N-heterocyclic Carbene-Amide Rhodium(I) Complexes: Structures, Dynamics and Catalysis

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Supporting Information

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Compound 3a Ground State

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1141.23378611 A.U. after 1 cycles
Imaginary frequencies: 0 (17.2)

Zero-point correction=	0.436082 (Hartree/Particle)
Thermal correction to Energy=	0.462730
Thermal correction to Enthalpy=	0.463674
Thermal correction to Gibbs Free Energy=	0.376916
Sum of electronic and zero-point Energies=	-1140.797704
Sum of electronic and thermal Energies=	-1140.771056
Sum of electronic and thermal Enthalpies=	-1140.770112
Sum of electronic and thermal Free Energies=	-1140.856870

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.97216	-0.0777	0.32016
2	17	0	0.39597	-0.5597	2.16791
3	8	0	-3.6839	-0.809	-1.784
4	8	0	-4.0236	-0.6338	0.53666
5	7	0	0.5039	2.57956	0.19643
6	7	0	-0.3009	1.23694	-1.3219
7	7	0	-1.9399	-0.9765	-0.2629
8	1	0	-1.6387	-0.8938	0.70861
9	6	0	3.28742	-1.9628	0.40737
10	1	0	2.68478	-2.8045	0.72482
11	6	0	3.87554	-0.9943	1.21837
12	1	0	3.82275	-0.9232	2.2975
13	6	0	3.18404	-0.3885	-1.4289
14	1	0	2.72642	-0.2156	-2.3965
15	6	0	3.7917	0.60648	-0.5947
16	1	0	3.86698	1.66571	-0.8139
17	6	0	3.84819	-1.7417	-1.0283
18	1	0	3.72619	-2.5689	-1.728
19	6	0	4.81443	-0.1567	0.30226
20	1	0	5.56594	0.45131	0.8065
21	6	0	5.30287	-1.2648	-0.6925
22	1	0	5.90762	-2.0408	-0.2069
23	1	0	5.83128	-0.8564	-1.5629
24	6	0	0.67017	1.32156	-0.344
25	6	0	-1.0623	2.41741	-1.3763
26	1	0	-1.8859	2.54144	-2.06
27	6	0	-0.5542	3.26257	-0.4252
28	1	0	-0.8525	4.25786	-0.1401

29	6	0	1.27178	3.07855	1.34734
30	1	0	0.86372	4.04455	1.65995
31	1	0	2.32649	3.20184	1.08111
32	1	0	1.19213	2.36294	2.17057
33	6	0	-0.5959	0.0411	-2.1353
34	1	0	0.26218	-0.1868	-2.7788
35	1	0	-1.4555	0.27754	-2.7685
36	6	0	-0.9233	-1.2084	-1.2822
37	1	0	-1.253	-1.993	-1.9755
38	1	0	-0.0185	-1.548	-0.7692
39	6	0	-3.2523	-0.8073	-0.6002
40	6	0	-5.5197	-0.4535	0.46283
41	6	0	-5.8983	-0.3134	1.94568
42	1	0	-5.6016	-1.2092	2.50234
43	1	0	-6.9826	-0.1781	2.0462
44	1	0	-5.392	0.55026	2.39115
45	6	0	-6.1567	-1.7083	-0.1649
46	1	0	-5.8522	-1.8203	-1.2087
47	1	0	-7.2506	-1.6258	-0.121
48	1	0	-5.8577	-2.6048	0.39187
49	6	0	-5.8482	0.82989	-0.3248
50	1	0	-5.5572	0.72898	-1.3735
51	1	0	-5.3232	1.6882	0.11276
52	1	0	-6.9273	1.02518	-0.2732

Compound 3a Transition State 1

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1141.21140166 A.U. after 1 cycles
Imaginary frequencies: 1 (-20.3)

Zero-point correction=	0.436766 (Hartree/Particle)
Thermal correction to Energy=	0.462343
Thermal correction to Enthalpy=	0.463288
Thermal correction to Gibbs Free Energy=	0.380384
Sum of electronic and zero-point Energies=	-1140.774635
Sum of electronic and thermal Energies=	-1140.749058
Sum of electronic and thermal Enthalpies=	-1140.748114
Sum of electronic and thermal Free Energies=	-1140.831018

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	2.36543	-0.2649	-0.0646
2	17	0	1.55435	-2.6029	-0.3919

3	8	0	-4.1992	-0.9402	-1.1765
4	8	0	-4.8145	-0.1797	0.96304
5	7	0	0.39715	2.22829	-0.4401
6	7	0	-0.6212	0.38488	-0.9885
7	7	0	-2.7427	-1.0052	0.63683
8	1	0	-2.6613	-0.7761	1.61931
9	6	0	4.46782	-1.0438	-0.367
10	1	0	4.44539	-1.7907	-1.1495
11	6	0	4.13801	-1.226	0.98034
12	1	0	3.80126	-2.1396	1.45055
13	6	0	3.87227	1.27879	-0.2231
14	1	0	3.64952	2.13506	-0.8447
15	6	0	3.53218	1.08624	1.15819
16	1	0	2.9915	1.75546	1.81579
17	6	0	5.10787	0.36719	-0.4799
18	1	0	5.67861	0.56974	-1.3864
19	6	0	4.56783	0.0699	1.71733
20	1	0	4.64711	0.00812	2.80282
21	6	0	5.84331	0.46469	0.89912
22	1	0	6.6591	-0.2619	1.00276
23	1	0	6.20254	1.47721	1.12363
24	6	0	0.60542	0.843	-0.5012
25	6	0	-1.5243	1.43007	-1.2132
26	1	0	-2.5186	1.24974	-1.5883
27	6	0	-0.8868	2.58769	-0.8756
28	1	0	-1.2227	3.61115	-0.9046
29	6	0	1.34998	3.28244	-0.0693
30	1	0	0.78783	4.15138	0.28769
31	1	0	1.94999	3.58809	-0.9336
32	1	0	2.00797	2.95084	0.72558
33	6	0	-1.0569	-0.9999	-1.2673
34	1	0	-0.2058	-1.5859	-1.611
35	1	0	-1.8146	-0.9467	-2.0533
36	6	0	-1.6453	-1.7187	-0.0354
37	1	0	-1.9903	-2.7026	-0.3797
38	1	0	-0.8484	-1.885	0.69285
39	6	0	-3.9408	-0.7338	0.03558
40	6	0	-6.2294	0.20087	0.59291
41	6	0	-6.7784	0.73122	1.92659
42	1	0	-6.7401	-0.049	2.69495
43	1	0	-7.8205	1.05087	1.80279
44	1	0	-6.1875	1.58675	2.27299
45	6	0	-6.9923	-1.0546	0.12885
46	1	0	-6.5803	-1.4424	-0.8063
47	1	0	-8.0492	-0.8031	-0.0283

48	1	0	-6.9371	-1.8384	0.89402
49	6	0	-6.2014	1.30417	-0.4824
50	1	0	-5.7867	0.9252	-1.42
51	1	0	-5.6006	2.15575	-0.1392
52	1	0	-7.223	1.66009	-0.6682

Compound 3a Transition State 2

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1141.20799157 A.U. after 1 cycles
Imaginary frequencies: 1 (-28.6)

Zero-point correction=	0.436405 (Hartree/Particle)
Thermal correction to Energy=	0.462094
Thermal correction to Enthalpy=	0.463038
Thermal correction to Gibbs Free Energy=	0.378821
Sum of electronic and zero-point Energies=	-1140.771586
Sum of electronic and thermal Energies=	-1140.745898
Sum of electronic and thermal Enthalpies=	-1140.744954
Sum of electronic and thermal Free Energies=	-1140.829170

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-2.6645	0.14471	-0.0017
2	17	0	-4.2921	2.01122	-0.141
3	8	0	4.09466	-1.5728	0.75976
4	8	0	5.11584	0.02303	-0.6357
5	7	0	-0.7014	2.63931	0.0402
6	7	0	0.41692	0.84287	0.55654
7	7	0	2.90853	-0.388	-0.846
8	1	0	2.98136	0.30774	-1.577
9	6	0	-4.2005	-1.2232	-0.9449
10	1	0	-4.7007	-0.6807	-1.7363
11	6	0	-4.4753	-1.1564	0.42529
12	1	0	-5.2211	-0.5423	0.91066
13	6	0	-1.9219	-1.8325	-0.482
14	1	0	-0.9511	-1.9197	-0.9515
15	6	0	-2.2105	-1.7589	0.92281
16	1	0	-1.5152	-1.7552	1.75332
17	6	0	-3.2117	-2.4053	-1.1422
18	1	0	-3.107	-2.7866	-2.1583
19	6	0	-3.6597	-2.2948	1.09269
20	1	0	-3.9548	-2.5754	2.10376
21	6	0	-3.7065	-3.3874	-0.0276

22	1	0	-4.7193	-3.7686	-0.2099
23	1	0	-3.0118	-4.218	0.15124
24	6	0	-0.8714	1.26144	0.18671
25	6	0	1.30916	1.91836	0.66145
26	1	0	2.33737	1.78962	0.95399
27	6	0	0.60586	3.04284	0.33801
28	1	0	0.91297	4.07482	0.29915
29	6	0	-1.6958	3.64131	-0.3923
30	1	0	-1.1533	4.54725	-0.6836
31	1	0	-2.4007	3.8617	0.41044
32	1	0	-2.275	3.26379	-1.2332
33	6	0	0.91548	-0.5334	0.70503
34	1	0	0.08674	-1.191	0.93521
35	1	0	1.61664	-0.5681	1.54567
36	6	0	4.05211	-0.7228	-0.1605
37	6	0	6.51956	-0.1545	-0.0913
38	6	0	7.31698	0.8555	-0.93
39	1	0	7.25097	0.60891	-1.9956
40	1	0	8.37237	0.83905	-0.6316
41	1	0	6.92843	1.8698	-0.7846
42	6	0	6.98615	-1.5991	-0.3502
43	1	0	6.39614	-2.3139	0.22913
44	1	0	8.04039	-1.6983	-0.0615
45	1	0	6.89936	-1.8441	-1.4158
46	6	0	6.53739	0.21259	1.40456
47	1	0	5.94416	-0.494	1.99058
48	1	0	6.14297	1.22515	1.55578
49	1	0	7.57139	0.19236	1.77202
50	6	0	1.6341	-1.0535	-0.5641
51	1	0	0.98292	-0.9248	-1.4351
52	1	0	1.82118	-2.1246	-0.4213

Compound 3b Ground State

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1372.25156837 A.U. after 1 cycles
Imaginary frequencies: 0 (11.3)

Zero-point correction=	0.518443 (Hartree/Particle)
Thermal correction to Energy=	0.549274
Thermal correction to Enthalpy=	0.550218
Thermal correction to Gibbs Free Energy=	0.452789
Sum of electronic and zero-point Energies=	-1371.733125
Sum of electronic and thermal Energies=	-1371.702294
Sum of electronic and thermal Enthalpies=	-1371.701350
Sum of electronic and thermal Free Energies=	-1371.79877

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-2.0911	-0.5297	-0.2873
2	17	0	-0.4713	-0.1655	-2.1295
3	8	0	3.42562	-2.7521	1.04803
4	8	0	3.91299	-1.289	-0.7283
5	7	0	-0.3989	1.35388	1.41821
6	7	0	0.21077	-0.7098	1.76882
7	7	0	1.78321	-1.9489	-0.3813
8	1	0	1.5463	-1.3045	-1.135
9	6	0	-3.6274	-1.83	-1.4046
10	1	0	-3.1137	-2.4272	-2.1475
11	6	0	-4.0293	-0.5015	-1.523
12	1	0	-3.8903	0.15191	-2.3751
13	6	0	-3.4551	-1.5844	0.99824
14	1	0	-3.0478	-2.0494	1.8892
15	6	0	-3.8689	-0.2174	0.87521
16	1	0	-3.8228	0.53707	1.65263
17	6	0	-4.2553	-2.3698	-0.0864
18	1	0	-4.2893	-3.4537	0.02514
19	6	0	-4.915	-0.1917	-0.2809
20	1	0	-5.5455	0.69538	-0.3457
21	6	0	-5.61	-1.5813	-0.0751
22	1	0	-6.2734	-1.8563	-0.9046
23	1	0	-6.1415	-1.6571	0.88159
24	6	0	-0.6959	0.05383	1.06113
25	6	0	1.06111	0.10518	2.53793
26	1	0	1.85703	-0.3014	3.14022
27	6	0	0.6755	1.40036	2.32111
28	1	0	1.07843	2.32669	2.69497
29	6	0	-1.1101	2.5475	0.90297
30	1	0	-1.682	2.99658	1.72573
31	1	0	-1.8187	2.17017	0.15773
32	6	0	0.35422	-2.1757	1.68345
33	1	0	-0.5766	-2.6538	2.01004
34	1	0	1.15764	-2.4646	2.36628
35	6	0	0.69511	-2.6788	0.25899
36	1	0	0.94991	-3.743	0.34856
37	1	0	-0.1815	-2.5794	-0.3868
38	6	0	3.07043	-2.055	0.06034
39	6	0	5.39638	-1.209	-0.4645
40	6	0	5.86767	-0.2584	-1.5765
41	1	0	5.62824	-0.674	-2.5616

42	1	0	6.95294	-0.1105	-1.5103
43	1	0	5.37254	0.71481	-1.4848
44	6	0	6.02249	-2.6085	-0.6175
45	1	0	5.65553	-3.2879	0.15604
46	1	0	7.11458	-2.5323	-0.5341
47	1	0	5.78192	-3.0266	-1.6025
48	6	0	5.63979	-0.6045	0.93204
49	1	0	5.28262	-1.278	1.71542
50	1	0	5.12371	0.35931	1.02328
51	1	0	6.71469	-0.4333	1.07524
52	6	0	-0.1771	3.58404	0.29487
53	6	0	-0.0789	4.8714	0.8616
54	6	0	0.58063	3.27321	-0.857
55	6	0	0.76776	5.84235	0.29087
56	1	0	-0.6665	5.11961	1.7448
57	6	0	1.42683	4.2414	-1.4241
58	1	0	0.49756	2.28558	-1.3071
59	6	0	1.52423	5.5274	-0.8531
60	1	0	0.83464	6.83332	0.73396
61	1	0	2.00316	3.99595	-2.3128
62	1	0	2.17835	6.27421	-1.2973

Compound 3b Transition State 1

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1372.22573433 A.U. after 1 cycles
Imaginary frequencies: 1 (-16.3)

Zero-point correction= 0.518850 (Hartree/Particle)
Thermal correction to Energy= 0.548763
Thermal correction to Enthalpy= 0.549707
Thermal correction to Gibbs Free Energy= 0.455090
Sum of electronic and zero-point Energies= -1371.706884
Sum of electronic and thermal Energies= -1371.676971
Sum of electronic and thermal Enthalpies= -1371.676027
Sum of electronic and thermal Free Energies= -1371.770645

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	2.19617	-1.1688	-0.1243
2	17	0	1.47881	-3.5592	-0.1688
3	8	0	-4.3026	-1.8428	-0.8211
4	8	0	-4.6542	-0.4311	1.02778
5	7	0	0.37172	1.08984	-1.497

6	7	0	-0.72	-0.7875	-1.3755
7	7	0	-2.6732	-1.4803	0.80058
8	1	0	-2.4818	-0.9766	1.65715
9	6	0	4.23456	-1.9984	0.42199
10	1	0	4.33303	-2.9765	-0.0284
11	6	0	3.55502	-1.6786	1.60375
12	1	0	3.03732	-2.3641	2.2618
13	6	0	3.84272	0.21147	-0.4123
14	1	0	3.87193	0.76059	-1.3457
15	6	0	3.14724	0.54708	0.798
16	1	0	2.54095	1.42338	0.99055
17	6	0	5.01232	-0.7229	0.00619
18	1	0	5.80917	-0.8563	-0.7254
19	6	0	3.90663	-0.2015	1.93314
20	1	0	3.70426	0.13128	2.95139
21	6	0	5.37964	-0.1288	1.40707
22	1	0	6.0698	-0.7669	1.97337
23	1	0	5.76492	0.8974	1.35261
24	6	0	0.52872	-0.239	-1.0763
25	6	0	-1.5887	0.15514	-1.9405
26	1	0	-2.5964	-0.1019	-2.2249
27	6	0	-0.9051	1.33159	-2.0217
28	1	0	-1.2048	2.30058	-2.3849
29	6	0	1.35734	2.18326	-1.4714
30	1	0	1.51949	2.5304	-2.5004
31	1	0	2.2967	1.77541	-1.1195
32	6	0	-1.2102	-2.1661	-1.1609
33	1	0	-0.4128	-2.8738	-1.3831
34	1	0	-2.0454	-2.318	-1.8485
35	6	0	-1.6823	-2.4363	0.28232
36	1	0	-2.0958	-3.4535	0.29352
37	1	0	-0.8166	-2.4242	0.94862
38	6	0	-3.9106	-1.3047	0.24407
39	6	0	-6.0721	-0.0514	0.66816
40	6	0	-6.4499	0.89951	1.81475
41	1	0	-6.3794	0.38442	2.77936
42	1	0	-7.4787	1.25674	1.68247
43	1	0	-5.778	1.76517	1.83522
44	6	0	-6.9553	-1.3134	0.66747
45	1	0	-6.6578	-1.9993	-0.1297
46	1	0	-8.0036	-1.0262	0.51355
47	1	0	-6.8798	-1.8323	1.63078
48	6	0	-6.0817	0.67444	-0.6911
49	1	0	-5.8077	-0.008	-1.4998
50	1	0	-5.3802	1.51795	-0.678

51	1	0	-7.0871	1.06836	-0.8883
52	6	0	0.93889	3.36241	-0.5969
53	6	0	1.2509	4.67631	-1.0027
54	6	0	0.28928	3.16334	0.64054
55	6	0	0.92855	5.77533	-0.1838
56	1	0	1.74578	4.84368	-1.9583
57	6	0	-0.0385	4.25998	1.45724
58	1	0	0.03084	2.15531	0.95692
59	6	0	0.28231	5.57004	1.04971
60	1	0	1.17467	6.78343	-0.5088
61	1	0	-0.5423	4.09436	2.40664
62	1	0	0.0285	6.41752	1.68179

Compound 3b Transition State 2

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1372.22199340 A.U. after 1 cycles
Imaginary frequencies: 1 (-27.3)

Zero-point correction=	0.518345 (Hartree/Particle)
Thermal correction to Energy=	0.548447
Thermal correction to Enthalpy=	0.549391
Thermal correction to Gibbs Free Energy=	0.452477
Sum of electronic and zero-point Energies=	-1371.703648
Sum of electronic and thermal Energies=	-1371.673546
Sum of electronic and thermal Enthalpies=	-1371.672602
Sum of electronic and thermal Free Energies=	-1371.769517

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	2.4593	-0.8796	-0.2571
2	17	0	4.29067	0.6981	-0.8858
3	8	0	-4.4499	-2.1631	-0.1239
4	8	0	-5.2682	-0.0344	0.45497
5	7	0	0.66335	1.5413	-1.3484
6	7	0	-0.5838	-0.2196	-1.0587
7	7	0	-3.0855	-0.5089	0.76568
8	1	0	-3.0604	0.44212	1.11056
9	6	0	3.9045	-1.8852	1.15877
10	1	0	4.48532	-1.1232	1.66162
11	6	0	4.12857	-2.4052	-0.1217
12	1	0	4.90584	-2.115	-0.8149
13	6	0	1.56898	-2.413	0.98702
14	1	0	0.61453	-2.2085	1.45288

15	6	0	1.80661	-2.9429	-0.3262
16	1	0	1.08301	-3.2052	-1.0881
17	6	0	2.82907	-2.7888	1.82165
18	1	0	2.73189	-2.714	2.90495
19	6	0	3.19594	-3.6356	-0.2658
20	1	0	3.42603	-4.3278	-1.0755
21	6	0	3.19417	-4.1797	1.20247
22	1	0	4.1774	-4.5474	1.52217
23	1	0	2.42542	-4.943	1.37836
24	6	0	0.7402	0.2217	-0.8977
25	6	0	-1.4053	0.77349	-1.6118
26	1	0	-2.4462	0.60484	-1.8306
27	6	0	-0.6222	1.87555	-1.7881
28	1	0	-0.8606	2.85347	-2.1721
29	6	0	1.70179	2.60493	-1.3014
30	1	0	1.67697	3.1265	-2.2655
31	1	0	2.67428	2.12144	-1.2024
32	6	0	-1.1889	-1.4801	-0.6004
33	1	0	-0.4255	-2.2444	-0.5356
34	1	0	-1.9301	-1.8059	-1.338
35	6	0	-4.2906	-1.0042	0.32718
36	6	0	-6.7121	-0.3049	0.08015
37	6	0	-7.3858	1.03373	0.41749
38	1	0	-7.2689	1.26666	1.48174
39	1	0	-8.4567	0.98191	0.18574
40	1	0	-6.9409	1.84777	-0.1658
41	6	0	-7.2581	-1.4497	0.95382
42	1	0	-6.7542	-2.3927	0.72725
43	1	0	-8.3325	-1.5709	0.76571
44	1	0	-7.1214	-1.2176	2.01704
45	6	0	-6.7973	-0.6179	-1.4255
46	1	0	-6.288	-1.5557	-1.6623
47	1	0	-6.3481	0.19334	-2.0117
48	1	0	-7.8508	-0.7071	-1.7201
49	6	0	-1.8835	-1.3452	0.77749
50	1	0	-1.1814	-0.9217	1.50345
51	1	0	-2.1625	-2.3537	1.10541
52	6	0	1.4619	3.58306	-0.1599
53	6	0	1.10963	4.92411	-0.4159
54	6	0	1.61543	3.15963	1.17951
55	6	0	0.90389	5.82903	0.6446
56	1	0	1.00581	5.26698	-1.4446
57	6	0	1.40626	4.05818	2.23926
58	1	0	1.91193	2.13266	1.38213
59	6	0	1.04758	5.39647	1.97575

60	1	0	0.63681	6.862	0.43304
61	1	0	1.5341	3.72313	3.26614
62	1	0	0.89115	6.09259	2.79664

Compound 3c Ground State

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1834.24436164 A.U. after 1 cycles
Imaginary frequencies: 0 (12.6)

Zero-point correction=	0.681196 (Hartree/Particle)
Thermal correction to Energy=	0.721037
Thermal correction to Enthalpy=	0.721981
Thermal correction to Gibbs Free Energy=	0.606460
Sum of electronic and zero-point Energies=	-1833.563165
Sum of electronic and thermal Energies=	-1833.523324
Sum of electronic and thermal Enthalpies=	-1833.522380
Sum of electronic and thermal Free Energies=	-1833.637901

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.02498	-1.886	0.2229
2	17	0	-0.7857	-2.2416	1.96026
3	8	0	-4.8197	-1.1314	-1.7797
4	8	0	-5.1898	-0.4902	0.45394
5	7	0	0.02745	1.04594	-0.4599
6	7	0	-1.1706	-0.5522	-1.3662
7	7	0	-3.4364	-1.8179	-0.0475
8	1	0	-3.1743	-1.6993	0.92813
9	6	0	1.80993	-4.0084	0.43513
10	1	0	1.01024	-4.6408	0.79869
11	6	0	2.63484	-3.173	1.19176
12	1	0	2.61118	-3.0194	2.26284
13	6	0	2.10846	-2.5921	-1.4928
14	1	0	1.69701	-2.3704	-2.4716
15	6	0	2.95591	-1.7332	-0.7183
16	1	0	3.29234	-0.7423	-0.9933
17	6	0	2.40811	-4.0419	-1.0009
18	1	0	2.0737	-4.8546	-1.6465
19	6	0	3.75429	-2.6718	0.23538
20	1	0	4.63642	-2.2416	0.70859
21	6	0	3.93679	-3.9313	-0.6773
22	1	0	4.32293	-4.8032	-0.1341
23	1	0	4.54903	-3.7322	-1.566

24	6	0	-0.0309	-0.3428	-0.6119
25	6	0	-1.8304	0.65368	-1.6449
26	1	0	-2.7639	0.68337	-2.1835
27	6	0	-1.0843	1.64981	-1.0904
28	1	0	-1.2631	2.70769	-1.0738
29	6	0	1.22247	1.87275	0.00431
30	6	0	-1.6719	-1.8452	-1.8705
31	1	0	-0.8122	-2.4678	-2.1362
32	1	0	-2.2484	-1.625	-2.7741
33	6	0	-2.5618	-2.6408	-0.8759
34	1	0	-3.1606	-3.3398	-1.4742
35	1	0	-1.9282	-3.2013	-0.1875
36	6	0	-4.5086	-1.1497	-0.5579
37	6	0	-6.4277	0.32655	0.18037
38	6	0	-6.7925	0.83423	1.58451
39	1	0	-6.9737	-0.0087	2.26058
40	1	0	-7.6992	1.45044	1.53797
41	1	0	-5.9767	1.43744	1.99857
42	6	0	-7.5285	-0.5868	-0.3923
43	1	0	-7.2411	-0.977	-1.372
44	1	0	-8.461	-0.0168	-0.497
45	1	0	-7.7145	-1.4283	0.28599
46	6	0	-6.0814	1.49404	-0.7646
47	1	0	-5.824	1.12631	-1.7614
48	1	0	-5.2378	2.06911	-0.363
49	1	0	-6.9457	2.16577	-0.8482
50	6	0	0.67228	3.26106	0.49969
51	6	0	0.45551	4.31565	-0.4209
52	6	0	0.3347	3.49281	1.85021
53	6	0	-0.0749	5.54957	-0.0101
54	1	0	0.7078	4.18044	-1.4684
55	6	0	-0.1971	4.72788	2.26652
56	1	0	0.49711	2.72329	2.59412
57	6	0	-0.4064	5.76435	1.34087
58	1	0	-0.2271	6.33798	-0.7434
59	1	0	-0.4426	4.87503	3.31544
60	1	0	-0.814	6.71926	1.66375
61	6	0	2.16967	2.08885	-1.2157
62	6	0	3.15697	3.10272	-1.1675
63	6	0	2.09398	1.30186	-2.3827
64	6	0	4.04141	3.31292	-2.2373
65	1	0	3.22324	3.74859	-0.2965
66	6	0	2.97454	1.51323	-3.4614
67	1	0	1.34833	0.52058	-2.4694
68	6	0	3.95682	2.51575	-3.3952

69	1	0	4.78842	4.10012	-2.1681
70	1	0	2.88766	0.89212	-4.3498
71	1	0	4.63666	2.67851	-4.2279
72	6	0	1.95011	1.15853	1.17842
73	6	0	1.19995	0.48657	2.16929
74	6	0	3.34723	1.25269	1.35665
75	6	0	1.82117	-0.0599	3.30619
76	1	0	0.12794	0.37001	2.06469
77	6	0	3.97115	0.71174	2.49589
78	1	0	3.96828	1.73281	0.61084
79	6	0	3.21099	0.05869	3.48329
80	1	0	1.20915	-0.5897	4.03013
81	1	0	5.04945	0.80333	2.60687
82	1	0	3.69232	-0.3571	4.36553

Compound 3c Transition State 1

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1834.20631764 A.U. after 1 cycles
Imaginary frequencies: 1 (-26.1)

Zero-point correction=	0.681181 (Hartree/Particle)
Thermal correction to Energy=	0.720280
Thermal correction to Enthalpy=	0.721224
Thermal correction to Gibbs Free Energy=	0.607815
Sum of electronic and zero-point Energies=	-1833.525137
Sum of electronic and thermal Energies=	-1833.486037
Sum of electronic and thermal Enthalpies=	-1833.485093
Sum of electronic and thermal Free Energies=	-1833.598502

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.35744	-2.1432	-0.208
2	17	0	0.18498	-4.1357	-1.2737
3	8	0	-5.0017	-1.1988	-1.474
4	8	0	-5.4397	-0.5817	0.75335
5	7	0	0.02354	0.99993	-0.6602
6	7	0	-1.2738	-0.6381	-1.3109
7	7	0	-3.5775	-1.7587	0.2806
8	1	0	-3.4582	-1.672	1.28189
9	6	0	2.92592	-3.7113	0.05926
10	1	0	2.80134	-4.4701	-0.6995
11	6	0	2.18498	-3.5813	1.2523
12	1	0	1.40381	-4.2439	1.60202

13	6	0	3.38873	-1.3854	0.09355
14	1	0	3.68033	-0.6132	-0.5958
15	6	0	2.6556	-1.2397	1.30558
16	1	0	2.32536	-0.3182	1.75408
17	6	0	4.12636	-2.7452	0.18547
18	1	0	4.95132	-2.8986	-0.51
19	6	0	2.93409	-2.5345	2.12146
20	1	0	2.67923	-2.507	3.1812
21	6	0	4.41958	-2.8255	1.72137
22	1	0	4.76452	-3.8188	2.03689
23	1	0	5.11559	-2.0509	2.06907
24	6	0	-0.0017	-0.4252	-0.7717
25	6	0	-1.9847	0.54654	-1.5122
26	1	0	-2.9812	0.55081	-1.9225
27	6	0	-1.183	1.56577	-1.1128
28	1	0	-1.373	2.62009	-1.1328
29	6	0	1.09443	1.91552	-0.0781
30	6	0	-1.9598	-1.897	-1.6788
31	1	0	-1.2459	-2.5971	-2.1062
32	1	0	-2.7133	-1.6369	-2.4257
33	6	0	-2.6458	-2.5994	-0.4906
34	1	0	-3.1727	-3.4699	-0.9028
35	1	0	-1.8815	-2.9743	0.19378
36	6	0	-4.6994	-1.1878	-0.2548
37	6	0	-6.7441	0.1248	0.46619
38	6	0	-7.1659	0.59957	1.86562
39	1	0	-7.2866	-0.2553	2.54038
40	1	0	-8.12	1.13807	1.80767
41	1	0	-6.4095	1.27019	2.28893
42	6	0	-7.7544	-0.8817	-0.1163
43	1	0	-7.4291	-1.2417	-1.0956
44	1	0	-8.733	-0.3964	-0.2255
45	1	0	-7.8706	-1.7391	0.55775
46	6	0	-6.4888	1.31588	-0.4776
47	1	0	-6.1817	0.97132	-1.4684
48	1	0	-5.7089	1.96853	-0.0657
49	1	0	-7.4093	1.90518	-0.5798
50	6	0	1.07378	1.81375	1.4774
51	6	0	1.8272	2.72605	2.25727
52	6	0	0.24022	0.90522	2.16101
53	6	0	1.79217	2.69254	3.66017
54	1	0	2.40439	3.50761	1.77278
55	6	0	0.1916	0.87615	3.56804
56	1	0	-0.3643	0.19967	1.60546
57	6	0	0.97595	1.75983	4.32858

58	1	0	2.38614	3.40522	4.22733
59	1	0	-0.4593	0.15937	4.06295
60	1	0	0.94125	1.73519	5.41494
61	6	0	0.72796	3.41197	-0.4436
62	6	0	1.22901	4.0449	-1.6011
63	6	0	-0.1571	4.15109	0.37892
64	6	0	0.86923	5.368	-1.9217
65	1	0	1.91277	3.52203	-2.2581
66	6	0	-0.521	5.46966	0.06119
67	1	0	-0.5721	3.69636	1.27269
68	6	0	-0.0074	6.08972	-1.0941
69	1	0	1.27836	5.82901	-2.8174
70	1	0	-1.2036	6.00843	0.71389
71	1	0	-0.2833	7.11218	-1.3403
72	6	0	2.45657	1.60567	-0.7623
73	6	0	3.69276	1.92076	-0.1604
74	6	0	2.47295	1.14574	-2.0991
75	6	0	4.90144	1.79358	-0.8704
76	1	0	3.74063	2.2444	0.87047
77	6	0	3.6779	1.00579	-2.8085
78	1	0	1.54343	0.88409	-2.5916
79	6	0	4.90365	1.33792	-2.2007
80	1	0	5.83802	2.03976	-0.376
81	1	0	3.65563	0.63685	-3.8307
82	1	0	5.83702	1.23606	-2.7485

Compound 3c Transition State 2

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1834.19622920 A.U. after 1 cycles
Imaginary frequencies: 1 (-19.1)

Zero-point correction=	0.680238 (Hartree/Particle)
Thermal correction to Energy=	0.719396
Thermal correction to Enthalpy=	0.720340
Thermal correction to Gibbs Free Energy=	0.606373
Sum of electronic and zero-point Energies=	-1833.515991
Sum of electronic and thermal Energies=	-1833.476833
Sum of electronic and thermal Enthalpies=	-1833.475889
Sum of electronic and thermal Free Energies=	-1833.589856

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-1.1572	-2.1682	0.11224

2	17	0	-3.5046	-1.4093	0.19197
3	8	0	5.6865	-1.0545	0.73042
4	8	0	6.08114	0.87708	-0.5541
5	7	0	-0.4426	1.09425	0.14453
6	7	0	1.32009	-0.1565	0.50429
7	7	0	4.16931	-0.2828	-0.8479
8	1	0	3.99769	0.42831	-1.547
9	6	0	-1.9232	-3.9992	-0.9186
10	1	0	-2.6768	-3.7026	-1.6357
11	6	0	-2.1025	-4.1808	0.46221
12	1	0	-3.0149	-4.0332	1.02209
13	6	0	0.39864	-3.5328	-0.5755
14	1	0	1.2636	-3.1204	-1.0756
15	6	0	0.20359	-3.7155	0.83382
16	1	0	0.86358	-3.4535	1.65122
17	6	0	-0.525	-4.5806	-1.2613
18	1	0	-0.3276	-4.7861	-2.3137
19	6	0	-0.819	-4.873	0.98227
20	1	0	-0.8811	-5.3394	1.96529
21	6	0	-0.4413	-5.7688	-0.245
22	1	0	-1.1805	-6.5557	-0.4419
23	1	0	0.56547	-6.2	-0.1709
24	6	0	-0.0583	-0.2664	0.26789
25	6	0	1.75001	1.17292	0.56523
26	1	0	2.77099	1.44413	0.77117
27	6	0	0.65802	1.94814	0.34137
28	1	0	0.58365	3.01736	0.32642
29	6	0	-1.8408	1.71301	0.0007
30	6	0	2.33322	-1.217	0.6307
31	1	0	1.8421	-2.1545	0.83924
32	1	0	2.9814	-0.982	1.48218
33	6	0	5.35098	-0.2251	-0.1472
34	6	0	7.44972	1.18254	0.02333
35	6	0	7.84116	2.45617	-0.7408
36	1	0	7.87778	2.26312	-1.8188
37	1	0	8.82978	2.80028	-0.4129
38	1	0	7.1144	3.25535	-0.5565
39	6	0	8.40532	0.01663	-0.2919
40	1	0	8.10325	-0.8936	0.23233
41	1	0	9.42189	0.28335	0.02438
42	1	0	8.42444	-0.1815	-1.3705
43	6	0	7.31741	1.4466	1.53495
44	1	0	7.00031	0.54491	2.06499
45	1	0	6.59156	2.24748	1.72261
46	1	0	8.288	1.76623	1.93533

47	6	0	3.21558	-1.3746	-0.6326
48	1	0	2.58108	-1.4514	-1.5219
49	1	0	3.77773	-2.3097	-0.5228
50	6	0	-2.5295	1.25904	-1.3194
51	6	0	-3.7223	1.90744	-1.7185
52	6	0	-1.9577	0.33583	-2.2149
53	6	0	-4.3485	1.60203	-2.9365
54	1	0	-4.1484	2.69119	-1.0994
55	6	0	-2.5723	0.03817	-3.4449
56	1	0	-1.0432	-0.1827	-1.9568
57	6	0	-3.7784	0.65812	-3.811
58	1	0	-5.2705	2.11203	-3.2064
59	1	0	-2.1092	-0.6894	-4.1082
60	1	0	-4.2582	0.42099	-4.7577
61	6	0	-1.6562	3.27416	-0.1617
62	6	0	-1.9366	4.18556	0.87638
63	6	0	-1.191	3.79424	-1.3949
64	6	0	-1.7639	5.57262	0.68915
65	1	0	-2.2979	3.82762	1.83309
66	6	0	-1.0068	5.17253	-1.5809
67	1	0	-0.9788	3.11533	-2.2159
68	6	0	-1.2961	6.0745	-0.5365
69	1	0	-1.9988	6.2534	1.50399
70	1	0	-0.6491	5.54215	-2.539
71	1	0	-1.1653	7.14439	-0.6806
72	6	0	-2.6053	1.44843	1.33469
73	6	0	-4.0124	1.42027	1.40971
74	6	0	-1.8807	1.36428	2.54369
75	6	0	-4.6713	1.32487	2.6465
76	1	0	-4.608	1.41431	0.50801
77	6	0	-2.5352	1.25728	3.78435
78	1	0	-0.7953	1.37619	2.53651
79	6	0	-3.9392	1.24516	3.84498
80	1	0	-5.7579	1.28519	2.66738
81	1	0	-1.9459	1.18288	4.69575
82	1	0	-4.451	1.16091	4.80094

Compound 4a Ground State

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1137.67166780 A.U. after 1 cycles
Imaginary frequencies: 0 (14.2)

Zero-point correction=	0.435634 (Hartree/Particle)
Thermal correction to Energy=	0.462674
Thermal correction to Enthalpy=	0.463618

Thermal correction to Gibbs Free Energy=	0.374351
Sum of electronic and zero-point Energies=	-1137.236034
Sum of electronic and thermal Energies=	-1137.208994
Sum of electronic and thermal Enthalpies=	-1137.208050
Sum of electronic and thermal Free Energies=	-1137.297317

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	2.02679	-0.082	0.00241
2	53	0	0.6698	2.32207	0.23841
3	6	0	4.12871	0.77516	-0.3748
4	1	0	4.20442	1.74199	0.10626
5	6	0	3.56416	0.49293	-1.6167
6	1	0	3.11124	1.19547	-2.3047
7	6	0	3.91493	-0.9886	-1.9394
8	1	0	3.80785	-1.2952	-2.9802
9	6	0	3.05251	-1.7622	-0.8957
10	1	0	2.4622	-2.6375	-1.1425
11	6	0	3.63201	-1.4715	0.38091
12	1	0	3.5482	-2.0789	1.27528
13	6	0	4.83933	-0.5268	0.09714
14	1	0	5.56776	-0.416	0.90066
15	6	0	5.33257	-1.0933	-1.2789
16	1	0	6.08052	-0.4529	-1.7629
17	1	0	5.69818	-2.1256	-1.2112
18	6	0	0.51785	-1.0526	0.94206
19	7	0	-0.5293	-1.7706	0.39636
20	6	0	-1.3912	-2.2473	1.3991
21	1	0	-2.2822	-2.8091	1.17029
22	6	0	-0.8698	-1.8391	2.59756
23	1	0	-1.2222	-1.9909	3.60459
24	7	0	0.29686	-1.1127	2.30389
25	6	0	1.13464	-0.453	3.31328
26	1	0	1.91017	0.11459	2.79559
27	1	0	1.59763	-1.1958	3.97441
28	1	0	0.53186	0.24193	3.90778
29	6	0	-0.7869	-1.9472	-1.0437
30	1	0	-1.585	-2.6867	-1.1493
31	1	0	0.11849	-2.3279	-1.5279
32	6	0	-1.2074	-0.6385	-1.7544
33	1	0	-0.3528	0.04096	-1.8084
34	1	0	-1.5093	-0.9087	-2.7752
35	7	0	-2.2867	0.07979	-1.0821
36	1	0	-2.0781	0.9677	-0.6338

37	6	0	-3.5539	-0.427	-1.0098
38	8	0	-3.8923	-1.553	-1.4606
39	8	0	-4.3915	0.47024	-0.3695
40	6	0	-5.8586	0.18	-0.158
41	6	0	-6.013	-1.0697	0.73032
42	1	0	-5.4508	-0.9435	1.66401
43	1	0	-5.654	-1.963	0.21258
44	1	0	-7.0717	-1.2098	0.98426
45	6	0	-6.551	0.0203	-1.5249
46	1	0	-6.3702	0.90449	-2.1481
47	1	0	-7.6342	-0.0796	-1.3772
48	1	0	-6.1828	-0.8653	-2.049
49	6	0	-6.3334	1.44788	0.56893
50	1	0	-6.163	2.33297	-0.0539
51	1	0	-5.7865	1.57929	1.50934
52	1	0	-7.4053	1.37488	0.7914

Compound 4a Transition State 1

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1137.64151715 A.U. after 1 cycles
Imaginary frequencies: 1 (-20.2)

Zero-point correction=	0.436293 (Hartree/Particle)
Thermal correction to Energy=	0.462245
Thermal correction to Enthalpy=	0.463189
Thermal correction to Gibbs Free Energy=	0.377824
Sum of electronic and zero-point Energies=	-1137.205224
Sum of electronic and thermal Energies=	-1137.179273
Sum of electronic and thermal Enthalpies=	-1137.178328
Sum of electronic and thermal Free Energies=	-1137.263693

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-2.1591	0.26322	-0.0112
2	53	0	-1.634	-2.535	-0.1494
3	6	0	-4.0687	-0.4047	1.06055
4	1	0	-3.8751	-1.3178	1.60508
5	6	0	-4.3488	-0.2788	-0.3046
6	1	0	-4.4205	-1.0768	-1.0313
7	6	0	-4.8125	1.1859	-0.5274
8	1	0	-5.3376	1.3912	-1.4602
9	6	0	-3.4826	1.95715	-0.3007
10	1	0	-3.1437	2.72973	-0.9759

11	6	0	-3.1902	1.8204	1.09773
12	1	0	-2.5758	2.45342	1.72542
13	6	0	-4.3504	0.9803	1.69701
14	1	0	-4.4539	1.00338	2.78179
15	6	0	-5.5554	1.46554	0.82265
16	1	0	-6.4537	0.84928	0.95354
17	1	0	-5.795	2.52667	0.9694
18	6	0	-0.2922	1.20356	-0.4975
19	7	0	0.90482	0.63867	-0.951
20	6	0	1.86692	1.60595	-1.2621
21	1	0	2.84419	1.3379	-1.6291
22	6	0	1.30453	2.82141	-1.0109
23	1	0	1.70129	3.8174	-1.1193
24	7	0	0.00596	2.57641	-0.5415
25	6	0	-0.8503	3.72864	-0.2289
26	1	0	-1.564	3.48601	0.54746
27	1	0	-1.3858	4.07105	-1.1217
28	1	0	-0.2162	4.54612	0.12952
29	6	0	1.27436	-0.7824	-1.0974
30	1	0	2.02203	-0.8445	-1.8924
31	1	0	0.39726	-1.36	-1.385
32	6	0	1.85193	-1.4009	0.19331
33	1	0	1.06929	-1.4491	0.9545
34	1	0	2.13956	-2.4315	-0.0508
35	7	0	2.99794	-0.678	0.76563
36	1	0	2.94355	-0.3179	1.70985
37	6	0	4.19939	-0.5571	0.1216
38	8	0	4.42253	-0.9414	-1.0532
39	8	0	5.11613	0.07056	0.95422
40	6	0	6.5503	0.29528	0.53093
41	6	0	6.58766	1.21734	-0.703
42	1	0	6.0382	2.14573	-0.5026
43	1	0	6.15187	0.72204	-1.5744
44	1	0	7.62881	1.47956	-0.9312
45	6	0	7.2216	-1.066	0.26782
46	1	0	7.12957	-1.7136	1.14818
47	1	0	8.28953	-0.9145	0.06411
48	1	0	6.76843	-1.5675	-0.5912
49	6	0	7.14502	0.98728	1.76723
50	1	0	7.05694	0.34177	2.64823
51	1	0	6.61984	1.92685	1.9737
52	1	0	8.20636	1.2082	1.59904

Compound 4a Transition State 2

Method: b3lyp/LanL2DZ
SCF Done: E(RB3LYP) = -1137.63995264 A.U. after 1 cycles
Imaginary frequencies: 1 (-22.6)

Zero-point correction=	0.436232 (Hartree/Particle)
Thermal correction to Energy=	0.462176
Thermal correction to Enthalpy=	0.463121
Thermal correction to Gibbs Free Energy=	0.377454
Sum of electronic and zero-point Energies=	-1137.203721
Sum of electronic and thermal Energies=	-1137.177776
Sum of electronic and thermal Enthalpies=	-1137.176832
Sum of electronic and thermal Free Energies=	-1137.262499

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-2.015	0.34623	0.01862
2	53	0	-4.1909	-1.4666	-0.1206
3	6	0	-3.6606	1.88692	0.42622
4	1	0	-4.4965	1.39393	0.90142
5	6	0	-3.3619	1.91449	-0.9401
6	1	0	-3.9251	1.45001	-1.7386
7	6	0	-2.2287	2.96013	-1.1234
8	1	0	-2.0632	3.32287	-2.138
9	6	0	-1.0342	2.22773	-0.4491
10	1	0	-0.057	2.19033	-0.9098
11	6	0	-1.3471	2.19011	0.95149
12	1	0	-0.6724	2.08725	1.7924
13	6	0	-2.7144	2.90873	1.1047
14	1	0	-2.984	3.22384	2.11253
15	6	0	-2.6075	3.99854	-0.0145
16	1	0	-3.5608	4.50619	-0.2084
17	1	0	-1.8147	4.73395	0.17399
18	6	0	-0.3222	-0.9392	0.24797
19	7	0	0.99228	-0.618	0.63567
20	6	0	1.7884	-1.7601	0.79483
21	1	0	2.8168	-1.7066	1.10927
22	6	0	1.00377	-2.832	0.48549
23	1	0	1.225	-3.8863	0.48335
24	7	0	-0.2576	-2.3308	0.14191
25	6	0	-1.3101	-3.2637	-0.2987
26	1	0	-1.831	-2.8674	-1.169
27	1	0	-2.05	-3.4183	0.48795
28	1	0	-0.8336	-4.2152	-0.5577
29	6	0	1.62703	0.70659	0.73444

30	1	0	2.33934	0.69337	1.56613
31	1	0	0.87701	1.45534	0.95222
32	6	0	2.38106	1.10985	-0.5573
33	1	0	1.70881	1.02848	-1.4178
34	1	0	2.68393	2.15811	-0.4467
35	7	0	3.57236	0.30468	-0.8355
36	1	0	3.55884	-0.4152	-1.5464
37	6	0	4.75812	0.53826	-0.1799
38	8	0	4.90502	1.40313	0.71565
39	8	0	5.73025	-0.3235	-0.6537
40	6	0	7.15695	-0.2746	-0.1417
41	6	0	7.16988	-0.6037	1.36272
42	1	0	6.68495	-1.5702	1.54834
43	1	0	6.65763	0.17095	1.93894
44	1	0	8.20817	-0.672	1.7118
45	6	0	7.75928	1.10919	-0.4487
46	1	0	7.67615	1.33412	-1.5189
47	1	0	8.82369	1.11	-0.1811
48	1	0	7.25483	1.894	0.12079
49	6	0	7.83095	-1.3799	-0.9682
50	1	0	7.76299	-1.1566	-2.0388
51	1	0	7.34956	-2.3472	-0.7851
52	1	0	8.89003	-1.4586	-0.6937

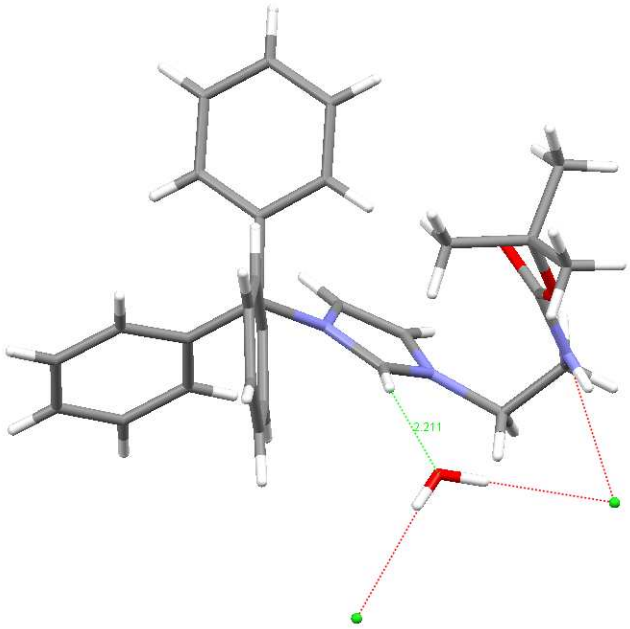


Figure S1. Crystal structure of **1c** showing the chloride counterion and the water molecule.

Table S1. Bond lengths (Å) and angles (°) for **1c**.

Bond lengths

C(4)-C(19)	1.5457(17)	C(22)-N(2)	1.3764(19)
C(12)-C(19)	1.5369(18)	C(23)-N(2)	1.4684(18)
C(18)-C(19)	1.5414(16)	C(23)-C(24)	1.514(2)
C(19)-N(1)	1.5016(16)	C(24)-N(3)	1.435(2)
C(20)-N(1)	1.3304(16)	C(25)-O(1)	1.2117(19)
C(20)-N(2)	1.3332(16)	C(25)-N(3)	1.343(2)
C(21)-C(22)	1.334(2)	C(25)-O(2)	1.344(2)
C(21)-N(1)	1.3895(16)	C(26)-O(2)	1.454(2)

Angles

C(5)-C(4)-C(3)	118.12(13)	C(21)-C(22)-N(2)	107.18(12)
C(5)-C(4)-C(19)	123.55(13)	N(2)-C(23)-C(24)	112.75(12)
C(3)-C(4)-C(19)	118.33(12)	N(3)-C(24)-C(23)	114.14(13)
C(7)-C(12)-C(11)	118.17(13)	O(1)-C(25)-N(3)	124.61(16)
C(7)-C(12)-C(19)	124.24(12)	O(1)-C(25)-O(2)	126.57(15)
C(11)-C(12)-C(19)	117.43(11)	N(3)-C(25)-O(2)	108.82(14)
C(17)-C(18)-C(13)	118.70(12)	O(2)-C(26)-C(27)	110.32(17)
C(17)-C(18)-C(19)	119.09(11)	O(2)-C(26)-C(29)	109.15(17)
C(13)-C(18)-C(19)	121.61(11)	O(2)-C(26)-C(28)	102.19(16)
N(1)-C(19)-C(12)	109.38(10)	C(20)-N(1)-C(21)	108.29(11)
N(1)-C(19)-C(18)	110.44(10)	C(20)-N(1)-C(19)	129.01(10)
C(12)-C(19)-C(18)	105.63(10)	C(21)-N(1)-C(19)	122.61(11)
N(1)-C(19)-C(4)	104.19(10)	C(20)-N(2)-C(22)	109.01(12)
C(12)-C(19)-C(4)	115.17(10)	C(20)-N(2)-C(23)	125.75(12)
C(18)-C(19)-C(4)	112.06(10)	C(22)-N(2)-C(23)	125.20(12)
N(1)-C(20)-N(2)	108.09(11)	C(25)-N(3)-C(24)	123.64(16)
C(22)-C(21)-N(1)	107.42(13)	C(25)-O(2)-C(26)	122.41(13)

Table S2. Bond lengths (Å) and angles (°) for $C_{18}H_{27}ClN_3O_2Rh$ (**3a**).

Bond lengths

Rh(1)-C(1)	2.204(2)	N(3)-C(14)	1.350(3)
Rh(1)-C(2)	2.206(2)	N(3)-C(13)	1.446(3)
Rh(1)-C(3)	2.083(2)	C(1)-C(2)	1.361(4)
Rh(1)-C(4)	2.083(2)	C(1)-C(5)	1.532(3)
Rh(1)-C(8)	2.026(2)	C(2)-C(6)	1.528(4)
Rh(1)-Cl(2)	2.3794(6)	C(3)-C(4)	1.401(3)
O(1)-C(14)	1.215(3)	C(3)-C(5)	1.533(3)
O(2)-C(14)	1.336(3)	C(4)-C(6)	1.526(3)
O(2)-C(15)	1.481(3)	C(5)-C(7)	1.535(4)
N(1)-C(8)	1.350(3)	C(6)-C(7)	1.534(4)
N(1)-C(10)	1.382(3)	C(9)-C(10)	1.322(4)
N(1)-C(11)	1.456(3)	C(12)-C(13)	1.511(4)
N(2)-C(8)	1.359(3)	C(15)-C(17)	1.509(4)
N(2)-C(9)	1.380(3)	C(15)-C(18)	1.510(4)
N(2)-C(12)	1.462(3)	C(15)-C(16)	1.512(4)

Angles

C(8)-Rh(1)-C(3)	96.49(8)	C(4)-Rh(1)-Cl(2)	156.56(7)
C(8)-Rh(1)-C(4)	97.38(9)	C(1)-Rh(1)-Cl(2)	98.52(6)
C(3)-Rh(1)-C(4)	39.31(9)	C(2)-Rh(1)-Cl(2)	97.68(7)
C(8)-Rh(1)-C(1)	157.93(10)	C(2)-C(1)-Rh(1)	72.12(14)
C(3)-Rh(1)-C(1)	66.77(9)	C(5)-C(1)-Rh(1)	93.75(13)
C(4)-Rh(1)-C(1)	78.93(9)	C(1)-C(2)-Rh(1)	71.93(13)
C(8)-Rh(1)-C(2)	159.36(10)	C(6)-C(2)-Rh(1)	93.78(14)
C(3)-Rh(1)-C(2)	79.27(9)	C(4)-C(3)-Rh(1)	70.35(13)
C(4)-Rh(1)-C(2)	66.49(9)	C(5)-C(3)-Rh(1)	98.59(14)
C(1)-Rh(1)-C(2)	35.95(10)	C(3)-C(4)-Rh(1)	70.33(13)
C(8)-Rh(1)-Cl(2)	93.22(6)	C(6)-C(4)-Rh(1)	98.84(15)
C(3)-Rh(1)-Cl(2)	159.00(7)		

Table S3. Bond lengths (Å) and angles (°) for $C_{18}H_{27}IN_3O_2Rh$ (**4a**).

Bond lengths

Rh(1)-C(1)	2.207(4)	N(9)-C(14)	1.458(6)
Rh(1)-C(2)	2.207(4)	C(10)-C(11)	1.314(7)
Rh(1)-C(4)	2.103(4)	C(11)-N(12)	1.380(6)
Rh(1)-C(5)	2.105(4)	N(12)-C(13)	1.454(6)
Rh(1)-C(8)	2.020(4)	C(14)-C(15)	1.513(7)
Rh(1)-I(1)	2.6597(5)	C(15)-N(16)	1.429(6)
C(1)-C(2)	1.355(6)	N(16)-C(17)	1.345(6)
C(1)-C(6)	1.532(6)	C(17)-O(18)	1.210(6)
C(2)-C(3)	1.523(6)	C(17)-O(19)	1.324(6)
C(3)-C(7)	1.526(7)	O(19)-C(20)	1.479(6)
C(3)-C(4)	1.527(6)	C(20)-C(22)	1.500(15)
C(4)-C(5)	1.379(6)	C(20)-C(220)	1.502(11)
C(5)-C(6)	1.524(7)	C(20)-C(210)	1.511(12)
C(6)-C(7)	1.529(7)	C(20)-C(230)	1.518(11)
C(8)-N(9)	1.356(5)	C(20)-C(23)	1.521(16)
C(8)-N(12)	1.357(5)	C(20)-C(21)	1.522(15)
N(9)-C(10)	1.383(6)		

Angles

C(8)-Rh(1)-C(4)	97.68(17)	C(1)-Rh(1)-I(1)	97.78(12)
C(8)-Rh(1)-C(5)	97.36(18)	C(2)-Rh(1)-I(1)	99.04(12)
C(4)-Rh(1)-C(5)	38.25(18)	C(2)-C(1)-Rh(1)	72.1(3)
C(8)-Rh(1)-C(1)	158.54(18)	C(6)-C(1)-Rh(1)	94.0(3)
C(4)-Rh(1)-C(1)	78.29(18)	C(1)-C(2)-Rh(1)	72.1(3)
C(5)-Rh(1)-C(1)	66.32(18)	C(3)-C(2)-Rh(1)	94.2(3)
C(8)-Rh(1)-C(2)	158.96(18)	C(5)-C(4)-Rh(1)	71.0(3)
C(4)-Rh(1)-C(2)	66.17(17)	C(3)-C(4)-Rh(1)	98.3(3)
C(5)-Rh(1)-C(2)	78.45(18)	C(4)-C(5)-Rh(1)	70.8(3)
C(1)-Rh(1)-C(2)	35.76(17)	C(6)-C(5)-Rh(1)	98.3(3)
C(8)-Rh(1)-I(1)	92.83(12)	N(9)-C(8)-Rh(1)	128.6(3)
C(4)-Rh(1)-I(1)	159.87(14)	N(12)-C(8)-Rh(1)	127.4(3)
C(5)-Rh(1)-I(1)	156.35(14)		

Table S4. Bond lengths (Å) and angles (°) for **3c**.

Bond Lengths

Rh(1)-C(18)	2.0549(18)
Rh(1)-C(31)	2.090(2)
Rh(1)-C(32)	2.096(2)
Rh(1)-C(37)	2.181(2)
Rh(1)-C(36)	2.199(2)
Rh(1)-Cl(2)	2.4283(6)
O(1)-C(23)	1.198(3)
O(2)-C(23)	1.346(3)
O(2)-C(24)	1.475(3)
N(1)-C(18)	1.361(2)
N(1)-C(21)	1.465(2)
N(1)-C(19)	1.381(2)
N(2)-C(12)	1.501(2)
N(2)-C(18)	1.368(2)
N(2)-C(20)	1.392(2)
N(3)-C(23)	1.339(3)
N(3)-C(22)	1.451(3)

C(12)-C(13)	1.546(3)
C(12)-C(9)	1.552(3)
C(12)-C(1)	1.538(3)
C(20)-C(19)	1.324(3)
C(21)-C(22)	1.514(3)
C(10)-C(11)	1.400(3)
C(25)-C(24)	1.490(4)
C(24)-C(28)	1.501(4)
C(24)-C(29)	1.499(4)
C(32)-C(31)	1.394(3)
C(32)-C(33)	1.530(3)
C(31)-C(35)	1.522(3)
C(36)-C(37)	1.358(4)
C(36)-C(33)	1.527(4)
C(33)-C(34)	1.532(4)
C(37)-C(35)	1.528(4)
C(35)-C(34)	1.540(3)

Angles

C(18)-Rh(1)-C(31)	92.76(8)
C(18)-Rh(1)-C(32)	98.34(8)
C(31)-Rh(1)-C(32)	38.90(9)
C(18)-Rh(1)-C(37)	150.36(10)
C(31)-Rh(1)-C(37)	66.32(10)
C(32)-Rh(1)-C(37)	78.78(9)
C(18)-Rh(1)-C(36)	163.77(9)
C(31)-Rh(1)-C(36)	78.79(10)
C(32)-Rh(1)-C(36)	66.39(9)
C(37)-Rh(1)-C(36)	36.13(10)
C(18)-Rh(1)-Cl(2)	94.60(5)
C(31)-Rh(1)-Cl(2)	146.36(7)
C(32)-Rh(1)-Cl(2)	165.81(6)
C(37)-Rh(1)-Cl(2)	92.79(7)
C(36)-Rh(1)-Cl(2)	100.11(7)
N(1)-C(18)-Rh(1)	121.26(13)
N(2)-C(18)-Rh(1)	134.27(13)
C(31)-C(32)-Rh(1)	70.33(13)
C(33)-C(32)-Rh(1)	98.49(15)
C(32)-C(31)-Rh(1)	70.76(13)
C(35)-C(31)-Rh(1)	98.66(16)
C(37)-C(36)-Rh(1)	71.22(13)
C(33)-C(36)-Rh(1)	94.39(14)
C(36)-C(37)-Rh(1)	72.65(14)
C(35)-C(37)-Rh(1)	94.75(15)
N(1)-C(18)-N(2)	103.48(15)

N(2)-C(12)-C(1)	111.52(15)
N(2)-C(12)-C(13)	109.61(15)
N(2)-C(12)-C(9)	105.20(15)
C(19)-C(20)-N(2)	107.59(18)
N(1)-C(21)-C(22)	112.73(16)
C(20)-C(19)-N(1)	106.75(17)
N(3)-C(22)-C(21)	114.17(17)
C(18)-N(2)-C(20)	110.42(15)
C(18)-N(2)-C(12)	129.75(15)
C(20)-N(2)-C(12)	119.82(15)
C(18)-N(1)-C(19)	111.73(16)
C(18)-N(1)-C(21)	124.65(15)
C(19)-N(1)-C(21)	123.53(16)
C(23)-O(2)-C(24)	120.9(2)
C(31)-C(32)-C(33)	105.5(2)
C(32)-C(31)-C(35)	106.6(2)
C(37)-C(36)-C(33)	106.1(2)
C(32)-C(33)-C(36)	100.65(17)
C(32)-C(33)-C(34)	100.9(2)
C(36)-C(33)-C(34)	101.3(2)
C(36)-C(37)-C(35)	107.4(2)
C(37)-C(35)-C(31)	100.08(18)
C(37)-C(35)-C(34)	100.6(2)
C(31)-C(35)-C(34)	100.5(2)
C(33)-C(34)-C(35)	93.58(18)

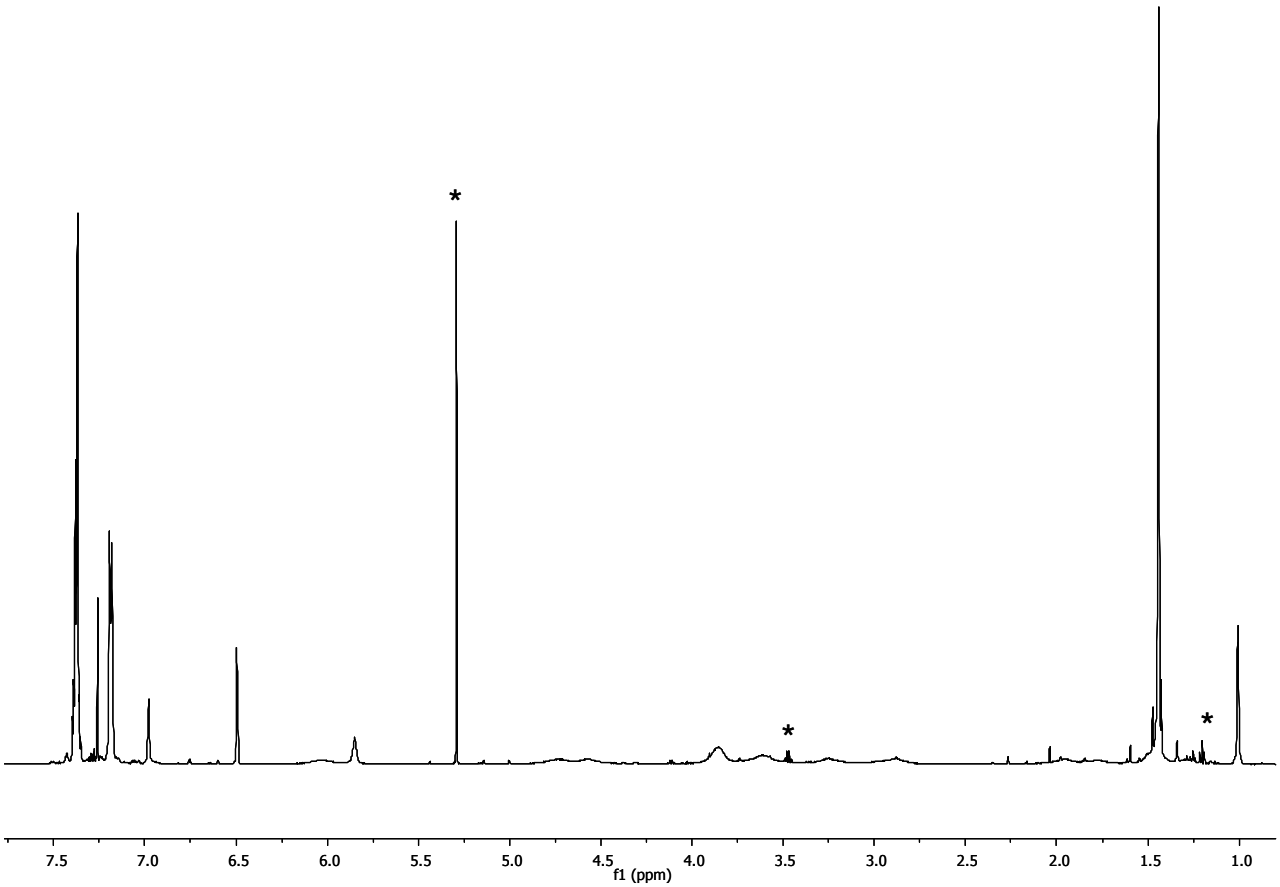


Figure S2. ^{1}H NMR of **3c** in $CDCl_3$, 298.15 K, 600 MHz (signals labelled with the asterisks solvents/impurities).

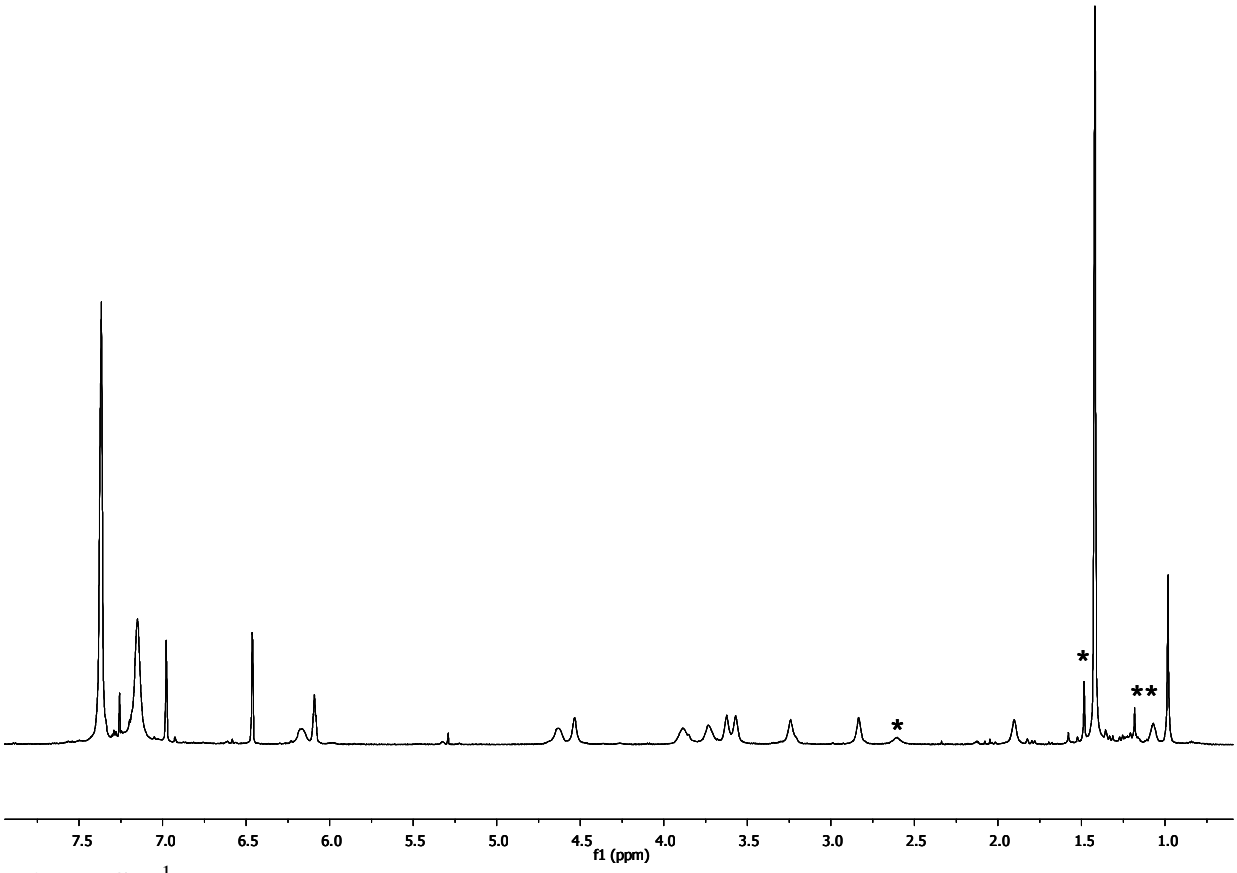


Figure S3. ^{1}H NMR of **3c** in $CDCl_3$, 253.15 K, 600 MHz (signals labelled with the asterisks impurities).

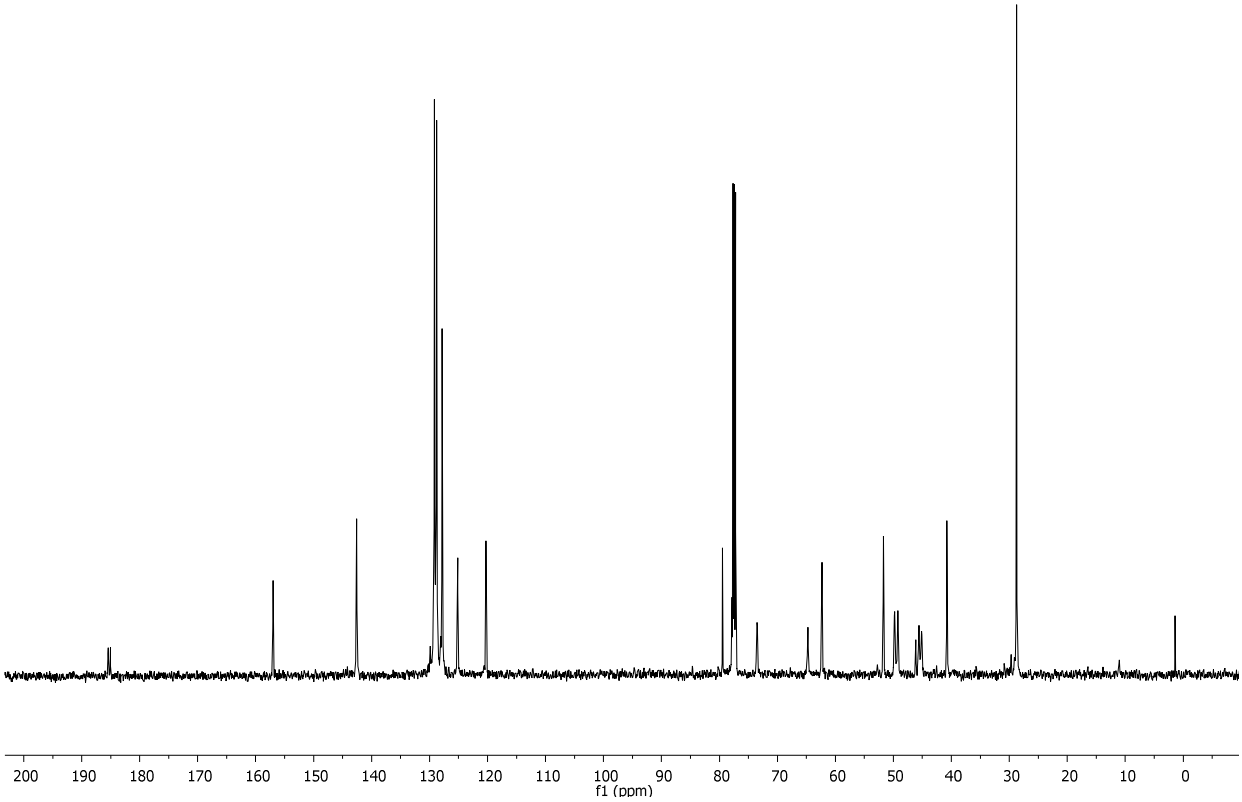


Figure S4. ^{13}C NMR of **3c** in $CDCl_3$, 253.15 K, 600 MHz.

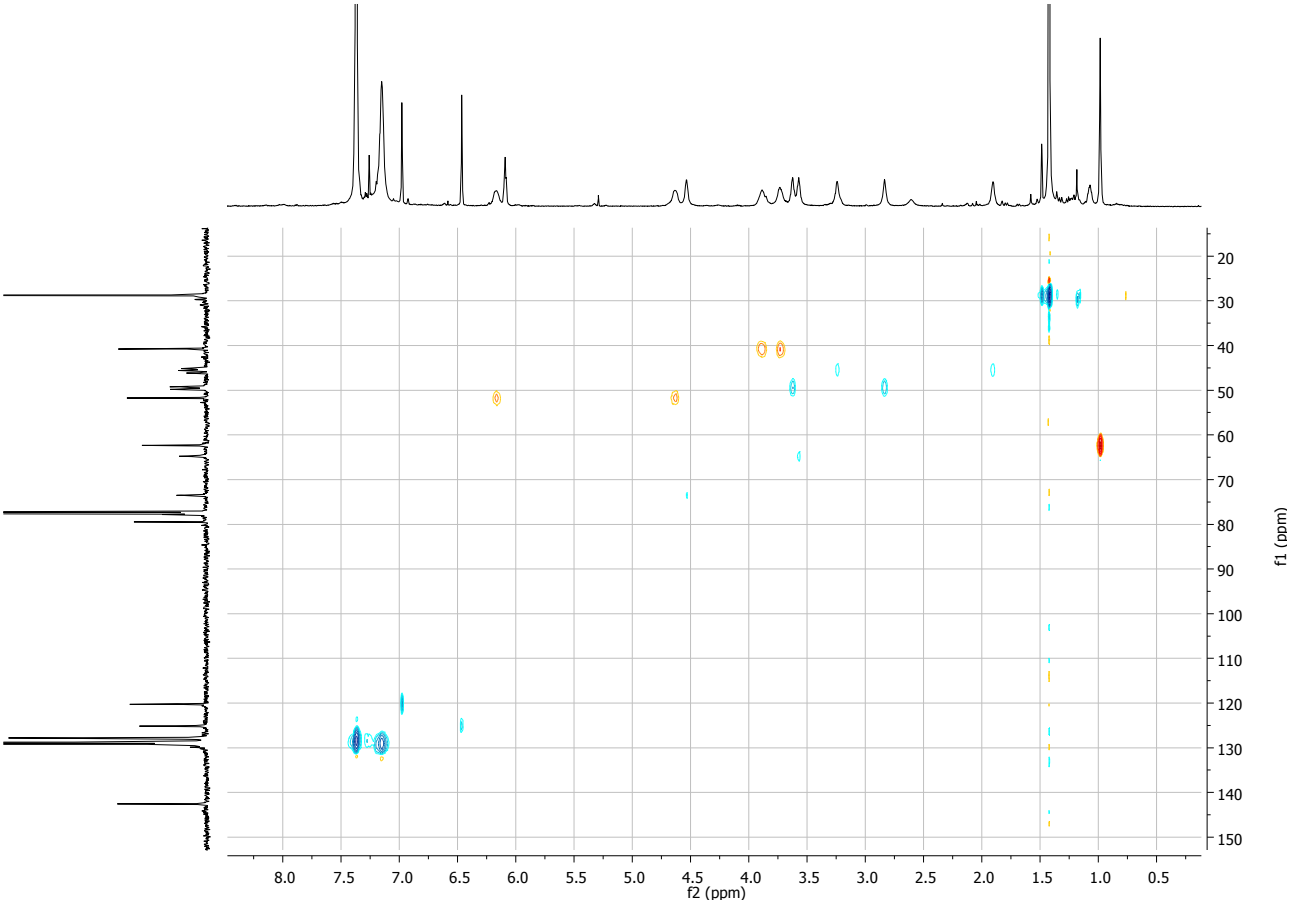


Figure S5. HSQC of **3c** in $CDCl_3$, 253.15 K, 600 MHz.

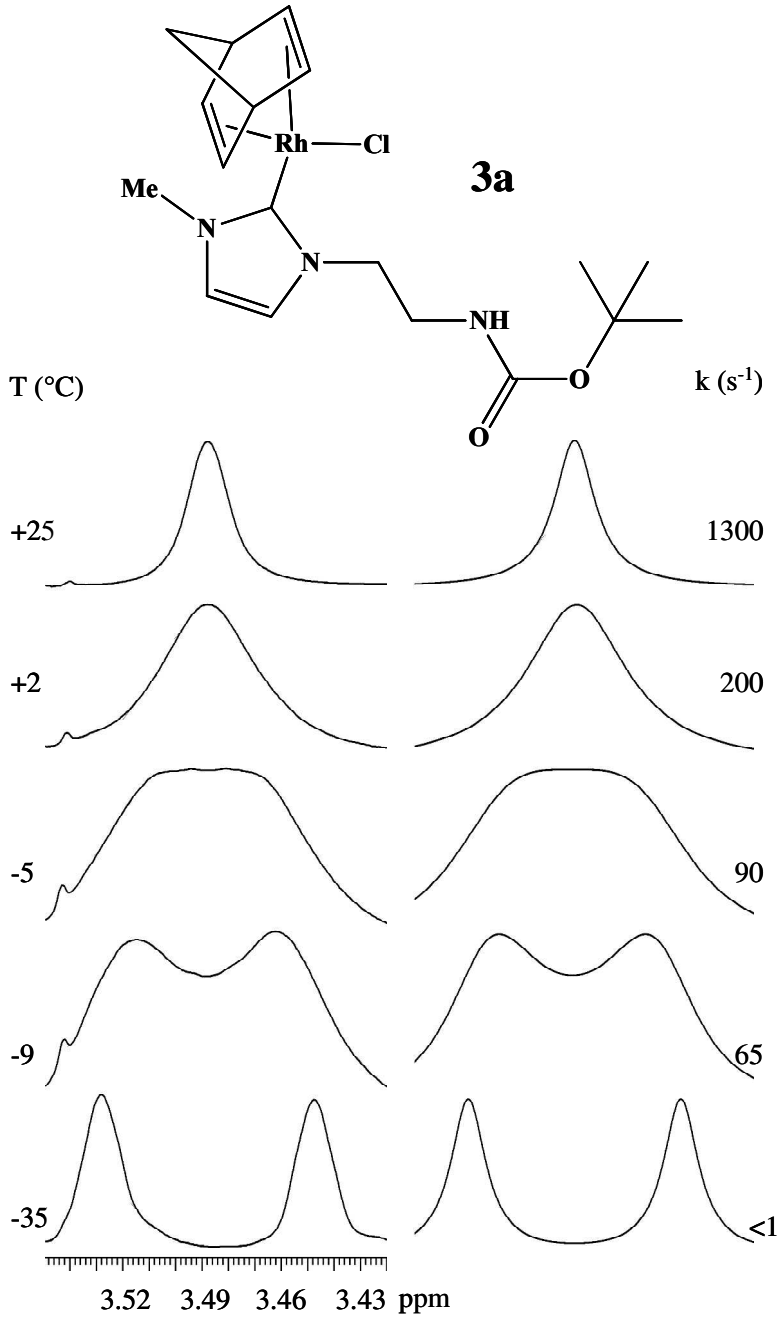


Figure S6. Variable temperature spectra of **3a** showing the evolution of a norbornadiene CH signal (^{1}H NMR at 600 MHz in CD_2Cl_2). On the right the simulations with the corresponding rate constants are reported.

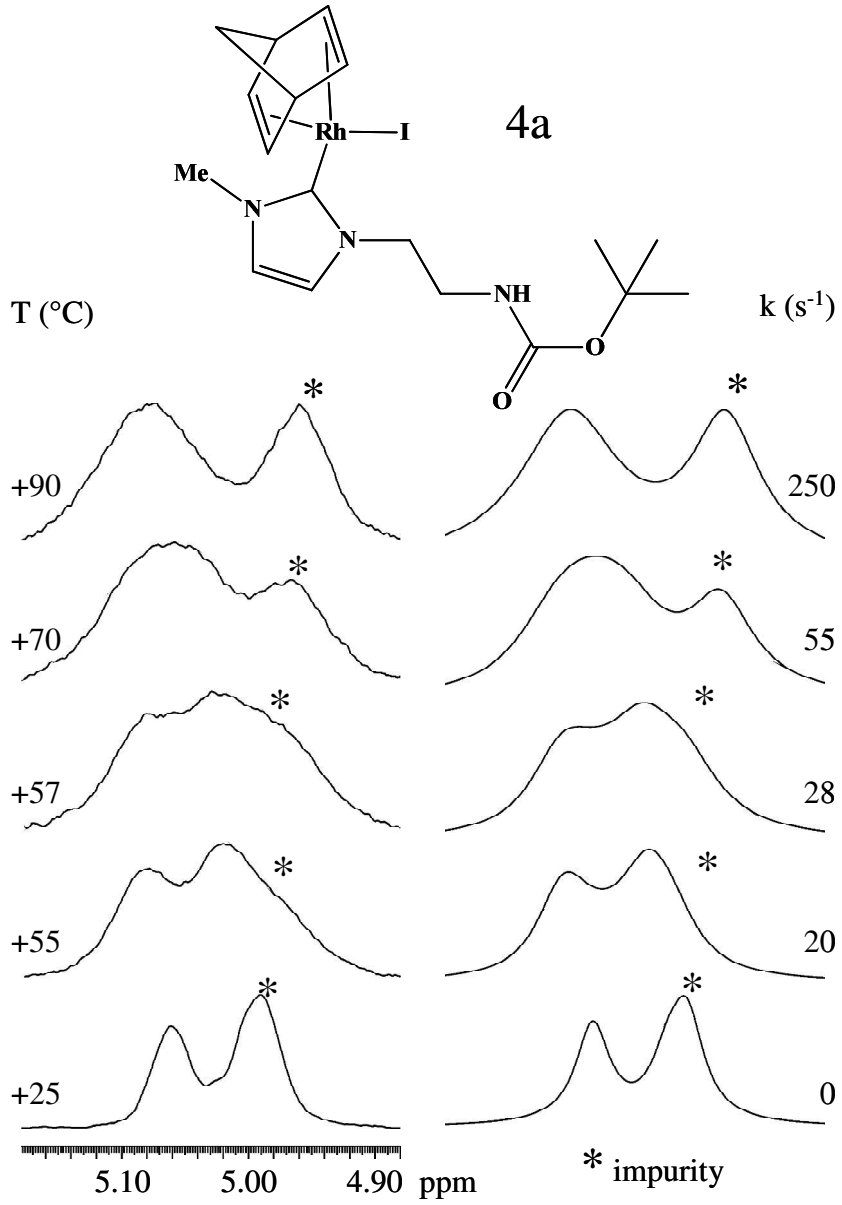


Figure S7. Variable temperature spectra of **4a** showing the evolution of a norbornadiene CH signal (^{1}H NMR at 300 MHz in $C_2D_2Cl_4$). On the right the simulations with the corresponding rate constants are reported.

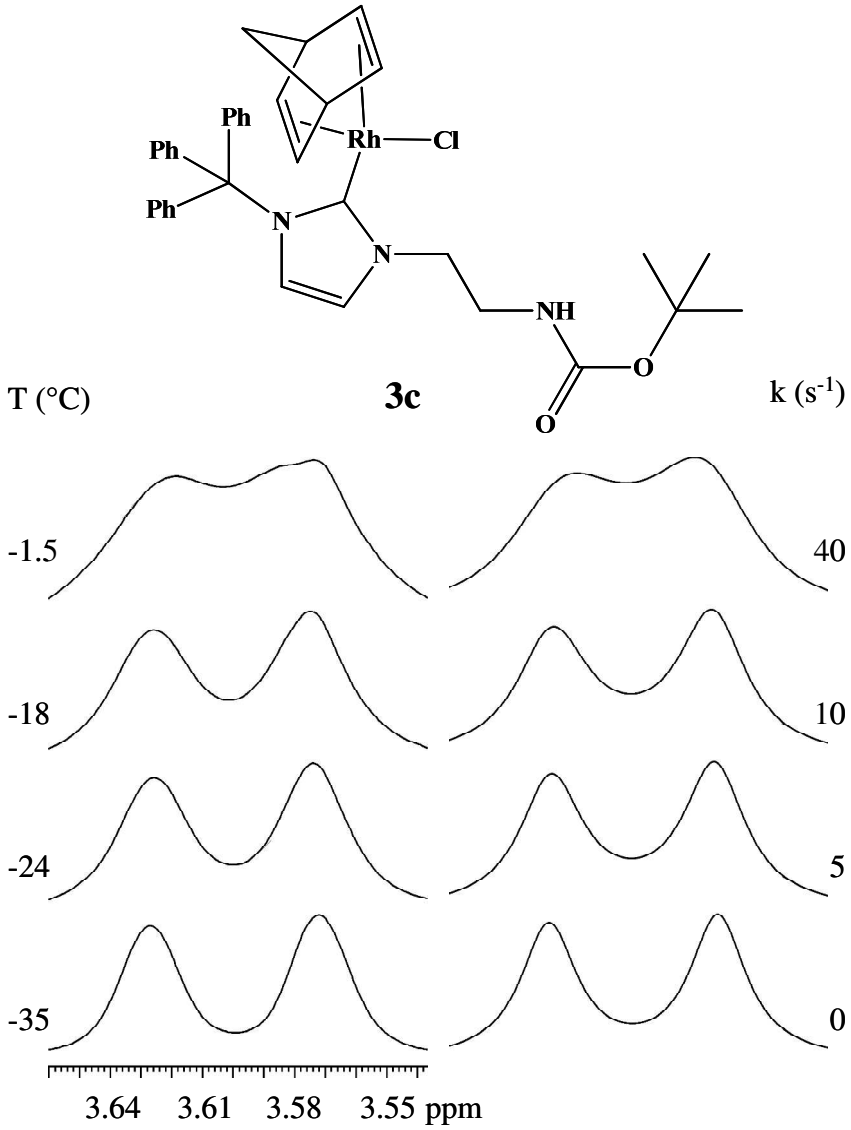
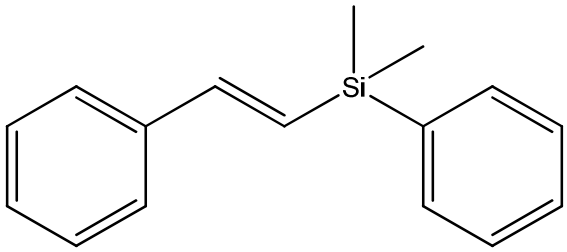


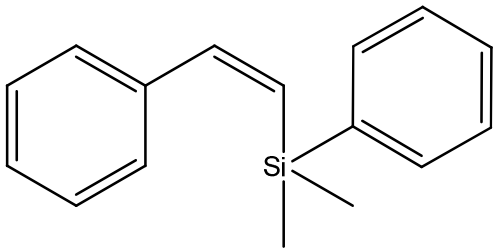
Figure S8. Variable temperature spectra of **3c** showing the evolution of a norbornadiene CH signal (^{1}H-NMR at 600 MHz in $CDCl_3$). On the right the simulations with the corresponding rate constants are reported.

Details and full characterization data for the catalysis

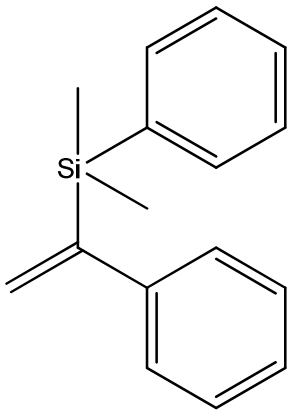
Hydrosilylation products: ^{1}H-NMR characterizations.



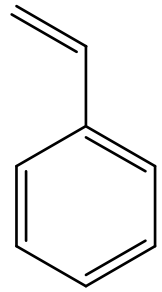
(E)-2- (dimethyl(phenyl)silyl)-1-phenyl-ethene (1s)[1]
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.6-7.2 (m, 5H), 7.0 (d, $J_{H,H}$ = 19 Hz, 1H), 6.6 (d, $J_{H,H}$ = 19 Hz, 1H), 0.36 (s, 6H) ppm.



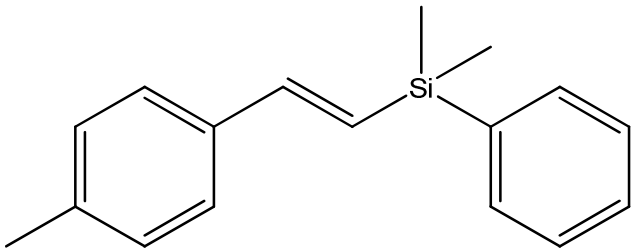
(Z)-2- (dimethyl(phenyl)silyl)-1-phenyl-ethene (2s)[2]
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.6-7.2 (m, 5H), 7.5 (d, $J_{H,H}$ = 15 Hz, 1H), 6.0 (d, $J_{H,H}$ = 15 Hz, 1H), 0.36 (s, 6H) ppm.



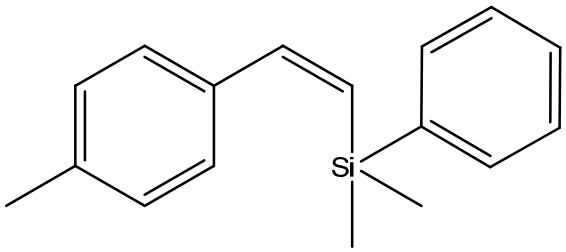
1-(dimethyl(phenyl)silyl)-1-phenyl-ethene (3s)[1]
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.6-7.3 (m, 5H), 5.98 (d, $J_{H,H}$ = 2.9 Hz, 1H,), 5.66 (d, $J_{H,H}$ = 2.9 Hz, 1H), 0.41 (s, 6H) ppm.



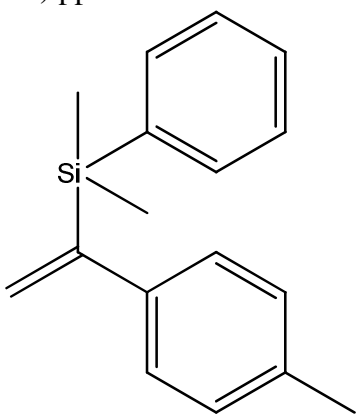
Styrene (4s)
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.10 (m, 5H), 6.69 (dd, $J_{H,H}$ = 18.0, 11.0 Hz, 1H), 5.74 (d, $J_{H,H}$ = 18.0, 1H), 5.22 (d, $J_{H,H}$ = 11.0 Hz, 1H).



(E)-2- (dimethyl(phenyl)silyl)-1-tolyl-ethene (5s)
^{1}H-NMR ($CDCl_3$): 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.

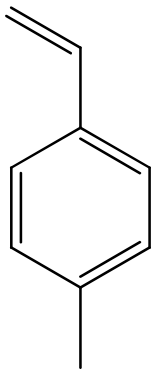


(Z)-2- (dimethyl(phenyl)silyl)-1-tolyl-ethene (6s)[3]
^{1}H-NMR ($CDCl_3$): δ 7.60–7.52 (m, 2H), 7.43 (d, $J_{H,H}$ = 15.3 Hz, 1H), 7.38–7.32 (m, 3H), 7.13 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.06 (d, $J_{H,H}$ = 8.1 Hz, 2H), 5.96 (d, $J_{H,H}$ = 15.0 Hz, 1H), 2.30 (s, 3H), 0.28 (s, 6H) ppm.

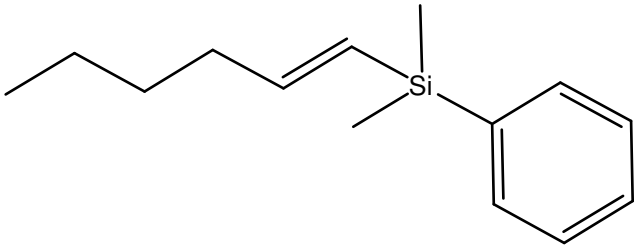


1-(dimethyl(phenyl)silyl)-1-tolyl-ethene (7s)

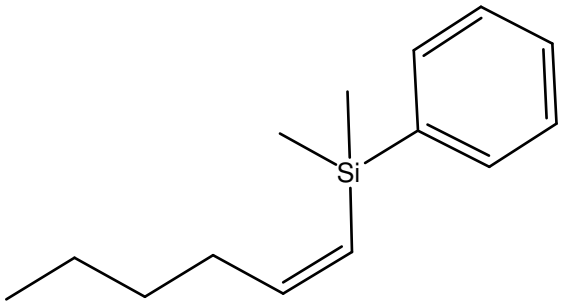
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.6-7.3 (m, 4H), 5.93 (d, 1H, $J_{H,H}$ = 2.9 Hz), 5.66 (d, 1H, $J_{H,H}$ = 2.9 Hz), 2.35 (s, 3H), 0.30 (s, 6H) ppm.



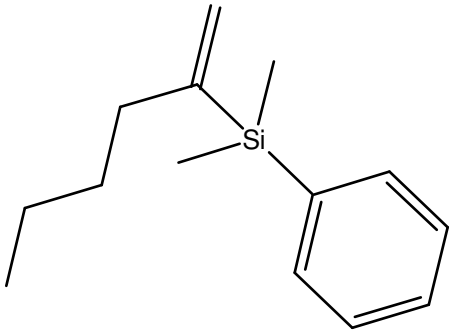
4-Methylstyrene (8s)
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.20 (d, $J_{H,H}$ = 8.0 Hz, 2H), 6.77 (dd, $J_{H,H}$ = 18.0, 11.0 Hz, 1H), 5.78 (d, $J_{H,H}$ = 18.0, 1H), 5.26 (d, $J_{H,H}$ = 11.0 Hz, 1H), 2.41 (s, 3H).



(E)-2- (dimethyl(phenyl)silyl)-1-hexene (9s)[4]
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.7-7.3 (m, 5H), 6.1 (dt, 1H, $J_{H,H}$ = 19 Hz, 6.2 Hz, CH_2CH=), 5.7 (d, 1H, $J_{H,H}$ = 19 Hz, SiCH=), 2.2-0.8 (m, 9H, ^{n}Bu), 0.30 (s, 6H, $SiMe_2$) ppm.

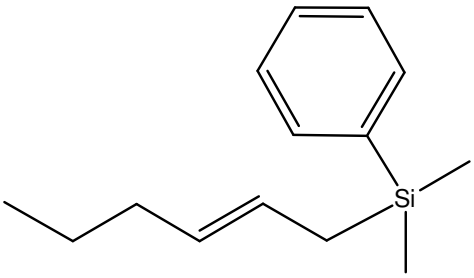


(Z)-2- (dimethyl(phenyl)silyl)-2-hexene (10s)[4]
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.7-7.3 (m, 5H, Ph), 6.4 (dt, 1H, $J_{H,H}$ = 14, 7.4 Hz, ^{n}BuCH=), 5.6 (d, 1H, $J_{H,H}$ = 14 Hz), 2.2-0.8 (m, 9H, ^{n}Bu), 0.38 (s, 6H, $SiMe_2$) ppm.



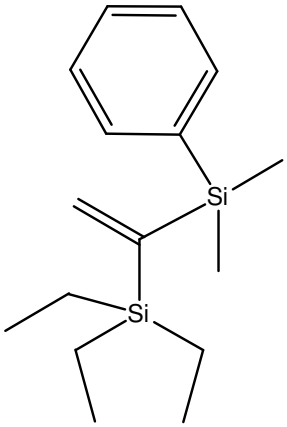
2-(dimethyl(phenyl)silyl)-1-hexene (11s)[4]

^{1}H NMR ($CDCl_3$, 300 MHz): 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, $SiMe_2$) ppm.



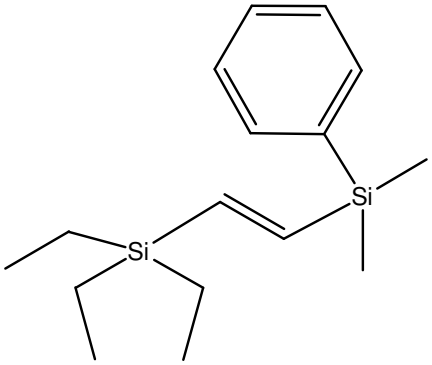
(E)-1-(Dimethylphenylsilyl)hex-2-ene (12s)[5]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.7-7.3 (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, $SiMe_2$) ppm.



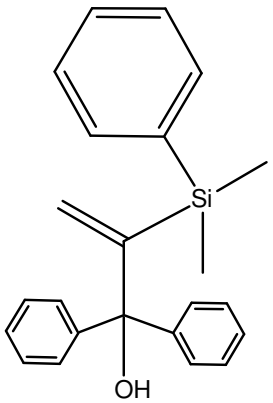
1-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene (13s)[6]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.19 (m, 5H,Ph), AB system (δ_A = 6.40, δ_B = 6.42, $J_{A,B}$ = 5.2, 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).



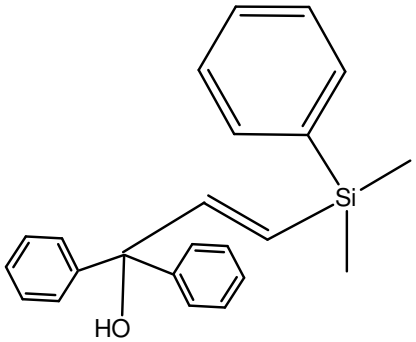
(E)-2-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene (14s)[6]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.15 (m, 5H,Ph), AB system (δ_A = 6.76, δ_B = 6.65, $J_{A,B}$ = 22.8, 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)ethane (15s)[7]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77-7.24 (m, 15H, Ph), 5.72 (d, $J_{H,H}$ = 1.8, 1H, CH_2), 5.28 (d, $J_{H,H}$ = 1.8, 1H, CH_2), 0.39 (s, 6H, CH_3).



(E)-2-(Dimethylphenylsilyl)-1-(CPh_2OH)ethene (16s)

^{1}H NMR ($CDCl_3$, 300 MHz): 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, 1H, =CHSi), 0.35 (s, 6H, CH_3).

Hydrosilylation: graphs of conversions and selectivities vs catalyst and time.

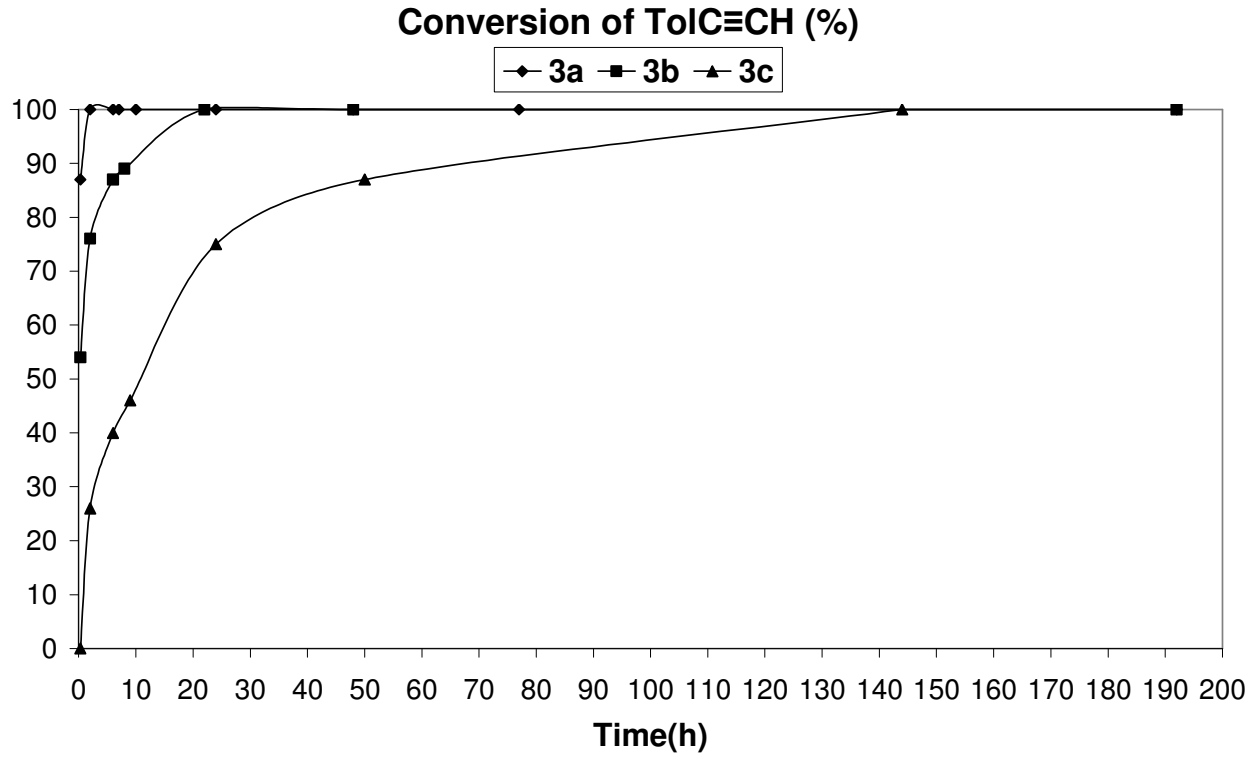


Figure S9. Reaction profile of conversion vs time for the hydrosilylation of TolC≡CH with complexes **3a**, **3b**, **3c**.

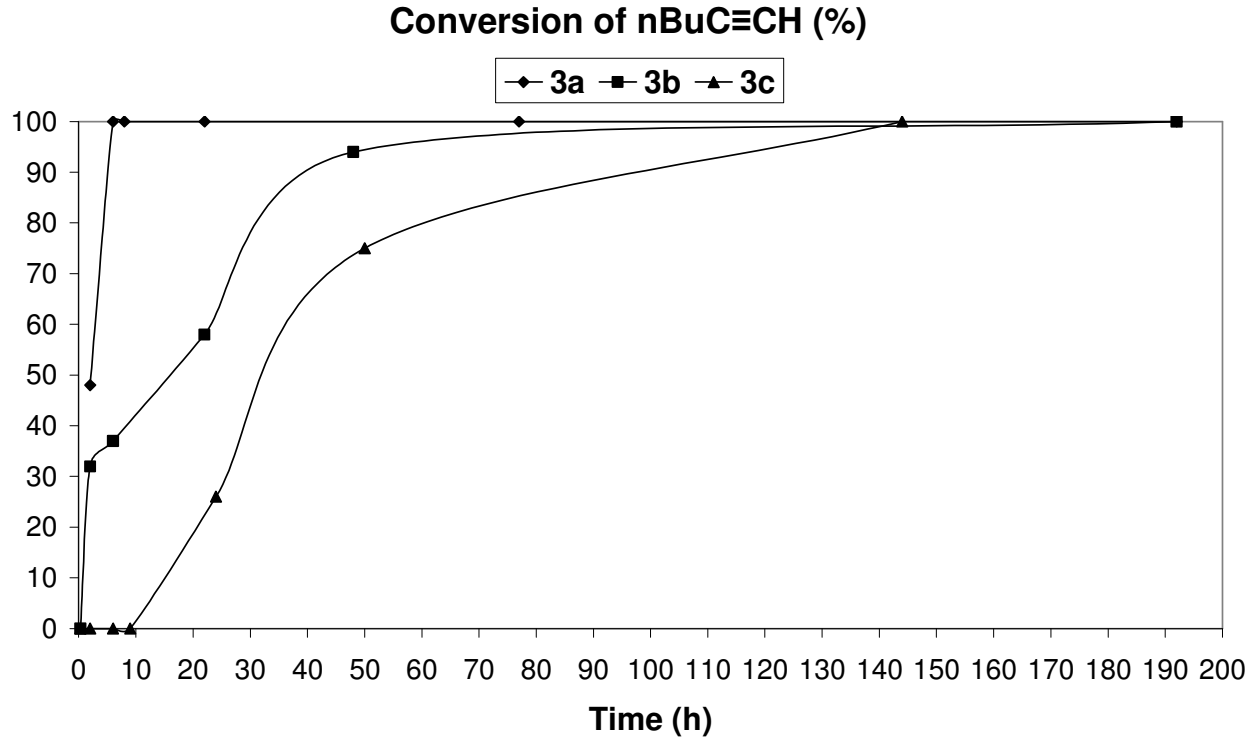


Figure S10. Reaction profile of conversion vs time for the hydrosilylation of ^{n}BuC≡CH with complexes **3a**, **3b**, **3c**.

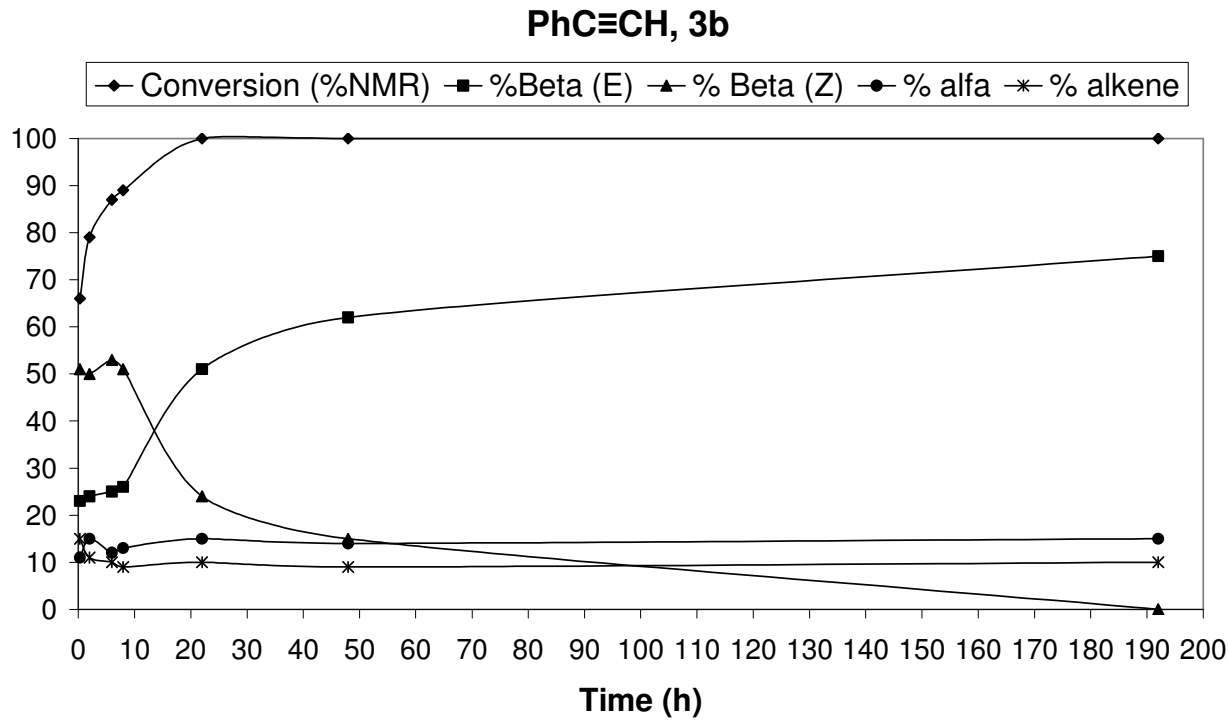


Figure S11. Reaction profile of conversion and selectivities vs time for the hydrosilylation of PhC≡CH with **3b**.

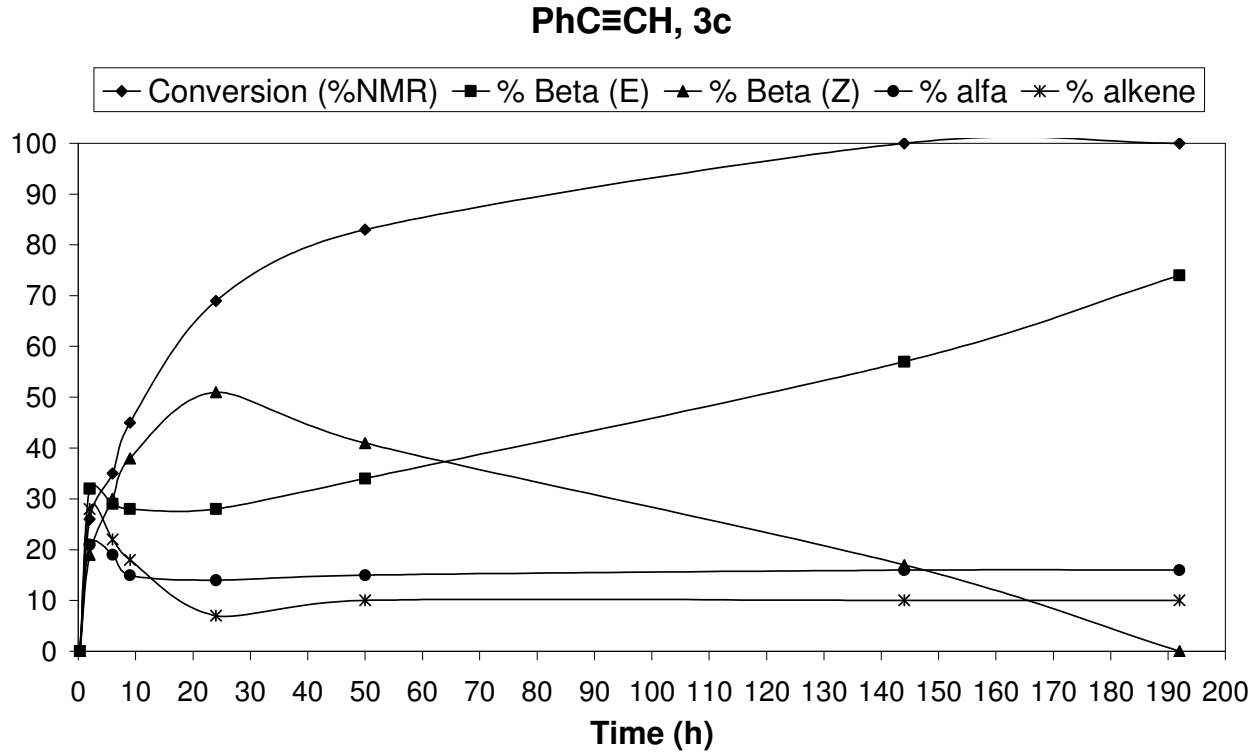


Figure S12. Reaction profile of conversion and selectivities vs time for the hydrosilylation of PhC≡CH with **3c**.

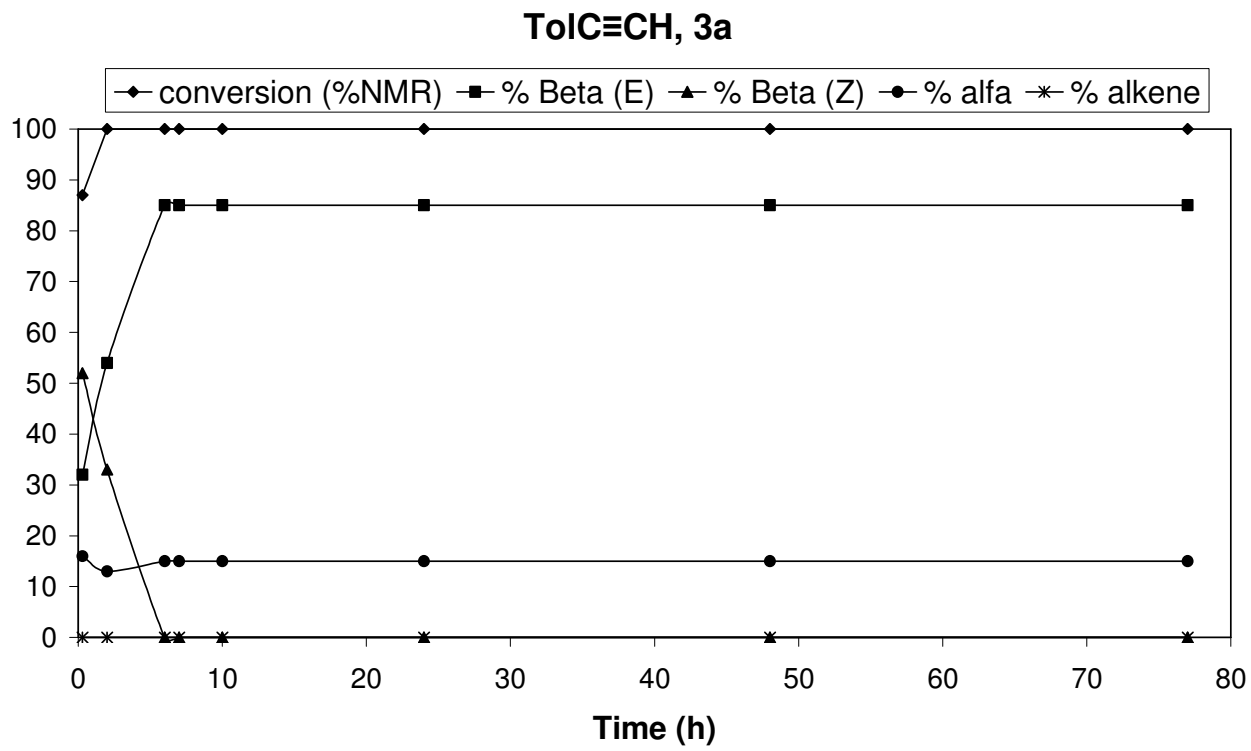


Figure S13. Reaction profile of conversion and selectivities vs time for the hydrosilylation of TolC≡CH with **3a**.

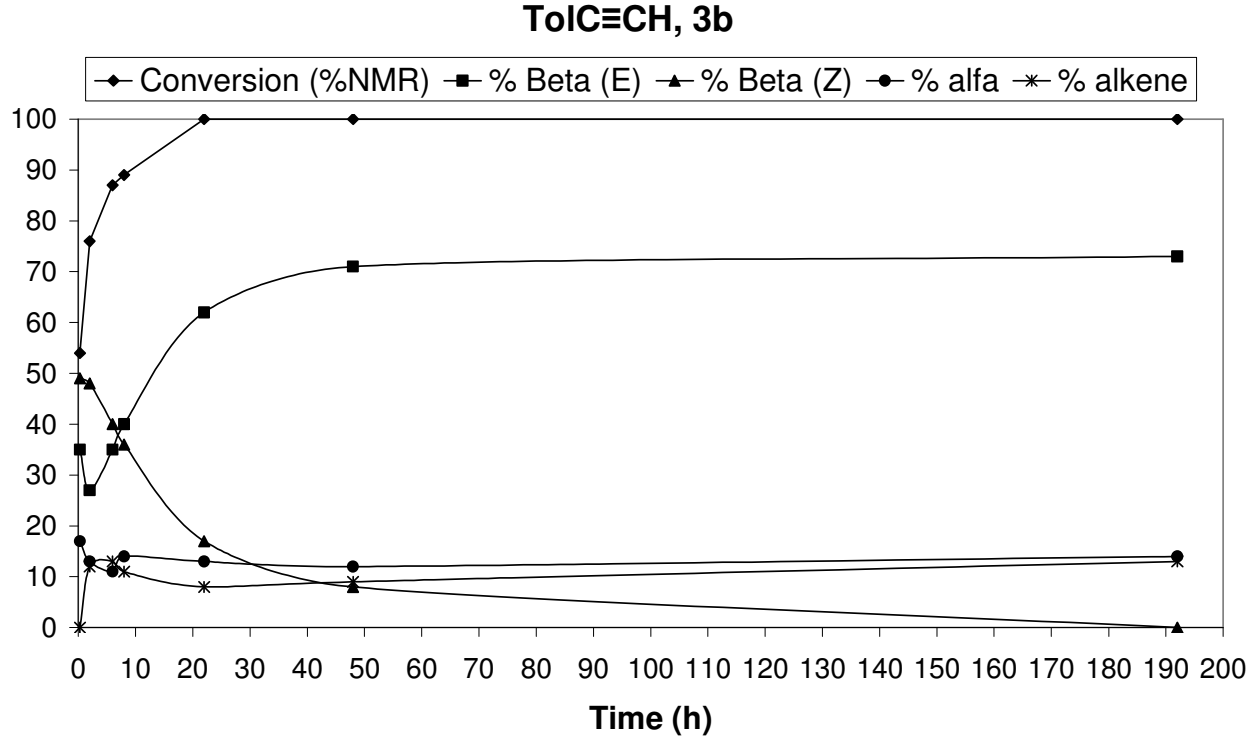


Figure S14. Reaction profile of conversion and selectivities vs time for the hydrosilylation of TolC≡CH with **3b**.

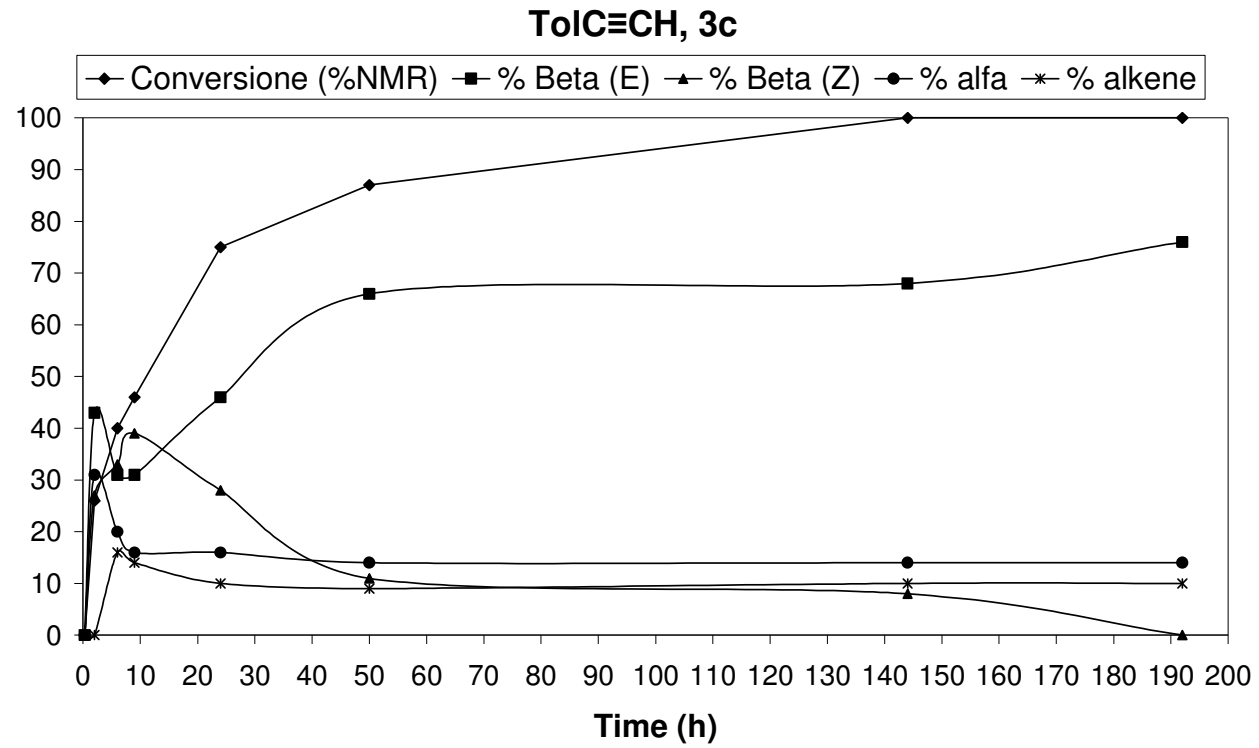


Figure S15. Reaction profile of conversion and selectivities vs time for the hydrosilylation of TolC≡CH with **3c**.

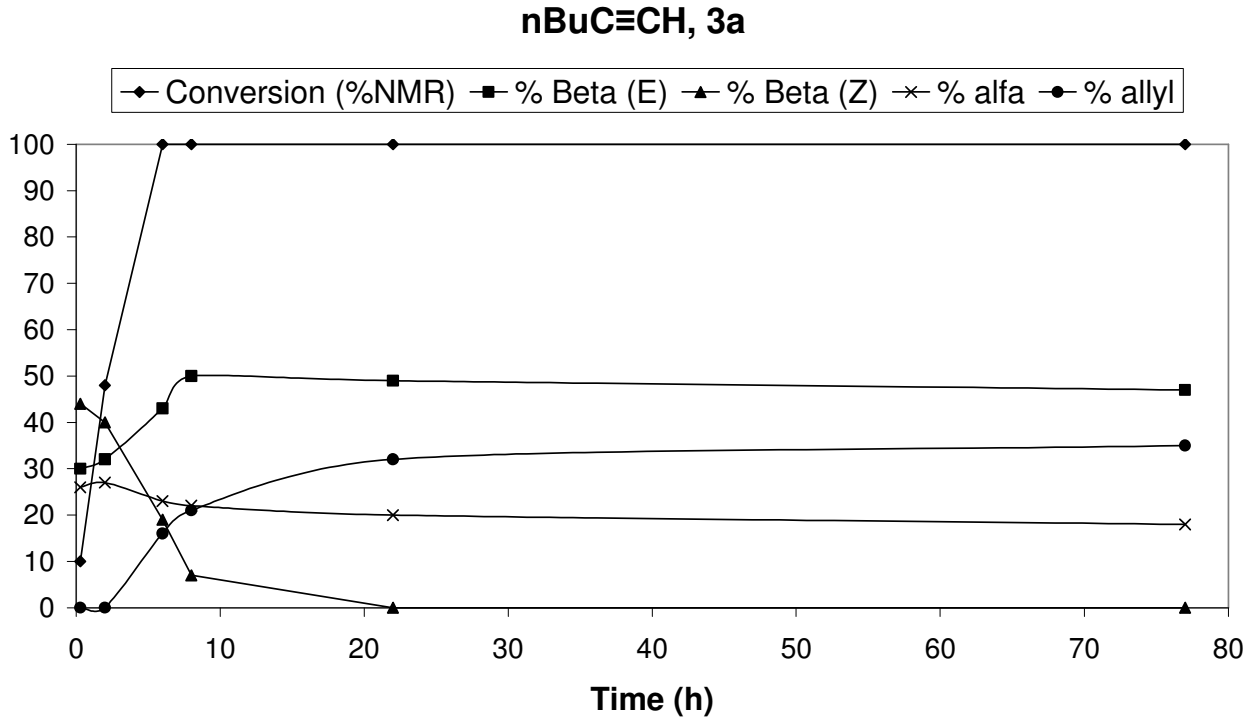


Figure S16. Reaction profile of conversion and selectivities vs time for the hydrosilylation of ^{n}BuC≡CH with **3a**.

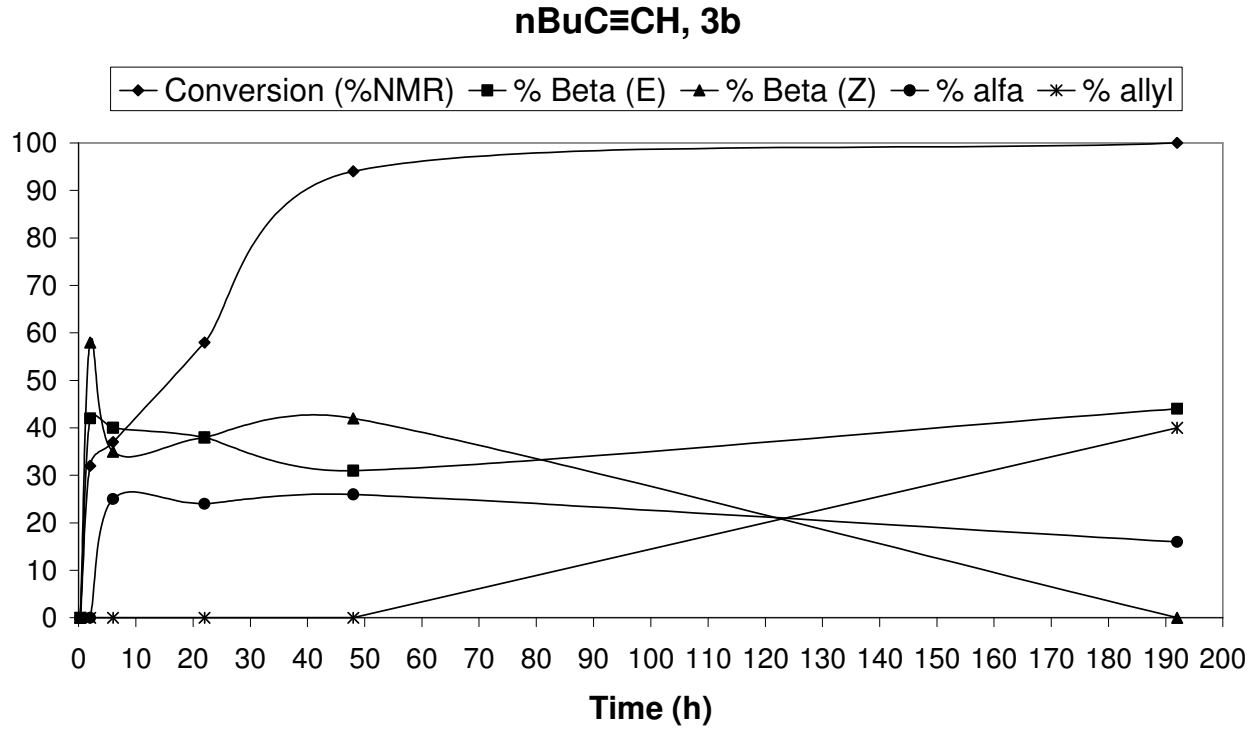


Figure S17. Reaction profile of conversion and selectivities vs time for the hydrosilylation of ^{n}BuC≡CH with **3b**.

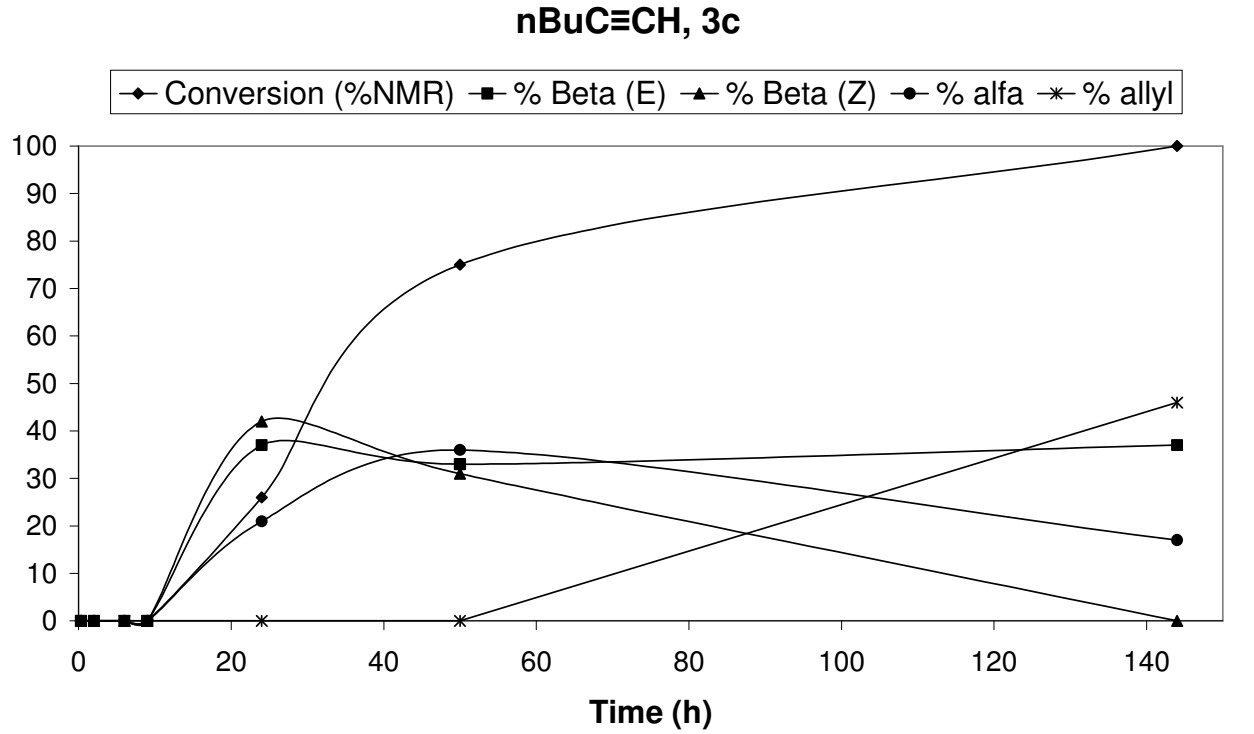


Figure S18. Reaction profile of conversion and selectivities vs time for the hydrosilylation of ^{n}BuC≡CH with **3a**.

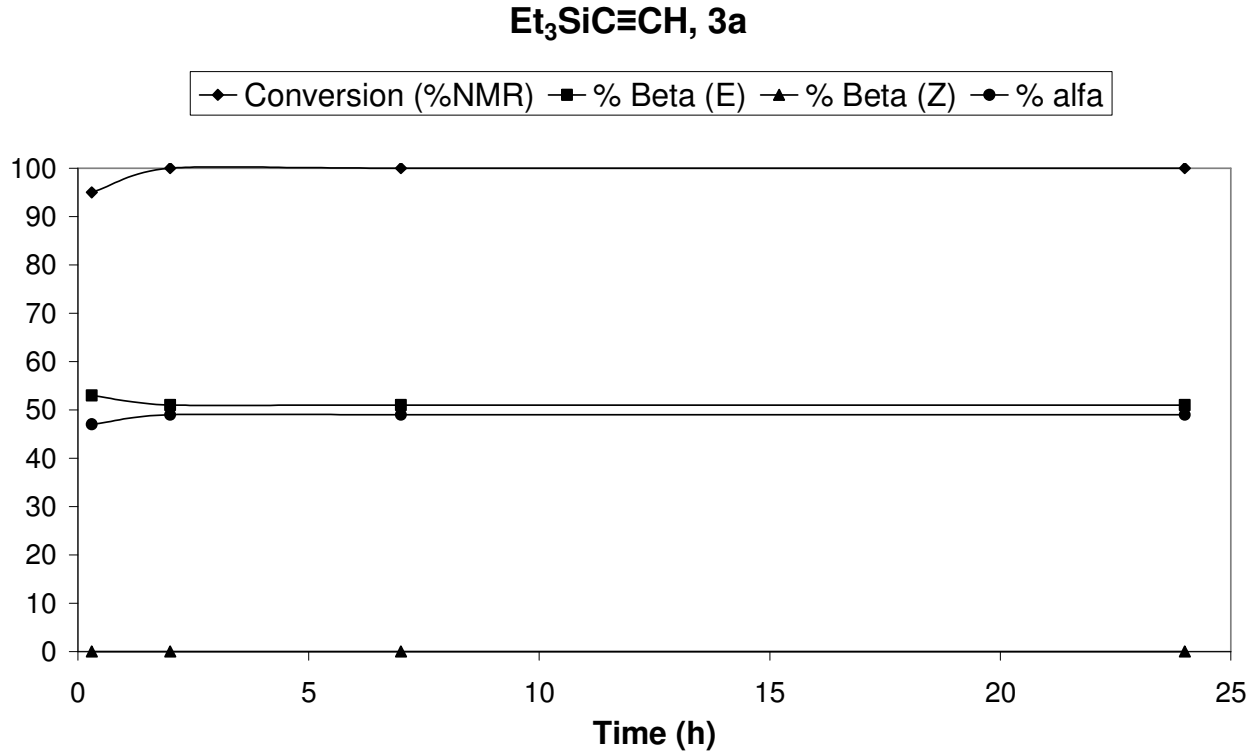


Figure S19. Reaction profile of conversion and selectivities vs time for the hydrosilylation of $Et_3SiC{\equiv}CH$ with **3a**.

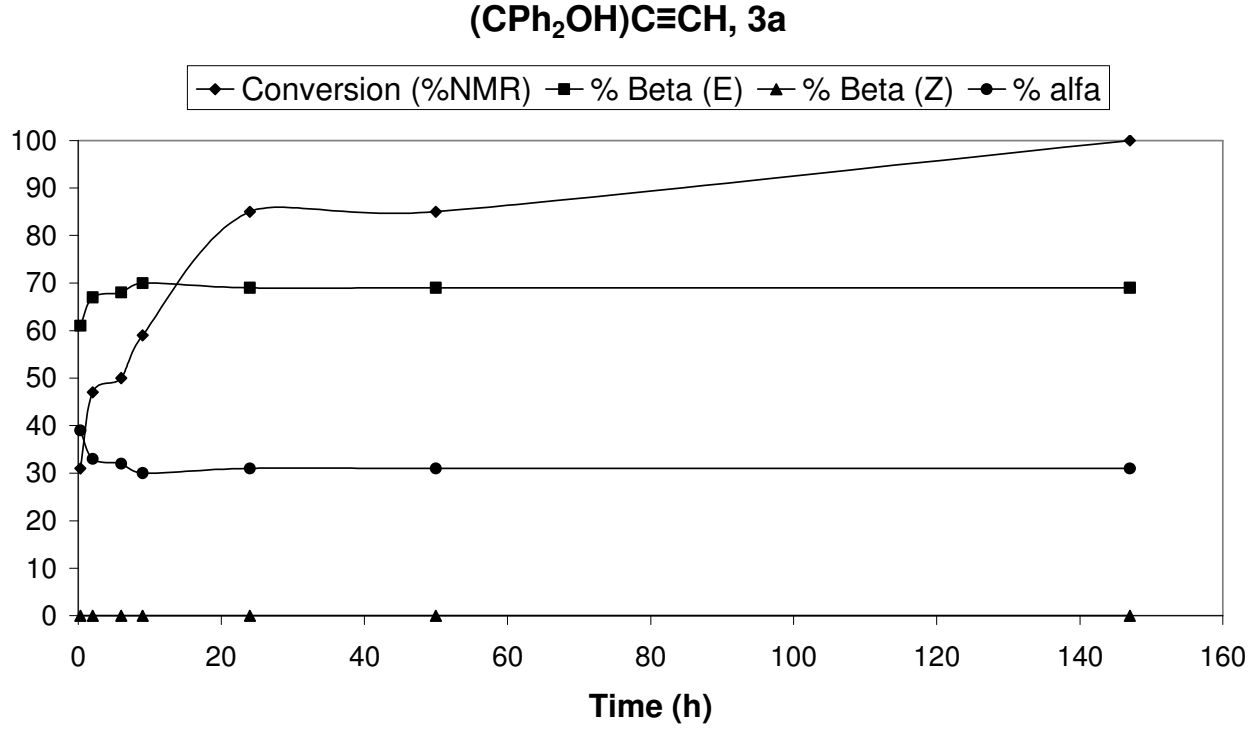


Figure S20. Reaction profile of conversion and selectivities vs time for the hydrosilylation of $(CPh_2OH)C{\equiv}CH$ with **3a**.

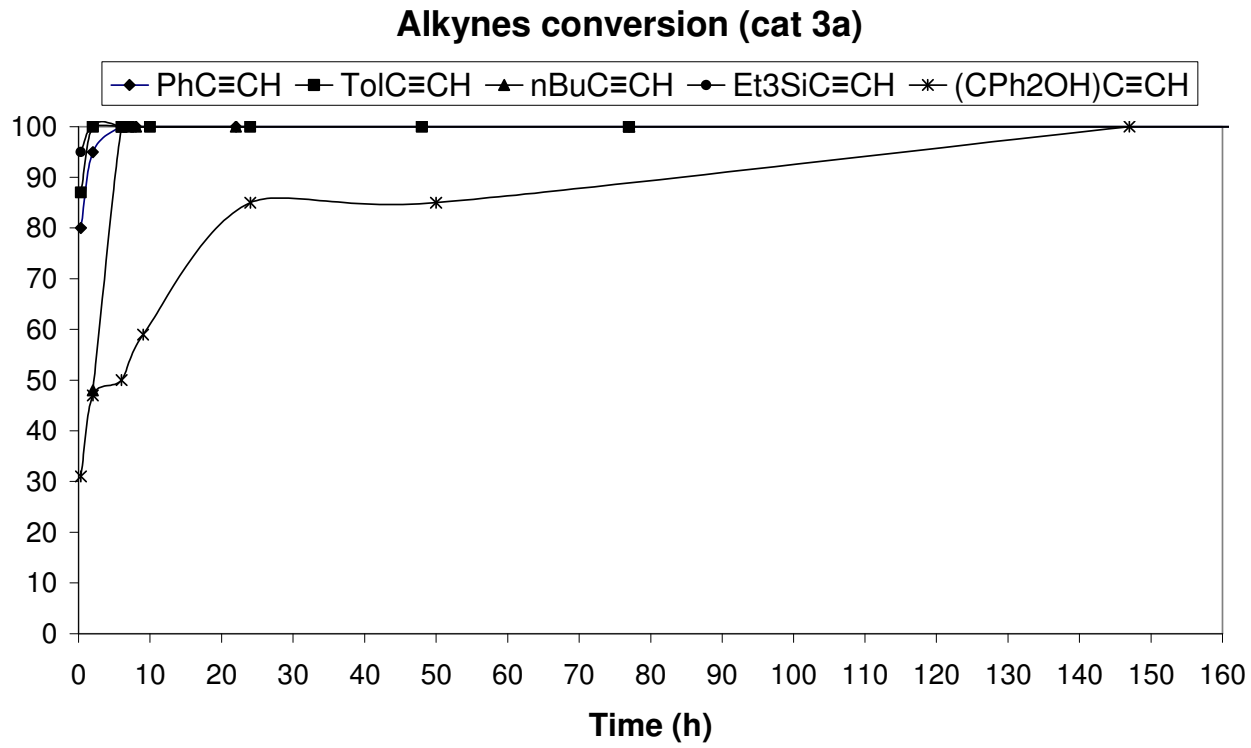


Figure S21. Conversions profile of catalyst **3a** with substrates: phenylacetylene, tolylacetylene, n-butylacetylene, triethylsilylacetylene, 1,1-diphenyl-2-propyn-1-ol.

Selected examples of conversions and selectivities calculations from ^{1}H-NMR.

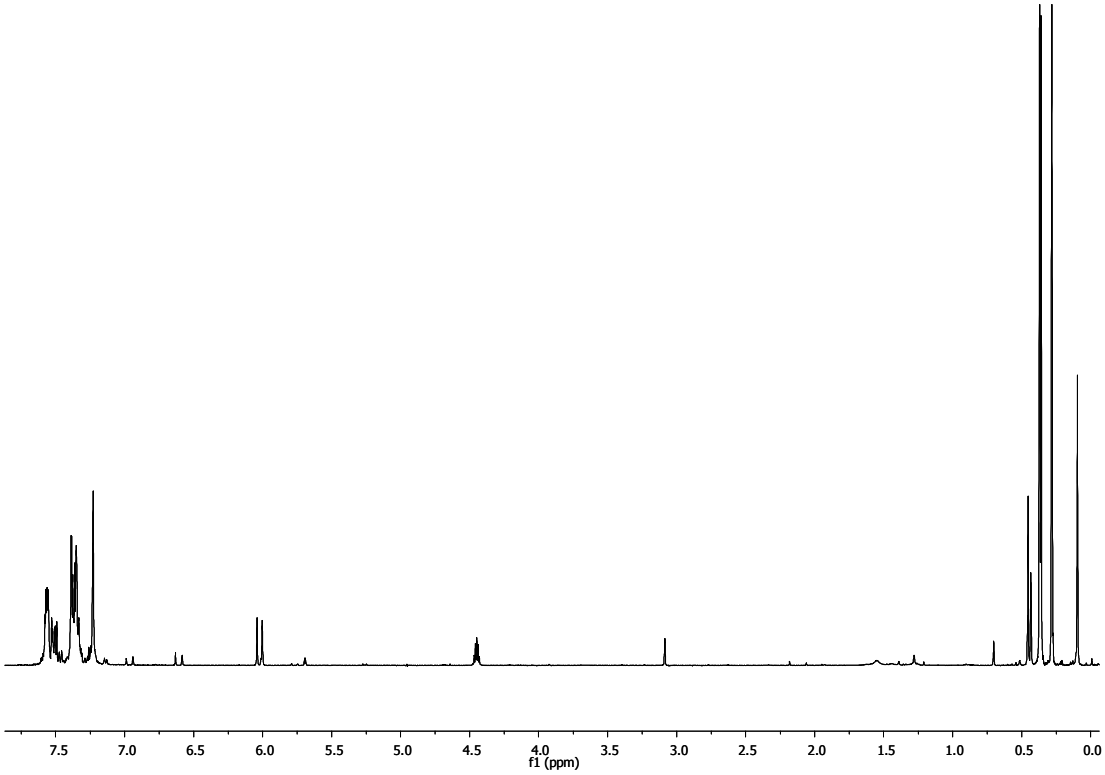


Figure S22. Hydrosilylation of PhC≡CH with 1% **3b**; *t* = 2 h, conversion = 79 %, selectivities: **1s**-β(E) = 24%; **2s**-β(Z) = 50%; **3s**-α = 15%; **4s**-styrene = 11%.

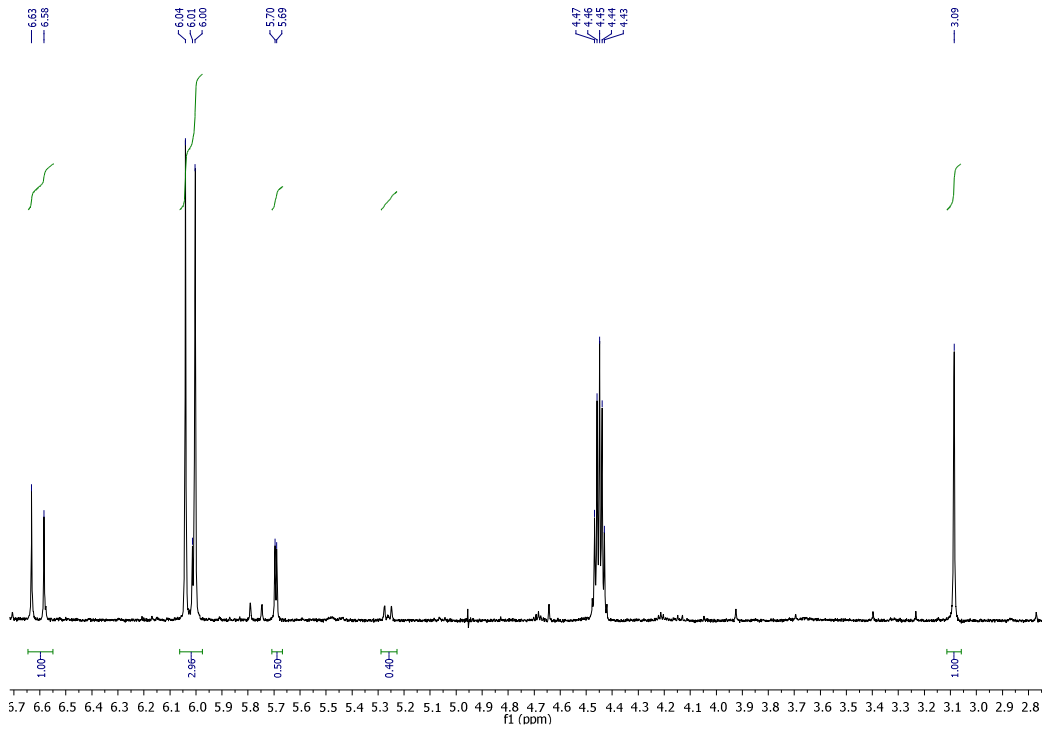


Figure S22A. Hydrosilylation of PhC≡CH with 1% **3b**; *t* = 2 h, conversion = 79 %, selectivities: **1s**-β(E) = 24%; **2s**-β(Z) = 50%; **3s**-α = 15%; **4s**-styrene = 11%. Enlargement.

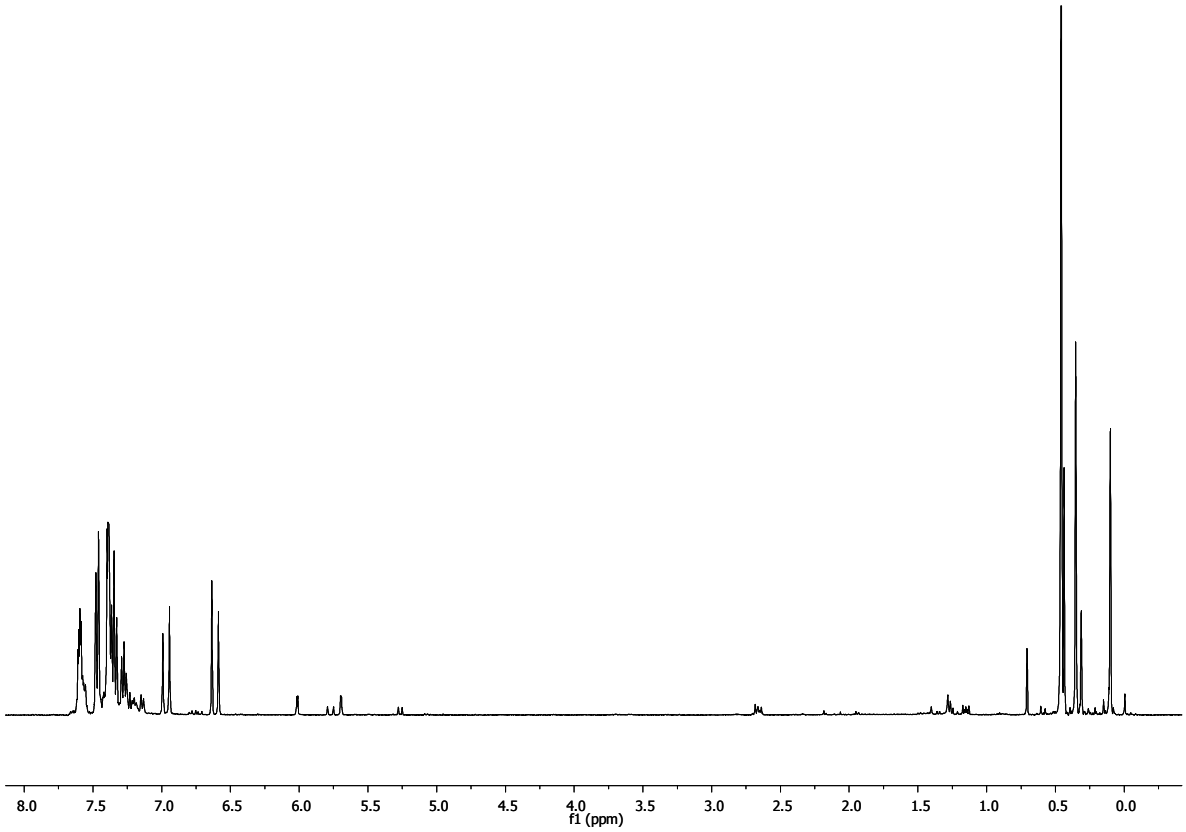


Figure S23. Hydrosilylation of PhC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **1s**-β(E) = 75%; **3s**-α = 15%; **4s**-styrene = 10%.

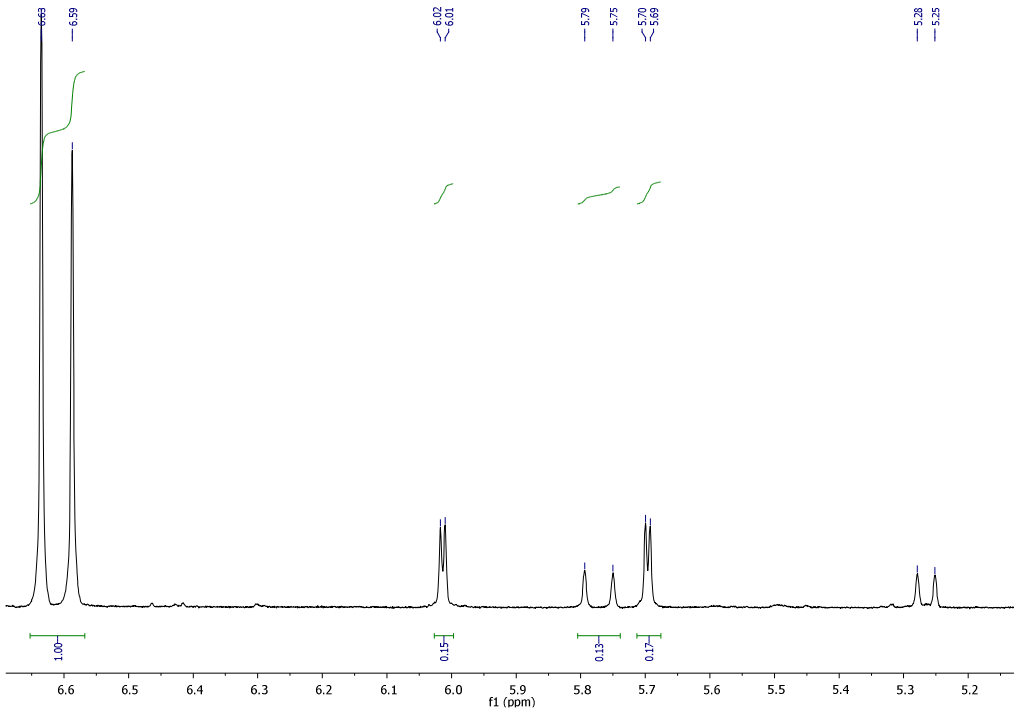


Figure S23A. Hydrosilylation of PhC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **1s**-β(E) = 75%; **3s**-α = 15%; **4s**-styrene = 10%. Enlargement.

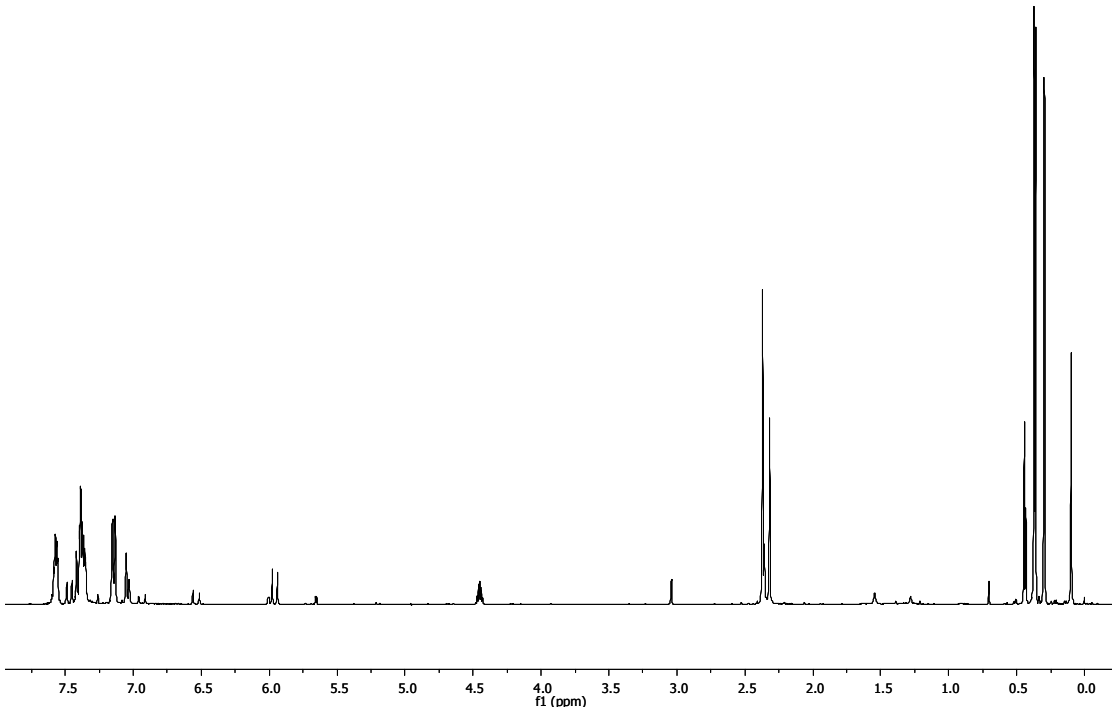


Figure S24. Hydrosilylation of TolC≡CH with 1% **3b**; *t* = 2 h, conversion = 76%, selectivities: **5s-**β(E) = 27%; **6s-**β(Z) = 48%; **7s-**α = 13%; **8s-**methylstyrene = 12%.

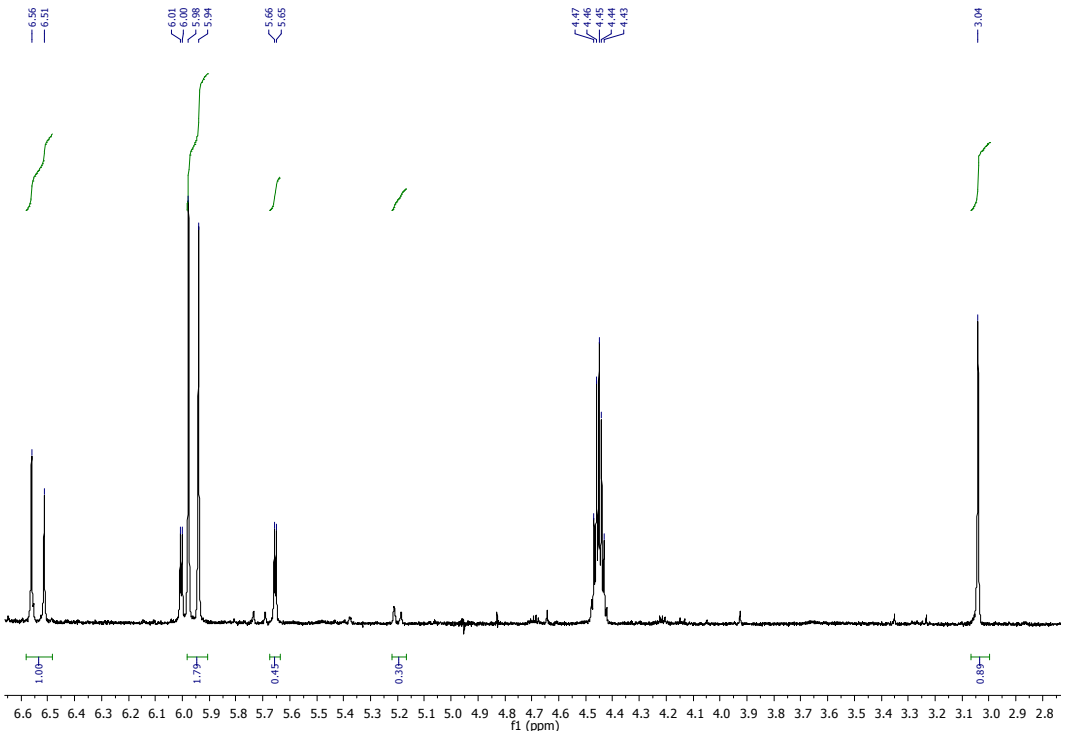


Figure S24A. Hydrosilylation of TolC≡CH with 1% **3b**; *t* = 2 h, conversion = 76%, selectivities: **5s-**β(E) = 27%; **6s-**β(Z) = 48%; **7s-**α = 13%; **8s-**methylstyrene = 12%. Enlargement.

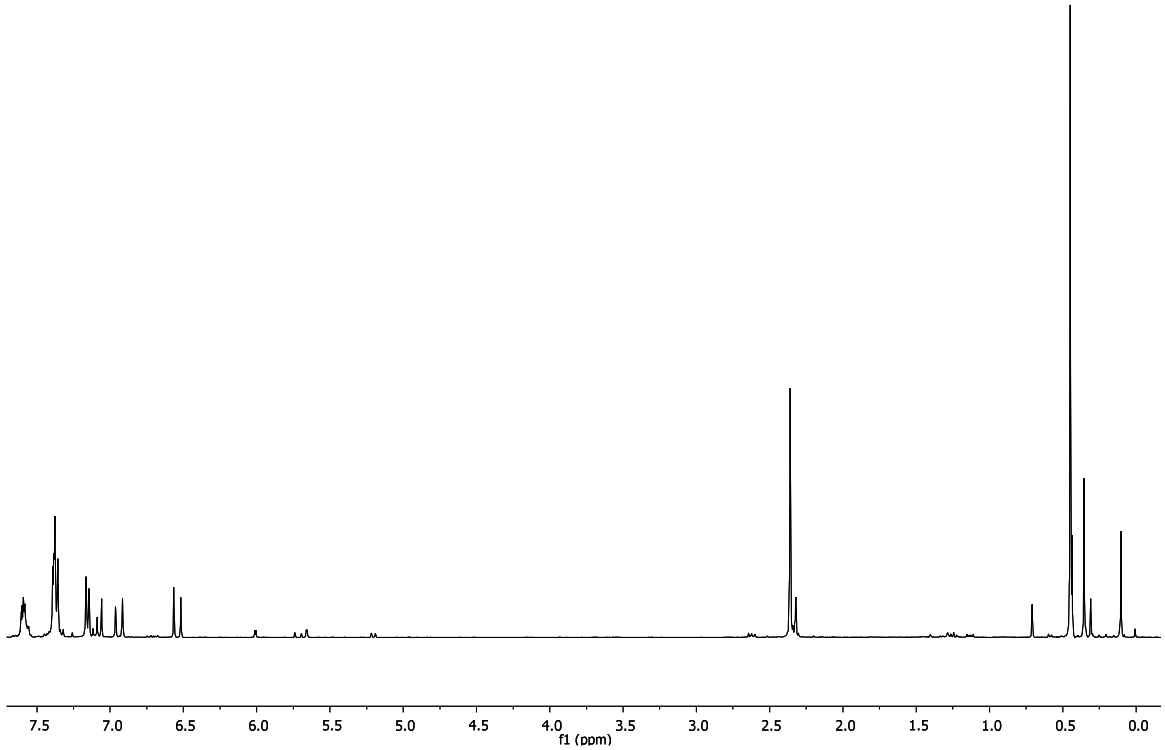


Figure S25. Hydrosilylation of TolC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **5s-**β(E) = 73%; **7s-**α = 14%; **8s-**methylstyrene = 13%.

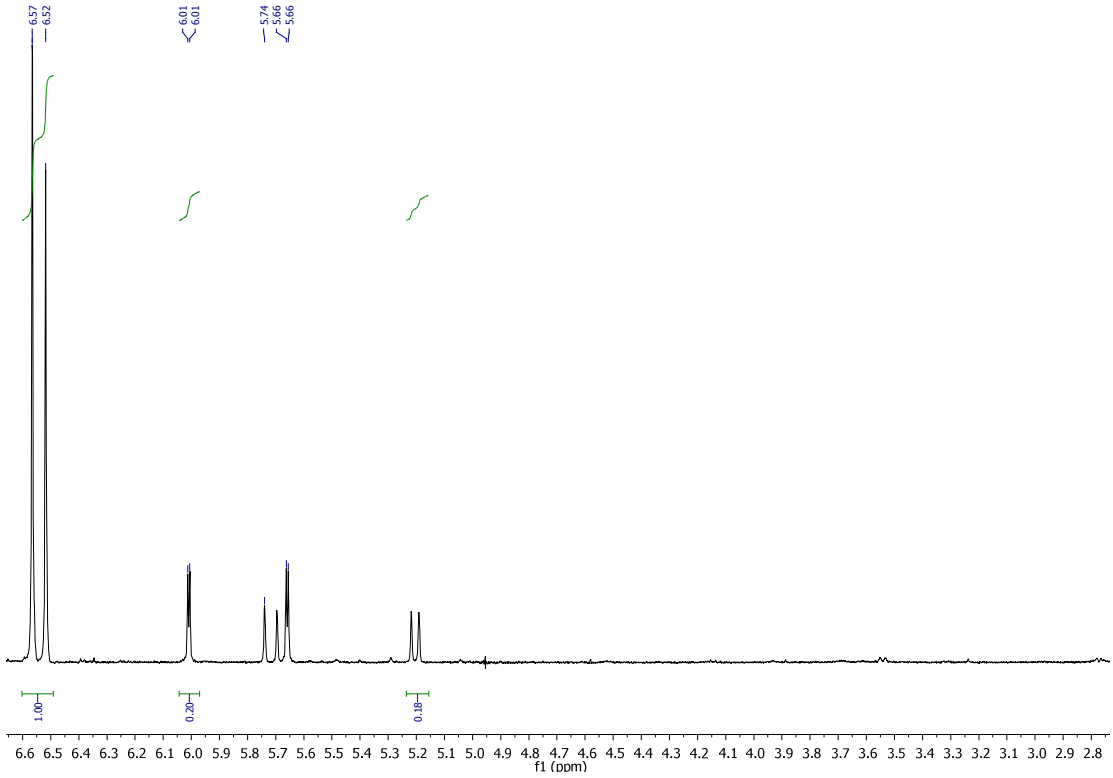


Figure S25A. Hydrosilylation of TolC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **5s-**β(E) = 73%; **7s-**α = 14%; **8s-**methylstyrene = 13%. Enlargement.

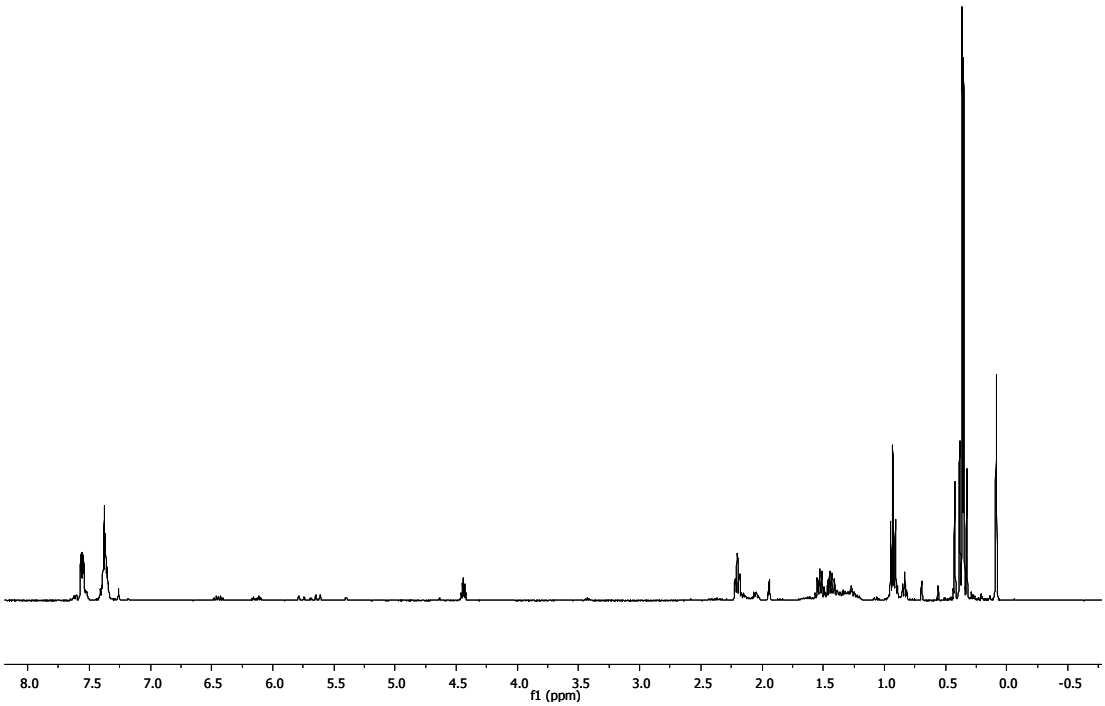


Figure S26. Hydrosilylation of ^{n}BuC≡CH with 1% **3b**; *t* = 22 h, conversion = 58%, selectivities: **9s-**β(E) = 38%; **10s-**β(Z) = 38%; **11s-**α = 24%.

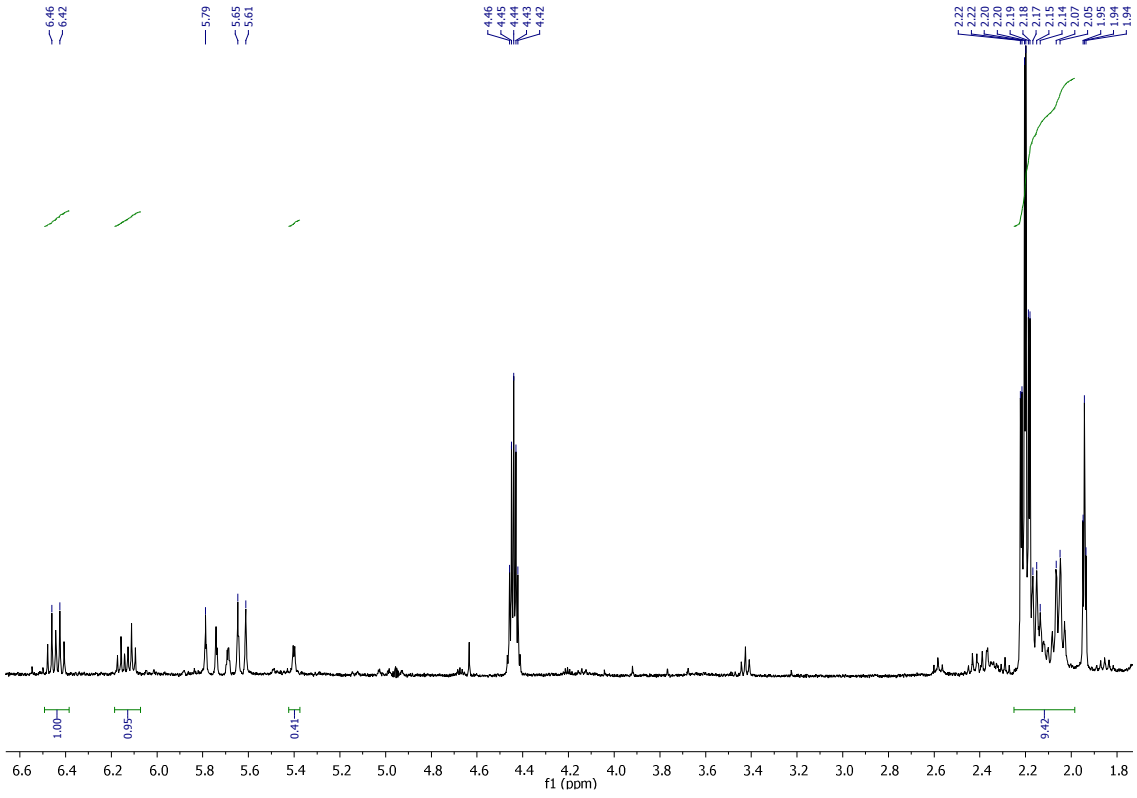


Figure S26A. Hydrosilylation of ^{n}BuC≡CH with 1% **3b**; *t* = 22 h, conversion = 58%, selectivities: **9s-**β(E) = 38%; **10s-**β(Z) = 38%; **11s-**α = 24%. Enlargement.

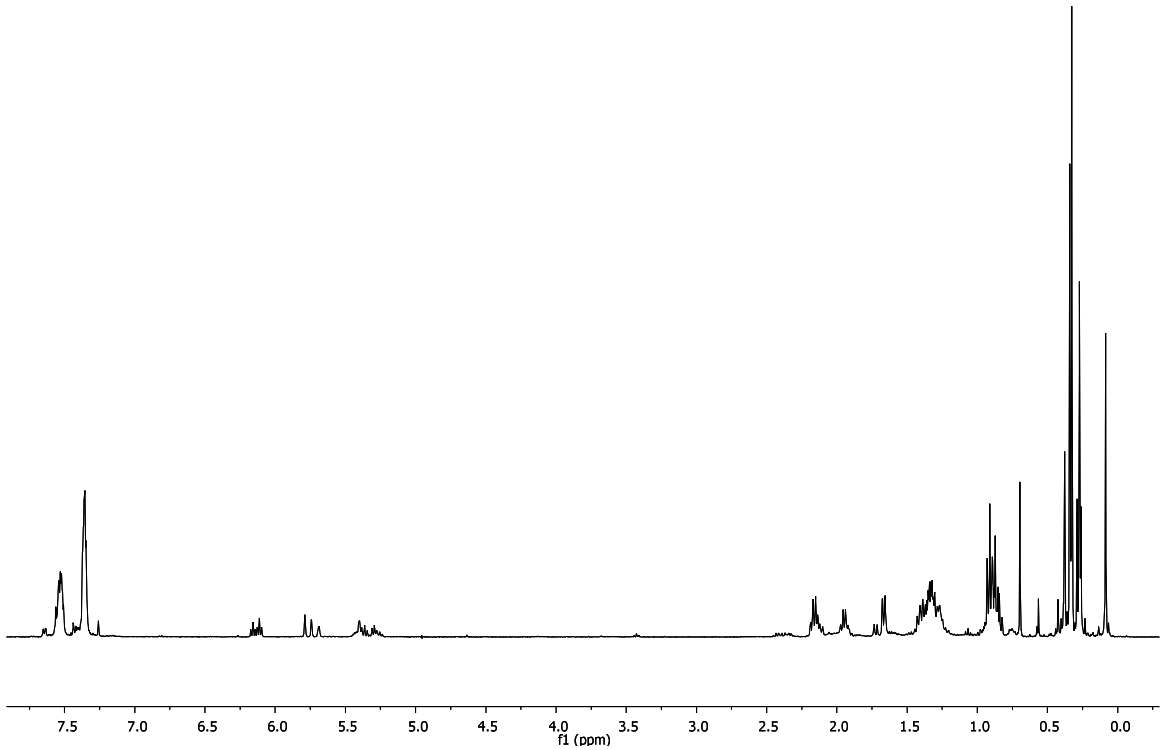


Figure S27. Hydrosilylation of ^{n}BuC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **9s-**β(E) = 44%; **11s-**α = 16%; **12s-**allyl = 40%.

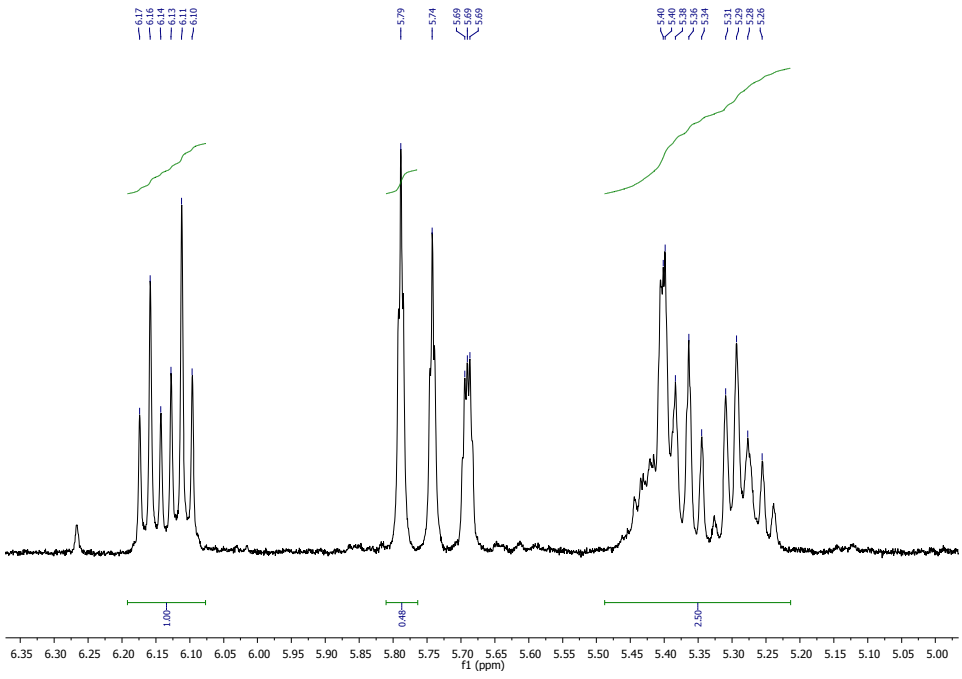


Figure S27A. Hydrosilylation of ^{n}BuC≡CH with 1% **3b**; *t* = 8 d, conversion > 99%, selectivities: **9s-**β(E) = 44%; **11s-**α = 16%; **12s-**allyl = 40%. Enlargement.

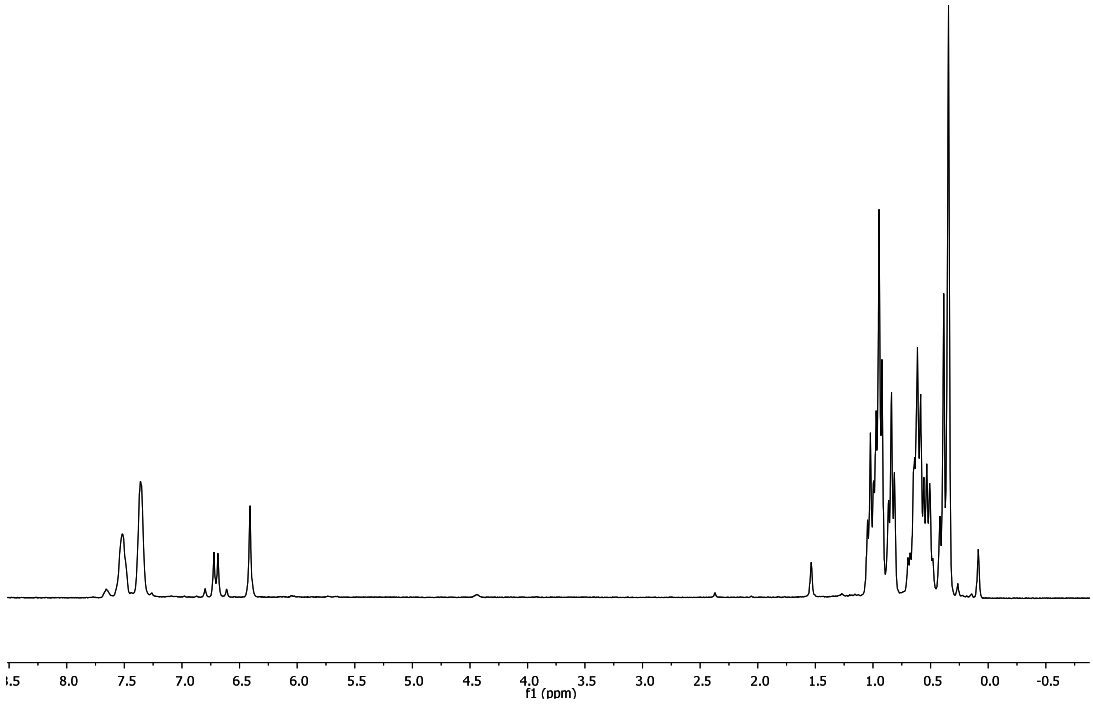


Figure S28. Hydrosilylation of $Et_3SiC{\equiv}CH$ with 1% **3a**; *t* = 20 min, conversion = 95 %, selectivities: **13s-**β(E) = 53%; **14s-**α = 47%.

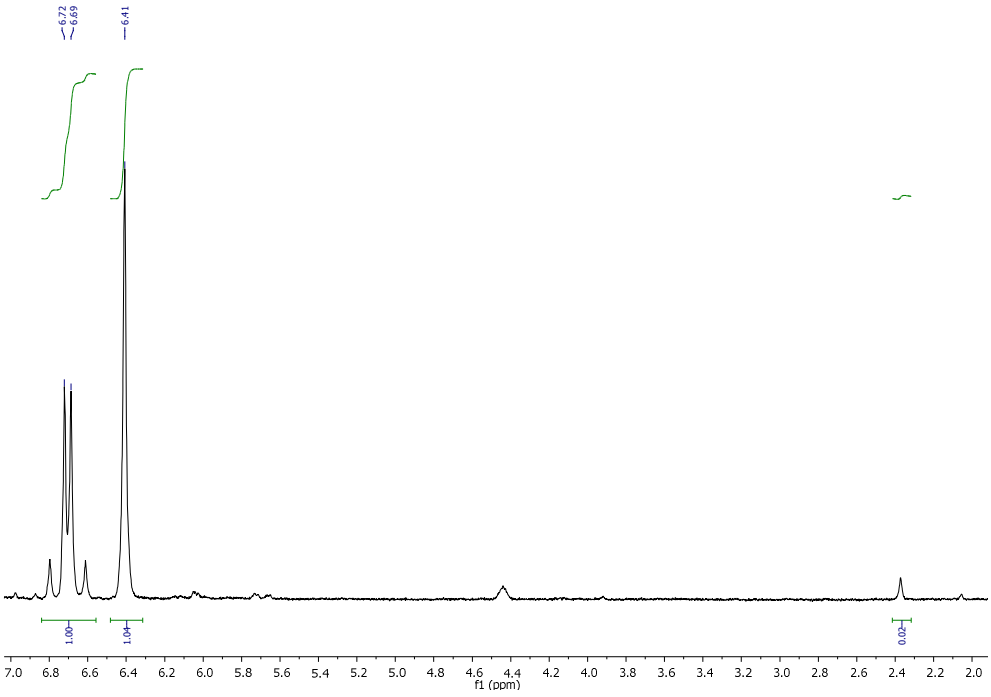


Figure S28A. Hydrosilylation of $Et_3SiC{\equiv}CH$ with 1% **3a**; *t* = 20 min, conversion = 95 %, selectivities: **13s-**β(E) = 53%; **14s-**α = 47%. Enlargement.

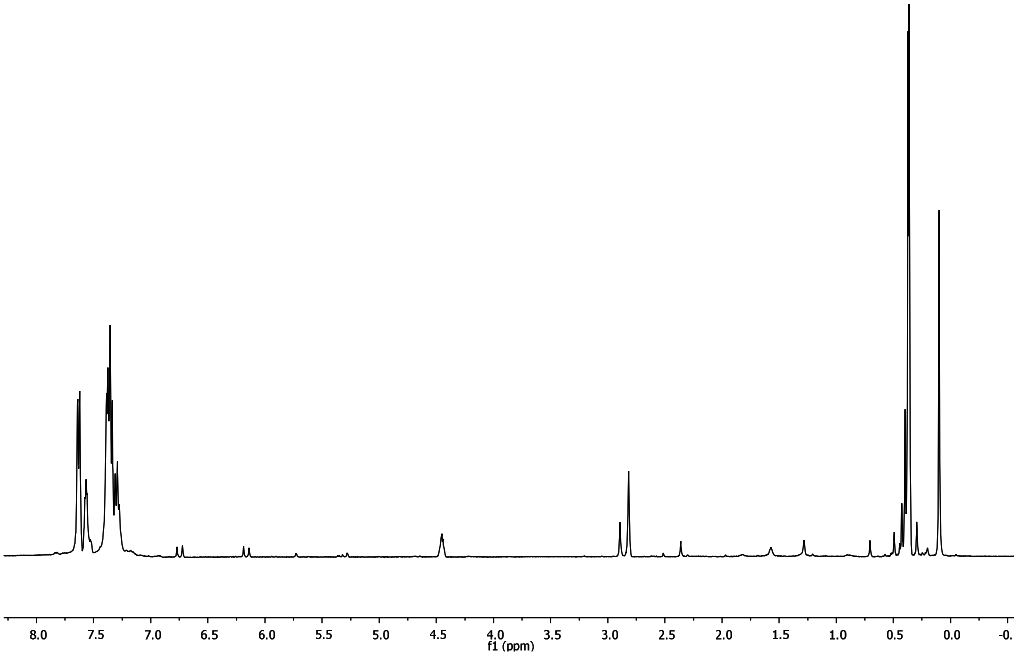


Figure S29. Hydrosilylation of (CPh_2OH)C≡CH with 1% **3a**; *t* = 2 h, conversion = 47 %, selectivities: **15s-**β(E) = 67%; **16s-**α = 33%.

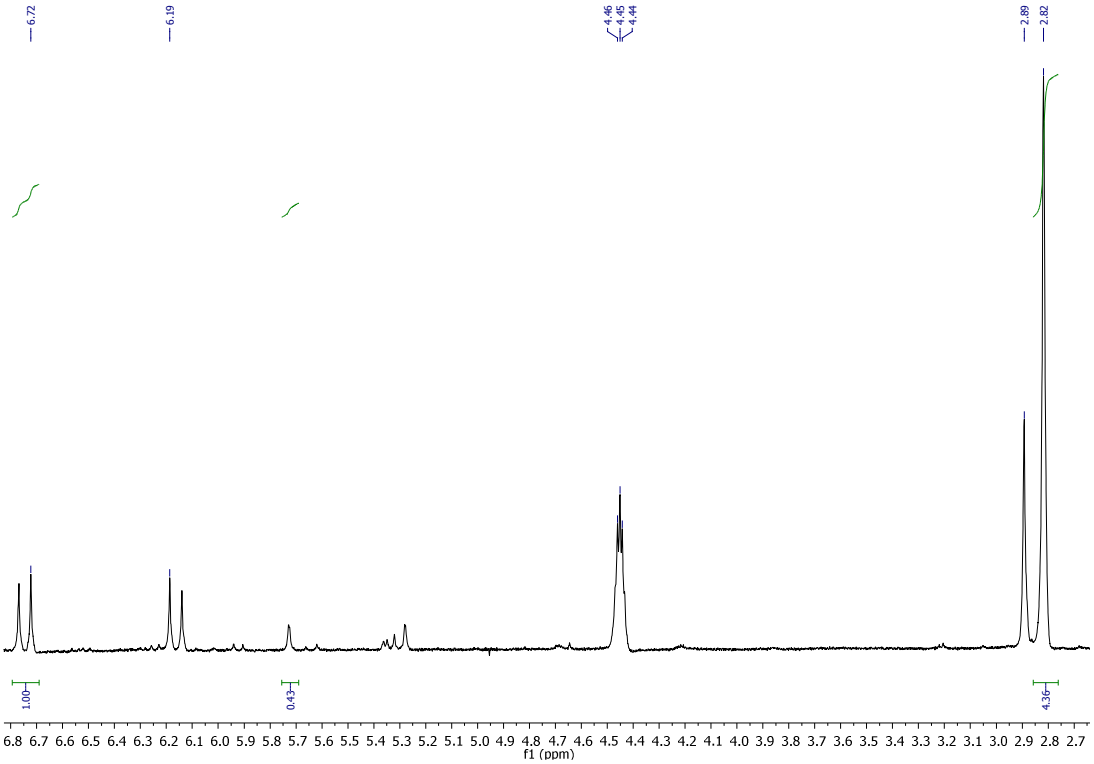
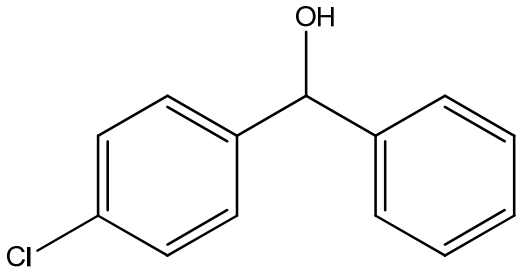
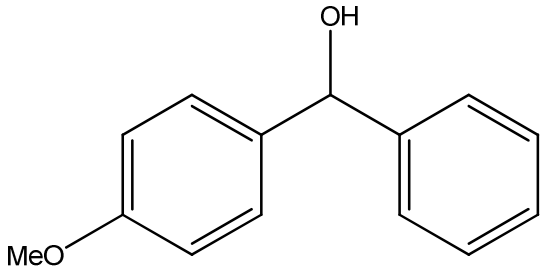


Figure S29A. Hydrosilylation of (CPh_2OH)C≡CH with 1% **3a**; *t* = 2 h, conversion = 47 %, selectivities: **15s-**β(E) = 67%; **16s-**α = 33%. Enlargement.

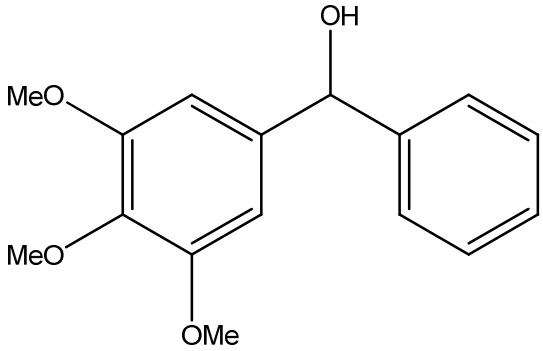
Addition of arylaldehydes to phenylboronic acid products: ^{1}H-NMR characterizations.



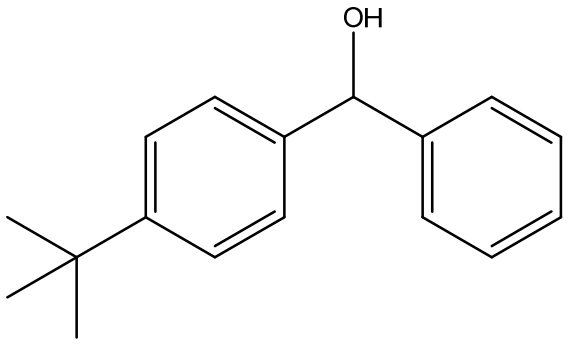
4-Chlorophenyl(phenyl)methanol[8]
^{1}H NMR (300 MHz, CDCl3): δ 7.35-7.23 (m, 9H), 5.81 (br s, 1H), 2.22 (s, 1H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ 143.3, 142.1, 133.1, 128.5, 128.4, 127.8, 127.7, 126.4, 75.3 ppm.



4-Methoxyphenyl(phenyl)methanol[9]
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.26 (m, 7H), 6.89-6.85 (m, 2H), 5.82 (brs, 1H), 3.79 (s, 3H), 2.14 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 144.0, 136.2, 128.4, 127.9, 127.3, 126.4, 113.9, 75.8, 55.2 ppm.

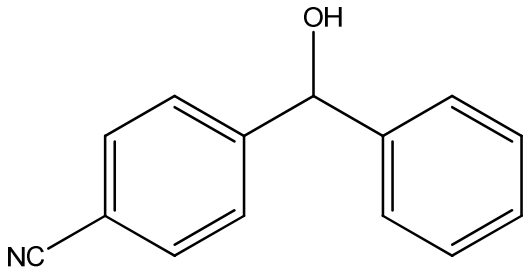


3,4,5 tri-methoxyphenyl(phenyl)methanol[10]
^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.39-7.19 (m, 3H), 6.61 (m, 2H), 5.78 (br s, 1H), 3.93 (s, 3H), 3.82 (s, 6H), 2.20 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 129.0, 127.9, 127.3, 105.0, 76.7, 60.8, 56.1 ppm.



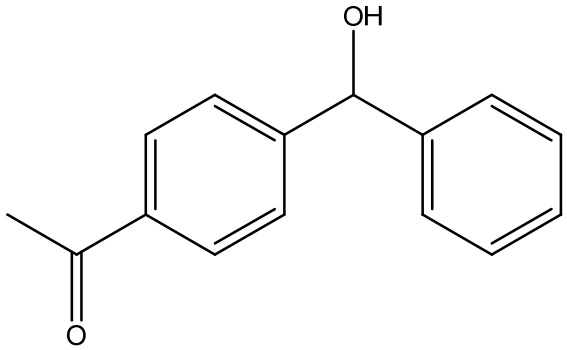
4-*tert*-Butylphenyl(phenyl)methanol[11]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.28 (m, 9H), 5.85 (br s, 1H), 2.06 (br s, 1H),1.39 (s, 9H) ppm**.**



4-Cyanophenyl(phenyl)methanol[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 2H), 7.45 (m, 2H), 7.33-7.23 (m, 5H), 5.78 (s, 1H), 3.05 (br s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.9, 142.7, 132.1, 128.7, 128.0, 126.9, 126.5, 118.7, 110.7, 75.3 ppm.



4-Acetylphenyl(phenyl)methanol[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93-7.91 (m, 2H), 7.51-7.49 (m, 2H), 7.37-7.26 (m, 5H), 5.89 (s, 1H), 2.57 (s, 3H), 2.40 (s, 1H), ppm. ^{13}C NMR (75 MHz, CDCl3): δ 198.2, 149.2, 143.2, 135.8, 128.5, 128.4, 127.6, 126.5, 126.4, 75.5, 26.4 ppm.

References

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