Supporting Information

for

Strikingly diverse reactivity of structurally identical silylene and stannylene

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Content:

[S1] Experimental Section

All manipulations were carried out under an inert gas atmosphere of dinitrogen using standard Schlenk technique and in a dinitrogen-filled MBRAUN MB 150-GI glove-box. All solvents were purified by MBRAUN MB SPS-800 solvent purification system. The starting material **1** and **2** were prepared using literature procedures. All other chemicals purchased from Aldrich were used without further purification. The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ using a Bruker 400 MHz spectrometer. Mass spectra were recorded using an AB Sciex 4800 plus MALDI TOF/TOF instrument.

Synthesis of [{PhC(N*t*Bu)$_2$}Si{N(SiMe$_3$)$_2$}]$_2$Cu$_2$Br$_2$ (4):

40 mL toluene was added into the mixture of compound **1** (0.419 g, 1 mmol) and CuBr (0.145 g, 1 mmol) in a 100 mL Schlenk flask. After 30 min the solution became colorless. It was stirred overnight at room temperature and was filtered and concentrated. Colorless crystals of **4** were found at 0 °C. Yield: 65% (0.400 g). Mp: 145-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.24 (*s*, 18H, Si*Me$_3$*), 0.46 (*s*, 18H, Si*Me$_3$*), 1.19 (*s*, 36H, C*Me$_3$*), 7.07-7.13 (*m*, 3H, Ph), 7.23-7.29 (*m*, 2H, Ph), 7.36-7.49 (*m*, 5H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 3.56 (Si*Me$_3$*), 4.92 (Si*Me$_3$*), 30.81 (C*Me$_3$*), 53.67 (*C*Me$_3$), 124.28, 126.36, 127.12, 127.18, 127.20, 128.01, 129.69, 130.05, 136.84 (Ph-*C*); 167.25 (N*C*N) ppm. $^{29}Si\{^{1}H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 5.72 (*Si*N(SiMe$_3$)$_2$); 6.80 (*Si*Me$_3$); 7.15 (*Si*Me$_3$) ppm. HRMS: *m/z* ($C_{42}H_{82}Cu_2Br_2N_6Si_6$): 1122.6686 [$M^+$]. Anal. Calcd. C, 44.78; H, 7.34; N, 7.46. Found: C, 44.76; H, 7.54; N, 7.64.

Synthesis of [{PhC(N*t*Bu)$_2$}Si{N(SiMe$_3$)$_2$}]$_2$Cu$_2$Cl$_2$ (5):

Compound **1** (0.419 g, 1 mmol) and CuCl (0.100g, 1 mmol) were taken in a 100 mL Schlenk flask and 40 mL toluene was added to it. The solution became colorless after 7 hour stirring at room temperature. Then it was filtered, concentrated, and stored at 0 °C overnight to afford colorless crystals. Yield: 65% (0.350 g). Mp: 110-114 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.23 (*s*, 18H, Si*Me$_3$*), 0.46 (*s*, 18H, Si*Me$_3$*), 1.18 (*s*, 36H, C*Me$_3$*), 7.06-7.13 (*m*, 2H, *Ph*), 7.22-7.27 (*m*, 2H, Ph), 7.29-7.35 (*m*, 2H, Ph), 7.39-7.45 (*m*, 4H, Ph) ppm; $^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 3.57 (Si*Me$_3$*), 4.97 (Si*Me$_3$*), 30.83 (C*Me$_3$*), 53.68 (*C*Me$_3$), 124.28, 126.22, 127.12, 127.20, 127.37, 128.01, 129.73, 130.00, 131.31, 136.84 (Ph-*C*), 167.40 (N*C*N) ppm. $^{29}Si\{^{1}H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 4.79 (*Si*N(SiMe$_3$)$_2$); 6.78 (*Si*Me$_3$); 7.17 (*Si*Me$_3$) ppm. MALDI: *m/z* ($C_{42}H_{82}Cu_2Cl_2N_6Si_6$): 1035.43 [M+H]$^+$. Anal. Calcd. C, 48.62; H, 7.97; N, 8.10. Found: C, 48.49; H, 7.78; N, 8.08.

Synthesis of PhC(N*t*Bu)$_2$SnBr (6):

Toluene (40 mL) was added to the mixture of **2** (0.510 g, 1 mmol) and CuBr (0.143g, 1

mmol) in a 100 mL Schlenk flask and the solution of the reaction mixture became pale yellow after overnight stirring at room temperature. The solution was filtered, concentrated to 10 mL and kept at 0 °C to afford colorless crystals of **6** suitable for single crystal X-ray analysis. Yield: 70% (0.300 g). Mp: 100-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.95 (*s*, 18H, C*Me*$_3$), 7.14-7.44 (*m*, 5H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 31.22 (C*Me*$_3$), 51.84 (*C*Me$_3$), 126.56, 127.57, 128.22, 136.59 (Ph-*C*), 173.86 (N*C*N) ppm. ^{119}Sn{^{1}H} NMR (149.18 MHz, $CDCl_3$, 298K): δ 68.45 ppm. HRMS: m/z ($C_{21}H_{41}N_3Si_3S$): 431.06 [M$^+$]. Anal Calcd: C, 41.90; H, 5.39; N, 6.52. Found: C, 41.64; H, 5.92; N, 6.67.

Synthesis of {PhC(NtBu)$_2$}Si{N(SiMe$_3$)$_2$}]$_2$Ag (9):

Two equivalent of **1** (0.420 g, 1 mmol) and one equivalent of $AgSbF_6$ (0.171g, 0.5 mmol) were taken in 40 mL toluene in a 100 mL Schlenk flask and the solution of the reaction mixture became colorless after overnight stirring at room temperature. The solution was filtered, concentrated to 15 mL and kept at 0 °C to afford colorless crystals of **9** suitable for single crystal X-ray analysis. Yield: 59% (0.350 g). Mp: 150-154^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.29 (*s*, 18H, Si*Me*$_3$), 0.47 (*s*, 18H, Si*Me*$_3$), 1.22 (s, 18H, C*Me*$_3$), 7.34-7.58 (*m*, 5H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 3.83 (Si*Me*$_3$), 5.34 (Si*Me*$_3$), 30.60 (C*Me*$_3$), 53.79 (*C*Me$_3$), 124.26, 125.56, 127.19, 127.25, 127.49, 127.73, 128.00, 129.24, 130.35, 136.84 (Ph-*C*), 167.64 (N*C*N) ppm. ^{29}Si NMR (79.495 MHz, $CDCl_3$, 298 K): δ 11.62 ppm (dd, ^{1}J ^{29}Si to ^{109}Ag = 333.05 and ^{1}J ^{29}Si to ^{107}Ag = 288.50 Hz), 8.61 (*m*, N(*Si*Me$_3$)$_2$), 7.16 (m, N(*Si*Me$_3$)$_2$) ppm. ^{19}F{^{1}H} NMR (376.66 MHz, $CDCl_3$, 298 K): δ -121 ppm (br). HRMS: *m/z* ($C_{42}H_{82}N_6Si_6AgSbF_6$): 947.50 [M-$SbF_6$]$^+$. Anal Calcd: C, 42.63; H, 6.99; N, 7.10. Found: C, 42.92; H, 6.75; N, 7.33.

Synthesis of {PhC(N*t*Bu)$_2$}Sn{N(SiMe$_3$)$_2$}]$_2$Ag (10):

Two equivalent of **2** (0.510 g, 1 mmol) and one equivalent of $AgSbF_6$ (0.171g, 0.5 mmol) were taken in 40 mL toluene in a 100 mL Schlenk flask and the solution of the reaction mixture became colorless after overnight stirring at room temperature. The solution was filtered, concentrated to 15 mL and kept at 0 °C to afford colorless crystals of **10** suitable for single crystal X-ray analysis. Yield: 56% (0.380 gm). Mp: 155-159^{o}C (Decomposed). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): 0.29 (*s*, 36H, Si*Me*$_3$), 1.04 (s, 36H, C*Me*$_3$), 7.17-7.46 (*m*, 10H, Ph) ppm; ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): 31.71 (C*Me*$_3$), 53.00 (*C*Me$_3$), 126.62, 127.05, 127.15, 127.49, 127.60, 128.29, 128.81, 134.09 (Ph-*C*), 170.29 (N*C*N) ppm; ^{119}Sn{^{1}H} NMR (149.18 MHz, $CDCl_3$, 298K): δ 99.15 ppm (dd, ^{1}J ^{119}Sn to ^{109}Ag = 4176.96 and ^{1}J ^{119}Sn to ^{107}Ag = 3668.40 Hz); ^{19}F{^{1}H} NMR (376.66 MHz, $CDCl_3$, 223 K): δ -120 ppm (br); HRMS: m/z ($C_{42}H_{82}N_6Si_4Sn_2AgSbF_6$): 1126.47 [M-$SbF_6$-H]$^+$; Anal Calcd: C,

36.97; H, 6.06; N, 6.16. Found: C, 36.57; H, 6.47; N, 6.52.

[S2] Crystal Data and Structure Refinements for 4, 5, 6, 9 and 10.

Crystallography reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo Kα radiation (λ = 0.710 73 Å) for **4** and **5**. The structures were solved by direct method and refined by full-matrix least-squares methods against F^2 (SHELXL-2014/6). Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC: CCDC no. 1474385(**4**), 1474386(**5**), 1535769(**6**), 1535770(**9**), 1535771(**10**).

Formula	$C_{49}H_{89}Br_2Cu_2N_6Si_6$ **(4)**	$C_{49}H_{90}Cl_2Cu_2N_6Si_6$ **(5)**
Formula weight	1217.70	1129.78
T, K	100(2)	100(2)
Color, Habit	Colorless, block	Colorless, block
Crystal System	Triclinic	Triclinic
Space Group	*P*-1	*P*-1
a, Å	11.0391(10)	11.0995(16)
b, Å	16.2036(16)	16.235(2)
c, Å	18.0379(16)	17.997(3)
α, deg	85.486(2)	84.770(4)
β, deg	72.999(2)	72.241(4)
γ, deg	75.928(2)	74.247(4)
V, Å^3	2992.8(5)	2972.4(8)
Z	2	2
d_{calcd}, g cm^{-3}	1.351	1.262
wavelength [Å]	0.71073	0.71073
μ (MoK_α)[mm^{-1}]	2.202	0.963
crystal size [mm^3]	0.2*0.1*0.1	0.2*0.1*0.1
Θ limits [°]	2.114 to 25.250	2.377 to 25.249
completeness to Θ (%)	99.9	99.9
reflns measured	64740	59699
independent reflns[a]	6450 [$R_{(int)}$ 0.1600]	6422 [$R_{(int)}$ 0.1502]
restraints	18	6
parameters	610	611
R_1(R_1 all data)[b]	0.0650 (0.1368)	0.0543 (0.1263)
wR_2(wR_1 all data)[c]	0.1310 (0.1546)	0.0857 (0.0996)
GOF	1.061	1.171

max., min peaks [eÅ-3]	1.843(-0.766)	0.586 (-0.575)

Crystal Data and Structure Refinements for 6, 9 and 10.

	6	9	10
Chemical formula	$C_{15}H_{23}BrN_2Sn$	$C_{42}H_{82}AgF_6N_6SbSi_6$	$C_{42}H_{79.50}AgF_6N_6SbSi_4Sn_2$
Formula weight	429.95 g/mol	1183.29 g/mol	1361.97 g/mol
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P* -1	$P\,2_1/_n$	*C* 2/*c*
Unit cell dimensions	*a* = 6.2709(19) Å	*a* = 14.897(6) Å	*a* = 15.748(3) Å
	b = 10.323(3) Å	*b* = 28.235(12) Å	*b* = 19.935(4) Å
	c = 13.767(5) Å	*c* = 14.912(7) Å	*c* = 20.701(4) Å
	α = 86.414(9)°	α = 90°	α = 90.00(3)°
	β = 84.020(8)°	β = 92.587(11)°	β = 107.03(3)°
	γ = 85.949(8)°	γ = 90°	γ = 90.00(3)°
Volume	882.8(5) Å^3	6266(5) Å^3	6214(2) Å^3
Z	2	4	4
Density (calculated)	1.618 g/cm^3	1.254 g/cm^3	1.456 g/cm^3
Absorption coefficient	3.701 mm^{-1}	0.907 mm^{-1}	1.661 mm^{-1}
F(000)	424	2448	2726
Theta range for data collection	2.41 to 27.66°	2.38 to 26.73°	2.30 to 22.32°
Index ranges	-7<=*h*<=7 -12<=*k*<=12 -16<=*l*<=16	-17<=*h*<=17 -33<=*k*<=33 -17<=*l*<=17	-18<=*h*<= 18 -23<=*k*<=23 -24<=*l*<= 24
Reflections collected	15506	102096	95896
Independent reflections	3205 [R(int)= 0.1081]	11322 R(int)= 0.0817]	5635 [R(int)= 0.1741]

Coverage of independent reflections	99.9%	99.9%	99.9%
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data/ restraints/ parameters	3205/6/178	11322/0/583	5635/48/380
Goodness-of-fit on F2	1.011	1.043	1.021
Δ/ σ max	0.001	0.003	0.001
Final R indices	2141 data; [$I>2\sigma(I)$] R_1= 0.0571, wR_2= 0.1313	8888 data; [$I>2\sigma(I)$] R_1= 0.0422, wR_2= 0.0835	3519 data; [$I>2\sigma(I)$] R_1= 0.0519, wR_2= 0.1157
	all data, R_1 = 0.0971, wR_2 = 0.1514	all data, R_1 = 0.0643, wR_2 = 0.0900	all data, R_1= 0.1040, wR_2 = 0.1479
Largest diff. peak and hole	0.866 and -0.724 eÅ^{-3}	0.829 and -0.440 eÅ^{-3}	1.020 and -0.729 eÅ^{-3}
R. M. S deviation from mean	0.136 eÅ^{-3}	0.076 eÅ^{-3}	0.107 eÅ^{-3}

[a] Observation criterion: $I>2\sigma(I)$. [b] $R_1=\Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$. [c] $wR2= \{\Sigma[w-(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

[S3]. Molecular Structures of $[MN(SiMe_3)_2]_4$ (M= Cu and Ag).

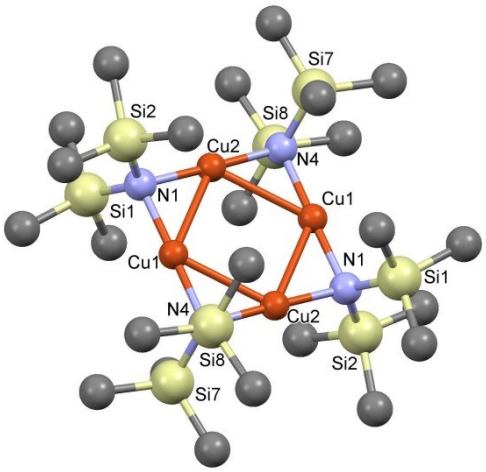

Figure S1. Molecular structure of $[CuN(SiMe_3)_2]_4$. Hydrogen atoms are not shown for clarity.

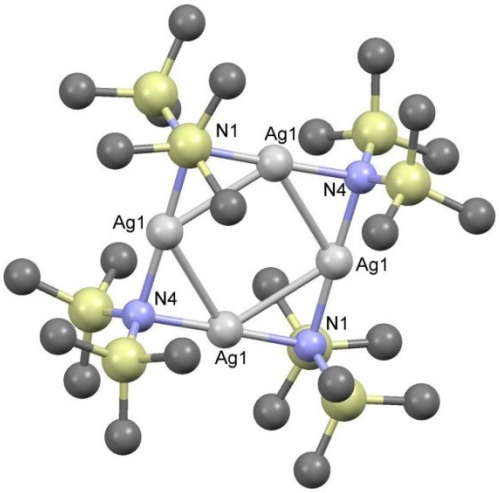

Figure S2. Molecular structure of $[AgN(SiMe_3)_2]_4$. Hydrogen atoms are not shown for clarity.

[S4] NMR Spectra

Compound **4**:

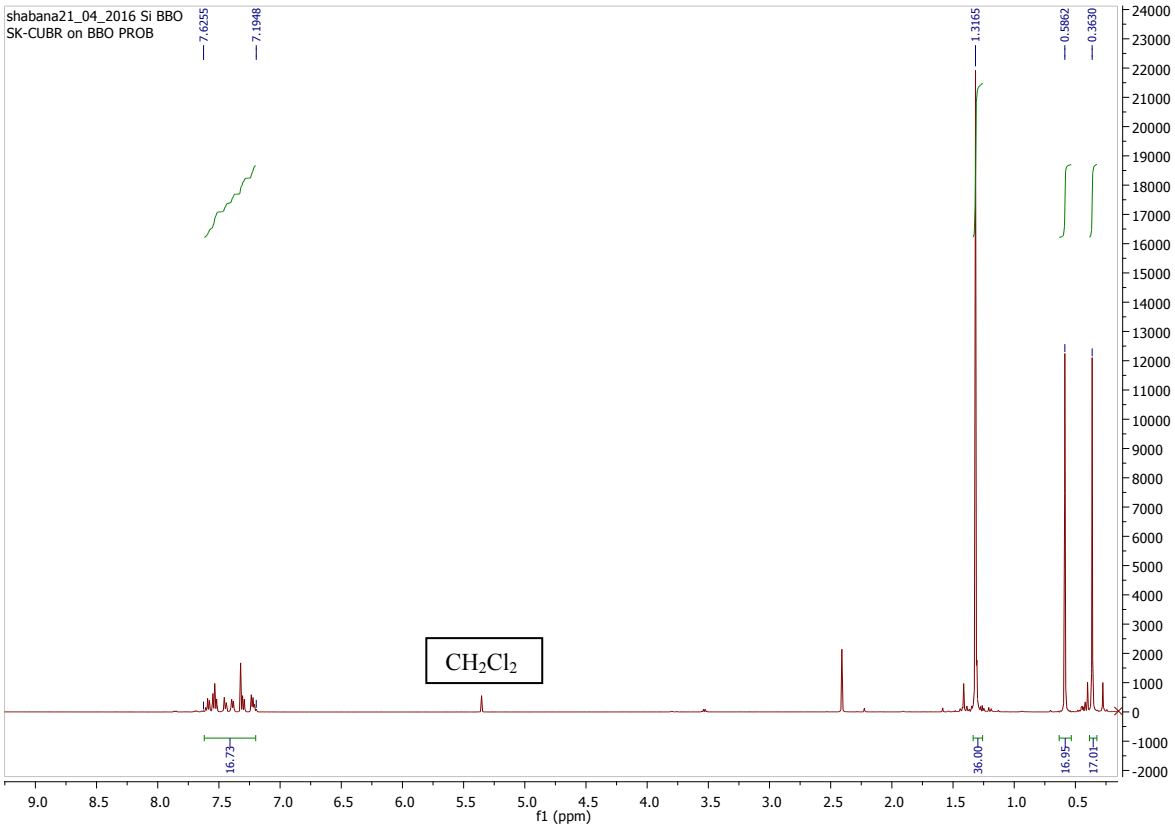

Figure S3. ^1H NMR of **4** in $CDCl_3$

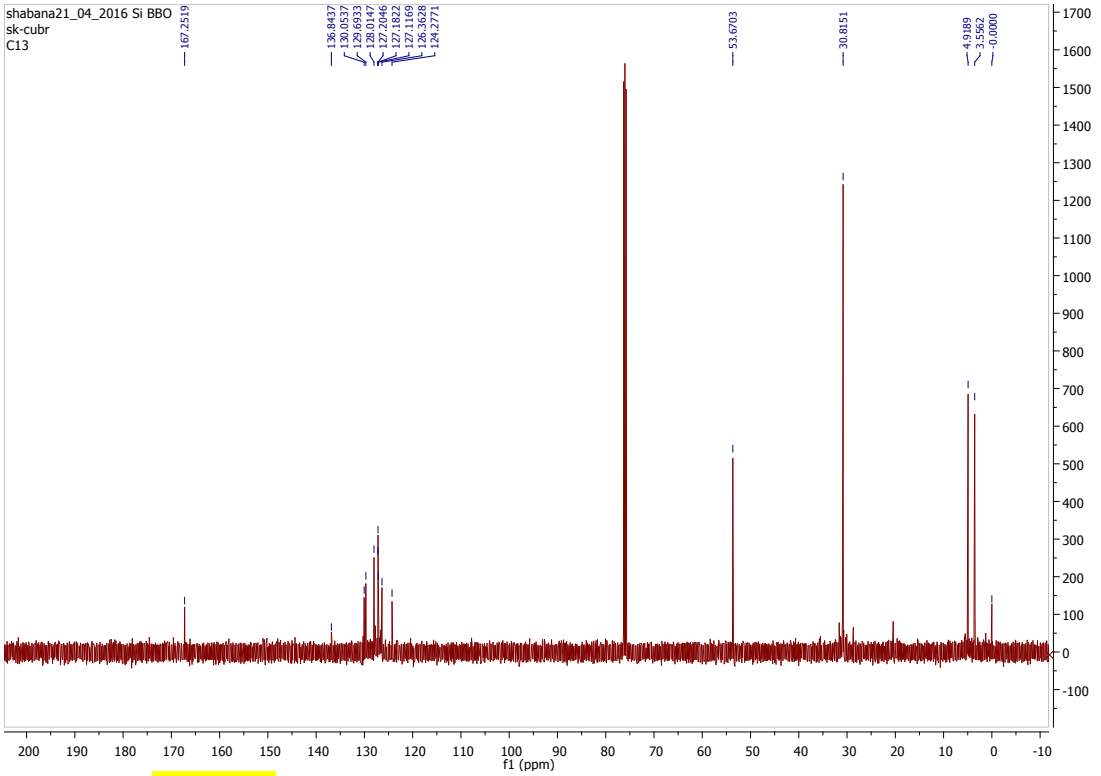

Figure S4. ^{13}C NMR of **4** in $CDCl_3$

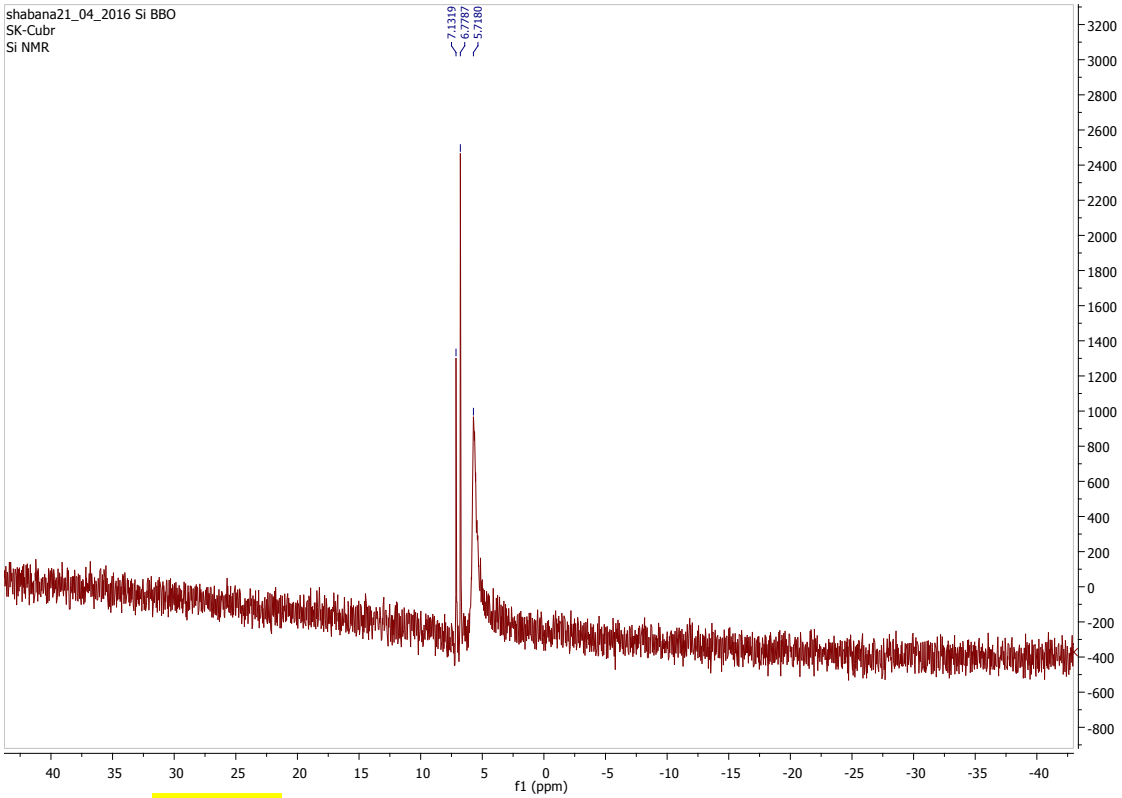

Figure S5. ^{29}Si NMR of **4** in $CDCl_3$

Compound **5**:

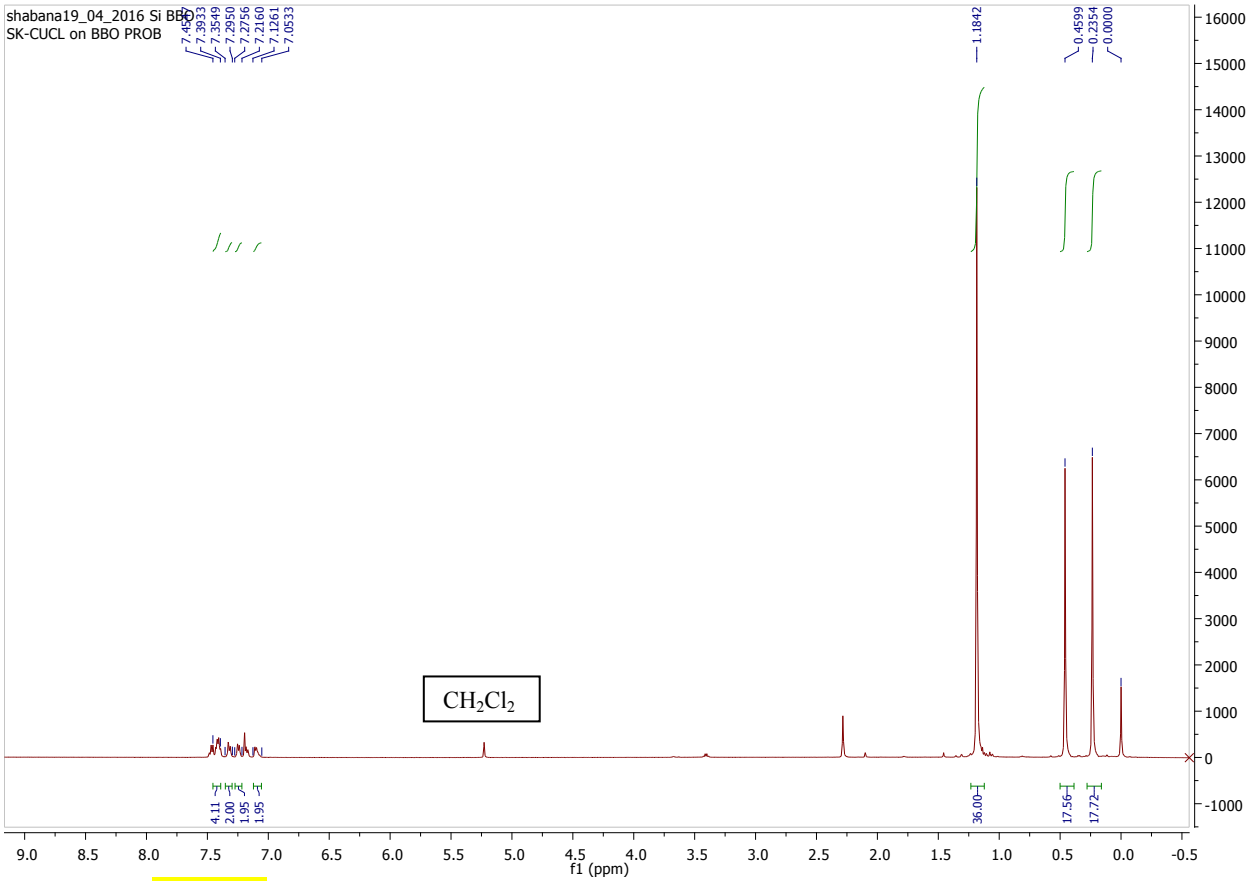

Figure S6. ^{1}H NMR of **5** in $CDCl_3$

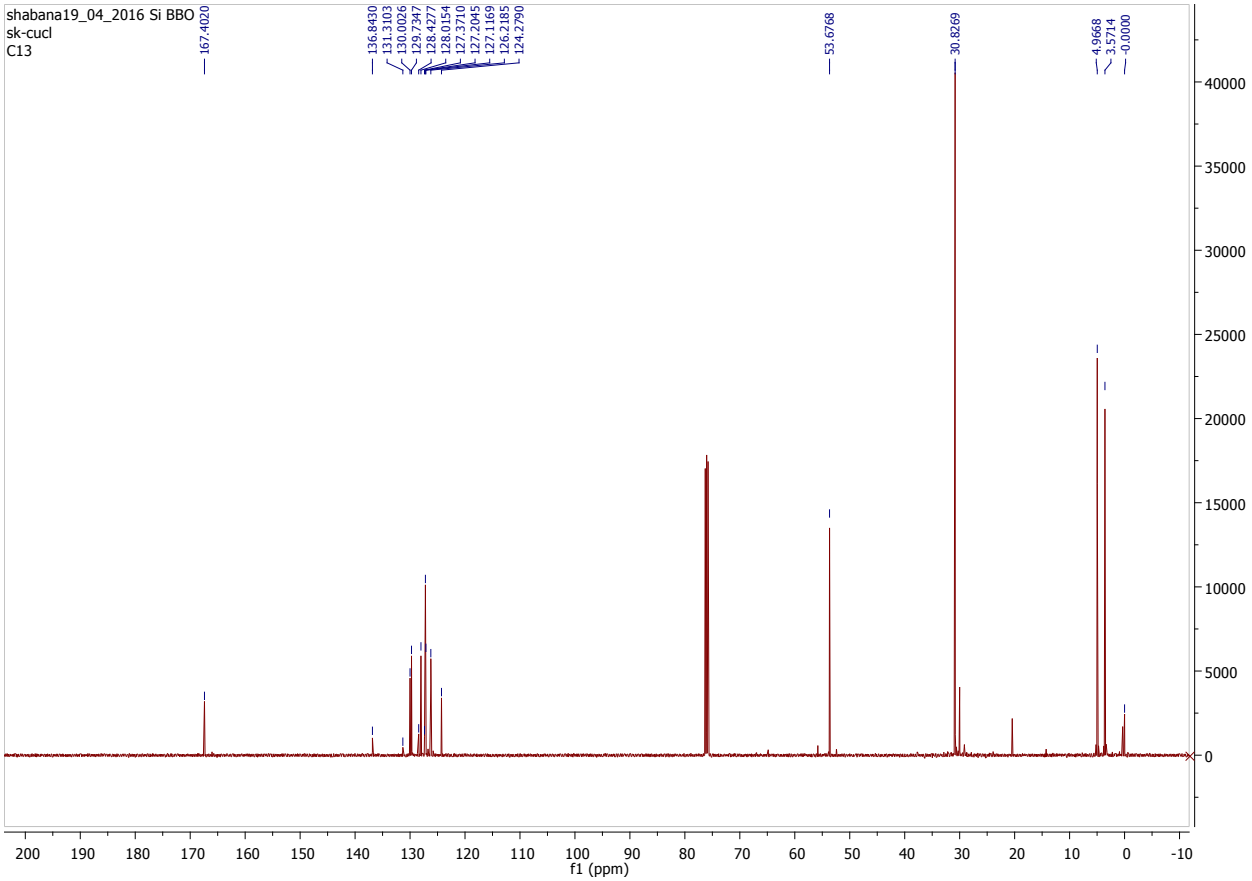

Figure S7. ^{13}C NMR of **5** in $CDCl_3$

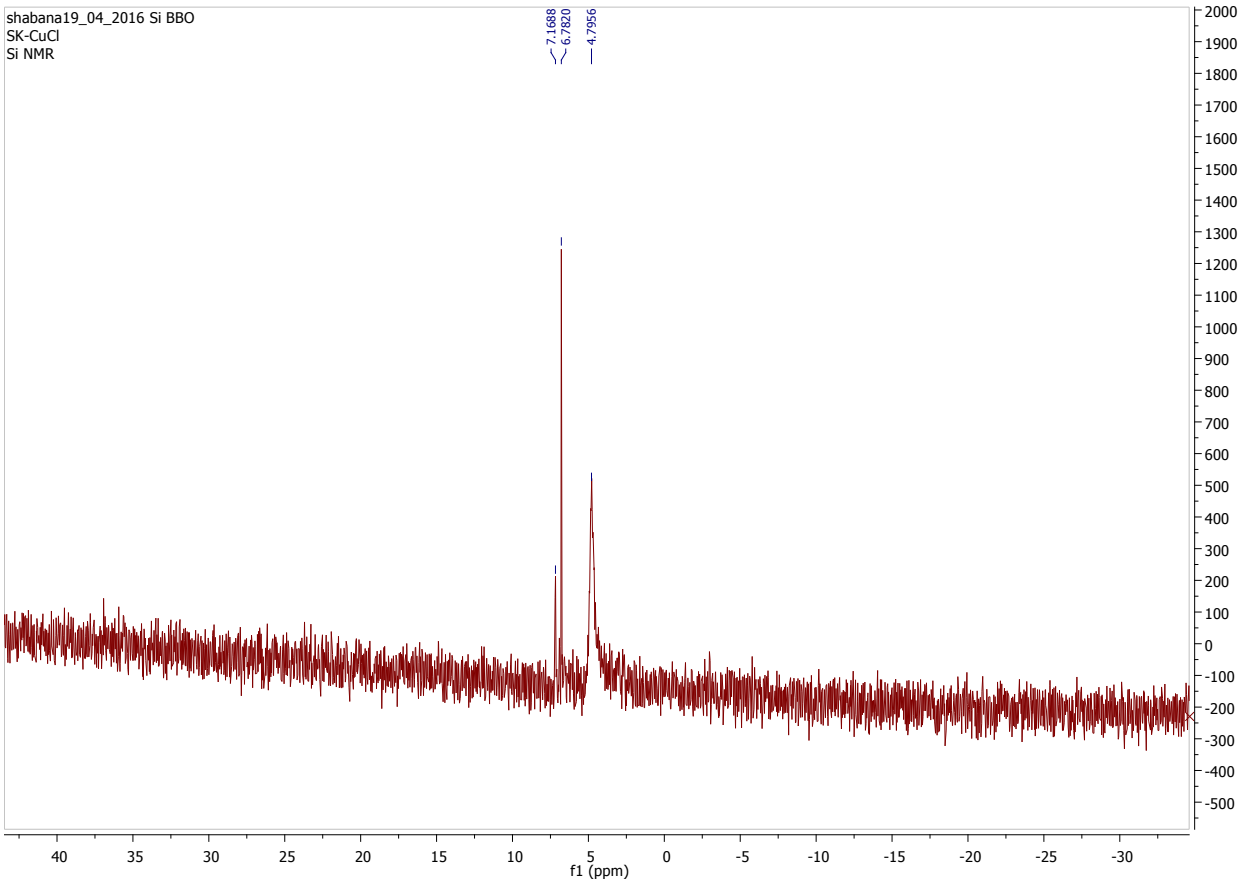

Figure S8. ^{29}Si NMR of **5** in $CDCl_3$

Compound **6**:

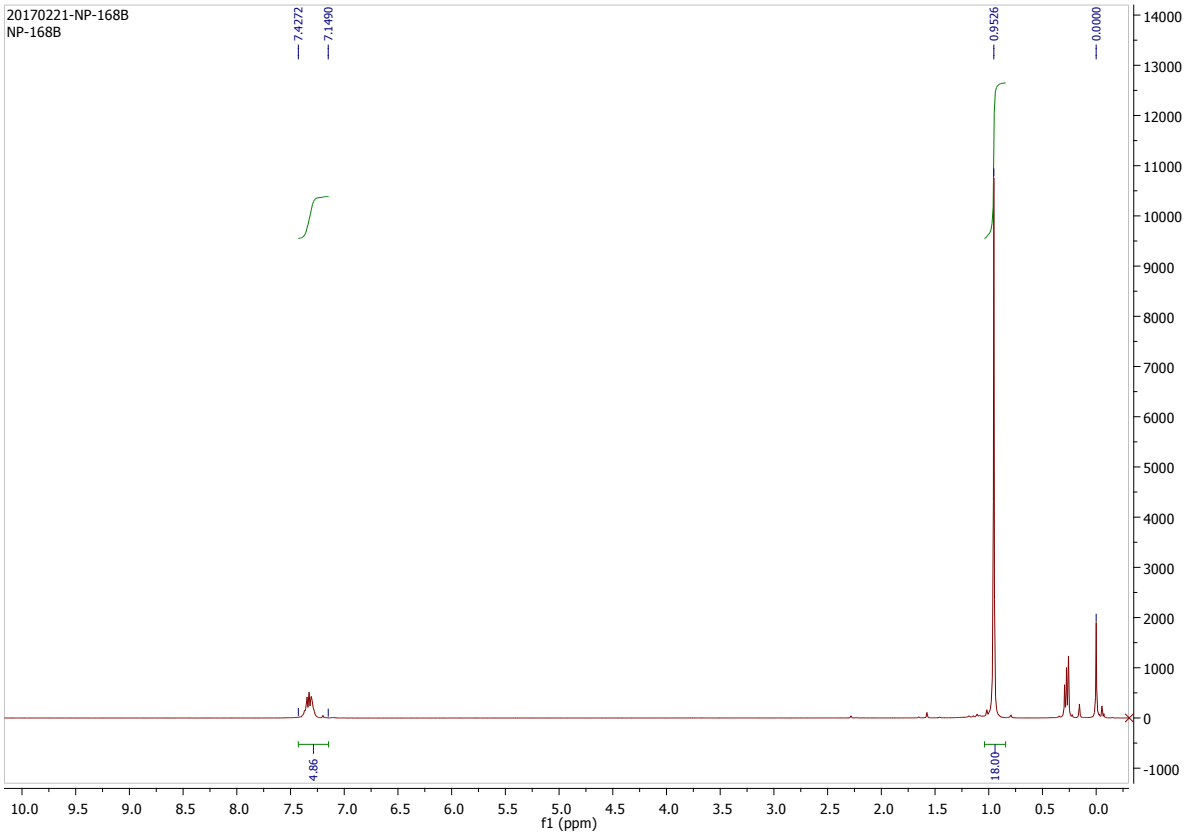

Figure S9. ^{1}H NMR of **6** in $CDCl_3$

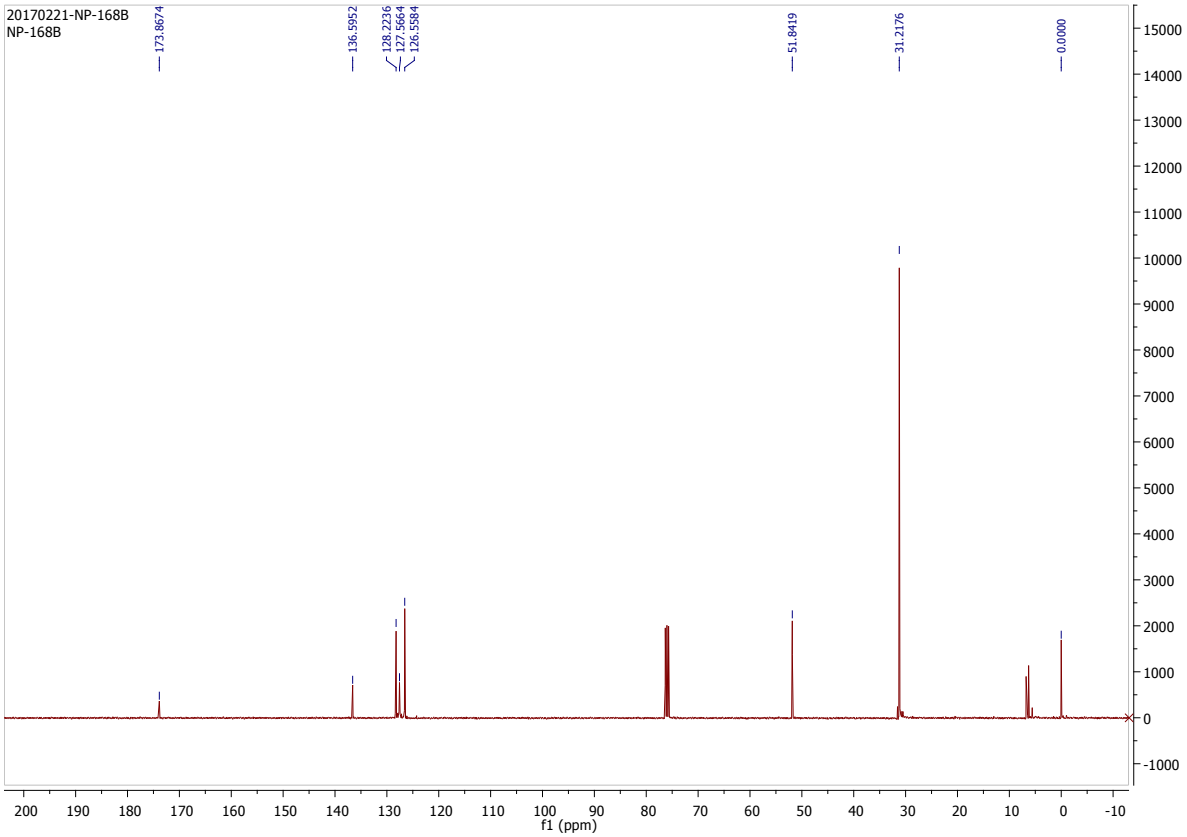

Figure S10. ^{13}C NMR of **6** in $CDCl_3$

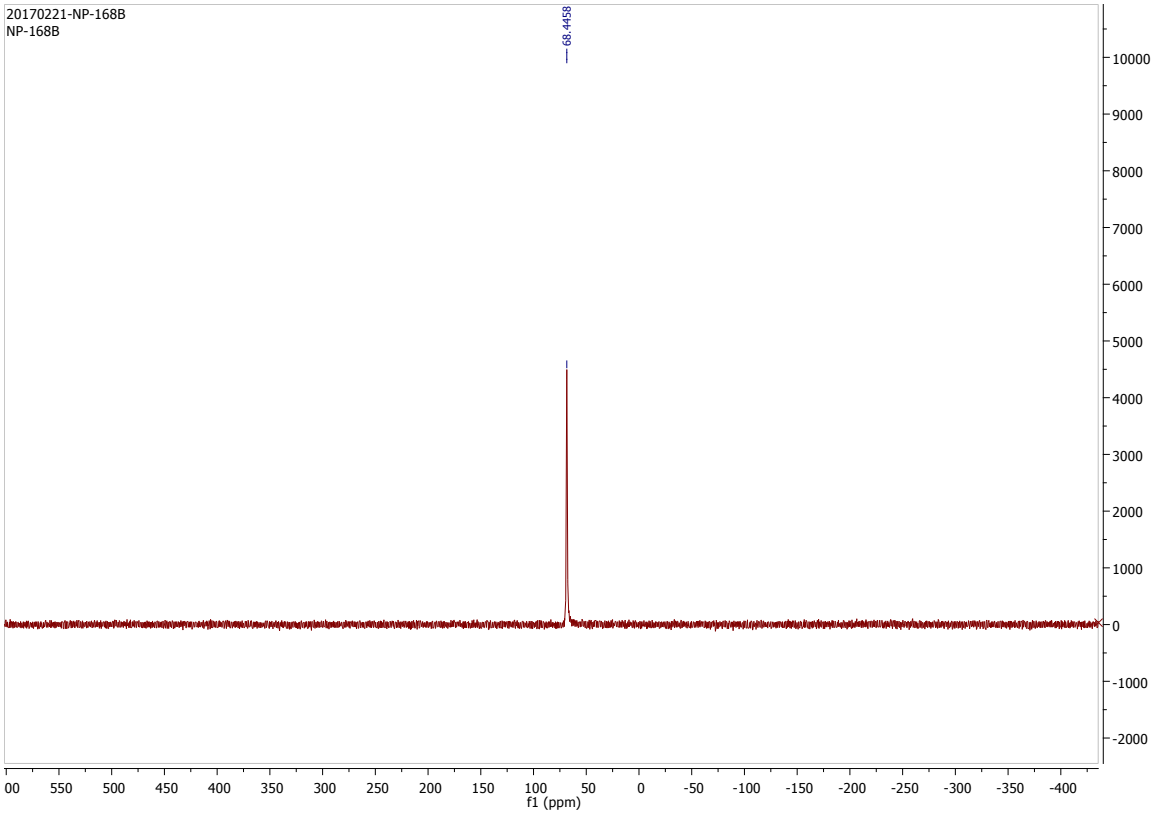

Figure S11. ^{119}Sn NMR of **6** in $CDCl_3$

Compound **9**:

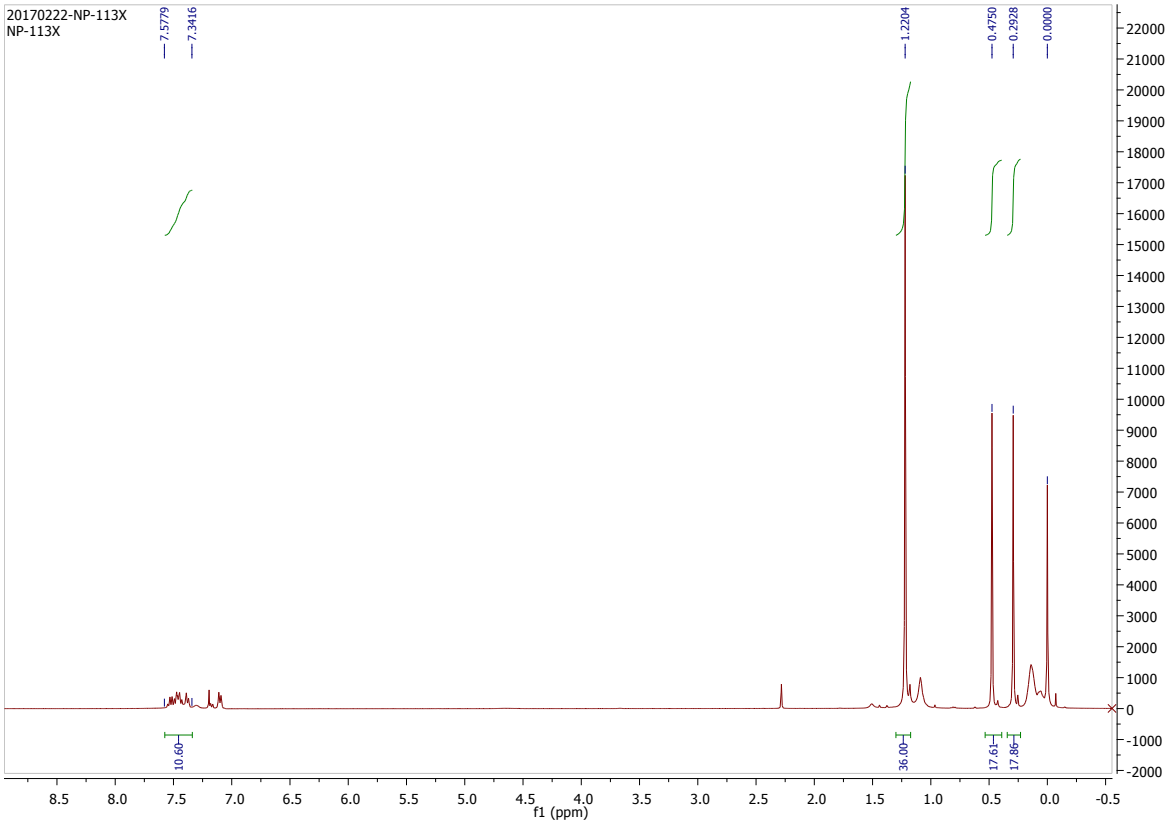

Figure S12. ^{1}H NMR of **9** in $CDCl_3$

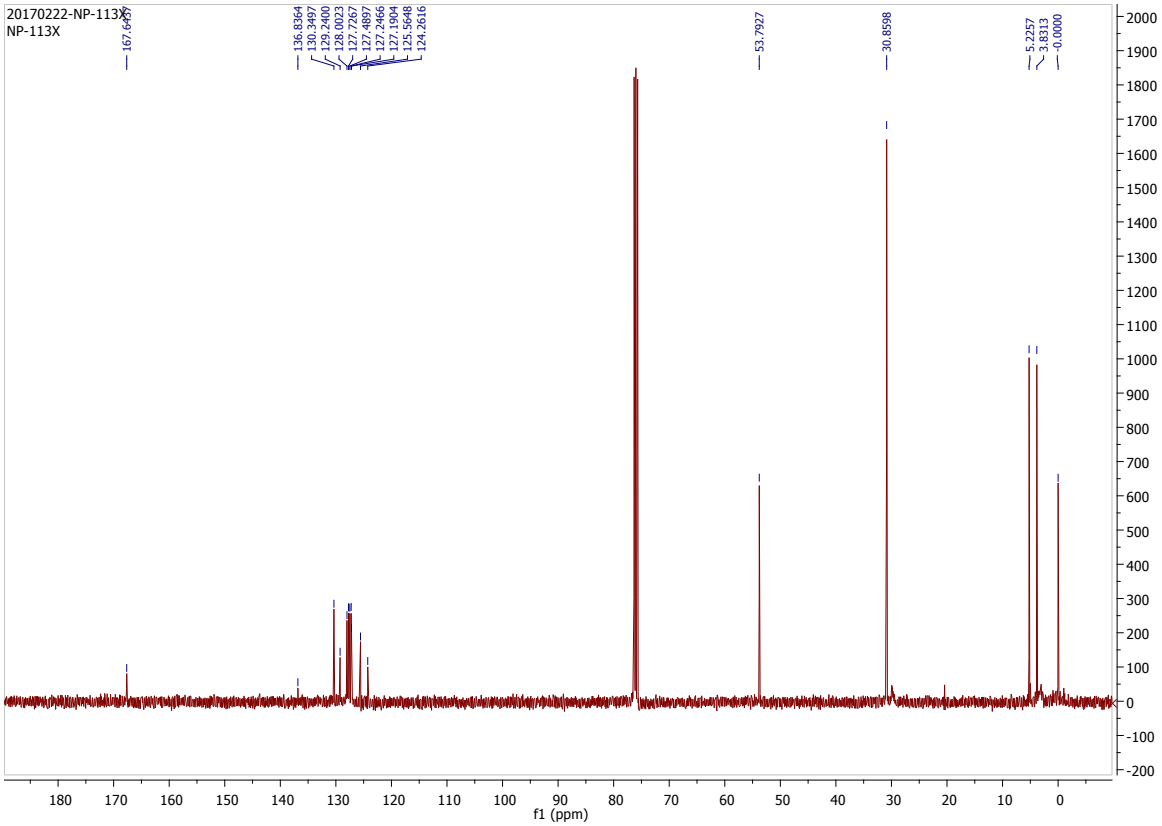

Figure S13. ^{13}C NMR of **9** in $CDCl_3$

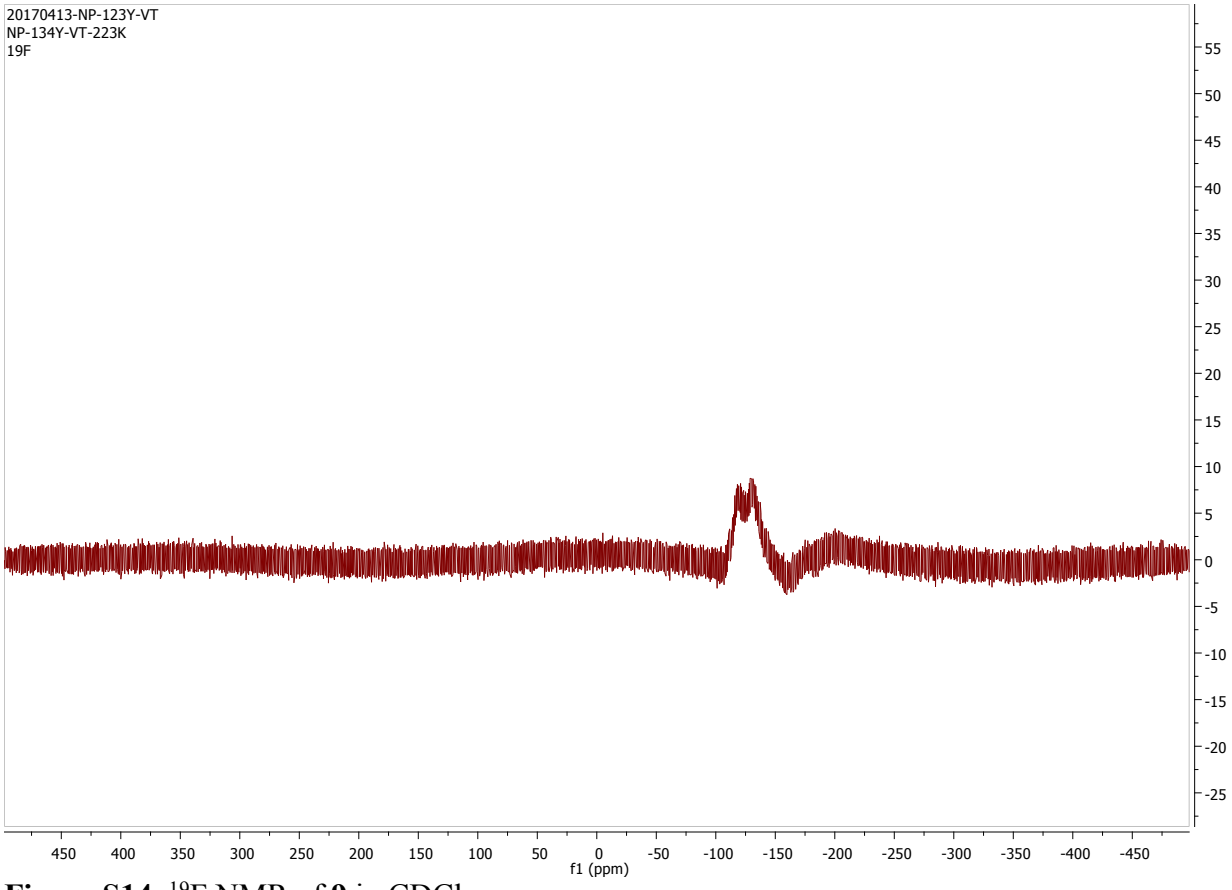

Figure S14. ^{19}F NMR of **9** in $CDCl_3$

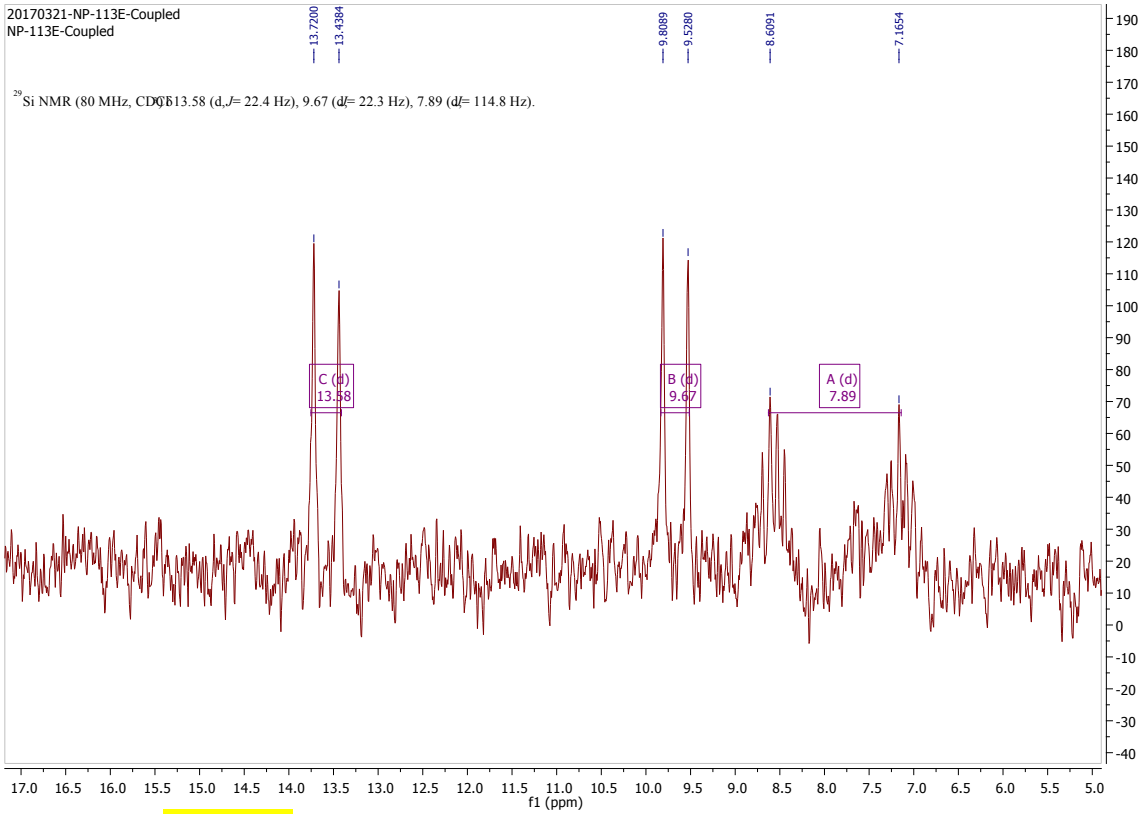

Figure S15. ^{29}Si NMR of **9** in $CDCl_3$

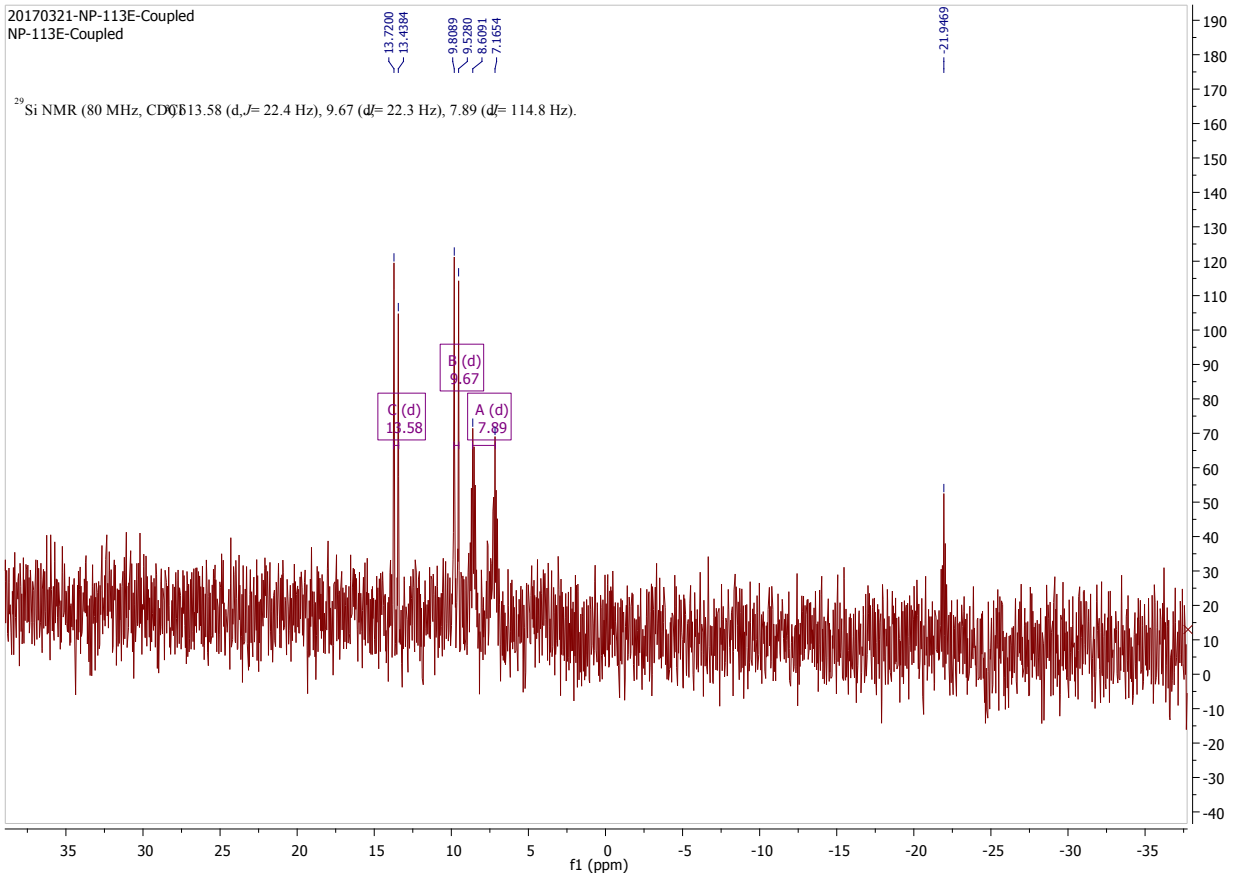

Figure S16. ^{29}Si NMR of **9** in $CDCl_3$

Compound **10**:

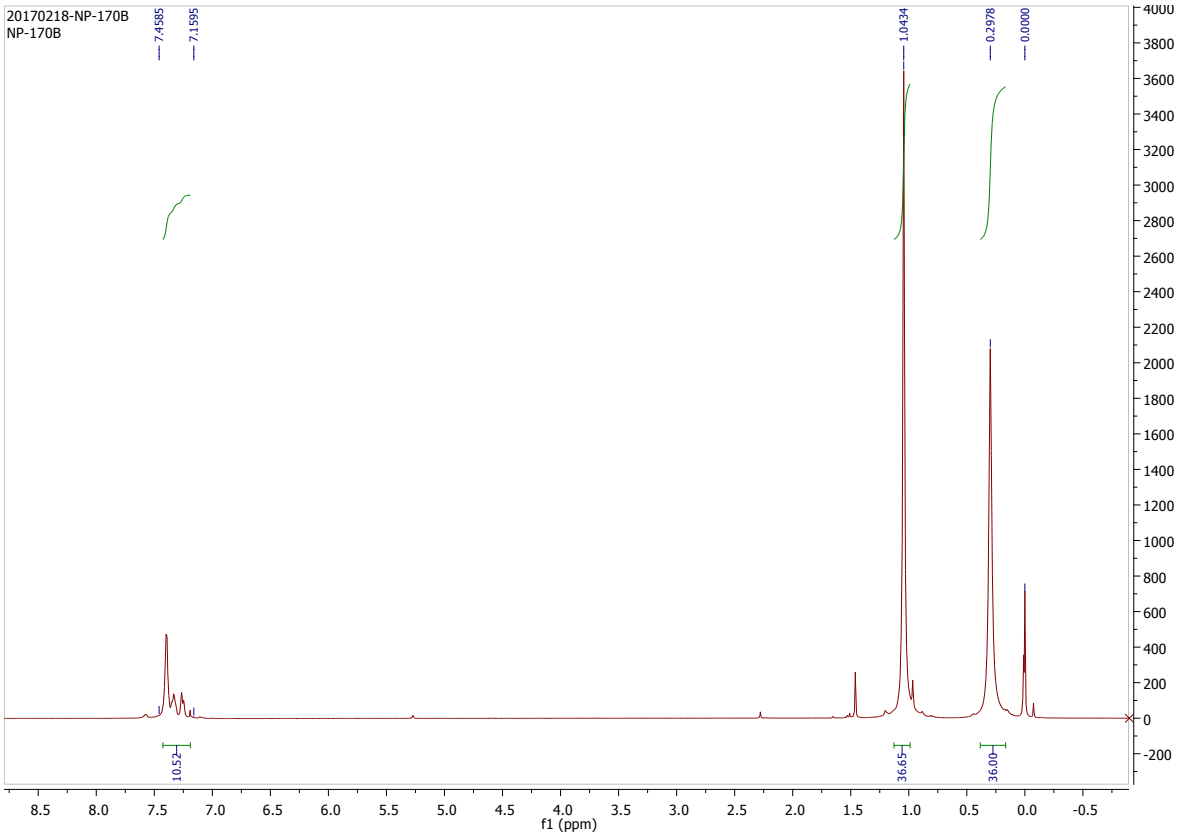

Figure S17. ^{1}H NMR of **10** in $CDCl_3$

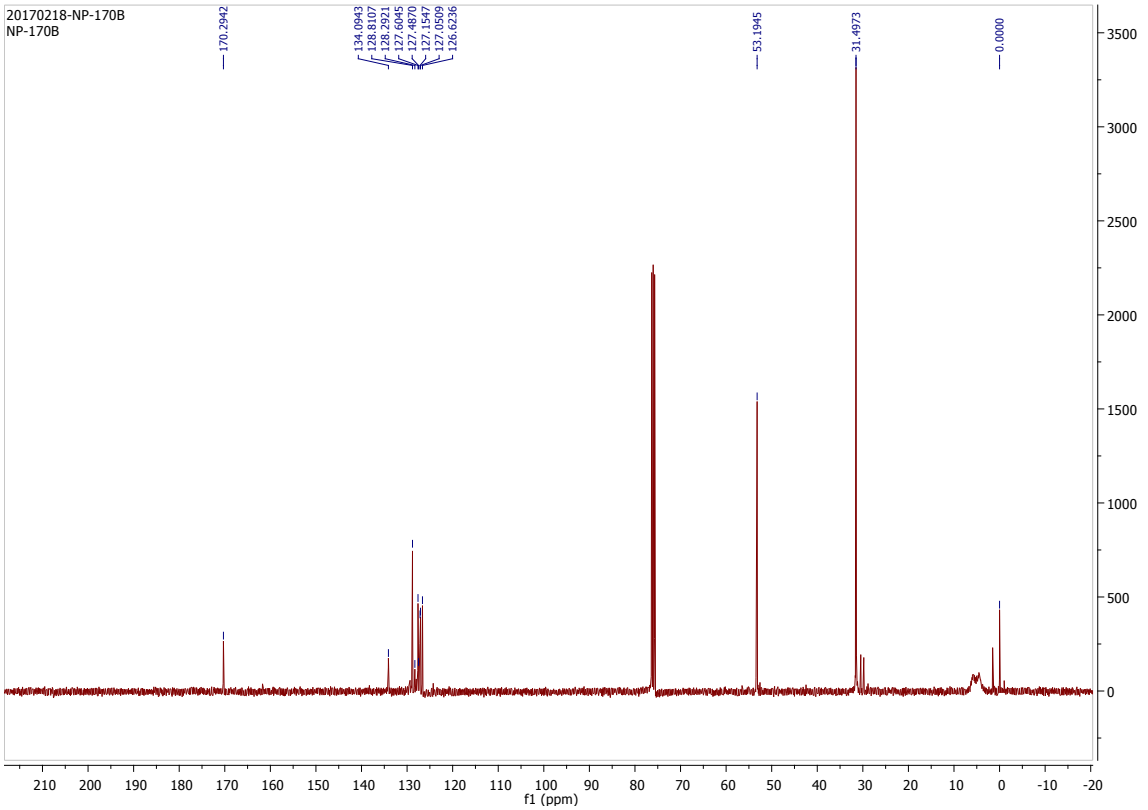

Figure S18. ^{13}C NMR of **10** in $CDCl_3$

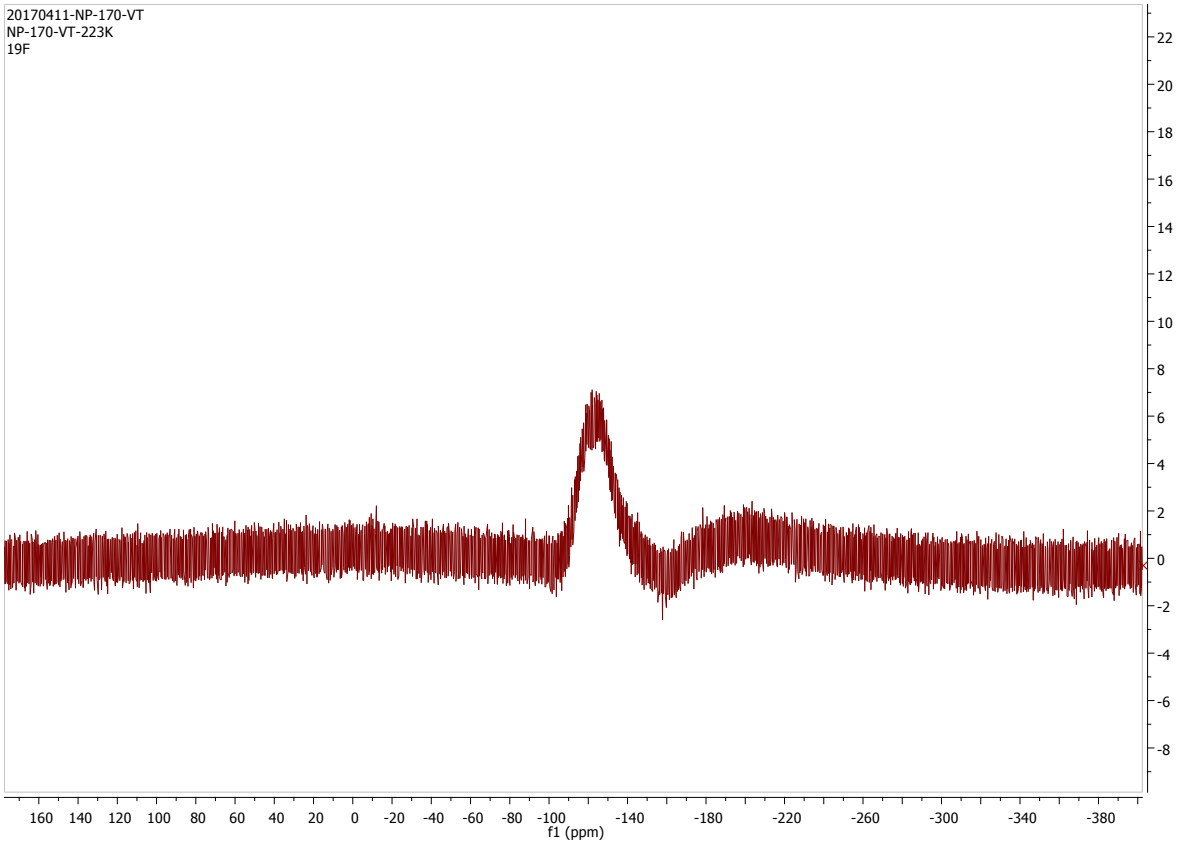

Figure S19. ^{19}F NMR of **10** in $CDCl_3$

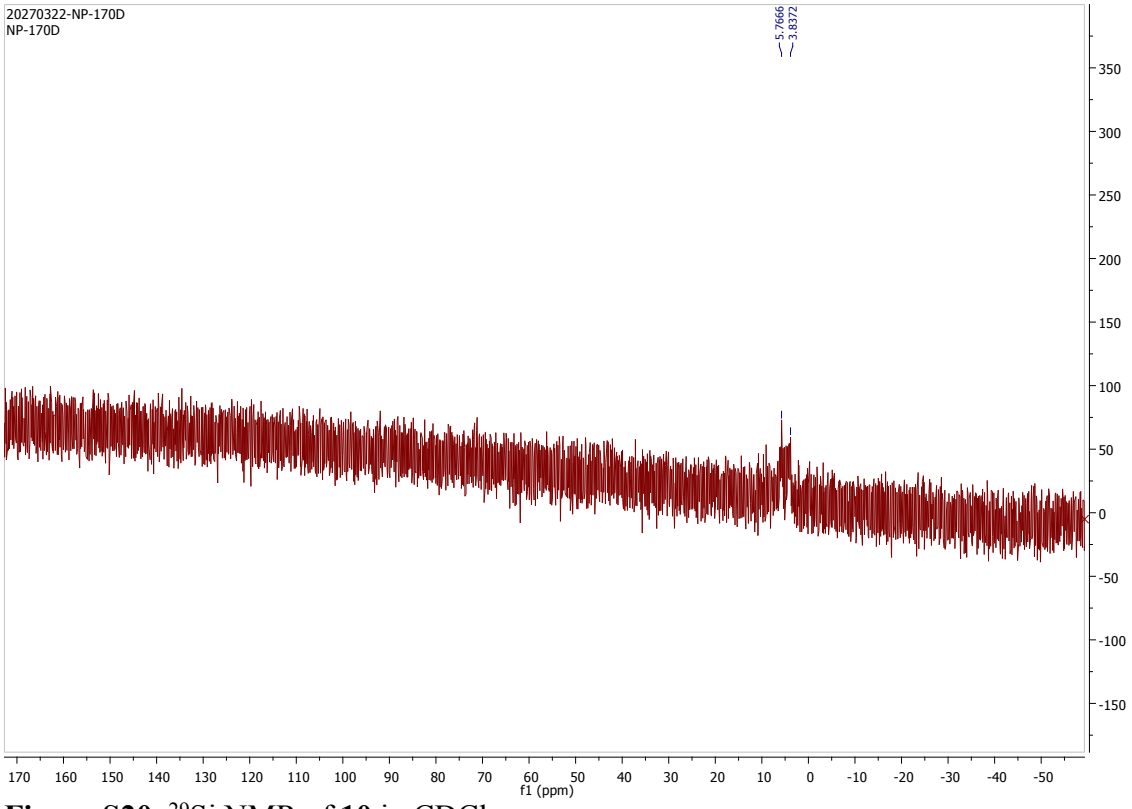

Figure S20. ^{29}Si NMR of **10** in $CDCl_3$

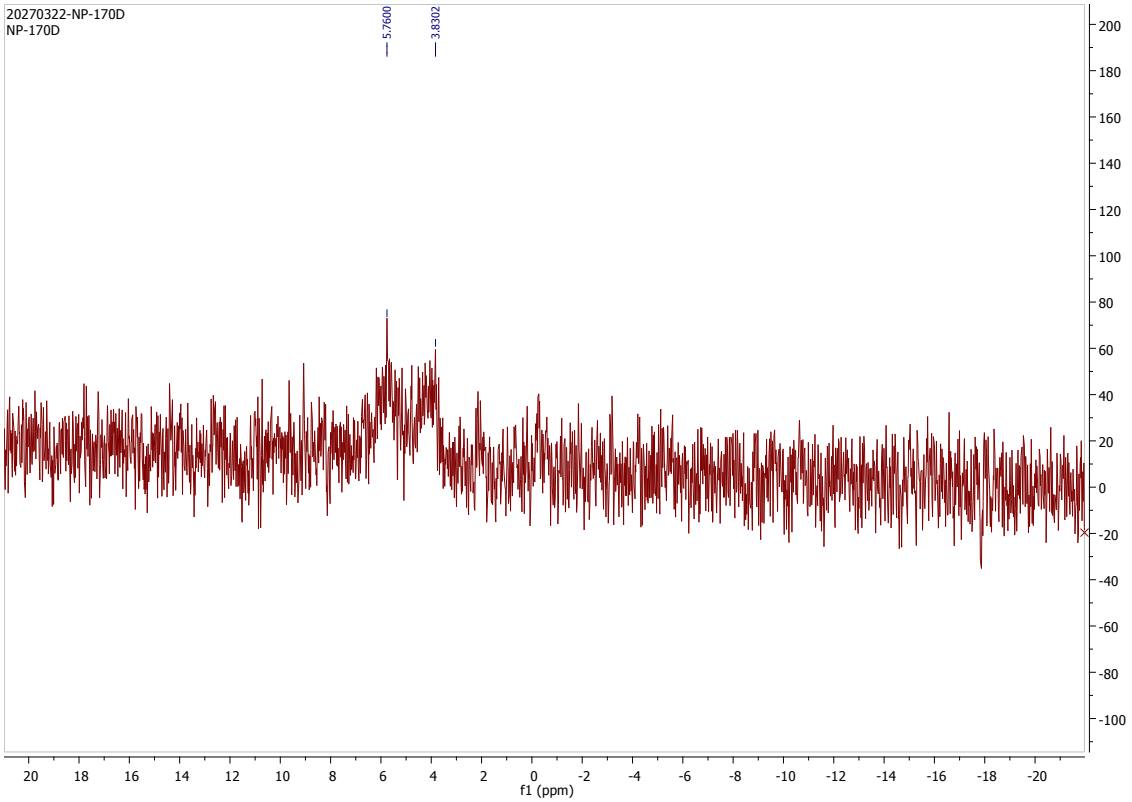

Figure S21. ^{29}Si NMR of **10** in $CDCl_3$

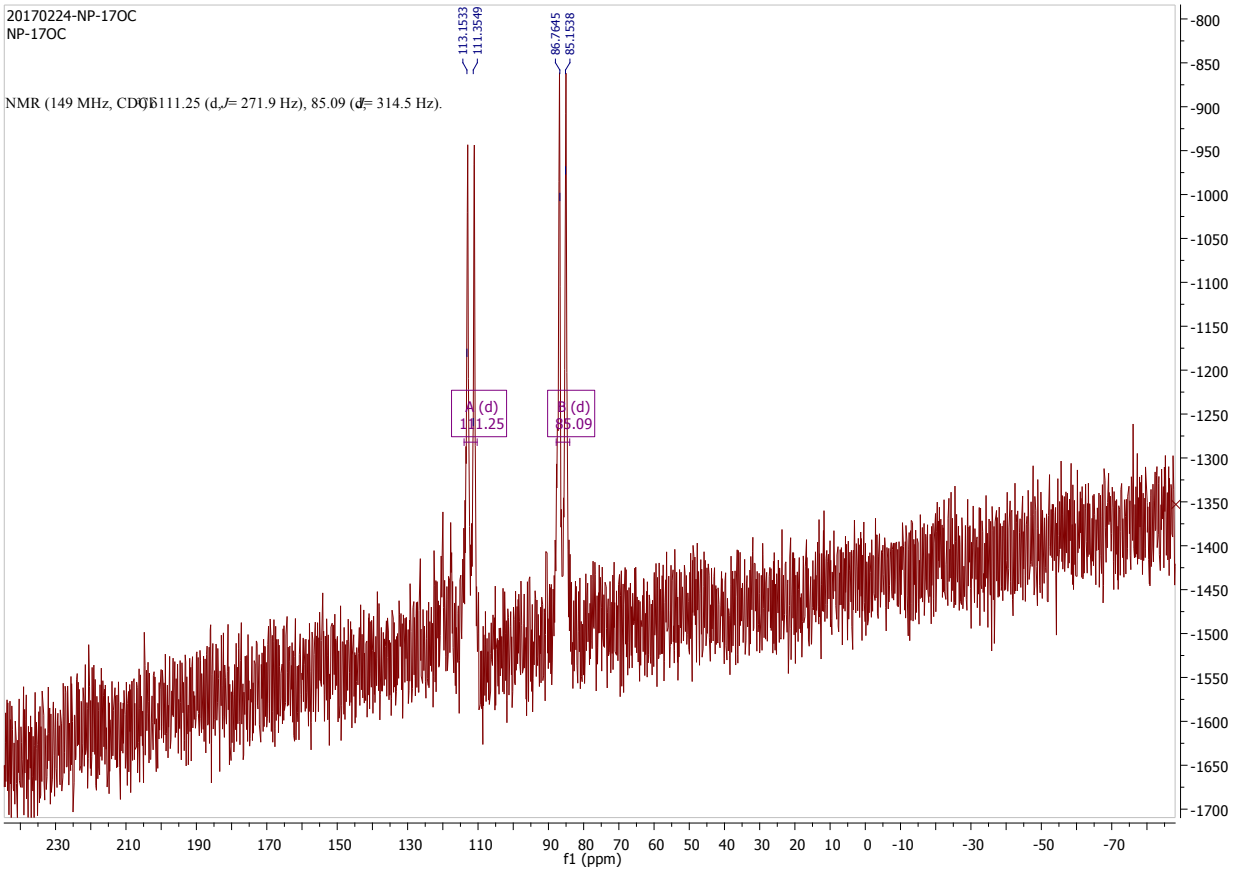

Figure S22. ^{119}Sn NMR of **10** in $CDCl_3$