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ARTICLE

Scandium alkyl and hydride complexes supported by a pentadentate diborate ligand: reactions with CO_2 and N_2O†

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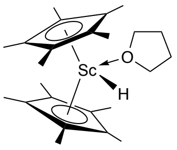
Alkyl and hydrido scandium complexes of the dianionic pentatdentate ligand B_2Pz_4Py are reported. The key starting material (B_2Pz_4Py)ScCl is readily prepared and alkylated with organolithium reagents RLi (R = CH_3, CH_2SiMe_3, CH_2SiMe_2Ph, $CH_2CH_2CH_3$ and CH_2CHMe_2) to form alkyl derivatives in 61-93% yields. These compounds are very thermally stable and do not undergo sigma bond metathesis reactions with dihydrogen. The hydrido complex was prepared from (B_2Pz_4Py)ScCl and $NaHBEt_3$ in 80% yield and was found to be more stable by 28 kcal mol^{-1} as a dimer, rather than a monomeric hydrido complex. However, the monomer is accessible through dissociation of the dimer at 80˚C. All of the compounds (B_2Pz_4Py)ScR react with water to form the bridging oxo dimer (B_2Pz_4Py)ScOSc(B_2Pz_4Py). The reactivity of the hydrido and methyl complexes towards carbon dioxide was explored; heating to 80˚C results in the formation of κ^2 formato and acetate complexes, respectively. The mechanisms were studied via density function theory and distinct transition states for insertion of CO_2 into the Sc-R (R = H, CH_3) were found, with the insertion into the Sc-CH_3 being more enthalpically difficult (by 18 kcal mol^{-1}) than insertion into Sc-H. The slow rate of reaction between [(B_2Pz_4Py)ScH]$_2$ and CO_2 is attributed to the barrier associated with dimer dissociation. In both insertion reactions, the kinetic products are κ^1 formato or acetate complexes that are only slightly less stable than the observed κ^2 derivatives. The κ^1 compounds can therefore be trapped by treating the κ^2 isomers with *tris*-pentafluorophenyl borane.

Introduction

Hydrides of the group 3 metals and lanthanides are extremely reactive compounds[1-3] that are key intermediates in several hydroelementation reactions[4-5] and C-H bond activation processes proceeding via a sigma bond metathesis mechanism.[6-10] Often they are generate *in situ*; when isolated, they tend to form dimers or higher oligomers[11-12] due to the high Lewis acidity and coordinative unsaturation of this family of compounds and the facility with which the hydride ligand can act to bridge metal centres. Thus, examples of monomeric group 3/lanthanide metal hydrides remain rare and in the province of compounds with highly sterically crowded or multidentate ligand environments.[13] Alternatively, they may be accessible via dissociation of a dimeric structure into more reactive monomeric hydrides through equilibrium processes.

This is even true for the smallest of this family of elements, scandium.[14-18] To date, very few monomeric Sc-H complexes have been reported and only one has been structurally characterized. *Bis*-(pentamethylcyclopentadienyl)scandium hydride is of unknown nuclearity, but its tetrahydrofuran (THF) adduct (**I**) is proposed to be monomeric as determined by solution molecular weight measurements.[6] Chen and co-workers recently reported the beta-diketiminato (Nacnac) supported monomeric compound **II** that features a terminal Sc-H moiety generated by addition of dihydrogen (H_2) across the Sc=N bond of a scandium imido precursor.[19] Evidently, in **II** the pendant amine donor is able to prevent transfer of the hydride to the imine functions of the Nacnac ligand, as has been observed in complexes with more conventional Nacnac or salicylaldiminato ligands.[20]



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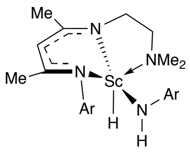
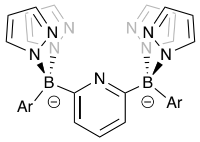


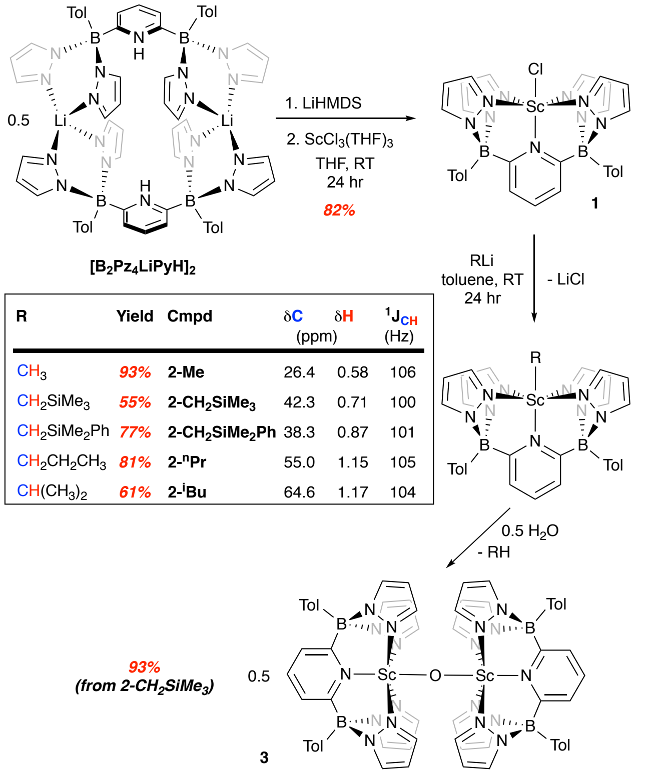
II



B_2Pz_4Py

It is thus clear that, in order to access and study monomeric Sc-H functions, both the steric and electronic properties of the ligands on scandium play an important role. We recently have developed a dianionic, pentadentate ligand system (**B_2Pz_4Py**) that provides a well-defined platform for chemistry in the sixth coordination site *trans* to the anchoring pyridyl donor. For example, we have been able to generate highly reactive imido radicals of Fe(III)[21] and Co(III)[22] using this ligand as a platform. Unlike the neutral, all-pyridyl ligand that inspired our thinking,[23-25] this dianionic ligand is suitable for exploring chemistry right across the d-block, including the early metals, and we hypothesized that it may be a viable ligand for supporting group 3 metal alkyls and hydrides. Herein we report the preparation of organoscandium compounds supported by the **B_2Pz_4Py** ligand and their reactions with CO_2[26-27] and N_2O.[28] Contrary to expectations, the hydride derivative is a ground state dimer, illustrating the high tendency of basic early metal hydrides to bridge these Lewis acidic metal centers. However, a monomeric Sc-H derivative is accessible via a dimer/monomer equilibrium upon heating and is highly reactive.

Results and discussion



R	Yield	Cmpd	δC (ppm)	δH (ppm)	$^1J_{CH}$ (Hz)
CH_3	93%	**2-Me**	26.4	0.58	106
CH_2SiMe_3	55%	**2-CH$_2$SiMe$_3$**	42.3	0.71	100
CH_2SiMe_2Ph	77%	**2-CH$_2$SiMe$_2$Ph**	38.3	0.87	101
$CH_2CH_2CH_3$	81%	**2-^{n}Pr**	55.0	1.15	105
$CH(CH_3)_2$	61%	**2-^{i}Bu**	64.6	1.17	104

Scheme 1 Synthesis of **1** and Sc(III) alkyl derivatives **2-R** and the reactions of **2-R** with water.

The *p*-tolyl substituted ligand precursor **$[B_2Pz_4LiPyH]_2$**[29] was deprotonated with lithium hexamethyl disilazane in THF and solid $ScCl_3$•$(THF)_3$ was added to the resulting solution (Scheme 1). Stirring for several hours led to formation of the Sc-Cl starting material **1** in excellent yield. Compound **1** was characterized crystallographically (Figure S1) and shown to be monomeric in the solid state. The Sc atom protrudes by 0.257(2)Å from the plane defined by the four pyrazolyl nitrogens; this is in contrast to related structures for Co(III) and Fe(III) compounds and is due to the larger size of the Sc(III) ion. The average Sc-N_{py} distance is 2.204(6) Å and the Sc-N_{py} bond length is longer at 2.306(3)Å, causing the pyridyl donor to tilt such that the angle between the planes defined by the six pyridyl atoms and the four N_{pz} atoms is 75.3(2)˚. Treatment of the chloro complex **1** with a variety of alkyllithium reagents smoothly affords the alkyl complexes **2-R** as colourless white or pale yellow solids in moderate to excellent yields; the lower yield of **2-CH$_2$SiMe$_3$** is attributable to its high solubility. The pattern of ligand resonances for all of the compounds **2-R** is indicative of C_{2v} symmetry, implying free rotation about the Sc-C bonds. The solid state structures of **2-Me** and **2-CH$_2$SiMe$_3$** were determined (Figure 1) and that of the latter shows that, as in several related Co and Fe structures,[21-22] the $SiMe_3$ group aligns with the "narrow groove" defined by the smaller of the N_{pz}-Sc-N_{pz} angles (N6-Sc1-N8, in this instance). Although these angles are smaller, this vector is the most sterically open in the coordination sphere sculpted by this ligand. However, the barrier to rotation by ≈ 90˚ to place the R group in the "wide groove" must be small and so, in solution, an averaged structure is always manifested, even at low temperatures. The resonances for the alpha carbon atoms exhibited some broadening due to the quadrupolar ^{45}Sc nucleus but were easily detectable in the ^{13}C NMR spectra, and the corresponding alpha hydrogen resonances in the ^{1}H NMR spectra were sharp; the values for these resonances are given in the Scheme 1 legend. The $^1J_{CH}$ coupling constants for the alpha C-H bonds are somewhat lower than in the free alkanes,[30] likely a reflection of the electropositive nature of the $(B_2Pz_4Py)Sc$ substituent rather than any alpha agostic interactions since there are no low energy C-H stretching bands in the IR spectra of compounds **2-Me** or **2-CH$_2$SiMe$_3$** (Figure S27). This is consistent with the normal Sc-C distances of 2.224(2) and 2.184(6) Å in **2-Me** and **2-CH$_2$SiMe$_3$**, respectively.[‡] The Sc-N_{py} (Sc1-N1) distances in **2-R** are slightly longer than in **1** as a consequence of the stronger *trans* influence for an alkyl group vs the chloro ligand.

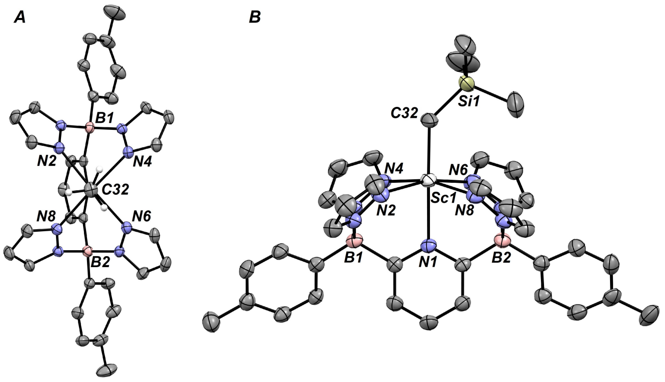


Figure 1 Molecular structures of **2-Me** (A) and **2-CH$_2$SiMe$_3$** (B). Except for those on C32 of **2-Me**, hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (˚) for **2-Me**: Sc1–N1, 2.342(1); Sc1–N2, 2.211(2); Sc1–N4, 2.195(2); Sc1–N6, 2.185(2); Sc1–N8, 2.222(2); Sc1–C32, 2.224(2); N2–Sc1–N8, 99.38(7); N2–Sc1–N4, 82.33(7); N4–Sc1–N6, 91.56(7); N6–Sc1–N8, 82.88(7). Selected bond lengths (Å) and angles (˚) for **2-CH$_2$SiMe$_3$**: Sc1–N1, 2.333(1); Sc1–N2, 2.244(2); Sc1–N4, 2.204(3); Sc1–N6, 2.192(2); Sc1–N8, 2.228(3); Sc1–C32, 2.185(6); N2–Sc1–N8, 96.78(8); N2–Sc1–N4, 82.91(8); N4–Sc1–N6, 91.21(8); N6–Sc1–N8, 85.19(8); Sc1–C32–Si1, 131.1(4).

Compounds **2-R** are highly sensitive to protic reagents, especially adventitious water; treatment of any of the compounds with H_2O leads to conversion to the Sc-O-Sc dimer **3**, Scheme 1. In all but the driest of media, small amounts of **3** can be detected, and it can be made preparatively in 93% yield with intentional addition of water. The molecular structure of **3** is shown in Figure 2, and despite short essentially equal Sc-O bonds of 1.8827(5)Å, the Sc1'-O1-Sc1 angle is slightly bent (166.62(14)˚) from linearity, probably due to packing forces. These data compare to distances of 1.910(5) and 1.925(5) Å and an angle of 174.1˚ for the related complex $[(C_5Me_4H)_2Sc]_2(\mu\text{-}O)$.[31]

While the signature reaction of organoscandium complexes supported by soft cyclopentadienyl ligands is sigma bond metathesis,[6, 32] this reactivity is largely absent in harder ligand environments where the more positively charged scandium center's orbitals are less available to interact with sigma bonds.[33-36] The coordinative saturation of compounds **2-R** exacerbates the low tendency to engage in sigma bond metathesis and, indeed, these alkyls are completely unreactive towards hydrogen, even with heating, and so the hydride **2-H** was not accessible via this route (Scheme 2). The *n*-propyl and *i*-butyl derivatives were prepared to see if beta elimination to **2-H** was possible; all compounds **2-R** are remarkably thermally robust, with **2-^{i}Bu** being the only compound that thermally converts to another species upon prolonged heating (Scheme 2). Isobutene was detected as a by-product and the other species was confirmed to be hydride **2-H** via its more efficient synthesis in 80% yield from **1** and $NaHBEt_3$ as shown in Scheme 2. Similarly, the deuteride *d_1*-**2-H** could be prepared using $LiDBEt_3$. In addition to familiar patterns for the ligand protons, a broad signal at 9.2 ppm in the ^1H NMR spectrum was observed and could be assigned as that due to Sc-*H* based on the observation of a sharper signal at this chemical shift in the $^2H\{^1H\}$ NMR spectrum. A comparison of the IR spectra for **2-H** and *d_1*-**2-H** suggested a band at 676 cm^{-1} (that shifted to 499 cm^{-1}) could be assigned to the Sc-H moiety. None of this spectroscopic data points definitively at a monomeric structure and all attempts to grow X-ray quality crystals of **2-H** were unsuccessful. Therefore we conducted DOSY NMR experiments on **2-Me**, **2-H** and **3**, which showed that **2-H** has a similar diffusion coefficient and hydrodynamic radius to that of **3**, not the definitively monomeric **2-CH_3** (Figures S33-S35). A solution molecular weight determination using the Signer method resulted in a value of 1190 g mol^{-1}, consistent with the calculated MW of 1105.22 g mol^{-1} for a dimeric structure. Finally, density functional theory (DFT) computations using the B3PW91 functional indicated that the dimer was favoured by 28.3 kcal mol^{-1} over the monomer in a monomer/dimer equilibrium. Thus, despite the pentadentate nature of the **B_2Pz_4Py** ligand, **2-H** is favoured in its dimeric form **[2-H]$_2$** as shown in Scheme 2.

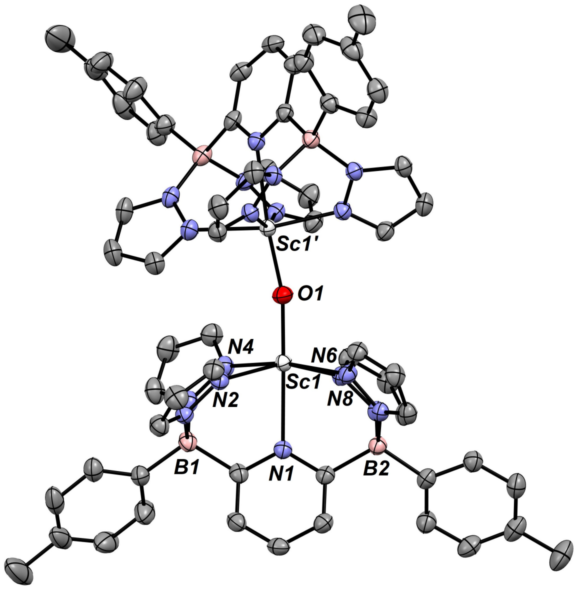
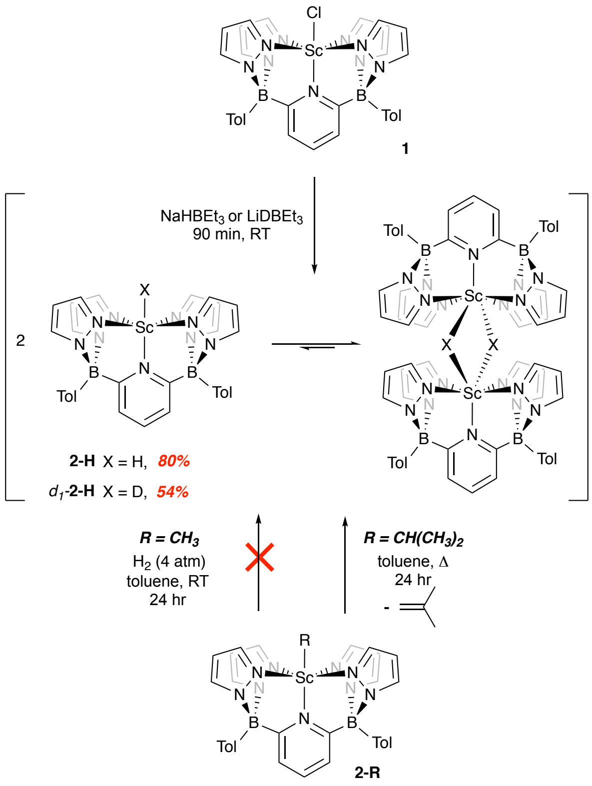


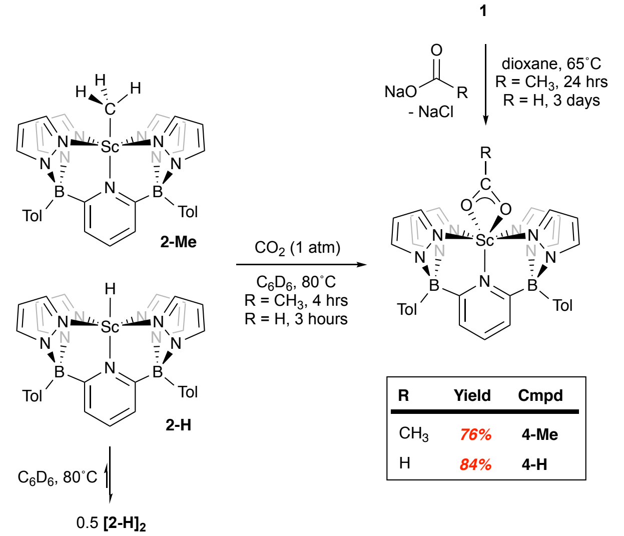
Figure 2. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Sc1–N1, 2.378(2); Sc1–N2, 2.275(2); Sc1–N4, 2.208(2); Sc1–N6, 2.226(2); Sc1–N8, 2.229(2); Sc1–O1, 1.8838(6); N2–Sc1–N8, 102.31(7); N2–Sc1–N4, 81.64(7); N4–Sc1–N6, 91.74(7); N6–Sc1–N8, 80.27(7); Sc1–O1–Sc1', 166.62(14).



Scheme 2 Synthesis of scandium hydride complex **3** and a lack of sigma bond metathesis.

Despite the fact that the dimeric form of **2-H** is favoured, we explored its reactivity with small molecules, including D_2, N_2O and CO_2. Assuming that reactivity proceeds through the monomer, barriers of at least 28 kcal mol^{-1} would be expected and, indeed, reaction of **2-H** did not proceed at room temperature with any of these reagents. Heating benzene or toluene solutions of **2-H** to 80°C under 1 atm of D_2 did not result in any production of *d_1*-**2-H**, suggesting that even the monomer was immune to this most facile of sigma bond metathesis processes.[6] When treated with an excess of N_2O at 80°C, however, clean conversion of **2-H** to the oxo-bridged dimer **3** was observed. Such reactions with other, monomeric electropositive metal hydrides (Hf-H[37] and Mg-H[38]) are quite facile at room temperature, resulting in M-OH complexes[39] that may or may not undergo further reactions to M-O-M complexes. Here, heating is required to generate the monomer, which undergoes reaction with N_2O to produce the unobserved presumed intermediate **2-OH** which reacts further with **2-H** to give **3** and H_2 in quantitative yield by ^1H NMR spectroscopy after 6 hours. The dihydrogen byproduct was identified by the signal at 4.47 ppm (C_6D_6) that disappeared once the sealed tube had been opened to a glove box atmosphere.

The accessibility of monomeric **2-H** through heating encouraged us to explore the reactions of **[2-H]$_2$** and genuinely monomeric **2-Me** with carbon dioxide (Scheme 3). Both reactions required heating to 80˚C for 3-4 hours in benzene in order to proceed to completion, and the products were identified as the acetate and formate complexes **4-Me** and **4-H**, respectively. While these insertion reactions were clean on a small scale (as determined by ^{1}H NMR spectroscopy), an alternate salt elimination route starting from **1** and sodium acetate or formate was employed for preparative scale experiments. This separate synthesis also confirmed the identity of the CO_2 insertion products **4-R**, which were structurally characterized by X-ray crystallography (Figure 3). The structures are very similar in terms of the metrical data associated with the molecular core, and there are no atypical distances or angles present. The κ^2 acetate and formate ligands lie along the axis that bisects the two wide N-Sc-N angles; since the steric bulk of the ligands is minimal, this must be an electronic preference.



Scheme 3. CO_2 insertion reactions of **2-Me** and **2-H** and separate synthesis of formate and acetate products **4-Me** and **4-H**.

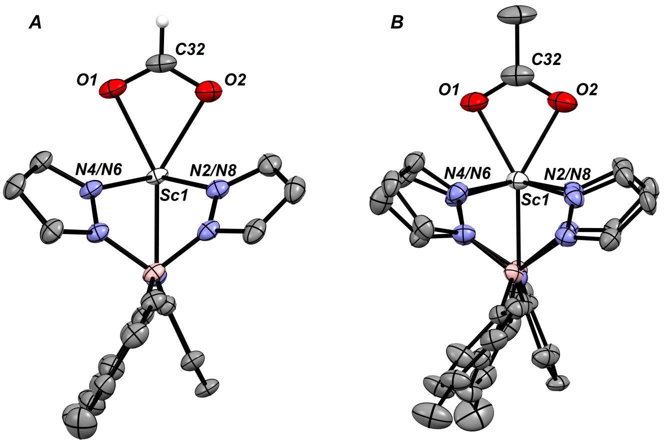


Figure 3. Molecular structures of **4-H** (A) and **4-Me** (B). Most hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (˚) for **4-H**: Sc1–N1, 2.311(1); Sc1–N2, 2.266(2); Sc1–N4, 2.208(2); Sc1–N6, 2.216(2); Sc1–N8, 2.265(2); Sc1–O1, 2.230(1); Sc1–O2, 2.256(2); C32–O1, 1.243(3); C32–O2, 1.255(3); N2–Sc1–N8, 102.48(7); N2–Sc1–N4, 80.55(7); N4–Sc1–N6, 92.37(7); N6–Sc1–N8, 80.16(7); O1–Sc1–O2, 58.199(7). Selected bond lengths (Å) and angles (˚) for **4-Me**: Sc1–N1, 2.358(6); Sc1–N2, 2.288(6); Sc1–N4, 2.213(7); Sc1–N6, 2.195(7); Sc1–N8, 2.231(7); Sc1–O1, 2.198(6); Sc1–O2, 2.216(7); C32–O1, 1.250(12); C32–O2, 1.281(12); N2–Sc1–N8, 102.4(2); N2–Sc1–N4, 79.0(2); N4–Sc1–N6, 91.6(2); N6–Sc1–N8, 81.5(2); O1–Sc1–O2, 59.1(2).

The reaction profiles for these insertion reactions were explored via DFT calculations at the B3PW91 level and were found to proceed through quite different transition states, despite having qualitatively similar rates. The relative energies of the reactants, intermediates, transition states and products (relative to **2-H** and **2-Me** at 0 kcal mol^{-1}) for each insertion are depicted in Figure 4, while the transition structures for the insertion step in each process are given in Figure 5. For both reactions, a weak, entropically disfavoured van der Waals complex with CO_2 was found, which leads to the insertion transition states. For the **2-Me** reaction, **TS$_{2\text{-Me}}$** is enthalpically 17 kcal mol^{-1} above the ground state of **2-Me**, and features a weak Sc-O interaction with one of the CO_2 oxygen atoms (Sc-O = 2.52Å) and a bent O-C-O angle of 161˚. The nascent C-C bond is not yet fully formed (C-C = 2.39Å), indicating an early transition state, and is likely due to the highly directional nature of the sp^3 hybridized orbital on the methyl group. This **TS$_{2\text{-Me}}$** connects to a κ^1 acetate complex in a highly exothermic path (-46.9 kcal mol^{-1} downhill) which converts to the even more stable κ^2 observed product via a nearly barrierless Sc-O bond rotation.

In contrast, the barrier to insertion into the Sc-H bond of **2-H** is much smaller, almost negligible relative to the energy of monomeric Sc-H; the barrier is only 0.8 kcal mol^{-1} starting from the van der Waals complex between **2-H** and CO_2. Therefore, the experimentally observed sluggishness of this reaction must be due to the need to dissociate **[2-H]$_2$** into the highly reactive monomer, creating an effective barrier of > 28 kcal mol^{-1} and accounting for the fact that production of **4-H** proceeds at

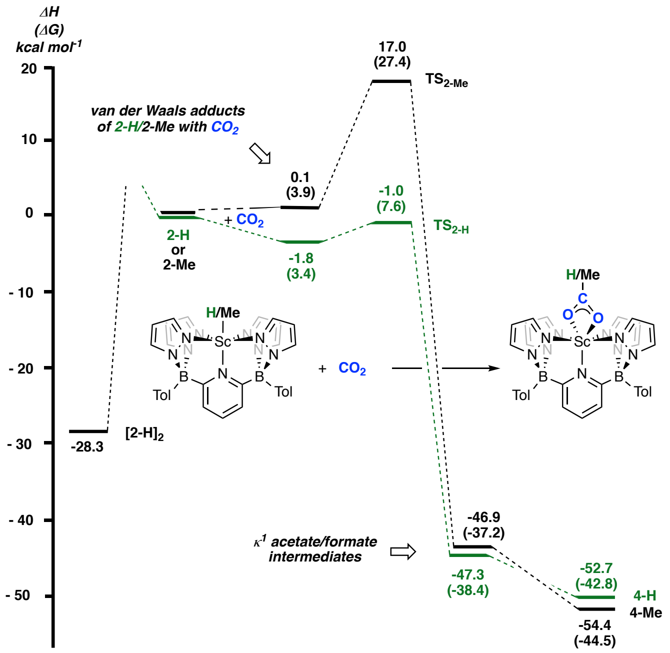


Figure 4. Computed reaction profile (DFT, B3PW91) for the insertion of CO$_2$ into the Sc-H and Sc-C bonds of **2-H** (green line) and **2-Me** (black line). ΔG values given in parentheses.

similar rates to those observed for **4-Me**. From monomeric **2-H**, the transition state for CO$_2$ insertion is unusual in that it can be characterized as a direct nucleophilic attack of the Sc-H moiety on unactivated CO$_2$; the O-C-O angle is only slightly bent (168°) and the closest Sc-O distance is 3.06Å. This is reflective of the high basicity of the hydride ligand in **2-H**. Charge density analysis indicates that the charge at H is -0.38 and the Wiberg bond index of the Sc-H is 0.8, indicating a significant degree of ionicity in the bond (1.0 would be a pure covalent bond). Natural bond analysis indicates that the Sc-H bond is indeed strongly polarized toward H (30% Sc and 70%H). Thus, while the forming C-H bond in **TS$_{2\text{-H}}$** is still quite long (2.15Å) the high hydricity of the scandium hydride makes it basic enough to react directly with CO$_2$ without Lewis acid activation of a carbon dioxide oxygen atom as seen in **TS$_{2\text{-Me}}$**.

As can be seen in the reaction profiles of Figure 4, the kinetic products of insertion are the κ^1 formate and acetate complexes that are only 5.4 (**4-H**) or 7.5 (**4-Me**) kcal mol^{-1} higher in energy than the κ^2 thermodynamic products. Accordingly, we attempted to trap the κ^1 isomers by treating with B(C$_6$F$_5$)$_3$ and found that compounds **4-R** undergo clean conversion to the μ-formato and acetato complexes **5-H** and **5-Me** (Scheme 4). Borate formation is signalled by boron chemical shifts of ≈ 0 ppm for each of compounds **5-R** and a $\Delta_{m,p}$ difference of 6.7 ppm and 6.9 ppm for **5-Me** and **5-H**, respectively, in the ^{19}F NMR spectra, suggesting that the compounds are best described as tending towards a "zwitterionic" resonance structure as opposed to the alternate "neutral" variant[40] shown in Scheme 4. The molecular structure of **5-H**, depicted in Figure 6, reveals metrical parameters that are consistent with this picture. The Sc-N distances are all somewhat shorter than those observed in other compounds reported here, consistent with a more positively charged Sc(III) center. The parameters associated with the bridging formato unit are similar to those observed in

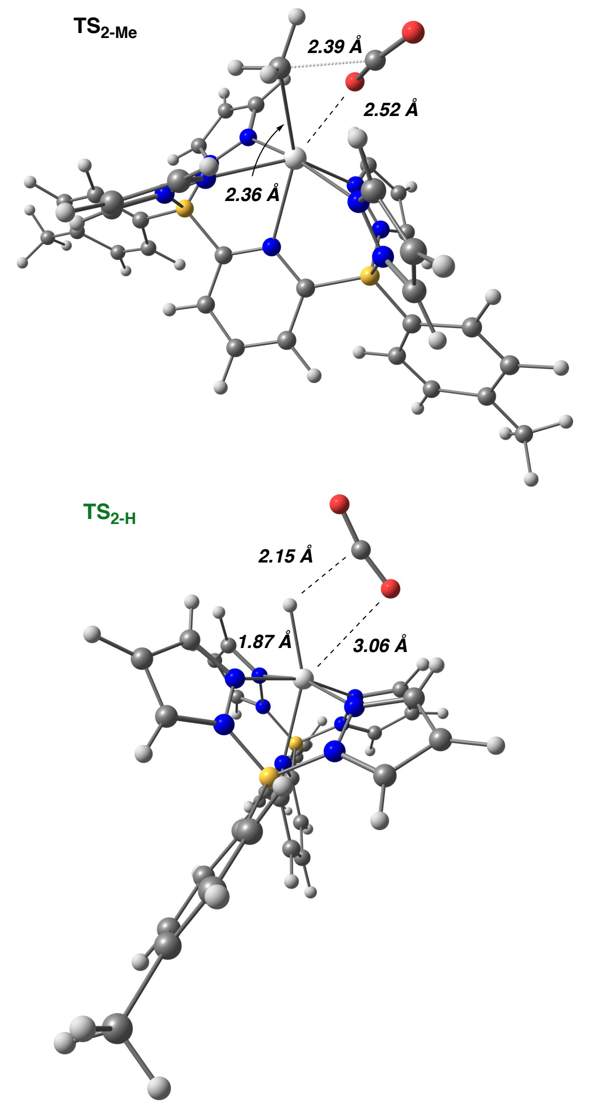
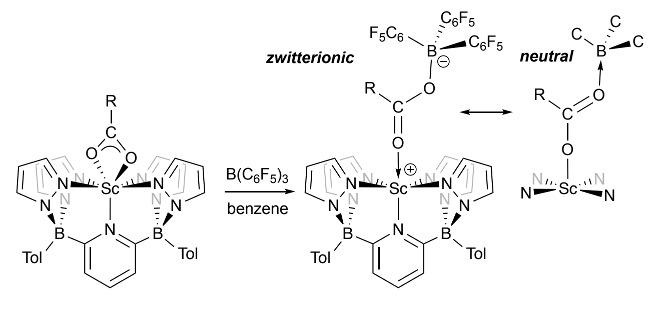


Figure 5. Computed transition state structures (DFT, B3PW91) for the insertion of CO$_2$ into the Sc-H and Sc-C bonds of **2-Me** (top) and **2-H** (bottom).



R	Yield	Cmpd
CH$_3$	*95%*	5-Me
H	*76%*	5-H

Scheme 4 Reactions of **4-R** with B(C$_6$F$_5$)$_3$.

the related Cp*$_2$Sc-OCO-B(C_6F_5)$_3$[40] we previously reported, with Sc1-O1 (2.056(2)Å) and O2-B3 (1.549(4)Å) distances more in line with dative and covalent bonds, respectively. Furthermore, the C50-O1 distance is slightly shorter than the C50-O2 distance, as would be expected. The Sc1-O1-C50 angle of 162.9(2)˚ is at first glance not consistent with a dative carbonyl to metal interaction, but in cases where ketones or aldehydes bind to d^0 centers such as this, sp hybridization at the oxygen is not uncommon.[41]

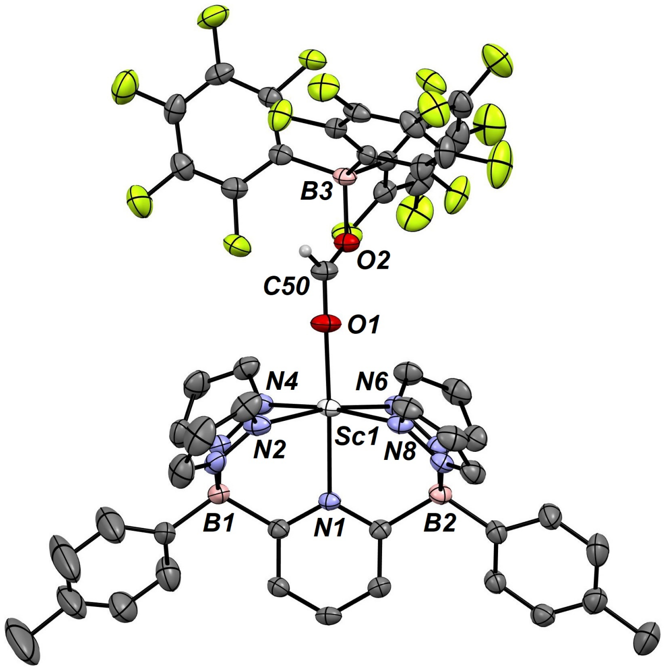


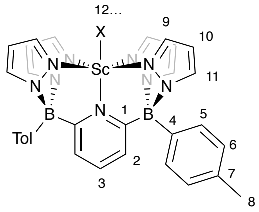
Figure 6. Molecular structure of **5-H**. Most hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (˚): Sc1–N1, 2.217(2); Sc1–N2, 2.219(2); Sc1–N4, 2.175(3); Sc1–N6, 2.170(3); Sc1–N8, 2.206(3); Sc1–O1, 2.056(2); O1-C50, 1.234(4); O2-C50, 1.256(4); O2-B3, 1.549(4); N2–Sc1–N8, 99.09(11); N2–Sc1–N4, 82.55(11); N4–Sc1–N6, 94.10(10); N6–Sc1–N8, 82.88(10); Sc1–O1–C50, 162.9(2); O1-C50-O2, 122.6(3); C50-O2-B3, 122.9(3).

Conclusions

The alkyl complexes supported by the B_2Pz_4Py ligand reported here are remarkably thermally stable, monomeric organoscandium compounds. The hydrido derivative **2-H** is highly reactive in its monomeric form. The Sc-H bond is highly ionic and therefore the hydrido ligand is significantly basic. This is evidenced by the facile dimerization of this species despite the six coordinate nature of the monomer; this dimerization may also be favoured by London dispersion forces[42] but the lack of dimerization in the chloro deriviative **1** and the alkyl complexes **2-R** point to the importance of the basicity of the hydride. Indeed, the facile reactions of the monomer with N_2O and CO_2, despite the lack of a vacant coordination site illustrate this notion.

Experimental

Selected procedures are described below; for general experimental details and the syntheses of compounds not included here, see the ESI.† NMR spectral assignments in the descriptions below are based on the following atom labelling scheme:



Synthesis of 1.

A 100 mL round bottom flask was charged with Li[tol-Pz_4B_2PyH] (1.963 g, 3.523 mmol) and *ca.* 30 mL of THF. LiHMDS (0.590 g, 3.526 mmol) was subsequently added as a solid to the white mixture. The mixture was stirred at 25 °C for 15 mins which resulted in a colourless solution. $ScCl_3(THF)_3$ (1.295 g, 3.523 mmol) was added as a solid to a stirred solution of the deprotonated ligand. The mixture was stirred at room temperature for 24 hours. Precipitation of the product as a white solid occurred over this time. The mixture was filtered through a coarse porosity frit, and the solid residue was subsequently washed with 10 mL of a 3:1 pentane:THF solution and 10 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (1.828 g, 2.903 mmol, 82%). Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of pentane onto a concentrated solution of **1** in benzene. ^{1}H NMR (500 MHz, C_6D_6): δ 8.14 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H9), 7.75 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H5), 7.55 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H11), 7.21 (d, $^3J_{HH}$ = 7.9, 1.3 Hz, 6H, H6 and H2), 6.67 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.79 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.33 (s, 6H, H8). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 171.4, (C1) 141.8 (C9), 140.3 (C4), 136.9 (C7), 136.3 (C11), 135.8 (C5), 135.4 (C3), 129.1 (C6), 128.5 (C2), 104.9 (C10), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.01. HRMS (APCI): Calcd m/z 630.2052 $(M+H)^+$, found m/z 630.2081 $(M+H)^+$. Elemental Analysis: Calcd. (%) for $C_{31}H_{29}B_2ClN_9Sc$: C, 59.13; H, 4.64; N, 20.02. Found: C, 59.42; H, 4.82; N, 19.33.

General Synthetic Method for compounds of 2-R.

A 20 mL scintillation vial was charged with **1** and 5 mL of toluene was added. The alkyl lithium was weighed separately in a 1 dram vial and dissolved in 2 mL of toluene. The solution of alkyl lithium was added dropwise into a stirred solution of **1**.The reaction mixture was left to stir for 24 hours at room temperature after which it was filtered through a 0.1 µm PTFE syringe filter to remove LiCl. The filtrate was transferred into a 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug and subsequently evaporated *in vacuo* to yield a colourless to pale yellow residue. The residue was triturated and sonicated with 20 mL of pentane. The suspension was then filtered through a medium porosity frit, washed with 2x3 mL of pentane and dried *in vacuo.* For **2-Me**: **1** (133 mg, 0.211 mmol) was reacted with MeLi (5 mg, 0.227 mmol, 1.08 equiv.)

to yield **2-Me** as a white solid (120 mg, 0.197 mmol, 93%). Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of pentane onto a concentrated solution of **2-Me** in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ 8.03 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.80 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H5), 7.50 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.34 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.21 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.74 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.84 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.33 (s, 6H, H8), 0.58 (s, 3H, H12). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 172.1 (C1), 140.7 (C9), 139.4 (C4), 136.8 (C7), 136.3 (C11), 136.1 (C5), 134.6 (C3), 129.0 (C6), 127.6 (C2), 104.7 (C10), 26.4 (C12), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ 0.12. Elemental Analysis: Calcd. (%) for $C_{32}H_{32}B_2N_9Sc$: C, 63.09; H, 5.29; N, 20.69. Found: C, 63.60; H, 5.14; N, 19.68.

Synthesis of 2-H.

A 20 mL scintillation vial was charged with **1** (113 mg, 0.179 mmol) and 5 mL of toluene was added. $NaHBEt_3$ (24 mg, 0.197 mmol, 1.10 equiv.) was weighed separately in a 1 dram vial and dissolved in 2 mL of toluene. The solution of $NaHBEt_3$ was added dropwise into a stirred solution of **1**. The reaction mixture was left to stir for 90 mins at room temperature after which it was filtered through a 0.1 μm PTFE syringe filter to remove NaCl. The filtrate was transferred into a 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug and subsequently evaporated *in vacuo* to yield a colourless residue. The residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (85 mg, 0.143 mmol, 80%). ^{1}H NMR (400 MHz, C_6D_6): δ 9.17 (br s, 1H, Sc*H*), 8.10 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.86 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H5), 7.53 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.47 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.22 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.77 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H3), 5.75 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.33 (s, 6H, H8). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 172.4 (C1), 142.0 (C9), 141.6 (C4), 136.6 (C7), 136.3 (C5), 136.1 (C11), 134.0 (C3), 128.9 (C6), 127.4 (C2), 104.4 (C10), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -1.01. HRMS (APCI): Calcd m/z 594.2286 M$^+$, found m/z 594.2288 M$^+$. Elemental Analysis: Calcd. (%) for $C_{31}H_{30}B_2N_9Sc$: C, 62.55; H, 5.08; N, 21.18. Found: C, 62.77; H, 5.21; N, 20.81.

Synthesis of 3.

Method A: A preweighed 25 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug was charged with **2-CH$_2$SiMe$_3$** (72 mg, 0.106 mmol) and dissolved in 10 mL of toluene. 10 μL of degassed deionized water was added to the solution under a positive flow of argon. The solution was stirred for 30 mins at room temperature before removing all solvents *in vacuo*. The residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (59 mg, 0.049 mmol, 93%). Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of pentane onto a concentrated solution of **3** in benzene. Method B: A J-Young NMR tube was charged with **2-H** (10 mg, 0.017 mmol) and dissolved in C_6D_6. The colourless solution was degassed by freeze-pump-thaw at -78 ^{o}C and backfilled with 1 atm of N_2O. The solution was heated to 80 ^{o}C for 18 hours to ensure complete formation of **2-H**. Quantitative conversion by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6): δ 7.94 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H5), 7.84 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H9), 7.56 – 7.50 (m, 6H, H2 and H11), 7.23 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H6), 6.84 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.81 (t, $^3J_{HH}$ = 2.1 Hz, 4H, H10), 2.32 (s, 6H, H8). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 172.6 (C1), 141.6 (C9), 141.5 (C4), 136. 7 (C7), 136.4 (C11), 136.3 (C5), 134.0 (C3), 129.0 (C6), 127.0 (C2), 104.2 (C10), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.43. Elemental Analysis: Calcd. (%) for $C_{62}H_{58}B_4N_{18}OSc$: C, 61.83; H, 4.85; N, 20.93. Found: C, 61.21; H, 4.97; N, 20.47.

Synthesis of 4-H

Method A: A J-Young NMR tube was charged with **2-H** (10 mg, 0.017 mmol) and dissolved in C_6D_6. The colourless solution was degassed by freeze-pump-thaw at -78 ^{o}C and backfilled with 1 atm of CO_2. The solution was heated to 80 ^{o}C for 18 hours to ensure complete formation of **4-H**. Quantitative conversion by NMR spectroscopy. Method B: A 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug was charged with both **1** (158 mg, 0.251 mmol) and HCOONa (18 mg, 0.265 mmol, 1.05 equiv.). The apparatus was connected to the vacuum line and 20 mL of 1,4-dioxane was vacuum transferred to the solid mixture at -78 ^{o}C. The cloudy white mixture was heated to 95 ^{o}C for 3 days after which the solvent was removed *in vacuo*. The residue was extracted with 20 mL toluene and filtered through a 0.1 μm PTFE syringe filter to remove NaCl and excess HCOONa. The filtrate was transferred into a 50 mL thick-walled glass vessel and subsequently evaporated *in vacuo* to yield a colourless residue. The residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (135 mg, 0.211 mmol, 84%). Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of pentane onto a concentrated solution of **4-H** in benzene. ^{1}H NMR (500 MHz, C_6D_6): δ 8.60 (s, 1H, H12), 8.40 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.82 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H5), 7.60 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.39 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.21 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.79 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H3), 5.83 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.33 (s, 6H, H8). ^{13}C NMR (101 MHz, C_6D_6) δ 178.1 (C12), 173.3 (C1), 142.1 (C9), 140.9 (C4), 136.8 (C7), 136.5 (C11), 136.3 (C5), 134.4 (C3), 129.0 (C6), 127.3 (C2), 104.3 (C10), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.43. $\nu_{C\text{-}O}$: 1566 cm^{-1}. HRMS (APCI): Calcd m/z 640.2340 (M+H)$^+$, found m/z 640.2311 (M+H)$^+$. Elemental Analysis: Calcd. (%) for $C_{32}H_{30}B_2N_9O_2Sc$: C, 60.13; H, 4.73; N, 19.72. Found: C, 61.39; H, 5.37; N, 18.63. Samples consistently analyzed high for carbon and hydrogen due to co-crystallized solvent molecules.

Synthesis of 5-H

Method A: A J Young NMR tube was charged with **4-H** (11 mg, 0.017 mmol) and dissolved in C_6D_6. A solution of $B(C_6F_5)_3$ (8.8 mg, 0.017mmol) in 0.1 mL of C_6D_6 was added to the J Young NMR tube. Immediate and quantitative conversion by ^{1}H NMR spectroscopy. Method B: A 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug was charged with **1** (118 mg, 0.187 mmol) and 15 mL of toluene was added. A solution of $B(C_6F_5)_3$ (101 mg, 0.197 mmol, 1.05 equiv.) and Et_3SiH (24 mg, 0.210 mmol, 1.10 equiv.) dissolved in 5 mL of toluene was added to the reaction mixture. The cloudy white suspension immediately turned into a clear solution. The apparatus was connected to the vacuum line and the solution was degassed by freeze-pump-thaw at -196 ºC and backfilled with 1 atm of CO_2. The reaction mixture was stirred overnight after which the solvent was removed *in vacuo*. The resulting residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (164 mg, 0.142 mmol, 76%). Single crystals suitable for X-ray diffraction were obtained by layering HMDSO onto a concentrated solution of **5-H** in benzene. ^{1}H NMR (500 MHz, C_6D_6) δ 8.12 (s, 1H, H12), 7.83 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H9), 7.62 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H5), 7.46 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H6), 7.16 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 6.62 (t, $^3J_{HH}$ = 7.9 Hz, 1H, H3), 5.76 (t, $^3J_{HH}$ = 2.3 Hz, 4H, H10), 2.33 (s, 6H, H8). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 172.9 (C12), 170.8 (C1), 148.5 (dm, $^1J_{CF}$ = 239 Hz, $[HCO_2B(C_6F_5)_3]^-$), 140.6 (dm, $^1J_{CF}$ = 251 Hz, $[HCO_2B(C_6F_5)_3]^-$), 140.2 (C9), 138.8 (C4), 137.7 (dm, $^1J_{CF}$ = 251 Hz, $[HCO_2B(C_6F_5)_3]^-$), 137.5 (C7), 137.3 (C11), 136.5 (C3), 135.6 (C5), 129.3 (C6), 128.8 (C2), 118.4 ($[HCO_2B(C_6F_5)_3]^-$), 105.4 (C10), 21.3 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ 0.01. ^{19}F NMR (471 MHz, C_6D_6) δ -135.08 (d, $^3J_{FF}$ = 24.4 Hz, *o*-F), -157.63 (t, $^3J_{FF}$ = 20.8 Hz, *p*-F), -164.56 (d, $^3J_{FF}$ = 22.8 Hz, *m*-F). $\nu_{C\text{-}O}$: 1614 cm^{-1}. Elemental Analysis: Calcd. (%) for $C_{50}H_{30}B_3F_{15}N_9O_2Sc$: C, 52.17; H, 2.63; N, 10.95. Found: C, 52.34; H, 2.73; N, 10.76.

Acknowledgements

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Notes and references

[‡] From the CCDC, the average Sc-C bond distance in 32 hits for Sc-CH_3 is 2.246 Å. The bond lengths range from 2.162 to 2.519Å. For Sc-CH_2TMS moieties, the average Sc-C bond distance is 2.234Å from 290 hits and the range is 2.115 to 2.350Å. The average Sc-C-Si angle is 130.7° ranging from 115.5 to 155.4˚.

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Electronic Supporting Information

Scandium Alkyl and Hydride Complexes Supported by a Pentadentate Diborate Ligand: Reactions with CO_2 and N_2O

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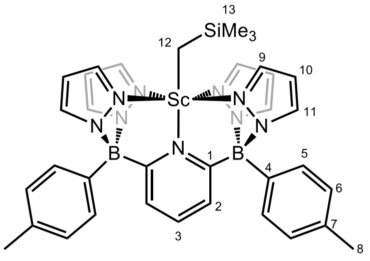
Experimental Details

General Considerations

Manipulation and storage of all oxygen and moisture sensitive materials was performed under an argon atmosphere in a MBRAUN glove box. Reactions were performed on a double manifold high vacuum line fitted with an OxisorBW scrubber (Matheson Gas products) argon purification cartridge, using standard techniques. Glassware was stored in a 135 °C oven prior to immediate transfer to the glovebox antechamber or assembly on the vacuum line and evacuated while hot. Tetrahydrofuran, toluene and pentane were dried and purified using a Grubbs/Down purification system,[1] and stored in evacuated 500 mL thick-walled vessels over sodium/benzophenone ketal. 1,4-Dioxane and C_6D_6 were dried over sodium/benzophenone ketal, and HMDSO was dried over calcium hydride. All dried solvents were degassed, vacuum transferred prior to use into thick-walled glass vessels for storage over activated molecular sieves (4 Å). Li[tol-Pz_4B_2PyH],[2] $ScCl_3(THF)_3$,[3] $LiCH_2SiMe_3$,[4] $LiCH_2SiMe_2Ph$,[5] Li^nPr[6] and $LiDBEt_3$[7] were prepared according to literature procedures. Li^iBu was synthesized using the same procedure for $LiCH_2SiMe_3$. MeLi (1.6 M in Et_2O), $NaBHEt_3$ (1.0 M in toluene), LiHMDS, LiD, BEt_3, HCOONa and NaOAc were purchased from Sigma-Aldrich and used as received. Solutions of MeLi, $NaHBEt_3$ and $LiDBEt_3$ were evaporated *in vacuo* and stored in a glove box freezer at -35 °C. LiHMDS and $B(C_6F_5)_3$ were sublimed prior to use. CO_2 (Coleman Instrument grade, 99.99%) was purchased from Air Liquide and used as received. Nuclear magnetic resonance spectroscopy experiments including ^1H, ^2H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, ^1H-^{13}C HMBC, ^1H-^{13}C HSQC and DOSY were performed on Bruker-400, Ascend-500 or Avance-600 spectrometers. DOSY experiments were ran at 298 K and sample were prepared in 0.7 mL of C_6D_6. The gradient amplitude was varied from 2% to 95% with an optimized δ (gradient pulse length) of 2600 μs and a Δ (diffusion time) of 0.075 s. All ^1H and $^{13}C\{^1H\}$ NMR spectra were internally referenced relative to $Si(CH_3)_4$ using residual solvent protons and naturally abundant ^{13}C resonances for all deuterated solvents. NMR spectra were processed and analyzed with MestReNova (v. 9.0.1-13254). X-ray crystallographic analyses were performed by Chris Gendy, Dr. Benjamin Gelfand, and Dr. Jian-Bin Li on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Crystals were coated in Fomblin Y HVAC 140/13 oil. Elemental analyses were performed by Johnson Li using a Perkin Elmer Model 2400 Series II analyser at the Instrumentation Facility of the Department of Chemistry, University of Calgary. Solution high-resolution mass spectrometry (APCI-MS) measurements were performed by Wade White on samples prepared in the glove box in a gas tight syringe. Headspace analysis was performed on an Agilent 7890B Gas Chromatograph. Infrared spectra were collected on a Nicolet Avatar FT-IR spectrometer, and samples were prepared either as a KBr pellet or thin film by evaporation of a benzene solution on AgCl plates.

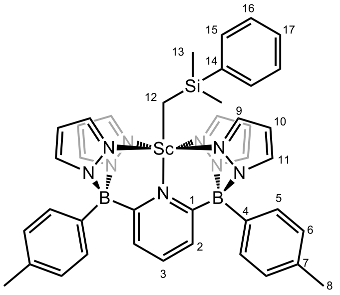
Synthesis of 2-CH_2SiMe_3



1 (115 mg, 0.183 mmol) was reacted with $LiCH_2SiMe_3$ (18 mg, 0.191 mmol, 1.05 equiv.) to yield **$2\text{-}CH_2SiMe_3$** as a pale yellow solid (68 mg, 0.100 mmol, 55%). Single crystals suitable for X-ray diffraction were obtained by layering HMDSO onto a concentrated solution of **$2\text{-}CH_2SiMe_3$** in benzene.

^1H NMR (500 MHz, C_6D_6): δ 8.10 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H9), 7.78 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H5), 7.45 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H11), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.72 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.85 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.32 (s, 6H, H8), 0.71 (s, 2H, H12), 0.21 (s, 9H, H13). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 172.2 (C1), 141.0 (C9), 140.7 (C4), 136.9 (C7), 136.5 (C11), 136.2 (C5), 134.5 (C3), 129.0 (C6), 127.4 (C2), 104.6 (C10), 42.3 (C12), 21.4 (C8), 3.8 (C13). ^{11}B NMR (161 MHz, C_6D_6) δ -0.01. Elemental Analysis: Calcd. (%) for $C_{35}H_{40}B_2N_9ScSi$: C, 61.69; H, 5.92; N, 18.50. Found: C, 60.74; H, 5.86; N, 18.10.

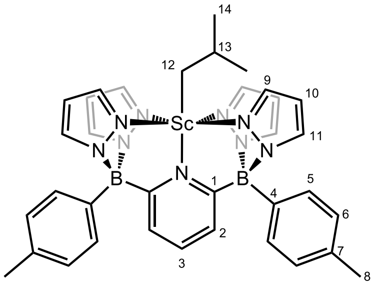
Synthesis of $2\text{-}CH_2SiMe_2Ph$



1 (88 mg, 0.140 mmol) was reacted with $LiCH_2SiMe_2Ph$ (23 mg, 0.147 mmol, 1.05 equiv.) to yield **$2\text{-}CH_2SiMe_2Ph$** as a pale yellow solid (80 mg, 0.108 mmol, 77%).

^1H NMR (500 MHz, C_6D_6): δ 7.91 (d, $^3J_{HH}$ = 2.0 Hz, 4H, H9), 7.80 – 7.75 (m, 6H, H5 and H15), 7.44 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H11), 7.38 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.34 (m, 2H, H16), 7.30 – 7.26 (m, 1H, H17), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.70 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H3), 5.82 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.32 (s, 6H, H8), 0.87 (s, 2H, H12), 0.29 (s, 6H, H13).$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 172.2 (C1), 146.2 (C14), 141.1 (C9), 140.6 (C4), 136.9 (C7), 136.5 (C11), 136.2 (C5), 134.5 (C3), 134.2 (C15), 129.0 (C6), 128.2 (C17), 128.0 (C16), 127.3 (C2), 104.6 (C10), 38.3 (C12), 21.4 (C8), 2.3 (C13). ^{11}B NMR (161 MHz, C_6D_6) δ -0.05. Elemental Analysis: Calcd. (%) for $C_{40}H_{42}B_2N_9ScSi$: C, 64.62; H, 5.69; N, 16.96. Found: C, 64.16; H, 5.41; N, 16.31.

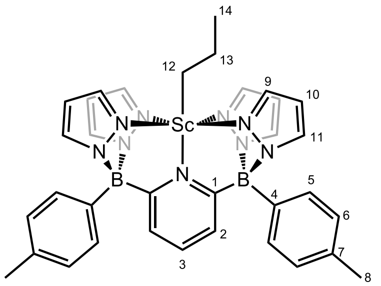
Synthesis of 2-^iBu



1 (62 mg, 0.098 mmol) was reacted with Li^iBu (7 mg, 0.109 mmol, 1.11 equiv.) to yield **2-^iBu** as a pale yellow solid (40 mg, 0.060 mmol, 61%).

^1H NMR (500 MHz, C_6D_6): δ 8.09 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.77 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H5), 7.45 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.39 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H2), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.73 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.86 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.50 (sept, $^3J_{HH}$ = 6.5 Hz, 1H, H13), 2.32 (s, 6H, H8), 1.19 (d, $^3J_{HH}$ = 6.4 Hz, 6H, H14), 1.17 (d, $^3J_{HH}$ = 6.7 Hz, 2H, H12). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 172.3 (C1), 140.9 (C4), 140.7 (C9), 136.8 (C7), 136.5 (C11), 136.2 (C5), 134.4 (C3), 129.0 (C6), 127.3 (C2), 104.6 (C10), 64.6 (C12), 31.9 (C13), 29.6 (C14), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ 0.08. Elemental Analysis: Calcd. (%) for $C_{35}H_{38}B_2N_9Sc$: C, 64.54; H, 5.88; N, 19.35. Found: C, 57.13; H, 4.71; N, 17.58. These data were obtained in triplicate and consistently low due to beta elimination during combustion.

Synthesis of 2-^{n}Pr



1 (79 mg, 0.125 mmol) was reacted with Li^{n}Pr (7 mg, 0.140 mmol, 1.12 equiv.) to yield **2-^{n}Pr** as an off-white solid (66 mg, 0.101 mmol, 81%).

^{1}H NMR (500 MHz, C_6D_6): δ 8.05 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.78 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H5), 7.45 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.74 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.85 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.32 (s, 6H, H8), 2.06 (m, 2H, H13), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, H14), 1.15 (m, 2H, H12). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 172.3 (C1), 140.8 (C4), 140.6 (C9), 136.8 (C7), 136.4 (C11), 136.2 (C5), 134.5 (C3), 129.0 (C6), 127.3 (C2), 104.7 (C10), 55.0 (C12), 25.4 (C13), 22.5 (C14), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.01. Elemental Analysis: Calcd. (%) for $C_{34}H_{36}B_2N_9Sc$: C, 64.08; H, 5.69; N, 19.78. Found: C, 62.73; H, 5.64; N, 19.05.

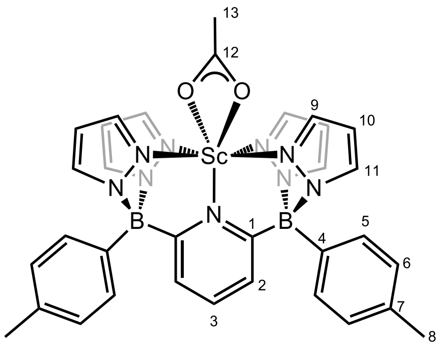
Synthesis of tol-Pz_4B_2PyScD (*d_1*-2-H)

Same synthetic procedure as **2-H** but used $LiDBEt_3$ instead of $NaHBEt_3$.

1 (104 mg, 0.165 mmol) was reacted with $LiDBEt_3$ (18 mg, 0.170 mmol, 1.03 equiv.) to yield ***d_1*-2-H** as a white solid (53 mg, 0.089 mmol, 54%).

^{2}H NMR (77 MHz, C_6H_6) δ 9.16.

Synthesis of tol-$Pz_4B_2PyScOOCCH_3$ (4-Me)



Method A: A J-Young NMR tube was charged with **2-Me** (10 mg, 0.017 mmol) and dissolved in C_6D_6. The colourless solution was degassed by freeze-pump-thaw at -78 °C and backfilled with 1 atm of CO_2. The solution was heated to 70 °C for 2 hours to ensure complete formation of **2-Me**. Quantitative conversion by NMR.

Method B: A 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug was charged with both **1** (125 mg, 0.199 mmol) and NaOAc (17 mg, 0.207 mmol, 1.04 equiv.). The apparatus was connected to the vacuum line and 20 mL of THF was vacuum transferred to the solid mixture at -78 °C. The cloudy white mixture was heated to 60 °C for 24 hours after which the solvent was removed *in vacuo*. The residue was extracted with 20 mL toluene and filtered through a 0.1 µm PTFE syringe filter to remove NaCl and excess NaOAc. The filtrate was transferred into a 50 mL thick-walled glass vessel and subsequently evaporated *in vacuo* to yield a colourless residue. The residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (98 mg, 0.150 mmol, 76%). Single crystals suitable for X-ray diffraction were obtained by slow vapour diffusion of pentane onto a concentrated solution of **4-Me** in benzene.

^{1}H NMR (500 MHz, C_6D_6): δ 8.47 (d, $^3J_{HH}$ = 2.1 Hz, 4H, H9), 7.85 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H5), 7.63 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H2), 7.41 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.21 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.81 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H3), 5.86 (t, $^3J_{HH}$ = 2.2 Hz, 4H, H10), 2.33 (s, 6H, H8), 1.82 (s, 3H, H13). ^{13}C NMR (101 MHz, C_6D_6) δ 189.1 (C12), 173.4 (C1), 142.1 (C9), 141.0 (C4), 136.7 (C7), 136.4 (C11), 136.3 (C5), 134.3 (C3), 129.0 (C6), 127.3 (C2), 104.3 (C10), 22.4 (C13), 21.4 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.29. $\nu_{C\text{-}O}$: 1535 cm^{-1}. Elemental Analysis: Calcd. (%) for $C_{32}H_{30}B_2N_9O_2Sc$: C, 60.67; H, 4.94; N, 19.30. Found: C, 61.83; H, 5.36; N, 18.05. These data were consistent over 3 trials and likely due to co-crystallized solvent.

Synthesis of [tol-Pz$_4$B$_2$PySc][MeCOOB(C$_6$F$_5$)$_3$] (5-Me)

A 50 mL thick-walled glass vessel equipped with a Kontes PTFE valve plug was charged with **4-Me** (49 mg, 0.075 mmol) and $B(C_6F_5)_3$ (40 mg, 0.078 mmol, 1.04 equiv.). 10 mL was added to dissolve the solids to give a colourless solution. The solution was stirred for 1 h after which the solvent was removed *in vacuo*. The resulting residue was triturated and sonicated with 20 mL of pentane. The white suspension was then filtered through a medium porosity frit and washed with 2x3 mL of pentane. The product was isolated as a white solid and dried *in vacuo* (83 mg, 0.071 mmol, 95%).

^{1}H NMR (500 MHz, C_6D_6) δ 7.65 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H5), 7.59 (d, $^3J_{HH}$ = 2.2 Hz, 4H, H9), 7.36 (d, $^3J_{HH}$ = 2.3 Hz, 4H, H11), 7.28 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H2), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H6), 6.64 (t, $^3J_{HH}$ = 7.8 Hz, 1H, H3), 5.73 (t, $^3J_{HH}$ = 2.3 Hz, 4H, H10), 2.32 (s, 6H, H8), 1.59 (s, 3H, H13). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 183.1 (C12), 171.3 (C1), 148.6 (dm, $^1J_{CF}$ = 240 Hz, $[MeCO_2B(C_6F_5)_3]^-$), 140.2 (dm, $^1J_{CF}$ = 251 Hz, $[MeCO_2B(C_6F_5)_3]^-$), 139.9 (C9), 138.7 (C4), 137.5 (dm, $^1J_{CF}$ = 262 Hz, $[MeCO_2B(C_6F_5)_3]^-$), 137.6 (C7), 137.5 (C11), 136.0 (C3), 135.7 (C5), 129.4 (C6), 128.2 (C2), 119.5 ($[MeCO_2B(C_6F_5)_3]^-$), 105.4 (C10), 24,3 (C13), 21.3 (C8). ^{11}B NMR (161 MHz, C_6D_6) δ -0.20. ^{19}F NMR (471 MHz, C_6D_6) δ -135.45 (d, $^3J_{FF}$ = 22.2 Hz, *o*-F), -158.54 (t, $^3J_{FF}$ = 20.9 Hz, *p*-F), -165.24 (t, $^3J_{FF}$ = 20.9 Hz, *m*-F). $\nu_{C\text{-}O}$: 1571 cm^{-1}.

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3. Hayes, P. G.; Piers, W. E. *Inorg. Synth.* **2010**, *35*, 20 – 24.
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Computational details.

All DFT calculations were carried out with the Gaussian 09 suite of programs.[i] Geometries were fully optimized in gas phase without symmetry constraints, employing the B3PW91 functional. [ii] The nature of the extrema was verified by analytical frequency calculations. The calculation of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. IRC calculations were performed to confirm the connections of the optimized transition states. Scandium atoms were treated with Stuttgart effective core potential and their associated basis set. [iii] For the other elements (H, C, O, N and B), Pople's double-ζ basis set 6-31G(d,p) was used. [iv]

Computational References

[i] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheesman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; A., R.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian Inc., 2009, Wallingford CT

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[iv] (a) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. Theor. Chem. Acc., 1973, 28, 213−222. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J. Chem. Phys. 1972, 56, 2257−2261.

Characterization data for new compounds

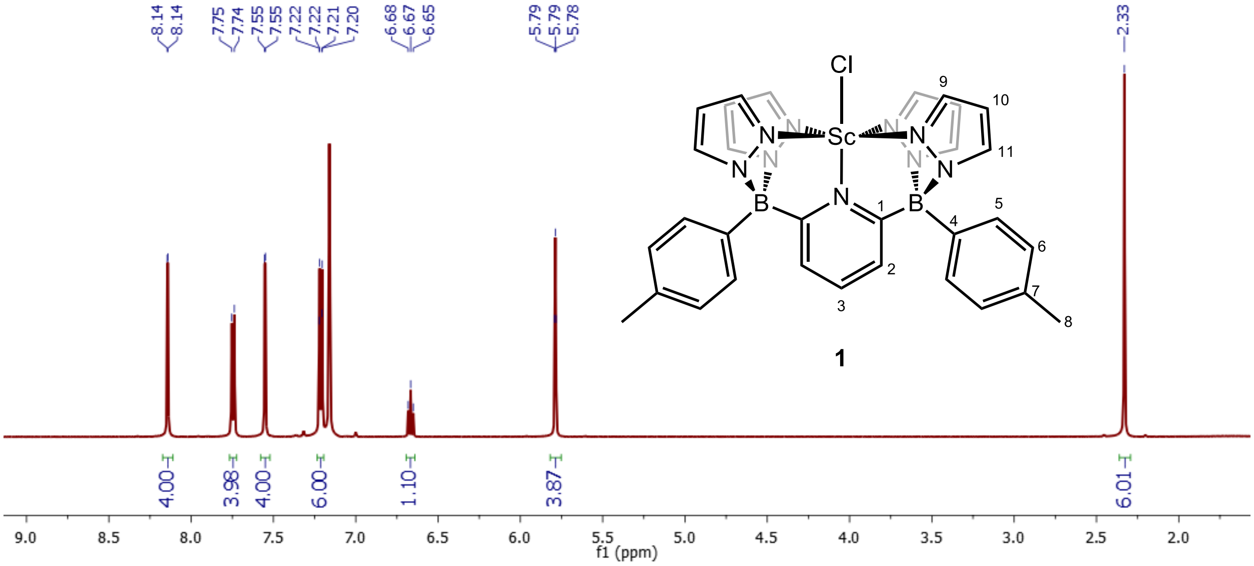

Figure S1: ^{1}H NMR spectrum of **1** in C_6D_6.

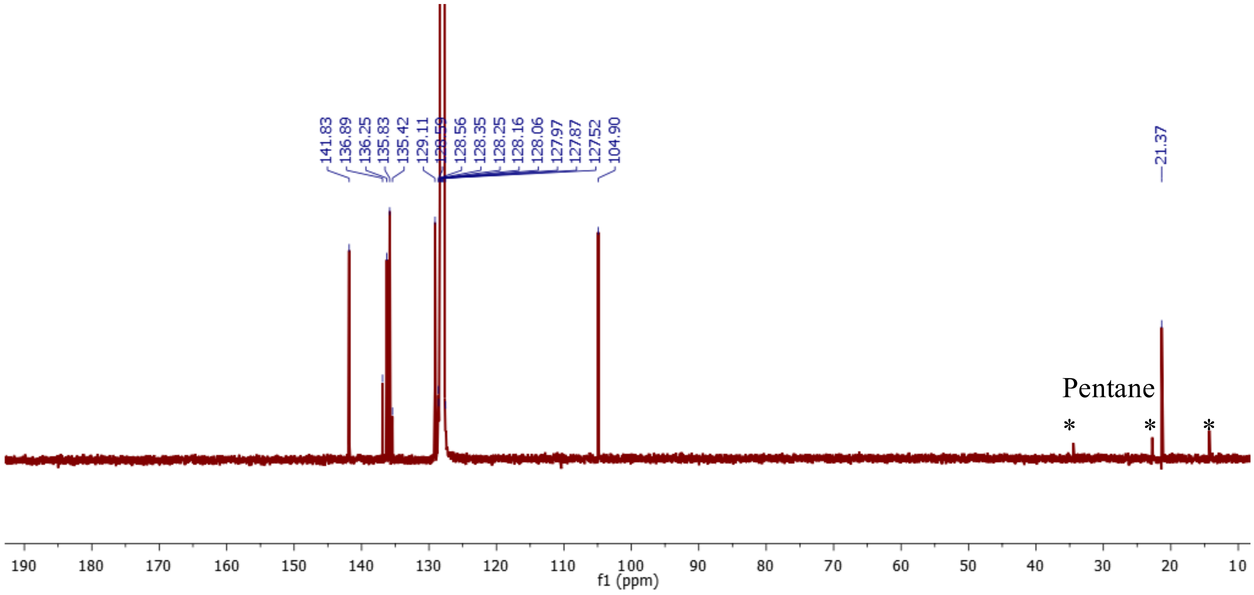

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

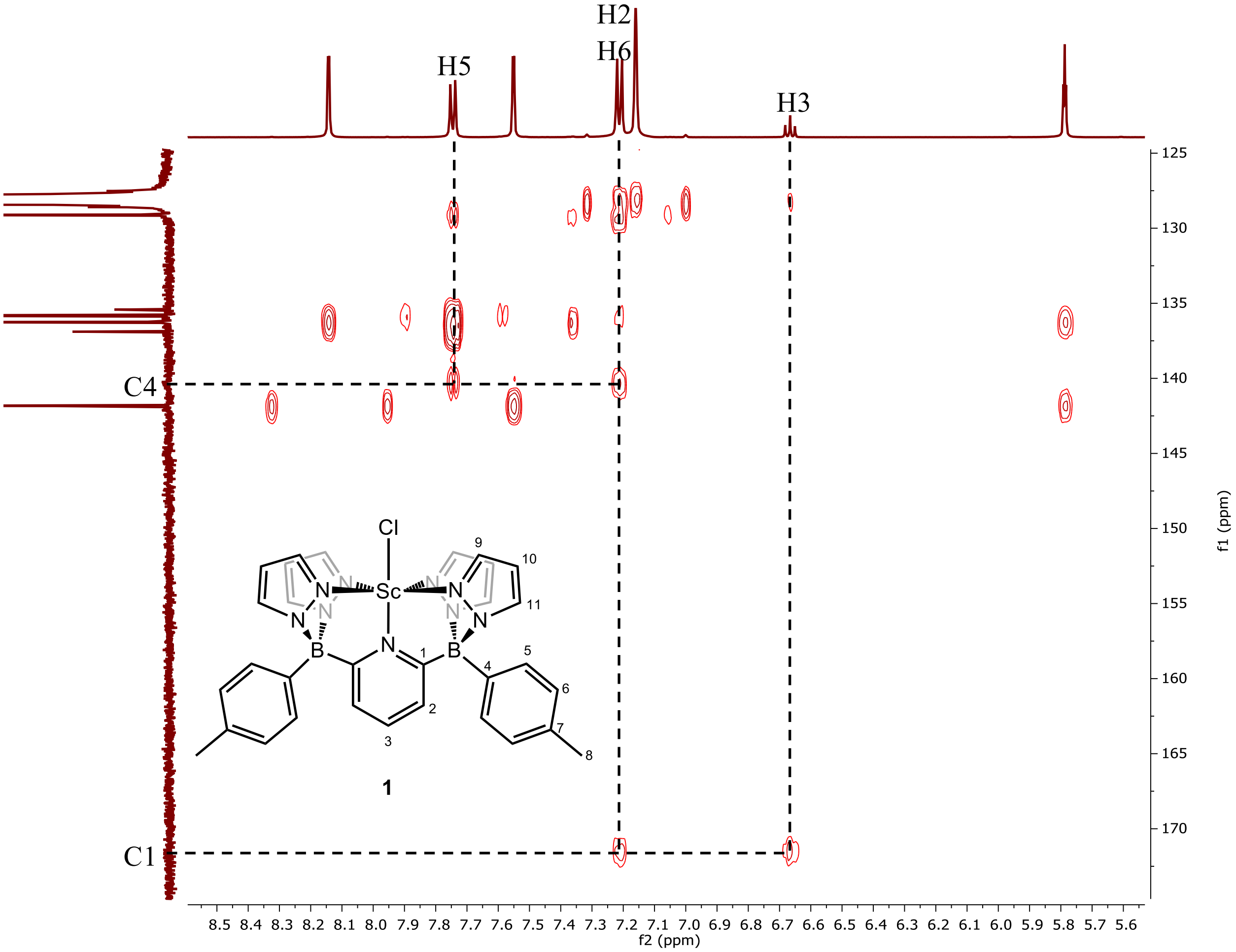

Figure S3: ^{1}H-^{13}C HMBC NMR spectrum of **1** for the determination of C1 and C4.

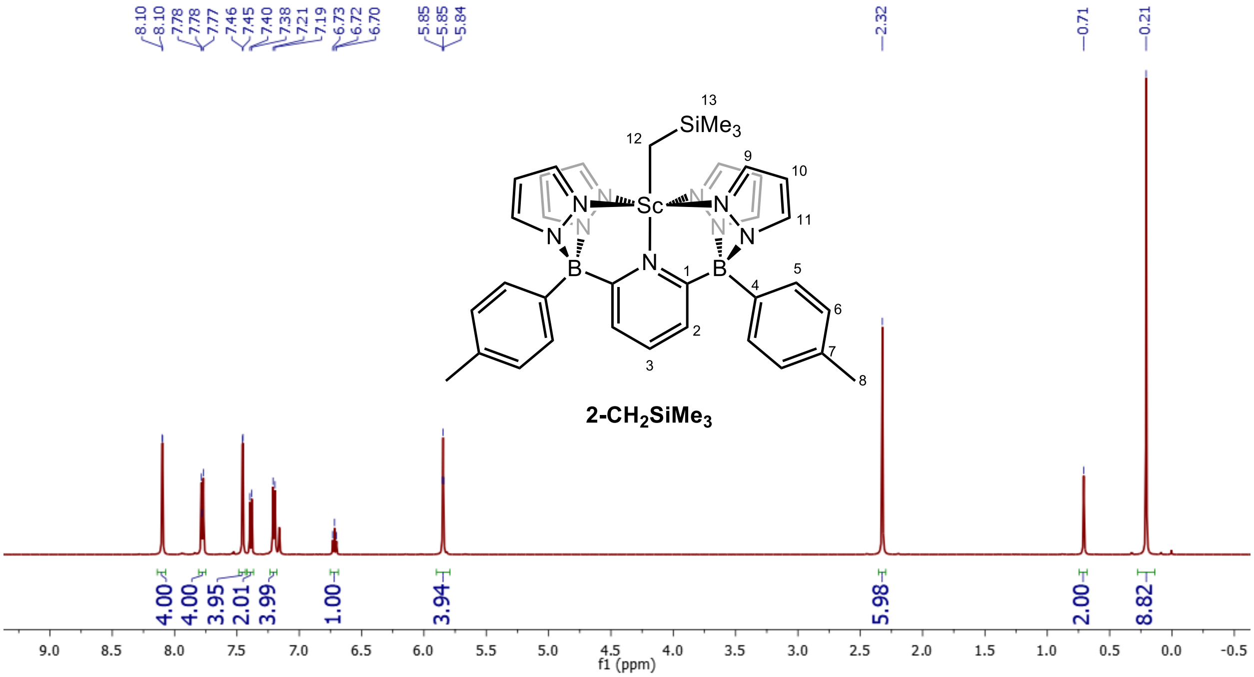

Figure S4: ^{1}H NMR spectrum of **$2\text{-CH}_2\text{SiMe}_3$** in C_6D_6.

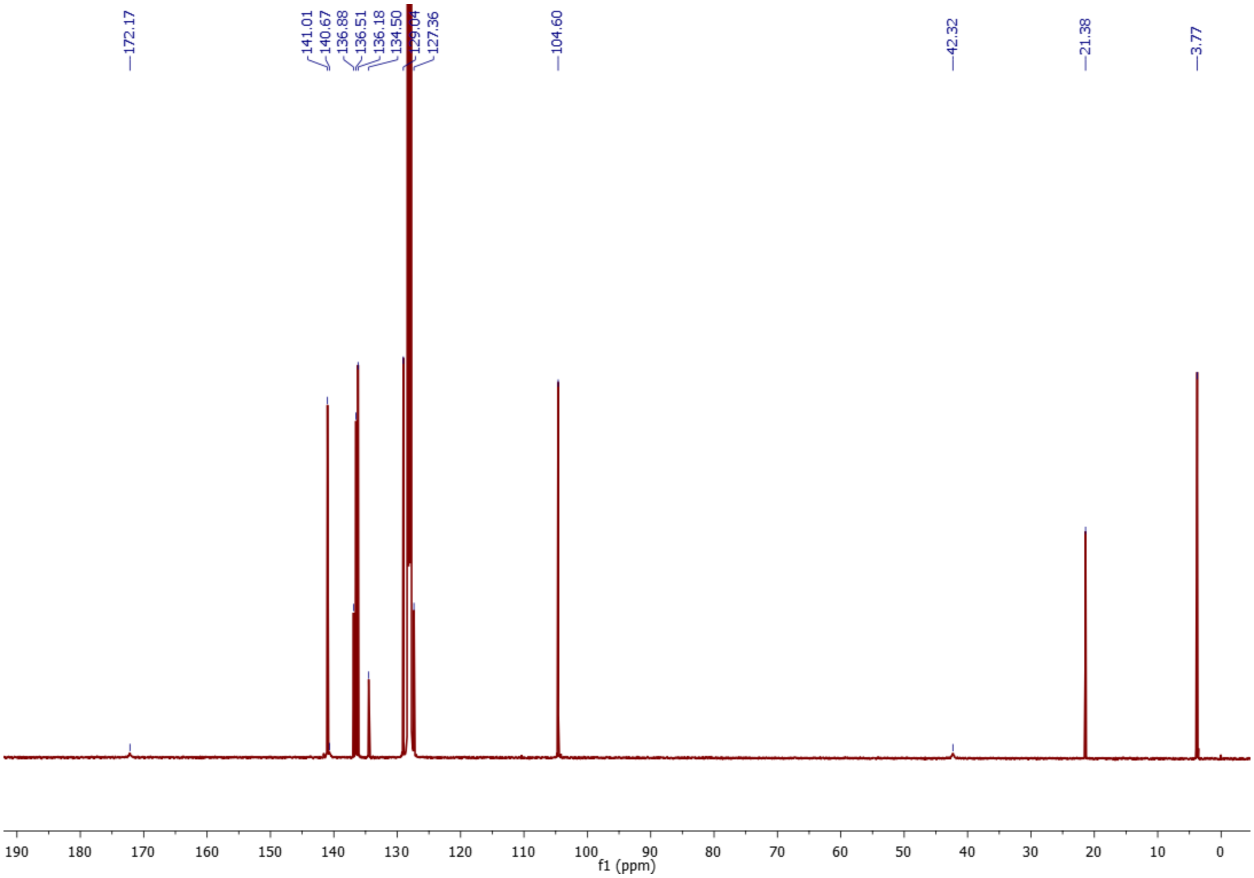

Figure S5: ^{13}C{^{1}H} NMR spectrum of **$2\text{-CH}_2\text{SiMe}_3$** in C_6D_6.

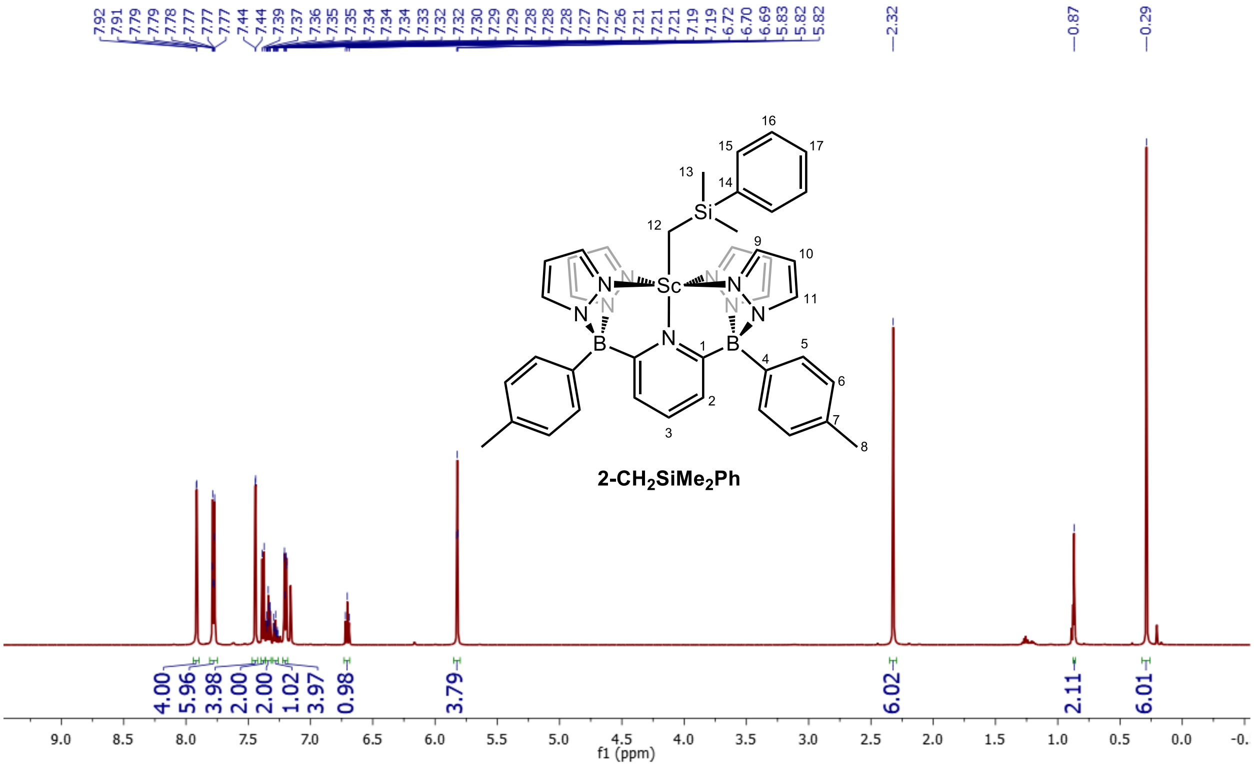

Figure S6: ^{1}H NMR spectrum of **2-CH$_2$SiMe$_2$Ph** in C$_6$D$_6$.

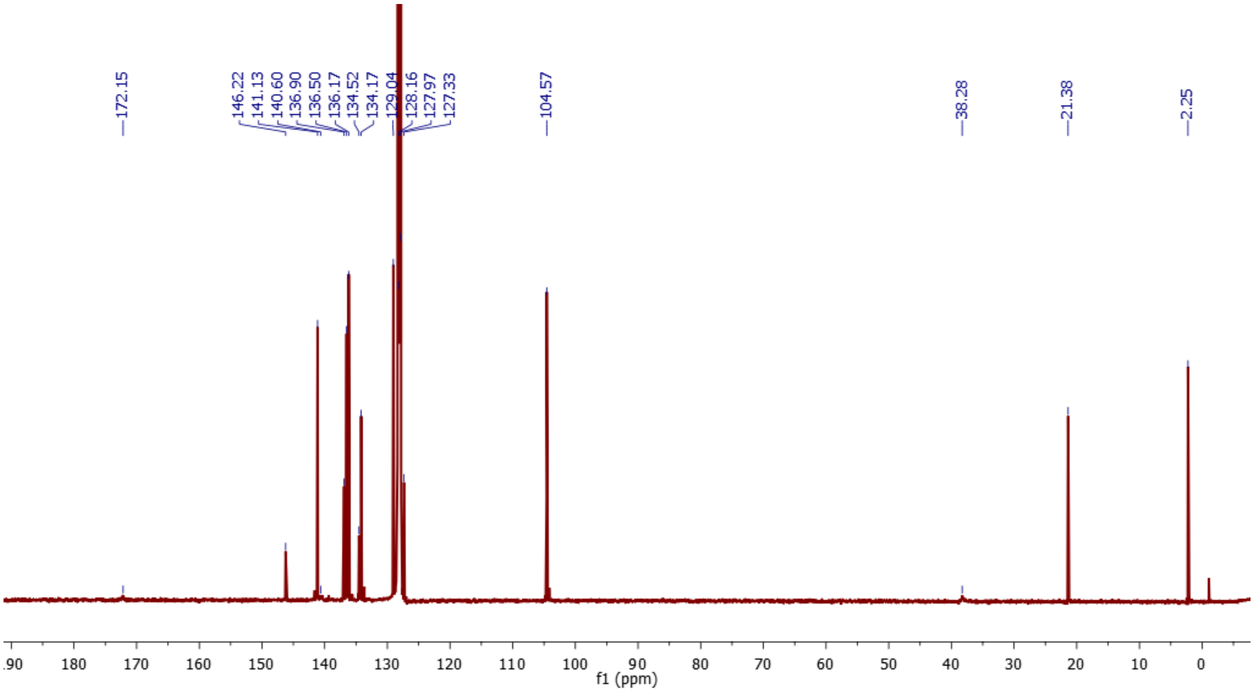

Figure S7: ^{13}C{^{1}H} NMR spectrum of **2-CH$_2$SiMe$_2$Ph** in C$_6$D$_6$.

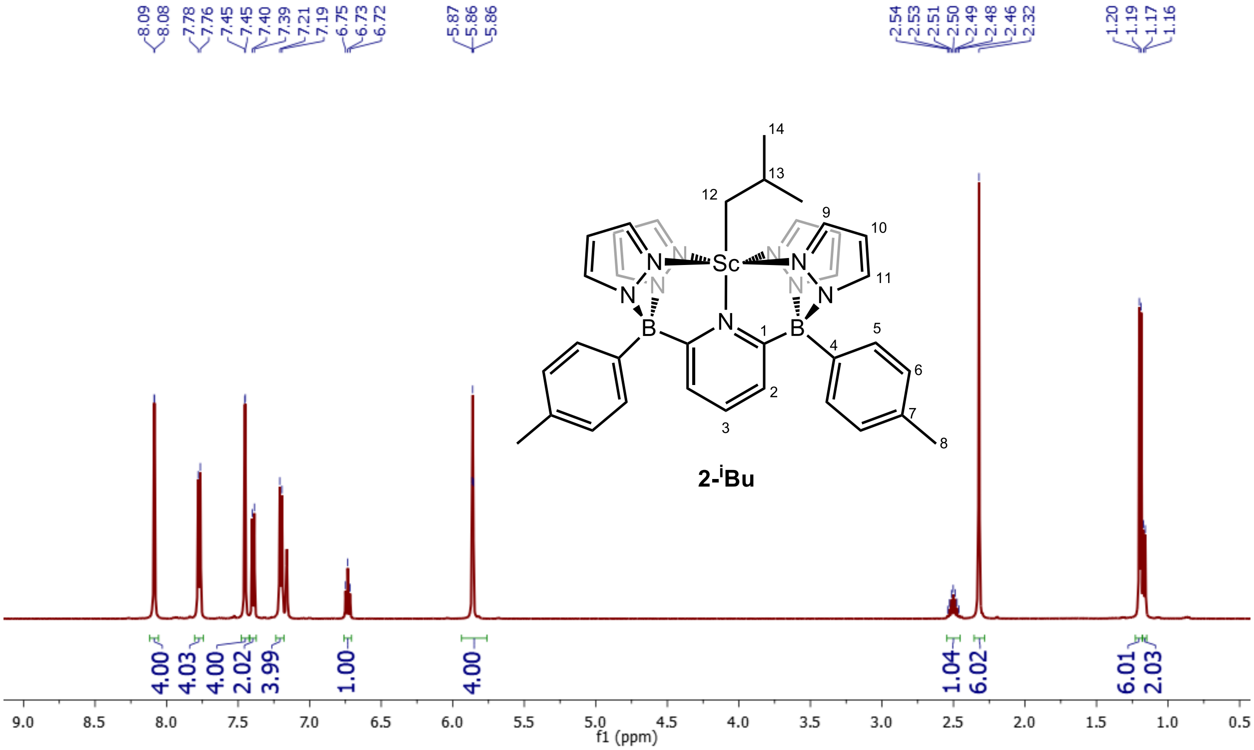

Figure S8: ^{1}H NMR spectrum of **2-$^{\mathbf{i}}$Bu** in C_6D_6.

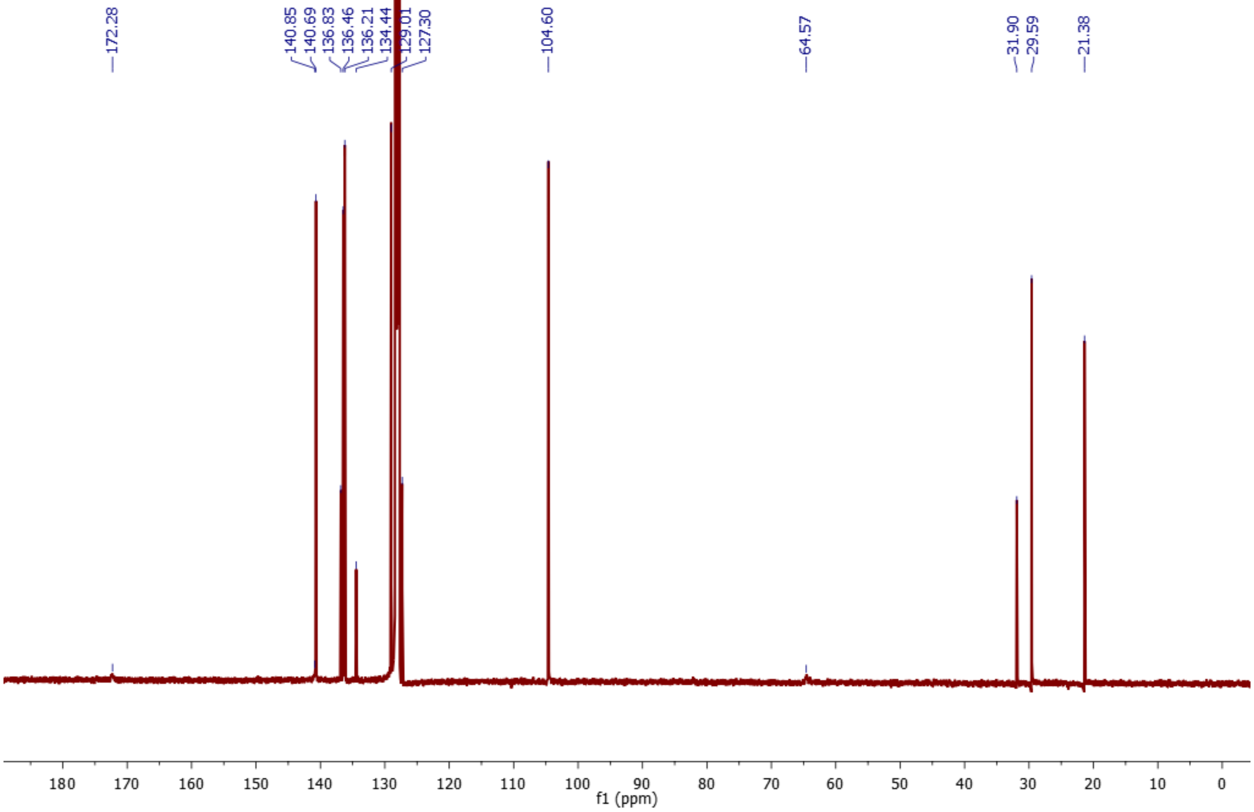

Figure S9: ^{13}C{^{1}H} NMR spectrum of **2-$^{\mathbf{i}}$Bu** in C_6D_6.

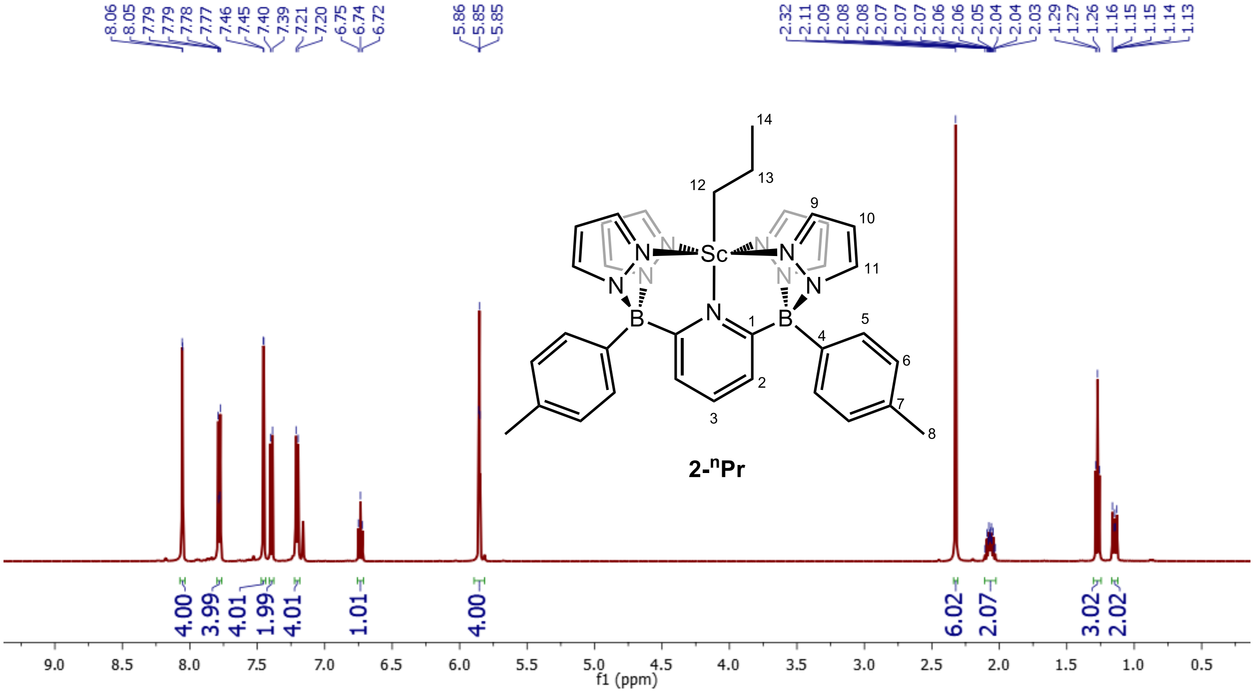

Figure S10: ^{1}H NMR spectrum of **2-$^{\mathbf{n}}$Pr** in C_6D_6.

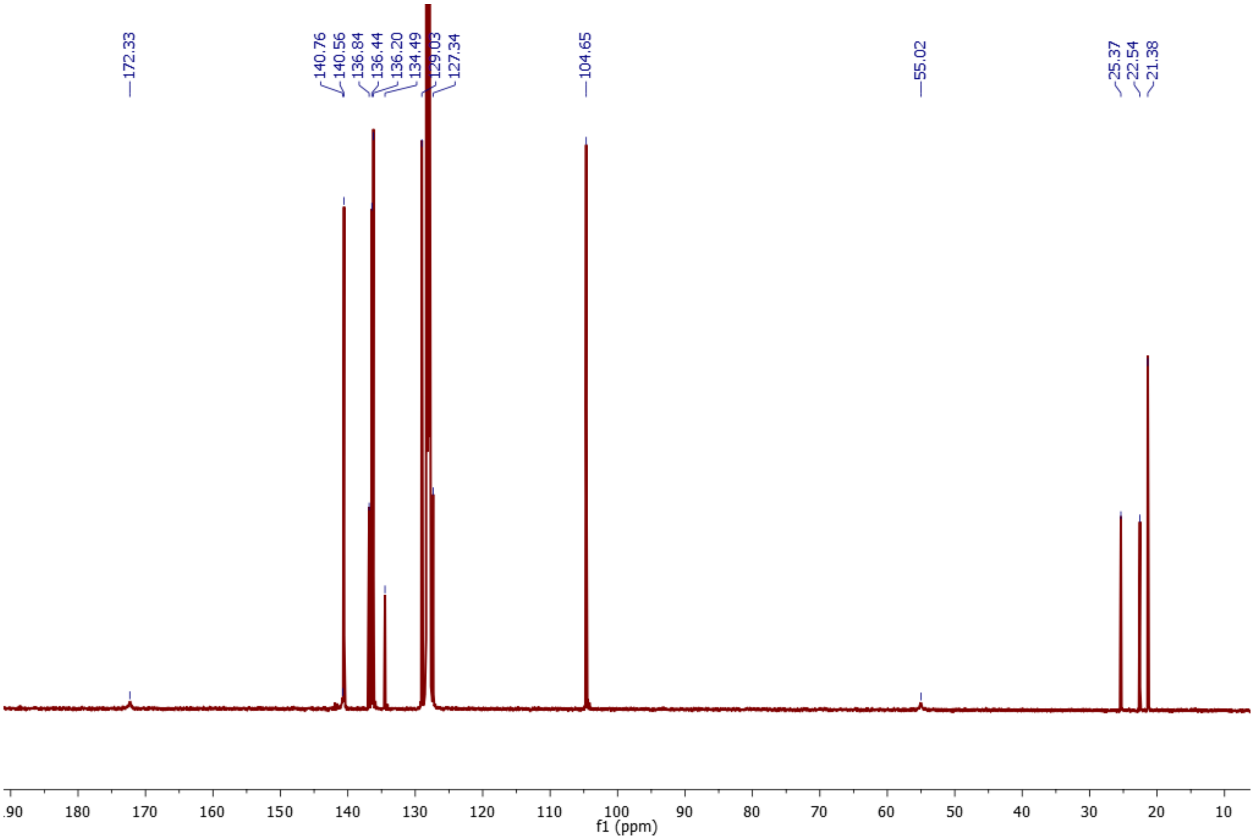

Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of **2-$^{\mathbf{n}}$Pr** in C_6D_6.

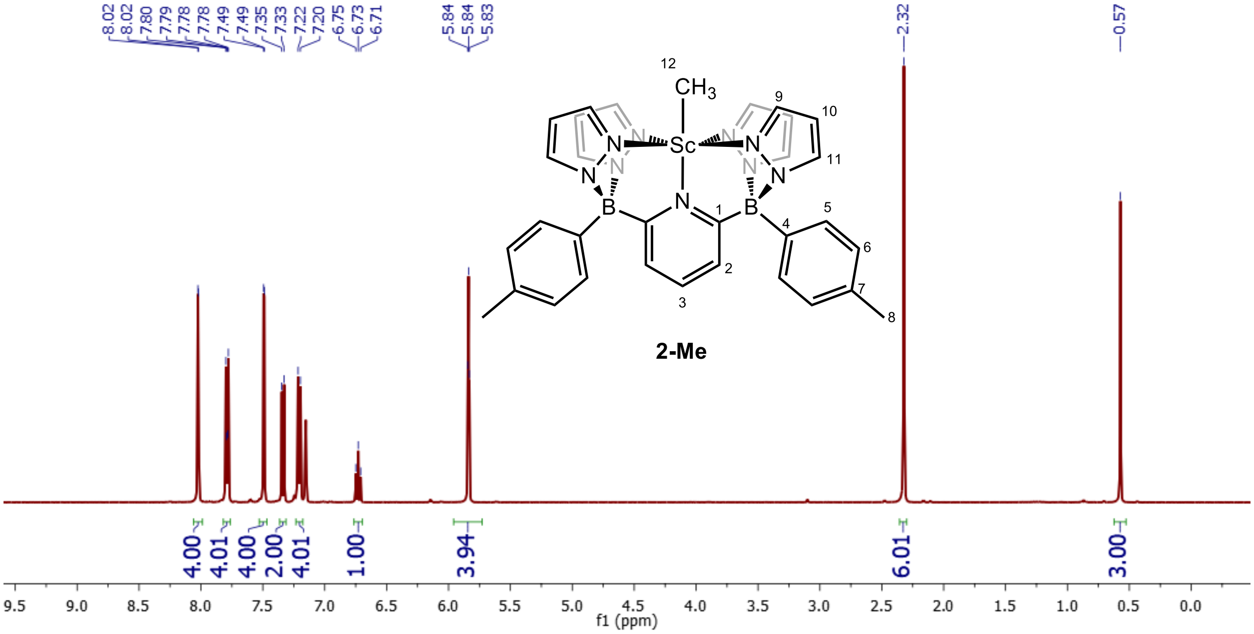

Figure S12: ^{1}H NMR spectrum of **2-Me** in C_6D_6.

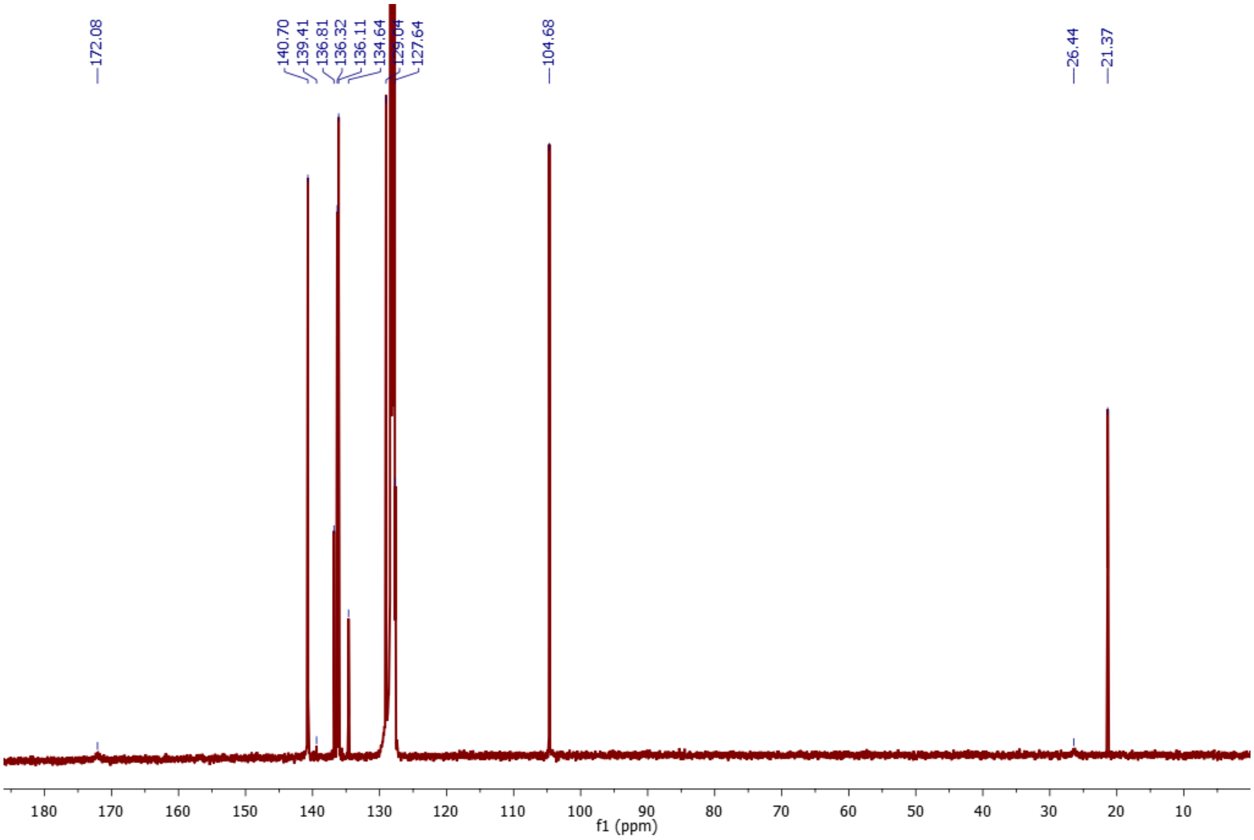

Figure S13: $^{13}C\{^1H\}$ NMR spectrum of **2-Me** in C_6D_6.

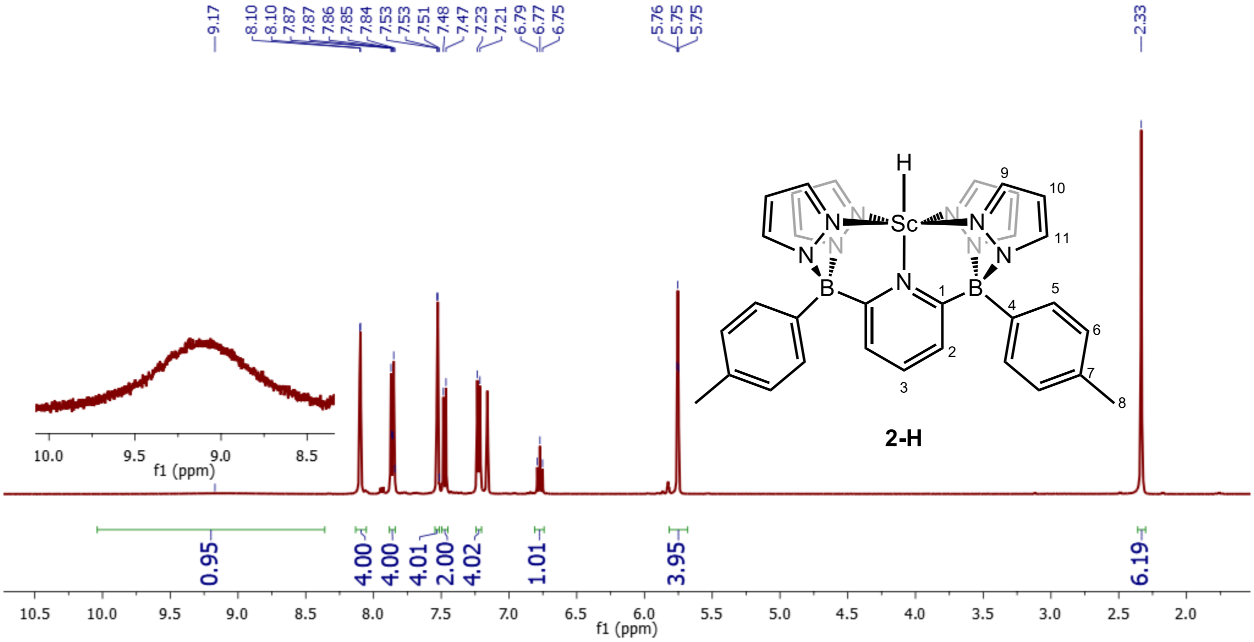

Figure S14: ^{1}H NMR spectrum of **2-H** in C_6D_6.

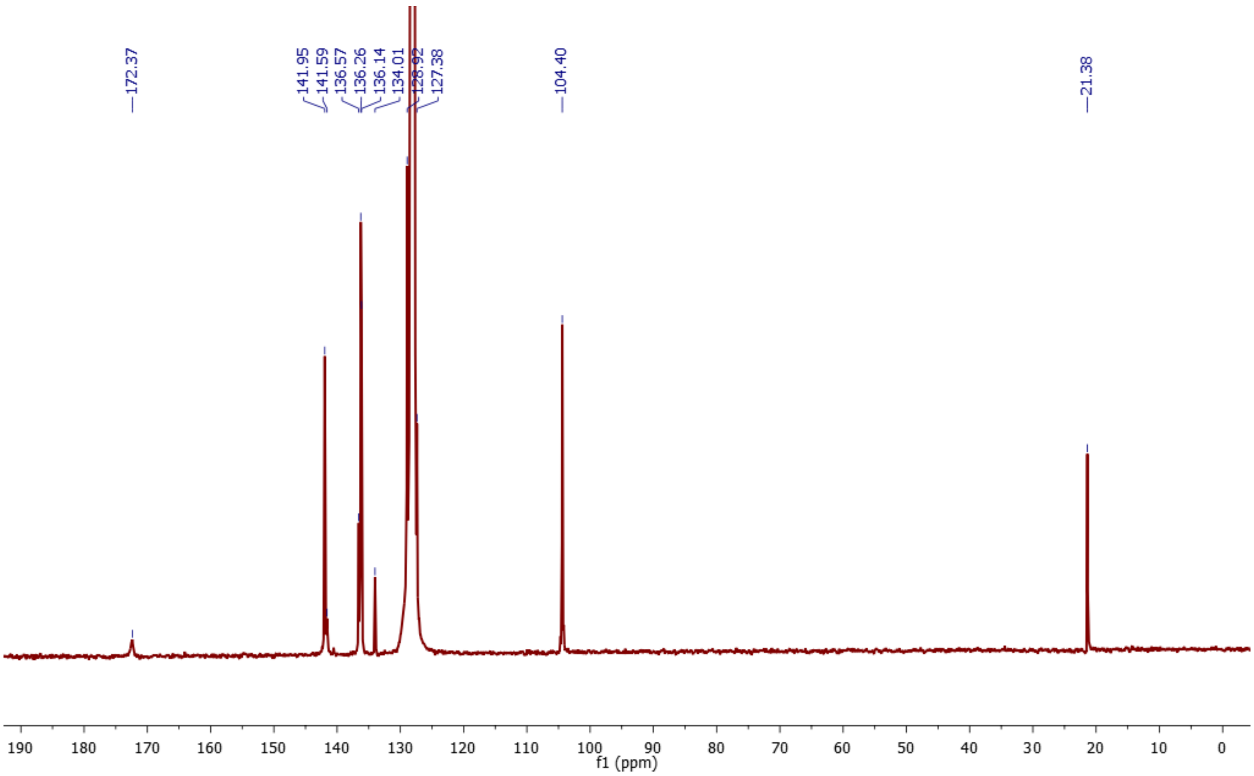

Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **2-H** in C_6D_6.

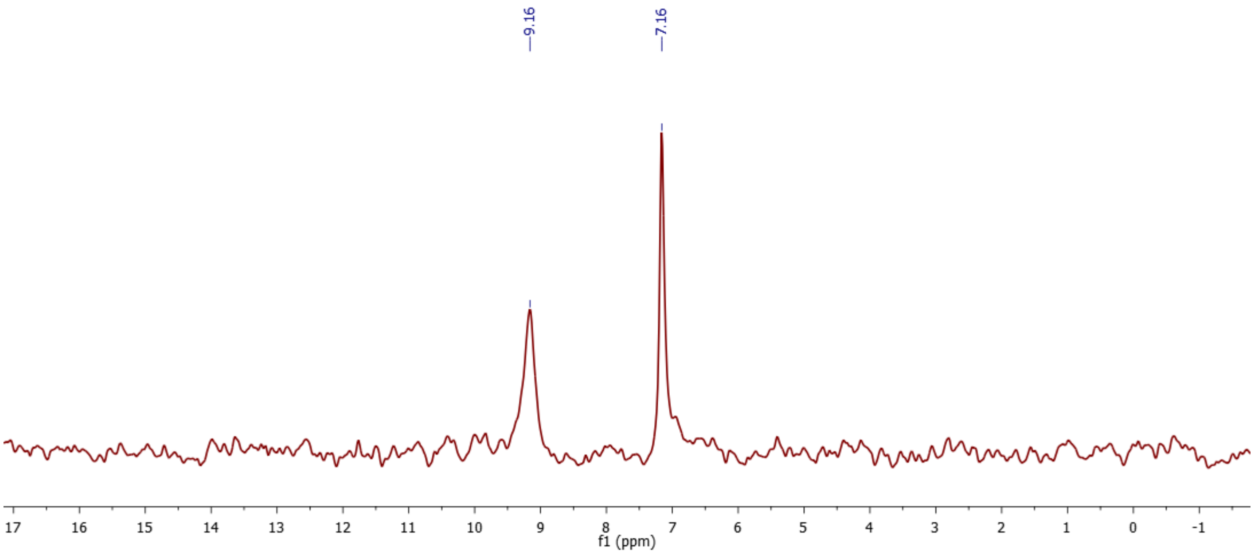

Figure S16: ^{2}H NMR spectrum of ***d_1*-2-H** in C_6H_6.

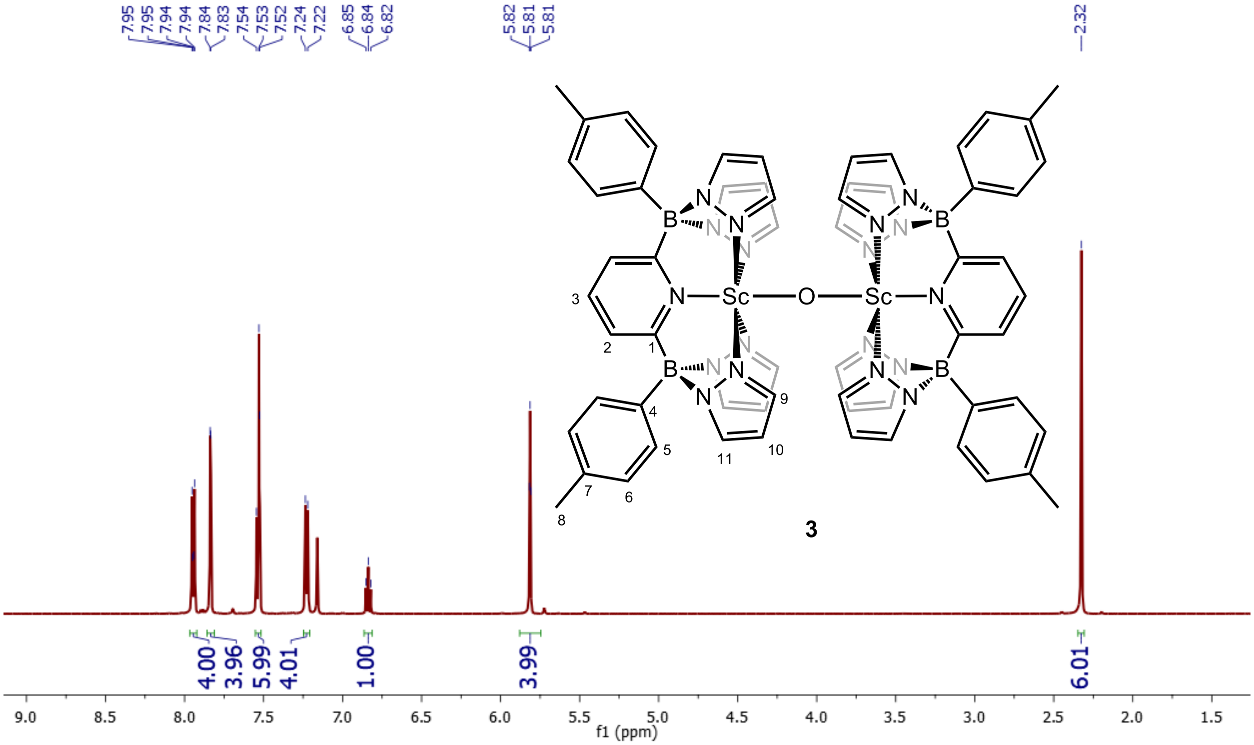

Figure S17: ^{1}H NMR spectrum of **3** in C_6D_6.

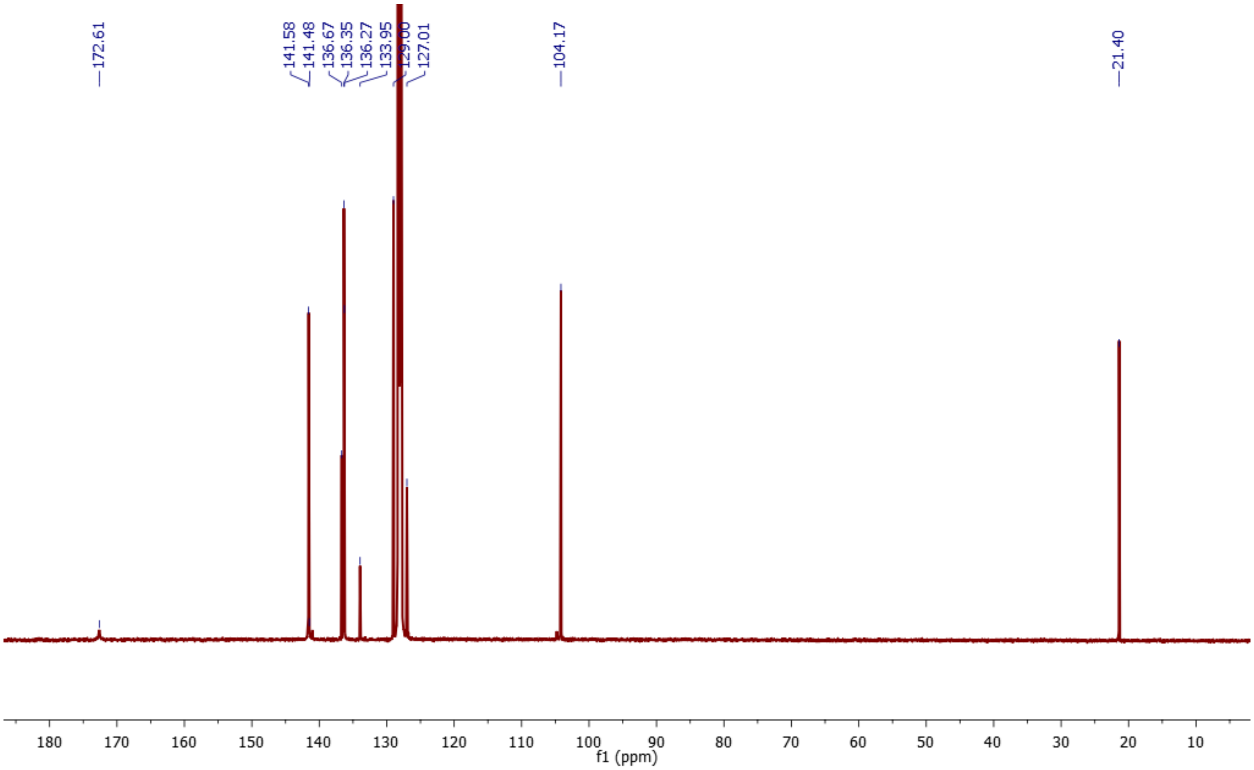

Figure S18: ^{13}C{^{1}H} NMR spectrum of **3** in C_6D_6.

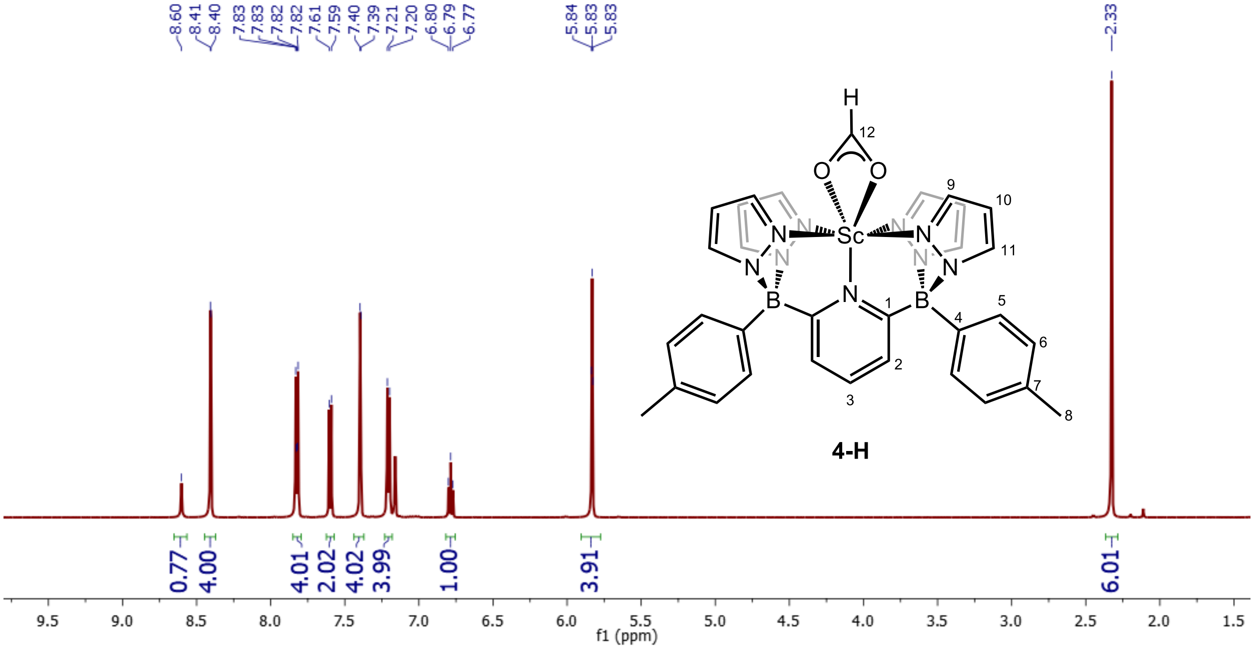

Figure S17: ^{1}H NMR spectrum of **4-H** in C_6D_6.

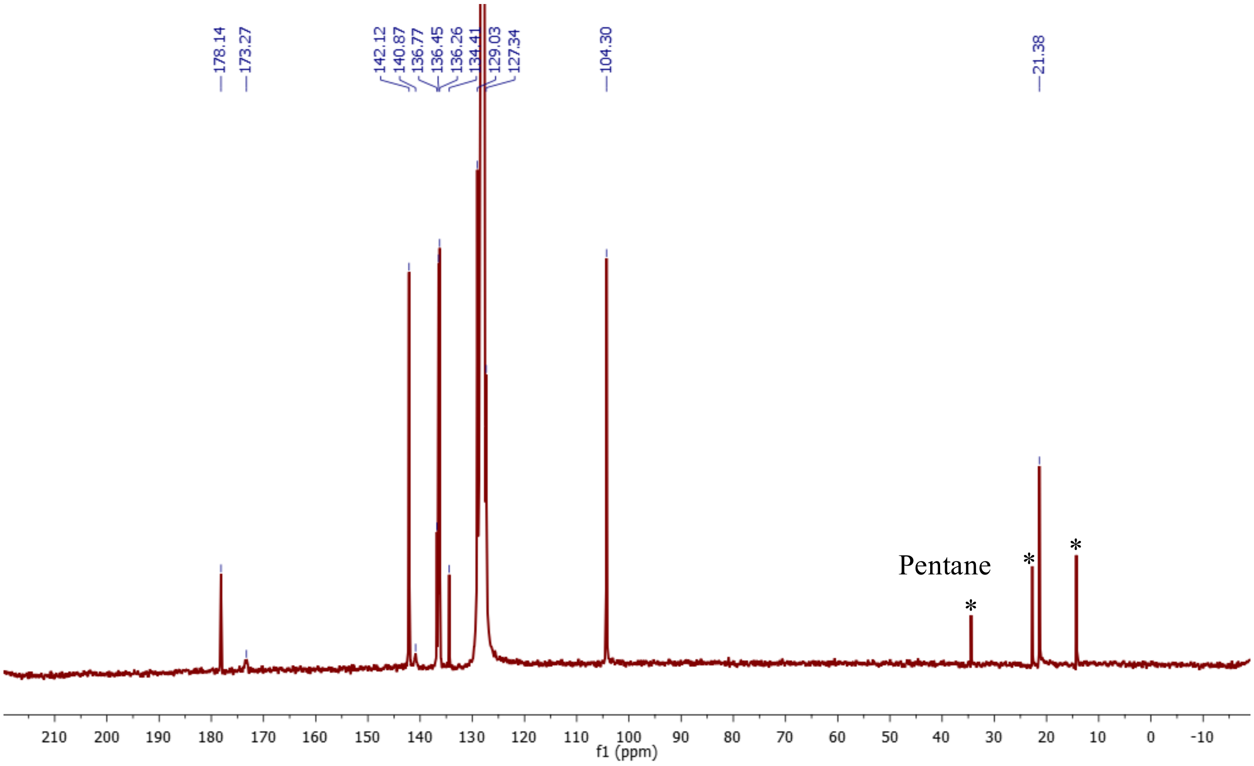

Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum of **4-H** in C_6D_6.

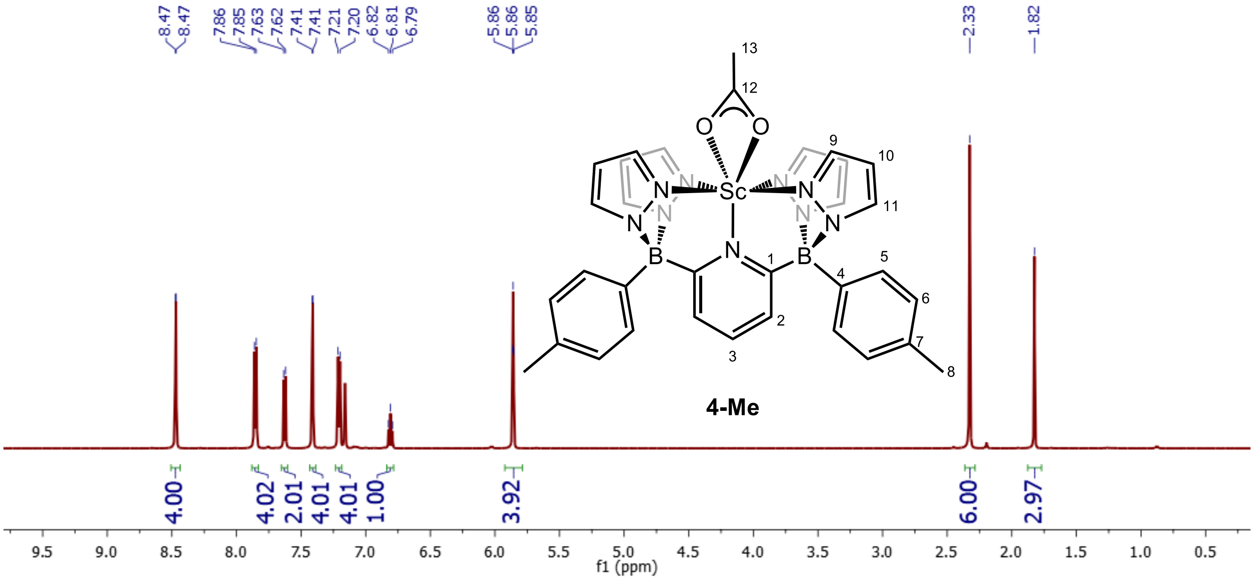

Figure S21: ^{1}H NMR spectrum of **4-Me** in C_6D_6.

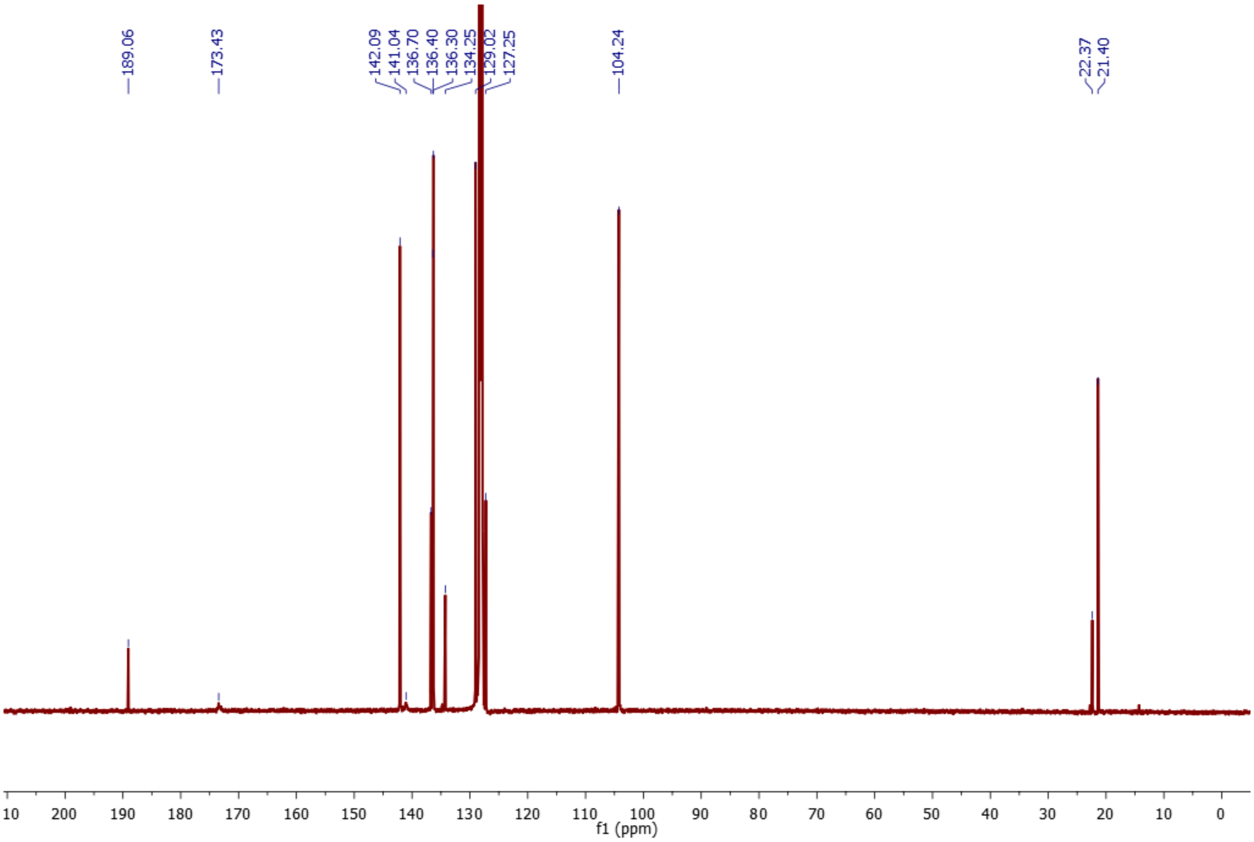

Figure S18: ^{1}H NMR spectrum of **4-Me** in C_6D_6.

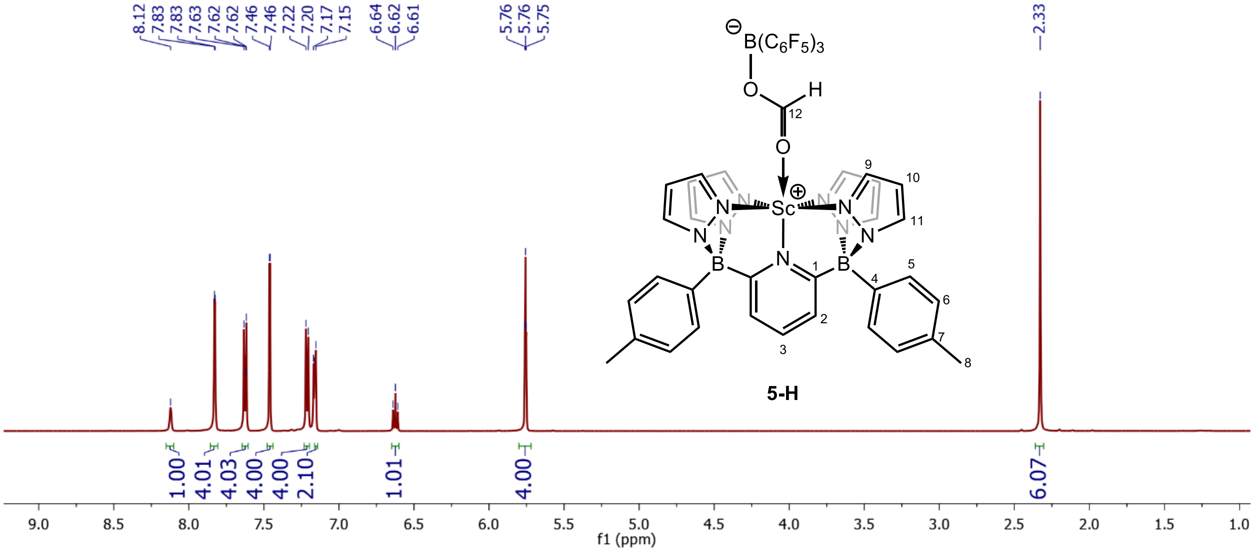

Figure S19: ^{1}H NMR spectrum of **5-H** in C_6D_6.

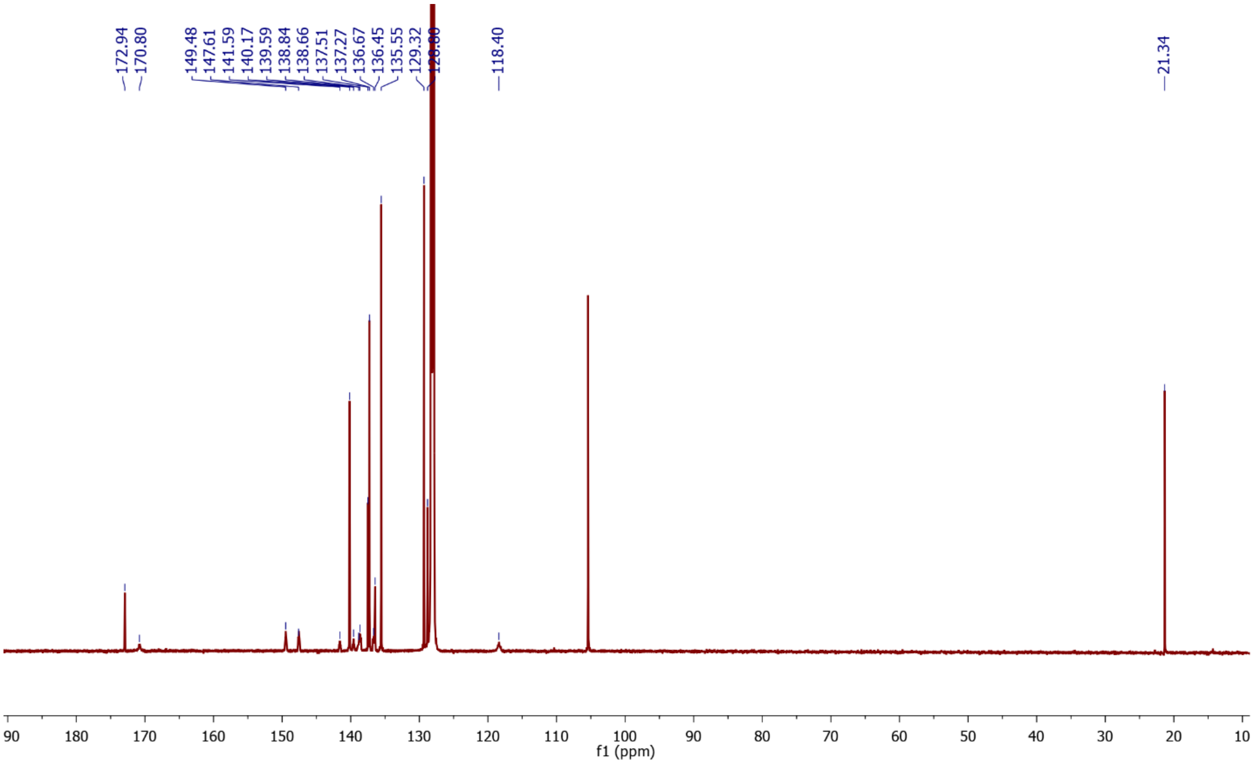

Figure S20: $^{13}C\{^1H\}$ NMR spectrum of **5-H** in C_6D_6.

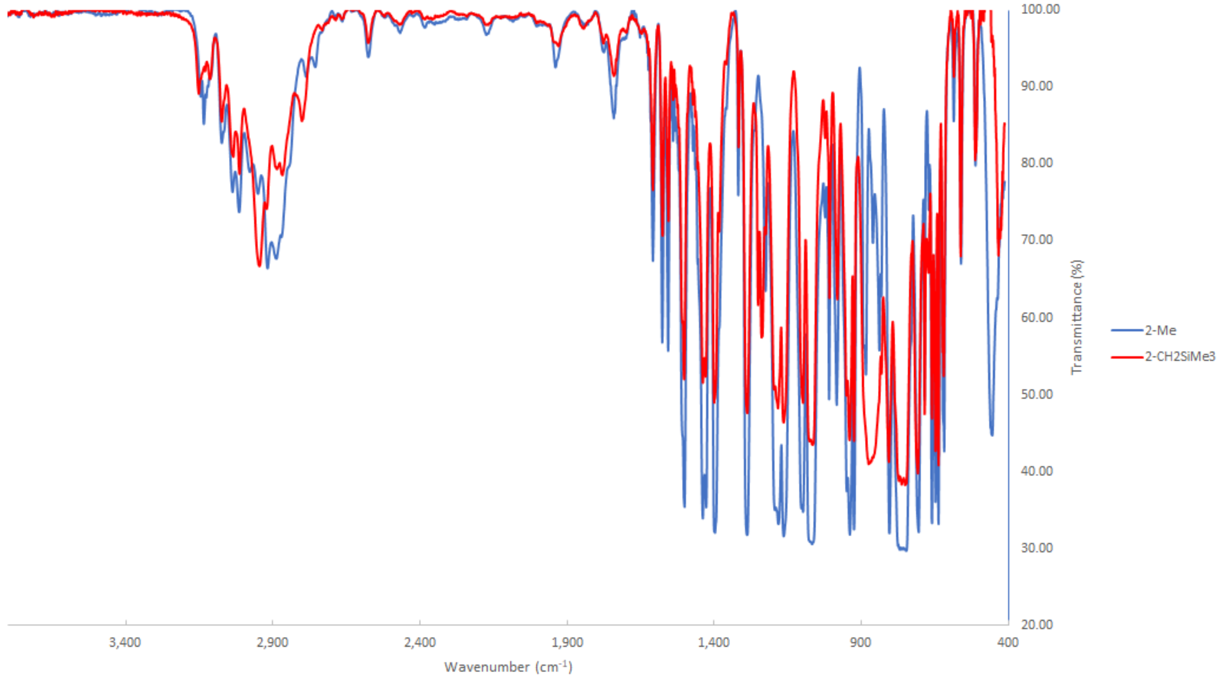

Figure S21: Superimposed FT-IR spectra of **2-Me** and **2-CH$_2$SiMe$_3$**, KBr pellet.

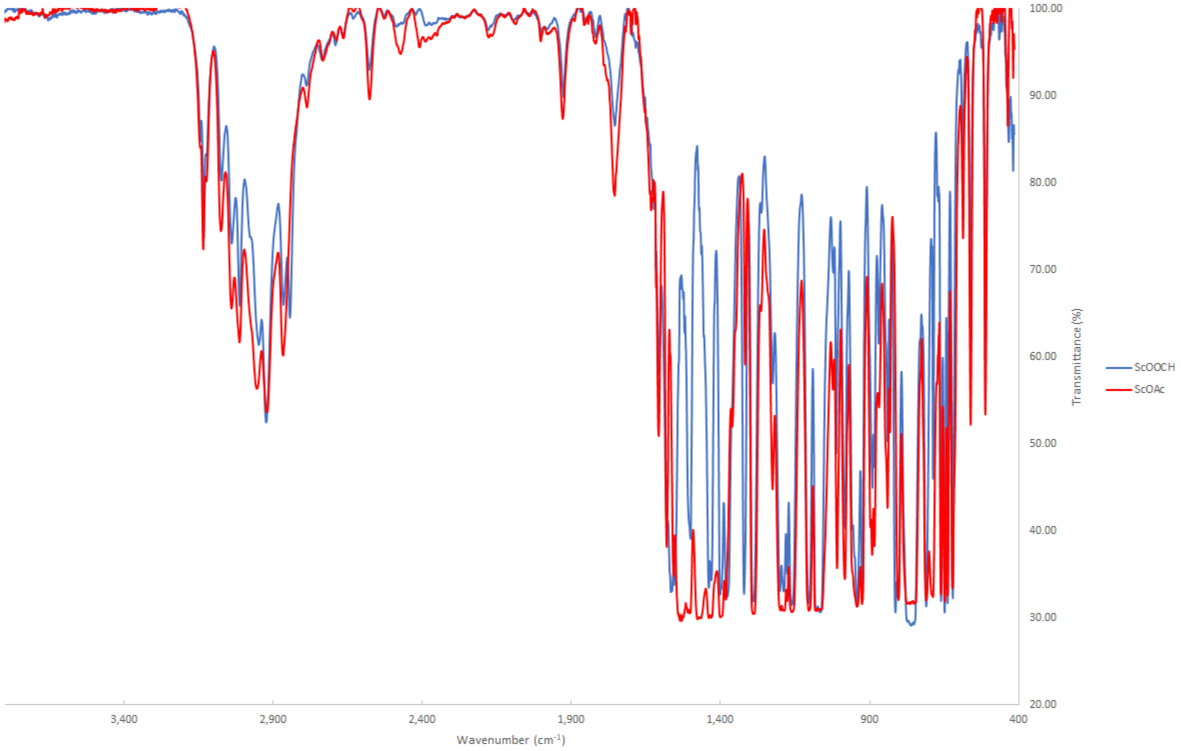

Figure S22: Superimposed FT-IR spectra of **4-H** and **4-Me**, KBr pellet.

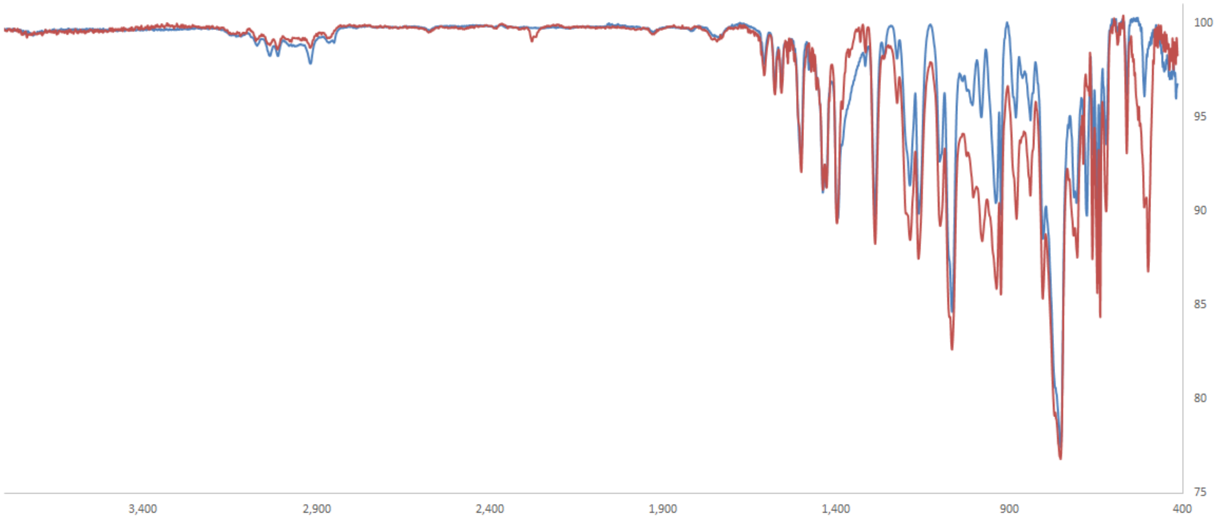

Figure S23: Superimposed FT-IR spectra of **2-H** and ***d*$_1$-2-H**, thin film on AgCl plates.

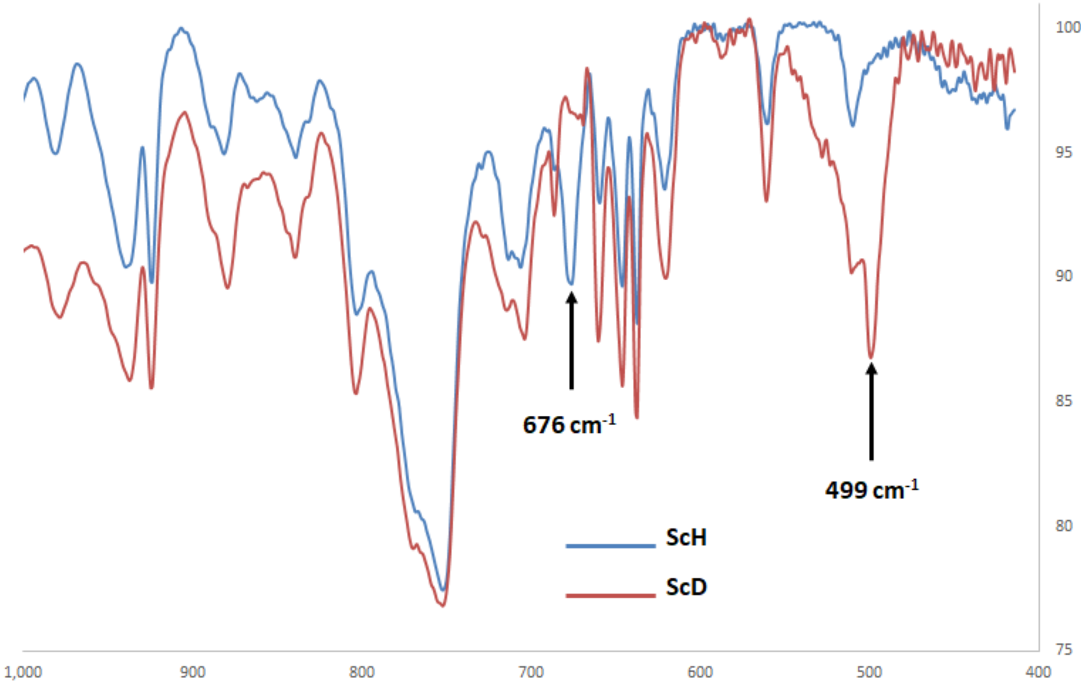

Figure S24: Zoomed in region of the superimposed FT-IR spectra of **2-H** and ***d*$_1$-2-H**.

$$MW_{ScH} = \frac{(mg_{ScH})(MW_{PhNNPh})(ml_{PhNNPh})}{(mg_{PhNNPh})(ml_{ScH})}$$

Mass of ScH = 10.1 mg
Mass of ScH = 10.2 mg
Molecular weight of azobenzene = 182.23 g/mol
V_i of ScH = 0.83 mL V_f of ScH = 0.24 mL
V_i of Azobenzene = 0.85 mL V_f of Azobenzene = 1.47 mL

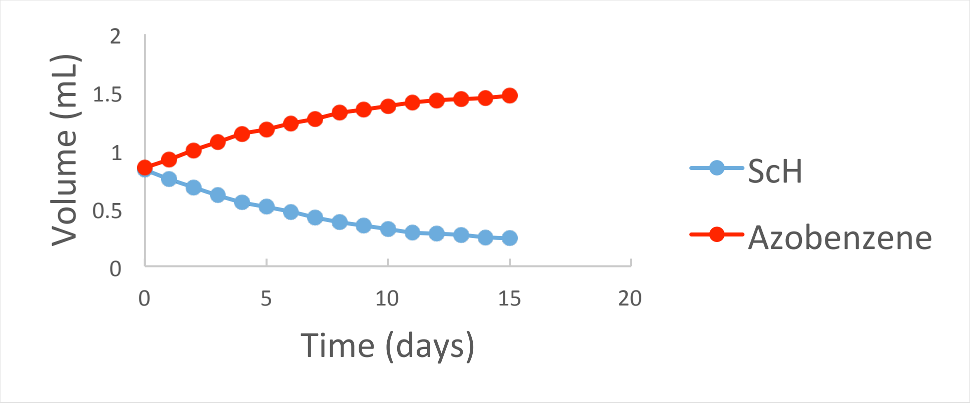

Figure S25: Signer method for the molecular weight determination of **2-H** in C_6H_6.

$$r = \frac{k_b T}{6\pi D\eta}$$

Where r = Hydrodynamic radius

k_b = Boltzmann constant = 1.38×10^{-23} J K^{-1}

T = Temperature = 298 K

D = Diffusion constant obtained from DOSY NMR spectrum

η = Viscosity of C_6D_6 at 298 K = 0.6392 mPa.s [8]

Complex	D (m^2/s)	r (Å)
2-H	4.80×10^{-10}	7.11
2-Me	6.88×10^{-10}	4.96
3	4.83×10^{-10}	7.07

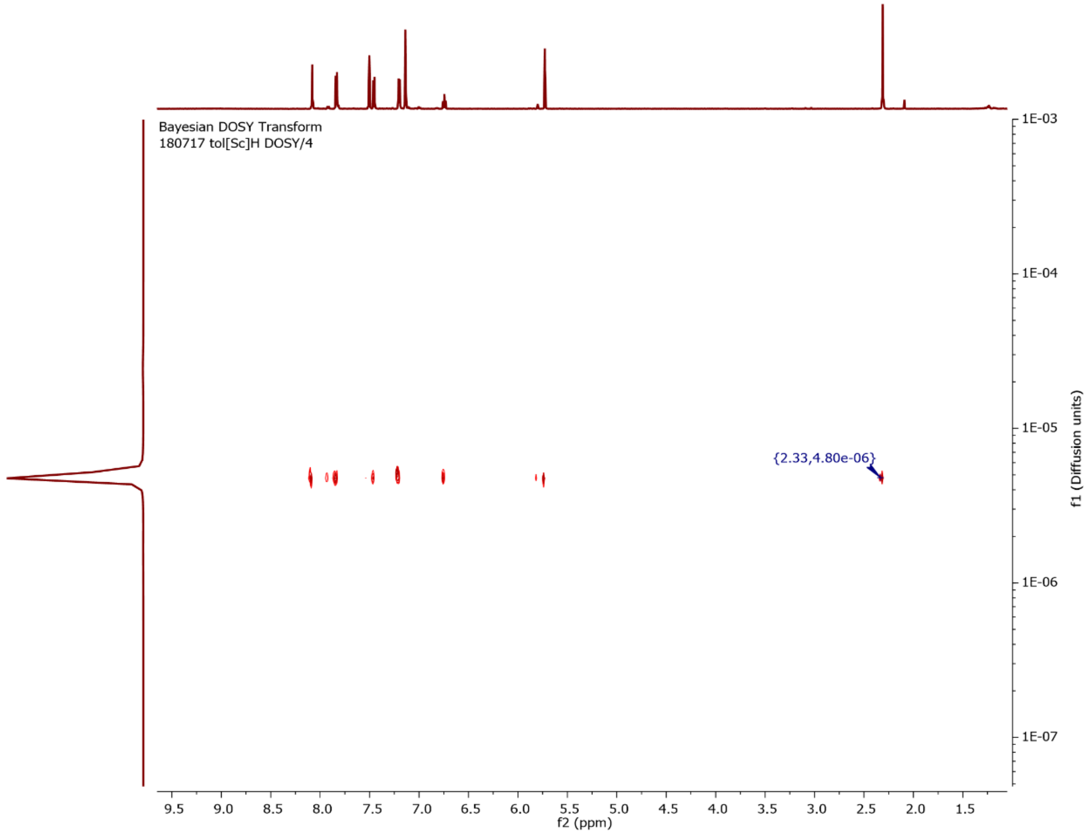

Figure S26: 2D DOSY spectrum of **2-H** in C_6D_6.

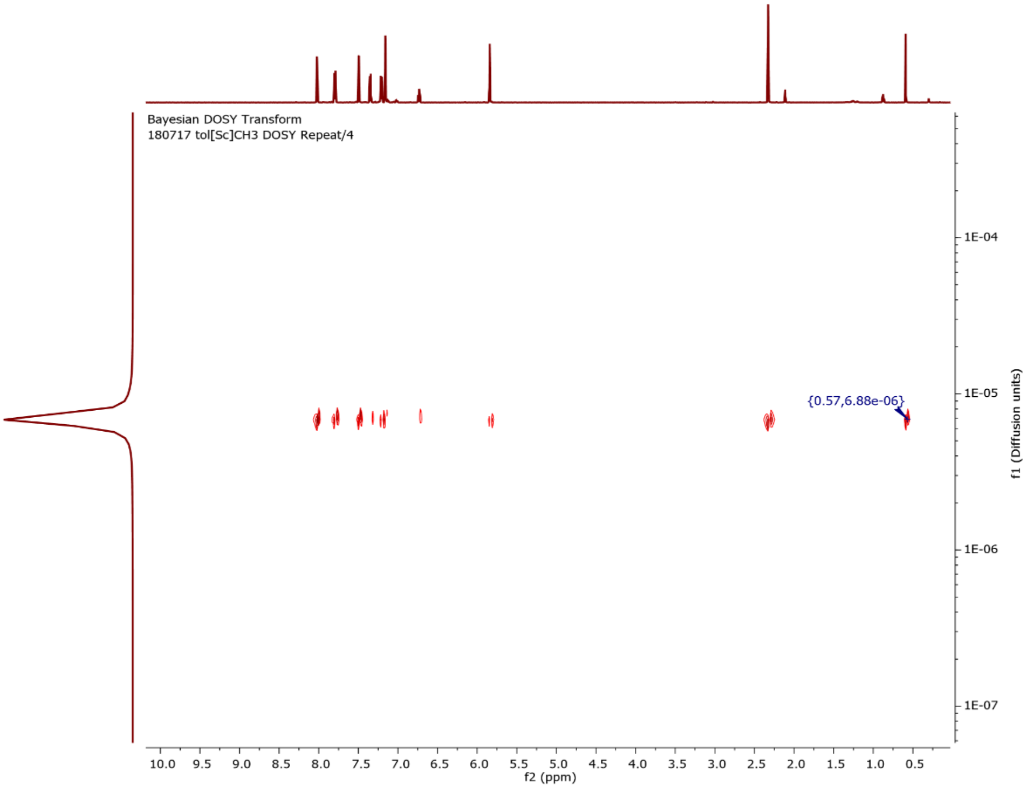

Figure S27: 2D DOSY spectrum of **2-Me** in C_6D_6.

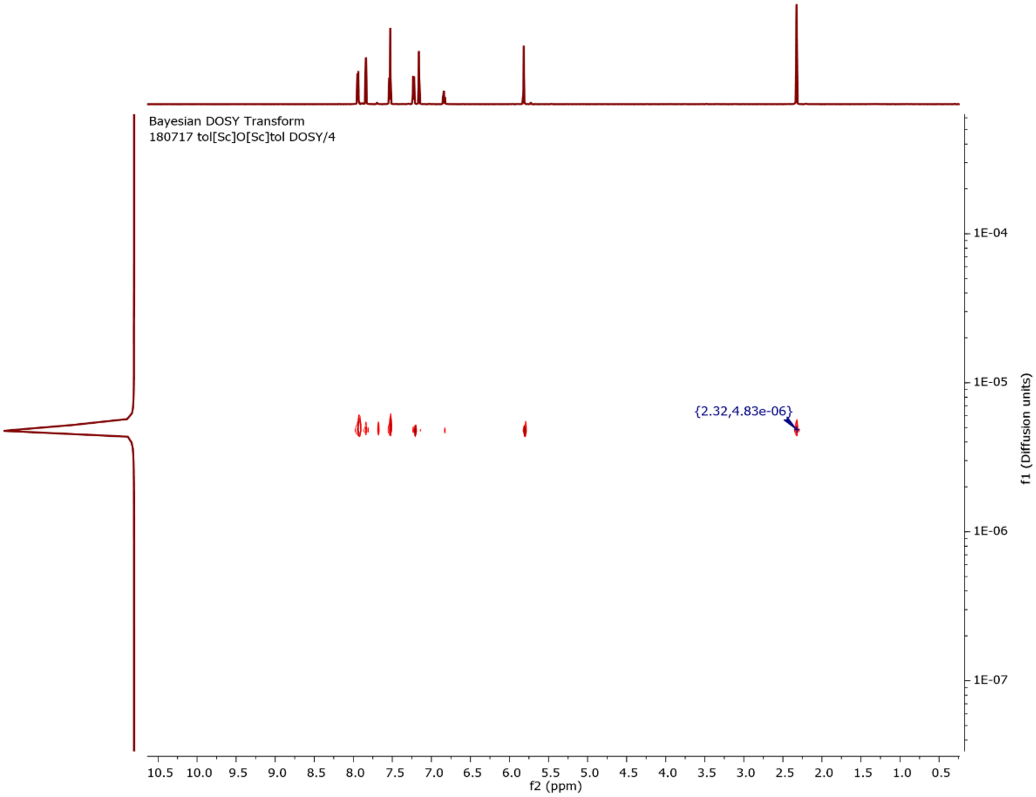

Figure S28: 2D DOSY spectrum of **3** in C_6D_6.

Table S1: Crystal data collection and refinement parameters for complexes.

	1	**2-Me**	**2-CH$_2$SiMe$_3$**
formula	$C_{31}H_{29}B_2ClN_9Sc$, 2(C_6H_6)	$C_{32}H_{32}B_2N_9Sc$, 2(C_6H_6)	$C_{35}H_{40}B_2N_9ScSi$
fw	785.88	765.46	681.43
crystal system	triclinic	triclinic	monoclinic
space group	P-1	P-1	C2/c
a **(Å)**	10.2171(2)	10.2075(9)	39.5534(15)
b **(Å)**	12.1118(4)	11.9288(10)	8.3472(3)
c **(Å)**	18.2907(4)	18.5503(16)	27.4331(9)
α (deg)	103.202(2)	104.426(4)	90
β (deg)	92.4060(10)	92.714(5)	126.713(2)
γ (deg)	113.9310(10)	112.543(4)	90
V **(Å^3)**	1990.99(9)	1994.4(3)	7260.7(5)
Z	2	2	8
T **(K)**	173(2)	173(2)	173(2)
Wavelength (Å)	1.54178	0.71073	0.71073
ρ_{calcd} (g·cm^{-3})	1.311	1.275	1.247
F**(000)**	820	804	2864
μ (mm^{-1})	2.539	0.229	0.274
crystal size, mm^3	0.198×0.111×0.053	0.2×0.2×0.2	0.27×0.20×0.16
transmission factors	0.646 – 0.754	0.6309 − 0.7461	0.6269 − 0.7456
θ **range (deg)**	2.510 − 68.228	3.348 − 26.000	3.110 − 25.000
data/restraints/param	7007/0/507	7825/0/506	6319/525/468
GOF	1.024	1.004	1.023
R_1 [I > 2σ(I)]	0.0790	0.0421	0.0403
wR_2 [all data]	0.2498	0.1096	0.1135
residual density, e/Å^3	0.580 and -0.888	0.436 and -0.401	0.376 and -0.365

Table S2: Data collection and structure refinement details for complexes.

	3	**4-H**	**4-Me**
formula	$C_{62}H_{46}B_4N_{18}OSc_2$	$C_{32}H_{30}B_2N_9O_2Sc$, 2(C_6H_6)	$C_{33}H_{32}B_2N_9O_2Sc$
fw	1204.42	795.45	653.25
crystal system	monoclinic	triclinic	orthorhombic
space group	P2/c	P-1	P212121
a **(Å)**	17.2544(3)	12.9337(7)	13.860(4)
b **(Å)**	11.7447(2)	13.0637(5)	14.896(5)
c **(Å)**	15.3640(2)	13.3321(7)	15.506(5)
α (deg)	90	67.293(2)	90
β (deg)	104.3550(10)	82.797(3)	90
γ (deg)	90	75.727(2)	90
V **($Å^3$)**	3016.27(8)	2012.73(17)	3201.3(18)
Z	2	2	4
T **(K)**	173(2)	173(2)	173(2)
Wavelength (Å)	1.54178	0.71073	0.71073
ρ_{calcd} ($g\cdot cm^{-3}$)	1.326	1.313	1.355
F**(000)**	1252	832.0	1360
μ (mm^{-1})	2.400	0.233	0.277
crystal size, mm^3	0.21×0.13×0.12	0.522×0.462×0.38	0.130×0.130×0.100
transmission factors	0.6219 − 0.7533	0.7270 − 0.9984	0.5506 − 0.7455
θ **range (deg)**	2.643 − 67.485	1.903 − 27.878	2.627 − 24.994
data/restraints/param	5307/0/395	9505/360/617	5646/0/428
GOF	1.058	1.021	1.013
R_1 [$I > 2\sigma(I)$]	0.0471	0.0550	0.0646
wR_2 [all data]	0.1355	0.1578	0.1452
residual density, e/$Å^3$	0.487 and -0.305	0.768 and -0.471	0.263 and -0.350

Table S3: Crystal data collection and refinement parameters for complex.

	5-H
formula	$C_{50}H_{30}B_3F_{15}N_9O_2Sc,2(C_3H_9O_{0.5}Si)$
fw	1313.60
crystal system	monoclinic
space group	C2/c
a **(Å)**	36.353(4)
b **(Å)**	12.6079(14)
c **(Å)**	30.349(3)
α (deg)	90
β (deg)	116.768(3)
γ (deg)	90
V **($Å^3$)**	12419(2)
Z	8
T **(K)**	173(2)
Wavelength (Å)	0.71073
ρ_{calcd} ($g \cdot cm^{-3}$)	1.405
F**(000)**	5360
μ (mm^{-1})	0.253
crystal size, mm^3	0.300×0.200×0.100
transmission factors	0.6335 − 0.7455
θ **range (deg)**	1.503 − 25.000
data/restraints/param	10596/0/820
GOF	1.016
R_1 [I > 2σ(I)]	0.0533
wR_2 [all data]	0.1482
residual density, e/$Å^3$	0.713 and -0.533

Cartesian coordinates of all optimized structures

ScH monomer **2-H**

73

C	7.99134	6.03529	5.56303
C	6.97736	6.44851	4.70778
N	5.88850	5.68562	4.91772
N	6.17092	4.75713	5.86249
C	7.43040	4.97301	6.26978
B	4.50846	5.60327	4.13501
C	4.62581	4.18139	3.32685
N	4.46018	3.00880	3.99684
C	4.60057	1.80606	3.37662
C	5.02144	1.76585	2.04198
C	5.26684	2.94497	1.35157
C	5.04724	4.15686	1.99214
Sc	4.78724	3.05389	6.33600
N	6.13918	1.30769	5.93074
N	5.83731	0.34583	5.02614
C	6.91131	-0.44545	4.84675
C	7.93473	-0.01592	5.68249
C	7.39529	1.08539	6.34488
B	4.45700	0.42133	4.24292
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C	3.02031	-2.06147	1.53819
C	3.40451	-3.32234	2.00416
C	4.13874	-3.37106	3.19348
C	4.49586	-2.20493	3.86781
C	3.04827	-4.57699	1.25236

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C	1.53385	0.08695	6.60532
C	2.22008	1.20820	7.06920
N	3.30502	4.67231	6.21558
N	3.35424	5.58056	5.21466
C	2.31984	6.43653	5.34789
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C	2.24646	4.96879	6.97968
C	4.23837	6.91911	3.22685
C	4.59523	8.21102	3.65617
C	4.26015	9.35572	2.93541
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C	3.12270	8.00167	1.32956
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C	3.19470	10.50328	0.94568
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H	5.22818	5.09176	1.47374
H	2.02149	1.83681	7.92606
H	5.18216	0.80660	1.56299
H	5.12430	8.33821	4.59762
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H	3.03867	0.05330	1.82459
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H	2.10522	-1.15793	4.83063
H	0.69489	6.56425	6.85044
H	4.56273	10.33178	3.31016
H	0.64399	-0.36733	7.01388
H	2.52243	7.90143	0.42723
H	8.98308	6.45094	5.65755
H	2.11599	-4.45797	0.69202
H	2.93227	-5.43048	1.92729
H	3.83065	-4.83926	0.52913
H	3.08538	11.38300	1.58728
H	2.26511	10.37591	0.38273
H	3.98609	10.72777	0.21956

ScH dimer **[2-H]$_2$**

146

C	8.02107	6.96586	11.95474
C	8.39582	5.73352	11.38955
C	9.68702	5.28178	11.71371
C	10.55980	6.02754	12.50436
C	10.18412	7.27147	13.02151
C	8.89019	7.72079	12.74056
B	7.33511	4.79975	10.59503
C	7.95728	3.80588	9.45030
N	7.21233	2.77636	8.96549
C	7.66706	2.00303	7.93960

C	8.84452	2.36002	7.27326
C	9.59203	3.44634	7.70544
C	9.16352	4.14590	8.82374
Sc	4.84563	2.76976	9.38048
H	3.28688	1.88706	10.19903
Sc	1.54920	2.75502	9.84586
H	3.11031	3.65374	9.05299
B	6.78105	0.72056	7.43452
C	7.56086	-0.41812	6.57733
C	6.87287	-1.29435	5.71716
C	7.50370	-2.35505	5.06936
C	8.86441	-2.61291	5.26176
C	9.55459	-1.78352	6.15073
C	8.91701	-0.72222	6.79131
C	9.55971	-3.73377	4.53589
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C	0.06096	-0.43015	7.28009
C	1.18280	-1.11216	7.73418
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C	-1.57179	2.08940	9.16663
N	-0.83296	2.67391	10.15117
C	-1.33657	2.82922	11.40512
C	-2.59026	2.29022	11.72245
C	-3.31209	1.58912	10.76814
C	-2.80339	1.50376	9.47989
B	-0.38876	3.42329	12.60209
C	-1.15959	3.93680	13.93259

C	-2.40199	4.59073	13.85624
C	-3.02035	5.14827	14.97396
C	-2.42295	5.08599	16.23702
C	-1.17001	4.47185	16.32640
C	-0.55501	3.92286	15.20225
C	-3.10694	5.65009	17.45395
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C	-0.55127	4.22115	6.31214
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C	1.03049	5.07433	7.57314
N	1.43175	4.52772	11.14418
N	0.52785	4.62397	12.14693
C	0.60422	5.85688	12.68950
C	1.58464	6.58200	12.02826
C	2.07951	5.69911	11.06940
N	1.33182	1.71876	11.88669
N	0.54235	2.17517	12.88614
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C	-2.51822	1.07468	4.13527
C	-3.83204	1.54569	4.21791
C	-4.22286	2.14797	5.41763
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C	-4.78929	1.40429	3.06450
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N	5.58966	1.35440	6.61041

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C	4.29372	2.23233	5.02678
C	3.88372	2.66024	6.28850
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N	6.18918	-0.02156	8.69189
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C	5.83259	-1.47899	10.33502
C	5.23564	-0.24990	10.62166
N	5.42511	3.28332	11.43945
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C	6.69899	4.08124	13.04512
C	5.71068	3.32819	13.66220
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N	5.31525	5.00268	9.09278
N	6.32185	5.64893	9.72501
C	6.46023	6.88487	9.20388
C	5.49865	7.06681	8.22029
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H	0.24251	6.23577	5.83846
H	-1.31154	3.98611	5.58456
H	-0.62350	0.83459	5.08206
H	-2.16690	0.63050	3.20565
H	-5.22772	2.55650	5.50789
H	-3.69241	2.74961	7.39395
H	-4.26521	1.41663	2.10388
H	-5.53028	2.20947	3.05746

H	-5.33999	0.45694	3.12164
H	-3.34922	0.97246	8.70849
H	-4.26052	1.12135	11.02285
H	-2.96840	2.38694	12.73372
H	2.87289	5.82743	10.34583
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H	-0.03427	6.13527	13.51273
H	2.41995	-0.05010	11.59591
H	1.39377	-0.76024	14.05331
H	-0.15916	1.40458	14.72482
H	-2.89717	4.68435	12.89268
H	-3.98189	5.64588	14.86159
H	-0.66170	4.43307	17.28810
H	0.43881	3.49704	15.31954
H	-3.71340	6.52609	17.20372
H	-2.38356	5.94554	18.21994
H	-3.77830	4.91076	17.90855
H	3.05596	3.29477	6.57423
H	3.85916	2.47226	4.06816
H	6.03157	0.87820	4.60115
H	4.67064	0.05936	11.48858
H	5.83645	-2.37579	10.93616
H	6.99961	-1.96404	8.48271
H	5.80409	-1.16700	5.56313
H	6.92474	-3.00079	4.41154
H	10.60704	-1.97480	6.35220
H	9.49412	-0.12902	7.49563
H	8.87548	-4.56155	4.32567
H	10.40017	-4.12668	5.11608
H	9.96114	-3.39222	3.57349

H	9.15906	1.78736	6.40812
H	10.49872	3.74019	7.18123
H	9.73255	4.99168	9.19224
H	4.03611	2.24556	12.62133
H	5.57505	3.16171	14.72011
H	7.51530	4.64328	13.46992
H	3.97990	5.54488	7.56929
H	5.32902	7.94689	7.61833
H	7.23507	7.54790	9.55637
H	10.01937	4.31064	11.35476
H	11.54903	5.63256	12.72851
H	8.55288	8.66990	13.15314
H	7.01097	7.33991	11.80410
H	11.80707	7.46685	14.43620
H	10.60780	8.76768	14.52304
H	11.77275	8.72262	13.19854

ScMe Monomer **2-Me**

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C	3.47868	6.81762	2.10711
C	4.23673	6.85356	3.29032
C	4.58715	8.13721	3.74876
C	4.25802	9.29556	3.04740
C	3.53834	9.23541	1.84968
C	3.14044	7.97198	1.40256
B	4.50028	5.52058	4.17619
N	3.33393	5.47606	5.24297
N	3.27511	4.55801	6.23407
C	2.19439	4.83337	6.97448
C	1.52416	5.94077	6.45679

C	2.28474	6.31674	5.35945
Sc	4.77317	2.93812	6.37536
N	3.23536	1.35498	6.24450
N	3.27413	0.42598	5.26254
C	2.20876	-0.39256	5.38939
C	1.45783	0.00941	6.48412
C	2.15075	1.10852	6.98936
B	4.43831	0.34671	4.19544
C	4.14219	-0.98482	3.31754
C	3.38156	-0.93644	2.13634
C	3.01412	-2.08562	1.43812
C	3.38384	-3.35606	1.88978
C	4.10557	-3.42766	3.08553
C	4.46385	-2.27417	3.78076
C	3.02566	-4.59690	1.11619
C	3.21145	10.48090	1.06976
N	5.87384	5.59362	4.96914
C	6.96588	6.35234	4.75887
C	7.98348	5.92379	5.60161
C	7.42053	4.85739	6.30078
N	6.15633	4.65354	5.90187
C	4.62797	4.11499	3.34434
N	4.45629	2.93340	3.99478
C	4.59945	1.74307	3.35375
C	5.03366	1.72317	2.02261
C	5.28784	2.91303	1.35425
C	5.06213	4.11393	2.01320
N	6.11358	1.18537	5.91597
N	5.80994	0.24630	4.98886
C	6.88350	-0.54013	4.78571

C	7.90984	-0.13083	5.62751
C	7.37169	0.95336	6.31875
C	5.10745	2.94183	8.56689
H	2.15054	7.12806	4.66191
H	5.24793	5.05747	1.51226
H	1.93260	1.72463	7.85069
H	5.19685	0.77149	1.52929
H	5.10747	8.24599	4.69747
H	5.65553	2.90467	0.33055
H	7.81576	1.56892	7.08886
H	3.04604	0.02489	1.75582
H	6.85417	-1.33434	4.05607
H	2.42346	-1.99270	0.52865
H	4.38124	-4.40149	3.48603
H	4.98400	-2.39101	4.72858
H	6.95431	7.14232	4.02415
H	3.12144	5.86281	1.72998
H	8.89472	-0.56226	5.72342
H	7.85108	4.23614	7.07398
H	2.05726	-1.20811	4.70044
H	0.62315	6.40817	6.82409
H	4.55518	10.26446	3.44449
H	0.54831	-0.43619	6.85748
H	2.55048	7.88879	0.49170
H	8.97874	6.33174	5.69301
H	2.09482	-4.46579	0.55605
H	2.90571	-5.46122	1.77650
H	3.80862	-4.84932	0.39009
H	3.09977	11.34865	1.72705
H	2.28474	10.36546	0.49947

H	4.00699	10.71774	0.35214
H	1.96285	4.23066	7.84178
H	4.66779	2.06156	9.06049
H	6.17901	2.92992	8.82645
H	4.68897	3.83577	9.05428

CO2

3

O	2.95015	0.13859	4.64268
C	2.09914	0.17047	5.43646
O	1.24678	0.20232	6.22920

ScH CO2 insertion adduct

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C	-1.12263	-3.96182	-2.40047
C	-0.34060	-3.96580	-1.23231
C	0.00898	-5.23684	-0.73951
C	-0.34289	-6.41441	-1.39644
C	-1.08562	-6.38700	-2.58117
C	-1.48331	-5.13543	-3.06061
B	-0.05273	-2.60715	-0.39515
N	-1.19713	-2.51754	0.68730
N	-1.22242	-1.55764	1.63895
C	-2.27024	-1.80339	2.43519
C	-2.95416	-2.93440	1.99121
C	-2.23577	-3.35649	0.88176
Sc	0.26784	0.05217	1.65442
N	1.66009	1.74853	1.16591
N	1.36747	2.66469	0.21037
C	2.45738	3.41731	-0.02798

C	3.48214	3.01230	0.81807
C	2.92802	1.96348	1.54955
B	-0.01855	2.57713	-0.56409
N	-1.16619	2.57060	0.51863
N	-1.20536	1.67336	1.52902
C	-2.25540	1.97803	2.30160
C	-2.92688	3.08421	1.78240
C	-2.19855	3.42889	0.65281
C	-1.43692	-7.65414	-3.31410
N	1.63964	-1.68872	1.27580
C	2.90557	-1.89422	1.67106
C	3.44557	-2.99460	1.00790
C	2.41441	-3.44045	0.19067
N	1.33406	-2.66090	0.38147
N	-0.07038	-0.02079	-0.67050
C	0.07440	-1.23059	-1.27705
C	0.48945	-1.28446	-2.61292
C	0.72643	-0.11302	-3.31884
C	0.50710	1.10530	-2.69086
C	0.09161	1.14470	-1.35476
C	-0.28950	3.88249	-1.48687
C	-1.07068	3.81238	-2.65334
C	-1.41911	4.94531	-3.38704
C	-1.00909	6.22064	-2.98728
C	-0.26654	6.31555	-1.80591
C	0.07287	5.17855	-1.07509
C	-1.34770	7.44247	-3.79895
O	2.96331	0.13880	4.65003
C	2.07792	0.16987	5.41697
O	1.25484	0.20272	6.24134

H	0.26536	0.11308	3.51810
H	-2.34392	4.22920	-0.05540
H	0.68405	2.03477	-3.22020
H	-2.45997	-1.16537	3.28684
H	0.65283	-2.24877	-3.08062
H	0.61004	5.31537	-0.13957
H	1.07865	-0.14909	-4.34731
H	3.34962	-1.25277	2.41981
H	-1.48128	-3.01721	-2.80135
H	2.38626	-4.25642	-0.51464
H	-2.09119	-5.07675	-3.96151
H	-0.04529	-7.37232	-0.97390
H	0.54621	-5.31995	0.20229
H	2.44005	4.18683	-0.78403
H	-1.43851	2.84775	-2.99355
H	4.43600	-3.41269	1.10556
H	3.36302	1.36625	2.33908
H	-2.39135	-4.19935	0.22734
H	-3.80795	3.57243	2.17045
H	0.04051	7.29533	-1.44474
H	-3.83694	-3.38912	2.41445
H	-2.02695	4.83583	-4.28320
H	4.47749	3.42379	0.89055
H	-0.65652	-7.92086	-4.03780
H	-2.37293	-7.54911	-3.87102
H	-1.54356	-8.49917	-2.62709
H	-0.56160	7.65920	-4.53311
H	-1.45227	8.32889	-3.16582
H	-2.28140	7.30938	-4.35370
H	-2.45573	1.39725	3.19094

ScH CO2 insertion TS

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C	7.40690	1.18582	6.27681
N	6.12328	1.37502	5.93110
N	5.80536	0.40414	5.03692
C	6.89140	-0.35475	4.80174
C	7.94232	0.10063	5.58677
Sc	4.72309	3.11950	6.32329
O	6.66060	3.17845	8.69067
C	5.82392	3.21012	9.52461
O	5.18290	3.24402	10.49879
B	4.41636	0.45411	4.26370
C	4.54108	1.83682	3.39345
N	4.39703	3.04593	4.00443
C	4.55912	4.21017	3.31550
C	4.97561	4.16969	1.97992
C	5.19609	2.95292	1.35088
C	4.95689	1.78344	2.05795
B	4.45117	5.64831	4.09334
C	4.18968	6.95033	3.16224
C	3.40919	6.88103	1.99530
C	3.06654	8.01389	1.25866
C	3.48173	9.28830	1.65594
C	4.22346	9.38261	2.83789
C	4.55708	8.24575	3.57155
C	3.14942	10.50982	0.84119
N	3.27096	4.75913	6.17908
C	2.21340	5.05708	6.94536
C	1.53178	6.15204	6.41526

C	2.26179	6.49961	5.28772
N	3.30322	5.65093	5.16492
N	3.25302	1.49022	6.29052
N	3.27208	0.53429	5.33612
C	2.22446	-0.29565	5.51926
C	1.50361	0.13069	6.62540
C	2.19713	1.25192	7.07967
N	6.14347	4.81848	5.82177
N	5.83891	5.73265	4.86556
C	6.93377	6.46326	4.58601
C	7.97731	6.04828	5.40267
C	7.42805	5.01577	6.15941
C	4.13773	-0.90225	3.41871
C	4.49363	-2.17259	3.90875
C	4.14790	-3.35049	3.24919
C	3.40501	-3.32422	2.06453
C	3.00074	-2.07365	1.58802
C	3.35538	-0.89964	2.25082
C	3.06051	-4.59150	1.32859
H	4.19907	3.18313	8.11327
H	2.11336	7.29563	4.57516
H	5.15279	5.09996	1.45232
H	2.01482	1.89034	7.93182
H	5.11972	0.81827	1.59210
H	5.09487	8.38189	4.50689
H	5.54980	2.91660	0.32296
H	7.86923	1.82932	7.01080
H	2.99142	0.04396	1.85226
H	6.85206	-1.16406	4.08935
H	2.39246	-2.01607	0.68732

H	4.45052	-4.30781	3.66952
H	5.03233	-2.25463	4.84989
H	6.90558	7.22540	3.82287
H	3.03702	5.91738	1.65697
H	8.94245	-0.30109	5.64713
H	7.88095	4.41622	6.93536
H	2.06639	-1.13537	4.86122
H	0.64366	6.63276	6.79671
H	4.53445	10.36184	3.19720
H	0.61356	-0.31639	7.04162
H	2.45909	7.90505	0.36215
H	8.98157	6.44235	5.44062
H	3.84368	-4.85400	0.60631
H	2.12542	-4.48923	0.76963
H	2.95555	-5.43811	2.01393
H	3.93933	10.72411	0.11038
H	3.04378	11.39724	1.47276
H	2.21799	10.37801	0.28236
H	2.02135	4.47755	7.83654

ScH CO_2 k^1 kinetic insertion product

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C	2.81944	-1.88742	1.75376
N	1.56640	-1.69694	1.31012
N	1.30335	-2.66613	0.40057
C	2.39924	-3.43237	0.24446
C	3.39366	-2.97784	1.10129
Sc	0.21944	0.05270	1.64423
O	0.47260	0.11509	3.61705
C	1.40446	0.13841	4.52870

O	2.60950	0.12592	4.32407
B	-0.05459	-2.60816	-0.40902
C	0.09508	-1.23050	-1.28441
N	-0.03171	-0.02084	-0.67163
C	0.11048	1.14482	-1.36172
C	0.51560	1.10554	-2.70056
C	0.73775	-0.11209	-3.32847
C	0.49954	-1.28340	-2.62311
B	-0.02541	2.57771	-0.57733
C	-0.28946	3.87921	-1.50714
C	-1.06813	3.80498	-2.67543
C	-1.40908	4.93432	-3.41782
C	-0.99437	6.21055	-3.02522
C	-0.25507	6.30981	-1.84235
C	0.07756	5.17611	-1.10301
C	-1.32463	7.42834	-3.84629
N	-1.29481	1.64333	1.46935
C	-2.37614	1.94257	2.20055
C	-3.01769	3.06243	1.67481
C	-2.24016	3.41970	0.58260
N	-1.20819	2.55773	0.47646
N	-1.30814	-1.53221	1.57644
N	-1.23349	-2.50957	0.64446
C	-2.26892	-3.35718	0.81395
C	-3.03653	-2.92538	1.88603
C	-2.38545	-1.77734	2.33328
N	1.58318	1.76417	1.20066
N	1.33115	2.67506	0.23005
C	2.43444	3.41936	0.02747
C	3.42299	3.01151	0.91407

C	2.83728	1.97084	1.63406
C	-0.33312	-3.96355	-1.25401
C	0.02552	-5.23551	-0.77083
C	-0.31621	-6.41052	-1.43797
C	-1.05672	-6.37956	-2.62382
C	-1.46388	-5.12726	-3.09379
C	-1.11387	-3.95646	-2.42337
C	-1.39574	-7.64331	-3.36825
H	1.00611	0.17223	5.56059
H	-2.35266	4.23069	-0.11919
H	0.68211	2.03542	-3.23219
H	-2.62848	-1.12526	3.16067
H	0.65361	-2.24770	-3.09354
H	0.61306	5.31694	-0.16733
H	1.08726	-0.14775	-4.35783
H	3.21201	-1.24186	2.52947
H	-1.47963	-3.01149	-2.81711
H	2.40666	-4.24515	-0.46515
H	-2.07039	-5.06613	-3.99545
H	-0.01138	-7.36937	-1.02280
H	0.56208	-5.32216	0.17082
H	2.45046	4.18491	-0.73273
H	-1.43978	2.83984	-3.01018
H	4.38452	-3.38546	1.23328
H	3.22238	1.37283	2.45061
H	-2.38997	-4.21201	0.16795
H	-3.91233	3.54883	2.03282
H	0.05563	7.29050	-1.48686
H	-3.93099	-3.38254	2.28108
H	-2.01457	4.82162	-4.31518

H	4.41746	3.41744	1.02191
H	-0.61279	-7.89556	-4.09435
H	-2.33277	-7.54242	-3.92425
H	-1.49387	-8.49562	-2.68902
H	-0.53733	7.63340	-4.58251
H	-1.42230	8.32047	-3.22015
H	-2.25953	7.29770	-4.39962
H	-2.62916	1.34694	3.06661

ScH eta2 coordination **TS**$_{\mathbf{2-H}}$

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C	-1.13747	-3.95450	-2.41891
C	-0.33409	-3.96367	-1.26511
C	0.02426	-5.23674	-0.78451
C	-0.33990	-6.41134	-1.44035
C	-1.10393	-6.37872	-2.61119
C	-1.51014	-5.12492	-3.07781
B	-0.03396	-2.60777	-0.42798
N	-1.18642	-2.50428	0.64762
N	-1.22273	-1.52972	1.58326
C	-2.27708	-1.76685	2.37413
C	-2.95287	-2.90709	1.94306
C	-2.22345	-3.34354	0.84637
Sc	0.30038	0.05486	1.62222
N	1.66478	1.76213	1.13565
N	1.38018	2.67254	0.17164
C	2.47738	3.41257	-0.07274
C	3.49685	3.00512	0.77821
C	2.93523	1.96773	1.52044
B	0.00347	2.57699	-0.60550

N	-1.15238	2.56085	0.47123
N	-1.20375	1.65091	1.46904
C	-2.26050	1.94955	2.23542
C	-2.92270	3.06485	1.72526
C	-2.18253	3.42090	0.60685
C	-1.46852	-7.64252	-3.34339
N	1.64076	-1.70106	1.25449
C	2.90782	-1.89964	1.65390
C	3.45438	-2.99202	0.98268
C	2.42935	-3.43978	0.15909
N	1.34302	-2.66924	0.35255
O	0.26223	0.12752	3.64205
C	1.29213	0.14885	4.43582
O	2.46677	0.12770	4.08381
N	-0.01435	-0.02120	-0.69358
C	0.10164	-1.23167	-1.30681
C	0.48379	-1.28789	-2.65196
C	0.71151	-0.11868	-3.36401
C	0.50282	1.10015	-2.73403
C	0.12019	1.14247	-1.38863
C	-0.27705	3.87826	-1.53104
C	-1.07711	3.80381	-2.68460
C	-1.43445	4.93350	-3.41885
C	-1.01540	6.21006	-3.03230
C	-0.25399	6.30941	-1.86348
C	0.09481	5.17546	-1.13210
C	-1.36414	7.42835	-3.84498
H	1.02647	0.18961	5.50892
H	-2.31893	4.22971	-0.09333
H	0.66256	2.02905	-3.26947

H	-2.48179	-1.11647	3.21269
H	0.62849	-2.25365	-3.12247
H	0.64756	5.31602	-0.20638
H	1.04283	-0.15684	-4.39928
H	3.32907	-1.25735	2.41534
H	-1.50360	-3.00809	-2.80881
H	2.40868	-4.25082	-0.55224
H	-2.13409	-5.06219	-3.96738
H	-0.03458	-7.37112	-1.02769
H	0.57855	-5.32430	0.14681
H	2.46755	4.17530	-0.83589
H	-1.45310	2.83840	-3.01365
H	4.44700	-3.40481	1.08103
H	3.34751	1.37098	2.32273
H	-2.37100	-4.19614	0.20291
H	-3.80643	3.55033	2.11068
H	0.06116	7.29031	-1.51250
H	-3.83844	-3.35738	2.36517
H	-2.05650	4.82071	-4.30480
H	4.49555	3.40884	0.84868
H	-0.70013	-7.90718	-4.08056
H	-2.41324	-7.53421	-3.88476
H	-1.56503	-8.49019	-2.65813
H	-1.45978	8.31773	-3.21458
H	-2.30519	7.29330	-4.38669
H	-0.58769	7.64124	-4.59043
H	-2.47690	1.35796	3.11362

ScH final product **4-H**

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Sc	11.67243	5.23640	6.69306
O	13.00013	3.56231	7.30802
O	12.04764	4.79940	8.85614
N	13.40399	5.62569	5.37019
N	13.61885	6.82761	4.79123
N	12.29795	7.27874	7.44959
N	12.68507	8.30116	6.65079
N	10.59477	6.57456	5.04847
N	9.55285	5.09128	7.48571
N	8.45703	4.94623	6.70352
N	10.88121	3.63027	5.39305
N	9.65127	3.68786	4.83622
C	14.36112	4.79387	4.93551
H	14.39430	3.77767	5.29857
C	15.20757	5.45736	4.04899
H	16.06859	5.06471	3.52952
C	14.69992	6.74680	3.98920
H	15.04049	7.60841	3.43731
C	12.17308	7.77263	8.69183
H	11.90448	7.11363	9.50389
C	12.45344	9.13799	8.69932
H	12.44039	9.81681	9.53868
C	12.76250	9.43132	7.37762
H	13.02523	10.36863	6.91214
C	13.40847	9.32085	4.30328
C	14.52165	10.00113	4.83065
H	14.89177	9.74160	5.81968
C	15.20529	10.98191	4.11430
H	16.05917	11.48011	4.56975
C	14.82310	11.32529	2.81383

C	13.74777	10.62775	2.25531
H	13.44273	10.84524	1.23338
C	13.06562	9.65207	2.98063
H	12.25439	9.12099	2.48905
C	15.53610	12.40767	2.04788
H	15.06470	13.38472	2.21276
H	15.51599	12.21651	0.97058
H	16.58191	12.49638	2.35736
C	11.14543	7.78208	4.73917
C	10.33219	8.81394	4.25675
H	10.77055	9.78720	4.06807
C	8.97541	8.60464	4.05999
H	8.33094	9.41385	3.72399
C	8.46104	7.33745	4.28994
H	7.40860	7.13437	4.12855
C	9.28720	6.31353	4.76733
C	3.73530	3.11254	2.17035
H	3.44030	2.09545	2.44661
H	3.89187	3.13828	1.08775
H	2.88357	3.76802	2.39140
C	4.96627	3.55287	2.91679
C	5.22508	3.10817	4.21728
H	4.54432	2.39946	4.68544
C	6.34799	3.54490	4.91764
H	6.52456	3.13113	5.90762
C	7.26593	4.46238	4.37351
C	7.01034	4.86397	3.05070
H	7.71212	5.52327	2.54607
C	5.89243	4.42765	2.34128
H	5.74135	4.76883	1.31882

C	9.11892	5.32647	8.73454
H	9.83330	5.43792	9.53656
C	7.72600	5.36405	8.76296
H	7.08067	5.53205	9.61198
C	7.35008	5.12872	7.44692
H	6.37063	5.08638	6.99628
C	11.46350	2.50149	4.96446
H	12.45154	2.24160	5.31351
C	10.60733	1.81630	4.10413
H	10.78275	0.88066	3.59506
C	9.46735	2.60477	4.05399
H	8.54042	2.46248	3.52154
C	12.79793	3.83897	8.52452
H	13.28346	3.23311	9.30623
B	12.71506	8.08114	5.08665
B	8.64209	4.85688	5.13679

ScMe CO2 insertion adduct

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C	3.79911	2.85121	0.46051
C	2.74039	3.28694	-0.32609
N	1.64749	2.55761	-0.03285
N	1.96712	1.62936	0.89958
C	3.25789	1.81162	1.21501
B	0.22632	2.49896	-0.73757
C	0.27142	1.07239	-1.54226
N	0.11756	-0.08967	-0.85311
C	0.19295	-1.29786	-1.47208
C	0.53849	-1.35852	-2.82771
C	0.77468	-0.19082	-3.54017

C	0.61827	1.03002	-2.89817
Sc	0.57586	-0.03888	1.49999
N	1.85245	-1.82839	1.00337
N	1.47382	-2.78205	0.12009
C	2.51749	-3.59449	-0.13065
C	3.60201	-3.18695	0.63577
C	3.12879	-2.07642	1.33266
B	0.05754	-2.67073	-0.58787
C	-0.31879	-4.01531	-1.41377
C	-1.15390	-3.97751	-2.54396
C	-1.58868	-5.13413	-3.18933
C	-1.21565	-6.40160	-2.73234
C	-0.41887	-6.46157	-1.58456
C	0.00684	-5.30054	-0.94187
C	-1.64812	-7.65182	-3.45095
C	1.08209	0.01223	3.66172
N	-0.99695	-1.59119	1.50873
N	-1.03567	-2.54279	0.54755
C	-2.10771	-3.33508	0.75702
C	-2.78302	-2.89284	1.88471
C	-2.04027	-1.79719	2.32269
N	-0.89045	1.61098	1.41475
N	-0.87280	2.50441	0.39920
C	-1.89951	3.36618	0.55476
C	-2.60171	3.02985	1.70263
C	-1.92261	1.92249	2.20903
C	-0.06152	3.81895	-1.63550
C	0.34053	5.10350	-1.22403
C	-0.00500	6.25486	-1.92881
C	-0.79351	6.18706	-3.08208

C	-1.24195	4.92420	-3.47970
C	-0.88727	3.77651	-2.77203
C	-1.13919	7.42430	-3.86705
H	-2.06067	4.16277	-0.15398
H	0.79208	1.95688	-3.43322
H	-2.19570	-1.15899	3.18155
H	0.64847	-2.32483	-3.30704
H	0.91650	5.21911	-0.30886
H	1.07534	-0.23161	-4.58477
H	3.63174	-1.45237	2.05845
H	-1.49519	-3.01844	-2.92508
H	2.42716	-4.40484	-0.83719
H	-2.23539	-5.04925	-4.06065
H	-0.13708	-7.43172	-1.17941
H	0.58474	-5.40719	-0.02686
H	2.69992	4.06319	-1.07432
H	-1.28562	2.82279	-3.10840
H	4.58270	-3.63591	0.68050
H	3.72241	1.19545	1.97246
H	-2.31690	-4.16198	0.09752
H	-3.47254	3.52172	2.10877
H	0.33408	7.22466	-1.56921
H	-3.67767	-3.30982	2.32168
H	-1.88480	4.83622	-4.35355
H	4.80689	3.23756	0.48125
H	-1.75700	-8.49436	-2.76117
H	-0.91161	-7.94639	-4.20906
H	-2.60315	-7.50883	-3.96555
H	-1.22387	8.30131	-3.21791
H	-2.08510	7.30712	-4.40437

H	-0.36657	7.64719	-4.61360
O	-2.17353	0.18676	5.58435
C	-1.41579	0.22376	6.47463
O	-0.67736	0.26182	7.37589
H	-2.11501	1.34574	3.10309
H	0.63710	-0.83608	4.20422
H	2.16561	-0.04112	3.85446
H	0.73482	0.94059	4.14060

ScMe CO2 insertion **TS**$_{\mathbf{2\text{-}Me}}$

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C	7.84234	6.08898	5.92649
C	6.92036	6.42542	4.94255
N	5.81403	5.67896	5.10438
N	5.99455	4.82982	6.14527
C	7.21161	5.08732	6.65828
B	4.53402	5.56474	4.18212
C	4.68906	4.14363	3.38611
N	4.46357	2.98056	4.05872
C	4.45784	1.78700	3.40893
C	4.78497	1.73518	2.04748
C	5.14664	2.89075	1.37131
C	5.08685	4.10212	2.04578
Sc	4.73496	3.00936	6.46959
N	6.19128	1.42385	5.66258
N	5.80052	0.37097	4.90423
C	6.88836	-0.31922	4.50337
C	8.02020	0.27688	5.03646
C	7.52600	1.36651	5.75489
B	4.35430	0.39711	4.26708

C	4.01984	-0.94763	3.42762
C	3.13684	-0.93419	2.33419
C	2.74404	-2.10102	1.67988
C	3.21147	-3.35295	2.09079
C	4.06055	-3.38981	3.20176
C	4.44338	-2.21963	3.85449
C	2.82411	-4.61163	1.36119
C	5.95441	2.40094	8.38994
N	3.31854	1.33864	6.44734
N	3.28717	0.43961	5.43682
C	2.25881	-0.40840	5.63982
C	1.60484	-0.05852	6.81300
C	2.31334	1.04267	7.28562
N	3.08572	4.48928	6.00686
N	3.25769	5.47204	5.09446
C	2.11839	6.18808	4.98644
C	1.17421	5.65830	5.85074
C	1.83236	4.59544	6.46798
C	4.34314	6.90711	3.28548
C	4.63339	8.18068	3.81027
C	4.36015	9.35699	3.11494
C	3.75879	9.32731	1.85305
C	3.41771	8.07428	1.33531
C	3.69773	6.90209	2.03599
C	3.49414	10.59256	1.08154
H	2.05524	7.02103	4.30468
H	5.35257	5.02523	1.54336
H	2.16499	1.63250	8.17937
H	4.80907	0.77637	1.54286
H	5.06298	8.26637	4.80543

H	5.46469	2.84866	0.33201
H	8.06559	2.10507	6.32911
H	2.72577	0.01201	1.99037
H	6.78881	-1.17597	3.85551
H	2.05747	-2.03722	0.83778
H	4.41838	-4.34978	3.56939
H	5.06824	-2.30879	4.74034
H	6.98235	7.14890	4.14428
H	3.37624	5.95948	1.60170
H	9.04735	-0.03468	4.92158
H	7.55049	4.54801	7.53064
H	2.06167	-1.20875	4.94489
H	0.16201	5.99780	6.01035
H	4.60722	10.31558	3.56747
H	0.74640	-0.54027	7.25591
H	2.91624	8.01294	0.37120
H	8.81946	6.51845	6.08799
H	2.76478	-5.46763	2.04050
H	3.56104	-4.86233	0.58791
H	1.85539	-4.50510	0.86384
H	3.33597	11.44435	1.74998
H	2.61217	10.49526	0.44107
H	4.34135	10.84319	0.43087
O	3.54951	3.74648	8.56776
C	4.52235	4.16979	9.11614
O	5.20748	4.82979	9.79783
H	1.46880	3.91362	7.22134
H	5.69231	1.35607	8.15580
H	7.02928	2.50941	8.20683
H	5.84351	2.46216	9.47921

ScMe CO2 insertion product **4-Me**

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C	-0.99684	3.86270	-2.85454
C	-0.19517	3.92715	-1.70169
C	0.19194	5.22012	-1.30294
C	-0.14211	6.35810	-2.03473
C	-0.90424	6.26783	-3.20389
C	-1.33987	4.99663	-3.58927
B	0.07204	2.62392	-0.77448
N	-1.05919	2.63716	0.32168
N	-1.09699	1.74643	1.33924
C	-2.13616	2.06263	2.12452
C	-2.80036	3.17283	1.60334
C	-2.08283	3.50480	0.46338
Sc	0.34467	0.10699	1.46165
O	0.65079	0.17777	3.41143
C	0.01990	0.23280	4.56381
O	-1.20098	0.25686	4.66913
C	-1.23720	7.49004	-4.01730
N	1.47294	2.69620	-0.02458
C	2.56874	3.43517	-0.27865
C	3.60176	3.01228	0.54843
C	3.04303	1.96911	1.28465
N	1.76699	1.77323	0.92155
C	0.15570	1.18411	-1.55322
N	0.00672	0.02493	-0.85368
C	0.11311	-1.18910	-1.46160
C	0.48830	-1.25464	-2.80848
C	0.72211	-0.09094	-3.52729

C	0.53204	1.13231	-2.90025
B	-0.01631	-2.56195	-0.57581
N	-1.14270	-2.45622	0.52006
N	-1.14898	-1.48981	1.46694
C	-2.19044	-1.71715	2.27957
C	-2.88764	-2.84558	1.84843
C	-2.18773	-3.28270	0.73341
N	1.71043	-1.64209	1.05068
N	1.38418	-2.62299	0.17597
C	2.45493	-3.41383	-0.02286
C	3.50321	-2.96452	0.77040
C	2.98044	-1.85190	1.42707
C	-0.32937	-3.92106	-1.40355
C	-1.13693	-3.91545	-2.55428
C	-1.52018	-5.08846	-3.20261
C	-1.12111	-6.34139	-2.72784
C	-0.35363	-6.37027	-1.55914
C	0.02072	-5.19311	-0.91390
C	-1.49740	-7.60831	-3.44866
C	0.93210	0.26471	5.77036
H	-2.23009	4.30160	-0.24845
H	0.70282	2.05713	-3.43931
H	-2.34799	-1.07125	3.13397
H	0.62435	-2.22362	-3.27493
H	0.74439	5.35461	-0.37603
H	1.04681	-0.13669	-4.56439
H	3.44600	-1.19974	2.15314
H	-1.49882	-2.96983	-2.94981
H	2.40841	-4.23930	-0.71589
H	-2.14746	-5.02821	-4.09000

H	-0.05469	-7.32896	-1.13930
H	0.57529	-5.27768	0.01764
H	2.54931	4.20823	-1.03091
H	-1.38636	2.90240	-3.18250
H	4.49262	-3.38760	0.85618
H	3.48658	1.35804	2.05867
H	-2.36033	-4.12750	0.08582
H	-3.67277	3.67122	1.99811
H	0.18455	7.33518	-1.68355
H	-3.77013	-3.28837	2.28484
H	-1.96413	4.89129	-4.47457
H	4.60437	3.40832	0.60506
H	-1.59780	-8.44971	-2.75624
H	-0.73363	-7.88460	-4.18640
H	-2.44324	-7.49741	-3.98752
H	-1.32736	8.37987	-3.38670
H	-2.17693	7.36444	-4.56351
H	-0.45520	7.69607	-4.75892
H	-2.31523	1.48857	3.02468
H	1.56645	-0.62714	5.77726
H	1.59505	1.13339	5.70904
H	0.34701	0.30988	6.68901

ScMe eta2 coordination TS

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C	0.00668	-5.27661	-1.07004
C	-0.34880	-3.98999	-1.51583
C	-1.18438	-3.94905	-2.64559
C	-1.58955	-5.10203	-3.31621
C	-1.18524	-6.36927	-2.88613

C	-0.38936	-6.43383	-1.73801
B	-0.00546	-2.65576	-0.65996
N	1.40823	-2.74539	0.05466
N	1.75071	-1.78907	0.94837
C	3.02473	-2.01223	1.30249
C	3.53347	-3.10914	0.60896
C	2.47237	-3.53527	-0.18030
Sc	0.41992	-0.04488	1.45281
N	-1.08857	-1.63469	1.44532
N	-1.10552	-2.57197	0.46801
C	-2.15932	-3.39020	0.66689
C	-2.84220	-2.97992	1.80251
C	-2.12626	-1.87479	2.25989
C	-1.58503	-7.61430	-3.63207
N	-1.02504	1.60172	1.40565
N	-1.00794	2.51457	0.40574
C	-2.03527	3.37119	0.57995
C	-2.73497	3.01144	1.72258
C	-2.05691	1.89531	2.20993
B	0.09607	2.53141	-0.72124
C	0.15727	1.11337	-1.53949
N	0.02748	-0.06339	-0.86621
C	0.10959	-1.26026	-1.51065
C	0.44635	-1.29068	-2.86889
C	0.66534	-0.10885	-3.56224
C	0.49505	1.09732	-2.89767
C	-0.19377	3.85974	-1.60551
C	-1.02222	3.82906	-2.74065
C	-1.37833	4.98376	-3.43593
C	-0.92937	6.24263	-3.02630

C	-0.14011	6.29873	-1.87306
C	0.20692	5.14026	-1.18069
C	-1.27605	7.48767	-3.79832
N	1.51153	2.58277	-0.00615
C	2.60496	3.32619	-0.25781
C	3.64924	2.87747	0.54122
C	3.09925	1.81630	1.25851
N	1.81758	1.63406	0.90870
O	1.10771	-0.03696	3.33735
C	0.40548	-0.00737	4.44461
C	1.22805	-0.00784	5.71351
O	-0.82393	0.01852	4.46577
H	-2.19808	4.18106	-0.11333
H	0.65256	2.03593	-3.41646
H	-2.26751	-1.25390	3.13372
H	0.56483	-2.24718	-3.36490
H	0.78153	5.24766	-0.26379
H	0.96216	-0.12749	-4.60850
H	3.49798	-1.38125	2.04167
H	-1.55069	-2.99122	-3.00609
H	2.41218	-4.34345	-0.89243
H	-2.23776	-5.01461	-4.18612
H	-0.08490	-7.40508	-1.35239
H	0.58347	-5.38894	-0.15512
H	2.57533	4.12029	-0.98753
H	-1.42226	2.87918	-3.08590
H	4.52232	-3.53792	0.66971
H	3.54818	1.18427	2.01183
H	-2.35093	-4.21118	-0.00547
H	-3.60461	3.49605	2.13993

H	0.19819	7.26489	-1.50313
H	-3.72558	-3.42519	2.23451
H	-2.02301	4.90450	-4.30924
H	4.65376	3.26943	0.59305
H	-2.53633	-7.48010	-4.15575
H	-1.68608	-8.47100	-2.95869
H	-0.83379	-7.88129	-4.38592
H	-1.35935	8.35817	-3.14033
H	-2.22289	7.37611	-4.33516
H	-0.50457	7.71766	-4.54389
H	-2.22024	1.30084	3.09809
H	1.89842	0.85713	5.71836
H	0.58003	0.02065	6.58962
H	1.85598	-0.90363	5.74467

ScMe final product **4-Me**

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Sc	3.74187	10.40085	5.38870
O	4.52826	11.40401	3.59620
O	2.38159	10.99927	3.74740
N	5.53254	7.79818	5.41372
N	2.34808	12.03946	7.80241
N	3.04424	7.24165	5.44378
N	5.03545	11.92105	6.35335
N	4.02395	9.38202	7.53547
N	2.63327	8.45549	5.00821
N	4.87802	12.30372	7.63938
N	5.44654	9.05734	4.93136
N	2.18421	11.58303	6.53851
C	4.67241	4.60829	5.53490

H	4.15448	4.84957	4.60971
C	2.05912	6.34297	5.26011
H	2.18247	5.31892	5.57680
C	1.16793	12.48218	8.27451
H	1.08400	12.85716	9.28275
C	5.17543	3.31687	5.68356
H	5.00963	2.58413	4.89592
C	6.70248	7.25213	5.02339
H	6.95918	6.24332	5.30488
C	0.20744	12.34804	7.28055
H	-0.83469	12.62562	7.33041
C	5.90312	2.95110	6.82002
C	7.39850	8.17959	4.26247
H	8.36522	8.05661	3.79794
C	0.98242	6.97498	4.65210
H	0.04305	6.53429	4.35387
C	4.82668	12.82870	12.17576
H	5.44289	12.41234	12.97052
C	3.26776	8.11109	9.88934
H	2.92142	7.61498	10.79324
C	5.83532	13.19935	7.95673
H	5.87791	13.63155	8.94380
C	4.61389	12.08770	11.01461
H	5.09157	11.11466	10.93240
C	6.08986	12.58692	5.86283
H	6.37805	12.44778	4.83178
C	3.65582	7.37475	8.78016
H	3.62776	6.29140	8.80245
C	3.34291	9.49429	9.82386
H	3.06637	10.09994	10.67929

C	5.61500	5.22623	7.63056
H	5.84105	5.96266	8.39764
C	4.05313	8.02180	7.60423
C	6.12675	3.93881	7.78415
H	6.71660	3.69999	8.66723
C	3.82983	12.56555	9.94968
C	0.89793	11.78231	6.20983
H	0.55379	11.52020	5.22046
C	4.84649	5.60269	6.51477
C	3.31836	13.86655	10.10873
H	2.76793	14.33115	9.29419
C	6.56317	9.29518	4.22943
H	6.69021	10.24456	3.73128
C	1.39568	8.29911	4.51222
H	0.88626	9.14427	4.07397
C	3.52102	14.61167	11.26917
H	3.10043	15.61291	11.34286
C	6.63866	13.40922	6.84579
H	7.49087	14.06701	6.76519
C	6.41822	1.54819	7.00224
H	5.69300	0.92815	7.54407
H	7.34926	1.53366	7.57722
H	6.60599	1.06131	6.04043
C	3.74295	10.12708	8.64110
C	4.26933	14.10122	12.33435
C	3.36414	11.46283	3.08850
C	3.16053	12.03767	1.71612
H	3.92071	12.78989	1.49995
H	2.15858	12.45940	1.62255
H	3.26124	11.22922	0.98362

C	4.46048	14.88680	13.60440
H	3.66872	14.66292	14.33035
H	4.43336	15.96475	13.41796
H	5.41521	14.64917	14.08355
B	3.71344	11.75920	8.54588
B	4.38759	7.13990	6.26908