

Supplementary Information

**Reaction of alkyne with dinickel-diphenylsilyl complexes.
An emissive disilane formed via the consecutive Si–C and
Si–Si bond-making processes**

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General Procedure	S2
Table S1 Selected bond distances and angles of 1 , 2 and [$\{M(PCy_3)\}_2(\mu-HSiPh_2)_2$] (M = Pd, Pt)	S6
Table S2 Crystallographic data of 1-3	S7
Figure S1. 1H and $^{13}C\{^1H\}$ NMR spectra of 1	S8
Figure S2. 1H NMR spectrum of 2	S9
Figure S3. $^{29}Si\{^1H\}$ NMR spectra of 1 and 2	S9
Figure S4. 1H and $^{13}C\{^1H\}$ NMR spectra of 3	S10

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled glovebox (Miwa MFG). Hexane, toluene, and THF were purified by using Grubbs-type solvent purification system (Glass Contour).¹ Cyclohexane and ether were distilled from sodium/benzophenone and stored under nitrogen. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on JEOL JNM-500 MHz or Bruker Biospin Avance III 400 MHz NMR spectrometers. Chemical shifts in ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the residual peaks of the solvents used.² The peak positions of the $^{29}\text{Si}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external SiMe_4 (δ 0) and 85% H_3PO_4 (δ 0) in C_6D_6 or $\text{THF-}d_8$, respectively. Infrared absorption spectrum (IR) was recorded on a JASCO FTIR-4100 spectrometer. Elemental analyses were performed using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. Fast atom bombardment mass spectrometry (FAB-MS) was also performed using a JEOL JMS-700 MStation at the same center. Melting points were measured using a Yanaco MP-J3 apparatus and were uncorrected. $[\text{Ni}(\text{cod})_2]$, PCy_3 and 1,2-bis(dimethylphosphino)ethane (dmpe) (Sigma-Aldrich), H_2SiPh_2 and $\text{PhC}\equiv\text{CPh}$ (Tokyo Chemical Industry) were purchased and used as received.

Preparation of $[\{\text{Ni}(\text{dmpe})\}_2(\mu\text{-SiHPh}_2)_2]$ (1**).** To a toluene solution (15 mL) of $[\text{Ni}(\text{cod})_2]$ (172 mg, 0.63 mmol) and dmpe (120 μL , 0.72 mmol) were added H_2SiPh_2 (130 μL , 0.70 mmol). The reaction mixture was allowed to stir for 45 h at room temperature, resulting in the formation of orange slurry. The precipitate was collected by filtration, washed with hexane (5 mL \times 3) and dried under vacuum to give **1** (97 mg, 40%). The crystals for X-ray crystallography were obtained by recrystallization from a THF/cyclohexane mixed solvents (1:8). Anal. calcd for $\text{C}_{36}\text{H}_{54}\text{Ni}_2\text{P}_4\text{Si}_2$: C, 55.13; H, 6.94; found: C, 54.55; H, 6.82. ^1H NMR (400 MHz, C_6D_6 , rt): δ 7.84 (d, 8H, C_6H_5 *ortho*, $J_{\text{H-H}} = 6.0$ Hz), 7.27–7.21 (m, 12H, C_6H_5 *meta* and *para*), 1.23 (br, 8H, PCH_2), 0.83–0.88 (br, 24H, PCH_3), –4.02 (br m, 2H, NiHSi). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF-}d_8$, rt): δ 148.7 (apparent quintet, C_6H_5 *ipso*, $^3J_{\text{P-C}} = 4.0$ Hz), 134.3 (C_6H_5 *ortho*), 126.2 (C_6H_5 *para*), 126.0 (C_6H_5 *meta*), 32.2 (m, PCH_2), 20.0 (br, PCH_3), 17.0 (br, PCH_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, $\text{THF-}d_8$, rt): δ 113.6 (apparent quintet,

$^2J_{\text{P-Si}} = 20$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , rt): δ 8.31. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1579br (Si-H). FAB-HRMS calcd for $\text{C}_{36}\text{H}_{54}\text{Ni}_2\text{P}_4\text{Si}_2$: 782.1422 [M^+]; found: 782.1440.

Preparation of $[\{\text{Ni}(\text{PCy}_3)\}_2(\mu\text{-SiHPh}_2)_2]$ (2**).** To a hexane solution (30 mL) of $[\text{Ni}(\text{cod})_2]$ (1.74 g, 6.33 mmol) and PCy_3 (2.53 g, 9.02 mmol) was added H_2SiPh_2 (1.60 mL, 8.62 mmol). The reaction mixture was stirred at room temperature for 20 h, causing an orange precipitate from the red solution. The precipitate was collected by filtration, washed with hexane (20 mL \times 2) and dried under vacuum to give **2** (3.20 g, 97%) as an orange solid. The crystals suitable for X-ray crystallography were obtained by recrystallization from a THF/ether mixed solvent (1:8). Anal. calcd for $\text{C}_{60}\text{H}_{88}\text{Ni}_2\text{P}_2\text{Si}_2$: C, 68.97; H, 8.49; found: C, 66.86; H, 8.68. ^1H NMR (400 MHz, C_6D_6 , rt): δ 8.11 (d, 8H, C_6H_5 *ortho*, $J_{\text{H-H}} = 7.4$ Hz), 7.34 (t, 8H, C_6H_5 *meta*, $J_{\text{H-H}} = 7.4$ Hz), 7.22 (t, 4H, C_6H_5 *para*, $J_{\text{H-H}} = 7.4$ Hz), 1.86–1.76 (m, 18H, PC_6H_{11}), 1.51 (br, 18H, PC_6H_{11}), 1.30 (m, 12H, PC_6H_{11}), 0.99 (m, 18H, PC_6H_{11}), -2.04 (m, NiHSi , $J_{\text{P-H}} = 15$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , rt): δ 144.7 (C_6H_5 *ipso*), 136.8 (C_6H_5 *ortho*), 128.3 (C_6H_5 *meta*), 127.6 (C_6H_5 *para*), 36.8 (apparent triplet, PCH, $|J_{\text{P-C}} + ^4J_{\text{P-C}}| = 8.3$ Hz), 30.7 (PCHCH₂), 27.8 (apparent triplet, PCHCH₂CH₂, $J = 5.1$ Hz), 26.6 (PCHCH₂CH₂CH₂). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6 , rt): δ 121.8 (m, $^2J_{\text{P-Si}} = 25$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , rt): δ 45.9. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1590br (Si-H).

Conversion of **2 into **1** by addition of dmpe.** To a toluene solution (20 mL) of **2** (1.21 g, 1.16 mmol) was added dmpe (390 μL , 2.34 mmol) and then the mixture was stirred at room temperature for 16 h. The solution was evaporated under reduced pressure to give an orange residue, which was washed with hexane (9 mL \times 3) and dried under vacuum to give **1** (815 mg, 90%) as a red solid.

Reaction of **1 with $\text{PhC}\equiv\text{CPh}$.** To a mixture of complex **1** (204 mg, 0.26 mmol) and $\text{PhC}\equiv\text{CPh}$ (196 mg, 1.10 mmol) was added 5 mL of toluene, followed by stirring at 60 °C for 22 h. The reaction solution was diluted in CH_2Cl_2 (20 mL) and filtered through Florisil to remove decomposition products. The solvent was evaporated under reduced pressure to give a yellow oil. The crude product was purified by a column chromatography on silica gel (eluent: CH_2Cl_2 /hexane = 1:10, $R_f = 0.18$), followed by recrystallization from toluene/hexane (1:7) to give 1,2-bis{(E)-1,2-diphenylethenyl}-1,1,2,2-tetraphenyldisilane (**3**: 80 mg, 43%) as colorless crystals. The NMR spectroscopic data of the reaction mixture before purification displayed almost complete

conversion into **3** and $[\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{dmpe})]_3$ (**4**). To isolate the Ni complex from the mixture, the solvent was removed under reduced pressure. The crude product was washed with hexane (2 mL \times 2) and recrystallized repeatedly with toluene/hexane (10:3) to give **4** as pale yellow solid (2.9 mg, 6%).

Data for **3**. Anal. calcd for $\text{C}_{52}\text{H}_{42}\text{Si}_2$: C, 86.38; H, 5.85; found: C, 86.34; H, 5.79. ^1H NMR (400 MHz, THF- d_8 , rt): δ 7.44 (d, 8H, SiC_6H_5 *ortho*, $J_{\text{H-H}} = 7.0$ Hz), 7.29 (t, 4H, SiC_6H_5 *para*, $J_{\text{H-H}} = 7.1$ Hz), 7.17 (t, 10H, C_6H_5 *meta* and $=\text{CH}$, $J_{\text{H-H}} = 6.9$ Hz), 7.01 (m, 6H, $=\text{CC}_6\text{H}_5$ *para* and *meta*), 6.91 (br, 6H, $=\text{CC}_6\text{H}_5$ *para* and *meta*), 6.78 (m, 8H, $=\text{CC}_6\text{H}_5$ *ortho*). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , rt): δ 145.2 ($=\text{CH}$), 142.5 ($=\text{CC}_6\text{H}_5$ *ipso*), 142.0 ($=\text{CSi}$), 138.0 ($=\text{CC}_6\text{H}_5$ *ipso*), 137.5 (SiC_6H_5 *ortho*), 135.6 (SiC_6H_5 *ipso*), 130.2 (SiC_6H_5 *para*), 129.7 ($=\text{CC}_6\text{H}_5$ *ortho*), 129.1 ($=\text{CC}_6\text{H}_5$ *meta*), 128.7 ($=\text{CC}_6\text{H}_5$ *ortho*), 128.4 ($=\text{CC}_6\text{H}_5$ *meta*), 128.2 (SiC_6H_5 *meta*), 127.9 ($=\text{CC}_6\text{H}_5$ *para*), 126.3 ($=\text{CC}_6\text{H}_5$ *para*).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6 , rt): δ -20.3. mp 171–173 °C. Data for **4**: ^1H NMR (400 MHz, THF- d_8 , rt): δ 7.48 (d, 4H, C_6H_5 *ortho*, $J_{\text{H-H}} = 6.8$ Hz), 7.21 (t, 4H, C_6H_5 *meta*, $J_{\text{H-H}} = 7.6$ Hz), 7.04 (t, 2H, C_6H_5 *para*, $J_{\text{H-H}} = 7.4$ Hz), 1.64 (m, 4H, PCH_2 , $J_{\text{P-H}} = 13$ Hz), 1.42 (apparent triplet, 12H, PCH_3 , $J_{\text{P-H}} = 3.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , rt): δ 138.2 (apparent triplet, C_6H_5 *ipso*, $^3J_{\text{P-C}} = 8.9$ Hz), 137.6 (d, $\equiv\text{CC}_6\text{H}_5$, $^2J_{\text{P-C}} = 13$ Hz), 129.3 (C_6H_5 *ortho*), 128.3 (C_6H_5 *meta*), 125.2 (C_6H_5 *para*), 30.3 (apparent triplet, PCH_2 , $|J_{\text{P-C}} + ^2J_{\text{P-C}}| = 22$ Hz), 15.6 (apparent triplet, PCH_3 , $|J_{\text{P-C}} + ^3J_{\text{P-C}}| = 11$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF- d_8 , rt): δ 22.5.

Cyclotrimerization of $\text{PhC}\equiv\text{CPh}$ catalyzed by **2.** To a toluene solution (5 mL) of $\text{PhC}\equiv\text{CPh}$ (56.3 mg, 0.32 mmol) was added catalytic amount of **2** (16.5 mg, 16 μmol). The reaction mixture was then stirred at 60 °C for 16 h. The reaction solution was diluted in CH_2Cl_2 (20 mL) and filtered through Florisil to remove decomposition products. The solvent was removed under vacuum to give pure hexaphenylbenzene (54.2 mg, 96 %). The ^1H NMR data of the product is consistent with that of the literature.⁴ A similar reaction of $\text{PhC}\equiv\text{CPh}$ (5.1 mg, 29 μmol) with **2** (7.5 mg, 7.2 μmol) in 4:1 ratio in C_6D_6 (0.6 mL) was performed at 60 °C for 9 h in an NMR sample tube. The ^1H NMR analysis of the reaction solution revealed the quantitative conversion of $\text{PhC}\equiv\text{CPh}$ into hexaphenylbenzene.

Crystallographic data. Single crystals of **1**, **2** and **3** suitable for X-ray diffraction study were mounted on MicroMounts (MiTeGen). The crystallographic data of **1**, **2** and **3** were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) at

113 K. Calculations were carried out using the program package Crystal Structure, version 4.0, for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F_2 by the full-matrix least-squares method using SHELXL-97.⁵ Hydrogen atoms, except for the bridging SiH hydrogens of **1** and **2**, were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. The bridging SiH hydrogens (H1) of **1** were found from the Fourier-difference electron-density and refined isotropically. Results of **1** contained severe disorder of the solvent molecule. Although the solvent molecule was calculated as cyclohexane, it would be also possible to involve THF or C₆D₆ molecules as the crystal solvent. The efforts to improve it were not successful. The bridging SiH hydrogens (H1) of **2** were found from the Fourier-difference electron-density and fixed. Results of complex **2** contained large range of U_{eq} values for hydrogens (Alert B by checkcif). High R_{int} and wR_2 values of **3** are attributed to the small number of diffraction due to poor quality of the crystals. Selected Bond Distances (Å) and Angles (deg) of **1**, **2** and $[\{M(PCy_3)\}_2(\mu-HSiPh_2)_2]$ (M = Pd,⁶ Pt⁷) are listed in Table S1. Crystallographic data and details of refinement of **1**, **2** and **3** are summarized in Table S2.

References

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Table S1. Selected Bond Distances (Å) and Angles (deg) of **1**, **2** and

$[\{M(PCy_3)\}_2(\mu\text{-HSiPh}_2)_2]$ (M = Pd, Pt)

	1	2	$[\{Pd(PCy_3)\}_2(\mu\text{-HSiPh}_2)_2]$	$[\{Pt(PCy_3)\}_2(\mu\text{-HSiPh}_2)_2]$
M–M	2.6417(5)	2.495(1)	2.691(1)	2.6985(3)
M–Si	2.2175(8)	2.215(2)	2.326(2)	2.326(2)
M–Si*	2.2402(8)	2.249(2)	2.384(2)	2.385(2)
M–P	2.1751(7)	2.173(2)	2.316(2)	2.268(2)
	2.2414(9)			
M–H	1.56(3)	1.415(1)	1.61	1.94(8)
Si*–H	1.69(2)	1.616(2)	1.63	1.88(7)
Si–M–Si*	107.32(3)	112.04(7)	110.32(7)	110.13(7)
M–Si–M*	72.68(3)	67.96(6)	69.68(7)	69.87(5)

Table S2. Crystallographic Data and Details of Refinement of **1**, **2** and **3**

	1 ·C ₆ H ₁₂	2	3
formula	C ₄₂ H ₆₆ Ni ₂ P ₄ Si ₂	C ₆₀ H ₈₈ Ni ₂ P ₂ Si ₂	C ₅₂ H ₄₂ Si ₂
fw	868.45	1044.87	723.07
cryst size/mm	0.11×0.15×0.21	0.15×0.20×0.20	0.25×0.28×0.32
cryst syst	monoclinic	monoclinic	monoclinic
cryst color	red	red	yellow
space group	<i>P</i> 2 ₁ / <i>n</i> (<i>No.</i> 14)	<i>P</i> 2 ₁ / <i>c</i> (<i>No.</i> 14)	<i>P</i> 2 ₁ / <i>c</i> (<i>No.</i> 14)
<i>a</i> /Å	12.421(2)	10.228(2)	21.774(9)
<i>b</i> /Å	13.104(3)	13.576(3)	9.170(3)
<i>c</i> /Å	14.176(3)	20.026(4)	22.267(8)
<i>β</i> /deg	111.783(2)	91.961(3)	113.51(1)
<i>V</i> /Å ³	2142.6(7)	2779.2(9)	4077(3)
<i>Z</i>	2	2	4
<i>D</i> _{calcd} /g cm ⁻³	1.346	1.249	1.178
<i>F</i> (000)	924	1124	1528
<i>μ</i> /mm ⁻¹	1.1131	8.150	0.1219
2 θ range, deg			
no. of reflns meads	17196	22419	28141
no. of unique reflns	4905	6363	8990
<i>R</i> _{int}	0.0541	0.1036	0.2416
no. of obsd reflns (<i>I</i> > 2 σ (<i>I</i>))	3288	3470	2845
no. of variables	230	302	487
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0333, 0.0455	0.0614, 0.1333	0.1204, 0.2638
<i>R</i> 1, <i>wR</i> 2 (<i>all data</i>)	0.0455, 0.0936	0.1376, 0.2409	0.2451, 0.3489
GOF on <i>F</i> ²	0.949	0.992	0.950

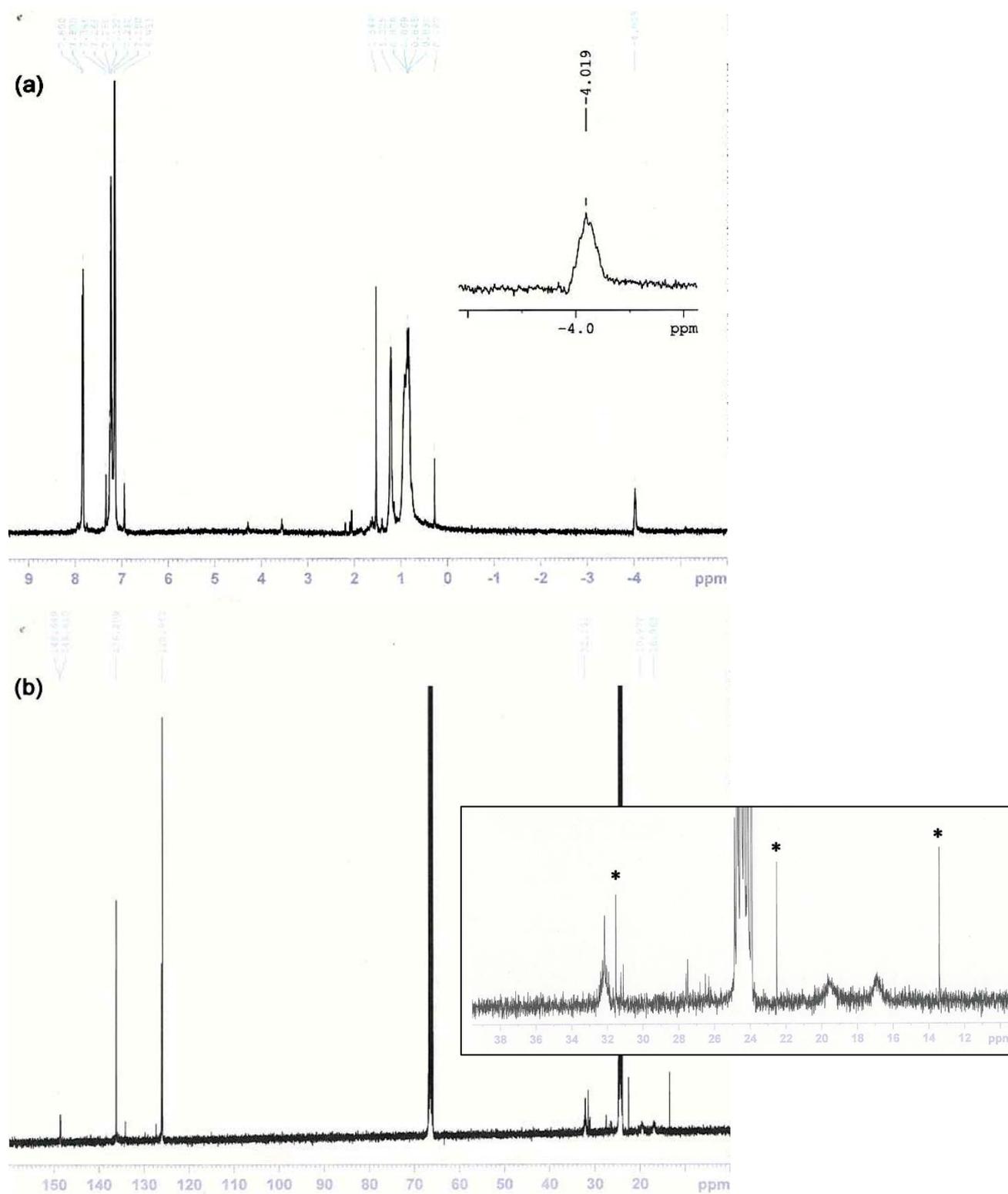


Figure S1. (a) ^1H NMR spectrum of **1** in C_6D_6 and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in $\text{THF-}d_8$.
(* = hexane)

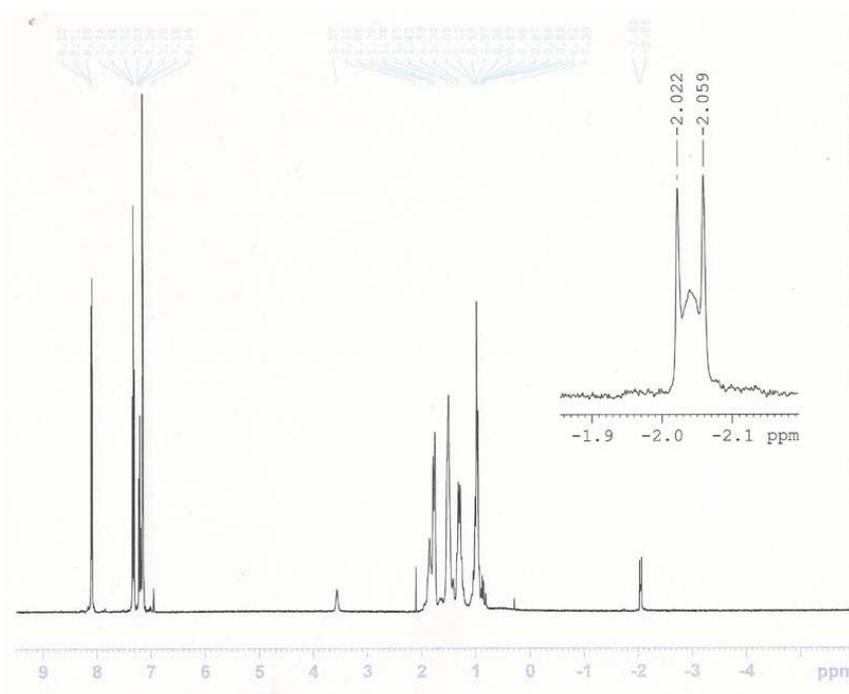


Figure S2. ^1H NMR spectrum of **2** in C_6D_6 .

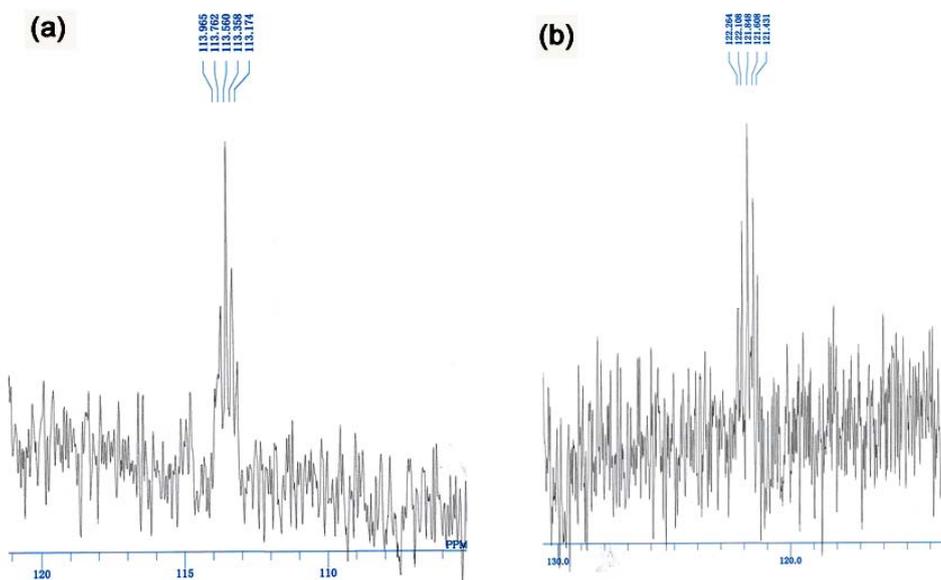


Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of (a) **1** in $\text{THF-}d_8$ and (b) **2** in C_6D_6 .

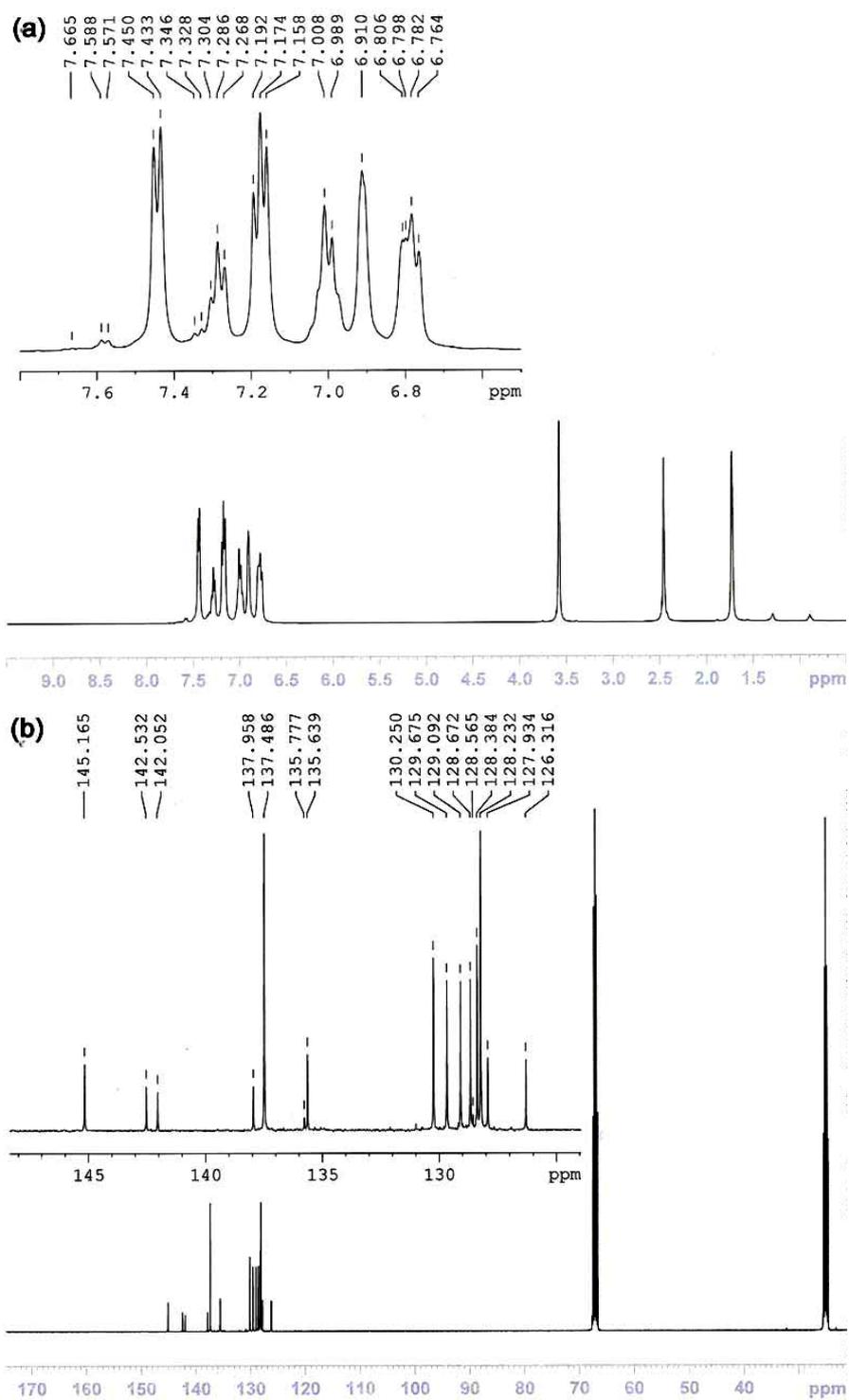


Figure S4. (a) ^1H and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3** in $\text{THF-}d_8$.