Electronic Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles for compound **1b**. Computational details, energies and optimized structures.

Olefin Isomerisation versus Hydrozirconation: A Case of Stable β-Hydrogen Containing Zr-Alkyl Derivative

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Molecular structure of 1b in the solid state

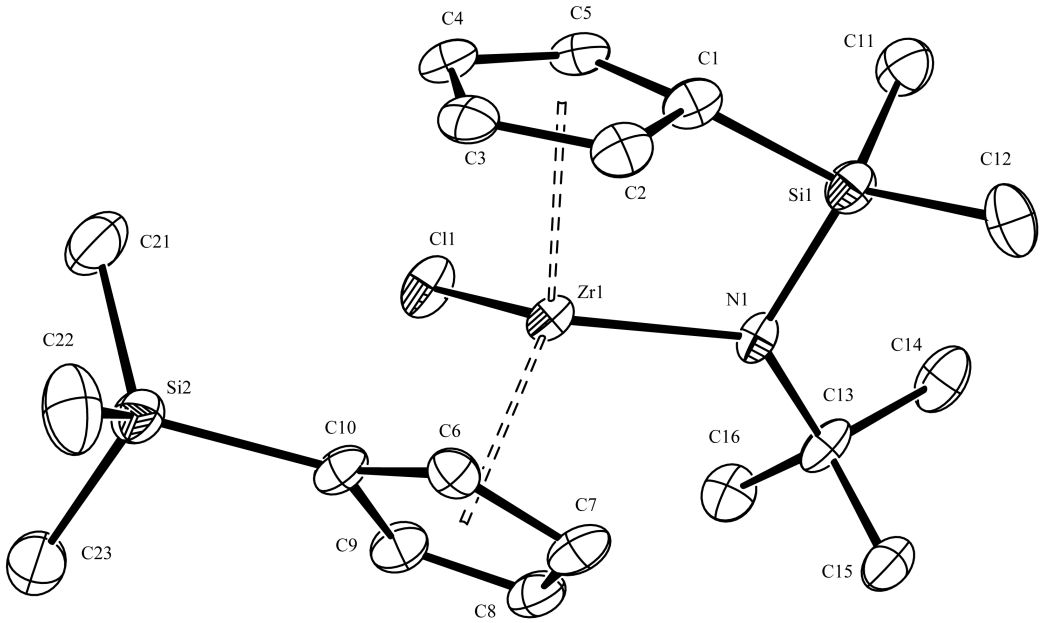


Table 1. Crystal data and structure refinement for **1b**.

Empirical formula	C19 H32 Cl N Si2 Zr
Formula weight	457.31
Temperature	200(2) K
Wavelength	0.71069 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.3620(13) Å α = 86.139(10) deg. b = 9.2080(10) Å β = 85.044(9) deg. c = 17.5130(14) Å γ = 76.824(12) deg.
Volume	1150.2(3) $Å^3$
Z, Calculated density	2, 1.320 Mg/m^3
Absorption coefficient	0.700 mm^{-1}
F(000)	476
Crystal size	0.34 x 0.33 x 0.24 mm
Theta range for data collection	3.16 to 27.50 deg.
Limiting indices	-9<=h<=9, -11<=k<=11, -22<=l<=22
Reflections collected / unique	22003 / 5209 [R(int) = 0.0722]
Completeness to theta = 27.50	98.6 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.724 and 0.652
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5209 / 0 / 217
Goodness-of-fit on F^2	0.986
Final R indices [I>2sigma(I)]	R1 = 0.0604, wR2 = 0.1657
R indices (all data)	R1 = 0.1227, wR2 = 0.2559
Largest diff. peak and hole	1.288 and -1.766 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **1b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zr(1)	7547(1)	4673(1)	2584(1)	28(1)
N(1)	8789(7)	2748(6)	3265(3)	32(1)
Si(1)	7565(3)	2978(2)	4174(1)	38(1)
Si(2)	5710(3)	7415(2)	782(1)	41(1)
Cl(1)	10205(2)	5936(2)	2345(1)	47(1)
C(1)	6101(10)	4855(8)	3916(4)	42(2)
C(2)	4585(9)	5161(9)	3407(4)	37(2)
C(3)	4525(10)	6550(8)	3019(4)	39(2)
C(4)	5980(10)	7132(8)	3263(5)	42(2)
C(5)	6939(10)	6109(9)	3787(5)	44(2)
C(6)	5215(10)	4553(8)	1614(4)	36(2)
C(7)	6301(11)	3073(8)	1723(4)	40(2)
C(8)	8116(11)	3043(9)	1408(5)	49(2)
C(9)	8218(10)	4478(8)	1113(4)	41(2)
C(10)	6418(9)	5466(8)	1234(4)	35(2)
C(11)	8953(13)	3218(10)	4983(5)	57(2)
C(12)	6082(12)	1587(11)	4454(6)	59(2)
C(13)	10294(10)	1357(8)	3094(5)	42(2)
C(14)	11219(12)	664(9)	3853(5)	54(2)
C(15)	9474(12)	172(9)	2778(6)	54(2)
C(16)	11860(10)	1779(9)	2551(6)	52(2)
C(21)	6293(15)	8892(10)	1342(6)	65(3)
C(22)	3120(13)	7816(12)	666(6)	71(3)
C(23)	7035(14)	7379(11)	-165(5)	65(3)

Table 3. Bond lengths [A] and angles [deg] for **1b**.

Zr(1)-N(1)	2.137(5)
Zr(1)-C(1)	2.480(8)
Zr(1)-C(2)	2.476(7)
Zr(1)-Cl(1)	2.4877(18)
Zr(1)-C(5)	2.517(7)
Zr(1)-C(7)	2.537(7)
Zr(1)-C(6)	2.541(7)
Zr(1)-C(10)	2.577(7)
Zr(1)-C(3)	2.579(6)
Zr(1)-C(8)	2.578(8)
Zr(1)-C(9)	2.591(7)
Zr(1)-C(4)	2.609(7)
N(1)-C(13)	1.518(8)
N(1)-Si(1)	1.761(6)
Si(1)-C(1)	1.866(8)
Si(1)-C(12)	1.879(9)
Si(1)-C(11)	1.870(9)
Si(2)-C(21)	1.875(9)
Si(2)-C(23)	1.848(9)
Si(2)-C(22)	1.884(10)
Si(2)-C(10)	1.890(7)
C(1)-C(5)	1.425(11)
C(1)-C(2)	1.454(10)
C(2)-C(3)	1.401(10)
C(2)-H(2)	0.9500
C(3)-C(4)	1.411(11)
C(3)-H(3)	0.9500
C(4)-C(5)	1.387(11)
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(6)-C(7)	1.424(10)
C(6)-C(10)	1.447(10)
C(6)-H(6)	0.9500
C(7)-C(8)	1.395(11)
C(7)-H(7)	0.9500
C(8)-C(9)	1.402(11)
C(8)-H(8)	0.9500
C(9)-C(10)	1.435(9)
C(9)-H(9)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(16)	1.533(11)
C(13)-C(15)	1.517(10)
C(13)-C(14)	1.576(11)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

N(1)-Zr(1)-C(1)	70.3(2)
N(1)-Zr(1)-C(2)	93.7(2)
C(1)-Zr(1)-C(2)	34.1(2)
N(1)-Zr(1)-Cl(1)	100.91(15)
C(1)-Zr(1)-Cl(1)	113.51(19)
C(2)-Zr(1)-Cl(1)	134.31(19)
N(1)-Zr(1)-C(5)	87.9(2)
C(1)-Zr(1)-C(5)	33.1(3)
C(2)-Zr(1)-C(5)	54.2(2)
Cl(1)-Zr(1)-C(5)	83.10(19)
N(1)-Zr(1)-C(7)	91.2(2)
C(1)-Zr(1)-C(7)	116.0(2)
C(2)-Zr(1)-C(7)	92.0(3)
Cl(1)-Zr(1)-C(7)	130.23(18)
C(5)-Zr(1)-C(7)	146.0(2)
N(1)-Zr(1)-C(6)	121.6(2)
C(1)-Zr(1)-C(6)	112.6(2)
C(2)-Zr(1)-C(6)	79.3(2)
Cl(1)-Zr(1)-C(6)	125.12(17)
C(5)-Zr(1)-C(6)	127.3(2)
C(7)-Zr(1)-C(6)	32.6(2)
N(1)-Zr(1)-C(10)	141.7(2)
C(1)-Zr(1)-C(10)	135.8(2)
C(2)-Zr(1)-C(10)	102.4(2)
Cl(1)-Zr(1)-C(10)	92.31(17)
C(5)-Zr(1)-C(10)	129.6(2)
C(7)-Zr(1)-C(10)	54.1(2)
C(6)-Zr(1)-C(10)	32.8(2)
N(1)-Zr(1)-C(3)	123.6(2)
C(1)-Zr(1)-C(3)	54.7(2)
C(2)-Zr(1)-C(3)	32.1(2)
Cl(1)-Zr(1)-C(3)	110.64(18)
C(5)-Zr(1)-C(3)	52.9(2)
C(7)-Zr(1)-C(3)	101.4(2)
C(6)-Zr(1)-C(3)	74.7(2)
C(10)-Zr(1)-C(3)	83.3(2)
N(1)-Zr(1)-C(8)	88.9(2)
C(1)-Zr(1)-C(8)	143.0(3)
C(2)-Zr(1)-C(8)	123.6(3)
Cl(1)-Zr(1)-C(8)	99.9(2)
C(5)-Zr(1)-C(8)	176.0(3)
C(7)-Zr(1)-C(8)	31.6(2)
C(6)-Zr(1)-C(8)	52.9(2)
C(10)-Zr(1)-C(8)	53.3(2)
C(3)-Zr(1)-C(8)	127.7(2)
N(1)-Zr(1)-C(9)	115.7(2)
C(1)-Zr(1)-C(9)	165.7(3)
C(2)-Zr(1)-C(9)	131.9(2)
Cl(1)-Zr(1)-C(9)	78.94(19)
C(5)-Zr(1)-C(9)	152.5(3)
C(7)-Zr(1)-C(9)	52.8(2)

C(6)-Zr(1)-C(9)	53.1(2)
C(10)-Zr(1)-C(9)	32.2(2)
C(3)-Zr(1)-C(9)	115.4(2)
C(8)-Zr(1)-C(9)	31.5(3)
N(1)-Zr(1)-C(4)	118.9(2)
C(1)-Zr(1)-C(4)	53.9(3)
C(2)-Zr(1)-C(4)	53.0(3)
Cl(1)-Zr(1)-C(4)	82.43(18)
C(5)-Zr(1)-C(4)	31.3(3)
C(7)-Zr(1)-C(4)	132.2(2)
C(6)-Zr(1)-C(4)	102.4(2)
C(10)-Zr(1)-C(4)	98.3(2)
C(3)-Zr(1)-C(4)	31.5(2)
C(8)-Zr(1)-C(4)	151.4(3)
C(9)-Zr(1)-C(4)	124.6(3)
C(13)-N(1)-Si(1)	121.5(5)
C(13)-N(1)-Zr(1)	133.5(5)
Si(1)-N(1)-Zr(1)	104.9(3)
N(1)-Si(1)-C(1)	94.8(3)
N(1)-Si(1)-C(12)	114.7(4)
C(1)-Si(1)-C(12)	111.4(4)
N(1)-Si(1)-C(11)	116.3(4)
C(1)-Si(1)-C(11)	107.1(4)
C(12)-Si(1)-C(11)	111.1(5)
N(1)-Si(1)-Zr(1)	41.78(17)
C(1)-Si(1)-Zr(1)	53.1(2)
C(12)-Si(1)-Zr(1)	123.1(3)
C(11)-Si(1)-Zr(1)	125.8(3)
C(21)-Si(2)-C(23)	108.3(5)
C(21)-Si(2)-C(22)	110.4(5)
C(23)-Si(2)-C(22)	110.6(5)
C(21)-Si(2)-C(10)	113.7(4)
C(23)-Si(2)-C(10)	105.9(4)
C(22)-Si(2)-C(10)	107.8(4)
C(5)-C(1)-C(2)	104.4(7)
C(5)-C(1)-Si(1)	120.0(6)
C(2)-C(1)-Si(1)	126.1(6)
C(5)-C(1)-Zr(1)	74.9(5)
C(2)-C(1)-Zr(1)	72.8(4)
Si(1)-C(1)-Zr(1)	89.9(3)
C(3)-C(2)-C(1)	109.1(7)
C(3)-C(2)-Zr(1)	78.0(4)
C(1)-C(2)-Zr(1)	73.1(4)
C(3)-C(2)-H(2)	125.4
C(1)-C(2)-H(2)	125.4
Zr(1)-C(2)-H(2)	115.5
C(2)-C(3)-C(4)	107.7(7)
C(2)-C(3)-Zr(1)	69.9(4)
C(4)-C(3)-Zr(1)	75.4(4)
C(2)-C(3)-H(3)	126.1
C(4)-C(3)-H(3)	126.1
Zr(1)-C(3)-H(3)	120.3
C(5)-C(4)-C(3)	108.4(7)
C(5)-C(4)-Zr(1)	70.7(4)
C(3)-C(4)-Zr(1)	73.0(4)
C(5)-C(4)-H(4)	125.8
C(3)-C(4)-H(4)	125.8
Zr(1)-C(4)-H(4)	122.2
C(4)-C(5)-C(1)	110.3(7)
C(4)-C(5)-Zr(1)	78.0(4)
C(1)-C(5)-Zr(1)	72.0(4)

C(4)-C(5)-H(5)	124.9
C(1)-C(5)-H(5)	124.9
Zr(1)-C(5)-H(5)	116.9
C(7)-C(6)-C(10)	108.3(6)
C(7)-C(6)-Zr(1)	73.6(4)
C(10)-C(6)-Zr(1)	74.9(4)
C(7)-C(6)-H(6)	125.9
C(10)-C(6)-H(6)	125.9
Zr(1)-C(6)-H(6)	117.6
C(8)-C(7)-C(6)	108.0(7)
C(8)-C(7)-Zr(1)	75.8(4)
C(6)-C(7)-Zr(1)	73.9(4)
C(8)-C(7)-H(7)	126.0
C(6)-C(7)-H(7)	126.0
Zr(1)-C(7)-H(7)	116.5
C(9)-C(8)-C(7)	109.1(7)
C(9)-C(8)-Zr(1)	74.8(4)
C(7)-C(8)-Zr(1)	72.6(4)
C(9)-C(8)-H(8)	125.5
C(7)-C(8)-H(8)	125.5
Zr(1)-C(8)-H(8)	119.0
C(8)-C(9)-C(10)	109.1(7)
C(8)-C(9)-Zr(1)	73.8(5)
C(10)-C(9)-Zr(1)	73.3(4)
C(8)-C(9)-H(9)	125.5
C(10)-C(9)-H(9)	125.5
Zr(1)-C(9)-H(9)	119.2
C(6)-C(10)-C(9)	105.5(6)
C(6)-C(10)-Si(2)	127.9(5)
C(9)-C(10)-Si(2)	125.2(6)
C(6)-C(10)-Zr(1)	72.2(4)
C(9)-C(10)-Zr(1)	74.4(4)
Si(2)-C(10)-Zr(1)	128.4(3)
Si(1)-C(11)-H(11A)	109.5
Si(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
Si(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Si(1)-C(12)-H(12A)	109.5
Si(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(16)-C(13)-N(1)	109.6(6)
C(16)-C(13)-C(15)	112.3(7)
N(1)-C(13)-C(15)	111.1(6)
C(16)-C(13)-C(14)	106.4(6)
N(1)-C(13)-C(14)	110.1(6)
C(15)-C(13)-C(14)	107.2(6)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Si(2)-C(21)-H(21A)	109.5
Si(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(2)-C(22)-H(22A)	109.5
Si(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(2)-C(23)-H(23A)	109.5
Si(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **1b**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zr(1)	20(1)	24(1)	42(1)	-7(1)	-4(1)	-5(1)
N(1)	25(3)	20(3)	53(4)	-1(2)	-8(2)	-5(2)
Si(1)	34(1)	36(1)	47(1)	-4(1)	-5(1)	-10(1)
Si(2)	40(1)	35(1)	44(1)	-3(1)	-6(1)	1(1)
Cl(1)	27(1)	37(1)	80(1)	-1(1)	-4(1)	-13(1)
C(1)	38(4)	40(4)	47(4)	-15(3)	-2(3)	-3(3)
C(2)	26(3)	48(4)	36(4)	-9(3)	2(3)	-5(3)
C(3)	29(3)	42(4)	40(4)	-12(3)	3(3)	5(3)
C(4)	35(4)	33(4)	58(5)	-24(3)	-1(3)	-1(3)
C(5)	33(4)	42(4)	58(5)	-25(4)	-12(3)	-1(3)
C(6)	31(4)	39(4)	41(4)	-11(3)	-4(3)	-12(3)
C(7)	51(4)	36(4)	37(4)	-8(3)	-6(3)	-15(3)
C(8)	40(4)	35(4)	71(6)	-24(4)	-9(4)	3(3)
C(9)	37(4)	41(4)	40(4)	-11(3)	-2(3)	1(3)
C(10)	31(3)	28(3)	43(4)	-12(3)	-5(3)	1(3)
C(11)	53(5)	47(5)	68(6)	-9(4)	-16(4)	-1(4)
C(12)	48(5)	63(6)	67(6)	2(5)	5(4)	-22(4)
C(13)	31(4)	22(3)	71(5)	-10(3)	-9(3)	0(3)
C(14)	49(5)	39(4)	70(6)	6(4)	-22(4)	5(4)
C(15)	57(5)	28(4)	77(6)	-12(4)	-5(4)	-8(4)
C(16)	26(4)	46(5)	82(6)	-17(4)	7(4)	0(3)
C(21)	89(7)	39(5)	66(6)	-2(4)	-18(5)	-9(5)
C(22)	58(6)	70(7)	75(7)	22(5)	-19(5)	0(5)
C(23)	71(6)	52(5)	63(6)	3(4)	10(5)	-5(5)

Experimental Part

General information. All manipulations were performed at an argon/vacuum manifold using standard Schlenk techniques or in a glove-box MBraun MOD System. Solvents were dried by known procedures and used freshly distilled. $Zr[\eta^5\text{-}C_5H_4Si(CH_3)_2\text{-}\eta^1\text{-}N^tBu]Cl_2$ and $Zr[\eta^5\text{-}C_5H_4Si(CH_3)_2\text{-}\eta^1\text{-}N^tBu](NMe_2)_2$ were prepared according to previous reports (ref 17 in article). Corresponding lithium salts $Li[C_5H_5]$, $Li[C_5H_4Si(CH_3)_2CH_2CH{=}CH_2]$ and $Li[C_5H_4Si(CH_3)_3]$, were prepared by addition of n-BuLi to diethyl ether solutions of the cyclopentadiene and subsequent precipitation in hexane, according to a modified procedure of previously reported synthesis (ref 16 in article). NMR spectra were recorded in a Bruker 400 Ultrashield. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported relative to tetramethylsilane. Coupling constants *J* are given in Hertz.

Preparation of $Zr[\eta^5\text{-}C_5H_4Si(CH_3)_2\text{-}\eta^1\text{-}N^tBu](\eta^5\text{-}C_5H_4R)Cl$ (R = H, 1a; $SiMe_3$, 1b). In a typical procedure, THF (10 mL) was added at room temperature to a dry mixture of $Zr[\eta^5\text{-}C_5H_4Si(CH_3)_2\text{-}\eta^1\text{-}N^tBu]Cl_2$ (0.50 g, 1.40 mmol) and $Li[C_5H_4R]$ (1.50 mmol, R = H, 0.11 g; $SiMe_3$, 0.23 g). Stirring the reaction mixture for ca. 12 hours at room temperature gave a yellow suspension. The solvent was removed under vacuum and hexane (2 x 5 mL) was then added to the oily residue, the resulting suspension was filtered and the yellow solution dried under vacuum to produce a yellow solid residue, which was identified as pure derivatives **1a-b**, respectively. **1a**: Yield: 72%. Anal. Calcd. for $C_{16}H_{24}ZrNSiCl$: C, 49.90; H, 6.28; N, 3.64. Found: C, 50.12; H, 5.86; N, 3.88. ^1H NMR (400 MHz, C_6D_6): δ 6.73, 6.31 (both m, each 1H, C_5H_4), 5.95 (s, 5H, C_5H_5), 5.90, 5.39 (both m, each 1H, C_5H_4), 1.24 (s, 9H, $C(CH_3)_3$), 0.52, 0.27 (both s, each 3H, $Si\text{-}(CH_3)_2$). ^{13}C APT NMR (100 MHz, C_6D_6): δ 124.5, 119.4, 118.4 (all +, C_5H_4), 108.1 (_, ipso-C_5H_4), 112.2 (+, C_5H_5), 110.2 (+, C_5H_4), 58.3 (_, $NC(CH_3)_3$), 34.9 (+, $C(CH_3)_3$), 4.8, 1.7 (both +, $Si\text{-}(CH_3)_2$). **1b**: Yield: 77%. Anal. Calcd. for $C_{19}H_{32}ZrNSi_2Cl$: C, 49.89; H, 7.06; N, 3.06. Found: C, 49.62; H, 7.10. ^1H NMR (400

MHz, C_6D_6): δ 6.73, 6.71, 6.48, 6.37, 6.13, 6.02, 5.71, 5.54 (all m, each 1H, C_5H_4), 1.26 (s, 9H, $C(CH_3)_3$), 0.52, 0.29 (both s, each 3H, Si-$(CH_3)_2$), 0.27 (s, 9H, Si-$(CH_3)_3$). ^{13}C APT NMR (100 MHz, C_6D_6): δ 125.3, 124.6 (both +, C_5H_4), 122.8 (_, ipso-C_5H_4), 120.9, 120.1, 118.3, 118.2 (+, C_5H_4), 114.6 (_, ipso-C_5H_4), 111.1, 109.7 (+, C_5H_4), 59.3 (_, N*C*$(CH_3)_3$), 35.4 (+, C(*C*$H_3)_3$), 5.7, 2.4 (both +, Si-$(CH_3)_2$), 0.85 (+, Si-$(CH_3)_3$).

Preparation of Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu][η^5-$C_5H_4SiMe_2(CH_2CH{=}CH_2)$]Cl (1c). Compound **1c** can be prepared in yields of ca. 80%, following an analogous procedure as that described above for **1b-c**, starting from Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu]Cl_2 (0.50 g, 1.40 mmol) and Li[$C_5H_4SiMe_2(CH_2CH{=}CH_2)$] (0.25 g, 1.50 mmol,). However, an alternative synthetic method is the addition, at room temperature, of an excess of $ClSiMe_3$ (0.40 mL, 3.06 mmol) to hexane solutions of Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu][η^5-$C_5H_4Si(CH_3)_2(CH_2CH{=}CH_2)$]$NMe_2$ (0.50 g, 1.02 mmol, the synthesis of this monoamido zirconium precursor is described in the next paragraph). The stirring of the mixture for ca. 12 hours and evaporation of the volatiles under vacuum produced a yellow oil which was identified as pure compound **1c**, obtained by this procedure in a "one pot reaction" directly from the diamido CGC zirconium compound in ca. 90% yield. Neither the non-substituted cyclopentadienyl monoamido zirconium compound nor the trimethylsilyl substituted cyclopentadienyl one could be prepared by an analogous procedure.

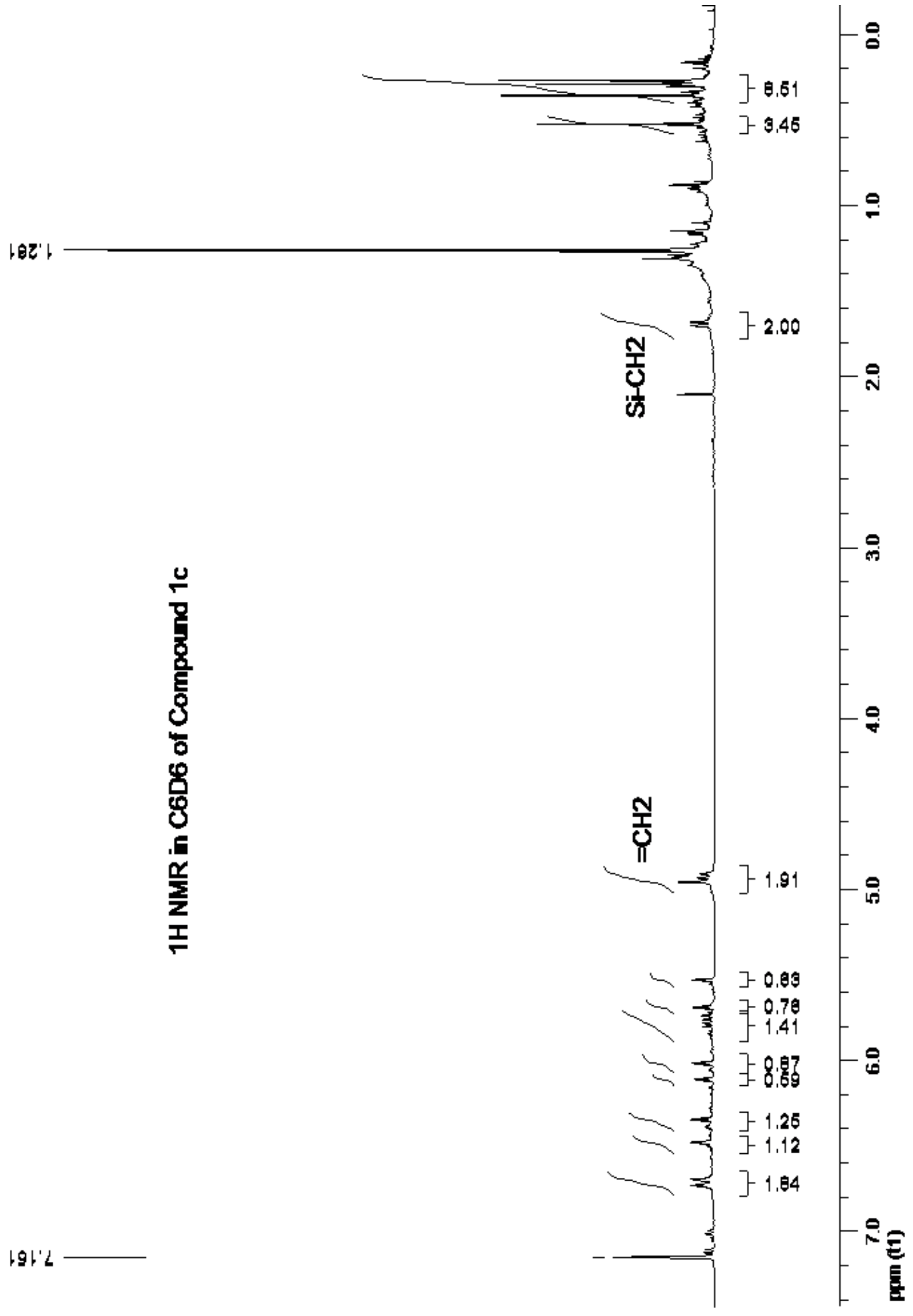
Data for **1c**: Anal. Calcd. for $C_{21}H_{34}ZrNClSi_2$: C, 52.18; H, 7.09; N, 2.90. Found: C, 52.17; H, 7.22; N, 3.42. ^{1}H NMR (plus HSQCGP, 400 MHz, C_6D_6): δ 6.73, 6.70, 6.48, 6.34, 6.11, 6.02 (all m, each 1H, C_5H_4), 5.76 (m, 1H, $^{trans}J_{HH}$ = 16.4, $^{cis}J_{HH}$ = 10.4, $^3J_{HH}$ = 8.0, =CH), 5.69, 5.53 (both m, each 1H, C_5H_4), 4.95 (dd, 1H, $^{trans}J_{HH}$ = 16.4, $^{cis}J_{HH}$ = 10.4, =CH_2), 4.96 (dd, 1H, $^{cis}J_{HH}$ = 10.4, $^3J_{HH}$ = 8.4, =CH_2), 1.69 (dd, 2H, $^3J_{HH}$ = 8.4, J_{HHgem} = 0.8, Si-CH_2), 1.26 (s, 9H, $C(CH_3)_3$), 0.53, 0.35, 0.29, 0.27 (all s, each 3H, Si$(CH_3)_2$). ^{13}C APT NMR (plus HSQCGP, 100 MHz, C_6D_6): δ 134.9 (+, =CH), 124.7, 123.6 (+, C_5H_4), 121.2 (_, C_5H_4-ipso), 120.2, 119.3, 117.6, 117.5 (+, C_5H_4), 113.8 (_,

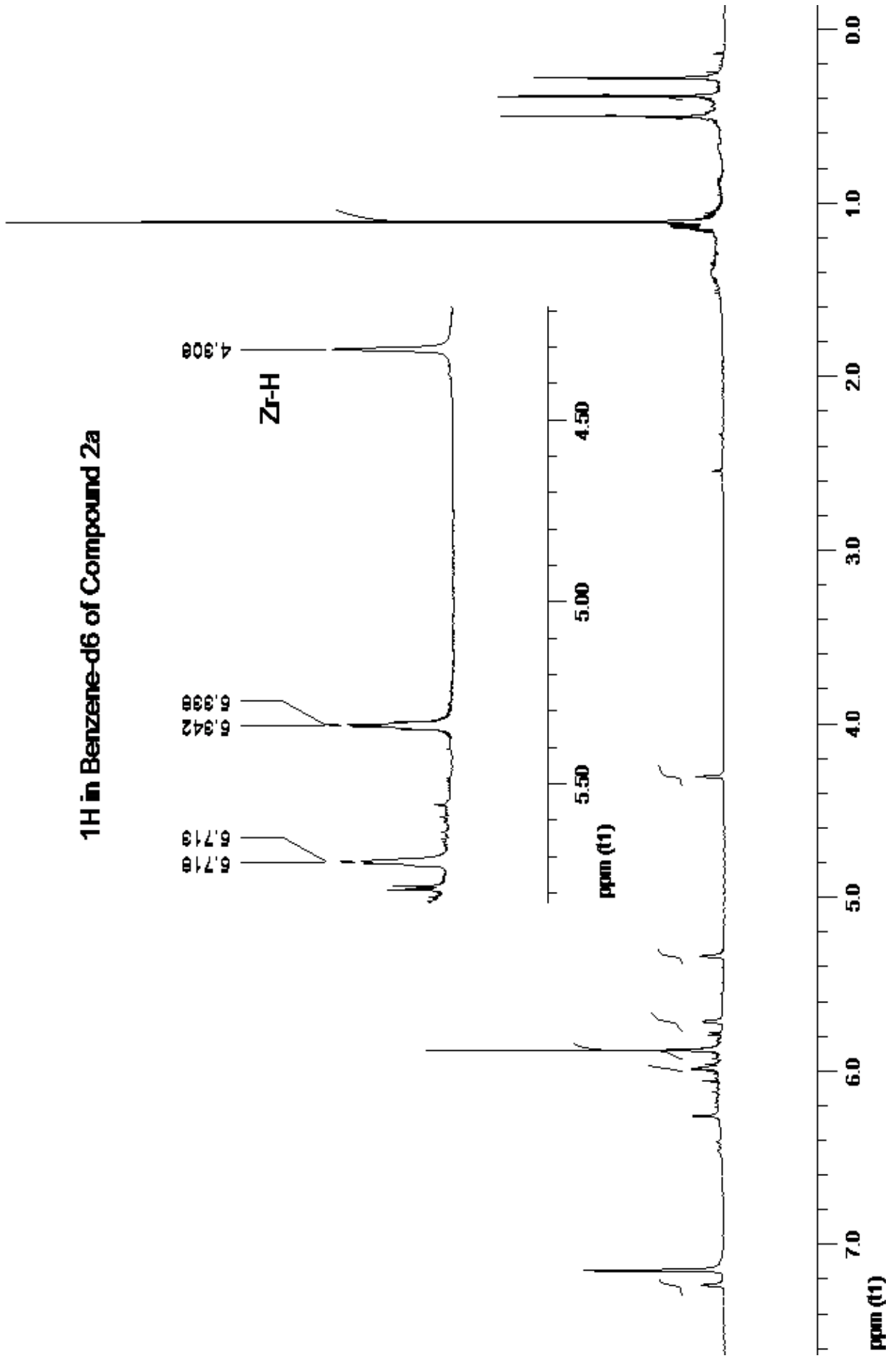
C_5H_4-ipso), 113.7 (_, $=CH_2$), 110.5, 108.8 (+, C_5H_4), 58.6 (_, N*C*$(CH_3)_3$), 34.7 (+, NC(*C*$H_3)_3$), 25.2 (_, Si-CH_2), 4.9, 1.7, -2.3, -2.6 (+, Si$(CH_3)_2$).

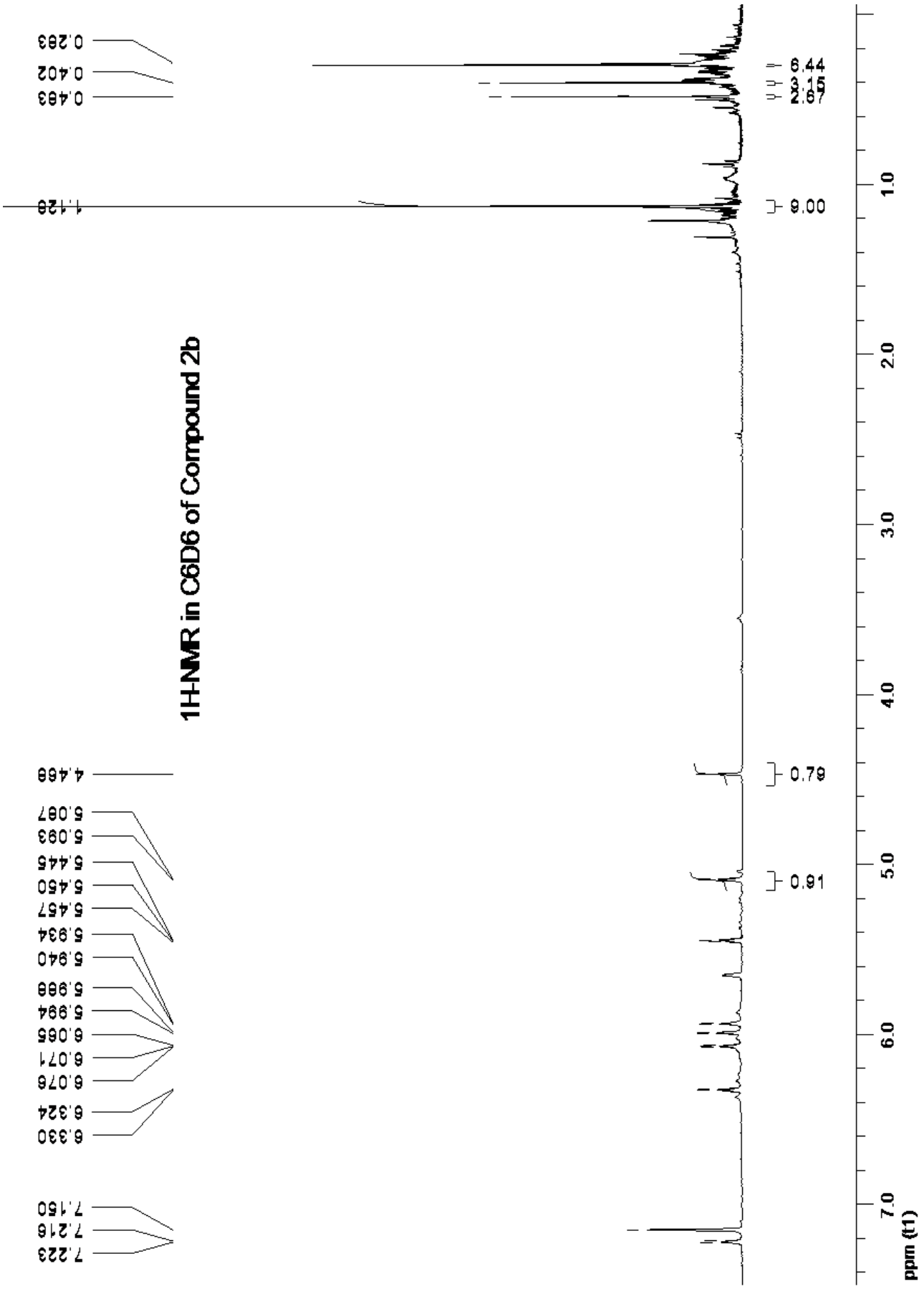
Preparation of Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu][η^5-$C_5H_4Si(CH_3)_2(CH_2CH=CH_2)$]$NMe_2$. A solution of the cyclopentadiene $C_5H_5SiMe_2(CH_2CH=CH_2)$ (0.13 g, 0.82 mmol) in toluene (10 mL) was added to dry Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu]$(NMe_2)_2$ (0.23 g, 0.63 mmol) and the mixture warmed up to 70ºC for ca. 48h. The resulting yellow suspension was allowed to reach room temperature, the toluene was evaporated to dryness and hexane (3 x 10 mL) was added to the residue. The yellow solution was filtered and the hexane removed under vacuum to give a beige solid which was identified as pure Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu][η^5-$C_5H_4Si(CH_3)_2(CH_2CH=CH_2)$]$NMe_2$: Yield: 96%. Anal. Calcd. for $C_{23}H_{40}ZrN_2Si_2$: C, 56.14; H, 8.21; N, 5.69. Found: C, 56.16; H, 8.16. ^{1}H NMR (plus HSQCGP, 400 MHz, C_6D_6): δ 6.54, 6.41, 6.33, 6.24, 6.20, 6.16, 6.04, 5.79 (all m, each 1H, C_5H_4), 5.75 (m, 1H, $^{trans}J_{HH}$ = 16.0, $^{cis}J_{HH}$ = 10.8, $^3J_{HH}$ = 8.0, =CH), 4.93 (dd, 1H, $^{trans}J_{HH}$ = 16.0, $=CH_2$), 4.94 (dd, 1H, $^{cis}J_{HH}$ = 10.8, $=CH_2$), 2.86, 2.86 (both s, each 3H, N$(CH_3)_2$), 1.64 (dd, 2H, $^2J_{HH}$ = 0.8, $^3J_{HH}$ = 8.0, Si-CH_2), 1.25 (s, 9H, C$(CH_3)_3$), 0.62, 0.46 (both s, each 3H, Si$(CH_3)_2$), 0.25, 0.25 (both s, each 3H, Si$(CH_3)_2$). ^{13}C APT NMR (plus HSQCGP, 100 MHz, C_6D_6): δ 134.8 (+, =CH), 123.5, 119.6, 117.2, 115.8, 114.9 (+, C_5H_4), 114.3 (_, ipso-C_5H_4), 114.0, (+, C_5H_4), 113.7 (_, $=CH_2$), 113.3, 111.9 (+, C_5H_4), 111.3 (_, C_5H_4-ipso), 57.2 (_, N*C*$(CH_3)_3$), 52.6, 50.4 (both s, each 3H, N$(CH_3)_2$), 35.1 (+, NC(*C*$H_3)_3$, 25.6 (_, Si-CH_2), 5.8, 2.4, -1.6, -1.9 (+, Si$(CH_3)_2$).

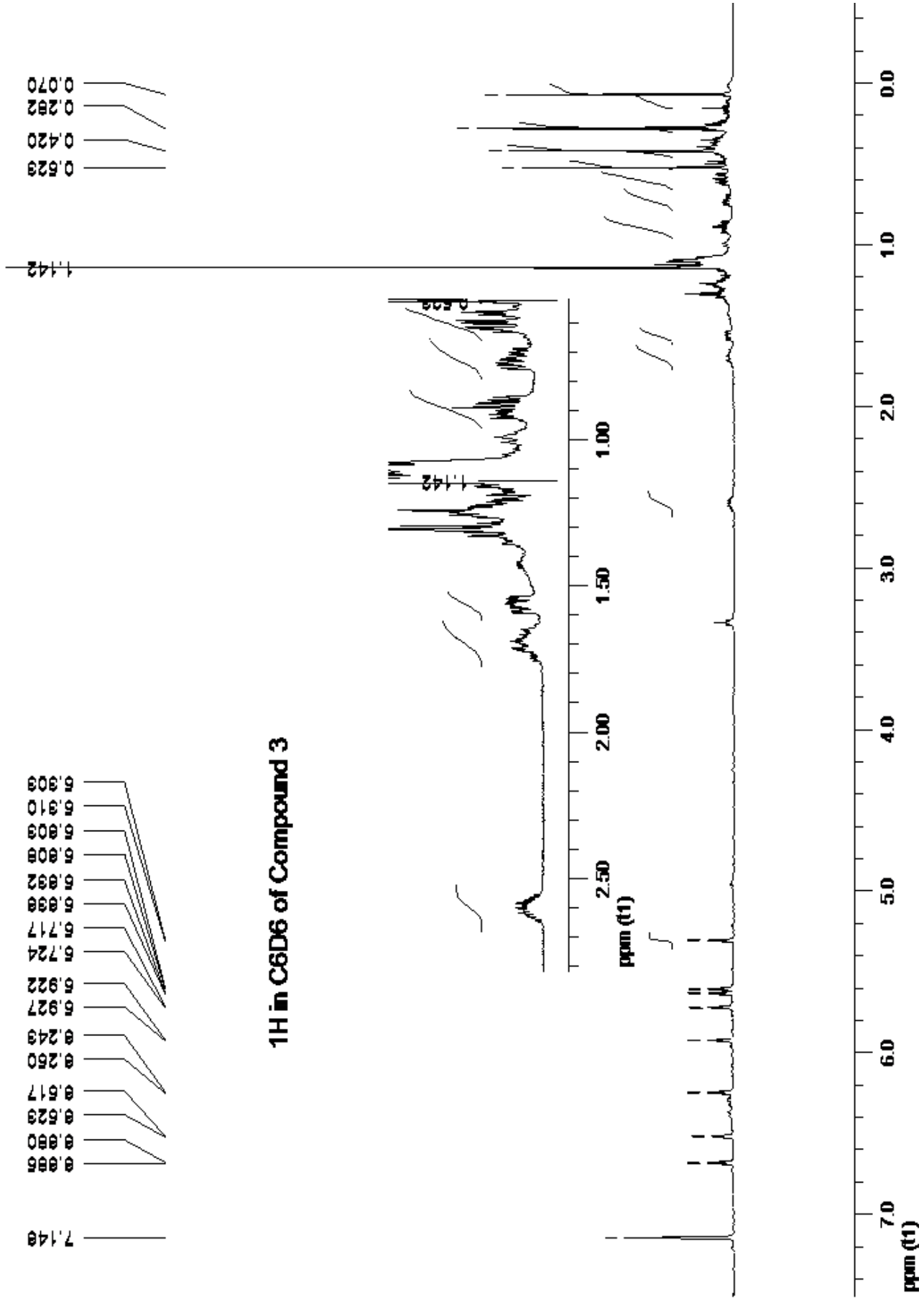
Preparation of Zr[η^5-$C_5H_4Si(CH_3)_2$-η^1-N^{t}Bu](η^5-C_5H_4R)H (R = H, 2a; $SiMe_3$, 2b). Following a general procedure, $NaHBEt_3$ (0.50 ml of a 1.0M solution in toluene, 0.50 mmol) was added to a THF (10 mL) solution of **1a-b** (0.46 mmol, R = H, 0.16 g **1a**; R = $SiMe_3$, 0.11 g **1b**), respectively, and the reaction mixture stirred at room temperature. Reaction times were from 2 hours for the synthesis of **2a** to ca. 12 hours for the preparation of **2b**. The solvent was removed under vacuum

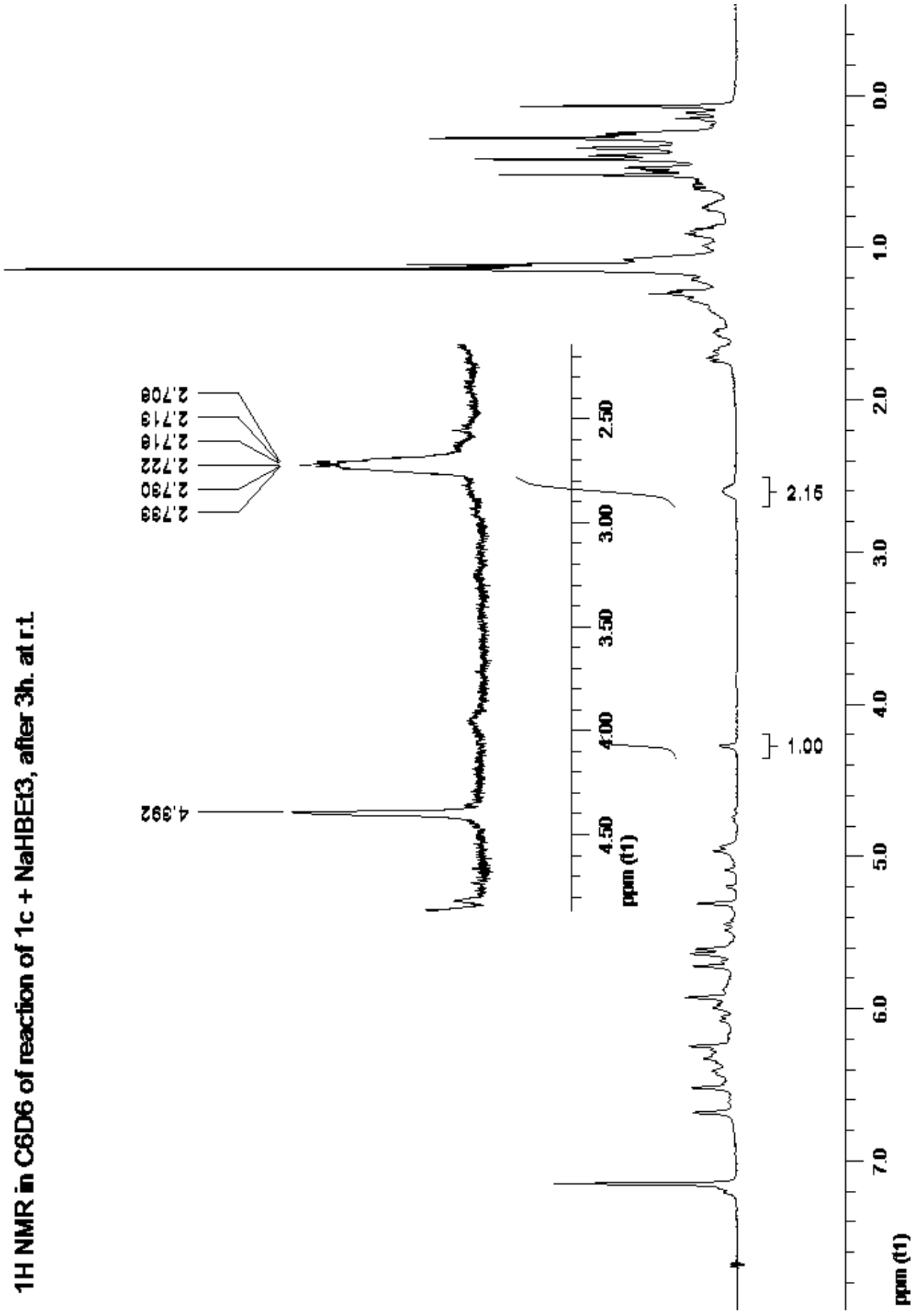
from the resulting yellow mixtures and hexane (2 x 5 mL) was then added to the oily residues, the resulting suspensions were filtered off from the white NaCl and the yellow solutions dried under vacuum to give a yellow oily-solids which were identified as pure derivatives **2a**-**b**, respectively. **2a**: Yield: 91%. Anal. Calcd. for $C_{16}H_{25}ZrNSi$: C, 54.80; H, 7.20; N, 4.0. Found: C, 55.43; H, 7.53; N, 3.77. ^{1}H NMR (400 MHz, C_6D_6): δ 7.23, 5.98 (both m, each 1H, C_5H_4), 5.88 (s, 5H, C_5H_5), 5.71, 5.34 (both m, each 1H, C_5H_4), 4.30 (s, 1H, Zr-H), 1.11 (s, 9H, $C(CH_3)_3$), 0.50, 0.38 (both s, each 3H, Si-$(CH_3)_2$). ^{13}C APT NMR (100 MHz, C_6D_6): δ 115.6, 114.7, 110.8, 108.4 (all +, C_5H_4), 107.0 (+, C_5H_5), 106.8 (_, ipso-C_5H_4), 57.9 (+, N*C*$(CH_3)_3$), 37.1 (+, C(*C*$H_3)_3$), 5.1, 3.1 (both +, Si-$(CH_3)_2$). **2b**: Yield: 85%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.22, 6.32, 6.07, 5.99, 5.94, 5.65, 5.45, 5.09 (all m, each 1H, C_5H_4), 4.47 (s, 1H, Zr-H), 1.13 (s, 9H, $C(CH_3)_3$), 0.48, 0.40 (both s, each 3H, Si-$(CH_3)_2$), 0.29 (s, 9H, Si-$(CH_3)_3$). ^{13}C APT NMR (100 MHz, C_6D_6): δ 117.7 (_, ipso-C_5H_4), 115.3, 114.8, 114.3, 113.5, 112.2, 110.8, 108.2, 107.2 (all +, C_5H_4), 106.4 (_, ipso-C_5H_4), 58.0 (_, N*C*$(CH_3)_3$), 37.2 (+, C(*C*$H_3)_3$), 5.1, 3.2 (both +, Si-$(CH_3)_2$), 1.2 (+, Si-$(CH_3)_3$).

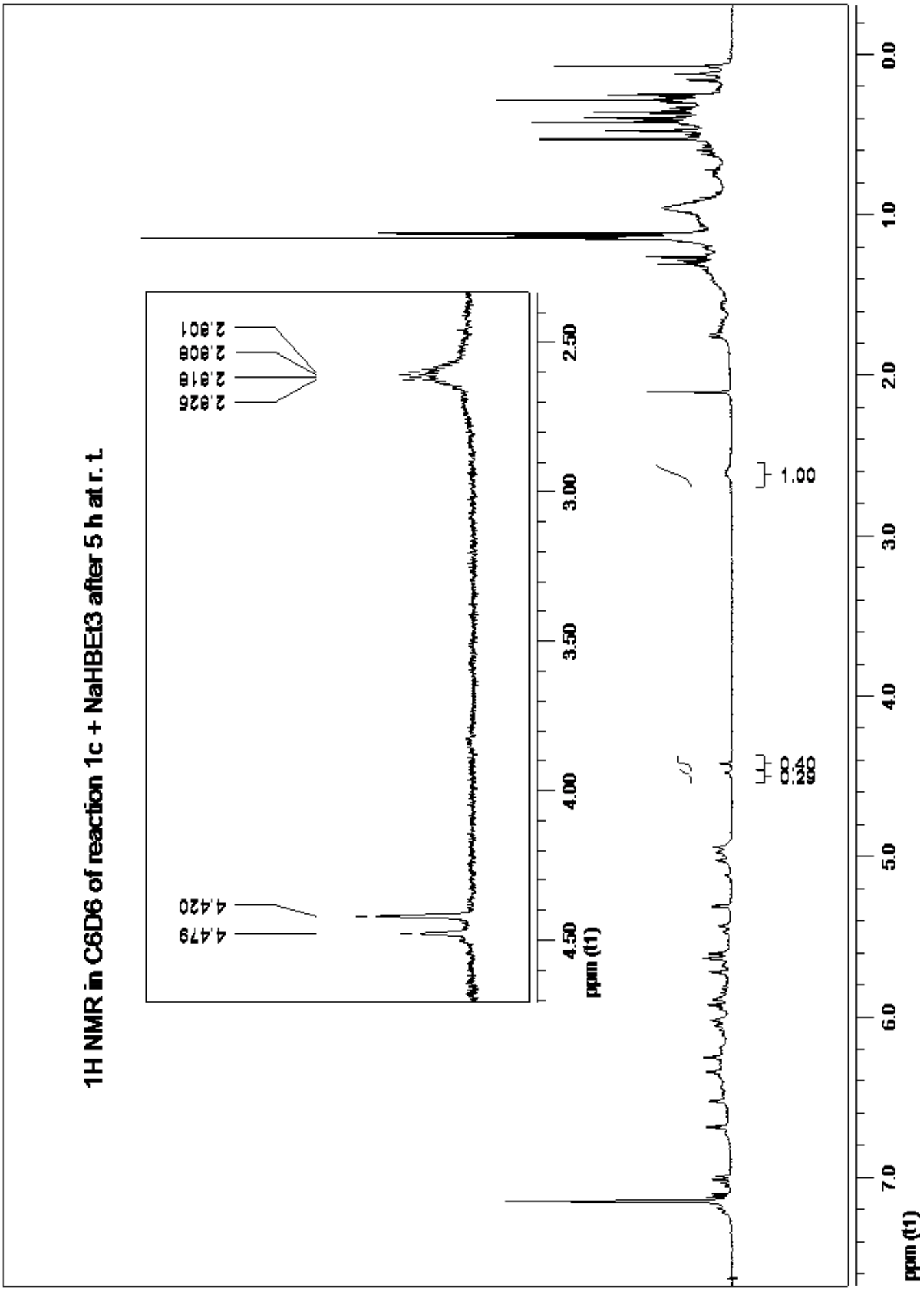

1H NMR in C6D6 of Compound 1c
7.161
1.281
Si-CH2
=CH2
6.51
3.45
2.00
1.91
0.83
0.78
1.41
0.87
0.69
1.25
1.12
1.84
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)

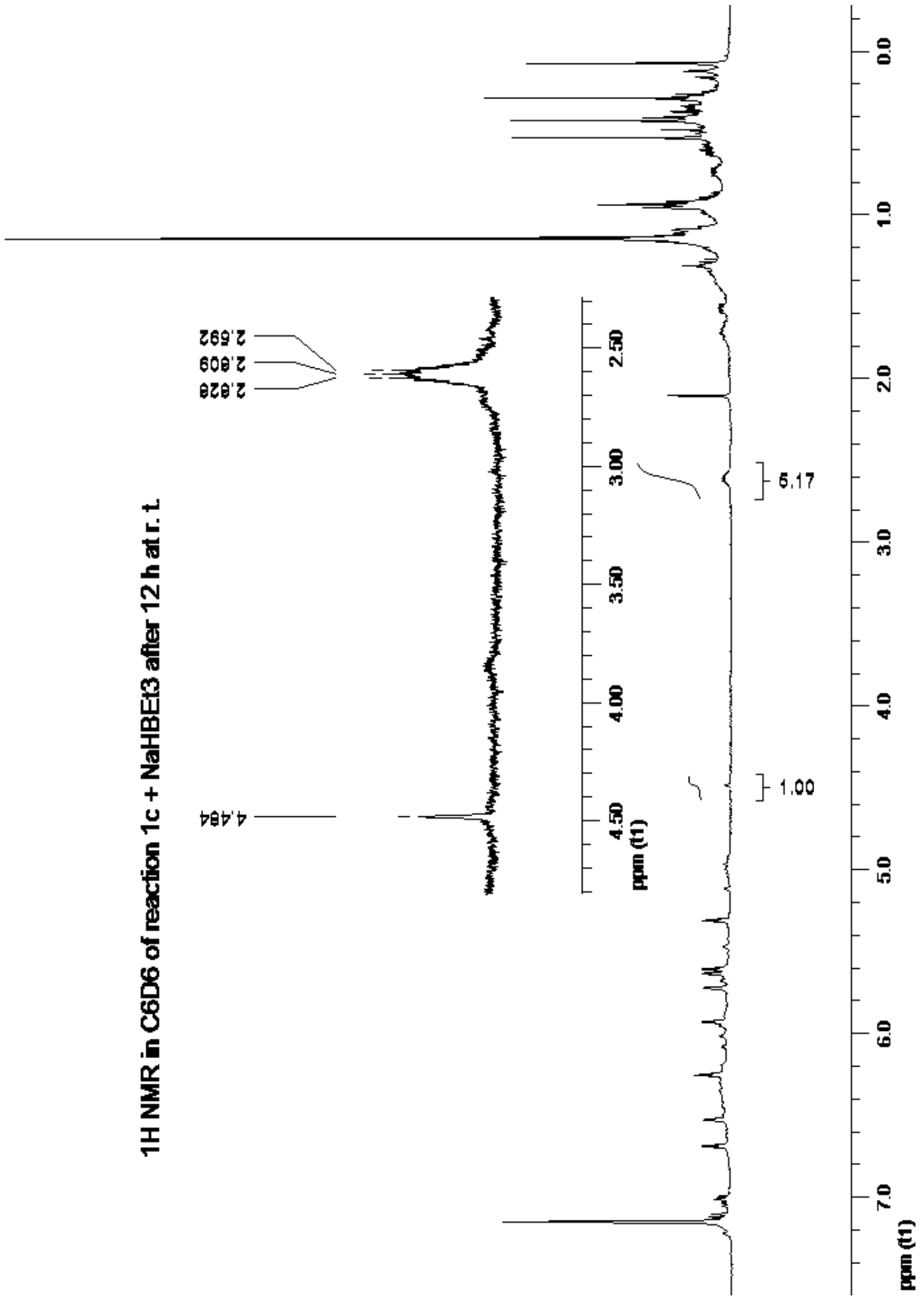

1H in Benzene-d6 of Compound 2a
Zr-H
4.308
6.718
6.713
6.342
6.338
5.50
5.00
4.50
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


1H-NMR in C6D6 of Compound 2b
0.283
0.402
0.483
1.128
4.468
5.087
5.093
5.445
5.450
5.457
5.934
5.940
5.988
5.994
6.065
6.071
6.076
6.324
6.330
7.150
7.216
7.223
6.44
3.15
2.67
9.00
0.79
0.91
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


1H in C6D6 of Compound 3
7.148
8.885
8.880
8.629
8.617
8.250
8.243
6.927
6.922
6.724
6.717
6.838
6.832
6.808
6.803
6.310
6.303
1.142
0.629
0.420
0.282
0.070
ppm (f1)


1H NMR in C6D6 of reaction of 1c + NaHBEt3, after 3h. at r.t.
4.392
2.788
2.780
2.722
2.718
2.713
2.708
2.15
1.00
4.50
4.00
3.50
3.00
2.50
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


1H NMR in C6D6 of reaction 1c + NaHBEt3 after 5 h at r. t.
4.479
4.420
2.825
2.819
2.808
2.801
4.50
4.00
3.50
3.00
2.50
ppm (f1)
1.00
0.40
0.29
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


1H NMR in C6D6 of reaction 1c + NaHBEt3 after 12 h at r. t.
4.484
2.828
2.809
2.692
6.17
1.00
ppm (f1)

Computational Details

HF method with B3LYP hybrid exchange-correlation energy functional as implemented in the Gaussian suite of programs[1] and LANL2DZ basis set were used for the theoretical study of the thermodynamic stability of each compound. Analytical gradients were used in order to determine the stationary points, and full optimizations were used in the optimization process. The stationary points have been identified as minima by checking that all the eigenvalues were positive in the approximate hessian matrix obtained during the optimization process.

Absolute and relative energies, and equilibrium population.

Table 5. The absolute (in atomic units, a.u.) and relative energies[a] (in a.u. and kcal·mol^{-1}) for the different metallacycles and the equilibrium population at 298K.

metallacycles	Absolute Energy (a.u.)	Relative Energy (a.u.)	Relative Energy (kcal/mol)	Equilibrium Population[b]
2c	-812.486853510	0.024091168	15.12	0.00 %
3	-812.510944678	0	0	99.87 %
4	-812.490283008	0.020661670	12.96	0.00 %
B-1	-812.504641902	0.006302776	3.95	0.13 %

[a] Energies relative to most stable compound, i.e. metallacycle **3**
[b] Populations obtained using the Boltzmann distribution equilibrium.

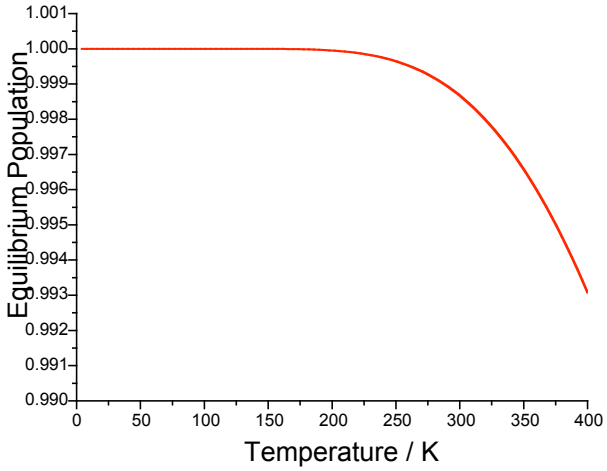


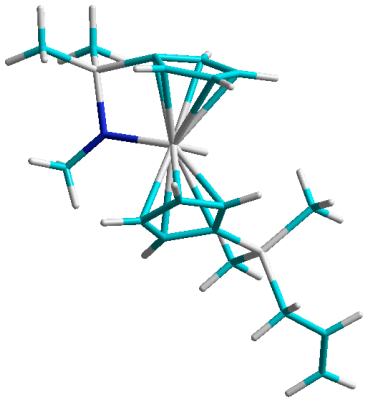
Figure 1. Equilibrium population (Boltzmann distribution) for the more stable metallacycle (**3**, see text) as a function of the temperature.

Optimized Structures
Cartesian coordinates for the DFT optimized structures (see above) in Angstroms.

- Hydrido compound **2c**

Standard orientation:

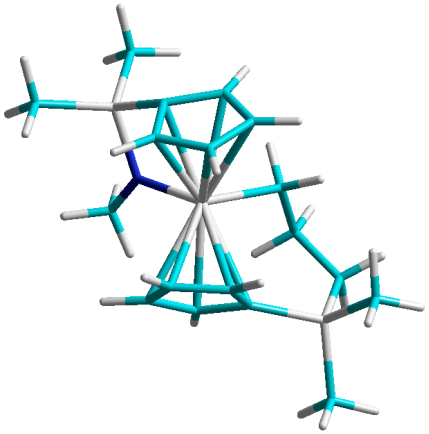
6	0.323596	0.743403	2.496118
6	1.076229	-1.142630	1.390518
6	1.771859	-0.014969	0.814546
6	1.288418	1.147127	1.511691
14	3.173302	-0.083961	-0.450437
6	3.075211	-1.688308	-1.447699
6	3.117107	1.438212	-1.579828
6	4.817656	-0.058067	0.555060
6	6.056004	-0.012137	-0.307345
6	6.928325	-1.027235	-0.497503
1	3.914838	-1.757058	-2.151211
1	3.119200	-2.571478	-0.795588
1	2.138518	-1.730305	-2.016355
1	3.926408	1.408028	-2.321447
1	2.162886	1.471498	-2.119385
1	3.222095	2.372089	-1.009955
1	4.784464	0.823445	1.214773
1	4.834747	-0.943146	1.206920
1	6.240038	0.931838	-0.827569
1	7.791472	-0.921164	-1.151051
1	6.804003	-1.989249	-0.002323
6	0.206377	-0.683965	2.428163
1	-0.182065	1.392893	3.199283
1	1.212973	-2.174940	1.093628
1	1.611342	2.166685	1.337450
1	-0.430862	-1.300583	3.048966
6	-2.046163	1.558983	-1.608770
6	-1.241572	2.589187	-1.019687
6	-1.665560	2.759098	0.334261
6	-2.720430	1.821821	0.586399
6	-2.970868	1.065483	-0.621992
1	-1.946078	1.194278	-2.621975
1	-0.462934	3.149980	-1.520353
1	-1.274790	3.483462	1.037642
1	-3.255045	1.711707	1.522242
14	-3.620063	-0.703086	-0.559131
6	-5.119125	-0.914801	0.577531
6	-3.970427	-1.432797	-2.268494
7	-2.101436	-1.340548	0.179923
40	-0.763692	0.262790	0.222585
1	0.105423	-0.104919	-1.374998
1	-6.006312	-0.434647	0.142619
1	-4.938945	-0.463525	1.561426
1	-5.357572	-1.975762	0.733311
1	-4.831545	-0.939495	-2.739755
1	-4.195720	-2.506033	-2.204745
1	-3.102390	-1.312365	-2.928295
6	-2.002077	-2.757627	0.586073
1	-2.787240	-3.032778	1.310891
1	-2.097734	-3.432066	-0.280780
1	-1.034170	-2.970178	1.053477



- Metallacycle **3:**

Standard orientation:

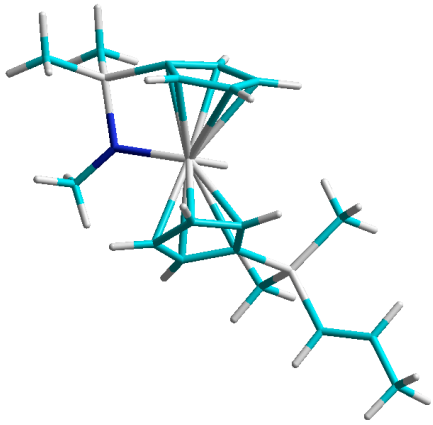
6	0.649419	1.234090	2.301225
6	1.420807	-0.856121	1.691315
6	2.183867	0.108478	0.935223
6	1.685398	1.400339	1.322008
14	3.625442	-0.243077	-0.225929
6	4.132558	1.383155	-1.067475
6	5.087724	-0.899322	0.797308
6	3.122407	-1.551943	-1.529495
6	1.611643	-1.910629	-1.585352
6	0.677959	-0.679716	-1.759709
1	4.441844	2.140850	-0.334762
1	4.980287	1.215206	-1.745973
1	3.309314	1.799680	-1.663081
1	5.953486	-1.112381	0.154299
1	5.401636	-0.171719	1.557349
1	4.819300	-1.829435	1.316581
1	3.425291	-1.174991	-2.519862
1	3.712160	-2.466140	-1.358460
1	1.463966	-2.609746	-2.426523
1	1.184258	0.079083	-2.383461
1	-0.212851	-0.989219	-2.333027
6	0.496309	-0.169275	2.538150
1	0.110370	2.028345	2.801315
1	1.556683	-1.929718	1.657148
1	2.051546	2.350551	0.952995
1	-0.202398	-0.626363	3.226599
6	-1.773162	1.290967	-1.825203
6	-0.820293	2.331073	-1.586191
6	-1.031509	2.821271	-0.259269
6	-2.105660	2.070724	0.320261
6	-2.578422	1.107306	-0.647444
1	-1.848911	0.711678	-2.735817
1	-0.087611	2.698346	-2.293301
1	-0.492447	3.632523	0.212878
1	-2.500888	2.206756	1.319706
14	-3.330935	-0.543206	-0.136530
6	-4.640454	-0.384233	1.222821
6	-4.025438	-1.533298	-1.593553
7	-1.768243	-1.182449	0.473192
40	-0.308975	0.279535	0.099477
1	-5.551134	0.090603	0.832809
1	-4.273444	0.224293	2.059059
1	-4.923046	-1.367718	1.622578
1	-4.928930	-1.056053	-1.997187
1	-4.296584	-2.552497	-1.285775
1	-3.291468	-1.614684	-2.405039
6	-1.684504	-2.507936	1.118701
1	-2.333124	-2.578739	2.009196
1	-1.982753	-3.312730	0.425819
1	-0.660442	-2.729857	1.441053
1	1.337598	-2.481804	-0.684047



- Hydrido compound **4:**

Standard orientation:

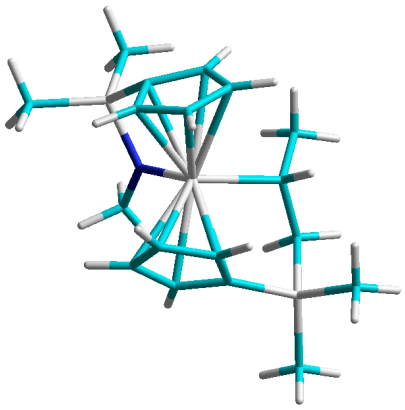
6	-0.512370	0.094051	-2.441831
6	-1.009469	-1.599214	-0.947807
6	-1.788735	-0.448006	-0.551733
6	-1.466452	0.591631	-1.490434
14	-3.107146	-0.392864	0.805155
6	-2.858174	-1.883752	1.950107
6	-3.017827	1.233391	1.775750
6	-4.792017	-0.521136	-0.039996
6	-5.811578	0.361639	0.092140
6	-7.160633	0.257366	-0.587390
1	-3.590214	-1.864768	2.768300
1	-2.991164	-2.831970	1.411645
1	-1.851918	-1.872474	2.387059
1	-3.803478	1.279009	2.541946
1	-2.046036	1.311938	2.277223
1	-3.136938	2.106664	1.120054
1	-4.956665	-1.382600	-0.697330
1	-7.973407	0.218426	0.153107
1	-7.350424	1.135771	-1.222173
6	-0.245448	-1.275937	-2.111695
1	-0.111780	0.636886	-3.288655
1	-1.021327	-2.559575	-0.447552
1	-1.894021	1.587026	-1.497695
1	0.424031	-1.938864	-2.644246
1	-5.682666	1.236284	0.735718
1	-7.223345	-0.639612	-1.214893
6	1.975019	1.852040	1.301019
6	0.990798	2.677495	0.664280
6	1.275919	2.701998	-0.735674
6	2.426654	1.878429	-0.965325
6	2.876708	1.342272	0.301439
1	2.007770	1.625245	2.357958
1	0.184048	3.200364	1.161194
1	0.732411	3.261128	-1.486660
1	2.894566	1.703464	-1.926686
14	3.751592	-0.323547	0.414439
6	5.144023	-0.523452	-0.853429
6	4.374546	-0.732257	2.153125
7	2.271450	-1.247208	-0.043396
40	0.733191	0.159041	-0.202647
1	0.025045	-0.063336	1.498830
1	6.001526	0.112465	-0.594480
1	4.806596	-0.243339	-1.859431
1	5.500327	-1.561724	-0.896354
1	5.219936	-0.087162	2.429031
1	4.716020	-1.774340	2.218502
1	3.580919	-0.593853	2.897653
6	2.317006	-2.715308	-0.200465
1	3.049859	-3.025004	-0.965239
1	2.591744	-3.211634	0.744892
1	1.340716	-3.113361	-0.498838



- Metallacycle **B-1:**

Standard orientation:

6	-1.096890	-1.048062	1.452261
6	-0.308130	-2.097937	2.282565
6	1.896853	0.392060	2.075952
6	1.014273	1.465344	2.412080
6	1.148905	2.470781	1.403949
6	2.108290	2.005831	0.444022
6	2.581068	0.704916	0.851087
1	2.015752	-0.522941	2.637391
1	0.376125	1.519110	3.284901
1	0.640202	3.425846	1.387057
1	2.425929	2.546024	-0.439750
14	3.132129	-0.637633	-0.348989
6	4.259610	0.000540	-1.730952
6	3.927210	-2.126106	0.507180
7	1.456995	-0.961833	-0.910884
40	0.182397	0.380945	0.073810
1	5.270497	0.201084	-1.350540
1	3.871007	0.931056	-2.164503
1	4.348892	-0.734564	-2.542562
1	4.909143	-1.861097	0.922581
1	4.076344	-2.957371	-0.195498
1	3.297054	-2.492215	1.327113
6	1.194962	-1.925722	-2.001106
1	1.457554	-1.514876	-2.991212
1	1.771640	-2.855559	-1.864555
1	0.137807	-2.215653	-2.031963
6	-0.767780	2.398300	-1.313717
6	-1.405357	0.283479	-1.988515
6	-2.254529	0.645595	-0.883514
6	-1.837016	1.956707	-0.465942
14	-3.469756	-0.526945	-0.049427
6	-4.457111	0.390765	1.284383
6	-4.650111	-1.301858	-1.317574
6	-2.255095	-1.783482	0.693686
1	-5.107409	1.157878	0.842569
1	-5.097090	-0.307637	1.840763
1	-3.798416	0.884596	2.010523
1	-5.271147	-2.080198	-0.852915
1	-5.322487	-0.547947	-1.748329
1	-4.096934	-1.766895	-2.144599
1	-2.759259	-2.504173	1.364909
1	-1.842098	-2.389870	-0.131725
6	-0.499217	1.358683	-2.258626
1	-0.267459	3.356379	-1.264085
1	-1.462109	-0.639189	-2.551546
1	-2.277067	2.531682	0.340191
1	0.245131	1.385253	-3.044310
1	0.353905	-1.638606	3.025336
1	-1.002815	-2.754696	2.836118
1	0.304199	-2.744191	1.637414
1	-1.564568	-0.351117	2.179533



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[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 03, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 2003