SUPPORTING INFORMATION

Ruthenium-Catalyzed Alkyne *trans*-Hydrometalation: Mechanistic Insights and Preparative Implications

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Supporting Crystallographic Information

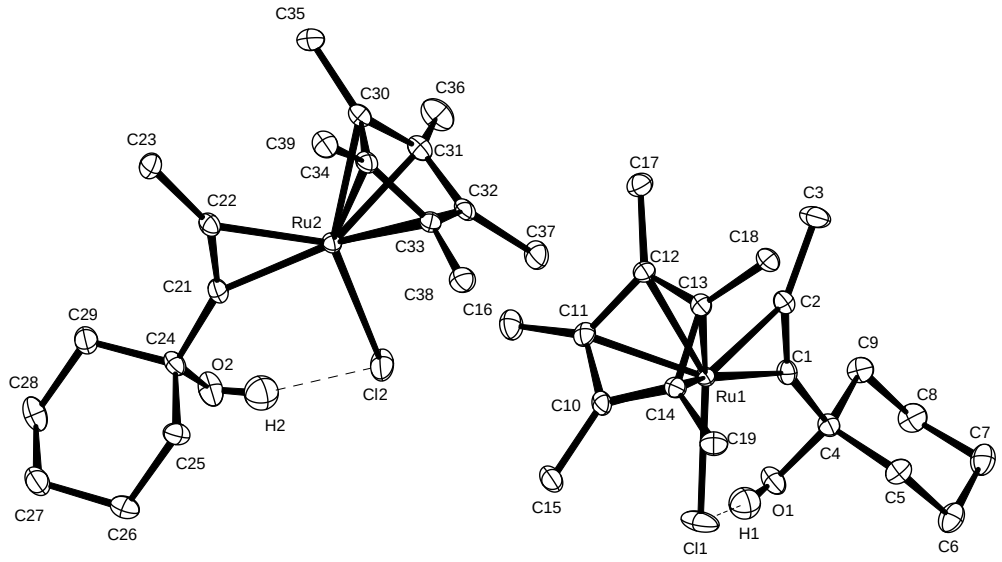


Figure S1. Molecular structure of **4**. Hydrogen atoms except for those attached to oxygen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of **4**: ($C_{19}H_{29}ClORu$), M_r = 409.94 g · mol^{-1}, red needle, crystal size 0.020 x 0.020 x 0.280 mm^3, monoclinic, space group $P2_1/n$, a = 8.7071(9) Å, b = 18.0486(19) Å, c = 23.181(3) Å, β = 97.786(2)°, V = 3609.4(7) Å^3, T = 100(2) K, Z = 8, D_{calc} = 1.509 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.017 mm^{-1}, Gaussian absorption correction (T_{min} = 0.86469, T_{max} = 0.98098), Bruker AXS Enraf-Nonius Mach3 Apex II IμS diffractometer, 2.257 < θ < 34.501°, 129000 measured reflections, 15152 independent reflections, 9885 reflections with $I > 2\sigma(I)$, R_{int} = 0.137.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.62	234	236	99.2	11.26	34.2	44.49	0.0247	0.0125
2.62 - 1.73	549	549	100.0	12.35	21.7	39.76	0.0377	0.0157
1.73 - 1.37	777	777	100.0	12.30	15.3	31.90	0.0513	0.0202
1.37 - 1.19	796	796	100.0	11.94	9.9	22.71	0.0783	0.0297
1.19 - 1.08	775	775	100.0	11.00	8.9	18.53	0.0962	0.0379
1.08 - 1.00	806	806	100.0	10.27	8.8	16.99	0.1055	0.0440
1.00 - 0.94	811	811	100.0	9.63	6.8	12.55	0.1305	0.0585
0.94 - 0.89	818	818	100.0	9.13	5.7	10.35	0.1575	0.0726
0.89 - 0.85	832	832	100.0	8.68	4.8	8.68	0.1867	0.0904
0.85 - 0.82	708	708	100.0	8.30	4.3	7.59	0.2119	0.1045
0.82 - 0.79	804	804	100.0	7.92	3.9	6.49	0.2311	0.1214
0.79 - 0.76	990	990	100.0	7.71	3.7	6.12	0.2494	0.1338
0.76 - 0.74	708	708	100.0	7.32	3.3	5.27	0.2708	0.1597
0.74 - 0.72	823	823	100.0	7.08	3.0	4.49	0.3172	0.1855
0.72 - 0.71	470	470	100.0	6.97	3.0	4.42	0.3059	0.1892
0.71 - 0.69	954	954	100.0	6.74	2.7	3.85	0.3403	0.2215
0.69 - 0.67	1060	1060	100.0	6.48	2.4	3.38	0.3832	0.2594
0.67 - 0.66	611	614	99.5	6.17	2.2	3.00	0.4116	0.3051
0.66 - 0.65	628	628	100.0	6.10	1.9	2.46	0.4575	0.3626
0.65 - 0.64	673	673	100.0	6.02	2.1	2.69	0.4586	0.3402
0.64 - 0.63	737	873	84.4	4.56	1.9	2.23	0.4708	0.4383
0.73 - 0.63	5550	5689	97.6	6.17	2.3	3.24	0.3857	0.2794
Inf - 0.63	15564	15705	99.1	8.34	6.1	10.88	0.1253	0.0825

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0469 [$I > 2\sigma(I)$], wR_2 = 0.1028, 411 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. Hydroxyl H atoms were refined using a rotating group refinement with with U_H = 1.5xUeq_O. Otherwise, H atoms were refined using a riding model with U_H = 1.2xUeq_C for the methylene groups and with U_H = 1.5xUeq_C for the methyl groups. S = 1.019, residual electron density 1.27 (1.02 Å from H26A)/ -1.53 (0.76 Å from Ru2) e Å^{-3}. **CCDC 1509642**.

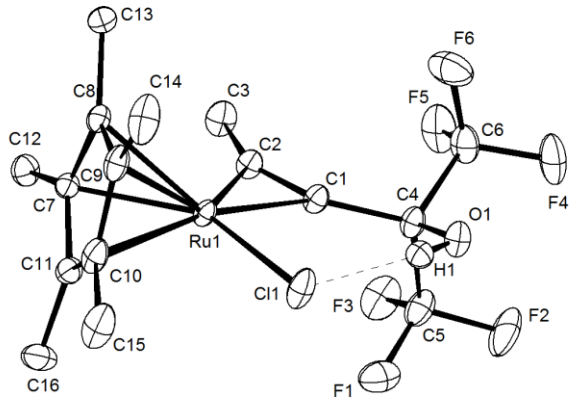


Figure S2. Molecular structure of **5**. Hydrogen atoms except for the one attached to the oxygen atom are omitted for clarity.

X-ray Crystal Structure Analysis of **5**: ($C_{16}H_{19}ClF_6ORu$), M_r = 477.83 g · mol^{-1}, dark red prism, crystal size 0.09 x 0.10 x 0.19 mm^3, monoclinic, space group $P2_1/c$, a = 14.0577(8) Å, b = 8.4937(3) Å, c = 15.6148(7) Å, β = 106.404(3)°, V = 1788.55(15) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.775 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 1.086 mm^{-1}, Gaussian absorption correction (T_{min} = 0.84477, T_{max} = 0.91547), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 4.201 < θ < 38.070°, 114114 measured reflections, 9751 independent reflections, 9109 reflections with $I > 2\sigma(I)$, R_{int} = 0.0313.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.38	155	173	89.6	10.64	118.6	72.77	0.0342	0.0116
2.38 - 1.59	359	362	99.2	15.04	127.6	91.96	0.0301	0.0098
1.59 - 1.25	540	540	100.0	15.72	80.7	88.15	0.0282	0.0092
1.25 - 1.09	512	512	100.0	15.64	55.8	83.56	0.0263	0.0093
1.09 - 0.99	515	515	100.0	15.05	52.1	75.29	0.0260	0.0097
0.99 - 0.92	497	497	100.0	14.18	39.0	69.21	0.0273	0.0108
0.92 - 0.86	568	568	100.0	13.54	31.7	63.37	0.0276	0.0114
0.86 - 0.82	476	476	100.0	12.89	24.1	58.78	0.0291	0.0125
0.82 - 0.78	571	571	100.0	12.36	22.9	54.20	0.0297	0.0130
0.78 - 0.75	520	520	100.0	11.69	21.1	50.90	0.0333	0.0140
0.75 - 0.72	611	611	100.0	11.17	17.4	46.54	0.0356	0.0152
0.72 - 0.70	457	457	100.0	10.66	16.3	42.49	0.0357	0.0161
0.70 - 0.68	512	512	100.0	10.39	14.6	41.43	0.0390	0.0172
0.68 - 0.66	576	576	100.0	9.96	12.7	35.73	0.0429	0.0185
0.66 - 0.65	315	315	100.0	9.44	12.1	35.22	0.0458	0.0199
0.65 - 0.63	708	708	100.0	9.23	10.0	31.17	0.0529	0.0218
0.63 - 0.62	388	388	100.0	8.88	9.4	29.07	0.0543	0.0228
0.62 - 0.60	823	823	100.0	8.50	8.4	26.84	0.0601	0.0252
0.60 - 0.59	496	496	100.0	8.07	7.1	23.68	0.0676	0.0287
0.59 - 0.58	666	669	99.6	7.65	5.5	20.05	0.0788	0.0338
0.68 - 0.58	3972	3975	99.9	8.76	9.0	28.25	0.0548	0.0236
Inf - 0.58	10265	10289	99.8	11.41	29.0	49.73	0.0312	0.0125

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0213 [$I > 2\sigma(I)$], wR_2 = 0.0577, 236 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The hydroxyl H atom was located on a difference Fourier synthesis and its coordinates were refined using an isotropic atomic displacement parameter. The H atoms were refined using a rotational group riding model with U_H = 1.5xUeq_C. S = 1.079, residual electron density 0.72 (1.22 Å from F5)/ -1.61 (0.60 Å from Ru1) e Å^{-3}. **CCDC 1509643**.

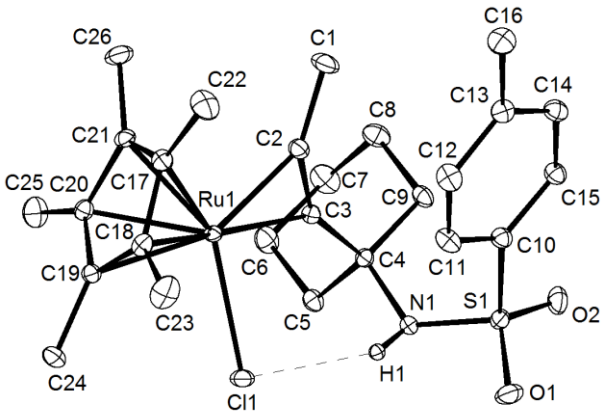


Figure S3. Molecular structure of **6**. Hydrogen atoms except for the one attached to the nitrogen atom are omitted for clarity.

X-ray Crystal Structure Analysis of **6**: ($C_{26}H_{36}ClNO_2RuS$), M_r = 563.14 g · mol^{-1}, purple prism, crystal size 0.050 x 0.119 x 0.190 mm^3, orthorhombic, space group *P*bca, a = 17.577(2) Å, b = 8.6560(12) Å, c = 32.749(4) Å, V = 4982.7(12) Å^3, T = 100(2) K, Z = 8, D_{calc} = 1.501 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.844 mm^{-1}, Gaussian absorption correction (T_{min} = 0.91515, T_{max} = 0.96193), Bruker AXS Kappa Mach3 APEX-II IμS diffractometer, 1.244 < θ < 33.891°, 166277 measured reflections, 10061 independent reflections, 9235 reflections with $I > 2\sigma(I)$, R_{int} = 0.0267.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.79	167	174	96.0	16.41	89.28	135.23	0.0165	0.0050
2.79 - 1.81	393	394	99.7	20.81	56.55	136.71	0.0158	0.0046
1.81 - 1.42	546	548	99.6	21.51	39.32	117.68	0.0157	0.0047
1.42 - 1.22	594	597	99.5	21.76	25.37	108.46	0.0189	0.0055
1.22 - 1.11	521	524	99.4	20.64	22.10	92.54	0.0210	0.0063
1.11 - 1.02	625	626	99.8	19.27	20.19	77.88	0.0226	0.0072
1.02 - 0.96	527	529	99.6	18.15	17.79	70.56	0.0247	0.0080
0.96 - 0.91	564	564	100.0	17.51	14.72	59.38	0.0294	0.0094
0.91 - 0.87	538	539	99.8	16.47	12.82	55.11	0.0331	0.0109
0.87 - 0.83	676	676	100.0	16.08	11.38	49.38	0.0359	0.0122
0.83 - 0.80	563	563	100.0	15.24	9.75	42.39	0.0403	0.0143
0.80 - 0.78	434	434	100.0	14.74	10.34	43.43	0.0406	0.0142
0.78 - 0.76	485	485	100.0	14.47	10.65	41.33	0.0403	0.0145
0.76 - 0.73	803	803	100.0	13.82	8.25	33.64	0.0489	0.0180
0.73 - 0.72	307	307	100.0	13.30	7.88	31.67	0.0500	0.0193
0.72 - 0.70	685	685	100.0	13.13	8.28	32.08	0.0521	0.0196
0.70 - 0.68	727	727	100.0	12.63	6.95	27.86	0.0585	0.0229
0.68 - 0.67	403	403	100.0	12.24	6.76	25.84	0.0630	0.0246
0.67 - 0.66	429	429	100.0	11.77	6.64	25.47	0.0627	0.0255
0.66 - 0.64	1069	1080	99.0	11.11	6.12	22.01	0.0680	0.0288
0.74 - 0.64	3887	3898	99.7	12.28	7.11	27.19	0.0579	0.0233
Inf - 0.64	11056	11087	99.7	15.81	16.02	56.28	0.0267	0.0101

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0259 [$I > 2\sigma(I)$], wR_2 = 0.0563, 300 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The amine H atom was located on a difference Fourier synthesis and its coordinates were refined using an isotropic atomic displacement parameter. The remaining H atoms were refined using a rotational group riding model with U_H = 1.5xUeq_C. S = 1.197, residual electron density 0.59 (0.67 Å from C2)/ -0.78 (1.43 Å from H3C) e Å^{-3}. **CCDC 1509644**.

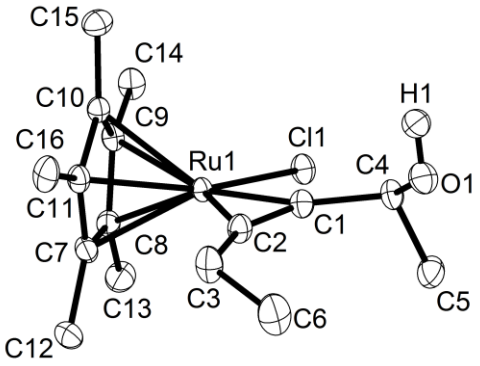


Figure S4. Molecular structure of **8** (triclinic form). Hydrogen atoms except for the one attached to the oxygen atom are omitted for clarity.

X-ray Crystal Structure Analysis of **8** (triclinic form): ($C_{16}H_{25}ClORu$), M_r = 369.88 g · mol^{-1}, red needle, crystal size 0.03 x 0.04 x 0.18 mm^3, triclinic, space group $P\bar{1}$, a = 8.4796(4) Å, b = 9.6569(3) Å, c = 11.3596(7) Å, α = 103.839(4)°, β = 95.099(5)°, γ = 111.774(3)°, V = 822.33(7) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.494 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.107 mm^{-1}, Gaussian absorption correction (T_{min} = 0.86700, T_{max} = 0.96887), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 3.440 < θ < 34.105°, 49987 measured reflections, 6754 independent reflections, 5811 reflections with $I > 2\sigma(I)$, R_{int} = 0.0889.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.52	102	105	97.1	13.32	155.92	54.16	0.0727	0.0164
2.52 - 1.71	240	240	100.0	10.68	117.75	44.65	0.0589	0.0188
1.71 - 1.36	341	341	100.0	9.99	80.35	38.79	0.0606	0.0210
1.36 - 1.19	336	336	100.0	9.68	54.29	33.78	0.0739	0.0236
1.19 - 1.08	337	337	100.0	9.38	44.57	29.58	0.0821	0.0257
1.08 - 1.00	365	365	100.0	9.01	44.06	28.70	0.0805	0.0275
1.00 - 0.94	341	341	100.0	8.60	38.26	25.01	0.0854	0.0304
0.94 - 0.90	312	312	100.0	8.25	29.09	21.97	0.0907	0.0350
0.90 - 0.86	331	331	100.0	7.98	24.87	19.84	0.0996	0.0393
0.86 - 0.82	423	423	100.0	7.46	21.03	17.00	0.1133	0.0454
0.82 - 0.79	352	352	100.0	7.15	20.76	16.37	0.1177	0.0484
0.79 - 0.77	287	287	100.0	6.91	17.74	14.19	0.1277	0.0545
0.77 - 0.75	304	304	100.0	6.64	16.81	13.14	0.1372	0.0592
0.75 - 0.73	359	359	100.0	6.41	14.70	11.83	0.1484	0.0671
0.73 - 0.71	383	383	100.0	6.09	12.62	10.51	0.1707	0.0780
0.71 - 0.69	426	426	100.0	5.90	12.45	9.76	0.1778	0.0838
0.69 - 0.68	236	236	100.0	5.48	9.77	7.70	0.1893	0.1057
0.68 - 0.66	521	521	100.0	5.47	8.90	7.04	0.2216	0.1195
0.66 - 0.65	262	262	100.0	5.12	8.19	6.37	0.2400	0.1383
0.65 - 0.64	292	292	100.0	5.11	8.00	6.00	0.2481	0.1471
0.64 - 0.63	209	226	92.5	4.53	7.65	5.49	0.2683	0.1628
0.73 - 0.63	2329	2346	99.3	5.48	9.95	7.83	0.2030	0.1088
Inf - 0.63	6759	6779	99.7	7.38	30.49	18.75	0.0881	0.0382

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0401 [$I > 2\sigma(I)$], wR_2 = 0.1047, 183 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The residual electron density close to Ru1 suggests some anharmonic displacement of the metal atom; it should be noted that the diffraction data were collected to a resolution of 0.63 Å. The hydroxyl H atom was located on a difference Fourier synthesis and its coordinates were refined using an isotropic atomic displacement parameter. The remaining H atoms were refined using a rotational group riding model with U_H = 1.5xUeq_C for the methyl groups and a riding model with U_H = 1.2xUeq_C for the CH and CH_2 groups. S = 1.049, residual electron density 1.54 (1.29 Å from H2C)/ -3.14 (0.70 Å from Ru1) e Å^{-3}. **CCDC 1509645**.

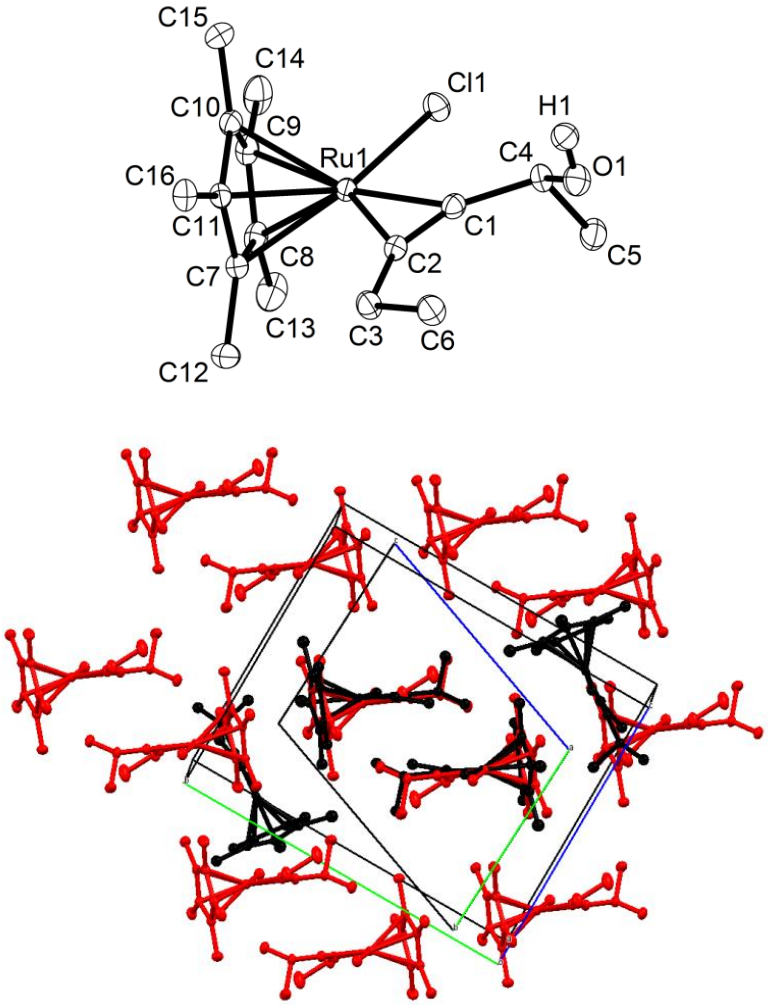


Figure S5. Top: Molecular structure of **8** (monoclinic form). Hydrogen atoms except for the one attached to the oxygen atom are omitted for clarity. Bottom: Superposition of the monoclinic (black) and triclinic (red) forms of **8.**

X-ray Crystal Structure Analysis of **8** (monoclinic form): ($C_{16}H_{25}ClORu$), M_r = 369.88 g · mol^{-1}, red needle, crystal size 0.030 x 0.036 x 0.270 mm^3, monoclinic, space group $P2_1/n$, a = 8.3798(3) Å, b = 15.161(2) Å, c = 13.0046(9) Å, β = 99.954(6)°, V = 1627.3(3) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.510 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 1.118 mm^{-1}, Gaussian absorption correction (T_{min} = 0.83733, T_{max} = 0.96860), Bruker AXS Enraf-

Nonius KappaCCD diffractometer, 3.913 < θ < 33.998°, 41215 measured reflections, 6627 independent reflections, 5075 reflections with $I > 2\sigma(I)$, R_{int} = 0.0757.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.61	103	110	93.6	10.69	95.37	48.01	0.0535	0.0155
2.61 - 1.74	242	242	100.0	9.18	76.65	42.08	0.0478	0.0178
1.74 - 1.38	341	341	100.0	8.62	55.15	34.54	0.0468	0.0209
1.38 - 1.20	352	352	100.0	8.29	31.77	27.17	0.0532	0.0259
1.20 - 1.09	343	343	100.0	7.81	29.62	23.69	0.0538	0.0290
1.09 - 1.01	354	354	100.0	7.49	28.34	21.73	0.0579	0.0318
1.01 - 0.95	337	337	100.0	7.29	24.42	19.28	0.0671	0.0356
0.95 - 0.90	376	376	100.0	6.74	18.58	15.61	0.0754	0.0446
0.90 - 0.86	348	348	100.0	6.52	16.25	13.86	0.0877	0.0516
0.86 - 0.83	305	305	100.0	6.25	13.65	12.36	0.0931	0.0609
0.83 - 0.80	367	367	100.0	5.89	12.86	11.13	0.1109	0.0683
0.80 - 0.77	398	398	100.0	5.76	10.68	9.44	0.1284	0.0807
0.77 - 0.75	320	320	100.0	5.43	12.18	9.27	0.1267	0.0804
0.75 - 0.73	364	364	100.0	5.17	8.52	7.43	0.1550	0.1098
0.73 - 0.71	392	392	100.0	4.96	8.95	7.03	0.1631	0.1144
0.71 - 0.70	194	194	100.0	4.89	8.21	6.71	0.1840	0.1259
0.70 - 0.68	479	479	100.0	4.58	7.36	5.70	0.1945	0.1474
0.68 - 0.67	242	243	99.6	4.58	5.83	4.79	0.2220	0.1811
0.67 - 0.65	551	552	99.8	4.31	6.00	4.49	0.2397	0.1943
0.65 - 0.64	446	447	99.8	3.66	5.59	3.86	0.2645	0.2378
0.74 - 0.64	2478	2481	99.9	4.48	6.96	5.40	0.2021	0.1609
Inf - 0.64	6854	6864	99.9	6.13	19.75	14.43	0.0732	0.0507

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0393 [$I > 2\sigma(I)$], wR_2 = 0.0831, 183 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The hydroxyl H atom was located on a difference Fourier synthesis and its coordinates were refined using an isotropic atomic displacement parameter. The remaining H atoms were refined using a rotational group riding model with U_H = 1.5xUeq_C for the methyl groups and a riding model with U_H = 1.2xUeq_C for the CH and CH_2 groups. S = 1.042, residual electron density 0.67 (0.66 Å from C1)/ -1.28 (0.68 Å from Ru1) e Å^{-3}. **CCDC 1509646**.

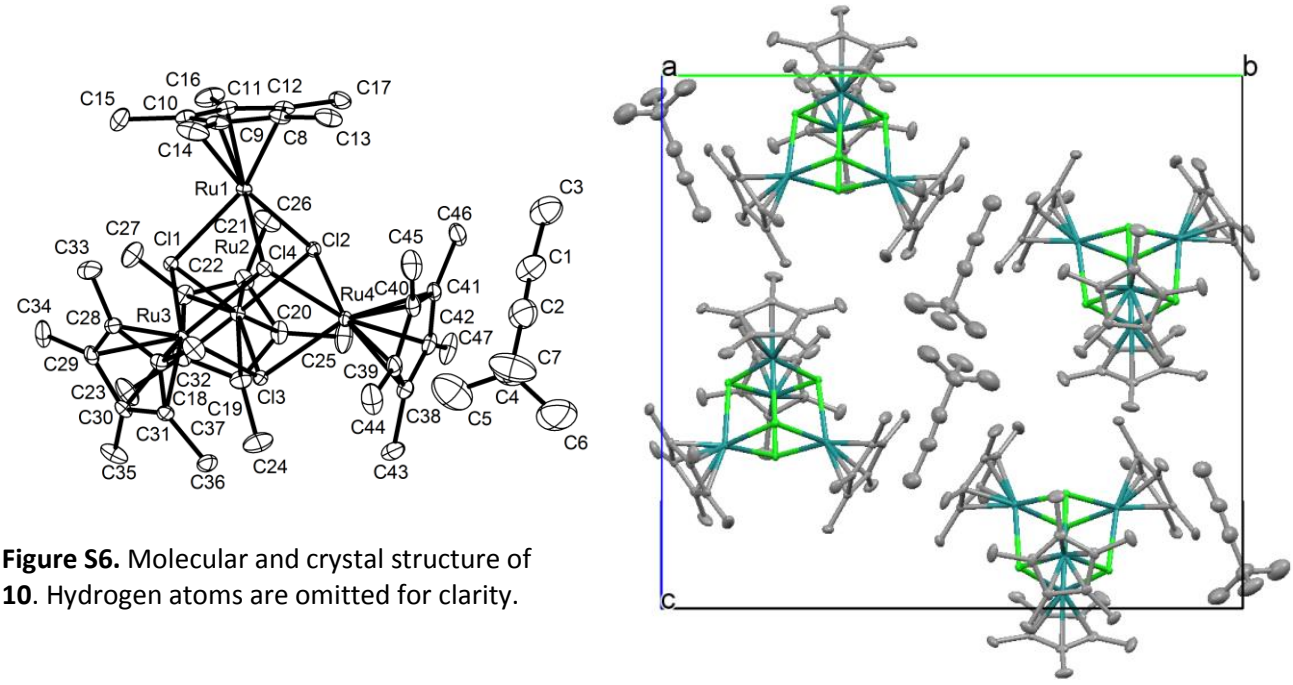


Figure S6. Molecular and crystal structure of **10**. Hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of **10**: $[C_{40}H_{60}Cl_4Ru_4]\cdot[C_7H_{12}]$, M_r = 1183.12 g · mol^{-1}, orange prism, crystal size 0.031 x 0.122 x 0.146 mm^3, monoclinic, space group $P2_1/n$, a = 11.375(8) Å, b = 21.717(15) Å, c = 19.940(14) Å, β = 94.351(14)°, V = 4912(6) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.600 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 1.454 mm^{-1}, Gaussian absorption correction (T_{min} = 0.87041, T_{max} = 0.97816), Bruker AXS Kappa Mach3 APEX-II IμS diffractometer, 3.392 < θ < 33.142°, 132567 measured reflections, 18486 independent reflections, 14850 reflections with $I > 2\sigma(I)$, R_{int} = 0.0452.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.45	373	382	97.6	9.06	54.71	75.54	0.0202	0.0077
2.45 - 1.63	871	871	100.0	9.99	47.60	69.83	0.0204	0.0087
1.63 - 1.29	1255	1258	99.8	9.92	24.78	48.07	0.0265	0.0119
1.29 - 1.12	1280	1294	98.9	9.24	22.57	43.73	0.0306	0.0143
1.12 - 1.02	1194	1223	97.6	8.37	18.37	33.02	0.0367	0.0179
1.02 - 0.94	1343	1377	97.5	7.75	14.15	27.04	0.0470	0.0237
0.94 - 0.88	1342	1375	97.6	7.28	11.57	22.18	0.0546	0.0295
0.88 - 0.84	1117	1157	96.5	6.76	11.39	19.34	0.0614	0.0332
0.84 - 0.80	1373	1396	98.4	6.58	8.79	15.59	0.0739	0.0417
0.80 - 0.77	1216	1239	98.1	6.26	9.12	15.40	0.0774	0.0447
0.77 - 0.74	1427	1455	98.1	5.95	7.52	13.05	0.0908	0.0539
0.74 - 0.72	1080	1095	98.6	5.80	7.91	12.50	0.0879	0.0542
0.72 - 0.70	1234	1249	98.8	5.52	6.08	9.84	0.1095	0.0706
0.70 - 0.68	1371	1383	99.1	5.39	5.63	8.96	0.1231	0.0785
0.68 - 0.66	1549	1554	99.7	5.20	4.17	7.11	0.1514	0.1047
0.66 - 0.65	870	872	99.8	5.03	4.35	6.77	0.1567	0.1073
0.65 - 0.63	1846	1847	99.9	4.85	4.14	6.29	0.1652	0.1168
0.63 - 0.62	1040	1043	99.7	4.62	4.44	6.44	0.1661	0.1196
0.62 - 0.61	1095	1097	99.8	4.52	4.12	5.93	0.1836	0.1314
0.61 - 0.60	1114	1141	97.6	3.49	3.76	4.79	0.1841	0.1675
0.60 - 0.59	757	1901	39.8	0.69	3.22	2.87	0.2402	0.2832
0.69 - 0.59	8969	10157	88.3	3.96	4.18	6.16	0.1621	0.1288
Inf - 0.59	24747	26209	94.4	6.03	11.41	19.33	0.0498	0.0380

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0308 [$I > 2\sigma(I)$], wR_2 = 0.1006, 520 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The H atoms were refined using a rotational group riding model with U_H = 1.5xUeq_C. S = 0.912, residual electron density 1.12 (1.20 Å from C2)/ -1.05 (0.36 Å from C7) e Å^{-3}. **CCDC 1509647**.

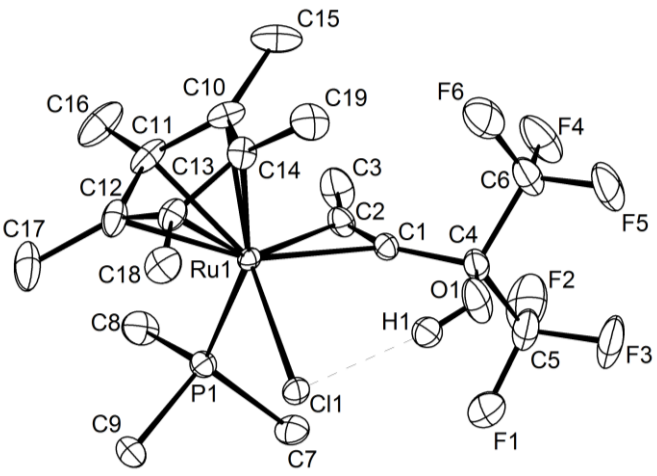


Figure S7. Molecular structure of **16**. Hydrogen atoms except for the one attached to the oxygen atom are omitted for clarity.

X-ray Crystal Structure Analysis of **16**: ($C_{19}H_{28}ClF_6OPRu$), M_r = 553.90 g · mol^{-1}, red prism, crystal size 0.07 x 0.08 x 0.12 mm^3, monoclinic, space group $P2_1/c$, a = 15.146(8) Å, b = 8.397(5) Å, c = 17.685(10) Å, β = 95.953(10)°, V = 2237(2) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.645 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.949 mm^{-1}, Gaussian absorption correction (T_{min} = 0.89128, T_{max} = 0.94420), Bruker AXS Enraf-Nonius Mach3 Apex II IμS diffractometer, 2.688 < θ < 32.206°, 66187 measured reflections, 7872 independent reflections, 6961 reflections with $I > 2\sigma(I)$, R_{int} = 0.040.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.82	126	129	97.7	9.08	108.1	88.03	0.0195	0.0076
2.82 - 1.87	294	294	100.0	10.61	74.5	85.52	0.0195	0.0081
1.87 - 1.46	431	431	100.0	10.81	57.5	75.54	0.0226	0.0090
1.46 - 1.27	425	425	100.0	11.08	29.7	57.67	0.0291	0.0116
1.27 - 1.15	421	421	100.0	10.46	25.4	49.11	0.0328	0.0136
1.15 - 1.07	398	398	100.0	9.85	27.3	46.64	0.0336	0.0144
1.07 - 1.00	474	474	100.0	9.52	22.3	39.04	0.0394	0.0168
1.00 - 0.95	392	392	100.0	8.94	18.9	34.44	0.0444	0.0202
0.95 - 0.91	400	400	100.0	8.67	15.8	29.35	0.0497	0.0235
0.91 - 0.87	478	478	100.0	8.32	12.9	24.73	0.0592	0.0285
0.87 - 0.84	396	396	100.0	7.87	11.6	22.20	0.0655	0.0322
0.84 - 0.81	496	496	100.0	7.70	10.9	19.91	0.0727	0.0355
0.81 - 0.79	361	361	100.0	7.52	10.9	19.48	0.0694	0.0369
0.79 - 0.77	399	399	100.0	7.29	9.6	17.09	0.0781	0.0418
0.77 - 0.75	433	433	100.0	7.00	8.5	15.37	0.0879	0.0481
0.75 - 0.73	497	497	100.0	6.88	8.9	14.96	0.0861	0.0479
0.73 - 0.72	259	259	100.0	6.88	8.6	13.82	0.0932	0.0509
0.72 - 0.70	567	567	100.0	6.40	7.0	11.52	0.1061	0.0625
0.70 - 0.69	315	315	100.0	6.48	7.0	11.58	0.1094	0.0651
0.69 - 0.67	786	820	95.9	5.65	6.8	10.61	0.1168	0.0742
0.77 - 0.67	2857	2891	98.8	6.41	7.7	12.67	0.0997	0.0591
Inf - 0.67	8348	8385	99.6	8.17	19.7	30.76	0.0396	0.0215

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0355 [$I > 2\sigma(I)$], wR_2 = 0.0856, 275 parameters. Several low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The hydroxyl H atom was located on a

difference Fourier map an refined using an isotropic atomic displacement parameter. Otherwise, H atoms were refined using a riding model with U_H = 1.5xUeq_C. *S* = 1.144, residual electron density 3.41 (0.64 Å from Ru1)/ -1.46 (0.60 Å from Ru1) e Å^{-3}. **CCDC 1509648**.

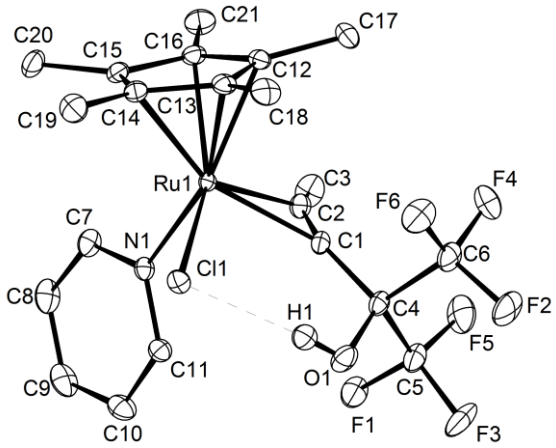


Figure S8. Molecular structure of **17**. Hydrogen atoms except for the one attached to the oxygen atom are omitted for clarity.

X-ray Crystal Structure Analysis of **17**: ($C_{21}H_{24}ClF_6NORu$), M_r = 556.93 g · mol^{-1}, orange prism, crystal size 0.08 x 0.09 x 0.22 mm^3, monoclinic, space group $P2_1/n$, a = 8.7929(13) Å, b = 12.2158(18) Å, c = 20.666(3) Å, β = 99.091(2)°, V = 2191.9(6) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.688 g · cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.901 mm^{-1}, Gaussian absorption correction (T_{min} = 0.83544, T_{max} = 0.94847), Bruker AXS Enraf-Nonius Mach3 Apex II IμS diffractometer, 2.601 < θ < 36.571°, 60003 measured reflections, 10566 independent reflections, 8833 reflections with $I > 2\sigma(I)$, R_{int} = 0.028.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.52	165	168	98.2	9.32	99.74	105.86	0.0181	0.0075
2.52 - 1.66	390	390	100.0	10.15	61.68	96.08	0.0155	0.0072
1.66 - 1.31	554	554	100.0	10.13	37.21	79.06	0.0181	0.0083
1.31 - 1.14	552	552	100.0	9.09	25.20	60.97	0.0224	0.0104
1.14 - 1.03	573	573	100.0	7.78	24.95	53.43	0.0243	0.0122
1.03 - 0.96	518	518	100.0	7.41	19.70	43.57	0.0279	0.0138
0.96 - 0.90	577	577	100.0	6.80	16.88	38.48	0.0318	0.0163
0.90 - 0.85	618	618	100.0	6.01	13.08	30.32	0.0368	0.0207
0.85 - 0.82	430	431	99.8	5.66	12.44	29.45	0.0385	0.0222
0.82 - 0.78	704	705	99.9	5.52	10.36	24.66	0.0448	0.0258
0.78 - 0.76	398	398	100.0	5.35	9.93	22.95	0.0484	0.0279
0.76 - 0.73	687	688	99.9	5.18	10.24	22.54	0.0498	0.0295
0.73 - 0.71	533	535	99.6	5.09	8.34	19.73	0.0555	0.0344
0.71 - 0.69	578	582	99.3	4.57	8.36	18.09	0.0577	0.0394
0.69 - 0.67	654	664	98.5	3.93	7.82	15.51	0.0613	0.0441
0.67 - 0.66	369	372	99.2	3.72	6.52	13.04	0.0717	0.0535
0.66 - 0.64	780	795	98.1	3.27	6.49	12.07	0.0701	0.0607
0.64 - 0.63	398	409	97.3	2.94	5.56	10.04	0.0822	0.0745
0.63 - 0.62	453	473	95.8	2.84	5.66	9.94	0.0788	0.0737
0.62 - 0.61	467	498	93.8	2.67	5.58	9.80	0.0807	0.0769
0.61 - 0.60	549	727	75.5	1.74	4.27	6.83	0.0947	0.1149
0.70 - 0.60	3959	4230	93.6	3.08	6.32	11.78	0.0703	0.0636
Inf - 0.60	10947	11227	97.5	5.45	15.77	31.36	0.0277	0.0215

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0221 [$I > 2\sigma(I)$], wR_2 = 0.0538, 290 parameters. Two low-angle reflections were shadowed by the beamstop and were removed before the final refinement cycles. The hydroxyl H atom was located on a difference Fourier map and refined using an isotropic atomic displacement parameter. Otherwise, H atoms were refined using a riding model with U_H = 1.5xUeq_C for the methyl groups and U_H = 1.2xUeq_C for the pyridinyl group. S = 1.023, residual electron density 0.67 (0.66 Å from C2)/ -0.56 (0.63 Å from Ru1) e Å^{-3}. **CCDC 1509649**.

General. Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon in flame-dried glassware. Anhydrous solvents were freshly distilled from appropriate drying agents and were transferred under Argon: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), CH_3CN (CaH_2), hexane, toluene (Na/K), EtOH, MeOH (Mg), Et_3N (MS), DMF (MS), DMAP (MS). Flash chromatography: Merck silica gel 60 (40-63 µm).

MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

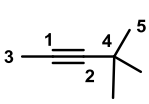
^{1}H, ^{13}C{^{1}H},^{19}F{^{1}H} (referenced externally to $BF_3{\cdot}Et_2O$), ^{31}P{^{1}H} (referenced externally to H_3PO_4), ^{29}Si{^{1}H} (referenced externally to TMS) and ^{119}Sn{^{1}H} (referenced externally to Me_4Sn) NMR spectra were recorded using a Bruker Avance VIII-300 or Bruker Avance III HD 400 MHz spectrometer. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves prior to use. ^{1}H NMR spectra (300.13 MHz or 400.1 MHz) were referenced to the residual protons of the deuterated solvent used. ^{13}C{^{1}H} NMR spectra (75.47 MHz or 101 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Where appropriate, resonances were assigned using 2D NMR homo- and heterocorrelation (COSY, HMBC, HSQC) and NOESY techniques. Chemical shifts (δ) are given in ppm, relative to TMS, coupling constants (J) in Hz. For clarity, Sn—H couplings of vinylic protons were omitted in the multiplet analysis but given in brackets (averaged over $^{117/119}$Sn).

Thermodynamic parameters for fluxional processes were determined through line shape analysis by extracting the exchange rates using the DNMR module in TopSpin 2.1, followed by data analysis using the Eyring-Polanyi equation.

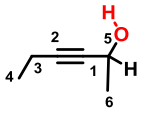
α:β is used to denote the ratio of the regioisomers formed by proximal:distal delivery of the R_3M residue while the *cis* and *trans* configuration nomenclature refers to the situation in which the H and MR_3 unit end up *trans* or *cis* to each other.

[Cp*RuCl]$_4$,[1] [Cp*Ru(MeCN)$_3$]PF_6,[2] [Cp*$RuCl_2$]$_n$[3] 2,5,5-trimethylhex-3-yn-2-ol,[4] trimethyl(nona-1,7-diyn-1-yl)silane,[5] trimethyltin hydride,[6] 6-bromo-1H-imidazole,[7] as well as some hydrostannylation products (Table 4, entries 1,[8] 3,[8] 6,[9] 9,[8] 12,[8] 13[8]) were prepared using literature methods. The spectra of these stannanes are contained in the SI of the cited references.

Reference Data for Alkyne Substrates Used in the π-Coordination Studies

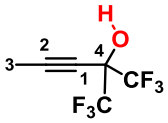


4,4-Dimethylpent-2-yne. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ 1.73 (s, 3H, C^3H), 1.18 (s, 9H, C^5H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K) δ 88.3 (C^2), 74.2 (C^1), 31.7 (C^5), 27.8 (C^4), 3.6 (C^3).



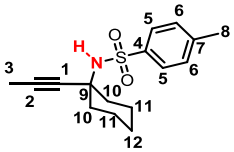
Hex-3-yn-2-ol. ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K) δ 4.45 (br qt, J = 7 Hz, 1 Hz, 1H, C^5H) 2.18 (dq, J_{HH} = 8 Hz, 1 Hz, 2H, C^3H), 1.95 (s, 1H, OH), 1.35 (d, J = 7 Hz, 3H, C^6H), 1.08 (t, J = 8 Hz, 3H, C^4H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) δ 85.4 (C^1), 81.3 (C^2), 58.1 (C^5), 24.5 (C^6), 13.7 (C^4), 12.1 (C^3).

1,1,1-Trifluoro-2-(trifluoromethyl)pent-3-yn-2-ol. Hexafluoroacetone (2 mL, 19.88 mmol) was



condensed into a Schlenk flask at –78 °C and pre-cooled Et_2O (2 mL) was added. The solution was then treated with a pre-cooled suspension of propynyl lithium (914 mg, 19.9 mmol) in Et_2O (15 mL) and stirring was continued at –78 °C for 2 h. The mixture was allowed to warm to RT where it was stirred for further 2 h. Aqueous work-up was followed by extraction with Et_2O and drying of the combined organic phases over Na_2SO_4. Evaporation of the solvent *in vacuo* afforded the title propargyl alcohol as a light yellow liquid (2.45 mL, 5 M in Et_2O, 61 %). Because of its volatility, 1,1,1-trifluoro-2-(trifluoromethyl)pent-3-yn-2-ol could only be obtained as a solution in Et_2O and was used as such in all preparative procedures. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ 4.90 (s, 1H, OH), 1.94 (s, 3H, C^3H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K) δ 122.3 (CF_3, $^{1}J_{CF}$ = 281 Hz), 87.8 (C^1), 71.8 (q, $^{2}J_{CF}$ = 33 Hz, C^4), 69.0 (C^2), 3.6 (C^3); $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K) δ −79.99 (s); IR (ṽ, film, cm^{-1}) 3178, 2985, 2282, 2882, 2253, 1387, 1220, 1160, 1090, 956, 720. ESI-MS for $C_6H_4OF_6$ [M-H^+] calcd. 205.00936, found 250.00933.

4-Methyl-N-(1-(prop-1-yn-1-yl)cyclohexyl)benzenesulfonamide. Following an adaptation from a

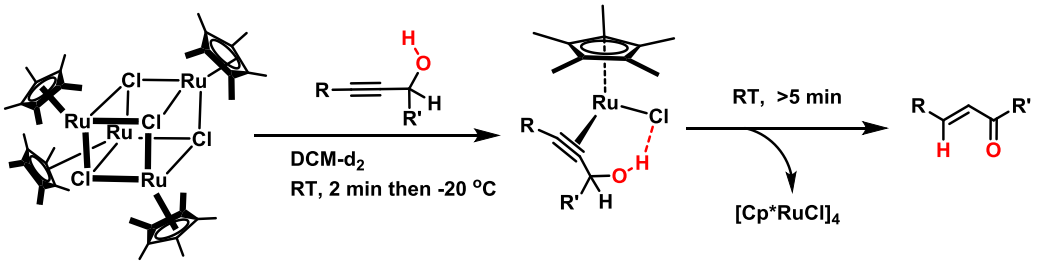


reported procedure,[10] $Bi(OTf)_3$ (242 mg, 0.37 mmol) and KPF_6 (68.1 mg, 0.37 mmol) were loaded in a Schlenk flask and dioxane (3 mL) was added. The mixture was stirred for 10 min at room temperature before 1-(prop-1-yn-1-yl)cyclohexan-1-ol (511 mg, 3.7 mmol), 4-methylbenzenesulfonamide (1.25 g, 171 mmol) and $CaSO_4$ were added. Stirring was continued for 16 h, after which the mixture was diluted with Et_2O and treated with silica. The supernatant was filtered off and the solid residue was washed with Et_2O (3 x 10 mL). The combined filtrates were evaporated and the solid residue was purified by flash chromatography (hexane/EtOAc 7/1) to afford the title compound as a white powder (140 mg, 13%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.79 (d, J = 8.0 Hz, 2H, C^5H or C^6H), 7.27 (d, J = 7.9 Hz, 2H, C^6H or C^5H), 4.74 (s, 1H, NH), 2.41 (s, 3H, C^8H), 2.27 – 1.07 (m, 10H, Cy), 1.36 (s, C^3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K) δ 141.8 (C^4), 138.6 (C^7), 128.2 (C^6), 126.8 (C^5), 80.9 (C^1), 78.3 (C^2), 53.8 (Cy), 38.4 (Cy), 24.2 (Cy), 21.7 (Cy), 20.6 (C^8), 2.5 (C^3); IR (ṽ, film, cm^{-1}) 3294, 2925, 2851, 1726, 1596, 1578, 1498, 1442, 1320, 1152, 1127, 891, 826, 801, 672, 603. ESI-MS for $C_{16}H_{20}NO_2S$ [M-H^+] calcd. 290.12237, found 290.12203.

Preparation of π-Complexes

Representative procedure: Preparation of Complex 5. $[Cp^*RuCl]_4$ (15 mg, 13.78 µmol) was added to a solution of 1,1,1-trifluoro-2-(trifluoromethyl)pent-3-yn-2-ol (18 µL, 16 mg, 57.4 µmol) in CH_2Cl_2 (2 mL) to give a cherry–red solution. Evaporation of the volatile components *in vacuo* afforded the title complex as a purple waxy powder (25 mg, 95 %). The compound was crystallised by storing a pentane solution of **5** at −20 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 8.03 (s, 1H, OH), 2.82 (s, 3H, C^3H), 1.75 (s, 15H, C^7); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 142.3 (C^1), 136.3 (C^2), 123.3 (q, $^1J_{CF3}$ = 283 Hz, CF_3), 92.6 (C^6), 80.8 (hept, $^2J_{CF}$ = 32 Hz, C^4), 14.3 (C^3), 10.4 (C^7); $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) δ −77.75 (s).

Complex 6. Prepared analogously by mixing $[Cp^*RuCl]_4$ (24 mg, 22.06 µmol) and 4-methyl-N-(1-(prop-1-yn-1-yl)cyclohexyl)benzenesulfonamide (25.7 mg, 88.2 µmol) in CD_2Cl_2 (0.6 mL) at RT, to give a purple solution. Full conversion was noted by NMR spectroscopy. The title complex is unstable at room temperature and was characterised *in situ* at −20 °C. Recrystallisation by slowly cooling a pentane solution of **6** from –30 to −80 °C in a cryostat over 7 days gave crystals suitable for X-ray crystallography. ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K) δ 7.36 (d, *J* = 8 Hz, 2H, C^9H or $C^{10}H$), 7.09 (d, *J* = 8 Hz, 2H, $C^{10}H$ or C^9H), 7.02 (br s, 1H, NH), 2.36 (s, 3H, $C^{13}H$), 2.24 (s, 3H, C^3H), 1.88 – 1.21 (m, 10H, C^5H, C^6H, C^7H), 1.59 (s, 15H, C^{15}); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 253 K) δ 146.5 (C^1), 141.9 (C^{11} or C^8) 140.2 (C^2), 137.4 (C^8 or C^{11}), 128.8 (C^{10} or C^9), 127.9 (C^9 or C^{10}), 88.7 (C^{14}), 68.3 (C^4), 37.0 (Cy), 29.7(Cy) 25.1 (Cy), 22.2 (Cy), 21.4 (C^{13}), 14.1 (C^3), 10.0 (C^{15}).



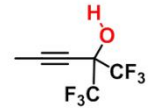
Compound 8. Compound **8** was generated by mixing $[Cp^*RuCl]_4$ (22 mg, 20.2 µmol) and hex-3-yn-2-ol (8.7 µL, 80.9 µmol) in an NMR tube in CD_2Cl_2 (0.5 mL) at −30 °C followed by warming of the mixture to RT for 2 min, to give a purple solution. The mixture was then cooled to −40 °C and placed in the probe of an NMR spectrometer pre-cooled to −40 °C. Full conversion was noted by NMR spectroscopy. The compound is unstable at RT and must be kept below −20 °C to prevent redox isomerization from occuring. Single crystals suitable for X-ray crystallography were obtained by generating compound **8** in a Schlenk flask in CH_2Cl_2, followed by evaporation of the volatile components *in vacuo* at −30 °C and re-dissolving the solid residue in cold pentane (−30 °C). The solution was then filtered at this temperature; the supernatant was placed in a cryostat and the temperature was gradually lowered from −30 °C to −75 °C over one week. ^{1}H NMR (400 MHz, CD_2Cl_2, 233K) δ 4.80 (q, *J* = 11 Hz, 1H, C^5H), 4.58 (s, 1H, OH), 2.99 (q, *J* = 7.4 Hz, 2H, C^3H) 1.70 (s, 15H, C^8H), 1.49 (t, *J* = 7.4 Hz, 3H, C^4H), 1.39 (d, *J* = 6.6 Hz, 3H, C^6H); $^{13}C\{^1H\}$ NMR (101 MHz, 233K) δ 150.7 (C^1), 133.3 (C^2), 88.7 (C^7) , 63.8 (C^4) , 23.8 (C^6) , 23.2 (C^5), 15.3 (C^3), 10.1 (C^8). Warming the sample to temperatures above −20 °C affords the redox isomerisation product **9** and $[Cp^*RuCl]_4$.

Binding and Hydrostannylation of a Non-functionalised Alkyne

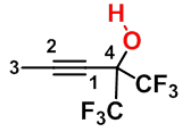
Complex / Cocrystals of 1 and 4,4-Dimethyl-2-pentyne (10). In an NMR tube, $[Cp^*RuCl]_4$ (9.7 mg, 9 µmol) was dissolved in CD_2Cl_2 (0.5 mL). To this, one equivalent of alkyne **10** was added at RT and the sample was equilibrated at −50 °C for 2 h before being inserted into the probe of an NMR spectrometer pre-cooled to −50 °C. A colour change from brown to purple was noted. 70% conversion was quantified by NMR spectroscopy (based on $[Cp^*RuCl]_4$). Dissociation of the substrate was observed when warming the sample to RT, concomitant with a colour change from purple to brown. Attempted crystallisation of the complex at −20°C furnished single crystals consisting of **1** with solute alkyne **10** in the crystal lattice. The complex observed in situ showed the following characteristic signals: ^{1}H NMR (400 MHz, CD_2Cl_2, 223K) δ 2.70 (s, 3H, C^3H), 1.66 (s, 15H, C^7H), 1.18(s, 9H, C^5H); $^{13}C\{^1H\}$ NMR (101 MHz, 223K) δ 159.3 (C^2), 131.1 (C^1), 89.7 (C^7), 36.1 (C^4), 30.6 (C^5), 10.1 (C^7), 10.0 (C^3).

Compound 11. A solution of trimethyltin hydride (33.8 µL, 184.8 µmol) in CH_2Cl_2 (2 mL) was added dropwise over 16 h to a stirred solution of **1** (5.02 mg, 4.62 µmol) and **10** (17.77 mg, 25 µL, 184.8 µmol) in CH_2Cl_2 (3 mL) at −65°C. An aliquot was analysed by NMR spectroscopy which indicated 92% conversion of the starting material and 95% isomer purity in favour of **11**. The mixture was then diluted with CH_2Cl_2 (3 mL) and passed through a short silica pad cooled to −20 °C. The volatile components were carefully removed *in vacuo* (20°C, 600 mbar) to avoid evaporation of the target compound. Compound **11** was isolated as a faint brown oil (44.3 mg, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298K) δ 6.05 (q, $^3J_{HH}$ = 7 Hz, $^3J_{SnH}$ = 156.2 Hz, 1H, C^1H), 1.72 (d, $^3J_{HH}$ = 7 Hz, 3H, C^5H), 1.03 (s, 9H, C^4H), 0.22 (s, 9H, $SnMe_3$); $^{13}C\{^1H\}$ NMR (101 MHz, 223K) δ 156.8 (C^2), 128.8 (C^1), 38.7 (C^3), 30.7 (C^4), 19.4 (C^5), −5.4 ($SnMe_3$); $^{119}Sn\{^1H\}$ NMR (112 MHz, CD_2Cl_2) δ −58.2 (s); IR (ṽ, film, cm^{-1}) 2960, 2923, 1461, 1360, 1260, 1189, 1095, 1017, 798, 710; EI-MS *m/z* (%) 247 (51.9), 165 (100), 151 (21.5) 135 (30.4). Trace amounts of Me_6Sn_2 and Me_4Sn were detected by NMR and GC-MS after the reaction was complete.

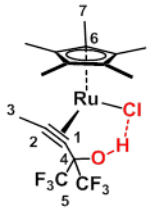
^{1}H, CD_2Cl_2, 298 K

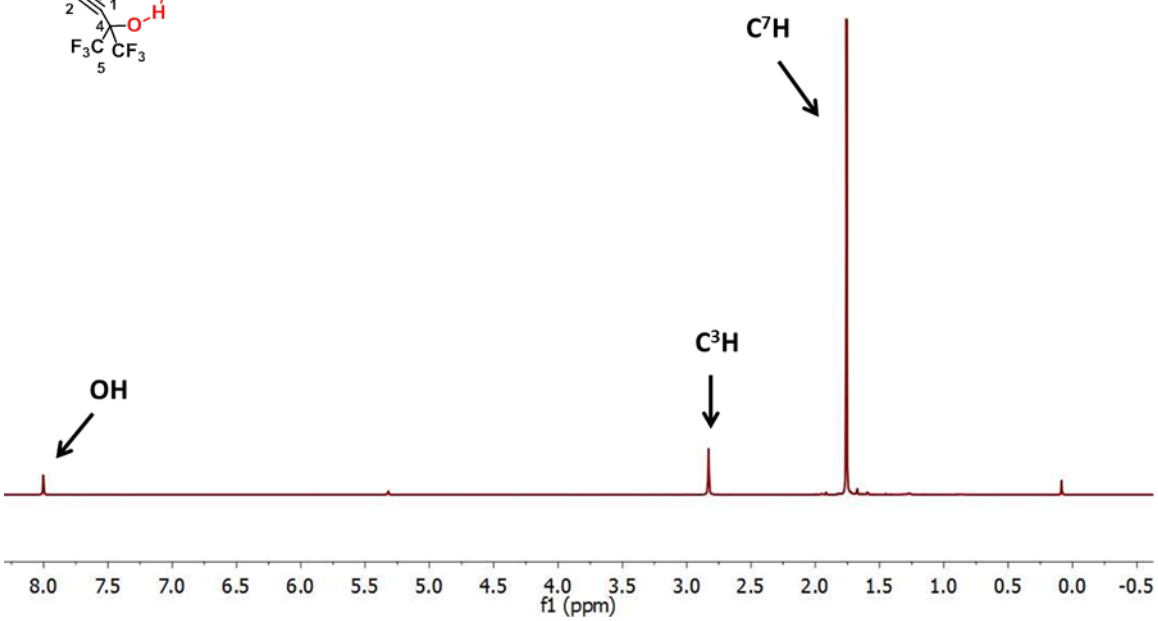


$^{13}C\{^1H\}$, CD_2Cl_2, 298 K

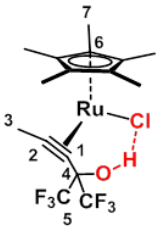


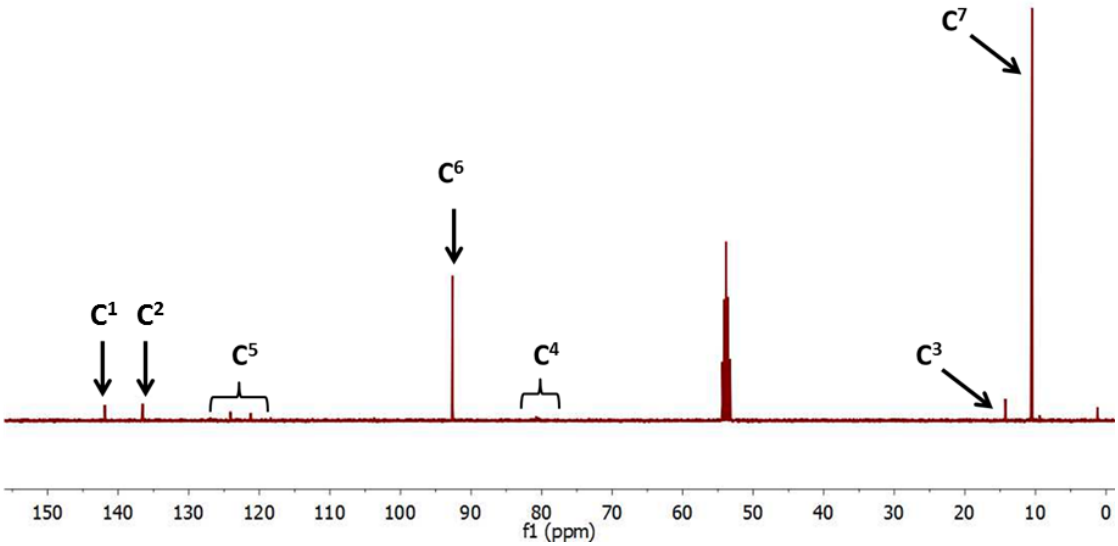
^{1}H, CD_2Cl_2, 298 K



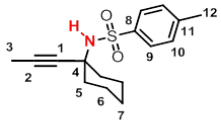


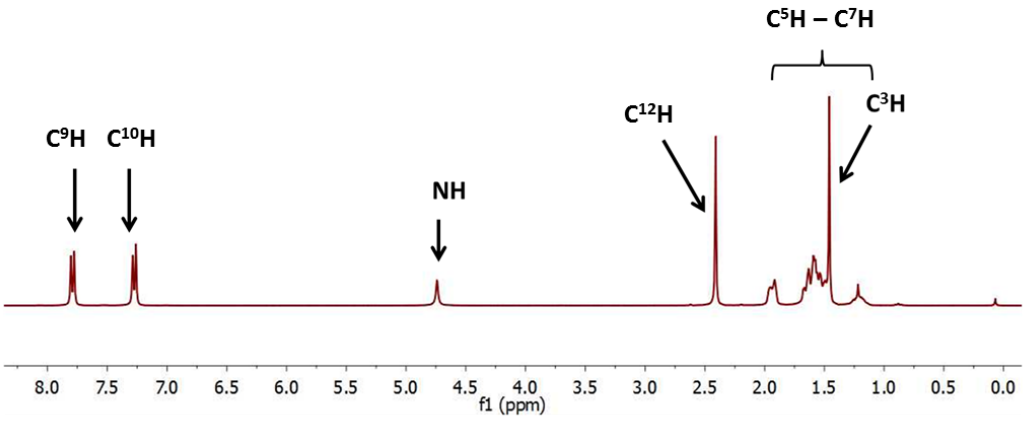
$^{13}C\{^{1}H\}$, CD_2Cl_2, 298 K



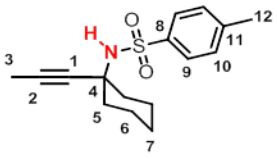


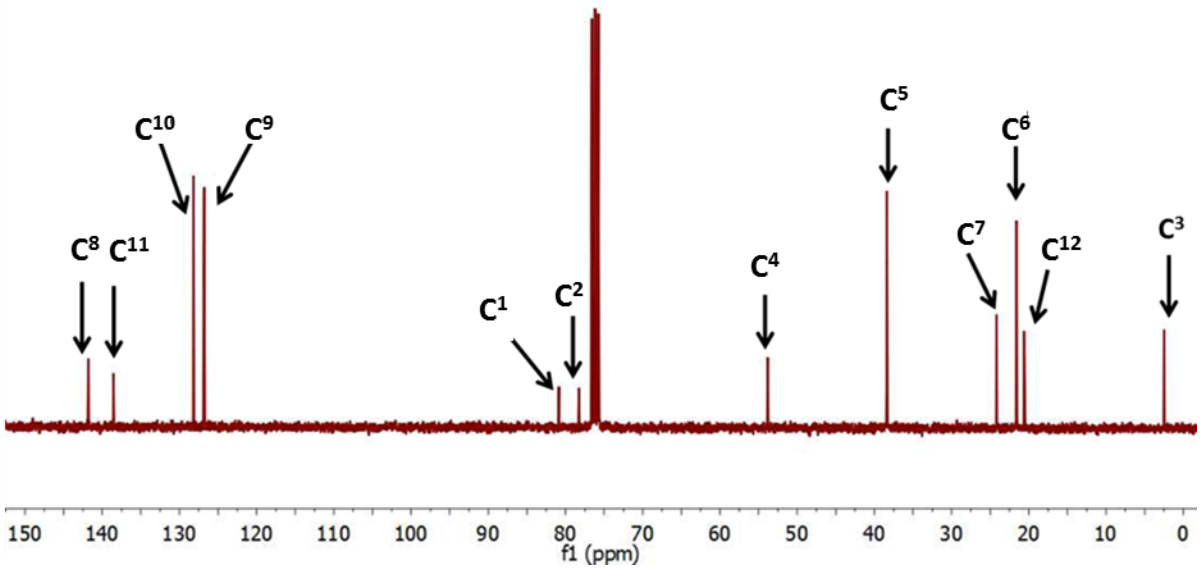
^{1}H, $CDCl_3$, 298 K



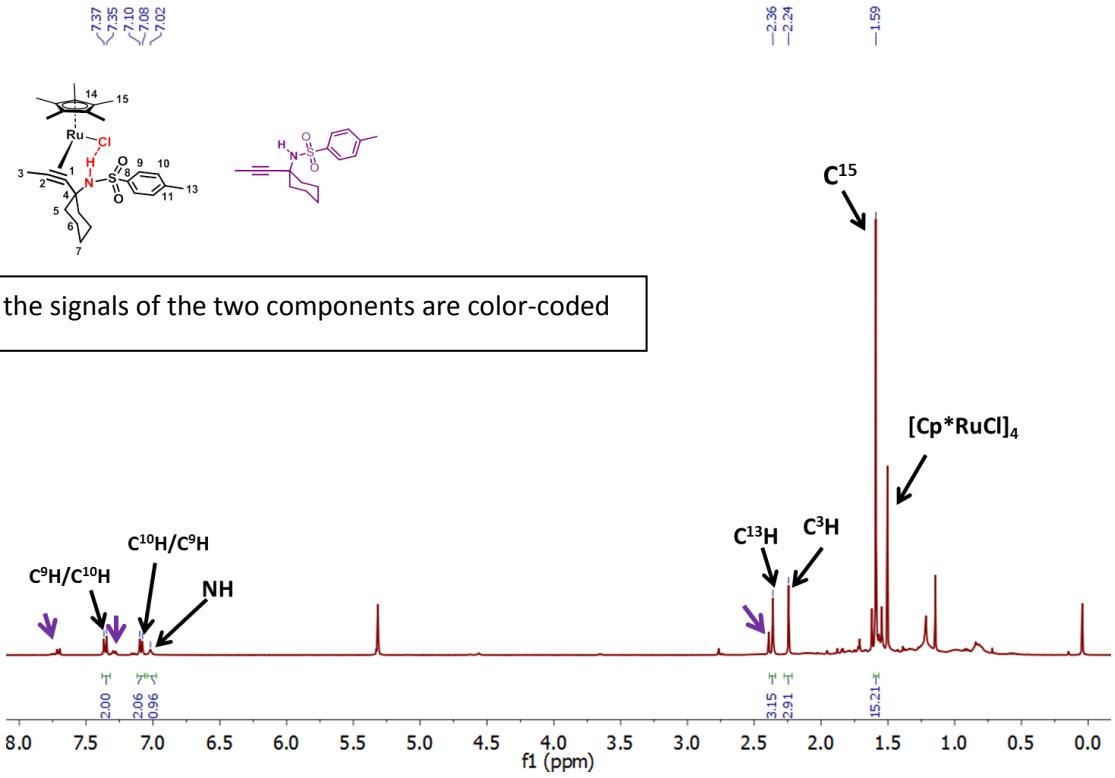


$^{13}C\{^1H\}$, $CDCl_3$, 298 K



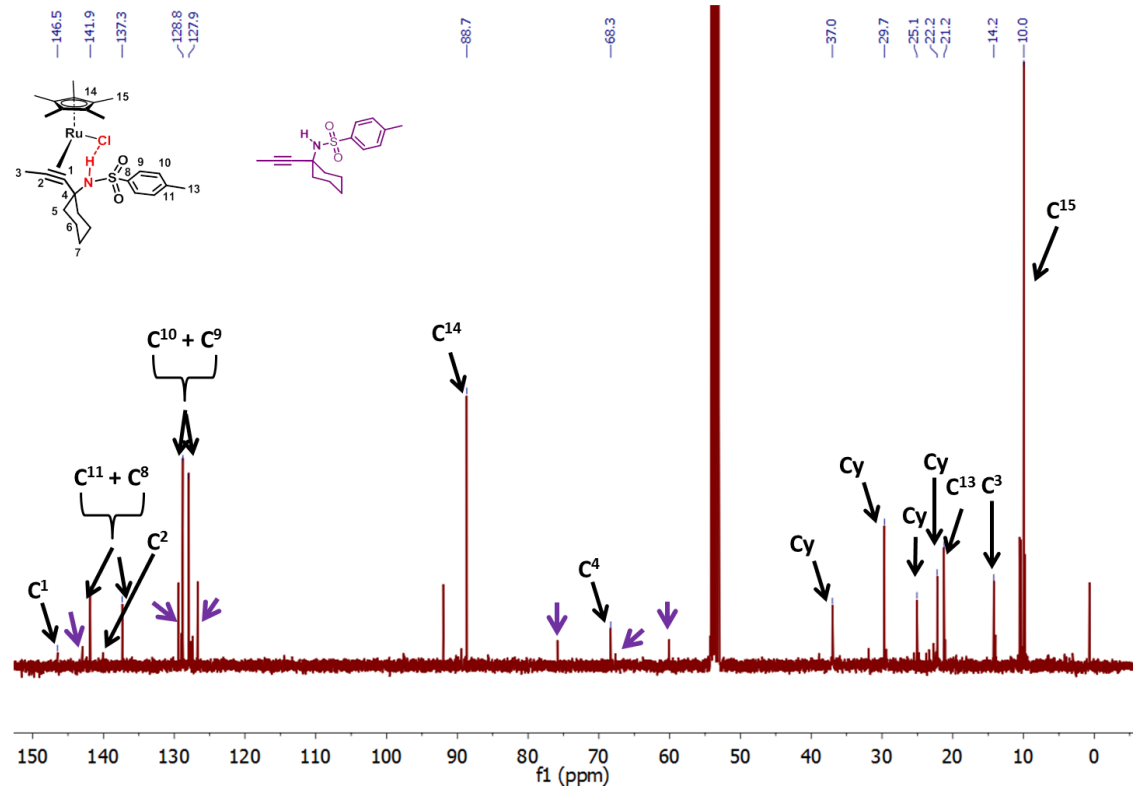


^{1}H NMR, CD_2Cl_2, 253 K

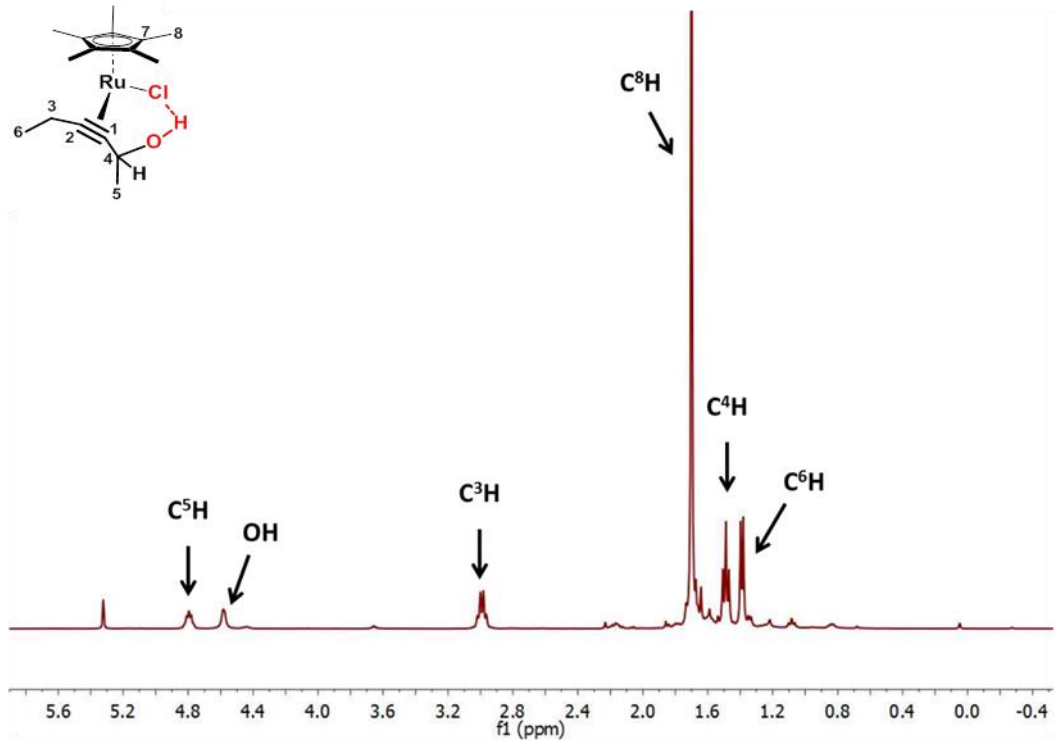


the signals of the two components are color-coded

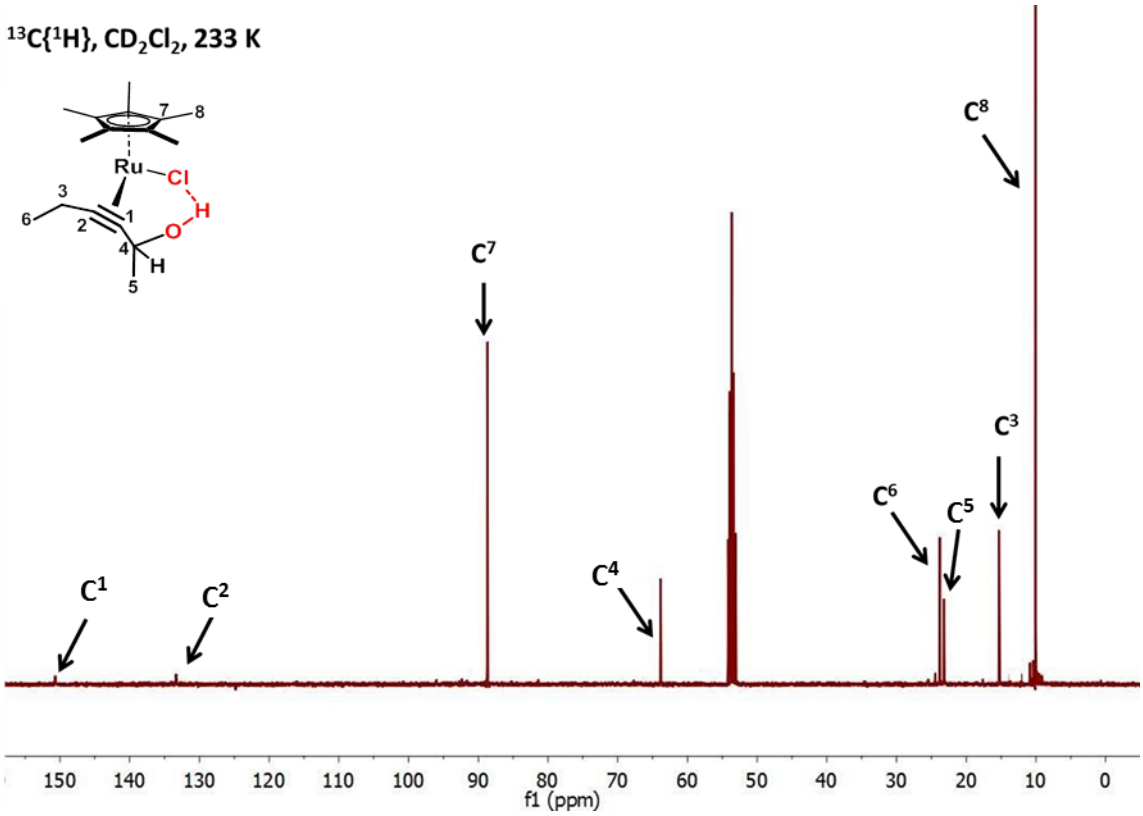
$^{13}C\{^1H\}$ NMR, CD_2Cl_2, 253 K



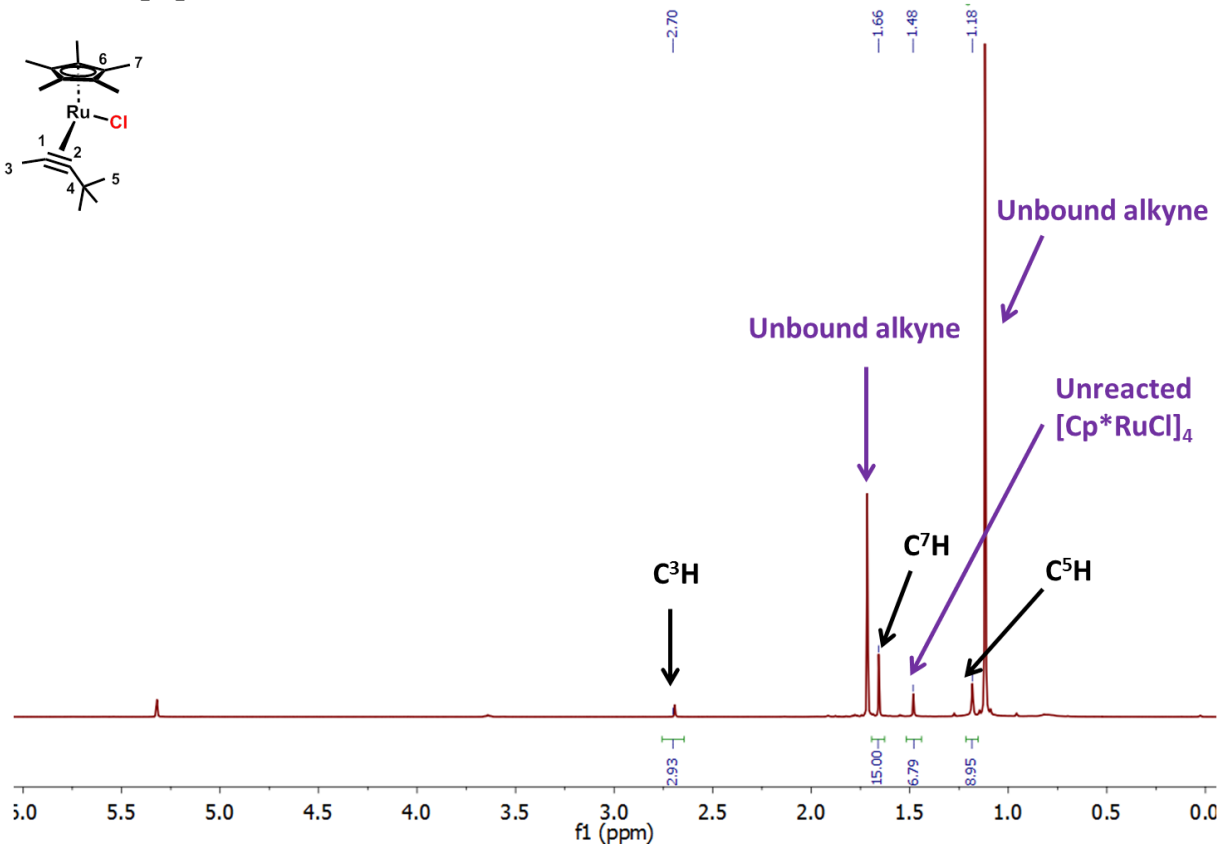
^{1}H, CD_2Cl_2, 233 K



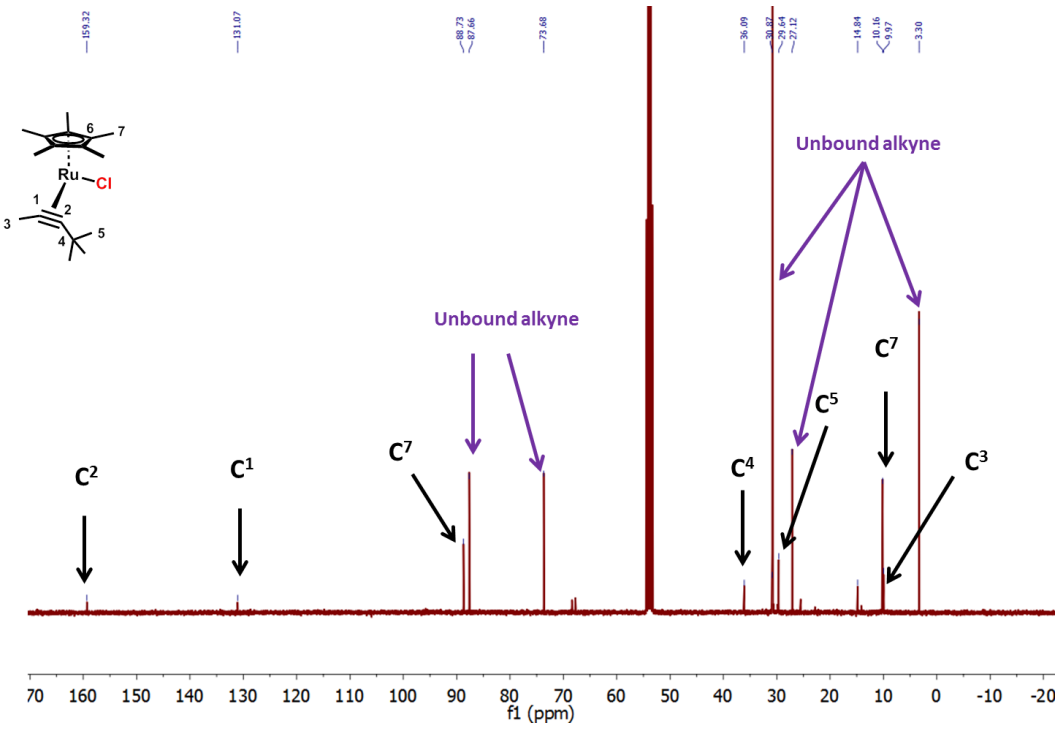
$^{13}C\{^{1}H\}$, CD_2Cl_2, 233 K



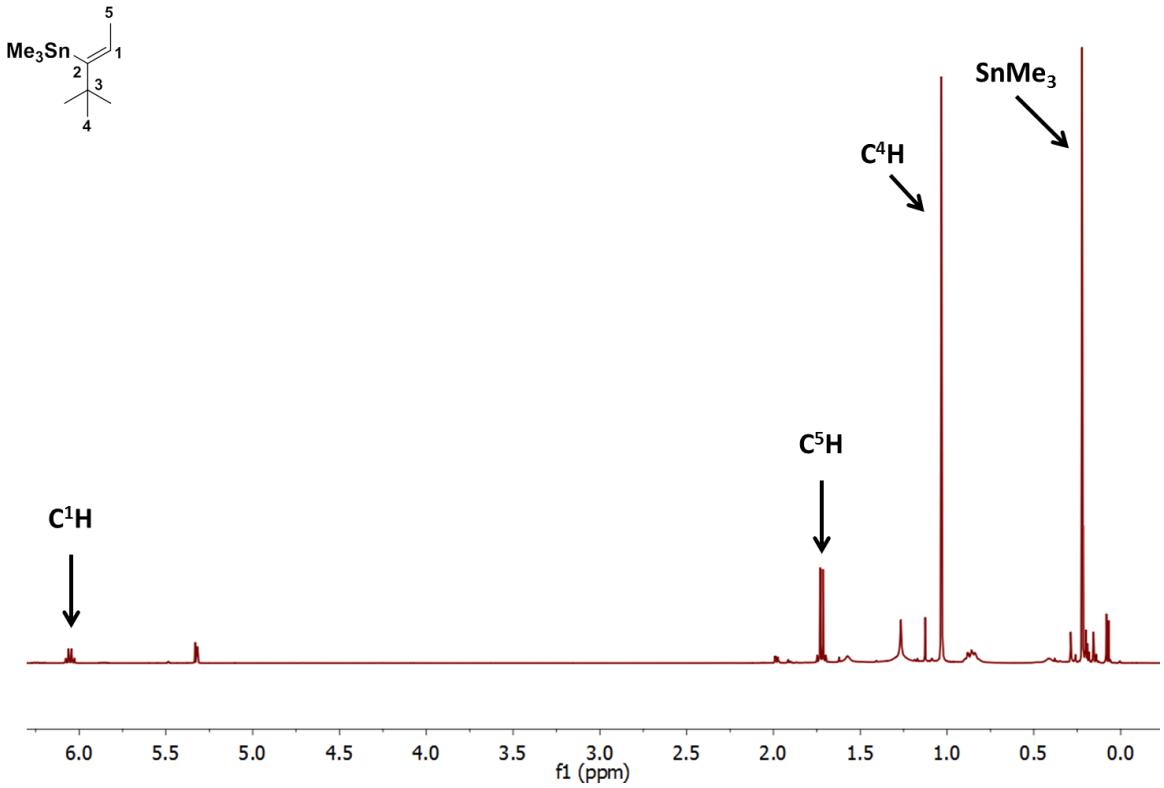
^{1}H NMR, CD_2Cl_2, 223 K



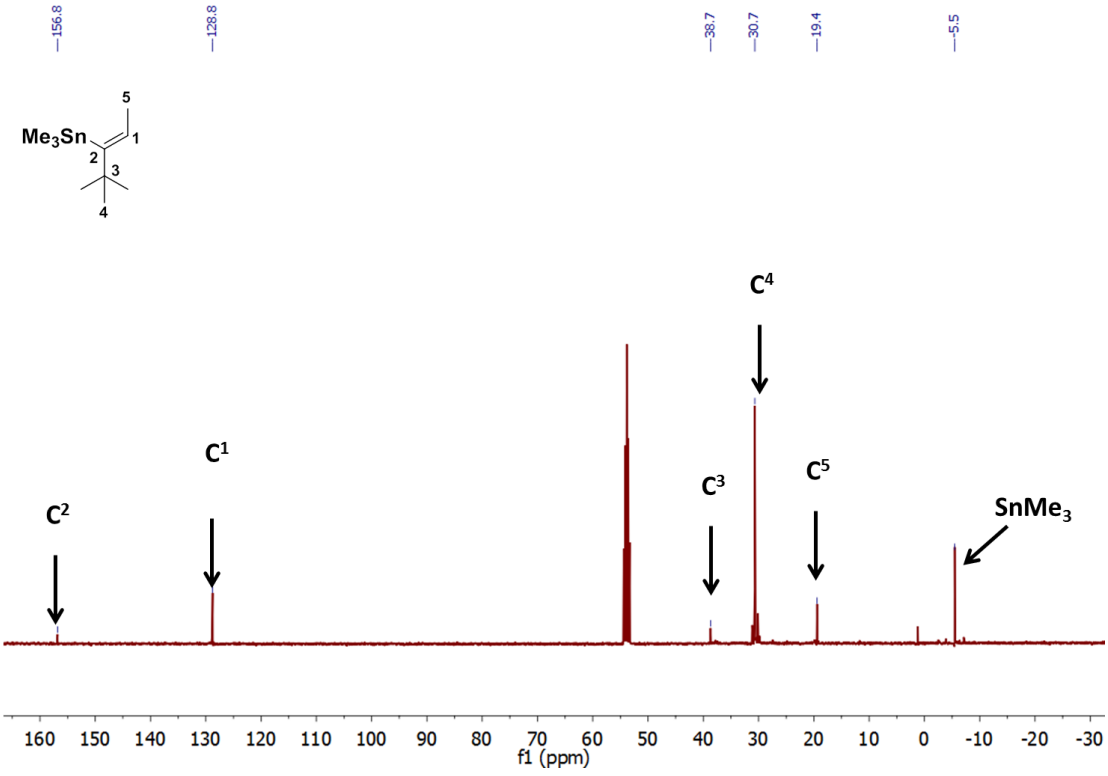
$^{13}C\{^1H\}$ NMR, CD_2Cl_2, 223 K



^{1}H NMR, CD_2Cl_2, RT

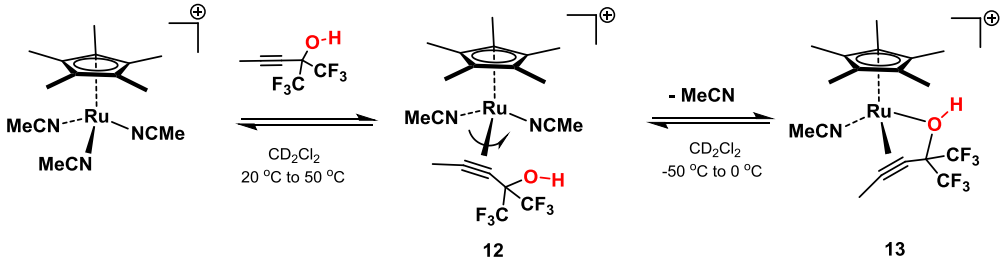


^{13}C{^{1}H} NMR, CD_2Cl_2, RT

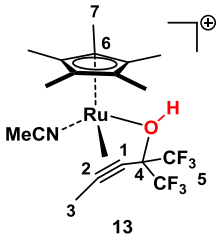


Binding to Cationic Catalysts

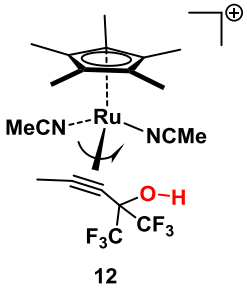
Measurements were performed on a Bruker 400 MHz spectrometer. Temperature control was achieved by employing a BCU unit. $^{19}F\{^{1}H\}$ NMR spectra were recorded from 240 K to 328 K and subjected to careful manual phase and baseline correction for accurate integration. The CF_3 resonances of the coordinated and free 1,1,1-trifluoro-2-(trifluoromethyl)pent-3-yn-2-ol were monitored. Lineshape analysis was performed for measurements ranging from 240 K (where full resolution of the resonances corresponding to the coordinated alkyne into two quartets was observed) and 277.5 K (where full coalescence of the signals was noted). The kinetic data were extracted by using the DNMR module of Topspin 2.1 (Bruker). The pair of exchanging signals were treated as an isolated spin system and was fitted using simple iterations on the chemical shifts, intensities and rate constants of the exchange process ($k_{exchange}$). The rate constants are tabulated in Table S1. Activation enthalpy ($\Delta H^{\ddagger}$), activation enthropy ($\Delta S^{\ddagger}$) and activation energy (E_A) were taken from least-squares linear fits on the corresponding Eyring plots.



Complexes 12 and 13. $[Cp^*Ru(MeCN)_3]PF_6$ (17 mg, 33.7 µmol) was placed in J-Young NMR tube and was dissolved in CD_2Cl_2 (0.6 mL). 1,1,1-Trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol (7.8 µL, 33.7 µmol) was added and the solution was placed in an NMR spectrometer probe pre-cooled to 240 K. The sample was allowed to equilibrate at this temperature for 30 min before the temperature was gradually raised to 298 K.



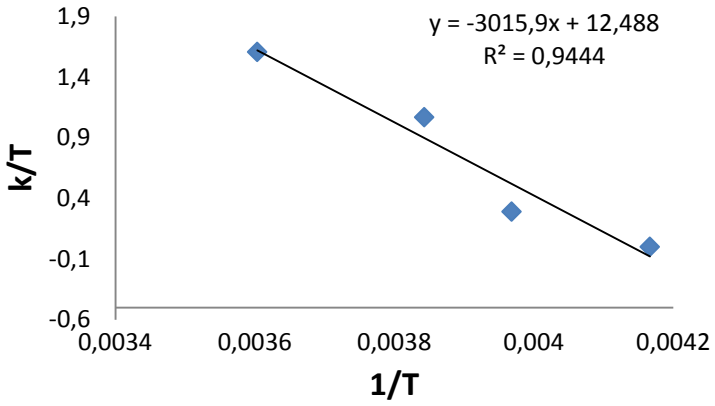
At −33 °C, 16.6% of 1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol was bound to give **13.** The rest of the sample consisted of $[Cp^*Ru(MeCN)_3]PF_6$ and unbound 1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol. Characterisation data for **13:** ^{1}H NMR (400 MHz, CD_2Cl_2, 240 K) δ 3.63 (s, OH), 2.48 (s, C^3H), 2.37 (coordinated MeCN), 1.51 (C^7H); ^{19}F NMR (376 MHz, CD_2Cl_2, 240 K) δ -76.62 (q, J_{FF} = 12 Hz, 3F), -77.2 (q, J_{FF} = 12 Hz, 3F).



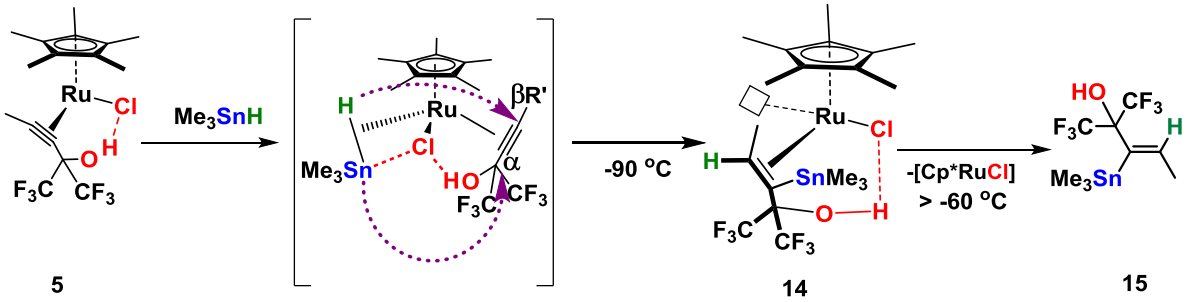
At 0 °C, resonances appear broad as free MeCN is freely exchanging with coordinated MeCN. Additionally, above room temperature, exchange between free and bound alkyne is also observed, hampering the analysis of complex **12** by ^{1}H NMR. Data for **12**: ^{19}F NMR (376 MHz, CD_2Cl_2, 273 K) δ -76.87 (s).

Table S1. Kinetic parameters for the alkyne exchange reaction with $[Cp^*Ru(MeCN)_3]PF_6$

Temp. (K)	$k_{exchange}$ (s^{-1})	k/T	1/T
240	0	0	0.004167
252	60	0.288	0.003968
260.2	233	1.068	0.003843
277.5	366	1.604	0.003604



Attempted Characterization of the Loaded Catalyst.

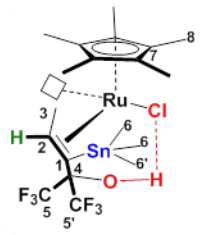


Complex 14. The π-complex **5** was generated in an NMR tube by mixing $[Cp^*RuCl]_4$ (7.3 mg, 6.71 µmol) with 1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol (7.5 µL, 26.84 µmol) in CD_2Cl_2 (0.5 mL) at room temperature, giving a cherry-red solution. (*vide supra)* The mixture was then cooled to −95 °C and Me_3SnH (4 µL, 26.84 µmol) was rapidly injected after which the tube was vigorously shaken and placed in the probe of an NMR spectrometer pre-cooled to −85 °C. A colour change to dark purple was noted. The resulting compound was characterized *in situ* by NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2, 188 K) δ 6.18 (1H, OH), 5.91 (q, *J* = 6 Hz, $^3J_{SnH}$ = 88 Hz, 1H, C^2H,), 2.25 (d, *J* = 6 Hz, 3H, C^3H), 1.42 (s, 15H, C^8H), 0.21 (br s, 3H, C^6H or $C^{6'}H$), 0.01 (br s, 6H, $C^{6'}H$ or C^6H); $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 188 K) δ −70.02 (br s, 3F, CF_3), -74.63 (q, J_{FF} = 10 Hz, 3F, CF_3); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 188 K) δ 122.5 (q, $^1J_{CF}$ = 289 Hz, C^5 or $C^{5'}$), 122.3 (q, $^1J_{CF}$ = 289 Hz, $C^{5'}$ or C^5), 86.5 (C^1/C^2), 83.4 (C^7), 82.4 (C^2/C^1), 80.7 (q, $^2J_{CF}$ = 28 Hz, C^4), 26.3 (s, $^3J_{SnC}$ = 45 Hz, C^3), 9.8 (s, C^8), -3.9 (C^6 or $C^{6'}$), −10.3 ($C^{6'}$ or C^6); $^{119}Sn\{^1H\}$ NMR (112 MHz, CD_2Cl_2, 188 K) δ 36.5 – 37.1 (m).

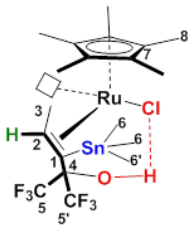
Gradual warming above −60 °C results in the conversion of **14** to $[Cp^*RuCl]_4$ and **15**, concomitant with a color change from purple to brown.

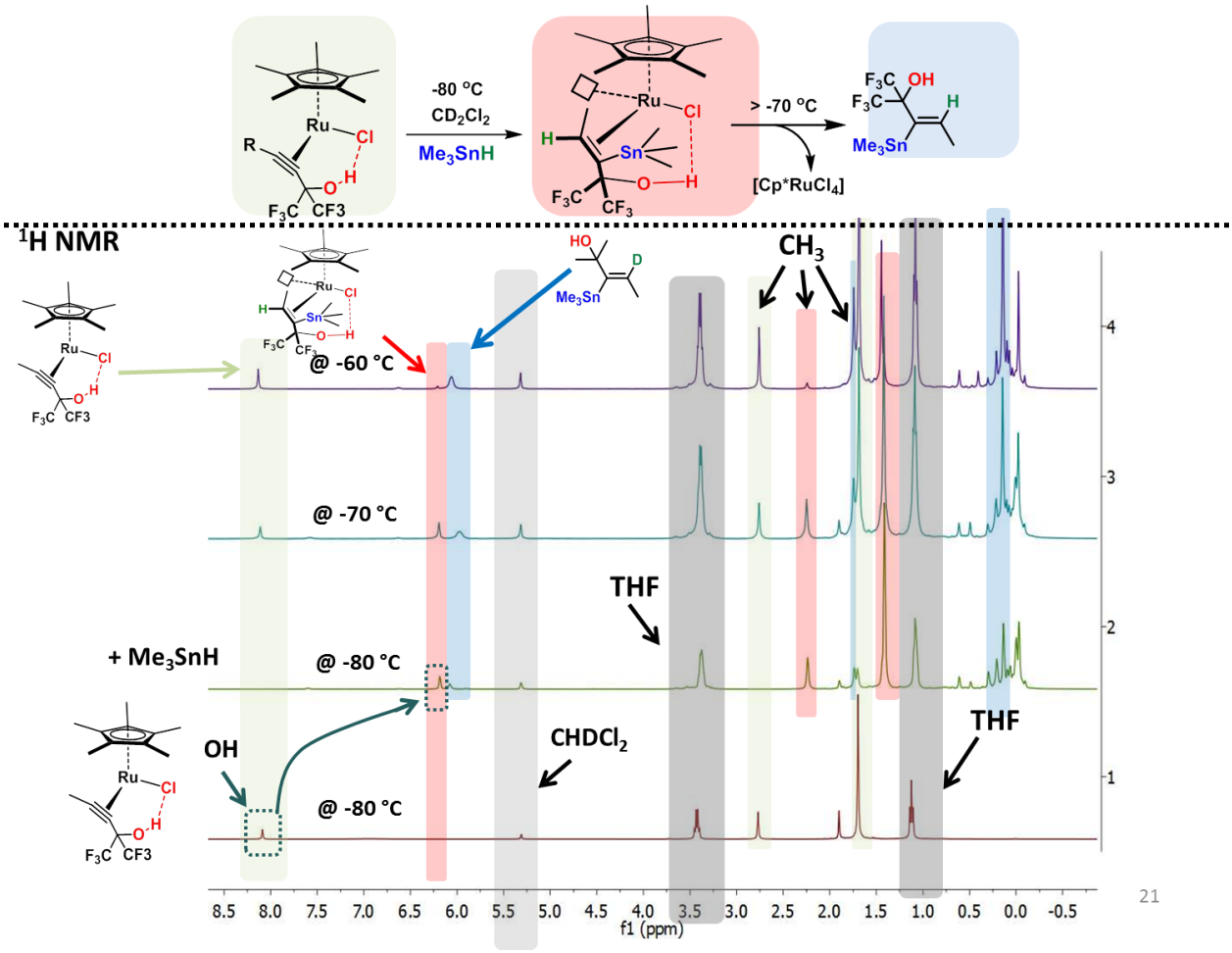
Compound 15. In addition to the protocol described above, **15** could also be prepared by mixing 1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol (50 µL, 0.1786 mmol) and $[Cp^*RuCl]_4$ (2.45 mg, 2.25 µmol) in CH_2Cl_2 (2 mL) followed by addition of Me_3SnH (29.8 µL, 0.198 mmol) over 5 minutes. The volatile components were removed *in vacuo* and the brown residue was passed through a silica plug (SiO_2, hexane/EtOAc 1/1). The solvent was removed *in vacuo* (40 °C, 200 mbar) to give **15** as a faint brown oil (54 mg, 81%). The compound is unstable on prolonged contact with silica. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.74 (dddt, *J* = 8.2, 6.9, 5.5, 1.4 Hz, $^3J_{SnH}$ = 124 Hz, 1H, C^2H), 1.87 (d, *J* = 6 Hz, 3H, C^3H), 0.27 (s, 9H, $SnMe_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 145.6 – 141.1 (m, C^1), 137.5 (C^2), 123.4 (q, $^1J_{CF}$ = 284 Hz, CF_3), 79.8 (q, $^2J_{CF}$ = 28 Hz, C^4), 19.8 ($^3J_{SnC}$ = 38.3 Hz, CH_3), -5.2 (s, $SnMe_3$, $^1J_{SnC}$ = 357 Hz). $^{119}Sn\{^1H\}$ NMR (112 MHz, CD_2Cl_2) δ -36.18 – -37.09 (m). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2) δ −75.63 (br s, $^4J_{SnF}$ = 8 Hz). IR (ṽ, film, cm^{-1}) 3596, 2970, 2919, 1717, 1662, 1377, 1250, 1210, 1109, 1045, 996, 844, 777, 715; ESI-MS calcd. for $C_9H_{13}NOF_6Sn$ [M-H^+] 370.98974; found 370.99006.

^{1}H, CD_2Cl_2, 188 K

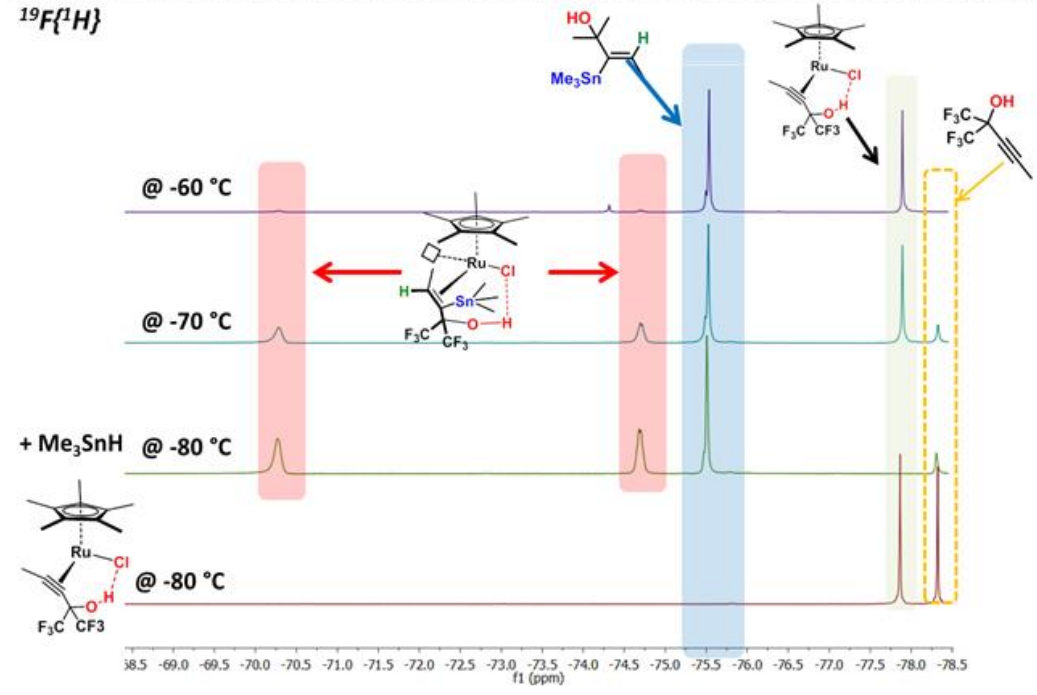


^{13}C{^{1}H} NMR, CD_2Cl_2, 188 K



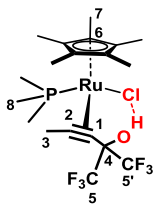

-80 °C
CD2Cl2
Me3SnH
> -70 °C
[Cp*RuCl4]
1H NMR
@ -60 °C
@ -70 °C
@ -80 °C
+ Me3SnH
@ -80 °C
CH3
THF
CHDCl2
THF
OH
f1 (ppm)

21


19F{1H}
@ -60 °C
@ -70 °C
+ Me3SnH
@ -80 °C
@ -80 °C
f1 (ppm)

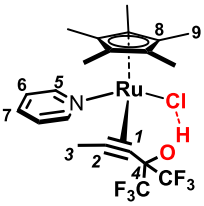
Emulation of the Loaded Catalyst.

Complex 16. A Schlenk flask was charged with $[Cp^*RuCl]_4$ (12.3 mg, 11.31 µmol) in CH_2Cl_2 (10 mL), and



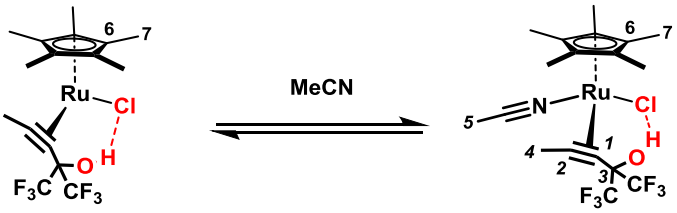
1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol (11 µL, 9.8 mg, 47.55 µmol) was added at room temperature, promoting a colour change from brown to cherry red. The mixture was cooled to −78 °C and a solution of PMe_3 (5 µL, 3.7 mg, 48.5 µmol) in CH_2Cl_2 (0.5 mL) was slowly added over 15 min. A colour change to light brown was noted. The solvent was removed *in vacuo*, giving the title compound as a brown powder (23 mg, 92%). Single crystals were obtained by dissolving compound **16** in pentane at RT and gradually cooling the resulting solution to −60 °C over one week. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 7.14 (s, 1H, OH), 2.17 (s, 3H, C^3), 1.48 (d, $^4J_{PH}$ = 1.7 Hz, 15H, C^7H), 1.13 (d, $^3J_{PH}$ = 9.5 Hz, 9H, C^8H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) δ 125.7 (apparent d, $^1J_{CF}$ = 286 Hz, C^5 and $C^{5'}$ overlapping), 96.6 (d, $^2J_{PC}$ = 3.2 Hz, C^6), 89.9 (d, $^2J_{PC}$ = 8.4 Hz, C^1), 78.5 (apparent t, $^2J_{CF}$ = 31 Hz, C^4), 71.9 (d, $^2J_{PC}$ = 6.7 Hz, C^2), 14.5 (d, $^2J_{PC}$ = 30.6 Hz, C^8), 10.1 (d, *J* = 4.6 Hz, C^3), 9.1 (s, C^7); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K) δ 11.11; $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) δ -76.15 (q, *J* = 10.1 Hz), −76.59 (q, *J* = 10.3 Hz).

Complex 17. $[Cp^*RuCl]_4$ (13.8 mg, 12.67 µmol) was dissolved in CD_2Cl_2 (2 mL) and 1,1,1-trifluoro-2(3-



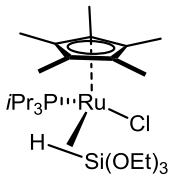
trifluoromethyl)pent-3yn-2-ol (14.2 mg, 50.7 µmol) was added to give a purple solution. The mixture was cooled to −78 °C and a solution of pyridine (4 µL, 3.9 mg, 49.45 mmol) in CD_2Cl_2 (2 mL) was added, promoting a colour change to brown. While keeping the mixture cold, an aliquot (0.6 mL) was transferred to an NMR tube pre-cooled to −60°C. NMR data analysis at −80 °C showed full conversion to **17**. Single crystals were obtained by solvent removal *in vacuo* at −50 °C, followed by dissolving the resulting brown powder in cold pentane (−20 °C) and gradually cooling the pentane solution from −20 °C to −60 °C over 3 days. ^{1}H NMR (400 MHz, CD_2Cl_2, 188 K) δ 8.15 (d, *J* = 6 Hz, 2H, C^5H), 7.83 (s, 1H, OH), 7.64 (t, *J* = 8 Hz, 1H, C^7H), 7.20 (pseudo t, 2H, C^6H), 2.27 (s, 3H, C^3H), 1.56 (s, 15H, C^9H). $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 185 K) δ −77.02 (br s, CF_3), −77.18 (br s, CF_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 185 K) δ 153.7 (C^5 or C^6), 136.4 (C^7), 124.5 (C^6 or C^5), 92.9 (C^8), 92.4 (C^1), C4 not observed, 80.2 (C^2), 9.9 (C^3), 9.2 (C^9).

Complex 18.



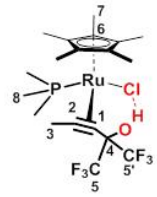
Prepared analogously to **17**, using $[Cp^*RuCl]_4$ (12 mg, 11.03 µmol) in CD_2Cl_2 (0.5 mL), 1,1,1-trifluoro-2(3-trifluoromethyl)pent-3yn-2-ol (12.35 mg, 44.11 µmol) and MeCN (2.5 µL, .2 mg, 47.86 µmol). The reaction was conducted directly in an NMR tube at −85 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 188 K) δ 7.72 (s, 1H, OH), 2.18 (br s, C^5), 1.90 (s, 1H, C^4), 1.45 (s, 15H, C^7); $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 185 K) δ −77.34 (br s), −77.69 (br s); The acquisition of $^{13}C\{^1H\}$ data was attempted but only broad resonances were obtained because of fast exchange between **18** and **5** even at −85 °C.

Cp*Ru(*i*Pr$_3$P)[σ-HSi(OEt)$_3$]Cl. [Cp*Ru(*i*Pr$_3$P)Cl][11] was generated in an NMR tube by mixing [Cp*RuCl]$_4$ **1** (10.5 mg, 9.15 µmol) with *i*Pr$_3$P (7.4 µL, 38.6 µmol) in CD_2Cl_2 (0.6 mL). $(EtO)_3SiH$ (7.1 µL, 38.6 µmol) was subsequently added, and the mixture was then cooled to −80 °C, promoting a colour change from deep blue to orange. The tube was placed in the probe of an NMR spectrometer pre-cooled to −80 °C. Full conversion to the title σ-complex was noted. ^{1}H NMR (400 MHz, CD_2Cl_2, 193 K) δ 3.73 (br q,6H, O<u>*CH*$_2$</u>CH_3), 2.98 (br s, 3H, *H*C$(CH_3)_2$), 1.56 (s, 15H, Me of Cp*), 1.29 – 0.93 (br m, 27H, OCH_2<u>*CH*$_3$</u> and $HC(CH_3)_2$, overlapping), -10.99 (d, $^2J_{PH}$ = 35.1 Hz, Ru σ-Si—H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 193 K) δ 97.4 (Cp*), 59.5 (O<u>*CH*$_2$</u>CH_3), 20.7 (d, J_{CP} = 16 Hz), 20.5 (d, J_{CP} = 13 Hz), 19.7 (br s), 18.2 (OCH_2<u>*CH*$_3$</u>), 10.2 (Me of Cp*); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 193 K) δ +52.89 (br s) (contains 10% free P^{i}Pr$_3$).

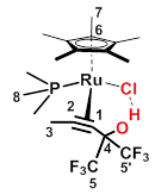


Formation of the σ-complex is reversible: upon warming of the sample to RT, full dissociation of $(EtO)_3SiH$ is observed.

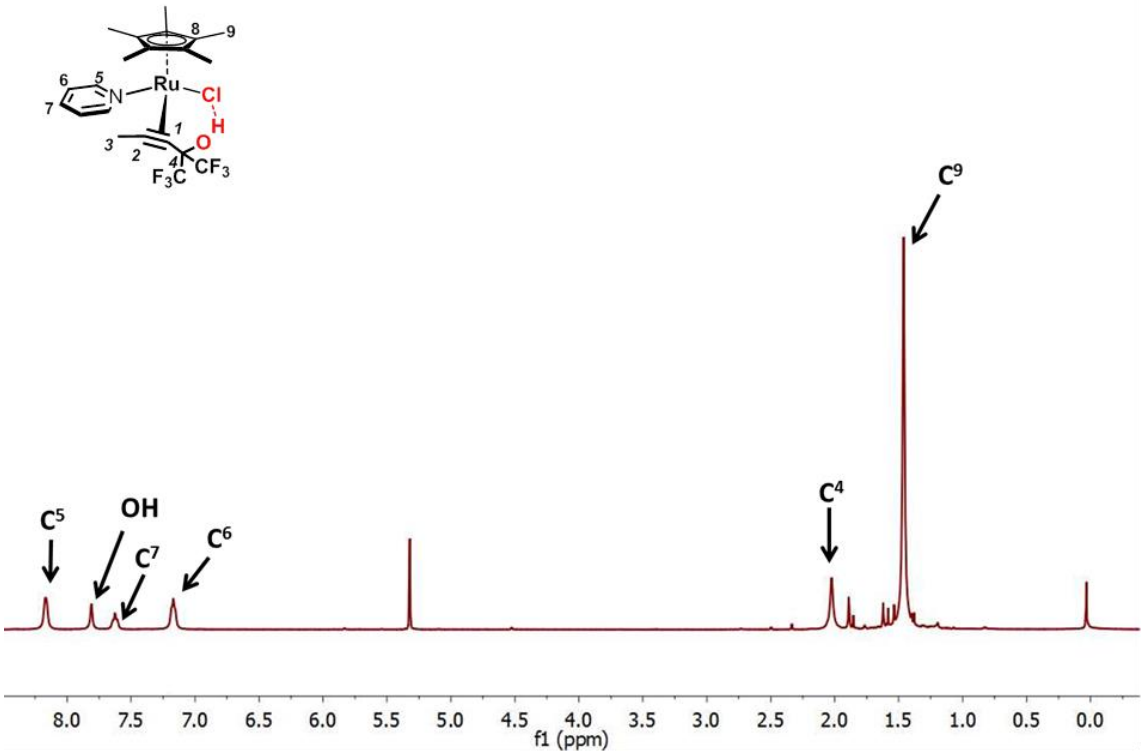
^{1}H, CD_2Cl_2, 298 K



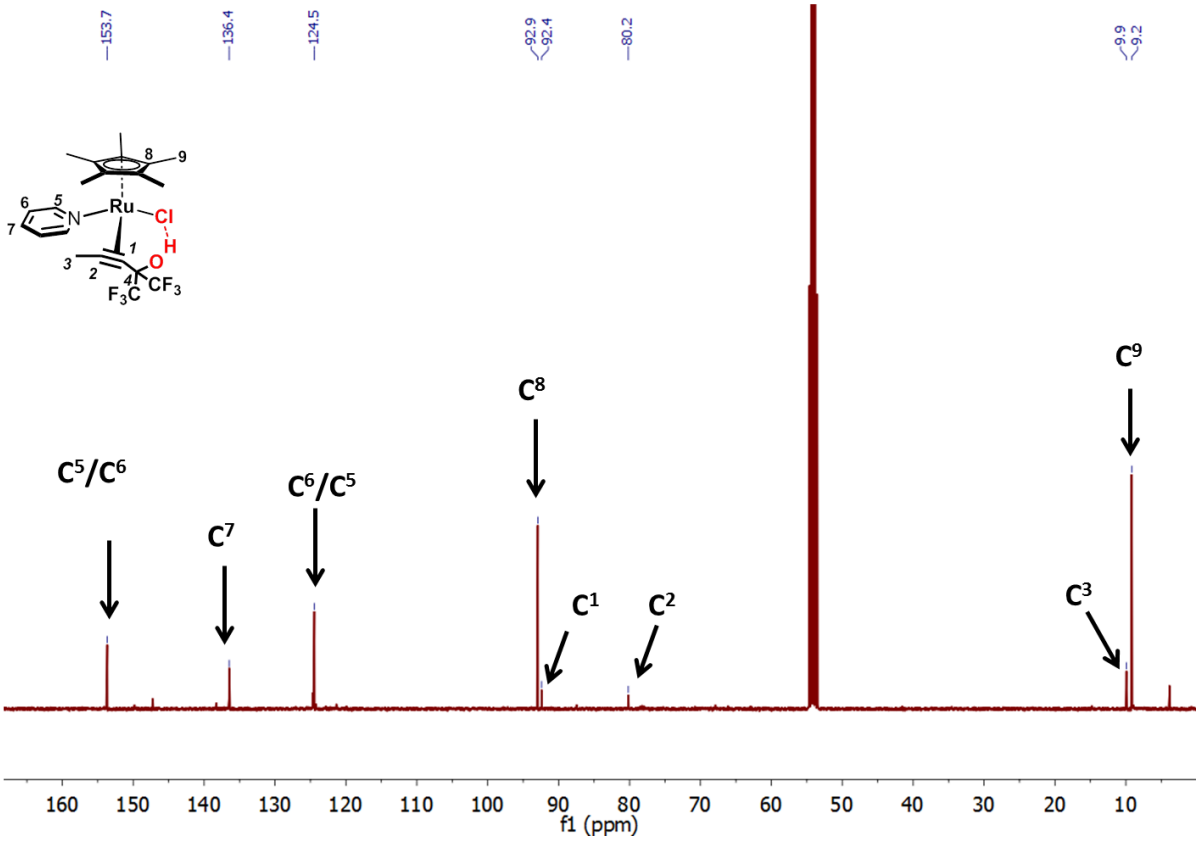
$^{13}C\{^{1}H\}$, CD_2Cl_2, 298 K

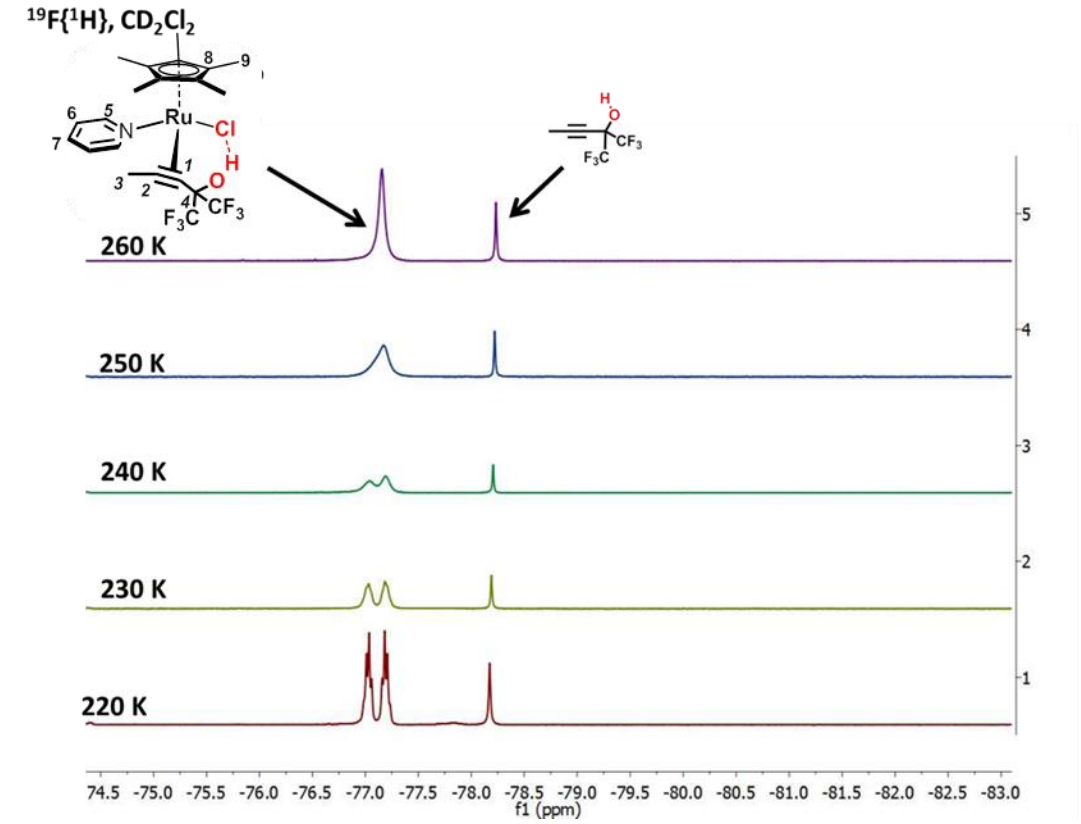


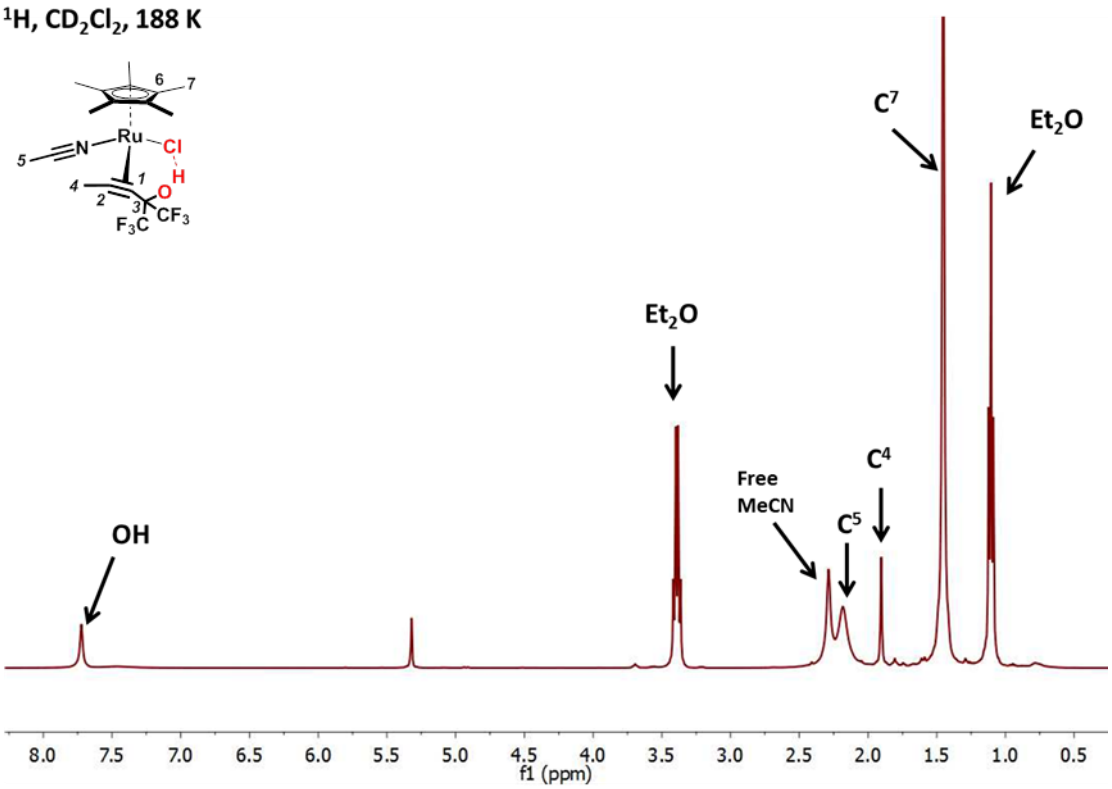
^{1}H, CD_2Cl_2, 188 K

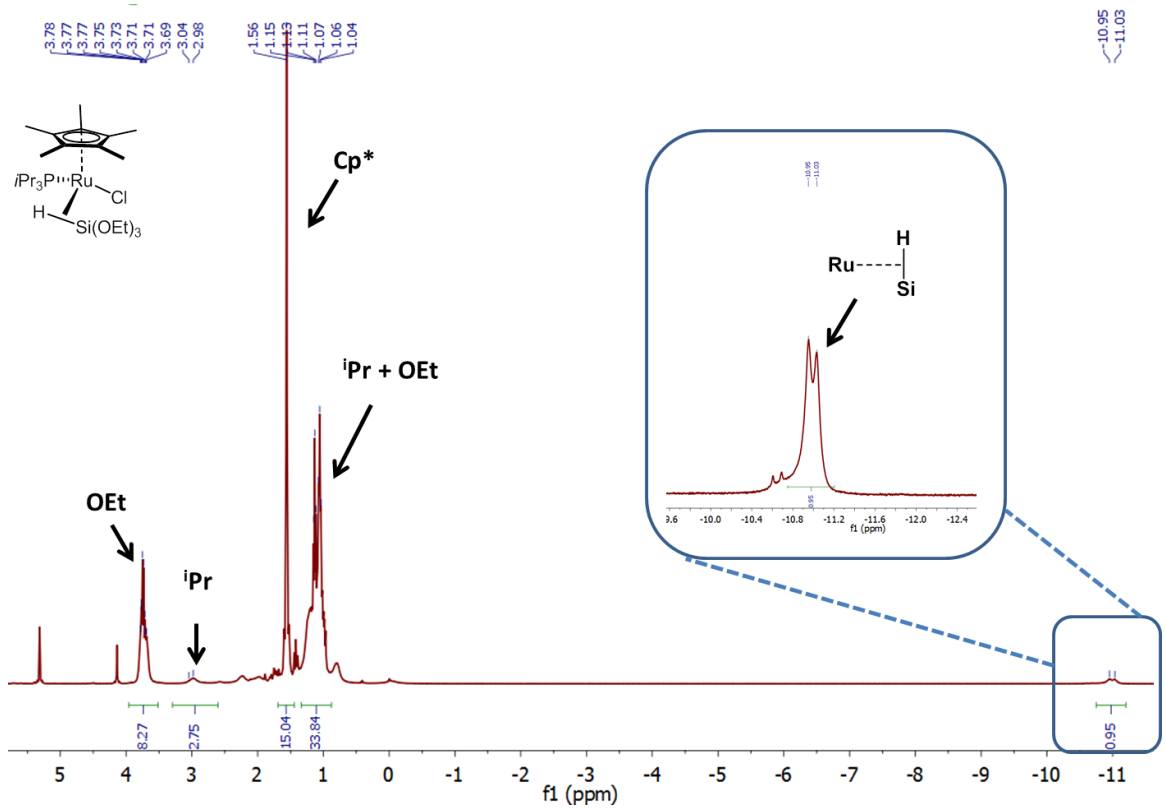


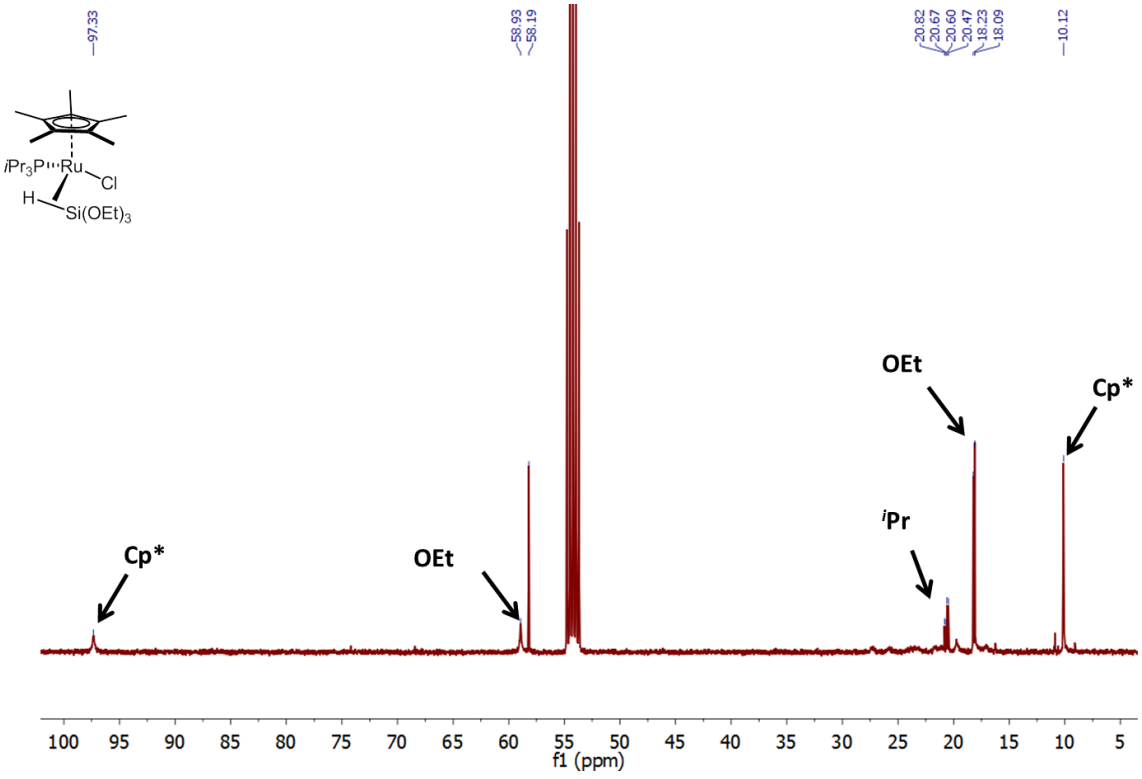
$^{13}C\{^1H\}$ NMR, CD_2Cl_2, 188 K



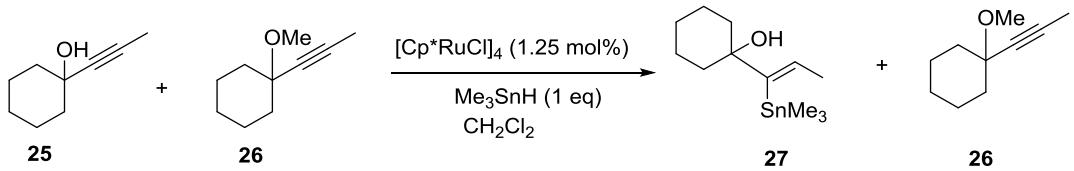

$^{19}F\{^1H\}$, CD_2Cl_2
260 K
250 K
240 K
230 K
220 K
74.5 -75.0 -75.5 -76.0 -76.5 -77.0 -77.5 -78.0 -78.5 -79.0 -79.5 -80.0 -80.5 -81.0 -81.5 -82.0 -82.5 -83.0
f1 (ppm)


^1H, CD_2Cl_2, 188 K
OH
Et_2O
Free MeCN
C^5
C^4
C^7
Et_2O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Cp*
iPr + OEt
OEt
iPr
Ru
H
Si
f1 (ppm)

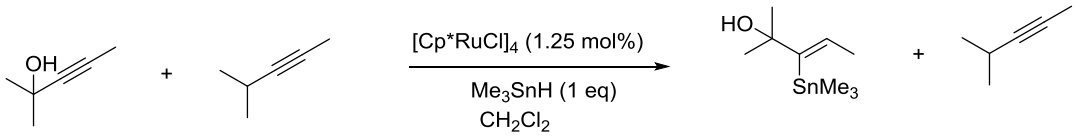

Cp*
OEt
OEt
Cp*
iPr
f1 (ppm)

Intermolecular Competition Experiments



25 **26** **27** **26**

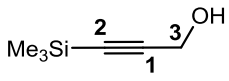
Compound 27. $[Cp^*RuCl]_4$ (1.6 mg, 6 µmol) was added was added to a solution of alkyne **25** (16.7 mg, 0.121 mmol) and alkyne **26**[12] (20 µL, 0.121 mmol) in CH_2Cl_2 (2 mL), resulting in formation of a purple colored solution. Me_3SnH (22.1 µL, 0.121 mmol) was then added dropwise over 5 min, causing a color change to pale brown. The mixture was stirred for 1 min before the volatile components were removed *in vacuo*. Analysis of the reaction mixture by ^1H and $^{119}Sn\{^1H\}$ NMR spectroscopy indicated an equimolar mixture of **27**[8] and **26**.



28 **29** **30** **29**

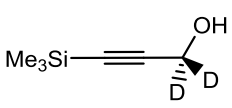
Compound 30. $[Cp^*RuCl]_4$ (2.45 mg, 2.25 µmol) was added to a solution of alkyne **28** (50 µL, 0.454 mmol) and alkyne **29** (52.4 µL, 0.454 mmol) in CH_2Cl_2 (4 mL), resulting in a purple colored solution. Me_3SnH (83.1 µL, 0.454 mmol) was then added dropwise over 5 min, promoting a color change to pale brown. The mixture was stirred for 1 min before the volatile components were removed *in vacuo* (200 mbar, 40 °C). Analysis of the reaction mixture by ^1H and $^{119}Sn\{^1H\}$ NMR spectroscopy indicated an equimolar mixture of **30** and **29**. Purification by flash chromatography (SiO_2, Hexane/EtOAc 9/1) afforded **30** as a colourless oil (108 mg, 90 %). ^1H NMR (400 MHz,CD_2Cl_2) δ 6.02 (q, J = 6.7 Hz, $^3J_{SnH}$ = 145 Hz, 1H, C^1H), 1.59 (d, J = 6.7 Hz, 3H, C^3H), 1.14 (s, 6H, C^5H), 0.07 (s, 9H, $^3J_{SnH}$ = 52 Hz, $SnMe_3$);.$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 155.0 (C^1), 130.3 (C^2), 75.4 (C^4), 30.6 (C^5), 18.7 (C^3), −6.1 ($SnMe_3$); $^{119}Sn\{^1H\}$ NMR (112 MHz, CD_2Cl_2) δ −56.4; IR (ṽ, film, cm^{-1}) 3442, 2972, 2915, 1620, 1446, 1361, 1313, 1121, 954, 902, 836, 71; EI-MS *m/z* (%) 246 (3.5), 231(29.6), 165(41.2), 82 (50.1), 67 (100).

Binding and Reactivity of a TMS-Capped Propargyl Alcohol

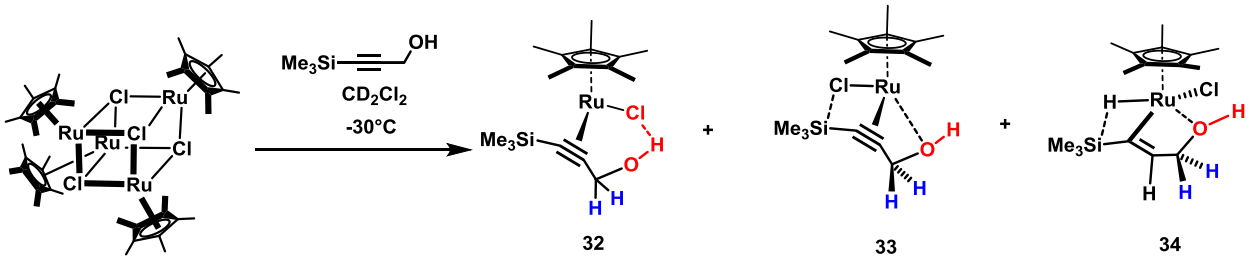


Compound 31. ^1H NMR (400 MHz, CD_2Cl_2, 253 K) δ 4.21 (br s, 2H, C^3H) 2.92 (s, 1H, OH), 0.12 (s, 9H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) δ 103.9 (C^1), 89.7 (C^2), 51.1 (C^3), -0.62 ($SiMe_3$); $^{29}Si\{^1H\}$ NMR (79 MHz, CD_2Cl_2, 253 K) δ −17.5 (s).

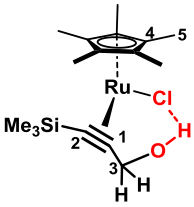
Compound [D_2]-31. *n*BuLi (7.28 mL, 1.6 M in hexanes, 11.65 mmol) was added to a solution of ethynyltrimethylsilane (1.64 mL, 11.65 mmol) in THF (20 mL) at −78°C and the resulting mixture was stirred at this temperature for 1 h. Subsequently, paraformaldehyde-d_2 (350 mg, 11.65 mmol) was added and stirring was continued at −78°C for 1 h before the mixture was allowed to warm to room temperature. After an additional 30 min, the mixture was quenched with water (20 mL) and the aqueous layer was extracted with pentane (2



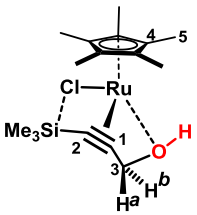
x 10 mL). The combined organic phases were evaporated to give [D_2]-**31** as a colorless viscous liquid (1.13 g, 75%). ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K) δ 2.92 (s, 1H, OH), 0.12 (s, 9H, $SiMe_3$).



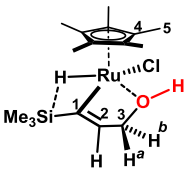
Complexes 32-34. Alkyne **31** (6.6 µL, 44.5 µmol) was added to an NMR tube containing $[Cp^*RuCl]_4$ (12 mg, 11.03 µmol) in CD_2Cl_2 (0.5 mL) at −20 °C. The solution was briefly warmed to 25°C for 1 min, affording a color change from brown to purple. The tube was then inserted into the probe of an NMR spectrometer pre-cooled to −30°C. All spectra were recorded at this temperature, showing a 75 % conversion of $[Cp^*RuCl]_4$ with the formation of **32**, **33** and **34** in a ratio of 5.5: 3.5: 1. The experiments involving [D_2]-**31** were carried out analogously. Characteristic data of the resulting complexes:



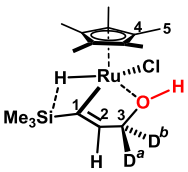
Compound **32**: ^{1}H NMR (400 MHz, CD_2Cl_2, 243K) δ 5.11 (br d, *J* = 6 Hz, 2H, C^3H), 2.49 (1H, OH), 1.64 (s, 15H, C^5H), 0.14 (s, 9H, $SiMe_3$); $^{13}C\{^1H\}$ NMR δ 152.1 (C^1), 143 (C^2), 88.0 (C^4), 60.2 (C^3), 10.6 (C^5), 0.13 ($SiMe_3$) $^{29}Si\{^1H\}$ NMR (79 MHz, CD_2Cl_2, 243K) −7.7 (s).



Compound **33**:^{1}H NMR (400 MHz, CD_2Cl_2, 243K) δ 5.06 (dd, *J* = 12Hz, 2Hz, 1H, C^3H^a/ C^3H^b), 4.45, (t, *J* = 12 Hz, 1H, C^3H^b/C^3H^a), 3.29 (dd, J= 12Hz, 2Hz, 1H, OH), 1.61 (s, 15H, C^5H), 0.24 (s, 9H, $SiMe_3$) $^{13}C\{^1H\}$ NMR δ 114.6 (C^1), 92.5 (C^2), 89.6 (C^4), 62.9 (C^3), 11.4 (C^5), 4.98 ($SiMe_3$); $^{29}Si\{^1H\}$ NMR (79 MHz, CD_2Cl_2, 243K) δ +1.2 (s).

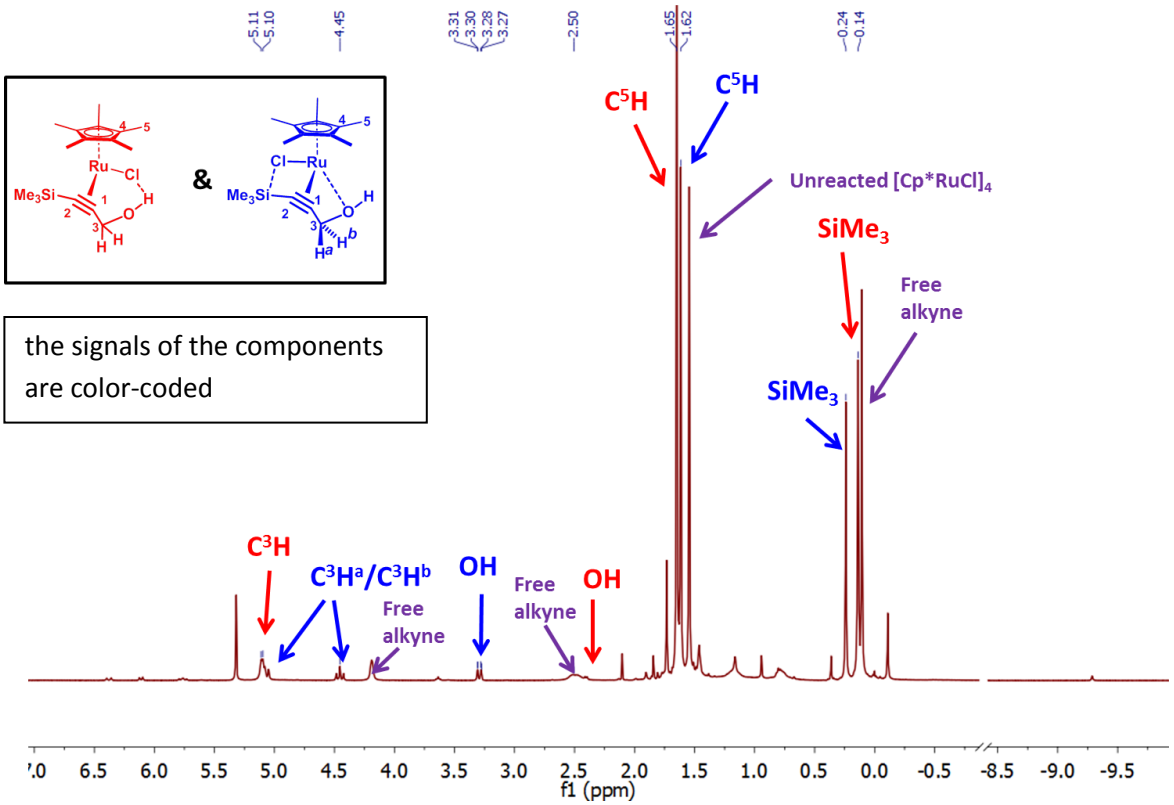


Compound **34**:^{1}H NMR (400 MHz, CD_2Cl_2, 243K) δ 6.38 (d, J_{HH}= 15 Hz, 1H, C^3H^a/C^3H^b), 6.11 (d, J_{HH} = 10 Hz, 1H, C^2H), 5.76 (dd, J_{HH}= 12 Hz, 1Hz, C^3H^b/C^3H^a), 3.62 (br t, J_{HH} = 6Hz, 1H, OH), 1.73 (s, 15H, C^5H), -0.11(s, 9H, $SiMe_3$), −9.28 (s, 1H, RuH) $^{13}C\{^1H\}$ NMR δ 172.1 (C^2), C^1 not observed, 93.4 (C^4), 69.0 (C^3), 10.2(C^5), 2.8 ($SiMe_3$); $^{29}Si\{^1H\}$ NMR (79 MHz, CD_2Cl_2, 243K) +7.6 (s).

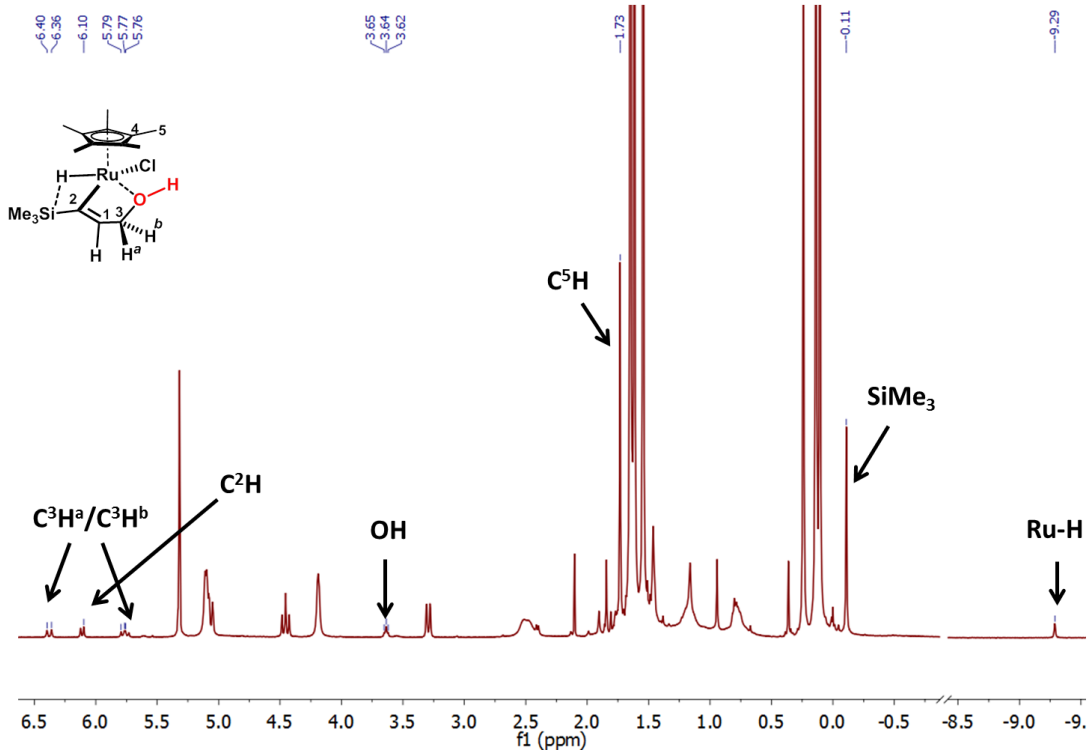


Compound **34-*d*$_2$** ^{1}H NMR (400 MHz, CD_2Cl_2, 243K) δ 6.11 (br s, 1H, C^2H), 3.62 (br t, J_{HH} = 6Hz, 1H, OH), 1.73 (s,15H, C^5H), −0.11 (s, 9H, $SiMe_3$), −9.28 (s, 1H, RuH) ^{2}H NMR(CH_2Cl_2, 243 K) 6.38 (br s, D^a/D^b), 5.78 (br s, D^b/D^a).

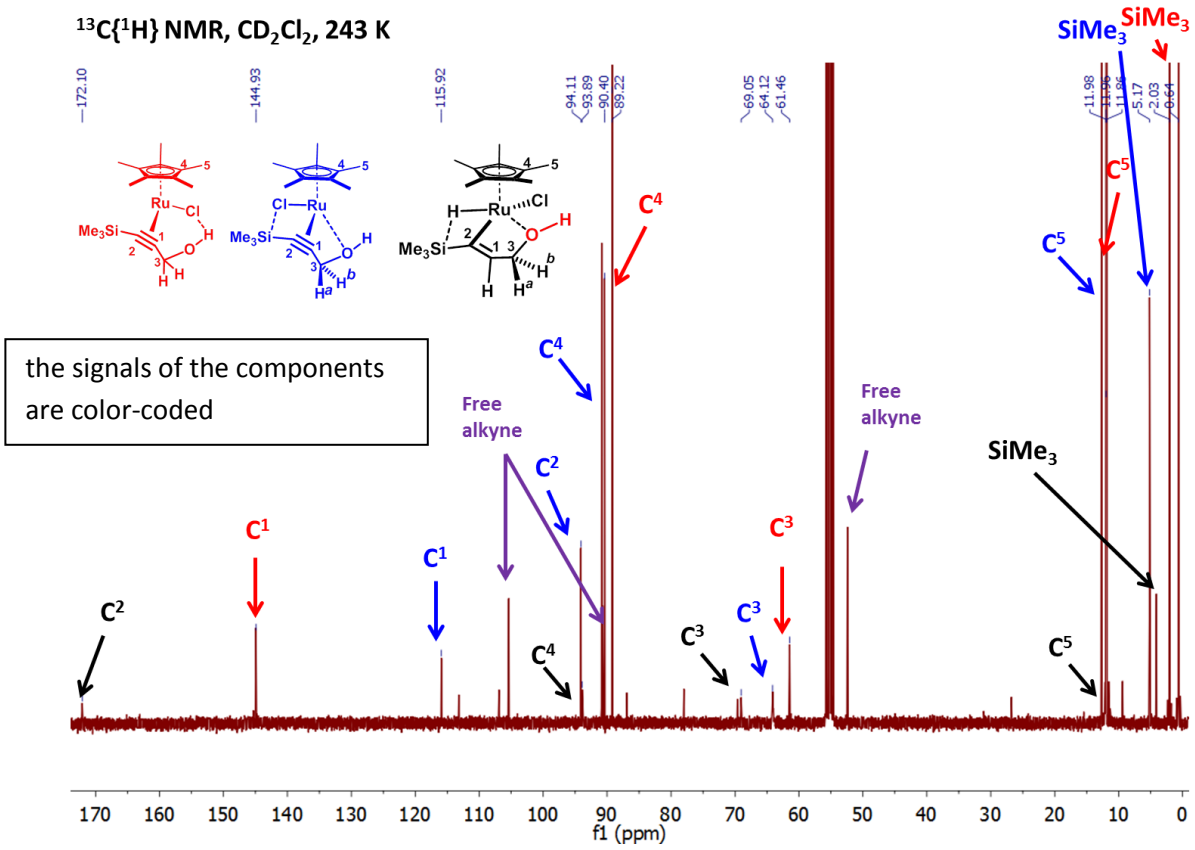
^{1}H NMR, CD_2Cl_2, 243 K



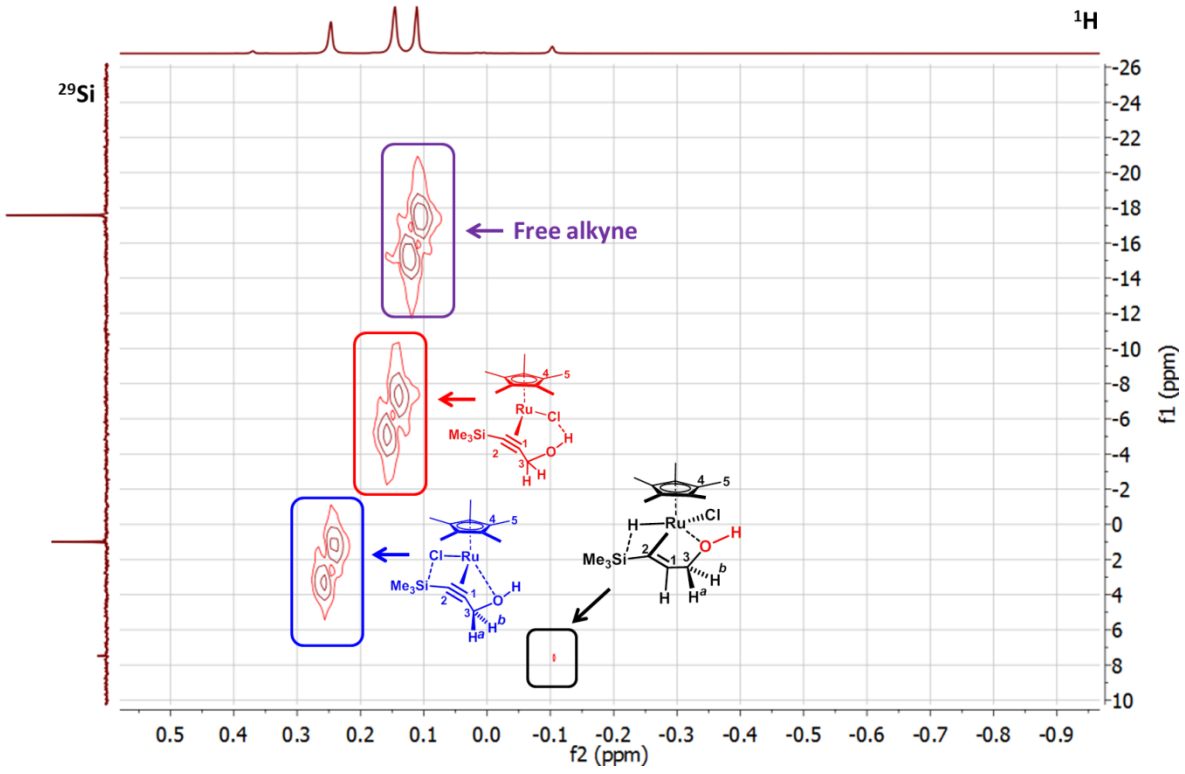
^{1}H NMR, CD_2Cl_2, 243 K - expansion



$^{13}C\{^1H\}$ NMR, CD_2Cl_2, 243 K



^{29}Si – ^1H HMBC, CD_2Cl_2, 243 K



Preparation of Substrates Used in Catalytic Hydrometallation Reactions

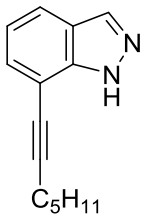
7-Methylocta-3,5-diyn-2-ol. aq. $BuNH_2$ (30 % in water, 10 mL) and CuCl (60 mg, 0.6 mmol, 10 mol%) were added to a two-neck flask and the resulting mixture was cooled to 0 °C. 3-Methylbut-1-yne (408 mg, 6.0 mmol) was introduced, followed by a few crystals of $NH_2OH{\cdot}HCl$ until the yellow color persisted. The solution was then allowed to warm to ambient temperature before 4-bromobut-3-yn-2-ol (900 mg, 6.0 mmol) was added over 5 min. During the course of the reaction, several portions of $NH_2OH{\cdot}HCl$ were added to maintain the yellow/green colour of the mixture. The mixture was stirred for 30 min before being transferred into a separating funnel and extracted with Et_2O (3 x 10 mL). The combined extracts were washed with sat. aq. $CuSO_4$ (10 mL) and sat. aq. NaCl (10 mL) before being dried over $MgSO_4$. The volatile components were removed *in vacuo* and the crude material was purified by flash chromatography (SiO_2, pentane/Et_2O 10:1) to give the title compound (81%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (qd, *J* = 6.6, 0.9 Hz, 1H), 2.63 (pD, *J* = 6.9, 0.9 Hz, 1H), 1.90 (br s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 87.0, 77.9, 69.1, 63.6, 58.8, 24.1, 22.4, 21.1.; IR (film, cm^{-1}) 2975, 2935, 1719, 1366, 1317, 1233, 1155, 1104, 1076, 1019. ESI-MS calcd. for $C_9H_{12}O$ [M-H$^+$] 136.08886, found 136.08882.

Nona-1,7-diyne K_2CO_3 (1.88 g, 13.6 mmol) was added to a solution of trimethyl(nona-1,7-diyn-1-yl)silane (1.3 g, 6.76 mmol) in MeOH (30 mL) and the resulting suspension was stirred at ambient temperature for 16 h. The mixture was then filtered through a frit and the filtrate was evaporated *in vacuo* (40 °C, 200 mbar). The resulting paste was dissolved in MTBE (40 mL) and the resulting ether layer was washed with water (2 x 20 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4. Evaporation of the volatile components *in vacuo* afforded nona-1,7-diyne (580 mg, 71%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09— 1.94 (m, 4H, C^{6}H and C^{3}H), 1.79(t, *J* = 2.5 Hz, 1H, C^{1}H), 1.62 (t, *J* = 2.54 Hz, 3H, C^{10}H), 1.51 – 1.39 (m, 4H, C^{5}H and C^{4}H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) 84.2 (C^2), 78.7 (C^7), 75.7 (C^8), 72.8 (C^1), 27.9 (C^5 or C^4), 27.5 (C^4 or C^5), 18.2 (C^6 or C^3), 18.0 (C^3 or C^6), 3.4 (C^{10}); IR (ṽ, film, cm^{-1}) 3307, 2936, 2860, 1440, 1434, 1248, 1077, 910, 840, 750, 630.

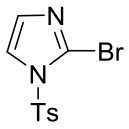
Compound S1. *n*BuLi (3.6 mL, 1.6 M in hexanes, 5.76 mmol, 1.2 eq) was added to a solution of nona-1,7-diyne (580 mg, 4.82 mmol) in THF (20 mL) at −78°C. The mixture was stirred at this temperature for 2 h before acetone (0.43 mL, 5.76 mmol) was added. Stirring was continued at −78°C for 1 h and at RT for 1 h, during which the colour of the mixture turned orange-red. Water (20 mL) was added and the mixture was extracted with pentane (3 x 40 mL). The combined organic phases were washed with water (10 mL) and dried over Na_2SO_4. Evaporation of the volatile components *in vacuo* afforded a yellow oil which was purified by flash chromatography (SiO_2, hexane/EtOAc 7/3) to give **31** as a faint yellow oil (400 mg, 46%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.22 – 2.10 (m, 4H, C^{8}H and C^{3}H), 1.88 (br s, 1H, OH), 1.76 (t, ^4J = 2.6 Hz, 3H, C^{11}H), 1.62 – 1.51 (m, 4H, C^{7}H and C^{6}H), 1.45 (s, 6H, C^{5}H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 83.2 (C^1), 79.7 (C^2), 76.4 (C^9), 73.3 (C^{10}), 62.8 (C^4), 29.4 (C^5), 26.0 (C^6), 25.6 (C^7), 16.0 (C^8), 15.8 (C^3), 0.90 (C^{11}); IR (ṽ, film, cm^{-1}) 3337, 2978, 2932, 2863, 1671, 1433, 1363, 1259, 1293, 944, 796; ESI-MS calcd. for $C_{12}H_{18}ONa$ [M+Na$^+$] 201.12498, found 201.12506.

Compound S2. A pressure Schlenk flask loaded with 7-bromo-1*H*-indazole (330 mg, 1.6749 mmol), copper(I) iodide (18 mg, 0.0945 mmol), DMF (3.3 mL) and triethylamine (1.2 mL, 8.61 mmol) was

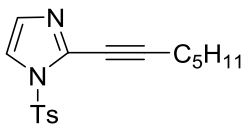
subjected to three freeze-pump-thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (109 mg, 0.0943 mmol) and heptyne (800 mg, 8.319 mmol, 5 equiv.) were added under argon. After stirring at 70 °C for 18 h (GC-MS control), the mixture was filtered through a short pad of silica which was rised with ethyl acetate. Evaporation of the combined filtrates in high vacuum at 45 °C followed by purification of the residue by flash chromatography (hexanes/ethyl acetate 10/1, 1% Et_3N) afforded 7-(hept-1-yn-1-yl)-1H-indazole as a pale brown oil (333 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (br s, 1H), 8.11 (s, 1H), 7.69 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.11 (dd, *J* = 8.1, 7.3 Hz, 1H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.66 (m, 2H), 1.46 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.8, 135.5, 129.7, 122.8, 121.0, 120.5, 106.4, 96.0, 75.7, 31.2, 28.4, 22.2, 19.6, 14.0; IR (ṽ, film, cm^{-1}) 3148, 3070, 2929, 2859, 2229, 1609, 1592, 1508, 1465, 1435, 1335, 1285, 1210, 1081, 1044, 950, 841, 784, 739, 659, 608; ESI-MS calcd. for $C_{14}H_{17}N_2$ [M+H$^+$] 213.13862; found 213.13868.



Compound S3. Triethylamine (0.1 mL, 0.72 mmol), 4-methylbenzenesulfonyl chloride (135 mg, 0.7081 mmol) and N.N-dimethylpyridin-4-amine (7.5 mg, 0.06139 mmol) were successively added to a stirred solution of 2-bromo-1*H*-imidazol (89 mg, 0.6056 mmol) in MeCN (2.4 mL) under argon. The mixture was stirred for 16 h; once the reaction was complete (TLC control), water (10 mL) and ethyl acetate (5 mL) were added. The aqueous phase was extracted twice, the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue purified by passing through a short pad of silica (hexanes → hexanes/ethyl acetate 5/1, 1% Et_3N) to give 2-bromo-1-tosyl-1*H*-imidazole as a pale yellow solid (170 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.61 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8, 133.7, 130.22, 130.18, 128.4, 122.3, 116.9, 21.8; IR (ṽ, film, cm^{-1}) 3157, 3122, 1595, 1519, 1493, 1431, 1382, 1328, 1251, 1193, 1176, 1159, 1121, 1083, 1023, 1015, 897, 813, 745, 702, 670, 652; ESI-MS calcd. for $C_{10}H_9BrN_2O_2SNa$ [M+Na$^+$] 322.94604; found 322.94640.



Compound S4. A pressure Schlenk flask loaded with 2-bromo-1-tosyl-1H-imidazole (495 mg, 1.6437 mmol), copper(I) iodide (16 mg, 0.0840 mmol), DMF (3.3 mL) and triethylamine (1.2 mL, 8.61 mmol) was subjected to three freeze-pump-thaw cycles. Next, tetrakis(triphenylphosphine)palladium(0) (96 mg, 0.0831 mmol) and heptyne (800 mg, 8.319 mmol, 5 equiv.) were added under argon. After stirring at 50°C for 15 h (GC-MS control), the mixture was filtered through a short pad of silica that was carefully washed with ethyl acetate. Evaporation of the combined filtrates in high vacuum at 45°C followed by purification of the residue by flash chromatography (hexanes/ethyl acetate 5/1, 1% Et_3N) afforded 2-(hept-1-yn-1-yl)-1-tosyl-1*H*-imidazole as a yellow orange solid (370 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 1.7 Hz, 1H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.64 (m, 2H), 1.44 (m, 2H), 1.36 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.2, 134.6, 131.2, 130.0, 129.3, 128.0, 119.1, 97.0, 69.8, 31.0, 27.6, 22.2, 21.7, 19.5, 13.9; IR (ṽ, film, cm^{-1}) 3147, 3114, 2952, 2929, 2869, 2848, 2232, 1595, 1518, 1493, 1464, 1421, 1401, 1373, 1366, 1309, 1285, 1215, 1193, 1162, 1114, 1086, 1057, 1020, 1002, 981, 969, 905, 809, 766, 726, 697, 668, 632, 610; ESI-MS calcd. for $C_{17}H_{20}N_2O_2SNa$ [M+Na$^+$] 339.11377; found 339.11395.



Compound S5. Potassium hydroxide (810 mg, 14.436 mmol) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1-tosyl-1*H*-imidazole (287 mg, 0.9070 mmol) in THF (9 mL)/CH_3OH (9 mL). After stirring for 2 h (TLC control), H_2O (10 mL) was added, followed by evaporation of all volatile components. An extractive work up with ethyl acetate followed by flash chromatographic purification of the crude product (hexanes/ethyl acetate 3:1 → 1:1, 1% Et_3N) afforded 2-(hept-1-yn-1-yl)-1*H*-imidazole as a colorless solid (110 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (br s, 1H), 7.05 (s, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.56 (m, 2H), 1.33 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 130.9, 123 (br), 91.3, 71.1, 31.0, 27.9, 22.2, 19.1, 13.9; IR (ṽ, film, cm^{-1}) 2951, 2927, 2863, 2724, 2634, 2503, 2238, 1832, 1572, 1465, 1454, 1420, 1392, 1375, 1341, 1298, 1231, 1124, 1108, 1018, 996, 941, 913, 752, 730, 711; ESI-MS calcd. for $C_{10}H_{14}N_2Na$ [M+Na$^+$] 185.10492; found 185.10494.

Compound S6. Triethylamine (0.5 mL, 3.587 mmol), 4-methylbenzenesulfonyl chloride (665 mg, 3.4881 mmol) and N,N-dimethylaminopyridine (18 mg, 0.1473 mmol) were successively added to a stirred solution of 6-bromopyridin-2(1*H*)-one (547 mg, 3.1438 mmol) in MeCN (12.6 mL) under argon. After stirring for 2 h, water (20 mL) and ethyl acetate (10 mL) were added. The water phase was extracted with ethyl acetate, the combined organic phases were dried over Na_2SO_4 and evaporated to give 6-bromo-1-tosylpyridin-2(1*H*)-one as an off-white solid that was used without further purification (975 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.37 (m, 3H), 7.08 (dd, *J* = 8.0, 0.5 Hz, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.9, 145.7, 141.7, 139.1, 133.2, 129.6, 129.1, 126.6, 113.9, 21.7; IR (ṽ, film, cm^{-1}) 3084, 3059, 1595, 1574, 1556, 1418, 1372, 1305, 1293, 1264, 1217, 1186, 1175, 1159, 1121, 1088, 1017, 988, 976, 911, 889, 878, 840, 809, 746, 734, 666, 638; ESI-MS calcd. for $C_{12}H_{10}Br_1N_1O_3SNa$ [M+Na$^+$] 349.94571; found 349.94587.

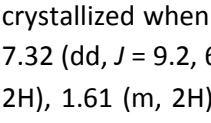
Compound S7. A pressure Schlenk flask loaded with 6-bromo-1-tosylpyridin-2(1*H*)-one (942 mg, 2.8703 mmol), copper(I)-iodide (28 mg, 0.1470 mmol) in DMF (5.7 mL), and triethylamine (2.0 mL, 14.349 mmol) was subjected to three freeze-pump-thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (170 mg, 0.1471 mmol) and heptyne (1380 mg, 14.350 mmol, 5 equiv.) were then added and the mixture stirred at 50 °C for 15 h (GC/MS control). For work up, the suspension was filtered through a short pad of silica which was washed with ethyl acetate. Evaporation of the combined filtrates in high vacuum at 45°C followed by flash chromatographic purification of the residue (hexanes/ethyl acetate 10/1, 1% Et_3N) afforded 6-(hept-1-yn-1-yl)-1-tosylpyridin-2(1*H*)-one as a yellow oil (697 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.60 (m, 2H), 1.39 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 145.3, 142.5, 139.9, 133.5, 129.5, 128.9, 125.6, 114.4, 92.6, 79.2, 31.0, 27.9, 22.2, 21.7, 19.2, 13.9; IR (ṽ, film, cm^{-1}) 2931, 2860, 2232, 1588, 1558, 1443, 1410, 1373, 1291, 1253, 1206, 1171, 1092, 1045, 1019, 990, 934, 905, 868, 810, 759, 732, 701, 666; ESI-MS calcd. for $C_{19}H_{21}NO_3SNa$ [M+Na$^+$] 366.11344; found 366.11366.

Compound S8. Potassium hydroxide (246 mg, 4.384 mmol) was added to a stirred solution of 6-(hept-1-yn-1-yl)-1-tosylpyridin-2(1*H*)-one (150 mg, 0.43675 mmol) in THF (3 mL)/CH_3OH (3 mL). The mixture was stirred for 30 min before

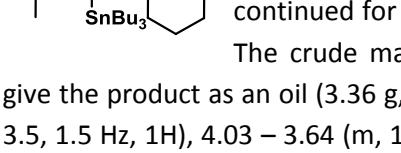
H_2O (4 mL) was added. An extractive work up followed by flash chromatography (hexanes/ethyl acetate 10:1 → ethyl acetate, 1% Et_3N) afforded 6-(hept-1-yn-1-yl)pyridin-2(1*H*)-one as a yellow oil, which crystallized when kept in the freezer at –20° (61 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.16 (br s, 1H), 7.32 (dd, *J* = 9.2, 6.9 Hz, 1H), 6.53 (dd, *J* = 9.2, 0.9 Hz, 1H), 6.31 (dd, *J* = 6.9, 0.9 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.61 (m, 2H), 1.37 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.6, 140.7, 130.0, 120.4, 110.7, 96.7, 74.0, 31.0, 27.7, 22.2, 19.4, 13.9; IR (ṽ, film, cm^{-1}) 3033, 2930, 2859, 2789, 2230, 1787, 1639, 1597, 1544, 1455, 1398, 1371, 1328, 1303, 1235, 1155, 1107, 1072, 980, 928, 859, 796, 720, 676, 648; ESI-MS calcd. for $C_{12}H_{16}NO$ [M+H$^+$] 190.12264; found 190.12259.

Directed *trans*-Hydrometalation

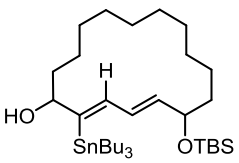
Compound S9. $[Cp^*RuCl_2]_n$ (27.3 mg, 0.094 mmol) was added to a solution of 1-(cyclohex-1-en-1-yl)-4-methylpent-1-yn-3-ol (1.77 g, 9.944 mmol)[13] in CH_2Cl_2 (50 mL), followed by dropwise addition of Bu_3SnH (2.8 mL, 10.43 mmol) over 1 h via syringe pump. Stirring was continued for another 5 min before the volatile components were removed *in vacuo*. The crude material was purified by flash chromatography (SiO_2, hexane/EtOAc) to give the product as an oil (3.36 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (h, *J* = 1.1 Hz, 1H), 5.58 (dh, J = 3.5, 1.5 Hz, 1H), 4.03 – 3.64 (m, 1H), 2.18 – 1.86 (m, 4H), 1.68 – 1.53 (m, 6H), 1.53 – 1.36 (m, 7H), 1.36 – 1.25 (m, 6H), 0.99 – 0.78 (m, 20H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.4, 143.3, 139.3, 123.8, 85.3, 33.6, 29.4, 28.9, 27.7, 25.6, 22.7, 22.2, 20.2, 17.7, 13.9, 12.0. ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ -51.6; IR (ṽ, film, cm^{-1}) 3449, 2955, 2924, 2871, 1597, 1459, 1364, 1266, 1236, 1201, 1137, 1076, 1021, 960, 924, 848, 802, 724, 665; ESI-MS calcuId. for $C_{24}H_{45}OSn$ [M-H+]: 469.24972, found 469.24941.



Compound S10. A solution of Bu_3SnH (2.19 µL, 8.1 µmol) in CH_2Cl_2 (160 µL) was added dropwise over 60 min via syringe pump to a solution of the corresponding alkyne (3 mg, 6.8 µmol) and $[Cp^*RuCl]_4$ (0.68 mg, 0.7 µmol) in CH_2Cl_2 (34 µL). All volatiles were evaporated and the residue was purified by flash chromatography (hexane/EtOAc 2/1) to afford the title stannane as a pale yellow oil (3.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 4H), 6.82 – 6.74 (m, 1H), 6.70 (d, *J* = 10.4 Hz, J_{SnH} = 112 Hz, 1H), 5.93 (dddd, *J* = 13.2, 10.5, 3.1, 1.2 Hz, 1H), 5.65 (ddd, *J* = 15.0, 7.1, 3.2 Hz, 1H), 4.48 (dd, *J* = 5.7, 2.1 Hz, 1H), 4.37 – 4.27 (m, 1H), 3.73 (s, 3H), 3.22 (s, 3H), 2.61 – 2.20 (m, 3H), 1.85 (s,*3*H), 1.52 – 1.41 (m, 3H), 1.39 – 1.22 (m, 8H), 1.02—0.94 (m, 7 H), 0.88 (d, *J* = 0.6 Hz, 18H), 0.00 (s, 3H), -0.21 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.9, 139.0, 138.6, 137.7, 127.0, 126.3, 126.0, 78.3, 77.8, 76.5, 51.09, 48.8, 36.7, 28.4, 26.6, 26.4, 25.1, 13.9, 13.0, 12.1, 10.5, -5.35, -5.73. ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ –51.88; IR (ṽ, film, cm^{-1}) 3513, 2927, 2954, 2855, 1716, 1648, 1436, 1462, 1361, 1387, 1255, 1196, 1064, 1081, 1026, 964, 836, 862, 775, 748, 700, 672, 542; ESI-MS calcd. for $C_{38}H_{66}O_4SiSnNa$ [M+Na$^+$] 757.36439, found: 757.36438.

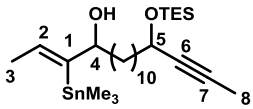


Compound S11. A solution of Bu_3SnH (9.30 µL, 34.6 µmol) in CH_2Cl_2 (0.15 mL) was added dropwise over 90 min via syringe pump to a solution of the substrate enyne (12.0 mg, 32.9 µmol) and $[Cp^*RuCl]_4$ (1.79 mg, 6.58 µmol, 20 mol%) in CH_2Cl_2 (0.2 mL). All volatile materials were evaporated and the residue was purified by flash chromatography (hexanes/*t*-butyl methyl ether 19:1) to afford title stannane as a pale yellow oil



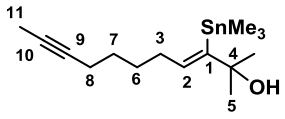
(17.9 mg, 83%, *syn*/*anti*-mixture of diol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 10.9 Hz, J_{SnH} = 119 Hz, 1H), 6.68 (d, *J* = 10.7 Hz, J_{SnH} = 117 Hz, 1H), 6.29 (ddd, *J* = 14.7, 10.9, 1.7 Hz, 1H), 6.08 (dd, *J* = 14.9, 10.7 Hz, 1H), 5.68 (dd, *J* = 14.7, 4.3 Hz, 1H), 5.59 (dd, *J* = 14.9, 8.4 Hz, 1H), 4.40 (dt, *J* = 4.9, 2.4 Hz, 1H), 4.31–4.20 (m, 2H), 4.07 (td, *J* = 9.0, 3.7 Hz, 1H), 1.78–1.57 (m, 5H), 1.56–1.42 (m, 18H), 1.38–1.28 (m, 20H), 1.27–1.10 (m, 32H), 1.04–0.98 (m, 10H), 0.92 (s, 9H), 0.90–0.89 (m, 9H), 0.88 (s, 9H), 0.06 (s, 9H), 0.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 151.2, 140.2, 140.0, 139.4, 139.3, 130.7, 128.8, 81.0, 80.4, 74.9, 71.8, 37.5, 36.9, 36.8, 36.6, 29.40, , 29.39, 29.0, 28.9, 28.5, 28.2, 28.0, 27.9, 27.74, 27.72, 27.70, 27.6, 27.5, 26.2, 26.1 (3C), 24.2, 23.8, 23.5, 21.8, 18.5, 18.4, 13.8, 11.5, 11.2, –4.1, –4.4, –4.6, –4.8. ^{119}Sn{^{1}H} NMR (150 MHz, $CDCl_3$): δ = –55.1, –56.2; IR (ṽ, film, cm^{-1}) 3373, 2926, 2854, 1461, 1253, 1070, 967, 835, 775, 667; ESI-MS calcd for $C_{34}H_{68}O_2SiSnNa$ [M+Na^{+}] 679.3902, found: 679.3903.

Compound S12. [Cp*RuCl]$_4$ (1.14 mg, 1.05 µmol) was added to a solution of the the diyne substrate



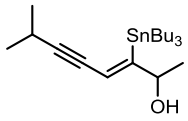
(16.5 mg, 0.042 mmol)[14] in CH_2Cl_2 (2 mL), giving a purple solution. Subsequently, a solution of Me_3SnH (7.7 µL, 0.042 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 10 min, during which the color changed to light brown. After the addition was complete, the volatile components were removed *in vacuo*, and the residue was purified by flash chromatography (hexane/EtOAc 9/1) to give the title compound as a pale yellow oil (21 mg, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.21 (dd, *J* = 6.6, 1.0 Hz, 1H, C^{2}H), 4.34 (ddt, *J* = 6.5, 4.3, 2.1 Hz, 1H, C^{4}H), 4.12 (q, *J* = 3.8 Hz, 1H, C^{5}H), 1.84 (d, *J* = 2.1 Hz, 3H, C^{8}H), 1.78 (d, *J* = 6.5 Hz, 3H, C^{3}H), 1.69 – 1.50 (m 4H, CH_2), 1.31 (br s, 16H), 1.00 (t, *J* = 7.0 Hz, 9H, CH_3 of TES), 0.67 (qd, *J* = 7.7, 1.7 Hz, 6H, CH_2 of TES), 0.25 (s, 9H, $SnMe_3$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 147.5 (C^{1}), 132.2 (C^{2}), 78.8 (C^{6}), 77.3 (C^{4}), 60.6 (C^{7}), 36.9 (CH_2), 35.5 (CH_2), 31.9 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 23.7 (CH_2), 23.0 (CH_2), 20.1 (CH_2), 16.4 (C^{3}), 4.3 (TES), 2.5 (TES), 0.9 (C^{8}), -9.8; ^{119}Sn{^{1}H} NMR (112 MHz, CD_2Cl_2) δ -53.86; IR (ṽ, film, cm^{-1}) 3469, 2854 2876, 1623, 1459, 1414, 1341, 1239, 1261, 1187, 1080, 1006, 770, 524; ESI-MS calcd. for $C_{27}H_{54}O_2SnNa$ (M+Na^{+}) 581.28066; found 581.28045.

Compound S13. [Cp*RuCl]$_4$ (5.3 mg, 4.75 µmol) was added to a solution of the starting diyne (35 mg,



0.196 mmol) in CH_2Cl_2 (4 mL) was added at room temperature, and the mixture was stirred for 1 minute, causing a color change from brown to purple. The mixture was then quickly cooled to −30 °C and a solution of Me_3SnH (36 µL, 0.196 mmol) in CH_2Cl_2 (2 mL) was added over 2 h. The volatile components were removed *in vacuo*. Purification of the residue by flash chromatography (SiO_2, hexane/EtOAc 9/1) afforded the title compound as a colorless oil (58 mg, 86 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.06 (t, ^{3}J = 7.2 Hz, 1H, C^{1}H), 2.17 – 2.00 (m, 4H), 1.74 (t, *J* = 2.6 Hz, 3H, C^{11}H), 1.48 (s, 1H, OH), 1.47 – 1.39 (m, 4H), 1.28 (s, 6H, C^{5}H), 0.19 (s, 9H, $SnMe_3$); ^{13}C{^{1}H} NMR (101 MHz, CH_2Cl_2) δ 151.7 (C^{1}), 134.0 (C^{2}, $^{3}J_{SnC}$ = 26 Hz), 76.7 (C^{9}),73.1 (C^{4} + C^{10}), 30.8 (C^{3}), 28.4 (C^{5}), 27.2 (C^{6}), 26.6 (C^{7}), 16.4 (C^{8}), 0.9 (C^{11}), −8.2 ($SnMe_3$, $^{1}J_{SnC}$ = 334 Hz); ^{119}Sn{^{1}H} NMR (112 MHz, CD_2Cl_2) δ −57.2 (s); IR (ṽ, film, cm^{-1}) 3440, 2970, 2920, 2857, 1618, 1458, 1360, 1123, 917, 713. ESI-MS calcd. for $C_{15}H_{28}OSnNa$ [M+Na^{+}] 367.10536; found 367.10568.

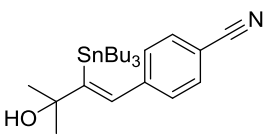
Compound S14. In a Schlenk flask, a solution of [Cp*RuCl]$_4$ (3.0 mg, 0.01 mmol) in CH_2Cl_2 (1 mL) was



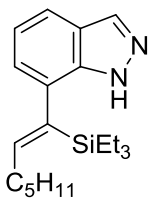
treated with 7-methylocta-3,5-diyn-2-ol (27.1 mg, 0.2 mmol) and the resulting mixture was stirred for 5 min. A solution of Bu_3SnH (62 µL, 0.23 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 1 h. Once the complete addition, the mixture was stirred for 10 min before the solvent was removed *in vacuo*. Purification of the residue by flash

chromatography (SiO_2, hexane/EtOAc 200/1) afforded the title compound as a colorless oil (62.8 mg, 74 %). ^{1}H NMR (400 MHz, CDCl3) δ 6.26 (dd, *J* = 2.1, 1.3 Hz, J_{SnH} = 111.8 Hz, 1H), 4.41 (qdd, *J* = 6.3, 3.5, 1.2 Hz, 1H), 2.68 (pd, *J* = 6.9, 2.1 Hz, 1H), 1.58 – 1.48 (m, 6H), 1.38 – 1.27 (m, 6H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 6H), 1.09 – 1.03 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). 13C{1H} NMR (101 MHz, $CDCl_3$) δ 164.5, 118.1, 97.3, 78.8, 74.9, 29.3, 27.6, 23.9, 22.9, 21.3, 13.9, 12.4, 10.7.; ^{119}Sn{^{1}H} δ -49.4; IR (ṽ, film, cm^{-1}) 2956, 2924, 2871, 2854, 1463; ESI-MS calcd. for $C_{21}H_{40}OSnNa$ [M+Na$^+$] 451.19948, found 451.19926.

Compound S15. $[Cp^*RuCl_2]_n$ (21.7 mg, 0.07 mmol) was added to a solution of 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzonitrile (1.31 g, 7.07 mmol)[15] in CH_2Cl_2 (35 mL), followed by dropwise addition of Bu_3SnH (2 mL, 7.42 mmol) over 1 h via syringe pump. Stirring was continued for 5 min before the volatile components were removed *in vacuo*. The crude material was purified by flash chromatography (SiO_2, hexane/EtOAc) to give the product as a pale brown oil (2.63 g, 78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.29 (s, 1H), 7.27 – 7.23 (m, 2H), 1.61 (s, 1H), 1.41 (s, 6H), 1.39 – 1.26 (m, 6H), 1.26 – 1.15 (m, 6H), 0.83 (t, J = 7.2 Hz, 9H), 0.79 – 0.55 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.5, 146.0, 135.4, 131.9, 129.0, 119.1, 110.4, 76.2, 31.1, 29.2, 27.5, 13.8, 12.9; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ -53.0; IR (ṽ, film, cm^{-1}) 3507, 2955, 2921, 2871, 2228, 1602, 1500, 1462, 1362, 1201, 1142, 1073, 1020, 959, 931, 876, 849, 823, 797, 724, 667, 594. ESI-MS calcd. for $C_{24}H_{39}NOSnNa$ [M+Na$^+$]: 500.19451, found 500.19430.



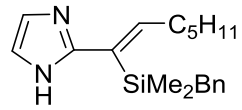
Compound S16. $[Cp^*RuCl_2]_n$ (24.6 mg, 0.08 mmol) was added to a solution of 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzaldehyde (1.51 g, 8.04 mmol)[15] in CH_2Cl_2 (40 mL), followed by dropwise addition of Bu_3SnH (2.27 mL, 8. 44 mmol) over 1 h via syringe pump. Stirring was continued for 5 min before the volatile components were removed *in vacuo*. The crude material was purified by flash chromatography (SiO_2, hexane/EtOAc) to give the product as a brownish oil (3.04 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.84 – 7.75 (m, 2H), 7.40 – 7.29 (m, 3H), 1.57 (d, J = 0.8 Hz, 1H), 1.43 (s, 6H), 1.40 – 1.25 (m, 6H), 1.25 – 1.12 (m, 6H), 0.82 (t, J = 7.2 Hz, 9H), 0.78 – 0.57 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.0, 162.9, 147.7, 136.0, 135.0, 129.7, 129.0, 76.2, 31.2, 29.2, 27.5, 13.8, 12.9; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ -52.8 ppm. IR (ṽ, film, cm^{-1}) 2955, 2921, 2871, 2853, 1700, 1600, 1565, 1462, 1418, 1139, 1074, 1048, 1018, 959, 932, 877, 723, 652, 628; ESI-MS calcd. for $C_{24}H_{39}O_2Sn$ [M-H$^+$]: 479.19769, found 479.19782.



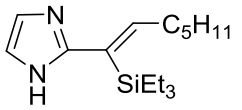
Compound S17. A solution of 7-(hept-1-yn-1-yl)-1*H*-indazole (20.0 mg, 0.0942 mmol) and tris(pentafluorophenyl)borane (49 mg, 0.0957 mmol) in CH_2Cl_2 (0.5 mL, 0.2 M) was stirred for 5 min before $[Cp^*RuCl]_4$ (1.8 mg, 0.001656 mmol) and triethylsilane (15 mg, 0.1290 mmol, 1.4 equiv.) were added. The mixture was stirred for 40 h, during which time additonal triethylsilane (2 x 1.4 equiv.) and $[Cp^*RuCl]_4$ (2 x 1.3 mol%) had to be added to ensure complete conversion. 1.4-Diazabicyclo[2.2.2]octan (106 mg, 0.945 mmol, 10 equiv.) was added and stirring was continued at 45°C for 24 h (NMR control). The solid was filtered off and washed with DCM, the combined filtrates were evaporated and the residue was purified by passing it through a short pad of silica using hexanes/ethyl acetate 5:1 as the eluent to give (Z)-7-(1-(triethylsilyl)hept-1-en-1-yl)-1*H*-indazole as a pale brown oil (20 mg, 65 %, α : β 99 : 1, Z/E 89:11 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, $CDCl_3$) for the major diastereoisomer δ 9.82 (br s, 1H), 8.06 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.10 (dd, *J* = 8.1, 7.0 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.38 (t, *J* =

7.5 Hz, 1H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.90 (m, 12H), 0.62 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for the major diastereoisomer δ 149.9, 139.1, 135.9, 135.3, 129.4, 124.9, 122.9, 121.0, 117.7, 32.5, 31.7, 29.5, 22.6, 14.0, 7.6, 4.6; IR (ṽ, film, cm^{-1}) 3259, 3065, 2953, 2924, 2873, 1605, 1509, 1459, 1425, 1377, 1327, 1238, 1210, 1076, 1004, 940, 873, 839, 789, 764, 746, 718, 695, 603; ESI-MS calcd. for $C_{20}H_{33}N_2Si$ $[M+H^+]$ 329.24075; found 329.24029.

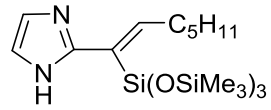
Compound S18. Benzyldimethylsilane (22 mg, 0.1464 mmol, 1.2 equiv.) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1*H*-imidazol (20 mg, 0.1233 mmol) and $[Cp^*RuCl]_4$ (1.7 mg, 0.001564 mmol) in CH_2Cl_2 (0.65 mL) at ambient temperature. Once the reaction was complete (15 min), the solvent was evaporated and the residue was purified by passing it through a pad of silica using hexanes/ethyl acetate 3:1, 1% Et_3N, as the eluent. (Z)-2-(1-(Benzyldimethylsilyl)hept-1-en-1-yl)-1H-imidazole was obtained as a colorless solid (34 mg, 88 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.22 (m, 2H), 7.10 (m, 1H), 6.99 (m, 3H), 6.73 (br s, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 2.36 (s, 2H), 2.23 (q, *J* = 7.5 Hz, 2H), 1.42 (m, 2H), 1.32 (m, 4H), 0.90 (m, 3H), 0.20 (s, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.2, 150.7, 140.0, 129.9, 128.3, 128.2, 128 (br), 124.2, 115 (br), 32.2, 31.6, 29.1, 26.4, 22.5, 14.0, -1.2; IR (ṽ, film, cm^{-1}) 2950, 2919, 2867, 2849, 2623, 2528, 1596, 1551, 1493, 1465, 1451, 1420, 1376, 1247, 1210, 1159, 1102, 1058, 1003, 958, 910, 894, 873, 833, 820, 795, 768, 747, 729, 715, 699, 675, 641; ESI-MS calcd. for $C_{19}H_{29}N_2Si$ $[M+H^+]$ 313.20945; found 313.20938.



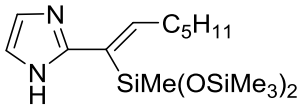
Compound S19. Triethylsilane (18 mg, 0.1548 mmol, 1.5 equiv.) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1*H*-imidazol (17 mg, 0.1048 mmol) and $[Cp^*RuCl]_4$ (1.6 mg, 0.001472 mmol) in CH_2Cl_2 (0.5 mL). Once the reaction was complete (7 h), the solvent was evaporated and the residue was purified by passing it through a pad of silica using hexanes/ethyl acetate 2:1, 1% Et_3N, as the eluent to give (Z)-2-(1-(triethylsilyl)hept-1-en-1-yl)-1*H*-imidazole as an oil (27 mg, 93 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (br s, 1H), 6.94 (s, 2H), 6.57 (t, *J* = 7.5 Hz, 1H), 2.25 (q, *J* = 7.5 Hz, 2H), 1.42 (m, 2H), 1.32 (m, 4H), 0.90 (m, 12H), 0.76 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.2, 151.1, 129.6, 121 (br), 32.1, 31.6, 29.3, 22.6, 14.0, 7.5, 4.6; IR data (ṽ, film, cm^{-1}) 2953, 2928, 2873, 1601, 1545, 1460, 1416, 1377, 1238, 1096, 1003, 891, 722, 699; ESI-MS calcd. for $C_{16}H_{31}N_2Si$ $[M+H^+]$ 279.22510, found 279.22525.



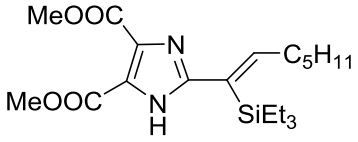
Compound S20. Tris(trimethylsiloxy)silane (47 mg, 0.1548 mmol, 1.4 equiv.) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1*H*-imidazol (18 mg, 0.1110 mmol) and $[Cp^*RuCl]_4$ (2.0 mg, 0.00184 mmol) in CH_2Cl_2 (0.55 mL). Once the reaction was complete (overnight), the solvent was evaporated and the residue was purified by passing it through a pad of silica using hexanes/ethyl acetate 10:1, 1% Et_3N, as the eluent to give the title compound as a pale grey solid (40 mg, 79 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (br s, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.93 (s, 1H), 2.41 (q, *J* = 7.6 Hz, 2H), 1.49 (m, 2H), 1.34 (m, 4H), 0.89 (m, 3H), 0.14 (s, 27H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.9, 149.1, 128.7 (br), 123.4, 114.4 (br), 32.2, 31.7, 29.1, 22.7, 14.0, 1.8; IR (ṽ, film, cm^{-1}) 3026, 2956, 2925, 2899, 2858, 2805, 2746, 1609, 1556, 1430, 1250, 1112, 1099, 1047, 833, 752, 735, 685, 655, 618; ESI-MS calcd. for $C_{19}H_{43}N_2O_3Si_4$ $[M+H^+]$ 459.23453; found 459.23466.



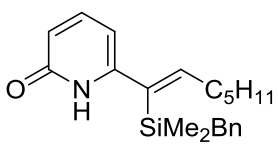
Compound S21. 1,1,1,3,5,5,5-Heptamethyl-trisiloxane (36 mg, 0.1618 mmol, 1.2 equiv.) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1*H*-imidazol (22 mg, 0.1356 mmol) and $[Cp^*RuCl]_4$ (1.6 mg, 0.001472 mmol) in CH_2Cl_2 (0.7 mL). Once the reaction was complete (30 min), the solvent was evaporated. The residue was purified by passing it through a pad of silica using hexanes/ethyl acetate 5:1, 1% Et_3N, as the eluent to give the title compound as a pale brown oil (44 mg, 84 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (br s, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 6.92 (s, 1H), 2.36 (q, *J* = 7.7 Hz, 2H), 1.49 (m, 2H), 1.34 (m, 4H), 0.89 (m, 3H), 0.31 (s, 3H), 0.15 (s, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.9, 149.3, 128.6 (br), 126.3, 114.5 (br), 32.2, 31.7, 29.2, 22.6, 14.0, 2.7, 1.9; IR data (ṽ, film, cm^{-1}) 3111, 3035, 2957, 2926, 2873, 2858, 2734, 1604, 1537, 1459, 1421, 1378, 1252, 1044, 840, 785, 755, 740, 688; ESI-MS calcd. for $C_{17}H_{37}N_2O_2Si_3$ $[M+H^+]$ 385.21574, found 385.21600.



Compound S22. Triethylsilane (12 mg, 0.1032 mmol, 1.4 equiv.) was added to a stirred solution of dimethyl 2-(hept-1-yn-1-yl)-1H-imidazole-4.5-dicarboxylate (21 mg, 0.075455 mmol) and $[Cp^*RuCl]_4$ (1.7 mg, 0.001564 mmol) in CH_2Cl_2 (0.4 mL). Once the reaction was complete (30 min), the solvent was evaporated and the residue purified by filtration through a short pad of silica using hexanes/ethyl acetate 2:1, 1% Et_3N, as the eluent to give the title compound as a dark yellow oil (23 mg, 77 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^1H NMR (400 MHz, $CDCl_3$) δ 9.39 (br s, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 6H), 2.29 (q, *J* = 7.5 Hz, 2H), 1.45 (m, 2H), 1.32 (m, 4H), 0.92 (m, 12H), 0.76 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.8, 159.7, 154.9, 152.8, 136.1, 127.8, 122.7, 52.5, 52.3, 32.4, 31.6, 29.0, 22.5, 13.9, 7.4, 4.5; IR (ṽ, film, cm^{-1}) 3261, 2953, 2931, 2874, 1740, 1712, 1602, 1562, 1504, 1440, 1393, 1314, 1271, 1236, 1203, 1166, 1080, 1003, 976, 816, 797, 771, 726; ESI-MS calcd. for $C_{20}H_{35}N_2O_4Si$ $[M+H^+]$ 395.23606; found 395.23581.



Compound S23. Benzyldimethylsilane (23 mg, 0.1530 mmol, 1.6 equiv.) was added to a stirred solution of 2-(hept-1-yn-1-yl)-1-tosyl-1*H*-imidazol (30 mg, 0.0948 mmol) and $[Cp^*RuCl]_4$ (1.25 mg, 0.001150 mmol,) in CH_2Cl_2 (0. 5 mL). After stirring the mixture for 46 h and adding 1.8 equiv. of benzyldimethylsilane in portions, the solvent was evaporated and the residue was purified by passing it through a short pad of silica using hexanes/ethyl acetate 10:1, 1% Et_3N, as the eluent to give the title compound as a colorless oil (20 mg, 45 %, α : β 2 : 98, Z/E > 99:1 for the major isomer (by NMR)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.30 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.16-7.10 (m, 3H), 7.03 (d, *J* = 1.6 Hz, 1H), 7.04-6.99 (m, 1H), 6.90-6.87 (m, 2H), 2.43 (s, 3H), 2.23-2.16 (m, 2H), 2.09 (s, 2H), 1.40-1.26 (m, 6H), 0.91 (t; *J* = 7 Hz, 3H), -0.27 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.5, 146.5, 145.9, 140.4, 135.1, 129.9, 128.4, 128.3, 127.9, 127.8, 126.8, 123.8, 119.3, 39.1, 31.7, 29.3, 25.7, 22.5, 21.6, 14.0, -2.7; IR (ṽ, film, cm^{-1}) 3155, 3118, 3080, 3059, 3024, 2955, 2927, 2857, 1597, 1526, 1493, 1452, 1373, 1307, 1293, 1246, 1191, 1178, 1151, 1088, 1039, 906, 812, 793, 761, 740, 699, 669; ESI-MS calcd. for $C_{26}H_{35}N_2O_2SSi$ $[M+H^+]$ 467.21830; found 467.21874.



Compound S24. Benzyldimethylsilane (18 mg, 0.1198 mmol, 1.3 equiv.) was added to a stirred solution of 6-(hept-1-yn-1-yl) pyridin-2(1*H*)-one (17.5 mg, 0.092465 mmol) and $[Cp^*RuCl]_4$ (1.2 mg, 0.001104 mmol) in CH_2Cl_2 (0.45 mL). Once the reaction was complete (10 min), the solvent was evaporated and the

residue passed through through a short pad of silica using hexanes → hexanes/ethyl acetate 5:1, 1% Et_3N, as the eluent to give the title compound as a colorless oil (26 mg, 83 %, α : β 99 : 1, Z/E > 99:1 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.18 (br s, 1H), 7.24 (dd, *J* = 9.2, 6.9 Hz, 1H), 7.24-7.18 (m, 2H), 7.09 (m, 1H), 7.01 (m, 2H), 6.39 (t, *J* = 7.5 Hz, 1H), 6.21 (dd, *J* = 9.2, 1 Hz, 1H), 5.60 (dd, *J* = 6.9, 1.0 Hz, 1H), 2.30 (s, 2H), 2.23 (q, *J* = 7.5 Hz, 2H), 1.45 (m, 2H), 1.33 (m, 4H), 0.91 (t, *J* = 7 Hz, 3H), 0.13 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 164.7, 152.9, 152.5, 141.6, 139.8, 135.3, 128.7, 128.6, 124.7, 116.6, 104.5, 33.0, 32.0, 29.3, 26.3, 23.0, 14.2, -1.8; IR (ṽ, film, cm^{-1}) 3080, 3059, 3024, 2955, 2925, 2857, 2785, 1643, 1595, 1547, 1493, 1452, 1396, 1366, 1249, 1205, 1155, 1057, 1011, 966, 905, 832, 816, 796, 761, 731, 697, 643, 617; ESI-MS calcd. for $C_{21}H_{29}NOSiNa$ [M+Na$^+$] 362.19106; found 362.19092.

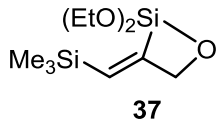
Compound S25. Benzyldimethylsilane (11 mg, 0.07319 mmol, 1.2 equiv.) was added to a stirred solution of 6-(hept-1-yn-1-yl)tosylpyridin-2(1*H*)-one (21 mg, 0.061144 mmol) and [Cp*RuCl]$_4$ (1.6 mg, 0.001472 mmol) in CH_2Cl_2 (0.3 mL). Once the reaction was complete (2 h), the solvent was evaporated and the residue passed through a pad of silica using hexanes → hexanes/ethyl acetate 10:1, 1% Et_3N, as the eluent to give the title compound as a yellow oil (29 mg, 96 %, α : β 17 : 83, Z/E > 99:1 for the major isomer (by NMR)). ^{1}H NMR (400 MHz, CD_2Cl_2) for the major regioisomer δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.72 (t, *J* = 7.8, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.17-7.09 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 7.03-6.96 (m, 1H), 6.94 (s, 1H), 6.90-6.84 (m, 2H), 2.35 (s, 3H), 2.24 (s, 2H), 2.15 (m, 2H), 1.27-1.20 (m, 6H), 0.87 (t, *J* = 7 Hz, 3H), -0.03 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 157.0, 155.8, 151.7, 146.2, 141.2, 140.45, 139.0, 133.5, 130.3, 128.8, 128.61, 128.1, 124.0, 123.4, 113.7, 40.3, 32.1, 30.3, 26.4, 22.9, 21.7, 14.20, -1.6; ^{1}H NMR (400 MHz, CD_2Cl_2) characteristic signals of the minor regioisomer δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 6.8 Hz, 1H), 6.91 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.28 (t, *J* = 7.5 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 2H), 2.09 (q, *J* = 7.4 Hz, 2H), 1.37-1.30 (m, 2H), 1.33-1.21 (m, 4H), 0.90 (t, *J* = 7 Hz, 3H), 0.02 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 165.2, 155.7, 151.8, 145.7, 140.50, 139.9, 134.4, 130.1, 128.71, 128.65, 128.3, 124.3, 120.8, 112.6, 32.6, 32.0, 29.6, 26.6, 23.0, 21.7, 14.17, -1.1; IR data (ṽ, film, cm^{-1}) 3059, 3024, 2956, 2928, 2857, 1591, 1551, 1493, 1450, 1421, 1375, 1265, 1244, 1201, 1171, 1120, 1092, 1055, 1019, 987, 904, 822, 811, 735, 699, 664; ESI-MS calcd. for $C_{28}H_{35}N_1O_3SSiNa$ [M+Na$^+$] 516.19991; found 516.20033.

Compound 35. Obtained by adding trimethyltin hydride (50.7 µL, 337.2 µmol) over 10 min to a solution alkyne **31** (50 µL, 337.2 µmol) in CH_2Cl_2 (2 mL) in the presence of [Cp*RuCl]$_4$ (5 mg, 4.59 µmol). ^{1}H NMR spectroscopy of the crude product indicated a mixture of isomers (*cis/*α: *trans/*β = 1:1), which were separated by flash chromatography (SiO_2, hexane/EtOAc 10/1). Data for the *trans/β* isomer (42 mg, 42%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.83 (t, *J* = 6 Hz, $^3J_{SnH}$ = 182 Hz, 1H, C^{1}H), 4.16 (pseudo t, *J* = 5 Hz, 2H, C^{3}H), 0.18 (s, J_{SnH} = 52 Hz, 9H, $SnMe_3$), 0.08 (s, 9H, $SiMe_3$) ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) δ 153.5 (J_{SnC} = 22 Hz, C^1), 146.1 (C^2), 67.0 (J_{SnC} = 67 Hz, C^3), −0.4 ($^1J_{SiC}$ = 6.4 Hz, $SiMe_3$), −6.4 ($^1J_{SnC}$ = 325 Hz, $SnMe_3$) ^{119}Sn{^{1}H} NMR (112 MHz, CD_2Cl_2) δ -49.1 (s) IR (ṽ, film, cm^{-1}) 3306, 2952, 1573, 1402, 1245, 1023, 912, 837, 687, 620, 413.

Compound 36. Data for the *cis/α* isomer (44 mg, 45%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.98 (t, ^4J = 2 Hz, $^3J_{SnH}$ = 113 Hz, C^{1}H), 4.41 (dd, *J* = 5 Hz, 2 Hz, 2H, $^3J_{SnH}$ = 43 Hz, 2H, C^{2}H), 1.71 (t, *J*= 5 Hz, 1H, OH), 0.13 (s, J_{SnH} = 53 Hz, 9H, $SnMe_3$), 0.11 (s, 9H, $SiMe_3$) ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) δ 171.3 (C^1), 142.2 (J_{SnC} = 58.8 Hz, C^2), 68.8 (J_{SnC} = 40 Hz, C^3), 0.9 (s, $SiMe_3$), −8.0 (J_{SnC} =

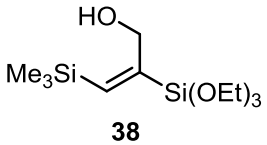
331 Hz, $SnMe_3$) $^{119}Sn\{^1H\}$ NMR (112 MHz, CD_2Cl_2) δ −39.4 (s) IR (ṽ, film, cm^{-1}) 3343, 2955, 2950, 1562, 1247, 1016, 957, 843, 762, 689, 612; ESI-MS calcd. for $C_9H_{21}OSiSn$ $[M\text{-}H^+]$ 293.03885; found 293.03908.

Compounds 37 and 38. Triethoxysilane (34 mg, 0.2070 mmol, 1.02 equiv.) was added to a stirred solution of alkyne **31** (26 mg, 0.2027 mmol) and $[Cp^*RuCl]_4$ (2.8 mg, 0.00258 mmol) in dichloromethane (1 mL). Once the reaction was complete (15 min) the solvent was evaporated to afford a mixture of compounds **37** and **38** as a brown oil (60 mg, quant., α : β 99 : 1, Z/E 57:43 for the major isomer (by NMR)). Passing the mixture of isomers though a silica pad afforded a pure sample of compound **38**, whereas compound **37** degraded on the column.



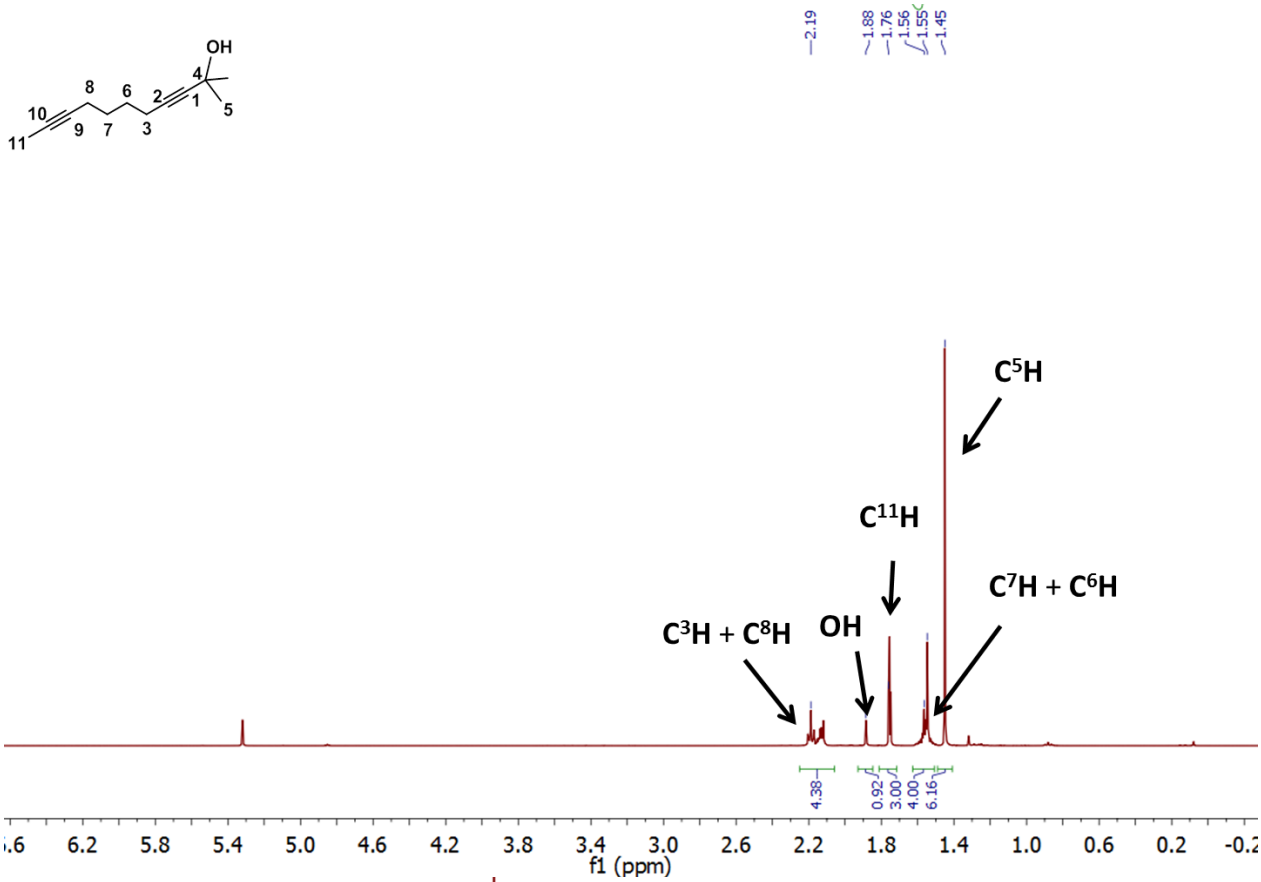
37

^1H NMR (400 MHz, CD_2Cl_2, major diastereoisomer): δ 7.33 (t, *J* = 1.5 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 2H), 3.72 (qd, *J* = 7.0, 1.8 Hz, 4H), 1.18 (t, *J* = 7.0 Hz, 6H), 0.14 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 162.0, 132.7, 70.3, 59.0, 18.3, −0.8; IR data (ṽ, ATR, cm^{-1}) 3457, 2974, 2957, 2926, 2895, 2855, 1556, 1482, 1443, 1390, 1295, 1261, 1248, 1166, 1101, 1074, 1004, 957, 916, 838, 781, 751, 731, 693, 628; ESI-MS calcd. for $C_{10}H_{22}O_3Si_2$ (M) 246.11075; found 246.11089.



38

^1H NMR (400 MHz, CD_2Cl_2, minor diastereoisomer): δ 6.43 (t, *J* = 1.2 Hz, 1H), 4.27 (dd, *J* = 6.3, 1.2 Hz, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 2.50 (t, *J* = 6.3 Hz, OH), 1.22 (t, *J* = 7.0 Hz, 9H), 0.15 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 155.3, 148.6, 65.8, 59.1, 18.3, 0.1; IR data (ṽ, ATR, cm^{-1}) 3457, 2974, 2957, 2926, 2895, 2855, 1556, 1482, 1443, 1390, 1295, 1261, 1248, 1166, 1101, 1074, 1004, 957, 916, 838, 781, 751, 731, 693, 628; ESI-MS calcd. for $C_{12}H_{28}O_4Si_2Na$ $(M+Na^+)$ 315.14184; found 315.14148.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2
10
1
5
9
7
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11
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1.76
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1.55
1.45
C5H
C11H
C7H + C6H
C3H + C8H
OH
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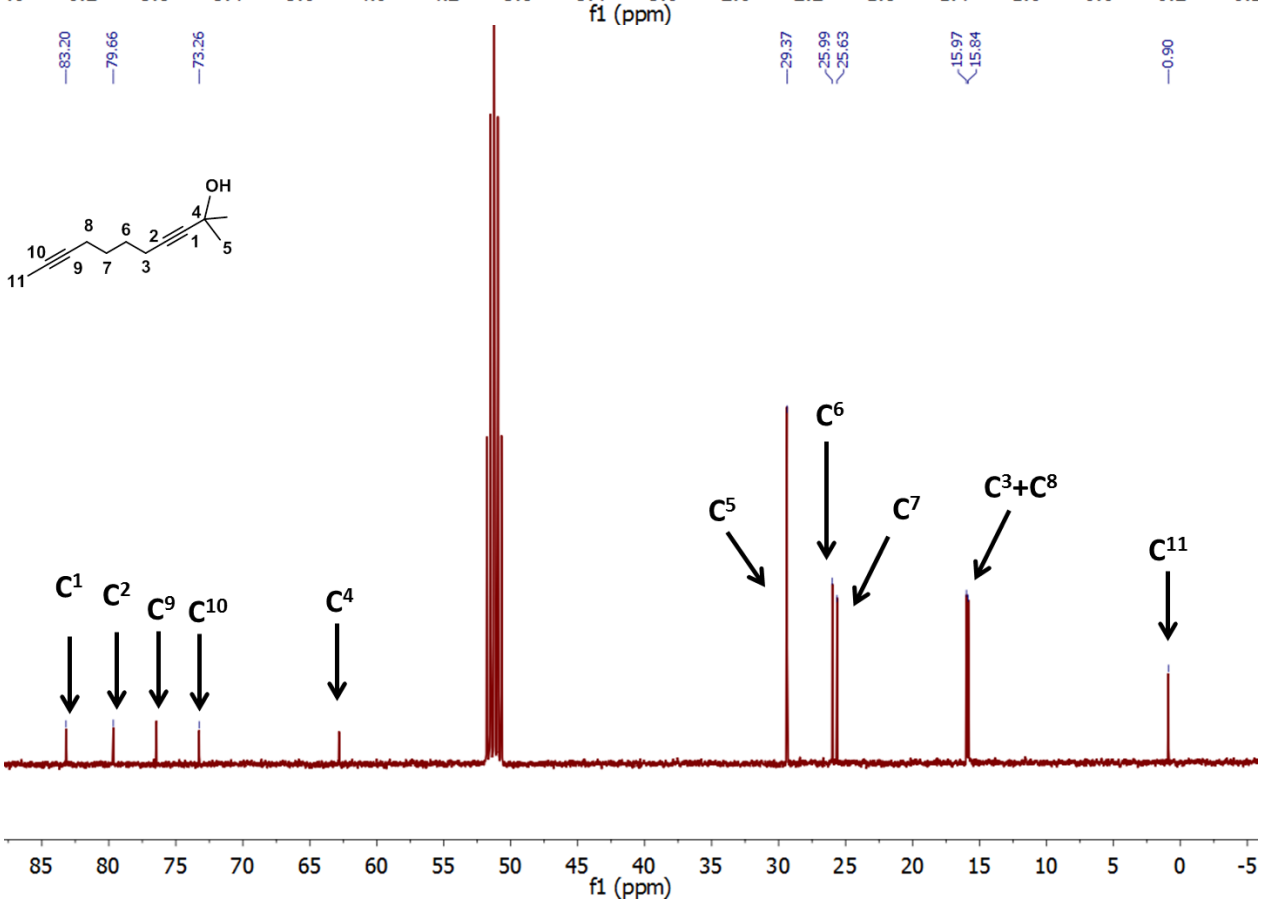
4.00
6.16
f1 (ppm)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2
10
1
5
9
7
3
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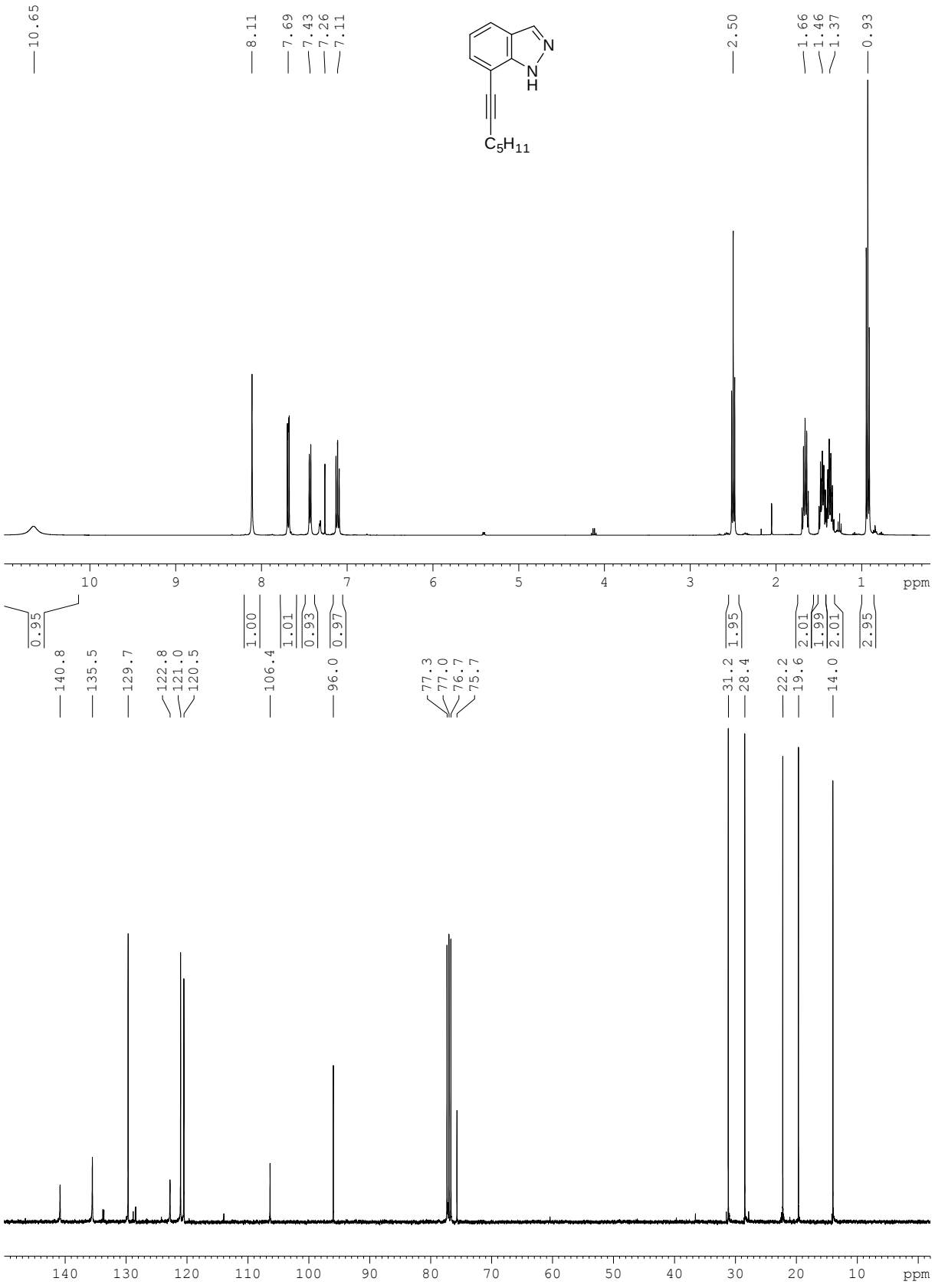
C1
C2
C9
C10
C4
C5
C6
C7
C3+C8
C11
f1 (ppm)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ppm
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1.01
0.93
0.97
1.95
2.01
1.99
2.01
2.95
140.8
135.5
129.7
122.8
121.0
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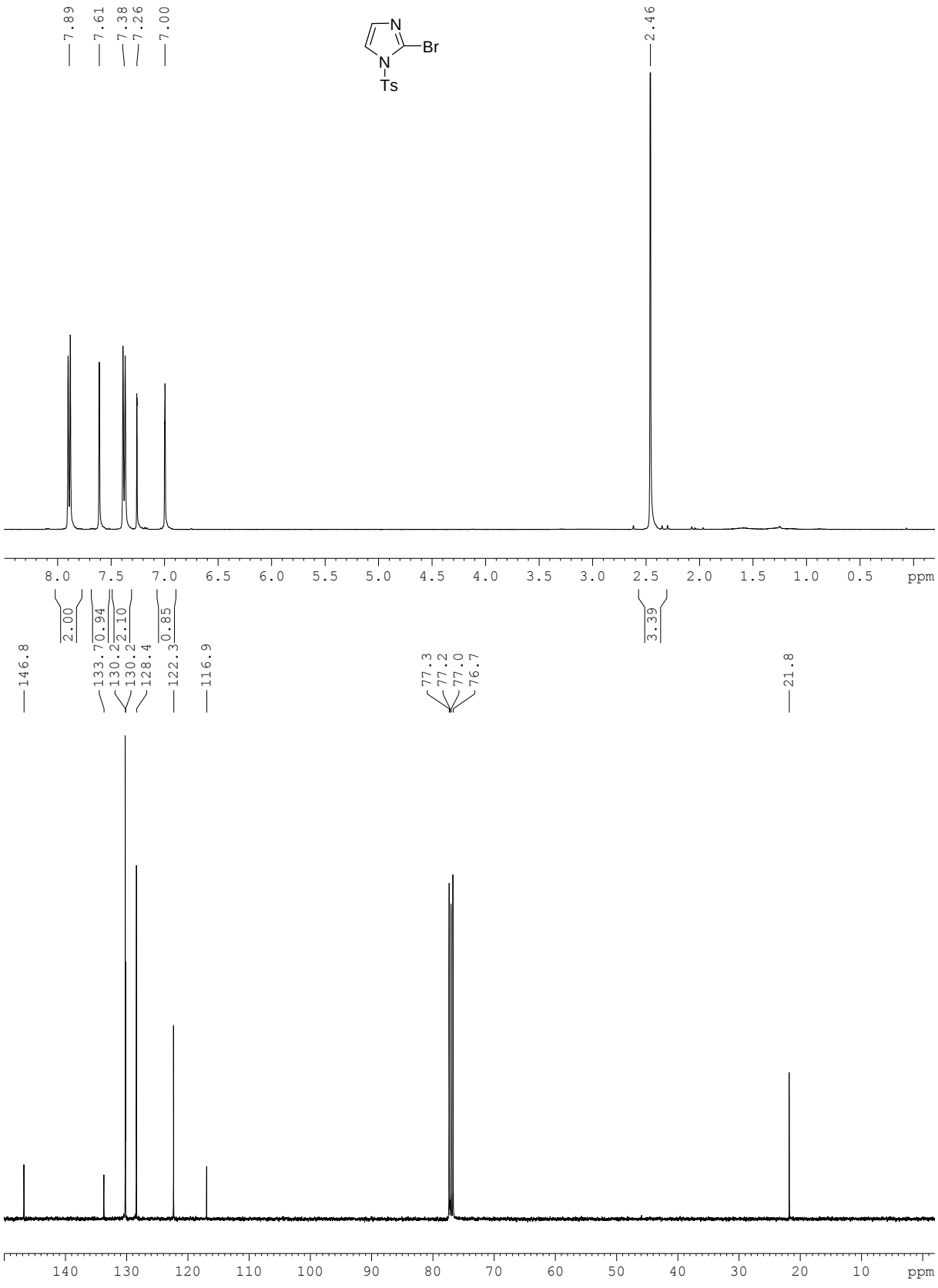
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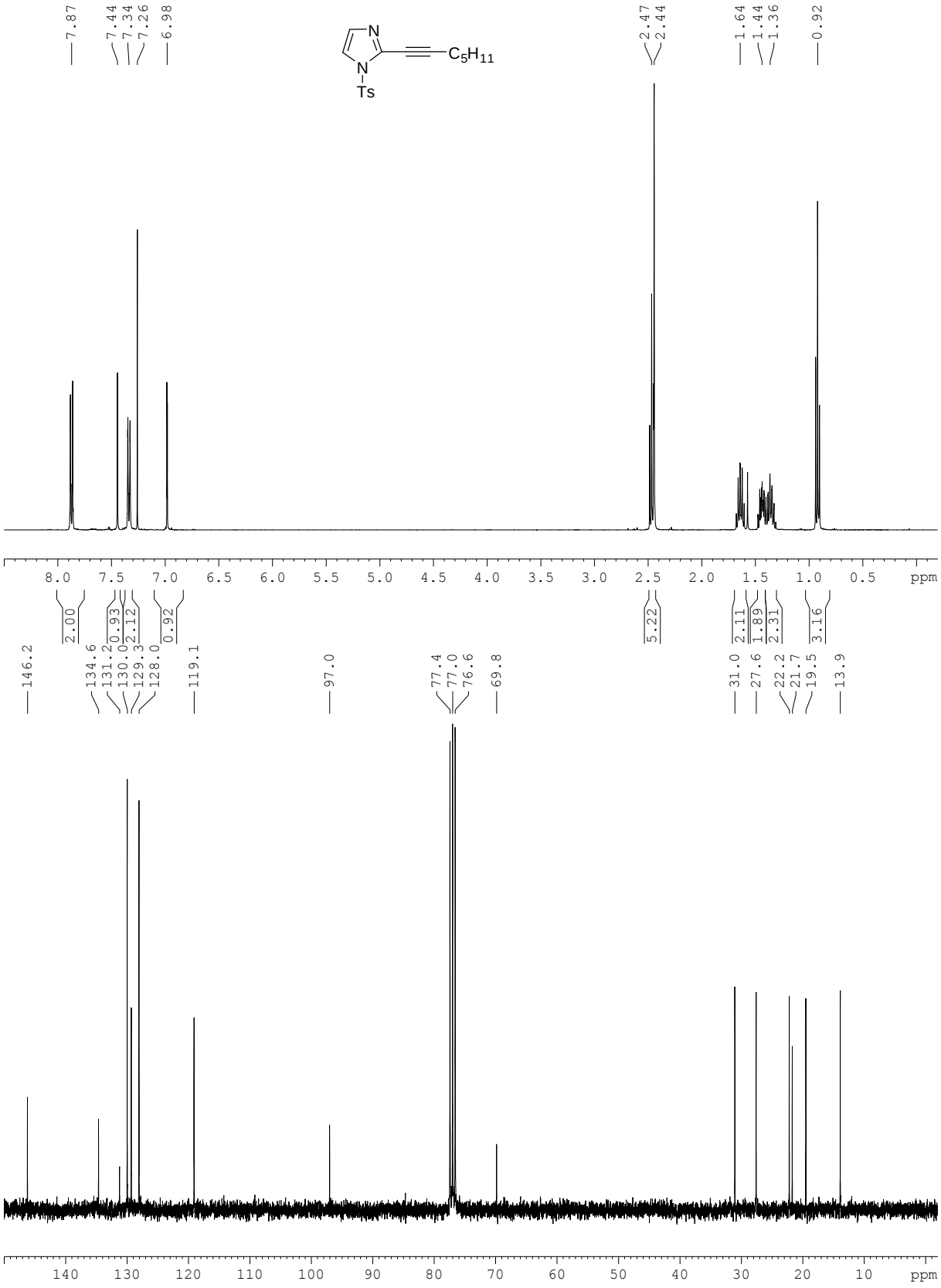
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N
Ts
C5H11
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0.93
2.12
0.92
5.22
2.11
1.89
2.31
3.16
146.2
134.6
131.2
130.0
129.3
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97.0
77.4
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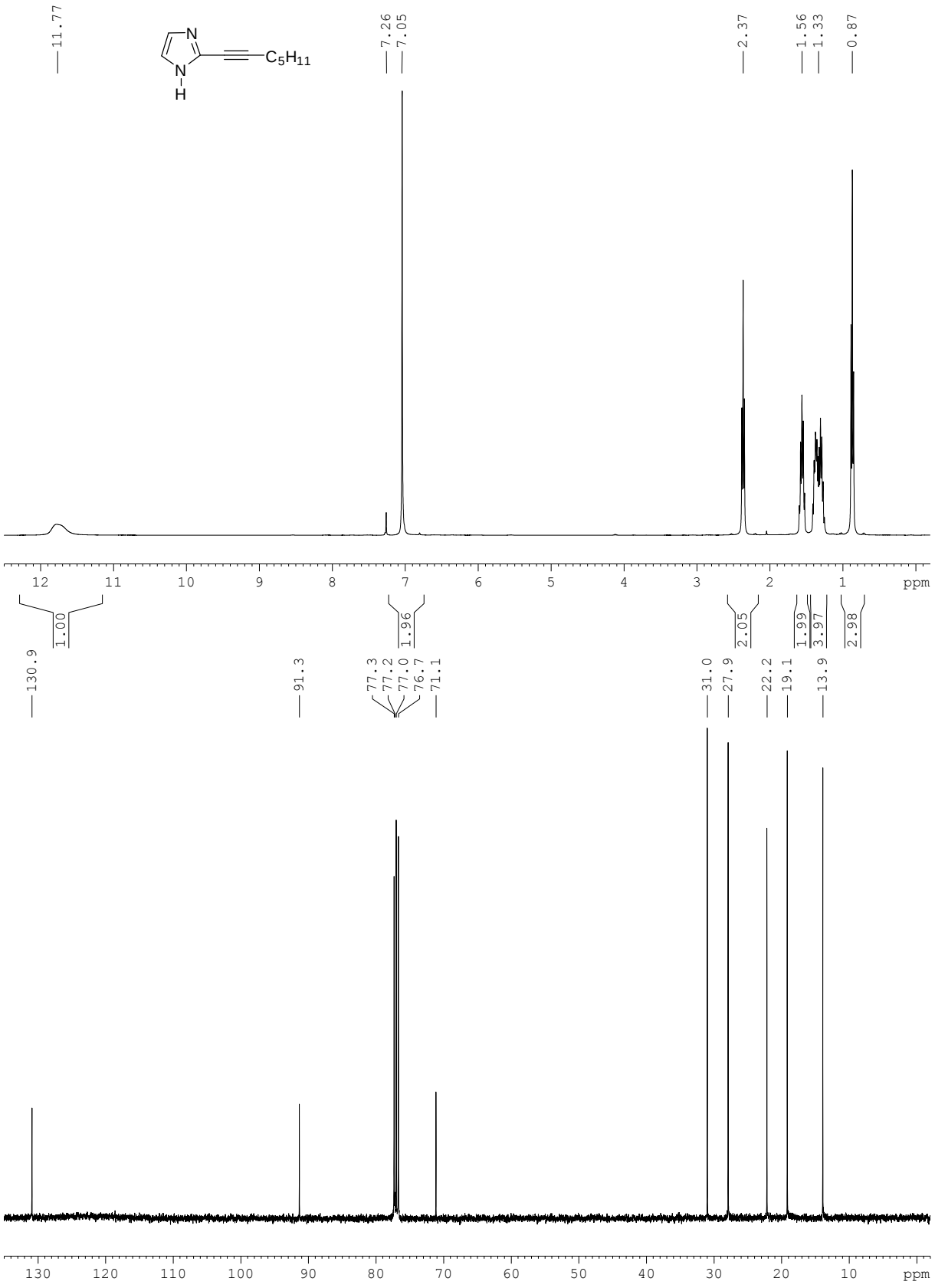
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7
6
5
4
3
2
1
ppm
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1.96
2.05
1.99
3.97
2.98
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77.2
77.0
76.7
71.1
31.0
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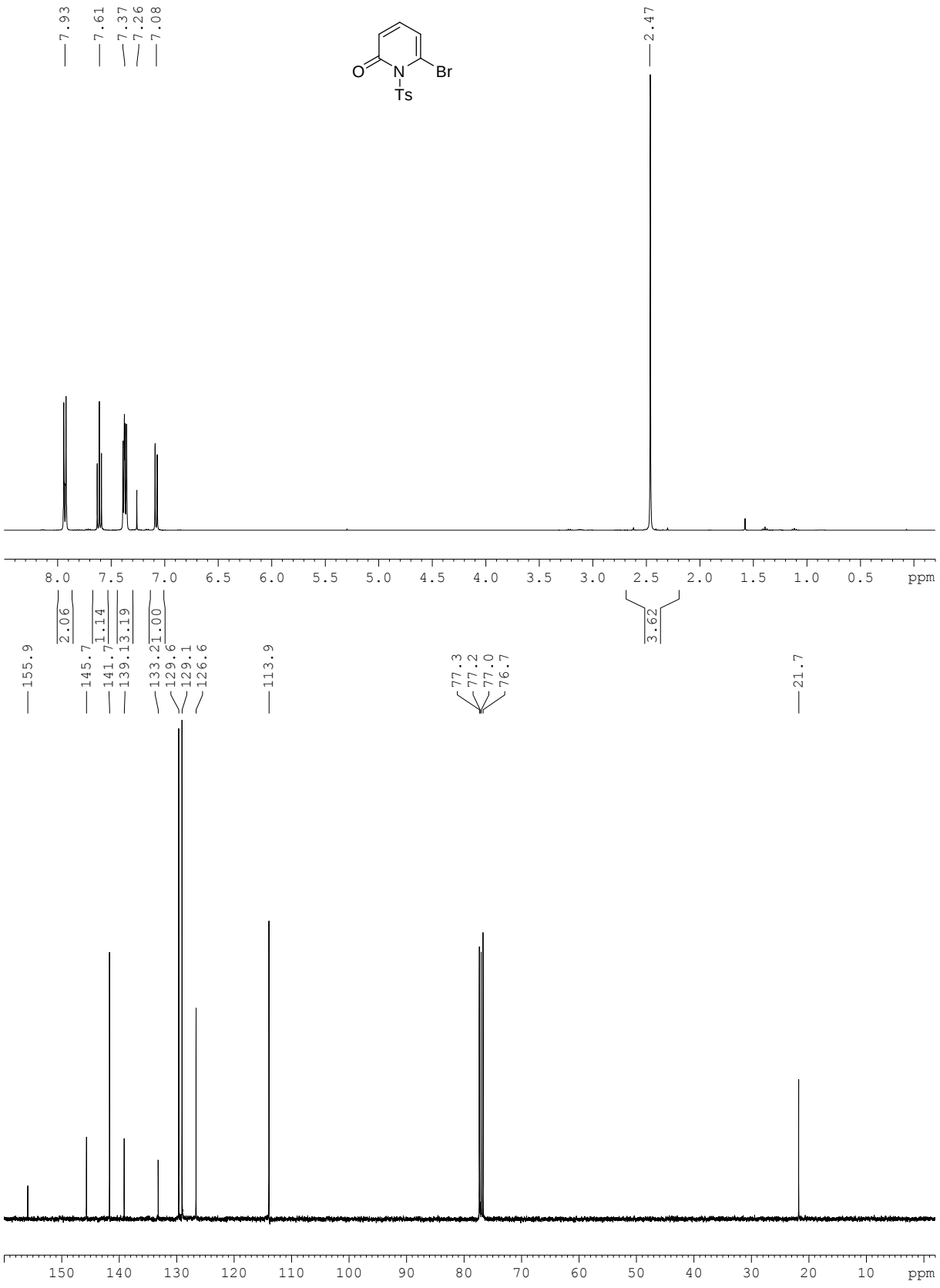
10
ppm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7.26
7.08
2.47
O
N
Br
Ts
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2.06
1.14
3.19
1.00
3.62
155.9
145.7
141.7
139.1
133.2
129.6
129.1
126.6
113.9
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77.2
77.0
76.7
21.7
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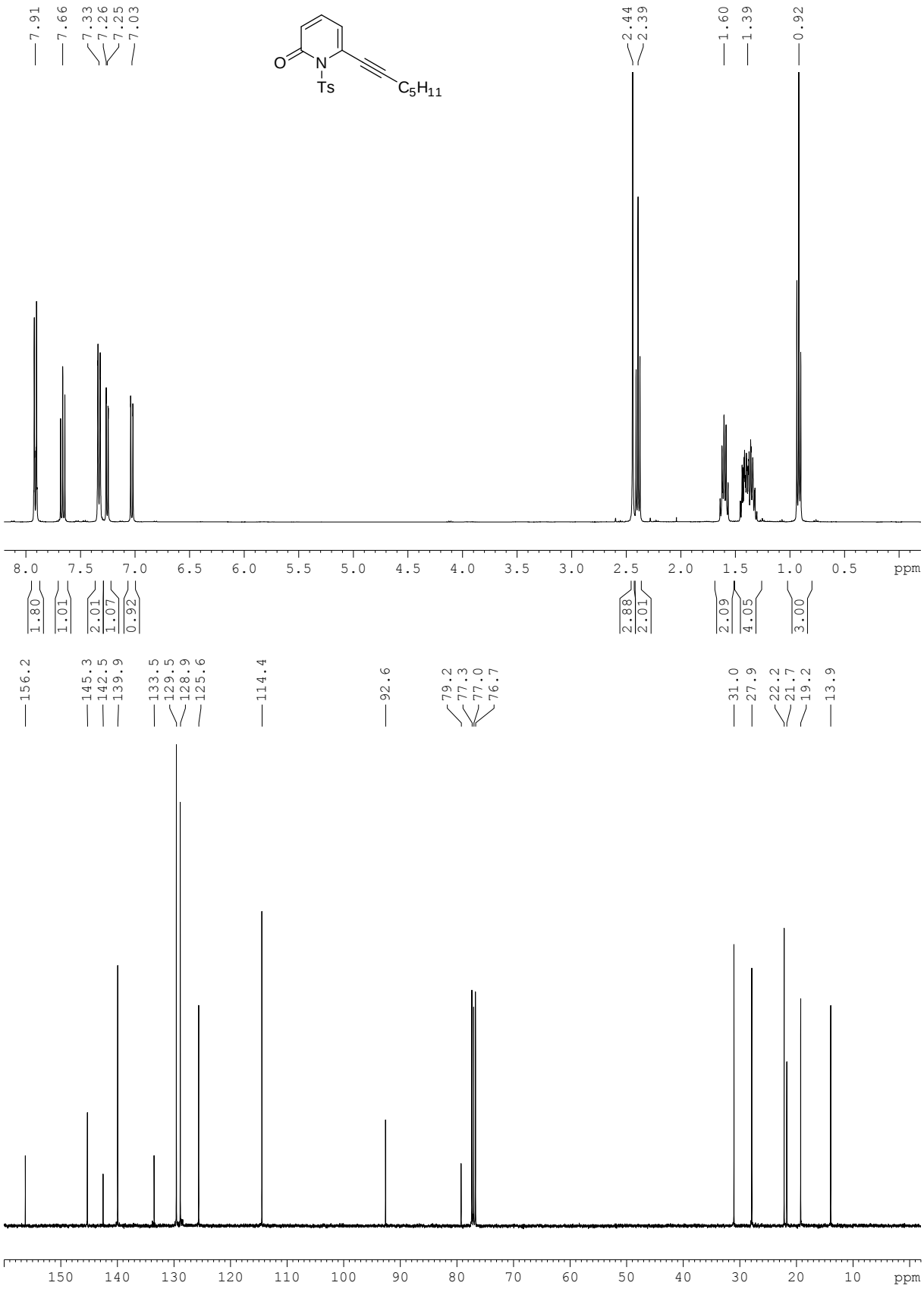
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O
N
Ts
C5H11
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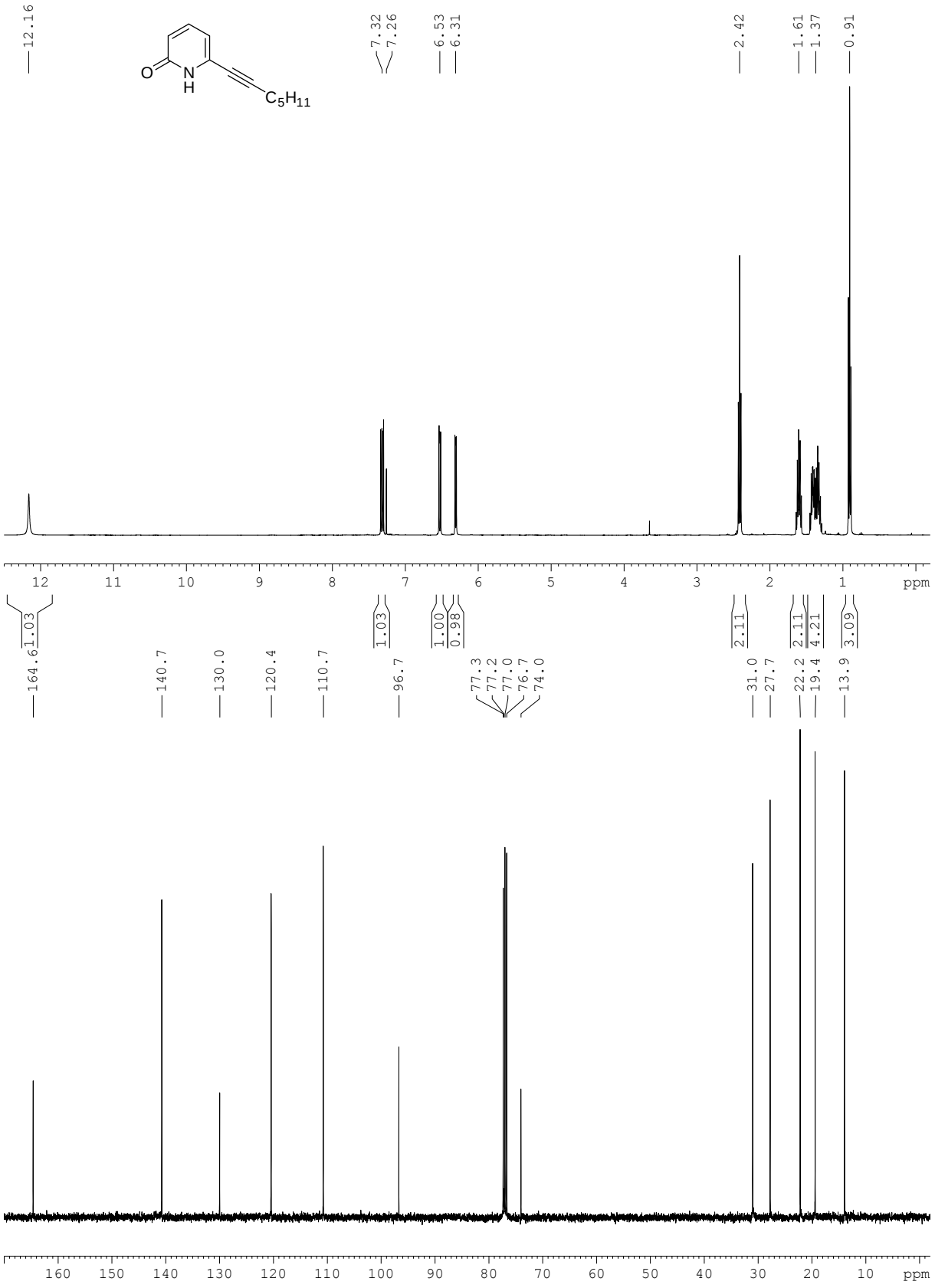
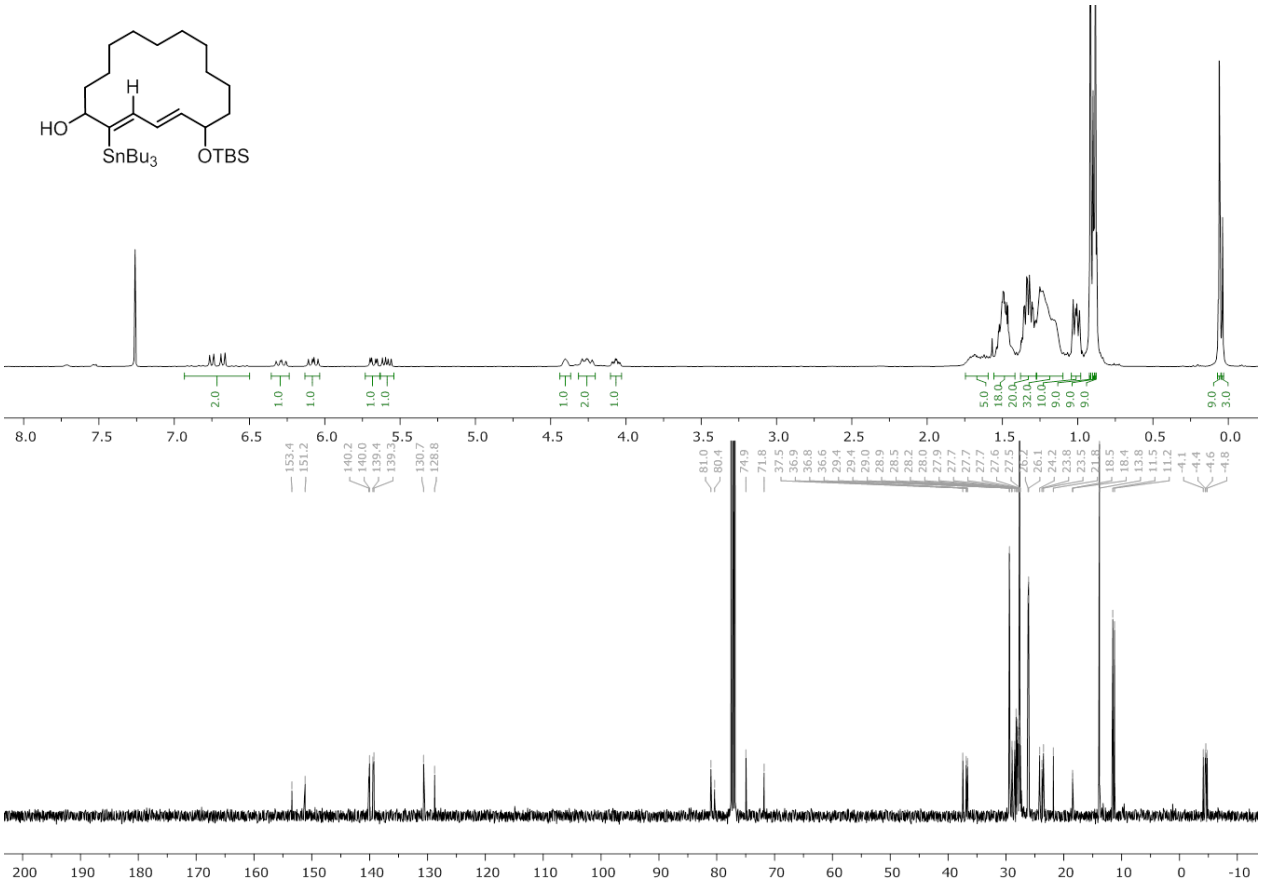
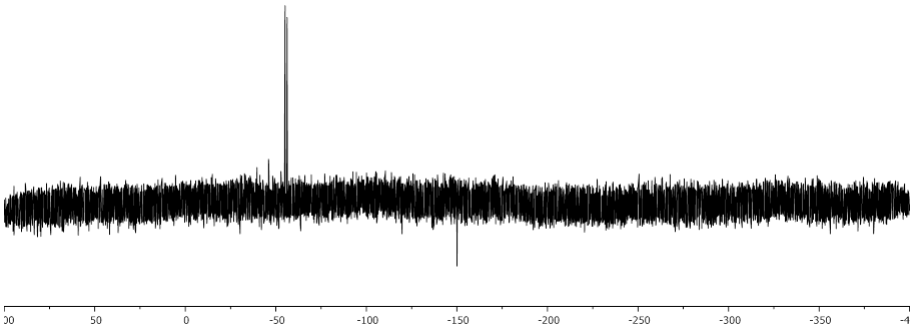
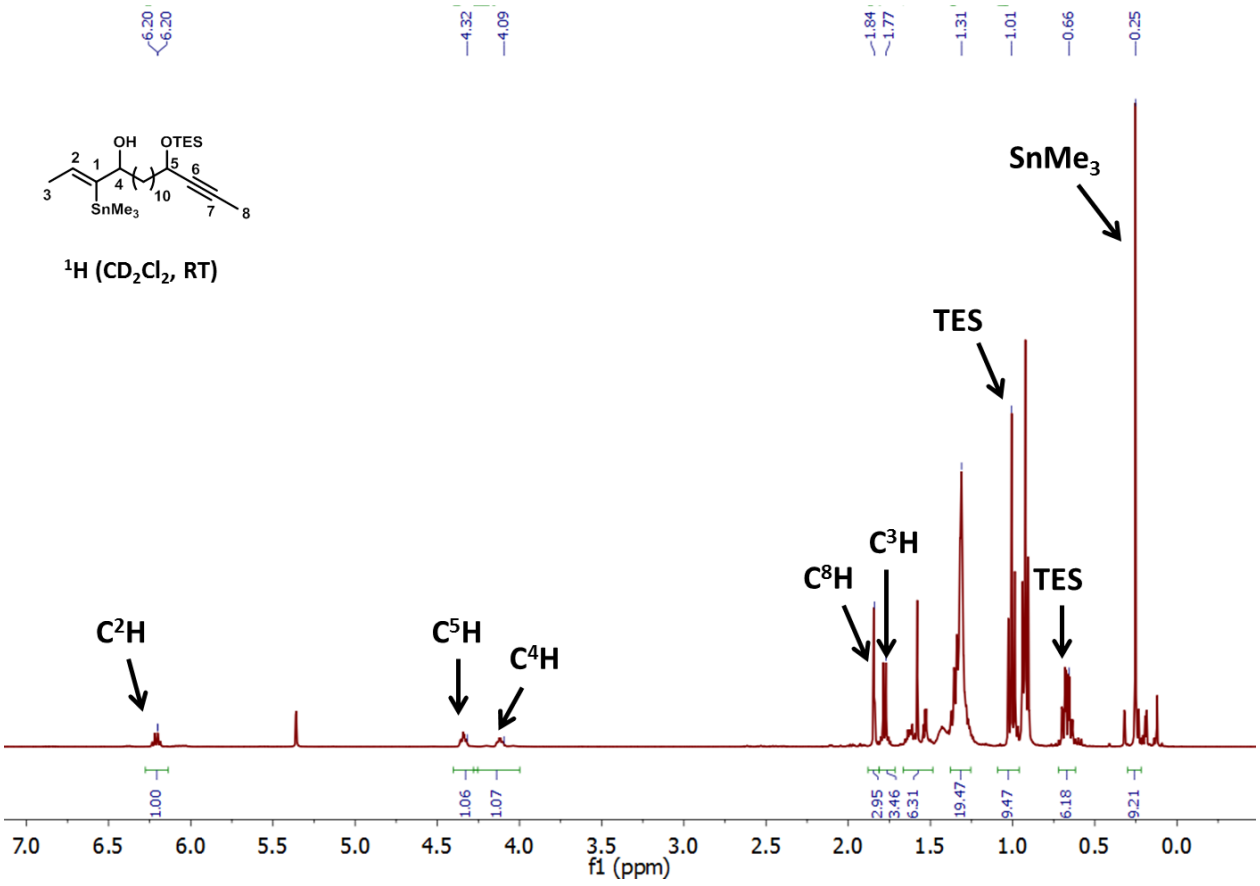
1.39
0.92
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.80
1.01
2.01
1.07
0.92
2.88
2.01
2.09
4.05
3.00
156.2
145.3
142.5
139.9
133.5
129.5
128.9
125.6
114.4
92.6
79.2
77.3
77.0
76.7
31.0
27.9
22.2
21.7
19.2
13.9
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

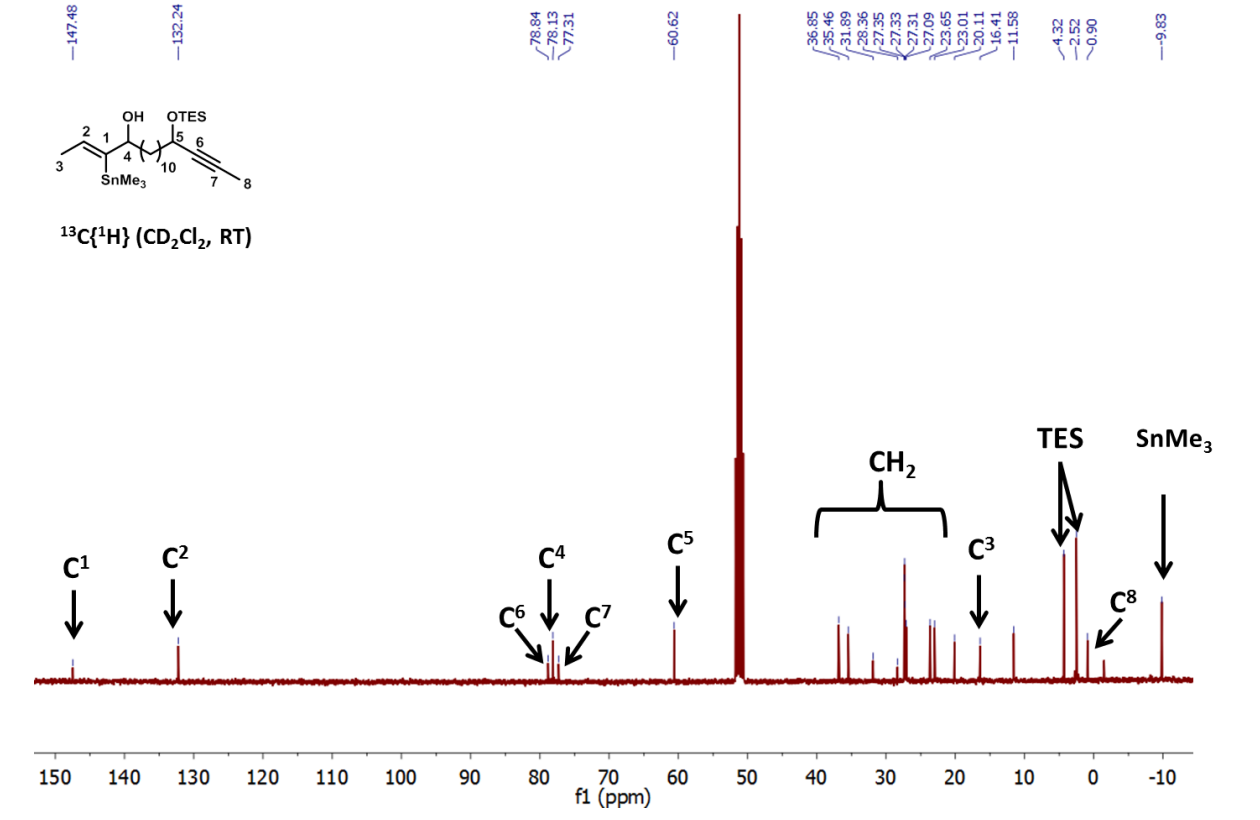

12.16
7.32
7.26
6.53
6.31
2.42
1.61
1.37
0.91
O
N
H
C5H11
ppm
1.03
1.03
1.00
0.98
2.11
2.11
4.21
3.09
164.6
140.7
130.0
120.4
110.7
96.7
77.3
77.2
77.0
76.7
74.0
31.0
27.7
22.2
19.4
13.9
ppm

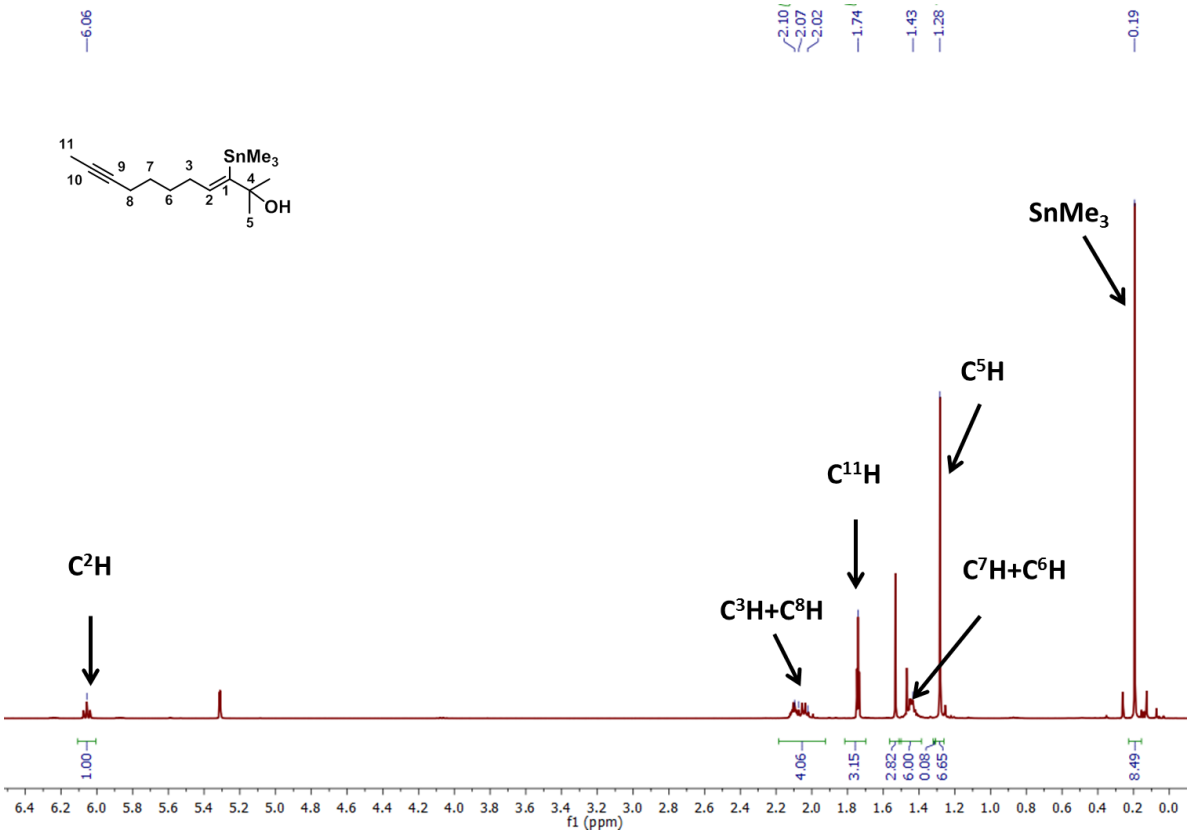


$^{119}Sn\{^{1}H\}$ NMR




OH
OTES
SnMe3
1H (CD2Cl2, RT)
SnMe3
TES
C3H
C8H
TES
C2H
C5H
C4H
f1 (ppm)


OH
OTES
SnMe3
13C{1H} (CD2Cl2, RT)
CH2
TES
SnMe3
C1
C2
C4
C6
C7
C5
C3
C8
f1 (ppm)


6.06
2.10
2.07
2.02
1.74
1.43
1.28
0.19
SnMe3
C2H
C3H+C8H
C11H
C5H
C7H+C6H
SnMe3
1.00
4.06
3.15
2.82
6.00
0.08
6.65
8.49
f1 (ppm)

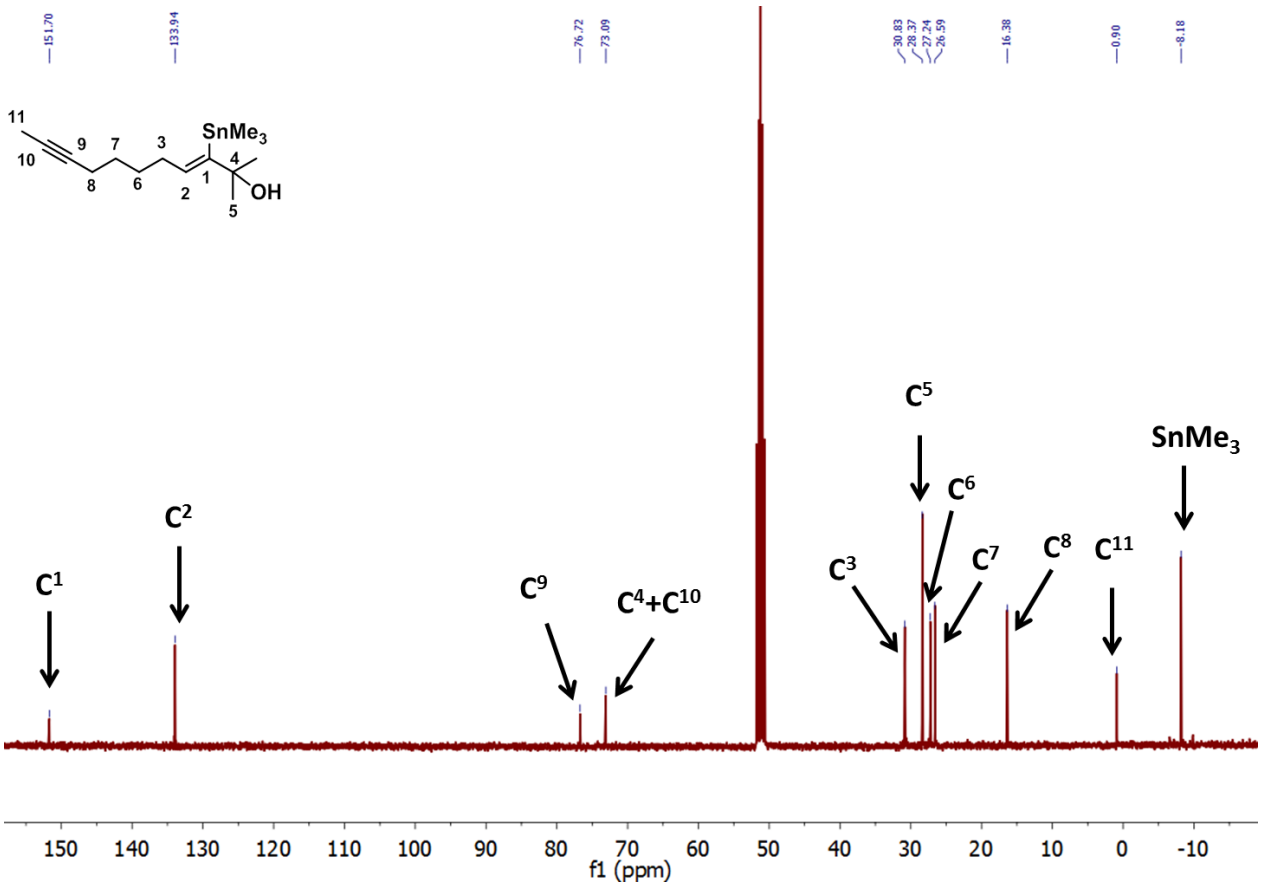

151.70
133.94
76.72
73.09
30.83
28.37
27.24
26.59
16.38
0.90
-8.18
SnMe3
C1
C2
C9
C4+C10
C3
C5
C6
C7
C8
C11
SnMe3
f1 (ppm)

Table 5, Entry 8

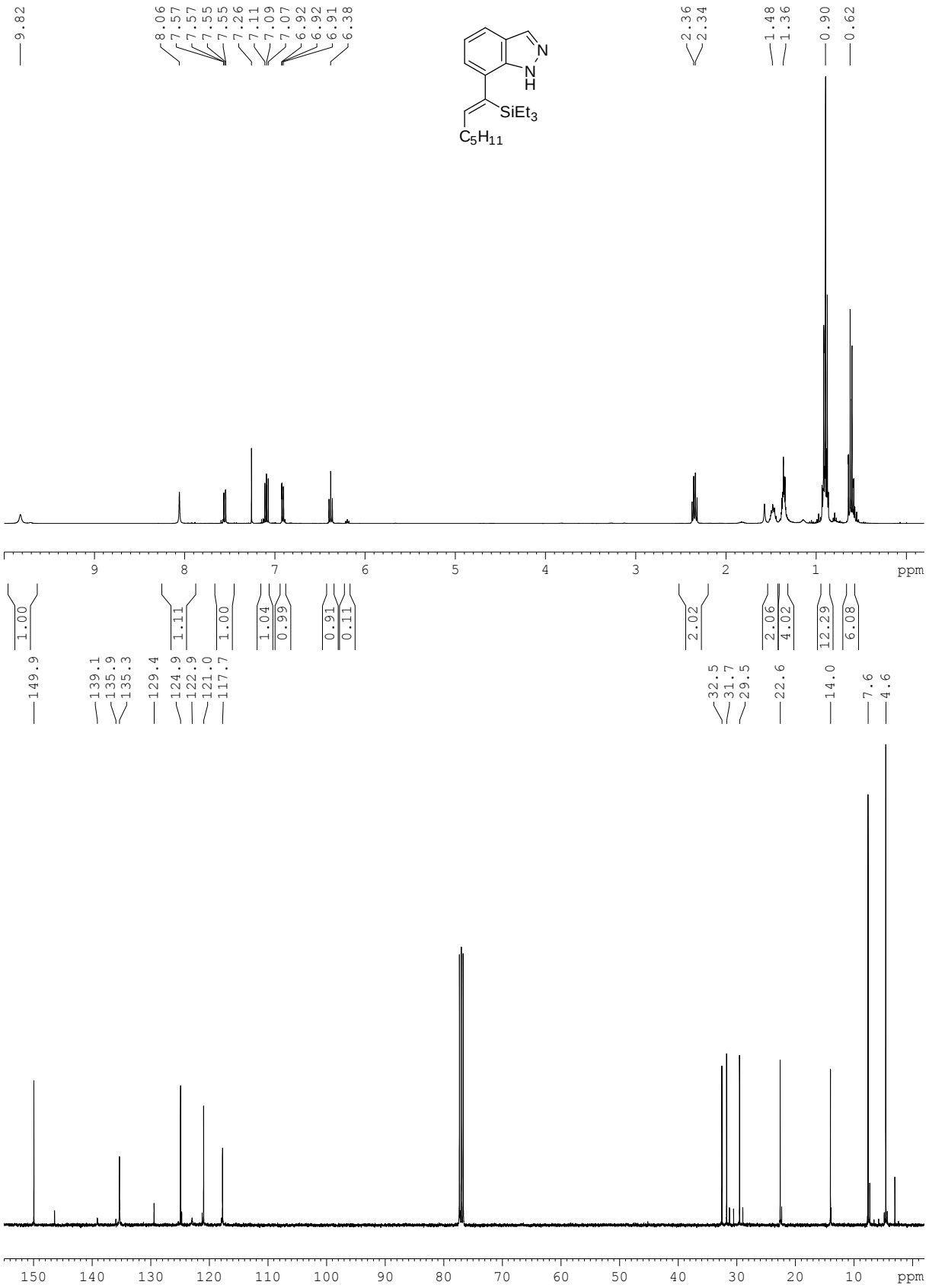


Table 5, Entry 9

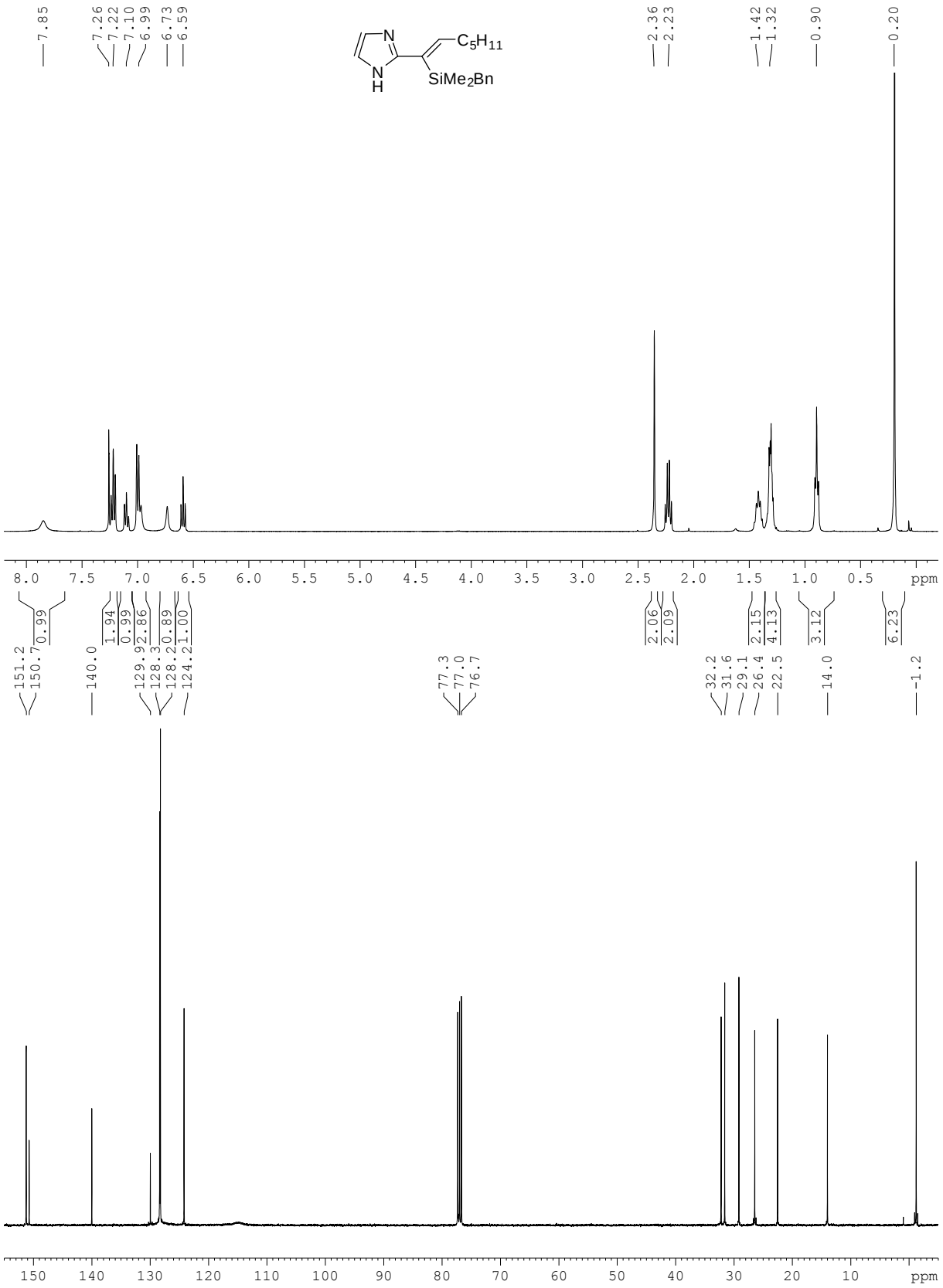


Table 5, Entry 10

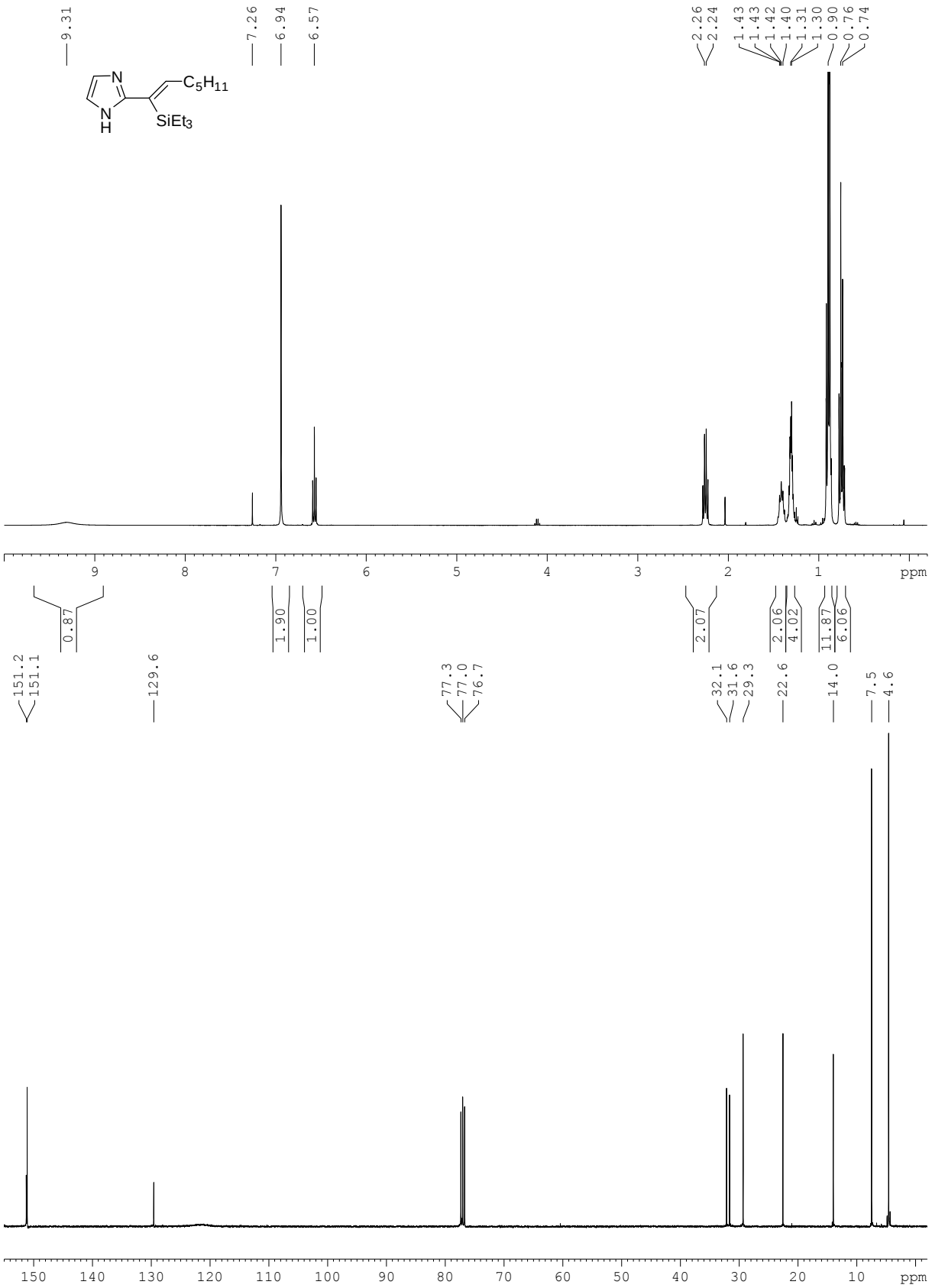


Table 5, Entry 11

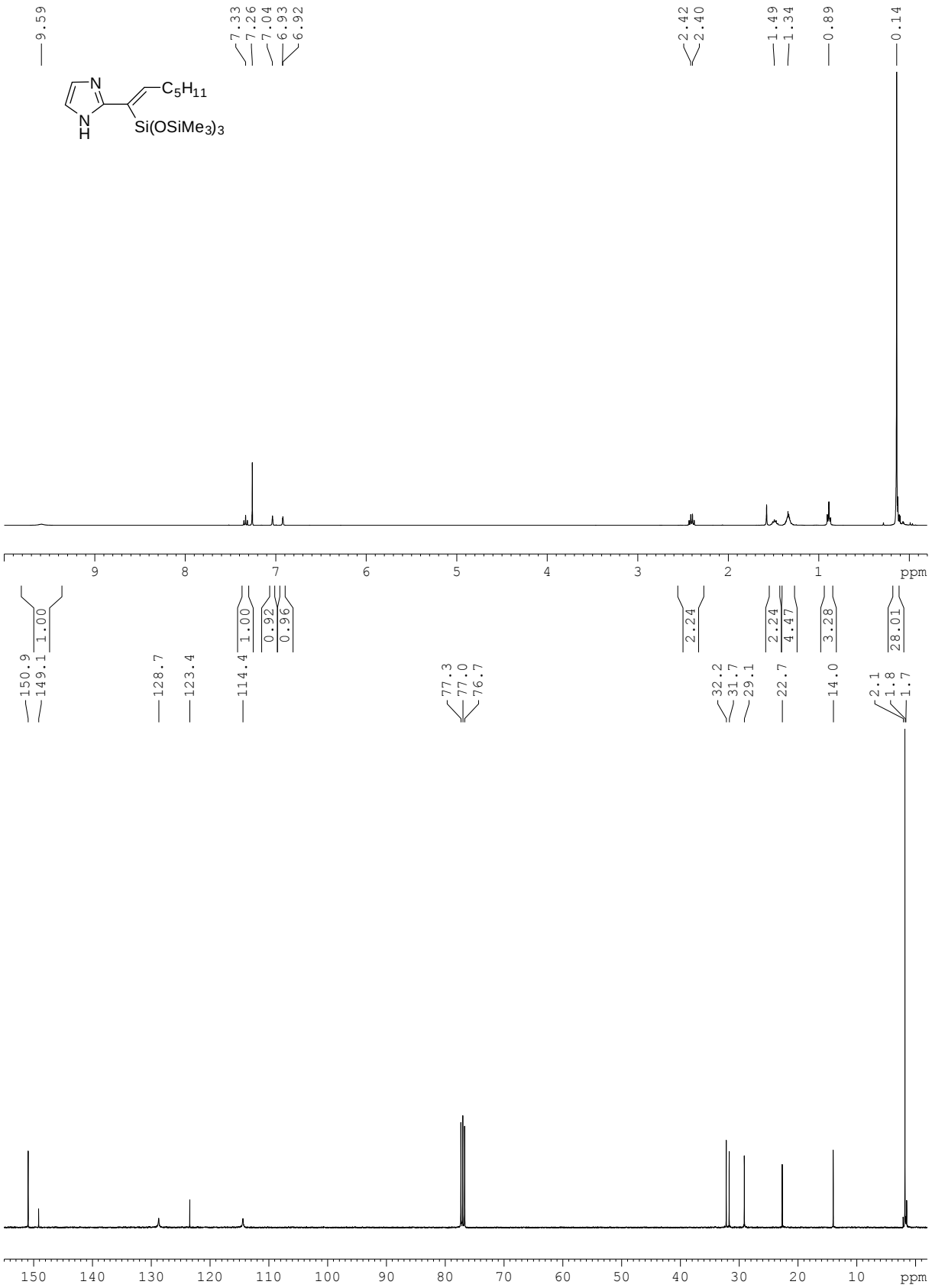


Table 5, Entry 12

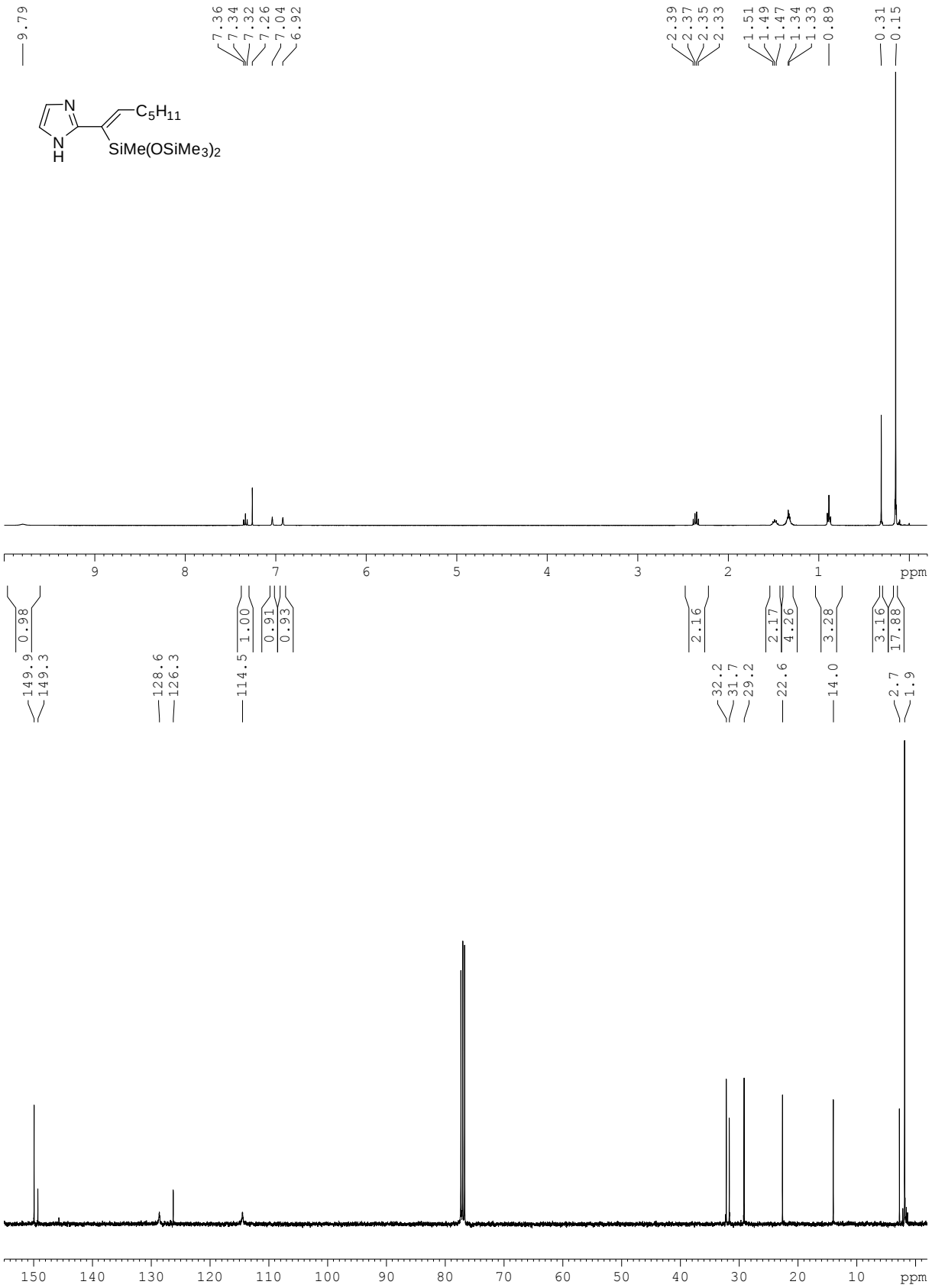


Table 5, Entry 13

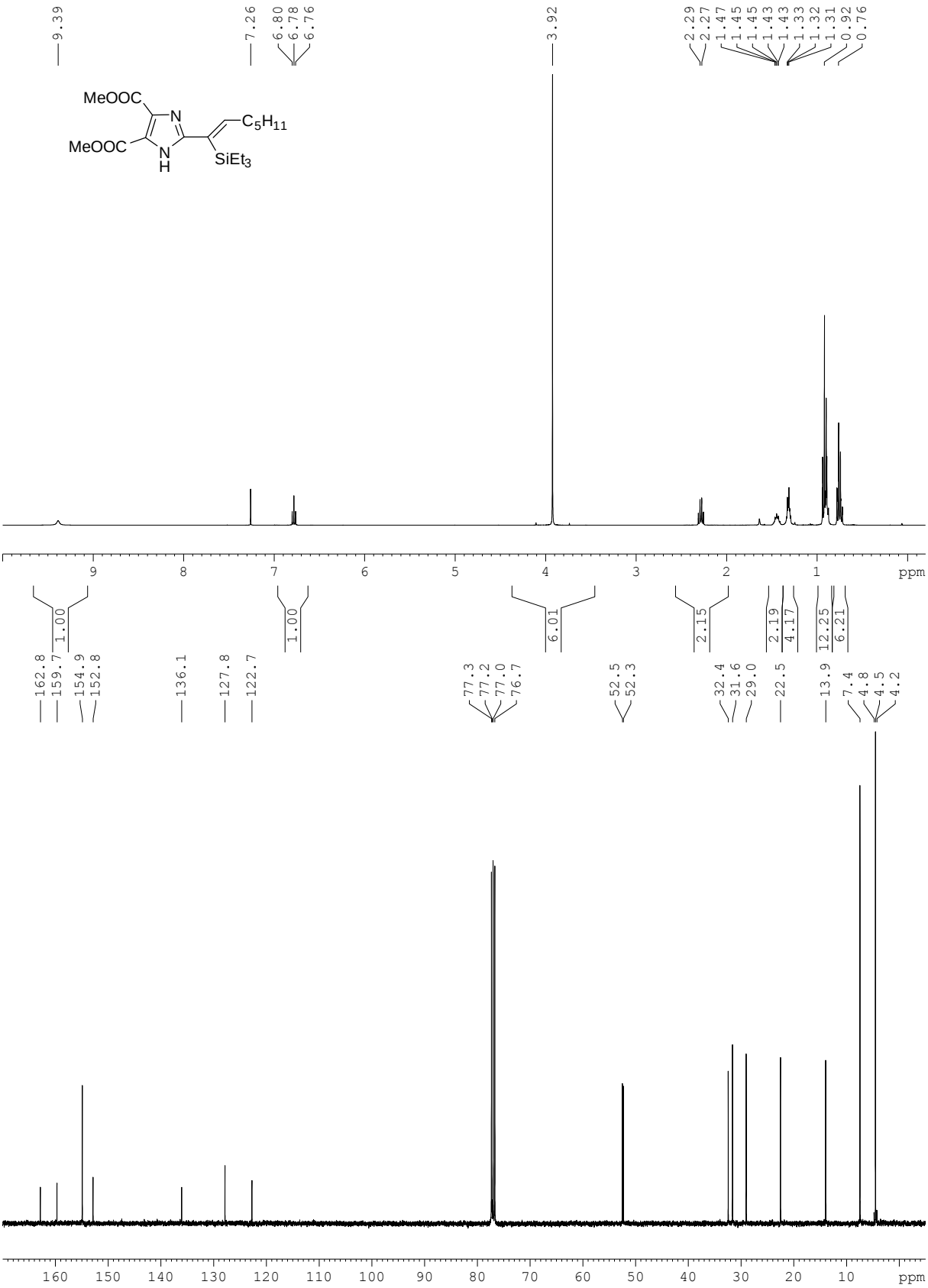


Table 5, Entry 14

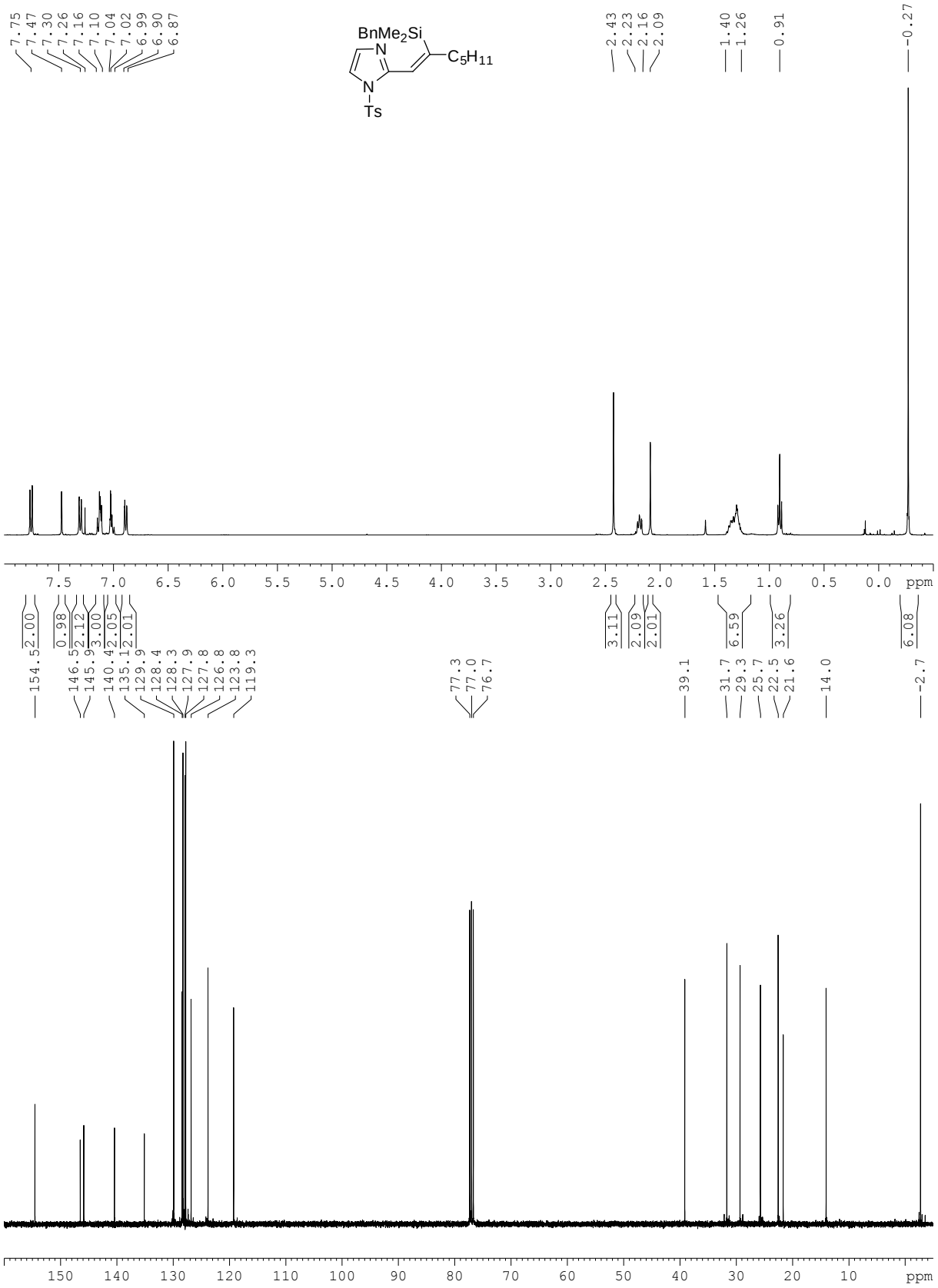


Table 5, Entry 15

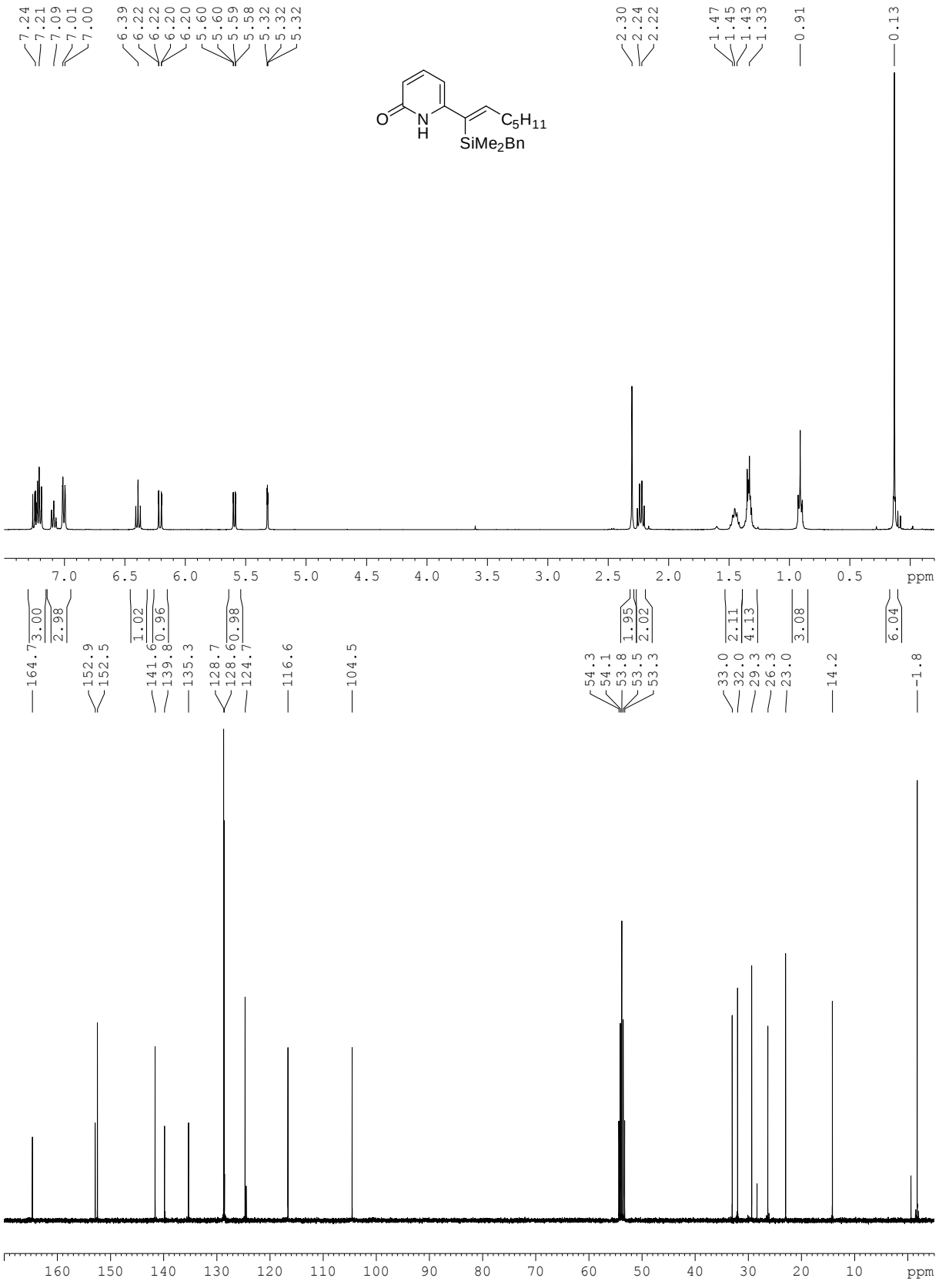


Table 5, Entry 16

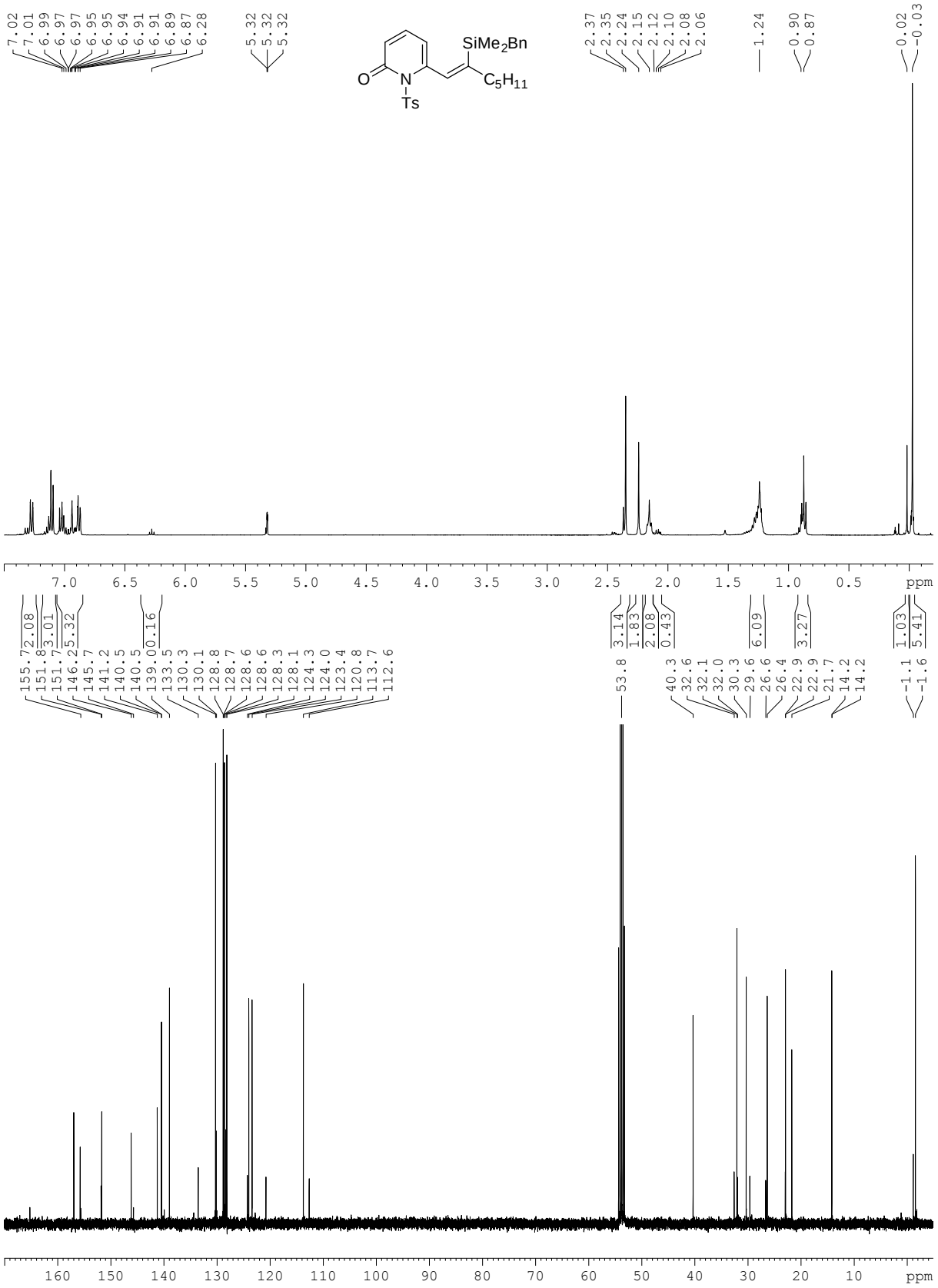


Table 5, Entry 16

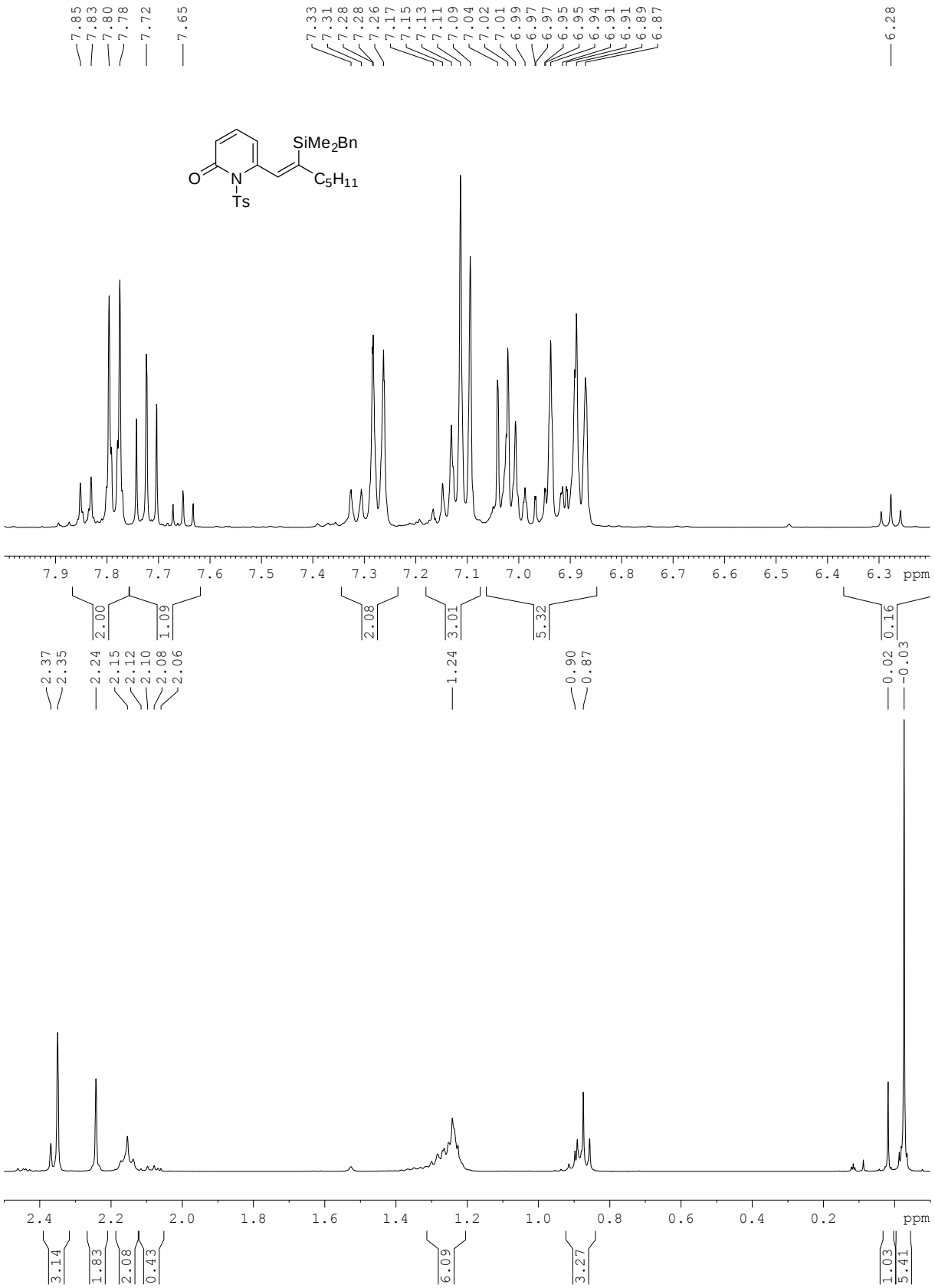
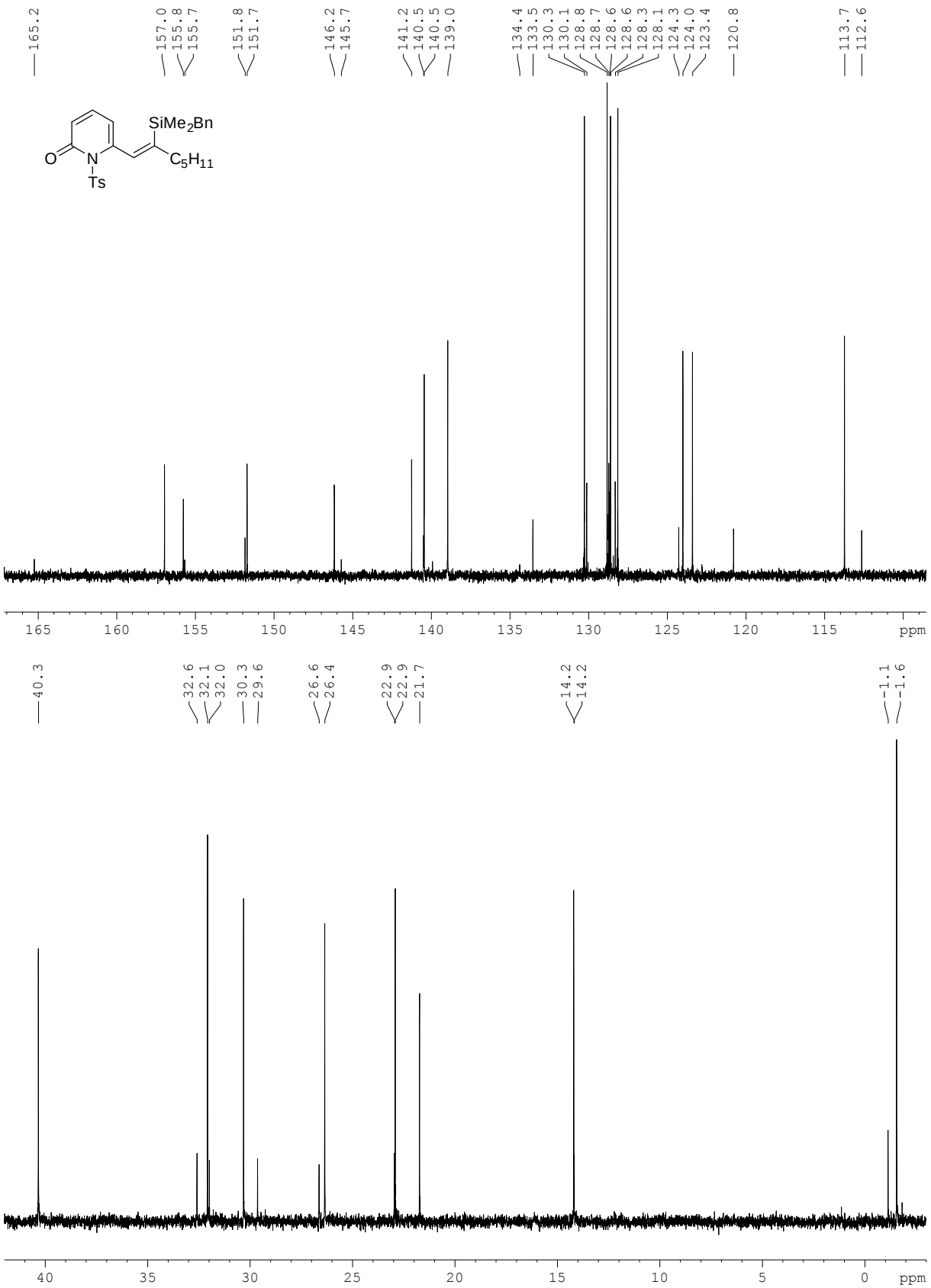
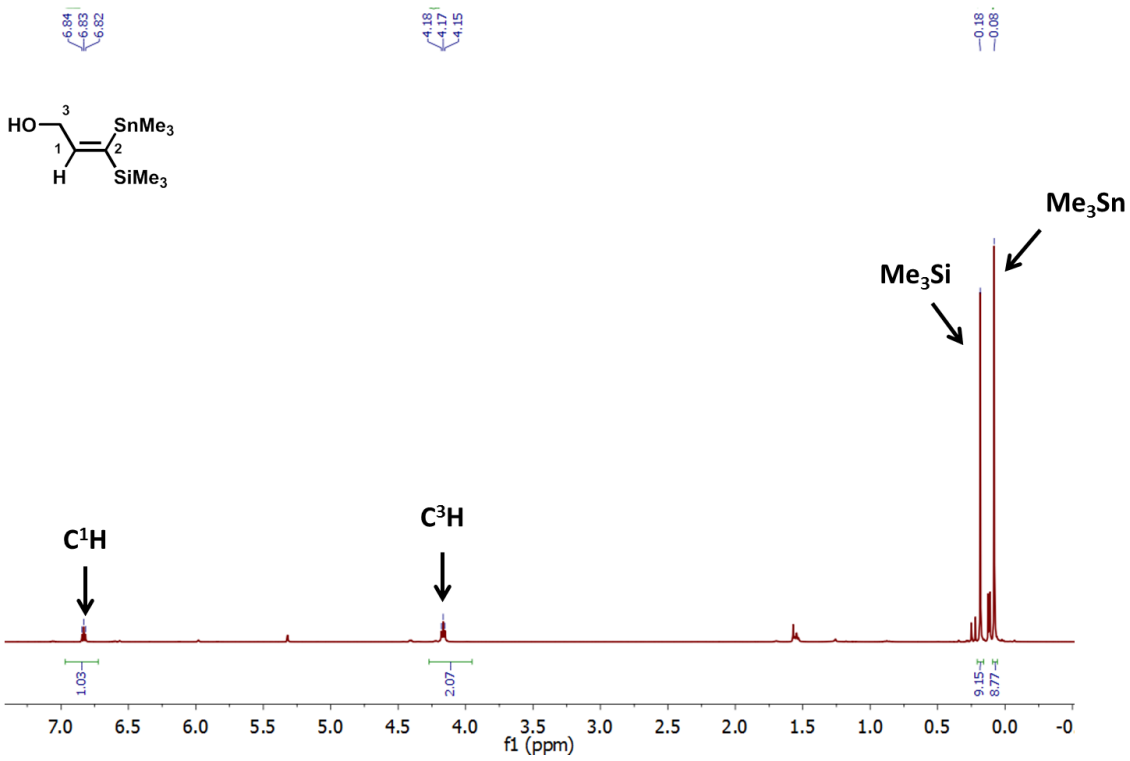


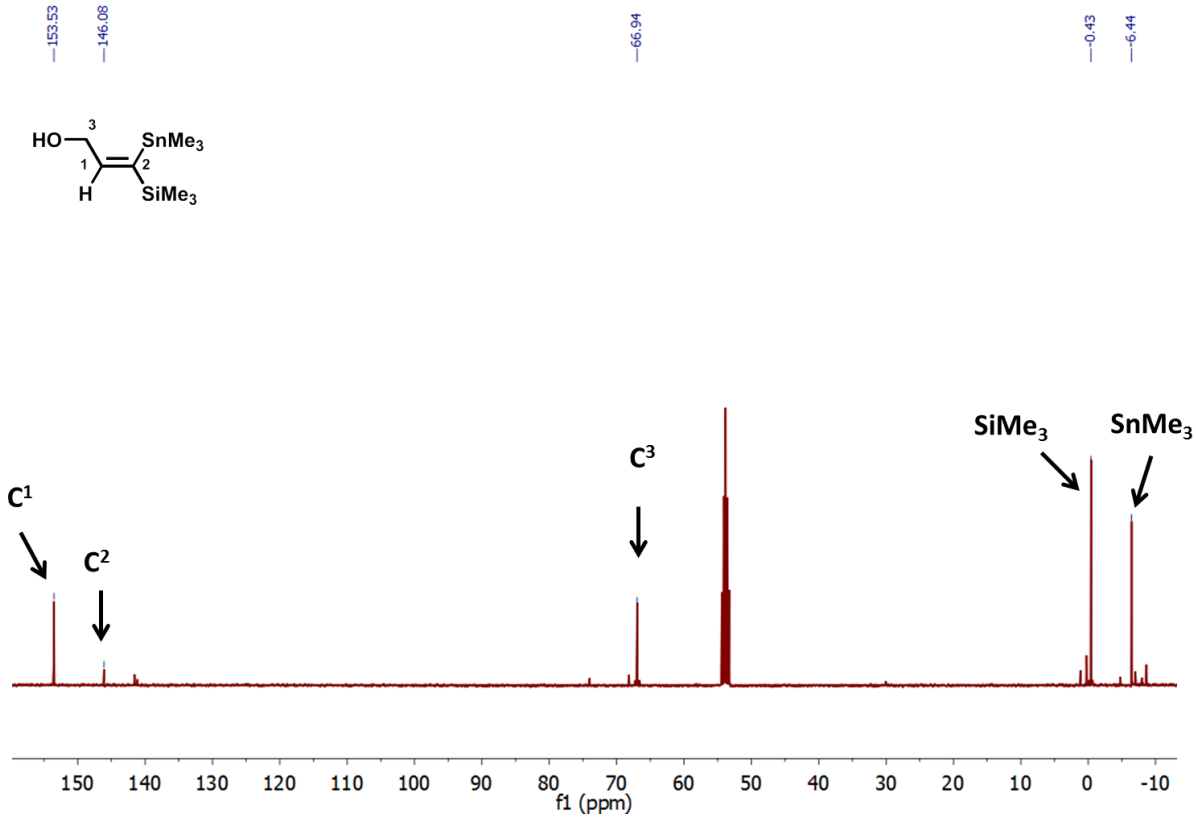
Table 5, Entry 16



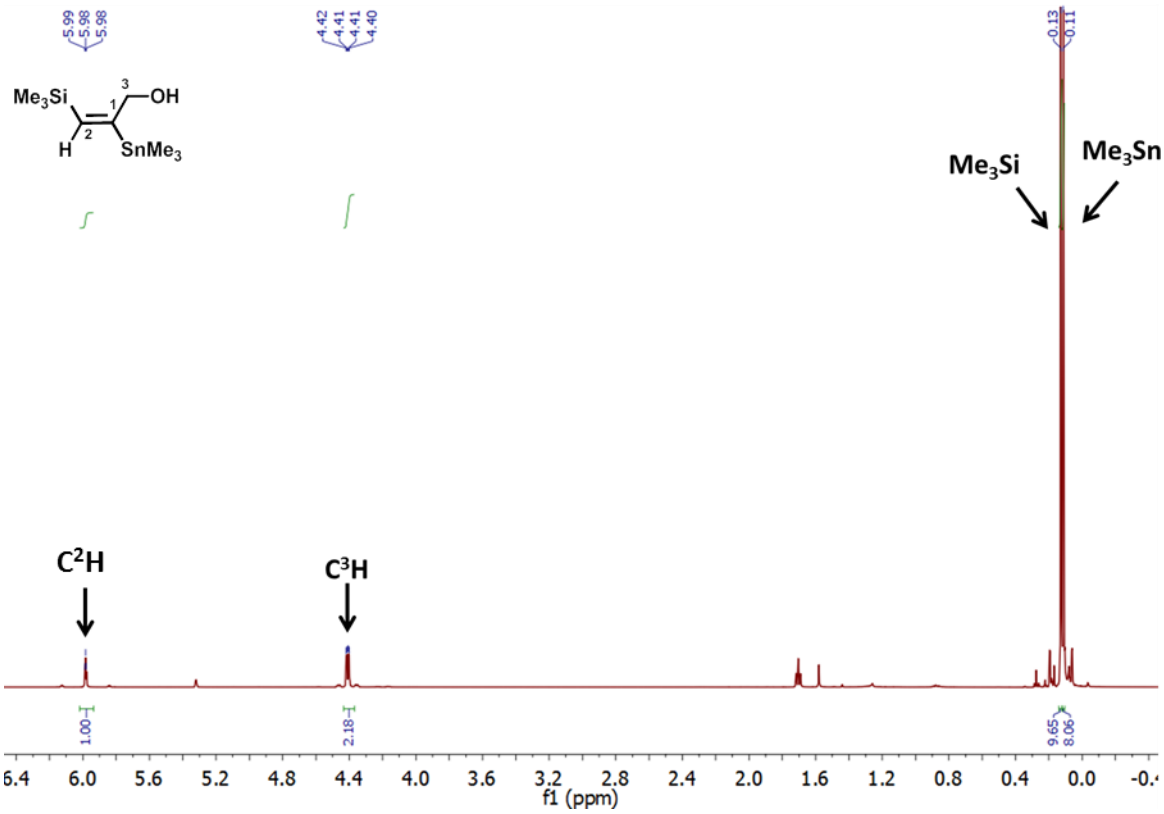
^{1}H NMR, CD_2Cl_2, 298 K



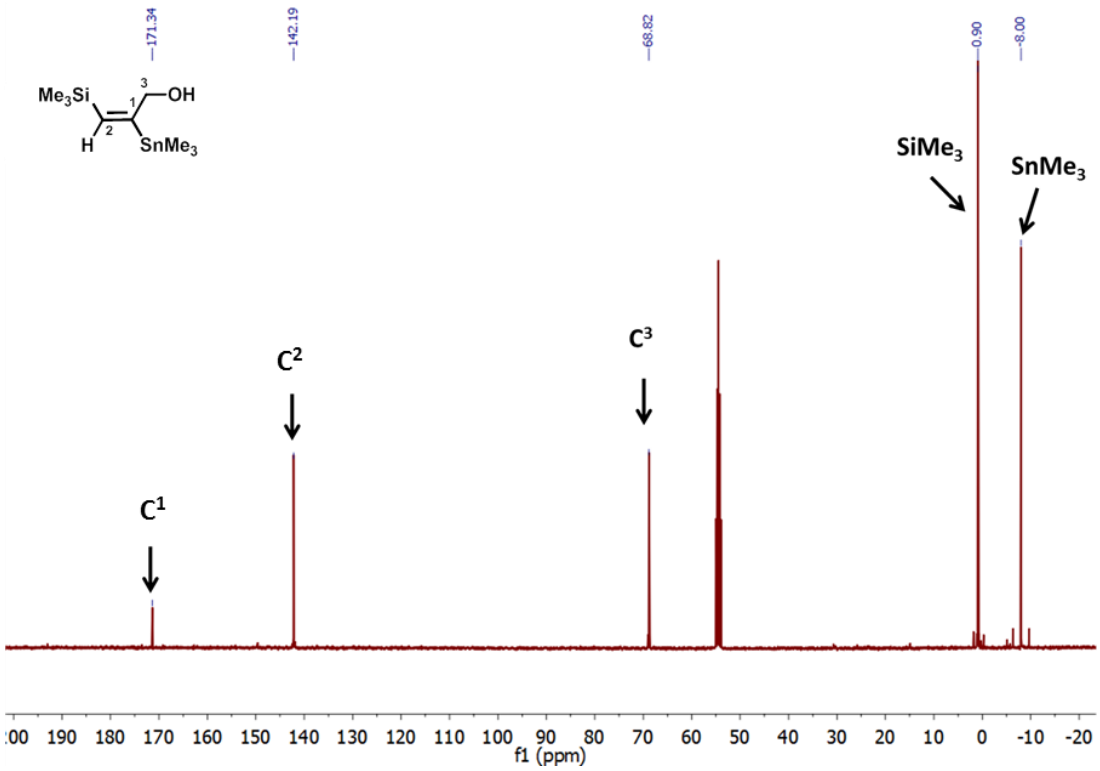
$^{13}C\{^1H\}$ NMR, CD_2Cl_2, 298 K

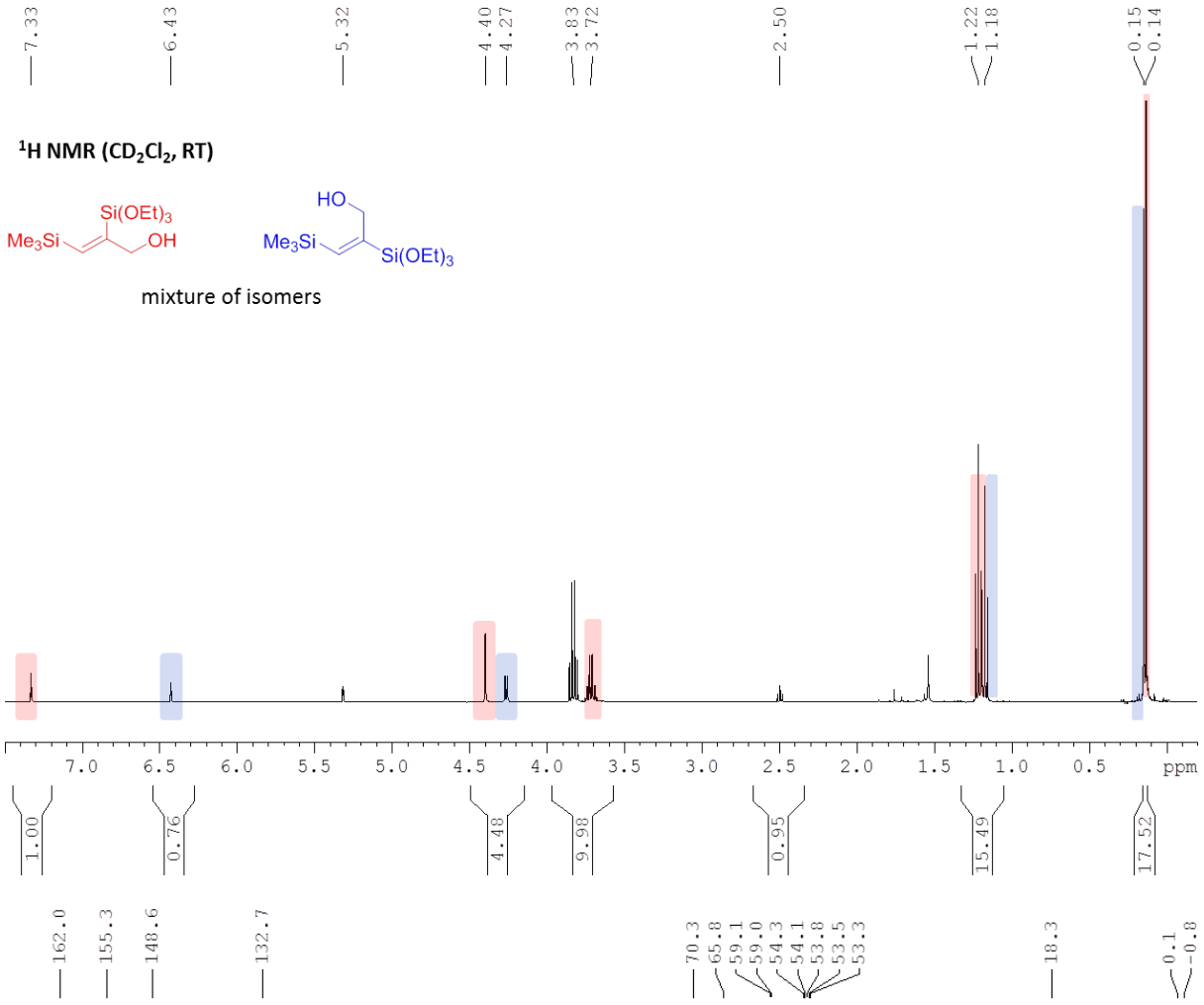


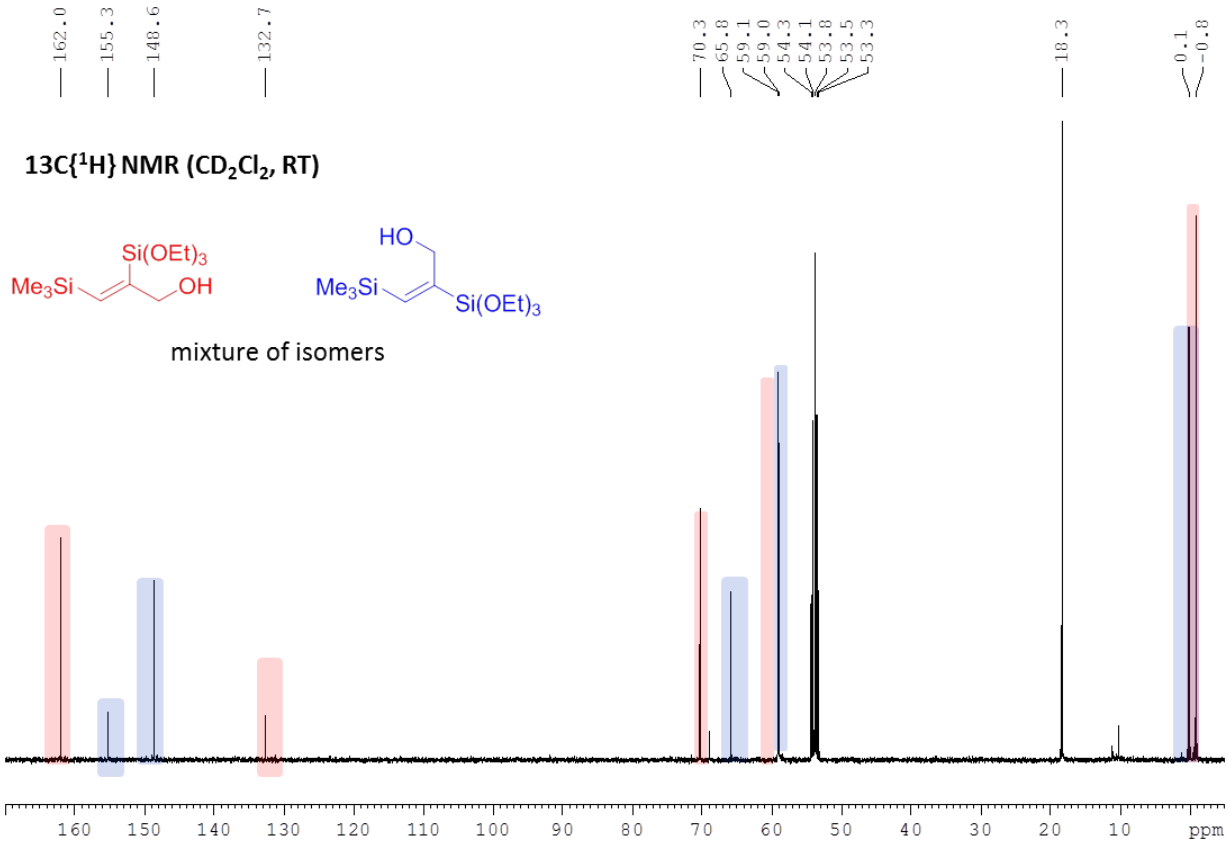
^{1}H NMR, CD_2Cl_2, 298 K



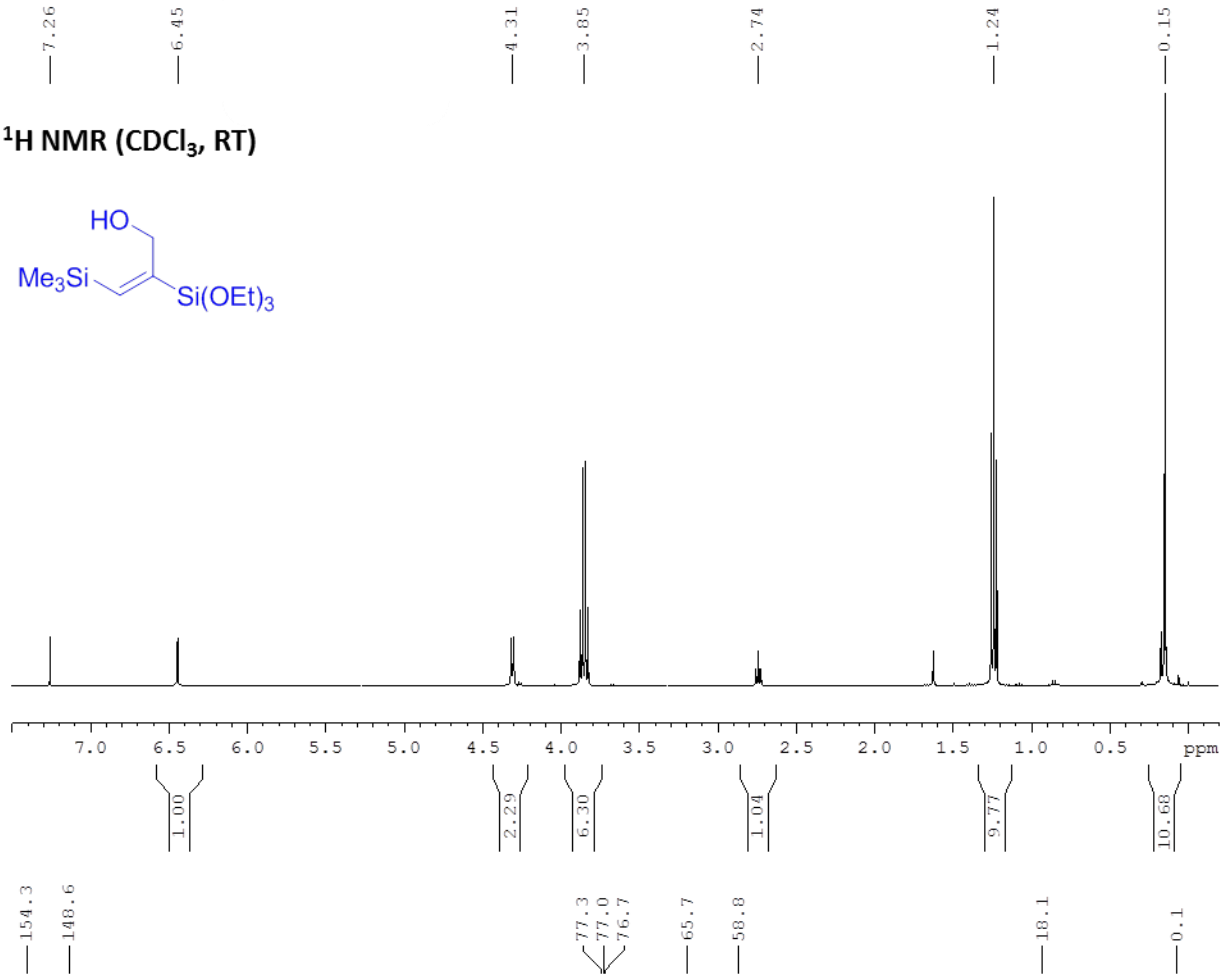
^{13}C{^{1}H} NMR, CD_2Cl_2, 298 K



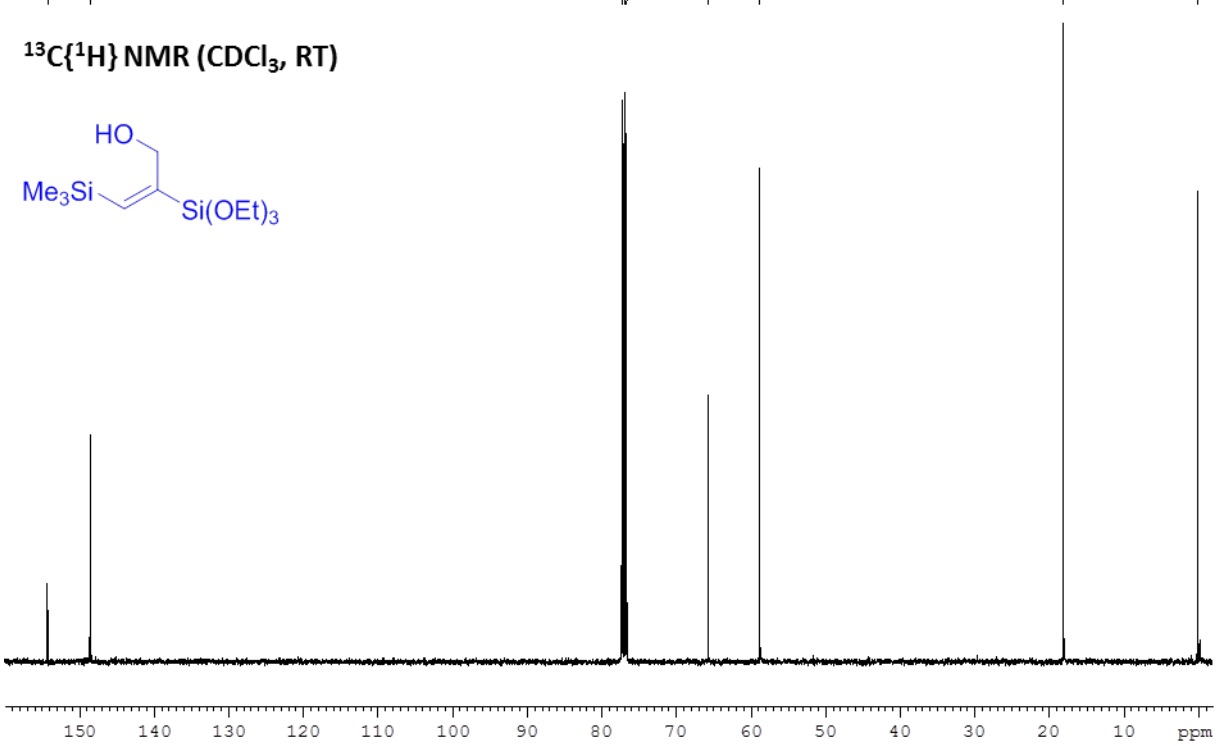

7.33
6.43
5.32
4.40
4.27
3.83
3.72
2.50
1.22
1.18
0.15
0.14
1H NMR (CD2Cl2, RT)
Si(OEt)3
Me3Si
OH
HO
Me3Si
Si(OEt)3
mixture of isomers
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.76
4.48
9.98
0.95
15.49
17.52


162.0
155.3
148.6
132.7
70.3
65.8
59.1
59.0
54.3
54.1
53.8
53.5
53.3
18.3
0.1
-0.8
13C{1H} NMR (CD2Cl2, RT)
Si(OEt)3
Me3Si
OH
HO
Me3Si
Si(OEt)3
mixture of isomers
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H NMR ($CDCl_3$, RT)



^{13}C{^{1}H} NMR ($CDCl_3$, RT)



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