Supporting Information

for

Coupling of N-Heterocyclic Carbenes to Terminal Alkynes at Half Sandwich Cobalt NHC Complexes

Katharina Lubitz and Udo Radius*

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

Corresponding author E-Mail address:
u.radius@uni-wuerzburg.de

1) Additional X-ray structures

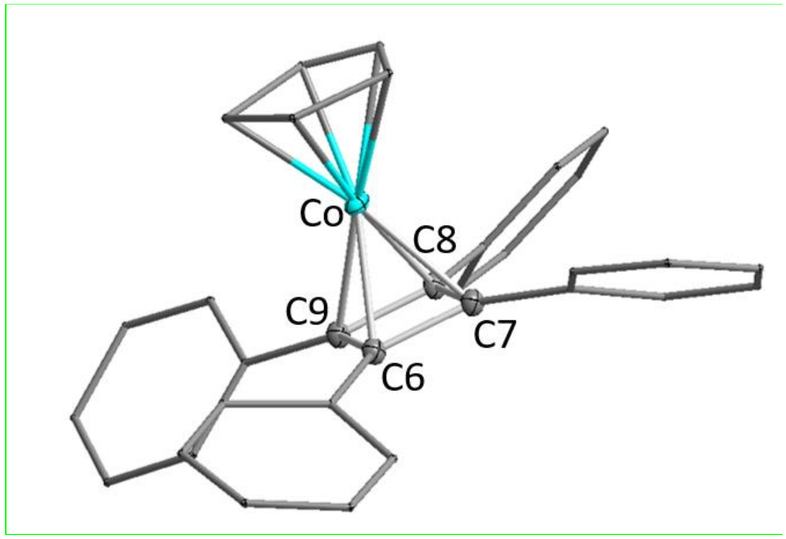


Figure S1: Molecular structure of [(η^5-C_5H_5)Co(η^4-C_4Ph_4)] (**5**) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond length [Å] and angles [°] in **5** Co–C6 1.977(7), Co–C7 1.983(7), Co–C8 1.974(7), Co–C9 1.976(7), Co–(η^4-C_4Ph_4)$_{Centroid}$ 1.6852(7), Co–(η^5-C_5H_5)$_{Centroid}$ 1.6670(7), C6–C7 1.441(10), C7–C8 1.464(7), C8–C9 1.458(9), C9–C6 1.466(8); η^5-C_5H_5)$_{Centroid}$–Co–(η^4-C_4Ph_4)$_{Centroid}$ 178.652(49), C6–C7–C8 91.2(6), C7–C8–C9 88.9(6), C8–C9–C6 89.4(6), C9–C6–C7 90.(6).

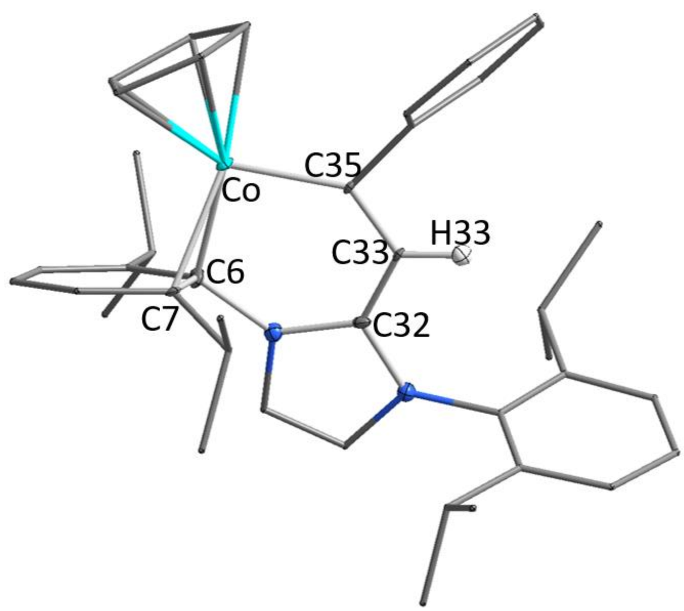


Figure S2: Preliminary molecular structure of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{$Dipp_2Im$})] (**6**) in the solid state.

2) NMR/IR/UV-Vis Spectra of Complexes (2-9)

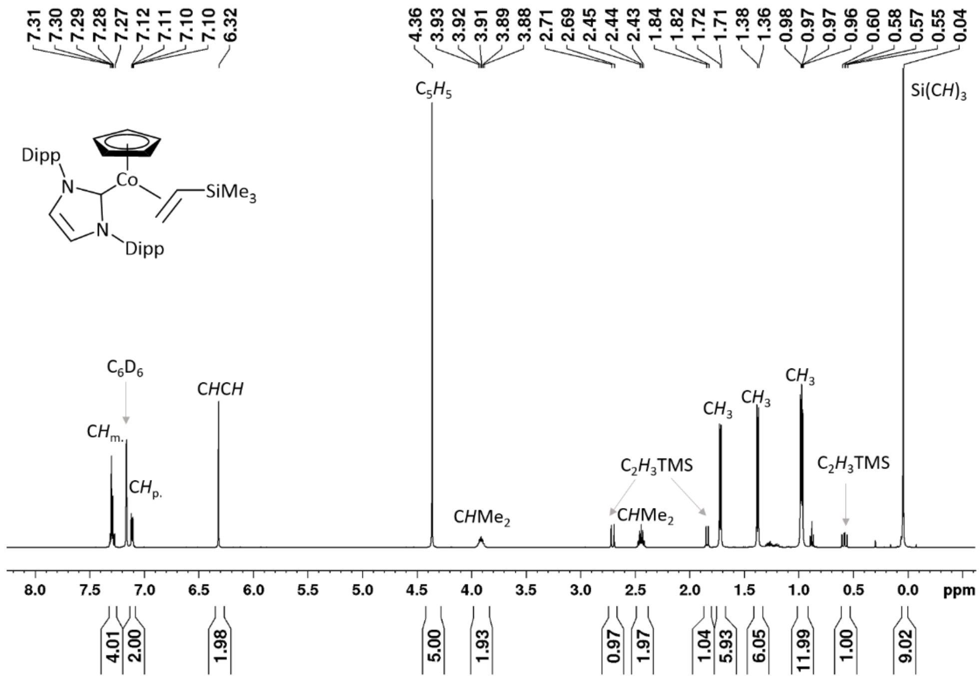


Figure S3: ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(Dipp_2Im)(\eta^2\text{-}C_2H_3SiMe_3)]$ (**2**) in C_6D_6.

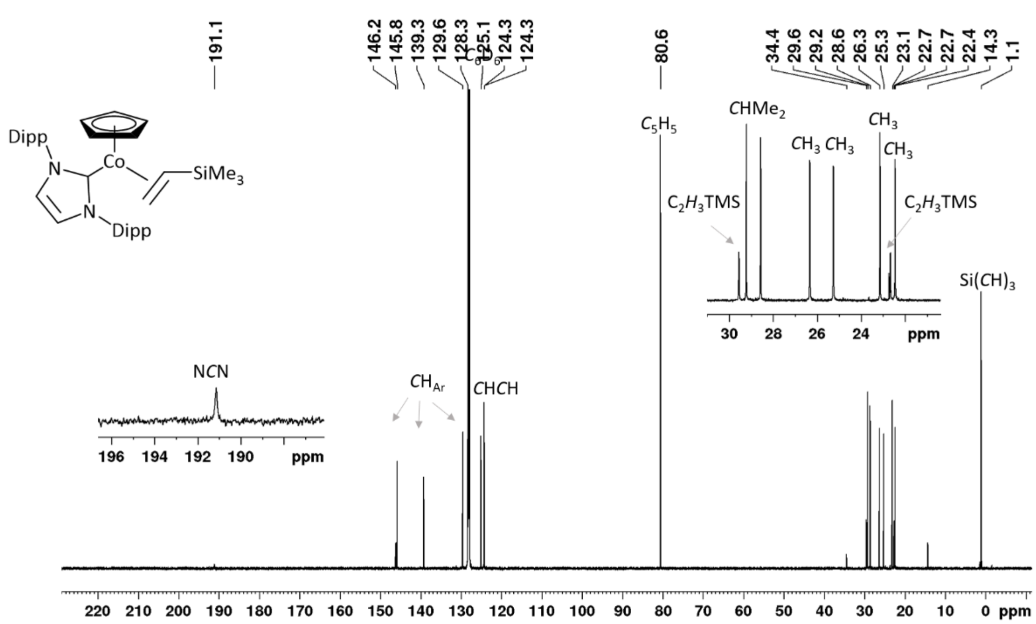


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(Dipp_2Im)(\eta^2\text{-}C_2H_3SiMe_3)]$ (**2**) in C_6D_6.

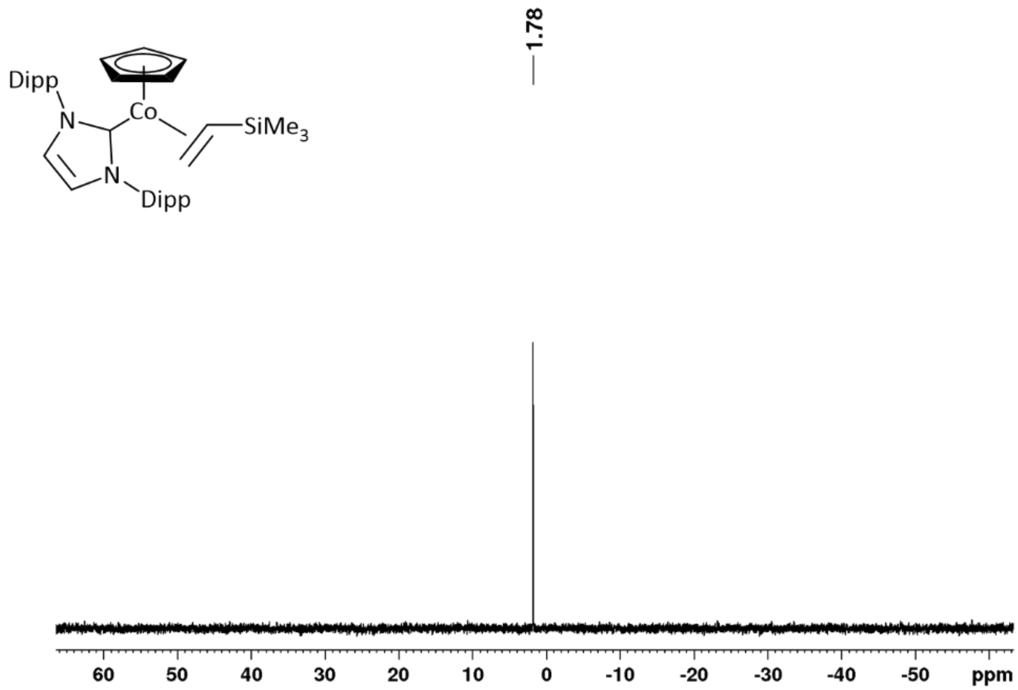


Figure S5: ^{29}Si NMR spectrum of [(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-$C_2H_3SiMe_3$)] (**2**) in C_6D_6.

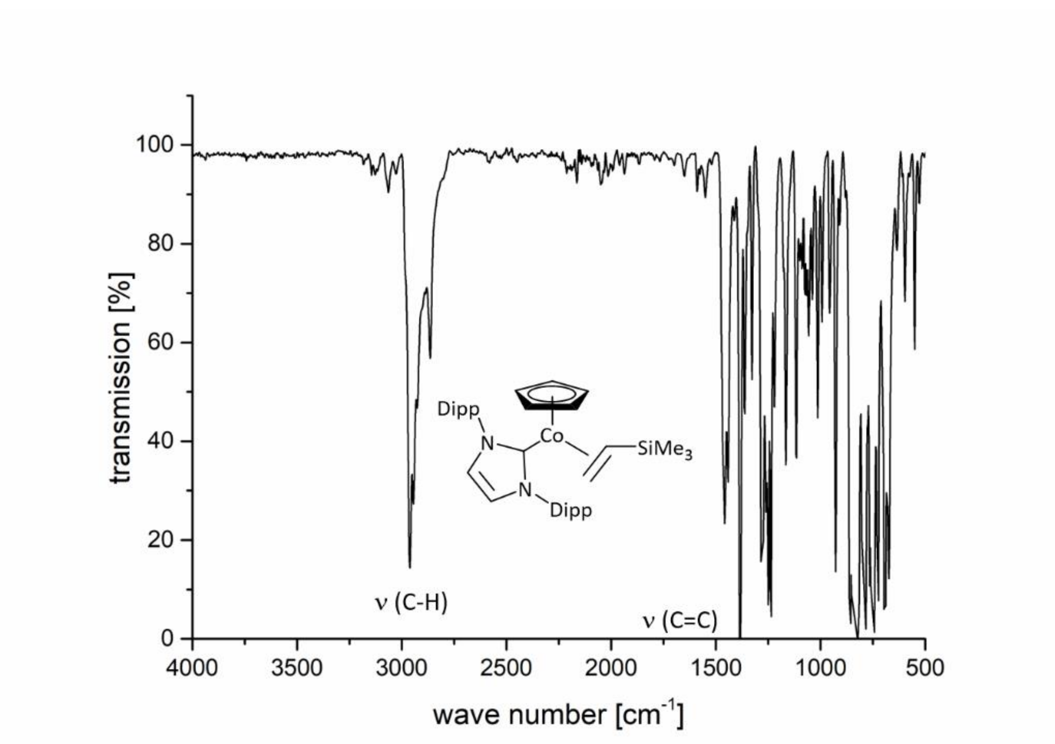


Figure S6: IR spectrum of [(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-$C_2H_3SiMe_3$)] (**2**).

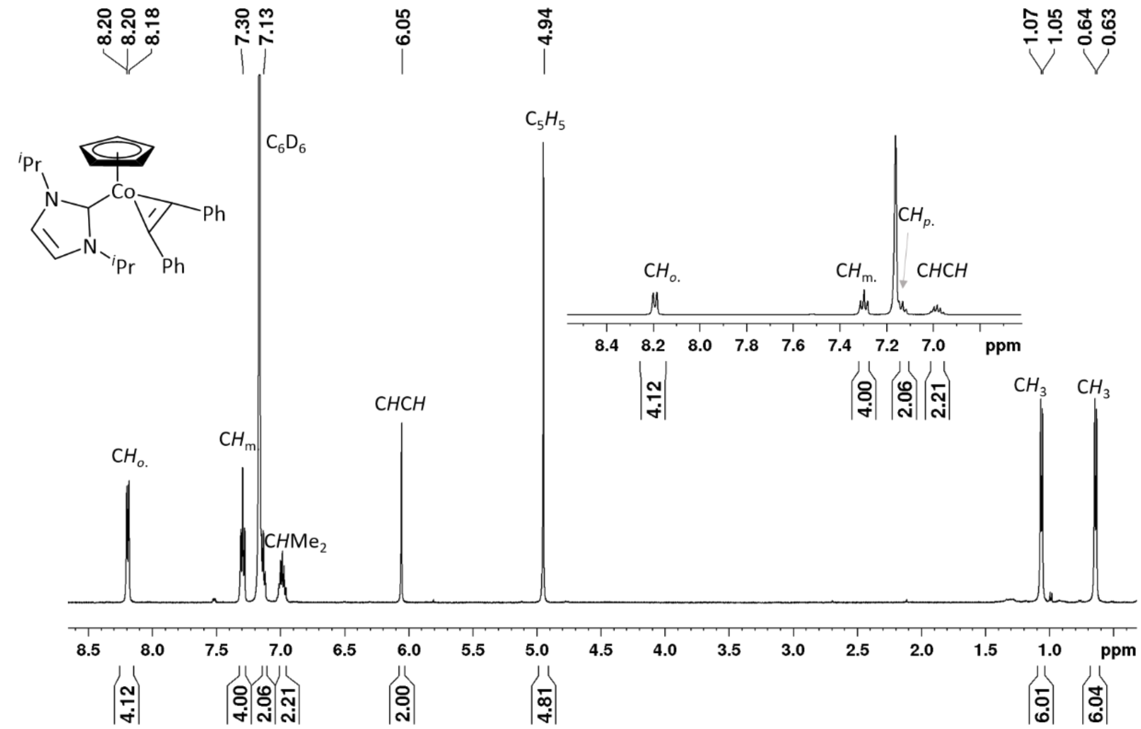


Figure S7: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co($^{i}Pr_2Im$)(η^2-C_2Ph_2)] (**3**) in C_6D_6.

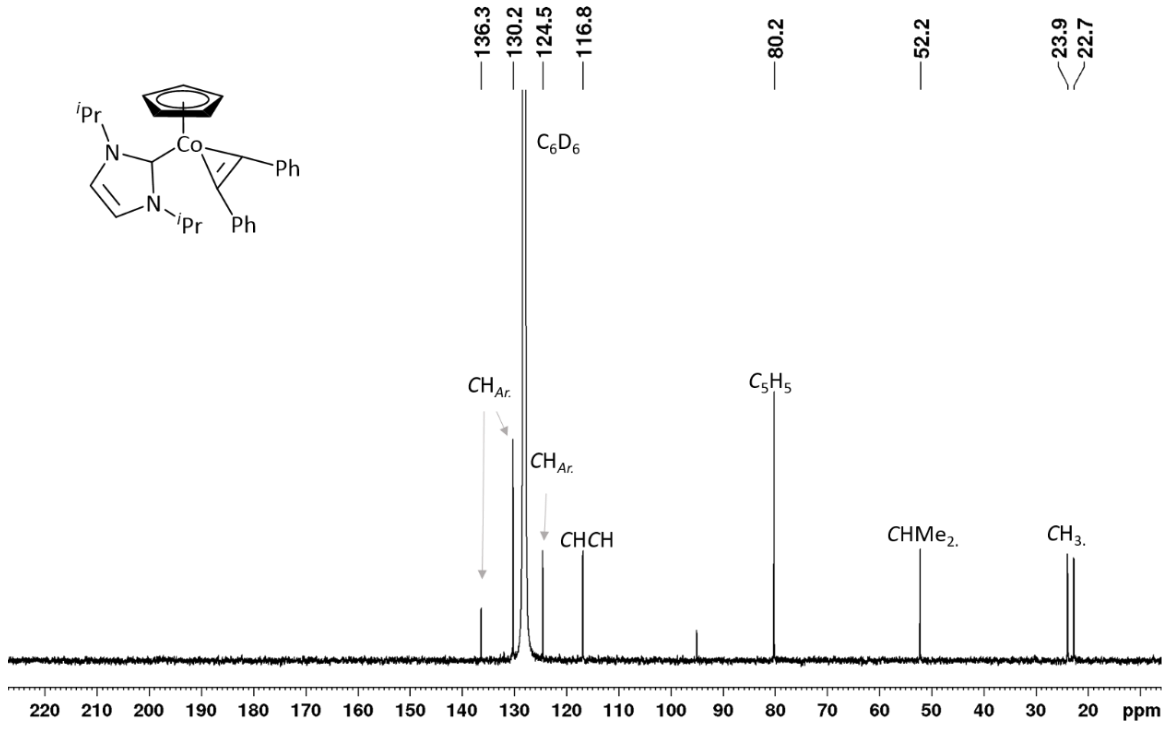


Figure S8: $^{13}C\{^1H\}$ NMR spectrum of [(η^5-C_5H_5)Co($^{i}Pr_2Im$)(η^2-C_2Ph_2)] (**3**) in C_6D_6. The resonances of the carbene carbon atom (183.0 ppm) and the alkyne carbon atoms (129.4 ppm) have been identified in a $^{13}C\{^1H\}$ HMBC experiment.

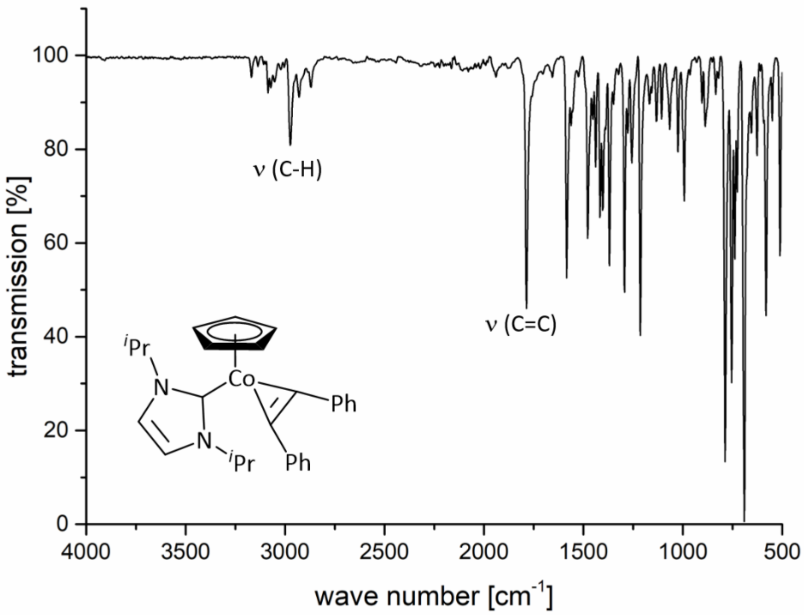


Figure S9: IR spectrum of [(η^5-C_5H_5)Co(^{i}Pr_2Im)(η^2-C_2Ph_2)] (**3**).

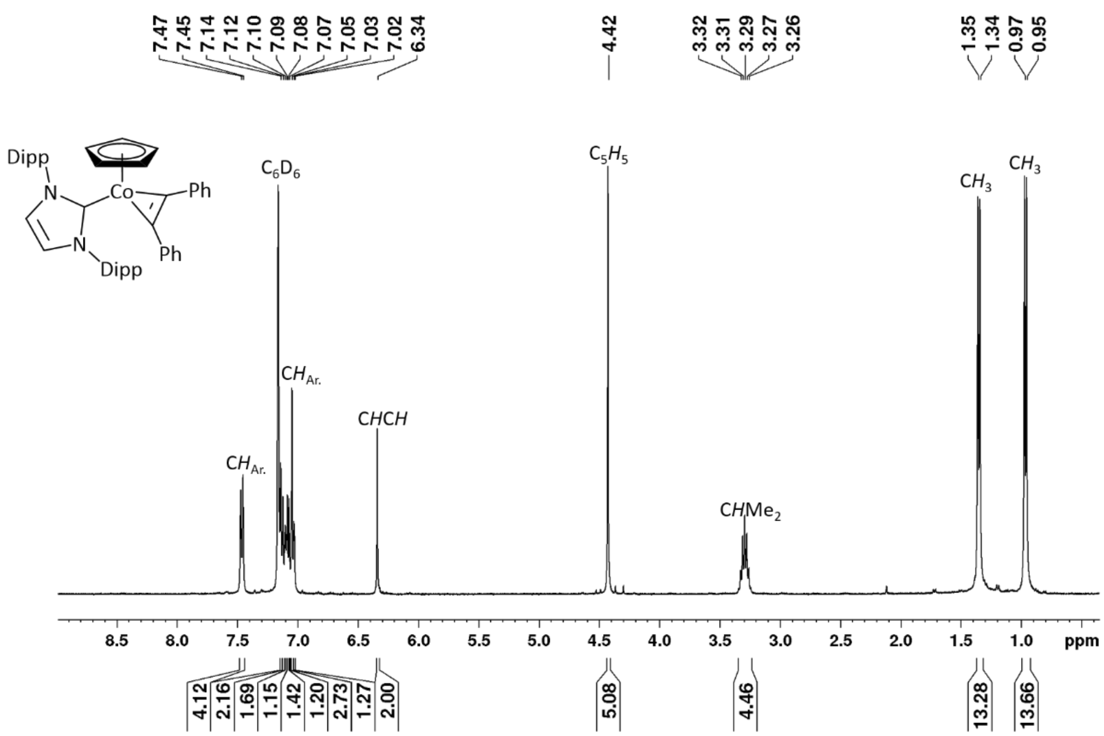


Figure S10: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co($Dipp_2$Im)(η^2-C_2Ph_2)] (**4**) in C_6D_6.

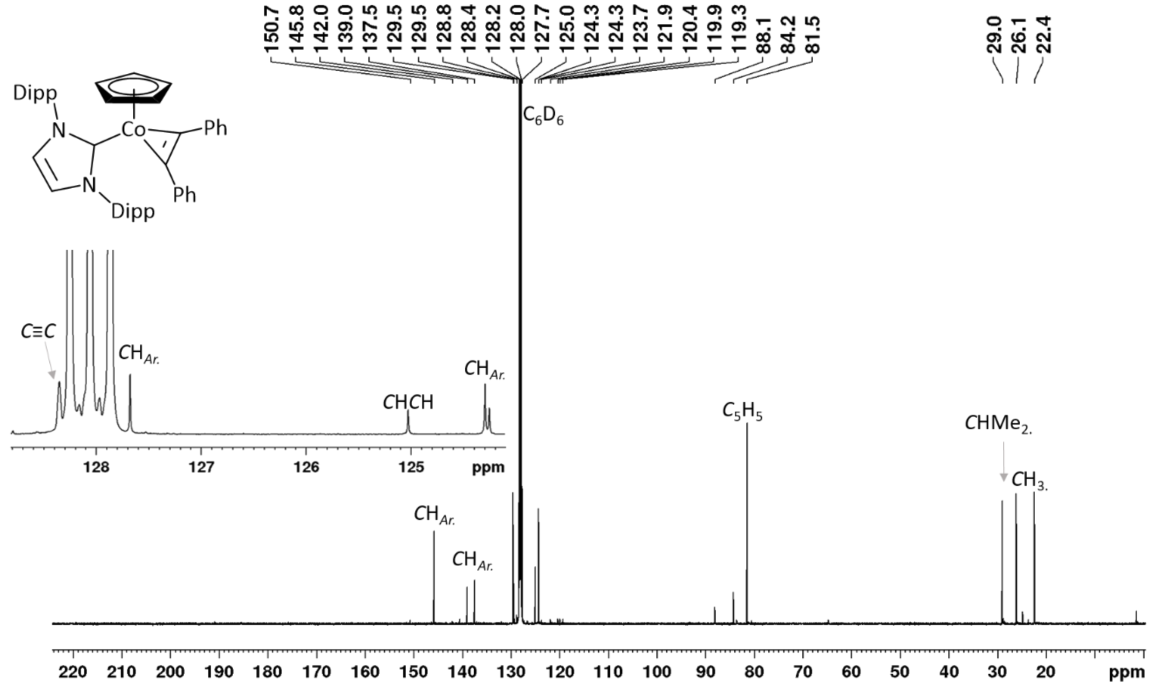


Figure S11: $^{13}C\{^1H\}$ NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(Dipp_2Im)(\eta^2\text{-}C_2Ph_2)]$ (**4**) in C_6D_6. The resonance of the carbene carbon atom have been identified in a $^{13}C\{^1H\}$ HMBC experiment at 196.6 ppm.

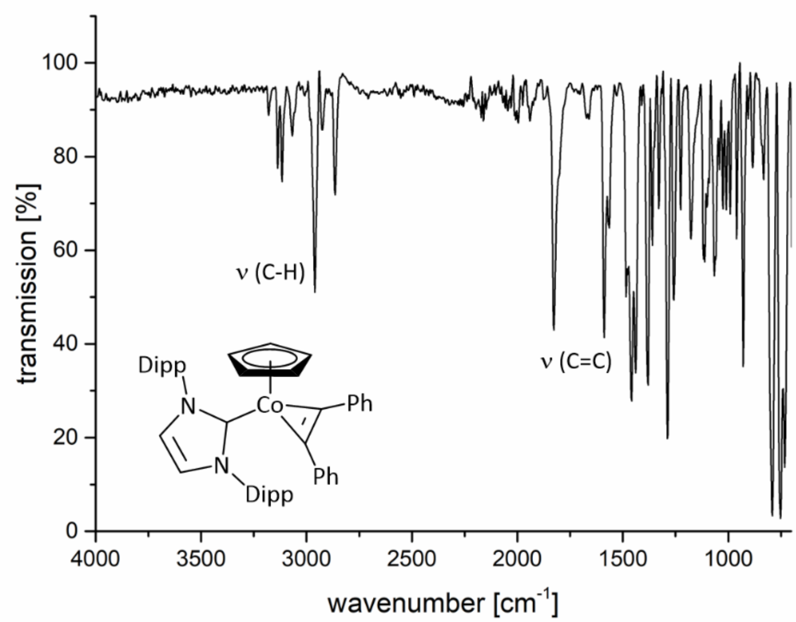


Figure S12: IR spectrum of $[(\eta^5\text{-}C_5H_5)Co(Dipp_2Im)(\eta^2\text{-}C_2Ph_2)]$ (**4**).

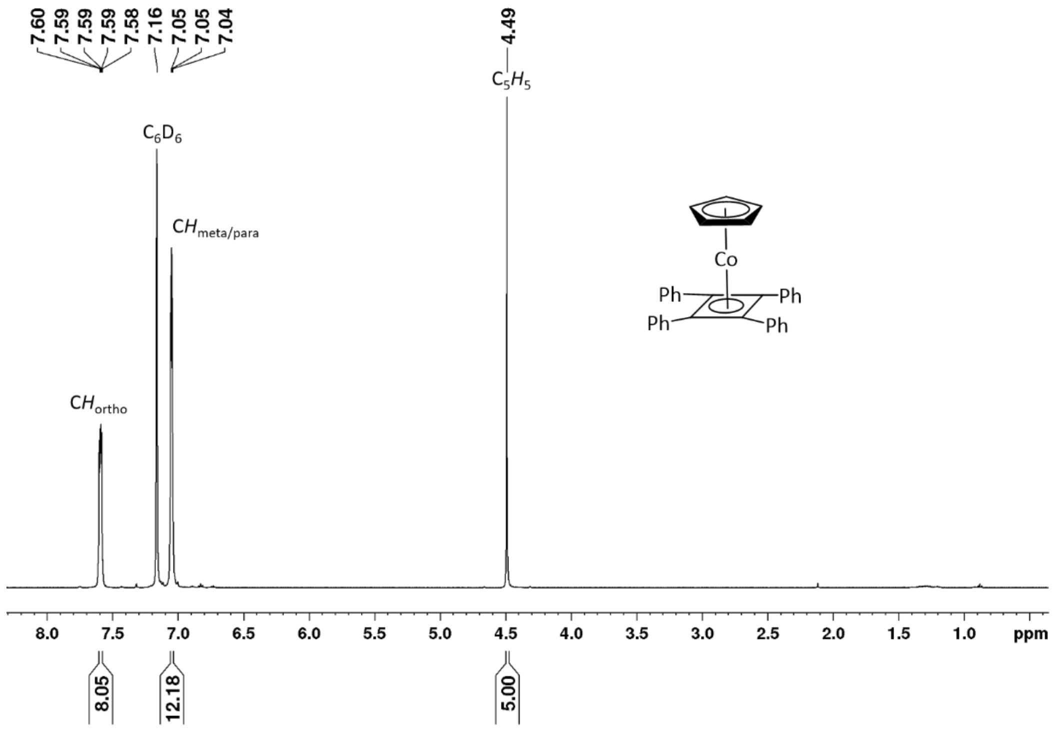


Figure S13: ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_4)]$ (**5**) in C_6D_6.

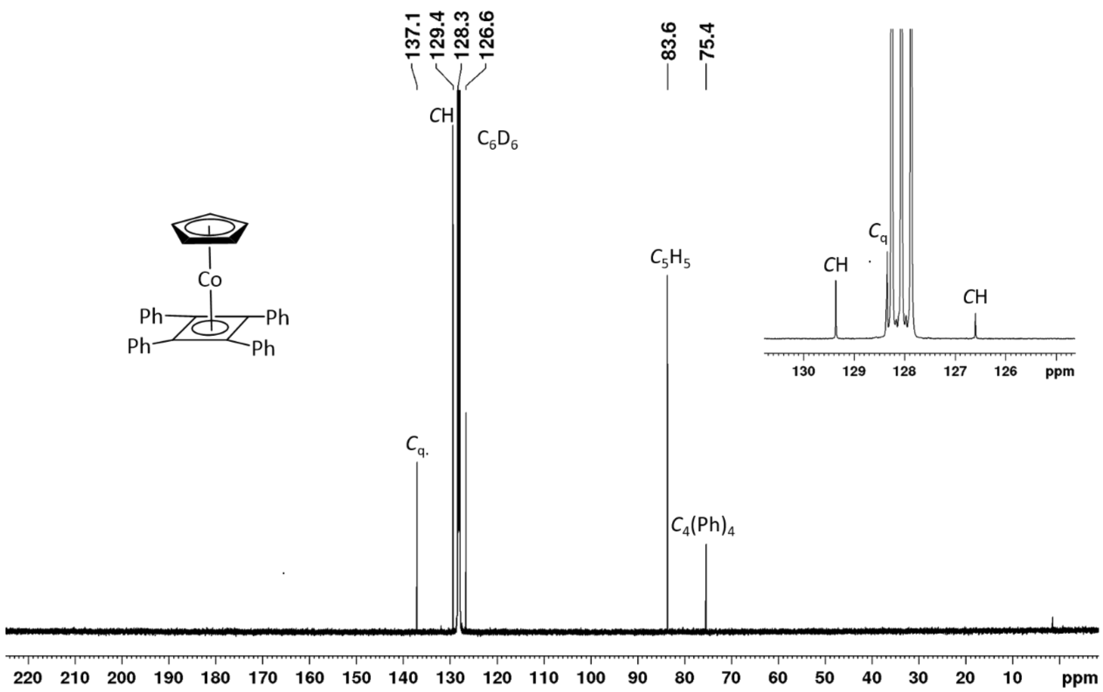


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_4)]$ (**5**) in C_6D_6.

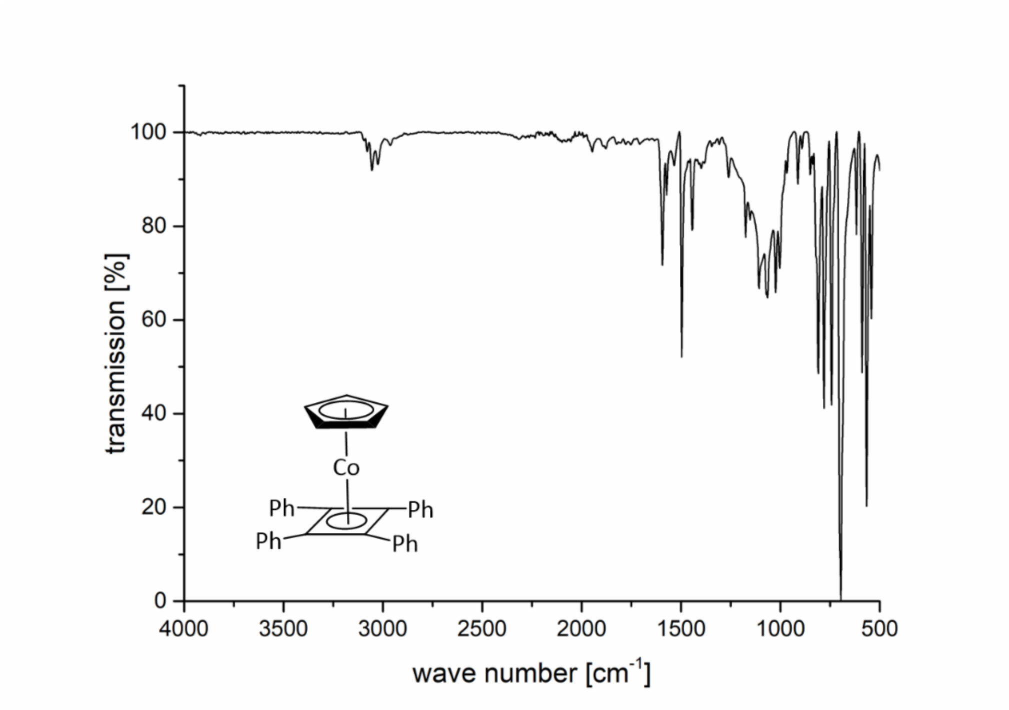


Figure S15: IR spectrum of [(η^5-C_5H_5)Co(η^4-C_4Ph_4)] (**5**).

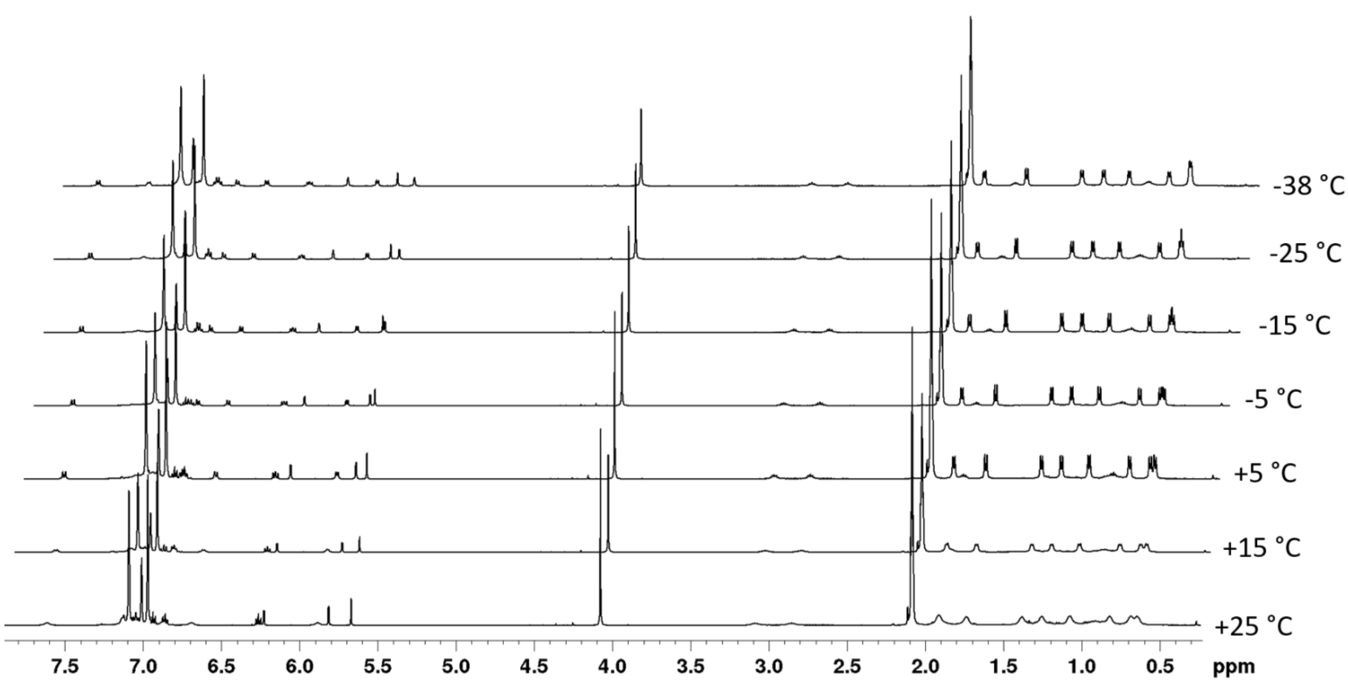


Figure S16: ^{1}H NMR spectra of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{Dipp$_2$Im})] (**6**) at different temperatures in d^8 toluene. The resonances of the methyl and methine protons of the Dipp *iso*-propyl groups are broadened at room temperature, presumably due to on/off coordination of one of the aryl ring π-system at the Co atom (see drawing below), associated with dynamics of the NHC unit of the complex. At temperatures below +10°C the resonances became sharp.

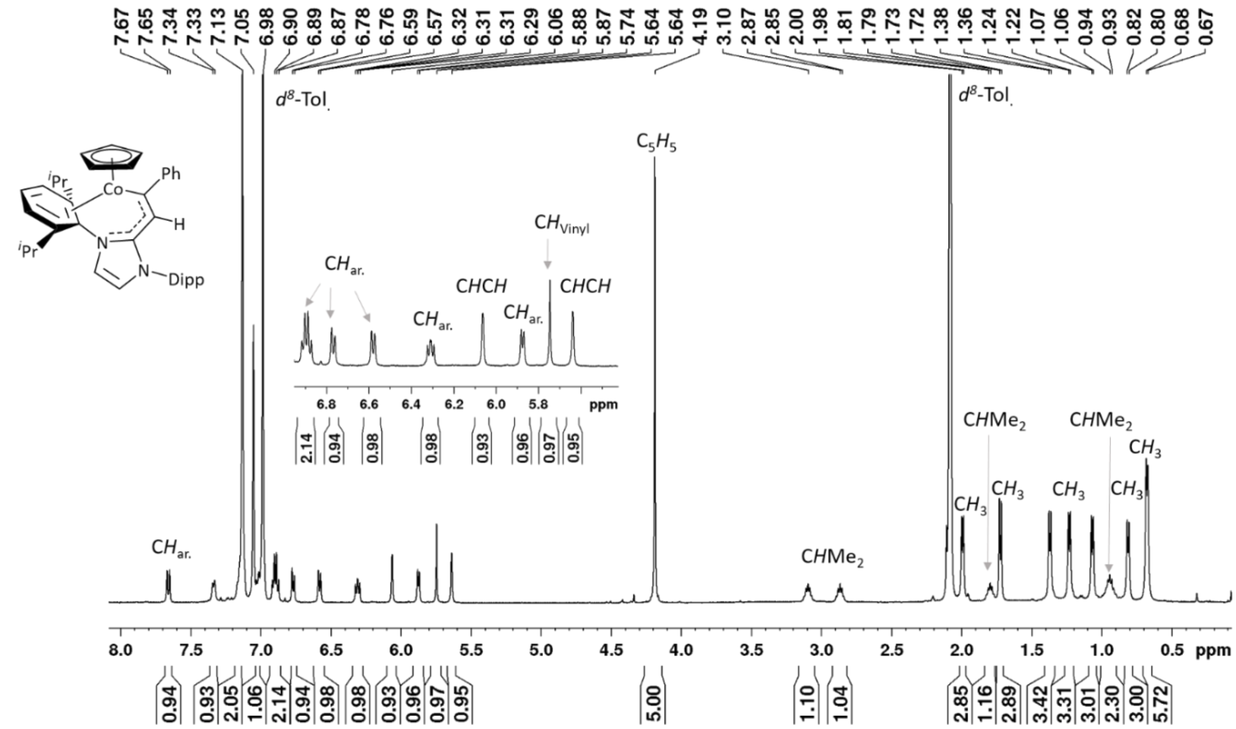


Figure S17: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{Dipp$_2$Im})] (**6**) at -38 °C in d^8 toluene.

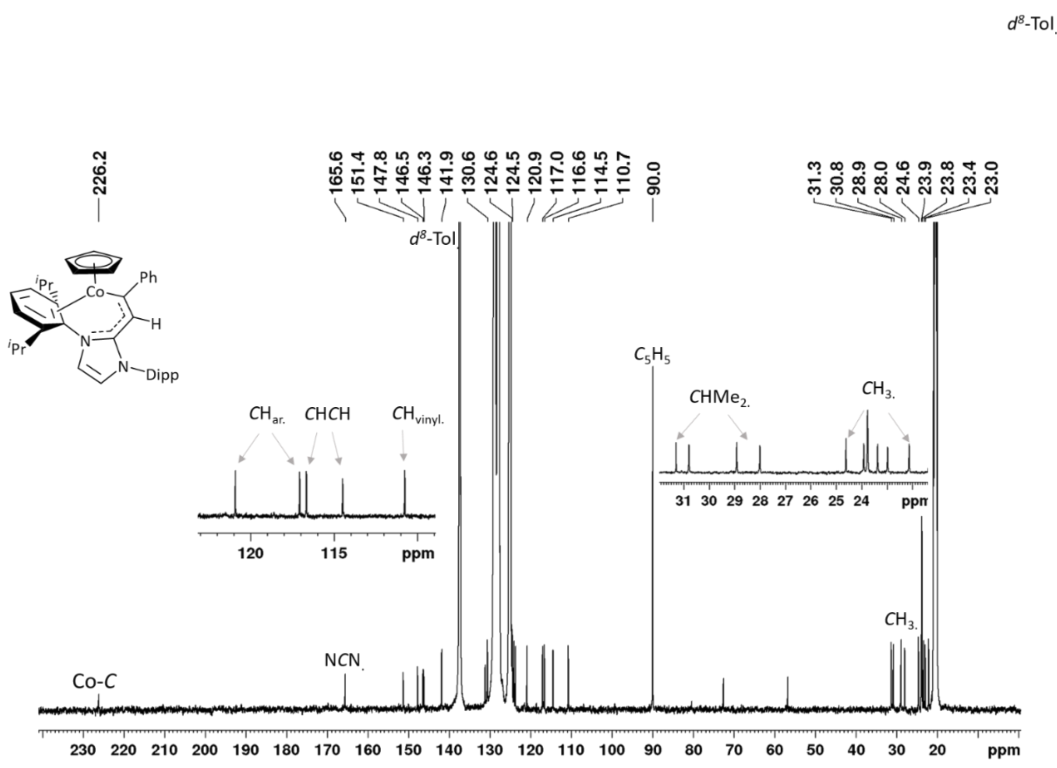


Figure S18: ^{13}C{^{1}H} NMR spectrum of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{Dipp$_2$Im})] (**6**) at -38 °C in d^8 toluene.

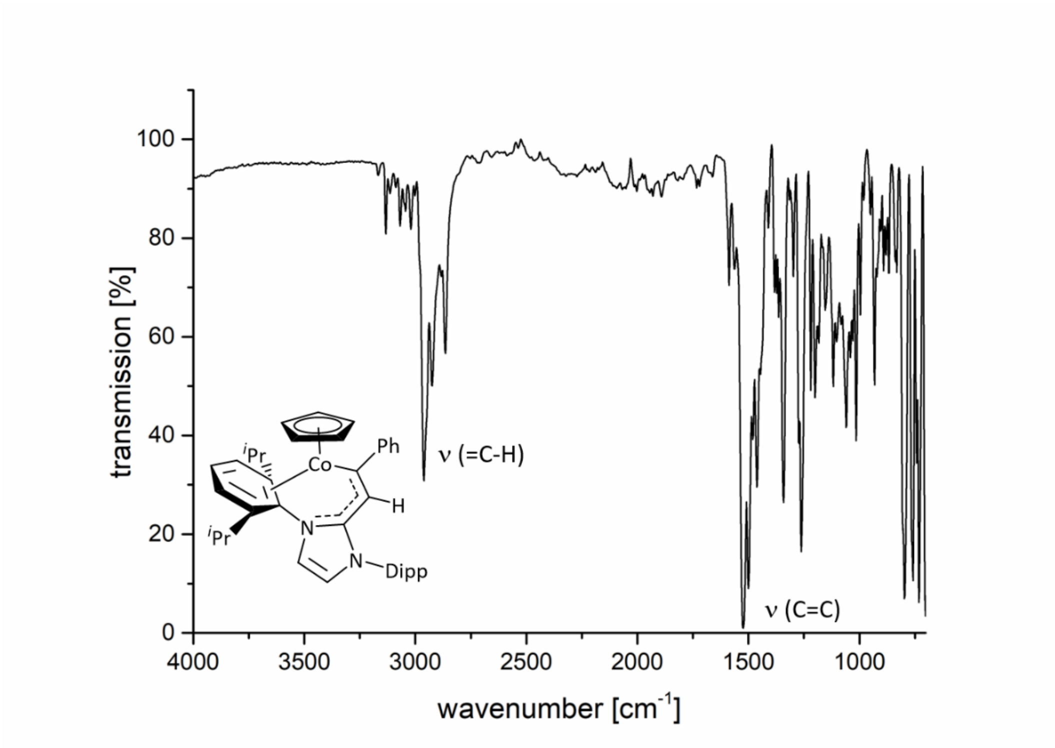


Figure S19: IR spectrum of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{Dipp$_2$Im})] (**6**).

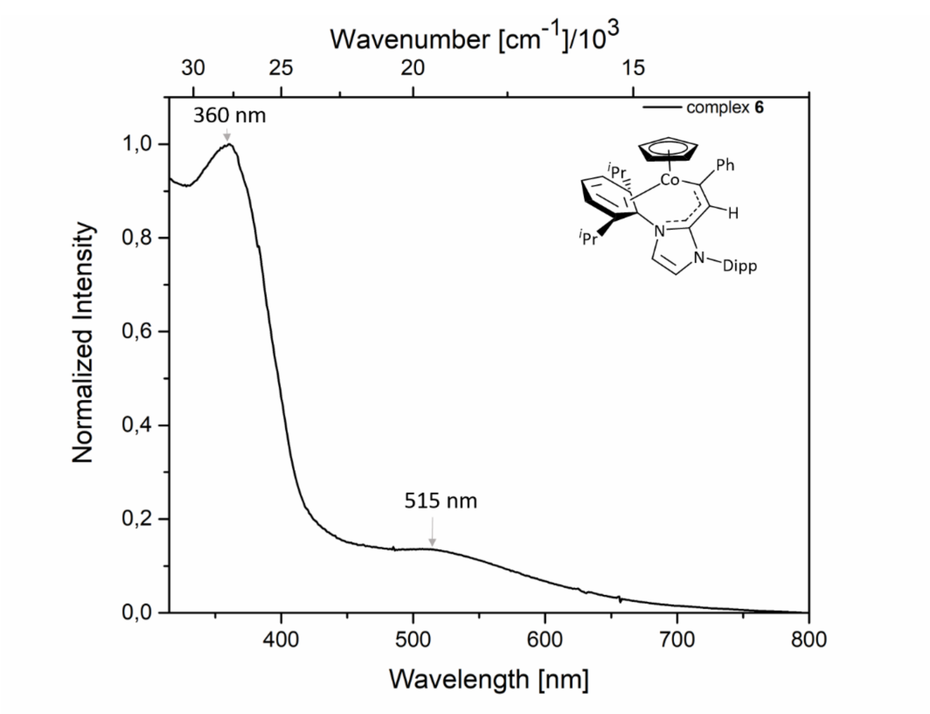


Figure S20: UV-Vis spectrum of [(η^5-C_5H_5)Co(–C{Ph}=C{H}{Dipp$_2$Im})] (**6**).

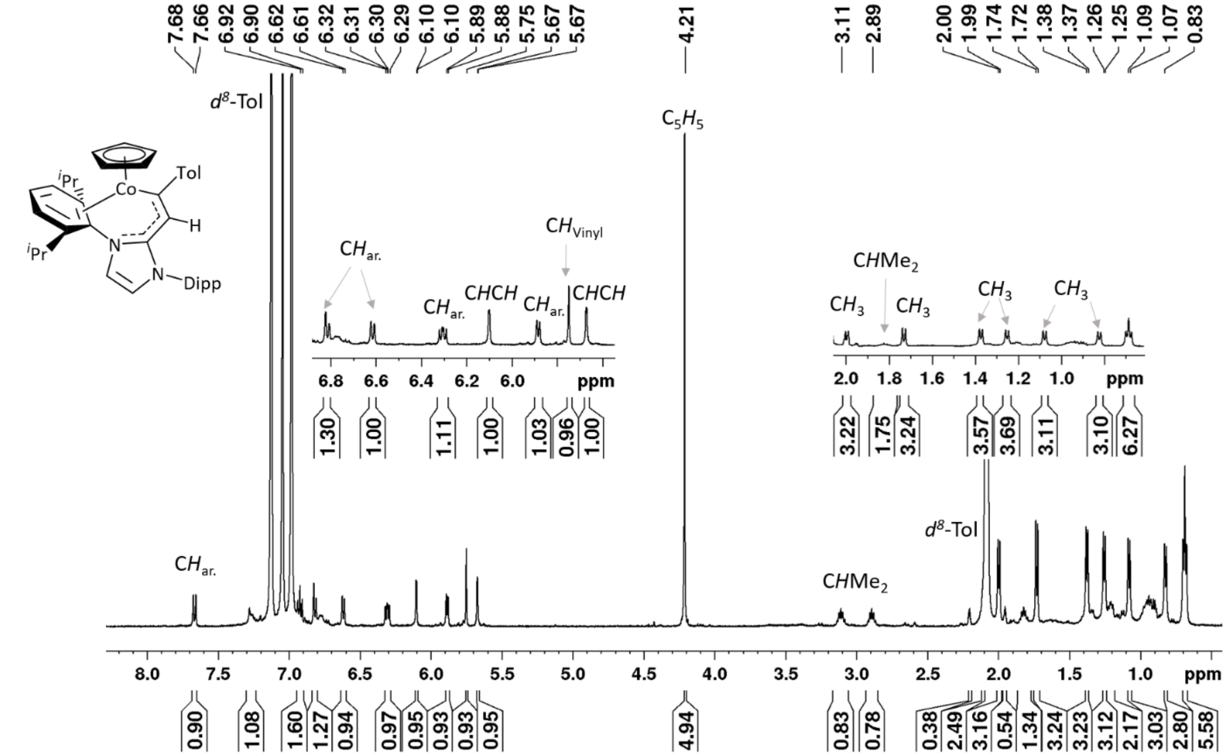


Figure S21: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co(–C{Tol}=C{H}{Dipp$_2$Im})] (**7**) at -38 °C in d^8 toluene.

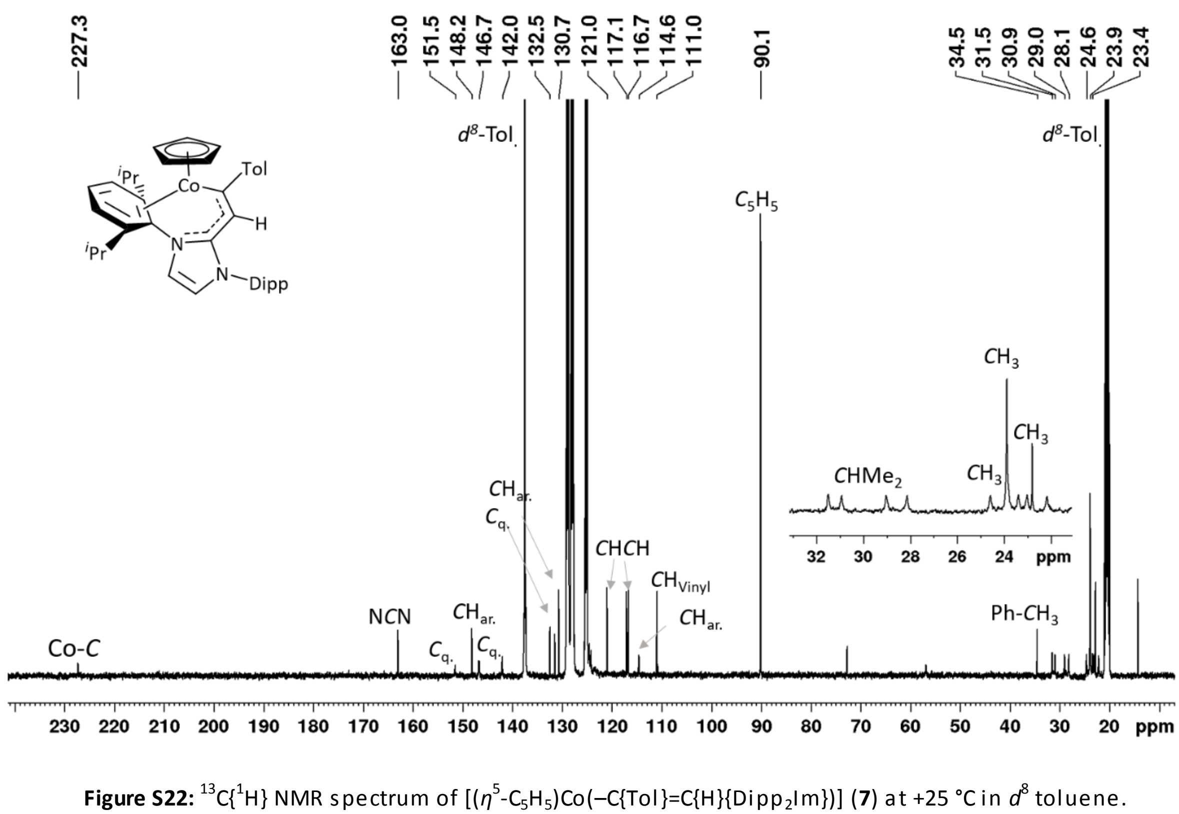


Figure S22: ^{13}C{^{1}H} NMR spectrum of [(η^5-C_5H_5)Co(–C{Tol}=C{H}{Dipp$_2$Im})] (**7**) at +25 °C in d^8 toluene.

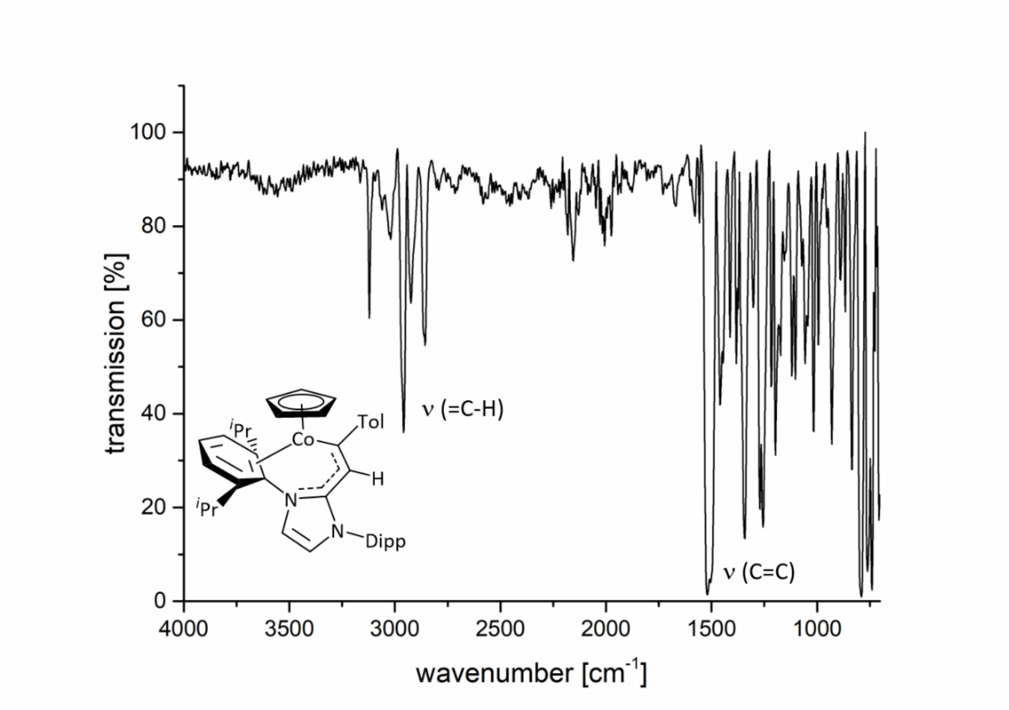


Figure S23: IR spectrum of [(η^5-C_5H_5)Co(–C{Tol}=C{H}{Dipp$_2$Im})] (**7**).

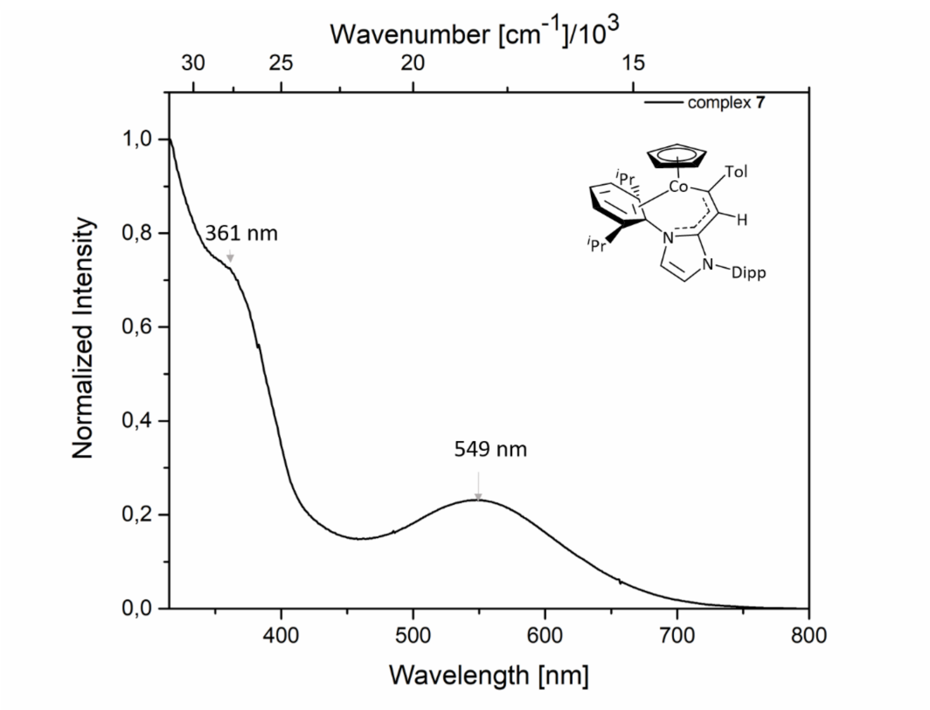


Figure S24: UV-Vis spectrum of [(η^5-C_5H_5)Co(–C{Tol}=C{H}{Dipp$_2$Im})] (**7**).

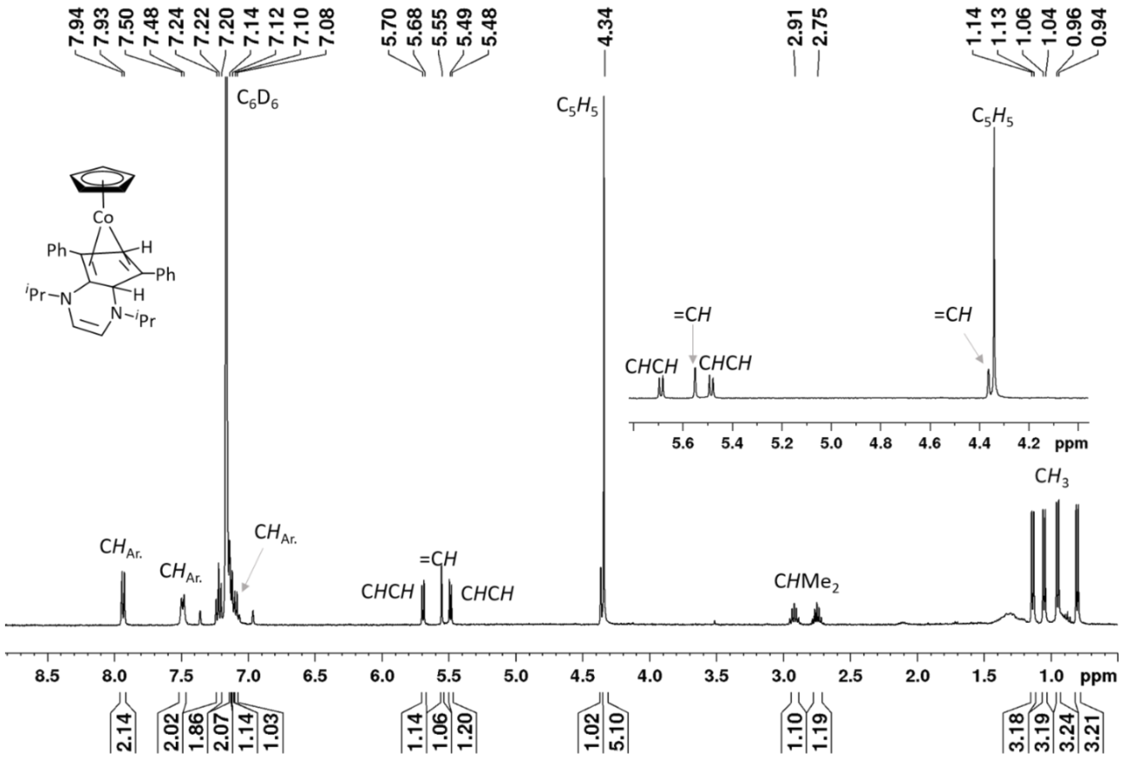


Figure S25: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co(η^4{(RER-NHC)$C_4H_2Ph_2$}] (**8**) in C_6D_6.

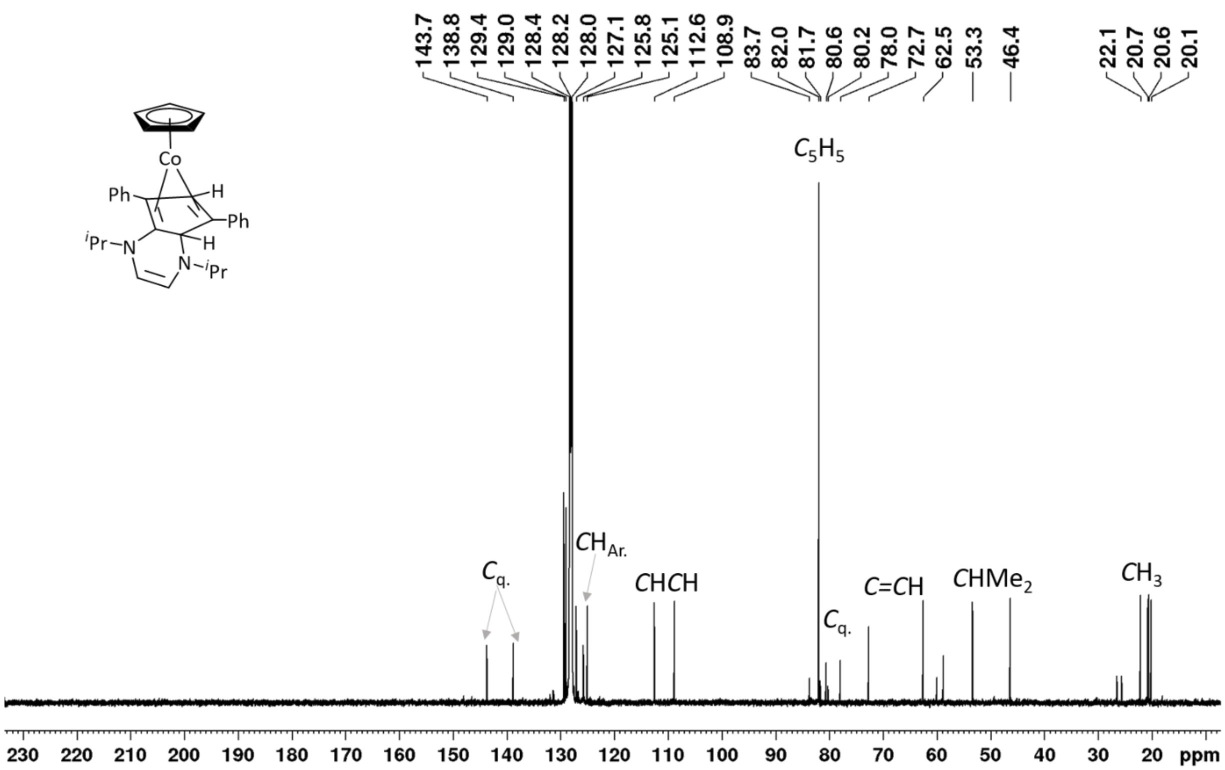


Figure S26: $^{13}C\{^1H\}$ NMR spectrum of [(η^5-C_5H_5)Co(η^4{(RER-NHC)$C_4H_2Ph_2$}] (**8**) in C_6D_6.

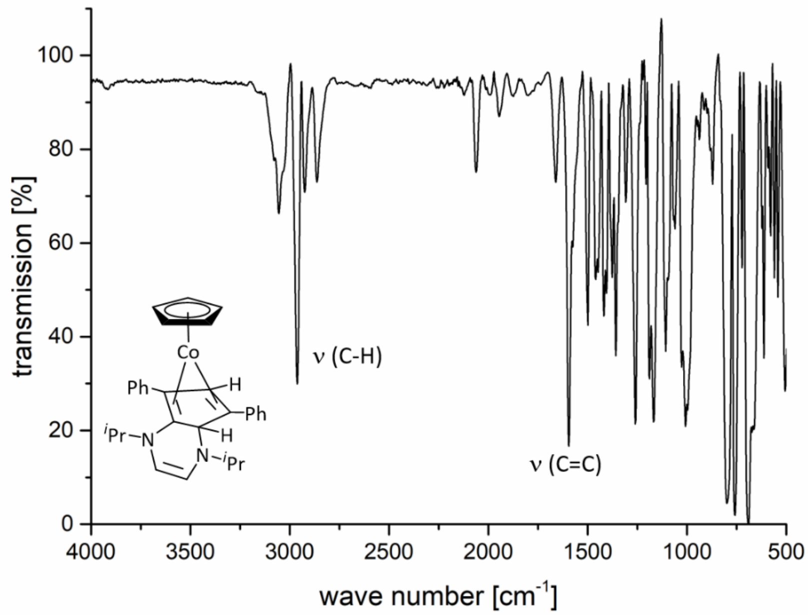


Figure 27: IR spectrum of [(η^5-C_5H_5)Co(η^4{(RER-NHC)$C_4H_2Ph_2$}] (**8**).

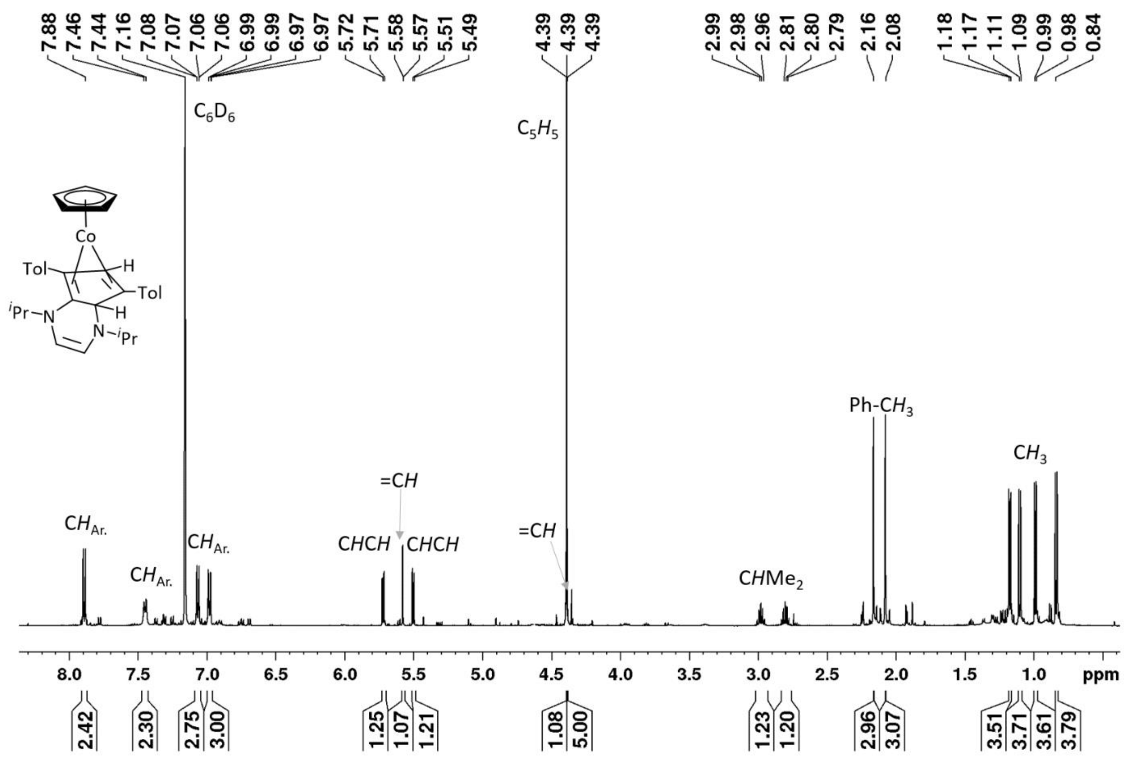


Figure S28: ^{1}H NMR spectrum of [(η^5-C_5H_5)Co(η^4{(RER-NHC)$C_4H_2Tol_2$}] (**9**) in C_6D_6.

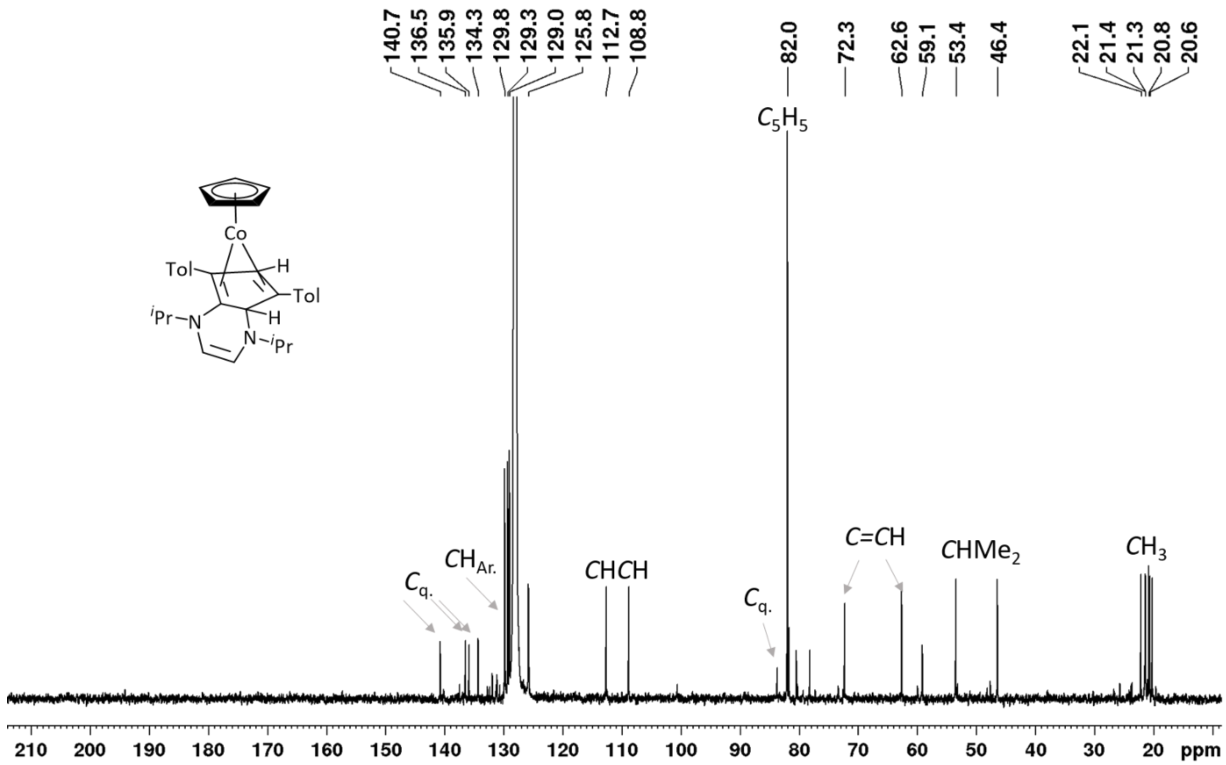


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of $[(\eta^5\text{-}C_5H_5)Co(\eta^4\{(RER\text{-}NHC)C_4H_2Tol_2\}]$ (**9**) in C_6D_6.

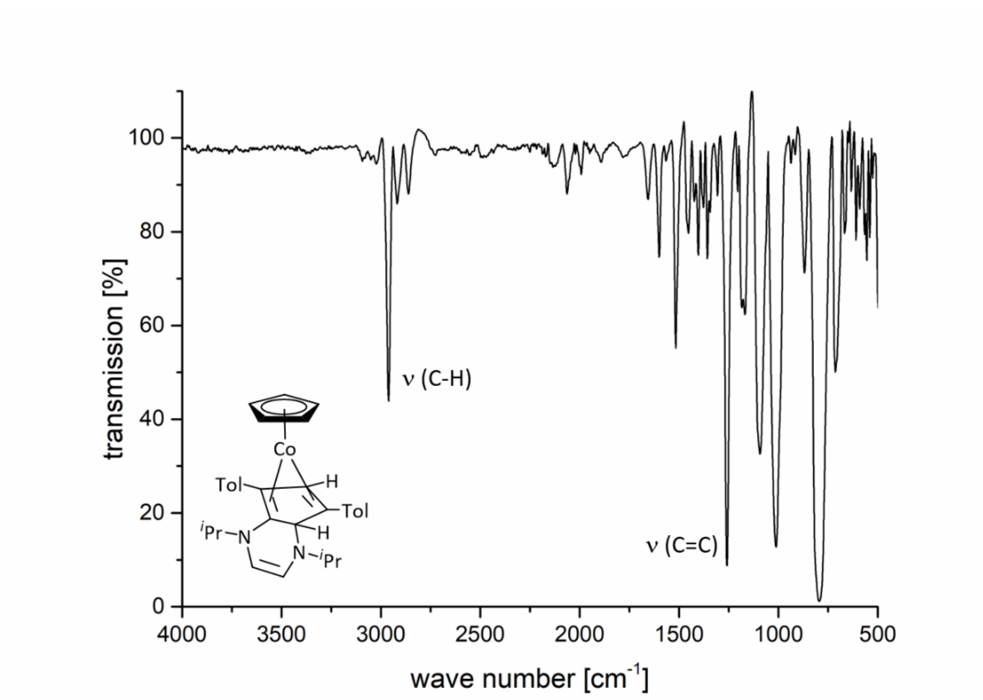


Figure S30: IR spectrum of $[(\eta^5\text{-}C_5H_5)Co(\eta^4\{(RER\text{-}NHC)C_4H_2Tol_2\}]$ (**9**).

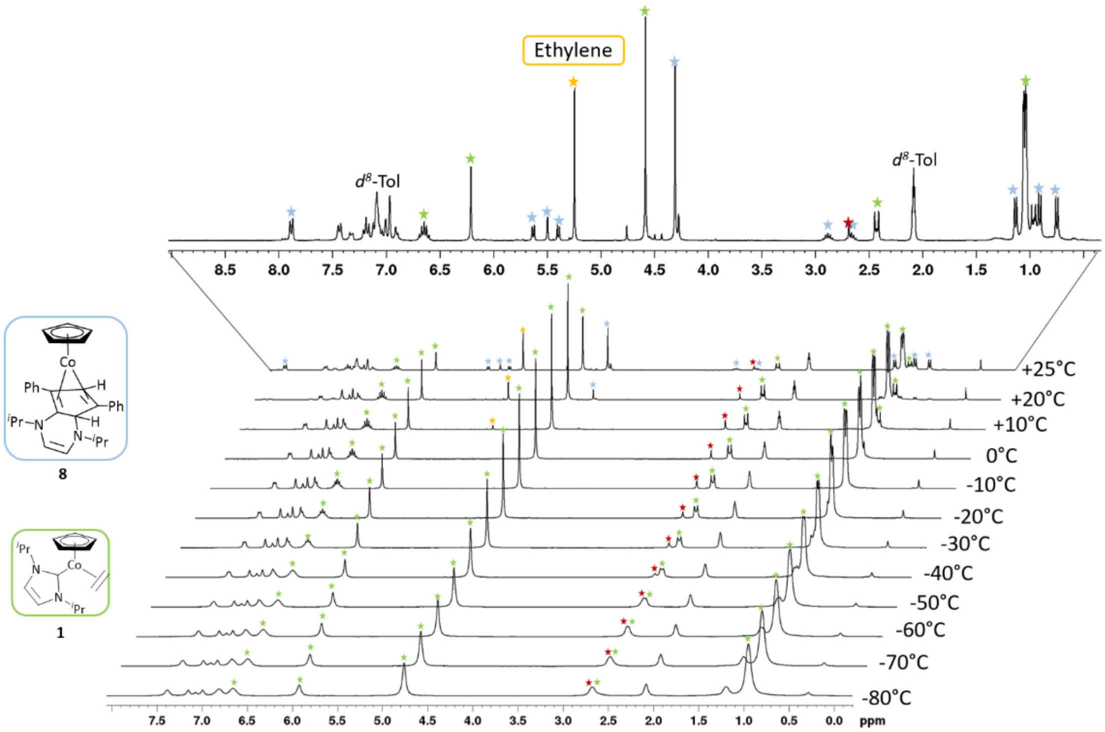


Figure S31: ^{1}H NMR spectra of the reaction of [(η^5-C_5H_5)Co(^{i}Pr$_2$Im)(η^2-C_2H_4)] **1** (green) with one equivalent phenylacetylene (red) in d^8-toluene at different temperatures starting at -80°C. This reaction leads directly [(η^5-C_5H_5)Co(η^4{(RER-NHC)$C_4H_2Ph_2$}] (**8**) (blue) (and **1**) at 20 °C. After the reaction has been completed, the NMR spectrum at top reveals a reaction mixture of **1** and **8** in a ratio round 1:1, as well as free ethylene (yellow). No resonances for any intermediate was detected.

3) NMR spectra of the experiments concerning the catalytic alkyne trimerization

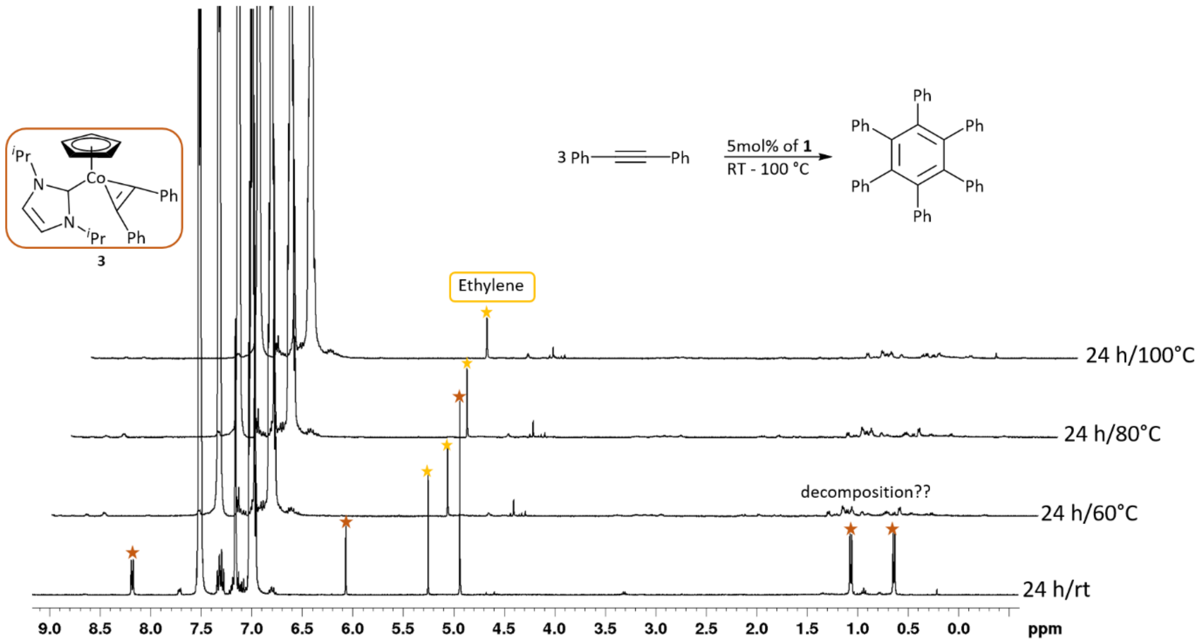


Figure S32: [1]H NMR spectra of the reaction of diphenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(iPr$_2$Im)(η^2-C_2H_4)] **1** (5mol%) in C_6D_6 at different temperatures. The NMR spectrum at room temperature reveals the resonances found for complex **3** (**brown**) and a singlet of free ethylene (**yellow**), eliminated from starting compound **1**. At higher temperatures complex **3** decomposes. All spectra reveal major amounts of diphenylacetylene and no [2+2+2] cycloaddition product of diphenylacetylene was formed.

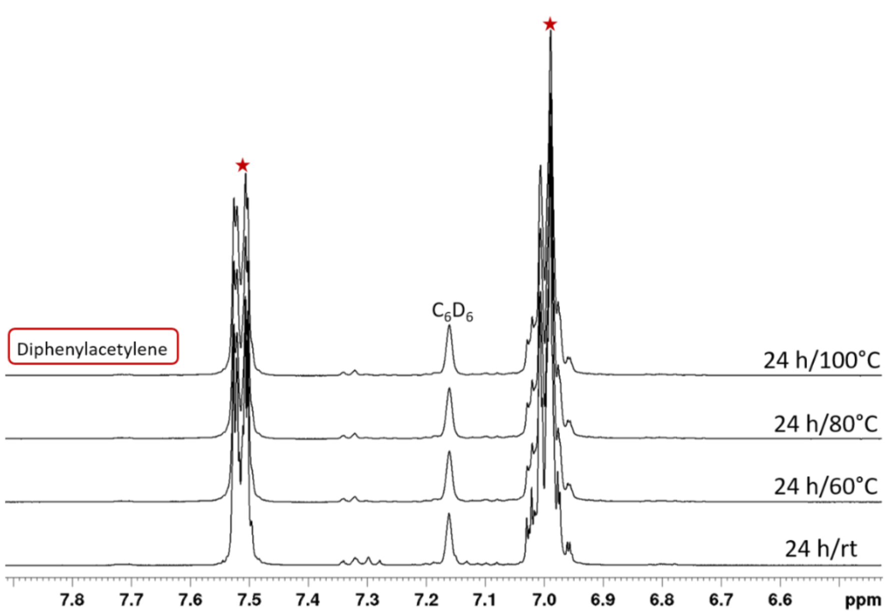


Figure S33: [1]H NMR spectra of the reaction of diphenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(iPr$_2$Im)(η^2-C_2H_4)] **1** (5mol%) in C_6D_6 at different temperatures, depicted is the aromatic region of the [1]H NMR spectra. Only the resonances of diphenylacetylene (**red**) were detected, even at high temperatures (100 °C). This result has been confirmed by $^{13}C\{^1H\}$ NMR spectroscopy and GC/MS analyses; the latter indicates only traces of hexaphenylbenzene (534.23), beside a major amount of diphenylacetylene (278.2).

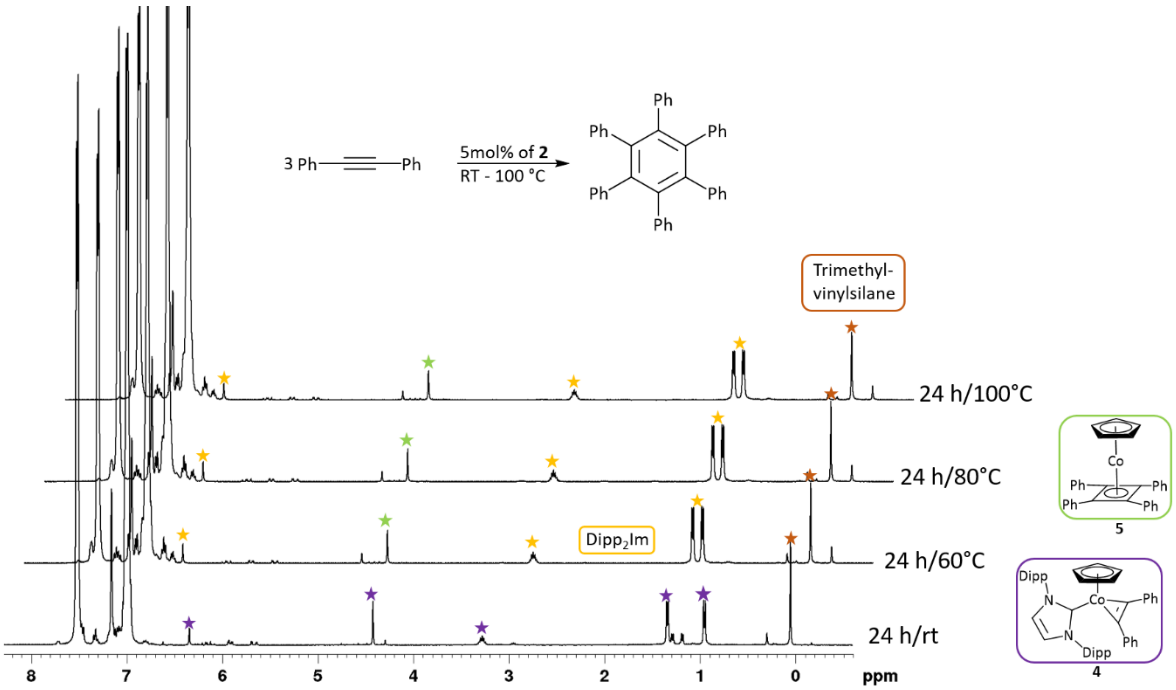


Figure S34: [1]H NMR spectra of the reaction of diphenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-$C_2H_3SiMe_3$)] **2** (5mol%) in C_6D_6 at different temperatures. [1]H NMR spectra at different temperatures of catalytically investigations of **2** (5mol%) in intermolecular [2+2+2] cycloaddition reaction of diphenylacetylene in C_6D_6. The spectrum at room temperature reveals the resonances detected for [(η^5-C_5H_5)Co(R^1_2Im)(η^2-C_2Ph_2)] **4** (**violet**), the spectra at higher temperatures reveals the resonances detected for [(η^5-C_5H_5)Co(η^4-C_4Ph_4)] **5** (**green**), along with uncoordinated Dipp$_2$Im (**yellow**).

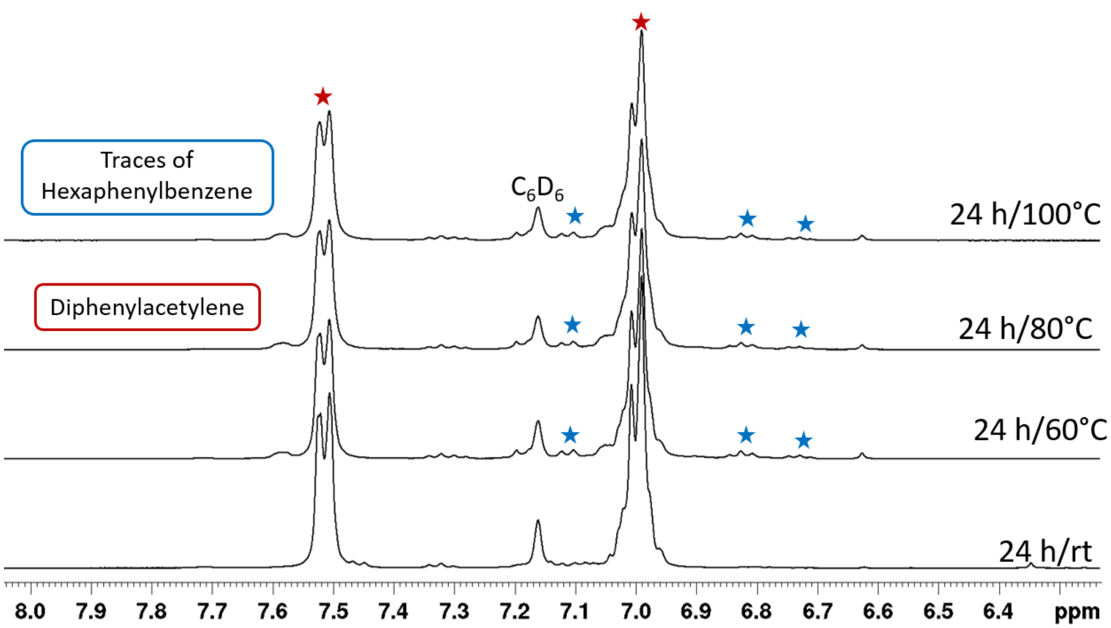


Figure S35: [1]H NMR spectra of the reaction of diphenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-$C_2H_3SiMe_3$)] **2** (5mol%) in C_6D_6 at different temperatures, shown is the aromatic region of the [1]H NMR spectra. Aside from signals of diphenylacetylene (**red**) signals for traces of hexaphenylbenzene (**blue**) at can be detected. Traces of hexaphenylbenzene (534.23) were also found in GC/MS analyses at 16.38 min, beside a major amount of diphenylacetylene (278.2).

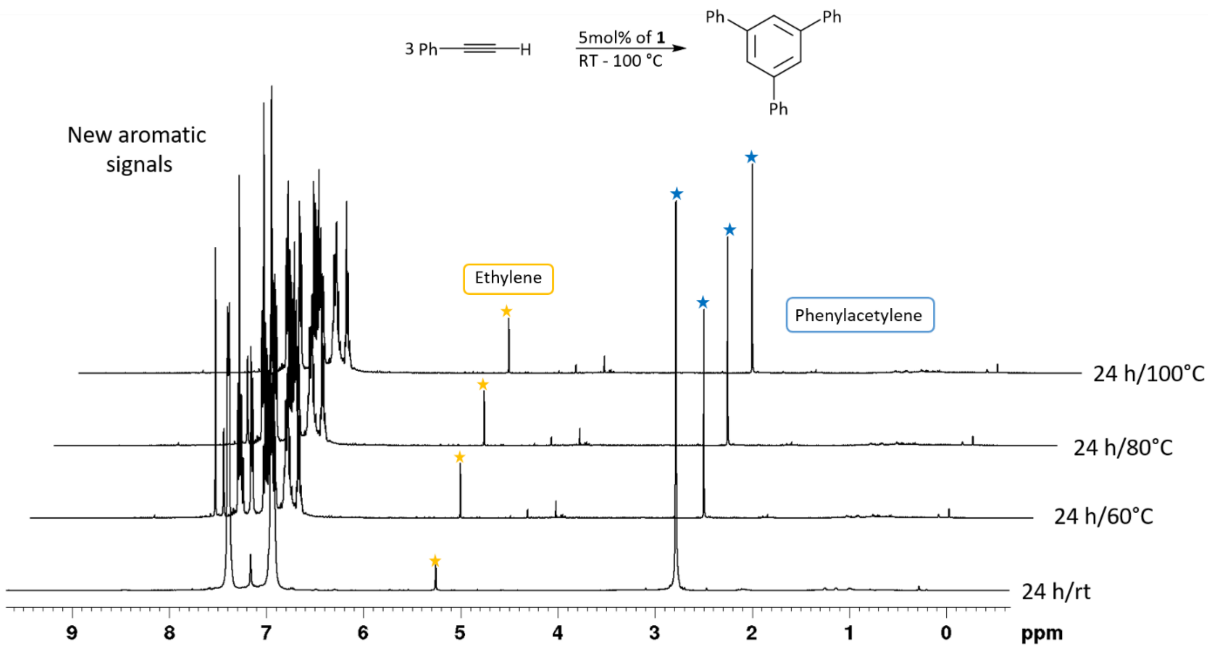


Figure S36: ^{1}H NMR spectra of the reaction of phenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(iPr$_2$Im)(η^2-C_2H_4)] **1** (5mol%) in C_6D_6 at different temperatures. The spectrum at room temperature reveals a singlet for eliminated ethylene (**yellow**) and the signals of phenylacetylene (**blue**). After heating (60 °C), new resonances can be detected in the aromatic region along with resonances for traces of complex **8**.

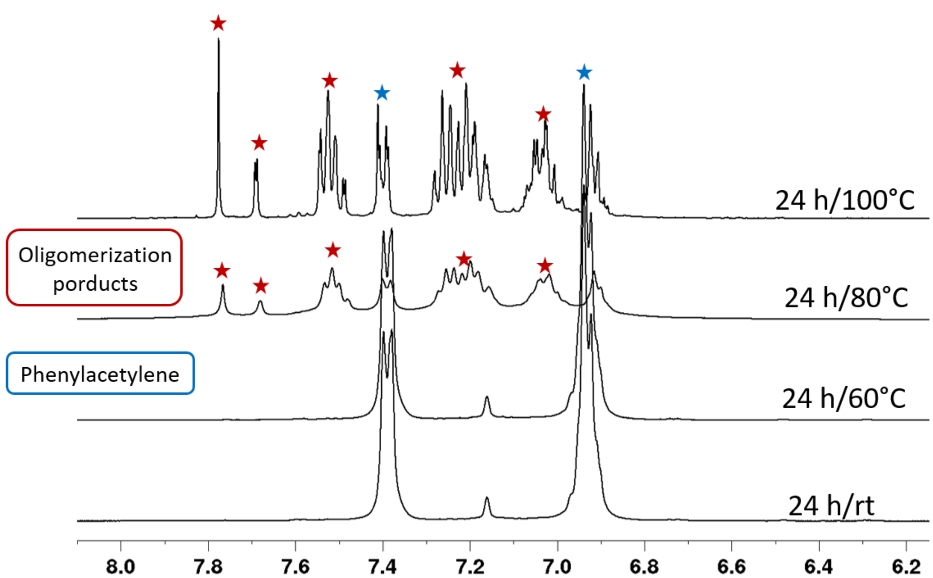


Figure S37: ^{1}H NMR spectra of the reaction of phenylacetylene with catalytic amounts of [(η^5-C_5H_5)Co(iPr$_2$Im)(η^2-C_2H_4)] **1** (5mol%) in C_6D_6 at different temperatures, shown is the aromatic region of the ^{1}H NMR spectra. At higher temperatures (80 °C) a set of new aromatic signals for different oligomerization products (**red**) was detected. GC/MS analyses reveal two different oligomerization products (306.1) at 2.94 min and 13.64 min. But even after prolonged heating (e.g. 100 °C for 24 h) there were still significant amounts of phenylacetylene (**blue**) detected in the NMR spectra as well as in the GC/MS traces of the reaction.

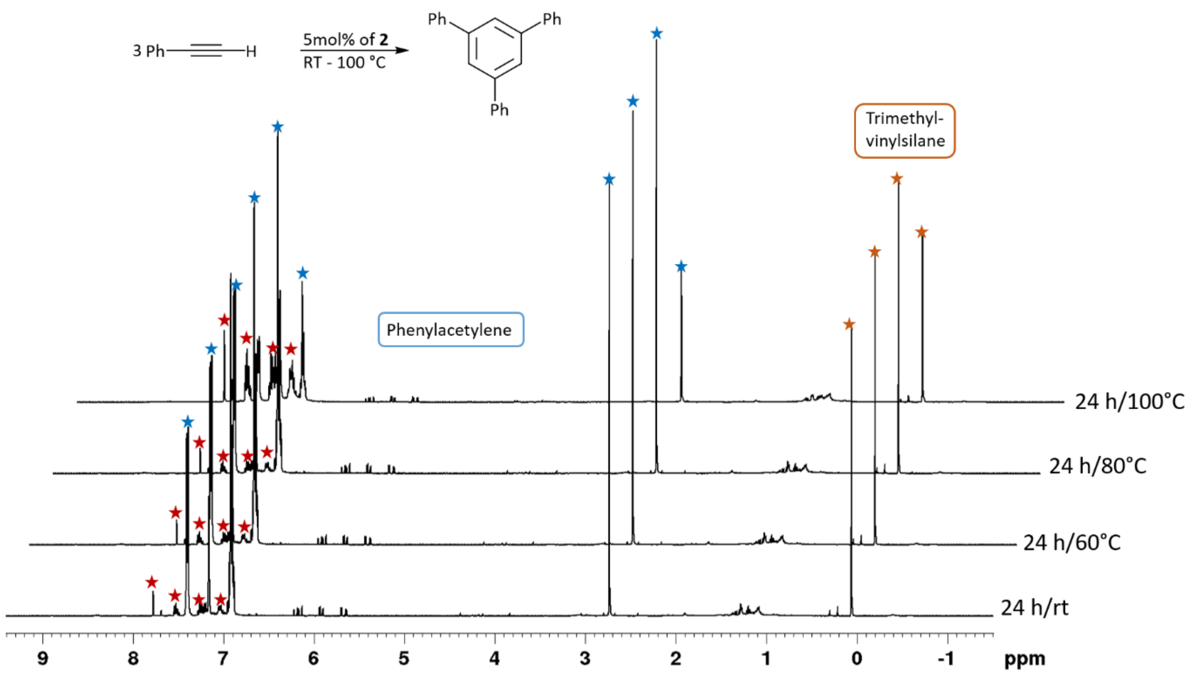


Figure S38: [1]H NMR spectra of the reaction of phenylacetylene with catalytic amounts of [(η[5]-C_5H_5)Co(Dipp$_2$Im)(η[2]-$C_2H_3SiMe_3$)] **2** (5mol%) in C_6D_6 at different temperatures. The spectra reveal the formation of new signals in the aromatic region (**red**) due to the formation of different [2+2+2] cycloaddition isomers, as well as the signals of phenylacetylene (**blue**). The resonances of uncoordinated trimethyl vinyl silane (**brown**) are also detected.

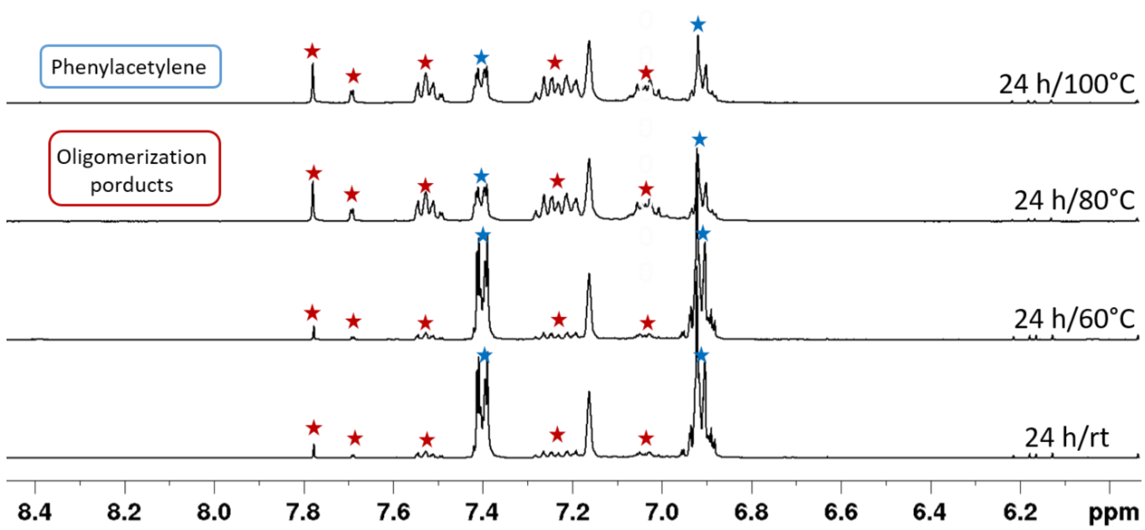


Figure S39: [1]H NMR spectra of the reaction of phenylacetylene with catalytic amounts of [(η[5]-C_5H_5)Co(Dipp$_2$Im)(η[2]-$C_2H_3SiMe_3$)] **2** (5mol%) in C_6D_6 at different temperatures, shown is the aromatic region of the [1]H NMR spectra. The spectra reveal the formation of new signals in the aromatic region (**red**) due to the formation of different [2+2+2] cycloaddition isomers, as well as the signals of phenylacetylene (**blue**). According to GC/MS analysis are two different oligomerization products (306.1) at 2.94 min and 13.64 min formed. But even after prolonged heating (e.g. 100 °C for 24 h) there were still significant amounts of phenylacetylene (**blue**) detected in the NMR spectra as well as in the GC/MS traces of the reaction.

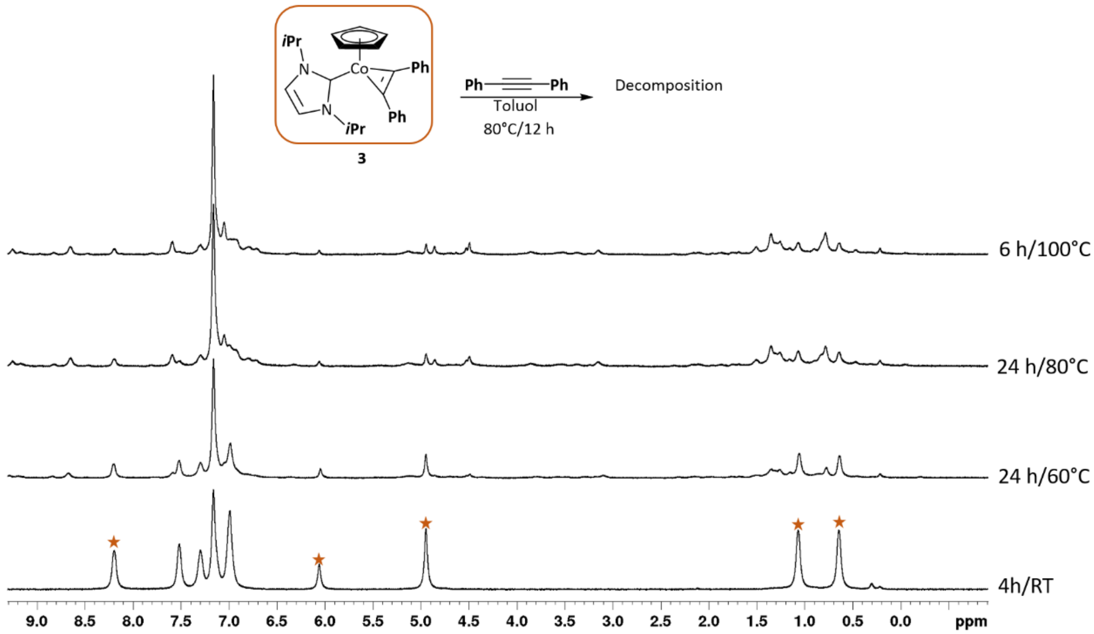


Figure S40: ^{1}H NMR spectra at different temperatures of the reaction of [(η^5-C_5H_5)Co(^{i}Pr_2Im)(η^2-C_2Ph_2)] **3** with additional of diphenylacetylene in C_6D_6. There is no reaction at room temperature and the spectrum reveals the resonances of **3** (**brown**) and diphenylacetylene. Applying higher temperatures leads to decomposition of **3**.

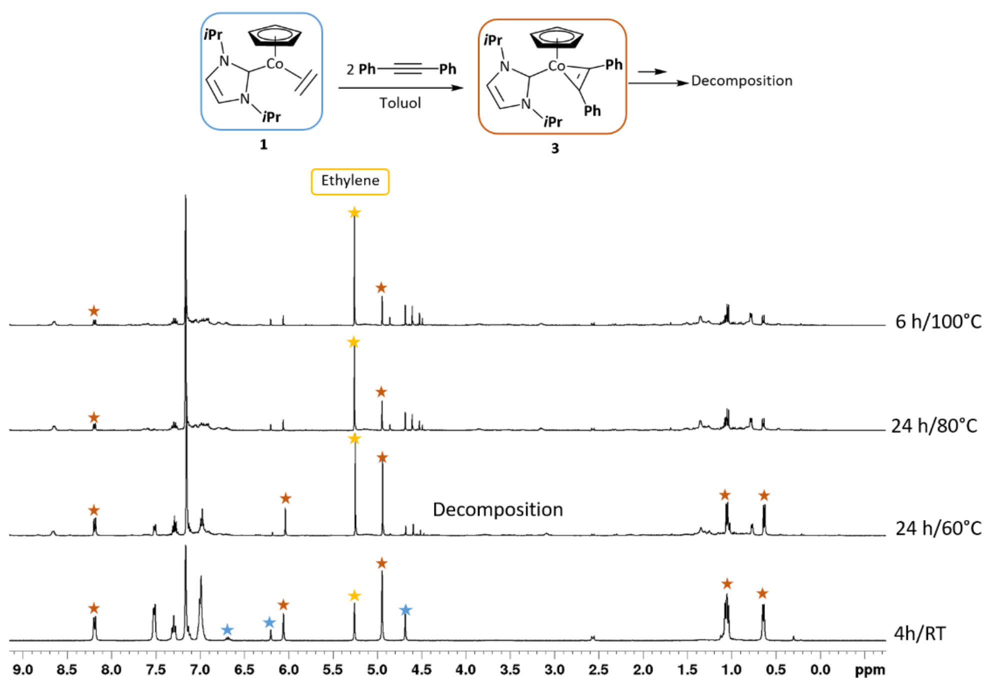


Figure S41: ^{1}H NMR spectra at different temperatures of the reaction of [(η^5-C_5H_5)Co(^{i}Pr_2Im)(η^2-C_2H_4)] **1** with two equivalents of diphenylacetylene in C_6D_6. The NMR spectrum at room temperature reveals resonances for the complexes [(η^5-C_5H_5)Co(^{i}Pr_2Im)(η^2-C_2H_4)] **1** (**blue**) and [(η^5-C_5H_5)Co(^{i}Pr_2Im)(η^2-C_2Ph_2)] **3** (**brown**) and diphenylacetylene. At elevated temperatures the decomposition of **3** can be observed.

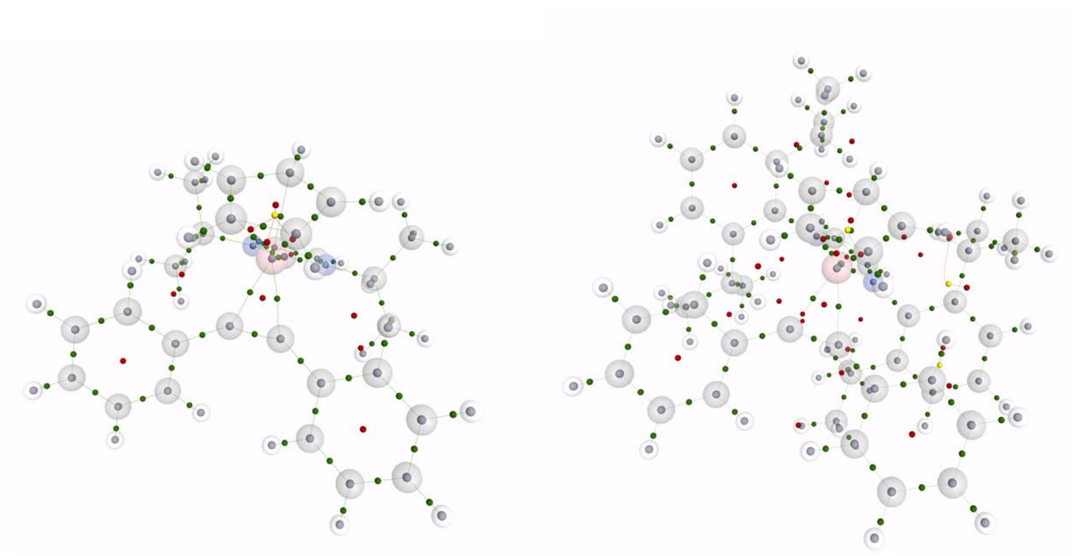
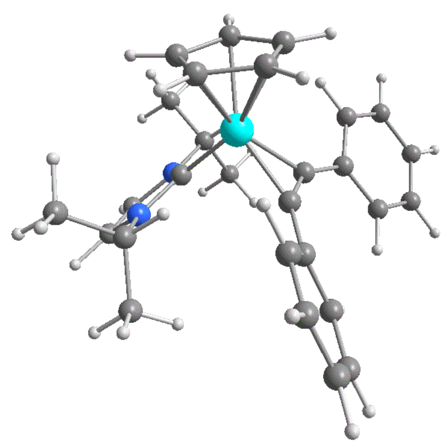


Figure S42: Bond critical (green) and ring critical (red) points calculated for [(η^5-C_5H_5)Co(^{i}Pr$_2$Im)(η^2-C_2Ph_2)] (left) and [(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-C_2Ph_2)] (right).

Computational details – Optimized Geometries

[(η^5-C_5H_5)Co(^{i}Pr$_2$Im)(η^2-C_2Ph_2)]



Energy = -2578.65598425711

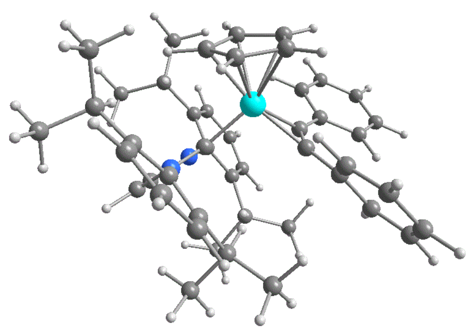
NIMAG = 0

Co	6.9825518	8.1960871	1.5512654
C	8.7282989	7.4622564	1.4869162
C	6.1412695	6.5600680	2.2081993
C	6.1437588	6.5499681	0.9088950
C	5.5140474	9.6241266	0.8887286
C	5.5493776	9.5981091	2.3176990
C	6.8605135	9.9550978	2.7463188
C	7.6424634	10.1671836	1.5614807
C	6.8031085	9.9932486	0.4096036
N	9.5441070	7.1045306	2.5371112
N	9.5005461	7.1963326	0.3775025
C	5.6439224	5.9656133	3.4221447
C	5.7249779	5.9180042	-0.3132961
H	4.6460839	9.3862499	0.2801785
H	4.7131385	9.3371543	2.9600865
H	7.1972035	10.0838101	3.7708221

H	8.6901007	10.4577993	1.5413268
H	7.0892272	10.1556012	-0.6254511
C	10.7739699	6.6426234	2.0906923
C	9.1761829	7.2086012	3.9606851
C	10.7467576	6.7009578	0.7333800
C	9.0776366	7.4227123	-1.0167362
C	5.1966960	4.6210090	3.4564089
C	5.5693787	6.7037389	4.6259926
C	5.4536535	6.6747084	-1.4774352
C	5.5743571	4.5114581	-0.4026563
H	11.5547035	6.3071751	2.7616921
H	8.1308325	7.5473280	3.9289424
C	9.2446988	5.8427987	4.6462735
C	10.0316378	8.2640805	4.6675765
H	11.4995990	6.4257916	0.0055287
H	8.0245465	7.7236714	-0.9191930
C	9.1622331	6.1319899	-1.8333703
C	9.8774496	8.5670299	-1.6469852
H	5.2393770	4.0263129	2.5440594
C	4.6998637	4.0557516	4.6279202
C	5.0661887	6.1363324	5.7954807
H	5.9048162	7.7416459	4.6171927
H	5.5756499	7.7576302	-1.4306350
C	5.0250899	6.0643274	-2.6542803
C	5.1584723	3.9040456	-1.5853527
H	5.8053611	3.8992331	0.4694792
H	8.6168844	5.1105594	4.1229893
H	8.8781015	5.9275356	5.6780911
H	10.2753164	5.4585433	4.6871588
H	9.9566928	9.2364065	4.1624489
H	11.0924503	7.9727039	4.6976120
H	9.6906513	8.3869782	5.7049768
H	8.5779913	5.3308312	-1.3632306
H	10.2018702	5.7898657	-1.9497366
H	8.7534099	6.3036746	-2.8381433

H	9.7916921	9.4849427	-1.0502892
H	9.4990545	8.7756160	-2.6574074
H	10.9445518	8.3129127	-1.7358132
H	4.3612205	3.0178929	4.6226794
C	4.6302748	4.8075750	5.8070765
H	5.0120559	6.7356233	6.7064807
H	4.8077020	6.6769046	-3.5314679
C	4.8751494	4.6746382	-2.7188699
H	5.0533232	2.8180815	-1.6242036
H	4.2410836	4.3616175	6.7233007
H	4.5463259	4.1967930	-3.6425939

[(η^5-C_5H_5)Co(Dipp$_2$Im)(η^2-C_2Ph_2)]



Energy = -3276.858758454

NIMAG = 0

Co	6.9053609	8.0107351	1.3919782
C	8.7488609	7.5338085	1.3900549
C	6.1272595	6.5326952	2.4032053
C	6.0954820	6.2417959	1.1362091
C	5.2982549	9.1084122	0.4437921
C	5.2674471	9.3182131	1.8583680
C	6.4946213	9.9180391	2.2549541
C	7.2999324	10.0286262	1.0771421
C	6.5491904	9.5550196	-0.0553789
N	9.5815409	7.2657419	2.4736282
N	9.6601391	7.5927504	0.3308510
C	5.5031974	6.2912111	3.6831247
C	5.5106775	5.4230368	0.1079572
H	4.4985208	8.6578596	-0.1362501
H	4.4502361	9.0418453	2.5183563
H	6.7588751	10.2543531	3.2508451
H	8.2966449	10.4571136	1.0427820
H	6.8734084	9.5496974	-1.0908299
C	10.9213142	7.1984275	2.0983340
C	10.9703837	7.4086545	0.7637548

C	4.6336824	5.1888127	3.8774865
C	5.6832308	7.1761613	4.7673885
C	5.1952705	5.9544559	-1.1643473
C	5.1781469	4.0655983	0.3463365
H	11.7057766	6.9996633	2.8165549
H	11.8082051	7.4309708	0.0796735
H	4.4583924	4.4990533	3.0517068
C	3.9801143	4.9926475	5.0914191
C	5.0283990	6.9762765	5.9816486
H	6.3526639	8.0249429	4.6306899
H	5.4892947	6.9802288	-1.3840877
C	4.5234333	5.1930009	-2.1192345
C	4.5263836	3.3022303	-0.6193719
H	5.4474008	3.6156424	1.3025928
H	3.3084485	4.1400410	5.2093189
C	4.1734530	5.8836415	6.1541081
H	5.1873163	7.6786459	6.8020841
H	4.2751859	5.6381229	-3.0847424
C	4.1804947	3.8626871	-1.8547839
H	4.2811462	2.2599791	-0.4058710
H	3.6609851	5.7272244	7.1044485
H	3.6610801	3.2657323	-2.6054830
C	9.2460476	7.0147106	3.8606693
C	9.2988679	8.0833832	4.7832696
C	9.0569626	5.6761702	4.2716203
C	9.1257187	7.7801223	6.1406969
C	8.8837649	5.4345387	5.6411274
C	8.9178733	6.4714031	6.5682866
H	9.1559781	8.5845920	6.8761502
H	8.7208467	4.4131084	5.9855568
H	8.7808695	6.2590972	7.6296931
C	9.3877530	7.7234674	-1.0864265
C	9.0330069	6.5646174	-1.8217473
C	9.6267168	8.9642247	-1.7202206
C	8.7900579	6.7193870	-3.1928650

C	9.3788390	9.0539418	-3.0982048
C	8.9401892	7.9524031	-3.8246063
H	8.4877951	5.8529989	-3.7796169
H	9.5395708	10.0045489	-3.6081801
H	8.7398195	8.0460713	-4.8932345
C	9.5878202	9.5183060	4.3566756
H	9.2947285	9.6094779	3.3003818
C	8.7845841	10.5570020	5.1579083
H	8.8842902	11.5493363	4.6952718
H	7.7162021	10.3063657	5.2042347
H	9.1508147	10.6449345	6.1914692
C	11.0925427	9.8412957	4.4655482
H	11.2858721	10.8788558	4.1543050
H	11.4377246	9.7295526	5.5044377
H	11.7010527	9.1820310	3.8331967
C	9.1063982	4.5052158	3.2965704
H	8.9051994	4.9020015	2.2909597
C	10.5089626	3.8620957	3.2905176
H	10.5443164	3.0273128	2.5749405
H	11.2910463	4.5798004	3.0093093
H	10.7564823	3.4644848	4.2865250
C	8.0443942	3.4328202	3.5857941
H	8.0352506	2.6916194	2.7736083
H	8.2566632	2.8878251	4.5176767
H	7.0418434	3.8708240	3.6682011
C	9.0138914	5.1721617	-1.1953937
H	8.5912715	5.2694511	-0.1829736
C	8.1639354	4.1508372	-1.9633741
H	8.6275524	3.8830274	-2.9254676
H	8.0866771	3.2255487	-1.3761601
H	7.1466741	4.5118633	-2.1536797
C	10.4499733	4.6128808	-1.0765006
H	10.9117247	4.5346646	-2.0725783
H	11.0971717	5.2341190	-0.4464312
H	10.4243429	3.6046100	-0.6376083

C	10.2272737	10.1672102	-0.9989970
H	10.1428694	9.9886815	0.0828055
C	11.7294970	10.2936039	-1.3309612
H	11.8751788	10.4778552	-2.4056758
H	12.1755695	11.1342415	-0.7791204
H	12.2875676	9.3839015	-1.0715596
C	9.5173603	11.4938282	-1.3206561
H	8.4366309	11.4399431	-1.1387896
H	9.9282297	12.3005199	-0.6960808
H	9.6699912	11.7888129	-2.3690104