N-Heterocyclic Carbene Rhodium(I) Complexes Containing an Axis of Chirality: Dynamics and Catalysis

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Supplementary Information

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Synthesis: additional experimental and characterization data

Synthesis of 1-benzyl-3-methyl-imidazolium bromide (1a).[1]

In a 100 mL round-bottom flask to a solution of 1-methylimidazole (0.24 mL, 3.0 mmol) in acetonitrile (15 mL), an equivalent molar amount of benzyl bromide (0.36 mL, 3.0 mmol) was added. After stirring for 12 h at room temperature, the solvent was removed under vacuum, and the resulting pale yellow, viscous oil was thoroughly washed with diethyl ether (3 x 10 mL), Etp and hexane. After separation from the washings the oil was kept under vacuum at 40 °C for several hours to yield 0.720 g (Y = 94%) of **1a**. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 10.58 (s, 1H, NCHN), 7.49-7.37 (m, 5H, Ph), 7.30 (bs, 1H, CH_{im}), 7.23 (bs, 1H, CH_{im}), 5.57 (s, 2H, CH_2Ph), 4.08 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9 (NCHN), 132.7 (C_q, Ph), 129.62 (Ph), 129.5 (Ph), 129.0 (Ph), 123.2 (CH_{im}), 121.6 (CH_{im}), 53.6 (CH_2Ph), 36.9 (CH_3). ESI-MS (MeOH, m/z): 173 (100) $[C_{11}H_{13}N_2]^+$; 79 (100), 81 (97) $[Br]^-$.

Synthesis of 1,3-dibenzyl-imidazolium bromide (1b).[2]

In a 100 mL round-bottom flask to a solution of 1-benzylimidazole (0.48 g, 3.0 mmol) in acetonitrile (15 mL), an equivalent molar amount of benzyl bromide (0.36 mL, 3.0 mmol) was added. After stirring for 12 h at room temperature, the solvent was removed under vacuum, and the resulting pale yellow, viscous oil was thoroughly washed with diethyl ether (10 mL) and Etp (10 mL). After separation from the washings the oil was kept under vacuum at 40 °C for several hours to yield 0.98 g (Y = 99%) of **1b**. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 10.59 (s, 1H, NCHN), 7.43 (m, 4H, Ph), 7.41 (d, 2H, $J_{H,H}$ = 1.5 Hz, CH_{im}), 7.28 (m, 6H, Ph), 5.50 (s, 4H, CH_2Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.3 (NCHN), 132.8 (C_q, Ph), 129.2 (Ph), 129.1 (Ph), 128.8 (Ph), 122.0 (CH_{im}), 53.0 (CH_2Ph). ESI-MS (MeOH, *m/z*): 249 (100) $[C_{17}H_{17}N_2]^+$; 79 (97), 81 (100) $[Br]^-$.

Synthesis of 1-tert-butylimidazole.[3]

In a 100 mL three-necked flask connected to two dropping funnels and a condenser, was placed 50 mL of distilled water. One dropping funnel contained a mixture of 40% aqueous glyoxal (11.5 mL,

0.10 mol) and 40% aqueous formaldehyde (8.1 mL, 0.10 mol), the other *tert*-butylamine (10.6 mL, 0.10 mol) and 25% aqueous ammonia (6.8 mL, 0.10 mol). The water was heated until boiling, and then both solutions were added simultaneously. The reaction mixture turned brown and was stirred for 30 min at 100 °C after complete addition and then cooled to room temperature. After removal of the water by rotatory evaporator, the crude product was purified via vacuum distillation (bp. 53°C/0.9 mbar) and 1-*tert*-butylimidazole was obtained as a very pale yellow liquid (1.49 g, 12%). ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 7.6 (s, 1H, NCHN), 7.1 (s, 1H, CH_{im}), 7.0 (s, 1H, CH_{im}), 1.6 (s, 9H, CH_3, ^{t}Bu). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 134.3 (NCHN), 129.1 (C_{im}), 116.3 (C_q, ^{t}Bu), 30.6 (CH_3, ^{t}Bu).

Synthesis of 1-benzyl-3-tert-butylimidazolium bromide (1d).[4]

In a Schlenk to a solution of 1-*tert*-butylimidazole (0.17 g, 1.40 mmol) in acetonitrile (5 mL), an equivalent molar amount of benzyl bromide (0.15 mL, 1.40 mmol) was added. After stirring for 48 h at room temperature, the solvent was removed under vacuum, and the resulting white solid was thoroughly washed with diethyl ether (2 x 4 mL). After separation from the washings the solid was kept under vacuum for 1 hour to yield 0.33 g (83%) of 1 h. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 10.66 (s, 1H, NCHN), 7.55 (dd, 1H, $^{3}J_{H,H} \approx {}^{4}J_{H,H}$ = 1.82 Hz, CH_{im}), 7.51 (m, 2H, Ph), 7.45 (dd, 1H, $^{3}J_{H,H} \approx {}^{4}J_{H,H}$ = 1.80 Hz, CH_{im}), 7.25 (m, 3H, Ph), 5.62 (s, 2H, CH_2Ph), (s, 9H, CH_3, ^{t}Bu). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.5 (NCHN), 133.3 (C_q, Ph), 129.0 (Ph), 128.1 (Ph), 122.0 (CH_{im}), 119.8 (CH_{im}), 60.2 (C_q, ^{t}Bu), 52.7 (CH_2Ph), 29.9 (CH_3, ^{t}Bu). ESI-MS (MeOH, *m/z*): 215 (100) $[C_{14}H_{19}N_2]^{+}$; 79 (100), 81 (97) $[Br]^{-}$.

Synthesis of 1-benzyl-3-methyl-imidazolin-2-ylidene silver bromide (2a).[5]

To a solution of **1a** (0.25 g, 0.97 mmol) in CH_2Cl_2 (10 mL) stirred in a Schlenk, Ag_2O (0.15 g, 0.63 mmol) was added. The reaction mixture was stirred for 2 h at room temperature; in the end of the reaction a colorless solution and a small amount of the black solid of Ag_2O was found in the Schlenk, which was subsequently filtered on Celite and the solvent was removed under vacuum to

afford 0.32 g (82%) of a white solid identified as **2a**. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 7.34-7.23 (m, 5H, Ph), 6.98 (d, 1H, $J_{H,H}$ = 1.8 Hz, CH_{im}), 6.93 (d, 1H, $J_{H,H}$ = 1.8 Hz, CH_{im}), 5.28 (s, 2H, CH_2Ph), 3.84 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 181.9 (s, C-Ag), 135.5 (C_q, Ph), 129.1 (Ph), 128.65 (Ph), 127.8 (Ph), 122.5 (CH_{im}), 121.1 (CH_{im}), 55.9 (CH_2Ph), 38.7 (CH_3). ESI-MS (MeOH, *m/z*): 173 (100) $[C_{11}H_{13}N_2]^+$; 451 (45) $[Ag(NHC)_2]^+$.

Synthesis of 1,3-dibenzyl-imidazolin-2-ylidene silver bromide (2b).[6]

To a solution of **1b**, (0.20 g, 0.61 mmol) in CH_2Cl_2 (ca. 10 mL) stirred in a Schlenk, Ag_2O (0.09 g, 0.39 mmol) was added. The reaction mixture was stirred for 2 h at room temperature and then filtered on a Celite pad. The solvent was removed under vacuum to afford 0.28 g (95%) of a white solid identified as **2b**. ^{1}H NMR (399.9 MHz, $CDCl_3$): δ 7.29-7.18 (m, 10 H, Ph), 6.99 (s, 2H, CH_{im}), 5.21 (s, 4H, CH_2Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 180.6 (s, C-Ag), 135.5 (C_q, Ph), 128.8 (Ph), 128.3 (Ph), 127.6 (Ph), 121.62 (C_{im}), 55.33 (CH_2Ph).

Synthesis of 1-benzyl-3-tert-butyl-imidazolin-2-ylidene silver bromide (2d).[7]

To a solution of **1d**, (0.066 g, 0.22 mmol) in CH_2Cl_2 (5 mL) stirred in a Schlenk, (0.026 g, 0.11 mmol) of Ag_2O was added. The suspension was stirred for 48 h and then filtrated on a Celite pad. The solvent was removed under vacuum and the white solid analyzed by NMR analysis. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.32-7.21 (m, 5H, Ph), 7.16 (d, 1H, $J_{H,H}$ = 1.9 Hz, CH_{im}), 6.90 (d, 1H, $J_{H,H}$ = 1.9 Hz, CH_{im}), 5.32 (s, 2H, CH_2Ph), 1.72 (s, 9H, ^{t}Bu). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 178.2 (s, C-Ag), 135.4 (C_q, Ph), 129.0 (Ph), 128.6 (Ph), 127.8 (Ph), 119.4 (CH_{im}), 57.9 (C_q, ^{t}Bu), 56.9 (CH_2Ph), 31.78 (^{t}Bu). ESI-MS (MeOH, *m/z*): 537 (100) $[Ag(NHC)_2]^+$, 321 (50) $[Ag(NHC)]^+$. In the ESI-MS(-) spectrum, no peaks were observed.

Table 1S. The most significant chemical shifts in ^{1}H NMR spectra of the rhodium(I)-NHC complexes **3a-d** acquired at 298 K.

Compounds	C*H*$_{im}$ δ (ppm)	C*H*$_2$Ph δ (ppm)	C*H*$_{NBD}$ δ (ppm)	*CH*$_2$(NBD) δ (ppm)
3a (Me)	6.76 (s) 6.65 (s)	5.72 (s)	4.84 (s) 3.72 (s) 3.36 (br s)	1.30 (m)
3b (Bz)	6.61 (s)	5.73 (br s)	4.78 (s) 3.60 (s) 3.20 (s)	1.20 (br d, $J_{H,H}$ = 1.4 Hz)
3c (Tr)	6.76 (d, $J_{H,H}$ = 2.0 Hz) 6.56 (d, $J_{H,H}$ = 2.0 Hz)	6.84 (d, $J_{H,H}$ = 15.0 Hz) 6.17 (d, $J_{H,H}$ = 15.0 Hz)	4.61 (s) 3.59 (s) 3.44 (s) 3.10 (s) 2.87 (s) 1.94 (s)	0.87 (m)
3d (^{t}Bu)	7.06 (d, $J_{H,H}$ = 2.0 Hz) 6.72 (d, $J_{H,H}$ = 2.0 Hz	6.41 (d, $J_{H,H}$ = 15.0 Hz) 6.27 (d, $J_{H,H}$ = 15.0 Hz)	4.84 (m) 4.70 (m) 3.81 (br s) 3.78 (br s) 3.47 (m)	1.36 (d, $J_{H,H}$ = 8.0 Hz) 1.31 (d, $J_{H,H}$ = 8.0 Hz)

Table 2S. Most significant chemical shifts in ^{13}C NMR spectra of the rhodium(I)-NHC complexes **3a-d** acquired at 298 K.

Compounds	NC*H*N δ (ppm)	C*H*$_{NBD}$ δ (ppm)	*C*^{7}H$_2$(NBD) δ (ppm)
3a	184.8 (d, $J_{C\text{-}Rh}$ = 57.8 Hz)	79.0 (d, $J_{C,Rh}$ = 6.0 Hz) 51.0 (d, $J_{C,Rh}$ = 2.5 Hz) 48.3 (d, $J_{C,Rh}$ = 12.8 Hz)	63.4 (d, $J_{C,Rh}$ = 5.2 Hz)
3b	185.4 (d, $J_{C\text{-}Rh}$ = 58.3 Hz)	79.1 (d, $J_{C,Rh}$ = 5.7 Hz) 51.0 (d, $J_{C,Rh}$ = 2.0 Hz) 48.5 (d, $J_{C,Rh}$ = 17.0 Hz)	63.3 (d, $J_{C,Rh}$ = 5.3 Hz)
3c	186.6 (d, $J_{C\text{-}Rh}$ = 55.1 Hz)	73.1 (s), 49.7 (s), 49.0 (s) 45.7 (d, $J_{C,Rh}$ = 13.0 Hz) 44.7 (d, $J_{C,Rh}$ = 10.8 Hz)	61.8 (d, $J_{C,Rh}$ = 5.8 Hz)
3d	183.0 (d, $J_{C\text{-}Rh}$ = 58.5 Hz)	74.9 (d, $J_{C,Rh}$ = 6.1 Hz) 71.8 (d, $J_{C,Rh}$ = 6.3 Hz) 48.2 (d, $J_{C,Rh}$ = 12.7 Hz) 46.3 (d, $J_{C,Rh}$ = 12.1 Hz)	62.7 (d, $J_{C,Rh}$ = 5.2 Hz)

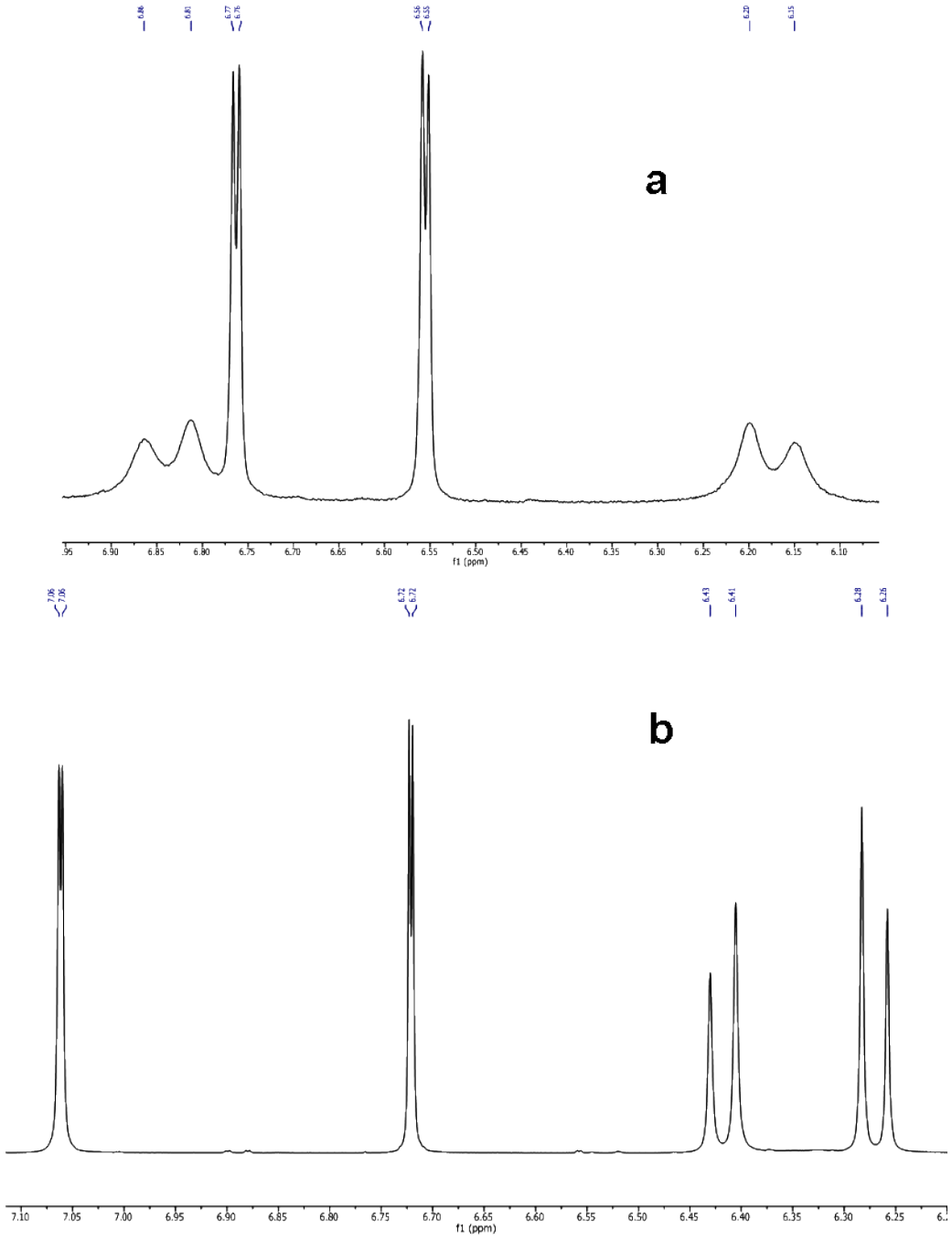


Fig. 1S (**a**) ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K) spectrum of **3c**; (**b**) ^{1}H NMR (599.7 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

Table 3S Crystal data, data collection and refinement parameters for **2b**, **3a** and **3b**.

	2b	**3a**	**3b**
formula	$C_{34}H_{32}AgBrN_4$	$C_{18}H_{20}ClN_2Rh$	$C_{24}H_{24}ClN_2Rh$
fw	684.42	402.72	478.81
T, K	296(2)	296(2)	296(2)
λ, Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	13.3816(14)	10.5190 (6)	11.3295(6)
b, Å	9.8169(11)	10.7555(6)	10.5864(6)
c, Å	23.974(3)	14.8470(9)	18.0379(9)
α, deg	90	90	90
β, deg	104.4500(10)	90.5320(10)	106.8260(10)
γ, deg	90	90	90
cell volume, $Å^3$	3049.8(6)	1679.67(17)	2070.82(19)
Z	4	4	4
D_c, g cm^{-3}	1.491	1.593	0.965
μ, mm^{-1}	2.000	1.173	0.965
F(000)	1384	816	1.536
crystal size, mm	0.20 x 0.15 x 0.12	0.20 x 0.15 x 0.10	0.25 x 0.25 x 0.10
θ limits, °	1.60 to 24.99	1.94 to 24.99	1.91 to 25.00
index ranges	$-15 \le h \le 15$, $-11 \le k \le 11$, $-28 \le l \le 28$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-17 \le l \le 17$	$-13 \le h \le 13$, $-12 \le k \le 12$, $-21 \le l \le 21$
Reflexions collected	28358	15678	19412
Independent reflections	5368 [R(int) = 0.0301]	2959 [R(int) = 0.0362]	3655 [R(int) = 0.0234]
completeness to θ = 25.00°	100.0%	100.0%	100.0%
data/restraints/parameters	5368 / 0 / 361	2959 / 0 / 200	3655 / 0 / 253
goodness on fit on F^2	1.051	1.051	1.044
R_1 ($I > 2\sigma(I)$)	0.0756	0.0319	0.0218
wR_2 (all data)	0.2494	0.0445	0.0261
largest diff peak and hole, e $Å^{-3}$	2.881 and –2.671	0.800 and –0.313	0.331 and –0.285

Molecular structure of ***2b***

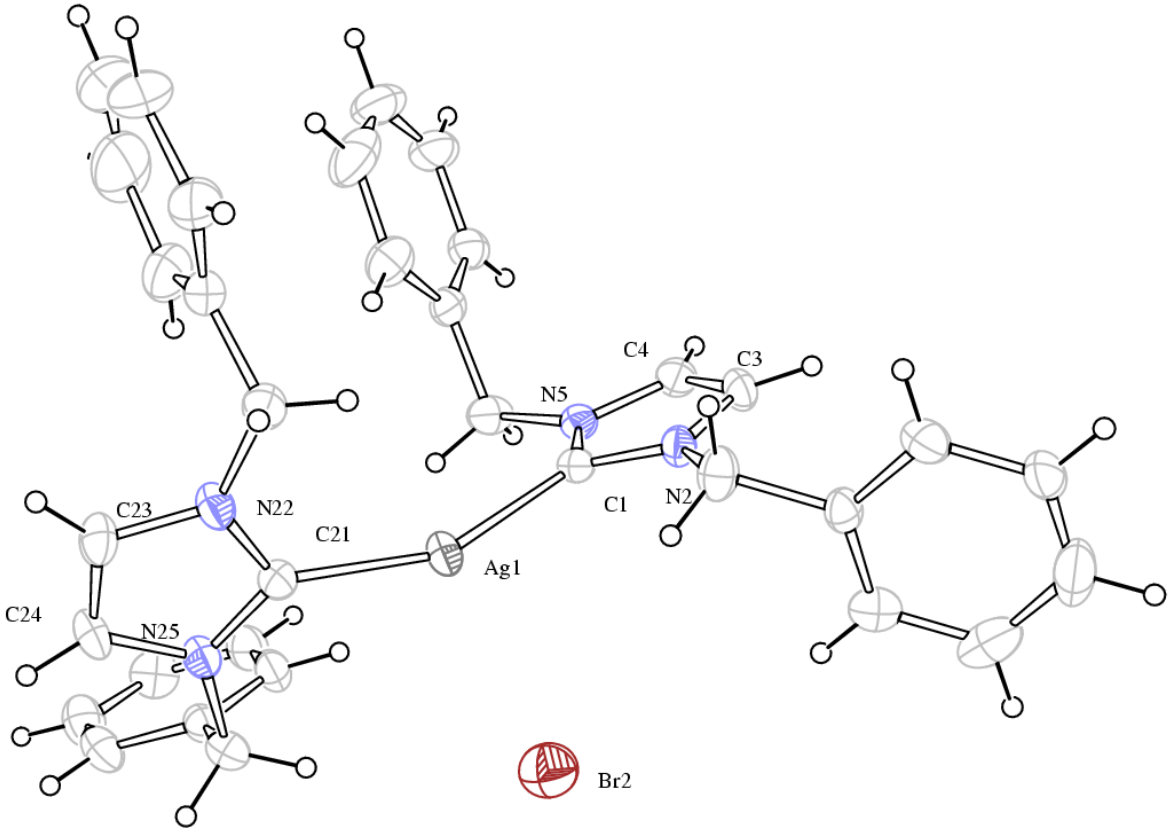


Fig. 2S. Crystal structure of $C_{34}H_{32}AgBrN_4$ (compound **2b**) depicted with thermal ellipsoids at 30% probability.

Table 4S. Most relevant bond lengths (Å) and angles (°) for **3a** and **3b**.

Description		**3a**	**3b**
Rh(1)-C(1)		2.019(4)	2.023(2)
Rh(1)-C(16)	Rh(1)-C(20)	2.083(4)	2.084(2)
Rh(1)-C(20)	Rh(1)-C(21)	2.098(4)	2.091(2)
Rh(1)-C(14)	Rh(1)-C(22)	2.194(4)	2.185(2)
Rh(1)-C(15)	Rh(1)-C(23)	2.213(4)	2.195(2)
Rh(1)-Cl(2)		2.3800(11)	2.3618(6)
C(1)-Rh(1)-C(16)	C(1)-Rh(1)-C(20)	97.00(15)	99.49(9)
C(1)-Rh(1)-C(20)	C(1)-Rh(1)-C(21)	99.27(15)	98.63(9)
C(16)-Rh(1)-C(20)	C(20)-Rh(1)-C(21)	39.25(16)	38.79(10)
C(1)-Rh(1)-C(14)	C(1)-Rh(1)-C(22)	156.71(16)	161.04(10)
C(16)-Rh(1)-C(14)	C(20)-Rh(1)-C(22)	66.99(17)	66.97(10)
C(20)-Rh(1)-C(14)	C(21)-Rh(1)-C(22)	79.23(17)	79.25(10)
C(1)-Rh(1)-C(15)	C(1)-Rh(1)-C(23)	161.52(16)	158.45(9)
C(16)-Rh(1)-C(15)	C(20)-Rh(1)-C(23)	79.41(17)	79.23(10)
C(20)-Rh(1)-C(15)	C(21)-Rh(1)-C(23)	66.44(17)	66.76(10)
C(14)-Rh(1)-C(15)	C(22)-Rh(1)-C(23)	36.44(15)	36.18(10)
C(1)-Rh(1)-Cl(2)	C(1)-Rh(1)-Cl(2)	90.57(10)	90.83(6)
C(16)-Rh(1)-Cl(2)	C(20)-Rh(1)-Cl(2)	156.05(13)	158.26(8)
C(20)-Rh(1)-Cl(2)	C(21)-Rh(1)-Cl(2)	160.57(13)	157.87(8)
C(14)-Rh(1)-Cl(2)	C(22)-Rh(1)-Cl(2)	98.19(13)	97.99(8)
C(15)-Rh(1)-Cl(2)	C(23)-Rh(1)-Cl(2)	100.01(14)	97.99(7)

Computational details

Compound **3a** Ground State

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -931.806133765 A.U. after 1 cycles

Lowest frequency = 25.4913

Zero-point correction= 0.344421

(Hartree/Particle)

Thermal correction to Energy= 0.364776

Thermal correction to Enthalpy= 0.365720

Thermal correction to Gibbs Free Energy= 0.292827

Sum of electronic and zero-point Energies= -931.461713

Sum of electronic and thermal Energies= -931.441358

Sum of electronic and thermal Enthalpies= -931.440414

Sum of electronic and thermal Free Energies= -931.513307

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.273080	0.000580	0.309303
2	17	0	-0.276918	0.235470	2.541669
3	7	0	1.300594	0.987847	-1.056368
4	7	0	0.141206	2.651357	-0.256780
5	6	0	-3.325057	-0.838947	0.917964
6	1	0	-3.575123	-0.457703	1.899992
7	6	0	-2.499972	-1.920484	0.617867

8	1	0	-1.974423	-2.558464	1.317181
9	6	0	-2.784706	0.187624	-1.206393
10	1	0	-2.831138	1.127208	-1.745686
11	6	0	-1.936786	-0.925997	-1.516434
12	1	0	-1.234160	-0.982239	-2.340563
13	6	0	-3.993985	-0.404790	-0.418612
14	1	0	-4.876213	0.230314	-0.334122
15	6	0	-2.642204	-2.178776	-0.910439
16	1	0	-2.301247	-3.149901	-1.270463
17	6	0	-4.146905	-1.796534	-1.123246
18	1	0	-4.838999	-2.468326	-0.600004
19	1	0	-4.421598	-1.712575	-2.182147
20	6	0	0.123377	1.278792	-0.394965
21	6	0	1.303639	3.201291	-0.823873
22	1	0	1.511776	4.258724	-0.813497
23	6	0	2.034618	2.155204	-1.322097
24	1	0	2.999791	2.137908	-1.800626
25	6	0	1.771356	-0.382958	-1.350865
26	1	0	1.917832	-0.482488	-2.434228
27	1	0	0.952079	-1.044653	-1.049533
28	6	0	3.054905	-0.744391	-0.614896
29	6	0	4.197156	-1.147492	-1.335955
30	6	0	3.102699	-0.704376	0.797497
31	6	0	5.379879	-1.508088	-0.660196
32	1	0	4.165165	-1.184556	-2.424284
33	6	0	4.284158	-1.061231	1.469846
34	1	0	2.223991	-0.401812	1.365229
35	6	0	5.425447	-1.463658	0.745368

36	1	0	6.255442	-1.819341	-1.225420
37	1	0	4.312122	-1.029999	2.556304
38	1	0	6.336553	-1.740460	1.270940
39	6	0	-0.893477	3.415040	0.454851
40	1	0	-1.729414	3.659314	-0.210906
41	1	0	-1.256464	2.813382	1.291215
42	1	0	-0.457232	4.340778	0.843122

Compound **3a** Transition State 1

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -931.785192408 A.U. after 1 cycles

Lowest frequency = -23.7718

Zero-point correction= 0.345171 (Hartree/Particle)

Thermal correction to Energy= 0.364326

Thermal correction to Enthalpy= 0.365270

Thermal correction to Gibbs Free Energy= 0.296228

Sum of electronic and zero-point Energies= -931.440021

Sum of electronic and thermal Energies= -931.420867

Sum of electronic and thermal Enthalpies= -931.419923

Sum of electronic and thermal Free Energies= -931.488965

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	45	0	-1.495933	0.036002	-0.009747
2	17	0	-3.372972	1.508994	0.672209
3	7	0	1.314287	1.337181	-0.836315
4	7	0	-0.036314	2.858561	-0.063794
5	6	0	-3.082523	-1.560975	-0.308765
6	1	0	-3.998222	-1.068939	-0.606640
7	6	0	-2.576754	-1.685591	0.989611
8	1	0	-3.027481	-1.317576	1.901739
9	6	0	-0.859277	-1.658995	-1.199163
10	1	0	-0.320248	-1.450737	-2.115826
11	6	0	-0.334666	-1.789642	0.131281
12	1	0	0.698050	-1.715101	0.447828
13	6	0	-2.194848	-2.455277	-1.213744
14	1	0	-2.597881	-2.704694	-2.195401
15	6	0	-1.369798	-2.658998	0.904123
16	1	0	-1.028816	-3.094189	1.843694
17	6	0	-1.854340	-3.624526	-0.229475
18	1	0	-2.735586	-4.213227	0.055474
19	1	0	-1.058685	-4.282826	-0.601121
20	6	0	0.014556	1.488363	-0.328791
21	6	0	1.160439	3.504091	-0.399071
22	1	0	1.300094	4.564096	-0.266070
23	6	0	2.009234	2.551164	-0.881232
24	1	0	3.026788	2.621910	-1.228492
25	6	0	1.990453	0.103460	-1.272861
26	1	0	2.347079	0.248653	-2.300879
27	1	0	1.252607	-0.689035	-1.298100
28	6	0	3.161113	-0.294627	-0.378147

29	6	0	4.338767	-0.811998	-0.955543
30	6	0	3.069734	-0.199500	1.027674
31	6	0	5.408339	-1.236378	-0.143868
32	1	0	4.422671	-0.885163	-2.038897
33	6	0	4.138772	-0.618206	1.839234
34	1	0	2.170506	0.208934	1.483485
35	6	0	5.311011	-1.140268	1.256927
36	1	0	6.311247	-1.633740	-0.601420
37	1	0	4.058360	-0.538512	2.920716
38	1	0	6.136881	-1.463793	1.885796
39	6	0	-1.154506	3.635060	0.507446
40	1	0	-2.002057	3.655457	-0.178289
41	1	0	-1.503529	3.180657	1.433869
42	1	0	-0.794304	4.651701	0.696566

Compound **3a** Transition State 2

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -931.784384124 A.U. after 1 cycles

Lowest frequency = -23.2189

Zero-point correction= 0.344868 (Hartree/Particle)

Thermal correction to Energy= 0.364072

Thermal correction to Enthalpy= 0.365016

Thermal correction to Gibbs Free Energy= 0.295804

Sum of electronic and zero-point Energies= -931.439517

Sum of electronic and thermal Energies= -931.420312

Sum of electronic and thermal Enthalpies= -931.419368

Sum of electronic and thermal Free Energies= -931.488580

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.269262	-0.256598	-0.198275
2	17	0	0.054421	-2.225261	-0.980729
3	7	0	1.534437	1.237965	-0.661000
4	7	0	0.079022	2.622280	0.175446
5	6	0	-2.778134	-1.802202	0.492073
6	1	0	-2.244292	-2.702344	0.763785
7	6	0	-3.131322	-1.389296	-0.797825
8	1	0	-2.931241	-1.909751	-1.725015
9	6	0	-2.726405	0.479028	1.222441
10	1	0	-2.356681	1.078181	2.045454
11	6	0	-3.092516	0.906891	-0.098172
12	1	0	-3.069481	1.911584	-0.497131
13	6	0	-3.502989	-0.844517	1.474351
14	1	0	-3.573345	-1.173767	2.511109
15	6	0	-4.081186	-0.172057	-0.628372
16	1	0	-4.676674	0.103730	-1.498849
17	6	0	-4.829037	-0.566062	0.689733
18	1	0	-5.454406	-1.460657	0.576925
19	1	0	-5.415053	0.259284	1.113982
20	6	0	0.206732	1.284131	-0.228510
21	6	0	1.268673	3.342206	-0.002094

22	1	0	1.358821	4.384970	0.254928
23	6	0	2.179275	2.471193	-0.521994
24	1	0	3.215137	2.609603	-0.782723
25	6	0	2.296274	0.099677	-1.248048
26	1	0	2.694095	0.447304	-2.209681
27	1	0	1.593513	-0.712746	-1.432441
28	6	0	3.431508	-0.364641	-0.347896
29	6	0	4.773530	-0.077353	-0.674727
30	6	0	3.154103	-1.107571	0.821519
31	6	0	5.825444	-0.509969	0.156678
32	1	0	4.999957	0.473161	-1.587455
33	6	0	4.201591	-1.535060	1.655461
34	1	0	2.124333	-1.365045	1.055052
35	6	0	5.540193	-1.236012	1.327843
36	1	0	6.856226	-0.286539	-0.109291
37	1	0	3.978107	-2.111596	2.550180
38	1	0	6.349070	-1.573512	1.972024
39	6	0	-1.119132	3.325937	0.651223
40	1	0	-1.720343	3.684299	-0.191860
41	1	0	-1.725951	2.682906	1.277220
42	1	0	-0.804009	4.189640	1.245323

Compound **3b** Ground State

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1162.82415997 A.U. after 1 cycles

Lowest frequency = 21.4369

Zero-point correction= 0.426602 (Hartree/Particle)

Thermal correction to Energy= 0.451159

Thermal correction to Enthalpy= 0.452103

Thermal correction to Gibbs Free Energy= 0.368312

Sum of electronic and zero-point Energies= -1162.397558

Sum of electronic and thermal Energies= -1162.373001

Sum of electronic and thermal Enthalpies= -1162.372057

Sum of electronic and thermal Free Energies= -1162.455848

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.004494	1.537974	0.266728
2	17	0	-0.000013	0.107623	2.268681
3	7	0	-1.091969	-0.825680	-1.355619
4	7	0	1.087375	-0.831707	-1.355830
5	6	0	0.706396	3.510886	1.222812
6	1	0	1.361428	3.278242	2.052960
7	6	0	-0.686225	3.514821	1.222794
8	1	0	-1.342579	3.285790	2.052902
9	6	0	0.725541	2.992250	-1.142095
10	1	0	1.365027	2.633827	-1.941279
11	6	0	-0.708225	2.996284	-1.142115
12	1	0	-1.349708	2.641528	-1.941335
13	6	0	1.153709	4.110367	-0.141996
14	1	0	2.188224	4.448644	-0.206034

15	6	0	-1.130117	4.116803	-0.142023
16	1	0	-2.162710	4.460894	-0.206093
17	6	0	0.014748	5.161568	-0.376438
18	1	0	0.017019	5.969560	0.365880
19	1	0	0.015928	5.574485	-1.392844
20	6	0	-0.000297	-0.116547	-0.896755
21	6	0	0.678962	-1.965009	-2.079414
22	1	0	1.379539	-2.671895	-2.492184
23	6	0	-0.689975	-1.961228	-2.079277
24	1	0	-1.394538	-2.664194	-2.491955
25	6	0	-2.499637	-0.459400	-1.079626
26	1	0	-2.988948	-0.202265	-2.028307
27	1	0	-2.451470	0.443618	-0.461029
28	6	0	-3.277575	-1.561779	-0.375261
29	6	0	-4.410960	-2.135126	-0.987132
30	6	0	-2.882309	-2.003265	0.907959
31	6	0	-5.145996	-3.142147	-0.330535
32	1	0	-4.723842	-1.794430	-1.973477
33	6	0	-3.614574	-3.009726	1.560477
34	1	0	-2.015241	-1.555360	1.390842
35	6	0	-4.746761	-3.582781	0.944791
36	1	0	-6.020142	-3.577188	-0.809617
37	1	0	-3.306573	-3.341721	2.549004
38	1	0	-5.311266	-4.360080	1.454852
39	6	0	2.497088	-0.473408	-1.079758
40	1	0	2.987915	-0.219120	-2.028424
41	1	0	2.454010	0.429914	-0.461227
42	6	0	3.268638	-1.580147	-0.375245

43	6	0	4.398421	-2.160475	-0.987211
44	6	0	2.871011	-2.018911	0.908179
45	6	0	5.127520	-3.171738	-0.330511
46	1	0	4.713139	-1.821923	-1.973706
47	6	0	3.597348	-3.029591	1.560814
48	1	0	2.006706	-1.565746	1.391110
49	6	0	4.725924	-3.609621	0.945026
50	1	0	5.998915	-3.612168	-0.809673
51	1	0	3.287560	-3.359461	2.549490
52	1	0	5.285842	-4.390175	1.455166

Compound **3b** Transition State 1 = TS2

Method: b3lyp/LanL2DZ O

SCF Done: E(RB3LYP) = -1162.79933611 A.U. after 1 cycles

Lowest frequency = -21.9230

Zero-point correction= 0.427127 (Hartree/Particle)

Thermal correction to Energy= 0.450623

Thermal correction to Enthalpy= 0.451567

Thermal correction to Gibbs Free Energy= 0.370966

Sum of electronic and zero-point Energies= -1162.372209

Sum of electronic and thermal Energies= -1162.348713

Sum of electronic and thermal Enthalpies= -1162.347769

Sum of electronic and thermal Free Energies= -1162.428370

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.138503	1.429270	-0.168248
2	17	0	-1.949883	2.198767	-1.303673
3	7	0	0.542554	-1.642057	0.680235
4	7	0	-1.340068	-1.414625	-0.385725
5	6	0	0.440855	3.620332	0.315901
6	1	0	-0.531175	4.078186	0.437616
7	6	0	1.097123	3.345502	-0.889816
8	1	0	0.736493	3.552415	-1.888567
9	6	0	1.603433	1.815819	1.377090
10	1	0	1.550185	1.204423	2.270059
11	6	0	2.282179	1.532883	0.143228
12	1	0	2.872937	0.661774	-0.108952
13	6	0	1.471520	3.363706	1.446751
14	1	0	1.236083	3.785565	2.423872
15	6	0	2.542494	2.916951	-0.518296
16	1	0	3.277646	2.936287	-1.322836
17	6	0	2.797557	3.808441	0.742870
18	1	0	2.819657	4.881061	0.512250
19	1	0	3.698268	3.518419	1.298897
20	6	0	-0.242265	-0.665291	0.044819
21	6	0	-1.236422	-2.762268	-0.021898
22	1	0	-2.007724	-3.478143	-0.252227
23	6	0	-0.055685	-2.908263	0.641100
24	1	0	0.412235	-3.780009	1.068301
25	6	0	1.874220	-1.509199	1.296737

26	1	0	1.834348	-1.959334	2.296945
27	1	0	2.084122	-0.455437	1.430182
28	6	0	2.985721	-2.170271	0.485213
29	6	0	4.014677	-2.869801	1.148763
30	6	0	3.028854	-2.056520	-0.921433
31	6	0	5.077013	-3.441159	0.422330
32	1	0	3.988938	-2.969476	2.233003
33	6	0	4.086403	-2.630924	-1.648510
34	1	0	2.234730	-1.529104	-1.445120
35	6	0	5.115557	-3.323094	-0.979689
36	1	0	5.864378	-3.978146	0.946008
37	1	0	4.108176	-2.539061	-2.731783
38	1	0	5.932623	-3.766729	-1.543407
39	6	0	-2.522419	-0.984007	-1.182422
40	1	0	-2.356308	0.046621	-1.496279
41	1	0	-2.555951	-1.622527	-2.074234
42	6	0	-3.823173	-1.103175	-0.402982
43	6	0	-4.097108	-0.217590	0.663402
44	6	0	-4.781987	-2.078966	-0.746551
45	6	0	-5.300598	-0.321989	1.381345
46	1	0	-3.377717	0.560178	0.906106
47	6	0	-5.992496	-2.180965	-0.032600
48	1	0	-4.590331	-2.752366	-1.581387
49	6	0	-6.251735	-1.304895	1.037473
50	1	0	-5.504611	0.368240	2.196695
51	1	0	-6.726227	-2.934134	-0.311006
52	1	0	-7.185117	-1.379684	1.590943

Compound **3c** Ground State

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1624.81891381 A.U. after 1 cycles

Lowest frequency = 23.7491

Zero-point correction= 0.589338 (Hartree/Particle)

Thermal correction to Energy= 0.622841

Thermal correction to Enthalpy= 0.623785

Thermal correction to Gibbs Free Energy= 0.522315

Sum of electronic and zero-point Energies= -1624.229576

Sum of electronic and thermal Energies= -1624.196073

Sum of electronic and thermal Enthalpies= -1624.195129

Sum of electronic and thermal Free Energies= -1624.296599

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.860890	-1.595642	-0.270403
2	17	0	2.262552	-0.808452	-2.188227
3	7	0	-0.435959	1.272066	0.256604
4	7	0	1.682478	1.100717	0.791525
5	6	0	1.784666	-3.665299	-0.273771
6	1	0	2.770654	-3.602816	-0.716222
7	6	0	0.560931	-3.745061	-0.944147
8	1	0	0.397899	-3.760374	-2.013911

9	6	0	0.705926	-2.625062	1.612810
10	1	0	0.915632	-2.048916	2.507252
11	6	0	-0.550208	-2.707003	0.929899
12	1	0	-1.467169	-2.203637	1.203856
13	6	0	1.484652	-3.921319	1.231019
14	1	0	2.338487	-4.179456	1.858197
15	6	0	-0.516283	-4.047251	0.136321
16	1	0	-1.474556	-4.417728	-0.227033
17	6	0	0.307000	-4.948318	1.118519
18	1	0	0.613048	-5.903119	0.672009
19	1	0	-0.204438	-5.119103	2.074383
20	6	0	0.616172	0.355038	0.322927
21	6	0	1.322121	2.436158	1.006934
22	1	0	2.025847	3.182980	1.333074
23	6	0	0.003548	2.546897	0.677790
24	1	0	-0.627567	3.414934	0.675848
25	6	0	-1.907405	0.969284	0.007569
26	6	0	3.038766	0.554337	1.067077
27	1	0	3.106822	-0.378624	0.500943
28	1	0	3.100795	0.319389	2.138137
29	6	0	-2.577611	2.288498	-0.526767
30	6	0	-3.050581	3.269907	0.378333
31	6	0	-2.687236	2.562894	-1.906533
32	6	0	-3.611374	4.474956	-0.075701
33	1	0	-2.988640	3.094064	1.448162
34	6	0	-3.248977	3.769029	-2.366059
35	1	0	-2.353032	1.835508	-2.635713
36	6	0	-3.714215	4.733298	-1.455581

37	1	0	-3.965881	5.206736	0.646332
38	1	0	-3.322918	3.948331	-3.435921
39	1	0	-4.150583	5.663407	-1.811576
40	6	0	-2.560588	0.563299	1.364004
41	6	0	-3.969862	0.577527	1.500756
42	6	0	-1.796898	0.172879	2.482586
43	6	0	-4.590947	0.204570	2.703250
44	1	0	-4.588374	0.904270	0.669564
45	6	0	-2.414743	-0.194782	3.693442
46	1	0	-0.715031	0.153818	2.425915
47	6	0	-3.814835	-0.186260	3.811613
48	1	0	-5.675777	0.226315	2.775217
49	1	0	-1.797505	-0.487938	4.539403
50	1	0	-4.291930	-0.470684	4.746270
51	6	0	-2.048370	-0.148461	-1.066243
52	6	0	-1.160074	-0.196477	-2.165027
53	6	0	-3.118986	-1.067505	-1.041315
54	6	0	-1.340740	-1.124719	-3.205489
55	1	0	-0.310650	0.474359	-2.219259
56	6	0	-3.305786	-1.993411	-2.084113
57	1	0	-3.810293	-1.088447	-0.208110
58	6	0	-2.421278	-2.024206	-3.177288
59	1	0	-0.619690	-1.145379	-4.017436
60	1	0	-4.141897	-2.687755	-2.036894
61	1	0	-2.564786	-2.739387	-3.983997
62	6	0	4.154634	1.511530	0.680920
63	6	0	4.943634	2.126382	1.675593
64	6	0	4.428165	1.776680	-0.680219

65	6	0	5.991077	3.000160	1.322633
66	1	0	4.745371	1.918116	2.726382
67	6	0	5.470748	2.651361	-1.032235
68	1	0	3.832569	1.283368	-1.445530
69	6	0	6.254562	3.266440	-0.034022
70	1	0	6.595637	3.465346	2.097909
71	1	0	5.678011	2.845464	-2.081994
72	1	0	7.063222	3.939116	-0.311089

Compound **3c** Transition State 1

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1624.78011288 A.U. after 1 cycles

Lowest frequency = -30.0559

Zero-point correction= 0.589301 (Hartree/Particle)

Thermal correction to Energy= 0.621965

Thermal correction to Enthalpy= 0.622910

Thermal correction to Gibbs Free Energy= 0.523694

Sum of electronic and zero-point Energies= -1624.190812

Sum of electronic and thermal Energies= -1624.158148

Sum of electronic and thermal Enthalpies= -1624.157203

Sum of electronic and thermal Free Energies= -1624.256419

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	45	0	1.128410	-1.737402	-0.196304
2	17	0	3.660005	-1.803208	-0.459956
3	7	0	-0.454852	1.311815	-0.229970
4	7	0	1.664850	1.399989	-0.773394
5	6	0	1.552843	-3.821210	0.495951
6	1	0	2.572895	-3.875724	0.846827
7	6	0	1.118252	-3.855208	-0.844165
8	1	0	1.741002	-3.970540	-1.722072
9	6	0	-0.396758	-2.612125	1.099208
10	1	0	-0.731419	-1.963570	1.889836
11	6	0	-0.857644	-2.651224	-0.248902
12	1	0	-1.660836	-2.075072	-0.675949
13	6	0	0.287038	-3.977002	1.369534
14	1	0	0.445145	-4.243070	2.414566
15	6	0	-0.423360	-4.039064	-0.799963
16	1	0	-0.902236	-4.368460	-1.722207
17	6	0	-0.579528	-4.929371	0.478740
18	1	0	-0.136085	-5.927367	0.366404
19	1	0	-1.620191	-5.009545	0.819159
20	6	0	0.684237	0.467877	-0.420566
21	6	0	1.199084	2.714907	-0.742685
22	1	0	1.840019	3.556147	-0.944167
23	6	0	-0.114190	2.666411	-0.406858
24	1	0	-0.806072	3.474420	-0.276377
25	6	0	-1.911284	0.937299	0.030059
26	6	0	-2.502182	0.181219	-1.200679
27	6	0	-3.898949	-0.052025	-1.263407

28	6	0	-1.728350	-0.192084	-2.318068
29	6	0	-4.487750	-0.679778	-2.372096
30	1	0	-4.544610	0.305240	-0.466788
31	6	0	-2.316172	-0.811998	-3.437713
32	1	0	-0.658628	-0.030166	-2.320656
33	6	0	-3.696661	-1.070993	-3.469603
34	1	0	-5.562406	-0.845256	-2.385025
35	1	0	-1.686961	-1.092408	-4.278948
36	1	0	-4.149469	-1.551902	-4.333170
37	6	0	-2.754516	2.267742	0.161869
38	6	0	-3.110175	2.820707	1.409416
39	6	0	-3.159285	2.958788	-1.007013
40	6	0	-3.851691	4.016552	1.489212
41	1	0	-2.825483	2.325910	2.329902
42	6	0	-3.891277	4.153604	-0.931646
43	1	0	-2.897658	2.563222	-1.983759
44	6	0	-4.245841	4.691021	0.321897
45	1	0	-4.117984	4.413870	2.465660
46	1	0	-4.185010	4.660862	-1.847338
47	1	0	-4.819305	5.612659	0.384066
48	6	0	-1.998952	0.192406	1.391757
49	6	0	-3.042665	-0.702417	1.706024
50	6	0	-1.089342	0.533210	2.419186
51	6	0	-3.181395	-1.230259	3.003436
52	1	0	-3.745400	-1.021101	0.947558
53	6	0	-1.218925	0.002740	3.714087
54	1	0	-0.268176	1.210443	2.210129
55	6	0	-2.274016	-0.878827	4.018458

56	1	0	-3.992574	-1.923364	3.212687
57	1	0	-0.497220	0.277540	4.479176
58	1	0	-2.379972	-1.287608	5.020143
59	6	0	3.037052	1.188958	-1.321657
60	1	0	3.015231	1.543680	-2.360555
61	1	0	3.247475	0.121234	-1.318245
62	6	0	4.098362	1.943065	-0.537143
63	6	0	4.767327	3.044912	-1.110359
64	6	0	4.448256	1.532692	0.768799
65	6	0	5.763056	3.736471	-0.392179
66	1	0	4.519869	3.356258	-2.124770
67	6	0	5.435294	2.225796	1.490049
68	1	0	3.967006	0.657053	1.195579
69	6	0	6.094990	3.331008	0.913609
70	1	0	6.275573	4.580517	-0.848400
71	1	0	5.702270	1.896991	2.491824
72	1	0	6.863405	3.861291	1.471839

Compound **3c** Transition State 2

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1624.77481776 A.U. after 1 cycles

Lowest frequency = -17.6133

Zero-point correction= 0.589310 (Hartree/Particle)

Thermal correction to Energy= 0.621789

Thermal correction to Enthalpy= 0.622733

Thermal correction to Gibbs Free Energy= 0.524529

Sum of electronic and zero-point Energies= -1624.185508

Sum of electronic and thermal Energies= -1624.153029

Sum of electronic and thermal Enthalpies= -1624.152085

Sum of electronic and thermal Free Energies= -1624.250288

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.322371	-1.466181	-0.030834
2	17	0	-0.586976	-2.740959	0.895900
3	7	0	-0.943240	0.877720	-0.755175
4	7	0	1.059871	1.383842	-1.475369
5	6	0	2.302625	-3.490695	-0.017022
6	1	0	1.538745	-4.235208	-0.191339
7	6	0	2.592220	-2.852121	1.198828
8	1	0	2.100278	-3.013500	2.148325
9	6	0	3.139813	-1.609922	-1.220257
10	1	0	3.111760	-1.187483	-2.217613
11	6	0	3.443156	-0.953749	0.020410
12	1	0	3.718559	0.079282	0.185271
13	6	0	3.445714	-3.115987	-0.993427
14	1	0	3.542943	-3.730633	-1.888326
15	6	0	3.918910	-2.078086	0.982524
16	1	0	4.445914	-1.753814	1.879848
17	6	0	4.661607	-3.032756	-0.011368
18	1	0	4.916964	-4.002154	0.435397

19	1	0	5.550472	-2.574569	-0.464165
20	6	0	0.386165	0.381049	-0.761629
21	6	0	0.210538	2.411678	-1.891520
22	1	0	0.564184	3.271440	-2.435880
23	6	0	-1.032842	2.097516	-1.447771
24	1	0	-1.946726	2.645998	-1.560525
25	6	0	-2.175921	0.333563	-0.019360
26	6	0	-2.689075	-0.962518	-0.706130
27	6	0	-3.931299	-1.505837	-0.303295
28	6	0	-2.038429	-1.551628	-1.806006
29	6	0	-4.476523	-2.628622	-0.943795
30	1	0	-4.501442	-1.029624	0.489343
31	6	0	-2.589011	-2.667256	-2.462003
32	1	0	-1.084429	-1.168901	-2.146896
33	6	0	-3.805448	-3.221504	-2.029937
34	1	0	-5.428261	-3.030321	-0.603176
35	1	0	-2.055041	-3.108895	-3.300487
36	1	0	-4.225951	-4.090559	-2.530711
37	6	0	-3.347315	1.385703	-0.177540
38	6	0	-3.700885	2.292196	0.843192
39	6	0	-4.085355	1.433668	-1.386906
40	6	0	-4.753929	3.212581	0.665879
41	1	0	-3.173944	2.281926	1.789295
42	6	0	-5.127424	2.355110	-1.571037
43	1	0	-3.847122	0.740607	-2.188199
44	6	0	-5.471257	3.253482	-0.540879
45	1	0	-5.009927	3.890783	1.476510
46	1	0	-5.673738	2.365506	-2.511208

47	1	0	-6.285298	3.961736	-0.675986
48	6	0	-1.810926	0.243529	1.492562
49	6	0	-2.398096	-0.693678	2.363736
50	6	0	-0.952987	1.217298	2.051795
51	6	0	-2.143349	-0.655917	3.745872
52	1	0	-3.010945	-1.493129	1.972819
53	6	0	-0.688018	1.254754	3.431930
54	1	0	-0.485782	1.962582	1.414301
55	6	0	-1.288876	0.317908	4.292117
56	1	0	-2.595465	-1.407574	4.388499
57	1	0	-0.019791	2.015425	3.830218
58	1	0	-1.087530	0.339925	5.360748
59	6	0	2.500145	1.551988	-1.750481
60	1	0	2.610673	1.810143	-2.811216
61	1	0	2.996898	0.605843	-1.598796
62	6	0	3.147242	2.636634	-0.893316
63	6	0	4.030122	3.564548	-1.482476
64	6	0	2.907102	2.703945	0.496893
65	6	0	4.671310	4.542563	-0.697637
66	1	0	4.219802	3.525142	-2.554193
67	6	0	3.543012	3.682408	1.280531
68	1	0	2.223073	1.996964	0.961014
69	6	0	4.428369	4.604501	0.687110
70	1	0	5.350278	5.252331	-1.164305
71	1	0	3.350777	3.725396	2.349970
72	1	0	4.919025	5.360796	1.294985

Compound **3d** Ground State 1

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1049.72619743 A.U. after 1 cycles

Lowest frequency = 29.9144

Zero-point correction= 0.429009 (Hartree/Particle)

Thermal correction to Energy= 0.453120

Thermal correction to Enthalpy= 0.454065

Thermal correction to Gibbs Free Energy= 0.374210

Sum of electronic and zero-point Energies= -1049.297188

Sum of electronic and thermal Energies= -1049.273077

Sum of electronic and thermal Enthalpies= -1049.272133

Sum of electronic and thermal Free Energies= -1049.351988

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.124237	-0.548410	0.313886
2	17	0	0.071470	-0.422501	2.469273
3	7	0	1.285637	0.731682	-0.976067
4	7	0	-0.067743	2.349144	-0.390048
5	6	0	-2.896308	-1.849154	0.949037
6	1	0	-3.192045	-1.586788	1.956941
7	6	0	-1.850822	-2.692533	0.569654
8	1	0	-1.161692	-3.214227	1.221437
9	6	0	-2.713853	-0.656152	-1.147087

10	1	0	-3.007695	0.257182	-1.650681
11	6	0	-1.640511	-1.523180	-1.531739
12	1	0	-0.971836	-1.375600	-2.372574
13	6	0	-3.710971	-1.545530	-0.342206
14	1	0	-4.714150	-1.142855	-0.198788
15	6	0	-2.002528	-2.929004	-0.960990
16	1	0	-1.458269	-3.777844	-1.375980
17	6	0	-3.562965	-2.908979	-1.100234
18	1	0	-4.050389	-3.743661	-0.580803
19	1	0	-3.899344	-2.857854	-2.143396
20	6	0	0.049646	0.966369	-0.398040
21	6	0	1.073271	2.939322	-0.974960
22	1	0	1.204802	4.002085	-1.069084
23	6	0	1.918894	1.928251	-1.332551
24	1	0	2.904632	1.957970	-1.766117
25	6	0	1.890995	-0.608033	-1.167964
26	1	0	1.937047	-0.818991	-2.244807
27	1	0	1.195125	-1.316007	-0.705883
28	6	0	3.278814	-0.729901	-0.556261
29	6	0	4.397499	-0.988757	-1.374633
30	6	0	3.453456	-0.610868	0.841401
31	6	0	5.681262	-1.126356	-0.810180
32	1	0	4.267835	-1.089088	-2.451743
33	6	0	4.734883	-0.745185	1.402806
34	1	0	2.589621	-0.426150	1.478087
35	6	0	5.852064	-1.002532	0.581101
36	1	0	6.537508	-1.328867	-1.449596
37	1	0	4.860519	-0.657318	2.479345

38	1	0	6.841159	-1.108836	1.021027
39	6	0	-1.249718	3.167431	0.085618
40	6	0	-2.205715	3.372637	-1.117347
41	1	0	-3.056842	3.997639	-0.819623
42	1	0	-1.690665	3.866386	-1.951209
43	1	0	-2.591642	2.410981	-1.470867
44	6	0	-0.741728	4.540504	0.595176
45	1	0	-0.349863	5.173637	-0.209975
46	1	0	-1.581444	5.078609	1.048758
47	1	0	0.034498	4.414062	1.358800
48	6	0	-1.974306	2.456697	1.247179
49	1	0	-2.384994	1.488933	0.937251
50	1	0	-1.297199	2.269233	2.086641
51	1	0	-2.802430	3.092258	1.586462

Compound **3d** Transition State 1

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1049.68940508 A.U. after 1 cycles

Lowest frequency = -28.9196

Zero-point correction= 0.430049 (Hartree/Particle)

Thermal correction to Energy= 0.453056

Thermal correction to Enthalpy= 0.454000

Thermal correction to Gibbs Free Energy= 0.377179

Sum of electronic and zero-point Energies= -1049.259356

Sum of electronic and thermal Energies= -1049.236349

Sum of electronic and thermal Enthalpies= -1049.235405

Sum of electronic and thermal Free Energies= -1049.312226

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.143308	-0.843579	-0.054700
2	17	0	-3.501906	-0.329552	0.666208
3	7	0	1.093772	1.321953	-0.956501
4	7	0	-0.650520	2.469852	-0.314295
5	6	0	-2.017866	-2.894603	-0.303571
6	1	0	-3.052131	-2.797464	-0.601492
7	6	0	-1.502694	-2.781658	0.999161
8	1	0	-2.065230	-2.588413	1.902248
9	6	0	0.083530	-2.229340	-1.205126
10	1	0	0.495248	-1.858039	-2.135612
11	6	0	0.617439	-2.116479	0.122294
12	1	0	1.543398	-1.654235	0.436597
13	6	0	-0.870714	-3.454283	-1.180812
14	1	0	-1.154182	-3.866006	-2.149314
15	6	0	-0.032408	-3.271825	0.933783
16	1	0	0.441344	-3.520755	1.883303
17	6	0	-0.138609	-4.387113	-0.159455
18	1	0	-0.753294	-5.239526	0.156617
19	1	0	0.840055	-4.733362	-0.516230
20	6	0	-0.210568	1.137259	-0.460946
21	6	0	0.337477	3.383584	-0.708652

22	1	0	0.205381	4.447623	-0.680780
23	6	0	1.423982	2.670131	-1.106252
24	1	0	2.388676	2.993692	-1.460719
25	6	0	2.128281	0.332310	-1.306046
26	1	0	2.465138	0.541722	-2.329723
27	1	0	1.677007	-0.648205	-1.316285
28	6	0	3.329634	0.352254	-0.364158
29	6	0	4.625506	0.152696	-0.883378
30	6	0	3.167024	0.519720	1.028220
31	6	0	5.742586	0.110677	-0.027363
32	1	0	4.765008	0.029318	-1.956459
33	6	0	4.282260	0.483145	1.883962
34	1	0	2.174138	0.686876	1.439379
35	6	0	5.573776	0.276032	1.360260
36	1	0	6.736324	-0.044371	-0.440894
37	1	0	4.144488	0.614861	2.954530
38	1	0	6.435118	0.247806	2.023216
39	6	0	-1.998131	2.982782	0.190376
40	6	0	-2.190701	2.500778	1.647448
41	1	0	-2.106489	1.420109	1.737025
42	1	0	-1.445291	2.984355	2.294951
43	1	0	-3.191743	2.777031	1.998606
44	6	0	-3.089478	2.548265	-0.815717
45	1	0	-4.078390	2.828720	-0.434665
46	1	0	-2.925201	3.057447	-1.776101
47	1	0	-3.097216	1.471210	-0.968803
48	6	0	-2.002331	4.535485	0.226720
49	1	0	-1.891964	4.984369	-0.768242

50	1	0	-2.979638	4.842672	0.614439
51	1	0	-1.240011	4.944496	0.901470

Compound **3d** Transition State 2

Method: b3lyp/LanL2DZ

SCF Done: E(RB3LYP) = -1049.68067717 A.U. after 1 cycles

Lowest frequency = -32.6543

Zero-point correction= 0.429922 (Hartree/Particle)

Thermal correction to Energy= 0.452995

Thermal correction to Enthalpy= 0.453939

Thermal correction to Gibbs Free Energy= 0.377106

Sum of electronic and zero-point Energies= -1049.250756

Sum of electronic and thermal Energies= -1049.227683

Sum of electronic and thermal Enthalpies= -1049.226738

Sum of electronic and thermal Free Energies= -1049.303571

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.129622	-0.800371	-0.146920
2	17	0	0.669759	-2.576399	-0.110244
3	7	0	1.543936	0.943281	-0.299019
4	7	0	-0.023147	2.390932	0.213459
5	6	0	-2.351834	-2.583565	0.459369
6	1	0	-1.692467	-3.332796	0.871780

7	6	0	-2.579185	-2.315234	-0.902563
8	1	0	-2.149481	-2.838530	-1.747289
9	6	0	-2.909172	-0.342237	0.998817
10	1	0	-2.756679	0.353890	1.810217
11	6	0	-3.162871	-0.056030	-0.383493
12	1	0	-3.326567	0.913200	-0.829736
13	6	0	-3.417929	-1.785924	1.246116
14	1	0	-3.573489	-2.074014	2.285559
15	6	0	-3.797368	-1.352724	-0.962756
16	1	0	-4.297834	-1.259982	-1.926847
17	6	0	-4.633243	-1.854491	0.262136
18	1	0	-5.017762	-2.874242	0.132796
19	1	0	-5.448048	-1.170538	0.532844
20	6	0	0.152246	1.034713	-0.172882
21	6	0	1.222558	3.015710	0.413400
22	1	0	1.333617	4.024631	0.760790
23	6	0	2.190454	2.117215	0.090553
24	1	0	3.263361	2.205919	0.099765
25	6	0	2.338935	-0.061673	-1.071159
26	1	0	2.506657	0.375334	-2.065086
27	1	0	1.736512	-0.962253	-1.174288
28	6	0	3.674317	-0.380979	-0.419544
29	6	0	4.880293	-0.050007	-1.072601
30	6	0	3.729715	-1.033997	0.832388
31	6	0	6.124938	-0.359946	-0.488784
32	1	0	4.848027	0.443307	-2.043341
33	6	0	4.969969	-1.335712	1.420409
34	1	0	2.803062	-1.324577	1.318684

35	6	0	6.171889	-0.999922	0.763443
36	1	0	7.046782	-0.104210	-1.006424
37	1	0	5.000970	-1.844240	2.381302
38	1	0	7.129959	-1.240618	1.218891
39	6	0	-1.277145	3.255468	0.116414
40	6	0	-2.310696	2.912746	1.213312
41	1	0	-2.913601	2.049453	0.955495
42	1	0	-1.808493	2.726989	2.170149
43	1	0	-2.993603	3.760752	1.346435
44	6	0	-1.842931	3.097244	-1.318691
45	1	0	-2.835944	3.559963	-1.386826
46	1	0	-1.182385	3.592638	-2.041495
47	1	0	-1.914107	2.046596	-1.601348
48	6	0	-0.908869	4.752975	0.305749
49	1	0	-0.158158	5.096245	-0.414205
50	1	0	-1.818853	5.338681	0.134861
51	1	0	-0.564363	4.972611	1.323993

Catalysis: additional graphs and experimental data

Reaction conditions: catalyst loading 1%, T = 25 °C

Fig. 3S-6S describe the reaction profiles of conversion for **3a**, **3d**, **4** and **5** with TolC≡CH, nBuC≡CH, Et_3SiC≡CH and (CPh_2OH)C≡CH, which confirm that catalyst **4** leads to reaction rates higher than all the other complexes employed.

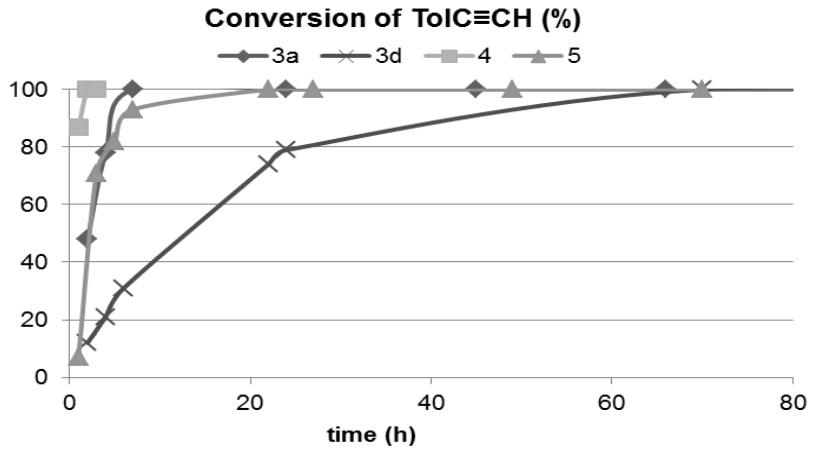


Fig. 3S. Reaction profile of conversion vs time for the hydrosilylation of TolC≡CH with complexes: **3a**, **3d**, **4** and **5** at 25°C with a catalyst loading of 1%.

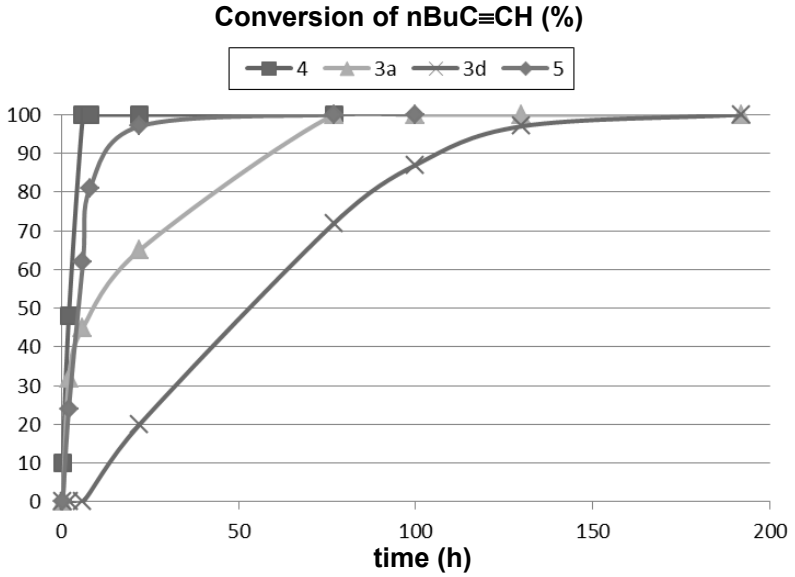


Fig. 4S. Reaction profile of conversion vs time for the hydrosilylation of nBuC≡CH with complexes: **3a**, **3d**, **4** and **5** at 25°C with a catalyst loading of 1%.

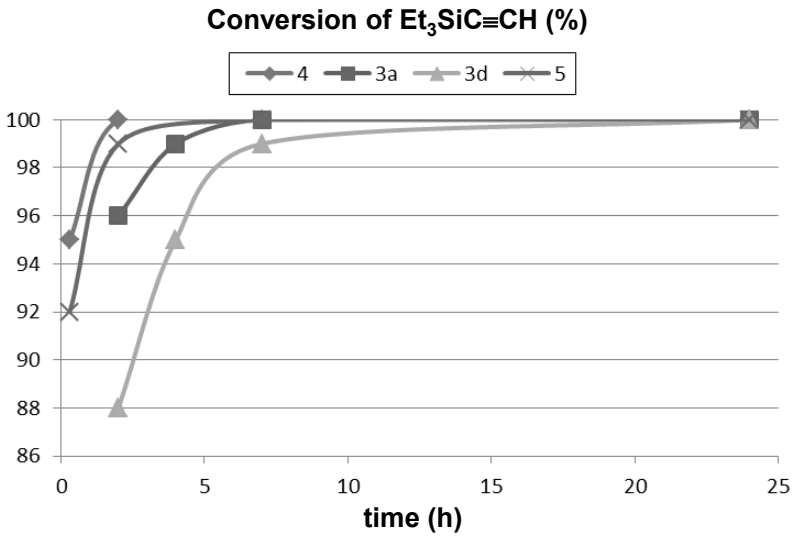


Fig. 5S. Reaction profile of conversion vs time for the hydrosilylation of $Et_3SiC{\equiv}CH$ with complexes: **3a**, **3d**, **4** and **5** at 25°C with a catalyst loading of 1%.

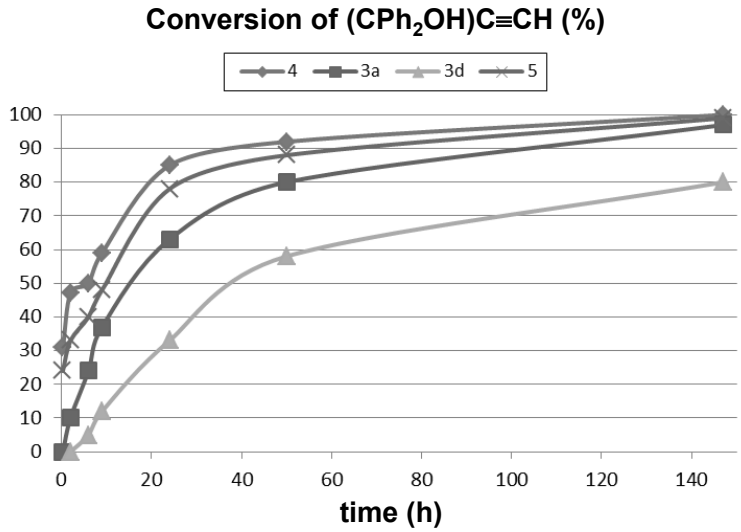


Fig. 6S. Reaction profile of conversion vs time for the hydrosilylation of $(CPh_2OH)C{\equiv}CH$ with complexes: **3a**, **3d**, **4** and **5** at 25°C with a catalyst loading of 1%.

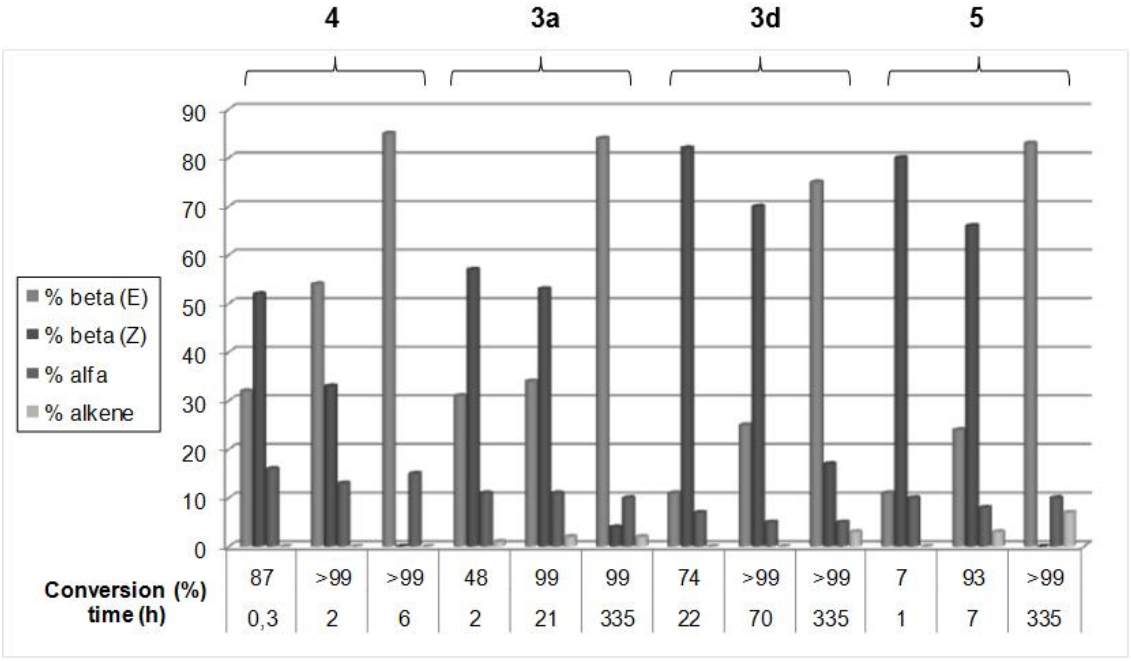
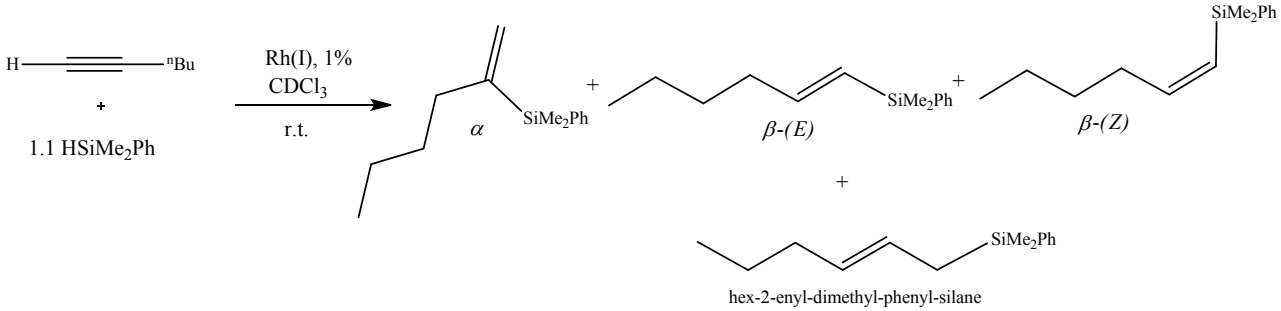


Fig. 7S Selectivity vs conversion and time for the hydrosilylation of tolylacetylene catalyzed by **3a**, **3d**, **4** and **5**. Catalyst loading of 1%.



Scheme 1S Hydrosylilation of nBuC≡CH with Rh(I) complexes.

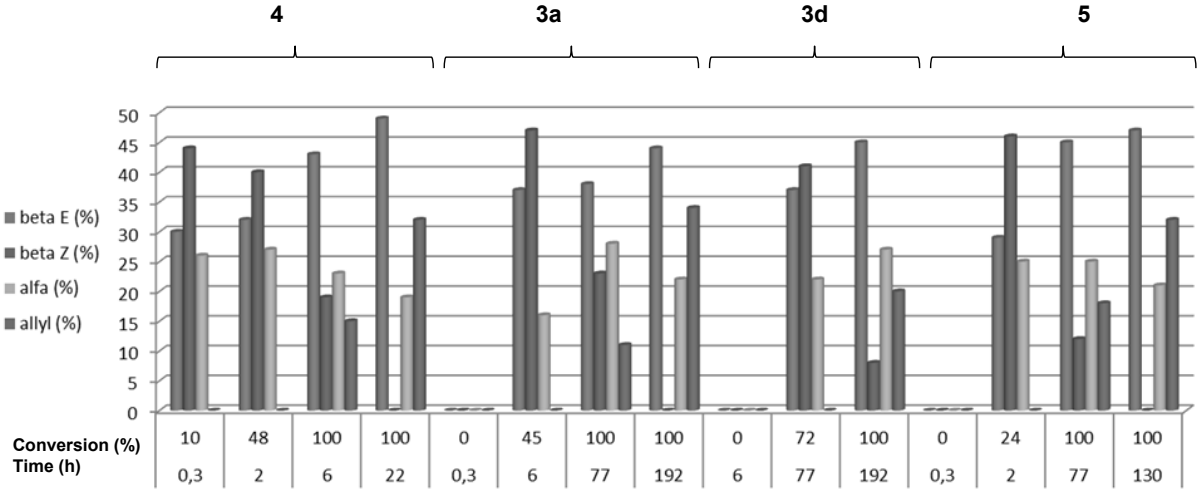


Fig. 8S Selectivity vs. conversion and time for the hydrosilylation of nBuC≡CH catalyzed by **3a**, **3d**, **4** and **5**. Catalyst loading of 1%.

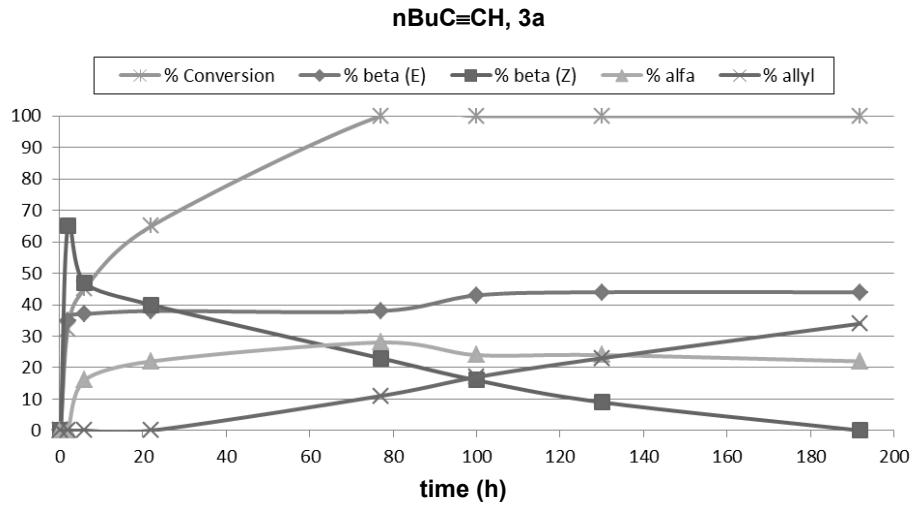
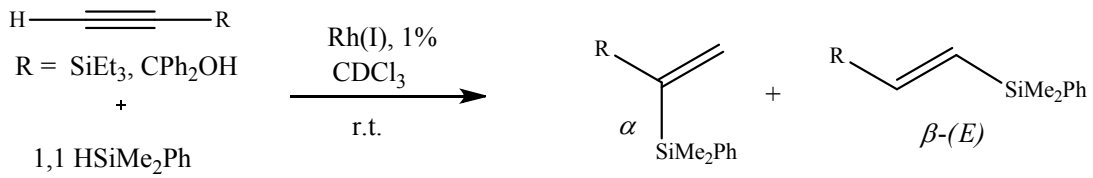


Fig. 9S Reaction profile of conversion and selectivity vs. time for the hydrosilylation of nBuC≡CH with **3a**; catalyst loading 1%.



Scheme 2S Hydrosylilation of $Et_3SiC{\equiv}CH$ and $(CPh_2OH)C{\equiv}CH$ with Rh(I) complexes.

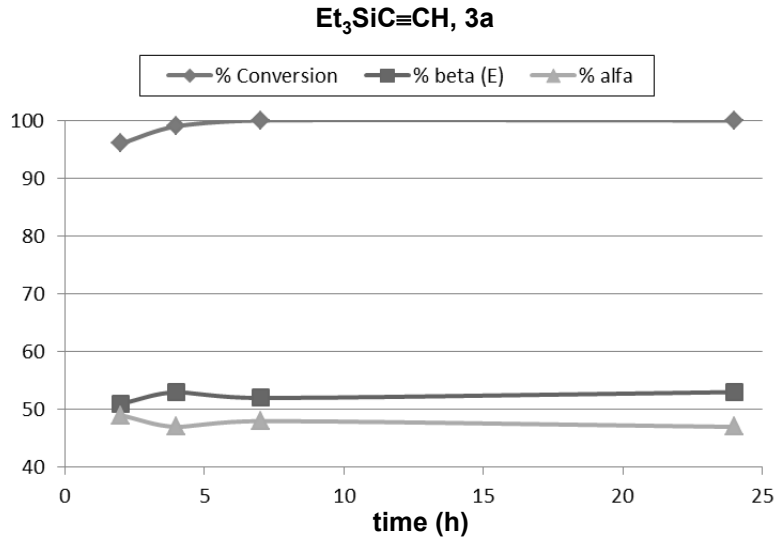


Fig. 10S Reaction profile of conversion and selectivity vs. time for the hydrosilylation of $Et_3SiC{\equiv}CH$ with **3a**; catalyst loading 1%.

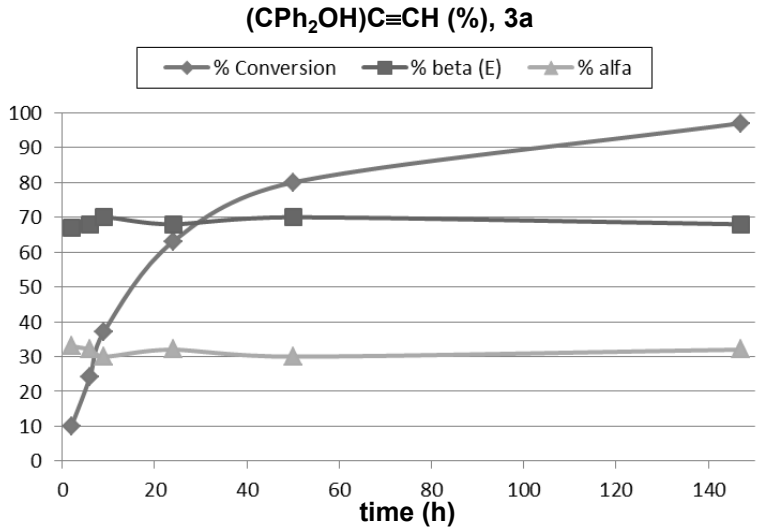


Fig. 11S Reaction profile of conversion and selectivity vs. time for the hydrosilylation of $(CPh_2OH)C{\equiv}CH$ with **3a**; catalyst loading 1%.

Reaction conditions: catalyst loading 0.1%, T = 25 °C

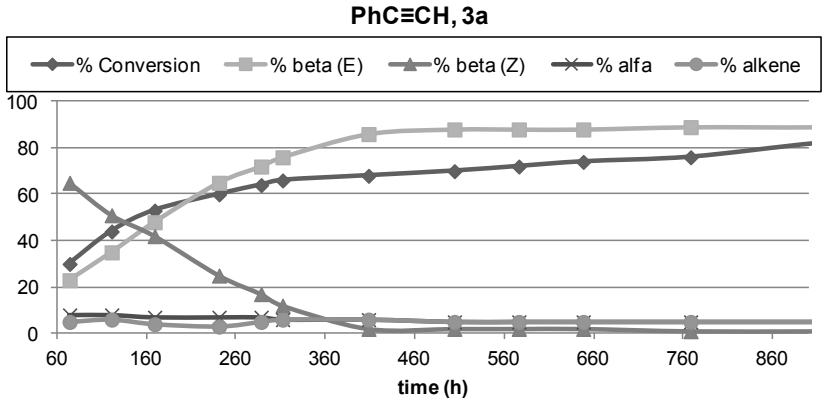


Fig. 12S Reaction profile of conversion and selectivities vs time for the hydrosilylation of PhC≡CH with **3a** (T = 25°C, catalyst loading = 0.1 %). Due to the long induction time and for sake of clarity, graphs start from a reaction time of 60 h.

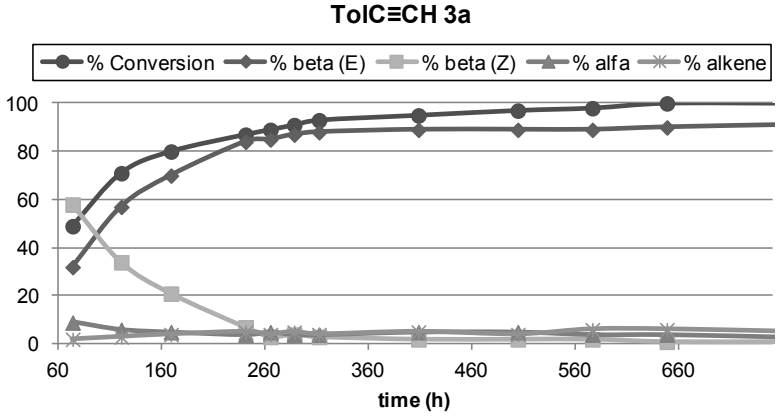


Fig. 13S Reaction profile of conversion and selectivities vs time for the hydrosilylation of TolC≡CH with **3a** (T = 25°C, catalyst loading = 0.1 %). Graphs start from a reaction time of 60 h for the sake of clarity due to the long induction time.

Reaction conditions: catalyst loading 0.1%, T = 60 °C

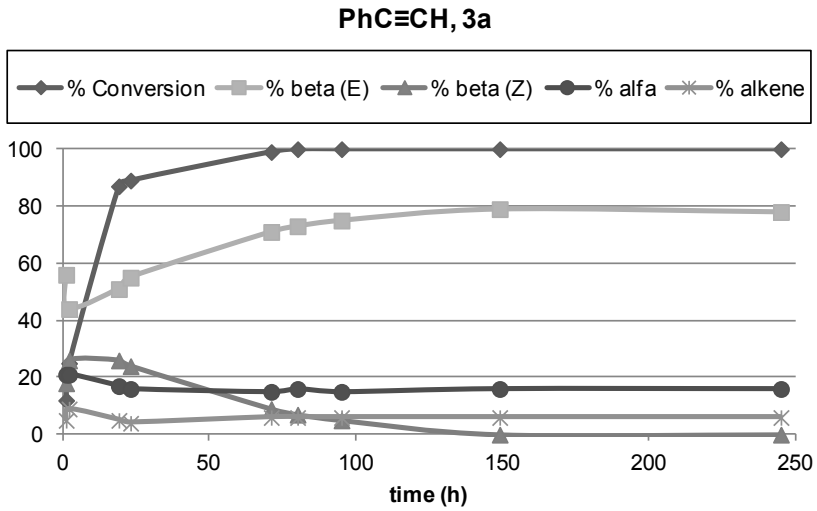


Fig. 14S Reaction profile of conversion and selectivities vs time for the PhC≡CH hydrosilylation of with **3a** (T = 60°C, catalyst loading = 0.1 %).

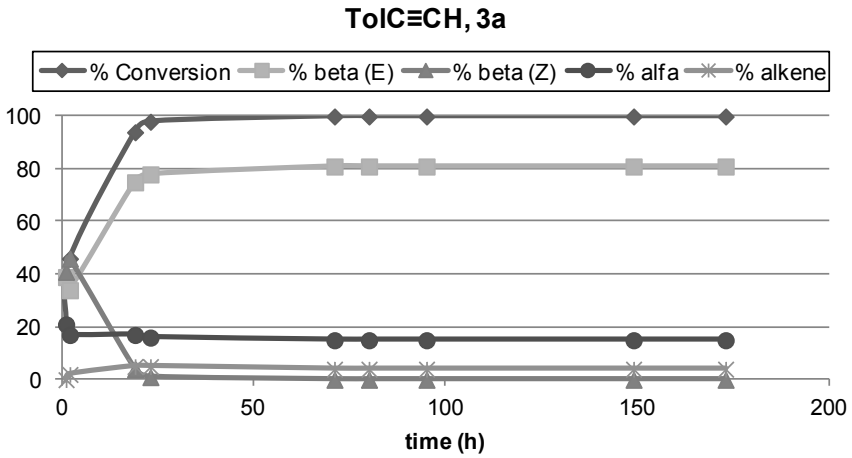
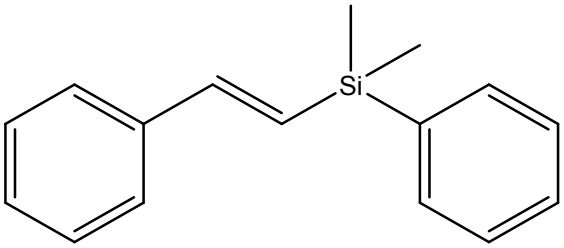


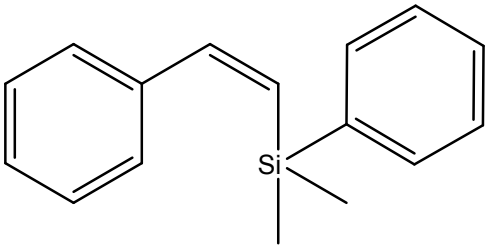
Fig. 15S Reaction profile of conversion and selectivities vs time for the hydrosilylation of TolC≡CH with **3a** (T = 60°C, catalyst loading = 0.1 %).

Details and full characterization data for the catalysis

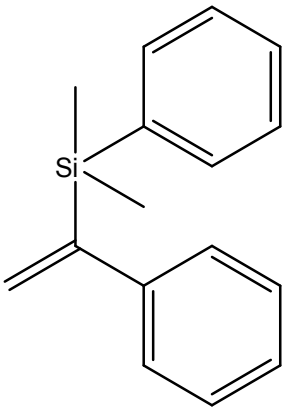
Hydrosilylation products: ^{1}H-NMR characterizations and selected examples of conversions and selectivities calculations from ^{1}H-NMR.



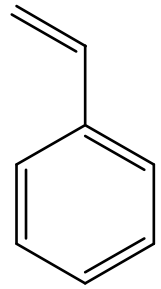
(*E*)-2- (dimethyl(phenyl)silyl)-1-phenyl-ethene[8]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.6-7.2 (m, 5H), 7.0 (d, $J_{H,H}$ = 19 Hz, 1H), 6.6 (d, $J_{H,H}$ = 19 Hz, 1H), 0.36 (s, 6H) ppm.



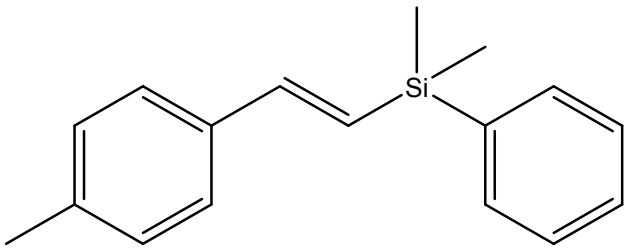
(*Z*)-2- (dimethyl(phenyl)silyl)-1-phenyl-ethene[9]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.6-7.2 (m, 5H), 7.5 (d, $J_{H,H}$ = 15 Hz, 1H), 6.0 (d, $J_{H,H}$ = 15 Hz, 1H), 0.36 (s, 6H) ppm.



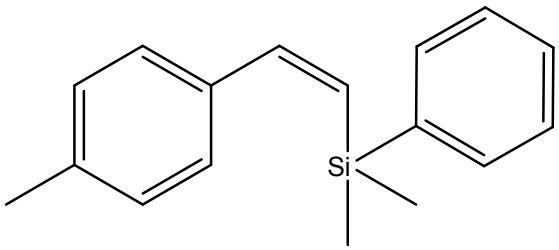
1-(dimethyl(phenyl)silyl)-1-phenyl-ethene[8]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.6-7.3 (m, 5H), 5.98 (d, $J_{H,H}$ = 2.9 Hz, 1H,), 5.66 (d, $J_{H,H}$ = 2.9 Hz, 1H), 0.41 (s, 6H) ppm.



Styrene
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.50-7.10 (m, 5H), 6.69 (dd, $J_{H,H}$ = 18.0, 11.0 Hz, 1H), 5.74 (d, $J_{H,H}$ = 18.0, 1H), 5.22 (d, $J_{H,H}$ = 11.0 Hz, 1H).

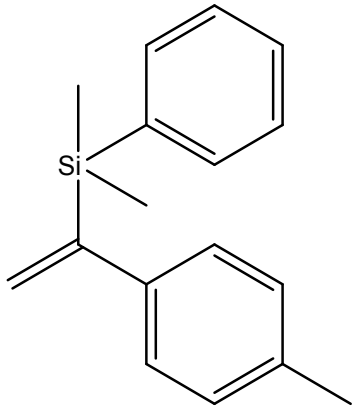


(*E*)-2- (dimethyl(phenyl)silyl)-1-tolyl-ethene
^{1}H-NMR (300.1 MHz, $CDCl_3$): δ 7.60-7.16 (m, 9H), 6.96 (d, $J_{H,H}$ = 19.2 Hz, 1H), 6.45 (d, $J_{H,H}$ = 19.2 Hz, 1H), 2.36 (s, 3H), 0.49 (s, 6H) ppm.

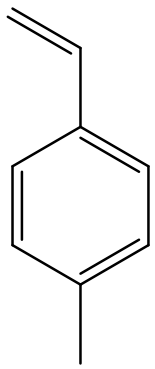


(*Z*)-2- (dimethyl(phenyl)silyl)-1-tolyl-ethene[10]

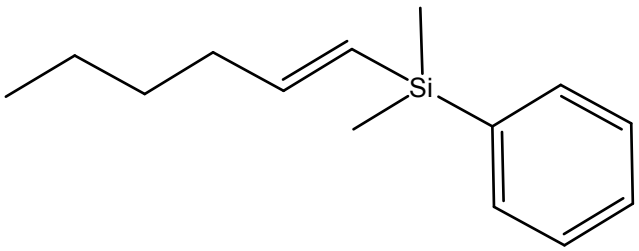
^{1}H-NMR (300.1 MHz, $CDCl_3$): δ 7.60–7.52 (m, 2H), 7.43 (d, $J_{H,H}$ = 15.3 Hz, 1H), 7.38–7.32 (m, 3H), 7.13 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.06 (d, $J_{H,H}$ = 8.1 Hz, 2H), 5.96 (d, $J_{H,H}$ = 15.0 Hz, 1H), 2.30 (s, 3H), 0.28 (s, 6H) ppm.



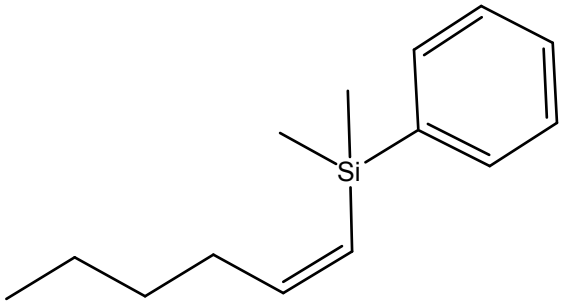
1-(dimethyl(phenyl)silyl)-1-tolyl-ethene
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.6-7.3 (m, 4H), 5.93 (d, 1H, $J_{H,H}$ = 2.9 Hz), 5.66 (d, 1H, $J_{H,H}$ = 2.9 Hz), 2.35 (s, 3H), 0.30 (s, 6H) ppm.



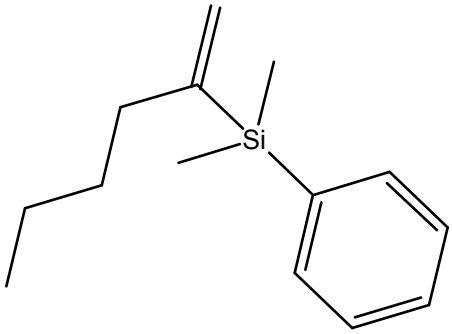
4-Methylstyrene
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.39 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.20 (d, $J_{H,H}$ = 8.0 Hz, 2H), 6.77 (dd, $J_{H,H}$ = 18.0, 11.0 Hz, 1H), 5.78 (d, $J_{H,H}$ = 18.0, 1H), 5.26 (d, $J_{H,H}$ = 11.0 Hz, 1H), 2.41 (s, 3H).



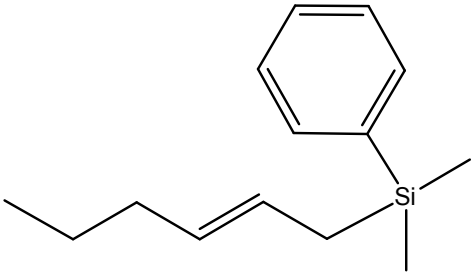
(*E*)-2- (dimethyl(phenyl)silyl)-1-hexene[11]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.70-7.30 (m, 5H, Ph), 6.12 (dt, 1H, $J_{H,H}$ = 19 Hz, 6.2 Hz, CH_2CH=), 5.72 (d, 1H, $J_{H,H}$ = 19 Hz, SiCH=), 2.22-0.80 (m, 9H, ^{n}Bu), 0.30 (s, 6H, $SiMe_2$).



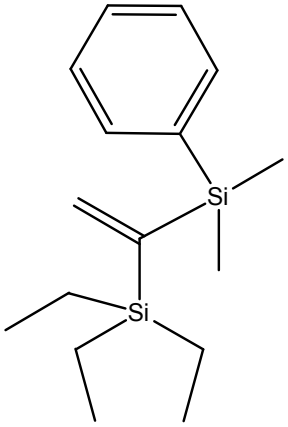
(Z)-2- (dimethyl(phenyl)silyl)-2-hexene[11]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.7-7.3 (m, 5H, Ph), 6.4 (dt, 1H, $J_{H,H}$ = 14.0, 7.4 Hz, ^{n}BuCH=), 5.6 (d, 1H, $J_{H,H}$ = 14.0 Hz), 2.2-0.8 (m, 9H, ^{n}Bu), 0.38 (s, 6H, $SiMe_2$).



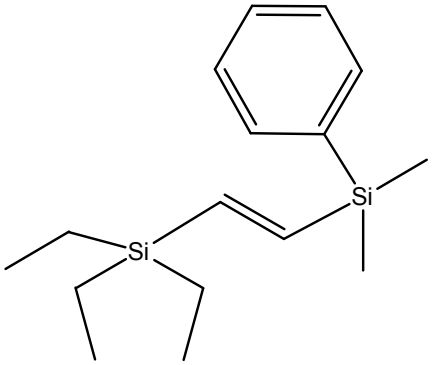
2-(dimethyl(phenyl)silyl)-1-hexene[11]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.7-7.3 (m, 5H), 5.76 (d, 1H, $J_{H,H}$ = 2.9 Hz), 5.38 (d, 1H, $J_{H,H}$ = 2.9 Hz), 2.2-0.8 (m, 9H), 0.41 (s, 6H, $SiMe_2$).



(*E*)-1-(Dimethylphenylsilyl)hex-2-ene (12s)[12]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.72-7.31 (m, 5H), 5.45-5.24 (m, 2H, $=CHCH_2CH_2$, $=CHCH_2Si$), 2.2-0.8 (m, 9H, $CH_2CH_2CH_3$,CH_2Si), 0.47 (s, 6H, $SiMe_2$).

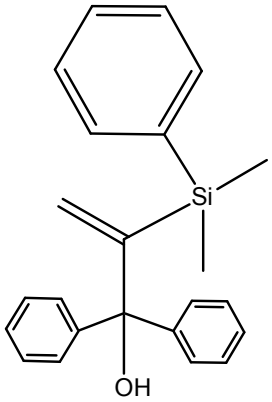


1-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene[13]
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.35-7.19 (m, 5H,Ph), AB system (δ_A = 6.40, δ_B = 6.42, $J_{A,B}$ = 5.2 Hz, 2H, CH), 0.64 (t, $J_{H,H}$ = 7.8 Hz, 6H, CH_2), 0.32 (q, $J_{H,H}$ = 7.8 Hz, 9H, CH_3), 0.19 (s, 6H, CH_3).



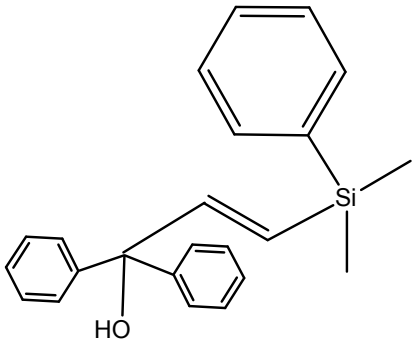
(*E*)-2-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene[13]

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.32-7.15 (m, 5H,Ph), AB system (δ_A = 6.76, δ_B = 6.65, $J_{A,B}$ = 22.8 Hz, 2H, CH), 0.76 (t, $J_{H,H}$ = 8.0 Hz, 6H, CH_2), 0.41 (q, $J_{H,H}$ = 8.0 Hz, 9H, CH_3), 0.15 (s, 6H, CH_3).



1-(Dimethylphenylsilyl)-1-(CPh_2OH)ethene[14]

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.77-7.24 (m, 15H, Ph), 5.72 (d, $J_{H,H}$ = 1.8 Hz, 1H, CH_2), 5.28 (d, $J_{H,H}$ = 1.8 Hz, 1H, CH_2), 0.39 (s, 6H, CH_3).



(*E*)-2-(Dimethylphenylsilyl)-1-(CPh_2OH)ethene

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.77-7.24 (m, 15H, Ph), 6.74 (d, $J_{H,H}$ = 18.8, 1H, =$CHCPh_2OH$), 6.16 (d, $J_{H,H}$ = 18.8 Hz, 1H, =CHSi), 0.35 (s, 6H, CH_3).

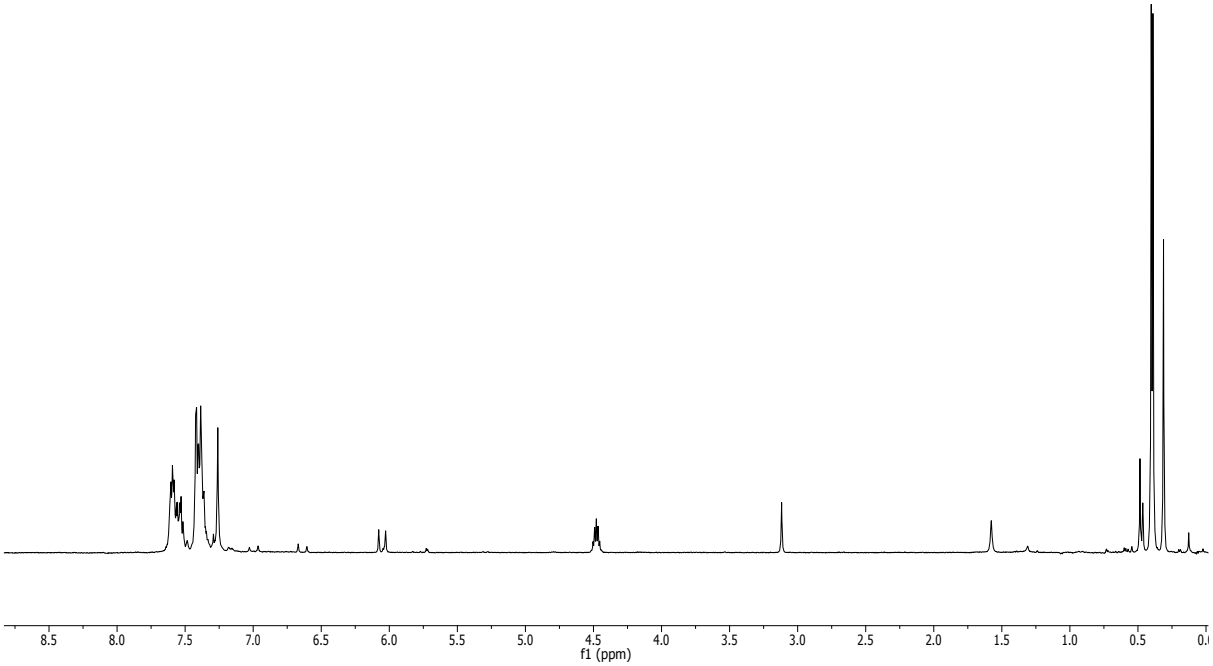


Fig. 16S Hydrosilylation of PhC≡CH catalysed by **5**. Reaction conditions (T = 25 °C; Catalyst loading = 1%; t = 2 h).

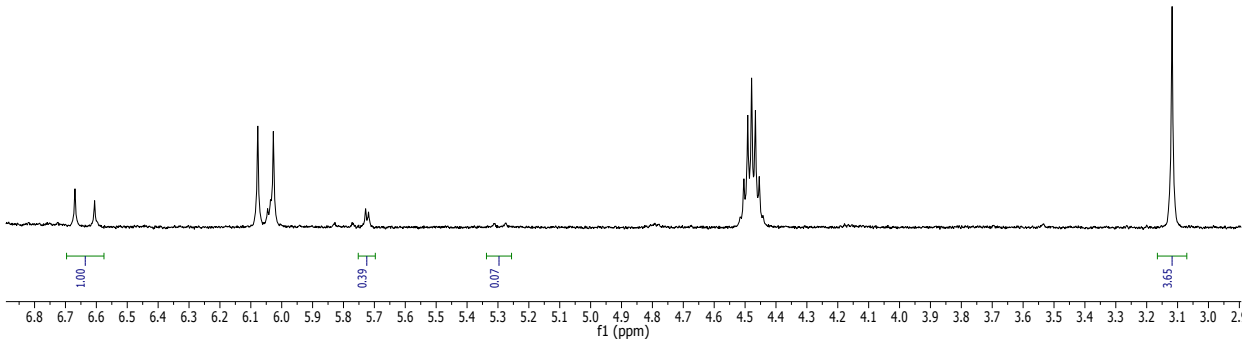


Fig. 17S Hydrosilylation of PhC≡CH catalysed by **5** (enlargement). Reaction conditions (T = 25 °C; Catalyst loading = 1%; t = 2 h). Conversion = 54 %, selectivities: **1s**-β(*E*) = 20%; **2s**-β(*Z*) = 70%; **3s**-α = 9%; **4s**-styrene = 1%.

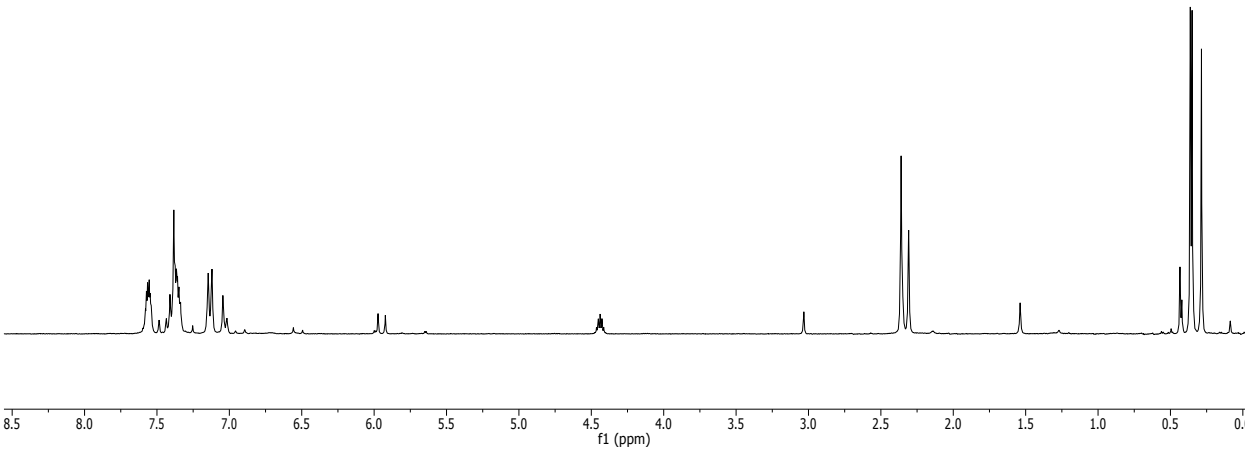


Fig. 18S Hydrosilylation of TolC≡CH catalysed by **5**. Reaction conditions (T = 25 °C; Catalyst loading = 1%; t = 2 h).

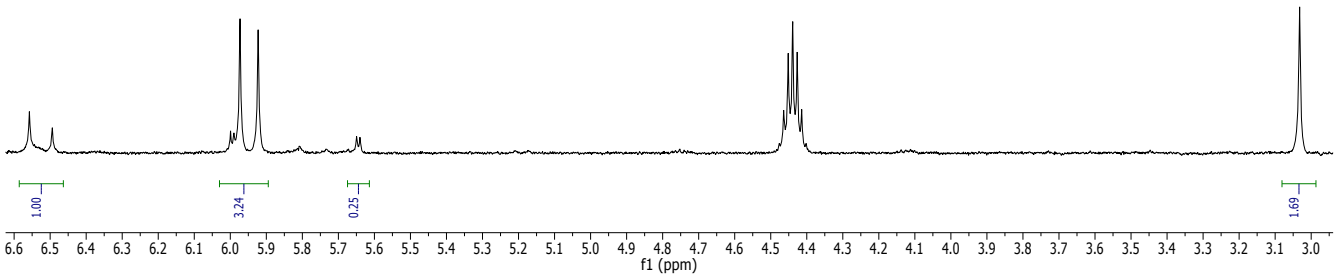


Fig. 19S Hydrosilylation of TolC≡CH catalysed by **5** (enlargement). Reaction conditions (T = 25 °C; Catalyst loading = 1%; t = 2 h). Conversion = 71 %, selectivities: **5s**-β(*E*) = 25%; **6s**-β(*Z*) = 69%; **7s**-α = 5%; **8s**-styrene = 1%.

For conversion and selectivity calculation methods used for the hydrosilylation of ^{n}BuC≡CH, $Et_3SiC{\equiv}CH$, and $(CPh_2OH)C{\equiv}CH$ see the NMR spectra reported in the supplementary information of ref. 15.

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