Supporting Information

Well-defined *N*-Heterocyclic Carbene Rh-hydroxide Complexes as Alkene Hydrosilylation and Dehydrogenative Silylation Catalysts

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Optimization studies

Table S 1 Solvent optimization for reaction: $HSiEt_3$ (4a) and styrene (5b)[a]

		T = 5 h			T = 24 h		
Entry	**Solvent**	**Conversion**	**6b**	**7b**	**Conversion**	**6b**	**7b**
1	Benzene	80	51	49	90	56	44
2	Dioxane	60	61	39	80	65	35
3	MeOH	7	32	68	8	40	60
4	THF	62	50	50	88	56	44
5	Toluene	70	53	47	92	58	42

[a]Reaction Conditions: **4a** (0.3 mmol), **5b** (0.3 mmol), [Rh(cod)(ICy)(OH)] (**3b**) (1.0 mol%), rt, solvent (1 mL)**.**
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 2 Temperature optimization for reaction: $HSiEt_3$ (4a) and styrene (5b)[a]

		T = 2.5 h			T = 5 h		
Entry	**Temp (°C)**	**Conversion**	**6b**	**7b**	**Conversion**	**6b**	**7b**
1	rt	32	53	47	70	55	45
2	60	93	60	40	93	65	35
3	80	93	65	35	94	67	33

[a]Reaction Conditions: **4a** (0.3 mmol), **5b** (0.3 mmol), [Rh(cod)(ICy)(OH)] (**3b**) (1.0 mol%), t, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 3 Reaction of $HSiEt_3$ (4a) with different concentrations of Styrene (5b)[a]

		T = 2.5 h			T = 5 h		
Entry	**Styrene (eq.)**	**Conversion**	**6b**	**7b**	**Conversion**	**6b**	**7b**
1	1	93	60	40	93	65	35
2	4	>99	19	82	>99	18	82
3	7	>99	11	89	>99	11	89
4	10	>99	5	95	>99	5	95

[a]Reaction Conditions: **4a** (0.3 mmol), **5b** (molar equivalence relative to **4a**), [Rh(cod)(ICy)(OH)] (**3b**) (1.0 mol%), 60 °C, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 4 Catalyst loading optimization for reaction: $HSiEt_3$ (4a) and styrene (5b)[a]

		T = 1 h			T = 2.5 h			T = 5 h		
Entry	**[Rh] 3b (mol%)**	**Conversion**	**6b**	**7b**	**Conversion**	**6b**	**7b**	**Conversion**	**6b**	**7b**
1	1.000	77	54	44	88	51	49	96	53	47
2	0.500	68	63	37	82	57	43	90	50	50
3	0.100	32	70	30	47	69	31	86	65	35
4	0.005	17	80	20	32	77	23	74	71	29
5	0.001	1	50	50	4	50	50	12	60	40

[a]Reaction Conditions: **4a** (0.3 mmol), **5b** (0.6 mmol), [Rh(cod)(ICy)(OH)] (**3b**) (mol% relative to **4a**), 60 °C, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 5 Reaction of $HSiEt_3$ (4a) with different concentrations of 1-hexene (5a)[a]

		T = 1 h			T = 2.5 h			T = 5 h		
Entry	**1-hexene (eq.)**	**Conversion**	**6a**	**7a**	**Conversion**	**6a**	**7a**	**Conversion**	**6a**	**7a**
1	1	35	54	46	54	52	48	55	47	53
2	2	53	85	15	88	94	6	>99	99	1
3	3	92	82	18	97	85	15	>99	84	16
4	5	>99	60	40	>99	77	23	>99	70	30

[a]Reaction Conditions: **4a** (0.3 mmol), **5a** (molar equivalence relative to **4a**), [Rh(cod)(ICy)(OH)] (**3b**) (1.0 mol%), 60 °C, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 6 Catalyst loading optimization for reaction: $HSiEt_3$ (4a) and 1-hexene (5a)[a]

		T = 4 h			T = 24 h		
Entry	**[3b] (mol%)**	**Conversion**	**6a**	**7a**	**Conversion**	**6a**	**7a**
1	1.00	99	99	1	>99	99	1
2	0.50	98	95	5	>99	98	2
3	0.10	90	88	12	93	94	6
4	0.05	90	85	15	92	88	12

[a]Reaction Conditions: **4a** (0.3 mmol), **5a** (0.6 mmol), [Rh(cod)(ICy)(OH)] (**3b**) (mol% relative to **4a**), 60 °C, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 7 Catalyst comparison for reaction: $HSiEt_3$ (4a) and styrene (5b) at 60 °C[a]

Entry	**[Rh(cod)(NHC)(OH)] NHC =**		**Conversion**	**6b**	**7b**
1	**3a**	IPr	94	64	36
2	**3b**	ICy	93	66	34
3	**3c**	IDD	94	66	34
4	**3d**	IGoofy	94	67	33

[a]Reaction Conditions: **4a** (0.3 mmol), **5b** (0.6 mmol), [Rh(cod)(NHC)(OH)] (**3a-d**) (0.02 mol%), 60 °C, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Table S 8 Catalyst comparison for reaction: $HSiEt_3$ (4a) and 1-hexene (5a) at rt[a]

			Conversion to Products (**6a** +**7a**) (%)/ Time (h)								
Entry	**[Rh(cod)(NHC)(OH)] NHC =**		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**24**
1	**3a**	IPr	3	6	9	17	20	24	27	28	42
2	**3b**	ICy	40	65	76	78	80	82	82	82	82
3	**3c**	IDD	30	45	54	65	74	76	77	78	89
4	**3d**	IGoofy	43	75	88	92	96	97	98	98	>99

[a]Reaction Conditions: **4a** (0.3 mmol), **5a** (0.6 mmol), [Rh(cod)(NHC)(OH)] (**3a-d**) (1.0 mol%), rt, Toluene (1mL).
Conversions and relative product yields as %; calculated from GC-MS (relative to concentration of **4a**) and confirmed by ^{1}H NMR.

Characterization data

triethyl(hexyl)silane **6a** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 – 1.20 (m, 8H), 0.89 – 0.85 (m, 12H), 0.58 – 0.40 (m, 8H); GC-MS *m/z* = 171 (M-C_2H_5, 100), 163, 143, 115.[1]

(*E*)-triethyl(hex-1-en-1-yl)silane **7a** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.08 (dt, *J* = 18.7, 6.3, 1H), 5.59 (dt, *J* = 18.7, 1.5, 1H), 2.04 - 1.94 (m, 2H); GC-MS *m/z* = 198 (M^+), 169 (M-C_2H_5, 100), 141, 113.[2]

triethyl(phenethyl)silane **6b** ^{1}H NMR (400MHz, C_6D_6, representative signals) δ 2.74 (t, *J* = 8.0, 2H), 1.02 (t, *J* = 8.0, 2H), 0.83 (q, *J* = 8.0, 9H), 0.66 (q, *J* = 8.0, 6H); GC-MS *m/z* 191 (M-C_2H_5, 100), 163, 135.[3]

(*E*)-triethyl(styryl)silane **7b** ^{1}H NMR (400MHz, C_6D_6) δ 7.20 (d, *J* = 19.0, 1H), 6.60 (d, *J* = 19.0, 1H), 1.19 (t, *J* = 7.9, 9H), 1.11 (t, *J* = 7.9, 6H); GC-MS *m/z* 218 (M^+), 189 (M-C_2H_5, 100), 161, 131.[2]

(4-chlorophenethyl)triethylsilane **6c** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 2.43 – 2.30 (m, 2H), 0.99 (t, *J* = 7.6, 2H); GC-MS *m/z* 225 (M-C_2H_5), 197, 169, 141, 115, 87 (100).[4]

(*E*)-(4-chlorostyryl)triethylsilane **7c** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.61 (d, *J* = 19.3, 1H), 6.17 (d, *J* = 19.3, 1H); GC-MS *m/z* 252 (M^+), 223 (M-C_2H_5, 100), 195, 167, 131.[5]

triethyl(octyl)silane **6d** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 – 1.19 (m, 12H), 0.98 – 0.84 (m, 12H), 0.60 – 0.44 (m, 8H); GC-MS *m/z* 200 (M-C_2H_5), 199 (100), 171, 115, 87.

(*E*)-triethyl(oct-1-en-1-yl)silane **7d** ^{1}H NMR (400MHz, $CDCl_3$, representative signals) δ 6.13 (dt, *J* = 18.7, 6.3, 1H), 5.63 (dt, *J* = 18.7, 1.5, 1H) 2.17 -2.08 (m, 2H); GC-MS *m/z* 226 (M^+), 207, 197 (M-C_2H_5, 100), 169.[6]

triethoxy(hexyl)silane **6e** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0, 6H), 1.67 – 1.47 (m, 17H), 0.94 – 0.82 (m, 3H), 0.70 – 0.58 (m, 2H); GC-MS *m/z* 248 (M^+), 203 (M-OC_2H_5, 100), 163, 149, 139, 119.[7]

triethoxy(phenethyl)silane **6f** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.13 (m, 5H), 3.83 (q, *J* = 7.0, 6H), 2.79 – 2.70 (m, 2H), 1.24 (t, *J* = 7.0, 9H), 1.04 – 0.96 (m, 2H); GC-MS *m/z* 268 (M^+), 240, 223, 195, 163 (100).[8]

(4-chlorophenethyl)triethoxysilane **6g** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 3.82 (q, *J* = 7.4, 6H), 2.75 – 2.65 (m, 2H), 0.99 – 0.91 (m, 2H); GC-MS *m/z* 287 (M-CH_3), 259 (100), 181.[9]

(*E*)-(4-chlorostyryl)triethoxysilane **7e** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.15 (d, *J* = 19.3, 1H); GC-MS *m/z* 285 (M-CH_3), 259, 207, 183, 181(100).[10]

triethoxy(octyl)silane **6h** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (q, *J* = 7.0, 6H), 1.58 – 1.26 (m, 21H), 0.97 (t, *J* = 6.7, 3H), 0.78 – 0.67 (m, 2H); GC-MS *m/z* 276 (M^+), 231, 207, 187, 163 (100), 149, 135, 119.[11]

hexyl(methyl)diphenylsilane **6i** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 4H), 7.43 – 7.28 (m, 6H), 1.44 – 1.20 (m, 8H), 1.12 – 1.04 (m, 2H), 0.81 – 0.93 (m, 3H), 0.56 (s, 3H); GC-MS *m/z* 281 (M^{-1}), 267 (M-CH_3), 225, 204, 197 (100), 183, 165, 121, 105.[12]

(*E*)-hex-1-en-1-yl(methyl)diphenylsilane **7f** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.21 (dt, *J* = 18.5, 6.2, 1H), 5.99 (dt, *J* = 18.5, 1.3, 1H), 0.95 (t, *J* = 7.2, 3H), 0.65 (s, 3H); GC-MS *m/z* 280 (M^+), 265, 223, 197 (100), 183, 145, 121, 105.[13]

methyl(phenethyl)diphenylsilane **6j** (300 MHz, $CDCl_3$, representative signals) δ 2.72 – 2.64 (m, 2H), 1.47 – 1.40 (m, 2H), 0.56 (s, 3H); GC-MS *m/z* 287 (M-CH_3), 224, 197 (100), 183, 165, 146, 121, 105.[12, 13]

(*E*)-methyldiphenyl(styryl)silane **7g** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.96 (d, *J* = 19.0, 1H), 6.75 (d, *J* = 19.0, 1H), 0.71 (s, 3H); GC-MS *m/z* 300 (M^+), 285, 222, 207 (100), 197, 183, 165, 155, 145, 129, 121, 105.[14]

(4-chlorophenethyl)(methyl)diphenylsilane **6k** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 2.72 – 2.63 (m, 2H), 1.46 – 1.37 (m, 2H), 0.55 (s, 3H); GC-MS *m/z* 321 (M-CH_3), 281, 258, 243, 207, 197 (100).[12]

(*E*)-(4-chlorostyryl)(methyl)diphenylsilane **7h** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5, 2H), 7.47 (d, *J* = 7.6, 2H), 7.43 – 7.26 (m, 10H), 6.97 (d, *J* = 19.1, 1H), 6.76 (d, *J* = 19.1, 1H), 0.72 (s, 3H); GC-MS *m/z* 334 (M^+), 319, 256, 241 (100), 222, 207, 183, 179, 165, 155, 121, 105.

methyl(octyl)diphenylsilane **6l** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 10H), 1.49 – 1.21 (m, 12H), 1.15 – 1.07 (m, 2H), 0.91 (t, *J* = 7.0, 3H), 0.58 (s, 3H); GC-MS *m/z* 295 (M-CH_3), 232, 197 (100), 183, 165, 121, 105.[12]

(*E*)-methyl(oct-1-en-1-yl)diphenylsilane **7i** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.21 (dt, *J* = 18.6, 6.2, 1H), 5.99 (dt, *J* = 18.5, 1.4, 1H), 0.65 (s, 3H); GC-MS *m/z* 308 (M^+), 293, 281, 223, 197 (100), 183, 145, 121, 105.

hexyltriphenylsilane **6m** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 0.89 (t, *J* = 7.4, 2H); GC-MS *m/z* 315 (M-C_2H_5), 282, 267, 259 (100), 181.

(*E*)-hex-1-en-1-yltriphenylsilane **7j** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 6.28 – 6.34 (m, 2H), 1.02 (t, *J* = 7.2, 2H); GC-MS *m/z* 342 (M^+), 260, 182 (100).[2]

phenethyltriphenylsilane **6n** ^{1}H NMR (300 MHz, $CDCl_3$, representative signals) δ 2.82 – 2.72 (m, 2H), 1.80 – 1.69 (m. 2H); GC-MS *m/z* 287 (M-C_6H_5), 281, 259 (100), 207, 181.

triphenyl(styryl)silane **7k** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 6H), 7.41 – 7.18 (m, 14H), 7.18 – 7.13 (m, 2H); GC-MS *m/z* 285 (M-C_6H_5), 259, 207, 181 (100), 105.[2]

triethyl(oct-1-en-2-yl)silane **8a** ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 – 5.42 (m, 2H), 1.92 – 2.0 (m, 2H); GC-MS *m/z* 226 (M^+), 197, 169, 115 (100), 87.[6]

Selected NMR Spectra

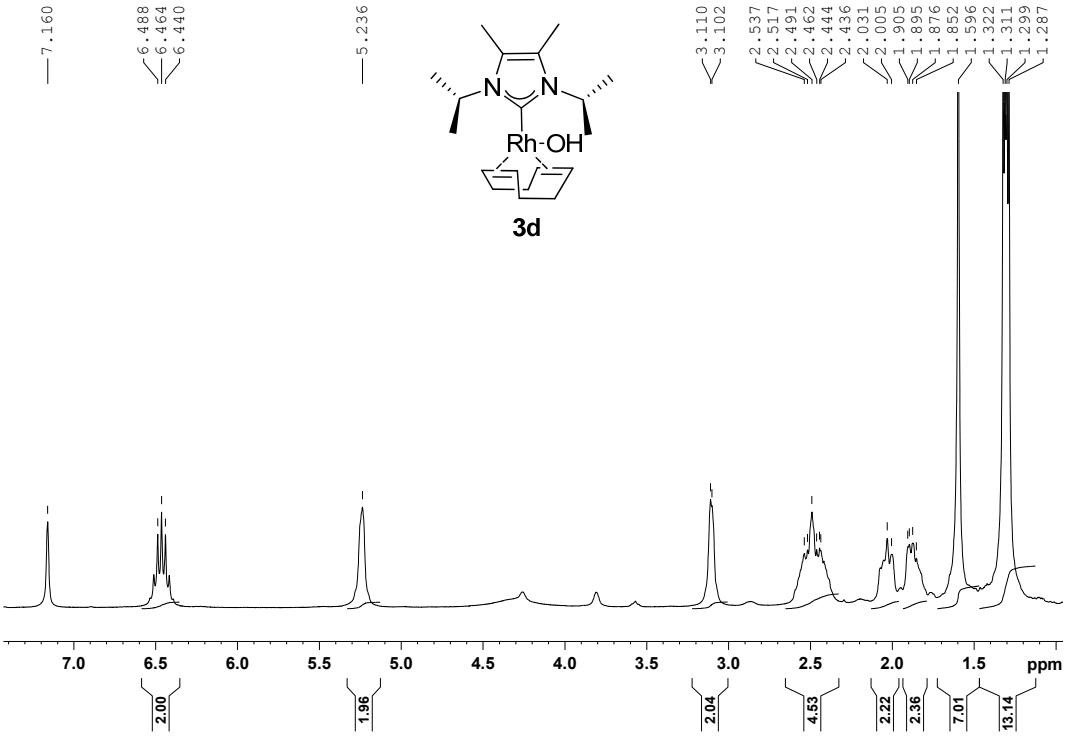

Figure S 1 ^{1}H NMR (300 MHz, C_6D_6) spectrum for complex **3d**

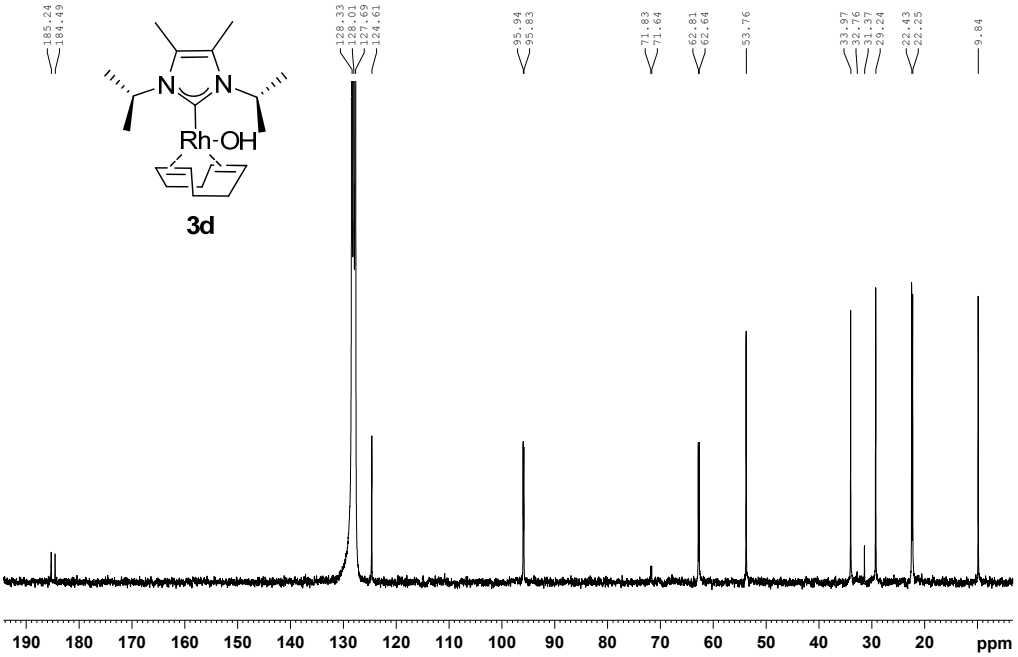

Figure S 2 ^{13}C NMR (75 MHz, C_6D_6) spectrum for complex **3d**

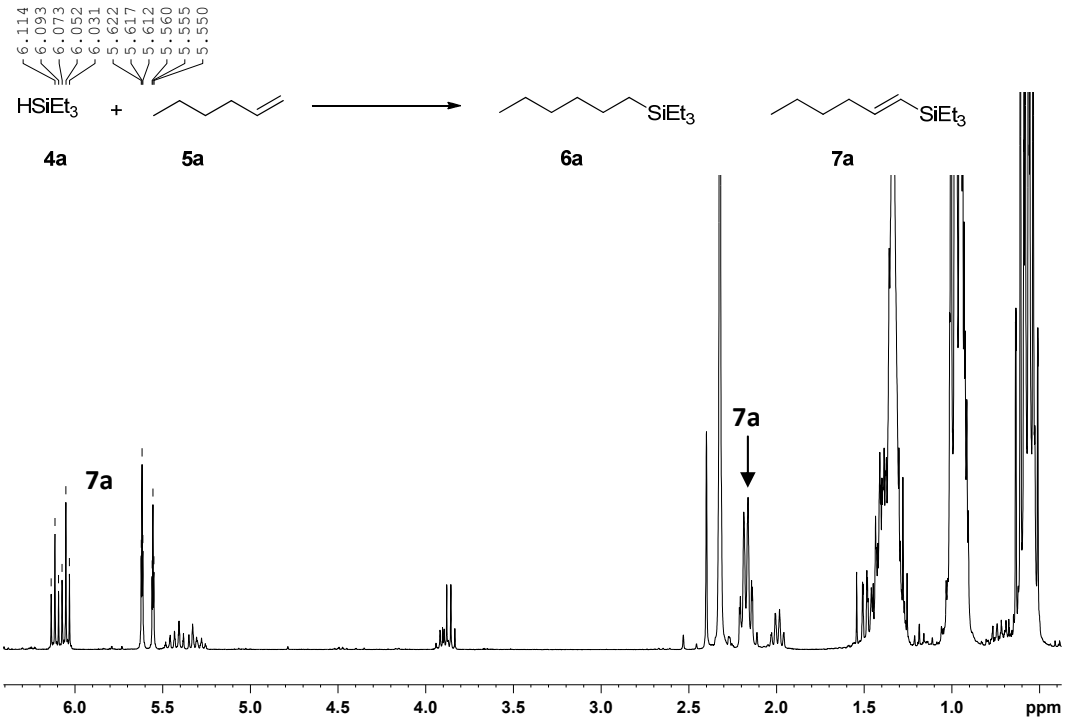

Figure S 3 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiEt_3$ (4a) + 1-hexene **(5a)**

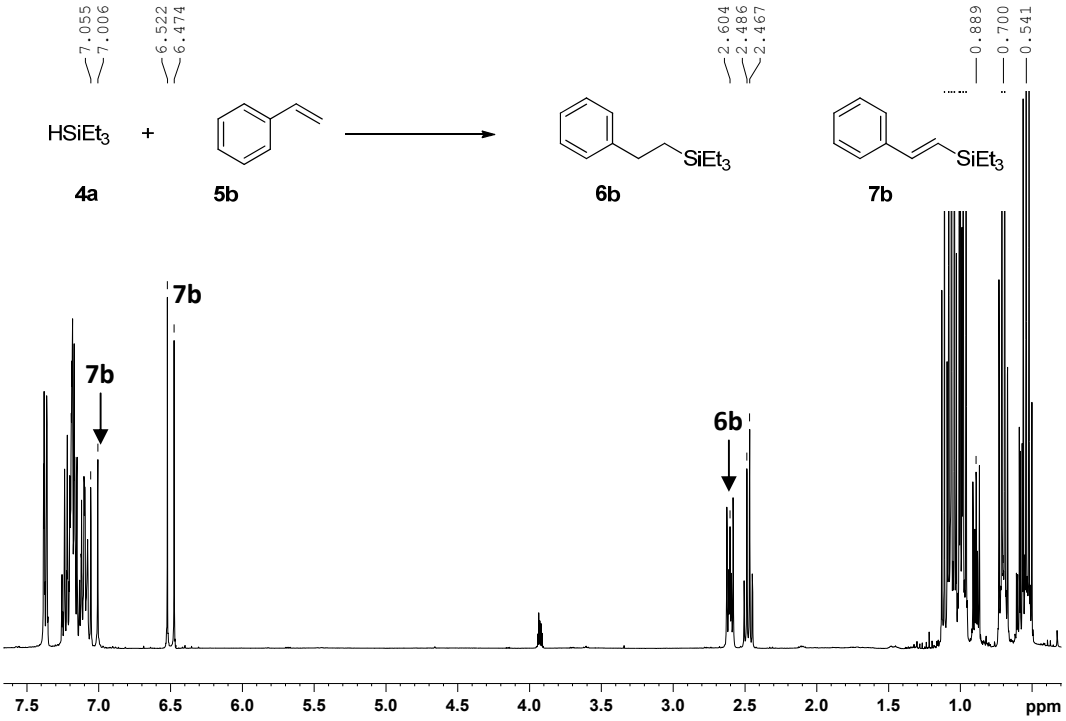

Figure S 4 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiEt_3$ (4a) + styrene **(5b)**

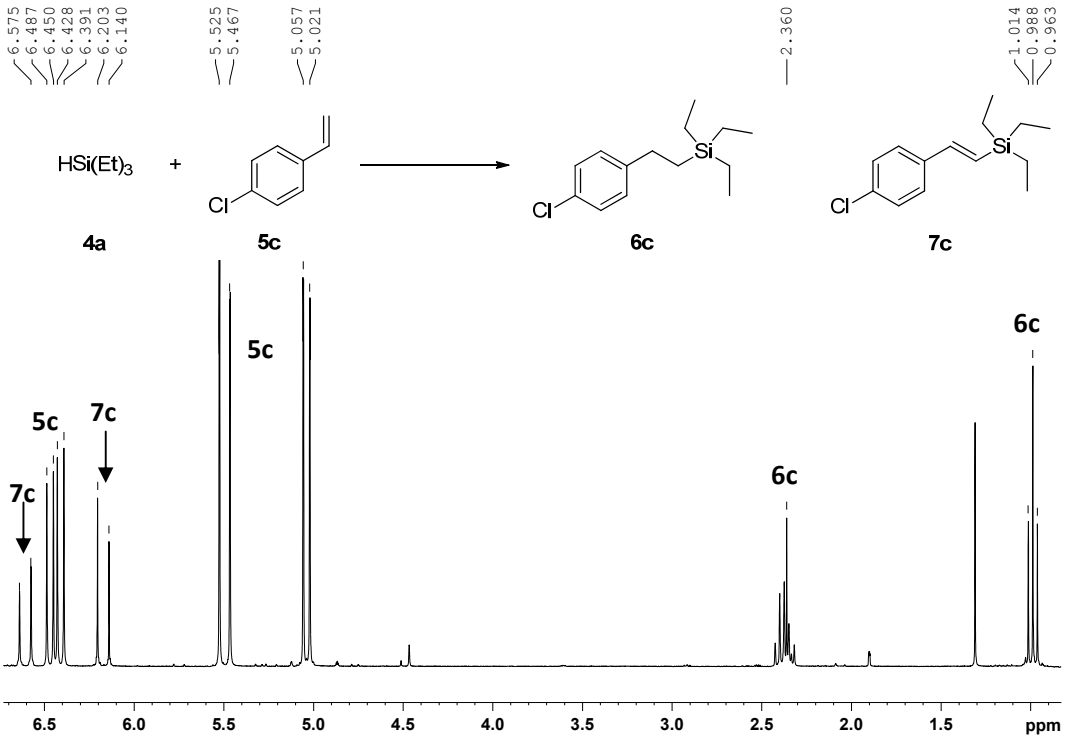

Figure S 5 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiEt_3$ (4a) + 4-chlorostyrene **(5c)**

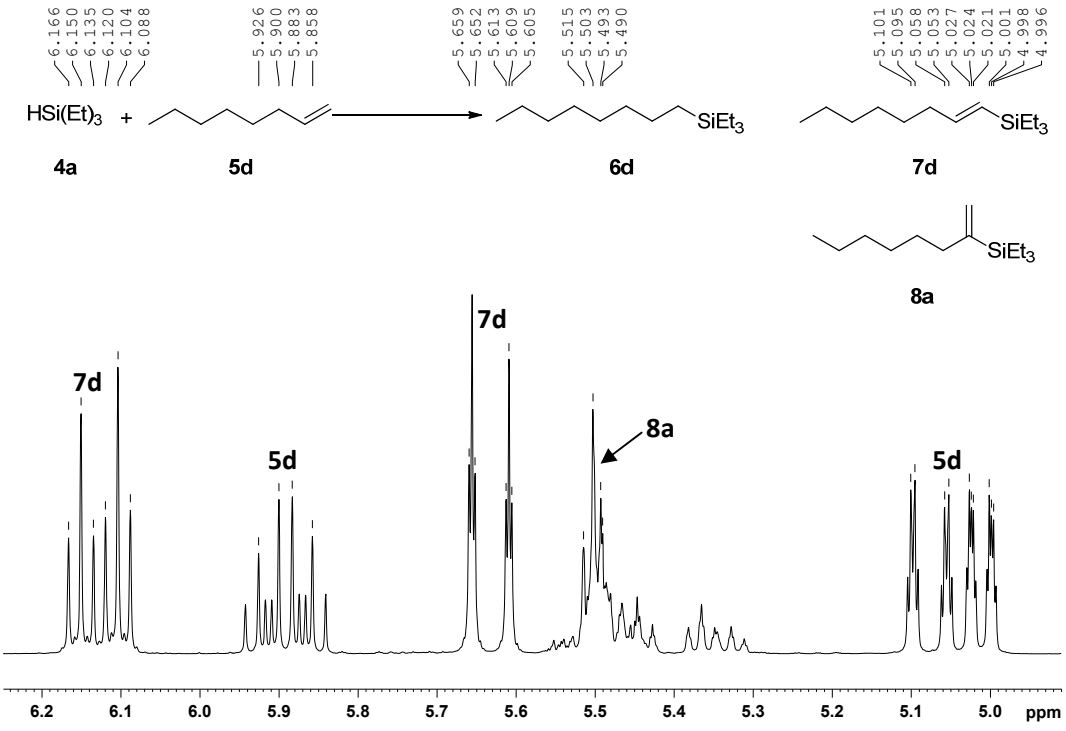

Figure S 6 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiEt_3$ (4a) + 1-octene **(5d)**

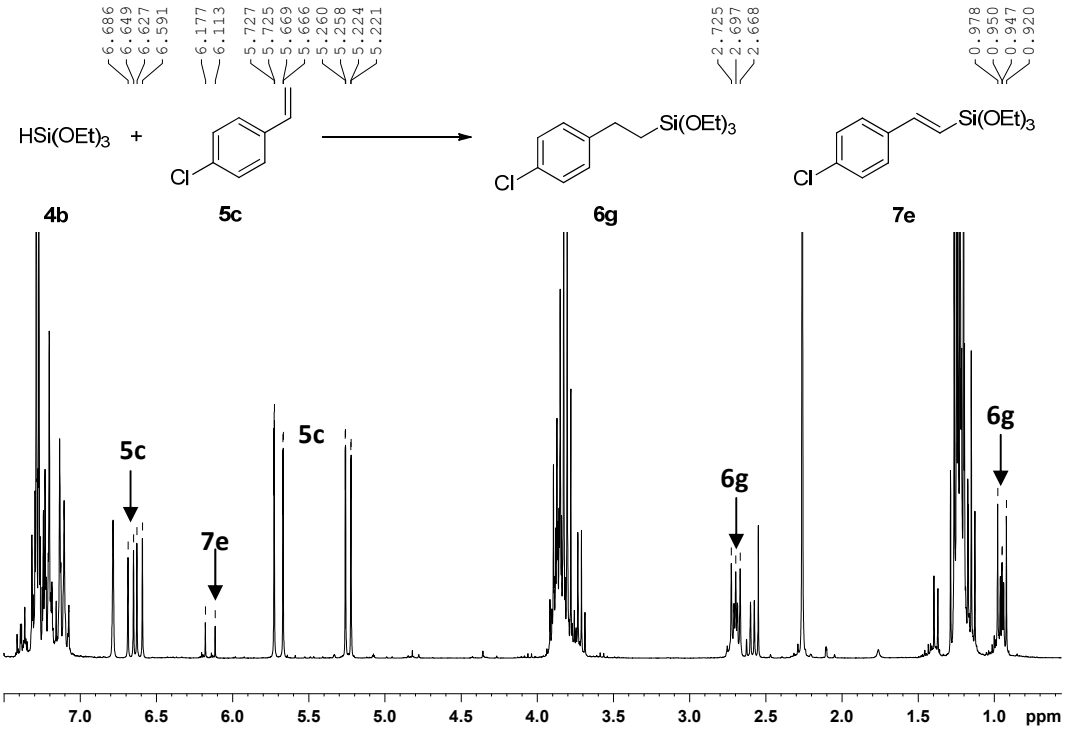

Figure S 7 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSi(OEt)_3$ (4b) + 4-chlorostyrene **(5c)**

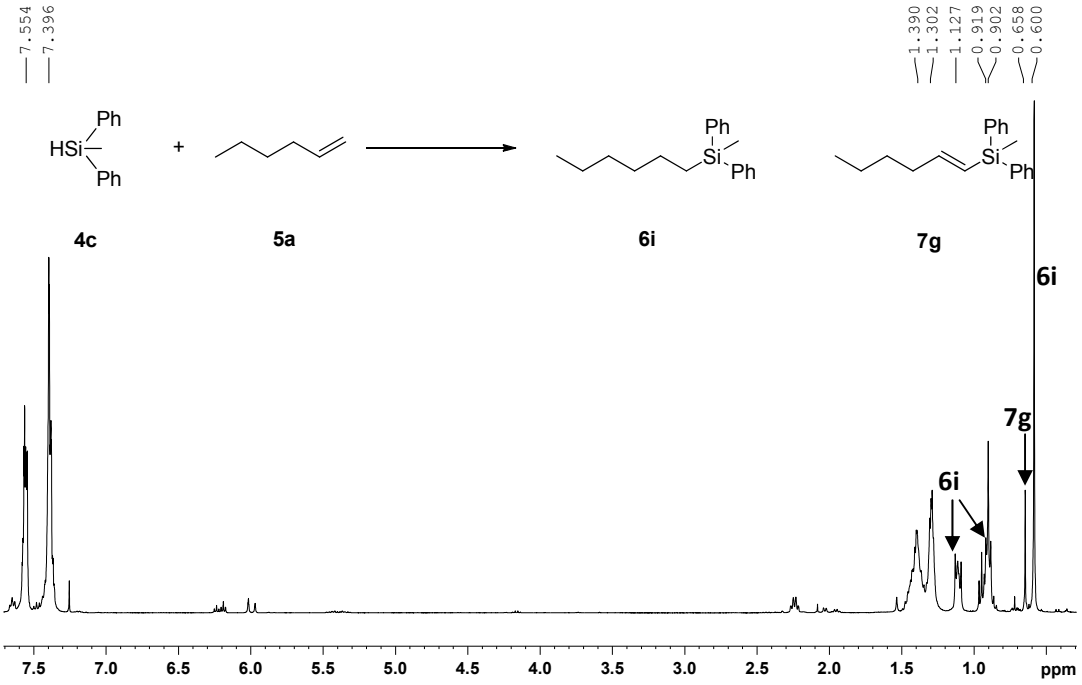

Figure S 8 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiPh_2Me$ (4c) + hexene **(5a)**

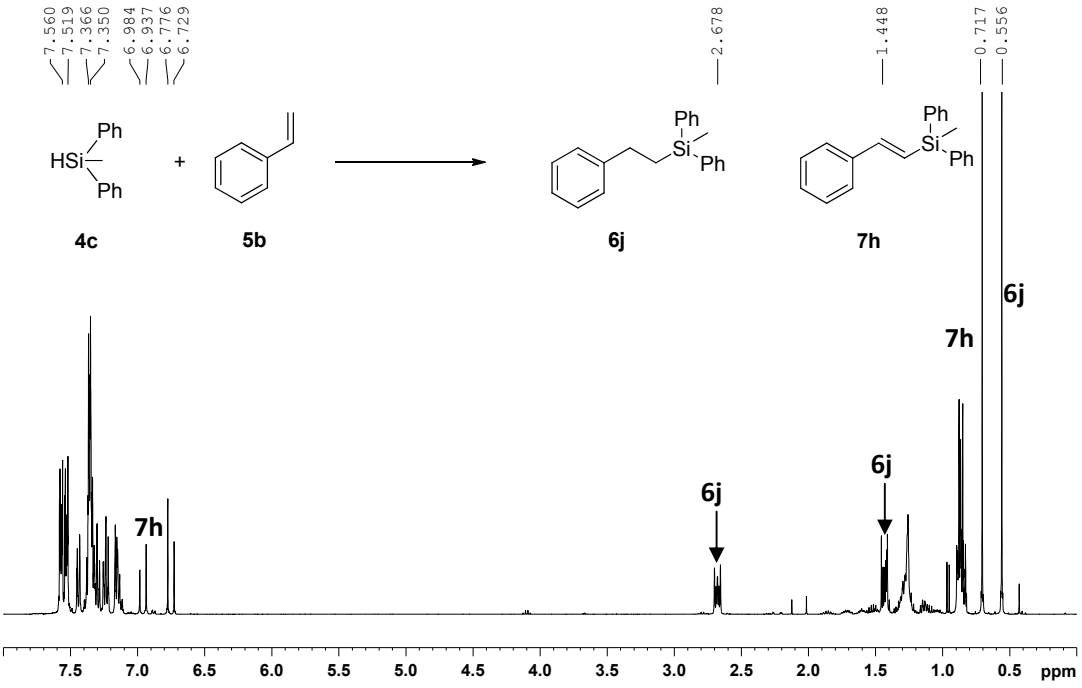

Figure S 9 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiPh_2Me$ (4c) + styrene **(5b)**

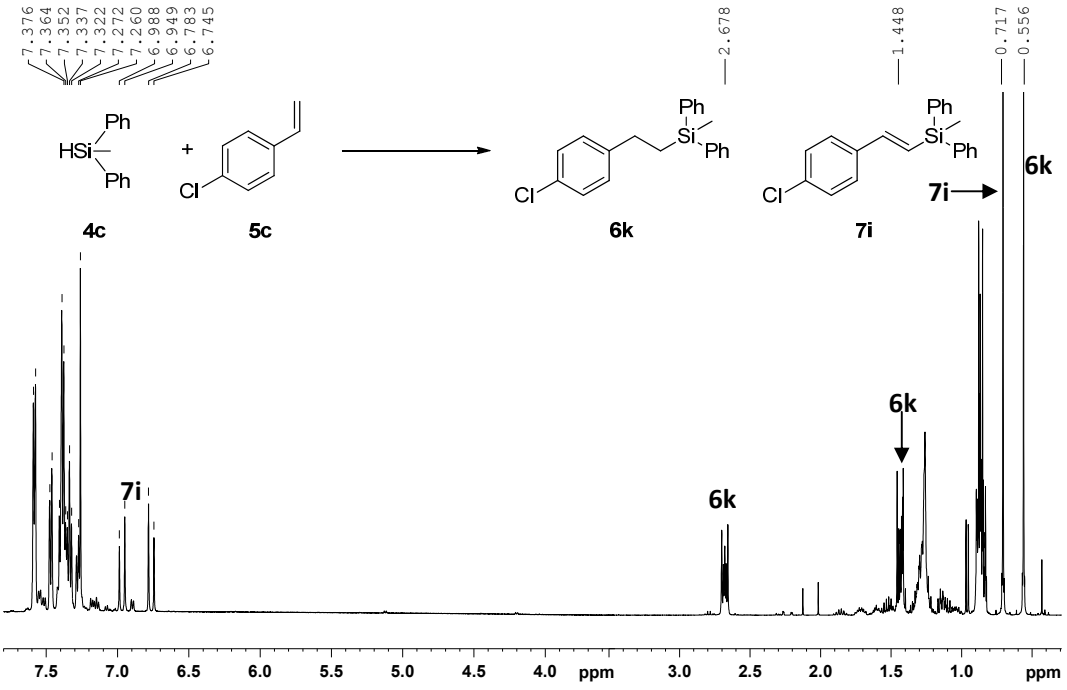

Figure S 10 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiPh_2Me$ (**4c**) + chlorostyrene (**5c**)

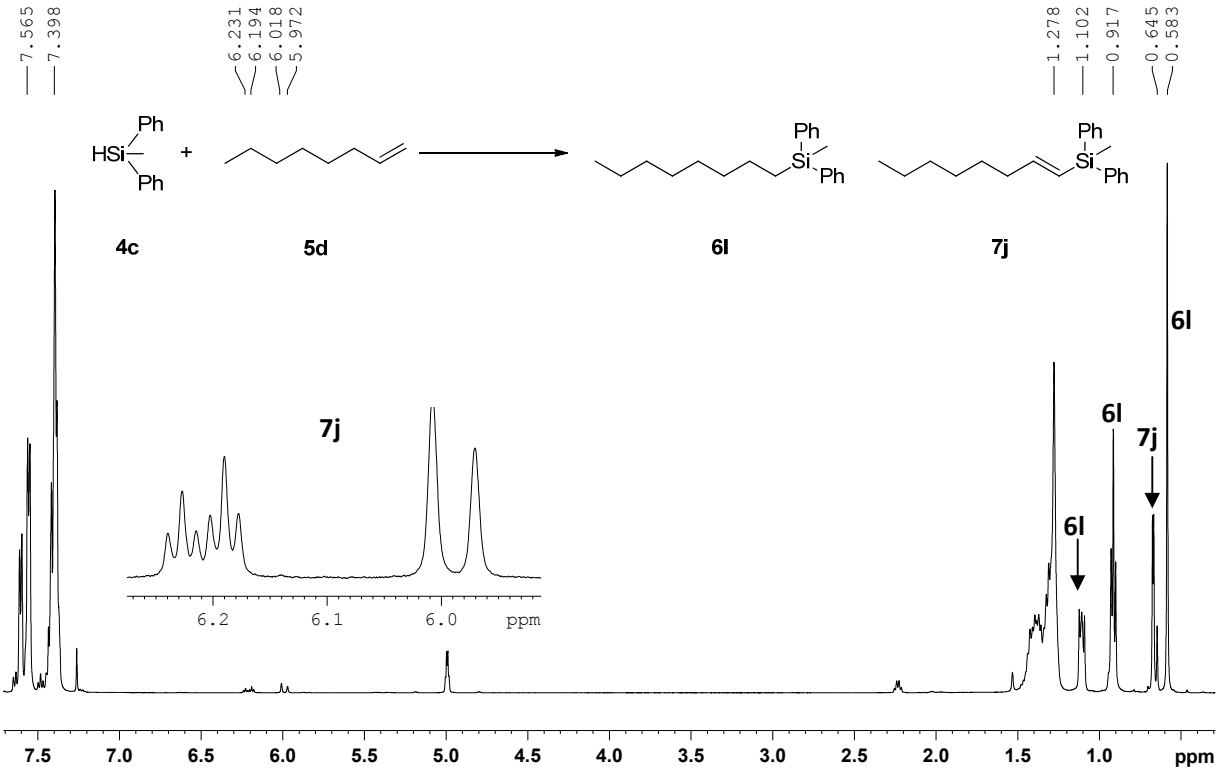

Figure S 11 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for the reaction $HSiPh_2Me$ (**4c**) + octene (**5d**)

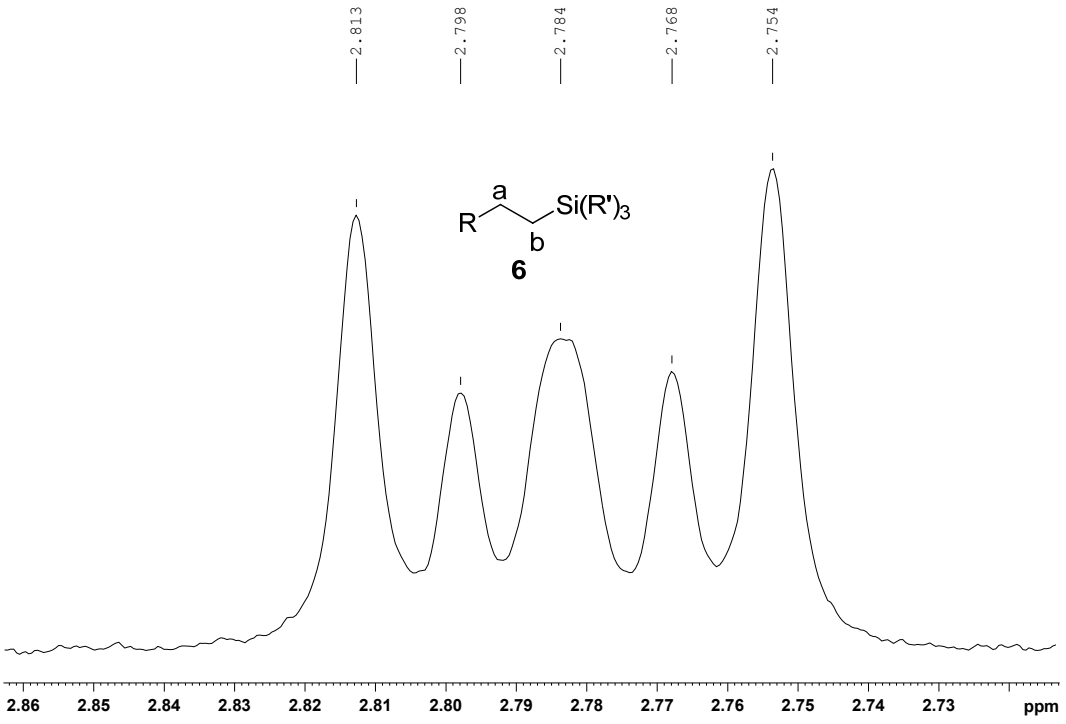

Figure S 12 ^{1}H NMR (300 MHz, $CDCl_3$) expanded region showing the splitting pattern for all CH_2 signals (a and b) of alkylsilane products **(6a-n)**

Single crystal x-ray diffraction data

Table S 9 Bond Lengths (Å) for [Ir(cod)(IDD)(OH)] **(3c)**

Rh(1)-O(1)	2.024(6)	C(11)-C(12)	1.538(5)
Rh(1)-C(1)	2.054(8)	C(11)-H(11A)	0.9900
Rh(1)-C(31)	2.109(8)	C(11)-H(11B)	0.9900
Rh(1)-C(32)	2.126(8)	C(12)-C(13)	1.533(5)
Rh(1)-C(35)	2.187(8)	C(12)-H(12A)	0.9900
Rh(1)-C(36)	2.210(8)	C(12)-H(12B)	0.9900
O(1)-H(1O)	0.9801	C(13)-C(14)	1.534(5)
C(1)-N(2)	1.356(10)	C(13)-H(13A)	0.9900
C(1)-N(5)	1.359(10)	C(13)-H(13B)	0.9900
N(2)-C(3)	1.391(10)	C(14)-C(15)	1.541(5)
N(2)-C(6)	1.465(10)	C(14)-H(14A)	0.9900
C(3)-C(4)	1.330(11)	C(14)-H(14B)	0.9900
C(3)-H(3A)	0.9500	C(15)-C(16)	1.530(5)
C(4)-N(5)	1.380(10)	C(15)-H(15A)	0.9900
C(4)-H(4A)	0.9500	C(15)-H(15B)	0.9900
N(5)-C(18)	1.470(10)	C(16)-C(17)	1.529(5)
C(6)-C(7)	1.526(5)	C(16)-H(16A)	0.9900
C(6)-C(17)	1.545(5)	C(16)-H(16B)	0.9900
C(6)-H(6A)	1.0000	C(17)-H(17A)	0.9900
C(7)-C(8)	1.527(5)	C(17)-H(17B)	0.9900
C(7)-H(7A)	0.9900	C(18)-C(19)	1.536(5)
C(7)-H(7B)	0.9900	C(18)-C(29)	1.547(5)
C(8)-C(9)	1.538(5)	C(18)-H(18A)	1.0000
C(8)-H(8A)	0.9900	C(19)-C(20)	1.534(5)
C(8)-H(8B)	0.9900	C(19)-H(19A)	0.9900
C(9)-C(10)	1.532(5)	C(19)-H(19B)	0.9900
C(9)-H(9A)	0.9900	C(20)-C(21)	1.544(5)
C(9)-H(9B)	0.9900	C(20)-H(20A)	0.9900
C(10)-C(11)	1.530(5)	C(20)-H(20B)	0.9900
C(10)-H(10A)	0.9900	C(21)-C(22)	1.534(5)
C(10)-H(10B)	0.9900	C(21)-H(21A)	0.9900

C(21)-H(21B)	0.9900	C(29)-H(29A)	0.9900
C(22)-C(23)	1.532(5)	C(29)-H(29B)	0.9900
C(22)-H(22A)	0.9900	C(31)-C(32)	1.418(12)
C(22)-H(22B)	0.9900	C(31)-C(38)	1.509(12)
C(23)-C(24)	1.538(5)	C(31)-H(31A)	0.9500
C(23)-H(23A)	0.9900	C(32)-C(33)	1.530(12)
C(23)-H(23B)	0.9900	C(32)-H(32A)	0.9500
C(24)-C(25)	1.534(5)	C(33)-C(34)	1.526(12)
C(24)-H(24A)	0.9900	C(33)-H(33A)	0.9900
C(24)-H(24B)	0.9900	C(33)-H(33B)	0.9900
C(25)-C(26)	1.533(5)	C(34)-C(35)	1.499(12)
C(25)-H(25A)	0.9900	C(34)-H(34A)	0.9900
C(25)-H(25B)	0.9900	C(34)-H(34B)	0.9900
C(26)-C(27)	1.544(5)	C(35)-C(36)	1.379(12)
C(26)-H(26A)	0.9900	C(35)-H(35A)	0.9500
C(26)-H(26B)	0.9900	C(36)-C(37)	1.493(12)
C(27)-C(28)	1.531(5)	C(36)-H(36A)	0.9500
C(27)-H(27A)	0.9900	C(37)-C(38)	1.522(13)
C(27)-H(27B)	0.9900	C(37)-H(37A)	0.9900
C(28)-C(29)	1.534(5)	C(37)-H(37B)	0.9900
C(28)-H(28A)	0.9900	C(38)-H(38A)	0.9900
C(28)-H(28B)	0.9900	C(38)-H(38B)	0.9900

Table S 10 Bond angles (°) for [Ir(cod)(I*i*-PrMe)(OH] **(3d)**

O(1)-Rh(1)-C(1)	89.4(3)	O(1)-Rh(1)-C(36)	89.5(3)
O(1)-Rh(1)-C(31)	157.0(3)	C(1)-Rh(1)-C(36)	167.4(3)
C(1)-Rh(1)-C(31)	94.4(3)	C(31)-Rh(1)-C(36)	81.8(3)
O(1)-Rh(1)-C(32)	163.1(3)	C(32)-Rh(1)-C(36)	90.4(3)
C(1)-Rh(1)-C(32)	94.2(3)	C(35)-Rh(1)-C(36)	36.6(3)
C(31)-Rh(1)-C(32)	39.1(3)	Rh(1)-O(1)-H(1O)	109.5
O(1)-Rh(1)-C(35)	87.4(3)	N(2)-C(1)-N(5)	104.4(6)
C(1)-Rh(1)-C(35)	155.9(3)	N(2)-C(1)-Rh(1)	129.2(6)
C(31)-Rh(1)-C(35)	97.8(3)	N(5)-C(1)-Rh(1)	126.3(6)
C(32)-Rh(1)-C(35)	82.6(3)	C(1)-N(2)-C(3)	111.0(6)

C(1)-N(2)-C(6)	125.5(7)	C(11)-C(10)-H(10A)	109.0
C(3)-N(2)-C(6)	123.3(6)	C(9)-C(10)-H(10A)	109.0
C(4)-C(3)-N(2)	106.2(7)	C(11)-C(10)-H(10B)	109.0
C(4)-C(3)-H(3A)	126.9	C(9)-C(10)-H(10B)	109.0
N(2)-C(3)-H(3A)	126.9	H(10A)-C(10)-H(10B)	107.8
C(3)-C(4)-N(5)	108.0(7)	C(10)-C(11)-C(12)	120.0(12)
C(3)-C(4)-H(4A)	126.0	C(10)-C(11)-H(11A)	107.3
N(5)-C(4)-H(4A)	126.0	C(12)-C(11)-H(11A)	107.3
C(1)-N(5)-C(4)	110.3(7)	C(10)-C(11)-H(11B)	107.3
C(1)-N(5)-C(18)	126.2(7)	C(12)-C(11)-H(11B)	107.3
C(4)-N(5)-C(18)	123.2(7)	H(11A)-C(11)-H(11B)	106.9
C(7)-C(6)-N(2)	110.4(8)	C(13)-C(12)-C(11)	107.9(13)
C(7)-C(6)-C(17)	112.1(9)	C(13)-C(12)-H(12A)	110.1
N(2)-C(6)-C(17)	106.5(7)	C(11)-C(12)-H(12A)	110.1
C(7)-C(6)-H(6A)	109.2	C(13)-C(12)-H(12B)	110.1
N(2)-C(6)-H(6A)	109.2	C(11)-C(12)-H(12B)	110.1
C(17)-C(6)-H(6A)	109.2	H(12A)-C(12)-H(12B)	108.4
C(8)-C(7)-C(6)	111.9(9)	C(14)-C(13)-C(12)	111.7(13)
C(8)-C(7)-H(7A)	109.2	C(14)-C(13)-H(13A)	109.3
C(6)-C(7)-H(7A)	109.2	C(12)-C(13)-H(13A)	109.3
C(8)-C(7)-H(7B)	109.2	C(14)-C(13)-H(13B)	109.3
C(6)-C(7)-H(7B)	109.2	C(12)-C(13)-H(13B)	109.3
H(7A)-C(7)-H(7B)	107.9	H(13A)-C(13)-H(13B)	107.9
C(7)-C(8)-C(9)	118.7(9)	C(13)-C(14)-C(15)	116.4(11)
C(7)-C(8)-H(8A)	107.6	C(13)-C(14)-H(14A)	108.2
C(9)-C(8)-H(8A)	107.6	C(15)-C(14)-H(14A)	108.2
C(7)-C(8)-H(8B)	107.6	C(13)-C(14)-H(14B)	108.2
C(9)-C(8)-H(8B)	107.6	C(15)-C(14)-H(14B)	108.2
H(8A)-C(8)-H(8B)	107.1	H(14A)-C(14)-H(14B)	107.3
C(10)-C(9)-C(8)	109.1(10)	C(16)-C(15)-C(14)	106.3(11)
C(10)-C(9)-H(9A)	109.9	C(16)-C(15)-H(15A)	110.5
C(8)-C(9)-H(9A)	109.9	C(14)-C(15)-H(15A)	110.5
C(10)-C(9)-H(9B)	109.9	C(16)-C(15)-H(15B)	110.5
C(8)-C(9)-H(9B)	109.9	C(14)-C(15)-H(15B)	110.5
H(9A)-C(9)-H(9B)	108.3	H(15A)-C(15)-H(15B)	108.7
C(11)-C(10)-C(9)	112.9(12)	C(17)-C(16)-C(15)	111.3(10)

C(17)-C(16)-H(16A)	109.4	C(23)-C(22)-H(22A)	109.5
C(15)-C(16)-H(16A)	109.4	C(21)-C(22)-H(22A)	109.5
C(17)-C(16)-H(16B)	109.4	C(23)-C(22)-H(22B)	109.5
C(15)-C(16)-H(16B)	109.4	C(21)-C(22)-H(22B)	109.5
H(16A)-C(16)-H(16B)	108.0	H(22A)-C(22)-H(22B)	108.0
C(16)-C(17)-C(6)	120.0(9)	C(22)-C(23)-C(24)	115.2(8)
C(16)-C(17)-H(17A)	107.3	C(22)-C(23)-H(23A)	108.5
C(6)-C(17)-H(17A)	107.3	C(24)-C(23)-H(23A)	108.5
C(16)-C(17)-H(17B)	107.3	C(22)-C(23)-H(23B)	108.5
C(6)-C(17)-H(17B)	107.3	C(24)-C(23)-H(23B)	108.5
H(17A)-C(17)-H(17B)	106.9	H(23A)-C(23)-H(23B)	107.5
N(5)-C(18)-C(19)	109.0(7)	C(25)-C(24)-C(23)	113.0(9)
N(5)-C(18)-C(29)	109.3(6)	C(25)-C(24)-H(24A)	109.0
C(19)-C(18)-C(29)	112.6(8)	C(23)-C(24)-H(24A)	109.0
N(5)-C(18)-H(18A)	108.6	C(25)-C(24)-H(24B)	109.0
C(19)-C(18)-H(18A)	108.6	C(23)-C(24)-H(24B)	109.0
C(29)-C(18)-H(18A)	108.6	H(24A)-C(24)-H(24B)	107.8
C(20)-C(19)-C(18)	113.1(8)	C(26)-C(25)-C(24)	113.7(10)
C(20)-C(19)-H(19A)	109.0	C(26)-C(25)-H(25A)	108.8
C(18)-C(19)-H(19A)	109.0	C(24)-C(25)-H(25A)	108.8
C(20)-C(19)-H(19B)	109.0	C(26)-C(25)-H(25B)	108.8
C(18)-C(19)-H(19B)	109.0	C(24)-C(25)-H(25B)	108.8
H(19A)-C(19)-H(19B)	107.8	H(25A)-C(25)-H(25B)	107.7
C(19)-C(20)-C(21)	115.9(8)	C(25)-C(26)-C(27)	115.3(9)
C(19)-C(20)-H(20A)	108.3	C(25)-C(26)-H(26A)	108.5
C(21)-C(20)-H(20A)	108.3	C(27)-C(26)-H(26A)	108.5
C(19)-C(20)-H(20B)	108.3	C(25)-C(26)-H(26B)	108.5
C(21)-C(20)-H(20B)	108.3	C(27)-C(26)-H(26B)	108.5
H(20A)-C(20)-H(20B)	107.4	H(26A)-C(26)-H(26B)	107.5
C(22)-C(21)-C(20)	110.6(8)	C(28)-C(27)-C(26)	109.8(8)
C(22)-C(21)-H(21A)	109.5	C(28)-C(27)-H(27A)	109.7
C(20)-C(21)-H(21A)	109.5	C(26)-C(27)-H(27A)	109.7
C(22)-C(21)-H(21B)	109.5	C(28)-C(27)-H(27B)	109.7
C(20)-C(21)-H(21B)	109.5	C(26)-C(27)-H(27B)	109.7
H(21A)-C(21)-H(21B)	108.1	H(27A)-C(27)-H(27B)	108.2
C(23)-C(22)-C(21)	110.9(8)	C(27)-C(28)-C(29)	111.5(8)

C(27)-C(28)-H(28A)	109.3	C(35)-C(34)-H(34A)	108.7
C(29)-C(28)-H(28A)	109.3	C(33)-C(34)-H(34A)	108.7
C(27)-C(28)-H(28B)	109.3	C(35)-C(34)-H(34B)	108.7
C(29)-C(28)-H(28B)	109.3	C(33)-C(34)-H(34B)	108.7
H(28A)-C(28)-H(28B)	108.0	H(34A)-C(34)-H(34B)	107.6
C(28)-C(29)-C(18)	116.4(7)	C(36)-C(35)-C(34)	125.6(8)
C(28)-C(29)-H(29A)	108.2	C(36)-C(35)-Rh(1)	72.7(5)
C(18)-C(29)-H(29A)	108.2	C(34)-C(35)-Rh(1)	107.7(5)
C(28)-C(29)-H(29B)	108.2	C(36)-C(35)-H(35A)	117.2
C(18)-C(29)-H(29B)	108.2	C(34)-C(35)-H(35A)	117.2
H(29A)-C(29)-H(29B)	107.3	Rh(1)-C(35)-H(35A)	89.7
C(32)-C(31)-C(38)	125.9(8)	C(35)-C(36)-C(37)	123.1(8)
C(32)-C(31)-Rh(1)	71.1(5)	C(35)-C(36)-Rh(1)	70.8(5)
C(38)-C(31)-Rh(1)	109.1(6)	C(37)-C(36)-Rh(1)	111.2(5)
C(32)-C(31)-H(31A)	117.0	C(35)-C(36)-H(36A)	118.5
C(38)-C(31)-H(31A)	117.0	C(37)-C(36)-H(36A)	118.5
Rh(1)-C(31)-H(31A)	89.8	Rh(1)-C(36)-H(36A)	88.1
C(31)-C(32)-C(33)	122.7(8)	C(36)-C(37)-C(38)	112.0(7)
C(31)-C(32)-Rh(1)	69.8(5)	C(36)-C(37)-H(37A)	109.2
C(33)-C(32)-Rh(1)	112.2(6)	C(38)-C(37)-H(37A)	109.2
C(31)-C(32)-H(32A)	118.7	C(36)-C(37)-H(37B)	109.2
C(33)-C(32)-H(32A)	118.7	C(38)-C(37)-H(37B)	109.2
Rh(1)-C(32)-H(32A)	88.0	H(37A)-C(37)-H(37B)	107.9
C(34)-C(33)-C(32)	113.0(7)	C(31)-C(38)-C(37)	114.4(7)
C(34)-C(33)-H(33A)	109.0	C(31)-C(38)-H(38A)	108.7
C(32)-C(33)-H(33A)	109.0	C(37)-C(38)-H(38A)	108.7
C(34)-C(33)-H(33B)	109.0	C(31)-C(38)-H(38B)	108.7
C(32)-C(33)-H(33B)	109.0	C(37)-C(38)-H(38B)	108.7
H(33A)-C(33)-H(33B)	107.8	H(38A)-C(38)-H(38B)	107.6
C(35)-C(34)-C(33)	114.3(7)		

Table S 11 Bond Lengths (Å) for [Ir(cod)(IDD)(OH)] **(3c)**

Rh(1)-C(1)	2.044(3)	C(10)-H(10C)	0.9800
Rh(1)-O(1)	2.074(3)	C(11)-C(13)	1.519(5)
Rh(1)-C(22)	2.097(4)	C(11)-C(12)	1.528(5)
Rh(1)-C(21)	2.131(4)	C(11)-H(11A)	1.0000
Rh(1)-C(26)	2.185(4)	C(12)-H(12A)	0.9800
Rh(1)-C(25)	2.198(3)	C(12)-H(12B)	0.9800
O(1)-H(1O)	0.9798(11)	C(12)-H(12C)	0.9800
C(1)-N(2)	1.362(5)	C(13)-H(13A)	0.9800
C(1)-N(5)	1.367(5)	C(13)-H(13B)	0.9800
N(2)-C(3)	1.408(5)	C(13)-H(13C)	0.9800
N(2)-C(6)	1.481(5)	C(21)-C(22)	1.395(5)
C(3)-C(4)	1.326(5)	C(21)-C(28)	1.530(5)
C(3)-C(9)	1.506(5)	C(21)-H(21A)	0.9500
C(4)-N(5)	1.411(4)	C(22)-C(23)	1.512(6)
C(4)-C(10)	1.502(5)	C(22)-H(22A)	0.9500
N(5)-C(11)	1.466(5)	C(23)-C(24)	1.540(6)
C(6)-C(8)	1.524(5)	C(23)-H(23A)	0.9900
C(6)-C(7)	1.529(5)	C(23)-H(23B)	0.9900
C(6)-H(6A)	1.0000	C(24)-C(25)	1.509(6)
C(7)-H(7A)	0.9800	C(24)-H(24A)	0.9900
C(7)-H(7B)	0.9800	C(24)-H(24B)	0.9900
C(7)-H(7C)	0.9800	C(25)-C(26)	1.371(6)
C(8)-H(8A)	0.9800	C(25)-H(25A)	0.9500
C(8)-H(8B)	0.9800	C(26)-C(27)	1.515(6)
C(8)-H(8C)	0.9800	C(26)-H(26A)	0.9500
C(9)-H(9A)	0.9800	C(27)-C(28)	1.523(6)
C(9)-H(9B)	0.9800	C(27)-H(27A)	0.9900
C(9)-H(9C)	0.9800	C(27)-H(27C)	0.9900
C(10)-H(10A)	0.9800	C(28)-H(28C)	0.9900
C(10)-H(10B)	0.9800	C(28)-H(28A)	0.9900

Table S 12 Bond Lengths (Å) for [Ir(cod)(IDD)(OH)] **(3c)**

C(1)-Rh(1)-O(1)	90.53(13)	C(8)-C(6)-C(7)	112.7(3)
C(1)-Rh(1)-C(22)	90.56(14)	N(2)-C(6)-H(6A)	106.4
O(1)-Rh(1)-C(22)	155.02(15)	C(8)-C(6)-H(6A)	106.4
C(1)-Rh(1)-C(21)	95.15(14)	C(7)-C(6)-H(6A)	106.4
O(1)-Rh(1)-C(21)	165.51(14)	C(6)-C(7)-H(7A)	109.5
C(22)-Rh(1)-C(21)	38.51(15)	C(6)-C(7)-H(7B)	109.5
C(1)-Rh(1)-C(26)	161.63(17)	H(7A)-C(7)-H(7B)	109.5
O(1)-Rh(1)-C(26)	88.90(14)	C(6)-C(7)-H(7C)	109.5
C(22)-Rh(1)-C(26)	97.64(16)	H(7A)-C(7)-H(7C)	109.5
C(21)-Rh(1)-C(26)	81.51(15)	H(7B)-C(7)-H(7C)	109.5
C(1)-Rh(1)-C(25)	161.88(16)	C(6)-C(8)-H(8A)	109.5
O(1)-Rh(1)-C(25)	88.72(14)	C(6)-C(8)-H(8B)	109.5
C(22)-Rh(1)-C(25)	82.64(15)	H(8A)-C(8)-H(8B)	109.5
C(21)-Rh(1)-C(25)	89.95(15)	C(6)-C(8)-H(8C)	109.5
C(26)-Rh(1)-C(25)	36.46(16)	H(8A)-C(8)-H(8C)	109.5
Rh(1)-O(1)-H(1O)	104(3)	H(8B)-C(8)-H(8C)	109.5
N(2)-C(1)-N(5)	105.5(3)	C(3)-C(9)-H(9A)	109.5
N(2)-C(1)-Rh(1)	127.9(3)	C(3)-C(9)-H(9B)	109.5
N(5)-C(1)-Rh(1)	126.6(3)	H(9A)-C(9)-H(9B)	109.5
C(1)-N(2)-C(3)	109.9(3)	C(3)-C(9)-H(9C)	109.5
C(1)-N(2)-C(6)	120.8(3)	H(9A)-C(9)-H(9C)	109.5
C(3)-N(2)-C(6)	128.7(3)	H(9B)-C(9)-H(9C)	109.5
C(4)-C(3)-N(2)	107.4(3)	C(4)-C(10)-H(10A)	109.5
C(4)-C(3)-C(9)	128.5(3)	C(4)-C(10)-H(10B)	109.5
N(2)-C(3)-C(9)	124.0(3)	H(10A)-C(10)-H(10B)	109.5
C(3)-C(4)-N(5)	107.5(3)	C(4)-C(10)-H(10C)	109.5
C(3)-C(4)-C(10)	128.6(3)	H(10A)-C(10)-H(10C)	109.5
N(5)-C(4)-C(10)	123.9(3)	H(10B)-C(10)-H(10C)	109.5
C(1)-N(5)-C(4)	109.6(3)	N(5)-C(11)-C(13)	112.5(3)
C(1)-N(5)-C(11)	121.7(3)	N(5)-C(11)-C(12)	111.9(3)
C(4)-N(5)-C(11)	128.8(3)	C(13)-C(11)-C(12)	113.2(3)
N(2)-C(6)-C(8)	110.9(3)	N(5)-C(11)-H(11A)	106.2
N(2)-C(6)-C(7)	113.5(3)	C(13)-C(11)-H(11A)	106.2

C(12)-C(11)-H(11A)	106.2	C(25)-C(24)-C(23)	112.9(3)
C(11)-C(12)-H(12A)	109.5	C(25)-C(24)-H(24A)	109.0
C(11)-C(12)-H(12B)	109.5	C(23)-C(24)-H(24A)	109.0
H(12A)-C(12)-H(12B)	109.5	C(25)-C(24)-H(24B)	109.0
C(11)-C(12)-H(12C)	109.5	C(23)-C(24)-H(24B)	109.0
H(12A)-C(12)-H(12C)	109.5	H(24A)-C(24)-H(24B)	107.8
H(12B)-C(12)-H(12C)	109.5	C(26)-C(25)-C(24)	125.3(4)
C(11)-C(13)-H(13A)	109.5	C(26)-C(25)-Rh(1)	71.3(2)
C(11)-C(13)-H(13B)	109.5	C(24)-C(25)-Rh(1)	110.1(2)
H(13A)-C(13)-H(13B)	109.5	C(26)-C(25)-H(25A)	117.3
C(11)-C(13)-H(13C)	109.5	C(24)-C(25)-H(25A)	117.3
H(13A)-C(13)-H(13C)	109.5	Rh(1)-C(25)-H(25A)	88.6
H(13B)-C(13)-H(13C)	109.5	C(25)-C(26)-C(27)	126.0(4)
C(22)-C(21)-C(28)	122.1(3)	C(25)-C(26)-Rh(1)	72.3(2)
C(22)-C(21)-Rh(1)	69.4(2)	C(27)-C(26)-Rh(1)	108.7(2)
C(28)-C(21)-Rh(1)	113.3(2)	C(25)-C(26)-H(26A)	117.0
C(22)-C(21)-H(21A)	119.0	C(27)-C(26)-H(26A)	117.0
C(28)-C(21)-H(21A)	119.0	Rh(1)-C(26)-H(26A)	89.0
Rh(1)-C(21)-H(21A)	87.3	C(26)-C(27)-C(28)	112.9(3)
C(21)-C(22)-C(23)	127.7(3)	C(26)-C(27)-H(27A)	109.0
C(21)-C(22)-Rh(1)	72.0(2)	C(28)-C(27)-H(27A)	109.0
C(23)-C(22)-Rh(1)	108.7(3)	C(26)-C(27)-H(27C)	109.0
C(21)-C(22)-H(22A)	116.1	C(28)-C(27)-H(27C)	109.0
C(23)-C(22)-H(22A)	116.1	H(27A)-C(27)-H(27C)	107.8
Rh(1)-C(22)-H(22A)	89.2	C(27)-C(28)-C(21)	112.1(3)
C(22)-C(23)-C(24)	113.1(4)	C(27)-C(28)-H(28C)	109.2
C(22)-C(23)-H(23A)	108.9	C(21)-C(28)-H(28C)	109.2
C(24)-C(23)-H(23A)	109.0	C(27)-C(28)-H(28A)	109.2
C(22)-C(23)-H(23B)	109.0	C(21)-C(28)-H(28A)	109.2
C(24)-C(23)-H(23B)	109.0	H(28C)-C(28)-H(28A)	107.9
H(23A)-C(23)-H(23B)	107.8		

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