Electronic Supplementary Materials

A Pt(0) complex with cyclic (alkyl)(amino)silylene and 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane ligands: synthesis, molecular structure and catalytic hydrosilylation activity

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Contents

1. NMR Spectra

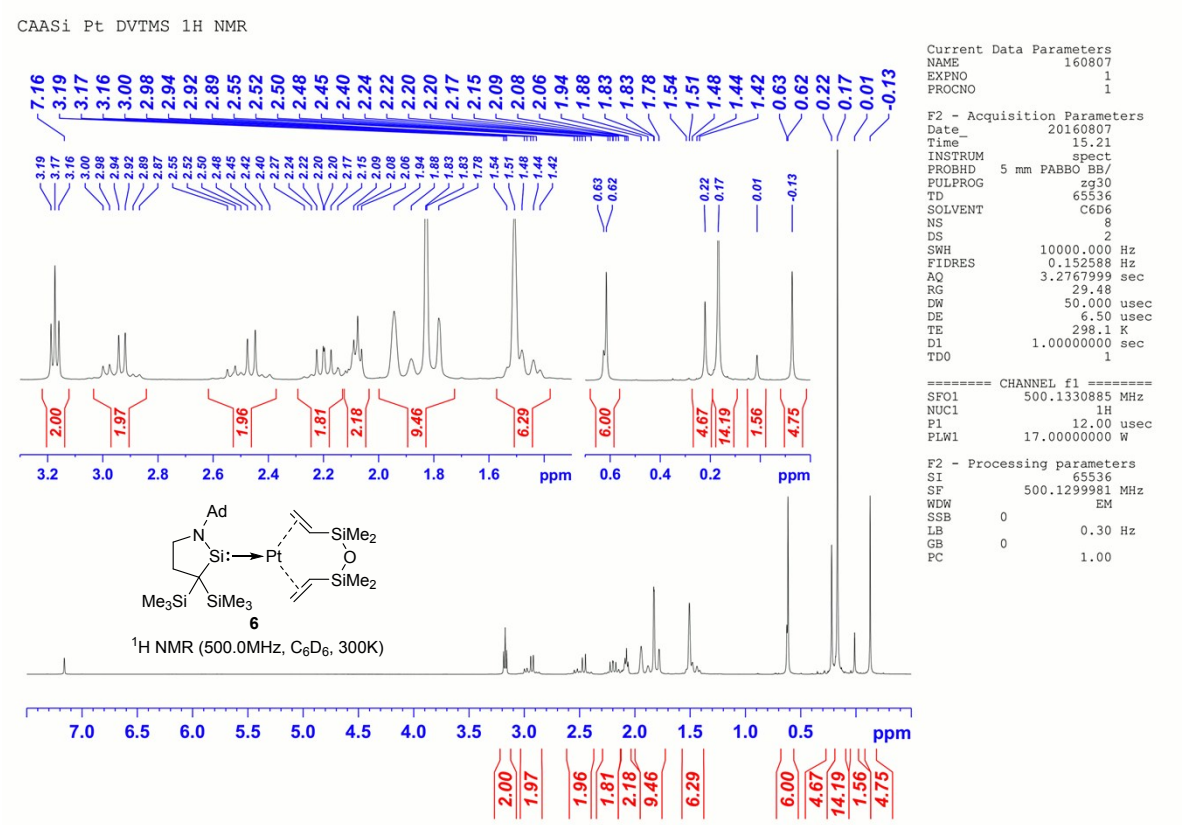


Figure S1. ^{1}H NMR spectrum of **6** in C_6D_6 at room temperature.

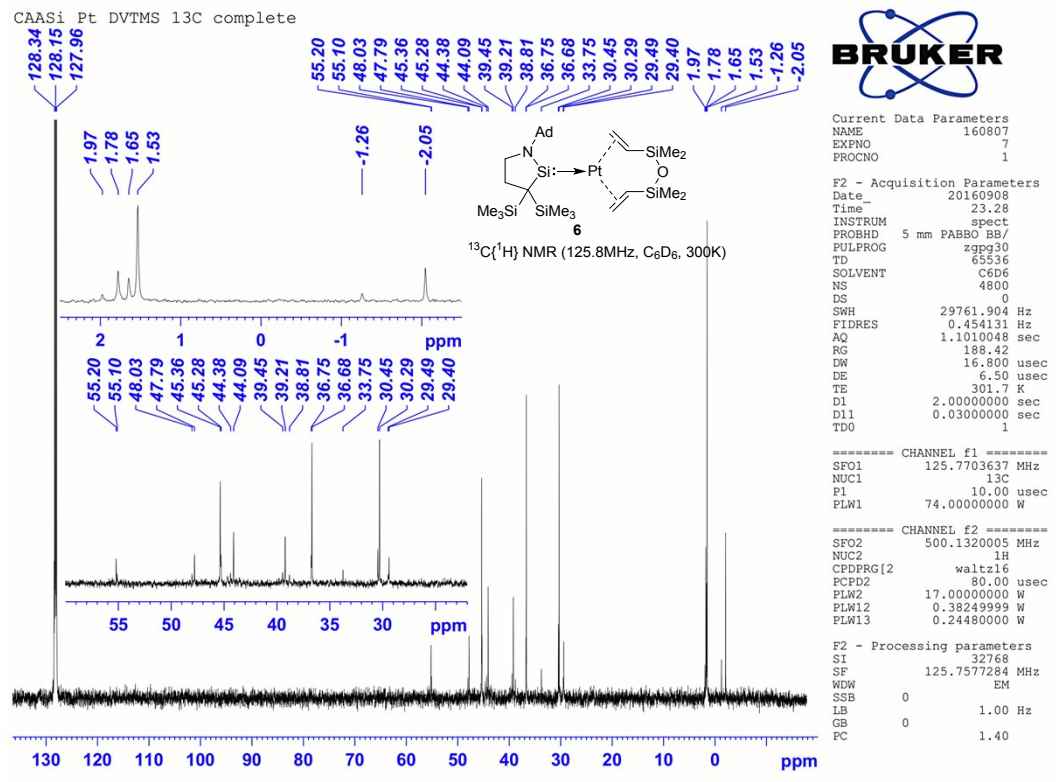


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6 at room temperature.

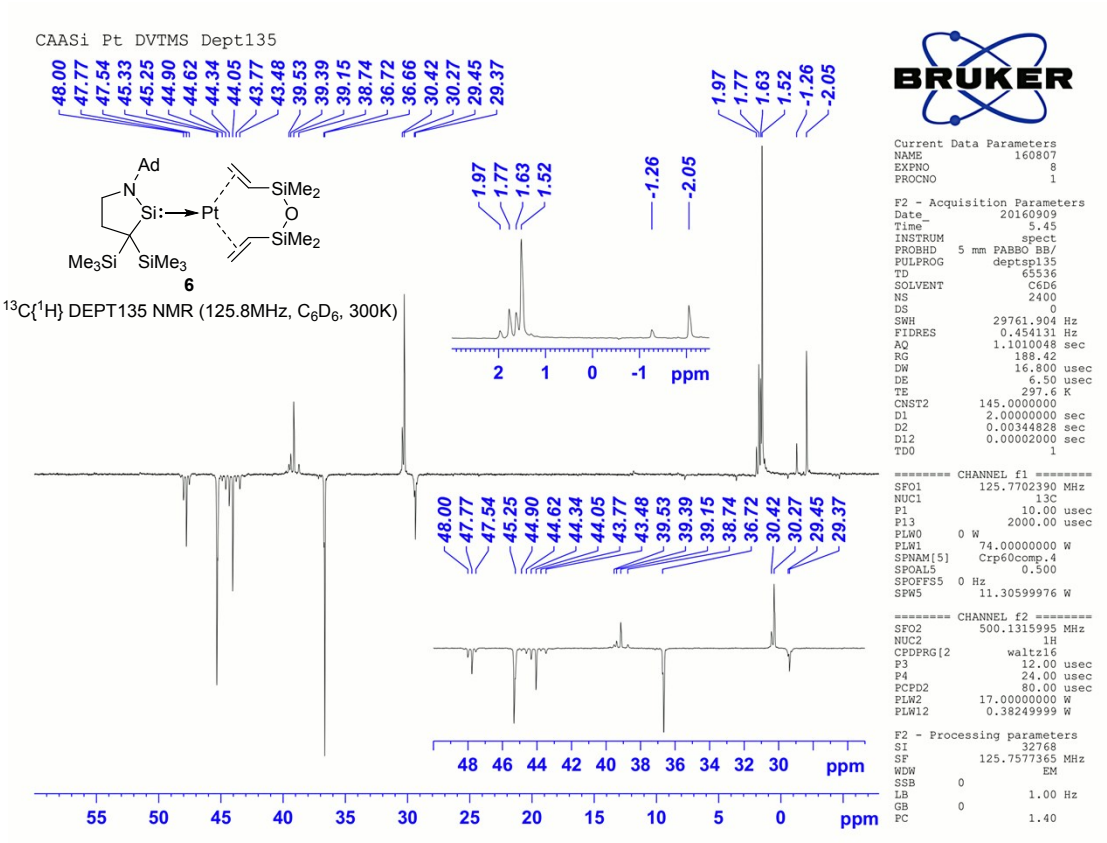


Figure S3. $^{13}C\{^{1}H\}$NMR (DEPT135) of **6** in C_6D_6 at room temperature.

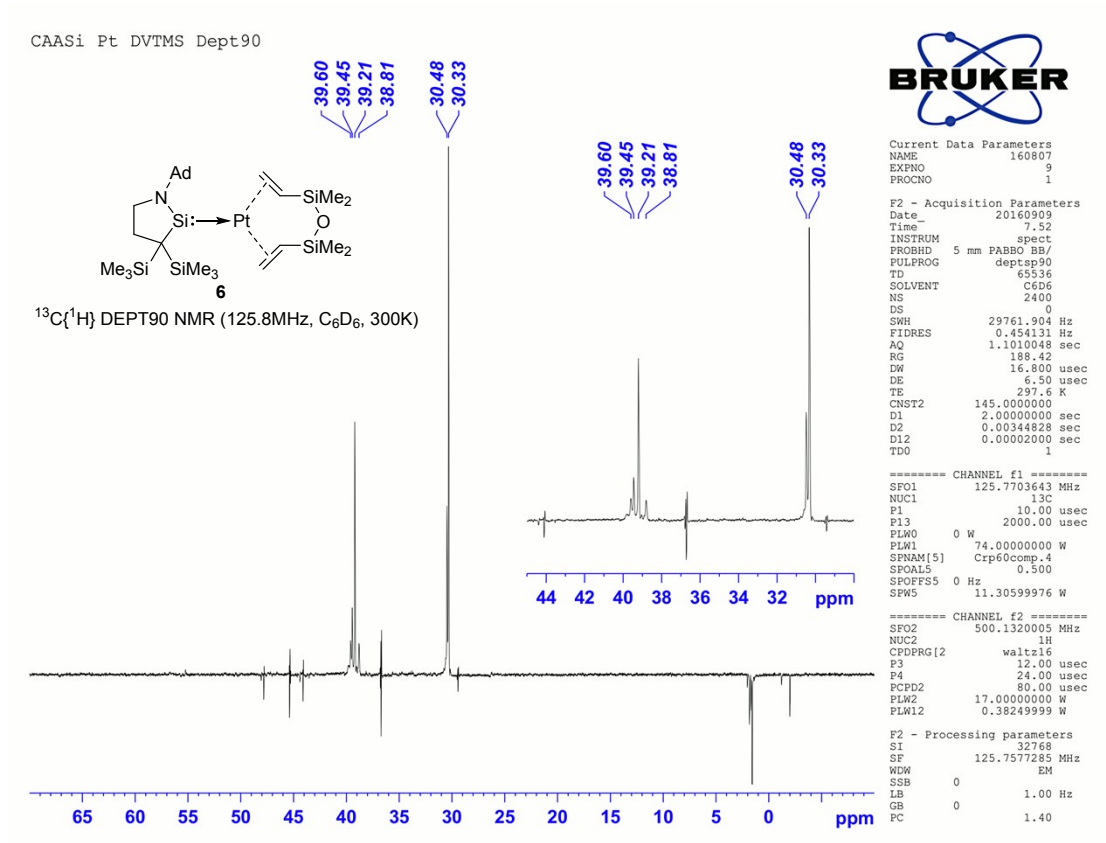


Figure S4. $^{13}C\{^{1}H\}$NMR (DEPT90) of **6** in C_6D_6 at room temperature.

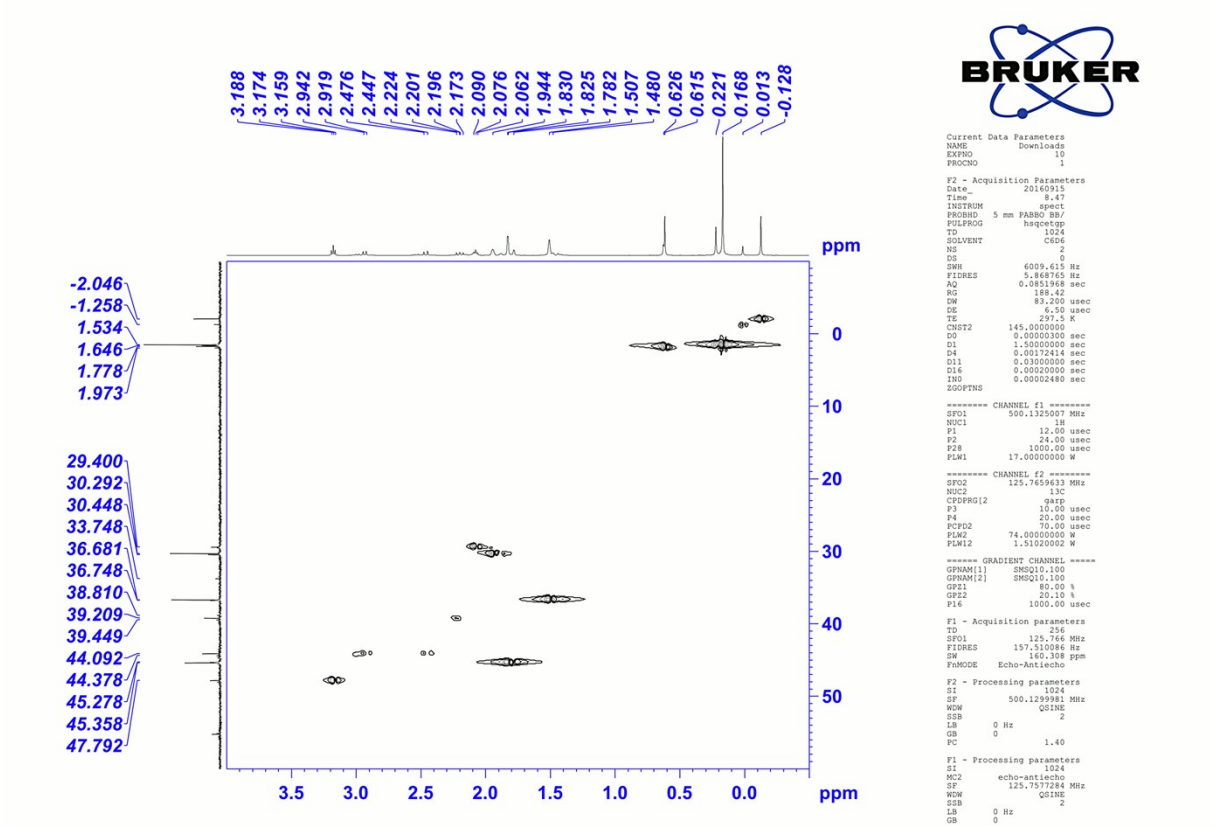


Figure S5. ^{13}C-^{1}H NMR (HMBC) of **6** in C_6D_6 at room temperature.

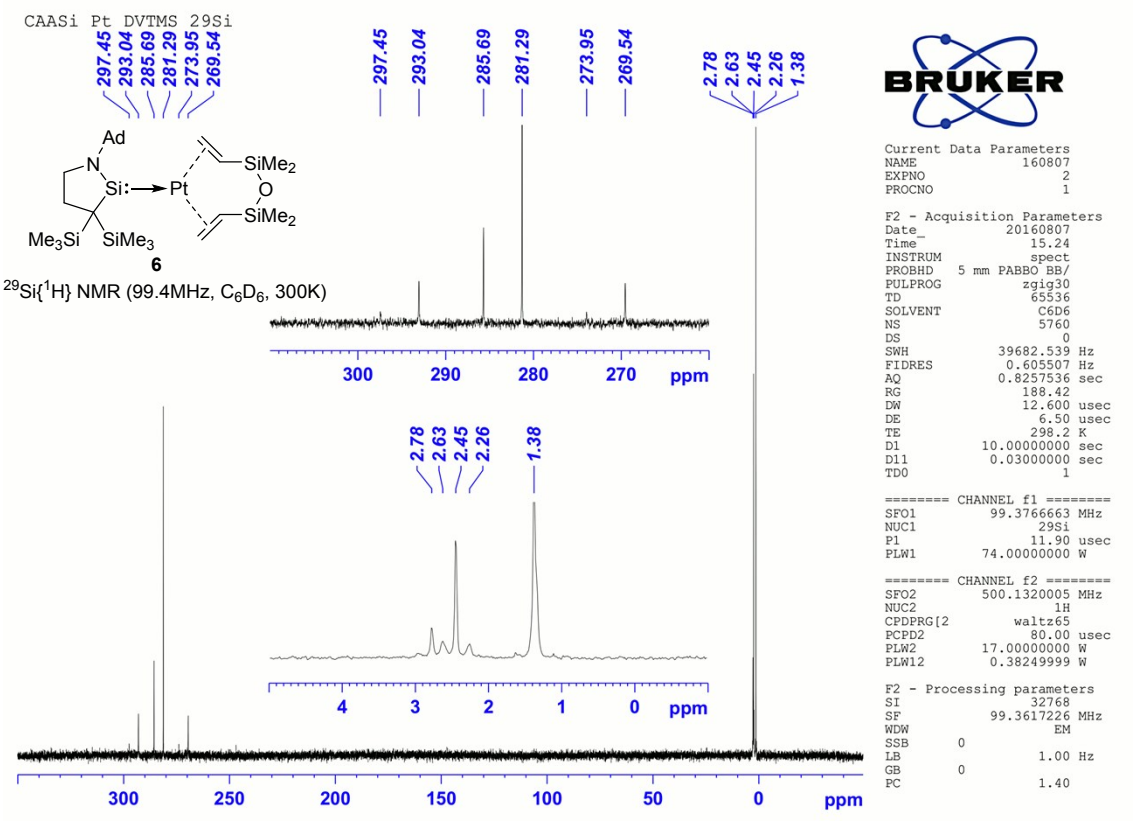


Figure S6 $^{29}Si\{^{1}H\}$NMR of **6** in C_6D_6 at room temperature.

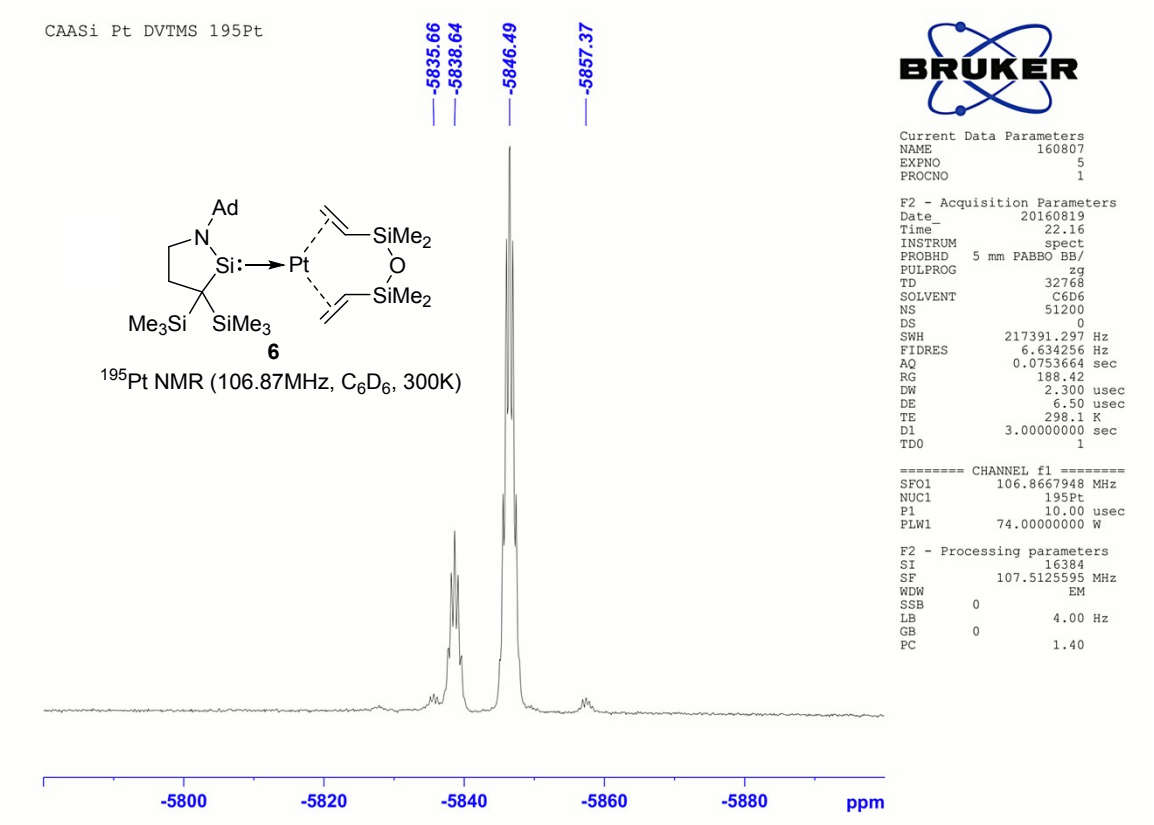


Figure S7. ^{195}Pt NMR of **6** in C_6D_6 at room temperature.

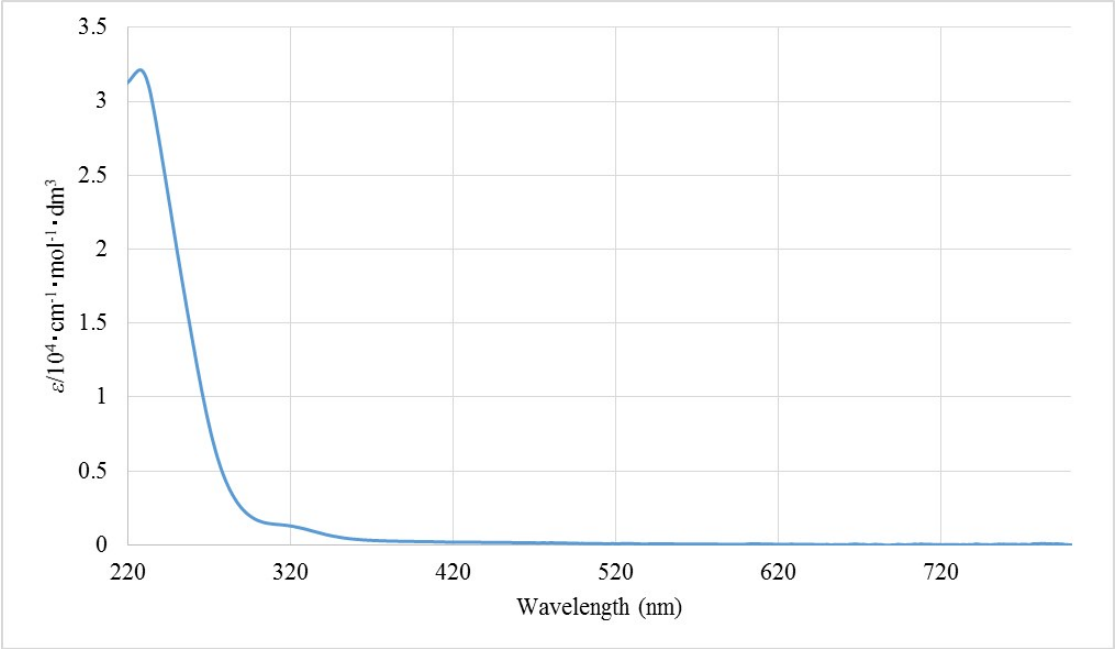


Figure S8. UV-vis spectrum of **6** in hexane at room temperature.

2. X-ray Analysis of 6

(a) Top view (b) Side view

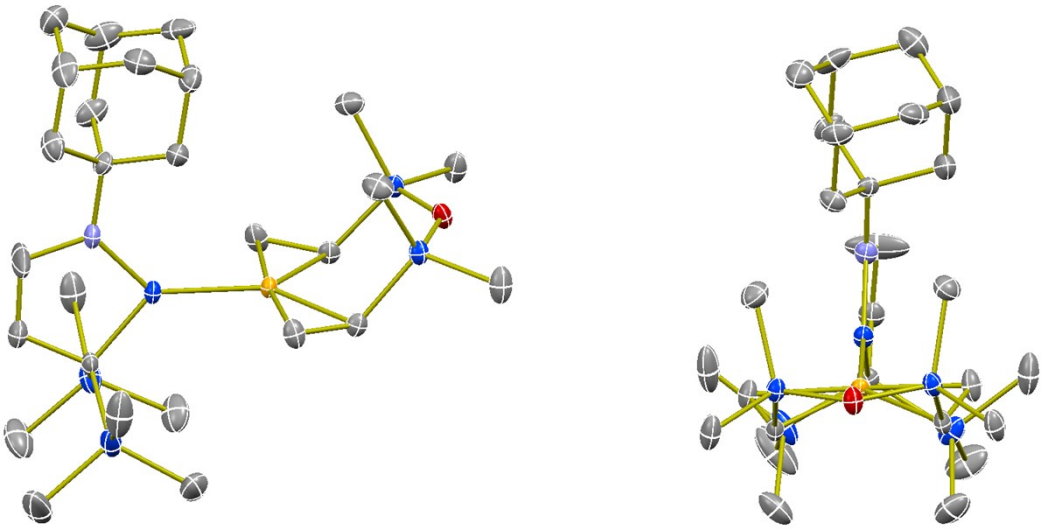


Figure S9. ORTEP drawings of complex **6**; top view (a) and side view (b). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

3. Hydrosilylation of Terminal Alkenes Catalysed by Platinum Complex 6

Hydrosilylation of 1-Hexene in the Presence of 6 (entry 1)

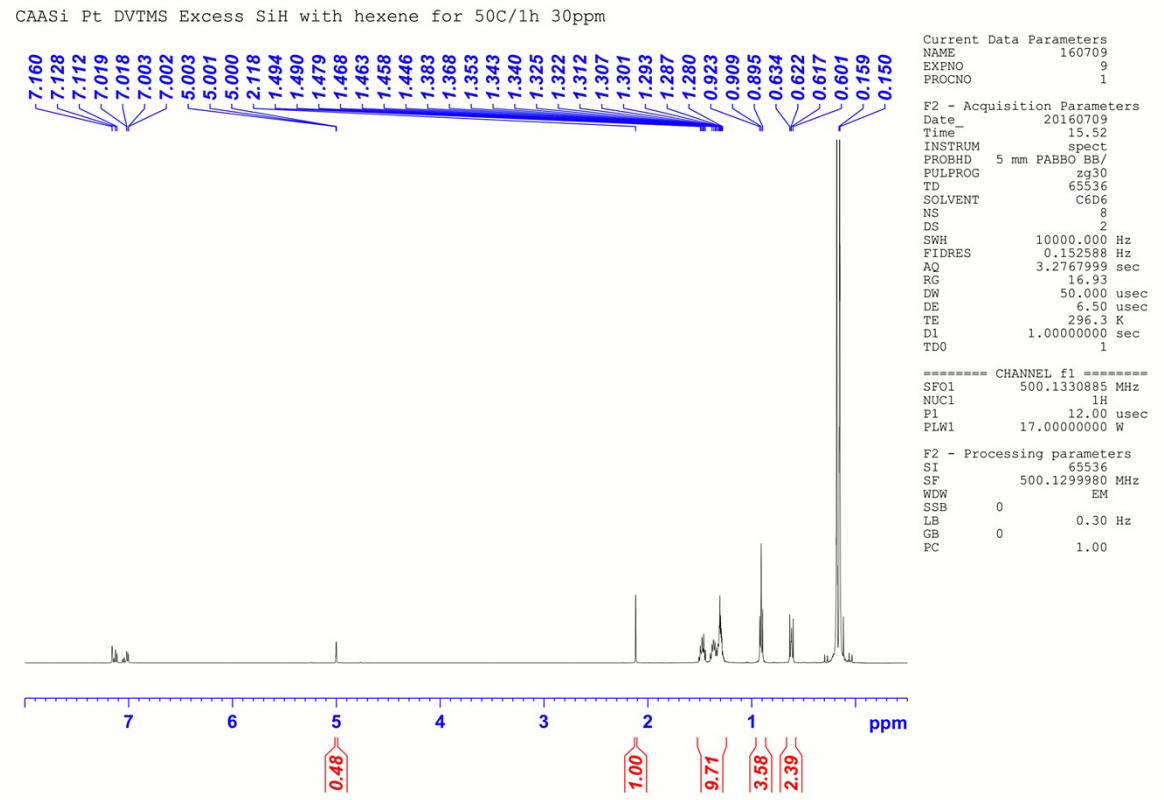


Figure S10. ^{1}H NMR spectrum of reaction mixture of entry 1 (C_6D_6, room temperature).

Hydrosilylation of 1-Hexene in the Presence of 6 (entry 2)

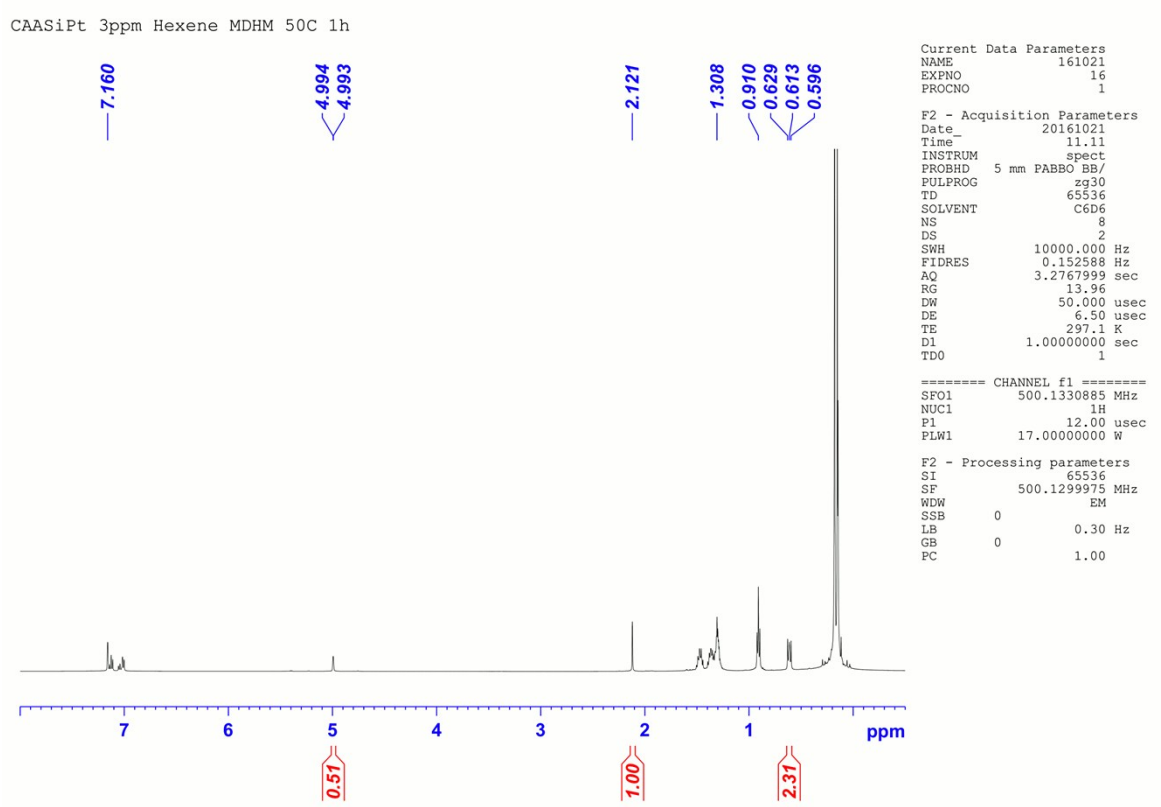


Figure S11. ^{1}H NMR spectrum of reaction mixture of entry 2 (C_6D_6, room temperature).

Hydrosilylation of Allyl Glycidyl Ether in the Presence of 6 (entry 6)

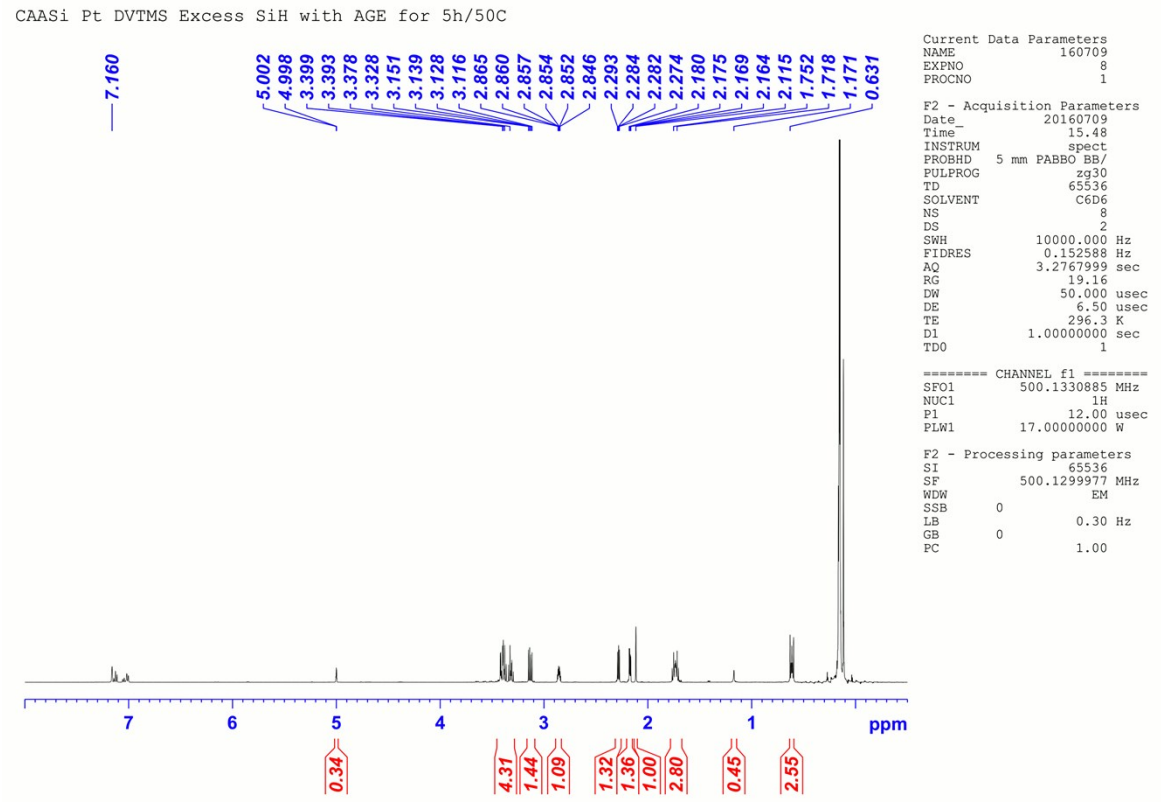


Figure S12. ^{1}H NMR spectrum of reaction mixture of entry 6 (C_6D_6, room temperature).

Hydrosilylation of Allyl Glycidyl Ether in the Presence of 6 (entry 7)

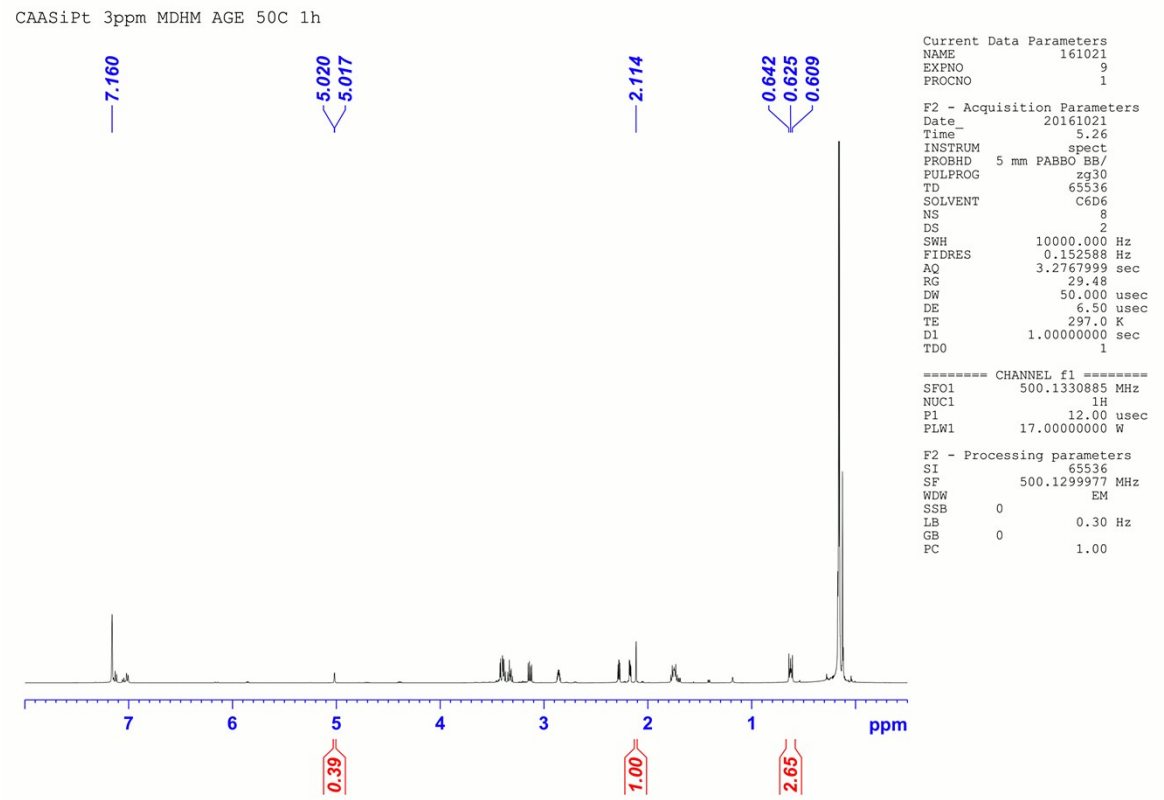


Figure S13. ^{1}H NMR spectrum of reaction mixture of entry 7 (C_6D_6, room temperature).

Hydrosilylation of Allylbis(trimethylsilyl)amine in the Presence of 6 (entry 11)

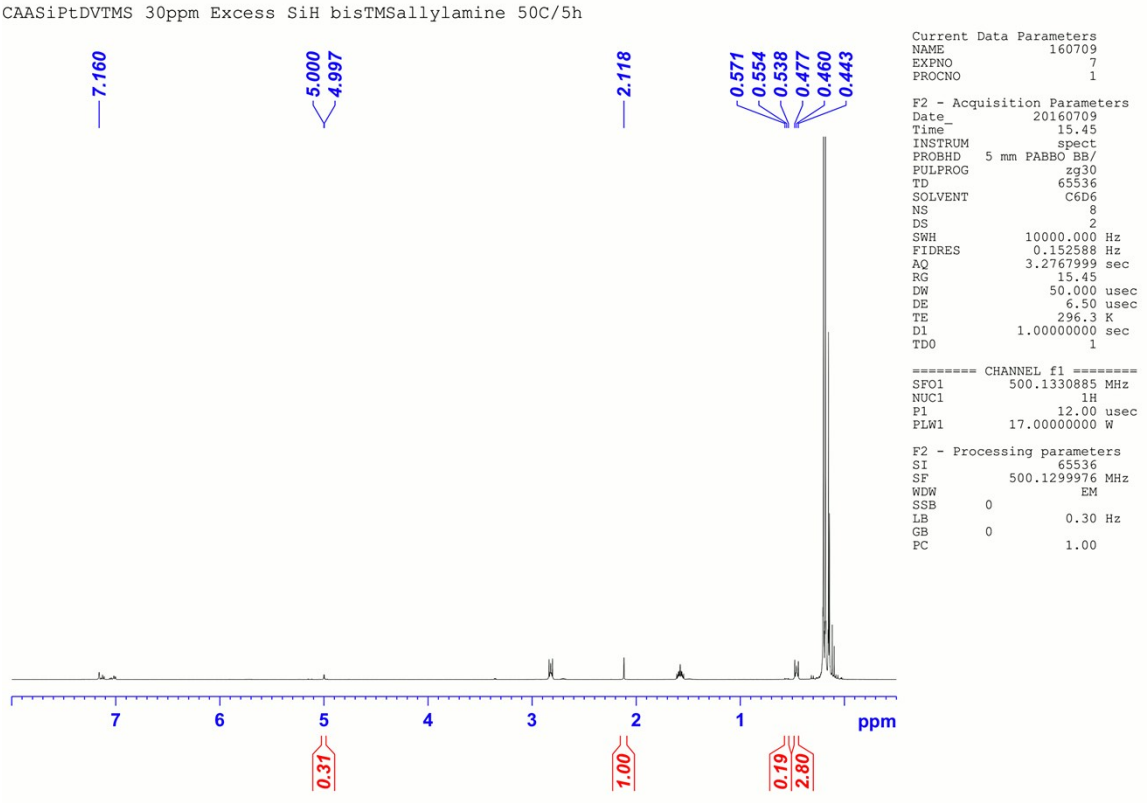


Figure S14. ^{1}H NMR spectrum of reaction mixture of entry 11 (C_6D_6, room temperature).

Hydrosilylation of Allylbis(trimethylsilyl)amine in the Presence of 6 (entry 12)

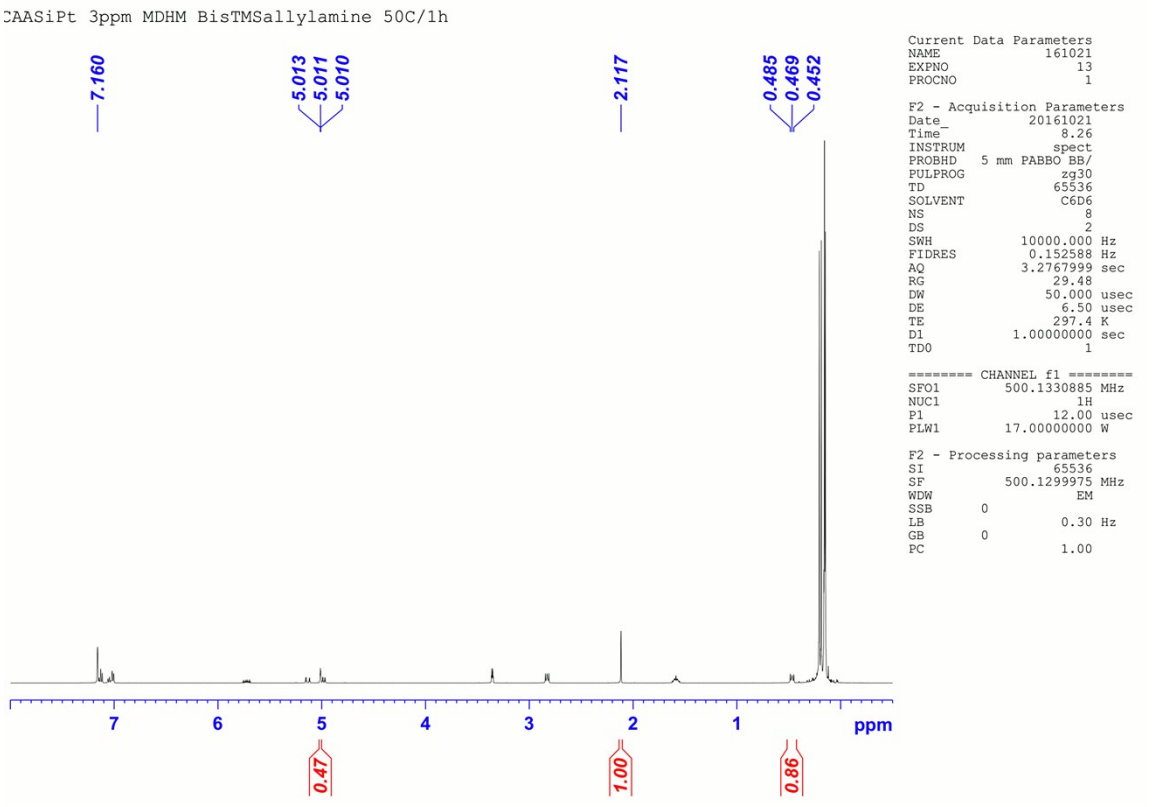


Figure S15. ^{1}H NMR spectrum of reaction mixture of entry 12 (C_6D_6, room temperature).

Hydrosilylation of Vinylcyclohexene Oxide in the Presence of 6 (entry 16)

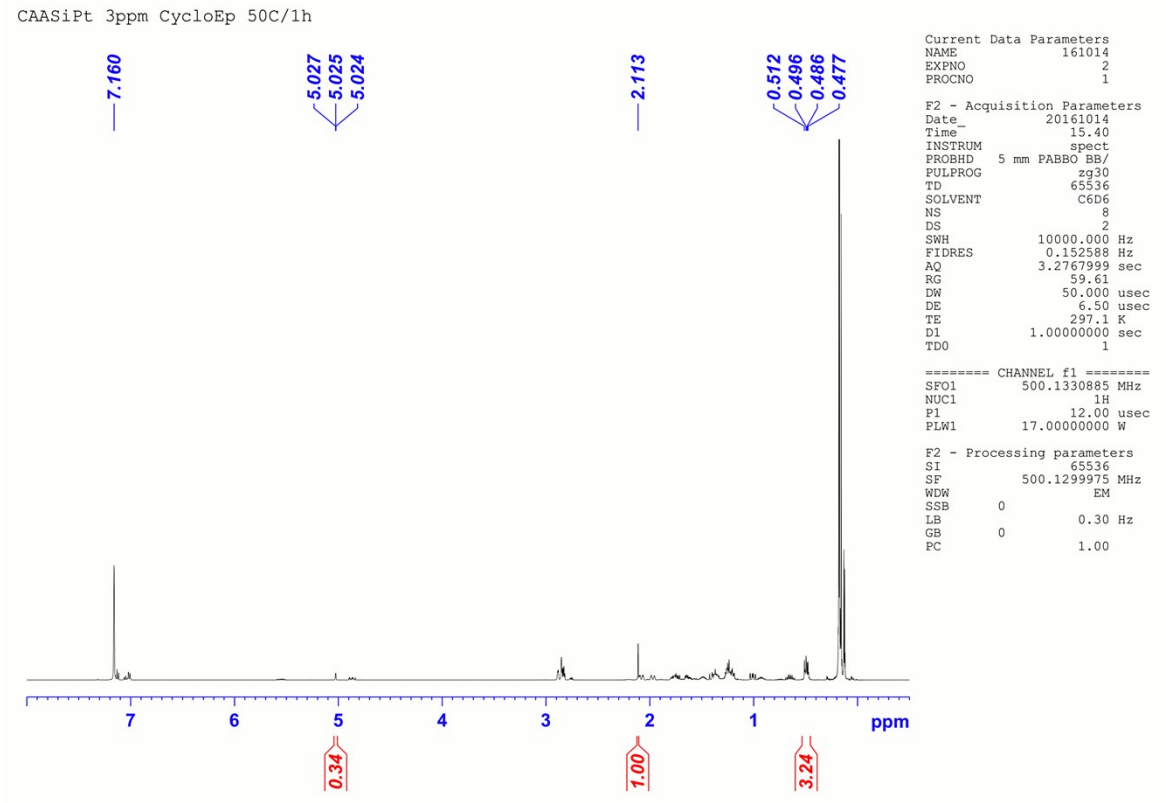


Figure S16. ^{1}H NMR spectrum of reaction mixture of entry 16 (C_6D_6, room temperature).

Hydrosilylation of Allyl Acetate in the Presence of 6 (entry 20)

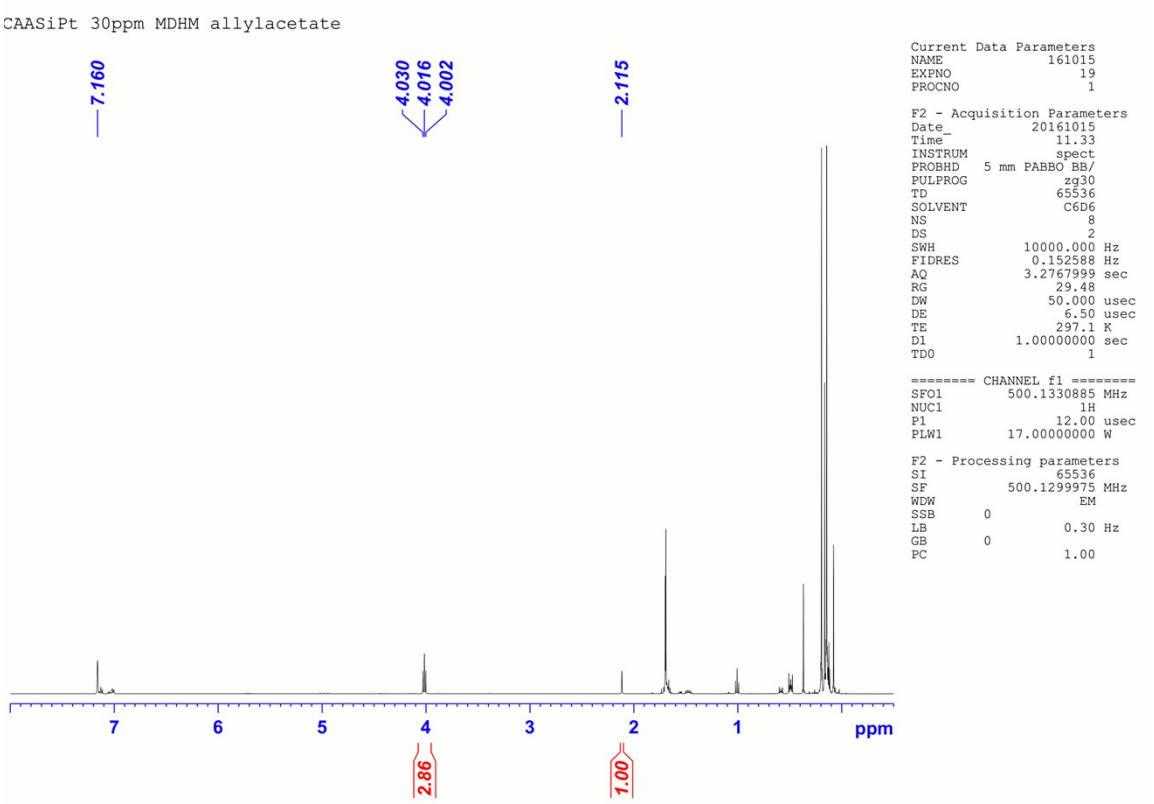


Figure S17. ^{1}H NMR spectrum of reaction mixture of entry 20 (C_6D_6, room temperature).

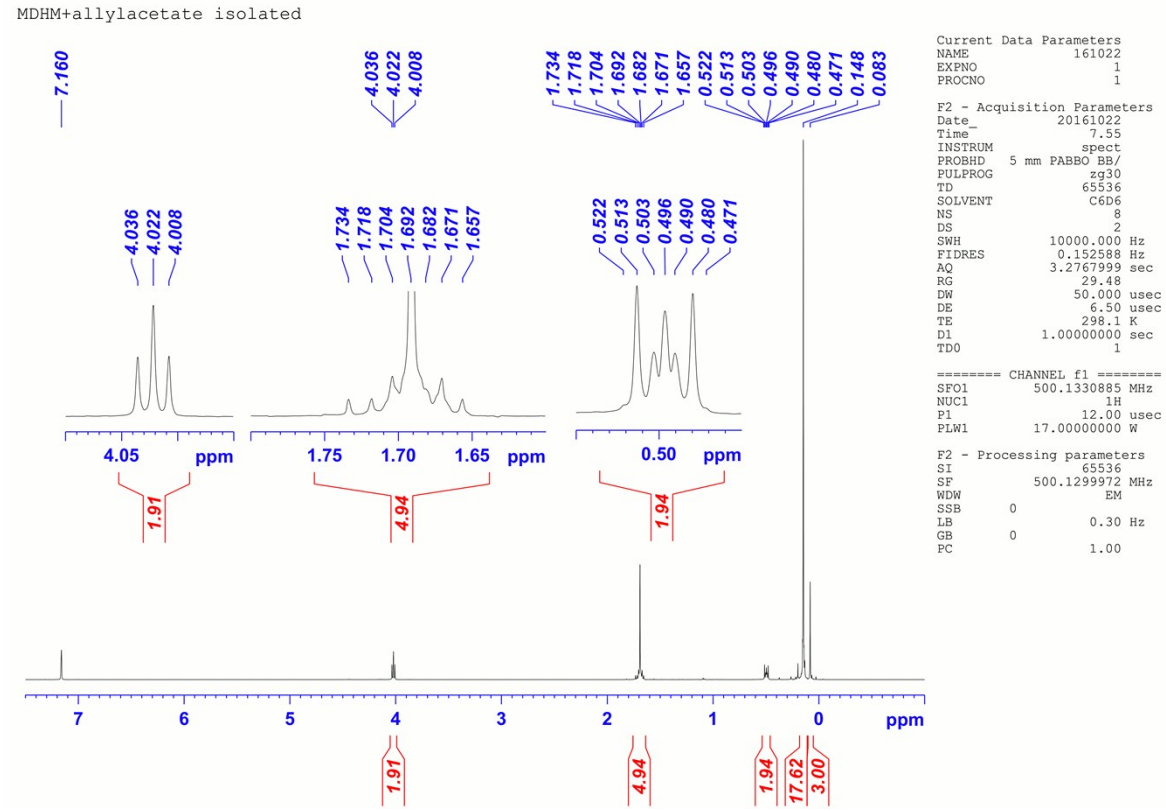


Figure S18. ^{1}H NMR spectrum of **10e** (entry 20, C_6D_6, room temperature).

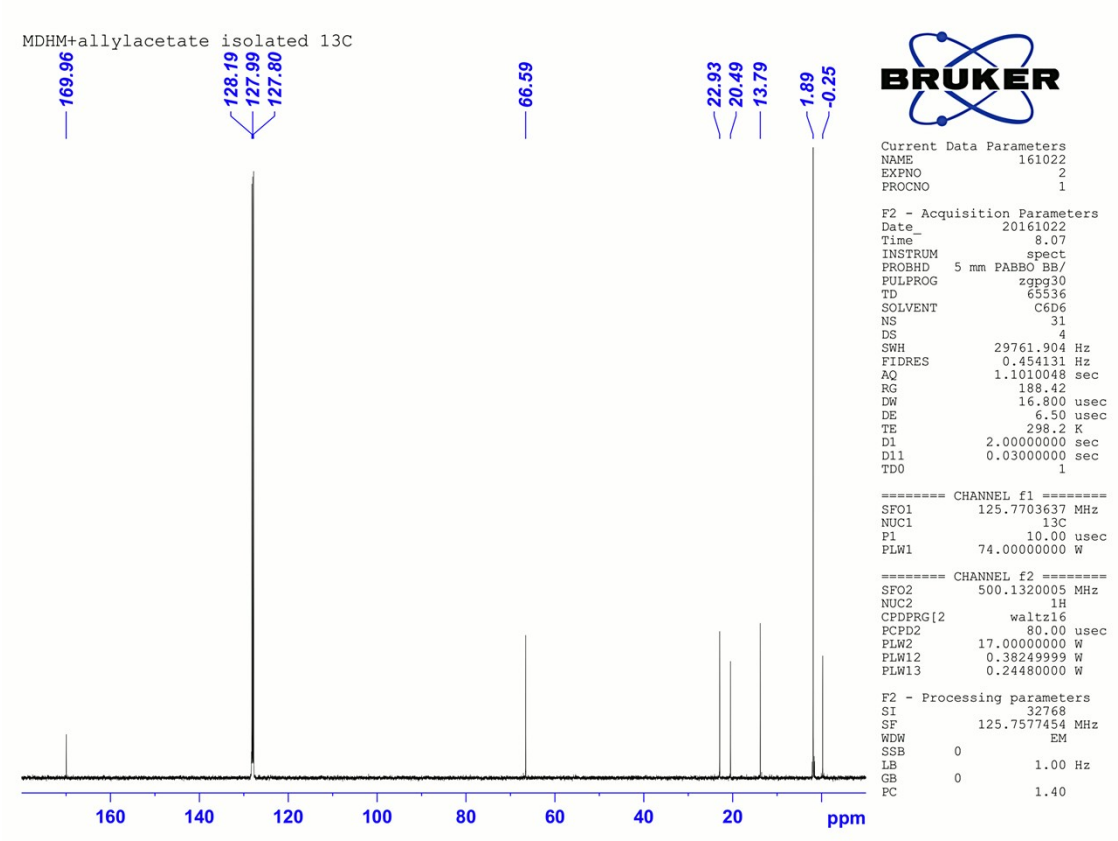


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **10e** (entry 20, C_6D_6, room temperature).

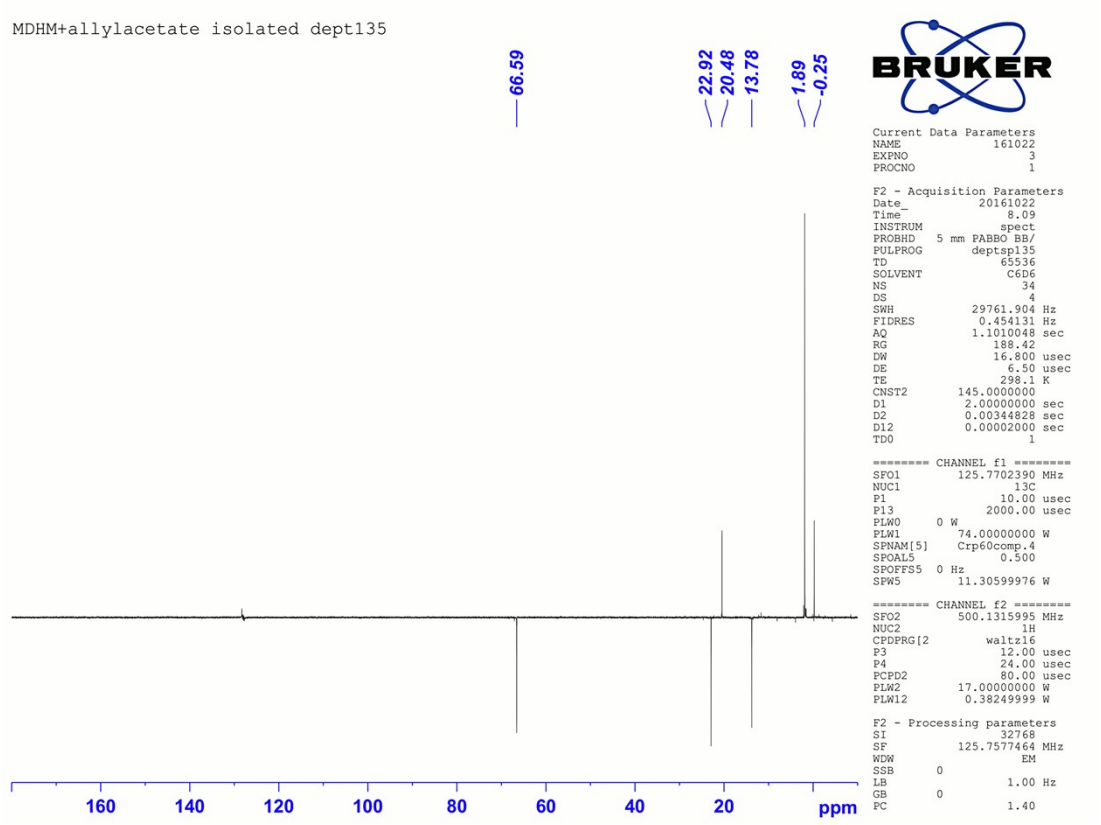


Figure S20. $^{13}C\{^{1}H\}$NMR (DEPT135) NMR spectrum of isolated **10e** (entry 20, C_6D_6, room temperature).

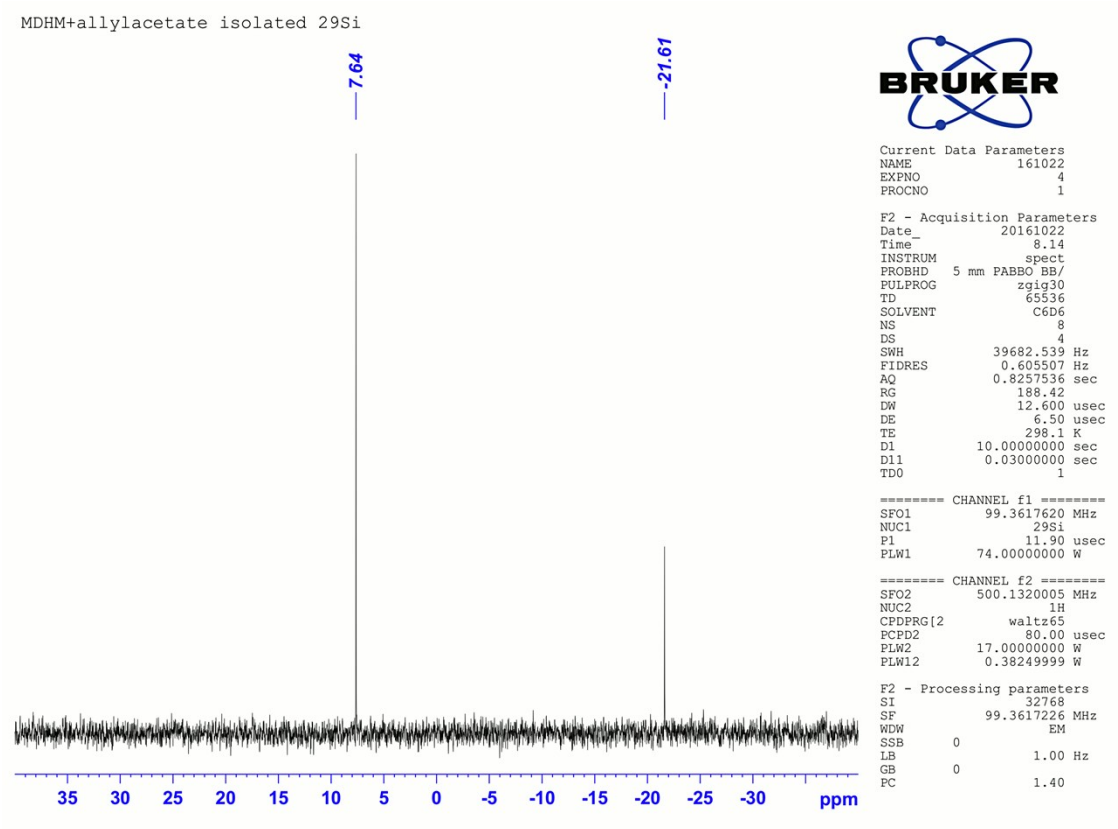


Figure S21. $^{29}Si\{^{1}H\}$ NMR spectrum of **10e** (entry 20, C_6D_6, room temperature).

Hydrosilylation of Allyl Acetate in the Presence of 7 (entry 21)

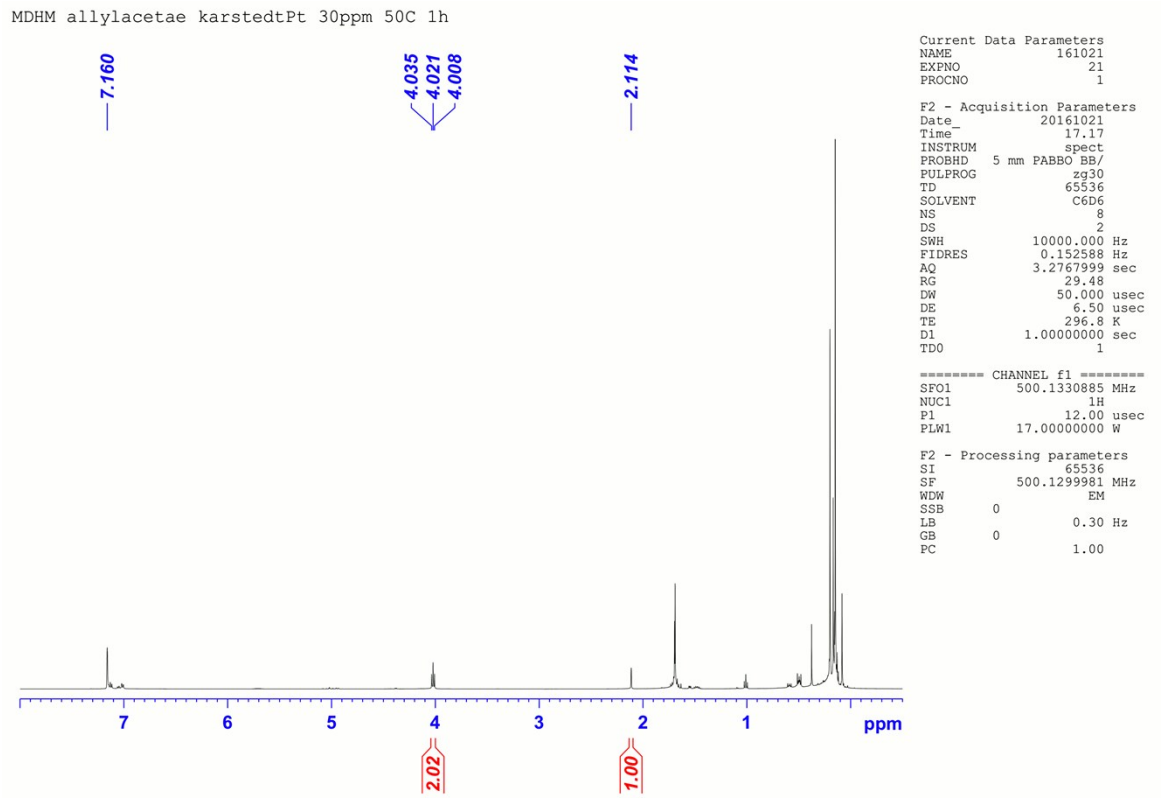


Figure S22. ^{1}H NMR spectrum of reaction mixture of entry 21 (C_6D_6, room temperature).

Hydrosilylation of Allyl Acetate in the Presence of 2 (entry 22)

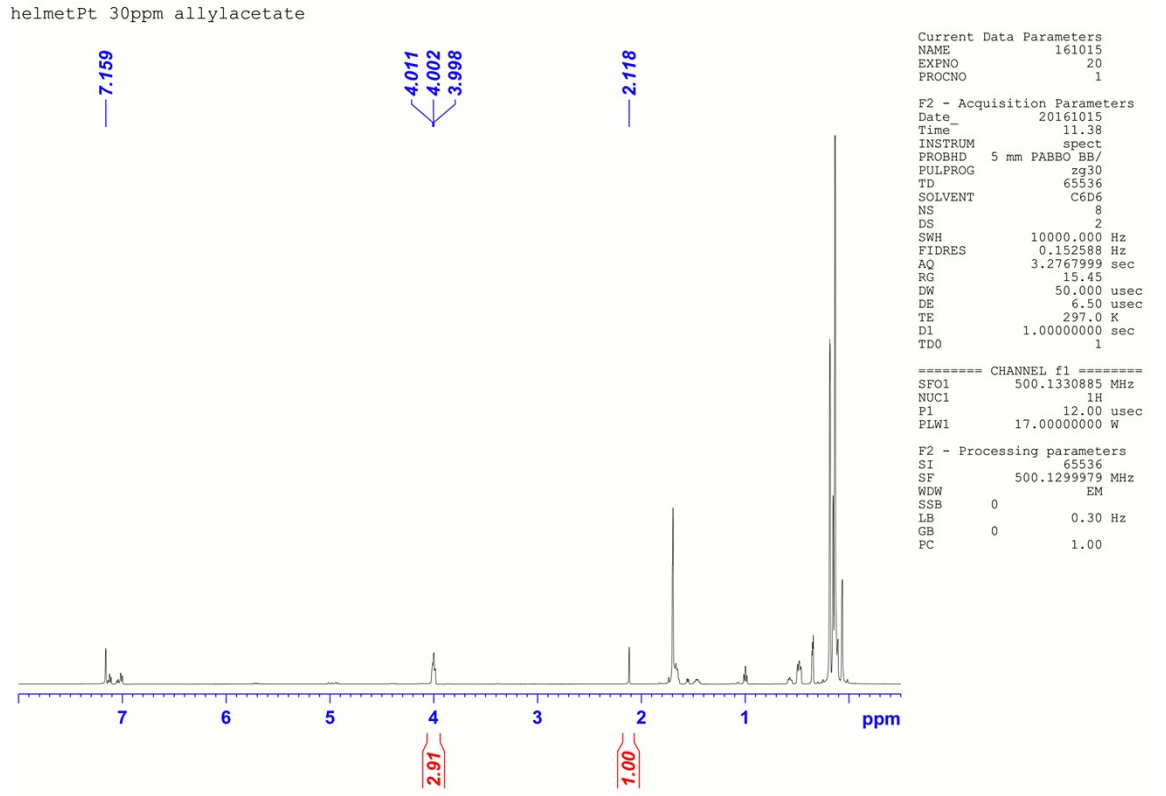


Figure S23. ^{1}H NMR spectrum of reaction mixture of entry 22 (C_6D_6, room temperature).

Hydrosilylation of Allyl Ethyl Ether in the Presence of 6 (entry 23)

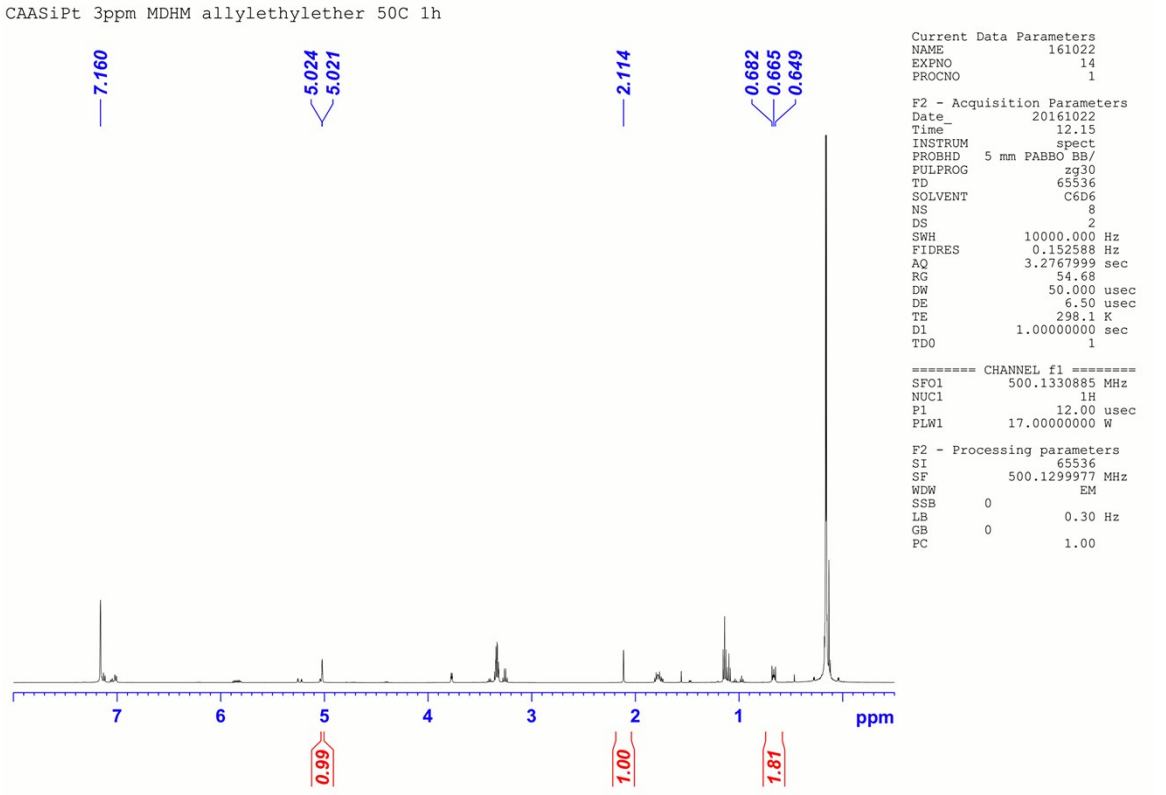


Figure S24. ^{1}H NMR spectrum of reaction mixture of entry 23 (C_6D_6, room temperature).

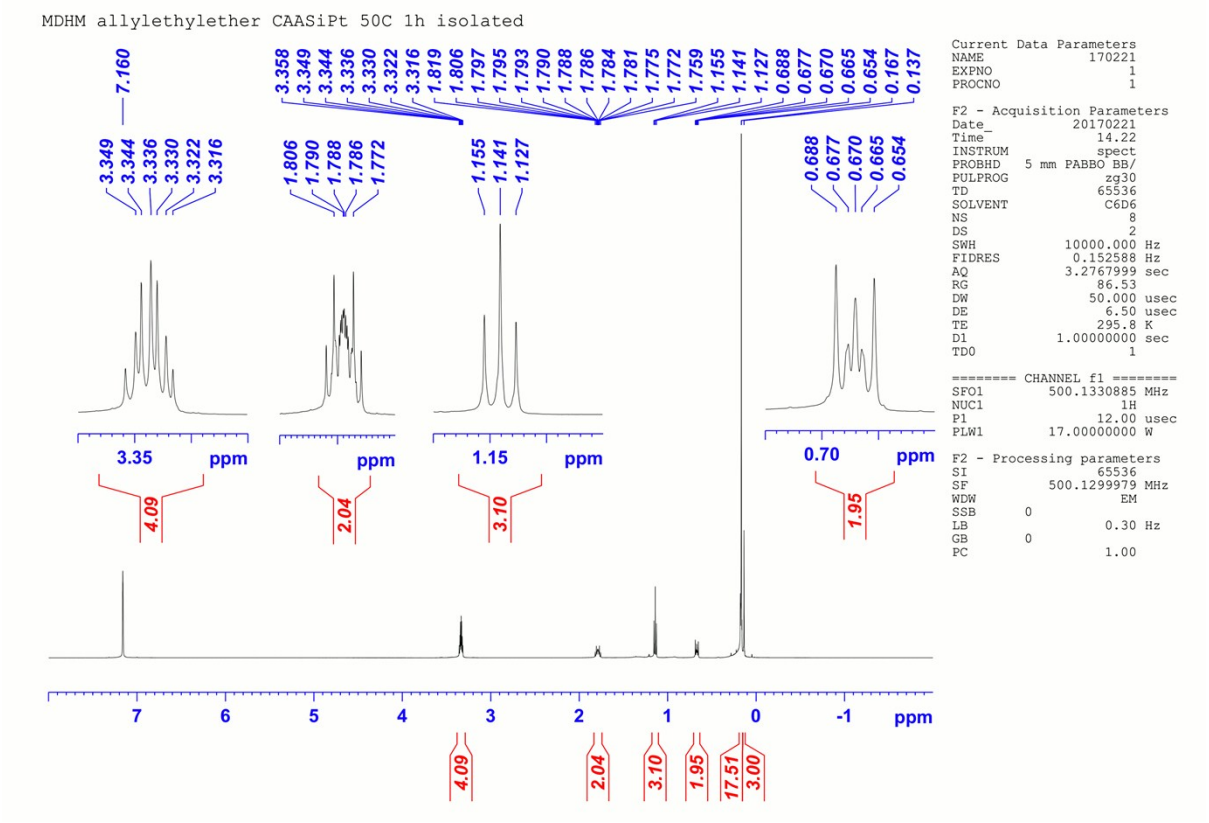


Figure S25. ^{1}H NMR spectrum of **10f** (C_6D_6, room temperature).

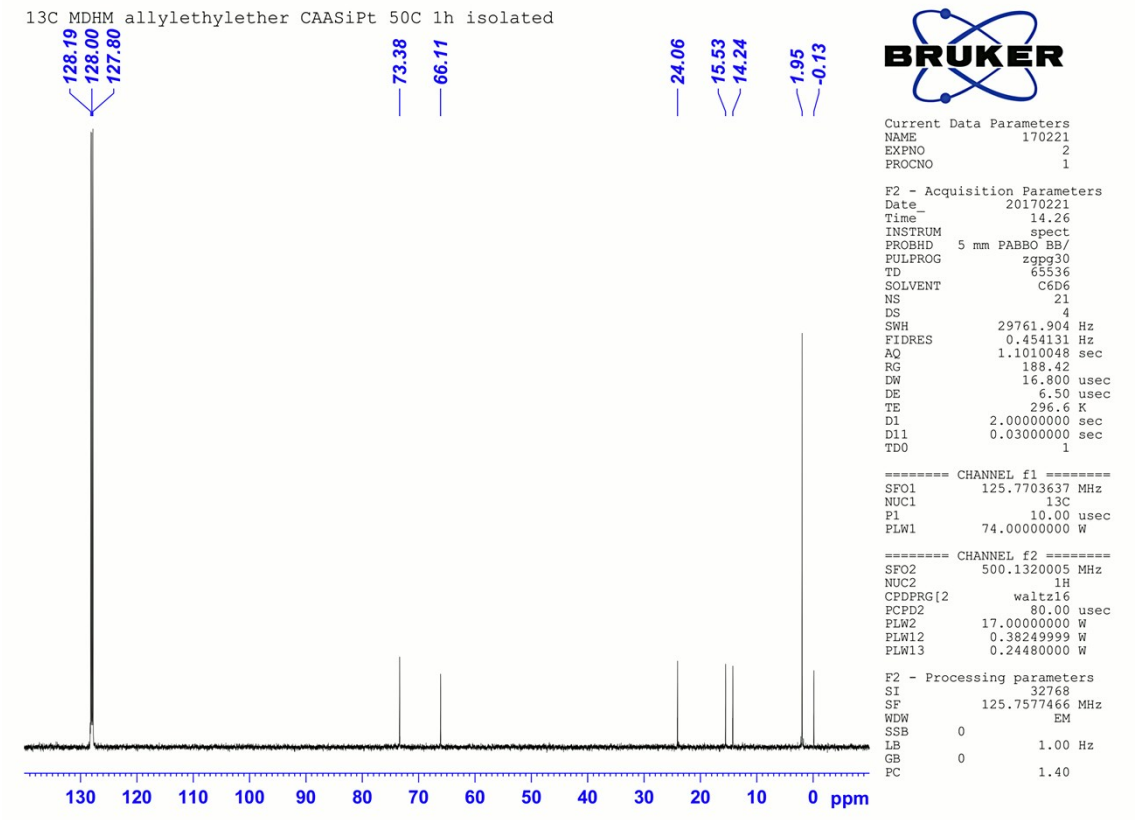


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **10f** (C_6D_6, room temperature).

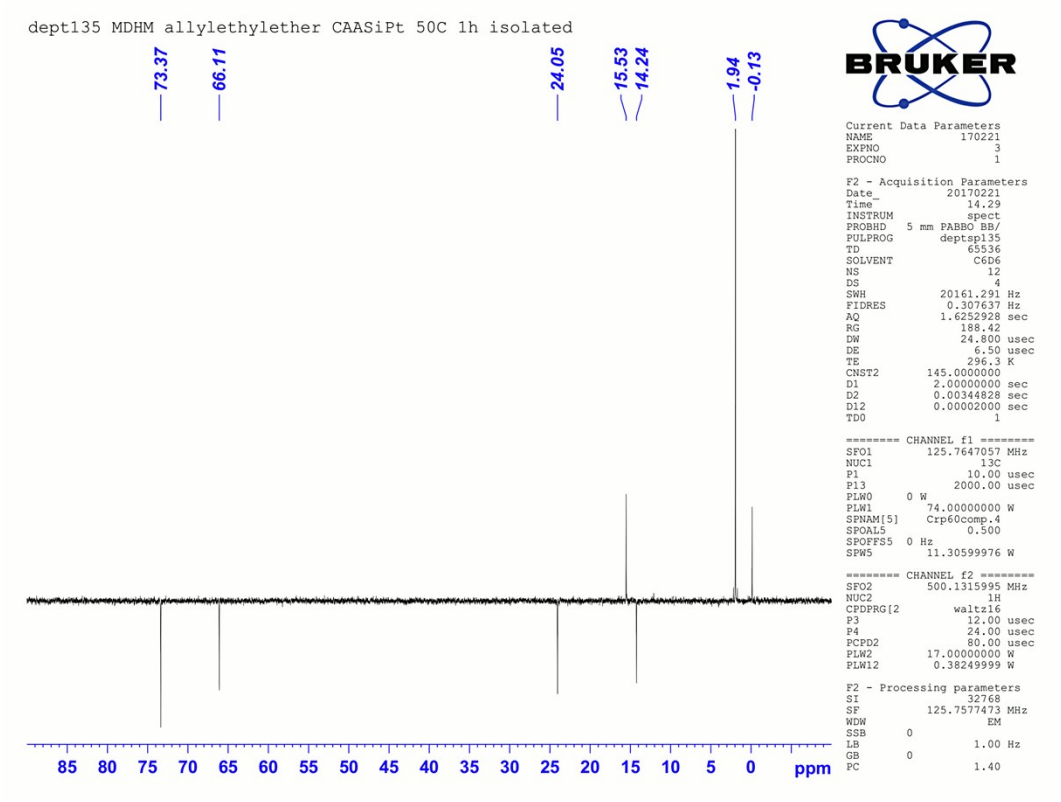


Figure S27. $^{13}C\{^{1}H\}$NMR (DEPT135) NMR spectrum of **10f** (C_6D_6, room temperature).

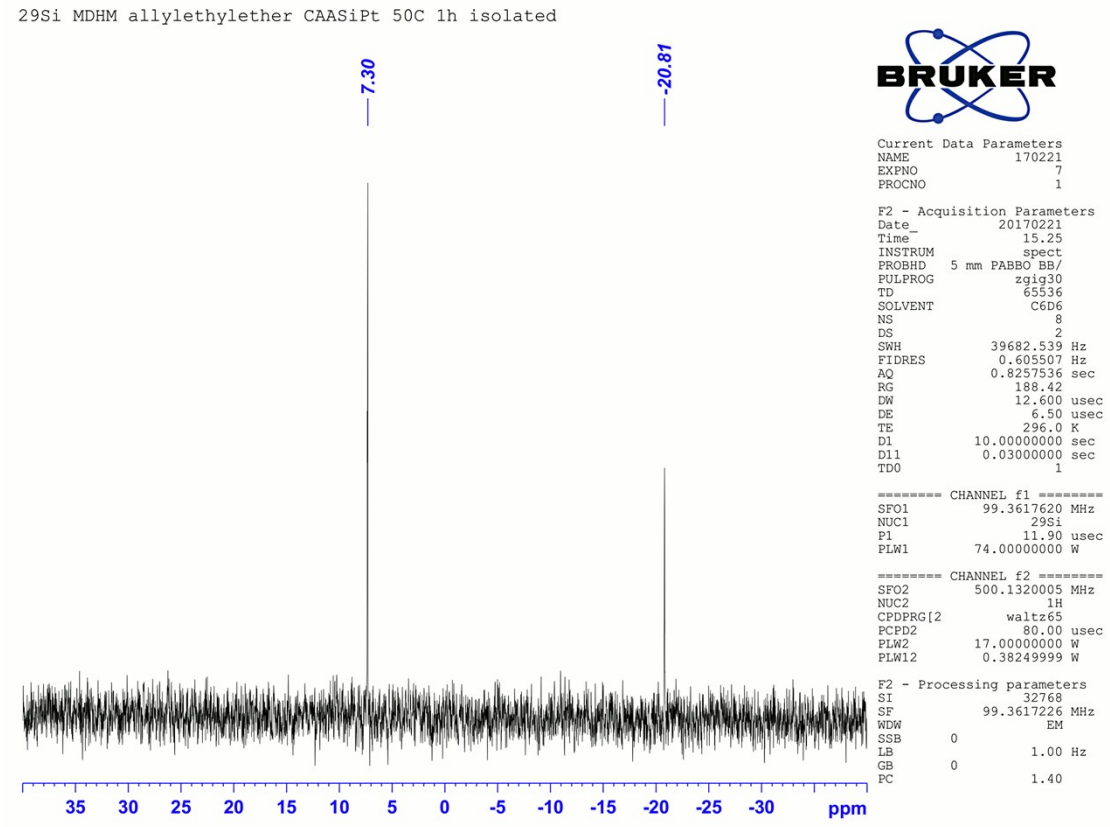


Figure S28. $^{29}Si\{^{1}H\}$NMR spectrum of **10f** (C_6D_6, room temperature).

Hydrosilylation of Allyl Ethyl Ether in the Presence of 7 (entry 24)

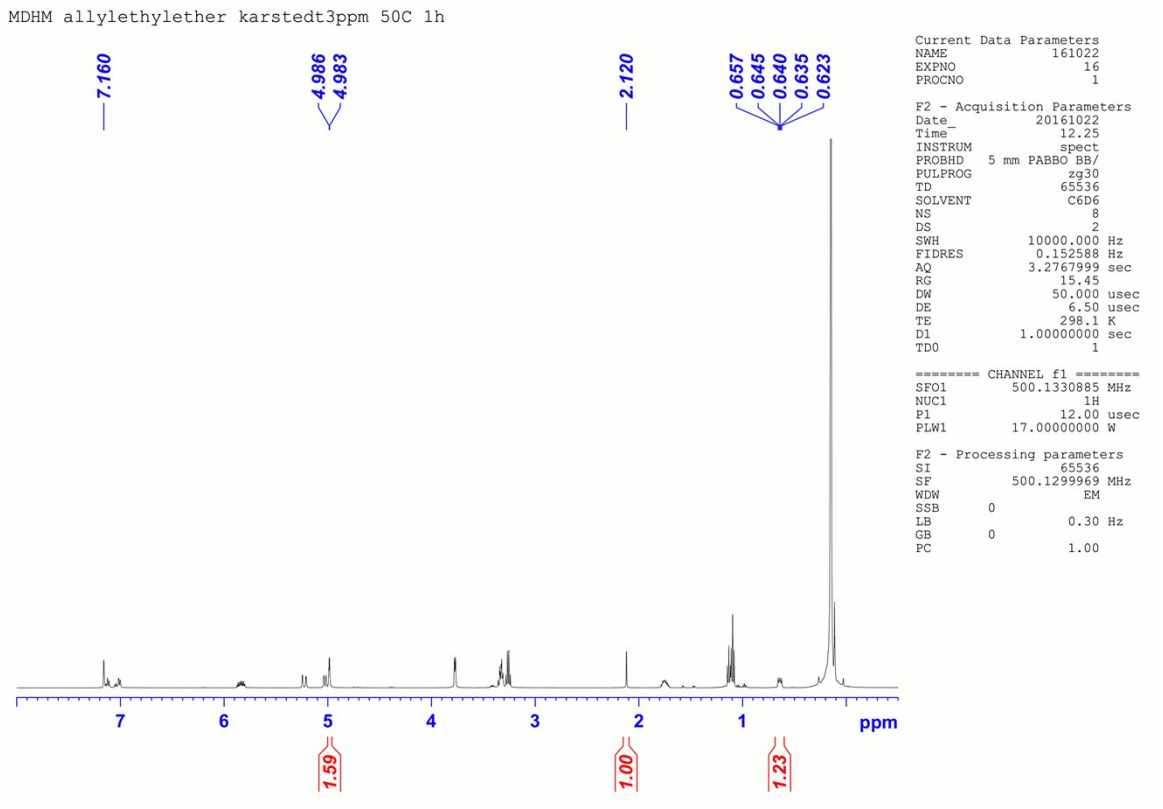


Figure S29. ^{1}H NMR spectrum of reaction mixture of entry 24 (C_6D_6, room temperature).

Hydrosilylation of Allyl Ethyl Ether in the Presence of 2 (entry 25)

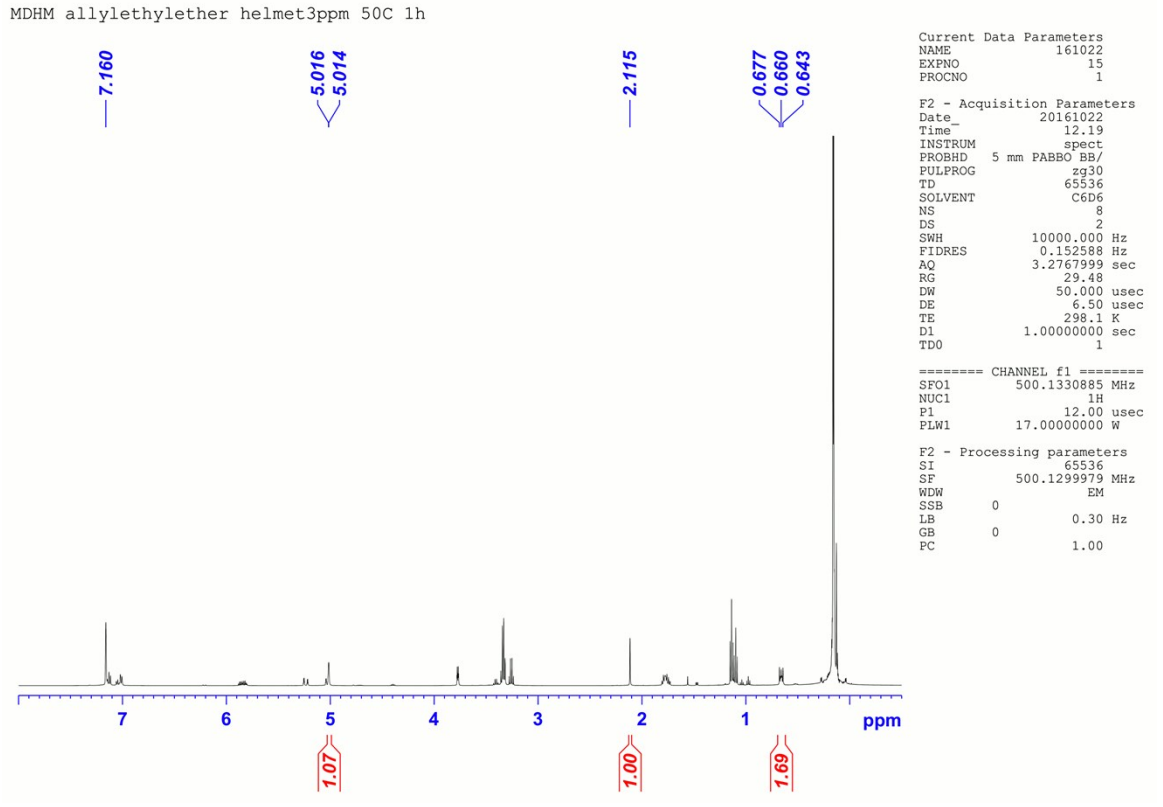
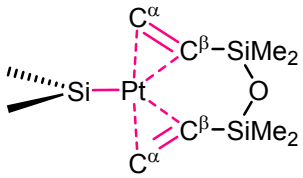


Figure S30. ^{1}H NMR spectrum of reaction mixture of entry 25 (C_6D_6, room temperature).

4. Theoretical Calculations

The geometry optimization of **6** was performed at the various levels of theory and the Pt–Si, Pt–C(vinyl) and C=C distances obtained at the PBE0/def2-tzvp level of theory is in good agreement with those obtained by X-ray diffraction study (Table 1).

Table S1. Selected Structural Parameters of $\mathbf{6}_{opt}$ and $\mathbf{2}_{opt}$ Calculated at Various Level of Theory.



Cpd	Functional/Basis Set	distances/Å [WBI]						NPA Charges	
		Si–Pt	Pt–C^{α}	Pt–C^{β}	C^{α}–C^{β}	Si–N(Ad)	Si–C($SiMe_3$)$_2$	Pt	Si
6a (exp)	XRD (mol. 1)	2.2504(8)	2.139(3) 2.145(3)	2.162(3), 2.151(3)	1.421(5) 1.422(4)	1.690(3)	1.870(3)	–	–
	XRD (mol. 2)	2.2481(8)	2.146(3), 2.147(3)	2.160(3) 2.158(3)	1.427(4) 1.422(4)	1.698(3)	1.873(3)	–	–
6a$_{opt}$	B3PW91-D3/B	2.255	2.163 2.172	2.183 2.178	1.421 1.423	1.715	1.875	0.221	1.441
	PBE0-D3/B	2.2633	2.152 2.161	2.169 2.164	1.421 1.423	1.715	1.879	0.231	1.446
	B3LYP-D3/B	2.268	2.197 2.202	2.222 2.218	1.417 1.421	1.720	1.890	0.213	1.405
	M06-2X/B	2.238	2.158 2.168	2.184 2.180	1.417 1.419	1.716	1.880	0.208	1.498
6b$_{opt}$	B3PW91-D3/B	2.259	2.174 2.163	2.180 2.183	1.422 1.421	1.718	1.903	0.219	1.446
TS$_{opt}$ (6a-6b)	B3PW91-D3/B	2.299	2.181 2.176	2.202 2.198	1.410 1.413	1.736	1.913	–	–
2(exp)	XRD[S1]	2.2572(13)	2.175(5) 2.170(5)	2.177(5) 2.181(5)	1.424(6) 1.415(6)	–	1.911-1.917	–	–
2$_{opt}$	B3PW91-D3/B[S1]	2.257	2.182	2.202	1.415	–	1.914-1.918	0.190	1.470

a. Basis B: SDD [Pt] and 6-311G(d) [H, C, N, O, Si]

Table S2. Atomic Coordinates of $\mathbf{6a}_{opt}$ at the B3PW91-D3/B Level of Theory (B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

Atom	X	Y	Z
Pt	-0.584395959265	-1.088374119769	0.008052072335
C	-0.741073032118	-1.641135797848	2.093830725154
H	0.100756766131	-2.235353696725	2.440457335456
H	-0.938901431050	-0.765982886407	2.709911930398
C	-1.802246772827	-2.266246241981	1.384840927670
H	-1.662889356702	-3.319298346977	1.131614690558
C	-0.713384280243	-0.689490585043	-2.123123229752
H	0.140491513916	-1.049993180876	-2.690751466741
H	-0.947997274848	0.356300438935	-2.315675607374
C	-1.752108107619	-1.592007725262	-1.760638547994
H	-1.566361156851	-2.646425806979	-1.977814896197
Si	-3.554704253506	-1.626395988032	1.399761357490
Si	-3.544203547239	-1.091148880968	-1.598952295456
O	-4.164859810087	-1.621707704987	-0.149485080647
C	-3.683617167666	0.778641908754	-1.671208371687
H	-3.354642416941	1.180660137938	-2.634527777169
H	-4.720395582051	1.092205868086	-1.516756238237
H	-3.081186535128	1.245423496139	-0.888163736560
C	-4.573447854764	-1.889474704587	-2.943779628534
H	-4.495909289682	-2.980089481245	-2.899446768801
H	-5.631061367277	-1.629300088978	-2.837585759210
H	-4.244675004976	-1.571186460962	-3.938182380331
C	-4.679308466176	-2.736973783197	2.403318596940
H	-4.353273417070	-2.794185840342	3.446632772458

H	-5.710258613582	-2.370028974978	2.390280439220
H	-4.685594413586	-3.753589886840	1.998637325524
C	-3.555263553047	0.125881191954	2.072973153420
H	-4.530111314830	0.599348860619	1.922904358725
H	-3.331274088136	0.156179295653	3.143975419587
H	-2.804930879351	0.732200697509	1.558259466978
Si	1.310081078026	0.126410104918	0.151763180641
C	3.100324158302	-0.417660120453	0.031977874408
N	1.641651892403	1.809172219949	0.138134703129
C	3.897891357297	0.909483745679	0.216153373260
Si	3.438439523738	-1.579456239798	1.500656079303
Si	3.371563601863	-1.185522652847	-1.689217318356
C	0.679659349315	2.922465104946	0.163011079376
C	3.041595642784	2.113909979366	-0.185665853869
H	4.182487086359	1.032854501481	1.267650372126
H	4.838066375943	0.915332087520	-0.346515111721
C	2.614695744028	-3.258347576566	1.309761900165
C	2.780419602208	-0.753858531606	3.068815540084
C	5.295920601484	-1.802404037234	1.725920733448
C	2.323909294419	-2.722775547359	-1.988981758181
C	5.182168684835	-1.656124424116	-1.927192884488
C	2.954629653109	0.113208102237	-2.998644848188
C	-0.719653354074	2.404121594993	0.524758700607
C	1.075239024413	3.974273693468	1.219473363255
C	0.600211858568	3.603128003601	-1.216989634399
H	3.382320750700	3.006358278123	0.345787524793
H	3.141153011608	2.322804108728	-1.257547023217
H	1.602434908941	-3.167676076876	0.907223918304
H	2.546854263749	-3.754687306407	2.283420334269
H	3.180217011992	-3.918046220118	0.646759073334
H	1.695412435601	-0.615123734442	3.040861943377
H	3.005605329118	-1.372844019536	3.943869493231
H	3.231786265861	0.227630347038	3.242853851532
H	5.504064868680	-2.350462814596	2.650948239609
H	5.749513328380	-2.359982525821	0.903027632819
H	5.812323768807	-0.839960869430	1.794129731286
H	1.344489088332	-2.669168833124	-1.507416683051
H	2.821721198996	-3.623820811897	-1.622703500672
H	2.160984281029	-2.856021583618	-3.063680447784
H	5.438982323084	-2.562830725626	-1.372636243178
H	5.869546498711	-0.867121482807	-1.608513263028
H	5.380976250103	-1.856114233808	-2.985578505917
H	1.977395524635	0.579667824894	-2.838539526565
H	2.940203299954	-0.341729601135	-3.994584368801
H	3.702585861560	0.911567796323	-3.019683104383
C	-1.743301418137	3.543001581759	0.550120407982
H	-0.682484000537	1.900746692887	1.498270666317
H	-1.029016145124	1.645691029159	-0.200249204937
C	0.058242388316	5.123895956795	1.242880553424
H	1.136550544959	3.485522448954	2.198969940200
H	2.066859041441	4.384324481385	1.001648246543
C	-0.417616708263	4.750852324521	-1.192803907708
H	0.321581331118	2.849891923027	-1.964315933296
H	1.584963077844	3.990359396706	-1.502352843783
C	-1.329012094453	4.578872070064	1.599314178688
C	-1.802310967148	4.199792863221	-0.833877070747
H	-2.725125133448	3.127595399060	0.804253303119
C	0.009356090867	5.784720878373	-0.141785083599
H	0.371283786446	5.860927699051	1.991987571900
H	-0.450725098788	5.222152607037	-2.182298026772
H	-1.311262443164	4.120018447315	2.595495241224
H	-2.059663487243	5.396086227873	1.637305500033
H	-2.544204036571	5.007572341486	-0.837622402597
H	-2.125950793231	3.467882797091	-1.583033155223
H	-0.695906162321	6.624548774333	-0.132564033688
H	0.992763449153	6.199386823254	-0.397211300865

(frequency analysis in the gas phase)
Thermochemistry at 298.150 K, 1.000 Atm
E(el) = -2759.050158515584
ZPVE = 0.775393237717
Enthalpie(0K) = -2758.274765277867
E(tr) = 0.001416284860
E(rot) = 0.001416284860
E(vib) = 0.818928139226
H-E(el) = 0.822704898852
Enthalpie = -2758.227453616732
S(el) = 0.000000000000
S(tr) = 0.000072830257

```
S(rot)       =    0.000060232164 (Symmetry number = 1)
S(vib)       =    0.000284214955
G-E(el)      =    0.698293649210
Free Energy  = -2758.351864866373 (0.0 kJ/mol relative to 6a_opt)
JOB name: ti510Dopt
```

Table S3. Atomic Coordinates of **6a$_{opt}$** at the PBE0-D3/B Level of Theory (B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

Atom	X	Y	Z
Pt	-0.614272729658	-1.099364982768	-0.013460823463
C	-0.755759438248	-1.586888455072	2.078145136074
H	0.086980485567	-2.173822811647	2.434718135301
H	-0.952243327970	-0.696741660912	2.672830317649
C	-1.821207862318	-2.228151231954	1.390901929270
H	-1.681866075391	-3.287431782994	1.164995849387
C	-0.739590289863	-0.761868331667	-2.144137272285
H	0.111366758215	-1.147078945810	-2.699941618553
H	-0.970253712837	0.278161794152	-2.369369502890
C	-1.783546893495	-1.644685667613	-1.751303476247
H	-1.604734457815	-2.706458159634	-1.936180587237
Si	-3.574830748213	-1.595534783677	1.409498744079
Si	-3.571229981564	-1.128065812741	-1.607382674621
O	-4.189759984485	-1.587560130663	-0.135321353057
C	-3.716620519332	0.734425511759	-1.778299295124
H	-3.384896271626	1.084578745768	-2.760992498240
H	-4.757388358053	1.047508170418	-1.650950239084
H	-3.125179094088	1.254439220430	-1.019399061957
C	-4.604670614873	-1.988219370525	-2.908313521644
H	-4.528589794211	-3.075551698653	-2.812386990907
H	-5.661939403493	-1.723142717244	-2.812550183271
H	-4.279590004979	-1.719651056682	-3.918333486558
C	-4.687207488992	-2.718529429291	2.410289928094
H	-4.360748933457	-2.776011480246	3.453335058653
H	-5.721918863012	-2.362679642546	2.399580275813
H	-4.684641639072	-3.734478707700	2.004106786717
C	-3.596750984059	0.150132157555	2.095211817671
H	-4.590217273018	0.595658732400	1.986223178729
H	-3.336288337150	0.178839625312	3.158035337216
H	-2.885413466713	0.786315669443	1.560214236679
Si	1.291706880090	0.116169587215	0.096520818238
C	3.090334130175	-0.415861774516	-0.011820749265
N	1.621704876915	1.799249815776	0.068576576274
C	3.876546636679	0.917738591865	0.149757960945
Si	3.442532802647	-1.533559626472	1.488817503706
Si	3.388580025610	-1.218889711184	-1.711268644684
C	0.679592792072	2.922110328223	0.144931019610
C	3.013249349429	2.103100019815	-0.275706592463
H	4.156445823701	1.063903284557	1.200020948068
H	4.818514095184	0.919092508623	-0.410541623301
C	2.644396323839	-3.228075161285	1.346551581321
C	2.768624094706	-0.673459172428	3.029817990063
C	5.300435149365	-1.724670455467	1.727944428222
C	2.357385360294	-2.771366249777	-1.976009457476
C	5.204788850836	-1.671936547777	-1.926746693095
C	2.964445244570	0.035401215965	-3.058558363945
C	-0.734463275389	2.408646241976	0.433324662914
C	1.065534666374	3.883895841954	1.283889136590
C	0.650358726033	3.700735466632	-1.180903585337
H	3.352129506902	3.013214278912	0.227156401394
H	3.101723394850	2.283116759867	-1.354152987487
H	1.626378949232	-3.163420266160	0.952074928931
H	2.592990877687	-3.701542857941	2.332591137629
H	3.212395820912	-3.897353238481	0.695151442791
H	1.680448031124	-0.559213578792	3.000009800013
H	3.007398746550	-1.259063223843	3.924016422839
H	3.197906294085	0.322719081595	3.173933050187
H	5.508638854990	-2.247018743020	2.667664031997
H	5.768173396581	-2.297400711031	0.923425552016
H	5.806068329833	-0.755371328296	1.777337521522
H	1.368074248745	-2.703439270049	-1.515096877435
H	2.849875503234	-3.657075661493	-1.567354200850
H	2.215323757965	-2.945658373047	-3.047841718234
H	5.478352782054	-2.548288455295	-1.332763705657
H	5.880991521072	-0.858632611334	-1.647096747981

```
H           5.406322394770   -1.916568288246   -2.975114568119
H           1.966115017602    0.468496477884   -2.937197219216
H           2.992849647061   -0.443121969678   -4.043179762168
H           3.682279694613    0.860921484655   -3.082377249837
C          -1.735693003499    3.562210477172    0.513542113236
H          -0.731703223112    1.842007629561    1.372552628061
H          -1.035250079164    1.704238254797   -0.348726955454
C           0.073713442686    5.049246590441    1.363433923218
H           1.084288767833    3.323180535875    2.226101846853
H           2.073507687621    4.283009024539    1.127223588470
C          -0.344140039590    4.862600454860   -1.099292577075
H           0.377749200247    3.010957955486   -1.989713846935
H           1.649506059313    4.088158517151   -1.411882670194
C          -1.330323495527    4.509829592292    1.642787693043
C          -1.745624303916    4.316696971020   -0.817451421852
H          -2.732042121017    3.150785440942    0.713106815851
C           0.074005700837    5.806990184437    0.032009547518
H           0.379973222872    5.723869131616    2.171720839352
H          -0.341483653240    5.404334647655   -2.052539471549
H          -1.348762019223    3.980440871191    2.603363312343
H          -2.046205648857    5.337250588484    1.720462301496
H          -2.471849842282    5.137833038297   -0.781293959559
H          -2.062607888825    3.647097395928   -1.626378409248
H          -0.614821778990    6.658825081078    0.084469692343
H           1.071688997042    6.217713140079   -0.168681304833
--------------------------------------------------------------------------------
(frequency analysis in the gas phase)
Thermochemistry at  298.150 K,    1.000 Atm
E(el)        = -2757.428705881179
ZPVE         =     0.777428787382
Enthalpie(0K) = -2756.651277093797
E(tr)        =     0.001416284860
E(rot)       =     0.001416284860
E(vib)       =     0.821182786096
H-E(el)      =     0.824959545722
Enthalpie    = -2756.603746335457
S(el)        =     0.000000000000
S(tr)        =     0.000072830257
S(rot)       =     0.000060260974 (Symmetry number = 1)
S(vib)       =     0.000288849056
G-E(el)      =     0.699158049227
Free Energy  = -2756.729547831952
JOB name: ti510Dopt2
```

Table S4. Atomic Coordinates of **6a$_{opt}$** at the B3LYP-D3/B Level of Theory (B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

```
--------------------------------------------------------------------------------
Atom              X                 Y                 Z
--------------------------------------------------------------------------------
Pt         -0.599794254203   -1.109076907576   -0.007822466935
C          -0.778531431424   -1.566453404526    2.133202154359
H           0.062588294164   -2.150814193604    2.493984097377
H          -0.952810024220   -0.656311895987    2.701291501184
C          -1.851345439768   -2.206420521360    1.464082846487
H          -1.720934998161   -3.269612071036    1.255662721830
C          -0.778370118692   -0.880400176367   -2.190529013709
H           0.068649808547   -1.299616639147   -2.724648151779
H          -0.986366038926    0.153932021580   -2.453030654403
C          -1.828527254558   -1.725196766047   -1.747977870981
H          -1.663433950689   -2.796407682119   -1.876992359023
Si         -3.611035933197   -1.570039831199    1.458733029708
Si         -3.616858408320   -1.189367483665   -1.596748297208
O          -4.212243246777   -1.596157682437   -0.095214963591
C          -3.752514495011    0.673968831766   -1.823795400647
H          -3.420444712510    0.993764967835   -2.816305433457
H          -4.789846589277    0.999796928732   -1.702853789095
H          -3.153732254121    1.209691381506   -1.083258803045
C          -4.677069084909   -2.091478026007   -2.856535346368
H          -4.600298516693   -3.175486181887   -2.729721505086
H          -5.732244125603   -1.822540742175   -2.749741891369
H          -4.371480129176   -1.854439696480   -3.880360319340
C          -4.728863569241   -2.679125666292    2.481007881252
H          -4.415621063119   -2.705302172893    3.529290040074
H          -5.766244070907   -2.332676281996    2.448436114938
H          -4.713678050384   -3.706058510793    2.104023265241
C          -3.643480019401    0.197203172185    2.104414689255
```

```
H          -4.647459504126    0.622944398036    2.017697060968
H          -3.349474686917    0.257272493795    3.156853669933
H          -2.963187480455    0.833364546674    1.532576682987
Si          1.302322694039    0.122694183433    0.081137072829
C           3.110619252878   -0.417667708483   -0.014436747067
N           1.627234621970    1.811349675095    0.041664384567
C           3.901785401468    0.926401266014    0.161916694792
Si          3.469055272137   -1.559243153851    1.479232729036
Si          3.422961475615   -1.205882192654   -1.730602414408
C           0.680438624660    2.946267649152    0.125003132440
C           3.038639020527    2.123445074095   -0.264383026172
H           4.175502973677    1.066485941725    1.212673574345
H           4.846097679890    0.933941141694   -0.391596006501
C           2.635950589890   -3.245862587699    1.344771713030
C           2.838596387410   -0.711513888265    3.054099733788
C           5.333837610509   -1.789233102115    1.685951912840
C           2.442092520216   -2.799072321750   -1.996216930572
C           5.257797318796   -1.597371099484   -1.970760345591
C           2.941254380905    0.031330978556   -3.084232596931
C          -0.765977642999    2.436153740196    0.288136050113
C           1.006060601394    3.835987923263    1.351488037584
C           0.742339801485    3.812053977641   -1.156985664778
H           3.362277336645    3.025017628416    0.261115001491
H           3.150264850616    2.322277249180   -1.335696132330
H           1.612919818110   -3.164748979643    0.970488431307
H           2.594744400251   -3.719247213845    2.331068649074
H           3.178827766592   -3.924292773464    0.682838064515
H           1.751910486277   -0.590812139990    3.056775062257
H           3.097988485115   -1.313994979487    3.930836652729
H           3.277976575864    0.278620669542    3.204574932952
H           5.551171935978   -2.295981455382    2.631858067103
H           5.771622418259   -2.389693180769    0.885443428928
H           5.862116901974   -0.831359781587    1.702297100338
H           1.456260271586   -2.770687576166   -1.528313314230
H           2.969531419321   -3.668732786143   -1.598028422209
H           2.297969625362   -2.971716792511   -3.067664475532
H           5.572232694459   -2.459860195281   -1.378081330579
H           5.909732360537   -0.760674184323   -1.704914636037
H           5.452113695122   -1.838910286035   -3.021009382050
H           1.915297350795    0.397076565083   -2.982290759513
H           3.019386781426   -0.441596413288   -4.068556184086
H           3.602548486937    0.902217183659   -3.093536713978
C          -1.761174751457    3.605808211605    0.383190993497
H          -0.837568555775    1.811451236293    1.183334782895
H          -1.026066394013    1.796438026906   -0.557770680702
C           0.020182501031    5.017585226936    1.442373014552
H           0.956076944159    3.219218369362    2.255398362224
H           2.027659950697    4.222265713845    1.284337960784
C          -0.248371867959    4.988946226513   -1.063572347472
H           0.514746141246    3.180270705824   -2.023266005990
H           1.754778943114    4.201628540878   -1.302300468011
C          -1.413033609735    4.479081596483    1.600695999685
C          -1.680285975814    4.447506133404   -0.902353943548
H          -2.771524694193    3.198224795253    0.495943938400
C           0.112347895455    5.860734727741    0.155366323546
H           0.282060543779    5.636235668009    2.308052255323
H          -0.178911845740    5.587784243845   -1.978579933333
H          -1.496885459603    3.890808604262    2.521825257033
H          -2.122993346379    5.309668271201    1.687575747276
H          -2.395983203980    5.276476733810   -0.858683121277
H          -1.954798156702    3.835622896952   -1.769371644052
H          -0.567623315289    6.717947377281    0.218478245374
H           1.124583359548    6.267116430550    0.041900430712
---------------------------------------------------------------------------
(frequency analysis in the gas phase)
Thermochemistry at  298.150 K,    1.000 Atm
E(el)        = -2759.658192670863
ZPVE         =     0.773679719782
Enthalpie(0K) = -2758.884512951081
E(tr)        =     0.001416284860
E(rot)       =     0.001416284860
E(vib)       =     0.817755789707
H-E(el)      =     0.821532549333
Enthalpie    = -2758.836660121530
S(el)        =     0.000000000000
S(tr)        =     0.000072830257
S(rot)       =     0.000060345008 (Symmetry number = 1)
S(vib)       =     0.000293819530
G-E(el)      =     0.694224051384
```

```
Free Energy   = -2758.963968619480
JOB name: ti510Dopt3
```

Table S5. Atomic Coordinates of **6a$_{opt}$** at the M06-2X/B Level of Theory

(B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

Atom	X	Y	Z
Pt	-0.597987834509	-1.110494976297	0.007798314090
C	-0.755164724763	-1.638212221715	2.094656198700
H	0.090519133301	-2.229406141411	2.433122111916
H	-0.942873532840	-0.750558433352	2.693510141180
C	-1.821221728704	-2.264193386404	1.401718725254
H	-1.682750762232	-3.316701766464	1.155421257993
C	-0.720950169704	-0.734419778420	-2.124265436192
H	0.138411213261	-1.106139702180	-2.674285253607
H	-0.947315000350	0.311845655510	-2.318670354290
C	-1.764847961952	-1.623922336333	-1.760359351765
H	-1.579454950756	-2.679805672426	-1.959692165172
Si	-3.564768713658	-1.607053974142	1.407382187692
Si	-3.549912359981	-1.105866713160	-1.600897210326
O	-4.165148007883	-1.607605111173	-0.142538516639
C	-3.684800525711	0.763393250190	-1.703430527354
H	-3.322016860359	1.151843087235	-2.659321366059
H	-4.729147254932	1.069831039715	-1.598492436367
H	-3.121919939749	1.254623389870	-0.904619223028
C	-4.588749371877	-1.907907239812	-2.931369368339
H	-4.519259911321	-2.997118658389	-2.877453727441
H	-5.642434648946	-1.639539447815	-2.822495559597
H	-4.263278349230	-1.602244061288	-3.929021260731
C	-4.703704573590	-2.687122502450	2.421354092993
H	-4.381176348824	-2.736772792009	3.464409142342
H	-5.727898304094	-2.306534101329	2.401561819341
H	-4.723656705370	-3.706920943927	2.029424225332
C	-3.552655522215	0.152458121572	2.060308272953
H	-4.528837778582	0.622820450547	1.914190409919
H	-3.321122682470	0.194975022655	3.128250310240
H	-2.808974062786	0.758693829444	1.534068322951
Si	1.278905904929	0.103768027205	0.120284972176
C	3.079782872187	-0.423453280985	0.001486342513
N	1.603287266886	1.788250069446	0.076069156874
C	3.868903956403	0.916666126634	0.141097598132
Si	3.468652463925	-1.538112210947	1.487735463975
Si	3.376197049386	-1.235288121067	-1.688430821445
C	0.656039363601	2.915753133119	0.143180282552
C	2.994391022990	2.098125364953	-0.291686147401
H	4.154107474290	1.079639265176	1.186295100896
H	4.803974251908	0.914100199421	-0.429411528974
C	2.724444565243	-3.254929896827	1.312560595103
C	2.772476922058	-0.717769148944	3.039723692407
C	5.331882466740	-1.675248637943	1.720946897603
C	2.311273243391	-2.764927208931	-1.975653247821
C	5.180094229499	-1.746080354634	-1.878674341636
C	3.001444431994	0.042524676276	-3.029120265890
C	-0.760636002008	2.400443867445	0.441626959423
C	1.044108768460	3.894282411664	1.272059315466
C	0.624303156388	3.679070794208	-1.195372387721
H	3.333794999415	3.013493027912	0.197226813338
H	3.067035273479	2.262006099400	-1.372340559563
H	1.700903890297	-3.219674032785	0.928845915337
H	2.700605385104	-3.754215540465	2.285659702232
H	3.310728892573	-3.885476704157	0.639644530527
H	1.681764212213	-0.637327499900	3.016346070551
H	3.035115927803	-1.299433376226	3.928253742307
H	3.171165168235	0.290025465864	3.186409221771
H	5.556172762558	-2.203249761784	2.652459284528
H	5.816172243538	-2.221820239109	0.909527758773
H	5.806136875965	-0.692026130715	1.784622162695
H	1.340244919848	-2.713182211215	-1.477521735923
H	2.812158971065	-3.669899580228	-1.625347156786
H	2.128744065708	-2.892865331058	-3.047052555910
H	5.399067127763	-2.658664266455	-1.318593227422
H	5.878626207615	-0.975088927393	-1.543270726863
H	5.400584317903	-1.953170995561	-2.930076681848
H	2.032729663876	0.533594268647	-2.887256982376
H	2.985661704524	-0.430898045594	-4.015079570661

```
H           3.766249508944    0.823603233088   -3.059744724746
C          -1.767787120689    3.555010011676    0.511292118955
H          -0.751810833858    1.845382001883    1.387428922166
H          -1.061559495270    1.693163393802   -0.336056917502
C           0.045284830063    5.060970828251    1.339649265188
H           1.064782925731    3.345210114438    2.219945181066
H           2.047300712819    4.297411006125    1.106720947047
C          -0.378754223912    4.840653531036   -1.127224186606
H           0.354220593189    2.978069886983   -1.994777331640
H           1.620585299315    4.070282302315   -1.427866221586
C          -1.360856588751    4.520979294619    1.630298103439
C          -1.782116708072    4.292455692480   -0.834360013249
H          -2.761805712567    3.144721231081    0.718125361837
C           0.039339765992    5.803649371671   -0.005430675077
H           0.351139194394    5.745939774088    2.136380753740
H          -0.380204727190    5.369406644161   -2.085241376295
H          -1.374792670829    4.003537395242    2.595720008530
H          -2.076575176647    5.347486442224    1.695700396955
H          -2.508513113282    5.111701784600   -0.807368615465
H          -2.096005804545    3.608768494558   -1.631279371377
H          -0.654127550028    6.650219980196    0.038421735899
H           1.034125118266    6.213434404788   -0.213410778217
--------------------------------------------------------------------------------
(frequency analysis in the gas phase)
Thermochemistry at  298.150 K,    1.000 Atm
E(el)        = -2758.680224191076
ZPVE         =     0.780777416354
Enthalpie(0K) = -2757.899446774722
E(tr)        =     0.001416284860
E(rot)       =     0.001416284860
E(vib)       =     0.824160362899
H-E(el)      =     0.827937122525
Enthalpie    = -2757.852287068551
S(el)        =     0.000000000000
S(tr)        =     0.000072830257
S(rot)       =     0.000060248770 (Symmetry number = 1)
S(vib)       =     0.000284692814
G-E(el)      =     0.703378448115
Free Energy  = -2757.976845742960
JOB name: ti510Dopt4
```

Table S6. Atomic Coordinates of **6b$_{opt}$** at the B3PW91-D3/B Level of Theory (B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

```
--------------------------------------------------------------------------------
Atom             X                 Y                 Z
--------------------------------------------------------------------------------
Pt         -0.865881083332   -0.554073587735   -0.320628682482
Si          0.885431967147    0.850587053571   -0.068504216524
N           2.575270095114    0.547197522766   -0.140378446850
C           3.365112151543    1.583568218501    0.539053749942
C           2.570693835588    2.890792116499    0.501505542713
C           1.040278660685    2.606028411086    0.571177292533
C          -0.443014225581   -1.466200500146    1.607375625243
C          -1.450356315415   -2.225524132320    0.951222729529
C          -1.546161081832    0.103655979164   -2.265507199037
C          -2.337452134160   -1.007193762463   -1.868198369159
H           0.569195388039   -1.860024344446    1.680244542514
H          -0.712019843153   -0.810221294632    2.432463901569
H          -1.102544585596   -3.121767904758    0.430386889401
H          -0.786718058282   -0.022023711616   -3.035216023065
H          -1.955721555304    1.110267816044   -2.219219081837
H          -2.061334387613   -1.973067029106   -2.297977820446
Si         -3.256207399165   -2.260472307908    1.431319334212
Si         -4.065959796296   -0.893997529920   -1.175492038667
O          -4.209858288690   -1.949091037997    0.104610163628
C          -4.407021328957    0.850637545254   -0.580738841435
H          -4.338672268483    1.587206820932   -1.387112663450
H          -5.410394766037    0.921302395587   -0.149617278767
H          -3.692739548129    1.140961538909    0.194356579868
C          -5.335671106529   -1.429137010359   -2.443922323074
H          -5.139898217181   -2.449464864650   -2.787317814751
H          -6.345880299711   -1.409878640306   -2.023452422604
H          -5.321285273260   -0.773138789023   -3.320159200895
C          -3.713613200714   -3.978568901942    2.021052694257
H          -3.147377923301   -4.257479137121    2.915459693427
H          -4.779073119905   -4.040490612135    2.262995048350
```

```
H          -3.507387271628   -4.725511018419    1.248270230411
C          -3.613032817171   -0.990923221746    2.762042818590
H          -4.669703679995   -1.027851166355    3.044423967586
H          -3.020836488342   -1.170259643290    3.665006982732
H          -3.400435822786    0.024102104791    2.420063919094
Si          0.136359782353    3.748299487398   -0.653054862316
Si          0.370993418471    2.632522218663    2.352443888119
H           2.814561495738    3.405751487831   -0.435396039274
H           2.909353258811    3.558812773007    1.301557073585
H           4.332163571111    1.725476509870    0.050549790394
H           3.570617586579    1.281278310853    1.573107366404
C           1.415180021258    1.458306754958    3.401627859232
H           2.437381992021    1.826932016792    3.528519496116
H           0.981421012698    1.355425022941    4.401815437563
H           1.474429794348    0.454584975595    2.967858656252
C           0.522907463166    4.358031800080    3.095433948757
H          -0.223553174999    5.040589217028    2.679552564564
H           0.359946189134    4.318912636150    4.177713626376
H           1.508773069756    4.801631848117    2.927457646062
C          -1.424733837984    2.078543545016    2.446392227039
H          -2.123102059699    2.899181865027    2.269315003490
H          -1.637067216053    1.297669007181    1.711220895832
H          -1.642418167093    1.668924955233    3.437615443085
C           0.681945462081    5.531300940846   -0.381409415974
H           0.234532827686    6.183282730172   -1.139162956491
H           0.381182037012    5.909570118467    0.598615890301
H           1.767818512914    5.642289138538   -0.457078104629
C          -1.731307862661    3.622702698055   -0.524154963744
H          -2.046814119277    2.581549129454   -0.434957102552
H          -2.130390800924    4.167487729394    0.335111206037
H          -2.200458637983    4.038121789741   -1.421891197686
C           0.640104055992    3.248004436558   -2.403880592792
H           0.224749172280    2.273063015428   -2.677608516813
H           0.266442659979    3.976003941035   -3.131736412887
H           1.725637500787    3.189829348773   -2.529598348974
C           3.262699594411   -0.698192128195   -0.523591057105
C           4.458201930342   -0.408955364289   -1.455412125933
C           3.776940103955   -1.440175454923    0.725443859355
C           2.301788975815   -1.628567703754   -1.280072967907
C           5.164170882273   -1.712990380676   -1.853199443807
H           5.184344613528    0.243029298823   -0.959614536672
H           4.096084315541    0.126455176798   -2.341078491933
C           4.477123351718   -2.745862585866    0.327418634206
H           4.474693105548   -0.802104914057    1.279703597339
H           2.928811720076   -1.640196388078    1.390781498503
C           2.996804163453   -2.933523524110   -1.681559273972
H           1.914423931072   -1.110958766559   -2.166103282844
H           1.432108918194   -1.858410498475   -0.656933699834
C           5.665617501999   -2.423902664418   -0.588457865929
C           4.184345221535   -2.624942332670   -2.597946018873
H           6.014713863689   -1.472597359617   -2.502165404098
C           3.488808117050   -3.650488690745   -0.418165777183
H           4.834150803711   -3.252482357232    1.231943425671
H           2.273779594474   -3.567157249041   -2.208107743585
H           6.388647347142   -1.789894301577   -0.059873642119
H           6.192478345000   -3.346636410020   -0.860148968132
H           4.684560723601   -3.553013816818   -2.900987048130
H           3.835526438990   -2.135815054937   -3.515750864011
H           3.970957223614   -4.599254262073   -0.683644049263
H           2.638173489102   -3.895514870810    0.229856387532
-----------------------------------------------------------------------------
(frequency analysis in the gas phase)
Thermochemistry at  298.150 K,    1.000 Atm
E(el)        = -2759.046678648038
ZPVE         =     0.774710589096
Enthalpie(0K) = -2758.271968058942
E(tr)        =     0.001416284860
E(rot)       =     0.001416284860
E(vib)       =     0.818509774376
H-E(el)      =     0.822286534002
Enthalpie    = -2758.224392114036
S(el)        =     0.000000000000
S(tr)        =     0.000072830257
S(rot)       =     0.000060329794 (Symmetry number = 1)
S(vib)       =     0.000288910932
G-E(el)      =     0.696446070280
Free Energy  = -2758.350232577758 (4.3 kJ/mol relative to 6a_opt)
JOB name: ti511_forward_end
```

Table S7. Atomic Coordinates of Transition State between **6a$_{opt}$** and **6b$_{opt}$** via Rotation of Pt-Si Bond (**TS$_{opt}$ (6a-6b)**) at the B3PW91-D3/B Level of Theory (B: SDD [Pt], 6-311G(d) [H, C, N, O, Si])

Atom	X	Y	Z
Pt	-1.015651590120	-0.448600869556	-0.731018097099
Si	0.848786427208	0.834510375132	-0.328850899443
N	2.548089533979	0.538150764194	-0.129641396590
C	3.346709228280	1.730057457485	0.172571516885
C	2.525118747471	2.960010270044	-0.182534892751
C	1.007052809884	2.696749563118	0.052180701414
C	-0.217226147133	-2.464649888913	-0.967754519192
C	-1.623902953821	-2.553112485717	-0.953414429706
C	-2.379881785043	1.243852798872	-0.817588243399
C	-3.138869798013	0.062965931571	-0.980471872586
H	0.320825594691	-2.580856545871	-1.905786067732
H	0.345817375743	-2.772984068813	-0.094570530366
H	-2.124970504955	-2.646835820180	-1.918880856052
H	-2.176979596808	1.874190386171	-1.677099610562
H	-2.425077356700	1.778713081261	0.122934975754
H	-3.377523714058	-0.214783230546	-2.010415340797
Si	-2.583612544392	-3.090006116822	0.556214560347
Si	-4.319015398393	-0.608445416051	0.311024968920
O	-3.993592753607	-2.211638133658	0.615630198141
C	-4.172519993525	0.344757452101	1.914814747333
H	-4.379798133307	1.411111639330	1.784500846936
H	-4.885744556160	-0.046017472385	2.647162150841
H	-3.173462819588	0.248623518248	2.345264776875
C	-6.067423193943	-0.524023033577	-0.353943252606
H	-6.159697437679	-1.084028970380	-1.289572253753
H	-6.778917713553	-0.952355203670	0.358714674470
H	-6.369112826641	0.509447208873	-0.551970578226
C	-3.073412020368	-4.893503694456	0.450096009087
H	-2.192309747093	-5.541436150983	0.405038807463
H	-3.667557948998	-5.191614479302	1.319562036313
H	-3.675318612114	-5.084372262805	-0.443337640438
C	-1.549281448427	-2.762331770375	2.086733850113
H	-2.120302544450	-2.968347204242	2.997221224690
H	-0.648014483927	-3.383556222819	2.113460177030
H	-1.229602392869	-1.716002399062	2.113902147528
Si	0.098151567953	3.863393941534	-1.160716356943
Si	0.555656976152	3.001548132186	1.886223423799
H	2.702033046599	3.174274708883	-1.243925584963
H	2.895533254720	3.836255038798	0.362686853793
H	4.268871195977	1.738849976109	-0.412901270869
H	3.639898026091	1.734697953570	1.226863695316
C	1.863640870567	2.278785689045	3.041120801191
H	2.822526529669	2.799808311909	2.976219566378
H	1.514111224539	2.374829580709	4.074721524770
H	2.036834237391	1.214847452510	2.853215127891
C	0.472216958971	4.848804117734	2.252798961762
H	-0.329381480243	5.352249343748	1.706674147285
H	0.288591182213	5.002972978556	3.321486800007
H	1.412713189565	5.352503972084	2.009695959089
C	-1.058738054742	2.182142555772	2.396498524733
H	-1.949678441413	2.686187318609	2.018031367534
H	-1.102053927947	1.142099773950	2.060445235592
H	-1.132967969285	2.180472840504	3.488947571659
C	1.072091356394	5.477815485752	-1.308840215166
H	0.527942645139	6.156193992348	-1.975466661821
H	1.171008802676	5.983614664159	-0.344410954916
H	2.074406438242	5.351657108000	-1.725318867480
C	-1.647240327555	4.410382664878	-0.666941480232
H	-2.356679980237	4.256294752675	-1.484473715973
H	-2.052225302626	3.900904690082	0.206517326268
H	-1.639547905224	5.481379029952	-0.442899993034
C	0.111593874148	3.070848615012	-2.873839338566
H	-0.400728814857	2.105294791605	-2.903849188479
H	-0.362427358358	3.728038728166	-3.610550462760
H	1.140471478059	2.901433361566	-3.210235699166
C	3.239259042713	-0.776968562592	-0.062264843718
C	4.755077902418	-0.644718217273	0.202832940527
C	2.643739378883	-1.615017471287	1.084611675508
C	3.074147273457	-1.521676308015	-1.396317190510
C	5.416330543540	-2.029110148265	0.274327056144

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H          4.936888281319   -0.110169752368    1.141070183760
H          5.232533265688   -0.071212636980   -0.598644007002
C          3.288547064526   -3.006153721096    1.140830094092
H          2.807336852854   -1.081773596079    2.029796477208
H          1.561786312249   -1.685777263286    0.952403252199
C          3.721991776451   -2.911725844135   -1.331933201561
H          3.534251205584   -0.919995535323   -2.190029040320
H          2.013242795291   -1.593379525955   -1.634436763833
C          4.789182630544   -2.846860760227    1.409125938370
C          5.222532687733   -2.755924447298   -1.061418829597
H          6.486941472427   -1.891082346351    0.467606357523
C          3.094712142957   -3.733450237296   -0.197518282156
H          2.824406346523   -3.585819600084    1.947653756434
H          3.566749183273   -3.425181372543   -2.288172122081
H          4.951756487129   -2.344783549016    2.371078879011
H          5.271553824683   -3.829547269545    1.477195447363
H          5.708903587026   -3.738577619457   -1.031423134962
H          5.698372462270   -2.189419094232   -1.871656104223
H          3.567272018980   -4.722525990837   -0.151601515335
H          2.033591467333   -3.906203707084   -0.394721008386
---------------------------------------------------------------------------
(frequency analysis in the gas phase)
Thermochemistry at  298.150 K,    1.000 Atm
E(el)        = -2759.024200634169
ZPVE         =     0.776461496466
Enthalpie(0K) = -2758.247739137704
E(tr)        =     0.001416284860
E(rot)       =     0.001416284860
E(vib)       =     0.818828999280
H-E(el)      =     0.822605758906
Enthalpie    = -2758.201594875263
S(el)        =     0.000000000000
S(tr)        =     0.000072830257
S(rot)       =     0.000060411845 (Symmetry number = 1)
S(vib)       =     0.000269963476
G-E(el)      =     0.702390015587
Free Energy  = -2758.321810618582 (78.9 kJ/mol relative to 6a_opt)
JOB name: ti511
```

Table S8. Transition Energies, Wavelengths, and Oscillator Strengths of the Electronic Transitions of $\mathbf{6}_{opt}$ Calculated at the TD-B3PW91-D3/B1 level (Basis B1: SDD for Pt atom and 6-311G(d) for H, C, N, O, Si atoms) Level of Theory

---

Excited State 1: Singlet-A	Excited State 5: Singlet-A
3.9397 eV 314.70 nm f=0.0213	4.9592 eV 250.01 nm f=0.1196
160 ->161 0.69920	156 ->161 0.35969
Excited State 2: Singlet-A	157 ->161 -0.18646
4.3177 eV 287.16 nm f=0.0029	158 ->161 0.55142
159 ->161 0.70125	
Excited State 3: Singlet-A	
4.7431 eV 261.40 nm f=0.0008	
156 ->161 0.26898	Excited State 6: Singlet-A
157 ->161 0.64377	5.1277 eV 241.79 nm f=0.0100
Excited State 4: Singlet-A	160 ->162 0.69338
4.7697 eV 259.94 nm f=0.0145	Excited State 7: Singlet-A
156 ->161 0.53261	5.1526 eV 240.62 nm f=0.0541
157 ->161 -0.19317	158 ->161 -0.11626
158 ->161 -0.40467	160 ->163 0.41907

160 ->164 0.52577

Excited State 8: Singlet-A
5.2777 eV 234.92 nm f=0.0228
159 ->163 0.55483
159 ->164 -0.29559
160 ->163 0.22967
160 ->164 -0.17701

Excited State 9: Singlet-A
5.3889 eV 230.07 nm f=0.1611
157 ->163 -0.12544
159 ->163 -0.23697
159 ->164 0.15874
160 ->163 0.45647
160 ->164 -0.38091

Excited State 10: Singlet-A
5.4583 eV 227.15 nm f=0.0260
155 ->161 0.63744
159 ->162 0.10164
160 ->165 -0.16411
160 ->166 0.16101

Excited State 11: Singlet-A
5.5795 eV 222.22 nm f=0.0220
159 ->162 0.50946
159 ->163 0.20882
159 ->164 0.20434
159 ->165 -0.28597
159 ->166 0.1392

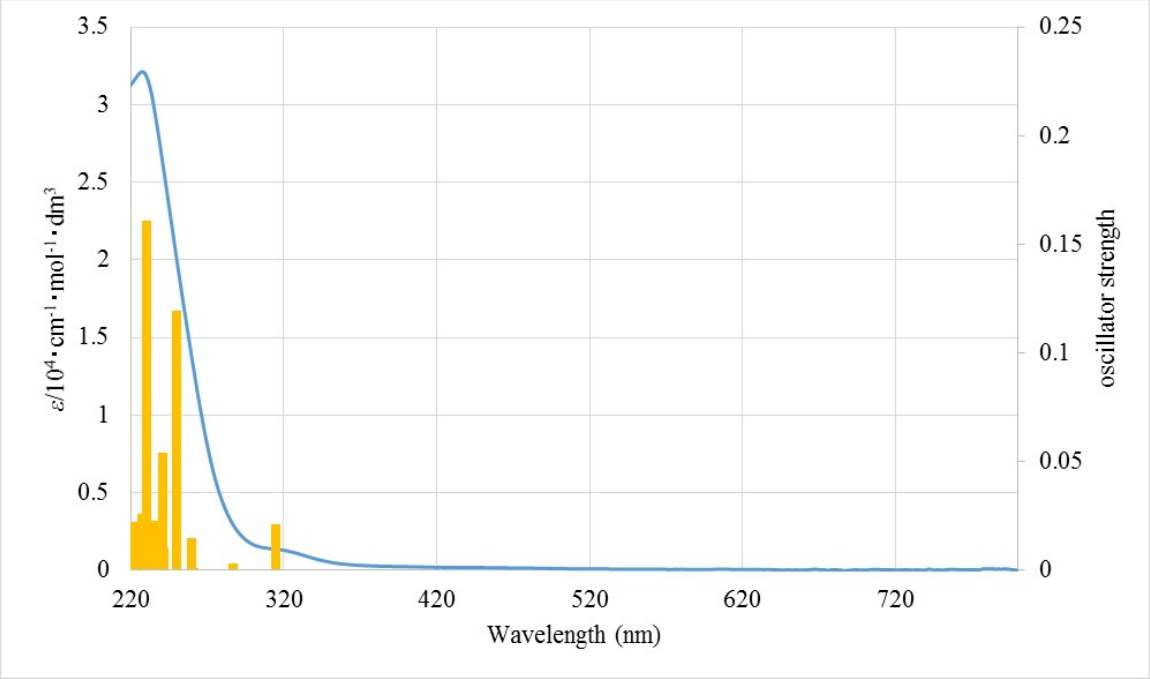
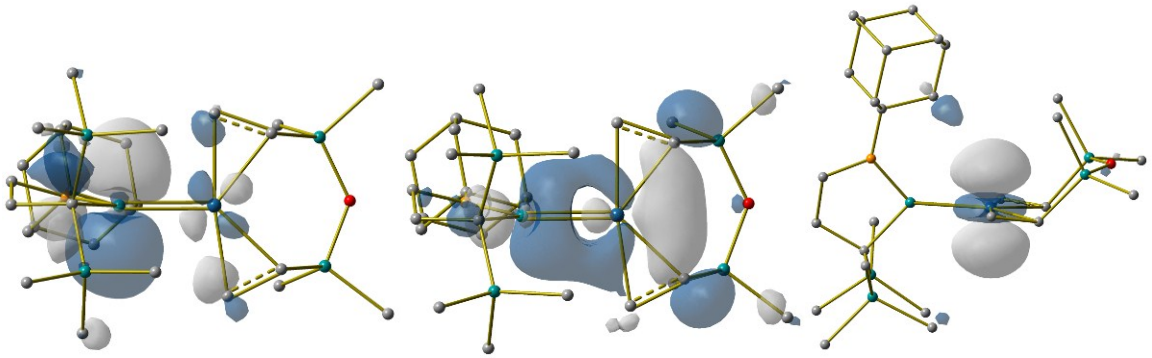
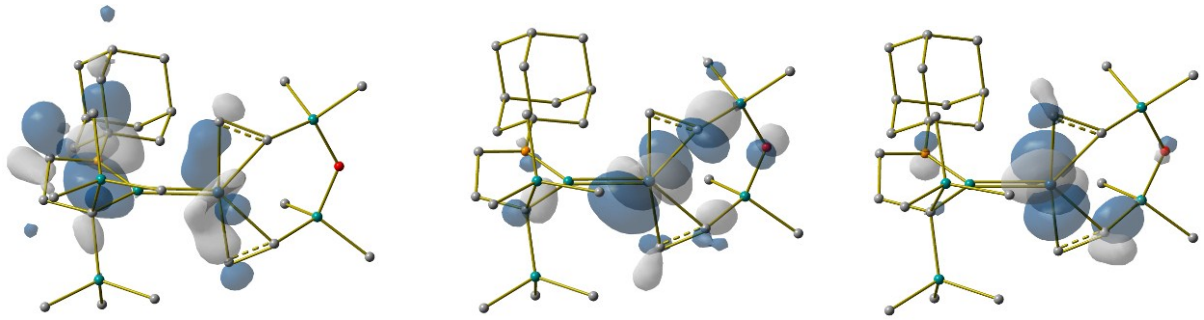


Figure S31. UV-vis absorption of **6** in hexane at room temperature. Superimposed vertical orange-yellow bars indicate band positions and oscillator strengths of **6a**$_{opt}$ at the B3PW91-D3/B level (Basis B: SDD for Pt atom and 6-311G(d) for Si, C, O, H atoms).

(a) LUMO (#161, -0.88 eV) (b) HOMO (#160, -5.61 eV) (c) HOMO-1 (#159, -6.20 eV)



(d) HOMO-2 (#158, -6.50 eV) (e) HOMO-3 (#157, -6.62 eV) (f) HOMO-4 (#156, -6.69 eV)



(g) HOMO-5 (#155, -7.15 eV) (h) HOMO-6 (#154, -7.30 eV)

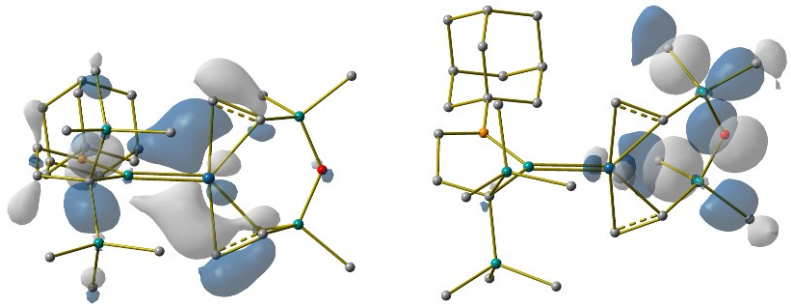


Figure S32. Frontier Kohn-Sham orbitals of **6a**$_{opt}$ at the B3PW91-D3/B level (Basis B: SDD for Pt atom and 6-311G(d) for H, C, N, O and Si atoms).

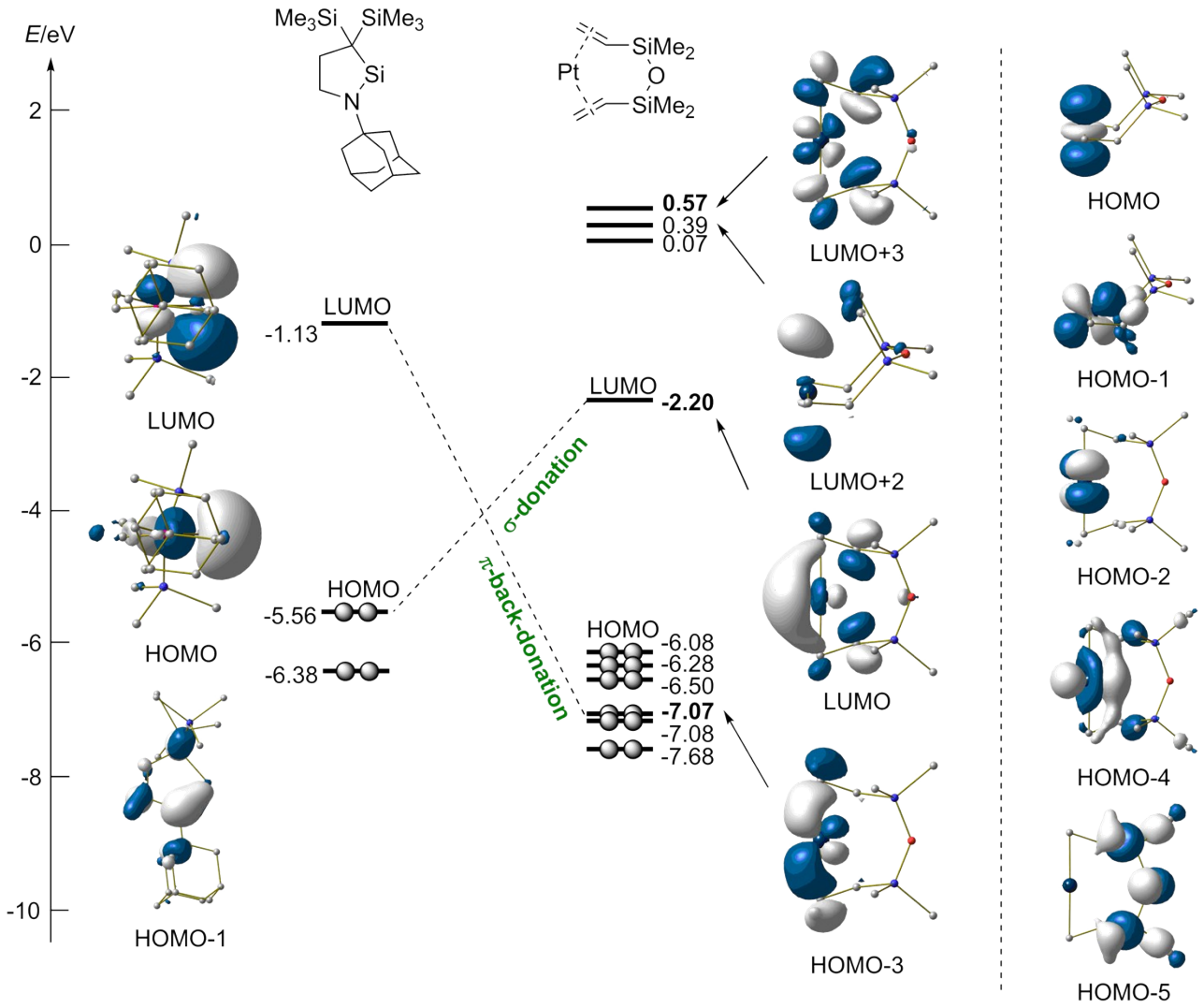


Figure S33. Important orbital interactions between cyclic (alkyl)(amino)silylene (left) and Pt(dvtms) (right) at the B3PW91-D3/B level of theory (Basis B: SDD for Pt atom and 6-311G(d) for H, C, N, O and Si atoms). Hydrogen atoms in the drawings are omitted for clarity.

5. References

S1. T. Kosai, S. Ishida and T. Iwamoto, *Angew. Chem. Int. Ed.*, 2016, **55**, 15554-15558.