Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Silylium Ion-promoted Dehydrogenative Cyclization: Synthesis of Silicon-containing Compounds Derived from Alkynes

Contents

General Procedure. All the reagents were of the highest grade available and were used without further purification. Benzyldimethylsilane (**1a**)[1] and trityl tetrakis(pentafluorophenyl)borate[2] were synthesized according to the previously reported method. Benzyldiisopropylsilane (**1b**) was prepared by the same method as **1a** except for use of chlorodiisopropylsilane as a starting material. The NMR spectral measurements were performed on a Varian 400-MR NMR spectrometers. The ^{1}H and ^{13}C chemical shifts are reported relative to the residual protonated solvent and the solvent, respectively, according to the literature.[3] High-resolution mass spectroscopy was measured by a JEOL GCMATE II corrected by perfluorokerosene. Elemental analysis was performed on a Thermo Scientific FLASH 2000 corrected by acetoanilide. Gel permeation column chromatography (GPC) was performed by a Japan Analytical Industry LC-918 using chloroform as an eluent.

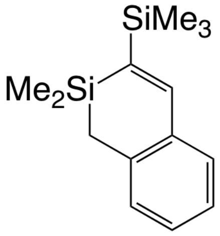
Preparation of Compounds.

Stoichiometric Cyclization

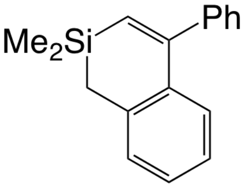
Method A. To a hydrosilane (0.20 mmol), an alkyne (0.30 mmol) and a base (0.30 mmol) in benzene (3 mL) was slowly added a benzene solution (5 mL) of trityl tetrakis(pentafluorophenyl)borate (203 mg, 0.22 mmol) at room temperature under Ar atmosphere, and the resulting solution was stirred for 15 min for **1a** or 30 min for **1b**. The reaction was quenched by 1 M HCl (or water in the cases of trimethylsilylacetylene), and then the organic layer was extracted. After extraction by hexane, the organic layers were combined and dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to remove volatiles, and the residue was purified by silica gel column (eluent: hexane). Further purification was carried out by GPLC to obtain each of products.

Method B. To trityl tetrakis(pentafluorophenyl)borate (203 mg, 0.22 mmol), an alkyne (0.60 mmol) and a base (0.30 mmol) in benzene (5 mL) was slowly added a benzene solution (2 mL) of a hydrosilane (0.20 mmol) at room temperature under Ar atmosphere, and the resulting solution was stirred for 15 min for **1a** or 30 min for **1b**. The following work-up was done according to Method A.

Catalytic Cyclization. To trityl tetrakis(pentafluoro-phenyl)borate (3.7 mg, 4.0 μmol) in benzene-*d*$_6$ (0.2 mL) was added a benzene-*d*$_6$ solution of hydrosilane **1a** or **1b** (0.22 mmol) and 1-hexyne (**3c**) (0.20 mmol) at room temperature under Ar atmosphere for 30 min for **1a** and for 90 min for **1b** monitored by ^{1}H NMR. The reaction was quenched by 2,6-lutidine (5 μL), and then all volatiles were removed under reduced pressure. Purification was achieved by GPLC to afford the sila-cyclic products **5ac** and **5bc** in 33% and 50% isolated yields, respectively.

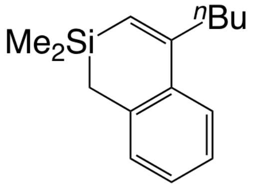


3-Trimethylsilyl-2,2-dimethyl-1,2-dihydro-2-silanaphthalene (4aa). 4aa was obtained as a colorless oil from the reaction using **1a** and trimethylsilylacetylene (**3a**) in 73% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.41 (s, 1H, C=CH–Ar), 7.2-7.1 (m, 4H, Ph), 2.06 (s, 2H, SiCH$_2$), 0.17 (s, 9H, SiMe$_3$), 0.13 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 153.0, 140.3, 136.3, 136.0, 131.7, 130.8, 127.6, 125.6, 19.6, –0.44, –1.7. HRMS: Calcd for $C_{14}H_{22}Si_2$ (M), 246.1260; Found, 246.1220.

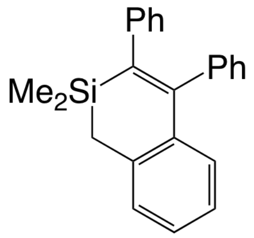


2,2-Dimethyl-4-phenyl-1,2-dihydro-2-silanaphthalene (4ab). 4ab was obtained as a white solid from the reaction using **1a** and phenylacetylene (**3b**) in 34% yield

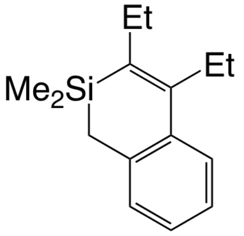
4ab: Mp: 77-78 ºC. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.4-7.3 (m, 5H, Ph*)*, 7.20 (d, 1H, *J* = 7.2 Hz, ArH), 7.11 (dt, 1H, *J* = 7.2 Hz, *J* = 1.6 Hz, ArH), 7.02 (t, 1H, *J* = 7.2 Hz, ArH), 6.97 (dd, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz, ArH), 6.10 (s, 1H, Si–CH=C), 2.19 (s, 2H, SiCH$_2$), 0.14 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 156.8, 145.1, 137.5, 137.4, 131.2, 129.4, 128.2, 128.0 (overlapped two signals), 127.3, 127.1, 125.0, 21.4, –3.7. HRMS: Calcd for $C_{17}H_{18}Si$ (M), 250.1178; Found, 250.1179. Anal. Calcd for **4ab** ($C_{17}H_{18}Si$): C, 81.54; H, 7.25. Found: C, 81.75; H, 7.49.



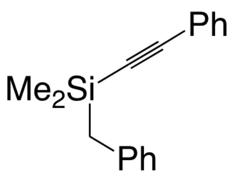
4-*n*-Butyl-2,2-dimethyl-1,2-dihydro-2-silanaphthalene (4ac): **4ac** was obtained as a colorless oil from the reaction using **1a** and 1-hexyne (**3c**) in 33% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (d, 1H, *J* = 7.6 Hz, ArH*)*, 7.2-7.0 (m, 3H, ArH), 5.86 (s, 1H, Si–CH=C), 2.60 (t, 2H, *J* = 7.6 Hz, C*H*$_2$(CH$_2$)CH$_3$), 2.05 (s, 2H, SiCH$_2$), 1.6-1.3 (m, 4H, CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.92 (t, 3H, *J* = 7.6 Hz, (CH$_2$)$_3$C*H*$_3$), 0.064 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 155.2, 137.3, 137.1, 131.5, 126.8, 125.7, 125.2, 124.2, 38.3, 30.8, 22.6, 21.7, 14.0, –3.5. HRMS: Calcd for $C_{15}H_{22}Si$ (M), 230.1491; Found, 230.1475.



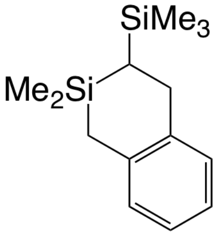
2,2-Dimethyl-3,4-diphenyl-1,2-dihydro-2-silanaphthalene (4ae): **4ae** was obtained as a white solid from the reaction using **1a** and diphenylacetylene (**3e**) in 77% yield. Mp: 128-130 ºC. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (d, 1H, *J* = 7.2 Hz, ArH), 7.15-7.05 (m, 6H, ArH), 7.0-6.9 (m, 4H, ArH), 6.8-6.7 (m, 3H, ArH), 2.30 (s, 2H, SiCH$_2$), 0.71 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 150.3, 143.0, 141.8, 140.5, 138.9, 136.3, 131.0, 130.6, 130.1, 128.0, 127.6, 127.5, 127.0, 126.1, 125.1, 124.7, 21.3, –3.7. HRMS: Calcd for $C_{23}H_{22}Si$ (M), 236.1491; Found, 236.1525. Anal. Calcd for **4ae** ($C_{23}H_{22}Si$): C, 84.61; H, 6.79. Found: C, 84.64; H, 6.52.



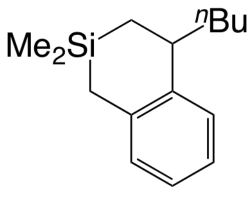
3,4-Diethyl-2,2-dimethyl-1,2-dihydro-2-silanaphthalene (4af): **4af** was obtained as a colorless oil from the reaction using **1a** and 3-hexyne (**3f**) in 34% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (d, 1H, *J* = 7.6 Hz, ArH), 7.15-7.05 (m, 2H, ArH), 7.04 (m, 1H, *J* = 7.6 Hz, ArH), 2.66 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 2.39 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 2.01 (s, 2H, SiCH$_2$), 1.09 (t, 3H, J = 7.6 Hz, CH_2CH$_3$), 1.03 (t, 3H, J = 7.6 Hz, CH_2CH$_3$), 0.06 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 148.3, 138.2, 137.8, 136.5, 131.0, 125.84, 125.82, 125.2, 24.2, 22.9, 21.7, 14.9, 14.6, –4.0. HRMS: Calcd for $C_{15}H_{22}Si$ (M), 230.1491; Found, 230.1496.



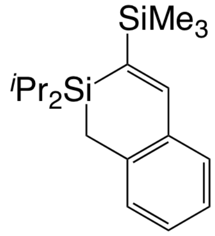
Benzyldimethyl(2-phenylethynyl)silane (6ag): **6ag** was also obtained as a colorless oil from the reaction using **1a** and phenyl(trimethylsilyl)acetylene (**3g**) in 54% yield. The spectroscopic data of **6ag** is consisted with the previous reported data.[4] ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.5-7.4 (m, 2H, ArH), 7.4-7.2 (m, 5H, ArH), 7.2-7.1 (m, 3H, ArH), 2.21 (s, 2H, SiCH_2Ph), 0.23 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): d 139.0, 131.9, 128.6, 128.4, 128.21, 128.16, 124.4, 123.0, 106.4, 92.5, 26.3, –2.1. HRMS: Calcd for $C_{17}H_{18}Si$ (M), 250.1178; Found, 250.1151.



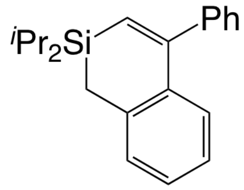
2,2-Dimethyl-3-trimethylsilyl-1,2,3,4-tetrahydro-2-silanaphthalene (5aa): **5aa** was obtained as a colorless oil from the reaction using **1a** and trimethylsilylacetylene (**3a**) in 12% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.15-7.0 (m, 4H, ArH), 2.80 (dd, 1H, J = 13.6 Hz, J = 4.0 Hz, CHCH_2Ar), 2.59 (dd, 1H, J = 14.0 Hz, J = 11.6 Hz, CHCH_2Ar), 2.02 (d, 1H, J = 14.4 Hz, SiCH$_2$Ar), 1.88 (d, 1H, J = 14.4 Hz, SiCH$_2$Ar), 0.17 (s, 3H, SiMe$_2$), 0.052 (s, 9H, SiMe$_3$), –0.036 (s, 3H, SiMe$_2$), –0.15 (dd, 1H, J = 11.6 Hz, J = 4.0 Hz, CHCH$_2$Ar). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 142.8, 138.2, 129.5, 127.4, 126.2, 124.7, 31.1, 21.6, 13.0, –0.57, –0.91, –1.3. HRMS: Calcd for $C_{14}H_{24}Si_2$ (M), 248.1417; Found, 248.1418.



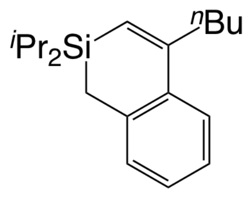
4-*n*-Butyl-2,2-Dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene (5ac): **5ac** was obtained as a colorless oil from the catalytic reaction using **1a** and **3c** in 33% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.15-7.05 (m, 4H, ArH), 2.8-2.7 (m, 1H, CH(^{n}Bu)), 2.04 (d, 1H, J = 14.8 Hz, SiCH$_2$Ar), 1.97 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 1.9-1.8 (m, 1H, ^{n}Bu), 1.65-1.5 (m, 1H, ^{n}Bu), 1.5-1.2 (m, 4H, ^{n}Bu), 0.99 (dd, 1H, J = 14.0 Hz, J = 4.8 Hz, SiCH_2CH), 0.93 (t, 3H, J = 7.2 Hz, ^{n}Bu), 0.51 (dd, 1H, J = 14.4 Hz, J = 8.8 Hz, SiCH_2CH), 0.10 (s, 3H, $SiMe_2$), 0.001 (s, 3H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 138.0, 130.2, 126.3, 125.9, 124.7, 40.0, 35.0, 30.4, 22.9, 20.8, 18.0, 14.1, –1.2, –1.6. HRMS: Calcd for $C_{15}H_{24}Si$ (M), 232.1647; Found, 232.1621.



2,2-Diisopropyl-3-trimethylsilyl-1,2-dihydro-2-silanaphthalene (4ba): **4ba** was obtained as a colorless oil from the reaction using **1b** and **3a** in 71% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (s, 1H, C=CH–Ar), 7.2-7.1 (m, 4H, ArH), 2.09 (s, 2H, $SiCH_2$), 1.2-1.0 (m, 2H, CH(CH_3)$_2$), 0.98 (d, 6H, J = 7.6 Hz, CH(CH_3)$_2$), 0.94 (d, 6H, J = 6.8 Hz, CH(CH_3)$_2$), 0.22 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.7, 136.8, 136.6, 136.5, 131.6, 131.0, 127.8, 125.4, 18.9, 18.1, 12.3, 11.6, 0.38. HRMS: Calcd for $C_{18}H_{30}Si_2$ (M), 302.1886; Found, 302.1884.

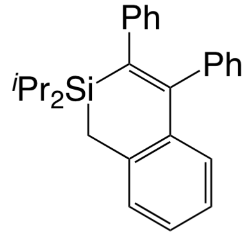


2,2-Diisopropyl-4-phenyl-1,2-dihydro-2-silanaphthalene (4bb): **4bb** was obtained as a colorless oil from the reaction using **1b** and **3b** in 67% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.4-7.3 (m, 5H, ArH), 7.21 (d, 1H, J = 7.6 Hz, ArH), 7.10 (td, 1H, J = 7.6 Hz, J = 1.6 Hz, ArH), 6.94 (d, 1H, J = 6.4 Hz, ArH), 6.08 (s, 1H, Si–CH=C), 2.23 (s, 2H, $SiCH_2$), 1.1-0.9 (m, 14H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 145.5, 137.79, 137.75, 131.2, 129.5, 128.3, 128.0, 127.4, 127.1, 124.9, 124.6, 18.3, 18.2, 15.4, 11.1. HRMS: Calcd for $C_{21}H_{26}Si$ (M), 306.1804; Found, 306.1845.

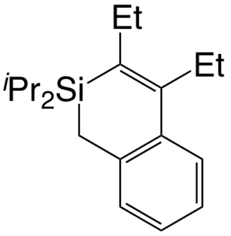


2,2-Diisopropyl-4-*n*-butyl-1,2-dihydro-2-silanaphthalene (4bc): **4bc** was obtained as a colorless oil from the reaction using **1b** with **3c** in 66% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, 1H, J = 7.6 Hz, ArH), 7.2-7.0 (m, 3H, ArH), 5.85 (s, 1H, Si–CH=C), 2.66 (t, 2H, J = 7.6 Hz, CH_2(CH_2)$_2$$CH_3$), 2.09 (s, 2H, $SiCH_2$), 1.6-1.3 (m, 4H, CH_2(CH_2)$_2$$CH_3$), 1.1-0.9 (m, 17H, C$H$(C$H_3$)$_2$ and

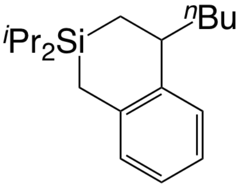
$CH_2(CH_2)_2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.8, 137.6, 137.4, 131.5, 126.9, 125.7, 125.1, 120.6, 38.6, 31.0, 22.5, 18.2, 18.1, 15.3, 14.0, 11.1. HRMS: Calcd for $C_{19}H_{30}Si$ (M), 286.2117; Found, 286.2112.



2,2-Diisopropyl-3,4-diphenyl-1,2-dihydro-2-silanaphthalene (4be): **4be** was obtained as a colorless oil from the reaction of **1b** and **3e** in 82% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, 1H, J = 6.8 Hz, ArH), 7.2-7.0 (m, 6H, ArH), 7.0-6.9 (m, 4H, ArH), 6.84 (d, 2H, J = 7.2 Hz, ArH), 6.70 (d, 1H, J = 7.6 Hz, ArH), 2.34 (s, 2H, $SiCH_2$), 1.1-1.0 (m, 2H, $CH(CH_3)_2$), 0.98 (d, 6H, J = 6.8 Hz, $CH(CH_3)_2$), 0.83 (d, 6H, J = 7.2 Hz, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.6, 143.4, 142.0, 139.2, 138.7, 136.9, 130.70, 130.65, 130.1, 128.6, 127.5 (overlapped two signals), 127.2, 126.1, 125.0, 124.7, 18.4, 18.0, 14.7, 11.6. HRMS: Calcd for $C_{24}H_{23}Si$ (M–^{i}Pr), 339.1569; Found, 339.1636.



3,4-Diethyl-2,2-diisopropyl-1,2-dihydro-2-silanaphthalene (4bf): **4bf** was obtained as a colorless oil from the reaction of **1b** and **3f** in 39% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34 (d, 1H, J = 8.0 Hz, ArH), 7.15-7.1 (m, 2H, ArH), 7.02 (t, 1H, J = 7.6 Hz, ArH), 2.69 (q, 2H, J = 7.6 Hz, CH_2CH_3), 2.38 (q, 2H, J = 7.6 Hz, CH_2CH_3), 2.04 (s, 2H, $SiCH_2$), 1.1-1.0 (m, 8H, CH_2CH_3 and $CH(CH_3)_2$), 0.97 (d, 6H, J = 6.4 Hz, $CH(CH_3)_2$), 0.89 (d, 6H, J = 7.2 Hz, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.2, 138.6, 136.9, 135.5, 130.8, 126.0, 125.8, 125.1, 24.3, 22.6, 18.7, 18.2, 15.1, 14.8, 14.5, 11.3. HRMS: Calcd for $C_{19}H_{30}Si$ (M), 286.2117; Found, 286.2134.



4-*n*-Butyl-2,2-Dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene (5bc): **5bc** was obtained as a colorless oil from the catalytic reaction using **1b** and **3c** in 50% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.05 (m, 4H, ArH), 2.7-2.6 (m, 1H, $CH(^nBu)$), 2.05 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 2.00 (d, 1H, J = 14.8 Hz, $SiCH_2Ar$), 1.95-1.85 (m, 1H, ^{n}Bu), 1.7-1.3 (m, 5H, ^{n}Bu and ^{i}Pr), 1.06 (dd, 1H, J = 14.8 Hz, J = 4.8 Hz, $SiCH_2CH$), 1.01 (brs, 7H, ^{i}Pr), 0.94 (t, 3H, J = 7.6 Hz, ^{n}Bu), 0.9-0.8 (m, 7H, ^{i}Pr), 0.37 (dd, 1H, J = 14.4 Hz, J = 10.0 Hz, $SiCH_2CH$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 138.6, 130.0, 125.9, 125.4, 124.6, 39.3, 35.3, 30.3, 23.0, 18.2, 18.14, 18.09, 17.9, 15.0, 14.2, 12.3, 11.8, 11.7. HRMS: Calcd for $C_{19}H_{32}Si$ (M), 288.2273; Found, 288.2297.

X-ray Crystallography. Single crystals of **4ab** and **4ae** suitable for XRD analyses were obtained. Each crystal was mounted on a glass fiber, and the diffraction data was collected on a Bruker APEX II CCD detector using graphite monochromated Mo $K\alpha$ radiation at 123 K.

All the structures were solved by the combination of the direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from the International Tables for X-ray Crystallography IV.[5] The refinement of all structures was carried out by full-matrix least-squares method of SHELXL-97.[6]

(1) J. W. Jenkins and H. W. Post, *J. Org. Chem.*, 1950, **15**, 552-555.

(2) E. Ihara, V. G. Young, Jr. and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 8277-8278.

(3) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

(4) Y. Nishihara, D. Saito, K. Tanemura, S. Noyori and K. Takagi, *Org. Lett.*, 2009, **11**, 3546-3549.

(5) J. A. Ibers and W. C. Hamilton, *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, U. K., **1974**; Vol. IV.

(6) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.

Table S1. Crystallographic data for **4ab** and **4ae**

	4ab	**4ae**
formula	$C_{34}H_{36}Si_2$	$C_{22}H_{20}Si$
fw	500.81	312.47
crystal cystem	triclinic	monoclinic
space group	P-1 (#2)	$P2_1/n$ (#14)
a, Å	9.8603(13)	9.7459(10)
b, Å	10.5873(14)	10.4452(11)
c, Å	14.4723(19)	18.2147(19)
α, deg	72.748(2)	90
β, deg	86.325(2)	99.690(1)
γ, deg	84.298(2)	90
V, Å^3	1434.8(3)	1827.8(3)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.159	1.136
μ(Mo $K\alpha$), mm^{-1}	0.144	0.126
total no. of data	8189	10169
no. of unique data (R_{int})	6222 (0.0171)	4132 (0.0174)
no. of params	329	219
$R1^a$	0.0449	0.0349
$wR2$ (all data)^b	0.0863	0.0764

[a] $I > 2.00\sigma(I)$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma(w(|F_o| - |F_c|)^2)/\Sigma wF_o^2\}^{1/2}$.

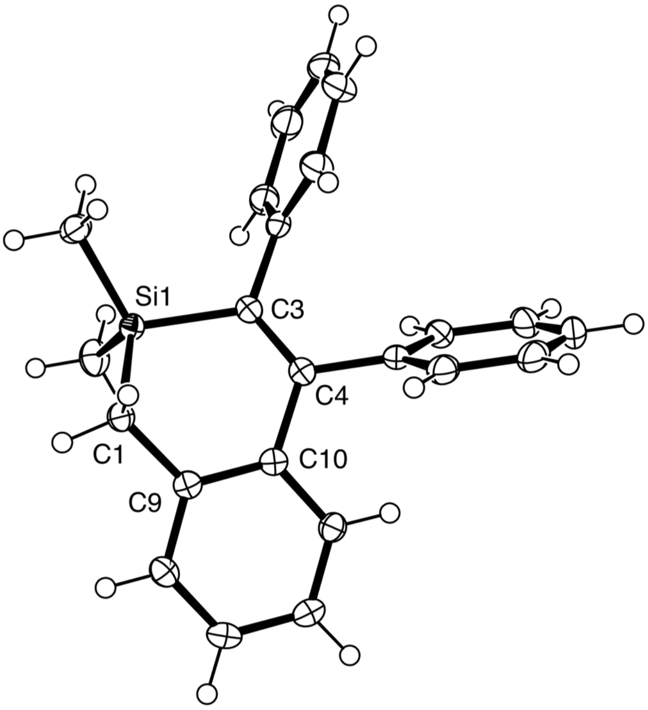


Fig. S1 Crystal structures of **4ae**, showing 50% probability thermal ellipsoids.

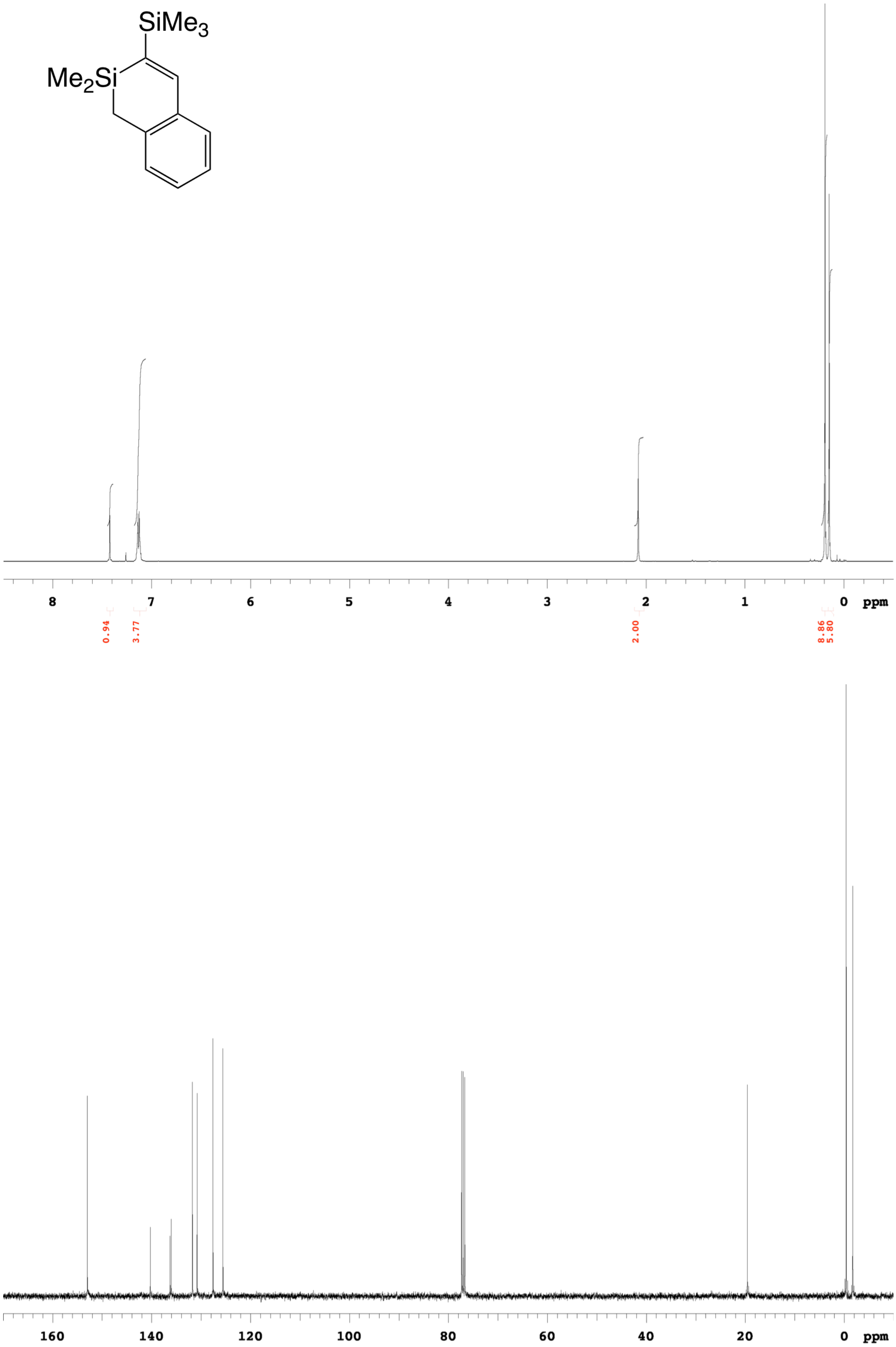


Fig. S2 ^{1}H and ^{13}C NMR spectra of **4aa**.

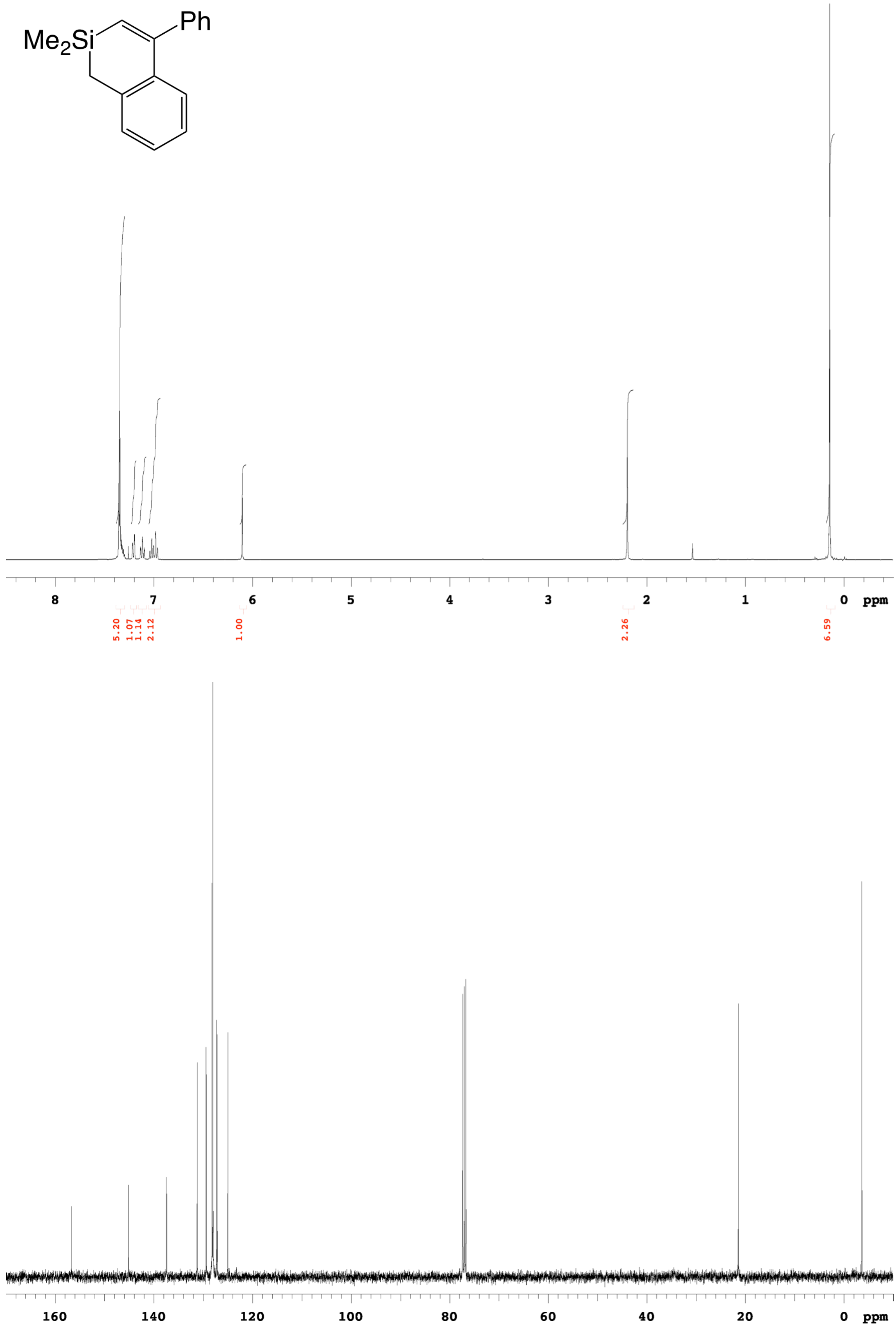


Fig. S3 ^{1}H and ^{13}C NMR spectra of **4ab**.

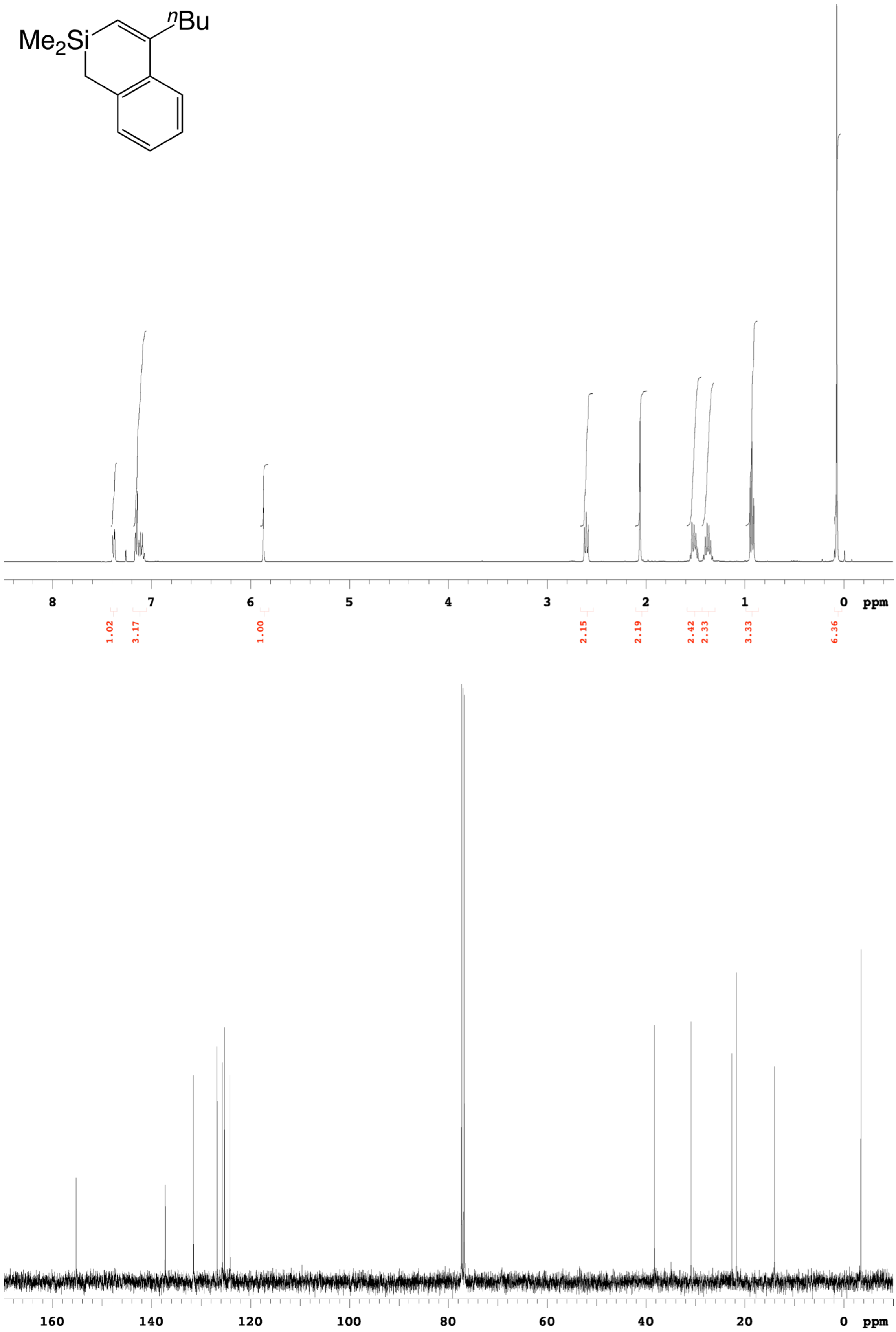


Fig. S4 ^{1}H and ^{13}C NMR spectra of **4ac**.

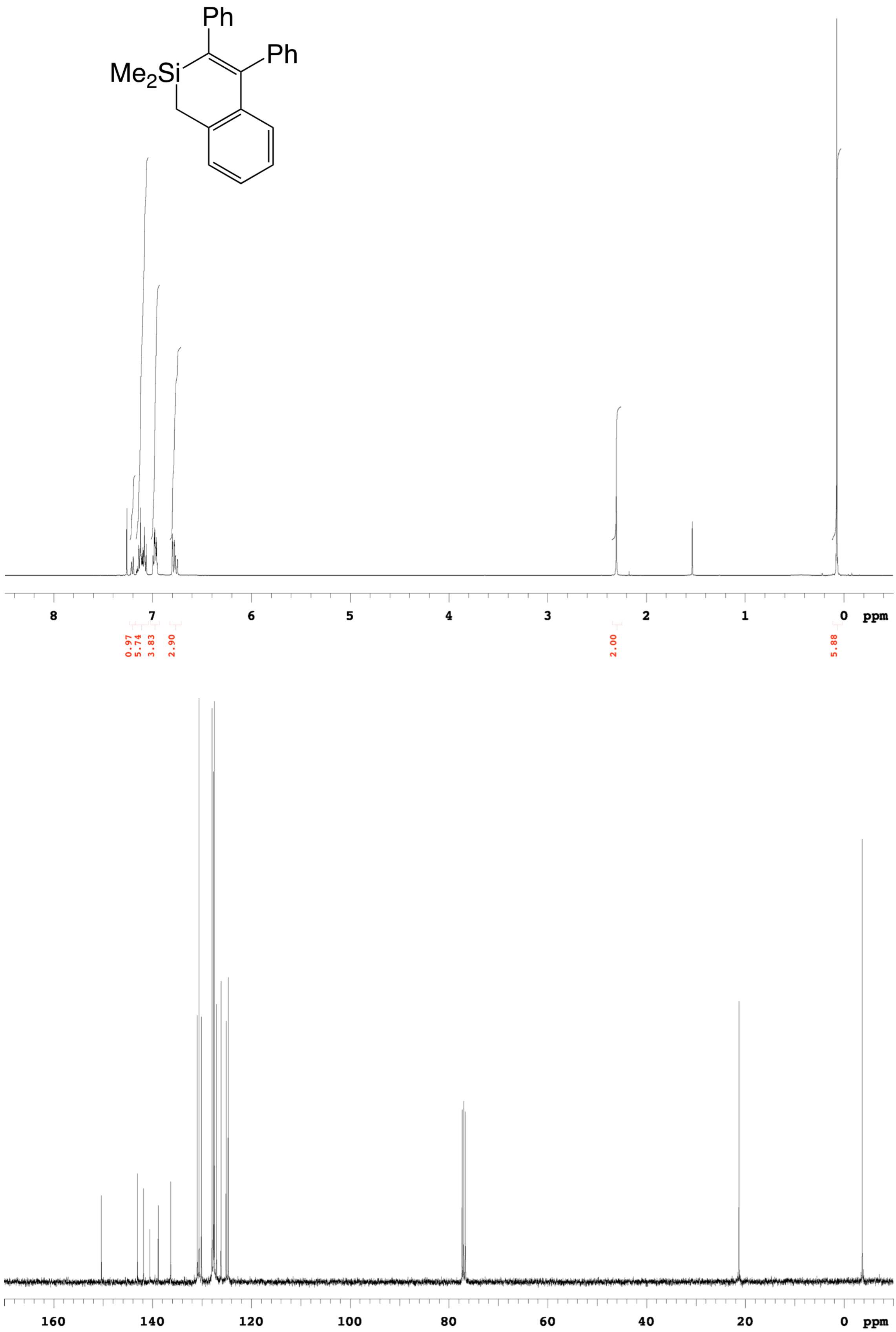


Fig. S5 ^{1}H and ^{13}C NMR spectra of **4ae**.

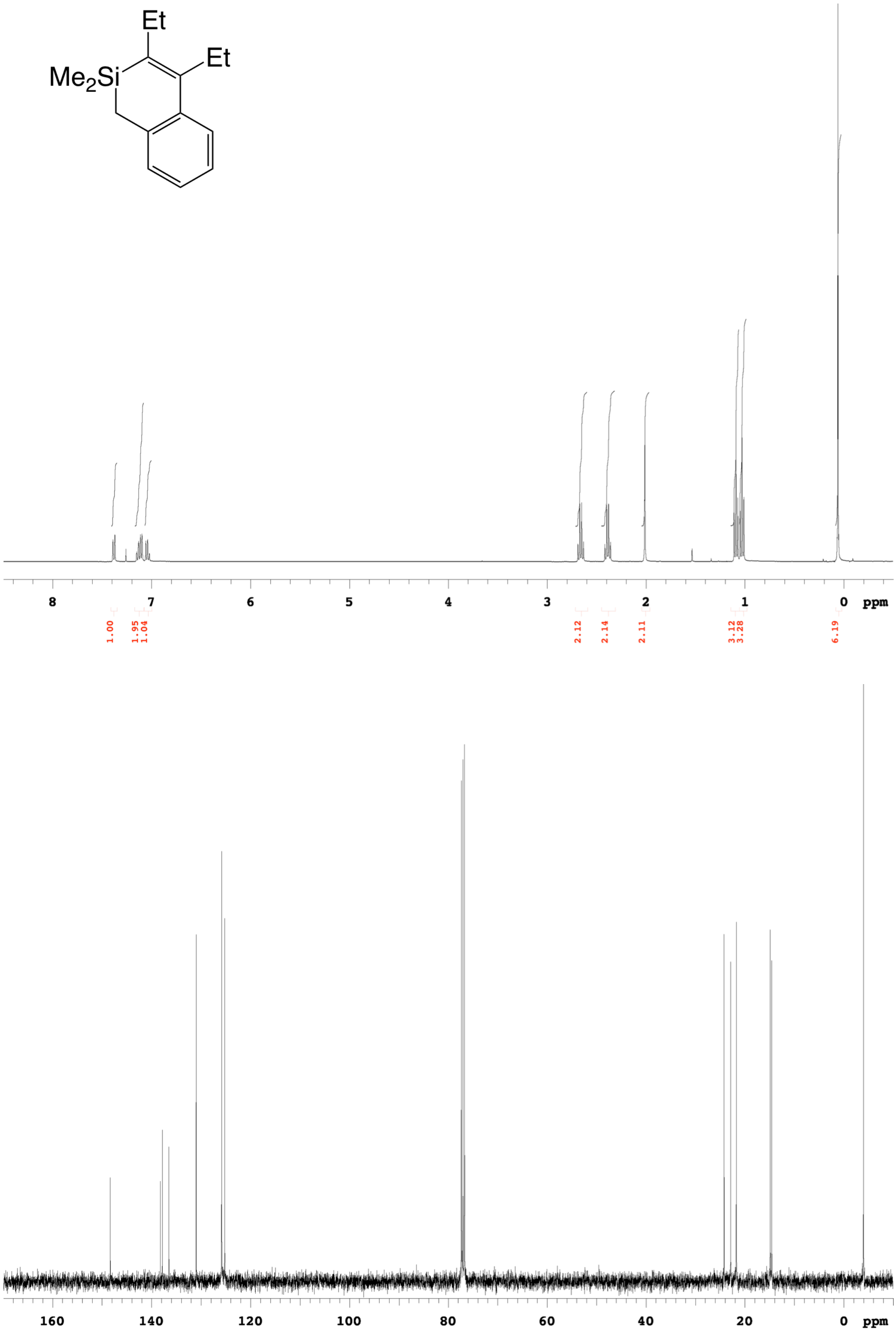


Fig. S6 ^{1}H and ^{13}C NMR spectra of **4af**.

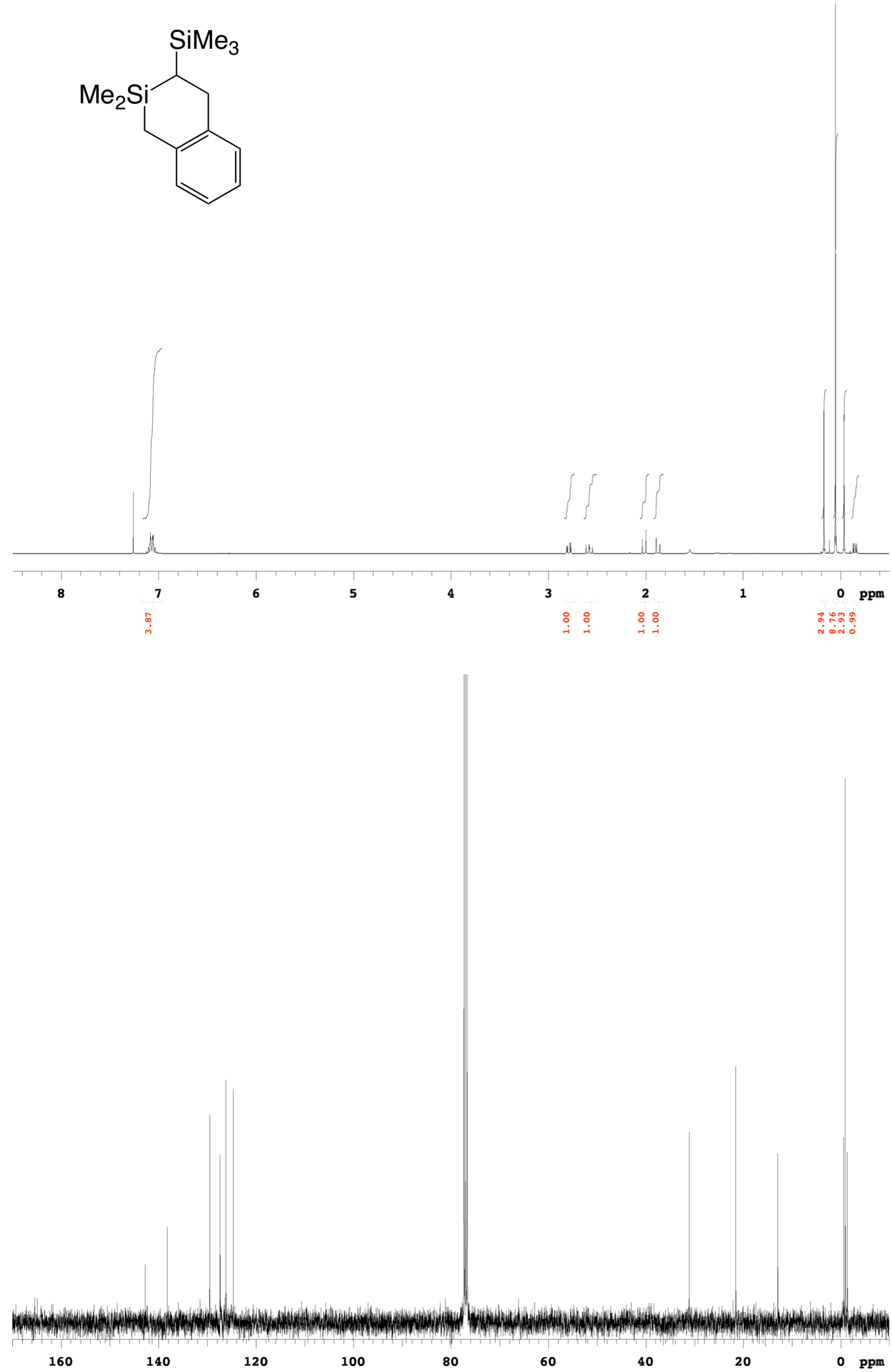


Fig. S7 ^{1}H and ^{13}C NMR spectra of **5aa**.

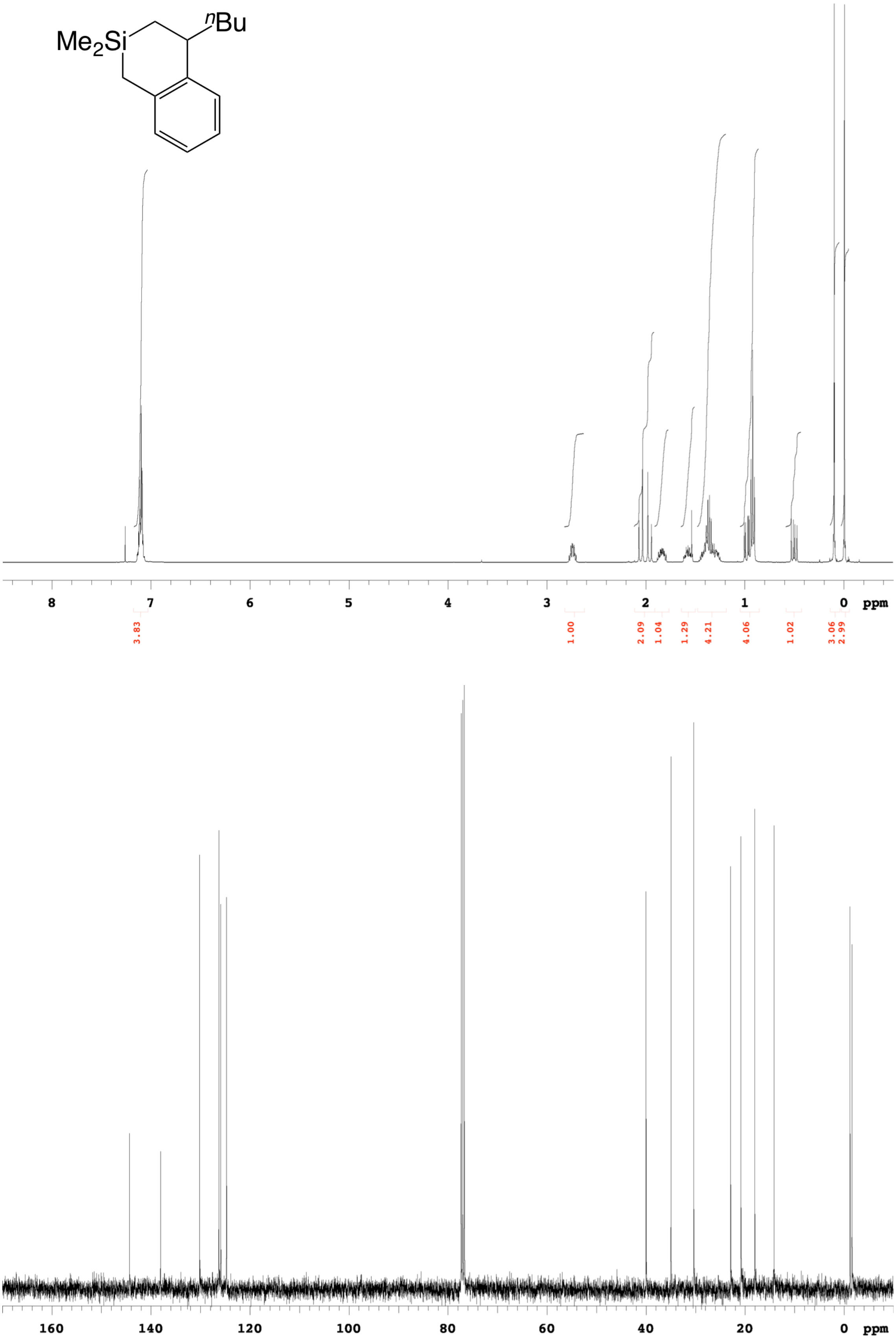


Fig. S8 ^{1}H and ^{13}C NMR spectra of **5ac**.

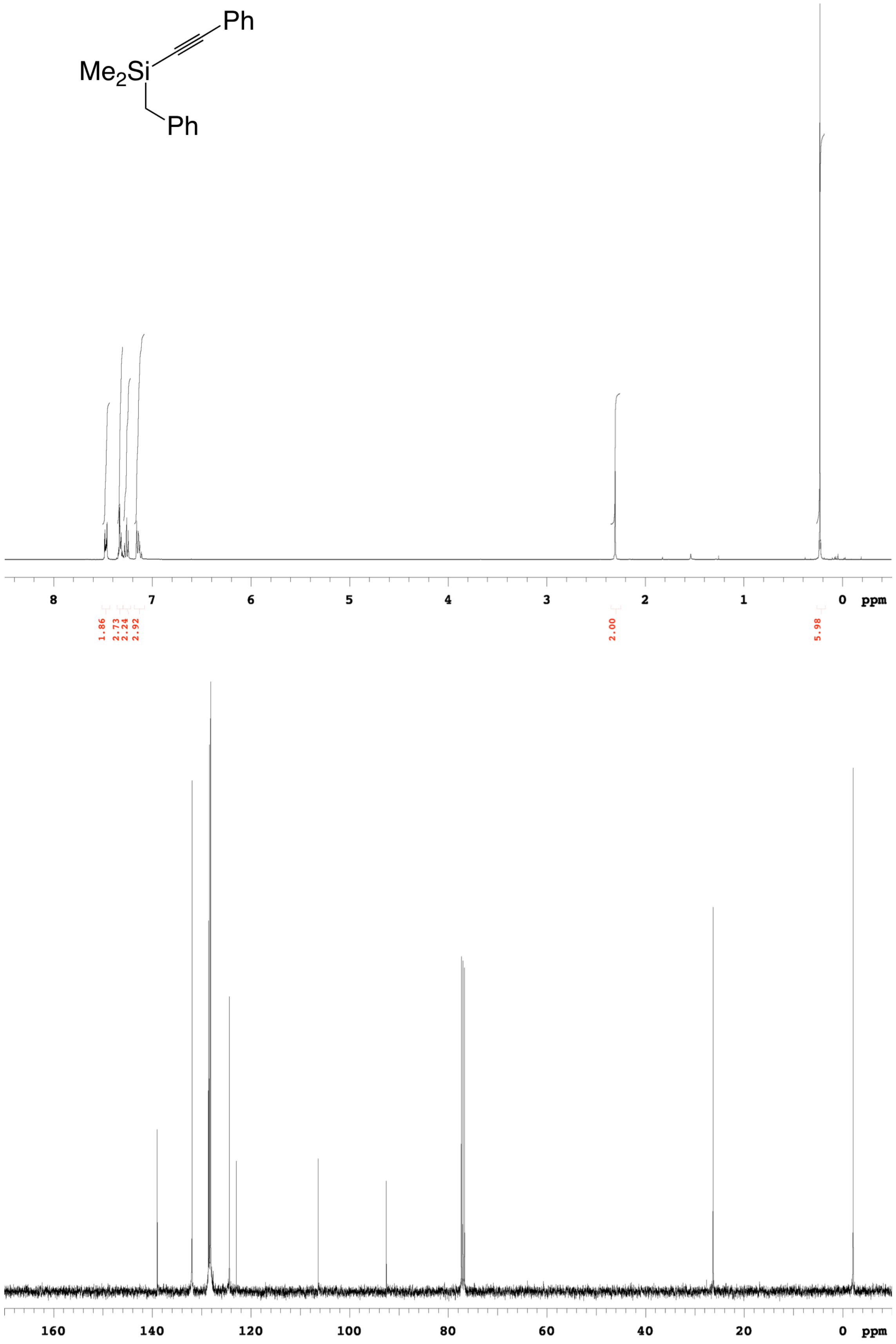


Fig. S9 ^{1}H and ^{13}C NMR spectra of **6ag**.

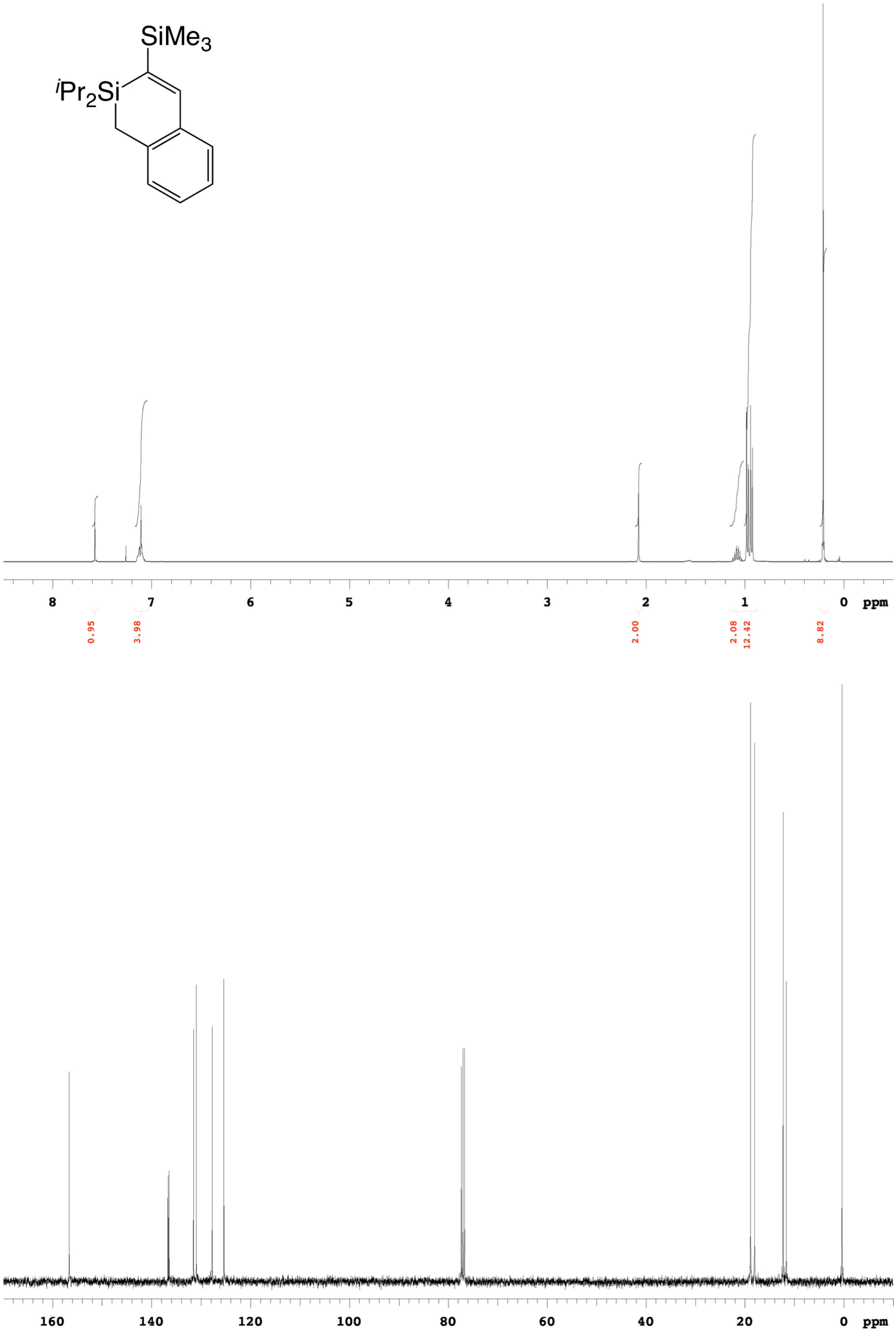


Fig. S10 ^{1}H and ^{13}C NMR spectra of **4ba**.

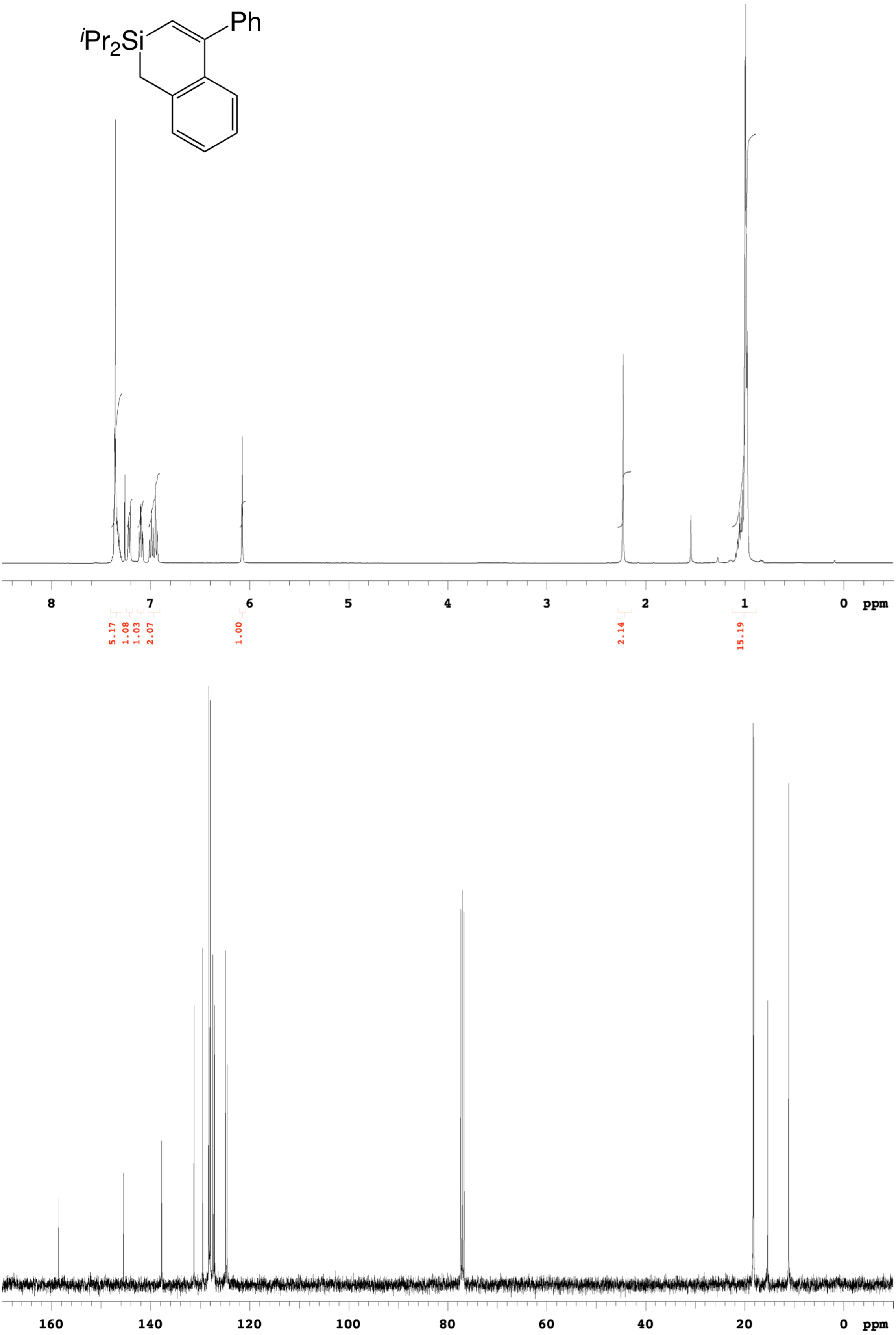


Fig. S11 ^{1}H and ^{13}C NMR spectra of **4bb**.

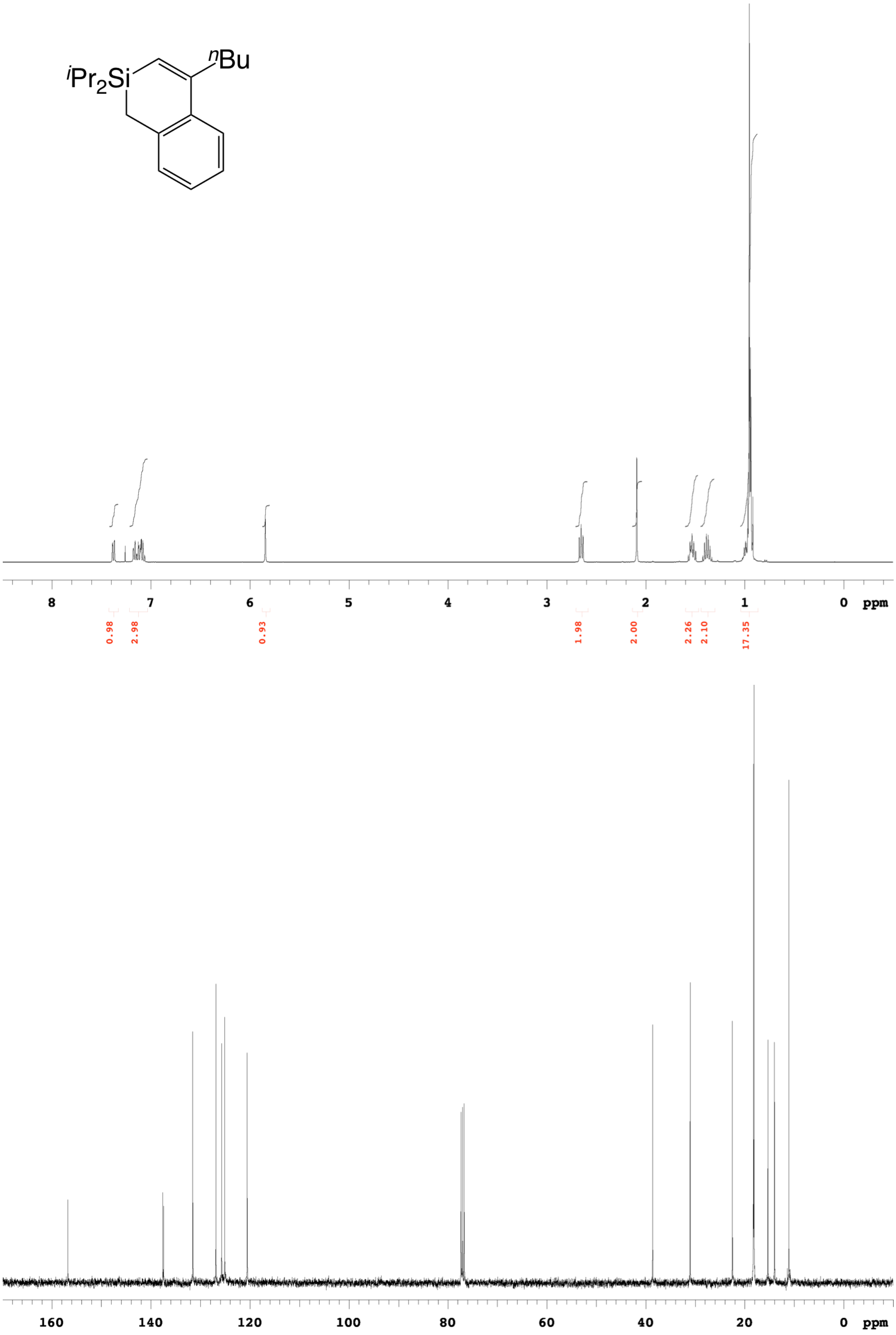


Fig. S12 ^{1}H and ^{13}C NMR spectra of **4bc**.

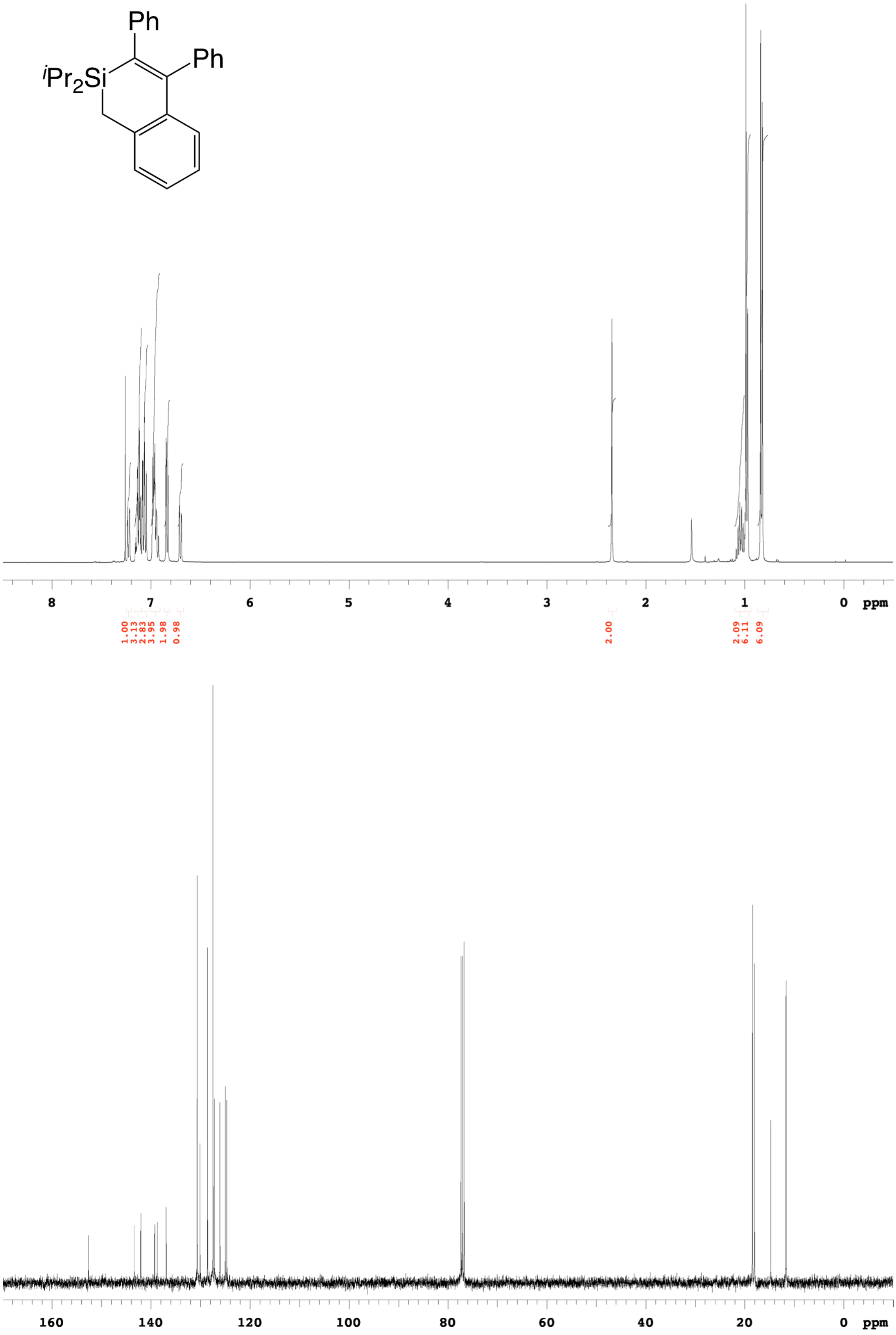


Fig. S13 ^{1}H and ^{13}C NMR spectra of **4be**.

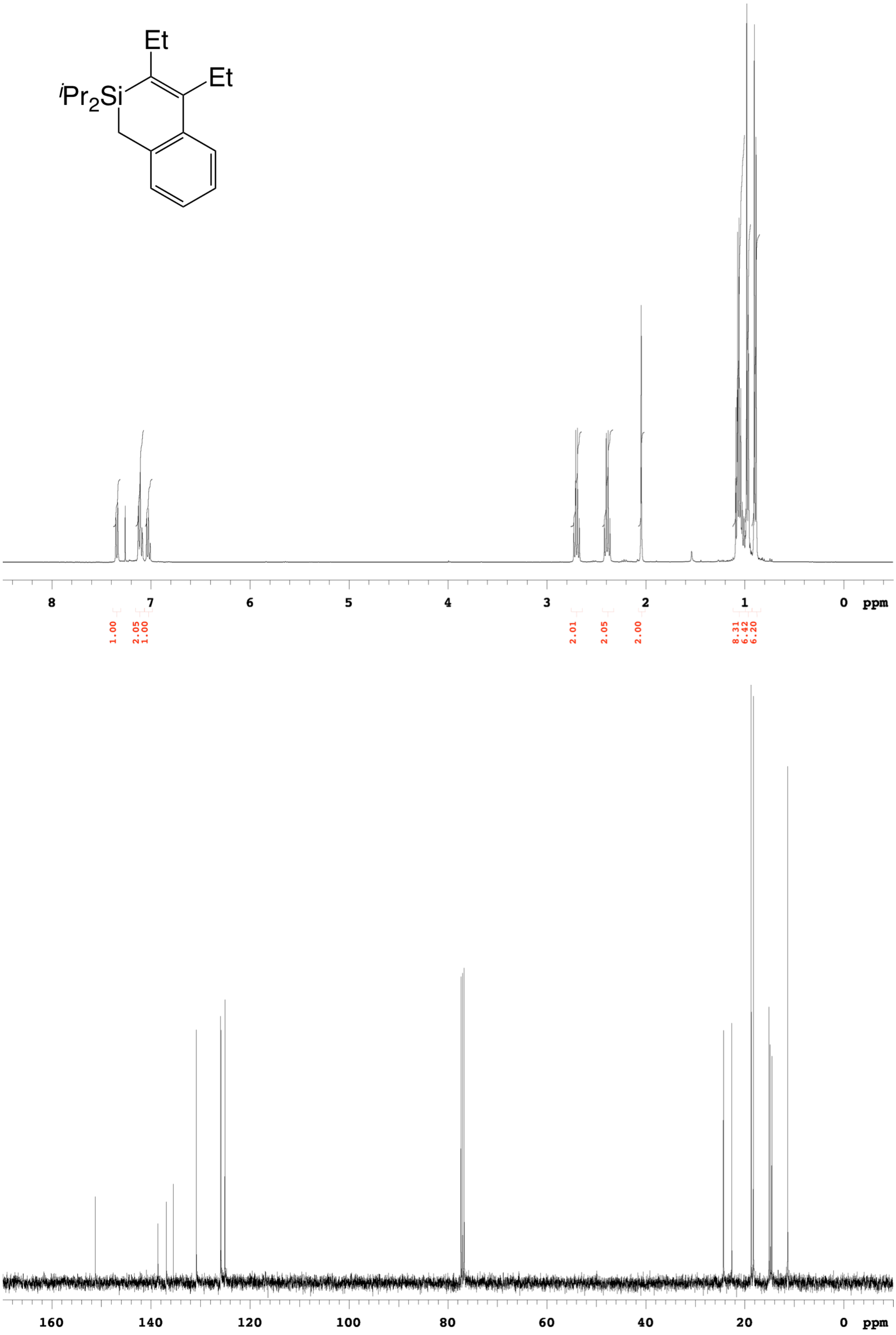


Fig. S14 ^{1}H and ^{13}C NMR spectra of **4bf**.

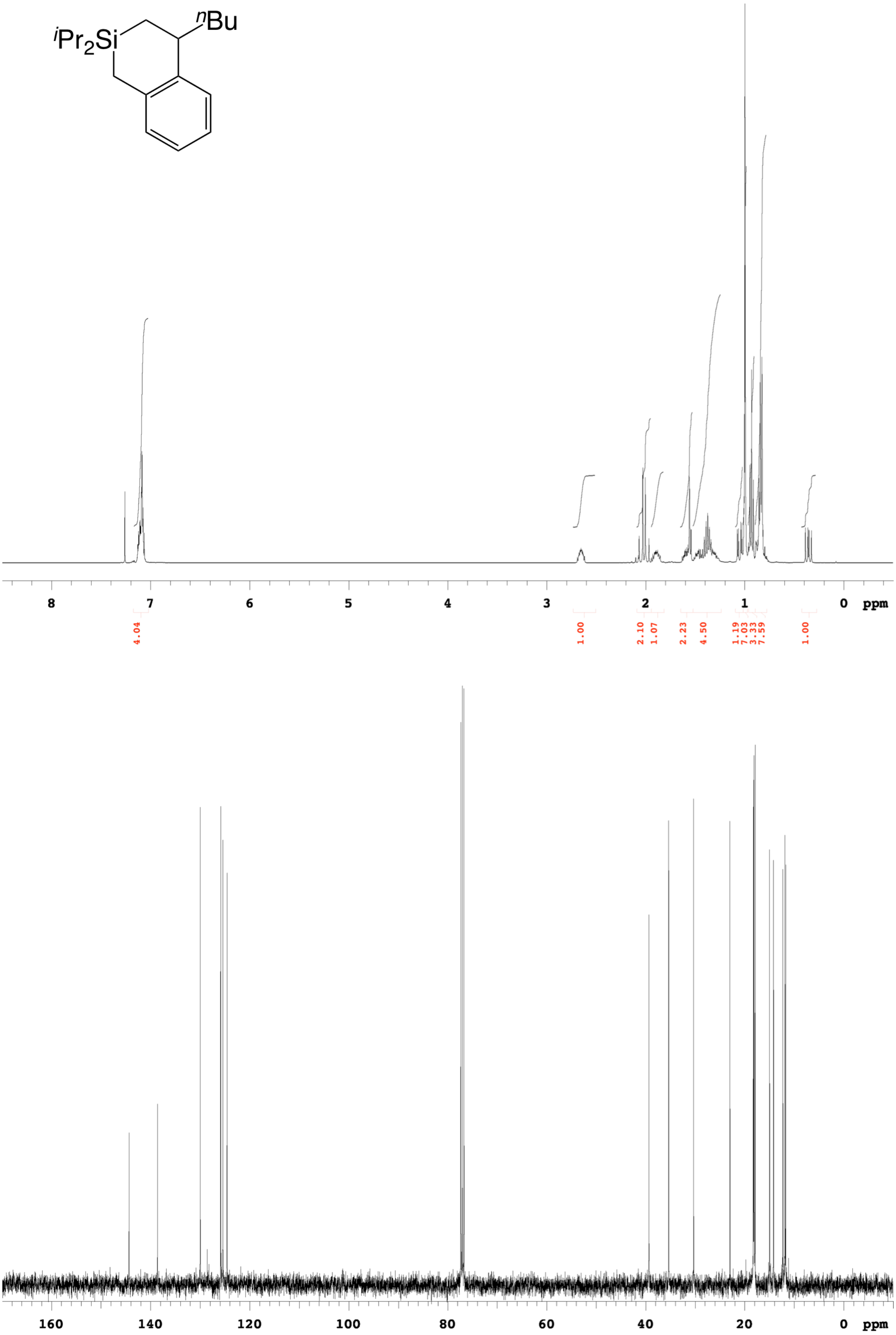


Fig. S15 ^{1}H and ^{13}C NMR spectra of **5bc**.