Direct synthesis of dicarbonyl PCP-iron hydride complexes and catalytic dehydrogenative borylation of styrene.

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Electronic Supplementary Material (ESI)

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Table of Contents

Monitoring over time by $^{31}P\{^{1}H\}$ NMR spectroscopy of the formation of **1c**

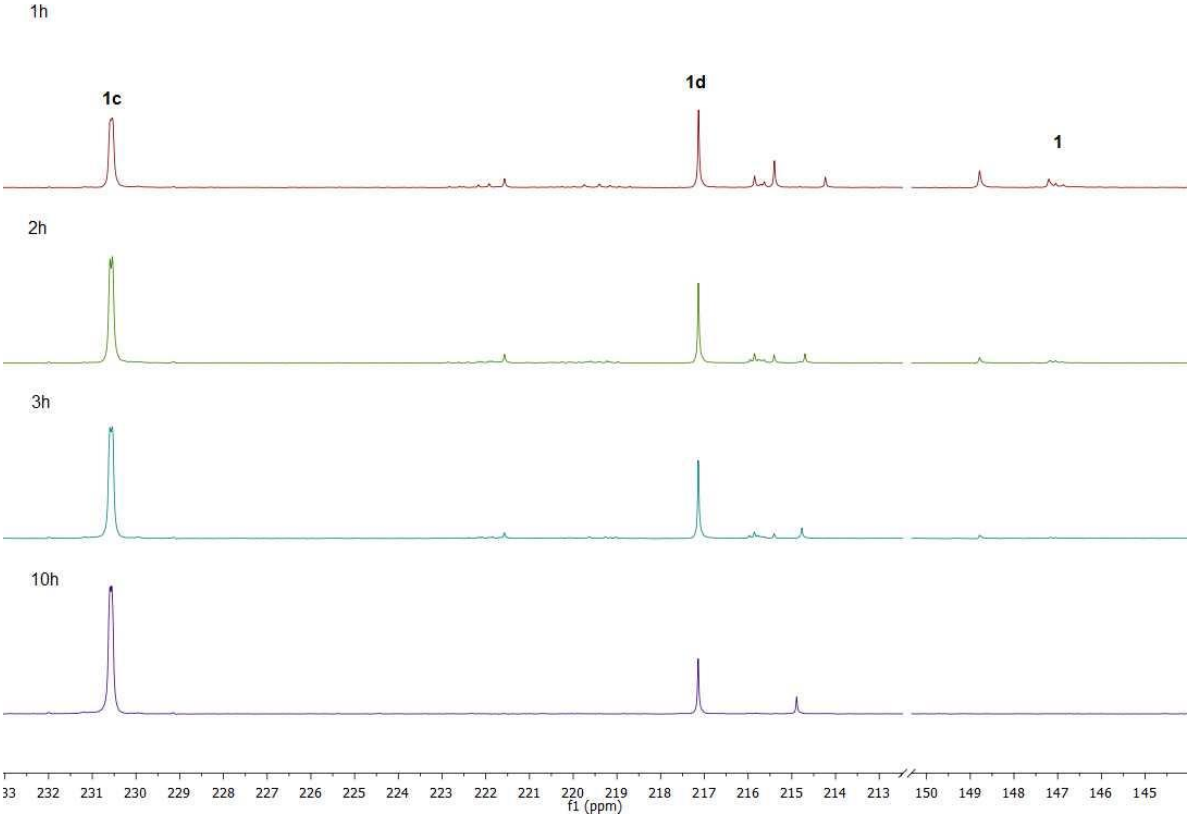


Figure S1: Monitoring over time by $^{31}P\{^{1}H\}$ NMR spectroscopy of the crude reaction in the presence of a slight excess of $Fe(CO)_5$ (ratio **1**:$Fe(CO)_5$ = 1:1.1, toluene, rt, UV (350 nm))

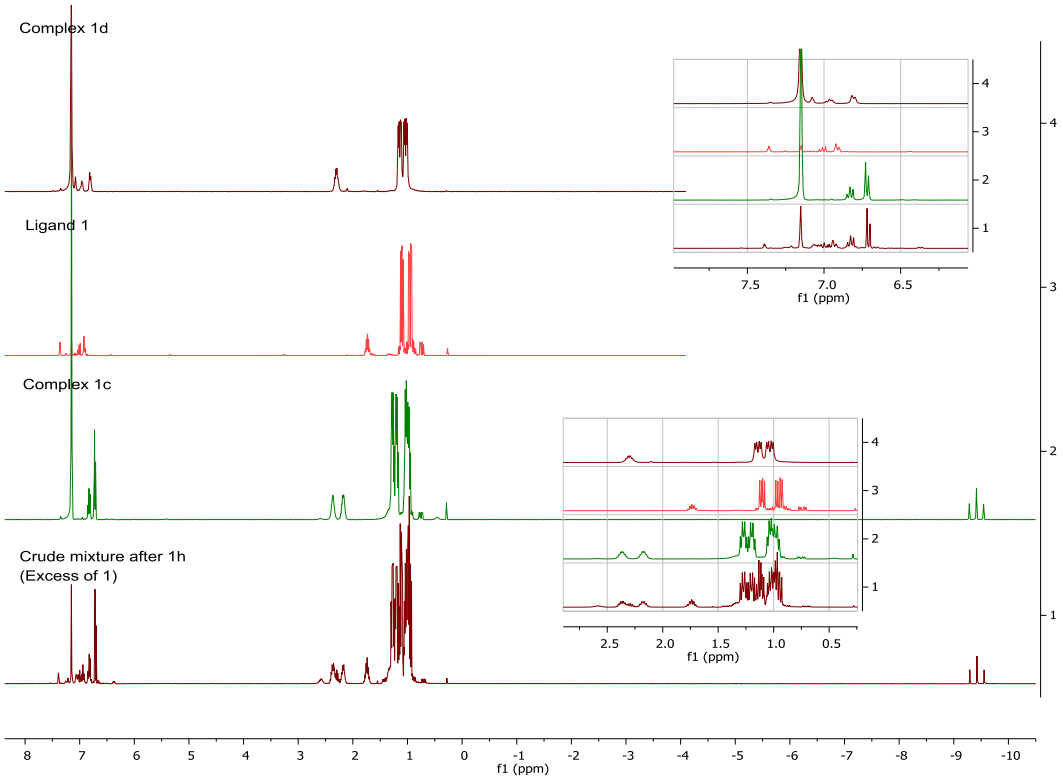


Figure S1_b: Bottom: ^{1}H NMR spectroscopy of the crude reaction in the presence of a slight excess of ligand after 1 h. (ratio **1**:$Fe(CO)_5$ = 1:0.9, toluene, rt, UV (350 nm)). Middle: ^{1}H NMR spectroscopy of complex **1c** and ligand **1**. Top: ^{1}H NMR spectroscopy of complex **1d**.

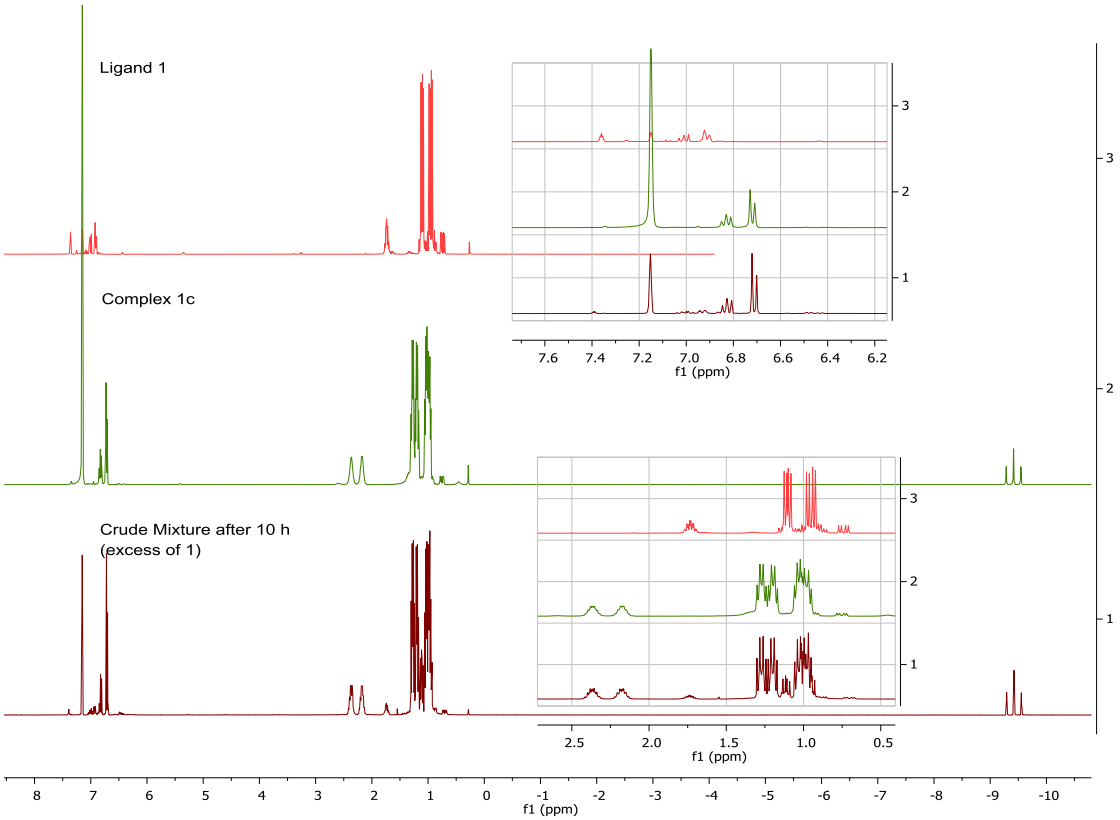


Figure S1_c: Bottom: ^{1}H NMR spectroscopy of the crude reaction in the presence of a slight excess of ligand after 10 h. (ratio **1**:$Fe(CO)_5$ = 1:0.9, toluene, rt, UV (350 nm)). Middle: ^{1}H NMR spectroscopy of complex **1c**. Top: ^{1}H NMR spectroscopy of ligand **1**.

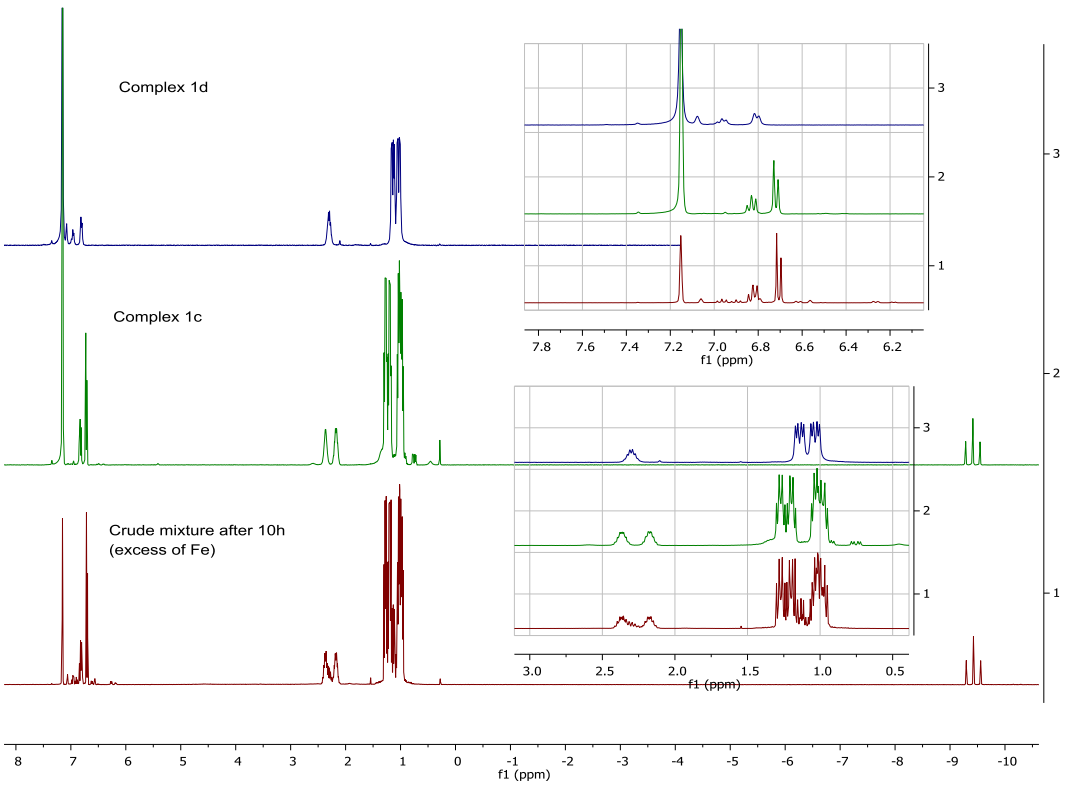


Figure S1_d: Bottom: ^{1}H NMR spectroscopy of the crude reaction in the presence of a slight excess of $Fe(CO)_5$ after 10h. (ratio **1**:$Fe(CO)_5$ = 1:1.1, toluene, rt, UV (350 nm)). Middle: ^{1}H NMR spectroscopy of complex **1c**. Top: ^{1}H NMR spectroscopy of complex **1d**.

^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR data for the complexes

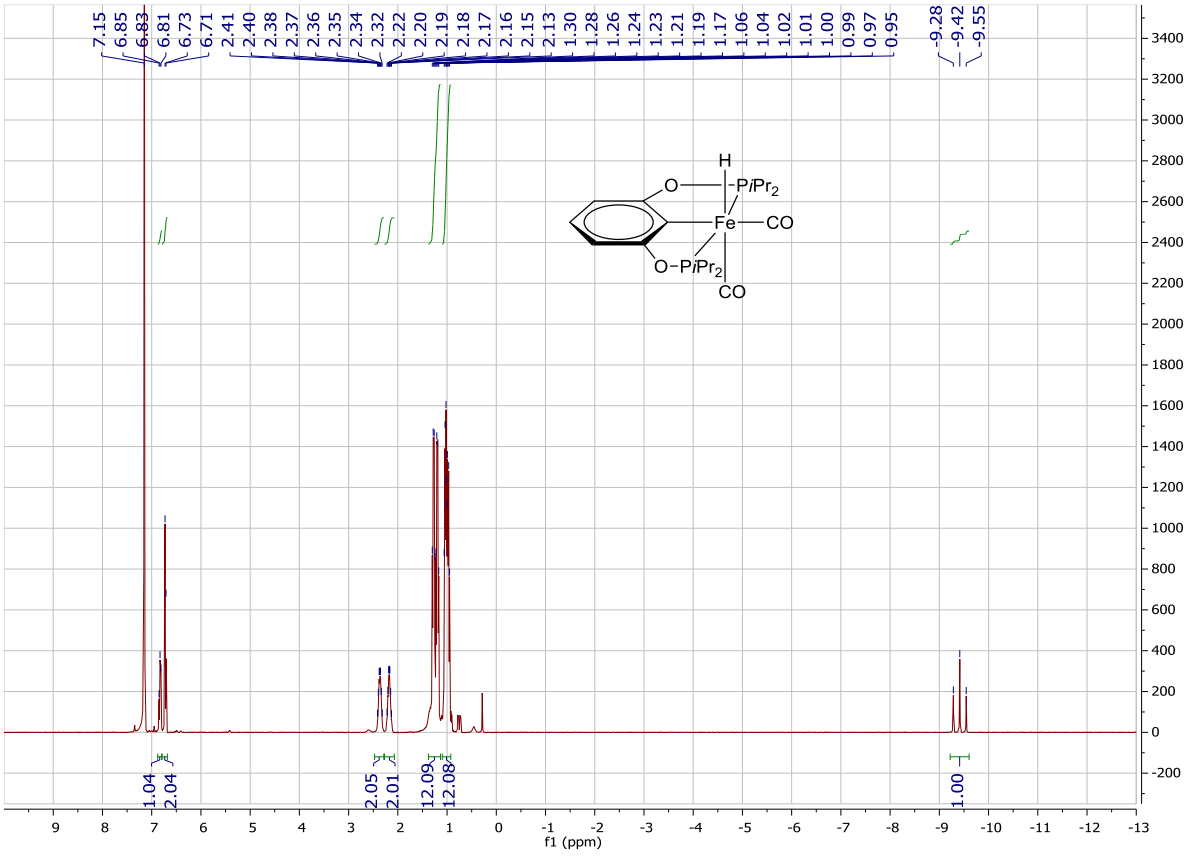


Figure S2: ^{1}H NMR spectrum of the complex **1c** in C_6D_6 recorded at 400MHz.

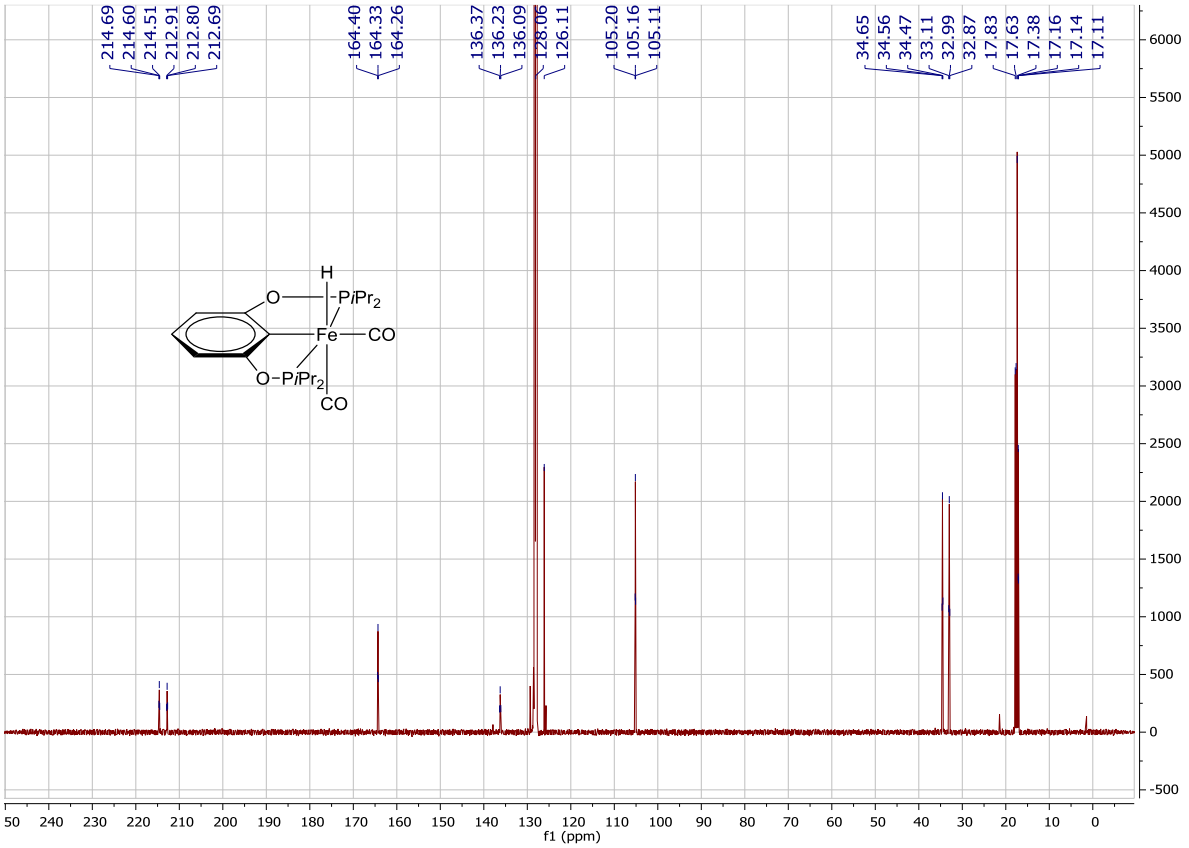


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **1c** in C_6D_6 recorded at 126 MHz.

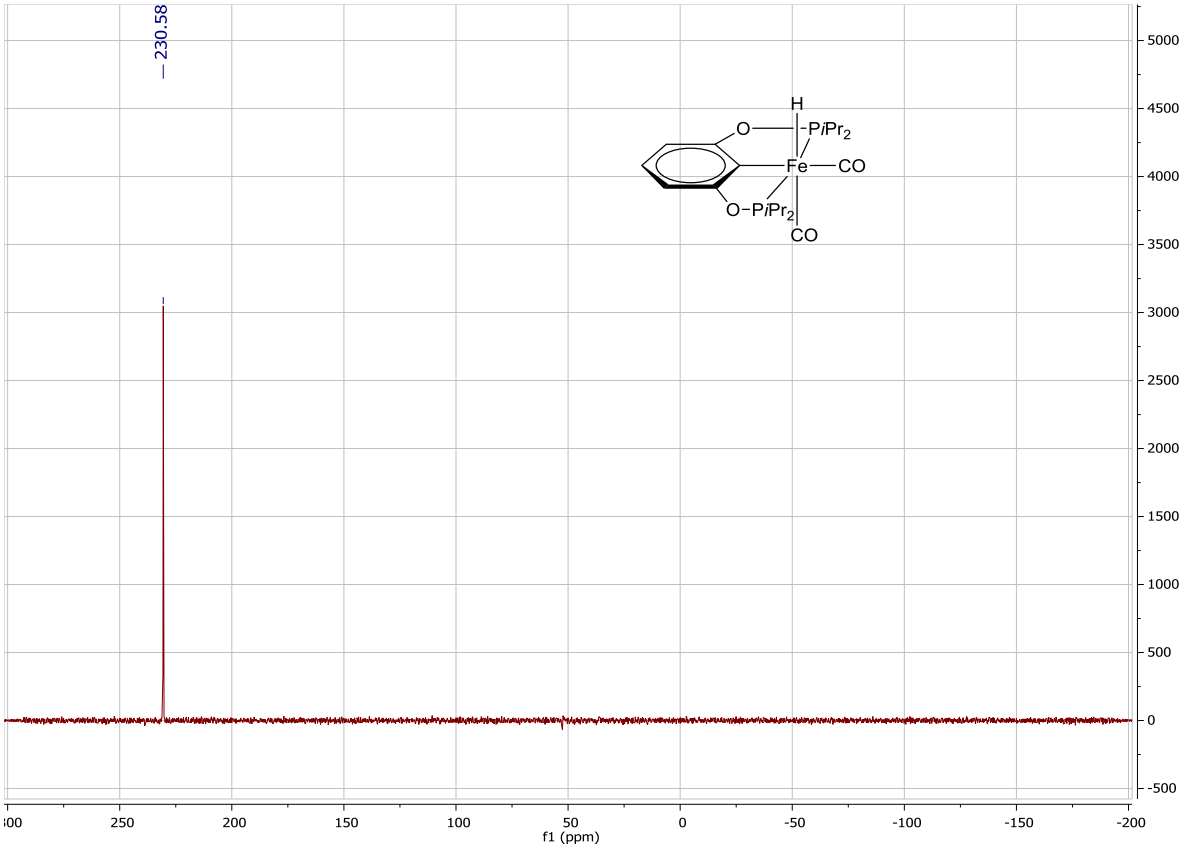


Figure S4: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **1c** in C_6D_6 recorded at 162 MHz.

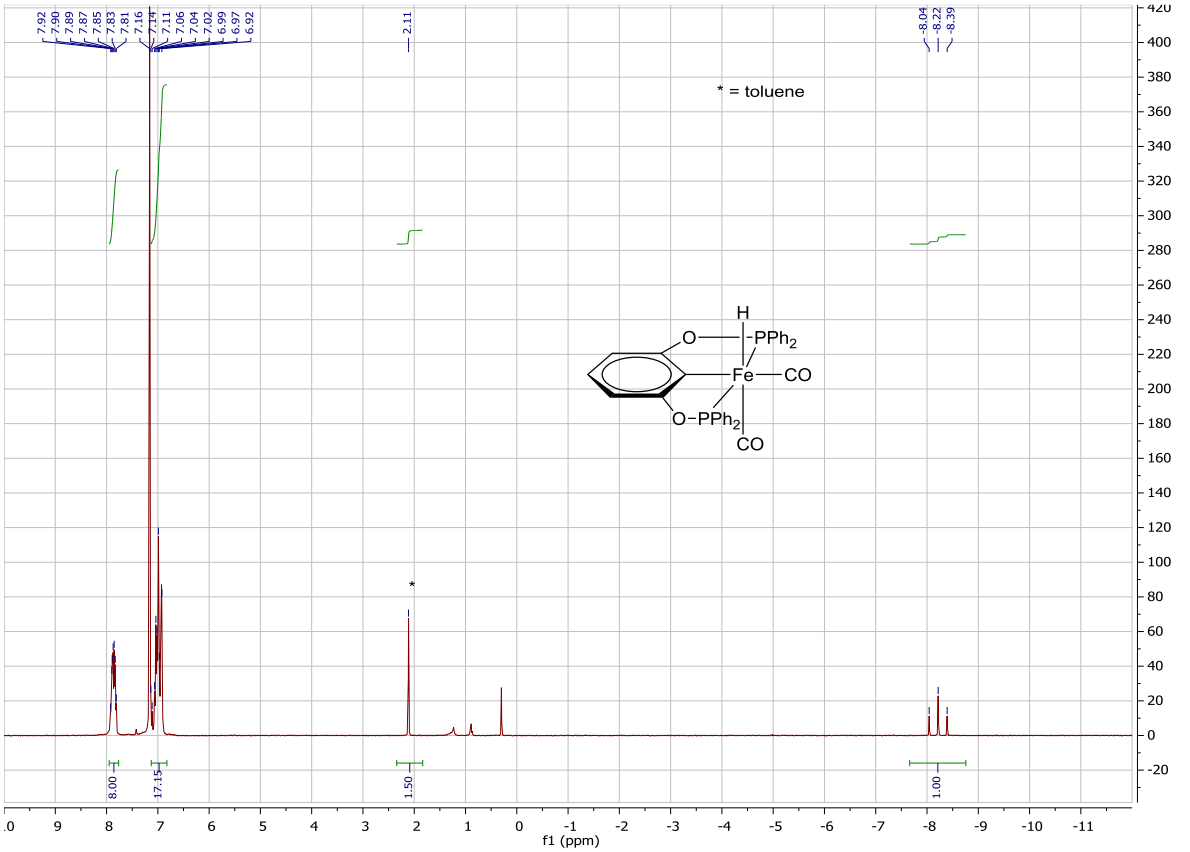


Figure S5: ^{1}H NMR spectrum of the complex **2c** in C_6D_6 recorded at 400MHz.

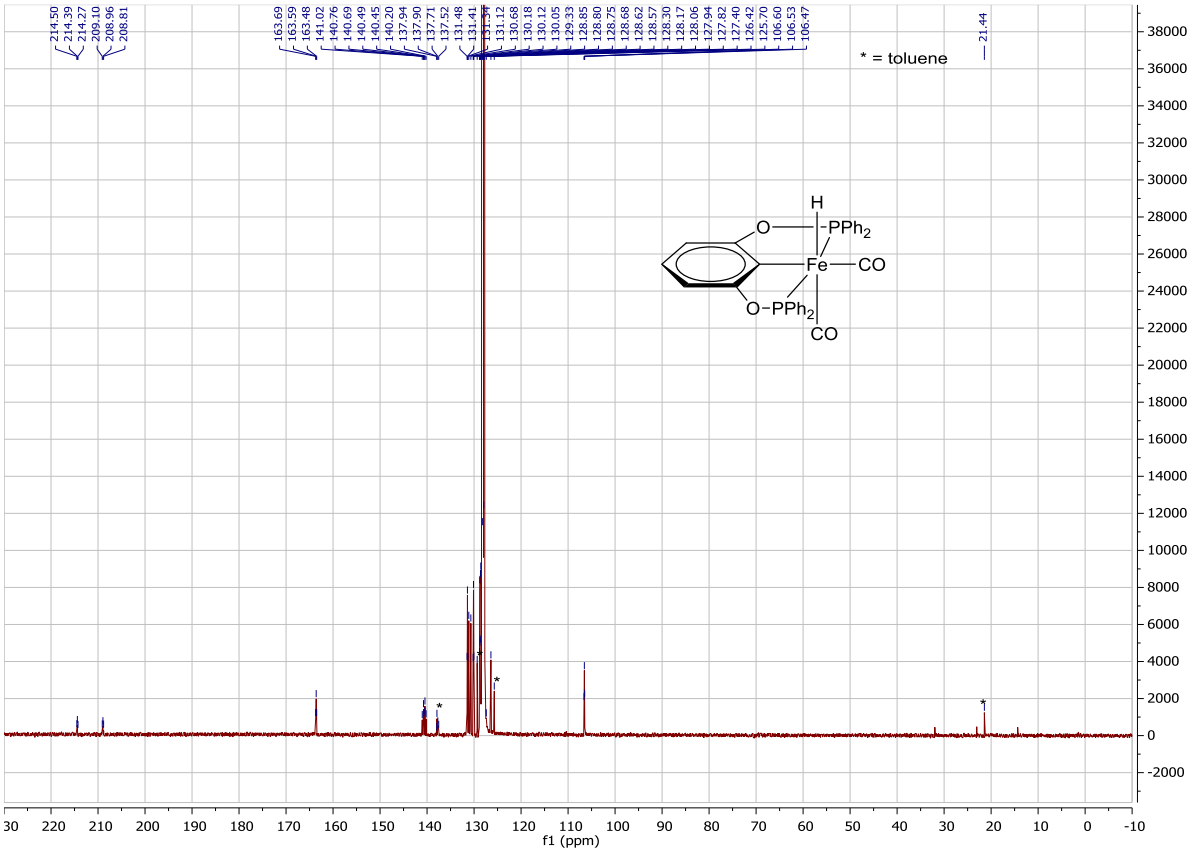


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **2c** in C_6D_6 recorded at 101 MHz.

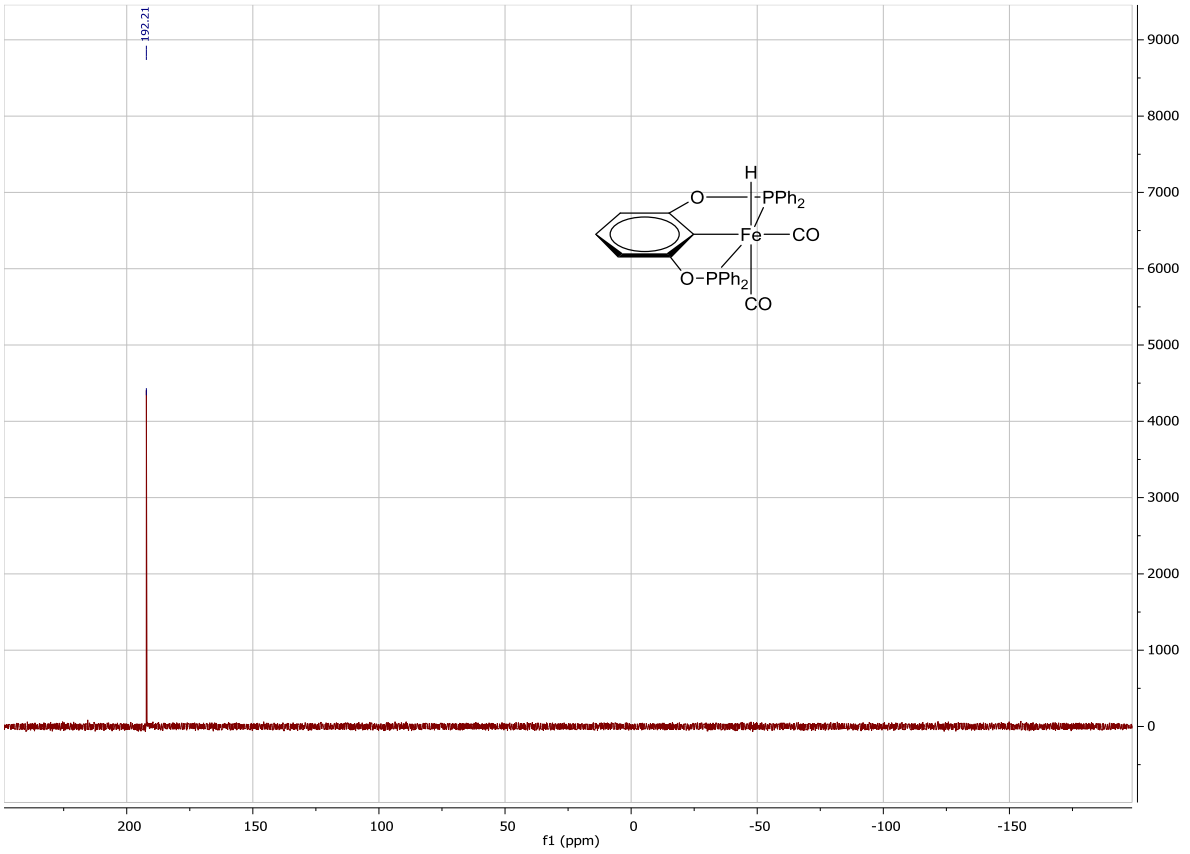


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **2c** in C_6D_6 recorded at 162 MHz.

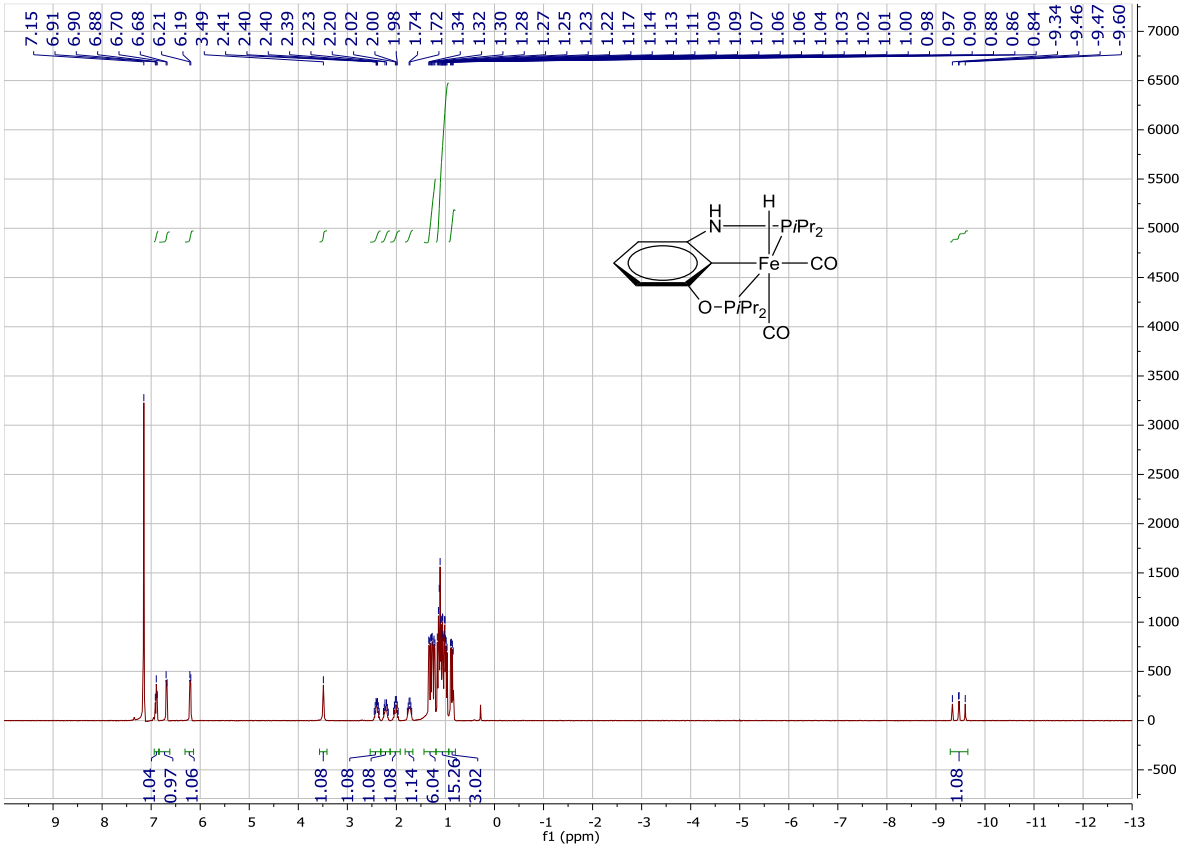


Figure S8: ^{1}H NMR spectrum of the complex **4c** in C_6D_6 recorded at 400MHz.

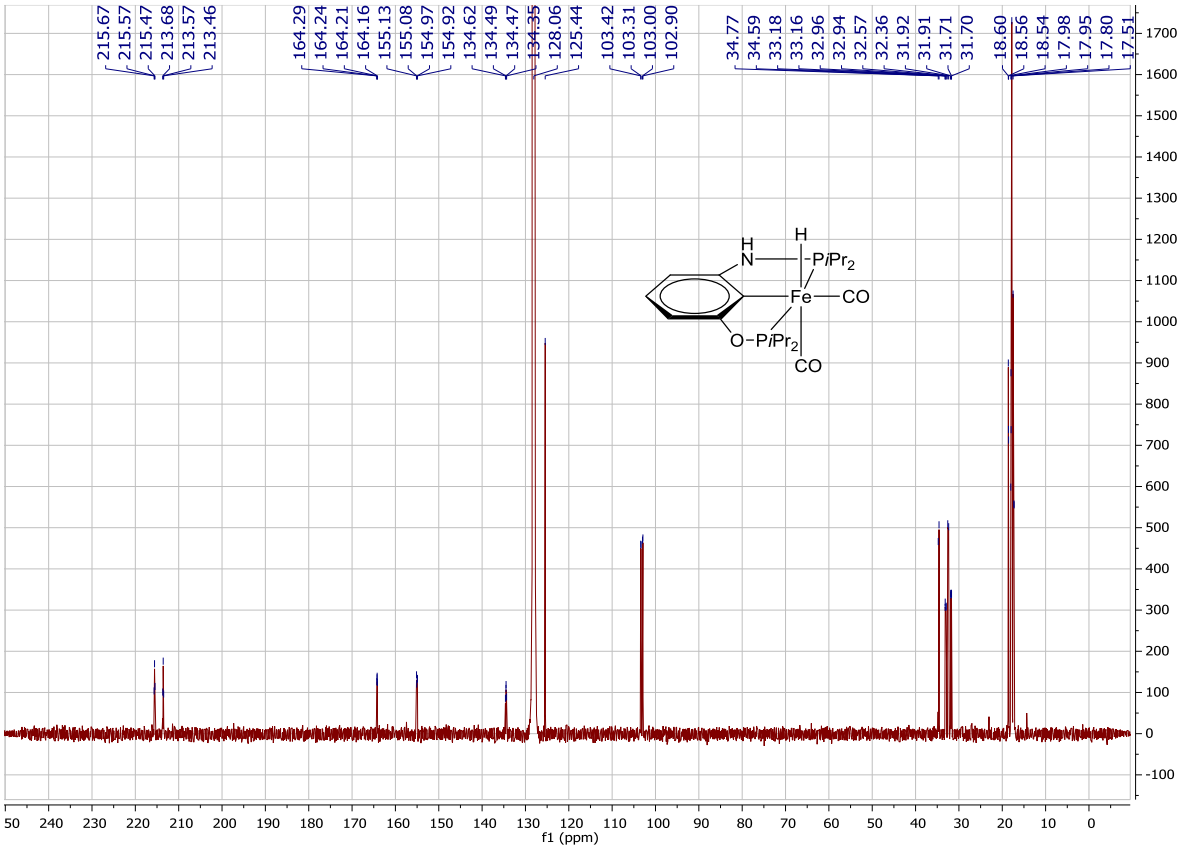


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **4c** in C_6D_6 recorded at 126 MHz.

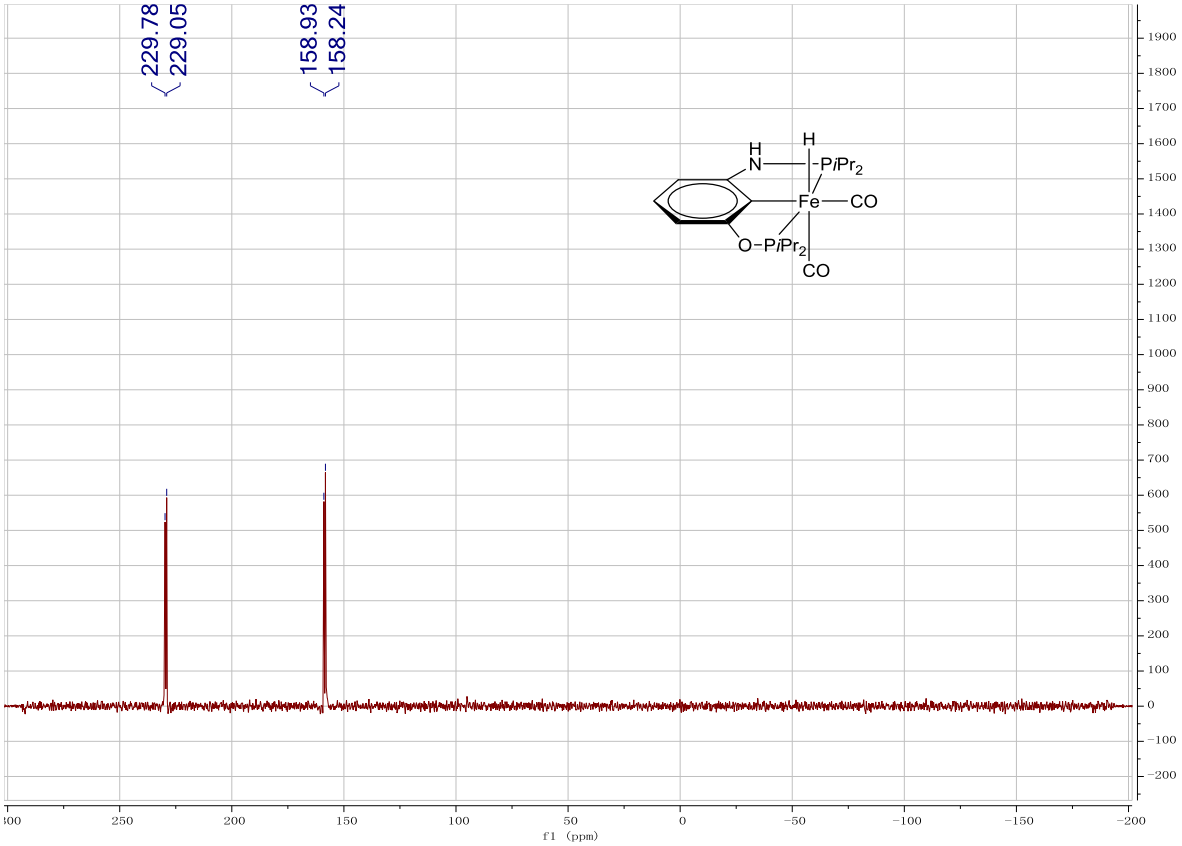


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **4c** in C_6D_6 recorded at 162 MHz.

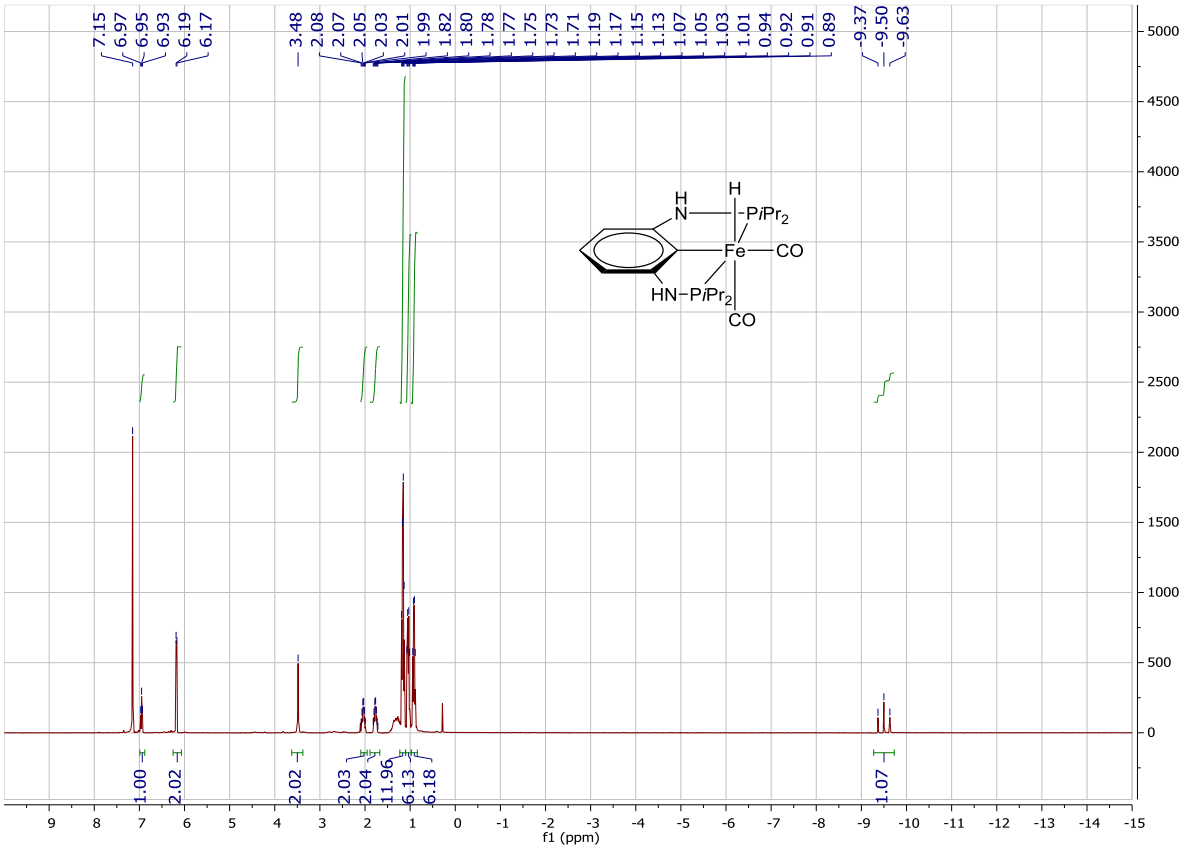


Figure S11: ^{1}H NMR spectrum of the complex **5c** in C_6D_6 recorded at 400MHz.

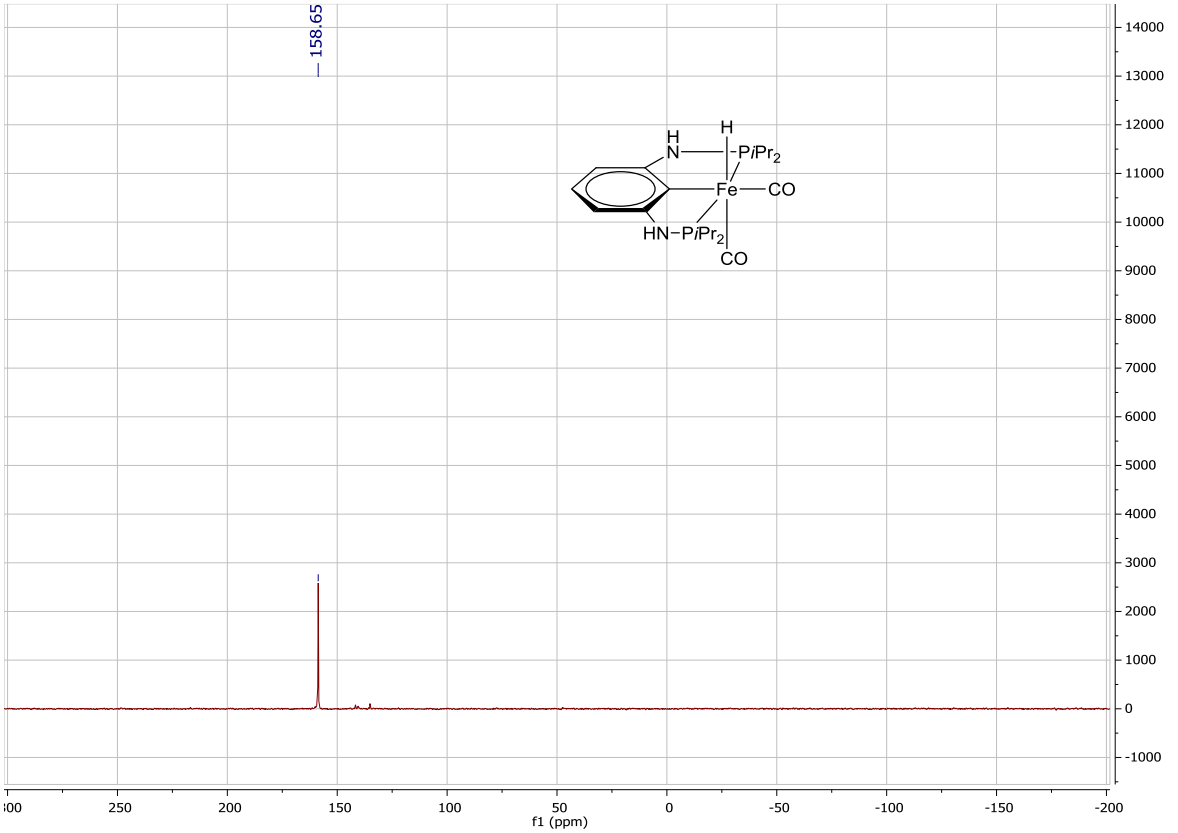


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **5c** in C_6D_6 recorded at 162 MHz.

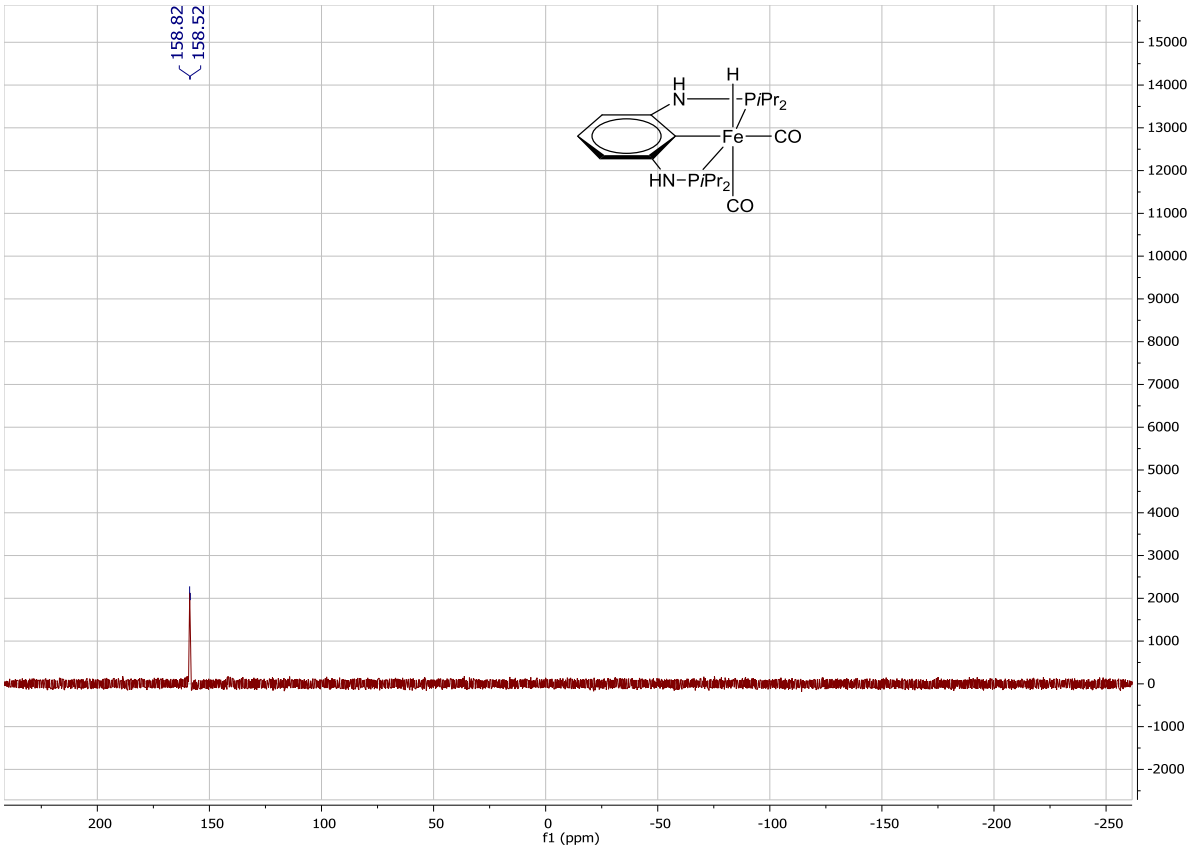


Figure S13: ^{31}P NMR spectrum of the complex **5c** in C_6D_6 recorded at 162 MHz.

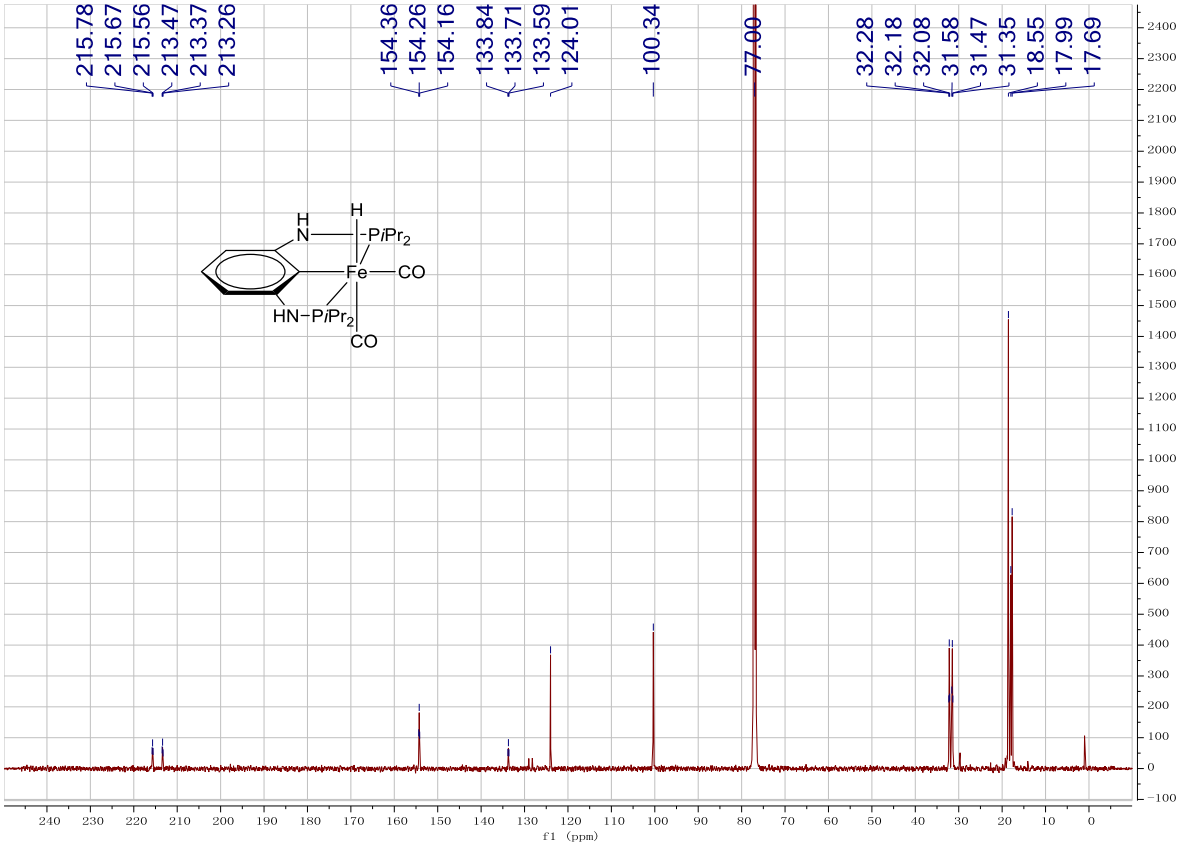


Figure S14: $^{13}C\{^1H\}$ NMR spectrum of the complex **5c** in C_6D_6 recorded at 125 MHz.

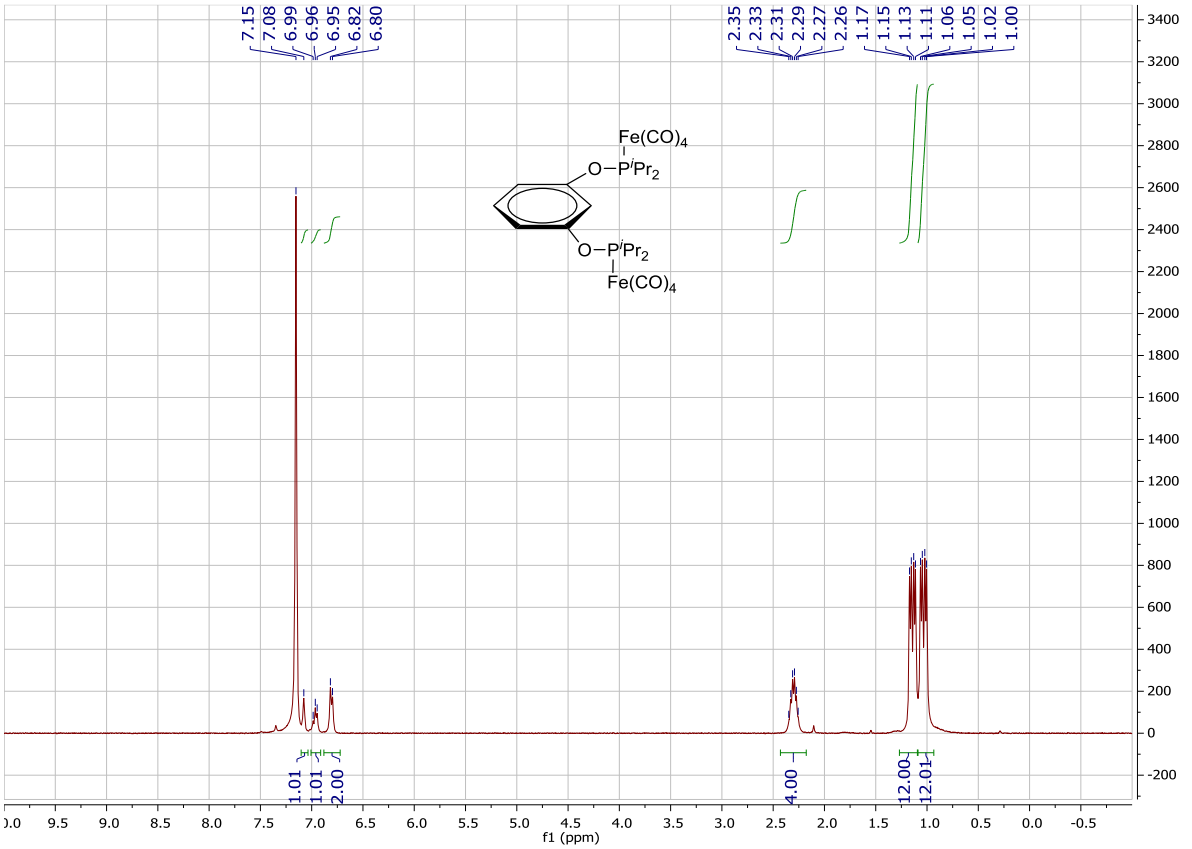


Figure S15: ^{1}H NMR spectrum of the complex **1d** in C_6D_6 recorded at 400MHz.

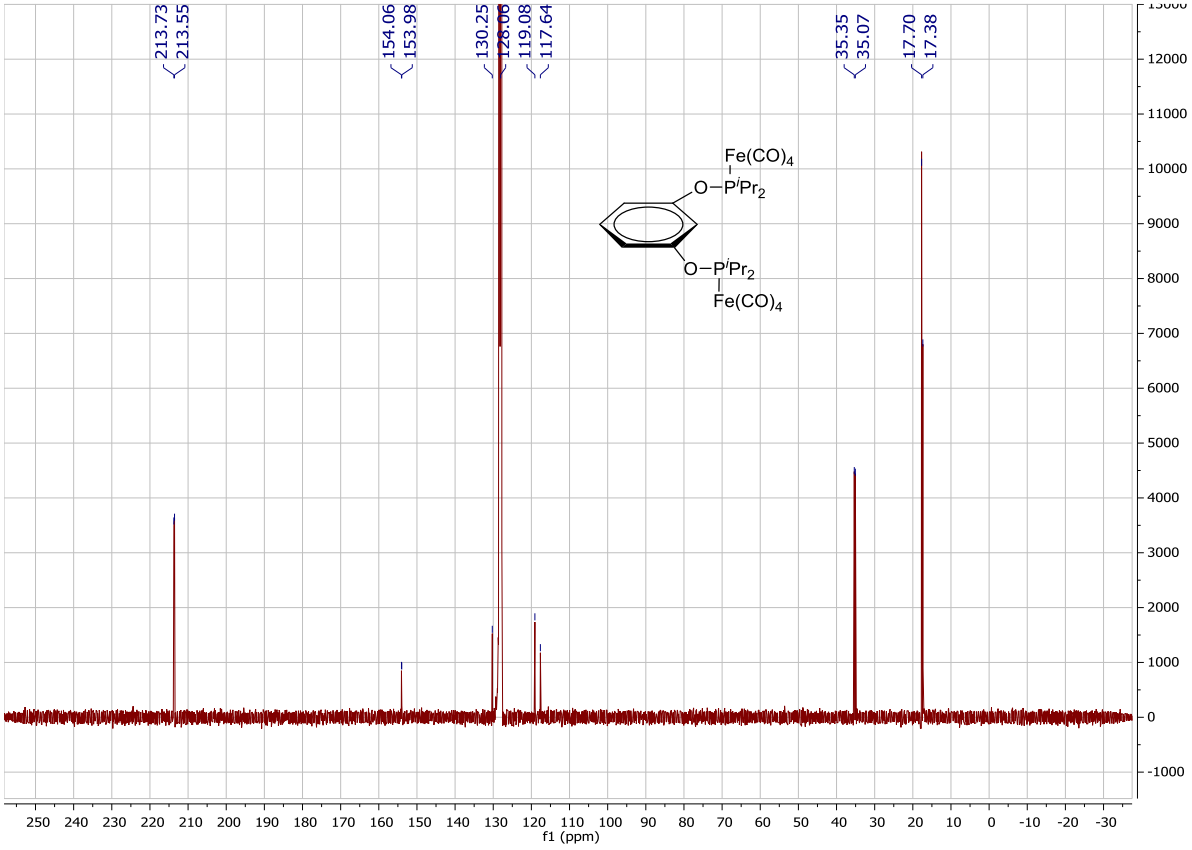


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **1d** in C_6D_6 recorded at 101 MHz.

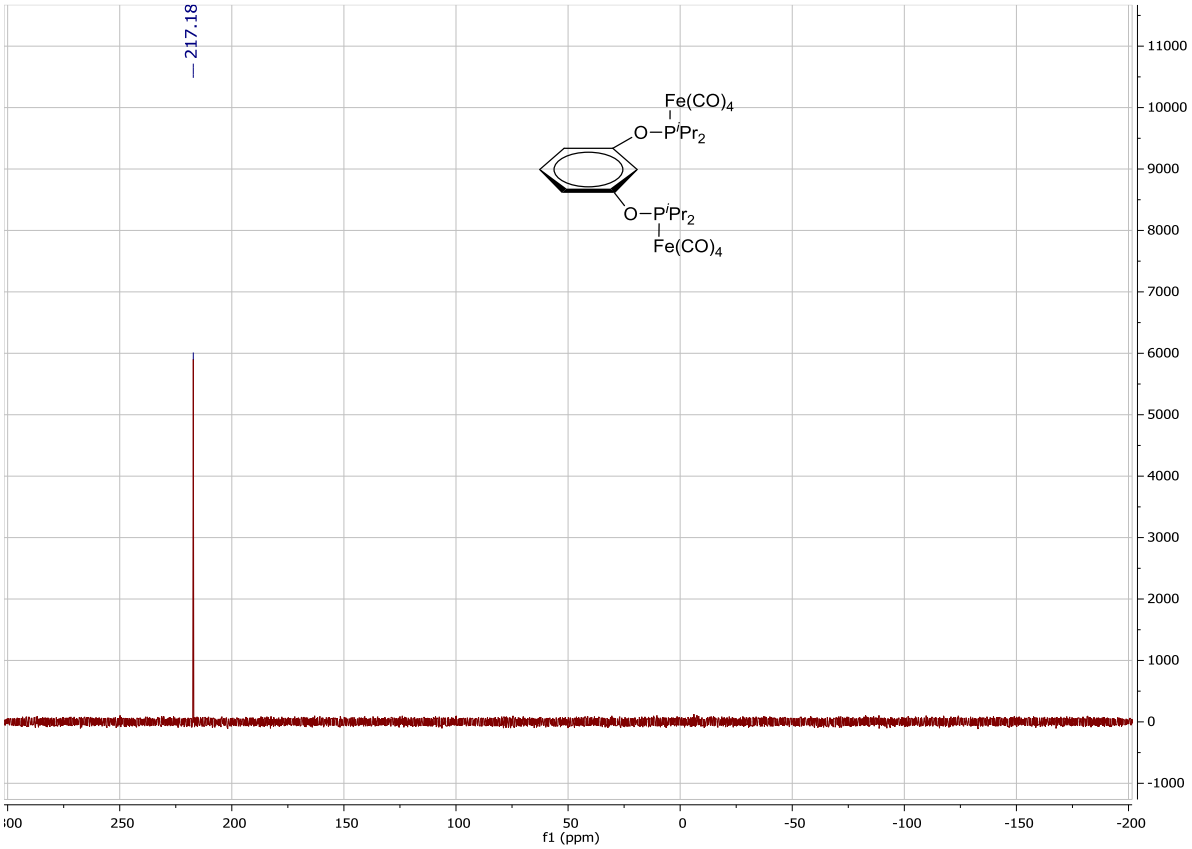


Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **1d** in C_6D_6 recorded at 162 MHz.

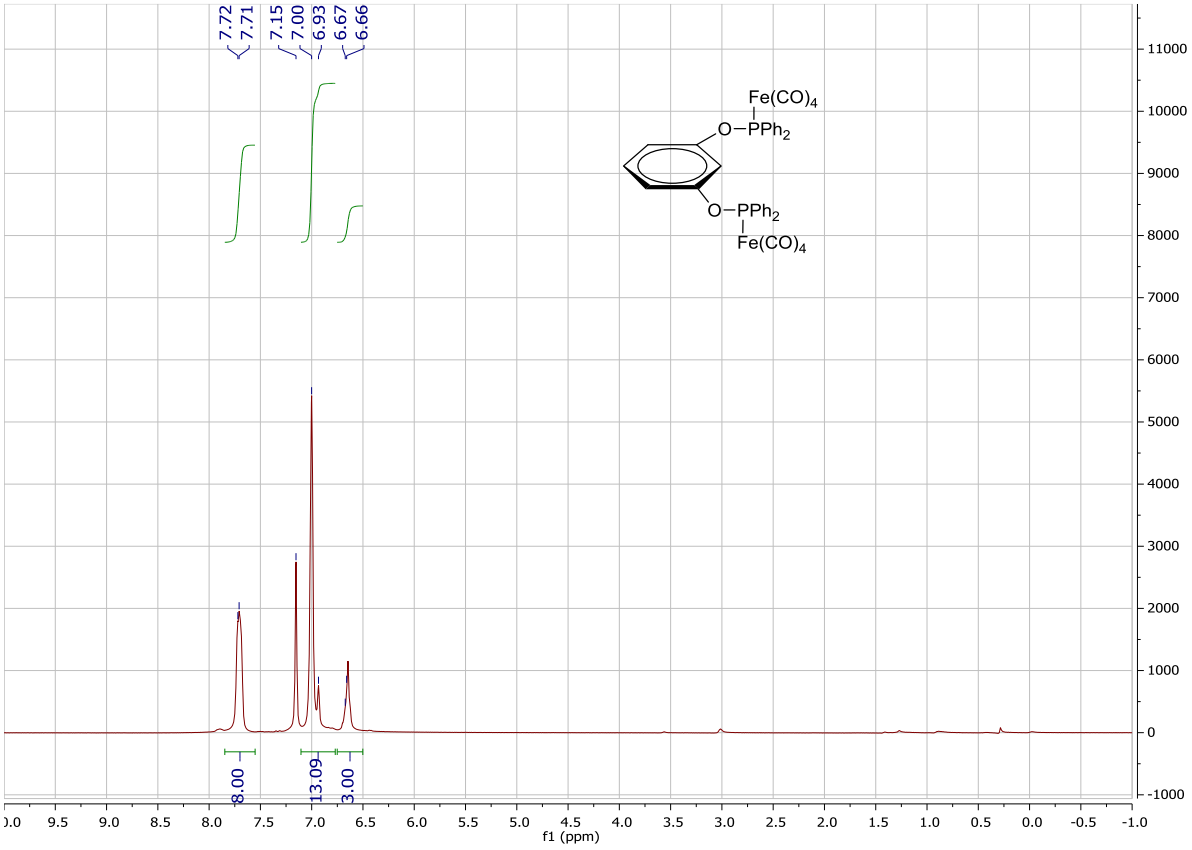


Figure S18: ^{1}H NMR spectrum of the complex **2d** in C_6D_6 recorded at 400MHz.

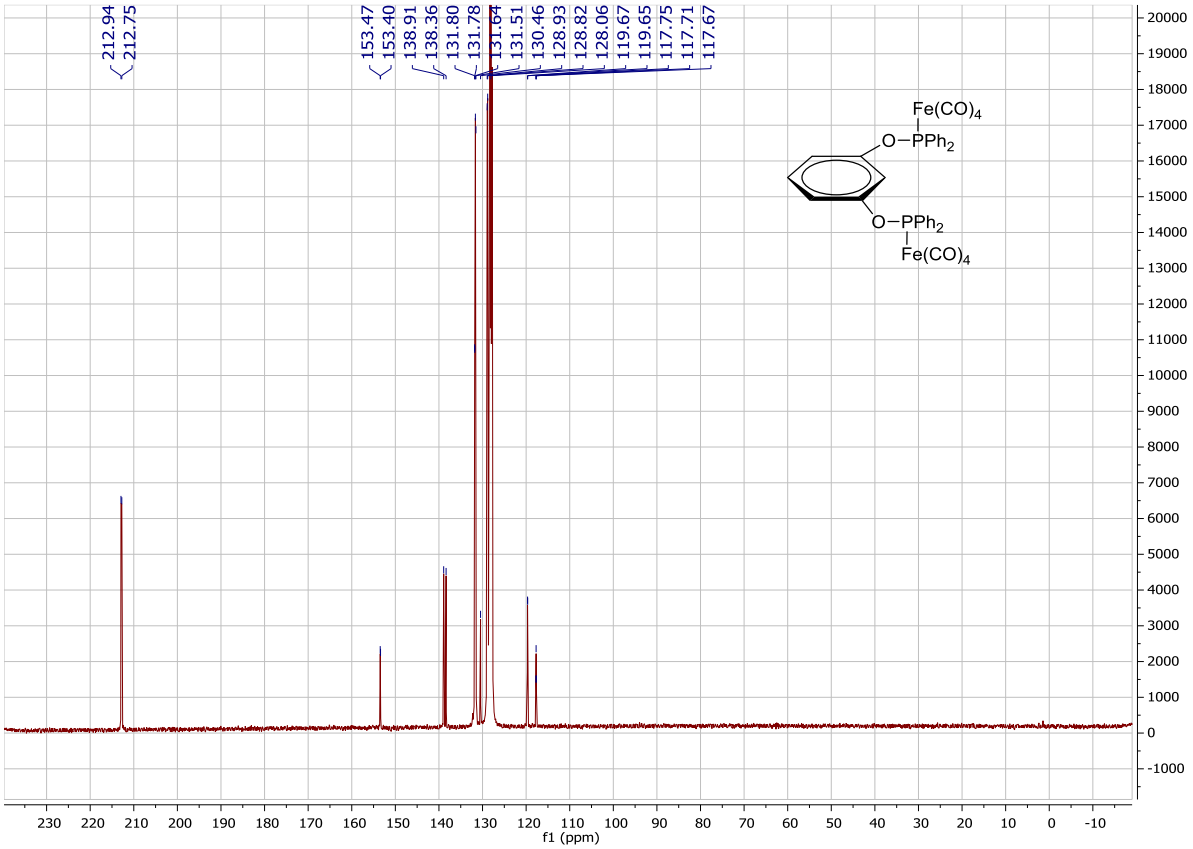


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of the complex **2d** in C_6D_6 recorded at 101 MHz.

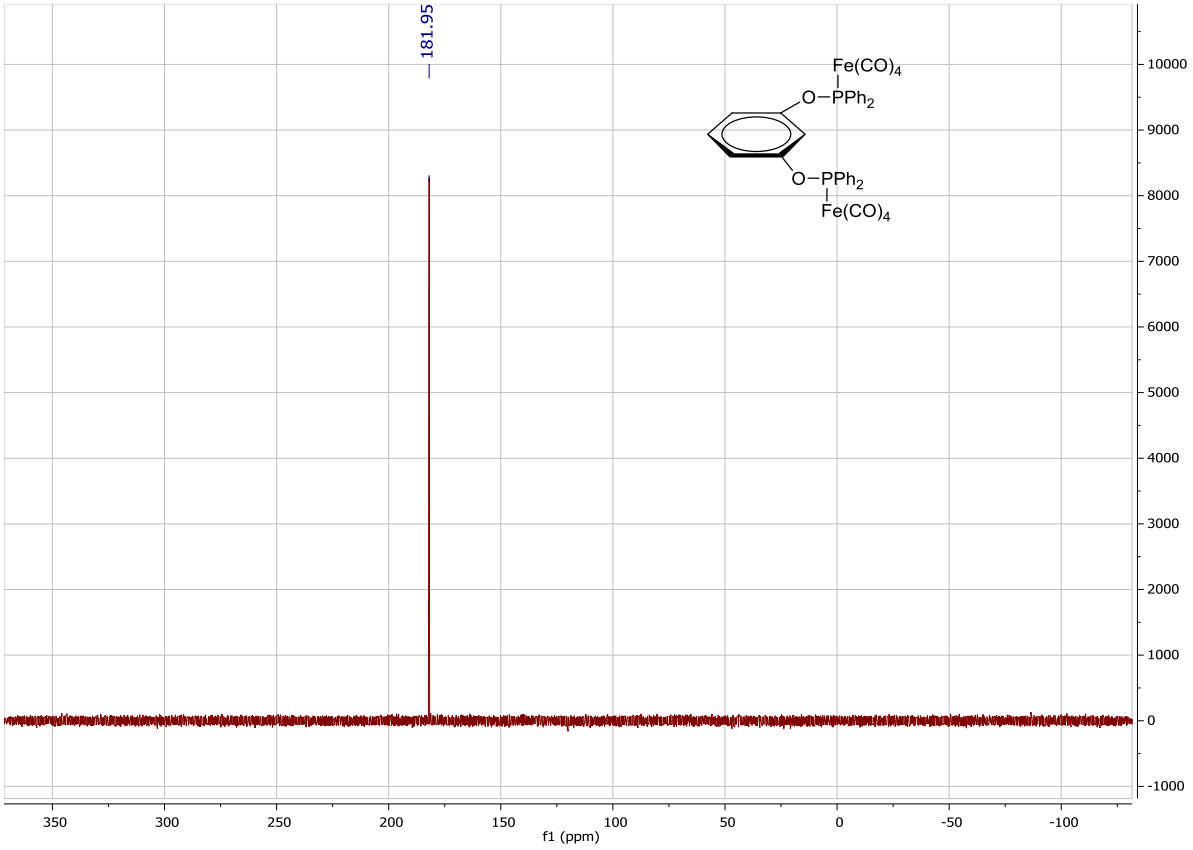


Figure S20: $^{31}P\{^{1}H\}$ NMR spectrum of the complex **2d** in C_6D_6 recorded at 162 MHz.

^{1}H, $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR data for the product of the catalysis

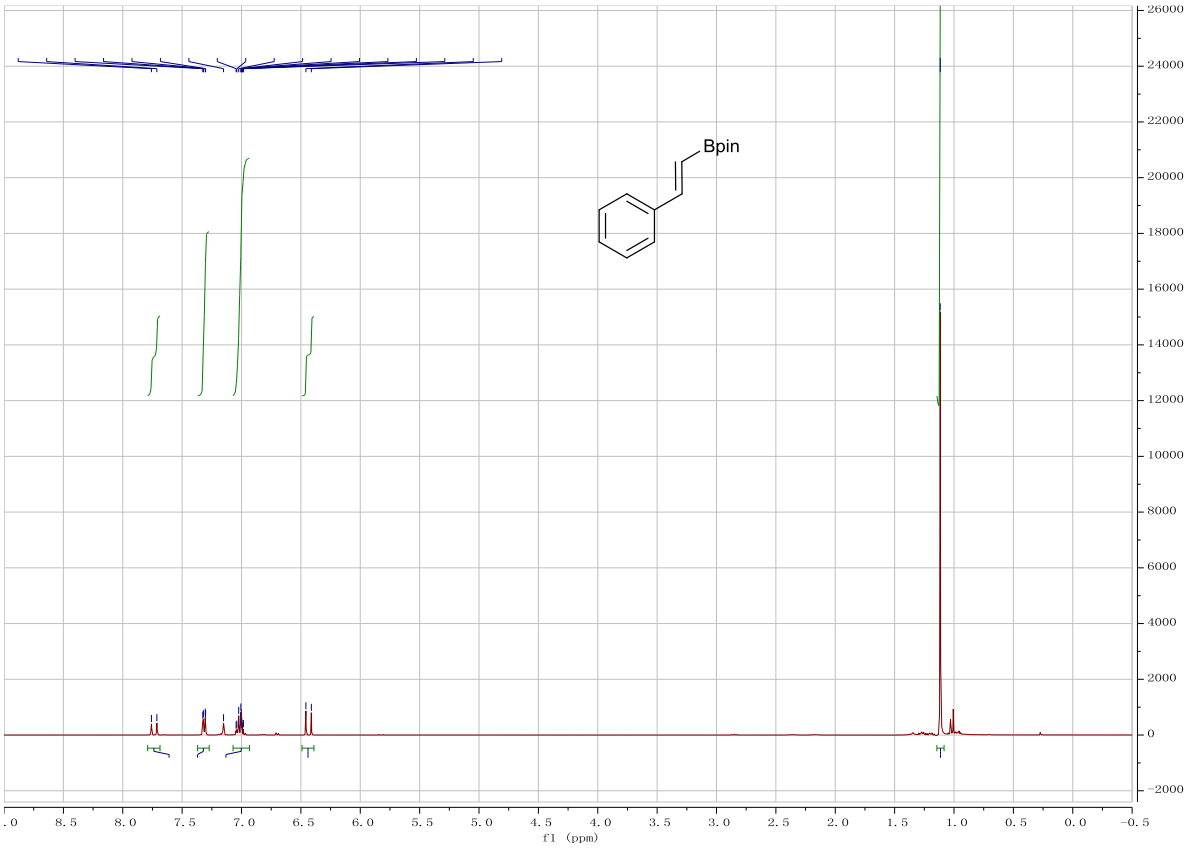


Figure S21: ^{1}H NMR spectrum of the compound **6** in C_6D_6 recorded at 400MHz.

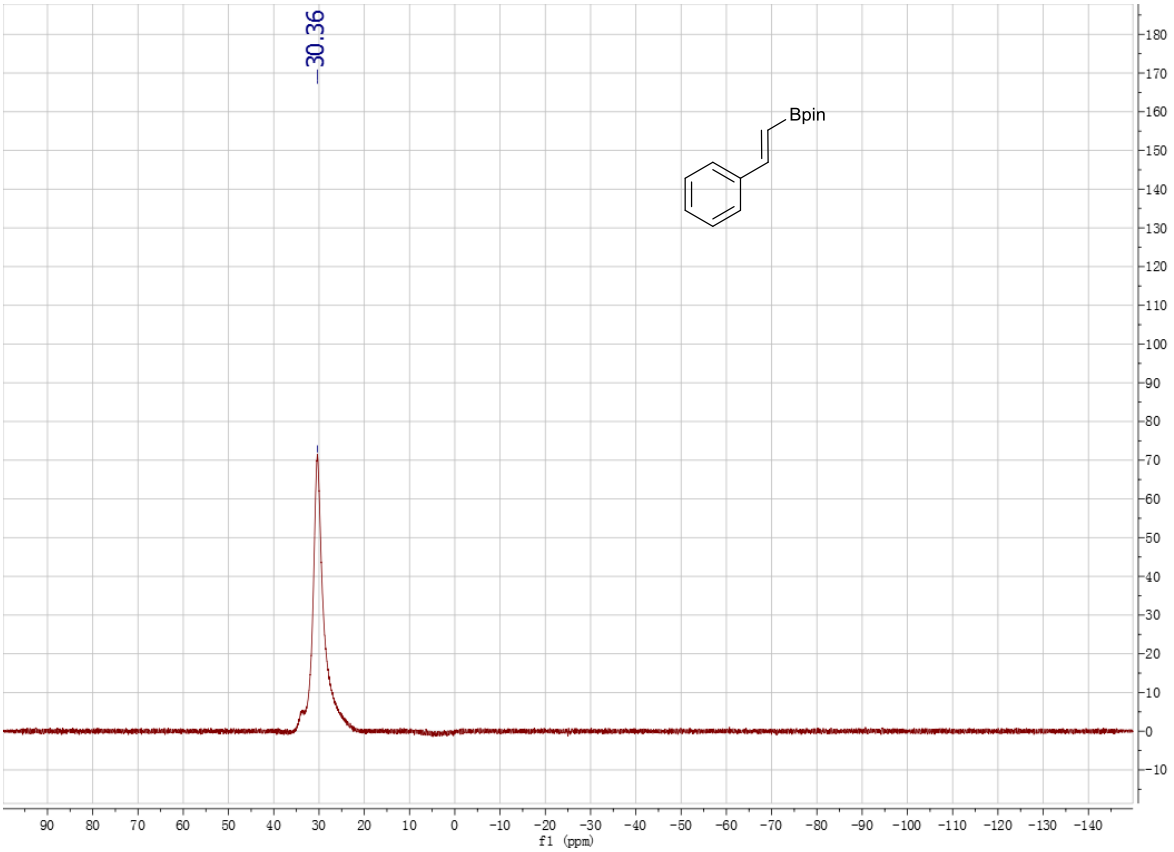


Figure S22: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **6** in C_6D_6 recorded at 128 MHz.

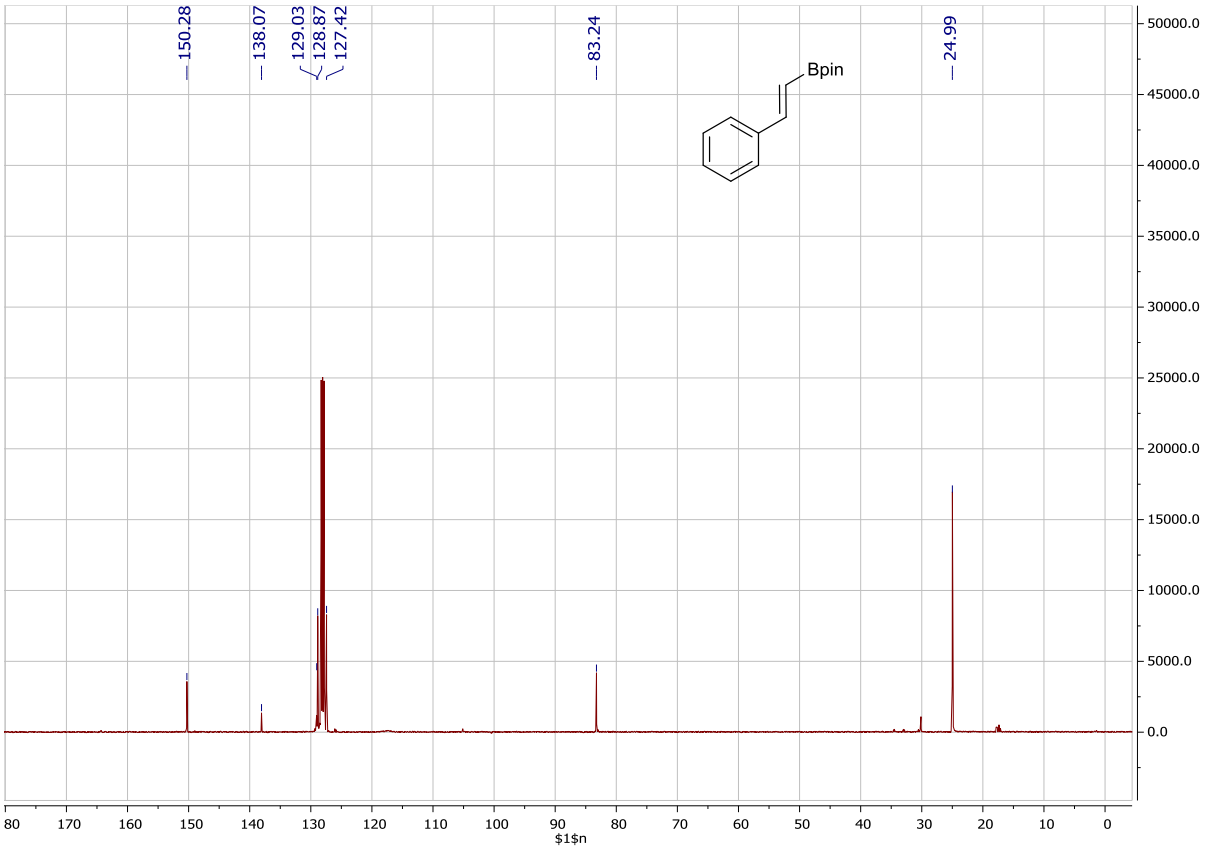


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **6** in C_6D_6 recorded at 101 MHz.

Typical ^{1}H NMR data for the crude mixture after the catalysis

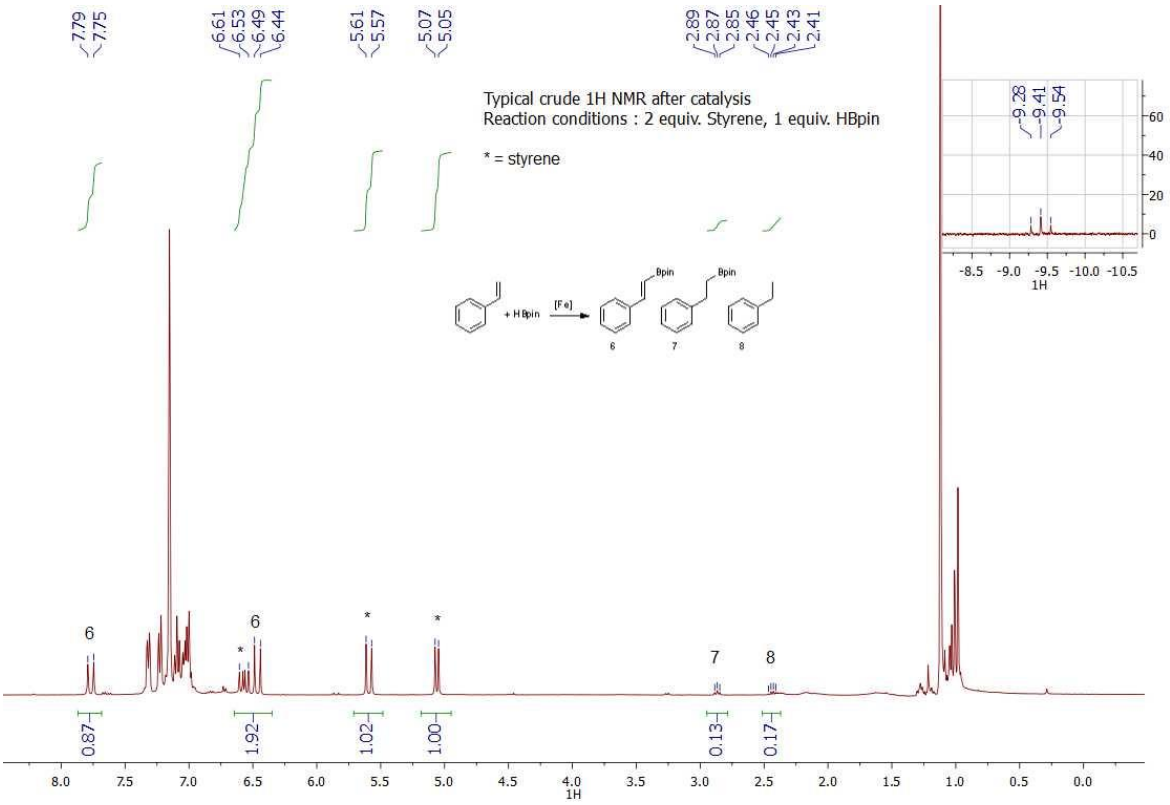


Figure S24: ^{1}H NMR spectrum of the crude mixture after a typical catalytic reaction with **1c** as catalyst in C_6D_6 recorded at 400 MHz.

NMR data for the crude mixture after the catalysis with 1d and conversion of 1d in 1c under UV irradiation

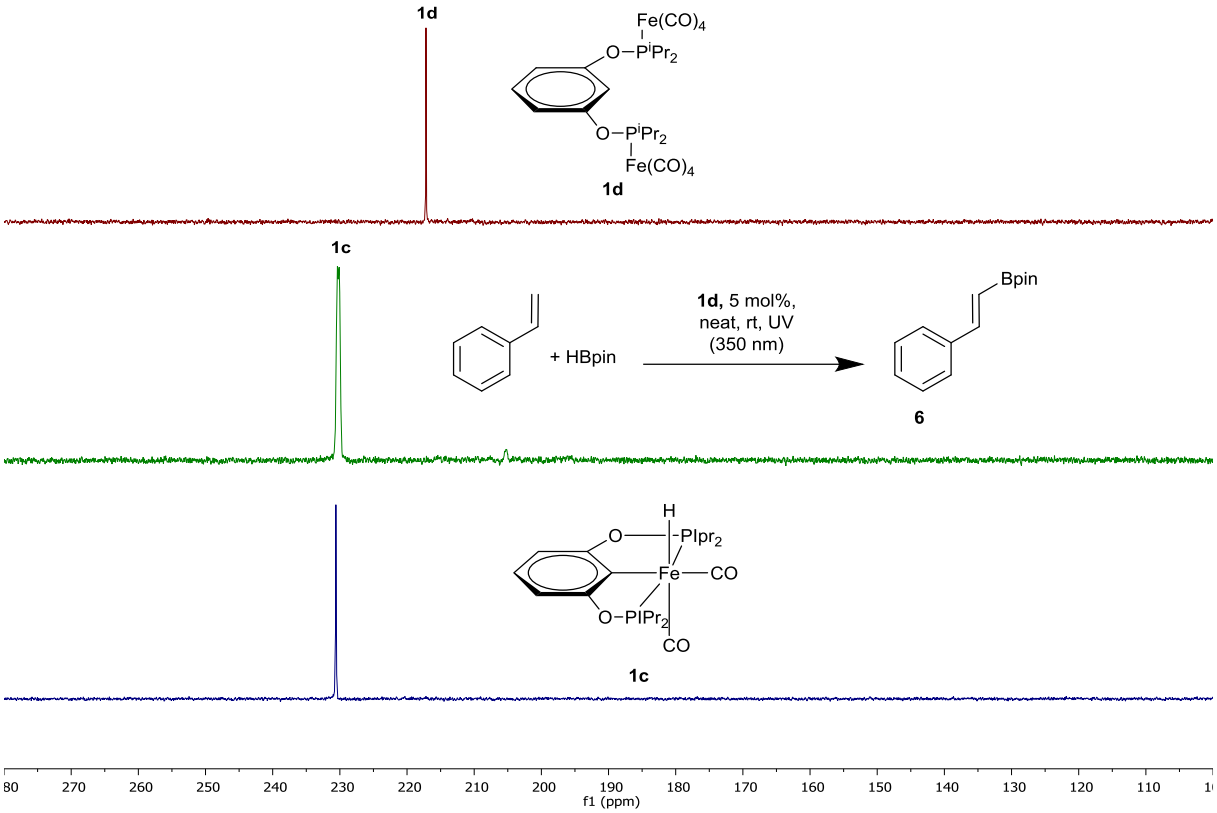


Figure S25: Comparison of the $^{31}P\{^{1}H\}$ NMR spectra of complex **1d** (top), of the crude reaction mixture after the dehydrogenative borylation of styrene catalyzed by **1d** (5 mol%) (middle) and of complex **1c** (bottom).

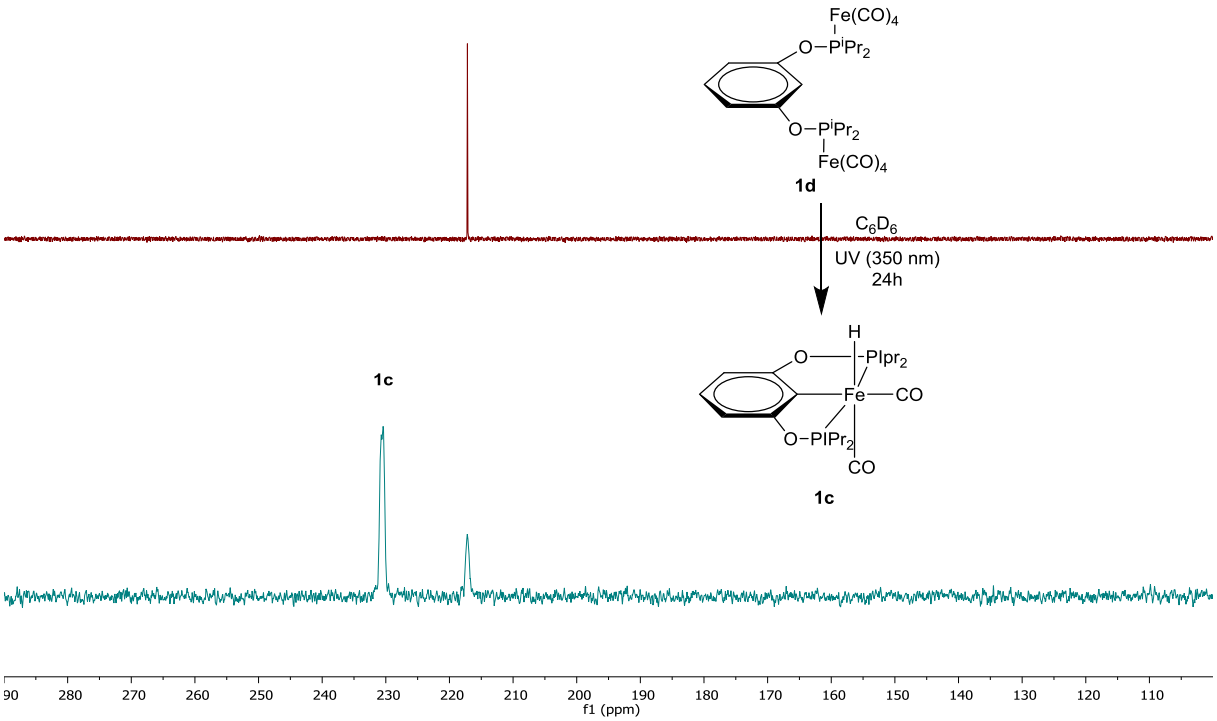


Figure S26: $^{31}P\{^{1}H\}$ NMR spectra of **1d** before (top) and after UV irradiation (350 nm) for 24h, in C_6D_6, showing the conversion of **1d** into **1c**.

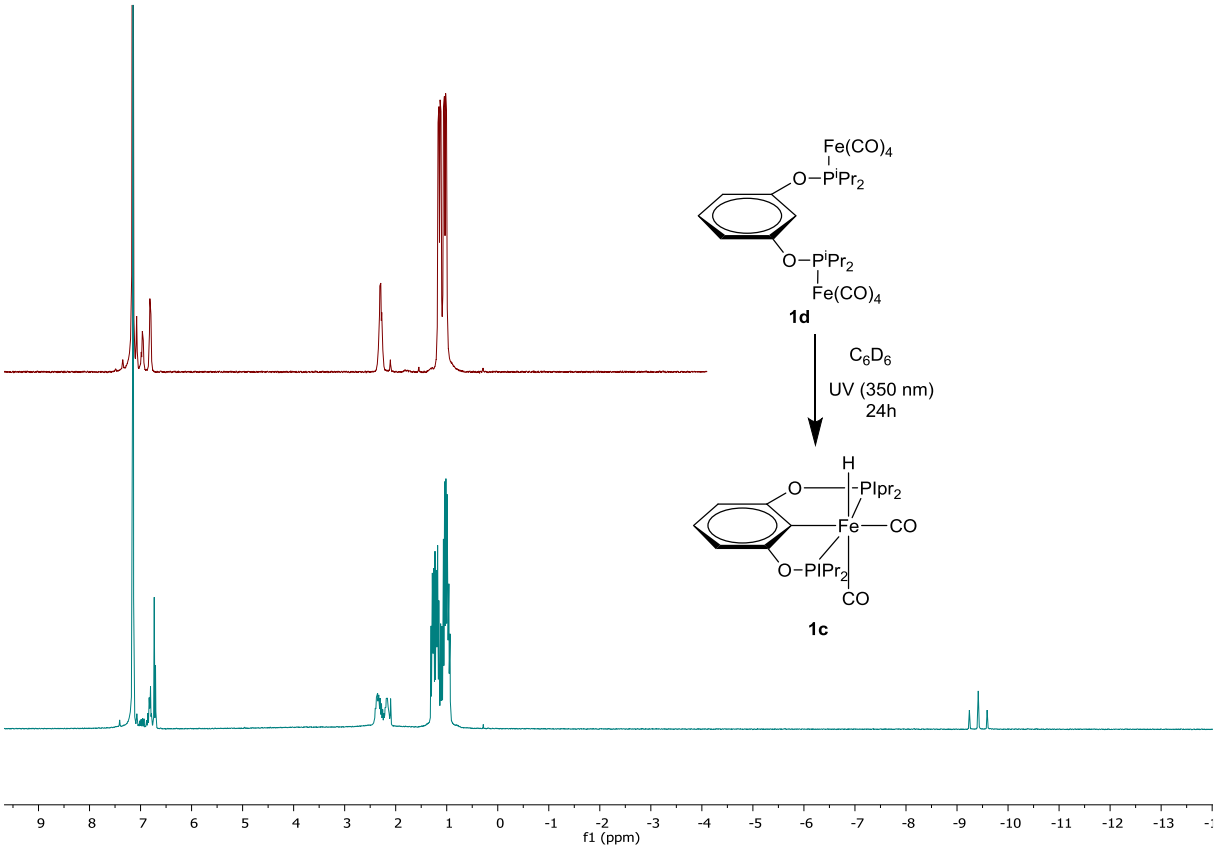


Figure S27: ^{1}H NMR spectra of **1d** before (top) and after UV irradiation (350 nm) for 24h, in C_6D_6 showing the conversion of **1d** into **1c**.

X-ray data for complexes 2d, 3d, 1c and 5c

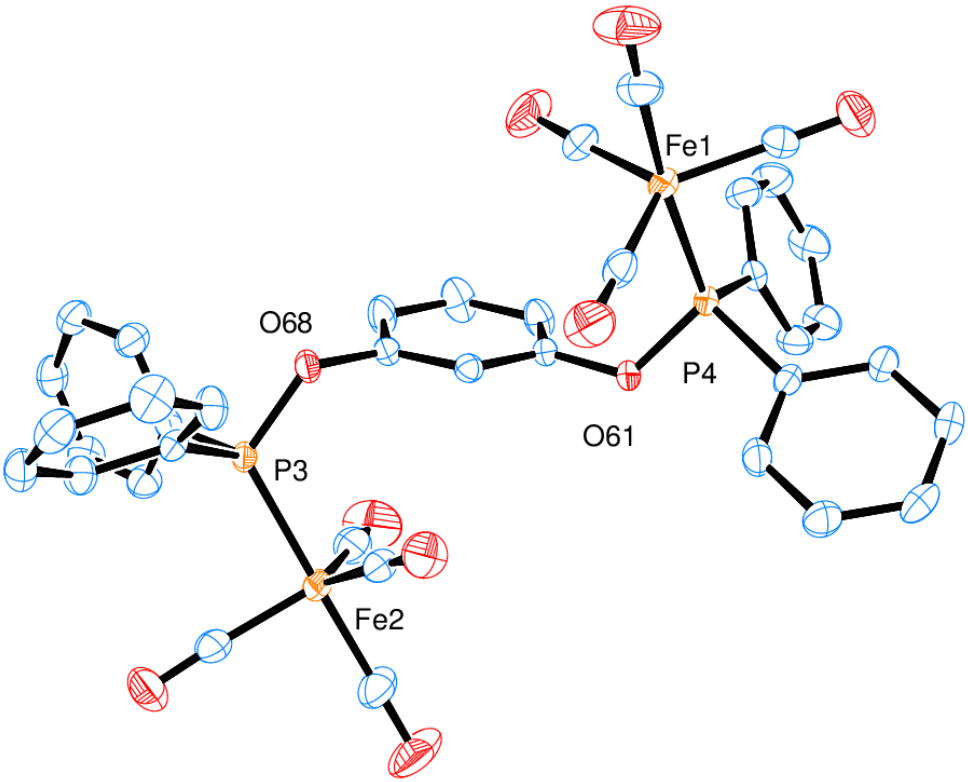


Figure S28: ORTEP view of the molecular structure of complex **2d** with thermal ellipsoids drawn at 50% probability. Hydrogens atoms were omitted for clarity.

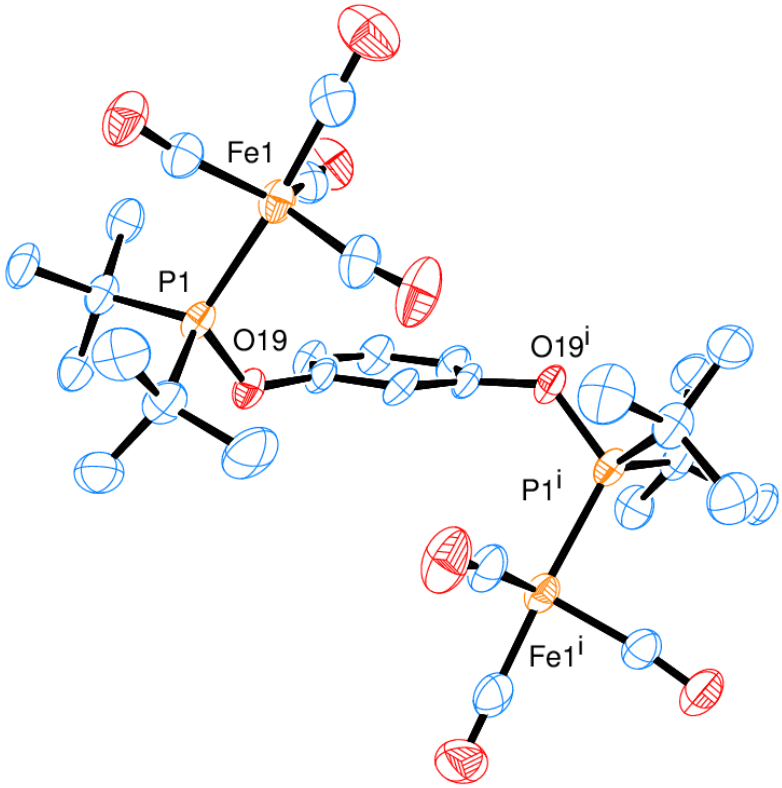


Figure S29: ORTEP view of the molecular structure of complex **3d** with thermal ellipsoids drawn at 50% probability. Hydrogens atoms were omitted for clarity.

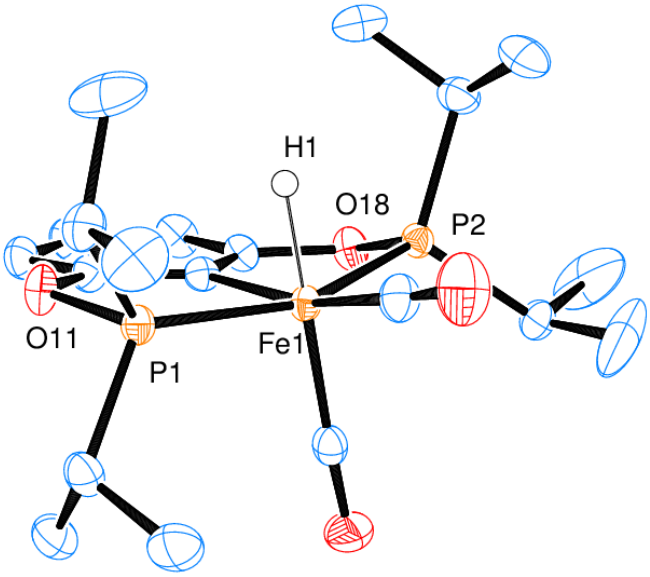


Figure S30: ORTEP view of the molecular structure of complex **1c** with thermal ellipsoids drawn at 50% probability. Hydrogens atoms, except the hydride, were omitted for clarity. Two molecules of **1c** are present in the unit cell, only one is depicted.

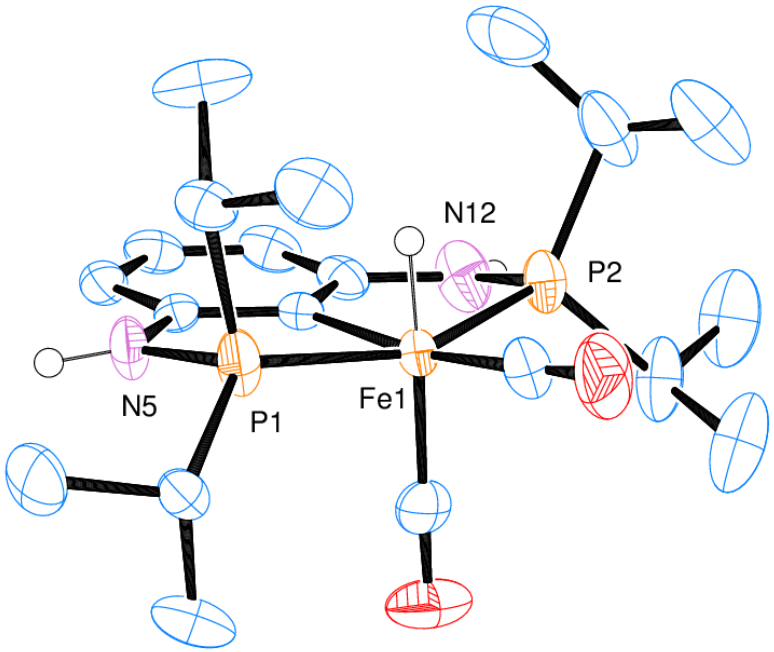
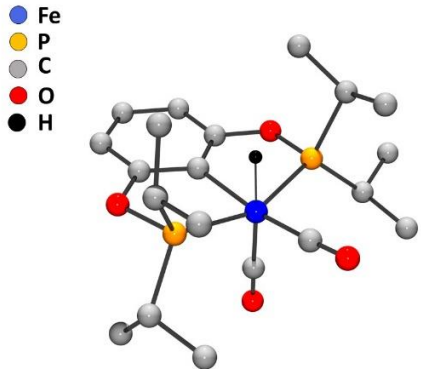


Figure S31: ORTEP view of the molecular structure of complex **5c** with thermal ellipsoids drawn at 50% probability. Hydrogens atoms, except the hydride and the NH, were omitted for clarity.

Calculations methods

Compound **1c**/DFT (H on carbon have been omitted in the picture for clarity)



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C	3.256276	-0.811844	-1.260517

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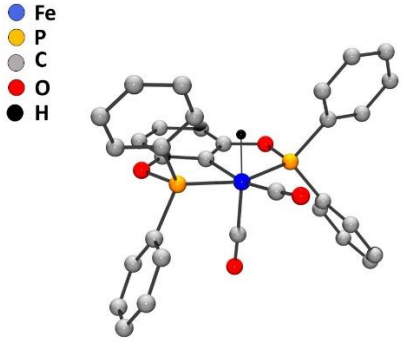
Compound **2c**/DFT (H on carbon have been omitted in the picture for clarity)



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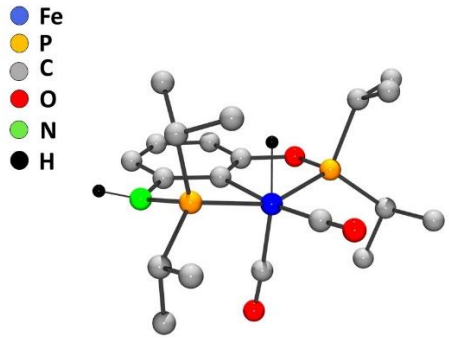
C	4.163796	-3.507097	-0.307038
C	-4.101120	-2.462020	-2.323272
C	-4.823197	-3.286524	-1.458259
C	3.787753	-1.146681	-1.747220
C	3.418859	-2.469109	0.249246
C	-3.304253	-1.443673	-1.809752
C	-4.745850	-3.090743	-0.080654
C	3.233421	-1.283948	-0.469157
C	-0.023758	-1.881756	-0.288659
C	-3.231949	-1.242526	-0.425665
C	-0.004386	0.352481	-1.873984
C	-3.950602	-2.069747	0.440573
C	4.448253	1.613585	0.170721
C	3.085583	1.553951	-0.152546
C	5.171967	2.773587	-0.084868
C	-4.456204	1.614737	-0.246316
C	-3.054906	1.609079	-0.243061
C	-0.003498	-0.181362	1.823527
C	2.460639	2.656328	-0.739680
C	1.180736	-0.221398	2.555068
C	-5.145752	2.785075	-0.549037
C	-2.355613	2.779102	-0.552748
C	4.545168	3.872342	-0.677061
C	-4.443499	3.951021	-0.858552
C	3.192632	3.812690	-1.006647
C	-3.049566	3.947242	-0.861363
C	-1.186929	-0.141654	2.556546
C	1.211299	-0.263498	3.947183
C	-1.218017	-0.181890	3.948772
C	-0.003953	-0.251969	4.633279
H	5.293761	-4.182026	-2.012160
H	4.958207	-2.079101	-3.290761
H	4.311673	-4.424613	0.255412
H	-4.154819	-2.616750	-3.397110

H	-5.441305	-4.084635	-1.859812
H	3.649970	-0.223416	-2.304381
H	-2.733767	-0.807608	-2.482816
H	-5.303312	-3.735237	0.593301
H	2.987513	-2.568976	1.240382
H	4.935730	0.752635	0.619233
H	-3.879406	-1.912889	1.512036
H	6.226207	2.820942	0.172811
H	-5.003756	0.704768	-0.018297
H	0.029856	1.379052	0.131952
H	-6.232093	2.786828	-0.548489
H	1.403379	2.603018	-0.979465
H	-1.269668	2.762334	-0.545482
H	5.114339	4.775022	-0.881570
H	-4.984700	4.861622	-1.100504
H	-2.501366	4.852976	-1.104648
H	2.161543	-0.294713	4.469631
H	2.704819	4.666127	-1.468912
H	-2.167388	-0.149889	4.472803
H	-0.004363	-0.283907	5.719038
O	-0.038695	-3.033320	-0.319385
O	-0.017225	0.711948	-2.974045
O	2.378888	-0.206606	1.855910
O	-2.382495	-0.039498	1.860433
P	2.136310	0.025177	0.194042
P	-2.129183	0.085481	0.189551
Fe	0.001246	-0.097644	-0.171705

Compound **4c**/DFT (H on carbon have been omitted in the picture for clarity)

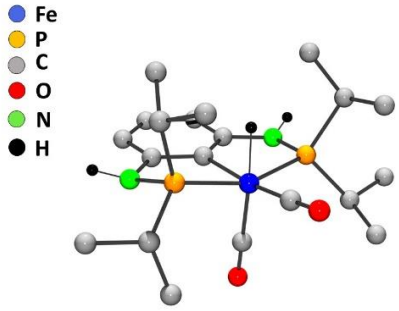


E: -1199.348536 u.a.

C	-1.209452	2.329418	-0.058515
C	-1.177314	3.723707	0.050617
C	0.058683	4.369127	0.117553
C	1.250655	3.647780	0.087903
C	1.172797	2.258538	-0.021401
C	-0.032617	1.568935	-0.098425
O	2.347930	1.525025	-0.043385
P	2.045851	-0.147194	0.061812
Fe	-0.082912	-0.437601	-0.272402
P	-2.203941	-0.097461	0.159258
N	-2.407882	1.595484	-0.144996
C	-0.147850	-0.142761	-2.025210
O	-0.196981	0.126064	-3.148282
C	-0.123959	-2.192798	-0.202827
O	-0.156699	-3.349039	-0.115496
C	3.388126	-0.735617	-1.087569
C	3.520617	-2.258882	-1.041708
C	3.126309	-0.233030	-2.506882
C	2.661501	-0.454628	1.801064
C	2.314007	-1.846538	2.328798
C	4.134925	-0.101186	1.994630
C	-3.619152	-0.800118	-0.843470
C	-3.867221	-2.280235	-0.546611
C	-3.379673	-0.562803	-2.333284
C	-2.752864	-0.370364	1.940153
C	-2.251222	0.779662	2.816167
C	-2.252283	-1.711615	2.483758
H	4.006591	-0.420415	-3.132106
H	2.280503	-0.754758	-2.961844
H	2.916079	0.839633	-2.524948
H	-4.286426	-0.802379	-2.900093
H	-2.576659	-1.206384	-2.703986
H	4.247905	-2.591824	-1.790522
H	4.307244	-0.269639	-0.711964
H	-3.104644	0.474418	-2.541124
H	2.566400	-2.746801	-1.269069
H	2.217385	4.136206	0.150339

H	-2.960701	-2.874092	-0.706502
H	-4.637776	-2.669106	-1.221580
H	0.090886	5.451921	0.202141
H	3.862428	-2.620830	-0.068484
H	-2.100502	4.297493	0.079629
H	-4.497996	-0.219795	-0.523765
H	4.367085	0.888793	1.591666
H	-4.213215	-2.450139	0.476412
H	-3.263068	2.061233	0.127870
H	4.790616	-0.836313	1.514995
H	-0.032396	-0.407353	1.232448
H	2.904963	-2.629012	1.843903
H	4.380542	-0.097441	3.062630
H	2.044685	0.278976	2.338731
H	1.257164	-2.080529	2.179842
H	-2.508575	-2.562609	1.848470
H	-3.852446	-0.368194	1.922356
H	-2.681356	1.743389	2.531920
H	-1.162609	-1.691025	2.577101
H	2.524961	-1.897710	3.402850
H	-1.162117	0.870238	2.739540
H	-2.675578	-1.892587	3.478266
H	-2.505212	0.589733	3.865109

Compound **5c**/DFT (H on carbon have been omitted in the picture for clarity)

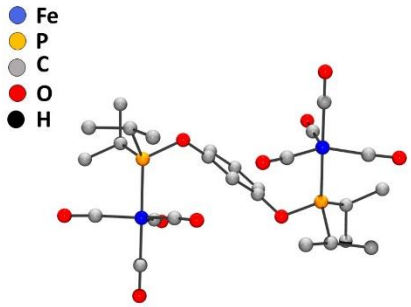


E: -1179.488064 u.a.

C	0.748468	3.782883	-0.245968
C	0.896279	2.389438	-0.231126
C	-0.206461	1.528497	-0.273416
C	-1.475439	2.110125	-0.363603
C	-1.657183	3.498711	-0.382212
C	-0.534370	4.322148	-0.320710
Fe	0.027045	-0.480565	-0.214505
C	0.169152	-2.204553	0.081852
O	0.239148	-3.337764	0.322603
N	2.157779	1.772082	-0.184402
P	2.126174	0.058406	0.027238
C	3.346433	-0.518992	-1.276633
H	2.973513	0.043922	-2.142726
N	-2.563068	1.209898	-0.425578
P	-2.129445	-0.373299	0.126521
C	-2.702524	-0.459516	1.912979
C	-2.224269	0.772790	2.681244
C	0.041616	-0.394536	-1.987304
O	0.092869	-0.267783	-3.135961
C	2.973028	-0.182741	1.681287
H	3.960336	0.286598	1.569765
C	-3.352863	-1.490556	-0.746354
H	-3.369337	-2.397115	-0.126248
C	2.203759	0.551712	2.779413
C	3.151788	-1.662978	2.018498
C	4.793507	-0.107757	-1.008741
C	3.214155	-2.010485	-1.589006
C	-4.761737	-0.893616	-0.801777
C	-2.852806	-1.854765	-2.143451
H	-3.800775	-0.462781	1.884988
C	-2.213348	-1.752837	2.566900
H	0.061540	-0.279270	1.276813
H	2.954452	2.324274	0.098036
H	1.619683	4.432480	-0.208166
H	-0.660780	5.401495	-0.332054
H	-2.654879	3.926589	-0.444240

H	-3.469556	1.582431	-0.173819
H	3.811012	-2.176483	1.313665
H	2.187873	-2.181624	2.020095
H	1.984952	1.588434	2.506945
H	2.787335	0.552304	3.707220
H	1.249280	0.054771	2.976747
H	3.589637	-1.771150	3.017398
H	-2.597394	-1.827282	3.590580
H	-2.533664	-2.650173	2.027337
H	-1.119917	-1.763892	2.612549
H	-2.537128	0.707000	3.729587
H	-1.132515	0.844385	2.650727
H	-2.622202	1.701780	2.263741
H	3.832306	-2.265230	-2.457255
H	3.543541	-2.639268	-0.756562
H	2.180647	-2.278954	-1.821226
H	5.415154	-0.321452	-1.885617
H	4.888022	0.962840	-0.797321
H	5.220260	-0.662512	-0.166077
H	-3.574947	-2.508527	-2.645631
H	-2.724847	-0.958050	-2.758132
H	-1.892187	-2.374287	-2.104286
H	-5.461971	-1.621705	-1.225948
H	-5.146685	-0.609284	0.183136
H	-4.777102	-0.009522	-1.447788

Compound **1d**/DFT (H on carbon have been omitted in the picture for clarity)



E: -1219.212577 u.a.

C	-3.118724	-2.213436	-1.434123
C	3.183814	-2.337355	-1.342181
C	-3.561085	0.128312	-2.274989
C	-0.050743	-0.503446	-1.953931
C	-3.459473	-0.772138	-1.041955
C	3.256276	-0.811844	-1.260517
C	-0.067642	-2.216553	0.157802
C	4.688085	-0.297906	-1.114719
C	-3.042036	-1.869859	2.173506
C	-2.936591	-0.384059	1.828405
C	-0.046813	1.512408	-0.179102
C	1.139056	2.239987	-0.258016
C	-1.225777	2.251068	-0.098371
C	2.615787	-1.681580	2.266220
C	2.874755	-0.290847	1.684452
C	1.175648	3.633004	-0.277463
C	-1.249163	3.644899	-0.114306
C	-2.170130	0.396647	2.894697
C	-0.034460	4.324900	-0.210948
C	2.353972	0.810158	2.610296
H	-3.919995	-2.629669	-2.054509
H	-2.193508	-2.243634	-2.017265
H	3.737921	-2.688060	-2.219548
H	-4.302361	-0.282497	-2.969733
H	-2.983335	-2.873930	-0.573164
H	2.154197	-2.695239	-1.430230
H	-2.605280	0.180195	-2.805358
H	2.822306	-0.394695	-2.179430
H	5.272963	-0.572400	-1.999798
H	3.635202	-2.810090	-0.464039
H	-4.414981	-0.755565	-0.500625
H	-3.854503	1.146066	-2.010922
H	-3.696666	-2.414127	1.486709
H	-2.057785	-2.349201	2.161254

H	5.186750	-0.744413	-0.247600
H	4.717807	0.790100	-1.012135
H	-3.454413	-1.988607	3.181631
H	2.969560	-2.489280	1.619402
H	-3.942365	0.046380	1.727316
H	-0.011523	-0.338096	1.320788
H	1.544885	-1.831917	2.433530
H	3.949824	-0.145570	1.525598
H	-1.177237	-0.035688	3.052320
H	3.124524	-1.780844	3.231485
H	2.126839	4.151251	-0.339038
H	-2.194732	4.172989	-0.049597
H	-2.713946	0.356294	3.845242
H	-2.042075	1.445832	2.615165
H	-0.030314	5.411107	-0.225132
H	1.266357	0.743295	2.718892
H	2.593100	1.805681	2.229561
H	2.803162	0.700049	3.603745
O	-0.006115	-0.489681	-3.110052
O	-0.078210	-3.341034	0.438848
O	2.329841	1.533231	-0.305470
O	-2.419809	1.561396	0.017021
P	-2.172331	-0.115733	0.149004
P	2.077368	-0.120533	0.006386
Fe	-0.055390	-0.493353	-0.178334