Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

NHC- Zn alkyl catalyzed cross-dehydrocoupling of amines and silanes

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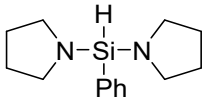
TS1. Crystallographic data and refinement parameters of 2b, 2c, 3 and 4.

Crystal Parameters	**2c** (exp_6252)	**3** (exp_6384)	**4** (exp_6203)
CCDC No.	2251323	2251324	2251325
Empirical formula	$C_{25}H_{23}NSi$	$C_{73}H_{80}N_8\ Zn_2$	$C_{58}H_{84}N_4\ Zn_2$
Formula weight	365.53	1200.19	968.07
T (K)	293(2) K	150(2) K	150(2) K
λ (Å)	1.54184 A	1.54184 A	0.71073 A
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	P -1	$P2_1/n$
a(Å)	6.8198(2)	11.3908(7)	12.3983(4)
b (Å)	11.6463(4)	12.4371(15)	15.3924(4)
c(Å)	12.6683(5)	12.7916(13)	14.3196(3)
α (°)	90.00	113.736(11)	90.00
β (°)	99.955(3)	104.197(7)	103.902(3)
γ (°)	90.00	95.841(7)	90.00
V(Å^3)	991.04(6)	1555.5(3)	2652.7(12)
Z	2	1	2
D_{calc} g cm^{-3}	1.225	1.281	1.212
μ (mm^{-1})	1.091	1.323	0.944
F(000)	388	634	1040
Theta range for data collection	3.542 to 70.597 deg	3.977 to 69.998 deg	3.176 to 71.671 deg
Limiting indices	$-8 \le h \le 5$, $-13 \le k \le 13$, $-14 \le l \le 15$	-13<=h<=10, -13<=k<=15, -15<=l<=15.	-15<=h<=10, -18<=k<=17, -17<=l<=17.
Reflections collected / unique	4118 / 2908 [R(int) = 0.0228]	11390 / 5847 [R(int) = 0.0393]	10004 / 5057 [R(int) = 0.0485]
Completeness to theta	99.8 %	99.9 %	97.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.79954	1.00000 and 0.95993	1.00000 and 0.83710
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2908 / 1 / 246	5847 / 3 / 373	5057 / 0 / 302
Goodness-of-fit on F^2	1.100	0.926	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0532, wR_2 = 0.1464	R_1 = 0.0687, wR_2 = 0.1934	R_1 = 0.0773, wR_2 = 0.2195
R indices (all data)	R_1 = 0.0547, wR_2 = 0.1483	R_1 = 0.0918, wR_2 = 0.2183	R_1 = 0.0838, wR_2 = 0.2301

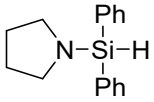
NMR spectroscopy data of aminosilanes:

1,1'-(phenylsilanediyl)dipyrrolidine (1a)[1]



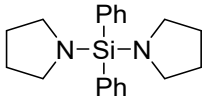
Yield: 95%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.66-7.64 (m, 2H, Ar-*H*), 7.42 (t, J = 4 Hz, 3H, Ar-*H*), 5.01 (s, 1H, Si-*H*), 3.10-3.07 (m, 8H, N-CH_2), 1.79-1.76 (m, 8H, CH_2) ppm.

1-(diphenylsilyl)pyrrolidine (1b)[1]



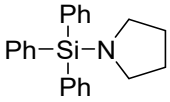
Yield: 96%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.69-7.67 (m, 4H, Ar-*H*), 7.23-7.21 (m, 6H, Ar-*H*), 5.66 (s, 1H, Si-*H*), 3.03-3.00 (m, 4H, N-CH_2), 1.54-1.51 (m, 4H, CH_2) ppm.

Diphenyldi(pyrrolidin-1-yl)silane (1c)[2]



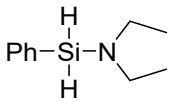
Yield: 95%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.66-7.64 (m, 4H, Ar-*H*), 7.19-7.16 (m, 6H, Ar-*H*), 3.03-3.00 (m, 8H, N-CH_2), 1.51-1.48 (m, 8H, CH_2) ppm.

1-(triphenylsilyl)pyrrolidine (1d)[2]



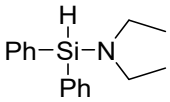
Yield: 95%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.63-7.61 (m, 6H, Ar-*H*), 7.14-7.12 (m, 9H, Ar-*H*), 3.01-2.98 (m, 4H, N-CH_2), 1.48-1.45 (m, 4H, CH_2) ppm.

***N*,*N*-diethyl-1-phenylsilanamine (1e)**[1]



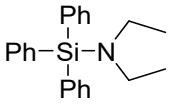
Yield: 96%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.42-7.39 (m, 2H, Ar-*H*), 6.99-6.98 (m, 3H, Ar-*H*), 4.91 (s, 1H, Si-*H*), 2.63-2.57 (m, 4H, N-CH_2), 0.73 (t, J = 8 Hz, 6H, CH_3) ppm.

***N*,*N*-diethyl-1,1-diphenylsilanamine (1f)**[1]



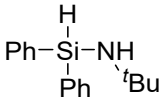
Yield: 94%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.55-7.52 (m, 4H, Ar-*H*), 7.32-7.28 (m, 6H, Ar-*H*), 5.24 (s, 1H, Si-*H*), 2.89-2.85 (m, 4H, N-CH_2), 0.95 (t, J = 4 Hz, 6H, CH_2) ppm.

***N*,*N*-diethyl-1,1,1-triphenylsilanamine (1g)**[3]



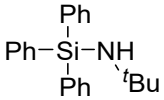
Yield: 92%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.78-7.75 (m, 6H, Ar-*H*), 7.23-7.21 (m, 9H, Ar-*H*), 3.00 (q, J = 8 Hz, 4H, N-CH_2), 0.95 (t, J = 6 Hz, 6H, CH_2) ppm.

***N*-tert-butyl-1,1-diphenylsilanamine (1h)**[1]



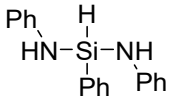
Yield: 95%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.60-7.57 (m, 4H, Ar-*H*), 7.11-7.09 (m, 6H, Ar-*H*), 5.60 (s, 1H, Si-*H*), 1.02 (s, 9H, N-CH_3), 0.84 (s, 1H, N-*H*) ppm.

***N*-tert-butyl-1,1,1-triphenylsilanamine (1i)**[2]



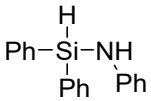
Yield: 93%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.85-7.83 (m, 6H, Ar-*H*), 7.22-7.20 (m, 9H, Ar-*H*), 1.29 (s, 1H, N-*H*), 1.10 (s, 9H, N-CH_3) ppm.

***N*,*N*',1-triphenylsilanediamine (2a)**[4]



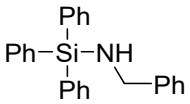
Yield: 94%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.98 (d, J = 8 Hz, 2H, Ar-*H*), 7.70-7.63 (m, 3H, Ar-*H*), 7.38 (t, J = 8 Hz, 4H, Ar-*H*), 7.04 (d, J = 8 Hz, 6H, Ar-*H*), 5.82 (s, 1H, Si-*H*), 4.11 (s, 2H, N-*H*) ppm.

_N_,1,1-triphenylsilanamine (2b)[4]



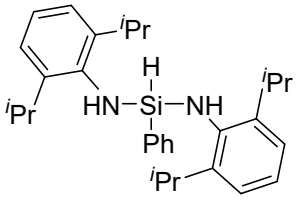
Yield: 97%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.57 (d, J = 8 Hz, 4H, Ar-*H*), 7.35-7.28 (m, 6H, Ar-*H*), 7.01 (t, J = 8 Hz, 2H, Ar-*H*), 6.62 (d, J = 8 Hz, 3H, Ar-*H*), 5.52 (s, 1H, Si-*H*), 3.75 (s, 1H, N-*H*) ppm.

_N_-benzyl-1,1,1-triphenylsilanamine (2c)[2]



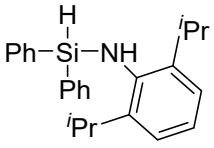
Yield: 90%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.61-7.59 (m, 5H, Ar-*H*), 7.11-7.08 (m, 15H, Ar-*H*), 3.91 (d, J = 8 Hz, 2H, N-CH_2) ppm.

_N_,_N_'-bis(2,6-diisopropylphenyl)-1-phenylsilanediamine (2d)[5]



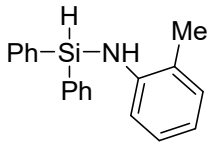
Yield: 85%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 8.03-8.01 (m, 2H, Ar-*H*), 7.67 (d, J = 4 Hz, 3H, Ar-*H*), 7.34-7.28 (m, 6H, Ar-*H*), 5.68 (s, 1H, Si-*H*), 3.52-3.48 (m, 4H, C*H*(CH_3)$_2$) 3.31 (d, J = 4 Hz, 2H, N-*H*), 1.39-1.32 (m, 24H, CH(CH_3)$_2$) ppm.

_N_-(2,6-diisopropylphenyl)-1,1-diphenylsilanamine (2e)[1]



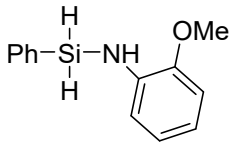
Yield: 90%. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ_H 7.85-7.83 (m, 4H, Ar-*H*), 7.60-7.56 (m, 6H, Ar-*H*), 7.32-7.27 (m, 3H, Ar-*H*), 5.82 (s, 1H, Si-*H*), 3.68-3.59 (m, 2H, C*H*(CH_3)$_2$) 3.37 (s, 1H, N-*H*), 1.35 (d, J = 4 Hz, 12H, CH(CH_3)$_2$) ppm.

1,1-diphenyl-*N*-(o-tolyl)silanamine (2f)



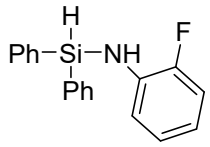
Yield: 94%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.58-7.50 (m, 4H, Ar-*H*), 7.30-7.24 (m, 6H, Ar-*H*), 7.20-7.16 (m, 1H, Ar-*H*), 6.95-6.93 (m, 1H, Ar-*H*), 6.83-6.79 (m, 1H, Ar-*H*), 6.64-6.60 (m, 1H, Ar-*H*), 4.86 (s, 1H, Si-*H*), 4.03 (s, 1H, N-*H*), 2.18 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 143.9 (Ar*C*-N), 135.6 (Ar-*C*), 134.7 (Ar-*C*), 134.6 (Ar-*C*), 129.9 (Ar-*C*), 128.3 (Ar-*C*), 127.7 (Ar-*C*), 119.0 (Ar-*C*), 116.7 (Ar-*C*), 19.1(*C*H_3) ppm. Elemental analysis: ($C_{19}H_{19}$NSi) (289.0); calcd. C 78.84, H 6.62, N 4.84; found C 78.67, H 6.52, N 4.72.

***N*-(2-methoxyphenyl)-1-phenylsilanamine (2g)**



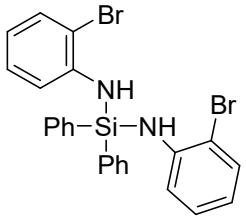
Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.67-7.61 (m, 1H, Ar-*H*), 7.48-7.42 (m, 1H, Ar-*H*), 7.31-7.26 (m, 3H, Ar-*H*), 7.13-7.07 (m, 2H, Ar-*H*), 6.86-6.81 (m, 1H, Ar-*H*), 6.67 (d, *J* = 8 Hz, 1H, Ar-*H*), 4.90 (s, 1H, Si-*H*), 4.87 (br, 1H, N-*H*), 3.61 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 156.4 (Ar*C*-N), 135.1 (Ar-*C*), 134.3 (Ar-*C*), 130.7 (Ar-*C*), 128.8 (Ar-*C*), 128.4 (Ar-*C*), 127.9 (Ar-*C*), 127.5 (Ar-*C*), 120.4 (Ar-*C*), 119.9 (Ar-*C*), 109.7 (Ar-*C*), 55.1 (O*C*H_3) ppm. Elemental analysis: ($C_{13}H_{15}$NOSi) (229.3); calcd. C 68.08, H 6.59, N 6.11; found C 67.88, H 6.44, N 5.97.

***N*-(2-fluorophenyl)-1,1-diphenylsilanamine (2h)**



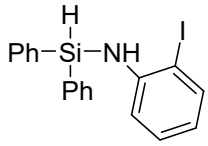
Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.67-7.65 (m, 4H, Ar-*H*), 7.47-7.38 (m, 6H, Ar-*H*), 7.01-6.95 (m, 1H, Ar-*H*), 6.85 - 6.75 (m, 2H, Ar-*H*), 6.68-6.63 (m, 1H, Ar-*H*), 5.62 (s, 1H, Si-*H*), 4.13 (br, 1H, N*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.8 (F attached Ar-*C*), 134.9 (Ar-*C*), 132.7 (Ar-*C*), 130.5 (Ar-*C*), 128.3 (Ar-*C*), 124.4 (Ar-*C*), 118.4 (Ar-*C*), 116.9 (Ar-*C*), 114.8(Ar-*C*) ppm. Elemental analysis: ($C_{18}H_{16}$FNSi) (293.4); calcd. C 73.68, H 5.50, N 4.77; found C 73.57, H 5.46, N 4.65.

***N*,*N*'-bis(2-bromophenyl)-1,1-diphenylsilanediamine (2i)**



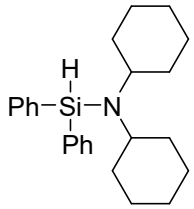
Yield: 94%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.67-7.65 (m, 2H, Ar-*H*), 7.55-7.50 (m, 3H, Ar-*H*), 7.34-7.27 (m, 8H, Ar-*H*), 7.15-7.11 (m, 2H, Ar-*H*), 6.97-6.86 (m, 1H, Ar-*H*), 6.55-6.51(m, 1H, Ar-*H*), 4.96 (br, 1H, N*H*), 4.84 (br, 1H, N*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 143.1 (Ar-C), 134.9 (Ar-C), 132.7 (Ar-C), 130.4 (Ar-C), 128.3 (Ar-C), 120.2 (Ar-C), 119.4 (Ar-C), 117.4 (Ar-C), 113.4 (Ar-C) ppm. Elemental analysis: ($C_{24}H_{20}Br_2N_2Si$) (524.3); calcd. C 54.98, H 3.84, N 5.34; found C 54.82, H 3.69, N 5.24.

N-(2-iodophenyl)-1,1-diphenylsilanamine (2j)



Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.69-7.65 (m, 5H, Ar-H), 7.47-7.38 (m, 6H, Ar-H), 7.05-7.01 (m, 1H, Ar-H), 6.79 (dd, *J* = 6.6 Hz, 1H, Ar-H), 6.46 (td, *J* =7.4 Hz, 1H, Ar-H), 5.60 (s, 1H, Si-H), 4.47 (br, 1H, NH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.8 (Ar-C), 134.9 (Ar-C), 132.7 (Ar-C), 130.5 (Ar-C), 128.3 (Ar-C), 124.4 (Ar-C), 118.4 (Ar-C), 116.9 (Ar-C), 115.0 (Ar-C), 114.8 (Ar-C) ppm. Elemental analysis: ($C_{18}H_{16}INSi$) (401.3); calcd. C 53.87, H 4.02, N 3.49; found C 53.65, H 3.86, N 3.41.

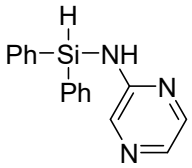
***N*,*N*-dicyclohexyl-1,1-diphenylsilanamine (2k)**



Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.67 - 7.59 (m, 4H, Ar-H), 7.42-7.36 (m, 6H, Ar-H), 4.97 (s, 1H, Si-H), 2.60-2.58 (m, 2H, Cy-H), 1.91-1.73 (m, 9H, Cy-H), 1.30-1.24 (m, 1H, Cy-H), 1.08-1.04 (m, 10H, Ar-H), ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 135.7 (Ar-C), 134.3 (Ar-C), 130.3 (Ar-

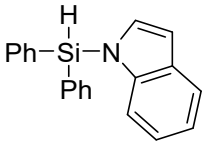
C), 129.9 (Ar-C), 128.1 (Ar-C), 127.9 (Ar-C), 53.0 (Cy-C), 34.4 (Cy-C), 26.2 (Cy-C), 25.3 (Cy-C) ppm. Elemental analysis: ($C_{24}H_{33}NSi$) (363.6); calcd. C 79.28, H 9.15, N 3.85; found C 79.11, H 9.05, N 3.73.

***N*-(diphenylsilyl)pyrazin-2-amine (2l)**



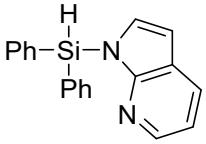
Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.83-7.78 (m, 1H, Ar-H), 7.74 (s, 1H, NH), 7.50-7.48 (m, 6H, Ar-H), 7.30-7.25 (m, 6H, Ar-H), 4.83 (s, 1H, Si-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 155.4 (Ar-C), 141.9 (Ar-C), 135.6 (Ar-C), 134.4 (Ar-C), 134.3 (Ar-C), 129.8 (Ar-C), 128.0 (Ar-C), 127.8 (Ar-C) ppm. Elemental analysis: ($C_{16}H_{15}N_3Si$) (277.4); calcd. C 69.28, H 5.45, N 15.15; found C 69.20, H 5.33, N 14.89.

1-(diphenylsilyl)-1H-indole (2m)



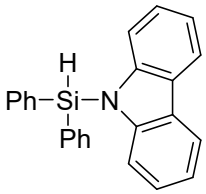
Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.58-7.56 (m, 1H, Ar-H), 7.40-7.34 (m, 2H, Ar-H), 7.14-7.05 (m, 9H, Ar-H), 6.95-6.88 (m, 2H, Ar-H), 6.63 (d, J = 3 Hz, 1H, C=CH), 6.10 (d, J = 3 Hz, 1H, C=CH), 4.92 (s, 1H, Si-H), ppm. Elemental analysis: ($C_{20}H_{17}NSi$) (299.4); calcd. C 80.22, H 5.72, N 4.68; found C 80.15, H 5.66, N 4.57.

1-(diphenylsilyl)-1H-pyrrolo[2,3-b]pyridine (2n)



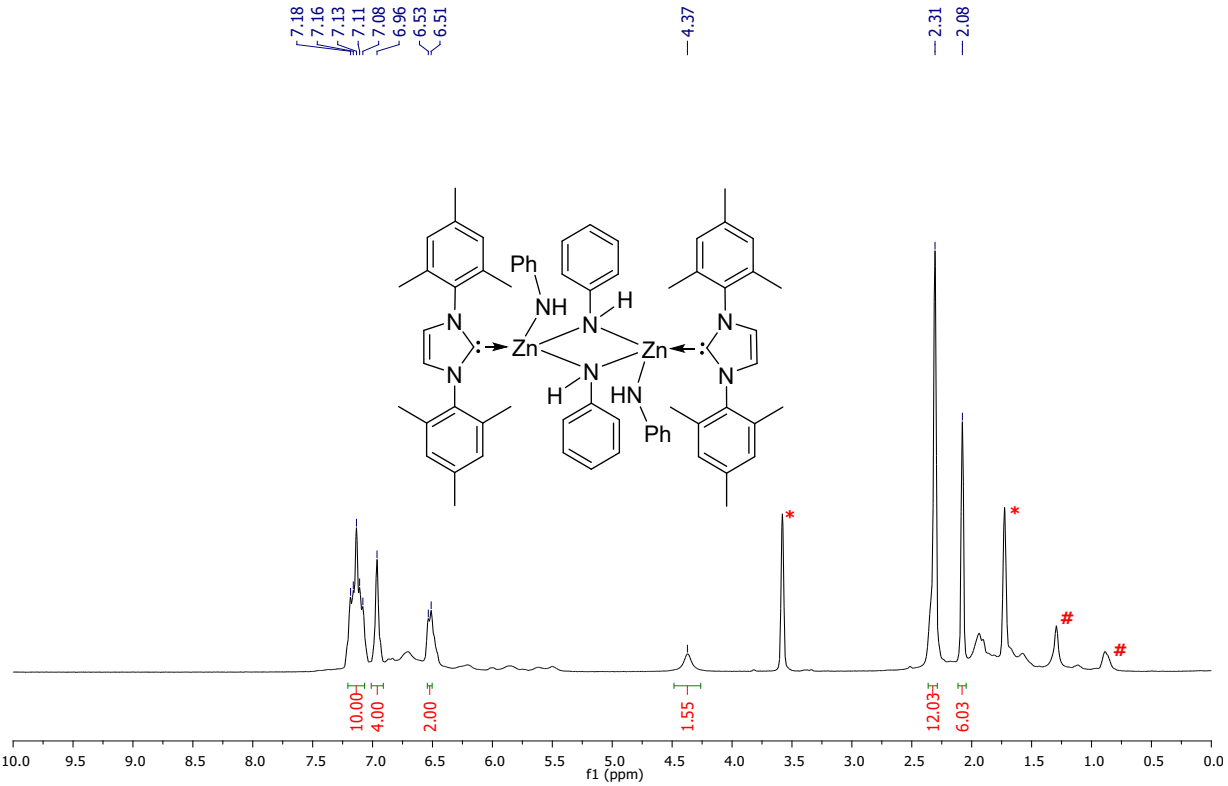
Yield: 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 8.35 (d, J = 7.9 Hz, 1H, C=CH), 7.98 (d, J = 7.3 Hz, 1H, Ar-H), 7.63-7.61 (m, 4H, Ar-H), 7.40-7.39 (m, 7H, Ar-H), 7.12 (d, J = 3 Hz, 1H, C=CH), 6.53 (d, J = 3 Hz, 1H, C=CH), 4.94 (s, 1H, Si-H), ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 142.6 (Ar-C), 135.6 (Ar-C), 134.3 (Ar-C), 129.8 (Ar-C), 128.1 (Ar-C), 127.9 (Ar-C), 115.8 (Ar-C), 100.6 (Ar-C) ppm. Elemental analysis: ($C_{19}H_{16}N_2Si$) (300.4); calcd. C 75.96, H 5.37, N 9.32; found C 75.81, H 5.29, N 9.25.

9-(diphenylsilyl)-9H-carbazole (2o)

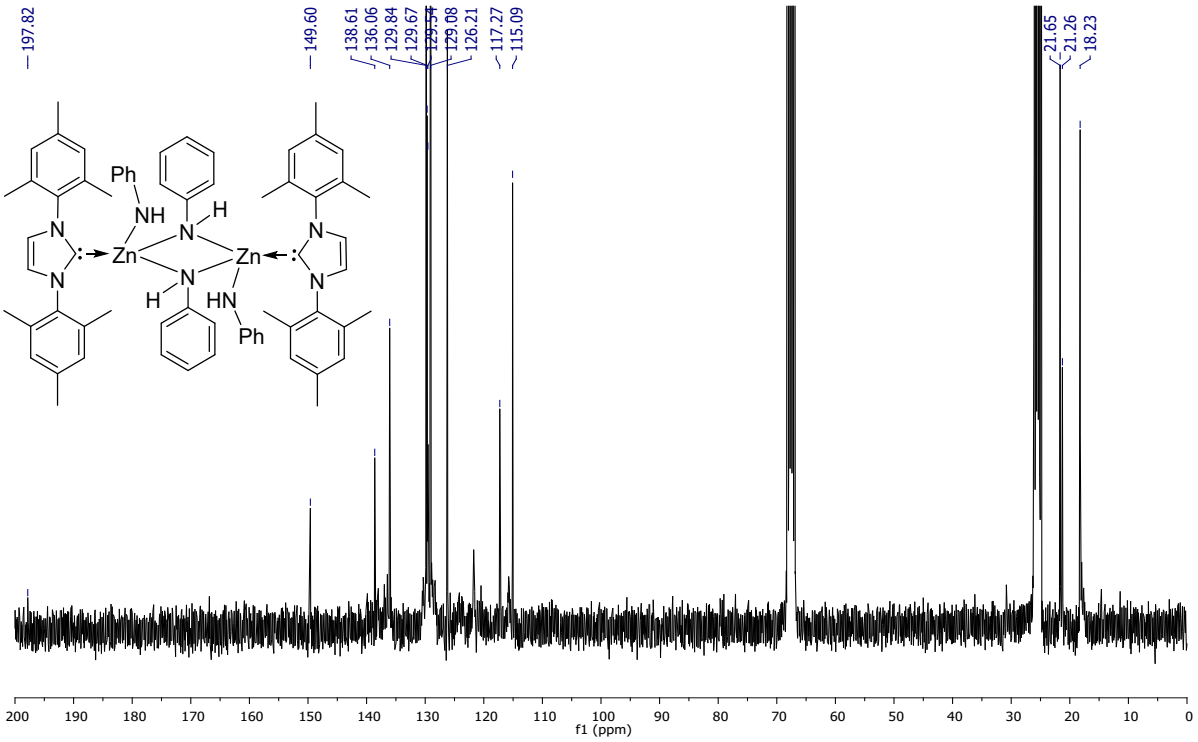


Yield: 88%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 8.02-8.00 (m, 2H, Ar-H), 7.52-7.48 (m, 4H, Ar-H), 7.39-7.34 (m, 2H, Ar-H), 7.30-7.25 (m, 4H, Ar-H), 7.15-7.11 (m, 2H, Ar-H), 7.09-7.07 (m, 4H, Ar-H), 4.85 (s, 1H, Si-H) ppm. Elemental analysis: ($C_{24}H_{19}NSi$) (349.5); calcd. C 82.48, H 5.48, N 4.01; found C 82.39, H 5.38, N 3.92.

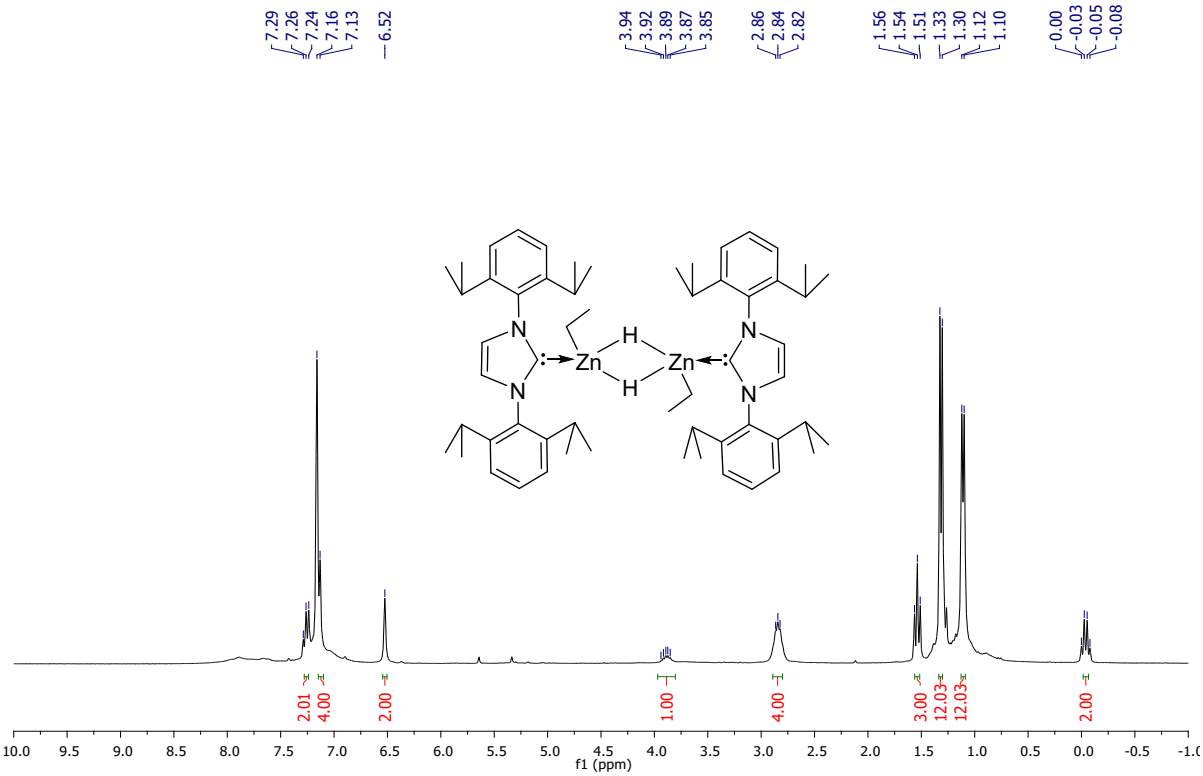
NMR spectra:



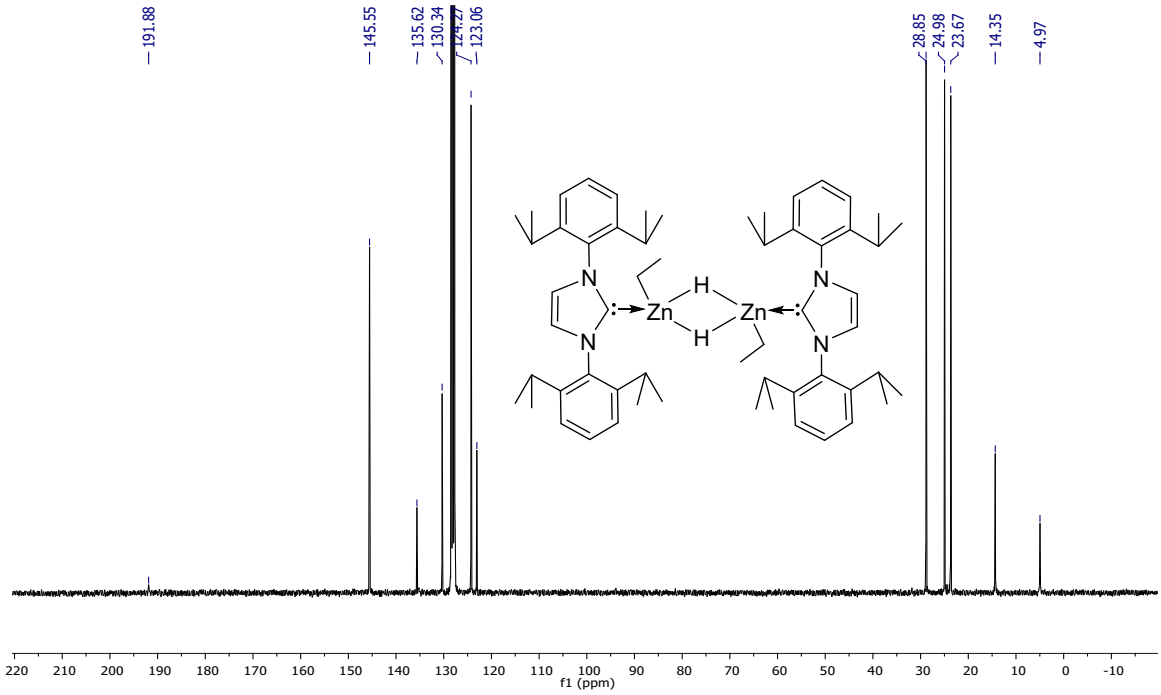
FS1: ^{1}H NMR spectrum (THF-d_8, 300 MHz, 25 °C) of compound **3** (# n-Hexane, * NMR solvent residual signals)



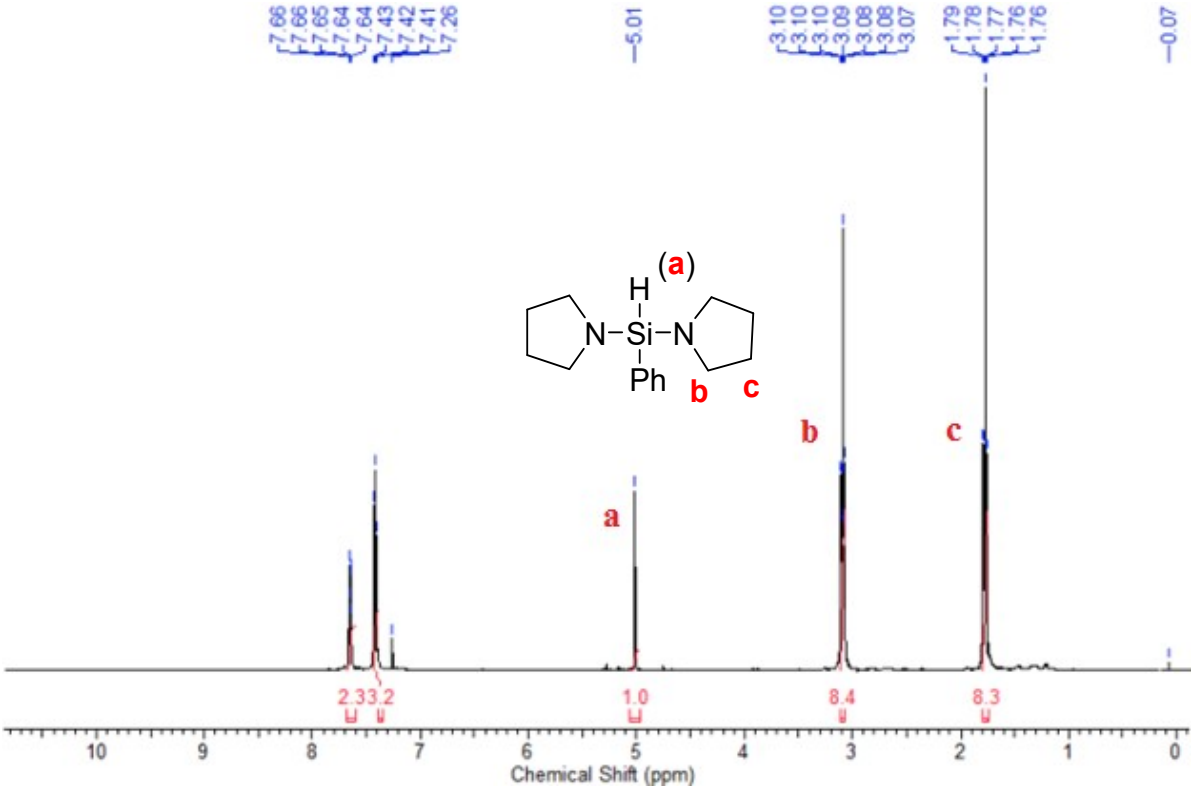
FS2: $^{13}C\{^{1}H\}$ NMR spectrum (THF-d_8, 75 MHz, 25 °C) of compound **3**



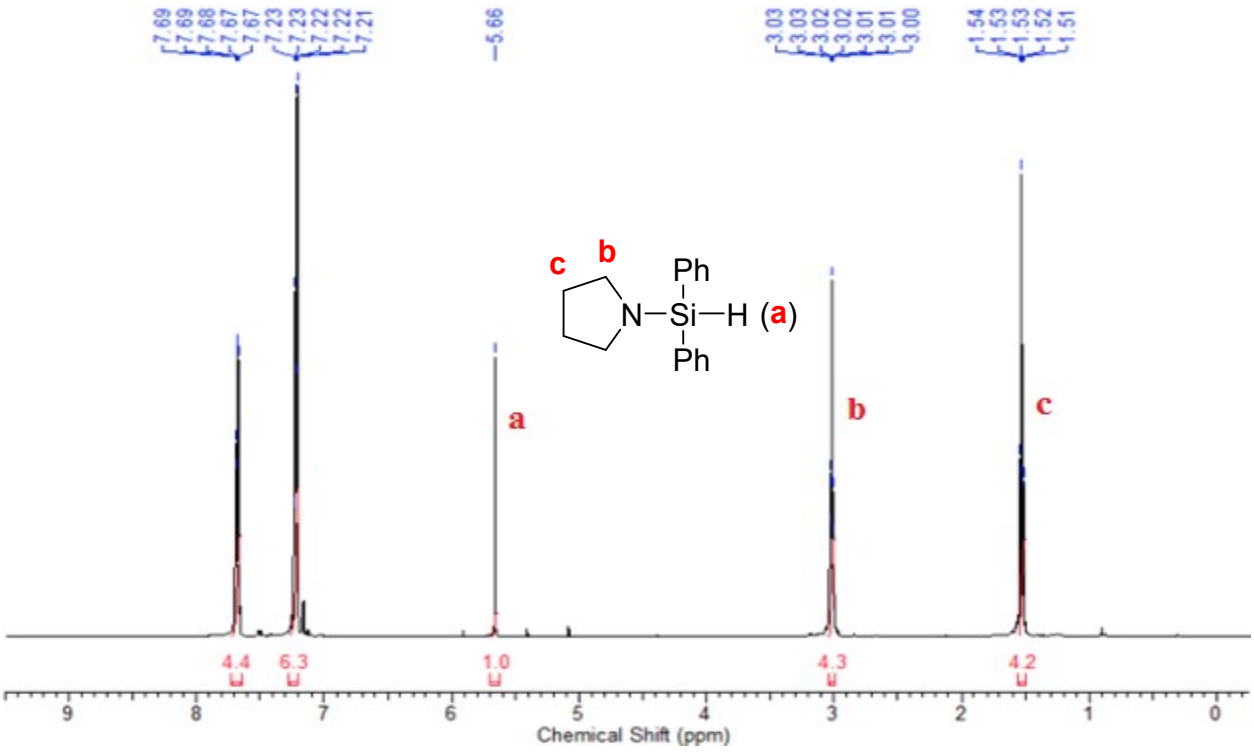
FS3: ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25 °C) of compound **4**



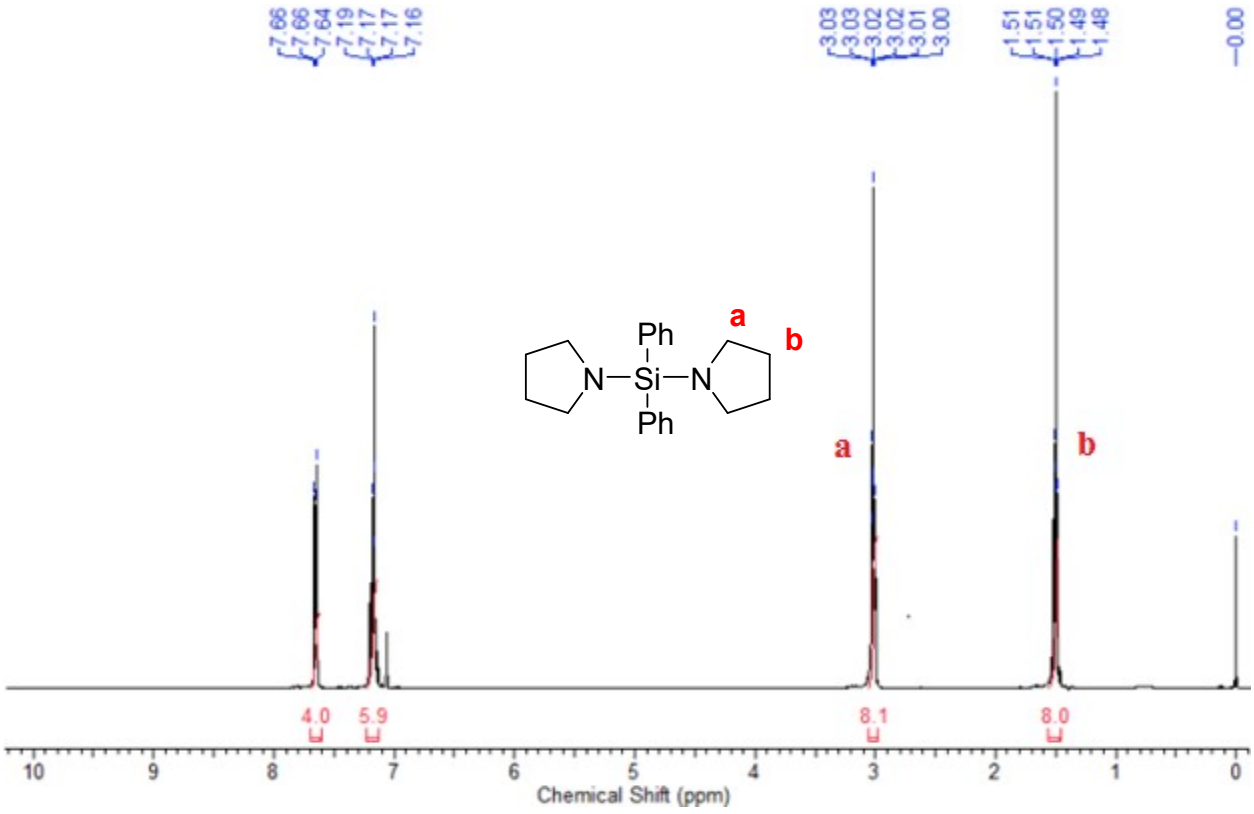
FS4: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 75 MHz, 25 °C) of compound **4**



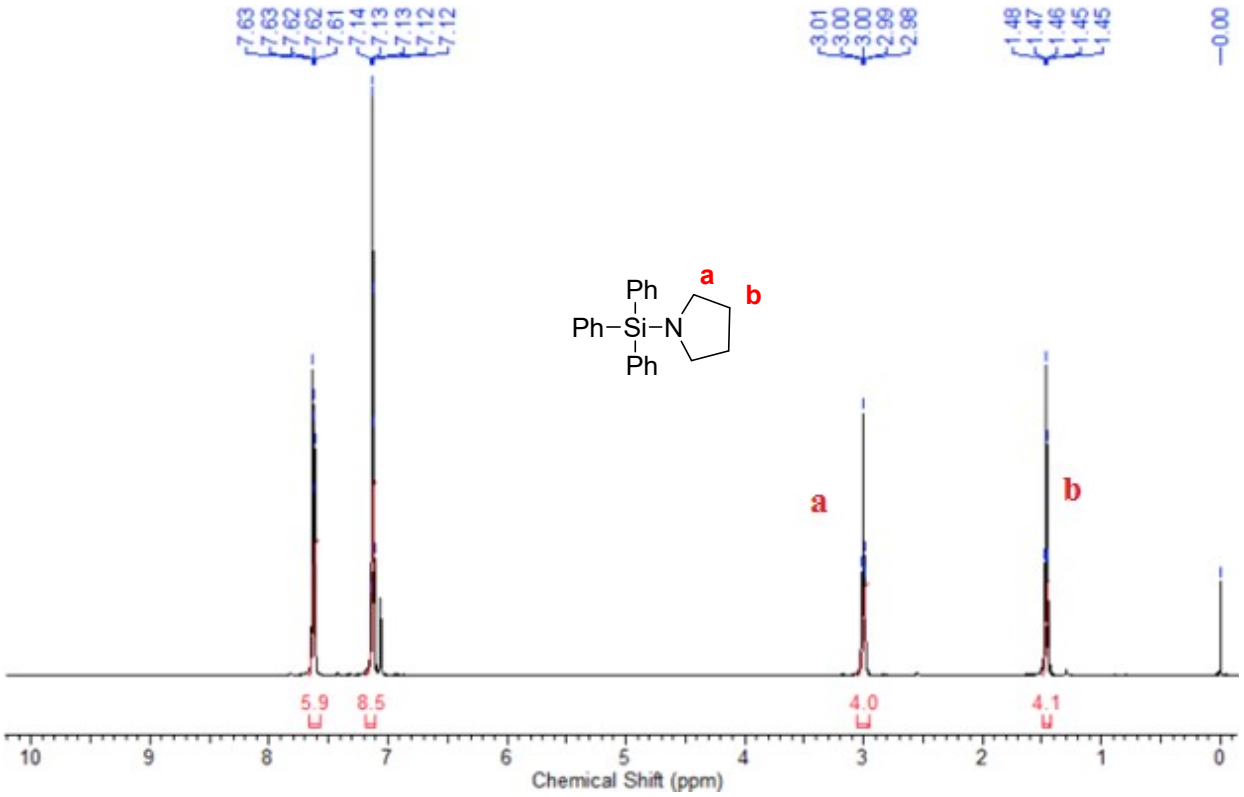
FS5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1a.**



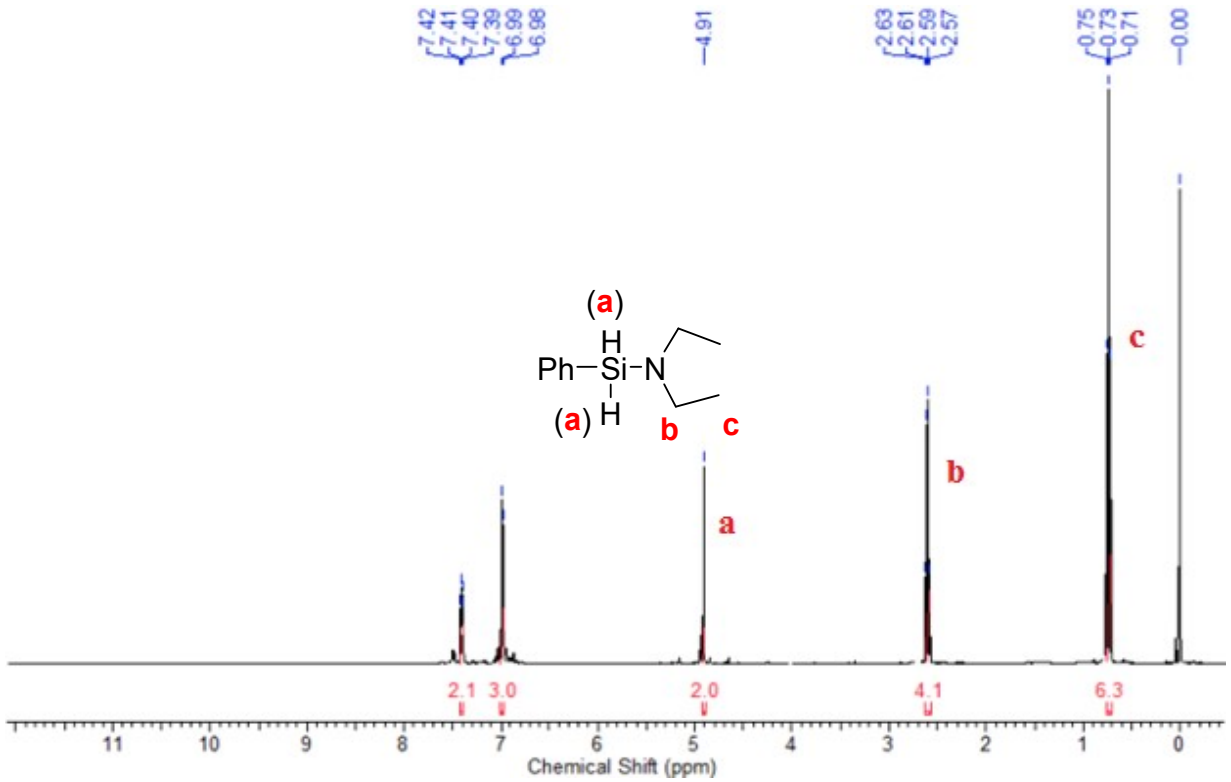
FS6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1b.**



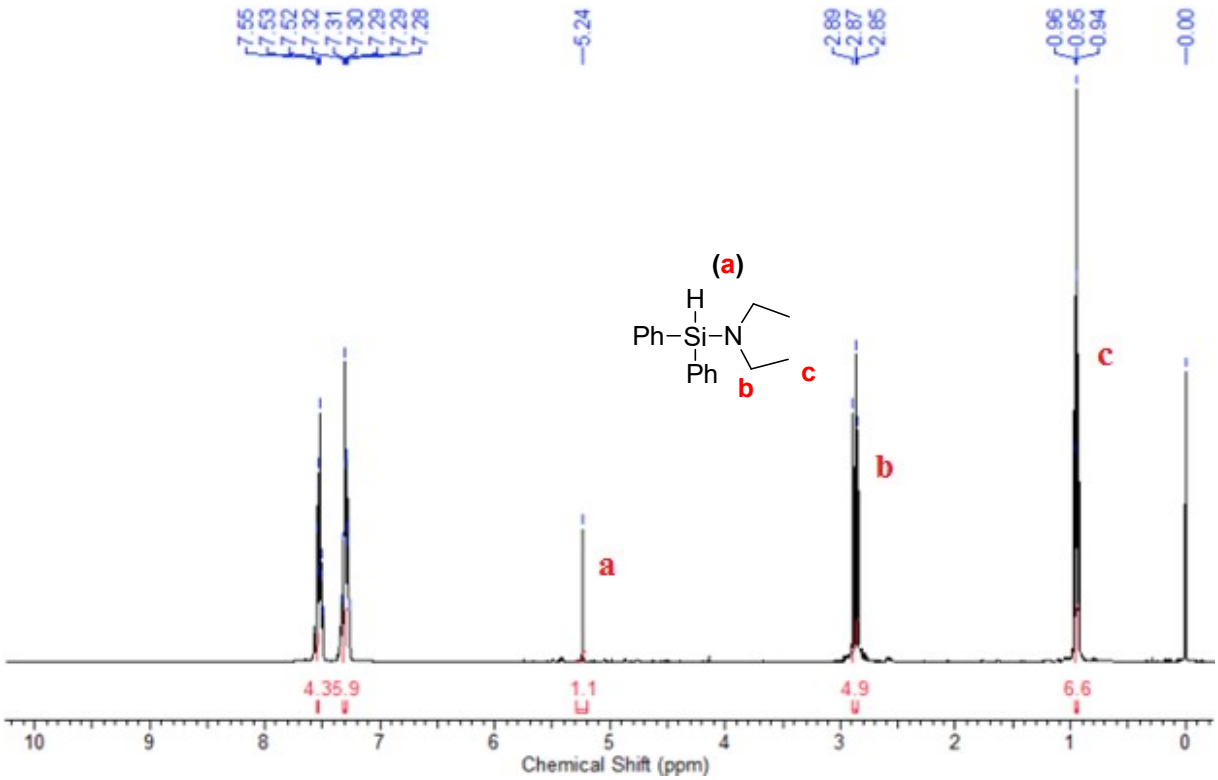
FS7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1c.**



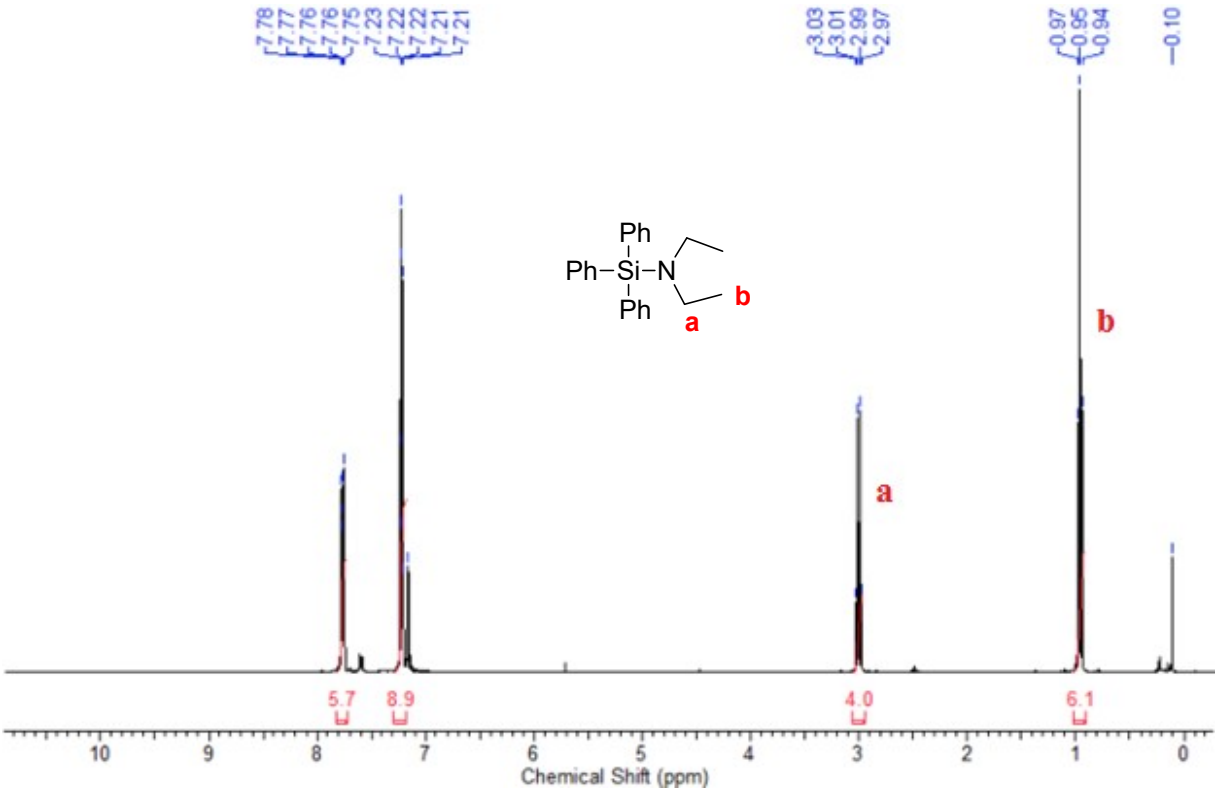
FS8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1d.**



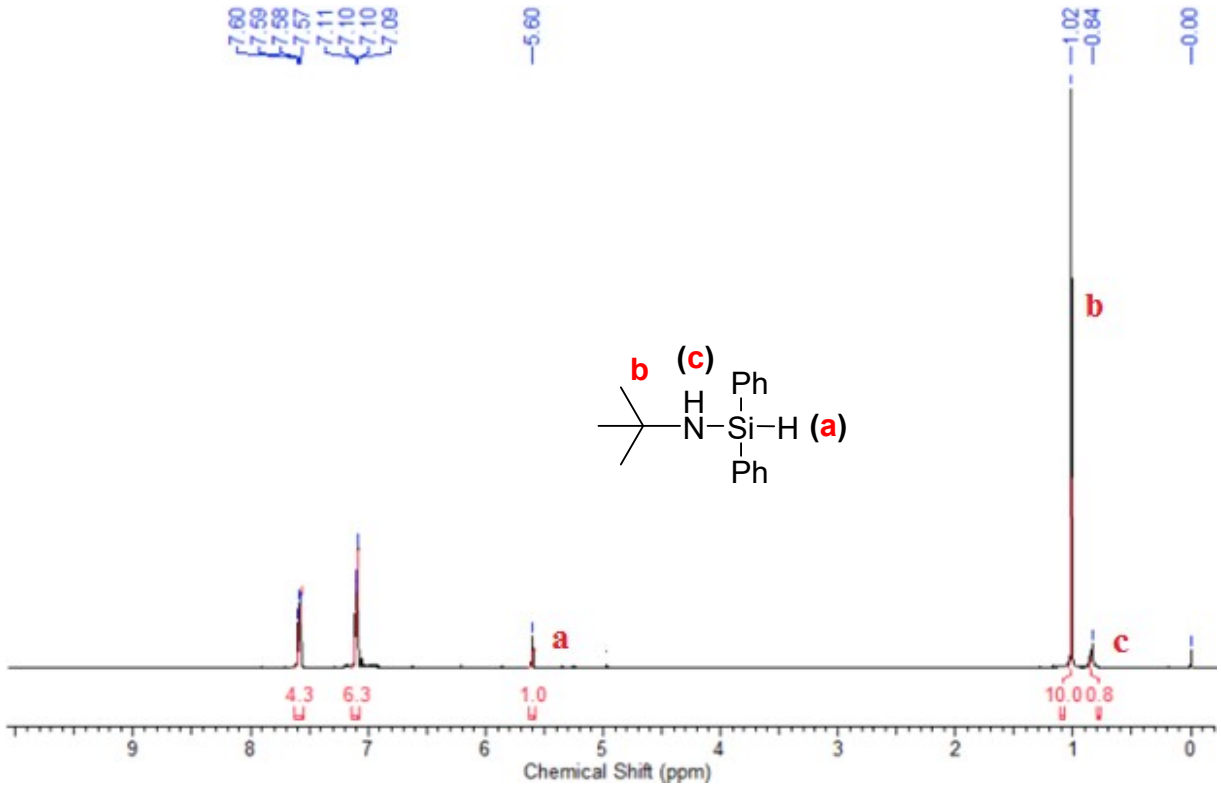
FS9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1e.**



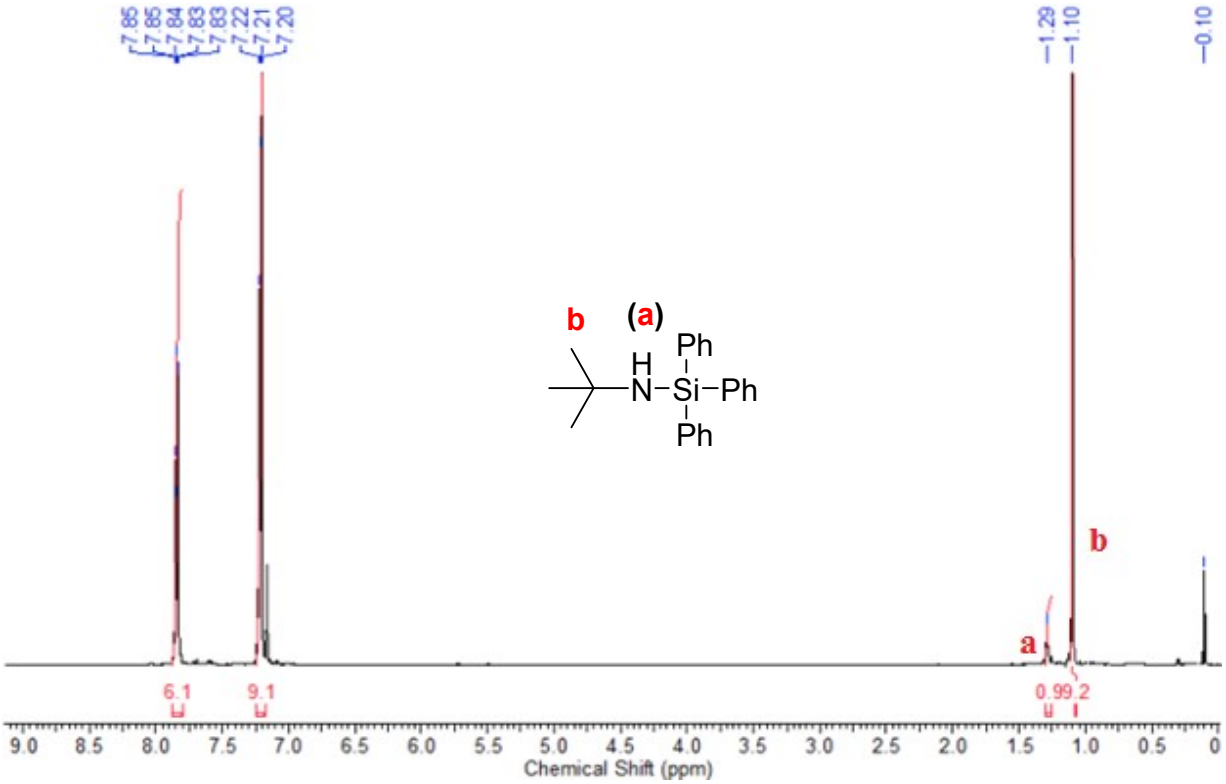
FS10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1f.**



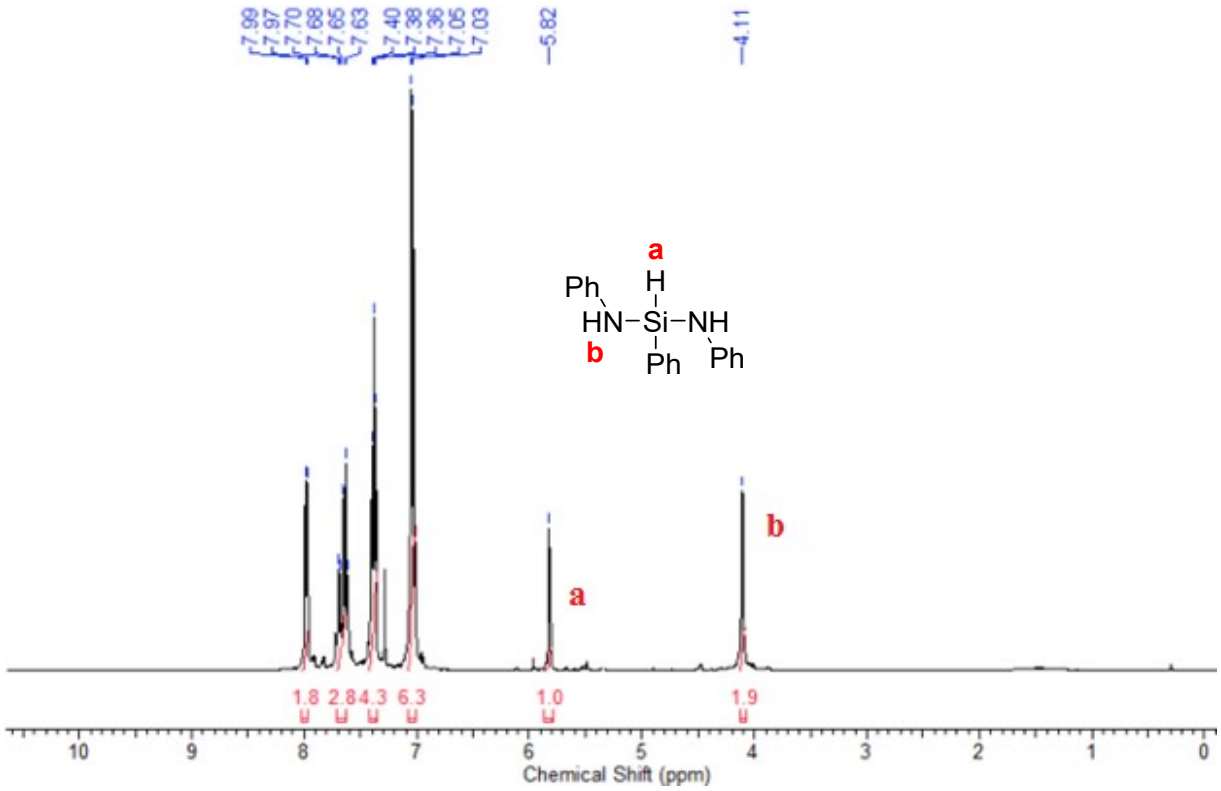
FS11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1g.**



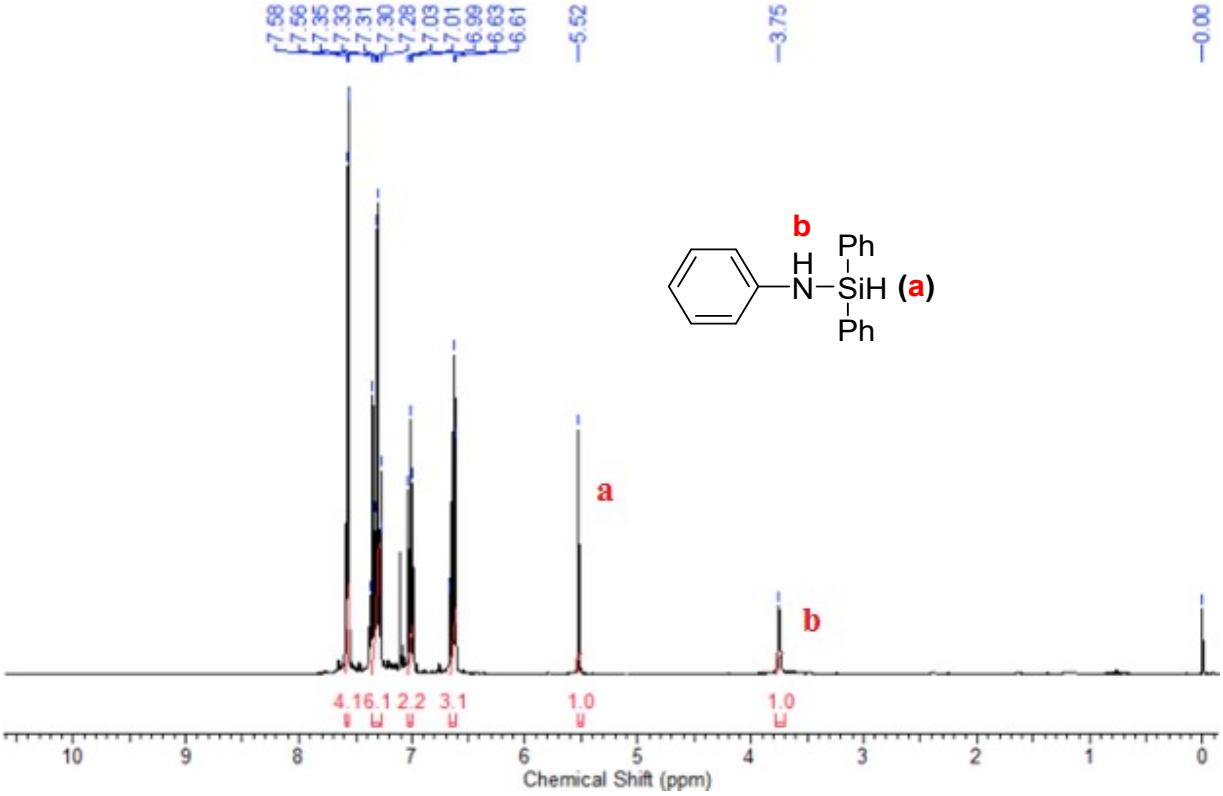
FS12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1h.**



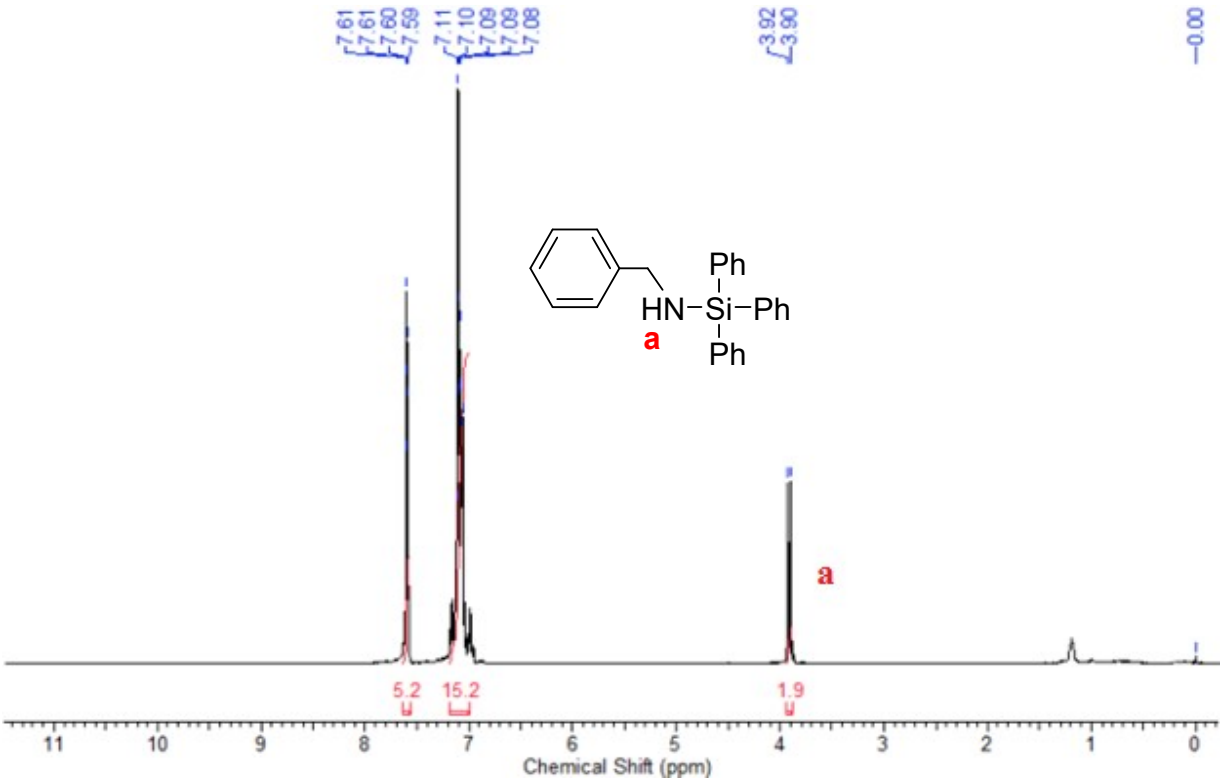
FS13. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **1i.**



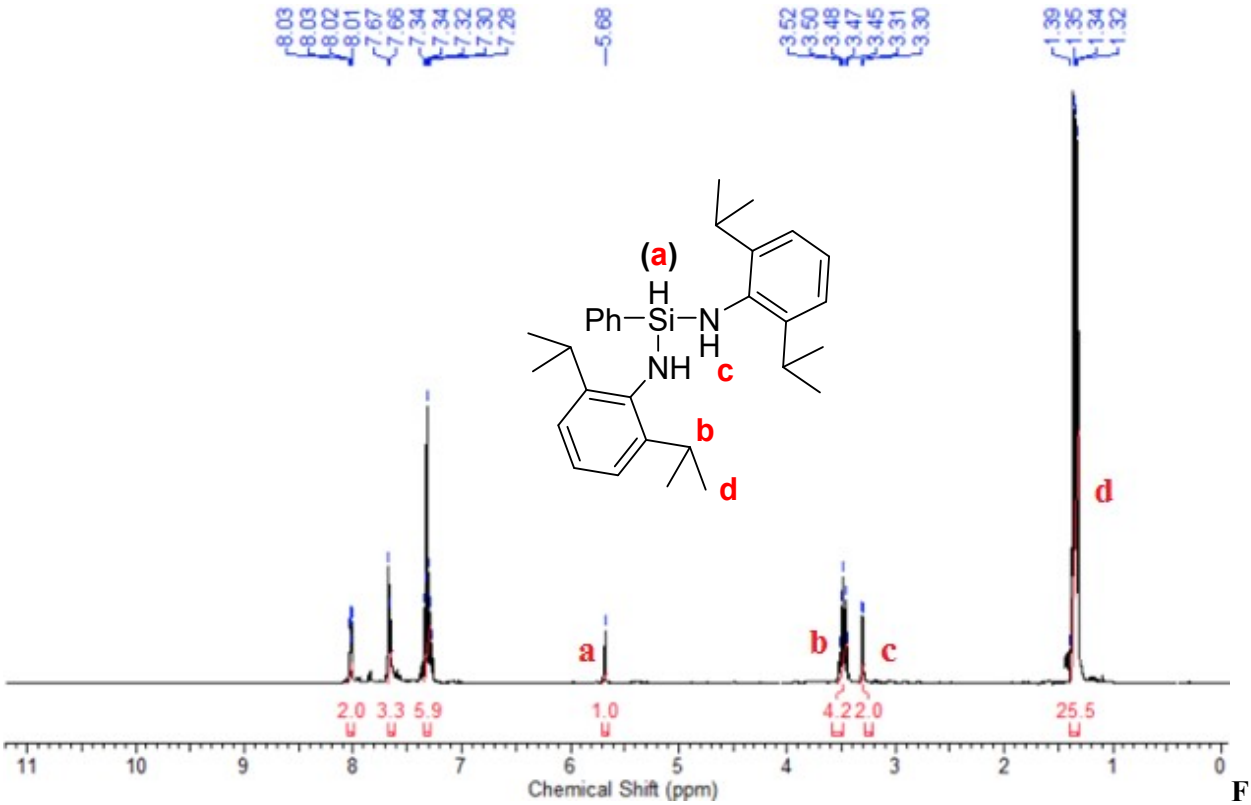
FS14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2a.**



FS15. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2b.**

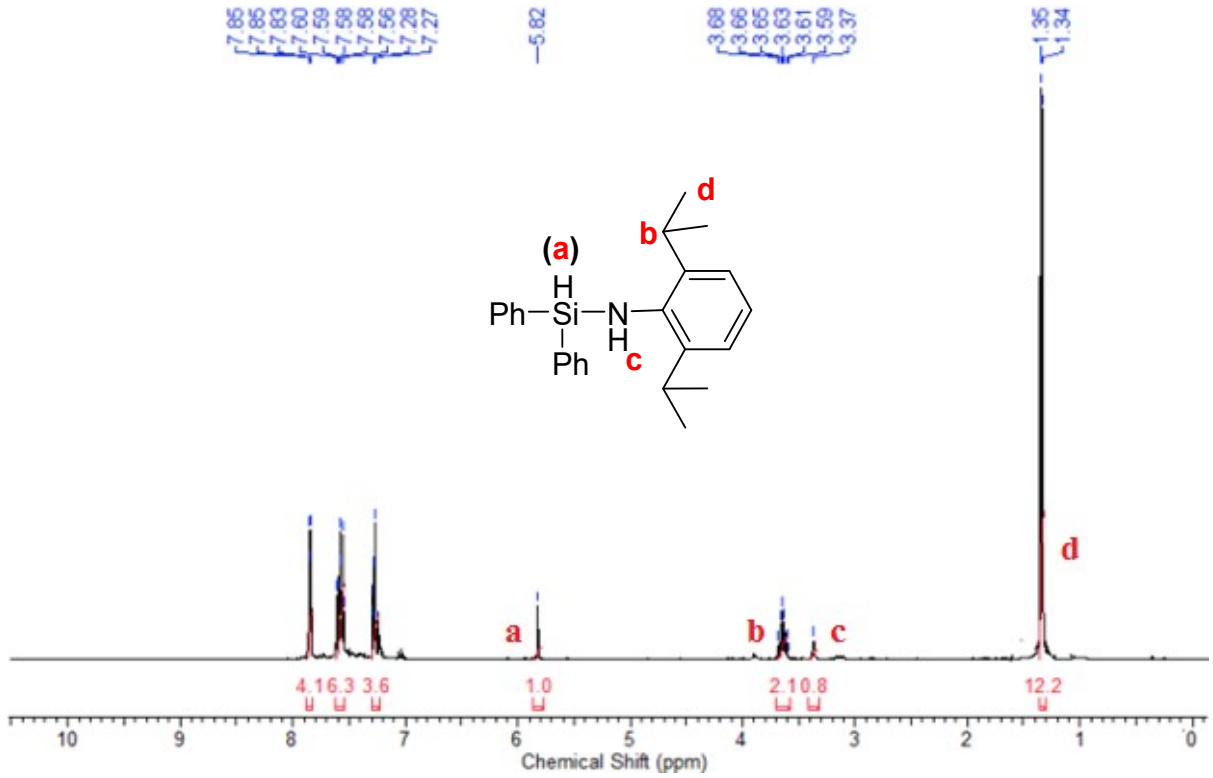


FS16. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2c.**

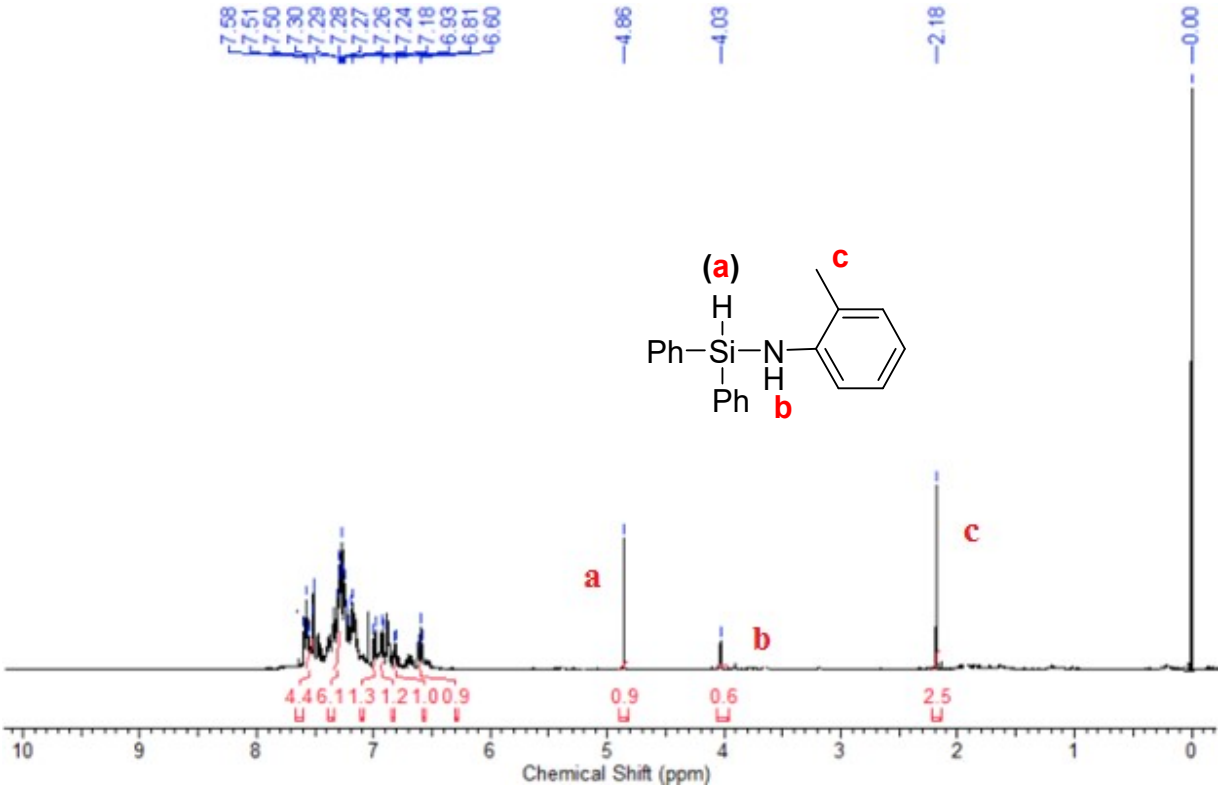


S17. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2d.**

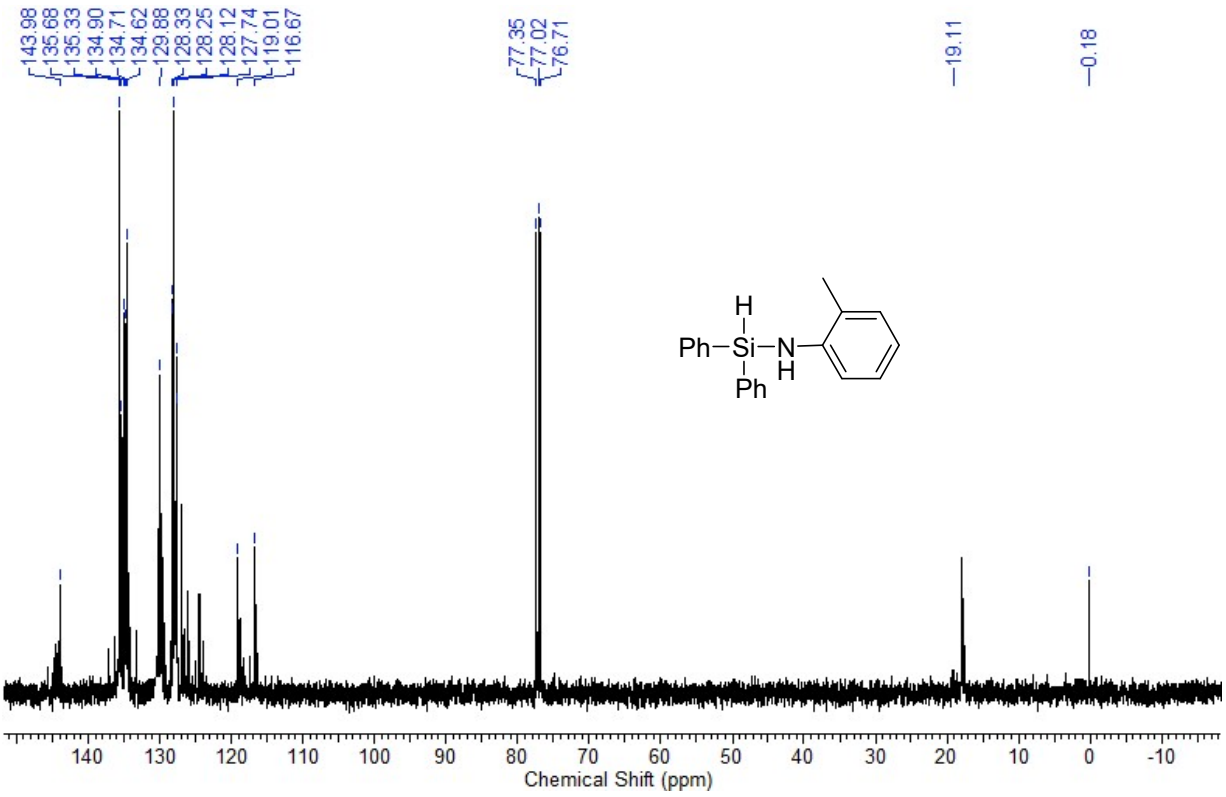
F



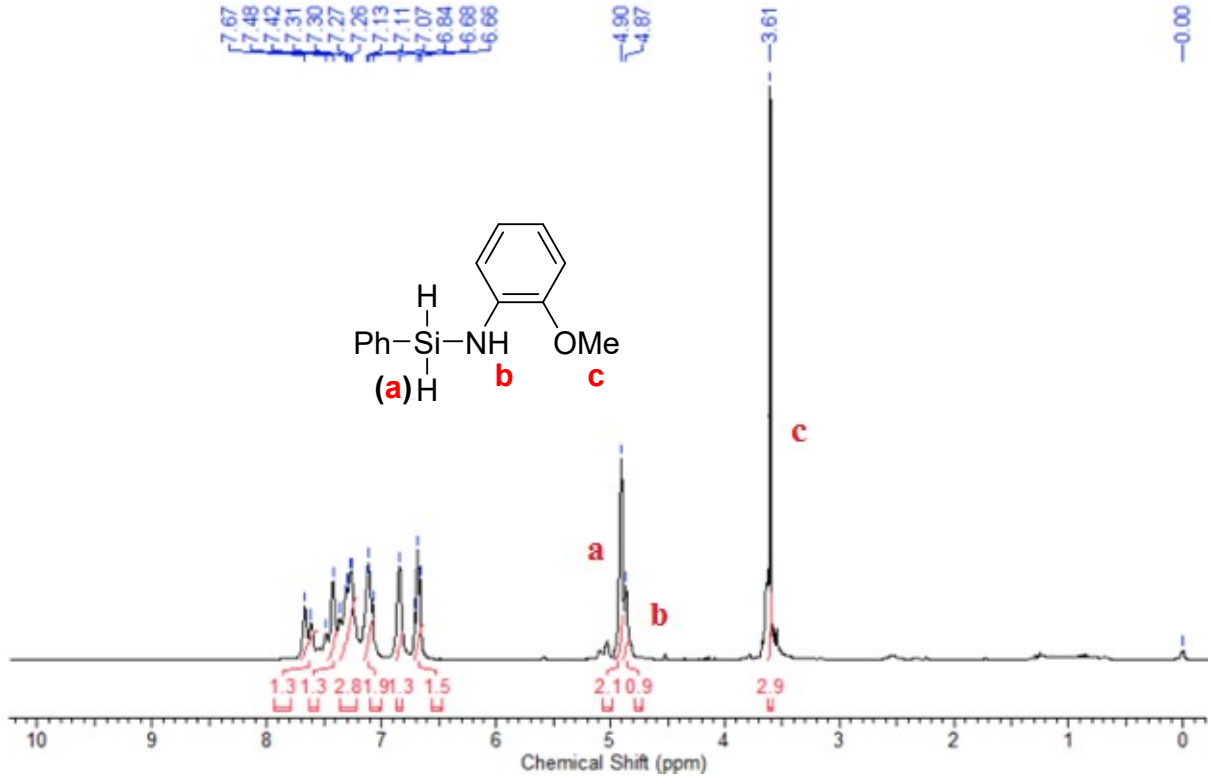
FS18. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2e.**



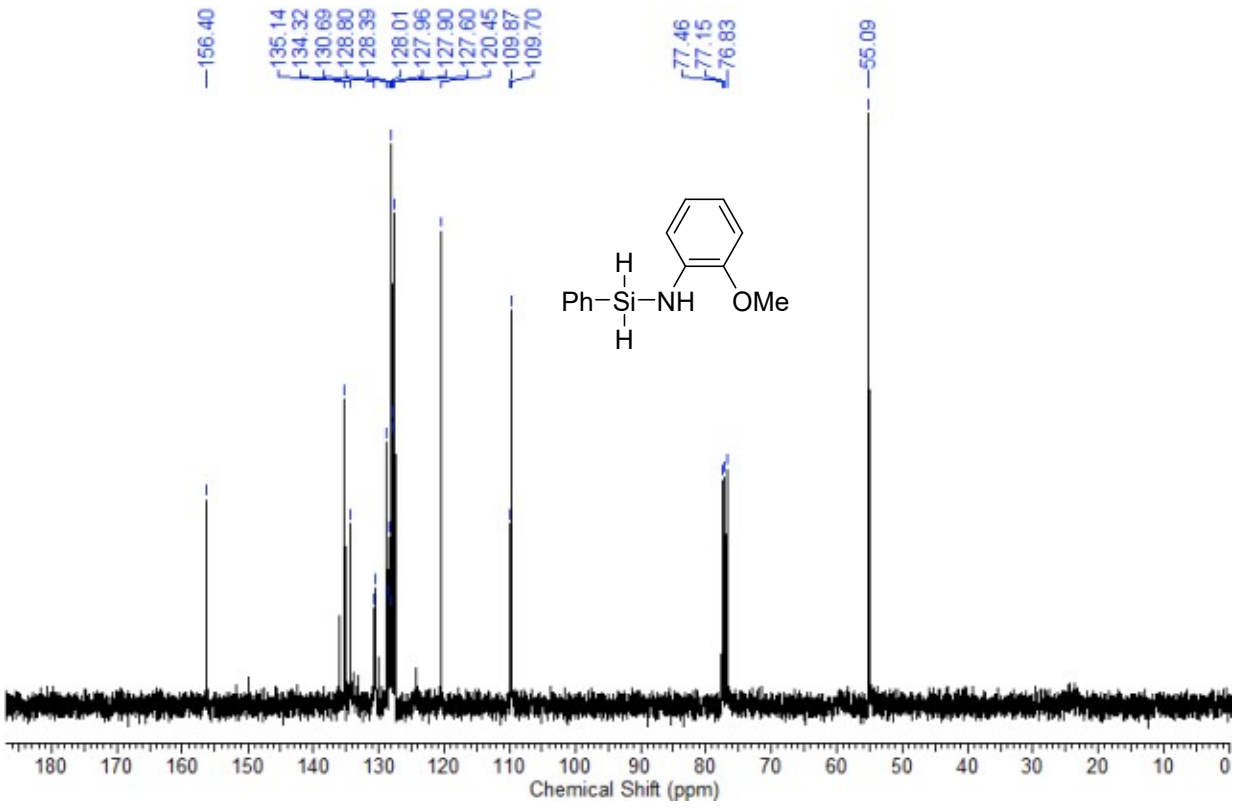
FS19. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2f.**



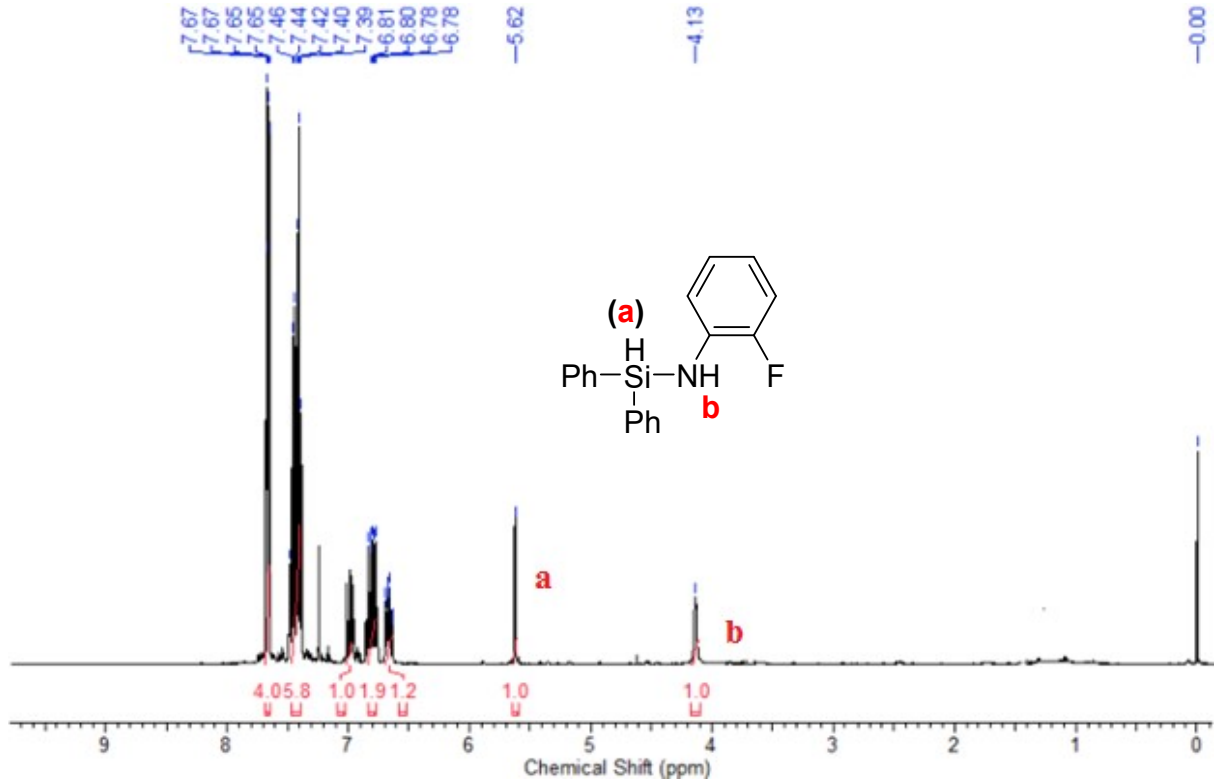
FS20. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2f.**



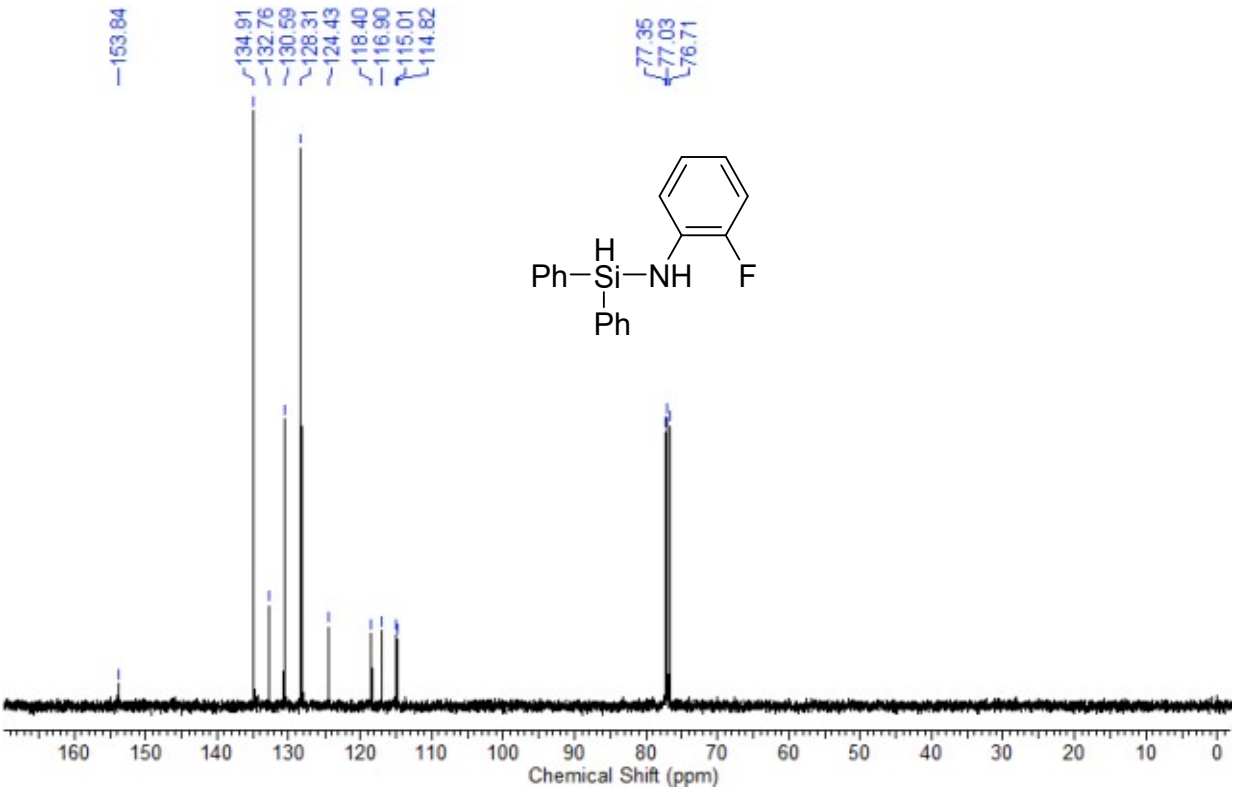
FS21. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2g.**



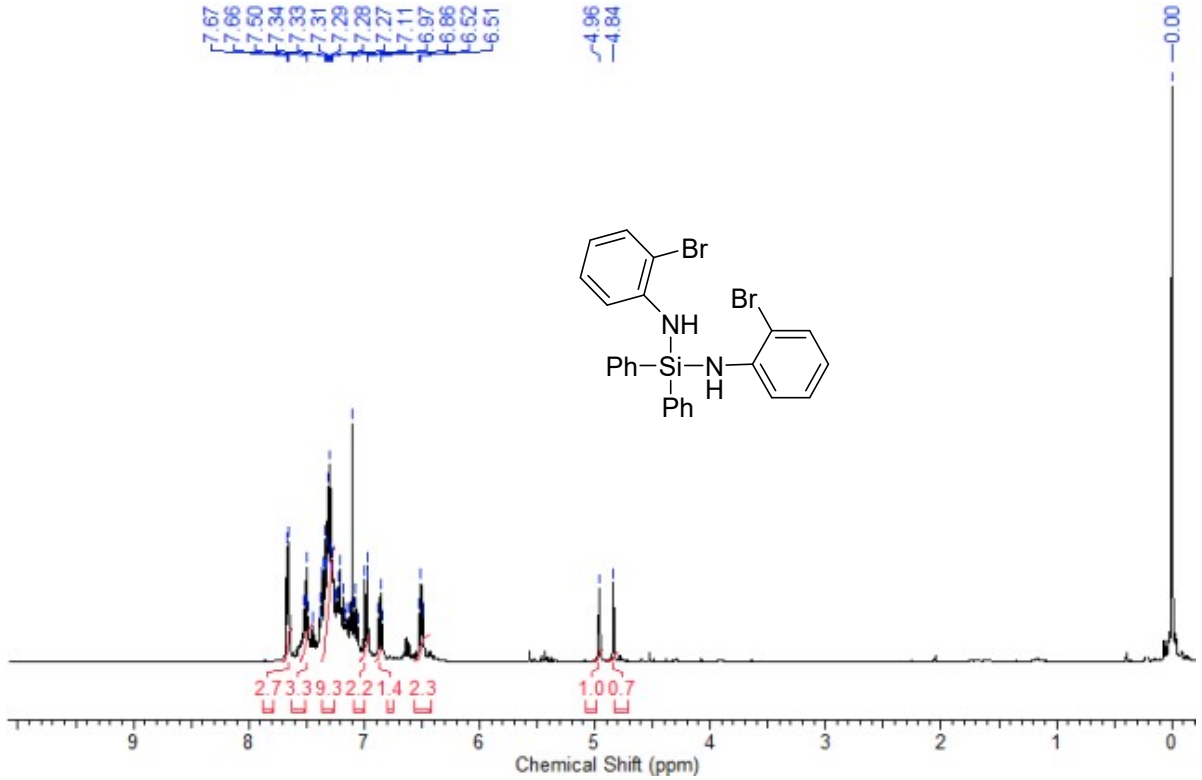
FS22. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2g.**



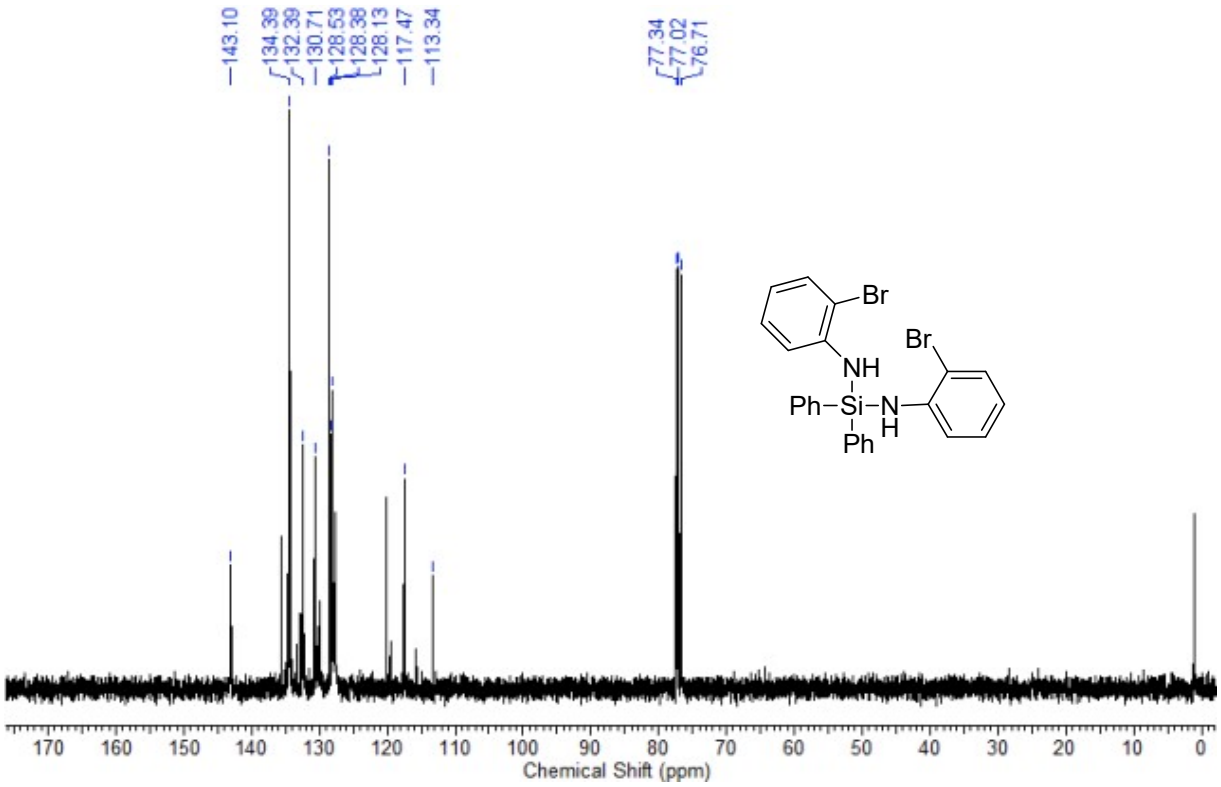
FS23. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2h.**



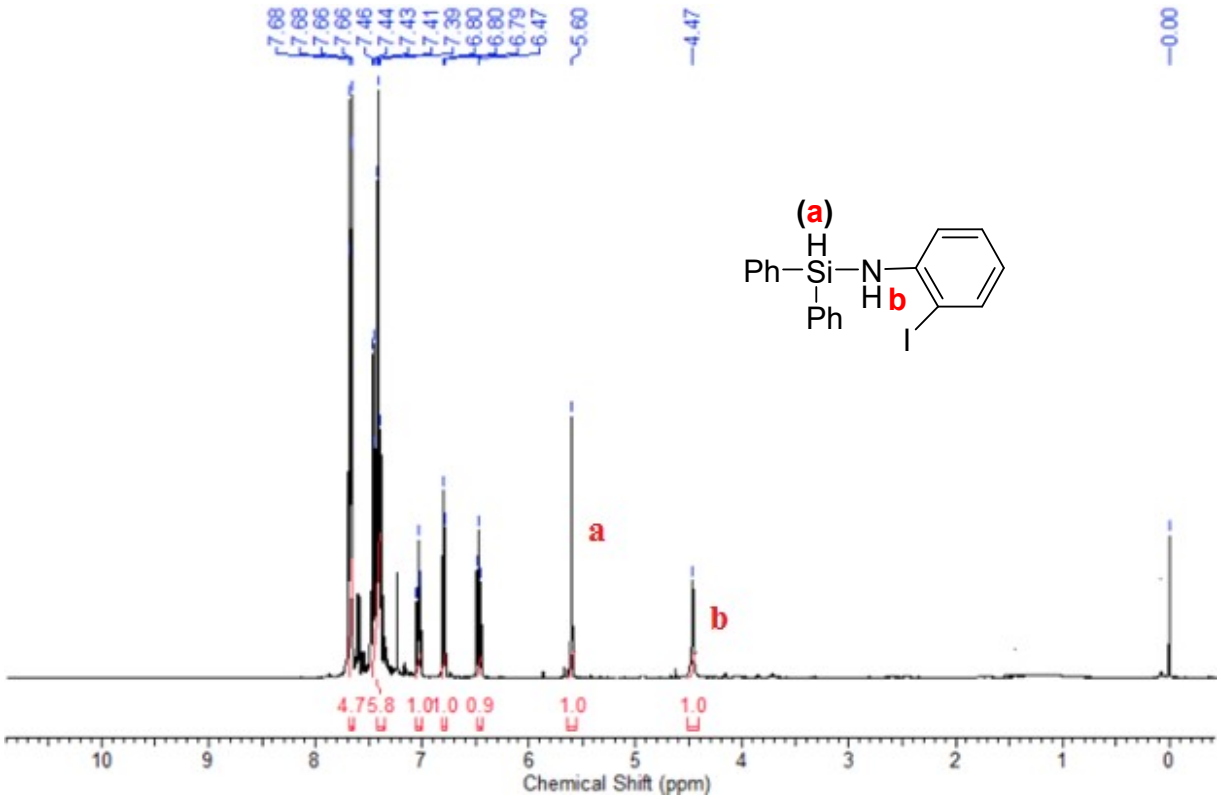
FS24. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2h.**



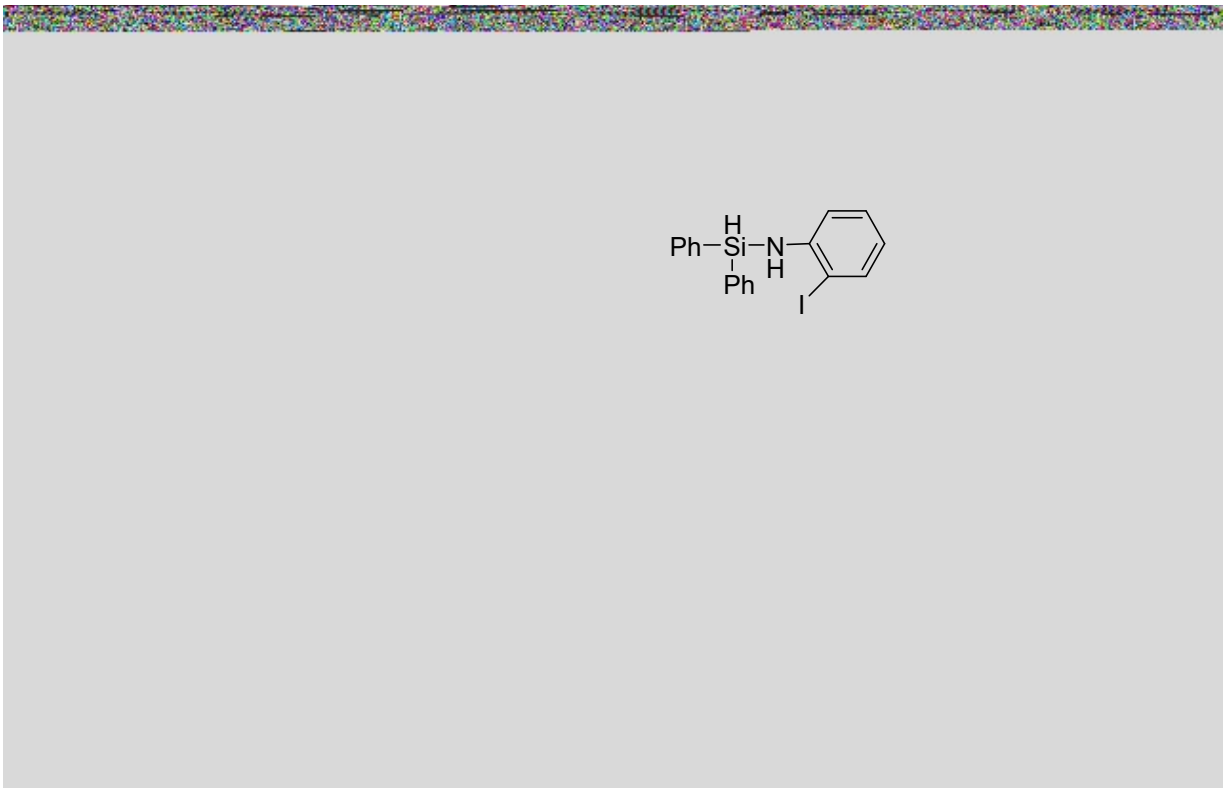
FS25. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2i.**



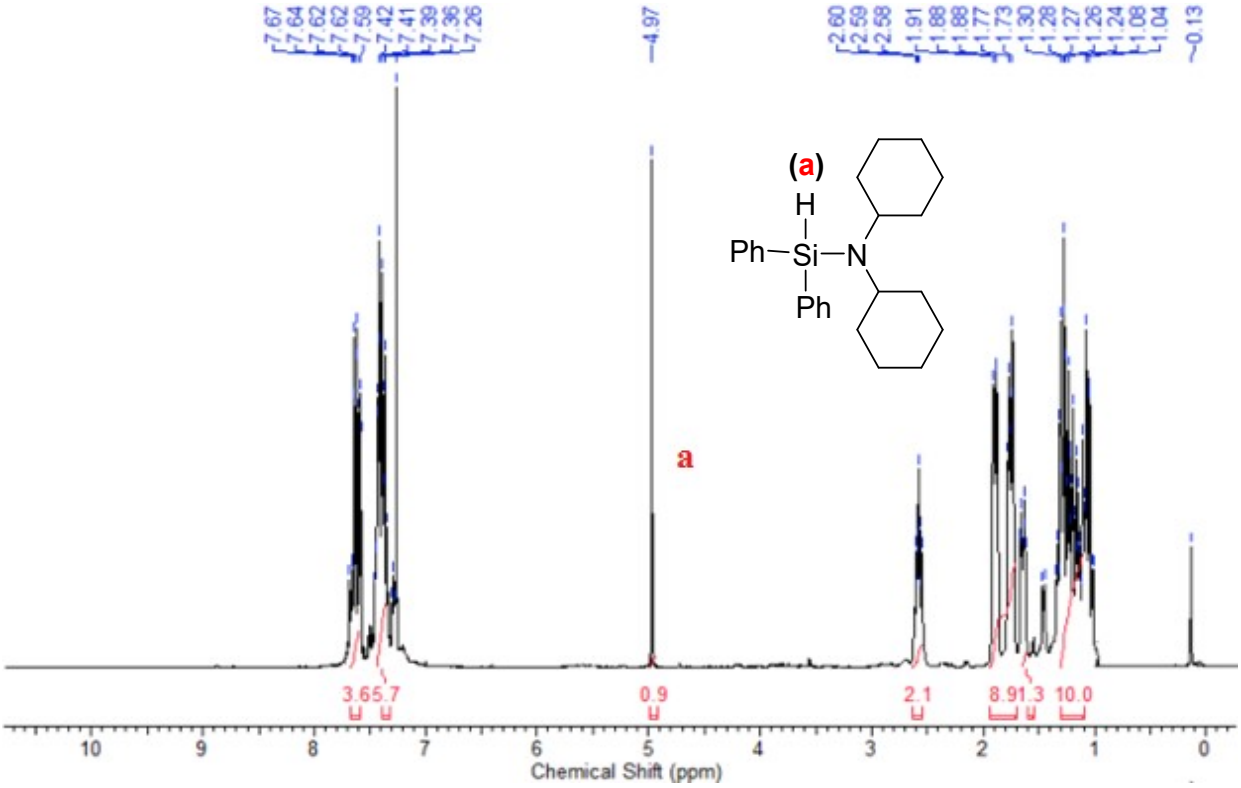
FS26. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2i.**



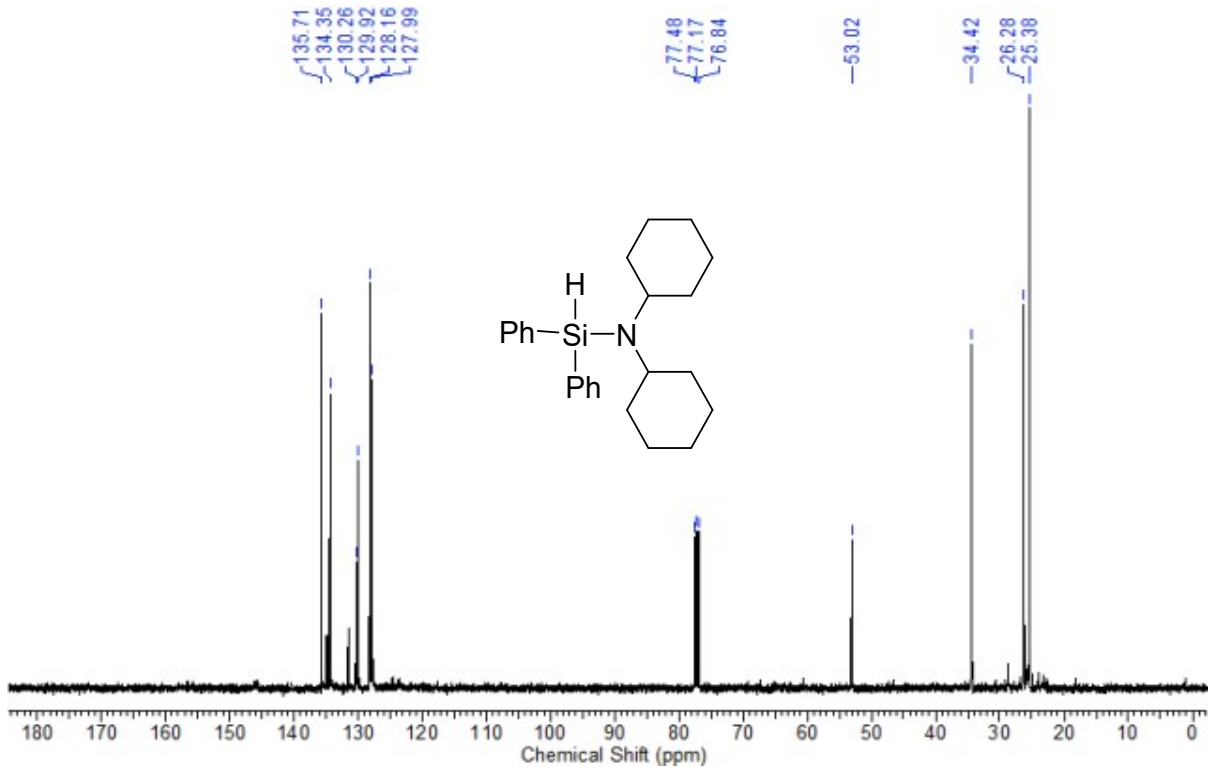
FS27. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2j.**



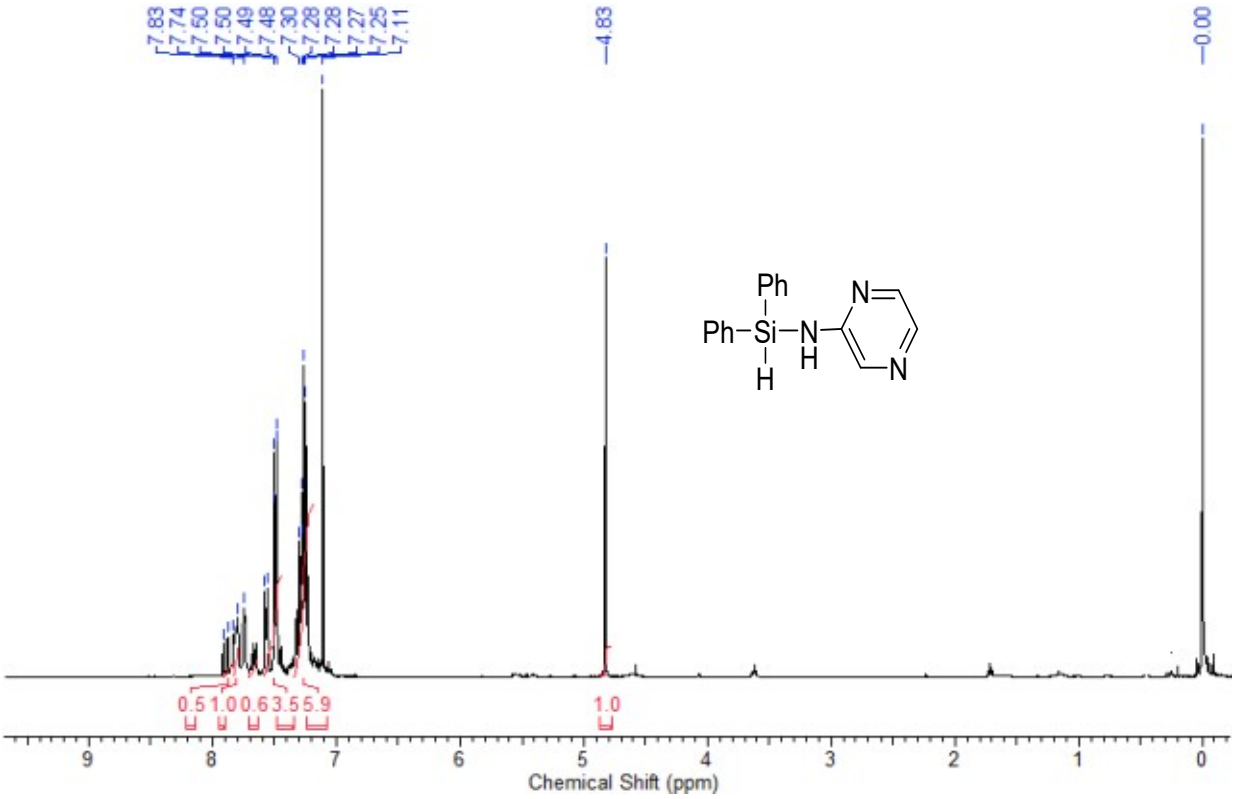
FS28. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2j.**



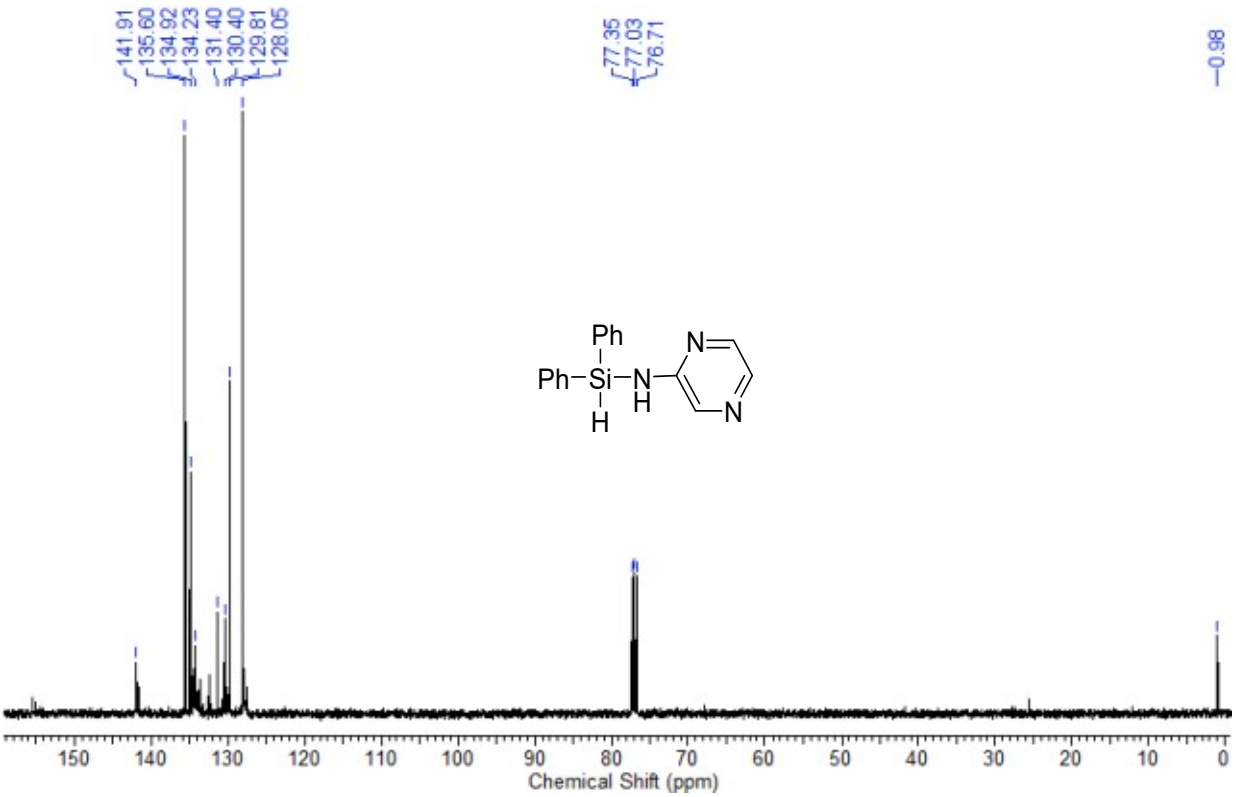
FS29. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2k.**



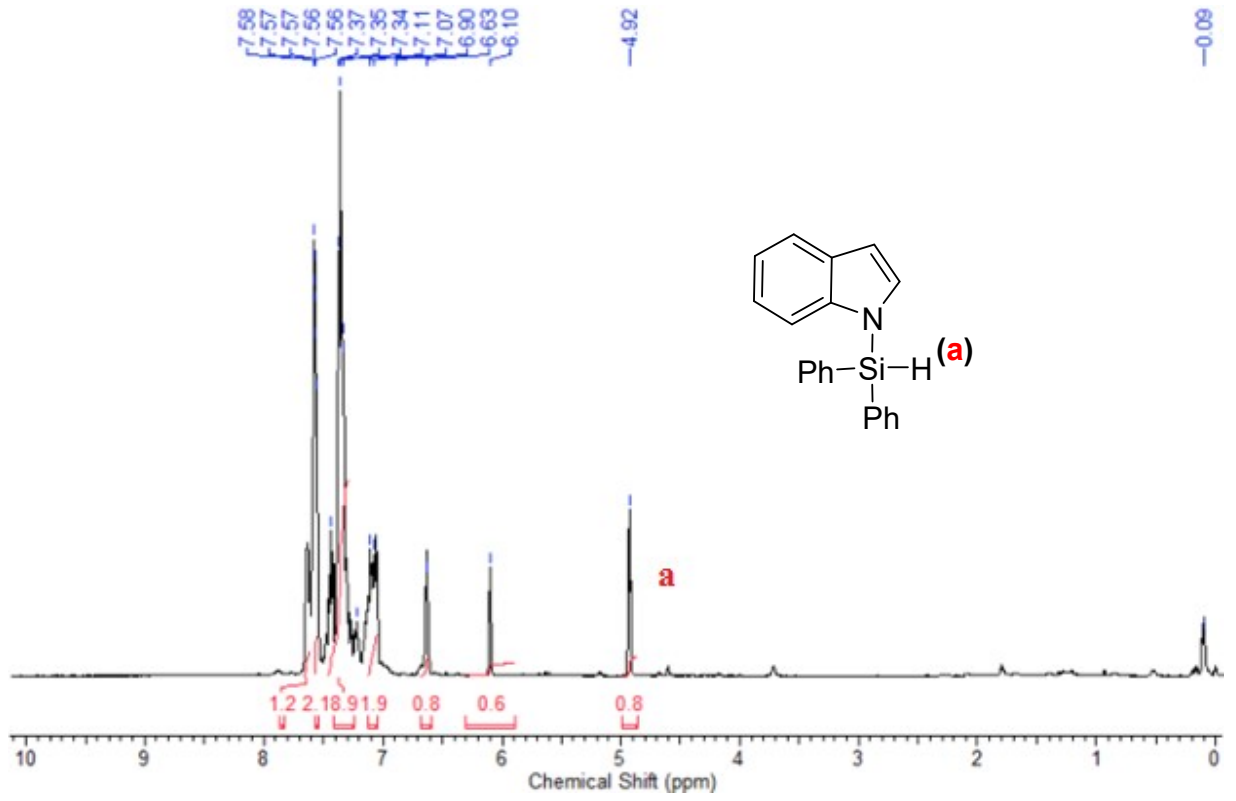
FS30. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2k.**



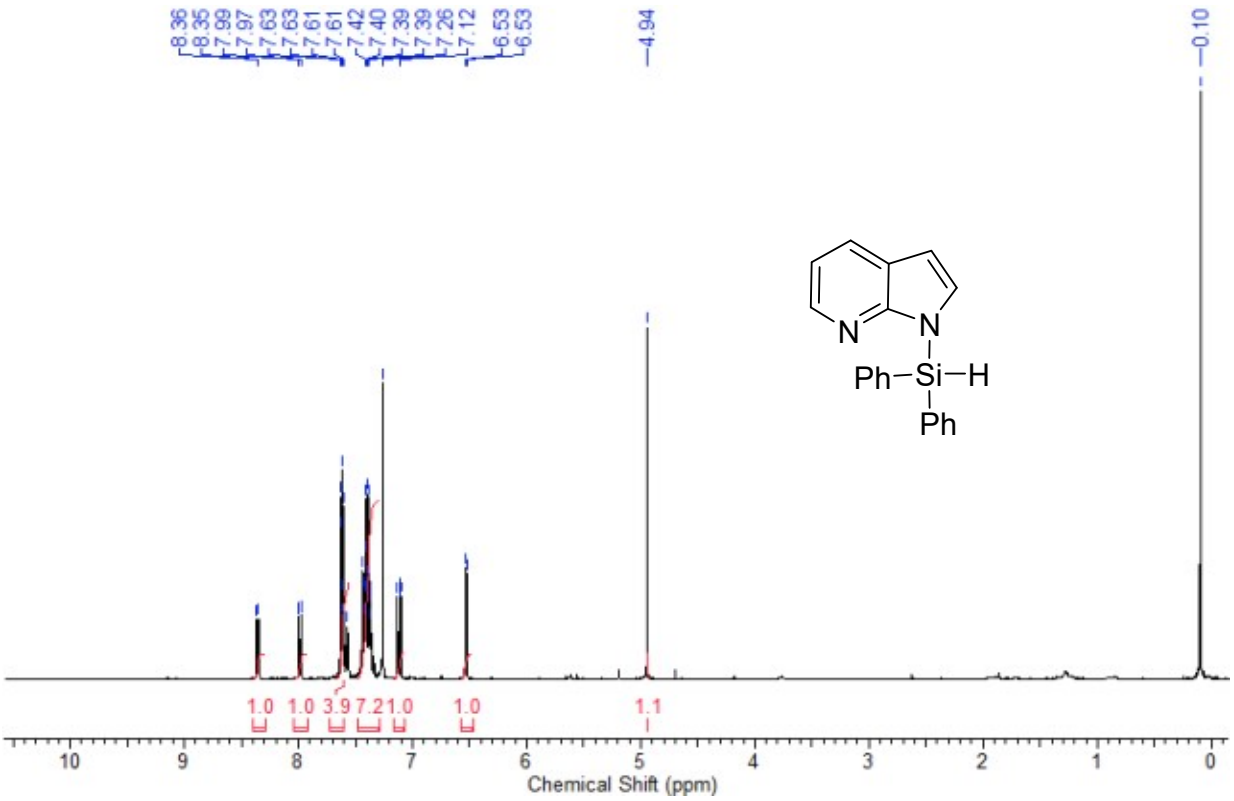
FS31. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2l.**



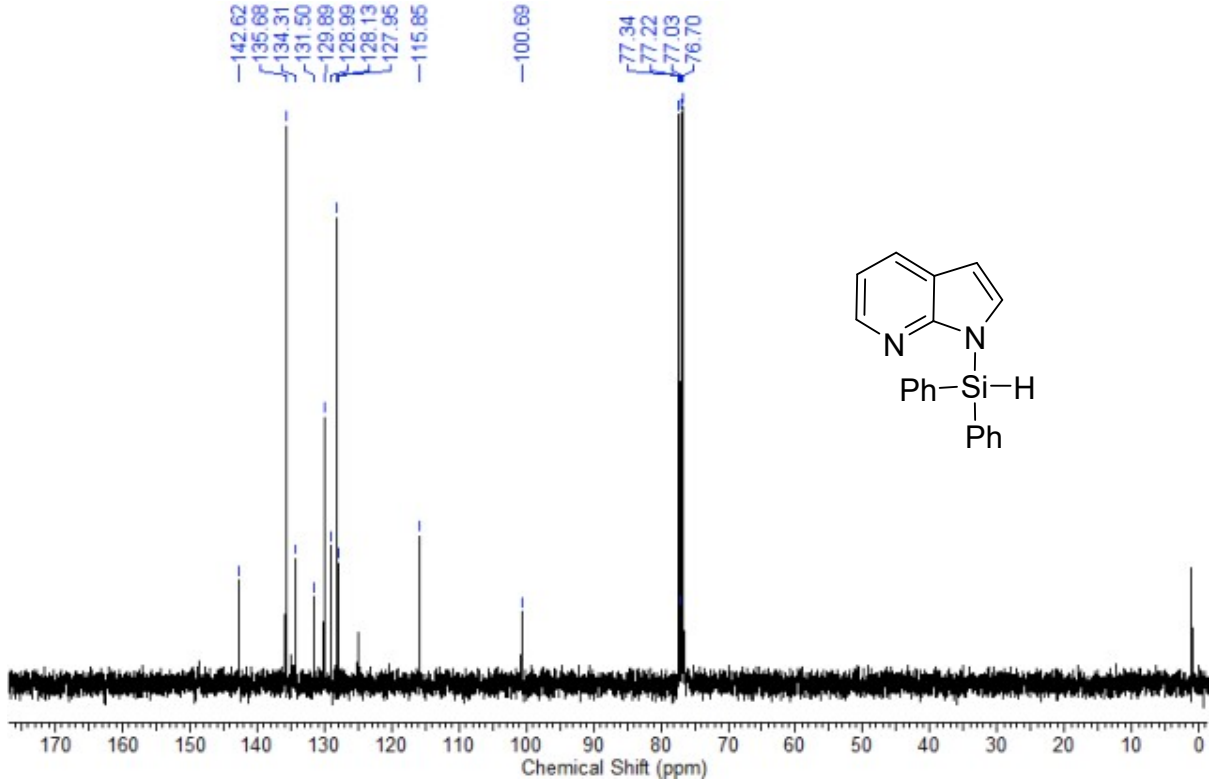
FS32. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2l.**



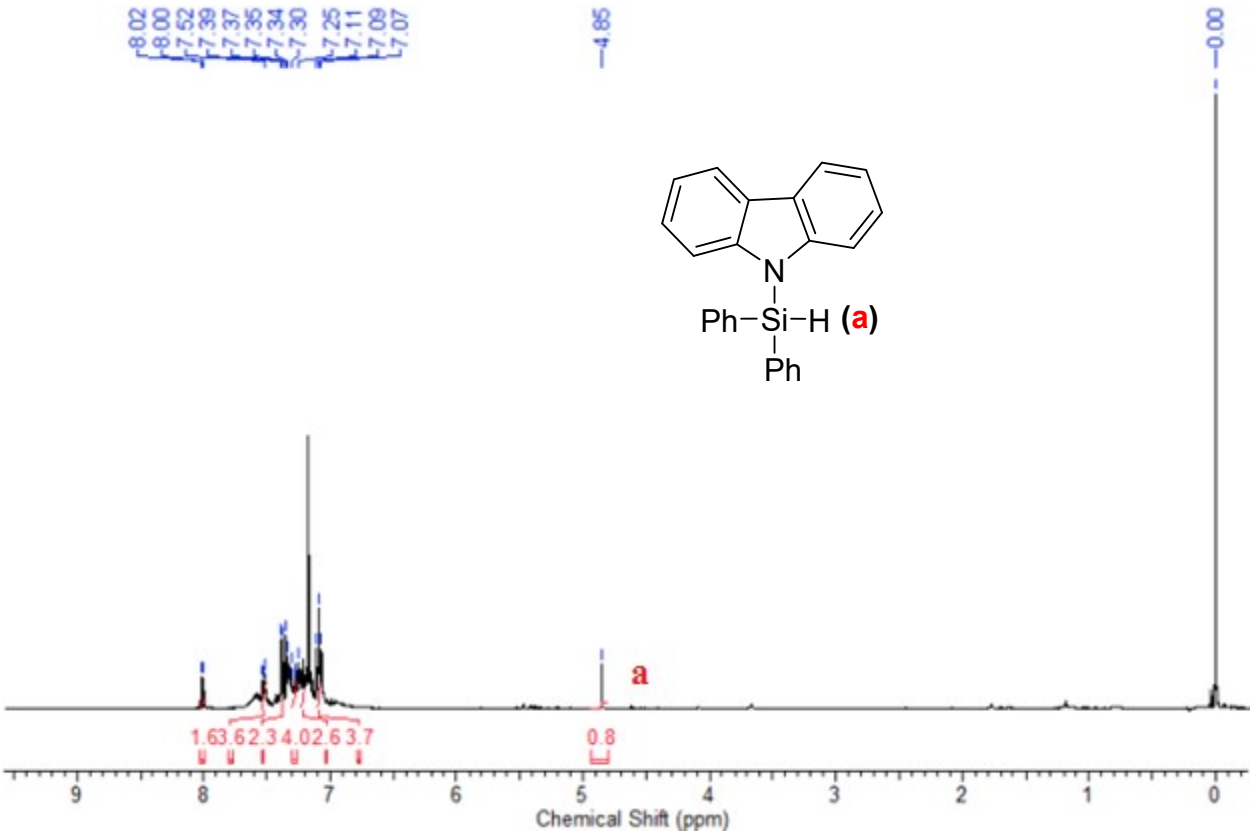
FS33. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2m.**



FS34. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2n.**



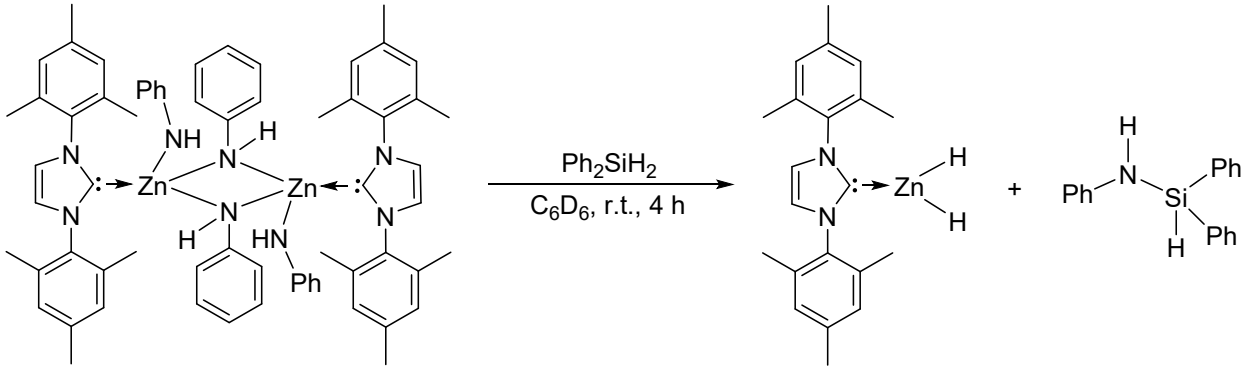
FS35. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of complex **2n.**



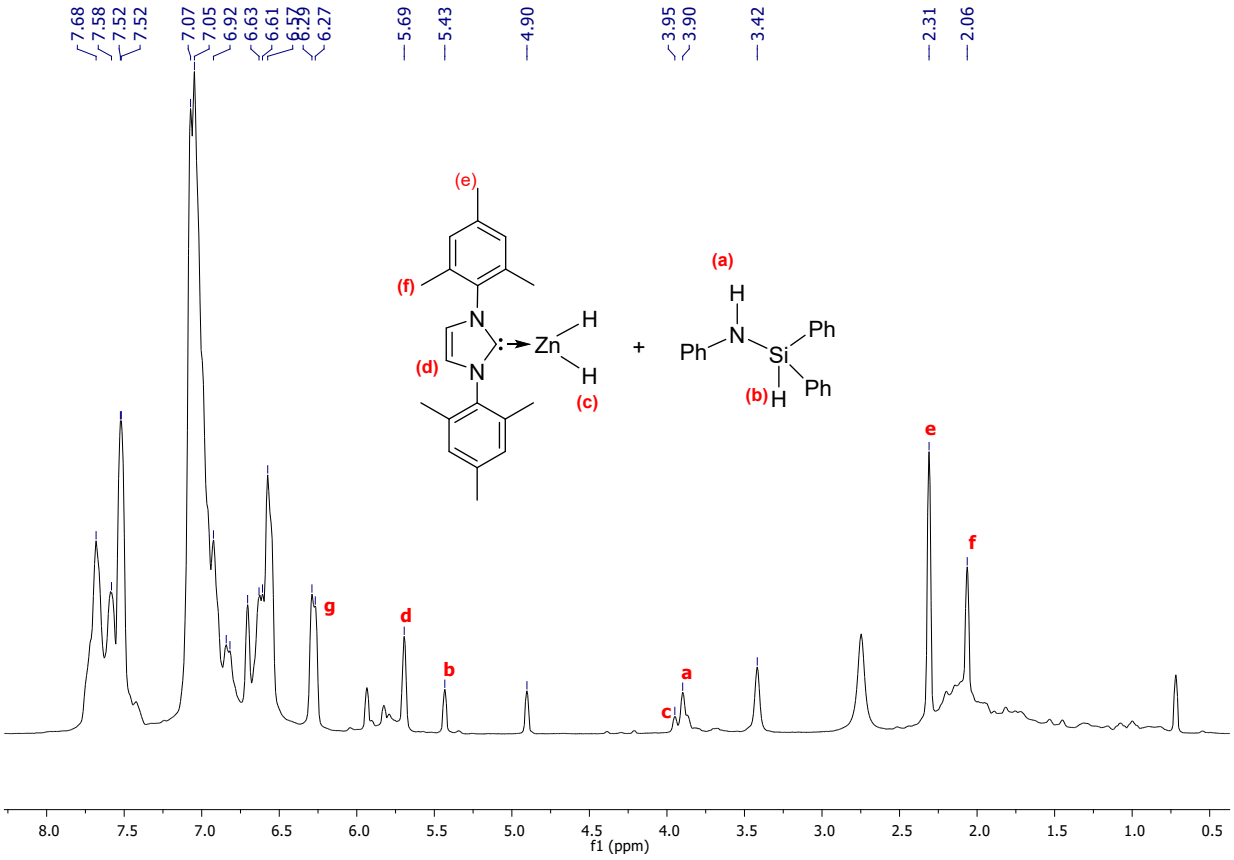
FS36. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of complex **2o.**

Stoichiometric reaction between Complex 3 and diphenylsilane:

Ph_2SiH_2 (0.5 mmol, 2 equiv) was added to a C_6D_6 solution of complex **3** (0.25 mmol, 1 equiv) in a screw cap NMR tube inside the glove box. After 4 hours, the progress of the reaction was monitored by ^{1}H NMR. Singlet peak at δ = 3.90 and 5.43 ppm correspond to N-H and Si-H proton respectively indicates for the formation of CDC product. Whereas singlet resonance at δ = 3.95 ppm indicates the formation of zinc hydride.



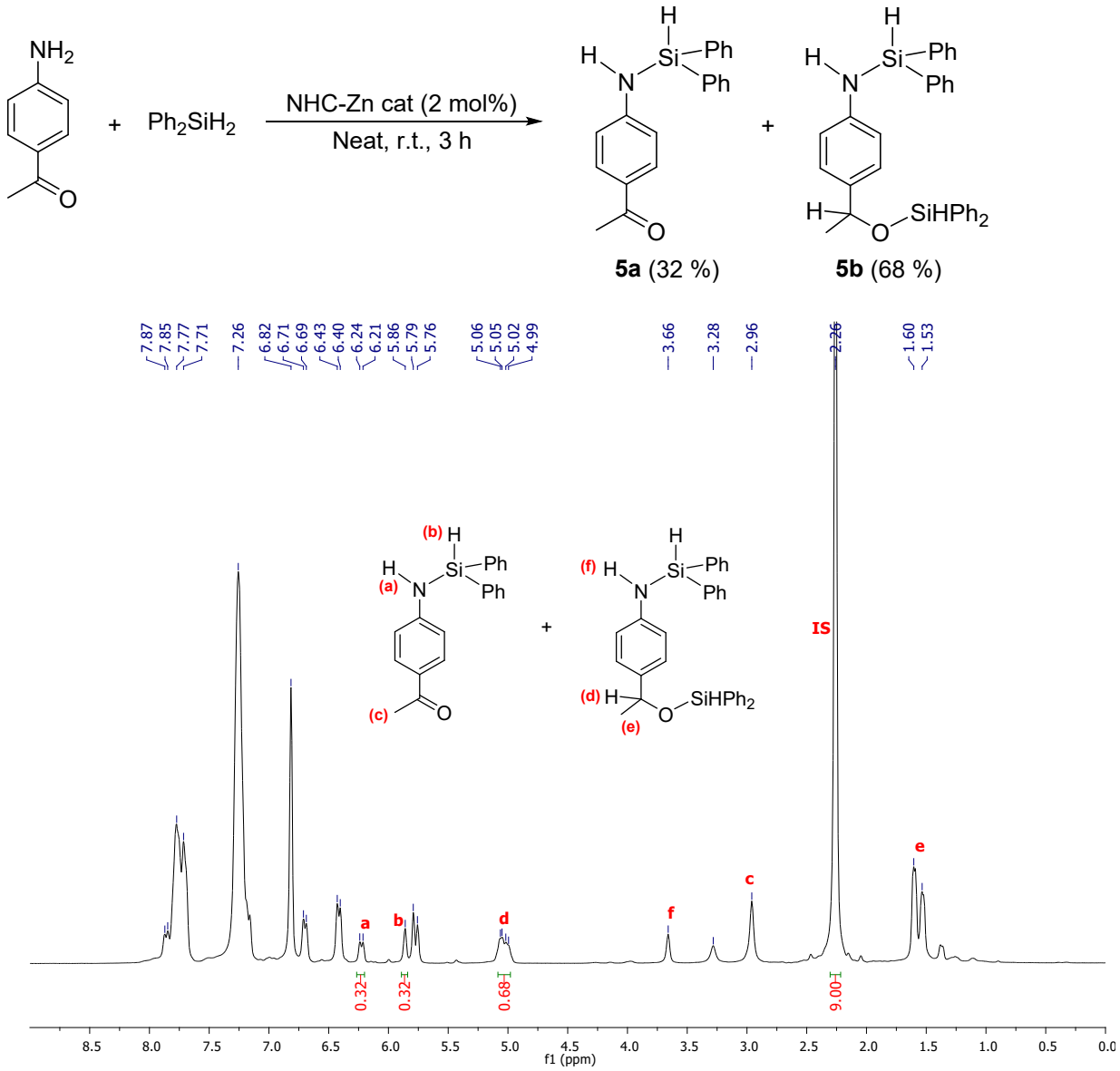
Complex **3**



FS37. ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25 °C) of the stoichiometric reaction between complex **3** and Ph_2SiH_2.

Competitive reactivity study of amine and carbonyl functionality in presence of Ph_2SiH_2:

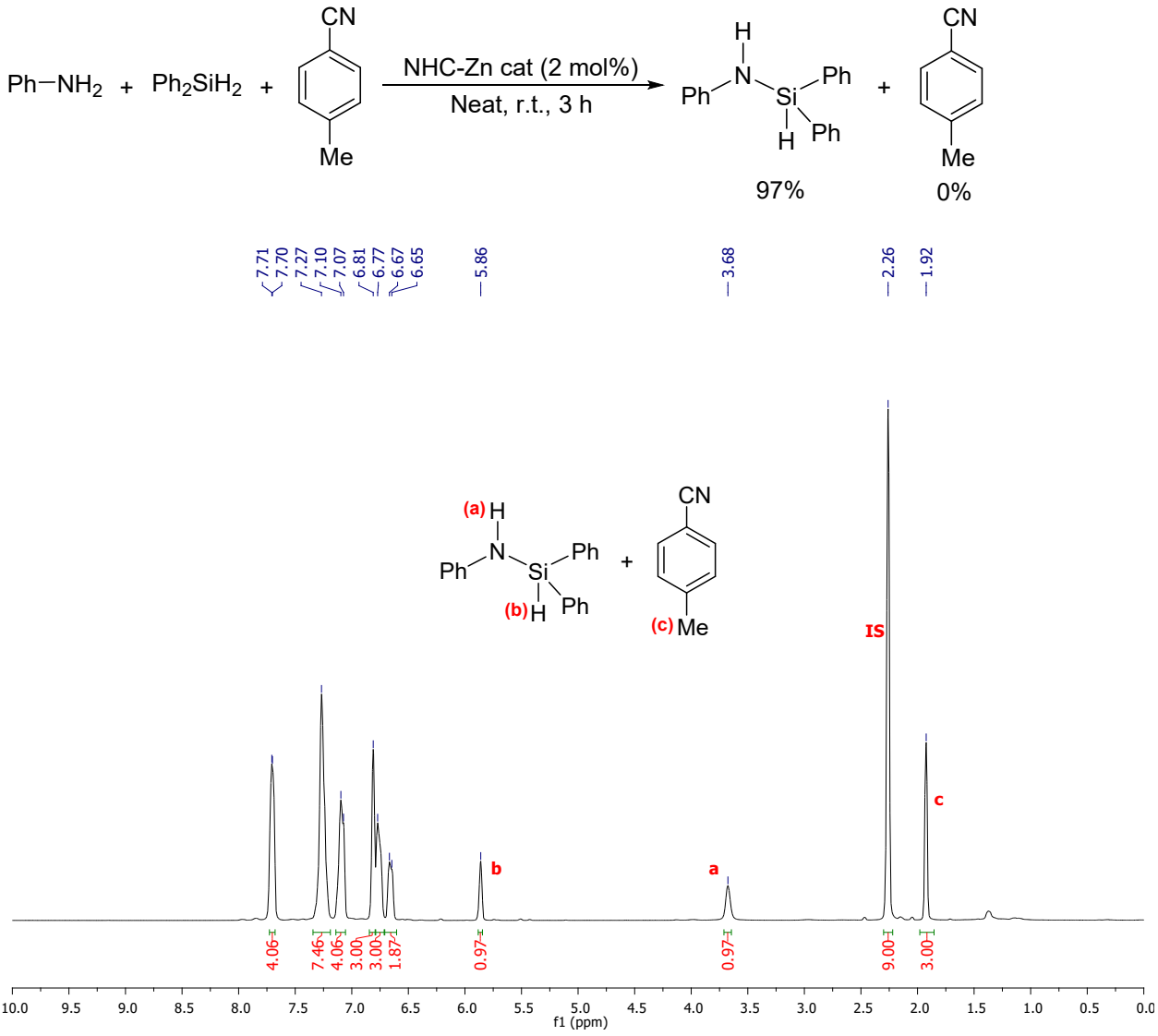
4-aminoacetophenone (0.25 mmol, 1 equiv.), Ph_2SiH_2 (0.25 mmol, 1 equiv.) and NHC-Zn catalyst (2 mol %) were charged in a Schlenk tube inside the glove box. The reaction mixture was stirred for 3 hours at room temperature in neat conditions. Upon completion of the reaction, the progress of the reaction was monitored by ^{1}H NMR with the help of mesitylene as the internal standard in C_6D_6 and a mixture of products was obtained. Doublet peak at δ = 6.23 ppm ($^1J_{HH}$ = 9 Hz) for N-H proton and singlet peak at δ = 5.86 ppm for Si-H proton are the indication of the formation of only CDC product **5a** [1-(4-((diphenylsilyl)amino)phenyl)ethan-1-one] (32% product formation), whereas quartet resonance at δ = 5.03 ppm ($^1J_{HH}$ = 7 Hz) indicates the formation of another product **5b** [N-(4-(1-((diphenylsilyl)oxy)ethyl)phenyl)-1,1-diphenylsilanamine] where both amine and carbonyl group reacted with silane (68% product formation).



FS38. ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25 °C) of the stoichiometric reaction between 4-aminoacetophenone and Ph_2SiH_2.

Selective CDC reaction of amine functionality over reduction of nitrile group in presence of 1 equiv. Ph_2SiH_2:

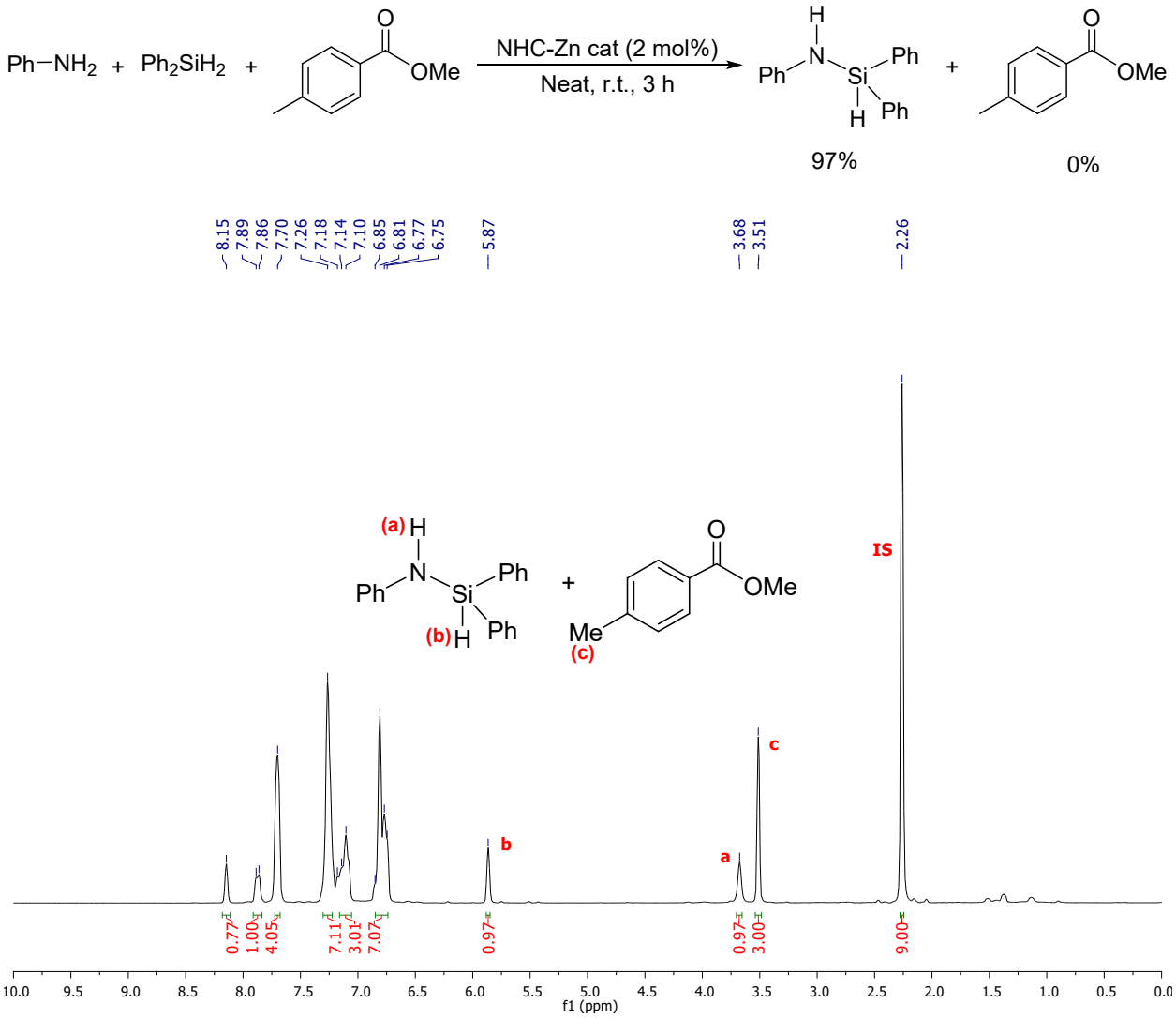
Aniline (0.25 mmol, 1 equiv.), 4-methylbenzonitrile (0.25 mmol, 1 equiv.), Ph_2SiH_2 (0.25 mmol, 1 equiv.) and NHC-Zn catalyst (2 mol %) were charged in a Schlenk tube inside the glove box. The reaction mixture was stirred for 3 hours at room temperature in neat conditions. Upon completion of the reaction, the progress of the reaction was monitored by ^{1}H NMR with the help of mesitylene as the internal standard in C_6D_6. Singlet peak at δ = 3.68 and 5.86 ppm correspond to N-H and Si-H proton respectively indicates for the formation of CDC product from aniline.



FS39. ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25 °C) of the reaction of aniline and 4-methylbenzonitrile in presence of one equiv. Ph_2SiH_2.

Selective CDC reaction of amine functionality over reduction of ester group in presence of 1 equiv. Ph_2SiH_2:

Aniline (0.25 mmol, 1 equiv.), Methyl *p*-toluate (0.25 mmol, 1 equiv.), Ph_2SiH_2 (0.25 mmol, 1 equiv.) and NHC-Zn catalyst (2 mol %) were charged in a Schlenk tube inside the glove box. The reaction mixture was stirred for 3 hours at room temperature in neat conditions. Upon completion of the reaction, the progress of the reaction was monitored by ^{1}H NMR with the help of mesitylene as the internal standard in C_6D_6. Singlet peak at δ = 3.68 and 5.87 ppm correspond to N-H and Si-H proton respectively indicates for the formation of CDC product from aniline.



FS40. ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25 °C) of the reaction of aniline and methyl *p*-toluate in presence of one equiv. Ph_2SiH_2.

References

1. X. Zhang, S. Zhou, X. Fang, L. Zhang, G. Tao, Y. Wei, X. Zhu, P. Cui and S. Wang, *Inorg. Chem*., 2020, **59**, 9683-9692.
2. M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon and T. P. Robinson, *Chem. Sci*., 2013, **4**, 4212-4222.
3. S. Anga, Y. Sarazin, J.-F. Carpentier and T. K. Panda, *ChemCatChem*, 2016, **8**, 1373-1378.
4. D. Gasperini, A. K. King, N. T. Coles, M. F. Mahon and R. L. Webster, *ACS Catal*., 2020, **10**, 6102-6112.
5. A. Baishya, T. Peddarao and S. Nembenna, *Dalton Trans*., 2017, **46**, 5880-5887.
6. C. Bellini, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Angew. Chem*., 2015, **127**, 7789-7793.
7. J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc*., 2011, **133**, 16782-16785.
8. W. Xie, H. Hu and C. Cui, *Angew. Chem*., 2012, **124**, 11303-11306.