Supporting Information

Tebbe-like and Phosphonioalkylidene and -alkylidyne Complexes of Scandium.

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---------- *Table of Contents* ----------

NMR Spectra:

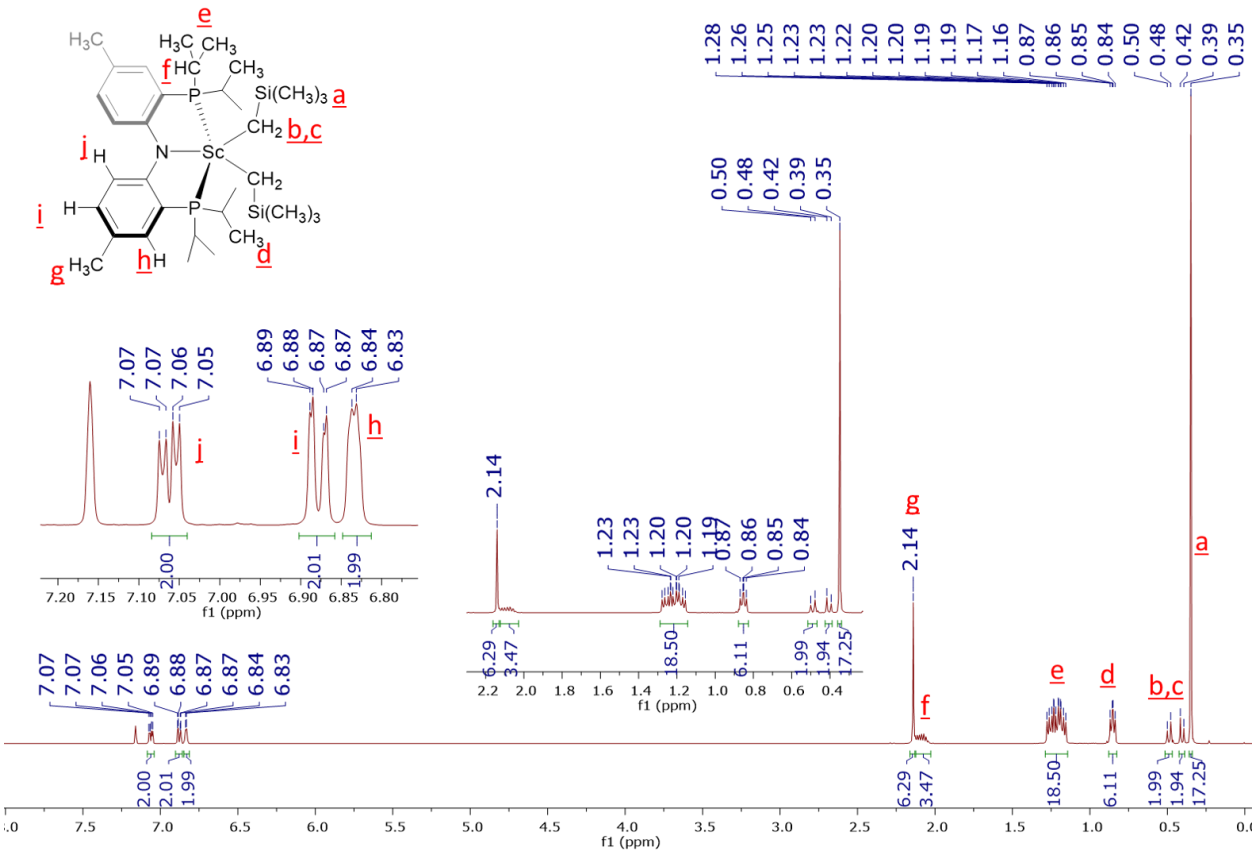


Figure S1. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

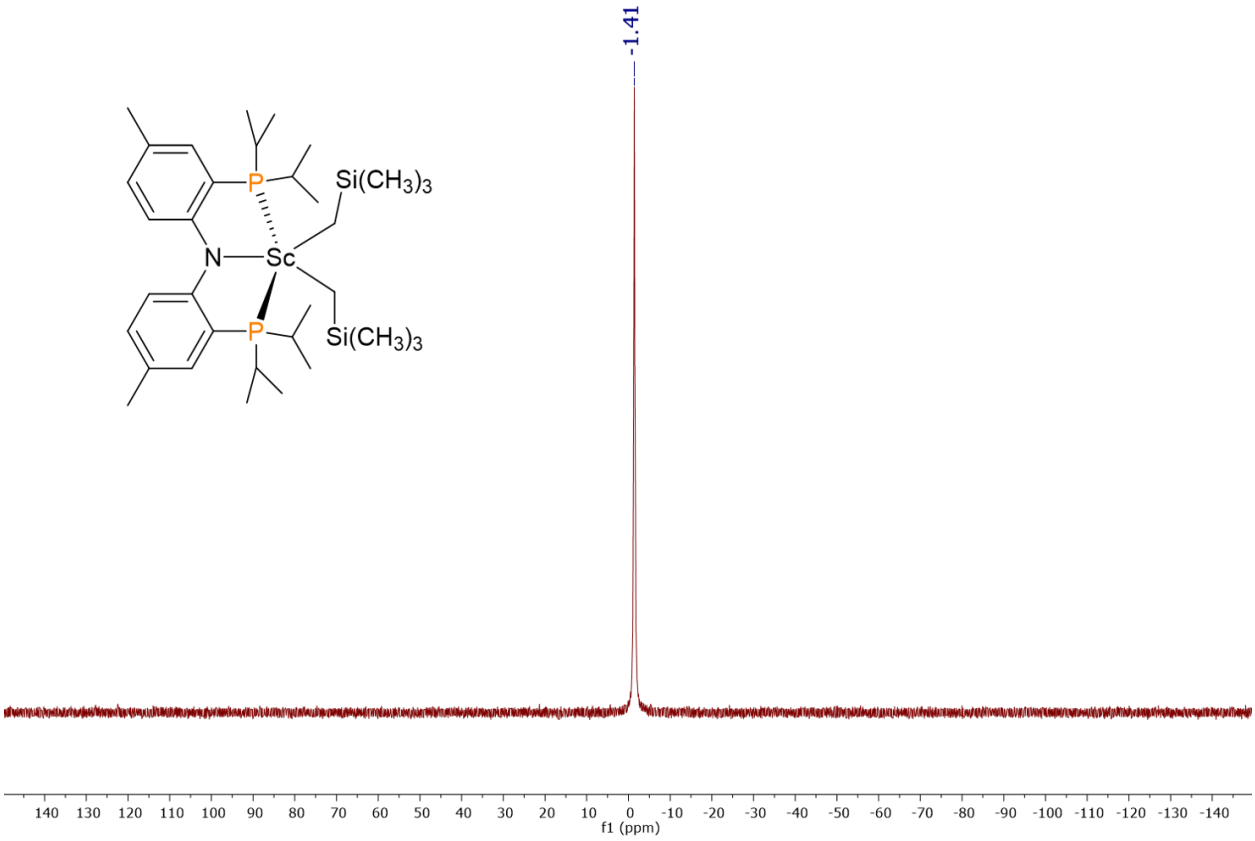


Figure S2. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

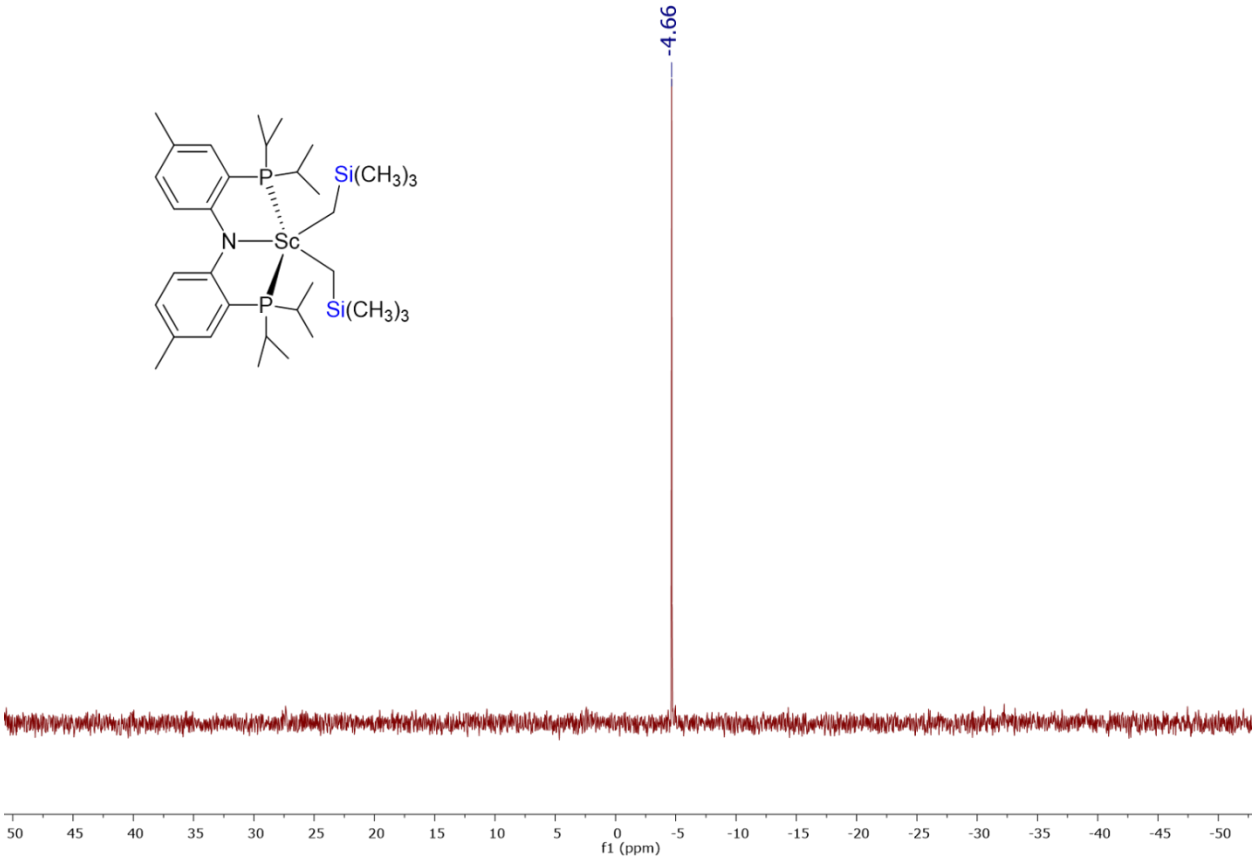


Figure S3. ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

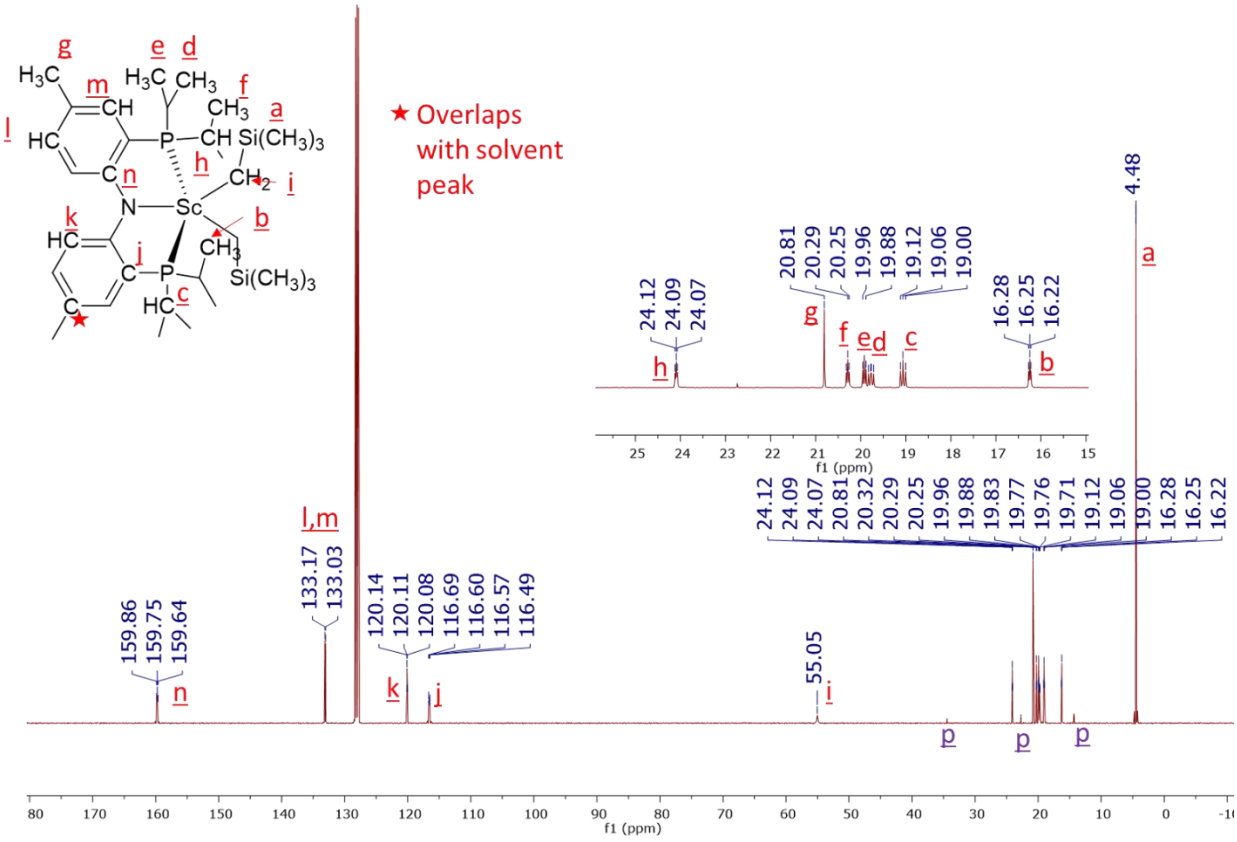


Figure S4. ^{13}C NMR (101 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**). Peaks labelled with p represent residual pentane.

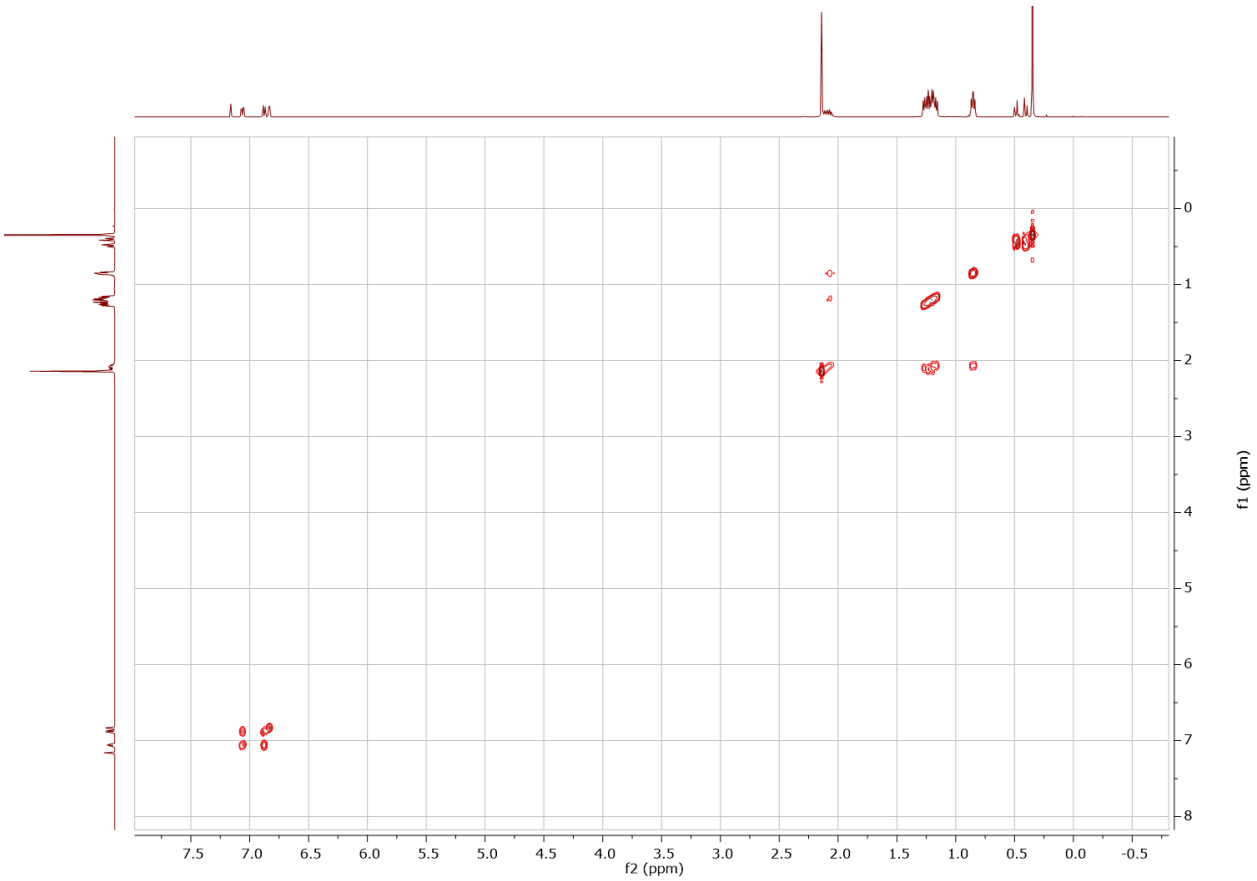


Figure S5. ^{1}H COSY NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

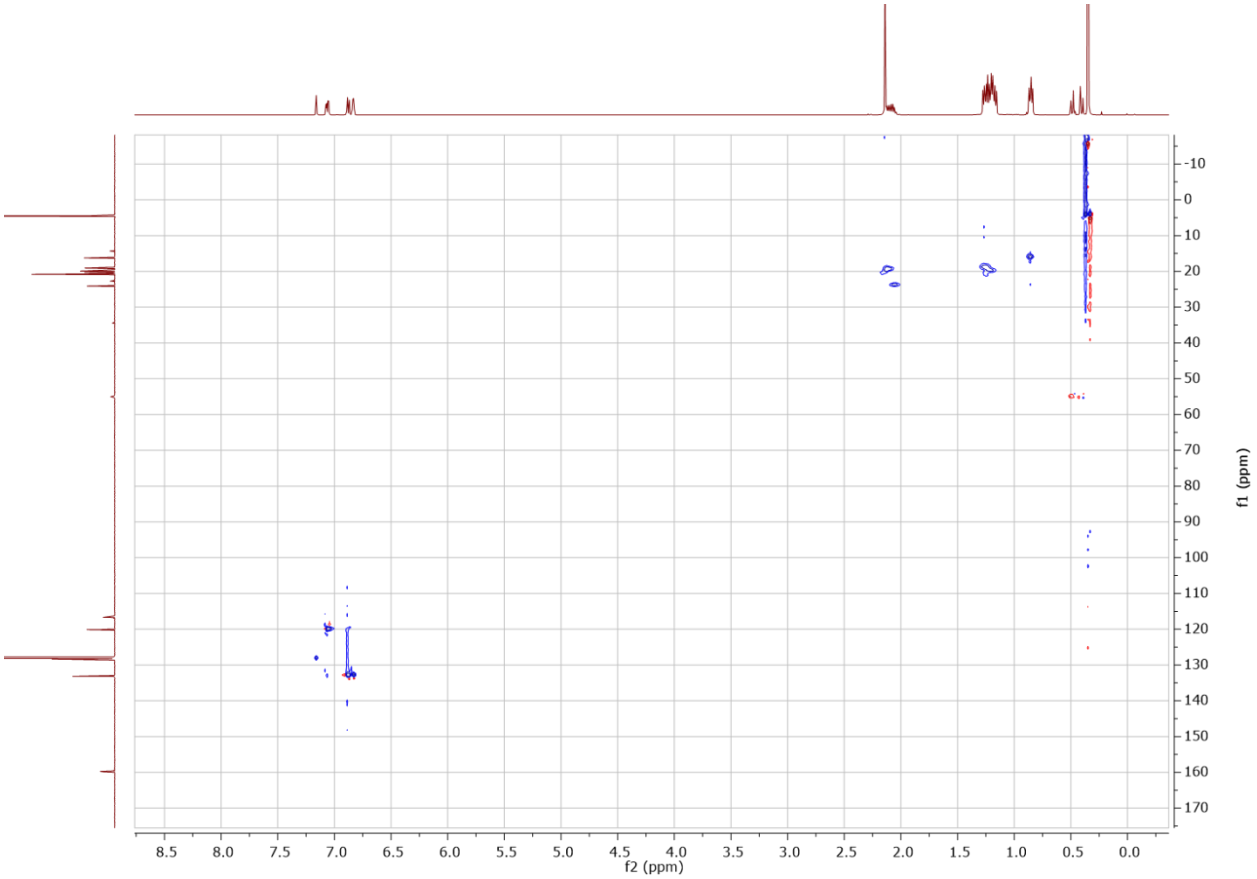


Figure S6. ^{1}H-^{13}C HSQC NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

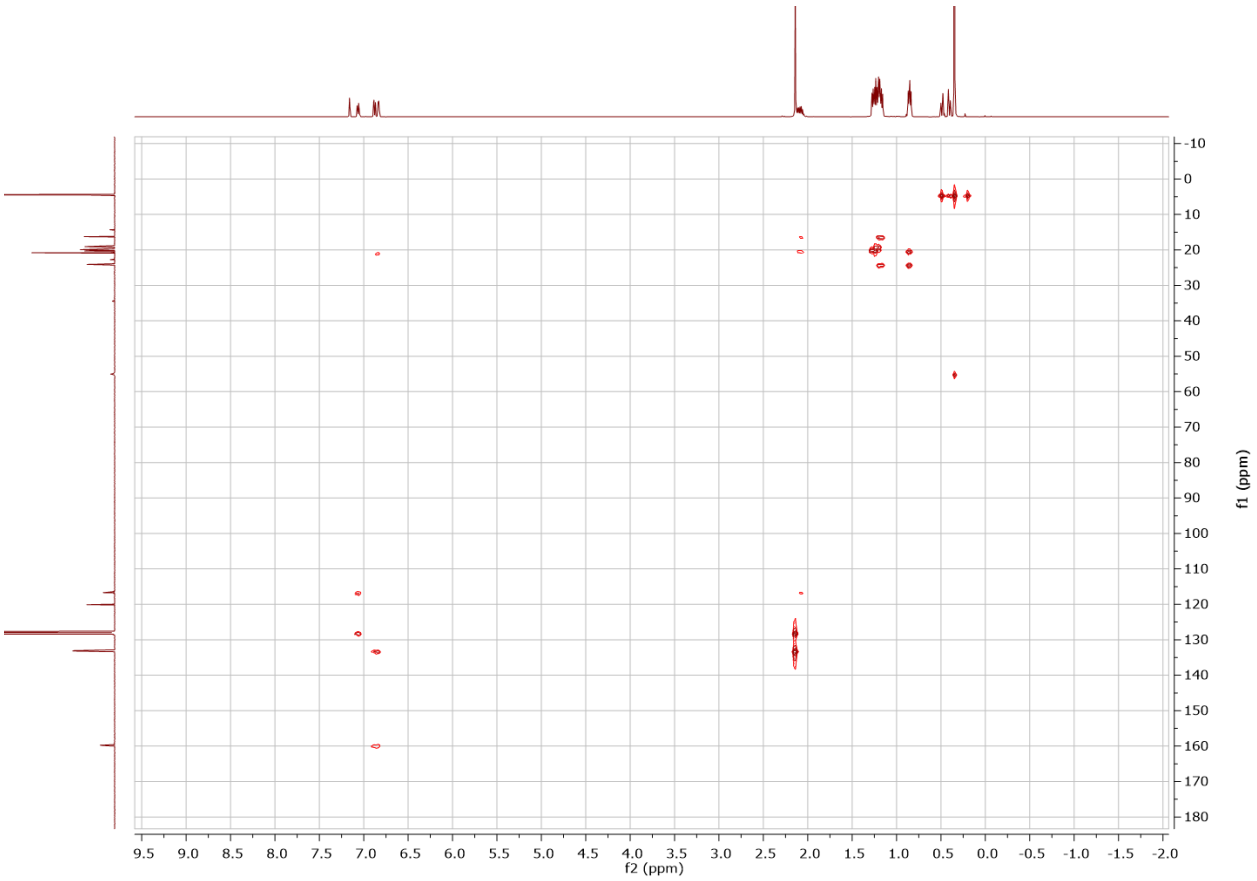


Figure S7. ^{1}H-^{13}C HSQC NMR (400 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_2SiMe_3)$_2$ (**1**).

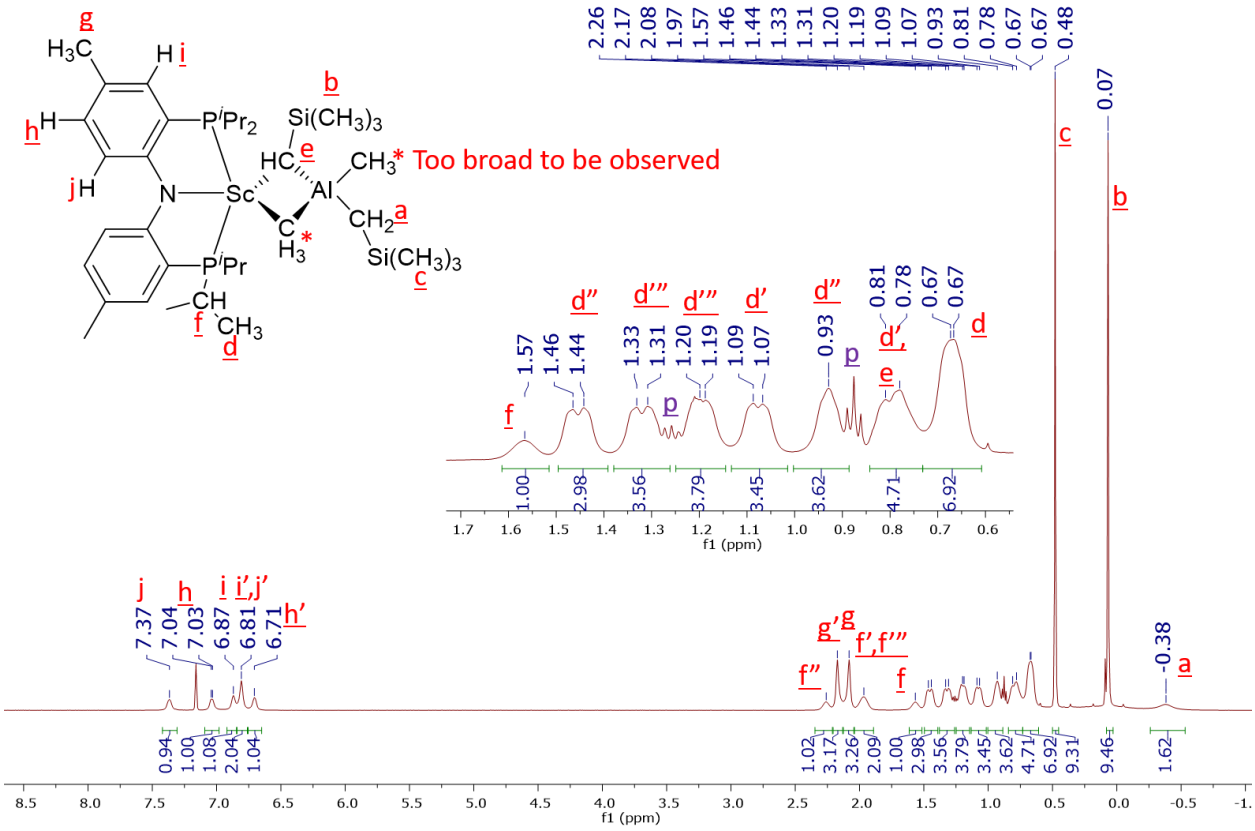


Figure S8. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**). Residual pentane is labelled with p.

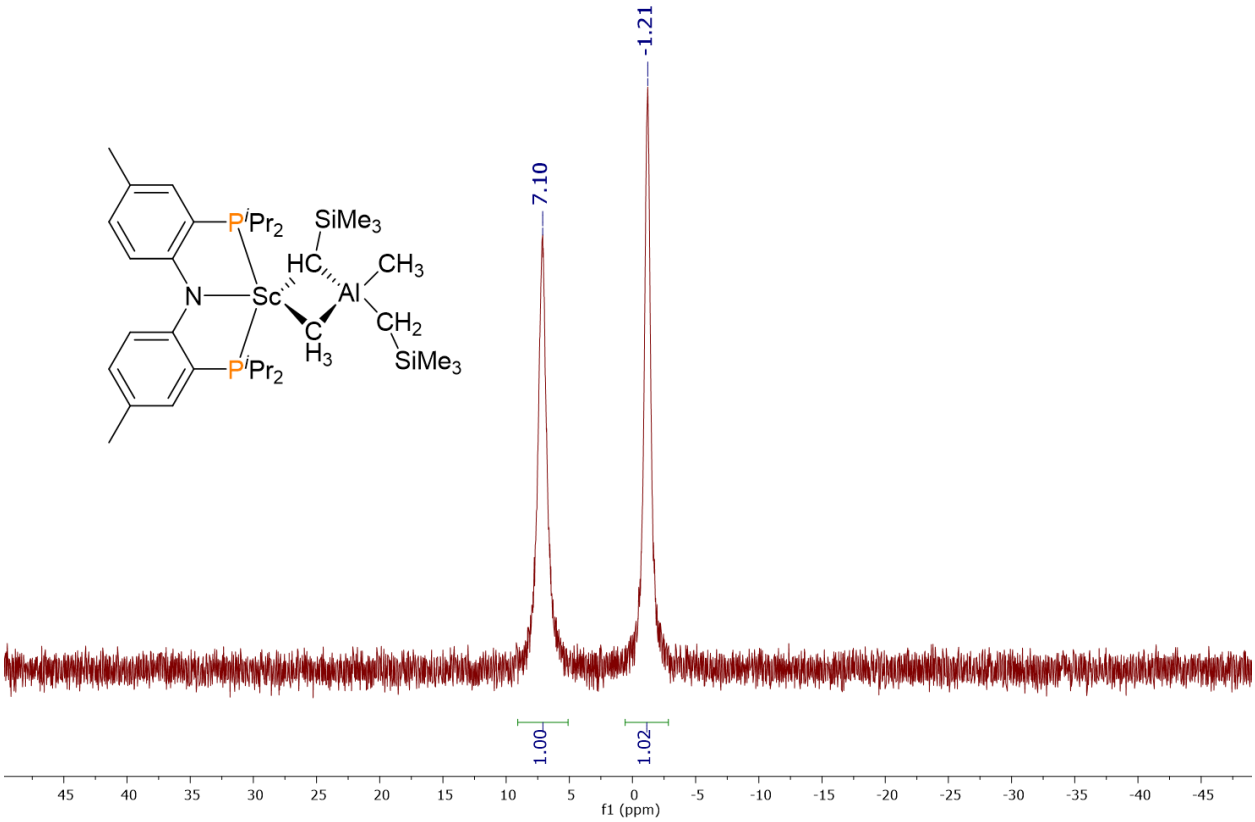


Figure S9. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

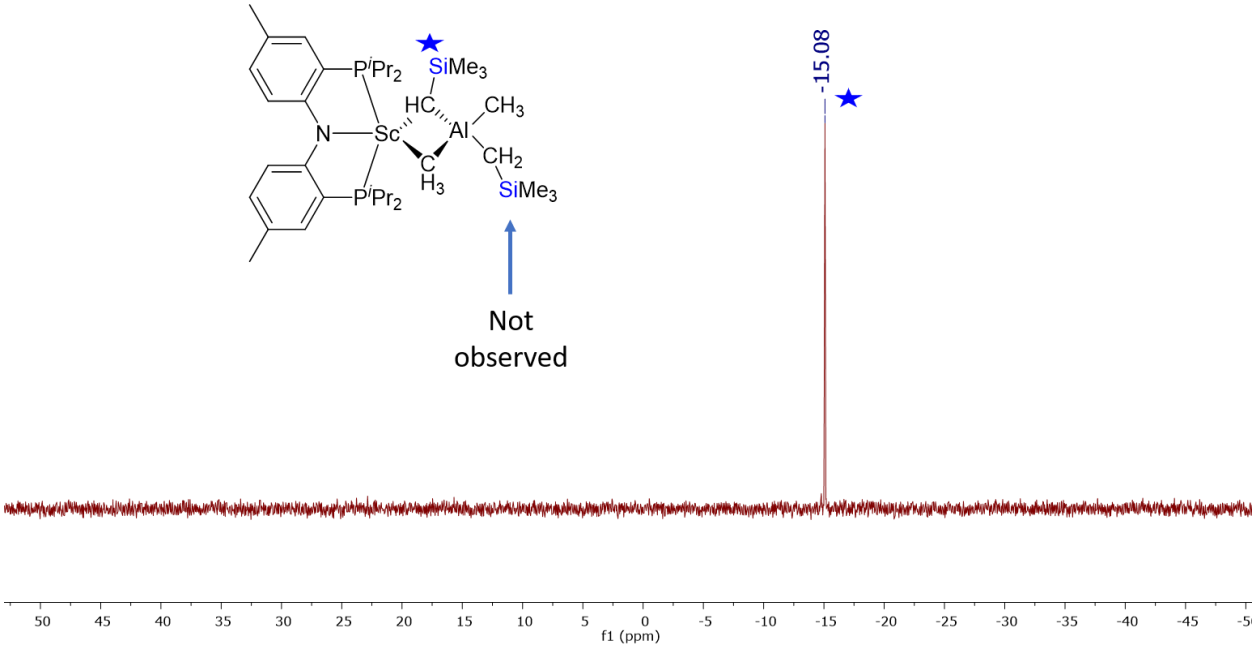


Figure S10. ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

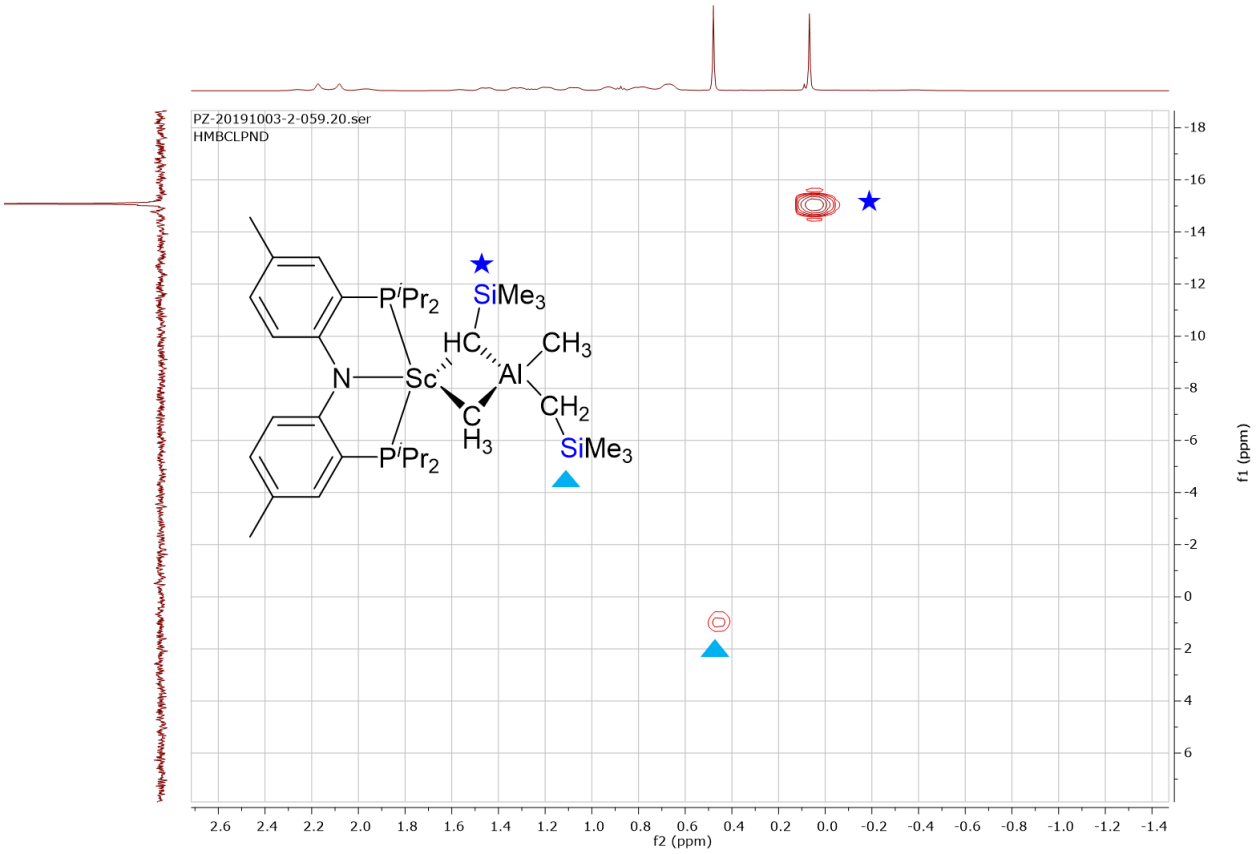


Figure S11. ^{1}H-^{29}Si HMBC NMR (400 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

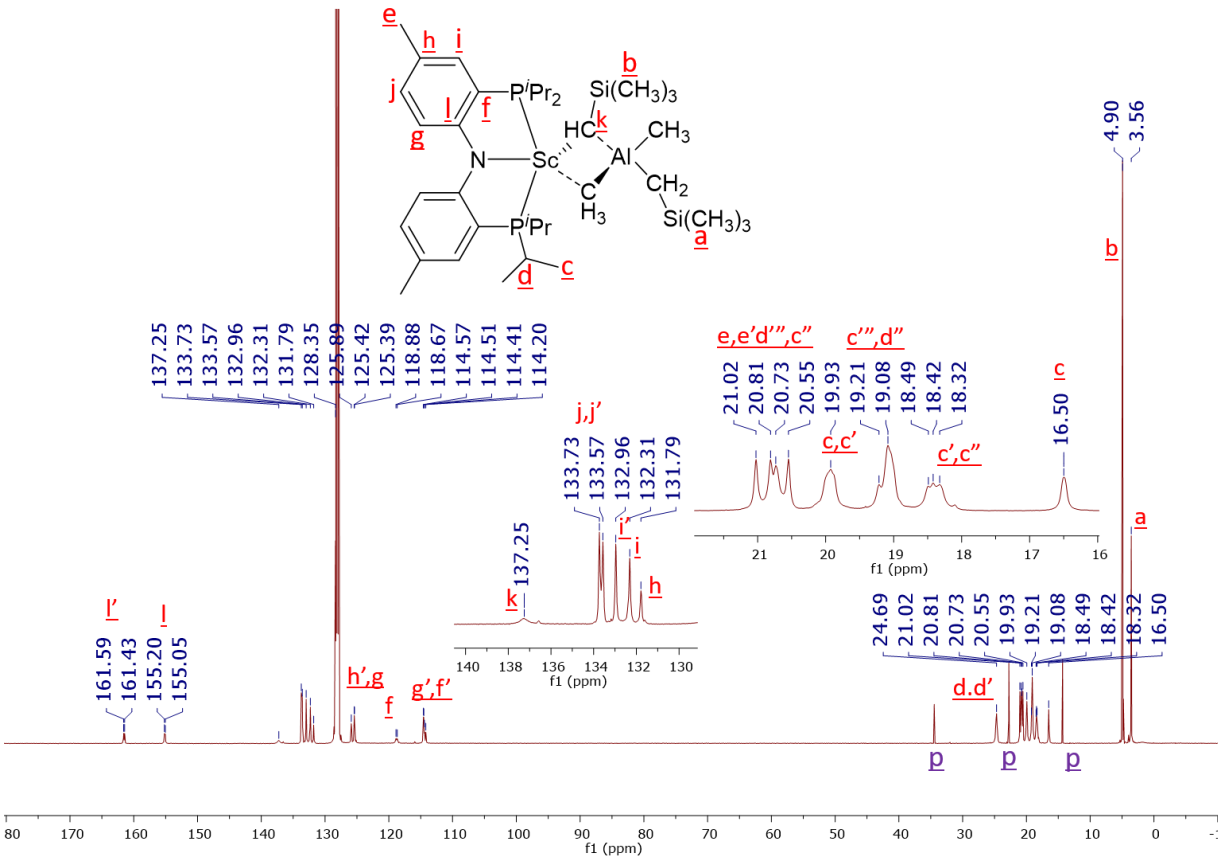


Figure S12. $^{13}C\{^{1}H\}$ NMR (126 MHz, benzene-d_6, 300 K; instrument used for collecting this spectrum is outfitted with a cryoprobe) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**). Residual pentane is labelled with p.

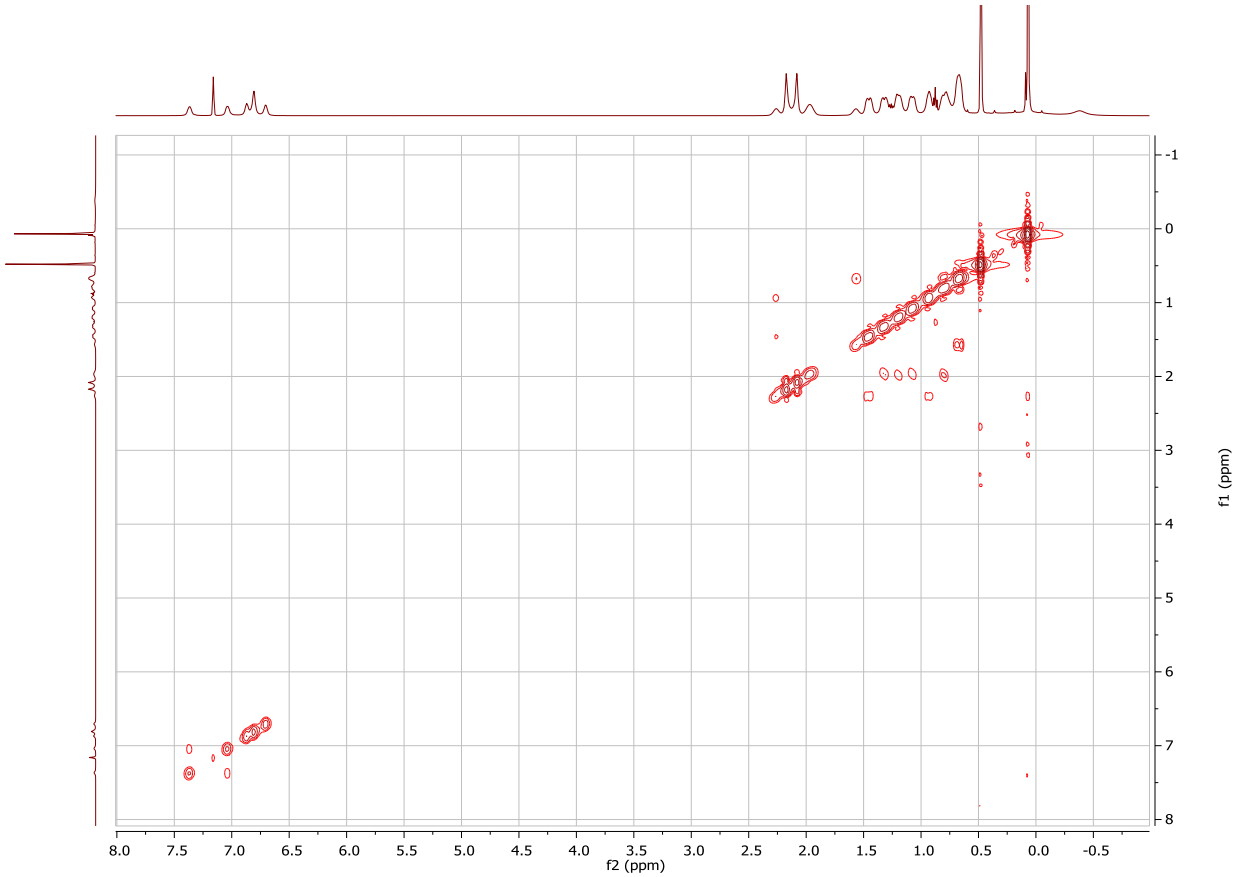


Figure S13. ^{1}H COSY NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

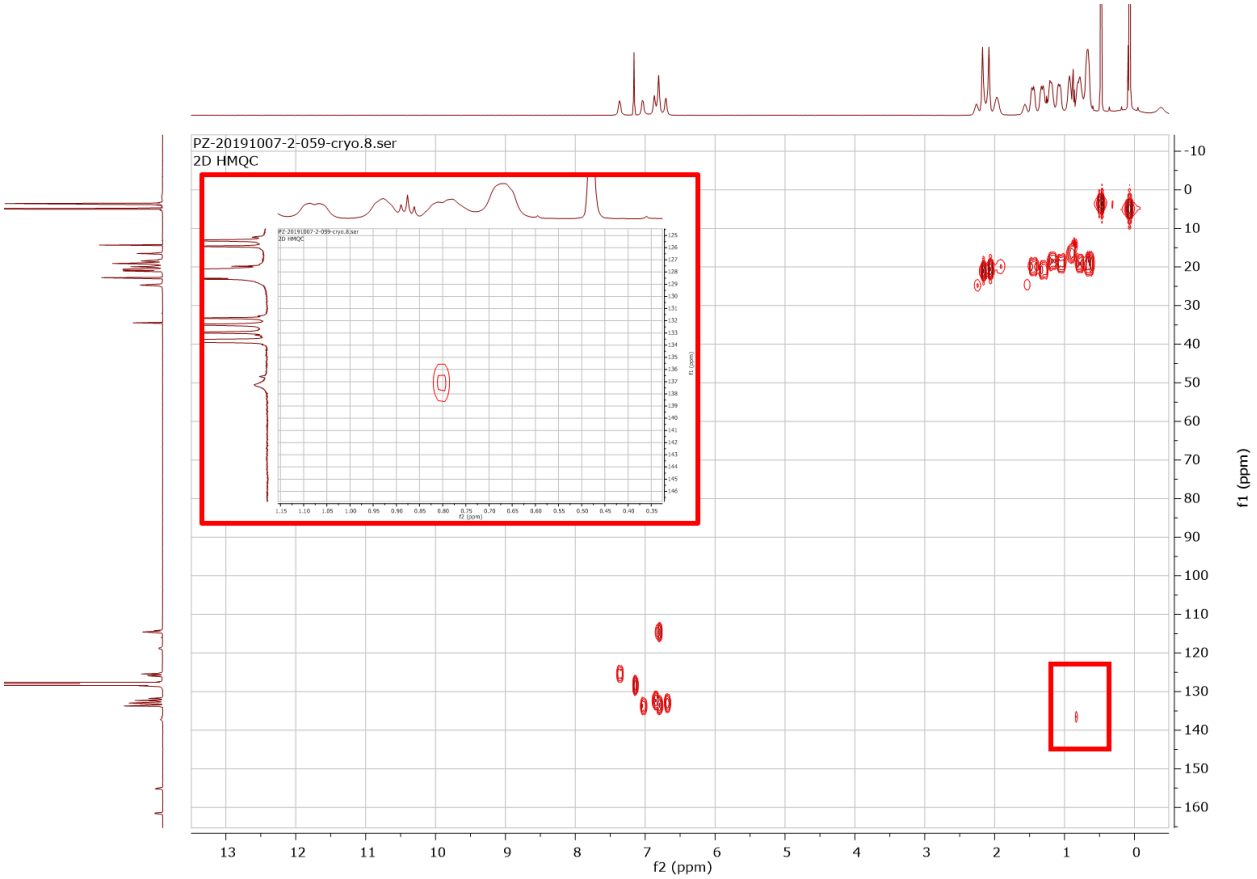


Figure S14. ^{1}H-^{13}C HMQC NMR (500 MHz, benzene-d_6, 300 K; instrument used for collecting this spectrum is outfitted with a cryoprobe) of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**). An inset of the same spectrum from 125 – 140 ppm in the f1 dimension and 0.35 – 1.15 ppm in the f2 dimension.

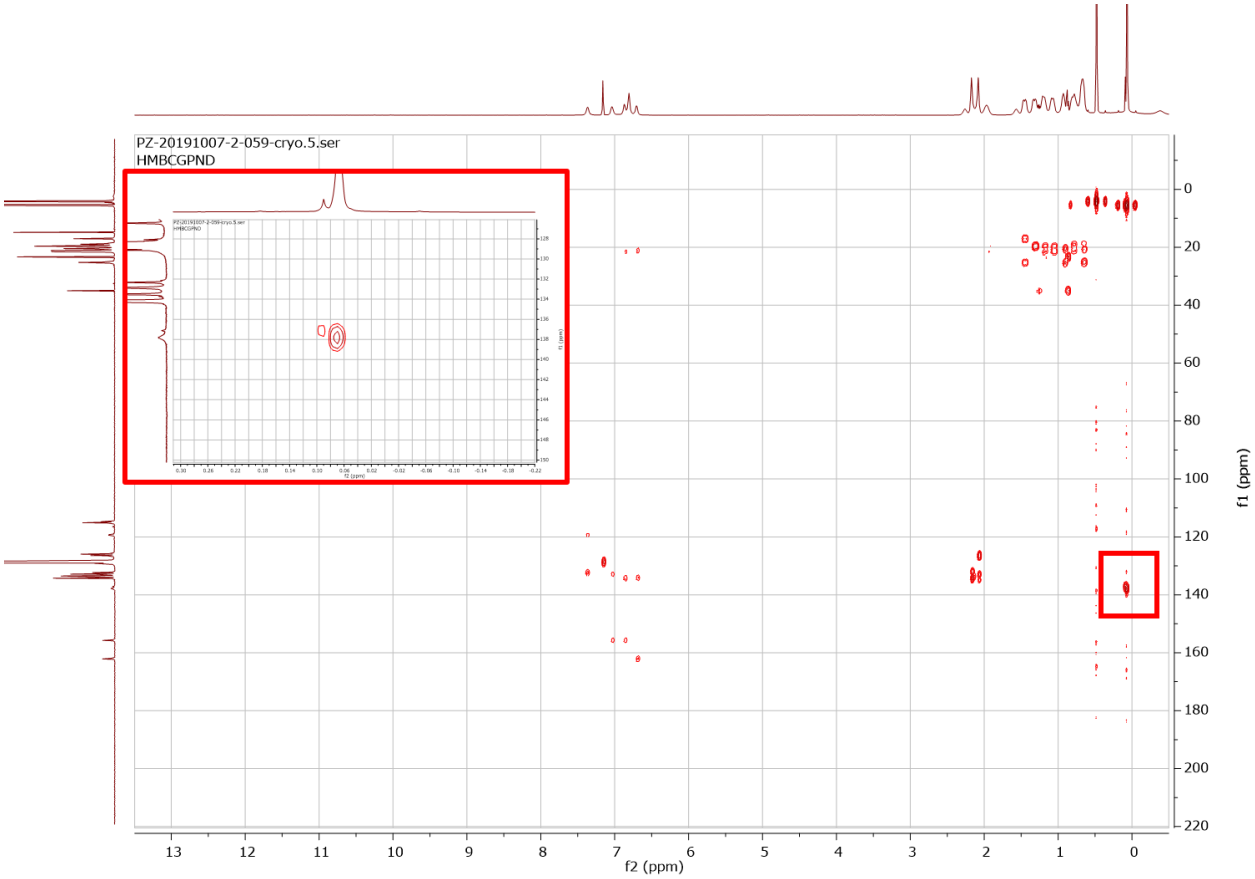


Figure S15. ^{1}H-^{13}C HMBC NMR (500 MHz, benzene-d_6, 300 K; instrument used for collecting this spectrum is outfitted with a cryoprobe) of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**). An inset of the same spectrum from 127 – 150 ppm in the f1 dimension and –0.22 – 1.15 ppm in the f2 dimension.

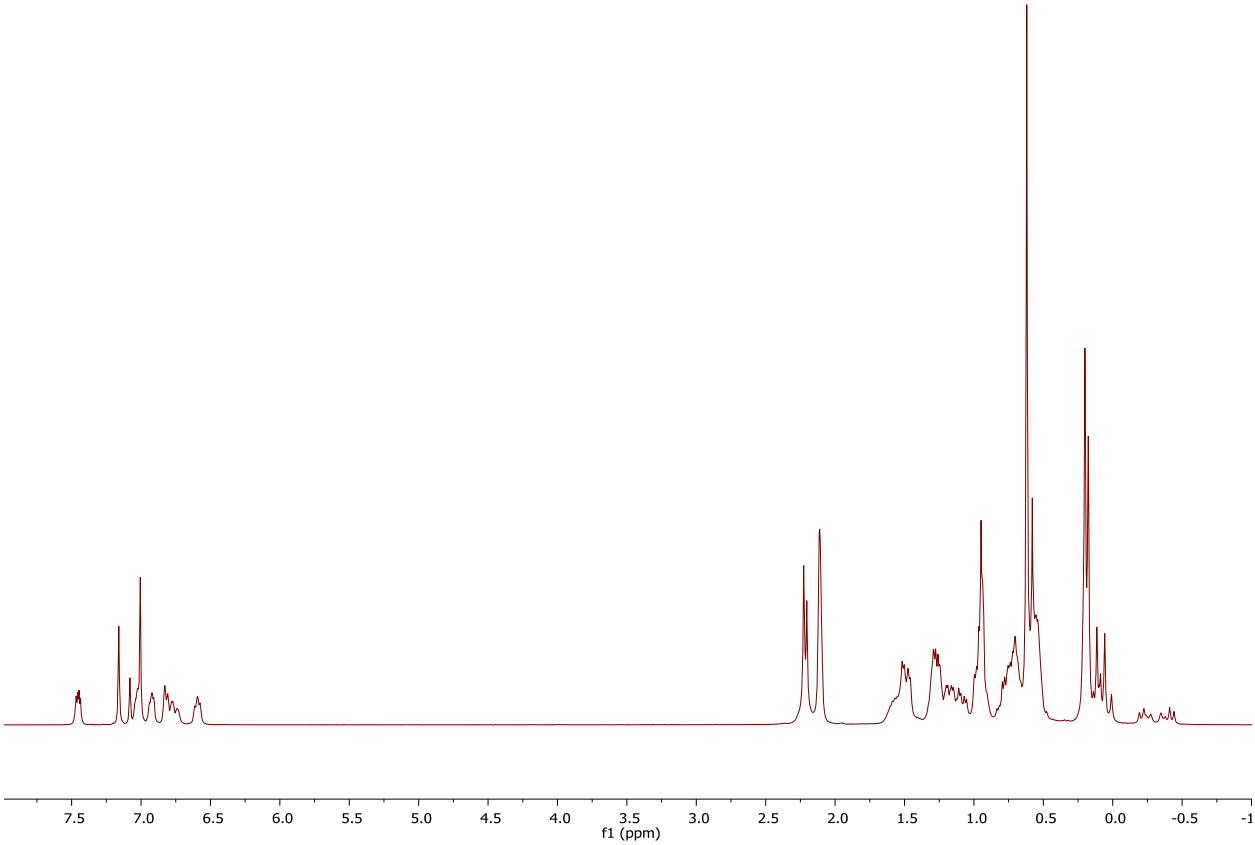


Figure S16. ^{1}H NMR (400 MHz, toluene-d_8, 199 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

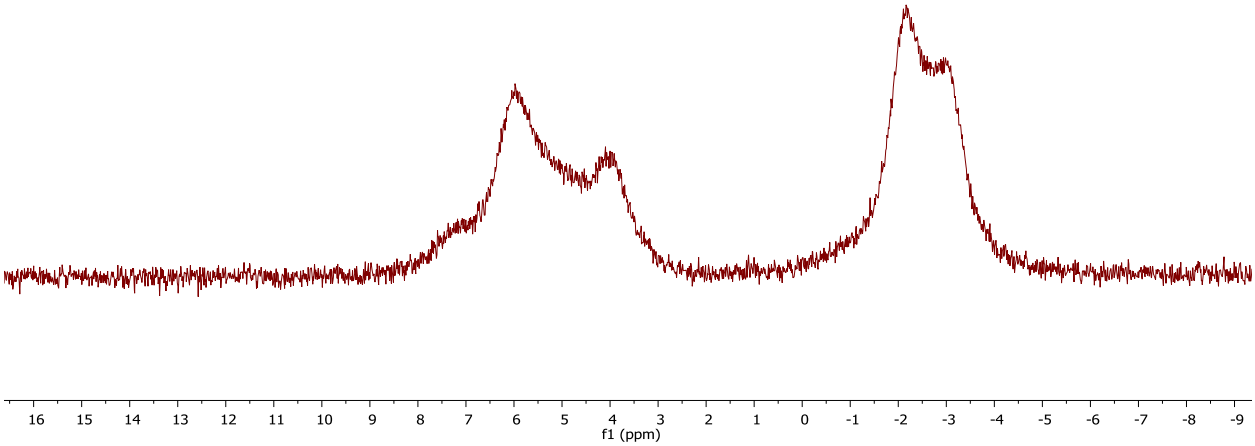


Figure S17. $^{31}P\{^{1}H\}$ NMR (162 MHz, toluene-d_8, 199 K) spectrum of (PNP)Sc(μ_2-$CHSiMe_3$)(μ_2-CH_3)[$Al(CH_3)(CH_2SiMe_3)$] (**2**).

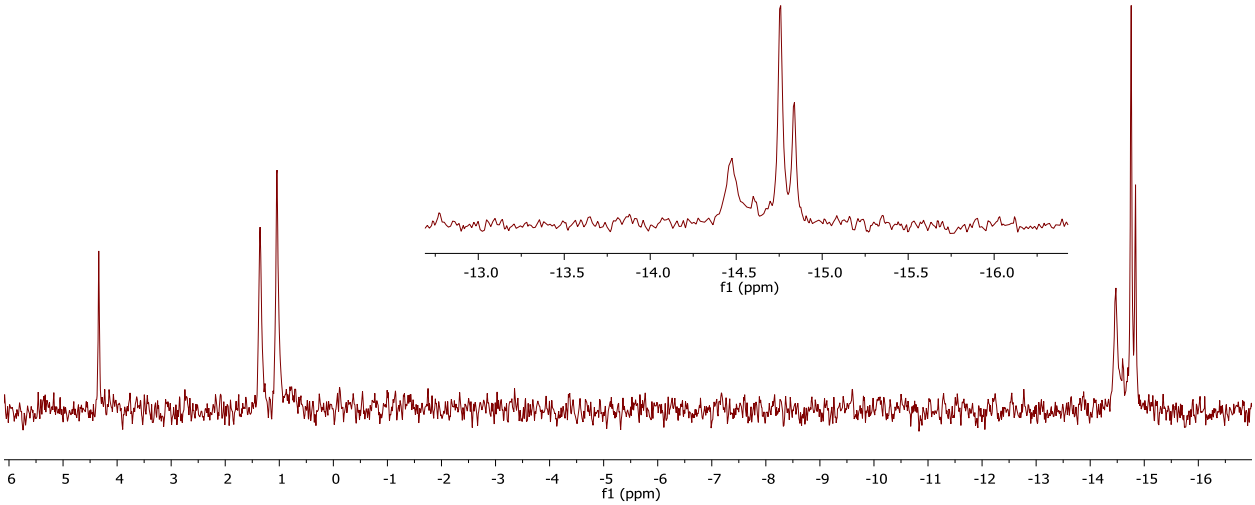


Figure S18. ^{29}Si INEPT NMR (79 MHz, toluene-d_8, 199 K) spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**).

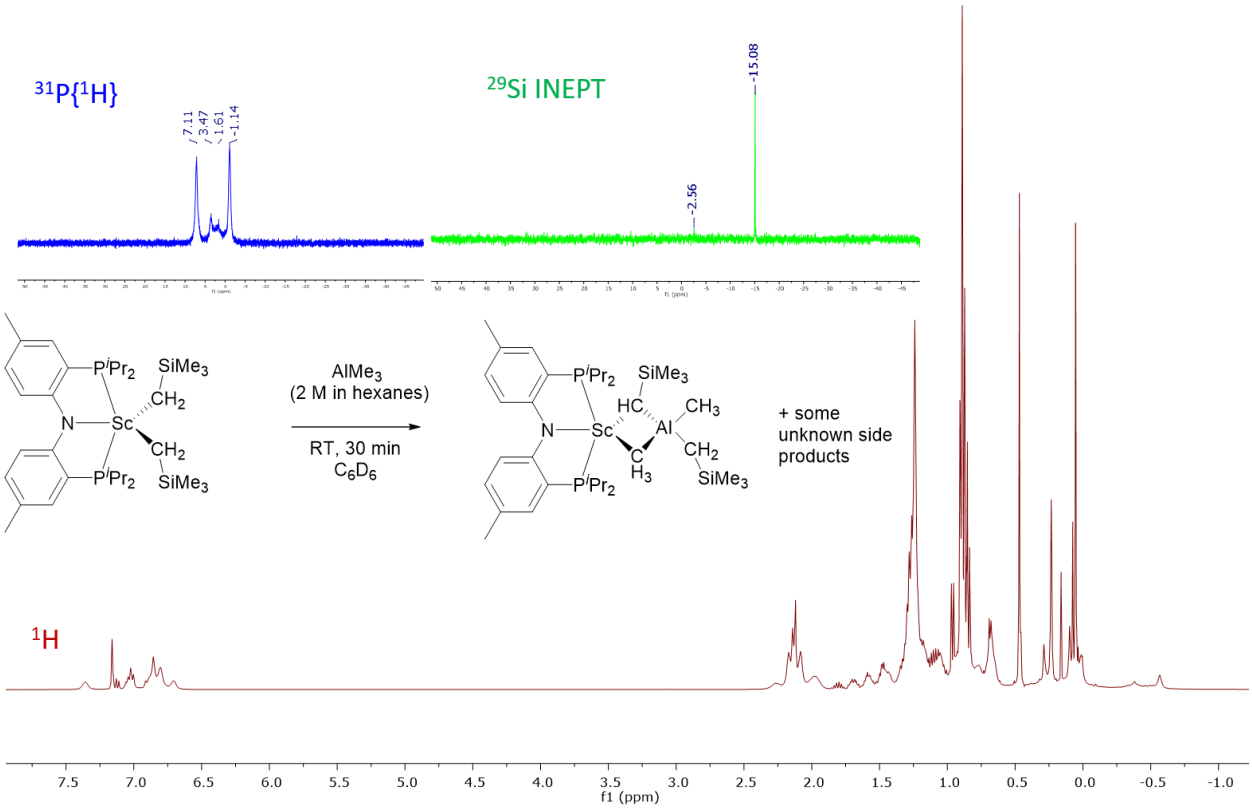


Figure S19. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K), ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectra of the reaction mixture produced following addition of about 1 equivalent of $AlMe_3$ to (PNP)Sc(CH_2SiMe_3)$_2$ after 30 minutes in benzene-d_6.

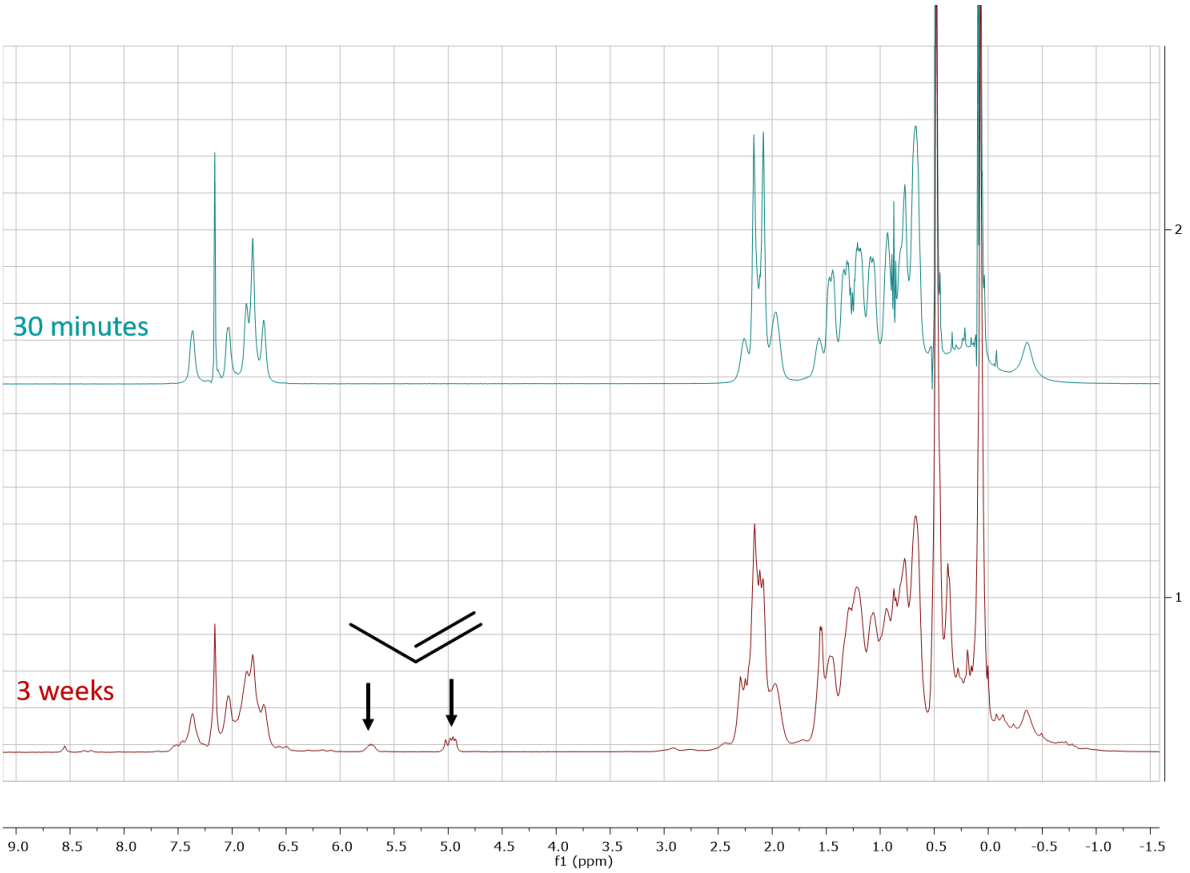


Figure S20. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), spectrum of (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**) after 30 minutes following dissolution in benzene-d_6 (top) and after 3 weeks at room temperature (bottom) displaying the formation of a significant quantity of propylene.

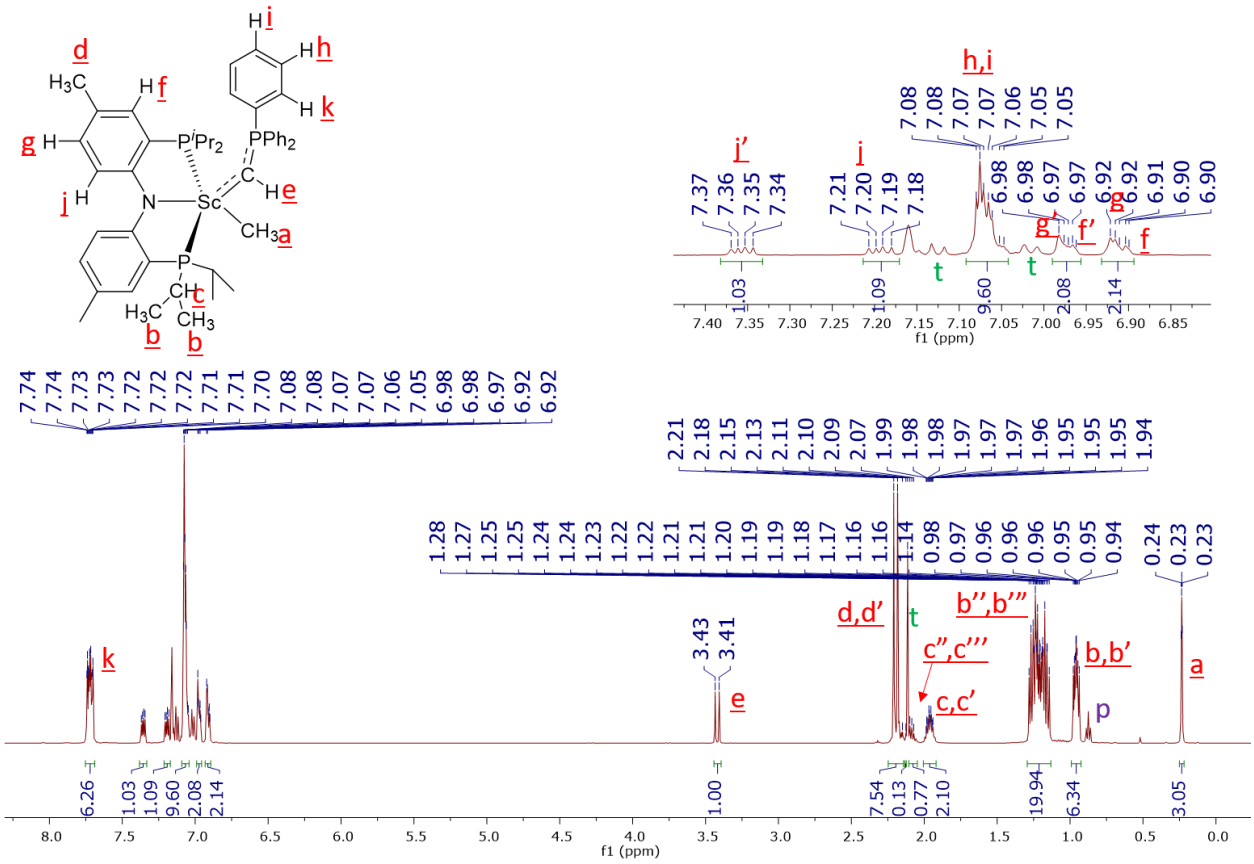


Figure S21. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**). Residual toluene and pentane are labelled with t and p, respectively.

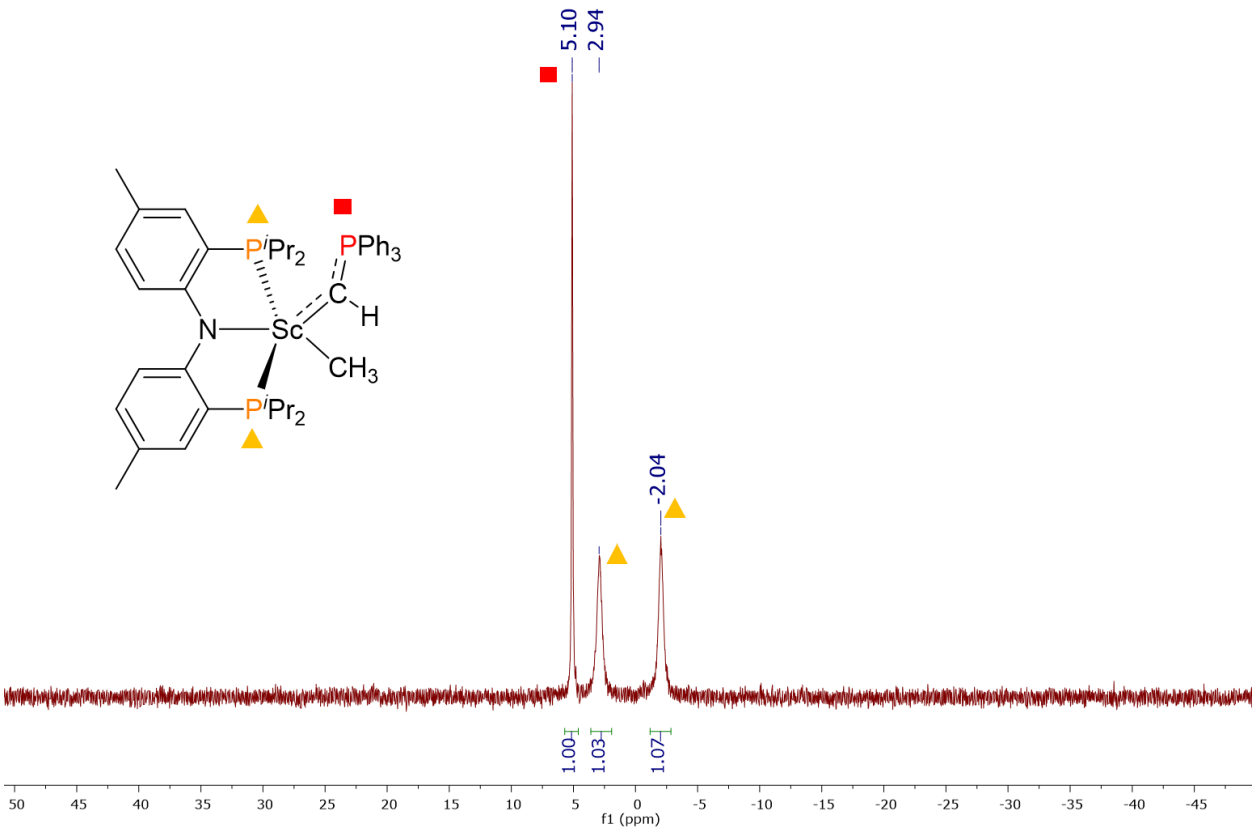


Figure S22. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**).

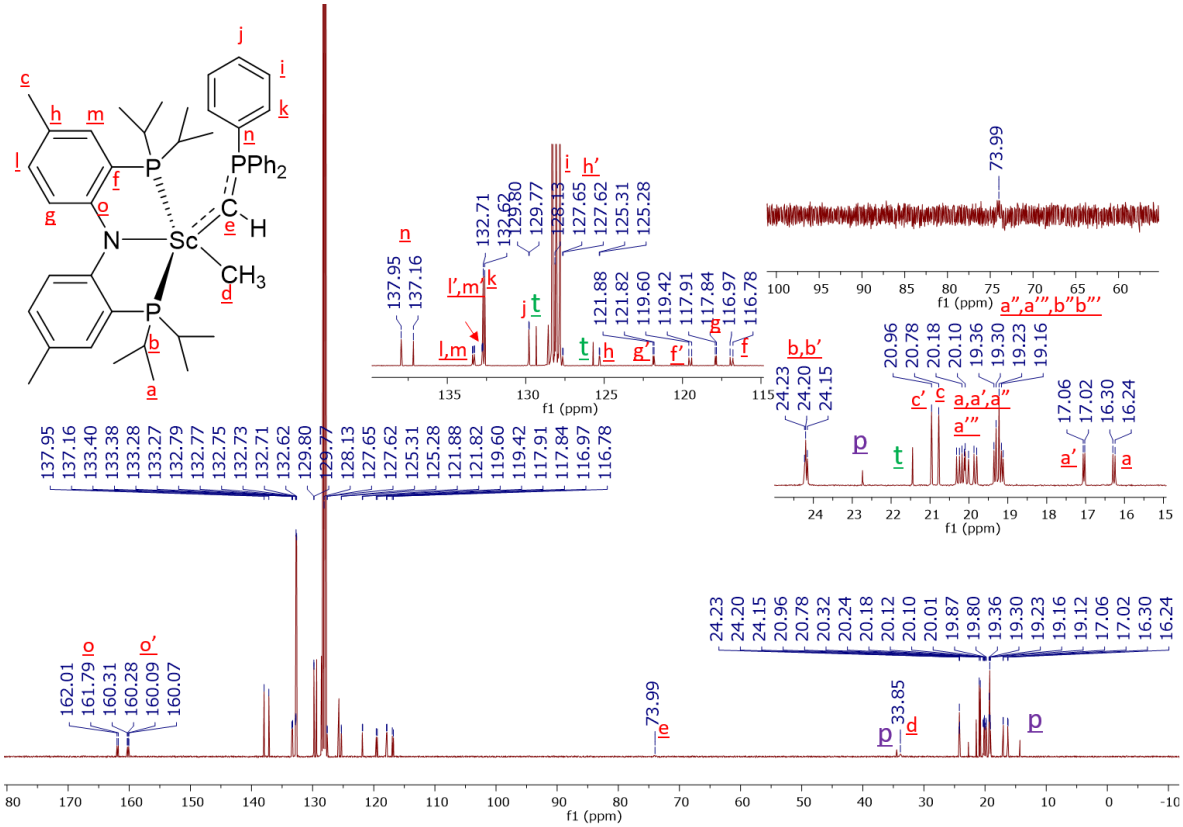


Figure S23. $^{13}C\{^{1}H\}$ NMR (101 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**). Residual toluene and pentane are labelled with t and p, respectively.

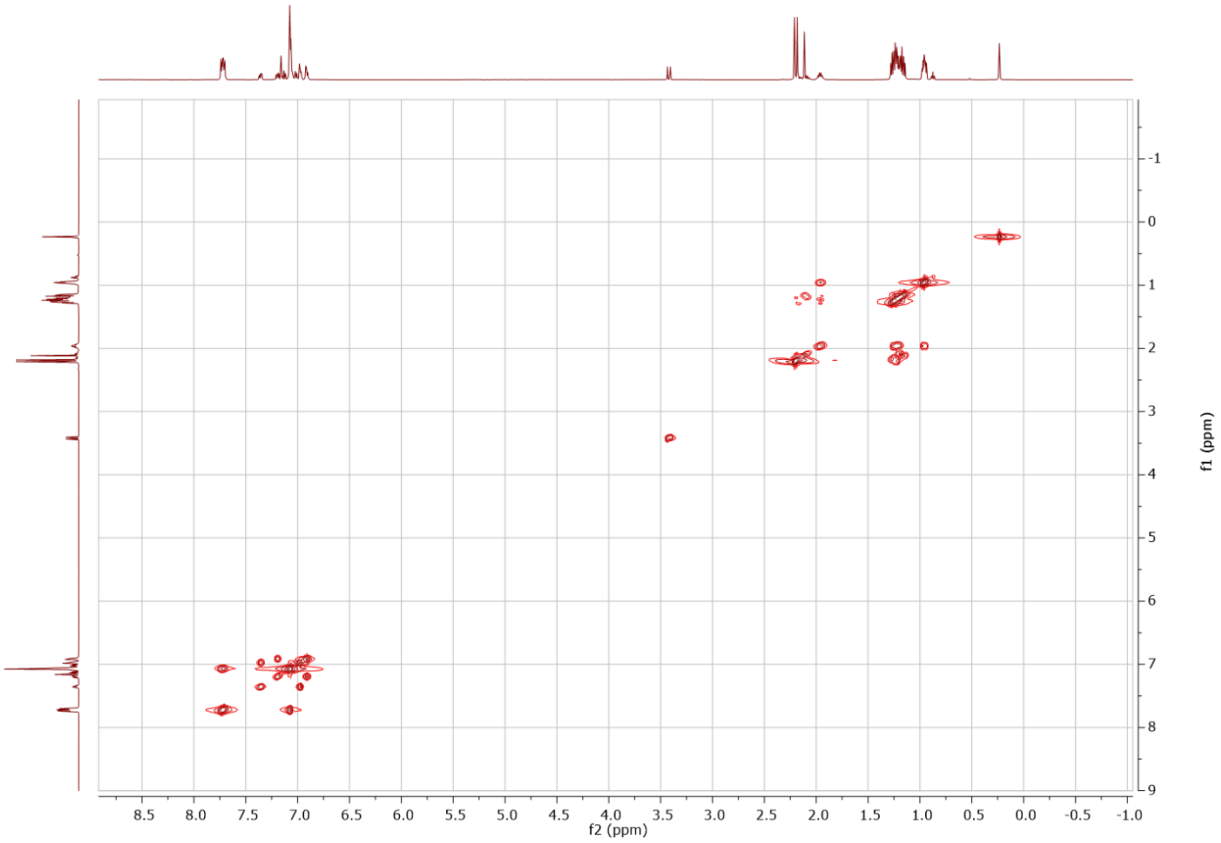


Figure S24. ^{1}H COSY NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**).

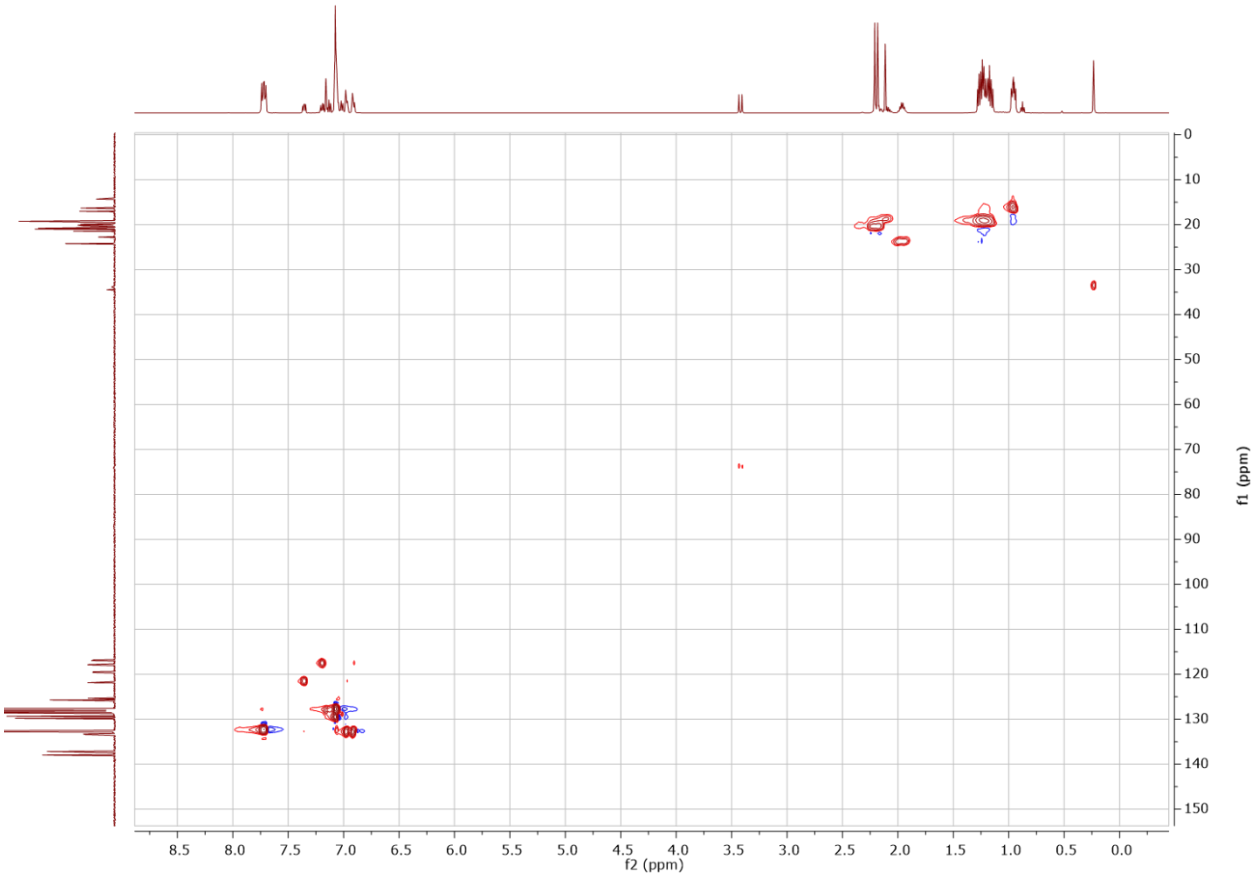


Figure S25. ^{1}H HSQC NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**).

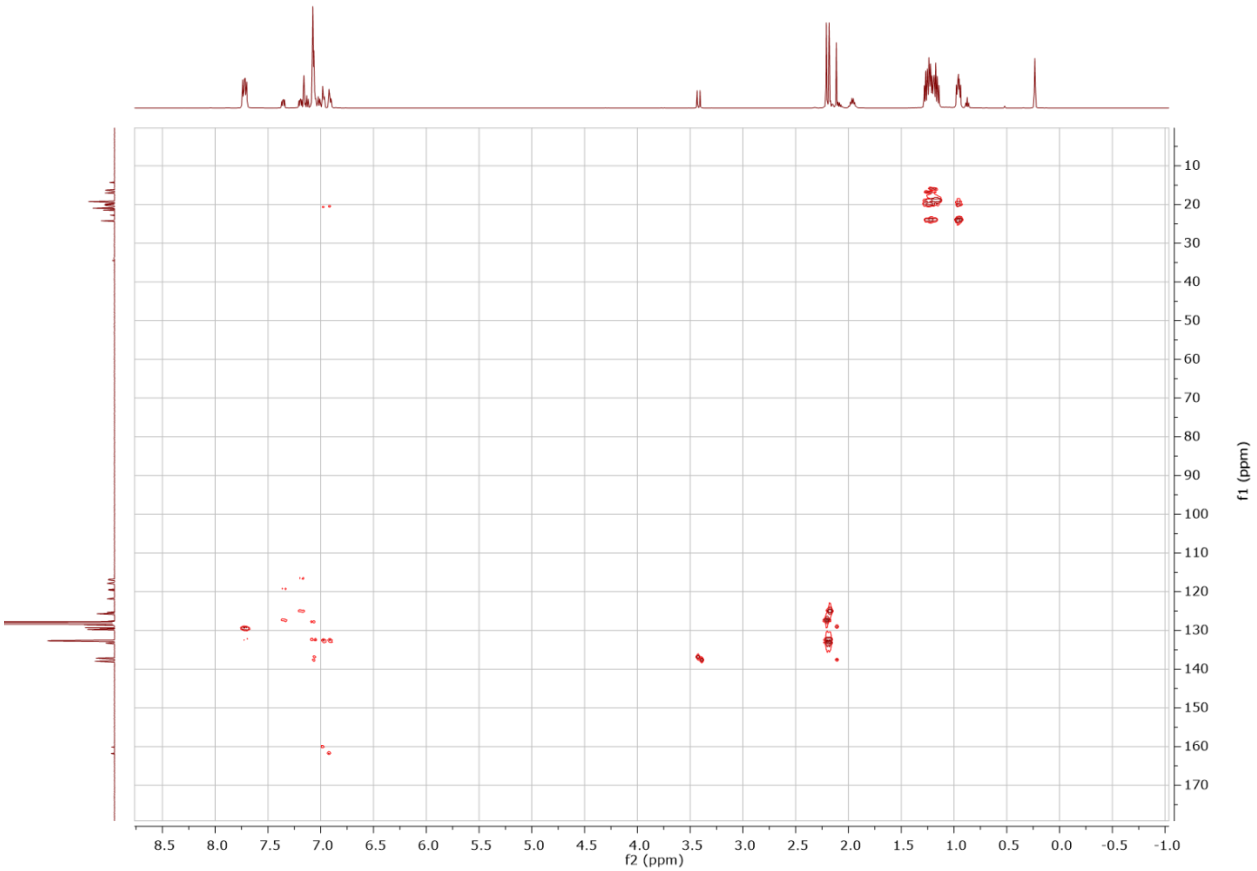


Figure S26. ^{1}H HMBC NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**).

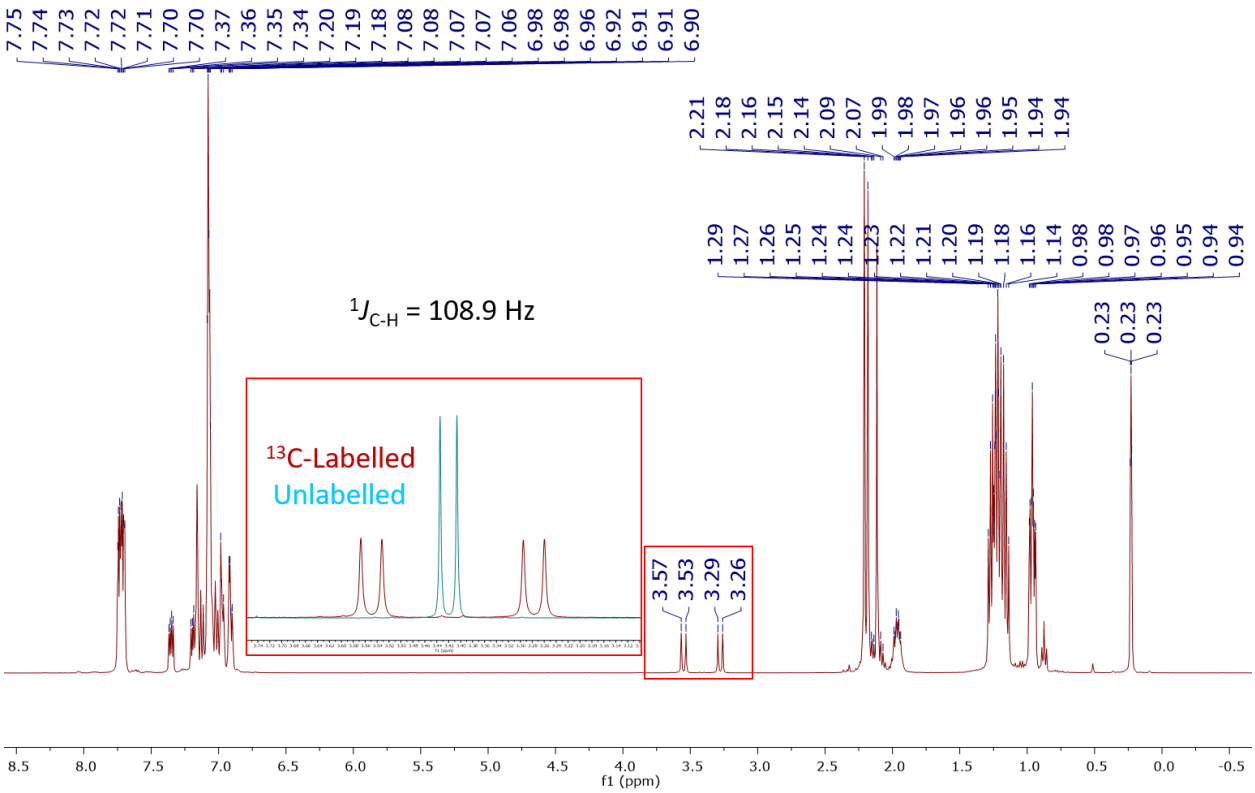


Figure S27. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(^{13}CHPPh$_3$)(CH$_3$) (**3-^{13}C**).

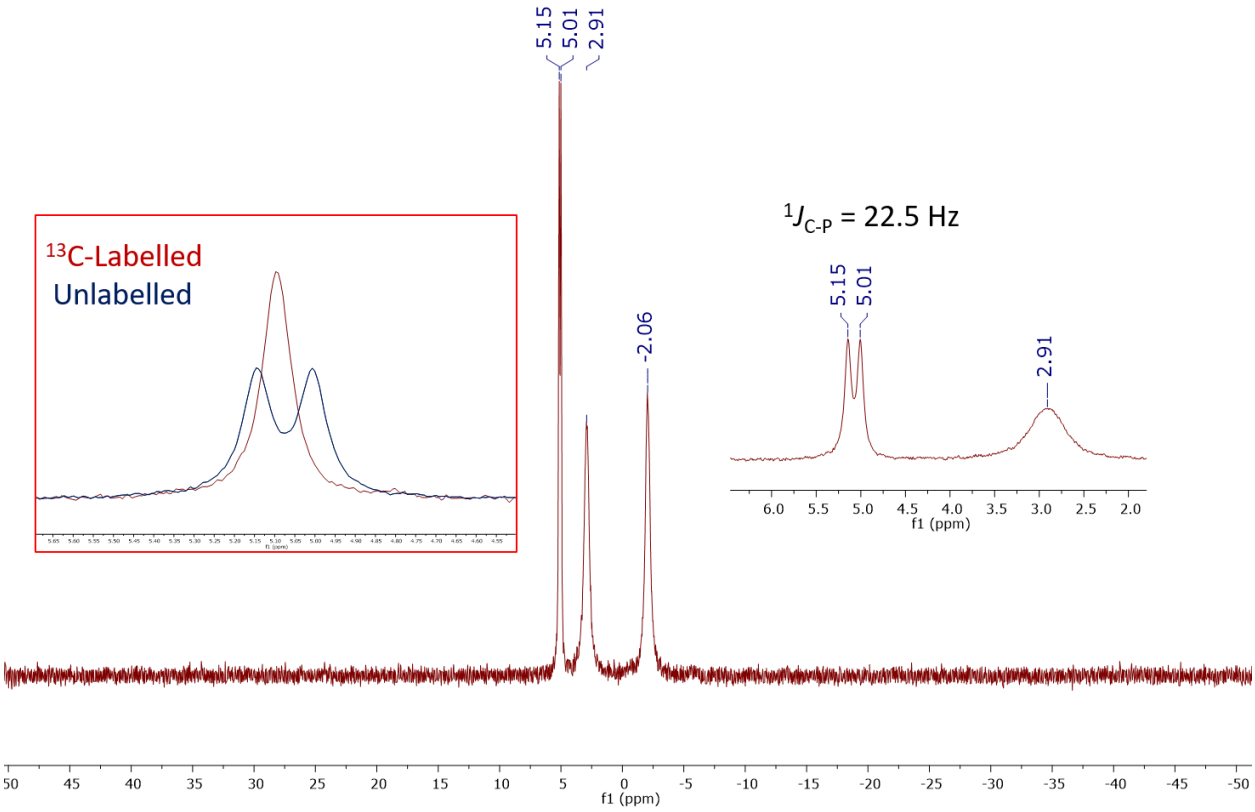


Figure S28. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc($^{13}CHPPh_3$)(CH_3) (**3-^{13}C**).

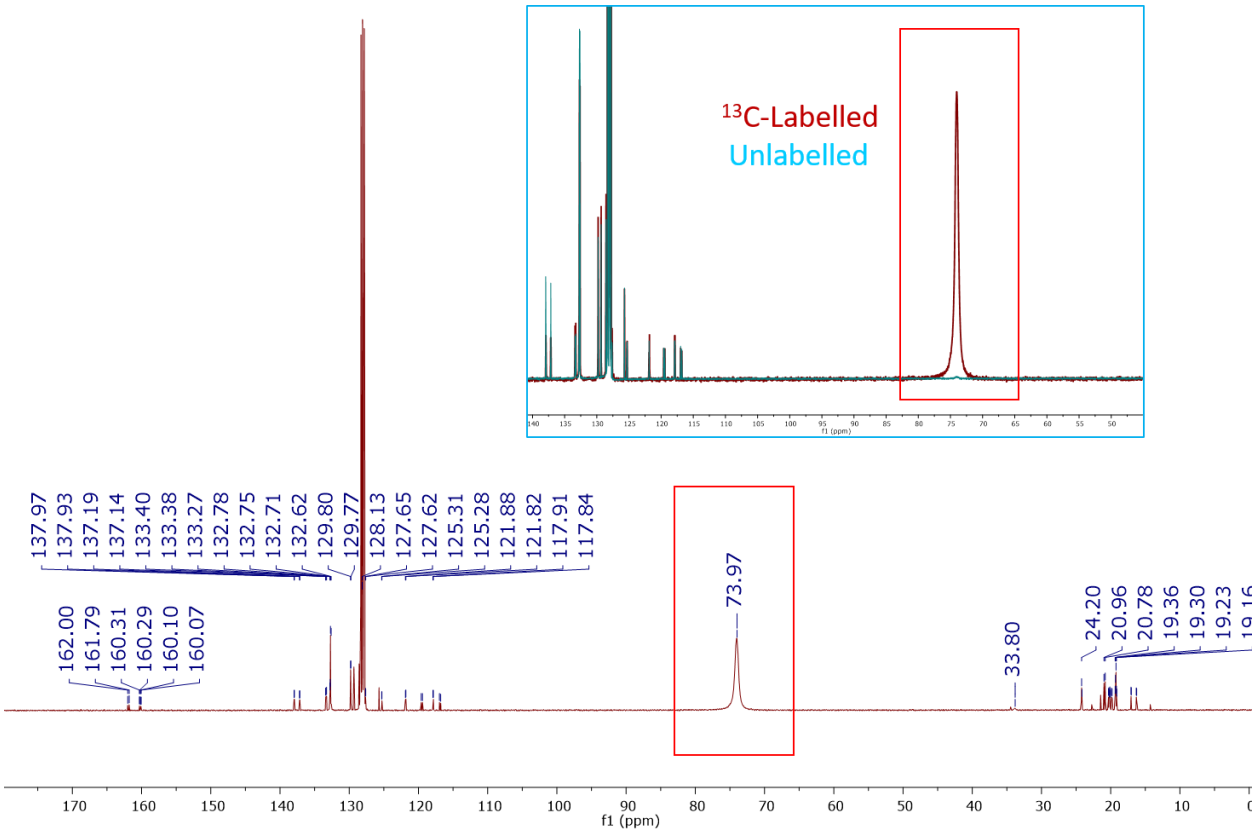


Figure S29. $^{13}C\{^{1}H\}$ NMR (101 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(^{13}CHPPh3)(CH_3) (**3-^{13}C**).

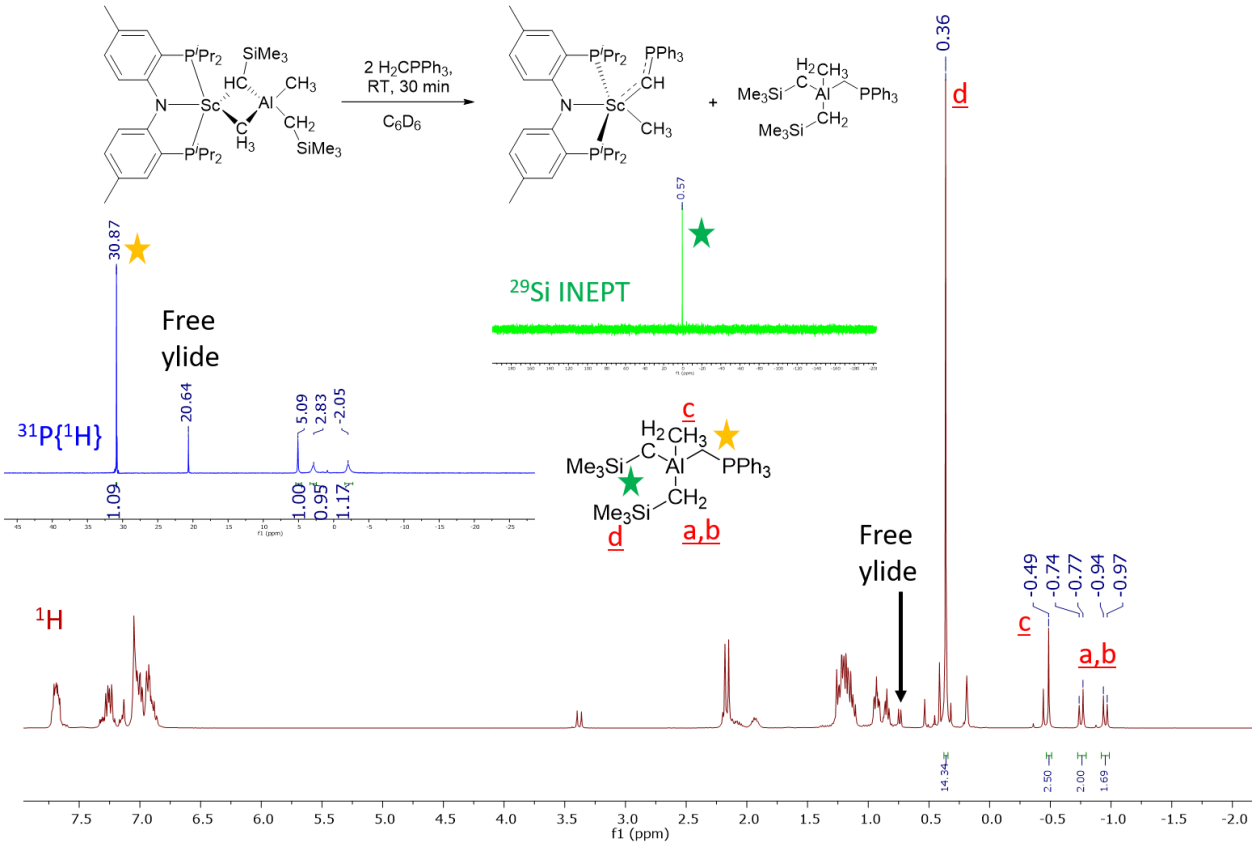


Figure S30. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K), ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectra of the reaction mixture produced following addition of about 2 equivalents of H_2CPPh_3 to (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] after 30 minutes.

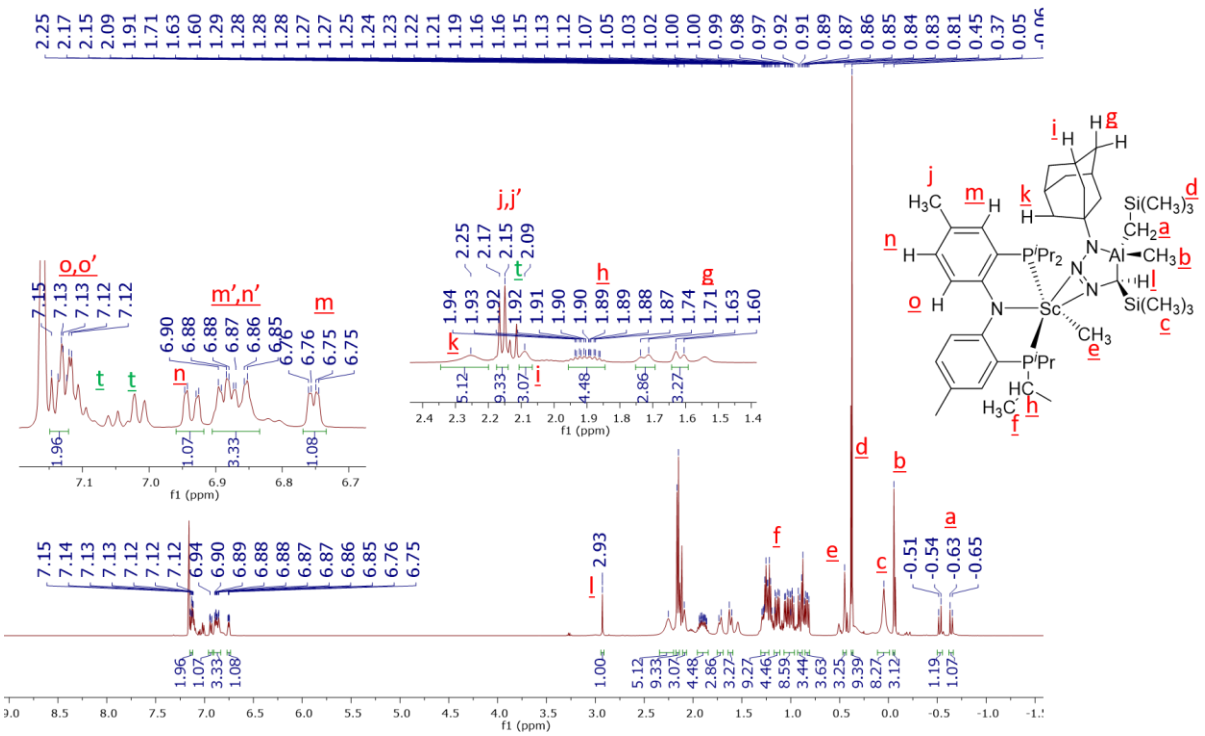


Figure S31. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**). Residual toluene is labelled with t. Unlabelled peaks correspond to impurity that could not be identified.

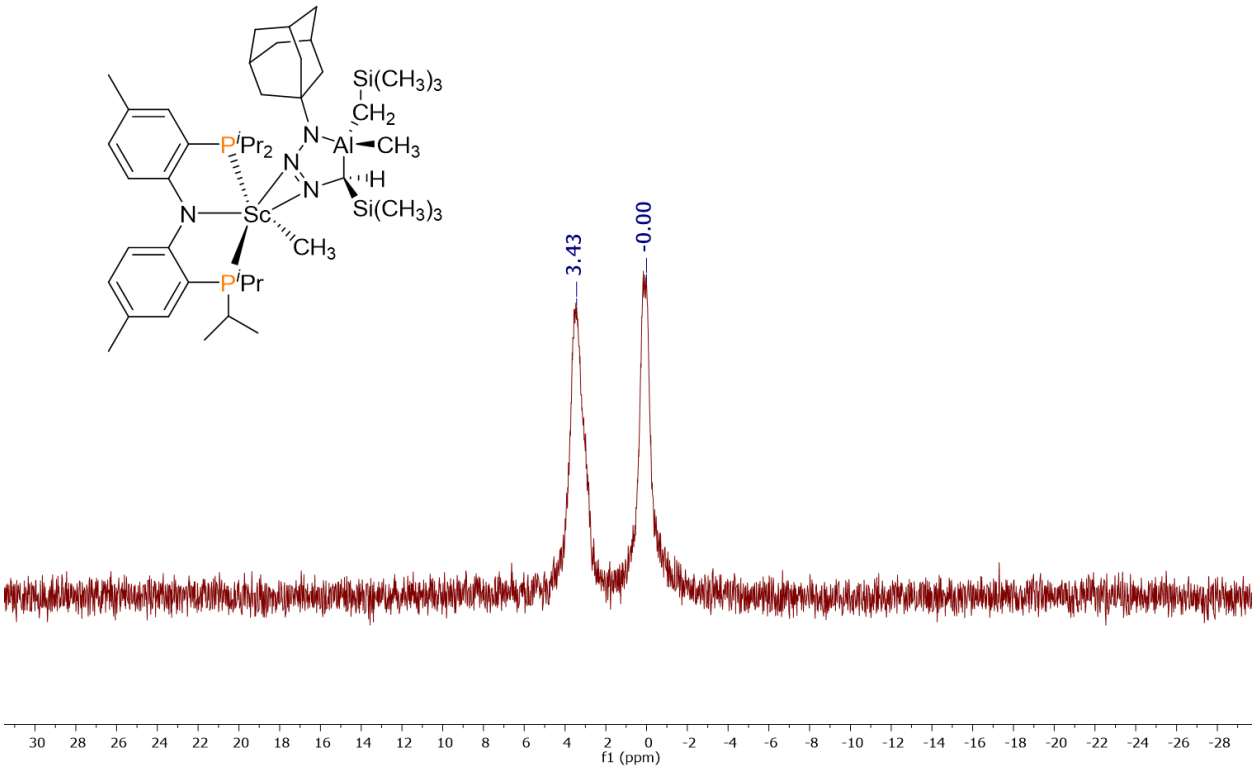


Figure S32. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**). An impurity has signals that overlap.

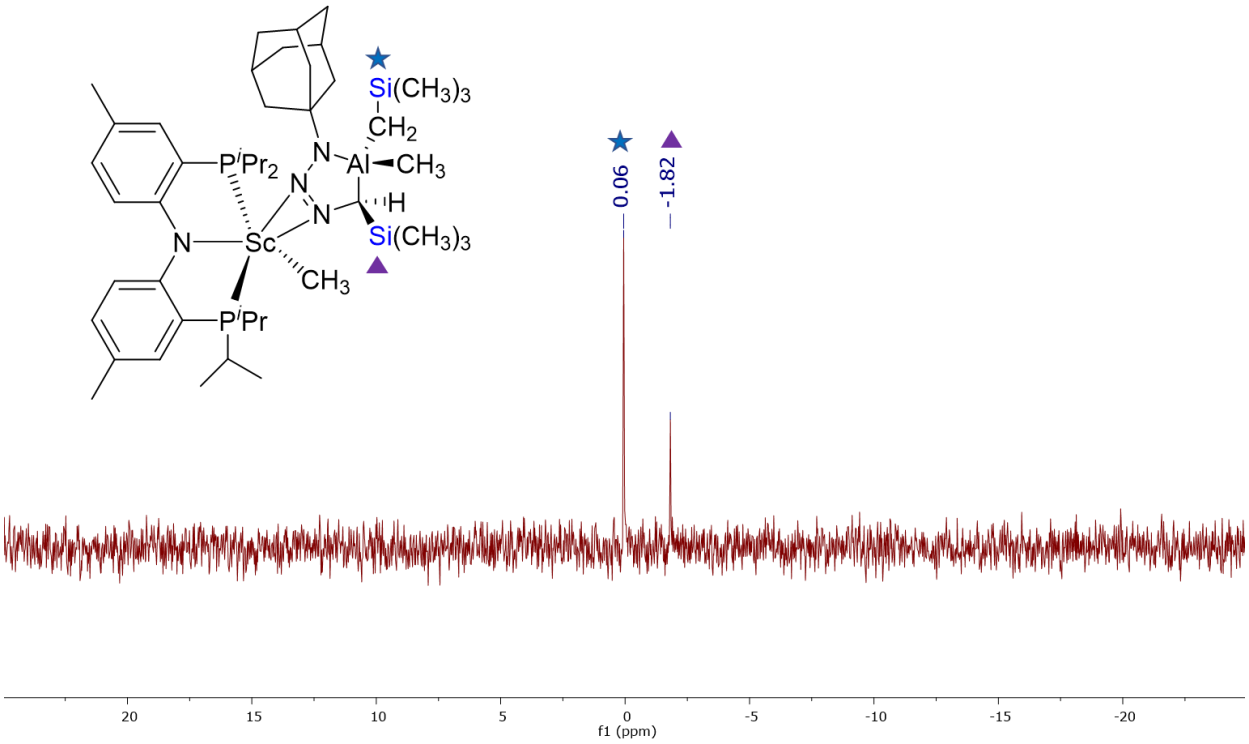


Figure S33. ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)($CH_2Si Me_3$)] (**4**).

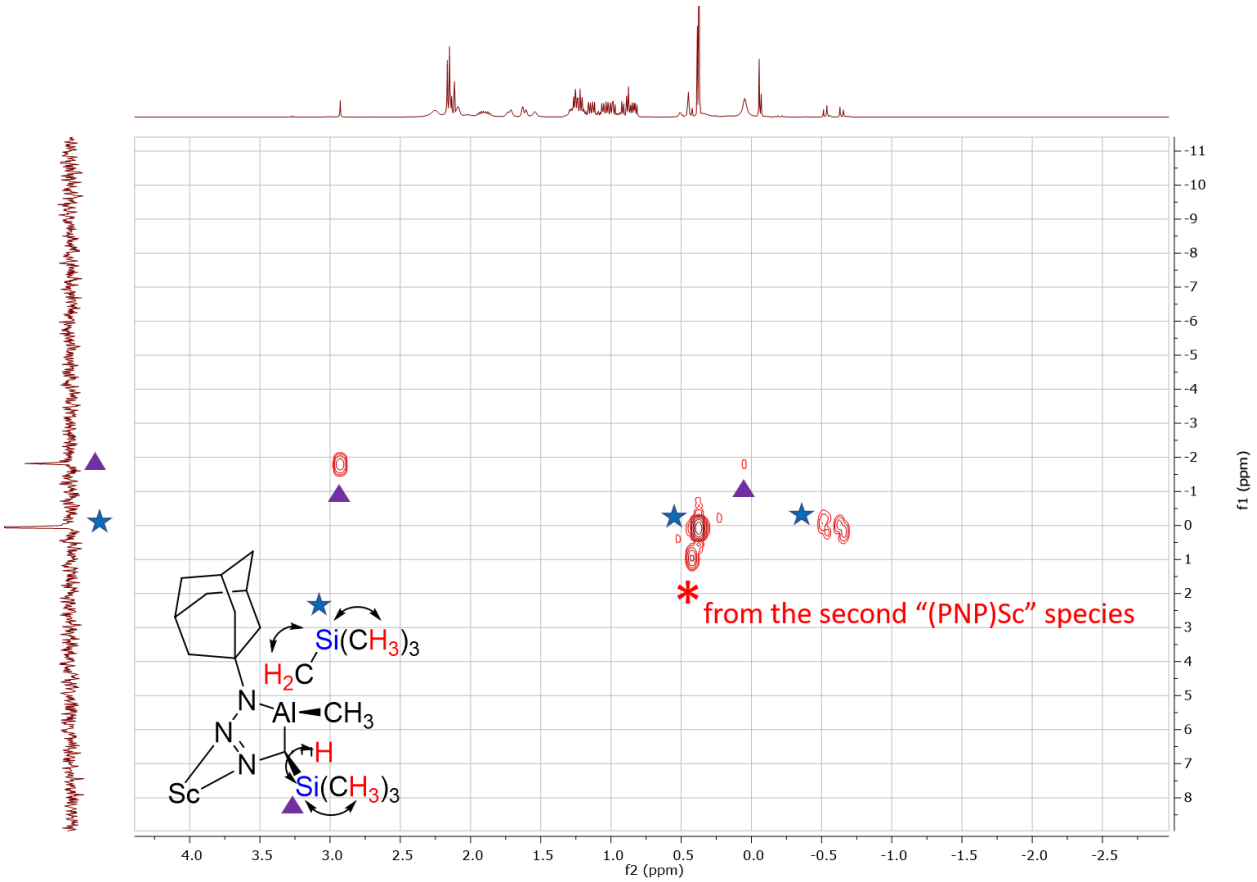


Figure S34. ^{29}Si-^{1}H HMBC (400 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**).

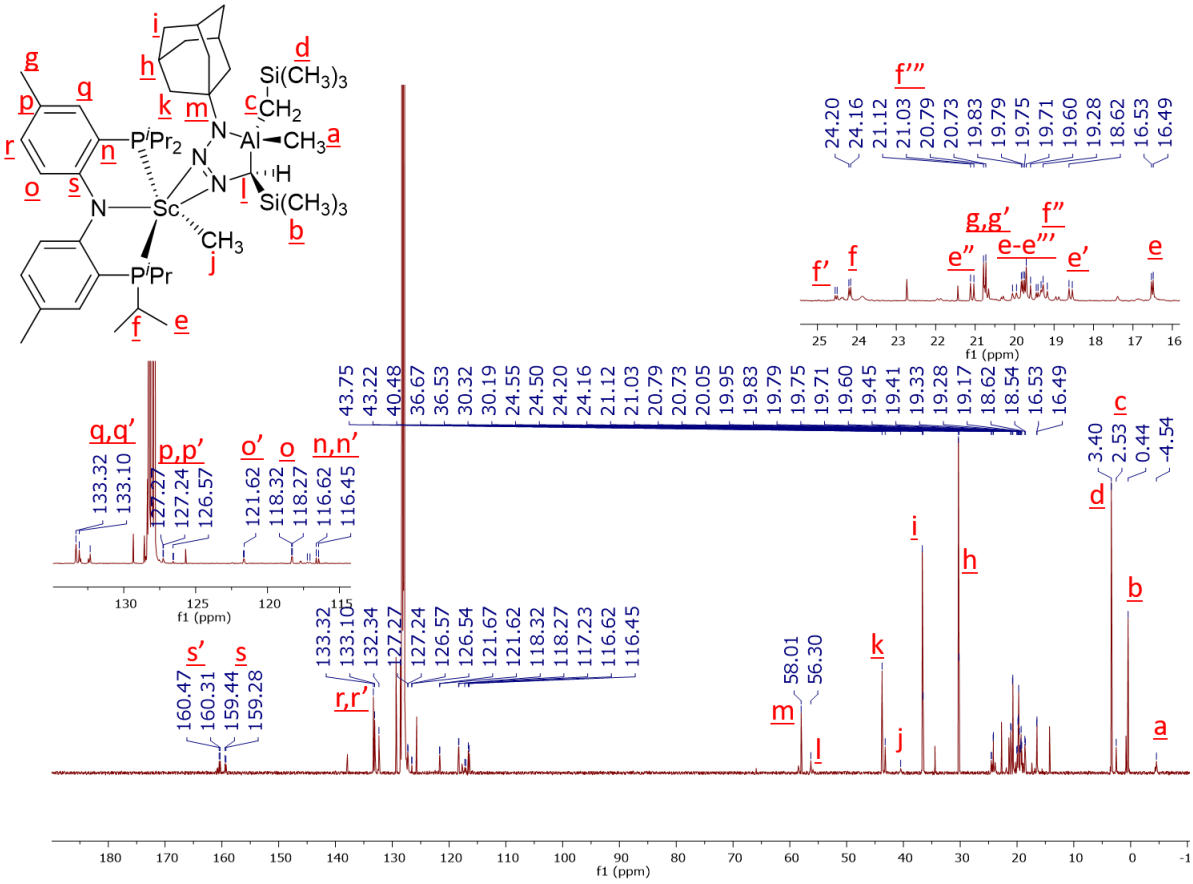


Figure S35. ^{13}C NMR (126 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)($CH_2Si Me_3$)] (**4**). Residual toluene and pentane are labelled with t and p respectively. Unlabelled peaks correspond to impurities that could not be identified.

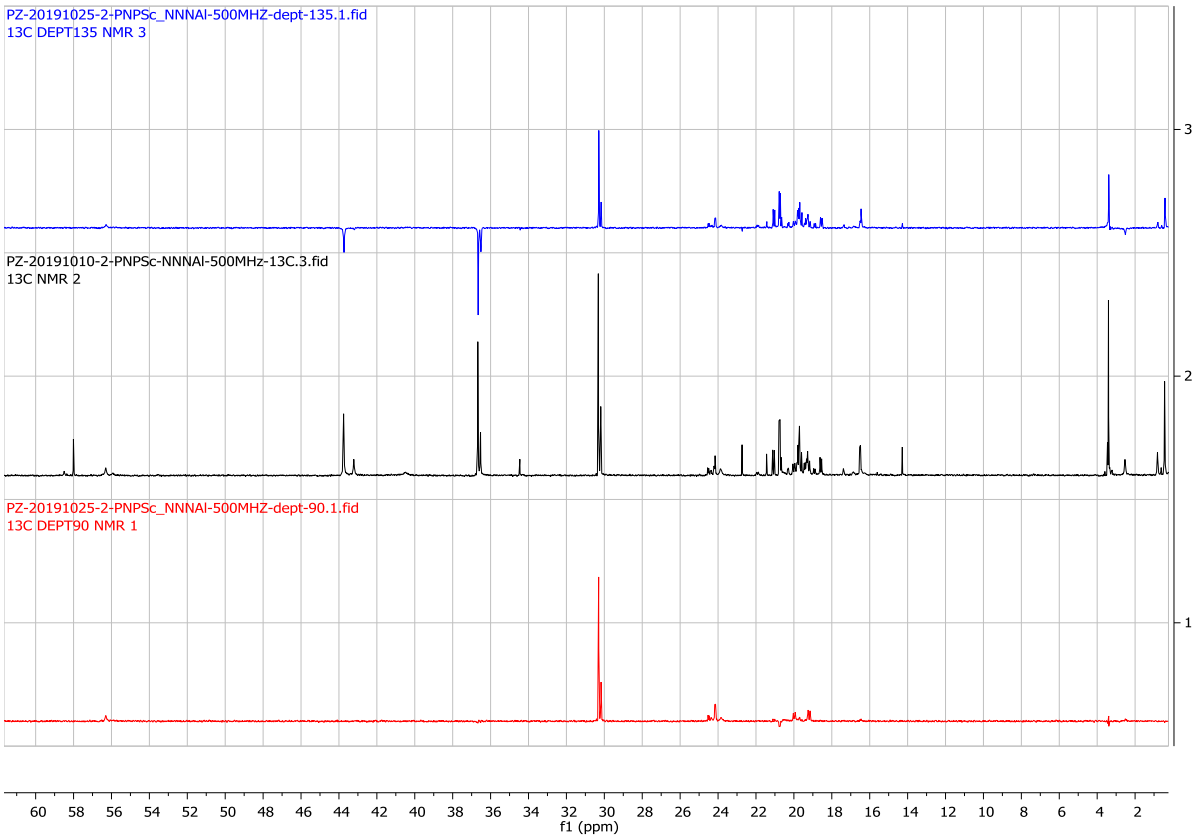


Figure S36. Aliphatic regions of $^{13}C\{^{1}H\}$, DEPT 90, DEPT 135 (126 MHz, benzene-d_6, 300 K) spectra of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**) used to assign carbons of [η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] ligand.

Figure S37. ^{1}H COSY (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**).

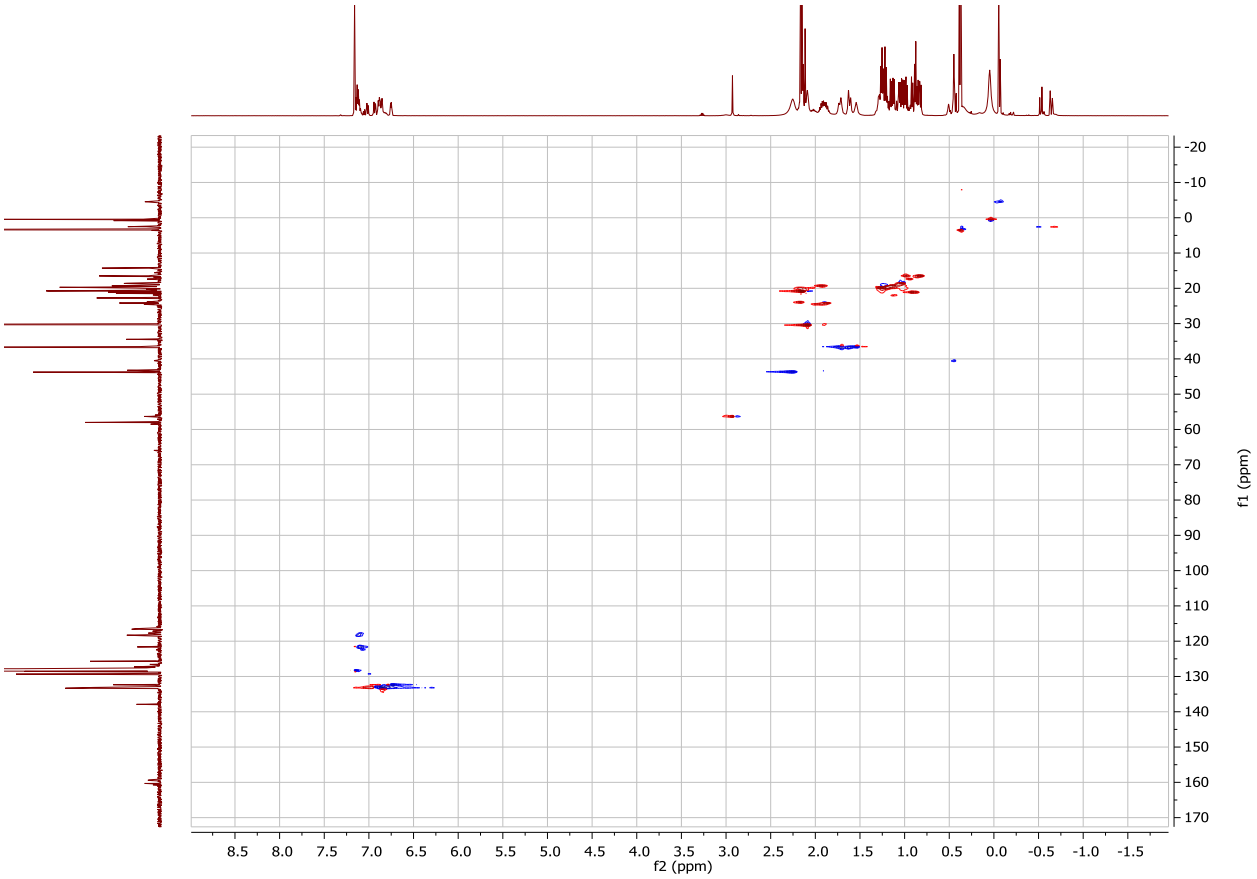


Figure S38. ^{1}H-^{13}C HSQC (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe$_3$Al(CH_3)(CH_2SiMe$_3$)] (**4**).

Figure S39. ^{1}H-^{13}C HMBC (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(CH_3)[η^2-N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)] (**4**).

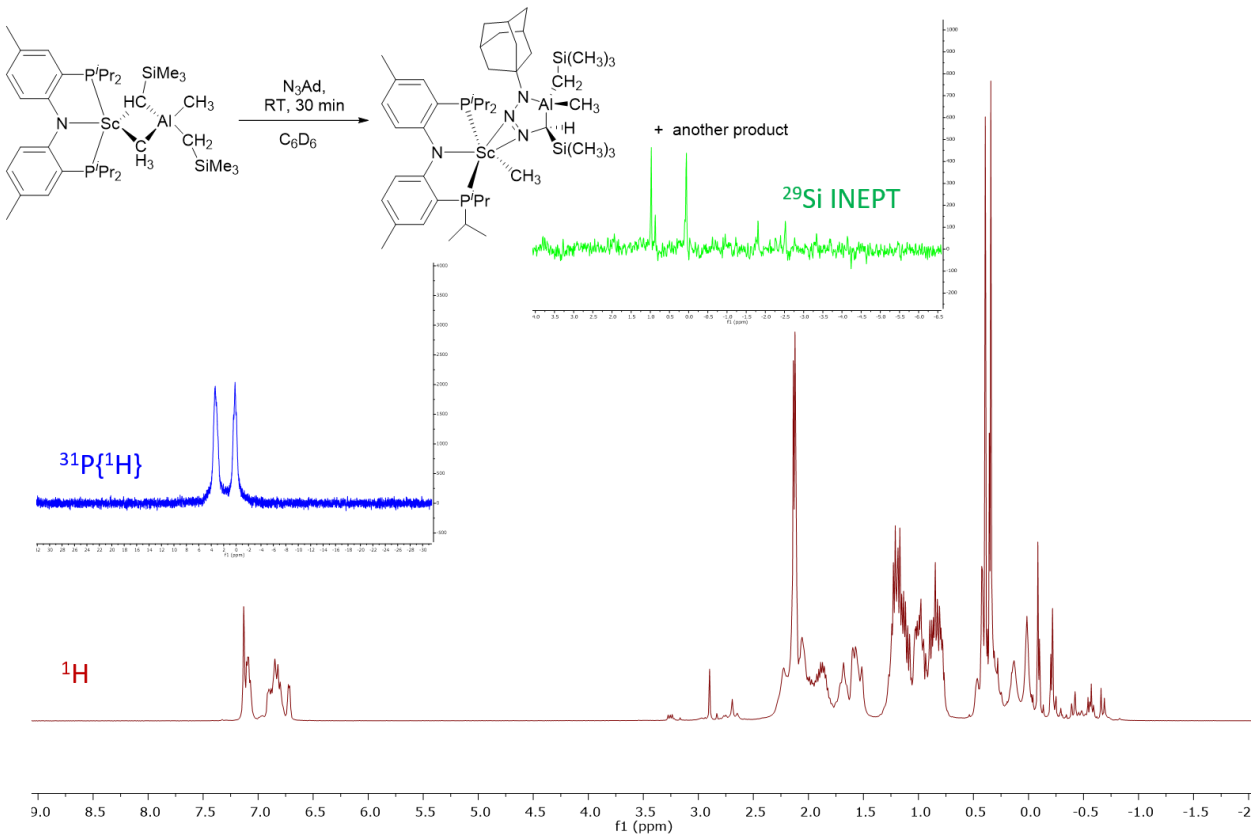


Figure S40. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K), ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K), spectra of the reaction mixture produced following addition of about 1 equivalent of N_3Ad to (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] after about 30 minutes.

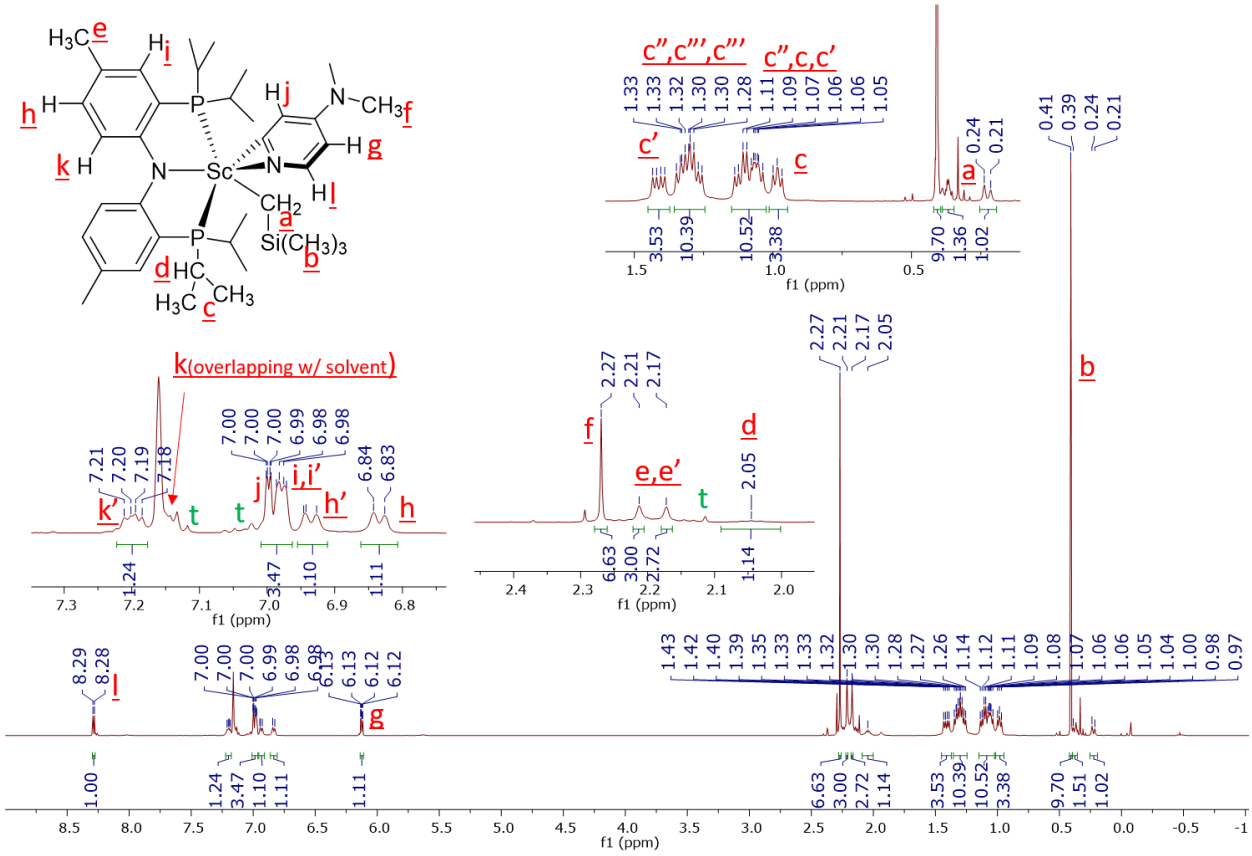


Figure S41. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**). Residual toluene is labelled with t. Unlabelled peaks correspond to impurities that could not be identified.

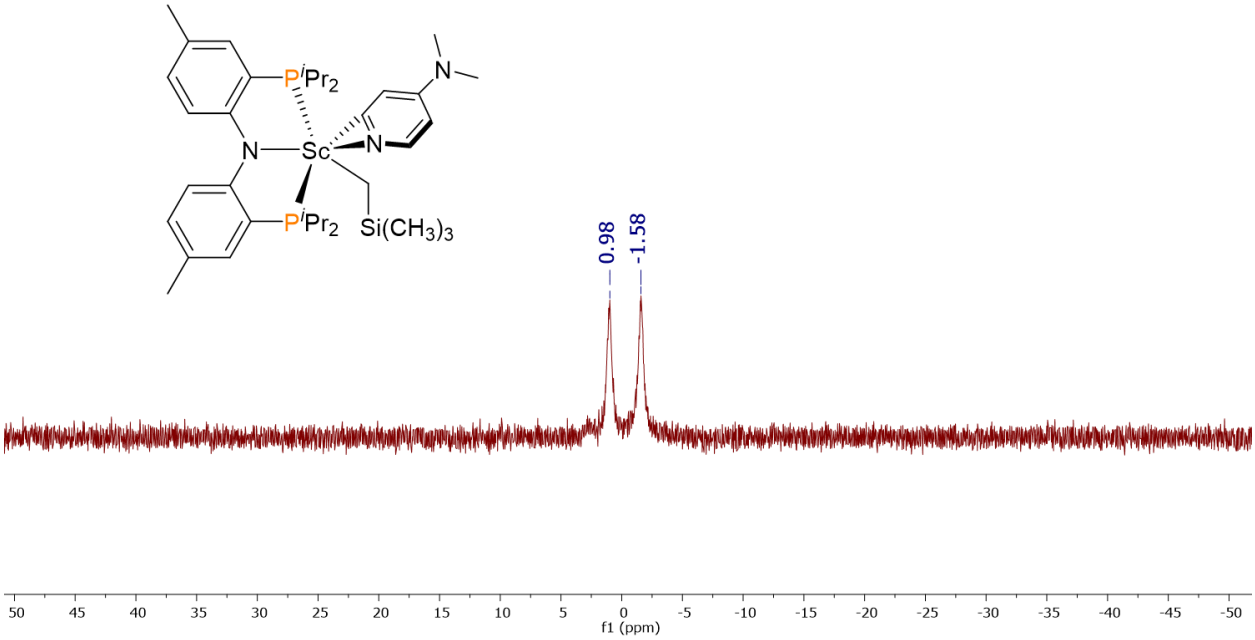


Figure S42. $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**). The unlabeled peak corresponds to the unidentified impurity.

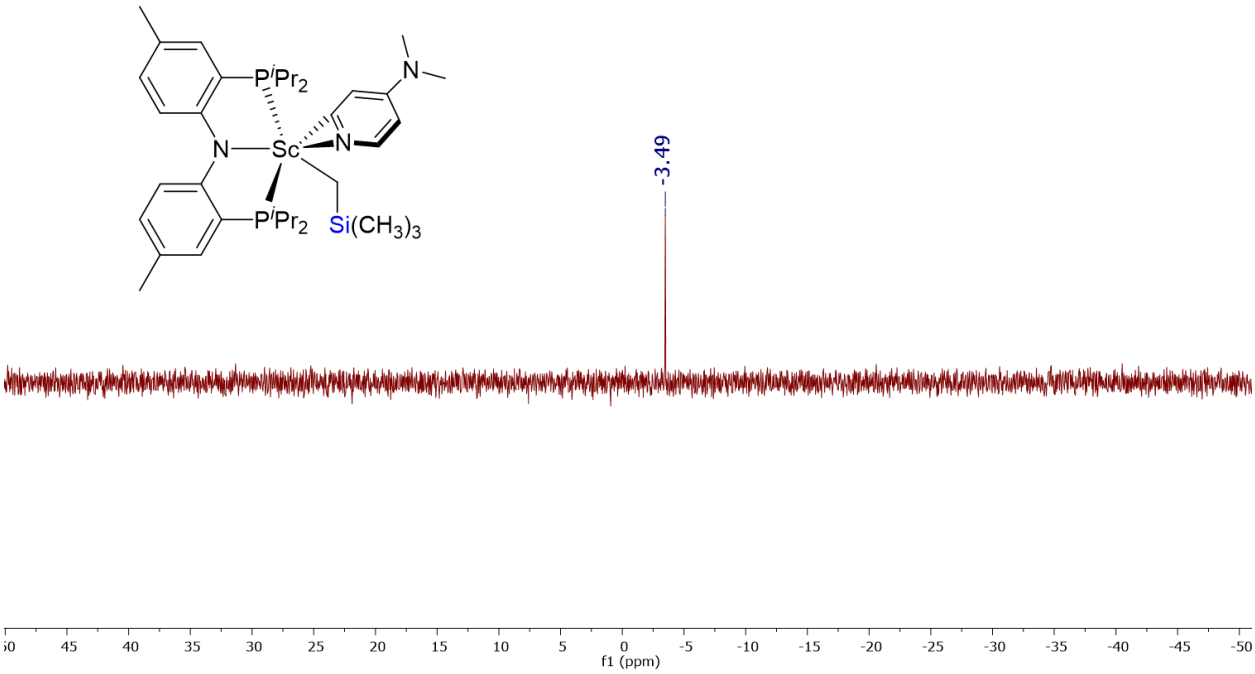


Figure S43. ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**).

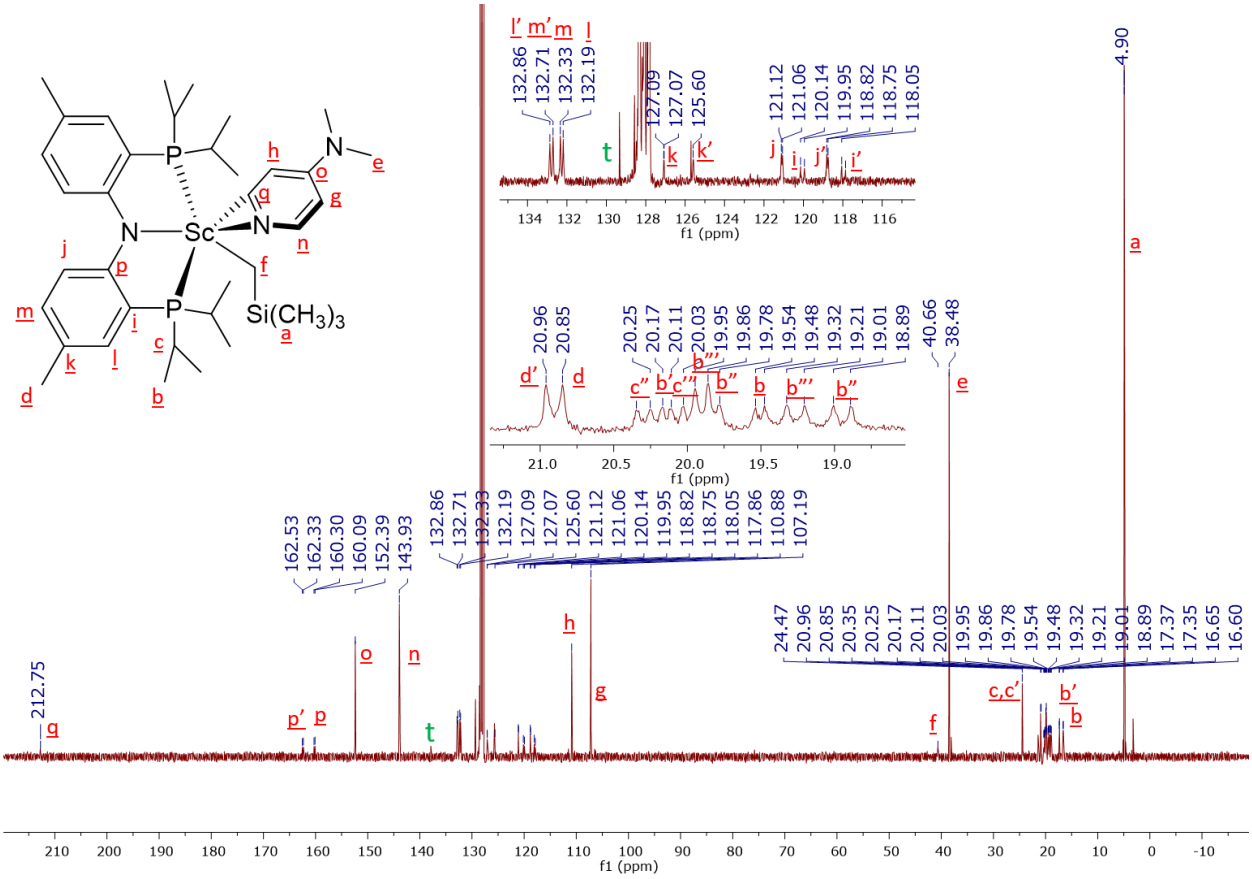


Figure S44. ^{13}C NMR (101 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**). Residual toluene is labelled with t. Unlabelled peaks correspond to impurities that could not be identified.

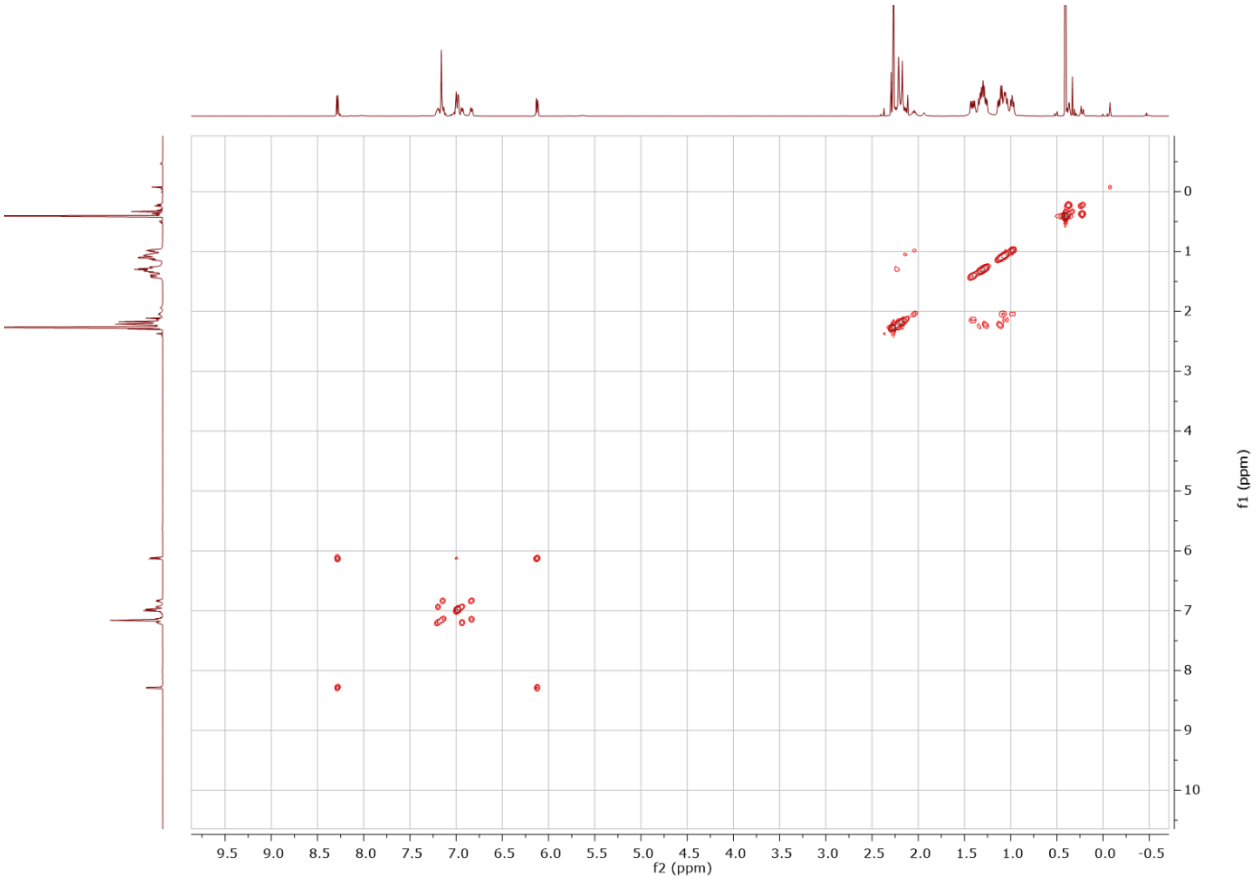


Figure S45. ^{1}H COSY NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**).

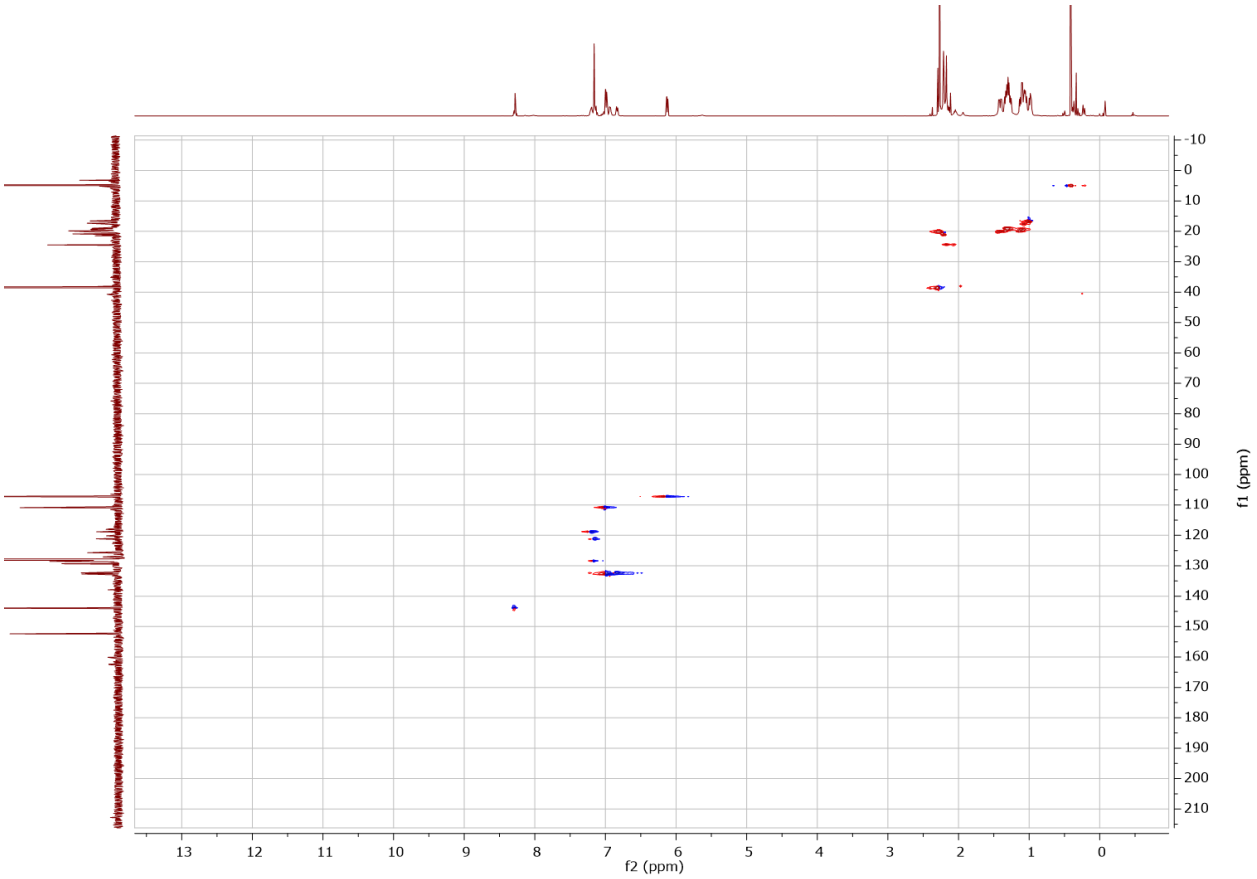


Figure S46. ^{1}H-^{13}C HSQC NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**).

Figure S47. ^{1}H-^{13}C HSQC NMR (400 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**).

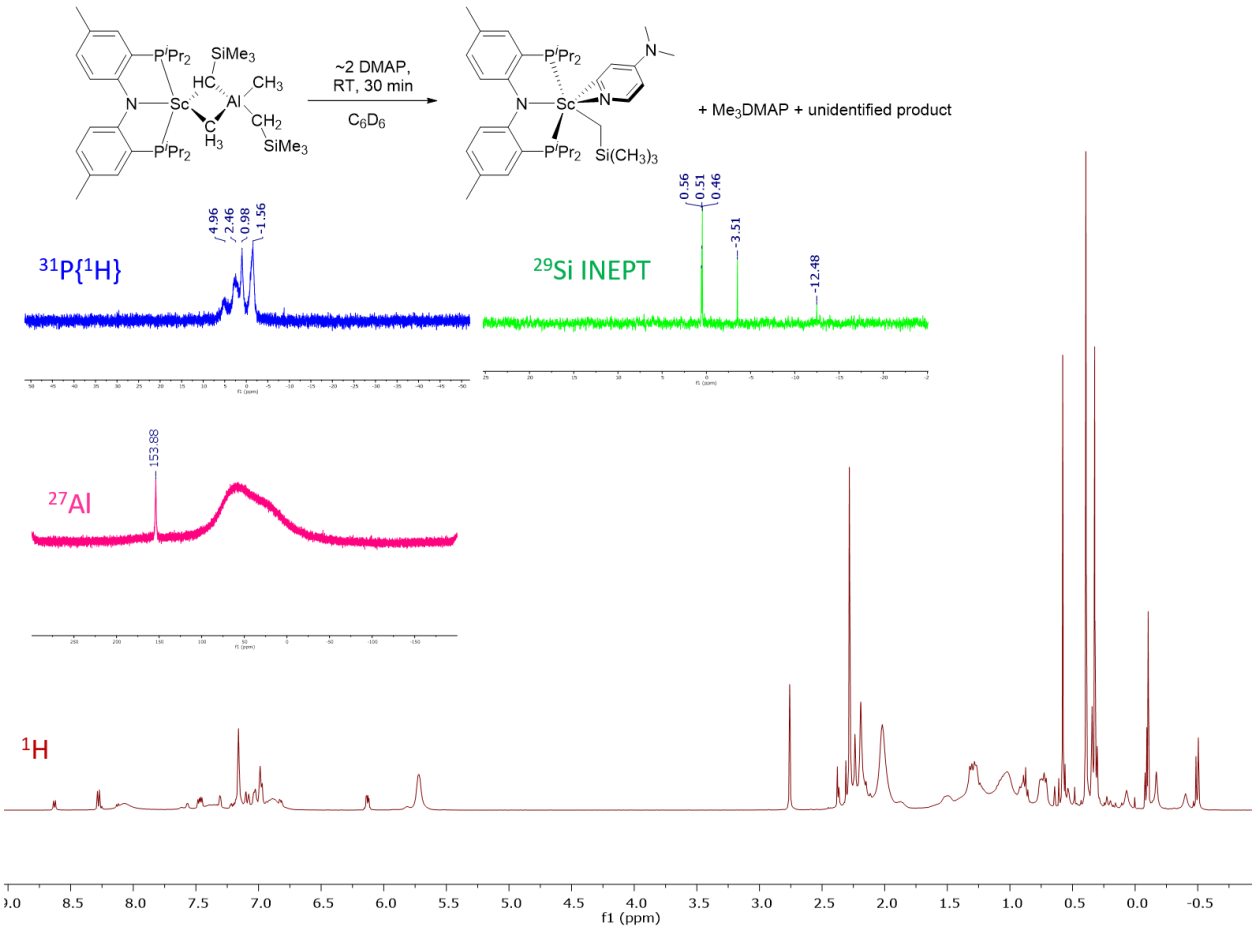


Figure S48. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K), ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K), ^{27}Al (104 MHz, benzene-d_6, 300 K) spectra of the reaction mixture produced following addition of about 2 equivalents of DMAP to (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] after 30 minutes.

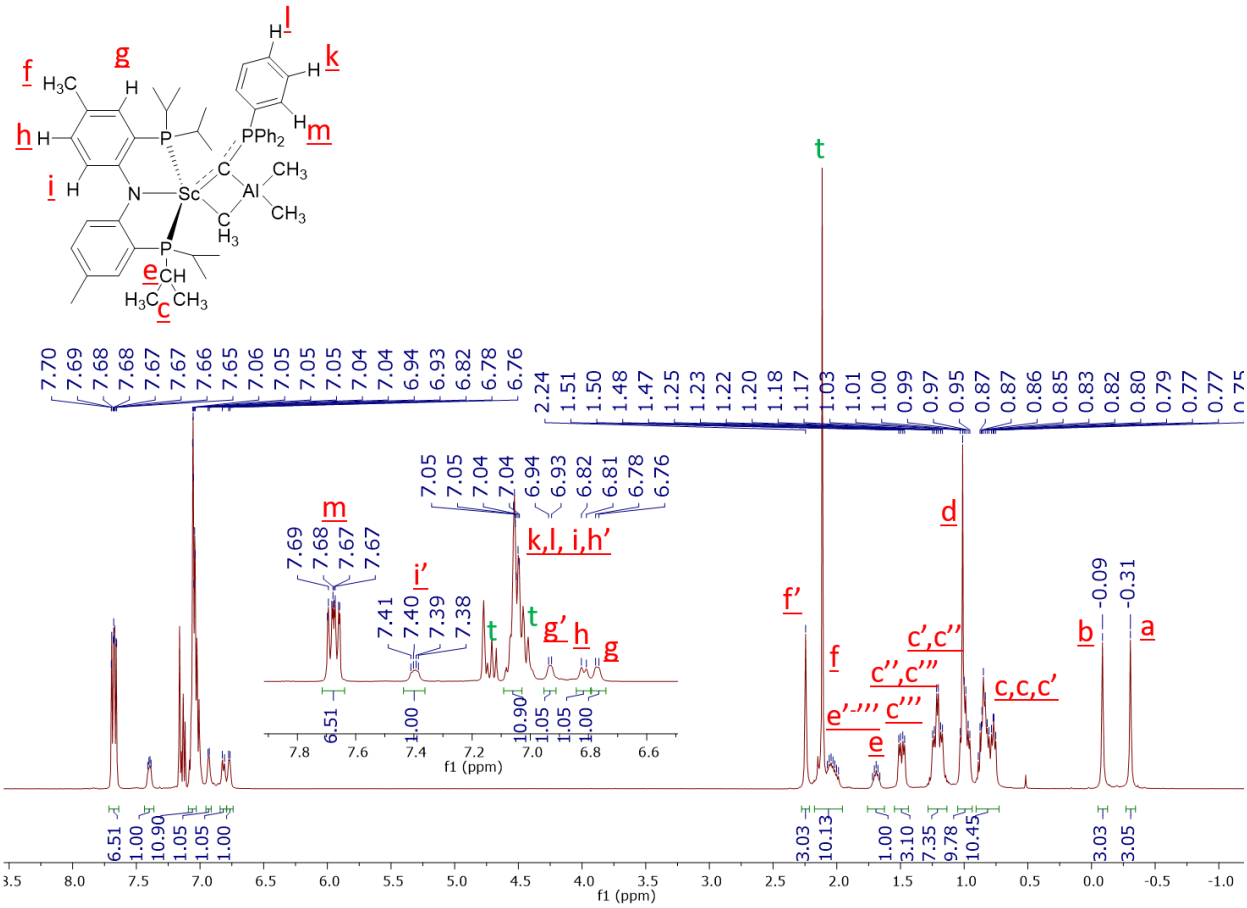


Figure S49. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6**). Residual toluene is labelled with t.

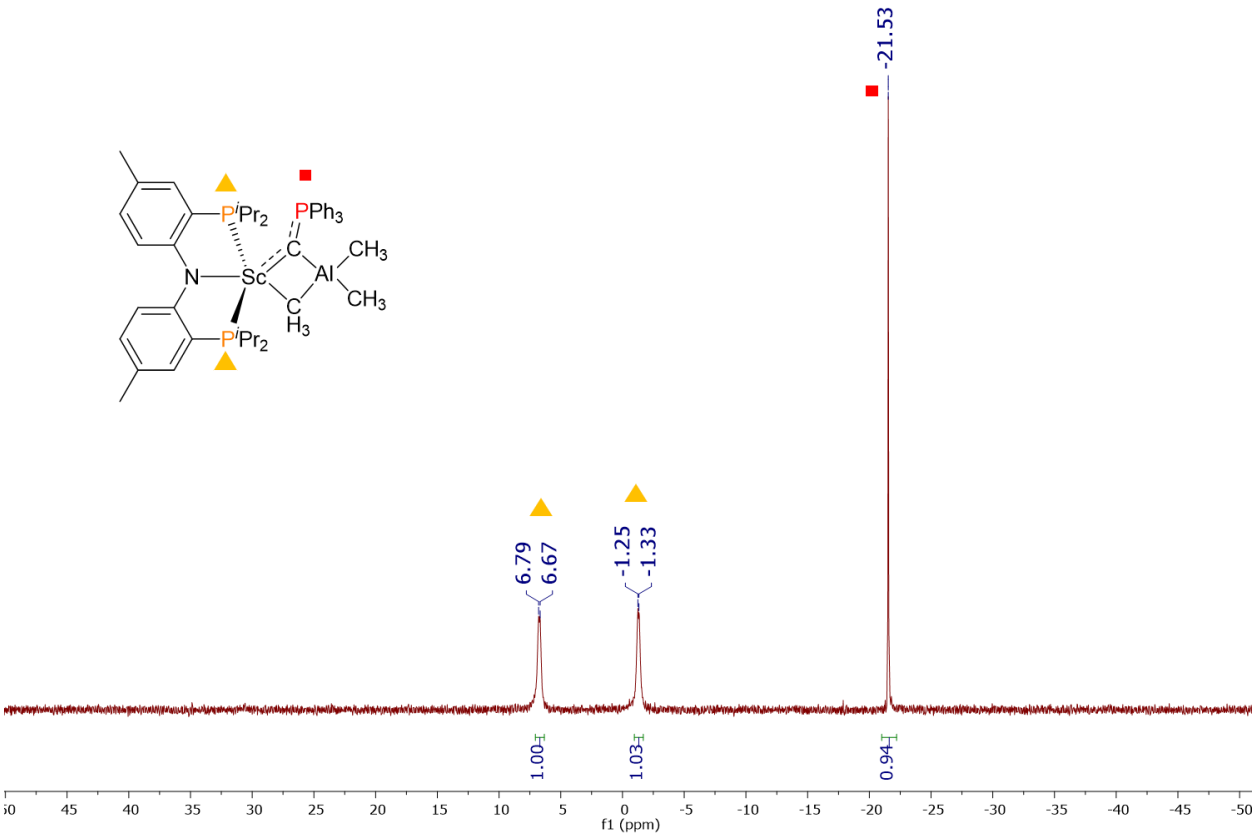


Figure S50. $^{31}P\{^{1}H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6**).

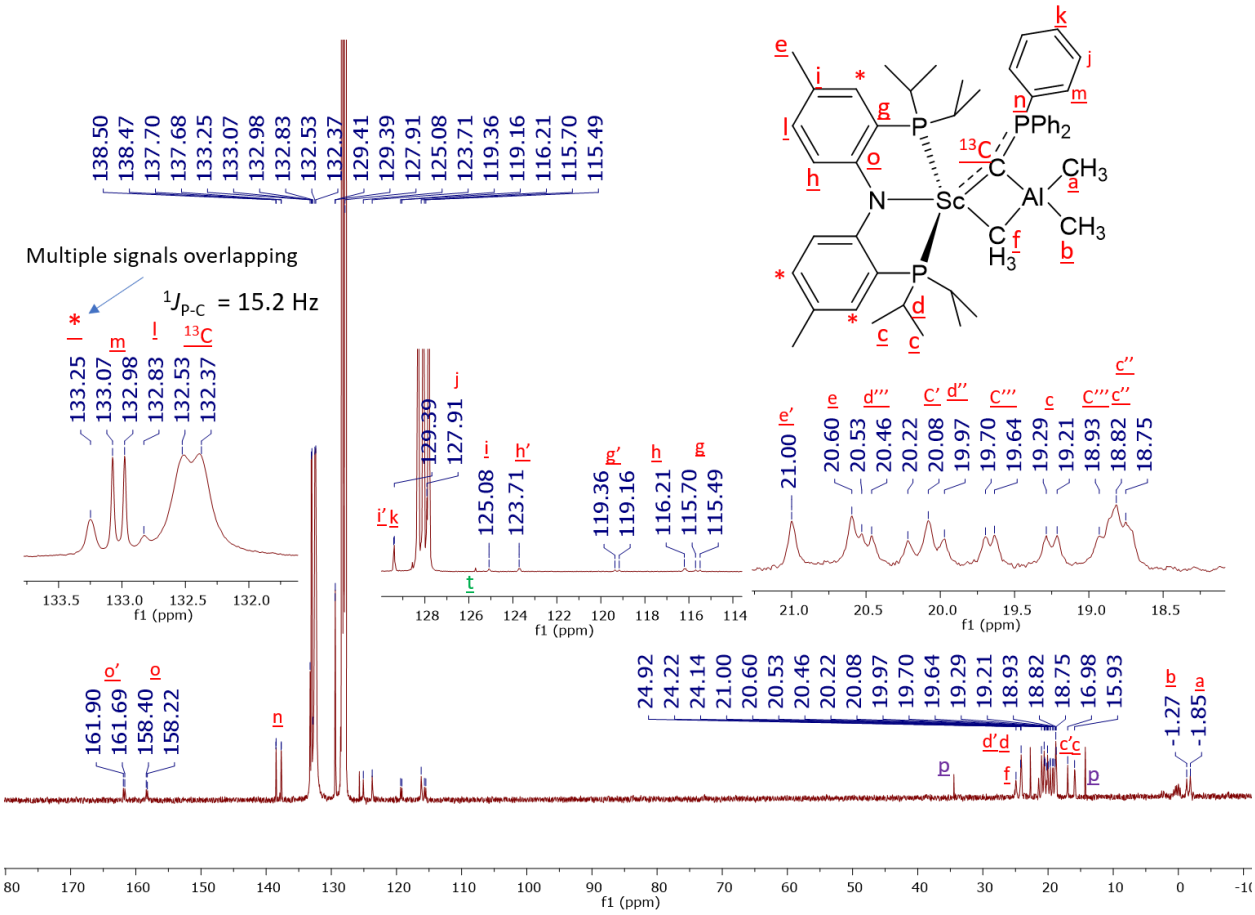


Figure S51. $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-^{13}CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6**). Residual toluene and pentane are labelled with t and p, respectively. The non-enriched spectrum is shown below for comparison.

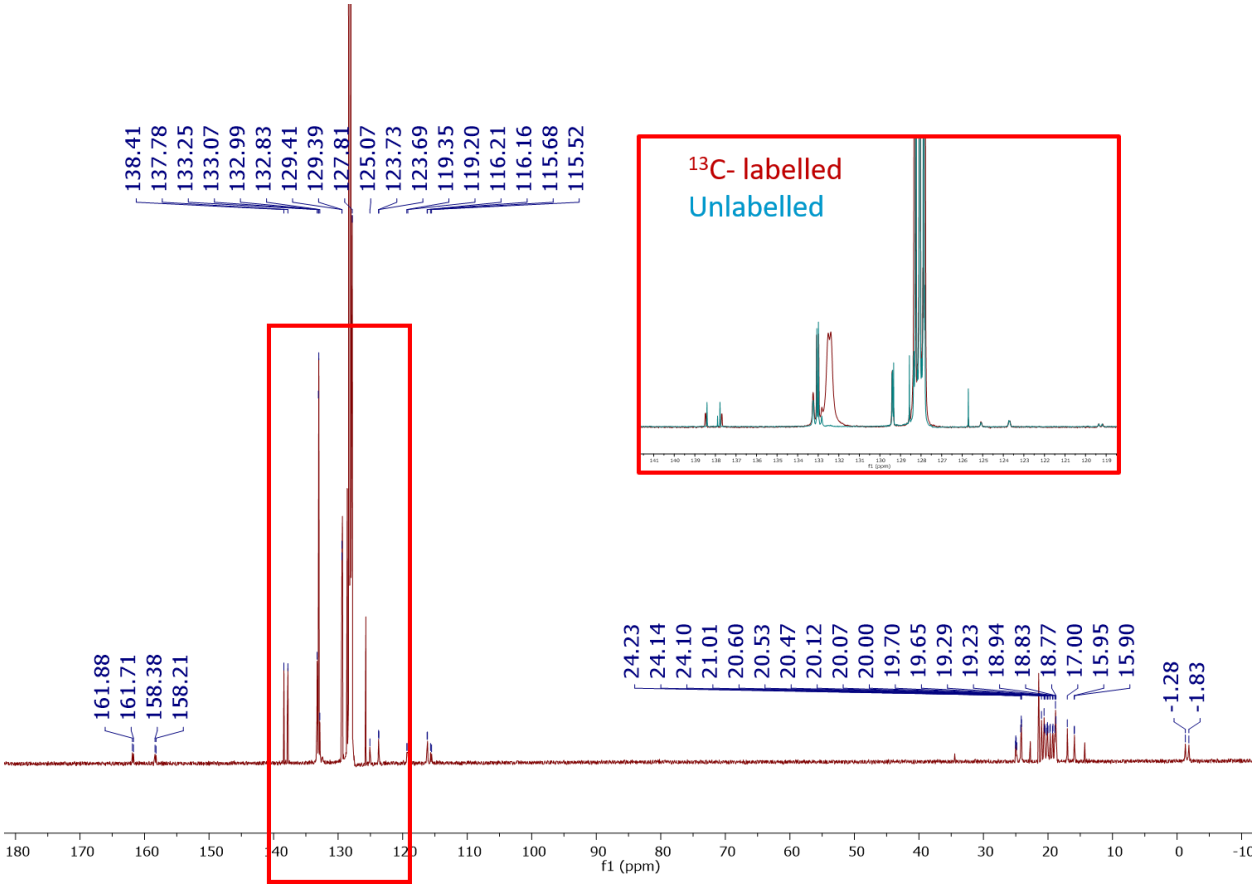


Figure S52. $^{13}C\{^{1}H\}$ NMR (126 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6**). Inset is an overlay of the region between 140 and 120 ppm for the labelled and unlabelled samples. Note that a higher frequency instrument was used to collect the spectrum of the unlabelled sample.

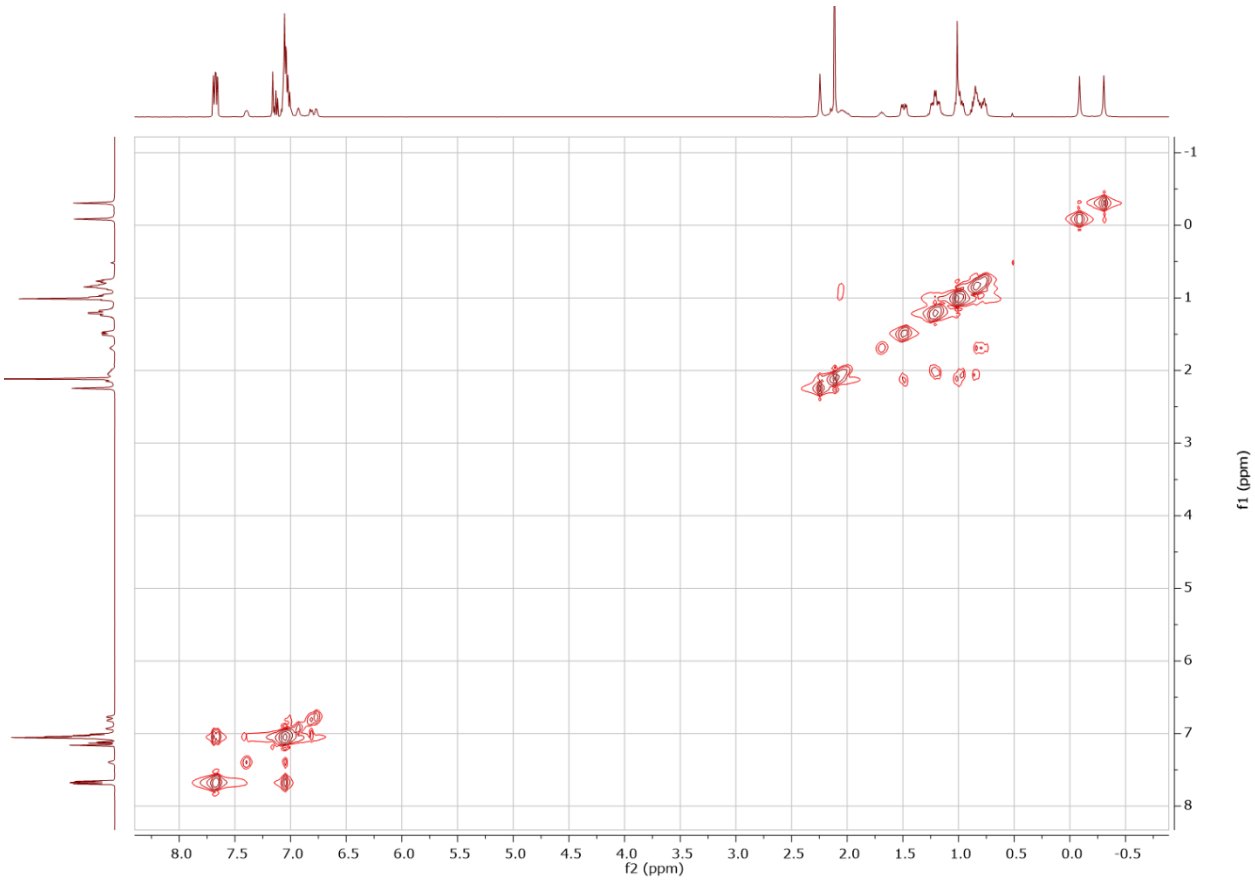


Figure S53. ^{1}H COSY NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6**).

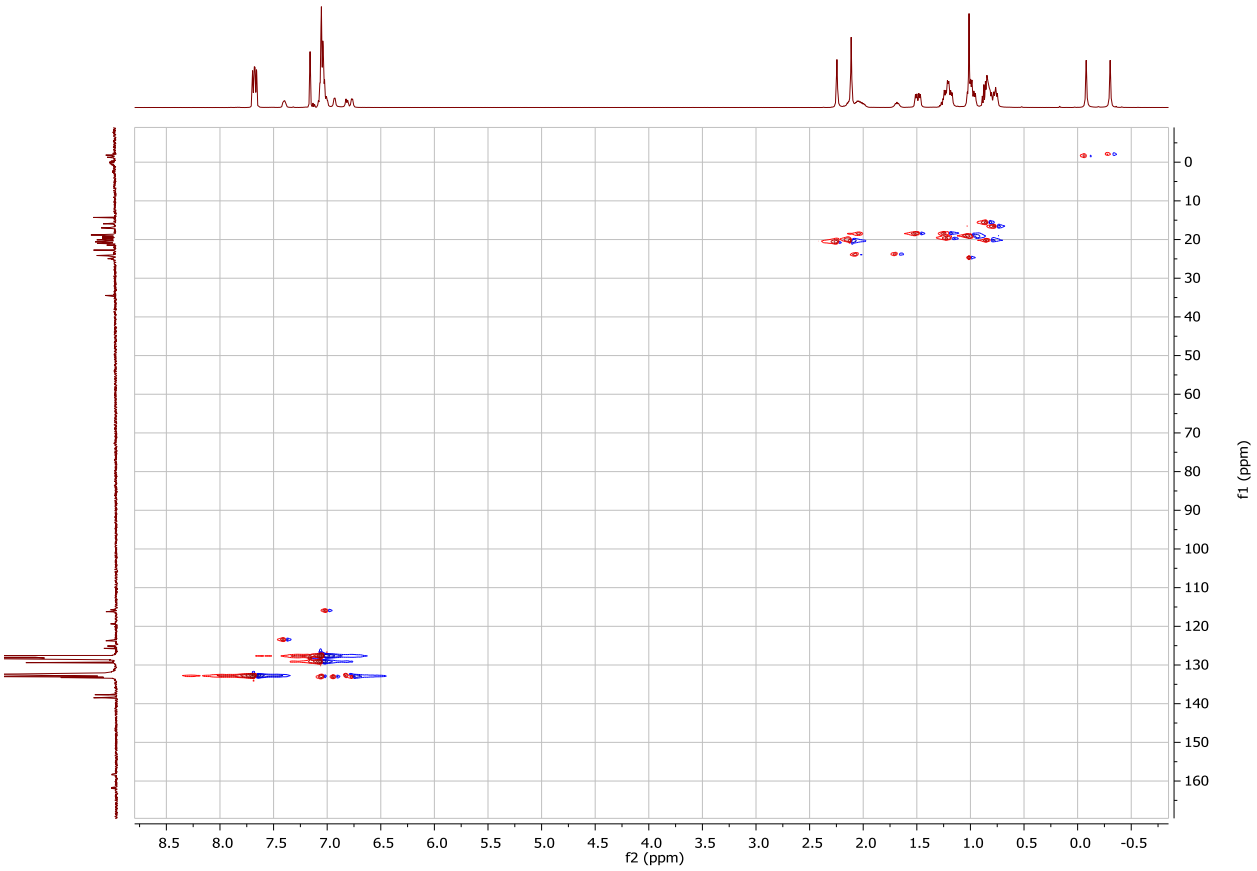


Figure S54. ^{1}H-^{13}C HSQC NMR (500 MHz, benzene-d_6, 300 K) spectrum of(PNP)Sc(μ_2-$^{13}CPPh_3$)(μ_2-CH_3)$AlMe_2$ (**6-^{13}C**). Note the lack of cross-peaks to the alkylidyne carbon.

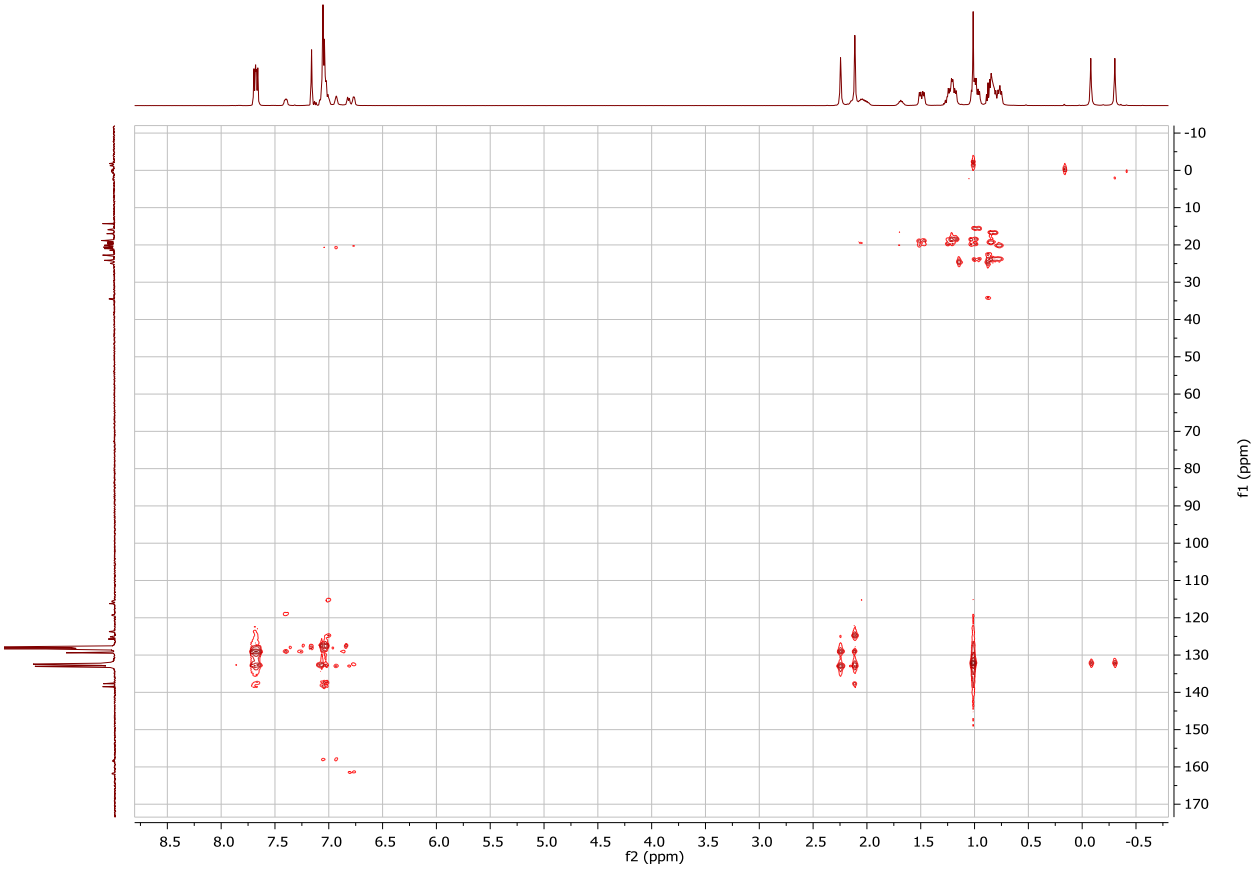


Figure S55. ^{1}H-^{13}C HMBC NMR (400 MHz, benzene-d_6, 300 K) spectrum of(PNP)Sc(μ_2-$^{13}CPPh_3$)(μ_2-CH_3)$AlMe_2$ (**6-^{13}C**). Note the strong cross-peaks to the alkylidyne carbon.

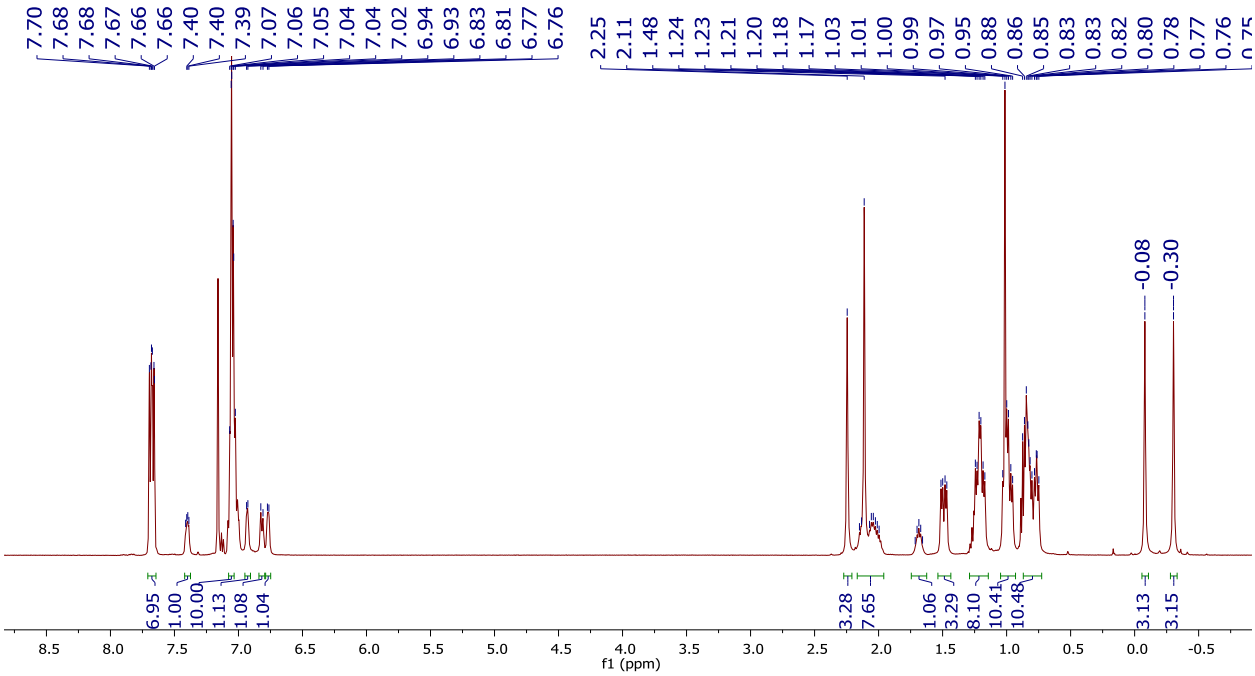


Figure S56. ^{1}H NMR (500 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-^{13}CPPh$_3$)(μ_2-CH$_3$)AlMe$_2$ (**6-^{13}C**).

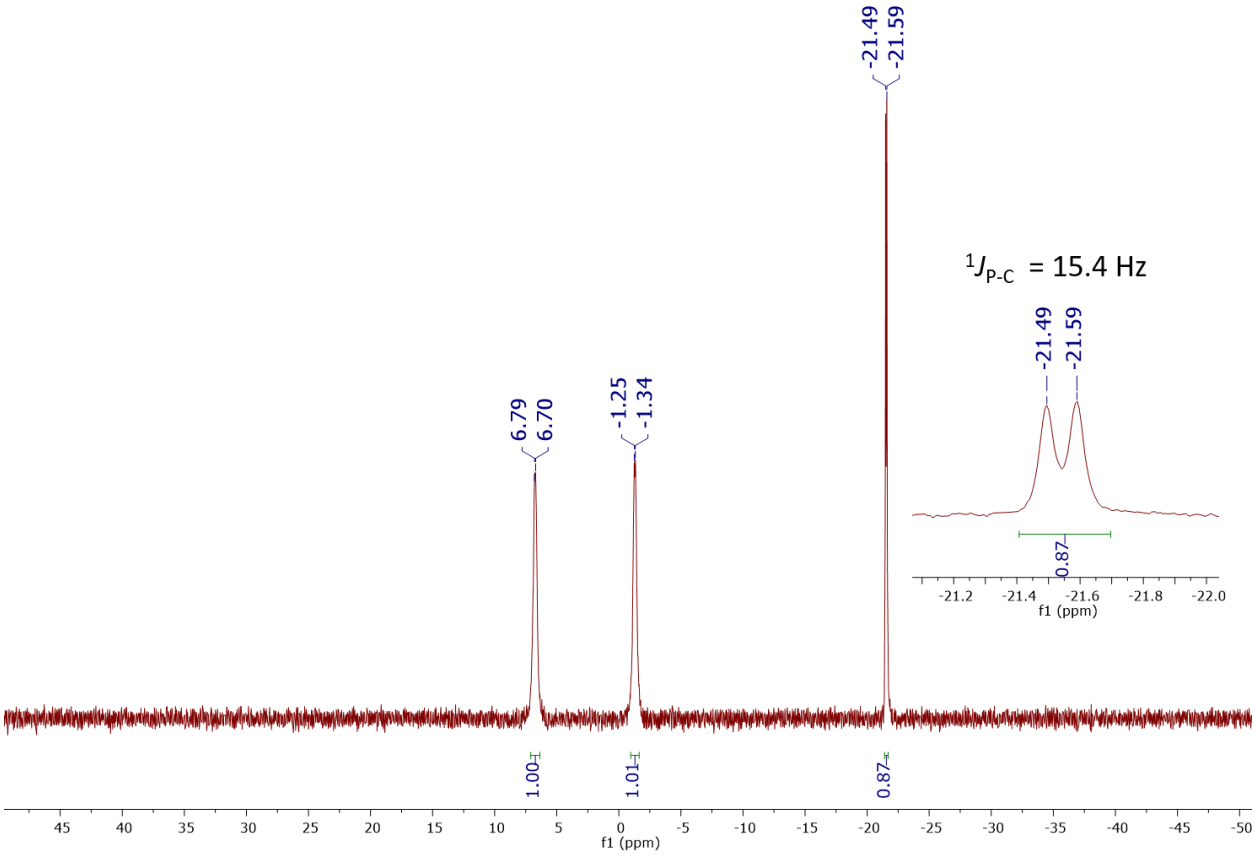


Figure S57. $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 300 K) spectrum of (PNP)Sc(μ_2-$^{13}CPPh_3$)(μ_2-CH_3)$AlMe_2$ (**6-^{13}C**).

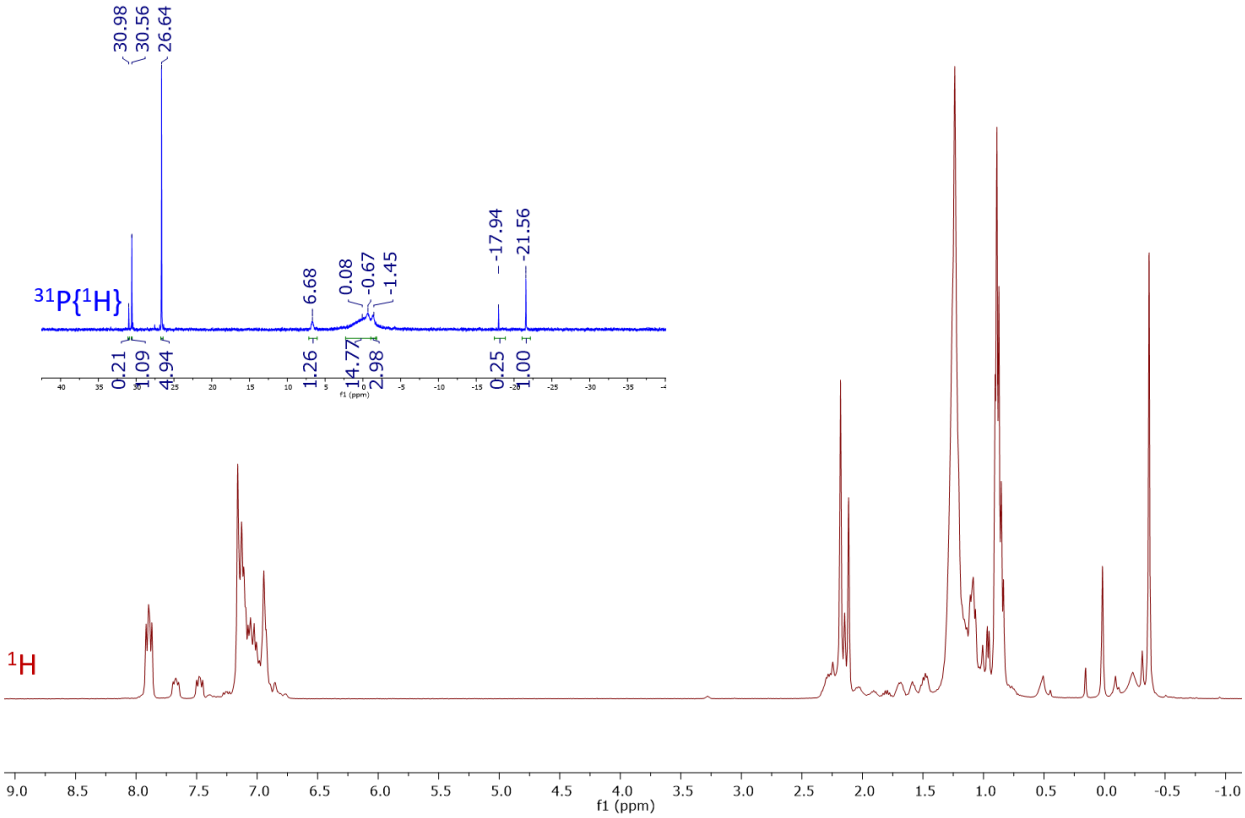


Figure S58. ^{1}H NMR (400 MHz, benzene-d_6, 300 K), ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K), spectra of the reaction mixture produced following addition of about 1 equivalent of $AlMe_3$ (2.0 M in hexanes) to (PNP)Sc($CHPPh_3$)(CH_3) in benzene-d_6 after 30 minutes.

X-Ray Crystallographic Information:

Crystallographic data are summarized Table S1-S2. Suitable crystals for X-ray analysis of **1** - **6** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker D8QUEST CMOS area detector or Bruker APEXII CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[1] producing a listing of non-averaged F 2 and $\int$(F 2) values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[2] The initial structures were determined by SHELXT.[3,4,3-5] The further structure determination was performed by Fourier transform method and refined by least squares method on SHELXL.[5‡] All reflections were used during refinement. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models, excluding those found from the difference map for structures of compounds **2**, **3**, and **6** mentioned in the main text of the article. The thermal ellipsoids were fixed by SHELXL restraints, RIGU and SIMU, and the bond lengths were fixed by DFIX.

Compound **1** crystal grew as a non-merohedral twin; the program CELL_NOW[6] was used to index the diffraction images and to determine the twinning mechanism. The crystal was twinned by a rotation of 180° about the 001 reciprocal direction. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[7] (minimum and maximum transmission 0.6054, 0.7456). There was a region of disordered solvent for which a reliable disorder model could not be devised; the X-ray data were corrected for the presence of disordered solvent using SQUEEZE.[4]

In the structure of compound **4** the adamantane moiety is disordered by a rotation of approximately 30° about the N4-C37 bond (the relative occupancies of the two disorder models are 0.53/0.47).

One of the Crystallographic Information Files of compound **6**, in the *C2/c* space group, called “9459” has a high R_{int} of 0.3215 with 6152 reflections out of 12920 with I > 2σ(I), which registerd A-level alerts in CheckCIF. This is due to weak diffraction of the sample. However, it does not appear that there is any error in the constitution of the structure solved using these data, supported by the same structural assignment being made in structure with CIF called “9543” which is of higher quality. Both 9459 and 9543 were submitted for the sake of completeness since they present compound **6** in both the space groups it tended to crystallize in practice.

These results were checked using the IUCR’s CheckCIF routine.

Table S1. Summary of Structure Determination of 1

Empirical formula	$C_{34}H_{62}NP_2ScSi_2$
Formula weight	647.92
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	12.6597(15)Å
b	14.6041(17)Å
c	14.8346(18)Å
α	109.894(5)°
β	105.782(5)°
γ	108.149(5)°
Volume	2220.6(5)Å^3
Z	2
d_{calc}	0.969 g/cm^3
μ	0.311 mm^{-1}
F(000)	704.0
Crystal size, mm	0.27 × 0.12 × 0.08
2θ range for data collection	3.222 - 55.104°
Index ranges	-16 ≤ h ≤ 15, -18 ≤ k ≤ 17, 0 ≤ l ≤ 19
Reflections collected	77246
Independent reflections	10173[R(int) = 0.0776]
Data/restraints/parameters	10173/0/377
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1093
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1155
Largest diff. peak/hole	0.57/-0.45 eÅ^{-3}

Table S2. Summary of Structure Determination of Compound 2

	2•(1/2 C_5H_{12})	**2**
Empirical formula	$C_{38.5}H_{73}AlNP_2ScSi_2$	$C_{36}H_{67}AlNP_2ScSi_2$
Formula weight	740.03	703.96
Temperature/K	100	100
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
A	13.9734(8)Å	10.9520(6)Å
B	17.3183(9)Å	14.0978(8)Å
C	21.9354(11)Å	27.7873(15)Å
A	67.158(2)°	90
B	77.272(3)°	100.030(2)°
Γ	68.459(2)°	90
Volume	4531.5(4)Å^3	4224.8(4)Å^3
Z	4	4
d_{calc}	1.085 g/cm^3	1.107 g/cm^3
M	0.330 mm^{-1}	0.351 mm^{-1}
F(000)	1612.0	1528.0
Crystal size, mm	0.35 × 0.13 × 0.05	0.24 × 0.18 × 0.13
2θ range for data collection	5.746 - 55.216°	5.78 - 55.1°
Index ranges	-18 ≤ h ≤ 18, -22 ≤ k ≤ 22, -28 ≤ l ≤ 28	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -36 ≤ l ≤ 36
Reflections collected	239059	175023
Independent reflections	20938[R(int) = 0.1115]	9729[R(int) = 0.0556]
Data/restraints/parameters	20938/176/927	9729/0/421
Goodness-of-fit on F^2	1.030	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.0950	R_1 = 0.0304, wR_2 = 0.0691
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1063	R_1 = 0.0389, wR_2 = 0.0729
Largest diff. peak/hole	0.49/-0.64 eÅ^{-3}	0.37/-0.33 eÅ^{-3}

Table S3. Summary of Structure Determination of Compound 3•(C_5H_{12})

Empirical formula	$C_{51}H_{71}NP_3Sc$
Formula weight	835.95
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	12.5485(5)Å
b	12.7502(5)Å
c	15.2081(6)Å
α	83.649(2)°
β	86.788(2)°
γ	85.681(2)°
Volume	2408.64(17)Å^3
Z	2
d_{calc}	1.153 g/cm^3
μ	0.286 mm^{-1}
F(000)	900.0
Crystal size, mm	0.29 × 0.11 × 0.03
2θ range for data collection	5.984 - 55.096°
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	59778
Independent reflections	11108[R(int) = 0.0519]
Data/restraints/parameters	11108/45/533
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1160
Final R indexes [all data]	R_1 = 0.0686, wR_2 = 0.1269
Largest diff. peak/hole	1.64/-0.84 eÅ^{-3}

Table S4. Summary of Structure Determination of Compound 4

Empirical formula	$C_{46}H_{82}AlN_4P_2ScSi_2$
Formula weight	881.21
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	12.969(2)Å
b	14.092(2)Å
c	14.336(2)Å
α	83.145(6)°
β	79.087(6)°
γ	87.572(6)°
Volume	2553.8(7)Å^3
Z	2
d_{calc}	1.146 g/cm^3
μ	0.304 mm^{-1}
F(000)	956.0
Crystal size, mm	0.44 × 0.42 × 0.11
2θ range for data collection	2.912 - 55.314°
Index ranges	-16 ≤ h ≤ 13, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	85162
Independent reflections	11796[R(int) = 0.0369]
Data/restraints/parameters	11796/0/620
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1301
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1380
Largest diff. peak/hole	1.52/-0.53 eÅ^{-3}

Table S5. Summary of Structure Determination of Compound 5•3(C_7H_8)

Empirical formula	$C_{58}H_{84}N_3P_2ScSi$
Formula weight	958.27
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	13.215(2)Å
b	15.972(3)Å
c	16.231(3)Å
α	64.146(6)°
β	84.121(5)°
γ	66.561(5)°
Volume	2818.1(9)Å^3
Z	2
d_{calc}	1.129 g/cm^3
μ	0.246 mm^{-1}
F(000)	1036.0
Crystal size, mm	0.18 × 0.15 × 0.07
2θ range for data collection	2.798 - 55.022°
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -20 ≤ l ≤ 21
Reflections collected	73135
Independent reflections	12930[R(int) = 0.0683]
Data/restraints/parameters	12930/162/598
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.1452
Final R indexes [all data]	R_1 = 0.0981, wR_2 = 0.1652
Largest diff. peak/hole	0.89/-0.56 eÅ^{-3}

Table S6. Summary of Structure Determination of Compound 6

	2(6)•3(C_7H_8)	**1/2[2(6)•1/2(C_7H_8)1/2(C_5H_{12})]**
Empirical formula	$C_{117}H_{152}Al_2N_2P_6Sc_2$	$C_{51}H_{69}AlNP_3Sc$
Formula weight	1916.10	860.92
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$
a	39.405(7)Å	16.6374(7)Å
b	11.884(2)Å	17.6783(7)Å
c	24.015(4)Å	33.7373(14)Å
β	97.304(5)°	97.6830(10)°
Volume	11154(3)Å^3	9833.8(7)Å^3
Z	4	8
d_{calc}	1.141 g/cm^3	1.163 g/cm^3
μ	0.270 mm^{-1}	0.298 mm^{-1}
F(000)	4104.0	3688.0
Crystal size, mm	0.28 × 0.05 × 0.03	0.48 × 0.16 × 0.08
2θ range for data collection	2.084 - 55.368°	5.21 - 55.138°
Index ranges	-51 ≤ h ≤ 51, -15 ≤ k ≤ 15, -31 ≤ l ≤ 19	-21 ≤ h ≤ 21, -23 ≤ k ≤ 22, -43 ≤ l ≤ 43
Reflections collected	142306	283447
Independent reflections	12920[R(int) = 0.3215]	22702[R(int) = 0.0721]
Data/restraints/parameters	12920/174/597	22702/498/1260
Goodness-of-fit on F^2	1.031	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0859, wR_2 = 0.2097	R_1 = 0.0530, wR_2 = 0.1074
Final R indexes [all data]	R_1 = 0.1975, wR_2 = 0.2602	R_1 = 0.0736, wR_2 = 0.1153
Largest diff. peak/hole	0.92/-0.68 eÅ^{-3}	0.45/-0.45 eÅ^{-3}

Computations

Computational Details

All density functional theory (DFT) calculations were performed using the Jaguar 9.1 quantum chemistry program.[8] All geometries are optimized with B3LYP hybrid functional[9a–b] along with Grimme's D3 dispersion correction[10] (B3LYP-D3). Main group atoms are described with 6-31G** basis set[11a–c] and Sc atom is treated with LACVP basis set which contains effective core potentials (ECP).[12a–c] The natural bond orbital (NBO) analysis was carried out using NBO 6.0 program[13a–c] in the Jaguar 9.1 suite. Electronic structures of the optimized geometries were re-evaluated with higher level basis sets, which are Dunning's correlation-consistent triple-ζ basis set, cc-pVTZ(-f)[14], for main group and LACV3P for Sc. Molecular orbitals of **6** are plotted by Chimera 1.14.[15]

Contour Plots of 2* Molecular Orbitals

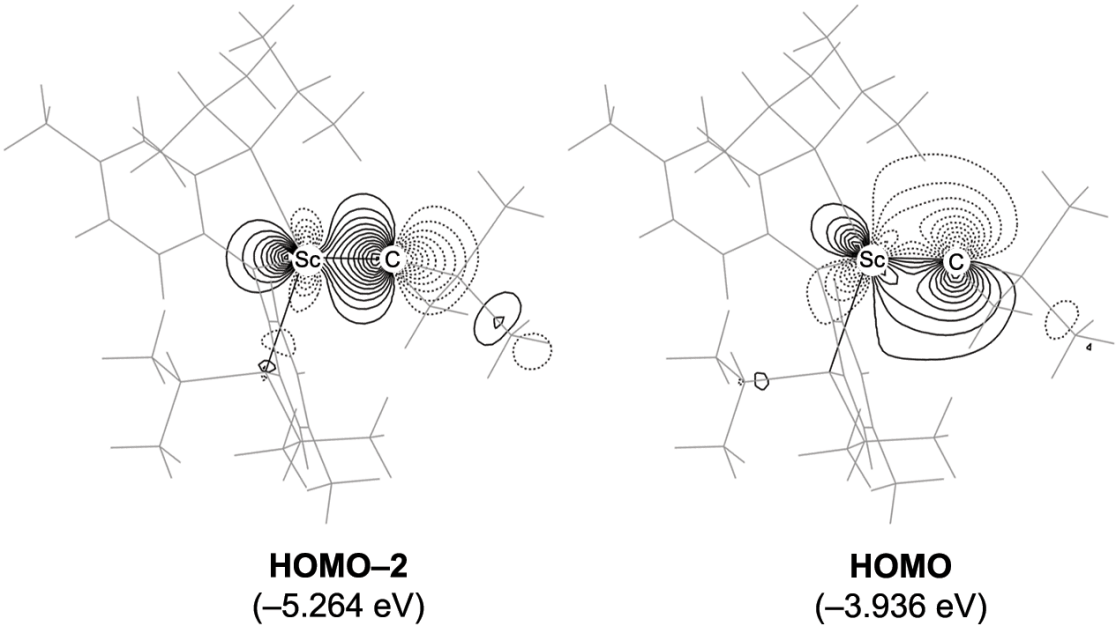
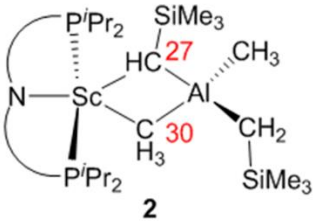


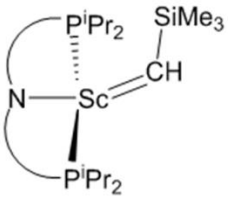
Figure S59. Contour plots of **2*** MO which show typical Schrock carbene nature.

Bond Information of Optimized Structures.



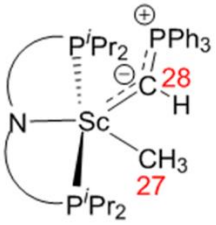
2

	Sc–C27	Sc–C30	Al–C27	Al–C30
Length(Å)	2.04	2.34	2.04	2.20
Mayer-Mulliken bond order	1.14	0.41	0.59	0.49



2*

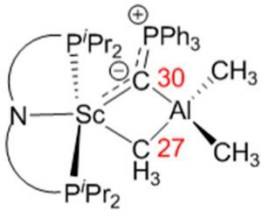
	Sc–C
Length(Å)	1.95
Mayer-Mulliken bond order	1.69



3

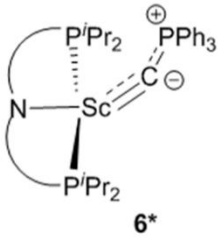
	Sc–C28	Sc–C27	C28–P
Length(Å)	2.10	2.22	1.69
Mayer-Mulliken bond order	1.02	0.84	1.39

Figure S60**.** Bond information of **2**, **2*** and **3**.



6

	Sc–C30	Sc–C27	Al–C30	Al–C27	C30–P
Length(Å)	1.99	2.34	2.02	2.17	1.68
Mayer-Mulliken bond order	1.31	0.58	0.34	0.54	1.42



6*

	Sc–C
Length(Å)	1.90
Mayer-Mulliken bond order	1.88

Figure S61. Bond information of **6** and **6***.

Cartesian Coordinates of All Optimized Geometries

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2

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Sc	7.278295994	9.847072601	4.083805084
P	8.509799957	10.699338913	1.811142087
P	7.178935051	10.591070175	6.694729805
N	7.190423965	12.026040077	4.093093872
H	6.275679111	10.004794121	-0.112637803
H	9.997303963	11.314104080	7.384210110
H	6.730054379	8.562604904	0.799782515
H	10.076177597	9.693366051	6.670030594
H	9.282841682	7.923368454	0.995536029
H	8.290827751	7.890747547	7.397003174
C	10.229556084	11.452233315	1.883069396
C	5.452954292	10.510973930	7.440726757
H	10.900519371	10.585227966	1.942138791
H	5.186794281	9.447100639	7.389514923
C	10.386986732	12.275910378	3.171792030
C	4.486220837	11.304303169	6.542402267
H	10.166955948	11.687616348	4.068502903
H	4.524403095	10.980148315	5.498787403
H	9.713388443	13.137778282	3.177482367
H	4.725316525	12.372673988	6.569398403
H	11.414605141	12.649048805	3.253214121
H	3.458027363	11.175703049	6.898689270
C	7.350327015	12.106335640	1.651069522
C	7.541125298	12.362481117	6.489087105
C	6.940625191	12.646786690	0.421585649
C	7.875768185	13.198153496	7.565435410
C	5.986613274	13.660602570	0.340454668
C	8.164709091	14.552124023	7.398149014
C	5.424388885	14.120382309	1.543747187
C	8.124385834	15.049956322	6.086489201

C	5.811445236	13.600356102	2.770601988
C	7.802467346	14.246212959	5.002413273
H	5.353877544	13.965472221	3.684771061
H	7.798677444	14.678833961	4.008184433
C	6.796240330	12.593331337	2.864669800
C	7.484887600	12.873533249	5.160926819
C	5.571091652	8.789743423	3.709735870
C	8.633329391	7.939186096	4.314910412
H	9.243337631	8.072036743	3.410008907
H	8.915208817	6.961207867	4.712635517
H	5.287170887	9.055910110	4.759034634
H	9.046016693	8.626194954	5.079572201
C	8.438487053	9.770765305	0.190146014
C	8.366504669	9.986907959	8.006712914
C	10.579245567	12.277986526	0.637665689
C	5.367617607	10.991466522	8.894948959
H	7.375357628	12.268073082	-0.499932975
H	7.919827461	12.778087616	8.567604065
H	4.659263134	14.892992973	1.511535883
H	8.361386299	16.097545624	5.908934593
H	8.681141853	10.470540047	-0.618839502
C	7.023560047	9.213312149	-0.028772892
C	9.480159760	8.639075279	0.190171853
C	8.120093346	8.497204781	8.291467667
H	8.168265343	10.561876297	8.919424057
C	9.818641663	10.252448082	7.576698303
H	10.574878693	11.674371719	-0.275482297
H	11.581045151	12.711250305	0.741227627
H	9.869292259	13.101465225	0.506116629
H	5.990882397	10.398421288	9.571029663
H	4.333153248	10.916293144	9.250159264
H	5.668439865	12.041340828	8.977408409
H	6.992599964	8.619173050	-0.949427307
H	10.504386902	9.009685516	0.299643129
H	9.428379059	8.089161873	-0.756331444

H	7.098670483	8.302281380	8.633625031
H	8.804800987	8.144806862	9.071323395
H	10.505917549	9.927671432	8.366433144
C	5.544216156	14.226188660	-0.988296926
H	6.199869156	13.901787758	-1.802160740
H	4.525661945	13.903643608	-1.236351490
H	5.540884495	15.322103500	-0.977278709
C	8.533775330	15.442506790	8.560748100
H	8.317880630	14.961770058	9.520008087
H	9.601990700	15.693857193	8.551810265
H	7.982473373	16.389476776	8.531296730
C	3.858248472	7.555406094	1.391911030
Si	3.990954399	8.887330055	2.738733053
C	3.768639565	10.591458321	1.918094397
C	2.518481016	8.657532692	3.924250126
H	4.666963100	7.622360229	0.657338679
H	3.900609970	6.552004814	1.829729915
H	2.909070730	7.646762371	0.849726140
H	3.740622520	11.381320000	2.677879095
H	4.599415779	10.835482597	1.247483134
H	2.838203907	10.648910522	1.338872790
H	2.559438944	7.677669048	4.414270401
H	2.532652378	9.420925140	4.712140560
H	1.556064487	8.735877991	3.403950691
C	6.967440605	5.881751060	2.425915718
Al	6.638329029	7.078047752	3.982136965
C	6.136025906	6.260876656	5.740045071
H	6.103608608	5.238025188	2.214485645
H	7.190353394	6.420012951	1.495543480
H	7.818234921	5.211492062	2.614231586
H	5.054731369	6.052585602	5.684567451
H	6.235710144	7.054786205	6.496721745
Si	6.964174271	4.705223083	6.363098621
C	6.462922573	4.328548908	8.159605026
C	6.472586632	3.240272522	5.264556885

C	8.864707947	4.832771301	6.340561390
H	6.762916565	5.145914555	8.827565193
H	5.376282692	4.214454651	8.250505447
H	6.928925991	3.408557653	8.532724380
H	6.949745655	2.308150053	5.588659286
H	5.387714386	3.082432032	5.280331612
H	6.761982918	3.424690247	4.223937988
H	9.255729675	4.852127552	5.316356182
H	9.225179672	5.732908249	6.853095055
H	9.316139221	3.968554020	6.842643738

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2*

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Sc	11.038753510	1.280474305	2.924827337
P	11.988267899	2.802769423	0.938193262
P	8.923414230	-0.399616510	3.176842928
N	11.138617516	0.020635501	1.186477900
C	13.170694351	4.249855995	0.993836462
H	13.660842896	4.326866150	0.014947548
C	12.406586647	5.557455540	1.260033846
H	13.114732742	6.388324261	1.356066108
H	11.839343071	5.498591900	2.196399689
H	11.710835457	5.808805943	0.454616249
C	14.228719711	4.005663395	2.084028244
H	14.904750824	4.867181778	2.144818783
H	14.828372002	3.113734961	1.887653351
H	13.755841255	3.859113455	3.060384274
C	10.831528664	3.034923792	-0.532886505
H	10.552905083	1.995248795	-0.747239769
C	9.549032211	3.788403511	-0.151329920
H	8.848444939	3.792613506	-0.994677544
H	9.744886398	4.830751419	0.119268425
H	9.042509079	3.310503721	0.695639491
C	11.519123077	3.620218754	-1.771871805

H	10.842130661	3.587605715	-2.633824825
H	12.419116974	3.053262949	-2.030538082
H	11.805858612	4.666676044	-1.620103121
C	12.983708382	1.369588017	0.353848994
C	14.253456116	1.469300151	-0.233194485
H	14.715851784	2.444745064	-0.356814623
C	14.949909210	0.343928874	-0.678528666
C	16.329832077	0.459380329	-1.281043768
H	16.439165115	-0.182963282	-2.161875486
H	17.100318909	0.155233800	-0.561395288
H	16.551790237	1.487184405	-1.584743142
C	14.332519531	-0.907826900	-0.524391770
H	14.855678558	-1.802361608	-0.855599105
C	13.080163002	-1.033362389	0.061865758
H	12.632102966	-2.013355732	0.194309935
C	12.375210762	0.096922882	0.517351866
C	10.084275246	-0.709399998	0.649798751
C	10.044540405	-1.127679825	-0.704890907
H	10.887531281	-0.900583208	-1.348320246
C	8.947921753	-1.795088410	-1.230914116
H	8.962018967	-2.083441496	-2.280530691
C	7.817772865	-2.091510534	-0.453102708
C	6.638369560	-2.831333876	-1.038623691
H	5.769907475	-2.794058084	-0.373305917
H	6.871477127	-3.889267206	-1.215361714
H	6.336756229	-2.405768394	-2.003095865
C	7.841147423	-1.675476193	0.878813744
H	6.970143318	-1.881683946	1.496109843
C	8.933677673	-0.999541104	1.444223881
C	7.157225132	0.136057839	3.486213207
H	6.492164135	-0.703688025	3.251596689
C	6.963958263	0.513799012	4.962853909
H	5.937640667	0.859633446	5.132493973
H	7.641457081	1.324429154	5.257626057
H	7.144150257	-0.332642287	5.632679462

C	6.813544273	1.306468010	2.550417900
H	5.777195454	1.628979683	2.704283476
H	6.932887077	1.030527472	1.498865128
H	7.457777500	2.173389435	2.750052452
C	9.228442192	-1.913779378	4.241228104
H	9.208254814	-1.524954081	5.267584324
C	10.648921013	-2.427861929	3.949450731
H	10.879668236	-3.279551983	4.599604130
H	11.397323608	-1.647426009	4.125199318
H	10.736436844	-2.761772871	2.909392595
C	8.174947739	-3.016447544	4.088339806
H	8.411140442	-3.853060484	4.756091118
H	8.160538673	-3.401556015	3.063817739
H	7.166384697	-2.669758081	4.338664055
C	12.402812004	1.214584589	4.325210571
H	11.989253044	1.874783874	5.120774746
Si	14.043824196	0.481825322	4.701578617
C	15.360874176	1.780712366	5.177927971
H	15.522084236	2.492024183	4.359859467
H	15.045975685	2.355920792	6.057206631
H	16.325710297	1.313392878	5.412946224
C	14.707861900	-0.457477808	3.186362982
H	14.008042336	-1.239406705	2.870549679
H	14.851265907	0.208948120	2.329022884
H	15.669464111	-0.938326120	3.403898239
C	13.984375954	-0.776043713	6.139363766
H	13.629437447	-0.303004503	7.063080311
H	13.294905663	-1.595767140	5.903965473
H	14.970058441	-1.214050770	6.343765259

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3

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Sc	11.816075325	2.051324129	3.443052530
P	12.356126785	4.002037048	1.560087681

P	11.330862999	-0.585710108	3.882022619
N	12.023221970	1.017601967	1.474872708
C	14.123449326	4.433642864	1.068051219
H	14.546435356	4.901200771	1.962180138
C	14.903303146	3.141935825	0.785173297
H	15.951118469	3.379186153	0.566224337
H	14.485682487	2.610875368	-0.077278234
H	14.890397072	2.461091995	1.637472272
C	14.240439415	5.410383701	-0.109872572
H	15.299008369	5.595129490	-0.330525607
H	13.779456139	6.380501747	0.099018313
H	13.779934883	4.997294426	-1.013782620
C	11.450284004	5.643915176	1.518863559
H	11.654605865	6.114526749	0.549644649
C	9.933045387	5.445450306	1.648528218
H	9.425550461	6.415317059	1.577274561
H	9.674375534	4.997136593	2.610763073
H	9.539755821	4.799375534	0.858682275
C	11.992945671	6.559225082	2.627908945
H	11.464569092	7.520254612	2.613557816
H	13.062090874	6.762292862	2.515165567
H	11.840847015	6.106946945	3.614465237
C	11.691989899	3.061378479	0.139756233
C	11.236430168	3.675747395	-1.037271857
H	11.317318916	4.755584240	-1.134956956
C	10.668776512	2.957900763	-2.089502335
C	10.214286804	3.630764961	-3.362747669
H	9.227079391	3.271617413	-3.676347017
H	10.905456543	3.431765318	-4.192434788
H	10.151089668	4.716956615	-3.242583990
C	10.541831970	1.571403623	-1.915750742
H	10.073325157	0.977030337	-2.698543072
C	10.981830597	0.937532604	-0.763672709
H	10.851027489	-0.134866670	-0.665872037
C	11.596373558	1.649823308	0.295845807

C	12.486668587	-0.302218854	1.384336233
C	13.246073723	-0.772722960	0.283685774
H	13.444787025	-0.095883057	-0.540801585
C	13.744253159	-2.067630529	0.239922553
H	14.325529099	-2.379664660	-0.626351833
C	13.544323921	-2.973181486	1.294567227
C	14.143414497	-4.358954906	1.257035255
H	13.710078239	-5.004260540	2.027554512
H	15.228281975	-4.331048012	1.426012635
H	13.983146667	-4.842083454	0.286283970
C	12.806370735	-2.518832207	2.388659477
H	12.642474174	-3.198103189	3.221847773
C	12.279356956	-1.220757842	2.453381300
C	9.569890022	-1.178712249	3.578543901
H	9.001867294	-0.777073443	4.427819252
C	9.034379959	-0.524415612	2.294829845
H	7.981421947	-0.792365193	2.147632599
H	9.594777107	-0.867281318	1.419537663
H	9.108780861	0.565556824	2.333835602
C	9.416726112	-2.704125643	3.538959026
H	8.374501228	-2.973786116	3.328762293
H	9.692613602	-3.175719023	4.487661362
H	10.038930893	-3.137055635	2.748140335
C	11.922751427	-1.549157500	5.372433662
H	11.740166664	-2.615901232	5.190994740
C	11.109651566	-1.110196471	6.601222992
H	11.452667236	-1.651256084	7.490968704
H	10.038316727	-1.306791306	6.486994267
H	11.241747856	-0.038034990	6.785738468
C	13.424530983	-1.327096105	5.600934029
H	13.746582985	-1.858014941	6.505170345
H	13.633641243	-0.260711312	5.727666378
H	14.027654648	-1.685126185	4.763064384
C	13.248334885	2.429058313	4.929066658
C	9.844080925	2.787496090	4.153478146

H	12.719613075	3.020910501	5.691206932
H	9.478427887	2.101120472	4.937360764
H	9.054543495	2.835893393	3.387428999
H	9.898883820	3.783669710	4.621764660
P	14.914551735	2.593001842	5.120443344
C	15.462245941	2.695968866	6.874166965
C	16.587394714	3.428098440	7.282281876
C	14.698159218	2.019816160	7.834960461
C	16.945545197	3.474792242	8.630041122
C	15.057904243	2.068222284	9.181191444
C	16.182130814	2.794685841	9.580636978
H	17.175704956	3.972153902	6.549046993
H	13.815175056	1.473450303	7.514838696
H	17.815355301	4.048944950	8.938114166
H	14.457515717	1.543869138	9.919777870
H	16.458534241	2.836601734	10.630822182
C	15.869676590	1.221382618	4.365409851
C	17.143808365	0.875454545	4.839823723
C	15.332344055	0.508176863	3.286360025
C	17.865947723	-0.155010596	4.234475613
C	16.054643631	-0.517537534	2.677390099
C	17.325994492	-0.851426303	3.150198460
H	17.571779251	1.402976871	5.687148571
H	14.339378357	0.738523126	2.922443390
H	18.850280762	-0.414349228	4.615051746
H	15.611496925	-1.053364754	1.844940543
H	17.890182495	-1.652683735	2.680621624
C	15.682751656	4.121949196	4.404420853
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References:

‡R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$, $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$; where n = the number of reflections and p = the number of parameters refined.

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