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Metal nitrene-like reactivity of a Si=N bond towards CO_2

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Contents:

1. Experimental methods and data

General considerations. All experiments and manipulations were carried out under dry oxygen free dinitrogen using standard Schlenk techniques or in an MBraun inert atmosphere glovebox containing an atmosphere of high purity dinitrogen. Hexane, diethylether, toluene and THF were dried by standard methods. Benzene-d_6 and THF-d_8 were stirred over a sonicated potassium mirror for a period of 48 hr and recondensed into a Schlenk tube containing activated 4 Å mol sieves. DCM-d_2 was stirred over CaH_2 for 24 hr and distilled into a Schlenk tube containing activated 4 Å mol sieves. NMR spectra were recorded on a Bruker AV 200, 400, or 500 Spectrometer. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual solvent signals as internal standards. ^{29}Si NMR spectra were externally calibrated with $SiMe_4$. ESI mass spectra were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer, and the raw data evaluated using the X-calibur computer program. Melting point samples were sealed in a glass capillary under dinitrogen. The starting materials NHC [:C{N(Pr^i)C(Me)}$_2$],[1] [{N(Dipp)(SiMe$_3$)}(NHC)ClSi:],[2] and [{N(Dipp)(SiMe$_3$)}ClSi:→Ni(NHC)$_2$] (**1**),[3] and [DippN=Si(OSiMe$_3$)Ni(Cl)(NHC)$_2$][4] were synthesized according to known literature procedures. All other reagents were used as received.

[DippN{(O)CO}$_2$SiNi(Cl)(NHC)$_2$], **3**. A solution of **1** (0.2 g, 0.27 mmol) in diethyl ether (15 mL) was cooled to -78 ^{o}C, and the atmosphere in the Schlenk flask exchanged for CO_2 (99.99 % purity). The reaction vessel was then sealed and rapidly stirred, whereupon an immediate color change from bright orange-yellow to pale yellow was observed. After stirring for 10 min at this temperature, the reaction mixture was warmed to ambient temperature, and the reaction stirred for a further 14 hrs. Subsequently, the reaction mixture was filtered and concentrated *in vacuo* to ~0.5 mL, and stored at 4 °C. After 5 days, a small crop of large pale yellow crystals of **3** had formed (60 mg, 37 %). M.p.: 142-149 ^{o}C (melt); ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = 0.07 (s, 9H, O-Si*Me$_3$*), 1.17 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, Dipp-Pr^i-C*H*$_3$), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, Dipp-Pr^i-C*H*$_3$), 1.62 (d, $^{3}J_{HH}$ = 7.2 Hz, 12H, NHC-Pr^i-C*H*$_3$), 1.67 (s, 12H, NHC-NC*Me*), 1.69 (d, $^{3}J_{HH}$ = 7.2 Hz, 12H, NHC-Pr^i-C*H*$_3$), 2.57 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, Dipp-Pr^i-C*H*), 3.24 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, Dipp-Pr^i-C*H*), 6.15 (sept, $^{3}J_{HH}$ = 7.2 Hz, 4H, NHC-Pr^i-C*H*), 7.14 (m, 2H, *m*-Ar-C*H*), 7.26 (m, 1H, *p*-Ar-C*H*); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ = 1.9 (O-Si*Me$_3$*), 10.2 (NHC-NC*Me*), 22.0 and 22.2 (NHC-Pr^i-*C*H$_3$), 24.6 and 24.7 (Dipp-Pr^i-*C*H$_3$), 29.0 (Dipp-Pr^i-*C*H), 54.1 (NHC-Pr^i-*C*H), 125.7 (NHC-N*C*Me), 124.0, 124.3, 129.0, 134.3, 145.7, and 146.0 (Ar-*C*), 147.4 (O=C(O)NDipp), 178.5 (NHC-*C*:); $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 80 MHz, 298 K): δ = 6.4 (O-*Si*Me$_3$), -47.1 (Ni-*Si*); IR, v/cm^{-1} (ATR, 298K): 1704, 1751 (symmetric and asymmetric O*C*=*O*); MS/ESI

m/z (%): 181.3 ([NHC+H]$^+$, 100); anal. calcd. for $C_{39}H_{66}ClN_5NiO_5Si_2$: C, 56.08 %; H, 7.96 %; N, 8.38 %; found: C, 55.92 %; H, 8.36%; N, 8.09 %.

N.B. Attempted controlled addition of a single equivalent of CO_2 to **1** led to mixtures of the mono CO_2 cycloaddition product, **2**, alongside both compounds **1** and **3**. Compound **2** could not be isolated in its pure form from this mixture. However, a single crystal of **3** could be picked in order to elucidate its solid state structure (see main text).

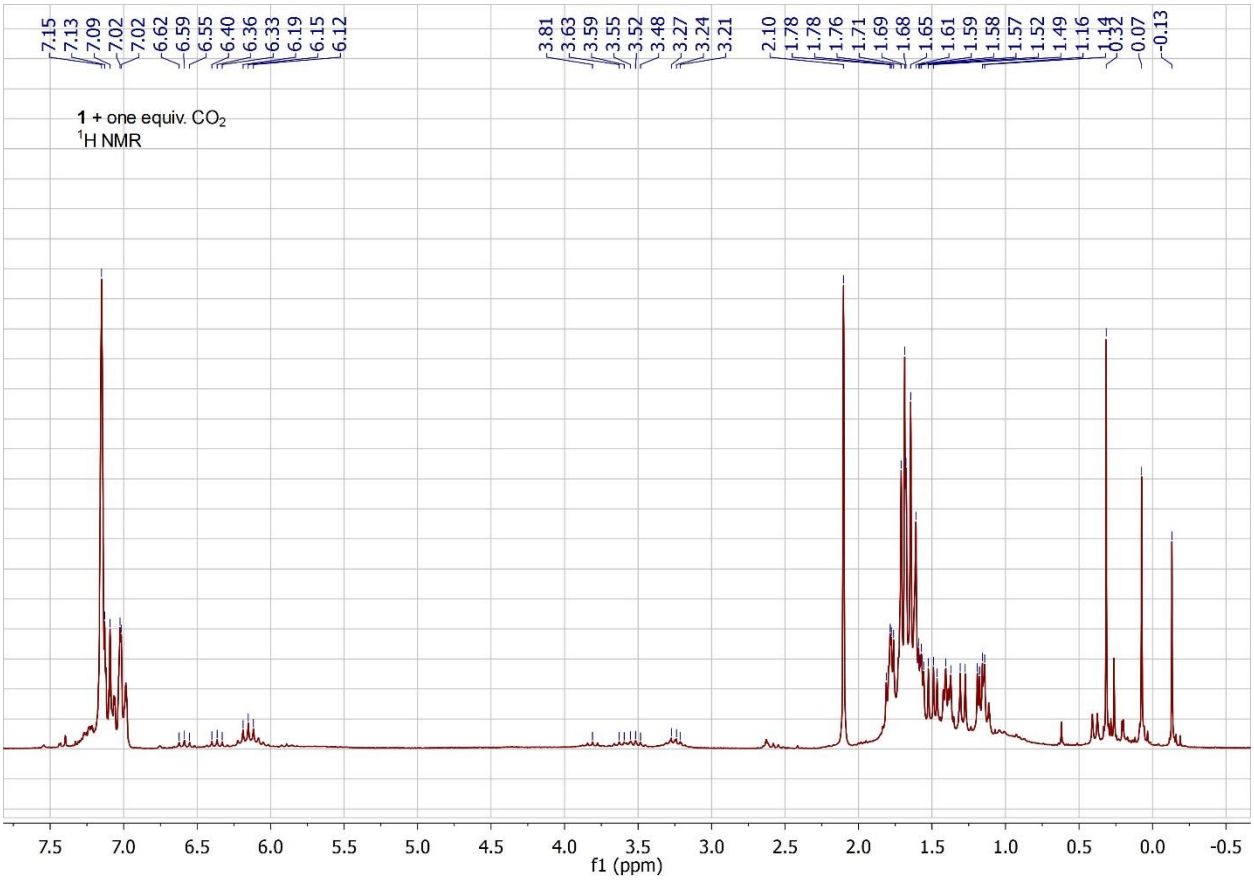

Figure S1. ^{1}H NMR spectrum of the reaction between **1** and one equiv. of CO_2, in C_6D_6 at 298 K.

[DippN{(CyN)CO}SiNi(Cl)(NHC)$_2$], **4**. A solution of **1** (0.2 g, 0.27 mmol) in diethyl ether (15 mL) was cooled to -78 ^{o}C, and CyNCO (35 µL, 0.27 mmol) was added. An immediate colour change from bright orange-yellow to near colourless was observed. The reaction mixture was warmed to ambient temperature, and the reaction stirred for a further 14 hrs. Subsequently, the reaction mixture was filtered and concentrated *in vacuo* to ~1 mL, and stored at 4 °C. After 2 weeks, a crop of large pale yellow crystals of **2** had formed (60 mg, 37 %). M.p.: 132-137 ^{o}C (dec.); ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ = 0.44 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Dipp-Pr^i-C*H*$_3$), 0.45 (s, 9H, O-Si*Me*$_3$), 1.02-1.20 (m, 4H, Cy-C*H*$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Dipp-Pr^i-C*H*$_3$), 1.42 (m, 2H, Cy-

C*H*$_2$), 1.57 (m, 2H, Cy-C*H*$_2$), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Dipp-Pr^i-C*H*$_3$),1.53 (s, 6H, NHC-NC*Me*), 1.63 (br, 6H, NHC-Pr^i-C*H*$_3$), 1.68 (d, $^3J_{HH}$ = 7.2 Hz, 6H, NHC-Pr^i-C*H*$_3$), 1.71 (NHC-NC*Me*), 1.74 (d, $^3J_{HH}$ = 7.2 Hz, 6H, NHC-Pr^i-C*H*$_3$), 1.76 (d, $^3J_{HH}$ = 7.2 Hz, 6H, NHC-Pr^i-C*H*$_3$), 1.82 (d, $^3J_{HH}$ = 6.8 Hz, 3H, Dipp-Pr^i-C*H*$_3$), 1.97 (m, 2H, Cy-C*H*$_2$), 3.61 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, Dipp-Pr^i-C*H*), 3.78 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, Dipp-Pr^i-C*H*), 3.79 (m, 1H, Cy-C*H*), 5.72 (v br, 2H, NHC-Pr^i-C*H*), 6.25 (br, 2H, NHC-Pr^i-C*H*), 6.98 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, *m*-Ar-C*H*), 7.10 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-Ar-C*H*), 7.24 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, *m*-Ar-C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ = 3.6 (O-Si*Me*$_3$), 10.5 and 10.6 (Dipp-Pr^i-*C*H$_3$), 22.1, 22.5, and 22.6 (NHC-Pr^i-*C*H$_3$), 24.7, 24.9, 25.7, and 25.9 (NHC-NC*Me*), 25.4, 26.5, and 26.7 (Cy-*C*H$_2$), 27.5 and 28.9 (Dipp-Pr^i-*C*H), 36.2 and 36.4 (Cy-C(H)*C*H$_2$), 53.3 (Cy-*C*H), 53.9 and 54.3 (NHC-Pr^i-*C*H), 123.9, 125.5, 125.6, and 126.4 (NHC-N*C*Me), 125.9, 128.4, 136.4, 145.4, 146.7, and 151.8 (Ar-*C*), 176.9 (v br, Cy-*C*NO), and 177.9 (v br, NHC-*C*:); $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz, 298 K): δ = 6.5 (O-*Si*Me$_3$), -8.4 (Ni-*Si*); IR, ν/cm^{-1} (ATR): 1663 (Cy*N*=*C*); MS/ESI m/z (%): 871.5 ([M+H]$^+$, 7); anal. calcd. for $C_{44}H_{77}ClN_6NiO_2Si_2$: C, 60.57 %; H, 8.90 %; N, 9.63 %; found: C, 60.35 %; H, 8.53%; N, 10.01 %.

[(NHC)$_2$Ni(CO)$_2$], **5**. A solution of **1** (0.2 g, 0.27 mmol) in toluene (10 mL) was cooled to -78 ^{o}C, and the atmosphere in the Schlenk flask exchanged for CO (99.999 % purity). The reaction vessel was then sealed and rapidly stirred, whereupon an immediate colour change from bright orange-yellow to pale yellow was observed. The reaction mixture was warmed to ambient temperature, and the reaction stirred for a further 14 hrs. Subsequently, all volatiles were removed from the reaction mixture *in vacuo*, the residue extracted in hexane (20 mL), and concentrated to ~5 mL. Storage at ambient temperature for 5 days led to the formation of a large crop of pale yellow crystals of **5** (70 mg, 55 %). M.p.: 110-117 ^{o}C (dec.); ^1H NMR (C_6D_6, 200 MHz, 298 K): δ = 1.19 (d, $^3J_{HH}$ = 7.3 Hz, 24H, NHC-Pr^i-C*H*$_3$), 1.81 (s, 12H, NHC-NC*Me*), 6.05 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, NHC-Pr^i-C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 298 K): δ = 10.5 (NHC-NC*Me*), 21.5 (NHC-Pr^i-*C*H$_3$), 52.7 (NHC-Pr^i-*C*H), 124.1 (NHC-N*C*Me), 198.8 (NHC-*C*:), 204.7 (Ni-*C*O); IR, ν/cm^{-1} (ATR): 1933 and 1856 (symmetric and asymmetric Ni*C*=*O*); MS/ESI m/z (%): 181.3 ([NHC+H]$^+$, 100); anal. calcd. for $C_{24}H_{40}N_4NiO_2$: C, 60.65 %; H, 8.48 %; N, 11.79 %; found: C, 60.23 %; H, 8.57 %; N, 11.39 %.

[(NHC)$_2$Ni(η^2-OCPh$_2$), **6**. A solution of **1** (0.2 g, 0.27 mmol) in toluene (10 mL) was cooled to -78 ^{o}C, and a solution of Ph$_2$CO (49 mg, 0.27 mmol) in toluene (5 mL) was added. The reaction mixture was warmed to ambient temperature, and stirred for 4 days, whereupon the reaction

colour had changed from bright yellow-orange to red-orange. Subsequently, all volatiles were removed from the reaction mixture *in vacuo*, the residue extracted in hexane (20 mL), and concentrated to ~3 mL. Storage at ambient temperature for 3 days led to the formation of a crop of orange-red crystals of **6** (50 mg, 31 %). M.p.: 121-125 °C (dec.); ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.95 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H, NHC-Pr^{i}-C*H*$_3$), 1.32 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H, NHC-Pr^{i}-C*H*$_3$), 1.62 (s, 6H, NHC-NC*Me*), 1.79 (s, 6H, NHC-NC*Me*), 6.07 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H, NHC-Pr^{i}-C*H*), 6.26 (sept, $^{3}J_{HH}$ = 7.3 Hz, 2H, NHC-Pr^{i}-C*H*), 7.10 (m, 2, *p*-Ar-C*H*), 7.25 (m, 4H, Ar-C*H*), 8.16 (m, 4H, Ar-C*H*); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ = 10.1 and 10.2 (NHC-NC*Me*), 21.6 and 22.2 (NHC-Pr^{i}-*C*H$_3$), 52.8 and 52.9 (NHC-Pr^{i}-*C*H), 79.7 ((Ph$_2$)*C*O), 123.8 and 124.4 (NHC-N*C*Me), 122.0, 127.0, 128.4, and 152.4 (Ph-*C*), 195.3 and 196.0 (NHC-*C*:); MS/ESI m/z (%): 181.3 ([NHC+H]$^{+}$, 100); anal. calcd. for $C_{35}H_{50}N_4NiO$: C, 60.89 %; H, 8.38 %; N, 9.31 %; found: C, 69.30 %; H, 8.79%; N, 9.33 %.

NMR and IR Spectra:

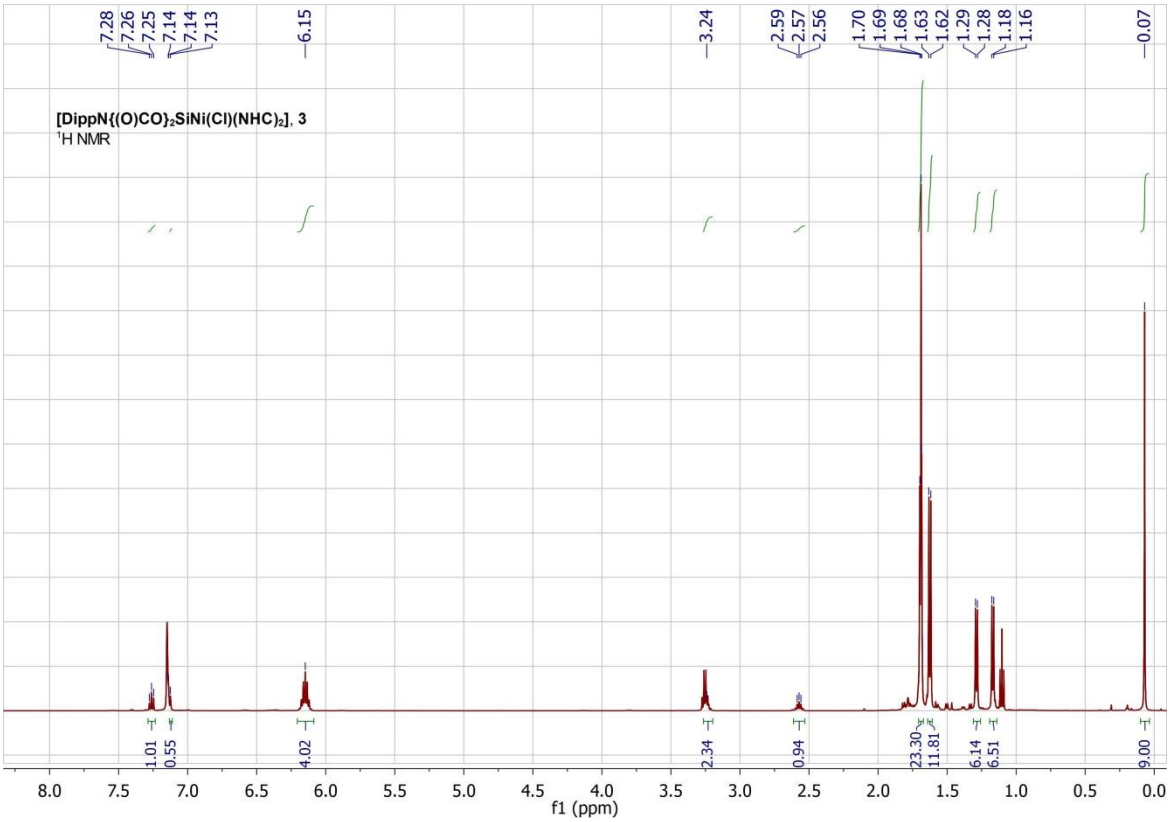

Figure S2. ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K.

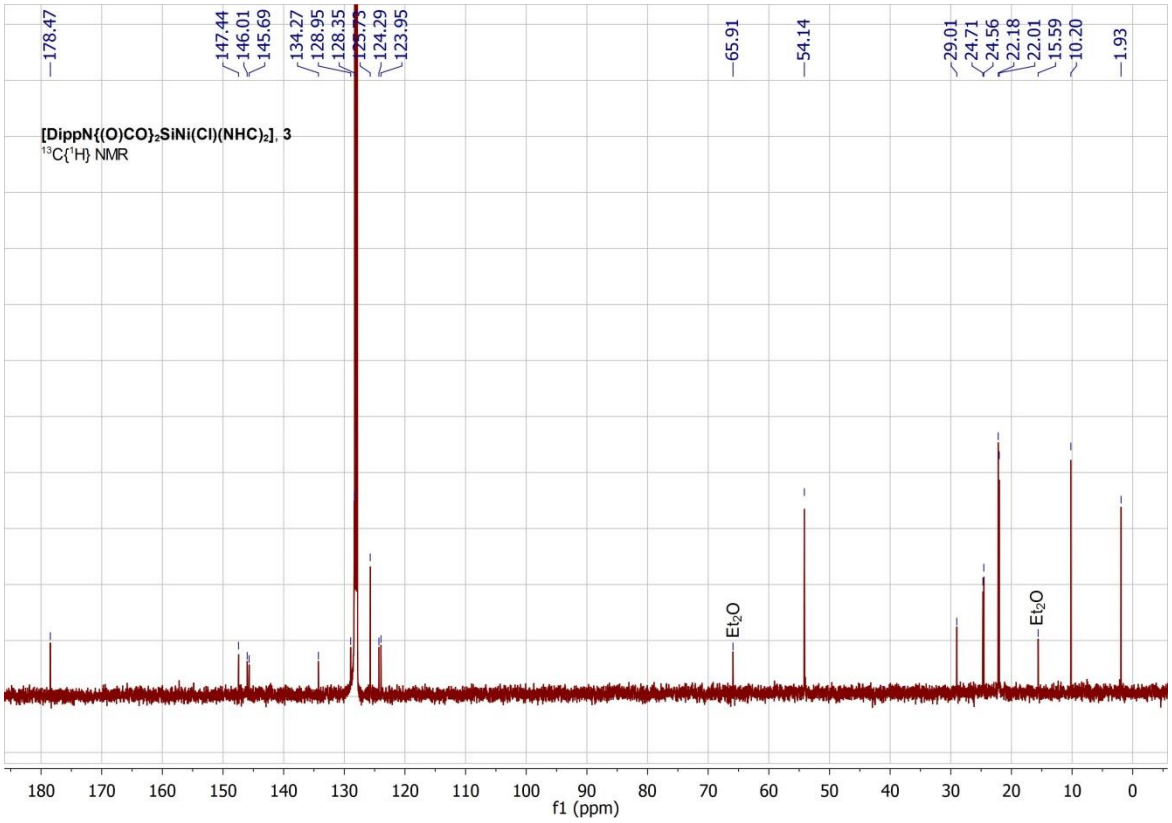

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 298 K.

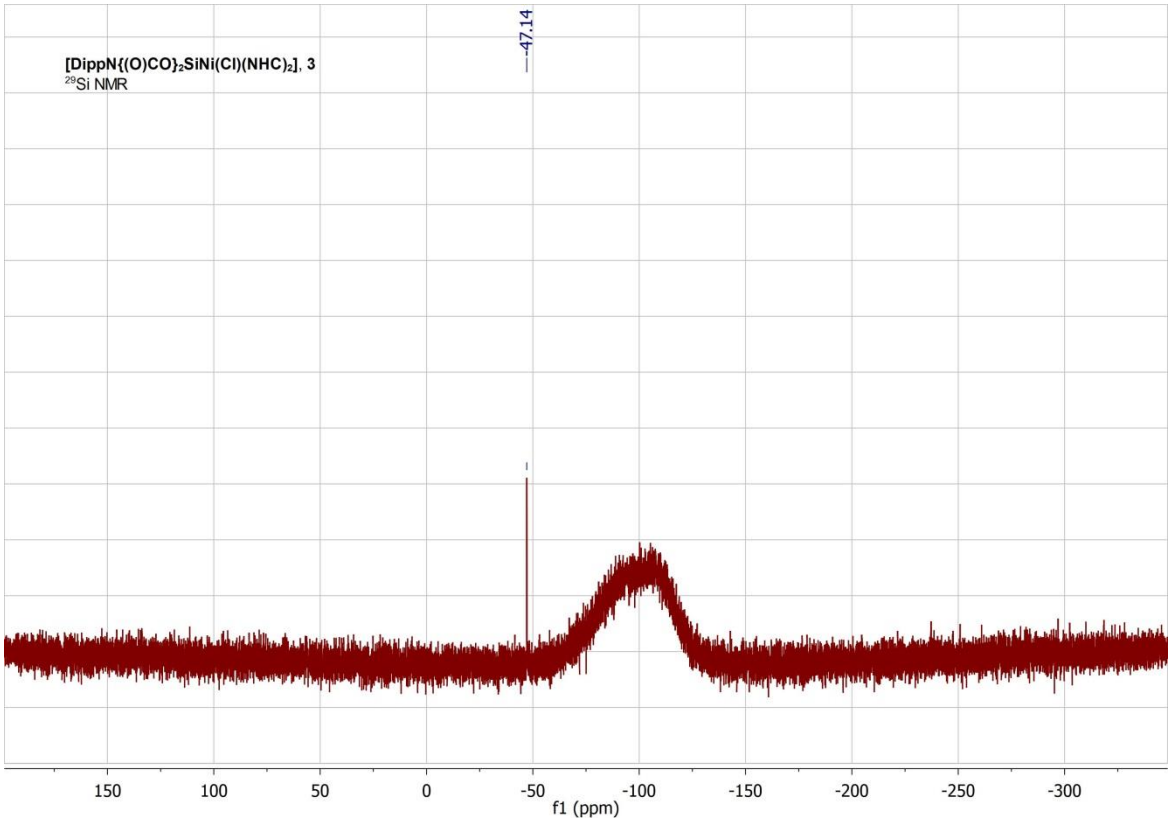

Figure S4. ^{29}Si NMR spectrum of **3** in C_6D_6 at 298 K.

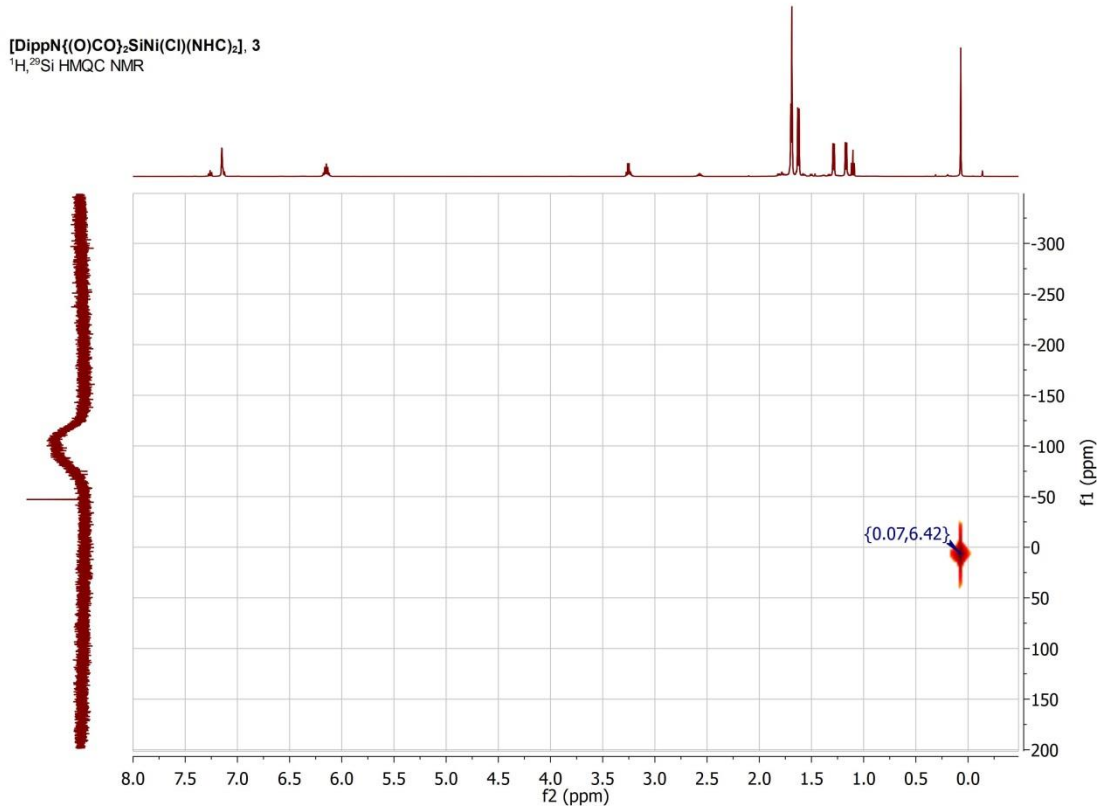

Figure S5. $^{1}H,^{29}Si$ HMQC NMR spectrum of **3** in C_6D_6 at 298 K.

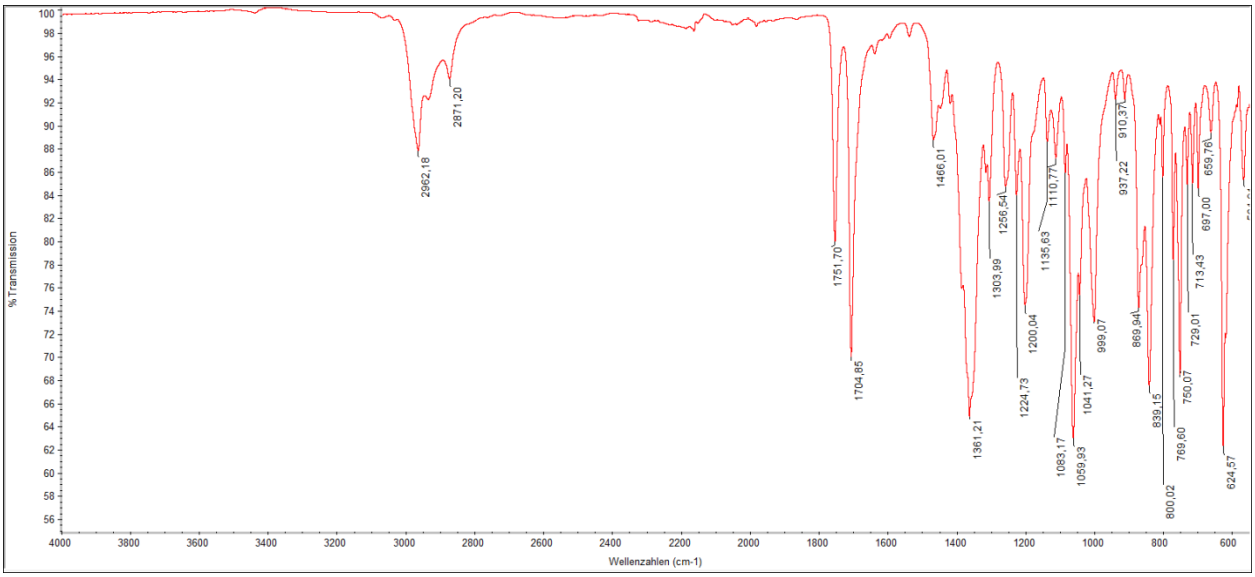

Figure S6. ATR IR spectrum of **3**.

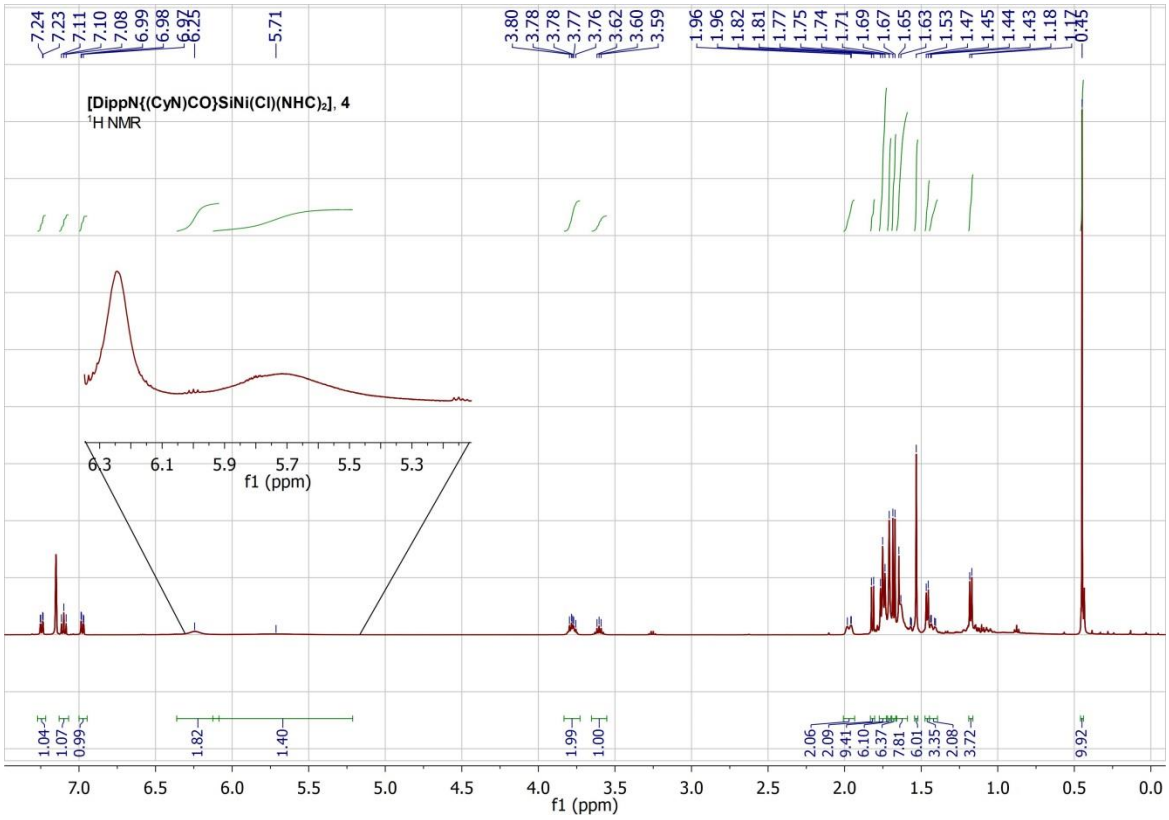

Figure S7. ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K.

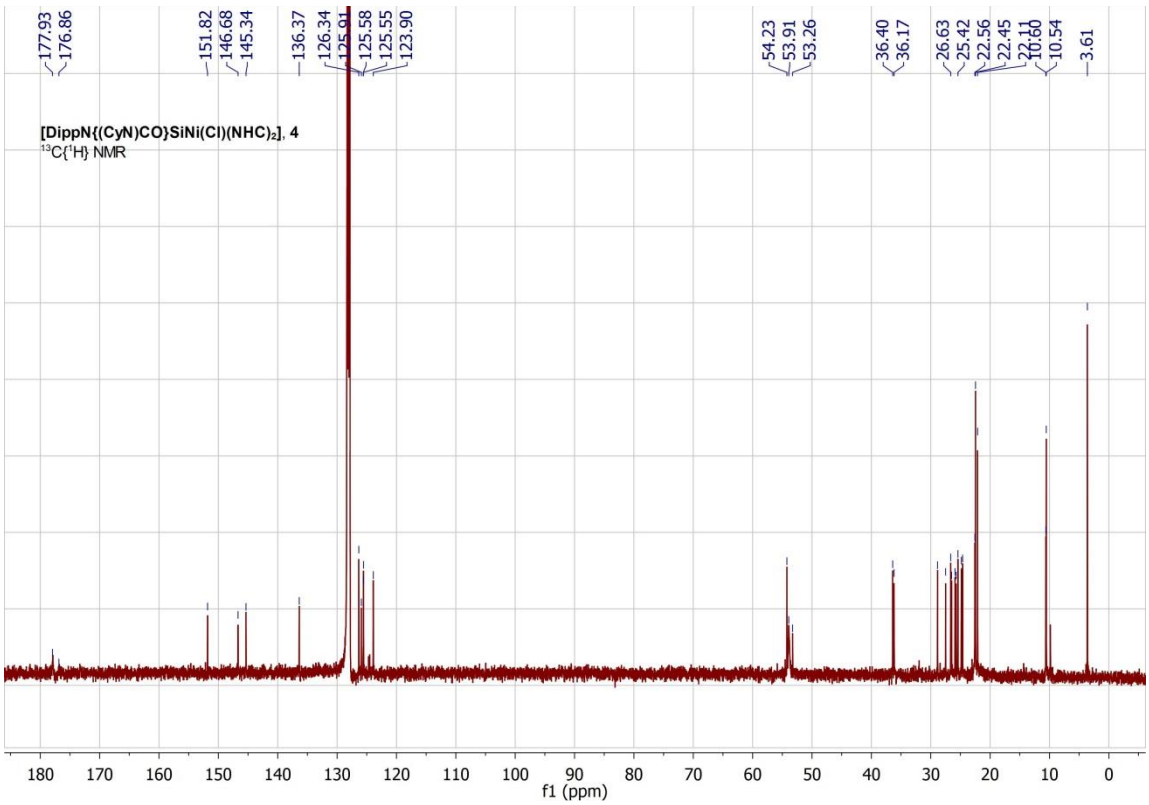

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 298 K.

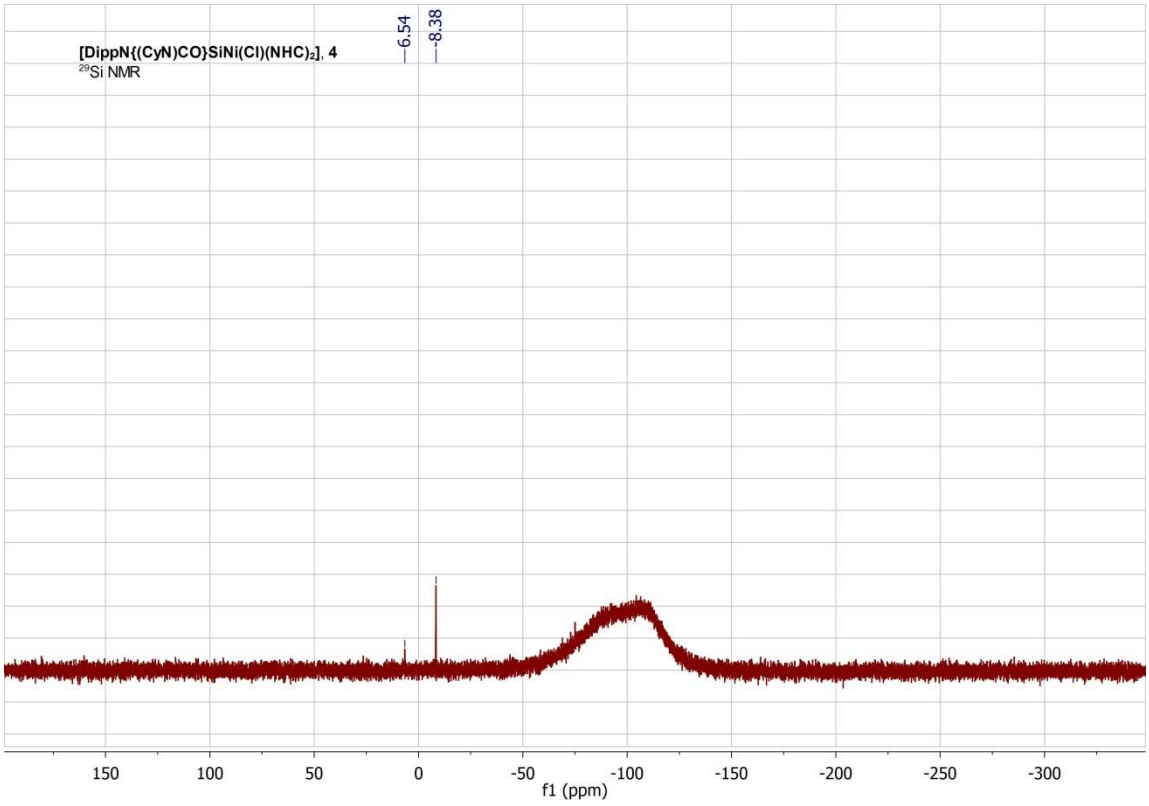

Figure S9. ^{29}Si NMR spectrum of **4** in C_6D_6 at 298 K.

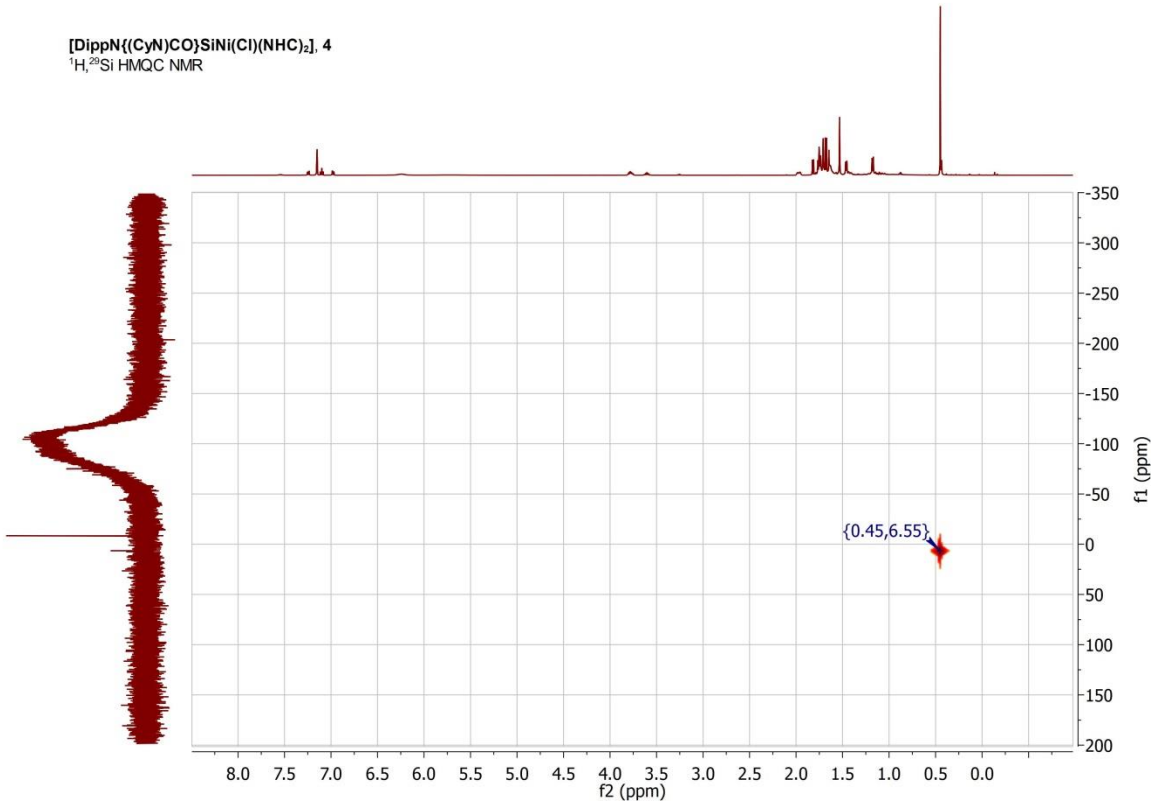

Figure S10. ^{1}H,^{29}Si HMQC NMR spectrum of **4** in C_6D_6 at 298 K.

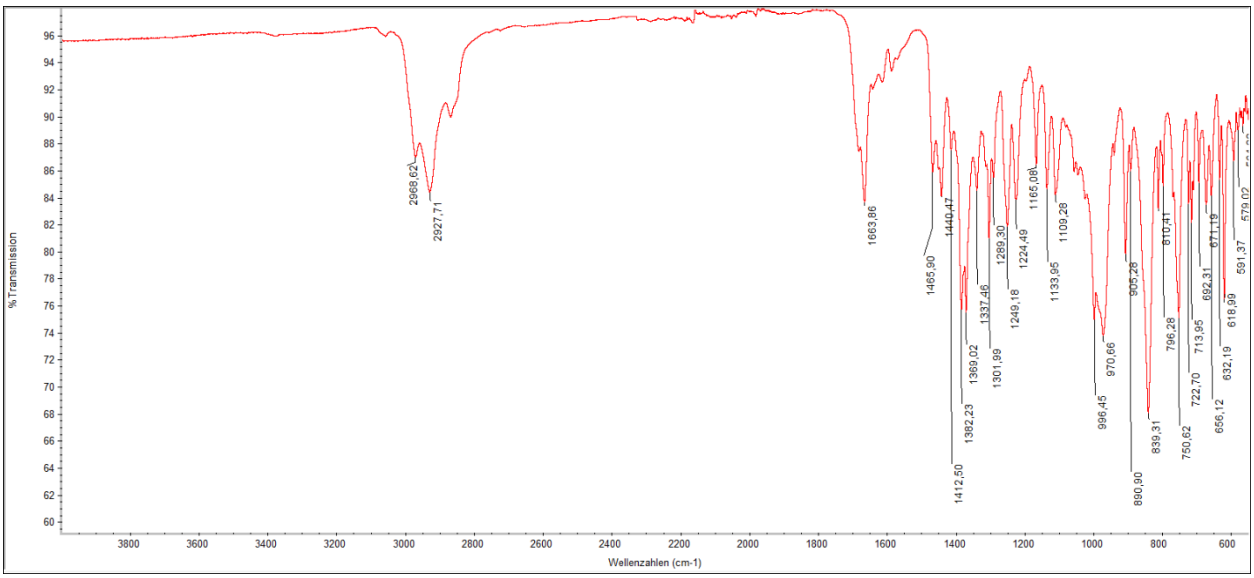

Figure S11. ATR IR spectrum of **4**.

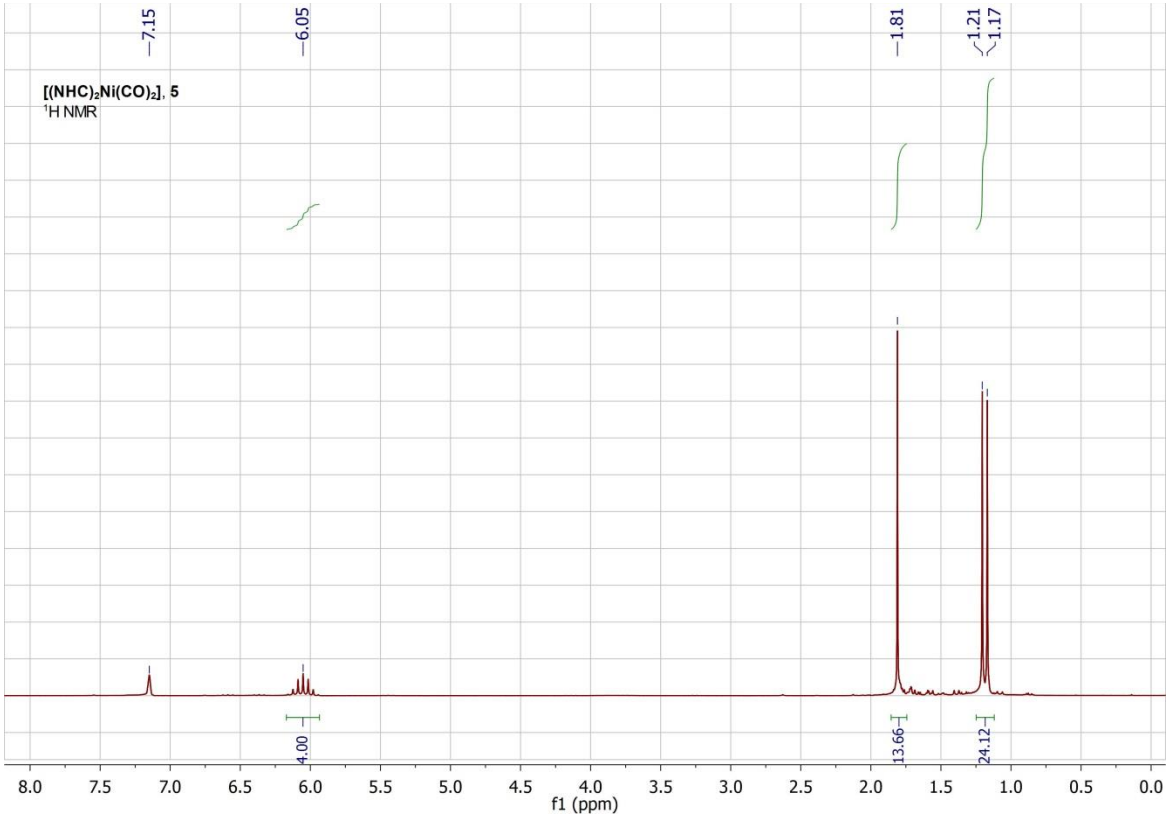

Figure S12. ^{1}H NMR spectrum of **5** in C_6D_6 at 298 K.

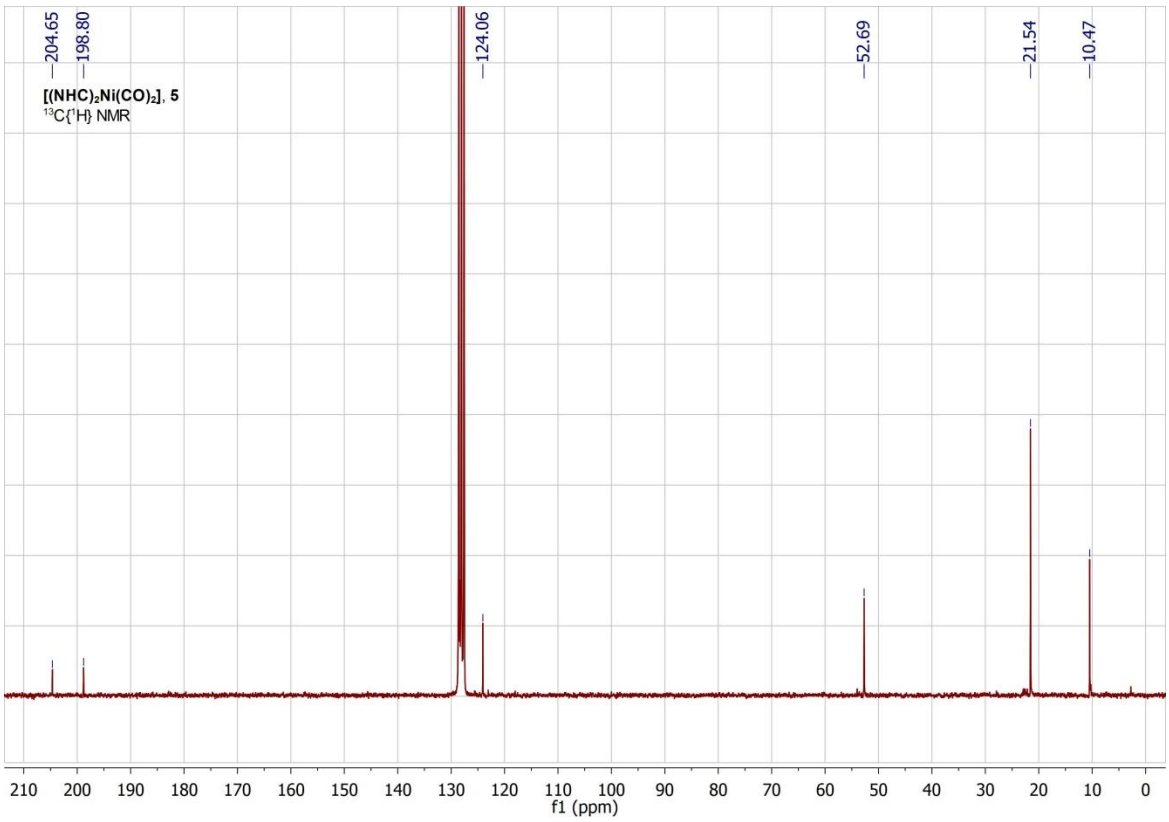

Figure S13. ^{13}C NMR spectrum of **5** in C_6D_6 at 298 K.

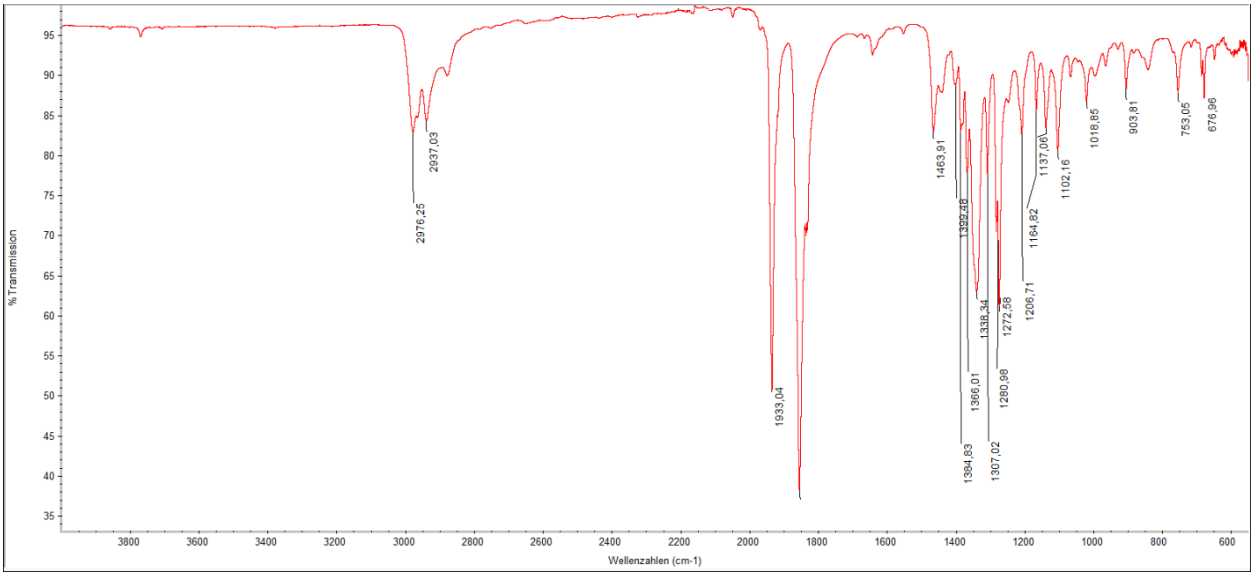

Figure S14. ATR IR spectrum of **5**.

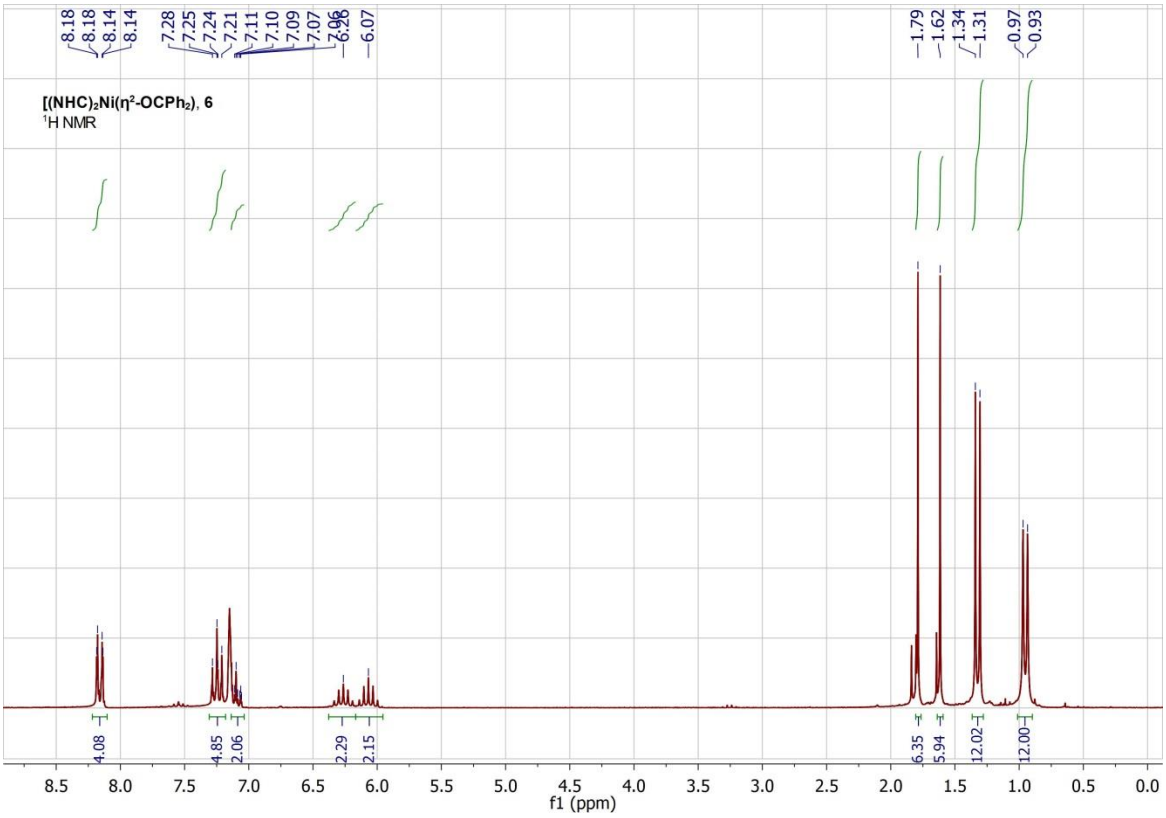

Figure S15. ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K.

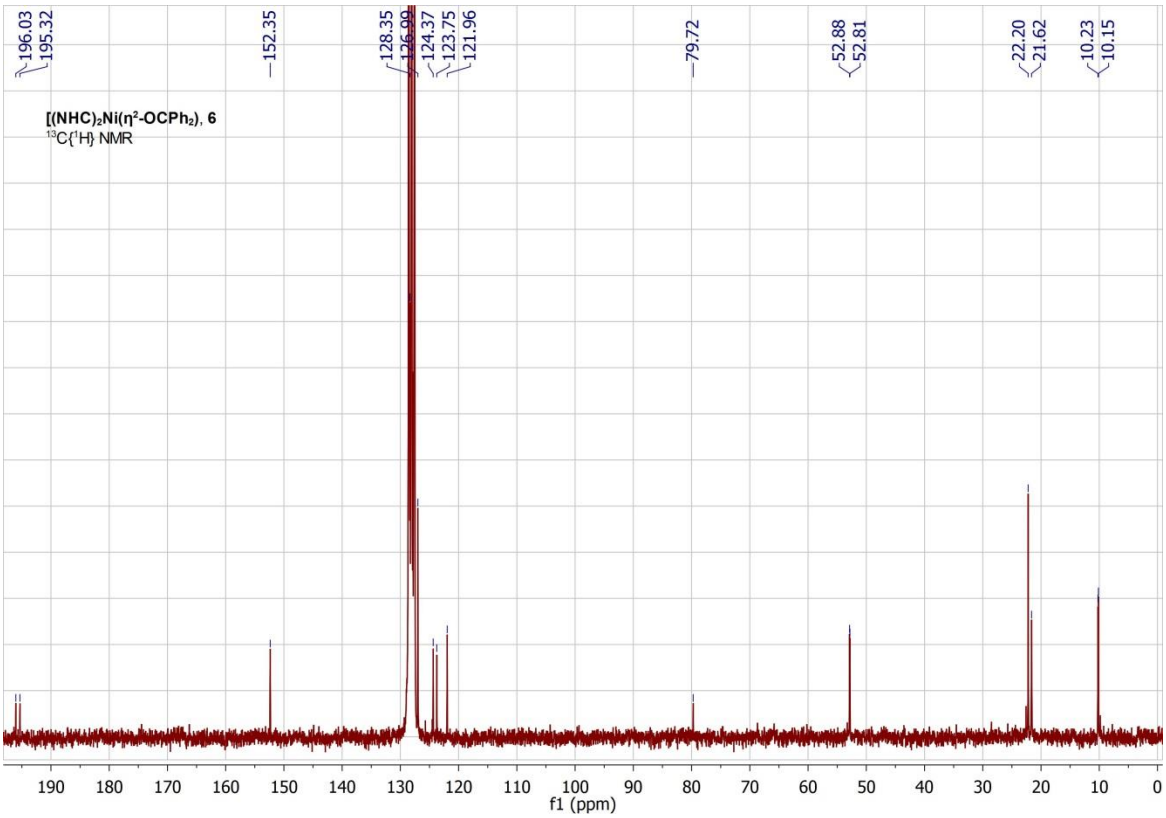

Figure S16. ^{13}C NMR spectrum of **6** in C_6D_6 at 298 K.

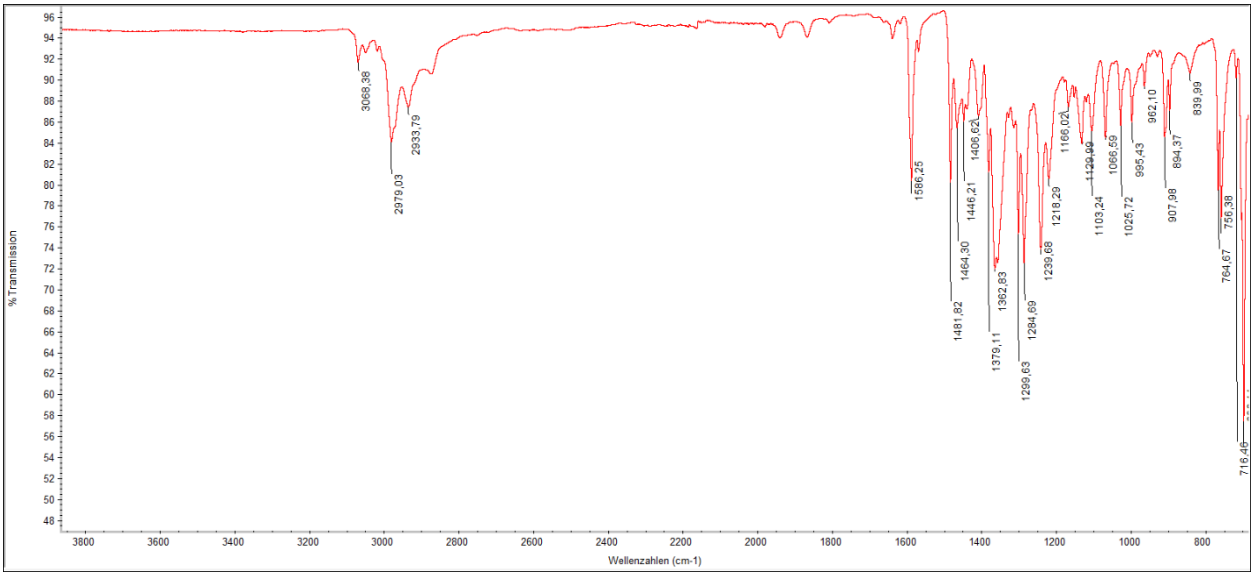

Figure S17. ATR IR spectrum of 6.

2. X-ray Crystallography

Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data was collected on an Oxford Diffraction SuperNova Atlas at 150 K (Cu-Kα radiation, λ= 1.54184 Å). The structures were solved by direct methods or using the SHELXT program[5] and refined on F^2 with the SHELX-2016 software package.[6] The positions of the H atoms were calculated and considered isotropically according to a riding model. Full crystal data, refinement and data collection details for **2**-**6** can be found in their CIFs.

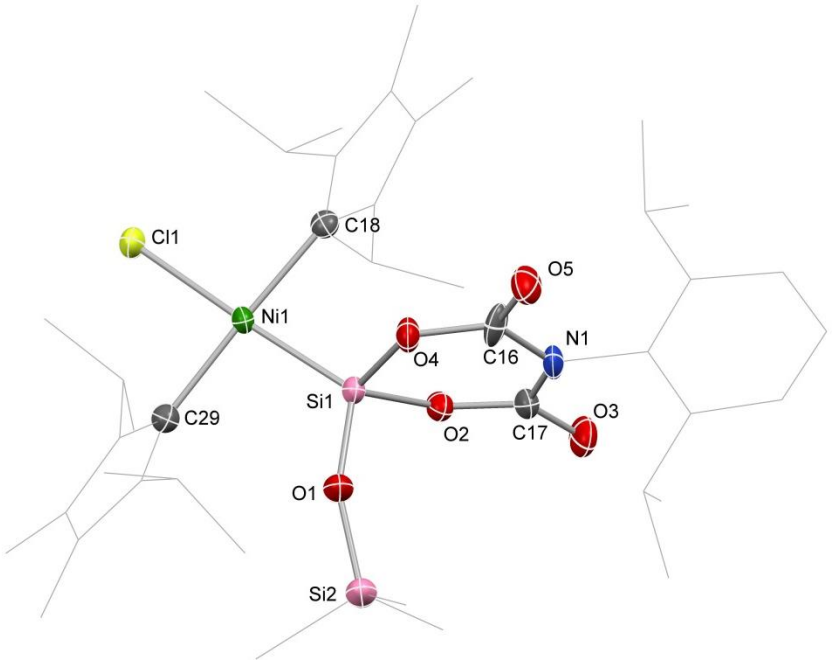

Figure S18. The molecular structure of a second polymorph **3a**, with thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°) for **3**: Si1-Ni1 2.148(2); Si1-O2 1.682(6); Si1-O3 1.682(5); C16-O4 1.20(1); C16-O2 1.338(9); C17-O5 1.23(1); C17-O3 1.335(9); C16-N1 1.42(1); C17-N1 1.37(1); Si1…N1 3.057(6); Si1-O2-C16 128.8(6); Si1-O3-C17 128.0(5); O3-C17-N1 118.6(7); O2-C16-N1 117.9(7); C16-N1-C17 125.6(7); O2-Si1-O3 98.1(3).

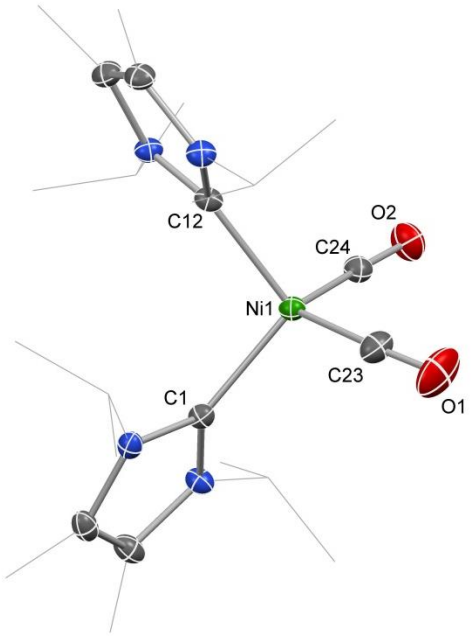

Figure S19. The molecular structure of **5**, with thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°) for **5**: C1-Ni1 2.015(1); C12-Ni1 2.019(1); C23-Ni1 1.763(2); C24-Ni1 1.766(1); C23-O1 1.152(2); C24-O2 1.157(2); C1-Ni1-C12 104.23(5); C1-Ni1-C23 107.72(7); C1-Ni1-C24 116.26(6); C12-Ni1-C23 116.17(7); C12-Ni1-C24 106.93(6); C23-Ni1-C24 105.95(7).

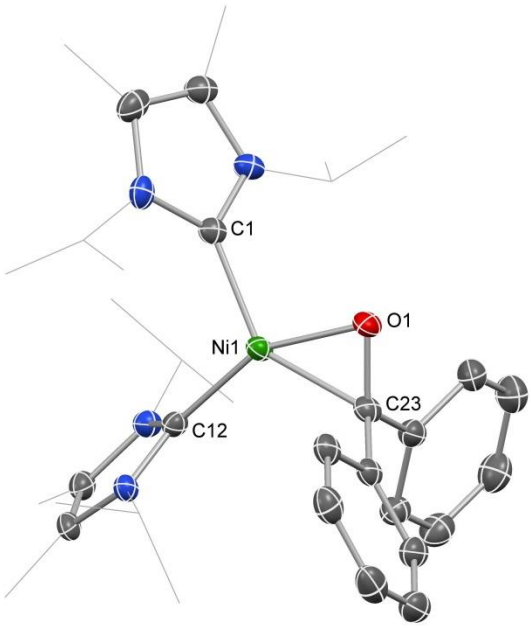

Figure S20. The molecular structure of **6**, with thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°) for **6**: Ni1-O1 1.870(2); C23-O1 1.344(4); C23-Ni1 1.959(3); C1- Ni1 1.951(3); C12-Ni1 1.907(3); O1-Ni1-C23 41.0(1); Ni1-O1-C23 73.1(2); Ni1-C23-O1 65.9(2); C1-Ni1-O1 100.6(1); C12-Ni1-C23 112.8(1); C1-Ni1-C12 105.5(1).

Table S1. Summary of crystal data for compounds **2**-**6**.

	2·(hexane)(Et_2O)	**3**	**3a**	**4**	**5**	**6**
empirical form.	$C_{43}H_{73}ClN_5NiO_{3.50}Si_2$	$C_{39}H_{66}ClN_5NiO_5Si_2$	$C_{39}H_{66}ClN_5NiO_5Si_2$	$C_{44}H_{77}ClN_6NiO_2Si_2$	$C_{24}H_{40}N_4NiO_2$	$C_{35}H_{50}N_4NiO$
formula wt	866.40	835.31	835.31	872.45	475.31	601.50
crystal syst.	monoclinic	triclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	*C2₁/c*	*P-1*	*P2₁/n*	*P-1*	*P2₁/n*	*P2₁2₁2₁*
a (Å)	32.1007(4)	9.3940(5)	13.8284(2)	11.2566(5)	12.52720(10)	10.2787(2)
b (Å)	12.4510(2)	11.9351(6)	14.3306(2)	12.7269(6)	15.8955(2)	15.5439(3)
c (Å)	25.1623(4)	20.7497(11)	24.1972(3)	17.1548(7)	13.02610(10)	21.1529(4)
α (deg.)	90	86.519(4)	90	89.747(4)	90	90
β (δεγ)	99.965(2)	79.694(4)	104.600(2)	85.046(3)	90.2270(10)	90
γ (deg.)	90	82.070(4)	90	86.160(4)	90	90
vol ($Å^3$)	9905.3(3)	2265.5(2)	4640.30(12)	2442.94(19)	2593.82(4)	3379.62(11)
Z	8	2	4	2	4	4
ρ(calc) ($g.cm^{-3}$)	1.162	1.225	1.196	1.186	1.217	1.182
μ (mm^{-1})	1.840	2.019	1.972	1.850	1.271	1.058
F(000)	3736	896	1792	944	1024	1296
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
reflns collect.	18637	15866	18884	17034	15095	13322
unique reflns	9314	10009	8759	9191	4759	6330
R_{int}	0.0265	0.0543	0.0263	0.0335	0.0203	0.0325
R1 [$I>2\sigma(I)$]	0.0359	0.0789	0.0307	0.0398	0.0159	0.0426
*w*R2 (all data)	0.1441	0.2067	0.1121	0.1241	0.0880	0.0962
CCDC No.	1851387	1851388	1851389	1851390	1851391	1851392

3. Computational methods and data

DFT calculations were performed at the B97-D/cc-pVTZ//B97-D/6-31G(d)[Ni: cc-pVTZ] level of theory.[7] Stationary points on the potential energy surface (PES) were characterised by harmonic vibrational frequency calculations. Transition states, which had one imaginary frequency, were analysed by intrinsic reaction coordinate (IRC) calculations to confirm the corresponding intermediates. Calculations were carried out using the GAUSSIAN 09 program suite.[8]

Table S2. Cartesian coordinates of CO_2 in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
C	1.304876	1.302539	-1.483446
O	2.222973	1.380837	-2.241148
O	0.386316	1.224046	-0.726105

Table S3. Cartesian coordinates of iminosilane **1** in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
Ni	0.901233	1.312724	0.437126
Si	-0.151515	-0.292843	-0.4937
Cl	1.929584	3.062658	1.514573
Si	0.717696	-2.327921	-2.642505
N	3.480546	0.275319	-0.537894
C	-0.796618	2.178264	0.426047
N	-1.732885	2.153907	1.417331
N	2.899343	-0.651271	1.33712
O	0.392662	-0.809029	-1.986167
C	-3.418112	-1.810089	-0.967404
C	2.475807	0.234491	0.385669
N	-1.418071	-1.011623	0.208805
N	-1.264058	3.071937	-0.494392
C	-4.433415	-3.930502	-0.270328
H	-5.222661	-4.6776	-0.380282
C	-2.389908	-3.154458	0.829929
C	-3.417385	-0.568104	-1.854228
H	-2.368826	-0.35993	-2.128606
C	-4.421137	-2.784955	-1.080548
H	-5.209455	-2.6582	-1.825582
C	4.554409	-0.533773	-0.143083
C	-2.37858	-1.977607	0.013838

C	-1.280105	-3.407554	1.845577
H	-0.608412	-2.538102	1.82171
C	3.411737	1.19104	-1.701225
H	2.346062	1.453785	-1.760771
C	-0.476804	3.400921	-1.703587
H	0.307103	2.628901	-1.721041
C	4.185922	-1.120367	1.044234
C	-2.798997	0.436239	2.913765
H	-3.629611	1.022879	3.331742
H	-2.513886	-0.319586	3.662024
H	-3.123792	-0.090886	2.00698
C	-3.412414	-4.103734	0.671283
H	-3.401796	-4.998961	1.299902
C	-1.561513	1.295704	2.615826
H	-0.763936	0.602367	2.321257
C	1.178577	-2.053755	-4.460526
H	0.332239	-1.602615	-5.006354
H	1.411311	-3.015862	-4.94954
H	2.049303	-1.391441	-4.589252
C	2.089859	-0.908643	2.55347
H	1.08603	-0.5579	2.27449
C	1.981831	-2.404147	2.889145
H	1.768992	-2.995466	1.987395
H	1.145309	-2.545634	3.589433
H	2.893447	-2.789351	3.367365
C	-2.757985	3.068002	1.150545
C	3.800111	0.500124	-3.019011
H	4.889555	0.404126	-3.131338
H	3.428612	1.109562	-3.85754
H	3.342597	-0.49603	-3.085647
C	5.827078	-0.702725	-0.915971
H	6.568645	-1.227487	-0.29675
H	6.258089	0.267067	-1.209096
H	5.679639	-1.293256	-1.835667
C	-3.935156	0.656649	-1.065223
H	-3.858697	1.576992	-1.669877
H	-3.348666	0.792675	-0.148214
H	-4.994214	0.507631	-0.793165
C	-2.463111	3.64962	-0.059216
C	0.216912	4.763119	-1.549049
H	-0.513044	5.58595	-1.500704
H	0.873428	4.93932	-2.416903
H	0.824065	4.759977	-0.631767
C	4.214155	2.472222	-1.426492
H	3.84719	2.948649	-0.506229

H	4.08984	3.169647	-2.27138
H	5.288372	2.25106	-1.321417
C	2.165987	-3.054343	-1.650266
H	3.014456	-2.352593	-1.596699
H	2.528469	-4.002612	-2.083646
H	1.849526	-3.263954	-0.613609
C	4.956774	-2.084814	1.893305
H	6.001441	-2.124924	1.553054
H	4.545306	-3.106404	1.839281
H	4.957435	-1.782269	2.951963
C	-0.455472	-4.65839	1.465311
H	-1.098434	-5.553433	1.434509
H	0.347544	-4.839703	2.200275
H	0.000415	-4.537786	0.46892
C	-1.831928	-3.538574	3.28227
H	-2.39988	-2.638205	3.565654
H	-1.008242	-3.679204	4.004689
H	-2.507388	-4.40615	3.368098
C	-3.957637	3.283152	2.020897
H	-4.480473	4.199843	1.711717
H	-3.680752	3.39229	3.080241
H	-4.671779	2.446089	1.945815
C	-4.199385	-0.719557	-3.173949
H	-3.876923	-1.612312	-3.734284
H	-4.03741	0.169477	-3.806231
H	-5.28385	-0.804036	-2.991858
C	2.592432	-0.049024	3.723118
H	3.611774	-0.342847	4.021243
H	1.927385	-0.188729	4.591087
H	2.589979	1.011587	3.431989
C	-0.783054	-3.466949	-2.549057
H	-1.056763	-3.719135	-1.513292
H	-0.580909	-4.408125	-3.091189
H	-1.671125	-2.999049	-3.003594
C	-1.072254	2.133244	3.807329
H	-0.153734	2.672188	3.531522
H	-0.858767	1.464548	4.657449
H	-1.835541	2.859223	4.129928
C	-1.30236	3.25272	-2.992278
H	-1.819892	2.281134	-3.010703
H	-0.620186	3.302485	-3.855575
H	-2.046016	4.054244	-3.104411
C	-3.266938	4.647156	-0.835594
H	-3.790862	4.179215	-1.686917
H	-2.645133	5.4633	-1.233813

H	-4.029855	5.093552	-0.181764

Table S3. Cartesian coordinates of **TS1** (+8.2 kcal/mol) in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
N	-2.919248	1.523095	-0.905867
C	-2.502224	0.259771	-0.604546
N	-3.590498	-0.358199	-0.05269
C	-4.697289	0.498867	-0.048502
C	-4.273746	1.687144	-0.59353
Ni	-0.85419	-0.607371	-1.063772
C	0.772804	-1.609654	-1.280537
N	0.968808	-2.907568	-0.889133
C	2.121071	-3.435117	-1.482264
C	2.682546	-2.417986	-2.217324
N	1.852185	-1.303864	-2.057978
C	-0.024608	-3.615446	-0.047764
C	0.621815	-4.436074	1.080653
C	2.609797	-4.840636	-1.307064
C	3.952909	-2.433986	-3.010877
C	1.996425	0.03117	-2.692968
C	1.581246	-0.016455	-4.171324
C	-3.565099	-1.791566	0.319969
C	-4.045851	-2.023777	1.759808
C	-6.046781	0.15627	0.507024
C	-5.063972	2.939601	-0.822393
C	-2.02329	2.49134	-1.584867
C	-2.284071	2.486013	-3.099248
Si	-0.084716	0.122047	0.769345
O	-0.58648	-0.698762	2.113841
Si	-0.299641	-0.787724	3.779456
C	-1.975114	-0.972455	4.638673
N	0.964612	1.36952	1.055599
C	2.260129	1.739701	0.712614
C	2.504486	2.919493	-0.062958
C	3.825066	3.31619	-0.329036
C	4.923183	2.579262	0.128443
C	4.690647	1.419765	0.878272
C	3.389292	0.991256	1.189836
C	1.365465	3.755616	-0.639281
C	1.412907	5.216164	-0.136732
C	3.225257	-0.278245	2.020921
C	4.002504	-0.212954	3.354289

C	0.751625	-2.339126	4.070104
C	0.597891	0.72797	4.460511
C	3.632731	-1.530005	1.213118
C	1.370304	3.731199	-2.185991
Cl	-1.701706	-1.339058	-3.079393
C	-0.984236	-4.436344	-0.922433
C	3.39168	0.634273	-2.481579
C	-4.300225	-2.647954	-0.723156
C	-2.093242	3.895305	-0.961929
C	-0.213787	2.696316	2.132293
O	0.526774	3.530801	2.559261
O	-1.324172	2.220728	2.002317
H	2.16368	-0.380198	2.274653
H	-5.380464	-2.436569	-0.732619
H	-4.164911	-3.712767	-0.473675
H	-3.881173	-2.457388	-1.720962
H	-6.772624	0.928676	0.215489
H	-6.03761	0.106448	1.608968
H	-6.418384	-0.809974	0.134339
H	-1.016554	2.088146	-1.40415
H	1.26973	0.648085	-2.145654
H	-0.586922	-2.800954	0.426655
H	3.717826	0.53343	-1.438563
H	3.340659	1.706882	-2.709189
H	4.136811	0.180561	-3.150522
H	-2.993859	4.440331	-1.27596
H	-1.222192	4.470124	-1.303009
H	-2.063972	3.835998	0.134826
H	5.942508	2.90089	-0.096741
H	3.990887	4.219184	-0.922587
H	-2.500457	-2.05038	0.276681
H	-2.644059	-0.135086	4.378589
H	-1.841518	-0.964088	5.734621
H	-2.481492	-1.913191	4.368905
H	0.423266	3.309166	-0.302482
H	-3.562962	-1.313323	2.443131
H	-3.768223	-3.045825	2.064218
H	-5.137568	-1.932665	1.851345
H	5.53833	0.832119	1.24064
H	-6.134948	2.729845	-0.690333
H	-4.920529	3.328516	-1.842277
H	-4.786983	3.740331	-0.117473
H	-2.189455	1.463827	-3.493734
H	-1.547678	3.138102	-3.595798
H	-3.292166	2.870055	-3.325182

H	3.041881	-1.610979	0.291134
H	3.480337	-2.446488	1.810651
H	4.698602	-1.478782	0.93348
H	-1.444666	-3.78878	-1.682155
H	-1.772204	-4.876019	-0.289089
H	-0.450747	-5.258106	-1.426602
H	2.328106	4.111815	-2.577169
H	0.566492	4.371345	-2.587552
H	1.222639	2.713128	-2.575456
H	2.288928	-0.620063	-4.762104
H	1.59132	1.008923	-4.576018
H	0.571172	-0.436297	-4.271368
H	4.760268	-1.883578	-2.500578
H	3.818729	-1.983008	-4.005281
H	4.288085	-3.471598	-3.151862
H	1.70703	-2.28336	3.523642
H	0.229299	-3.254086	3.746958
H	0.987588	-2.44811	5.143062
H	1.049161	0.480299	5.437506
H	-0.091439	1.572525	4.615388
H	1.397284	1.072386	3.790422
H	5.089348	-0.159536	3.178361
H	3.799815	-1.115147	3.956042
H	3.706609	0.671053	3.939282
H	1.049185	-5.380656	0.717372
H	-0.158987	-4.682643	1.816557
H	1.404603	-3.857811	1.591705
H	3.384792	-5.056926	-2.055988
H	1.797282	-5.571132	-1.442343
H	3.049339	-5.009172	-0.309799
H	1.399657	5.248505	0.960786
H	0.545077	5.780633	-0.519691
H	2.326272	5.720708	-0.493589

Table S4. Cartesian coordinates of **2** (-24.1 kcal/mol) in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
Ni	-0.996397	-0.3192	-1.024812
Cl	-1.943678	-0.649587	-3.111605
Si	-0.203387	0.021941	0.939198
Si	0.039455	-1.646211	3.542033
O	-0.873753	1.237271	2.019689
C	-2.596171	0.50901	-0.395487

N	-3.722622	-0.137101	0.036104
N	-2.919213	1.833604	-0.396098
O	0.532837	2.932112	2.732653
O	-0.05476	-1.342439	1.884169
N	0.690834	-2.679342	-1.356368
N	1.16126	1.181431	1.237447
N	1.633074	-0.950735	-2.27189
C	0.568024	-1.322923	-1.501105
C	2.48651	1.552502	0.87681
C	3.357352	-0.702967	1.793297
H	2.31274	-0.773656	2.106322
C	0.323706	1.926232	2.080157
C	-4.644918	-2.163555	-1.089695
H	-5.70516	-1.883177	-0.996028
H	-4.584249	-3.263957	-1.086255
H	-4.246534	-1.787382	-2.041659
C	-6.118739	0.417044	0.787184
H	-6.784517	1.28867	0.712628
H	-6.086916	0.112053	1.846883
H	-6.578614	-0.40541	0.219286
C	-4.758939	0.776555	0.269356
C	-4.252129	2.022433	-0.010242
C	-1.960424	2.854834	-0.88054
H	-0.993056	2.330322	-0.870192
C	1.842455	0.461904	-2.678653
H	1.219582	1.02514	-1.967749
C	2.378557	-2.068794	-2.66654
C	3.564123	0.662293	1.145204
C	-0.319692	-3.470846	-0.616344
H	-0.849485	-2.717893	-0.022233
C	3.300432	0.910763	-2.50594
H	3.710035	0.58315	-1.542438
H	3.331508	2.007338	-2.524868
H	3.937211	0.542234	-3.322057
C	-1.85308	4.064637	0.060031
H	-2.75361	4.692481	0.03182
H	-1.009563	4.686194	-0.272329
H	-1.657823	3.74374	1.093184
C	5.130942	2.298654	0.220045
H	6.154011	2.59062	-0.02759
C	4.064336	3.163351	-0.043812
H	4.25596	4.134655	-0.504811
C	-3.805711	-1.615836	0.075728
H	-2.769705	-1.938573	-0.08548
C	-1.708483	-1.974401	4.190145

H	-2.338328	-1.078591	4.058448
H	-1.691574	-2.21574	5.267235
H	-2.192784	-2.813559	3.664303
C	1.627765	3.790462	-0.119378
H	0.66607	3.337418	0.133944
C	2.736291	2.808287	0.252129
C	-4.25641	-2.137858	1.449438
H	-3.698483	-1.645188	2.257717
H	-4.056089	-3.220336	1.498049
H	-5.333574	-1.990976	1.6137
C	4.87051	1.050812	0.796704
H	5.695497	0.364362	0.998388
C	1.781761	-3.16208	-2.08626
C	-4.944604	3.348953	0.075129
H	-6.029305	3.194284	0.166528
H	-4.766762	3.957665	-0.824453
H	-4.613346	3.936833	0.947188
C	-2.27682	3.228017	-2.33782
H	-2.305222	2.318056	-2.95565
H	-1.493157	3.902065	-2.719295
H	-3.245291	3.748259	-2.414446
C	3.61307	-1.842536	0.782112
H	2.948081	-1.754808	-0.087092
H	3.436718	-2.822554	1.257655
H	4.656331	-1.818213	0.423791
C	-1.315282	-4.125698	-1.586568
H	-1.751093	-3.36186	-2.246602
H	-2.12029	-4.611385	-1.010293
H	-0.824973	-4.896711	-2.202049
C	1.598642	4.092066	-1.635372
H	2.547431	4.540531	-1.972457
H	0.790889	4.809702	-1.856877
H	1.418256	3.182045	-2.226626
C	1.318893	0.709176	-4.102166
H	1.915848	0.149758	-4.840524
H	1.411106	1.78287	-4.335153
H	0.266272	0.40755	-4.183468
C	3.598913	-2.027298	-3.535026
H	4.473185	-1.61799	-3.00236
H	3.436606	-1.410308	-4.431576
H	3.850738	-3.045098	-3.865987
C	1.121878	-3.189334	3.73886
H	0.654148	-4.07986	3.289235
H	1.303835	-3.40577	4.805874
H	2.101821	-3.042515	3.256074

C	0.802381	-0.200611	4.491628
H	1.774267	0.1069	4.078508
H	0.965674	-0.492516	5.54427
H	0.144971	0.681689	4.482971
C	4.234469	-0.880735	3.053188
H	5.306137	-0.884711	2.795751
H	4.001776	-1.839741	3.54474
H	4.059602	-0.067732	3.774904
C	0.310505	-4.455276	0.380708
H	0.717132	-5.350844	-0.109807
H	-0.472942	-4.783164	1.081758
H	1.102199	-3.960772	0.959177
C	2.194264	-4.600637	-2.15592
H	2.936599	-4.73428	-2.955524
H	1.340273	-5.259887	-2.374119
H	2.650078	-4.946232	-1.212987
C	1.754281	5.101595	0.687718
H	1.728654	4.886623	1.763604
H	0.920531	5.78052	0.440988
H	2.697492	5.618292	0.442248

Table S5. Cartesian coordinates of **IM2** (-7.7 kcal/mol) in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
C	0.553227	4.315737	0.440074
N	1.003705	3.019531	0.725752
C	0.968945	2.239801	-0.40222
N	0.449812	3.036662	-1.380212
C	0.190523	4.322127	-0.88625
C	1.684562	2.532312	1.955937
C	1.065364	3.010193	3.278811
C	0.405051	2.593248	-2.801471
C	1.506371	3.283257	-3.623482
Ni	1.734334	0.48452	-0.563053
C	2.489891	-1.275182	-0.411386
N	3.221262	-1.745477	0.650866
C	3.716422	-3.027532	0.376304
C	3.262819	-3.362842	-0.876841
N	2.512808	-2.27619	-1.335936
C	3.651067	-0.84683	1.751295
C	3.464225	-1.453939	3.150642
C	1.943696	-2.084597	-2.694681
C	3.070832	-1.803831	-3.702229

C	4.531879	-3.849717	1.327925
C	3.451172	-4.644339	-1.630401
C	-0.433605	5.431736	-1.677624
C	0.500154	5.439932	1.429348
Cl	3.679081	1.287118	-1.479847
Si	-0.045983	-0.530561	0.100387
C	-1.721314	-2.228637	-0.073209
N	-2.196454	-0.90039	-0.418916
C	-3.515606	-0.529777	0.071482
C	-3.656092	0.718302	0.729733
C	-4.882588	1.01206	1.353443
C	-5.958796	0.122997	1.292904
C	-5.846216	-1.027907	0.507752
C	-4.649486	-1.359211	-0.155671
C	-2.620479	1.834929	0.636084
C	-2.271487	2.471975	1.991576
C	-4.711276	-2.475901	-1.201765
C	-5.224766	-3.815465	-0.630078
O	-0.370048	-2.211186	-0.16917
O	-0.30367	-0.341686	1.731068
Si	-0.729611	-1.212926	3.116886
C	-2.599602	-1.19661	3.372105
C	-0.124219	-2.999429	2.95146
C	0.121041	-0.310482	4.552
C	-3.147729	2.908925	-0.346866
O	-2.355877	-3.175263	0.34263
C	1.005733	-3.227647	-3.112364
C	-0.99046	2.734897	-3.424446
C	3.183158	2.868692	1.884238
C	5.088056	-0.357807	1.506464
C	-5.616362	-2.013313	-2.372047
H	-1.686799	1.446879	0.210434
H	5.806539	-1.190222	1.564803
H	5.355819	0.381207	2.278453
H	5.154545	0.116546	0.518191
H	4.875798	-4.763777	0.823726
H	3.948326	-4.153941	2.212857
H	5.421615	-3.309028	1.686577
H	1.339301	-1.178599	-2.602161
H	0.639646	1.525222	-2.74766
H	1.543713	1.44499	1.907809
H	-1.758475	2.267899	-2.796717
H	-0.987809	2.209737	-4.391475
H	-1.256531	3.785891	-3.610496
H	1.559172	-4.119459	-3.441565

H	0.391813	-2.876057	-3.955303
H	0.335649	-3.496586	-2.284674
H	-6.897062	0.355176	1.801901
H	-6.716669	-1.670421	0.364687
H	2.981003	0.016181	1.660517
H	-0.801894	-3.563286	2.292116
H	-0.102031	-3.50007	3.935393
H	0.88357	-3.063767	2.511575
H	-3.711926	-2.639734	-1.617991
H	2.462208	-1.884537	3.272519
H	3.587912	-0.650046	3.893497
H	4.214955	-2.225846	3.369856
H	-4.99921	1.96665	1.869543
H	4.197772	-5.269173	-1.120116
H	3.803193	-4.468626	-2.658023
H	2.513568	-5.220209	-1.694826
H	3.661278	-0.937975	-3.368811
H	2.624147	-1.576843	-4.683686
H	3.735158	-2.674055	-3.823581
H	-3.400686	2.455047	-1.316088
H	-2.381859	3.685124	-0.497331
H	-4.056833	3.381756	0.059278
H	3.62125	2.480435	0.95468
H	3.70364	2.424192	2.748776
H	3.329147	3.960827	1.920688
H	-6.650812	-1.855102	-2.024692
H	-5.632782	-2.789274	-3.156352
H	-5.237968	-1.077216	-2.80412
H	1.313505	4.359521	-3.752325
H	1.532485	2.825048	-4.625222
H	2.482559	3.136452	-3.142608
H	-1.490008	5.218572	-1.90987
H	0.085862	5.608001	-2.630408
H	-0.400136	6.36564	-1.098672
H	-0.278662	0.710471	4.666339
H	1.209074	-0.230528	4.397495
H	-0.045126	-0.843093	5.504369
H	-3.00802	-0.175005	3.407333
H	-2.844685	-1.694916	4.327325
H	-3.123391	-1.734609	2.567277
H	-3.16549	2.885752	2.484762
H	-1.561596	3.29594	1.829556
H	-1.810955	1.731656	2.660179
H	1.318553	4.055595	3.502314
H	1.484042	2.385887	4.082118

H	-0.023646	2.889989	3.288885
H	0.194038	6.364307	0.920205
H	1.484431	5.620617	1.891147
H	-0.218276	5.248329	2.24292
H	-4.599961	-4.152917	0.206453
H	-5.208856	-4.584621	-1.420098
H	-6.266812	-3.719753	-0.281737
O	-0.700831	-0.395696	-2.209965
C	-1.934217	-0.400639	-2.013131
O	-2.938948	-0.075024	-2.610845

Table S6. Cartesian coordinates of **3** (-37.6 kcal/mol) in Scheme 2, in Angstrom (Å).

Atomtype	X coordinates	Y coordinates	Z coordinates
Ni	1.776405	-1.247146	-0.096407
Cl	3.203895	-3.045618	0.01059
Si	0.443654	0.425462	-0.21927
Si	1.004782	3.56506	-0.039437
N	-0.518044	-2.874825	0.763647
O	-0.542665	0.537984	1.189126
O	-0.795108	0.28854	-1.412083
N	4.001808	0.534714	-0.796158
N	-2.565598	0.858407	0.028987
O	-2.394849	1.132095	2.309342
N	3.672295	0.46131	1.34689
O	-2.902671	0.283869	-2.175422
C	3.195073	-0.009211	0.157682
N	-0.37676	-2.788649	-1.402506
C	-2.113032	0.45393	-1.258601
C	0.207642	-2.328449	-0.25826
C	-1.844839	0.869386	1.253647
C	-3.971194	1.210893	0.117672
O	1.024847	1.950941	-0.47367
C	-4.352604	2.528564	-0.209771
C	-4.902169	0.230716	0.513286
C	-3.346099	3.567938	-0.692713
H	-2.333972	3.162011	-0.554033
C	0.214789	-2.492284	-2.731983
H	0.852341	-1.617283	-2.539559
C	-0.124031	-2.674838	2.18014
H	0.549718	-1.809757	2.138713
C	4.804905	1.261369	1.145796
C	-4.491991	-1.200976	0.843189

H	-3.396302	-1.280492	0.799407
C	-1.516733	-3.721591	0.264034
C	0.677539	-3.883354	2.689946
H	0.05321	-4.790127	2.727769
H	1.037446	-3.67498	3.710937
H	1.541054	-4.060475	2.033041
C	-6.256648	0.60198	0.579806
H	-6.996865	-0.141944	0.880885
C	-1.304055	-2.297336	3.089001
H	-1.90098	-1.48276	2.659751
H	-0.896636	-1.945595	4.049597
H	-1.957095	-3.155768	3.298515
C	-2.286867	-4.342101	-2.130359
H	-2.926262	-5.089079	-1.639137
H	-1.680721	-4.858629	-2.890802
H	-2.942976	-3.627144	-2.652596
C	5.010452	1.311422	-0.211855
C	3.797422	0.226955	-2.230161
H	2.820334	-0.278407	-2.24839
C	-5.717844	2.856141	-0.130428
H	-6.037039	3.868475	-0.385746
C	-1.431174	-3.659967	-1.106937
C	6.054596	2.071381	-0.970574
H	5.63951	2.973688	-1.45146
H	6.519383	1.458752	-1.75716
H	6.847924	2.397483	-0.28259
C	-6.665242	1.903459	0.263289
H	-7.722203	2.173746	0.319814
C	-2.455669	-4.525922	1.109099
H	-3.211525	-3.897936	1.604649
H	-1.920502	-5.085625	1.891391
H	-2.986914	-5.253444	0.479142
C	-0.824734	-2.090488	-3.790645
H	-1.383224	-2.959052	-4.168171
H	-0.283011	-1.650912	-4.643445
H	-1.526841	-1.340637	-3.401891
C	-3.540391	3.82785	-2.205151
H	-4.542654	4.246047	-2.395799
H	-3.441726	2.88939	-2.770607
H	-2.791251	4.550041	-2.57115
C	3.05578	0.054144	2.630357
H	2.102375	-0.397979	2.324259
C	3.675559	1.498773	-3.08419
H	2.954984	2.192717	-2.626921
H	3.306242	1.2181	-4.083196

H	4.64105	2.008154	-3.215424
C	-0.053121	3.812142	1.509454
H	-1.117031	3.601574	1.320636
H	0.018456	4.854023	1.867614
H	0.26478	3.147713	2.328958
C	5.57526	1.942396	2.235501
H	6.534427	2.305059	1.838754
H	5.791027	1.261025	3.072203
H	5.033156	2.812313	2.643927
C	0.304751	4.550525	-1.496278
H	0.929229	4.430131	-2.398012
H	0.256326	5.628613	-1.263072
H	-0.714029	4.215959	-1.74853
C	4.847438	-0.776844	-2.731058
H	5.861088	-0.346487	-2.717277
H	4.611733	-1.06056	-3.769663
H	4.824959	-1.676698	-2.098844
C	-3.424257	4.87978	0.117115
H	-2.63812	5.575038	-0.220495
H	-3.286382	4.688262	1.192664
H	-4.398384	5.376126	-0.022491
C	2.798502	4.077411	0.289609
H	3.245847	3.466476	1.089306
H	2.864774	5.138309	0.586969
H	3.41802	3.939409	-0.612063
C	-4.930853	-1.579029	2.275401
H	-6.027197	-1.533188	2.376985
H	-4.48328	-0.887935	3.005136
H	-4.614657	-2.606046	2.521061
C	1.113405	-3.660078	-3.170564
H	1.878207	-3.854065	-2.404161
H	1.608366	-3.403287	-4.121606
H	0.518225	-4.57352	-3.331394
C	3.894016	-1.034	3.318516
H	4.037164	-1.877883	2.627694
H	3.364332	-1.388463	4.217807
H	4.877055	-0.64773	3.630961
C	-5.060433	-2.175464	-0.213918
H	-6.162663	-2.150354	-0.213698
H	-4.738379	-3.207188	0.001273
H	-4.707069	-1.893035	-1.217463
C	2.720771	1.253936	3.531148
H	2.048835	0.911884	4.333386
H	2.200265	2.035331	2.957395
H	3.614527	1.687837	4.001671

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