Electronic Supplementary Material (ESI) for Chemical Science.

Intermolecular C–H Silylations of Arenes and Heteroarenes with Mono-, Bis-, and Tris(trimethylsiloxy)hydrosilanes: Control of Silane Redistribution under Operationally Diverse Approaches

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1. General

^{1}H NMR spectra were recorded on a Bruker Avance III HD 400 (400 MHz) and Bruker Avance III 500 (500 MHz). Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, hept = heptet, m = multiplet, br = broad), and coupling constants (*J*, Hz). ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 (101 MHz) and Bruker Avance III 500 (126 MHz). Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{29}Si NMR spectra were recorded on a Bruker Avance III 500 (99 MHz). ^{19}F NMR spectra were recorded on a Bruker Advance III HD 400 (376 MHz) spectrometer without proton decoupling. ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (162 MHz). High-resolution mass spectrometry was performed on a JEOL AccuTOF DART (positive mode). Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Solvents were purified under a positive pressure of dry argon by a two-column solid-state purification system (JC Meyer Solvent System, Irvine, CA) and stored over activated 4 Å molecular sieves. $CDCl_3$ (Aldrich) was distilled and stored over activated 4 Å molecular sieves prior to use. 25mm 0.2 μm PTFE Syringe filters from VWR were used in workup procedures.

1.1 Reagents

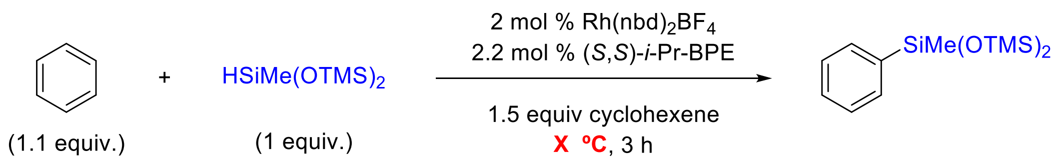
$[Rh(nbd)Cl]_2$ was purchased from Strem and was used as received. (*S*)-(-)-XylBINAP was purchased from Ambeed and was used as received. $[Rh(1,5\text{-hexadiene})Cl]_2$ was purchased from Aldrich and Ambeed and was used as received.

Tris(trimethylsiloxy)silane (Ambeed), 1,1,1,3,5,5,5-Heptamethyltrisiloxane (Aldrich), Pentamethyldisloxane (Gelest), Cyclohexene (Aldrich), 2,3-Dimethyl-2-butene (Aldrich), Furan (Aldrich), 2-Methylfuran (Oakwood), *N*-Methylpyrrole (Oakwood), 1-Methylindole (Oakwood), Fluorobenzene (Oakwood), Chlorobenzene (Oakwood), 2-*tert*-Butylfuran (Ambeed), 2,3-Dimethylfuran (Ambeed), 2-Ethylfuran (Ambeed), Anisole (Aldrich), Benzofuran (Oakwood), Thiophene (Aldrich), Benzothiophene (Aldrich) *tert*-Butylbenzene (Aldrich), and Diphenylether (Ambeed) were distilled prior to use. Naphthalene (Oakwood) was recrystallized in ethanol.

2. Synthesis and characterization of C-H silylation products

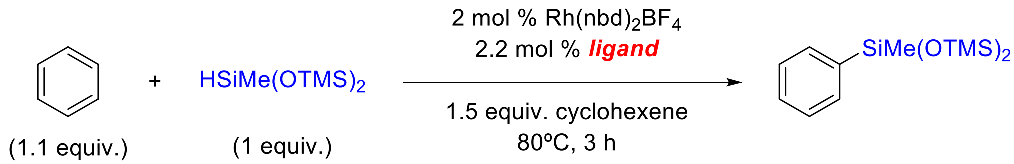
2.1 Optimization of reaction conditions for Si-1

Table S1. Temperature screening



entry	temperature	conv.
1	22 ºC	0%
2	40 ºC	0%
3	60 ºC	7%
4	80 ºC	45%

Table S2. Ligand Screening



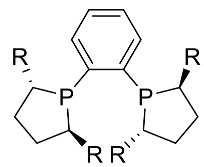
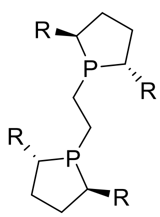
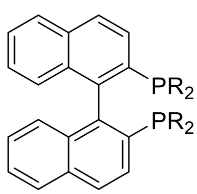
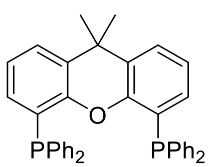
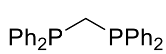
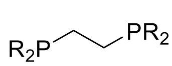
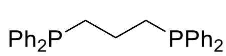
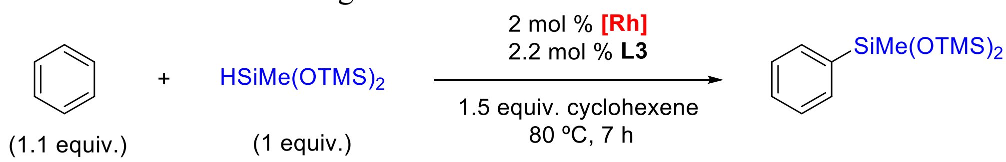
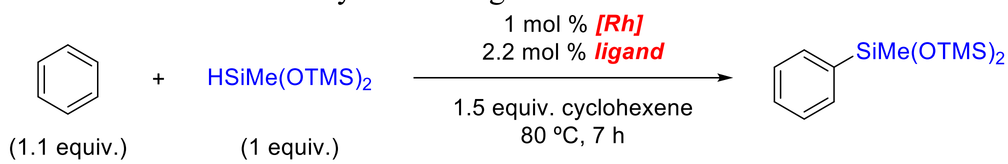
entry	***ligand***		conv.
1		R= Et (**L1**)	<1%
2		R= Ph (**L2**)	0%
3		R= *i*-Pr (**L2a**)	3%
4		R= Et (**L2b**)	21%
5		R = Ph (*R)* (**L3**)	<1%
6		R = 3,5-dimethyl-Ph (*S*) (**L4**)	11%
7		**L5**	0%
8		**L6**	0%
9		R= cyclohexyl (**L7**)	3%
10		R= Ph (**L7a**)	0%
11		**L8**	0%

Table S3. Rh salt screening



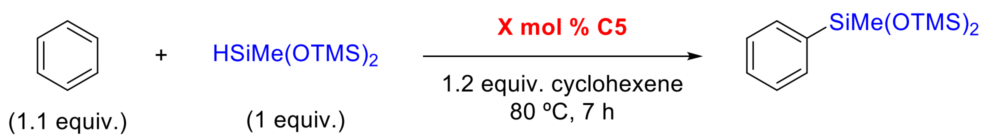
entry	[Rh]	conv.	yield
1	$Rh(nbd)_2BF_4$	45% conv	61%
2	$Rh(cod)BF_4$	0% conv	-
3	$[Rh(OMe)cod]_2$	70% conv	53%
4	$[RhCl(coe)_2]_2$	69% conv	51%
5	$[RhCl(ethylene)_2]_2$	75% conv	57%
6	$[RhCl(CO)_2]_2$	0% conv	-
7	$[RhCl(1,5\text{-hexadiene})]_2$	66% conv	54%
8	$[RhCl(nbd)]_2$	42% conv	32%

Table S4. Preformed catalyst screening



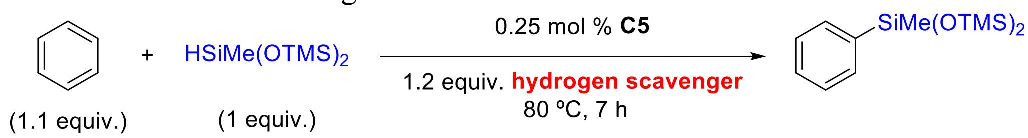
entry	[Rh]	ligand	conv.
1a	$Rh(nbd)_2BF_4$	**L3**	74%
1b	**C1**		5%
2a	$[RhCl(nbd)]_2$	**L3**	42%
2b	**C2**		67%
3a	$RhCl(coe)_2]_2$	**L3**	69%
3b	**C3**		69%
4a	$[RhCl(ethylene)_2]_2$	**L3**	75%
4b	**C4**		75%
5a	$[RhCl(1,5\text{-hexadiene})]_2$	**L3**	66%
5b	**C5**		83%

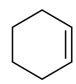
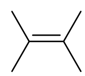
Table S5. Alkene screening



entry	catalyst loading	conv.
1	0.25 mol %	69% conv
2	0.5 mol %	74% conv
3	1 mol %	68% conv

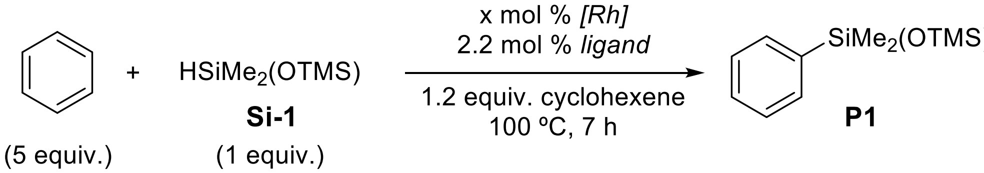
Table S6. Alkene screening



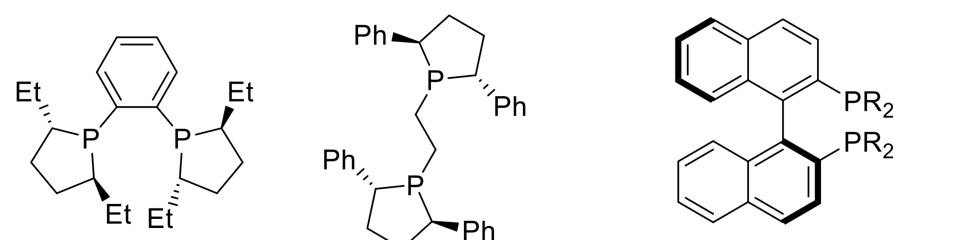
entry	hydrogen scavenger	conv.
1	No hydrogen scavenger	9% conv
2		80% conv
3		19% conv

2.2 Optimization of reaction conditions for Si-2

Table S7. Ligand and rhodium salt screening



entry	[Rh]	ligand	condition	conv.; yield	Si-redistribution
1	$[Rh(1,5\text{-hexadiene})Cl]_2$	**L1**	1 mol % [Rh]	<5%; -	54%
2	$[Rh(1,5\text{-hexadiene})Cl]_2$	**L2**	1 mol % [Rh]	72%; 55%	28%
3	$[Rh(1,5\text{-hexadiene})Cl]_2$	**L3**	1 mol % [Rh]	44%; -	18%
4	$[Rh(1,5\text{-hexadiene})Cl]_2$	**L4**	1 mol % [Rh]	74%; 57%	26%
5	$[Rh(nbd)Cl]_2$	**L4**	1 mol % [Rh]	81%; 53%	19%
6	$[Rh(coe)_2Cl]_2$	**L4**	1 mol % [Rh]	74%; 55%	26%
7	$[Rh(ethylene)_2Cl]_2$	**L4**	1 mol % [Rh]	77%; 64%	23%
8	$Rh(nbd)_2BF_4$	**L4**	2 mol % [Rh]	48%; -	52%

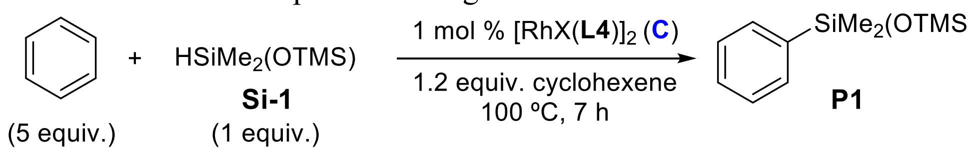


L1 **L2**

L3: R = Ph (*rac*)

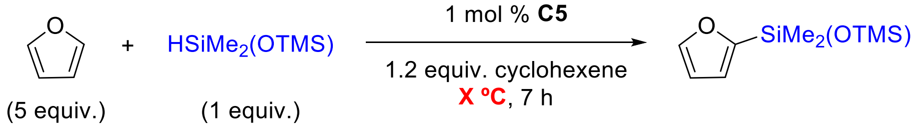
L4: R = 3,5-dimethyl-Ph (*S*)

Table S8. Preformed complex screening



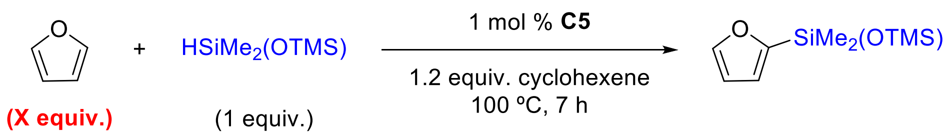
entry	[Rh] / L	preformed catalyst	conv.	Si-redistribution
1	$[Rh(nbd)Cl]_2$ / **L4**	**C1**	79%	21%
2	$[Rh(coe)_2Cl]_2$ / **L4**	**C2**	78%	22%
3	$[Rh(ethylene)_2Cl]_2$ / **L4**	**C3**	82%	18%
4	$[Rh(1,5\text{-hexadiene})Cl]_2$ / **L4**	**C4**	93%	7%

Table S9. Temperature screening



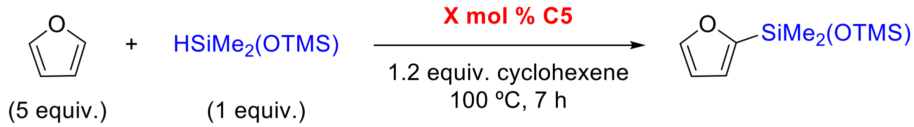
entry	temperature	conv.
1	80 ºC	65%
2	100 ºC	71%
3	120 ºC	66%

Table S10. Arene equivalence screening



entry	arene equivalence	conv.
1	5	66%
2	7	58%
3	10	58%
4	13.8	71%

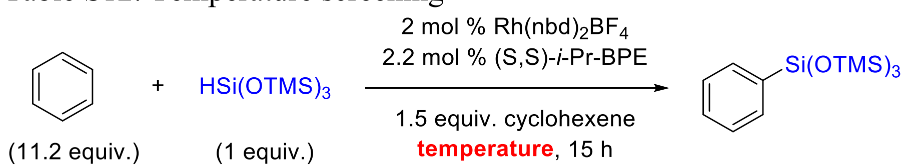
Table S11. Catalyst loading screening



entry	catalyst loading	conv.
1	1 mol %	71%
2	1.25 mol %	72%
3	1.5 mol %	73%
4	1.75 mol %	71%

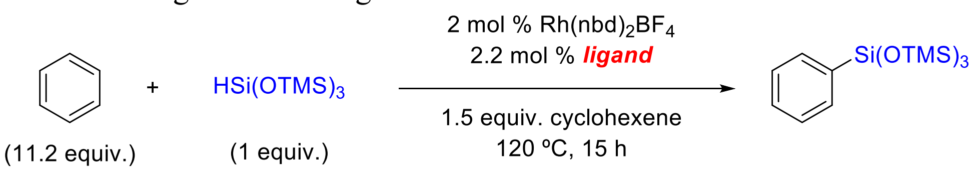
2.3 Optimization of reaction conditions for Si-3

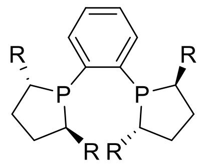
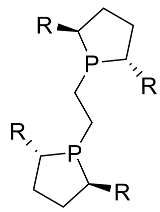
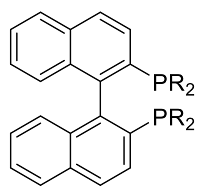
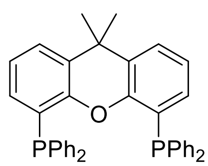
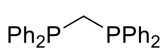
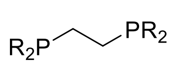
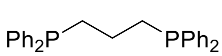
Table S12. Temperature screening



entry	temperature	conv.	yield
1	22 ºC	<1%	-
2	40 ºC	<1%	-
3	60 ºC	<1%	-
4	80 ºC	7%	-
5	100 ºC	37%	30%
6	120 ºC	59%	59%

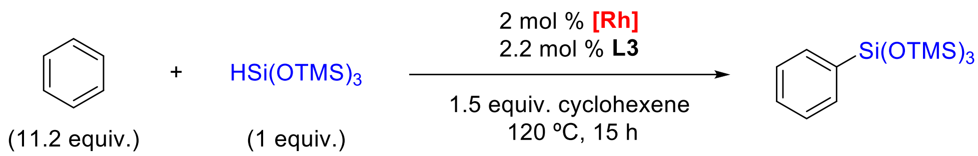
Table S13. Ligand Screening



entry	*ligand*		conv.
1		R= Et (**L1**)	8%
2		R= Ph (**L2**)	<1%
3		R= *i*-Pr (**L2a**)	94%
4		R= Et (**L2b**)	31%
5		R = Ph (*R*) (**L3**)	7%
6		R = 3,5-dimethyl-Ph (*S*) (**L4**)	52%
7		**L5**	<1%
8		**L6**	<1%
9		R= cyclohexyl (**L7**)	15%
10		R= Ph (**L7a**)	<1%
11		**L8**	<1%

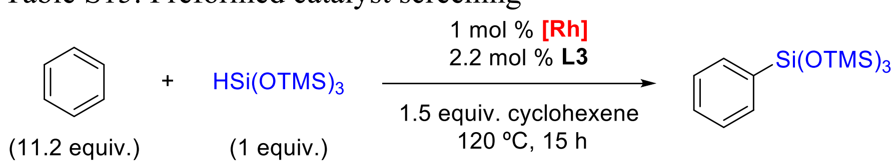
(*S*)-(-)-XylBINAP ($76/ mmol)
(*S*,*S*)-*i*-Pr-BPE ($295.7/ mmol)

Table S14. Rh salt screening



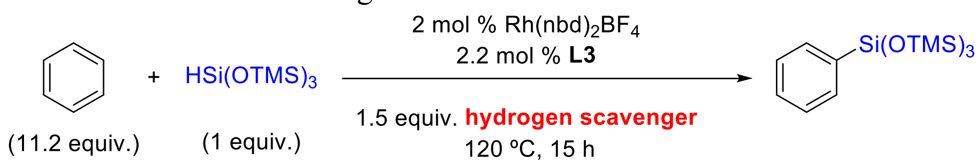
entry	[Rh]	conv.	yield
1	$Rh(nbd)_2BF_4$	63%	61%
2	$Rh(cod)_2BF_4$	6%	-
3	$Rh(cod)_2OTf$	7%	-
4	$[RhCl(coe)_2]_2$	41%	31%
5	$[RhCl(ethylene)_2]_2$	33%	31%
6	$[RhCl(CO)_2]_2$	0%	-
7	$[RhCl(1,5\text{-hexadiene})]_2$	28%	22%
8	$[RhCl(nbd)]_2$	42%	32%

Table S15. Preformed catalyst screening



entry	[Rh]	*ligand*	conv.	yield
1a	$Rh(nbd)_2BF_4$	**L3**	41%	31%
1b	**C1**		8%	-
2a	$[RhCl(nbd)]_2$	**L3**	42%	32%
2b	**C2**		18%	-
3a	$RhCl(coe)_2]_2$	**L3**	58%	58%
3b	**C3**		<1%	-
4a	$[RhCl(ethylene)_2]_2$	**L3**	33%	31%
4b	**C4**		24%	23%

Table S16. Alkene screening



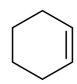
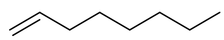
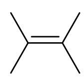
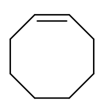
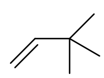
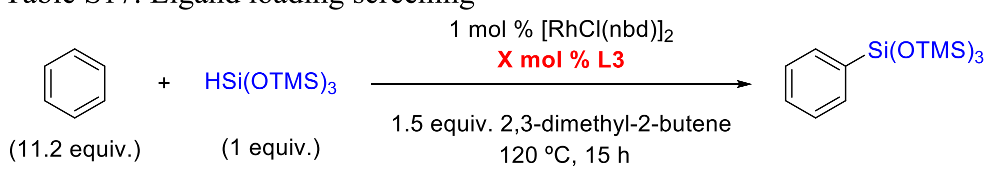
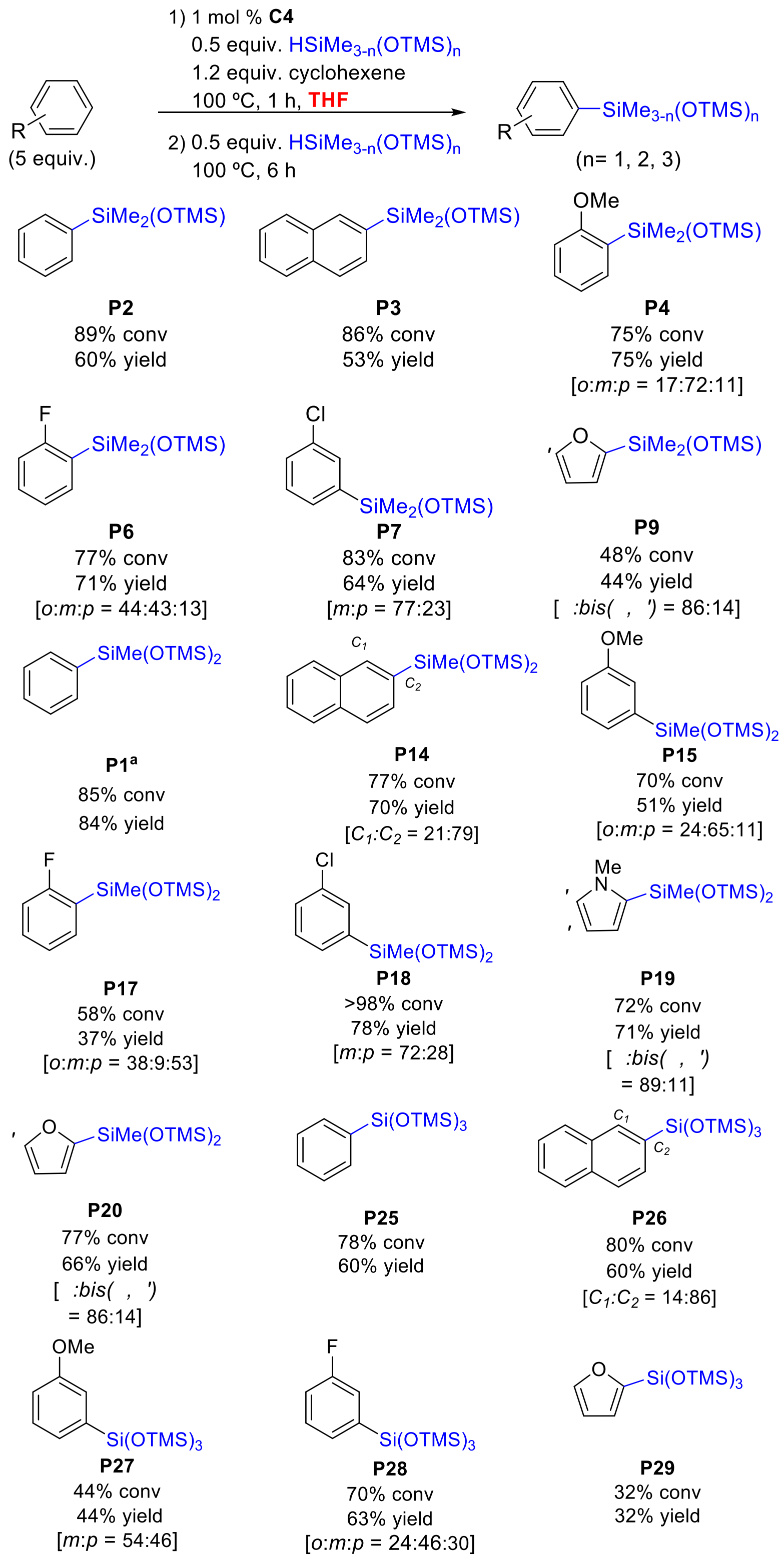
entry	hydrogen scavenger	conv.	yield
1	No hydrogen scavenger	14%	-
2		58%	58%
3		12%	-
4		70%	69%
5		19%	-
6		49%	24%

Table S17. Ligand loading screening



entry	ligand loading	conv.	yield
1	1 mol %	93%	92%
2	2 mol %	95%	92%
3	2.2 mol %	92%	71%
4	3.5 mol %	81%	78%

2.4 Portion-wise C—H silylation of arenes and heteroarenes with solvent and various siloxysilanes



2.5 Synthesis of [RhCl(Xyl-BINAP)]$_2$ (C4)

In a N_2-filled glovebox, an oven-dried vial was charged with [Rh(1,5-hexadiene)Cl]$_2$ (112.8 mg, 0.26 mmol, 1 equiv.), (*S*)-(-)-XylBINAP (400 mg, 0.54 mmol, 2.1 equiv.), and THF (4 ml). After 20 h of stirring at 22 °C, a dark brown solution was obtained. Solvent was removed by evaporation and rinsed with *n*-hexanes. Brown solid form of [RhCl(XylBINAP)]$_2$ (**C4**) was obtained after evaporation. The resulting solid was collected by filtration and washed with cold *n*-hexanes (95% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.33 (s, 10H), 7.09 (q, *J* = 7.1 Hz, 4H), 6.82 (t, *J* = 7.7 Hz, 2H), 6.61 (s, 4H), 6.42 (d, *J* = 8.6 Hz, 2H), 6.05 (s, 3H), 2.27 (t, *J* = 12.1 Hz, 3H), 2.12 (d, *J* = 7.4 Hz, 3H), 2.04 (s, 2H), 1.91 (s, 2H), 1.62 (s, 2H), 1.15 (d, *J* = 22.2 Hz, 5H), 0.79 (t, *J* = 6.7 Hz, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.71 (d, *J* = 194.5, 200.0 Hz). X-ray data is shown at the end of SI.

2.6 Redistribution reaction in control experiment

Redistribution control experiment with Si-1

In a N_2-filled glovebox, an oven-dried pressure tube was charged with [RhCl(XylBINAP)]$_2$ (**C4**, 17.5 mg, 1 mol %), (*S*)-(-)-XylBINAP (7.3 mg, 1 mol %), or [Rh(1,5-hexadiene)Cl]$_2$ (8.7 mg, 1 mol %) and **Si-1** (148.4 mg, 1 mmol). After stirring for 7 h at 100 ºC, the reaction mixture was cooled to 22 °C. Conversion to redistribution byproducts were monitored by ^{1}H NMR and ^{29}Si NMR. Note that due to the high volatility of some expected byproducts, the percentile of the observed redistribution is an approximate value based on ^{1}H NMR analysis.

Table S18. Redistribution control experiment of **Si-1**

1 mol % **X** + $HSiMe_2(OTMS)$ (**Si-1**) —(100 °C, 7 h)→ redistribution byproduct(s)

	hydrosilane redistribution		
	0.5 h	3 h	7 h
Si-1	<5%	<5%	<5%
[Rh(1,5-hexadiene)Cl]$_2$	6%	55%	67%
L4	<5%	<5%	<5%
C4	<5%	<5%	<5%

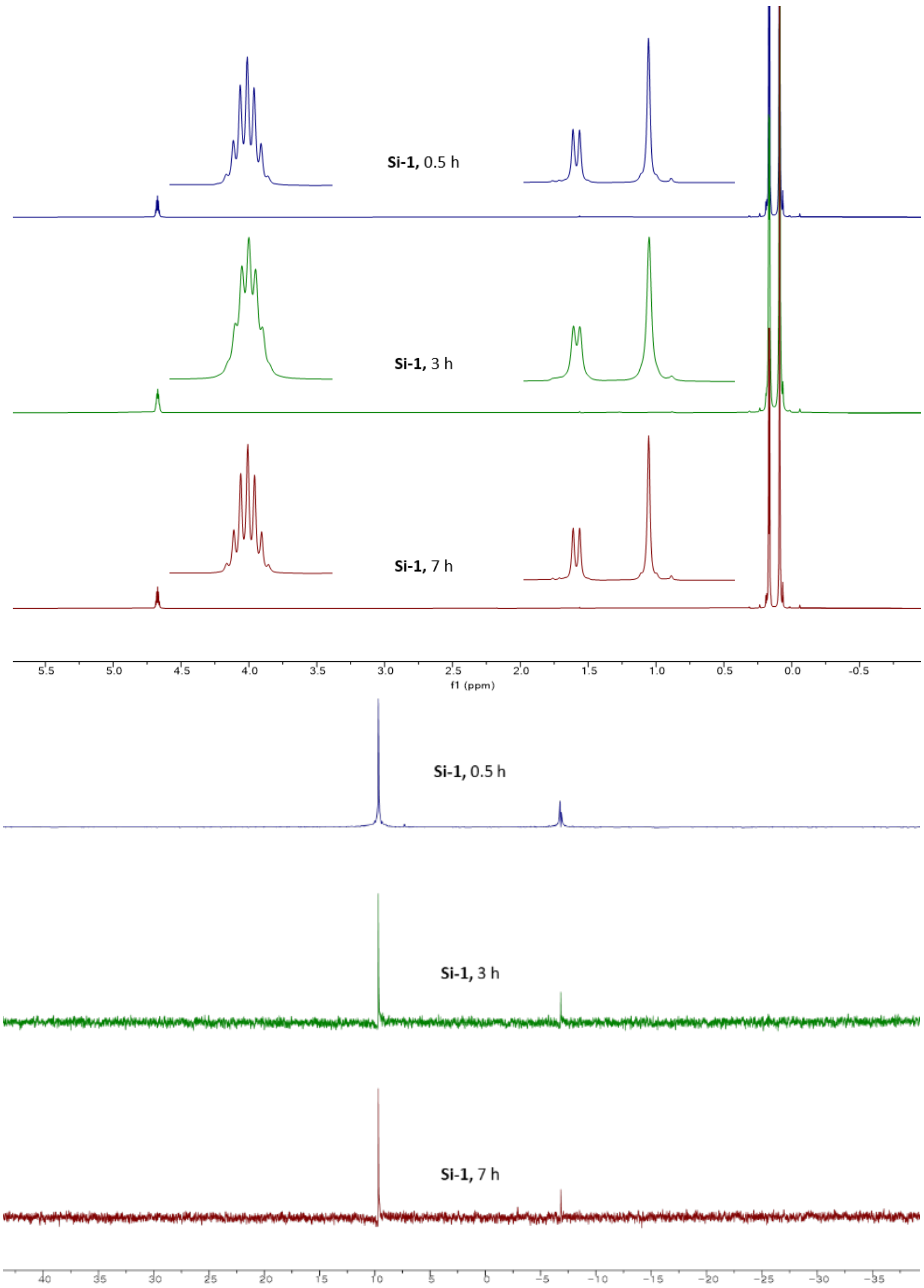


Figure S1. ^{1}H and ^{29}Si spectra of **Si-1** redistribution.

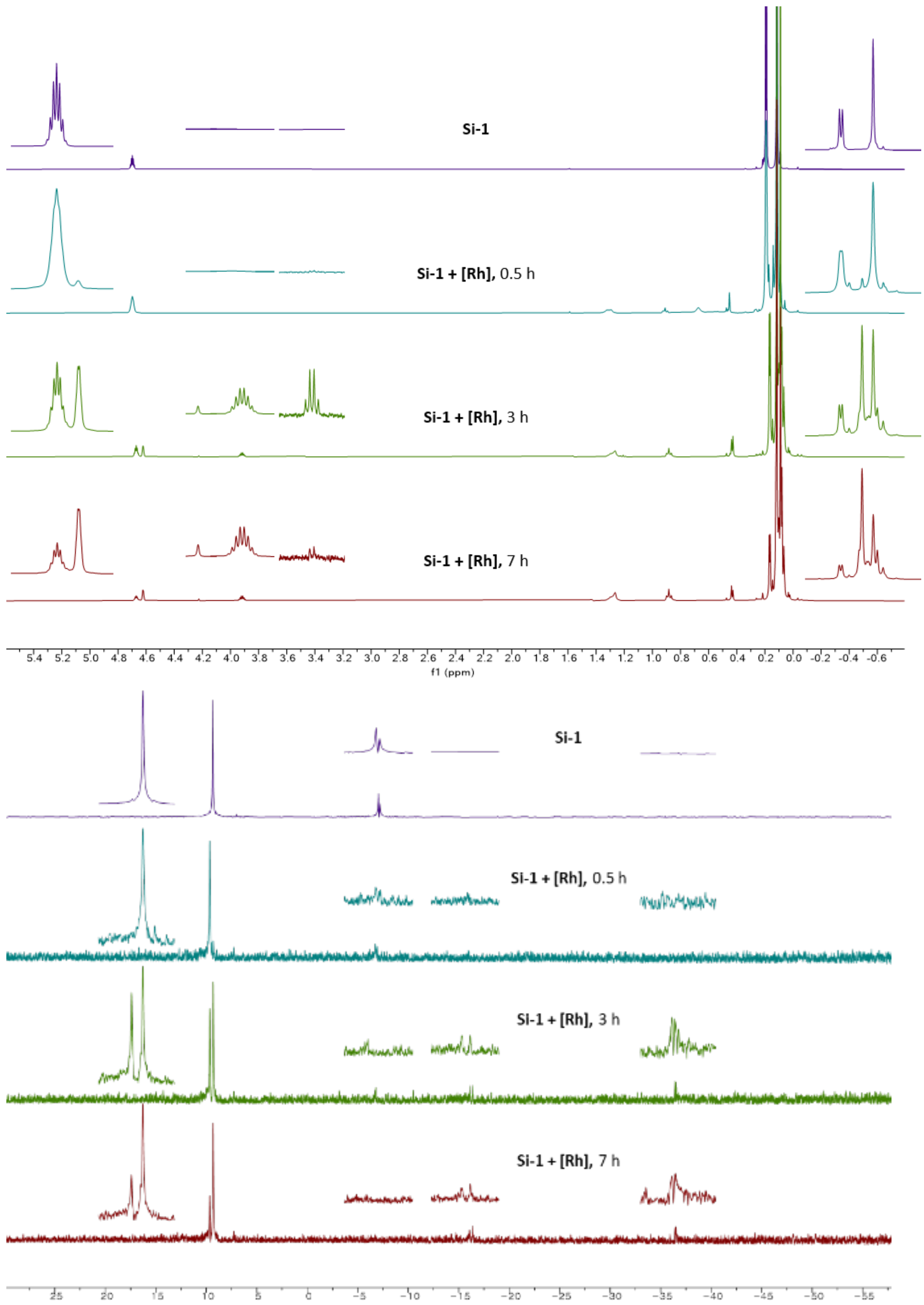
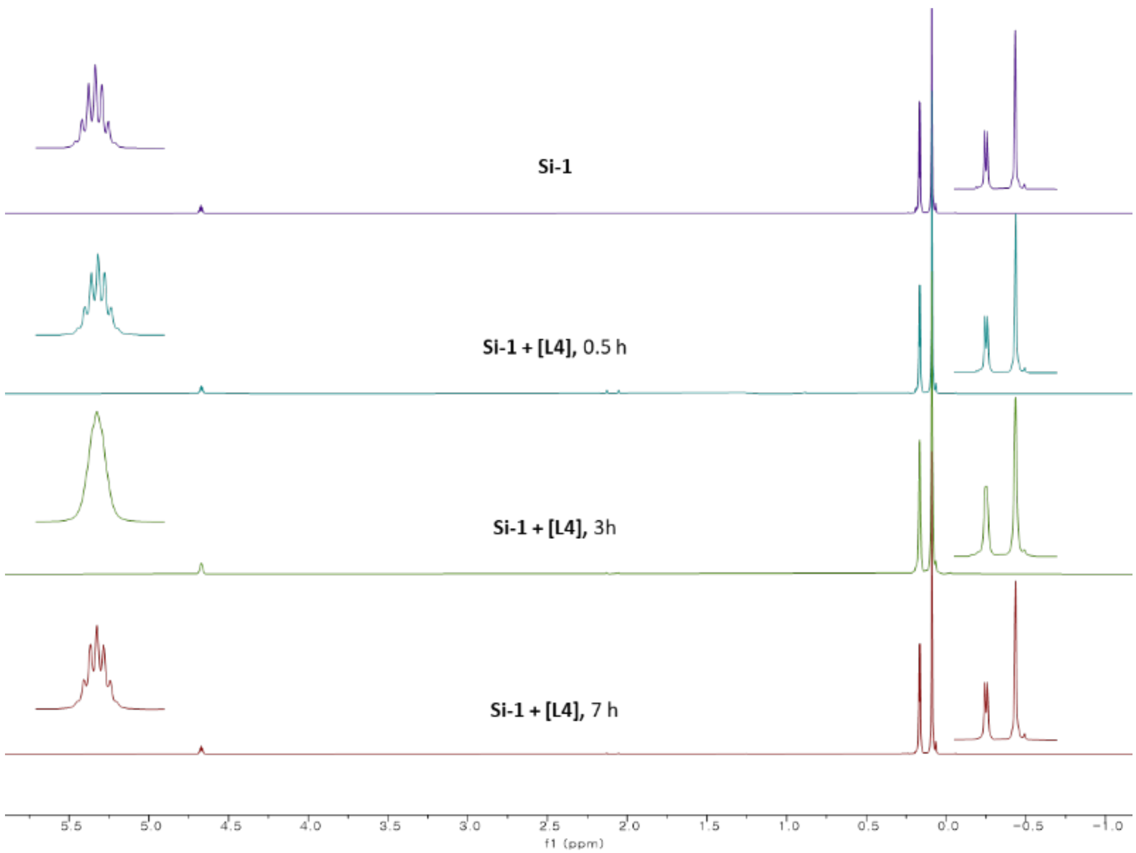


Figure S2. ^{1}H and ^{29}Si spectra of **Si-1** redistribution tendency with $[Rh(1,5\text{-hexadiene})Cl]_2$.



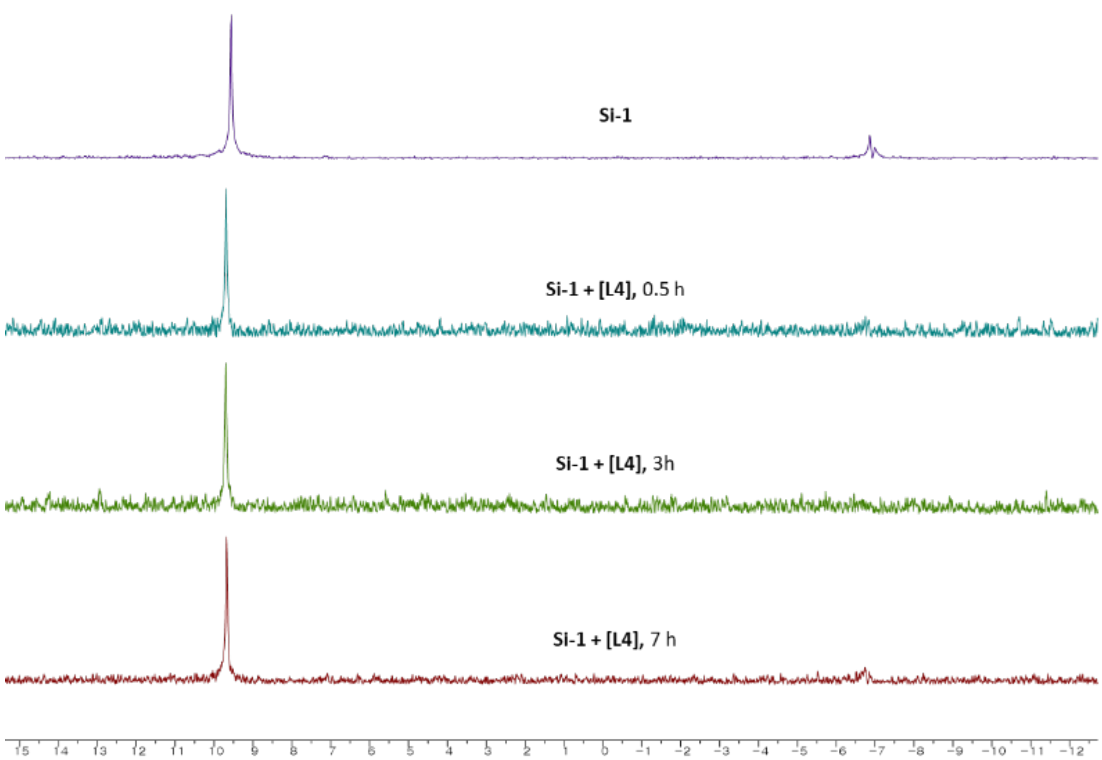


Figure S3. ^{1}H and ^{29}Si spectra of **Si-1** redistribution tendency with **L4**.

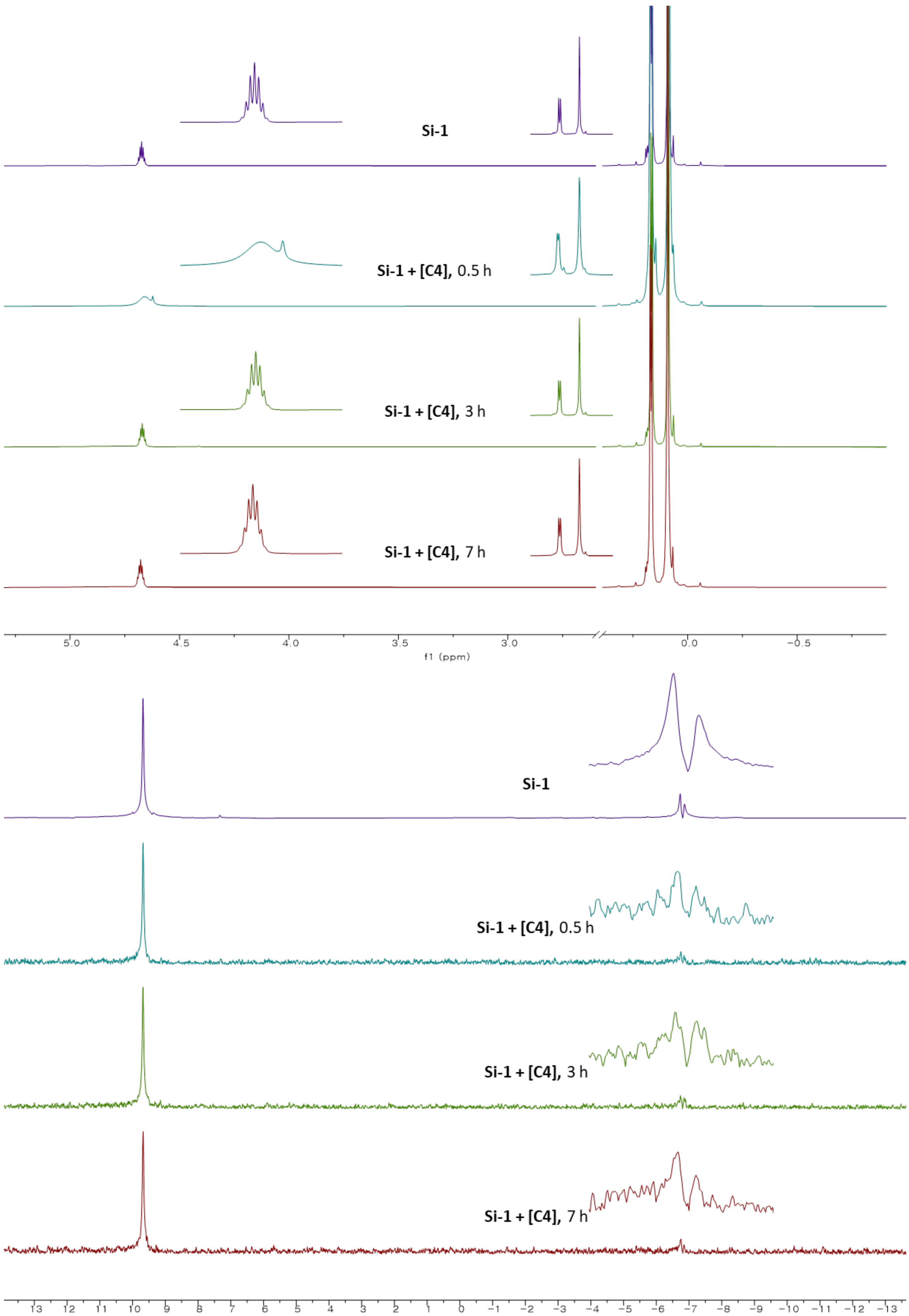


Figure S4. ^{1}H and ^{29}Si spectra of **Si-1** redistribution tendency with **C4.**

Redistribution control experiment with Si-2

In a N_2-filled glovebox, an oven-dried pressure tube was charged with $[RhCl(XylBINAP)]_2$ (**C4**, 17.5 mg, 1 mol %), (*S*)-(-)-XylBINAP (7.3 mg, 1 mol %), or $[Rh(1,5\text{-hexadiene})Cl]_2$ (8.7mg, 1 mol %) and **Si-2** (222.5 mg, 1 mmol). After stirring for 7 h at 80 ºC, the reaction mixture was cooled to 22 °C. Conversion to redistribution byproducts were monitored by ^{1}H NMR. Note that due to the high volatility of some expected byproducts, the percentile of the observed redistribution is an approximate value based on ^{1}H NMR analysis.

Table S19. Redistribution control experiment of **Si-2**

0.25 mol % **X** + $HSiMe(OTMS)_2$ (**Si-2**) $\xrightarrow[7\ h]{80\ °C}$ redistribution byproduct(s)

	hydrosilane redistribution		
	0.5 h	1 h	7 h
Si-2	<5%	<5%	<5%
$[Rh(1,5\text{-hexadiene})Cl]_2$	6%	8%	21%
L4	<5%	<5%	<5%
C4	<5%	<5%	8%

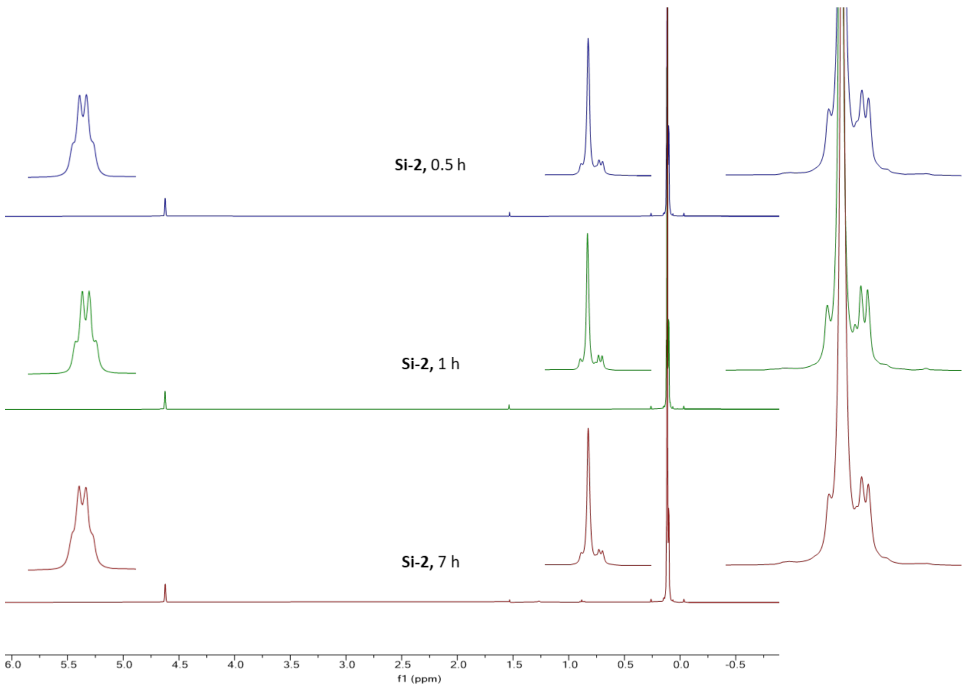


Figure S5. [1]H spectra of **Si-2** redistribution.

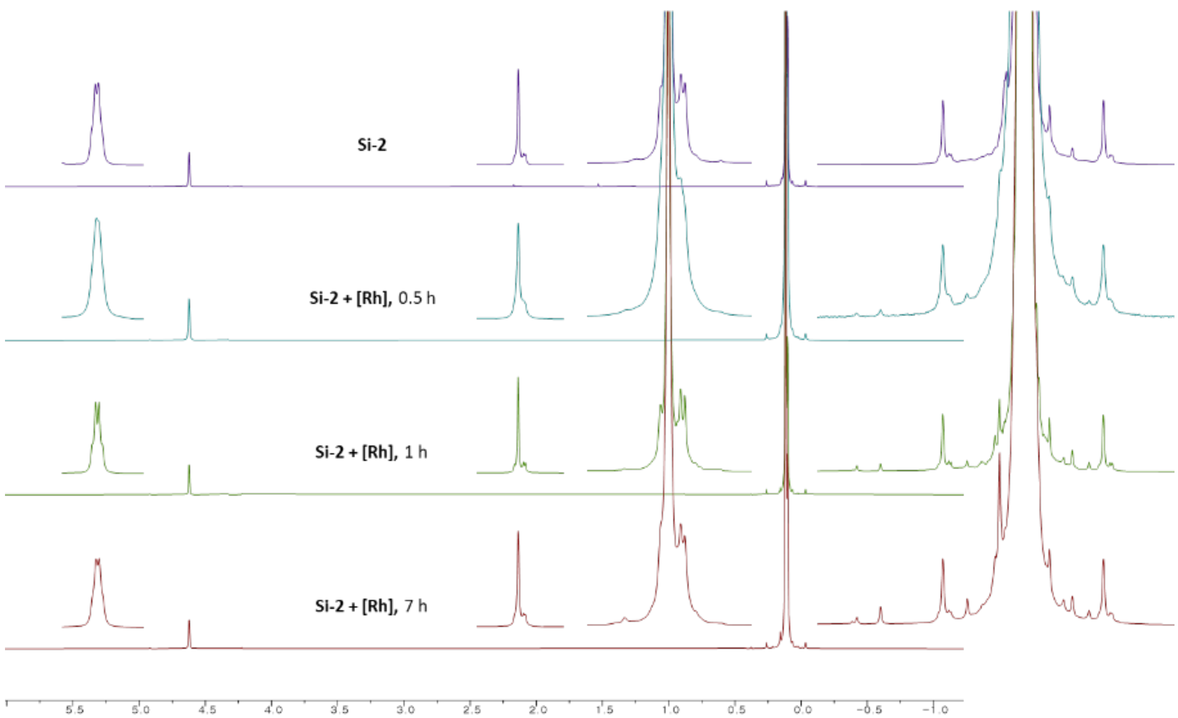


Figure S6. [1]H spectra of **Si-2** redistribution tendency with [Rh(1,5-hexadiene)Cl]$_2$.

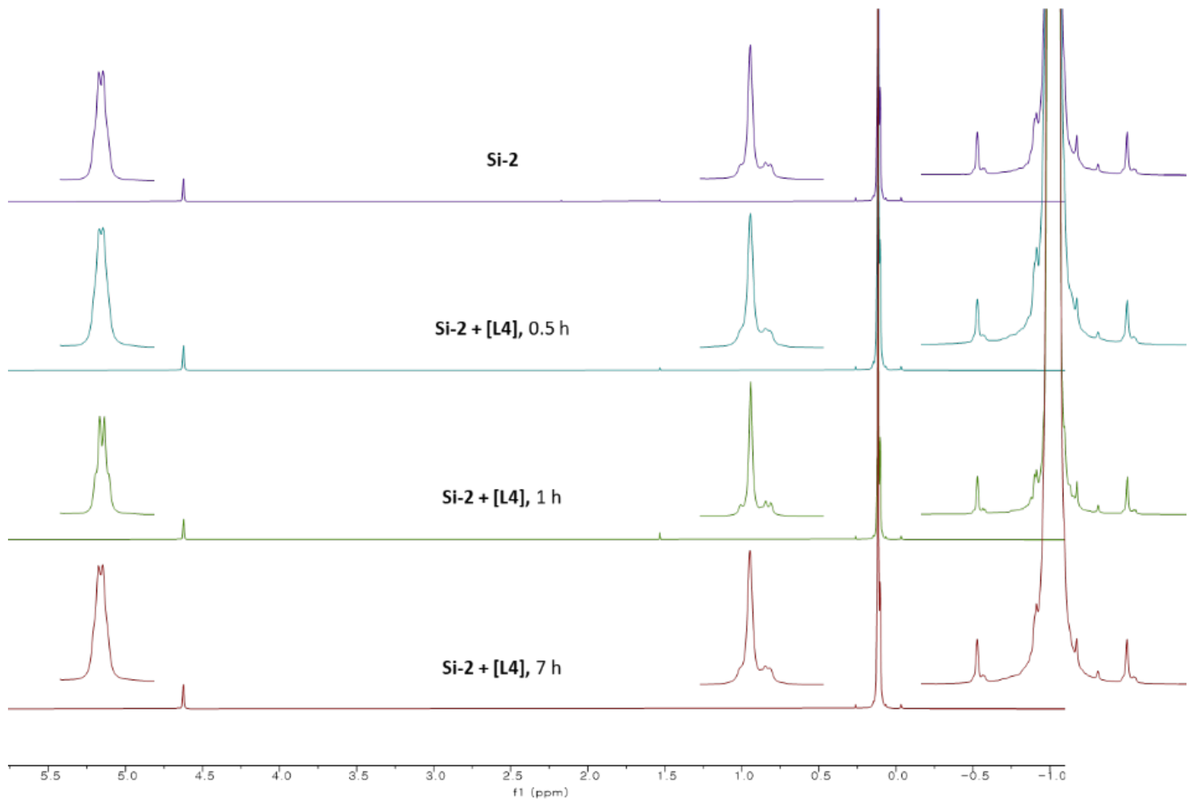


Figure S7. [1]H spectra of **Si-2** redistribution tendency with **L4**.

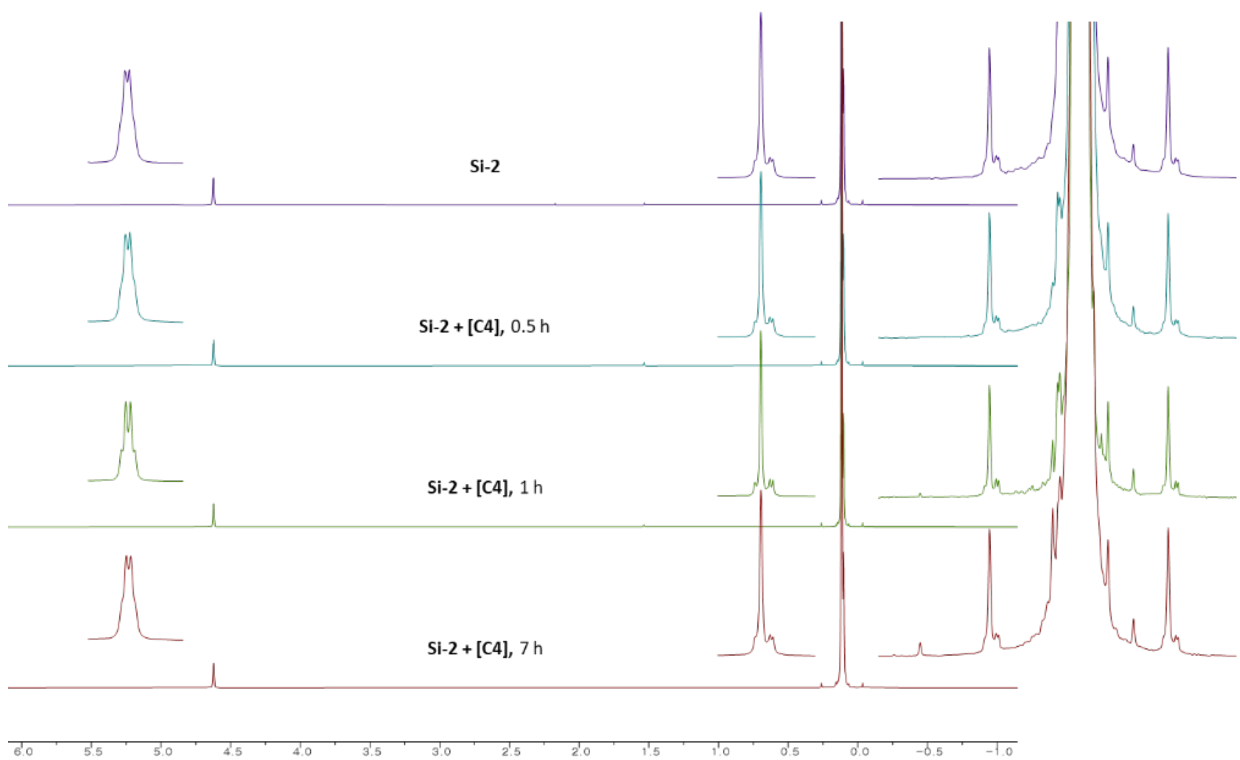


Figure S8. [1]H spectra of **Si-2** redistribution tendency with **C4.**

Redistribution control experiment with Si-3

In a N_2-filled glovebox, an oven-dried pressure tube was charged with $[Rh(nbd)Cl]_2$ (4.6 mg, 1 mol %) and **Si-3** (296.7 mg, 1 mmol). After stirring for 15 h at 120 ºC, the reaction mixture was cooled to 22 °C. Conversion to redistribution byproducts were monitored by ^{1}H NMR. Note that due to the high volatility of some expected byproducts, the percentile of the observed redistribution is an approximate value based on ^{1}H NMR analysis.

Table S20. Redistribution control experiment of **Si-3**

1 mol % **X** + $HSi(OTMS)_3$ (**Si-3**) → (120 °C, 15 h) redistribution byproduct(s)

	hydrosilane redistribution			
	0.5 h	1 h	5 h	15 h
Si-3	<5%	<5%	<5%	<5%
$[Rh(nbd)Cl]_2$	<5%	9%	10%	13%

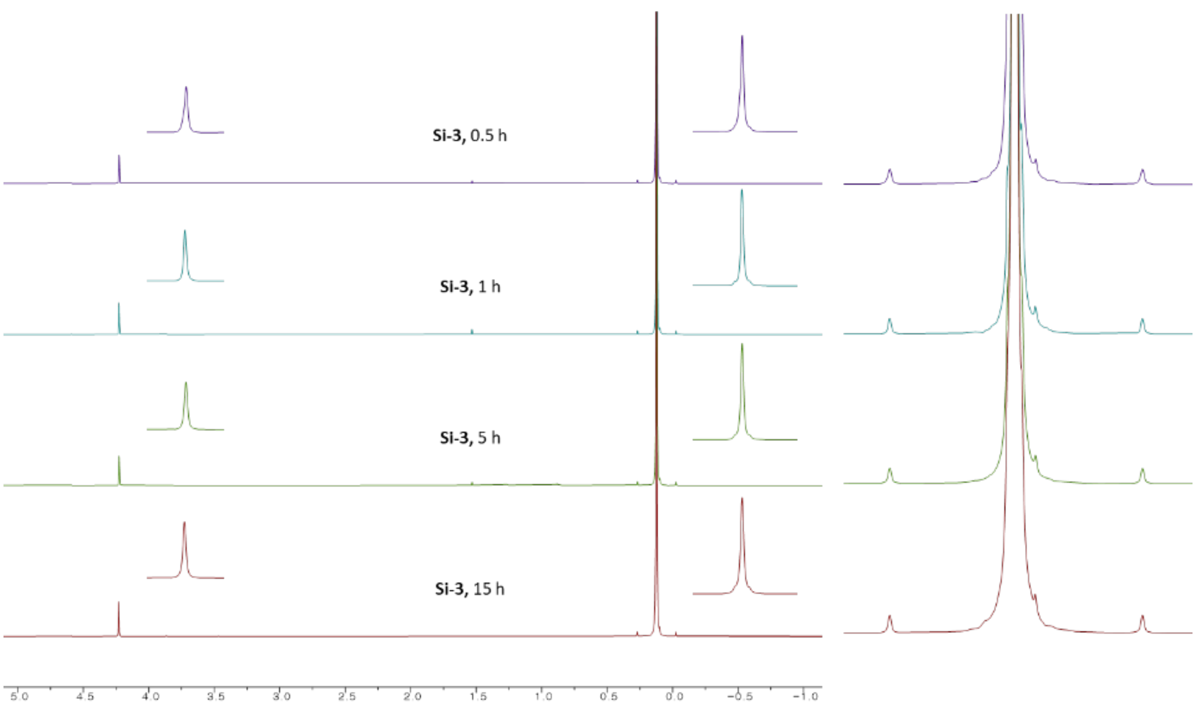


Figure S9. ^{1}H spectra of **Si-3** redistribution.

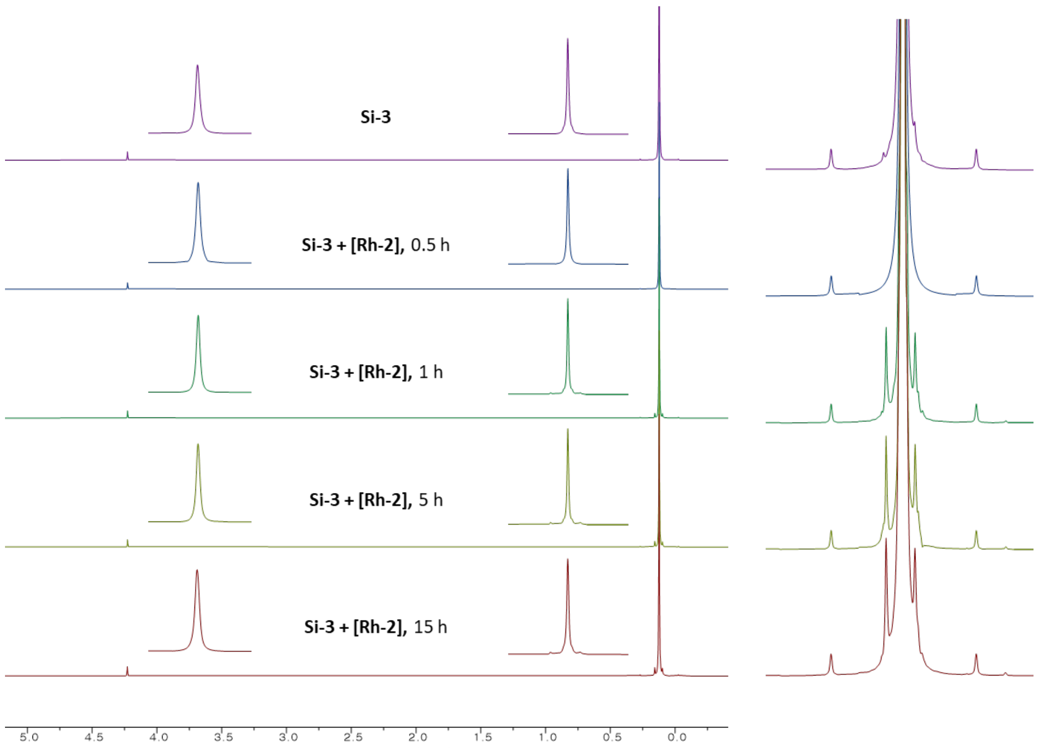


Figure S10. ^{1}H spectra of **Si-3** redistribution tendency with $[Rh(nbd)Cl]_2$.

2.7 Representative procedure for Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-1 (Procedure A1)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (8.7 mg, 1 mol %) and benzene (195.3 mg, 5 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-1** (74.2 mg, 0.5 equiv.) and cyclohexene (49.3 mg, 1.2 equiv.) were added. The reaction mixture was allowed to stir for 7 h at 100 °C (93% conv., 71% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P1**) as a colorless liquid [71% isolated yield (80 mg)]

2.8 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-1 (Procedure A2)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (8.7 mg, 1 mol %) and benzene (195.3 mg, 5 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-1** (37.1 mg, 0.5 equiv.) and cyclohexene (49.3 mg, 1.2 equiv.) were added. The reaction mixture was allowed to stir for 1 h at 100 °C. To the mixture, **Si-1** (37.1 mg, 0.5 equiv.) was added and allowed to stir for 6 h at 100 °C (95% conv., 85% yield by ^{1}H NMR analysis).

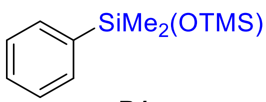
Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P1**) as a colorless liquid [85% isolated yield (95 mg)].

2.9 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-1 with solvent (Procedure A3)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (8.7 mg, 1 mol %) and benzene (195.3 mg, 5 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-1** (37.1 mg, 0.5 equiv.), cyclohexene (49.3 mg, 1.2 equiv.) and THF (328.9 mg, 1.35 M) were added. The reaction mixture was allowed to stir for 1 h at 100 °C. To the mixture, **Si-1** (37.1 mg, 0.5 equiv.) was added and allowed to stir for 6 h at 100 °C (89% conv., 60% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P1**) as a colorless liquid [60% isolated yield (67 mg)].

1,1,1,3,3-Pentamethyl-3-phenyldisiloxane (P1)



P1

Procedure A1: 93% conv., 71% isolated yield (80 mg)

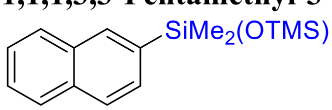
Procedure A2: 95% conv., 85% isolated yield (95 mg)

Procedure A3: 89% conv., 60% isolated yield (67 mg)

Procedure E: 32% conv.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.43 (dd, *J* = 4.8, 1.8 Hz, 3H), 0.40 (s, 6H), 0.17 (s, 9H). Spectroscopic data were consistent with those previously reported.[1]

1,1,1,3,3-Pentamethyl-3-(naphthalen-2-yl)disiloxane (P2)



P2

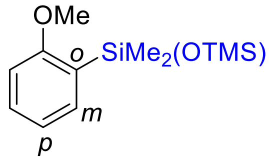
Procedure A1: 53% conv., 41% isolated yield (56 mg)

Procedure A2: 58% conv., 46% isolated yield (63 mg)

Procedure A3: 86% conv., 53% isolated yield (73 mg)

^{1}NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.98 – 7.88 (m, 3H), 7.74 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.57 (dd, *J* = 6.2, 3.3 Hz, 2H), 0.52 (s, 6H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.57, 131.85, 131.61, 130.86, 127.36, 126.18, 125.69, 124.90, 124.29, 123.80, 0.00, -1.07. HRMS (EI+) calcd for $[C_{15}H_{23}OSi_2]^+$ $[M+H]^+$: 275.1282, found: 275.12761.

1-(2-methoxyphenyl)-1,1,3,3,3-pentamethyldisiloxane and regioisomers (P3)



P3

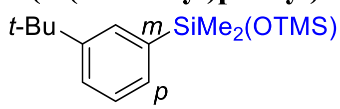
Procedure A1: 57% conv., 55% isolated yield (70 mg) [*o*:*m*:*p* = 24:61:15]

Procedure A2: 75% conv., 60% isolated yield (76 mg) [*o*:*m*:*p* = 23:61:16]

Procedure A3: 75% conv., 75% isolated yield (95 mg) [*o*:*m*:*p* = 17:72:11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 1H), 7.37 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 0.26H), 7.32 (dd, *J* = 8.2, 7.2 Hz, 1.16H), 7.14 (dt, *J* = 7.1, 1.0 Hz, 1.16H), 7.12 – 7.10 (m, 1.14H), 7.01 – 6.96 (m, 0.31H), 6.93 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1.78H), 6.83 (d, *J* = 8.2 Hz, 0.26H), 3.84 (s, 3H), 3.83 (s, 1H), 3.80 (s, 0.73H), 0.33 (s, 8.47H), 0.32 (s, 2.06H), 0.13 – 0.12 (m, 3.64H), 0.11 (s, 9.14H), 0.10 (s, 3.01H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.01, 160.66, 159.07, 142.01, 135.18, 134.64, 131.43, 131.12, 129.08, 127.86, 125.38, 120.53, 119.16, 118.52, 114.65, 113.54, 109.54, 55.21, 55.14, 54.99, 2.12, 1.53, 1.14, 1.04. HRMS (EI+) calcd for $[C_{14}H_{32}O_4Si_4]^+$ $[M+H]^+$: 275.1282, found: 275.12761.

1-(3-(*tert*-Butyl)phenyl)-1,1,3,3,3-pentamethyldisiloxane and regioisomer (P4)

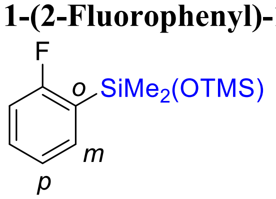


P4 [*m*:*p* = 66:34]

Procedure A1: 59% conv., 48% isolated yield (67 mg) [*m*:*p* = 66:34]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.52 (dd, *J* = 8.1, 1.7 Hz, 1.05H), 7.47 – 7.40 (m, 2.06H), 7.38 (dq, *J* = 7.2, 1.3 Hz, 1.01H), 7.36 – 7.30 (m, 1.02H), 1.37 (d, *J* = 1.6 Hz, 9H), 1.36 (d, *J* = 1.5 Hz, 3.7H), 0.35 (d, *J* = 1.6 Hz, 6.19H), 0.34 (d, *J* = 1.6 Hz, 2.54H), 0.14 – 0.11 (m, 13.41H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.22, 150.12, 139.83, 136.84, 133.05, 130.24, 129.90, 127.55, 126.37, 124.78, 31.56, 31.42, 2.15, 1.17. HRMS (EI+) calcd for $[C_{15}H_{29}OSi_2]^+$ $[M+H]^+$: 281.17515, found: 281.17577.

1-(2-Fluorophenyl)-1,1,3,3,3-pentamethyldisiloxane and regioisomers (P5)



P5 [*o*:*m*:*p* = 52:33:15]

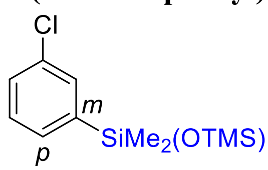
Procedure A1: 66% conv., 66% isolated yield (80 mg) [*o*:*m*:*p* = 67:28:5]

Procedure A2: 74% conv., 72% isolated yield (87 mg) [*o*:*m*:*p* = 47:39:14]

Procedure A3: 77% conv., 71% isolated yield (86 mg) [*o*:*m*:*p* = 44:43:13]

^{1}H NMR (400 MHz, $CDCl_3$) 7.55 – 7.46 (m, 1.41H) 7.37 (tdd, *J* = 9.9, 6.9, 2.2 Hz, 1.38H), 7.33 – 7.29 (m, 0.47H), 7.23 (dd, *J* = 9.1, 2.7 Hz, 0.51H), 7.15 (t, *J* = 7.3 Hz, 0.94H), 7.09 – 7.02 (m, 0.81H), 6.99 (t, *J* = 8.4 Hz, 0.94H), 0.38 (d, *J* = 1.2 Hz, 6H), 0.33 (d, *J* = 3.3 Hz, 4.09H), 0.12 (s, 9.6H), 0.10 (d, *J* = 5.2 Hz, 6.16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.22, 165.83, 163.97, 161.51, 143.46 (d, *J* = 3.8 Hz), 135.25 (d, *J* = 11.3 Hz), 135.08 (d, *J* = 7.4 Hz), 131.67 (d, *J* = 8.2 Hz), 129.65 (d, *J* = 6.9 Hz), 128.58 (d, *J* = 3.0 Hz), 126.14 (d, *J* = 29.9 Hz), 123.87 (d, *J* = 2.9 Hz), 119.44 (d, *J* = 18.4 Hz), 116.18 (d, *J* = 21.0 Hz), 114.87 (d, *J* = 7.0 Hz), 114.78 (d, *J* = 25.4 Hz), 2.07, 2.02, 1.57 (d, *J* = 1.5 Hz), 0.94.^{19}F NMR (376 MHz, $CDCl_3$) δ -101.12 – -101.43 (m), -111.89 (tt, *J* = 9.4, 6.2 Hz), -113.92 (tdd, *J* = 9.0, 5.2, 1.2 Hz). HRMS (EI+) calcd for $[C_{11}H_{20}FOSi_2]^+$ $[M+H]^+$: 243.1031, found: 243.10344

1-(2-Chlorophenyl)-1,1,3,3,3-pentamethyldisiloxane and regioisomers (P6)



P6 [*m*:*p* = 78:22]

Procedure A1: 60% conv., 50% isolated yield (65 mg) (*m*:*p* = 78:22)

Procedure A2: 77% conv., 76% isolated yield (98 mg) (*m*:*p* = 60:40)

Procedure A3: 83% conv., 64% isolated yield (83 mg) (*m*:*p* = 77:23)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 1.18H), 7.46 (d, *J* = 1.9 Hz, 0.32H), 7.41 (dt, *J* = 6.9, 1.3 Hz, 0.91H), 7.37 – 7.33 (m, 1.5H), 7.32 – 7.27 (m, 1H), 0.33 (s, 5.8H), 0.32 (s, 1.67H), 0.11 (s, 8.48H), 0.09 (s, 2.85H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.01, 134.52, 134.28, 132.95, 131.03, 129.36, 128.07, 2.09, 0.98 (d, *J* = 4.4 Hz). HRMS (EI+) calcd for $[C_{11}H_{20}ClOSi_2]^+$ $[M+H]^+$: 259.0736, found: 259.07467.

1-Methyl-2-(1,1,3,3,3-pentamethyldisiloxaneyl)-1*H*-pyrrole and regioisomer and 1-methyl-2,4-bis(1,1,3,3,3-pentamethyldisiloxaneyl)-1*H*-pyrrole (P7)

P7 [α:β:bis(α,β') = 84:6:10]

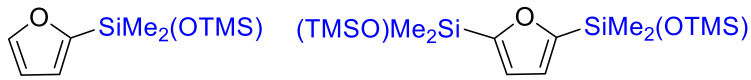
Procedure A1: 64% conv., 48% isolated yield (54 mg) [α:β:bis(α,β') = 72:13:15]

Procedure A2: 67% conv., 65% isolated yield (74 mg) [α:β:bis(α,β') = 72:13:15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (t, *J* = 2.0 Hz, 1H), 6.71 (s, 0.15H), 6.71 (s, 0.18H), 6.43 (dd, *J* = 3.5, 1.5 Hz, 0.98H), 6.42 (s, 0.09H), 6.28 (t, *J* = 2.1 Hz, 0.13H), 6.18 (dd, *J* = 3.5, 2.4 Hz, 1.01H), 3.91 (s, 0.13H), 3.80 (s, 2.93H), 3.70 (s, 0.38H), 0.40 (s, 0.75H), 0.39 (s, 5.84H), 0.31 (s, 0.95H), 0.12 (s, 12.54H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.25, 132.72, 127.64, 126.67, 122.81, 118.96, 118.31 (d, *J* = 16.5 Hz), 113.14, 107.71, 36.69, 35.63, 1.77, 1.47. HRMS (EI+) calcd for

$[C_{10}H_{22}NOSi_2]^+$ $[M+H]^+$: 228.1234, found: 228.12406 calcd for $[C_{15}H_{36}NO_2Si_4]^+$ $[M+H]^+$: 374.1818, found: 374.1823.

1-(Furan-2-yl)-1,1,3,3,3-pentamethyldisiloxane and regioisomer and 2,5-bis(1,1,3,3,3-penta methyldisiloxaneyl) furan (P8)



P8 [*α*:*β*:bis(*α*,*α*') = 80:2:18]

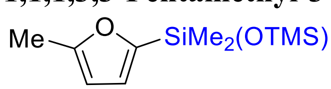
Procedure A1: 71% conv., 71% isolated yield (102 mg) [*α*:bis(*α*,*α*') = 83:17]

Procedure A3: 48% conv., 44% isolated yield (63 mg) [*α*:bis(*α*,*α*') = 86:14]

Procedure E: 65% conv., 49% isolated yield (53 mg) [*α*:bis(*α*,*α*') = 92:8] trace amounts of *β* present in ^{1}H NMR

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.6 Hz, 0.94H), 7.58 (s, 0.02H), 7.49 (d, *J* = 1.7 Hz, 0.03H), 7.40 (s, 0.03H), 6.68 (d, *J* = 3.2 Hz, 0.95H), 6.65 (s, 0.44H), 6.38 (dd, *J* = 3.3, 1.6 Hz, 1H), 0.34 (s, 8.72H), 0.28 (s, 0.29H), 0.10 (s, 0.49H), 0.06 (d, *J* = 1.8 Hz, 14.32H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.87, 159.83, 119.85 (d, *J* = 4.0 Hz), 119.43, 109.61 – 109.01 (m), 1.83 (d, *J* = 2.7 Hz), 0.50 (d, *J* = 11.5 Hz). HRMS (EI+) calcd for $[C_9H_{19}O_2Si_2]^+$ $[M+H]^+$: 215.0918, found: 215.09161 calcd for $[C_{14}H_{33}O_3Si_4]^+$ $[M+H]^+$: 361.1501, found: 361.1495.

1,1,1,3,3-Pentamethyl-3-(5-methylfuran-2-yl)disiloxane (P9)

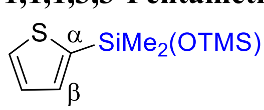


P9

Procedure A1: 71% conv., 50% isolated yield (57 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 3.1 Hz, 1H), 5.96 (dq, *J* = 3.1, 1.0 Hz, 1H), 2.35 – 2.31 (m, 3H), 0.31 (s, 6H), 0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.90, 156.22, 120.90, 105.47, 13.59, 1.68, 0.31. HRMS (EI+) calcd for $[C_{10}H_{21}O_2Si_2]^+$ $[M+H]^+$: 229.1075, found: 229.10681.

1,1,1,3,3-Pentamethyl-3-(thiophen-2-yl)disiloxane and regioisomer (P10)

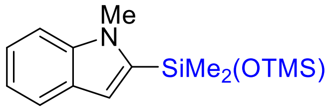


P10 [*α*:*β* = 95:5]

Procedure A1: 20 h. 44% conv., 41% isolated yield (47 mg) [α:β = 95:5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.51 (dt, *J* = 2.6, 1.1 Hz, 0.05H), 7.39 (dd, *J* = 4.8, 2.6 Hz, 0.06H), 7.36 (s, 0.08H), 7.32 (dd, *J* = 3.3, 0.9 Hz, 0.99H), 7.20 (dd, *J* = 4.6, 3.3 Hz, 0.99H), 0.40 (s, 6.37H), 0.34 (s, 0.26H), 0.10 (s, 11.23H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.73, 134.01, 130.42, 127.88,1.81. HRMS (EI+) calcd for $[C_{11}H_{25}O_2SSi_3]^+$ $[M+H]^+$: 305.0878, found: 305.08748.

1-Methyl-2-(1,1,3,3,3-pentamethyldisiloxaneyl)-1*H*-indole (P11)

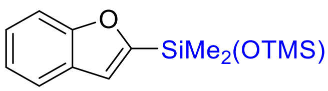


P11

Procedure A1: 52% conv., 49% isolated yield (136 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.26 (ddd, *J* = 8.2, 6.3, 1.2 Hz, 1H), 7.11 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.73 (d, *J* = 0.9 Hz, 1H), 3.92 (s, 3H), 0.47 (s, 6H), 0.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 139.93, 128.13, 122.13, 120.88, 119.05, 111.11, 109.07, 32.78, 1.82, 1.44. HRMS (EI+) calcd for $[C_{14}H_{24}NOSi_2]^+$ $[M+H]^+$: 278.1391, found: 278.13991.

1-(Benzofuran-2-yl)-1,1,3,3,3-pentamethyldisiloxane (P12)



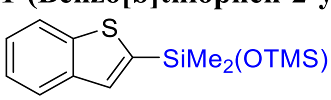
P12

Procedure A1: 51% conv., 45% isolated yield (119 mg)

Procedure E: 81% conv., 60% isolated yield (79 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.37 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.09 (d, *J* = 1.1 Hz, 1H), 0.51 (s, 6H), 0.20 (d, *J* = 0.7 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.43, 157.78, 127.74, 124.48, 122.27, 121.17, 116.08, 111.35, 1.72, 0.31. HRMS (EI+) calcd for $[C_{13}H_{21}O_2Si_2]^+$ $[M+H]^+$: 265.1075, found: 265.10728.

1-(Benzo[b]thiophen-2-yl)-1,1,3,3,3-pentamethyldisiloxane (P40)



P40

Procedure A1: 20 h. 51% conv., 45% isolated yield (119 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.49 (s, 1H), 7.33 (tt, *J* = 7.8, 6.0 Hz, 2H), 0.43 (s, 6H), 0.11 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 143.62, 141.92, 141.05, 131.02, 124.47, 124.12, 123.81, 122.43, 2.06 (d, *J* = 2.9 Hz), 1.84. HRMS (EI+) calcd for $[C_{13}H_{21}OSSi_2]$ [M]: 280.0773, found: 280.07703.

2.10 Representative procedure for Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-2 (Procedure B1)

In a N_2-filled glovebox, an oven-dried pressure tube was charged with **C4** (2.3 mg, 0.25 mol %) and benzene (43 mg, 1.1 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-2** (111.3 mg, 0.5 equiv.) and cyclohexene (49.3 mg, 1.2 equiv.) were added. The reaction mixture was allowed to stir for 7 h at 80 °C (88% conv., 70% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P13**) as a colorless liquid [70% isolated yield (105 mg)].

2.11 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-2 (Procedure B2)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (2.3 mg, 0.25 mol %) and benzene (43 mg, 1.1 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-2** (55.6 mg, 0.5 equiv.) and cyclohexene (49.3 mg, 1.2 equiv.) were added. The reaction mixture was allowed to stir for 1 h at 80 °C. To the mixture, **Si-2** (55.6 mg, 0.5 equiv..) was added and allowed to stir for 6 h at 80 °C (80% conv., 77% yield by ^{1}H NMR analysis).

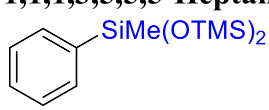
Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P13**) as a colorless liquid [77% isolated yield (115 mg)].

2.12 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-2 with solvent (Procedure B3)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (2.3 mg, 0.25 mol %) and benzene (43 mg, 1.1 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-2** (55.6 mg, 0.5 equiv.), cyclohexene (49.3 mg, 1.2 equiv.) and THF (328.9 mg, 1.35 M) were added. The reaction mixture was allowed to stir for 1 h at 80 °C. To the mixture, **Si-2** (55.6 mg, 0.5 equiv.) was added and allowed to stir for 6 h at 80 °C (85% conv., 84% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P13)** as a colorless liquid [84% isolated yield (125 mg)].

1,1,1,3,5,5,5-Heptamethyl-3-phenyltrisiloxane (P13)



P13

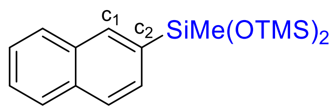
Procedure B1: 88% conv., 70% isolated yield (104 mg)

Procedure B2: 80% conv., 77% isolated yield (115 mg)

Procedure B3: 85% conv., 84% isolated yield (125 mg)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.38 – 7.32 (m, 3H), 0.27 (s, 3H), 0.10 (s, 18H). Spectroscopic data were consistent with those previously reported.[2]

1,1,1,3,5,5,5-Heptamethyl-3-(naphthalen-2-yl)trisiloxane and regioisomer (P14)



P14 [c_1:c_2 = 44:56]

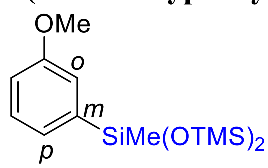
Procedure B1: 97% conv., 95% isolated yield (165 mg) [c_1:c_2 = 21:79]

Procedure B2: 82% conv., 79% isolated yield (138 mg) [c_1:c_2 = 19:81]

Procedure B3: 77% conv., 70% isolated yield (122 mg) [c_1:c_2 = 21:79]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.8 Hz, 1.5H), 7.92 – 7.83 (m, 4.57H), 7.67 (ddd, *J* = 8.1, 2.4, 1.2 Hz, 1.52H), 7.52 (ddd, *J* = 7.2, 3.5, 1.5 Hz, 3.05H), 0.40 (d, *J* = 1.7 Hz, 2.39H), 0.39 (s, 3H), 0.18 (d, *J* = 1.7 Hz, 13.85H), 0.17 (s, 18.83H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.13, 134.24, 134.15, 132.96, 129.67, 128.47, 127.86, 127.00, 126.53, 125.92, 2.06, 0.24. HRMS (EI+) calcd for $[C_{17}H_{29}O_2Si_3]^+$ $[M+H]^+$: 349.147, found: 349.14624.

3-(2-Methoxyphenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and regioisomers (P15)



P15 [*o*:*m*:*p* = 24:65:11]

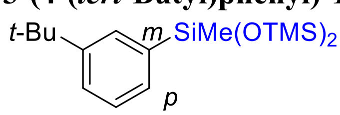
Procedure B1: 3 equiv. arene. 88% conv., 83% isolated yield (136 mg) (*o*:*m*:*p* = 24:64:11)

Procedure B2: 3 equiv. arene. 60% conv., 40% isolated yield (66 mg) (*o*:*m*:*p* = 21:66:13)

Procedure B3: 3 equiv. arene. 70% conv., 51% isolated yield (84 mg) (*o*:*m*:*p* = 24:65:11)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.8 Hz, 0.08H), 7.50 – 7.47 (m, 0.81H), 7.36 (ddd, *J* = 7.8, 6.5, 1.8 Hz, 0.17H), 7.29 (t, *J* = 7.7 Hz, 0.97H), 7.14 (dq, *J* = 7.1, 1.0 Hz, 1.02H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.91 (dddd, *J* = 9.4, 6.4, 1.9, 0.9 Hz, 1.76H), 6.81 (d, *J* = 8.2 Hz, 0.14H), 3.82 (s, 4.46H), 3.79 (s, 0.4H), 0.29 – 0.27 (m, 0.73H), 0.27 (d, *J* = 1.0 Hz, 3.52H), 0.26 – 0.24 (m, 1.34H), 0.12 (d, *J* = 0.9 Hz, 18.86H), 0.11 – 0.08 (m, 14.92H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.18, 160.80, 158.97, 140.26, 135.62, 134.91, 131.40, 129.96, 129.01, 125.71, 120.36, 118.55, 115.10, 113.42, 109.36, 55.20, 55.12, 54.74, 2.01. Spectroscopic data were consistent with those previously reported.[2]

3-(4-(*tert*-Butyl)phenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and regioisomer (P16)

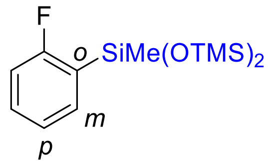


P16 [m:p= 67:33]

Procedure B1: 3 equiv. arene. 55% conv., 49% isolated yield (87 mg) [*m*:*p* = 67:33]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (q, *J* = 1.6 Hz, 0.76H), 7.51 (dd, *J* = 8.2, 1.6 Hz, 0.93H), 7.45 – 7.36 (m, 2.84H), 7.31 (d, *J* = 7.5 Hz, 0.53H), 1.35 (q, *J* = 1.7 Hz, 9.36H), 1.34 (d, *J* = 1.4 Hz, 3.76H), 0.29 (d, *J* = 1.5 Hz, 2.97H), 0.28 – 0.26 (m, 1.82H), 0.13 (d, *J* = 1.5 Hz, 28.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.44, 149.98, 138.13, 135.18, 133.28, 130.52, 130.22, 127.46, 126.54, 124.67, 34.82, 31.55, 31.41, 2.04 (d, J = 1.3 Hz), 0.42, 0.29. HRMS (EI+) calcd for $[C_{17}H_{35}O_2Si_3]^+$ $[M+H]^+$: 355.1939, found: 355.19538.

3-(2-Fluorophenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and regioisomers (P17)



P17 [*o*:*m*:*p* = 41:41:18]

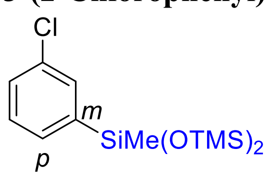
Procedure B1: 3 equiv. arene. 64% conv., 64% isolated yield (101 mg) [*o*:*m*:*p* = 41:33:26]

Procedure B2: 3 equiv. arene. 51% conv., 47% isolated yield (74 mg) [*o*:*m*:*p* = 47:37:16]

Procedure B3: 3 equiv. arene. 58% conv., 37% isolated yield (59 mg) [*o*:*m*:*p* = 39:40:21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dddd, J = 12.4, 7.4, 4.7, 1.9 Hz, 1.59H), 7.40 – 7.32 (m, 1.52H), 7.32 – 7.29 (m, 1.14H), 7.22 (dd, J = 9.0, 2.8 Hz, 0.02H), 7.16 – 7.10 (m, 0.99H), 7.09 – 7.02 (m, 1.42H), 6.98 (t, J = 8.4 Hz, 0.86H), 0.33 (d, J = 1.4 Hz, 3H), 0.27 (s, 3.12H), 0.27 (s, 1.39), 0.11 (d, J = 3.8 Hz, 43.41H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.40, 165.99, 163.90, 161.44, 141.73 (d, J = 4.0 Hz), 135.57 (d, J = 10.8 Hz), 135.37 (d, J = 7.5 Hz), 134.38 (d, J = 3.9 Hz), 131.92 (d, J = 8.3 Hz), 129.61 (d, J = 6.9 Hz), 128.87 (d, J = 3.0 Hz), 124.71 (d, J = 29.3 Hz), 123.77 (d, J = 3.0 Hz), 119.68 (d, J = 18.6 Hz), 116.46 (d, J = 21.0 Hz), 114.94 (d, J = 5.4 Hz), 114.72 (d, J = 11.0 Hz), 1.98 (d, J = 1.6 Hz), 1.88. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.28 (q, J = 6.5 Hz), -111.41 (tt, J = 9.4, 6.2 Hz), -113.85 -114.07 (m). HRMS (EI+) calcd for $[C_{13}H_{26}FO_2Si_3]^+$ $[M+H]^+$: 317.1219, found: 317.12275

3-(2-Chlorophenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and regioisomers (P18)



P18 [*m*:*p* = 69:31]

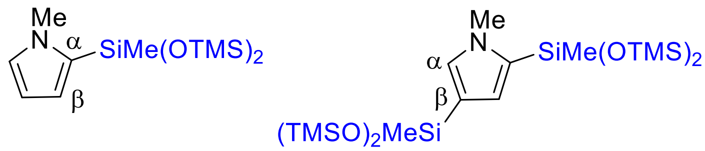
Procedure B1: 3 equiv. arene. 89% conv., 81% isolated yield (135 mg) [*m*:*p* = 71:29]

Procedure B2: 3 equiv. arene. 87% conv., 82% isolated yield (136 mg) [*m*:*p* = 79:21]

Procedure B3: 3 equiv. arene. >98% conv., 78% isolated yield (130 mg) [*m*:*p* = 74:26]

^{1}H NMR (400 MHz, $CDCl_3$) 7.51 – 7.47 (m, 1.22H), 7.46 (d, J = 1.9 Hz, 0.28H), 7.41 (dt, J = 7.1, 1.2 Hz, 0.87H), 7.37 – 7.31 (m, 1.47H), 7.29 (d, J = 7.4 Hz, 0.76H), 0.27 (s, 3H), 0.26 (s, 1.32H), 0.12 (s, 19.96H), 0.10 (d, J = 2.0 Hz, 9.94H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.29, 136.99, 135.83, 134.76, 134.16, 133.36, 133.23, 131.27, 129.61, 129.30, 128.02, 127.73, 1.98, 1.82. HRMS (EI+) calcd for $[C_{13}H_{26}ClO_2Si_3]^+$ $[M+H]^+$: 333.0924, found: 333.09257.

2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-1-methyl-1*H*-pyrrole and regioisomer (P19) and 2,5-bis(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-1-methyl-1*H*-pyrrole and regioisomer (P36+P37)



P19, P36, P37 [*α*:*β*: bis(*α*,*α*'): bis(*α*,*β*') = 23:2:60:15]

Procedure B1: 100 °C. 80% conv., 77% isolated yield (116 mg) [*α*:*β*:bis(*α*, *α*'):bis(*α*,*β*') = 75:7:11:7]

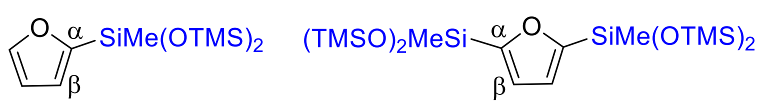
Procedure B2: 100 °C. 62% conv., 62% isolated yield (93 mg) [*α*:*β*:bis(*α*,*α*'):bis(*α*,*β*') = 81:3:10:6]

Procedure B3: 100 °C. 72% conv., 71% isolated yield (107 mg) [*α*:bis(*α*,*α*') = 89:11]

Procedure D: 100 °C. >98% conv., 86% isolated yield (224 mg) [bis(*α*,*α*'):bis(*α*,*β*') = 67:33]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 1.5 Hz, 0.5H), 6.79 (t, *J* = 1.9 Hz, 0.76H), 6.72 (t, *J* = 1.8 Hz, 0.06H), 6.69 (s, 0.03H), 6.55 (d, *J* = 1.5 Hz, 0.52H), 6.47 (dd, *J* = 3.5, 1.5 Hz, 0.75H), 6.44 (s, 2H), 6.28 (dd, *J* = 2.5, 1.6 Hz, 0.06H), 6.17 (dd, *J* = 3.5, 2.3 Hz, 0.76H), 3.89 (s, 2.84H), 3.79 (s, 2.18H), 3.78 (s, 1.65H), 0.37 (s, 6.36H), 0.36 (s, 5.93H), 0.35 (s, 2.17H), 0.16 (dd, *J* = 3.6, 1.7 Hz, 72.04H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.81, 132.75, 132.42, 131.45, 126.45, 125.23, 119.57, 118.88, 116.26, 107.69, 77.27, 76.96, 76.64, 37.12, 36.62, 36.39, 27.81, 26.60, 1.85, 1.71, 0.95 (d, *J* = 2.6 Hz). HRMS (EI+) calcd for $[C_{12}H_{28}NO_2Si_3]^+$ $[M+H]^+$: 302.1422, found: 302.14334. HRMS (EI+) calcd for $[C_{19}H_{48}NO_4Si_6]^+$ $[M+H]^+$: 522.2193, found: 522.22122.

3-(Furan-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and regioisomer (P20) and 2,5-bis(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)furan and regioisomer (P34+P35)



P20, P34, P35 [*α*:*β*:bis(*α*,*α*'): bis(*α*,*β*') = 65:2:5:28]

Procedure B1: 100 °C. 92% conv., 75% isolated yield (108 mg) [*α*:bis(*α*,*α*'):bis(*α*,*β*') = 75:21:4]

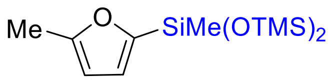
Procedure B2: 100 °C. 45% conv., 45% isolated yield (65 mg) [*α*:bis(*α*,*α*'):bis(*α*,*β*') = 75:21:4]

Procedure B3: 100 °C. 72% conv., 71% isolated yield (102 mg) [(*α*:bis(*α*,*α*') = 89:11]

Procedure D: 100 °C. >98% conv., 86% isolated yield (152 mg) [bis(*α*,*α*'):bis(*α*,*β*') = 67:33]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.6 Hz, 1.01H), 7.57 (s, 0.08H), 7.47 (t, *J* = 1.6 Hz, 0.03H), 7.41 (s, 0.03H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.66 (s, 0.09H), 6.65 (s, 0.85H), 6.37 (dd, *J* = 3.3, 1.6 Hz, 1.06H), 0.28 (d, *J* = 1.2 Hz, 5.86H), 0.11 (d, *J* = 1.1 Hz, 39.43H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.04, 158.15, 158.01, 151.86, 146.30, 123.75, 120.15 (d, *J* = 3.9 Hz), 119.67 (t, *J* = 2.6 Hz), 109.26, 1.97, 1.83 (dd, *J* = 5.5, 2.4 Hz), 0.20, 0.10. HRMS (EI+) calcd for $[C_{11}H_{25}O_3Si_3]^+$ $[M+H]^+$: 289.1106, found: 289.11113 calcd for $[C_{18}H_{45}O_5Si_6]^+$ $[M+H]^+$: 509.1877, found: 509.18761.

1,1,1,3,5,5,5-Heptamethyl-3-(5-methylfuran-2-yl)trisiloxane (P21)

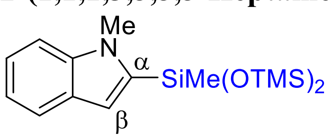


P21

Procedure B1: 100 °C. 86% conv., 74% isolated yield (112 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, J = 3.1 Hz, 1H), 5.95 (dq, J = 2.9, 1.0 Hz, 0.93H), 2.33 (d, J = 1.0 Hz, 2.88H), 0.27 (s, 3.56H), 0.11 (s, 17.97H). Trace amounts of β silylation product observed in ^{1}H NMR. Spectroscopic data were consistent with those previously reported.[3]

2-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-1-methyl-1*H*-indole and regioisomer (P22)

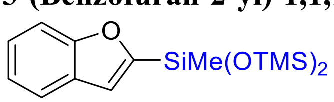


P22 [α:β = 64:36]

Procedure B1: 67% conv., 66% isolated yield (116 mg) [α:β = 60:40]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 0.5H), 7.63 (d, J = 7.9 Hz, 1H), 7.55 (s, 0.11H), 7.33 (t, J = 7.0 Hz, 1.86H), 7.23 (dd, J = 8.3, 2.1 Hz, 1.46H), 7.16 – 7.06 (m, 2.56H), 6.74 (s, 1H), 3.88 (s, 3H), 3.79 (s, 1.8H), 0.41 (s, 3H), 0.34 (s, 1.8H), 0.13 (d, J = 3.6 Hz, 32H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.74, 139.38, 138.02, 135.85, 132.24, 128.08, 122.15 (d, J = 2.4 Hz), 121.38, 120.96, 119.28, 118.98, 111.67, 109.12 (d, J = 5.6 Hz), 108.59, 77.27, 76.96, 76.64, 32.73 (d, J = 3.1 Hz), 1.90, 1.75, 0.85. HRMS (EI+) calcd for $[C_{16}H_{30}NO_2Si_3]^+$ $[M+H]^+$: 352.1579, found: 352.15799.

3-(Benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (P23)

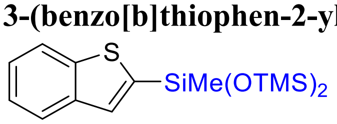


P23 [α:β = 79:21]

Procedure B1: 1 mmol **Si-2**, 100 °C. 90% conv., 88% isolated yield (298 mg) [α:β = 60:40]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 0.07H), 7.73 – 7.69 (m, 1.07H), 7.69 (s, 0.1H), 7.63 (dd, J = 8.2, 1.1 Hz, 1.15H), 7.39 (ddd, J = 8.3, 7.1, 1.3 Hz, 1.21H), 7.35 (d, J = 1.4 Hz, 0.03H), 7.31 (td, J = 7.4, 1.0 Hz, 1.06H), 7.26 (s, 0.12H), 7.14 (d, J = 1.0 Hz, 1.04H), 0.50 (s, 3H), 0.48 (s, 0.38H), 0.29 – 0.26 (m, 18H), 0.26 (s, 2.37H). Spectroscopic data were consistent with those previously reported.[2]

3-(benzo[b]thiophen-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (P24)

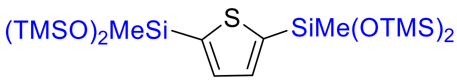


P24

Procedure B1: 1 mmol **Si-2**, 30 h, 100 °C. 67% conv., 44% isolated yield (156 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 1H), 7.86 – 7.81 (m, 1H), 7.50 (s, 1H), 7.38 – 7.30 (m, 2H), 0.37 (s, 3H), 0.15 (s, 18H). Spectroscopic data were consistent with those previously reported.[3]

2,5-Bis(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)thiophene (P38)

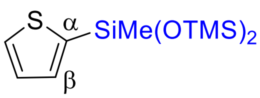


P38

Procedure D: 30 h, 100 °C. 75% conv., 40% isolated yield (69 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 0.32 (s, 6H), 0.11 (s, 36H). Spectroscopic data were consistent with those previously reported.[3]

1,1,1,3,5,5,5-Heptamethyl-3-(thiophen-2-yl)trisiloxane and regioisomer (P39)



P39 [: = 97:3]

Procedure D: 30 h, 100 °C. 75% conv., 40% isolated yield (69 mg) (α:β = 79:21)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 4.6, 0.9 Hz, 0.99H), 7.53 (d, J = 1.2 Hz, 0.03H), 7.37 – 7.35 (m, 0.05H), 7.32 (dd, J = 3.3, 0.9 Hz, 1H), 7.20 (d, J = 1.0 Hz, 0.04H), 7.17 (dd, J = 4.6, 3.3 Hz, 1.04H), 0.33 (s, 3.26H), 0.28 (d, 0.25H), 0.12 (s, 22.27H). Spectroscopic data were consistent with those previously reported.[4]

2.13 Representative procedure for Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-3 (Procedure C1)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with [Rh(nbd)Cl]$_2$ (2.3 mg, 1 mol %), (*S*)-(-)-XylBINAP (7.3 mg, 2 mol %), and benzene (437.4 mg, 11.2 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-3** (148.3 mg, 1 equiv.) and 2,3-dimethyl-2-butene (63.1 mg, 1.5 equiv.) were added. The reaction mixture was allowed to stir for 15 h at 120 °C (95% conv., 92% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P25**) as a colorless liquid [92% isolated yield (171 mg)]

2.14 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-3 (Procedure C2)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with [Rh(nbd)Cl]$_2$ (2.3 mg, 1 mol %), (*S*)-(-)-XylBINAP (7.3 mg, 2 mol %), and benzene (437.4 mg, 11.2 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-3** (74.1 mg, 0.5 equiv.) and 2,3-dimethyl-2-butene (63.1 mg, 1.5 equiv.) were added. The reaction mixture was allowed to stir for

11 h at 120 °C. To the mixture, **Si-3** (74.1 mg, 0.5 equiv.) was added and allowed to stir for 14 h at 120 °C (96% conv., 92% yield by ^{1}H NMR analysis).

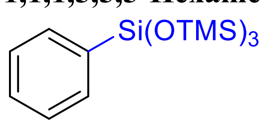
Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P25**) as a colorless liquid [92% isolated yield (171.5 mg)].

2.15 Representative procedure for portion-wise Rh-catalyzed C—H silylation of arenes and heteroarenes with Si-3 with solvent (Procedure C3)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with $[Rh(nbd)Cl]_2$ (2.3 mg, 1 mol %), (*S*)-(-)-XylBINAP (7.3 mg, 2 mol %), and benzene (437.4 mg, 11.2 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-3** (74.1 mg, 0.5 equiv.), 2,3-dimethyl-2-butene (63.1 mg, 1.5 equiv.), and THF (328.9 mg, 1.35 M) were added. The reaction mixture was allowed to stir for 1 h at 120 °C. To the mixture, **Si-3** (74.1 mg, 0.5 equiv.) was added and allowed to stir for 14 h at 120 °C (78% conv., 60% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P25**) as a colorless liquid [60% isolated yield (171.5 mg)].

1,1,1,5,5,5-Hexamethyl-3-phenyl-3-((trimethylsilyl)oxy)trisiloxane (P25)



P25

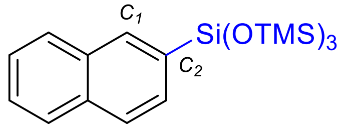
Procedure C1: 95% conv., 92% isolated yield (172 mg)

Procedure C2: 80% conv., 77% isolated yield (144 mg)

Procedure C3: 78% conv., 60% isolated yield (112 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 110.7 Hz, 2H), 7.35 (ddd, *J* = 13.7, 7.5, 5.8 Hz, 3H), 0.12 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.69, 133.97, 129.62, 127.65, 2.18. HRMS (EI+) calcd for $[C_{15}H_{33}O_3Si_4]^+$ $[M+H]^+$: 373.1501, found: 373.15063.

1,1,1,5,5,5-hexamethyl-3-(naphthalen-2-yl)-3-((trimethylsilyl)oxy)trisiloxane and regioisomer (P26)



P26 [c_1:c_2 = 37:63]

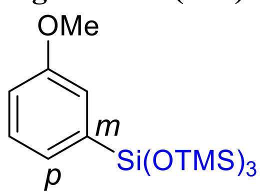
Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 70% conv., 66% isolated yield (151 mg) [c_1:c_2 = 14:86]

Procedure C2: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 66% conv., 64% isolated yield (147 mg) [c_1:c_2 = 16:84]

Procedure C3: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 80% conv., 60% isolated yield (138 mg) [c_1:c_2 = 14:86]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 (s, 0.19H), 7.88 – 7.76 (m, 2.5H), 7.65 – 7.59 (m, 1.17H), 7.52 – 7.44 (m, 1.46H), 7.00 (s, 0.18H), 0.14 (d, *J* = 1.6 Hz, 31H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 135.55, 134.98, 134.16, 133.13, 132.89, 130.73, 130.18, 130.07, 128.49, 127.84, 127.33, 126.89, 126.70, 126.54, 125.85, 110.36, 109.12, 65.82, 64.71, 1.94, 1.92. HRMS (EI+) calcd for $[C_{19}H_{34}O_3Si_4]^+$ $[M+H]^+$: 423.1658, found: 423.16477.

3-(2-Methoxyphenyl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane and regioisomer (P27)



P27 [*m*:*p* = 55:45]

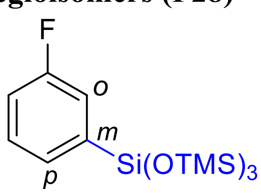
Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 53% conv., 34% isolated yield (69 mg) [*m*:*p* = 53:47]

Procedure C2: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 51% conv., 45% isolated yield (91 mg) [*m*:*p* = 55:45]

Procedure C3: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 44% conv., 44% isolated yield (89 mg) [*m*:*p* = 54:46]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 1.61H), 7.29 (s, 1.22H), 7.14 (dt, *J* = 7.2, 1.1 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.88 (d, *J* = 2.0 Hz, 1.62H), 3.82 (s, 3H), 3.81 (s, 3H), 0.12 (s, 27H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.85, 158.85, 137.20, 135.52, 128.91, 126.92, 126.35, 119.08, 115.31, 113.34, 55.17, 55.09, 1.91, 1.83. HRMS (EI+) calcd for $[C_{16}H_{35}O_4Si_4]^+$ $[M+H]^+$: 403.1607, found: 403.16095.

3-(2-Fluorophenyl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane and regioisomers (P28)



P28 [*o*:*m*:*p* = 25:54:21]

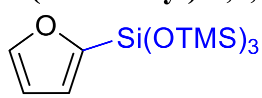
Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 71% conv., 71% isolated yield (140 mg) [*o*:*m*:*p* = 25:54:21]

Procedure C2: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 53% conv., 53% isolated yield (104 mg) [*o*:*m*:*p* = 43:35:21]

Procedure C3: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 70% conv., 63% isolated yield (123 mg) [*o*:*m*:*p* = 24:46:30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 0.9H), 7.40 – 7.34 (m, 0.14H), 7.32 – 7.30 (m, 1H), 7.22 (dd, *J* = 9.3, 3.2 Hz, 0.99H), 7.12 (d, *J* = 7.3 Hz, 0.09H), 7.07 – 7.02 (m, 0.8H), 7.00 (d, *J* = 4.8 Hz, 0.36H), 6.96 (d, *J* = 8.4 Hz, 0.09H), 0.13 (s, 8.71H), 0.12 – 0.11 (m, 30.74H), 0.11 (s, 10.98H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.15 (d, *J* = 248.2 Hz), 162.55 (d, *J* = 247.1 Hz), 138.72 (d, *J* = 4.6 Hz), 136.34 (d, *J* = 10.2 Hz), 135.98 (d, *J* = 7.6 Hz), 132.02 (d, *J* = 8.3 Hz), 131.44 (d, *J* = 3.8 Hz), 129.51 (d), 123.64 (d, *J* = 3.1 Hz), 120.29 (d, *J* = 18.9 Hz), 116.56 (d, *J* = 21.1 Hz), 114.92, 1.86, 1.78. ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.61 (d, *J* = 5.9 Hz), -111.29 (tt, *J* = 9.4, 6.3 Hz), -114.11 (tdd, *J* = 9.0, 4.1, 2.3 Hz). HRMS (EI+) calcd for $[C_{15}H_{32}FO_3Si_4]^+$ $[M+H]^+$: 391.1407, found: 391.14122.

3-(Furan-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (P29)



P29

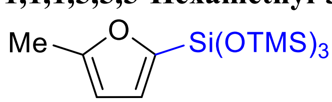
Procedure C1: 85% conv., 73% isolated yield (134 mg)

Procedure C2: 48% conv.

Procedure C3: 32% conv., 32% isolated yield (58 mg)

[85% conv., 74% isolated yield (134 mg)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.6 Hz, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.36 (dd, *J* = 3.3, 1.6 Hz, 1H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.23, 146.36, 120.96, 109.25, 1.73. HRMS (EI+) calcd for $[C_{13}H_{31}O_4Si_4]^+$ $[M+H]^+$: 363.1294, found: 363.12899.

1,1,1,5,5,5-Hexamethyl-3-(5-methylfuran-2-yl)-3-((trimethylsilyl)oxy)trisiloxane (P30)

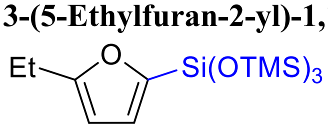


P30

Procedure C1: 20 h. 55% conv., 45% isolated yield (85 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (dd, *J* = 45.8, 3.1 Hz, 1H), 5.97 – 5.90 (m, 1H), 2.31 (d, *J* = 1.0 Hz, 3H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.26, 153.38, 122.15, 105.49, 13.75, 1.76. HRMS (EI+) calcd for $[C_{14}H_{33}O_4Si_4]^+$ $[M+H]^+$: 377.145, found: 377.14378.

3-(5-Ethylfuran-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (P31)

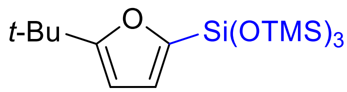


P31

Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 37% conv., 34% isolated yield (67 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, J = 3.1 Hz, 1H), 5.94 (dt, J = 3.1, 0.9 Hz, 1H), 2.67 (qd, J = 7.6, 1.0 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96, 153.17, 121.88, 103.98, 21.68, 12.56, 1.74. HRMS (EI+) calcd for $[C_{15}H_{35}O_4Si_4]^+$ $[M+H]^+$: 391.1607, found: 391.15954.

3-(5-*tert*-Butyl)furan-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (P32)

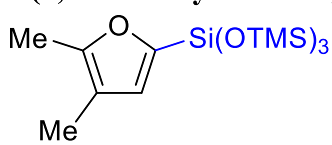


P32

Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 70% conv., 66% isolated yield (140 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, J = 3.2 Hz, 1H), 5.93 (d, J = 3.2 Hz, 1H), 1.29 (s, 9H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.50, 152.96, 121.61, 101.91, 32.90, 29.37, 1.74. HRMS (EI+) calcd for $[C_{17}H_{39}O_4Si_4]^+$ $[M+H]^+$: 419.192, found: 419.19218.

3-(4,5-Dimethylfuran-2-yl)-1,1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (P33)



P33

Procedure C1: 1.5 mol % $[Rh(nbd)Cl]_2$, 20 h. 39% conv., 31% isolated yield (60 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 2.21 (s, 3H), 1.93 (s, 3H), 0.11 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.70, 124.60, 113.71, 11.74, 9.86, 1.78. HRMS (EI+) calcd for $[C_{15}H_{35}O_4Si_4]^+$ $[M+H]^+$: 391.1607, found: 391.16063.

2.16 Representative procedure for Rh-catalyzed double C—H silylation with Si-2 (Procedure D)

In a N_2- filled glovebox, an oven-dried pressure tube was charged with **C4** (2.3 mg, 0.25 mol %) and furan (68.1 mg, 1 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture, **Si-2** (556.3 mg, 2.5 equiv.) and cyclohexene (197.1 mg, 2.4 equiv.) were added. The reaction mixture was allowed to stir for 7 h at 100 °C (>98% conv., 60% yield by ^{1}H NMR analysis).

Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired products (**P34**, **P35**, **P20)** as a colorless liquid [60% isolated yield (108 mg)].

2.17 Representative procedure for acceptorless Rh-catalyzed C—H silylation with Si-1 (Procedure E)

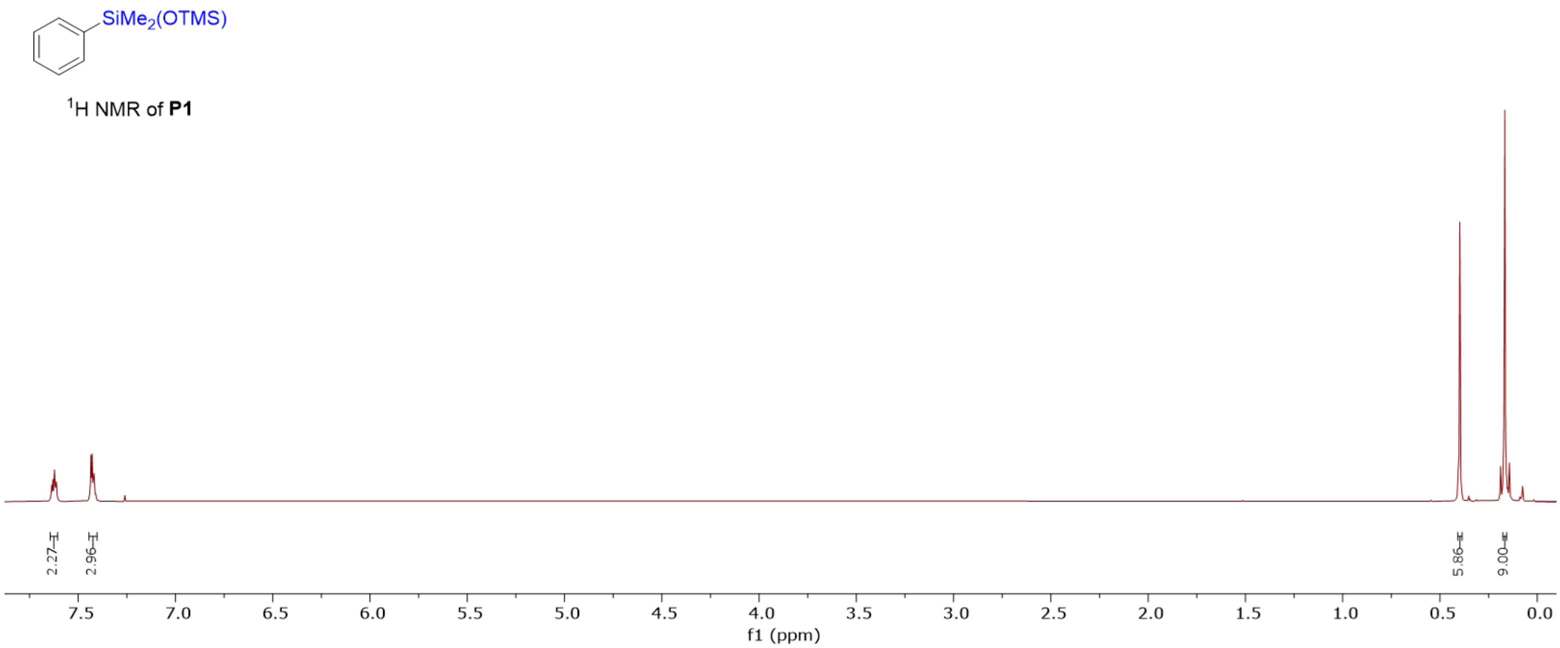
In a N_2-filled glovebox, an oven-dried pressure tube was charged with **C4** (8.7 mg, 1 mol %) and furan (170.2 mg, 5 equiv.). The reaction was allowed to stir for 10 minutes at 22 °C. To the mixture,

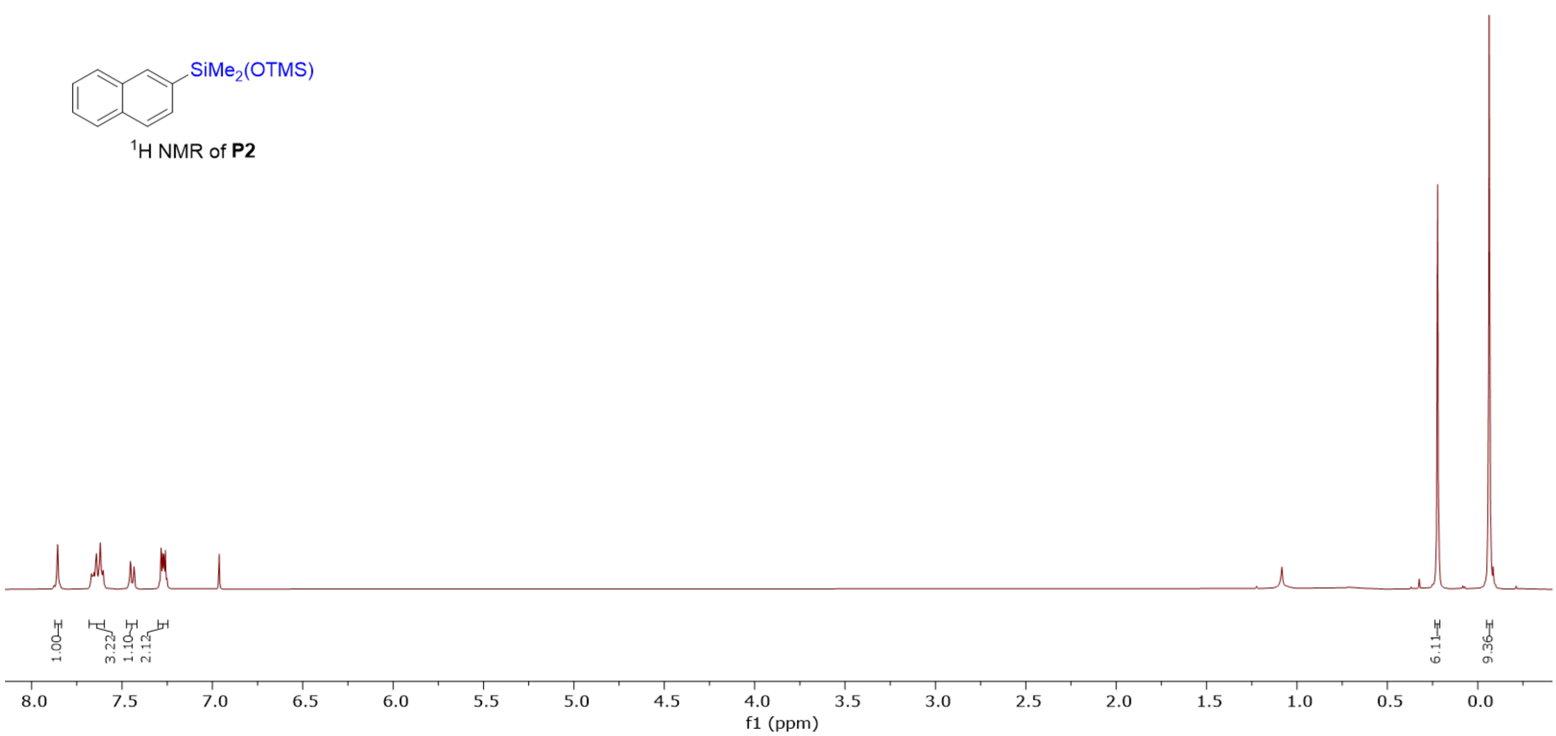
Si-1 (74.2 mg, 0.5 equiv.) was added. The reaction mixture was allowed to stir for 7 h at 100 °C (65% conv., 49% yield by ^{1}H NMR analysis).

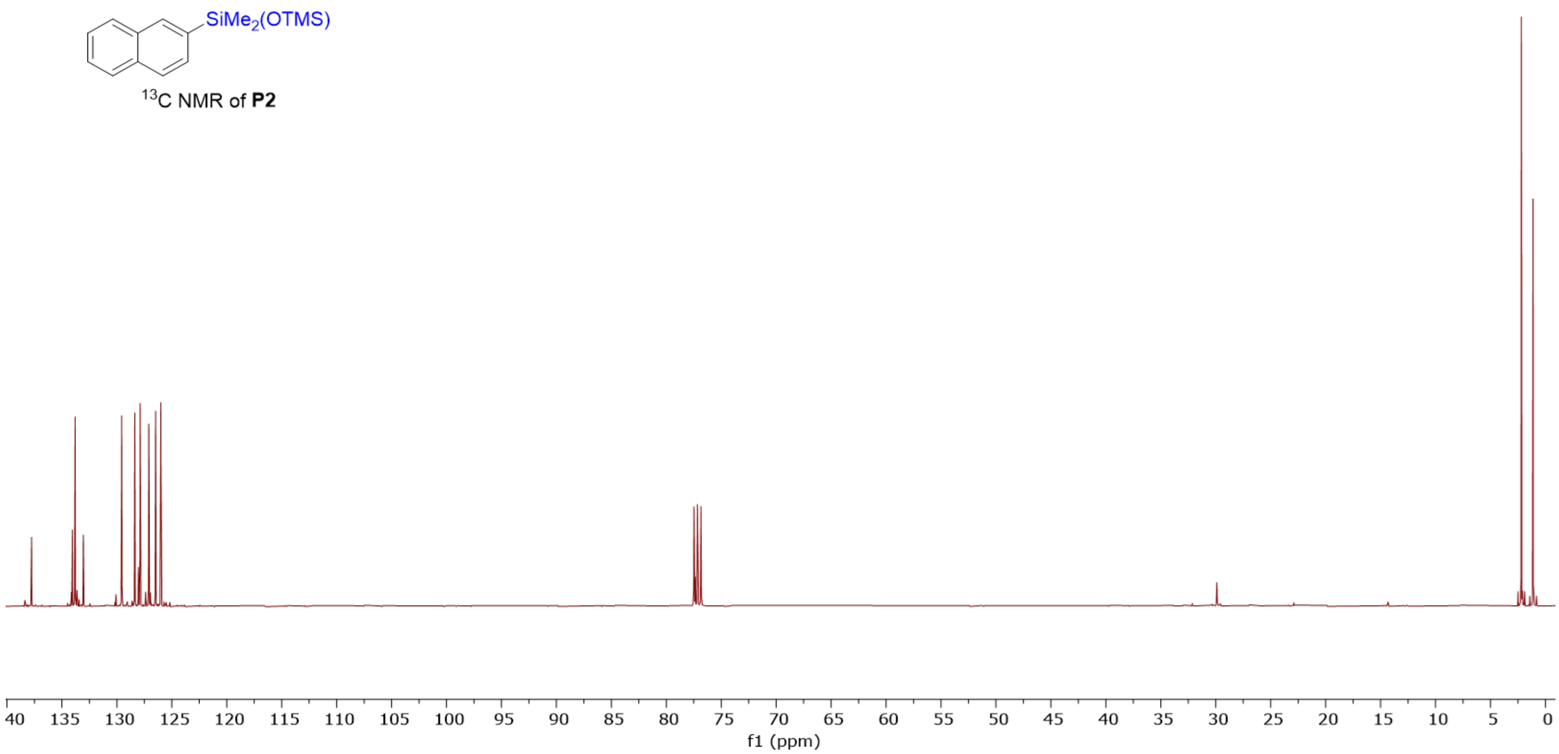
Isolated yield was obtained after the following workup procedure was done outside the glovebox. Evaporation of the crude mixture, diluting the residue with *n*-hexanes, and filtration through a syringe filter by rinsing with *n*-hexanes was done. The filtrate was then purified by silica gel chromatography affording the desired product (**P9)** as a colorless liquid [49% isolated yield (71 mg)].

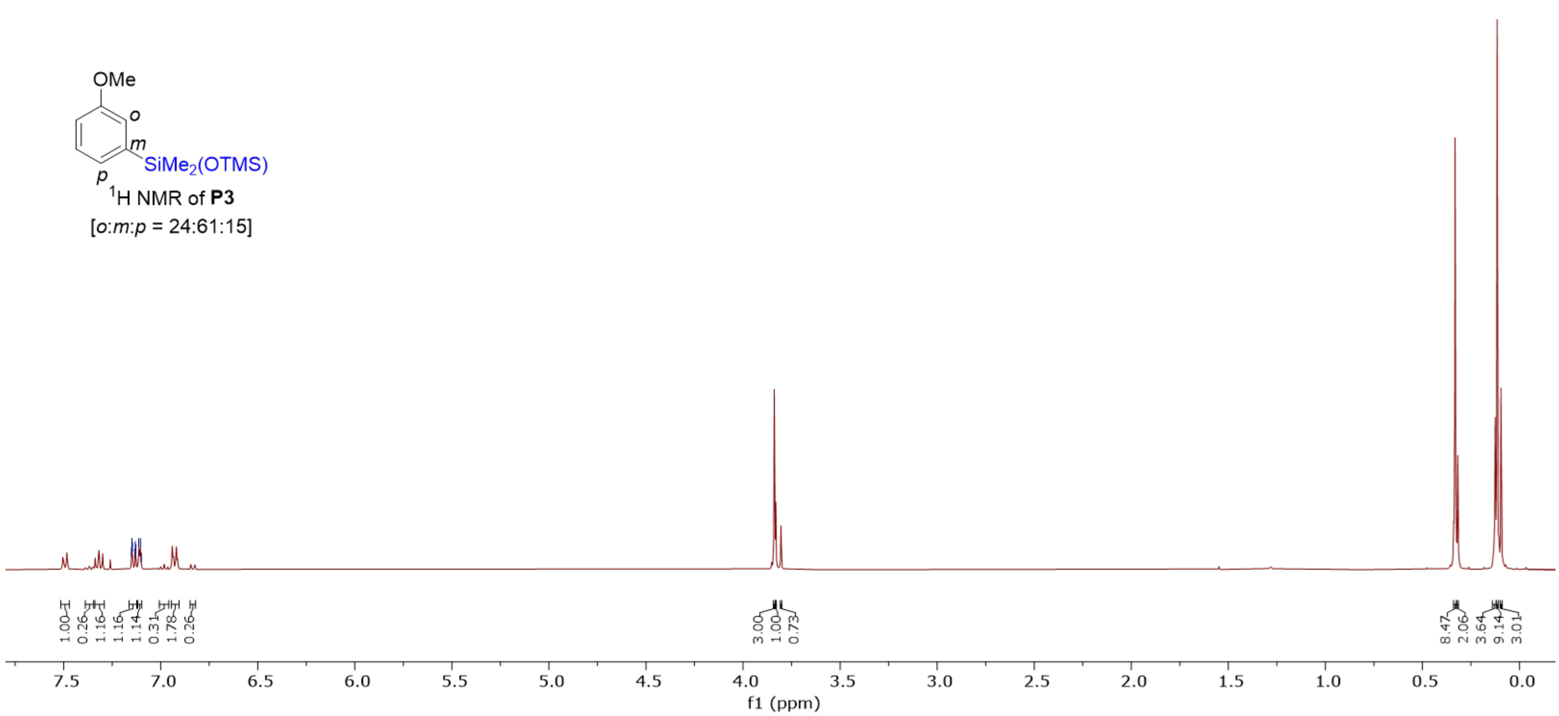
3. NMR spectra

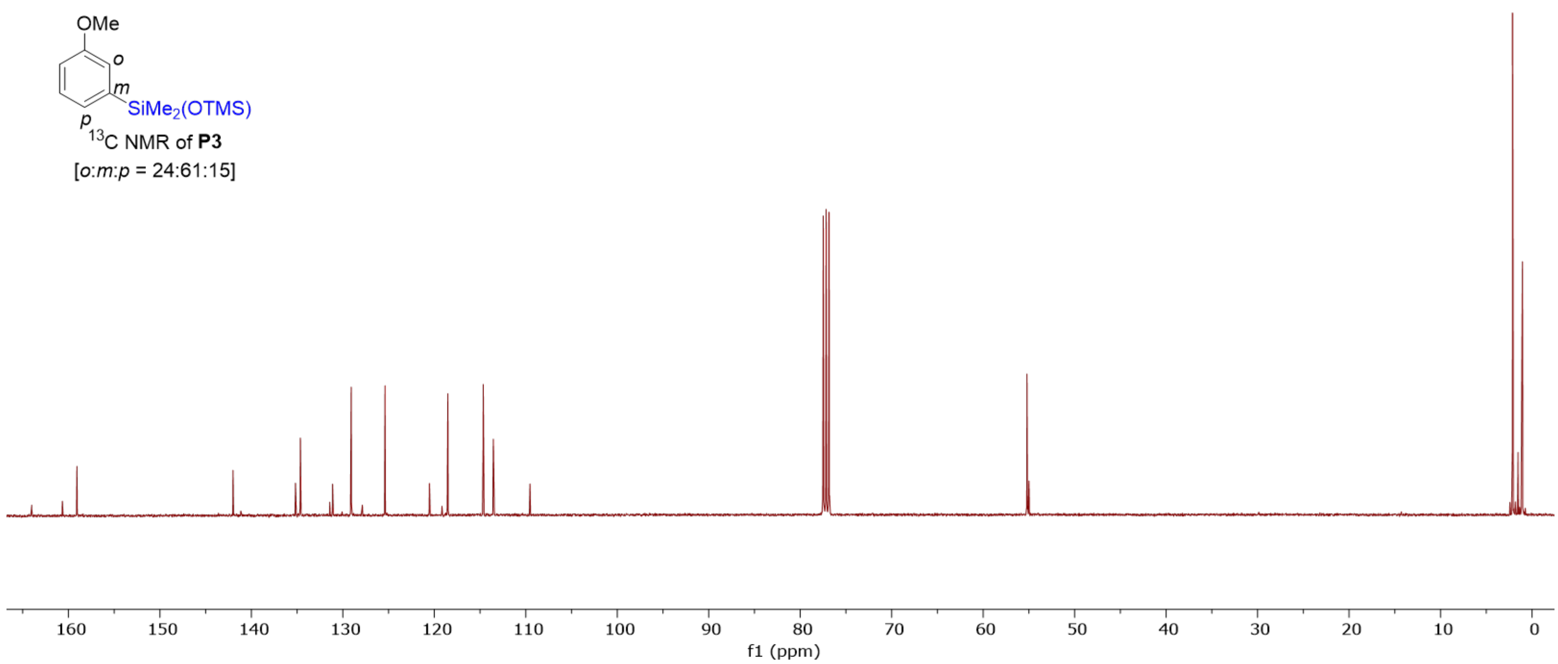
3.1 C—H silylation products

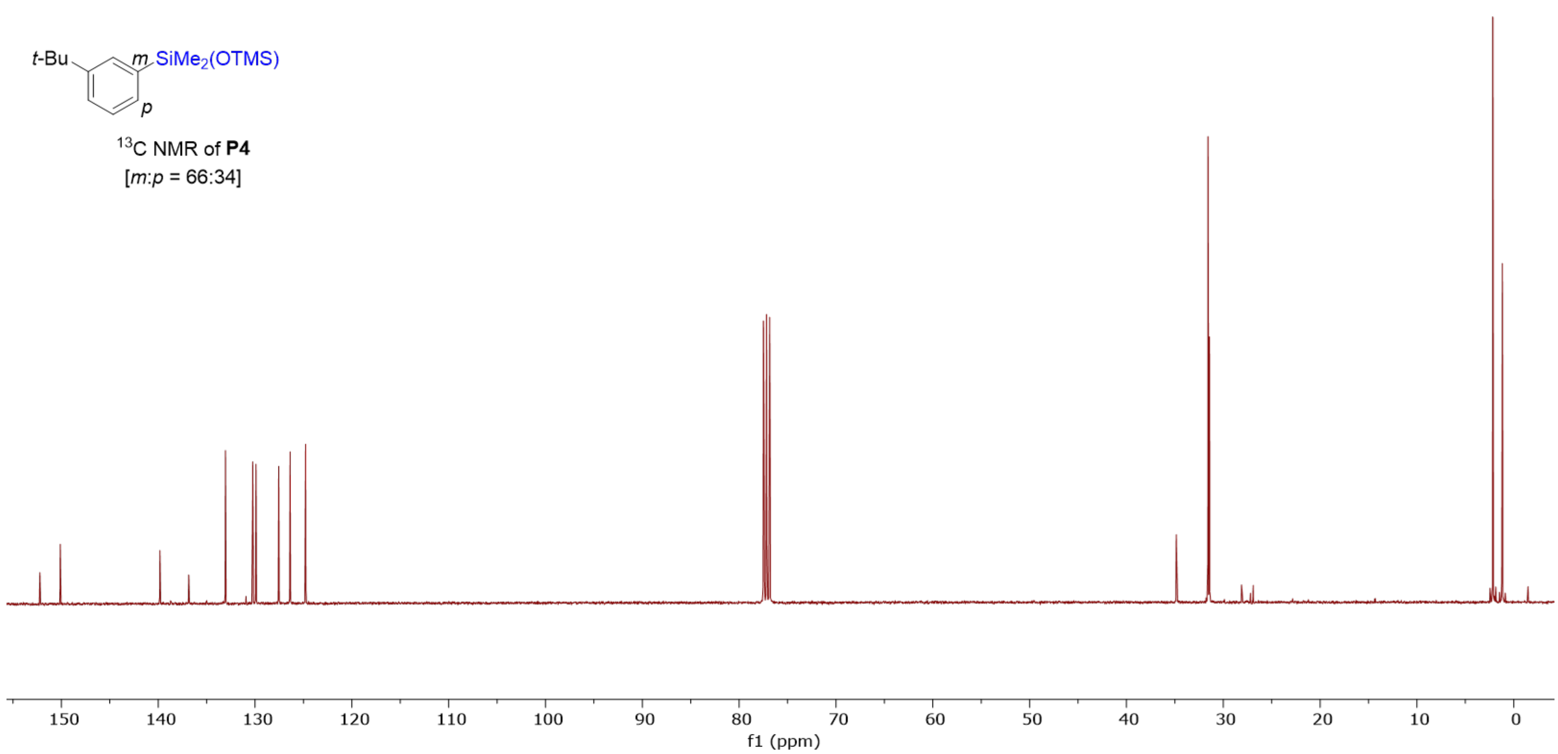


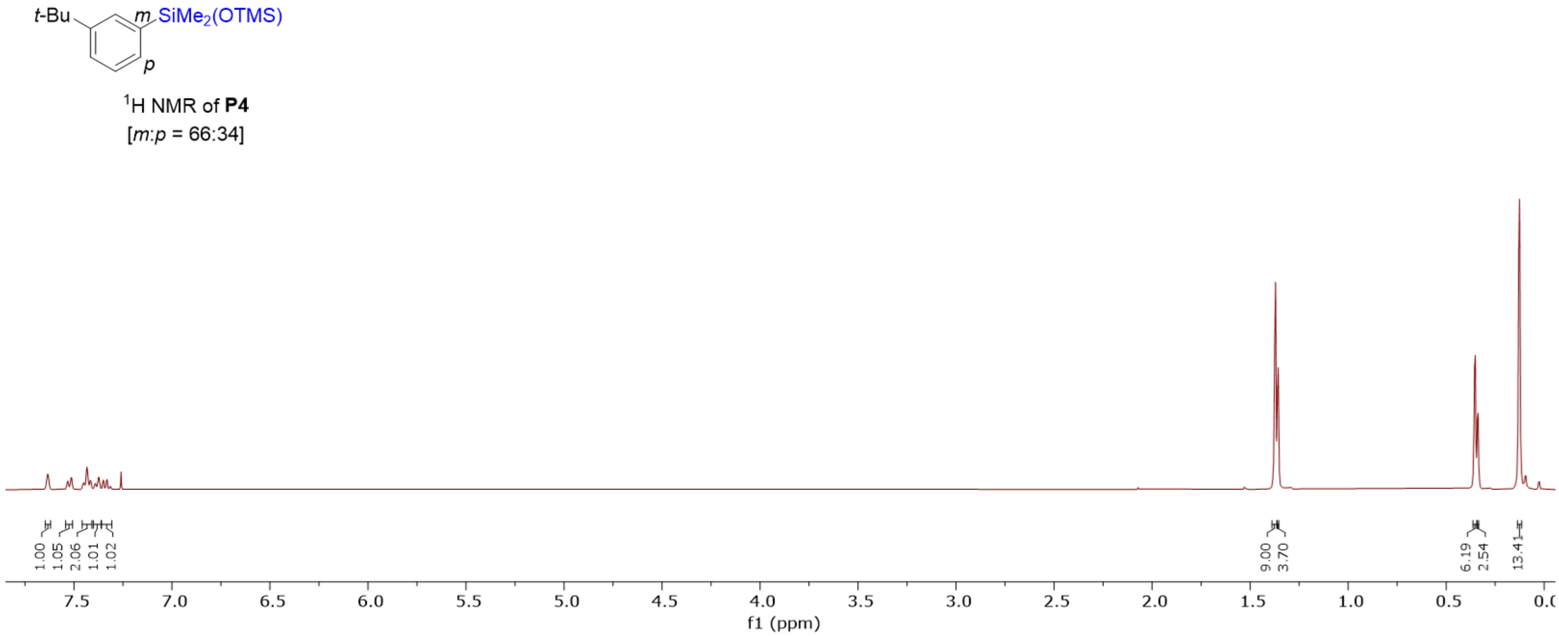


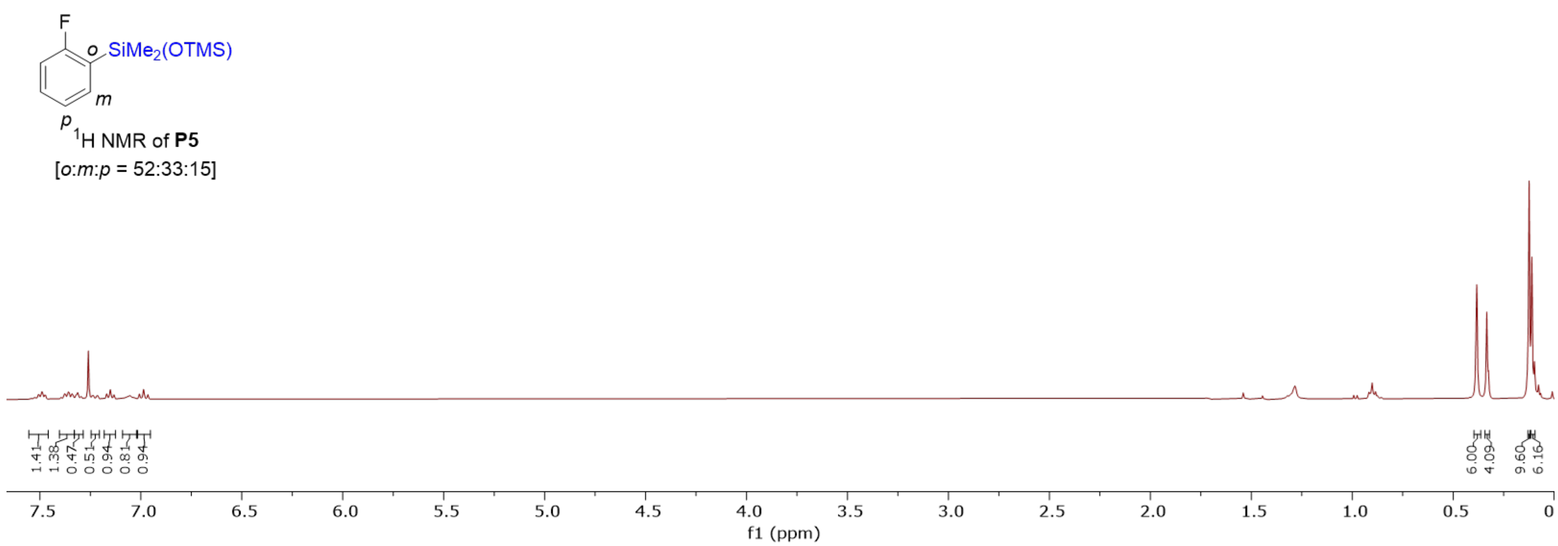

SiMe2(OTMS)
13C NMR of P2
f1 (ppm)

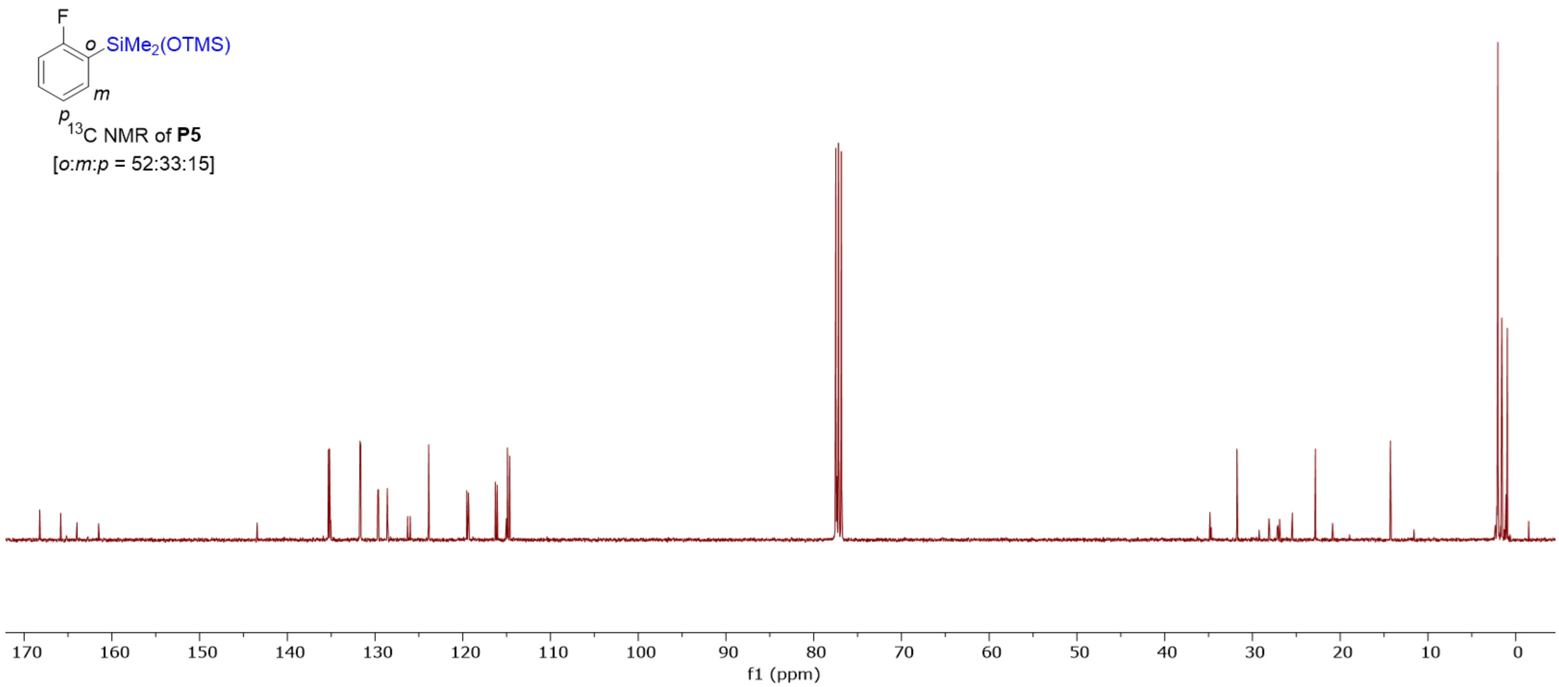

OMe
o
m
p
SiMe2(OTMS)
1H NMR of P3
[o:m:p = 24:61:15]
f1 (ppm)

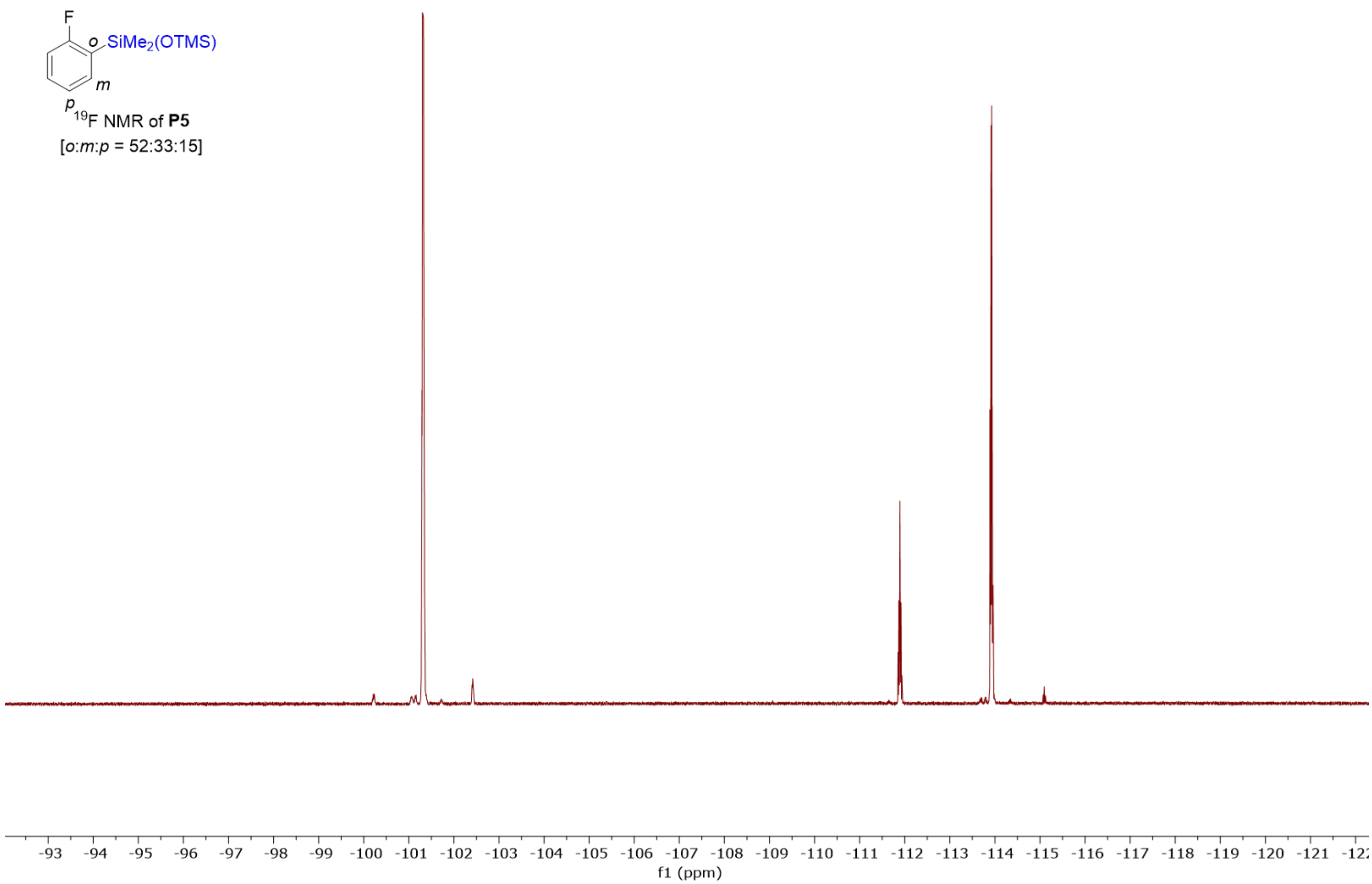

OMe
o
m
SiMe2(OTMS)
p
13C NMR of P3
[o:m:p = 24:61:15]
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

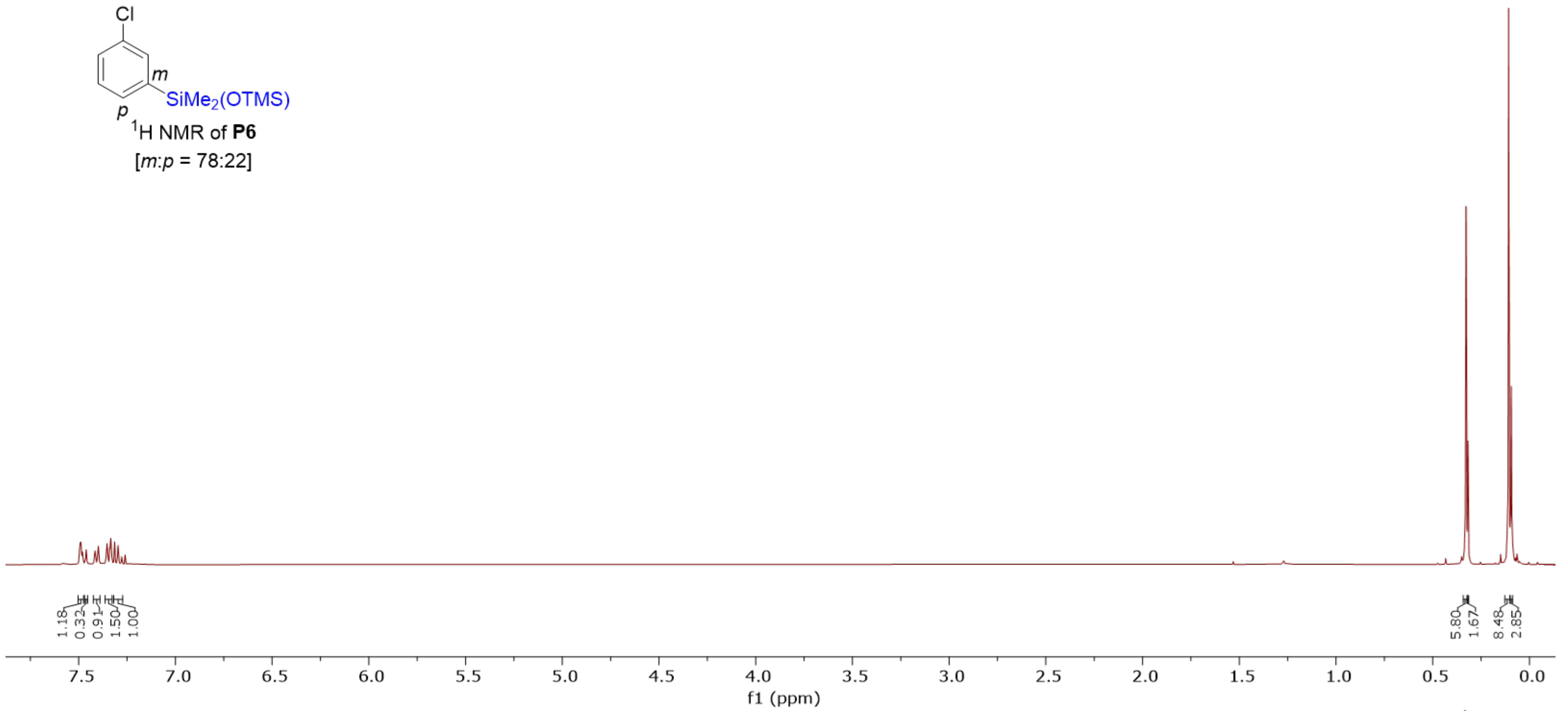

t-Bu
m
SiMe2(OTMS)
p
13C NMR of P4
[m:p = 66:34]
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

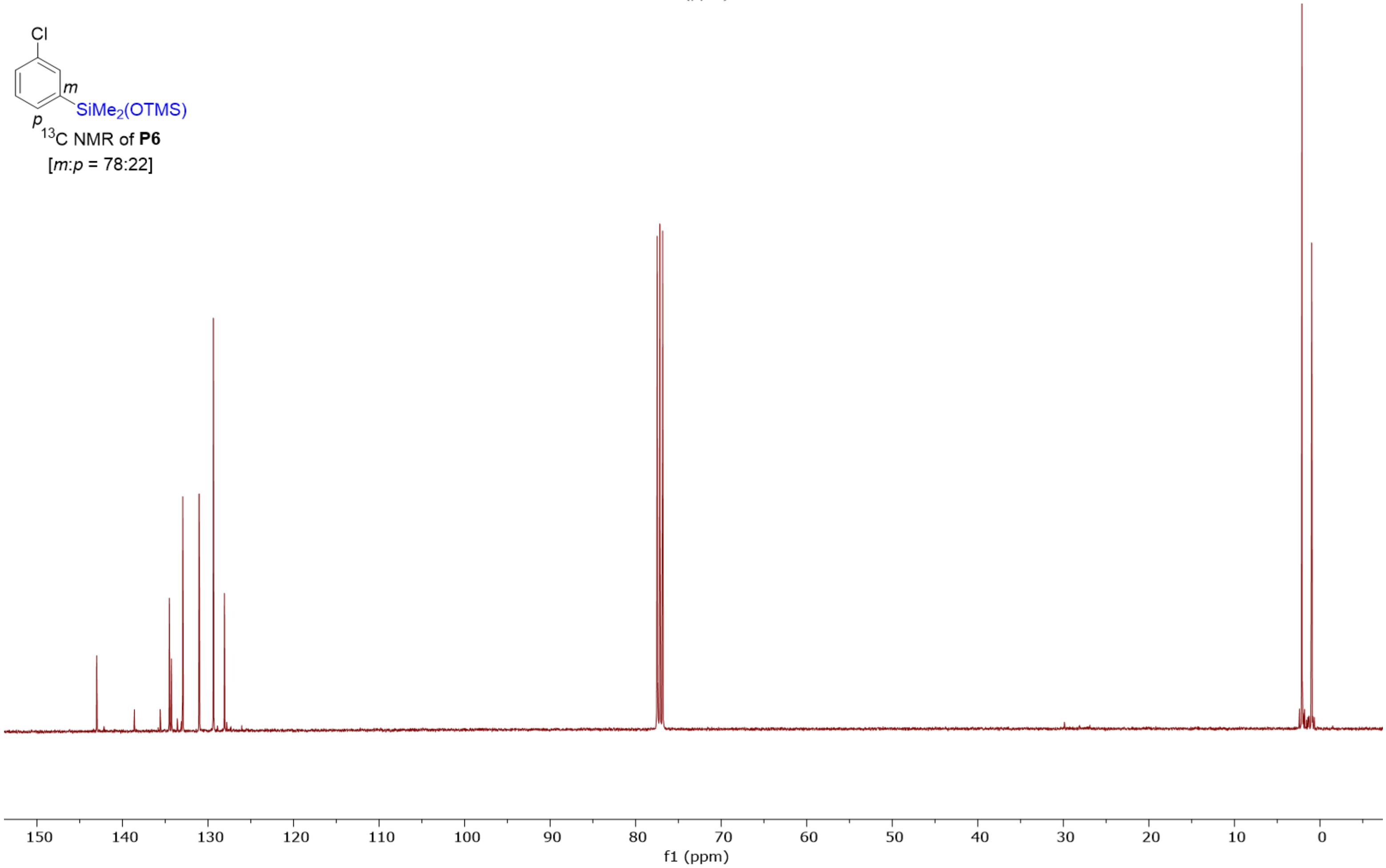

t-Bu
m
SiMe2(OTMS)
p
1H NMR of P4
[m:p = 66:34]
1.00
1.05
2.06
1.01
1.02
9.00
3.70
6.19
2.54
13.41
f1 (ppm)

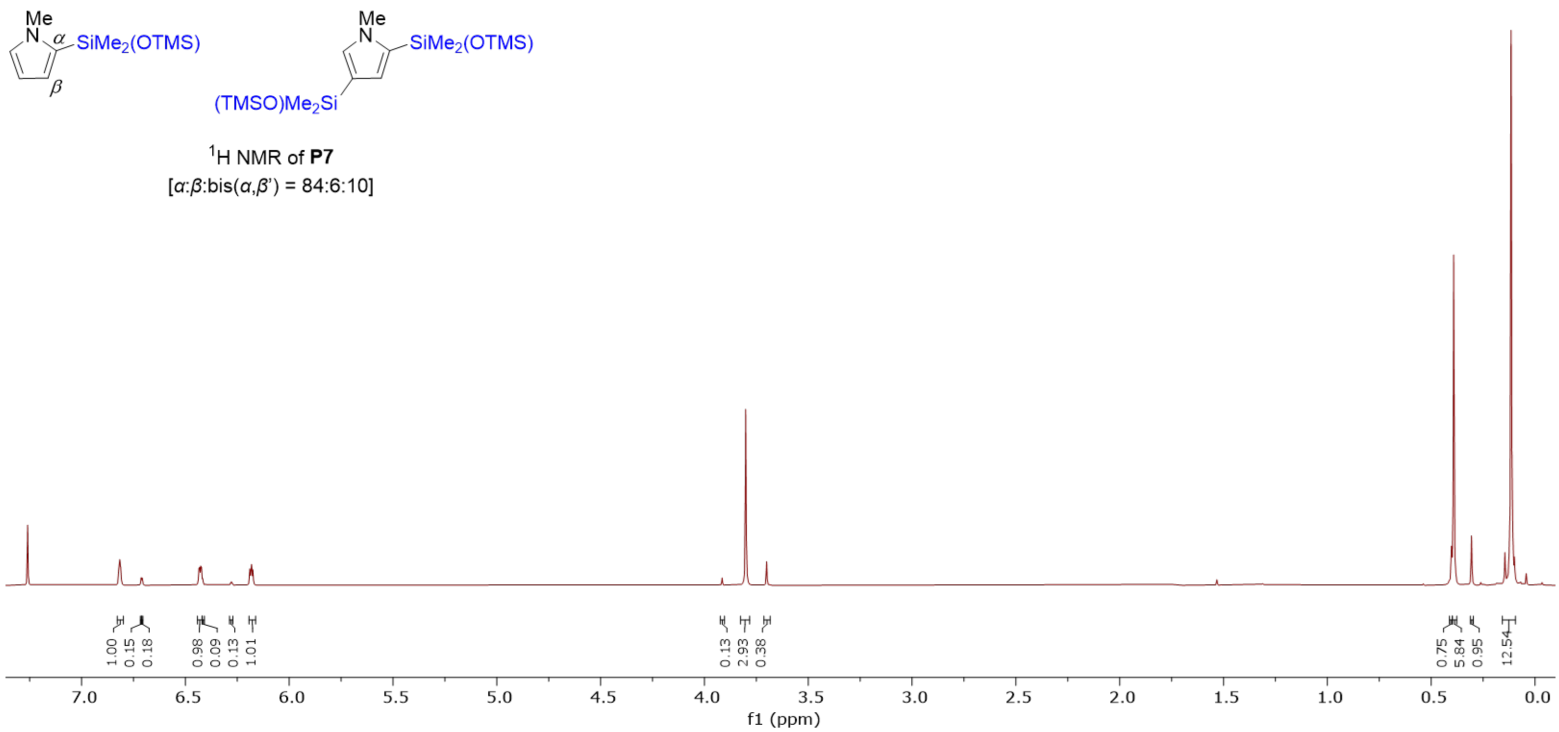

F
o
SiMe2(OTMS)
m
p
1H NMR of P5
[o:m:p = 52:33:15]
1.41
1.38
0.47
0.51
0.94
0.81
0.94
6.00
4.09
9.60
6.16
f1 (ppm)


F
o
SiMe2(OTMS)
m
p
13C NMR of P5
[o:m:p = 52:33:15]
f1 (ppm)

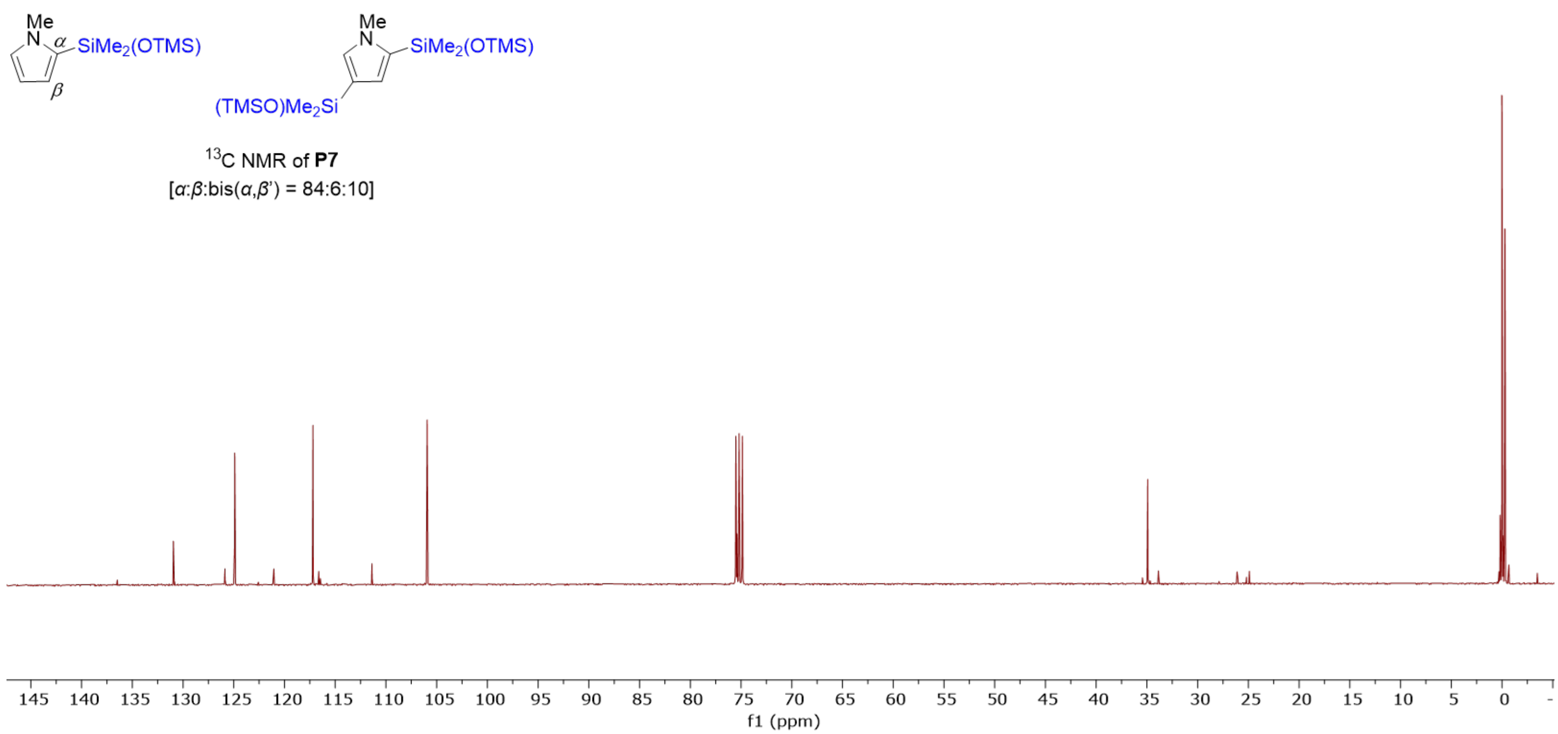

F
o
SiMe2(OTMS)
m
p
19F NMR of P5
[o:m:p = 52:33:15]
f1 (ppm)


Cl
m
SiMe2(OTMS)
p
1H NMR of P6
[m:p = 78:22]
1.18
0.32
0.91
1.50
1.00
5.80
1.67
8.48
2.85
f1 (ppm)

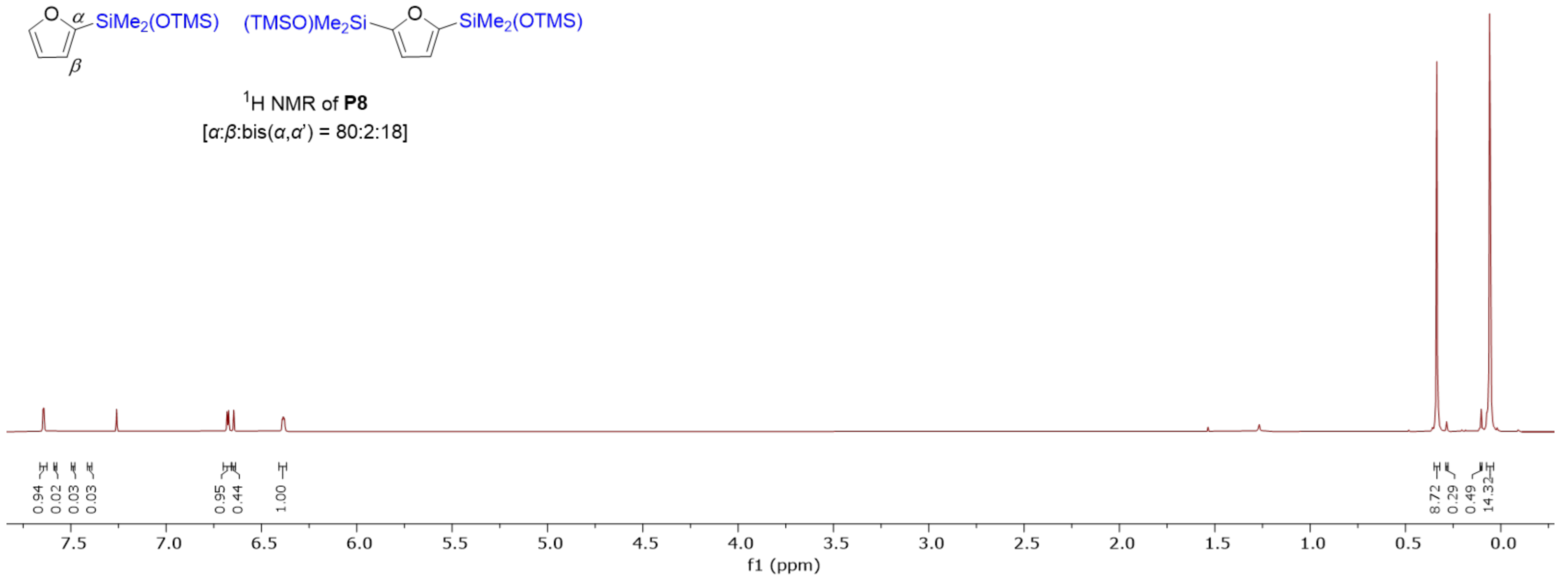

Cl
m
SiMe2(OTMS)
p
13C NMR of P6
[m:p = 78:22]
f1 (ppm)

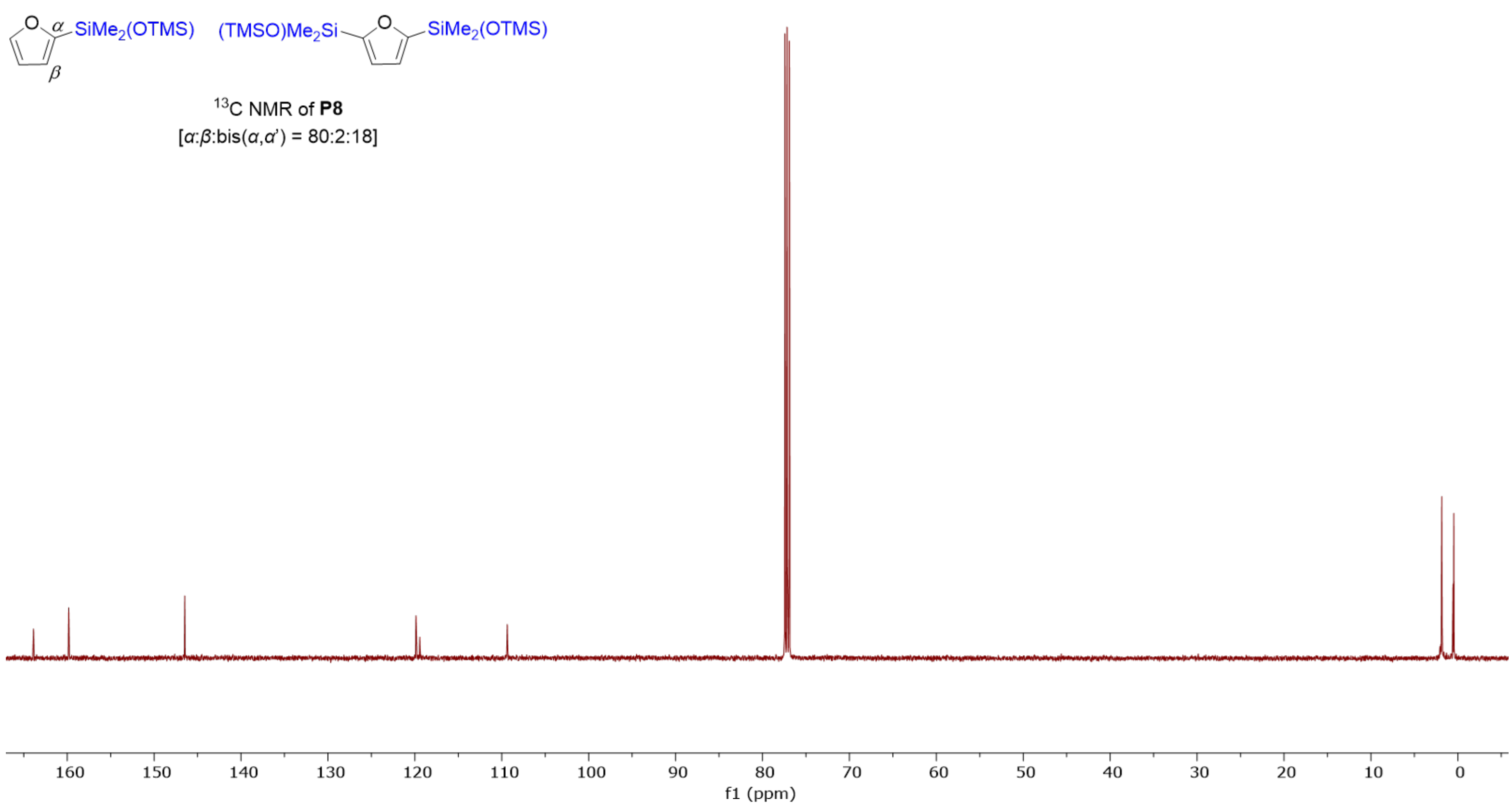


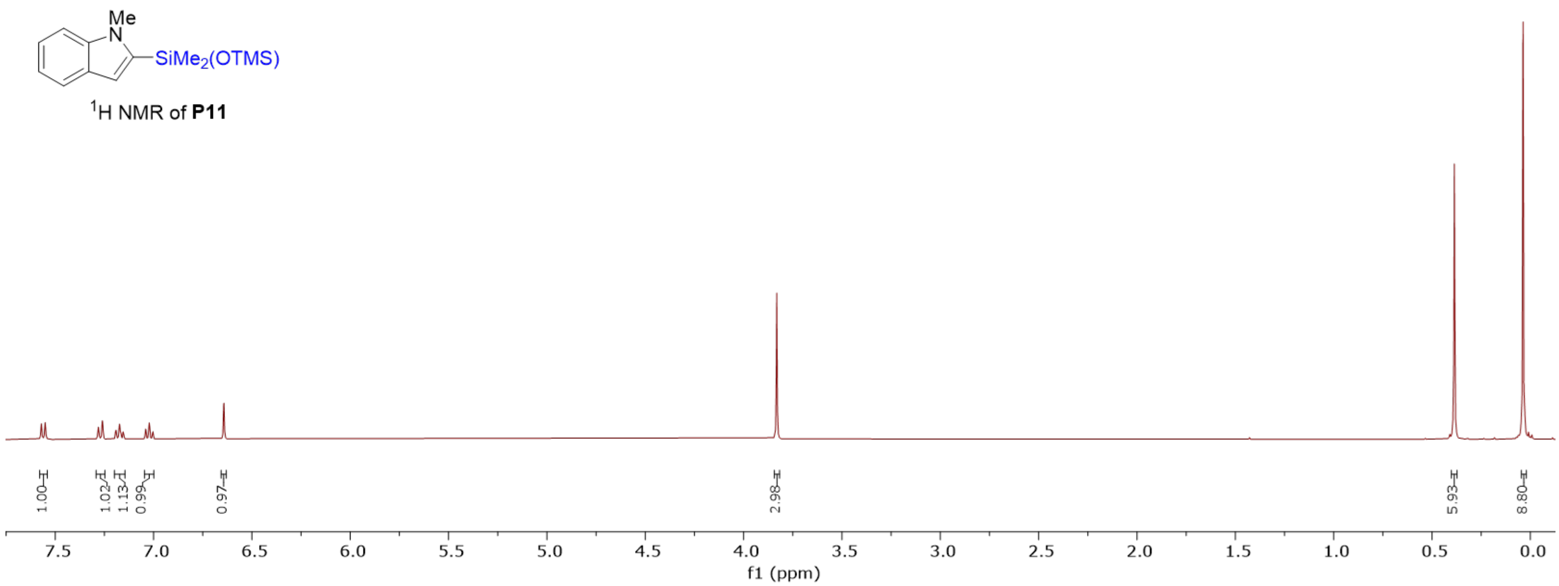
^{1}H NMR of **P7**
[α:β:bis(α,β') = 84:6:10]

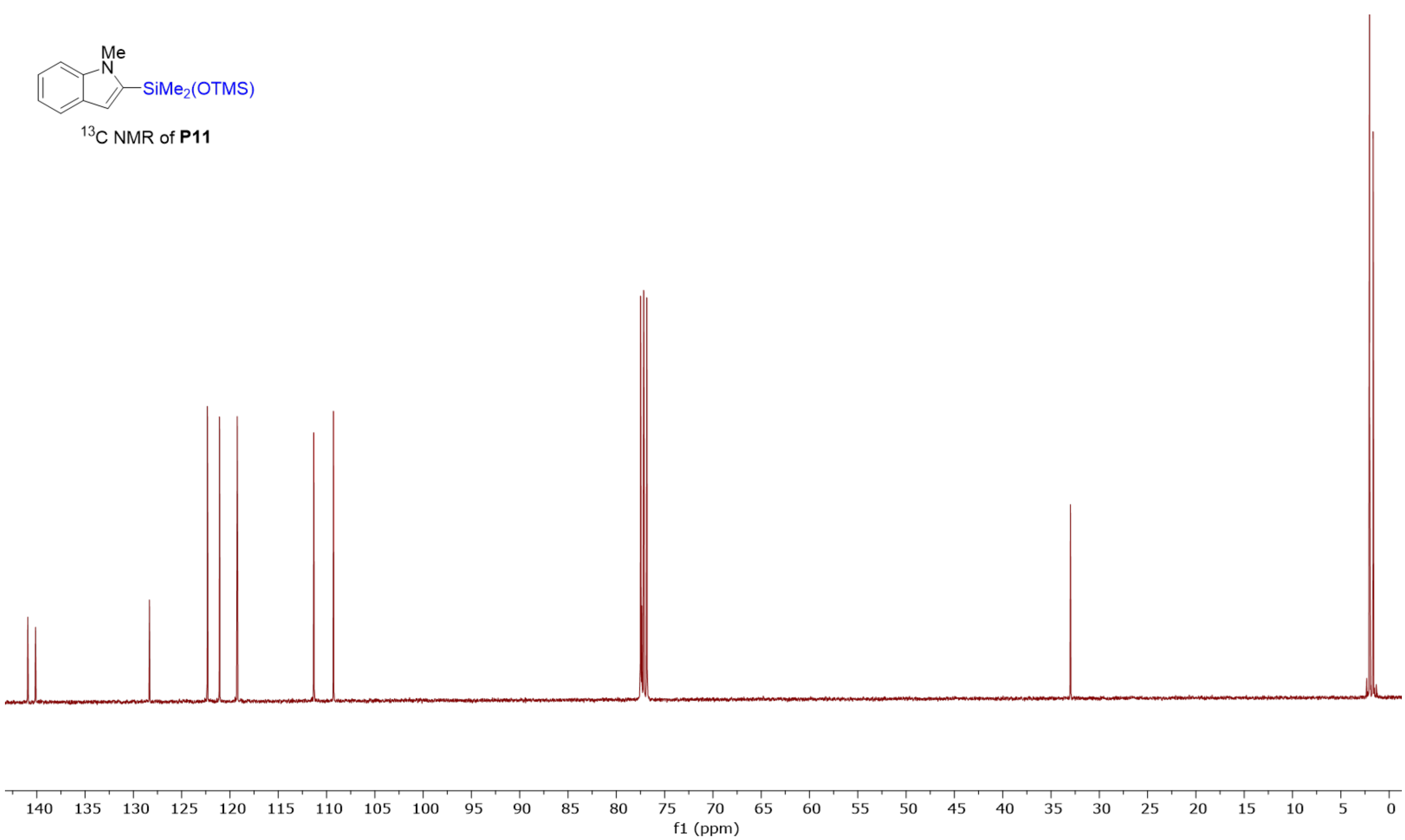


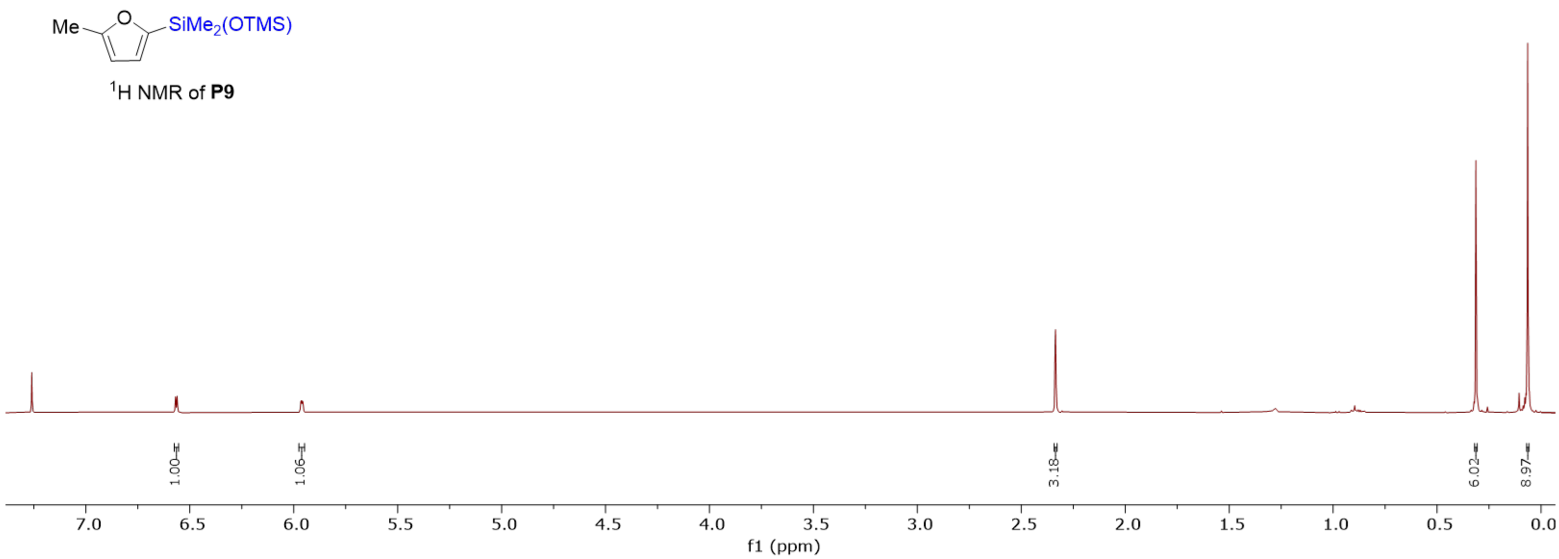
^{13}C NMR of **P7**
[α:β:bis(α,β') = 84:6:10]

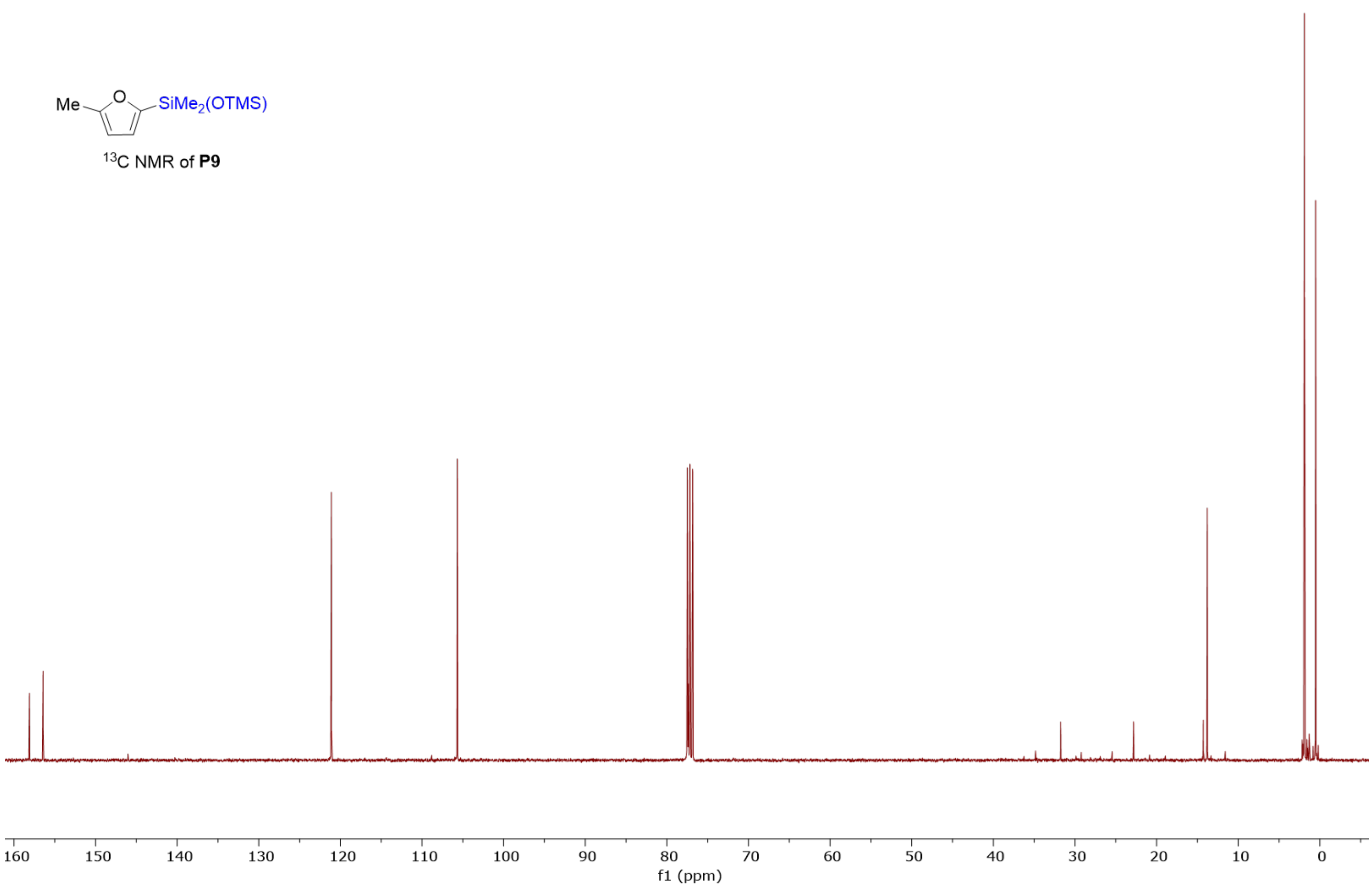

SiMe2(OTMS)
(TMSO)Me2Si
SiMe2(OTMS)
α
β
1H NMR of P8
[α:β:bis(α,α') = 80:2:18]
0.94
0.02
0.03
0.03
0.95
0.44
1.00
8.72
0.29
0.49
14.32
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

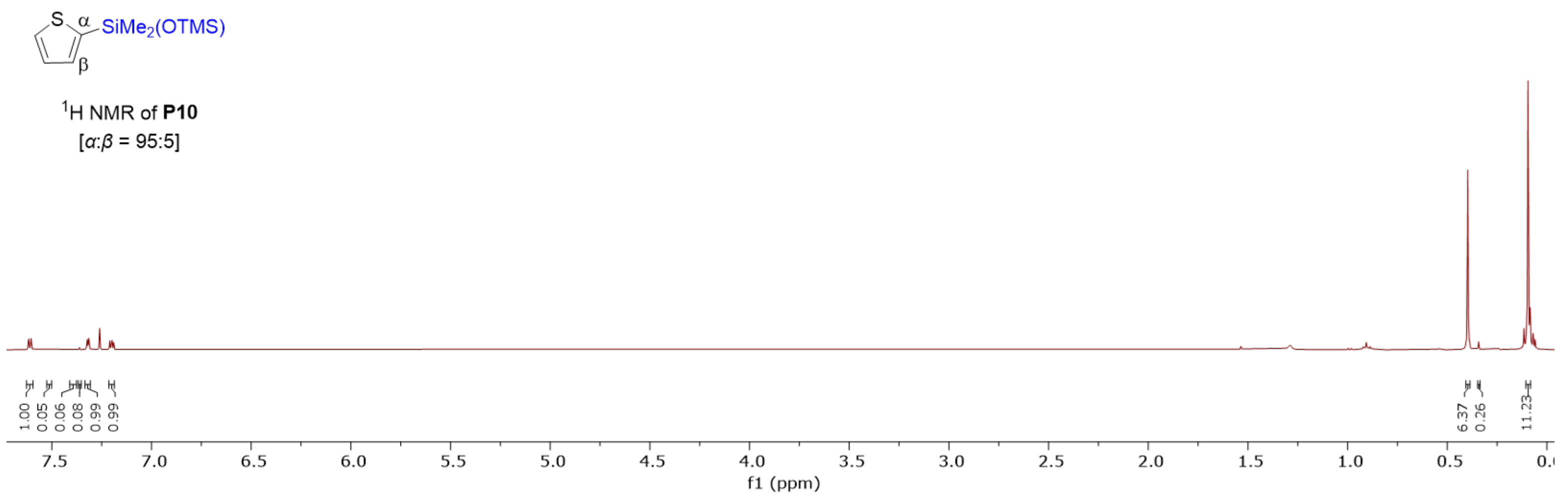

SiMe2(OTMS)
(TMSO)Me2Si
SiMe2(OTMS)
α
β
13C NMR of P8
[α:β:bis(α,α') = 80:2:18]
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

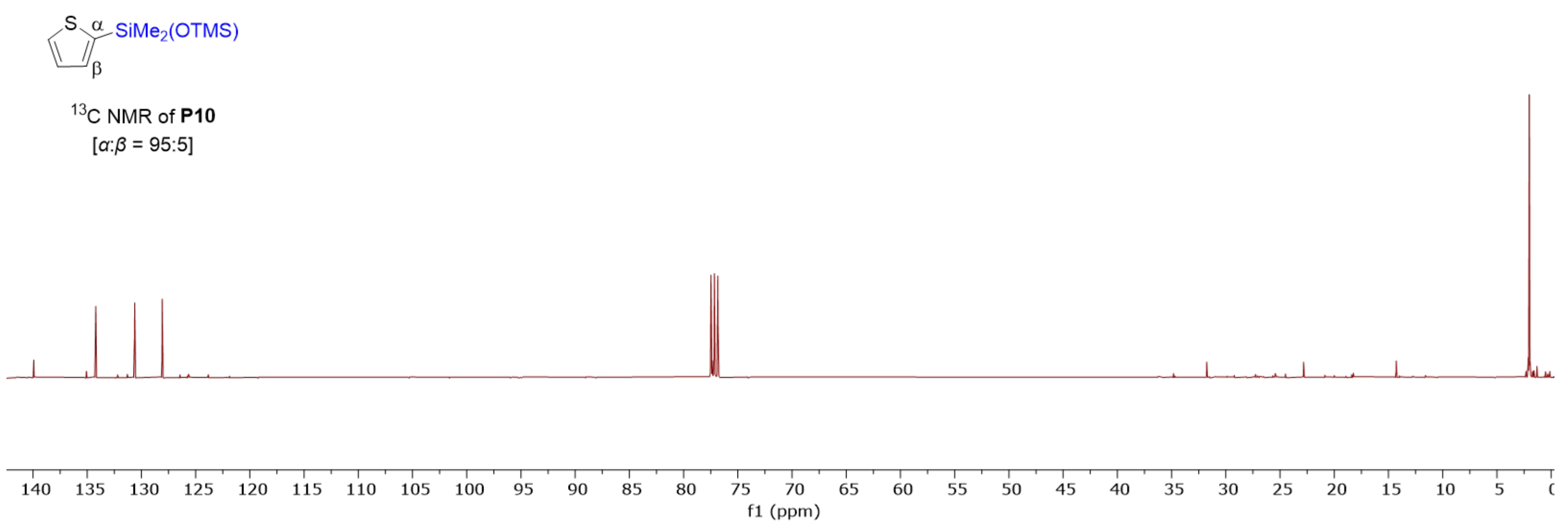

Me
N
SiMe2(OTMS)
1H NMR of P11
1.00
1.02
1.13
0.99
0.97
2.98
5.93
8.80
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

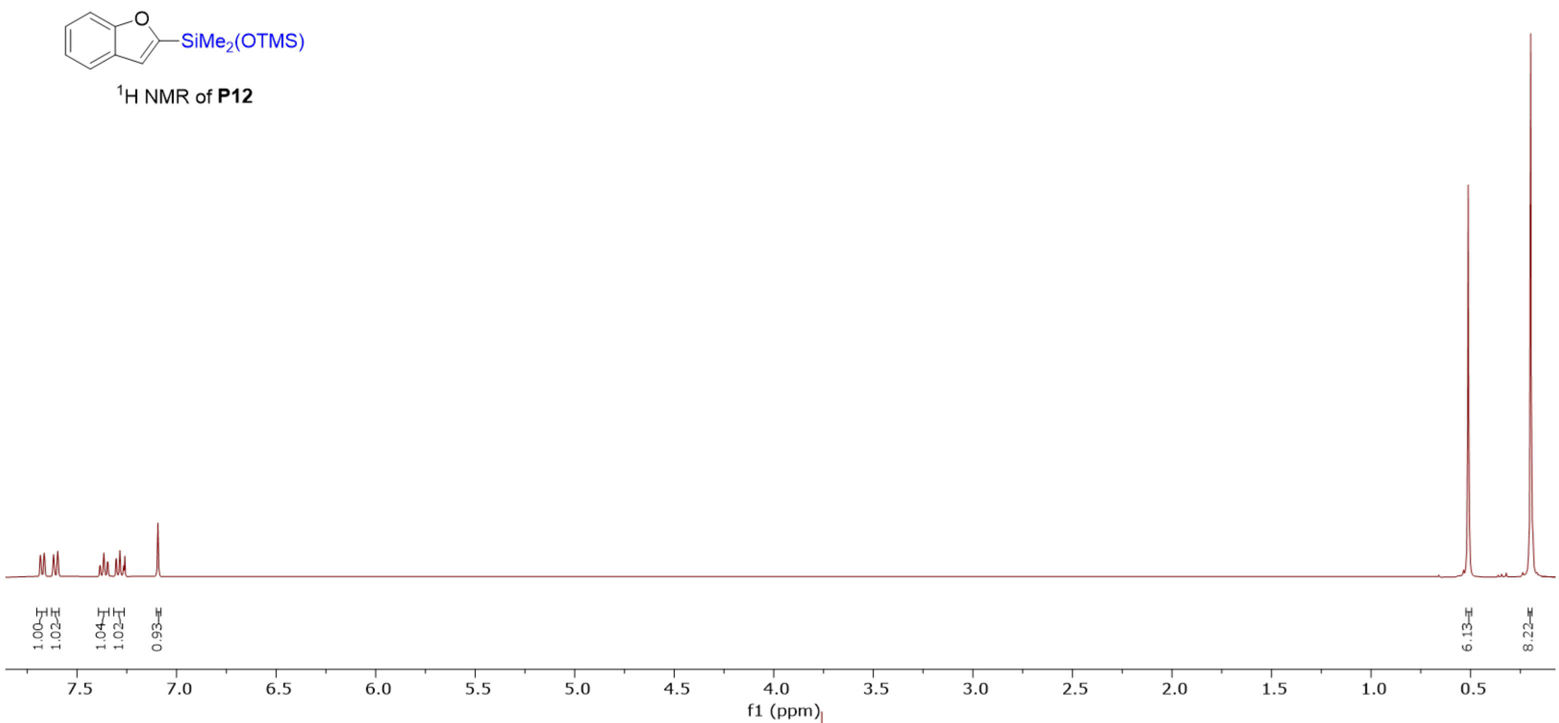

Me
N
SiMe2(OTMS)
13C NMR of P11
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

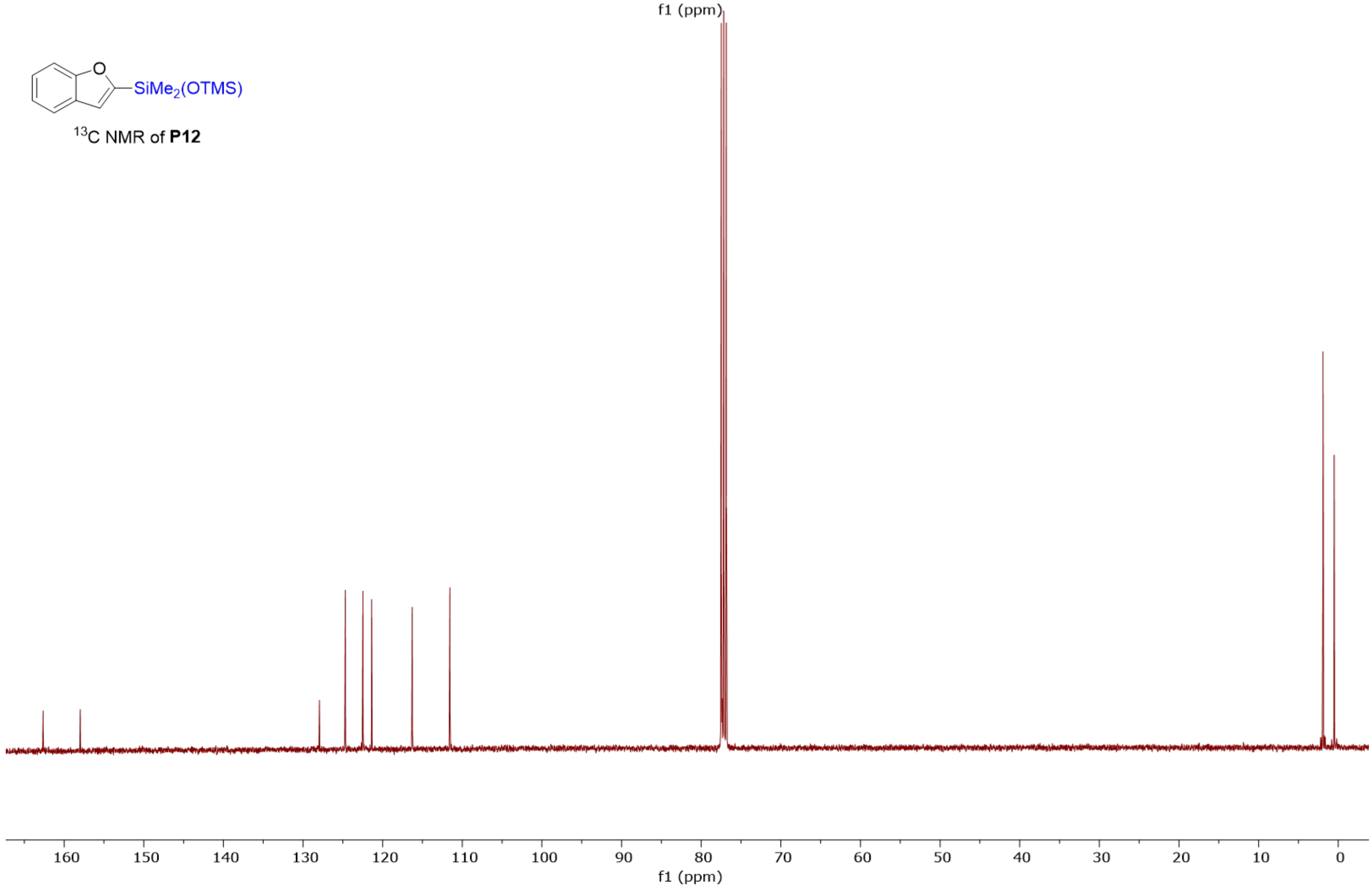

Me
O
SiMe2(OTMS)
1H NMR of P9
1.00
1.06
3.18
6.02
8.97
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

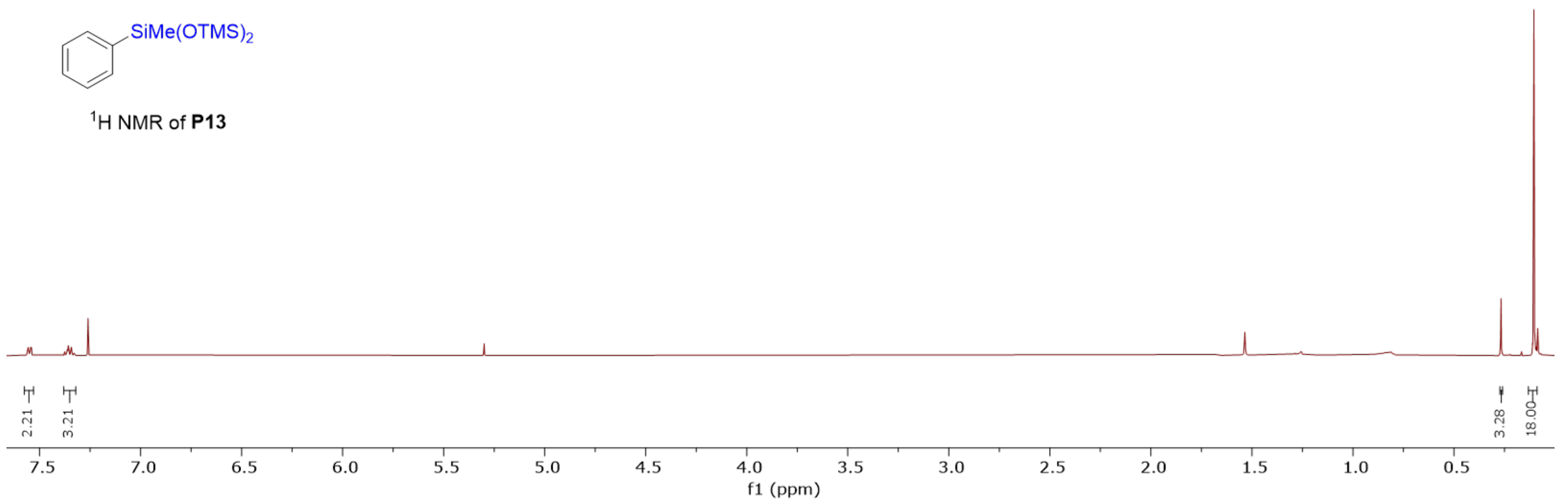

Me
O
SiMe2(OTMS)
13C NMR of P9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

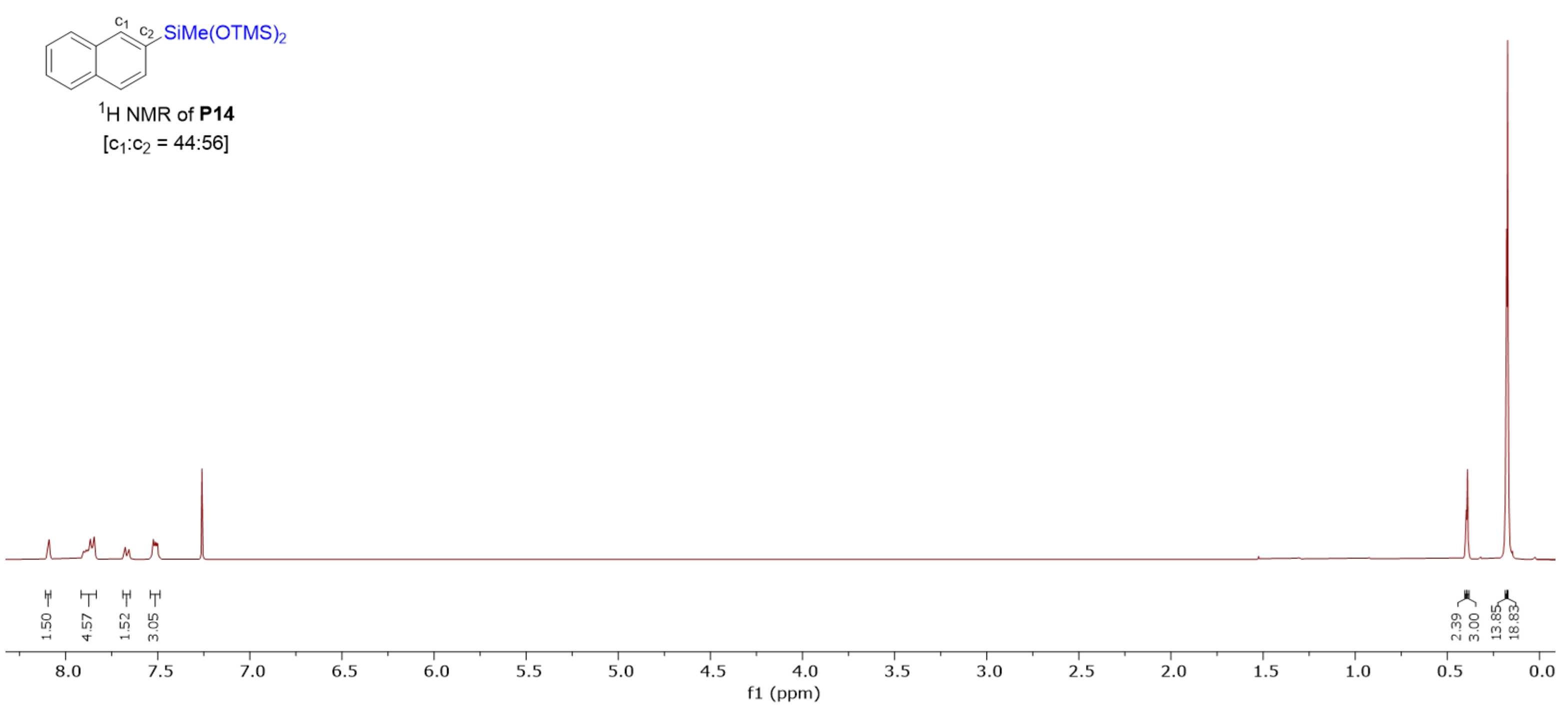

S
α
SiMe2(OTMS)
β
1H NMR of P10
[α:β = 95:5]
1.00
0.05
0.06
0.08
0.99
0.99
6.37
0.26
11.23
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

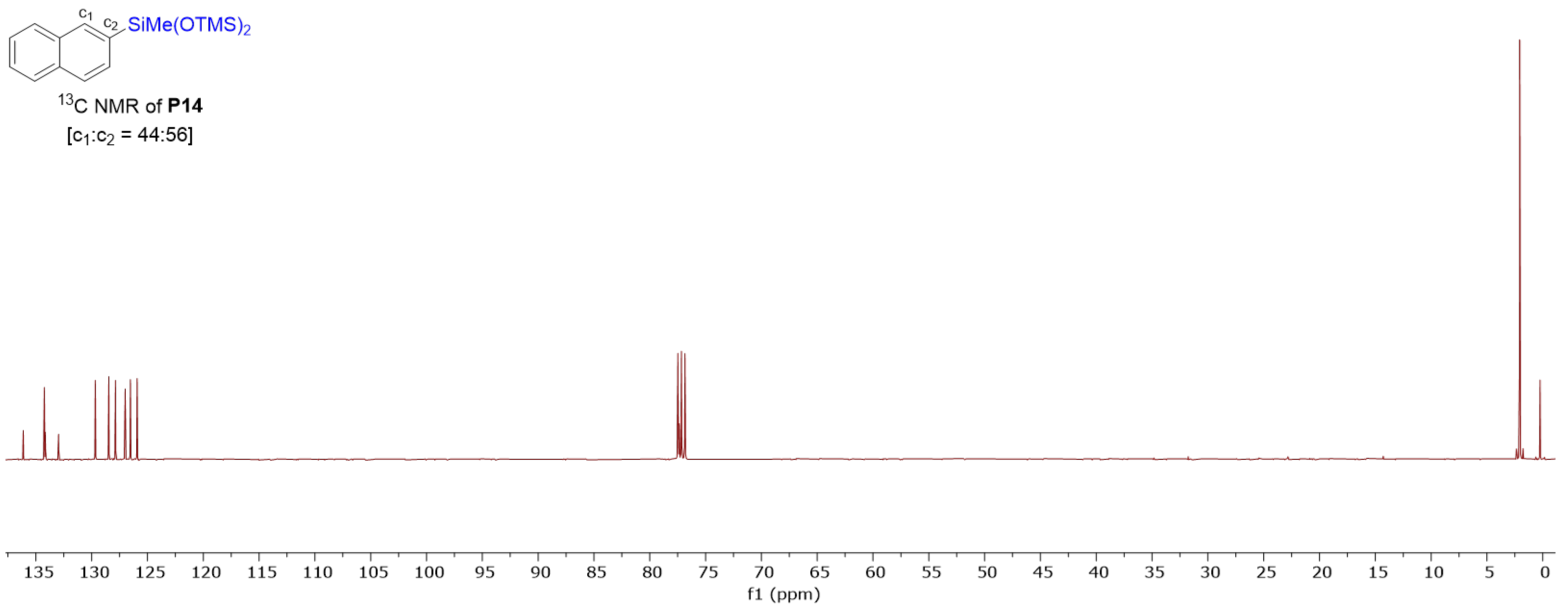

S
α
SiMe2(OTMS)
β
13C NMR of P10
[α:β = 95:5]
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

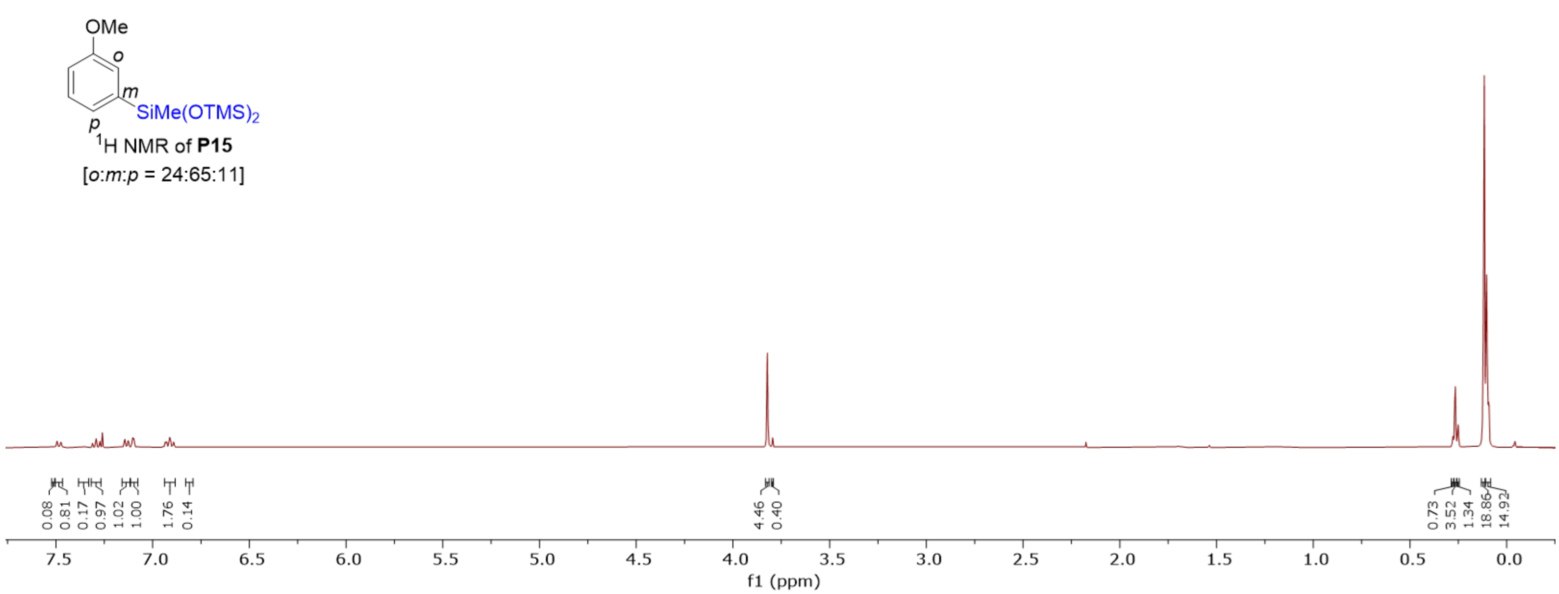

SiMe2(OTMS)
1H NMR of P12
1.00
1.02
1.04
1.02
0.93
6.13
8.22
f1 (ppm)

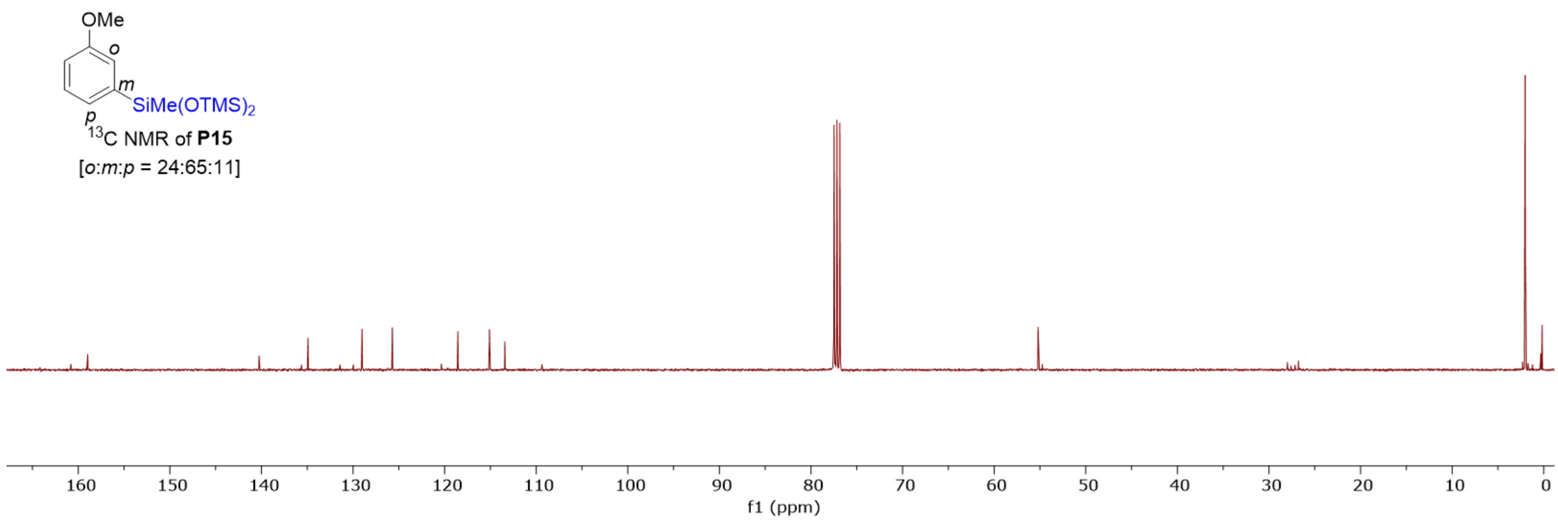

SiMe2(OTMS)
13C NMR of P12
f1 (ppm)

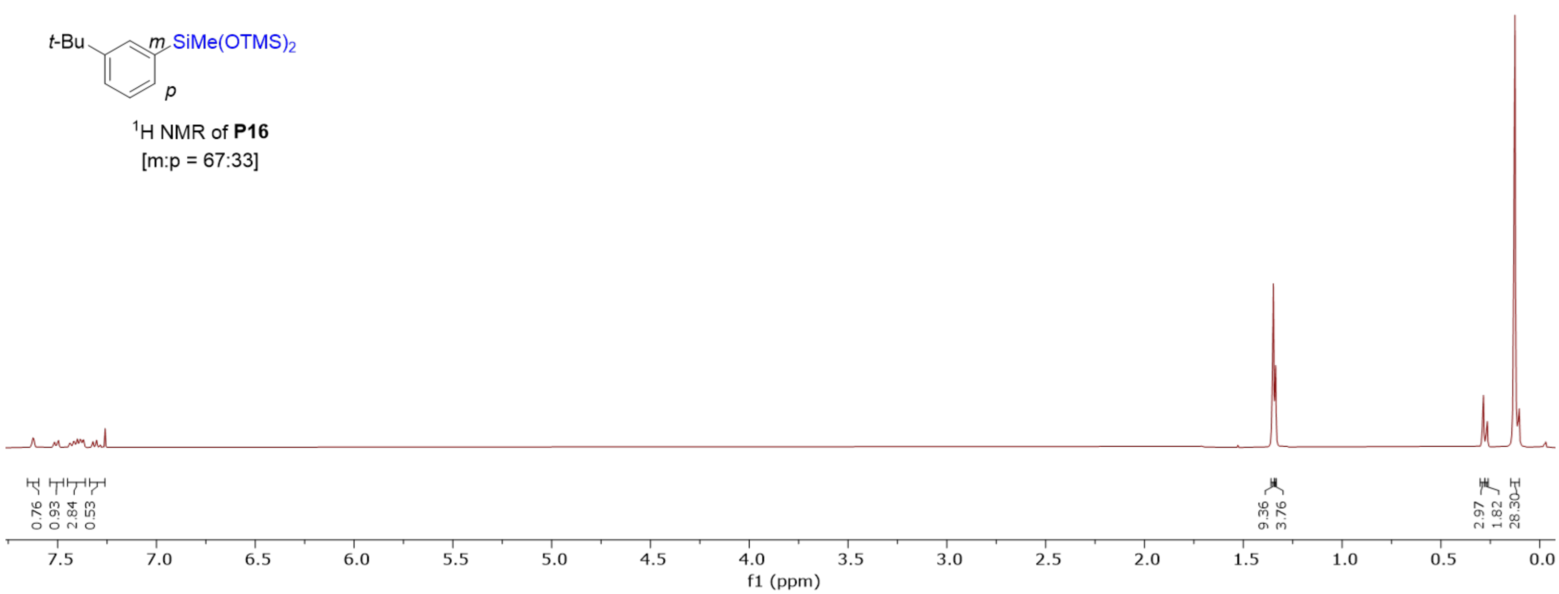

SiMe(OTMS)2
1H NMR of P13
2.21
3.21
3.28
18.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

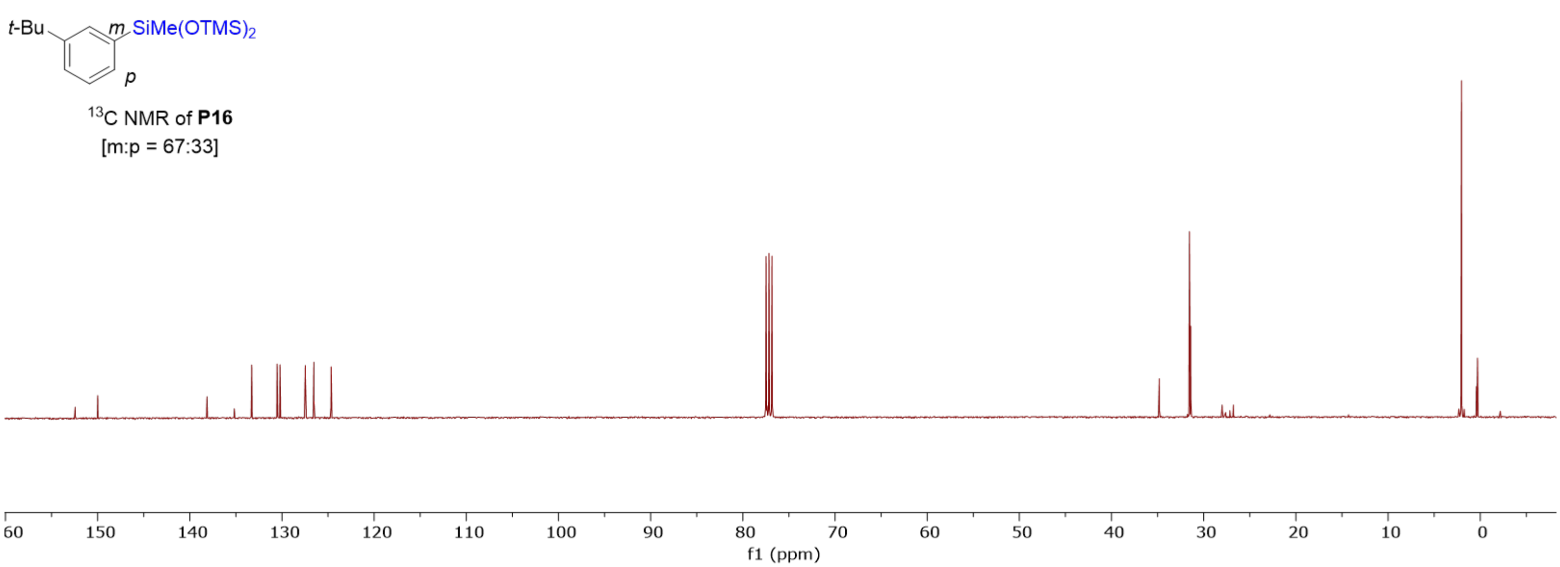

c1
c2
SiMe(OTMS)2
1H NMR of P14
[c1:c2 = 44:56]
1.50
4.57
1.52
3.05
2.39
3.00
13.85
18.83
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

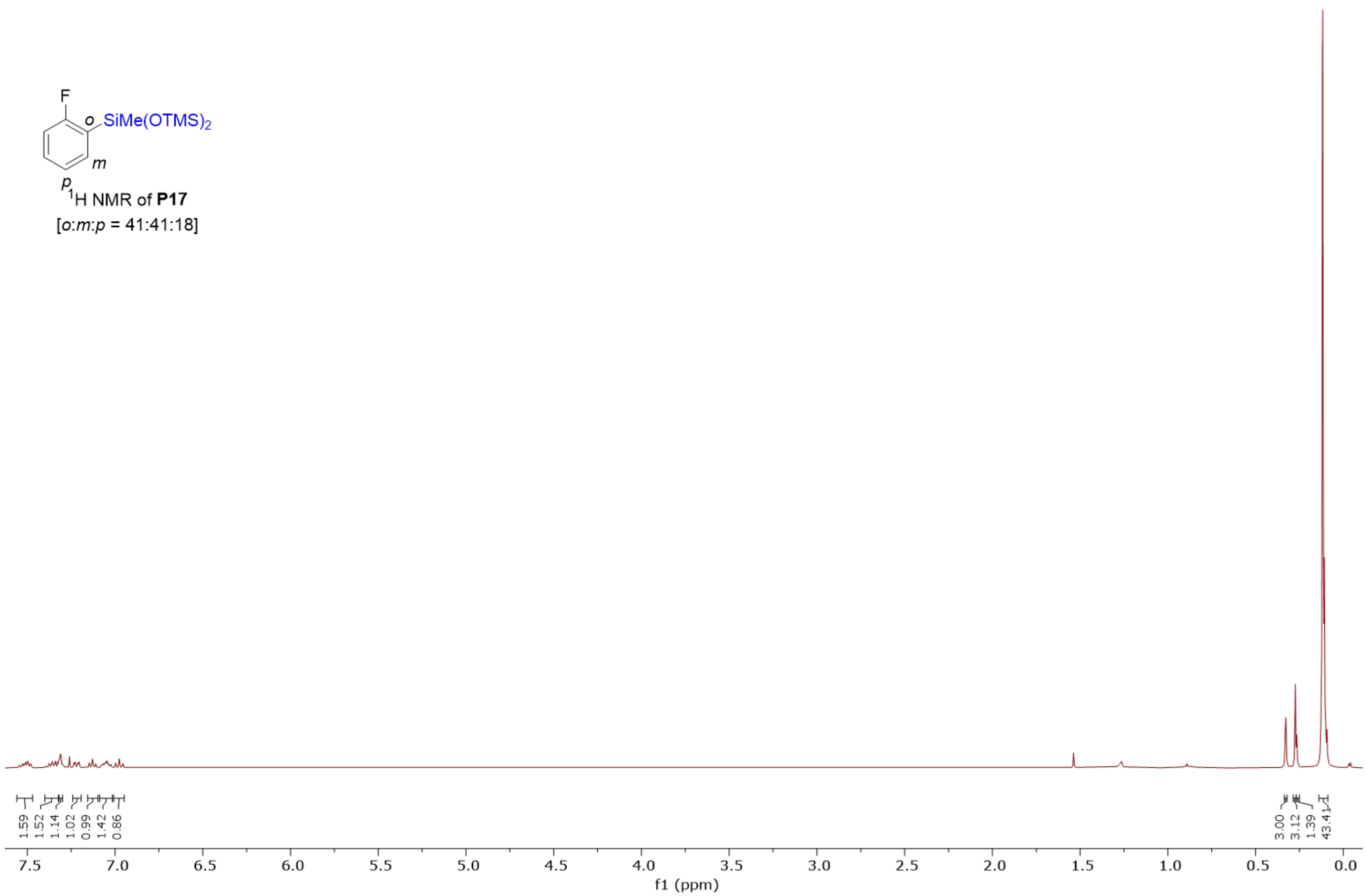

SiMe(OTMS)2
c1
c2
13C NMR of P14
[c1:c2 = 44:56]
f1 (ppm)

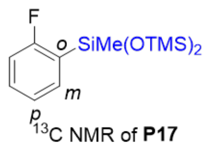

OMe
o
m
p
SiMe(OTMS)2
1H NMR of P15
[o:m:p = 24:65:11]
f1 (ppm)


OMe
o
m
p
SiMe(OTMS)2
13C NMR of P15
[o:m:p = 24:65:11]
f1 (ppm)


t-Bu
m
SiMe(OTMS)2
p
1H NMR of P16
[m:p = 67:33]
f1 (ppm)

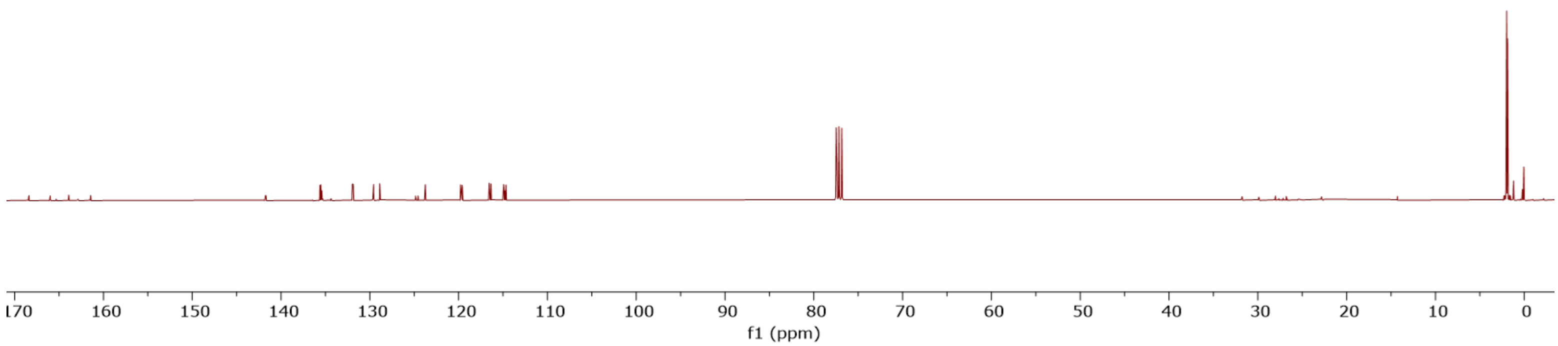

t-Bu
m
SiMe(OTMS)2
p
13C NMR of P16
[m:p = 67:33]
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

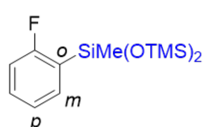

F
o
SiMe(OTMS)2
m
p
1H NMR of P17
[o:m:p = 41:41:18]
1.59 1.52 1.14 1.02 0.99 1.42 0.86
3.00 3.12 1.39 43.41
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



^{13}C NMR of **P17**

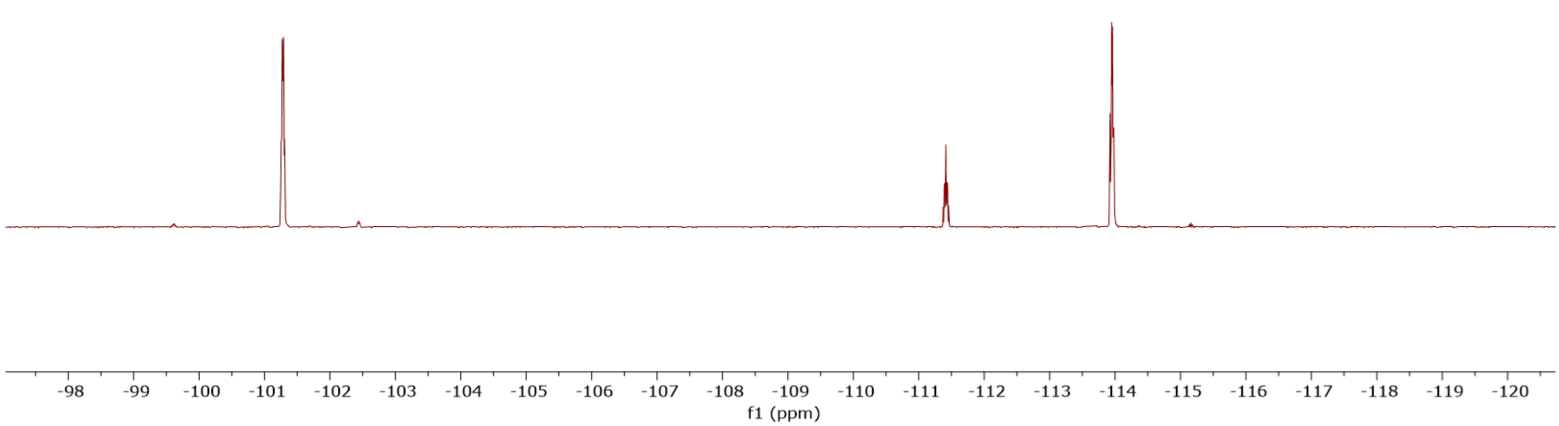
[*o*:*m*:*p* = 41:41:18]

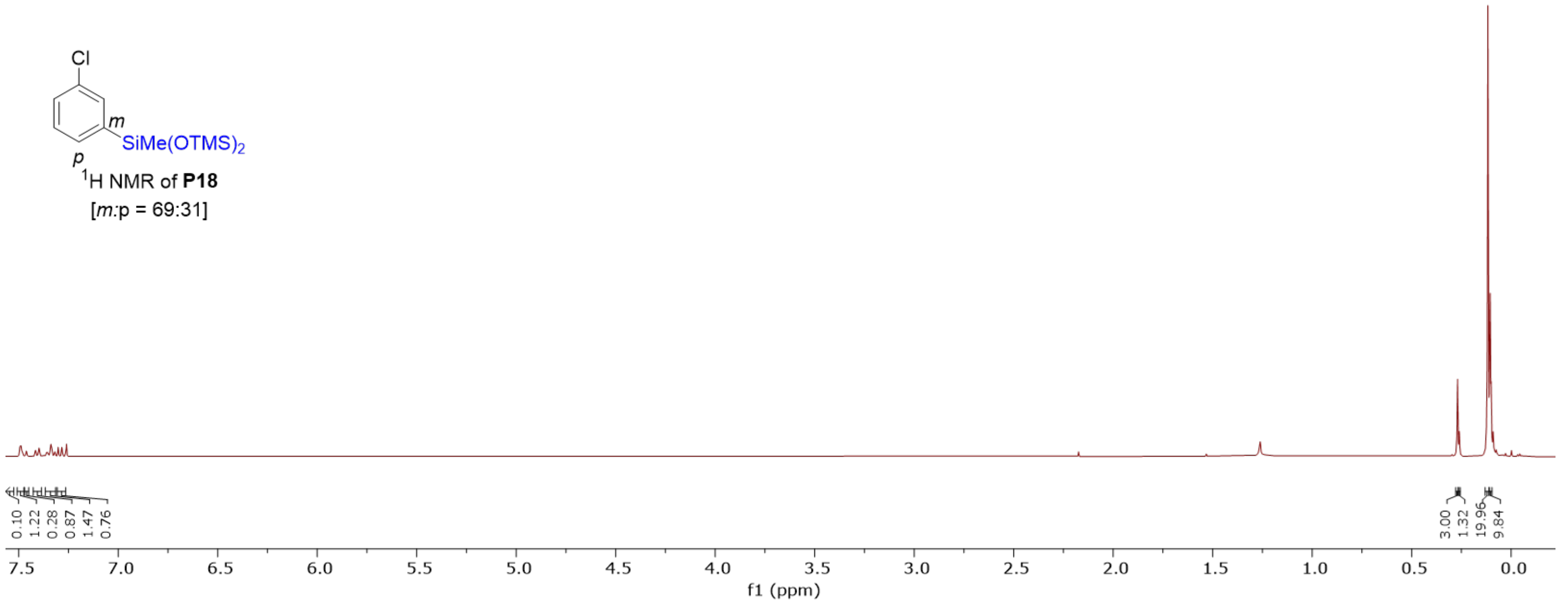


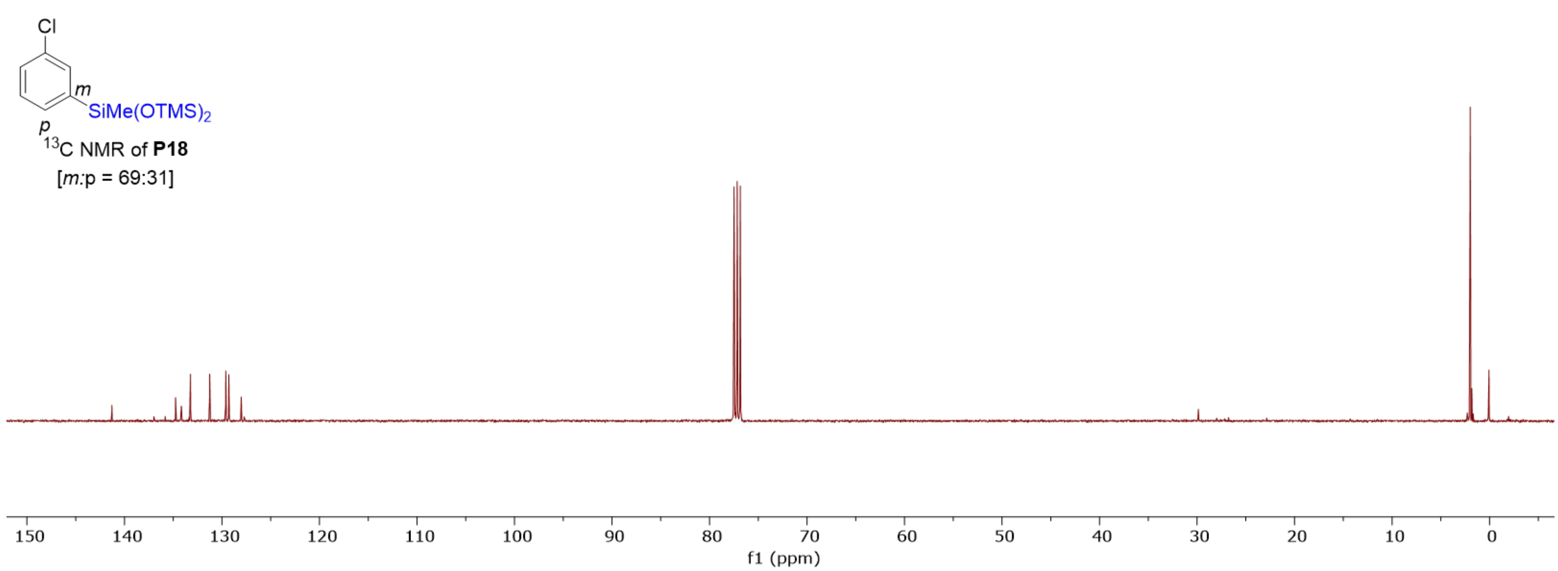


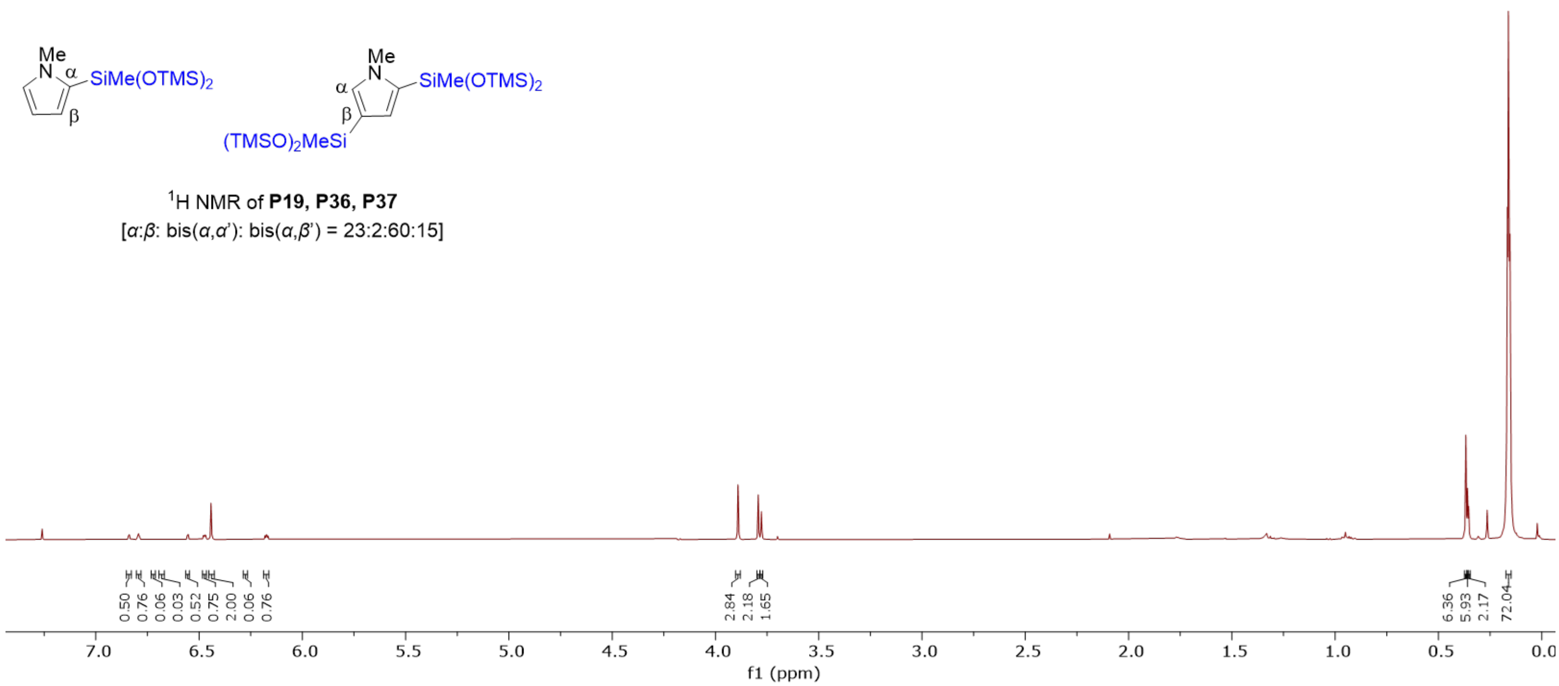
^{19}F NMR of **P17**

[*o*:*m*:*p* = 41:41:18]



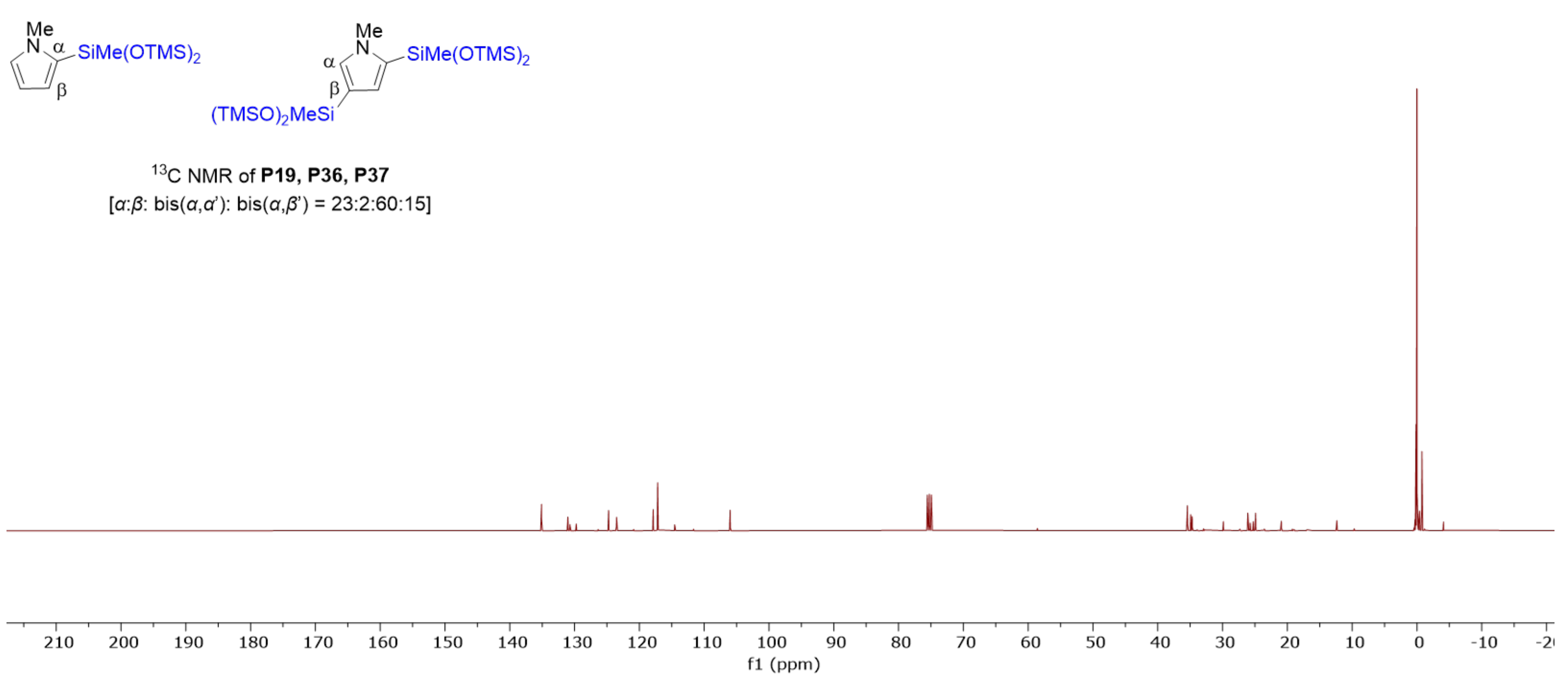

Cl
m
SiMe(OTMS)2
p
1H NMR of P18
[m:p = 69:31]
f1 (ppm)


Cl
m
SiMe(OTMS)2
p
13C NMR of P18
[m:p = 69:31]
f1 (ppm)



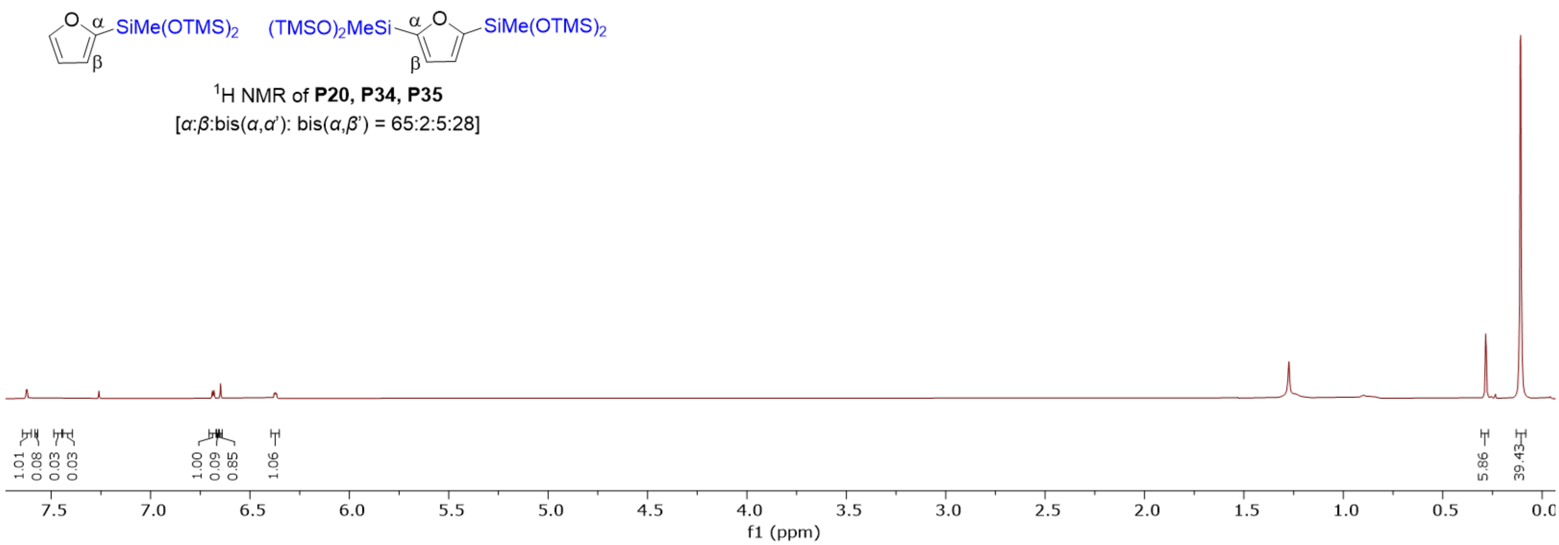
^{1}H NMR of **P19, P36, P37**

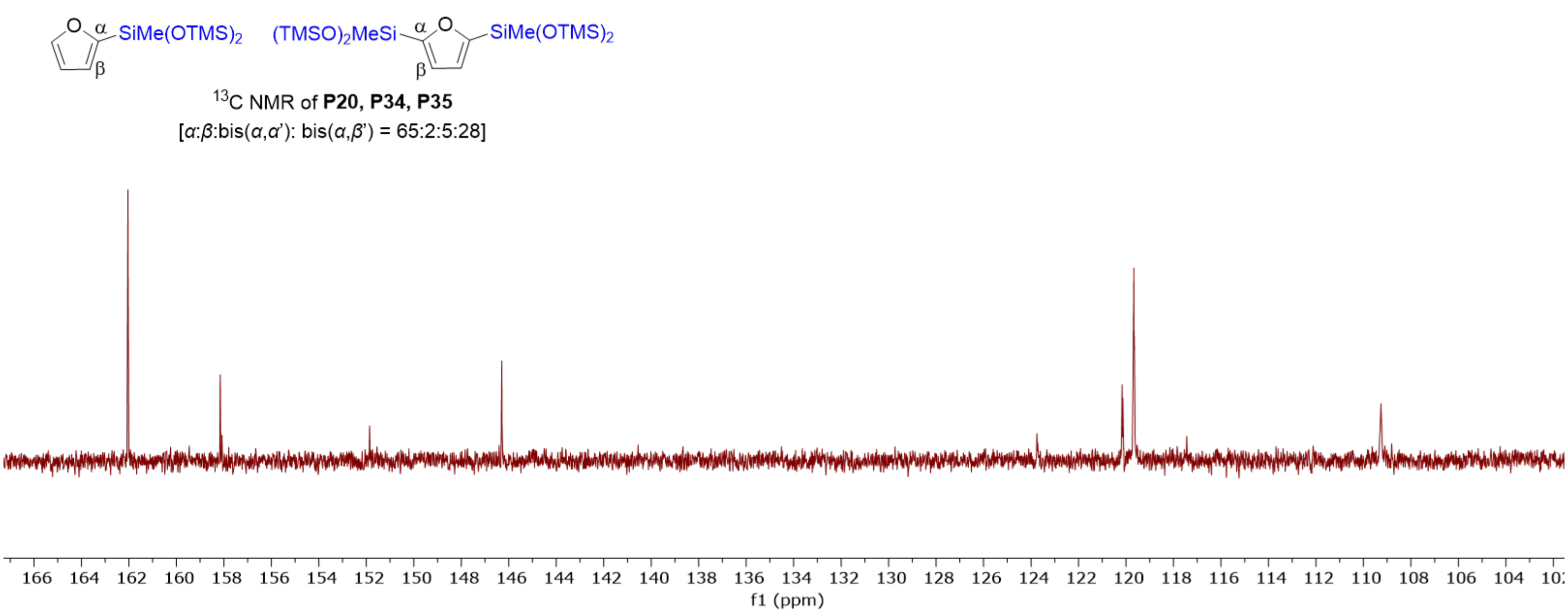
[α:β: bis(α,α'): bis(α,β') = 23:2:60:15]

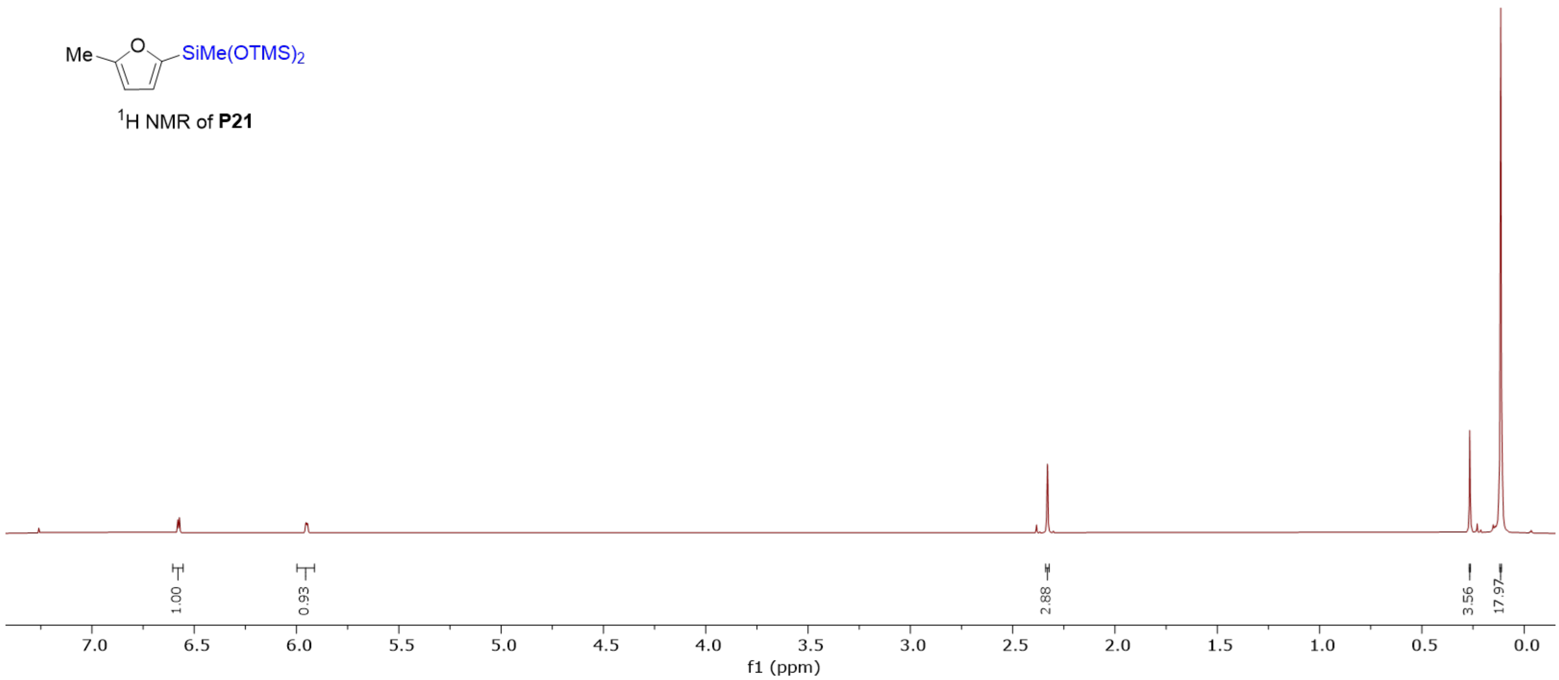


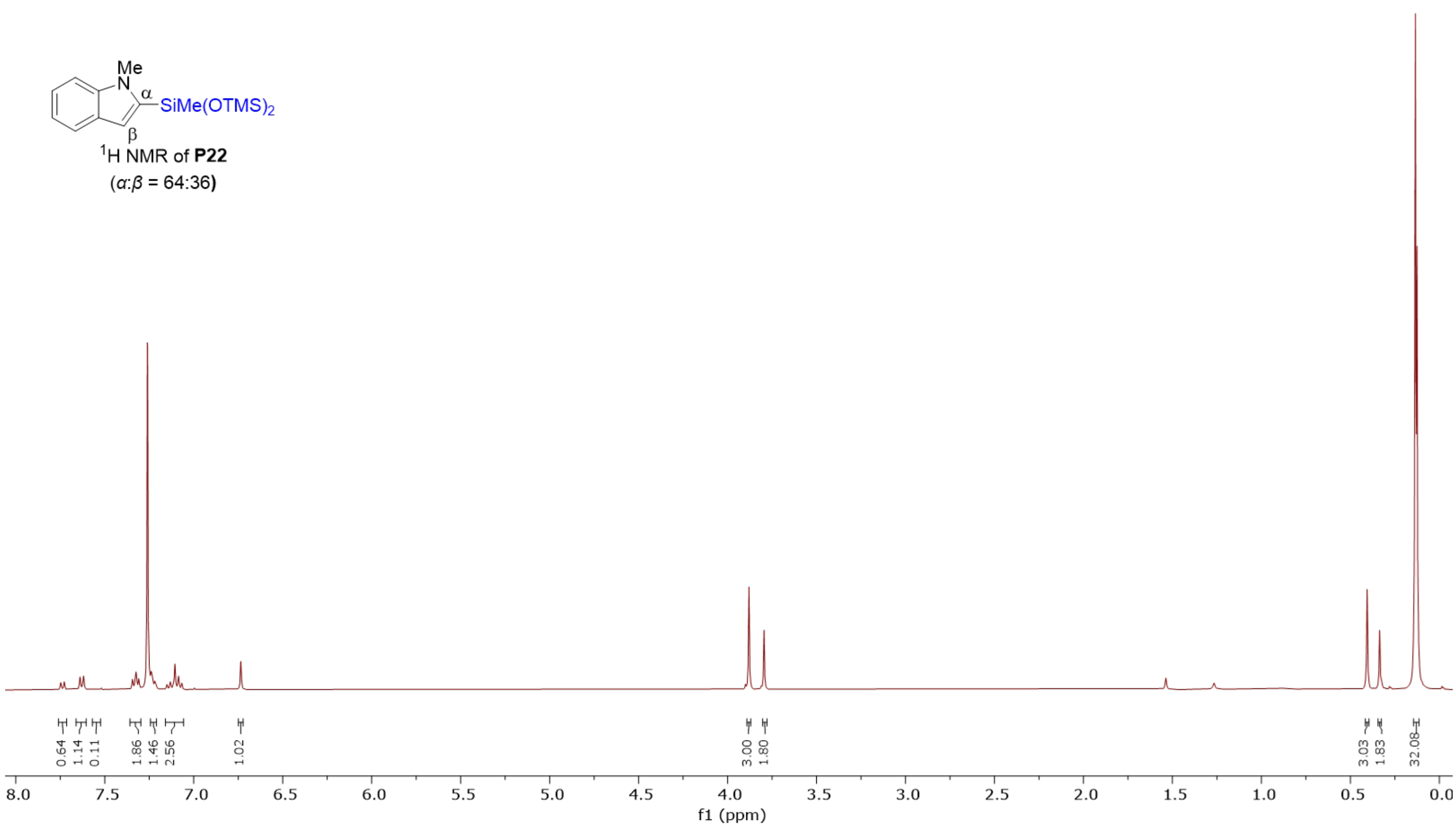
^{13}C NMR of **P19, P36, P37**

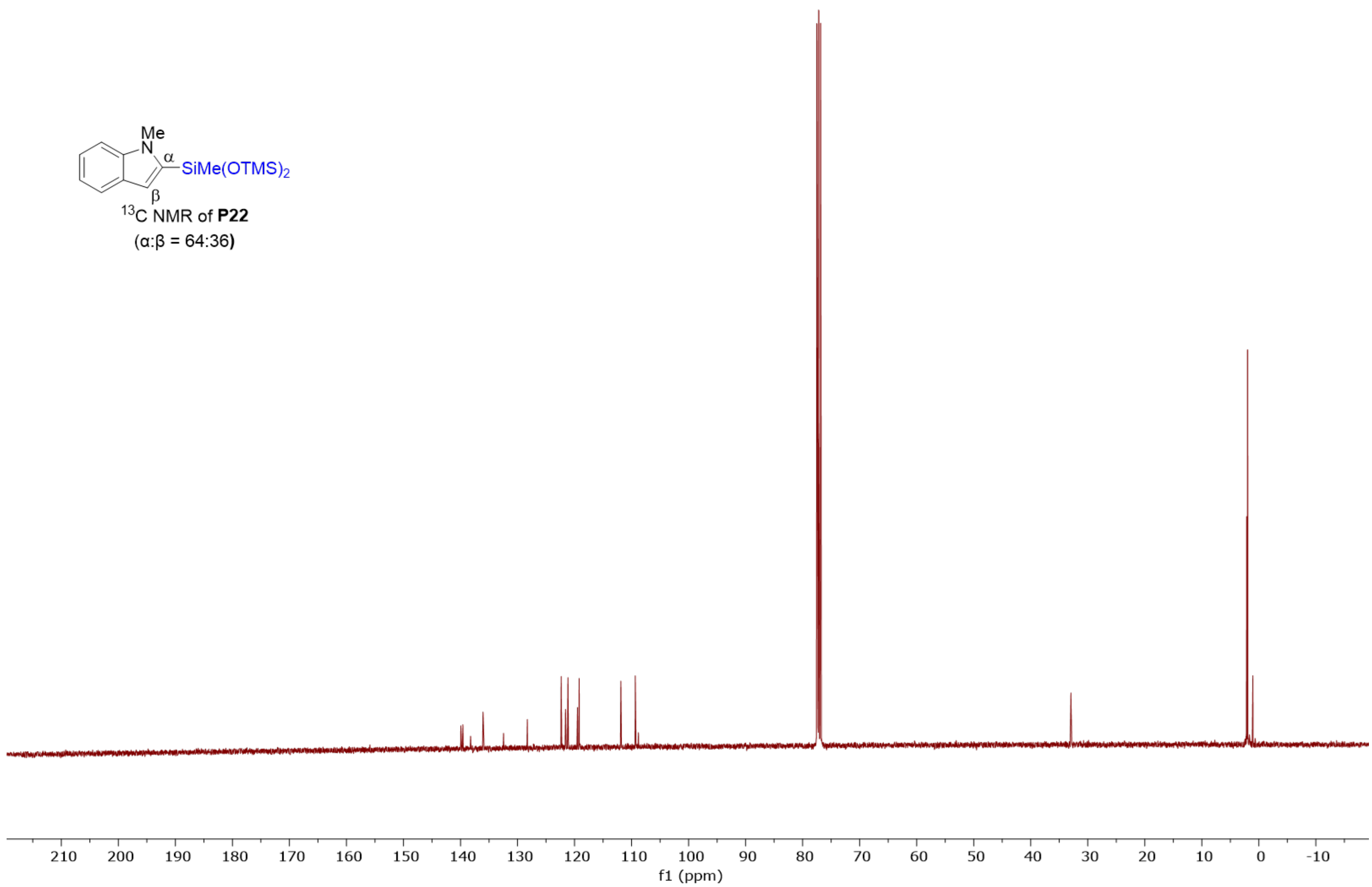
[α:β: bis(α,α'): bis(α,β') = 23:2:60:15]


SiMe(OTMS)2
(TMSO)2MeSi
SiMe(OTMS)2
1H NMR of P20, P34, P35
[α:β:bis(α,α'): bis(α,β') = 65:2:5:28]
f1 (ppm)

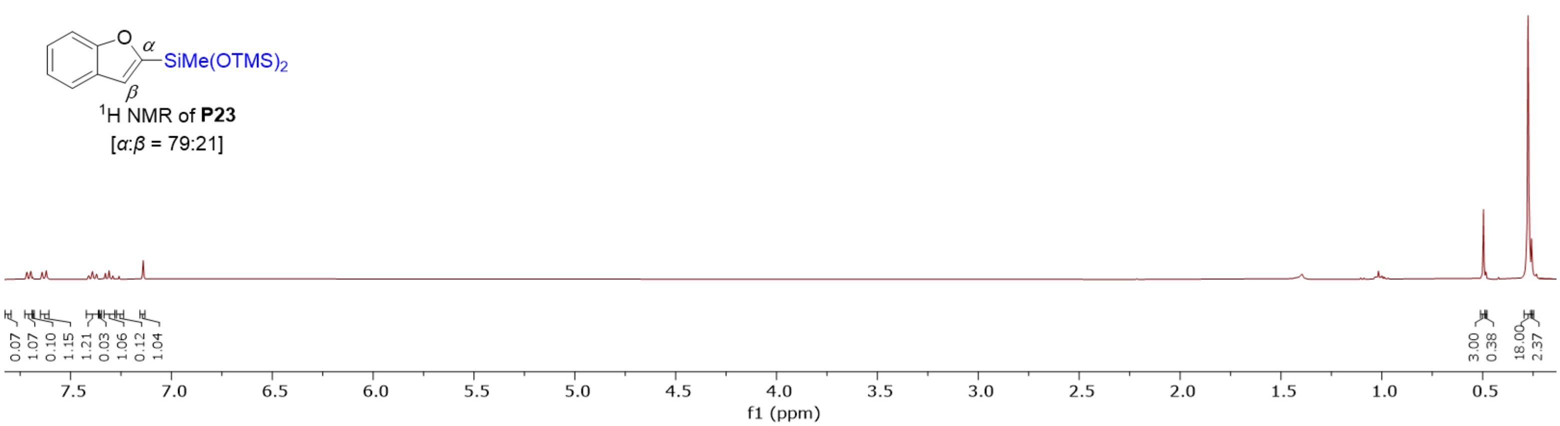

SiMe(OTMS)2
(TMSO)2MeSi
SiMe(OTMS)2
13C NMR of P20, P34, P35
[α:β:bis(α,α'): bis(α,β') = 65:2:5:28]
f1 (ppm)


Me
O
SiMe(OTMS)2
1H NMR of P21
1.00
0.93
2.88
3.56
17.97
f1 (ppm)

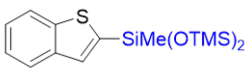

Me
N
α
SiMe(OTMS)2
β
1H NMR of P22
(α:β = 64:36)
0.64
1.14
0.11
1.86
1.46
2.56
1.02
3.00
1.80
3.03
1.83
32.08
f1 (ppm)



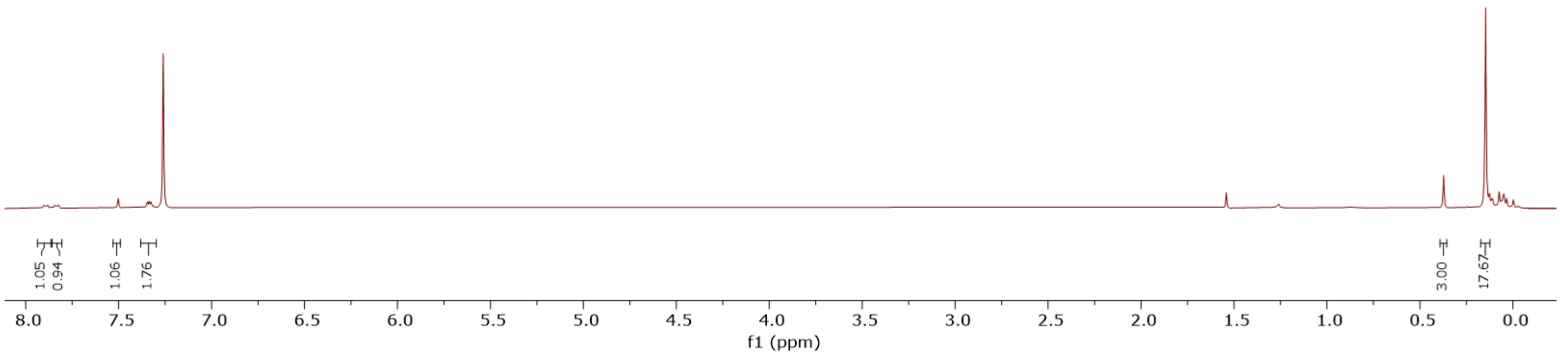
Me
N
α
SiMe(OTMS)2
β
13C NMR of P22
(α:β = 64:36)
f1 (ppm)

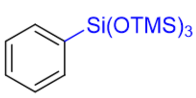


O
α
SiMe(OTMS)2
β
1H NMR of P23
[α:β = 79:21]
f1 (ppm)

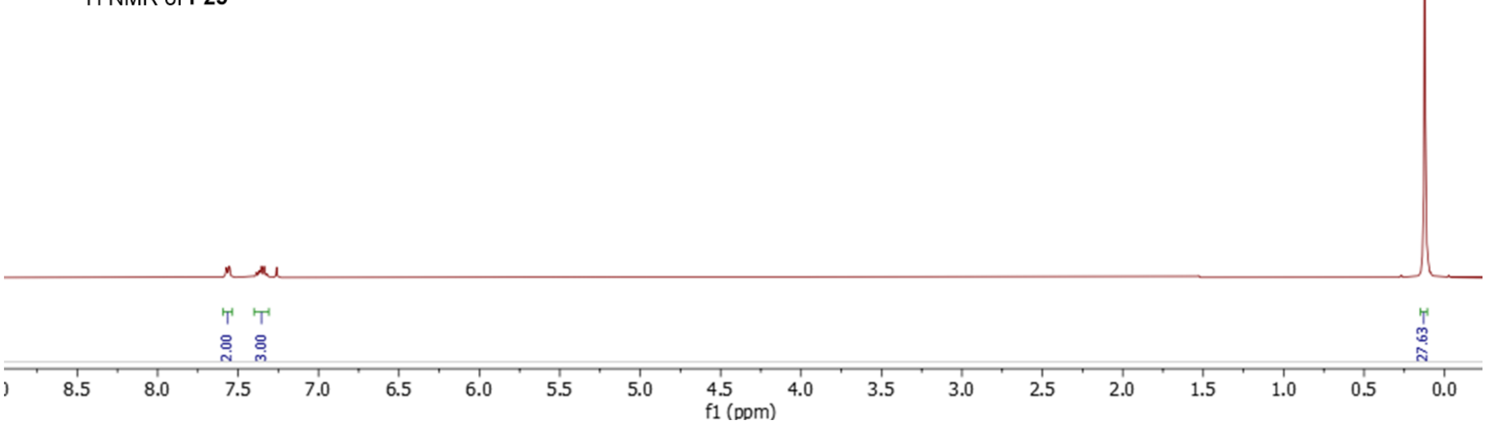


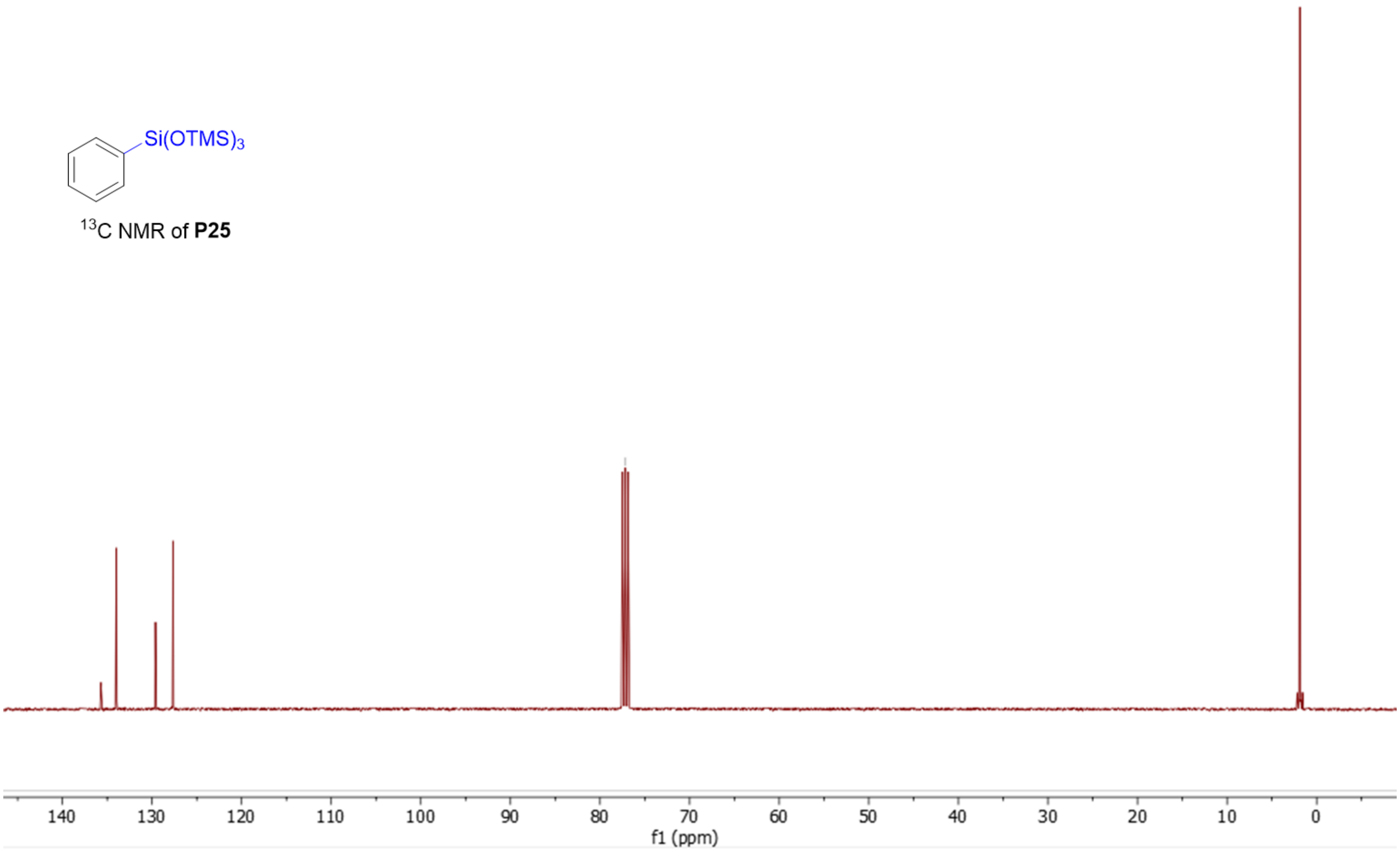
^1H NMR of **P24**

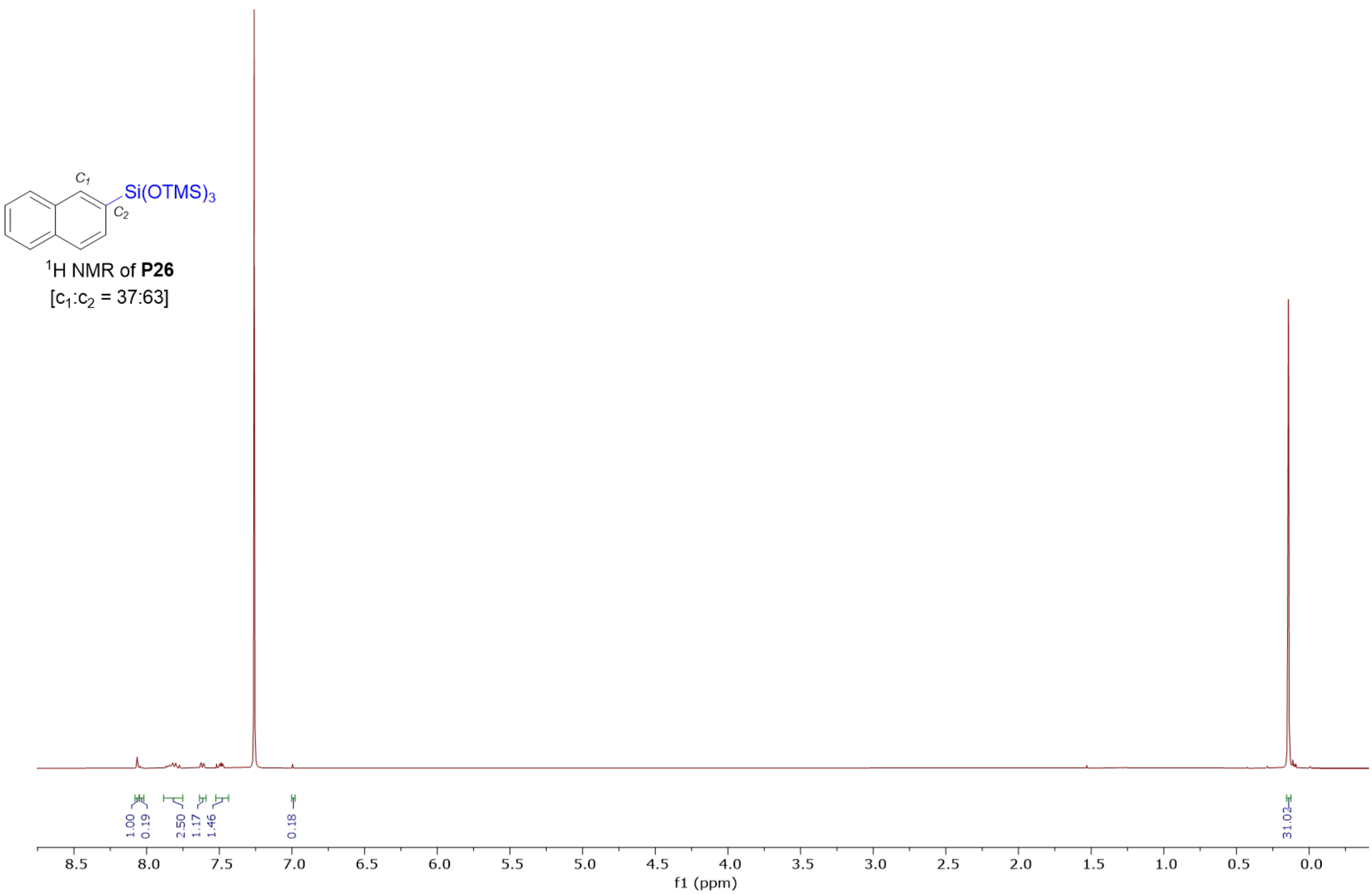




^1H NMR of **P25**

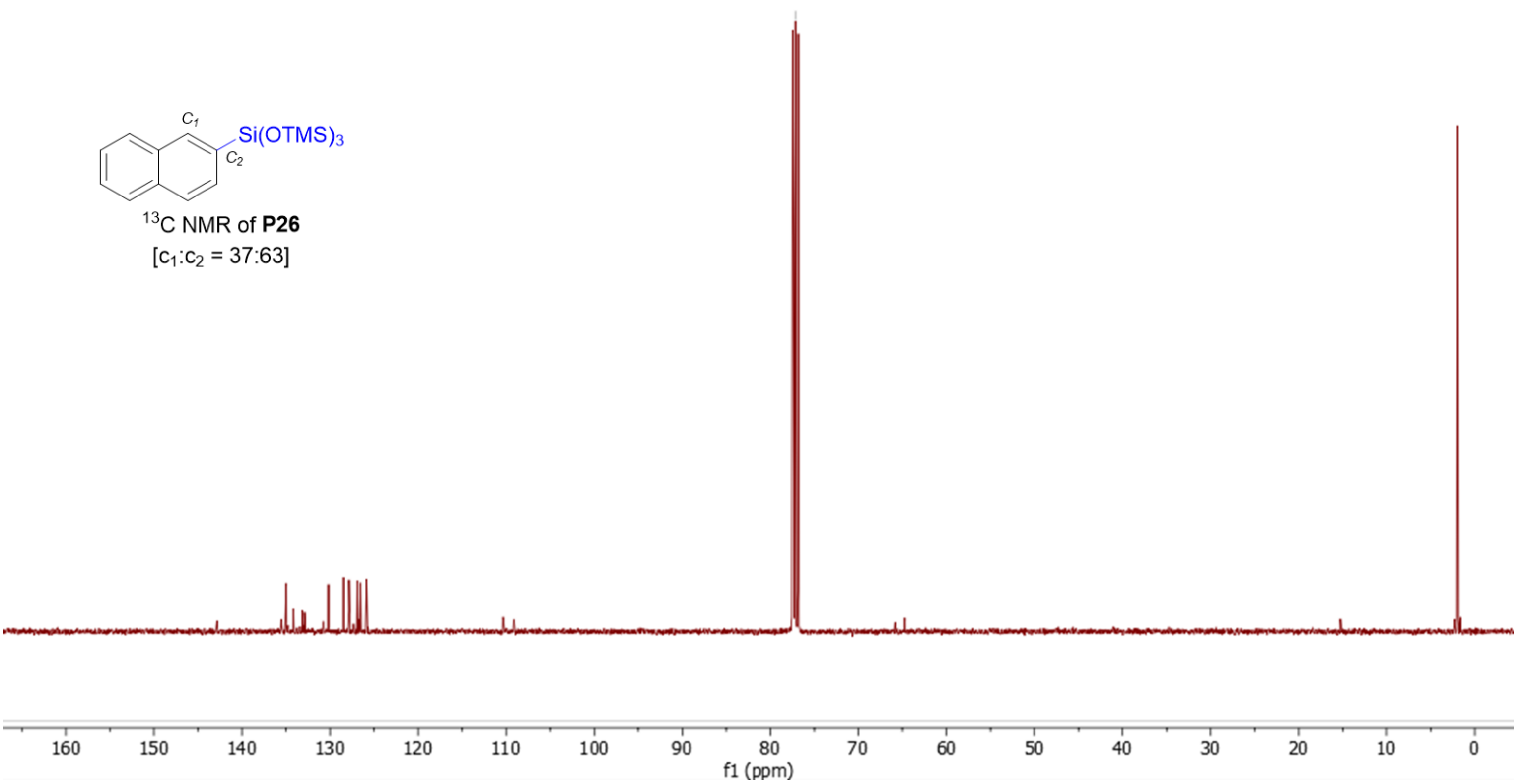


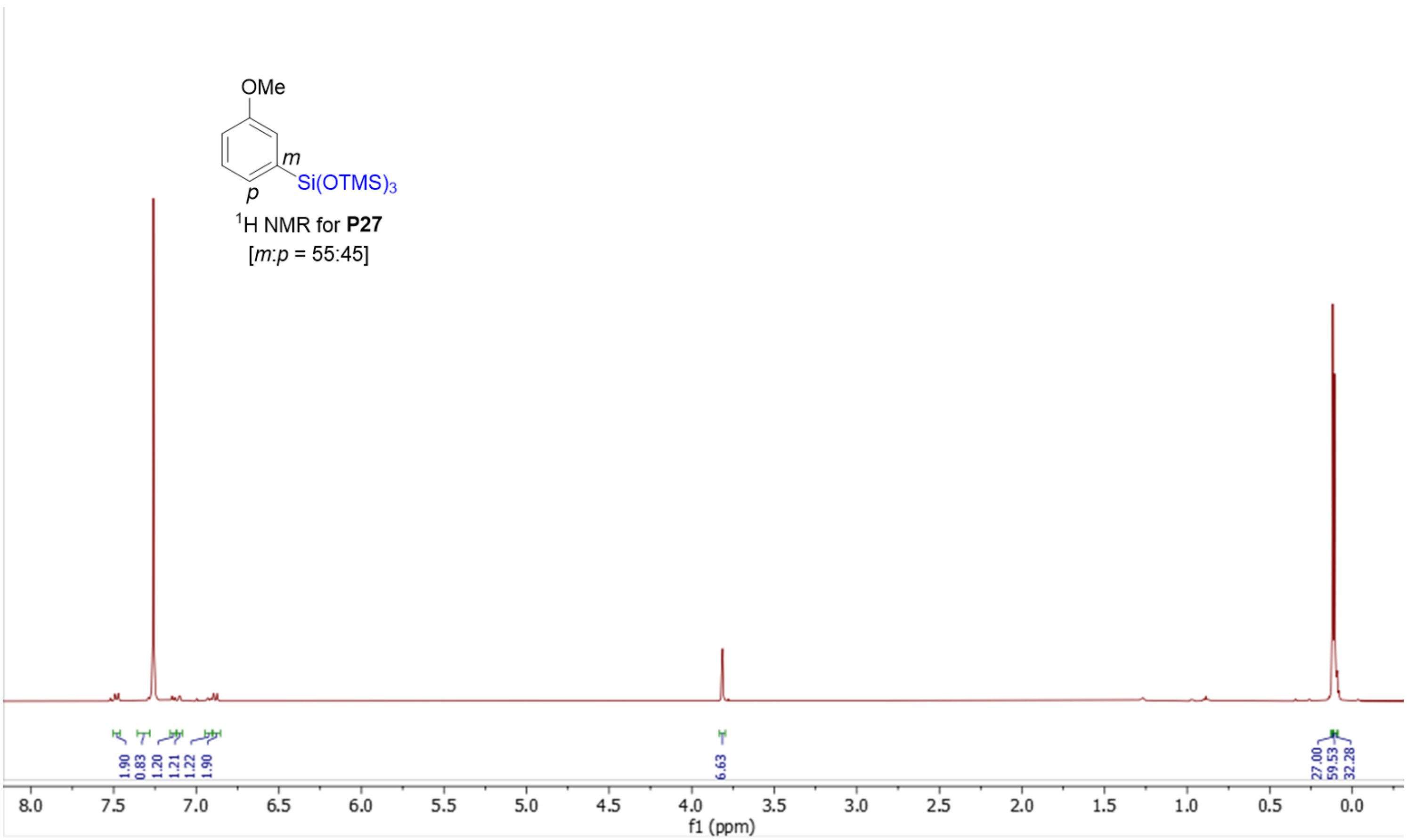

Si(OTMS)3
13C NMR of P25
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

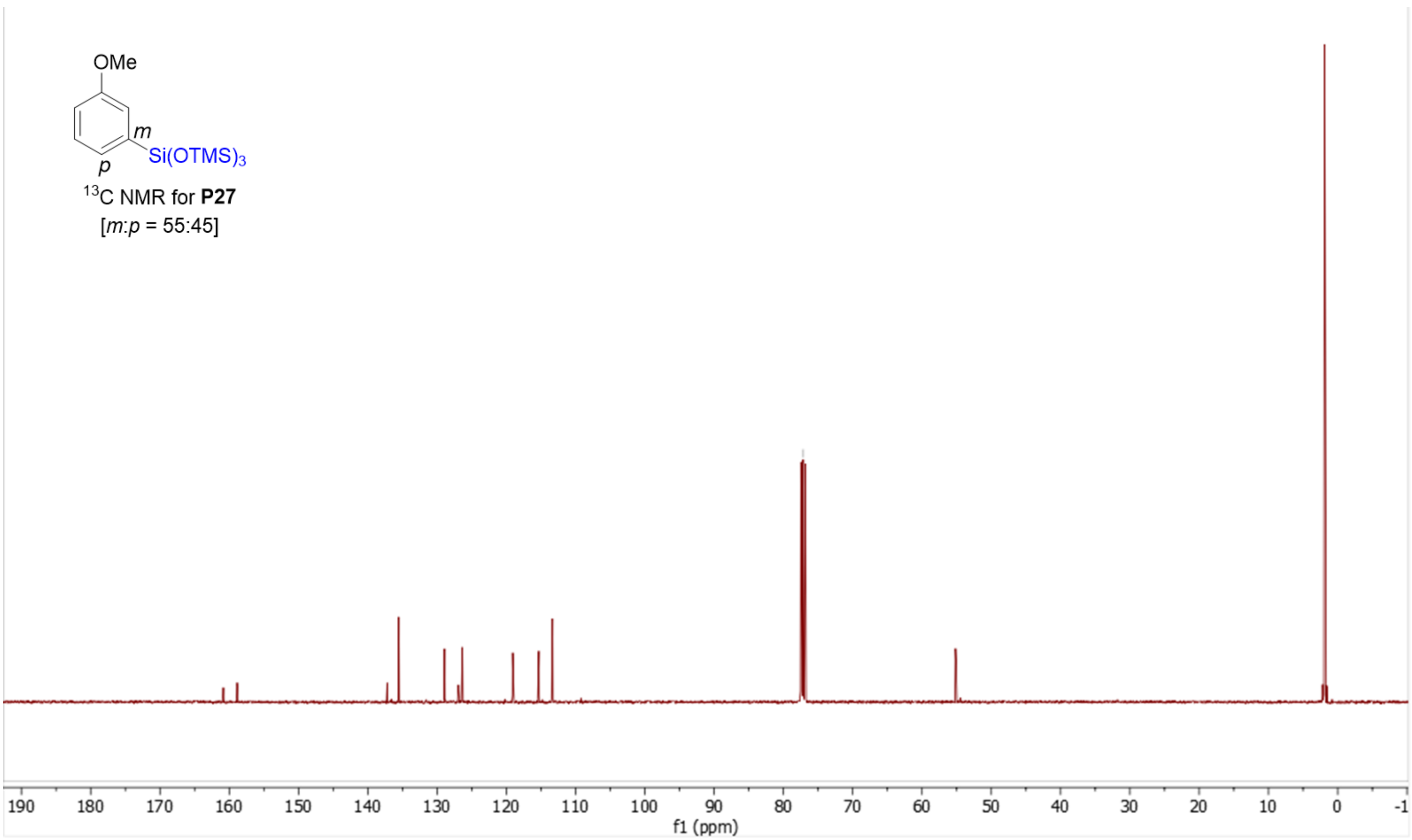


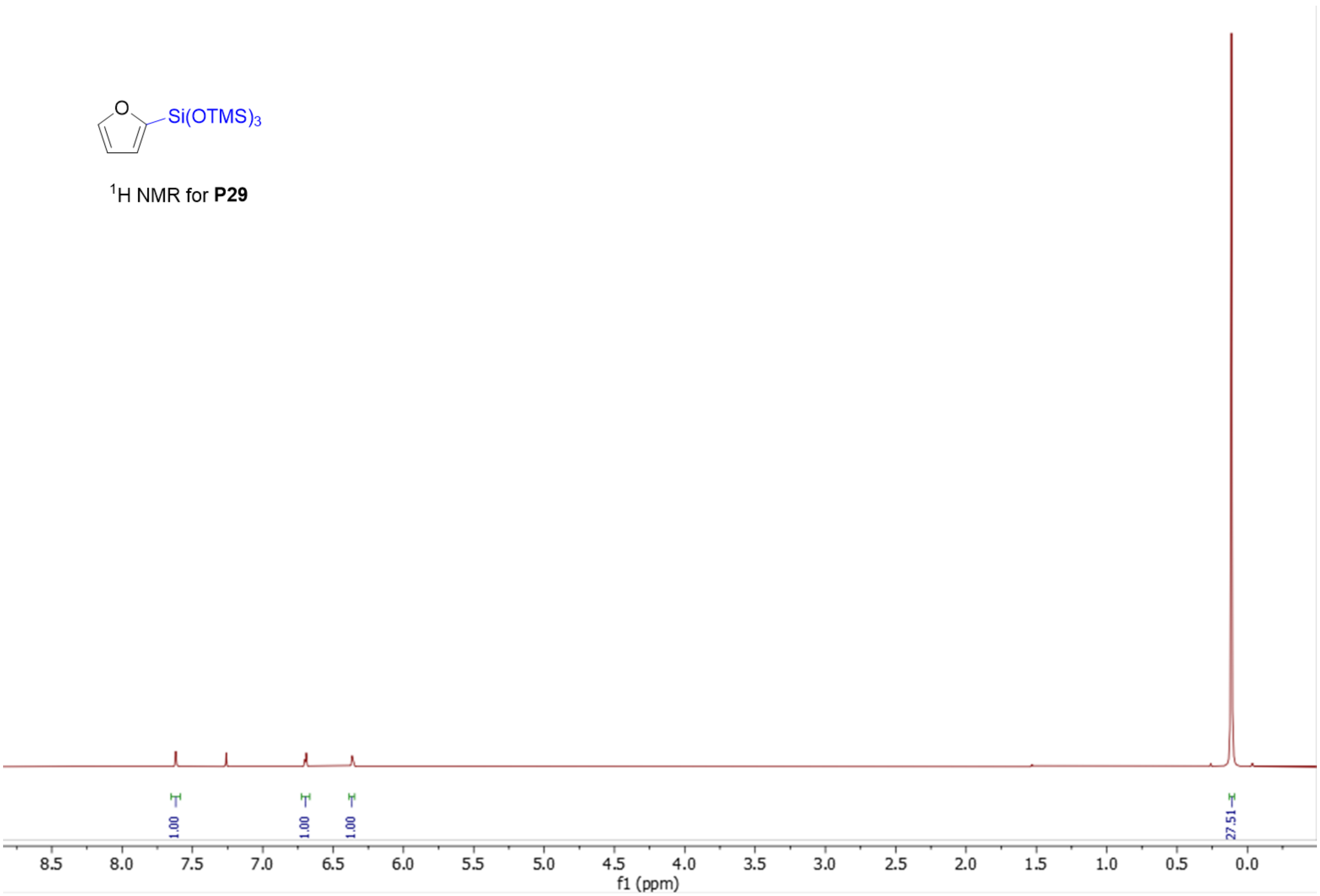
[1]H NMR of **P26**

[c_1:c_2 = 37:63]

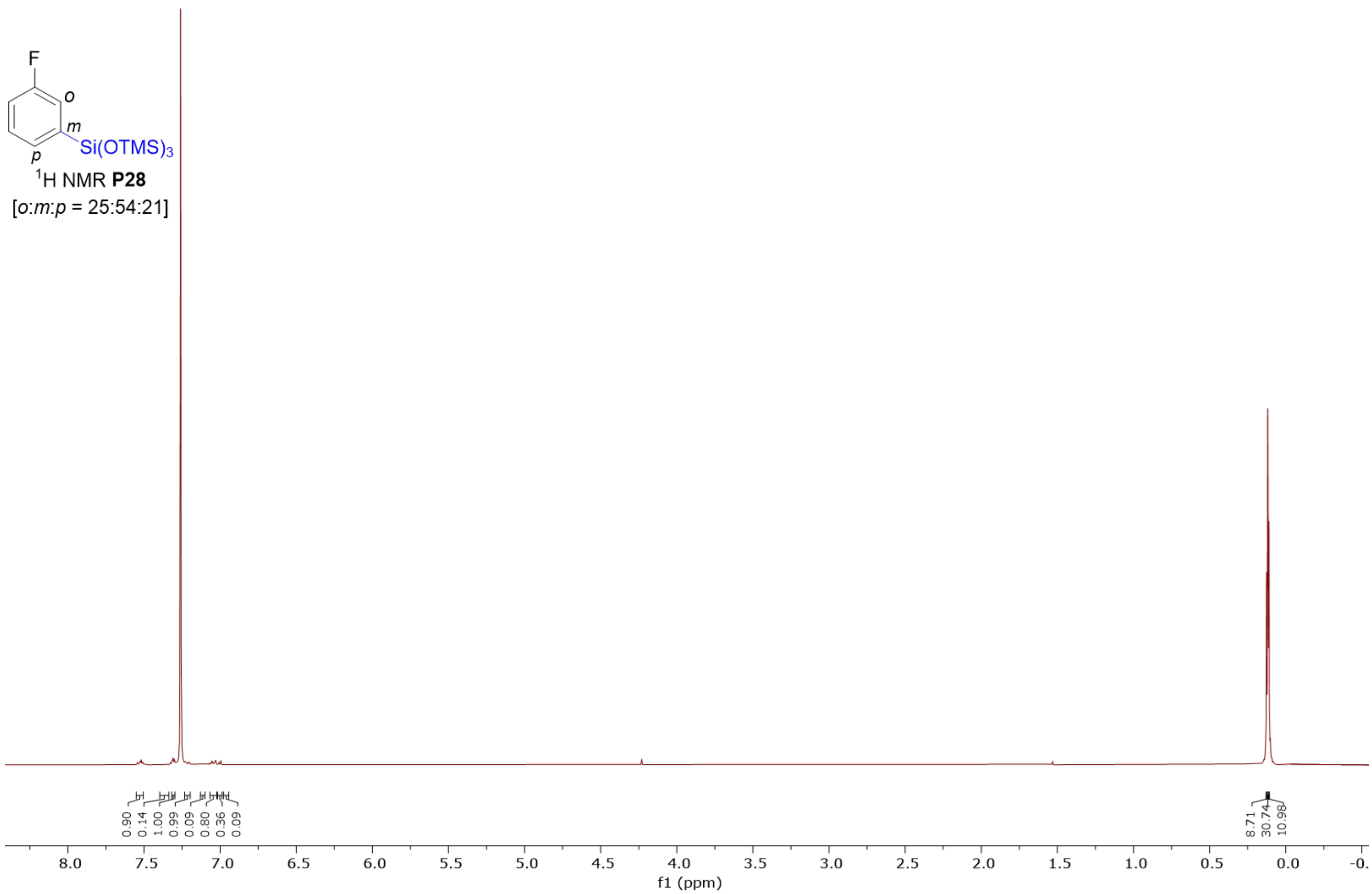

C1
Si(OTMS)3
C2
13C NMR of P26
[c1:c2 = 37:63]
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

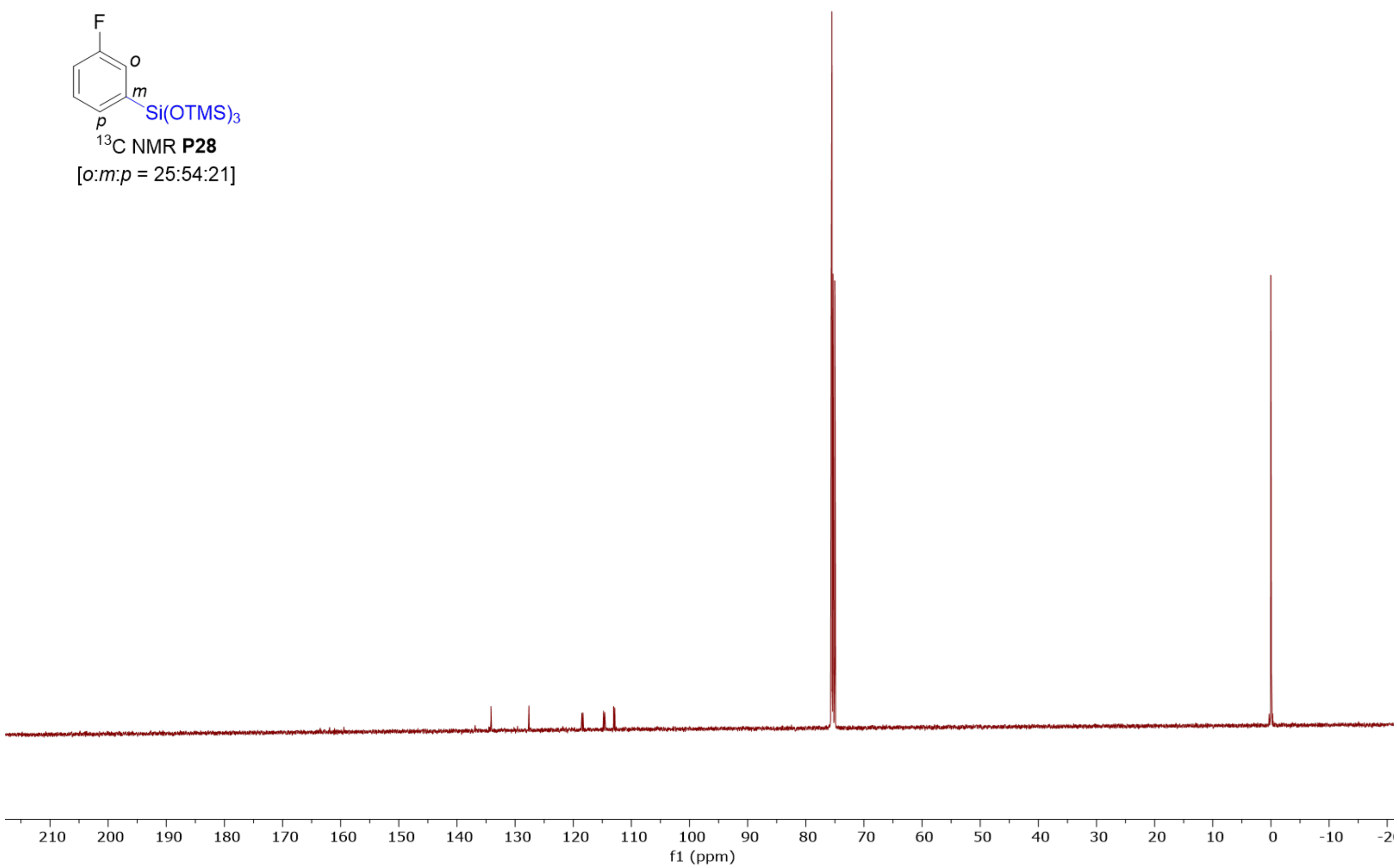

OMe
m
Si(OTMS)3
p
1H NMR for P27
[m:p = 55:45]
1.90
0.83
1.20
1.21
1.22
1.90
6.63
27.00
59.53
32.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
m
Si(OTMS)3
p
13C NMR for P27
[m:p = 55:45]
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

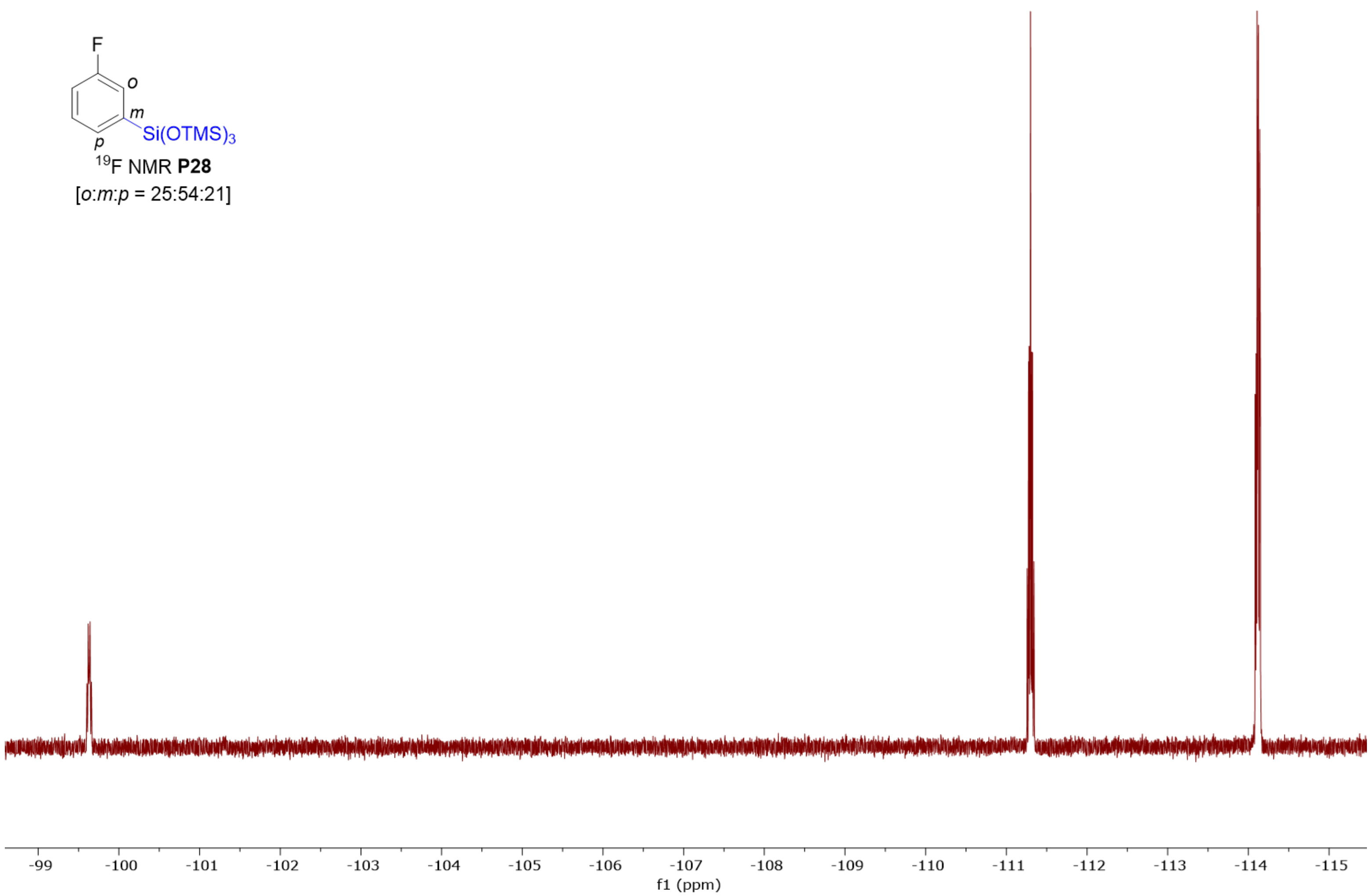


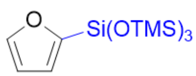
[1]H NMR for **P29**


F
o
m
p
Si(OTMS)3
1H NMR P28
[o:m:p = 25:54:21]
0.90
0.14
1.00
0.99
0.09
0.80
0.36
0.09
8.71
30.74
10.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

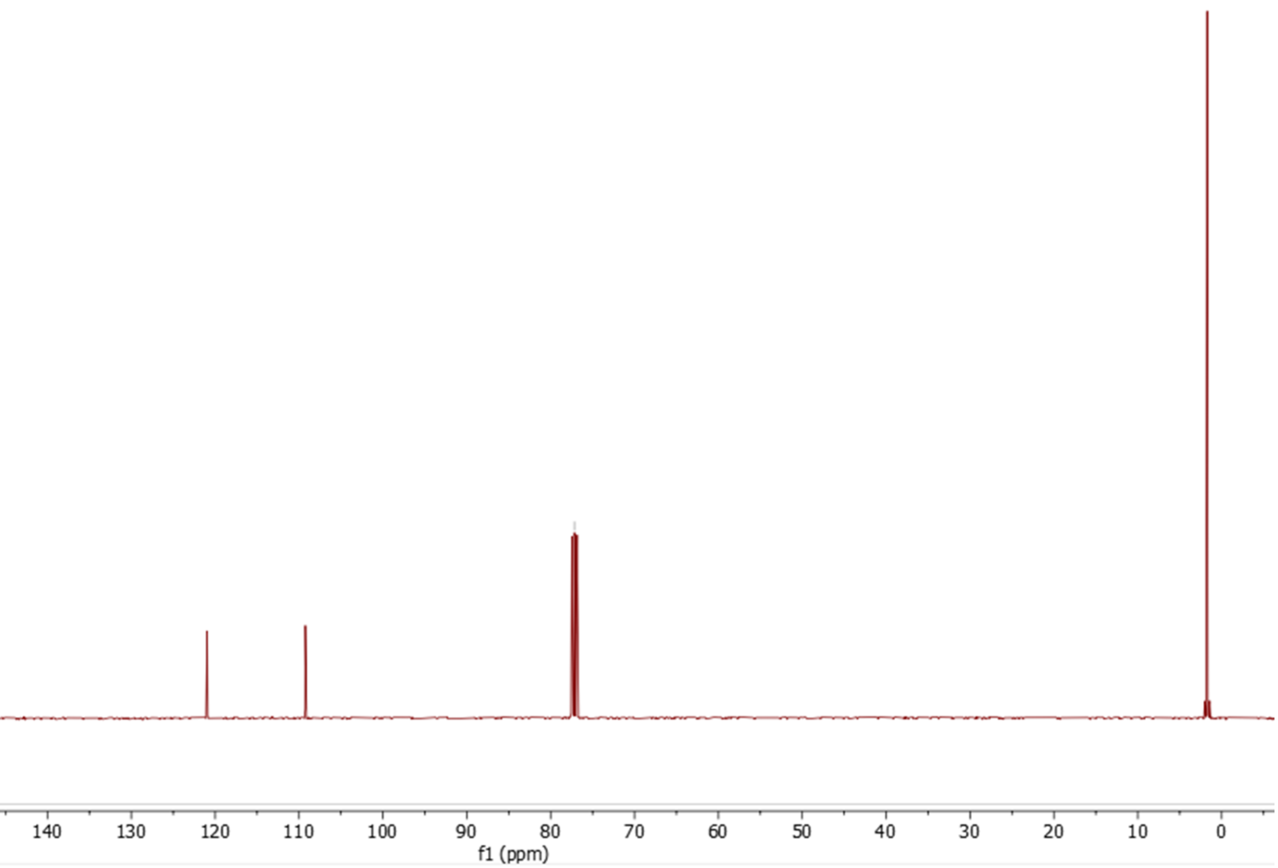


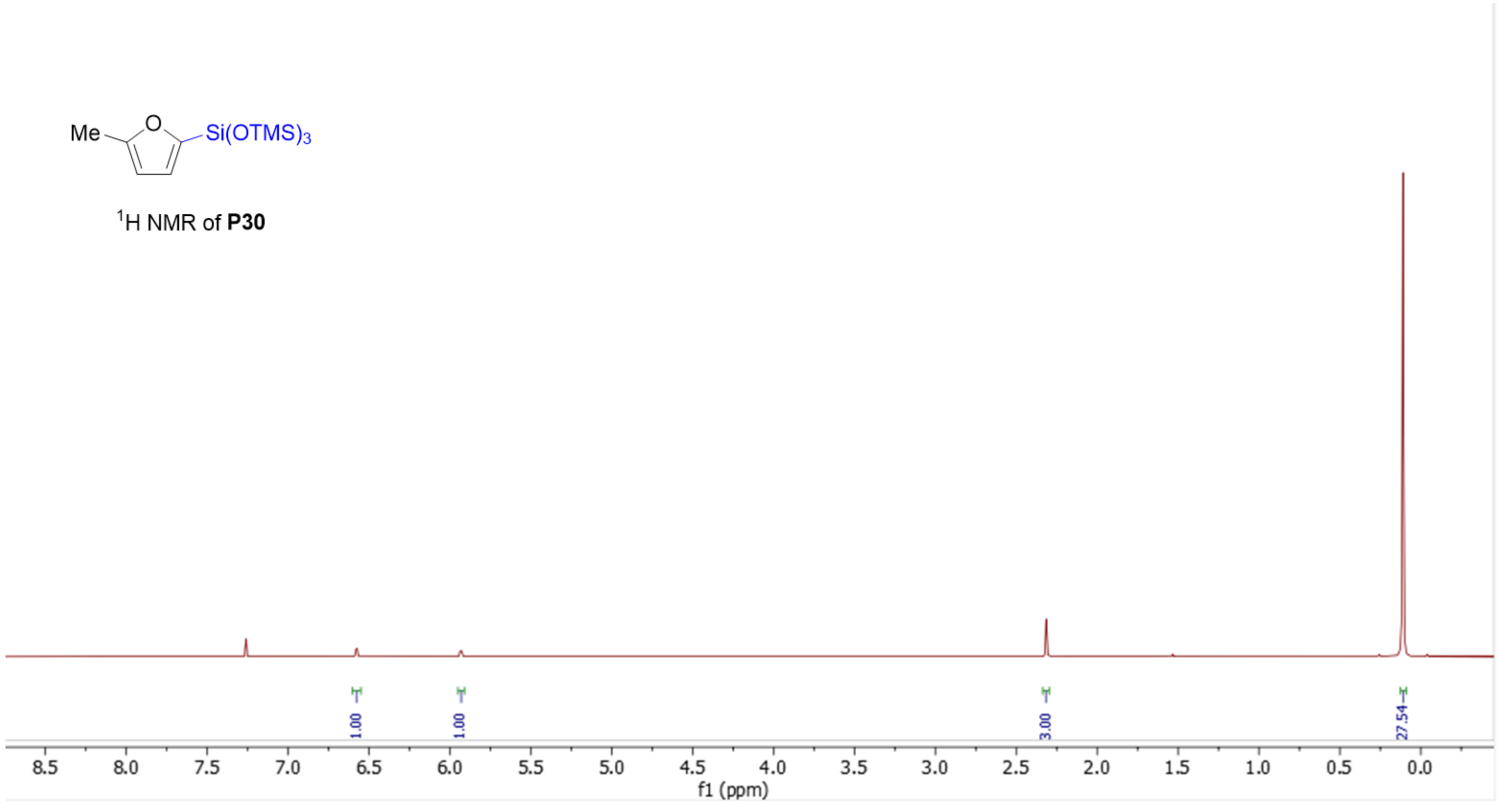
^{13}C NMR **P28**
[*o*:*m*:*p* = 25:54:21]


F
o
m
p
Si(OTMS)3
19F NMR P28
[o:m:p = 25:54:21]
-99
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
f1 (ppm)

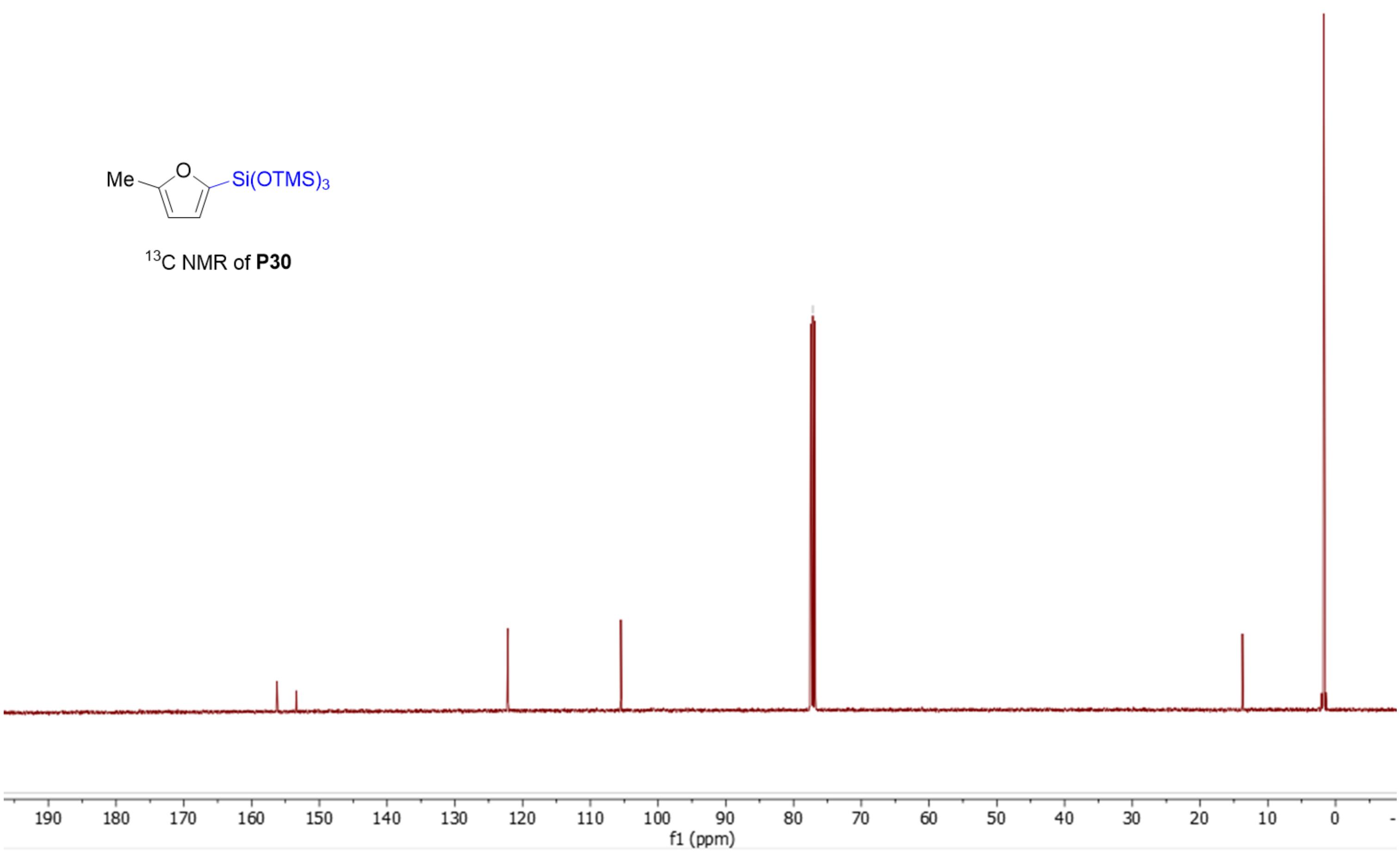


^{13}C NMR of **P29**

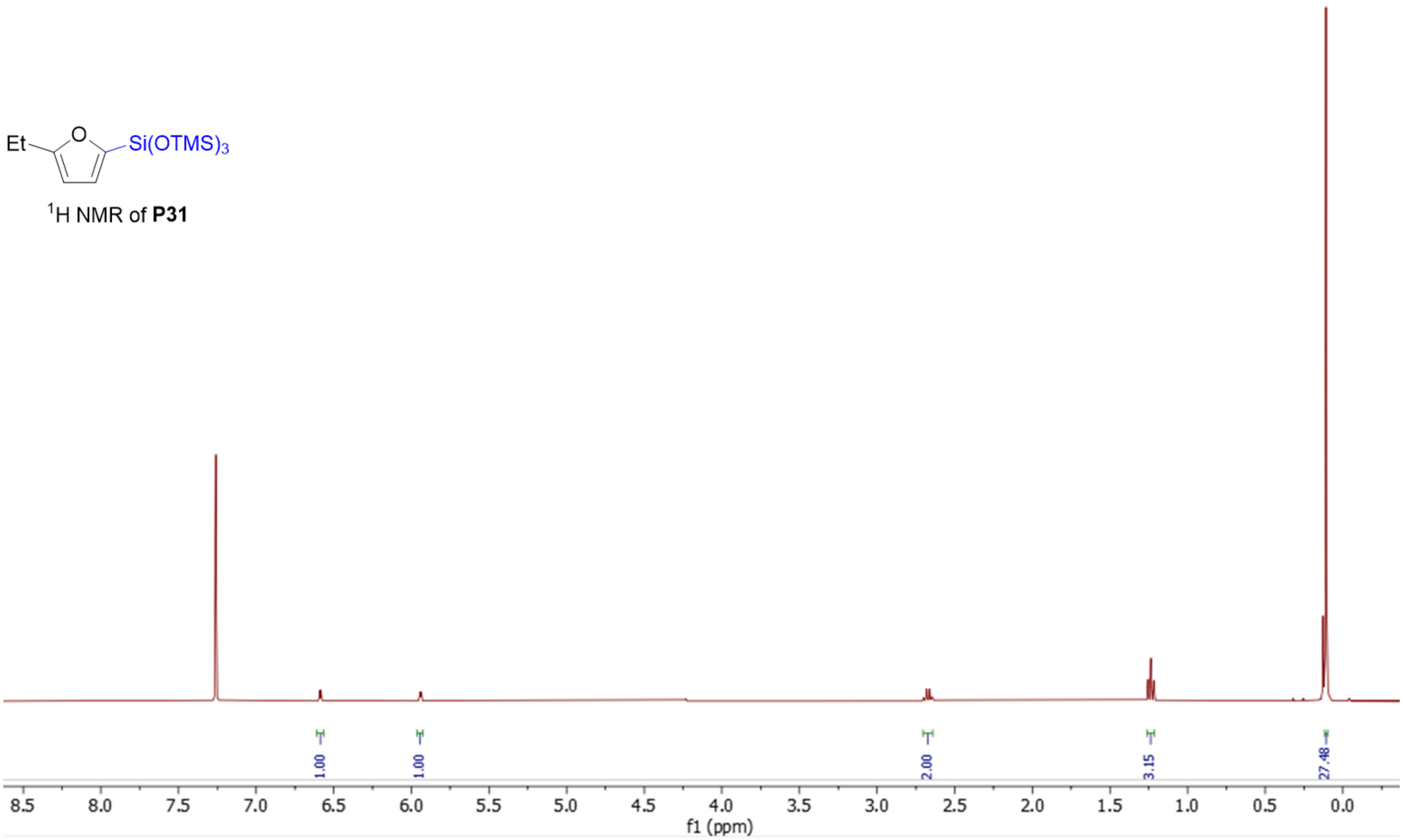




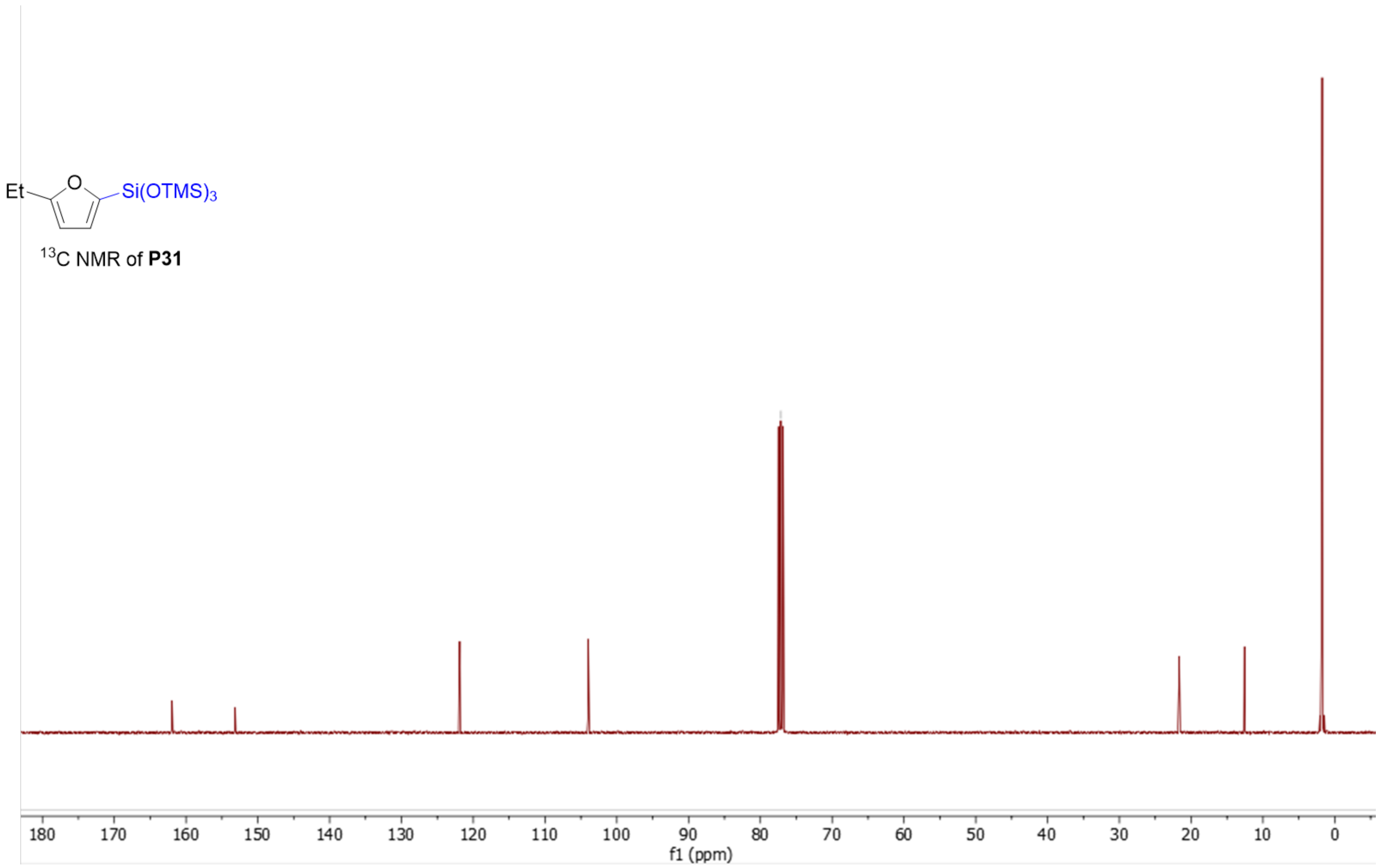
^{1}H NMR of **P30**

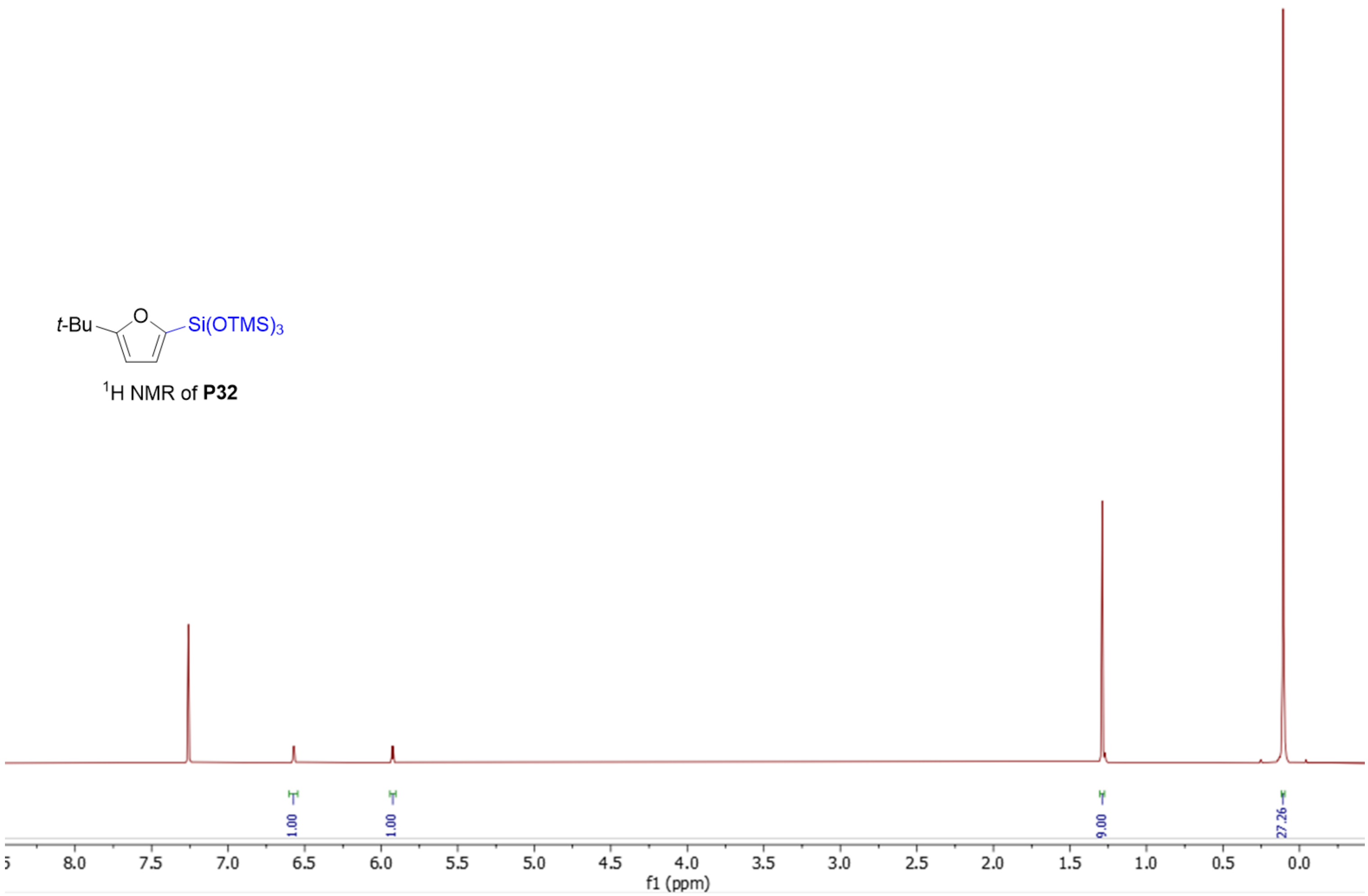


^{13}C NMR of **P30**

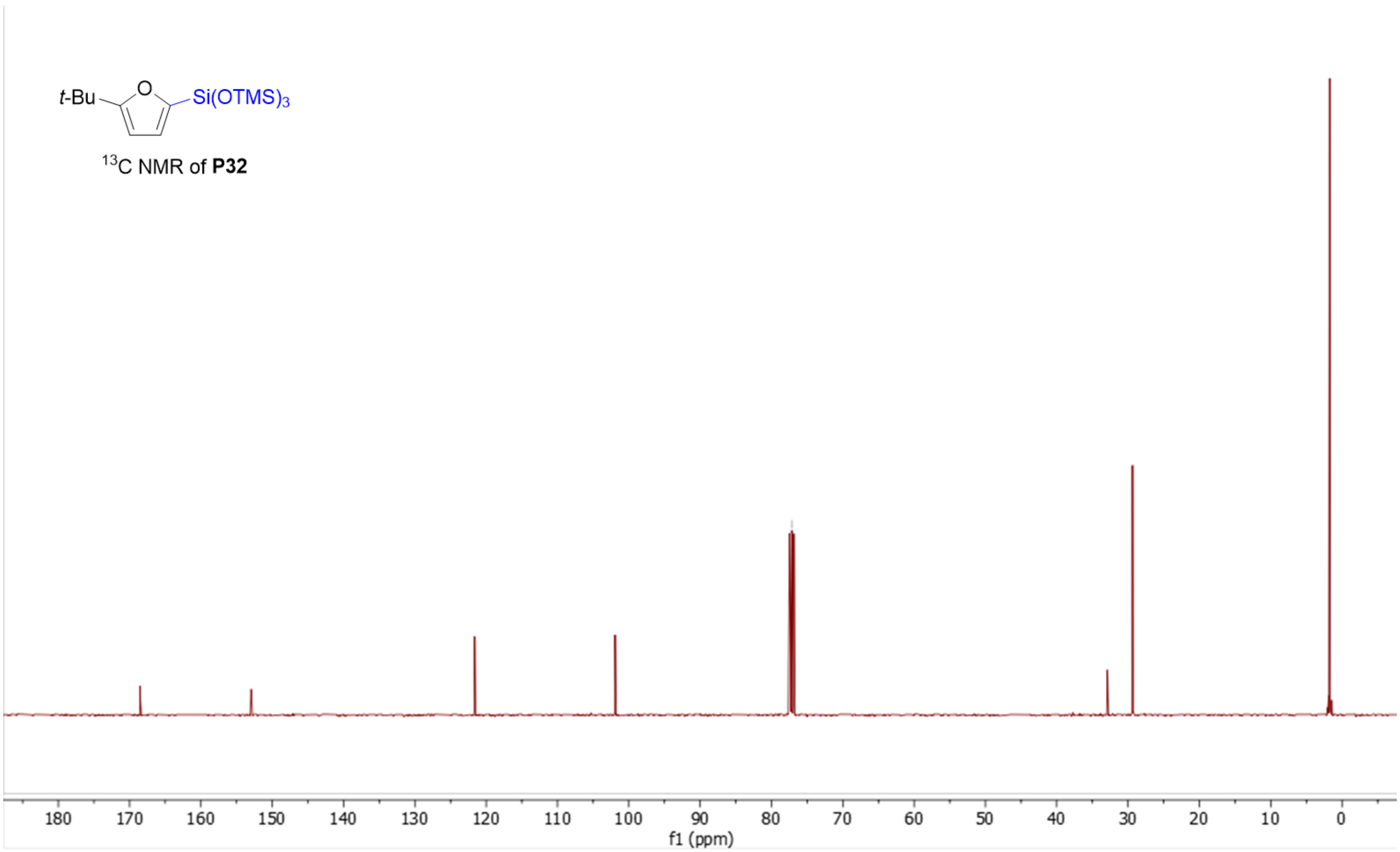


Et
O
Si(OTMS)3
1H NMR of P31
1.00
1.00
2.00
3.15
27.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

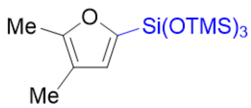

Et
O
Si(OTMS)3
13C NMR of P31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


t-Bu
O
Si(OTMS)3
1.00
1.00
9.00
27.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

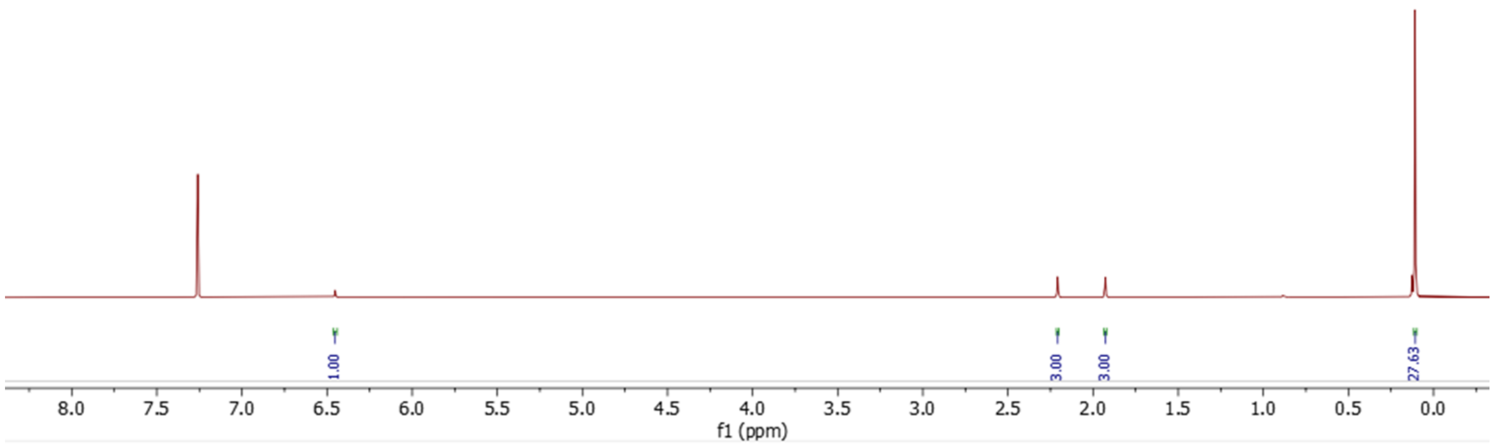
^{1}H NMR of **P32**

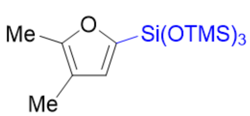


^{13}C NMR of **P32**

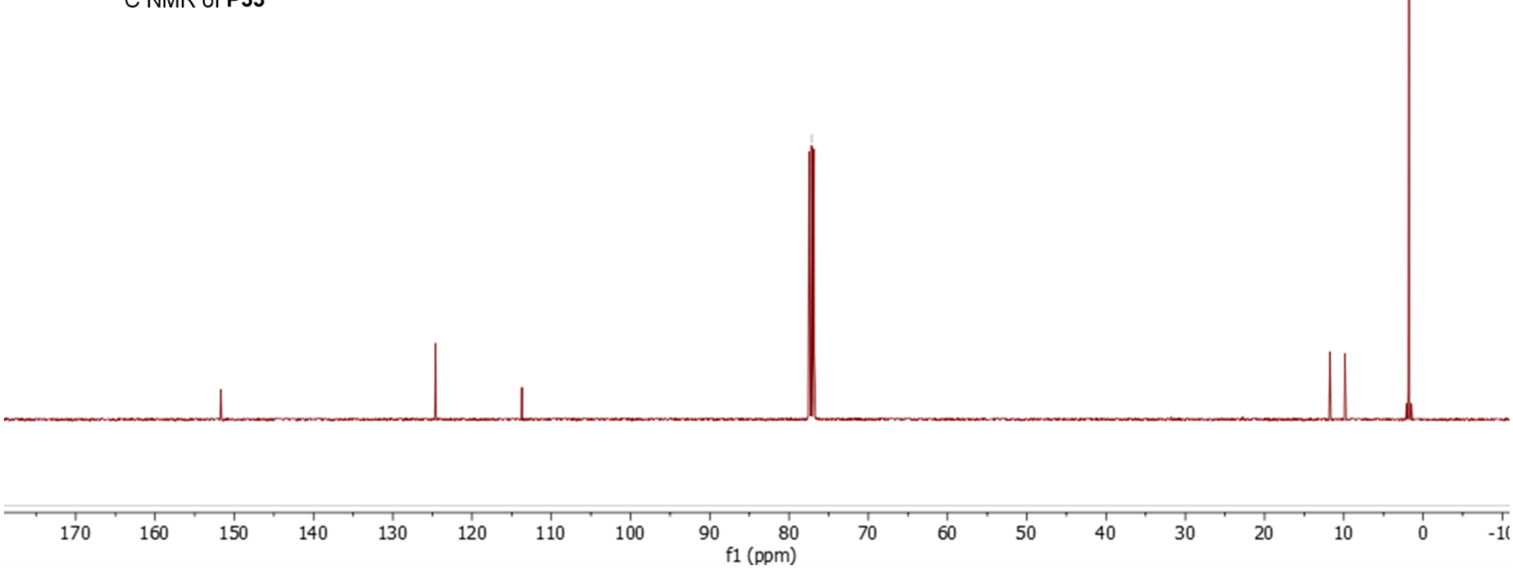


^{1}H NMR of **P33**

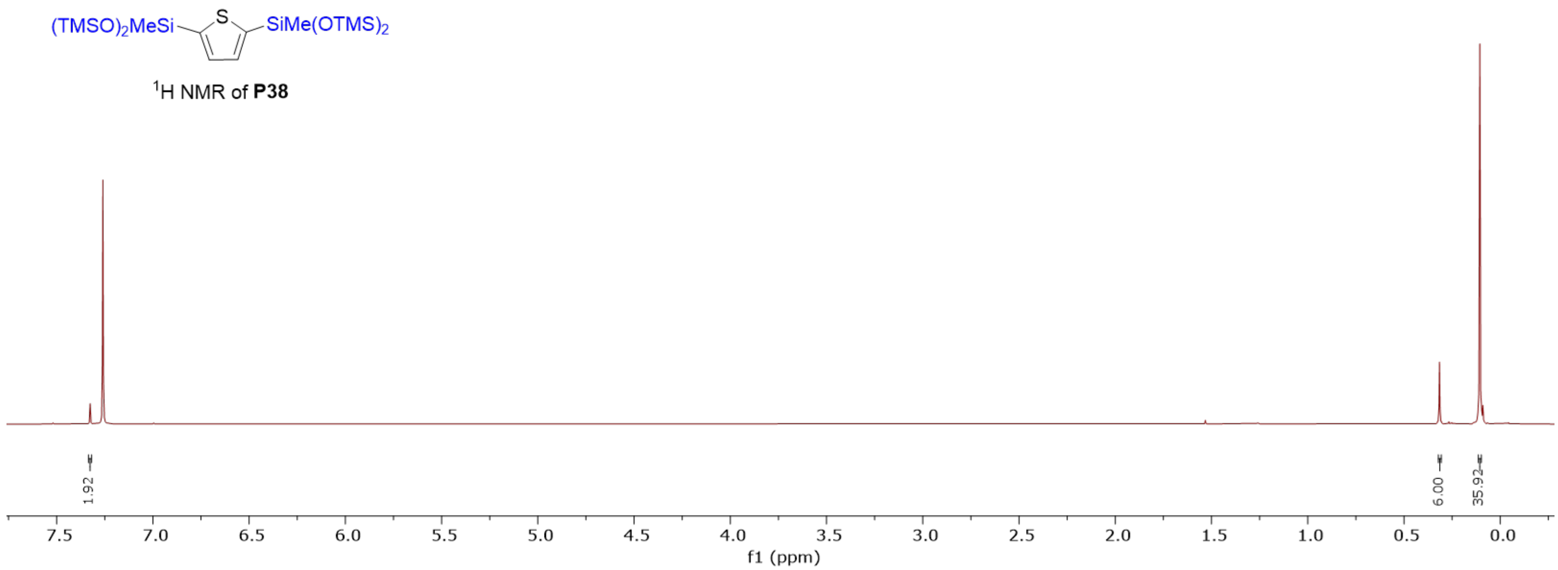


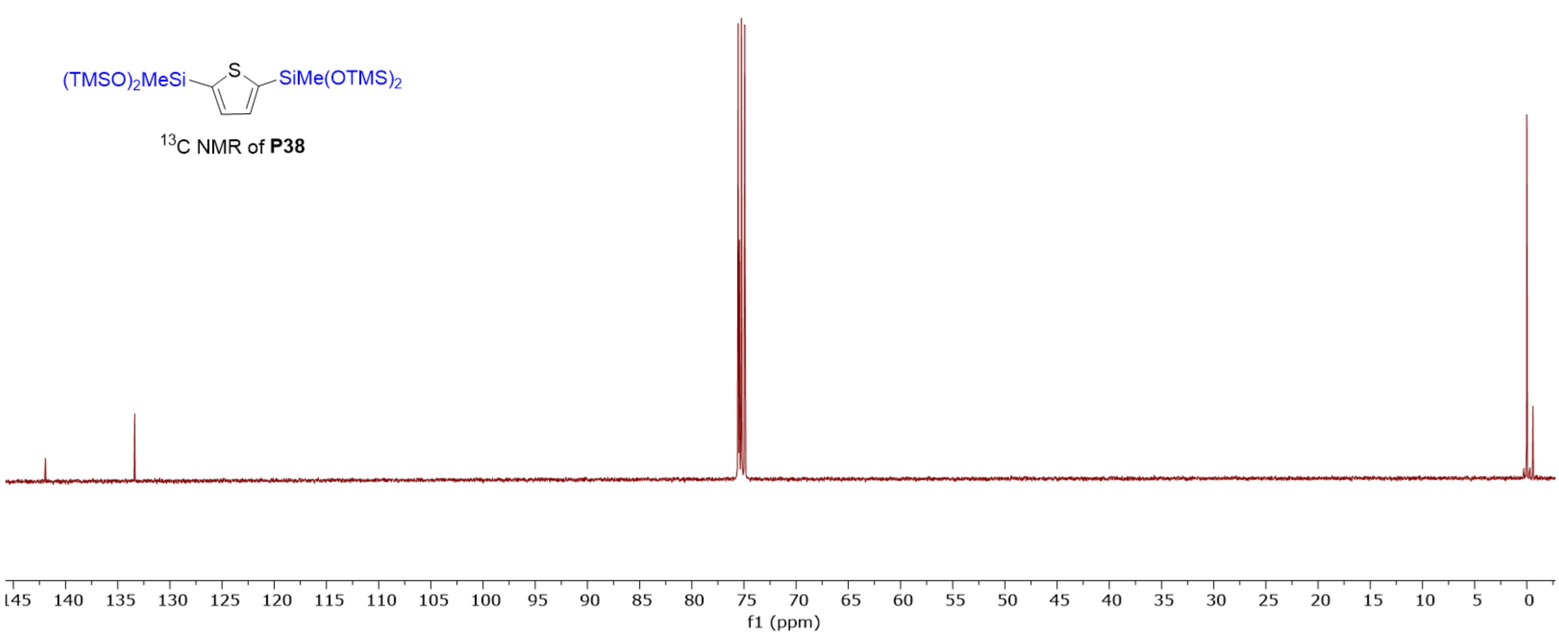


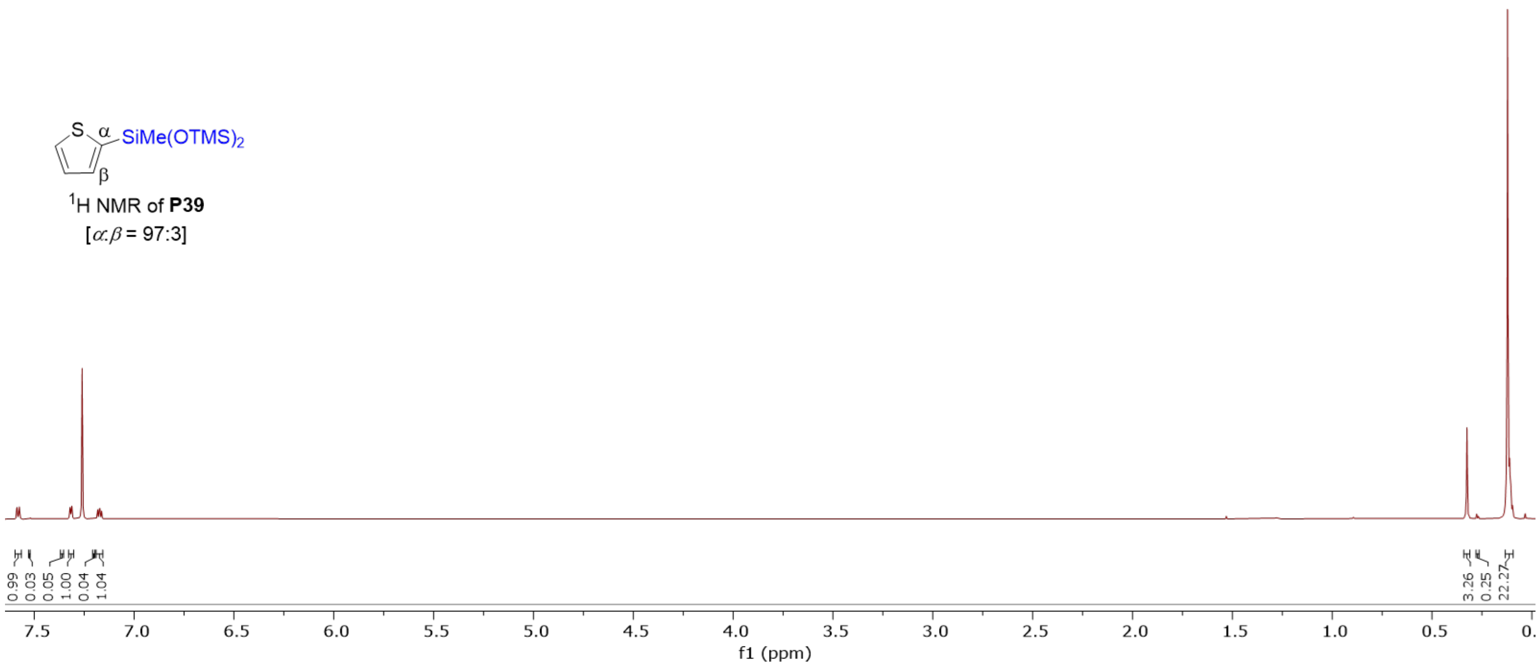
^{13}C NMR of **P33**



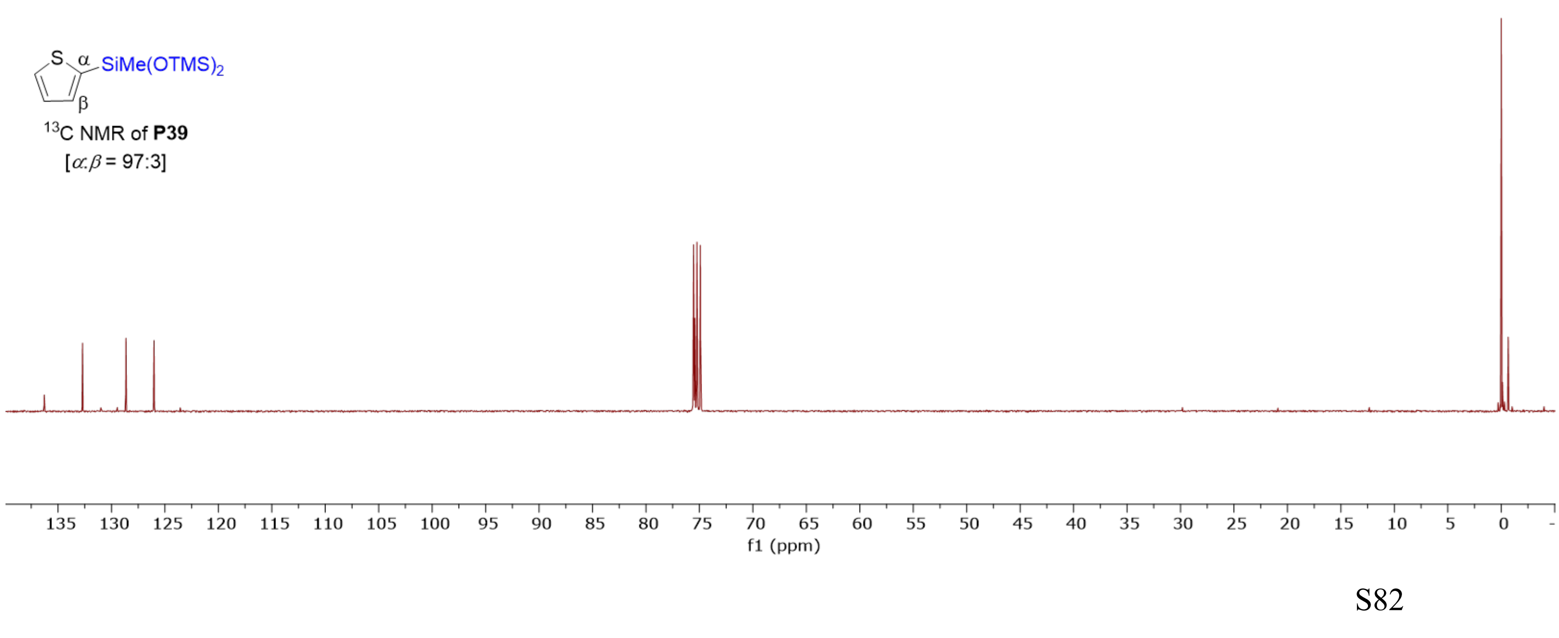
P34


(TMSO)2MeSi
S
SiMe(OTMS)2
1H NMR of P38
1.92
6.00
35.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


(TMSO)2MeSi
S
SiMe(OTMS)2
13C NMR of P38
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

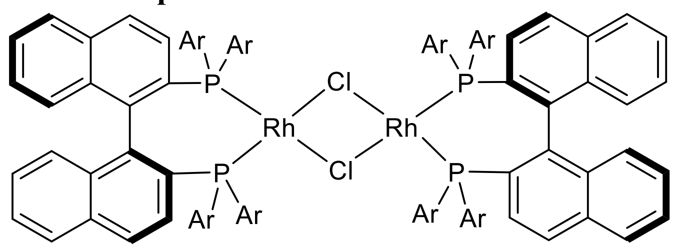


S
α
SiMe(OTMS)2
β
1H NMR of P39
[α:β = 97:3]
0.99
0.03
0.05
1.00
0.04
1.04
3.26
0.25
22.27
f1 (ppm)



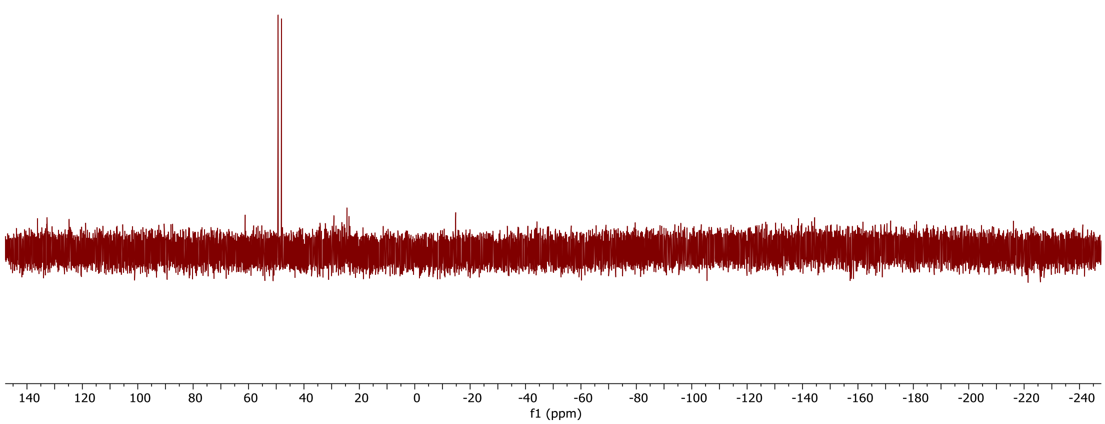
S
α
SiMe(OTMS)2
β
13C NMR of P39
[α:β = 97:3]
f1 (ppm)

3.2 Rh complex

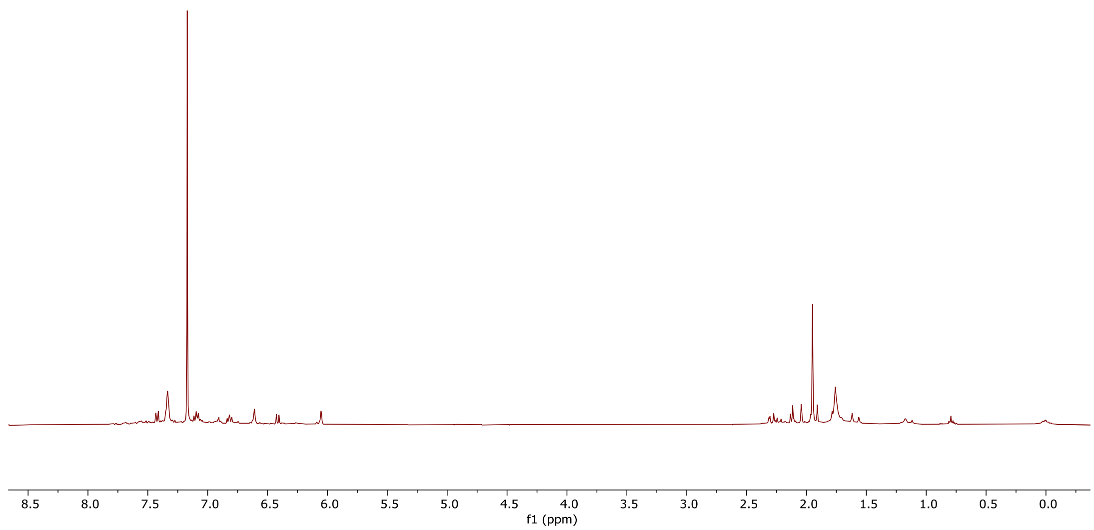


$[RhX(\mathbf{L4})]_2$ (**C4**)

^{31}P NMR of **C4**



^{1}H NMR of **C4**



4. Crystallographic data

Table S21. Crystal data and structure refinement for **C4**.

Empirical formula	$C_{104}H_{96}Cl_2P_4Rh_2$
Formula weight	1746.40
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, b, c	14.3389(8), 23.8027(13), 24.6313(13)
α, β, γ	90, 90, 90
Volume/Å^3	8406.8(8)
Z	4
ρ_{calc}g/cm^3	1.380
μ/mm^{-1}	0.582
F(000)	3616.0
Crystal size/mm^3	0.179 × 0.089 × 0.062
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 55.03
Index ranges	$-18 \leq h \leq 18$, $-30 \leq k \leq 30$, $-32 \leq l \leq 32$
Reflections collected	148406
Independent reflections	19287 [R_{int} = 0.1133, R_{sigma} = 0.0674]
Data/restraints/parameters	19287/0/1026
Goodness-of-fit on F^2	1.019

Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.0945
Final R indexes [all data]	R_1 = 0.0625, wR_2 = 0.1035
Largest diff. peak/hole / e Å^{-3}	1.15/-0.45
Flack parameter	-0.03(3)

Table S22. Fractional Atomic Coordinates (×10^4) and Equiv.alent Isotropic Displacement Parameters (Å^2×10^3) for **C4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	***x***	***y***	***z***	**U(eq)**
Rh01	6023.1(3)	6588.8(2)	7103.0(2)	25.55(10)
Rh02	4512.3(3)	5982.2(2)	6094.8(2)	26.12(10)
P03	5853.7(10)	7007.4(6)	7883.7(6)	24.5(3)
Cl04	6075.6(10)	6372.2(6)	6143.1(6)	29.7(3)
Cl05	4356.4(10)	6516.5(6)	6928.0(6)	34.7(3)
P06	3013.8(10)	5757.2(6)	6141.3(6)	26.2(3)
P07	4572.9(11)	5638.8(6)	5269.8(6)	25.4(3)
P08	7500.4(11)	6408.4(6)	7266.5(6)	28.3(3)
C009	2254(4)	4685(2)	5905(2)	27.2(12)
C00A	5542(4)	5971(3)	9444(2)	36.1(13)
C00B	2504(4)	5212(2)	5687(2)	25.5(12)
C00C	5624(4)	6032(2)	8478(2)	29.6(12)
C00D	1980(4)	4427(3)	3888(3)	33.9(13)
C00E	1789(4)	5487(3)	7024(3)	34.2(14)
C00F	5696(4)	6614(2)	8510(2)	27.3(12)
C00G	4835(4)	7470(2)	7849(2)	26.6(12)
C00H	1998(4)	4244(2)	5588(2)	29.5(13)
C00I	8119(4)	5570(3)	8682(3)	39.8(16)
C00J	4138(4)	7479(2)	8240(2)	31.4(13)
C00K	5597(5)	6555(3)	9493(2)	37.6(14)
C00L	2679(4)	5474(2)	6804(2)	29.7(13)
C00M	8083(4)	5989(3)	9086(3)	37.7(15)
C00N	1783(4)	3905(3)	4123(3)	37.2(15)
C00O	1087(4)	6050(2)	4614(2)	30.1(12)
C00P	729(4)	6764(3)	5801(2)	36.5(15)
C00Q	2463(4)	5292(2)	5134(2)	24.1(12)
C00R	8459(4)	7661(3)	8279(2)	29.9(13)
C00S	2292(4)	6758(2)	4487(2)	30.5(13)
C00T	6409(4)	5870(2)	3992(2)	32.2(13)
C00U	2665(4)	6875(3)	5915(2)	33.9(14)
C00V	5604(4)	5864(2)	4301(2)	28.5(12)
C00W	8016(4)	4718(3)	6406(3)	35.4(14)
C00X	1280(4)	6307(3)	5943(2)	31.9(13)
C00Y	449(5)	6406(3)	4393(2)	34.9(13)
C00Z	4747(4)	7817(2)	7393(2)	31.0(13)
C010	6824(4)	7494(2)	8046(2)	24.7(12)

Atom	*x*	*y*	*z*	U(eq)
C011	2132(5)	7336(3)	5748(3)	36.1(15)
C012	8206(4)	5521(3)	5093(3)	40.8(16)
C013	5554(4)	5711(2)	8944(3)	33.2(13)
C014	3355(4)	7823(3)	8177(3)	37.3(15)
C015	8422(4)	6914(2)	7101(3)	30.0(12)
C016	2193(4)	4882(2)	4208(2)	29.3(13)
C017	3376(4)	5153(2)	7070(3)	33.0(13)
C018	4341(5)	3892(3)	3914(3)	47.8(17)
C019	6477(4)	5636(2)	5103(3)	30.6(13)
C01A	2246(4)	6357(2)	6012(2)	27.5(12)
C01B	2040(4)	6208(2)	4660(2)	27.4(12)
C01C	2200(4)	4832(2)	4787(2)	26.8(12)
C01D	9349(4)	6808(3)	7233(2)	34.0(14)
C01E	7789(4)	5743(2)	6924(2)	30.3(13)
C01F	698(4)	6949(3)	4219(3)	37.0(15)
C01G	2738(4)	5846(2)	4887(2)	25.1(12)
C01H	3304(5)	8167(3)	7726(3)	41.7(16)
C01I	3998(5)	8176(3)	7331(2)	37.2(14)
C01J	3652(4)	6020(2)	4906(2)	26.6(12)
C01K	7974(4)	5699(3)	8152(3)	37.9(15)
C01L	9342(4)	7472(3)	8451(3)	37.0(14)
C01M	3888(4)	6584(2)	4744(2)	29.1(12)
C01N	6736(4)	8074(2)	7937(2)	30.1(12)
C01O	-300(4)	6710(3)	5729(3)	38.8(15)
C01P	7933(4)	6554(3)	8933(3)	34.5(13)
C01Q	7802(4)	6683(3)	8370(2)	29.6(13)
C01R	8636(4)	5602(3)	6685(3)	33.0(14)
C01S	1561(5)	5179(3)	7480(3)	37.5(15)
C01T	4373(4)	4106(3)	4473(3)	36.8(14)
C01U	7666(4)	7290(2)	8222(2)	28.3(12)
C01V	10067(5)	7828(3)	8508(3)	44.8(17)
C01W	8168(4)	7437(3)	6906(2)	33.3(14)
C01X	7264(4)	5765(2)	4255(3)	32.9(14)
C01Y	5516(5)	5069(2)	8906(3)	43.1(15)
C01Z	1176(5)	7276(3)	5701(3)	40.8(16)
C020	1991(4)	4300(2)	5020(2)	29.3(13)
C021	9676(4)	4943(3)	6151(3)	39.3(15)
C022	5687(4)	6870(3)	9022(2)	33.9(14)
C023	1788(4)	3840(2)	4676(3)	36.4(15)
C024	4410(4)	4682(2)	4585(2)	30.6(13)
C025	7809(4)	6261(2)	7982(2)	30.3(13)
C026	2606(6)	7878(3)	5597(3)	50.8(19)
C027	7304(4)	5646(2)	4805(3)	30.9(13)
C028	5619(4)	5750(2)	4852(2)	27.9(12)

Atom	*x*	*y*	*z*	U(eq)
C029	10035(5)	7216(3)	7154(3)	42.4(16)
C02A	3230(4)	6932(2)	4545(3)	32.5(13)
C02B	7062(4)	5354(2)	6899(3)	34.0(14)
C02C	2255(5)	4863(3)	7729(2)	37.1(15)
C02D	8187(5)	6275(4)	10029(3)	52(2)
C02E	3944(5)	8568(3)	6849(3)	52.1(19)
C02F	8349(4)	8238(2)	8160(2)	31.6(13)
C02G	4387(4)	3745(2)	4917(3)	38.6(15)
C02H	3161(5)	4846(3)	7532(3)	38.3(15)
C02I	8053(5)	6835(3)	9874(3)	46.4(17)
C02J	8765(4)	5087(2)	6422(2)	32.5(14)
C02K	8221(5)	5868(3)	9650(3)	46.4(18)
C02L	562(5)	5169(3)	7692(3)	50.8(18)
C02M	1595(4)	7120(3)	4275(3)	35.5(14)
C02N	11049(5)	7101(3)	7288(3)	53.5(19)
C02O	7172(4)	4837(3)	6639(3)	35.9(14)
C02P	7478(4)	8435(3)	7995(2)	32.6(13)
C02Q	4452(4)	4506(2)	5543(2)	30.9(12)
C02R	9134(5)	8603(3)	8216(3)	38.7(15)
C02S	6391(5)	5990(3)	3396(3)	43.5(16)
C02T	7914(4)	6973(3)	9348(3)	38.4(15)
C02U	8829(5)	7866(3)	6854(3)	40.0(15)
C02V	4433(5)	3928(2)	5447(3)	39.0(15)
C02W	3900(5)	4498(3)	7811(3)	52.7(19)
C02X	5567(6)	6835(3)	10040(3)	50.9(18)
C02Y	9971(5)	8398(3)	8382(3)	46.1(17)
C02Z	6332(5)	4456(3)	6589(3)	49.0(18)
C030	4438(4)	4886(2)	5115(2)	28.7(12)
C031	8550(6)	8454(3)	6728(3)	54(2)
C032	9743(5)	7742(3)	6970(3)	43.3(17)
C033	4459(6)	3520(3)	5915(3)	54.0(19)
C034	2613(5)	7831(4)	8603(3)	65(2)

Table S23. Distances (Å) and angles (°) of **C4**

Distances (Å)				Angles (°)			
Rh01-P03	2.1794(15)	C00X-C01A	1.401(8)	P03-Rh01-Cl04	164.26(5)	C02H-C017-C00L	120.4(6)
Rh01-Cl04	2.4210(14)	C00Y-C01F	1.408(9)	P03-Rh01-Cl05	94.54(5)	C027-C019-C028	120.7(6)
Rh01-Cl05	2.4345(15)	C00Z-C01I	1.382(8)	P03-Rh01-P08	92.01(6)	C00U-C01A-P06	117.4(4)
Rh01-P08	2.1986(16)	C010-C01N	1.414(8)	Cl04-Rh01-Cl05	80.95(5)	C00U-C01A-C00X	118.8(5)
Rh02-Cl04	2.4292(14)	C010-C01U	1.370(8)	P08-Rh01-Cl04	96.16(5)	C00X-C01A-P06	123.3(4)
Rh02-Cl05	2.4247(15)	C011-C01Z	1.384(10)	P08-Rh01-Cl05	164.68(6)	C00O-C01B-C01G	117.6(5)
Rh02-P06	2.2173(15)	C011-C026	1.503(9)	Cl05-Rh02-Cl04	80.98(5)	C00S-C01B-C00O	122.9(5)
Rh02-P07	2.1920(16)	C012-C027	1.504(9)	P06-Rh02-Cl04	169.73(5)	C00S-C01B-C01G	119.5(5)

P03-C00F	1.819(6)	C013-C01Y	1.531(8)	P06-Rh02-Cl05	89.64(5)	C016-C01C-C00Q	122.1(5)
P03-C00G	1.831(6)	C014-C01H	1.381(9)	P07-Rh02-Cl04	98.70(5)	C020-C01C-C00Q	119.5(5)
P03-C010	1.854(6)	C014-C034	1.494(9)	P07-Rh02-Cl05	169.70(6)	C020-C01C-C016	118.4(5)
P06-C00B	1.862(6)	C015-C01D	1.391(8)	P07-Rh02-P06	89.79(6)	C015-C01D-C029	121.0(6)
P06-C00L	1.831(6)	C015-C01W	1.382(8)	C00F-P03-Rh01	121.80(19)	C01R-C01E-P08	126.7(5)
P06-C01A	1.831(6)	C016-C01C	1.431(8)	C00F-P03-C00G	104.5(3)	C01R-C01E-C02B	118.2(5)
P07-C01J	1.836(6)	C017-C02H	1.387(9)	C00F-P03-C010	103.4(2)	C02B-C01E-P08	115.1(4)
P07-C028	1.838(6)	C018-C01T	1.470(9)	C00G-P03-Rh01	108.8(2)	C02M-C01F-C00Y	119.1(6)
P07-C030	1.842(6)	C019-C027	1.396(8)	C00G-P03-C010	103.5(2)	C01B-C01G-C00Q	120.1(5)
P08-C015	1.833(6)	C019-C028	1.403(8)	C010-P03-Rh01	113.11(18)	C01J-C01G-C00Q	120.0(5)
P08-C01E	1.841(6)	C01B-C01G	1.434(8)	Rh01-Cl04-Rh02	95.77(5)	C01J-C01G-C01B	119.8(5)
P08-C025	1.851(6)	C01C-C020	1.421(8)	Rh02-Cl05-Rh01	95.53(5)	C014-C01H-C01I	122.2(6)
C009-C00B	1.411(8)	C01D-C029	1.396(9)	C00B-P06-Rh02	121.15(19)	C00Z-C01I-C01H	117.9(6)
C009-C00H	1.360(8)	C01E-C01R	1.392(8)	C00L-P06-Rh02	112.9(2)	C00Z-C01I-C02E	120.5(6)
C00A-C00K	1.398(9)	C01E-C02B	1.397(8)	C00L-P06-C00B	100.1(3)	C01H-C01I-C02E	121.5(6)
C00A-C013	1.379(9)	C01F-C02M	1.355(9)	C00L-P06-C01A	106.6(3)	C01G-C01J-P07	123.6(4)
C00B-C00Q	1.376(8)	C01G-C01J	1.376(8)	C01A-P06-Rh02	112.68(19)	C01G-C01J-C01M	119.6(5)
C00C-C00F	1.392(8)	C01H-C01I	1.392(9)	C01A-P06-C00B	101.7(3)	C01M-C01J-P07	115.3(4)
C00C-C013	1.383(8)	C01I-C02E	1.511(9)	C01J-P07-Rh02	103.86(18)	C00I-C01K-C025	121.5(6)
C00D-C00N	1.400(9)	C01J-C01M	1.441(8)	C01J-P07-C028	104.0(3)	C01V-C01L-C00R	121.5(6)
C00D-C016	1.375(8)	C01K-C025	1.422(8)	C01J-P07-C030	107.7(3)	C02A-C01M-C01J	120.6(5)
C00E-C00L	1.386(9)	C01L-C01V	1.350(9)	C028-P07-Rh02	119.8(2)	C02P-C01N-C010	121.4(6)
C00E-C01S	1.382(9)	C01M-C02A	1.347(8)	C028-P07-C030	96.3(3)	C00M-C01P-C01Q	118.8(6)
C00F-C022	1.401(8)	C01N-C02P	1.375(8)	C030-P07-Rh02	123.4(2)	C00M-C01P-C02T	118.4(6)
C00G-C00J	1.389(8)	C01P-C01Q	1.431(8)	C015-P08-Rh01	121.7(2)	C02T-C01P-C01Q	122.8(6)
C00G-C00Z	1.400(8)	C01P-C02T	1.429(9)	C015-P08-C01E	107.5(3)	C01P-C01Q-C01U	117.3(5)
C00H-C020	1.406(8)	C01Q-C01U	1.504(8)	C015-P08-C025	99.4(3)	C025-C01Q-C01P	120.8(6)
C00I-C00M	1.411(10)	C01Q-C025	1.387(8)	C01E-P08-Rh01	107.5(2)	C025-C01Q-C01U	121.9(5)
C00I-C01K	1.356(9)	C01R-C02J	1.400(8)	C01E-P08-C025	102.7(3)	C01E-C01R-C02J	121.6(6)
C00J-C014	1.398(8)	C01S-C02C	1.390(10)	C025-P08-Rh01	116.22(19)	C00E-C01S-C02C	118.4(6)
C00K-C022	1.386(8)	C01S-C02L	1.525(9)	C00H-C009-C00B	122.5(6)	C00E-C01S-C02L	120.6(6)
C00K-C02X	1.505(9)	C01T-C024	1.399(8)	C013-C00A-C00K	121.5(6)	C02C-C01S-C02L	120.9(6)
C00L-C017	1.417(8)	C01T-C02G	1.390(9)	C009-C00B-P06	119.4(4)	C024-C01T-C018	121.6(6)
C00M-C01P	1.413(9)	C01V-C02Y	1.399(10)	C00Q-C00B-P06	121.1(4)	C02G-C01T-C018	121.6(6)
C00M-C02K	1.431(9)	C01W-C02U	1.400(9)	C00Q-C00B-C009	119.2(5)	C02G-C01T-C024	116.8(6)
C00N-C023	1.371(9)	C01X-C027	1.385(9)	C013-C00C-C00F	120.5(5)	C00R-C01U-C01Q	117.5(5)
C00O-C00Y	1.361(8)	C020-C023	1.415(8)	C016-C00D-C00N	120.5(6)	C010-C01U-C00R	120.4(5)
C00O-C01B	1.422(8)	C021-C02J	1.505(8)	C01S-C00E-C00L	121.6(6)	C010-C01U-C01Q	122.1(5)
C00P-C00X	1.390(8)	C024-C030	1.395(8)	C00C-C00F-P03	118.2(4)	C01L-C01V-C02Y	120.7(6)
C00P-C01O	1.491(9)	C029-C02N	1.516(10)	C00C-C00F-C022	119.0(5)	C015-C01W-C02U	120.8(6)
C00P-C01Z	1.397(9)	C029-C032	1.394(10)	C022-C00F-P03	122.7(4)	C027-C01X-C00T	121.6(6)
C00Q-C01C	1.439(8)	C02B-C02O	1.395(9)	C00J-C00G-P03	123.4(5)	C011-C01Z-C00P	122.1(6)
C00Q-C01G	1.506(7)	C02C-C02H	1.388(10)	C00J-C00G-C00Z	118.9(5)	C00H-C020-C01C	119.0(5)
C00R-C01L	1.409(9)	C02D-C02I	1.399(11)	C00Z-C00G-P03	117.6(4)	C00H-C020-C023	121.5(6)
C00R-C01U	1.448(8)	C02D-C02K	1.347(11)	C009-C00H-C020	120.0(5)	C023-C020-C01C	119.5(6)

C00R-C02F	1.413(8)	C02F-C02P	1.394(9)	C01K-C00I-C00M	120.9(6)	C00K-C022-C00F	121.2(6)
C00S-C01B	1.423(8)	C02F-C02R	1.428(8)	C00G-C00J-C014	120.6(6)	C00N-C023-C020	120.5(6)
C00S-C02A	1.415(8)	C02G-C02V	1.377(9)	C00A-C00K-C02X	121.0(6)	C030-C024-C01T	121.7(6)
C00S-C02M	1.419(8)	C02H-C02W	1.510(9)	C022-C00K-C00A	118.1(6)	C01K-C025-P08	120.0(5)
C00T-C00V	1.382(8)	C02I-C02T	1.351(9)	C022-C00K-C02X	120.9(6)	C01Q-C025-P08	121.2(4)
C00T-C01X	1.409(9)	C02O-C02Z	1.513(9)	C00E-C00L-P06	125.5(5)	C01Q-C025-C01K	118.6(6)
C00T-C02S	1.495(8)	C02Q-C02V	1.397(8)	C00E-C00L-C017	118.8(6)	C019-C027-C012	118.6(6)
C00U-C011	1.400(9)	C02Q-C030	1.389(8)	C017-C00L-P06	115.2(5)	C01X-C027-C012	122.5(6)
C00U-C01A	1.392(8)	C02R-C02Y	1.358(10)	C00I-C00M-C01P	119.3(6)	C01X-C027-C019	118.8(6)
C00V-C028	1.386(8)	C02U-C031	1.488(10)	C00I-C00M-C02K	122.5(6)	C00V-C028-P07	124.3(5)
C00W-C02J	1.389(9)	C02U-C032	1.373(10)	C01P-C00M-C02K	118.1(7)	C00V-C028-C019	118.9(5)
C00W-C02O	1.369(9)	C02V-C033	1.509(9)	C023-C00N-C00D	120.7(6)	C019-C028-P07	116.2(4)
				C00Y-C00O-C01B	120.9(5)	C01D-C029-C02N	121.3(7)
				C00X-C00P-C01O	121.5(6)	C032-C029-C01D	117.2(6)
				C00X-C00P-C01Z	117.8(6)	C032-C029-C02N	121.5(6)
				C01Z-C00P-C01O	120.6(6)	C01M-C02A-C00S	121.5(5)
				C00B-C00Q-C01C	119.7(5)	C01E-C02B-C02O	121.3(6)
				C00B-C00Q-C01G	120.6(5)	C01S-C02C-C02H	122.1(6)
				C01C-C00Q-C01G	119.6(5)	C02K-C02D-C02I	120.0(7)
				C01L-C00R-C01U	122.7(6)	C00R-C02F-C02R	118.9(6)
				C01L-C00R-C02F	118.3(6)	C02P-C02F-C00R	119.1(5)
				C02F-C00R-C01U	119.0(5)	C02P-C02F-C02R	122.0(6)
				C01B-C00S-C02M	118.7(5)	C02V-C02G-C01T	123.4(6)
				C02A-C00S-C01B	122.0(5)	C017-C02H-C02W	118.7(6)
				C02A-C00S-C02M	119.3(6)	C02C-C02H-C017	120.4(6)
				C00V-C00T-C01X	118.0(6)	C02C-C02H-C02W	120.9(6)
				C00V-C00T-C02S	121.8(6)	C02T-C02I-C02D	120.9(7)
				C01X-C00T-C02S	120.1(6)	C00W-C02J-C01R	117.7(6)
				C01A-C00U-C011	120.6(6)	C00W-C02J-C021	121.0(5)
				C00T-C00V-C028	121.9(6)	C01R-C02J-C021	121.3(6)
				C02O-C00W-C02J	122.7(6)	C02D-C02K-C00M	121.5(7)
				C00P-C00X-C01A	121.7(6)	C01F-C02M-C00S	121.6(6)
				C00O-C00Y-C01F	121.4(6)	C00W-C02O-C02B	118.5(6)
				C01I-C00Z-C00G	121.5(6)	C00W-C02O-C02Z	123.0(6)
				C01N-C010-P03	120.1(4)	C02B-C02O-C02Z	118.4(6)
				C01U-C010-P03	120.5(4)	C01N-C02P-C02F	120.9(6)
				C01U-C010-C01N	119.0(5)	C030-C02Q-C02V	120.8(6)
				C00U-C011-C026	119.9(6)	C02Y-C02R-C02F	120.5(6)
				C01Z-C011-C00U	118.9(6)	C02I-C02T-C01P	120.9(7)
				C01Z-C011-C026	121.1(6)	C01W-C02U-C031	121.6(7)
				C00A-C013-C00C	119.6(5)	C032-C02U-C01W	118.0(6)
				C00A-C013-C01Y	120.1(6)	C032-C02U-C031	120.2(6)
				C00C-C013-C01Y	120.3(6)	C02G-C02V-C02Q	118.2(6)
				C00J-C014-C034	120.0(6)	C02G-C02V-C033	121.5(6)
				C01H-C014-C00J	118.7(6)	C02Q-C02V-C033	120.3(6)

C01H-C014-C034	121.2(6)	C02R-C02Y-C01V	120.1(6)
C01D-C015-P08	121.2(4)	C024-C030-P07	122.3(4)
C01W-C015-P08	118.6(5)	C02Q-C030-P07	118.4(4)
C01W-C015-C01D	119.7(6)	C02Q-C030-C024	119.0(5)
C00D-C016-C01C	120.4(6)	C02U-C032-C029	123.2(6)

Table S24. Anisotropic Displacement Parameters (Å^2×10^3) for **C4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
Rh01	26.6(2)	24.3(2)	25.7(2)	-2.09(18)	-0.68(19)	0.50(18)
Rh02	23.7(2)	24.8(2)	29.9(2)	-3.12(19)	-1.0(2)	-0.65(18)
P03	24.0(7)	25.2(7)	24.3(7)	-0.7(6)	-0.2(6)	-0.3(5)
Cl04	27.0(7)	32.4(7)	29.7(7)	-5.2(6)	0.9(6)	-4.5(6)
Cl05	25.5(7)	42.0(8)	36.6(7)	-12.4(6)	-1.0(6)	-0.8(6)
P06	23.5(7)	25.7(7)	29.6(8)	-2.2(6)	-1.2(6)	0.3(6)
P07	23.2(7)	22.8(7)	30.4(8)	-0.8(6)	-1.1(6)	-1.0(6)
P08	27.9(8)	23.8(7)	33.4(8)	0.0(6)	1.8(6)	-2.2(6)
C009	21(3)	28(3)	33(3)	2(2)	4(2)	-2(2)
C00A	31(3)	44(3)	33(3)	11(3)	7(3)	-4(3)
C00B	22(3)	22(3)	33(3)	-4(2)	0(2)	0(2)
C00C	22(3)	35(3)	32(3)	1(2)	1(2)	-2(3)
C00D	36(3)	37(3)	29(3)	-5(3)	-3(3)	-5(3)
C00E	31(3)	35(3)	37(4)	-6(3)	0(3)	0(3)
C00F	24(3)	29(3)	29(3)	2(2)	2(2)	-1(2)
C00G	25(3)	25(3)	30(3)	-7(2)	1(2)	0(2)
C00H	27(3)	24(3)	37(3)	3(2)	5(3)	-3(2)
C00I	26(3)	38(4)	56(4)	11(3)	1(3)	5(3)
C00J	28(3)	31(3)	35(3)	-3(3)	2(3)	-3(2)
C00K	36(3)	46(4)	31(3)	-1(3)	-2(3)	-2(3)
C00L	32(3)	31(3)	27(3)	2(2)	0(3)	-4(3)
C00M	27(3)	47(4)	39(4)	14(3)	-3(3)	-2(3)
C00N	37(4)	29(3)	46(4)	-10(3)	-8(3)	-5(3)
C00O	26(3)	30(3)	34(3)	0(2)	-1(3)	-4(2)
C00P	35(4)	41(4)	33(3)	-5(3)	1(3)	9(3)
C00Q	22(3)	20(3)	31(3)	-1(2)	-1(2)	1(2)
C00R	27(3)	35(3)	28(3)	-4(3)	2(2)	-4(3)
C00S	34(3)	26(3)	31(3)	4(2)	1(3)	-1(2)
C00T	35(3)	26(3)	36(3)	0(3)	5(3)	-1(2)
C00U	32(3)	32(3)	37(3)	-8(3)	-3(3)	2(3)

	U11	U22	U33	U23	U13	U12
C00V	25(3)	27(3)	33(3)	1(2)	-3(2)	2(2)
C00W	38(4)	25(3)	43(4)	-4(3)	-9(3)	7(3)
C00X	28(3)	34(3)	34(3)	-7(3)	-1(2)	-2(2)
C00Y	31(3)	37(3)	37(3)	-1(3)	-4(3)	-4(3)
C00Z	32(3)	35(3)	25(3)	-6(3)	-5(2)	3(2)
C010	30(3)	21(3)	23(3)	-3(2)	3(2)	-1(2)
C011	44(4)	30(3)	34(3)	-9(3)	-2(3)	3(3)
C012	26(3)	47(4)	49(4)	6(3)	-2(3)	0(3)
C013	23(3)	36(3)	40(3)	4(3)	0(3)	0(2)
C014	26(3)	46(4)	40(4)	-11(3)	2(3)	0(3)
C015	30(3)	27(3)	33(3)	-5(3)	1(3)	-2(2)
C016	27(3)	29(3)	32(3)	0(2)	-2(2)	-4(2)
C017	32(3)	35(3)	32(3)	-4(3)	-3(3)	-3(2)
C018	46(4)	37(4)	60(4)	-20(3)	10(4)	-1(3)
C019	31(3)	22(3)	38(3)	-2(3)	1(3)	-5(2)
C01A	29(3)	24(3)	29(3)	-1(2)	1(2)	4(2)
C01B	28(3)	27(3)	28(3)	-2(2)	0(2)	-2(2)
C01C	19(3)	26(3)	36(3)	-2(2)	2(2)	0(2)
C01D	36(3)	32(3)	33(3)	-7(2)	3(3)	-3(3)
C01E	29(3)	24(3)	38(3)	-4(2)	-2(3)	0(2)
C01F	36(4)	39(3)	36(3)	5(3)	-4(3)	7(3)
C01G	28(3)	24(3)	23(3)	-5(2)	3(2)	-2(2)
C01H	34(4)	45(4)	47(4)	-15(3)	-10(3)	11(3)
C01I	42(4)	36(3)	34(3)	-7(3)	-3(3)	7(3)
C01J	30(3)	24(3)	26(3)	-5(2)	2(2)	0(2)
C01K	32(3)	34(3)	47(4)	2(3)	4(3)	4(3)
C01L	35(4)	39(3)	37(3)	-2(3)	-3(3)	2(3)
C01M	30(3)	25(3)	32(3)	-2(2)	2(2)	-9(3)
C01N	32(3)	27(3)	31(3)	-9(3)	0(3)	-1(2)
C01O	35(4)	47(4)	35(3)	-7(3)	-3(3)	14(3)
C01P	22(3)	44(3)	37(3)	10(3)	-4(3)	0(3)
C01Q	18(3)	37(3)	34(3)	4(3)	-2(2)	-2(2)
C01R	28(3)	29(3)	42(4)	-2(3)	-7(3)	1(2)
C01S	39(4)	43(4)	30(3)	-6(3)	0(3)	-9(3)
C01T	28(3)	34(3)	49(4)	-5(3)	-3(3)	3(3)
C01U	30(3)	28(3)	27(3)	2(2)	2(2)	1(2)
C01V	30(3)	54(4)	51(4)	-11(3)	-8(3)	-2(3)
C01W	34(3)	35(3)	32(3)	-1(3)	7(3)	-2(3)
C01X	29(3)	29(3)	40(4)	1(3)	8(3)	1(2)
C01Y	48(4)	36(3)	45(4)	8(3)	4(4)	-4(3)
C01Z	48(4)	32(3)	42(4)	-5(3)	-2(3)	12(3)
C020	24(3)	27(3)	37(3)	-5(2)	-2(3)	-3(2)
C021	36(4)	33(3)	49(4)	-5(3)	-3(3)	5(3)
C022	33(3)	37(3)	32(3)	-4(3)	3(3)	-4(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C023	35(3)	24(3)	50(4)	0(3)	-4(3)	-8(3)
C024	27(3)	27(3)	38(3)	-1(2)	0(3)	0(2)
C025	22(3)	29(3)	40(4)	6(3)	0(3)	2(2)
C026	60(5)	28(4)	65(5)	-2(3)	-6(4)	3(3)
C027	29(3)	25(3)	38(3)	-3(3)	3(3)	-2(2)
C028	26(3)	24(3)	34(3)	-1(2)	5(3)	-1(2)
C029	36(4)	50(4)	41(4)	-17(3)	8(3)	-8(3)
C02A	33(3)	25(3)	39(3)	6(3)	2(3)	-1(2)
C02B	34(3)	24(3)	45(4)	-1(3)	3(3)	3(2)
C02C	50(4)	38(4)	23(3)	2(3)	-2(3)	-8(3)
C02D	45(4)	75(6)	35(4)	19(4)	-4(3)	3(4)
C02E	56(5)	57(4)	43(4)	6(3)	-6(4)	22(4)
C02F	34(3)	33(3)	28(3)	-8(2)	4(3)	-6(3)
C02G	34(3)	20(3)	62(4)	-6(3)	-3(3)	-3(3)
C02H	43(4)	36(3)	37(4)	-3(3)	-13(3)	-1(3)
C02I	49(4)	56(4)	35(4)	0(3)	-4(3)	-4(3)
C02J	33(3)	31(3)	34(3)	-4(3)	-3(3)	7(2)
C02K	36(4)	56(5)	47(4)	20(4)	-7(3)	6(3)
C02L	41(4)	73(5)	38(4)	5(4)	9(3)	-5(4)
C02M	36(4)	29(3)	40(4)	1(3)	1(3)	4(3)
C02N	39(4)	63(5)	58(5)	-26(4)	7(4)	-10(4)
C02O	34(3)	29(3)	44(4)	7(3)	-6(3)	-2(3)
C02P	40(3)	26(3)	32(3)	-1(3)	4(3)	-3(3)
C02Q	25(3)	32(3)	35(3)	2(2)	1(3)	0(3)
C02R	47(4)	31(3)	38(3)	-11(3)	7(3)	-10(3)
C02S	43(4)	49(4)	39(4)	11(3)	5(3)	11(3)
C02T	36(4)	46(4)	34(3)	9(3)	-4(3)	-2(3)
C02U	52(4)	32(3)	36(3)	-4(3)	11(3)	-7(3)
C02V	33(3)	30(3)	54(4)	6(3)	3(3)	-1(3)
C02W	51(4)	59(5)	48(4)	10(4)	-18(4)	1(4)
C02X	57(5)	65(5)	31(3)	-4(3)	5(3)	-4(4)
C02Y	32(4)	53(4)	53(4)	-19(4)	3(3)	-16(3)
C02Z	45(4)	31(4)	71(5)	-6(3)	-1(4)	-7(3)
C030	23(3)	24(3)	39(3)	-2(2)	-3(3)	-3(2)
C031	76(5)	37(4)	49(4)	9(3)	14(4)	-19(4)
C032	46(4)	35(3)	49(4)	-13(3)	15(3)	-14(3)
C033	65(5)	31(3)	66(5)	13(3)	5(4)	-2(3)
C034	35(4)	91(7)	69(6)	8(5)	14(4)	7(4)

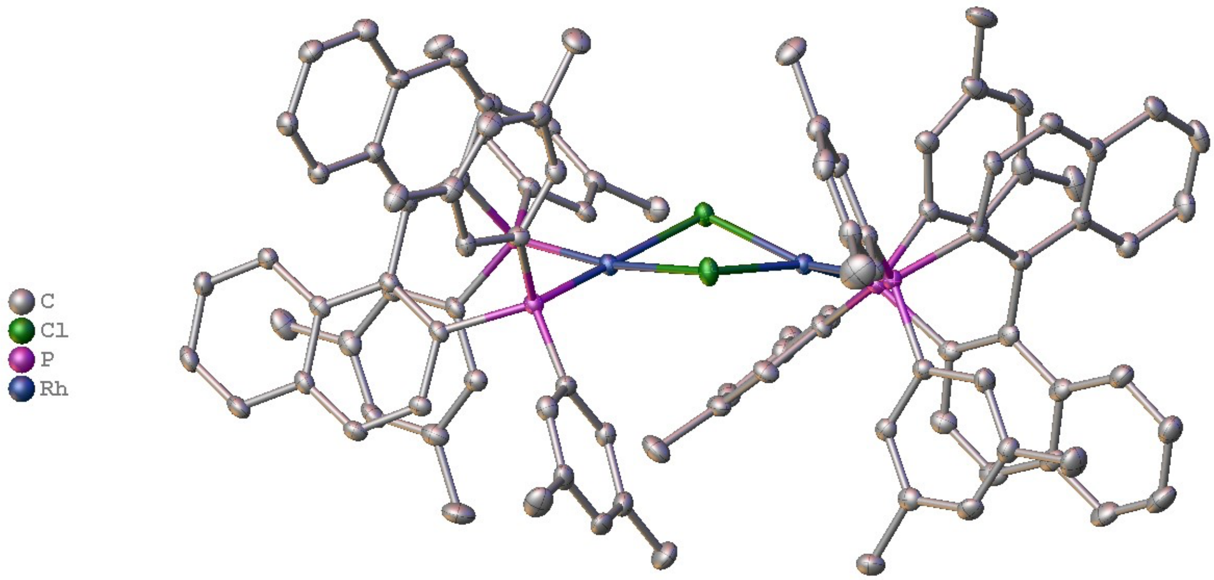
Table S25**:** Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for **C4**

	x	*y*	*z*	**U(eq)**
H009	2264.95	4636.98	6287.75	33
H00A	5495.1	5747.65	9762.37	43
H00C	5622.33	5853.59	8132.49	36
H00D	1966.78	4466.13	3504.44	41
H00E	1325.71	5713.44	6856.39	41
H00H	1823.82	3897.6	5750.01	35
H00I	8245.84	5191.95	8782.1	48
H00J	4193.15	7249.37	8554.24	38
H00N	1644.31	3592.15	3897.53	45
H00O	893.51	5691.23	4739.58	36
H00U	3319.55	6915.13	5962.24	41
H00V	5024.01	5940.17	4129.75	34
H00W	8091.14	4367.72	6225.51	43
H00X	993.38	5950.94	5994.87	38
H00Y	-179.49	6284.81	4354.53	42
H00Z	5213.8	7804.59	7119.04	37
H01A	8309.18	5114.19	5099.46	61
H01B	8173.74	5663.03	5466.37	61
H01C	8721.73	5704.46	4901.78	61
H016	2335.53	5233.08	4043.49	35
H017	3994.09	5148.6	6930.87	40
H01D	3844.41	4084.56	3713.29	72
H01E	4216.89	3487.68	3919.23	72
H01F	4941.31	3962.68	3735.97	72
H019	6494.18	5550.91	5480.05	37
H01G	9518	6452.68	7377.62	41
H01H	244.76	7191.92	4065.4	44
H01I	2776.61	8404.41	7684.22	50
H01K	7983.64	5406.97	7889.22	45
H01L	9428.57	7084.31	8528.81	44
H01M	4513.12	6711.86	4776.54	35
H01N	6151.32	8218.45	7820.4	36
H01J	-475.16	6312.03	5745.18	58
H01O	-480.97	6865.69	5376.59	58
H01P	-619.72	6915.25	6019.48	58
H01R	9138.77	5861.37	6700.4	40

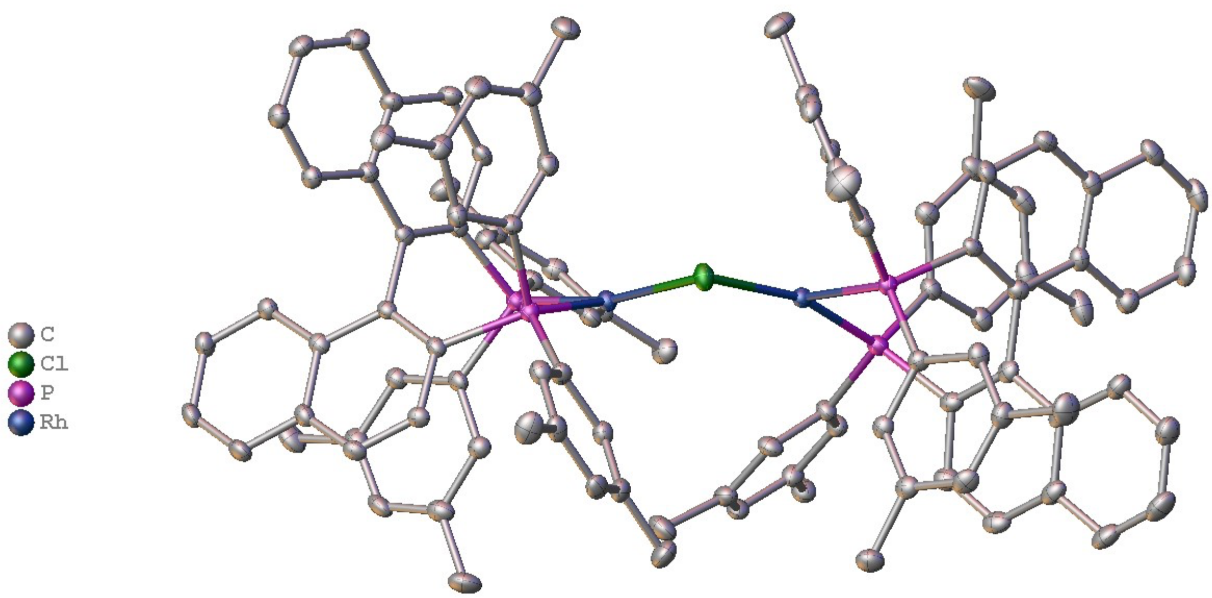
	x	*y*	*z*	U(eq)
H01V	10649.68	7690.67	8634.6	54
H01W	7538.43	7505.2	6806.88	40
H01X	7825.13	5775.45	4051.07	39
H01Q	5945.39	4905.49	9172.05	65
H01S	5698.01	4950.45	8539.98	65
H01T	4879.81	4940.27	8981.76	65
H01Z	811.39	7591.4	5598.12	49
H02A	9821.53	5226.96	5876.24	59
H02B	9625.34	4573.44	5977.49	59
H02C	10173.34	4933.64	6423.82	59
H022	5743.27	7266.88	9047.34	41
H023	1653.94	3482.62	4830.37	44
H024	4416.05	4941.43	4291.09	37
H02D	2341.31	8019.89	5257.06	76
H02E	3275.23	7811.01	5549.98	76
H02F	2509.05	8154.58	5886.07	76
H02G	3399.69	7302.84	4442.7	39
H02H	6479.83	5441.89	7062.76	41
H02I	2104.37	4651.59	8044.23	45
H02J	8254.37	6182.48	10401.97	62
H02K	3554.18	8398.03	6566.48	78
H02L	4572.19	8632.83	6705.91	78
H02M	3670.12	8926.2	6962.8	78
H02N	4364.48	3352.33	4851.2	46
H02O	8060.39	7121.95	10142.1	56
H02P	8339.42	5492.28	9758.62	56
H02Q	165.79	4960.69	7437.71	76
H02R	330.67	5554.72	7726.46	76
H02S	547.06	4985.15	8047.88	76
H02T	1759.87	7490.25	4169.08	43
H02U	11087.93	6790.35	7548.24	80
H02V	11331.03	7438.07	7446.65	80
H02W	11384.27	6999.35	6955.3	80
H02X	7396.55	8824.07	7922.7	39
H02Y	4474.96	4641.17	5905.82	37
H02Z	9069.84	8991.83	8136.79	46
H02	5752.35	5949.02	3259.73	65
H	6800.91	5725.35	3206.72	65
HA	6607.27	6374.9	3330.9	65
H1	7803.05	7354.3	9253.12	46
H2	4218.59	4262.8	7542.05	79
HB	3607.78	4258.59	8085.81	79
HC	4354.1	4747.55	7985.3	79
H3	6097.96	6707.27	10258.73	76

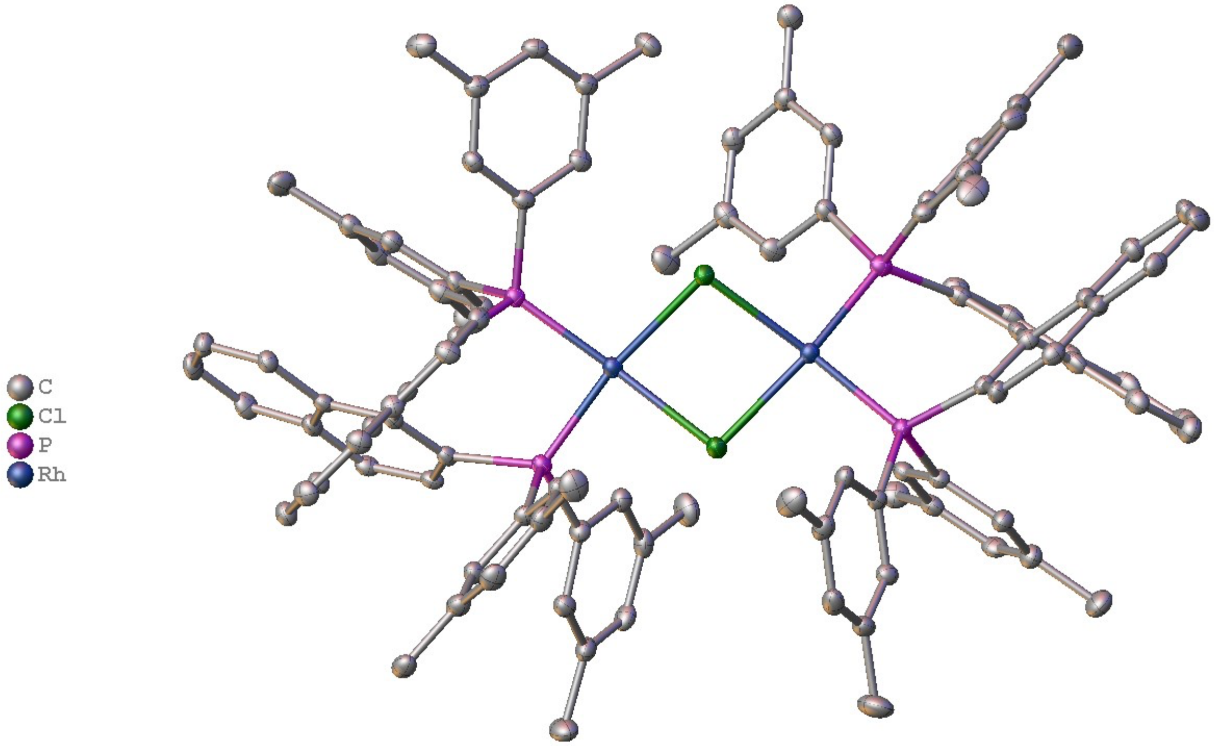
	x	*y*	*z*	U(eq)
HD	4984.37	6735.27	10224.82	76
HE	5599.56	7242.98	9994.26	76
H4	10491.8	8642.99	8412.1	55
H5	5912.23	4519.68	6897.03	73
HF	6537.34	4063.14	6588.7	73
HG	6002.77	4537.75	6249.69	73
H03A	7882.04	8465.1	6643.6	81
H03B	8905.66	8588.9	6413.96	81
H03C	8677.83	8694	7041.83	81
H032	10198.37	8027.15	6921.53	52
H03D	3860.29	3322.7	5940	81
H03E	4573.84	3725.03	6253.72	81
H03F	4959.88	3246.16	5856.88	81
H03G	2469.53	7445.45	8713.65	97
H03H	2050.56	8008.68	8455.96	97
H03I	2833.77	8044.94	8917.5	97

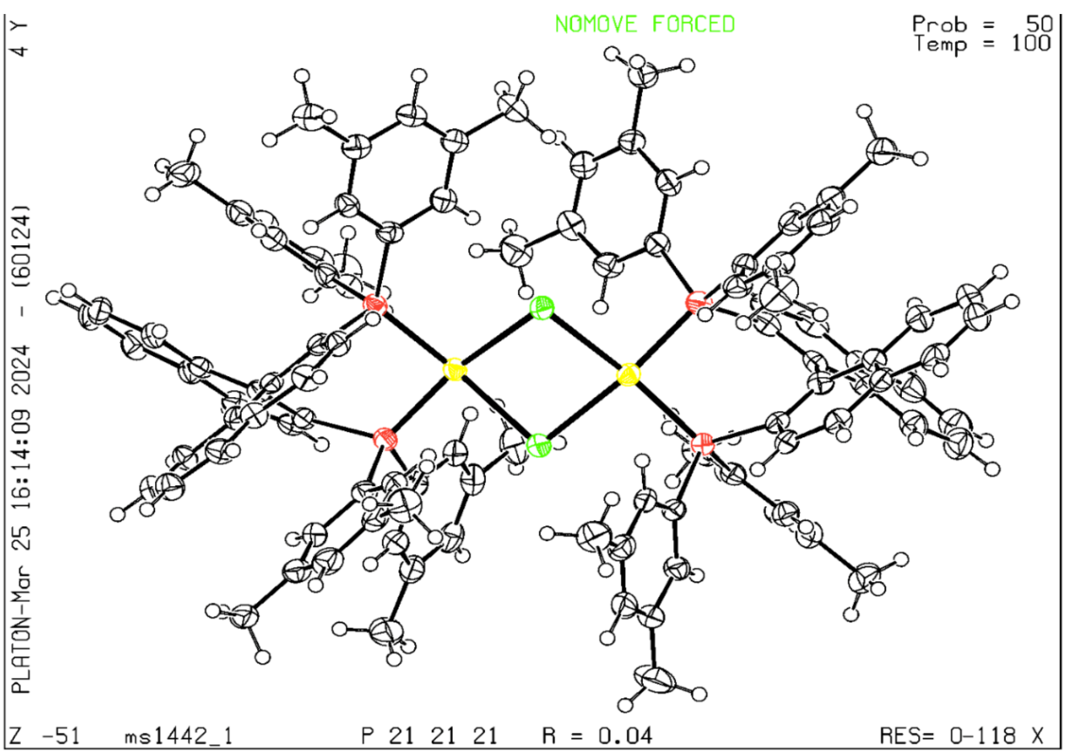
Figure S11: Single crystal x-ray structure of **C4** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.



Additional Figures:







Experimental:

Dark brown single crystals of **C4** suitable for X-ray diffraction studies were grown via layering pentanes onto chlorobenzene solution. Single-crystal X-ray diffraction studies were conducted at Los Alamos National Laboratory on a Bruker D8 Quest diffractometer using a Mo Kα (λ = 0.71073 Å) IμS 3.0 Microfocus source X-ray generator and a Photon II detector at 100(1) K. Data collection and cell parameter determinations were performed via the SMART software package.[5] Data reduction was performed via the SAINT software package.[6] Absorption corrections were carried out via the multiscan SADABS method.[7] Structure solution, refinement, and publication materials were generated via SHELXT, SHELXL, and Olex2.[8-10] Hydrogen atoms were attached via the riding model at calculated positions. Crystallographic data for **C4** has been deposited in the Cambridge Structural Data base (2351158).

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