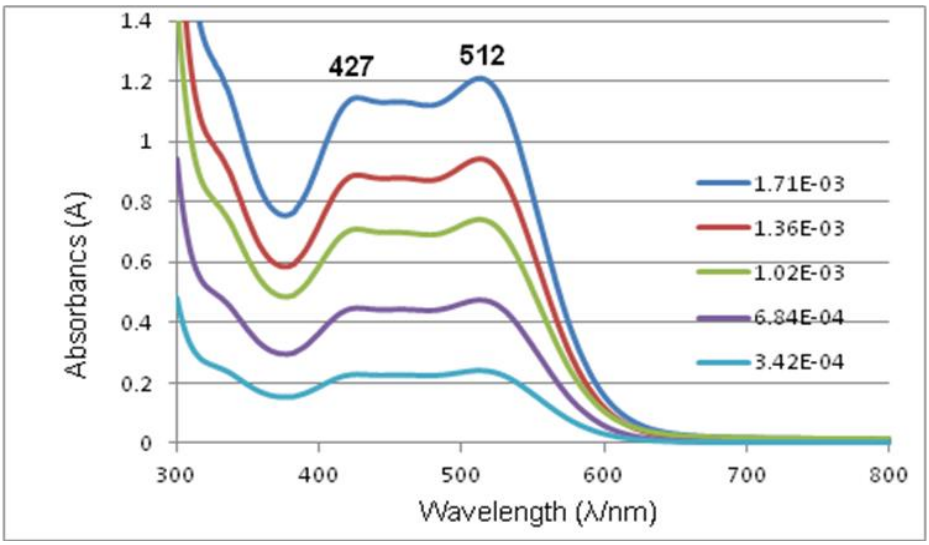


Figure S36: UV/vis spectra of **5**-*E* in hexane at different concentrations.

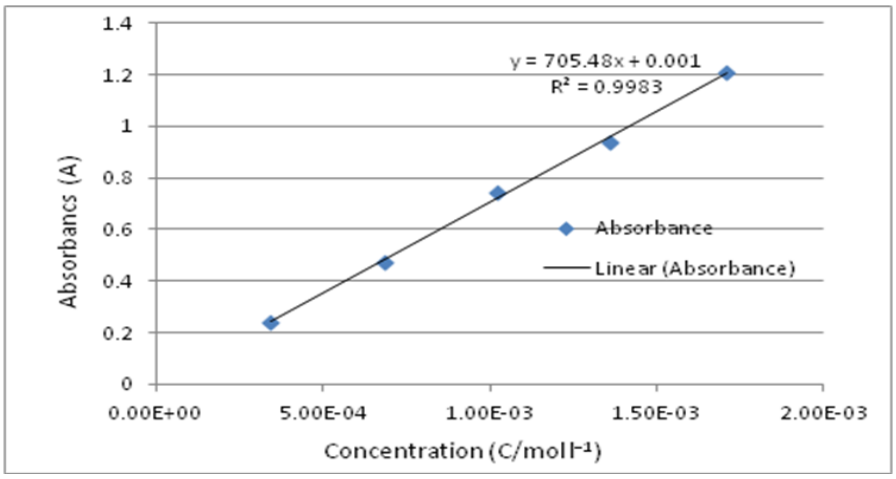


Figure S37: Linear regression of **5**-*E* at 512 nm.

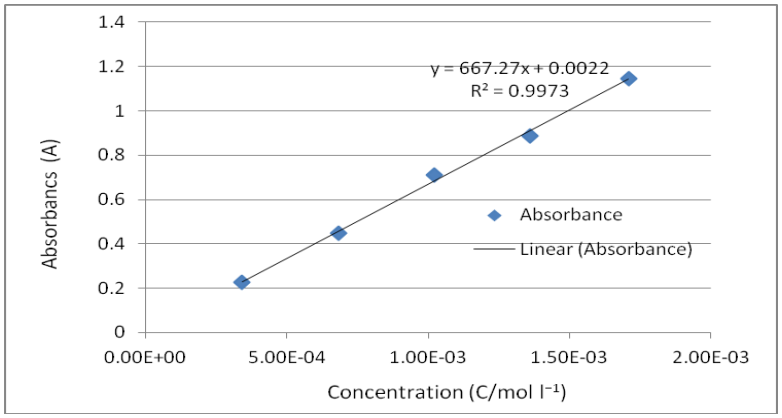


Figure S38: Linear regression of **5**-*E* at 427 nm.

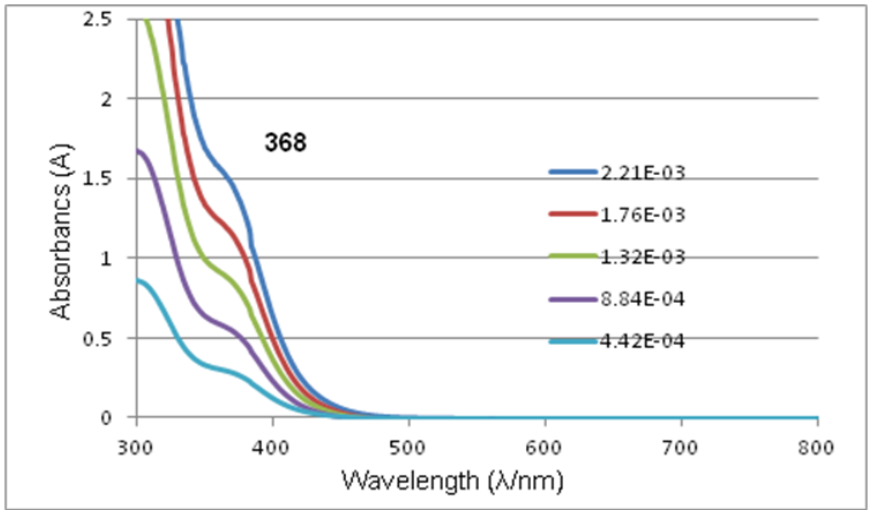


Figure S39: UV/vis spectra of **6** in THF at different concentrations.

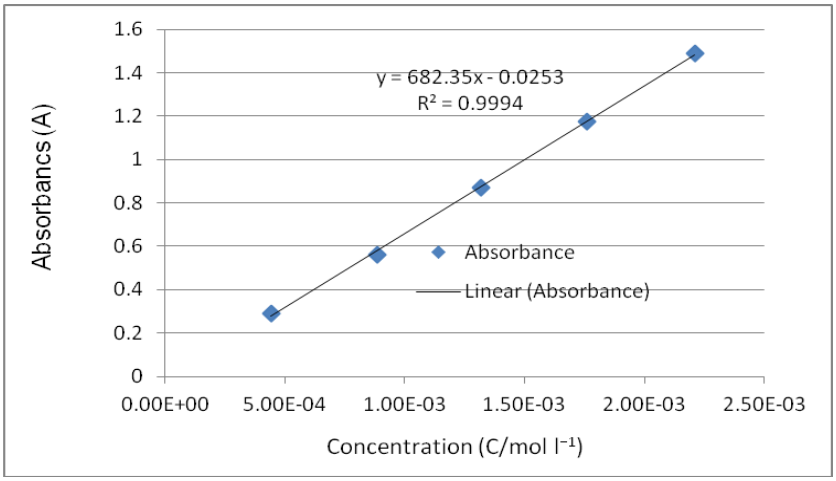


Figure S40: Linear regression of **6** at 368 nm.

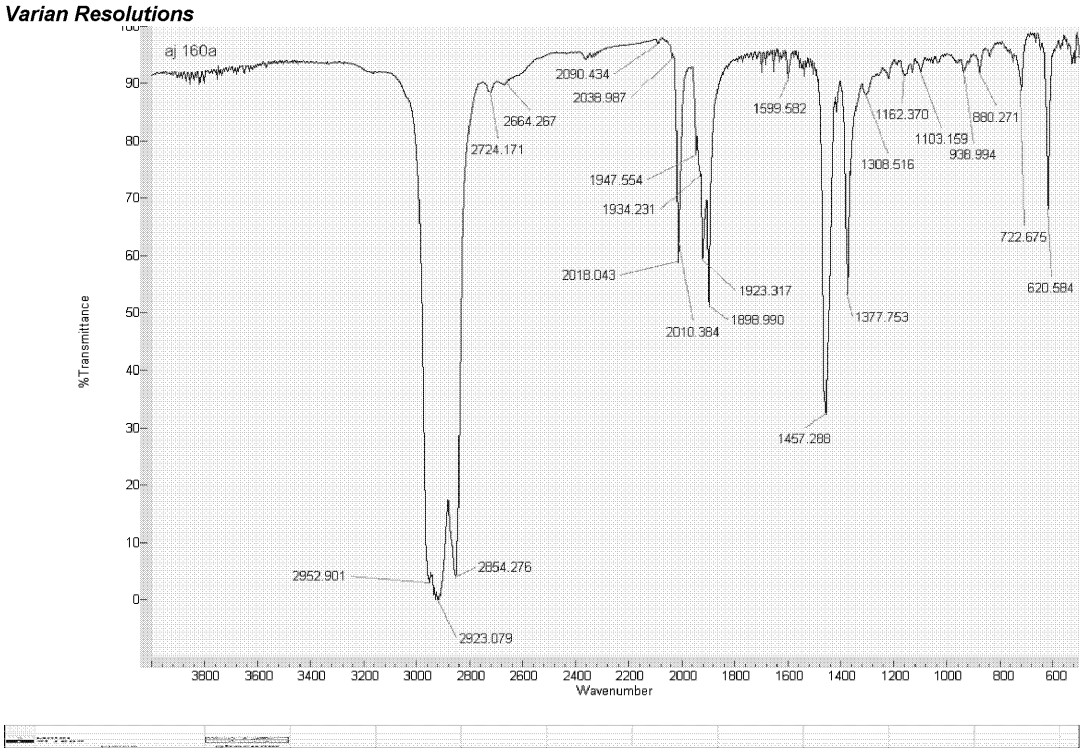


Figure S41: IR spectrum of **5**-*Z*.

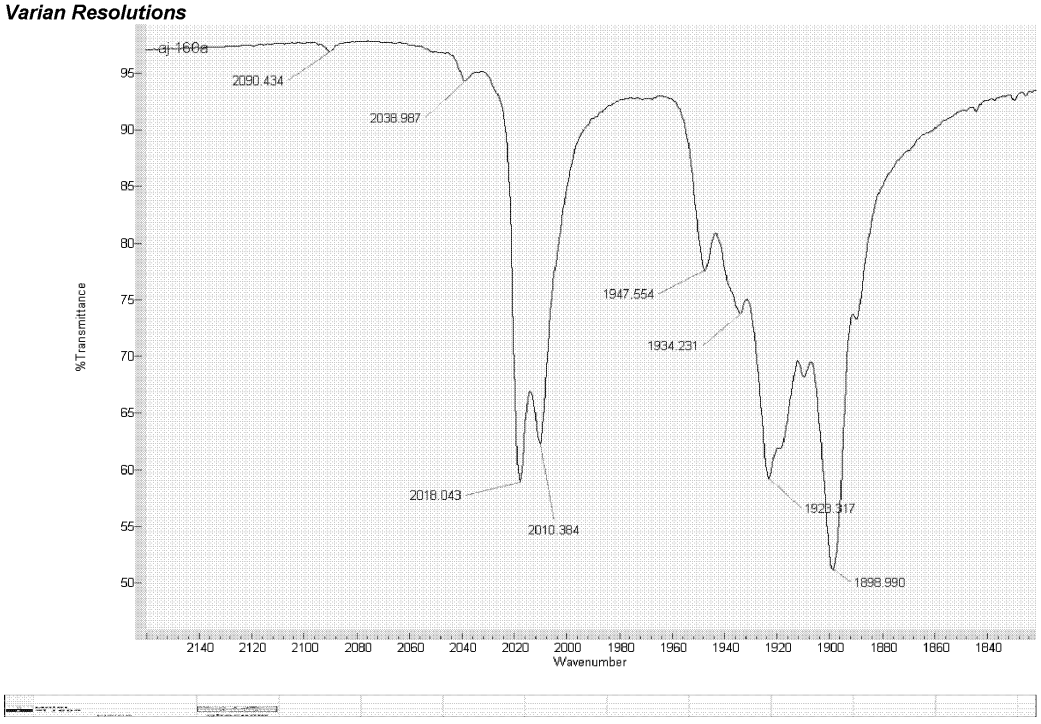


Figure S42: IR spectrum of **5**-*Z* (zoom).

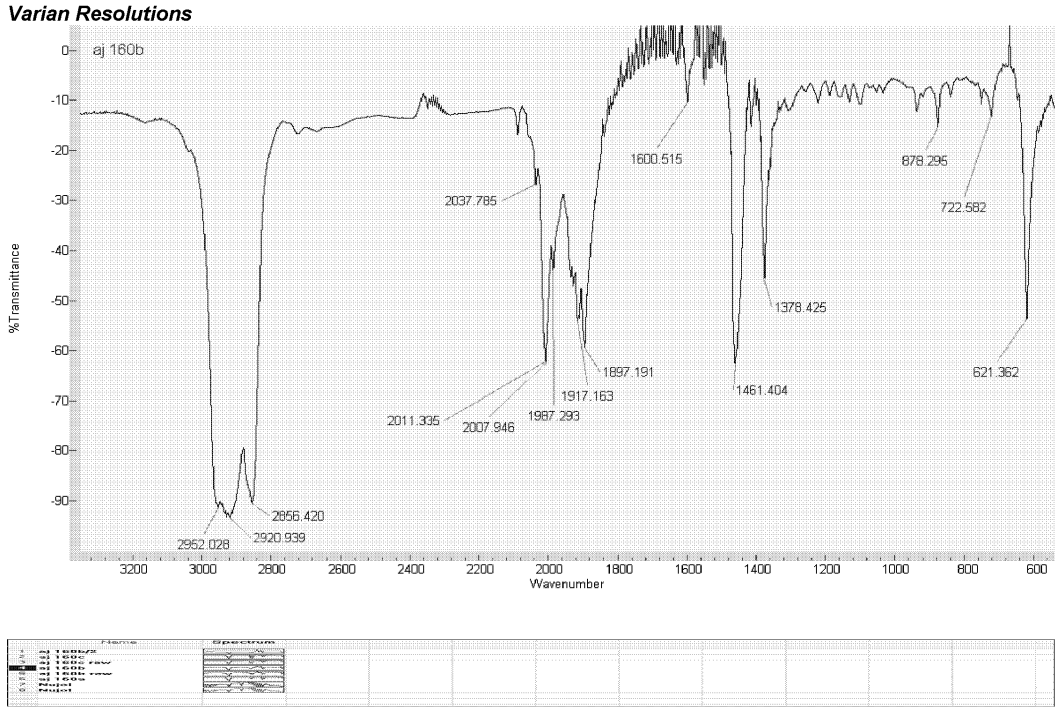


Figure S43: IR spectrum of **5**-*E*.

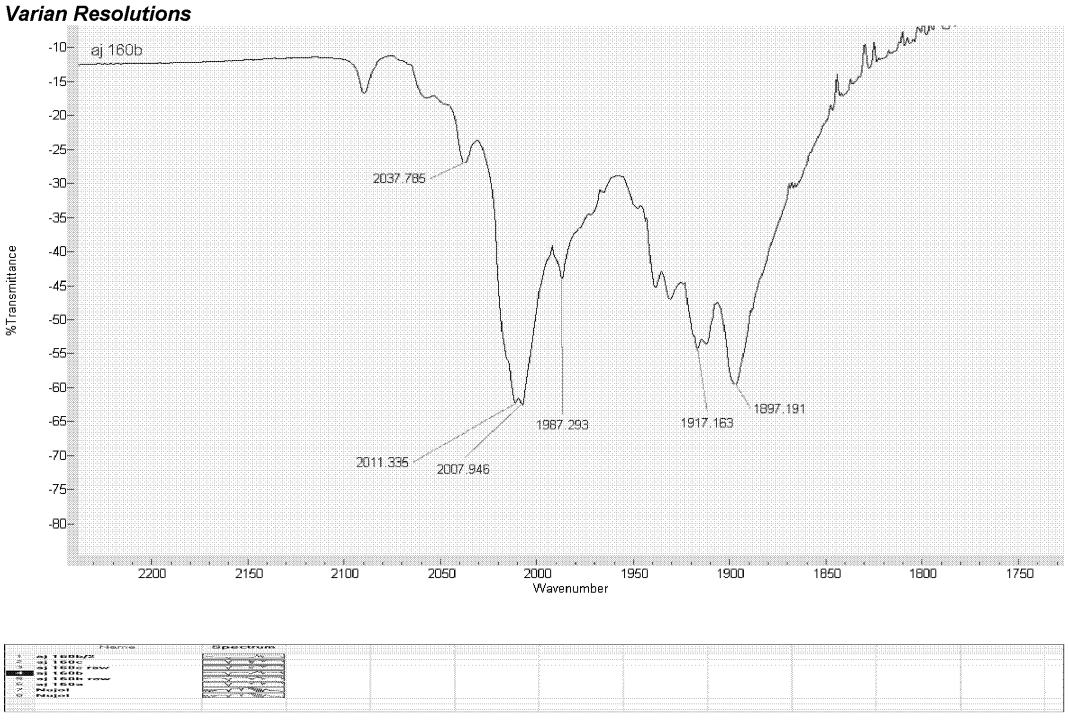


Figure S44: IR spectrum of **5**-*E* (zoom).

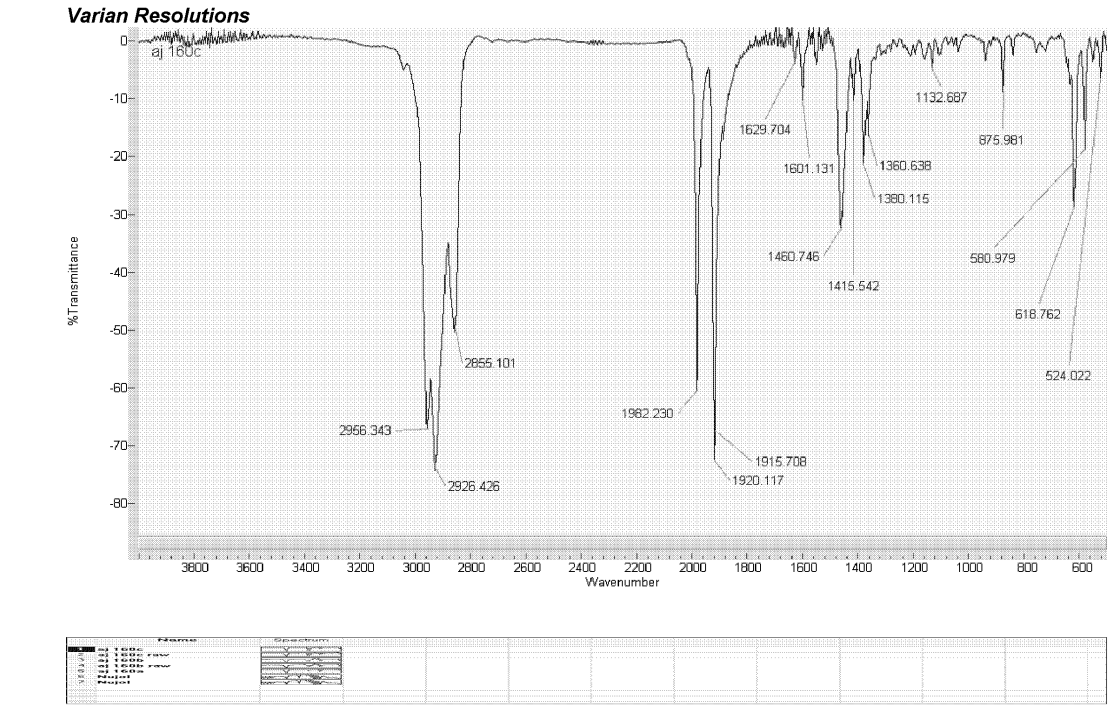


Figure S45: IR spectrum of **6**.

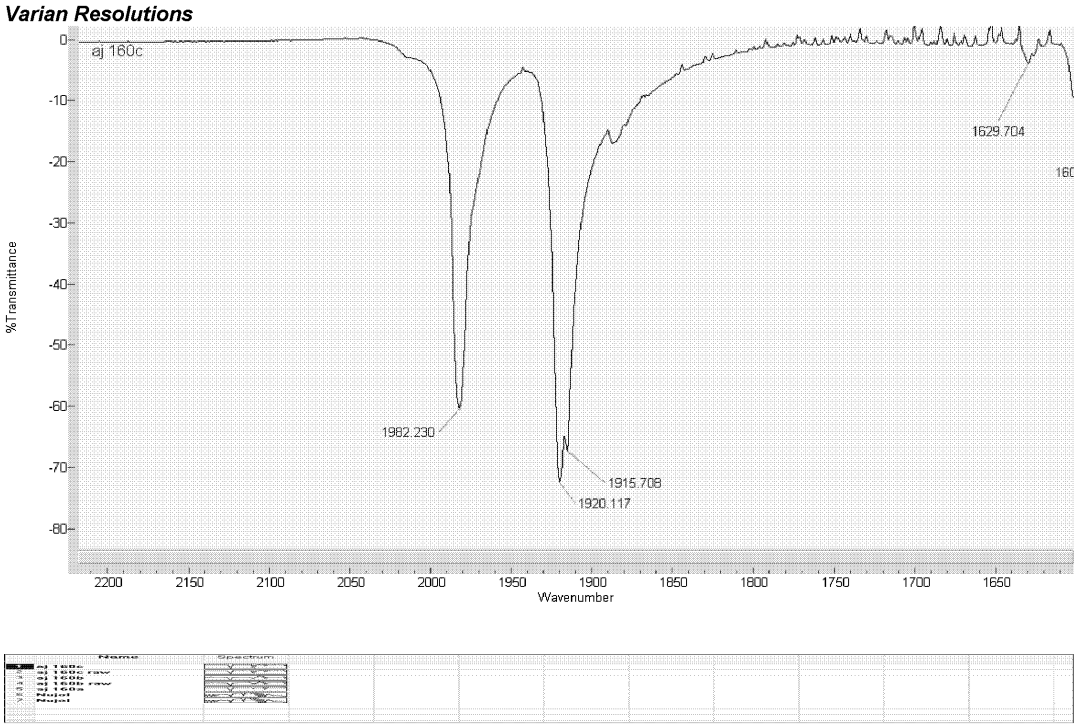


Figure S44: IR spectrum of **6** (zoom).

Table S1. Crystal data and structure refinement for **4**-*E*.

Identification code	sh3241a	
Empirical formula	C56 H89 Cl Ge N2 Si2	
Formula weight	954.51	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.3816(11) Å	α= 90°.
	b = 10.9027(6) Å	β= 90.840(3)°.
	c = 25.5288(13) Å	γ = 90°.
Volume	5672.3(5) $Å^3$	
Z	4	
Density (calculated)	1.118 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	2064	
Crystal size	0.16 x 0.15 x 0.05 mm^3	
Theta range for data collection	1.60 to 28.33°.	
Index ranges	-20<=h<=27, -14<=k<=13, -31<=l<=34	
Reflections collected	48361	
Independent reflections	14017 [R(int) = 0.1264]	
Completeness to theta = 28.33°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9707 and 0.9035	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14017 / 179 / 589	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1011	
R indices (all data)	R1 = 0.1802, wR2 = 0.1332	
Largest diff. peak and hole	0.827 and -0.923 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **5**-*E*•C_5H_{12}.

Identification code	sh3359	
Empirical formula	C60H89 Cl Fe Ge N2 O4 Si2 x .25 C5 H12	
Formula weight	1140.44	
Temperature	122(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.2910(4) Å	α= 89.1430(10)°.
	b = 19.9842(5) Å	β= 88.102(2)°.
	c = 24.8636(7) Å	γ = 76.122(2)°.
Volume	6407.6(3) $Å^3$	
Z	4	
Density (calculated)	1.182 Mg/m^3	
Absorption coefficient	0.818 mm^{-1}	
F(000)	2434	
Crystal size	0.34 x 0.29 x 0.15 mm^3	
Theta range for data collection	1.05 to 27.10°.	
Index ranges	-17<=h<=17, -25<=k<=25, -31<=l<=31	
Reflections collected	105034	
Independent reflections	28114 [R(int) = 0.0436]	
Completeness to theta = 27.10°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8872 and 0.7684	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	28114 / 504 / 1408	
Goodness-of-fit on F^2	1.427	
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1620	
R indices (all data)	R1 = 0.0967, wR2 = 0.1744	
Largest diff. peak and hole	2.142 and -0.789 $e.Å^{-3}$	

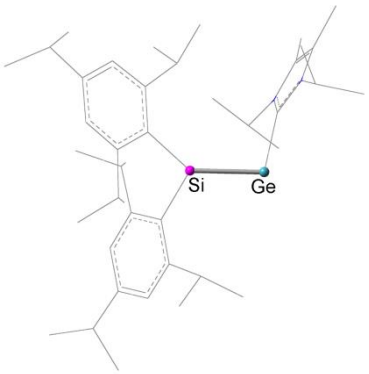
Table S3. Crystal data and structure refinement for **6**.

Identification code	sh3315	
Empirical formula	C59 H89 Cl Fe Ge N2 O3 Si2	
Formula weight	1094.39	
Temperature	132(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 19.6288(5) Å	α= 90°.
	b = 24.6607(7) Å	β= 90°.
	c = 24.6974(7) Å	γ = 90°.
Volume	11955.0(6) $Å^3$	
Z	8	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.873 mm^{-1}	
F(000)	4672	
Crystal size	0.65 x 0.49 x 0.20 mm^3	
Theta range for data collection	1.56 to 27.92°.	
Index ranges	-25<=h<=17, -31<=k<=32, -31<=l<=32	
Reflections collected	104743	
Independent reflections	14312 [R(int) = 0.0577]	
Completeness to theta = 27.92°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8448 and 0.6026	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14312 / 200 / 646	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.0995	
R indices (all data)	R1 = 0.0732, wR2 = 0.1131	
Largest diff. peak and hole	1.184 and -0.536 $e.Å^{-3}$	

Computational Details

TDDFT calculation of NHC-stabilized silagermenylidene, $Tip_2Si{=}Ge{:}NHC^{iPr_2Me_2}$ (II):

The calculation was performed using X-ray coordinates of **II** in the presence of heptane as the solvent in Tomasi's Polarized Continuum Model (PCM) at the at the B3LYP level of theory and 6-31G(d,p) basis set, using *Gaussian 09* suite of programs.[S1]

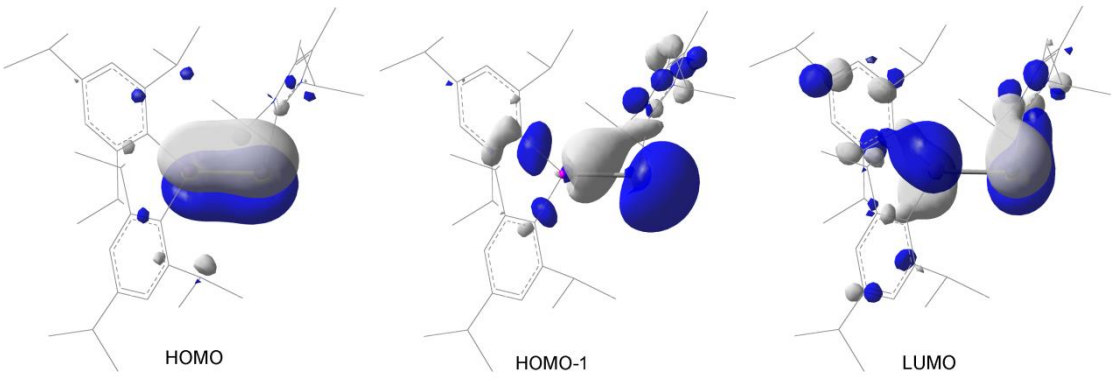


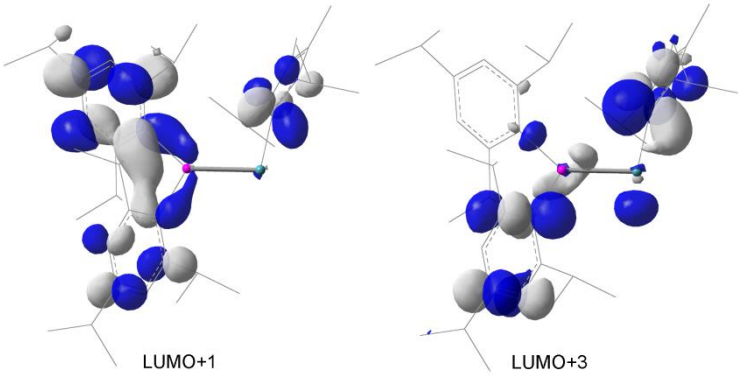
TDDFT output section:

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      2.8237 eV  439.08 nm
f=0.2150  <S**2>=0.000
     186 -> 187        0.65859
     186 -> 188        0.11108
     186 -> 190       -0.16433
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -4075.13936484
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:      Singlet-A      3.1436 eV  394.40 nm
f=0.0531  <S**2>=0.000
     185 -> 187       -0.10320
     186 -> 187       -0.13050
     186 -> 188        0.67695

 Excited State   3:      Singlet-A      3.3653 eV  368.42 nm
f=0.0836  <S**2>=0.000
     185 -> 187        0.54228
     186 -> 188        0.15366
     186 -> 190        0.39857

 Excited State   4:      Singlet-A      3.4244 eV  362.06 nm
f=0.0198  <S**2>=0.000
     185 -> 187       -0.41294
     186 -> 189       -0.24211
     186 -> 190        0.50002
```

```
 Excited State   5:      Singlet-A      3.4660 eV  357.71 nm
f=0.0094  <S**2>=0.000
     185 -> 187       -0.10328
     186 -> 189        0.65678
     186 -> 190        0.21756

 Excited State   6:      Singlet-A      3.6781 eV  337.09 nm
f=0.0100  <S**2>=0.000
     186 -> 191        0.69103

 Excited State   7:      Singlet-A      3.8296 eV  323.76 nm
f=0.0124  <S**2>=0.000
     186 -> 192        0.66052
     186 -> 194        0.10587

 Excited State   8:      Singlet-A      4.2175 eV  293.98 nm
f=0.1432  <S**2>=0.000
     185 -> 188        0.49449
     186 -> 193       -0.47357

 Excited State   9:      Singlet-A      4.2292 eV  293.16 nm
f=0.1301  <S**2>=0.000
     185 -> 188        0.46036
     186 -> 193        0.51926

 Excited State  10:      Singlet-A      4.4742 eV  277.11 nm
f=0.0345  <S**2>=0.000
     182 -> 187        0.11140
     185 -> 189        0.63318
     185 -> 190       -0.25113
```

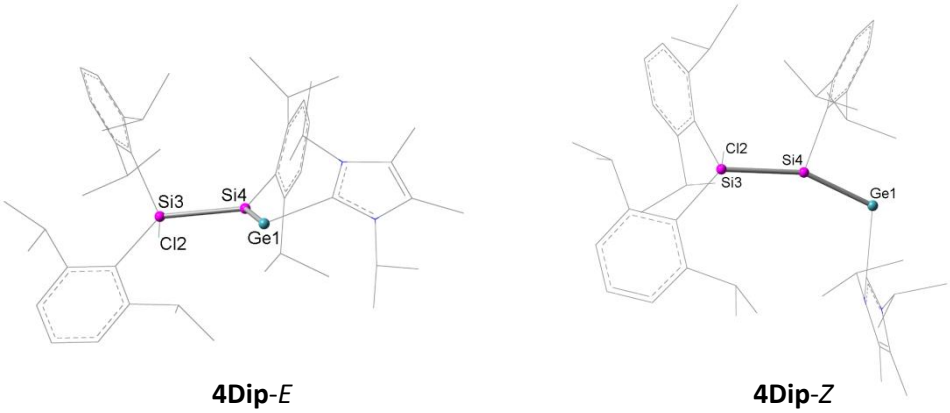
Contour plots of II at 0.04 isosurface:





Theoretical calculation of NHC-stabilized silagermenylidene, Tip(SiTip$_2$Cl)Si=Ge:NHC^{iPr_2Me_2} (4).

DFT calculations were performed on model systems **4Dip**-*E* and **4Dip**-*Z* (Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$ instead of Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) at the B3LYP level of theory with the 6-31G(d,p) basis set using *Gaussian 03* suite of programs.[S2] Compounds **4Dip**-*E* and **4Dip**-*Z* were optimized at the stationary point with number of imaginary frequency NIMAG = 0. The ^{29}Si{^{1}H} NMR and ^{13}C{^{1}H} NMR for **4Dip**-*E* and **4Dip**-*Z* were computed at the GIAO level with SCRF (solvent=benzene) correction, 6-311+G(2d,p) basis set on Ge, Si and Cl atoms, and 6-31G(d,p) basis set on C, N and H atoms.



	4Dip-*E*	**4Dip**-*Z*
E_{abs}[Hartree]	-5056.562259	-5056.555114
E_{rel} [kcal mol^{-1}]	0.00	+4.48
H [Hartree]	-5056.498292	-5056.491162
H [kcal mol^{-1}]	0.00	+4.47
G[Hartree]	-5056.657683	-5056.650280
G [kcal mol^{-1}]	0.00	+4.64

NIMAG	0	0

Cartesian coordinates of calculated stationary points

4Dip-*E*

Ge	1.66978100	-1.45096800	-0.08428900
Cl	-2.88697700	1.21540300	-1.86807000
Si	-2.00765300	-0.09084600	-0.40229000
Si	0.37995500	0.32052500	-0.61329300
N	4.51694100	-0.50278100	-0.80833800
N	4.25384000	-0.82268800	1.32407400
C	-2.99068200	-1.70791400	-0.91079900
C	-4.41713000	-1.70894800	-0.81912300
C	-5.14258100	-2.80695000	-1.30378300
H	-6.22494700	-2.80068800	-1.21804900
C	-4.51925600	-3.89427200	-1.89937300
C	-3.13511500	-3.90992900	-1.98104400
H	-2.63349100	-4.76200100	-2.42936300
C	-2.36566800	-2.85305200	-1.47798700
C	-5.26241700	-0.58496200	-0.21159100
H	-4.60552200	0.23024100	0.08221400
C	-5.98684500	-1.04309000	1.06954200
H	-6.68120300	-1.86609500	0.86888200
H	-6.56565400	-0.21451300	1.49239400
H	-5.27606500	-1.37661300	1.83022000
C	-6.26669800	-0.00652200	-1.22781200
H	-5.75923700	0.33566100	-2.13317500
H	-6.79738800	0.84633200	-0.78988600
H	-7.02099000	-0.74498000	-1.51912300
C	-0.85713400	-3.01017200	-1.54490500
H	-0.43550700	-2.24259200	-0.89399800
C	-0.27085200	-2.75326300	-2.94314600
H	-0.50495400	-3.57019100	-3.63556500
H	0.81636200	-2.65007200	-2.85472300
H	-0.65683500	-1.82272300	-3.37022900
C	-0.35981000	-4.35382200	-0.98223000
H	-0.79811200	-4.56020000	-0.00101700
H	0.72838900	-4.32093500	-0.86619500
H	-0.60590200	-5.19265700	-1.64197800
C	-2.49822100	0.42185900	1.40611100
C	-2.35575800	-0.60336500	2.38975300
C	-2.80760800	-0.39267900	3.69850700
H	-2.70053800	-1.18608900	4.43260300
C	-3.38363600	0.81303300	4.07426700
C	-3.45858800	1.84237500	3.14552600
H	-3.87264900	2.79777400	3.45210900
C	-3.00496100	1.68987200	1.82645900
C	-1.65767500	-1.94031000	2.12181100
H	-1.31646500	-1.96524700	1.08389700
C	-0.37594200	-2.07119100	2.96643100
H	0.25526200	-1.18866600	2.83690300
H	0.19920800	-2.94488200	2.64153800
H	-0.60456300	-2.18419800	4.03174700

C	-2.57887300	-3.15519200	2.32662200
H	-2.94511500	-3.20814300	3.35768500
H	-2.03545900	-4.08423400	2.12206500
H	-3.44349100	-3.11628100	1.66017000
C	-3.09244000	2.94003500	0.93979200
H	-2.50562200	2.76791200	0.03914000
C	-4.54160100	3.23968300	0.50861400
H	-4.97406300	2.41891100	-0.06618700
H	-4.57309200	4.13735000	-0.11883200
H	-5.17990700	3.41862500	1.38163500
C	-2.49015400	4.19026400	1.61240700
H	-3.08249400	4.52989300	2.46891500
H	-2.46142100	5.01295700	0.89026700
H	-1.46888900	4.01312500	1.95377100
C	0.65824300	2.22341100	-0.74010800
C	0.35179000	2.90406700	-1.95641000
C	0.39919900	4.30187600	-1.99805300
H	0.15586200	4.81995100	-2.91966300
C	0.75484200	5.04411800	-0.87607600
C	1.13623700	4.38543300	0.28523900
H	1.45883200	4.96801100	1.14370900
C	1.12452900	2.98506500	0.36710600
C	0.09500900	2.14574500	-3.25936100
H	-0.33187000	1.17037400	-2.99927500
C	-0.88655400	2.83227000	-4.22214400
H	-1.81440200	3.11313800	-3.71981300
H	-1.13871100	2.15124200	-5.04154900
H	-0.45326500	3.73123300	-4.67531900
C	1.43310600	1.87812500	-3.97602200
H	1.92256600	2.81895100	-4.25260800
H	1.27443800	1.29454200	-4.89028500
H	2.11322100	1.32157000	-3.32743500
C	1.69571100	2.35302500	1.63812400
H	1.74499800	1.27185500	1.47220600
C	3.13888700	2.84277500	1.87480600
H	3.78242900	2.60555100	1.02165200
H	3.56600900	2.37200800	2.76641400
H	3.18363300	3.92497400	2.03368400
C	0.82402100	2.58875900	2.88287200
H	0.71628300	3.65714000	3.10217500
H	1.27631000	2.11739000	3.76348600
H	-0.17601800	2.16682100	2.75355600
C	3.57542600	-0.72988500	0.14628000
C	5.79517200	-0.48605000	-0.23616700
C	5.62888800	-0.68650200	1.10634400
C	4.16530400	-0.58976100	-2.25032300
H	3.08653500	-0.40865100	-2.25936900
C	4.83303700	0.47888000	-3.11697800
H	4.72876800	1.47222200	-2.67149300
H	4.33348300	0.49726100	-4.08945100
H	5.89141400	0.28257100	-3.29975000
C	4.37951000	-2.02370300	-2.74653400
H	5.43460100	-2.31606700	-2.73306400
H	4.01333400	-2.11753700	-3.77344800

H	3.80894400	-2.71271300	-2.11671500
C	7.06721800	-0.26081000	-0.98923900
H	7.13424500	0.75298100	-1.39649900
H	7.18365700	-0.96212700	-1.82096100
H	7.92019300	-0.40315700	-0.32333300
C	6.67057200	-0.72407400	2.17844500
H	7.66498400	-0.69633500	1.72931100
H	6.61126400	-1.63611300	2.78007800
H	6.59496100	0.12964400	2.85952500
C	3.56142800	-1.28244200	2.55582400
H	2.51066900	-1.05831700	2.34652000
C	3.69944400	-2.80133700	2.70618600
H	4.73685900	-3.09858100	2.89158100
H	3.34016700	-3.30949900	1.80732400
H	3.09481500	-3.14106900	3.55258900
C	3.95173100	-0.52263500	3.82514300
H	4.92250300	-0.82767800	4.22211400
H	3.20476600	-0.73579900	4.59542800
H	3.96303100	0.55658900	3.66079400
H	0.76344500	6.13002300	-0.91836300
H	-3.74707900	0.95919600	5.08785600
H	-5.10627000	-4.72348400	-2.28504500

4Dip-*Z*

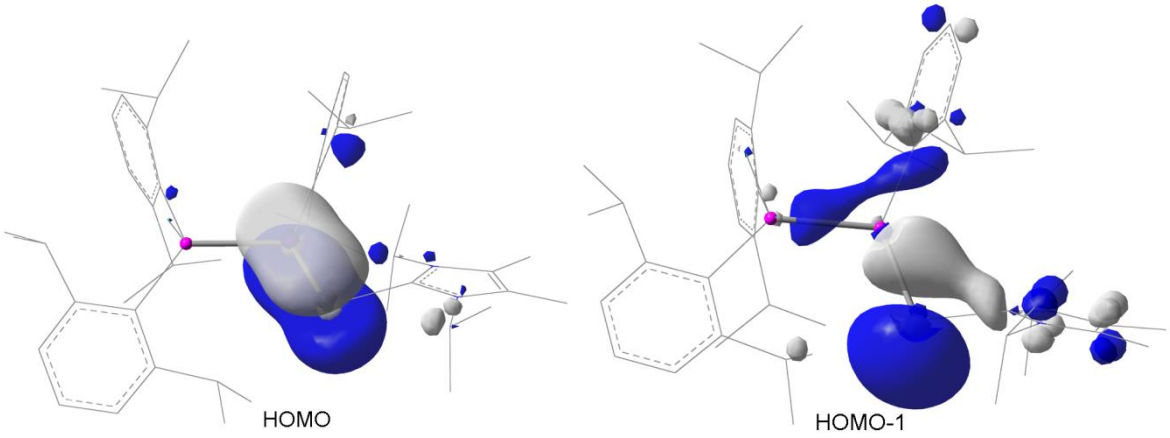
Ge	-2.35140800	1.60372300	0.11701000
Cl	2.11950000	-0.12107700	-2.57494700
Si	1.55054800	-0.65841700	-0.56892700
Si	-0.24260700	0.91094100	-0.16309200
N	-4.50431600	-0.25231400	-0.94904000
N	-4.23293600	-0.53655000	1.18782700
C	1.47283600	-2.58539000	-0.82276000
C	2.68629700	-3.28597800	-1.11554700
C	2.66148000	-4.67574200	-1.29312000
H	3.59034600	-5.19564900	-1.50631400
C	1.48181500	-5.40218400	-1.21656700
C	0.29770900	-4.72842200	-0.96388200
H	-0.63096900	-5.28930900	-0.92625300
C	0.27211400	-3.34007800	-0.76322400
C	4.06013500	-2.63260600	-1.29190800
H	3.96417300	-1.56167400	-1.13411400
C	4.58810800	-2.82293100	-2.72806900
H	4.77160400	-3.87866800	-2.95486200
H	5.53688900	-2.28974400	-2.85566100
H	3.87867200	-2.43532300	-3.46355500
C	5.08791800	-3.13517700	-0.26005600
H	4.74745700	-2.95271400	0.76239400
H	6.04021400	-2.61112000	-0.39478000
H	5.28332500	-4.20757200	-0.36835300
C	-1.10732400	-2.73005600	-0.53719100
H	-0.99975900	-1.67608400	-0.26490900
C	-1.87358900	-3.41125900	0.61134700
H	-2.09075700	-4.46191900	0.39436000
H	-2.83077200	-2.90692200	0.77137900
H	-1.30462000	-3.37801300	1.54597200
C	-1.93153100	-2.77967500	-1.83643300
H	-1.44264000	-2.21513900	-2.63602100
H	-2.92376600	-2.35420700	-1.66677000
H	-2.05962800	-3.81060600	-2.18401200
C	2.91508800	-0.30170400	0.75974700
C	4.03528900	0.56798700	0.60012900
C	5.03784600	0.58287700	1.58138200
H	5.90420800	1.22067700	1.43747100
C	4.94530700	-0.18002800	2.73751500
C	3.81166800	-0.95382500	2.94559300
H	3.71209900	-1.51449100	3.87045800
C	2.79241500	-1.02325400	1.98694200
C	4.23663600	1.52904100	-0.57780200
H	3.31555400	1.56591500	-1.15600500
C	4.50342600	2.97297600	-0.10757000
H	3.72049600	3.32440700	0.56733800
H	4.52165800	3.64267700	-0.97369400
H	5.46833000	3.07249500	0.40152300
C	5.36559300	1.06702100	-1.51947800
H	6.32305500	1.00949700	-0.98912500

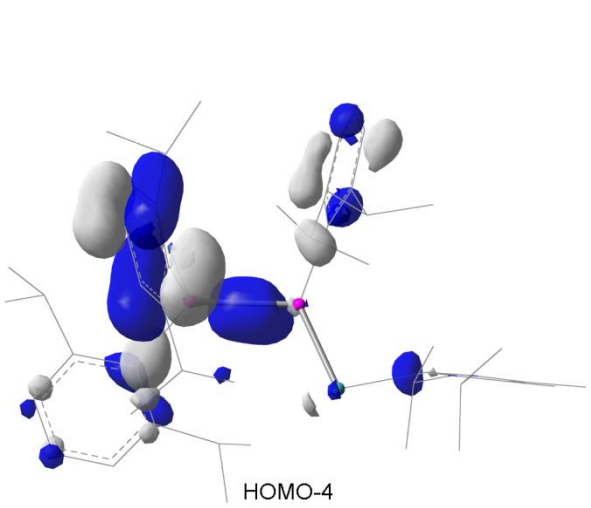
H	5.48431800	1.77779300	-2.34467000
H	5.15992700	0.08664300	-1.95470200
C	1.57062200	-1.87088900	2.36442000
H	0.83629700	-1.81341800	1.55531700
C	1.92004900	-3.35854500	2.55645900
H	2.37844900	-3.78277400	1.66118800
H	1.01759300	-3.93772100	2.78160500
H	2.61473200	-3.49473000	3.39227600
C	0.86532200	-1.32432600	3.62204600
H	1.51204800	-1.38494500	4.50339300
H	-0.03544700	-1.91180800	3.83474100
H	0.56904800	-0.28055600	3.49492200
C	0.57226900	2.67909400	-0.07267300
C	0.87030700	3.27513700	1.18574500
C	1.27667500	4.61492900	1.25042100
H	1.49511200	5.06150200	2.21642200
C	1.39513300	5.38744800	0.10148100
C	1.08746400	4.82398100	-1.13046300
H	1.15834700	5.43548000	-2.02549700
C	0.66622700	3.49122500	-1.23836600
C	0.71961800	2.52646400	2.50884400
H	0.51780400	1.47760000	2.26018700
C	1.98751100	2.56304000	3.37966300
H	2.85612200	2.17506500	2.84248800
H	1.84625000	1.95196400	4.27822100
H	2.22140200	3.57986800	3.71393800
C	-0.49806000	3.04233500	3.29839700
H	-0.37631400	4.09742100	3.56773500
H	-0.62414800	2.47383200	4.22822000
H	-1.41398800	2.94995700	2.70643700
C	0.26486100	2.99707500	-2.62849200
H	0.09289000	1.91709500	-2.56011500
C	-1.06305400	3.64100900	-3.07187700
H	-1.85684300	3.43709500	-2.34632300
H	-1.37356100	3.24948200	-4.04832800
H	-0.96456700	4.72852300	-3.16402000
C	1.35594400	3.22100700	-3.69032400
H	1.53257300	4.28620900	-3.87664100
H	1.05430200	2.76931600	-4.64192000
H	2.30389900	2.76713700	-3.39111100
C	-3.66855000	0.03000500	0.08714500
C	-5.61090300	-0.97866200	-0.49699800
C	-5.44021700	-1.15799600	0.84964500
C	-4.29427600	0.39427400	-2.27343600
H	-3.23828600	0.68418800	-2.23380900
C	-4.48778700	-0.53276400	-3.47571800
H	-3.95896700	-1.47919500	-3.35093200
H	-4.07377300	-0.03485800	-4.35749200
H	-5.53961100	-0.74076300	-3.68579700
C	-5.13571500	1.67141300	-2.37468300
H	-6.20763400	1.45083500	-2.41446000
H	-4.86927600	2.21334400	-3.28712900
H	-4.94212500	2.32913800	-1.52322300
C	-6.72147700	-1.46975700	-1.36917500

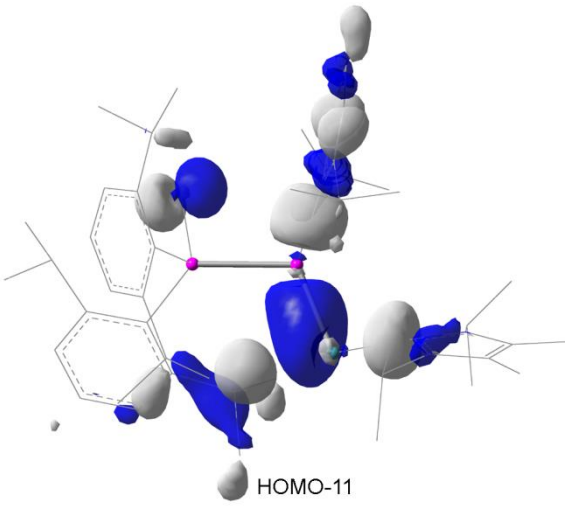
H	-6.38483000	-2.23315600	-2.07797800
H	-7.18029600	-0.66047600	-1.94518900
H	-7.50531800	-1.91645300	-0.75475400
C	-6.31574300	-1.89674300	1.81070500
H	-7.24840500	-2.18106000	1.31985000
H	-6.57836800	-1.28709000	2.68029400
H	-5.84476400	-2.81461200	2.17730200
C	-3.69295600	-0.23920200	2.54221300
H	-2.67844400	0.11338100	2.32778200
C	-4.46624500	0.92461900	3.17139600
H	-5.50002800	0.65215800	3.40828400
H	-4.47318900	1.78408100	2.49555200
H	-3.97610400	1.22896800	4.10103700
C	-3.58705900	-1.45666900	3.46239800
H	-4.55479100	-1.77919900	3.85365700
H	-2.96522000	-1.18371500	4.32022900
H	-3.11081400	-2.30120100	2.96053000
H	1.71462900	6.42427100	0.16696600
H	5.73690000	-0.15094600	3.48121700
H	1.48526500	-6.47890100	-1.36259400

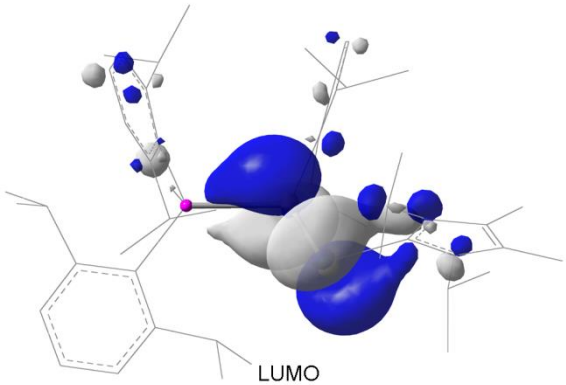
Contour plots at 0.04 isosurface:

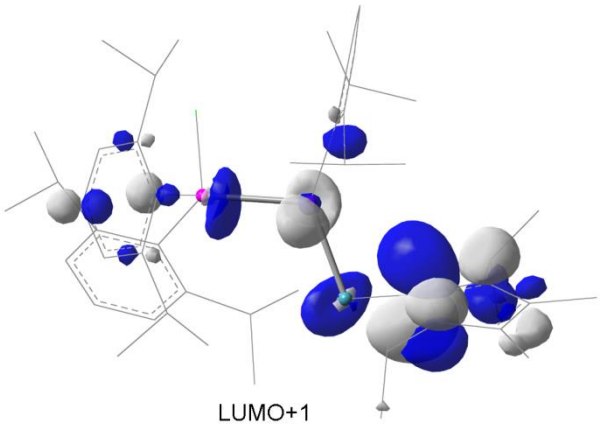
4Dip-*E*



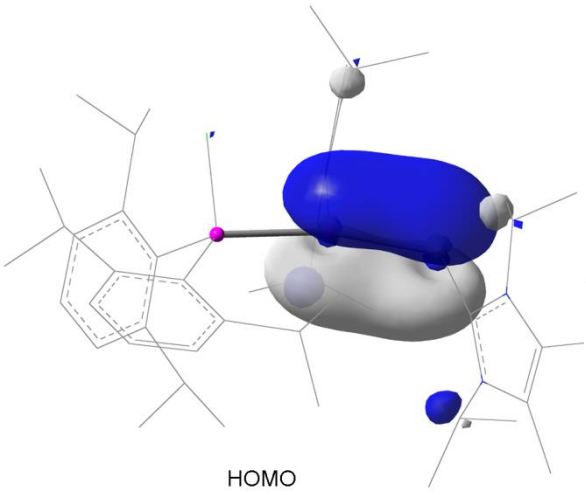


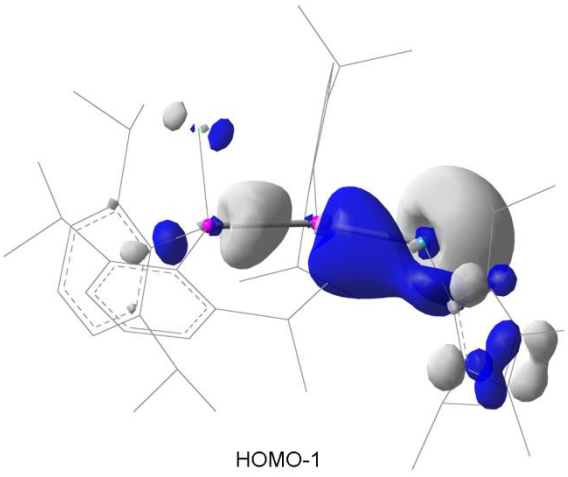


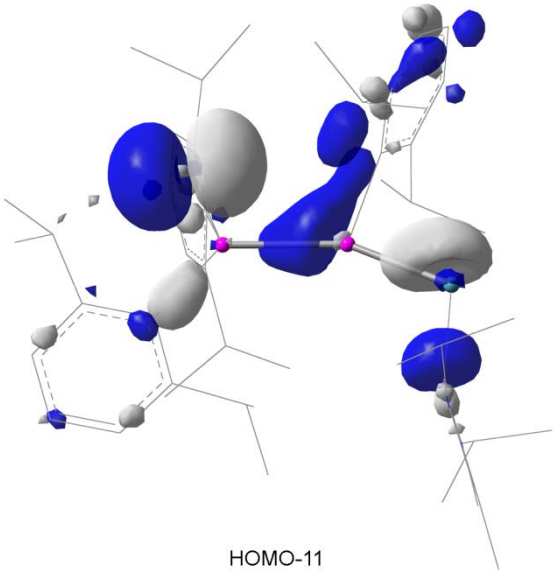




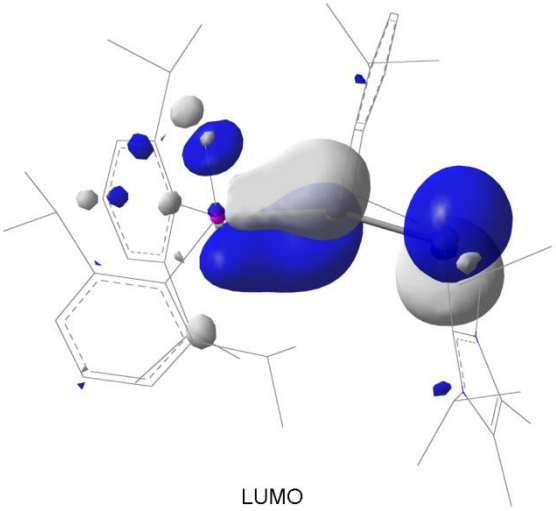
4Dip-*Z*



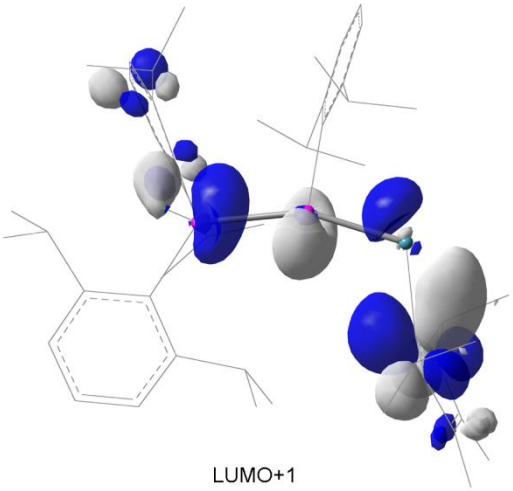




HOMO-11



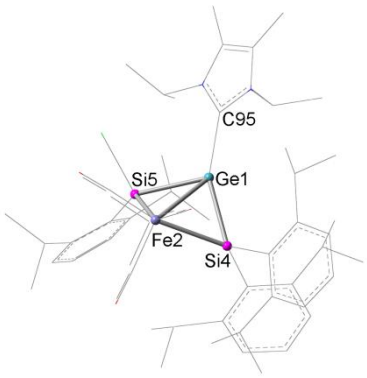
LUMO



LUMO+1

Theoretical calculation of 6:

DFT calculation was performed on simpler model system **6Dip** (Dip instead of Tip) at the B3LYP level of theory [basis sets: 6-311++G(d,p) for Ge, 6-31G(d,p) for Si, Cl, C, N, O and H, LANL2DZ for Fe], using *Gaussian 03* suite of programs. Compounds **6Dip** was optimized at the stationary point with number of imaginary frequency NIMAG = 0. The ^{29}Si NMR for **6Dip** was computed at the GIAO level with SCRF(solvent=toluene) correction, 6-311+G(2d,p) basis set on Ge, Si and Cl atoms, 6-31G(d,p) basis set on C, N, O and H atoms, LANL2DZ for Fe.



Cartesian coordinates of 6Dip:

Ge	0.59819	-0.75008	0.46536
Fe	-0.58078	-0.10179	-1.8522
Cl	-1.0064	-3.79794	-0.72573
Si	0.14034	1.54105	-0.22528
Si	-1.42136	-1.7029	-0.3521
N	2.85593	-2.69265	-0.79362
N	3.07825	-2.24589	1.32477
O	-0.86168	-2.26295	-3.79275
O	-2.80611	1.42036	-2.9427
O	1.51324	1.02191	-3.55569
C	1.47066	2.85983	-0.7968
C	2.88886	2.71442	-0.76395
C	3.71203	3.81374	-1.04789
H	4.79067	3.69488	-0.99977
C	3.18762	5.04727	-1.40822
C	1.8114	5.17868	-1.52791
H	1.39302	6.12364	-1.86119
C	0.95062	4.11054	-1.24158
C	3.62115	1.39721	-0.50246
H	2.87131	0.61684	-0.35114
C	4.47173	0.99819	-1.72725
H	3.88066	1.01553	-2.64528
H	4.88941	-0.00618	-1.59282
H	5.314	1.68472	-1.86308
C	4.52265	1.4312	0.74675
H	5.28992	2.20807	0.66406
H	5.04217	0.47259	0.8615
H	3.95433	1.62353	1.65933
C	-0.53322	4.34919	-1.51074
H	-1.0883	3.45778	-1.20271
C	-0.79182	4.51753	-3.02248
H	-0.29899	5.41546	-3.41067
H	-1.86497	4.61082	-3.22071
H	-0.41427	3.65915	-3.58604
C	-1.09815	5.53742	-0.7116
H	-0.95234	5.39862	0.36289
H	-2.17094	5.64969	-0.8975
H	-0.61665	6.47708	-1.00253
C	-0.80653	2.4498	1.25155
C	-0.01101	3.01838	2.29655

C	-0.58397	3.86609	3.2533
H	0.04334	4.2892	4.03231
C	-1.93587	4.176	3.22943
C	-2.73376	3.58437	2.26365
H	-3.79834	3.79529	2.26136
C	-2.21284	2.71192	1.29361
C	1.47318	2.72066	2.50323
H	1.81582	2.0945	1.67853
C	2.33841	3.99493	2.50893
H	2.1999	4.57036	1.59062
H	3.40039	3.74034	2.59243
H	2.09254	4.64256	3.357
C	1.68352	1.90785	3.79711
H	1.36589	2.47257	4.67981
H	2.74308	1.65948	3.92946
H	1.10515	0.97797	3.77399
C	-3.26592	2.08668	0.37377
H	-2.77626	1.33154	-0.24056
C	-3.94135	3.11531	-0.5563
H	-4.40864	3.918	0.02474
H	-4.72573	2.63154	-1.14699
H	-3.24122	3.57159	-1.25724
C	-4.35813	1.36601	1.19143
H	-3.9324	0.65976	1.90591
H	-5.01851	0.80632	0.52344
H	-4.9803	2.07545	1.74726
C	-3.09226	-1.91429	0.57753
C	-3.19207	-2.05447	1.98969
C	-4.45658	-2.1964	2.57913
H	-4.53224	-2.28599	3.65926
C	-5.61382	-2.24384	1.81222
C	-5.51682	-2.17084	0.42784
H	-6.41778	-2.24785	-0.17379
C	-4.27806	-2.01126	-0.20635
C	-1.98738	-2.11517	2.92749
H	-1.08517	-2.05491	2.3147
C	-1.94361	-0.92509	3.90383
H	-1.89304	0.02737	3.36755
H	-1.06231	-0.99385	4.55327
H	-2.82712	-0.90066	4.55138
C	-1.93565	-3.45888	3.68163
H	-2.7951	-3.58651	4.34843
H	-1.03215	-3.51598	4.29969
H	-1.9271	-4.30215	2.98389
C	-4.268	-2.03577	-1.73496
H	-3.26217	-1.77056	-2.07366
C	-5.22737	-1.00938	-2.36538
H	-6.27337	-1.23477	-2.13117
H	-5.12678	-1.02109	-3.45589
H	-5.01325	0.00571	-2.02127
C	-4.56183	-3.45584	-2.26031
H	-3.84954	-4.18098	-1.85764
H	-4.49358	-3.47931	-3.35357
H	-5.57082	-3.77843	-1.97947

C	2.29164	-1.99674	0.2331
C	4.00129	-3.35763	-0.35597
C	4.13585	-3.08597	0.97813
C	2.23835	-2.82394	-2.14623
H	1.29596	-2.29415	-2.03104
C	3.03847	-2.11953	-3.24413
H	3.24962	-1.08303	-2.98665
H	2.43738	-2.12038	-4.15833
H	3.98029	-2.62642	-3.47268
C	1.92864	-4.28348	-2.50281
H	2.80845	-4.82207	-2.86458
H	1.18729	-4.28446	-3.30598
H	1.49483	-4.81948	-1.65707
C	4.89566	-4.19866	-1.2127
H	5.80747	-4.44076	-0.6642
H	5.19673	-3.68044	-2.1259
H	4.42529	-5.14209	-1.50225
C	5.20138	-3.57305	1.90988
H	5.80578	-4.33037	1.40828
H	4.78674	-4.03817	2.80812
H	5.87421	-2.77076	2.22806
C	2.70284	-1.84693	2.71079
H	1.94888	-1.06873	2.56568
C	3.852	-1.22565	3.51176
H	4.56117	-1.96688	3.8847
H	3.42455	-0.71901	4.38136
H	4.39371	-0.48057	2.92509
C	2.03418	-3.01927	3.43818
H	1.17909	-3.39295	2.86942
H	1.67498	-2.68221	4.41536
H	2.72826	-3.84868	3.60569
C	-0.74811	-1.44659	-2.97347
C	-1.95252	0.81825	-2.43675
C	0.7276	0.60184	-2.81061
H	3.84479	5.88627	-1.62027
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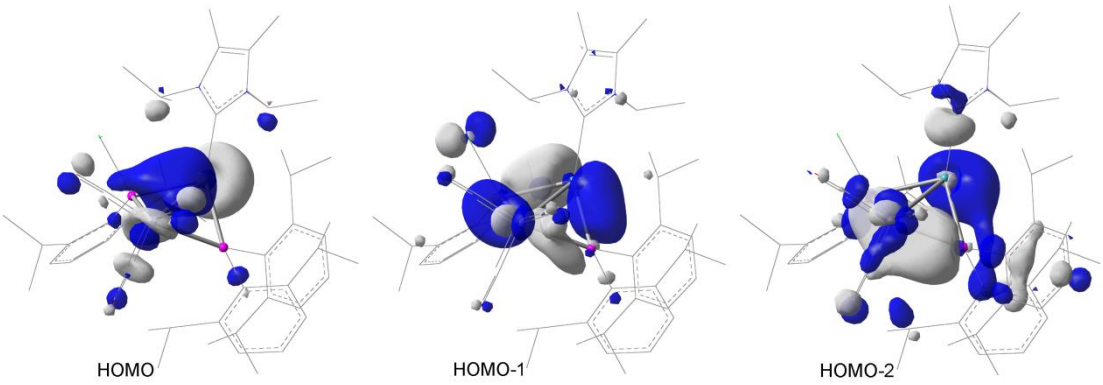
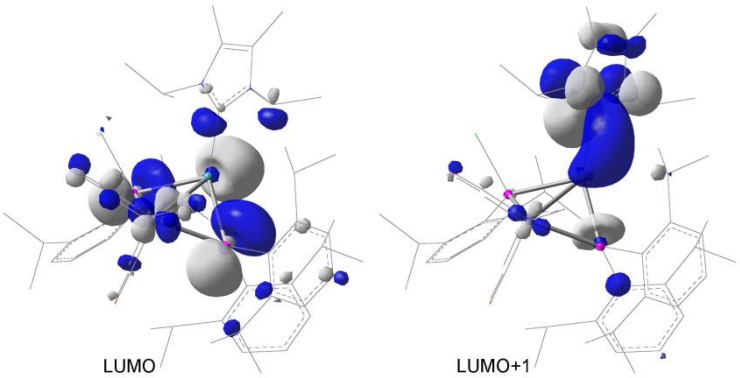
H	-6.58365	-2.3574	2.28933

Contour plots of 6Dip at 0.04 isosurface:





References:

S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

S2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.