Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Catalytic Oxidative Coupling Promoted by Bismuth TEMPOxide Complexes

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Contents

Synthetic Procedures

General

All manipulations were performed under dry nitrogen using standard Schlenk-line techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300.1 (^{1}H) and 75.4 (^{13}C) MHz or a Varian DirectDrive 600 MHz spectrometer equipped with a triple-resonance HCN cryogenic probe operating at 25 K, operating at 600.1 (^{1}H) and 150.9 (^{13}C) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University. Bi(NON^{Ar}) (**1a**$^{\bullet}$)[S1] and [Bi(NON$^{t\text{Bu}}$)]$_2$ ([**1b**]$_2$)[S2] were prepared according to published procedures.

*Synthesis of Bi(NON^{Ar})(OTEMP) (**2a**)*

A solution of TEMPO (0.023 g, 0.15 mmol.) in hexane (5 mL) was added drop wise to a solution of **1a** (0.10 g, 0.15 mmol.) in hexane (5 mL) resulting in an immediate colour change from deep red to orange. The resulting solution was concentrated *in vacuo* to ca. 1 mL and stored at –30 °C overnight to give orange crystals of **2a**. Yield 0.079 g (64 %)

Anal. Calcd. for $C_{37}H_{64}BiN_3O_2Si_2$ (*848.09*): C, 52.40; H, 7.61; N, 4.95 %. Found C, 52.36; H, 7.57; N, 5.10 %.

^{1}H NMR (C_7D_8, 300 MHz, 263 K): δ 7.23 (d, *J* = 7.6 Hz, 2H, *m*-C_6H_3)*, 6.93 (t, *J* = 7.6 Hz, 2H, *p*-C_6H_3), 4.05, 3.77 (sept, *J* = 6.7 Hz, 2H, C*H*Me$_2$), 1.62 (d, *J* = 6.7 Hz, 6H, CH*Me$_2$*), 1.37 (m, 12H, CH*Me$_2$*), 1.25 (d, *J* = 6.7 Hz, 6H, C*H*Me$_2$), 1.11 (br, 6H, C*Me$_2$*), 0.91 (br, 6H, C*Me$_2$*), 0.55, 0.33 (s, 6H, Si*Me$_2$*).

^{1}H NMR (C_7D_8, 300 MHz, 313 K): δ* 7.00 (t, *J* = 7.6 Hz, 2H, *p*-C_6H_3), 3.90 (br, 4H, C*H*Me$_2$), 1.48 (br, 12H, C*Me$_2$*), 1.28 (d, *J* = 6.7 Hz, 18H, CH*Me$_2$*), 0.41 (s, 6H, Si*Me$_2$*).

* *m*-C_6H_3 resonances overlapping with D_8-toluene resonances

^{13}C NMR (C_6D_6, 300 MHz, 298 K): 141.7, 125.5, 124.3 (br) (*C$_6$*H$_3$)*, 35.4, 29.0, 28.7, 26.1 (br), 25.3, 24.6 (CH*Me$_2$*, *C*HMe$_2$, C*Me$_2$*, *C*Me$_2$, *C*H$_2$), 3.79 (Si*Me$_2$*).

* one *C$_6$*H$_3$ resonance not observed

*Synthesis of Bi(NON^{tBu})(OTEMP) (**2b**)*

A solution of TEMPO (0.049 g, 0.32 mmol.) in hexane (5 mL) was added dropwise to a solution of **1b** (0.15 g, 0.16 mmol.) in hexane (5 mL) resulting in an immediate colour change from orange-red to pale yellow. The resulting solution was concentrated *in vacuo* to ca. 1 mL and stored at –30 °C overnight to give orange crystals of **2b**. Yield 0.164 (82 %)

Anal. Calcd. for $C_{37}H_{64}BiN_3O_2Si_2$ (639.78): C, 39.42; H, 7.56; N, 6.57. Found C, 39.43; H, 7.68; N, 6.43.

^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 1.48 (br, 4H, C*H*$_2$), 1.27 (br, 2H, C*H*$_2$), 1.32 (br, 12H, CMe$_2$) 1.27 (s, 18H, C*Me*$_3$), 0.55, 0.43 (s, 6H, Si*Me*$_2$)

^{1}H NMR (C_6D_6, 600 MHz, 333 K): δ 1.48 (d, *J* = 7.6 Hz, 4H, C*H*$_2$), 1.41 (br, 2H, C*H*$_2$) 1.32 (br, 12H, CMe$_2$) 1.27 (s, 18H, C*Me*$_3$), 0.50, 0.41 (s, 6H, Si*Me*$_2$).

^{13}C NMR (C_6D_6, 600 MHz): δ 59.9 (*C*Me$_2$), 53.1 (*C*Me$_3$), 40.6 (*C*H$_2$)*, 37.3 (C*Me*$_3$), 17.6 (*C*H$_2$), 8.2, 6.5 (Si*Me*$_2$)

* two overlapping *C*H$_2$ resonances

General procedure for catalytic studies

1a (0.011 g, 0.013 mmol.) or **1b** (0.008 g, 0.013 mmol.) was added to a Young's NMR tube containing a mixture of TEMPO (0.020 g, 0.13 mmol.) and $PhSiH_3$ (0.005 g, 0.13 mmol.) in C_6D_6 (0.5 mL). The reaction mixture was heated to 70 °C and monitored at regular intervals using ^1H NMR spectroscopy.

Figure S1 VT ^{1}H NMR spectra of Bi(NON^{Ar})(OTEMP) (**2a**) in C_7D_8

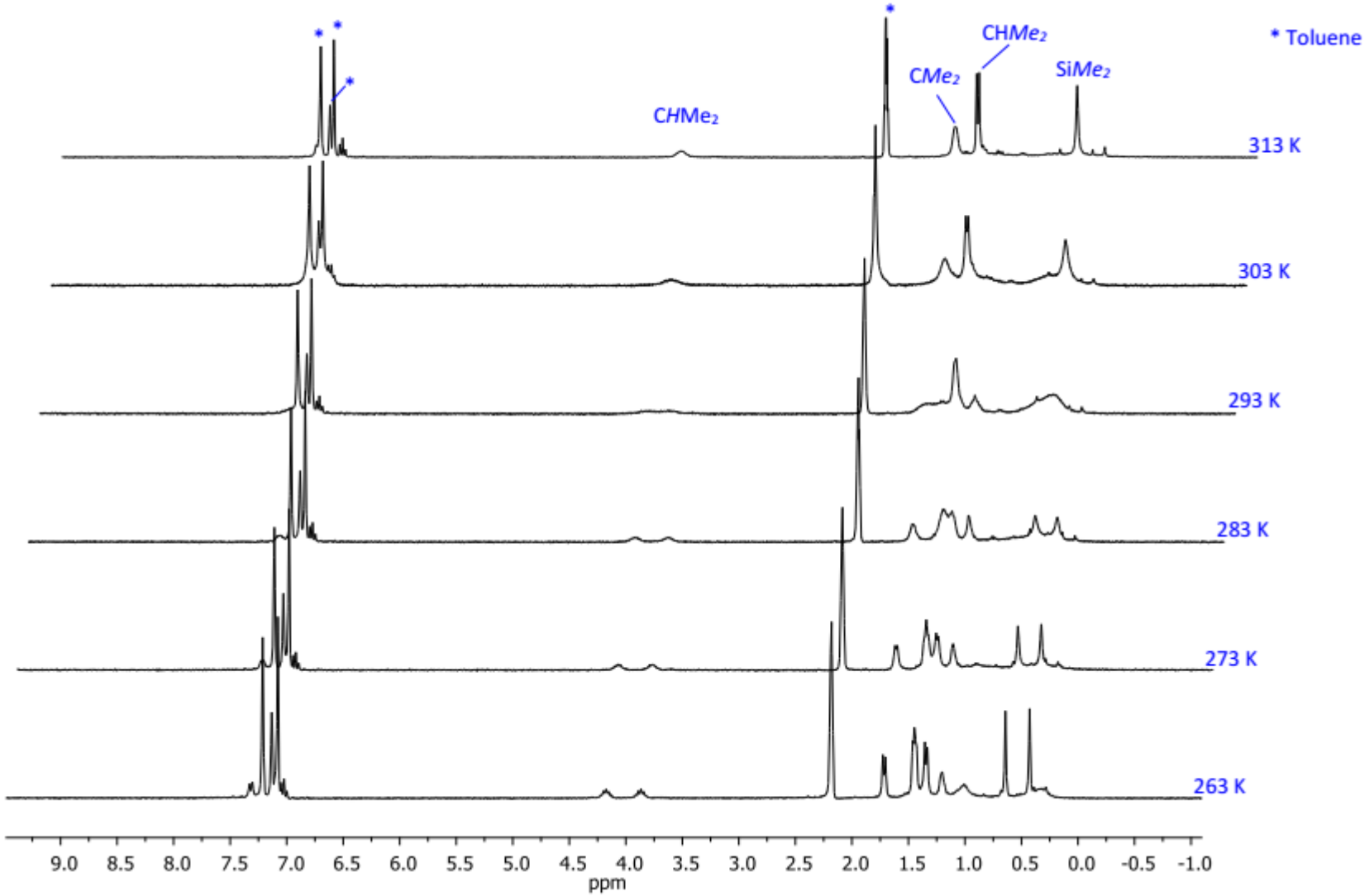


Figure S2 ^{1}H NMR spectra of Bi(NON$^{t\mathrm{Bu}}$)(OTEMP) (**2b**) in C_6D_6 at 298 K (top) and 333 K (bottom)

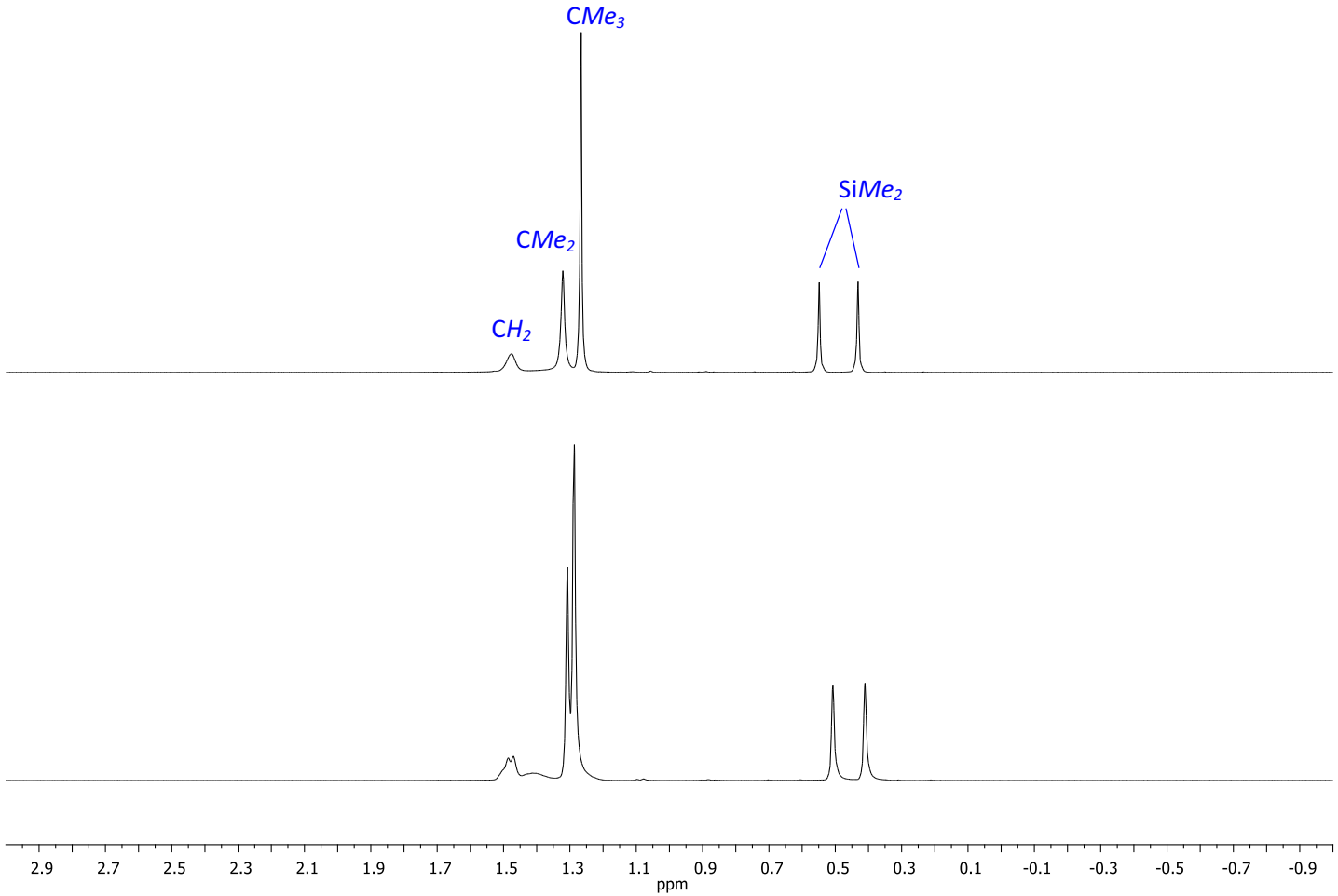


Figure S3 VT ^{1}H NMR spectra of a mixture of Bi(NON^{Ar})$^{\bullet}$ (**1a**$^{\bullet}$) and Bi(NON^{Ar})(OTEMP) (**2a**) in C_6D_6

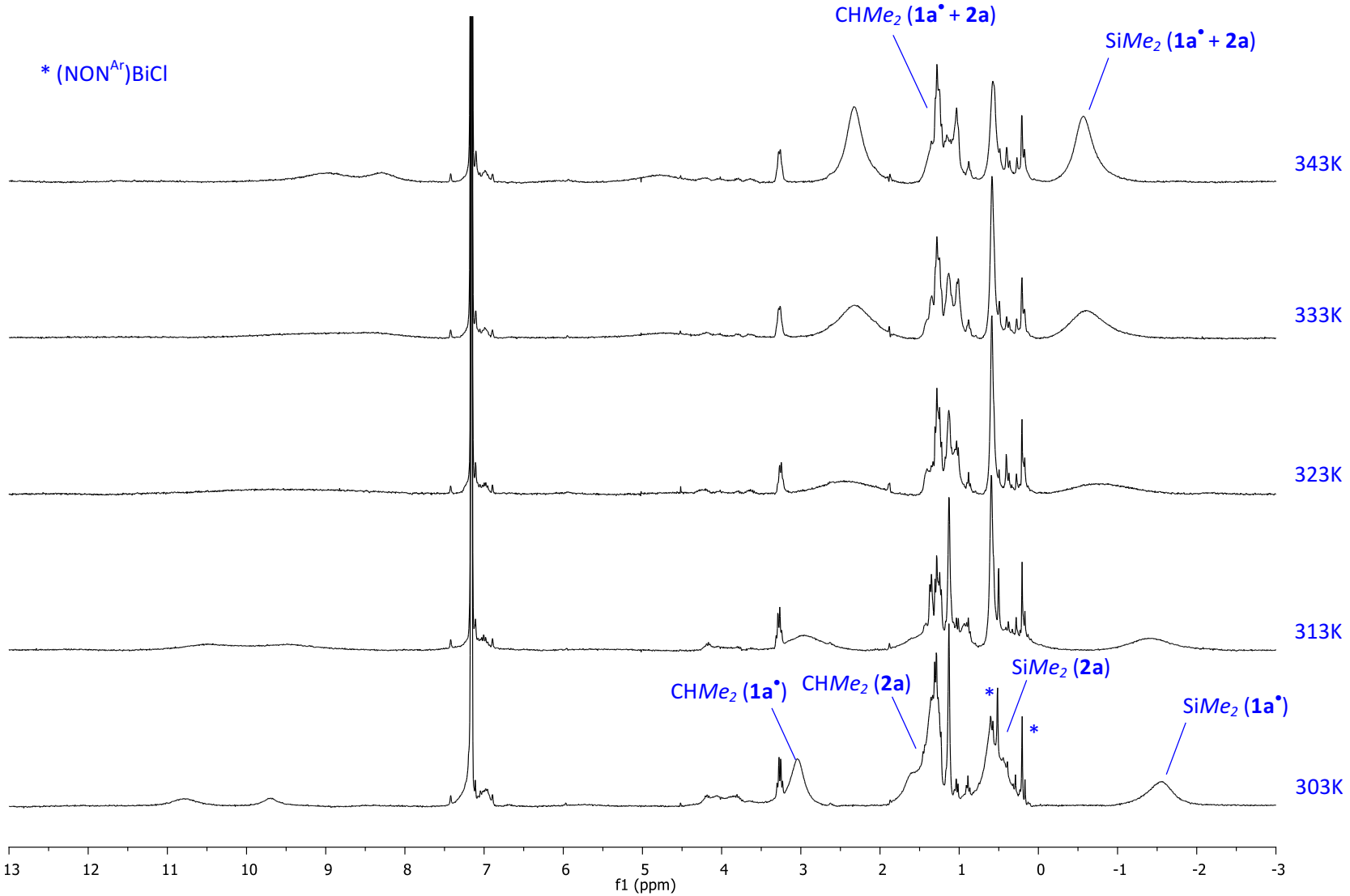


Figure S4 ^{1}H NMR spectra of a mixture of Bi(NON$^{t\text{Bu}}$)(OTEMP) (**2b**) and [Bi(NON$^{t\text{Bu}}$)]$_2$ ([**1b**]$_2$) at 298 K (bottom) and 343 K (top)

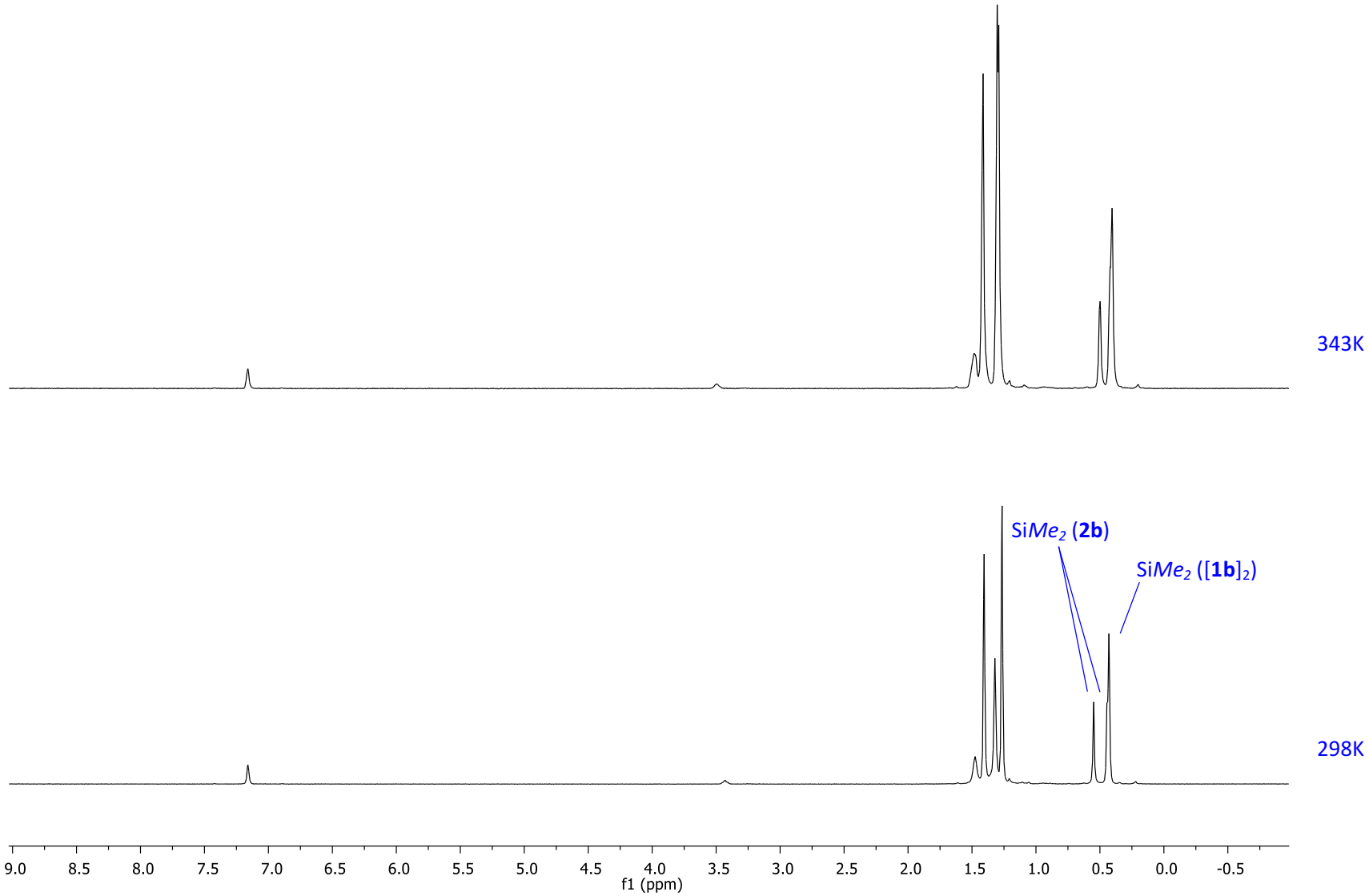


Figure S5 ^{1}H NMR spectrum of the irreversible reaction of Bi(NON^{Ar})(TEMPO) (**2a**) and [Bi(NON^{tBu})]$_2$ ([**1b**]$_2$)

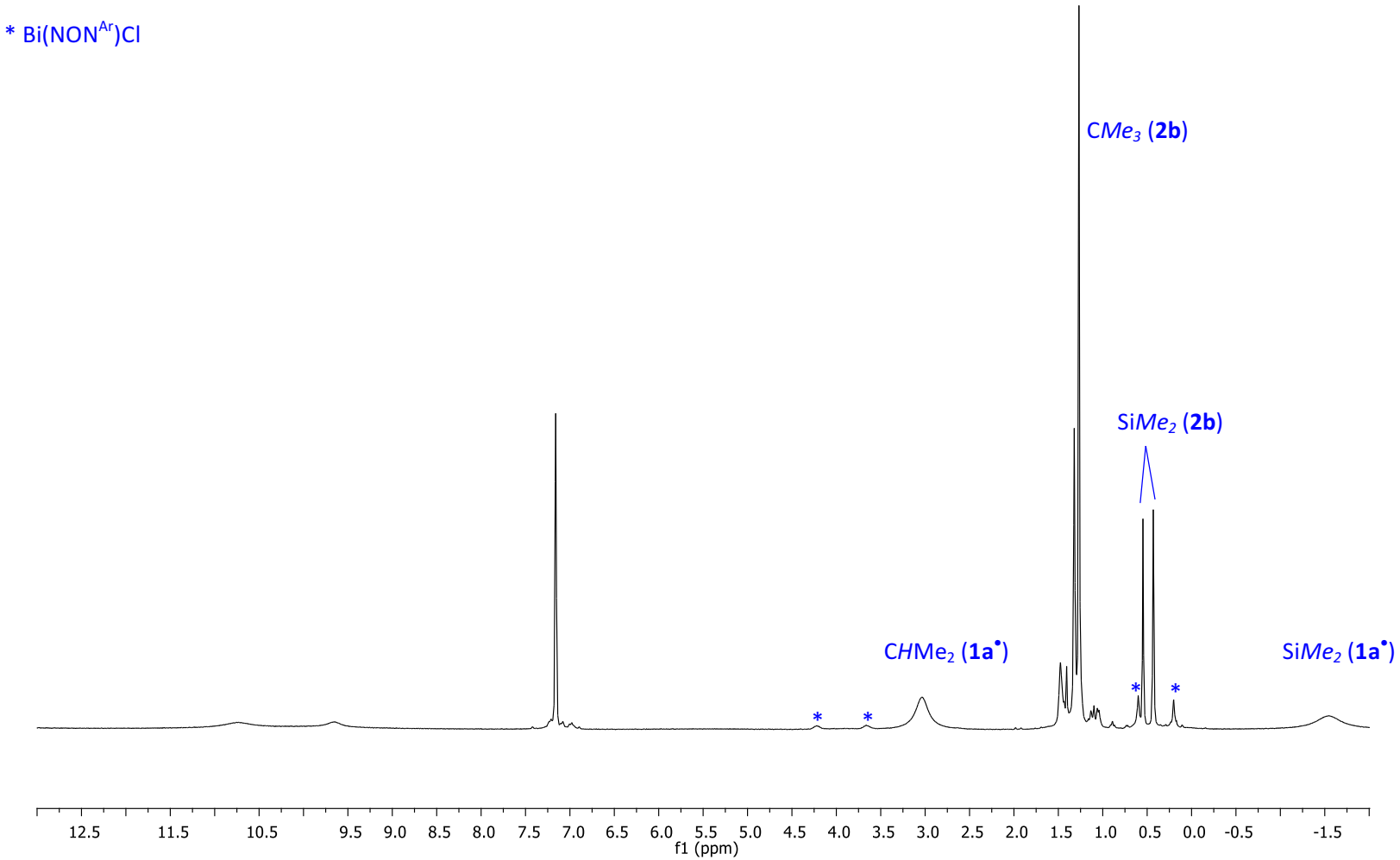


Figure S6 ^{1}H NMR spectra of dehydrosilylation catalysis initiated by Bi(NON^{Ar})(OTEMP) (**2a**) (10 mol%) at 343 K in C_6D_6

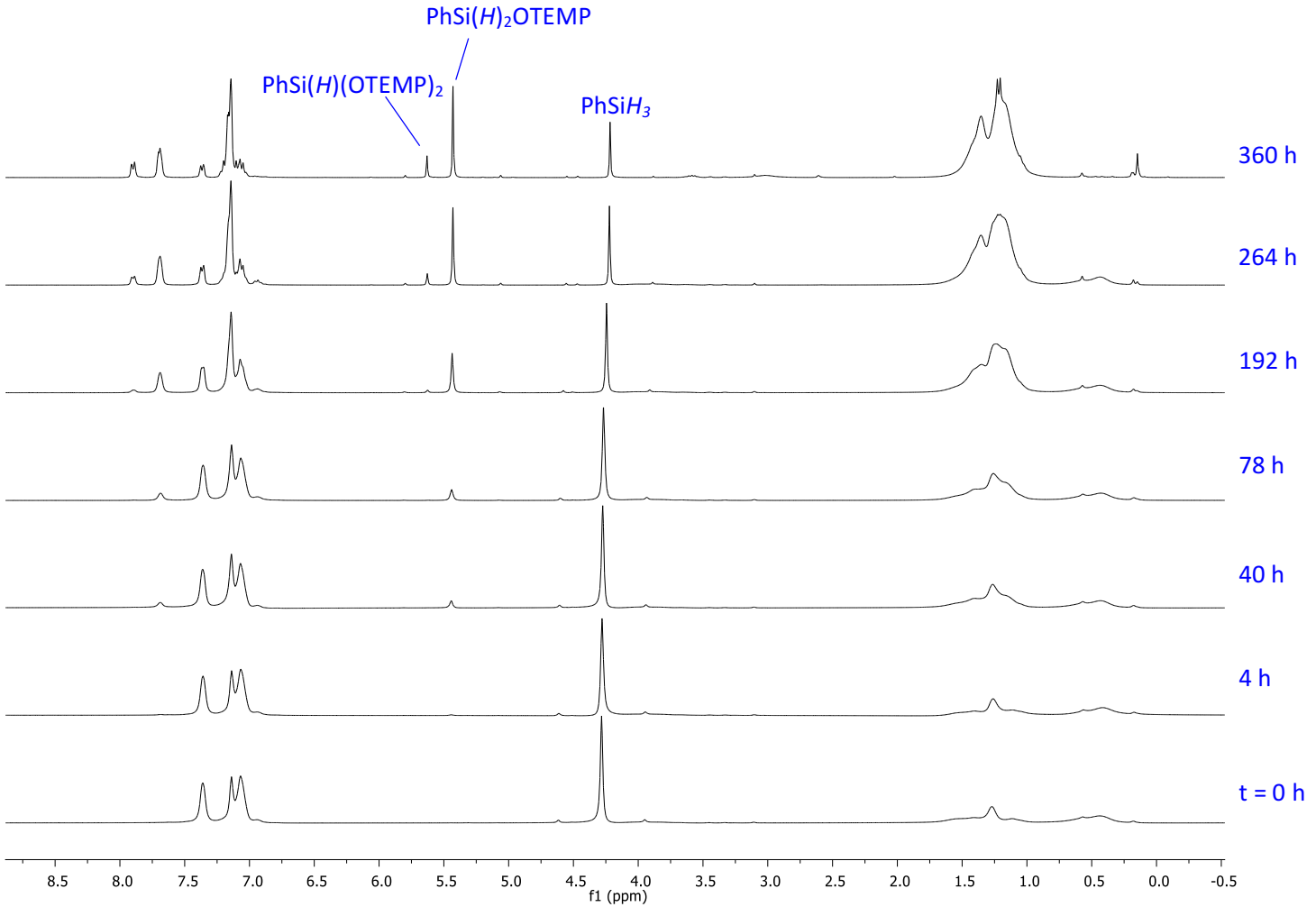


Figure S7 Plot of product formation from the catalytic dehydrosilylation initiated by Bi(NON^{Ar})(OTEMP) (**2a**) (10 mol%)

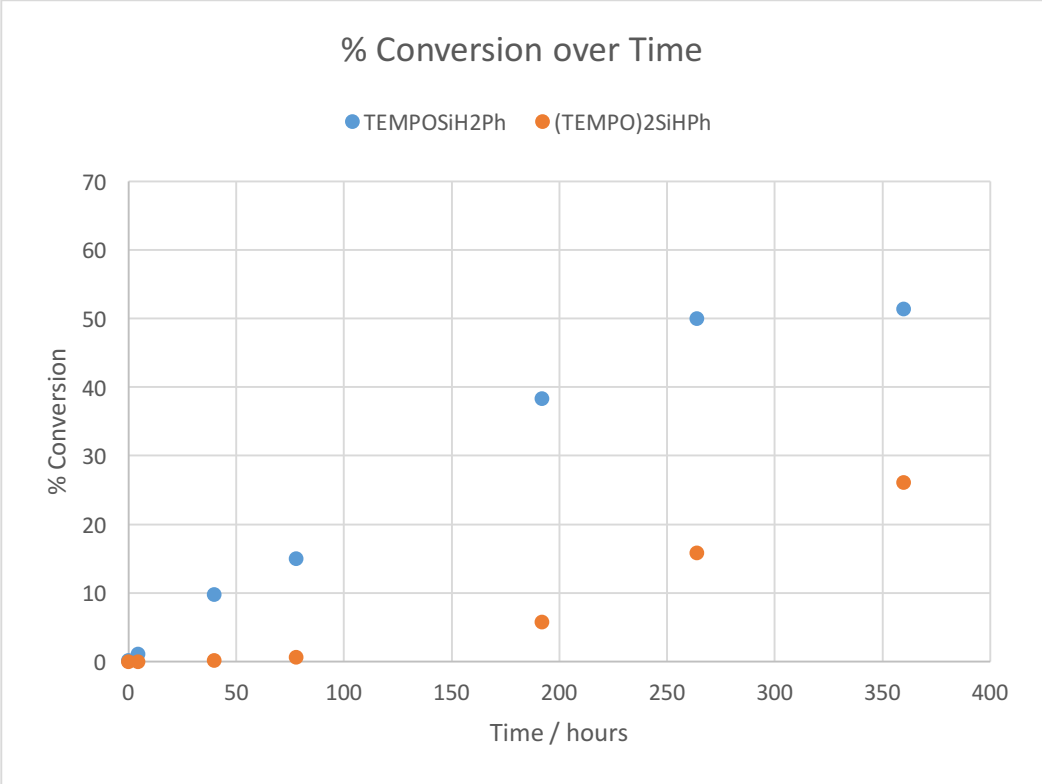


Figure S8 ^{1}H NMR spectra of dehydrosilylation catalysis initiated by Bi(NON^{tBu})(OTEMP) (**2b**) (10 mol%) at 343 K in C_6D_6

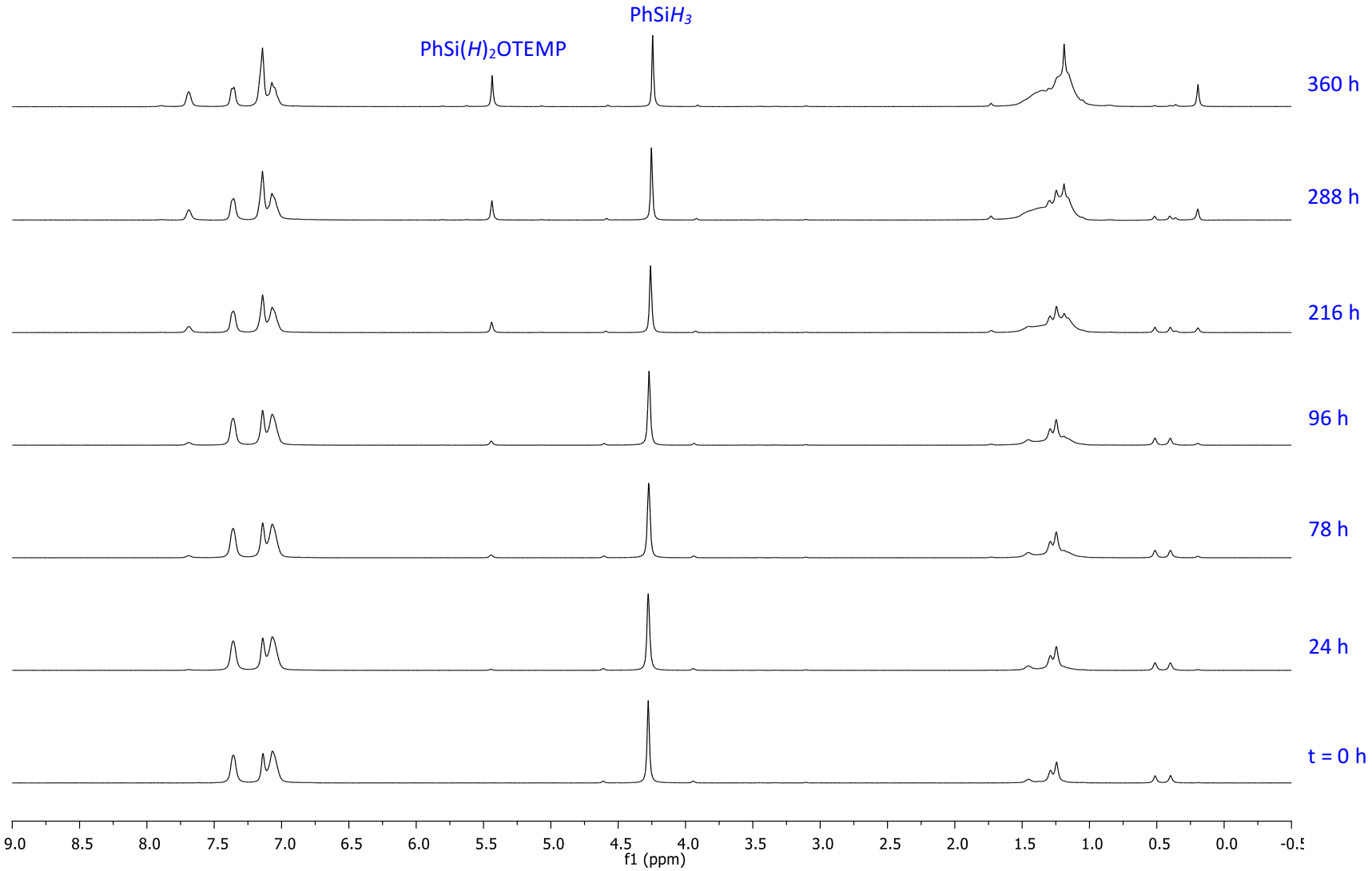
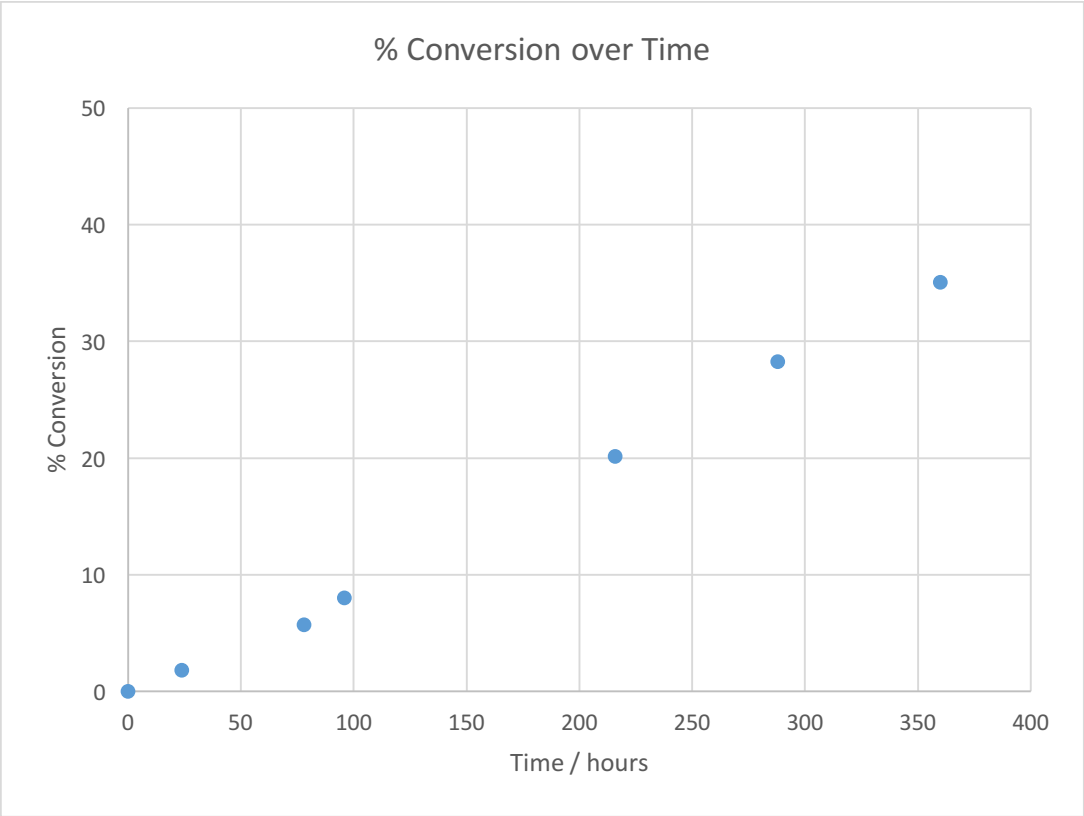


Figure S9 Plot of product formation from the catalytic dehydrosilylation initiated by Bi(NON^{tBu})(OTEMP) (**2b**) (10 mol%)



Calculation for Gibbs free energy[S3]

The rate constant (k_C) at coalescence temperature (T_C) can be approximated by:

$$k_c = \frac{\pi(\Delta\delta)}{\sqrt{2}} \qquad \text{(eq. 1)}$$

where:

Δδ=difference in chemical shift (in Hz) at the slow exchange limit

Using the Eyring equation, the free energy of activation ($\Delta G^{\ddagger}$) can be calculated:

$$k_c = \frac{kT_c}{h} e^{(-\Delta G^{\ddagger}/RT_c)} \qquad \text{(eq. 2)}$$

where:

k = Boltzmann constant (1.381×10^{-23} J K^{-1})

h = Planck constant (6.626×10^{-34} J s)

R = gas constant (8.314 J mol^{-1} K^{-1})

T_c = coalescence temperature (K)

Substitution of the fundamental constants gives the equation:

$$\Delta G^{\ddagger} = (1.914\times10^{-2})(T_C)[10.319 + \log_{10}\left(\frac{T_c}{k_c}\right)]$$

Calculation of Gibbs free energy of activation: concentration dependence

Concentration: 0.0118 mol L^{-1}

The coalescence temperature (T_c) was found to be approximately 26 °C (299 K). The lowest exchange limit is found at – 40 °C with the two proton resonances for the C*H*Me_2 separated by Δδ 67.4 Hz.

$$k_c = \frac{\pi(67.4)}{\sqrt{2}}$$

$$k_c = 149.72\ s^{-1}$$

The free energy of activation ($\Delta G^{\ddagger}$) can be calculated using eq. 2:

$$\Delta G^{\ddagger} = (1.914\times10^{-2})(299)[10.319 + \log_{10}\left(\frac{299}{149.72}\right)]$$

$$\boldsymbol{\Delta G^{\ddagger} = 60.77\ kJ\ mol^{-1}}$$

Concentration: 0.0236 mol L^{-1}

The coalescence temperature (T_c) was found to be approximately 23 °C (296 K). The lowest exchange limit is found at – 40 °C with the two proton resonances for the C*H*Me_2 separated by Δδ 64.4 Hz.

$$k_c = \frac{\pi(64.4)}{\sqrt{2}}$$

$$k_c = 143.06\ s^{-1}$$

The free energy of activation ($\Delta G^{\ddagger}$) can be calculated using eq. 2:

$$\Delta G^{\ddagger} = (1.914\times10^{-2})(296)[10.319 + \log_{10}\left(\frac{296}{143.06}\right)]$$

$$\boldsymbol{\Delta G^{\ddagger} = 60.25\ kJ\ mol^{-1}}$$

Concentration: 0.0354 mol L^{-1}

The coalescence temperature (T_c) was found to be approximately 24 °C (297 K). The lowest exchange limit is found at – 40 °C with the two proton resonances for the C*H*Me_2 separated by Δδ 66.9 Hz.

$$k_c = \frac{\pi(66.9)}{\sqrt{2}}$$

$$k_c = 148.61\ s^{-1}$$

The free energy of activation ($\Delta G^{\ddagger}$) can be calculated using eq. 2:

$$\Delta G^{\ddagger} = (1.914\times10^{-2})(297)[10.319 + \log_{10}\left(\frac{297}{148.61}\right)]$$

$$\boldsymbol{\Delta G^{\ddagger} = 60.37\ kJ\ mol^{-1}}$$

Calculation of Gibbs free energy of activation: solvent dependence

THF

Concentration: 0.0118 mol L^{-1}

The coalescence temperature (T_c) was found to be approximately 16 °C (289 K). The lowest exchange limit is found at – 40 °C with the two proton resonances for the C*H*Me_2 separated by Δδ 51.58 Hz.

$$k_c = \frac{\pi(51.58)}{\sqrt{2}}$$

$$k_c = 162.04\ s^{-1}$$

The free energy of activation ($\Delta G^{\ddagger}$) can be calculated using eq. 2:

$$\Delta G^{\ddagger} = (1.914\times10^{-2})(289)[10.319 + \log_{10}\left(\frac{289}{162.04}\right)]$$

$$\boldsymbol{\Delta G^{\ddagger} = 58.47\ kJ\ mol^{-1}}$$

Crystallography

Crystals were covered in inert oil and suitable single crystals were selected under a microscope and mounted on an Agilent SuperNova diffractometer fitted with an Atlas (**2a**) or EOS S2 (**2b**) detector. Data were collected at the temperature indicated using focused microsource Mo Kα radiation at 0.71073 Å. Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods.[S4] Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS,[S5] refined on F^2 using all data by full matric least-squares procedures with SHELXL-97,[S6] within OLEX-2.3,[S7] or WinGX.[S8] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate unless otherwise stated. The functions minimized were Σw(F2o-F2c), with w = [σ2(F2o) + *a*P2 + *b*P]-1, where P = [max(Fo)2 + 2F2c]/3. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Notes:

2b: The molecule lies on a mirror plane. The methyl carbon atoms of the *t*Bu group are disordered and were modelled over two positions. The anisotropic displacement factors of the carbon atoms were constrained to be equal for each component using the EADP command.

Table S1 Crystal structure and refinement data for Bi(NON^{Ar})(OTEMP) (**2a**) and Bi(NON^{tBu})(OTEMP) (**2b**)

	2a	**2b**
CCDC number	1582724	1582725
Empirical formula	$C_{37}H_{64}BiN_3O_2Si_2$	$C_{21}H_{48}BiN_3O_2Si_2$
M_r	848.07	639.78
Radiation (wavelength [Å])	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
T [K]	120.0(1)	120.0(1)
Crystal size [mm]	0.20 × 0.09 × 0.06	0.47 × 0.29 × 0.22
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$ (No.2)	*Pnma* (No. 62)
a [Å]	9.8235(5)	11.8697(3)
b [Å]	11.3232(4)	17.1607(4)
c [Å]	19.8873(11)	13.7508(3)
α [°]	96.254(3)	90
β [°]	91.689(4)	90
γ [°]	115.381(4)	90
V [Å^3]	1979.57(18)	2800.94(11)
Z	2	4
$D_{calc.}$ [mg m^{-3}]	1.423	1.517
Absorption coefficient [mm^{-1}]	4.547	6.4
2θ range for data collection [°]	6.9248 to 52.7428	7.1236 to 58.6874
Reflections collected	12880	8659
Independent reflections (R_{int})	7996 (0.0458)	3412 (0.0276)
Data/restraints/parameters	7996 / 0 / 410	3412 / 0 / 139
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.038 wR_2 = 0.083	$R1$ = 0.024 wR_2 = 0.050
Final R indices (all data)	$R1$ = 0.045 wR_2 = 0.087	$R1$ = 0.031 wR_2 = 0.052
GOOF on F^2	1.027	1.036
Largest diff. peak/hole [e.Å^{-3}]	5.02* and –1.50	0.75 and –1.20

* close to bismuth

Figure S10 ORTEP of Bi(NON^{Ar})(OTEMP) (**2a**). Ellipsoids at 30 % probability (hydrogen atoms omitted)

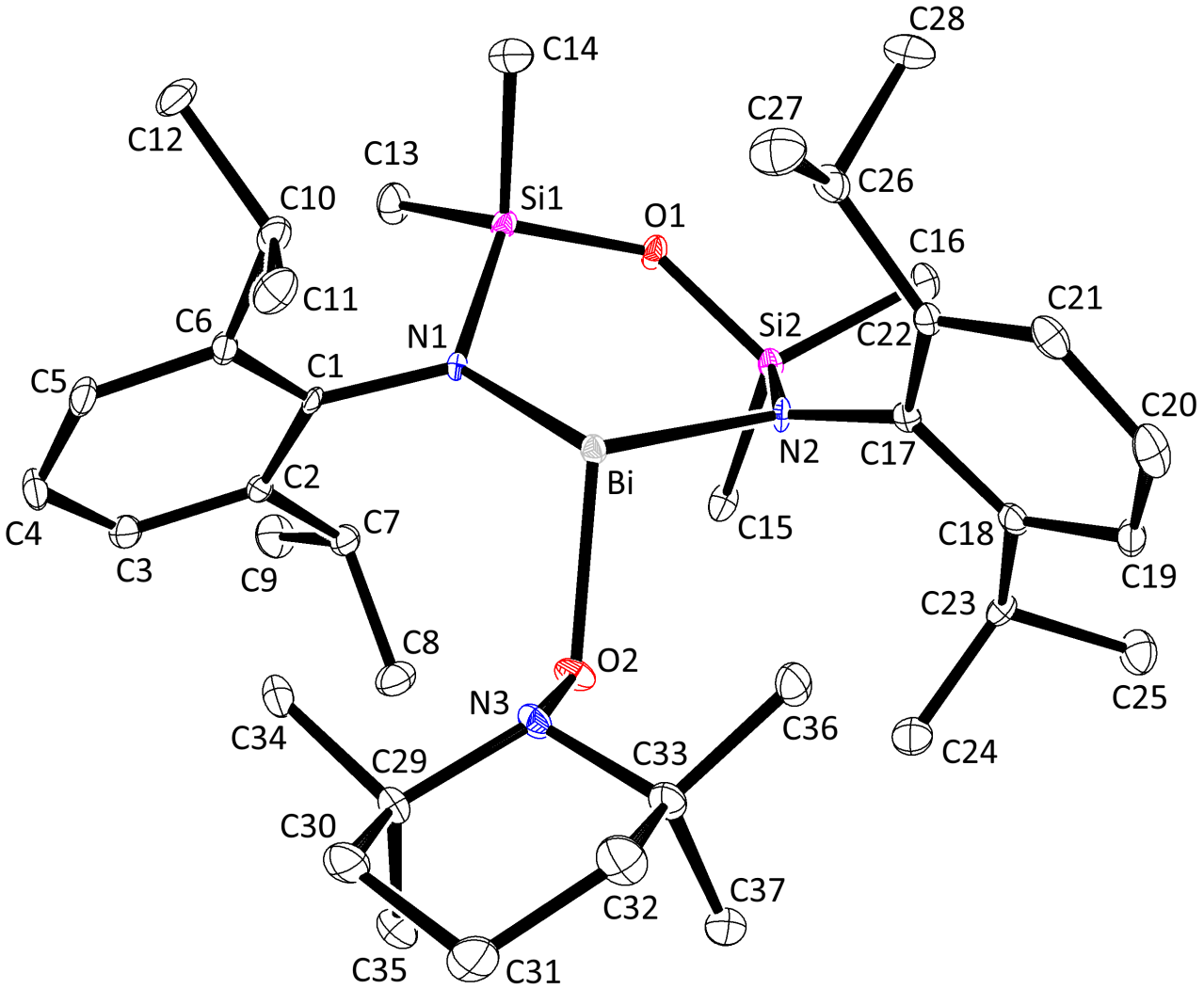
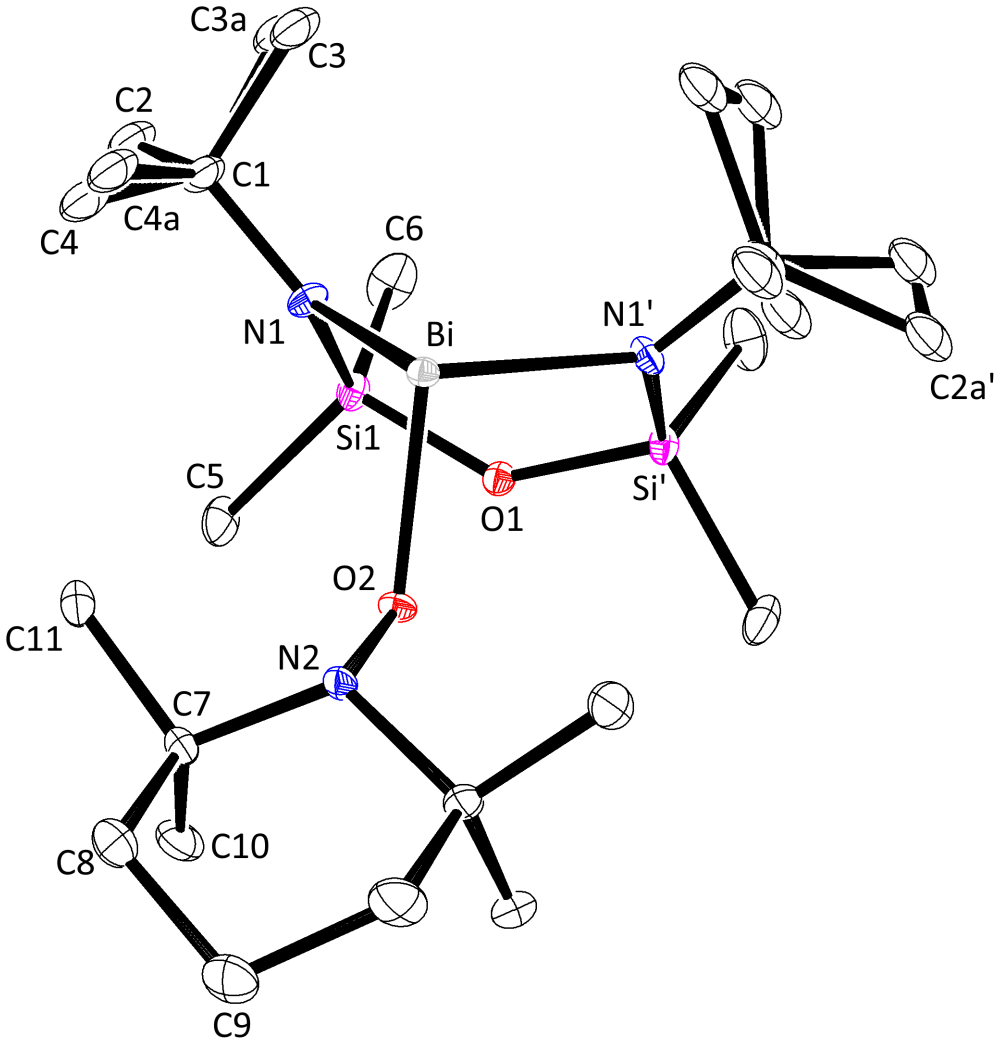


Figure S11 ORTEP of Bi(NON^{tBu})(OTEMP) (**2b**). Ellipsoids at 30 % probability (' = *x*, 3/2–*y*, *z*, hydrogen atoms omitted)



Computational Methods

General

All structural optimisations were carried out with the Gaussian 09 suite of programs (Revision D.01)[S9] using the density functional method (DFT) with the PBE0 hybrid functional[S10] and the balanced, polarised def2-TZVP basis-set[S11] of triple-ζ quality. Frequency calculations at the same level of theory were employed to ensure that the obtained structures are minima on the potential energy surface.

The bonding was analysed using the Natural Bond Orbital (NBO) approach[S12] using the NBO 6.0 program[S13] and Wiberg Bond Indices (WBI) were computed.[S14]

Additional Morokuma-Ziegler Energy Decomposition Analyses (EDA)[S15] were carried out at the previously obtained structures with the ADF2014 program.[S16] The PBE functional[S17] and the TZ2P (Slater Type Orbital) basis set[S18] were employed along with the relativistic ZORA Hamiltonian.[S19]

Molecular and MO graphics and were rendered with GaussView 5.0.9[S20] and CYLview (Build 561).[S21]

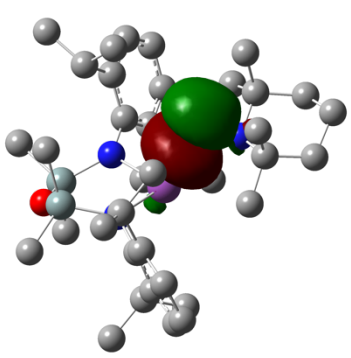
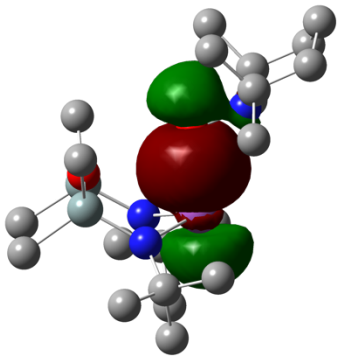
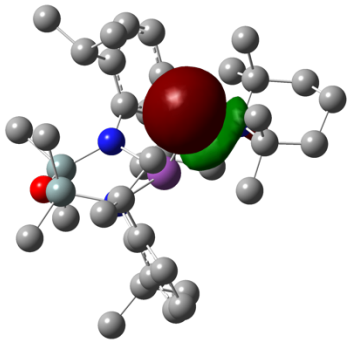
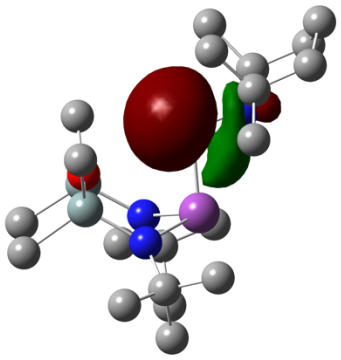
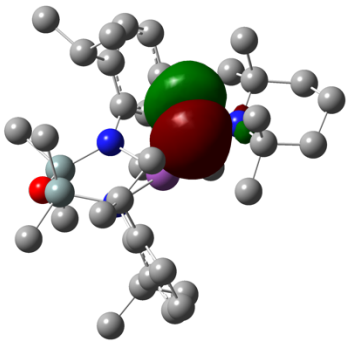
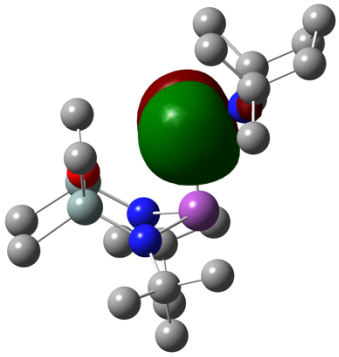
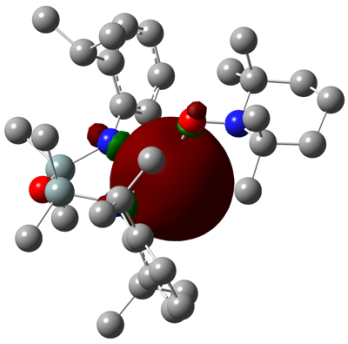
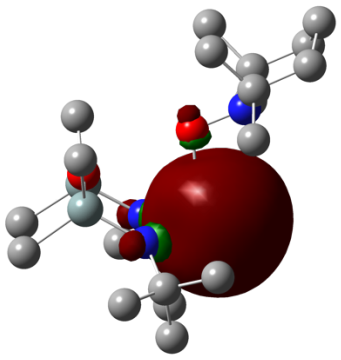
NBO Analysis

Natural Bond Orbitals (NBOs) are orbitals that have been localised to one or two nuclei (or in the case of multiple centre bonds or strong delocalisation, more than two nuclei) with the additional condition to maximise the density (the occupation) of these orbitals. Hence, NBOs are the molecular orbital analogue of finding the Lewis structure, *i.e*. assigning electron pairs to atoms as either "core electrons" or "lone pairs") and bonds in optimally compact form.

Table S2 Results of the Natural Bond Orbital (NBO) analysis for Bi(NON^{R})(OTEMP).

	Bi(NON^{Ar})(OTEMP) (**2a**)	Bi(NON^{tBu})(OTEMP) (**2b**)
r(Bi,O)	2.12 Å	2.15 Å
WBI(Bi,O)	0.38	0.47
Bi−O (bond)	*n/a*	**Bi** : 13.0 % = 4.2 % *s*-; 94.9 % *p*- **O** : 87.0 % = 18.4 % *s*-; 81.5 % *p*-
Bi (lone-pair)	92.7 % *s*-; 7.2 % *p*-	87.9 % *s*-; 12.1 % *p*-
O (lone-pair)	14.2 % *s*-; 85.7 % *p*- 99.9 % *p*- 99.9 % *p*-	13.7 % *s*-; 86.2 % *p*- 99.9 % *p*-

Figure S12 Plots of the Natural Bonding Orbitals of Bi(NON^{Ar})(OTEMP) (**2a**) and Bi(NON^{tBu})(OTEMP) (**2b**). Hydrogen atoms have been omitted for clarity.

Bi(NON^{Ar})(OTEMP) (**2a**)	Bi(NON^{tBu})(OTEMP) (**2b**)
	
	
	
	

Energy Decomposition Analyses

In general, the interaction energy ΔE_{int} between two systems can be calculated as the difference between the energies of the individual systems E_1 and E_2 and the energy of the entire system where both fragments are in contact E_{total}.

$$\Delta E_{int} = E_{total} - (E_1 + E_2)$$

In the case of a chemical bond (*e.g.* a covalent bond, a donor-acceptor bond, or weak molecular interactions) that is being described within the realm of molecular orbital theory (*e.g.* Kohn-Sham DFT or *ab-initio* wave function methods), the interaction energy ΔE_{int} can be decomposed into individual contributions to the total value. In the case of the Morokuma-Ziegler Energy Decomposition Analysis (MZ-EDA) these term describe electrostatic interactions, Pauli repulsive orbital interactions, and attractive orbital interactions:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

The term ΔE_{elstat} corresponds to the classical electrostatic interaction between the two charge distributions (electrons and nuclei) of the fragments in the structure they assume in the interacting complex and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing 4-electron repulsive interactions between occupied orbitals and is equated with repulsive steric interactions. ΔE_{Pauli} is calculated by orthonormalising the two molecular wave functions after ΔE_{elstat} has been determined. The orbital interaction ΔE_{orb} is then determined by allowing the molecular wave function to relax to its optimal value in an SCF procedure. ΔE_{orb} represents the energy change by allowing the two fragment wave functions to mix and hence includes effects such as charge transfer (*i.e.* interactions between occupied orbitals on one fragment with unoccupied orbitals on the other; specifically including the HOMO-LUMO interactions) and polarization (*i.e.* orbital mixing on one fragment due to the presence of the other) and is usually attractive.

Table S3 Results of the Energy Decomposition Analyses (EDA) for the "covalent" interaction. All energies in kcal/mol. The total interaction energy of the two fragments is given by the interaction energy $\Delta E_{int.}$ which is the sum of the Pauli repulsion ΔE_{Pauli}, the electrostatic interaction ΔE_{elstat} and the orbital interaction ΔE_{orb}.

	Bi(NON^{Ar})(OTEMP) (**2a**)	Bi(NON^{tBu})(OTEMP) (**2b**)
ΔE_{Pauli}	213.02	214.30
ΔE_{elstat}	−119.35	−119.52
ΔE_{orb}	−131.92	−134.37
ΔE_{int}	**−38.26**	**−39.59**

Table S4 Results of the Energy Decomposition Analyses (EDA) for for the "ionic" interaction. All energies in kcal/mol. The total interaction energy of the two fragments is given by the interaction energy $\Delta E_{int.}$ which is the sum of the Pauli repulsion ΔE_{Pauli}, the electrostatic interaction ΔE_{elstat} and the orbital interaction ΔE_{orb}.

	Bi(NON^{Ar})(OTEMP) (**2a**)	Bi(NON^{tBu})(OTEMP) (**2b**)
ΔE_{Pauli}	184.13	180.24
ΔE_{elstat}	−206.25	−210.11
ΔE_{orb}	−132.01	−130.01
ΔE_{int}	**−154.13**	**−159.88**

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Cartesian Coordinates

Bi(NON^{Ar})(OTEMP) (**2a**)

Bi	0.058590	0.093363	-0.530899
Si	-1.143904	-3.073237	0.105285
Si	1.516146	-2.367532	1.434805
O	0.319699	-3.297155	0.801154
O	-0.150318	1.801544	0.753929
N	-1.461305	-1.357529	0.121082
N	1.722350	-0.986436	0.394622
N	-0.330200	2.895667	-0.139914
C	-2.810950	-0.903212	0.152770
C	-3.431544	-0.656818	1.400550
C	-4.734111	-0.174923	1.426486
H	-5.205688	0.022816	2.382759
C	-5.441625	0.063067	0.261913
H	-6.454827	0.446725	0.303925
C	-4.847363	-0.209215	-0.953961
H	-5.408328	-0.042384	-1.867804
C	-3.547422	-0.699659	-1.035865
C	-2.711392	-0.882585	2.712748
H	-1.841652	-1.503855	2.495513
C	-2.198809	0.431846	3.297948
H	-1.510549	0.935541	2.615899
H	-3.030096	1.113711	3.501269
H	-1.676506	0.252179	4.242366
C	-3.568110	-1.618388	3.739596
H	-2.961183	-1.885753	4.608820
H	-4.391082	-0.997273	4.103025

H	-3.999437	-2.533945	3.329502
C	-2.995579	-1.018078	-2.411869
H	-2.011888	-1.471516	-2.275211
C	-2.820112	0.224366	-3.283332
H	-2.436363	-0.052497	-4.269284
H	-3.771635	0.742499	-3.429519
H	-2.122418	0.941537	-2.843875
C	-3.870350	-2.040815	-3.136948
H	-4.045525	-2.926622	-2.523087
H	-4.846609	-1.619037	-3.389574
H	-3.396891	-2.357639	-4.070183
C	-2.448927	-4.012926	1.047880
H	-3.454457	-3.800445	0.677100
H	-2.264943	-5.084558	0.928086
H	-2.424587	-3.785552	2.114780
C	-1.008547	-3.841582	-1.598611
H	-1.971548	-3.900520	-2.109512
H	-0.313104	-3.305884	-2.250139
H	-0.628686	-4.861660	-1.486331
C	0.991296	-1.929163	3.178586
H	1.839648	-1.691141	3.824178
H	0.317363	-1.069924	3.191791
H	0.467179	-2.779050	3.624960
C	3.060243	-3.411389	1.448234
H	3.916900	-2.901814	1.892913
H	2.866662	-4.317556	2.029579
H	3.336423	-3.715251	0.436294
C	2.974970	-0.618943	-0.163241

C	3.978296	-0.034650	0.649868
C	5.147155	0.424980	0.058786
H	5.909586	0.881585	0.678856
C	5.366276	0.314715	-1.303687
H	6.280177	0.695347	-1.745330
C	4.423448	-0.321651	-2.083484
H	4.616664	-0.461225	-3.142044
C	3.240490	-0.815536	-1.538895
C	3.810089	0.088394	2.150398
H	3.154517	-0.721939	2.467827
C	3.117323	1.385382	2.551520
H	3.002599	1.437364	3.638232
H	3.703267	2.252368	2.234172
H	2.124894	1.459296	2.105032
C	5.115711	-0.081244	2.920208
H	4.905877	-0.159030	3.989987
H	5.656132	-0.979685	2.612454
H	5.784239	0.773599	2.788958
C	2.337225	-1.628042	-2.446615
H	1.452072	-1.912071	-1.870593
C	1.882243	-0.866752	-3.689350
H	1.193430	-1.475716	-4.281384
H	1.376457	0.069044	-3.436868
H	2.729100	-0.613338	-4.331910
C	3.016225	-2.937560	-2.850386
H	3.314660	-3.516028	-1.974322
H	2.339583	-3.552433	-3.450261
H	3.912885	-2.746191	-3.445557

C	-1.603159	3.588354	0.190784
C	-1.760277	4.781522	-0.759316
H	-1.925275	4.392251	-1.770680
H	-2.670609	5.317257	-0.473391
C	-0.562867	5.704965	-0.782115
H	-0.436589	6.200846	0.185071
H	-0.713251	6.502937	-1.515403
C	0.664801	4.894872	-1.134967
H	1.566058	5.515794	-1.134731
H	0.549367	4.499771	-2.150962
C	0.908853	3.716492	-0.184656
C	-2.750334	2.635845	-0.107449
H	-2.679055	2.258765	-1.128912
H	-3.700400	3.167165	-0.014899
H	-2.778112	1.793255	0.580269
C	-1.722930	4.035495	1.652614
H	-1.414455	3.232775	2.321845
H	-2.766922	4.273441	1.871022
H	-1.130427	4.920003	1.880329
C	2.014153	2.871685	-0.807461
H	2.335578	2.056522	-0.159078
H	2.893633	3.493279	-0.990567
H	1.692047	2.465800	-1.770779
C	1.389728	4.224524	1.181519
H	0.868065	5.125954	1.500345
H	2.454321	4.465647	1.130774
H	1.253681	3.460777	1.945208

Bi(NON$^{t\text{Bu}}$)(OTEMP) (**2b**)

Bi	-0.898401	-0.163647	0.000000
Si	1.572894	-1.684283	1.542760
O	1.954170	-1.254366	0.000000
O	0.589676	1.345012	0.000000
N	-0.121058	-1.357775	1.640052
N	-0.064689	2.602260	0.000000
C	-1.106185	-1.814868	2.635784
C	2.631724	-0.631093	2.663460
H	2.429303	-0.825760	3.720173
H	3.692305	-0.832507	2.485950
H	2.452152	0.428755	2.472065
C	2.072157	-3.476738	1.797178
H	2.159431	-3.735095	2.854569
H	1.379902	-4.179564	1.327772
H	3.057060	-3.626277	1.344007
C	0.246712	3.298256	1.270767
C	-0.427488	4.672924	1.234066
H	-1.512956	4.522644	1.263402
H	-0.154901	5.209352	2.148319
C	-0.078506	5.479524	0.000000
H	0.982801	5.747162	0.000000
H	-0.629075	6.425040	0.000000
C	1.743900	3.425286	1.580973
H	2.254455	2.489954	1.350383
H	1.880254	3.636062	2.644716
H	2.228627	4.226737	1.025558
C	-0.396458	2.493920	2.393989

H	-1.456395	2.326653	2.184416
H	-0.319738	3.041447	3.336761
H	0.096789	1.529854	2.523030
C	-0.428498	-2.594230	3.763050
H	-1.162629	-2.841045	4.534068
H	0.000913	-3.528714	3.402186
H	0.360360	-2.002125	4.233491
C	-2.135645	-2.740795	1.979140
H	-2.720404	-2.211661	1.219433
H	-1.636979	-3.581402	1.492559
H	-2.843662	-3.132490	2.715138
C	-1.843079	-0.636606	3.277776
H	-2.373914	-0.033494	2.534932
H	-2.588118	-0.993295	3.994256
H	-1.144464	0.016211	3.803211
Si	1.572894	-1.684283	-1.542760
N	-0.121058	-1.357775	-1.640052
C	-1.106185	-1.814868	-2.635784
C	2.631724	-0.631093	-2.663460
H	2.429303	-0.825760	-3.720173
H	3.692305	-0.832507	-2.485950
H	2.452152	0.428755	-2.472065
C	2.072157	-3.476738	-1.797178
H	2.159431	-3.735095	-2.854569
H	1.379902	-4.179564	-1.327772
H	3.057060	-3.626277	-1.344007
C	-0.428498	-2.594230	-3.763050
H	-1.162629	-2.841045	-4.534068

H	0.000913	-3.528714	-3.402186
H	0.360360	-2.002125	-4.233491
C	-2.135645	-2.740795	-1.979140
H	-2.720404	-2.211661	-1.219433
H	-1.636979	-3.581402	-1.492559
H	-2.843662	-3.132490	-2.715138
C	-1.843079	-0.636606	-3.277776
H	-2.373914	-0.033494	-2.534932
H	-2.588118	-0.993295	-3.994256
H	-1.144464	0.016211	-3.803211
C	0.246712	3.298256	-1.270767
C	-0.427488	4.672924	-1.234066
H	-1.512956	4.522644	-1.263402
H	-0.154901	5.209352	-2.148319
C	1.743900	3.425286	-1.580973
H	2.254455	2.489954	-1.350383
H	1.880254	3.636062	-2.644716
H	2.228627	4.226737	-1.025558
C	-0.396458	2.493920	-2.393989
H	-1.456395	2.326653	-2.184416
H	-0.319738	3.041447	-3.336761
H	0.096789	1.529854	-2.523030

Ishida-Iwamoto

Bi	0.078397	-0.017366	-0.677816
C	1.476553	1.627147	0.205830
C	2.758535	0.766101	0.368788
H	3.192775	0.545432	-0.610639

H	3.529651	1.332120	0.904202
C	2.530421	-0.561122	1.087220
H	2.176661	-0.342507	2.103258
H	3.501341	-1.058355	1.218512
C	1.535832	-1.507987	0.366407
C	-0.036620	-4.226739	0.953449
H	-0.303035	-4.875165	1.794181
H	0.583527	-4.813197	0.274327
H	-0.964155	-3.975429	0.436484
C	-0.375577	-1.943533	2.882183
H	-0.866614	-2.755461	3.428543
H	-1.139830	-1.342181	2.389113
H	0.131753	-1.321418	3.621014
C	3.556779	-1.499721	-2.100467
H	3.975444	-2.178762	-2.850460
H	4.393749	-1.106903	-1.517644
H	3.096414	-0.670522	-2.638948
N	-2.831778	0.007836	-0.307919
C	-3.616803	1.145343	0.222204
C	-4.865050	1.318624	-0.648424
H	-5.469088	2.122575	-0.216567
H	-4.547555	1.655281	-1.642014
C	-3.516619	-1.288871	-0.518421
C	-3.874314	-2.045837	0.766083
H	-4.723908	-1.611106	1.290743
H	-3.024054	-2.062917	1.447477
H	-4.133998	-3.079227	0.521843
C	2.237589	-3.354572	2.755511

H	1.800735	-3.982222	3.539077
H	2.762695	-2.536391	3.255197
H	2.976157	-3.954637	2.224020
C	3.407255	-3.936281	-0.444970
H	3.892122	-4.385189	-1.317796
H	2.848277	-4.722882	0.062627
H	4.200382	-3.597757	0.226671
C	-5.668889	0.044470	-0.798982
H	-6.521197	0.211107	-1.464335
H	-6.089560	-0.265346	0.162771
C	-2.590144	-2.171382	-1.348968
H	-2.292708	-1.660046	-2.267195
H	-3.103581	-3.096553	-1.622566
H	-1.694022	-2.447187	-0.792368
C	0.208055	4.200215	1.621418
H	0.117741	4.631265	2.623914
H	-0.799454	4.128112	1.210728
H	0.773073	4.908896	1.013948
C	2.656800	2.899999	2.761914
H	2.410433	3.482785	3.655046
H	3.364080	3.486602	2.170540
H	3.166511	1.993514	3.097997
C	2.427035	2.013203	-2.767500
H	2.491262	2.773495	-3.552564
H	1.774468	1.222603	-3.148648
H	3.428823	1.599630	-2.637266
C	1.068088	-3.173943	-2.253077
H	1.572073	-3.821607	-2.977208

H	0.577829	-2.377013	-2.819759
H	0.290167	-3.762704	-1.765724
C	-4.001804	1.027337	1.702912
H	-3.151316	0.684265	2.292408
H	-4.833575	0.344516	1.872634
H	-4.302134	2.007859	2.081104
C	-4.769168	-1.034198	-1.364215
H	-5.303835	-1.983326	-1.469141
H	-4.449433	-0.735024	-2.368937
C	-2.757814	2.390021	0.049523
H	-2.437165	2.487275	-0.989392
H	-1.876944	2.343760	0.688069
H	-3.326471	3.283167	0.320496
C	-0.026038	1.558134	3.021193
H	-0.416292	2.233547	3.788469
H	0.546986	0.781430	3.530178
H	-0.870102	1.079398	2.522341
C	0.202520	3.732045	-1.798363
H	-0.338513	4.256486	-1.012056
H	-0.485500	3.021413	-2.265308
H	0.476972	4.464765	-2.563726
C	3.079027	4.129724	-0.767314
H	2.793625	4.783329	0.058472
H	3.281664	4.762394	-1.636937
H	4.017431	3.638204	-0.495338
O	-1.699138	-0.179467	0.522211
Si	1.055006	2.527635	1.835222
Si	0.830127	-2.716146	1.670447

Si	2.350306	-2.497208	-1.051570
Si	1.761273	2.859221	-1.216313