Supplementary Information

Reversible CO_2 insertion into the silicon-nitrogen σ-bond of an N-heterocyclic iminosilane.

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1.0. General considerations

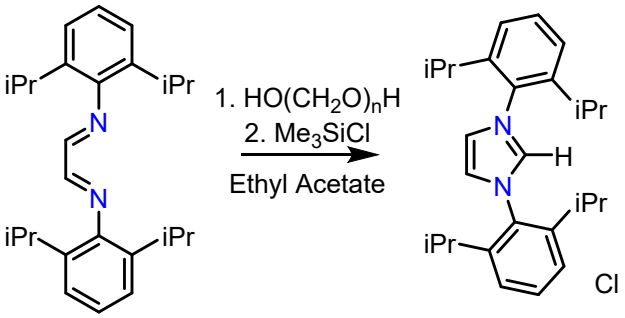
Moisture sensitive reactions were performed using standard Schlenk and glove box techniques in vacuo or under an atmosphere of N_2. All non-deuterated solvents were predried over activated molecular sieves (48 hours) and were further dried over the appropriately sized molecular sieves (3 or 4 Å). Deuterated solvents were obtained from Cambridge Isotope Laboratories, which were degassed and stored over 4 Å molecular sieves. **IPrNSiMe$_3$**[1] was prepared according to literature procedures.

Single crystal X-ray diffraction (SXRD) data were collected using a SuperNova Atlas (Dual) diffractometer using Cu Kα radiation of wavelength 1.54184 Å. Suitable crystals were selected and mounted on a nylon loop and the crystal was kept at 150 K during data collection. TGA data were collected using a *Netzsch STA 449C Jupiter* instrument, with graphs being calibrated to 100%. ATR-IR spectra were recorded on a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer. Thermogravimetric analysis (TGA) measurements were made using a PerkinElmer STA6000 TGA instrument.

^{1}H and ^{13}C{^{1}H} NMR was conducted using a Bruker Advance III 500 MHz instrument. Elemental analysis was carried out using a Carlo Erba CE1108 elemental analyser (London Metropolitan University). Accurate mass data was collected using a Waters LTC Premier XE ESI Q-TOF mass spectrometer.

2.0. Synthetic procedures.

2.1. Synthesis of 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (IPrHCl).

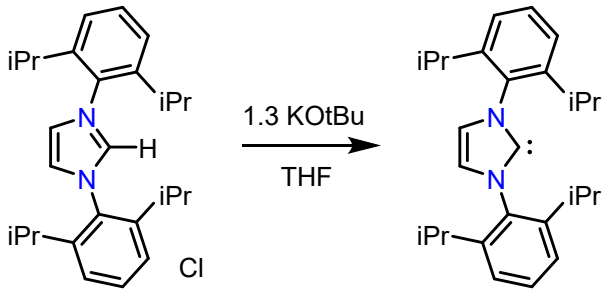


The synthesis was adapted from reference 2.

A round-bottom flask was loaded with N,N'-bis(2,6-diisopropylphenyl)ethanediimine (8.01g, 21.3mmol), paraformaldehyde (639mg, 21.3mmol) and ethyl acetate (200 mL) and heated to 70 °C. In a 250ml conical flask, trimethylsilyl chloride (2.31g, 21.3mmol) was dissolved in ethyl acetate (50 mL). The solution of trimethylsilyl chloride was added to the previous solution in the round bottom flask dropwise with magnetic stirring. The resulting reaction mixture was heated at 70 °C for 24 hours with magnetic stirring. After 24 hours, the flask was cooled to 0 °C in an ice bath to yield an off-white precipitate. The resulting precipitate was collected under vacuum filtration and washed with cold ethyl acetate (3 × 50 mL). The off-white powder was collected by filtration to give an off-white solid. Total yield: 6.93g (87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ =8.15(d,) δ = 7.29 (m, $^3J_{H–H}$ = 7.4 Hz, 2H, *meta*-C*H*), 7.19 (d, $^3J_{H–H}$ = 7.8 Hz, 4H, *para*-C*H*), 6.62 (s, 2H, NHC C*H*), 2.96 (sept, $^3J_{H–H}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (d, $^3J_{H–H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.20 (d, $^3J_{H–H}$ = 6.9, 12H, CH(C*H*$_3)_2$).

2.2. Synthesis of 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene (IPr).

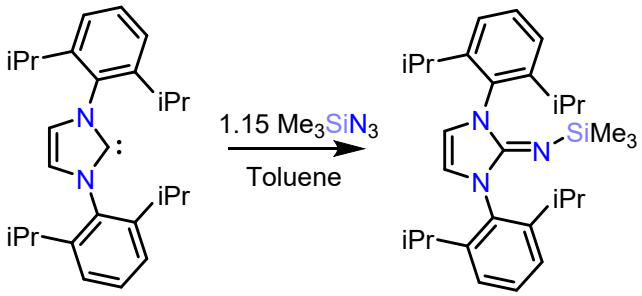


The synthesis was adapted from reference 3.

A Schlenk flask was loaded with 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (4.00g, 9.41mmol) and 1.3 equivalents of dehydrated potassium tert-butoxide (1.37g, 12.22mmol) and tetrahydrofuran (50 mL). The solution was allowed to stir overnight. Volatile materials were removed from the milky yellow mixture under vacuum, and the residue was extracted with ether (40 mL), filtered and concentrated to 10 mL. The concentrated solution was store in the freezer overnight and gave an off-white solid of IPr. The volatile materials were removed under vacuum and pale yellow solids were dried and collected. Total yield: 2.29g (57.2%).

^{1}H NMR (500 MHz, C_6D_6) δ = 7.29 (m, $^3J_{H–H}$ = 7.4 Hz, 2H, *meta*-C*H*), 7.19 (d, $^3J_{H–H}$ = 7.8 Hz, 4H, *para*-C*H*), 6.62 (s, 2H, NHC C*H*), 2.96 (sept, $^3J_{H–H}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (d, $^3J_{H–H}$ = 6.9Hz, 12H, CH(C*H*$_3)_2$), 1.20 (d, $^3J_{H–H}$ = 6.9, 12H, CH(C*H*$_3)_2$).

2.3. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)-1,3-dihydro-2*H*-imidazol-2-imine (**IPrNSiMe$_3$**).

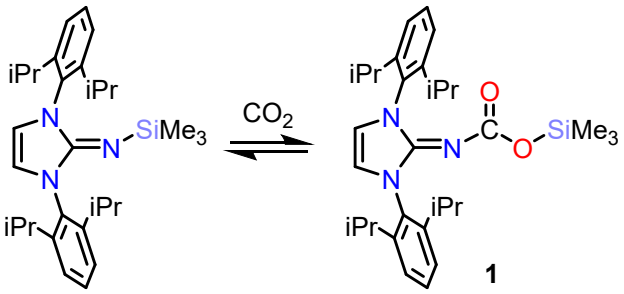


The synthesis was adapted from reference 4,5.

A Schlenk flask was loaded with1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (2.15g, 5.53mmol), 1.15 equivalent of azidotrimethylsilane (0.73g, 6.36mmol) and toluene (30mL), heated to 120 °C in an oil bath with stirring for 3 days. The dark brown solution was filtered to give clear orange solution. The volatile materials were removed under vacuum and the pale orange solids were dried and collected. Total yield:1.91g (88.8%).

^{1}H NMR (500 MHz, C_6D_6) δ = 7.22 (m, $^3J_{H–H}$ = 7.7 Hz, 2H, *meta*-C*H*), 7.14 (d, $^3J_{H–H}$ = 7.8 Hz, 4H, *para*-C*H*), 5.94 (s, 2H, NHC C*H*), 3.16 (sept, $^3J_{H–H}$ = 6.8 Hz, 4H, C*H*(CH_3)), 1.37 (d, $^3J_{H–H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)), 1.19 (d, $^3J_{H–H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)), -0.17 (s, NSiCC*H*$_3$).

2.4. Synthesis of $IPrNCO_2SiMe_3$ (**1**).



A solution of $IPrNSiMe_3$ (50 mg, 0.105 mmol) in hexane (10 mL) was stirred for 30 minutes and filtered via cannula into a Schlenk flask. The solution was placed under 1 atmosphere of CO_2 and the Schlenk flask sealed and placed into the – 35 °C freezer overnight. Colourless crystals of **1** (41.6 mg, 76%) formed which were characterized by X-ray crystallography, IR spectroscopy, and elemental analysis. Upon dissolution, partial dissociation of CO_2 occurred to yield a mixture of **$IPrNSiMe_3$** and **1**. NMR assignments were derived from difference between pure **$IPrNSiMe_3$** and the equilibrium mixture.

^{1}H NMR (500 MHz, C_6D_6) δ = 7.22 (m, $^3J_{H–H}$ = 7.4 Hz, 2H, *meta*-C*H*), 7.12 (d, $^3J_{H–H}$ = 7.4 Hz, 4H, *para*-C*H*), 6.07 (s, 2H, NHC C*H*), 3.06 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.45 (d, $^3J_{H–H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.34 (d, $^3J_{H–H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 0.2 (s, 9H, Si(C*H*$_3)_3$).

Further resonances associated with **$IPrNSiMe_3$** are present at 30% of total concentration:

^{1}H NMR (500 MHz, C_6D_6) δ = 7.22 (m, $^3J_{H–H}$ = 7.4 Hz, 2H, *meta*-C*H*), 7.14 12 (d, $^3J_{H–H}$ = 7.4 Hz, 2H, *para*-C*H*), 5.94 (s, 2H, NHC C*H*), 3.16 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.38 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, CH(C*H*$_3)_2$), 1.19 (sept, $^3J_{H–H}$ = 6.9 Hz, 4H, CH(C*H*$_3)_2$), -0.18 (s, 9H, Si(C*H*$_3)_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ = 158.1 (*C*O_2), 152.1 (carbonic *C*), 146.9 (*ortho*-*C*), 133.2 (*ipso*-*C*), 129.9 (*para*-*C*), 124.3 (*meta*-*C*), 116.7 (NHC *C*H), 29.2 (*C*H$(CH_3)_2$), 24.7 (CH(*C*H$_3)_2$), 23.7 (CH(*C*H$_3)_2$), 0.1 (Si(*C*H$_3)_3$).

Further resonances associated with **$IPrNSiMe_3$** can be found at:

^{13}C NMR (126 MHz, C_6D_6) δ = 148.0 (*ortho*-*C*), 141.3 (carbonic *C*), 135.2 (*ipso*-*C*), 129.4 (*para*-*C*), 123.9 (*meta*-*C*), 113.8 (NHC *C*H), 28.9 (*C*H$(CH_3)_2$), 24.4 (CH(*C*H$_3)_2$), 23.5 (CH(*C*H$_3)_2$), 3.5 (Si(*C*H$_3)_3$).

IR (solid, ATR, neat, cm^{-1}): 2959, 2865, 1615, 1595, 1574, 1556, 1466, 1429, 1362, 1323, 1248, 1203, 1132, 1054, 1034, 983, 938, 875, 846, 805, 775, 740, 705.

Elemental analysis (%) calcd for C, 71.63; H, 8.73; N, 8.08. Found: C, 69.62; H, 8.35; N, 7.73.

3.0. NMR spectra.

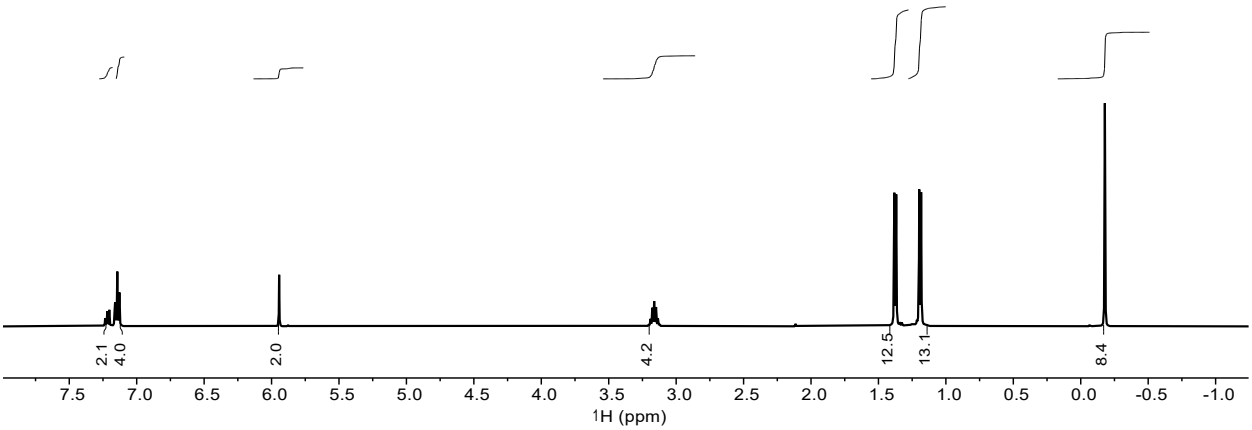


Figure S1. ^{1}H NMR (500 MHz, C_6D_6) of **IPrNSiMe$_3$**.

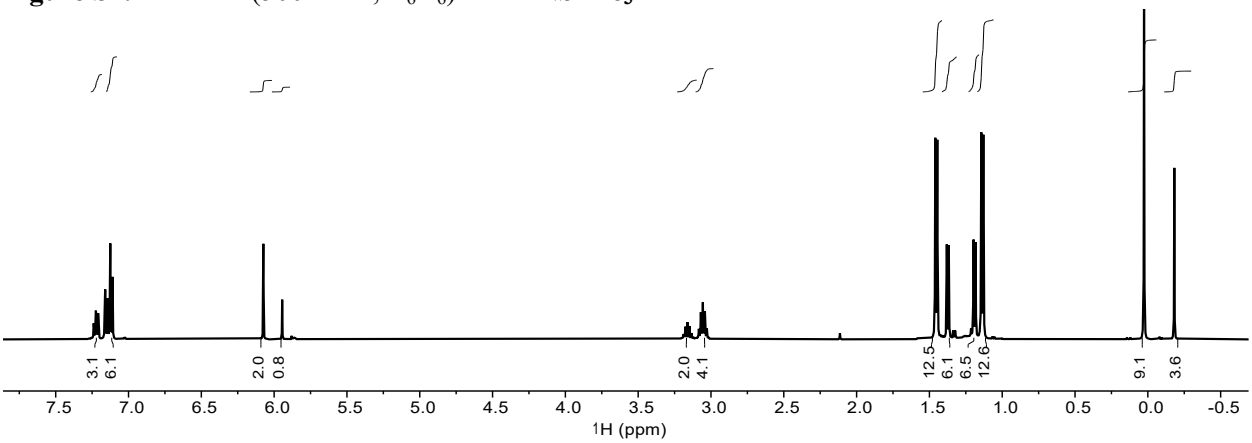


Figure S2. ^{1}H NMR (500 MHz, C_6D_6) of equilibrium mixture of **IPrNSiMe$_3$** and **1**.

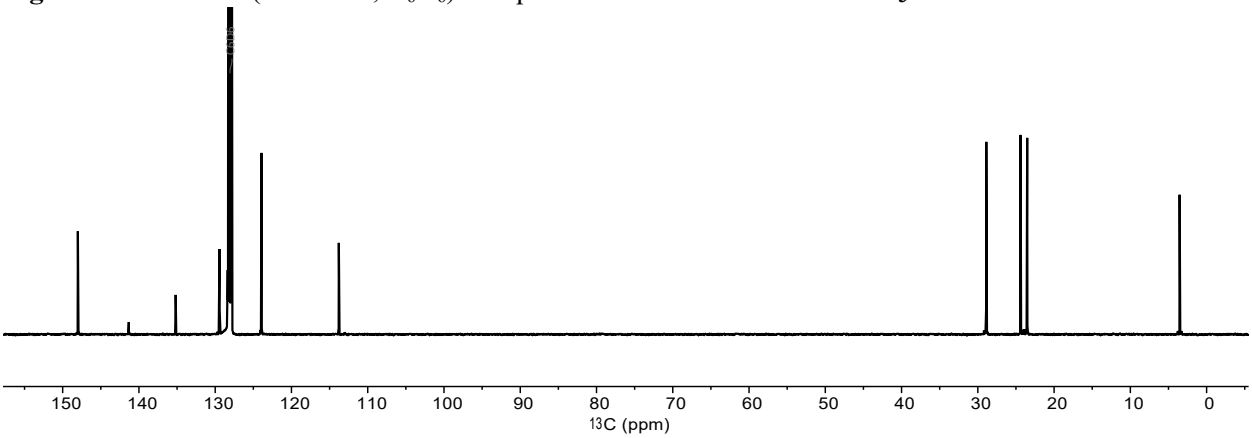


Figure S3. ^{13}C NMR (126 MHz, C_6D_6) of **IPrNSiMe$_3$**.

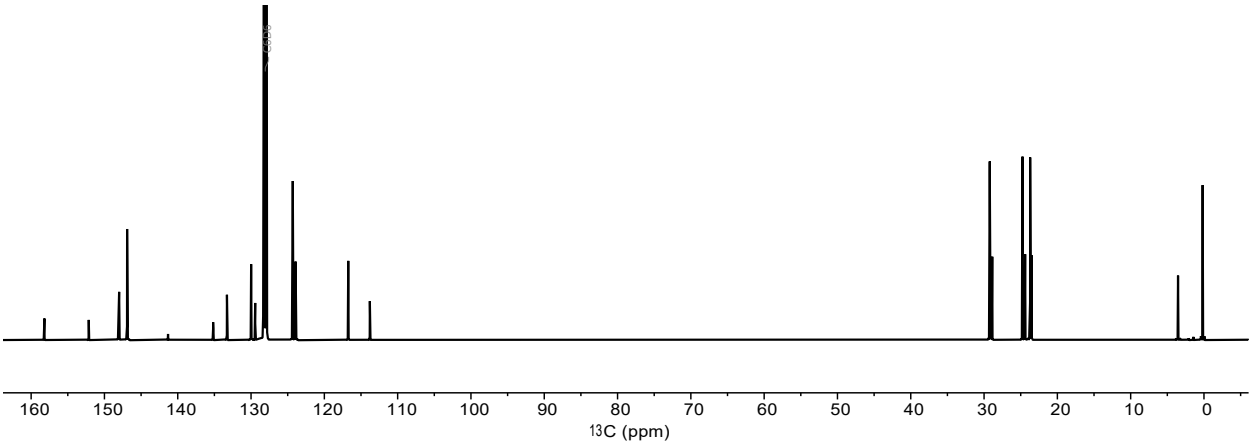


Figure S4. ^{13}C NMR (126 MHz, C_6D_6) of equilibrium mixture of **IPrNSiMe$_3$** and **1**.

4.0. Variable temperature (VT) NMR.

The binding equilibrium between CO_2 to $IPrNSiMe_3$ was observed to be undergoing slow chemical exchange relative to the ^1H NMR timescale (500 MHz). Distinct ^1H NMR resonances were observable for **1** and **IPrNSiMe$_3$** over the viable temperature range (298K to 333k; Figure 5) and their relative integrations were used in conjunction with the known pressure of CO_2. K_{CO2} values were determined using the equation:

$$K_{CO2} = \frac{[1]}{[IPrNSiMe_3]} \times P_{CO2}$$

Where P_{CO2} (in atm) is known based on initial pressurization of the sample, and 1 atm was used as the standard state definition for CO_2 gas. For **IPrNSiMe$_3$** and **1**, the standard state is defined to be 1 M at 298 K in toluene. Pressure is assumed to vary with temperature in accordance with Guy Lussac's Law for a closed system (P1/T1 = P2/T2). This treatment for determining P_{CO2} at various T was applied for both the case of VT NMR with a pressurized J Young tube, which is unambiguously a closed system.

Thermodynamic binding parameters were subsequently extracted from the van't Hoff analysis (Figure S6), with ΔG° at 298 K determined using the equations:

$$ln(K_{CO2}) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

$$\Delta G^\circ = -RT \cdot ln(K_{CO2})$$

$$\Delta G^\circ = \Delta H^\circ - (T \cdot \Delta S^\circ)$$

The rate of self-exchange, i.e. the interconversion of **IPrNSiMe$_3$** and **1** via loss of CO_2, in which $k_{ex} << |\Delta v|$, was determined from the relative intensity of the peaks associated with each species at a given temperature (Figure S7).[6] The rate constant for CO_2 loss from **1** was extracted at each T using equations:

$$rate_{ex} \cong rate_{loss} = k_{loss} \cdot [1]$$

$$k_{loss} = \frac{rate_{ex}}{[1]}$$

Obtaining k_{loss} at various temperatures followed by constructing Eyring plots of $\ln(k_{loss}/T)$ vs 1/T (Figure S8) allows for the extraction of activation parameters for H_2 loss (ΔH‡ loss, ΔS‡ loss, and ΔG‡ loss). The experiment was repeated in triplicate at a range of concentrations, and the error values cited in the manuscript were propagated from the three runs.

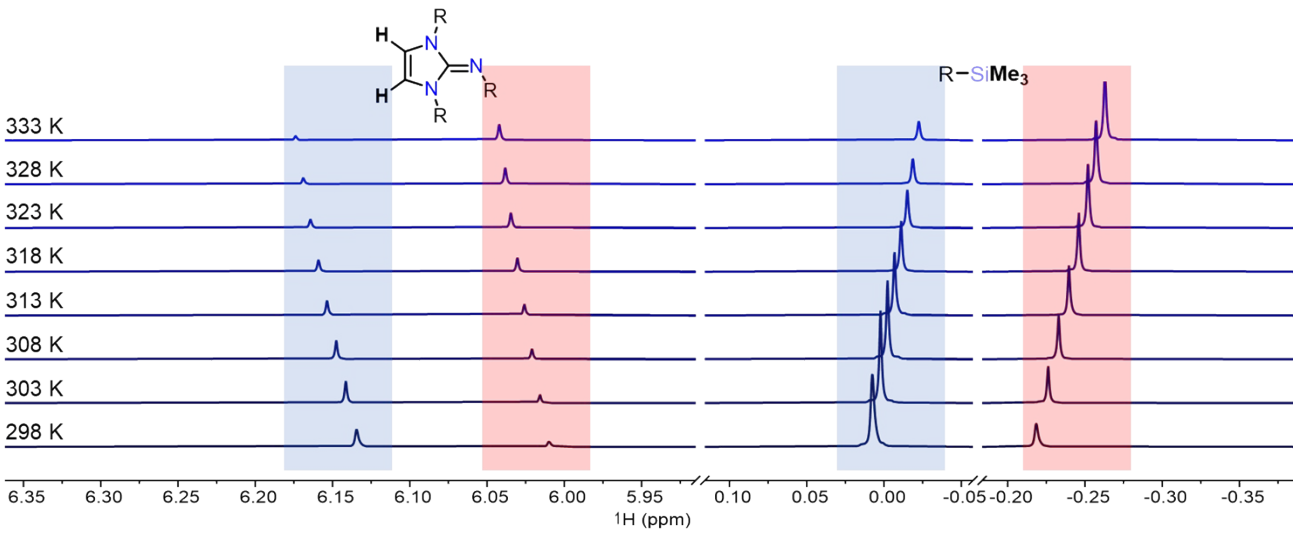
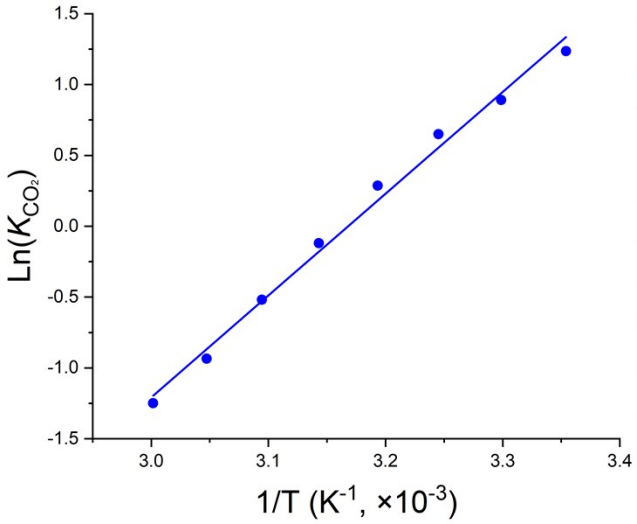


Figure S5. Example variable temperature ^{1}H NMR (500 MHz, d^{8}-toluene) spectra of the equilibrium between **IPrNSiMe$_3$** and **1** and CO_2. Temperature range of 298 to 333 K at 5 K increments.



Equation	y = a + b*x
Plot	Ln[conc]
Weight	No Weighting
Intercept	-22.75681 ± 0.82
Slope	7183.14891 ± 26
Residual Sum of S	0.04337
Pearson's r	0.99607
R-Square (COD)	0.99216
Adj. R-Square	0.99085

Figure S6. Example van't Hoff plot of the natural log of the equilibrium constant vs 1/temperature foir the equilibrium between IPrNSiMe$_3$ and **1** and CO_2.

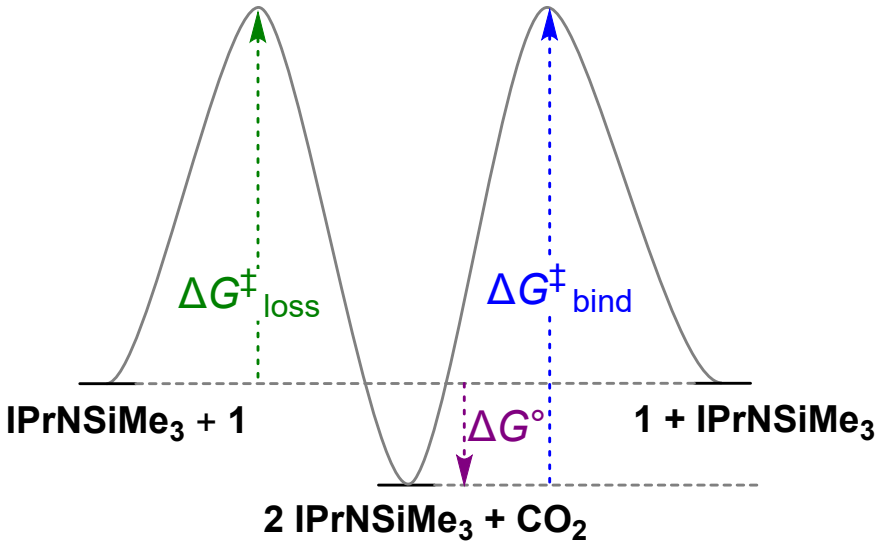
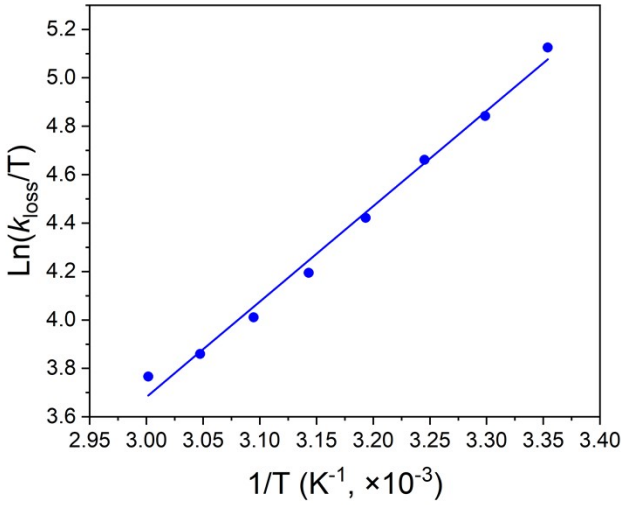


Figure S7. Proposed mechanism of self-exchange and associated thermodynamic parameters.



Equation	y = a + b*x
Plot	Ln(Kloss/T)
Weight	No Weighting
Intercept	-8.13848 ± 0.468
Slope	3940.03712 ± 14
Residual Sum of	0.01391
Pearson's r	0.99582
R-Square (COD)	0.99165
Adj. R-Square	0.99026

Figure S8. Example Eyring plot of the natural log of k_{loss}/Temperature vs 1/Temperature for the equilibrium between **IPrNSiMe$_3$** and **1** and CO_2.

5.0. FTIR spectra of compounds.

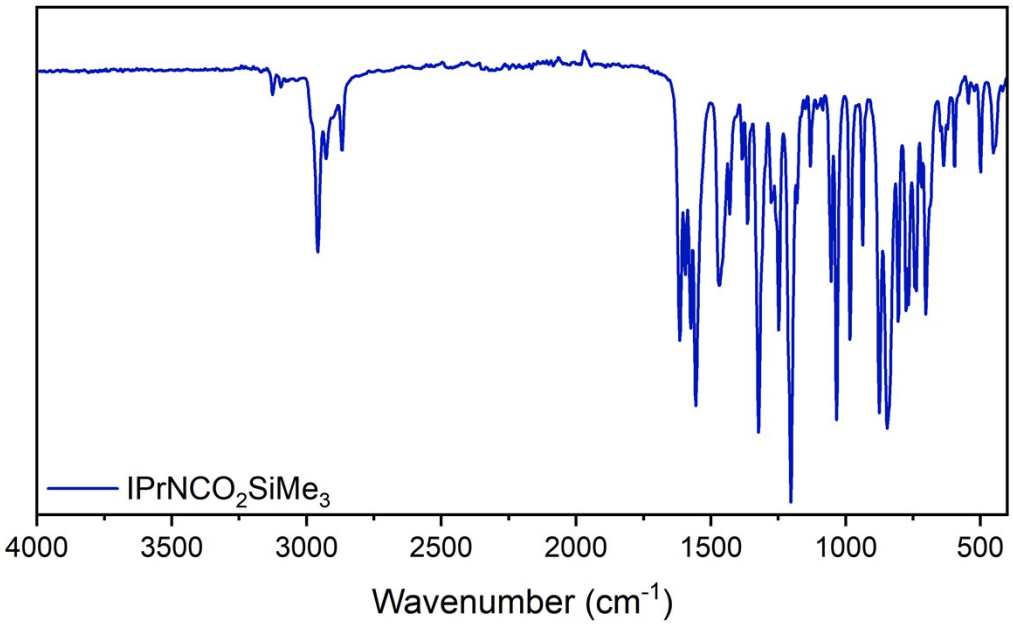


Figure S9. FTIR spectrum of solid **IPrNSiMe$_3$**.

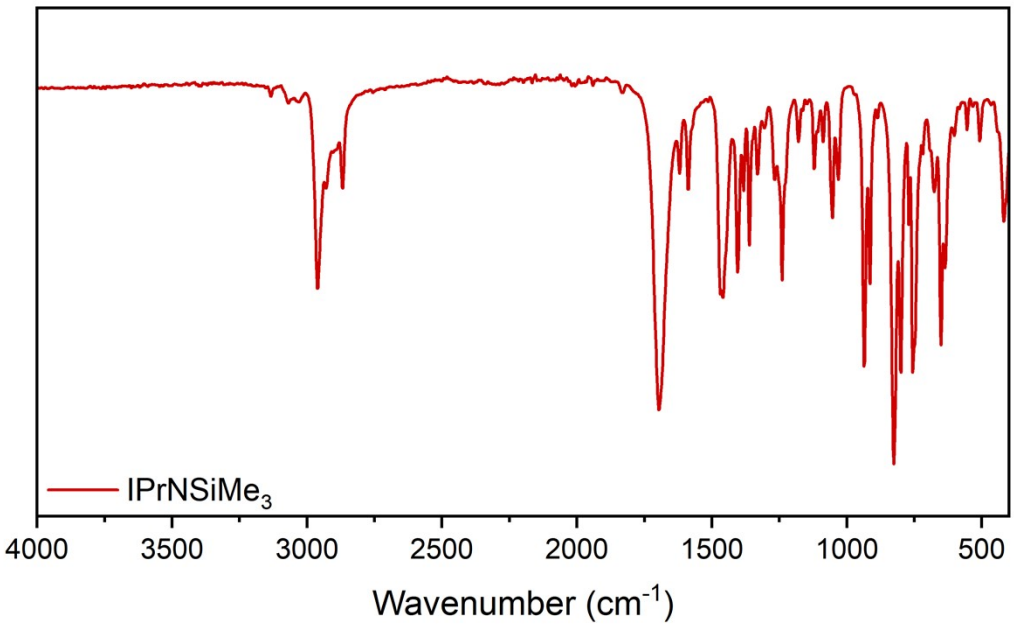


Figure S10. FTIR spectrum of solid **1**.

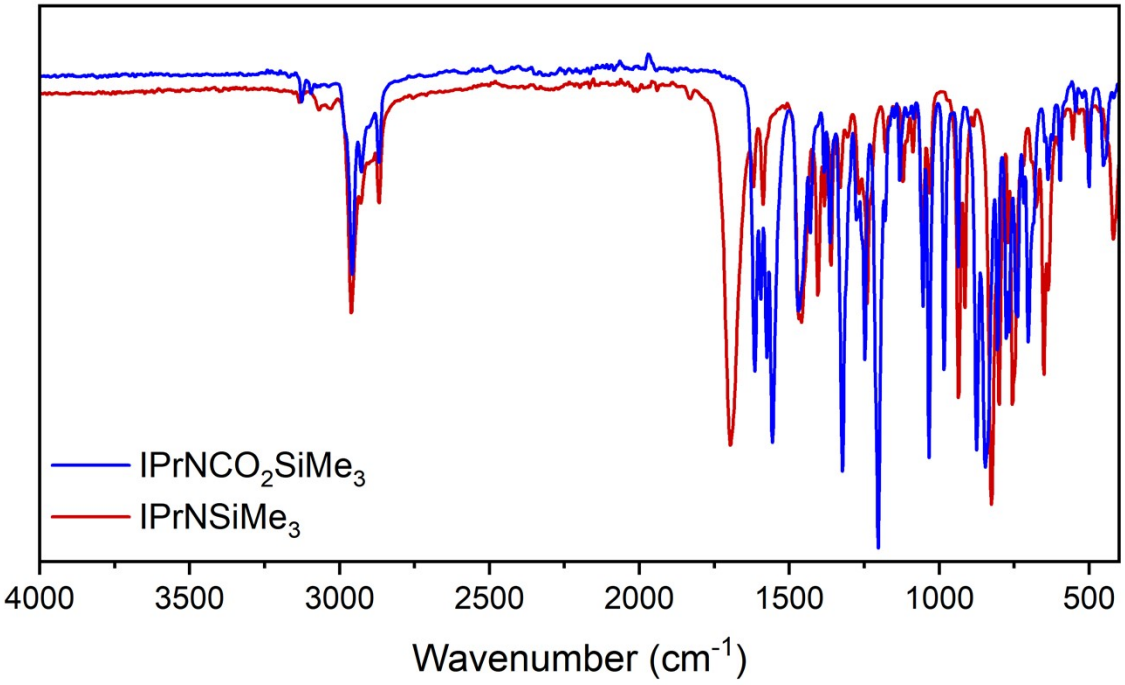


Figure S11. FTIR overlay of solid **IPrNSiMe$_3$** and **1**.

6.0. Thermogravimetric analysis.

Thermogravimetric analysis (TGA) measurements were made using a PerkinElmer STA6000 TGA instrument, with a sensitivity of 0.1 mg and used N2 as the shield gas. The samples were heated from 30 °C to 500 °C, at a heating rate of 10 °C/min.

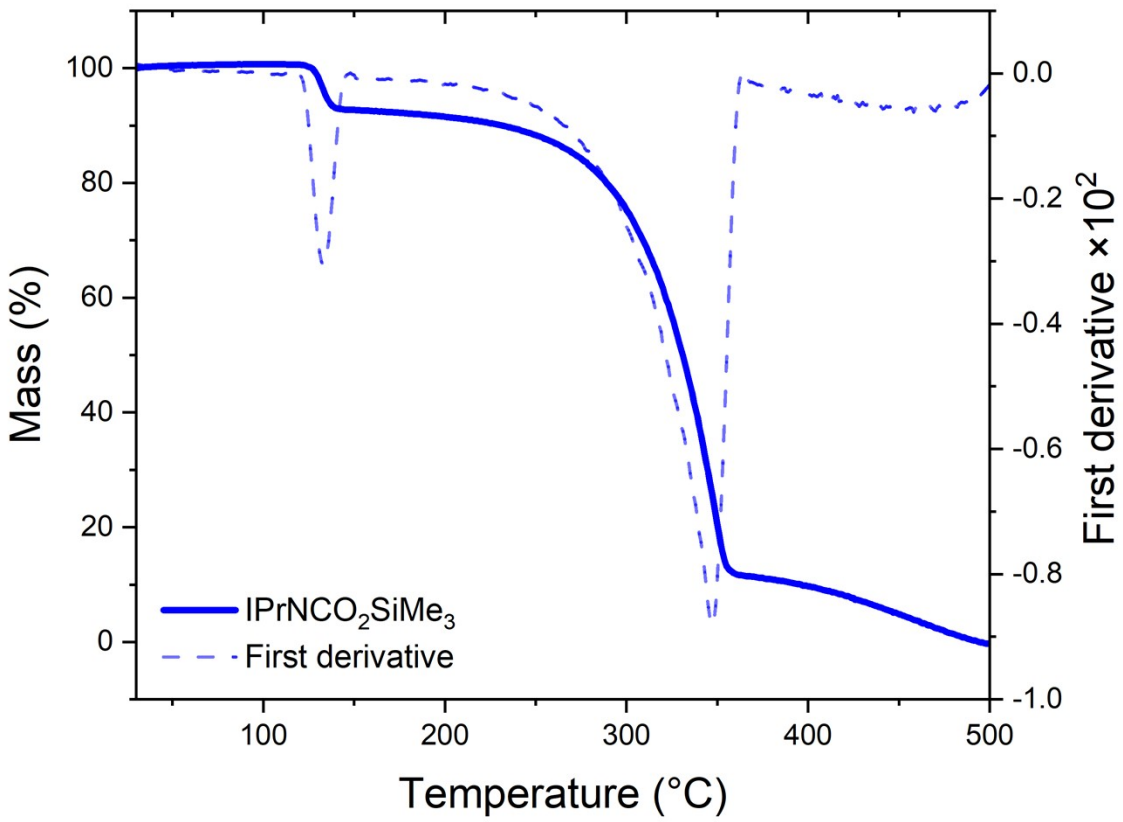


Figure S 12. Thermogravimetric plot of **1**. Solid line represents the mass loss (%), dashed line represents the first derivative of the curve.

7.0. Crystallographic Data.

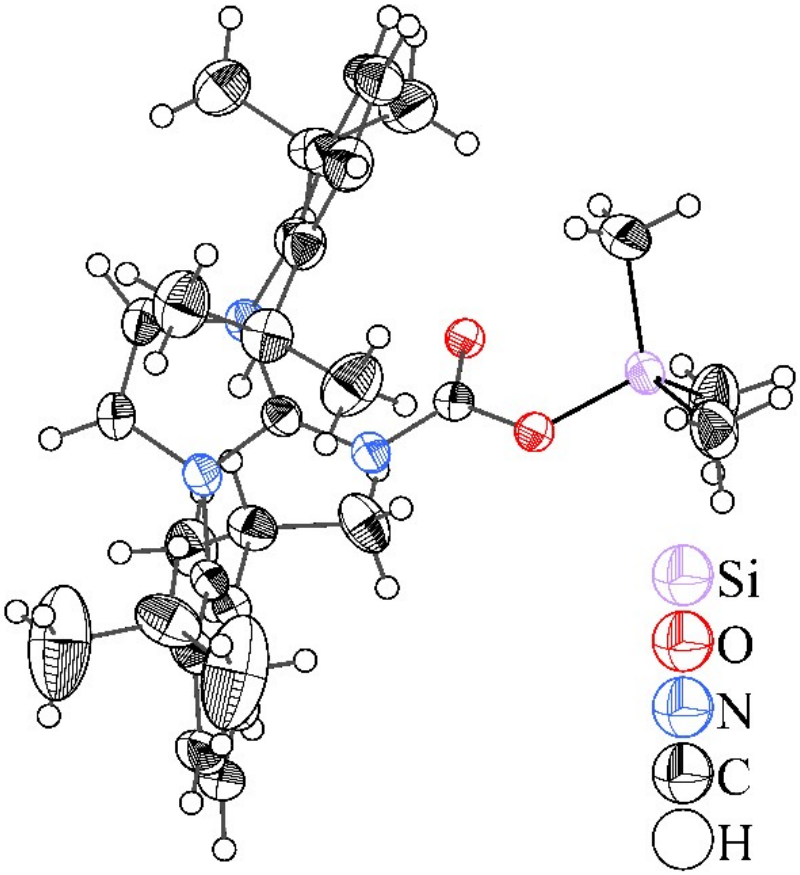


Figure S13. Structure of **1**. The thermal ellipsoids are drawn at 50% probability level.

Table S1. Crystal data and structure refinement for **1**.

Identification code	2384340 (CCDC)
Empirical formula	$C_{31}H_{45}N_3O_2Si$
Formula weight	519.79
Temperature/K	150.01(10)
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	27.23555(7)
b/Å	27.23555(7)
c/Å	17.39351(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	12902.07(9)
Z	16
ρ_{calc}g/cm^3	1.070
μ/mm^{-1}	0.857
F(000)	4512.0
Crystal size/mm^3	0.319 × 0.204 × 0.169
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.864 to 156.328
Index ranges	$-33 \leq h \leq 34$, $-34 \leq k \leq 34$, $-20 \leq l \leq 22$
Reflections collected	151242
Independent reflections	6825 [R_{int} = 0.0359, R_{sigma} = 0.0110]
Data/restraints/parameters	6825/0/345
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	0.44/-0.38

8.0. Density Functional Theory Calculations

Geometry optimizations and frequency calculations were performed using the Gaussian program package (versions 16). Optimized geometries were calculated from crystal structure coordinates where available. Energy minima were confirmed by the presence of no imaginary frequencies in the vibrational calculation. Relaxed surface scans were performed with BP86 functional and def2-SVP basis set. Transition states were optimized as such with the full basis set and confirmed by the presence of a single imaginary frequency productive to the reaction coordinate. After identification of minima and transition states, single point calculations were performed with methods described below with benzene as the implicit solvent.

Of the methods investigated, most reproduced the experimental IR and solid-state parameters of both **1** and **IPrNSiMe$_3$** (Table S2). However, the energies of the reaction vary significantly, with huge discrepancies in the overall reaction enthalpy as well as the barriers to conversion, demonstrating the sensitivity of even this simple reaction to a high degree of computational variance (Figure S14). The methodology BP86 with the scalar relativistically recontracted version of the Aldrichs triple-z basis set (def2-TZVP) produced results in keeping with the experimental observation of reaction reversibility, and are within error of the experimentally determined thermodynamic parameters.

Table S2. Top: Calculated stretching frequencies of **IPrNSiMe$_3$**, **IPrNCO$_2$SiMe$_3$**, and intermediate species in comparison to experimental data. Bottom: Calculated bond metrics of calculated and experimental **IPrNSiMe$_3$** and **IPrNCO$_2$SiMe$_3$**.

		IR (cm^{-1})			
Compound	Method	C=N	C=N (scaled)	CO_2	CO_2 (scaled)
IPrNSiMe$_3$	Experimental		1699	-	-
	BP86/def2-TZVP(D3)	1697	1721	-	-
	PBE/6-311++g(D3)	1781	1704	-	-
	B3LYP/def2-TZVP(D3)	1735	1674	-	-
	M062X/6-311++g(D3)	1774	1774	-	-
IPrNCO$_2$SiMe$_3$	Experimental		1613		1558
	BP86/def2-TZVP(D3)	1594	1616	1588	1610
	PBE/6-311++g(D3)	1670	1598	1581	1513
	B3LYP/def2-TZVP(D3)	1623	1566	1511	1458
	M062X/6-311++g(D3)	1637	1637	1567	1567
Intermediate1	BP86/def2-TZVP(D3)	1484	1505	1794	1819
	PBE/6-311++g(D3)	1578	1510	1684	1612
	B3LYP/def2-TZVP(D3)	1550	1496	1783	1721
	M062X/6-311++g(D3)	1587	1587	1678	1678

		Distances (Å)					
Compound	Method	C=N	N-Si	N-C	C-O1	C-O2	O2-Si
IPrNSiMe$_3$	Experimental	1.263	1.677	-	-	-	-
	BP86/def2-TZVP(D3)	1.271	1.715	-	-	-	-
	PBE/6-311++g(D3)	1.270	1.730	-	-	-	-
	B3LYP/def2-TZVP(D3)	1.266	1.691	-	-	-	-
	M062X/6-311++g(D3)	1.270	1.730	-	-	-	-
IPrNCO$_2$SiMe$_3$	Experimental	1.319	-	1.343	1.227	1.364	1.671
	BP86/def2-TZVP(D3)	1.309	-	1.363	1.240	1.366	1.737
	PBE/6-311++g(D3)	1.320	-	1.351	1.258	1.358	1.762
	B3LYP/def2-TZVP(D3)	1.308	-	1.351	1.229	1.354	1.693
	M062X/6-311++g(D3)	1.325	-	1.355	1.261	1.356	1.759

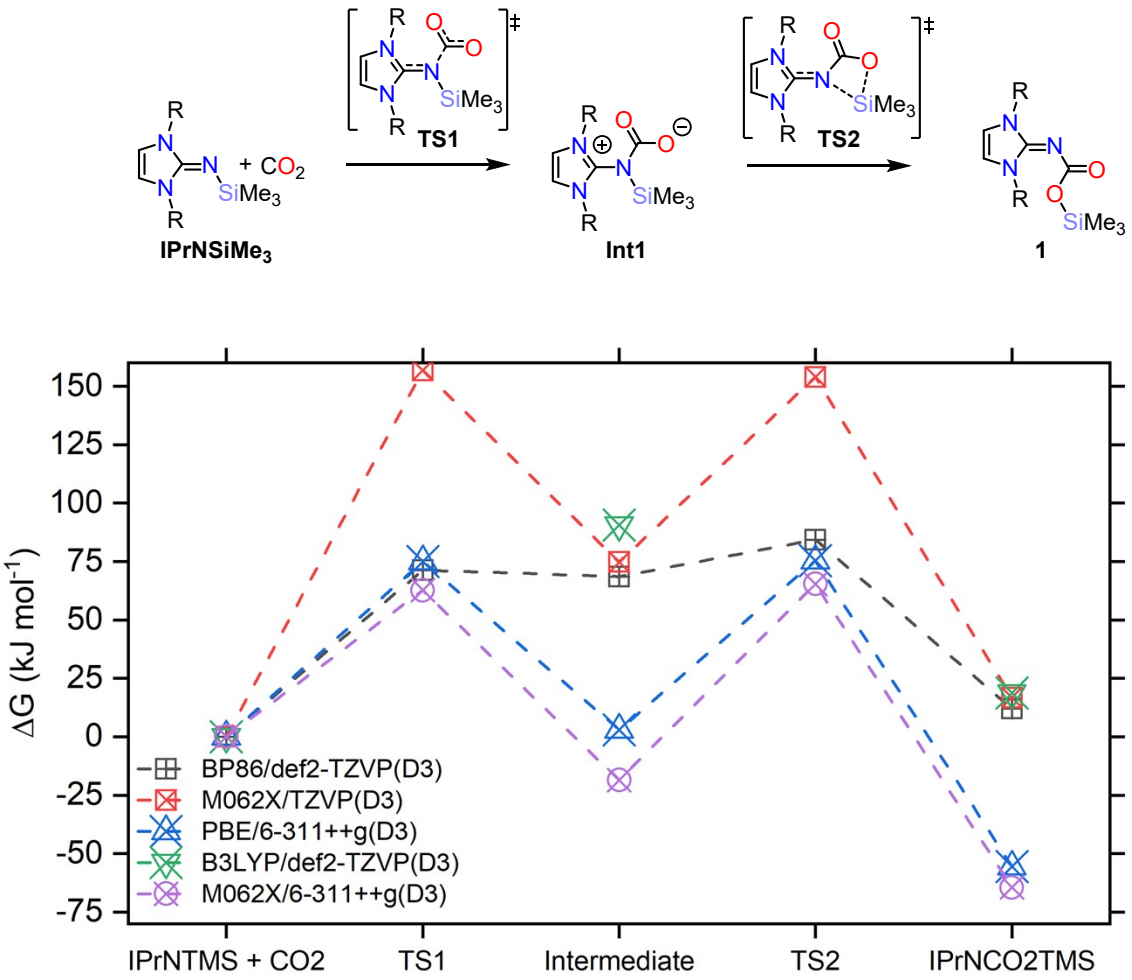


Figure S14. Top: Scheme showing calculated reaction pathway. Bottom: Dependence of reaction energetics on computational methodology.

8.1. Optimized coordinates

The optimized structures are from the methodology discussed in the manuscript, BP86-def2-TZVP-d3.

CO_2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.17525800
O	0.00000000	0.00000000	-1.17525800

$IPrNSiMe_3$

C	0.09787100	-0.00012800	-0.15071000
C	-0.51555700	0.00094100	-2.39323100
C	0.84857400	0.00104500	-2.35045700
N	1.23470300	0.00046200	-1.00557900
H	-1.20126100	0.00126200	-3.24577900
H	1.58592000	0.00146300	-3.15877000
N	0.11667400	-0.00089100	1.12043900
N	-0.98832600	0.00022600	-1.07244100
C	-2.37839400	0.00017000	-0.71868200
C	-3.05355700	1.24325500	-0.56927700
C	-3.05340400	-1.24298000	-0.56909700
C	-4.43207300	1.21479000	-0.27307600
C	-4.43190800	-1.21464500	-0.27286000
C	-5.11661100	0.00004300	-0.12659600
H	-4.98067700	2.16298300	-0.15617900
H	-4.98038900	-2.16288600	-0.15579200
H	-6.19378900	-0.00001300	0.10516200
C	2.59203300	0.00021000	-0.53950200
C	3.24937700	1.24229000	-0.32468400
C	3.24924100	-1.24210900	-0.32561300
C	4.59221700	1.21409400	0.10509500
C	4.59207000	-1.21437800	0.10420800
C	5.25946500	-0.00025800	0.31852500
H	5.12545600	2.16311200	0.27637900
H	5.12520700	-2.16358000	0.27480600
H	6.30868400	-0.00045000	0.65522600
C	-2.33460900	2.57842800	-0.76602100
H	-1.24600800	2.36350300	-0.78999500
C	-2.71104400	3.21017000	-2.12493800
H	-2.47621400	2.53037000	-2.96954100
H	-3.79647500	3.44294300	-2.17275500
H	-2.15457800	4.15774700	-2.28618800
C	-2.58301700	3.56463400	0.39251000
H	-1.97898200	4.48542300	0.25185100
H	-3.64702400	3.87800800	0.45225900
H	-2.30447100	3.12034200	1.36956300
C	-2.33428100	-2.57805200	-0.76586100
H	-1.24568900	-2.36302800	-0.78929000
C	-2.71009300	-3.20937700	-2.12515300
H	-3.79550700	-3.44211400	-2.17351000
H	-2.47486500	-2.52931800	-2.96943500
H	-2.15355500	-4.15690700	-2.28643700
C	-2.58310300	-3.56465700	0.39222300
H	-3.64706500	-3.87831100	0.45131200
H	-1.97879300	-4.48526700	0.25158900
H	-2.30516400	-3.12061400	1.36956300
C	2.55258800	2.58022200	-0.57084600
H	1.48965800	2.35903000	-0.80041800
C	3.14942600	3.30218200	-1.79882000
H	4.21897000	3.55713200	-1.63872400
H	3.08877000	2.67326000	-2.71102600
H	2.60551700	4.24928900	-2.00090800
C	2.57388600	3.48366000	0.67857700
H	2.11716700	2.97163800	1.54888700
H	3.60788300	3.77865300	0.95792300
H	2.00457100	4.41864800	0.49148200
C	2.55231400	-2.57978400	-0.57274800
H	1.48949900	-2.35830500	-0.80256200
C	2.57304300	-3.48386100	0.67622700
H	3.60691300	-3.77904900	0.95583500
H	2.11601300	-2.97221600	1.54659300
H	2.00373200	-4.41871400	0.48844500
C	3.14944500	-3.30117500	-1.80091100
H	3.08923700	-2.67171900	-2.71278000
H	4.21888000	-3.55644400	-1.64059900
H	2.60541200	-4.24805600	-2.00372400
Si	-0.44457100	-0.00086600	2.74131700

C	-2.33449300	-0.00014600	2.96968100
H	-2.80627100	0.89257600	2.50825700
H	-2.80705700	-0.89248600	2.50832600
H	-2.59384800	0.00000900	4.05107100
C	0.24527100	1.53767400	3.62101100
H	-0.05844500	1.55827400	4.68994600
H	1.35476200	1.54875600	3.58036100
H	-0.12043400	2.47448200	3.14933600
C	0.24436200	-1.54005700	3.62053800
H	-0.12168000	-2.47650700	3.14841100
H	1.35385300	-1.55159200	3.57995000
H	-0.05943900	-1.56099000	4.68943500

TS1

C	0.06162400	0.02423900	-0.12423600
C	-0.53526200	0.29400600	-2.32151300
C	0.82091000	0.14668800	-2.28199500
N	1.18982700	-0.03186500	-0.95098100
H	-1.20890000	0.45982900	-3.16564700
H	1.56125000	0.14832000	-3.08608900
N	0.07886500	0.03019200	1.20032900
N	-1.01116100	0.21510000	-1.01228700
C	-2.41251500	0.36531200	-0.68267900
C	-2.84792000	1.57990900	-0.08080500
C	-3.32317700	-0.67224200	-1.04336000
C	-4.21638100	1.69152000	0.24380200
C	-4.68116000	-0.49278500	-0.70577400
C	-5.12252400	0.66422300	-0.05040000
H	-4.57871600	2.61343200	0.72315900
H	-5.40752700	-1.27886700	-0.96339000
H	-6.18610200	0.77446400	0.21495400
C	2.55805600	-0.28207900	-0.54426300
C	3.52353300	0.75543700	-0.67597600
C	2.90878200	-1.59309300	-0.10713800
C	4.84858600	0.46079100	-0.28746600
C	4.24494100	-1.81854100	0.27765800
C	5.20564800	-0.80018500	0.20062400
H	5.61489800	1.24709400	-0.36852200
H	4.54471200	-2.81479000	0.63343400
H	6.24403300	-0.99869400	0.51058700
C	-1.91782000	2.77927800	0.09741000
H	-0.87521700	2.41405300	0.16939100
C	-1.99897100	3.68402200	-1.15564900
H	-1.74035300	3.13017300	-2.08197700
H	-3.02136000	4.09986200	-1.28601800
H	-1.29167800	4.53457500	-1.06250900
C	-2.18597900	3.59390500	1.37574300
H	-1.39366800	4.35955700	1.50135200
H	-3.15869900	4.13041000	1.34209900
H	-2.17597300	2.95146500	2.27873400
C	-2.90905600	-1.90825500	-1.85163200
H	-1.80632500	-2.01338100	-1.76848300
C	-3.25829100	-1.71293800	-3.34749500
H	-4.35779700	-1.63705200	-3.48488200
H	-2.81231200	-0.79252700	-3.77447200
H	-2.90005700	-2.57456200	-3.94935400
C	-3.54005200	-3.22515300	-1.35336200
H	-4.63973100	-3.23980400	-1.50621300
H	-3.12540100	-4.08210700	-1.92406900
H	-3.34093800	-3.40295200	-0.27906500
C	3.21953000	2.12586000	-1.28697000
H	2.11867900	2.24298600	-1.31538100
C	3.76673100	2.20284800	-2.73206400
H	4.87510100	2.12698600	-2.74506400
H	3.37897300	1.38913700	-3.38032300
H	3.49081500	3.17052800	-3.20198400
C	3.76649400	3.29615300	-0.44519600
H	3.35557400	3.26107400	0.58113000
H	4.87635000	3.29507700	-0.39661400
H	3.46255000	4.26145400	-0.90214400
C	1.90904100	-2.75238900	-0.14716300
H	0.92703200	-2.35261800	0.18100400
C	2.26051300	-3.91610900	0.79649200
H	3.15948700	-4.47155800	0.45443700
H	2.44759000	-3.57065500	1.83334200
H	1.42438000	-4.64491500	0.82779300
C	1.74694100	-3.28141900	-1.59265700
H	1.41522300	-2.49062400	-2.29531800
H	2.70950200	-3.68720300	-1.97047200
H	0.99708700	-4.10012000	-1.62723100
Si	-0.74021600	-0.91988100	2.48495500

C	-1.69967300	-2.35660700	1.69790500
H	-2.58705300	-1.98761700	1.14713100
H	-1.08344000	-2.96868000	1.00674000
H	-2.06084200	-3.03139100	2.50385300
C	-1.97604900	0.13156600	3.45711600
H	-2.43260800	-0.47529500	4.26869200
H	-1.46351500	0.99803700	3.91967300
H	-2.79523400	0.50129600	2.80611500
C	0.54661000	-1.66476900	3.65532600
H	1.25304800	-2.32624400	3.11381400
H	1.12756400	-0.86395000	4.15051800
H	0.03631400	-2.27404100	4.43255900
C	0.94816700	1.47444500	1.91593100
O	0.96606500	1.33813000	3.12064900
O	1.24842800	2.23591600	1.01493200

Intermediate 1

C	0.05551400	0.03757400	-0.15887000
C	-0.55319200	0.20426500	-2.34982300
C	0.80706800	0.07480800	-2.30918700
N	1.17956900	-0.04008300	-0.97459200
H	-1.23298800	0.32567800	-3.19651500
H	1.54677100	0.05384800	-3.11382200
N	0.06379500	0.12194900	1.17949800
N	-1.01991600	0.17801100	-1.03734900
C	-2.41860700	0.33681200	-0.69076000
C	-2.84507900	1.57043100	-0.12417900
C	-3.32837700	-0.72030300	-0.99244300
C	-4.20776900	1.68525200	0.22485100
C	-4.67878200	-0.53635100	-0.62985200
C	-5.11301600	0.64267000	-0.00898700
H	-4.56424000	2.62315000	0.67735700
H	-5.40557700	-1.33568200	-0.84083800
H	-6.17103100	0.75641000	0.27623500
C	2.54953700	-0.26000000	-0.54815300
C	3.48955400	0.80280500	-0.64760100
C	2.91768800	-1.56767300	-0.11934800
C	4.80777200	0.53666300	-0.21827600
C	4.24636200	-1.76446800	0.30604100
C	5.18026200	-0.71940400	0.27289000
H	5.55633800	1.34214400	-0.26945400
H	4.55979500	-2.75849200	0.65753200
H	6.21240700	-0.89315200	0.61667200
C	-1.92645100	2.78509000	0.00054000
H	-0.87174300	2.44861500	-0.03681400
C	-2.15163200	3.72585400	-1.20707100
H	-1.98066600	3.20589800	-2.17300700
H	-3.18821500	4.12669600	-1.22123500
H	-1.45296100	4.58707000	-1.15775200
C	-2.08375900	3.54516800	1.33057300
H	-1.31396300	4.34036600	1.39515200
H	-3.07745600	4.03348100	1.42754200
H	-1.93610600	2.87499100	2.20034600
C	-2.92565300	-1.98082800	-1.76825400
H	-1.82150300	-2.08379800	-1.70056000
C	-3.30046700	-1.83259700	-3.26340000
H	-4.40228900	-1.76336200	-3.38399500
H	-2.86554900	-0.92416200	-3.72620400
H	-2.95005600	-2.71131700	-3.84476500
C	-3.54664000	-3.28172600	-1.21817600
H	-4.64839200	-3.30257900	-1.35351400
H	-3.13892900	-4.15627700	-1.76659500
H	-3.33048800	-3.42504200	-0.14174400
C	3.16923900	2.16090400	-1.27522500
H	2.06688800	2.25423600	-1.32031200
C	3.74098800	2.23032900	-2.71121800
H	4.85062900	2.17333600	-2.70514400
H	3.37740700	1.40299900	-3.35678400
H	3.45667300	3.18795600	-3.19644100
C	3.67294500	3.34901200	-0.43262700
H	3.22482600	3.31401500	0.57818700
H	4.78086900	3.36792700	-0.35097100
H	3.36639500	4.30322000	-0.91066300
C	1.96030200	-2.75688400	-0.23061800
H	0.93109700	-2.37793400	-0.06164300
C	2.20960000	-3.86508900	0.80773200
H	3.16988300	-4.39364000	0.62983900
H	2.22207000	-3.46781400	1.84222100
H	1.40754800	-4.62978100	0.74757800
C	2.01009000	-3.34553100	-1.66139000
H	1.76149300	-2.58819400	-2.43235200

H	3.02455000	-3.73643600	-1.88888100
H	1.29008600	-4.18478100	-1.76595600
Si	-0.63989700	-0.88147800	2.52033900
C	-1.44929600	-2.39944000	1.71082700
H	-2.32354300	-2.09794200	1.10081400
H	-0.76224600	-2.99413700	1.07418700
H	-1.82246000	-3.07437600	2.51122800
C	-2.01399000	0.01243600	3.46096000
H	-2.44495300	-0.67028900	4.22534300
H	-1.61152000	0.90712300	3.97366700
H	-2.83511500	0.32260900	2.78170400
C	0.72692000	-1.49635600	3.67676100
H	1.64872600	-1.73048100	3.10535400
H	0.98632200	-0.71702000	4.41775000
H	0.40272100	-2.41875800	4.20545900
C	0.77128600	1.45280500	1.80351800
O	0.71276200	1.41125700	3.03400600
O	1.17079100	2.24472800	0.94583700

TS2

C	0.05755900	0.07836200	-0.26886300
C	-0.54706600	0.28847500	-2.44768400
C	0.81604300	0.18537500	-2.40598500
N	1.18826300	0.05041200	-1.07068200
H	-1.22931500	0.41507200	-3.29195600
H	1.55890000	0.18895200	-3.20814900
N	0.01332700	0.04774000	1.06968700
N	-1.01477000	0.22516000	-1.13590200
C	-2.40061200	0.42471200	-0.76334800
C	-2.76329000	1.64299100	-0.12411300
C	-3.35313700	-0.57917700	-1.10071900
C	-4.12030300	1.80784600	0.22448200
C	-4.69533800	-0.34564500	-0.73649300
C	-5.07543900	0.82589800	-0.06879400
H	-4.43291500	2.73558900	0.72779200
H	-5.45708800	-1.10283400	-0.97796500
H	-6.12836900	0.97952600	0.21617800
C	2.55268700	-0.19929700	-0.64102500
C	3.47636600	0.88051000	-0.60529100
C	2.92327700	-1.54034000	-0.34168500
C	4.79688200	0.58185600	-0.20891200
C	4.25501800	-1.76992200	0.05894000
C	5.18113000	-0.72046900	0.13289500
H	5.53666400	1.39542500	-0.16112300
H	4.57431900	-2.79281200	0.30837200
H	6.21594200	-0.92282900	0.45207700
C	-1.78249600	2.79494700	0.10294800
H	-0.74730400	2.41176300	0.00999700
C	-1.97412000	3.86999100	-0.99238100
H	-1.84390000	3.44852600	-2.01109000
H	-2.98924000	4.31909100	-0.94327700
H	-1.23420700	4.68765200	-0.86454400
C	-1.88255300	3.41046500	1.51191600
H	-1.07135500	4.15248300	1.65410700
H	-2.84898400	3.93389900	1.67471100
H	-1.76692700	2.64082500	2.30062400
C	-2.99623300	-1.84352100	-1.89038700
H	-1.89262800	-1.96418300	-1.85636300
C	-3.41328300	-1.69253600	-3.37293100
H	-4.51640000	-1.60107000	-3.46368500
H	-2.97273800	-0.79348700	-3.85061900
H	-3.09794200	-2.57952300	-3.96172000
C	-3.61262900	-3.12952000	-1.30197700
H	-4.72056100	-3.12815900	-1.37474200
H	-3.25232500	-4.01474200	-1.86649400
H	-3.33473500	-3.26537800	-0.23853500
C	3.11951600	2.30200900	-1.04167200
H	2.01389600	2.37950200	-1.03820600
C	3.63249100	2.56963100	-2.47620000
H	4.74145500	2.51773300	-2.52021500
H	3.24109700	1.83658900	-3.21231400
H	3.32947500	3.58285100	-2.81499200
C	3.63960700	3.37696400	-0.06745700
H	3.25737400	3.18446500	0.95253800
H	4.74952400	3.42108400	-0.04660600
H	3.28234300	4.37813900	-0.38818300
C	1.96603600	-2.71792300	-0.54110600
H	0.92938900	-2.33735500	-0.42703700
C	2.14312800	-3.84263400	0.49495500
H	3.11475600	-4.36774800	0.37940600
H	2.07887600	-3.45768100	1.53194200

H	1.34725300	-4.60517100	0.36730200
C	2.10202600	-3.27670300	-1.97767100
H	1.91134400	-2.49962600	-2.74597100
H	3.12481000	-3.67427000	-2.14991800
H	1.38158000	-4.10489000	-2.14614200
Si	-0.59217800	-0.93928100	2.71333800
C	-1.44883300	-2.31546000	1.65275100
H	-2.26390500	-1.88344500	1.03562400
H	-0.74702600	-2.85133900	0.97700900
H	-1.90428900	-3.07692800	2.32372400
C	-2.08606800	-0.23047900	3.65599800
H	-2.74191300	-1.05002800	4.01978700
H	-1.77133700	0.39162000	4.51749900
H	-2.70301100	0.40353100	2.98322400
C	0.60303200	-1.98220900	3.77818000
H	1.58538400	-2.08294400	3.26743200
H	0.80385800	-1.47557100	4.74433600
H	0.21437600	-3.00392900	3.97211300
C	0.72314200	1.01049100	1.87998600
O	0.49830400	0.63091300	3.10347600
O	1.33161200	1.98536800	1.44720700

IPrNCO$_2$SiMe$_3$

C	0.53969600	0.48445400	-0.34535700
C	0.51415600	2.61787400	-1.16730100
C	1.82265000	2.25572800	-1.01485800
N	1.84120200	0.95441700	-0.50240800
H	0.06503000	3.53746000	-1.55300000
H	2.74765500	2.80028600	-1.22515700
C	-0.78887500	-1.11771900	0.78831200
O	-1.32496200	-0.43725300	1.67615800
O	-1.15589500	-2.41414600	0.56543000
Si	-2.32507500	-3.21105300	1.57370600
N	0.25044700	-0.74925500	-0.01396100
C	-4.01126600	-2.38153900	1.41190900
H	-4.78038100	-2.93439800	1.99290400
H	-3.96329900	-1.33953800	1.78549500
H	-4.33878200	-2.35306500	0.35169800
C	-2.35981700	-4.94730600	0.83382800
H	-1.35598900	-5.41920400	0.87534300
H	-3.06753800	-5.59997300	1.38816800
H	-2.67983700	-4.92425700	-0.22883800
C	-1.71193200	-3.25515200	3.35706100
H	-0.70803300	-3.72528900	3.41843400
H	-1.63964500	-2.22664500	3.76323300
H	-2.40362800	-3.84252100	3.99830200
N	-0.28003600	1.54136500	-0.74774400
C	-1.71837200	1.50755100	-0.85304400
C	-2.49290500	2.19273700	0.12288100
C	-2.30847300	0.82509800	-1.95108900
C	-3.89305200	2.18842800	-0.03623100
C	-3.71604800	0.83951400	-2.04787000
C	-4.50176700	1.51652800	-1.10587000
H	-4.51987500	2.71389800	0.70137500
H	-4.20316400	0.31632000	-2.88621000
H	-5.59910500	1.52005600	-1.20501900
C	3.01656700	0.23295600	-0.08230400
C	3.55105700	0.50277100	1.20740400
C	3.59773200	-0.71432900	-0.96529200
C	4.70315000	-0.21081300	1.59680700
C	4.74804200	-1.39954600	-0.52193200
C	5.29653100	-1.15216700	0.74356900
H	5.14134400	-0.02907600	2.59049500
H	5.21992400	-2.14469100	-1.18189300
H	6.19505500	-1.69989700	1.07023100
C	-1.85875900	2.93478200	1.29915000
H	-0.78525700	2.65604400	1.32221400
C	-1.94894700	4.46470800	1.10337200
H	-1.47216600	4.79251100	0.15606400
H	-3.00627700	4.80528800	1.07742000
H	-1.44564100	4.99666600	1.93835600
C	-2.46064800	2.50427300	2.65174800
H	-1.92709400	3.00919700	3.48475500
H	-3.53347100	2.78060400	2.73578300
H	-2.35851800	1.40968300	2.77972200
C	-1.48484800	0.11004900	-3.02316400
H	-0.41379700	0.21716600	-2.75509600
C	-1.67516500	0.76845000	-4.40715900
H	-2.72437300	0.68021700	-4.76108000
H	-1.41905300	1.84809800	-4.38541300
H	-1.02681600	0.27838500	-5.16395300

C	-1.79247900	-1.40161700	-3.06566100
H	-2.84833800	-1.59379000	-3.35356200
H	-1.14735700	-1.90622100	-3.81541900
H	-1.60772200	-1.87518300	-2.08061500
C	2.89013700	1.48920300	2.17245100
H	2.21097800	2.13613200	1.57790100
C	3.90767800	2.41978400	2.86257500
H	4.57099300	1.86760800	3.56155400
H	4.55354400	2.94282200	2.12694000
H	3.37769500	3.18971000	3.46132700
C	2.01770400	0.74381400	3.20860900
H	1.19743800	0.17609300	2.72509900
H	2.62893400	0.03124600	3.80259200
H	1.55554200	1.46532900	3.91525000
C	3.00030900	-1.02798400	-2.33597400
H	2.19116700	-0.29062500	-2.52138400
C	2.35095300	-2.42964900	-2.33832100
H	3.10857300	-3.22275700	-2.15968700
H	1.57482400	-2.49868500	-1.54989400
H	1.87456500	-2.63586300	-3.32036000
C	4.03156300	-0.87157800	-3.47252900
H	4.48752200	0.14040500	-3.47834500
H	4.85599000	-1.61106100	-3.38733900
H	3.54756500	-1.03407900	-4.45852700

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