Supplementary Information for:

Selective Enzymatic Oxidation of Silanes to Silanols

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Table of Contents

Safety statement

CO is flammable and highly toxic and can be fatal at high doses. It has to be used in a fume hood equipped with a CO detector. The silane reagents are volatile and work with them should be performed with caution (in a fume hood). Other than that, no unexpected or unusually high safety concerns were raised with these methods.

Materials and Methods

General

Hydrosilanes **1a**, **1d**, **1i**–**l**, and silanol **2a** were purchased from commercial vendors. Hydrosilanes **1b**, **1c**, and **1e**–**h** were synthesized according to procedures previously described.[1] All other chemicals and reagents were obtained from commercial suppliers (Sigma-Aldrich, VWR, Alfa Aesar) and used without further purification. Unless stated otherwise, all reactions were carried out under aerobic conditions. Synthetic reactions were monitored using thin layer chromatography (Merck 60 gel plates) using a UV-lamp for visualization. Silica gel chromatography was performed using AMD Silica Gel 60, 230–400 mesh. ^{1}H and ^{13}C NMR were recorded on a Bruker Prodigy 400 MHz instrument. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constant (Hz), integration. Electrocompetent *Escherichia coli* (*E. coli*) cells were prepared following the protocol of Sambrook *et al.*[2] Phusion polymerase and *Dpn*I were purchased from New England Biolabs (NEB, Ipswich, MA).

Site-saturation library generation

Site-saturation mutagenesis for amino acid residue 87 was performed using primers containing degenerate codons (NNK; Table S7). Double-site-saturation of amino

acid residues 181 and 184 and residues 327 and 328 was performed using primers bearing degenerate codons (NDT, VHG, TGG) as per the “22 codon trick” (Tables S8 and S9).[3] For each library, two separate PCRs were performed, each using vector-specific primers at the 5’ and 3’ ends of the sequence (005 and 006, Table S6) and a mutagenic primer. Afterwards, the remaining template was digested with *Dpn*I. The two resulting overlapping fragments that contained the base-pair substitutions were then assembled in a second PCR using flanking primers 005 and 006 resulting in the full-length mutated gene. The pET22(b)+ vector (Novagen) was amplified using flanking primers 007 and 008 (Table S6) in a long-range PCR. The PCR conditions were as follows (final concentrations): Phusion HF buffer 1x, 0.2 mM dNTPs each, 0.5 µM forward primer, 0.5 µM reverse primer, and 0.02 U/µl Phusion polymerase. The purified gene and the pET22(b)+ vector were then assembled using the Gibson assembly protocol.[4] The assembly product was used to transform electrocompetent *E. cloni*® EXPRESS BL21 (DE3) cells (Lucigen, Middleton, WI) with a Gene Pulser Xcell (Bio-Rad, Hercules, CA). SOC medium[5] (0.75 mL) was added to electroporated cells, and they were incubated for 45 min at 37 °C and 220 rpm before being plated on Luria-Bertani (LB) agar plates (100 µg/mL ampicillin). Gel purification was performed with a Zymoclean Gel DNA Recovery Kit (Zymo Research Corp, Irvine, CA). Plasmids were isolated with a QIAprep Spin Miniprep Kit (Qiagen, Hilden, Germany). Generated sequences were sequenced by Laragen using primers T7 and 006 (Table S6).

General protein expression protocol

The following protocol was used for large scale (25–250 mL culture) protein expression. Single colonies of *E. coli* BL21(DE3) cells transformed with the plasmid encoding the protein of interest were picked with sterile toothpicks and grown overnight in Luria-Bertani medium supplemented with ampicillin (100 µg/mL final concentration, LB_{amp}) at 37 °C and 220 rpm. The preculture was used to inoculate an expression culture (2% v/v preculture) in Terrific Broth supplemented with ampicillin (100 µg/mL final concentration, TB_{amp}) in an unbaffled 125-mL – 1-L

Erlenmeyer flask. The expression culture was grown at 37 °C and 220 rpm for 3.5 hours and then cooled on ice for 30 min. Isopropyl β-D-glucopyranoside (IPTG, 0.5 mM final concentration), 5-aminolevulinic acid (Ala, 1.0 mM final concentration) as well as $FeCl_3$ (3.5 μM final concentration), and trace metal mix[6] (1000x, 0.6 μL per 100 mL culture) were added, and the proteins were expressed at 22 °C and 180 rpm for 20–22 h. Following expression, the cultures were centrifuged at 10 °C and 4,000 *g* for 10 min. The cell pellets were then resuspended in potassium phosphate buffer (0.1 M, pH 8.0, 5–25 mL).

Expression of P450s in 96-well deep-well plates: Single colonies from *E. coli* BL21(DE3) cells transformed with plasmids of P450 site-saturation mutagenesis libraries were picked from LB_{amp} agar plates using sterile toothpicks and grown in 300 μL of LB_{amp} in 2-mL 96-deep-well plates at 37 °C and 220 rpm (80% humidity) for 12–18 hours. The preculture (50 μL) was used to inoculate 0.6 mL of TB_{amp} medium in 2-mL 96-well deep-well plates. The expression culture plate was incubated at 37 °C and 220 rpm (80% humidity) for 3.5 hours and then chilled on ice for 30 minutes. TB_{amp} (50 μL) containing isopropyl β-D-glucopyranoside (IPTG, 0.5 mM final concentration), 5-aminolevulinic acid (Ala, 1.0 mM final concentration) as well as $FeCl_3$ (3.5 μM final concentration), and trace metal mix[6] (1000x, 0.6 μL per 100 mL culture) were added, and the proteins were expressed at 22 °C and 220 rpm for 20–24 h. Cells were pelleted at 10 °C and 4,000 *g* for 10 min.

Lysis

Cells were lysed by sonication of 5–10 mL resuspended whole cells in potassium phosphate buffer (0.1 M, pH 8) on ice for 1.5 minutes at 30% amplitude (1 second on, 2 second off) using a QSonica Q500 Sonicator and a 1/8-inch tip. The sonicated cell mixture was clarified via centrifugation at 4 °C and 20,000 *g* for 10 min. The lysate contained the expressed enzymes, and it was used for reactions and protein concentration determination.

CO binding assay

The CO binding assay was performed with lysate. The lysate (1 mL) and excess sodium dithionite (ca. 1 mg) were added to a cuvette. The absorbance was read at 450 nm and 490 nm. CO was bubbled through the lysate for ca. 1 min and absorbances at 450 nm and 490 nm were reread. Beer's law was used to determine protein concentration ($A_{450–450} = \varepsilon_{450–490} \times l \times c$; $l = 1$ cm, $\varepsilon_{450\text{-}490} = 0.091\ cm^{-1}\mu M^{-1}$).[7] The concentrations calculated are an average of three samples.

Reaction screening in 96-well plates

The cell pellets in the 2-mL 96-well plates were resuspended in 390 µL potassium phosphate buffer (0.1 M, pH 8) by vortexing. Dimethylphenylsilane (**1a**, 400 mM in MeCN, 10 µL, 10 mM final concentration) was added to each well. The plates were then immediately covered with a pierceable foil cover (USA Scientific) and shaken at room temperature and 60 rpm for 3–4 h. Afterwards, cyclohexane (900 µL) was added to each well, the plate was sealed with a silicon mat and vortexed for a few seconds. The phases were separated by centrifugation at 15 °C and 20,000 *g* for 10 min. Two hundred µL of the supernatant were moved to a 2-mL glass GC screw top vial with a glass insert, and the mixture was analyzed via GC-FID using method A as specified in the Methods section.

Small-scale biocatalytic reactions with $P450_{BM3}$ variants

Unless stated otherwise, small-scale reactions were set up aerobically on 400-µL-scale. Suspensions of *E. coli* cells expressing the appropriate enzyme or the corresponding lysate were adjusted to the desired protein concentration with potassium phosphate buffer (0.1 M, pH 8) and 386 µL (for whole cell reactions) or 390 µL (for lysate reactions) of the mixture were placed in a 2-mL glass GC screw top vial. A glucose solution (1.0 M in potassium phosphate buffer, 4 µL, for whole cell reactions) or NADPH (3.9 mg, 10 mM final concentration, for lysate reactions) was added, followed by hydrosilane **1a** (400 mM in MeCN, 10 µL, 10 mM final concentration). The vials were then sealed with a cap and moved to a shaker. After

shaking at the indicated temperature and 60 rpm for 4–48 h, cyclohexane (900 µL) and acetophenone (40 mM in cyclohexane, 20 µL) as internal standard were added. The mixture was vortexed for a few seconds, and the phases were separated by centrifugation at 15 °C and 20,000 *g* for 10 min. Two hundred µL of the organic phase were moved to a 2-mL glass GC screw top vial with a glass insert and analyzed via GC-FID using method A as specified in the Methods section. All reactions were done at least in triplicate (technical replicates).

Small-scale biocatalytic reactions with various hydrosilanes

For silanols **2a**–**2k**: Pelleted *E. coli* cells expressing $P450_{SiOx3}$ from 25–50 mL cultures were resuspended in potassium phosphate buffer (5–10 mL, 0.1 M, pH 8), and 390 µL of the mixture were placed in a 2-mL glass GC screw top vial. The corresponding hydrosilane **1** (200 mM in MeCN, 10 µL, 5.0 mM final concentration) was added, and the vials were then sealed with a cap. After shaking at room temperature and 60 rpm for 24 h, cyclohexane (900 µL) and acetophenone (40 mM in cyclohexane, 20 µL) as internal standard were added. The mixture was vortexed for a few seconds and the phases were separated by centrifugation at 15 °C and 20,000 *g* for 10 min. Two hundred µL of the organic phase were moved to a 2-mL glass GC screw top vial with a glass insert and analyzed by GC-FID using the methods specified in the Methods section. All reactions were done in triplicate (technical replicates).

For silanol **2l**: Pelleted *E. coli* cells expressing $P450_{SiOx3}$ from 25–50 mL cultures were resuspended in potassium phosphate buffer (5–10 mL, 0.1 M, pH 8), and 1 mL of the mixture was placed in a 2-mL glass GC screw top vial. Pentamethyldisiloxane (**1l**, 1.07 µL, 5.0 mM final concentration) was added, and the vials were then sealed with a cap. After shaking at room temperature and 60 rpm for 24 h, diethyl ether (500 µL) was added. The mixture was vortexed for a few seconds, and the phases were separated by centrifugation at 15 °C and 20,000 *g* for 10 min. Two hundred µL of the organic phase were moved to a 2-mL glass GC screw top vial with a glass insert, and acetophenone (40 mM in cyclohexane, 8 µL) was added as internal standard.

The reaction was analyzed by GC-FID using method D as specified in the Methods section. The reaction was done in triplicates (technical replicates).

Enzyme-catalyzed hydrosilane oxidation

Control reactions

Table S1. Control reactions for the formation of dimethylphenylsilanol (**2a**). BSA = bovine serum albumin.

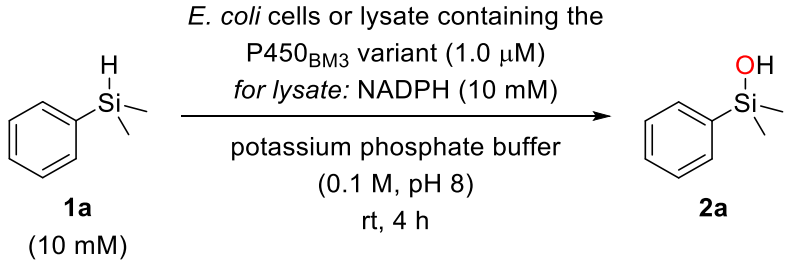
Entry	Catalyst/Additive	Concentration	Yield of 2a	TTN
1	-	-	0.2%	n.a.
2	Hemin	1 µM	0.2%	n.a.
3	BSA	1 µM	0.2%	n.a.
4	Hemin + BSA	1 µM/1 µM	0.2%	n.a.
5	Hemin + $Na_2S_2O_4$	1 µM/10 mM	0.2%	n.a.
6	Hemin + $Na_2S_2O_4$	10 µM/10 mM	1.0 ± 0.1%	10 ± 1
7	Hemin + BSA	1 µM/1 µM	0.2%	n.a.
8	Hemin + BSA + $Na_2S_2O_4$	1 µM/1 µM/10 mM	0.2%	n.a.
9	*E. coli* BL21(DE3)	-	0.3%	n.a.
10	*E. coli* lysate	-	0.3%	n.a.

Experiments were performed on 400-µL scale in potassium phosphate buffer (0.1 M, pH 8) with hydrosilane **1a** (10 µL of a 400 mM solution in MeCN, 10 mM final concentration). Hemin was added as a 1 mM suspension/solution in MeCN or DMSO (0.4 µL or 4 µL), BSA as a 1 mM solution in potassium phosphate buffer (0.4 µL), and $Na_2S_2O_4$ (0.9 mg) was added as a solid. Experiments to determine *E. coli* cell and lysate background reactions were performed with *E. cloni*® EXPRESS BL21(DE3) cells containing a pET22b(+) plasmid encoding a variant of tryptophane

synthase subunit B from *thermotoga maritima* (uniprot P50909) as a control. Lysis was performed as described above. Reactions were performed in triplicate, and TTNs reported are the average of three experiments. n.a. = not applicable.

Catalytic performance of $P450_{BM3}$ variants

Table S2. Evolutionary lineage for the oxidation of **1a**.



1a (10 mM) → **2a**

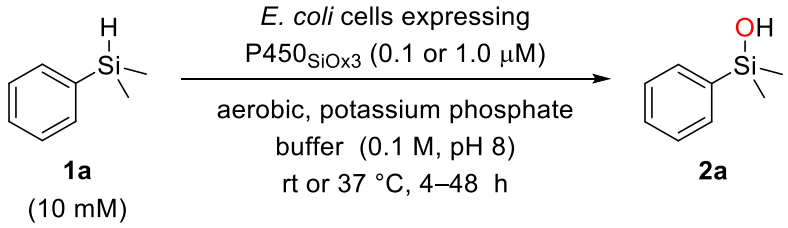
Entry	Variant (Mutations)	Conditions	Yield of 2a	TTN
1[a]		whole cells	2.1 ± 0.3%	210 ± 25
2	$P450_{BM3}$ WT	whole cells, anaerobic[b]	0.2%	n.a.
3		whole cells, anaerobic[b,c]	0.2%	n.a.
4[a]	$P450_{SiOx1}$ (F87G)	whole cells	3.1 ± 0.1%	310 ± 10
5[a]	$P450_{SiOx2}$ (F87G, A328L)	whole cells	8.5 ± 1.3%	850 ± 130
6[a]	$P450_{SiOx3}$ (F87G, A328L, L181D, A184H)	whole cells	12 ± 2.4%	1200 ± 240
7[a]	$P450_{BM3}$ WT	lysate	18 ± 1.4%	1740 ± 140
8[a]	$P450_{SiOx3}$	lysate	36 ± 1.5%	3620 ±150

Experiments were performed as described above for small-scale biocatalytic reactions with $P450_{BM3}$ variants at 1.0 μM protein concentration for 4 h at room temperature. n.a. = not applicable. [a] The average of biological duplicates and triplicate runs is given, six runs in total. [b] The reactions were set up anaerobically in a Coy chamber. [c] An oxygen depletion system was used. Cells were resuspended

in 310 µL potassium phosphate buffer (0.1 M, pH 8), 20 µL of a stock solution containing glucose oxidase (from *Aspergillus niger*, 1,000 U/mL) and catalase (from bovine liver, 14,000 U/mL) in double-distilled water, and 60 µL of a glucose solution (250 mM in potassium phosphate buffer) were added.

Optimization of reaction conditions

Table S3. Performance of $P450_{SiOx3}$ under various reaction conditions.



Entry	Temperature	Protein Concentration	Time	Yield of 2a	TTN
1[a]	rt	1.0 µM	4 h	12 ± 2%	1,200 ± 240
2	37 °C	1.0 µM	4 h	18 ± 3%	1,750 ± 310
3	37 °C	1.0 µM	48 h	24 ± 0.6%	2,400 ± 60
4	rt	0.1 µM	4 h	1.6 ± 0.1%	1,560 ± 50
5	rt	0.1 µM	24 h	2.0 ± 0.1%	2,020 ± 120
6	rt	0.1 µM	48 h	3.1 ± 0.1%	3,110 ± 30
7	37 °C	0.1 µM	4 h	2.5 ± 0.1%	2,500 ± 10
8	37 °C	0.1 µM	24 h	9.9 ± 0.5%	9,870 ± 490
9	37 °C	0.1 µM	48 h	19 ± 0.2%	19,100 ± 190

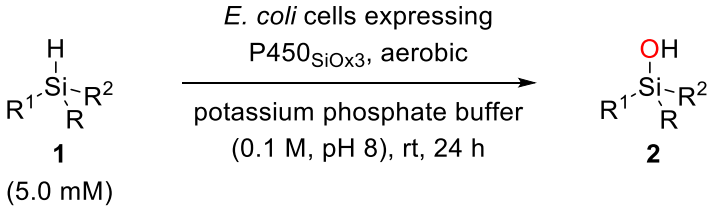
Experiments were performed as described earlier for small-scale biocatalytic reactions with $P450_{BM3}$ variants. Yields and TTN are given as an average of triplicate runs (technical replicates). [a] See Table S2, entry 6.

Preparative-scale reaction

Single colonies of *E. coli* BL21(DE3) cells carrying a plasmid encoding $P450_{SiOx3}$ were picked with sterile toothpicks and grown overnight in 2 × 5 mL LB_{amp} at 37 °C and 220 rpm. Each preculture was used to inoculate an expression culture in TB_{amp} (250 mL). The expression cultures were grown at 37 °C and 180 rpm for 3.5 hours and then cooled on ice for 30 min. Isopropyl β-D-glucopyranoside (IPTG, 0.5 mM final concentration), 5-aminolevulinic acid (Ala, 1.0 mM final concentration) as well as $FeCl_3$ (3.5 µM final concentration) and trace metal mix[6] (1000x, 0.6 µL per 100 mL culture) were added, and the proteins were expressed at 22 °C and 180 rpm overnight. Following expression, the cultures were centrifuged at 10 °C and 4,000 *g* for 10 min. The cell pellets were then resuspended in potassium phosphate buffer (100 mM, pH 8.0, 25 mL per pellet), and the cell suspensions were combined. The protein concentration in the whole-cell suspension was determined to 8.8 µM by lysis of an aliquot, and the CO binding assay as described earlier. A solution of dimethylphenylsilane (**1a**, 400 mM in MeCN, 625 µL, 0.25 mmol) was added to the 50 mL of the cell suspension and the reaction mixture was shaken at 180 rpm for 3 d at 37 °C. Afterwards, the mixture was extracted with cyclohexane (3 × 300 mL) and the solvent was removed under reduced pressure. Drying *in vacuo* delivered dimethylphenylsilanol (**2a**, 29 mg, 76%) as a clear liquid.

Substrate Scope

Table S4. Substrate scope reactions.



Silanol	GC Method	Protein Concentration	Yield	TTN
2a	A	9.0	>99 ± 6.4%	550 ± 35
2b	B	9.0	94 ± 4.1%	520 ± 25
2c	B	8.1	59 ± 1.3%	360 ± 10
2d	B	9.0	79 ± 3.7%	440 ± 20
2e	B	9.0	58 ± 7.6%	320 ± 40
2g	B	8.1	64 ± 2.5%	400 ± 15
2i	E	9.0	9 ± 1.6%	50 ± 10
2j	C	9.0	17 ± 1.1%	95 ± 5
2k	C	9.0	14 ± 0.4%	80 ± 5
2l	D	9.0	18 ± 1.5%	100 ± 10
2l[a]	D	negative control	7 ± 1%	n.a.

Experiments were performed as described earlier for small-scale biocatalytic reactions with various hydrosilanes. Yields and TTN are given as average of triplicate runs (technical replicates). [a]Negative control in potassium phosphate buffer (0.1 M, pH 8) without whole cells added under otherwise identical reaction conditions. n.a. = not applicable.

Gas Chromatography

GC-FID data were collected on an Agilent 7820A GC system with a DB-WAXetr column (30 m × 0.32 mm, 0.25-μm film thickness) using the following parameters: Helium carrier gas, column flow 2.5 mL/min, split ratio 20:1, injection temperature 250 °C, detector temperature 300 °C, and one of the temperature programs specified below.

Methods

Method A:

	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial	--	110	1
Ramp	20	120	0
Ramp	70	260	2

Method B:

	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial	--	110	2
Ramp	12	140	0
Ramp	40	260	1

Method C:

	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial	--	110	2
Ramp	15	140	0
Ramp	40	200	0

Method D:

	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial	--	50	1
Ramp	20	60	0
Ramp	70	260	0.7

Method E:

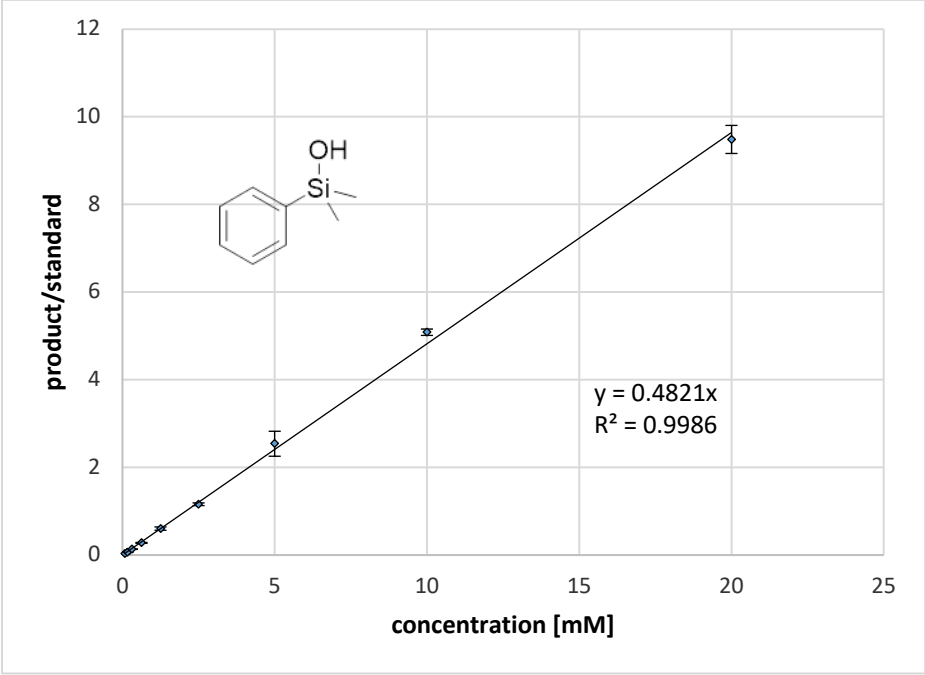
	Rate (°C/min)	Temperature (°C)	Hold time (min)
Initial	--	140	1
Ramp	70	260	2.3

Calibration curves

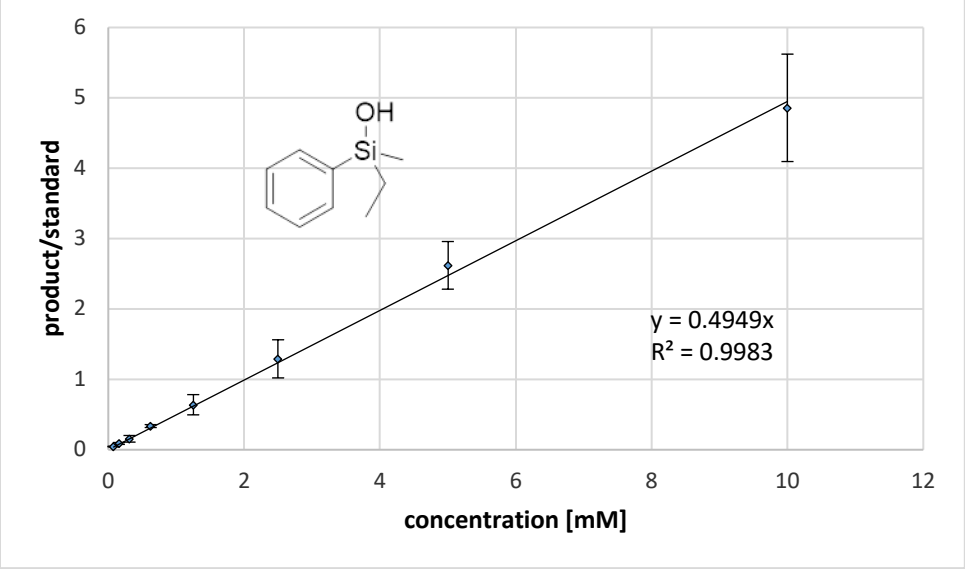
For silanols **2a**–**k**, a dilution series of the corresponding authentic standard (800 mM–1.56 mM in MeCN) was prepared and 10 µL of these solutions were added to 390 µL of potassium phosphate buffer (0.1 M, pH = 8), resulting in final product concentrations of 20 mM – 78.1 µM. This was followed by the addition of cyclohexane (900 µL) and acetophenone (20 µL of a 40 mM solution in cyclohexane) as internal standard. The mixtures were vortexed for a few seconds and then centrifuged at 15 °C and 20,000 *g* for 10 min. Two hundred µL of the supernatant were moved to a 2-mL glass GC screw top vial with a glass insert, and the mixture was analyzed via GC-FID. The series were performed in triplicates. For silanol **2l**, a 2 mM solution of the silanol in potassium phosphate buffer (2 mL, 0.1 M, pH 8) was prepared. From this solution, a dilution series was prepared, resulting in 1-mL samples of 1 mM, 0.5 mM, 0.25 mM, 125 µM, 62.5 µM, and 31.25 µM concentrations. Et_2O (500 µL) was added to each of the samples, the mixture was vortexed for a few second and then centrifuged at 4 °C and 20,000 *g* for 10 min. Two hundred µL of the supernatant were moved to a 2-mL glass GC screw top vial with a glass insert, acetophenone (8 µL of a 40 mM solution in cyclohexane) was added, and the mixture was analyzed via GC-FID. The series were performed in triplicates.

The standard curves plot the ratio of product area to internal standard area on the GC (y-axis) against product concentration in mM (x-axis).

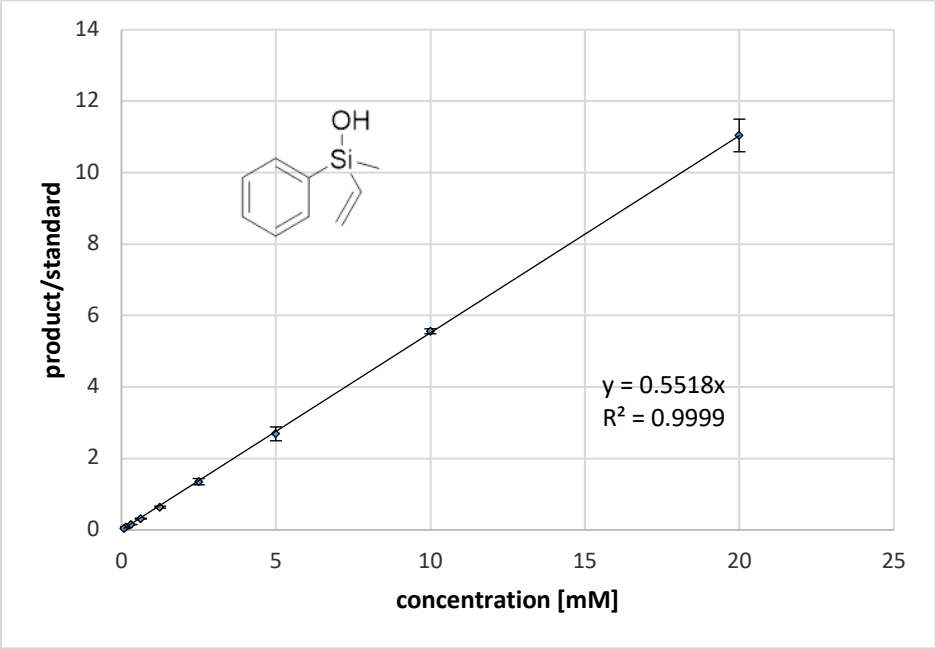
Dimethylphenylsilanol (**2a**)
Method A



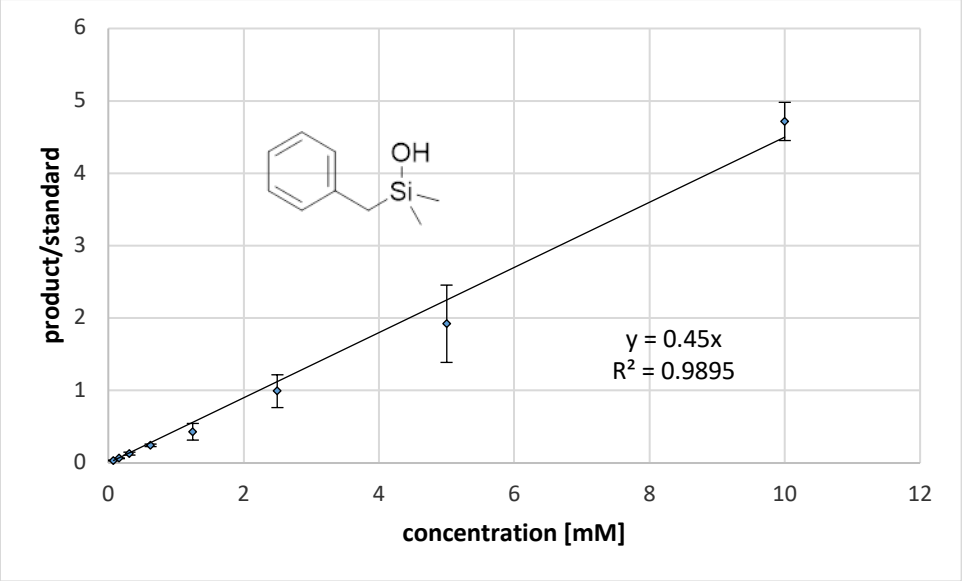
Methylethylphenylsilanol (**2b**)
Method B



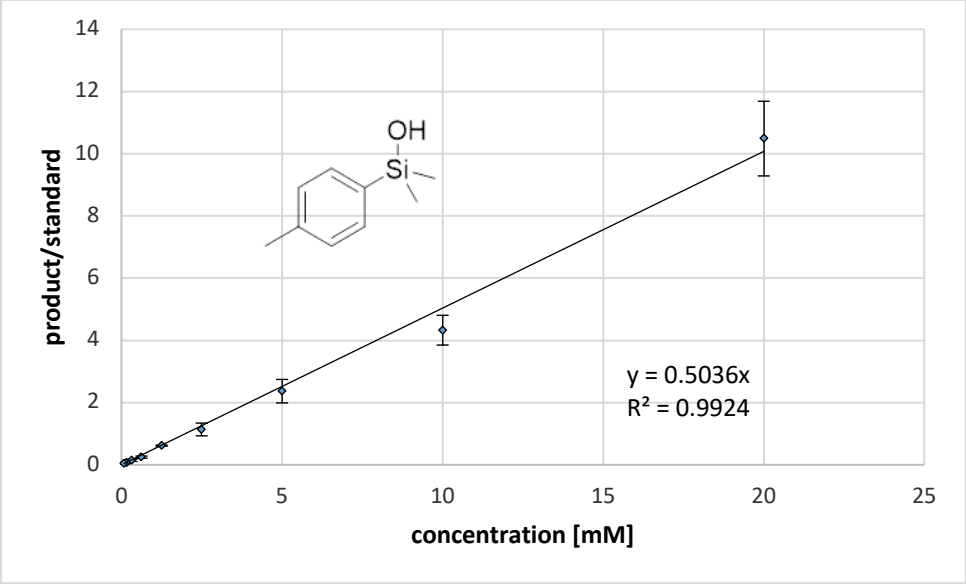
Methyl(phenyl)vinylsilanol (**2c**)
Method B



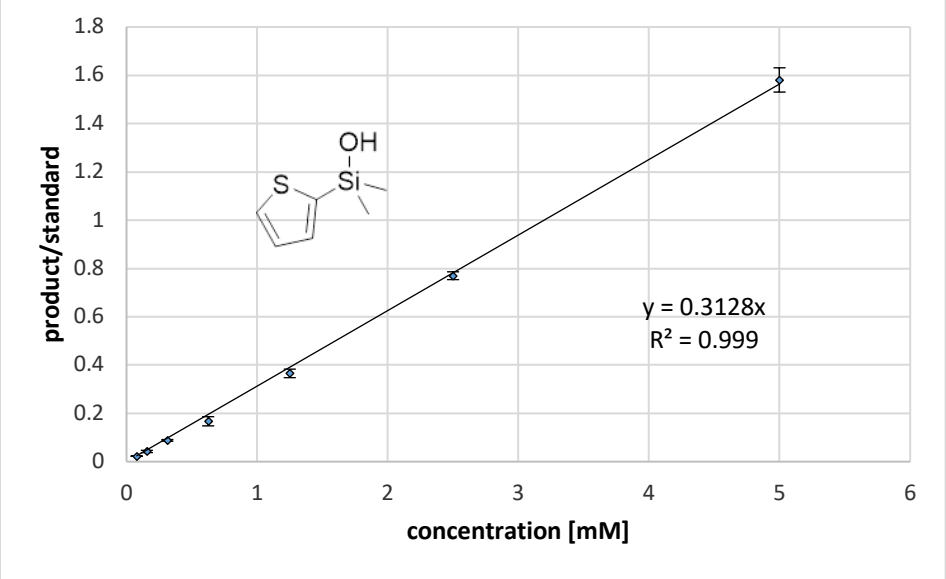
Benzyldimethylsilanol (**2d**)
Method B



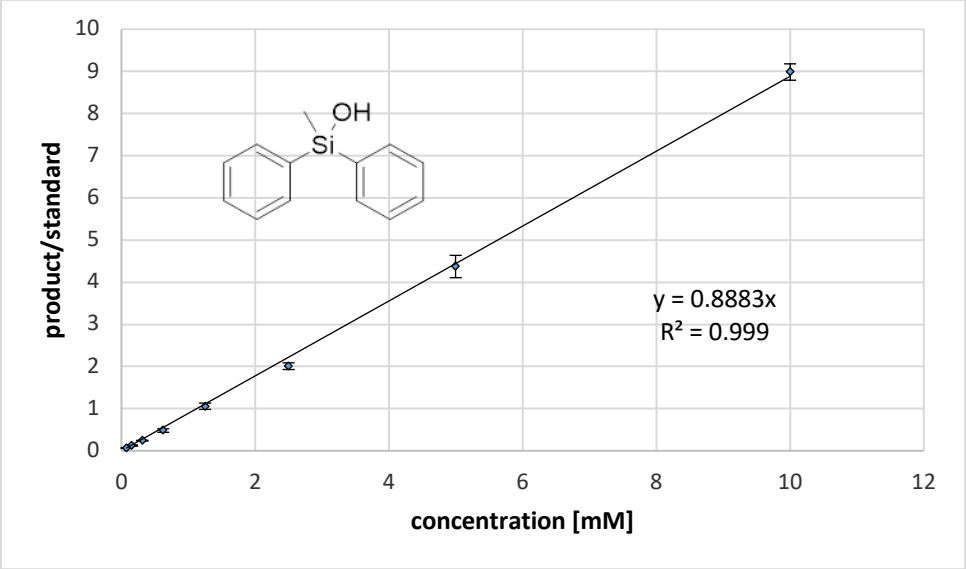
Dimethyl(*p*-tolyl)silanol (**2e**)
Method B



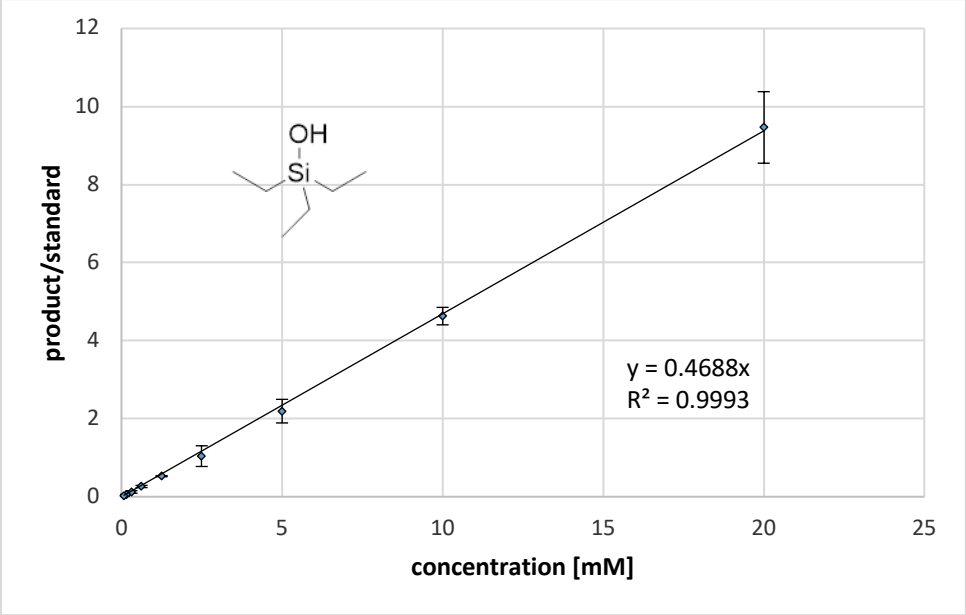
Dimethyl(thiophen-2-yl)silanol (**2g**)
Method B



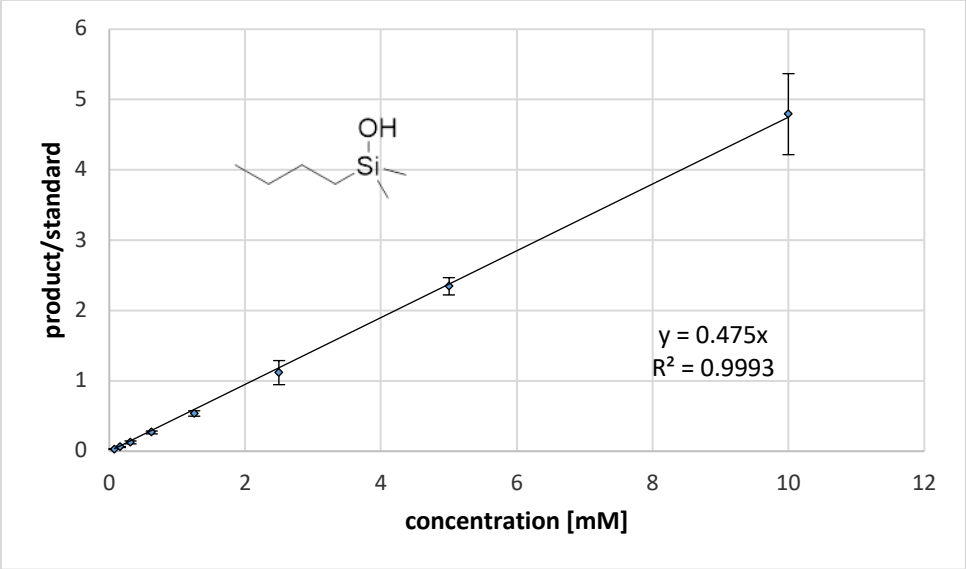
Methyldiphenylsilanol (**2i**)
Method E



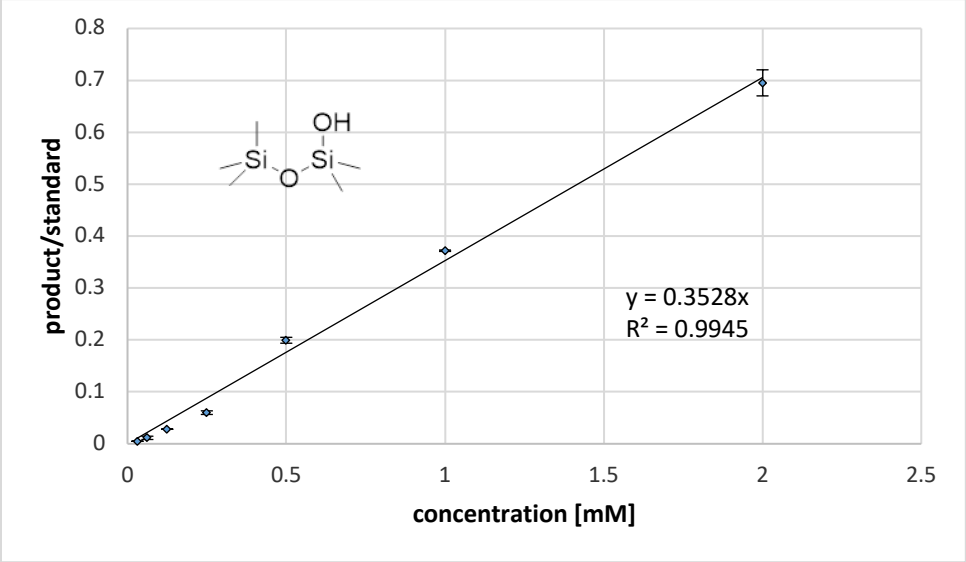
Triethylsilanol (**2j**)
Method C



Butyldimethylsilanol (**2k**)
Method C

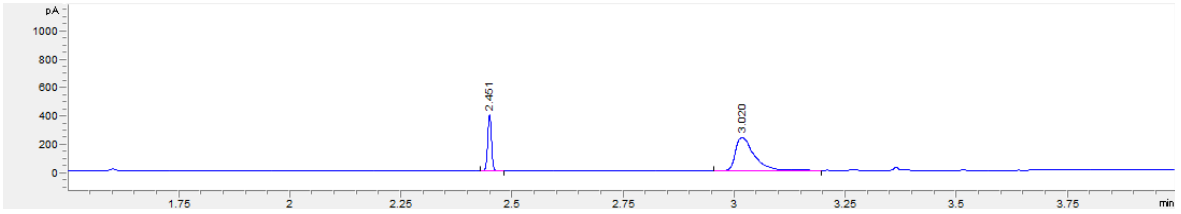


Pentamethyldisiloxanol (**2l**)
Method D

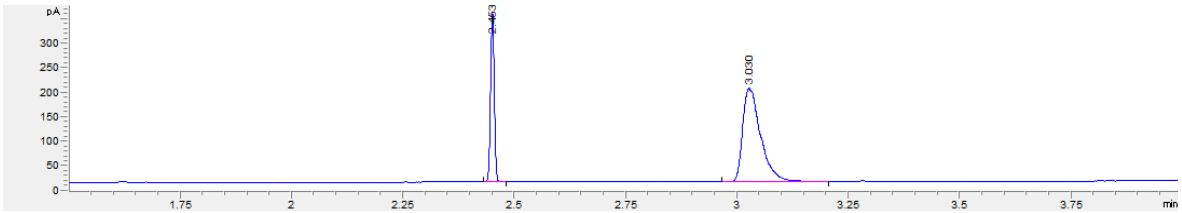


GC Traces

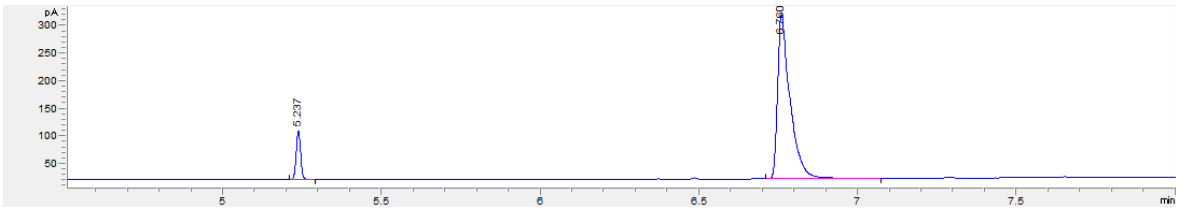
PhMe$_2$SiOH (**2a**) – standard:



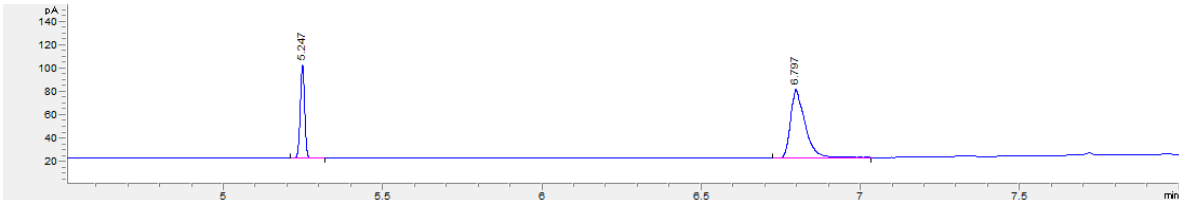
PhMe$_2$SiOH (**2a**) – enzymatic reaction:



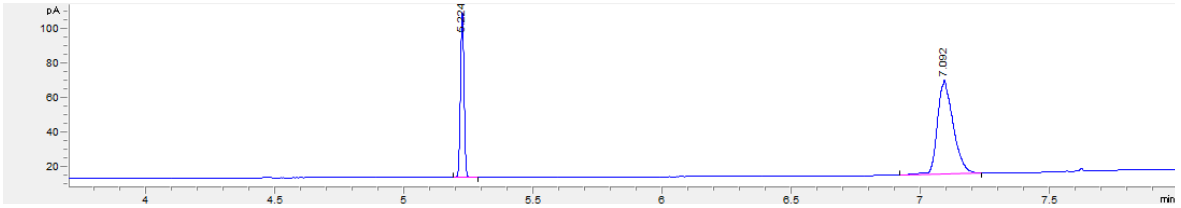
Ethyl(methyl)(phenyl)silanol (**2b**) – standard:



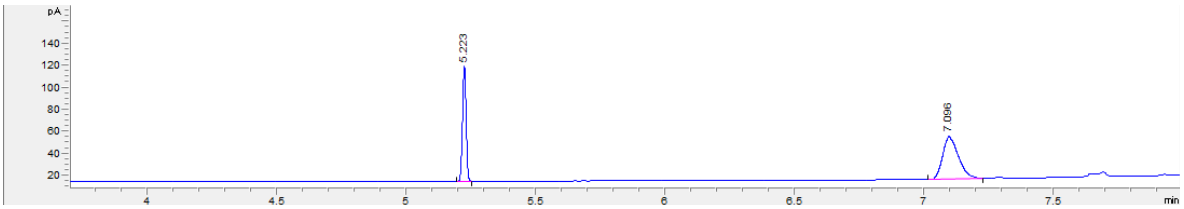
Ethyl(methyl)(phenyl)silanol (**2b**) – enzymatic reaction:



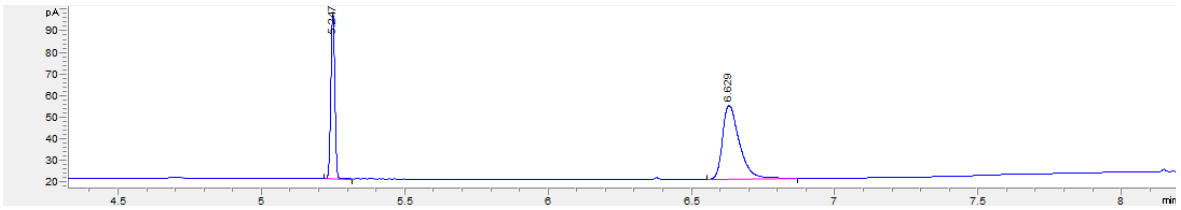
Methyl(phenyl)(vinyl)silanol (**2c**) – standard:



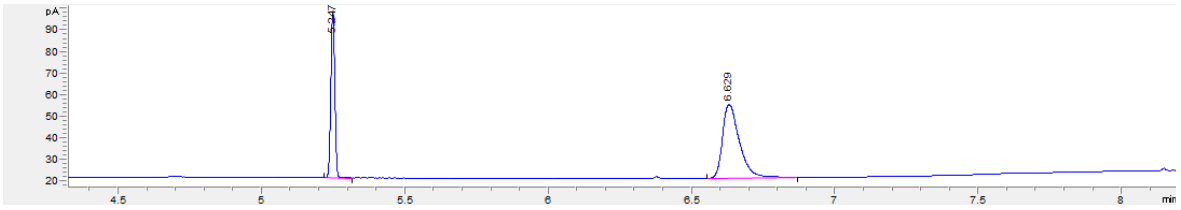
Methyl(phenyl)(vinyl)silanol (**2c**) – enzymatic reaction:



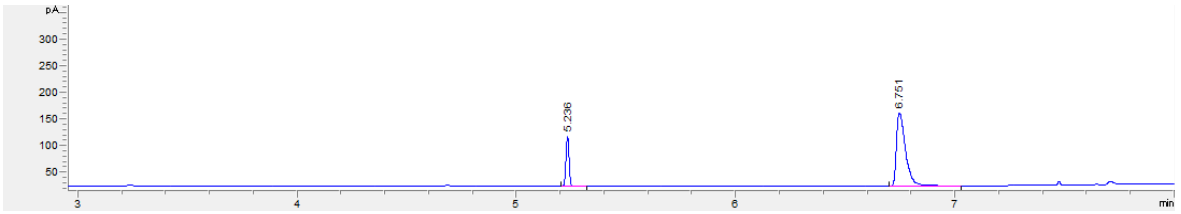
Benzyldimethylsilanol (**2d**) – standard:



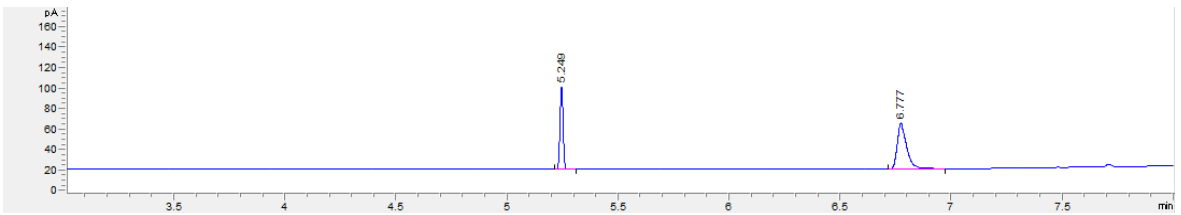
Benzyldimethylsilanol (**2d**) – enzymatic reaction:



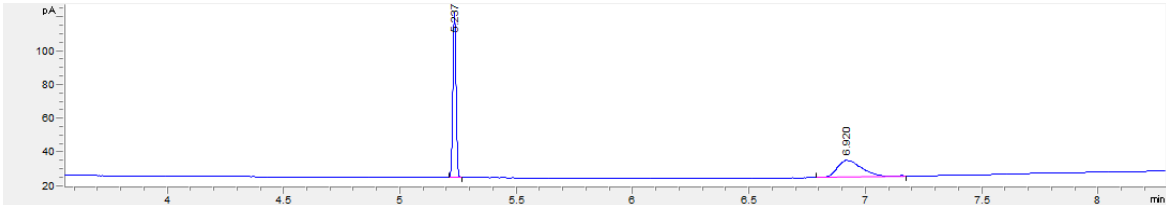
Dimethyl(*p*-tolyl)silanol (**2e**) – standard:



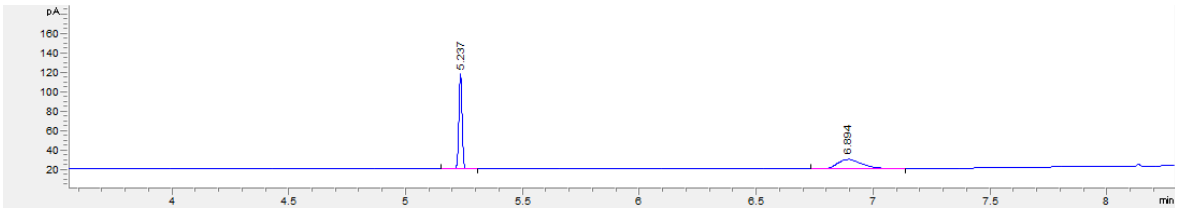
Dimethyl(*p*-tolyl)silanol (**2e**) – enzymatic reaction:



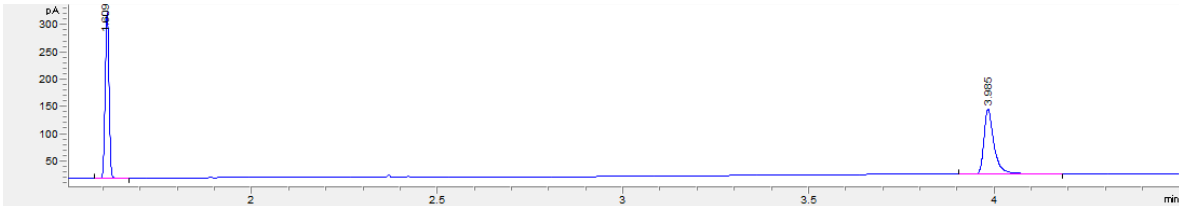
Dimethyl(thiophen-2-yl)silanol (**2g**) – standard:



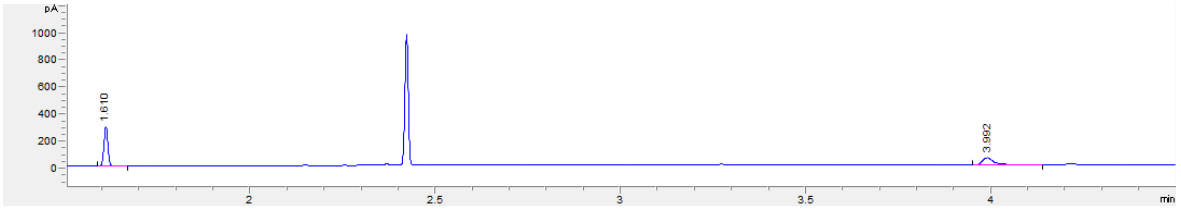
Dimethyl(thiophen-2-yl)silanol (**2g**) – enzymatic reaction:



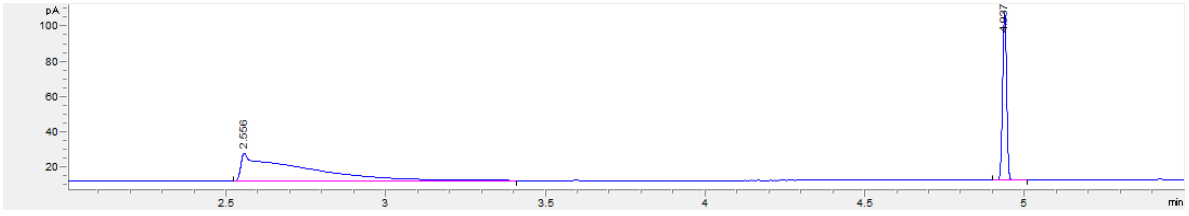
Methyldiphenylsilanol (**2i**) – standard:



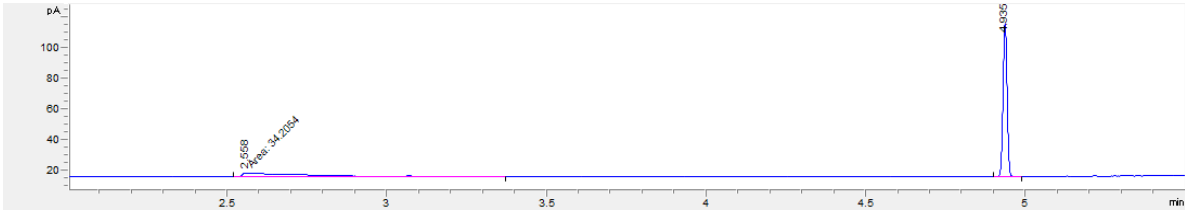
Methyldiphenylsilanol (**2i**) – enzymatic reaction:
*Note: The retention time of the starting hydrosilane **1i** is 2.43 min.*



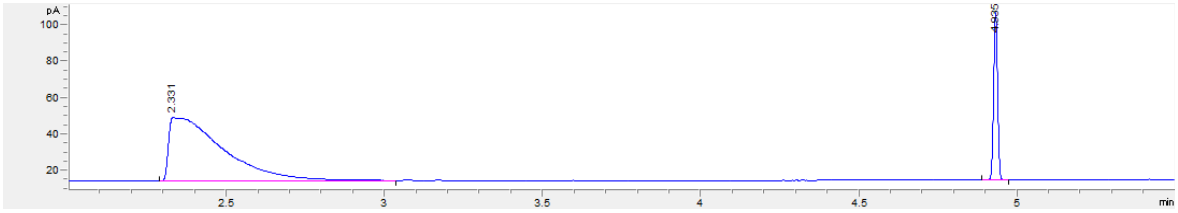
Triethylsilanol (**2j**) – standard:



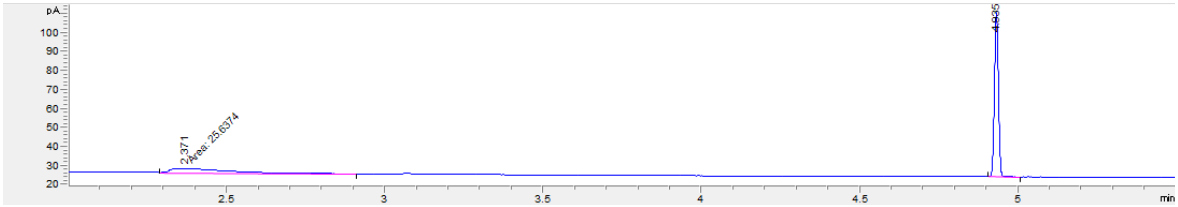
Triethylsilanol (**2j**) – enzymatic reaction:



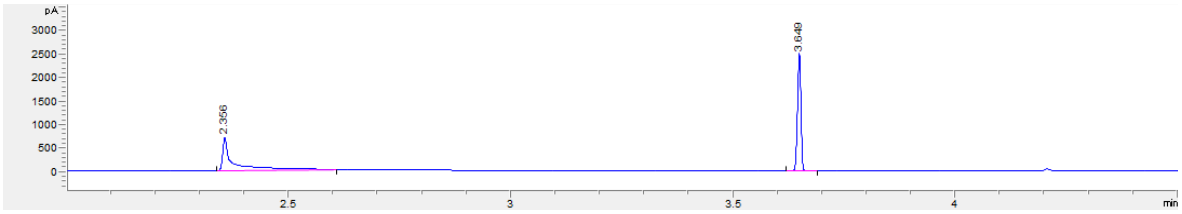
Butyldimethylsilanol (**2k**) – standard:



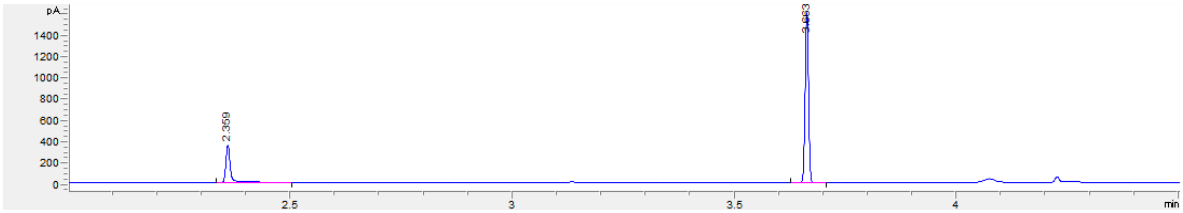
Butyldimethylsilanol (**2k**) – enzymatic reaction:



Pentamethyldisiloxanol (**2l**) – standard:



Pentamethyldisiloxanol (**2l**) – enzymatic reaction:



Sequence of primers and variants

Table S5. Amino acid sequences of mutants relative to wild type ($P450_{BM3}$ WT).

Variant:	Amino acid substitutions:
$P450_{BM3}$ WT	-
$P450_{SiOx1}$	$P450_{BM3}$ F87G
$P450_{SiOx2}$	$P450_{SiOx1}$ A328L
$P450_{SiOx3}$	$P450_{SiOx2}$ L181D A184H

Sequences of the heme domain of all variants:

$P450_{BM3}$ WT:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAGATAAACCGGTT
CAAGCTTTGATGAAAATTGCGGATGAATTAGGAGAAATCTTTAAATTCGAGGCGCCTGGTCGTGTAACGCGCTACTTATC
AAGTCAGCGTCTAATTAAAGAAGCATGCGATGAATCACGCTTTGATAAAAACTTAAGTCAAGCGCTTAAATTTGTACGTG
ATTTTGCAGGAGACGGGTTATTTACAAGCTGGACGCATGAAAAAAATTGGAAAAAAGCGCATAATATCTTACTTCCAAGC
TTCAGTCAGCAGGCAATGAAAGGCTATCATGCGATGATGGTCGATATCGCCGTGCAGCTTGTTCAAAAGTGGGAGCGTC
TAAATGCAGATGAGCATATTGAAGTACCGGAAGACATGACACGTTTAACGCTTGATACAATTGGTCTTTGCGGCTTTAAC
TATCGCTTTAACAGCTTTTACCGAGATCAGCCTCATCCATTTATTACAAGTATGGTCCGTGCACTGGATGAAGCAATGAA
CAAGCTGCAGCGAGCAAATCCAGACGACCCAGCTTATGATGAAAACAAGCGCCAGTTTCAAGAAGATATCAAGGTGATG
AACGACCTAGTAGATAAAATTATTGCAGATCGCAAAGCAAGCGGTGAACAAAGCGATGATTTATTAACGCATATGCTAAA
CGGAAAAGATCCAGAAACGGGTGAGCCGCTTGATGACGAGAACATTCGCTATCAAATTATTACATTCTTAATTGCGGGA
CACGAAACAACAAGTGGTCTTTTATCATTTGCGCTGTATTTCTTAGTGAAAAATCCACATGTATTACAAAAAGCAGCAGAA
GAAGCAGCACGAGTTCTAGTAGATCCTGTTCCAAGCTACAAACAAGTCAAACAGCTTAAATATGTCGGCATGGTCTTAAA
CGAAGCGCTGCGCTTATGGCCAACTGCTCCTGCGTTTTCCCTATATGCAAAAGAAGATACGGTGCTTGGAGGAGAATAT
CCTTTAGAAAAAGGCGACGAACTAATGGTTCTGATTCCTCAGCTTCACCGTGATAAAACAATTTGGGGAGACGATGTGG
AAGAGTTCCGTCCAGAGCGTTTTGAAAATCCAAGTGCGATTCCGCAGCATGCGTTTAAACCGTTTGGAAACGGTCAGCG
TGCGTGTATCGGTCAGCAGTTCGCTCTTCATGAAGCAACGCTGGTACTTGGTATGATGCTAAAACACTTTGACTTTGAAG
ATCATACAAACTACGAGCTCGATATTAAAGAAACTTTAACGTTAAAACCTGAAGGCTTTGTGGTAAAAGCAAAATCGAAAA
AAATTCCGCTTGGCGGTATTCCTTCACCTAGCACTGAACAGT

$P450_{SiOx1}$:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAGATAAACCGGTT
CAAGCTTTGATGAAAATTGCGGATGAATTAGGAGAAATCTTTAAATTCGAGGCGCCTGGTCGTGTAACGCGCTACTTATC
AAGTCAGCGTCTAATTAAAGAAGCATGCGATGAATCACGCTTTGATAAAAACTTAAGTCAAGCGCTTAAATTTGTACGTG
ATTTTGCAGGAGACGGGTTAGGTACAAGCTGGACGCATGAAAAAAATTGGAAAAAAGCGCATAATATCTTACTTCCAAGC
TTCAGTCAGCAGGCAATGAAAGGCTATCATGCGATGATGGTCGATATCGCCGTGCAGCTTGTTCAAAAGTGGGAGCGTC
TAAATGCAGATGAGCATATTGAAGTACCGGAAGACATGACACGTTTAACGCTTGATACAATTGGTCTTTGCGGCTTTAAC
TATCGCTTTAACAGCTTTTACCGAGATCAGCCTCATCCATTTATTACAAGTATGGTCCGTGCACTGGATGAAGCAATGAA
CAAGCTGCAGCGAGCAAATCCAGACGACCCAGCTTATGATGAAAACAAGCGCCAGTTTCAAGAAGATATCAAGGTGATG
AACGACCTAGTAGATAAAATTATTGCAGATCGCAAAGCAAGCGGTGAACAAAGCGATGATTTATTAACGCATATGCTAAA
CGGAAAAGATCCAGAAACGGGTGAGCCGCTTGATGACGAGAACATTCGCTATCAAATTATTACATTCTTAATTGCGGGA
CACGAAACAACAAGTGGTCTTTTATCATTTGCGCTGTATTTCTTAGTGAAAAATCCACATGTATTACAAAAAGCAGCAGAA
GAAGCAGCACGAGTTCTAGTAGATCCTGTTCCAAGCTACAAACAAGTCAAACAGCTTAAATATGTCGGCATGGTCTTAAA
CGAAGCGCTGCGCTTATGGCCAACTGCTCCTGCGTTTTCCCTATATGCAAAAGAAGATACGGTGCTTGGAGGAGAATAT

CCTTTAGAAAAAGGCGACGAACTAATGGTTCTGATTCCTCAGCTTCACCGTGATAAAACAATTTGGGGAGACGATGTGG
AAGAGTTCCGTCCAGAGCGTTTTGAAAATCCAAGTGCGATTCCGCAGCATGCGTTTAAACCGTTTGGAAACGGTCAGCG
TGCGTGTATCGGTCAGCAGTTCGCTCTTCATGAAGCAACGCTGGTACTTGGTATGATGCTAAAACACTTTGACTTTGAAG
ATCATACAAACTACGAGCTCGATATTAAAGAAACTTTAACGTTAAAACCTGAAGGCTTTGTGGTAAAAGCAAAATCGAAAA
AAATTCCGCTTGGCGGTATTCCTTCACCTAGCACTGAACAGT

$P450_{SiOx2}$:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAGATAAACCGGTT
CAAGCTTTGATGAAAATTGCGGATGAATTAGGAGAAATCTTTAAATTCGAGGCGCCTGGTCGTGTAACGCGCTACTTATC
AAGTCAGCGTCTAATTAAAGAAGCATGCGATGAATCACGCTTTGATAAAAACTTAAGTCAAGCGCTTAAATTTGTACGTG
ATTTTGCAGGAGACGGGTTAGGTACAAGCTGGACGCATGAAAAAAATTGGAAAAAAGCGCATAATATCTTACTTCCAAGC
TTCAGTCAGCAGGCAATGAAAGGCTATCATGCGATGATGGTCGATATCGCCGTGCAGCTTGTTCAAAAGTGGGAGCGTC
TAAATGCAGATGAGCATATTGAAGTACCGGAAGACATGACACGTTTAACGCTTGATACAATTGGTCTTTGCGGCTTTAAC
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CAAGCTGCAGCGAGCAAATCCAGACGACCCAGCTTATGATGAAAACAAGCGCCAGTTTCAAGAAGATATCAAGGTGATG
AACGACCTAGTAGATAAAATTATTGCAGATCGCAAAGCAAGCGGTGAACAAAGCGATGATTTATTAACGCATATGCTAAA
CGGAAAAGATCCAGAAACGGGTGAGCCGCTTGATGACGAGAACATTCGCTATCAAATTATTACATTCTTAATTGCGGGA
CACGAAACAACAAGTGGTCTTTTATCATTTGCGCTGTATTTCTTAGTGAAAAATCCACATGTATTACAAAAAGCAGCAGAA
GAAGCAGCACGAGTTCTAGTAGATCCTGTTCCAAGCTACAAACAAGTCAAACAGCTTAAATATGTCGGCATGGTCTTAAA
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TGCGTGTATCGGTCAGCAGTTCGCTCTTCATGAAGCAACGCTGGTACTTGGTATGATGCTAAAACACTTTGACTTTGAAG
ATCATACAAACTACGAGCTCGATATTAAAGAAACTTTAACGTTAAAACCTGAAGGCTTTGTGGTAAAAGCAAAATCGAAAA
AAATTCCGCTTGGCGGTATTCCTTCACCTAGCACTGAACAGT

$P450_{SiOx3}$:

ATGACAATTAAAGAAATGCCTCAGCCAAAAACGTTTGGAGAGCTTAAAAATTTACCGTTATTAAACACAGATAAACCGGTT
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TAAATGCAGATGAGCATATTGAAGTACCGGAAGACATGACACGTTTAACGCTTGATACAATTGGTCTTTGCGGCTTTAAC
TATCGCTTTAACAGCTTTTACCGAGATCAGCCTCATCCATTTATTACAAGTATGGTCCGTGCAGATGATGAACATATGAAC
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CGAAACAACAAGTGGTCTTTTATCATTTGCGCTGTATTTCTTAGTGAAAAATCCACATGTATTACAAAAAGCAGCAGAAGA
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TTTAGAAAAAGGCGACGAACTAATGGTTCTGATTCCTCAGCTTCACCGTGATAAAACAATTTGGGGAGACGATGTGGAA
GAGTTCCGTCCAGAGCGTTTTGAAAATCCAAGTGCGATTCCGCAGCATGCGTTTAAACCGTTTGGAAACGGTCAGCGTG
CGTGTATCGGTCAGCAGTTCGCTCTTCATGAAGCAACGCTGGTACTTGGTATGATGCTAAAACACTTTGACTTTGAAGAT
CATACAAACTACGAGCTCGATATTAAAGAAACTTTAACGTTAAAACCTGAAGGCTTTGTGGTAAAAGCAAAATCGAAAAAA
ATTCCGCTTGGCGGTATTCCTTCACCTAGCACTGAACAGT

Primers

Table S6. Primer sequences.

Primer	Sequence
005	AACTTTAAGAAGGAGATATACATATGACAATTAAAGAAATGCCTCAGCCA
006	CAGTGCTAGGTGAAGGAATACCGCCAAGCGGAA
007	TGGCTGAGGCATTTCTTTAATTGTCATATGTATATCTCCTTCTTAAAGTT
008	TTCCGCTTGGCGGTATTCCTTCACCTAGCACTG
T7	TAATACGACTCACTATAGGG

Table S7. Primers for 87 single site-saturation library generation.

87NNK_for	TGCAGGAGACGGGTTA**NNK**ACAAGCTGGACGCATG
87NNK_rev	CATGCGTCCAGCTTGT**MNN**TAACCCGTCTCCTGCA

Table S8. Primers for 327/328 double site-saturation library generation.

327NDT_328NDT_for	GCTTATGGCCA**NDTNDT**CCTGCGTTTTCC
327NDT_328NDT_rev	GGAAAACGCAGG**AHNAHN**TGGCCATAAGC
327VHG_328VHG_for	GCTTATGGCCA**VHGVHG**CCTGCGTTTTCC
327VHG_328VHG_rev	GGAAAACGCAGG**CDBCDB**TGGCCATAAGC
327NDT_328VHG_for	GCTTATGGCCA**NDTVHG**CCTGCGTTTTCC
327NDT_328VHG_rev	GGAAAACGCAGG**CDBAHN**TGGCCATAAGC
327VHG_328NDT_for	GCTTATGGCCA**VHGNDT**CCTGCGTTTTCC
327VHG_328NDT_rev	GGAAAACGCAGG**AHNCDB**TGGCCATAAGC
327NDT_328TGG_for	GCTTATGGCCA**NDTTGG**CCTGCGTTTTCC
327NDT_328TGG_rev	GGAAAACGCAGG**CCAAHN**TGGCCATAAGC
327TGG_328NDT_for	GCTTATGGCCA**TGGNDT**CCTGCGTTTTCC
327TGG_328NDT_rev	GGAAAACGCAGG**AHNCCA**TGGCCATAAGC
327VHG_328TGG_for	GCTTATGGCCA**VHGTGG**CCTGCGTTTTCC
327VHG_328TGG_rev	GGAAAACGCAGG**CCACDB**TGGCCATAAGC
327TGG_328VHG_for	GCTTATGGCCA**TGGVHG**CCTGCGTTTTCC
327TGG_328VHG_rev	GGAAAACGCAGG**CDBCCA**TGGCCATAAGC
327TGG_328TGG_for	GCTTATGGCCA**TGGTGG**CCTGCGTTTTCC
327TGG_328TGG_rev	GGAAAACGCAGG**CCACCA**TGGCCATAAGC

Table S9. Primers for 181/184 double site-saturation library generation.

181NDT_184NDT_for	GGTCCGTGCA**NDT**GATGAA**NDT**ATGAACAAGC
181NDT_184NDT_rev	GCTTGTTCAT**AHN**TTCATC**AHN**TGCACGGACC
181VHG_184VHG_for	GGTCCGTGCA**VHG**GATGAA**VHG**ATGAACAAGC
181VHG_184VHG_rev	GCTTGTTCAT**CDB**TTCATC**CDB**TGCACGGACC
181NDT_184VHG_for	GGTCCGTGCA**NDT**GATGAA**VHG**ATGAACAAGC
181NDT_184VHG_rev	GCTTGTTCAT**CDB**TTCATC**AHN**TGCACGGACC
181VHG_184NDT_for	GGTCCGTGCA**VHG**GATGAA**NDT**ATGAACAAGC
181VHG_184NDT_rev	GCTTGTTCAT**AHN**TTCATC**CDB**TGCACGGACC
181NDT_184TGG_for	GGTCCGTGCA**NDT**GATGAA**TGG**ATGAACAAGC
181NDT_184TGG_rev	GCTTGTTCAT**CCA**TTCATC**AHN**TGCACGGACC

181TGG_184NDT_for	GGTCCGTGCA**TGG**GATGAA**NDT**ATGAACAAGC
181TGG_184NDT_rev	GCTTGTTCAT**AHN**TTCATC**CCA**TGCACGGACC
181VHG_184TGG_for	GGTCCGTGCA**VHG**GATGAA**TGG**ATGAACAAGC
181VHG_184TGG_rev	GCTTGTTCAT**CCA**TTCATC**CDB**TGCACGGACC
181TGG_184VHG_for	GGTCCGTGCA**TGG**GATGAA**VHG**ATGAACAAGC
181TGG_184VHG_rev	GCTTGTTCAT**CDB**TTCATC**CCA**TGCACGGACC
181TGG_184TGG_for	GGTCCGTGCA**TGG**GATGAA**TGG**ATGAACAAGC
181TGG_184TGG_rev	GCTTGTTCAT**CCA**TTCATC**CCA**TGCACGGACC

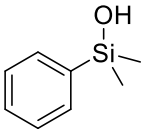
Syntheses and characterization of authentic standards

Syntheses

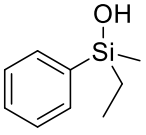
Silanol **2a** was purchased from commercial vendors. Other silanols were synthesized as described below.

General Procedure 1 (GP 1): According to a literature procedure,[8] the hydrosilane (1–5 mmol, 1.0 equiv) was added dropwise to a suspension of Pd/C (10 w-%, 0.1–0.4 mol-%) and H_2O (3 equiv) in ethyl acetate (0.8–1 M). The mixture was stirred at room temperature until H_2 evolution ceased (0.5–4 h). The suspension was filtered over neutral Al_2O_3 with ethyl acetate, and the solvent was removed under reduced pressure. Column chromatography on silica gel (eluent: hexanes/ethyl acetate) was carried out if necessary.

Dimethyl(phenyl)silanol (2a). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.41 (s, 6H), 2.05 (br s, 1H), 7.37–7.43 (m, 3H), 7.59–7.62 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 0.0, 128.0, 133.2, 139.2 ppm. GC (DB-WAXetr, Method A): t_R = 3.02 min.

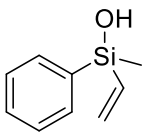


Ethyl(methyl)(phenyl)silanol (2b). Obtained from **1b** (0.15 g, 1.0 mmol) according to GP1 as a clear liquid (0.17 g, 1.0 mmol, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 1H), 0.83–0.88 (m, 2H), 0.99–1.03 (m, 3H), 1.81 (br s, 1H), 7.36–7.41 (m, 3H), 7.58–7.60 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (101



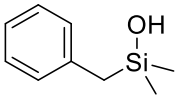
MHz, $CDCl_3$): δ = –2.1, 6.8, 8.3, 128.0, 129.8, 133.4, 138.3 ppm. GC (DB-WAXetr, Method B): t_R = 6.76 min.

Methyl(phenyl)(vinyl)silanol (2c). According to a literature procedure,[1c] the



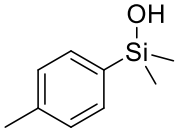
hydrosilane **1c** (0.37 mmol, 1.0 equiv) was dropwise added to a solution of [Ru(*p*-cymene)$_2$Cl$_2$] (0.88 mol-%) and H_2O (12 equiv) in MeCN (0.5 M). The mixture was stirred at room temperature until H_2 evolution ceased (45 min). The solvent was evaporated, the residue was filtered over neutral Al_2O_3 with hexanes and the solvent was removed under reduced pressure. Silanol **1c** (55 mg, 4.3 mmol, 90%) was obtained as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 3H), 1.83 (br s, 1H), 5.89 (dd, *J* = 20.3, 3.9 Hz, 1H), 6.14 (dd, *J* = 14.8, 3.9 Hz, 1H), 6.31 (dd, *J* = 20.3, 14.8 Hz, 1H), 7.36–7.44 (m, 3H), 7.60–7.62 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = –1.56, 128.1, 130.0, 133.7, 134.8, 136.6, 137.3 ppm. (DB-WAXetr, Method B): t_R = 7.10 min. The spectroscopic data are in accordance with those reported.[9]

Benzyldimethylsilanol (2d). Obtained from **1d** (0.15 g, 1.0 mmol) according to



GP1. The crude product was purified via column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford **2d** (65 mg, 0.39 mmol, 39% yield) as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 (s, 6H), 1.60 (br s, 1H), 2.18 (s, 2H), 7.06 (m_c, 2H), 7.10 (m_c, 1H), 7.24 (m_c, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = –0.6, 28.2, 124.4, 128.3, 128.6, 139.1 ppm. GC (DB-WAXetr, Method B): t_R = 6.61 min. The spectroscopic data are in accordance with those reported.[10]

Dimethyl(*p*-tolyl)silanol (2e). Obtained from **1e** (0.15 g, 1.0 mmol) according to



GP1. The crude product was purified via column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford **2e** (0.10 g, 0.67 mmol, 67% yield) as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (s, 6H), 1.80 (br s, 1H), 2.37 (s, 3H), 7.22 (m_c, 2H), 7.50 (m_c, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 0.2, 21.6, 128.9, 133.3, 135.7, 139.8 ppm. GC (DB-WAXetr,

Method B): t_R = 6.75 min. The spectroscopic data are in accordance with those reported.[11]

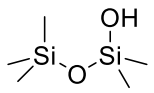
Dimethyl(thiophen-2-yl)silanol (2g). Obtained from **1g** (0.14 g, 1.0 mmol) according GP1 as a clear liquid (0.15 g, 0.92 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.47 (s, 6H), 2.05 (br s, 1H), 7.22 (dd, *J* = 4.7, 3.3 Hz, 1H), 7.37 (dd, *J* = 3.3, 0.8 Hz, 1H), 7.64 (dd, 4.7, 0.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 1.1, 128.4, 131.3, 134.8, 138.7 ppm. (DB-WAXetr, Method B): t_R = 6.77 min. The spectroscopic data are in accordance with those reported.[12]

Methyldiphenylsilanol (2i). Obtained from **1i** (0.85 g, 4.3 mmol) according to GP1 yield as a clear liquid (0.92 g, 4.3 mmol, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.68 (s, 3H), 2.34 (br s, 1H), 7.36–7.45 (m, 6H), 7.62 (m_c, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = –1.1, 128.1, 130.0, 134.1, 137.2 ppm. (DB-WAXetr, Method E): t_R = 3.99 min. The spectroscopic data are in accordance with those reported.[12]

Triethylsilanol (2j). Obtained from **1j** (0.50 g, 4.3 mmol) according to GP1 as a clear liquid (0.53 g, 4.0 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55–0.62 (m, 6H), 0.94–0.99 (m, 9H), 1.88 (br s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 5.9, 6.7 ppm. GC (DB-WAXetr, Method C): t_R = 2.56 min. The spectroscopic data are in accordance with those reported.[8]

Butyldimethylsilanol (2k). Obtained from **1k** (0.50 g, 4.3 mmol) according to GP1 in as a clear liquid (0.47 g, 0.36 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 6H), 0.57–0.61 (m, 2H), 0.88 (m_c, 3H), 1.29–1.37 (m, 4H), 1.94 (br s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = –0.2, 13.9, 17.6, 25.5, 26.5 ppm. GC (DB-WAXetr, Method C): t_R = 2.33 min. The spectroscopic data are in accordance with those reported.[13]

Pentamethyldisiloxanol (2l). Obtained from **1l** (0.15 g, 4.3 mmol) according to GP1

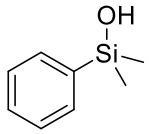


as a clear liquid (0.17 mg, 4.3 mmol, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 9H), 0.12 (s, 6H), 1.97 (br s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 0.6, 1.9 ppm. GC (DB-WAXetr, Method D): t_R = 2.37 min.

NMR Spectra

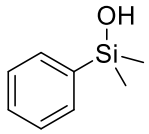
Dimethyl(phenyl)silanol (2a)

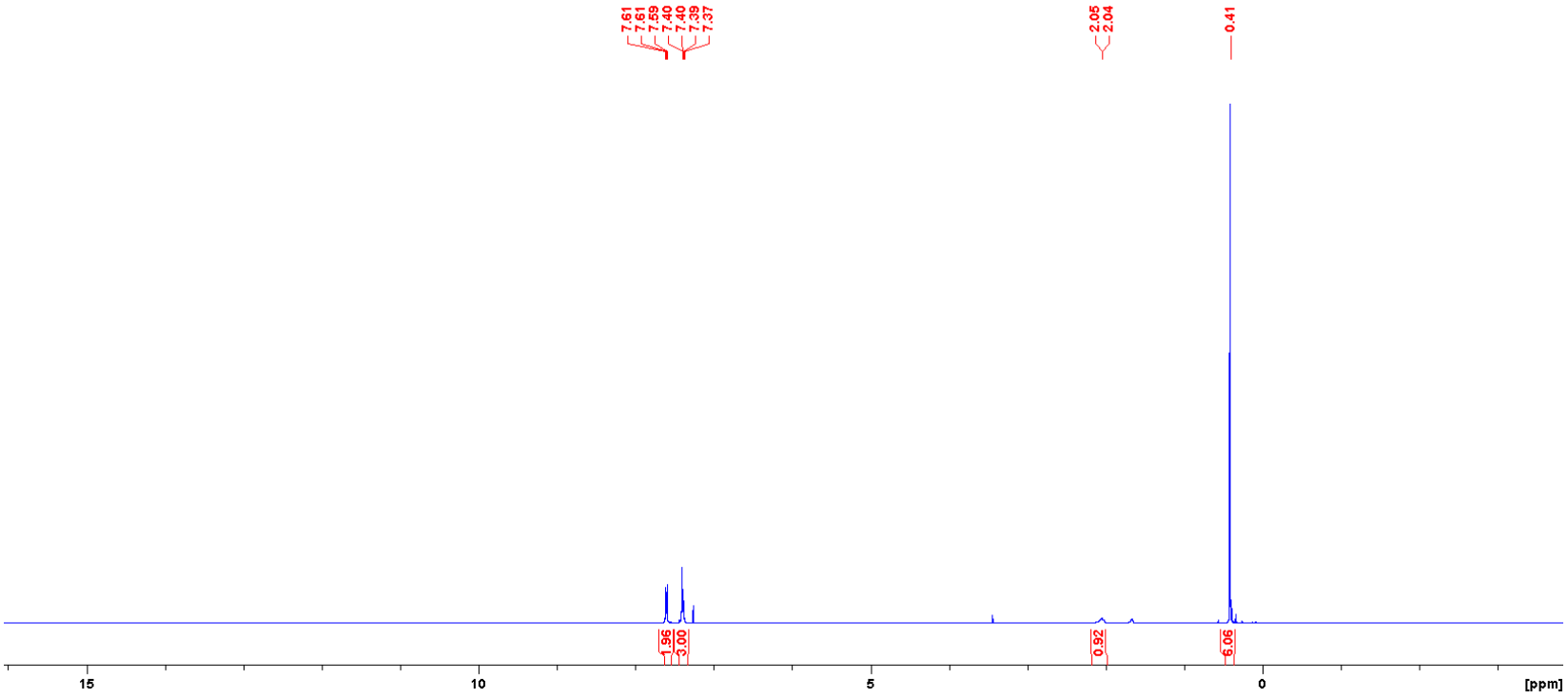
^{1}H NMR (400 MHz, $CDCl_3$):
enzymatic reaction



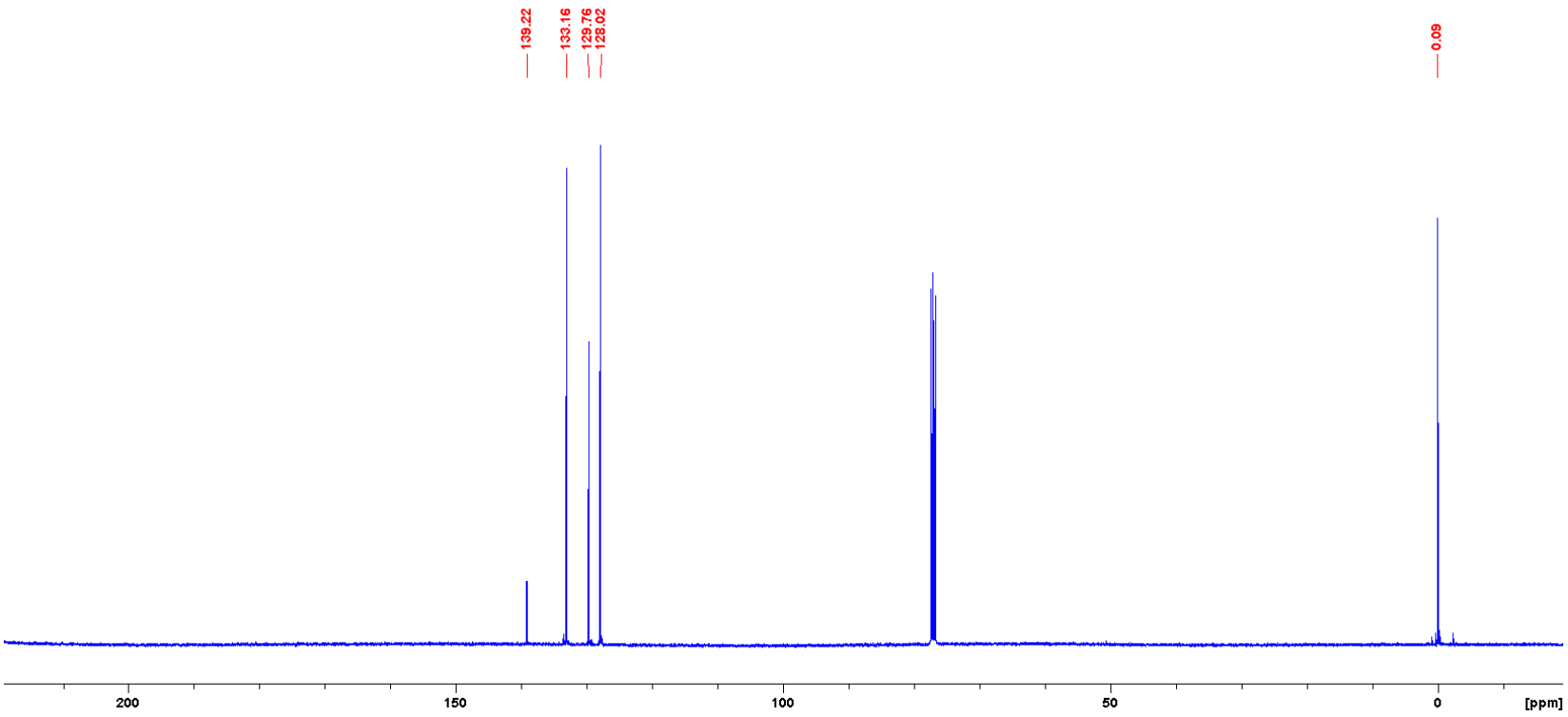
^{1}H NMR (400 MHz, $CDCl_3$):

authentic standard



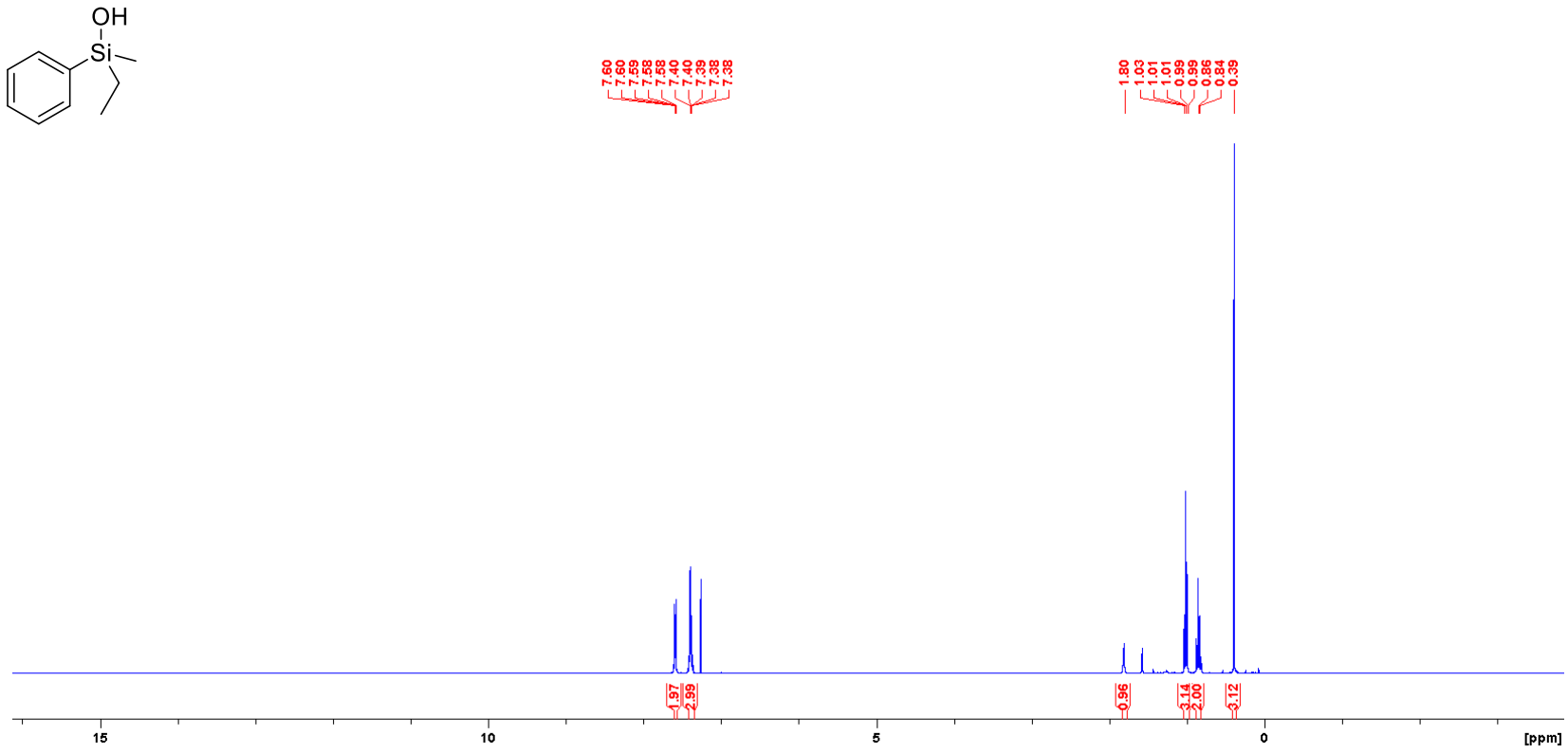


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):

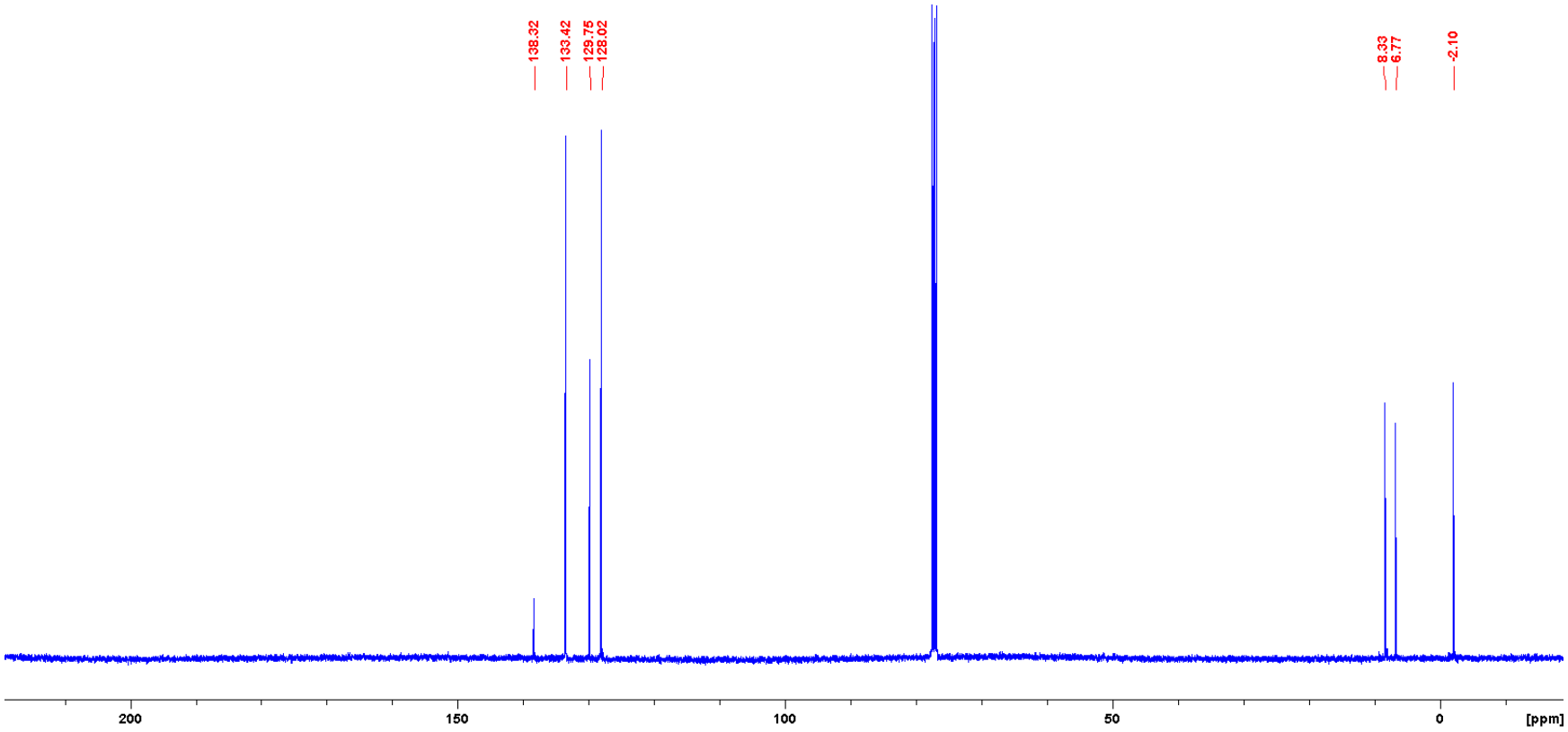


Ethyl(methyl)(phenyl)silanol (2b)

^{1}H NMR (400 MHz, $CDCl_3$):

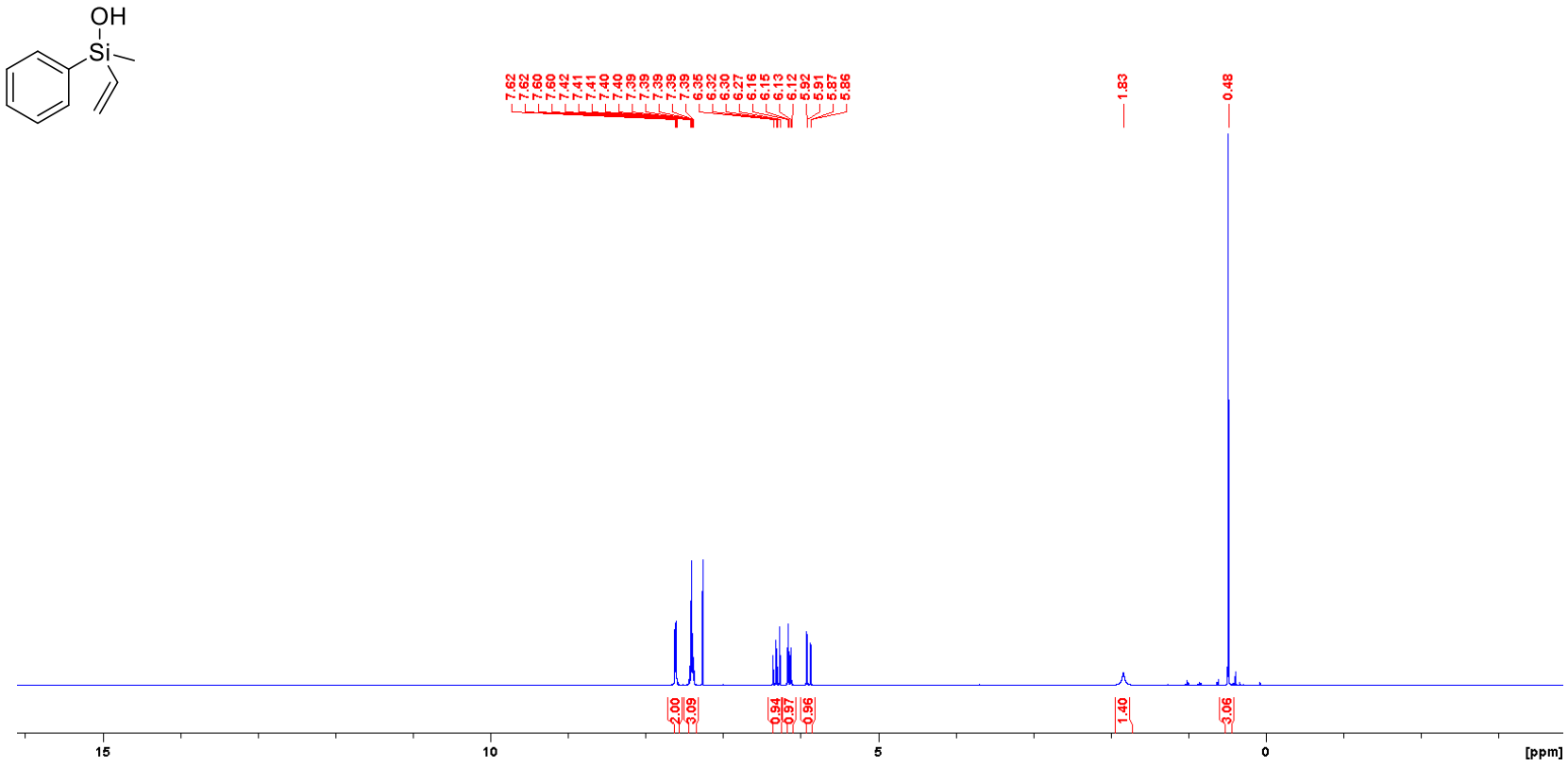


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):

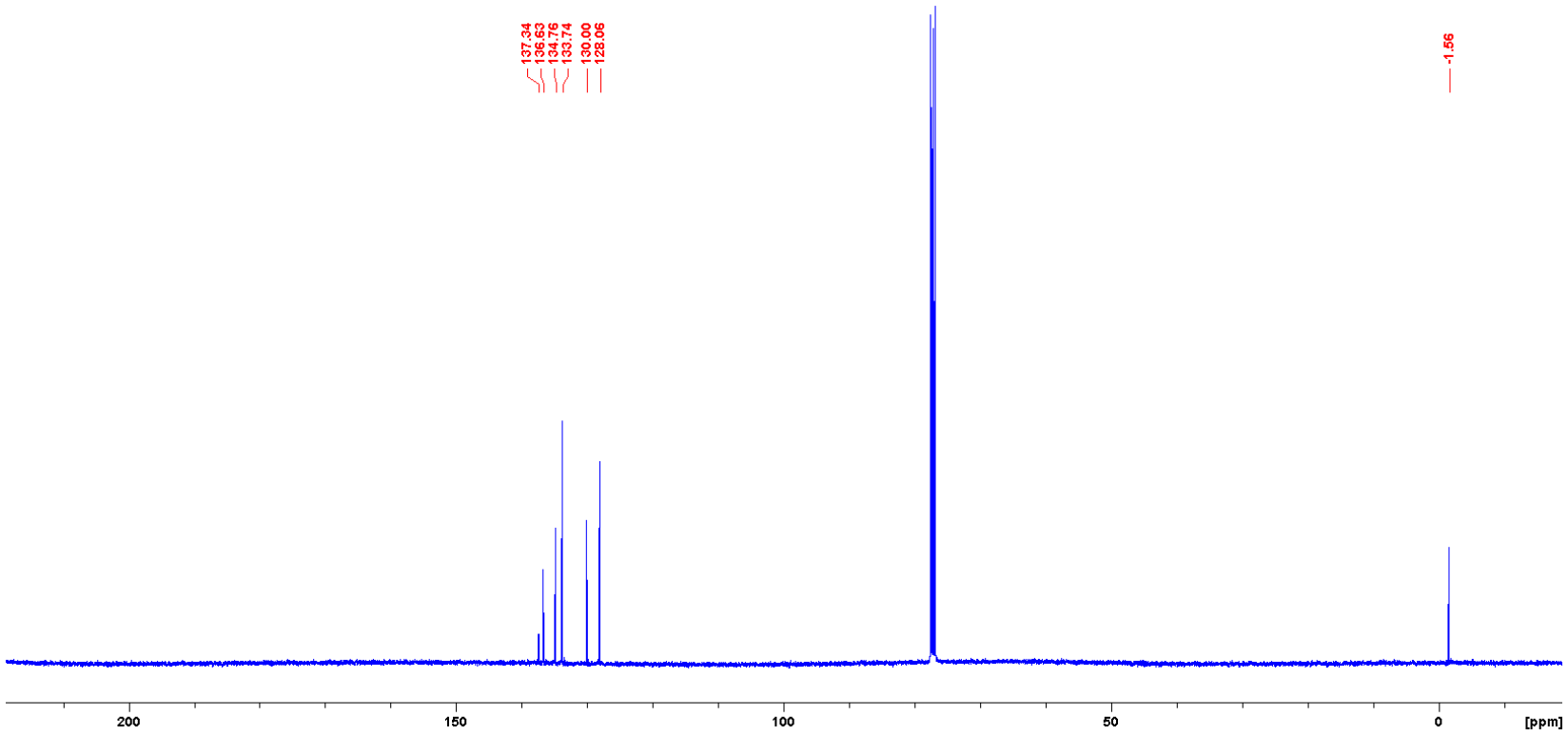


Methyl(phenyl)(vinyl)silanol (2c)

^{1}H NMR (400 MHz, $CDCl_3$):

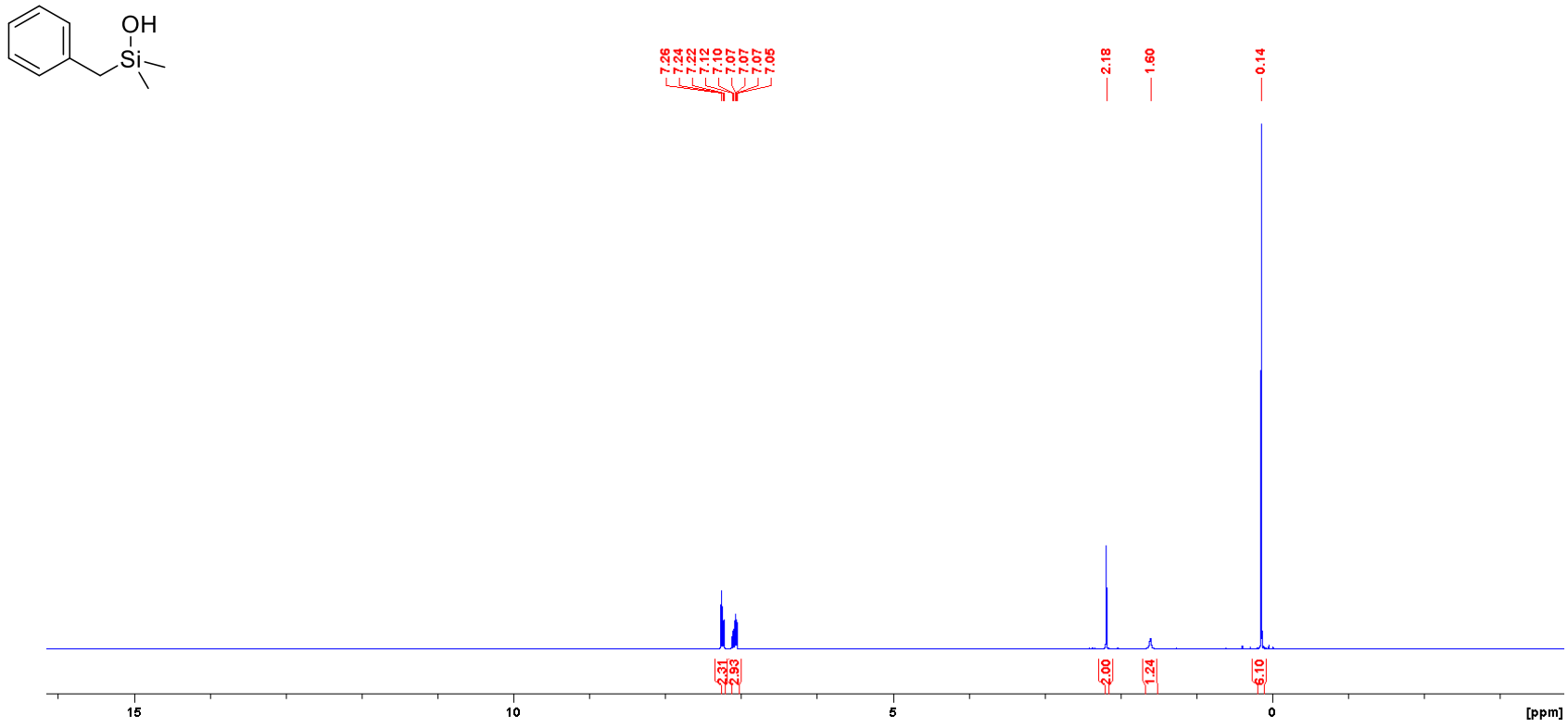


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):

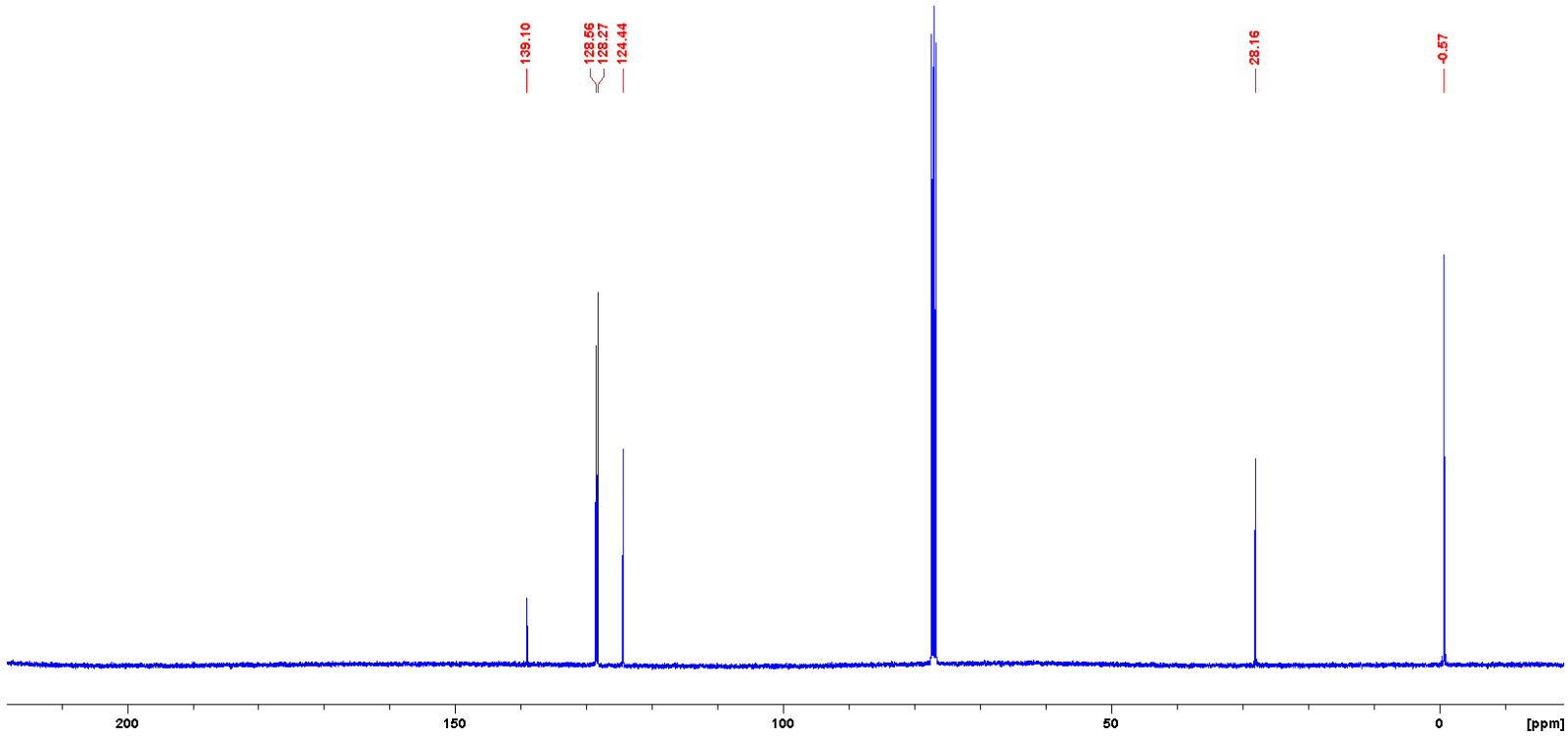


Benzyldimethylsilanol (2d)

^{1}H NMR (400 MHz, $CDCl_3$):

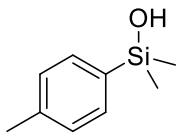


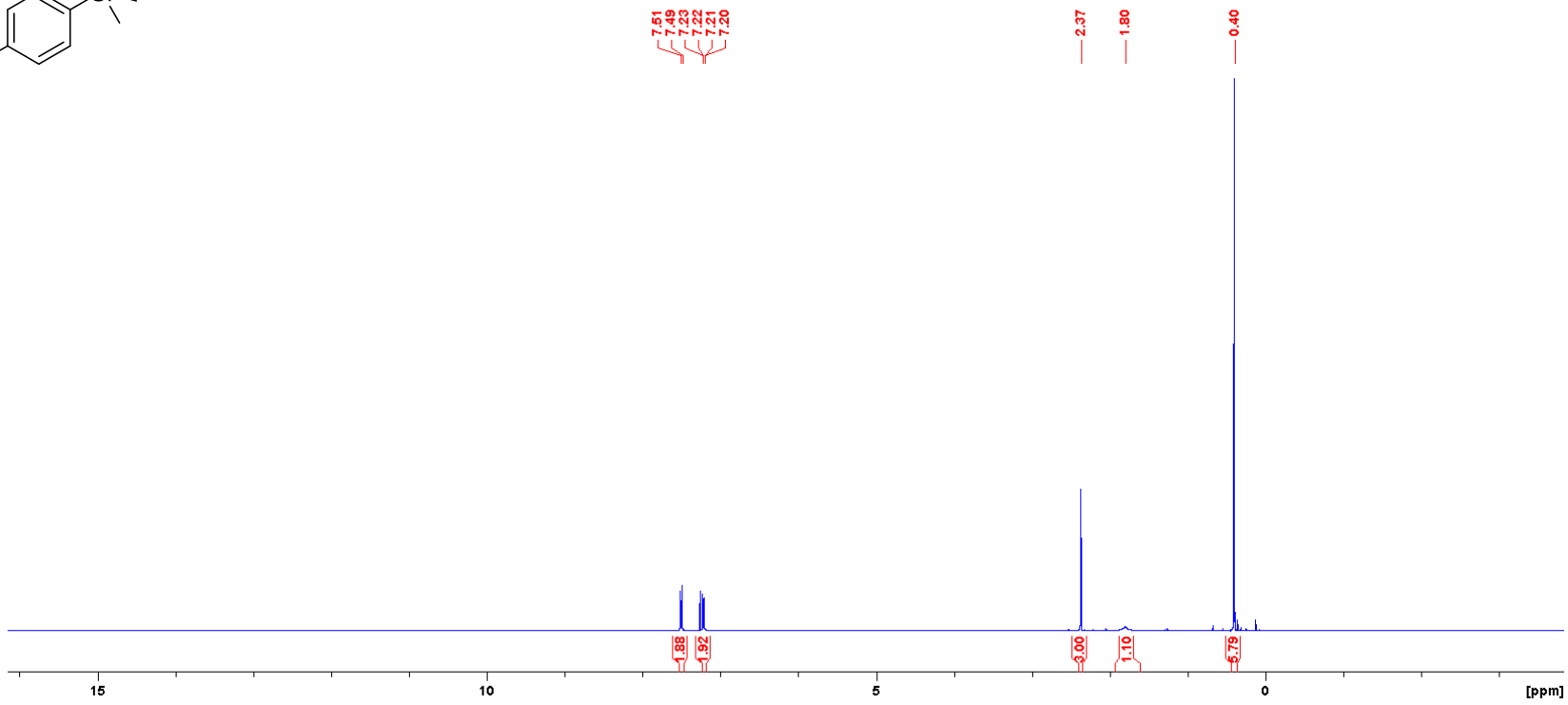
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



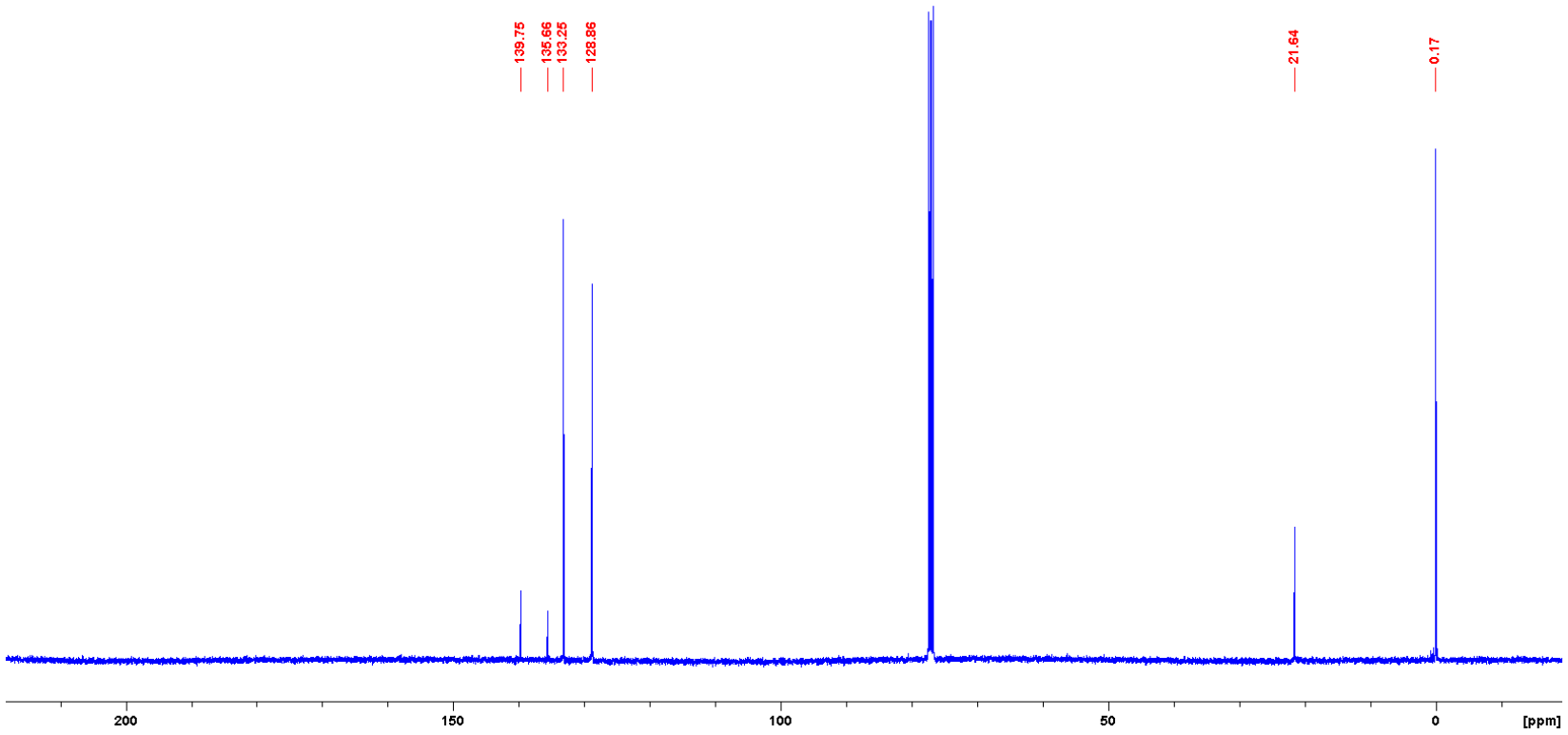
Dimethyl(*p*-tolyl)silanol (2e)

^{1}H NMR (400 MHz, $CDCl_3$):



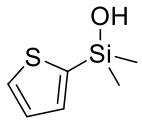


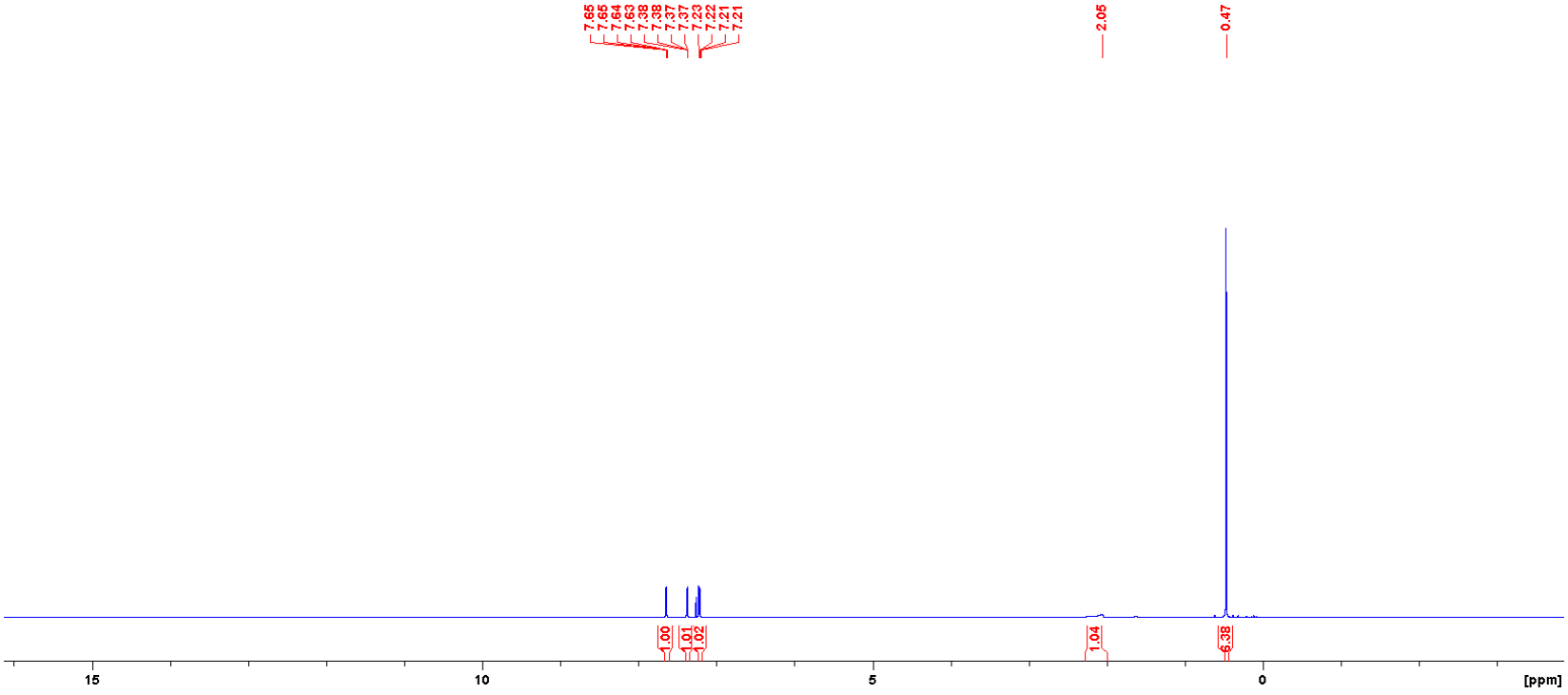
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



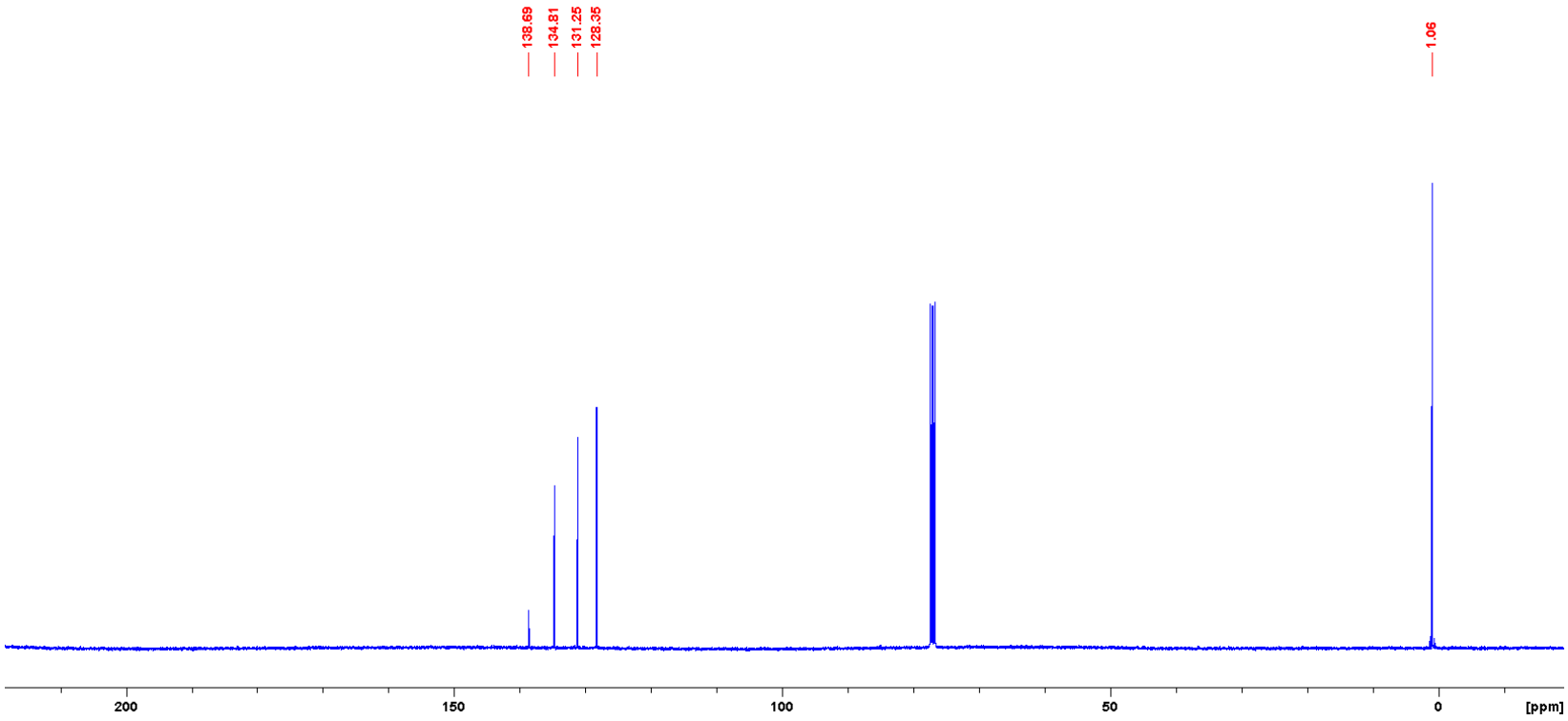
Dimethyl(thiophen-2-yl)silanol (2g)

^{1}H NMR (400 MHz, $CDCl_3$):



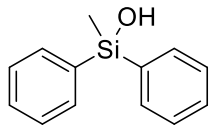


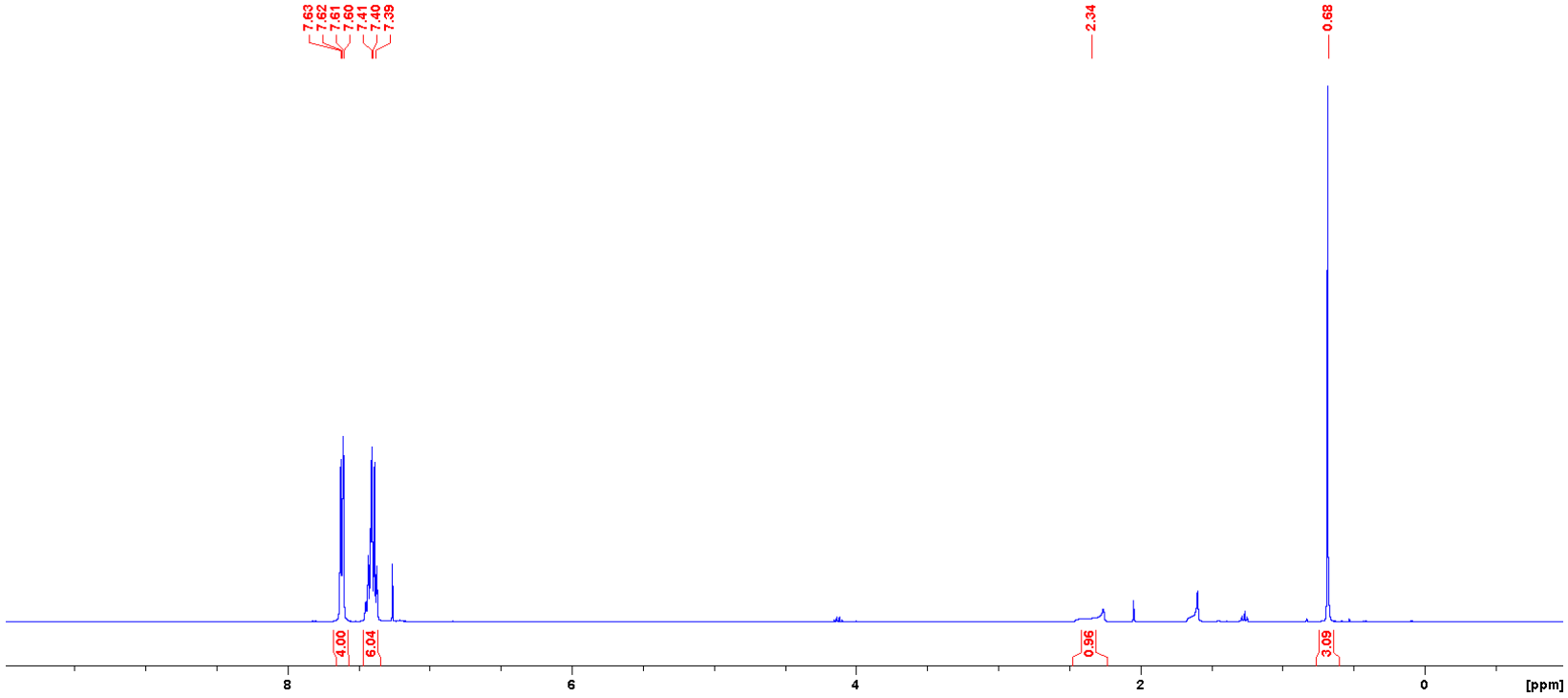
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



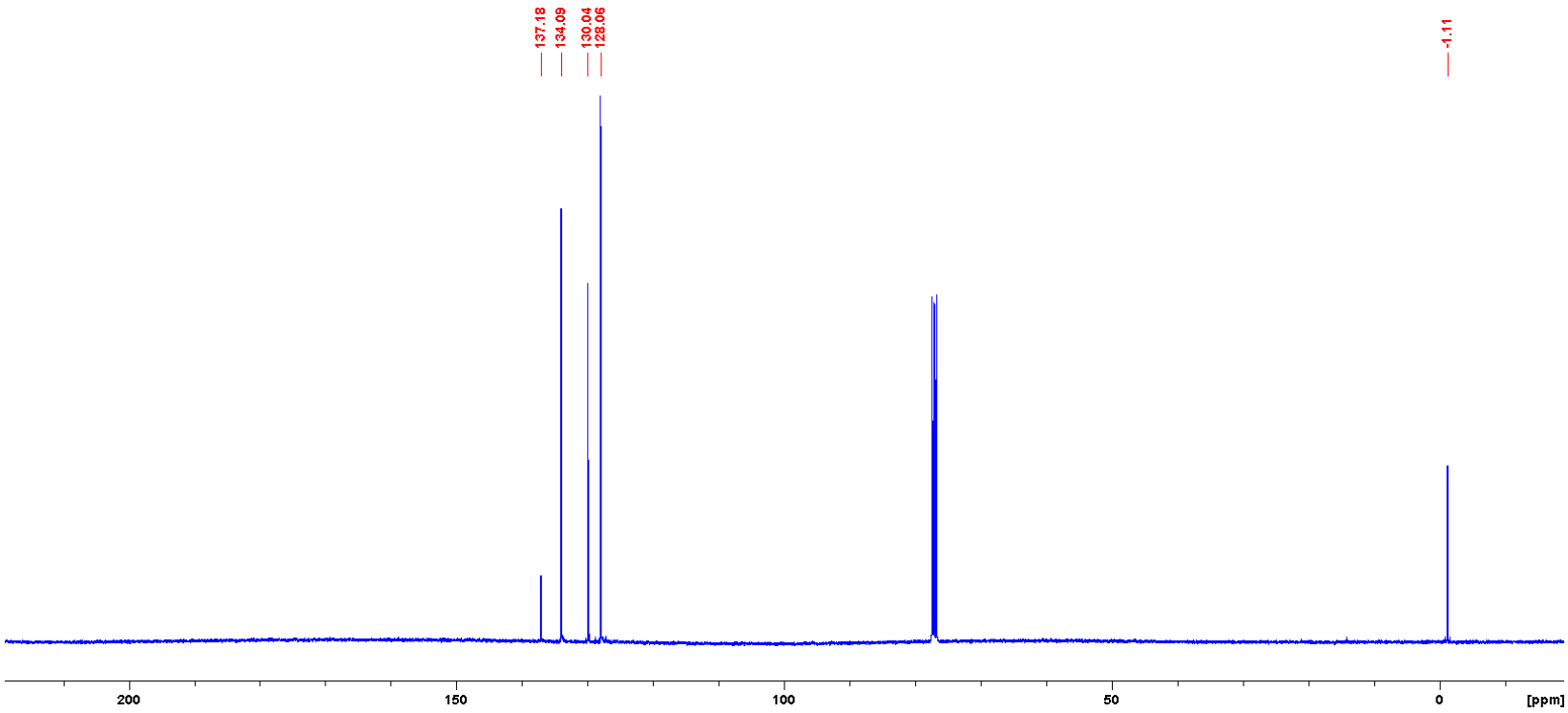
Methyldiphenylsilanol (2i)

^{1}H NMR (400 MHz, $CDCl_3$):



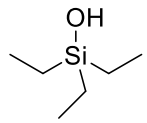


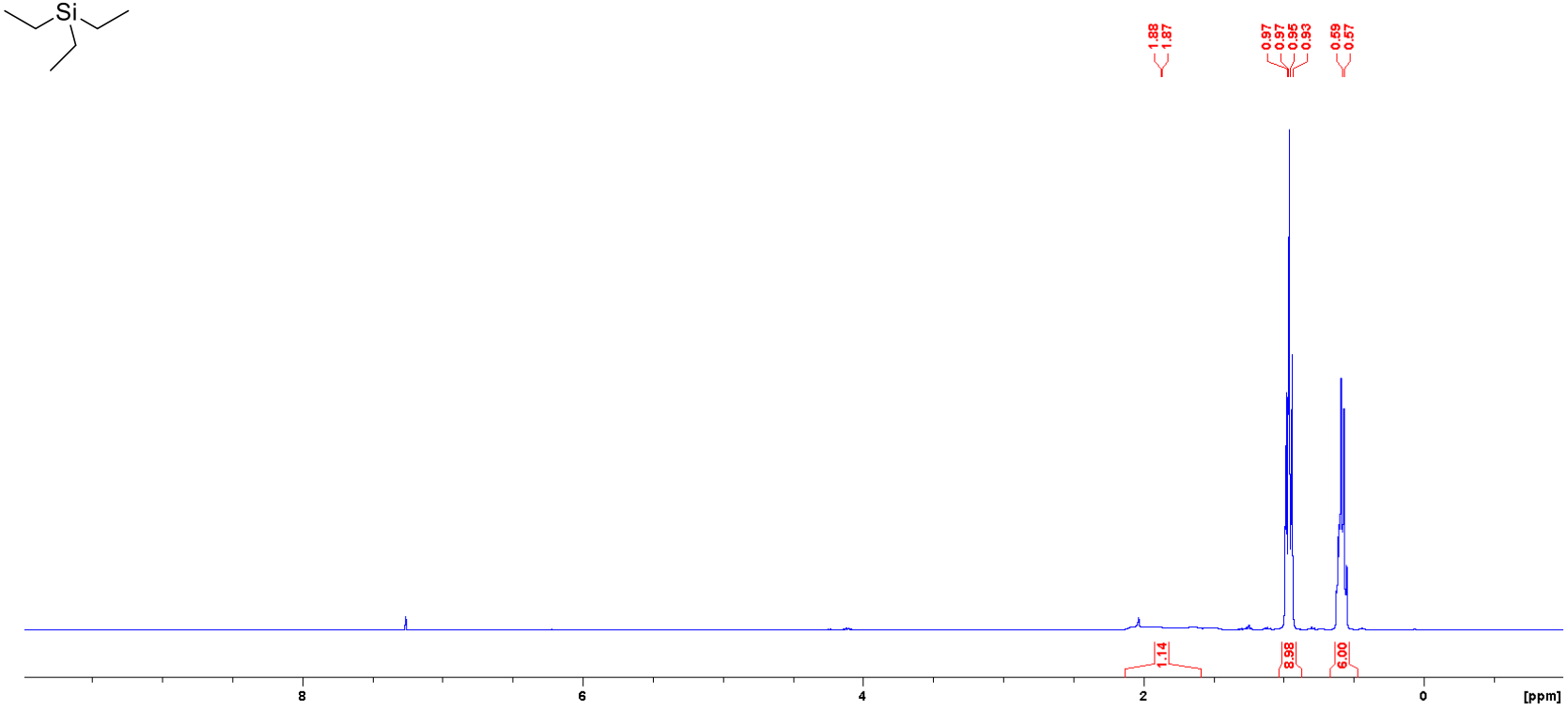
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



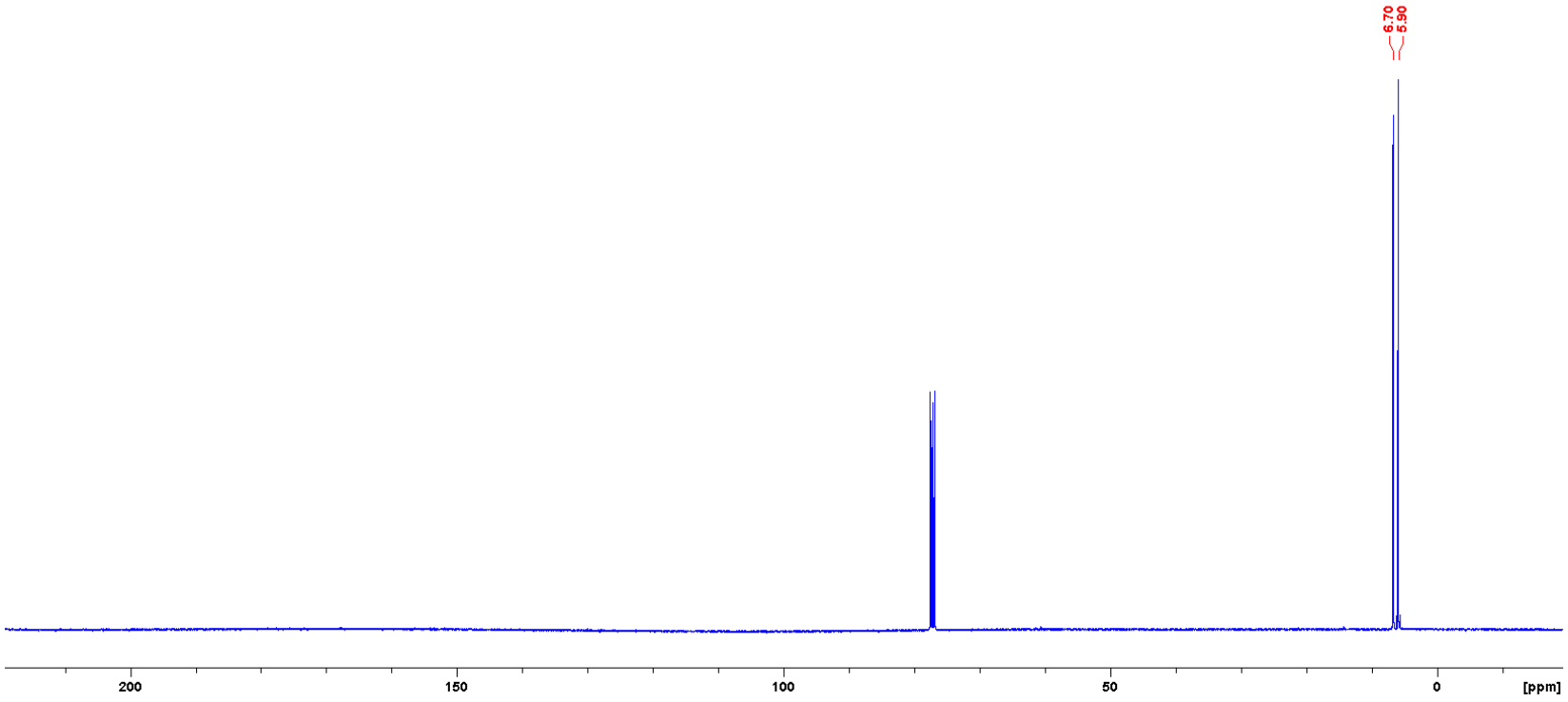
Triethylsilanol (2j)

^{1}H NMR (400 MHz, $CDCl_3$):



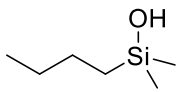


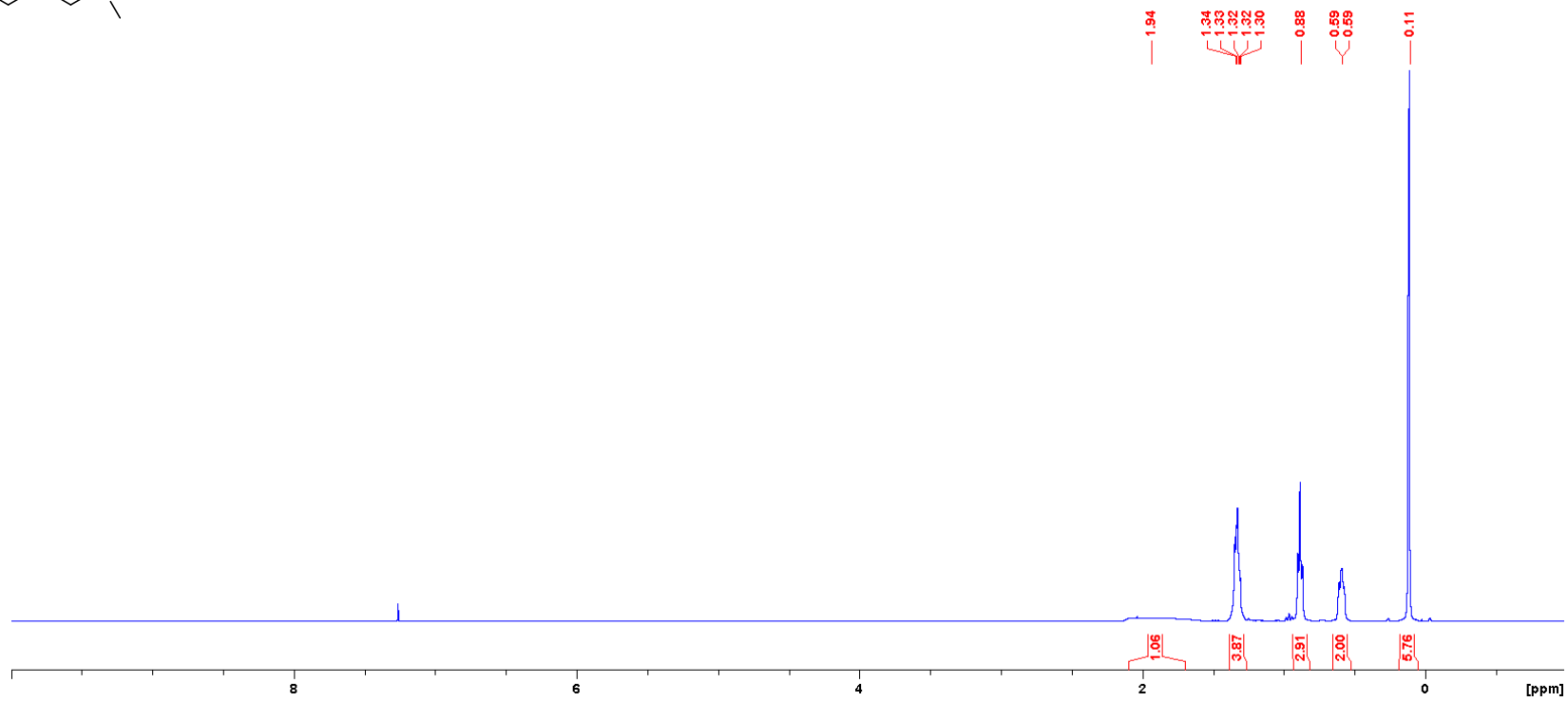
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



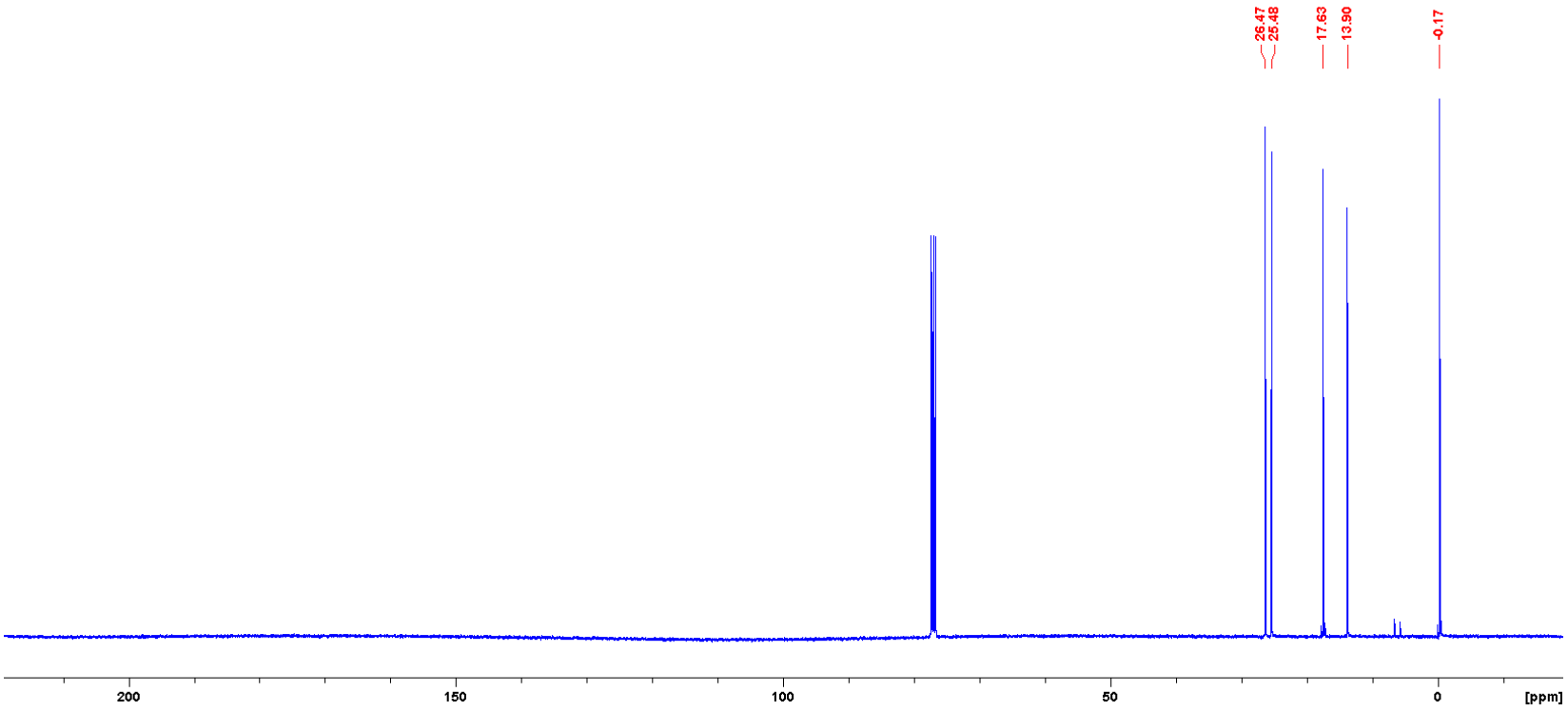
Butyldimethylsilanol (2k)

^{1}H NMR (400 MHz, $CDCl_3$):



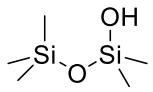


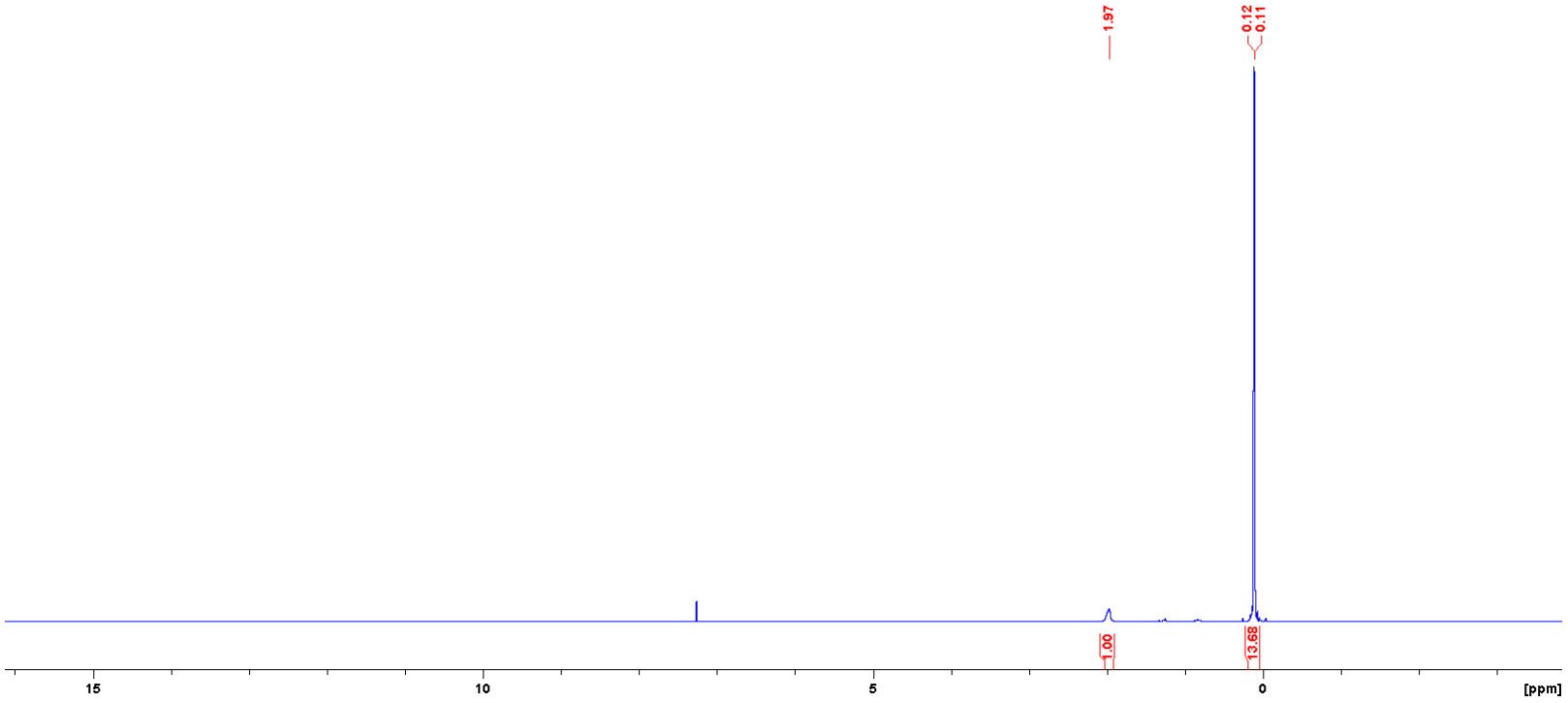
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



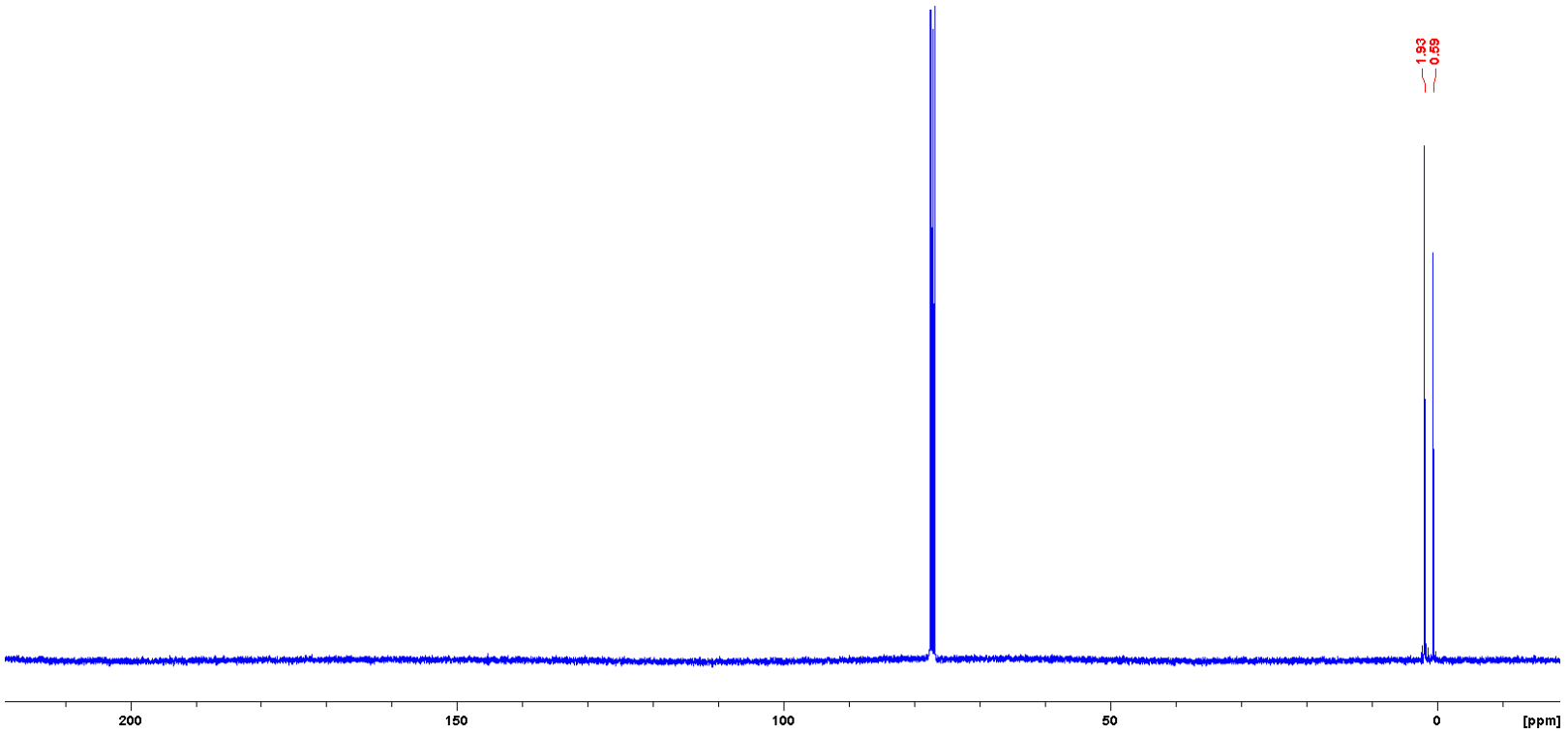
Pentamethyldisiloxanol (2l)

^{1}H NMR (400 MHz, $CDCl_3$):





$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$):



Computational Methods

Quantum Mechanics (Density Functional Theory) calculations

Density Functional Theory (DFT) calculations were carried out using Gaussian09.[14] A truncated model containing the porphyrin pyrrole core, Fe center, and a methanethiol to mimic cysteine as Fe-axial ligand was used. Geometry optimizations and frequency calculations were performed using (U)B3LYP[15] functional with the SDD basis set for iron and 6-31G(d) on all other atoms. Transition states had one negative force constant corresponding to the desired reaction coordinate. All stationary points were verified as minima or first-order saddle points by a vibrational frequency analysis. Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the optimized transition states connect the corresponding desired reactants and products. Enthalpies and entropies were calculated for 1 atm and 298.15 K. A correction to the harmonic oscillator approximation, as discussed by Truhlar and co-workers, was also applied to the entropy calculations by raising all frequencies below 100 cm^{-1} to 100 cm^{-1}[16] using Goodvibes v.1.0.1 python script.[17]
Single-point energy calculations were performed using the dispersion-corrected functional (U)B3LYP-D3(BJ)[18] with the Def2TZVP basis set on all atoms. The CPCM polarizable conductor model (diethyl ether, $\varepsilon = 4$)[19] to have an estimation of the dielectric permittivity in the enzyme active site was used during both the optimizations and single point calculations. The use of a dielectric constant $\varepsilon = 4$ has been proved to be a good and general model to account for electronic polarization and small backbone fluctuations in enzyme active sites.[20]
The methodology employed in this study, based on the use of (U)B3LYP density functional, has been extensively proved to accurately perform in the computational modeling of iron-oxo chemistry.[21]
Optimized DFT structures are illustrated with CYLView.[22]

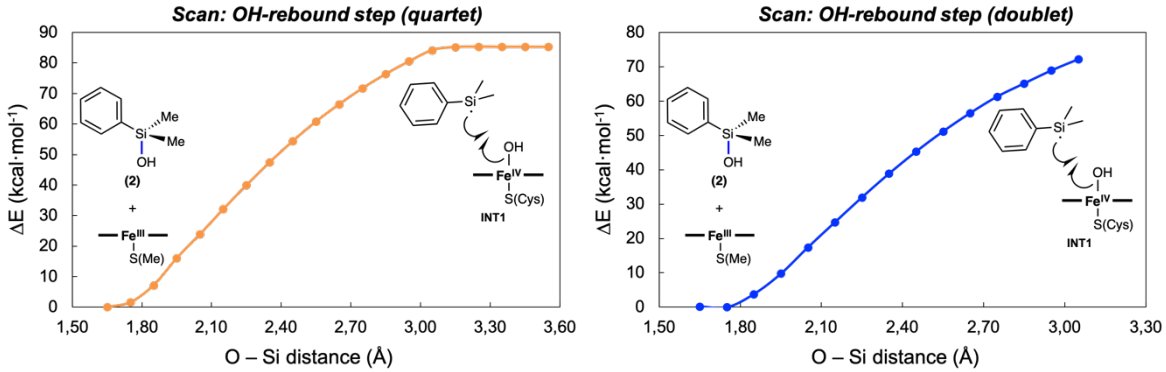
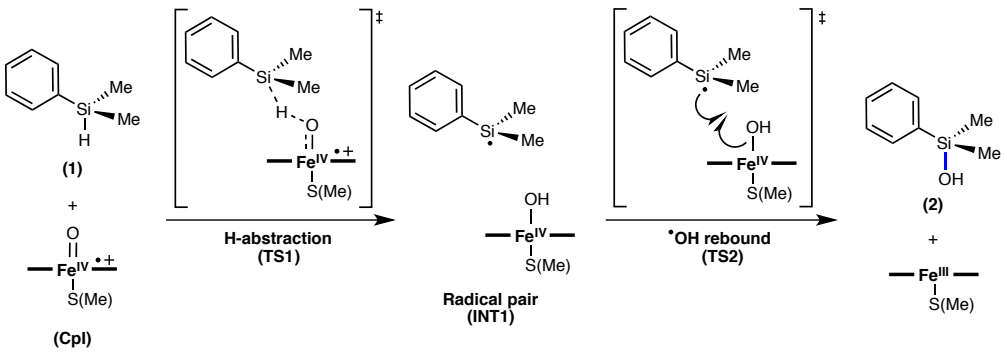


Figure S1. Relaxed scan calculations along the new Si–O bond formation coordinate in porphyrin-Fe-oxo catalyzed Si–H oxidations. The scan along the Si–O bond coordinate starts from the radical intermediate (**INT1**), generated after the first Si–H abstraction step (**TS1**) considering $PhMe_2SiH$ (**1a**) as substrate and considering both quartet and doublet electronic states. Scan calculations show the OH-rebound step (**TS2**) forms the new Si–O bond during the second step of the reaction mechanism corresponding to a barrierless process that generates the final product **2a**.



Substrate	spin state	$\Delta G^{\ddagger}$ TS1	ΔG INT1	$\Delta E^{\ddagger}$ TS1	ΔE INT1
$PhMe_2SiH$	doublet	20.6	7.0	7.0	-9.4
(1a)	**quartet**	**18.1**	**6.6**	**5.2**	**-9.3**
$BnMe_2SiH$	doublet	20.2	**8.1**	6.8	-8.3
	quartet	**19.6**	**8.4**	**6.7**	**-7.6**
$PhSiH_3$	doublet	21.3	7.1	8.9	-8.5
	quartet	**19.0**	**5.7**	**6.4**	**-9.6**
$BnSiH_3$	doublet	22.0	9.4	9.5	-6.4
	quartet	**20.7**	**8.8**	**8.0**	**-6.7**
$Me_2HSi–O–SiMe_2H$	doublet	19.9	-[a]	6.6	-[a]
	quartet	**17.7**	**7.6**	**4.8**	**-8.7**

[a] $Me_2HSi–O–SiMe_2H$ INT1 in the doublet electronic state could not be optimized.

Figure S2. Computed Gibbs energy barriers (***ΔG*‡ TS1**) and electronic activation barriers (***ΔE*‡ TS1**) for the rate-limiting H-abstraction step in porphyrin-Fe-oxo catalyzed Si–H oxidations for different hydrosilane substrates and the corresponding radical intermediate (***ΔG* INT1** and ***ΔE* INT1**) stabilities. Two electronic states (doublet and quartet) are considered. Electronic and Gibbs energies are given in kcal·mol^{-1}.

The phenyl (Ph) group substituent on the silicon center does not help stabilizing the silyl radical as compared to the benzyl (Bn) substituent, because orbital overlap between the phenyl π-aromatic system and the silicon 3p-orbital is difficult due to the long Si–C σ-bond and poor overlap between C_{2p} and Si_{3p} orbitals (see Ref. 23).

Figure S3. DFT optimized geometries for the lowest in energy H-abstraction transition states (**TS1**) and radical intermediates (**INT1**) of porphyrin-Fe-oxo catalyzed Si–H oxidation reactions involving **a**) $BnMe_2SiH$ and **b**) $Me_2HSi–O–SiMe_2H$ substrates. Distances are given in Å, angles in degrees, and spin densities (ρ_{spin}(Si)) in atomic units.

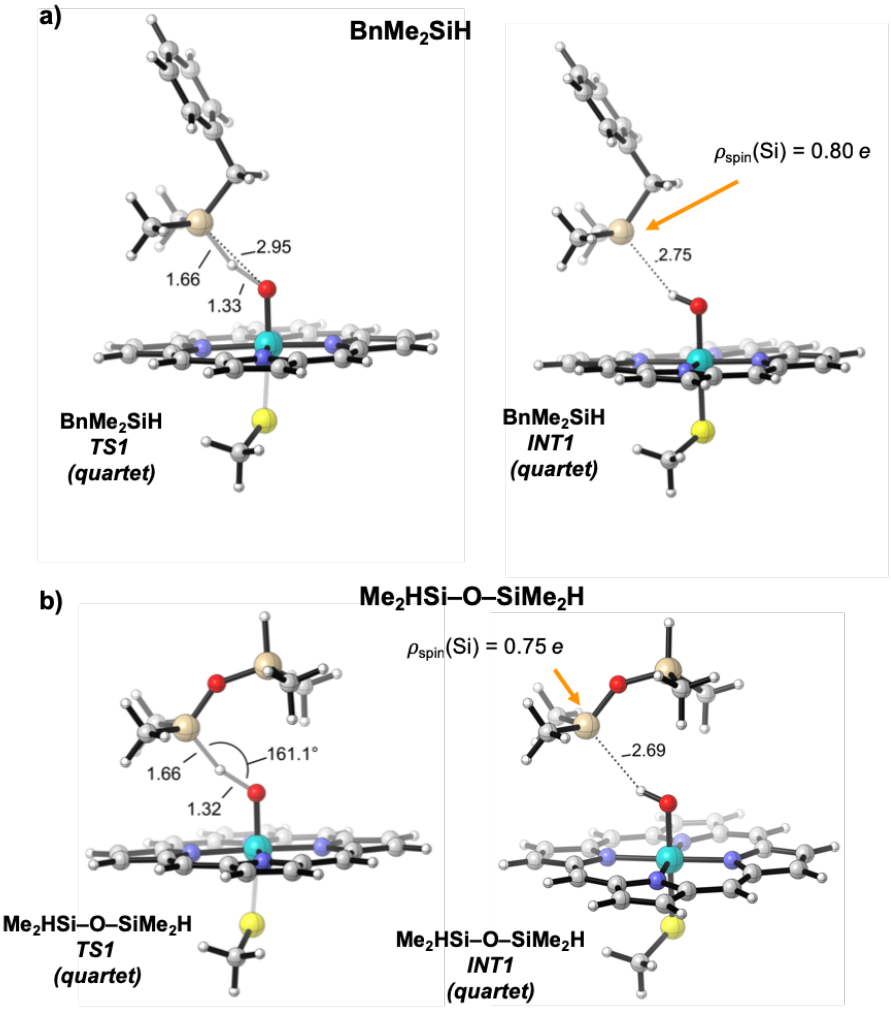


Figure S4. Spin density distribution in DFT optimized lowest in energy H-abstraction transition states (**TS1**) and radical intermediates (**INT1**) considering **a**) $PhMe_2SiH$ (**1a**), **b**) $BnMe_2SiH$ (**1d**), and **c**) $Me_2HSi–O–SiMe_2H$ as substrates. Spin density in the intermediate is highly localized on the Si atom, without delocalization on the neighboring substituents.

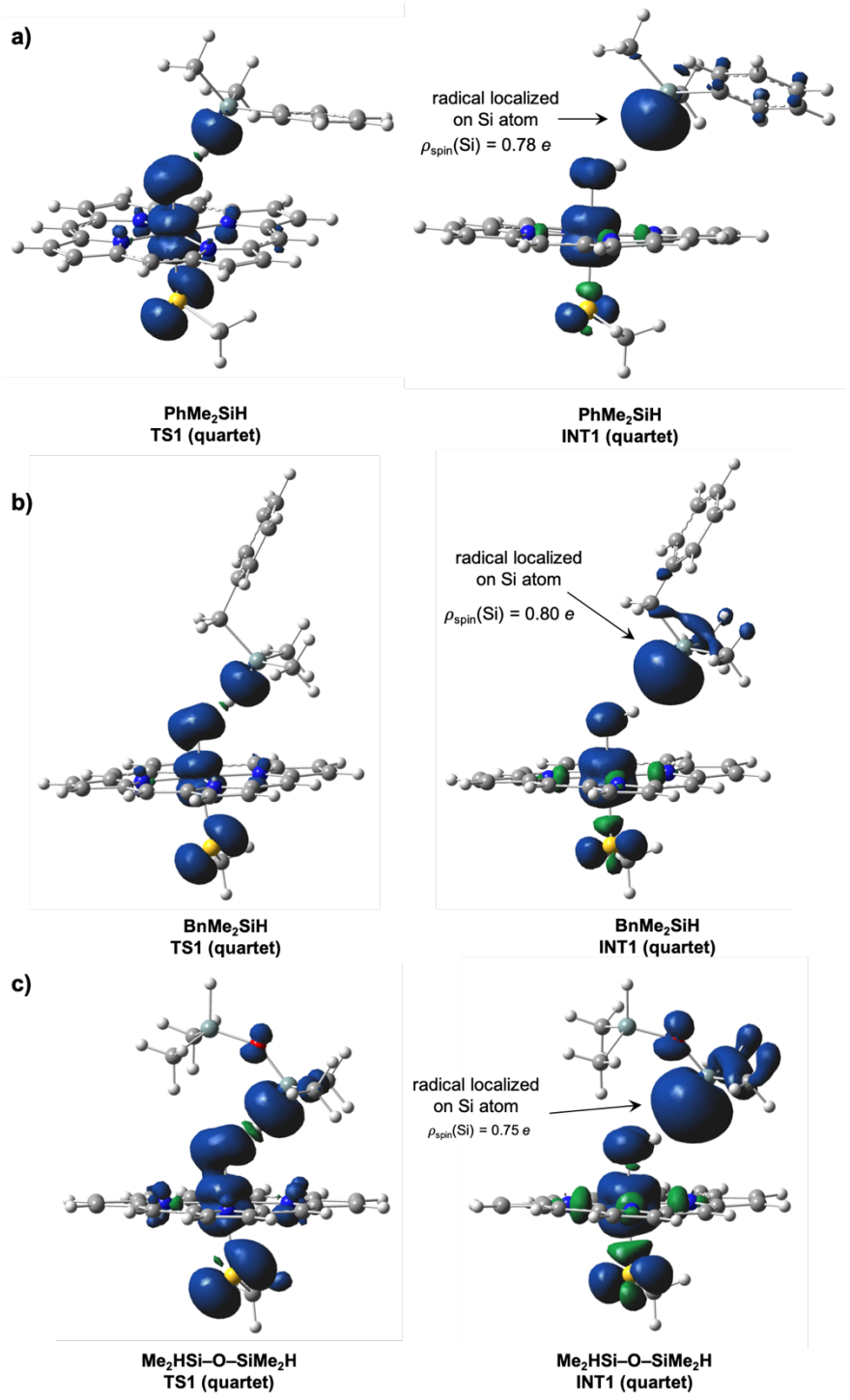
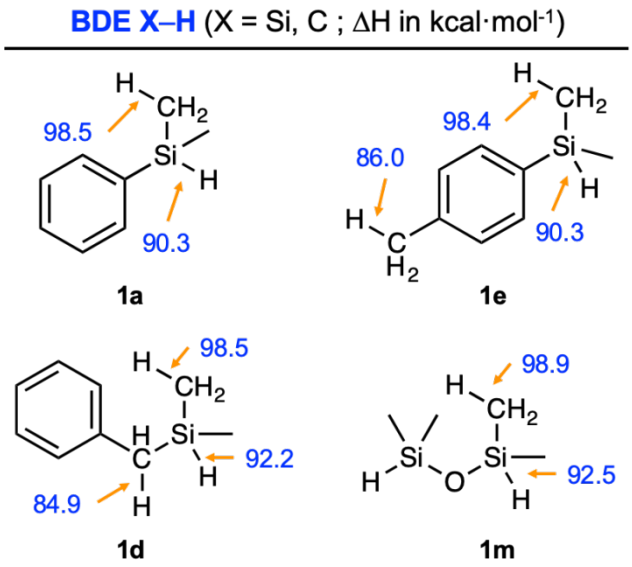


Figure S5. Bond Dissociation Energies (BDE) for selected X–H (X = Si, C) bonds computed at (U)B3LYP/Def2TZVP // (U)B3LYP/6-31G(d)+SDD(Fe) level. BDE is defined as the change in enthalpy, ΔH, for homolysis of the X–H bond: ΔH X-H(g) → A•(g) + X•(g)



Direct conjugation of the methyl group to the phenyl ring decreases the computed C–H BDE by ca. 12 kcal·mol^{-1} (BDE = 86.0 kcal·mol^{-1} for $PhCH_2$–H in **1e**; and BDE = 98.4 kcal·mol^{-1} for $PhHSi(CH_3)CH_2$–H in **1e**).
Direct conjugation of the silyl group to the phenyl ring decreases the computed Si–H BDE by only ca. 2 kcal·mol^{-1} (BDE = 90.3 kcal·mol^{-1} for **1a** and **1e**; BDE = 92.2 and 92.5 kcal·mol^{-1} for **1d** and **1m**, respectively).

The high chemoselectivity observed for enzymatic Si–H oxidations over other possible C–H oxidations can be directly attributed to the lower bond dissociation energies (BDE) of the Si–H bonds as compared to the sterically accessible C–H bonds from neighboring Si–Me groups.
On the other hand, lower BDEs are found for C–H bonds directly conjugated to the phenyl ring (in **1d** and **1e**), as compared to Si–H ones. The latter indicates that the enzyme active site is preventing the substrates to bind in catalytic poses that could allow the remote *para*-CH_3 group in **1e**, and the sterically hindered benzylic CH_2 group in **1d**, to be close enough to the catalytic Fe-oxo to react with it through an H-abstraction TS.

Table S10. Energies of all DFT optimized structures. Energies and thermochemistry parameters (at T = 298.15 K and P = 1 atm) of all computationally characterized stationary points: Electronic energies (E), electronic energies from high level single point calculations (E (SP)), Zero point energy (ZPE), enthalpy (H), entropic term (T·S), quasi-harmonic corrected entropic term (T·S-qh), free energy (G(T)), quasi-harmonic corrected free energy (G(T)-qh). All energies are given in a.u.

Structure	E/au	ZPE/au	H/au	T.S/au	T.qh-S/au	G(T)/au	qh-G(T)/au	E/au SP
$BnMe_2SiH$ - INT1 doublet	-2266.515737	0.521202	-2265.956618	0.112582	0.099124	-2266.069200	-2266.055742	-3407.159543370
$BnMe_2SiH$ - INT1 quartet	-2266.515328	0.521243	-2265.956057	0.114954	0.099965	-2266.071011	-2266.056022	-3407.158322640
$BnMe_2SiH$ - TS1 doublet	-2266.493424	0.515976	-2265.940412	0.109155	0.097840	-2266.049567	-2266.038253	-3407.135394300
$BnMe_2SiH$ - TS1 quartet	-2266.494717	0.515661	-2265.942104	0.110045	0.098343	-2266.052149	-2266.040447	-3407.135559810
Fe-OH reduced, doublet	-1626.402321	0.327591	-1626.050823	0.074449	0.072655	-1626.125272	-1626.123478	-2766.825006130
Fe-OH singlet	-1626.234697	0.329233	-1625.882021	0.072493	0.071021	-1625.954514	-1625.953041	-2766.655548200
Fe-OH triplet	-1626.258064	0.328431	-1625.905521	0.075720	0.073366	-1625.981240	-1625.978886	-2766.677979470
Fe-oxo doublet	-1625.614413	0.317637	-1625.273163	0.074664	0.072514	-1625.347827	-1625.345677	-2766.021307700
Fe-oxo quartet	-1625.614147	0.317678	-1625.272893	0.075247	0.073058	-1625.348140	-1625.345951	-2766.020965580
$PhMe_2SiH$ - INT1 doublet	-2227.202345	0.493542	-2226.672235	0.108773	0.096662	-2226.781008	-2226.768898	-3367.823277960
$PhMe_2SiH$ - INT1 quartet	-2227.202138	0.493387	-2226.672003	0.111331	0.097534	-2226.783333	-2226.769537	-3367.823089250
$PhMe_2SiH$ - TS1 doublet	-2227.178279	0.488463	-2226.654173	0.105668	0.095097	-2226.759840	-2226.749270	-3367.797101390
$PhMe_2SiH$ - TS1 quartet	-2227.179828	0.488016	-2226.656282	0.104047	0.095603	-2226.760329	-2226.751885	-3367.799972480
$[BnMe_2Si]^+$	-640.096402	0.194480	-639.889780	0.049072	0.048272	-639.938852	-639.938052	-640.306612183

$[BnMe_2Si]^-$	-640.253956	0.192619	-640.048831	0.051470	0.049682	-640.100301	-640.098513	-640.469745873
benzyl(dimethyl)silane (**1d**,) $BnMe_2SiH$	-640.906867	0.201718	-640.692558	0.050860	0.049021	-640.743419	-640.741579	-641.124964833
$[PhMe_2Si]^+$	-600.784131	0.166037	-600.606928	0.047229	0.046601	-600.654157	-600.653529	-600.973221168
$[PhMe_2Si]^-$	-600.940985	0.164714	-600.765024	0.048283	0.047177	-600.813307	-600.812201	-601.134044453
phenyldimethylsilane (**1a**), $PhMe_2SiH$	-601.591838	0.173874	-601.406626	0.047895	0.046455	-601.454522	-601.453081	-601.786939477
$Me_2HSi\text{-}O\text{-}SiMe_2H$ - TS1 doublet	-2440.785437	0.484403	-2440.263976	0.105623	0.098096	-2440.369598	-2440.362072	-3581.419541110
$Me_2HSi\text{-}O\text{-}SiMe_2H$ - TS1 quartet	-2440.785424	0.484844	-2440.262687	0.110550	0.100144	-2440.373238	-2440.362831	-3581.422328230
$[Me_2HSi\text{-}O\text{-}SiMe_2]^-$	-814.542275	0.161392	-814.367166	0.055068	0.051578	-814.422234	-814.418744	-814.751928188
$Me_2HSi\text{-}O\text{-}SiMe_2H$	-815.196441	0.170660	-815.011982	0.055118	0.050839	-815.067100	-815.062821	-815.408718805
$Me_2HSi\text{-}O\text{-}SiMe_2H$ - INT1 quartet	-2440.805027	0.490574	-2440.275584	0.115372	0.101398	-2440.390956	-2440.376982	-3581.443857210
$PhSiH_3$ - INT1 doublet	-2148.549811	0.434736	-2148.081819	0.102867	0.090054	-2148.184686	-2148.171873	-3289.122346540
$PhSiH_3$ - INT1 quartet	-2148.549841	0.434820	-2148.081824	0.102597	0.090524	-2148.184421	-2148.172349	-3289.124151320
$PhSiH_3$ - TS1 doublet	-2148.526152	0.429022	-2148.064997	0.097751	0.088230	-2148.162749	-2148.153228	-3289.094705590
$PhSiH_3$ - TS1 quartet	-2148.526745	0.429561	-2148.065331	0.096783	0.088233	-2148.162115	-2148.153565	-3289.098690270
$BnSiH_3$ - INT1 doublet	-2187.863145	0.462701	-2187.365858	0.106905	0.092786	-2187.472762	-2187.458643	-3328.456585310
$BnSiH_3$ - INT1 quartet	-2187.863014	0.462779	-2187.365653	0.108159	0.093421	-2187.473812	-2187.459074	-3328.457060480
$BnSiH_3$ - TS1 doublet	-2187.841236	0.456881	-2187.350872	0.101347	0.091040	-2187.452219	-2187.441912	-3328.431325750
$BnSiH_3$ - TS1 quartet	-2187.841758	0.457287	-2187.351163	0.101278	0.091173	-2187.452441	-2187.442336	-3328.433621740

$PhSiH_3$	-522.937826	0.115557	-522.814280	0.040570	0.039009	-522.854849	-522.853288	-523.087513806
$BnSiH_3$	-562.253712	0.143556	-562.101001	0.042870	0.041952	-562.143871	-562.142953	-562.425103201

Table S11. Cartesian coordinates of optimized stationary points. XYZ structures

Fe-oxo doublet

Fe	0.09068	0.04068	-0.37939
N	1.83605	-0.95266	-0.13980
N	-0.89460	-1.72644	-0.26448
N	1.05836	1.79050	-0.13876
N	-1.67215	1.01450	-0.29077
C	3.08986	-0.39855	-0.03343
C	-2.25773	-1.91646	-0.32449
C	2.02949	-2.30951	-0.20327
C	-0.33662	-2.98888	-0.30988
C	2.41247	1.97551	-0.02837
C	-2.92496	0.46144	-0.36070
C	0.50933	3.04679	-0.17617
C	-1.86043	2.37699	-0.31610
C	4.09459	-1.43348	-0.01736
C	-2.56321	-3.32535	-0.37428
C	3.43656	-2.61979	-0.13012
C	-1.37430	-3.98778	-0.37116
C	2.72585	3.38297	0.01082
C	-3.92886	1.49569	-0.41868
C	1.54214	4.04953	-0.08544
C	-3.26727	2.68562	-0.39240
H	5.15897	-1.25569	0.06688
H	-3.56427	-3.73506	-0.41559
H	3.84700	-3.62104	-0.15463
H	-1.19645	-5.05491	-0.40603
H	3.72545	3.78847	0.09999
H	-4.99492	1.31577	-0.47166
H	1.36532	5.11737	-0.09009
H	-3.67640	3.68738	-0.41901
C	3.36165	0.96044	0.03249
C	-3.20406	-0.90259	-0.36357
C	-0.84991	3.32642	-0.26413
C	1.02069	-3.26252	-0.29772
H	4.40215	1.25703	0.12022
H	-4.24738	-1.19695	-0.42043
H	-1.14425	4.37100	-0.28694
H	1.32109	-4.30445	-0.34481
O	0.16369	0.04653	-2.00171
S	-0.02840	-0.38366	2.20800
C	-1.71003	-0.04437	2.80906
H	-2.41412	-0.73229	2.32525
H	-1.74465	-0.22260	3.88791
H	-2.01527	0.98066	2.58484

Fe-oxo quartet

Fe	0.08915	0.03752	-0.38148
N	1.84386	-0.93800	-0.14395
N	-0.87793	-1.73359	-0.26855
N	1.04202	1.79902	-0.13287
N	-1.68226	0.99739	-0.29264
C	3.09253	-0.37167	-0.03502
C	-2.24030	-1.93627	-0.32358
C	2.05071	-2.29267	-0.20696
C	-0.30896	-2.99200	-0.30818
C	2.39414	1.99619	-0.02474
C	-2.92998	0.43436	-0.36525
C	0.48141	3.04986	-0.16972
C	-1.88194	2.35864	-0.31459
C	4.10692	-1.39711	-0.01883
C	-2.53272	-3.34783	-0.36634
C	3.46050	-2.58965	-0.13292
C	-1.33799	-3.99971	-0.36270
C	2.69501	3.40652	0.01420
C	-3.94273	1.45992	-0.42362
C	1.50509	4.06221	-0.08013
C	-3.29131	2.65532	-0.39322
H	5.16942	-1.20918	0.06711
H	-3.53015	-3.76661	-0.40403
H	3.88046	-3.58694	-0.15715
H	-1.15077	-5.06535	-0.39330
H	3.69105	3.82105	0.10156
H	-5.00709	1.27095	-0.47893
H	1.31840	5.12838	-0.08481
H	-3.70891	3.65362	-0.41826
C	3.35230	0.98928	0.03428
C	-3.19645	-0.93226	-0.36663
C	-0.88043	3.31703	-0.25739
C	1.05028	-3.25469	-0.29918
H	4.39020	1.29469	0.12266
H	-4.23681	-1.23695	-0.42285
H	-1.18436	4.35891	-0.27799
H	1.35913	-4.29421	-0.34440
O	0.17116	0.07540	-2.00313
S	-0.02502	-0.38302	2.20488
C	-1.70981	-0.05937	2.80592
H	-2.40803	-0.75244	2.32096
H	-1.74294	-0.24022	3.88442
H	-2.02379	0.96350	2.58401

Fe-OH singlet

Fe	0.08220	0.09047	-0.18783
N	1.69434	-1.18403	-0.14281
N	-1.18637	-1.56929	-0.22614
N	1.29320	1.61827	-0.15735
N	-1.51773	1.26841	-0.24891
C	3.01509	-0.83888	-0.07113
C	-2.54439	-1.56364	-0.32414
C	1.65885	-2.55974	-0.16170
C	-0.80019	-2.88697	-0.26237
C	2.67497	1.60718	-0.08825
C	-2.84407	0.89495	-0.33108
C	0.93029	2.94952	-0.16112
C	-1.51515	2.63881	-0.24909
C	3.84524	-2.01812	-0.04507
C	-3.05080	-2.91798	-0.40198
C	3.00145	-3.08735	-0.10525
C	-1.96602	-3.73904	-0.36475

C	3.18042	2.95809	-0.05715
C	-3.68784	2.06713	-0.37232
C	2.10337	3.78721	-0.10288
C	-2.86461	3.14894	-0.31940
H	4.92647	-2.01293	0.00754
H	-4.09739	-3.18328	-0.48181
H	3.24874	-4.14137	-0.11120
H	-1.93628	-4.82046	-0.40736
H	4.23025	3.21715	-0.00576
H	-4.76825	2.04309	-0.43658
H	2.08314	4.86948	-0.09705
H	-3.12597	4.19936	-0.33163
C	3.47564	0.47682	-0.04400
C	-3.32364	-0.40661	-0.36400
C	-0.37061	3.42773	-0.20463
C	0.51084	-3.34492	-0.22919
H	4.54881	0.63102	0.01320
H	-4.39948	-0.53381	-0.43911
H	-0.50499	4.50497	-0.20612
H	0.65628	-4.42069	-0.25820
O	0.04073	-0.17854	-1.98296
S	0.04747	-0.31543	2.00192
C	-1.61760	-0.03736	2.69043
H	-2.33839	-0.74204	2.26446
H	-1.55627	-0.20980	3.76920
H	-1.95975	0.98184	2.49588
H	0.91902	-0.52784	-2.21809

Fe-OH triplet

Fe	0.06062	-0.00524	-0.22430
N	1.13312	1.70983	-0.21601
N	1.77354	-1.06433	-0.09795
N	-1.63976	1.06642	-0.23386
N	-1.00154	-1.70614	-0.27277
C	0.63856	2.99271	-0.14334
C	1.88422	-2.43255	-0.03868
C	2.50479	1.82463	-0.20309
C	3.05450	-0.57202	-0.12017
C	-1.75692	2.43557	-0.18192
C	-0.50857	-2.98630	-0.19471
C	-2.91624	0.57470	-0.38172
C	-2.36344	-1.82216	-0.41002
C	1.72609	3.93740	-0.11081
C	3.27520	-2.81106	-0.00126
C	2.88024	3.21528	-0.15564
C	3.99995	-1.65964	-0.05901
C	-3.14485	2.81331	-0.27018
C	-1.59015	-3.93465	-0.28948
C	-3.86130	1.66193	-0.40302
C	-2.73778	-3.21436	-0.43060
H	1.60284	5.01162	-0.06026
H	3.63109	-3.83212	0.04791
H	3.90174	3.57330	-0.14519
H	5.07544	-1.53715	-0.06216
H	-3.50427	3.83410	-0.24776
H	-1.46706	-5.00956	-0.25617
H	-4.93184	1.54087	-0.50817
H	-3.75346	-3.57437	-0.53313
C	-0.70417	3.33884	-0.11616
C	0.82918	-3.33313	-0.06664
C	-3.26176	-0.76558	-0.47710
C	3.40564	0.76992	-0.18094
H	-0.95061	4.39457	-0.07108
H	1.07060	-4.38983	-0.01705
H	-4.31393	-1.00658	-0.58770
H	4.46310	1.01294	-0.18012
O	0.11469	-0.04052	-2.05676
S	0.10849	-0.05702	2.08643
C	-1.60223	0.02603	2.72788
H	-2.20352	-0.80290	2.34644
H	-1.53235	-0.05932	3.81709
H	-2.08202	0.97381	2.47452
H	0.40153	0.84961	-2.33055

Fe-OH reduced, doublet

Fe	0.06553	-0.00047	-0.20232
N	1.54887	-1.38720	-0.14283
N	-1.34669	-1.45351	-0.26957
N	1.48616	1.45040	-0.14329
N	-1.40909	1.38614	-0.27739
C	2.90071	-1.17387	-0.08337
C	-2.70434	-1.29948	-0.35522
C	1.37129	-2.74609	-0.16052
C	-1.10877	-2.80123	-0.27242
C	2.84589	1.29781	-0.08073
C	-2.75844	1.17142	-0.36517
C	1.24786	2.79949	-0.16396
C	-1.23151	2.74275	-0.28836
C	3.60402	-2.43844	-0.06373
C	-3.35110	-2.59425	-0.40273
C	2.65477	-3.41410	-0.11138
C	-2.35995	-3.52678	-0.35086
C	3.49195	2.59280	-0.05897
C	-3.46188	2.43584	-0.42219
C	2.49997	3.52467	-0.11023
C	-2.51342	3.41185	-0.37416
H	4.68111	-2.54572	-0.02020
H	-4.42139	-2.74833	-0.46962
H	2.79146	-4.48879	-0.11587
H	-2.44754	-4.60649	-0.36627
H	4.56313	2.74796	-0.01223
H	-4.53773	2.54201	-0.49204
H	2.58817	4.60442	-0.11453
H	-2.64872	4.48652	-0.39583
C	3.51419	0.07636	-0.05059
C	-3.37165	-0.07808	-0.40035
C	-0.00547	3.40178	-0.23118
C	0.14597	-3.40428	-0.21998
H	4.59926	0.10036	-0.00315
H	-4.45560	-0.10211	-0.47056
H	-0.02938	4.48811	-0.24454
H	0.17084	-4.49063	-0.22873
O	0.14208	0.00598	-2.07383
S	0.05786	-0.00883	2.17383
C	-1.67274	0.02952	2.78663
H	-2.24187	-0.83382	2.42778

H	-1.66053	0.00562	3.88225
H	-2.19090	0.93891	2.46612
H	1.09461	-0.00937	-2.26467

BnMe$_2$SiH - TS1 doublet

Fe	1.52402	0.06213	-0.02247
N	2.33779	0.61078	-1.79804
N	1.72681	-1.88135	-0.53804
N	1.51793	2.00000	0.56090
N	0.87322	-0.48509	1.78375
C	2.56437	1.88988	-2.24046
C	1.36076	-2.97565	0.20454
C	2.68696	-0.21817	-2.83354
C	2.16823	-2.37108	-1.74471
C	1.87173	3.08806	-0.19479
C	0.62802	-1.76657	2.22589
C	1.12137	2.49532	1.77548
C	0.56622	0.34271	2.84291
C	3.07179	1.86686	-3.59296
C	1.58892	-4.18809	-0.54494
C	3.14742	0.55927	-3.96086
C	2.08956	-3.81239	-1.75371
C	1.68972	4.30352	0.56333
C	0.14190	-1.74227	3.58259
C	1.22562	3.93510	1.78897
C	0.10622	-0.43507	3.96590
H	3.33219	2.74719	-4.16652
H	1.38550	-5.18575	-0.17725
H	3.48255	0.13930	-4.90056
H	2.38307	-4.43749	-2.58735
H	1.89984	5.29778	0.19022
H	-0.12276	-2.62154	4.15597
H	0.97323	4.56280	2.63404
H	-0.19503	-0.01873	4.91865
C	2.35389	3.04409	-1.49806
C	0.84328	-2.92701	1.49301
C	0.67984	1.72662	2.84508
C	2.61383	-1.60508	-2.81273
H	2.58996	3.99131	-1.97290
H	0.59964	-3.87088	1.97069
H	0.40104	2.24817	3.75541
H	2.92789	-2.13398	-3.70715
O	0.01476	0.18416	-0.78700
S	3.89249	-0.07901	0.63988
C	4.03579	-1.24874	2.03732
H	3.69460	-2.24904	1.75444
H	5.09837	-1.31145	2.29696
H	3.47512	-0.91034	2.91242
H	-1.19986	0.03306	-0.12444
C	-3.70568	0.25939	-1.33184
Si	-2.75479	-0.07713	0.29630
H	-3.40000	1.24808	-1.69523
H	-3.36196	-0.47233	-2.07305
C	-5.20420	0.18846	-1.16273
C	-5.94823	1.32702	-0.80845
C	-5.89511	-1.02441	-1.32756
C	-7.33081	1.25747	-0.62830
H	-5.43709	2.27903	-0.68341
C	-7.27760	-1.09680	-1.14809
H	-5.34225	-1.91775	-1.60962
C	-8.00308	0.04422	-0.79609
H	-7.88392	2.15450	-0.36139
H	-7.78895	-2.04580	-1.28869
H	-9.07960	-0.01041	-0.65893
C	-3.11558	1.24175	1.60175
H	-2.86392	2.24247	1.23283
H	-4.17768	1.23792	1.87702
H	-2.52780	1.05864	2.50799
C	-3.08381	-1.82029	0.94926
H	-2.79326	-2.57958	0.21442
H	-2.51397	-2.00267	1.86701
H	-4.14884	-1.95636	1.17512

BnMe$_2$SiH - TS1 quartet

Fe	-1.56152	0.09374	-0.04040
N	-1.40173	1.92471	0.80584
N	-0.84408	-0.73443	1.69355
N	-2.33722	0.90541	-1.69211
N	-1.90657	-1.74513	-0.76770
C	-1.69039	3.12364	0.20706
C	-0.66964	-2.06887	1.95091
C	-0.89808	2.22904	2.04941
C	-0.42679	-0.06854	2.82112
C	-2.49816	2.24416	-1.95474
C	-1.56092	-2.94261	-0.18494
C	-2.80442	0.24312	-2.80075
C	-2.42353	-2.05749	-2.00054
C	-1.37680	4.21411	1.09790
C	-0.12017	-2.25473	3.27457
C	-0.88526	3.65874	2.24057
C	0.03028	-1.01280	3.81409
C	-3.06430	2.42971	-3.27174
C	-1.88809	-4.03560	-1.06771
C	-3.25580	1.18948	-3.79540
C	-2.42624	-3.48704	-2.19247
H	-1.51770	5.26117	0.86175
H	0.10709	-3.21589	3.71800
H	-0.53843	4.15546	3.13772
H	0.40740	-0.74307	4.79238
H	-3.28578	3.39245	-3.71440
H	-1.71903	-5.08050	-0.84035
H	-3.66671	0.91807	-4.75941
H	-2.78891	-3.98737	-3.08128
C	-2.20087	3.27802	-1.07813
C	-0.99206	-3.10003	1.07313
C	-2.85520	-1.13575	-2.94801
C	-0.44505	1.31022	2.98833
H	-2.38513	4.29118	-1.42161
H	-0.78885	-4.11480	1.40135
H	-3.24824	-1.52590	-3.88165
H	-0.07785	1.70363	3.93119
O	0.02498	0.16532	-0.73851
S	-3.64571	0.09601	1.17467
C	-4.25133	-1.60824	1.39729
H	-3.53598	-2.18734	1.99065

H	-5.19571	-1.55852	1.94796
H	-4.40465	-2.10809	0.43818
H	1.14271	-0.02600	-0.05135
C	3.64469	0.24232	-1.30272
Si	2.75010	-0.17128	0.34228
H	3.27676	-0.45849	-2.06223
H	3.31796	1.24310	-1.61123
C	5.14912	0.17888	-1.20064
C	5.84336	-1.01764	-1.44946
C	5.89883	1.30780	-0.82767
C	7.23286	-1.08404	-1.33119
H	5.28659	-1.90281	-1.74913
C	7.28834	1.24459	-0.70854
H	5.38559	2.24816	-0.63896
C	7.96336	0.04711	-0.95850
H	7.74558	-2.02063	-1.53596
H	7.84454	2.13463	-0.42485
H	9.04518	-0.00259	-0.86907
C	3.11315	-1.94583	0.89270
H	2.79297	-2.66857	0.13356
H	4.18723	-2.08960	1.06576
H	2.58313	-2.17698	1.82334
C	3.20229	1.07431	1.69450
H	2.92506	2.09376	1.40318
H	2.68104	0.83787	2.62840
H	4.28160	1.05947	1.89214

$BnMe_2SiH$ - INT1 doublet

Fe	-1.73483	0.07941	0.00925
N	-1.60479	2.04451	0.45880
N	-0.79688	-0.37946	1.73089
N	-2.65954	0.54207	-1.72154
N	-1.98025	-1.87744	-0.37679
C	-1.97645	3.09640	-0.34007
C	-0.47076	-1.63695	2.18402
C	-1.07567	2.59250	1.60221
C	-0.38560	0.50229	2.70506
C	-2.88561	1.79974	-2.22325
C	-1.47157	-2.93073	0.34652
C	-3.19518	-0.33766	-2.62865
C	-2.59955	-2.42655	-1.47375
C	-1.68357	4.34363	0.32243
C	0.18074	-1.54296	3.46556
C	-1.13204	4.03160	1.52806
C	0.22625	-0.21930	3.79131
C	-3.56745	1.70879	-3.49233
C	-1.79931	-4.17596	-0.30110
C	-3.76558	0.38527	-3.74007
C	-2.50463	-3.86434	-1.42402
H	-1.88237	5.32141	-0.09729
H	0.53775	-2.39126	4.03561
H	-0.77995	4.69983	2.30349
H	0.63142	0.24279	4.68249
H	-3.85608	2.56051	-4.09488
H	-1.51617	-5.15258	0.07029
H	-4.24751	-0.07905	-4.59091
H	-2.91755	-4.53149	-2.16981
C	-2.55985	2.99325	-1.59601
C	-0.76150	-2.82977	1.53407
C	-3.18678	-1.71993	-2.51475
C	-0.52007	1.88314	2.65756
H	-2.80269	3.91554	-2.11354
H	-0.43311	-3.75116	2.00372
H	-3.64412	-2.29338	-3.31439
H	-0.14143	2.45221	3.50034
O	-0.15214	0.12599	-0.88704
S	-3.77194	0.19453	1.12662
C	-4.16277	-1.44266	1.84326
H	-3.37967	-1.76676	2.53345
H	-5.09794	-1.32642	2.40067
H	-4.30233	-2.19948	1.06820
H	0.59337	0.12895	-0.24277
C	3.99923	0.52099	-1.24893
Si	3.14465	-0.15547	0.33364
H	3.55173	0.01804	-2.11400
H	3.75566	1.58646	-1.33501
C	5.49486	0.31218	-1.21889
C	6.07195	-0.86523	-1.72561
C	6.35002	1.27545	-0.65601
C	7.45151	-1.07171	-1.67356
H	5.43155	-1.62129	-2.17441
C	7.72988	1.07110	-0.60287
H	5.92784	2.19886	-0.26567
C	8.28835	-0.10492	-1.11021
H	7.87336	-1.98792	-2.07914
H	8.37001	1.83517	-0.16887
H	9.36259	-0.26373	-1.07168
C	3.72179	0.76303	1.89010
H	4.79695	0.61245	2.05682
H	3.53957	1.84025	1.80791
H	3.18481	0.39448	2.77100
C	3.37558	-2.02958	0.51107
H	2.83549	-2.39893	1.38977
H	2.99328	-2.56040	-0.36767
H	4.43712	-2.28572	0.62892

$BnMe_2SiH$ - INT1 quartet

Fe	-1.78178	0.06910	0.00167
N	-1.63279	2.02666	0.47629
N	-0.82931	-0.41675	1.72087
N	-2.69826	0.55533	-1.71748
N	-2.03775	-1.88078	-0.40370
C	-1.99975	3.09078	-0.30753
C	-0.50789	-1.68019	2.15488
C	-1.09097	2.55684	1.62347
C	-0.40181	0.45082	2.69870
C	-2.91863	1.82148	-2.20393
C	-1.53057	-2.94459	0.30703
C	-3.24482	-0.31027	-2.63327
C	-2.66408	-2.41547	-1.50315
C	-1.69438	4.32759	0.36818
C	0.15950	-1.60623	3.43025
C	-1.13763	3.99689	1.56651
C	0.21922	-0.28671	3.76982
C	-3.60458	1.74914	-3.47150
C	-1.86839	-4.18093	-0.35224

C	-3.81298	0.43002	-3.73382
C	-2.57719	-3.85402	-1.46866
H	-1.88762	5.31183	-0.03876
H	0.51648	-2.46359	3.98656
H	-0.77520	4.65310	2.34744
H	0.63894	0.16256	4.66082
H	-3.88932	2.60962	-4.06333
H	-1.58840	-5.16289	0.00727
H	-4.30125	-0.02074	-4.58829
H	-2.99662	-4.51112	-2.21969
C	-2.58652	3.00561	-1.56366
C	-0.81329	-2.86245	1.49144
C	-3.24923	-1.69330	-2.53489
C	-0.52944	1.83321	2.66582
H	-2.82588	3.93504	-2.06990
H	-0.48730	-3.79211	1.94629
H	-3.71403	-2.25392	-3.33926
H	-0.13921	2.39224	3.51003
O	-0.18179	0.10758	-0.87566
S	-3.78532	0.18491	1.15880
C	-4.20284	-1.46530	1.82850
H	-3.42047	-1.82337	2.50252
H	-5.13175	-1.34936	2.39608
H	-4.35998	-2.19521	1.03137
H	0.54656	0.13538	-0.21949
C	4.09903	0.38221	-1.33976
Si	3.23268	-0.00976	0.33124
H	3.66068	-0.26795	-2.10583
H	3.85041	1.41422	-1.61393
C	5.59531	0.19160	-1.26534
C	6.18231	-1.05215	-1.55635
C	6.44179	1.24343	-0.87385
C	7.56251	-1.23777	-1.46107
H	5.54901	-1.87880	-1.87065
C	7.82234	1.06018	-0.77783
H	6.01224	2.21806	-0.65275
C	8.39050	-0.18255	-1.06954
H	7.99190	-2.20789	-1.69870
H	8.45545	1.89218	-0.47966
H	9.46528	-0.32543	-0.99769
C	3.79329	1.17829	1.70197
H	4.87171	1.08202	1.88715
H	3.58763	2.22078	1.43483
H	3.26675	0.95836	2.63730
C	3.49299	-1.81846	0.84405
H	2.95724	-2.03122	1.77575
H	3.12049	-2.50542	0.07616
H	4.55819	-2.03288	1.00470

$PhMe_2SiH$ - TS1 doublet

Fe	1.12562	0.16235	0.08281
N	1.44812	2.11918	-0.34235
N	1.49871	-0.31296	-1.84555
N	0.96176	0.62867	2.04493
N	0.97795	-1.77959	0.52920
C	1.37607	3.17535	0.53106
C	1.46669	-1.56310	-2.41086
C	1.68427	2.66296	-1.57913
C	1.73497	0.56462	-2.87770
C	0.97059	1.88363	2.59657
C	1.02502	-2.84099	-0.34764
C	0.76733	-0.24126	3.08584
C	0.79202	-2.33236	1.77802
C	1.57559	4.42015	-0.17459
C	1.70134	-1.47579	-3.83243
C	1.76700	4.10222	-1.48337
C	1.86771	-0.15598	-4.12113
C	0.77395	1.80323	4.02495
C	0.85068	-4.08338	0.36212
C	0.65022	0.48225	4.32959
C	0.71039	-3.76829	1.68045
H	1.56836	5.39779	0.29005
H	1.73047	-2.32396	-4.50448
H	1.94966	4.76384	-2.32040
H	2.06163	0.30666	-5.08038
H	0.74273	2.65661	4.69020
H	0.84932	-5.06129	-0.10222
H	0.49499	0.02216	5.29709
H	0.56944	-4.43373	2.52260
C	1.15816	3.07112	1.89808
C	1.24120	-2.74558	-1.71690
C	0.69246	-1.62337	2.96789
C	1.82225	1.94468	-2.75995
H	1.13713	3.99322	2.47062
H	1.24904	-3.66982	-2.28633
H	0.54312	-2.19603	3.87798
H	2.00882	2.51002	-3.66773
O	-0.51262	0.46764	-0.22206
S	3.58398	0.16398	0.34194
C	4.20115	-1.52931	0.03805
H	3.95147	-1.86698	-0.97222
H	5.29276	-1.49513	0.12601
H	3.80778	-2.24441	0.76505
H	-1.54903	-0.45909	-0.09827
C	-4.32118	-0.02806	-0.31624
C	-5.01376	0.48414	0.79898
C	-4.68941	0.45141	-1.58956
C	-6.03398	1.42563	0.65048
H	-4.75805	0.14273	1.79920
C	-5.70796	1.39295	-1.74391
H	-4.17594	0.08563	-2.47573
C	-6.38367	1.88219	-0.62271
H	-6.55572	1.80213	1.52667
H	-5.97488	1.74476	-2.73719
H	-7.17702	2.61568	-0.74078
Si	-2.93569	-1.28748	-0.11190
C	-3.08366	-2.21741	1.52755
H	-2.27650	-2.95269	1.61724
H	-3.01511	-1.54261	2.38768
H	-4.04065	-2.75127	1.58830
C	-2.85374	-2.47675	-1.57974
H	-2.74746	-1.94363	-2.53065
H	-1.99160	-3.14494	-1.47560
H	-3.76007	-3.09324	-1.63380

$PhMe_2SiH$ - TS1 quartet

Fe	-1.18305	0.11965	0.14974

N	-2.60421	0.99147	-0.95096
N	-0.31707	1.90878	0.47697
N	-2.15278	-1.64361	0.02971
N	0.22265	-0.76015	1.35649
C	-3.69024	0.38384	-1.53141
C	0.84635	2.15358	1.16711
C	-2.68848	2.32020	-1.28932
C	-0.70032	3.11164	-0.06045
C	-3.29830	-1.89966	-0.68098
C	1.29351	-0.14742	1.95506
C	-1.75147	-2.85074	0.55558
C	0.29137	-2.08444	1.71254
C	-4.46824	1.35120	-2.27166
C	1.19077	3.55141	1.07920
C	-3.84710	2.55157	-2.12165
C	0.22956	4.14685	0.31907
C	-3.63986	-3.29783	-0.58887
C	2.06428	-1.11142	2.70633
C	-2.67925	-3.88756	0.17596
C	1.44215	-2.31365	2.55551
H	-5.37211	1.12106	-2.82115
H	2.06098	3.99984	1.54126
H	-4.13257	3.51605	-2.52186
H	0.14598	5.18581	0.02671
H	-4.50267	-3.75215	-1.05897
H	2.95906	-0.87901	3.26934
H	-2.58999	-4.92693	0.46524
H	1.71671	-3.27379	2.97376
C	-4.02075	-0.95845	-1.40653
C	1.59262	1.20773	1.86122
C	-0.61871	-3.06220	1.33154
C	-1.80945	3.31101	-0.87617
H	-4.91361	-1.30279	-1.91905
H	2.48696	1.55624	2.36810
H	-0.43704	-4.07493	1.67793
H	-1.99714	4.32221	-1.22368
O	-0.23877	-0.16979	-1.27219
S	-2.42056	0.27565	2.22621
C	-1.67901	1.52538	3.32547
H	-1.65617	2.51155	2.85633
H	-2.27671	1.56162	4.24157
H	-0.65767	1.23333	3.59189
H	0.95815	-0.75524	-1.26583
C	3.81530	-0.33335	-1.12993
C	4.01324	0.98313	-1.59422
C	4.70399	-0.81827	-0.15055
C	5.05495	1.77595	-1.11015
H	3.34494	1.39779	-2.34584
C	5.75011	-0.03053	0.33609
H	4.58417	-1.82696	0.23683
C	5.92803	1.26950	-0.14299
H	5.18717	2.78688	-1.48748
H	6.42708	-0.43189	1.08631
H	6.74170	1.88407	0.23364
Si	2.39804	-1.38584	-1.79723
C	2.55543	-3.18944	-1.24667
H	2.54840	-3.28537	-0.15591
H	1.71393	-3.77301	-1.63736
H	3.48208	-3.63903	-1.62626
C	2.30539	-1.26684	-3.68509
H	1.44134	-1.82757	-4.05968
H	2.19859	-0.22933	-4.02018
H	3.20896	-1.68234	-4.14930

$PhMe_2SiH$ - INT1 doublet

Fe	1.32245	0.15676	0.15281
N	1.97639	1.83488	-0.75089
N	2.06045	-0.94743	-1.35481
N	0.68410	1.25581	1.72260
N	0.66897	-1.51678	1.05916
C	1.80166	3.12487	-0.31502
C	1.89428	-2.29933	-1.54350
C	2.68662	1.91519	-1.92233
C	2.75137	-0.48663	-2.44956
C	0.68628	2.62449	1.82058
C	0.71382	-2.79701	0.55708
C	0.12019	0.78345	2.88280
C	0.11593	-1.61215	2.31650
C	2.40565	4.04584	-1.24811
C	2.51108	-2.70205	-2.78268
C	2.96179	3.29627	-2.23878
C	3.05067	-1.58162	-3.33865
C	0.11289	3.02724	3.08135
C	0.15993	-3.71903	1.51579
C	-0.22951	1.88698	3.74285
C	-0.20041	-2.98676	2.60856
H	2.40153	5.12245	-1.13563
H	2.52112	-3.71624	-3.16119
H	3.50614	3.62788	-3.11369
H	3.59112	-1.48315	-4.27137
H	-0.00121	4.05490	3.40183
H	0.07925	-4.78763	1.36267
H	-0.68824	1.78286	4.71777
H	-0.64313	-3.33014	3.53481
C	1.18740	3.50379	0.86973
C	1.25738	-3.16637	-0.66712
C	-0.13092	-0.54981	3.17552
C	3.06965	0.83950	-2.71002
H	1.12349	4.56526	1.08540
H	1.21509	-4.21602	-0.93939
H	-0.58057	-0.77664	4.13671
H	3.62501	1.05320	-3.61743
O	-0.27013	0.37209	-0.70094
S	3.33130	0.03346	1.31546
C	4.13750	-1.56696	0.94977
H	4.40721	-1.64963	-0.10552
H	5.04897	-1.60601	1.55505
H	3.49342	-2.40489	1.22830
H	-0.97230	-0.12722	-0.22592
C	-4.62083	0.01592	-0.74999
C	-5.46205	0.55554	0.24672
C	-4.72695	0.55168	-2.05160
C	-6.37553	1.56879	-0.04500
H	-5.40752	0.17687	1.26466
C	-5.63909	1.56495	-2.34674
H	-4.09023	0.17162	-2.84682
C	-6.46779	2.07662	-1.34398
H	-7.01650	1.96206	0.74010
H	-5.70422	1.95600	-3.35893

H	-7.17810	2.86680	-1.57251
Si	-3.36593	-1.31861	-0.34767
C	-2.96254	-2.41746	-1.83817
H	-2.63392	-1.82882	-2.70076
H	-2.15335	-3.11081	-1.58391
H	-3.83778	-3.00882	-2.13994
C	-3.86534	-2.34742	1.16461
H	-3.06344	-3.04678	1.42448
H	-4.05698	-1.72085	2.04200
H	-4.77345	-2.93002	0.95756

$PhMe_2SiH$ - INT1 quartet

Fe	1.37142	-0.09276	0.16635
N	2.86202	-0.41297	-1.13924
N	0.92021	-2.05054	0.14792
N	1.90163	1.85202	0.29156
N	-0.15424	0.24185	1.45358
C	3.71198	0.52810	-1.66889
C	-0.15940	-2.65385	0.75083
C	3.25077	-1.62207	-1.66320
C	1.56527	-3.03407	-0.56140
C	2.88031	2.48456	-0.43215
C	-1.07361	-0.67771	1.89886
C	1.31035	2.81716	1.07251
C	-0.45796	1.42877	2.07814
C	4.64642	-0.10364	-2.56861
C	-0.17730	-4.05930	0.43181
C	4.36565	-1.43551	-2.55952
C	0.89536	-4.29660	-0.37376
C	2.91949	3.88444	-0.08799
C	-1.99535	-0.04812	2.81030
C	1.95153	4.08894	0.84828
C	-1.60916	1.25426	2.92729
H	5.41694	0.42140	-3.11852
H	-0.92481	-4.75777	0.78565
H	4.85429	-2.23369	-3.10345
H	1.21067	-5.22969	-0.82281
H	3.60547	4.60222	-0.51929
H	-2.81993	-0.55476	3.29487
H	1.67424	5.01046	1.34394
H	-2.05046	2.03816	3.52957
C	3.72070	1.87924	-1.35753
C	-1.09494	-2.02483	1.55950
C	0.22440	2.62709	1.91507
C	2.66502	-2.84846	-1.38882
H	4.45428	2.50526	-1.85483
H	-1.89090	-2.63449	1.97419
H	-0.13418	3.48708	2.47134
H	3.07467	-3.72344	-1.88277
O	0.25174	0.23846	-1.23825
S	2.81868	-0.35625	1.95936
C	2.33372	-1.82844	2.93142
H	2.42264	-2.74607	2.34582
H	3.01701	-1.88124	3.78519
H	1.31099	-1.73094	3.30438
H	-0.60804	0.56117	-0.89446
C	-4.42741	0.29531	-0.97512
C	-4.76693	-0.84569	-1.73374
C	-5.09867	0.48342	0.25225
C	-5.73890	-1.74578	-1.29628
H	-4.26757	-1.03307	-2.68147
C	-6.07206	-0.41412	0.69254
H	-4.86221	1.34548	0.87127
C	-6.39625	-1.53234	-0.08109
H	-5.98551	-2.61310	-1.90355
H	-6.58069	-0.24047	1.63768
H	-7.15436	-2.23224	0.26047
Si	-3.09127	1.48125	-1.55050
C	-2.96751	1.56632	-3.43992
H	-2.13914	2.22027	-3.73349
H	-2.78413	0.58126	-3.88137
H	-3.89129	1.96960	-3.87669
C	-3.27588	3.20451	-0.77953
H	-3.23181	3.16867	0.31406
H	-2.46468	3.85583	-1.12337
H	-4.22878	3.66852	-1.06840

$BnMe_2SiH$

C	3.99150	0.26165	-1.60145
Si	2.91394	0.99698	-0.20021
H	3.59058	-0.73270	-1.83789
H	3.83733	0.88077	-2.49492
C	5.46241	0.17146	-1.27106
C	5.99737	-0.96953	-0.64977
C	6.33501	1.23615	-1.55185
C	7.35198	-1.04385	-0.31932
H	5.34454	-1.81173	-0.43076
C	7.69017	1.16534	-1.22285
H	5.94756	2.12705	-2.04138
C	8.20604	0.02458	-0.60317
H	7.74072	-1.94079	0.15643
H	8.34430	2.00184	-1.45597
H	9.26107	-0.03313	-0.34949
H	1.50510	1.01300	-0.70820
C	3.43421	2.77184	0.19195
H	4.47736	2.81316	0.52618
H	3.33788	3.41977	-0.68737
H	2.80953	3.19445	0.98790
C	2.98480	-0.08792	1.34660
H	2.35880	0.32915	2.14444
H	2.62750	-1.10344	1.13838
H	4.00915	-0.16479	1.72917

$[BnMe_2Si]^+$

C	3.94576	0.53740	-1.79974
Si	3.64544	0.11535	-0.02865
H	3.52901	-0.15530	-2.53128
H	3.76049	1.57443	-2.07974
C	5.41563	0.25531	-1.47613
C	5.95017	-1.04763	-1.62764
C	6.25852	1.28055	-0.98084
C	7.28127	-1.30560	-1.31444

H	5.32255	-1.84215	-2.02123
C	7.58881	1.01150	-0.66936
H	5.87236	2.29068	-0.87597
C	8.10095	-0.27864	-0.83514
H	7.68193	-2.30486	-1.45176
H	8.22782	1.81027	-0.30679
H	9.13957	-0.48353	-0.59453
C	3.67374	1.42374	1.28821
H	4.41713	1.19102	2.05801
H	3.86723	2.42080	0.88567
H	2.68966	1.43106	1.77573
C	3.31129	-1.63385	0.49427
H	2.30301	-1.66887	0.92834
H	3.35423	-2.33715	-0.34072
H	4.01363	-1.95040	1.27270

phenyldimethylsilane (**1a**), $PhMe_2SiH$

C	5.33768	-0.10941	-1.16325
C	6.25577	-0.81757	-1.96060
C	5.85532	0.66437	-0.10575
C	7.63050	-0.75899	-1.71528
H	5.89360	-1.42485	-2.78747
C	7.22705	0.72807	0.14555
H	5.18055	1.22922	0.53537
C	8.11876	0.01470	-0.66055
H	8.31839	-1.31581	-2.34667
H	7.60104	1.33272	0.96803
H	9.18729	0.06272	-0.46702
Si	3.48115	-0.20011	-1.50003
H	3.31477	-1.05795	-2.71306
C	2.77171	1.51737	-1.85581
H	3.26019	1.97691	-2.72260
H	1.69674	1.45956	-2.06544
H	2.90818	2.18963	-1.00003
C	2.56545	-1.00090	-0.05079
H	1.49033	-1.06712	-0.25730
H	2.93517	-2.01471	0.14068
H	2.69300	-0.41924	0.87020

$[PhMe_2Si]^+$

C	5.40928	0.18899	-1.10683
C	6.32021	0.26518	-2.19159
C	5.90982	-0.10187	0.18816
C	7.67875	0.06001	-1.98424
H	5.96485	0.48484	-3.19357
C	7.26965	-0.30766	0.38609
H	5.23608	-0.16537	1.03692
C	8.15138	-0.22625	-0.69806
H	8.37037	0.12092	-2.81827
H	7.64613	-0.53017	1.37926
H	9.21362	-0.38706	-0.53973
Si	3.64121	0.46933	-1.37160
C	2.98130	0.86984	-3.05202
H	3.68884	0.65336	-3.85590
H	2.05239	0.31543	-3.22805
H	2.73088	1.93906	-3.08921
C	2.43716	0.40117	0.03060
H	1.69879	-0.38791	-0.16189
H	2.90794	0.21577	0.99838
H	1.88623	1.34929	0.07795

$[BnMe_2Si]_{\top\top\|}$

C	4.05800	0.49210	-1.68560
Si	2.96630	0.21950	-0.12040
H	3.68220	-0.16750	-2.47680
H	3.90430	1.52260	-2.02740
C	5.52140	0.22960	-1.42220
C	6.06970	-1.05350	-1.59250
C	6.37190	1.25360	-0.97040
C	7.41600	-1.30430	-1.32160
H	5.43420	-1.86060	-1.95030
C	7.71850	1.00540	-0.69870
H	5.97360	2.25740	-0.83980
C	8.24800	-0.27610	-0.87130
H	7.81630	-2.30450	-1.46790
H	8.35610	1.81680	-0.35660
H	9.29660	-0.46970	-0.66250
C	3.46030	1.41930	1.26890
H	4.50810	1.26800	1.56190
H	3.34490	2.46320	0.95640
H	2.83550	1.26250	2.15550
C	3.07470	-1.58160	0.47770
H	2.45010	-1.73230	1.36550
H	2.73580	-2.28120	-0.29460
H	4.10790	-1.84450	0.74190

$[PhMe_2Si]_{\top}$

C	5.34640	-0.06490	-1.15800
C	6.27300	0.11140	-2.20830
C	5.86600	-0.22170	0.14520
C	7.64700	0.14460	-1.96830
H	5.91720	0.22980	-3.22930
C	7.23920	-0.18910	0.38950
H	5.18860	-0.36630	0.98380
C	8.13560	-0.00520	-0.66720
H	8.33740	0.28880	-2.79560
H	7.61110	-0.30550	1.40450
H	9.20570	0.01990	-0.47860
Si	3.49960	-0.16200	-1.49180
C	3.00360	0.82370	-3.03800
H	3.53660	0.48300	-3.93200
H	1.93050	0.71090	-3.22910
H	3.21220	1.89420	-2.90650
C	2.47540	0.37380	0.01550
H	1.40600	0.26360	-0.19650
H	2.70090	-0.22910	0.90160
H	2.66290	1.42690	0.26560

$Me_2HSi\text{-}O\text{-}SiMe_2H$

Si	-2.84693	1.53819	-0.42570
H	-3.92288	2.07660	-1.31656
O	-2.66616	-0.08868	-0.71827
Si	-3.08930	-1.40774	-1.63810
H	-2.28942	-2.55038	-1.10705
C	-3.35260	1.78749	1.36845
H	-2.58874	1.39736	2.05173
H	-3.48852	2.85351	1.58968
H	-4.29576	1.27548	1.59150
C	-1.23353	2.42616	-0.80936
H	-0.41742	2.05195	-0.17966
H	-0.94062	2.28700	-1.85646
H	-1.33047	3.50400	-0.62842
C	-4.92239	-1.79168	-1.44497
H	-5.18670	-1.95398	-0.39359
H	-5.54326	-0.97145	-1.82566
H	-5.18935	-2.69876	-2.00176
C	-2.64696	-1.12971	-3.44715
H	-1.58069	-0.90545	-3.56723
H	-2.87045	-2.02395	-4.04253
H	-3.21706	-0.29476	-3.87279

$[Me_2HSi\text{-}O\text{-}SiMe_2]_{TTI}$

Si	-3.20310	1.42070	0.11210
H	-4.53370	1.22040	0.76610
O	-2.81780	0.04990	-0.75540
Si	-3.43390	-1.29960	-1.52520
C	-1.89360	1.67890	1.43560
H	-0.90290	1.82550	0.98910
H	-2.12350	2.56450	2.04110
H	-1.83460	0.81690	2.10990
C	-3.30530	2.90190	-1.04450
H	-2.34710	3.07830	-1.54780
H	-4.06890	2.75530	-1.81710
H	-3.56350	3.81090	-0.48670
C	-4.60300	-0.77990	-2.92840
H	-5.46330	-0.21800	-2.54890
H	-4.07530	-0.14760	-3.65600
H	-4.98270	-1.66310	-3.45530
C	-1.95950	-2.27470	-2.20720
H	-1.27930	-2.58260	-1.40620
H	-2.30230	-3.17560	-2.72910
H	-1.39180	-1.66060	-2.91970

$Me_2HSi\text{-}O\text{-}SiMe_2H$ - TS1 doublet

Fe	-0.93140	-0.01584	0.11374
N	-0.84159	-0.28571	2.10707
N	-0.56554	-1.96954	-0.16140
N	-1.43247	1.93468	0.38935
N	-1.24660	0.21112	-1.87457
C	-1.00680	0.67586	3.06996
C	-0.51122	-2.63968	-1.35961
C	-0.55818	-1.44685	2.77806
C	-0.32549	-2.91809	0.80840
C	-1.50535	2.59706	1.58819
C	-1.09089	-0.74751	-2.84572
C	-1.68369	2.87252	-0.57667
C	-1.52846	1.38397	-2.54141
C	-0.82164	0.10664	4.38358
C	-0.21054	-4.03508	-1.14353
C	-0.54338	-1.21451	4.20205
C	-0.09637	-4.20808	0.20294
C	-1.81266	3.99316	1.37228
C	-1.30804	-0.17520	-4.15366
C	-1.91969	4.16494	0.02676
C	-1.57527	1.14601	-3.96425
H	-0.89983	0.65976	5.31088
H	-0.11483	-4.77303	-1.92987
H	-0.34508	-1.97279	4.94876
H	0.11339	-5.11724	0.75194
H	-1.92836	4.72749	2.15923
H	-1.25068	-0.72628	-5.08373
H	-2.14349	5.06977	-0.52375
H	-1.78444	1.90536	-4.70690
C	-1.31631	2.01323	2.83446
C	-0.75027	-2.07432	-2.60872
C	-1.72358	2.62080	-1.94475
C	-0.32096	-2.67896	2.17662
H	-1.41443	2.65670	3.70353
H	-0.66578	-2.72698	-3.47235
H	-1.93273	3.46091	-2.59985
H	-0.11902	-3.52246	2.82978
O	0.70913	0.52210	-0.02654
S	-3.38910	-0.30318	0.10486
C	-3.79868	-1.89633	-0.68168
H	-3.34567	-2.73604	-0.14831
H	-4.88792	-2.00481	-0.68355
H	-3.45224	-1.90966	-1.72092
H	1.70351	-0.39155	-0.02809
Si	3.19230	-1.05185	-0.06119
C	3.35724	-2.19980	-1.54553
H	3.12270	-1.67595	-2.47852
H	4.38310	-2.58350	-1.61844
H	2.67589	-3.05322	-1.45324
C	3.52777	-1.94411	1.56349
H	3.41387	-1.26680	2.41674
H	2.83254	-2.78044	1.69764
H	4.55076	-2.34174	1.57704
O	4.25922	0.21321	-0.22244
Si	4.34014	1.87495	-0.39258
H	5.79820	2.18637	-0.48142
C	3.59802	2.72688	1.10994
H	4.09655	2.41715	2.03581
H	3.68873	3.81720	1.02589
H	2.53323	2.47850	1.19370
C	3.47911	2.41643	-1.97410
H	3.57110	3.50044	-2.11754
H	3.90551	1.92245	-2.85492
H	2.41181	2.16960	-1.92551

$Me_2HSi\text{-}O\text{-}SiMe_2H$ - TS1 quartet

Fe	-0.97805	-0.02491	0.10601
N	-0.85795	-0.21111	2.11611
N	-0.42784	-1.99369	-0.07873
N	-1.58184	1.86797	0.30015
N	-1.29534	0.06176	-1.87501
C	-1.06957	0.78103	3.03823
C	-0.30699	-2.70382	-1.24445
C	-0.45950	-1.31845	2.82927
C	-0.09623	-2.86018	0.93473
C	-1.69097	2.58273	1.46829
C	-1.02933	-0.92148	-2.80017
C	-1.96012	2.72428	-0.70489
C	-1.70535	1.15777	-2.59207
C	-0.81646	0.28641	4.36955
C	0.12185	-4.05507	-0.96372
C	-0.43791	-1.01563	4.23939
C	0.25296	-4.15133	0.38907
C	-2.13036	3.93121	1.18865
C	-1.30075	-0.43541	-4.13093
C	-2.29889	4.01844	-0.15784
C	-1.72314	0.85324	-4.00184
H	-0.91632	0.87391	5.27329
H	0.28756	-4.81743	-1.71436
H	-0.16187	-1.71936	5.01426
H	0.54904	-5.00931	0.97926
H	-2.29098	4.69269	1.94115
H	-1.17617	-1.01778	-5.03501
H	-2.62611	4.86685	-0.74525
H	-2.01565	1.54942	-4.77746
C	-1.45643	2.08438	2.74191
C	-0.57615	-2.20400	-2.51548
C	-2.02795	2.39814	-2.05182
C	-0.10415	-2.54792	2.28845
H	-1.58912	2.76591	3.57638
H	-0.42535	-2.87434	-3.35616
H	-2.34323	3.17585	-2.74040
H	0.18712	-3.33000	2.98278
O	0.66897	0.50844	-0.04705
S	-3.15734	-0.97185	0.49415
C	-3.81851	-1.69726	-1.04124
H	-3.17384	-2.51573	-1.37829
H	-4.80840	-2.10708	-0.81837
H	-3.89354	-0.95260	-1.83687
H	1.70205	-0.31421	-0.02022
Si	3.26528	-0.87718	-0.06046
C	3.51813	-1.98731	-1.56325
H	3.24530	-1.46905	-2.48894
H	4.57002	-2.29188	-1.63996
H	2.90257	-2.89056	-1.48414
C	3.68771	-1.76968	1.54536
H	3.51150	-1.12667	2.41443
H	3.07612	-2.67162	1.65958
H	4.74441	-2.06703	1.54935
O	4.23835	0.46516	-0.20145
Si	4.23839	2.12369	-0.40182
H	5.67618	2.52466	-0.34305
C	3.28585	2.95590	0.98836
H	3.70947	2.70994	1.96911
H	3.30278	4.04740	0.87674
H	2.24050	2.62520	0.97406
C	3.53272	2.58760	-2.08308
H	3.60123	3.67063	-2.24641
H	4.07351	2.09030	-2.89668
H	2.47585	2.30311	-2.15185

Me_2HSi-O-$SiMe_2H$ - INT1 quartet

Fe	-1.12118	-0.07434	0.19858
N	-0.71989	0.76454	1.99157
N	-0.20457	-1.77816	0.79386
N	-2.00001	1.62759	-0.40067
N	-1.62620	-0.95533	-1.53350
C	-0.96621	2.06138	2.36437
C	-0.03018	-2.92138	0.05183
C	-0.09510	0.16478	3.05964
C	0.34912	-2.02707	2.02777
C	-2.06991	2.80926	0.29731
C	-1.24253	-2.20409	-1.96687
C	-2.67145	1.83668	-1.58086
C	-2.33927	-0.39230	-2.56381
C	-0.49798	2.28371	3.71010
C	0.67122	-3.91023	0.83134
C	0.03550	1.10757	4.14284
C	0.89952	-3.35863	2.05755
C	-2.78603	3.79555	-0.47508
C	-1.74816	-2.43898	-3.29591
C	-3.16493	3.19140	-1.63435
C	-2.43437	-1.32070	-3.66238
H	-0.57548	3.22565	4.23783
H	0.93372	-4.89837	0.47552
H	0.49064	0.88293	5.09894
H	1.39125	-3.79933	2.91538
H	-2.97322	4.81047	-0.14847
H	-1.58681	-3.34822	-3.86076
H	-3.72535	3.60669	-2.46213
H	-2.95028	-1.11841	-4.59223
C	-1.58158	3.02597	1.57679
C	-0.49414	-3.12068	-1.24288
C	-2.84966	0.89894	-2.58637
C	0.39331	-1.13370	3.09003
H	-1.71328	4.01444	2.00439
H	-0.27621	-4.07407	-1.71310
H	-3.39843	1.20686	-3.47034
H	0.86802	-1.46897	4.00642
O	0.45921	0.52888	-0.49341
S	-3.07225	-0.77566	1.22802
C	-3.67418	-2.30430	0.42405
H	-2.92831	-3.10046	0.49048
H	-4.57131	-2.61469	0.96927
H	-3.93354	-2.13335	-0.62303
H	1.19081	-0.02875	-0.15064
Si	3.78744	-0.73647	-0.19224
C	3.97619	-2.08513	-1.50771
H	3.50512	-1.79001	-2.45103
H	5.03885	-2.28538	-1.70240
H	3.50656	-3.01543	-1.16814
C	4.59664	-1.25443	1.43803
H	4.47905	-0.48195	2.20501
H	4.14422	-2.18026	1.81112
H	5.67127	-1.42986	1.29127

O	4.50596	0.67180	-0.72026
Si	4.18432	2.19355	-1.33767
H	5.52079	2.84089	-1.49391
C	3.12820	3.17402	-0.13154
H	3.60950	3.25891	0.84973
H	2.94635	4.18862	-0.50789
H	2.15680	2.68225	0.00222
C	3.34732	2.06428	-3.01693
H	3.21029	3.05989	-3.45767
H	3.93872	1.46470	-3.71856
H	2.35745	1.60196	-2.92080
C	-4.53565	-0.17544	-0.12277
C	-5.13541	1.08196	0.08805
C	-5.08778	-1.01175	-1.11289
C	-6.24442	1.48617	-0.65656
H	-4.73499	1.75228	0.84565
C	-6.19691	-0.61092	-1.85953
H	-4.65022	-1.98996	-1.30045
C	-6.77756	0.63970	-1.63248
H	-6.69381	2.45907	-0.47486
H	-6.60931	-1.27376	-2.61589
H	-7.64159	0.95293	-2.21265
Si	-3.02438	-0.70130	0.85645
H	-3.07895	-0.10516	2.22296
H	-2.99049	-2.18898	0.95851

$PhSiH_3$ - TS1 doublet

Fe	0.98282	0.10272	0.04476
N	1.53380	1.75545	-0.99991
N	1.47443	-1.02990	-1.56379
N	0.72377	1.21269	1.70221
N	0.60075	-1.55263	1.11426
C	1.51629	3.04828	-0.54098
C	1.35208	-2.39508	-1.66579
C	1.89897	1.82804	-2.31852
C	1.85149	-0.58867	-2.81514
C	0.82871	2.57719	1.79185
C	0.59879	-2.84474	0.65092
C	0.36730	0.78002	2.95403
C	0.26017	-1.63237	2.44707
C	1.88551	3.96111	-1.59846
C	1.68989	-2.82858	-3.00113
C	2.12046	3.20278	-2.70382
C	1.99652	-1.70941	-3.71243
C	0.52478	3.01657	3.13231
C	0.23627	-3.75823	1.70758
C	0.23984	1.89807	3.85604
C	0.02993	-3.00583	2.82389
H	1.95034	5.03618	-1.48958
H	1.67982	-3.85867	-3.33391
H	2.42007	3.52409	-3.69310
H	2.29175	-1.62992	-4.75082
H	0.53721	4.04849	3.45914
H	0.16234	-4.83226	1.59409
H	-0.03216	1.81949	4.90083
H	-0.25098	-3.33288	3.81678
C	1.19441	3.43164	0.75481
C	0.94324	-3.23858	-0.64009
C	0.15658	-0.54878	3.30927
C	2.04421	0.73710	-3.17085
H	1.23205	4.49281	0.98148
H	0.89136	-4.29996	-0.86303
H	-0.11760	-0.75370	4.33955
H	2.33421	0.94093	-4.19697
O	-0.62414	0.30640	-0.54790
S	3.44167	-0.09742	0.39327
C	3.83285	-1.77993	0.97051
H	3.54829	-2.51406	0.20797
H	4.91391	-1.84838	1.12538
H	3.30745	-2.01691	1.89908
H	-1.62686	-0.18782	0.13790

$PhSiH_3$ - TS1 quartet

Fe	-1.04394	0.06997	0.07144
N	-2.42179	1.21399	-0.82209
N	-0.08331	1.71464	0.72117
N	-2.11215	-1.58442	-0.36542
N	0.30218	-1.09763	1.07863
C	-3.54083	0.78664	-1.49163
C	1.08977	1.76113	1.43554
C	-2.42928	2.58394	-0.90953
C	-0.39506	3.01717	0.41886
C	-3.27386	-1.63640	-1.09470
C	1.40106	-0.66828	1.78048
C	-1.77667	-2.89019	-0.08991
C	0.30074	-2.46961	1.17527
C	-4.26391	1.91599	-2.03072
C	1.51516	3.12856	1.60483
C	-3.57406	3.03106	-1.66997
C	0.59266	3.90857	0.97506
C	-3.69221	-3.00532	-1.26923
C	2.11295	-1.79739	2.33286
C	-2.76150	-3.78280	-0.64911
C	1.43168	-2.91440	1.95436
H	-5.18019	1.84232	-2.60241
H	2.40864	3.43308	2.13458
H	-3.80391	4.06734	-1.88230
H	0.57111	4.98668	0.88034
H	-4.58152	-3.31296	-1.80416
H	3.01164	-1.72449	2.93200
H	-2.72846	-4.86176	-0.56834
H	1.65573	-3.94978	2.17708
C	-3.94547	-0.53586	-1.61592
C	1.77605	0.66140	1.93971
C	-0.65570	-3.30714	0.61782
C	-1.49101	3.42834	-0.33202
H	-4.85756	-0.72781	-2.17241
H	2.68402	0.85853	2.50100
H	-0.52682	-4.37571	0.75894
H	-1.61829	4.49560	-0.48430
O	-0.13806	0.01185	-1.39445
S	-2.27779	-0.10887	2.15892
C	-1.46755	0.86816	3.46477
H	-1.39680	1.92328	3.19088
H	-2.05463	0.75736	4.38152

H	-0.45981	0.48146	3.65197
H	0.96783	-0.67804	-1.49634
C	3.92517	-0.54993	-1.53870
C	4.36447	0.58332	-2.25211
C	4.69477	-0.97430	-0.43756
C	5.52744	1.26140	-1.88468
H	3.79494	0.93808	-3.10847
C	5.86000	-0.29931	-0.06827
H	4.38273	-1.84445	0.13511
C	6.27864	0.82055	-0.79131
H	5.84987	2.13069	-2.45202
H	6.44316	-0.64895	0.78002
H	7.18620	1.34616	-0.50596
Si	2.34996	-1.44706	-2.02833
H	2.23726	-1.48305	-3.51662
H	2.39160	-2.84478	-1.50938
H	4.21474	1.80277	0.04510
H	4.88667	1.62527	-1.59492
H	3.30389	2.40513	-1.36681
H	-1.09713	0.16592	0.16569
C	-5.01467	0.43599	0.53307
C	-5.82723	-0.41988	-0.24096
C	-5.21502	0.45513	1.93006
C	-6.81055	-1.20929	0.35415
H	-5.69437	-0.46316	-1.31969
C	-6.19810	-0.33421	2.52543
H	-4.60008	1.09760	2.55614
C	-6.99882	-1.16817	1.73902
H	-7.43127	-1.85575	-0.26068
H	-6.34115	-0.29950	3.60221
H	-7.76429	-1.78416	2.20316
Si	-3.67494	1.46036	-0.25739
H	-3.99163	1.77394	-1.68020
H	-3.39587	2.70267	0.51734

$PhSiH_3$ - INT1 doublet

Fe	1.19256	-0.11312	-0.09900
N	1.85682	-1.67731	0.97522
N	1.86382	1.14779	1.31097
N	0.61628	-1.37186	-1.57085
N	0.51081	1.44934	-1.17440
C	1.72384	-3.00791	0.66092
C	1.65468	2.50634	1.36690
C	2.54180	-1.62763	2.16439
C	2.54089	0.81342	2.45880
C	0.65552	-2.74318	-1.53913
C	0.50145	2.77030	-0.79045
C	0.06706	-1.02654	-2.78286
C	-0.02460	1.40943	-2.44210
C	2.32573	-3.81913	1.69139
C	2.23238	3.04223	2.57383
C	2.84045	-2.96450	2.61740
C	2.79039	1.99606	3.24463
C	0.12429	-3.27835	-2.76835
C	-0.07252	3.57985	-1.83483
C	-0.23197	-2.21538	-3.54191
C	-0.38927	2.73873	-2.86043
H	2.34940	-4.90130	1.68275
H	2.20510	4.08747	2.85411
H	3.37118	-3.19719	3.53169
H	3.31172	2.00217	4.19328
H	0.04475	-4.33434	-2.99252
H	-0.19850	4.65352	-1.77885
H	-0.66993	-2.21619	-4.53182
H	-0.83365	2.97934	-3.81765
C	1.15170	-3.51459	-0.49643
C	1.01043	3.26762	0.40261
C	-0.21883	0.26463	-3.20333
C	2.88408	-0.47308	2.85219
H	1.11978	-4.59315	-0.61064
H	0.92690	4.33516	0.57800
H	-0.65730	0.38636	-4.18842
H	3.42339	-0.58529	3.78695
O	-0.42757	-0.26920	0.73089
S	3.21187	-0.03359	-1.23140
C	3.96635	1.61615	-1.00205

$PhSiH_3$ - INT1 quartet

Fe	-1.18057	0.03522	0.10819
N	-2.68992	0.89896	-0.89335
N	-0.36307	1.83696	0.45021
N	-2.06179	-1.76747	-0.12178
N	0.36131	-0.84478	1.07855
C	-3.74845	0.26495	-1.49908
C	0.86357	2.09154	1.01997
C	-2.88622	2.24534	-1.08511
C	-0.86997	3.05454	0.06609
C	-3.20477	-2.03845	-0.83071
C	1.47953	-0.22389	1.58264
C	-1.60179	-2.97458	0.35026
C	0.48557	-2.17971	1.38749
C	-4.62084	1.23841	-2.10988
C	1.12150	3.50937	1.01520
C	-4.09135	2.46445	-1.84702
C	0.04433	4.10656	0.43292
C	-3.48325	-3.45274	-0.79270
C	2.34218	-1.19646	2.20405
C	-2.49420	-4.03137	-0.05629
C	1.72307	-2.40584	2.08985
H	-5.52324	0.99442	-2.65571
H	2.01851	3.96980	1.40907
H	-4.46487	3.43876	-2.13498
H	-0.12610	5.15887	0.24489
H	-4.33005	-3.92352	-1.27539
H	3.29212	-0.96456	2.66790
H	-2.35703	-5.07680	0.18860
H	2.05973	-3.37279	2.44128
C	-3.99030	-1.10022	-1.48757
C	1.73051	1.14190	1.54074
C	-0.42818	-3.17356	1.06321
C	-2.05546	3.25669	-0.62811
H	-4.87171	-1.45928	-2.00857
H	2.66525	1.49362	1.96464
H	-0.19397	-4.18802	1.36904
H	-2.33336	4.27963	-0.85984
O	-0.27130	-0.14666	-1.46800

S	-2.37836	0.10702	2.08283
C	-1.52668	1.19617	3.28039
H	-1.48401	2.22857	2.92677
H	-2.10800	1.15848	4.20728
H	-0.51475	0.83710	3.48389
H	0.49082	-0.73447	-1.29955
C	4.42569	-0.58807	-1.50911
C	4.58344	0.77563	-1.83712
C	5.26704	-1.13116	-0.51458
C	5.55275	1.55804	-1.21018
H	3.94655	1.22698	-2.59442
C	6.23727	-0.34934	0.11193
H	5.16869	-2.17771	-0.23547
C	6.38284	0.99762	-0.23433
H	5.66345	2.60399	-1.48398
H	6.88312	-0.79015	0.86695
H	7.13953	1.60679	0.25281
Si	3.10532	-1.62243	-2.32083
H	2.82753	-1.17680	-3.71527
H	3.44347	-3.07418	-2.27556

$BnSiH_3$ - TS1 doublet

Fe	1.35898	0.07580	0.05099
N	2.47074	0.87998	-1.44672
N	1.80349	-1.77107	-0.65676
N	1.12538	1.89448	0.87747
N	0.39036	-0.74292	1.60725
C	2.71802	2.21391	-1.64960
C	1.36682	-2.97026	-0.14592
C	3.04773	0.22465	-2.50192
C	2.47417	-2.07817	-1.82270
C	1.56471	3.08666	0.36157
C	0.15132	-2.07845	1.81857
C	0.45461	2.20814	2.03162
C	-0.18150	-0.08785	2.67680
C	3.47433	2.40501	-2.86612
C	1.79793	-4.05973	-0.98938
C	3.67577	1.16874	-3.39793
C	2.48033	-3.50610	-2.02893
C	1.15928	4.18027	1.21113
C	-0.59899	-2.27036	3.03618
C	0.46903	3.63351	2.25075
C	-0.80402	-1.03458	3.57016
H	3.79841	3.36572	-3.24533
H	1.58787	-5.10464	-0.79986
H	4.20178	0.90040	-4.30514
H	2.94864	-4.00288	-2.86895
H	1.38370	5.22233	1.02269
H	-0.91316	-3.23254	3.41999
H	0.00805	4.13267	3.09339
H	-1.32272	-0.77039	4.48278
C	2.30549	3.23908	-0.80802
C	0.60032	-3.11506	1.00423
C	-0.15277	1.28563	2.87826
C	3.04542	-1.15527	-2.68508
H	2.58095	4.25125	-1.08856
H	0.32838	-4.12527	1.29499
H	-0.64493	1.67066	3.76606
H	3.53775	-1.54117	-3.57240
O	-0.02247	0.20245	-0.98262
S	3.59549	-0.24395	1.09189
C	3.45996	-1.45303	2.44741
H	3.13538	-2.42382	2.05565
H	4.44989	-1.57871	2.89653
H	2.74579	-1.12474	3.20686
H	-1.20369	0.10922	-0.44796
C	-3.89482	0.09617	-1.58791
Si	-2.80546	0.05863	-0.01898
H	-3.11828	1.23751	0.84220
H	-3.09201	-1.18016	0.76230
H	-3.63802	0.99731	-2.15687
H	-3.62217	-0.76515	-2.20899
C	-5.36484	0.07281	-1.24406
C	-6.07698	1.26600	-1.03509
C	-6.05366	-1.14317	-1.09762
C	-7.43153	1.24529	-0.69924
H	-5.56379	2.21871	-1.14626
C	-7.40817	-1.16619	-0.76185
H	-5.52220	-2.07874	-1.25778
C	-8.10415	0.02851	-0.56042
H	-7.96282	2.18183	-0.54974
H	-7.92118	-2.11934	-0.66145
H	-9.15934	0.01157	-0.30155

$BnSiH_3$ - TS1 quartet

Fe	-1.40355	0.06281	0.01445
N	-1.29632	1.98644	0.62638
N	-0.38984	-0.49632	1.70184
N	-2.48223	0.61215	-1.57943
N	-1.68782	-1.87136	-0.44680
C	-1.78733	3.08028	-0.04087
C	-0.07424	-1.77609	2.08313
C	-0.63878	2.47691	1.73064
C	0.13515	0.32986	2.66978
C	-2.81111	1.89203	-1.94985
C	-1.16731	-2.96296	0.20764
C	-3.02687	-0.20974	-2.53441
C	-2.32982	-2.36464	-1.55625
C	-1.44671	4.29012	0.66652
C	0.67144	-1.75981	3.31982
C	-0.73216	3.91550	1.76408
C	0.80291	-0.45383	3.68205
C	-3.56782	1.87759	-3.18138
C	-1.50918	-4.17392	-0.49700
C	-3.70157	0.57373	-3.54403
C	-2.23216	-3.80287	-1.59053
H	-1.72233	5.28720	0.34770
H	1.03882	-2.64175	3.82878
H	-0.29965	4.54084	2.53451
H	1.29937	-0.04087	4.55082
H	-3.94311	2.76093	-3.68205
H	-1.22199	-5.16943	-0.18328
H	-4.20977	0.15951	-4.40539
H	-2.66070	-4.42974	-2.36193
C	-2.49567	3.04135	-1.23726

C	-0.42672	-2.92605	1.38404
C	-2.96304	-1.59639	-2.52693
C	0.03121	1.71399	2.67978
H	-2.82653	3.98952	-1.64956
H	-0.09637	-3.87667	1.79141
H	-3.43692	-2.12371	-3.34903
H	0.50404	2.24439	3.50042
O	0.04392	0.16664	-0.92500
S	-3.29703	0.05266	1.52999
C	-3.72940	-1.65480	1.99261
H	-2.89205	-2.12363	2.52084
H	-4.58591	-1.61319	2.67222
H	-3.97598	-2.25685	1.11506
H	1.20990	0.10077	-0.36132
C	3.89131	0.05619	-1.53567
Si	2.83092	0.06995	0.05480
H	3.13846	-1.14051	0.87269
H	3.16504	1.27687	0.86842
H	3.60571	-0.82339	-2.12445
H	3.62346	0.93966	-2.12692
C	5.36772	0.04174	-1.22156
C	6.06091	-1.17006	-1.06121
C	6.08304	1.23989	-1.05554
C	7.42224	-1.18448	-0.75380
H	5.52714	-2.10939	-1.18826
C	7.44436	1.22781	-0.74809
H	5.56663	2.18946	-1.17798
C	8.12111	0.01498	-0.59517
H	7.93828	-2.13474	-0.64211
H	7.97772	2.16790	-0.63180
H	9.18159	0.00469	-0.35846

$BnSiH_3$ - INT1 quartet

Fe	-1.61365	0.05254	0.03233
N	-1.51395	2.03175	0.42266
N	-0.60564	-0.33220	1.74381
N	-2.57535	0.43982	-1.68642
N	-1.81766	-1.91823	-0.28856
C	-1.93100	3.05139	-0.39503
C	-0.23116	-1.56653	2.21889
C	-0.96241	2.62543	1.53391
C	-0.17780	0.58788	2.67287
C	-2.84704	1.67784	-2.21812
C	-1.26211	-2.93622	0.45272
C	-3.11705	-0.47857	-2.55290
C	-2.45188	-2.51690	-1.35027
C	-1.64943	4.32350	0.22249
C	0.47245	-1.41875	3.46776
C	-1.05550	4.05961	1.41962
C	0.49950	-0.08543	3.75196
C	-3.55837	1.53285	-3.46500
C	-1.57733	-4.20823	-0.14664
C	-3.73196	0.19835	-3.66863
C	-2.32099	-3.94934	-1.25830
H	-1.88194	5.28373	-0.21987
H	0.87813	-2.24044	4.04390
H	-0.69547	4.75822	2.16396
H	0.93456	0.41357	4.60836
H	-3.88307	2.35953	-4.08376
H	-1.25907	-5.16547	0.24609
H	-4.22540	-0.30182	-4.49208
H	-2.73696	-4.64932	-1.97152
C	-2.54029	2.89688	-1.63343
C	-0.51787	-2.78371	1.61341
C	-3.07975	-1.85574	-2.39744
C	-0.35117	1.96290	2.58891
H	-2.81978	3.79682	-2.17122
H	-0.15108	-3.68343	2.09648
H	-3.54548	-2.46231	-3.16716
H	0.04427	2.56737	3.39866
O	-0.02560	0.09881	-0.87345
S	-3.58792	0.15682	1.22628
C	-3.94724	-1.47752	1.96461
H	-3.14131	-1.79005	2.63342
H	-4.86620	-1.36282	2.54836
H	-4.10291	-2.24008	1.19849
H	0.68771	0.15759	-0.20776
C	4.42095	0.39501	-1.18174
Si	3.54820	0.01851	0.47951
H	3.78102	-1.39922	0.88948
H	4.06032	0.91401	1.56110
H	3.98428	-0.24882	-1.95267
H	4.20226	1.43193	-1.45866
C	5.90723	0.16351	-1.05005
C	6.46724	-1.09770	-1.31786
C	6.76498	1.19615	-0.63306
C	7.83856	-1.31661	-1.18253
H	5.82085	-1.90929	-1.64429
C	8.13648	0.97820	-0.49729
H	6.35187	2.18034	-0.42358
C	8.68005	-0.27977	-0.77068
H	8.25071	-2.29791	-1.40319
H	8.78187	1.79381	-0.18143
H	9.74827	-0.44936	-0.66712

$BnSiH_3$ - INT1 doublet

Fe	-1.59476	0.05290	0.03682
N	-1.49677	2.03195	0.42928
N	-0.57575	-0.33333	1.73561
N	-2.58057	0.44335	-1.67208
N	-1.79987	-1.91783	-0.28740
C	-1.92392	3.05231	-0.38271
C	-0.19513	-1.56864	2.20565
C	-0.93836	2.62464	1.53706
C	-0.14430	0.58552	2.66533
C	-2.86024	1.68155	-2.19780
C	-1.23542	-2.93685	0.44493
C	-3.12927	-0.47432	-2.53418
C	-2.44419	-2.51425	-1.34454
C	-1.63941	4.32384	0.23488
C	0.51481	-1.42202	3.45067
C	-1.03515	4.05892	1.42654
C	0.54001	-0.08939	3.73848
C	-3.58548	1.53800	-3.43689
C	-1.55380	-4.20771	-0.15529
C	-3.75841	0.20349	-3.64151

C	-2.30925	-3.94676	-1.25845
H	-1.87795	5.28442	-0.20351
H	0.92585	-2.24422	4.02228
H	-0.67077	4.75674	2.16949
H	0.97869	0.40823	4.59384
H	-3.91859	2.36533	-4.05029
H	-1.22980	-5.16552	0.23131
H	-4.25980	-0.29601	-4.46056
H	-2.73127	-4.64529	-1.96954
C	-2.54721	2.89982	-1.61418
C	-0.48179	-2.78528	1.59971
C	-3.08546	-1.85197	-2.38267
C	-0.31980	1.96037	2.58669
H	-2.83397	3.80071	-2.14653
H	-0.10872	-3.68485	2.07817
H	-3.55779	-2.45800	-3.14879
H	0.07978	2.56291	3.39583
O	-0.02369	0.10672	-0.89561
S	-3.57452	0.14731	1.23501
C	-3.90784	-1.48361	1.99291
H	-3.09273	-1.78139	2.65725
H	-4.82251	-1.37244	2.58424
H	-4.06380	-2.25560	1.23632
H	0.70406	0.16094	-0.24350
C	4.36930	0.36320	-1.21153
Si	3.49305	-0.00868	0.44858
H	3.74210	-1.41864	0.87474
H	3.98372	0.90609	1.52369
H	3.94736	-0.29577	-1.97785
H	4.13631	1.39350	-1.50113
C	5.85810	0.15622	-1.06786
C	6.43952	-1.09867	-1.31924
C	6.69672	1.20637	-0.65567
C	7.81318	-1.29458	-1.17281
H	5.80815	-1.92354	-1.64176
C	8.07052	1.01139	-0.50881
H	6.26682	2.18597	-0.45884
C	8.63553	-0.24054	-0.76599
H	8.24214	-2.27140	-1.38093
H	8.70093	1.84016	-0.19701
H	9.70557	-0.39225	-0.65382

$BnSiH_3$

C	3.92972	0.28308	-1.61720
Si	2.84466	0.73335	-0.11891
H	2.97366	-0.29743	0.94703
H	3.25497	2.04744	0.44690
H	3.56003	-0.66607	-2.02460
H	3.76580	1.04402	-2.39023
C	5.39823	0.18021	-1.27172
C	5.95509	-1.03506	-0.84267
C	6.23772	1.30308	-1.34770
C	7.30643	-1.12681	-0.50400
H	5.32369	-1.91881	-0.78032
C	7.58938	1.21435	-1.00978
H	5.82791	2.25388	-1.68177
C	8.13040	-0.00176	-0.58563
H	7.71593	-2.08011	-0.17963
H	8.22075	2.09629	-1.08192
H	9.18286	-0.07259	-0.32484
H	1.41124	0.81980	-0.51987

$PhSiH_3$

C	5.35754	0.04311	-1.23993
C	6.07222	-1.16684	-1.16187
C	6.05484	1.23900	-0.98708
C	7.42988	-1.18319	-0.83574
H	5.56733	-2.10966	-1.36166
C	7.41269	1.22747	-0.66047
H	5.53591	2.19314	-1.04910
C	8.10231	0.01518	-0.58359
H	7.96291	-2.12889	-0.78234
H	7.93213	2.16305	-0.47023
H	9.15963	0.00446	-0.33235
Si	3.52256	0.06058	-1.64619
H	3.18947	-1.06105	-2.56643
H	2.67808	-0.09007	-0.42691
H	3.15806	1.35029	-2.29358

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