Ferrocenophanes with Gallium and Silicon as Alternating Bridges

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Experimental Section

General Information. Manipulations were done using standard Schlenk and glovebox techniques (N_2 as inert gas), unless noted differently. Solvents were dried using an MBraun Solvent Purification System and stored under nitrogen over 3 Å molecular sieves. All solvents for NMR spectroscopy were degassed prior to use and stored under nitrogen over 3 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz Avance NMR spectrometer at 25 ºC in C_6D_6 and toluene-D_8, respectively (^1H at 500.28 MHz; ^{13}C at 125.80 MHz). ^1H chemical shifts were referenced to the residual protons of the deuterated solvents (δ 7.15 for C_6D_6 and 2.08 for toluene-D_8); ^{13}C chemical shifts were referenced to the C_6D_6 signal at δ 128.00 and the toluene-D_8 signal at δ 20.43. Mass spectra were measured on a VG 70SE and are reported in the form *m/z* (rel intens) [M^+] where "*m/z*" is the mass observed, 'rel intens' is intensity of the peak relative to the most intense peak and "M^+" is the molecular ion or fragment; only characteristic mass peaks are reported. For isotopic pattern, only the mass peak of the isotopoloque or isotope with the highest natural abundance is listed. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyzer using V_2O_5 to promote complete combustion.

Chemicals. Ferrocene (98%), *n*BuLi (2.5 M in hexanes), *t*BuLi (1.7 M in pentane), Me_2SiCl_2 (99%) and C_6D_6 (99.6 atom % D) were purchased from Sigma Aldrich. [D_8]toluene (99.5 atom % D) was purchased from Cambridge Isotope Laboratories, Inc. $GaCl_3$ (Alfa Aesar, 99.999%), 1-bromo-4-(bromomethyl)benzene (Alfa-Aesar, 98%) and $C_2Br_2Cl_4$ (Alfa-Aesar, 98%) were purchased from VWR. $(LiC_5H_4)_2Fe\cdot 2/3tmeda$,[1] $(BrC_5H_4)_2Fe$,[2] $\mathbf{1}^{\mathbf{Me}}$,[3] and $Ar'GaCl_2$[4] were synthesized following literature procedures.

Species 1-bromo-4-[(dimethylamino)methyl]benzene[5-7] and 1-[(dimethylamino)-methyl]-4-trimethylsilylbenzene[8-9] are known compounds that were synthesized in a similar way compared to the literature (see details below).

Gel Permeation Chromatography (GPC). Molecular weights and polydispersity indices (PDI = M_w/M_n) of $\mathbf{6a_x}$ and $\mathbf{6b_x}$ were obtained by GPC using a Viscotek VE 2001 Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, in-line degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, and VE 3580 refractometer. The solvent thf, stabilized with 0.025% butylated hydroxytoluene (Fisher) and containing 0.1 w/w% nBu_4NBr, was used as the chromatography eluent at a flow rate of 1.0 mL min^{-1}. Samples were dissolved in the eluent (2 mg/mL) and filtered (Whatman, PTFE membrane, 0.2 µm) before analysis. Calibration of the refractive index detector was performed using polystyrene standards purchased from Viscotek.

MALDI-TOF Mass Spectrometry. MALDI-TOF mass spectra were collected on a 4700 Proteomics Analyzer (Applied Biosystems) equipped with a Nd:Yag laser, operating at 335 nm. Positive ion mass spectra were obtained in linear or reflector mode over a range of 500 - 5000 *m/*z. Each spectrum was an accumulation of 12500 laser shots over 100 points on the sample (125 shots/point). Laser intensity was varied for each sample. Solutions of the analytes (10 mg/mL toluene solution) and benzo[α]pyrene (20 mg/mL toluene solution) were prepared and then mixed in a 1:10 ratio. The resulting solutions were drop-cast by micropipette into sample wells and allowed to evaporate for 3 h in an inert atmosphere glovebox prior to sample analysis.

Electrochemistry. A computer controlled system, consisting of a HEKA potentiostat PG590 (HEKA, Mahone Bay, NS, Canada) was used for the cyclic voltammetry experiments. Data was collected using a multifunction DAQ card (PCI 6251 M Series, National Instruments Austin, Texas) and in-house software written in the LabVIEW environment. Glassy carbon (BAS, 3 mm) was used as the working electrode. The quasi-reference electrode (QRE) was a silver wire and all measurements were made against the QRE. A loop of gold wire was used as the auxiliary electrode. Before each measurement, 1 mM solutions of **6a** and **6b** were freshly prepared in dry CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. The electrolyte was dried overnight under high vacuum at 100 °C. The scan rate for the CVs reported was 50 mV/s. The measurements were conducted inside a glovebox and taken at ambient temperature (25 °C).

1-Bromo-4-[(dimethylamino)methyl]benzene. Dimethylamine (ca. 30 mL, 0.40 mol) was added dropwise to a cold (0 °C) suspension of 1-bromo-4-(bromomethyl)benzene (25.25 g, 101.0 mmol) in hexane (50 mL). The reaction mixture was warmed up to r.t. and stirred for 16 h. The solid was filtered off and all volatiles were removed from the filtrate under vacuum. Flask-to-flask condensation (50 °C, high vacuum) gave the pure product as a colorless oil (21.09 g, 98%). ^1H NMR (C_6D_6): δ 1.98 (s, 6H, CH_3), 3.02 (s, 2H, CH_2), 6.95 (d, 2H, C_6H_4), 7.26 (d, 2H, C_6H_4).

1-[(Dimethylamino)methyl]-4-trimethylsilylbenzene. *t*BuLi (1.6 M in pentane, 69.0 mL, 110 mmol) was added dropwise to a cold (-78 °C) solution of 1-bromo-4-[(dimethylamino)methyl]benzene (10.70 g, 49.98 mmol) in thf (75 mL). The reaction mixture was stirred for 15 min at -78 °C, followed by the dropwise addition of chlorotrimethylsilane (19.0 mL, 150 mmol). The resultant reaction mixture was warmed up to r.t. and stirred for 16 h, resulting in a pale yellow solution with white precipitate. The solid was filtered off and all volatiles were removed under vacuum. Flask-to-flask condensation (65 °C, high vacuum) gave the pure product as a colorless oil (9.85 g, 95%). ^1H NMR (C_6D_6): δ 0.22 (s, 9H, $SiMe_3$), 2.10 (s, 6H, NMe_2), 3.30 (s, 2H, CH_2), 7.40 (d, 2H, C_6H_4), 7.49 (d, 2H, C_6H_4).

Dichloro{2-[(dimethylamino)methyl]-5-(trimethylsilyl)phenyl-κ^{2}C,N}gallane (5). *t*BuLi (1.6 M in pentane, 17.0 mL, 27.2 mmol) was added dropwise to a cold (0 °C) solution of 1-[(dimethylamino)methyl]-4-trimethylsilylbenzene (5.25 g, 25.3 mmol) in hexane (40 mL). The reaction mixture was warmed up to r.t. and stirred for 16 h, yielding a pale yellow solution with a white precipitate. The solid lithium salt was filtered off, washed with hexane (2 x 20 mL) and dried under high vacuum. The cold slurry (-78 °C) of the white solid in Et_2O (15 mL) was added dropwise to a cold (-78 °C) solution of $GaCl_3$ (3.00 g, 17.0 mmol) in Et_2O (20 mL). The reaction mixture was warmed up to r.t. and stirred for 16 h, resulting in a pale yellow solution with a white precipitate. The solid was filtered off and all volatiles were removed from the filtrate under high vacuum, resulting in a pale yellow solid as the crude product. Pure product **5** was obtained by sublimation (120 °C, high vacuum) as a white crystalline solid (3.83 g, 65%). ^{1}H NMR (C_6D_6): δ 0.20 (s, 9H, $SiMe_3$), 1.88 (s, 6H, NMe_2), 3.08 (s, 2H, CH_2), 6.78 (d, 1H, C_6H_3), 7.50 (d, 1H, C_6H_3), 8.08 (s, 1H, C_6H_3). ^{13}C NMR (C_6D_6): δ -1.05 ($SiMe_3$), 45.29 (CH_2), 65.47 (NMe_2), 124.24, 134.47, 139.66, 142.17 (C_6H_3). EIMS (70 eV) *m/z*: 347 (16) [M^+], 330 (100) [M^+ - Me], 289 (8) [M^+ - CH_2NMe_2], 206 (18) [M^+ - $GaCl_2$], 58 (38) [$C_3H_8N^+$]. HRMS (EI; *m/z*): calcd for $C_{12}H_{20}GaCl_2NSi$, 346.9989; found, 346.9989. Anal. Calcd for $C_{12}H_{20}GaCl_2NSi$: C, 41.53; H, 5.81; N, 4.04. Found: C, 40.92; H, 6.06; N, 3.80.

General Procedure for the Synthesis of 6a, 6b, 6a$_x$ and 6b$_x$. *n*BuLi (2.5 M in hexanes) was added dropwise to a cold (-78 °C) solution of **1^{Me}** in dry thf (30-35 mL). After the addition of *n*BuLi, the reaction mixture was stirred for 30 min at -78 °C, followed by the addition of a solution of $RGaCl_2$ (R = Ar′ and *p*-$SiMe_3$Ar′) in thf (20-30 mL). The reaction mixture was warmed up to r.t. and stirred for another 3 h, resulting in a red solution. All volatiles were removed in vacuum, resulting in a red paste which was extracted with toluene (35 mL). All volatiles were removed from the toluene solution, yielding a red paste. Hexane (50 mL) was added to the red paste and the mixture was stirred vigorously for 16 h, resulting in a red solution and a red gummy residue. The residue was filtered off and washed with hexane (2 x 5 mL). The combined hexane phase was concentrated to ca. 20 mL and kept at -78 °C for 16 h, resulting in red crystals of pure **6a** or **6b**. The residue was redissolved in toluene (5 mL) and the resulting solution was added dropwise to well-stirred hexane (30 mL), resulting in a red solution with red gummy material sticking to the glass wall. The red solution was syringed off, leaving a gummy material behind, from which all volatiles were removed in high vacuum, yielding a sticky red solid (**6a$_x$** or **6b$_x$**).

6a and 6a$_x$. As described in general procedure, **1^{Me}** (1.18 g, 2.01 mmol) in thf (35 mL), *n*BuLi (1.66 mL, 4.15 mmol), and **4** (0.533 g, 1.94 mmol) in thf (30 mL) resulted in **6a** as red crystals (0.355 g, 29%) and **6a$_x$** as a sticky red solid (0.374 g, 31%).

Assignments of ^{1}H NMR signals of **6a** are based on the ^{1}H NMR data of **6b** (see below). ^{1}H NMR of **6a** ([D$_8$]toluene): δ 0.22 (s, 3H, $SiMe_2$), 0.72 (s, 3H, $SiMe_2$), 1.60 (s, 6H, NMe_2), 3.15 (s, 2H, CH_2), 3.80 (m, 2H, CH-β), 4.14 (m, 2H, CH-α), 4.21 (m, 2H, CH-α, 4.23 (m, 2H, CH-β), 4.25 (m, 2H, CH-β), 4.40 (m, 2H, CH-β), 4.52 (m, 2H, CH-α), 4.82 (m, 2H, CH-α), 6.91 (d, 1H, CH-3), 7.20 (t, 1H, CH-4), 7.33 (t, 1H, CH-5), 8.15 (d, 1H, CH-6). ^{13}C NMR of **6a** ([D$_8$]toluene): δ 0.45, 5.29 ($SiMe_2$), 45.37 (NMe_2), 66.25 (CH_2), 70.59, 70.72, 70.77, 71.20, 72.55, 72.79, 75.58, 76.85 (α- and β-C), 70.83, 71.03 (*ipso*-C of Cp rings), 127.28, 127.36, 136.71, 144.15, 149.88 (C_6H_3) [Note: one C_6H_3 peak is buried under the solvent peak]. EIMS (70 eV) *m/z*: 629 (100) [M^+], 428 (24)

[$C_{22}H_{24}Fe_2Si^+$], 411 (12) [$C_{21}H_{19}Fe_2Si^+$]. HRMS (EI; *m/z*): calcd for $C_{31}H_{34}Fe_2GaNSi$, 629.0433; found, 629.0415. Anal. Calcd for $C_{31}H_{34}Fe_2GaNSi$: C, 59.09; H, 5.44; N, 2.22. Found: C, 59.07; H, 5.27; N, 2.12.

^{1}H NMR of **6a$_x$** (C_6D_6): δ 0.47-0.77 (multiple peaks, 6H, $SiMe_2$), 1.70-1.85 (multiple peaks with one major broad peak at 1.78, 6H, NMe_2), 3.27 (broad peak, 2H, CH_2), 3.85-4.86 (multiple peaks, 16H, Cp), 6.72-7.11 (br. peaks, 1H, C_6H_4), 7.22-7.32 (br. peaks, 1H, C_6H_4), 7.33-7.44 (br. peaks, 1H, C_6H_4), 7.94-8.44 (br. peaks, 1H, C_6H_4). ^{13}C NMR of **6a$_x$** (C_6D_6): δ -0.45 (br. peak, $SiMe_2$), 45.93 (br. peak, NMe_2), 66.92 (br. peak, CH_2), 68.30-76.30 (multiple peaks, Cp), 124.50-151.00 (multiple peaks, C_6H_4).

6b and 6b$_x$. As described in general procedure, **1^{Me}** (1.07 g, 1.82 mmol) in thf (30 mL), *n*BuLi (1.53 mL, 3.83 mmol), and **5** (0.621 g, 1.79 mmol) in thf (20 mL) resulted in **6b** as red crystals (0.518 g, 41%) and **6b$_x$** as a sticky red solid (0.389 g, 31%). A series of NOE experiments was performed in order to assign every resonance of the ^{1}H NMR spectrum (C_6D_6) of **6b**: δ 0.35 (s, 3H, $SiMe_2$), 0.40 (s, 9H, $SiMe_3$), 0.79 (s, 3H, $SiMe_2$), 1.63 (s, 6H, NMe_2), 3.18 (s, 2H, CH_2), 3.93 (m, 2H, CH-α), 4.26 (m, 2H, CH-α), 4.28 (m, 2H, CH-β), 4.35 (m, 2H, CH-β), 4.40 (m, 2H, CH-β), 4.48 (m, 2H, CH-β), 4.65 (m, 2H, CH-α), 5.06 (m, 2H, CH-α), 7.03 (d, 1H, CH-3), 7.57 (d, 1H, CH-4), 8.62 (s, 1H, CH-6). ^{13}C NMR of **6b** (C_6D_6) δ 0.64 ($SiMe_3$), -0.60, 5.17 ($SiMe_2$), 45.48 (NMe_2), 66.24 (CH_2), 70.59, 70.82, 70.83, 71.21, 72.54, 72.94, 75.68, 76.94 (α- and β-C), 70.95 (*ipso*-C of Cp), 124.43, 132.74, 138.59, 142.11, 145.28, 149.16 (C_6H_3). Note: One signal for *ipso*-C of Cp was detected in the ^{13}C NMR spectrum in C_6D_6; the other signal for *ipso*-C of Cp overlapped with another Cp signals. The ^{13}C NMR was also measured in [D$_8$]toluene and signals for two 4*ipso*-C atoms of Cp were observed.] ^{1}H NMR of **6b** ([D$_8$]toluene): δ 0.27 (s, 3H, $SiMe_2$), 0.39 (s, 9H, $SiMe_3$), 0.75 (s, 3H, $SiMe_2$), 1.64 (s, 6H, NMe_2), 3.20 (s, 2H, CH_2), 3.85 (m, 2H, CH-α), 4.20 (m, 2H, CH-α), 4.24 (m, 2H, CH-β), 4.30 (m, 2H, CH-β), 4.33 (m, 2H, CH-β), 4.44 (m, 2H, CH-β), 4.57 (m, 2H, CH-α), 4.95 (m, 2H, CH-α), 7.00 (d, 1H, CH-3), 7.51 (d, 1H, CH-4), 8.51 (s, 1H, CH-6). ^{13}C NMR of **6b** (C_6D_6): δ -0.63 ($SiMe_3$), 0.59, 5.14 ($SiMe_2$), 45.47 (NMe_2), 66.32 (CH_2), 70.55, 70.75, 70.81, 71.19, 72.51, 72.87, 75.62, 76.94 (α- and β-C), 70.89, 71.15 (*ipso*-C of Cp rings), 124.43, 132.69, 138.42, 142.08, 145.22, 149.09 (C_6H_3). EIMS (70 eV) *m/z*: 701 (100) [M$^+$], 428 (24) [$C_{22}H_{24}Fe_2Si^+$], 411 (12) [$C_{21}H_{19}Fe_2Si^+$]. HRMS (EI; *m/z*): calcd for $C_{34}H_{42}Fe_2GaNSi_2$, 701.0810; found, 701.0810. Anal. Calcd for $C_{34}H_{42}Fe_2GaNSi_2$: C, 58.15; H, 6.03; N, 1.99. Found: C, 58.42; H, 6.07; N, 1.95.

^{1}H NMR of **6b$_x$** (C_6D_6): δ 0.16-0.46 (multiple peaks, 9H, $SiMe_3$), 0.47-0.80 (multiple peaks, 6H, $SiMe_2$), 1.55-2.15 (multiple peaks with one major br. peak at 1.80, 6H, NMe_2), 3.00-3.65 (multiple peaks with one major br. peak at 3.30, 2H, CH_2), 3.85-5.10 (multiple peaks, 16H, Cp), 6.72-7.11 (multiple peaks, 1H, C_6H_3), 7.39-7.67 (multiple peaks, 1H, C_6H_3), 8.30-8.80 (multiple peaks, 1H, C_6H_3). ^{13}C NMR of **6b$_x$** (C_6D_6): δ -1.40-0.00 (multiple peaks, $SiMe_2$ and $SiMe_3$), 45.93 (br. peak, NMe_2), 66.91 (br. peak, CH_2), 68.30-76.30 (multiple peaks, Cp), 124.00-150.00 (multiple peaks, C_6H_3).

Crystal Structure Determination of 6a and 6b. A clear orange plate-like crystal of **6a** ($C_{31}H_{34}Fe_2GaNSi$) having the approximate dimensions of 0.18 × 0.15 × 0.08 mm was coated with oil, collected onto the aperture of a mounted Micromount^{TM}(MiTeGen, USA) mounted onto the goniometer head, which was quickly transferred to the cold stream of the Oxford cryo-jet. The same procedure was applied for mounting a clear yellow needle-like crystal of **6b** ($C_{34}H_{42}Fe_2GaNSi_2$) having the approximate dimensions of 0.18 × 0.08 × 0.05 mm. All measurements were made on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using monochromated Mo K_α radiation at -100 °C. An initial orientation matrix and cell was determined from 10 frames using ϕ-scans. Data =was collected using ϕ- and ω-scans.[10] Cell parameters were initially retrieved using the COLLECT[10] software and then refined with the HKL DENZO and SCALEPACK software[11] using 16029 (**6a**) and 17143 (**6b**) observed reflections from the data collection, respectively. Data reduction was performed with the HKL DENZO and SCALEPACK software,[11] which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarization effects. A multiscan absorption correction was applied (SCALEPACK).[11] The structure was solved using direct methods (SIR-2004)[12] and refined by full-matrix least-squares method on F^2 with SHELXL97-2.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C-H bond distances 0.95/0.98/0.99 Å) and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom. Neutral atom scattering factors for non-hydrogen atoms and anomalous dispersion coefficients are contained in the SHELXTL-NT 6.14 program library.[14]

Table S1. Crystal Data for the Compounds **6a** and **6b**.

Compound reference	**6a**	**6b**
Chemical formula	$C_{31}H_{34}Fe_2GaNSi$	$C_{34}H_{42}Fe_2GaNSi_2$
Formula Mass	630.10	702.29
Crystal system	Monoclinic	Monoclinic
a/Å	27.7463(2)	9.63300(10)
b/Å	11.3739(2)	10.86300(10)
c/Å	17.6834(3)	31.8490(4)
α/°	90.00	90.00
β/°	96.8620(8)	99.9950(6)
γ/°	90.00	90.00
Unit cell volume/Å^3	5540.62(14)	3282.20(6)
Temperature/K	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$
No. of formula units per unit cell, Z	8	4
Radiation type	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	2.063	1.784
No. of reflections measured	28035	33427
No. of independent reflections	15486	9546
R_{int}	0.0370	0.0519
Final R_1 values ($I > 2\sigma(I)$)	0.0377	0.0353
Final $wR(F^2)$ values (all data)	0.0844	0.0806
Goodness of fit on F^2	1.016	1.022
CCDC number	878280	878281

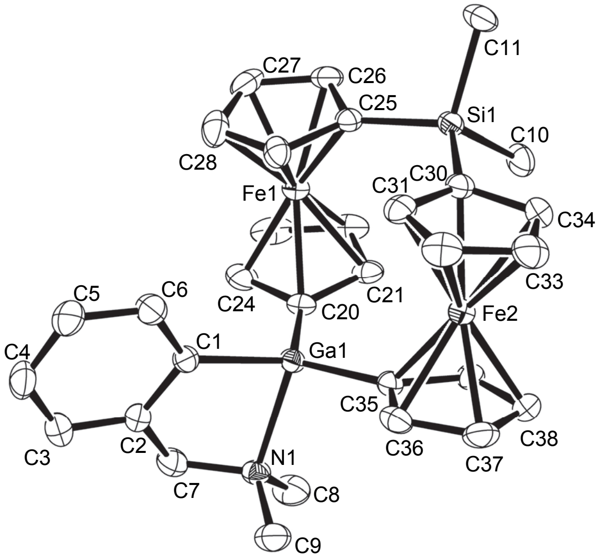

Figure S1. Molecular structure of **6a** with thermal ellipsoids at the 50% probability level**.** Hydrogen atoms are omitted for clarity. Only one of two independent molecules is shown. Selected atom-atom distances [Å] for **6a** (values for the second independent molecule shown in braces): Ga1-N1 2.1585(18) {2.158(2)}; Ga1-C1 1.983(2) {1.980(3)}; Ga1-C20 1.952(2) {1.962(2)}; Ga1-C35 1.962(2) {1.948(2)}; Fe1···Fe2 5.2777(5) {5.3281(4)}; C20···C35 3.362(3) {3.375(3)}, C25···C30 3.095(3) {3.115(3)}. Tilt angles between the least square planes of the C atoms of the Cp rings are 1.44(13)° {4.44(13)} (at Fe1) and 6.71(11)° {5.23(13)} (at Fe2).

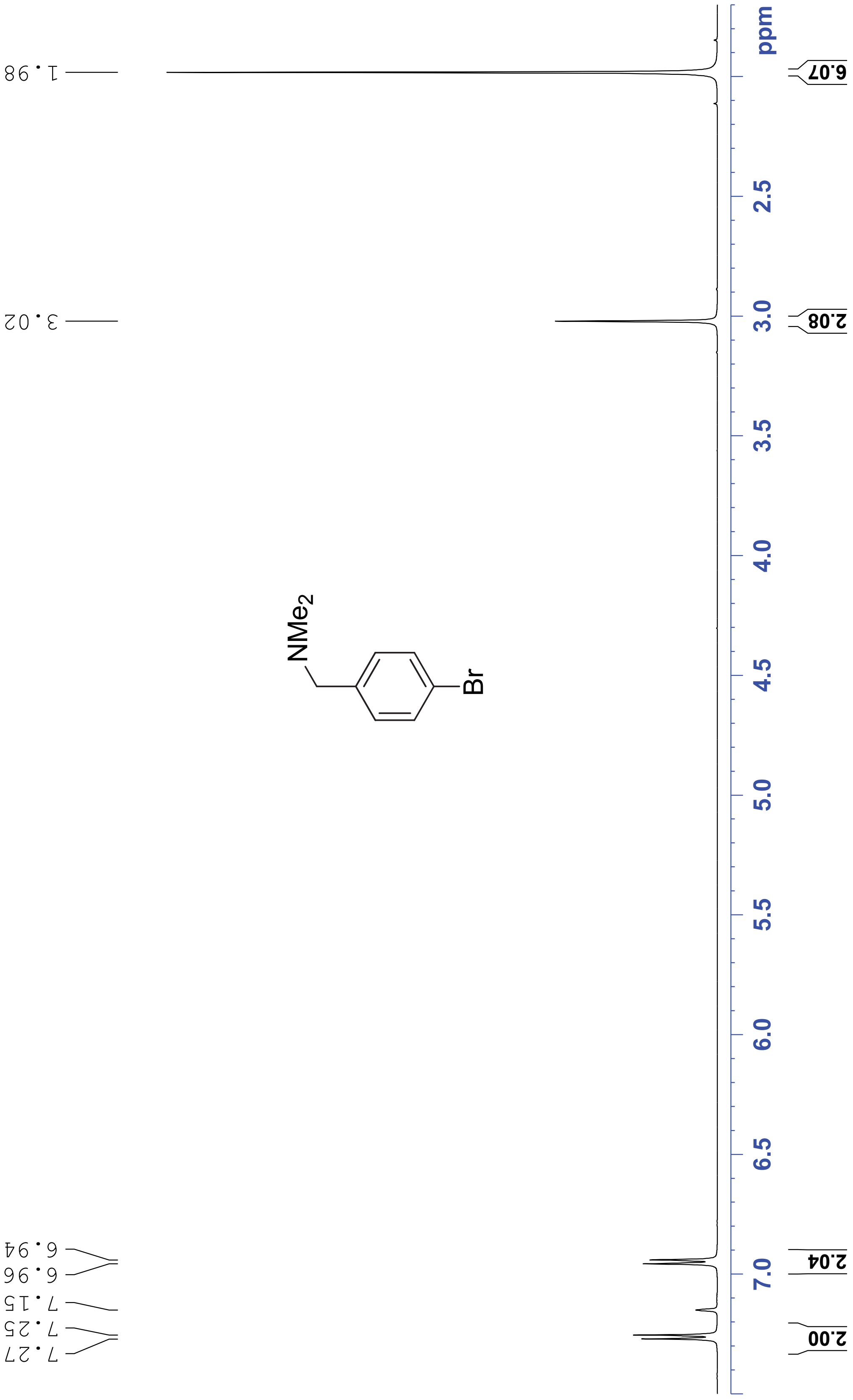

Figure S2. ^{1}H NMR spectrum of 1-bromo-4-[(dimethylamino)methyl]benzene in C_6D_6.

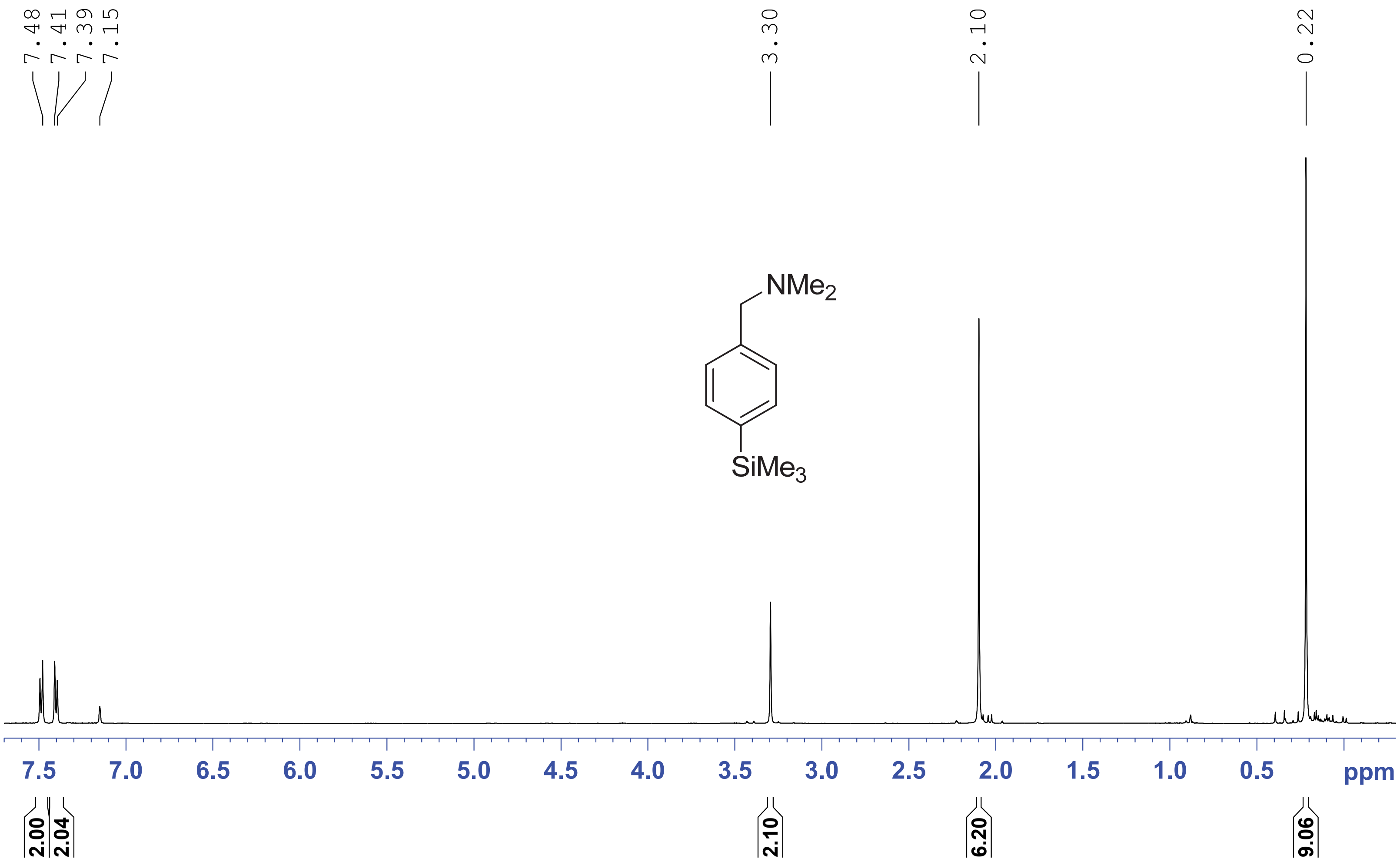

Figure S3. ^{1}H NMR spectrum of 1-[(dimethylamino)methyl]-4-trimethylsilylbenzene in C_6D_6.

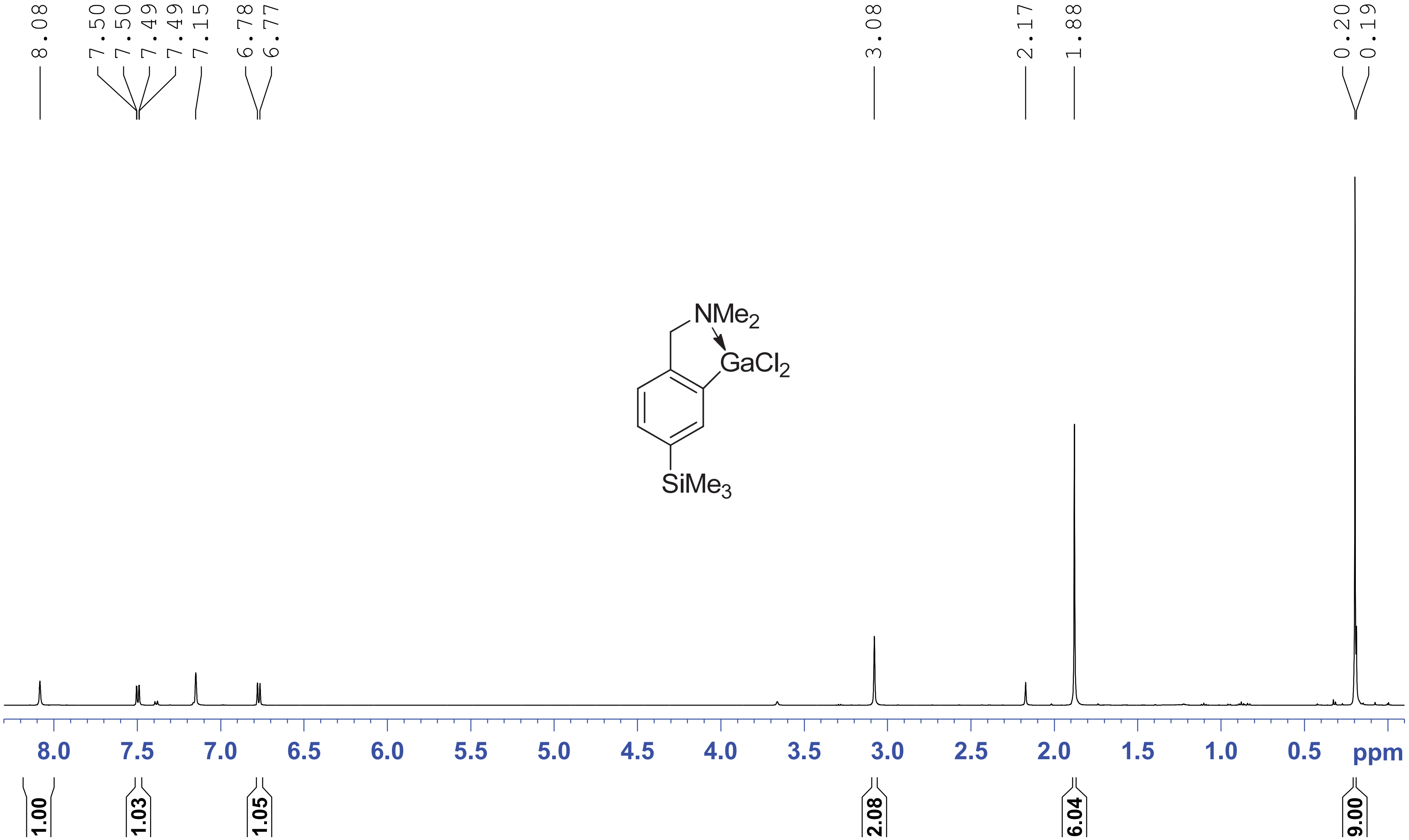

Figure S4. ^{1}H NMR spectrum of **5** in C_6D_6.

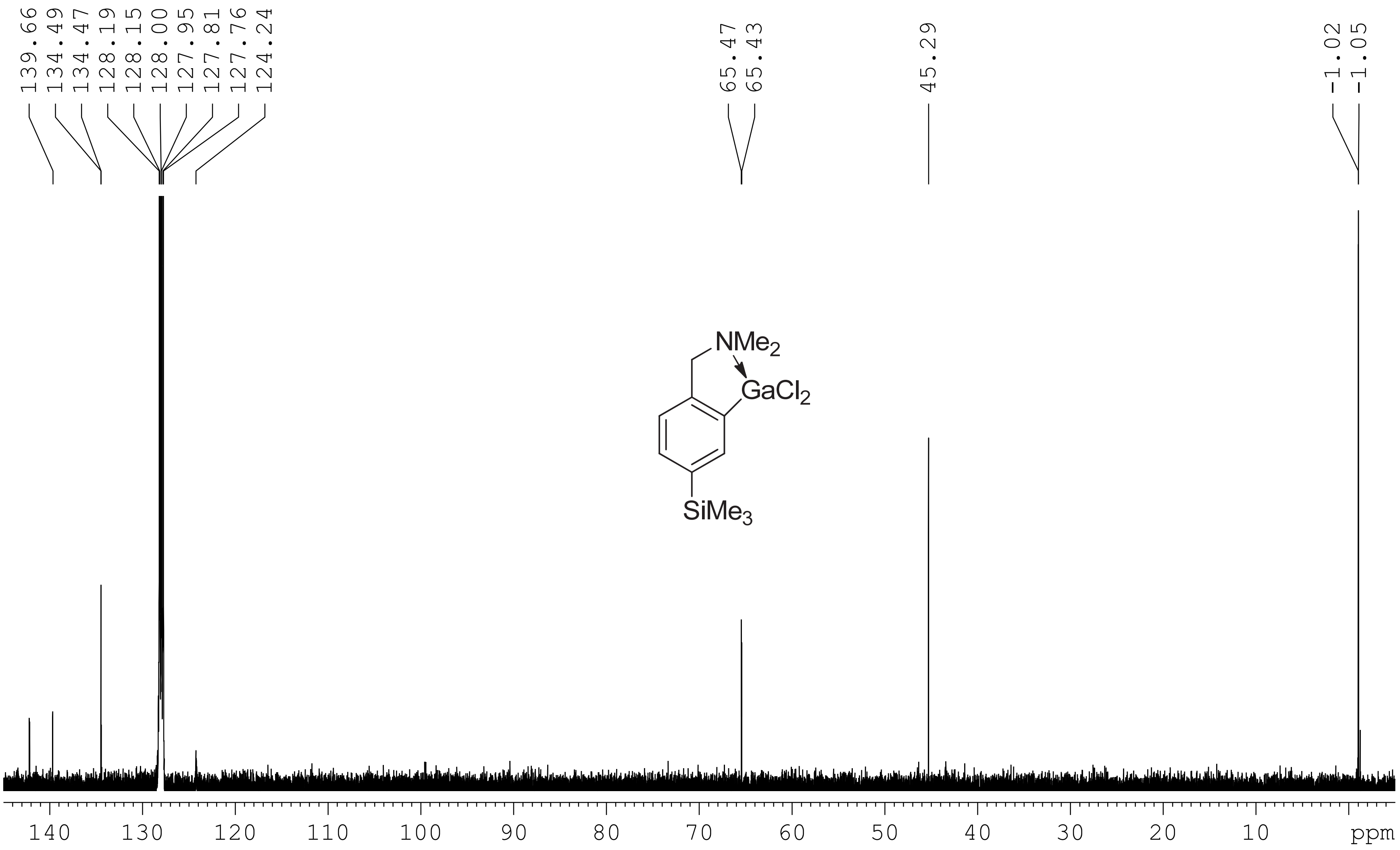

Figure S5. ^{13}C NMR spectrum of **5** in C_6D_6.

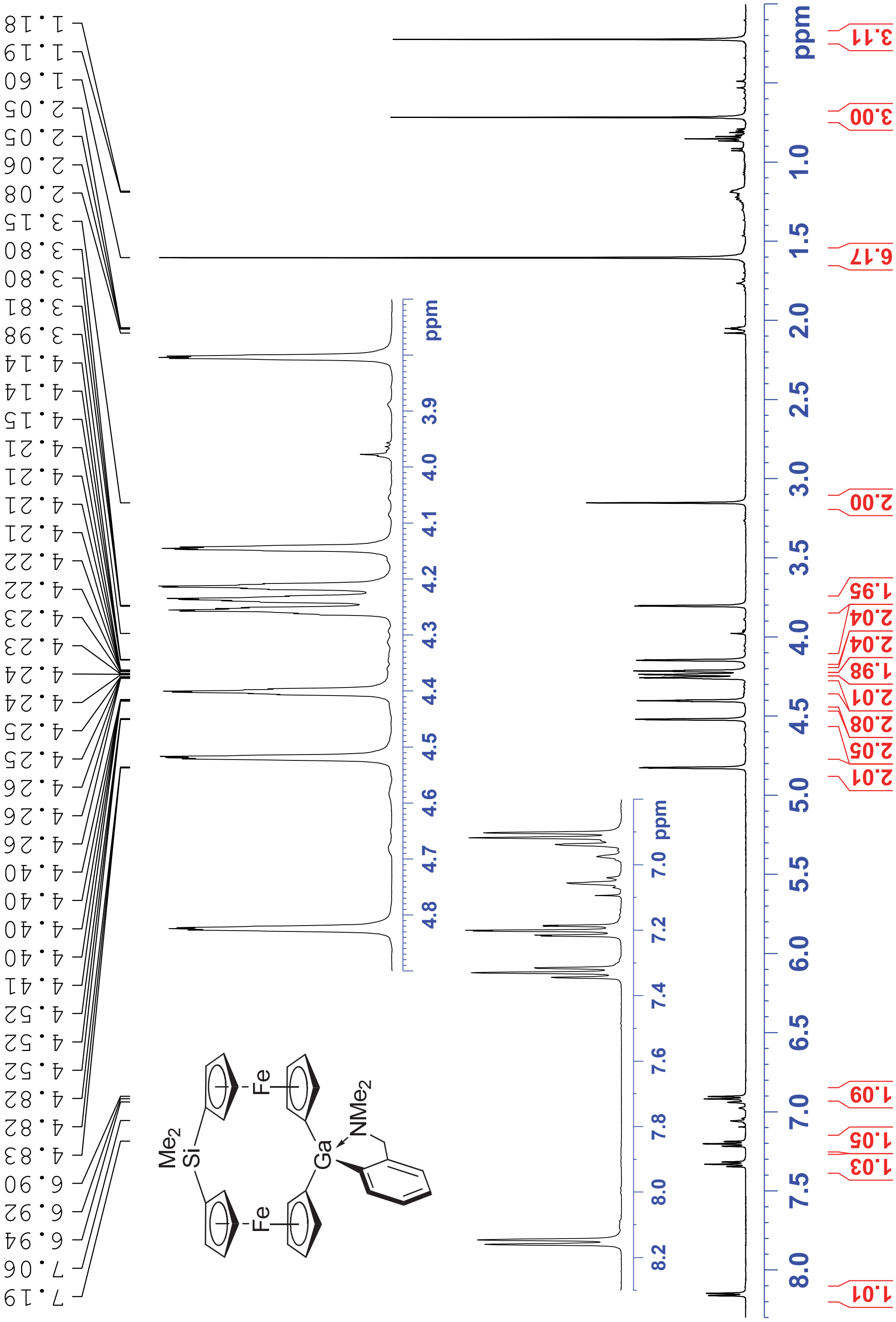

Figure S6. ^{1}H NMR spectrum of **6a** in [D$_8$]toluene at r.t.

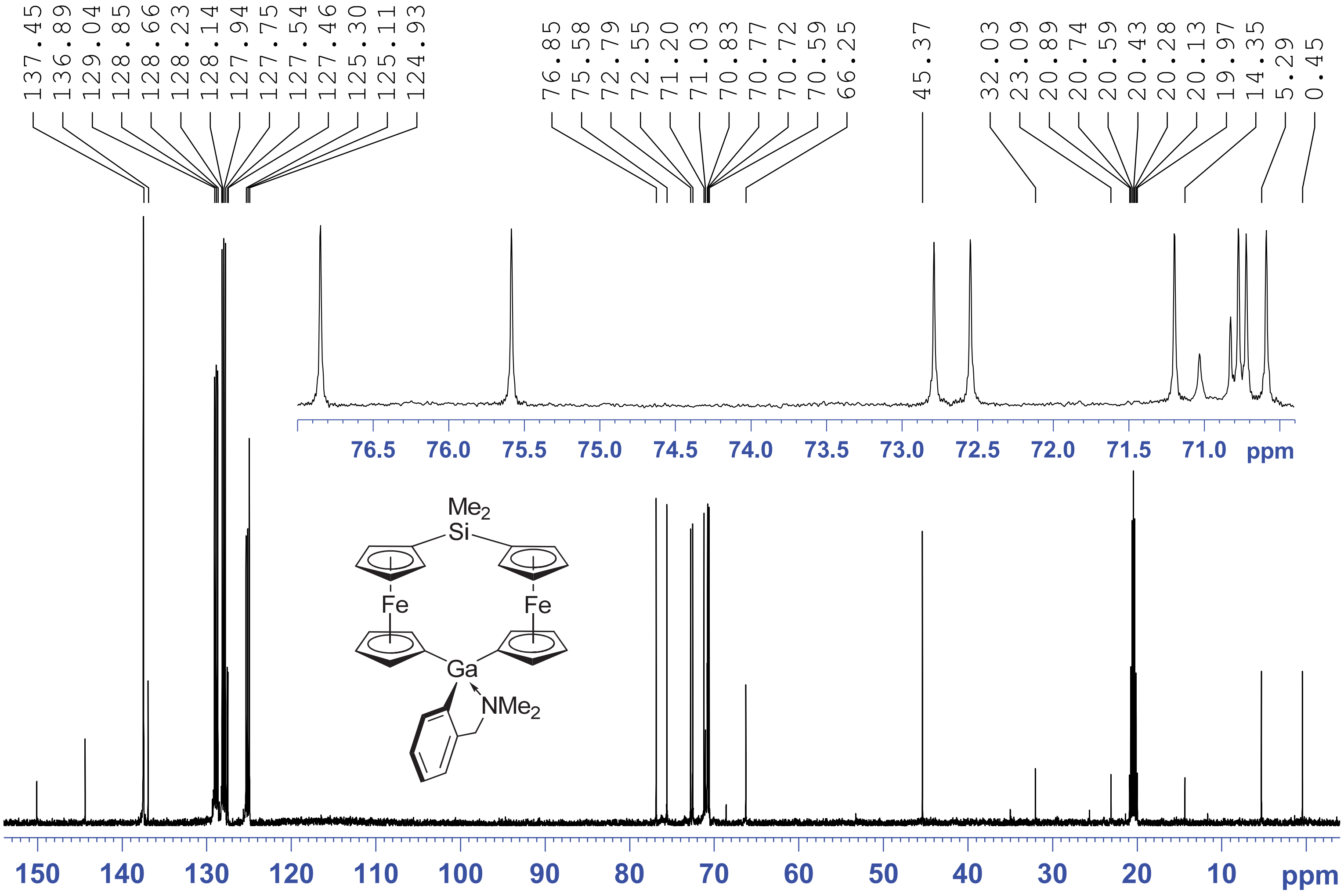

Figure S7. ^{13}C NMR spectrum of **6a** in [D$_8$]toluene at r.t.

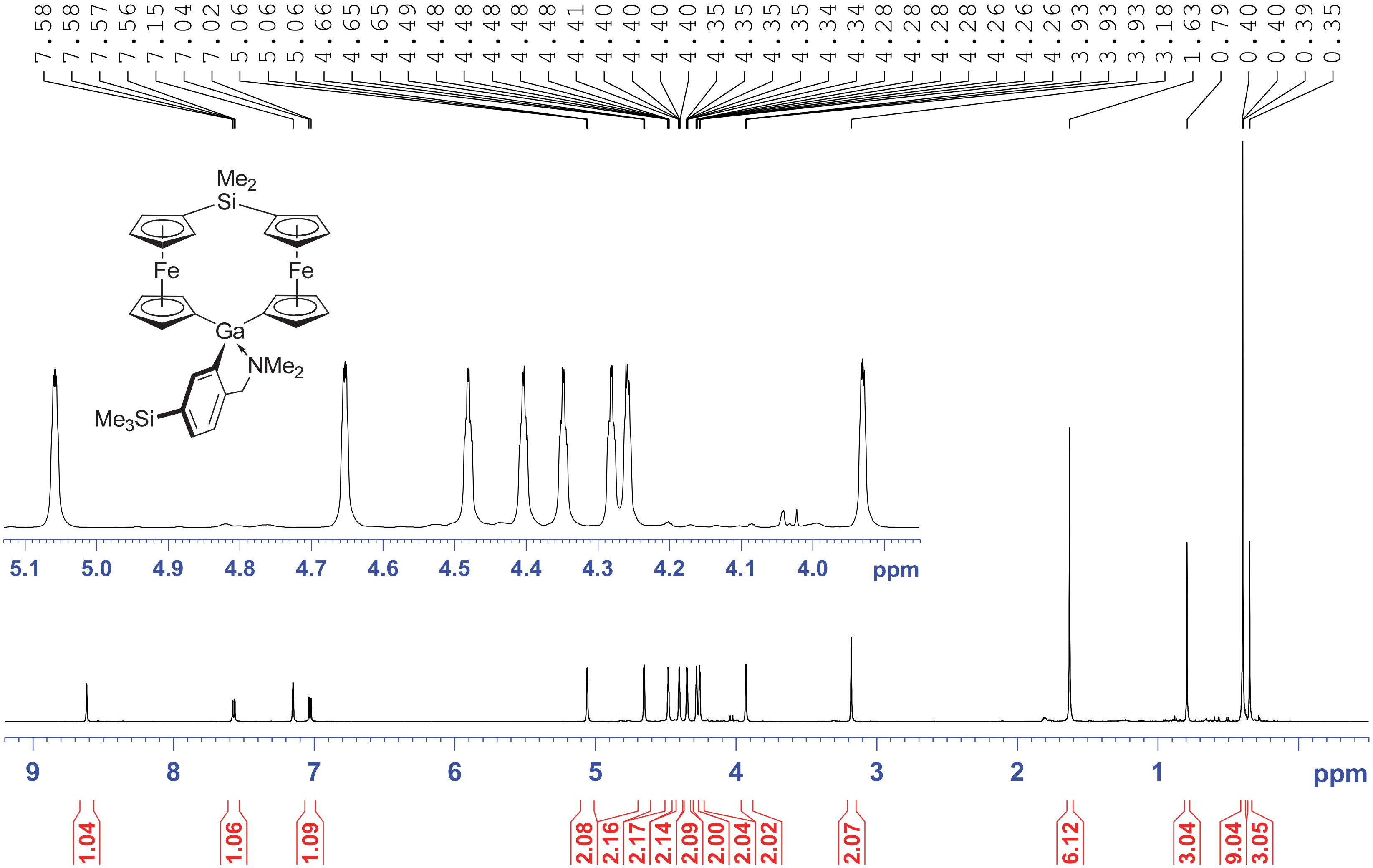

Figure S8. ^{1}H NMR spectrum of **6b** in C_6D_6 at r.t.

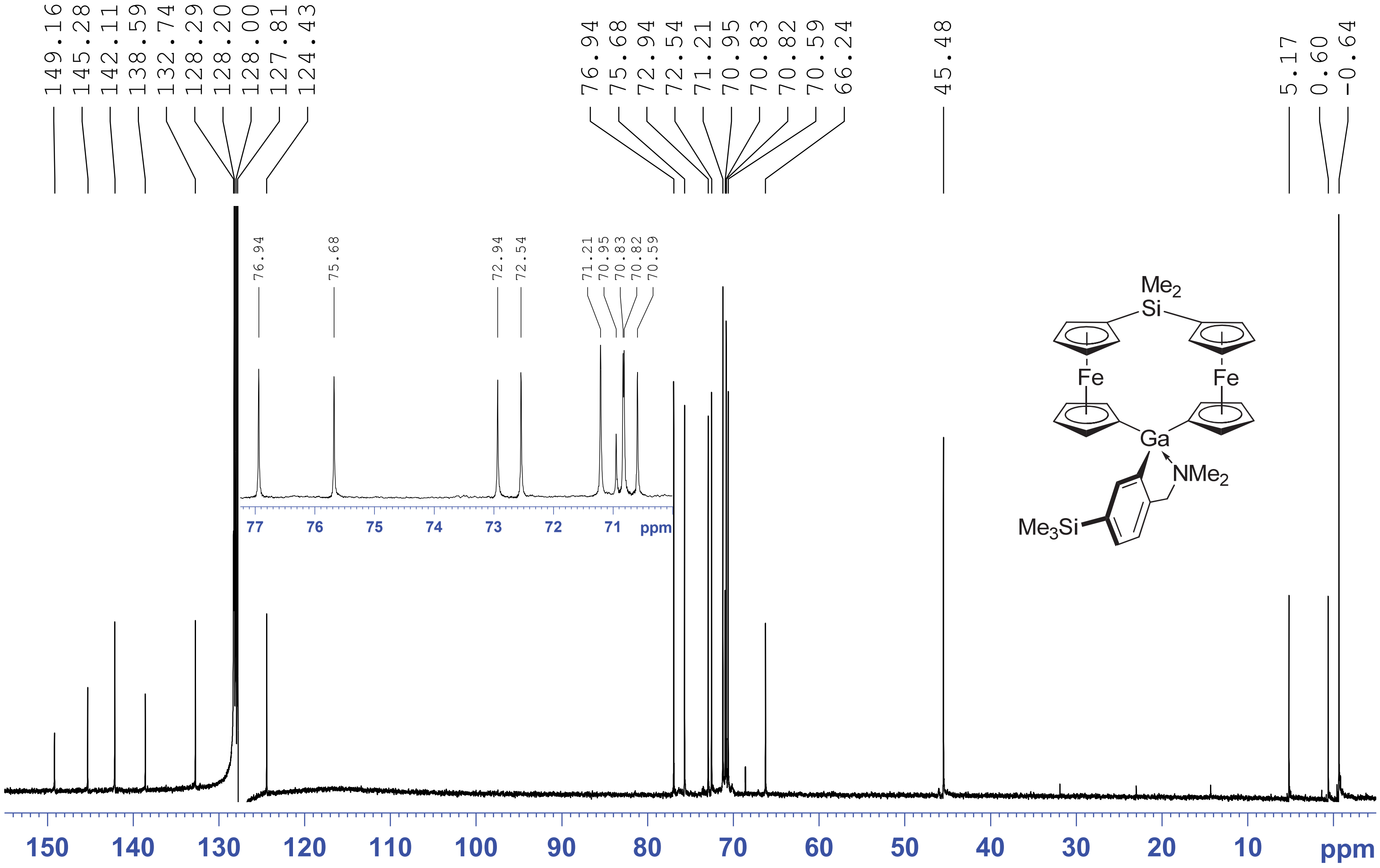

Figure S9. ^{13}C NMR spectrum of **6b** in C_6D_6 at r.t.

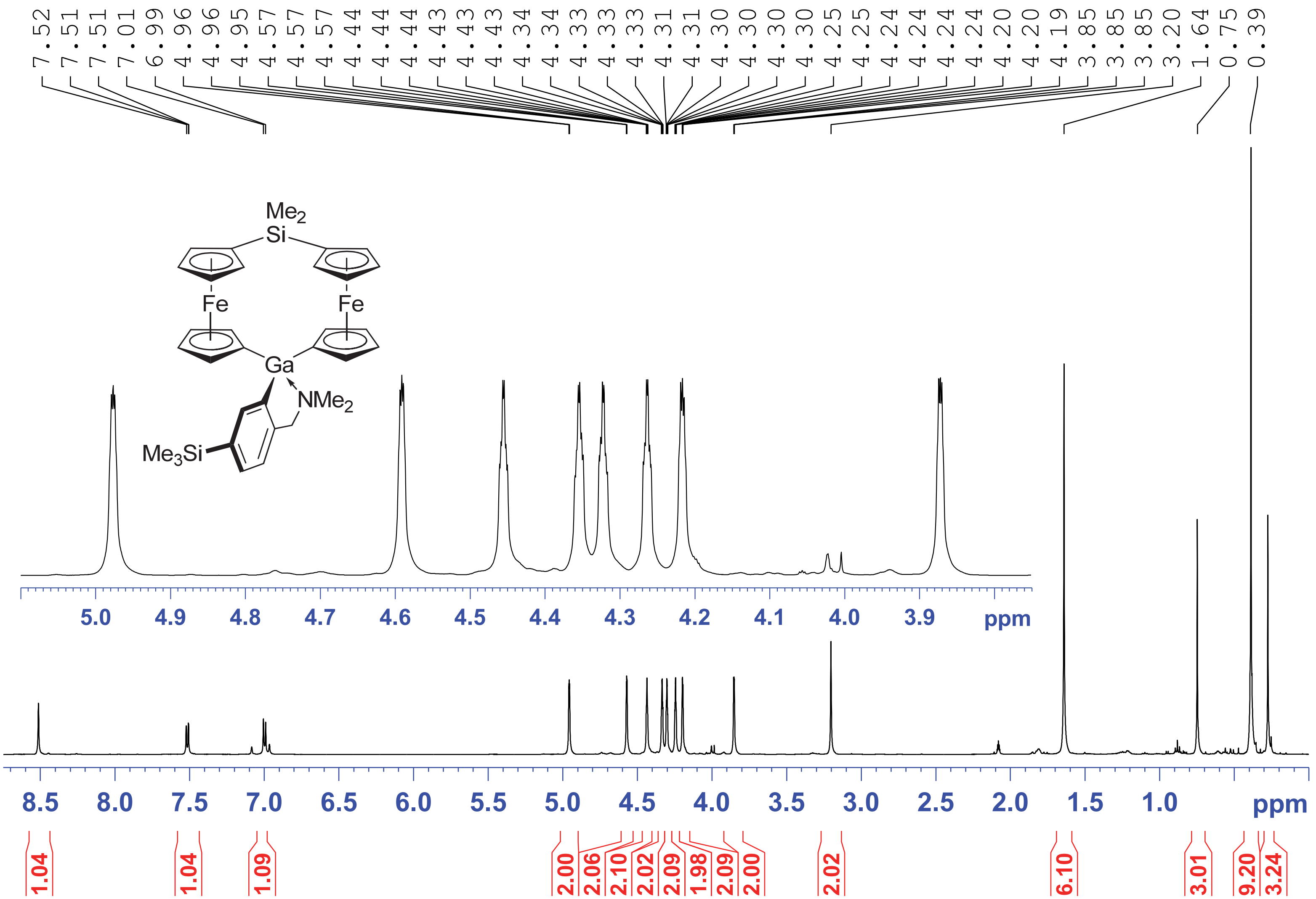

Figure S10. ^{1}H NMR spectrum of **6b** in [D$_8$]toluene at r.t.

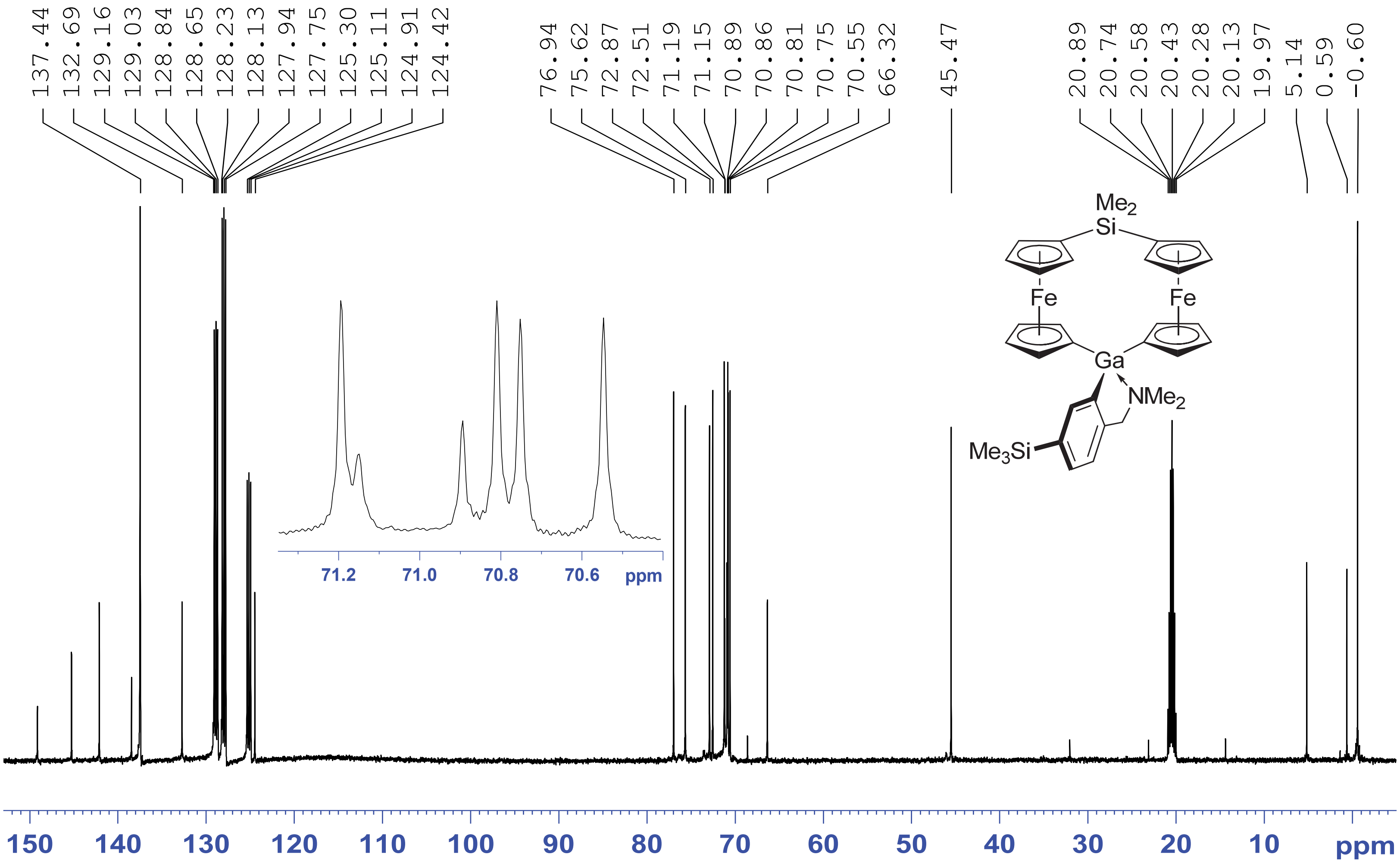

Figure S11. ^{13}C NMR spectrum of **6b** in [D$_8$]toluene at r.t.

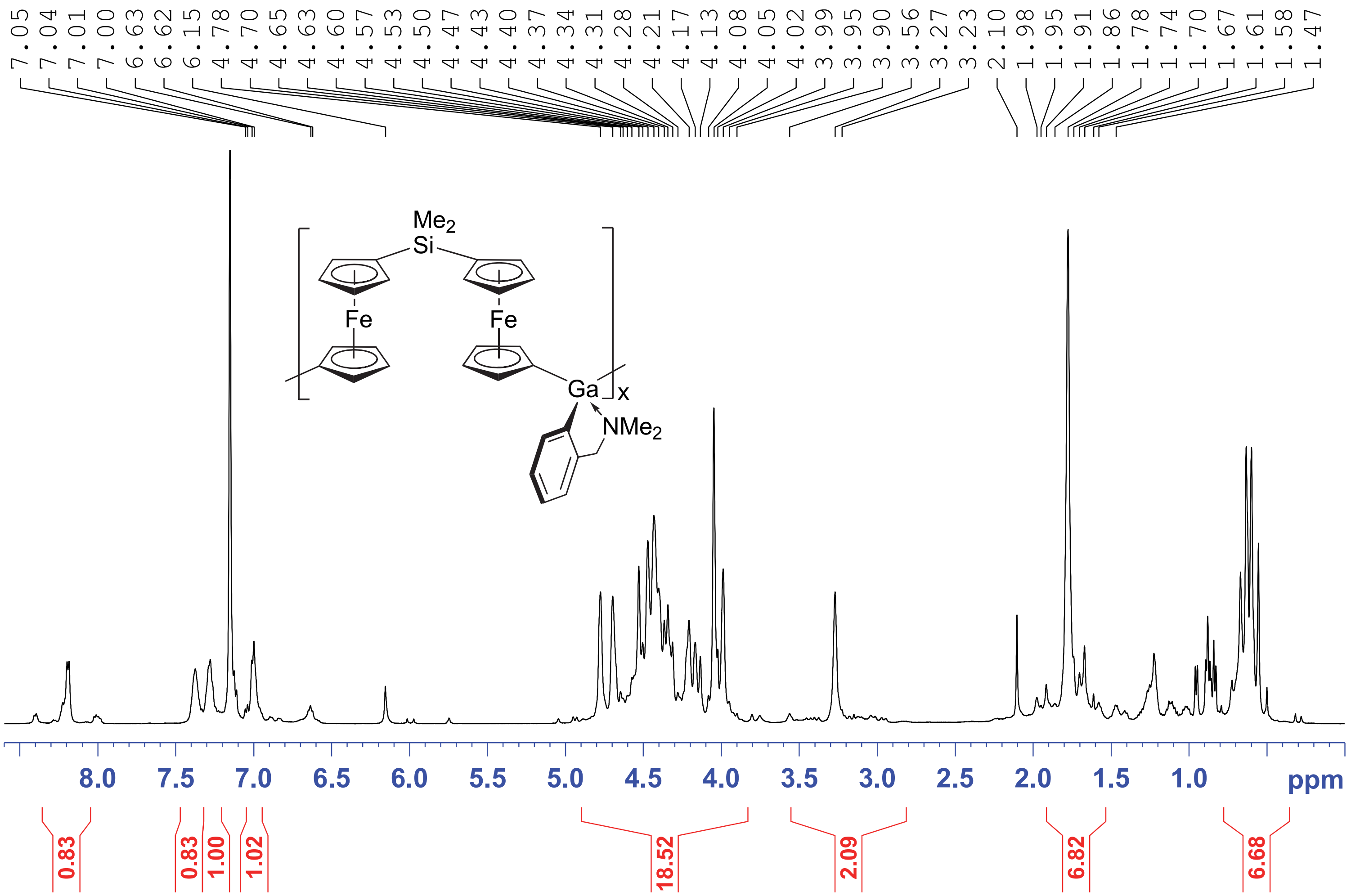

Figure S12. ^{1}H NMR spectrum of **6a$_x$** in C_6D_6 at r.t.

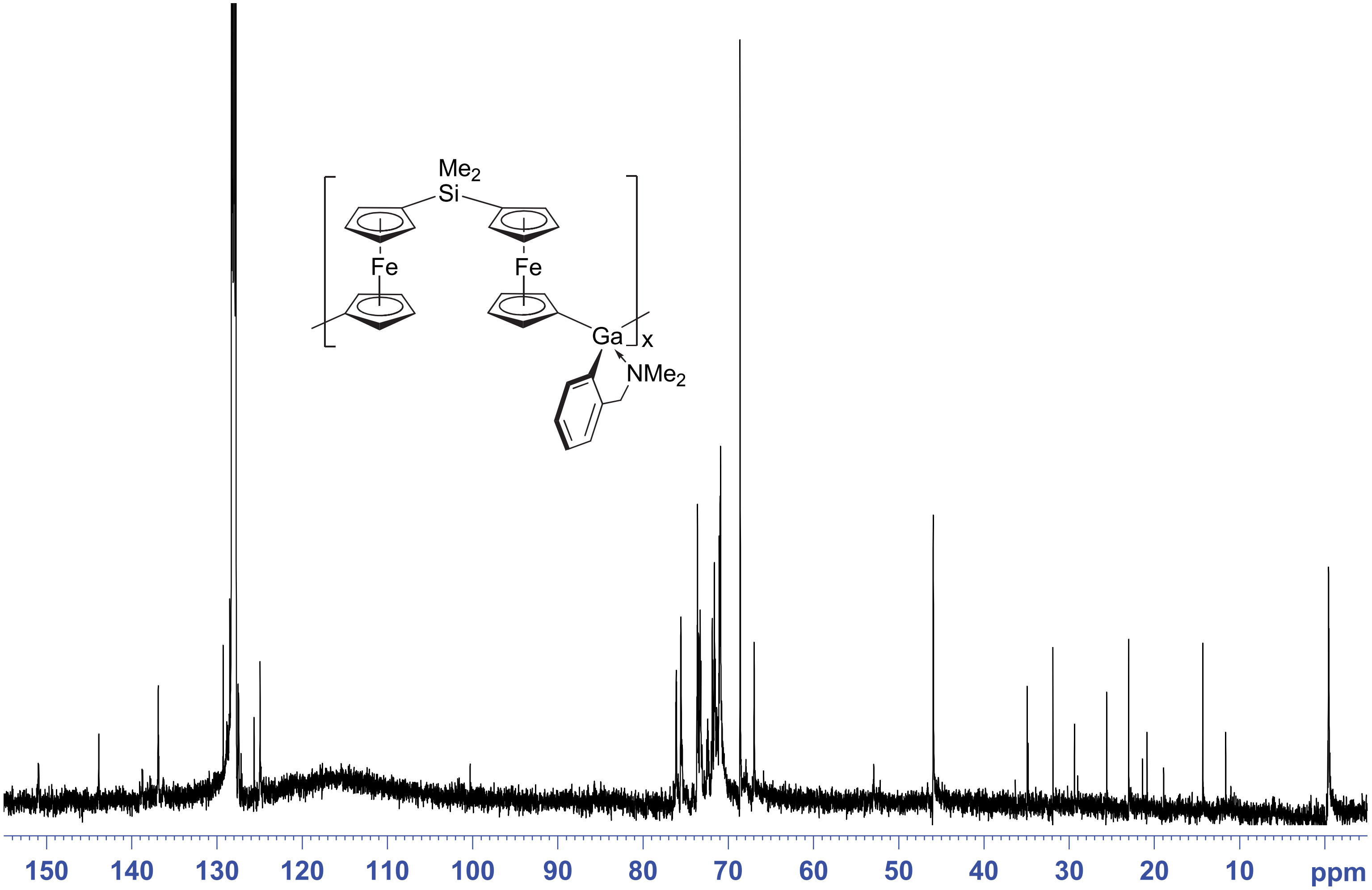

Figure S13. ^{13}C NMR spectrum of $\mathbf{6a_x}$ in C_6D_6 at r.t.

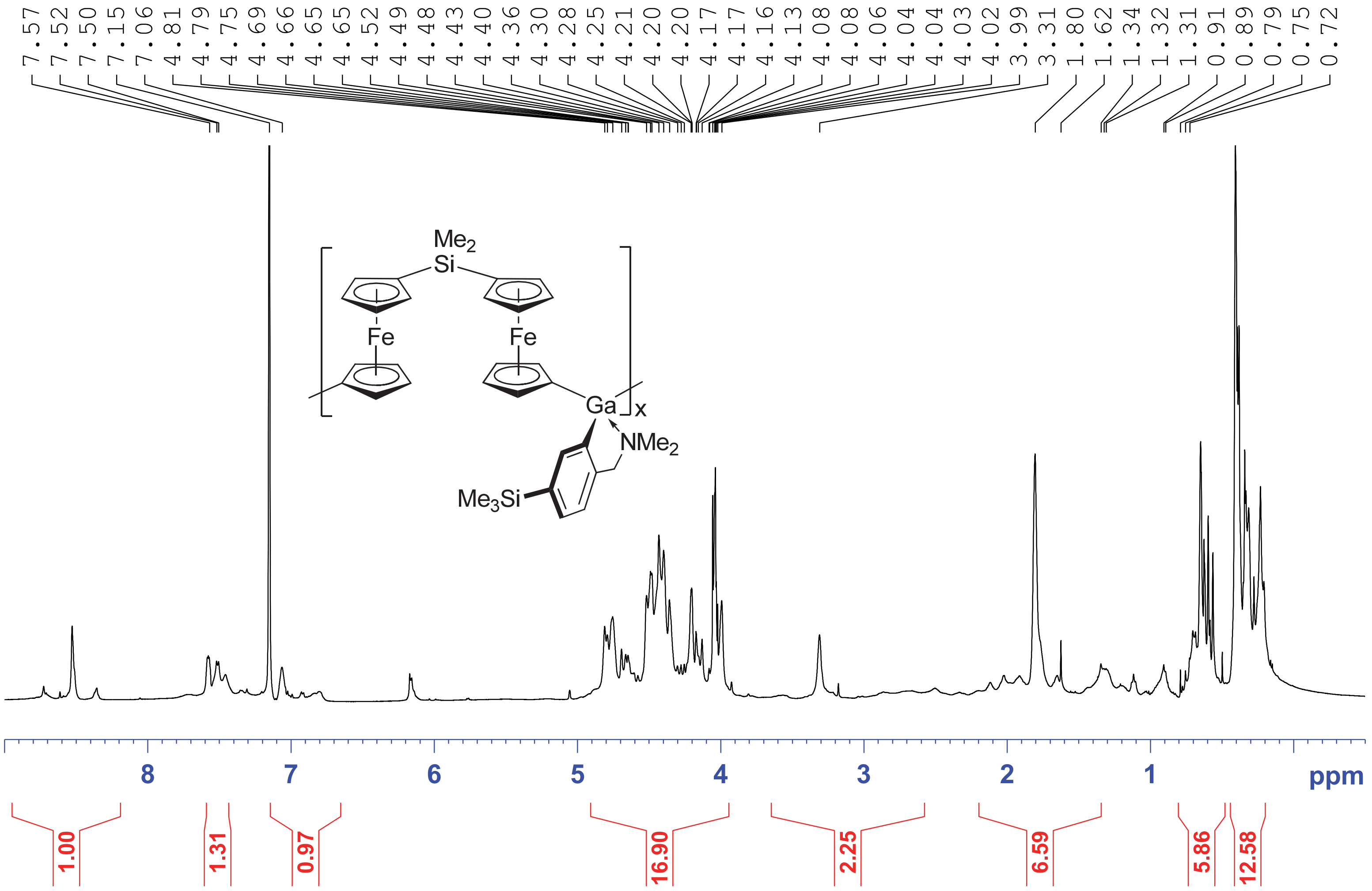

Figure S14. ^{1}H NMR spectrum of **6b$_x$** in C_6D_6 at r.t.

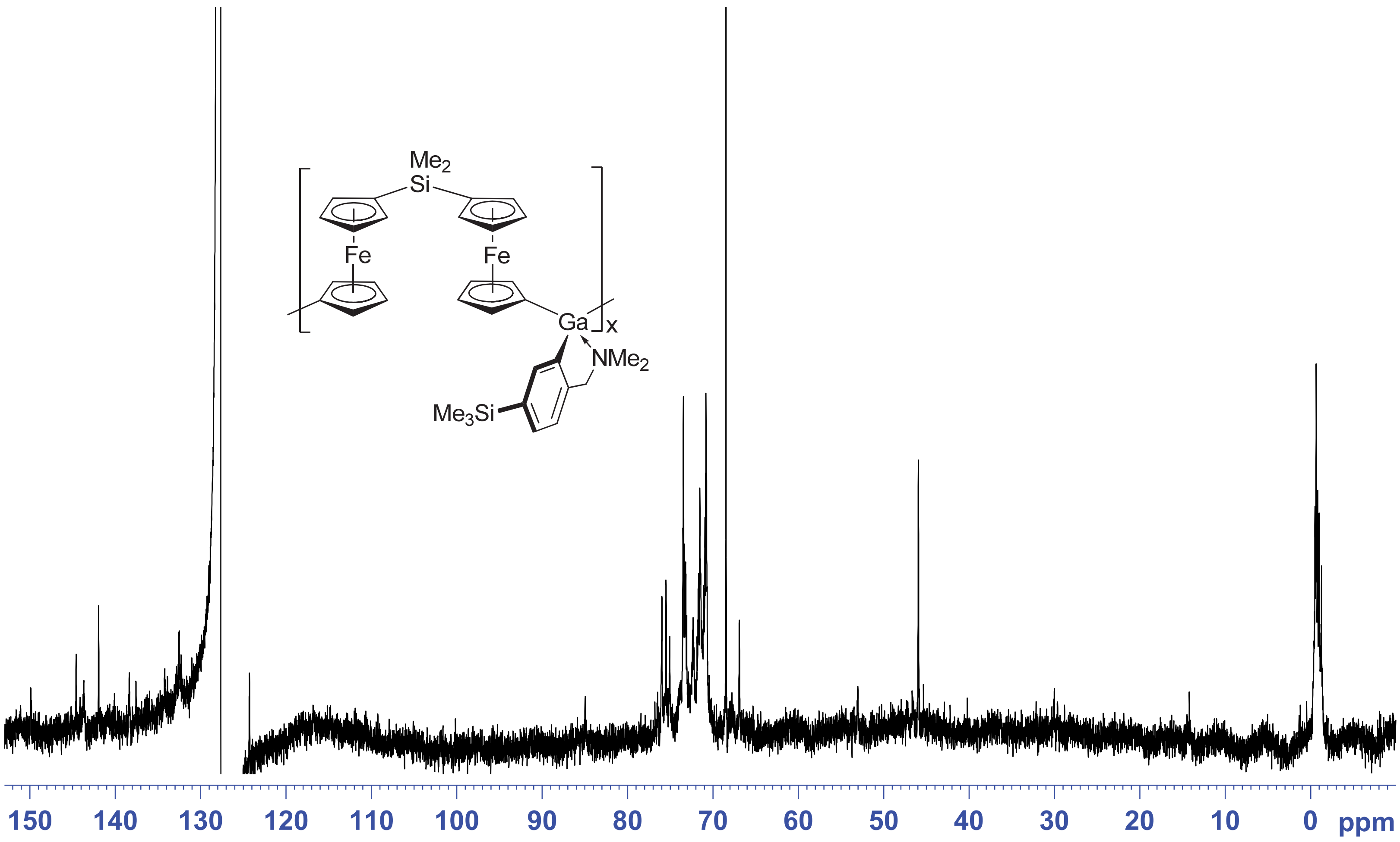

Figure S15. ^{13}C NMR spectrum of **6b$_x$** in C_6D_6 at r.t.

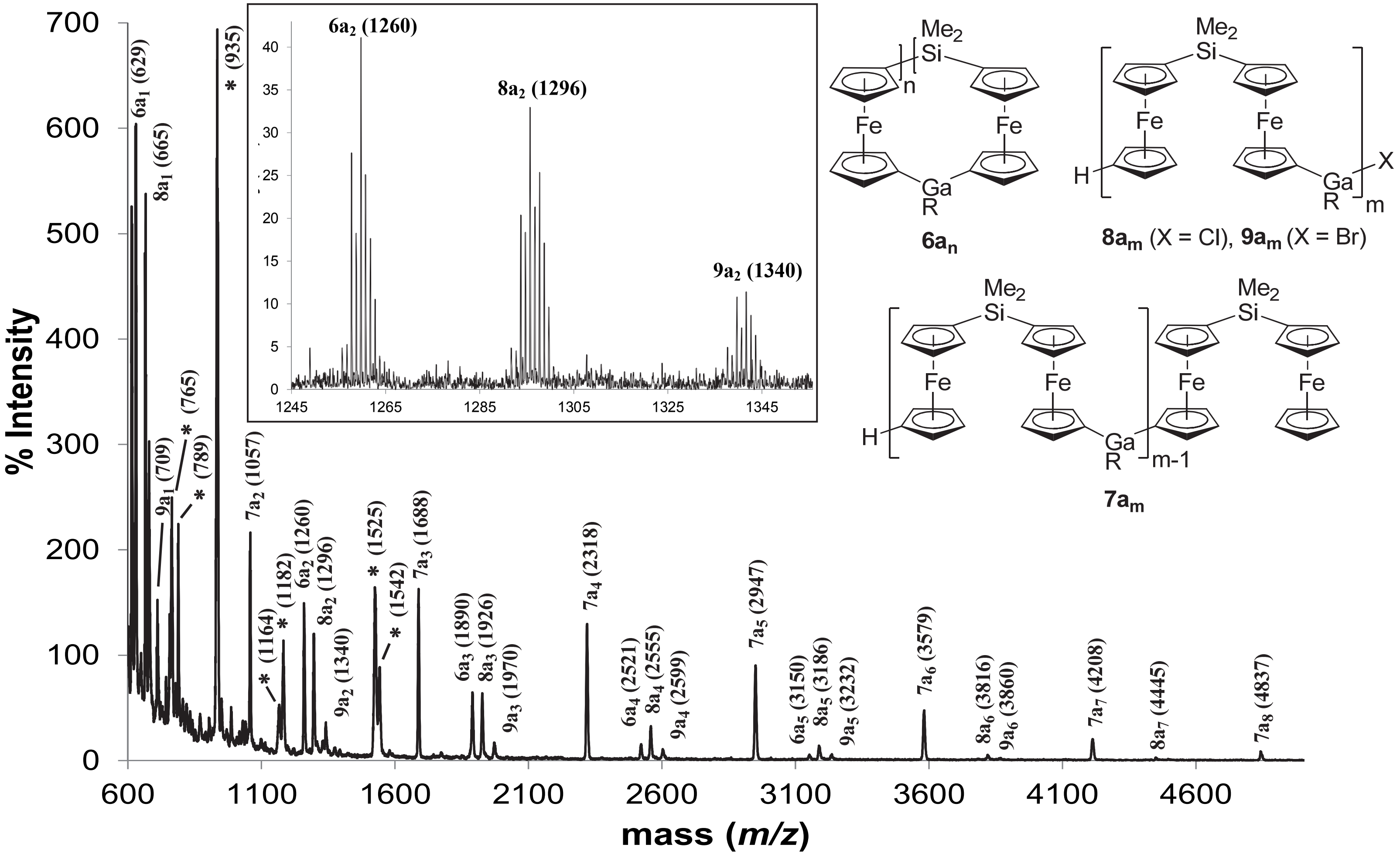

Figure S16. MALDI-TOF (linear mode) spectrum of **$6a_x$** [box shows HR (reflector mode) MALDI-TOF spectrum; asterisk indicates unassigned peaks; see also Fig. S17].

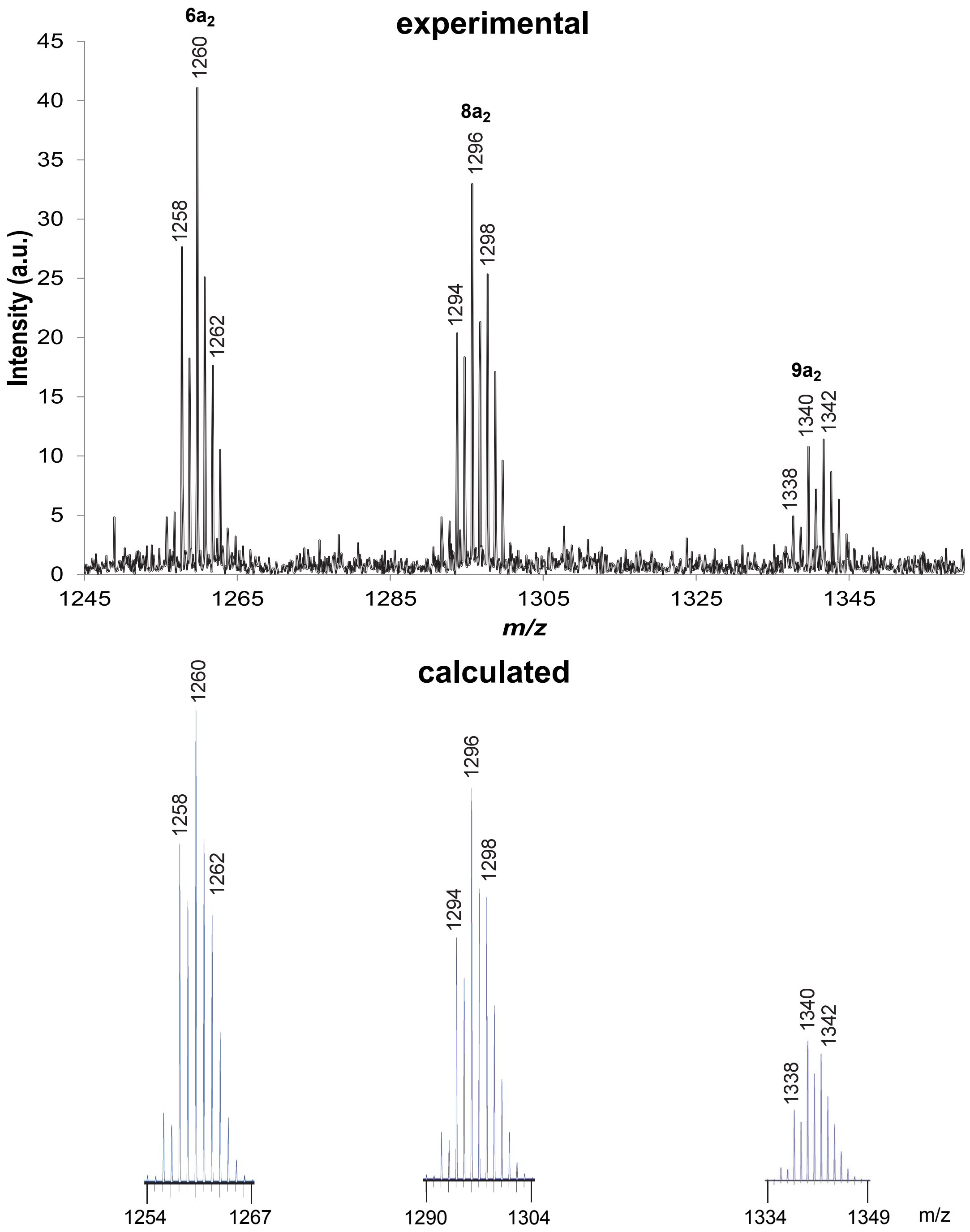

Figure S17. Selected highly resolved mass peaks of **6a$_x$** (MALDI-TOF; reflector mode; see Fig. S16) and their calculated isotopic pattern.

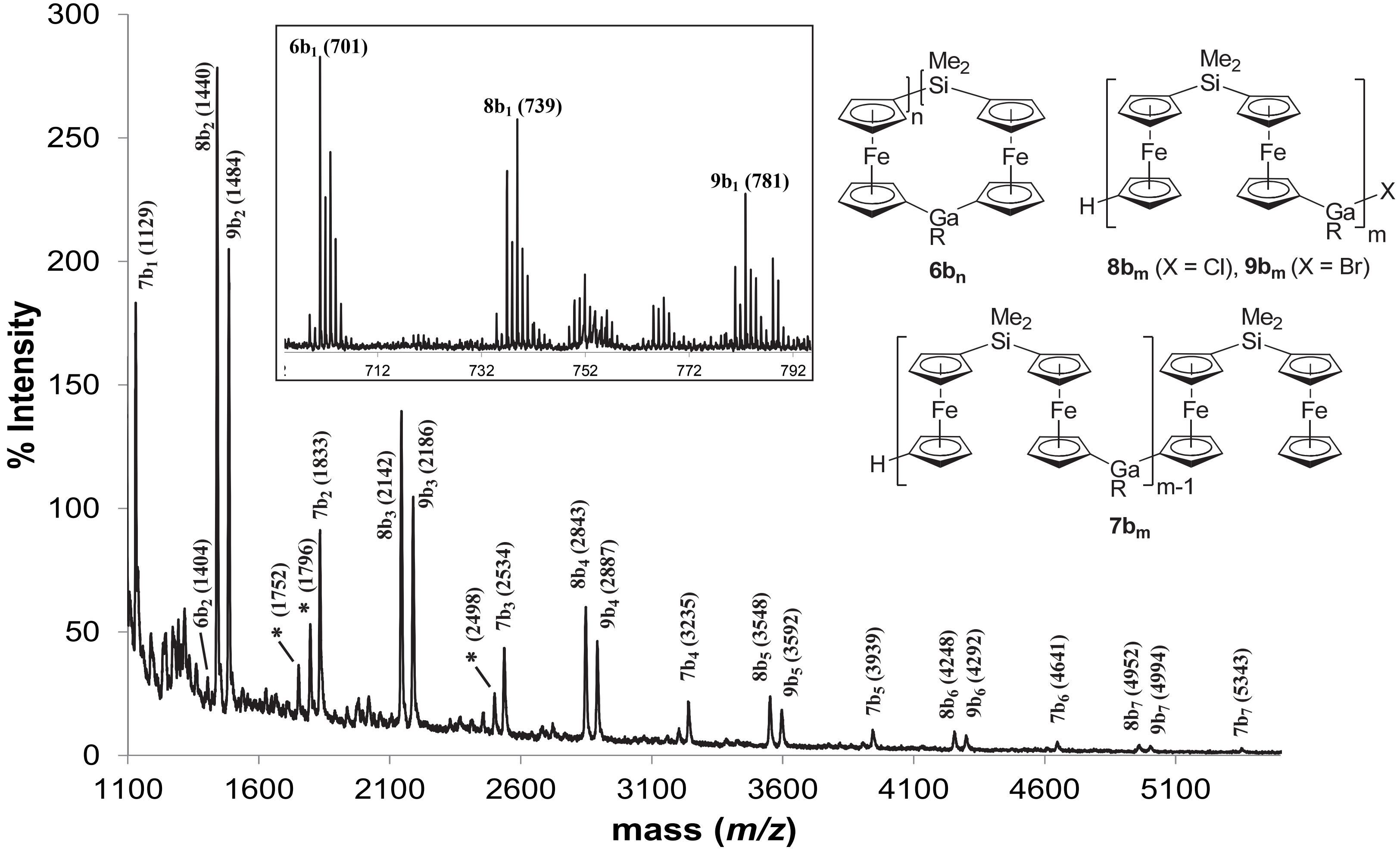

Figure S18. MALDI-TOF (linear mode) spectrum of **6b**$_x$ [box shows HR (reflector mode) MALDI-TOF spectrum; asterisk indicates unassigned peaks; see also Fig. S19].

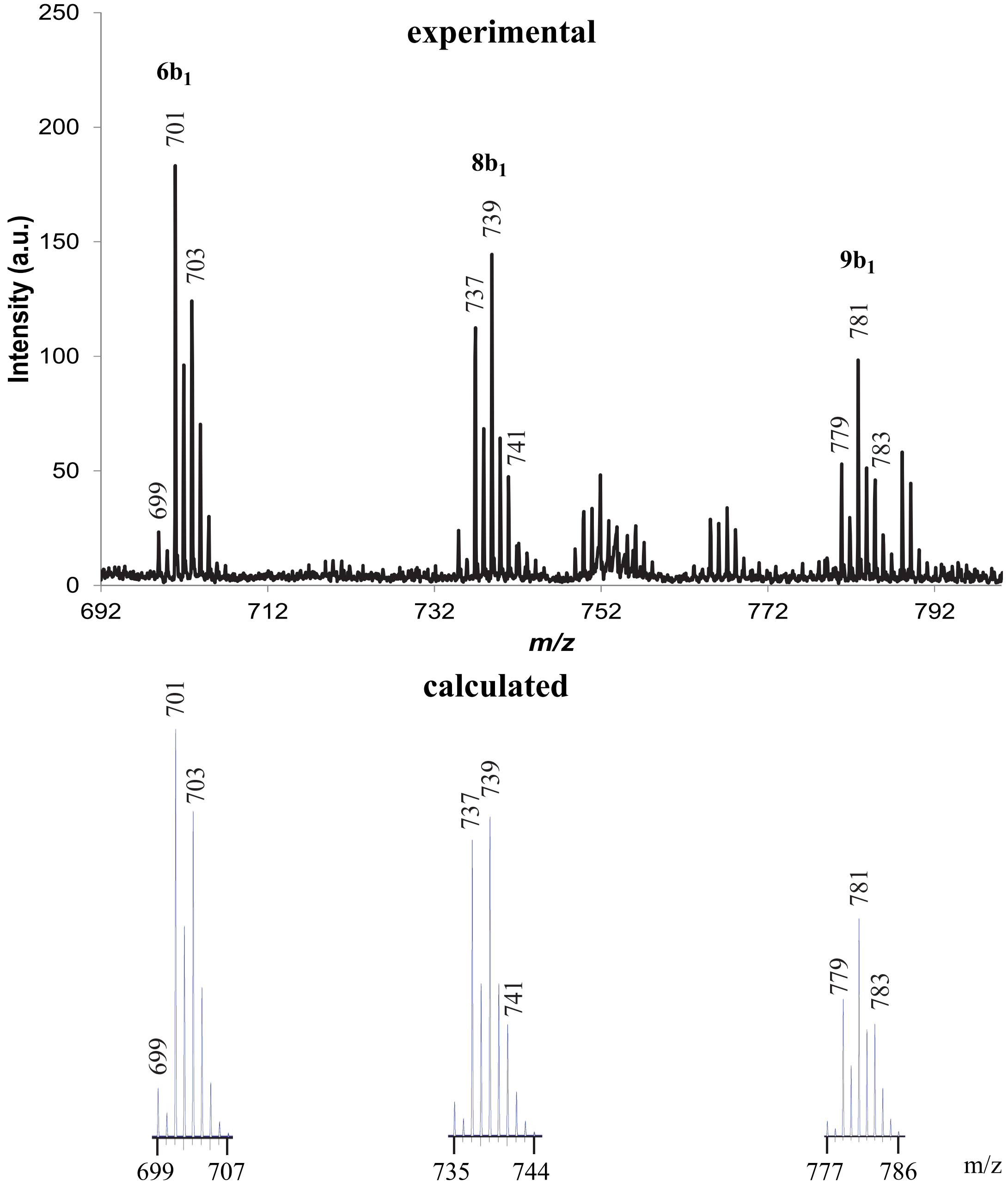

Figure S19. Selected highly resolved mass peaks of **6b$_x$** (MALDI-TOF; reflector mode; see Fig. S18) and their calculated isotopic pattern.

Table S4. GPC results of **6a**$_x$ and **6b**$_x$.

Sample	M_n [kDa]	M_w [kDa]	PDI	DP_w
6a$_x$	2.11	3.08	1.46	5
6b$_x$	2.69	7.05	2.62	10

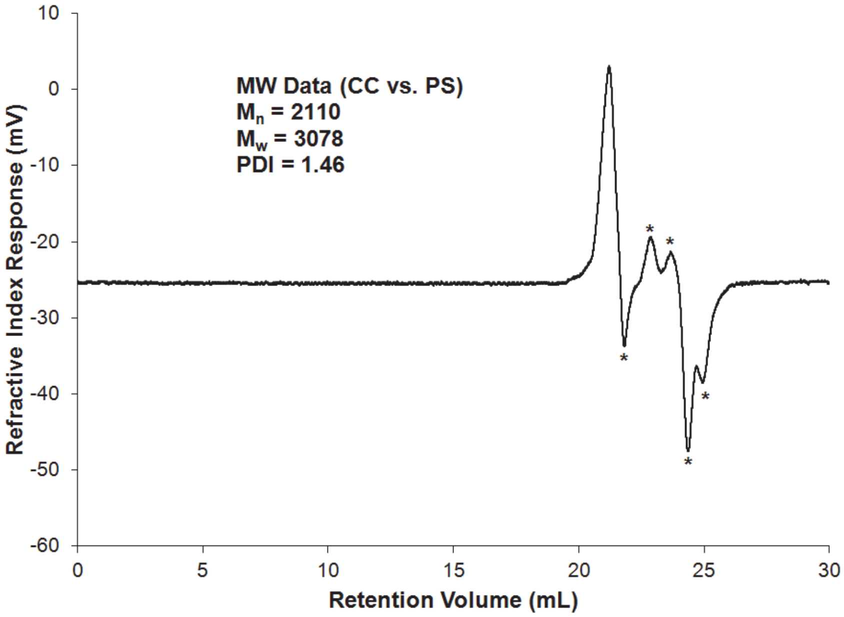

Figure S20. GPC trace of polymer **6a**$_x$ (*denotes fluctuations in RI associated with sample injections).

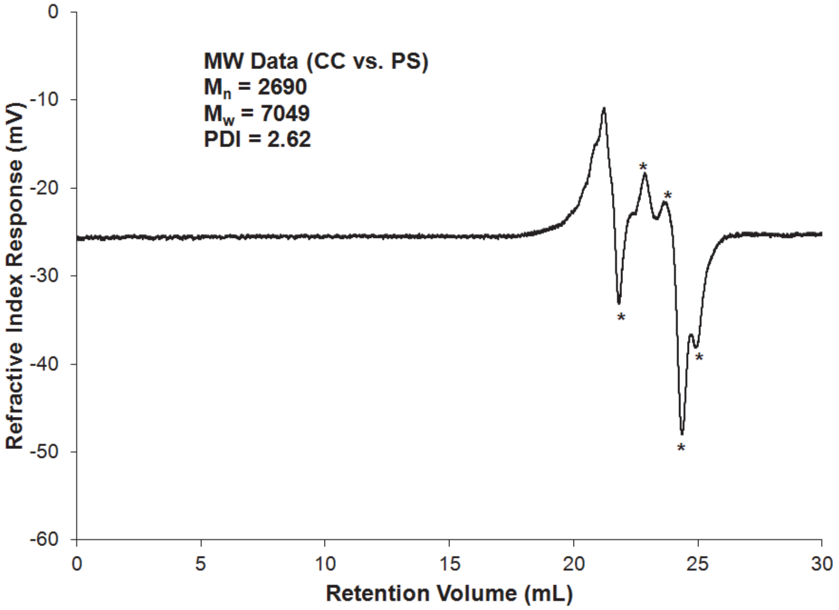

Figure S21. GPC trace of polymer **6b**$_x$ (*denotes fluctuations in RI associated with sample injections).

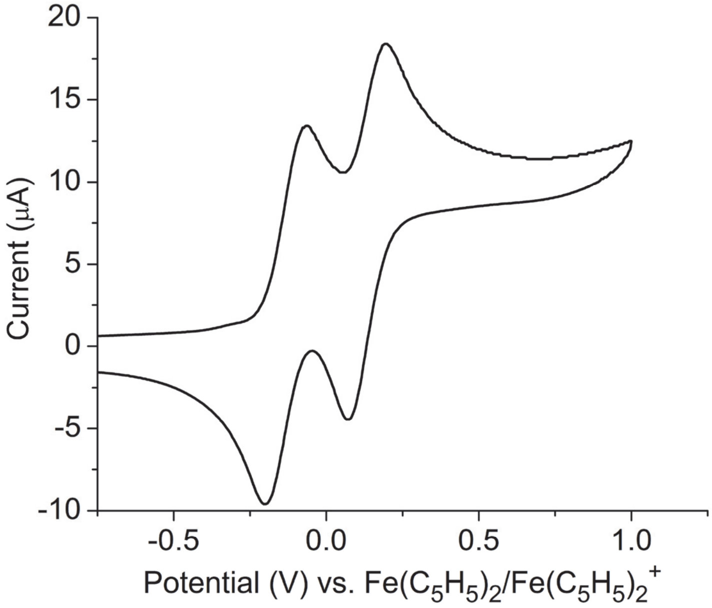

Figure S22. Cyclic voltammogram of **6a** (1 mM) in CH_2Cl_2 at 25 °C using NBu_4PF_6 (0.1 M) as supporting electrolyte using a scan rate of 50 mV/s. The measured E°′ for the two principal peaks is -0.134 and -0.133 V, respectively.

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