Supporting Information

Estimation of σ-Donation and π-Backdonation of Cyclic Alkyl(amino) carbene Containing Compounds

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Content:

(1) Computation Details:

All calculations were performed in Gaussian09 suite programs.[S1] Compounds were optimized using the global-hybrid meta-GGA to DFT functional, R/U-M06-2X[S2] with def2-SVP[S3] basis sets for all atoms and with effective core potential (ECP) for palladium and platinum. The stationary points were located with the Berny algorithm[S4] using redundant internal coordinates. Geometries were fully optimized without symmetry constraints. Harmonic force constants were computed at the optimized geometries to confirm if they were located at minima or saddle point on the potential energy surface.[S5] The NMR chemical shifts were computed at U/R-B3LYP/TZVP level of theory using GIAO method,[S6] implemented in Gaussian09. The NBO[S7] analyses were computed at R/U-M06-2X/def2-TZVP[S8] level on optimized geometries using the NBO 3.1 program implemented in Gaussian09. The donor–acceptor interactions were inspected by using charge decomposition analysis (CDA).[S9] CDA is a valuable tool for analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on electron donation. The CDA calculations were performed by using the AOMix program[S10] with the R/U-M06-2X/def2-TZVP method. Molecular orbital (MO) compositions and the overlap populations were calculated by using the AOMix program.[S11] Analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) were performed by using AOMix-CDA.[S12] For the study of CDA and NBO analysis we truncate the –Dipp group by –Me group to reduce computational cost.

Table S1. Calculated bond distance, Natural bond order and Wiberg bond order for compound **1** to **18** at the R/U-M06-2X/def2-TZVP level of theory.

No.	C_{carb}-E bond			N-C_{carb} bond		
	Calculated bond distance (Å)	Natural bond order	Wiberg bond order	Calculated bond distance	Natural bond order	Wiberg bond order
1	2.114	0.297	0.217	1.303	1.216	1.568
2	1.969	0.691	0.633	1.300	1.196	1.596
3	1.090	0.767	0.860	1.287	1.194	1.606
4	1.943	0.737	0.626	1.303	1.179	1.556
5	1.845	0.896	1.182	1.379	0.976	0.846
6	1.856	0.955	1.102	1.339	1.070	1.331
7	1.877	0.951	1.059	1.343	1.064	1.314
8	1.874	0.828	0.909	1.300	1.221	1.652
9	1.212	1.151	1.675	1.365	1.008	1.170
10	1.851	0.8641	0.802	1.392	0.970	1.161
11	1.848	1.042	1.201	1.368	1.012	1.233
12	1.947	0.730	0.737	1.465	0.784	0.958
	1.900	1.064	1.329	1.374	0.965	1.162
13	1.991	0.549	0.603	1.307	1.212	1.551
14	1.886	0.597	0.675	1.330	1.139	1.382
15	2.112	0.582	0.608	1.314	0.982	1.079
16	1.997	0.509	0.754	1.325	0.899	1.056
17	1.996	0.602	0.748	1.325	0.845	1.013
19	1.804	1.237	1.577	1.337	1.052	1.256
20	1.926	1.018	1.239	1.378	0.980	1.143

Table S2. Atomic partial NPA charges of some selected atoms at R/U-M06-2X/def2-TZVP//R/U-M06-2X/def2-SVP level.

No.	$q(C_{carb})$	q(E)	q(N)
1	0.114	0.689	-0.406
2	0.141	1.198	-0.369
3	0.398	0.288	-0.343
4	0.158	1.395	-0.404
5	-0.249	1.091	-0.455
6	-0.082	0.522	-0.443

7	-0.052	0.109	-0.466
8	0.278	0.846	-0.346
9	0.722	-0.637	-0.484
10	-0.289	1.580	-0.474
11	-0.172	0.546	-0.475
12	-0.464 -0.303	1.306	-0.524 -0.493
13	0.331	0.445	-0.428
14	0.142	-0.070	-0.449
15	0.146	-0.070	-0.449
16	0.191	-0.367	-0.442
17	0.206	-0.356	-0.442
19	0.158	-0.461	-0.137
20	-0.161	0.413	-0.501
22	0.139	1.207	-0.425

Table S3. Computed components for ^{15}N NMR chemical shift anisotropic tensors at R/U-B3LYP/TZVP level of theory.

compounds	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	% of N→C_{cAAC} π-donation
1	-135.8	69.8	97.2	10.5	
2	-103.2	30.6	112.3	13.3	28%
3	-96.7	52.2	127.5	27.7	27%
4	-54.2	39.2	113.0	32.6	27%
5	61.3	130.4	156.9	116.2	15%
6	-33.3	97.7	110.1	58.1	20%
7	-20.4	95.7	108.5	61.3	24%
8	-162.9	8.5	113.5	-13.6	32%
9	5.3	102.8	188.1	98.8	9%
10	77.7	131.3	174.9	127.9	14%
11	11.5	95.3	138.8	81.9	9.9%
12	98.6	189.0	225.3	171.0	1%
	56.3	109.2	160.5	108.6	6%
13	-121.5	58.8	101.9	13.1	24%

14	-66.4	101.1	139.3	58.0	21%
15	-62.5	115.6	220.8	91.3	22%
16	-77.4	88.7	106.3	39.2	22%
17	-71.3	92.6	109.4	43.4	21%
19	-83.8	90.5	129.7	45.5	19%
20	16.6	97.2	148.7	87.5	16%
22	-51.7	52.1	111.1	37.1	26%

Table S4. Optimized Cartesian coordinates (in Å) at R/U-M06-2X/def2-SVP level of theory and the energies E (in a.u.) at the R/U-M06-2X/def2-TZVP//R/U-M06-2X/def2-SVP level of theory using G09 program package.

Cy-cAAC·LiOTf (**1**)
E = -1921.34669974

S	-3.30654	-0.48051	-0.15409
F	-3.95904	-2.97456	-0.53957
F	-5.21206	-1.93718	0.87169
F	-5.42265	-1.55703	-1.23667
O	-2.36232	-0.96545	0.88946
O	-2.59284	-0.54524	-1.45880
O	-4.05124	0.72590	0.13473
C	-4.55973	-1.82295	-0.27206
N	1.77554	0.54643	0.04199
C	0.49289	0.60734	-0.17617
C	2.49504	1.85019	0.32552
C	1.38233	2.85988	-0.00867
C	0.06168	2.05191	-0.05299
C	3.72837	2.00898	-0.56063
C	2.93336	1.91105	1.78964
C	-0.83590	2.44525	-1.24106
C	-1.43792	3.83809	-1.06682
C	-2.25976	3.90332	0.21987
C	-1.39670	3.54296	1.42816
C	-0.76092	2.16337	1.25621
C	2.48113	-0.71279	0.04913
C	2.54896	-1.45981	1.24160
C	3.27794	-2.65399	1.22122
C	3.89365	-3.10408	0.05919
C	3.75329	-2.38405	-1.12247
C	3.03601	-1.18473	-1.15677
C	1.77847	-1.08532	2.49885
C	2.64859	-1.12375	3.75785
C	0.55489	-1.99670	2.66051
C	2.78068	-0.50996	-2.49576
C	4.06040	-0.29812	-3.30736
C	1.75309	-1.32157	-3.29471
H	1.35994	3.67876	0.72406
H	1.57449	3.31053	-0.99482
H	3.46832	2.03735	-1.62635
H	4.45195	1.19760	-0.38991
H	4.21903	2.96040	-0.31108
H	3.49343	2.84240	1.95281
H	3.59506	1.06820	2.03769
H	2.07710	1.90762	2.47646
H	-0.25302	2.37878	-2.17526
H	-1.65241	1.71052	-1.32344
H	-2.06589	4.07850	-1.93726
H	-0.63548	4.59750	-1.03645
H	-3.09125	3.18226	0.14970
H	-2.70021	4.90331	0.34881
H	-0.61279	4.30911	1.56338
H	-2.00083	3.54819	2.34734
H	-1.55708	1.40264	1.23209
H	-0.12210	1.91893	2.12134
H	3.34711	-3.25062	2.13254
H	4.46097	-4.03582	0.06715
H	4.19385	-2.76974	-2.04368
H	1.39856	-0.06457	2.37877
H	3.55812	-0.51591	3.64852
H	2.95813	-2.15132	4.00019
H	2.08154	-0.74304	4.61942
H	0.00745	-1.73978	3.57892
H	0.85786	-3.05290	2.72494
H	-0.15235	-1.88599	1.82651
H	2.32957	0.47196	-2.30621
H	3.83996	0.27078	-4.22224
H	4.50279	-1.25654	-3.61702
H	4.81817	0.25248	-2.73205
H	0.80741	-1.41827	-2.74127
H	2.12918	-2.33455	-3.50341
H	1.53386	-0.83135	-4.25430
Li	-0.93616	-0.92143	-0.48013

(Cy-cAAC)→Si(Cl_2)=P-Tip (**2**)
E = -3088.93364398

Cl	-0.32078	0.72892	2.16908
Cl	-0.17285	-1.88054	0.25353
P	-1.23191	1.13925	-1.40865

Si	-0.07774	0.21893	0.10683
N	2.88254	0.09056	0.24237
C	1.80491	0.79446	0.06764
C	2.15483	2.26090	-0.14136
C	3.61712	2.32900	0.34296
H	4.23035	3.01389	-0.25731
H	3.63467	2.69136	1.38206
C	4.17040	0.90160	0.28730
C	4.97884	0.55640	1.52992
H	4.40397	0.72933	2.44769
H	5.86241	1.21007	1.55278
H	5.32366	-0.48677	1.50606
C	5.03198	0.62733	-0.94499
H	4.56151	0.96041	-1.87782
H	5.26921	-0.44243	-1.02398
H	5.97628	1.17680	-0.82838
C	1.25569	3.24317	0.63567
H	0.20526	3.05395	0.36633
H	1.35308	3.05152	1.71448
C	1.59372	4.69250	0.29477
H	0.94430	5.35970	0.87987
H	2.63189	4.92715	0.59160
C	1.41553	4.94546	-1.20042
H	1.64065	5.99295	-1.44990
H	0.36073	4.76527	-1.46918
C	2.30255	4.00424	-2.01153
H	3.36284	4.24857	-1.82425
H	2.13779	4.14856	-3.08939
C	2.02590	2.54017	-1.66658
H	2.70574	1.88124	-2.22828
H	1.00342	2.28694	-1.98655
C	2.94671	-1.36122	0.29073
C	3.00372	-2.05682	-0.93428
C	3.10618	-3.44950	-0.88122
H	3.13800	-4.01434	-1.81438
C	3.14489	-4.12567	0.33088
H	3.22608	-5.21334	0.34803
C	3.04677	-3.41630	1.52042
H	3.03077	-3.95621	2.46877
C	2.92675	-2.02374	1.53454
C	2.67303	-1.35037	2.87791
H	2.52528	-0.27297	2.70743
C	3.82756	-1.55997	3.86698
H	3.62687	-1.01075	4.79855
H	4.79954	-1.23373	3.47737
H	3.91563	-2.62523	4.12795
C	1.38172	-1.88829	3.51367
H	0.53314	-1.83773	2.82316
H	1.13390	-1.29814	4.40807
H	1.51513	-2.93533	3.82603
C	2.88399	-1.40105	-2.30428
H	2.94193	-0.31307	-2.18050
C	4.01666	-1.82850	-3.24478
H	3.98313	-1.23283	-4.16852
H	3.91096	-2.88417	-3.53511
H	5.00966	-1.70457	-2.78996
C	1.52243	-1.70006	-2.94707
H	1.50734	-1.31983	-3.97939
H	0.69975	-1.21651	-2.40428
H	1.32976	-2.78332	-2.97557
C	-2.79780	0.33407	-0.73607
C	-3.57221	0.99930	0.24937
C	-4.76551	0.42092	0.68858
H	-5.35653	0.94114	1.44545
C	-5.22531	-0.80045	0.19409
C	-4.45349	-1.44455	-0.76955
H	-4.80364	-2.40269	-1.16082
C	-3.25312	-0.90567	-1.24535
C	-2.50128	-1.64057	-2.34541
H	-1.44070	-1.38696	-2.22598
C	-2.94353	-1.12032	-3.71704
H	-2.77455	-0.03632	-3.79403
H	-4.01635	-1.31387	-3.87501
H	-2.38108	-1.61616	-4.52385
C	-2.61702	-3.16176	-2.26863
H	-3.62700	-3.51657	-2.52588
H	-2.36785	-3.52594	-1.26131
H	-1.92054	-3.62420	-2.98459
C	-3.17541	2.36397	0.79840
H	-2.07870	2.40922	0.78377
C	-3.69297	3.46945	-0.12800
H	-4.79341	3.45094	-0.17111
H	-3.30608	3.33401	-1.14846
H	-3.37865	4.46162	0.23255
C	-3.61717	2.60433	2.24125
H	-4.70807	2.72537	2.32885
H	-3.15935	3.52955	2.62227
H	-3.30759	1.77432	2.89293
C	-6.52450	-1.40705	0.68930
H	-6.64651	-2.37287	0.17168
C	-6.48118	-1.68555	2.19434
H	-6.38438	-0.74807	2.76324
H	-5.62595	-2.32534	2.45358
H	-7.40412	-2.18529	2.52566
C	-7.72484	-0.52698	0.32828
H	-7.65314	0.45137	0.82819
H	-8.66709	-0.99949	0.64497
H	-7.77145	-0.34770	-0.75505

Cy-cAACH^{+} OTf^{-} (**3**)

E = -1914.35140553

S	0.28546	2.83160	0.07419
F	2.11584	1.25516	-0.94823
F	2.23038	3.29223	-1.64055
F	2.91194	2.79024	0.33708
O	-0.54329	2.52263	-1.11065
O	0.16988	1.78704	1.12097
O	0.29133	4.20408	0.53330
C	1.98825	2.53731	-0.58143
N	-0.39314	-1.23258	0.33897
C	-1.00317	-0.17026	-0.05454
C	-1.33825	-2.25805	0.92994
C	-2.59368	-1.39426	1.17261
C	-2.45047	-0.13623	0.28235
C	-0.79912	-2.89473	2.19970
C	-1.56055	-3.35226	-0.11811
C	-2.82006	1.17467	1.00971
C	-4.32258	1.25189	1.26422
C	-5.10051	1.18673	-0.04859
C	-4.74664	-0.07853	-0.82789

C	-3.23876	-0.19794	-1.05249
C	0.98802	-1.49098	-0.01214
C	1.27740	-1.77457	-1.36345
C	2.60760	-2.03893	-1.69758
C	3.61084	-2.00676	-0.73656
C	3.30373	-1.66611	0.57395
C	1.99287	-1.37868	0.96862
C	0.24693	-1.70529	-2.48196
C	0.27999	-2.94177	-3.38432
C	0.43730	-0.42017	-3.30102
C	1.76257	-0.89131	2.39215
C	2.18081	-1.93901	3.43216
C	2.52571	0.41336	2.65444
H	-0.51750	0.57736	-0.68241
H	-3.50667	-1.96748	0.96139
H	-2.62880	-1.08849	2.22881
H	-0.62298	-2.15843	2.99252
H	0.13324	-3.43935	1.99624
H	-1.54308	-3.61770	2.56264
H	-2.18588	-4.14161	0.32088
H	-0.60268	-3.80058	-0.42148
H	-2.07169	-2.97253	-1.01207
H	-2.23659	1.25210	1.93755
H	-2.49994	2.01460	0.37393
H	-4.55156	2.18357	1.80107
H	-4.63921	0.42430	1.92426
H	-4.84509	2.06932	-0.65841
H	-6.18393	1.22811	0.13655
H	-5.11095	-0.96199	-0.27560
H	-5.25733	-0.09042	-1.80196
H	-2.88924	0.63909	-1.68057
H	-3.00848	-1.12849	-1.59529
H	2.86281	-2.25536	-2.73602
H	4.64329	-2.21798	-1.01815
H	4.10414	-1.59142	1.31188
H	-0.75634	-1.66386	-2.03933
H	0.17457	-3.87077	-2.80527
H	1.22062	-3.00167	-3.95077
H	-0.53878	-2.89571	-4.11678
H	-0.31033	-0.37067	-4.10654
H	1.43662	-0.40437	-3.76162
H	0.34221	0.48776	-2.68768
H	0.69521	-0.65578	2.50531
H	1.89782	-1.60251	4.44033
H	3.27384	-2.06710	3.42674
H	1.73238	-2.92570	3.25929
H	2.17413	1.21291	1.99699
H	3.60859	0.27360	2.51799
H	2.35609	0.73232	3.69343

$(Me_2\text{-cAAC})\rightarrow SiCl_4$ (**4**)
E = -2965.94706273

C	-0.43856	-0.18837	3.13216
C	-1.56280	0.12410	2.13113
C	-0.83230	0.01317	0.79007
C	0.88401	0.10929	2.42572
H	-0.54171	0.38813	4.06159
H	-0.47784	-1.25700	3.39024
N	0.45921	0.03309	0.95986
C	1.52113	0.04656	-0.05009
C	2.13647	-1.17324	-0.42031
C	1.99659	1.28567	-0.54218
C	3.26428	-1.11454	-1.24466
C	3.13663	1.27172	-1.35384
C	3.77936	0.09195	-1.69454
H	3.74339	-2.04804	-1.54290
H	3.51376	2.21922	-1.74108
H	4.66732	0.11087	-2.32781
C	1.63556	-2.56567	-0.06046
H	0.75931	-2.46862	0.59499
C	1.31705	2.63817	-0.36376
H	0.42044	2.50814	0.25695
C	0.85726	3.14982	-1.73976
H	0.18846	4.01350	-1.61636
H	1.72591	3.46994	-2.33564
H	0.31293	2.37868	-2.29696
C	2.22002	3.70400	0.27067
H	3.09574	3.90328	-0.36460
H	1.66286	4.64795	0.36028
H	2.58753	3.43298	1.26757
C	2.70273	-3.42241	0.63571
H	2.25798	-4.37385	0.96240
H	3.51863	-3.66915	-0.05948
H	3.15143	-2.93370	1.50946
C	1.17890	-3.29396	-1.33461
H	2.04896	-3.54974	-1.95903
H	0.66144	-4.22707	-1.06855
H	0.48949	-2.68206	-1.92643
C	-2.73245	-0.85072	2.31010
H	-3.15007	-0.69327	3.31594
H	-3.53073	-0.67319	1.57719
H	-2.40819	-1.89325	2.21398
C	-2.10457	1.55967	2.30235
H	-2.95147	1.74045	1.62980
H	-2.44323	1.66973	3.34278
H	-1.34963	2.32819	2.08909
C	1.93772	-0.93496	2.76218
H	1.56831	-1.94971	2.57488
H	2.86773	-0.77452	2.19949
H	2.16544	-0.84820	3.83443
C	1.44453	1.49354	2.73190
H	2.37670	1.65407	2.17578
H	0.73970	2.29812	2.48853
H	1.67571	1.54630	3.80482
Si	-1.82598	-0.14418	-0.87171
Cl	-0.69598	-0.27176	-2.60822
Cl	-3.89954	-0.29500	-1.11402
Cl	-1.72495	-2.31478	-0.40258
Cl	-1.97639	2.04953	-0.87830

$(Me_2\text{-cAAC}\cdot)(Cl_2)Si\text{-}Si(Cl_2)(\cdot CAAc\text{-}Me_2)$ (**5**)
E = -4324.34746607

Si	7.71169	3.01545	2.97636
Si	6.23816	4.59865	4.05214
Cl	6.85564	2.84216	1.06983
Cl	9.53937	3.95107	2.60711
Cl	7.04122	4.69110	5.99012
Cl	4.38719	3.67803	4.32725
N	9.08830	1.07631	4.54450
N	4.92875	6.62211	2.53062

C	8.06725	1.33734	3.65503
C	7.06267	0.17504	3.65419
C	7.68270	-0.79804	4.68761
H	8.20912	-1.61173	4.16256
H	6.92859	-1.26528	5.33595
C	8.69813	0.00950	5.51307
C	5.63959	0.63045	4.02902
H	5.63981	1.13090	5.00903
H	5.33319	1.39370	3.29388
C	4.59992	-0.48839	3.99529
H	4.81732	-1.23324	4.77995
H	3.61132	-0.06736	4.23403
C	4.57599	-1.17787	2.63358
H	3.86130	-2.01474	2.63443
H	4.22494	-0.45802	1.87363
C	5.97318	-1.65953	2.25056
H	5.96049	-2.12364	1.25263
H	6.29694	-2.44582	2.95548
C	6.97454	-0.50325	2.26390
H	6.66294	0.24707	1.52171
H	7.96959	-0.85615	1.95714
C	8.01664	0.63254	6.73923
H	7.26007	1.36897	6.43134
H	8.74079	1.14132	7.38704
H	7.52335	-0.15183	7.33181
C	9.89009	-0.83722	5.94094
H	10.39258	-1.28601	5.07212
H	9.53889	-1.64622	6.59744
H	10.62969	-0.23988	6.49233
C	10.45463	1.48815	4.37008
C	11.03438	2.46413	5.20495
C	12.37574	2.80657	5.00488
H	12.83347	3.55816	5.65086
C	13.12623	2.22991	3.98956
H	14.16720	2.52117	3.84117
C	12.54076	1.27809	3.16313
H	13.12988	0.82380	2.36434
C	11.21450	0.88031	3.34405
C	10.26129	3.19072	6.29028
H	9.20011	2.92390	6.18050
C	10.74026	2.76804	7.68480
H	10.74044	1.67599	7.80976
H	10.09933	3.20619	8.46492
H	11.77026	3.11721	7.85685
C	10.37386	4.71294	6.14639
H	10.06521	5.04176	5.14395
H	11.40687	5.05335	6.31481
H	9.73203	5.21233	6.88668
C	10.63848	-0.17936	2.42182
H	9.72204	-0.55684	2.89254
C	10.25827	0.42318	1.06500
H	11.14382	0.86437	0.58168
H	9.50209	1.21322	1.17339
H	9.85367	-0.35117	0.39498
C	11.57809	-1.37457	2.23849
H	11.05922	-2.18105	1.69938
H	11.92409	-1.77136	3.20448
H	12.46612	-1.10812	1.64626
C	5.92166	6.30875	3.43551
C	6.94749	7.45020	3.50495
C	6.38075	8.46701	2.48376
H	5.85852	9.27866	3.01601
H	7.16431	8.93350	1.87061
C	5.37236	7.70719	1.60588
C	8.37045	6.97552	3.15714
H	8.63267	6.17394	3.86831
H	8.38923	6.51824	2.15723
C	9.43827	8.06174	3.27007
H	10.42268	7.62079	3.04970
H	9.26905	8.84054	2.50670
C	9.43246	8.69981	4.65646
H	9.73497	7.94251	5.40090
H	10.16976	9.51492	4.71253
C	8.03594	9.20708	5.00686
H	7.75869	10.02555	4.31899
H	8.02500	9.63669	6.02014
C	7.00546	8.08042	4.91923
H	6.00991	8.44999	5.20368
H	7.27024	7.29718	5.64551
C	6.07778	7.10022	0.38504
H	5.36285	6.62786	-0.29939
H	6.80503	6.33623	0.69744
H	6.61016	7.88660	-0.16993
C	4.21360	8.59261	1.16618
H	4.60281	9.41158	0.54445
H	3.69450	9.02773	2.03216
H	3.47833	8.02798	0.57587
C	3.54907	6.23584	2.65372
C	2.97046	5.30064	1.77182
C	1.61577	4.98647	1.92259
H	1.15906	4.26742	1.24002
C	0.84967	5.54889	2.93399
H	-0.20191	5.27914	3.04283
C	1.43365	6.45834	3.80774
H	0.83240	6.90109	4.60385
C	2.77379	6.82871	3.67706
C	3.75434	4.58838	0.68460
H	4.81947	4.81814	0.83562
C	3.59040	3.06631	0.76851
H	2.54955	2.76667	0.57399
H	3.87843	2.68930	1.75978
H	4.22548	2.57566	0.01694
C	3.33018	5.07500	-0.70701
H	3.98157	4.64629	-1.48366
H	3.36445	6.17031	-0.79219
H	2.29619	4.76309	-0.92165
C	3.34811	7.84318	4.64983
H	4.28247	8.21856	4.21392
C	3.68387	7.18389	5.99213
H	4.42920	6.38512	5.87316
H	2.77859	6.74129	6.43599
H	4.08430	7.92574	6.70039
C	2.42884	9.05034	4.85582
H	2.11073	9.48718	3.89758
H	2.95275	9.82694	5.43261
H	1.52391	8.78251	5.42119

(Me_2-cAAC)→(Cl)Si-Si(Cl)←(CAAc-Me_2) (**6**)

E = -3170.39276947

Cl	1.14359	-0.76877	1.74037

Cl	-1.14276	-0.78785	-1.73102
Si	1.01722	1.04865	0.58278
Si	-1.01711	1.04202	-0.59313
N	3.54808	0.48204	-0.71283
N	-3.54846	0.48956	0.70766
C	2.33610	1.05146	-0.72326
C	2.29389	2.06131	-1.88444
C	3.79037	2.28865	-2.17408
C	4.53136	1.03396	-1.70616
C	1.58035	1.40887	-3.08521
C	1.61988	3.39947	-1.56598
C	5.86557	1.38408	-1.05230
C	4.80933	0.03494	-2.83215
C	3.93267	-0.59298	0.16677
C	4.49834	-0.28831	1.42395
C	4.90253	-1.35019	2.23728
C	4.73687	-2.67051	1.83790
C	4.13408	-2.94976	0.61847
C	3.71129	-1.92631	-0.23518
C	4.62137	1.12443	1.98051
C	6.06969	1.47873	2.34240
C	3.73646	1.30440	3.22240
C	2.94563	-2.31055	-1.49257
C	3.72514	-3.28070	-2.38640
C	1.58830	-2.91756	-1.11963
C	-2.33641	1.05895	0.71234
C	-2.29455	2.08132	1.86251
C	-3.79113	2.31207	2.14891
C	-4.53204	1.05236	1.69456
C	-1.62015	3.41584	1.52994
C	-1.58161	1.44173	3.07052
C	-5.86600	1.39529	1.03639
C	-4.81042	0.06589	2.83150
C	-3.93276	-0.59475	-0.16060
C	-4.49751	-0.30353	-1.42137
C	-4.90102	-1.37406	-2.22363
C	-4.73555	-2.69003	-1.81009
C	-4.13372	-2.95623	-0.58727
C	-3.71170	-1.92370	0.25573
C	-4.62025	1.10316	-1.99305
C	-3.73464	1.26988	-3.23629
C	-6.06839	1.45351	-2.35951
C	-2.94696	-2.29434	1.51773
C	-1.58895	-2.90437	1.15236
C	-3.72680	-3.25538	2.42104
H	3.97863	2.50893	-3.23474
H	4.13854	3.15102	-1.58468
H	0.49859	1.33858	-2.91062
H	1.94061	0.39002	-3.28232
H	1.74798	2.01935	-3.98572
H	0.54129	3.28090	-1.39412
H	1.75254	4.07716	-2.42411
H	2.06825	3.86584	-0.67726
H	5.74503	2.14309	-0.27038
H	6.53592	1.79330	-1.82190
H	6.34444	0.49406	-0.61859
H	3.91043	-0.22047	-3.40529
H	5.24025	-0.88780	-2.42016
H	5.54281	0.47321	-3.52362
H	5.33866	-1.13442	3.21470
H	5.05732	-3.48438	2.49012
H	3.96507	-3.98792	0.32620
H	4.25825	1.82727	1.21602
H	6.13966	2.53509	2.64231
H	6.76679	1.30695	1.51226
H	6.41285	0.87313	3.19469
H	3.76271	2.35307	3.55410
H	4.10296	0.67906	4.05132
H	2.69583	1.02203	3.02306
H	2.74186	-1.39524	-2.06251
H	3.84933	-4.25562	-1.89129
H	4.72648	-2.90867	-2.64355
H	3.17301	-3.45797	-3.32111
H	1.00193	-2.22505	-0.50458
H	1.72375	-3.85256	-0.55313
H	1.00788	-3.14262	-2.02659
H	-3.97987	2.54412	3.20697
H	-4.13888	3.16789	1.54981
H	-2.06799	3.87262	0.63597
H	-0.54149	3.29526	1.35994
H	-1.75316	4.10282	2.38060
H	-1.74960	2.06177	3.96440
H	-0.49978	1.36958	2.89711
H	-1.94190	0.42501	3.27833
H	-6.53663	1.81301	1.80115
H	-6.34474	0.50055	0.61234
H	-5.74510	2.14560	0.24618
H	-5.54457	0.51164	3.51746
H	-3.91182	-0.18259	3.40816
H	-5.24066	-0.86162	2.42968
H	-5.33643	-1.16874	-3.20362
H	-5.05539	-3.51083	-2.45388
H	-3.96484	-3.99119	-0.28382
H	-4.25757	1.81413	-1.23591
H	-4.10070	0.63579	-4.05873
H	-2.69414	0.98960	-3.03334
H	-3.76063	2.31498	-3.57912
H	-6.76591	1.29065	-1.52793
H	-6.41107	0.83875	-3.20540
H	-6.13822	2.50658	-2.67080
H	-2.74426	-1.37299	2.07821
H	-1.00933	-3.11998	2.06213
H	-1.00233	-2.21777	0.53093
H	-1.72331	-3.84508	0.59513
H	-4.72870	-2.88128	2.67299
H	-3.17565	-3.42219	3.35824
H	-3.84975	-4.23568	1.93635

(Me_2-cAAC)→Si=Si←(CAAc-Me_2) (**7**)

E = -2249.84264386

Si	0.11003	0.94383	0.59695
N	-0.96236	3.33769	-0.48777
C	-2.69571	1.79606	-0.32318
C	-2.17599	4.17078	-0.76854
C	0.98271	4.49002	0.50947
C	1.05019	3.76119	-1.83949
C	0.36762	3.87700	-0.60691
C	0.52008	2.97091	-3.02716
C	2.31337	4.34967	-1.95605
C	-1.19389	2.05281	-0.17280

C	0.38026	4.51037	1.90783
C	-2.16905	5.46631	0.03812
C	0.45589	3.80760	-4.30962
C	2.24776	5.06113	0.33573
C	-2.27297	4.54454	-2.24987
C	-3.29556	0.93587	0.79026
C	2.90469	5.01023	-0.88682
C	-3.28710	3.22021	-0.30227
C	0.18520	5.93762	2.43604
C	-2.93867	1.09579	-1.67163
C	1.26246	3.72923	2.89154
C	1.38004	1.72331	-3.26325
H	-0.49119	2.62332	-2.78186
H	2.84792	4.27407	-2.90511
H	-0.59311	3.99986	1.86495
H	-1.30797	6.09522	-0.23237
H	-2.14429	5.27095	1.11710
H	-3.08694	6.02928	-0.18567
H	-0.02207	3.22949	-5.11435
H	1.46659	4.07358	-4.65449
H	-0.10688	4.74146	-4.17699
H	2.73211	5.54344	1.18727
H	-3.16331	5.17059	-2.40467
H	-2.35409	3.66935	-2.90541
H	-1.39141	5.12858	-2.54958
H	-3.05028	1.34308	1.78264
H	-2.90965	-0.09118	0.73656
H	-4.39147	0.90736	0.68045
H	3.88968	5.46610	-1.00016
H	-3.56618	3.47472	0.73218
H	-4.19055	3.30607	-0.92393
H	-0.39075	6.57079	1.74951
H	1.15901	6.42403	2.59975
H	-0.33648	5.91482	3.40467
H	-4.02138	0.97635	-1.83157
H	-2.47511	0.09829	-1.67516
H	-2.52534	1.66294	-2.51686
H	1.43295	2.70348	2.53917
H	0.77449	3.68055	3.87667
H	2.23615	4.22644	3.02223
H	0.96178	1.12284	-4.08520
H	1.40859	1.09446	-2.36367
H	2.41023	2.00305	-3.53490
Si	-0.11003	-0.94383	-0.59695
N	0.96236	-3.33769	0.48777
C	2.69571	-1.79606	0.32318
C	2.17599	-4.17078	0.76854
C	-0.98271	-4.49002	-0.50947
C	-1.05019	-3.76119	1.83949
C	-0.36762	-3.87700	0.60691
C	-0.52008	-2.97091	3.02716
C	-2.31337	-4.34967	1.95605
C	1.19389	-2.05281	0.17280
C	-0.38026	-4.51037	-1.90783
C	2.16905	-5.46631	-0.03812
C	-0.45589	-3.80760	4.30962
C	-2.24776	-5.06113	-0.33573
C	2.27297	-4.54454	2.24987
C	3.29556	-0.93587	-0.79026
C	-2.90469	-5.01023	0.88682
C	3.28710	-3.22021	0.30227
C	-0.18520	-5.93762	-2.43604
C	2.93867	-1.09579	1.67163
C	-1.26246	-3.72923	-2.89154
C	-1.38004	-1.72331	3.26325
H	0.49119	-2.62332	2.78186
H	-2.84792	-4.27407	2.90511
H	0.59311	-3.99986	-1.86495
H	1.30797	-6.09522	0.23237
H	2.14429	-5.27095	-1.11710
H	3.08694	-6.02928	0.18567
H	0.02207	-3.22949	5.11435
H	-1.46659	-4.07358	4.65449
H	0.10688	-4.74146	4.17699
H	-2.73211	-5.54344	-1.18727
H	3.16331	-5.17059	2.40467
H	2.35409	-3.66935	2.90541
H	1.39141	-5.12858	2.54958
H	3.05028	-1.34308	-1.78264
H	2.90965	0.09118	-0.73656
H	4.39147	-0.90736	-0.68045
H	-3.88968	-5.46610	1.00016
H	3.56618	-3.47472	-0.73218
H	4.19055	-3.30607	0.92393
H	0.39075	-6.57079	-1.74951
H	-1.15901	-6.42403	-2.59975
H	0.33648	-5.91482	-3.40467
H	4.02138	-0.97635	1.83157
H	2.47511	-0.09829	1.67516
H	2.52534	-1.66294	2.51686
H	-1.43295	-2.70348	-2.53917
H	-0.77449	-3.68055	-3.87667
H	-2.23615	-4.22644	-3.02223
H	-0.96178	-1.12284	4.08520
H	-1.40859	-1.09446	2.36367
H	-2.41023	-2.00305	3.53490

$[(Me_2\text{-cAAC})PPh_2]^+Cl^-$ (**8**)
E = -2100.26033759

C	-0.13916	-0.47551	-0.39370
C	-0.19930	-1.46020	-1.56051
C	1.19811	-1.28147	-2.17236
H	1.64361	-2.16967	-2.65264
H	1.15064	-0.50885	-2.95674
C	2.12202	-0.78745	-1.05933
C	-0.41263	-2.88256	-0.98776
H	-1.46371	-3.05021	-0.71862
H	0.21393	-3.09466	-0.11176
H	-0.13118	-3.59743	-1.77334
C	-1.29041	-1.21810	-2.60675
H	-2.29829	-1.24302	-2.17502
H	-1.21882	-2.02962	-3.34520
H	-1.15238	-0.27667	-3.15177
C	3.13082	0.22210	-1.57198
H	2.64913	1.05276	-2.10502
H	3.73685	-0.35921	-2.29428
H	3.77173	0.60667	-0.76523
C	2.87129	-1.89938	-0.33721
H	3.51469	-1.48712	0.45331
H	3.49078	-2.36506	-1.13205

H	2.20818	-2.66438	0.08586
C	1.54506	0.56265	1.07479
C	1.90674	1.92132	0.97090
C	2.51370	2.52082	2.07974
H	2.80527	3.57030	2.01605
C	2.74278	1.81588	3.25229
H	3.23089	2.30052	4.09870
C	2.31960	0.49687	3.35117
H	2.46165	-0.04409	4.28815
C	1.70531	-0.15861	2.28101
C	1.59149	2.81018	-0.22284
H	1.15719	2.18382	-1.01486
C	0.54945	3.86377	0.18229
H	0.23298	4.44494	-0.69636
H	0.97964	4.56414	0.91411
H	-0.34325	3.41002	0.63335
C	2.83056	3.51366	-0.78805
H	2.56117	4.07111	-1.69688
H	3.63157	2.80963	-1.04143
H	3.23030	4.24027	-0.06525
C	1.18341	-1.56728	2.53359
H	0.74301	-1.95311	1.60346
C	2.28310	-2.53975	2.97562
H	2.68578	-2.25062	3.95774
H	3.11536	-2.57852	2.26375
H	1.86859	-3.55346	3.07607
C	0.07815	-1.53117	3.60038
H	-0.71669	-0.81846	3.34082
H	0.49189	-1.23228	4.57485
H	-0.36299	-2.53204	3.72457
C	-2.87187	-1.00946	0.49302
C	-2.85238	-2.13467	1.32917
H	-2.02391	-2.27696	2.02730
C	-3.87708	-3.07705	1.27239
H	-3.84295	-3.95536	1.91821
C	-4.94913	-2.88705	0.40103
H	-5.75644	-3.61954	0.35984
C	-4.99412	-1.75202	-0.40849
H	-5.83672	-1.59469	-1.08323
C	-3.96267	-0.81549	-0.36340
H	-4.00411	0.06705	-1.00521
C	-2.04743	1.62088	-0.30743
C	-3.03086	2.43611	0.27364
H	-3.43422	2.18422	1.25805
C	-3.49594	3.56672	-0.39238
H	-4.26365	4.18888	0.06960
C	-2.97135	3.90939	-1.63964
H	-3.32962	4.79961	-2.15820
C	-1.98422	3.11384	-2.21676
H	-1.56406	3.37804	-3.18836
C	-1.52492	1.97450	-1.55528
H	-0.74399	1.37342	-2.02158
N	1.08280	-0.15469	-0.10519
P	-1.49627	0.19475	0.71198
Cl	3.88046	-2.53280	-3.43394

Me_2-cAAC=O (**9**)
E = -910.742303245

C	-2.61517	-0.68130	1.09406
C	-2.78539	-0.33959	-0.39591
C	-1.34216	-0.17973	-0.87694
C	-1.20521	-0.19898	1.51798
H	-3.39691	-0.23249	1.72440
H	-2.67202	-1.77269	1.22515
N	-0.51882	-0.10513	0.20899
C	0.89050	0.08668	0.07140
C	1.72872	-1.04337	-0.01364
C	1.41516	1.39168	-0.01311
C	3.11129	-0.84235	-0.05636
C	2.80459	1.54575	-0.05541
C	3.64869	0.44077	-0.05075
H	3.77769	-1.70487	-0.11602
H	3.23115	2.54877	-0.11493
H	4.73066	0.57979	-0.07819
C	1.16606	-2.44240	-0.19853
H	0.09928	-2.41201	0.05907
C	0.51952	2.60340	-0.20480
H	-0.50416	2.30784	0.05475
C	0.51084	2.98903	-1.69058
H	-0.17439	3.83242	-1.86556
H	1.51791	3.29316	-2.01600
H	0.18871	2.13619	-2.30419
C	0.90642	3.79095	0.67744
H	1.88978	4.19751	0.39746
H	0.17445	4.60373	0.56186
H	0.94715	3.51326	1.74092
C	1.83987	-3.48662	0.69225
H	1.33794	-4.45943	0.58463
H	2.89462	-3.63283	0.41528
H	1.80660	-3.19536	1.75244
C	1.25323	-2.82444	-1.68253
H	2.30355	-2.86161	-2.01107
H	0.80590	-3.81554	-1.85285
H	0.72262	-2.08478	-2.29856
C	-3.46400	-1.44691	-1.19888
H	-4.51146	-1.56767	-0.88436
H	-3.43782	-1.19740	-2.26854
H	-2.94610	-2.40805	-1.06217
C	-3.50635	0.99306	-0.63747
H	-3.48442	1.23868	-1.70861
H	-4.55512	0.92205	-0.31229
H	-3.03223	1.82109	-0.09082
C	-0.52199	-1.20552	2.44548
H	-0.50532	-2.21353	2.01144
H	0.51226	-0.90045	2.66558
H	-1.07454	-1.25421	3.39492
C	-1.24251	1.15666	2.23334
H	-0.22166	1.54038	2.38055
H	-1.81875	1.90456	1.67309
H	-1.70986	1.03894	3.22155
O	-0.99206	-0.10876	-2.03551

$(Cy\text{-}cAAC\cdot)_2SiCl_2$ (**10**)
E = -3114.33884015

Cl	-0.95338	-1.34465	1.98130
Si	-0.00005	-0.00009	0.69105
N	2.62229	-0.44468	-0.38531
C	1.33874	-0.92019	-0.19642
Cl	0.95318	1.34429	1.98164
N	-2.62238	0.44488	-0.38535

C	3.25655	-1.01874	-1.61459
C	3.47531	0.03230	0.67909
C	3.98705	1.34822	0.66584
C	4.89931	1.72871	1.65574
H	5.30448	2.74193	1.64323
C	5.28293	0.85795	2.66580
H	5.98774	1.17948	3.43396
C	4.75164	-0.42424	2.69001
H	5.04160	-1.11265	3.48623
C	3.86287	-0.86308	1.70538
C	3.04549	-0.10178	-2.82574
H	3.41615	-0.59595	-3.73623
H	3.59098	0.84245	-2.70413
H	1.98637	0.13771	-2.97033
C	4.75014	-1.27671	-1.44039
H	5.12749	-1.77638	-2.34429
H	4.94639	-1.92450	-0.57671
H	5.31170	-0.34317	-1.29804
C	3.56483	2.40914	-0.33764
H	2.71530	2.00291	-0.90965
C	4.70007	2.75469	-1.31007
H	5.12329	1.86425	-1.79435
H	5.52067	3.25507	-0.77311
H	4.34530	3.44028	-2.09553
C	3.10327	3.68933	0.37426
H	2.68937	4.40953	-0.34634
H	3.94758	4.18666	0.87344
H	2.34004	3.47342	1.13257
C	3.35186	-2.28873	1.80849
H	2.79977	-2.51043	0.89047
C	4.47834	-3.32083	1.92563
H	4.05849	-4.33779	1.90087
H	5.02598	-3.21692	2.87409
H	5.20830	-3.23269	1.10776
C	2.37861	-2.42136	2.98442
H	1.58828	-1.66168	2.93705
H	2.91370	-2.29878	3.93940
H	1.90203	-3.41400	2.98736
C	-1.33873	0.92015	-0.19653
C	-2.48177	2.33745	-1.76467
H	-2.99948	3.12439	-1.19158
H	-2.45374	2.66668	-2.81227
C	-3.25653	1.01892	-1.61469
C	-3.47552	-0.03199	0.67900
C	-3.86304	0.86341	1.70531
C	-4.75187	0.42462	2.68990
H	-5.04182	1.11302	3.48611
C	-5.28320	-0.85756	2.66568
H	-5.98800	-1.17908	3.43386
C	-4.89962	-1.72833	1.65563
H	-5.30480	-2.74154	1.64315
C	-3.98739	-1.34787	0.66571
C	-4.75008	1.27716	-1.44060
H	-5.12732	1.77668	-2.34463
H	-4.94625	1.92519	-0.57708
H	-5.31180	0.34375	-1.29805
C	-3.04554	0.10176	-2.82572
H	-3.59213	-0.84188	-2.70453
H	-1.98655	-0.13888	-2.96943
H	-3.41498	0.59631	-3.73649
C	-3.35175	2.28895	1.80856
H	-2.79933	2.51055	0.89072
C	-2.37886	2.42132	2.98484
H	-2.91440	2.29922	3.93964
H	-1.90175	3.41370	2.98778
H	-1.58890	1.66122	2.93796
C	-4.47801	3.32133	1.92535
H	-5.20749	3.23369	1.10699
H	-4.05782	4.33817	1.90116
H	-5.02625	3.21730	2.87343
C	-3.56527	-2.40879	-0.33781
H	-2.71584	-2.00258	-0.90998
C	-4.70067	-2.75436	-1.31006
H	-5.52114	-3.25482	-0.77297
H	-4.34599	-3.43990	-2.09561
H	-5.12402	-1.86393	-1.79421
C	-3.10358	-3.68897	0.37400
H	-3.94778	-4.18621	0.87345
H	-2.34013	-3.47308	1.13209
H	-2.68994	-4.40923	-0.34669
C	2.48198	-2.33738	-1.76452
H	2.99987	-3.12426	-1.19148
H	2.45391	-2.66662	-2.81212
C	-1.07712	2.09648	-1.16692
C	-0.55164	3.35092	-0.42838
C	-0.04183	1.78313	-2.27293
C	-0.34935	4.54000	-1.37020
H	0.41381	3.10058	0.03568
H	-1.22923	3.62266	0.39461
C	0.22367	2.94625	-3.22959
H	0.89755	1.50243	-1.76990
H	-0.36066	0.90616	-2.84630
C	0.64426	4.20599	-2.48149
H	0.00271	5.40855	-0.79213
H	-1.31520	4.83519	-1.81636
H	1.00388	2.64845	-3.94820
H	-0.67797	3.15515	-3.82919
H	0.75429	5.05311	-3.17538
H	1.63679	4.03005	-2.03498
C	1.07734	-2.09671	-1.16661
C	0.55237	-3.35126	-0.42786
C	0.04168	-1.78380	-2.27239
C	0.35042	-4.54049	-1.36958
H	-0.41314	-3.10122	0.03621
H	1.23010	-3.62270	0.39511
C	-0.22351	-2.94702	-3.22900
H	-0.89771	-1.50358	-1.76909
H	0.35989	-0.90659	-2.84575
C	-0.64343	-4.20692	-2.48077
H	-0.00131	-5.40911	-0.79141
H	1.31633	-4.83541	-1.81579
H	-1.00403	-2.64956	-3.94743
H	0.67809	-3.15552	-3.82881
H	-0.75320	-5.05412	-3.17462
H	-1.63598	-4.03139	-2.03414

$(Cy\text{-}cAAC)_2Si$ (**11**)

E = -1960.37188692

Si	0.00019	-0.22512	-0.00072
N	-2.65895	-0.49958	-0.58412

C	-1.47684	-1.18795	-0.55581
N	2.65889	-0.49961	0.58408
C	-1.69259	-2.48350	-1.34909
C	-3.76095	-1.12858	-1.36175
C	-2.86010	0.72872	0.13203
C	-3.23983	0.68482	1.49249
C	-3.51737	1.88670	2.15164
H	-3.82346	1.86071	3.19957
C	-3.38818	3.10900	1.50489
H	-3.61216	4.03711	2.03319
C	-2.93794	3.14356	0.19051
H	-2.78883	4.10723	-0.30083
C	-2.65126	1.97144	-0.51627
C	-1.90270	-3.66691	-0.38748
H	-2.25728	-4.54538	-0.94862
H	-2.63930	-3.43726	0.39495
H	-0.96842	-3.94164	0.11449
C	-0.54034	-2.79623	-2.30412
H	0.41750	-2.83390	-1.76887
H	-0.45459	-2.01521	-3.07217
H	-0.71135	-3.76305	-2.80465
C	-4.83422	-1.70633	-0.43156
H	-5.62619	-2.17805	-1.03110
H	-5.28979	-0.89768	0.15795
H	-4.43413	-2.45745	0.26048
C	-4.44891	-0.14673	-2.30714
H	-5.24107	-0.67589	-2.85698
H	-3.74372	0.26558	-3.03859
H	-4.91341	0.68119	-1.75130
C	-3.25376	-0.59943	2.30756
H	-3.03691	-1.43413	1.62757
C	-4.59595	-0.86159	2.99710
H	-5.43196	-0.89091	2.28563
H	-4.81625	-0.08050	3.74043
H	-4.56659	-1.82304	3.53138
C	-2.12788	-0.55104	3.34935
H	-2.04195	-1.51681	3.87087
H	-2.33073	0.22529	4.10366
H	-1.16654	-0.32200	2.86664
C	-2.07102	2.11434	-1.91843
H	-1.88558	1.10211	-2.30889
C	-3.02154	2.86603	-2.86135
H	-2.63112	2.84572	-3.88996
H	-3.10095	3.92267	-2.56356
H	-4.03559	2.44726	-2.86737
C	-0.72193	2.85015	-1.89070
H	-0.00100	2.34336	-1.23517
H	-0.84896	3.88790	-1.54366
H	-0.29565	2.88693	-2.90517
C	1.47646	-1.18777	0.55574
C	1.69200	-2.48332	1.34906
C	2.98603	-2.19776	2.14150
H	2.71682	-1.78941	3.12762
H	3.58795	-3.10333	2.30829
C	3.76060	-1.12868	1.36191
C	2.86015	0.72860	-0.13207
C	2.65115	1.97133	0.51618
C	2.93762	3.14348	-0.19063
H	2.78841	4.10714	0.30071
C	3.38788	3.10896	-1.50501
H	3.61172	4.03709	-2.03333
C	3.51738	1.88665	-2.15169
H	3.82357	1.86068	-3.19960
C	3.24002	0.68475	-1.49252
C	1.90193	-3.66673	0.38738
H	2.63840	-3.43708	-0.39516
H	0.96756	-3.94135	-0.11449
H	2.25651	-4.54528	0.94840
C	0.53974	-2.79590	2.30412
H	0.71021	-3.76310	2.80409
H	-0.41821	-2.83266	1.76901
H	0.45460	-2.01527	3.07261
C	4.44841	-0.14679	2.30739
H	5.24042	-0.67591	2.85749
H	3.74307	0.26569	3.03860
H	4.91308	0.68104	1.75154
C	4.83412	-1.70662	0.43210
H	5.28979	-0.89810	-0.15750
H	4.43424	-2.45794	-0.25984
H	5.62598	-2.17815	1.03194
C	2.07124	2.11409	1.91848
H	1.88634	1.10180	2.30904
C	0.72184	2.84933	1.89118
H	0.84825	3.88707	1.54386
H	0.29599	2.88616	2.90584
H	0.00083	2.34211	1.23607
C	3.02180	2.86619	2.86103
H	4.03600	2.44778	2.86669
H	2.63178	2.84579	3.88979
H	3.10072	3.92285	2.56316
C	3.25441	-0.59956	-2.30747
H	3.03701	-1.43416	-1.62753
C	4.59713	-0.86187	-2.99593
H	4.81803	-0.08089	-3.73920
H	4.56818	-1.82340	-3.53007
H	5.43258	-0.89109	-2.28378
C	2.12936	-0.55128	-3.35016
H	2.33295	0.22477	-4.10457
H	1.16767	-0.32190	-2.86831
H	2.04365	-1.51720	-3.87145
C	-2.98664	-2.19778	-2.14143
H	-2.71749	-1.78953	-3.12762
H	-3.58871	-3.10326	-2.30808

(Cy-cAACH)Si(CMe_2)=CAAc-Cy (**12**)
E = -2193.84643150

Si	-0.00327	-0.63512	-0.70242
N	-2.51654	0.64984	-0.54454
C	-1.87571	-0.61303	-0.16969
H	-1.89241	-0.71513	0.92766
N	2.53483	-0.64007	0.68245
C	-2.82327	-1.76012	-0.70556
C	-3.86740	-0.99493	-1.54504
H	-3.58794	-1.01640	-2.60914
H	-4.86634	-1.44798	-1.48596
C	-3.89696	0.46426	-1.04198
C	-4.98798	0.60746	0.04151
H	-4.69290	0.11861	0.97978
H	-5.92451	0.14711	-0.30711
H	-5.20279	1.65923	0.26238

C	-4.22449	1.43038	-2.18120
H	-4.23740	2.47115	-1.82708
H	-5.21793	1.19305	-2.58978
H	-3.48329	1.35959	-2.98928
C	-2.11234	-2.83661	-1.54700
H	-1.30272	-3.28109	-0.94158
H	-1.62331	-2.37125	-2.41616
C	-3.05783	-3.94731	-2.00693
H	-3.84160	-3.52239	-2.65806
H	-2.50551	-4.67578	-2.61970
C	-3.70856	-4.64081	-0.81237
H	-2.92309	-5.14199	-0.21999
H	-4.40311	-5.42628	-1.14692
C	-4.43032	-3.62716	0.07297
H	-4.82963	-4.11813	0.97360
H	-5.30316	-3.22721	-0.46930
C	-3.49707	-2.48713	0.48567
H	-2.70537	-2.91480	1.12314
H	-4.03704	-1.76415	1.11380
C	-4.28619	3.90612	1.07645
H	-3.97640	4.96237	1.09365
H	-4.98239	3.75267	1.91519
H	-4.83501	3.74118	0.13815
C	-2.26860	3.32942	2.46168
H	-1.39727	2.66696	2.56700
H	-2.89510	3.22927	3.36160
H	-1.89817	4.36532	2.42065
C	-3.07258	2.98033	1.20151
H	-3.41710	1.94682	1.31721
C	-2.16143	3.02097	-0.01341
C	-1.58579	4.25231	-0.35306
H	-1.90691	5.15489	0.17239
C	-0.59584	4.33318	-1.31796
H	-0.16021	5.29617	-1.58946
C	-0.11068	3.16010	-1.89031
H	0.72934	3.22960	-2.57852
C	-0.92881	0.06772	-3.29204
H	-1.05276	0.82451	-4.08467
H	-1.92297	-0.20180	-2.92894
H	-0.46730	-0.82512	-3.74315
C	1.31829	0.93686	-2.83440
H	2.01567	1.44889	-2.16112
H	1.17742	1.56817	-3.72730
H	1.78959	0.00846	-3.17348
C	-1.78925	1.85241	-0.71966
C	-0.66442	1.91024	-1.59607
C	-0.03264	0.64547	-2.18261
C	1.16095	-0.66889	0.68258
C	0.71736	-1.04331	2.12069
C	2.05969	-1.18029	2.88543
H	2.27182	-0.25244	3.44053
H	2.04991	-2.00232	3.61514
C	3.14161	-1.38275	1.81868
C	3.32012	-2.87843	1.50922
H	4.16399	-3.04869	0.82928
H	2.41572	-3.30004	1.04918
H	3.52477	-3.42541	2.44136
C	4.49175	-0.80296	2.22794
H	5.22380	-0.89494	1.41189
H	4.87402	-1.36106	3.09477
H	4.41625	0.25628	2.50669
C	-0.08094	0.14421	2.71713
H	0.57880	1.02730	2.73234
H	-0.91906	0.41230	2.05721
C	-0.62721	-0.15326	4.11232
H	-1.19567	0.71549	4.47825
H	0.20523	-0.30651	4.82190
C	-1.50381	-1.40326	4.08664
H	-1.92518	-1.60524	5.08294
H	-2.35870	-1.23169	3.40768
C	-0.70034	-2.60547	3.59481
H	-1.33428	-3.50488	3.55311
H	0.09580	-2.82428	4.32726
C	-0.08907	-2.35683	2.21428
H	-0.88936	-2.33819	1.46662
H	0.55927	-3.19917	1.93199
C	1.78984	2.99910	0.86846
H	2.01608	3.76665	0.11204
H	1.42992	3.51130	1.77485
H	0.97184	2.37578	0.47842
C	4.10772	3.01842	1.85658
H	5.03114	2.44844	2.03742
H	3.74004	3.39942	2.82065
H	4.36785	3.89218	1.24055
C	3.03096	2.16057	1.18555
H	2.72114	1.38775	1.90155
C	3.55682	1.44349	-0.04964
C	4.30923	2.14939	-0.99095
H	4.50817	3.21098	-0.83264
C	4.81630	1.51830	-2.12510
H	5.40510	2.08537	-2.84793
C	4.57626	0.16603	-2.33070
H	4.97948	-0.32396	-3.22009
C	2.88142	-2.36255	-3.00213
H	3.37454	-1.87650	-3.85841
H	1.83391	-2.03261	-2.96430
H	2.87992	-3.44695	-3.18759
C	4.94820	-2.80219	-1.64552
H	5.55893	-2.53937	-2.52319
H	4.79538	-3.89192	-1.65800
H	5.53268	-2.54242	-0.75092
C	3.30701	0.06888	-0.28066
C	3.81545	-0.58121	-1.42323
C	3.60285	-2.06459	-1.68296
H	2.96041	-2.44710	-0.88108

$(Me_2\text{-cAAC})_2NiCl_2$ (**13**)

E = -4099.72409692

Ni	0.00000	0.00000	0.00000
Cl	0.78810	-1.57208	1.40613
N	0.36924	1.89022	2.37035
C	0.76966	1.34085	1.25415
C	1.42833	2.68371	3.12341
C	2.68818	2.30973	2.33121
H	3.21821	1.49976	2.85470
H	3.37807	3.16075	2.23726
C	2.19577	1.79404	0.97038
C	1.10550	4.17501	3.09691
H	1.01265	4.56295	2.07559
H	1.91384	4.72203	3.60245

H	0.16945	4.37587	3.63691
C	1.53703	2.23288	4.57459
H	1.76223	1.16128	4.64226
H	0.61757	2.44700	5.13756
H	2.36310	2.78647	5.04465
C	2.11592	2.92682	-0.07281
H	3.13563	3.27960	-0.28957
H	1.52433	3.78065	0.28406
H	1.64489	2.57416	-0.99809
C	3.08095	0.67676	0.41580
H	2.69679	0.31186	-0.55145
H	3.11756	-0.17751	1.10398
H	4.09877	1.06313	0.25267
C	-0.98000	1.90279	2.91255
C	-1.33512	1.00022	3.94138
C	-2.54600	1.20237	4.61183
H	-2.82711	0.51243	5.40930
C	-3.39758	2.24565	4.27576
H	-4.32930	2.39535	4.82340
C	-3.07240	3.07001	3.20801
H	-3.76825	3.85313	2.90219
C	-1.87824	2.91373	2.49429
C	-0.55016	-0.25659	4.28251
H	0.38223	-0.26095	3.70225
C	-1.36608	-1.47180	3.81937
H	-1.67229	-1.35395	2.77294
H	-2.26771	-1.59163	4.44085
H	-0.76151	-2.38734	3.88695
C	-0.23145	-0.40046	5.77463
H	0.39012	-1.29346	5.93558
H	-1.15030	-0.53409	6.36526
H	0.30320	0.46680	6.18294
C	-1.69953	3.77754	1.25234
H	-0.75091	3.51017	0.76505
C	-2.82340	3.44882	0.25737
H	-2.61462	3.91526	-0.71568
H	-3.78869	3.82778	0.62831
H	-2.90050	2.36829	0.09240
C	-1.72468	5.28360	1.54064
H	-1.57075	5.84112	0.60501
H	-0.95802	5.60119	2.25734
H	-2.70330	5.58662	1.94298
Cl	-0.78810	1.57208	-1.40613
N	-0.36924	-1.89022	-2.37035
C	-0.76966	-1.34085	-1.25415
C	-1.42833	-2.68371	-3.12341
C	-2.68818	-2.30973	-2.33121
H	-3.21821	-1.49976	-2.85470
H	-3.37807	-3.16075	-2.23726
C	-2.19577	-1.79404	-0.97038
C	-1.10550	-4.17501	-3.09691
H	-1.01265	-4.56295	-2.07559
H	-1.91384	-4.72203	-3.60245
H	-0.16945	-4.37587	-3.63691
C	-1.53703	-2.23288	-4.57459
H	-1.76223	-1.16128	-4.64226
H	-0.61757	-2.44700	-5.13756
H	-2.36310	-2.78647	-5.04465
C	-2.11592	-2.92682	0.07281
H	-3.13563	-3.27960	0.28957
H	-1.52433	-3.78065	-0.28406
H	-1.64489	-2.57416	0.99809
C	-3.08095	-0.67676	-0.41580
H	-2.69679	-0.31186	0.55145
H	-3.11756	0.17751	-1.10398
H	-4.09877	-1.06313	-0.25267
C	0.98000	-1.90279	-2.91255
C	1.33512	-1.00022	-3.94138
C	2.54600	-1.20237	-4.61183
H	2.82711	-0.51243	-5.40930
C	3.39758	-2.24565	-4.27576
H	4.32930	-2.39535	-4.82340
C	3.07240	-3.07001	-3.20801
H	3.76825	-3.85313	-2.90219
C	1.87824	-2.91373	-2.49429
C	0.55016	0.25659	-4.28251
H	-0.38223	0.26095	-3.70225
C	1.36608	1.47180	-3.81937
H	1.67229	1.35395	-2.77294
H	2.26771	1.59163	-4.44085
H	0.76151	2.38734	-3.88695
C	0.23145	0.40046	-5.77463
H	-0.39012	1.29346	-5.93558
H	1.15030	0.53409	-6.36526
H	-0.30320	-0.46680	-6.18294
C	1.69953	-3.77754	-1.25234
H	0.75091	-3.51017	-0.76505
C	2.82340	-3.44882	-0.25737
H	2.61462	-3.91526	0.71568
H	3.78869	-3.82778	-0.62831
H	2.90050	-2.36829	-0.09240
C	1.72468	-5.28360	-1.54064
H	1.57075	-5.84112	-0.60501
H	0.95802	-5.60119	-2.25734
H	2.70330	-5.58662	-1.94298

$(Me_2\text{-cAAC})_2Ni$ (**14**)

E = -3179.16397326

Ni	-0.00903	-1.04355	-0.08768
N	-2.84020	-0.50173	0.38219
C	-1.78318	-1.30508	0.49032
C	-4.15828	-1.00339	0.90240
C	-3.82509	-2.48707	1.11131
H	-4.19135	-3.06403	0.24785
H	-4.31300	-2.89260	2.01018
C	-2.28438	-2.58162	1.17229
C	-4.54356	-0.28997	2.20223
H	-3.81935	-0.47585	3.00575
H	-5.52537	-0.65412	2.53757
H	-4.61985	0.79529	2.04003
C	-5.28880	-0.80068	-0.10660
H	-5.08779	-1.32037	-1.05210
H	-5.45336	0.26665	-0.31692
H	-6.21728	-1.21328	0.31425
C	-1.75461	-2.58989	2.61383
H	-2.13599	-3.47114	3.15335
H	-2.05327	-1.68790	3.16852
H	-0.65636	-2.62663	2.60830
C	-1.78288	-3.83285	0.45027
H	-0.68965	-3.90984	0.53065

H	-2.04222	-3.80016	-0.61901
H	-2.23387	-4.73564	0.89355
C	-2.75884	0.82023	-0.17111
C	-3.00003	1.00200	-1.54782
C	-3.05116	2.30786	-2.04381
H	-3.23934	2.46969	-3.10700
C	-2.85015	3.40177	-1.20852
H	-2.90570	4.41474	-1.61068
C	-2.53137	3.19905	0.12952
H	-2.31014	4.05777	0.76634
C	-2.46137	1.91087	0.66985
C	-3.07514	-0.17009	-2.51275
H	-3.21150	-1.08583	-1.92220
C	-1.72753	-0.31138	-3.23025
H	-0.92148	-0.44936	-2.49181
H	-1.50727	0.58648	-3.82960
H	-1.73474	-1.18361	-3.90239
C	-4.22987	-0.05954	-3.50927
H	-4.29858	-0.97606	-4.11360
H	-4.08099	0.77855	-4.20650
H	-5.19297	0.09273	-3.00045
C	-1.93197	1.71923	2.08120
H	-2.13745	0.68522	2.38342
C	-0.40733	1.88119	2.06148
H	0.01460	1.72752	3.06680
H	-0.12383	2.88926	1.72007
H	0.04845	1.14424	1.37938
C	-2.57278	2.65650	3.10568
H	-2.21799	2.40857	4.11680
H	-3.67034	2.58506	3.09977
H	-2.30217	3.70610	2.91605
N	2.81392	-0.37299	-0.54794
C	1.75101	-1.14515	-0.75846
C	4.10341	-0.76224	-1.21558
C	3.59230	-1.82123	-2.20439
H	3.45895	-1.35574	-3.19334
H	4.30830	-2.64824	-2.32164
C	2.22067	-2.28450	-1.66743
C	5.10265	-1.32246	-0.19854
H	4.73449	-2.23641	0.28457
H	6.04479	-1.56412	-0.71123
H	5.32012	-0.57537	0.57905
C	4.76099	0.42118	-1.92566
H	4.10615	0.84843	-2.69550
H	5.03614	1.21437	-1.21457
H	5.67906	0.07113	-2.41968
C	2.33452	-3.56155	-0.82043
H	2.73976	-4.38369	-1.43134
H	2.98939	-3.42201	0.05196
H	1.34451	-3.85527	-0.44610
C	1.21490	-2.52197	-2.79364
H	0.22870	-2.76251	-2.36806
H	1.09914	-1.61917	-3.41256
H	1.54339	-3.35089	-3.44104
C	2.77276	0.78569	0.29861
C	2.47418	2.03775	-0.27477
C	2.56237	3.17369	0.53506
H	2.33962	4.15332	0.10762
C	2.90373	3.07337	1.87969
H	2.97403	3.97174	2.49518
C	3.11017	1.82119	2.44752
H	3.31650	1.74215	3.51669
C	3.03828	0.65640	1.67637
C	1.93960	2.16871	-1.69117
H	2.11649	1.21821	-2.21189
C	0.42053	2.36395	-1.63223
H	-0.06088	1.51401	-1.12025
H	0.16509	3.28443	-1.08401
H	-0.00299	2.44096	-2.64559
C	2.61155	3.28932	-2.48653
H	2.26365	3.27456	-3.52992
H	2.36171	4.27894	-2.07546
H	3.70701	3.19083	-2.48502
C	3.10417	-0.69856	2.36186
H	3.21233	-1.46460	1.58451
C	1.76568	-0.96717	3.06029
H	1.76034	-1.97052	3.51421
H	1.58327	-0.22685	3.85565
H	0.94257	-0.91026	2.33010
C	4.27429	-0.83275	3.33720
H	4.31834	-1.85694	3.73591
H	5.23779	-0.61007	2.85607
H	4.16258	-0.15437	4.19634

$(Cy\text{-}cAAC)_2Pd$ (**15**)

E = -2032.22438236

Pd	0.00005	0.54894	-0.00005
N	-3.03659	-0.15651	-0.11273
N	3.03655	-0.15668	0.11276
C	-2.06465	0.67023	-0.42758
C	-2.69217	1.84092	-1.16835
C	-4.14031	1.39544	-1.47616
H	-4.88055	2.19905	-1.35143
H	-4.20737	1.05110	-2.52036
C	-4.43580	0.21926	-0.52943
C	-2.80917	-1.37868	0.61282
C	-2.84961	-1.37553	2.02038
C	-2.75573	-2.60475	2.68207
H	-2.78701	-2.62621	3.77317
C	-2.60162	-3.79244	1.97667
H	-2.54100	-4.74215	2.51074
C	-2.47294	-3.76123	0.59192
H	-2.28210	-4.68808	0.04757
C	-2.55463	-2.55809	-0.11461
C	-2.62380	3.07397	-0.23910
H	-3.21234	2.89127	0.67491
H	-1.57375	3.17628	0.08295
C	-3.08504	4.35728	-0.92928
H	-4.15937	4.28994	-1.17445
H	-2.97924	5.20657	-0.23720
C	-2.29413	4.61203	-2.21217
H	-2.65821	5.52097	-2.71483
H	-1.23664	4.79142	-1.95125
C	-2.37144	3.40659	-3.14842
H	-1.77196	3.58446	-4.05409
H	-3.41488	3.27022	-3.48533
C	-1.88346	2.14525	-2.44017
H	-0.82968	2.26147	-2.13416
H	-1.91567	1.27118	-3.11231
C	-5.26474	0.63116	0.68900

H	-4.84522	1.51305	1.19108
H	-5.32414	-0.19380	1.41392
H	-6.28667	0.87539	0.36528
C	-5.14654	-0.93368	-1.23604
H	-6.14579	-0.59498	-1.54622
H	-5.26975	-1.79983	-0.56901
H	-4.60482	-1.25414	-2.13523
C	-2.84361	-0.09125	2.83433
H	-3.07324	0.74143	2.15766
C	-1.42550	0.15261	3.36744
H	-0.70973	0.19346	2.53043
H	-1.12353	-0.65323	4.05549
H	-1.37755	1.10823	3.91257
C	-3.86777	-0.08691	3.97054
H	-3.87102	0.89212	4.47183
H	-3.62403	-0.84159	4.73334
H	-4.88633	-0.29086	3.60972
C	-2.23253	-2.53938	-1.60016
H	-2.53092	-1.56256	-2.00382
C	-0.71245	-2.64731	-1.77847
H	-0.44192	-2.60582	-2.84517
H	-0.33853	-3.59802	-1.36683
H	-0.20274	-1.81832	-1.25781
C	-2.96350	-3.62775	-2.38812
H	-2.77258	-3.50800	-3.46468
H	-4.05046	-3.59187	-2.22271
H	-2.61272	-4.63194	-2.10674
C	2.06471	0.67018	0.42762
C	2.69235	1.84077	1.16843
C	4.14045	1.39513	1.47622
H	4.88076	2.19868	1.35148
H	4.20751	1.05079	2.52042
C	4.43581	0.21893	0.52948
C	2.80904	-1.37878	-0.61284
C	2.84947	-1.37553	-2.02039
C	2.75555	-2.60468	-2.68219
H	2.78681	-2.62605	-3.77330
C	2.60142	-3.79243	-1.97689
H	2.54078	-4.74209	-2.51104
C	2.47272	-3.76132	-0.59214
H	2.28186	-4.68821	-0.04786
C	2.55445	-2.55823	0.11449
C	1.88366	2.14514	2.44025
H	0.82989	2.26146	2.13424
H	1.91580	1.27105	3.11237
C	2.37174	3.40641	3.14855
H	3.41517	3.26994	3.48545
H	1.77227	3.58431	4.05421
C	2.29453	4.61189	2.21234
H	1.23705	4.79137	1.95141
H	2.65867	5.52079	2.71503
C	3.08543	4.35713	0.92944
H	4.15976	4.28970	1.17463
H	2.97970	5.20644	0.23739
C	2.62411	3.07387	0.23922
H	3.21266	2.89114	-0.67478
H	1.57408	3.17627	-0.08286
C	5.14641	-0.93411	1.23608
H	5.26950	-1.80027	0.56904
H	4.60466	-1.25451	2.13527
H	6.14570	-0.59553	1.54623
C	5.26479	0.63074	-0.68894
H	4.84538	1.51267	-1.19103
H	5.32411	-0.19424	-1.41387
H	6.28675	0.87484	-0.36522
C	2.84347	-0.09116	-2.83421
H	3.07322	0.74142	-2.15746
C	1.42531	0.15284	-3.36713
H	1.37737	1.10850	-3.91220
H	0.70966	0.19371	-2.53003
H	1.12317	-0.65294	-4.05519
C	3.86751	-0.08675	-3.97052
H	3.87073	0.89233	-4.47172
H	3.62367	-0.84135	-4.73338
H	4.88611	-0.29077	-3.60983
C	2.23232	-2.53966	1.60003
H	2.53067	-1.56286	2.00378
C	0.71225	-2.64766	1.77830
H	0.20252	-1.81862	1.25775
H	0.44171	-2.60635	2.84500
H	0.33836	-3.59834	1.36651
C	2.96332	-3.62807	2.38792
H	2.61255	-4.63224	2.10647
H	2.77239	-3.50839	3.46449
H	4.05028	-3.59215	2.22252

$(Me_2\text{-cAAC})_2Pt$ (**16**)
E = -1790.22089796

Pt	-0.00001	0.96535	-0.00007
N	-2.89377	0.28615	0.48581
C	-1.86414	1.08941	0.70448
N	2.89374	0.28609	-0.48588
C	-2.37313	2.26669	1.53629
C	-3.77257	1.82634	2.01476
H	-3.70274	1.43595	3.04175
H	-4.49738	2.65358	2.02434
C	-4.21645	0.69529	1.07367
C	-2.42856	3.49707	0.61722
H	-3.07137	3.32600	-0.25899
H	-1.41974	3.73149	0.24926
H	-2.82313	4.36132	1.17389
C	-1.43695	2.55615	2.71048
H	-0.44080	2.83796	2.33984
H	-1.32000	1.66726	3.34920
H	-1.84312	3.37578	3.32461
C	-5.17242	1.16872	-0.02269
H	-6.13008	1.45832	0.43312
H	-5.36694	0.35667	-0.73752
H	-4.77771	2.03414	-0.57067
C	-4.88045	-0.45299	1.83115
H	-5.82291	-0.08916	2.26563
H	-4.24749	-0.81434	2.65143
H	-5.11260	-1.29601	1.16368
C	-2.79481	-0.93324	-0.27317
C	-2.48788	-2.12893	0.40853
C	-2.53079	-3.32645	-0.31073
H	-2.30075	-4.26341	0.20045
C	-2.83509	-3.34159	-1.66769
H	-2.87027	-4.28741	-2.21088
C	-3.04629	-2.14339	-2.33885

H	-3.22047	-2.15307	-3.41677
C	-2.00419	-2.15086	1.84997
H	-2.17397	-1.15562	2.28367
C	-3.01684	-0.91762	-1.66434
C	-2.73640	-3.18667	2.70757
H	-2.42913	-3.09287	3.75964
H	-2.49239	-4.21109	2.38854
H	-3.82839	-3.07017	2.65319
C	-0.49065	-2.39969	1.87367
H	0.04635	-1.63193	1.29130
H	-0.25346	-3.38652	1.44496
H	-0.11142	-2.37900	2.90739
C	-3.09208	0.36703	-2.47478
H	-3.14704	1.20945	-1.77286
C	-4.30395	0.42378	-3.40852
H	-5.25216	0.27231	-2.87397
H	-4.23630	-0.34429	-4.19372
H	-4.34681	1.40071	-3.91229
C	-1.79189	0.53488	-3.27225
H	-1.79897	1.49010	-3.81991
H	-1.67880	-0.27961	-4.00562
H	-0.92434	0.52792	-2.59349
C	1.86410	1.08933	-0.70464
C	2.37305	2.26643	-1.53672
C	3.77248	1.82600	-2.01514
H	3.70262	1.43542	-3.04206
H	4.49728	2.65325	-2.02489
C	4.21639	0.69512	-1.07385
C	1.43682	2.55565	-2.71093
H	1.84295	3.37518	-3.32522
H	0.44068	2.83750	-2.34030
H	1.31987	1.66665	-3.34948
C	2.42850	3.49699	-0.61789
H	2.82305	4.36113	-1.17473
H	3.07132	3.32610	0.25834
H	1.41969	3.73148	-0.24996
C	4.88033	-0.45332	-1.83115
H	4.24733	-0.81478	-2.65136
H	5.11245	-1.29624	-1.16355
H	5.82280	-0.08962	-2.26571
C	5.17242	1.16873	0.02237
H	6.13007	1.45821	-0.43352
H	5.36693	0.35681	0.73737
H	4.77776	2.03427	0.57020
C	2.79481	-0.93316	0.27334
C	2.48794	-2.12903	-0.40809
C	2.53088	-3.32638	0.31146
H	2.30088	-4.26346	-0.19950
C	2.83516	-3.34118	1.66843
H	2.87035	-4.28687	2.21185
C	3.04632	-2.14281	2.33930
H	3.22049	-2.15223	3.41722
C	3.01686	-0.91722	1.66449
C	2.00433	-2.15136	-1.84956
H	2.17424	-1.15628	-2.28355
C	2.73646	-3.18753	-2.70678
H	2.42926	-3.09404	-3.75889
H	2.49232	-4.21182	-2.38741
H	3.82846	-3.07115	-2.65238
C	0.49077	-2.40003	-1.87325
H	-0.04618	-1.63202	-1.29114
H	0.25344	-3.38669	-1.44424
H	0.11159	-2.37963	-2.90700
C	3.09207	0.36764	2.47460
H	3.14687	1.20988	1.77244
C	4.30407	0.42476	3.40815
H	5.25221	0.27315	2.87352
H	4.23656	-0.34305	4.19361
H	4.34696	1.40186	3.91159
C	1.79196	0.53560	3.27218
H	1.79903	1.49096	3.81959
H	1.67901	-0.27871	4.00576
H	0.92434	0.52839	2.59351

$(Et_2\text{-cAAC})_2Pt$ (**17**)

E = -1947.43968944

Pt	-0.00005	-0.65382	-0.00012
N	-2.92031	0.02999	-0.23406
C	-1.91387	-0.77008	-0.55550
N	2.92030	0.02972	0.23405
C	-2.49795	-1.93526	-1.36249
C	-3.90034	-1.43142	-1.75970
H	-3.82933	-0.93378	-2.74058
H	-4.65917	-2.22025	-1.84841
C	-4.28476	-0.38745	-0.70471
C	-2.49793	-3.16490	-0.40569
H	-2.54079	-2.81341	0.63890
H	-1.50668	-3.63745	-0.49383
C	-1.61692	-2.18914	-2.59788
H	-0.59140	-2.37557	-2.24145
H	-1.56692	-1.24848	-3.17349
C	-5.08979	-0.98675	0.44996
H	-6.07287	-1.31114	0.07868
H	-5.25267	-0.23484	1.23473
H	-4.58392	-1.85429	0.89453
C	-5.07026	0.77782	-1.29956
H	-6.03418	0.40005	-1.67047
H	-4.53733	1.23317	-2.14375
H	-5.27160	1.55483	-0.54759
C	-2.75810	1.24746	0.51645
C	-2.51618	2.44354	-0.19130
C	-2.49546	3.64165	0.52753
H	-2.31352	4.57836	-0.00295
C	-2.67839	3.65854	1.90624
H	-2.66554	4.60504	2.44920
C	-2.83099	2.46136	2.59438
H	-2.91183	2.47234	3.68325
C	-2.16751	2.46490	-1.67137
H	-2.39398	1.47508	-2.09190
C	-2.86013	1.23465	1.92120
C	-2.95909	3.51601	-2.45450
H	-2.75690	3.41752	-3.53121
H	-2.66586	4.53531	-2.16177
H	-4.04290	3.42099	-2.29423
C	-0.65872	2.69030	-1.83382
H	-0.08288	1.91352	-1.30262
H	-0.36910	3.67261	-1.42761
H	-0.37574	2.66608	-2.89790
C	-2.86775	-0.04799	2.73766
H	-2.98661	-0.89051	2.04417

C	-3.99549	-0.09907	3.77180
H	-4.98456	0.06698	3.32195
H	-3.85280	0.66332	4.55248
H	-4.00595	-1.07873	4.27199
C	-1.50427	-0.21818	3.42008
H	-1.46293	-1.17555	3.96302
H	-1.32882	0.59368	4.14403
H	-0.69865	-0.20706	2.66924
C	1.91372	-0.77020	0.55541
C	2.49757	-1.93548	1.36243
C	3.89996	-1.43179	1.75983
H	3.82888	-0.93414	2.74069
H	4.65870	-2.22071	1.84864
C	4.28463	-0.38790	0.70486
C	1.61637	-2.18927	2.59774
H	0.59079	-2.37528	2.24125
H	1.56667	-1.24871	3.17355
C	2.49757	-3.16510	0.40561
H	2.54042	-2.81356	-0.63896
H	1.50635	-3.63768	0.49376
C	5.07024	0.77728	1.29975
H	4.53728	1.23270	2.14390
H	5.27173	1.55425	0.54778
H	6.03409	0.39941	1.67074
C	5.08967	-0.98736	-0.44972
H	6.07266	-1.31193	-0.07835
H	5.25276	-0.23550	-1.23449
H	4.58367	-1.85481	-0.89433
C	2.75831	1.24726	-0.51640
C	2.51644	2.44329	0.19146
C	2.49574	3.64147	-0.52727
H	2.31384	4.57813	0.00331
C	2.67864	3.65847	-1.90598
H	2.66581	4.60501	-2.44886
C	2.83127	2.46135	-2.59422
H	2.91214	2.47243	-3.68309
C	2.86043	1.23457	-1.92115
C	2.16790	2.46451	1.67157
H	2.39452	1.47469	2.09201
C	2.95944	3.51565	2.45468
H	2.75736	3.41710	3.53142
H	2.66608	4.53494	2.16204
H	4.04324	3.42074	2.29430
C	0.65909	2.68971	1.83417
H	0.08330	1.91288	1.30299
H	0.36931	3.67201	1.42803
H	0.37621	2.66542	2.89827
C	2.86824	-0.04797	-2.73776
H	2.98737	-0.89055	-2.04438
C	3.99586	-0.09865	-3.77203
H	4.98495	0.06765	-3.32232
H	3.85283	0.66376	-4.55263
H	4.00653	-1.07827	-4.27231
C	1.50473	-0.21841	-3.42006
H	1.46357	-1.17572	-3.96313
H	1.32899	0.59350	-4.14388
H	0.69920	-0.20761	-2.66913
C	-2.07714	-3.32156	-3.50971
H	-3.12706	-3.20014	-3.82063
H	-1.46407	-3.35305	-4.42157
H	-1.98088	-4.30062	-3.01879
C	-3.60067	-4.20019	-0.62070
H	-3.67343	-4.52465	-1.66764
H	-3.40737	-5.09121	-0.00630
H	-4.58765	-3.81297	-0.32777
C	2.07614	-3.32203	3.50936
H	3.12603	-3.20091	3.82049
H	1.46290	-3.35361	4.42110
H	1.97977	-4.30095	3.01816
C	3.60038	-4.20032	0.62063
H	3.67306	-4.52484	1.66755
H	3.40720	-5.09131	0.00614
H	4.58736	-3.81299	0.32781

(Me_2-cAAC)Se (**19**)

E = -3237.07683689

C	-2.20883	-0.64329	1.88071
C	-2.66005	-0.32210	0.44284
C	-1.33396	-0.19862	-0.30573
C	-0.74975	-0.17239	2.01244
H	-2.85487	-0.17424	2.63667
H	-2.25083	-1.73181	2.03730
N	-0.33335	-0.10175	0.57621
C	1.04201	0.10243	0.20889
C	1.87441	-1.02096	0.02742
C	1.53096	1.41401	0.03610
C	3.23327	-0.80182	-0.21685
C	2.89875	1.57841	-0.20504
C	3.75013	0.48517	-0.30901
H	3.89466	-1.65938	-0.35493
H	3.29787	2.58629	-0.33517
H	4.81483	0.63581	-0.49369
C	1.34551	-2.44644	-0.01392
H	0.28469	-2.42542	0.27405
C	0.63216	2.64074	-0.01488
H	-0.38888	2.32689	0.24144
C	0.59090	3.19338	-1.44661
H	-0.12150	4.02945	-1.51077
H	1.58214	3.56893	-1.74443
H	0.28377	2.41417	-2.15615
C	1.06643	3.74352	0.95588
H	2.04840	4.15124	0.67243
H	0.34784	4.57591	0.92801
H	1.13973	3.38894	1.99273
C	2.09530	-3.38132	0.94052
H	1.62036	-4.37349	0.95244
H	3.13682	-3.52254	0.61496
H	2.11683	-2.99494	1.96888
C	1.41280	-2.98562	-1.44926
H	2.45826	-3.05450	-1.78777
H	0.97298	-3.99301	-1.49848
H	0.86544	-2.32775	-2.13732
C	-3.54180	-1.42940	-0.13349
H	-4.45085	-1.53402	0.47844
H	-3.82662	-1.19123	-1.16665
H	-3.00980	-2.39215	-0.14044
C	-3.40041	1.02089	0.34244
H	-3.62963	1.23875	-0.70955
H	-4.33988	0.96938	0.91310
H	-2.79982	1.85236	0.73869

C	0.09522	-1.17538	2.79474
H	0.00916	-2.18666	2.37811
H	1.15557	-0.88290	2.80586
H	-0.26438	-1.20394	3.83350
C	-0.62141	1.19443	2.68716
H	0.42524	1.52855	2.67061
H	-1.24316	1.95909	2.20435
H	-0.93578	1.10871	3.73701
Se	-1.18574	-0.13965	-2.10243

$(Me_2\text{-cAAC})_2Ge$ (**20**)
E = -3747.90359754

N	-2.74803	-0.73646	0.21317
C	-1.54066	-1.32908	0.29630
C	-3.92772	-1.63070	0.45009
C	-3.23814	-2.99865	0.57886
H	-3.28679	-3.52133	-0.38914
H	-3.72793	-3.63689	1.32882
C	-1.76751	-2.70992	0.91950
C	-4.72977	-1.23431	1.68931
H	-4.13423	-1.26192	2.60982
H	-5.57356	-1.92955	1.80590
H	-5.13997	-0.22318	1.56298
C	-4.86981	-1.60071	-0.75241
H	-4.34545	-1.89388	-1.67128
H	-5.30562	-0.60062	-0.89341
H	-5.69020	-2.31324	-0.58227
C	-1.55852	-2.58697	2.44369
H	-1.85846	-3.52858	2.93046
H	-2.14294	-1.76826	2.88203
H	-0.50027	-2.39317	2.66338
C	-0.82660	-3.79680	0.42377
H	0.21268	-3.48537	0.60004
H	-0.96081	-4.00563	-0.64655
H	-1.00821	-4.73074	0.97737
C	-2.95110	0.65925	-0.09799
C	-3.06268	1.07736	-1.44270
C	-3.40072	2.41016	-1.70045
H	-3.50440	2.73928	-2.73622
C	-3.58571	3.32415	-0.67203
H	-3.85444	4.35767	-0.89555
C	-3.38743	2.91956	0.64137
H	-3.47654	3.64906	1.44865
C	-3.05508	1.59848	0.95743
C	-2.74536	0.19087	-2.63818
H	-2.48551	-0.81136	-2.26548
C	-1.51549	0.74734	-3.37041
H	-0.65493	0.81471	-2.68787
H	-1.72350	1.75164	-3.76990
H	-1.25055	0.09967	-4.21989
C	-3.91765	0.07715	-3.62013
H	-3.67422	-0.63720	-4.42069
H	-4.12114	1.04735	-4.09804
H	-4.84355	-0.25371	-3.13221
C	-2.73513	1.28663	2.41397
H	-2.49955	0.21681	2.48539
C	-1.48931	2.06367	2.86766
H	-1.21615	1.76754	3.89180
H	-1.69016	3.14644	2.87342
H	-0.63177	1.86440	2.21199
C	-3.89340	1.61217	3.36580
H	-3.64131	1.29034	4.38726
H	-4.83614	1.13064	3.07821
H	-4.07120	2.69759	3.40240
N	2.69977	-0.24151	-0.67611
C	1.52343	-0.95686	-0.70631
C	3.67636	-0.56081	-1.75255
C	2.77623	-1.35070	-2.70562
H	2.29758	-0.64227	-3.40076
H	3.33680	-2.08615	-3.30172
C	1.68062	-1.99426	-1.83079
C	4.86382	-1.37201	-1.21521
H	4.56127	-2.33047	-0.77818
H	5.57137	-1.57635	-2.03195
H	5.39274	-0.78939	-0.44659
C	4.24528	0.68290	-2.43040
H	3.45707	1.28312	-2.89938
H	4.79293	1.30936	-1.71074
H	4.94977	0.37169	-3.21565
C	2.16561	-3.35329	-1.26719
H	2.78710	-3.87443	-2.01189
H	2.75240	-3.24383	-0.34542
H	1.31575	-4.00514	-1.03762
C	0.41342	-2.22653	-2.64965
H	-0.41127	-2.55519	-2.00356
H	0.09659	-1.30322	-3.14925
H	0.59369	-3.00050	-3.41342
C	2.98773	0.72000	0.34728
C	2.69586	2.09295	0.14966
C	3.03600	2.99579	1.16290
H	2.82470	4.05732	1.01800
C	3.61539	2.57194	2.35224
H	3.87269	3.29676	3.12635
C	3.84022	1.21675	2.55934
H	4.25978	0.87798	3.50901
C	3.52156	0.27339	1.57858
C	1.98982	2.65010	-1.08167
H	1.75839	1.80211	-1.74406
C	0.65910	3.32829	-0.71947
H	-0.00927	2.64414	-0.18072
H	0.83038	4.22091	-0.09733
H	0.14670	3.65626	-1.63741
C	2.86293	3.66998	-1.82824
H	2.38506	3.95829	-2.77685
H	2.97684	4.58579	-1.22827
H	3.86882	3.29243	-2.04821
C	3.68397	-1.20025	1.91583
H	3.45652	-1.77396	1.01007
C	2.66403	-1.61098	2.98546
H	2.70442	-2.69750	3.16004
H	2.87521	-1.10577	3.94109
H	1.64648	-1.33910	2.66978
C	5.10333	-1.55407	2.36882
H	5.19276	-2.63926	2.52791
H	5.85922	-1.25225	1.63062
H	5.35097	-1.06193	3.32154
Ge	0.05124	-0.16950	0.25421

$(Me_2\text{-cAAC})_2Si_2S_4$ (**22**)
E = -3842.93255987

Si	-1.04598	-0.49646	-0.88066
N	-3.80183	-0.66332	-0.03567
C	-2.67818	-1.30830	-0.20038
C	-2.91636	-2.81605	-0.09871
C	-3.88935	0.72820	0.36319
C	-3.75607	0.97334	1.74706
C	-4.06778	1.76436	-0.56769
C	-3.49832	-0.13274	2.76151
H	-3.83485	-1.08433	2.32473
C	-4.18612	1.55543	-2.06677
H	-3.98791	0.49744	-2.28323
C	-3.80056	2.29795	2.18150
H	-3.67882	2.51709	3.24270
C	-4.11587	3.07350	-0.07269
H	-4.24559	3.89729	-0.77658
C	-3.97997	3.34286	1.28110
H	-4.00654	4.37302	1.63923
C	-5.59151	1.92986	-2.55500
H	-5.75536	3.01483	-2.46484
H	-6.38317	1.43454	-1.97343
H	-5.71562	1.65881	-3.61401
C	-4.28781	0.06528	4.05821
H	-4.19596	-0.82906	4.69107
H	-5.35545	0.24621	3.86272
H	-3.90040	0.91318	4.64134
C	-5.02687	-1.54044	-0.18338
C	-3.13026	2.35894	-2.83390
H	-3.30791	3.44181	-2.74212
H	-3.16904	2.09499	-3.90079
H	-2.11832	2.13004	-2.47530
C	-1.99892	-0.26331	3.04915
H	-1.56410	0.69473	3.37015
H	-1.43451	-0.57908	2.16008
H	-1.81759	-1.00720	3.84021
C	-2.49912	-3.61549	-1.33859
H	-1.42635	-3.49499	-1.54081
H	-3.03309	-3.28906	-2.23941
H	-2.70875	-4.67967	-1.15212
C	-2.12555	-3.34594	1.11400
H	-1.04333	-3.31202	0.93967
H	-2.42675	-4.39022	1.28844
H	-2.34500	-2.77048	2.02460
C	-4.43588	-2.90074	0.19839
H	-4.91769	-3.71664	-0.35709
H	-4.59688	-3.08491	1.27198
C	-6.16977	-1.08309	0.71063
H	-5.88715	-1.07238	1.77187
H	-7.01092	-1.77953	0.58516
H	-6.51146	-0.07667	0.42988
C	-5.45852	-1.53244	-1.65254
H	-6.21133	-2.31899	-1.80443
H	-5.90676	-0.57319	-1.93521
Si	1.04602	0.49648	0.88075
N	3.80183	0.66332	0.03564
C	2.67818	1.30830	0.20036
C	2.91632	2.81604	0.09855
C	3.88935	-0.72822	-0.36314
C	3.75605	-0.97344	-1.74700
C	4.06780	-1.76433	0.56778
C	3.49826	0.13259	-2.76150
H	3.83480	1.08421	-2.32477
C	4.18613	-1.55533	2.06685
H	3.98783	-0.49735	2.28327
C	3.80055	-2.29807	-2.18138
H	3.67880	-2.51726	-3.24257
C	4.11592	-3.07350	0.07285
H	4.24564	-3.89724	0.77678
C	3.98000	-3.34292	-1.28092
H	4.00658	-4.37310	-1.63901
C	5.59155	-1.92962	2.55510
H	5.75550	-3.01457	2.46497
H	6.38317	-1.43424	1.97352
H	5.71563	-1.65852	3.61410
C	4.28770	-0.06549	-4.05822
H	4.19582	0.82882	-4.69111
H	5.35534	-0.24641	-3.86275
H	3.90026	-0.91341	-4.64129
C	5.02686	1.54048	0.18318
C	3.13033	-2.35889	2.83402
H	3.30808	-3.44175	2.74228
H	3.16909	-2.09489	3.90090
H	2.11837	-2.13009	2.47541
C	1.99884	0.26314	-3.04908
H	1.56402	-0.69491	-3.37002
H	1.43446	0.57897	-2.16002
H	1.81749	1.00699	-3.84018
C	2.49913	3.61558	1.33837
H	1.42638	3.49508	1.54067
H	3.03317	3.28925	2.23919
H	2.70872	4.67975	1.15179
C	2.12541	3.34578	-1.11417
H	1.04320	3.31181	-0.93978
H	2.42654	4.39007	-1.28871
H	2.34485	2.77027	-2.02473
C	4.43582	2.90073	-0.19867
H	4.91765	3.71669	0.35672
H	4.59675	3.08483	-1.27228
C	6.16971	1.08307	-0.71087
H	5.88700	1.07226	-1.77209
H	7.01085	1.77954	-0.58553
H	6.51143	0.07668	-0.43007
C	5.45863	1.53262	1.65231
H	4.60049	1.72364	2.31426
H	5.90692	0.57341	1.93503
S	1.49178	0.74465	2.82790
S	0.68664	-1.46146	0.00063
S	-0.68665	1.46146	-0.00048
S	-1.49166	-0.74455	-2.82783
H	-4.60034	-1.72343	-2.31444
H	6.21143	2.31920	1.80407

(2) ^{15}N-HMBC measurements

Two dimentional heteronuclear multiple-bond correlation spectroscopy (^{15}N-HMBC) is an important NMR technique. It provides more informations than a routine NMR measurements. We use 3-bond coupling of ^{1}H–^{15}N correlation spectroscopy of cyclic alkyl(amino) carbenes (cAACs) to shade light on the nature carbene-element (C_{cAAC}-E) bonds. ^{15}N-HMBC spectra of three different types of compounds are given below (Figures S3-S5). Replacement of Me_2-cAAC by Et_2-cAAC or Cy-cAAC has a negligible effect on chemical shift values (δ) of ^{15}N nuclei (I = 1/2) of series of compounds.

The chemical shift values of ^{13}C nuclei of all the compounds (**1-22**) do not follow similar trend like that of ^{15}N nuclei. The chemical shift values obtained from ^{15}N-HMBC measurements provides the true reflections the σ-donation and π-backdonation of cyclic alkyl(amino) carbenes (cAACs).

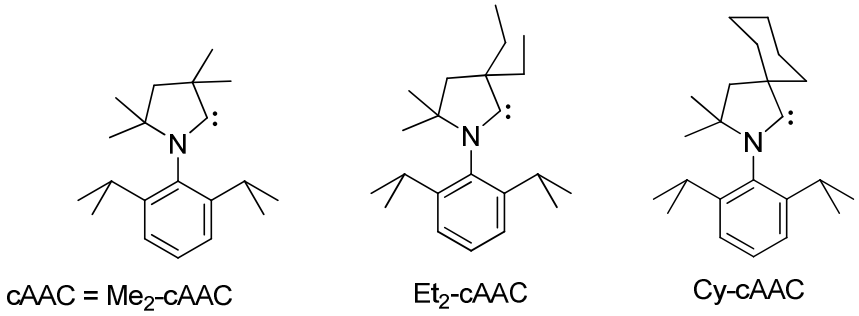


Figure S1. Cyclic alkyl(amino) carbenes (cAAC); Dimethyl (Me_2-cAAC; left), diethyl (Et_2-cAAC; middle) and cycloxehyl (Cy-cAAC; right) substituted cAACs.

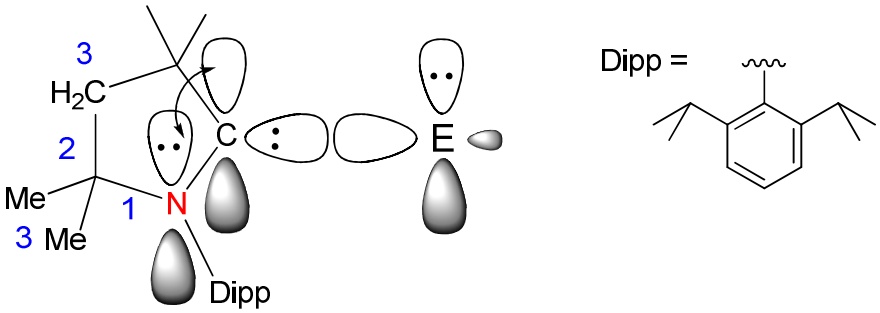


Figure S2. 3-bond coupling of ^{1}H–^{15}N nuclei of cAAC containing compounds. E is the elements or metals.

Table S5. Chemical shift values (δ) obtained from ^{15}N-HMBC measurements.

Compound	Compound No.	C_{cAAC}–N bond distance (Å)	^{15}N (δ ppm)	Solvents	Weight of compounds (mg)	Duration of measurements (minutes)
Cy-cAAC·LiOTf	**1**	1.315(3)	-159.0	THF-d_8	28	15

(Cy-cAAC)Si(Cl_2)=P-Tip	**2**	1.301	-160.7	C_6D_6	16	20
Cy-cAACH$^+$ OTf	**3**	1.290	-148.1	$CDCl_3$	15	20
(Me_2-cAAC)$SiCl_4$	**4**	1.303 (2)	-164.1	THF-d_8	17	20
(Cy-cAAC·)(Cl_2)Si-Si(Cl_2)(·CAAc-Cy)	**5**	1.376(6)	No signal	THF-d_8	15	30
(Me_2-cAAC)(Cl)Si-Si(Cl)(CAAc-Me_2)	**6**	1.336(3)-1.337(2)	-208.5	C_6D_6	20	30
(Me_2-cAAC)Si=Si(CAAc-Me_2)	**7**	1.342(5)	-206.0	C_6D_6	14	20
[(Me_2-cAAC)PPh_2]$^+Cl^-$	**8**	1.302(18)	-130.3	DMSO-d_6	15	30
Me_2-cAAC=O	**9**	1.374 (10)	-241.0	$CDCl_3$	15	20
(Cy-cAAC·)$_2SiCl_2$	**10**	1.400(2)-1.403(2)	No signal	C_6D_6	17	30
(Cy-cAAC)$_2$Si	**11**	1.382(16)-1.373(16)	-230.5	C_6D_6	12	30
(Cy-cAACH)Si(CMe_2)=CAAc-Cy	**12**	1.461(3) (1.465)	-315.2	THF-d_8	12	30
		1.383(3)	-256.5			
(Me_2-cAAC)$_2NiCl_2$	**13**	1.3154(18)-1.3148(18)	-160.6, -161.0	THF-d_8	15	30
(Me_2-cAAC)$_2$Ni	**14**	1.3381(16)/1.3420(16) Å	No Signal, broad ^{1}H signal	THF-d_8	25	30
(Cy-cAAC)$_2$Pd	**15**	1.3267(18)	-175.0	THF-d_8	11	30
(Me_2-cAAC)$_2$Pt	**16**	1.3231(15)	-180.1	THF-d_8	15	30
(Et_2-cAAC)$_2$Pt	**17**	1.3267(18)	-180.0	THF-d_8	20	30

$(Me_2\text{-}cAAC)_2Zn$	**18**	1.376(2)	-245.0	THF-d_8	25	20
$(Me_2\text{-}cAAC)Se$	**19**	1.323(2)	-187.5	C_6D_6	25	30
$(Me_2\text{-}cAAC)_2Ge$	**20**	1.3666(19)	-222.5	THF-d_8	23	20
$(Me_2\text{-}cAACH)_2O$	**21**	1.4352(18)-1.4353(19)	-307.9	THF-d_8	28	30
$(Me_2\text{-}cAAC)_2Si_2S_4$	**22**	1.342(5) (1.343)	-173.0	THF-d_8	15	20
$(Me_2\text{-}cAAC)S$	**23**	-	199.8	THF-d_8	15	20
(^{iPr}NHC)HCl			-196.3	$CDCl_3$ or DMSO-d_6	20	30
(^{iPr}NHC)			-185.1	C_6D_6	20	30
(^{iPr}NHC)$SiCl_2$			-191.8	C_6D_6	20	30
(^{iPr}NHC)$_2NiCl_2$			-190.9	C_6D_6	20	30

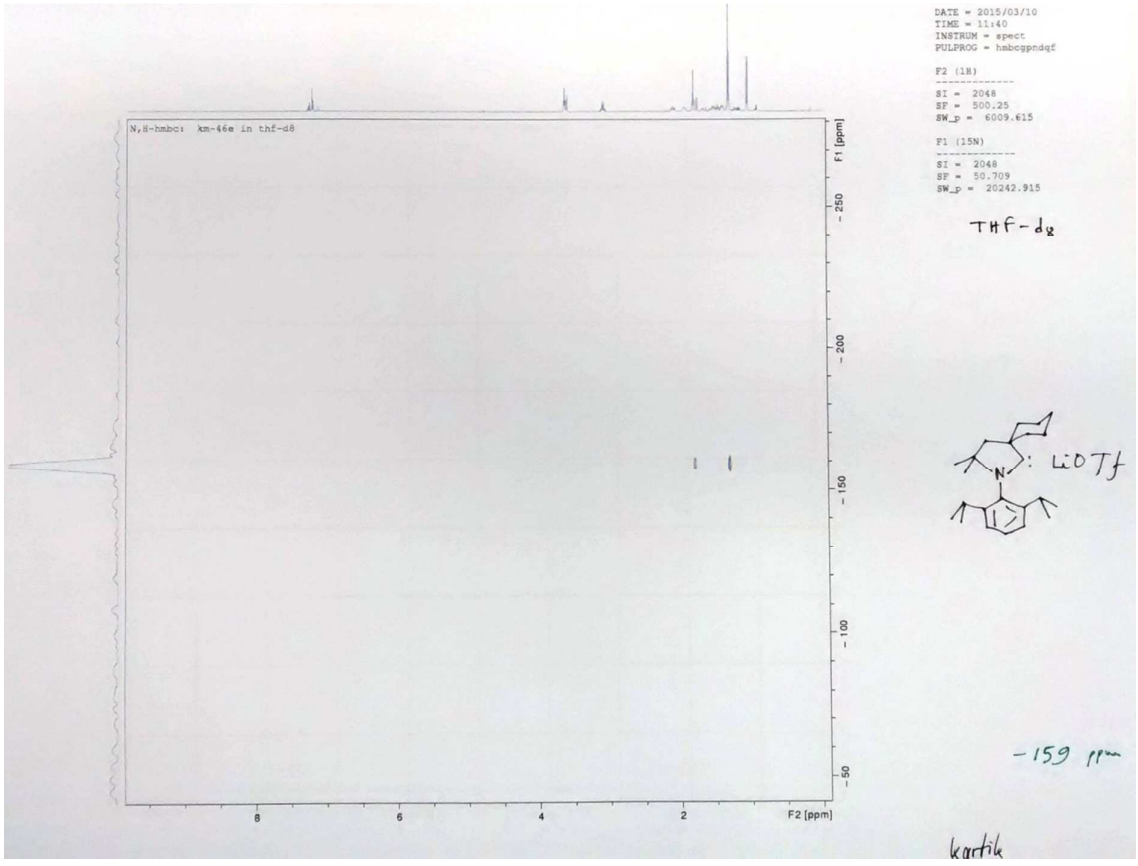


Figure S3. ^{15}N-HMBC NMR spectrum of (Cy-cAAC)LiOTf (**1**).

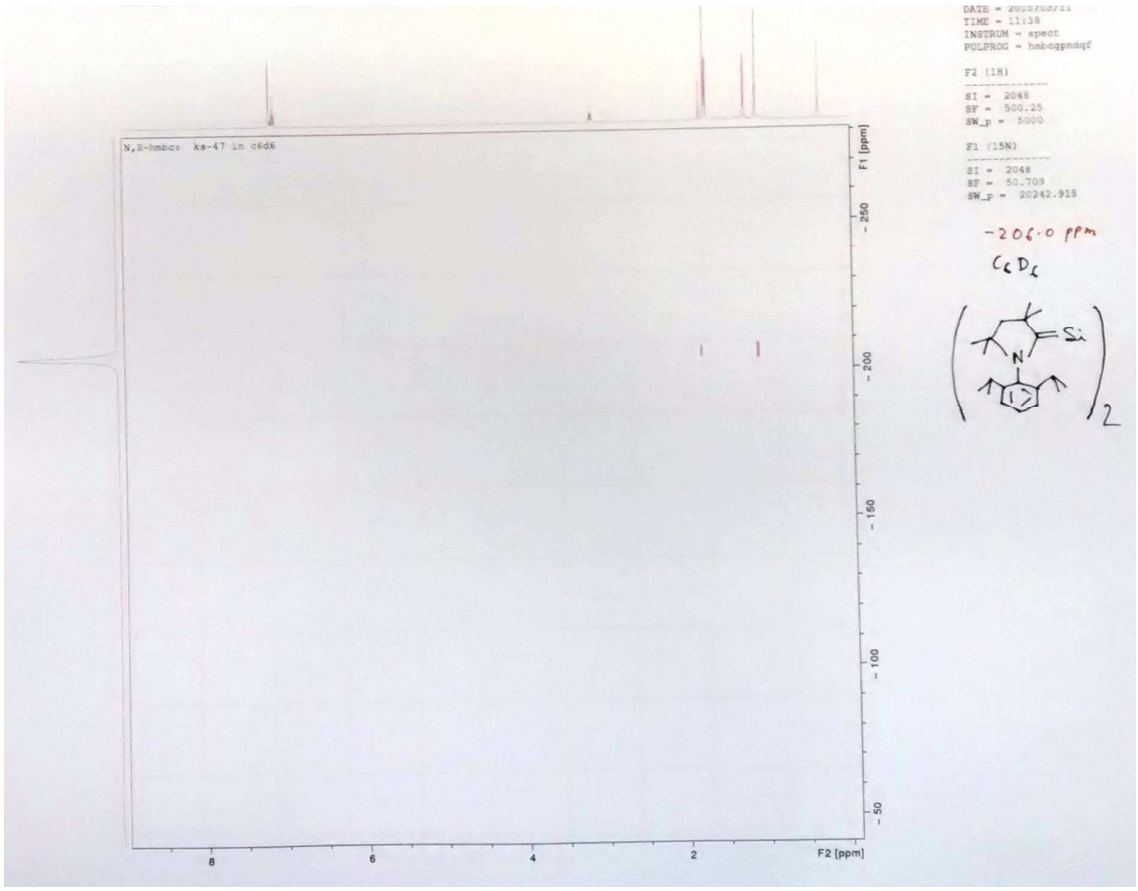


Figure S4. ^{15}N-HMBC NMR spectrum of $(Me_2\text{-cAAC})_2Si_2$ (**7**).

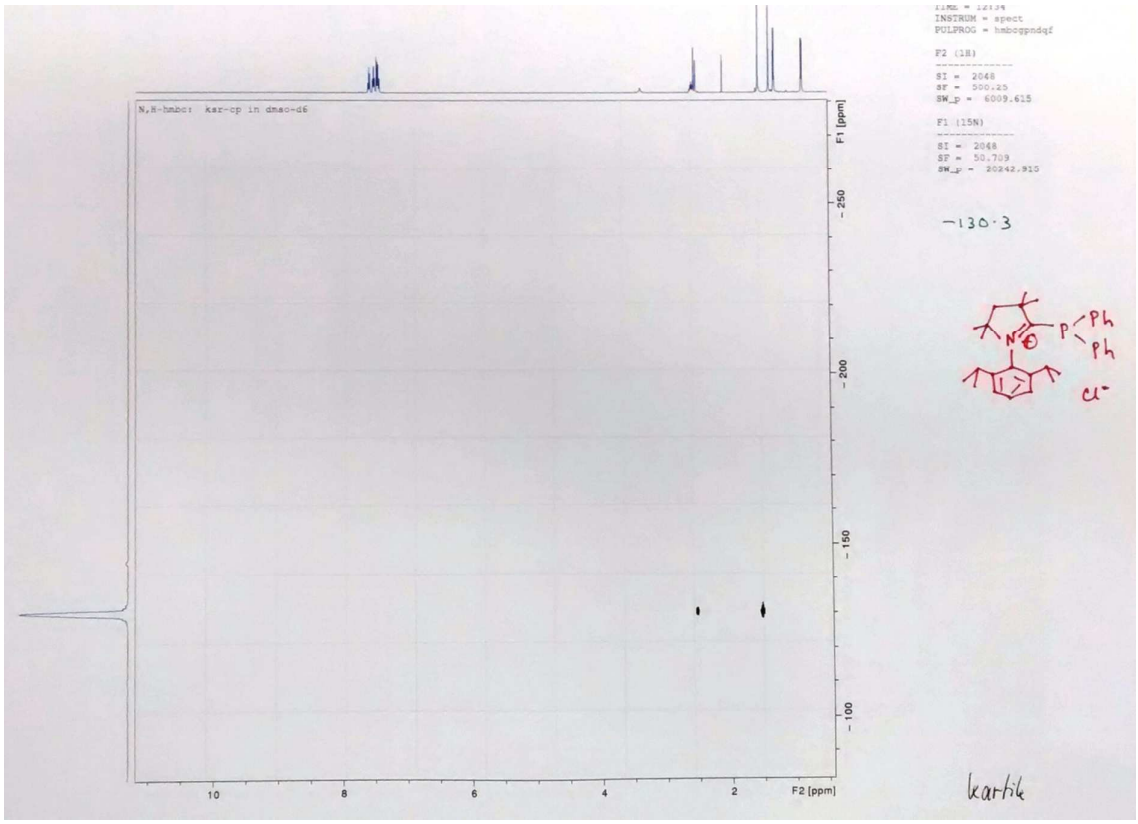
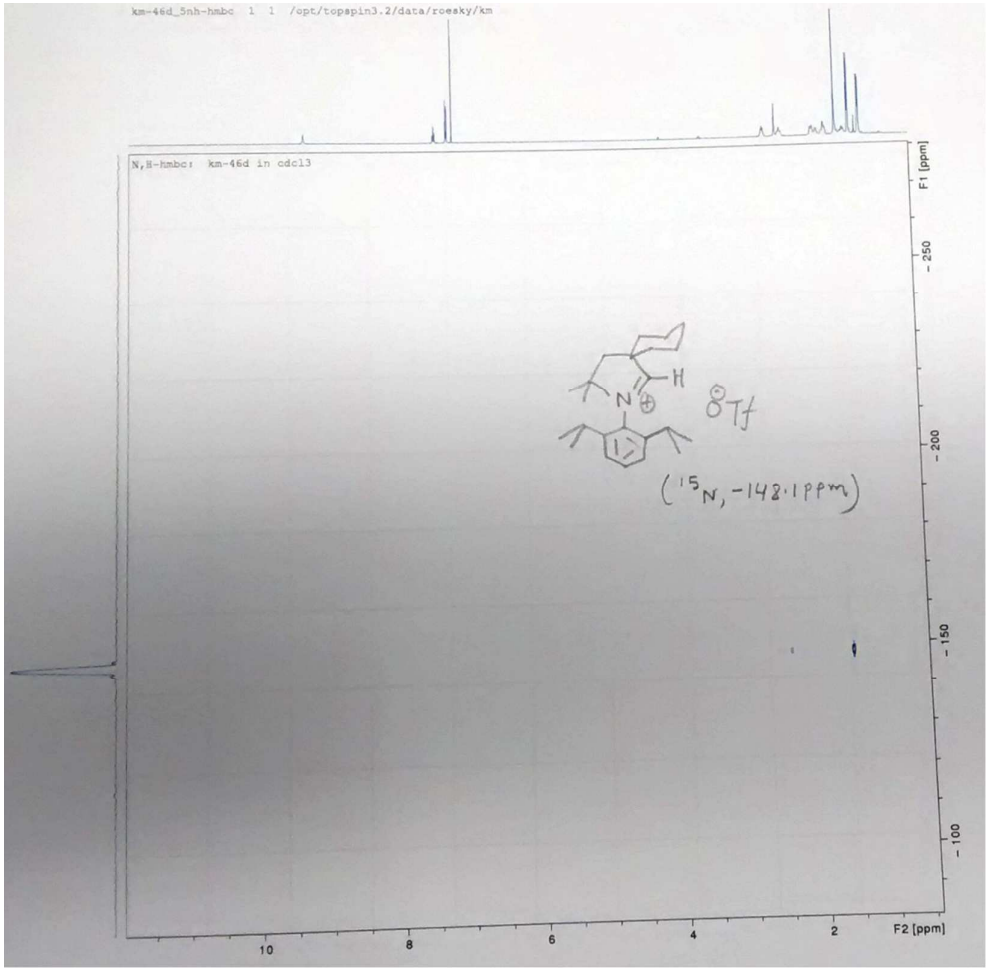
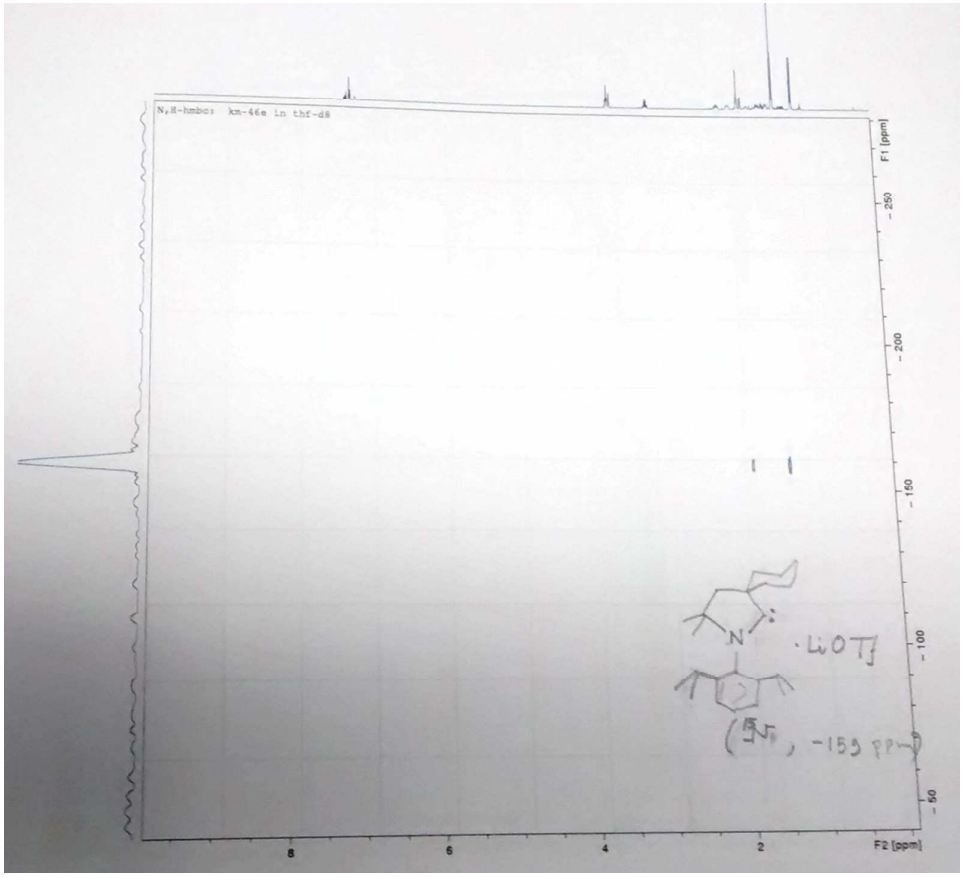
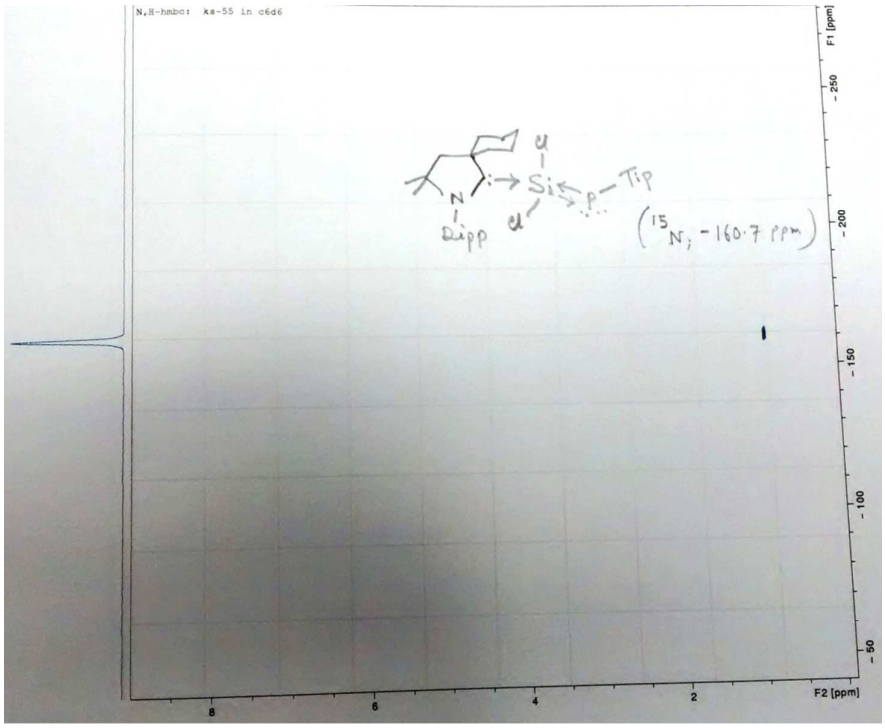
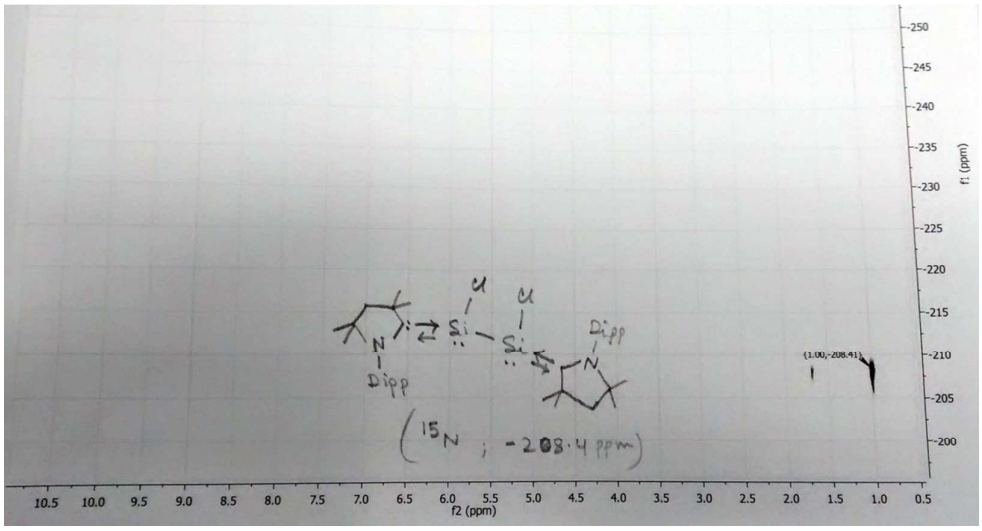


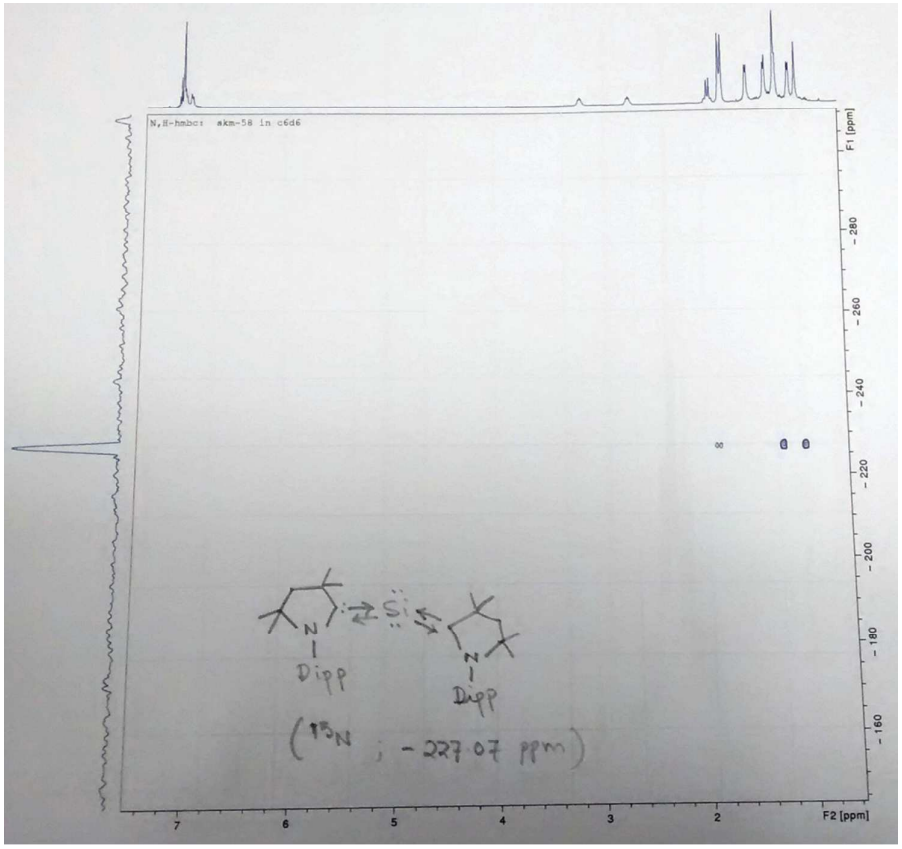
Figure S5. ^{15}N-HMBC NMR spectrum of $[(Me_2\text{-cAAC})PPh_2]^+Cl^-$ (**8**).

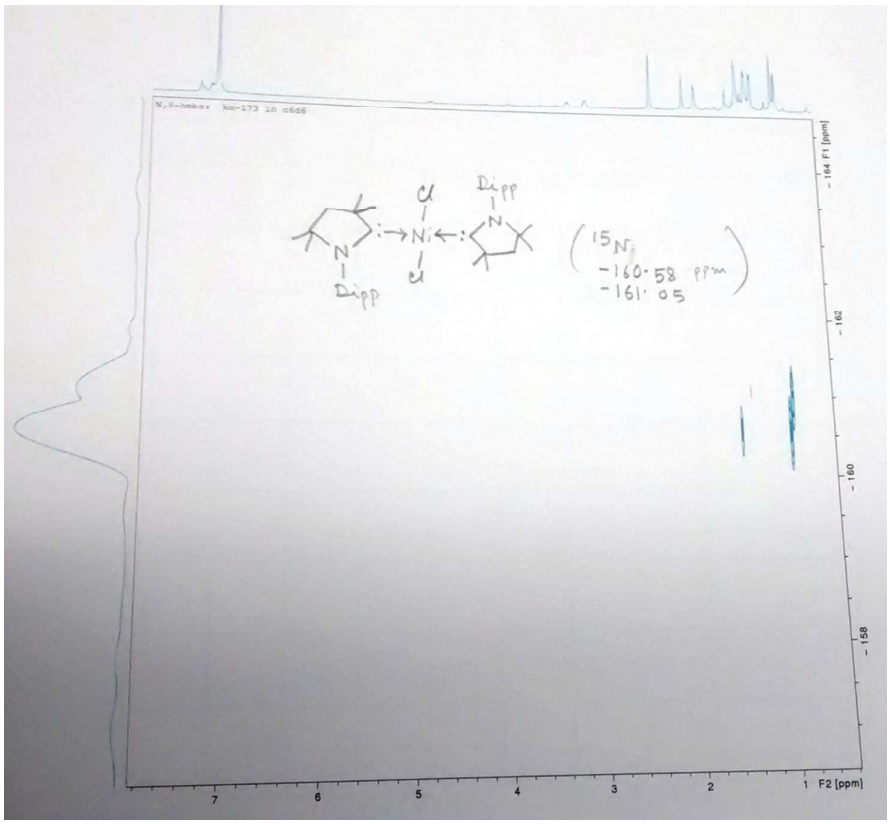

km-46d_5nh-hmbc 1 1 /opt/topspin3.2/data/roesky/km
N,H-hmbc: km-46d in cdcl3
F1 [ppm]
- 250
- 200
- 150
- 100
10
8
6
4
2
F2 [ppm]
H
N
⊕
OTf
(^{15}N, -148.1 ppm)

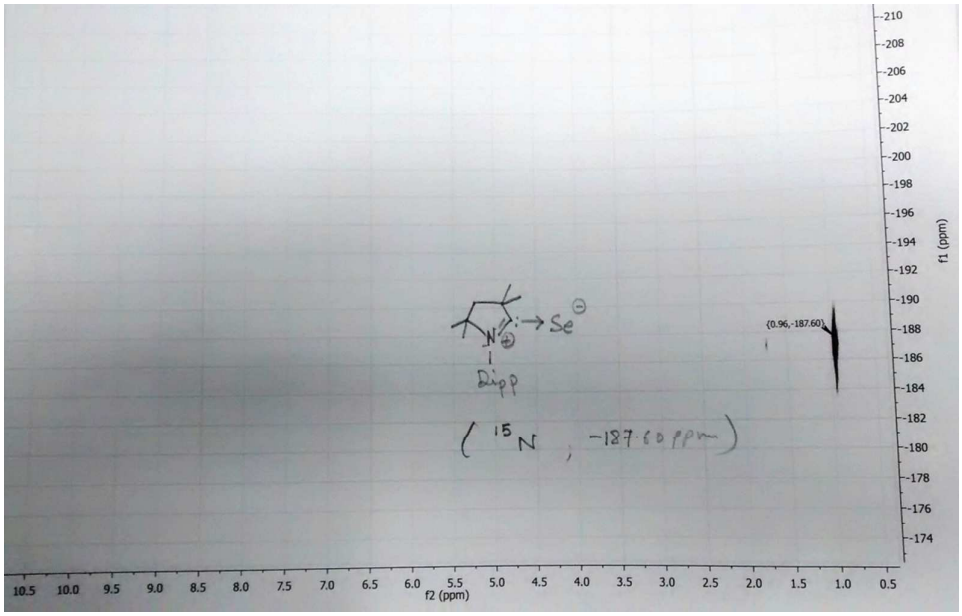

N,H-hmbc: km-46e in thf-d8
F1 [ppm]
250
200
150
100
50
8
6
4
2
F2 [ppm]
N
·LiOTf
(5F), -159 ppm


N,H-hmbc: ks-55 in c6d6
F1 [ppm]
F2 [ppm]
Dipp
Tip
(^{15}N; -160.7 ppm)

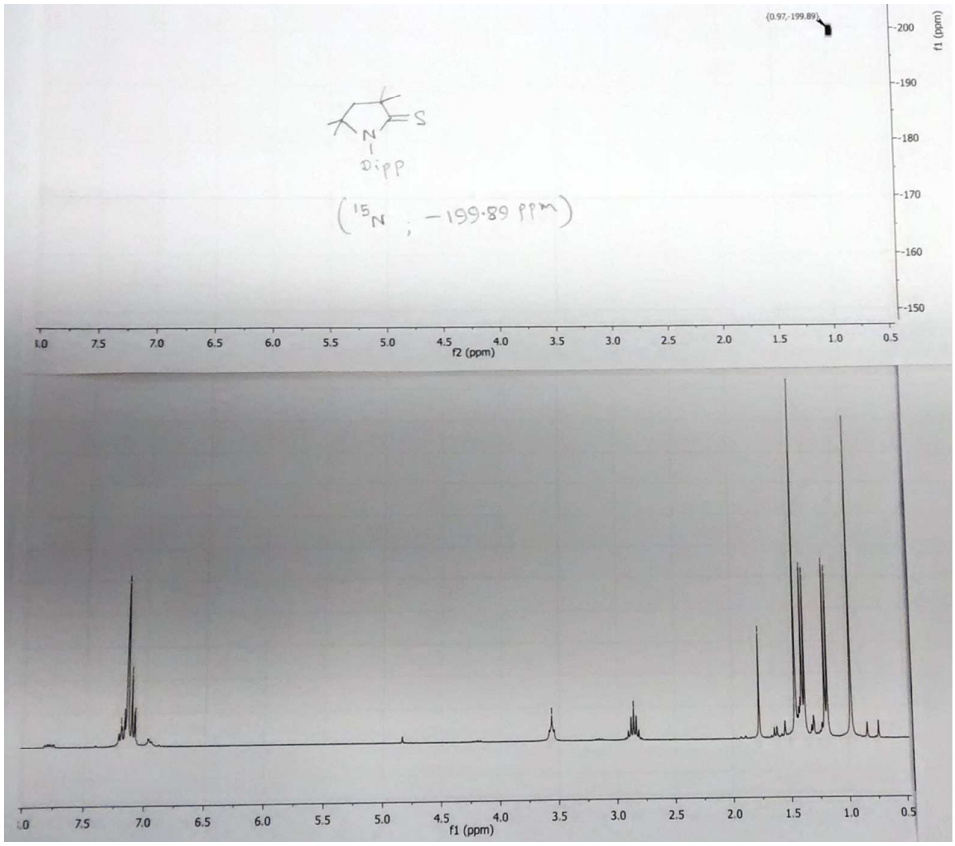

f1 (ppm)
f2 (ppm)
Dipp
Dipp
(^{15}N ; -208.4 ppm)


N,H-hmbc: akm-58 in c6d6
F1 [ppm]
F2 [ppm]
Dipp
Dipp
(^{15}N ; -227.07 ppm)

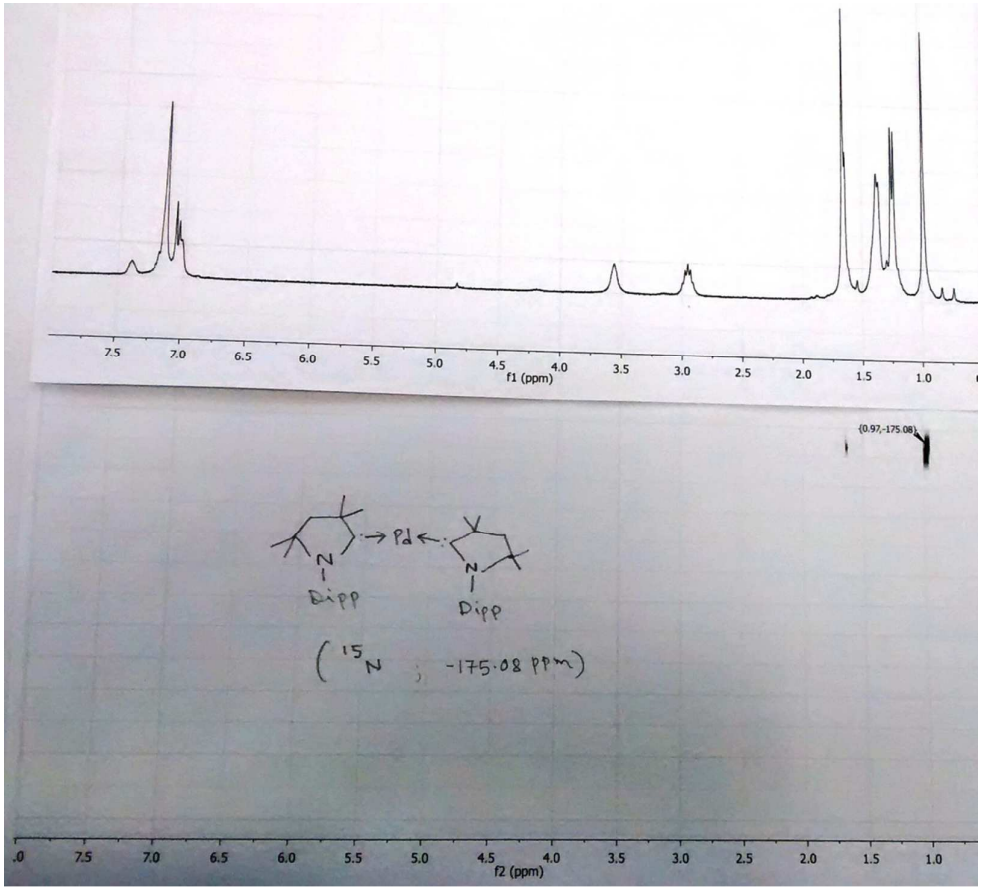

N,H-hmbc: km-173 in c6d6
F1 [ppm]
F2 [ppm]
Cl
Dipp
Dipp
Cl
(^{15}N
-160.58 ppm
-161.05)

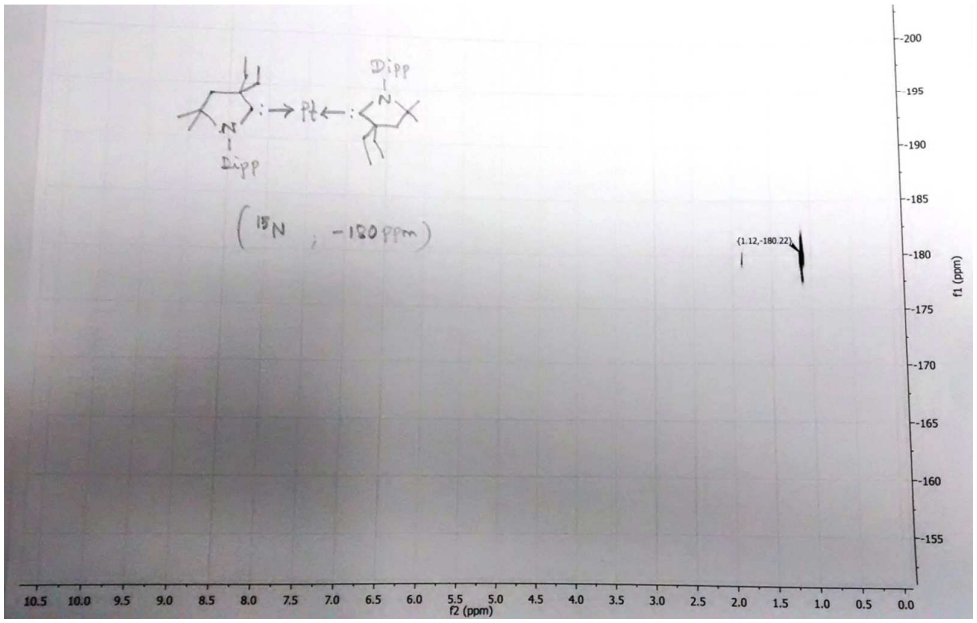


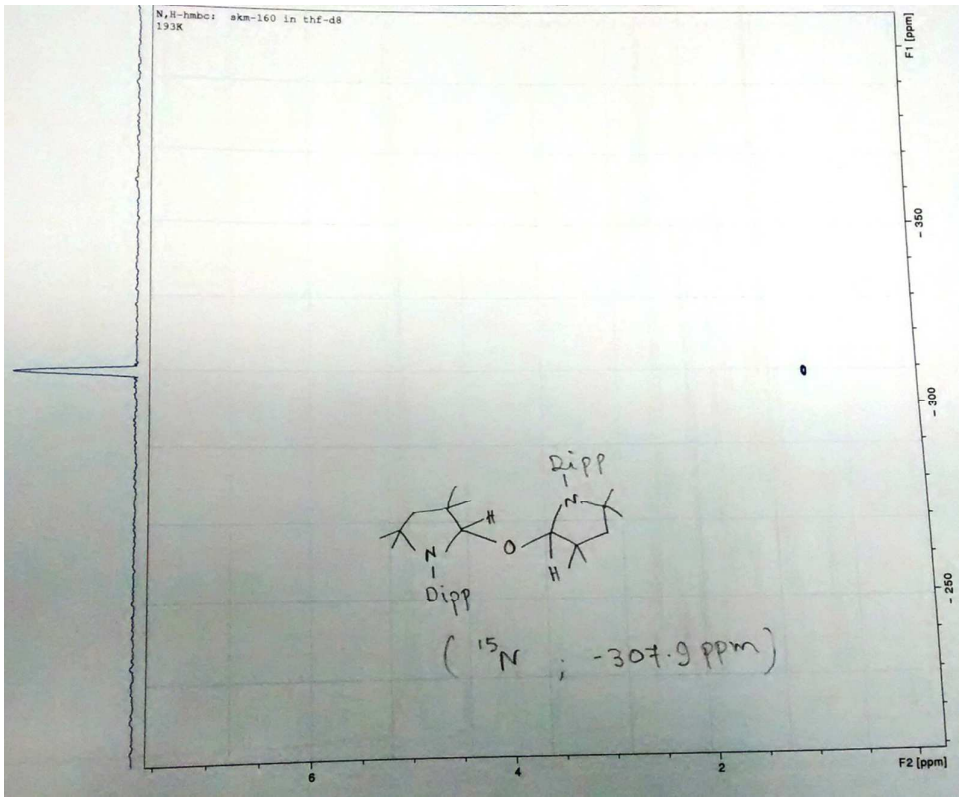
(^{15}N ; −187.60 ppm)

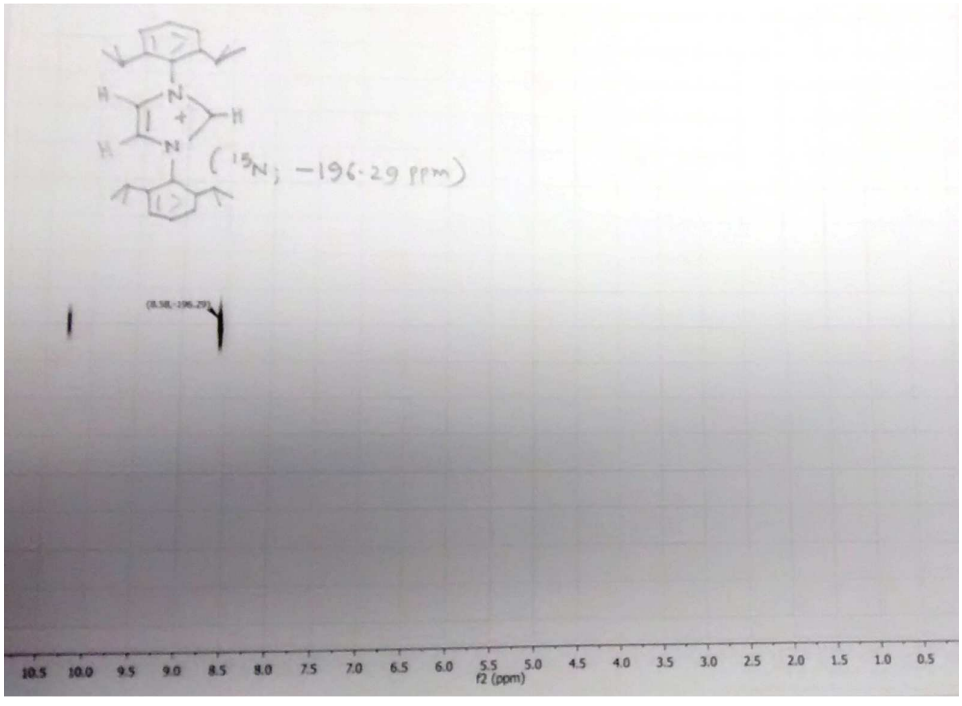


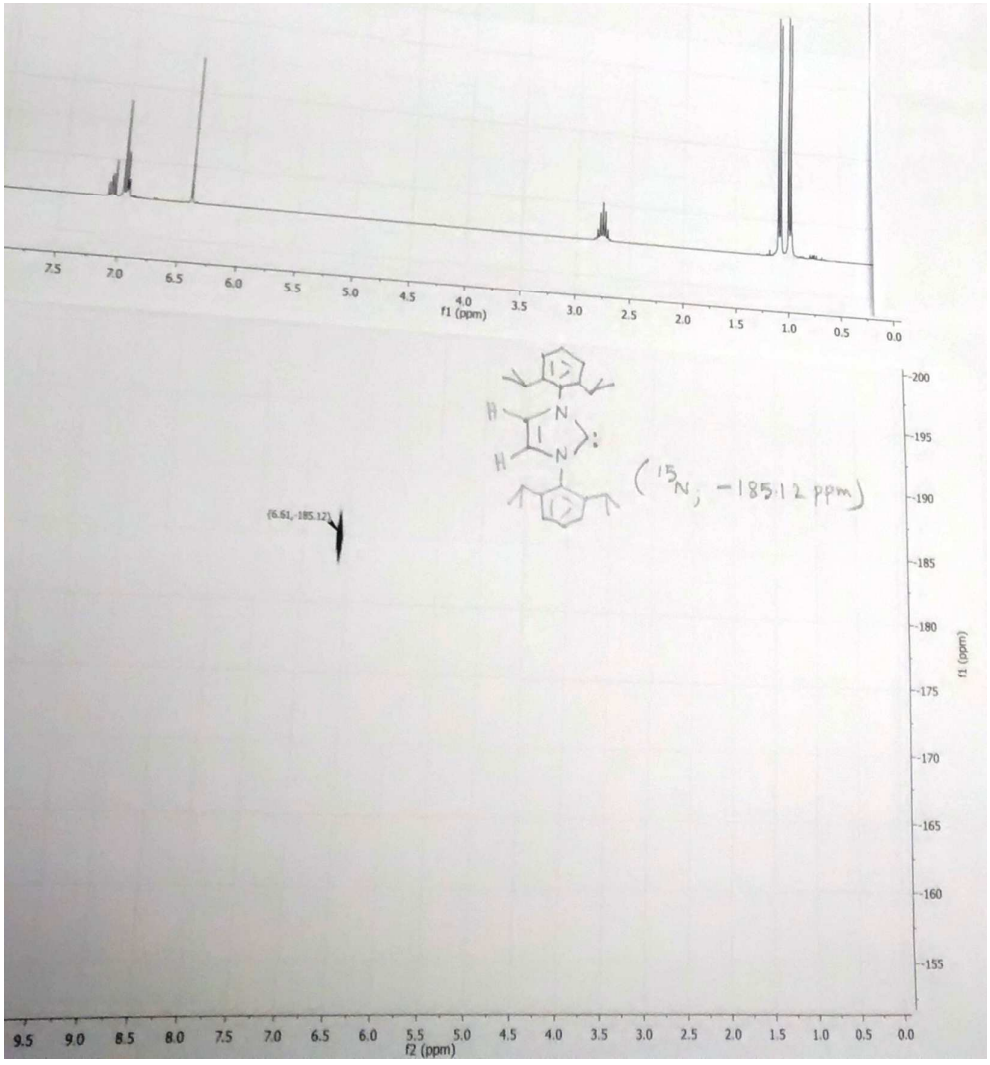
(^{15}N ; −199.89 ppm)

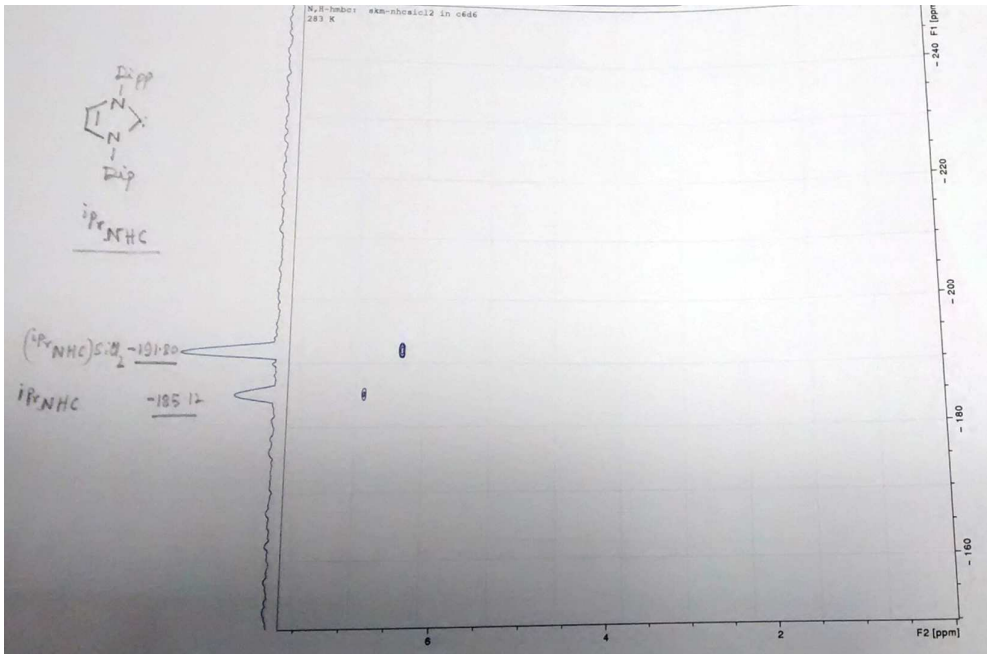

f1 (ppm)
(0.97,-175.08)
Dipp
Pd
Dipp
(^{15}N ; -175.08 ppm)
f2 (ppm)

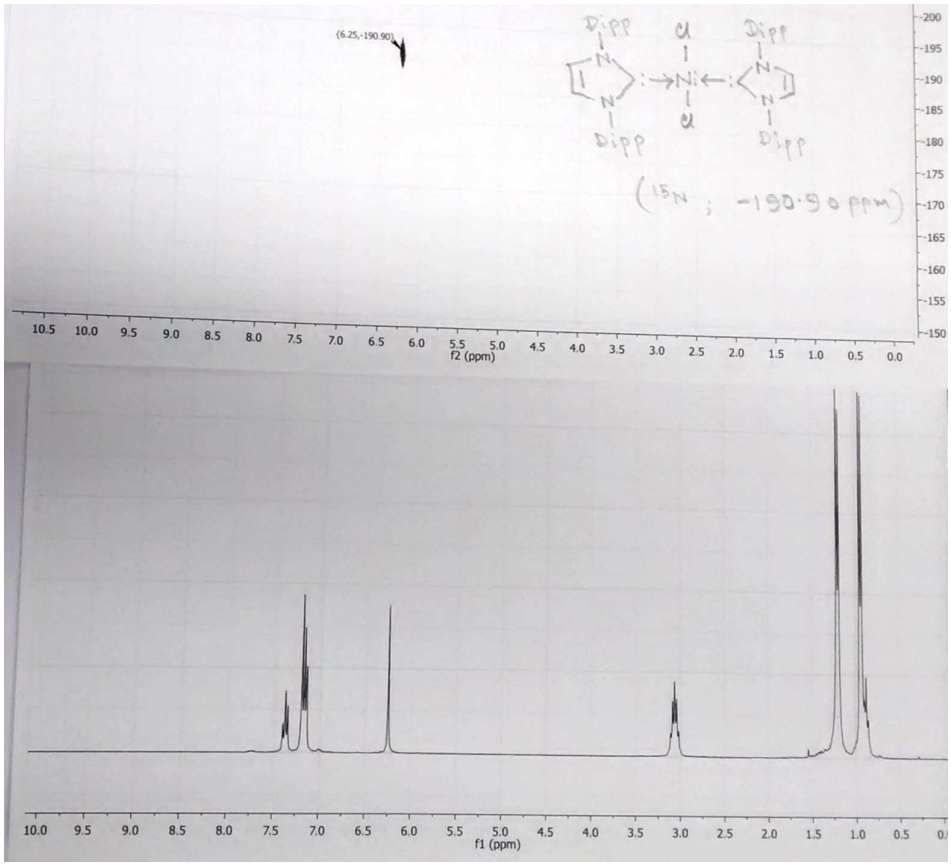

Dipp
Pt
Dipp
(^{15}N ; -180 ppm)
(1.12,-180.22)
f1 (ppm)
f2 (ppm)

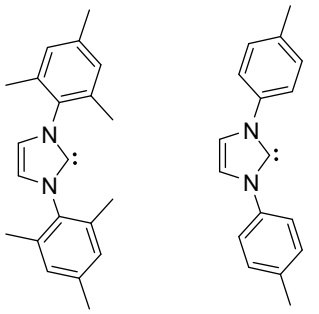

N,H-hmbc: akm-160 in thf-d8
193K
F1 [ppm]
- 350
- 300
- 250
F2 [ppm]
6
4
2
Dipp
Dipp
(^{15}N ; -307.9 ppm)


(^{15}N; -196.29 ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)


f1 (ppm)
f2 (ppm)
(6.61, -185.12)
(^{15}N; −185.12 ppm)


N,H-hmbc ekm-nhcsalc12 in c6d6
283 K
Dipp
iPr$_2$NHC
(^{iPr_2}NHC) ^{15}N −191.80
^{iPr_2}NHC −185.12
F2 [ppm]
F1 [ppm]

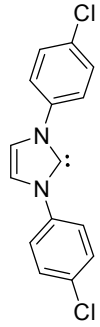




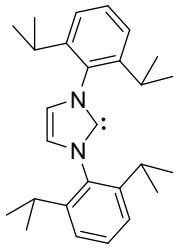
^{Mes}NHC

^{15}N (δ, -178.85 ppm)

^{15}N (δ, -171.0 ppm)

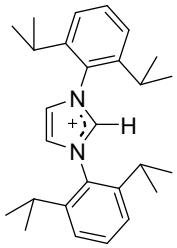


^{15}N (δ, -174.0 ppm)



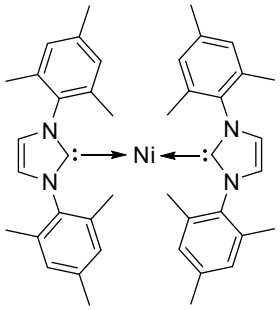
^{iPr}NHC

^{15}N (δ, -185.12 ppm)



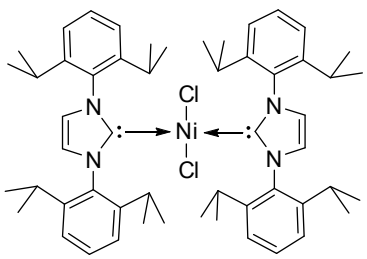
^{iPr}NHC.HCl

^{15}N (δ, -196.30 ppm)



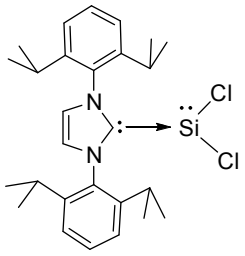
(^{Mes}NHC)$_2$Ni

^{15}N (δ, -193.92 ppm)



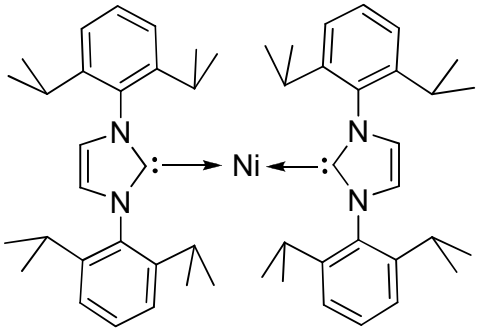
(^{iPr}NHC)$_2$NiCl$_2$

^{15}N (δ, -190.90 ppm)



(^{iPr}NHC)SiCl$_2$

^{15}N (δ, -191.80 ppm)



$(^{iPr}NHC)_2Ni$

^{15}N (δ, -197.58 ppm)

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