Supporting Information

Selective Hydrosiloxane Synthesis via Dehydrogenative Coupling of Silanols with Hydrosilanes Catalyzed by Fe Complexes Bearing a Tetradentate PNNP Ligand

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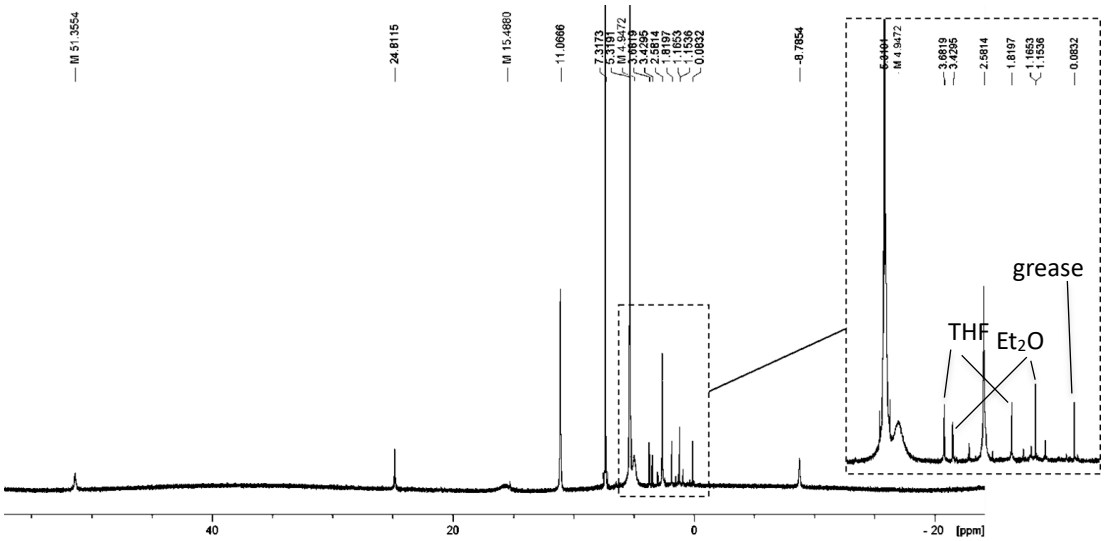
Contents

Compound characterization data

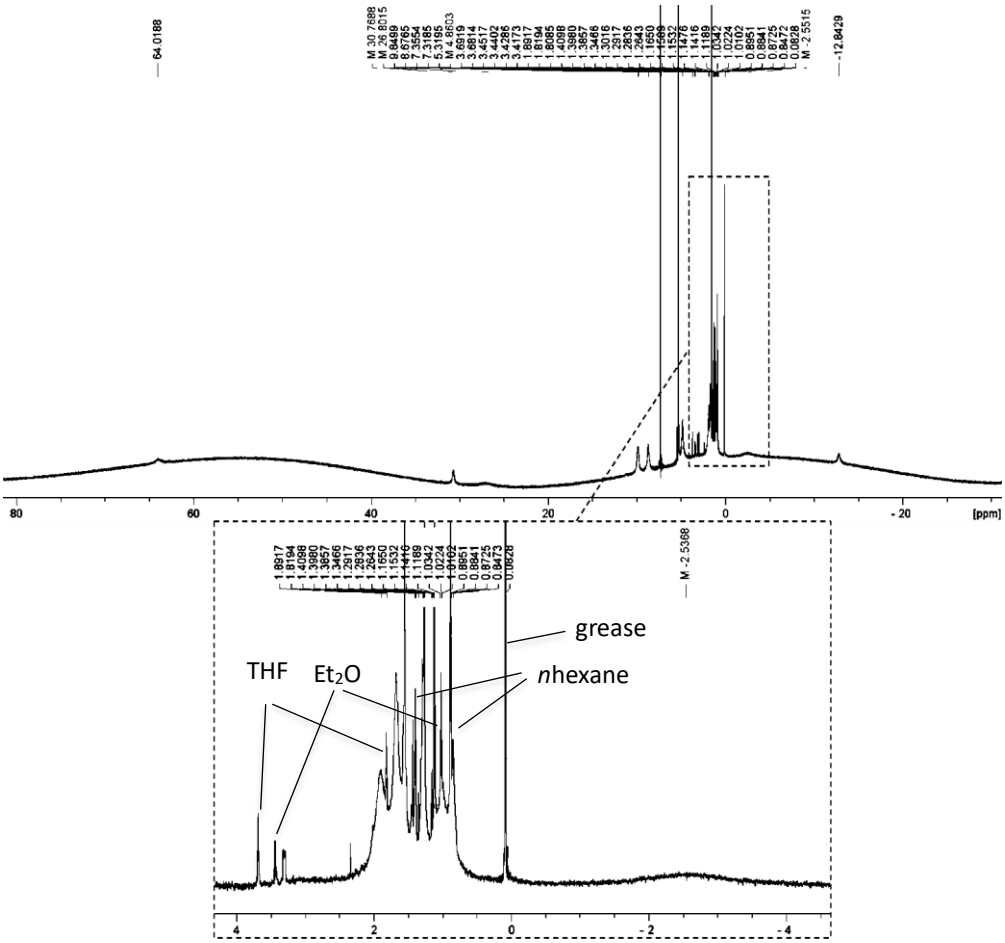
[$FeCl_2$(PNNP-Ph)] (1a)

^{1}H NMR:



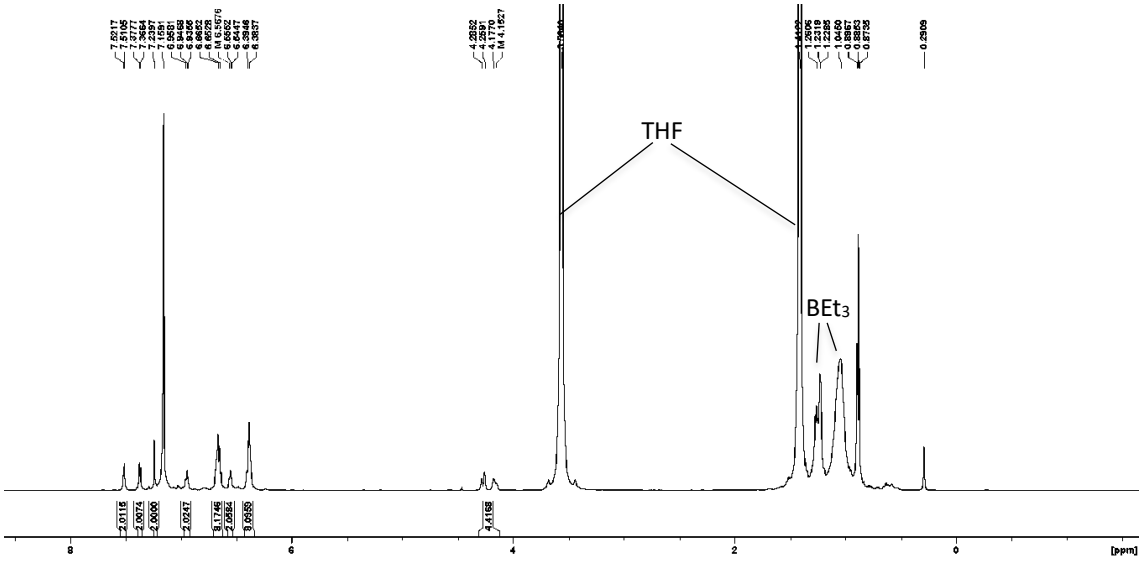
[$FeBr_2$(PNNP-Cy)] (1b)

^{1}H NMR:

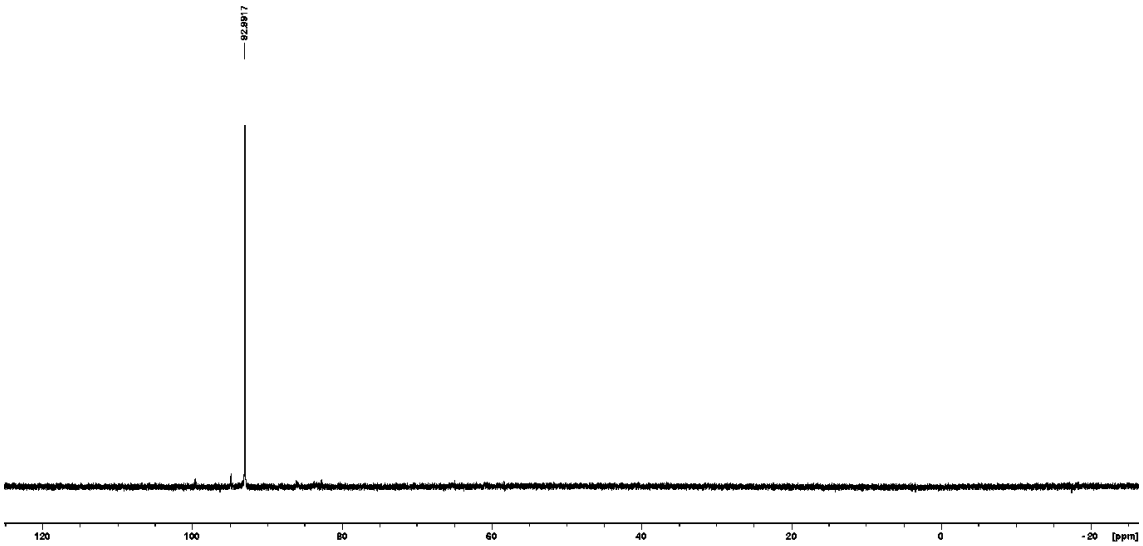


[Fe(PNNP-Ph)]$_2$(μ-N$_2$) (2a)

^{1}H NMR:

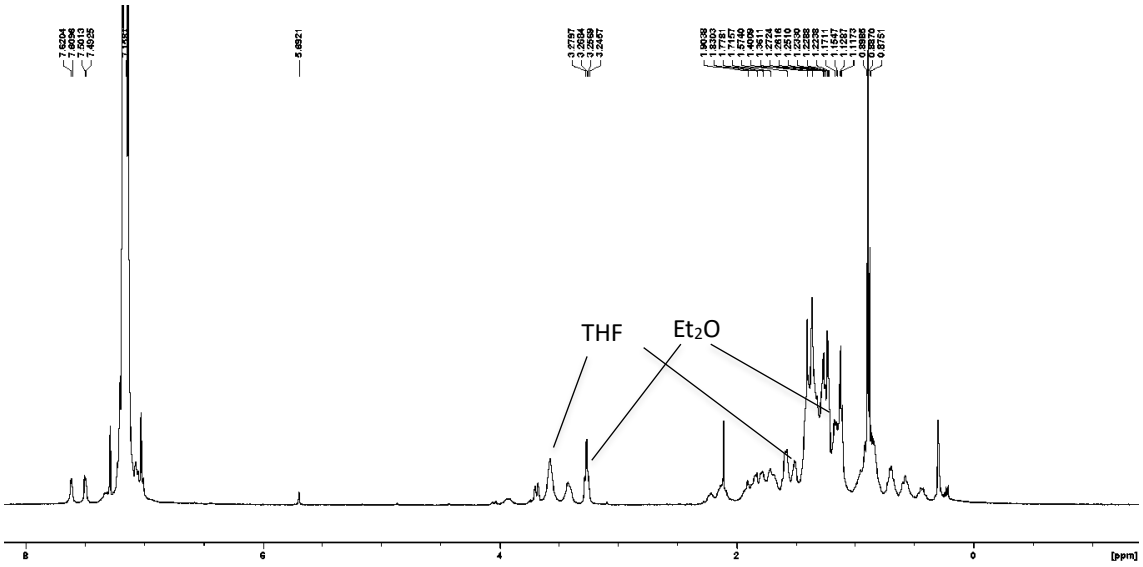


^{31}P{^{1}H} NMR:

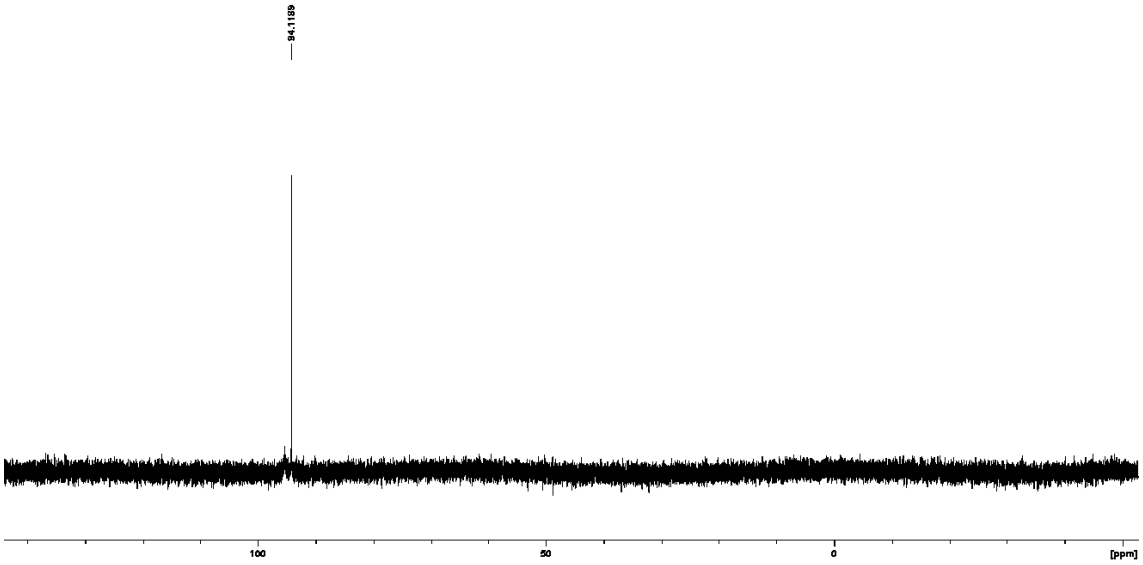


[Fe(PNNP-Cy)]$_2$(μ-N$_2$) (2b)

^{1}H NMR:

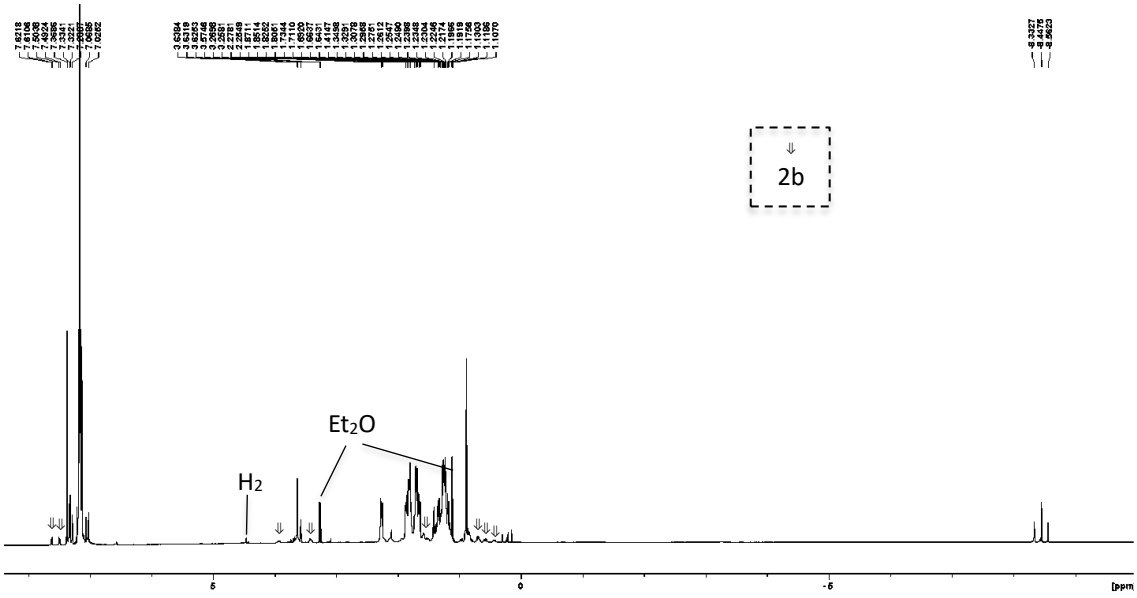


^{31}P{^{1}H} NMR:

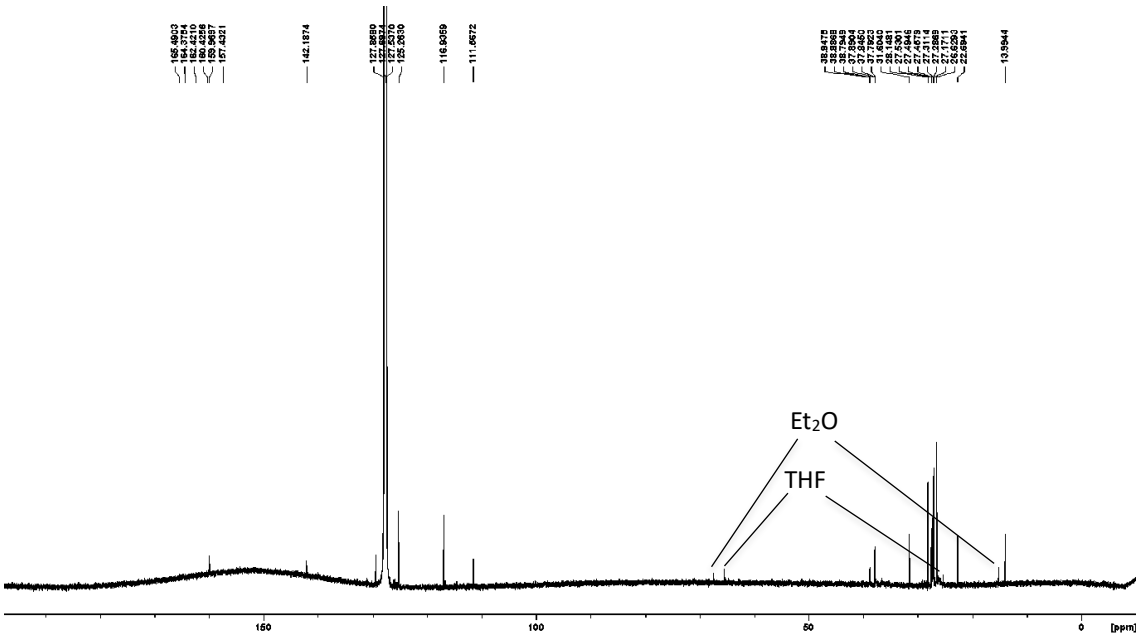


[Fe(H)$_2$(PNNP-Cy)] (3b)

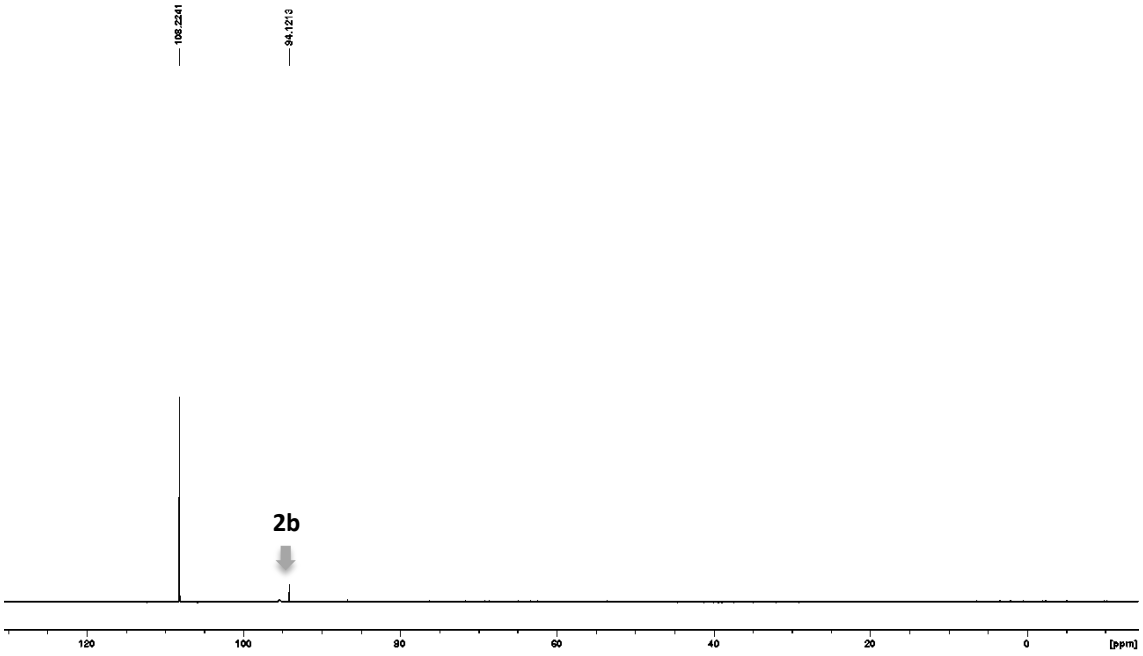
^{1}H NMR:



^{13}C{^{1}H} NMR:

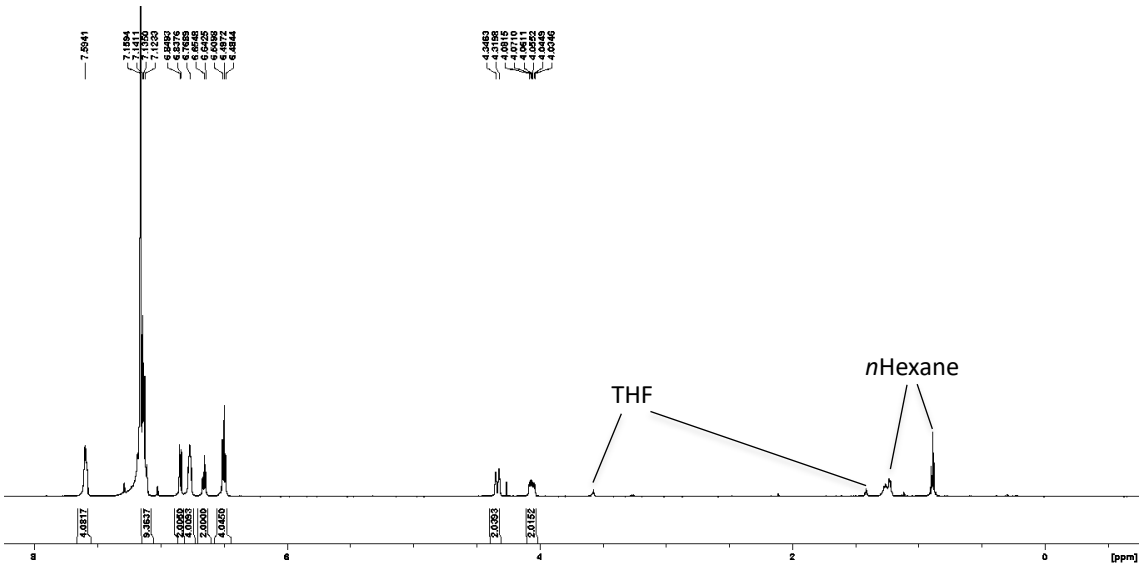


$^{31}P\{^{1}H\}$ NMR:

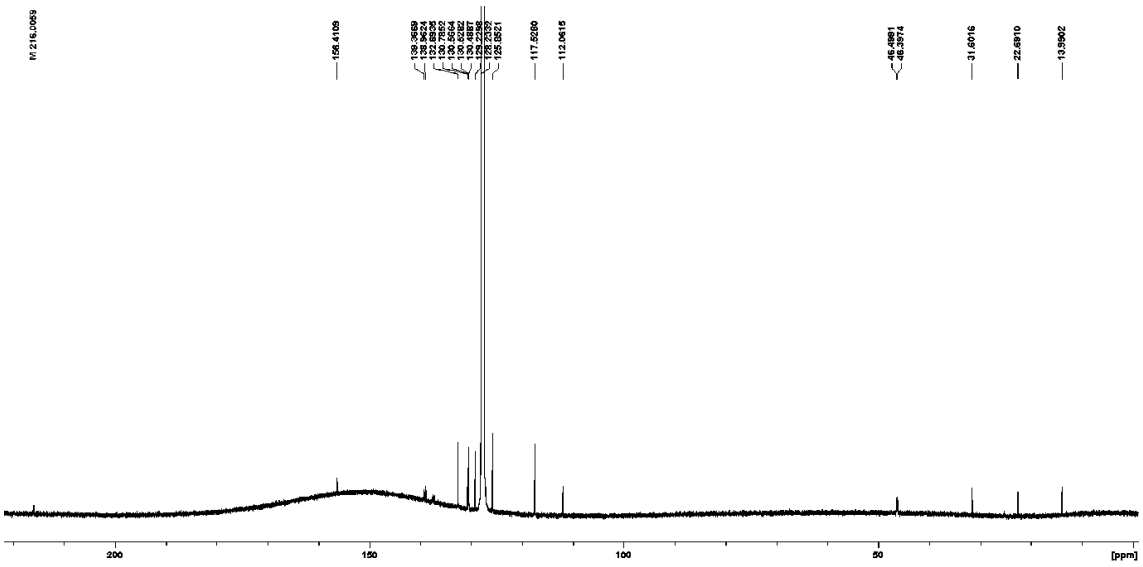


[Fe(PNNP-Ph)(CO)] (4a)

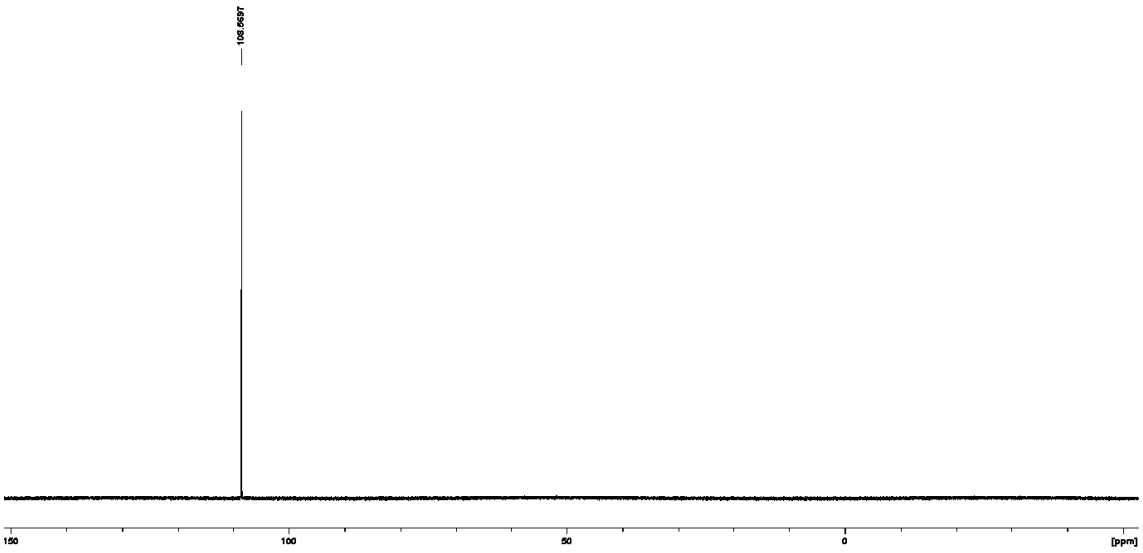
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:

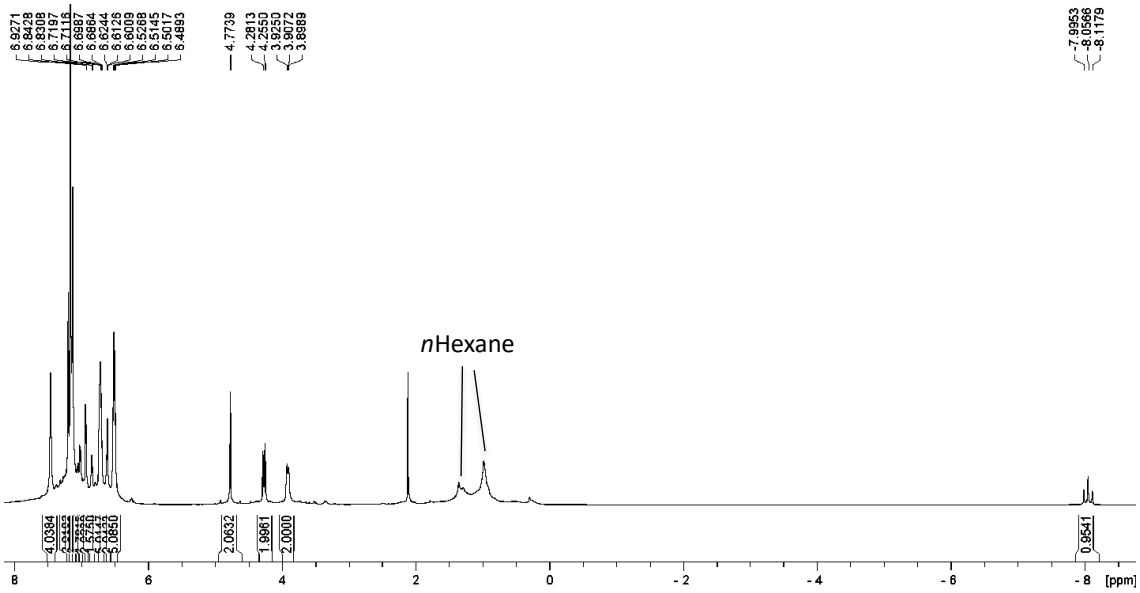


$^{31}P\{^{1}H\}$ NMR:

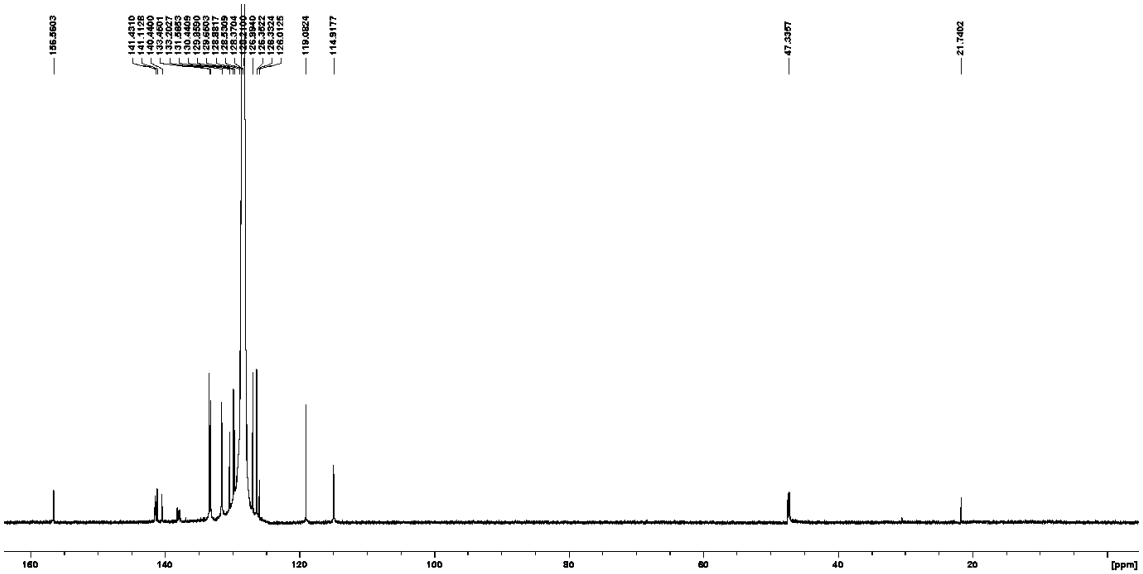


[Fe(η^2-HSiH$_2$Ph)(PNNP-Ph)] (5a)

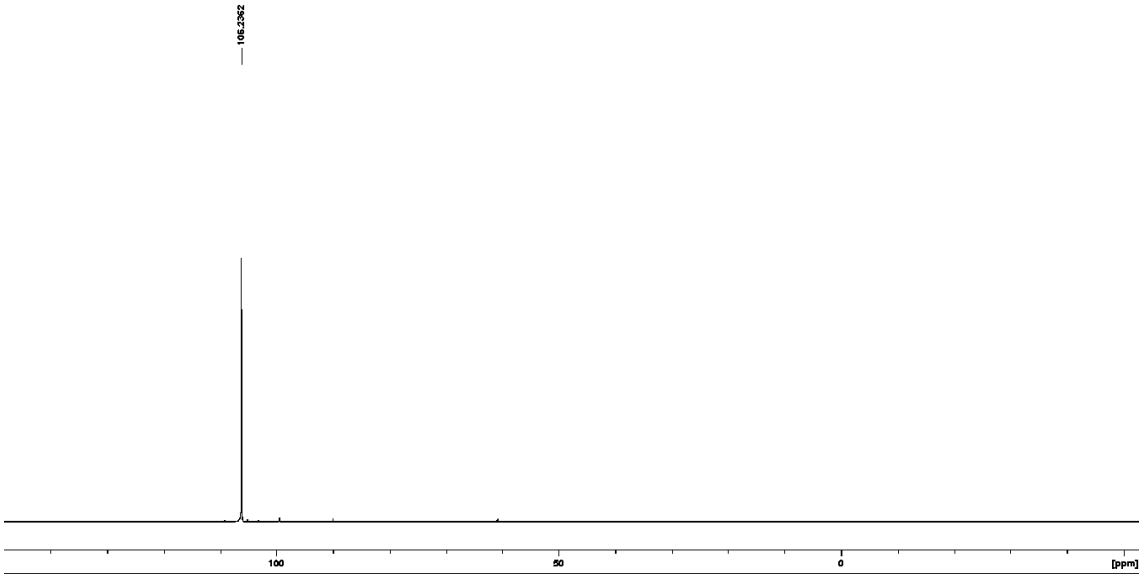
^{1}H NMR:



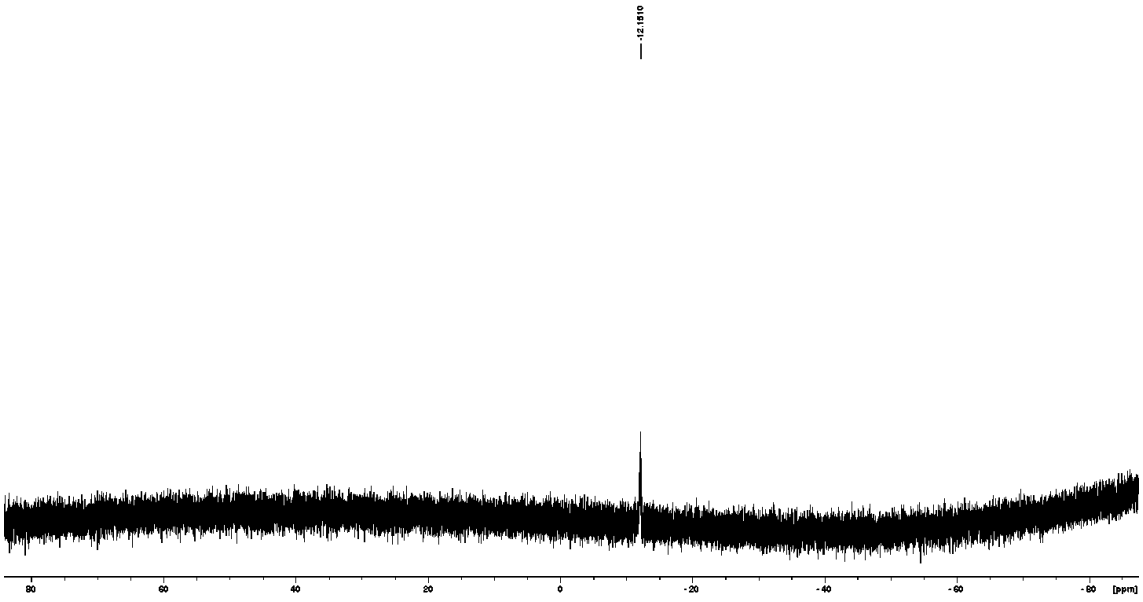
^{13}C{^{1}H} NMR:



$^{31}P\{^{1}H\}$ NMR:



$^{29}Si\{^{1}H\}$ NMR:



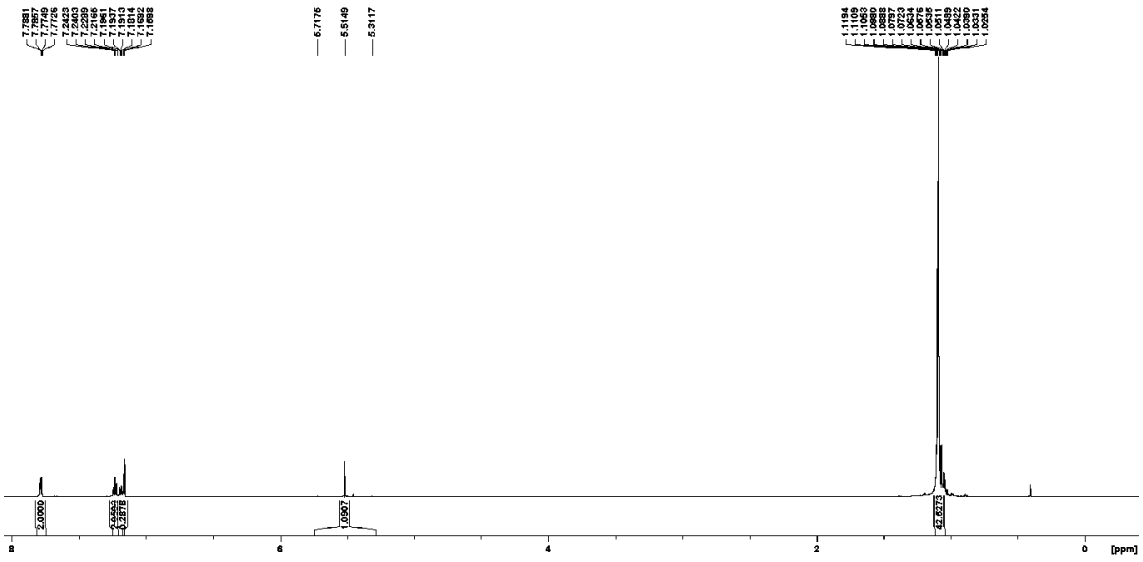
Compounds characterization data of hydrosiloxanes

The final product was characterized by ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR as well as HRMS. $(Me_3SiO)(SiH_2Ph)$,[1] $(Me_3SiO)_2(SiHPh)$,[1,2] $((tBuO)_3SiO)(SiH_2Ph)$,[1] $(Me_3SiO)(SiHPh_2)$[3] and $(Me_3SiO)(SiHPhMe)$[2] were identified by comparing their ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR data with those previously reported. 4-Methylphenylsilane[4] was synthesized by following the reported procedures.

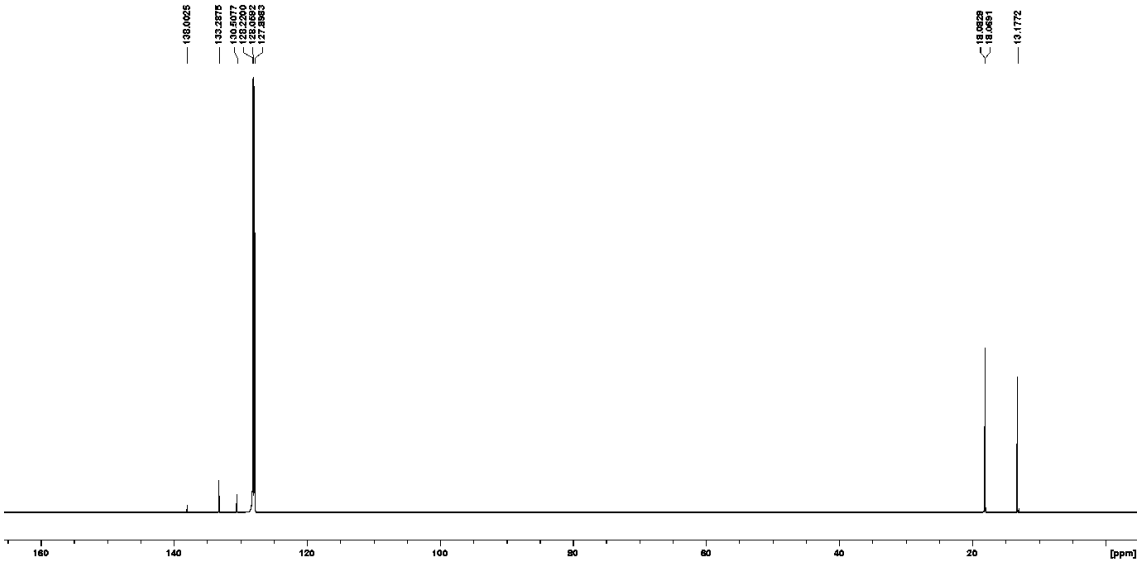
$(iPr_3SiO)_2(SiHPh)$ Using $PhSiH_3$ (32.4 mg, 0.30 mmol) and iPr_3SiOH (108.1 mg, 0.62 mmol). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): δ 7.72 (d, 2H, J = 1.50 Hz, Ar-*H*), 7.21-7.18 (m, 3H, Ar-*H*), 5.39 (s, 1H, $^{1}J_{SiH}$ = 246.6 Hz), 0.98-0.89 (m, 42H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6, 25 °C): δ 137.6, 132.8, 130.1, 128.1, 17.7, 12.8 ppm. $^{29}Si\{^{1}H\}$ NMR (119 MHz, C_6D_6, 25 °C): δ 9.5, –49.2 ppm.

HRMS (ESI): m/z calcd for $[C_{23}H_{48}O_2Si_3H]^+$ (M+H): 453.3040 ; found 453.3029.

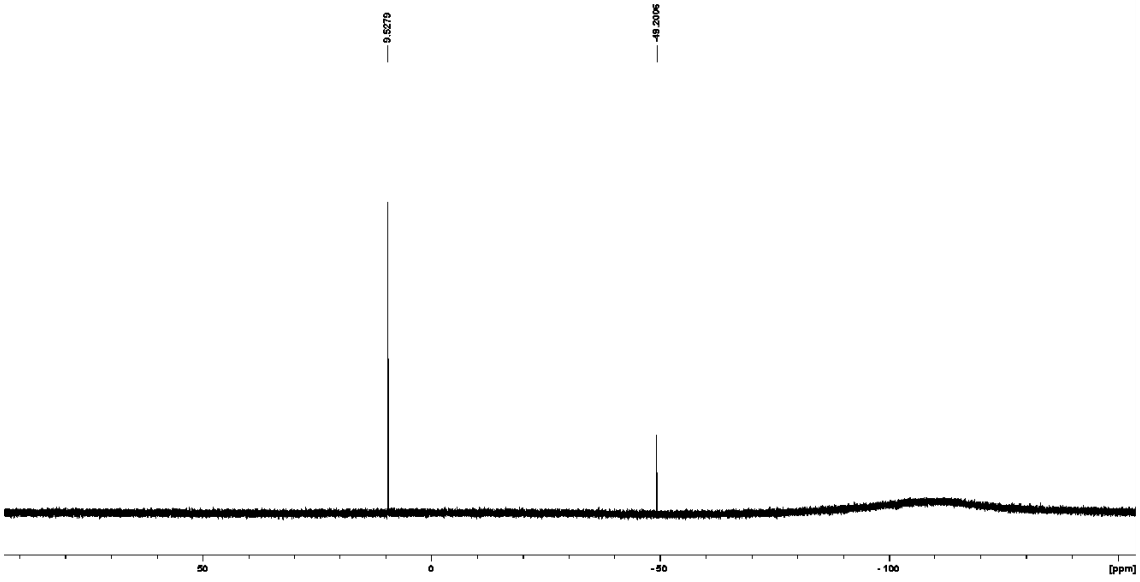
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:



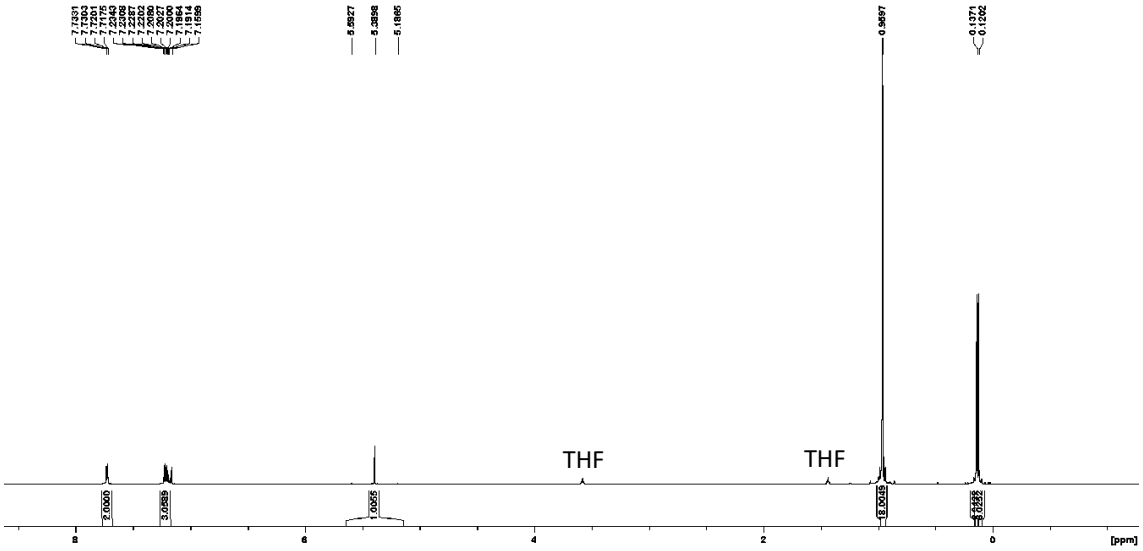
$^{29}Si\{^{1}H\}$ NMR:



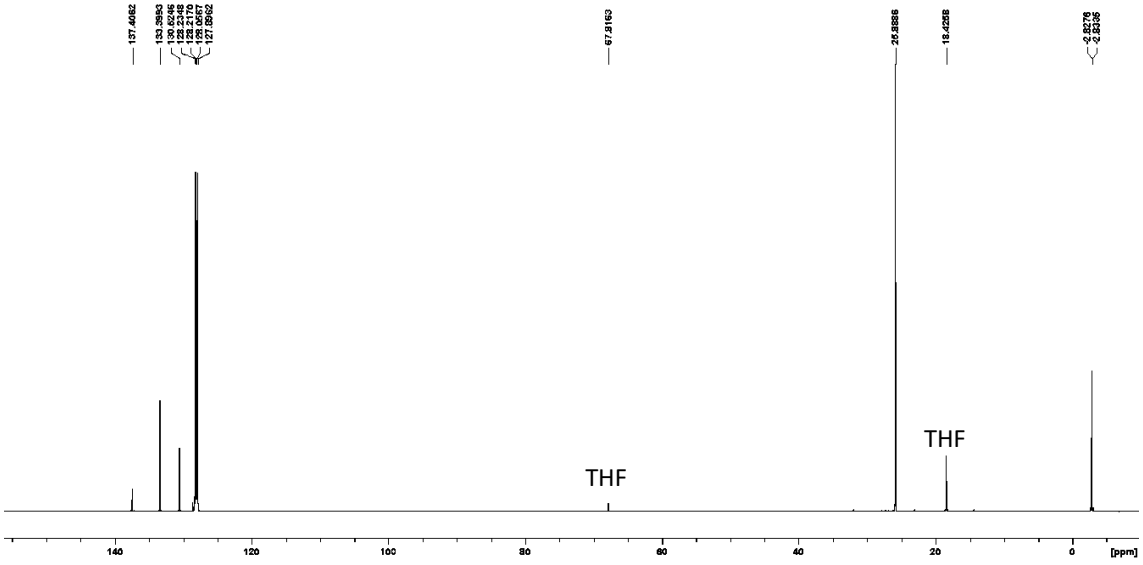
(tBuMe$_2$SiO)$_2$(SiHPh) Using $PhSiH_3$ (32.4 mg, 0.30 mmol) and tBuMe$_2$SiOH (108.1 mg, 0.62 mmol). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): δ 7.73 (dd, 2H, J = 7.74, 1.62 Hz, Ar-*H*), 7.23-7.19 (m, 3H, Ar-*H*), 5.39 (s, 1H, $^{1}J_{Si,\,H}$ = 243.8 Hz, Si*H*), 0.96 (s, 18H), 0.14 (s, 6H), 0.12 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6, 25 °C): δ 137.4, 133.4, 130.5, 128.2, 25.9, 18.4, –2.8 ppm. $^{29}Si\{^{1}H\}$ NMR (119 MHz, C_6D_6, 25 °C): δ 13.2, –48.5 ppm.

HRMS (ESI): m/z calcd for $[C_{18}H_{36}O_2Si_3H]^+$ (M+H): 369.2101 ; found 369.2111.

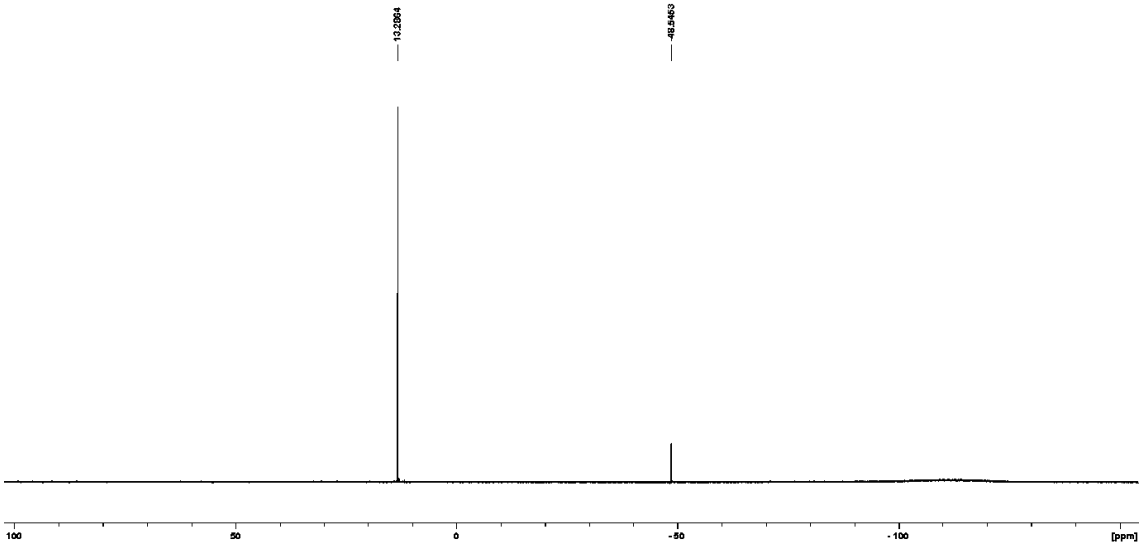
^{1}H NMR:



^{13}C{^{1}H} NMR:



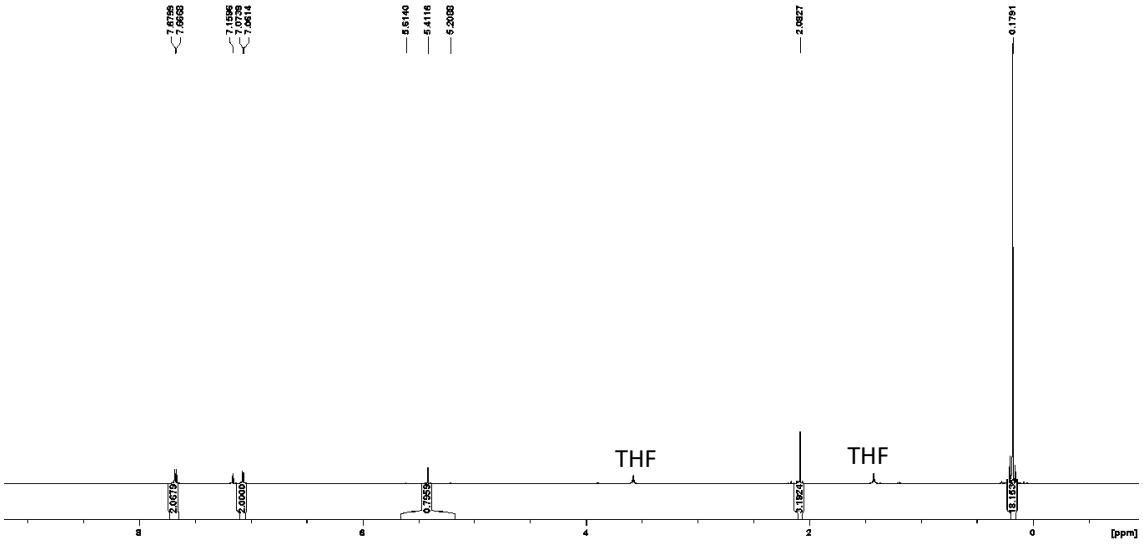
$^{29}Si\{^{1}H\}$ NMR:



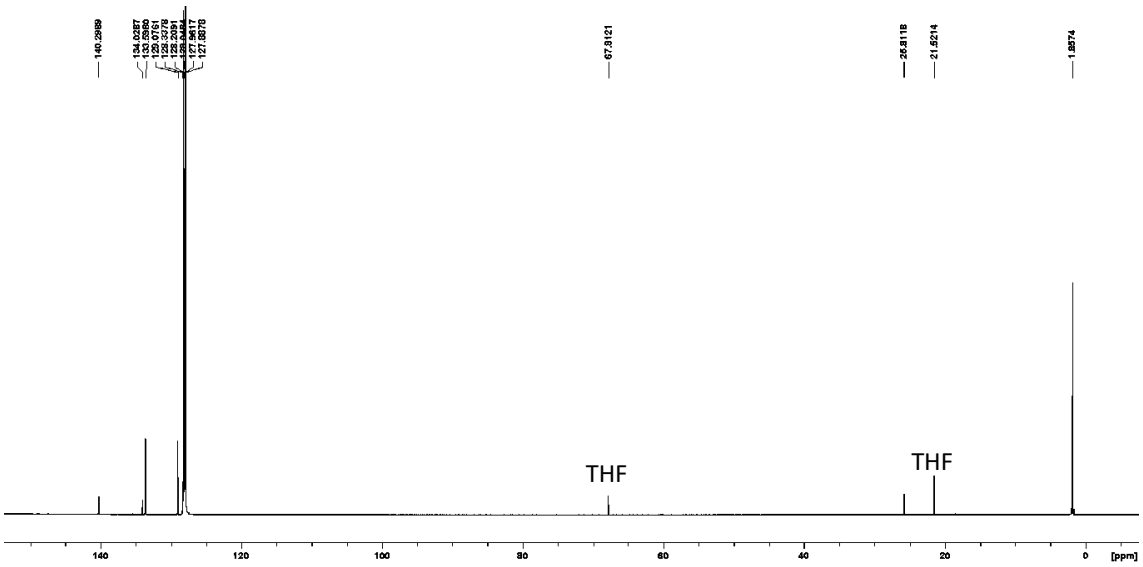
$(Me_3SiO)_2(SiHTol)$ Using $TolSiH_3$ (36.6 mg, 0.30 mmol) and Me_3SiOH (56.1 mg, 0.62 mmol). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): δ 7.67 (d, 2H, *J* = 7.87, Ar-*H*), 7.07 (d, 2H, *J* = 7.07, Ar-*H*), 5.41(s, 1H, $^{1}J_{Si,\,H}$ = 243.3 Hz, Si*H*), 2.08 (s, 3H, PhC*H*$_3$), 0.17 (s, 18H, Si(C*H*$_3$)$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6, 25 °C): δ 139.9, 133.6, 133.2, 128.7, 25.4, 1.5 ppm. $^{29}Si\{^{1}H\}$ NMR (119 MHz, C_6D_6, 25 °C): δ 10.2, –48.1 ppm.

HRMS (ESI): m/z calcd for $[C_{18}H_{36}O_2Si_3H]^+$ (M+H): 369.2101 ; found 369.2111.

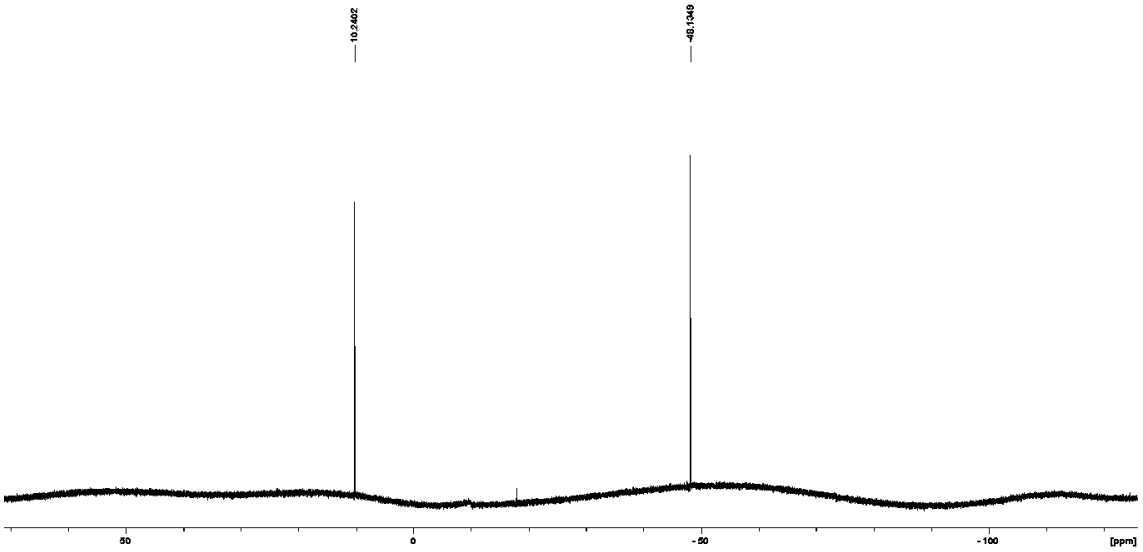
^{1}H NMR:



$^{13}C\{^{1}H\}$ NMR:

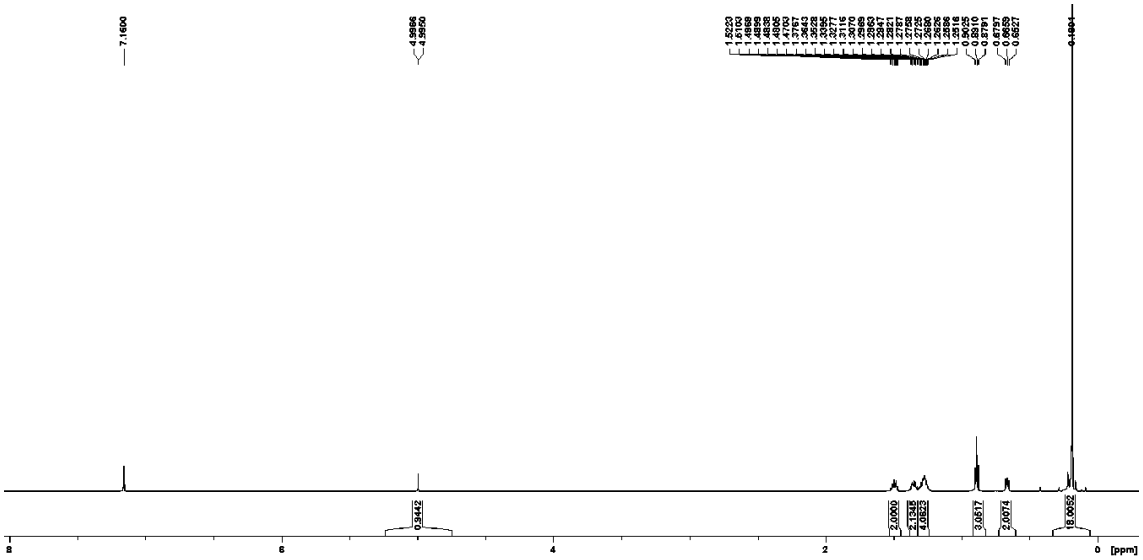


$^{29}Si\{^{1}H\}$ NMR:

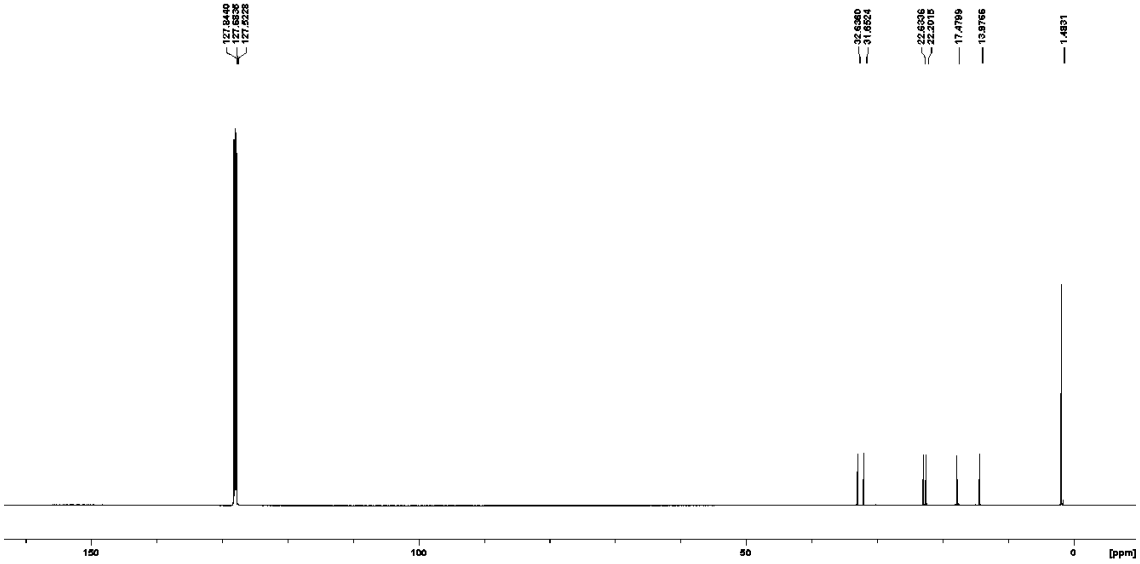


($Me_3SiO)_2(SiHnHex)$ Using *n*$HexSiH_3$ (34.8 mg, 0.30 mmol) and Me_3SiOH (56.0 mg, 0.62 mmol). ^1H NMR (600 MHz, C_6D_6, 25 °C): δ 5.0 (s, 1H, $^1J_{Si,H}$ = 232.4 Hz, Si*H*), 1.50 (quin, 2H, *J* = 7.80, $SiCH_2CH_2$), 1.35 (quin, 2H, *J* = 7.35, $SiCH_2CH_2CH_2$), 1.32-1.23 (m, 4H, CH_2CH_2CH3), 0.89 (t, 3H, *J* = 7.02, CH_3), 0.66 (t, 2H, *J* = 8.01, $SiCH_2$), 0.19 (s, 18H, $Si(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 25 °C): δ 32.6, 31.7, 22.6, 22.2, 17.5, 14.0, 1.5 ppm. $^{29}Si\{^1H\}$ NMR (119 MHz, C_6D_6, 25 °C): δ 9.00, –36.0 ppm.
HRMS (ESI): m/z calcd for $[C_{12}H_{32}O_2Si_3H]^+$ (M+H): 293.1788 ; found 293.1787.

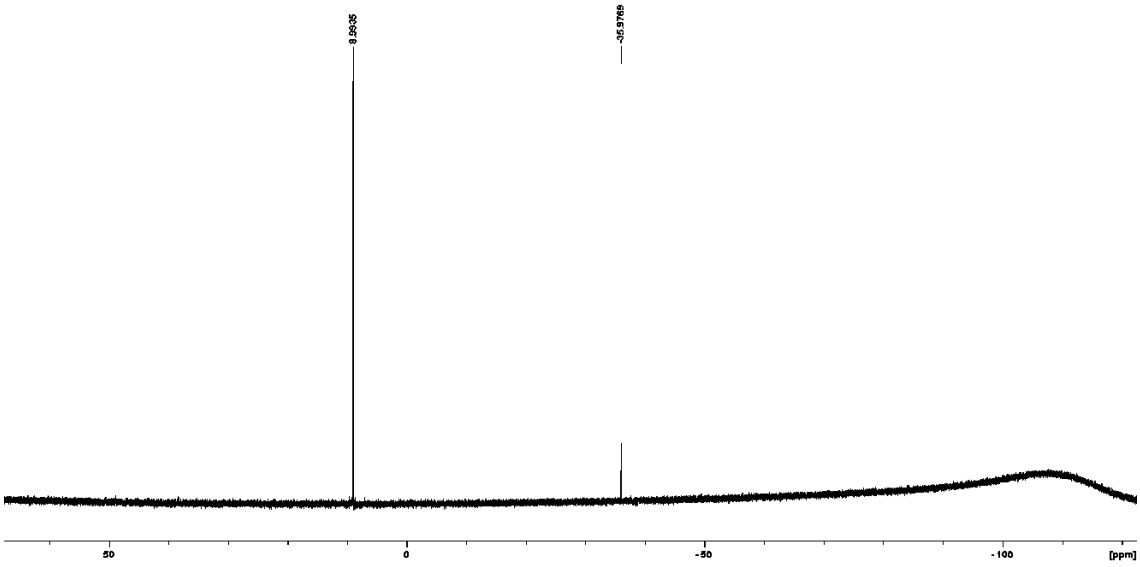
^1H NMR



$^{13}C\{^{1}H\}$ NMR:



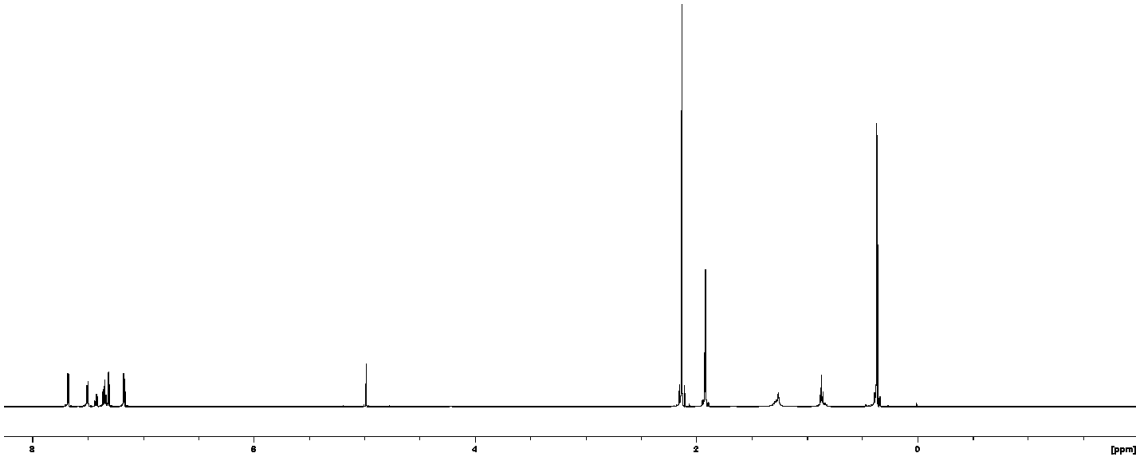
$^{29}Si\{^{1}H\}$ NMR:



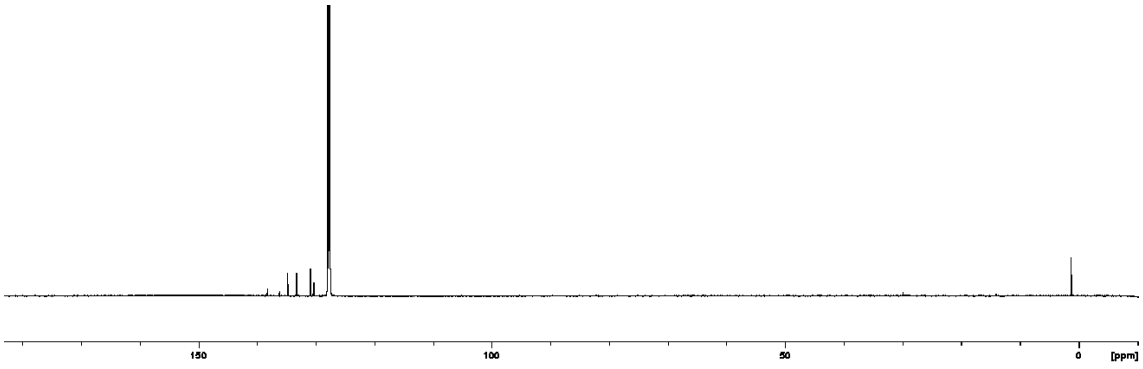
(thiophen-2-ylMe$_2$SiO)$_2$(SiHPh) Using $PhSiH_3$ (32.4 mg, 0.30 mmol) and **t**hiophen-2-ylMe$_2$SiOH (98.1 mg, 0.62 mmol). ^{1}H NMR (600 MHz, CD_3CN): δ 7.72 (dd, 2H, *J* = 4.59, 0.87 Hz, Ar-*H*), 7.55 (dd, 2H, *J* = 7.21, 1.38 Hz, Ar-*H*), 7.42 (dt, 2H, *J* = 7.47, 1.41 Hz, Ar-*H*), 7.34 (t, 2H, *J* = 7.32 Hz, Ar-*H*), 7.31 (dd, 2H, *J* = 3.36, 0.84 Hz, Ar-*H*), 7.23-7.21 (m, 2H, Ar-*H*), 5.45 (s, 1H, $^{1}J_{SiH}$ = 248.9 Hz, Si*H*), 0.39 (s, 6H, SiC*H*$_3$), 0.38 (s, 6H, SiC*H*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 138.2, 136.1, 134.7, 133.2, 130.8, 130.3. 128.0, 1.27, 1.26 ppm. $^{29}Si\{^{1}H\}$ NMR (119 MHz, C_6D_6): δ –3.5, –47.7 ppm.

HRMS (ESI): m/z calcd for $[C_{18}H_{24}O_2S_2Si_3H]^+$ (M+H): 421.0604 ; found 421.0604.

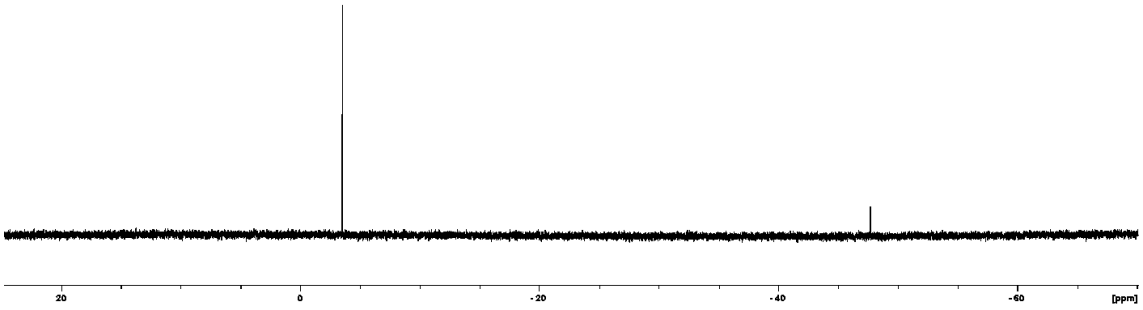
^1H NMR:



$^{13}C\{^1H\}$ NMR:



$^{29}Si\{^1H\}$ NMR:



Single crystal X-ray diffraction studies.

The single crystal X-ray diffraction measurements of **1a**, **1b**, **2a**, **2b, 3b, 4a** and **5a** was performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirrore monochromated Mo Kα radiation. The determination of crystal systems and unit cell parameters and data processing were performed with the *CrystalClear* program package. The data sets were corrected for Lorentz and polarzation effects and absorption. The structure was solved by direct methods using SIR2014 program,[5] and refined by full-matrix least squares calculations on F^2 for all reflections (SHELXL-2014/7),[6] using Yadokari-XG 2009.[7]

Table S1. Crystallographic data of **1a**, **1b**, **2a**, **2b, 3b, 4a, 5a**

	1a	**1b**	**2a**	**2b**	**3b**	**4a**	**5a**
Emprical formula	$C_{38}H_{30}Cl_2FeN_2P_2$	$C_{38}H_{54}Br_2FeN_2P_2$	$C_{40}H_{34}FeN_3OP_2$	$C_{82}H_{122}Fe_2N_6P_4$	$C_{40}H_{34}FeN_3OP_2$	$C_{39}H_{30}FeN_2OP_2$	$C_{44}H_{38}FeN_2P_2Si$
Formula weifht	703.33	816.42	690.49	1427.44	658.63	660.44	740.64
Temperature/*K*	93 (2)	93 (2)	93 (2)	93 (2)	93 (2)	93 (2)	93 (2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	Ortho	triclinic	triclinic
Space group	P 21/c	P 21/c	P-1	P 2/n	P na21	P-1	P-1
a / Å	12.0414 (19)	18.299 (5)	9.785 (2)	26.075 (4)	15.1645 (19)	9.8699 (9)	96.735 (9)
b / Å	20.358 (3)	14.140 (4)	12.336 (2)	10.1672 (15)	13.1906 (19)	10.7795 (13)	12.1191 (8)
c / Å	14.058 (2)	15.178 (5)	14.142 (3)	28.018 (4)	16.823 (2)	16.578 (2)	17.8980 (18)
α / °	90	90	92.154 (4)	90	90	82.081 (11)	70.273 (16)
β / °	107.348 (3)	107.351 (7)	103.057 (5)	93.366 (3)	90	75.1840 (10)	74.867 (16)
γ / °	90	90	101.480 (5)	90	90	65.260 (8)	67.391 (14)
Volume / Å^3	3289.4 (9)	374.6 (19)	1623.5 (6)	7415.0 (19)	3365.1 (8)	1547.7 (3)	1802.4 (4)
Z	4	4	2	4	4	2	2
*R*1 / %	0.029	0.0744	0.0507	0.0771	0.0338	0.0519	0.0576
*wR*2 / %	0.0644	0.189	0.104	0.1849	0.0802	0.1322	0.1111
GOF	1.028	1.107	1.063	1.128	1.022	1.07	1.672

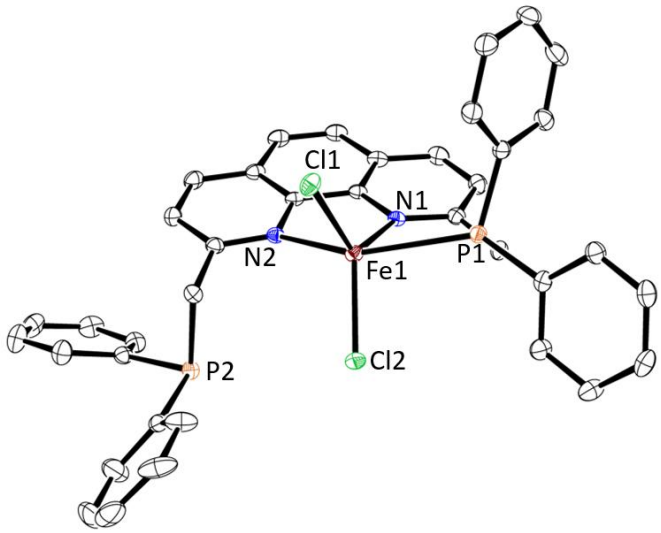


Figure S-1. Molecular structure of **1b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

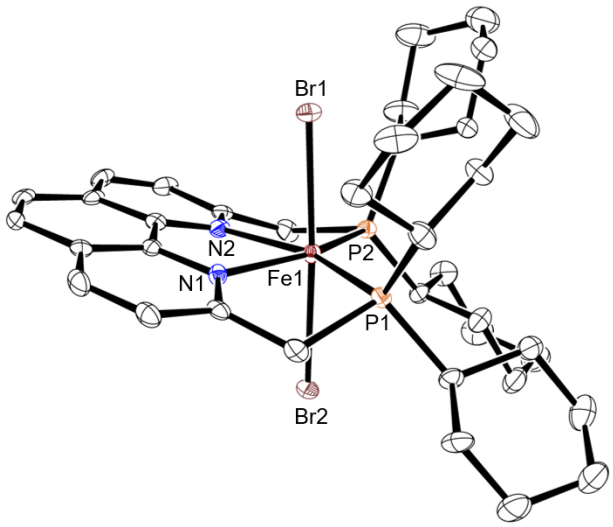


Figure S-2. Molecular structure of **1b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

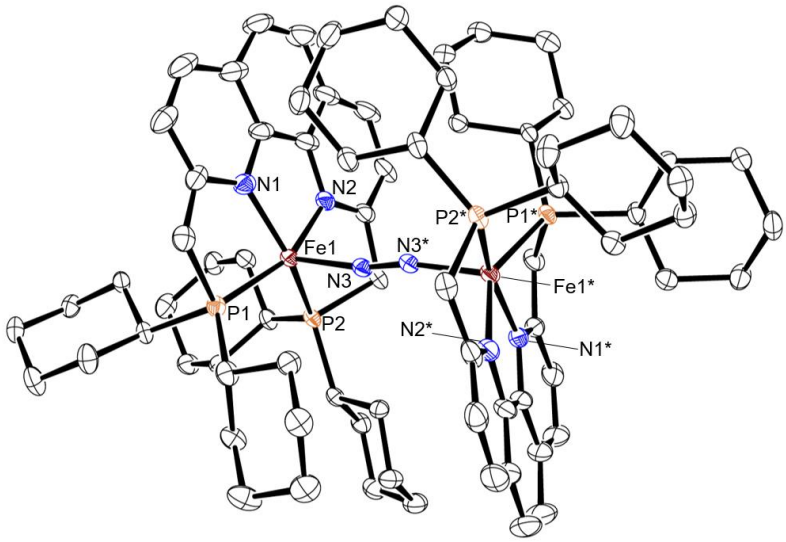


Figure S-3. Molecular structure of **2b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

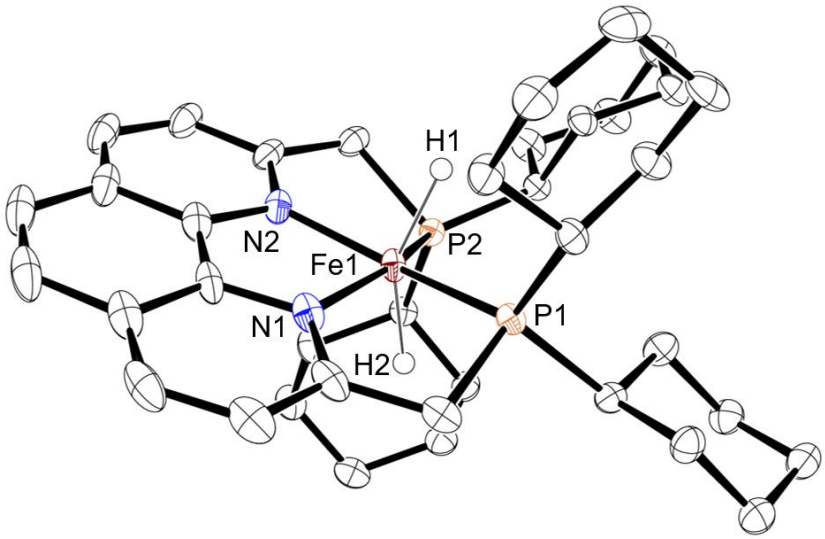


Figure S-4. Molecular structure of **3b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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