SUPPORTING INFORMATION

SYNTHESIS OF NOVEL PHOSPHININE COORDINATION COMPOUNDS AND THEIR REACTIVITY TOWARD SMALL MOLECULES

Dissertation zur Erlangung des

Doktorgrades der Naturwissenschaften

DOCTOR RERUM NATURALIUM

am Institut für Anorganische Chemie

der Fakultät für Chemie und Pharmazie

der Universität Regensburg

vorgelegt von

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aus Aschau am Inn

Regensburg 2020

Supporting Information

Chapter 2

Halide-Substituted Phosphacyclohexadienyl Iron Complexes:Covalent Structures vs. Ion Pairs

S1 NMR Spectra

[Cp*Fe(1-F-PC$_5$Ph$_3$H$_2$)] (2-F)

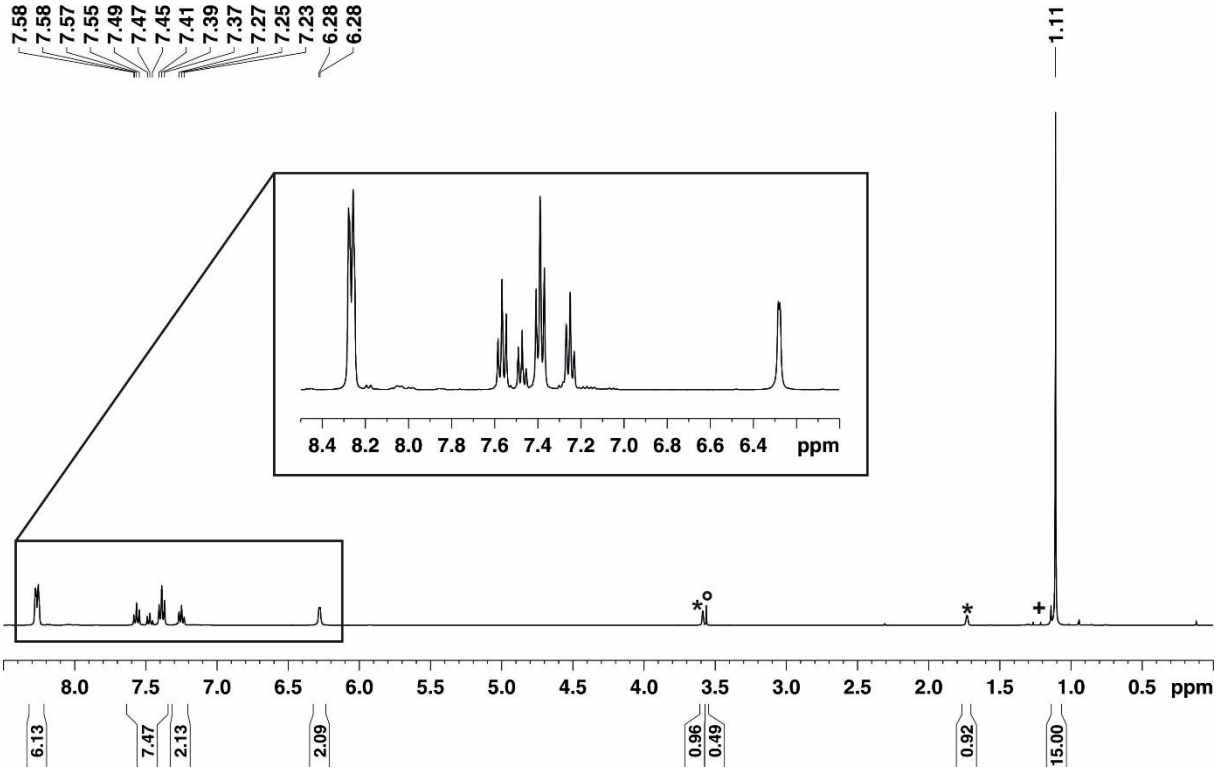

Figure S1 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-F-PC$_5$Ph$_3$H$_2$)] (**2-F**); * [D$_8$]THF; ° [18]crown-6; + impurities.

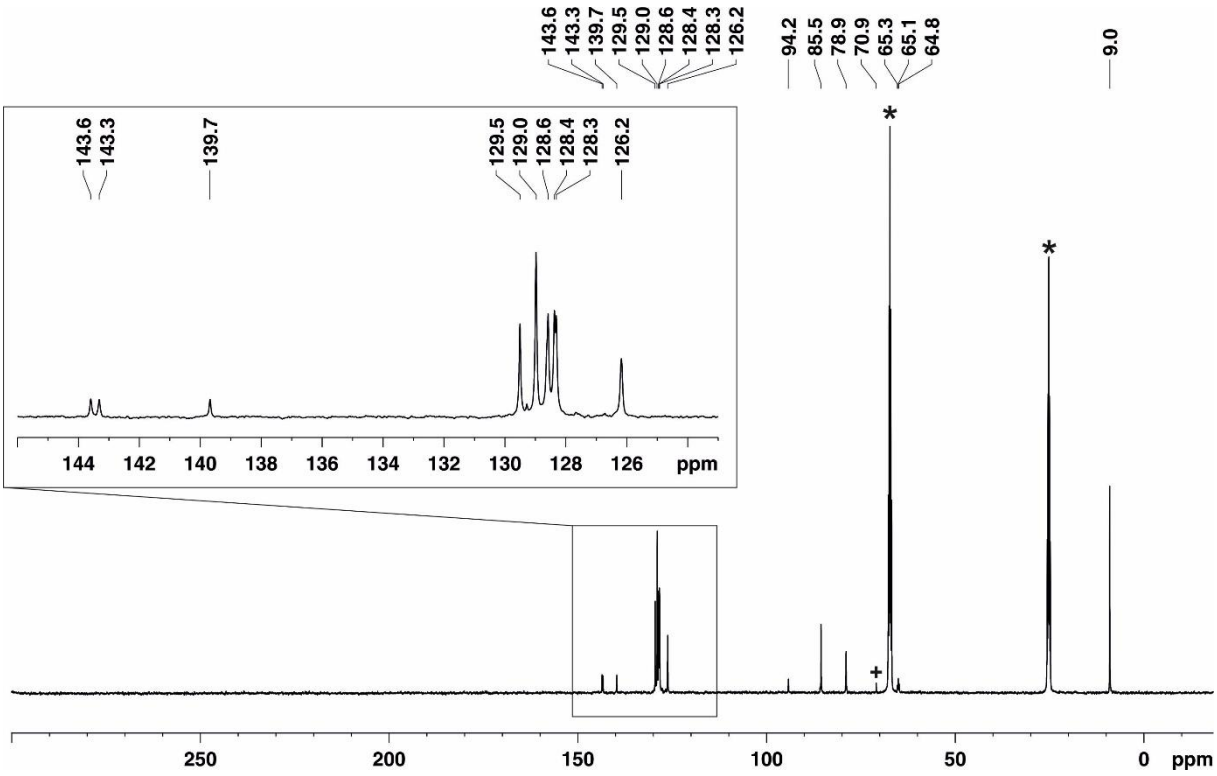

Figure S2 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-F-PC$_5$Ph$_3$H$_2$)] (**2-F**); * [D$_8$]THF; + impurity.

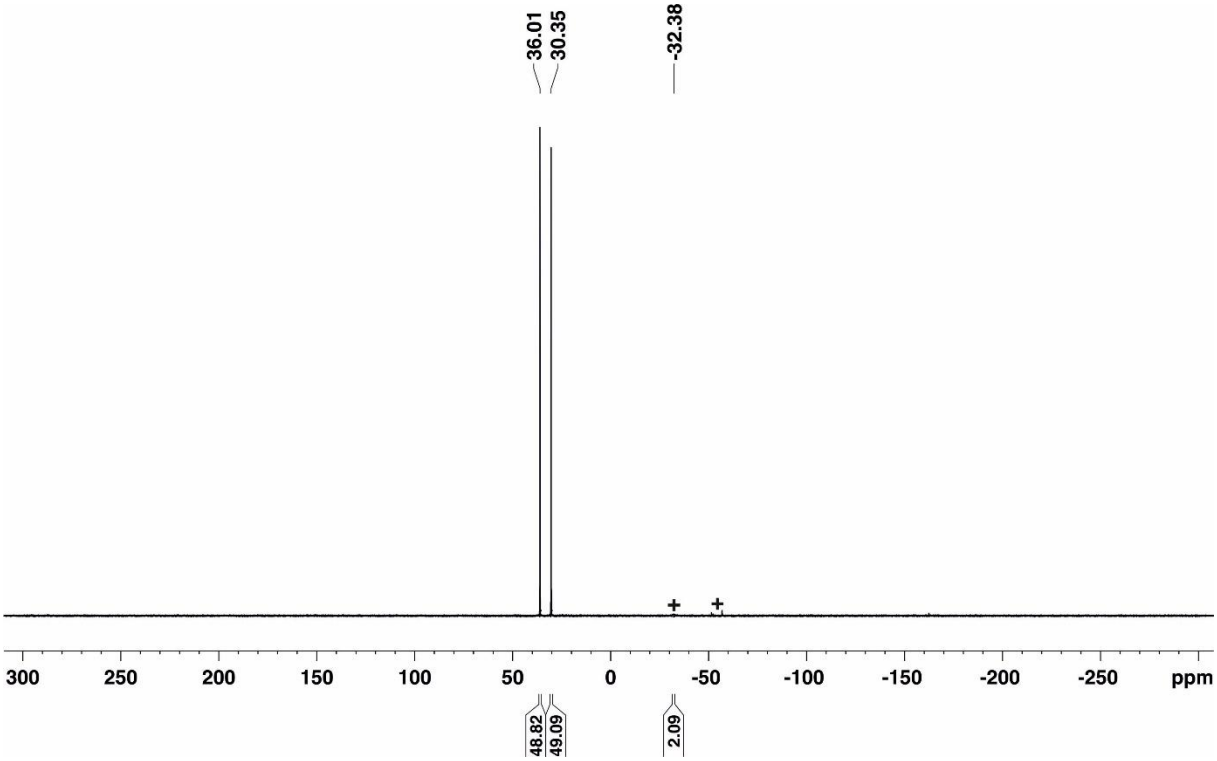

Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(1\text{-}F\text{-}PC_5Ph_3H_2)]$ (**2-F**); + impurities.

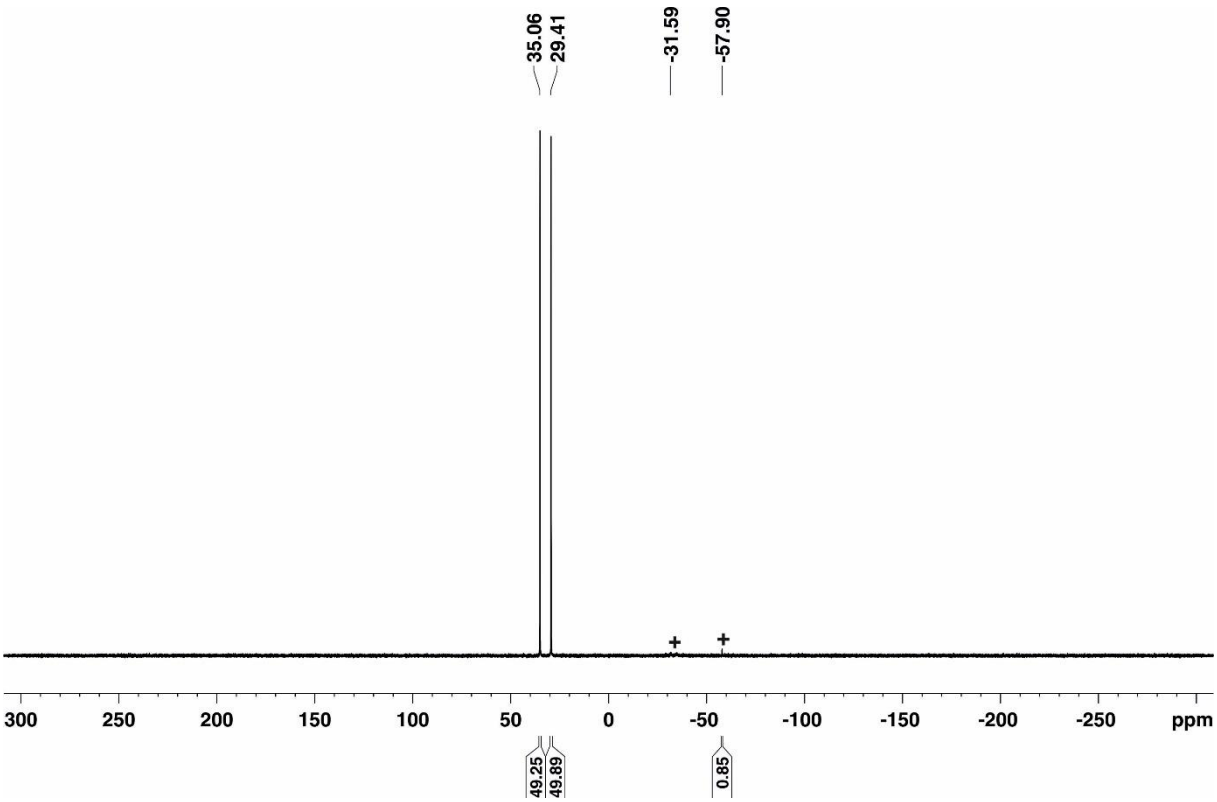

Figure S4 ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(1\text{-}F\text{-}PC_5Ph_3H_2)]$ (**2-F**); + impurities.

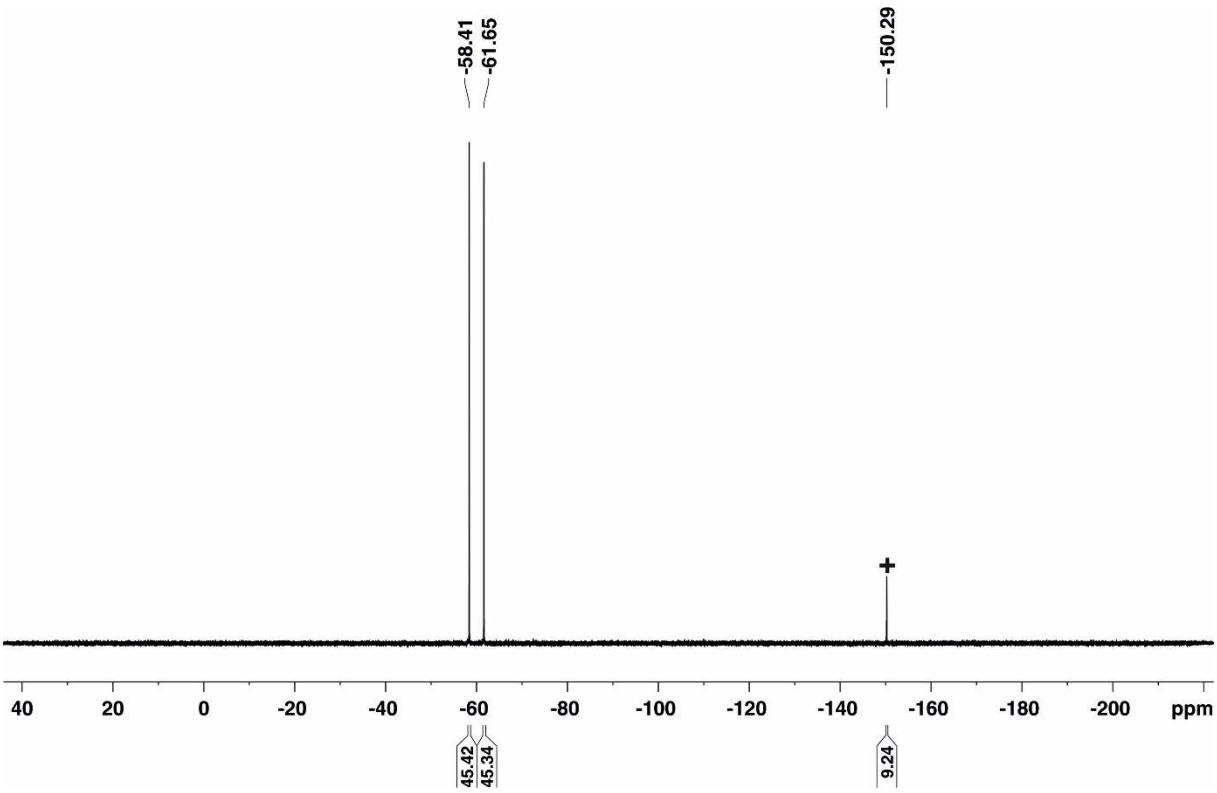

Figure S5 $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, $[D_8]$THF) of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**); + KBF_4.

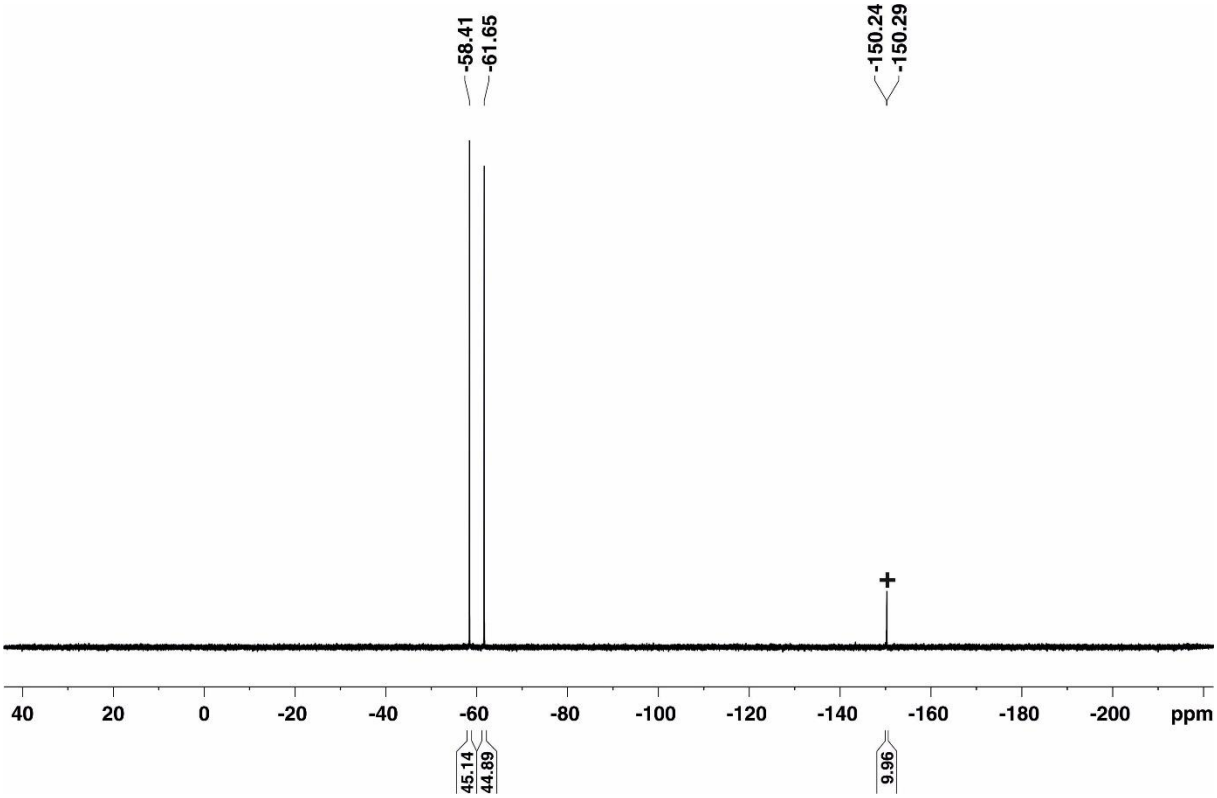

Figure S6 ^{19}F NMR spectrum (376.50 MHz, 300 K, $[D_8]$THF) of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**); + KBF_4.

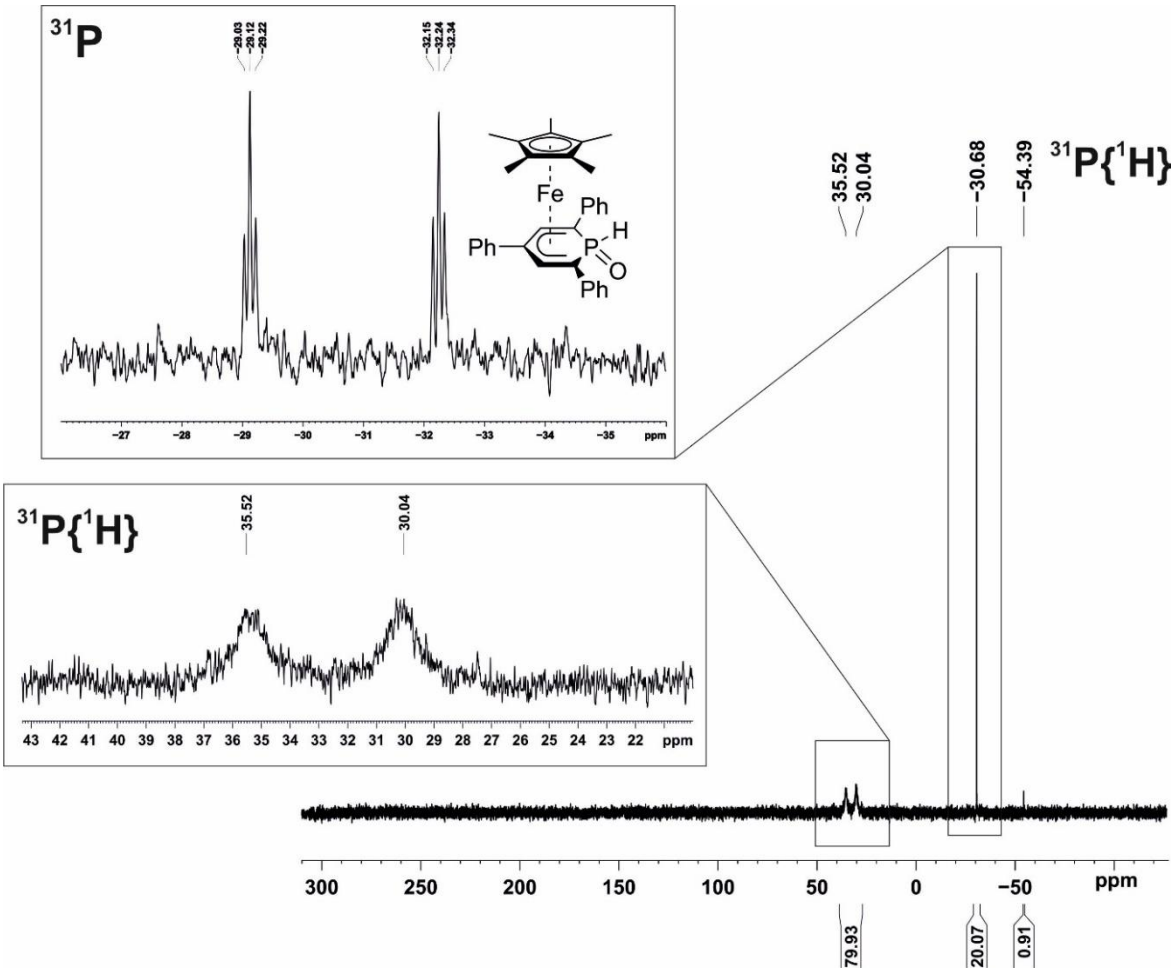

Figure S7 $^{31}P\{^{1}H\}$ and ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_3]MeCN$) of $[Cp^*Fe(1\text{-}F\text{-}PC_5Ph_3H_2)]$ (**2-F**); hydrolysis product $[Cp^*Fe\{1\text{-}H\text{-}1\text{-}O\text{-}PC_5Ph_3H_2)]$ (**2-OH**) at −30.7 ppm.

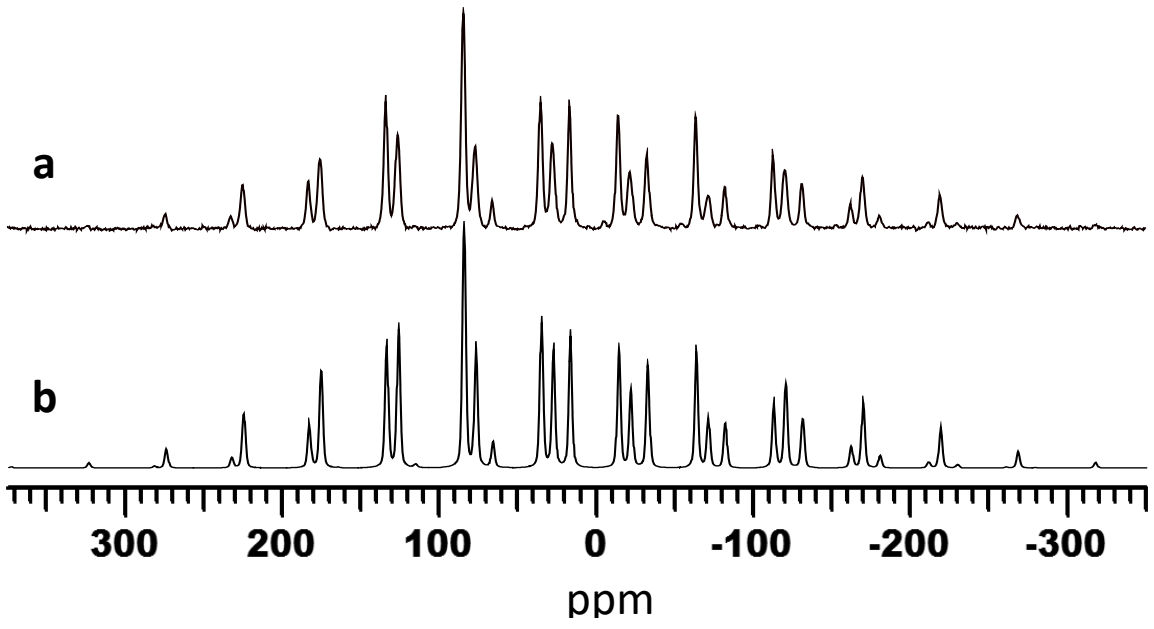

Figure S8 ^{31}P CP MAS spectrum (6 kHz, 300 K) of $[Cp^*Fe(1\text{-}F\text{-}PC_5Ph_3H_2)]$ (**2-F**); a) experimental spectrum (δ_{iso} = 35.5 ppm, 28.0 ppm; J_{PF} = 930 Hz), b) simulated spectrum.

[Cp*Fe(1-Cl-PC$_5$Ph$_3$H$_2$)] (2-Cl)

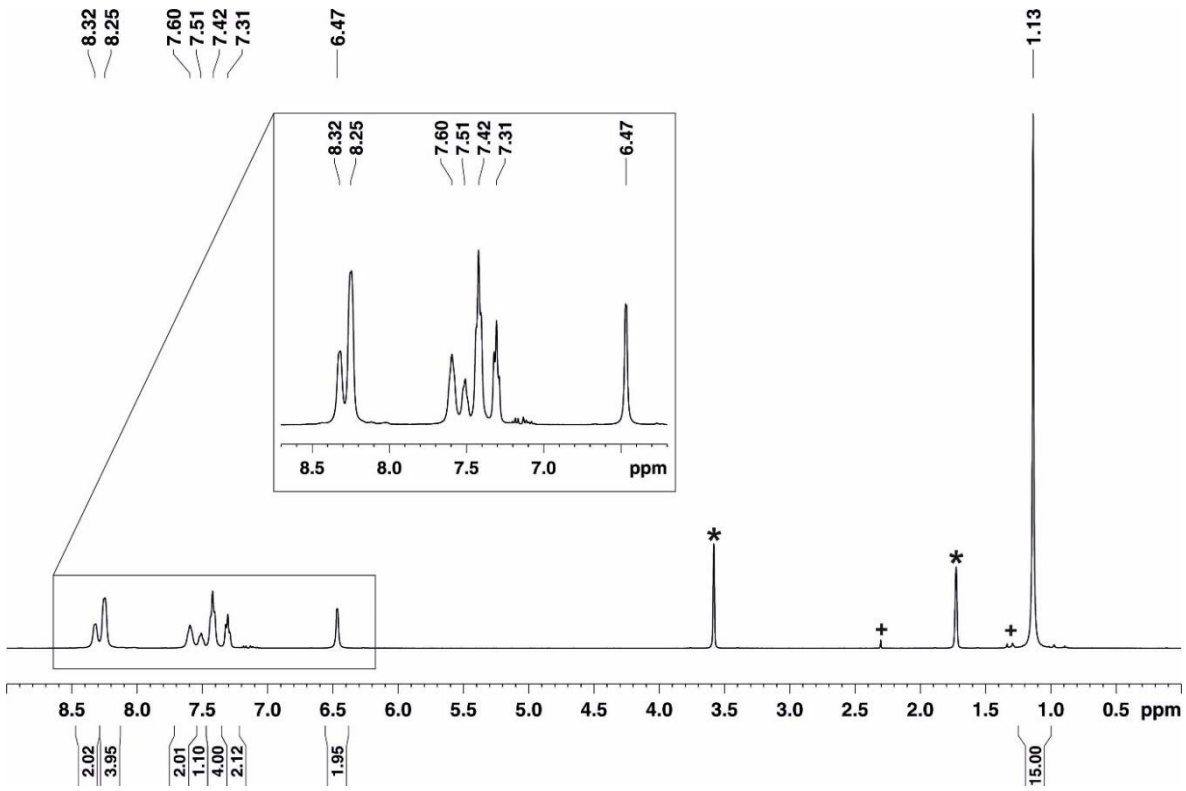

Figure S9 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Cl-PC$_5$Ph$_3$H$_2$)] (**2-Cl**), * [D$_8$]THF, + impurities.

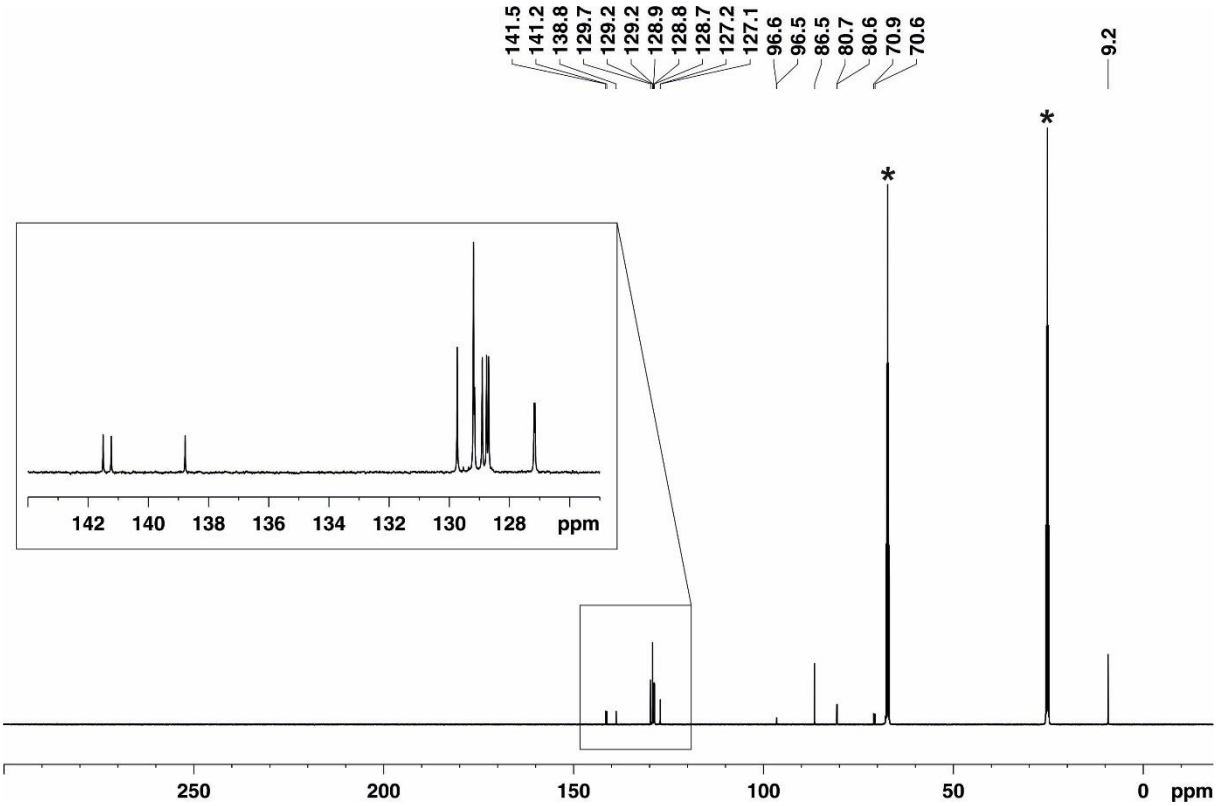

Figure S10 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) [Cp*Fe(1-Cl-PC$_5$Ph$_3$H$_2$)] (**2-Cl**); * [D$_8$]THF.

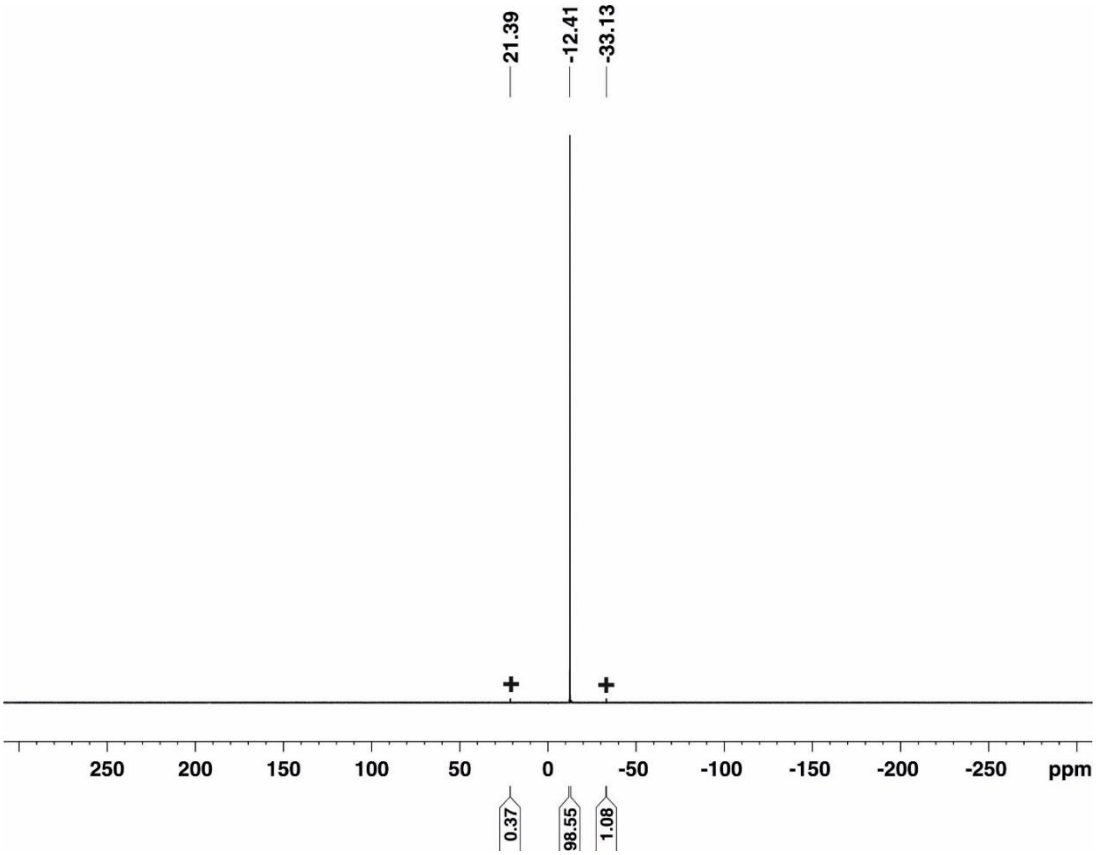

Figure S11 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(1\text{-}Cl\text{-}PC_5Ph_3H_2)]$ (**2-Cl**); + impurities.

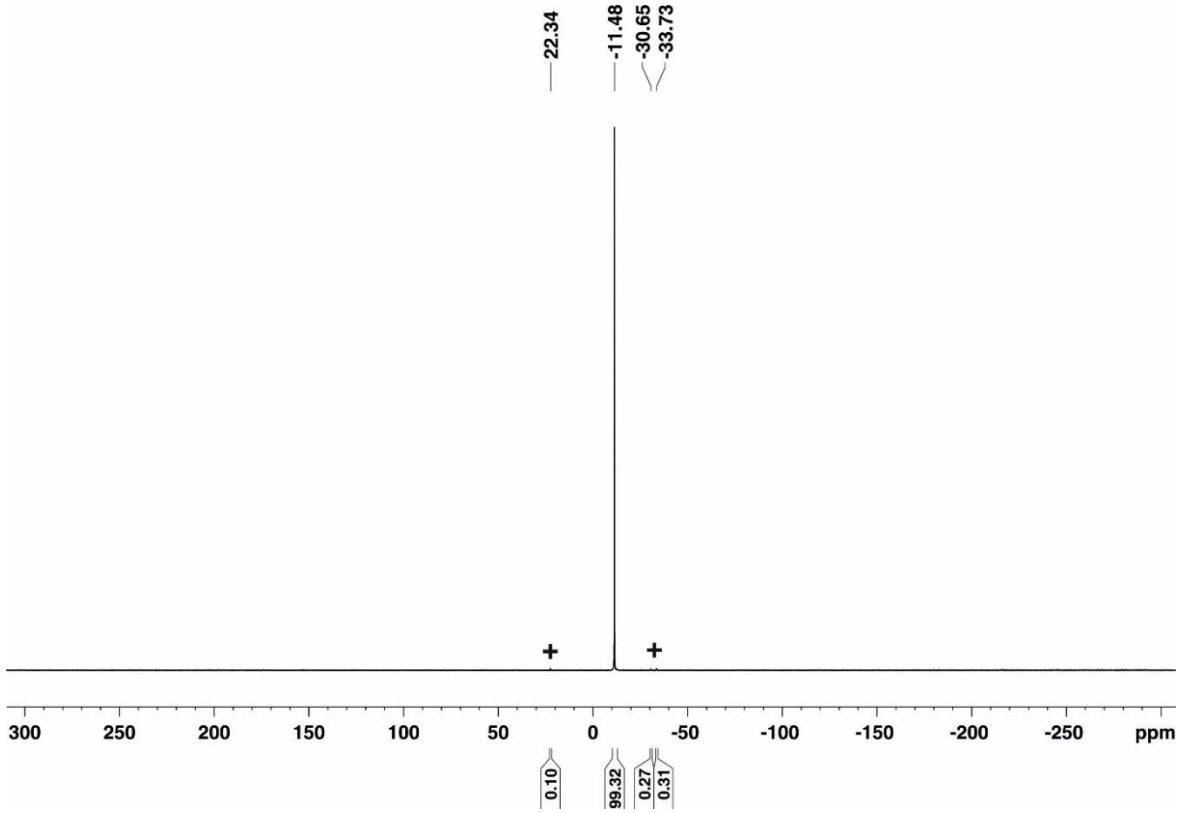

Figure S12 ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(1\text{-}Cl\text{-}PC_5Ph_3H_2)]$ (**2-Cl**); + impurities.

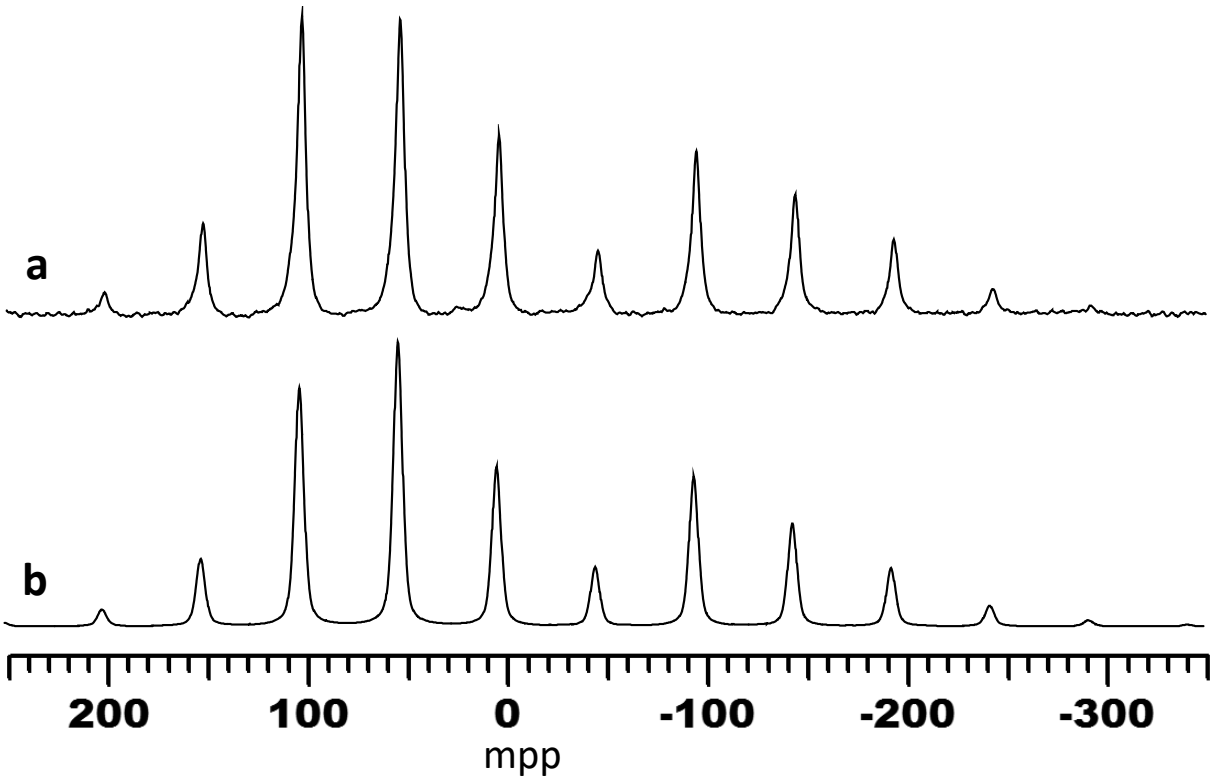

Figure S13 ^{31}P CP MAS spectrum (6 kHz, 300 K) of [Cp*Fe(1-Cl-$PC_5Ph_3H_2$)] (**2-Cl**); a) experimental spectrum (δ_{iso} = 3.8 ppm), b) simulated spectrum.

[Cp*Fe($PC_5Ph_3H_2$)]Br (2-Br)

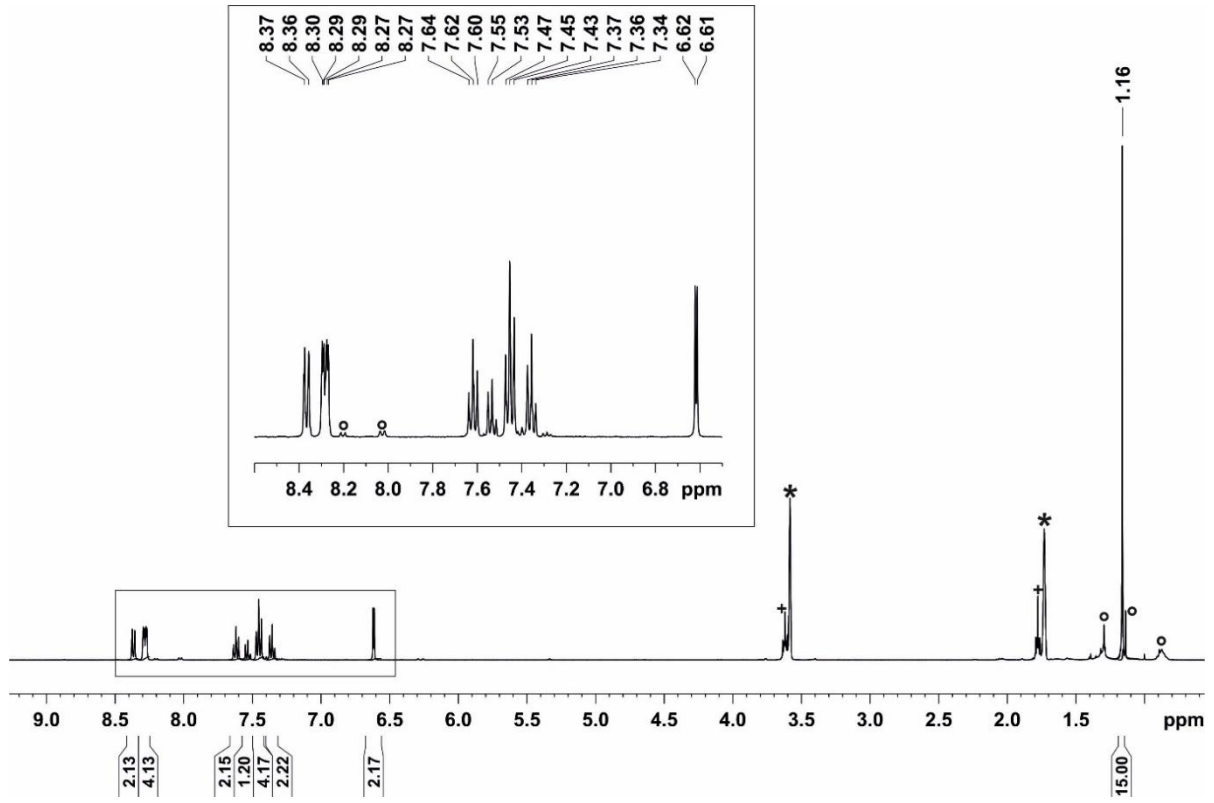

Figure S14 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**). * [D_8]THF; ° impurities; + THF.

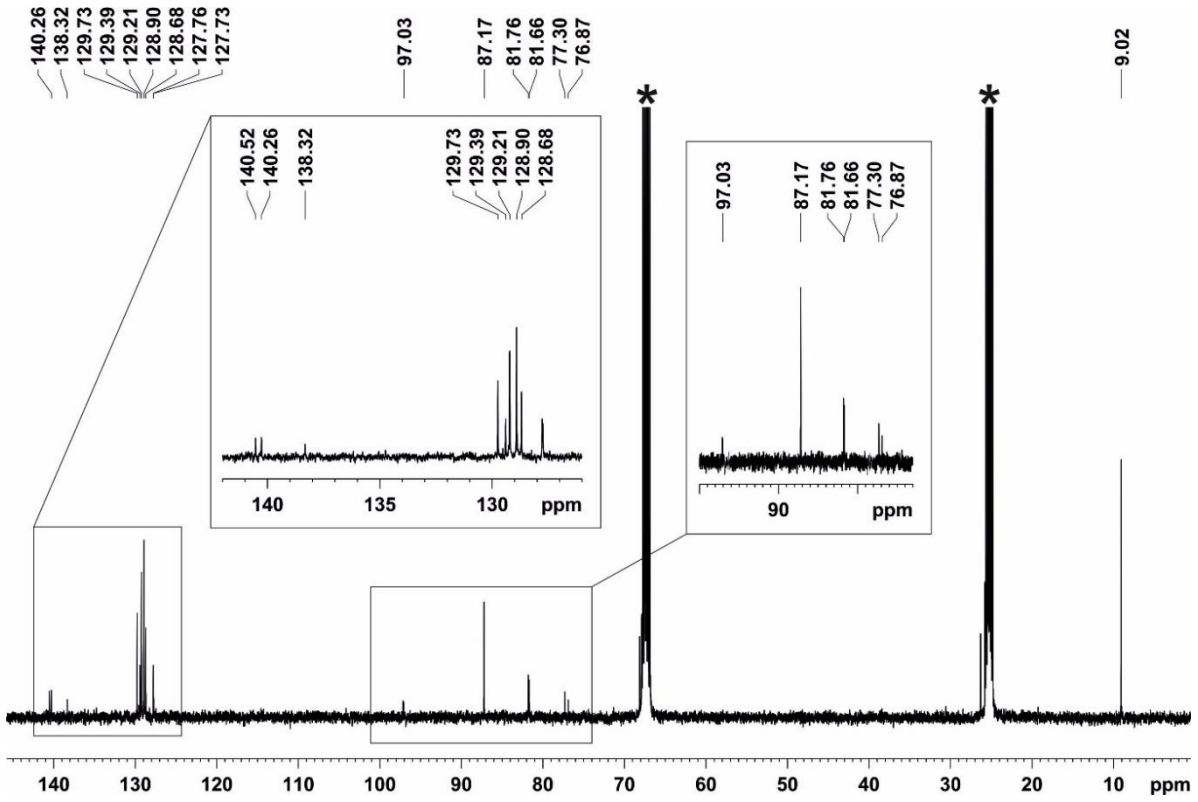

Figure S15 $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**); * [D_8]THF.

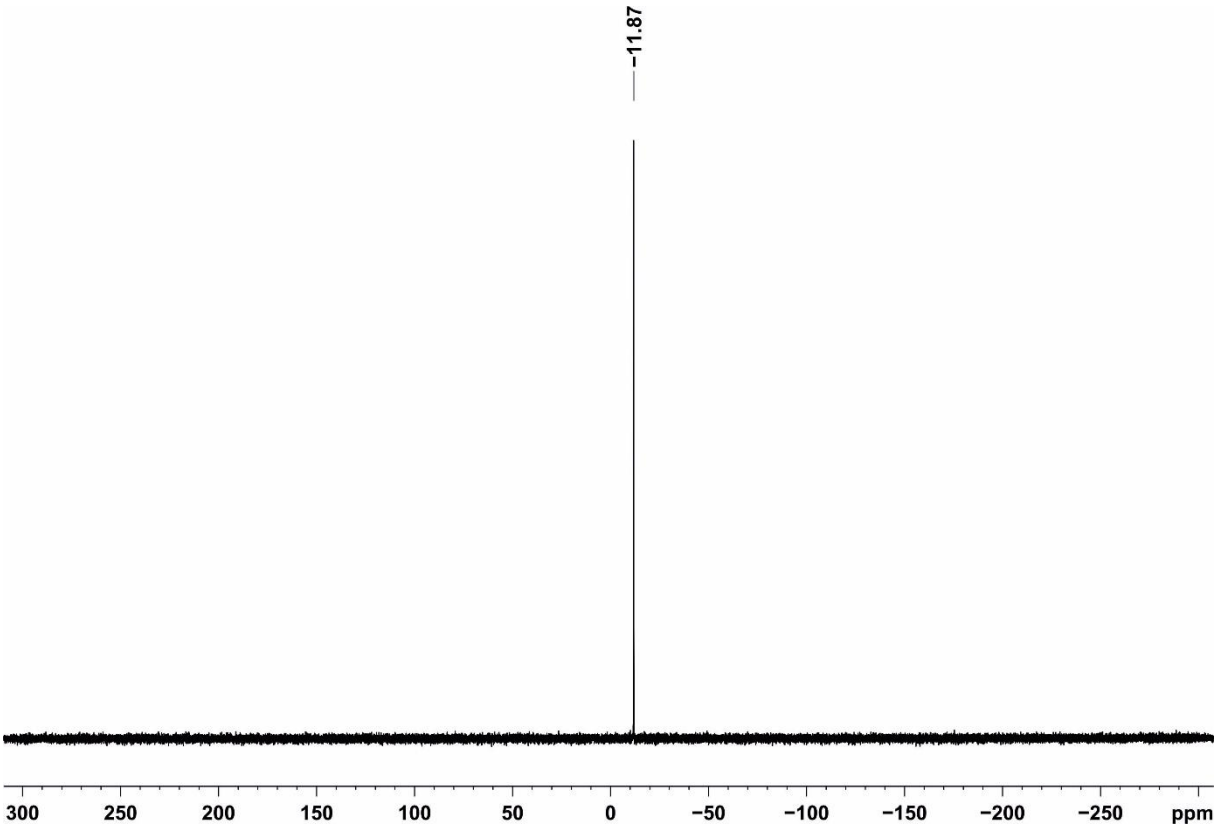

Figure S16 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**).

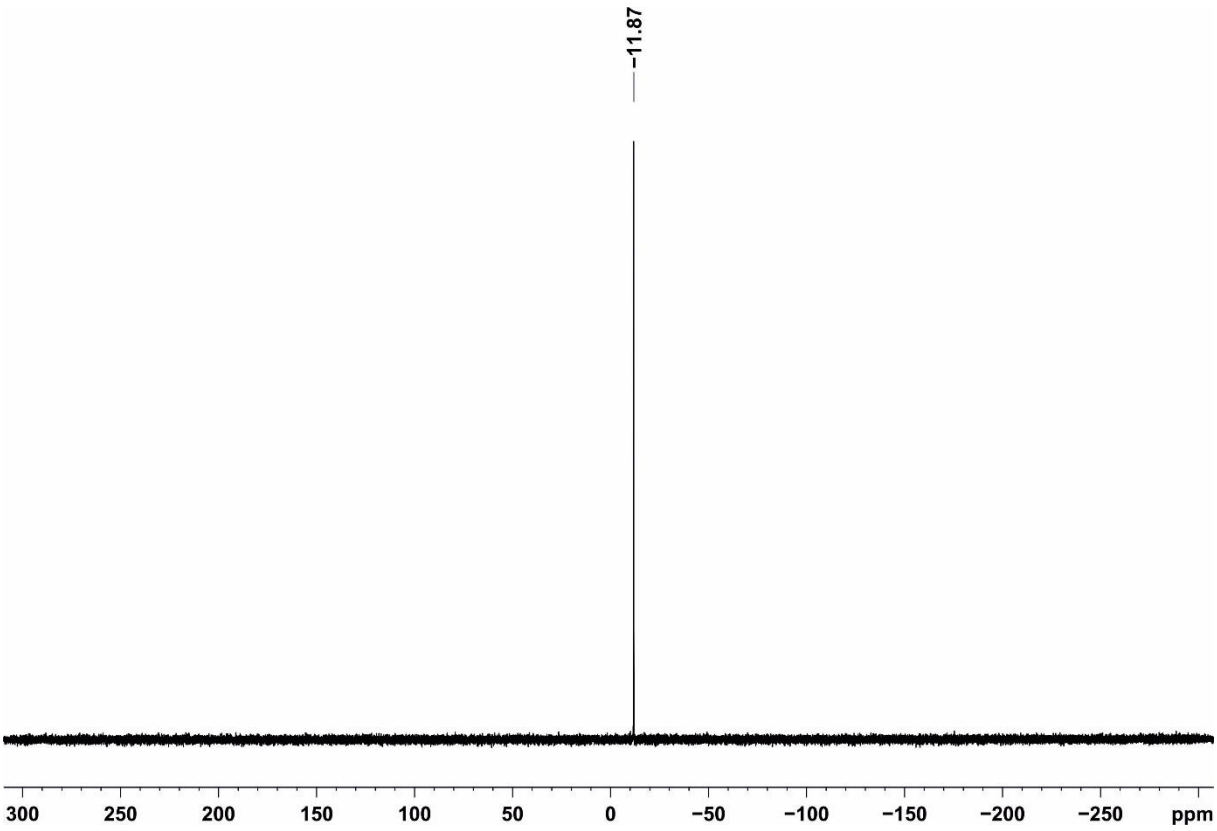

Figure S17 ^{31}P NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(PC$_5$Ph$_3$H$_2$)]Br (**2-Br**).

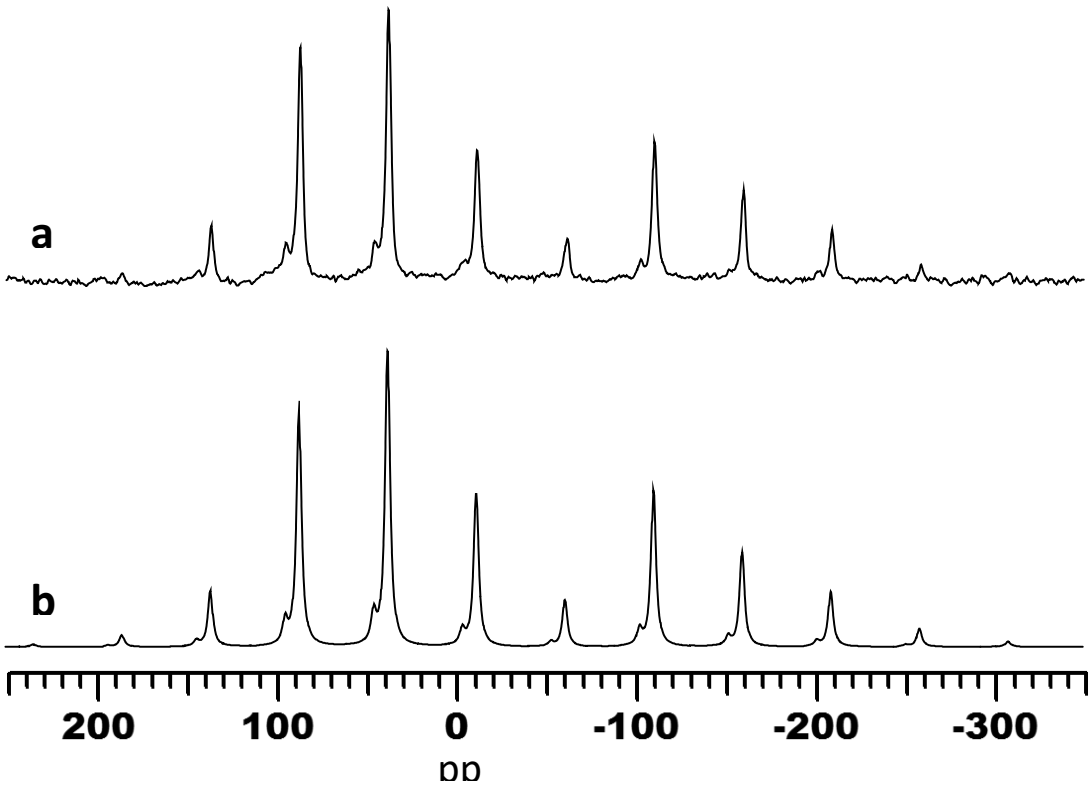

Figure S18 ^{31}P CP MAS spectrum (6 kHz, 300 K) of [Cp*Fe(PC$_5$Ph$_3$H$_2$)]Br (**2-Br**); a) experimental spectrum (δ_{iso} = −12.2 ppm), b) simulated spectrum.

[Cp*Fe($PC_5Ph_3H_2$)]I (2-I)

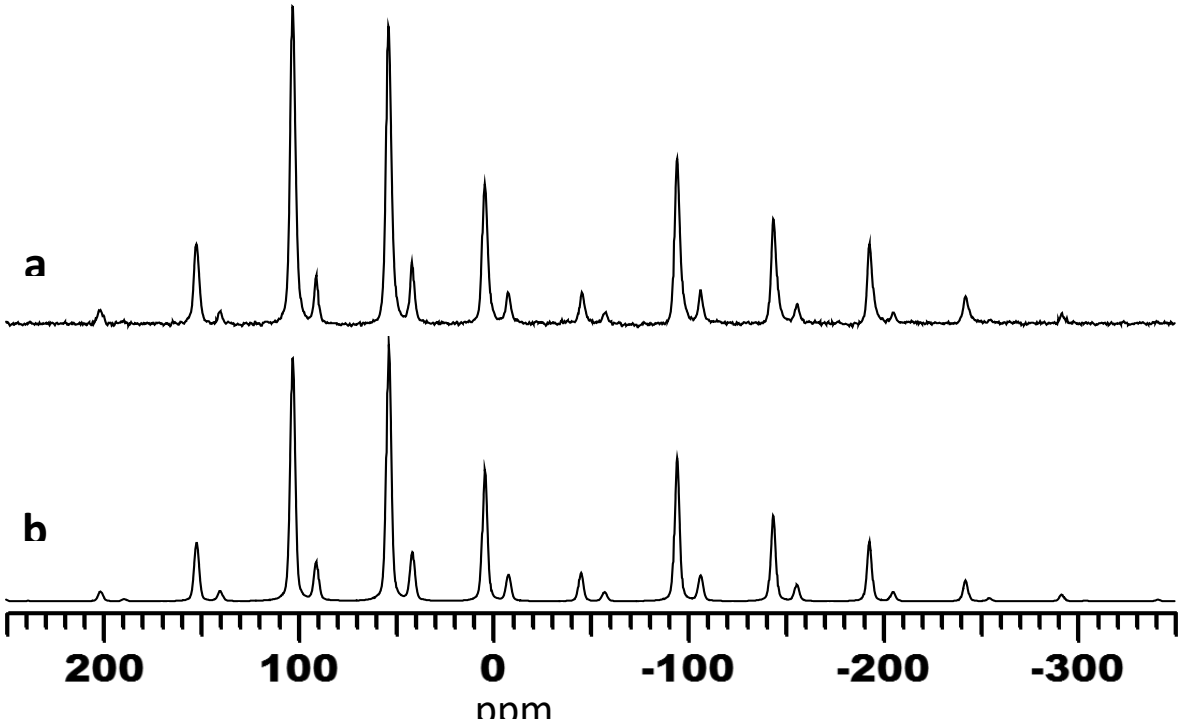

Figure S19 ^{31}P CP MAS spectrum (6 kHz, 300 K) of [Cp*Fe($PC_5Ph_3H_2$)]I (**2-I**); a) experimental spectrum (δ_{iso} = 4.1 ppm), b) simulated spectrum.

[Cp*Fe($PC_5Ph_3H_2$)][BAr^F_4] (2-[BAr^F_4])

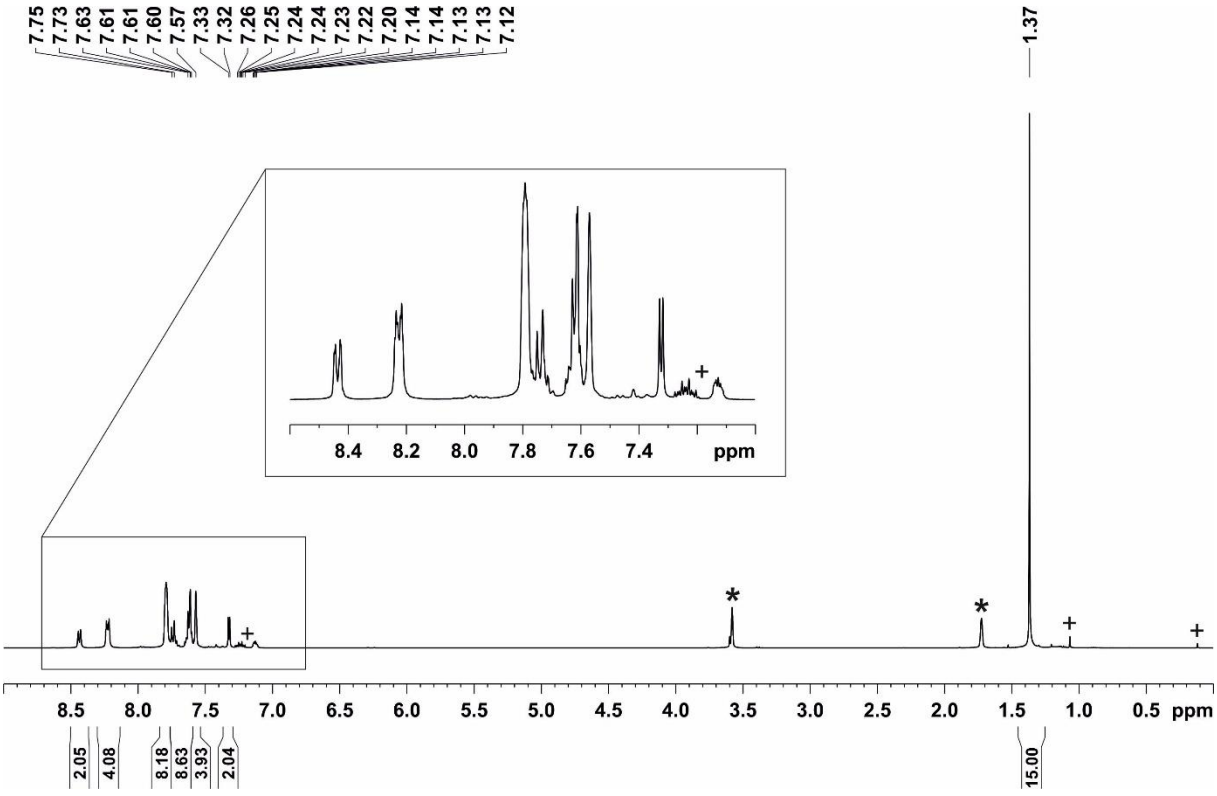

Figure S20 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of [Cp*Fe($PC_5Ph_3H_2$)][BAr^F_4] (**2-[BAr^F_4]**); * [D_8]THF; + impurities.

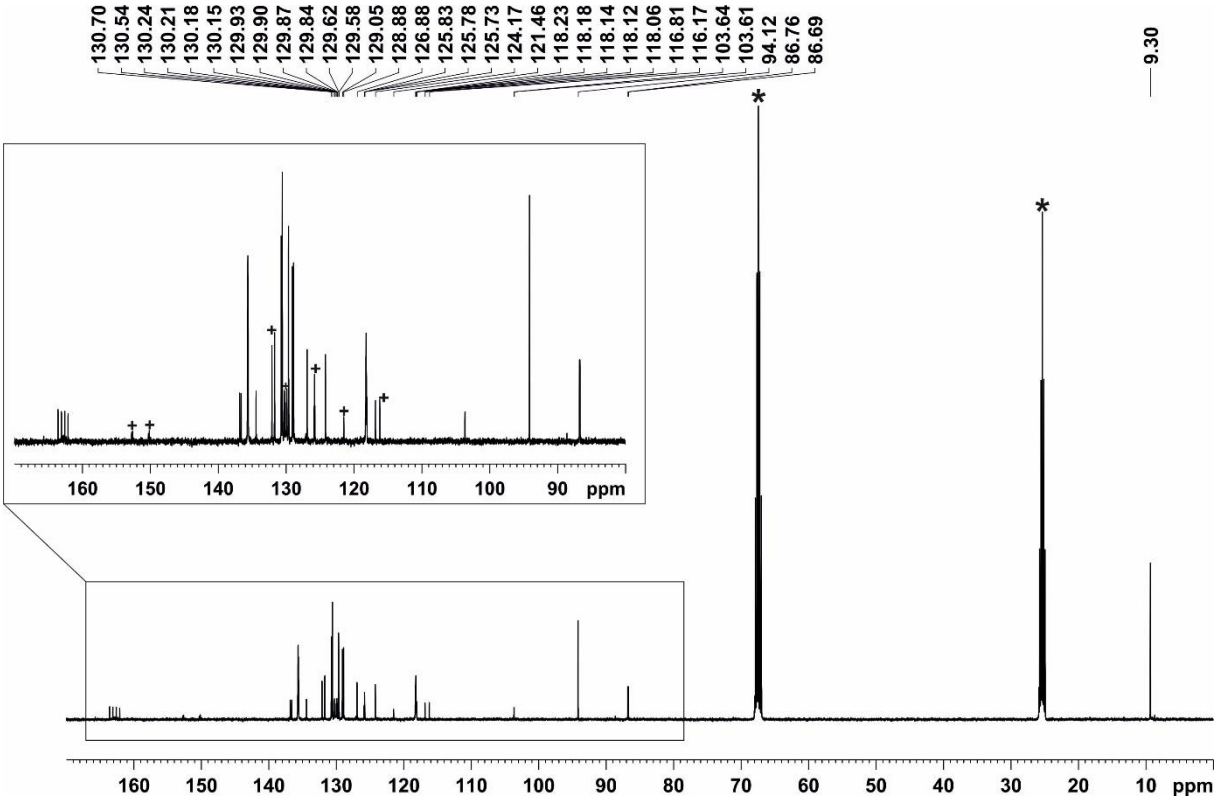

Figure S21 $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**); * $[D_8]$THF, + impurities.

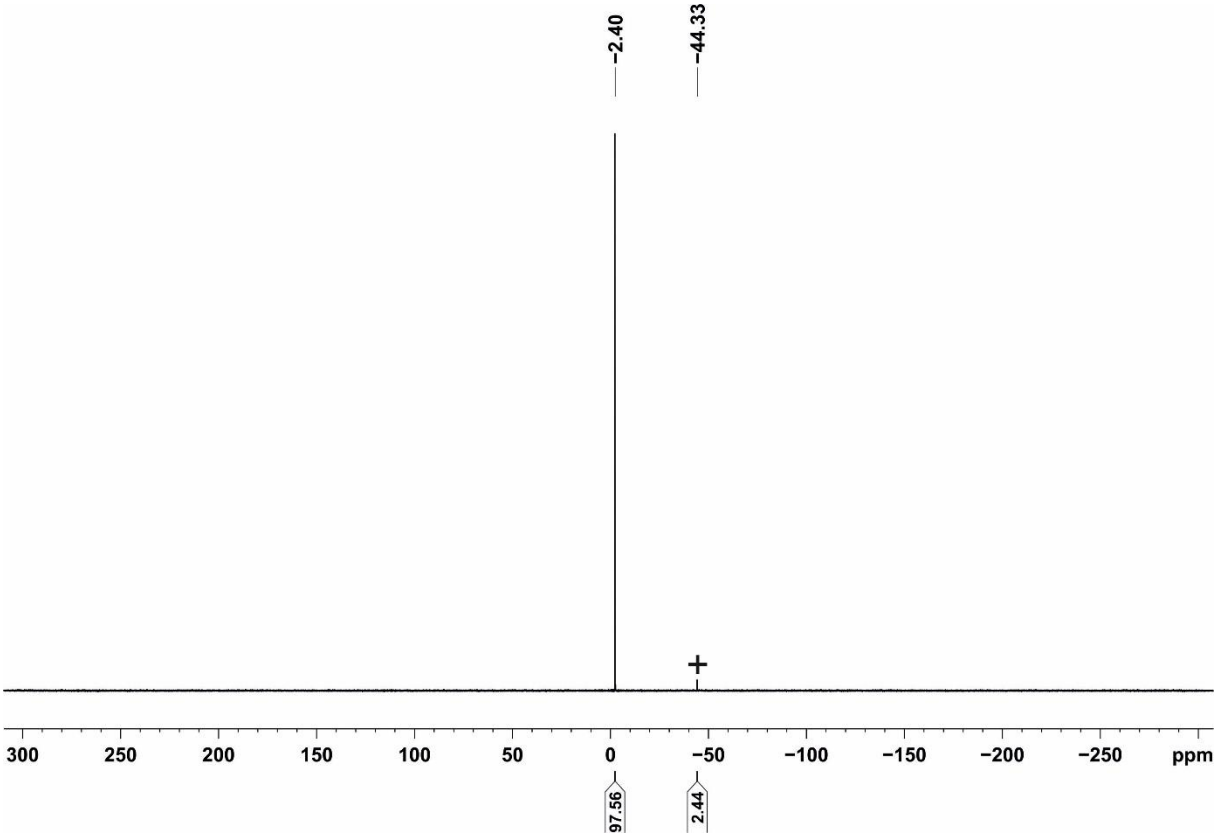

Figure S22 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**); + impurity.

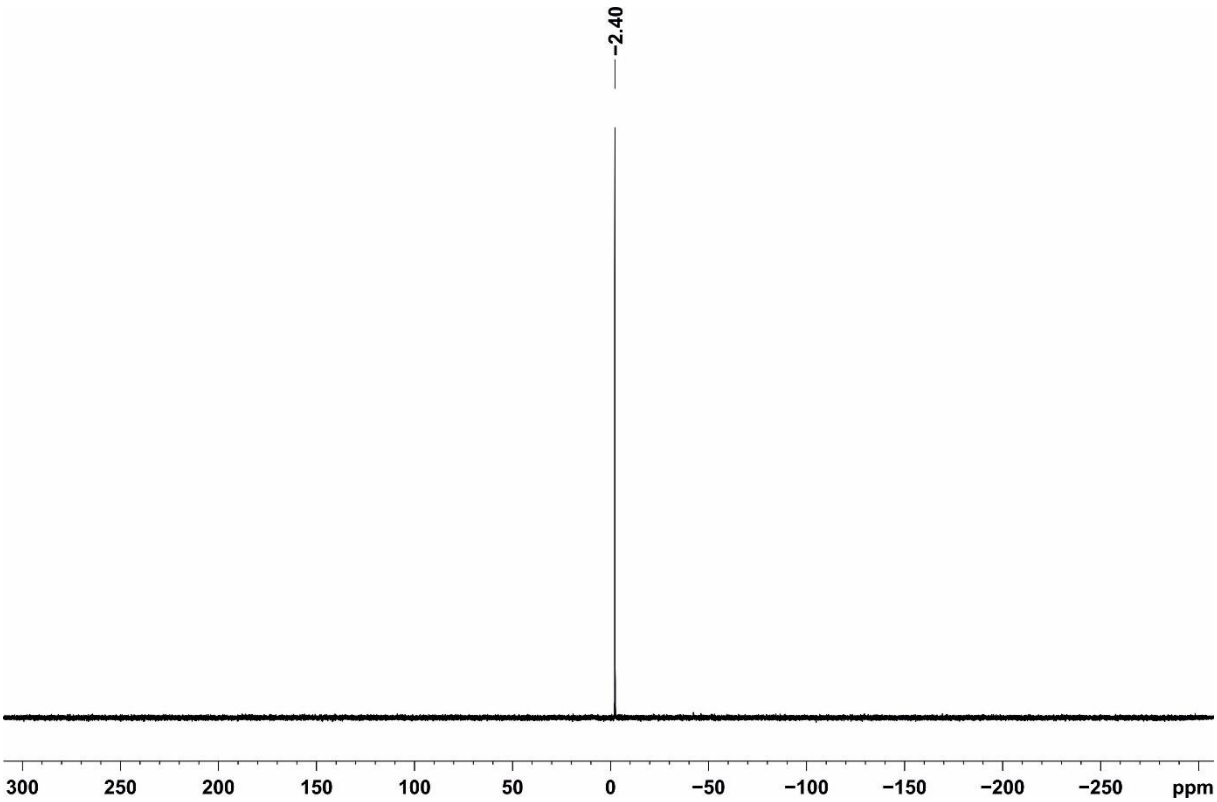

Figure S23 ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]THF$) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**).

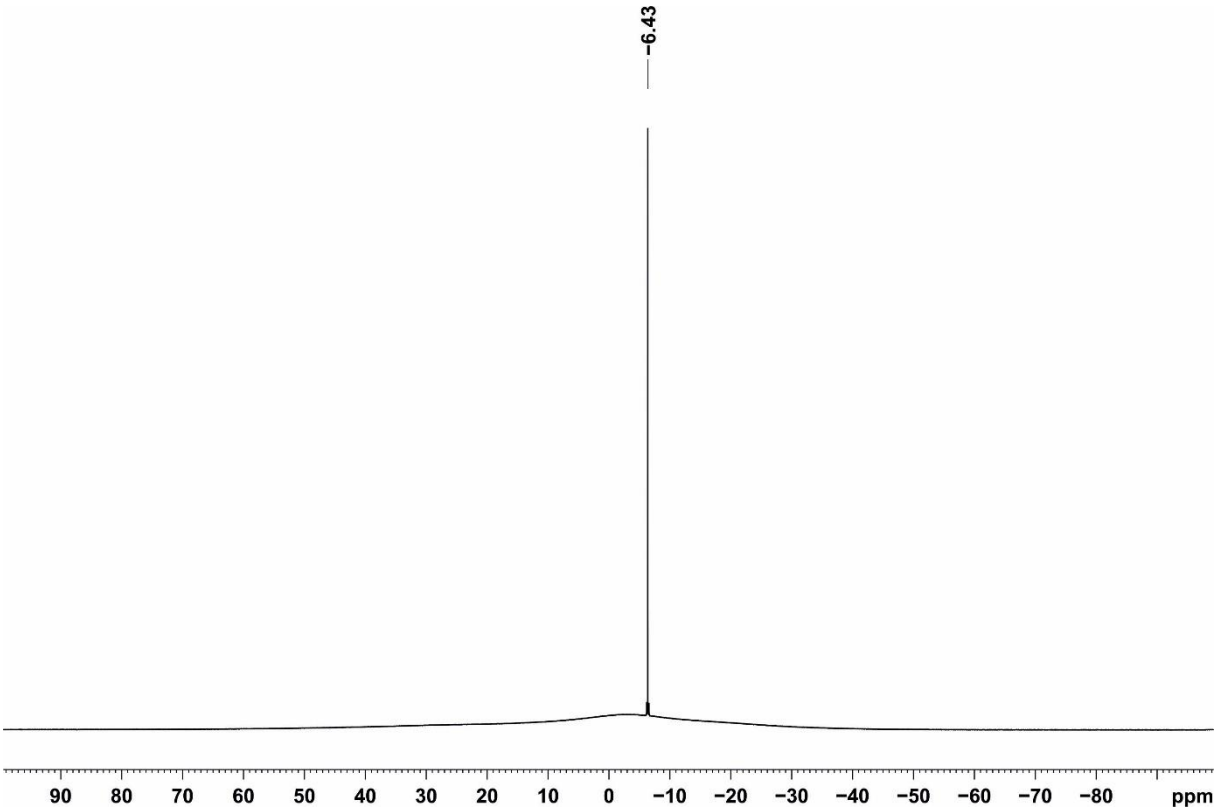

Figure S24 $^{11}B\{^1H\}$ NMR spectrum (128.38 MHz, 300 K, $[D_8]THF$) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**).

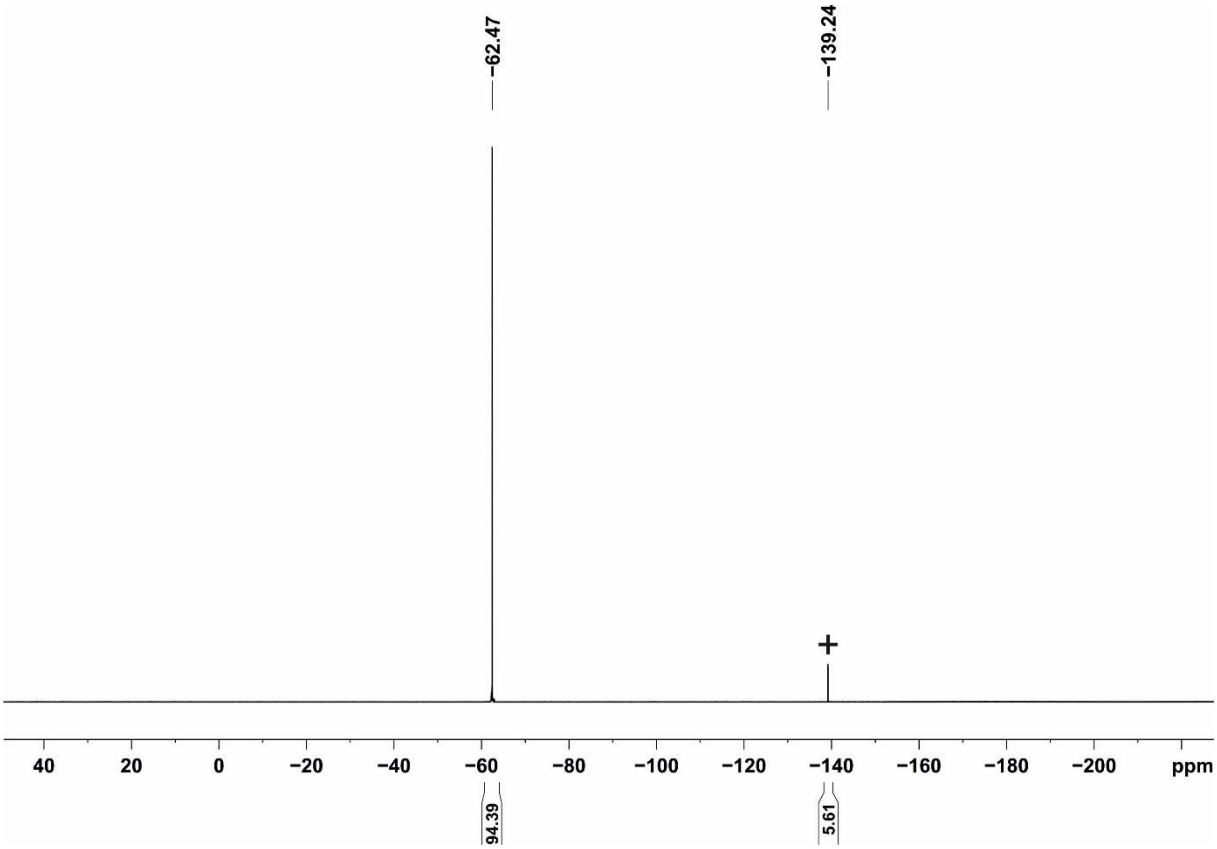

Figure S25 $^{19}F\{^{1}H\}$ NMR spectrum (376.66MHz, 300 K, $[D_8]$THF) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**); + impurity.

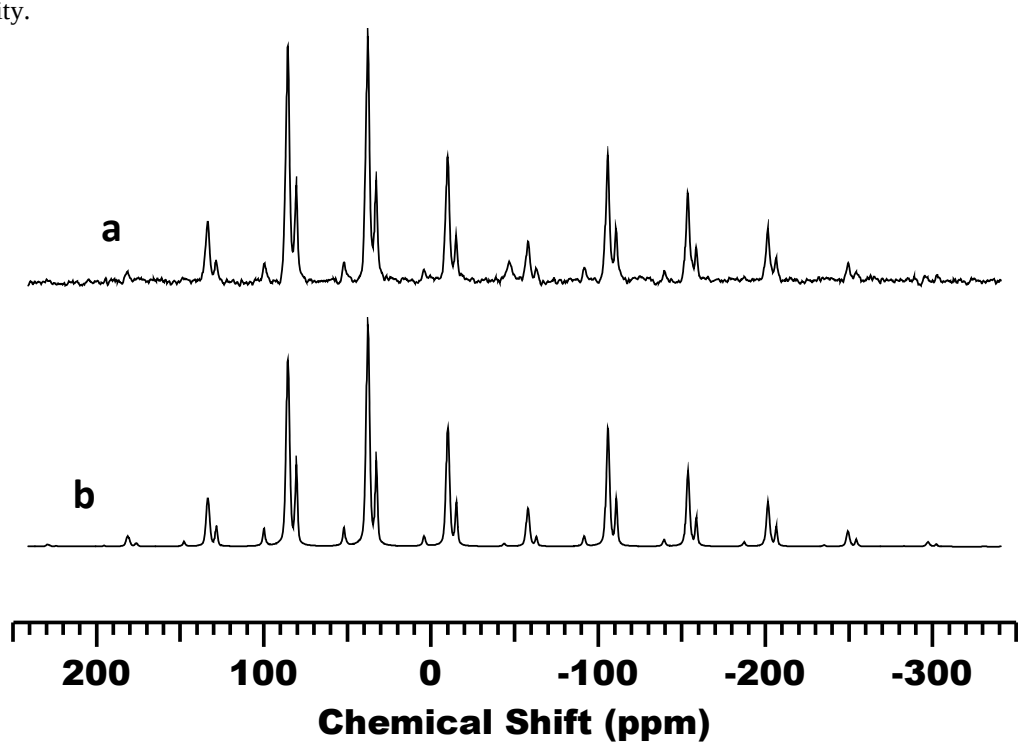

Figure S26 ^{31}P CP MAS spectrum (6 kHz, 300 K) of $[Cp^*Fe(PC_5Ph_3H_2)][BAr^F{}_4]$ (**2-[BAr$^F{}_4$]**); a) experimental spectrum (δ_{iso} = −8.9 ppm), b) simulated spectrum.

S2 UV-vis Spectra

[Cp*Fe(1-F-$PC_5Ph_3H_2$)] (2-F)

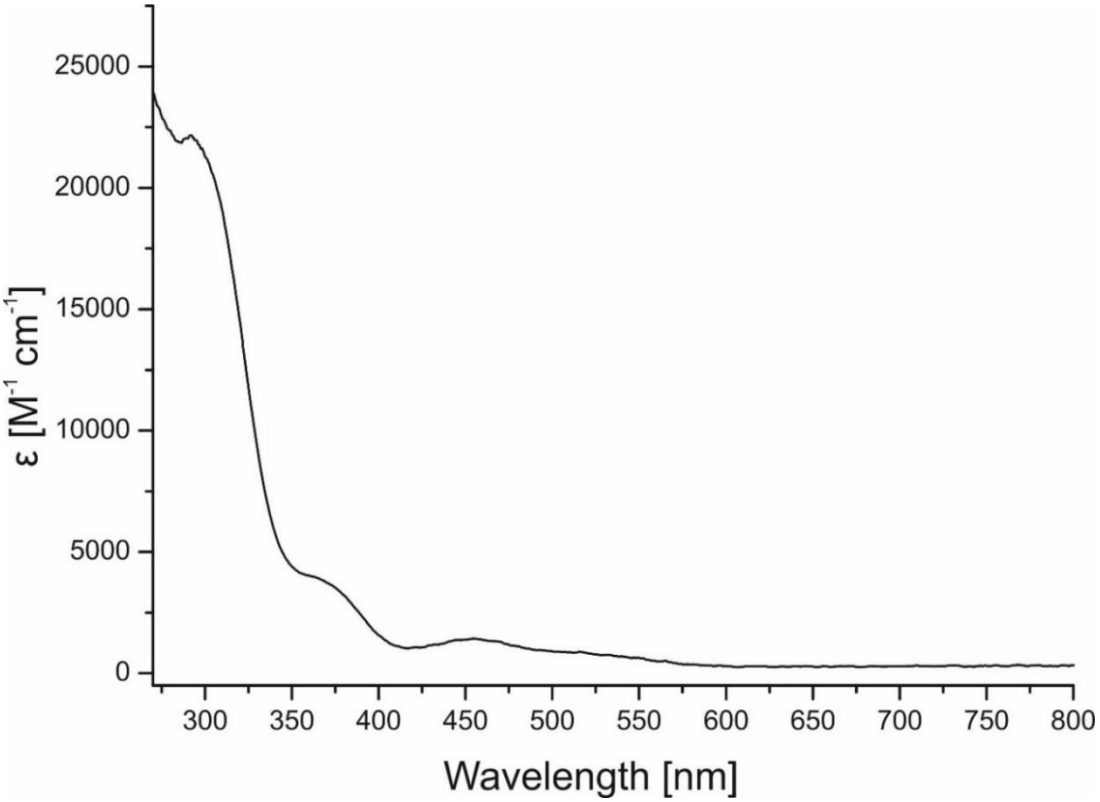

Figure S27 UV/vis spectrum of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**) in THF.

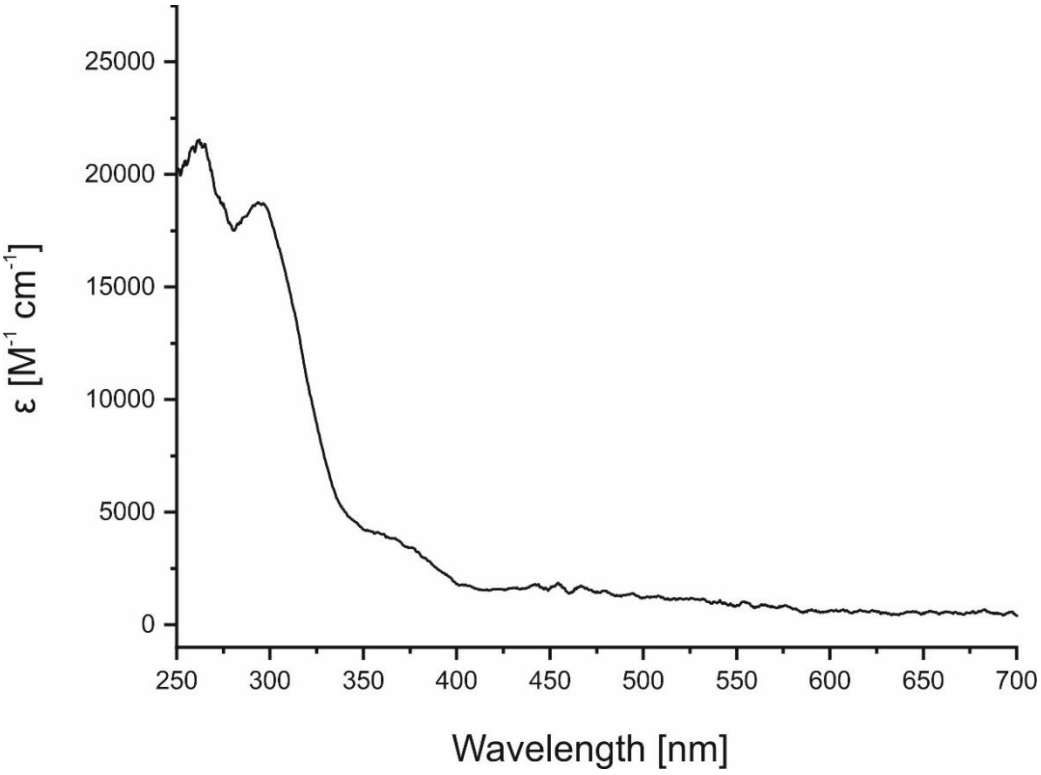

Figure S28 UV/vis spectrum of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**) in MeCN.

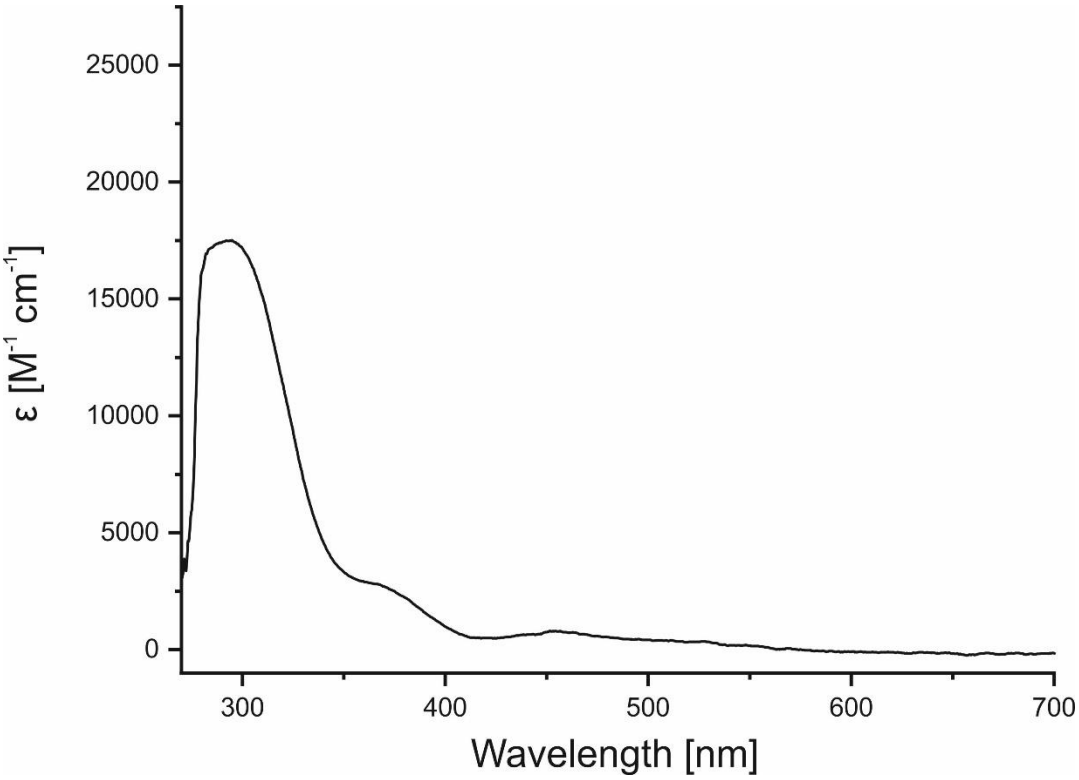

Figure S29 UV/vis spectrum of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**) in fluorobenzene.

[Cp*Fe(1-Cl-$PC_5Ph_3H_2$)] (2-Cl)

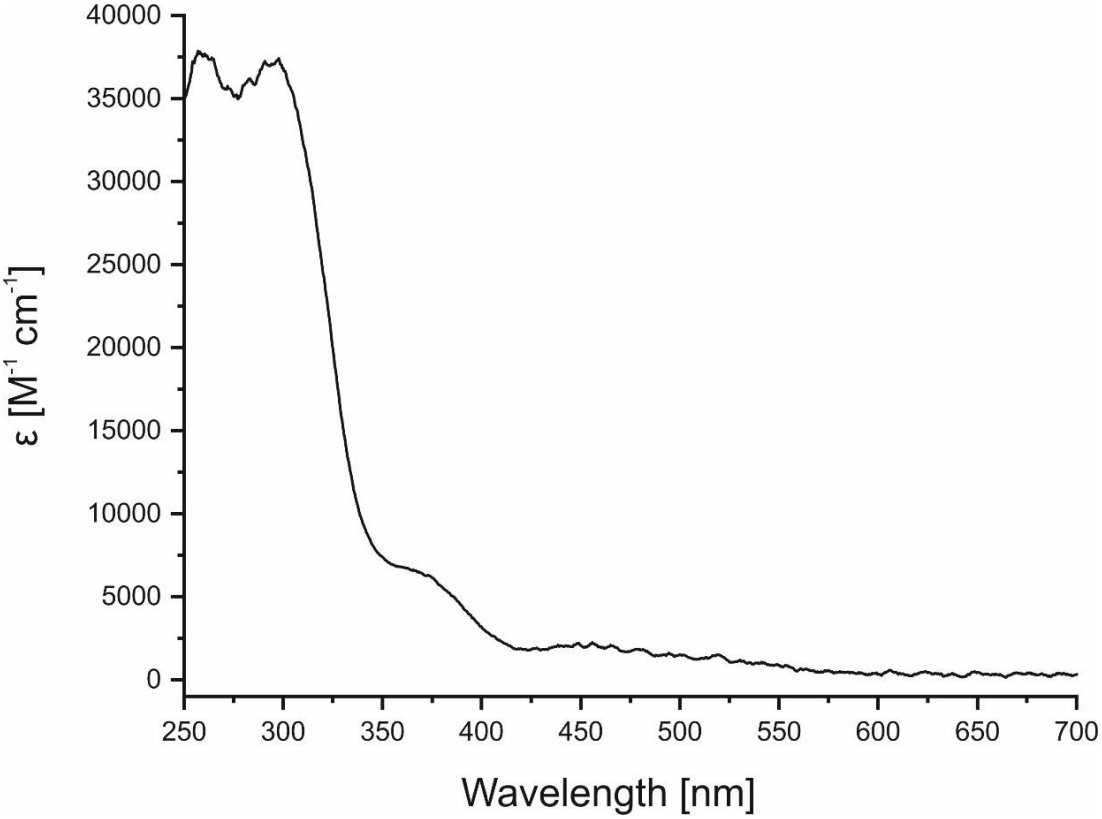

Figure S30 UV/vis spectrum of [Cp*Fe(1-Cl-$PC_5Ph_3H_2$)] (**2-Cl**) in THF.

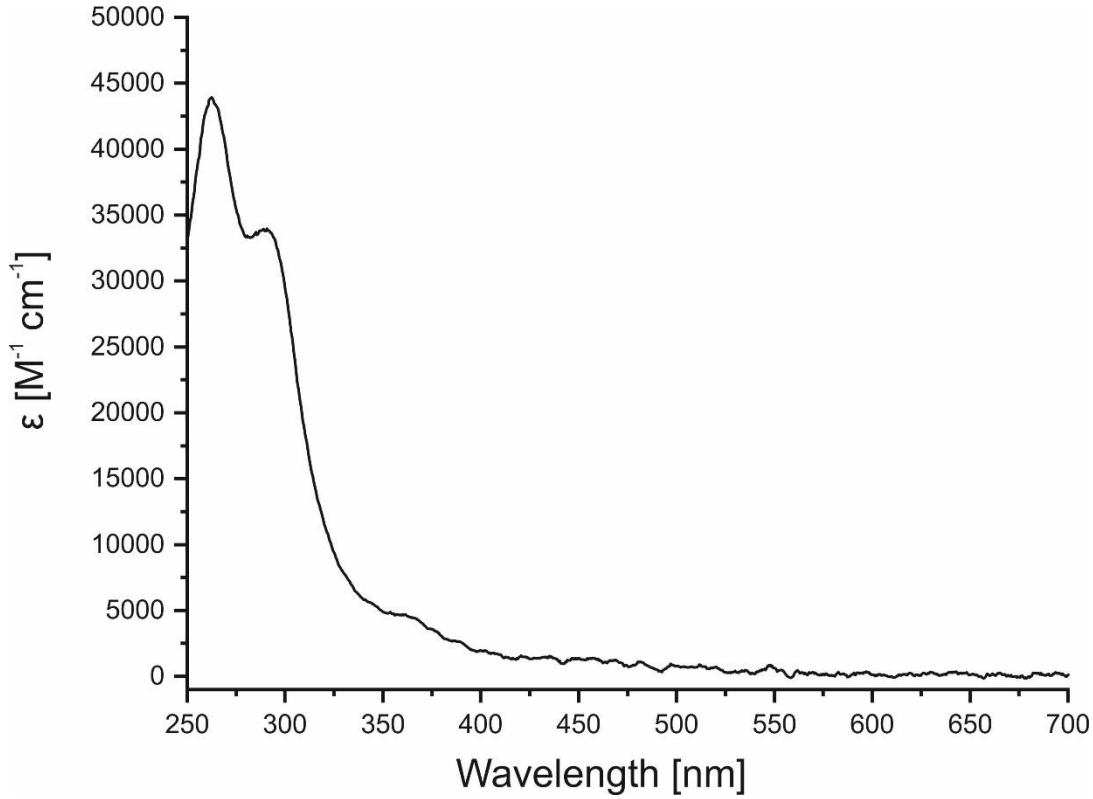

Figure S31 UV/vis spectrum of [Cp*Fe(1-Cl-$PC_5Ph_3H_2$)] (**2-Cl**) in MeCN.

[Cp*Fe($PC_5Ph_3H_2$)]Br (2-Br)

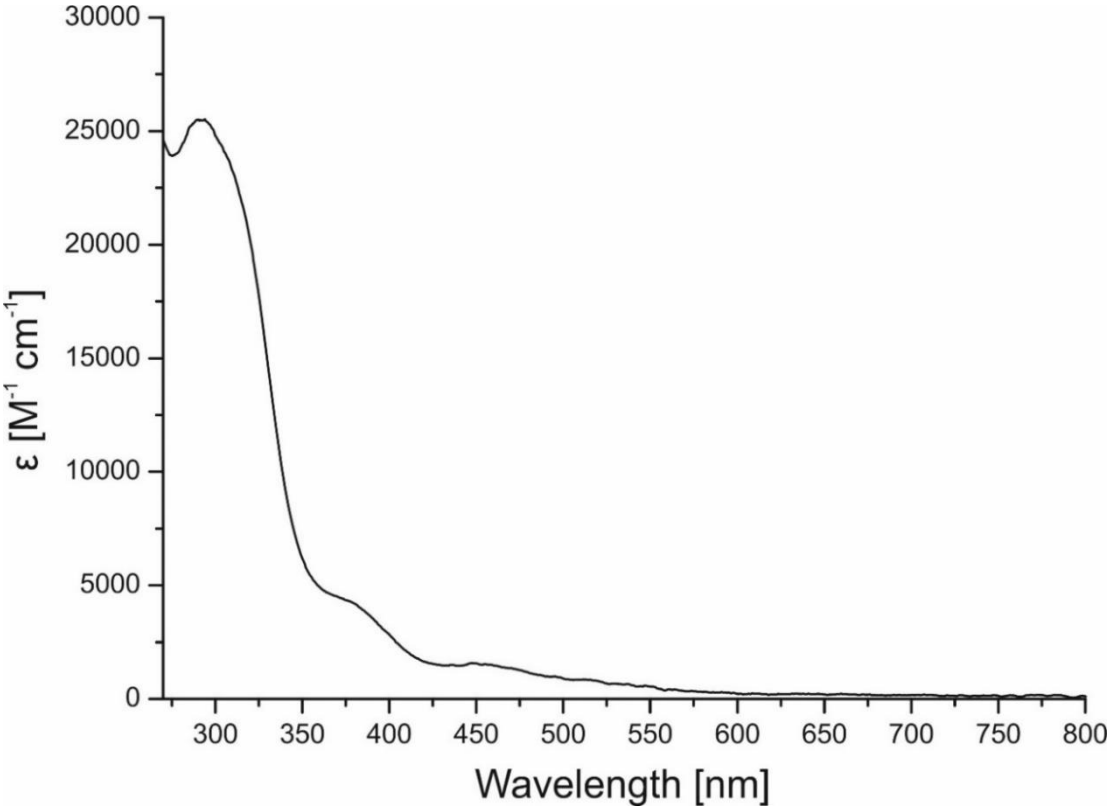

Figure S32 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**) in THF.

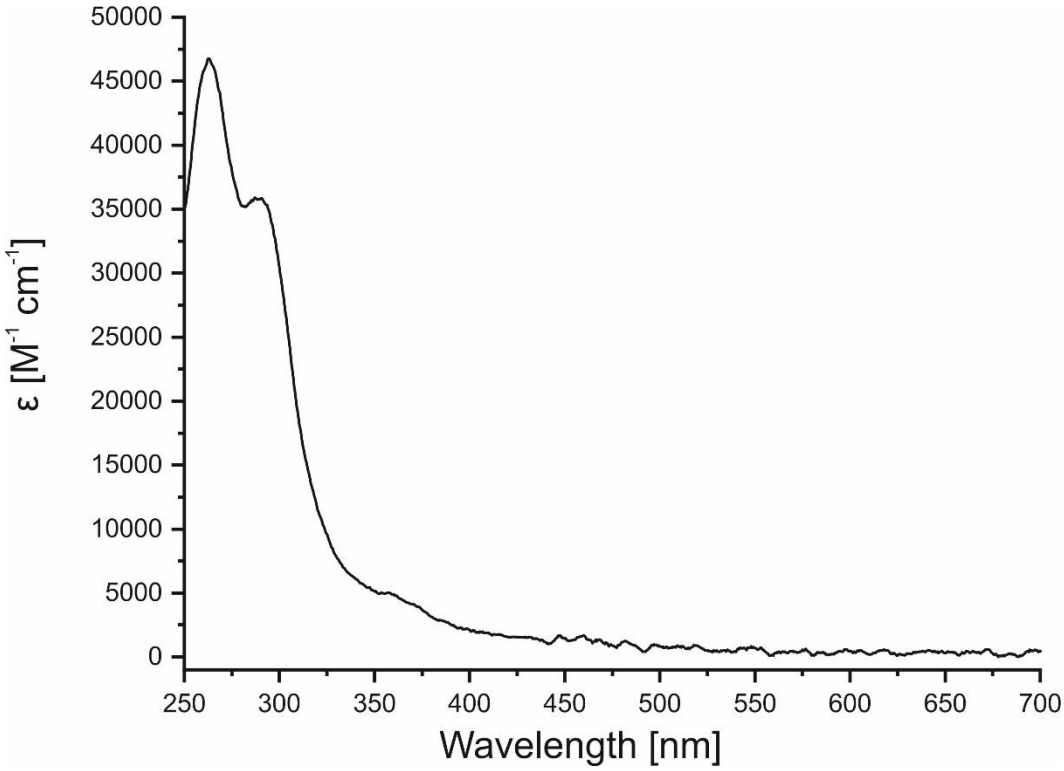

Figure S33 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**) in MeCN

[Cp*Fe($PC_5Ph_3H_2$)]I (2-I)

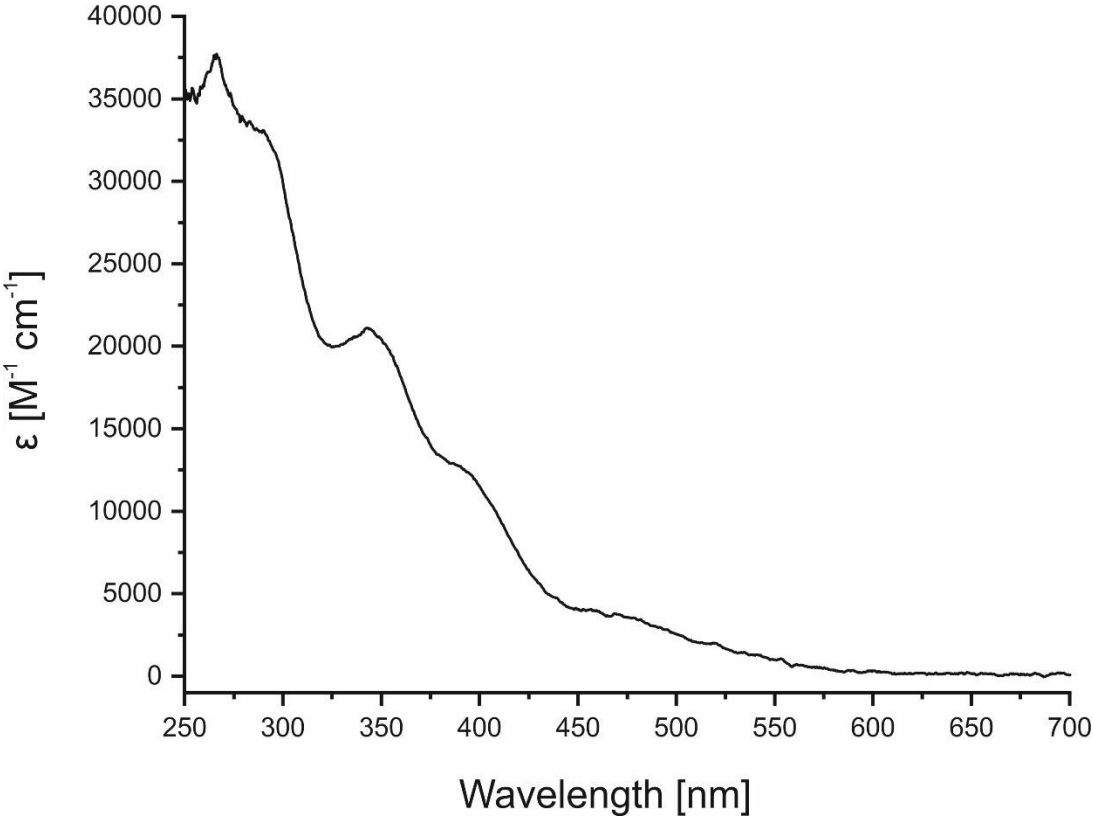

Figure S34 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)]I (**2-I**) in THF.

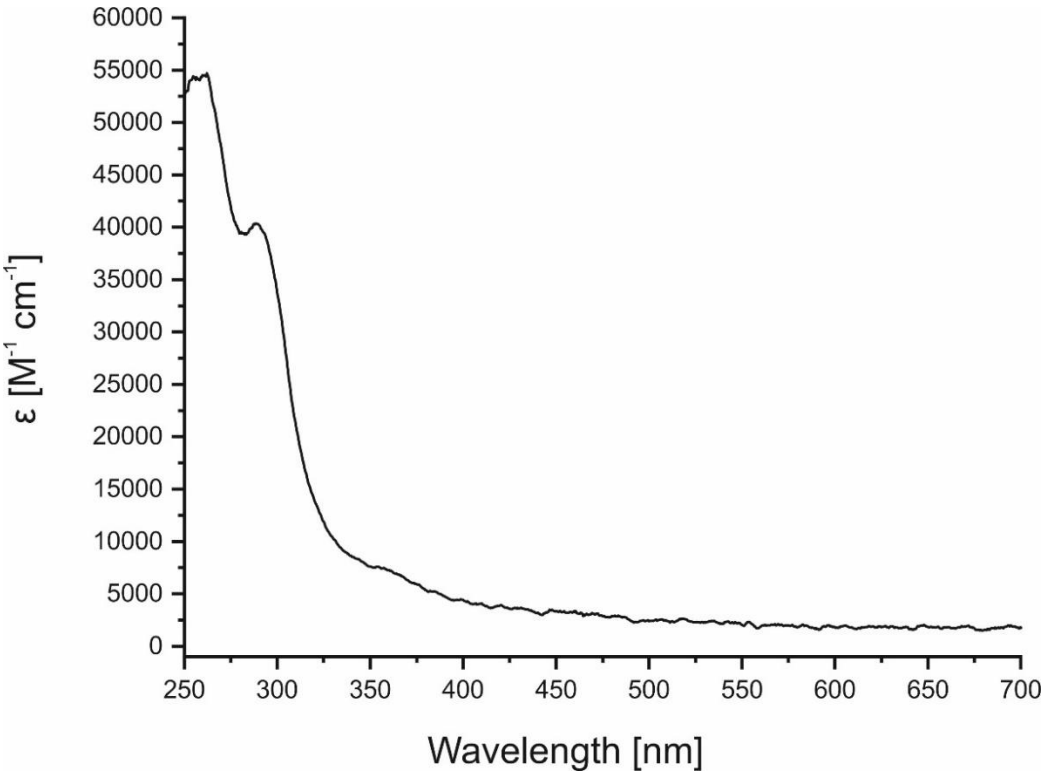

Figure S35 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)]I (**2-I**) in MeCN.

[Cp*Fe($PC_5Ph_3H_2$)][BAr^F_4] (2-[BAr^F_4])

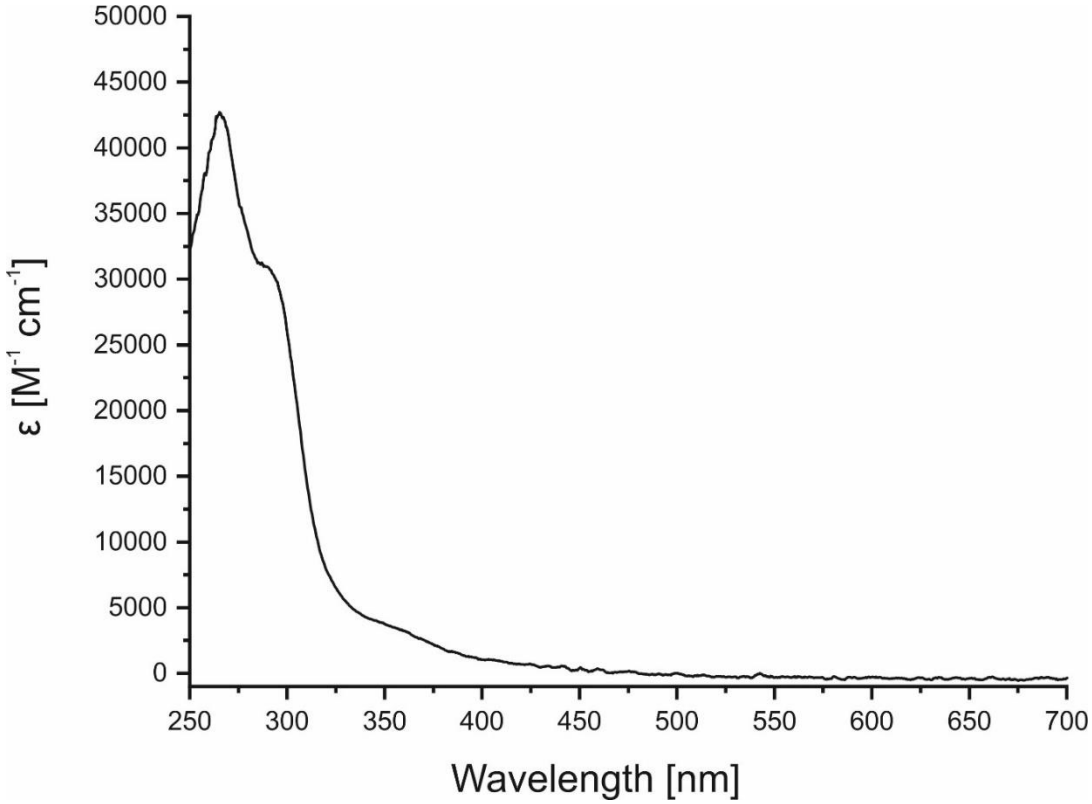

Figure S36 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)][BAr^F_4] (**2-[BAr^F_4]**); in THF.

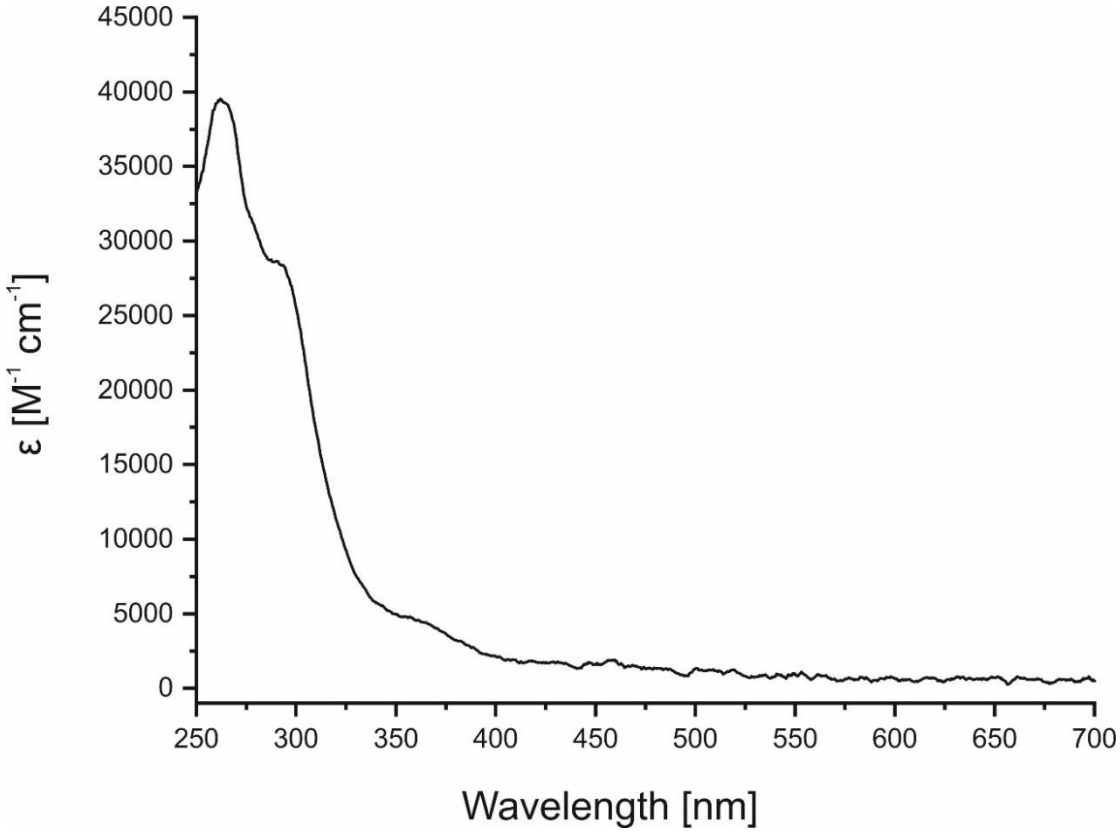

Figure S37 UV/vis spectrum of [Cp*Fe($PC_5Ph_3H_2$)][BAr^F_4] (**2-[BAr^F_4]**); in MeCN.

S3 X-ray crystallography

Table S1. Crystallographic data and structure refinement of **2-F**, **2-Cl**, **2-Br and 2-[BAr$^F_4$]**.

	2-F	**2-Cl**	**2-Br**	**2-[BAr$^F_4$]**
Empirical formula	$C_{33}H_{32}FFeP$	$C_{33}H_{32}ClFeP$	$C_{36.5}H_{36}BrFeP$	$C_{71}H_{48}BF_{26}FeP$
Formula weight / g·mol^{-1}	534.40	550.85	641.38	1492.72
Temperature / K	123.0(2)	123.0(1)	123.0(1)	123.0(3)
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a / Å	9.8569(9)	9.1507(2)	9.1777(3)	12.6489(3)
b / Å	16.2027(9)	17.2127(3)	15.9039(3)	15.4269(3)
c / Å	16.704(1)	17.3417(3)	20.7207(6)	18.5654(4)
α /°	82.018(5)	90	90	111.641(2)
β /°	81.061(7)	92.979(2)	97.231(3)	101.302(2)
γ /°	84.369(6)	90	90	96.394(2)
V / Å^3	2601.8(3)	2727.8(1)	3000.4(1)	3234.4(1)
Z	4	4	4	2
ρ_{calc} / g cm^{-1}	1.364	1.341	1.420	1.533
μ / mm^{-1}	5.437	6.028	6.264	3.202
F(000)	1120.0	1152.0	1324.0	1508.0
Crystal size / mm^3	0.295 × 0.204 × 0.122	0.123 × 0.070 × 0.068	0.110 × 0.087 × 0.033	0.45 × 0.34 × 0.26
Radiation / Å	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)	CuK_α (λ = 1.5478)
2Θ range for data collection /°	5.398 – 150.098	7.24 – 147.176	7.028 − 147.666	7.304 – 134.666
Diffractometer	GV1000, TitanS2	Agilent Technologies SuperNova	Agilent Technologies SuperNova	Agilent Technologies Gemini Ultra R
Index ranges	−12 ≤ h ≤ 12 −20 ≤ k ≤ 12 −20 ≤ l ≤ 19	−11 ≤ h ≤ 9 −21 ≤ k ≤ 21 −21 ≤ l ≤ 21	−11 ≤ h ≤ 11 −18 ≤ k ≤ 19 −25 ≤ l ≤ 25	−15 ≤ h ≤ 14 −18 ≤ k ≤ 18 −22 ≤ l ≤ 22
Reflections collected	16567	9182	25723	56256
Independent reflections	9969 [R_{int} = 0.0866, R_{sigma} = 0.0867]	5361 [R_{int} = 0.0270, R_{sigma} = 0.0258]	5971 [R_{int} = 0.0405, R_{sigma} = 0.0329]	11394 [R_{int} = 0.0366, R_{sigma} = 0.0244]
Data/restraints/parameters	9969/0/659	5361/282/461	5971/42/382	11394/132/980
Goodness-of-fit on F^2	1.052	1.067	1.069	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0939, wR_2 = 0.2424	R_1 = 0.0452, wR_2 = 0.1261	R_1 = 0.0443, wR_2 = 0.1156	R_1 = 0.0500, wR_2 = 0.1206
Final R indexes [all data]	R_1 = 0.1336, wR_2 = 0.2809	R_1 = 0.0517, wR_2 = 0.1310	R_1 = 0.0559, wR_2 = 0.1284	R_1 = 0.0530, wR_2 = 0.1227
Largest diff. peak/hole / e Å^{-3}	1.51/−1.38	0.58/−0.43	0.93/−0.81	0.82/−0.48

S4 Cyclic voltammetry

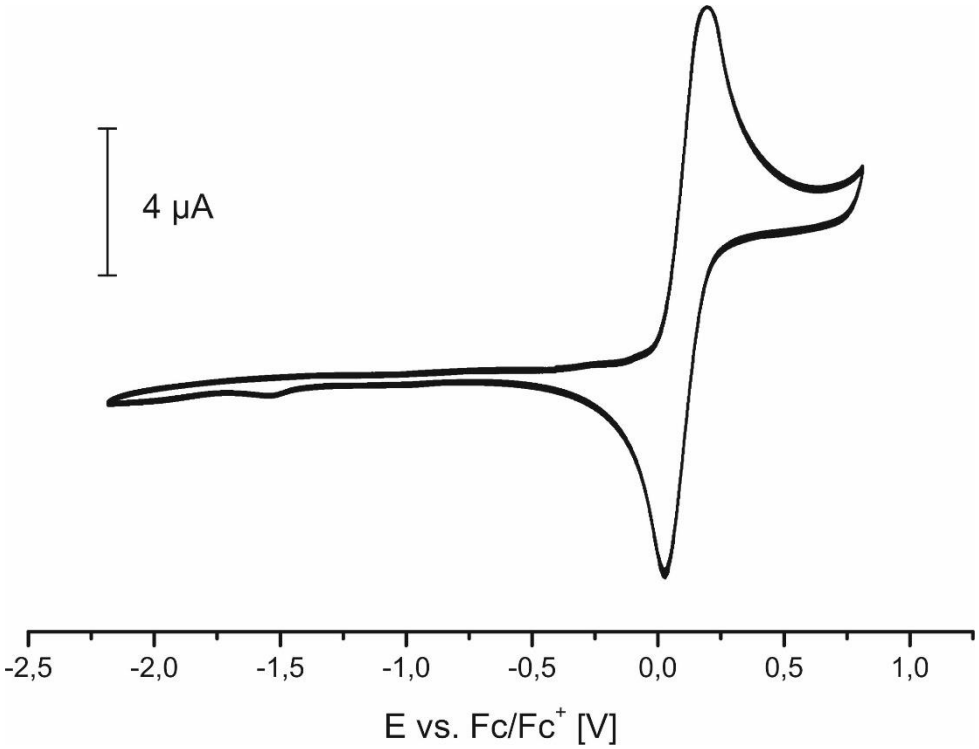

Figure S38 Cyclic voltammogram of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**).

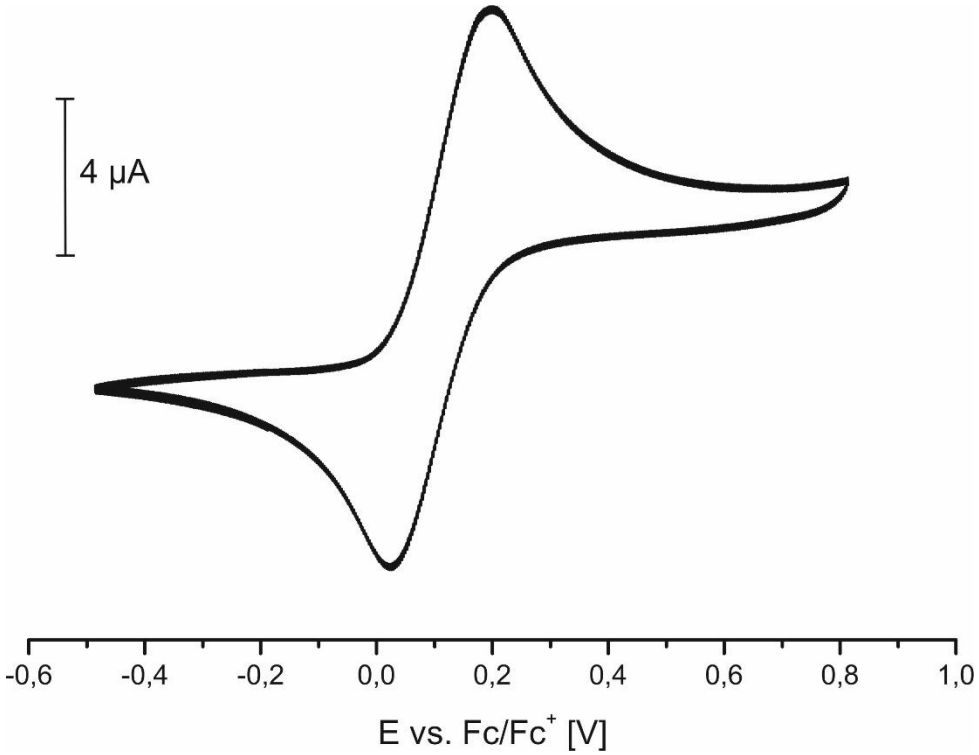

Figure S39 Cyclic voltammogram of of [Cp*Fe(1-F-$PC_5Ph_3H_2$)] (**2-F**).

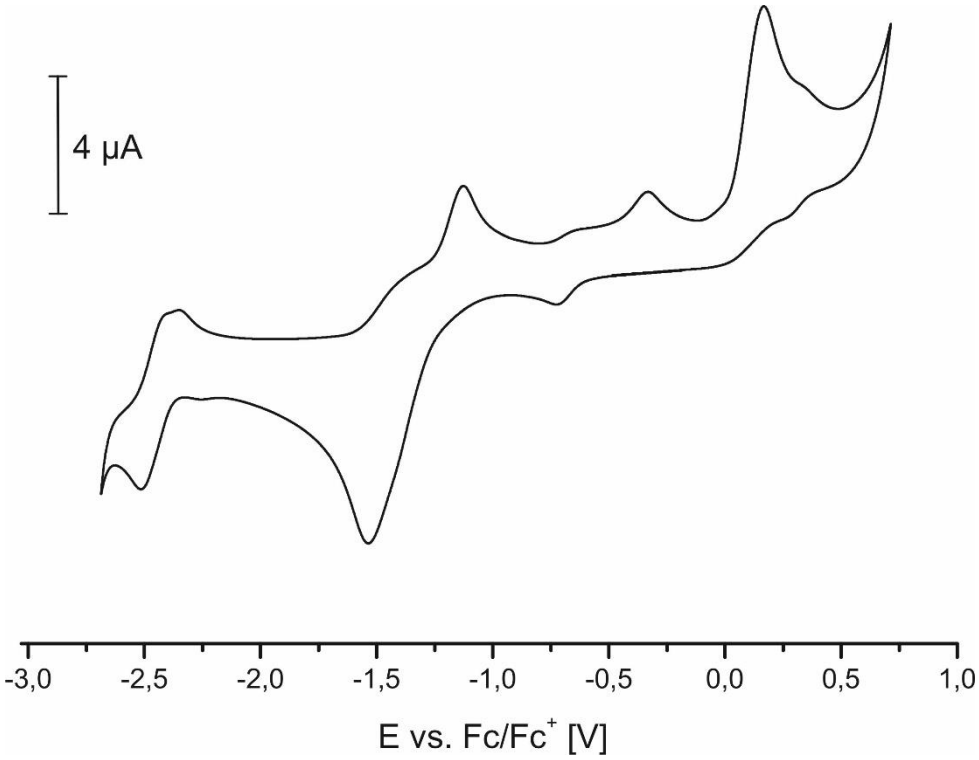

Figure S40 Cyclic voltammogram of [Cp*Fe(1-Cl-$PC_5Ph_3H_2$)] (**2-Cl**).

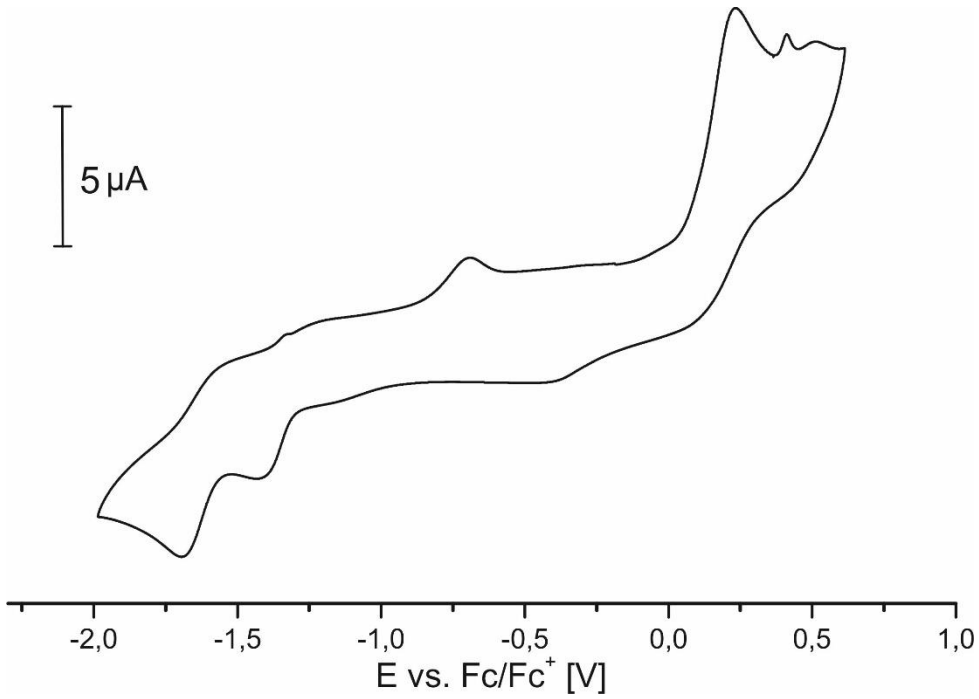

Figure S41 Cyclic voltammogram of [Cp*Fe($PC_5Ph_3H_2$)]Br (**2-Br**).

S5 DFT calculations

Computational Details: Density-functional theory based geometry optimizations were carried out with ADF at the OPBE/TZ2P level of theory,[1] by using a convergence criteria of 1 x 10^{-5} E_h and the integration grid was set to very good. The nature of stationary points was verified by subsequent analytical frequency analysis. For consideration of relativistic effects, the Zeroth Order Regular Approximation (ZORA) was used.[2]

The resulting wavefunction was further supplied to ADF's EPR/NMR program to calculate the ^{31}P NMR chemical shielding σ_{calc}. These values are relative to a bare phosphorus nucleus and can be converted to chemical shifts δ relative to an appropriate reference system, for which we used complex **2-[BAr$^F_4$]** without considering the weakly coordinating anion (named as **2**$^+$).

The ^{31}P NMR chemical shielding σ_{calc} of cation **2**$^+$ were calculated at the same level of theory (σ_{calc} = 365.7, δ_{exp} = −8.9 ppm) to obtain the relationship: δ_{calc}(P-X) = 374.6 ppm – σ_{calc}(P-X). The reported shielding contributions are rounded to one decimal place.

XYZ coordinates of optimized geometries

2-F covalent:

H 8.848778412228748 15.28436988172099 14.5259828909638
C 8.183682497296241 14.41987947870702 14.51981058532992
C 7.248265553622029 14.41250649909113 15.67822367287828
H 8.802877824341779 13.52301809855836 14.46907249399285
H 7.596127453315599 14.4667137744416 13.59099075445407
Fe 7.473773850275949 14.24252748164906 17.7446669904434
C 6.554925376452998 13.26117040629368 16.17552299473623
C 6.736847224633649 15.56840227759131 16.34388840796995
P 9.80579911995606 15.40498204714075 18.64546416362747
C 9.578798602359889 13.80758959512221 17.86847795774602
C 8.743291434048386 12.80344216946154 18.41436684975196
H 8.83019247898909 11.79034919887436 18.0333793736934
C 7.757664678339168 13.0202708675353 19.41269403898502
C 7.436626153772548 14.35827655115529 19.76543579888594
H 6.52296671331819 14.49981435036554 20.33703842931517
C 8.169472967997221 15.50005341671837 19.36070385086141
C 5.587658868505083 13.70824176078819 17.13505324275545
C 5.705574187608218 15.13336802533543 17.24943705730616
C 6.682938441969039 11.88147899691427 15.62024655961807
C 7.05976524368009 16.97980390847264 15.9886575187762
F 10.78869962926045 15.07774319003735 19.94015045891567
C 10.62556582324849 13.42821581321253 16.87941187374766
C 7.066962325253901 11.88079602205124 20.067356449663
C 7.780821169966449 16.83880970588984 19.8822861364961
C 4.515418103599207 12.88288999338998 17.76239392767239
C 4.776985791115001 16.02271038374183 18.00556585814678
H 6.300159183309771 11.12109981964985 16.3034756196225
H 6.098674965195288 11.80057945054154 14.69212062157484
H 7.716230335956849 11.62642920682642 15.37192473956521
H 8.118322545653669 17.11594356820691 15.75395118624966
H 6.48512296456116 17.27564887930774 15.09866070476677
H 6.802335380071624 17.67563253717118 16.78747639677179
C 11.28494022473894 14.40361146614215 16.11234109188259
C 11.06906836498966 12.10266202160811 16.73379303150695
C 6.93734817300516 10.61551205115435 19.47546913326585
C 6.603781351741255 12.02267911721289 21.38462454122642
C 7.024801132657839 16.98137502338988 21.05854242121135
C 8.24170842735486 18.02118514187289 19.27870472550923
H 4.251990956430164 13.23173058186498 18.76397964644386
H 3.604481096907302 12.93944790366909 17.14896080988938
H 4.788170552620059 11.83007711214366 17.84431612665394
H 5.255263446292197 16.94852565173574 18.32769721335568
H 3.926810531642068 16.29628465505418 17.36373504706137
H 4.365347320465817 15.53585209126461 18.89296284896118
H 10.99091267892033 15.44477821489784 16.22206226550869
C 12.30903559179769 14.07360504562896 15.23421314071193
C 12.09193090185245 11.76878966585681 15.85219979620025
H 10.64236621652951 11.30989258931254 17.34325882220312
H 7.28791164794255 10.44857890889458 18.4613601776269
C 6.353257433890452 9.553858304893863 20.15563568975643
C 6.014895712695092 10.96307743821278 22.06631177722112
H 6.738727261951253 12.96906474705567 21.90256324133227
H 6.691415699594542 16.10243992286643 21.60437813948614
C 6.717747764358676 18.23300319801962 21.58095324710372
C 7.937397434261107 19.27267527060884 19.79926507344564
H 8.864431881246604 17.94984343401655 18.39101759599351
H 12.79518558278762 14.86103293960138 14.65895450351007
C 12.71753538636676 12.7502575495474 15.08983280858053
H 12.41348571832643 10.73041774154935 15.77651224594724
H 6.265154491088006 8.586004267646629 19.66328120121527
C 5.880781843961063 9.720938788433211 21.45471846668677
H 5.673311018703559 11.10876019750189 23.09035756584543
H 6.135913697439609 18.30032310925517 22.49977438388191
C 7.164393723169371 19.39079149040714 20.95151652985814
H 8.313968184371763 20.16531179951223 19.30052962114325
H 13.52245779246456 12.48960799838102 14.40423352987885
H 5.423831307078496 8.888410575613335 21.98741537436613
H 6.927752764765355 20.37099704447204 21.36267606389258

2-F covalent (ZORA):

H 8.851043208262377 15.36665747558417 14.56362955320303
C 8.196606518485096 14.49464963141041 14.53251545874769
C 7.258928213156909 14.44461567191855 15.68772120935117
H 8.826233306345435 13.60708167181006 14.45882019384569
H 7.609888048909186 14.55985611053347 13.6044304616237
Fe 7.47434193504449 14.24139786154776 17.74649455774625
C 6.590066049902746 13.26971047647632 16.16324956044867
C 6.720145202811576 15.57676122755162 16.37107638521805
P 9.808486846288684 15.40020176609807 18.64430211019413
C 9.571361673810737 13.80507462051527 17.86586059259893
C 8.733930644424474 12.80312308888034 18.41343832763925
H 8.816702706910124 11.78981786854565 18.03282838225632
C 7.749865695466379 13.0240438565084 19.41215718241062
C 7.431584115880987 14.36393671106963 19.75943552927535
H 6.517130699471272 14.51027146606985 20.32813975016058
C 8.169245832085858 15.50169882236622 19.35157769520817
C 5.608764130440781 13.67959673394525 17.12566895430028
C 5.696440600479463 15.10468442421108 17.26607119323206
C 6.753690335991172 11.90222328196711 15.58783316905545

C 7.014195099479884 17.00014423923181 16.0410542217832
F 10.78688588979385 15.06831971076323 19.94195857497672
C 10.61577128995399 13.42124513724364 16.8757042291665
C 7.057268920760076 11.88811501974113 20.07057762275357
C 7.784876733277936 16.84309629381785 19.86998442491222
C 4.54812799895719 12.82315974654629 17.73012203300089
C 4.748104634708549 15.96095579129236 18.03575455172869
H 6.387667990433829 11.12266441997222 16.2584637211639
H 6.175293878101986 11.82039958895873 14.65632781964126
H 7.794111783018916 11.67670412775778 15.34127661897076
H 8.069068282014811 17.16094348109759 15.80595469239036
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C 11.04804712529517 12.09301940373668 16.72302191146882
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C 6.589930863637264 12.03763496738621 21.38544989416274
C 7.026434842182285 16.99084879005111 21.04380089718491
C 8.254419582993192 18.02232330862582 19.26750391822349
H 4.287441394900442 13.13320648340586 18.74495761870071
H 3.6337222725173 12.89347328976715 17.12361163633999
H 4.830404835733646 11.77078048554837 17.77235720117242
H 5.208084044622874 16.88825777948418 18.37943432968786
H 3.895909560913867 16.23250162389869 17.39600896432074
H 4.34166487869352 15.4476958251967 18.91049566186755
H 10.99993783980214 15.43783199150108 16.23005943171283
C 12.30702592244752 14.06102455957707 15.23659833609557
C 12.06894818219311 11.7552784225799 15.84097569625511
H 10.61395001643763 11.30024690408706 17.32692203050217
H 7.286178685267682 10.44540682858332 18.47544433460103
C 6.348500881142627 9.560634135953988 20.17257167434168
C 6.001210979876333 10.98158146782925 22.0723150511463
H 6.721626769242567 12.98739382447366 21.89769474488527
H 6.686200546458872 16.11440770241134 21.58911698801882
C 6.725183652130802 18.24428098388768 21.56462776866418
C 7.956166510039312 19.27568011962428 19.78661241148863
H 8.879075822813492 17.94726820287767 18.38167241075674
H 12.80066567148647 14.84745548954245 14.66662976909509
C 12.70403762876289 12.73528320130628 15.08503739241358
H 12.38129466834662 10.71465310044978 15.75977315952248
H 6.264192043326475 8.589401290714362 19.68655799305143
C 5.871700806876615 9.735300931677703 21.46880983260421
H 5.656338870851077 11.1334160348581 23.09422722524697
H 6.141041078238988 18.31537258640966 22.48154446081519
C 7.180498804321452 19.39895704634088 20.93616861897891
H 8.339528449310896 20.16567755088561 19.28862428844257
H 13.50731655884308 12.47149020877075 14.39892667677662
H 5.415089965489807 8.905418288409415 22.0056374464353
H 6.948422810716746 20.38062445505211 21.34608914673898

2-F ionic:

F 4.77603972258574 10.41918526860883 16.040594201447
Fe 5.262503341460431 7.208659797603139 13.53343564074923
P 5.187169521082525 7.914612910993651 11.34800509961074
C 4.04269924551406 6.667861245524756 11.85237091361835
C 3.302873842959242 6.75316207608079 13.04942388728995
H 2.714375188966959 5.884847922307993 13.32638805317465
C 3.252298449568636 7.862153476371923 13.93184602716851
C 4.130744104016761 8.9628906740123 13.73823886728204
H 4.24625328806046 9.683192087691886 14.5904734715131
C 4.930683535325711 9.156336849930339 12.58829292817072
C 6.618057621756764 5.656124356178227 13.57206859551997
C 5.766495039532467 5.609042618008263 14.72652836455389
C 5.948724534266463 6.82868311186344 15.46141025304469
C 6.901138652293049 7.635610300306527 14.75829811140504
C 7.306460530891894 6.917250770260481 13.58488058487407
C 6.894432962851341 4.541066831399015 12.62371529998034
H 6.079232487330938 3.818861104243671 12.57344996318314
H 7.792058421935496 4.000932055804434 12.95722431692408
H 7.087209919674924 4.896867743917871 11.60892675555674
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H 5.570095610116697 3.881939787634304 15.94842795261521
H 4.743514932965664 3.735398006877923 14.39944871005901
C 5.397264117001357 7.158077989933204 16.80137199620087
H 5.222539097895461 8.233547337819145 16.90345087147798
H 6.13291558176105 6.860820231590193 17.56351460374302
H 4.469644717516459 6.625514698630723 17.01721227586434
C 7.456153357609827 8.914284516045484 15.27029959943038
H 7.992941319783749 9.472461166421777 14.50207306423209
H 8.172111743937414 8.684770042641567 16.07312446183368
H 6.665344693802605 9.551715853391737 15.69265383958961
C 8.3956255941156 7.327105300185848 12.65262730945103
H 8.283499503956929 6.883881763528491 11.66099523900006
H 9.361488729741859 6.994560783677877 13.05910992673379
H 8.44773834991816 8.410852667302928 12.53304858367568
C 3.885675698950922 5.485209332648033 10.9616545313553
C 4.159464350919247 5.608755490445226 9.590792407887564
H 4.5168577030958 6.560669232155862 9.202686894350332
C 3.960113149259574 4.551082257996864 8.711181300517316
H 4.178062758407205 4.686349485473353 7.652722843474072
C 3.469202047092489 3.335003635789012 9.175233274351619
H 3.305541912100872 2.50643687696118 8.487996575842674
C 3.17947937464066 3.195017751172266 10.52985020044381
H 2.789402212701736 2.251661593002218 10.910038955903
C 3.385334850872881 4.251872613757025 11.40802843712423
H 3.155850356609895 4.098429074788611 12.45833781225269
C 2.254911741370738 7.865329579443615 15.035133996048
C 1.120146435308928 7.03812513255249 14.96036792904662
H 0.9610904232197149 6.383754798830717 14.10616556005722
C 0.1395071015814776 7.071155429245384 15.94425030499586
H -0.734123785797131 6.426849993286822 15.85358335284654
C 0.2644960843184576 7.938923642806089 17.02603603516709
H -0.5041350504537525 7.968268737120824 17.7978231078547
C 1.369868687095447 8.781712286557408 17.09563658095723
H 1.473081209922342 9.480406484444856 17.92536325710825
C 2.355293754225224 8.758936857676215 16.11412748644939
H 3.215137938794915 9.442204603069614 16.19627919900997
C 5.676612862561391 10.43040045208079 12.39091922477142
C 5.778780983592404 11.39335304649638 13.41003969562398
H 5.379848451498202 11.19352014995812 14.41386054351439
C 6.415159897755442 12.60513453685343 13.16288241066336
H 6.482444070802683 13.33499397792301 13.96916722994614
C 6.957163135100851 12.89357890539948 11.91353317313129
H 7.449359751687041 13.8484358959134 11.73094088844608
C 6.851093501133935 11.95197076509402 10.89290161967151
H 7.251662503995479 12.16515851878053 9.902616755243086
C 6.214898262594451 10.74038922307546 11.12966990992888
H 6.119440638802818 10.03235094638681 10.30766620696946

2-F ionic (ZORA):

F 4.774521172747752 10.41829928024846 16.04191103707986
Fe 5.260541950516929 7.210222955570882 13.53196010239933
P 5.190777543589685 7.914510847630222 11.35074864804051
C 4.047218465848442 6.667487105957546 11.85510242003543
C 3.308482145971614 6.750929309428561 13.05280898985172
H 2.723926332005823 5.880760872117039 13.33148543643751
C 3.256116282609864 7.859512730734288 13.93516866900083
C 4.134450541769568 8.960029134814418 13.74240618833891
H 4.251698519264162 9.678856647998765 14.59626103070405
C 4.933349000015566 9.154318384199033 12.59212303166712
C 6.605684025115531 5.655839452051743 13.57001182044447
C 5.756205136640829 5.616945630244645 14.72615586216099
C 5.945011947387445 6.838642833336509 15.45582707372419
C 6.898269238365638 7.639140483114499 14.74694993008898
C 7.298214773549905 9.01456843216882 13.57575925114759
C 6.877571724886872 4.535694330103102 12.62659651981975
H 6.062696456569192 3.812847872626818 12.58483196937983
H 7.777026203907275 3.998364728769092 12.95918377731353
H 7.065136502253186 4.88544562752596 11.60888209045974
C 4.966069689414065 4.447811026255468 15.20891394259992
H 4.036822979786674 4.750715945990044 15.6971510449378
H 5.555759730006502 3.894365712469707 15.95313190660833
H 4.722284578729241 3.748056438110681 14.40797009866351

C 5.399273260838869 7.175555423596041 16.79607392276618
H 5.224071660596833 8.251558398467907 16.89240602010508
H 6.139004915366812 6.883247609821764 17.55594962686606
H 4.473450773172933 6.643251001618498 17.01921987720536
C 7.460505463562866 8.917010819062799 15.25302313992803
H 7.990510005364691 9.474145471427194 14.47958769055554
H 8.184116338346158 8.685694784821756 16.04825671792289
H 6.675419490500305 9.555412176868531 15.68299150638225
C 8.386710125724832 7.316549911315224 12.639405302327
H 8.270483817302868 6.870030041564049 11.64985369932853
H 9.35188428261689 6.981563654647002 13.04509062854444
H 8.442832130436507 8.399485349643308 12.51568826436786
C 3.891363902750953 5.485089301665512 10.96377793991024
C 4.170092090513267 5.608541465155662 9.594146822483467
H 4.531213760857017 6.559515531196191 9.207529739457986
C 3.970911722382711 4.552169920557732 8.713278715369697
H 4.19301261493991 4.687537525169869 7.655835995406947
C 3.474813439129173 3.337462668324688 9.174651656061132
H 3.311108243406106 2.50992676815906 8.486402300993388
C 3.179764583839751 3.197694693788352 10.52787433462814
H 2.785282945763575 2.255531025519255 10.90608325771391
C 3.385719616436059 4.253183834197591 11.40733084270397
H 3.151622359239302 4.099518997344316 12.45643513302982
C 2.258810810869556 7.860776232699402 15.03848827311833
C 1.126469342617164 7.030704330392387 14.96377741424966
H 0.9700495510205465 6.374530724581096 14.11065103817717
C 0.1447195802486201 7.062844774956379 15.94628146918767
H -0.7269470591491983 6.416097831283277 15.85566633010575
C 0.2660378526480584 7.932703917135361 17.02647786664124
H -0.5035026885601043 7.961362219275149 17.7971979908519
C 1.368846135114984 8.778474602444847 17.09576887283282
H 1.469136704795573 9.478980261493454 17.92415130567438
C 2.355332511246585 8.756586577742542 16.11560793952728
H 3.213032820732526 9.442238311673469 16.19744112662719
C 5.679711549190086 10.42833250584688 12.39535730413565
C 5.776809105600436 11.3932552603001 13.41270458366462
H 5.375662875011879 11.19437422765279 14.41562565813989
C 6.411346882823434 12.60571351917254 13.16526554193148
H 6.474544644712851 13.33709634239583 13.97032303211626
C 6.956545203795308 12.8929524810604 11.91732540597646
H 7.447227876602589 13.84837782353068 11.73443957296372
C 6.855574024534018 11.94931622301049 10.89839535374248
H 7.258712702326099 12.16133229840707 9.909052464643997
C 6.221079241640948 10.73713290258814 11.13542567670859
H 6.129498026885189 10.02791120495278 10.31416591147138

2-Cl covalent:

Fe 2.346062289427311 4.738498144511878 11.30797134993799
P 2.292280982691718 3.441125258907343 8.891513405556163
C 1.536543250495625 5.001779049491136 9.335501889120204
C 2.284459070396094 6.106720218758745 9.806672986622866
H 1.806514647540022 7.080882040152915 9.840439474187308
C 3.619898484060065 6.039851383177102 10.28250771501918
C 4.199759660942444 4.76087171552877 10.49475448572415
H 5.110041954729843 4.736206872505735 11.08789592629445
C 3.636619773264262 3.535944148842013 10.06548243189223
C 0.5871508588144749 4.463905521522158 12.39891488298092
C 1.224141786757585 5.695381432253956 12.76125021459815
C 2.535612086138203 5.387281900860773 13.2510690237223
C 2.716651242908604 3.966971845207872 13.16371409102489
C 1.505519852119416 3.395526404027554 12.63481693306781
Cl 3.200810936678895 3.78725599930246 6.973509364004297
C 0.1682345294895592 5.218016158425474 8.790738293066028
C 4.392712558781557 7.273753089125393 10.57296964062405
C 4.392864489741981 2.270048703790309 10.26279201818654
C -0.8511727275769296 4.31084831129426 12.04603199134834
C 0.5452676962240842 7.023648804280588 12.81459551421383
C 3.478278338123923 6.333702427721525 13.91435252170914
C 3.866566022883082 3.203228795017221 13.7286585758325
C 1.174065775956712 1.943784569086133 12.56212826556438
C -0.6998949692546296 4.136896782095612 8.565159605830297
C -0.2836741831337394 6.487701215321339 8.393461625516183
C 3.793105421470444 8.504652631681461 10.87794052807053
C 5.789880518412788 7.255172281293193 10.44224430887093
C 5.78383308615792 2.26650620571284 10.46184675045785
C 3.763616287615906 1.018632751447621 10.1559559613098
H -1.237263948163402 5.15023066974988 11.46579746121607
H -1.438491198383345 4.255248086971863 12.97449547696646
H -1.048122821926529 3.397527890422268 11.48329160305934
H -0.1322871441515188 7.179625729368929 11.97136427943344
H 1.254711485469958 7.852831204937259 12.83866417843026
H -0.05892587517314527 7.093087214263045 13.73075912072766
H 4.52471759542187 6.068476825722862 13.74441572363842
H 3.311158325158099 6.314891897643873 15.00106562460442
H 3.343908364729109 7.36366836031504 13.58170575082228
H 4.040458010558962 2.262122827094877 13.20558122198175
H 3.663756132870244 2.962502246266859 14.78242730840694
H 4.797887500118256 3.774039063893143 13.70360937694671
H 0.5280740144973126 1.708488422232887 11.71268765765498
H 0.6388166951650668 1.642965904058125 13.47472216163626
H 2.065025134230085 1.319923352420214 12.48781442285206
H -0.3714471561939122 3.134412367346416 8.829648617896959
C -1.956318926915237 4.31460957592536 8.001116130405498
C -1.543253953304505 6.669164233577269 7.832208514339245
H 0.3649999598496233 7.355501413805111 8.482453410631573
C 4.552692315010896 9.652569166883572 11.06791584521689
H 2.714493909973825 8.576889025090052 10.98031674471302
C 6.552892626149478 8.401636560595687 10.63587051243567
H 6.28982058109696 6.336360881296692 10.14580304952448
H 6.335085392707699 3.202795566367575 10.49034677973055
C 6.498771100663582 1.080202706732358 10.58391839913538
C 4.475794765501644 -0.1678881260950816 10.27602389267255
H 2.695312605549775 0.9812852593072188 9.959800343820584
H -2.598679140031931 3.449174783499151 7.841362772840439
C -2.393503145456228 5.5853370247339 7.636701233778046
H -1.852854602117185 7.66847810937008 7.527738041100841
C 5.939824865884272 9.608602538822025 10.95547823758821
H 4.054226420911426 10.59101519021864 11.30808545512971
H 7.634672787972545 8.351056557479865 10.51893049163355
H 7.577899283443705 1.119288216988268 10.72912326334972
C 5.849893826291512 -0.1478183891529058 10.50046658701542
H 3.950663153584284 -1.118409521373698 10.18706608606227
H -3.377023723460151 5.726868335349963 7.19116045091139
H 6.534385901919339 10.50872304620346 11.10355669720132
H 6.410325836244235 -1.077088148661412 10.59124215562663

2-Cl covalent (ZORA):

Fe 2.346777735284987 4.738773661471026 11.3069137352862
P 2.292593576712549 3.441490184325311 8.891133309103695
C 1.535526034313386 4.999131956215652 9.343103772884961
C 2.282118390604303 6.105427442482468 9.813808937367808
H 1.802579574660825 7.078540136040242 9.849864949610476
C 3.617975568343621 6.039345265209489 10.28795739255015
C 4.196337834835831 4.760136471437175 10.50125335524681
H 5.105204291507588 4.734331909531374 11.09624722781027
C 3.631510873199701 3.5361076589166 10.07110239241717
C 0.5905574136590114 4.465366535606129 12.39152345830527
C 1.227042963384284 5.697108391938756 12.75219498656757
C 2.539045833685802 5.389922820766886 13.24131666697571
C 2.720589878775765 3.969573634430641 13.15540343008461
C 1.50963603615829 3.397552903753924 12.62689522173056
Cl 3.204265170772309 3.794167765503252 6.975796221303897
C 0.1672482392128 5.214565769560827 8.797702704063843
C 4.391087209626548 7.272946197410544 10.57828869971653
C 4.387516871568387 2.269763846092915 10.26715444450102
C -0.8480348740923063 4.311018132491369 12.04104778939401
C 0.5478304064925967 7.025100815030153 12.80397398825633
C 3.481886142367399 6.336639412722522 13.90361384686093
C 3.870759137034768 3.207212231709659 13.72135081876775
C 1.177846399095545 1.946013182777711 12.55475859223656
C -0.6995535168889244 4.132926704063209 8.571209127873727
C -0.2847786152055888 6.48345318179211 8.399128499874497
C 3.792269546555322 8.505399115909421 10.87728270312689
C 5.788315320649904 7.252304896814125 10.45137039590929

C 5.778446781718529 2.265733015309979 10.46445877290668
C 3.758239785069524 1.018824534700923 10.15852363447184
H -1.236474743524752 5.150525651342739 11.46291648782556
H -1.432598864209637 4.253545158090101 12.97096647370664
H -1.045071893540056 3.398204938187723 11.4778602873721
H -0.1301933686172004 7.179548894339507 11.96102075280768
H 1.256987362943508 7.85437745635411 12.82645182624118
H -0.05557385661162378 7.095369548822915 13.72039889551609
H 4.528183789452008 6.074340384195623 13.72913147758686
H 3.318430890442805 6.314108072621963 14.99064590313492
H 3.343872352415423 7.367027503859085 13.57436137081598
H 4.043073373246866 2.264099394873418 13.20174316107152
H 3.669230048919486 2.971028555020864 14.77623557302982
H 4.802361226628626 3.777171055362087 13.69257257142753
H 0.5343886068139619 1.710290419668796 11.70368283891492
H 0.6398422786627962 1.646802962935095 13.46606481137256
H 2.068686298369853 1.321904320236115 12.48380979567735
H -0.3710413096856695 3.130898079580374 8.836732197982869
C -1.954947730264967 4.309404252098349 8.005000338436561
C -1.543435531989889 6.663781568419828 7.835918215803059
H 0.3631771424502137 7.351579557795557 8.488602571208826
C 4.552616418783573 9.652822615601311 11.06553882468117
H 2.713596809125382 8.579646060670145 10.9758340137213
C 6.552098217364279 8.398249885965678 10.64338044612745
H 6.287927715300986 6.33213408720056 10.15918868168445
H 6.329690355332834 3.201842364480526 10.49403653211146
C 6.493368694638956 1.079367756898832 10.58351370160844
C 4.47039001420099 -0.1678129940819517 10.2753848499413
H 2.689936173230143 0.9816828115223062 9.963309772358556
H -2.596303445042163 3.443521939813721 7.844537183735225
C -2.392428549870039 5.579456436800073 7.639507091625853
H -1.85323029272274 7.6626421478841 7.530623110026026
C 5.939769499950488 9.606806857432513 10.95726577609725
H 4.054625362000094 10.59258236279277 11.30089356907505
H 7.633997821675376 8.345916001776953 10.52959456646226
H 7.572520884444269 1.118154187057523 10.72762904765926
C 5.844456609596961 -0.1482553724934786 10.49845165311267
H 3.945170996010426 -1.118003447607886 10.18505833713577
H -3.375246776870934 5.720076087170757 7.19245302188368
H 6.53494336124336 10.50658717324089 11.10397789880382
H 6.404848827448392 -1.07761146150724 10.5869175227167

2-Cl ionic:

C -5.627056288930349 -10.28078996688393 7.608638966790141
H -5.703466628908835 -9.842259297217128 6.616097560890709
C -6.795443206592336 -10.70609732401382 8.228119962050917
H -7.744034734715594 -10.62357688979711 7.699211277393067
C 0.5169041687920242 -11.39760760594442 6.36728241058067
C 0.06142352034524071 -11.81375237426003 7.661823972104611
C -1.196902387359916 -12.47963398664488 7.494468287174231
C -1.518744894687282 -12.47741495831723 6.095362143891363
C -0.4492867425876232 -11.82558337041281 5.394066729502937
C 0.8239926377419859 -11.74582743904717 8.932926150969001
H 1.585586559895305 -10.96500292138489 8.922462666766286
H 1.341769092409457 -12.70672395668534 9.070854087734874
H 0.1740381014806615 -11.60052268324179 9.806938322842381
C -1.925397887574378 -13.19712085644687 8.571029610203516
H -2.984385945201265 -13.33128001671735 8.344575602742035
H -1.827897577104303 -12.69758850702788 9.542872923786762
H -1.483280406143914 -14.19937026647881 8.674607523159262
C -2.665056089967984 -13.20890604933427 5.483204902759666
H -2.890425711834232 -12.86478662571471 4.472414423532921
H -3.573459605005849 -13.13138166875041 6.085304511420662
H -2.415868505554267 -14.27708975723177 5.413101351582099
C -0.2557474196792111 -11.76983876660829 3.918527488351914
H -1.19118864059998 -11.85562704317486 3.365588585158219
H 0.3835659120590895 -12.61070786187188 3.613784692542911
H 0.2405895273511839 -10.85159940362101 3.596644612131867
C 1.855130747981897 -10.81075674504567 6.071198369550142
H 2.20366880230858 -10.15710377285894 6.873182882696645
H 1.863500811506497 -10.23849871902828 5.141397186122092
H 2.588383360207379 -11.62347307937199 5.969212763218201
C -2.181496109755648 -9.092464902653022 5.391220253484311
C -3.149283648135415 -9.748547160619919 6.178235303522005
H -3.967374640278148 -10.23459631704598 5.65743088923322
C -3.171265246909901 -9.829514097284896 7.593247500645972
C -2.057530221433742 -9.363158903255478 8.339184738393318
H -2.052360086672401 -9.57845773129503 9.410814387861636
C -0.9603866600826685 -8.650560164616165 7.806272610563251
C -2.380287769325536 -8.958304913163252 3.922193626989467
C -1.738281771137887 -7.920581269246092 3.228825445421974
H -1.074294704494132 -7.24851753320735 3.769172495215405
C -1.951252564278072 -7.7123294283476 1.871223570755021
H -1.440130294569306 -6.89265777508321 1.368382453048186
C -2.824091721929566 -8.532717393922066 1.163995670097809
H -2.998676573045091 -8.368417545922195 0.1019225531741757
C -3.480795940256014 -9.560603922678936 1.835333514156278
H -4.172088278351383 -10.2089645395835 1.298522300234386
C -3.261857832489413 -9.770463636431575 3.191108903999815
H -3.787642860121221 -10.58904073170348 3.673704686782421
C -4.385972424185104 -10.3570904473133 8.265791433810332
C -4.362901084514754 -10.8411061548137 9.581935667126865
H -3.434291807473333 -10.90268650728132 10.16075043946563
C -5.535828144829022 -11.26821277860513 10.19431486992246
H -5.482415526550922 -11.64377113288863 11.2150780758458
C -6.753939741978358 -11.21325125118959 9.524280143926754
H -7.668913559482513 -11.54651778438761 10.01280923726764
C 0.07863535298794498 -8.070203777721376 8.698682665893564
C 0.2074275646959052 -8.444844242857403 10.04597622169698
H -0.4043341105956574 -9.236283914063254 10.49082174986355
C 1.145710631260535 -7.822061620653137 10.86101286581096
H 1.221113513804921 -8.136831790931184 11.90082813891545
C 1.972342726813016 -6.81805452981876 10.36551653454982
H 2.702087477126637 -6.333828000539854 11.01352924082606
C 1.847384902202541 -6.428263763460894 9.03444581894146
H 2.470832355725887 -5.630620802695558 8.632703747738367
C 0.9100006975488032 -7.044132199521412 8.215902134233485
H 0.8088423868255075 -6.701535312189914 7.187160770049754
P -0.6903685520839934 -8.431116795715454 6.069063882349812
Fe -1.320744834648472 -10.53327697966663 6.744255487789947
Cl -1.545891028202433 -11.06410785758885 11.59548246533051

2-Cl ionic (ZORA):

C -5.62283453646574 -10.29312919827957 7.605544287177802
H -5.698443091990667 -9.858690996428866 6.6113056121816
C -6.791425964349949 -10.71831965519313 8.224213553088877
H -7.738936909916371 -10.6398325110782 7.693035353160982
C 0.51185645075329 -11.38900720920075 6.367009970567723
C 0.05707937713125207 -11.80450825079955 7.66181499192844
C -1.201136813531066 -12.47026993619692 7.495341486638085
C -1.523857186413899 -12.46842399676035 6.096526360191786
C -0.4545977964428447 -11.81744670384104 5.394450334554579
C 0.8206666533392905 -11.73728286224553 8.932317419608088
H 1.582057524638467 -10.95651261491625 8.921748798664039
H 1.338561121420538 -12.69820216777357 9.06839275667943
H 0.1715098527053218 -11.5927291189661 9.806777232840352
C -1.928115147384643 -13.1885092196326 8.572325278581454
H -2.986793881845784 -13.32441175494533 8.346370671815196
H -1.830845895896891 -12.68886353346829 9.543957504218604
H -1.484089432884331 -14.18981985064558 8.675185630222249
C -2.670676597603727 -13.19994379289634 5.485610746989782
H -2.896035793546036 -12.85690726056943 4.474601752257225
H -3.578712744377104 -13.12118459056496 6.087848073888114
H -2.421787767524821 -14.26810338723532 5.416756946576861
C -0.2607875443481564 -11.76308312733574 3.919017986017777
H -1.195754320445877 -11.85110428370977 3.365961370952608
H 0.3798670011962886 -12.60340189254465 3.616151507708891
H 0.2342167146322459 -10.84465657766993 3.596105254625459
C 1.849779886924703 -10.80209273323364 6.07004387083527
H 2.198577795371481 -10.1482078416286 6.871515401845574
H 1.85753698893217 -10.23028317872247 5.14009838114869
H 2.582708259039919 -11.61487314976436 5.967989669644975
C -2.179408467575548 -9.096042204058348 5.39245366026119
C -3.146099930681071 -9.754148764422164 6.17882251324456

H -3.961709291637859 -10.243414117533313 5.657568209925616
C -3.168665218971374 -9.835389692842515 7.593494476127264
C -2.054080900044455 -9.370696681390042 8.338784289232988
H -2.045679123784052 -9.591450668163812 9.40944879943879
C -0.9584771028686949 -8.655955281096086 7.805854763512839
C -2.37799241340648 -8.961449840578938 9.323436510299936
C -1.734862794794551 -7.924304029730895 3.230759051692069
H -1.069812173081797 -7.25351459925627 3.771138982584457
C -1.947945197614012 -7.714583467071635 1.873624365678462
H -1.435684400228696 -6.895426243737898 1.371393692803762
C -2.822307999725937 -8.532718243273534 1.16615448672627
H -2.997033417934317 -8.367259837242429 0.1044278256954181
C -3.480518588663327 -9.559675821744301 1.836910806822756
H -4.17331915021644 -10.20616927534551 1.300062060711041
C -3.261339014190315 -9.771062997635179 3.192192593254911
H -3.78870257310226 -10.58879057182764 3.67413962221507
C -4.383081606253152 -10.36448746620713 8.265258823570989
C -4.361784117168291 -10.84274314164846 9.583232289517763
H -3.434331588082665 -10.90006476296709 10.16433401208254
C -5.534939799455747 -11.2696620264019 10.19483395436847
H -5.48281238365619 -11.64073351586474 11.21716804083193
C -6.751592806761908 -11.22007084937504 9.522261222993492
H -7.666778046290341 -11.55320326350418 10.01019776516648
C 0.08190745839368725 -8.076786898034962 8.697648263745423
C 0.206350949160575 -8.445942967273782 10.04656066142941
H -0.4086823280378035 -9.233627367891708 10.49348685876324
C 1.144623450805467 -7.822813445703773 10.86101637661807
H 1.216435144914126 -8.133427351561988 11.90219649048623
C 1.975532298926417 -6.823746224817126 10.36346532684689
H 2.705173730697004 -6.339126619818459 11.01107673100396
C 1.854793007620213 -6.439195693957047 9.03074039022626
H 2.481524310940165 -5.645291870544255 8.627078377450317
C 0.9173784902792489 -7.055344402679377 8.212806092743005
H 0.8198105681560892 -6.71607933852597 7.182747252875318
P -0.6885970367333764 -8.434350435454405 6.069364945137347
Fe -1.322151132002127 -10.53071702947989 6.744210640707605
Cl -1.549328353904347 -11.05635149309629 11.59561532945823

2-Br covalent:

C -5.204043176333155 -9.929840145928706 7.850055107970602
H -5.375923630149495 -9.378115664076597 6.929128360875604
C -6.300042942889207 -10.33996464384067 8.601436194032976
H -7.305905512628309 -10.13065803246501 8.239695746077464
C 0.659747327949454 -11.51318294954947 6.49351380712851
C -0.347052140300006 -12.12220840056357 7.311616983768523
C -1.470920257813839 -12.42709891959359 6.476053821200175
C -1.166632407270504 -11.98004984886917 5.147420504332116
C 0.1570519965248597 -11.41421743428508 5.16005616496321
C -0.1502602555286869 -12.54923197878068 8.728253379619071
H 0.4163645614051941 -11.81728925512839 9.309363579159092
H 0.4177496083831329 -13.4904137319321 8.75411915296452
H -1.095013806596215 -12.73446725014086 9.242412987595992
C -2.666021587355769 -13.23366842672207 6.857401283526314
H -3.565259948639067 -12.92894919868904 6.316317953086091
H -2.890357662385208 -13.17580831781998 7.923144962082955
H -2.48532410333047 -14.2912420055963 6.616471368144105
C -1.984964387609435 -12.25602386440614 3.931428989574926
H -1.842598415571198 -11.50587269264758 3.152662441844831
H -3.053886617315308 -12.307002924783 4.151815320760383
H -1.695667031663244 -13.22937993499734 3.509120612185522
C 0.9555442399264357 -11.01140921177843 3.967296429612757
H 0.3246983591516373 -10.73262011414159 3.123028218350925
H 1.582232570040494 -11.85510200521035 3.643045051201192
H 1.622618490551211 -10.17216620100816 4.179188590001924
C 2.060033442969914 -11.23608967834276 6.916728218598862
H 2.132030558833453 -10.90250020129 7.953022998373775
H 2.544762363755277 -10.4864654535809 6.290097826695421
H 2.645472828043758 -12.16319495000438 6.828471455432627
C -1.950856221975325 -8.818729411889809 5.245550918734947
C -2.878879151798701 -9.493370197932212 6.072624436244101
H -3.721055580543401 -9.996907441421278 5.605531125052268
C -2.757114495701719 -9.640672773532346 7.479639871391899
C -1.527609603173222 -9.288678723962374 8.094353774827413
H -1.398661245867354 -9.591680285933116 9.128798608989138
C -0.4638437855578448 -8.613778870298345 7.451356001901809
C -2.245831500770439 -8.646950131454993 3.797758278605591
C -1.240344830547333 -8.291370533506493 2.883827588128633
H -0.2206080855331814 -8.174036945613089 3.241059191994246
C -1.521236274432728 -8.069092760386352 1.541820657431213
H -0.7133671837840786 -7.79492860874787 0.864164333719174
C -2.823909734924793 -8.186044764048049 1.064084383421222
H -3.046629464448162 -8.008271449942647 0.01307000232174724
C -3.840579971610303 -8.510735295704819 1.956867401733744
H -4.871443024860269 -8.576960063447663 1.61047873289777
C -3.55697627047462 -8.731370116361651 3.30001975497273
H -4.385324676854609 -8.939242733975611 3.972294707181245
C -3.890001541827241 -10.16826296549167 8.281049080032703
C -3.725800357226785 -10.8122691317041 9.516197136782166
H -2.730038052717151 -11.01120538292594 9.90084758949364
C -4.81914357112068 -11.22033440248849 10.27035214967188
H -4.655369713533509 -11.72191794977966 11.22345406191496
C -6.115380931261376 -10.99328812255165 9.815443350364232
H -6.971766036505011 -11.31177301278137 10.407727611889
C 0.7425168549028196 -8.229057038370405 8.2333226840378
C 0.7298992582737317 -8.169177485807952 9.636889309913453
H -0.173762317858233 -8.412715385817394 10.18992071063789
C 1.843905221902611 -7.751028586546836 10.35681547387348
H 1.79143889553038 -7.708283240674118 11.44423750585744
C 3.007476831960679 -7.365371551631649 9.698609166706774
H 3.877104746138586 -7.031098571935659 10.26238559273555
C 3.033232803959201 -7.39360929683484 8.306820050440132
H 3.927735917772355 -7.078960277144771 7.77029297636537
C 1.921065610998255 -7.815924243836436 7.590617298061205
H 1.956335200745517 -7.816614667789898 6.503576719890352
P -0.6500086825971179 -7.774446884817652 5.883168506265945
Fe -1.10640796143156 -10.40044337260967 6.44487528733316
Br -1.693032162561384 -5.735180511016907 6.39440185143668

2-Br covalent (ZORA):

C -5.200934079332085 -9.934506178004824 7.847661246864045
H -5.371900570937475 -9.385461005078497 6.925133276593189
C -6.297460275877953 -10.34246884449498 8.599028394577603
H -7.302851727379047 -10.13435436022712 8.235688529360232
C 0.6550010531519211 -11.50665679062966 6.498479893831989
C -0.3534753122889527 -12.11518252590296 7.314063797317061
C -1.476412340666973 -12.41768617657078 6.476367589217443
C -1.169257748766133 -11.97029884371327 5.148506194256011
C 0.1545271188551235 -11.40486307402383 5.164409435501175
C -0.1595012951807826 -12.5436304496368 8.730502867462279
H 0.4078136954996596 -11.81349024331111 9.312927454955979
H 0.4064556954235929 -13.48587945109193 8.75588309770383
H -1.105201934164875 -12.72750547562162 9.243078594572287
C -2.673208816745803 -13.2229411457429 6.854630748807192
H -3.57135352847585 -12.91491012560634 6.313870861378351
H -2.898046319824674 -13.16765393384891 7.920240895775168
H -2.494053124485981 -14.27991877849099 6.610658070405279
C -1.98511683594506 -12.24603549263986 3.930975148094861
H -1.838566231616518 -11.49787023764687 3.151343599873606
H -3.054653989487766 -12.29361923230305 4.148490573531991
H -1.697231316999309 -13.22093081806422 3.511652511041413
C 0.9559506946676055 -11.00035110363873 3.974360088606458
H 0.3271475070765268 -10.72450211603836 3.12783326253412
H 1.586588699754428 -11.84210872223459 3.653295420303754
H 1.619012704499763 -10.15858785105302 4.188189662118901
C 2.05506758406991 -11.23270876783261 6.923831389421249
H 2.1267164108508 -10.90114327471537 7.960622084744286
H 2.542004009208197 -10.48330377695623 6.298987253020774
H 2.6380639471471 -12.16107110539303 6.834407613410822
C -1.946188729295696 -8.824068165916417 5.245875145414841
C -2.875304690164817 -9.498787421787178 6.071917651678627
H -3.716108057463425 -10.00389397836872 5.604357440656874
C -2.754514530392598 -9.644891620610798 7.478909195927613
C -1.524049823213608 -9.294498281295912 8.092170420539198
H -1.392854035582797 -9.599375870884552 9.12563806360528

C -0.461246452323003 -8.620036040990982 7.446721020816208
C -2.24122669102931 -8.651093692387347 3.798206940996752
C -1.236158258020126 -8.293099769543915 2.885153445180211
H -0.2165531421733814 -8.176281529525008 3.242494500293399
C -1.517142996955634 -8.067652914059021 1.543905275383742
H -0.7094663835825049 -7.791667819987741 0.8669697065591673
C -2.819591595017778 -8.183749331462764 1.066070347216698
H -3.04240571565435 -8.003675837384757 0.01560294187682874
C -3.835915716697579 -8.510667809725369 1.95807214665955
H -4.8666781440942 -8.576323103114072 1.611690604628167
C -3.552156633592581 -8.73430386823846 3.300479672980324
H -4.380306928807491 -8.944045762345949 3.972228489254842
C -3.887517333297323 -10.17167493091924 8.280425898523646
C -3.72449267177107 -10.81151949181625 9.517592542547868
H -2.729300892632603 -11.00865872344622 9.904174664436583
C -4.818370123240643 -11.21732467572 67 10.27179843710877
H -4.655447503747549 -11.71568145089635 11.22658627708351
C -6.113974362928787 -10.99203122458915 9.814956914006897
H -6.970796868397526 -11.30880292088531 10.40728423111019
C 0.7453711182658286 -8.233760893397132 8.227521101417782
C 0.7325360358585484 -8.168676675003958 9.630526458872001
H -0.1709902818203783 -8.410923421845528 10.18414006274786
C 1.845997271011318 -7.747004230712672 10.34889556410172
H 1.793472916790934 -7.700388146826418 11.43602332434908
C 3.009008998728365 -7.362667979194409 9.689440120938363
H 3.878219693831721 -7.02564166378795 10.25196714061139
C 3.034872897651932 -7.395948672836558 8.297986658669835
H 3.928994226287404 -7.082460194225088 7.760416213233013
C 1.923312210176379 -7.821950022380849 7.583451887464095
H 1.958599730486039 -7.826973357566798 6.496546650186549
P -0.6504939531133898 -7.773091337006147 5.882971414249056
Fe -1.107340865803344 -10.39913067670058 6.44526895012583
Br -1.69588608991907 -5.744017349739645 6.397610554021646

2-Br ionic:

Br 4.702835316031802 11.02176042080282 16.82749975965076
Fe 5.256947835266335 7.178459962727941 13.51159513663749
P 5.212941722922913 7.890405929270915 11.32831064459165
C 4.029146512547516 6.672375651716423 11.8066222443197
C 3.27049258097353 6.761825011598634 12.98847222024507
H 2.604852290466887 5.933052223225441 13.20663911000958
C 3.259956420881189 7.844715475991302 13.90182755145612
C 4.148476941615372 8.936826583550696 13.70679435715321
H 4.220190889514393 9.663650904540889 14.52513401948982
C 4.959410322612603 9.135606719136357 12.56479131401066
C 6.614321395650352 5.626459424433372 13.54390052830316
C 5.76147913026348 5.565310569925058 14.69664307622153
C 5.928027389774736 6.78230574938515 15.44126417618489
C 6.887444874717731 7.59382268215864 14.75070007039217
C 7.301762337202264 6.886609366425398 13.57329841494852
C 6.894447456717799 4.519194896011778 12.58762667855337
H 6.076061686301677 3.801693094636016 12.52282611798208
H 7.785625930867392 3.971047293208769 12.92525988219045
H 7.10011808074136 4.883617326676345 11.57847986034691
C 5.010659419719276 4.365533340921844 15.16486575960599
H 4.141633793135578 4.630366815093002 15.76904196577281
H 5.670521782620479 3.759435492379665 15.80205086760515
H 4.683033125845744 3.724592456845832 14.34441265848854
C 5.351952208169854 7.103893797985041 16.77345303113771
H 5.155081246191919 8.17565421646205 16.8944871982019
H 6.080387830051883 6.818771500251931 17.54670231971507
H 4.430180753631 57 6.556886729087482 16.97598006238478
C 7.467335377353776 8.855438104516683 15.27581204168333
H 7.947861894131261 9.451202299925146 14.49906388800428
H 8.240504809478006 8.593320277046258 16.01313285132
H 6.728773239853102 9.480180649793031 15.79481407459768
C 8.399967041905354 7.303730265166561 12.65555536777956
H 8.299260161748252 6.867534133328846 11.65965100865957
H 9.360268410398392 6.966568592662106 13.07111759577132
H 8.456335860154041 8.38812541629925 12.54564821601944
C 3.848481424750997 5.509705149678368 10.89585329338981
C 4.082482790038776 5.665260649134479 9.52118802603597
H 4.422316001699134 6.627621166678523 9.1431413747819
C 3.861693718354082 4.624889961560574 8.626046882367941
H 4.046816163560328 4.782746813139201 7.564566404500666
C 3.390974361095182 3.397072346995843 9.079889766460614
H 3.211440668852131 2.582050825199967 8.380597277333814
C 3.14269052702924 3.225827139308163 10.43930336593473
H 2.770084604270462 2.271849973365073 10.81014974467136
C 3.369036860892794 4.265221875471154 11.33286653869471
H 3.174533805120788 4.09166167348189 12.38714544392279
C 2.281882511710267 7.846967335992435 15.01838102614278
C 1.648936409357878 6.673541951287398 15.46288863431238
H 1.921491650725411 5.704059054735258 15.055428293667
C 0.6715178255008777 6.710504259216254 16.44715293487159
H 0.2027427006659749 5.783201243314383 16.77377020874046
C 0.2969887765756167 7.925623064665345 17.01778541750257
H -0.4688768349329758 7.956159301446052 17.79152172130781
C 0.9175608426419433 9.094241442112315 16.59542343847511
H 0.6551136712094524 10.05174416269181 17.04084239078142
C 1.896343506177425 9.059564892785032 15.60798558444325
H 2.365899155185868 9.994791121734156 15.31979609468478
C 5.726224850308415 10.39652814727151 12.37468578947939
C 5.825389618643894 11.37331622055678 13.37878227754102
H 5.407767742348759 11.2254423135087 14.37951695749907
C 6.483958181617999 12.57285641246274 13.13370924752875
H 6.541986182222595 13.30640022980109 13.93645146069939
C 7.055612398436668 12.83557280636125 11.89275678354061
H 7.56644252369361 13.78002826953146 11.70849691478385
C 6.955274918747553 11.88196826531962 10.88248503371414
H 7.379165627326783 12.07534960476255 9.897984955699199
C 6.295779545696444 10.6839940417636 11.12087798046547
H 6.207093485027263 9.967797315155009 10.30544594683959

2-Br ionic (ZORA):

Br 4.699540533814827 10.99895242105617 16.81054872965624
Fe 5.255107582139251 7.182797359594392 13.51248059328561
P 5.21483065532082 7.892148887053989 11.33323777078388
C 4.032662174652303 6.674001367670802 11.81386726153854
C 3.275752610035335 6.76271694082627 12.9967829745866
H 2.613691647628985 5.932174104032059 13.21841333450812
C 3.264904988516721 7.846250350369302 13.90880506798038
C 4.153971397928967 8.937450311820697 13.71400604136364
H 4.229692714405015 9.661219613248024 14.53588564731066
C 4.962620356459676 9.136185588391022 12.57061431801286
C 6.607863085367654 5.634538996813105 13.53838522502638
C 5.75561142764754 5.571784091972869 14.69130814007381
C 5.922217163756366 6.787966400151628 15.43713265770021
C 6.881172459775366 7.600305583784988 14.74733427685632
C 7.294903501106968 6.894753768491159 13.5690574737345
C 6.887846815109067 4.52912775361163 12.58011711293663
H 6.071191372139178 3.809760917674272 12.51715384706607
H 7.781437795426688 3.983279311993554 12.91455880719938
H 7.089249958099 04 4.895192954192558 11.57082875297352
C 5.006789470971866 4.370749101441283 15.15914414482632
H 4.140356959068161 4.633803514153066 15.76747643410264
H 5.669522537162648 3.763536154871197 15.79200227243041
H 4.676139071036082 3.731826936253206 14.33853122280521
C 5.346678616245276 7.109305170993981 16.76946506928001
H 5.146200222111222 8.180814392486315 16.88844792828179
H 6.077277160839178 6.828003530171355 17.5418348798856
H 4.427290236969411 6.559337469092738 16.97386750072277
C 7.460534975207065 8.861196063316873 15.27435894599729
H 7.943741925740559 9.456614789311937 14.49923814986737
H 8.23114364159993 8.597789687504019 16.01365422242272
H 6.720293247068944 9.486032430143505 15.79134983752599
C 8.391960996457003 7.3136793940493 12.65093345360014
H 8.290971722114801 6.878187075709508 11.65487637462161
H 9.3525734328267 6.977017121424796 13.06575289102202
H 8.447048528152372 8.398089346577862 12.54198909741923
C 3.852774213681994 5.51058134285701 10.90386662726179
C 4.088698818958854 5.665219678517774 9.529678063525385
H 4.430485149960574 6.62673241364504 9.151591624948084
C 3.867296576487094 4.625213071037925 8.634602598016635

H 4.054205071627489 4.782515857276701 7.573490654509334
C 3.393533326989785 3.398649316641303 9.087919425652752
H 3.213302095815052 2.58393873395376 8.388654790861672
C 3.142852892564096 3.228448867313332 10.44676104319044
H 2.767481514338782 2.275600816258818 10.81733276676119
C 3.370086806282071 4.267427032417337 11.34025631270551
H 3.173175551436085 4.094456713503744 12.39400336224297
C 2.286888116436144 7.849783013338801 15.02510731066134
C 1.657993380576673 6.67693307803335 15.47556228010117
H 1.934674552114063 5.70634782884666 15.07392293929755
C 0.6793343438745215 6.716229097410042 16.45822070826607
H 0.2136341582036459 5.78934491132761 16.78993293345957
C 0.2995540836195959 7.933295132626587 17.02065528865428
H -0.4674101537178223 7.965717544757873 17.7930491230186
C 0.9158021206782178 9.101496924604332 16.59171060942331
H 0.6483967289226007 10.06058711645367 17.03042862333099
C 1.896155026864615 9.064503976267609 15.60615334183741
H 2.361556066875453 9.99931175824346 15.31047568346222
C 5.730885077045743 10.39621006311345 12.38008569133275
C 5.827629829064382 11.37454108381676 13.38251706338651
H 5.408910206467422 11.22729699570574 14.3832171005964
C 6.485872887969442 12.57386476797051 13.13655803505383
H 6.542102619207214 13.30872681226494 13.93804626050296
C 7.059274337831964 12.83506796449941 11.8963867007466
H 7.569760717818343 13.77942743131347 11.71144161953547
C 6.961096269413946 11.87993679408046 10.88769832803159
H 7.386408336246878 12.07189660589064 9.903684907571403
C 6.301970831781803 10.68215407003609 11.12691464070103
H 6.215069850594734 9.965072302200417 10.31223280297725

2-I covalent:

C -5.193293242554167 -9.957666662741731 7.873934408198249
H -5.367402978709629 -9.395492532090708 6.95977915203851
C -6.286845947055292 -10.36978618367826 8.627713636825057
H -7.293758428541769 -10.15179296453358 8.274184015335504
C 0.6615132782774775 -11.55190388430834 6.518605048995473
C -0.363057712205861 -12.17129039157666 7.305860673957584
C -1.47031986829242 -12.45937073555595 6.443467667222829
C -1.137164980366602 -11.9940903440963 5.128071702108229
C 0.1869341188920708 -11.43075542675081 5.176321950561547
C -0.1954010512887435 -12.61953528160485 8.71953380383485
H 0.3516231577776179 -11.89258225101433 9.32545783518774
H 0.3806147182730209 -13.55583373490287 8.742995590570295
H -1.149996297601954 -12.82180127333117 9.20822275076816
C -2.678673914070376 -13.26156683842123 6.790516745460306
H -3.561685711993855 -12.9496406225926 6.227247800875159
H -2.930326823625203 -13.20605827274113 7.850358332289836
H -2.498038402073409 -14.31921657550029 6.550108689923321
C -1.931609727463331 -12.25013640691063 3.89233135757015
H -1.763599533120694 -11.49528788590793 3.123446645108104
H -3.005690185394687 -12.29059723341906 4.088270022950699
H -1.643691370123986 -13.22321818525631 3.468578699545077
C 1.010814002918791 -11.0069631231499 4.008293087479971
H 0.3977832182613857 -10.73013791075512 3.150344713453905
H 1.658522278839746 -11.8380660090663 3.693267405608155
H 1.658745090501474 -10.15930387950396 4.244896984424494
C 2.05313256657929 -11.28600456169587 6.975950644960148
H 2.103360974587949 -10.96097493935405 8.016327176146769
H 2.556249523754927 -10.53452376430108 6.366519166831522
H 2.635045197048817 -12.21585509727521 6.893789598910838
C -1.952481535148652 -8.852207333497013 5.254869895019117
C -2.875976491883416 -9.527134309938758 6.085841299688315
H -3.72010778248989 -10.03021905670669 5.621753553680835
C -2.748042110967213 -9.676638457968622 7.491960595562084
C -1.516987157802659 -9.325867482635976 8.104023806902871
H -1.384810925914776 -9.630388876996353 9.137672435438891
C -0.4544434033975897 -8.651511211013501 7.459401176853503
C -2.254943472086865 -8.6739029927089 3.810103439995956
C -1.253175503736561 -8.319141038891731 2.892011728742459
H -0.2303977108323753 -8.209695926426937 3.243204822692504
C -1.541451290498002 -8.088864281872951 1.553027162136685
H -0.7368048847532868 -7.814968431879767 0.8715302306132329
C -2.847910982365338 -8.196607381957463 1.083625525350444
H -3.076541840507833 -8.011982708001064 0.03507451960637342
C -3.860698510858553 -8.520594778387391 1.981061830705276
H -4.894042865822952 -8.57921763848949 1.640895387279268
C -3.569836513281014 -8.749187649681259 3.321209264917236
H -4.394816424570916 -8.955203505612666 3.998145958851077
C -3.878228879965163 -10.20669004239681 8.295512479379212
C -3.709511259256806 -10.863326715041 9.523214596329515
H -2.712402424703323 -11.07001119425924 9.900034630603221
C -4.800542038914851 -11.27376110977734 10.27947427141818
H -4.6339163886052 -11.78532518519085 11.22673900902348
C -6.098158316043803 -11.03599923187011 9.834081491747986
H -6.952675418829106 -11.35606080803827 10.42820071511878
C 0.7521592274914711 -8.262989244057994 8.237514372145643
C 0.7379614614047143 -8.190244794431136 9.640317592519342
H -0.1667394055176457 -8.427343682435703 10.19445413079441
C 1.851792405907768 -7.765590671626002 10.3565020499794
H 1.798977565644812 -7.711902928506884 11.44337020127172
C 3.015444360479468 -7.386119359729383 9.69478321113886
H 3.884594645364916 -7.045957975397424 10.25573994053467
C 3.042481881792203 -7.427658798987606 8.303368040727646
H 3.937207465367867 -7.117779852508104 7.764554433731734
C 1.930673546550033 -7.856651516211795 7.590810194203692
H 1.966514573661439 -7.869497729985262 6.503749060997539
P -0.634861447163617 -7.825735946298531 5.884327711546915
Fe -1.098331541282606 -10.43115334951579 6.448163857512802
I -1.723113651831589 -5.537386800930622 6.413516342398319

2-I covalent (ZORA):

C -5.189943465005625 -9.962936089157507 7.864737297646919
H -5.362786582519063 -9.408119753289959 6.946040141616071
C -6.284747352110079 -10.37095032828042 8.618516583155577
H -7.290865488033321 -10.1572608116537 8.260529912650574
C 0.6599782117652362 -11.54260085926588 6.499719438537675
C -0.3526384858514345 -12.15473884350952 7.307587377701243
C -1.47272983684814 -12.45011264295632 6.464039355797981
C -1.159588259389362 -11.99542852242091 5.140089958488766
C 0.1651211417020066 -11.43263171975114 5.164112243372153
C -0.1645367997503396 -12.59148259399503 8.722198594092244
H 0.39842827898276 -11.86378991928363 9.311919182219144
H 0.4037484617312463 -13.53237471488582 8.744080823868737
H -1.112177673997257 -12.78113476086485 9.228939379059341
C -2.673495778299952 -13.2534032562294 6.833565675325066
H -3.567769439286946 -12.94160639907608 6.288582143416886
H -2.904055161123967 -13.20034212615364 7.898075595952274
H -2.495751872035661 -14.31013276158873 6.58761157425174
C -1.971864627964745 -12.26191238121654 3.918240709812601
H -1.818938853939483 -11.51093078501346 3.142605187787173
H -3.04244163367735 -12.30585992662437 4.13122477021412 8
H -1.686355588237171 -13.23615322985257 3.495883020517081
C 0.9718554166414103 -11.0218756230841 3.97983180475666
H 0.3467627476963339 -10.74588785346741 3.130603163838 07
H 1.607231127833836 -11.86043981176963 3.659911975505813
H 1.630638188990997 -10.17834350756513 4.19984910262774
C 2.058702143624582 -11.27348589400294 6.932393842487862
H 2.126501321664045 -10.94654301048249 7.970921740650187
H 2.549907638481451 -10.5225282122726 6.312833580885247
H 2.640046059292195 -12.20272387045426 6.841536473259769
C -1.944412244367979 -8.854162938336414 5.25334597903514
C -2.870147691991896 -9.529488283266762 6.081965214025426
H -3.71301967367267 -10.03263330936509 5.616131795436597
C -2.744493450425698 -9.678907938469774 7.48808712028861
C -1.512143010044115 -9.331794386147825 8.099201104882253
H -1.378420717303272 -9.639580849874896 9.131432525470229
C -0.4499645288097161 -8.656722421474342 7.45425578258293
C -2.245937144391692 -8.675934028286116 3.808071976507293
C -1.24423739559962 -8.319293449731772 2.891033359478158
H -0.2220457685285942 -8.208079420864438 3.242787758604371
C -1.531797322269893 -8.08840187666164 1.552155188796108
H -0.7270300560110118 -7.813069230056764 0.8715707896436228
C -2.837418524608771 -8.197769713113169 1.081622474438674
H -3.065433045105821 -8.013068127191955 0.03308314966553141

C -3.850314396609449 -8.523191342225527 1.978081605856946
H -4.883240604832169 -8.582894290592213 1.637234969141798
C -3.560143584188074 -8.752105650338297 3.318082357701077
H -4.385332372187563 -8.959121765183564 3.994226413832834
C -3.875774132806551 -10.20666057213537 8.291405081700399
C -3.7096510176378 -10.85324829305126 9.52456287636849
H -2.713576695948058 -11.05522398011436 9.906303781917838
C -4.801883735689816 -11.25943022736925 10.28093678712219
H -4.636932363914184 -11.7630525798556 11.23258514853684
C -6.098458847555244 -11.02737554259965 9.830317018770666
H -6.953983415739569 -11.34408685142611 10.42453930111969
C 0.7569087505810452 -8.270998057316199 8.23398775319502
C 0.7427521811655572 -8.203356171813876 9.636822559381079
H -0.1617178046664116 -8.442799363463896 10.19004397525305
C 1.856026109880892 -7.780938377820565 10.35473773041341
H 1.802972721310069 -7.731612350194884 11.44167713132183
C 3.019400468262011 -7.398336795685869 9.694821304540563
H 3.888274015944249 -7.060114146887757 10.25713284898572
C 3.046223873112908 -7.43390584688323 8.30351597217561
H 3.940501930705683 -7.121024516389955 7.765949707079011
C 1.934893400968406 -7.860863398943785 7.58927531241996
H 1.970901843584413 -7.867874060452597 6.502368239378701
P -0.6318112722610857 -7.820973287071704 5.883991204952873
Fe -1.099294728976393 -10.42994653464139 6.446144746150584
I -1.727126708253363 -5.538777298215376 6.420753475387945

2-I ionic:

C -5.632704844212171 -10.23447245603148 7.580037761873743
H -5.706648424267013 -9.784931764516232 6.592253503141932
C -6.802738093858489 -10.65231692050664 8.201369833010622
H -7.752772367555518 -10.55371306375384 7.677938197606275
C 0.5143408307290362 -11.38416333916601 6.336573694881699
C 0.06279523627803428 -11.80352703724158 7.631581455141682
C -1.19491327276602 -12.47066340614871 7.466557620592513
C -1.521077857607713 -12.46487195026798 6.0684353643108
C -0.4529929569660145 -11.8131488081843 5.365114818125972
C 0.8370898794965408 -11.74118731815306 8.89541471122868
H 1.573381569111976 -10.93649576099388 8.897827134852252
H 1.38687259763412 -12.68763290062872 9.005131413412972
H 0.2017512417191919 -11.6437391873863 9.78575357565386
C -1.919539996780583 -13.19963521364586 8.537481520710937
H -2.984785046333104 -13.30818441971507 8.327421949975568
H -1.797286845401864 -12.73741363197881 9.524787038623547
H -1.496023990426671 -14.21249732193785 8.608812984481203
C -2.667558721285245 -13.1975799596119 5.458352771368323
H -2.89686239734284 -12.85214050178175 4.448960516501019
H -3.574280069091004 -13.1242047399499 6.063472136262966
H -2.415583876678745 -14.26488644165311 5.38538617536162
C -0.2608350558649102 -11.76045352326027 3.889451726650206
H -1.19666136902241 -11.84623045767732 3.337271685985945
H 0.3767550239346124 -12.60335085175207 3.58678221387124
H 0.2373504057088226 -10.84420742293015 3.564940494320353
C 1.852677930273401 -10.79872048201869 6.038612463308795
H 2.203120318371655 -10.14448697921179 6.839318339496084
H 1.861214019186657 -10.22819847276712 5.107814549183954
H 2.584729315361448 -11.61257702411762 5.937505960461534
C -2.184068564306965 -9.085208767954413 5.348747386929414
C -3.150154637264906 -9.741541074758933 6.137782105401477
H -3.966724767994995 -10.23380951976613 5.620332633536557
C -3.175640832290119 -9.809198843803472 7.553335465752354
C -2.069634580583235 -9.323700501546192 8.295882673638566
H -2.086642998422767 -9.491977654152398 9.371830862131583
C -0.9651366860433139 -8.626760631527675 7.761035284595662
C -2.381840106949415 -8.956225949753227 3.879413468168235
C -1.733866819167874 -7.924511803781952 3.182415981774665
H -1.066190772620958 -7.253876056918536 3.720014227922858
C -1.94587604408126 -7.719582504312103 1.824247840465062
H -1.430265391791841 -6.904536015795028 1.318564519380579
C -2.82358078054407 -8.537407987007855 1.120084541139435
H -2.997507428407969 -8.375625796233914 0.05754514815196767
C -3.486201232142517 -9.559203031055361 1.794922148945681
H -4.181478541180968 -10.20511977908461 1.260407316095018
C -3.268378996228912 -9.765839585635571 3.151305639995489
H -3.799467776666178 -10.57958532441063 3.636263242507148
C -4.389526660731767 -10.33099083894463 8.2300200004667
C -4.368092480440858 -10.83032406442455 9.539735375821142
H -3.443550183323238 -10.91294635818202 10.11647461530143
C -5.541074668461581 -11.24968756337836 10.15626937186876
H -5.484213652451967 -11.63664899162373 11.17212823160164
C -6.761112893742284 -11.17262027153819 9.492154930514522
H -7.677273457245618 -11.50020846741224 9.981921590386179
C 0.06839876763628927 -8.038202407081773 8.653121171738391
C 0.2176162246113354 -8.419997928849879 9.995773480813659
H -0.3718606586924051 -9.222734157124457 10.44364949020897
C 1.149198329872485 -7.787983145476282 10.81059737296582
H 1.23754367088652 -8.111314358831203 11.84630358448849
C 1.952547952982973 -6.765008177227428 10.31578147575498
H 2.678545253710626 -6.273084596873253 10.96192261845838
C 1.809769266113574 -6.367330619963954 8.989059731195722
H 2.415274474567356 -5.555323693501935 8.58883957725285
C 0.8773123857753131 -6.993519619158578 8.172747409698705
H 0.76006108427888 -6.644776245920815 7.147859888134491
P -0.6898764232147255 -8.425630788970505 6.022940988784187
Fe -1.32321486062068 -10.51979615388671 6.717269578519127
I -1.4726289502728 -11.31705060667501 12.1492428049256

2-I ionic (ZORA):

C -5.625885479251607 -10.25021202453117 7.580104448990389
H -5.702042958810829 -9.797294107633117 6.594163928306984
C -6.794156084780342 -10.67111684507343 8.202290577432882
H -7.745151228198477 -10.57162572118376 7.681058734181477
C 0.5128102835244848 -11.37473919342643 6.329067095412975
C 0.05952817148600995 -11.79904080873508 7.621697521014668
C -1.197054105786806 -12.46632297572623 7.452167641517401
C -1.521301947328684 -12.45563969145359 6.053754769251312
C -0.45250845254348 -11.80094842284977 5.354537480989095
C 0.8315161564258183 -11.74243259504136 8.887298599893052
H 1.572174436437553 -10.94204175827762 8.892196278309916
H 1.375276711729922 -12.69212106888382 8.996962179408696
H 0.195037698383073 -11.64184988390705 9.776116760556196
C -1.921035238520752 -13.20121148163823 8.519530856584067
H -2.98482799356473 -13.31537283329447 8.306174688451909
H -1.804491168100932 -12.73963403186809 9.507354944590743
H -1.491499442037666 -14.21134982439464 8.590537753030082
C -2.666280467126829 -13.18704786846726 5.439455878135235
H -2.892434303054586 -12.83996605140014 4.430088584182506
H -3.574619743582415 -13.1142848520083 6.041993234722312
H -2.414124527526489 -14.25407111742781 5.365579829251024
C -0.2576695134941386 -11.74254596011535 3.879539715266141
H -1.192165181695394 -11.82795548601285 3.325372008709596
H 0.3819877533533463 -12.58317656942098 3.575518885022918
H 0.2393745046736926 -10.82431401181248 3.559368010957987
C 1.850808749408873 -10.78658209744171 6.035221768061587
H 2.198987574640539 -10.13439071993077 6.838358806783697
H 1.859928104589819 -10.21320944487653 5.106319151385975
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S6 References

[1] a) E. van Lenthe, E. J. Baerends, *J. Comput. Chem.* **2003**, *24*, 1142–1156; b) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931–967; c) ADF 2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, *http://www.scm.com*; d) C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391–403.

[2] a) E. van Lenthe, A. Ehlers, E.-J. Baerends, *J. Chem. Phy.* **1999**, *110*, 8943–8953; b) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phy.* **1994**, *101*, 9783–9792; c) E. van Lenthe, E. J. Baerends, J. G. Snijders, *J. Chem. Phy.* **1993**, *99*, 4597–4610.

Supporting Information

Chapter 3

A Phosphinine-Derived 1-Phospha-7-Bora-Norbornadiene: Frustrated Lewis Pair Type Activation Toward Triple Bonds

S1 NMR Spectra

S1.1 NMR Spectra of 2

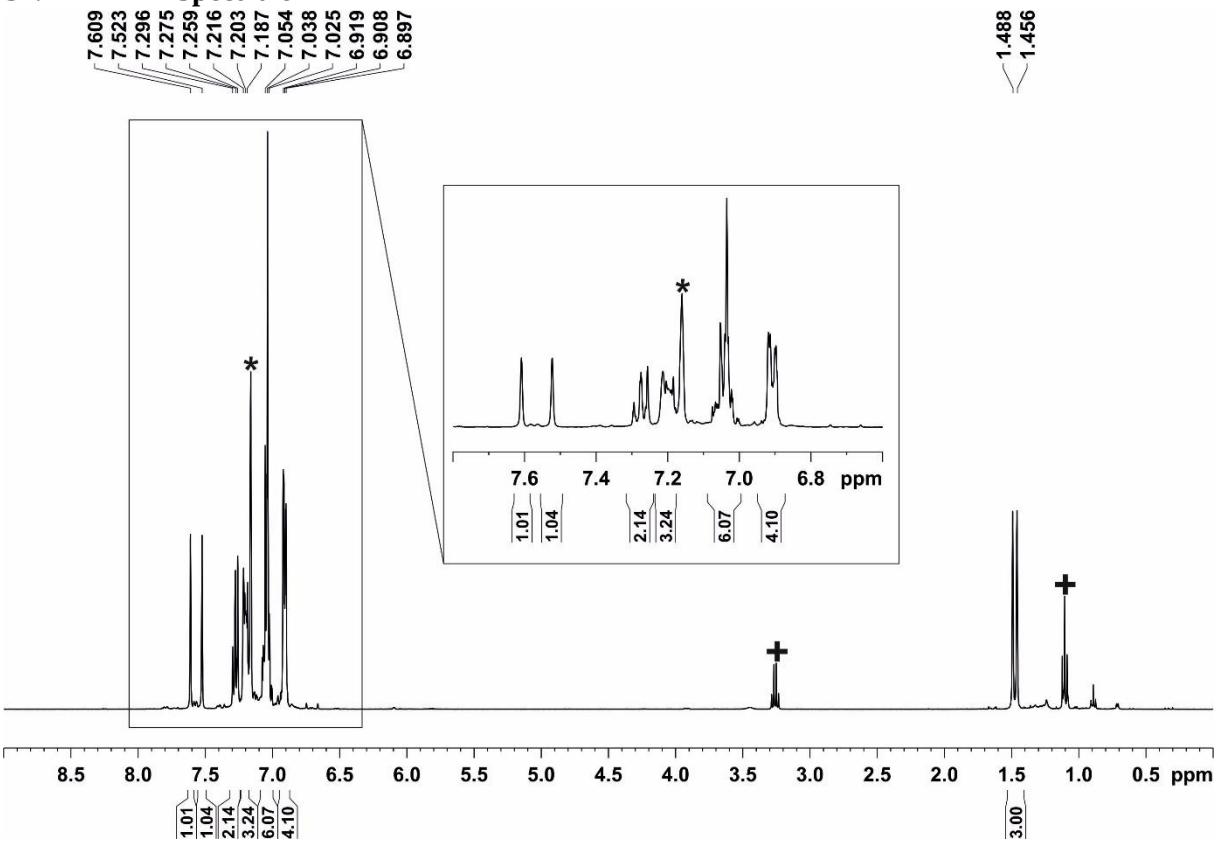


Figure S1. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **2**; * C_6D_6; + diethylether.

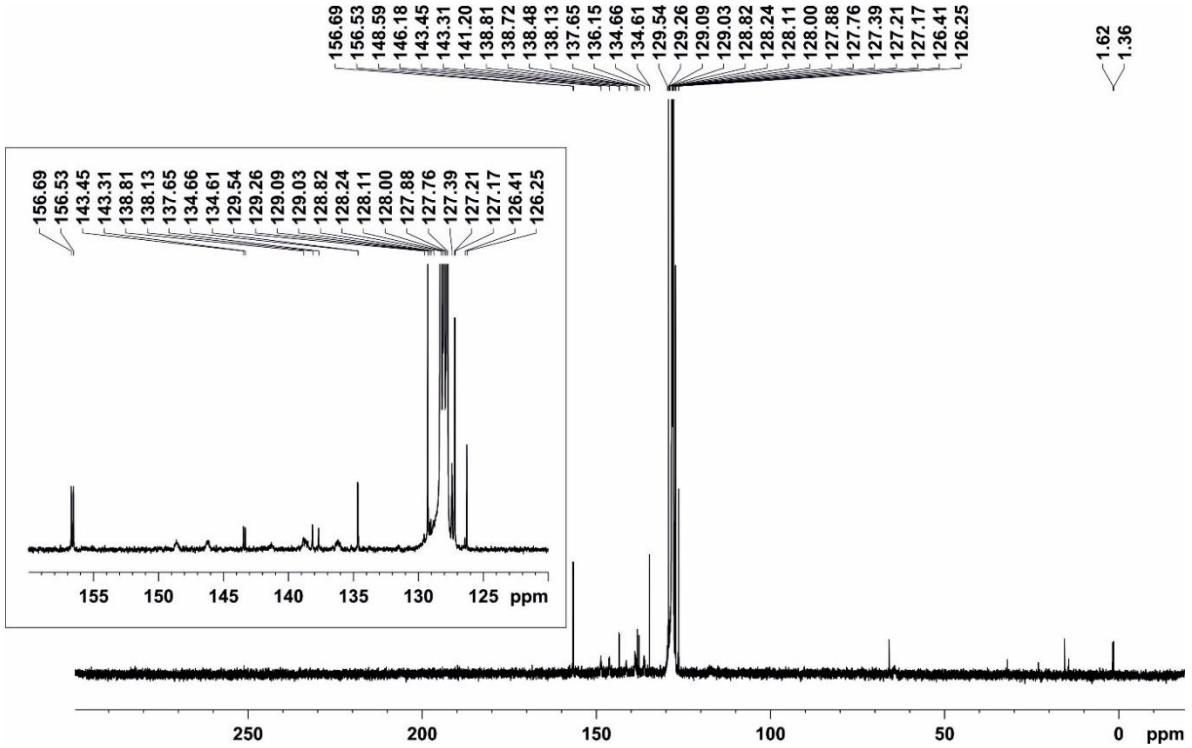


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **2**.

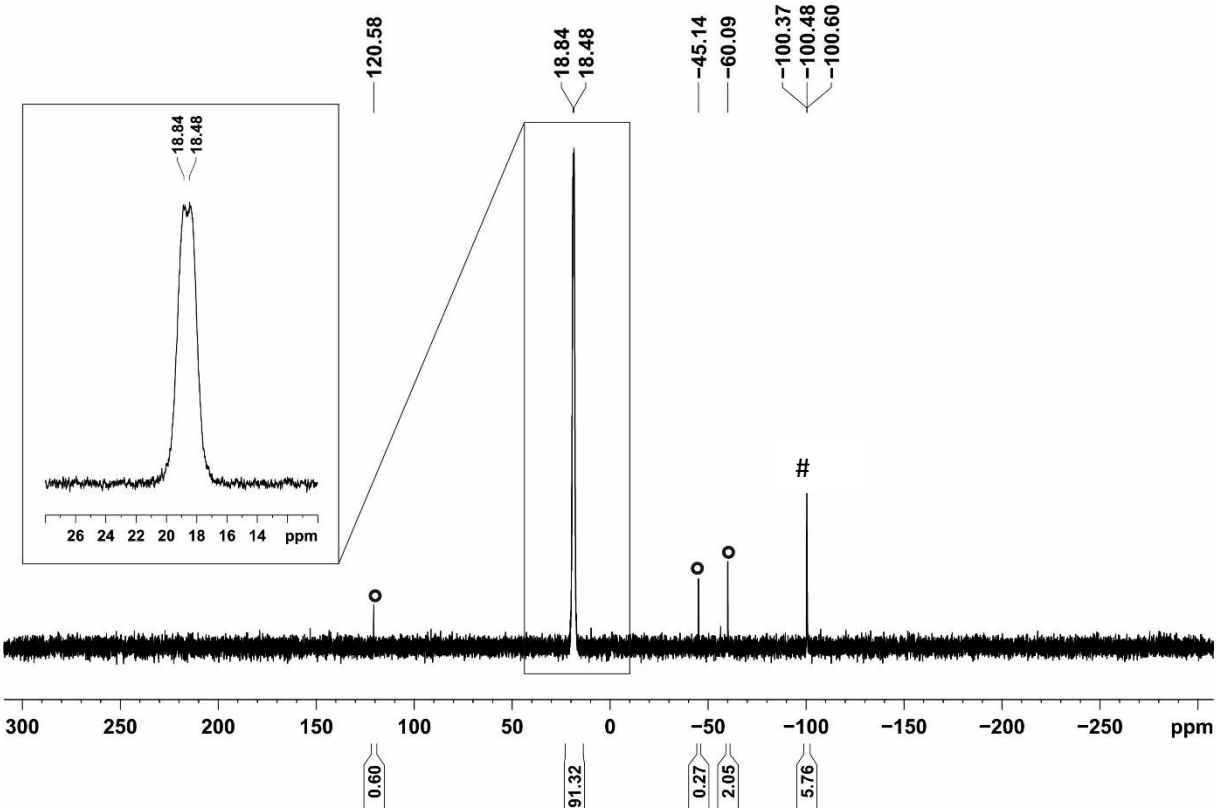


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **2**; # **Iso-2a**; ° impurities or isomers of **2**.

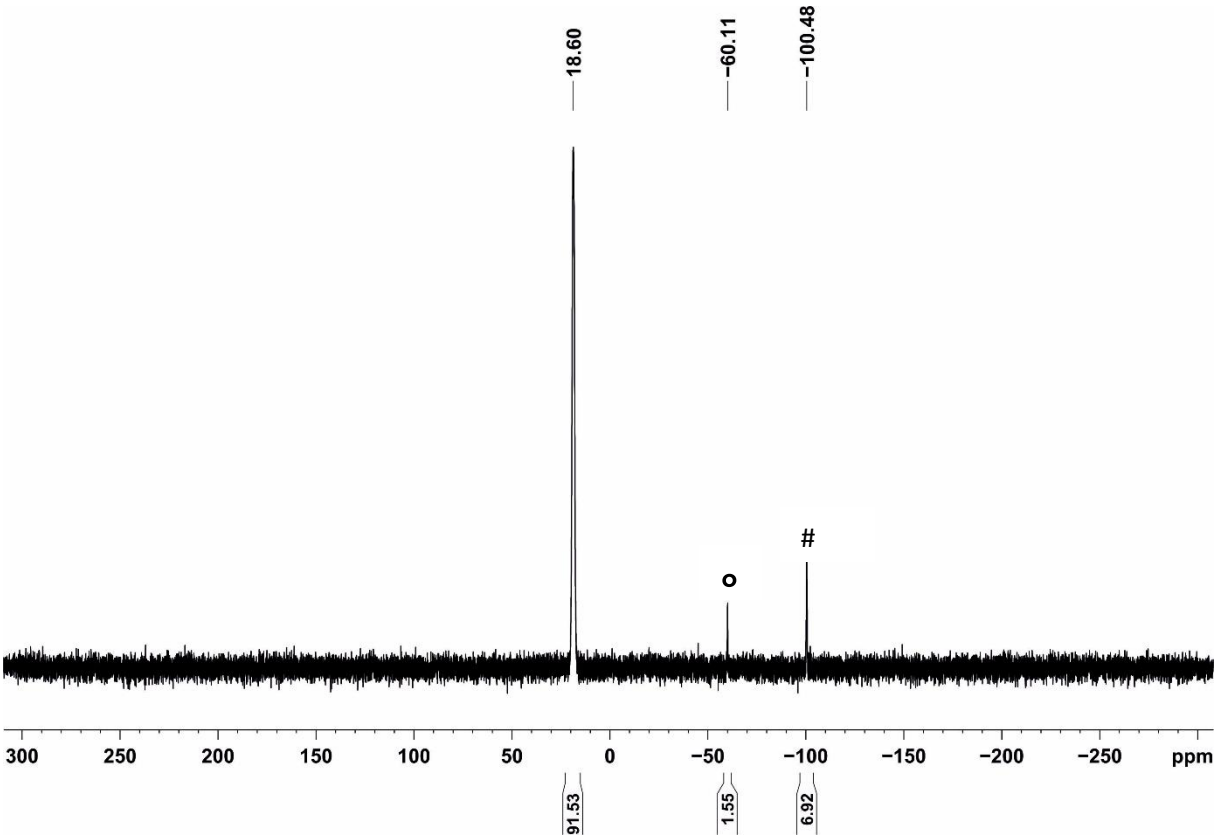


Figure S4. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **2**; # **Iso-2a**; ° impurity or isomer of **2**.

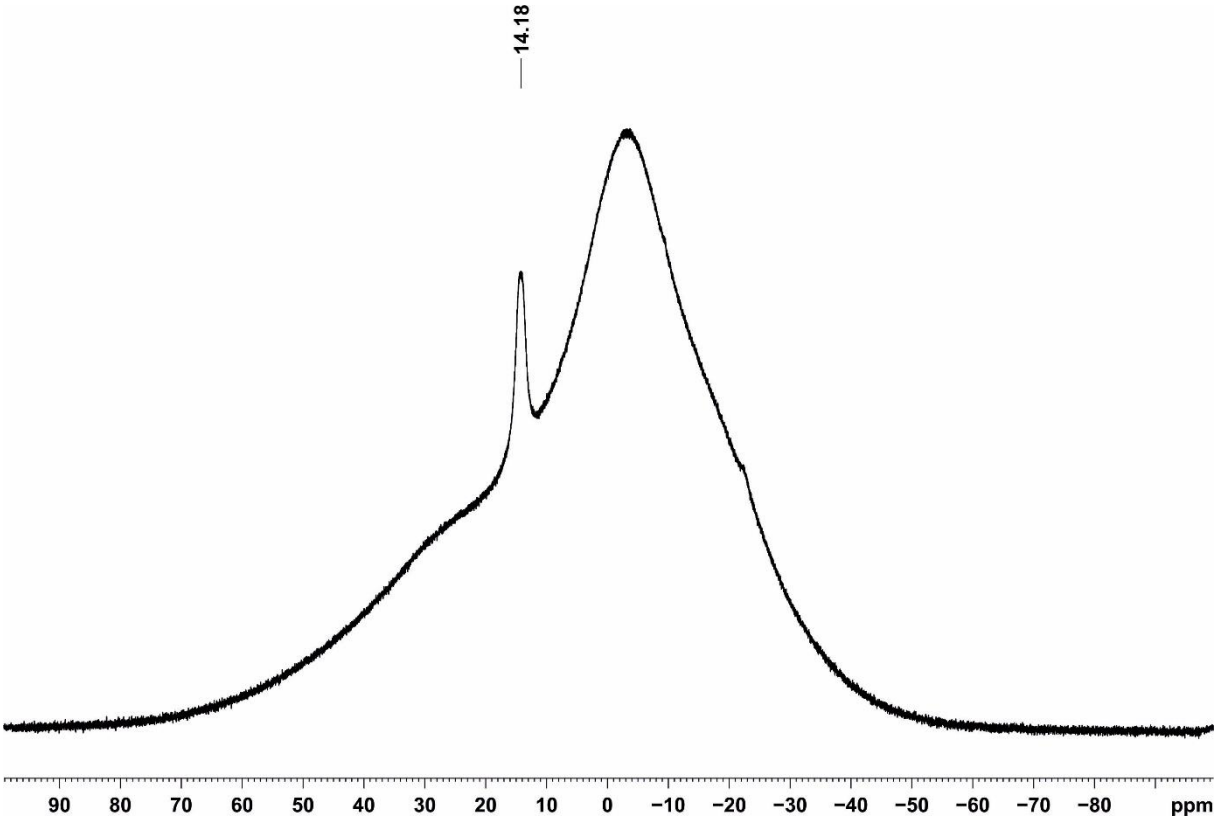


Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **2**.

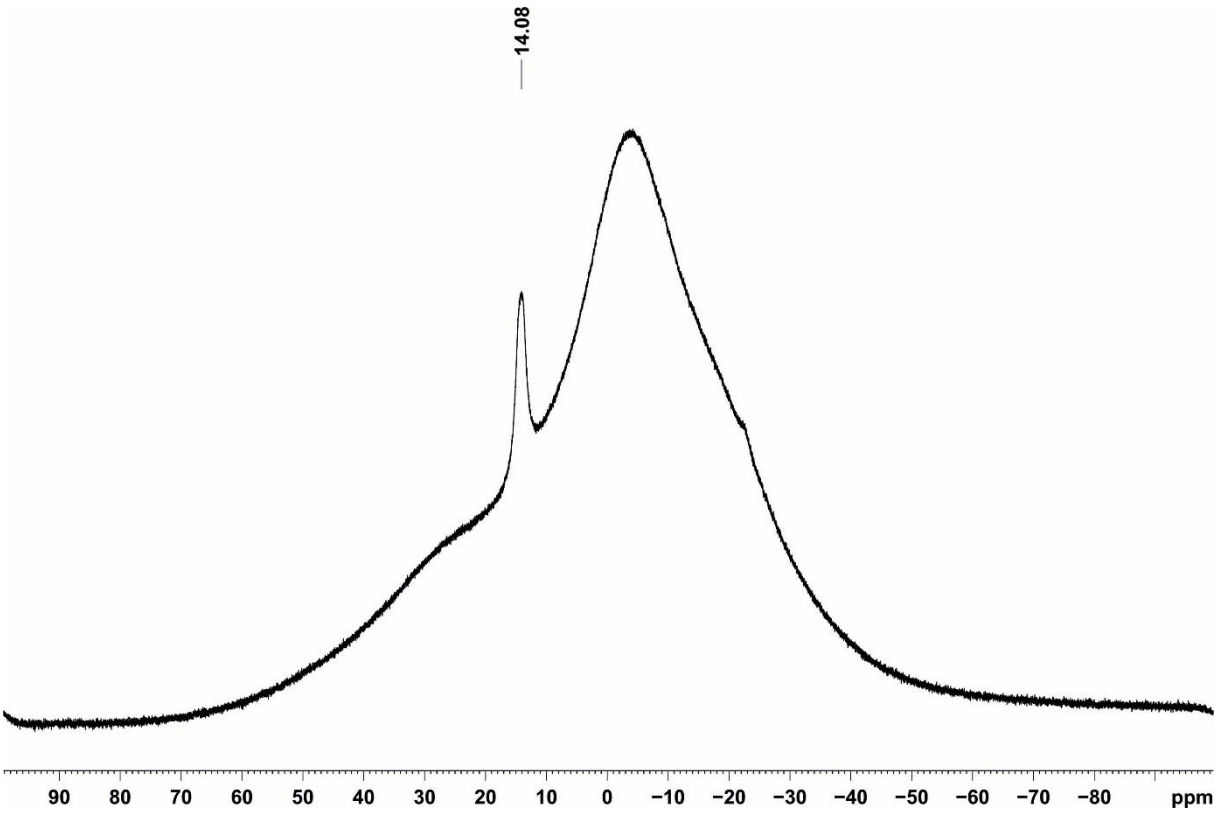


Figure S6. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **2**.

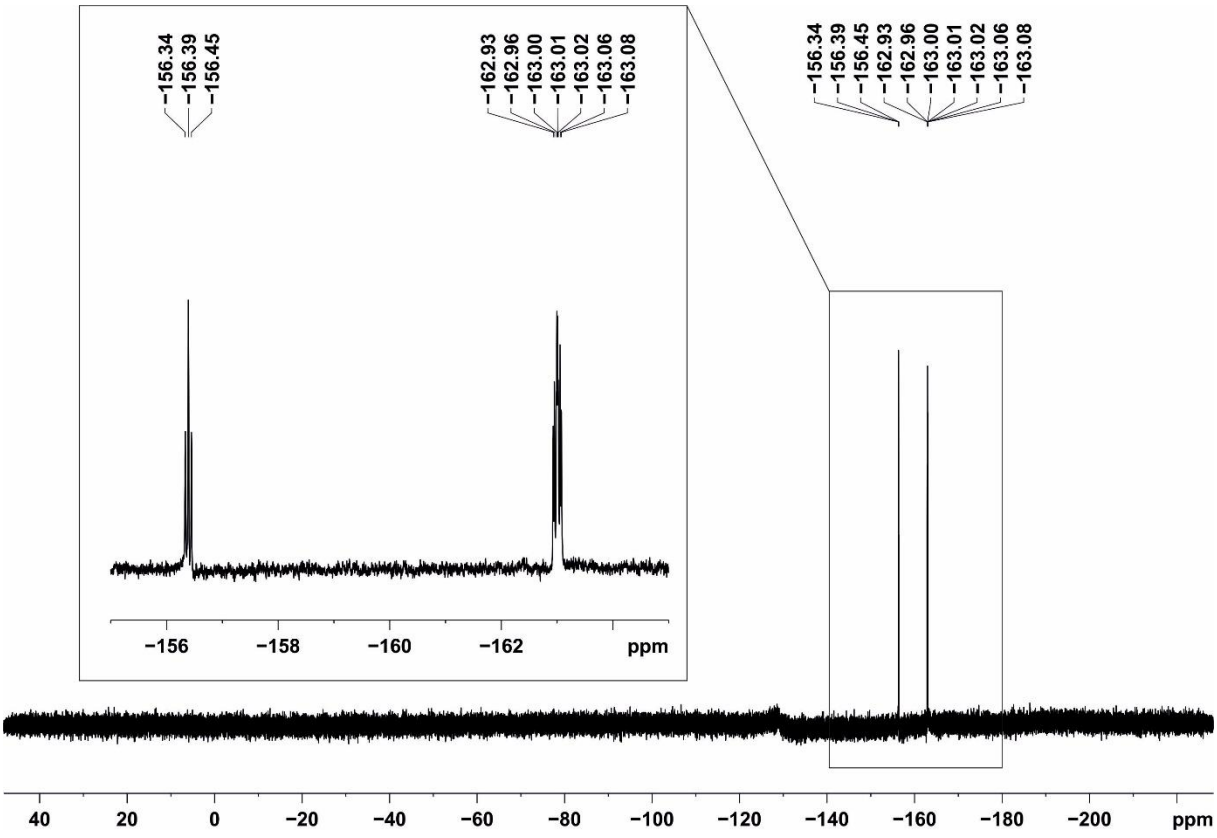


Figure S7. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **2**.

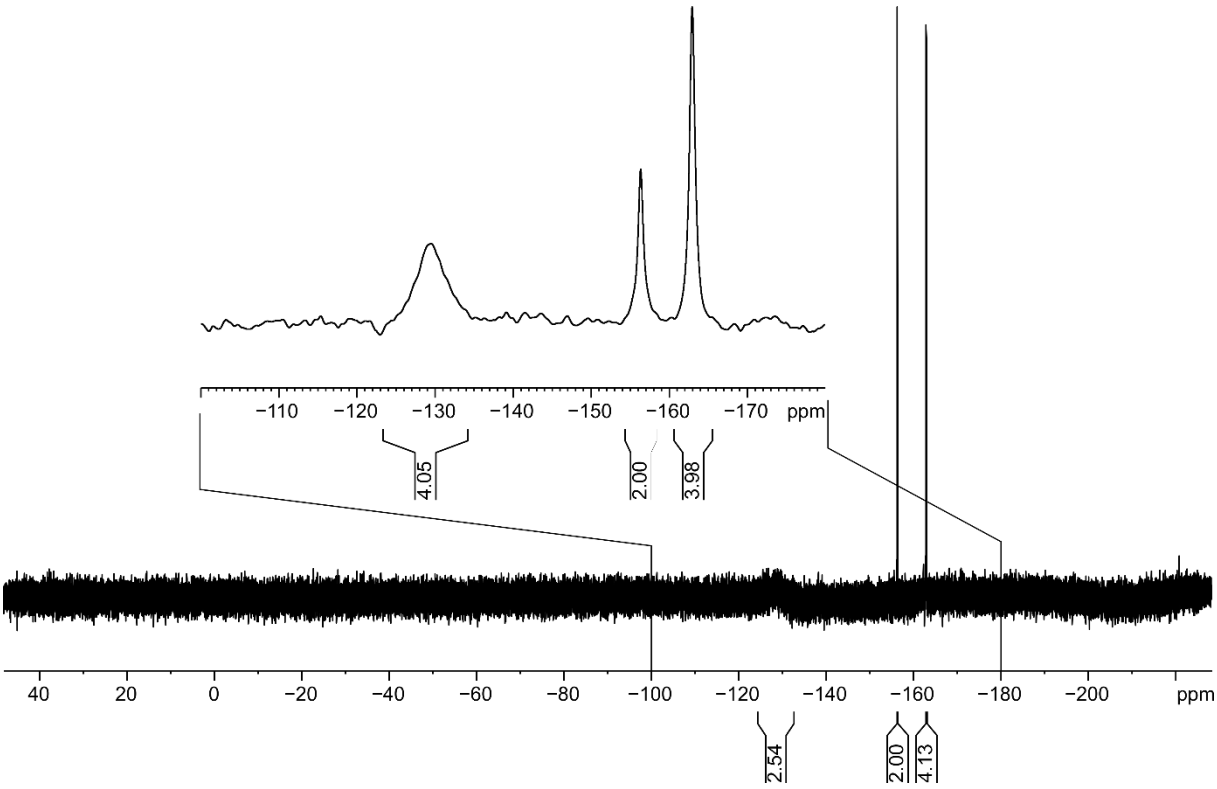


Figure S8. ^{19}F NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **2**. Full spectrum: processed with WDW=EM and LB=1 Hz. The baseline was corrected automatically. Zoomed part: processed with WDW=EM and LB=300 Hz. The baseline was corrected manually by defining baseline points and applying cubic spline baseline correction.

S1.2 NMR Spectra of 3a

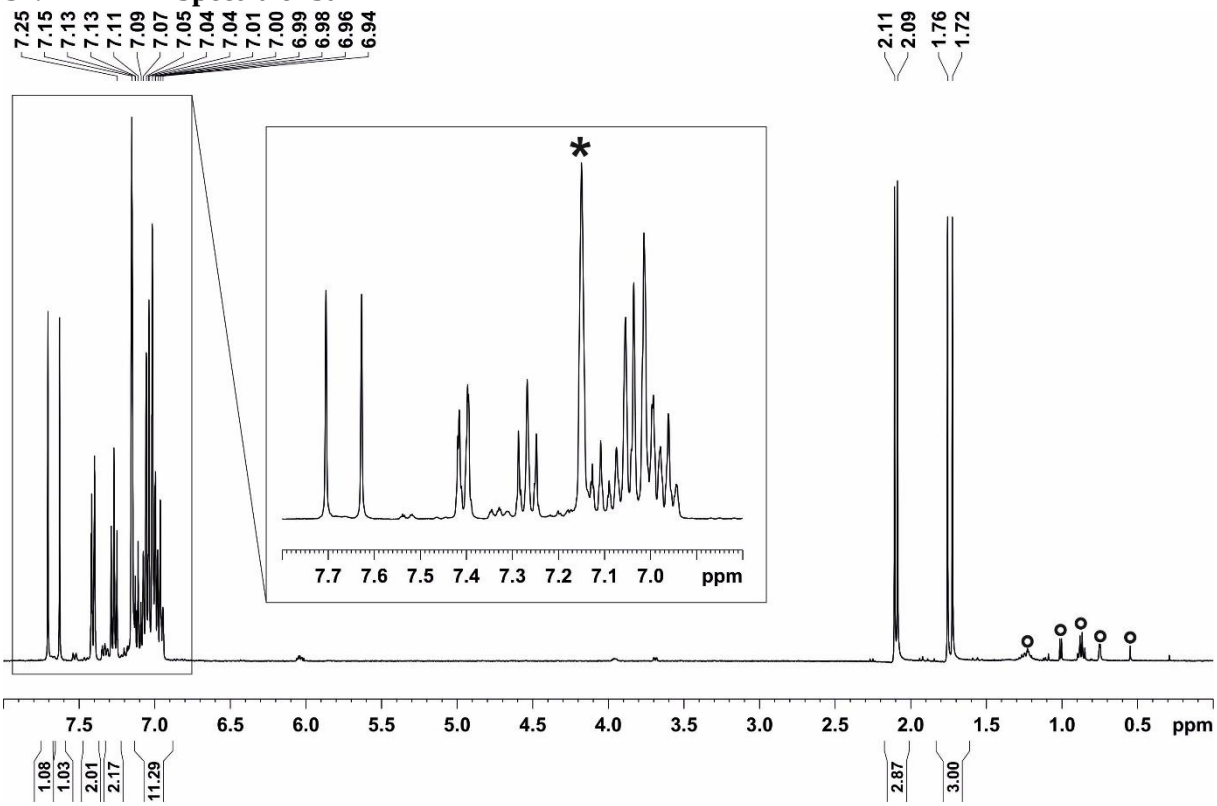


Figure S9. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **3a**; * C_6D_6; ° impurities and *n*-hexane.

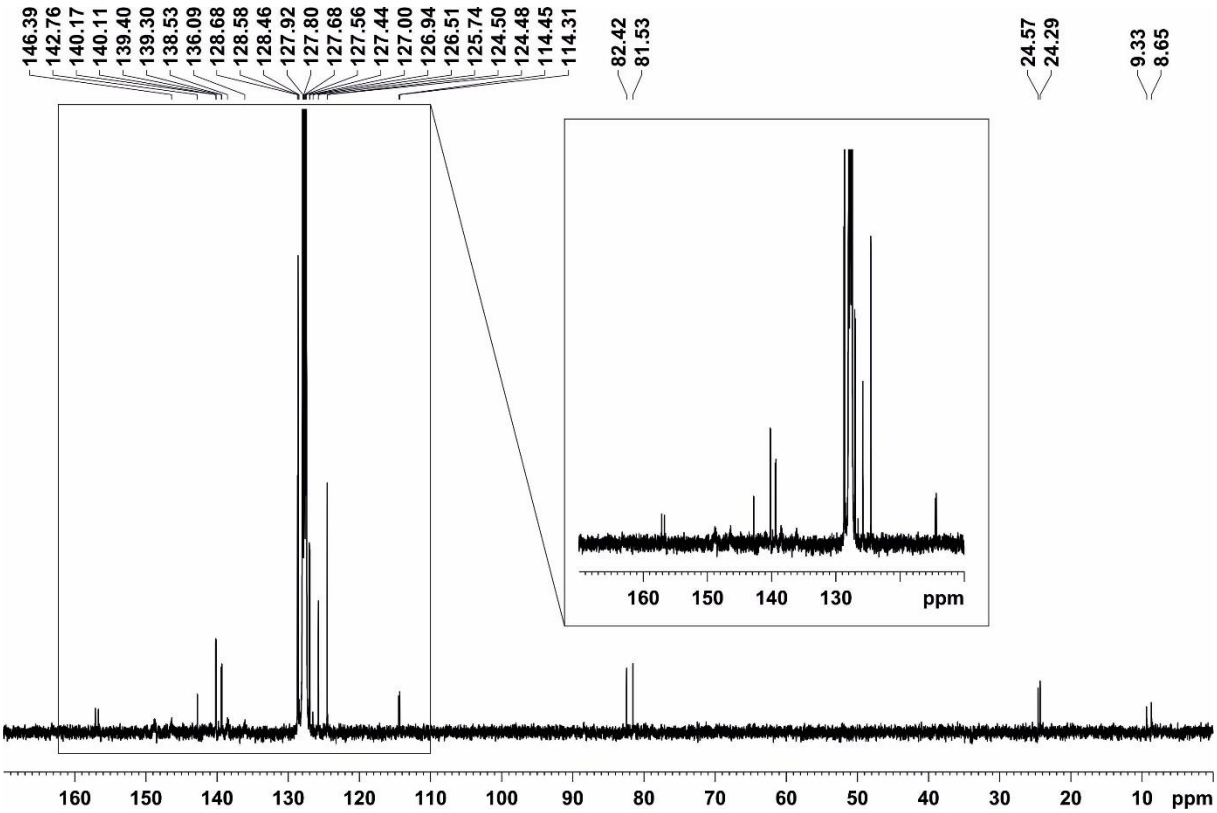


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **3a**.

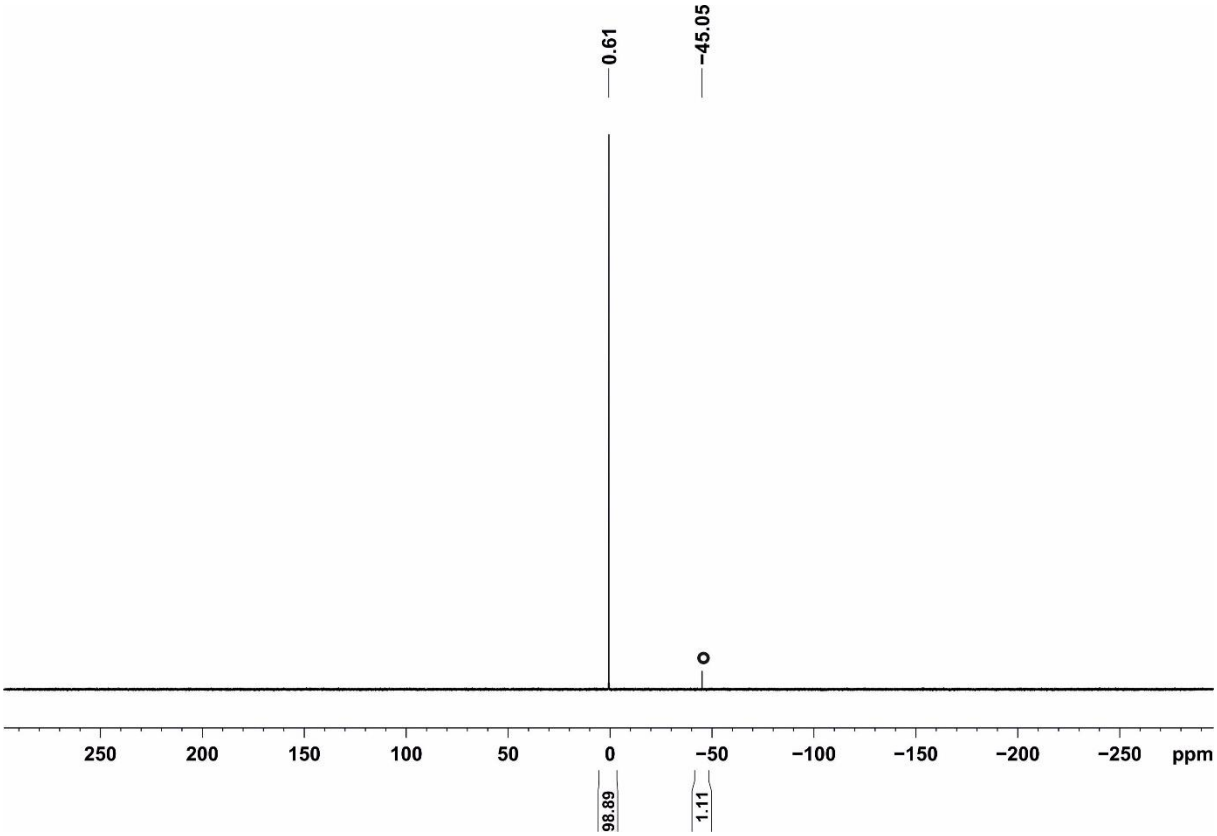


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3a**; ° impurity

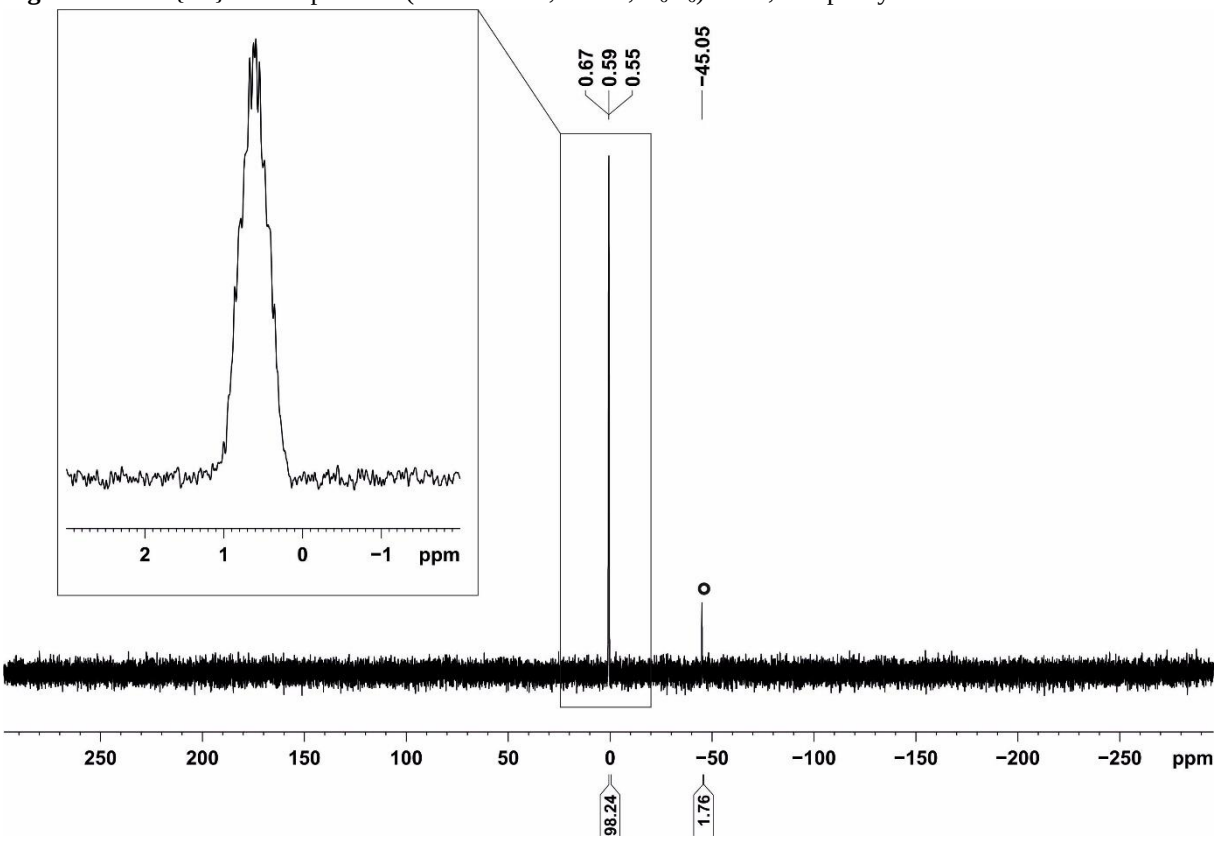


Figure S12. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3a**; ° impurity.

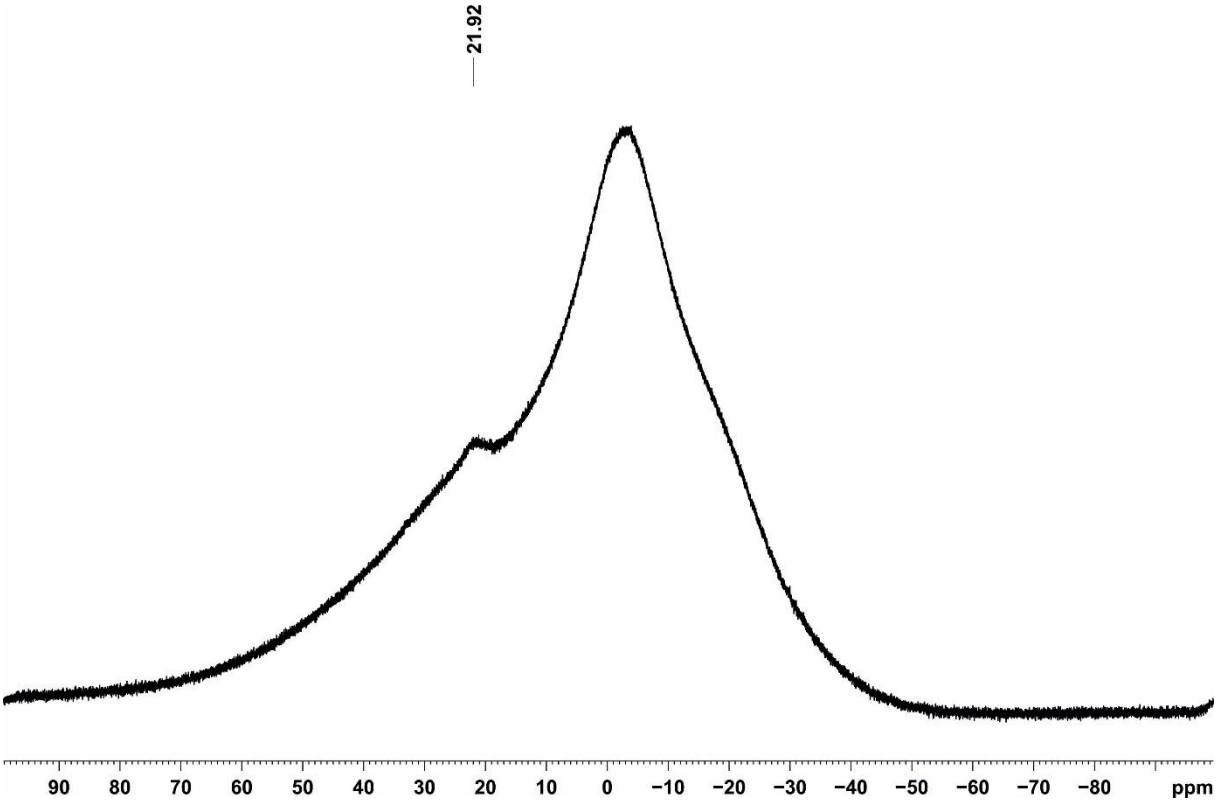


Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3a**.

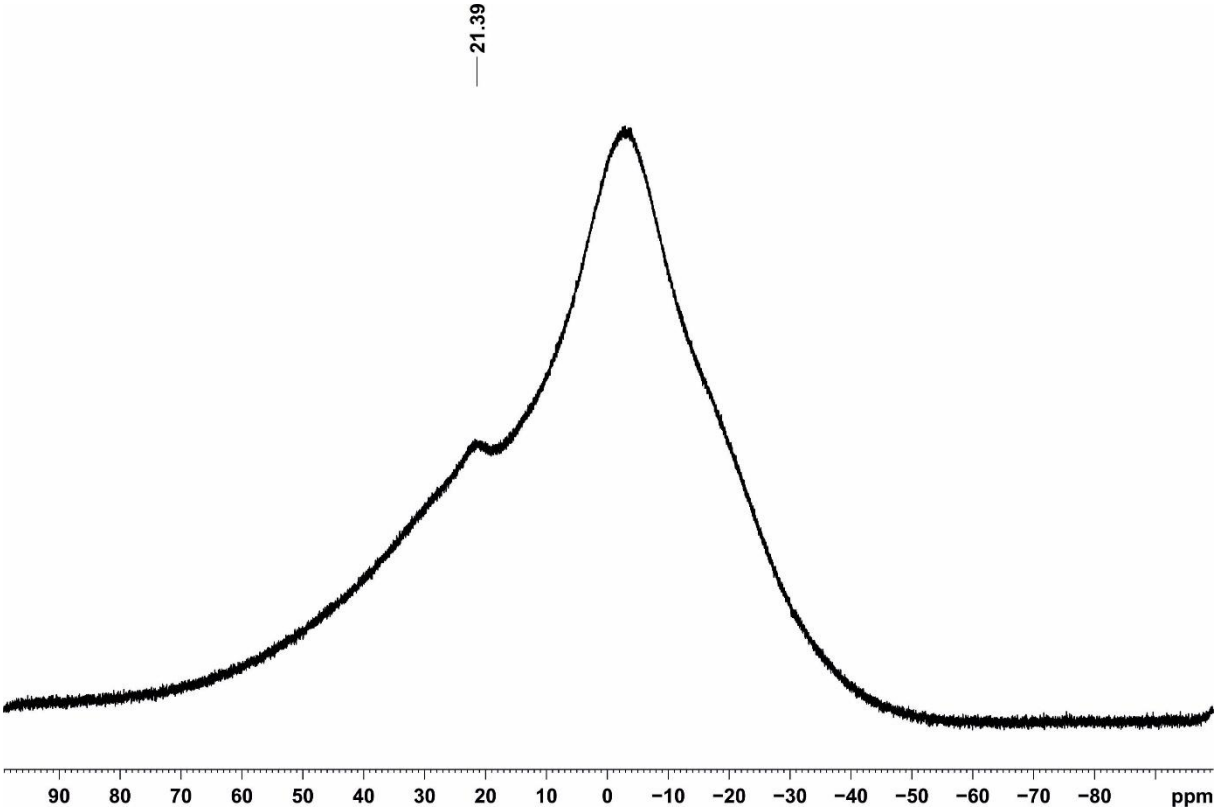


Figure S14. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3a**.

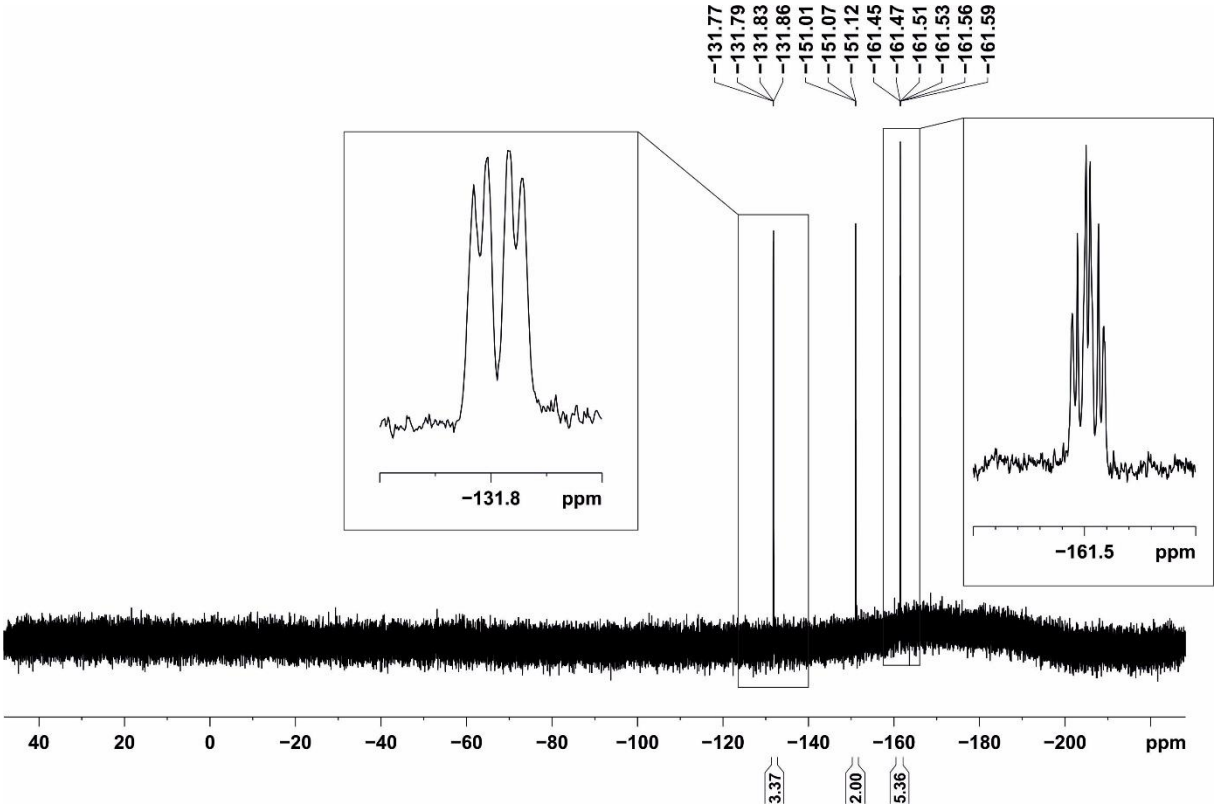


Figure S15. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **3a**. The integrals for the $^{19}F\{^{1}H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.3 NMR Spectra of 3b

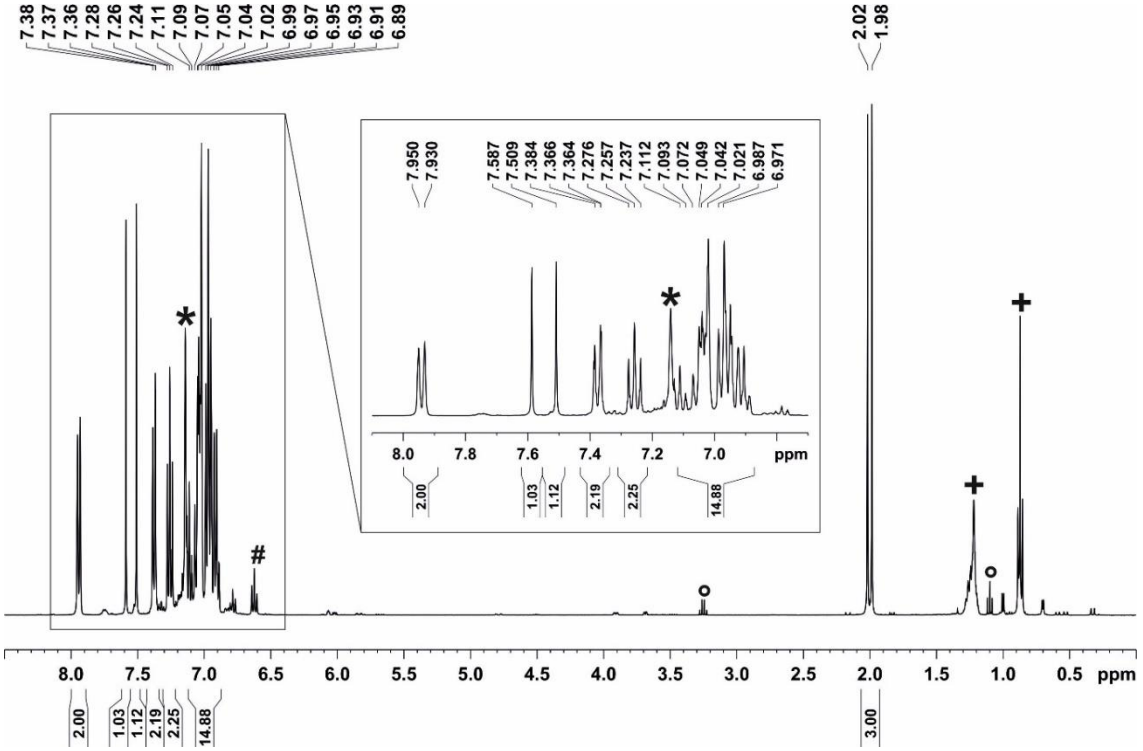


Figure S16. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **3b** ; * C_6D_6; + *n*-hexane; ° diethyl ether; # impurity.

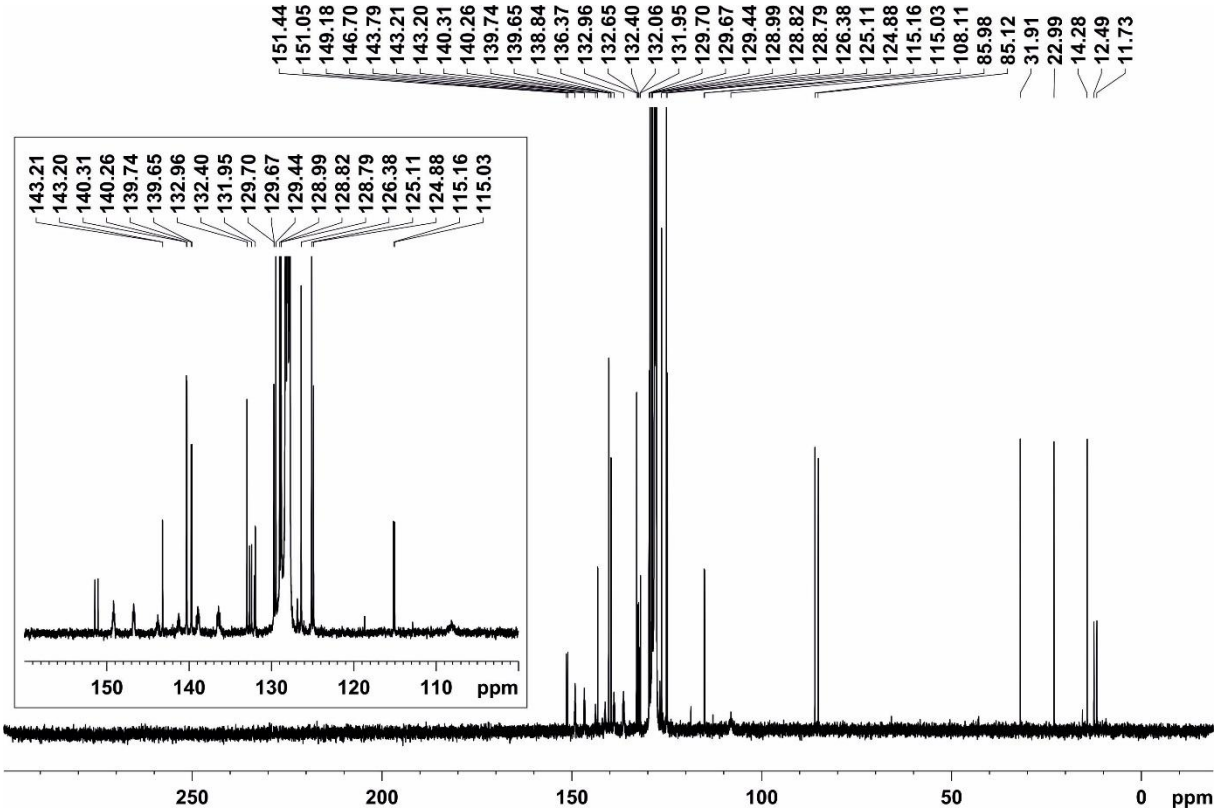


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **3b**.

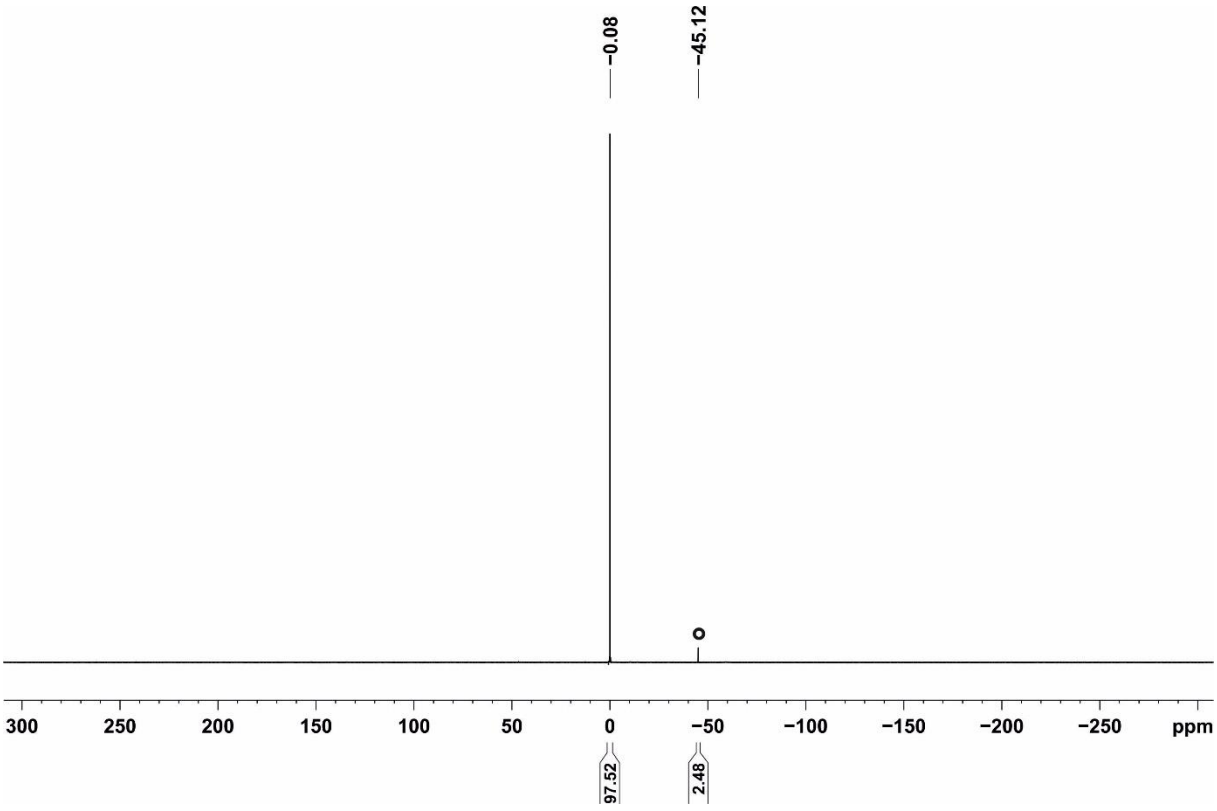


Figure 18. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3b**; ° impurity.

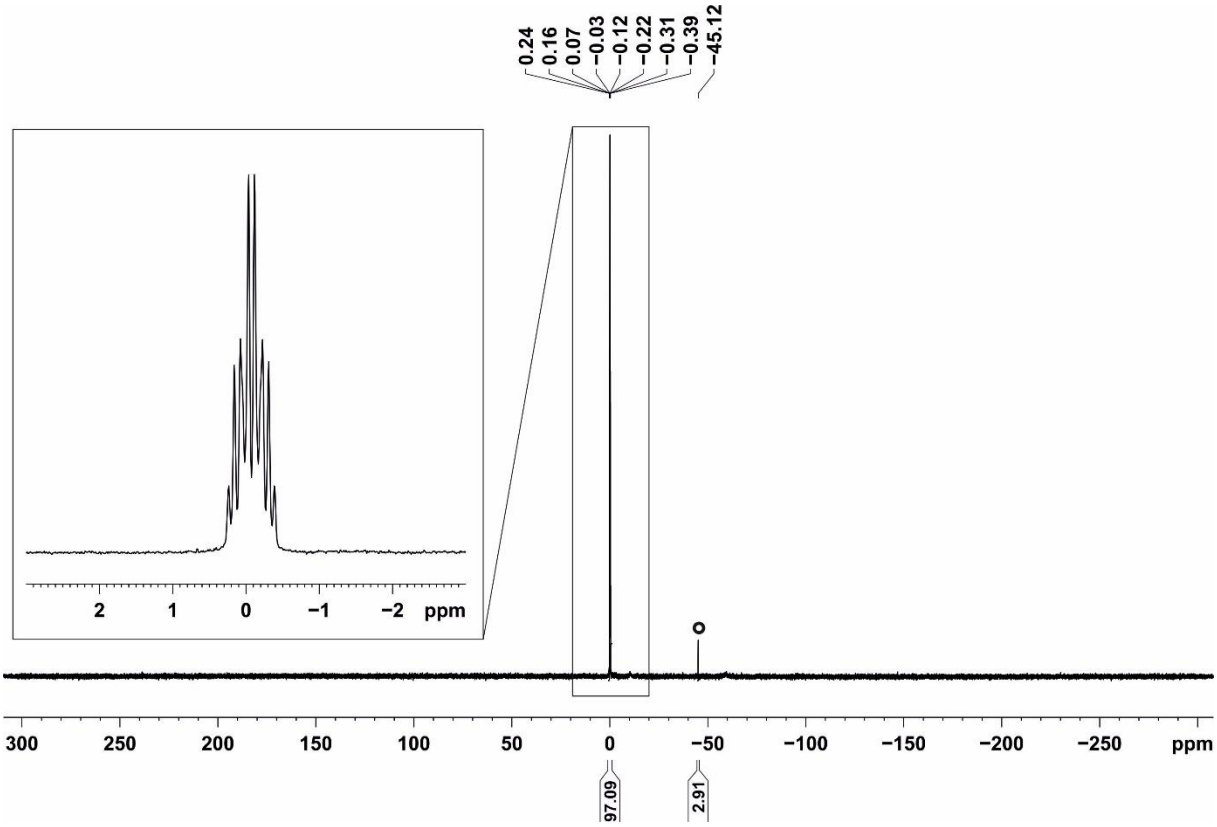


Figure S19. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3b**; ° impurity.

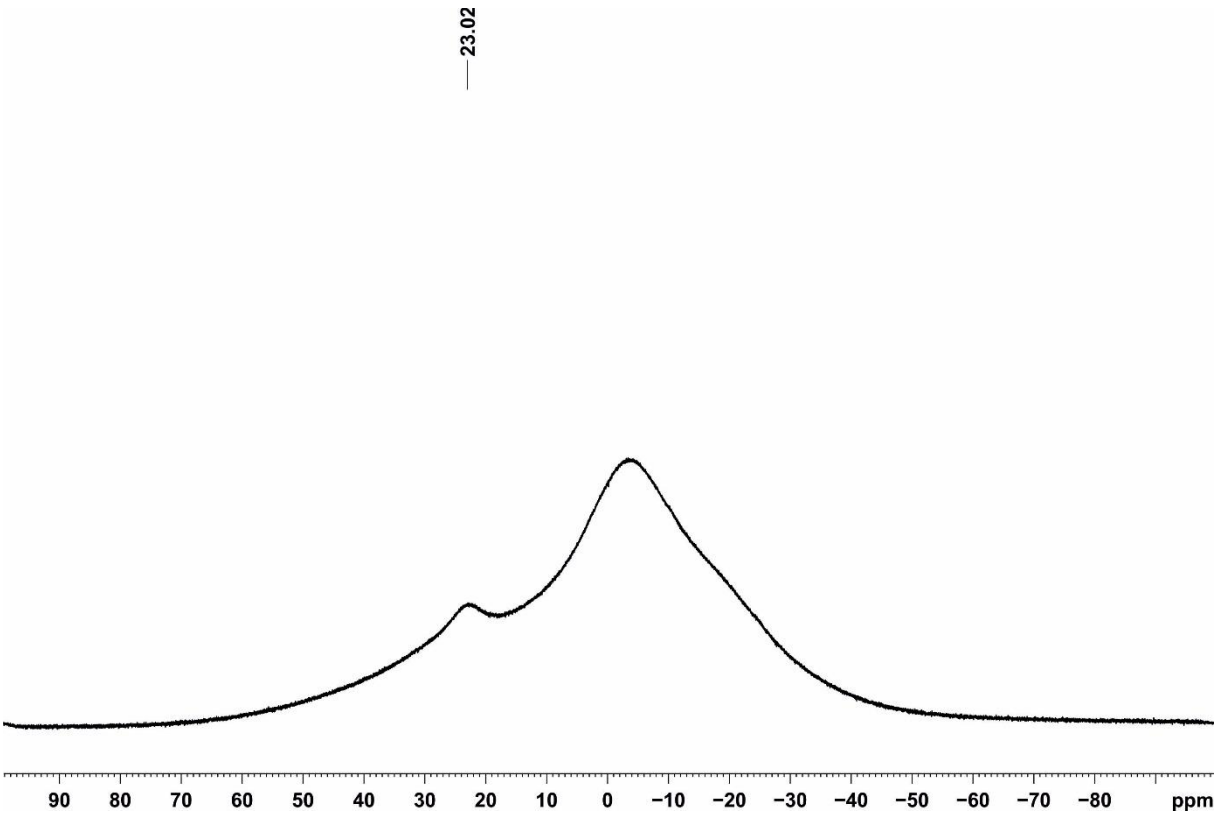


Figure S20. $^{11}B\{^1H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of 3**b**.

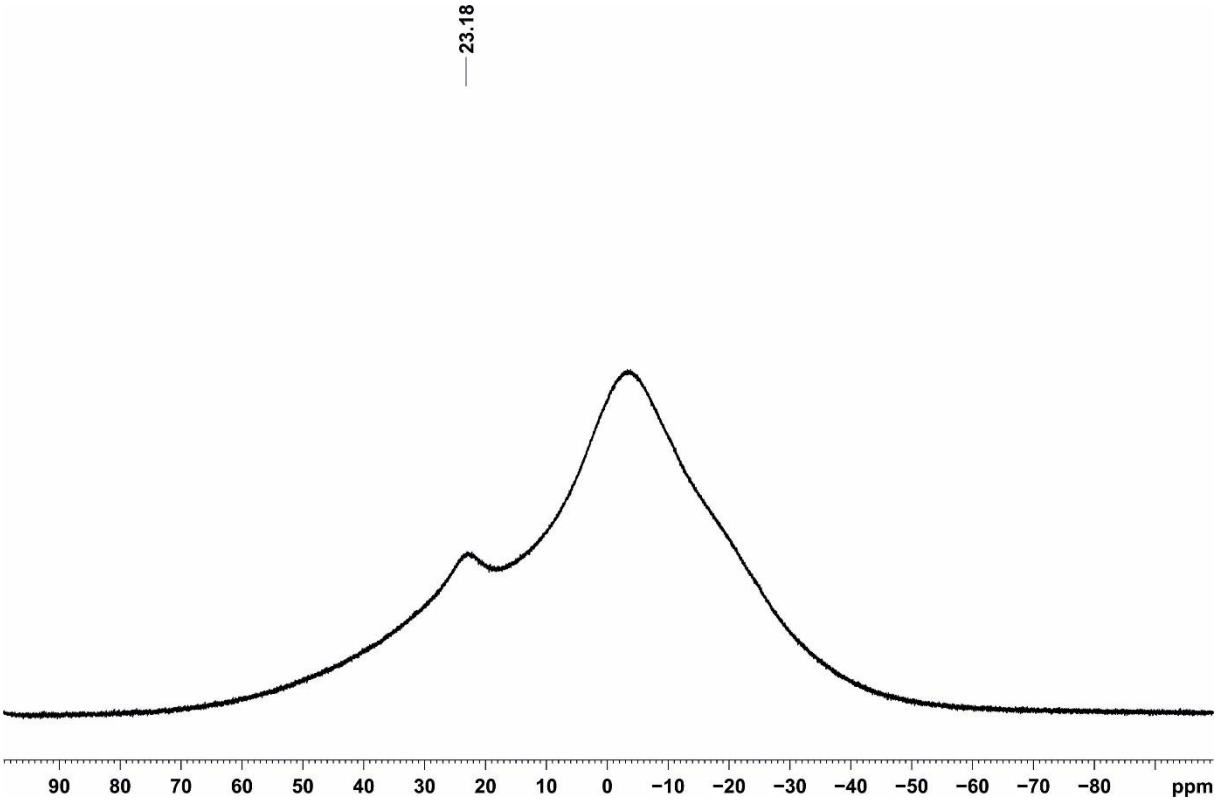


Figure S21. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3b**.

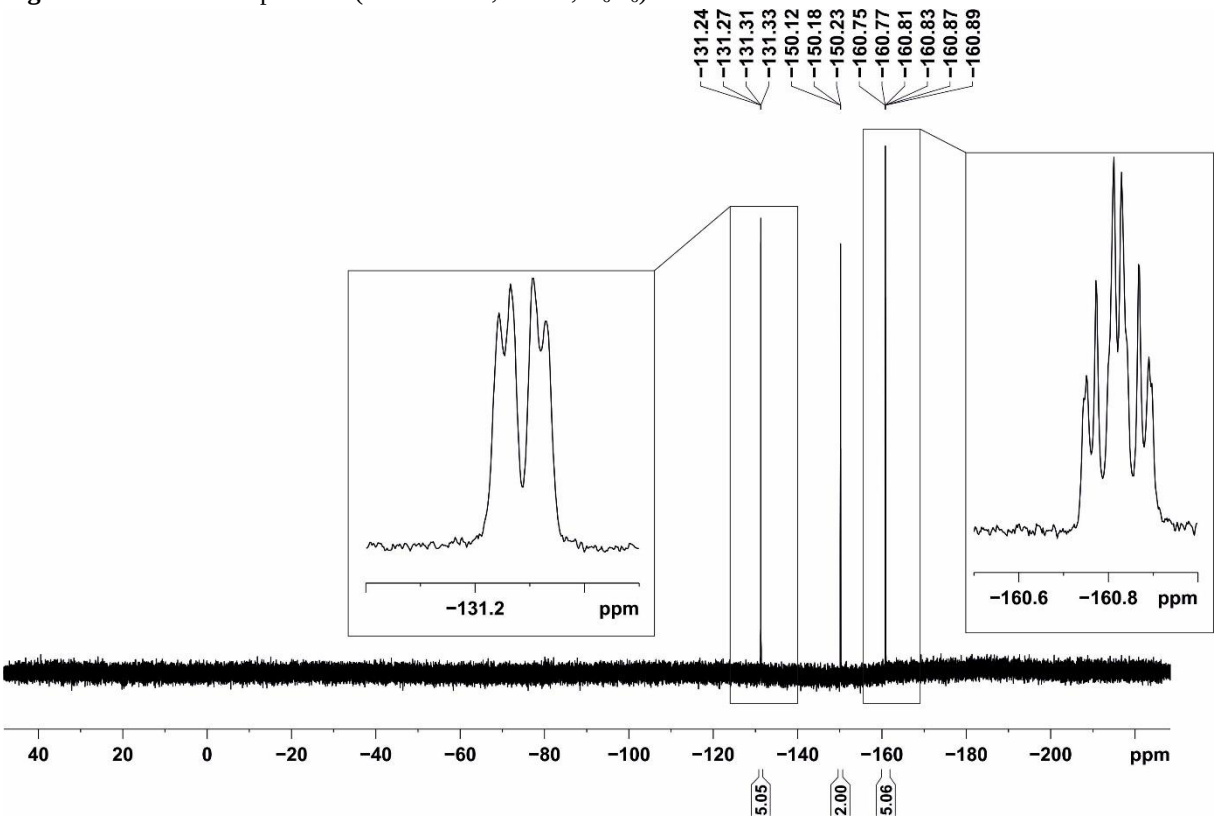


Figure S22. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **3b**. The integrals for the $^{19}F\{^1H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.4 NMR Spectra of 3c

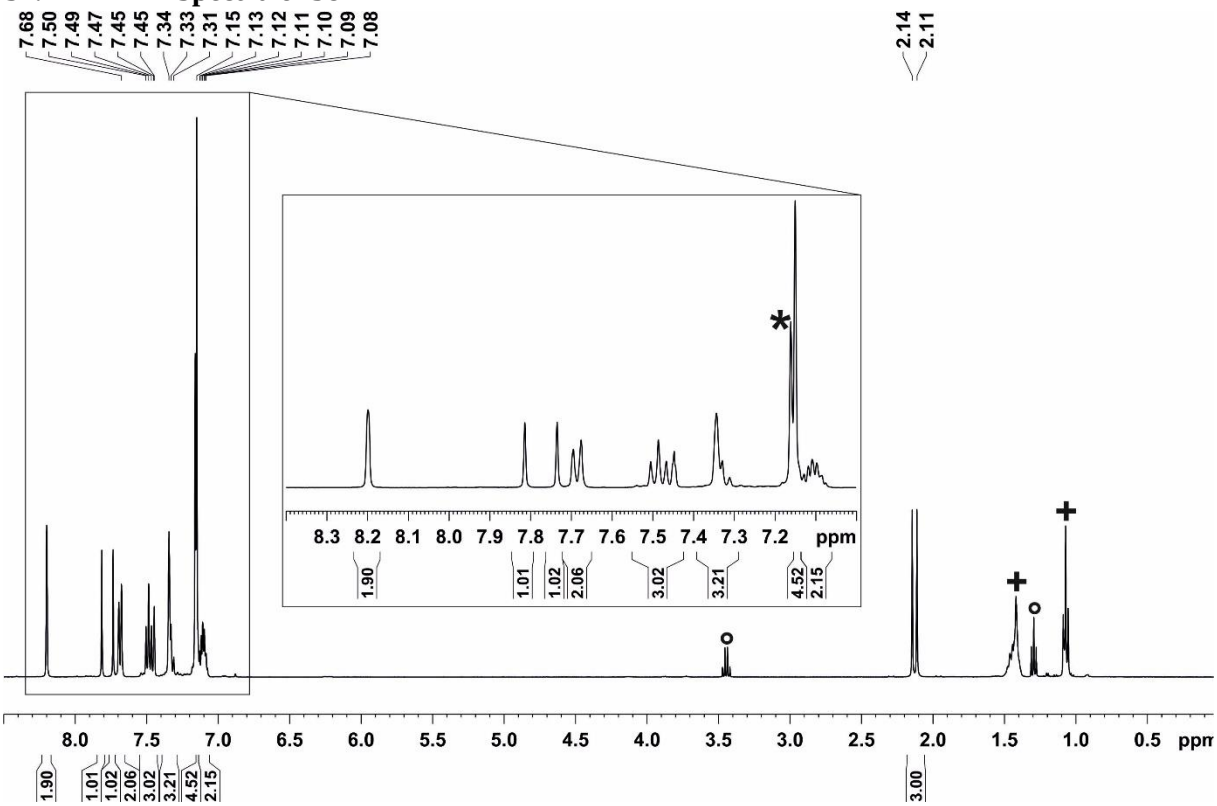


Figure S23. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **3c** ; * C_6D_6; + *n*-hexane; ° diethyl ether.

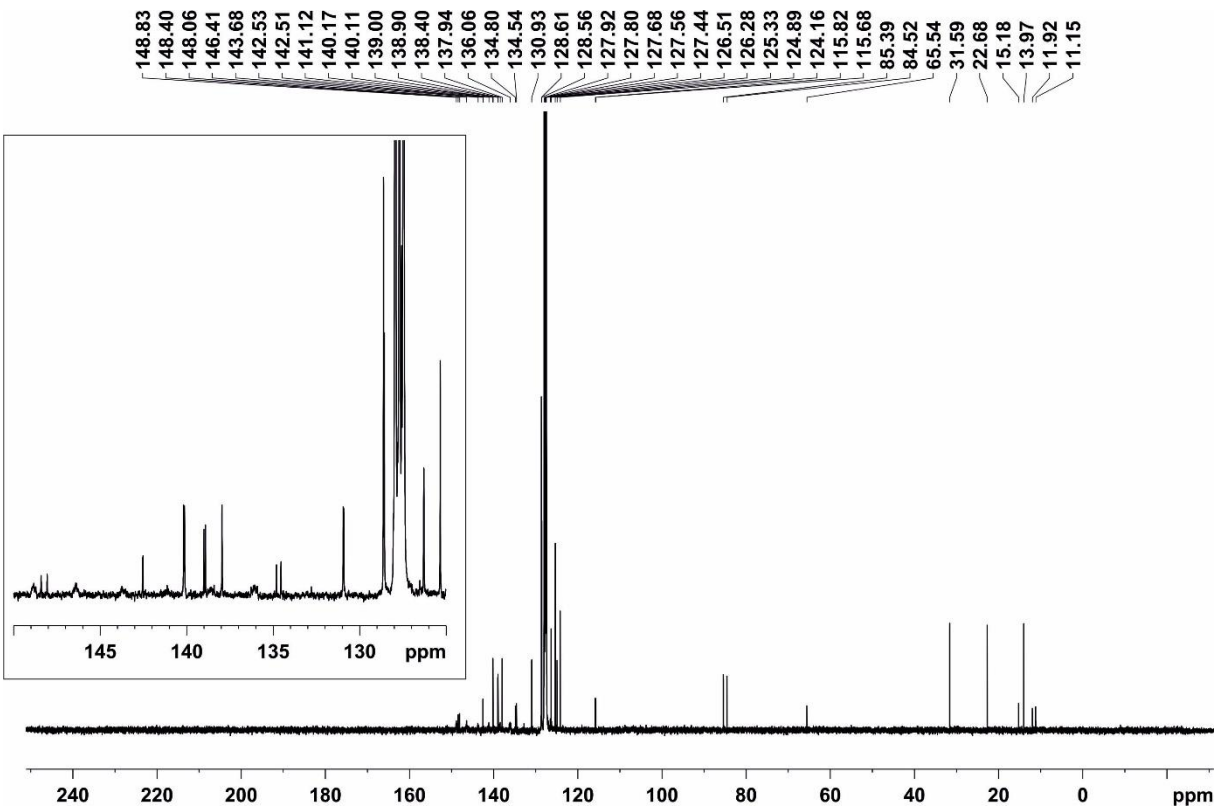


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **3c**.

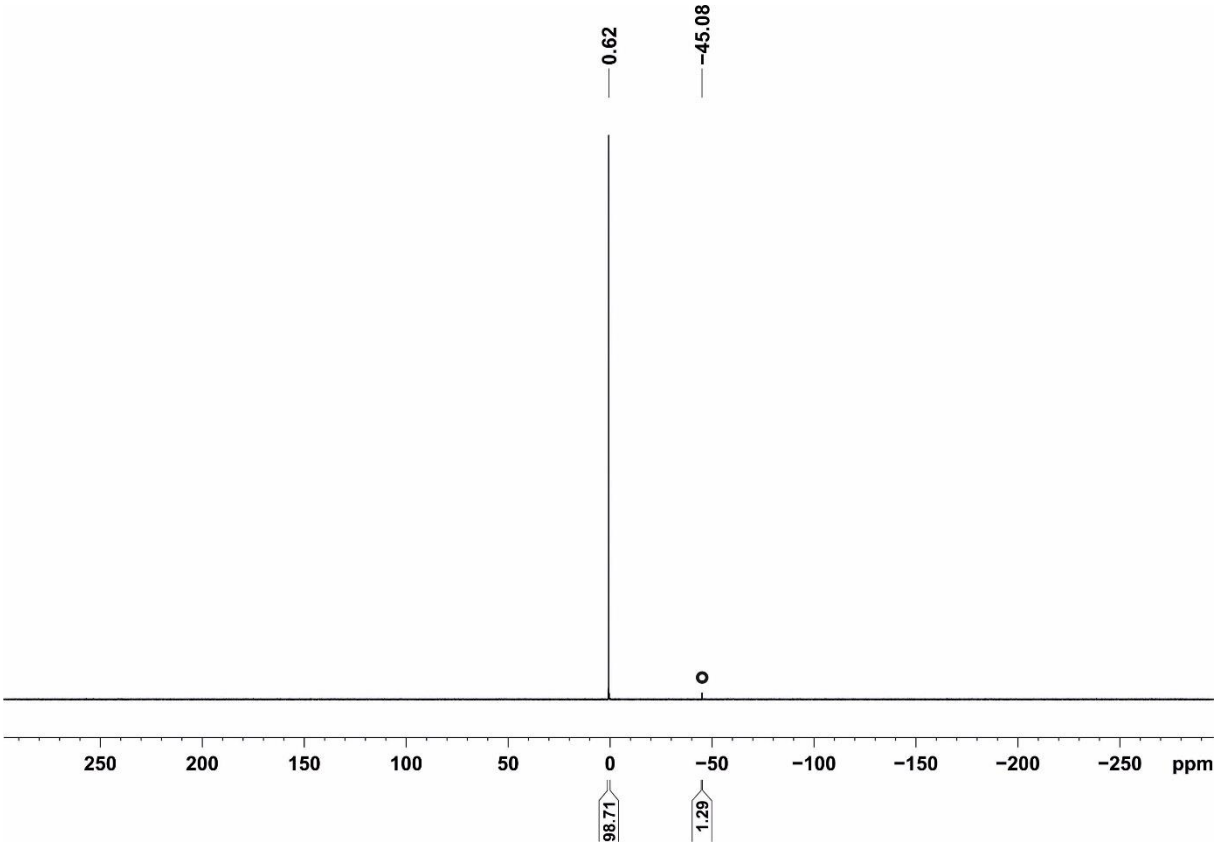


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3c**; ° impurity.

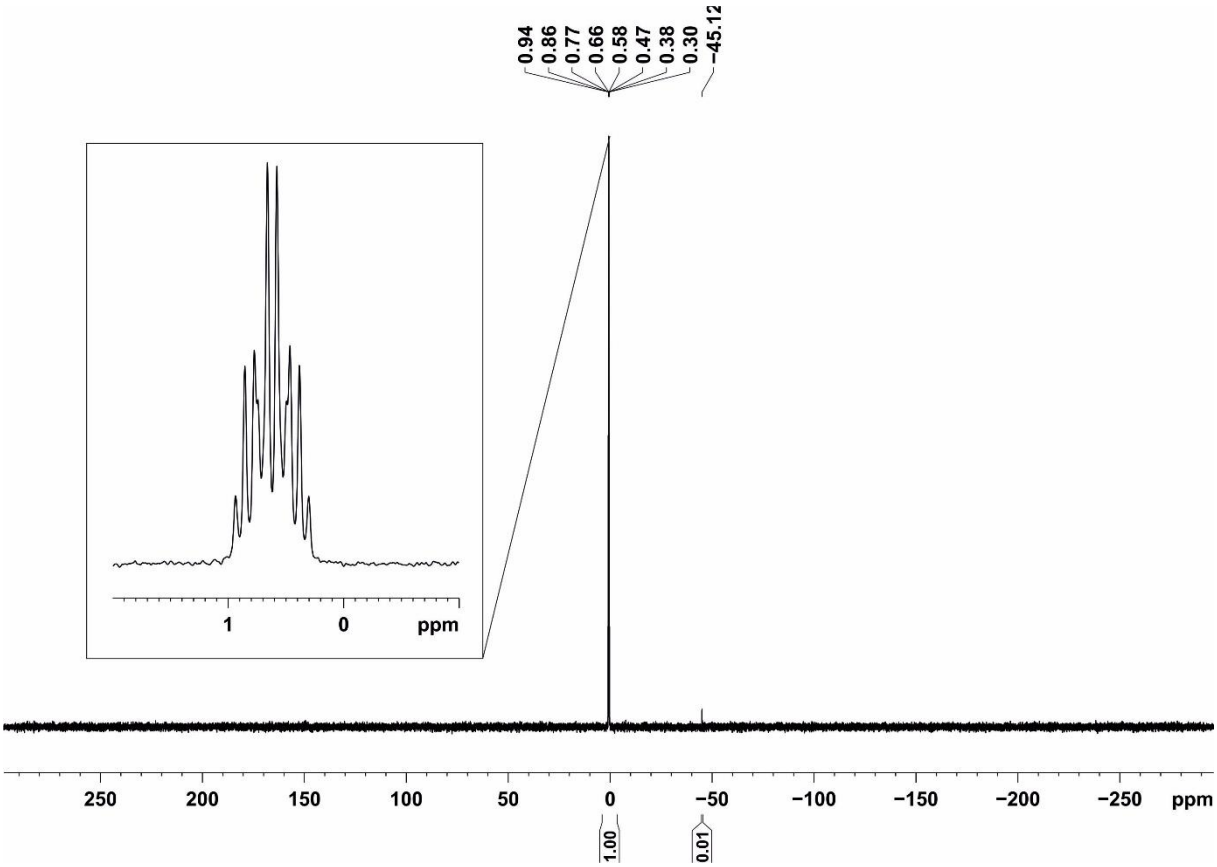


Figure S26. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3c**.

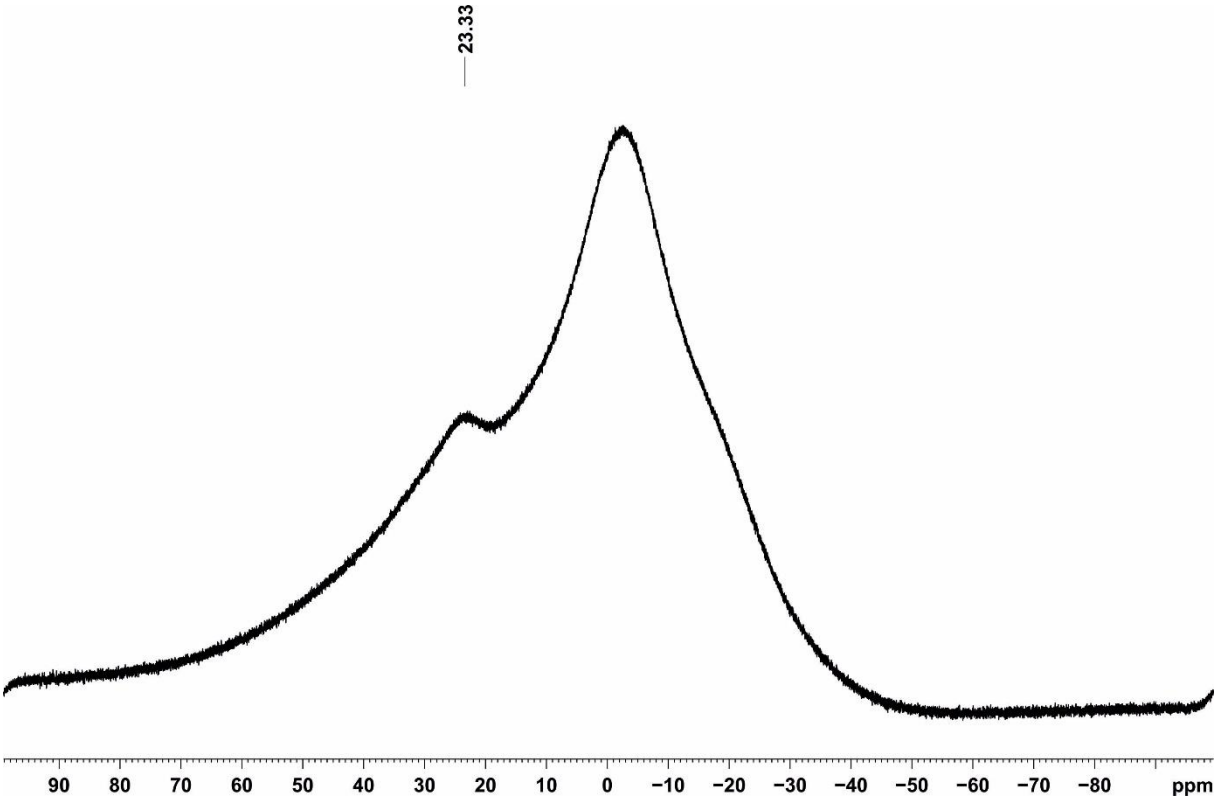


Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3c**.

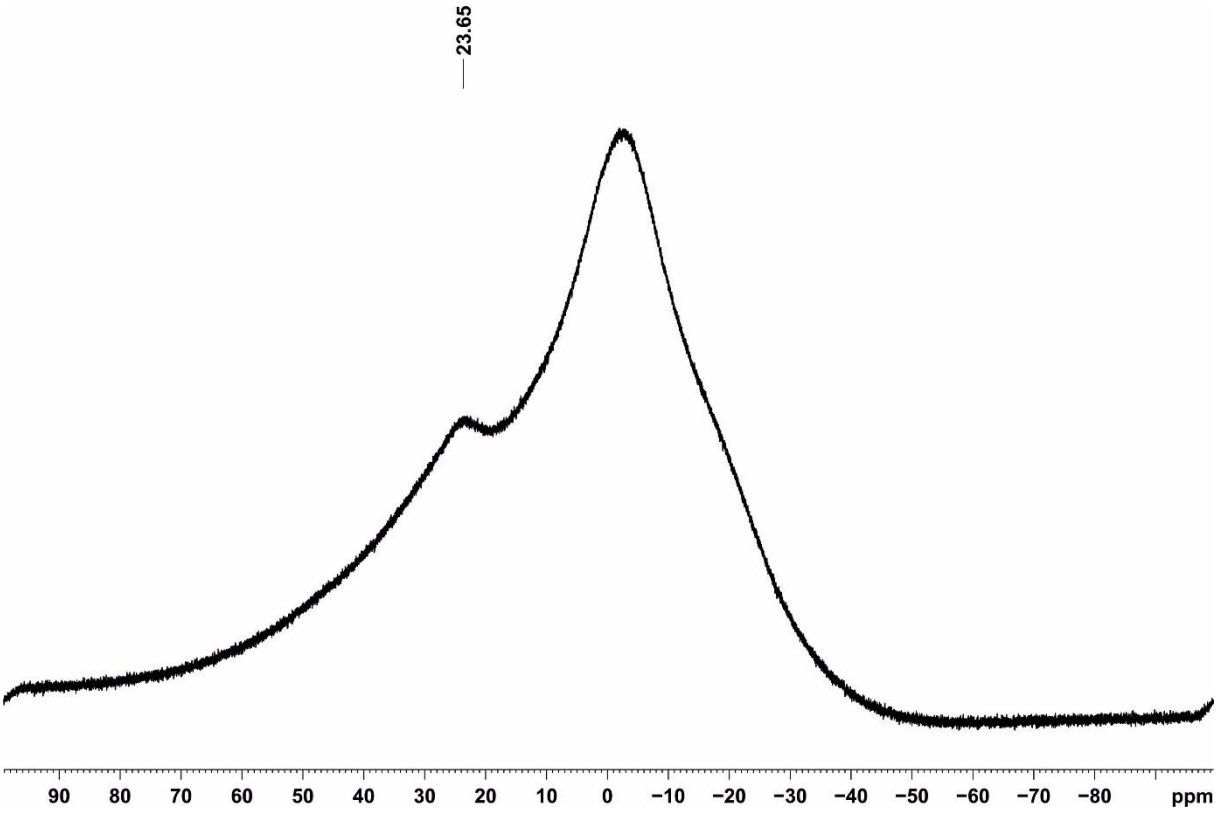


Figure S28. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3c**.

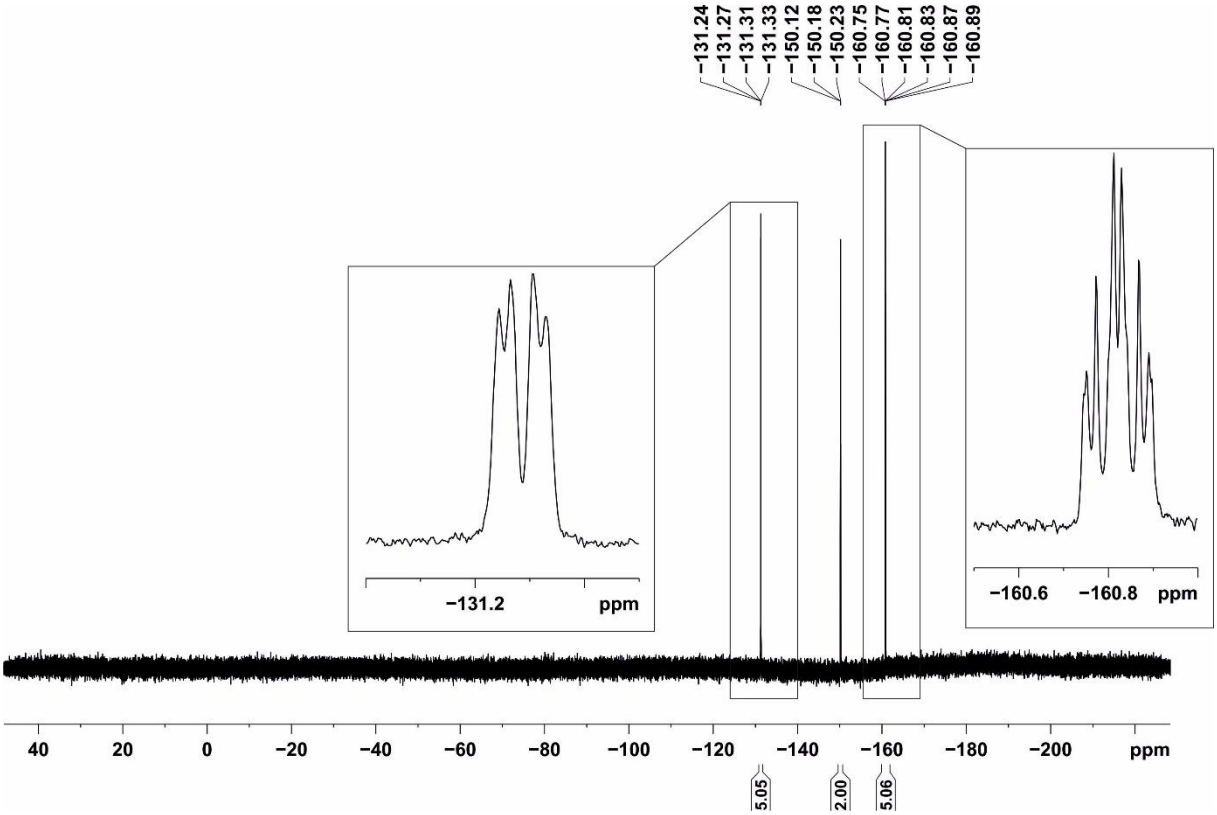


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **3c**. The integrals for the $^{19}F\{^{1}H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.5 NMR Spectra of 3d

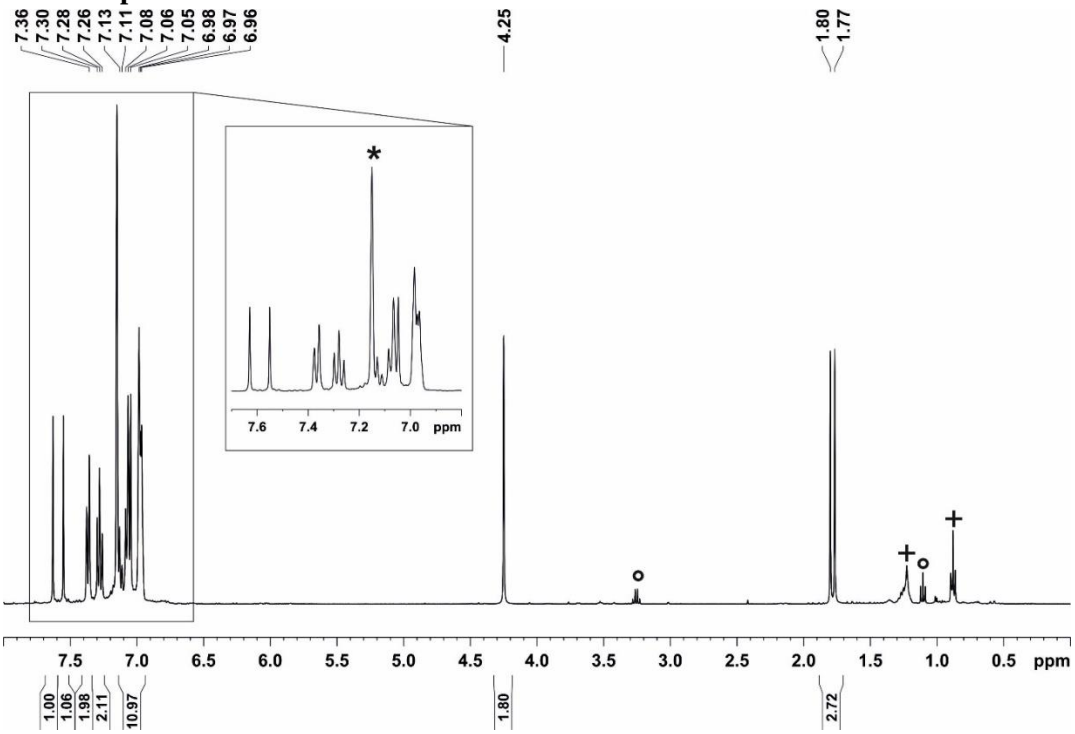


Figure S30. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **3d**; * C_6D_6; + *n*-hexane, ° diethylether.

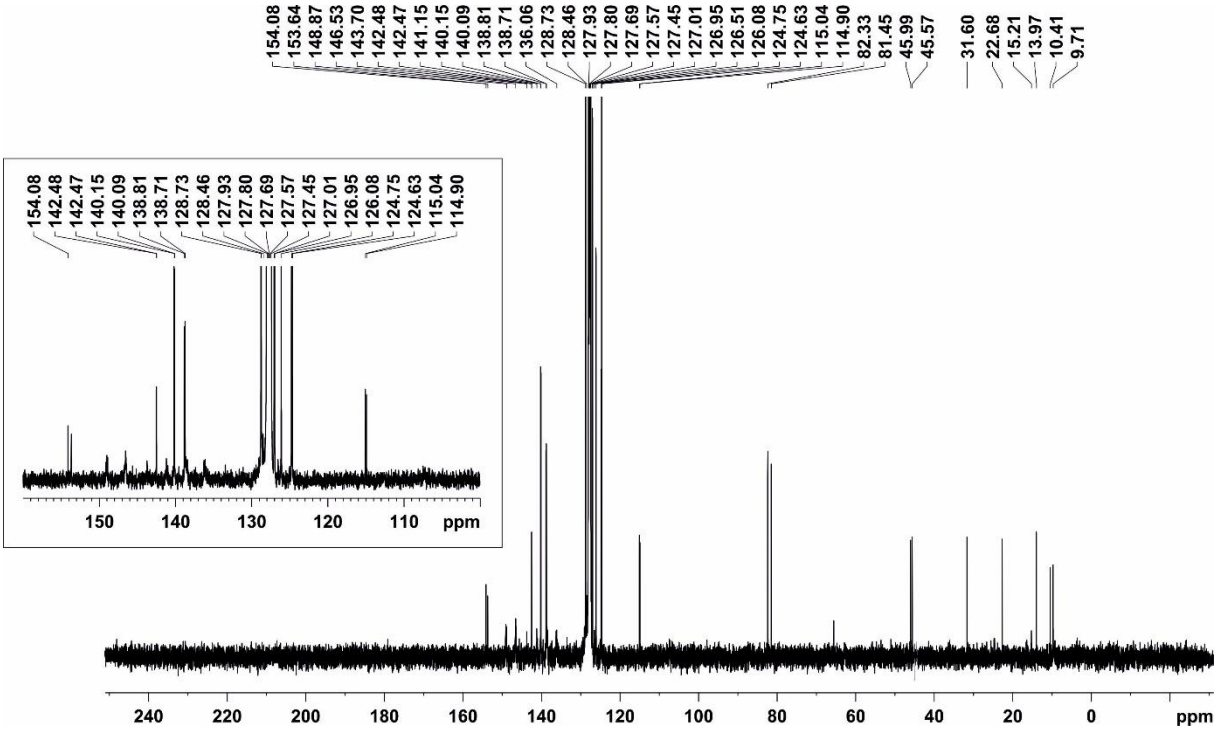


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **3d**.

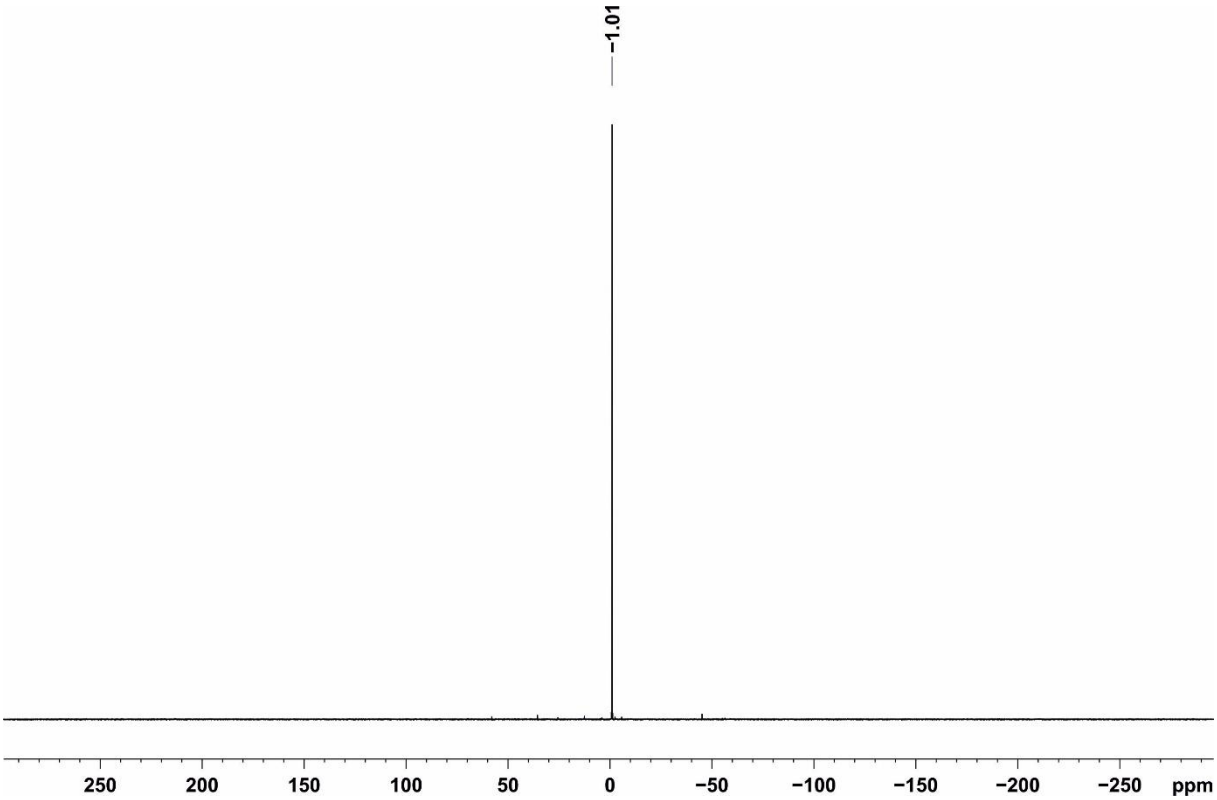


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3d**.

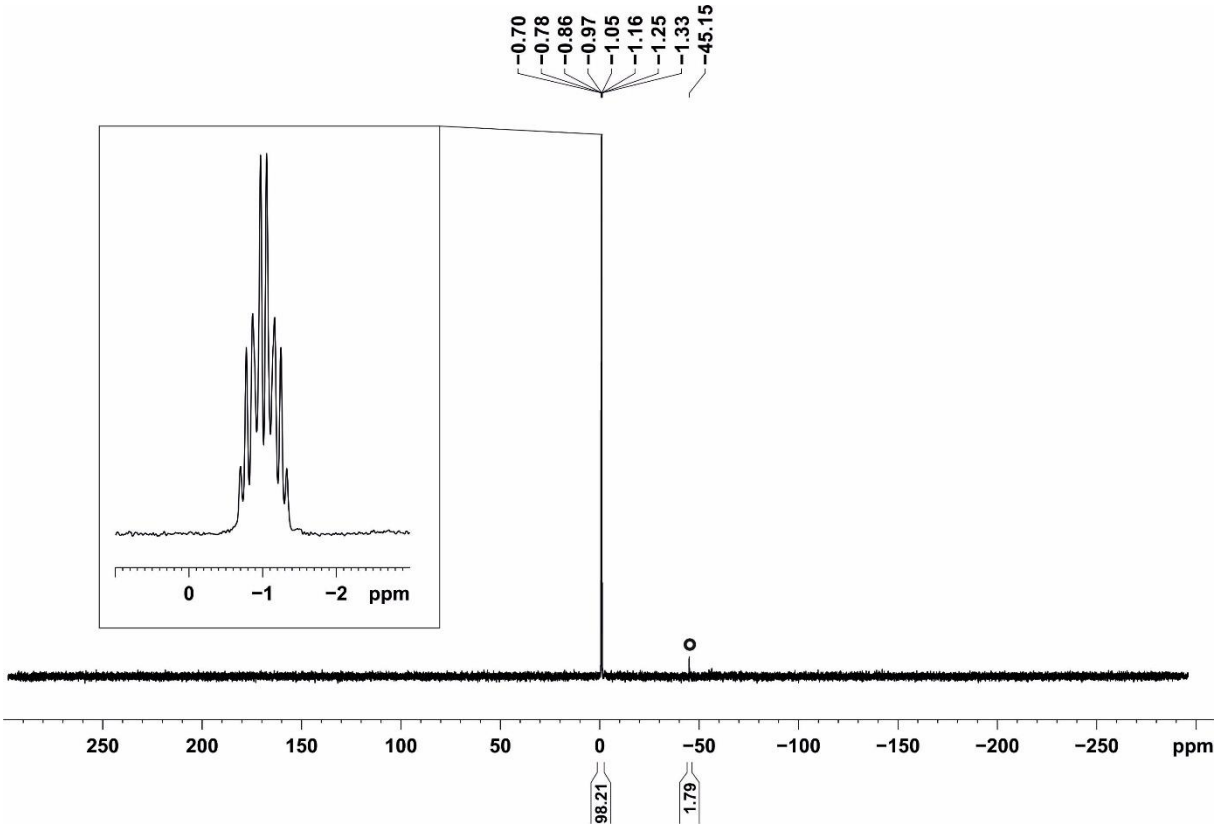


Figure S33. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3d**; ° impurity.

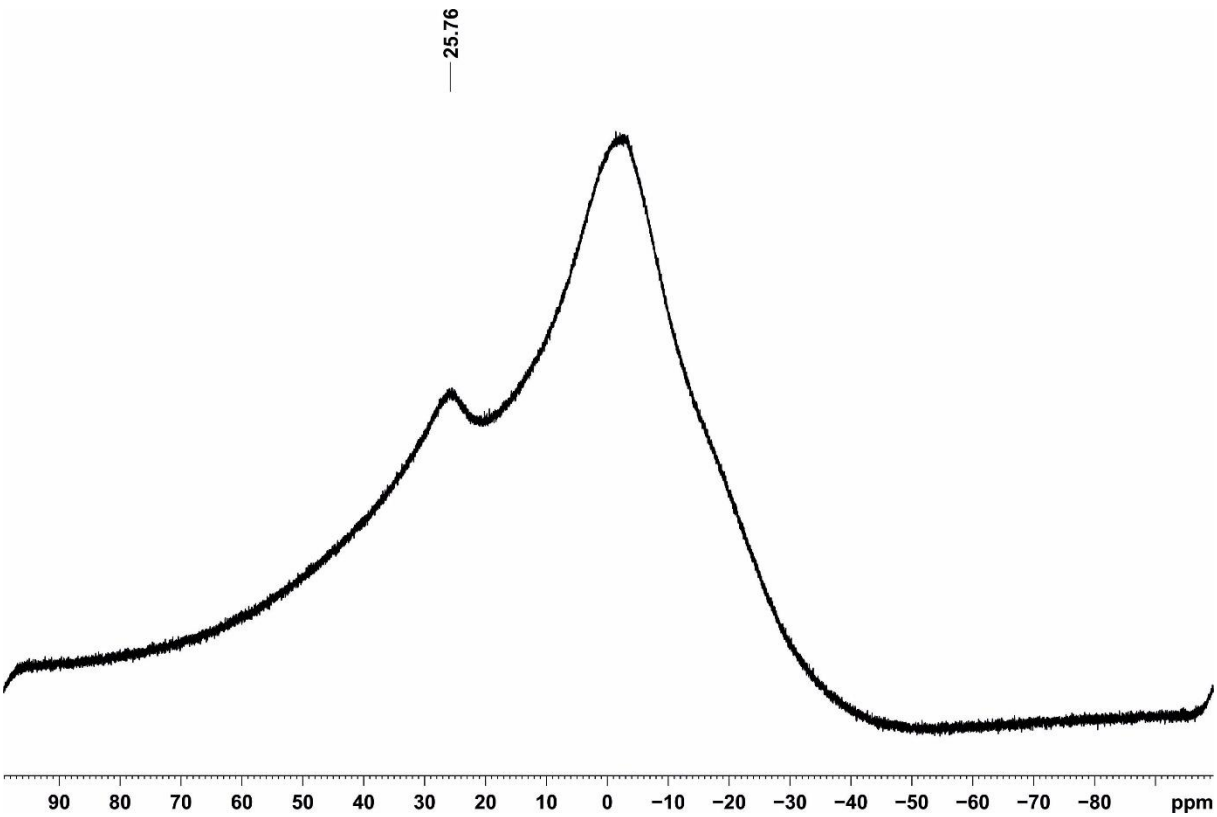


Figure S34. $^{11}B\{^1H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3d**.

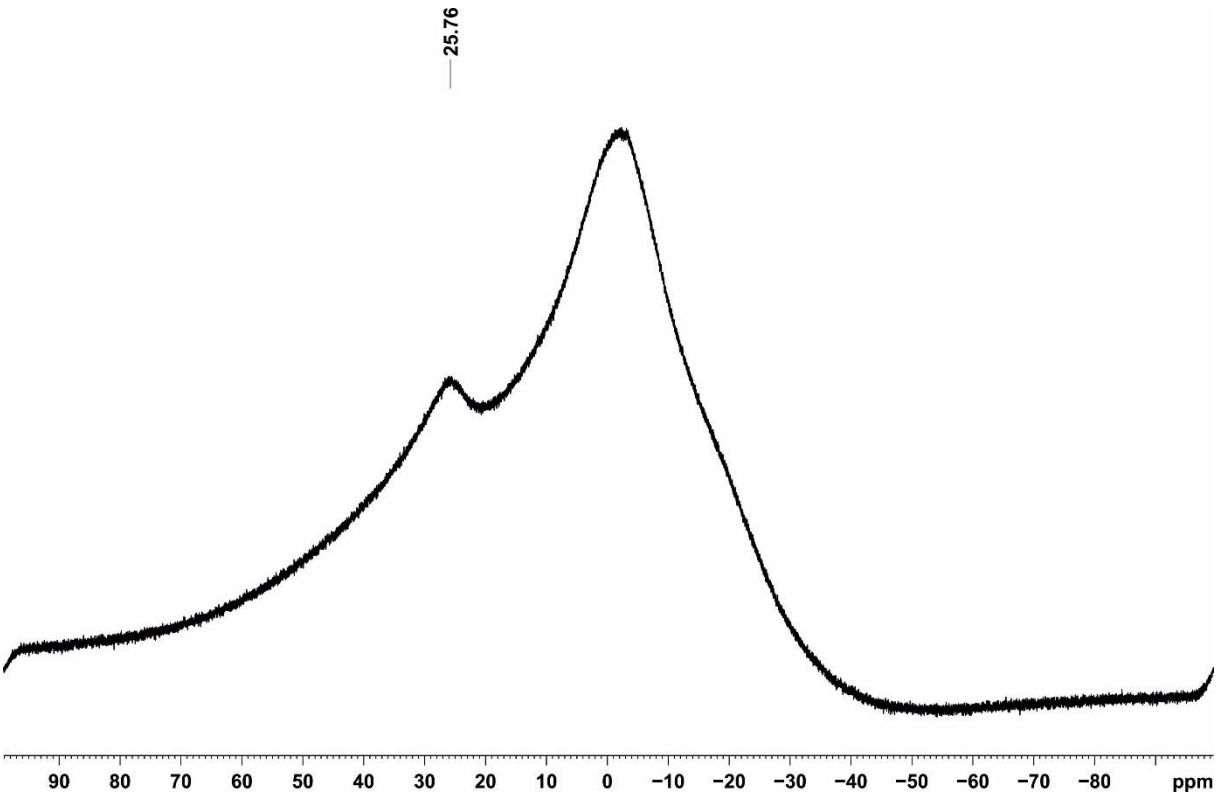


Figure S35. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3d**.

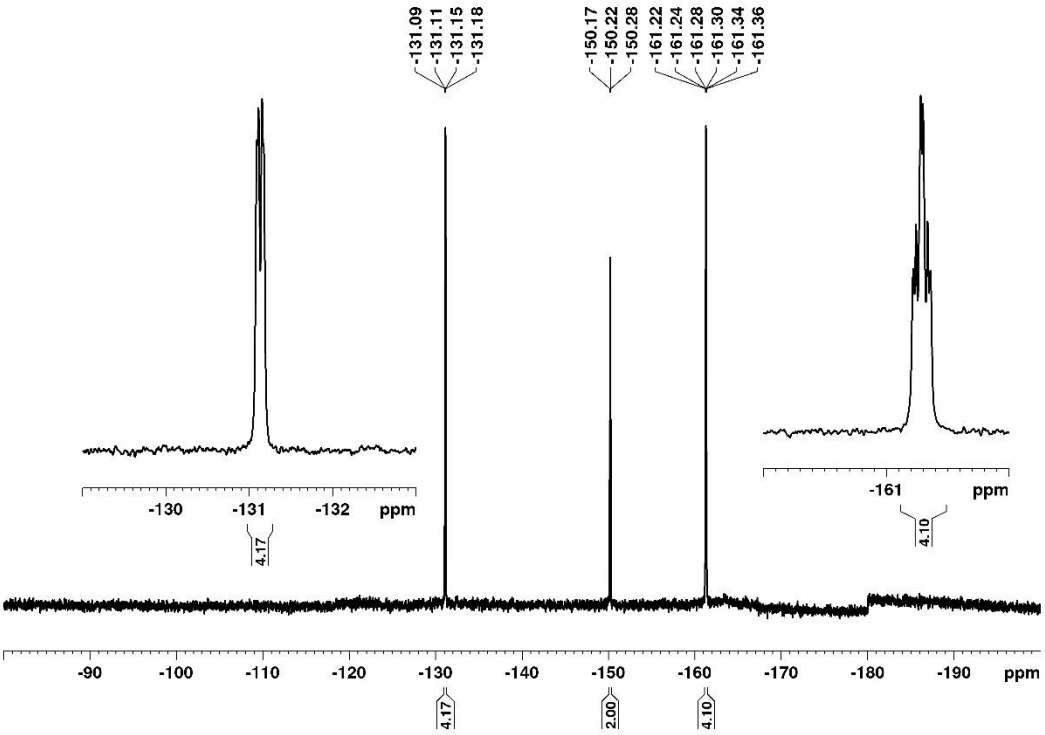


Figure S36. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **3d** with baseline correction.

S1.6 NMR Spectra of 3e

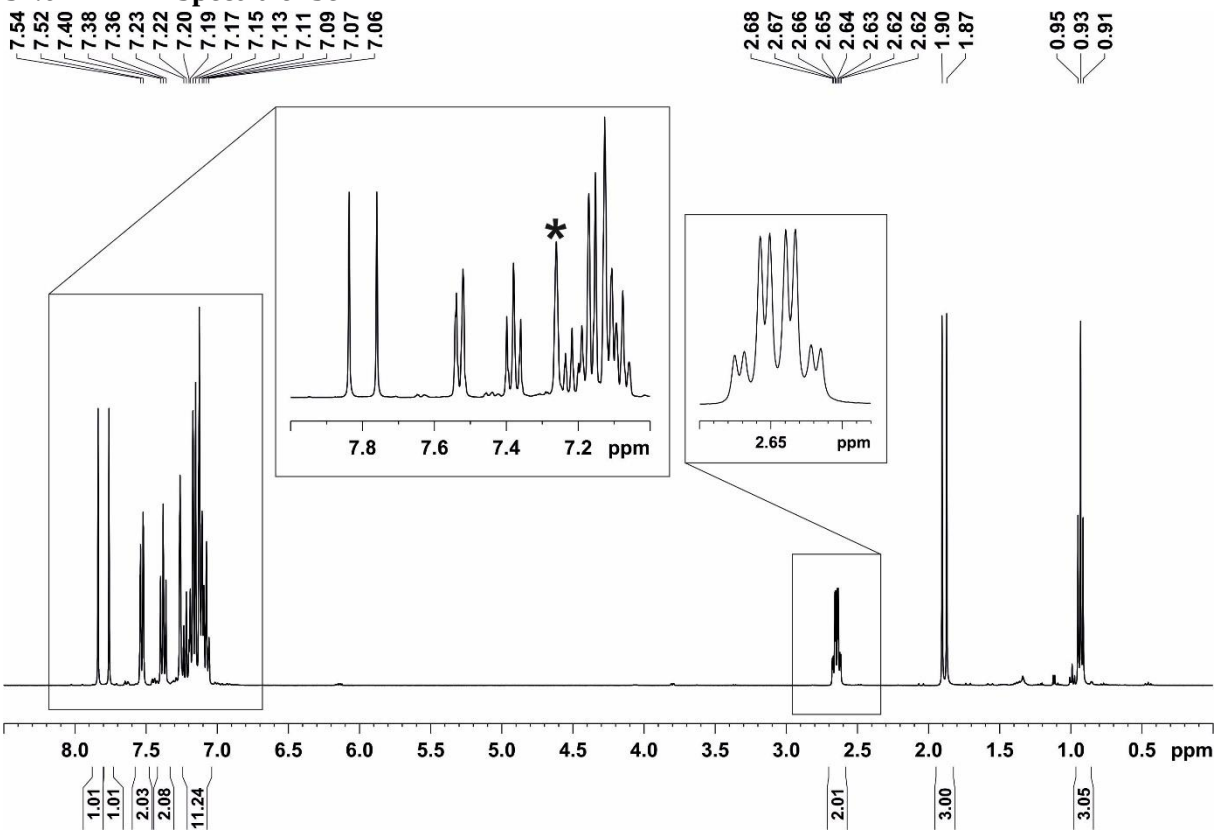


Figure S37. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **3e**; * C_6D_6.

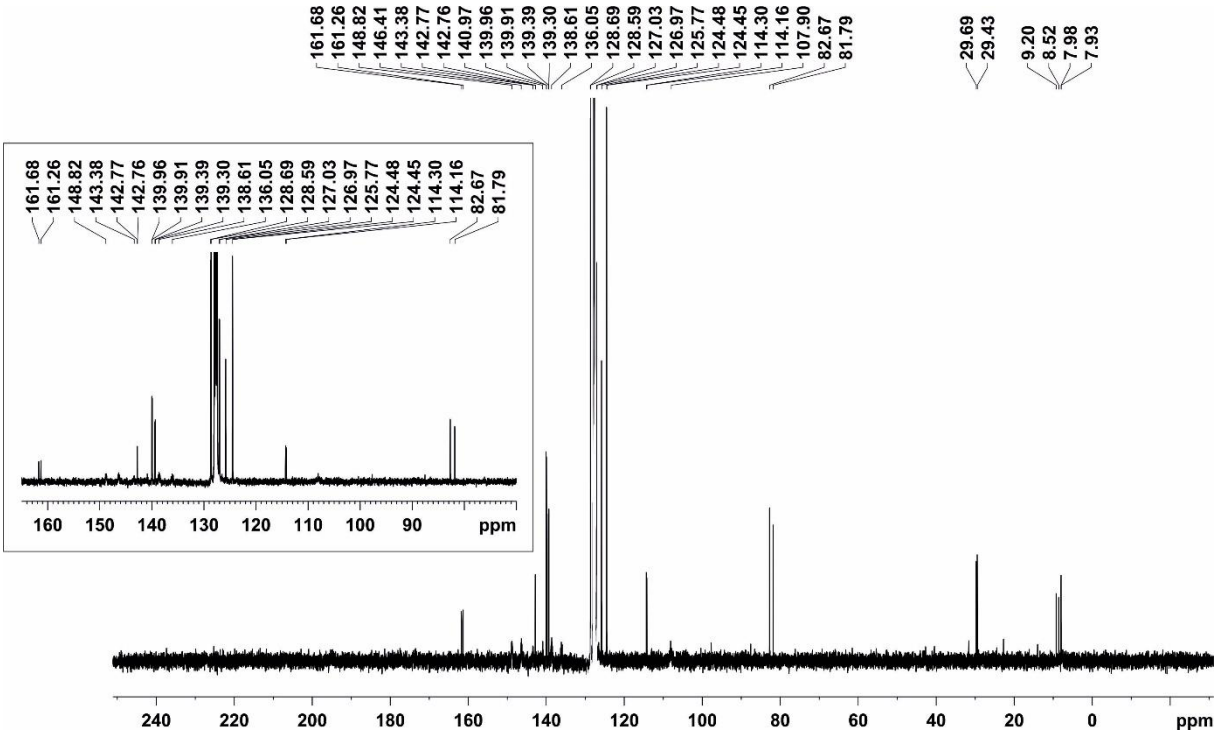


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **3e**.

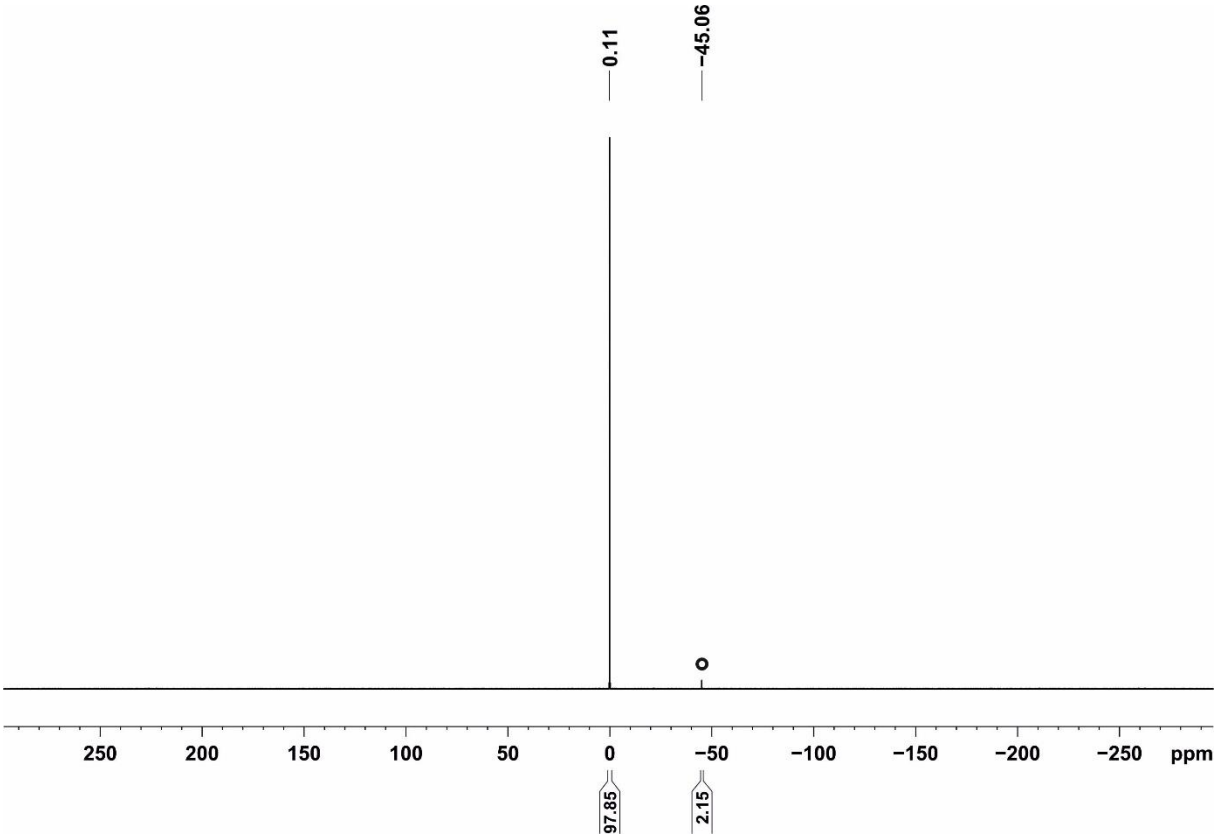


Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3e**; ° impurity.

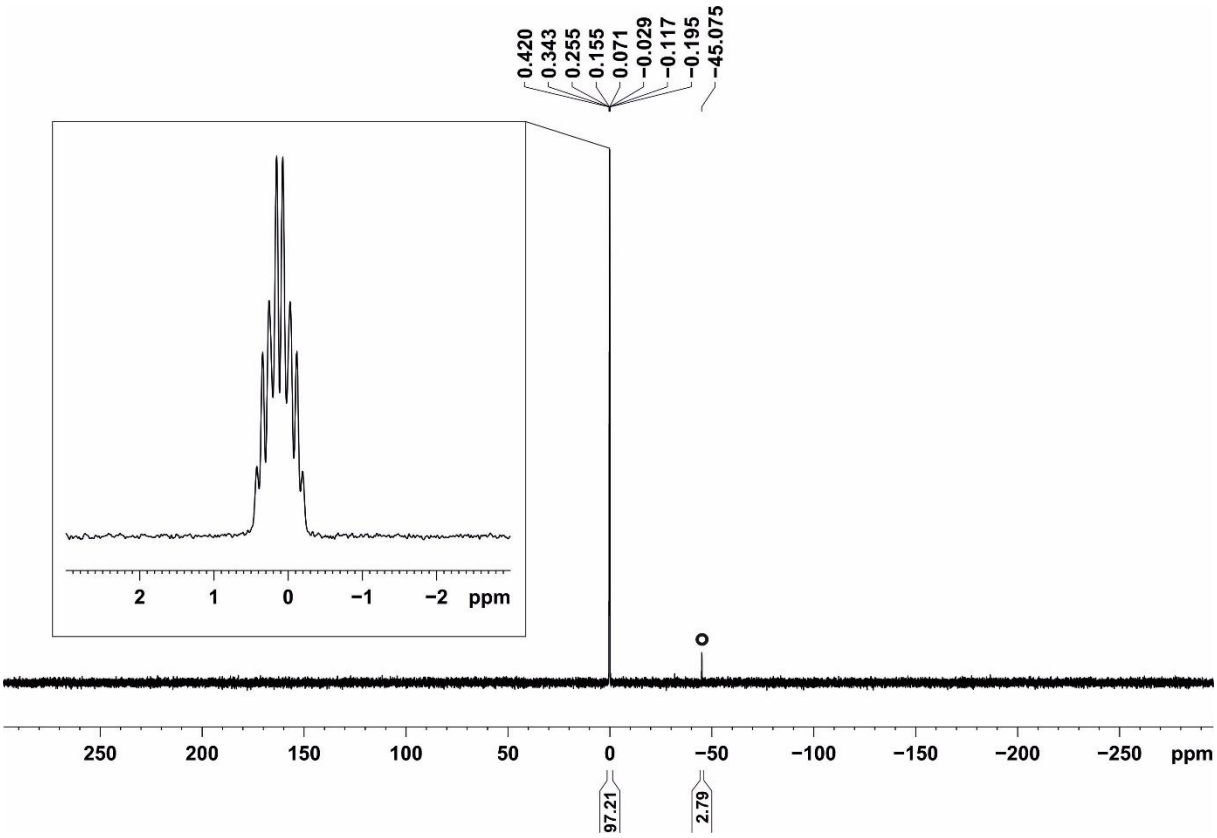


Figure S40. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3e**; ° impurity.

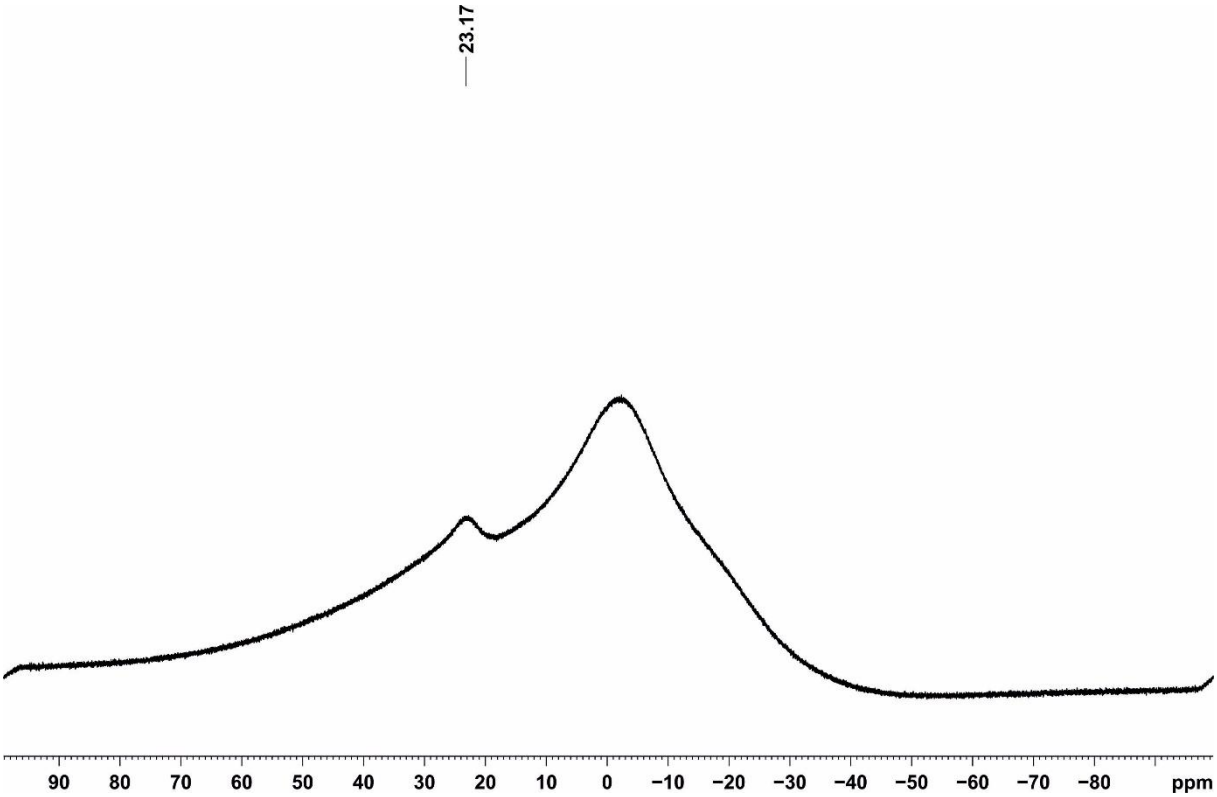


Figure S41. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3e**.

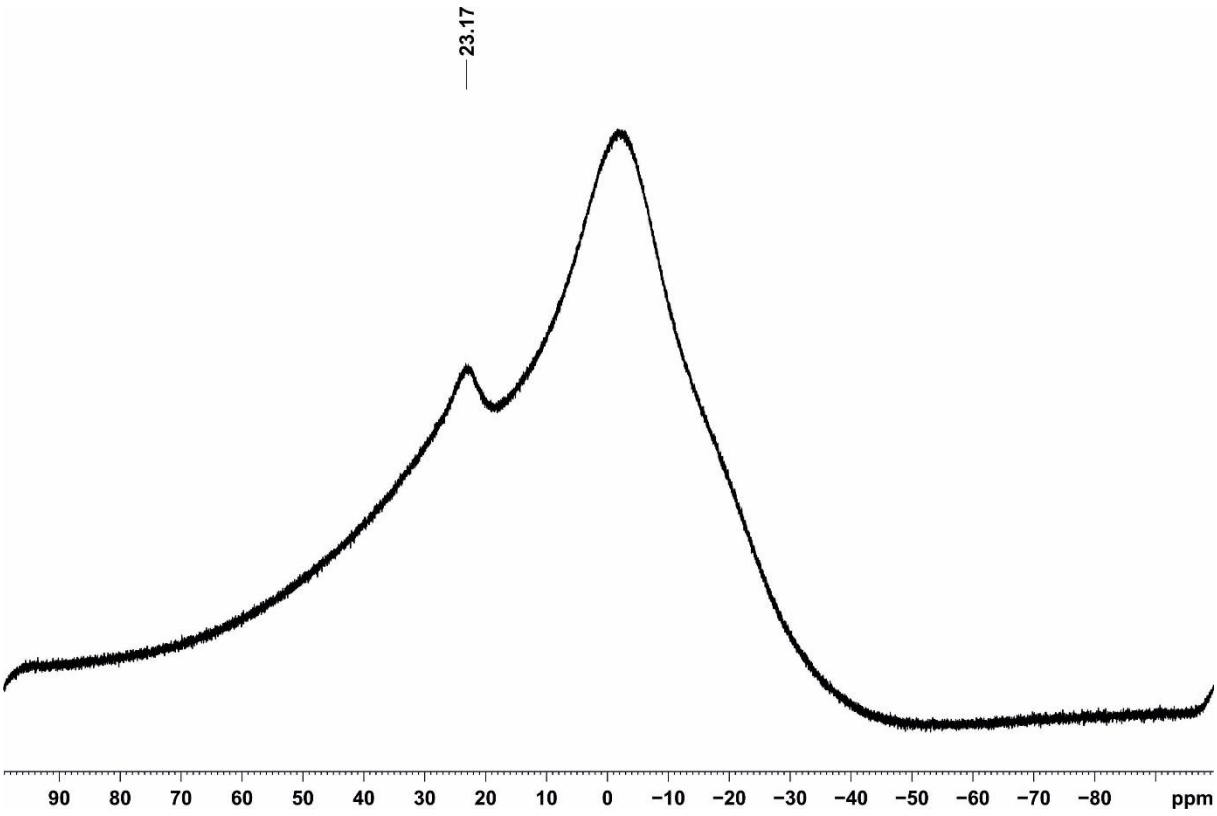


Figure S42. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **3e**.

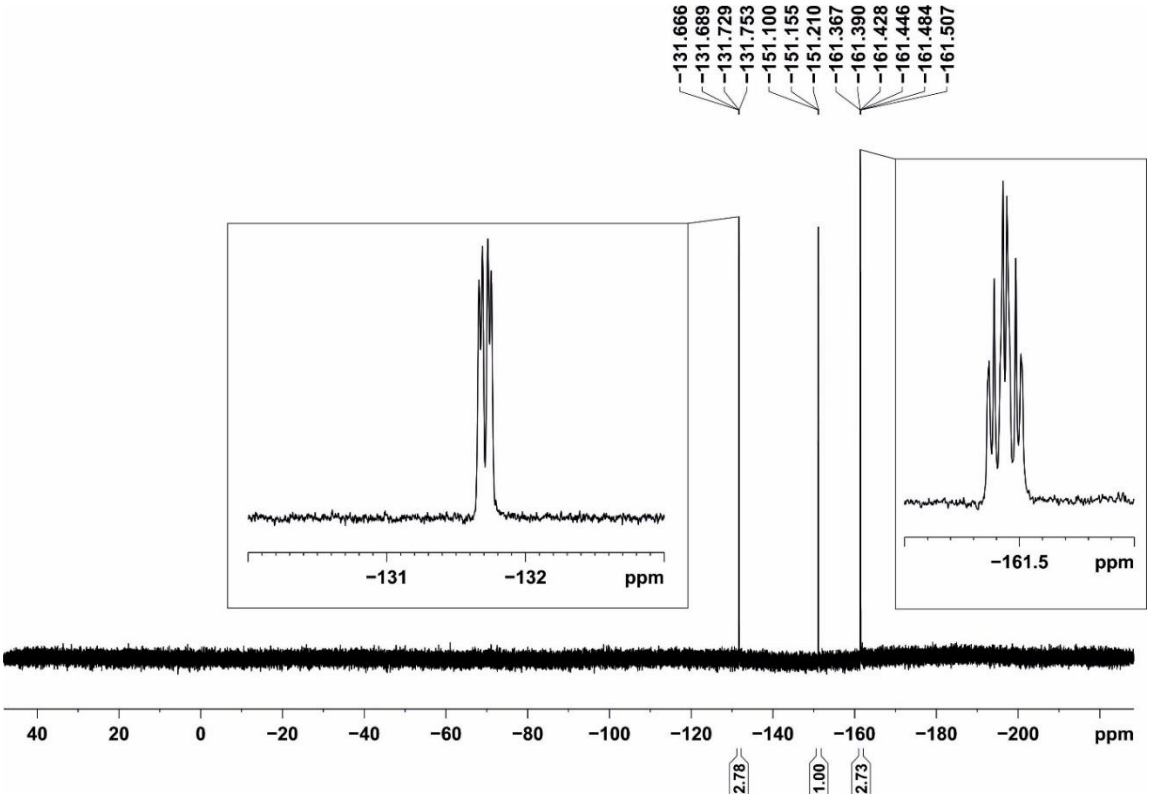


Figure S43. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **3e**. The integrals for the $^{19}F\{^{1}H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.7 NMR Spectra of 4

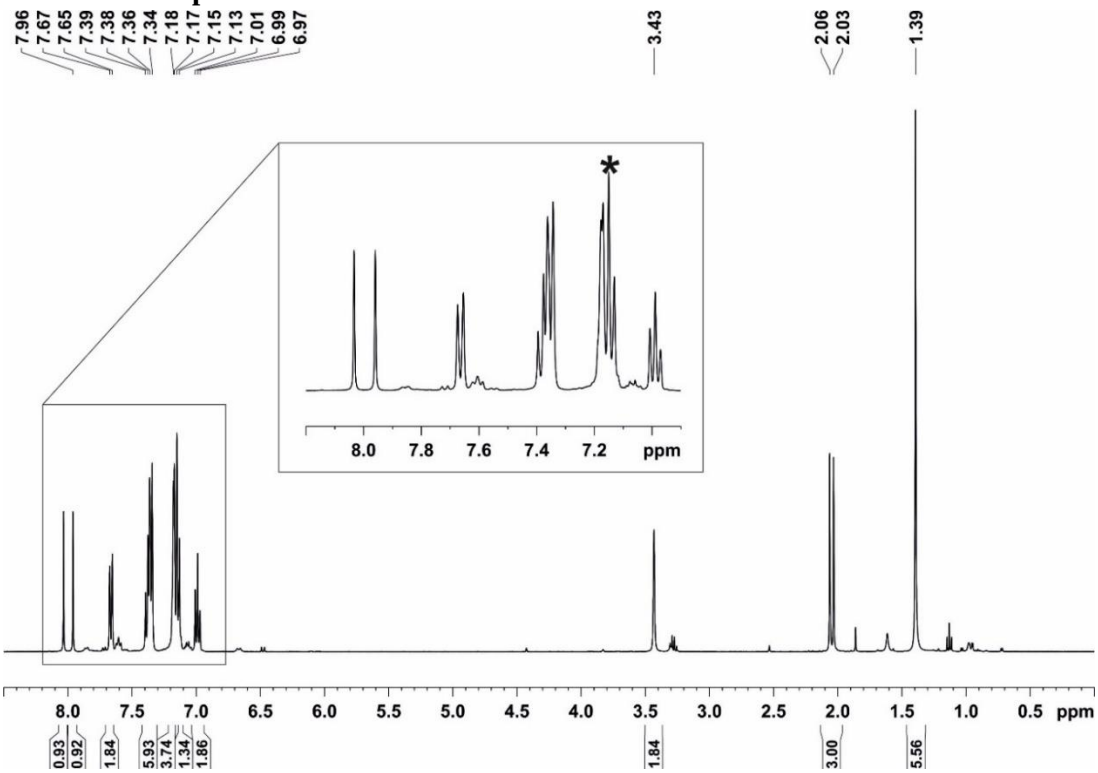


Figure S44. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **4**; * C_6D_6.

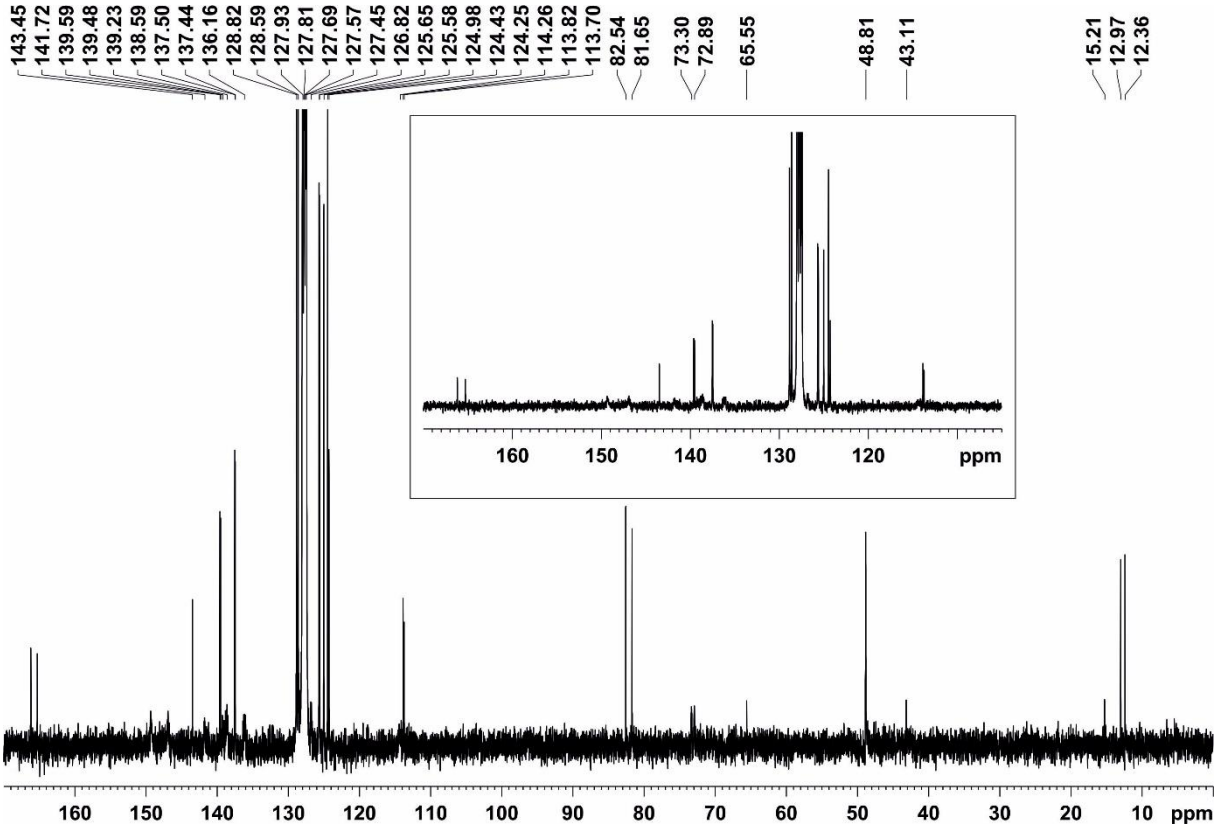


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **4**.

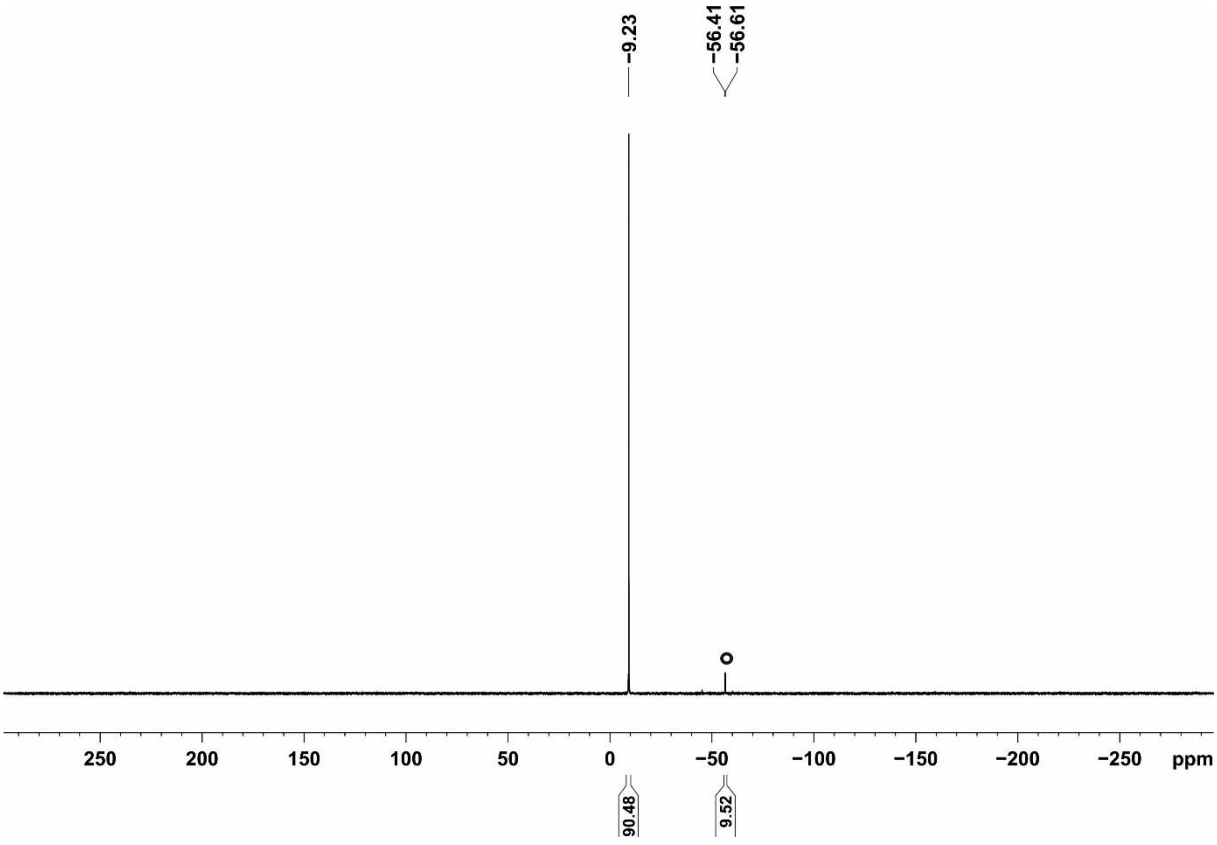


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4**; ° impuritiy.

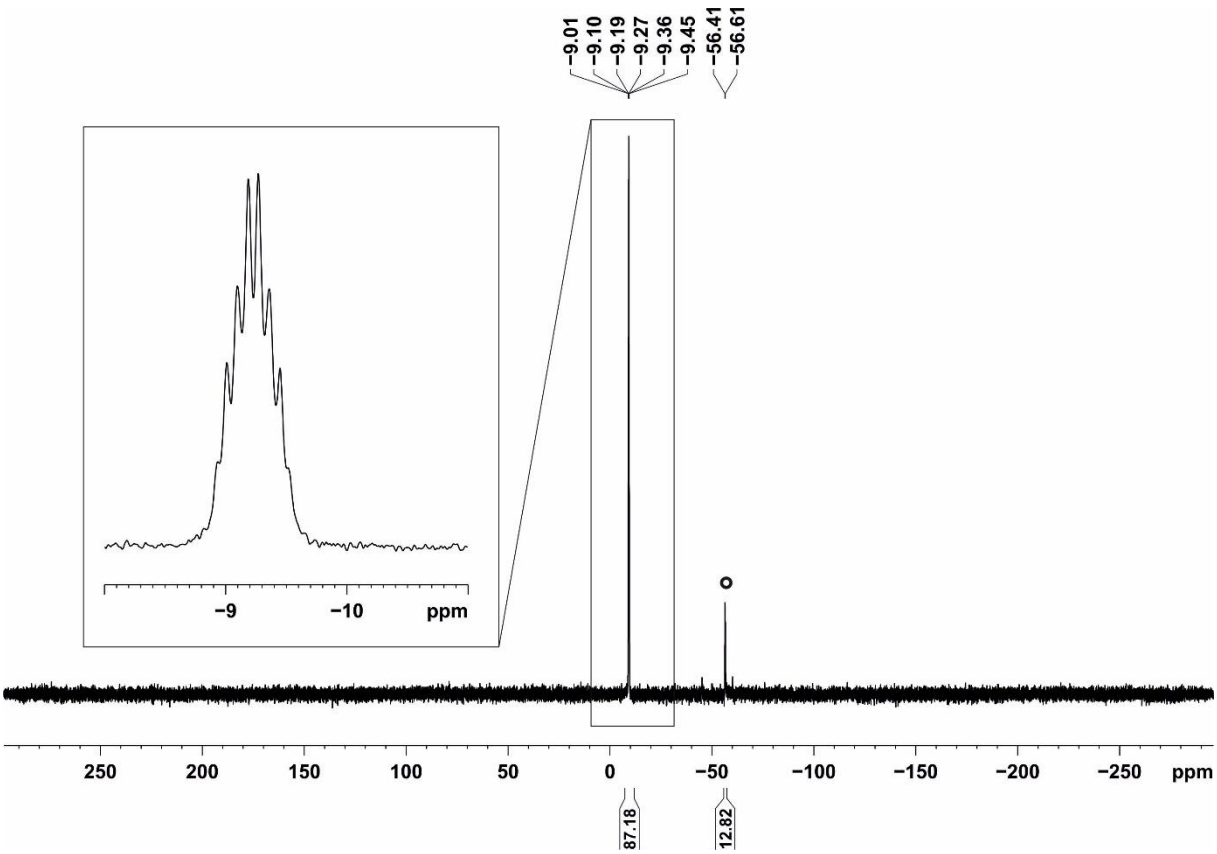


Figure S47. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4**; ° impurity.

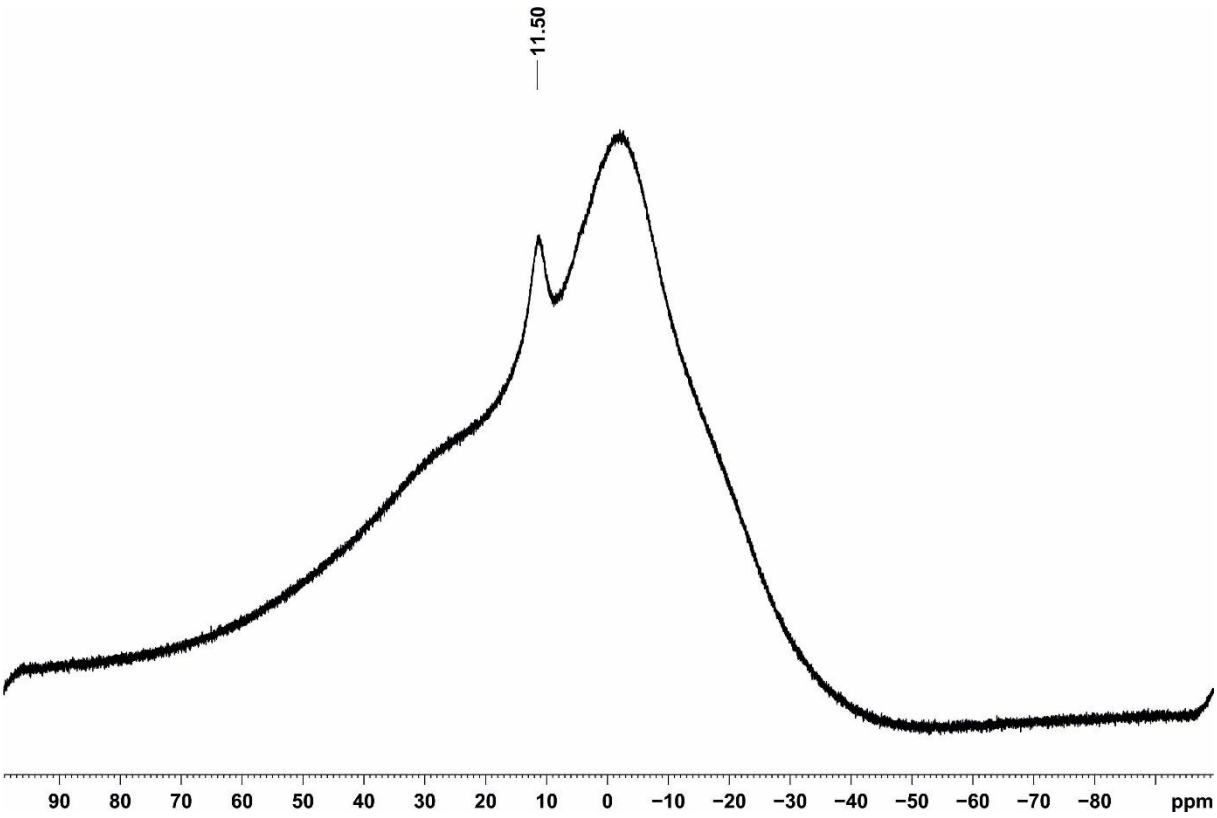


Figure S48. $^{11}B\{^1H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **4**.

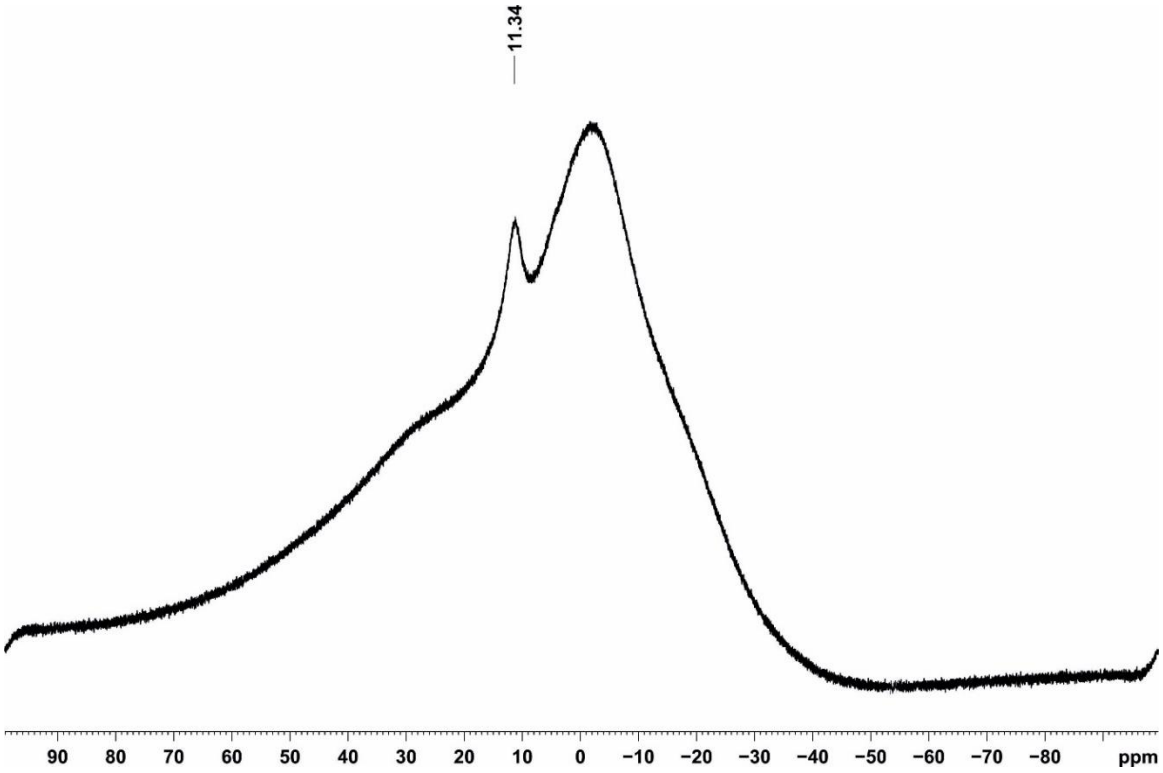


Figure S49. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **4**.

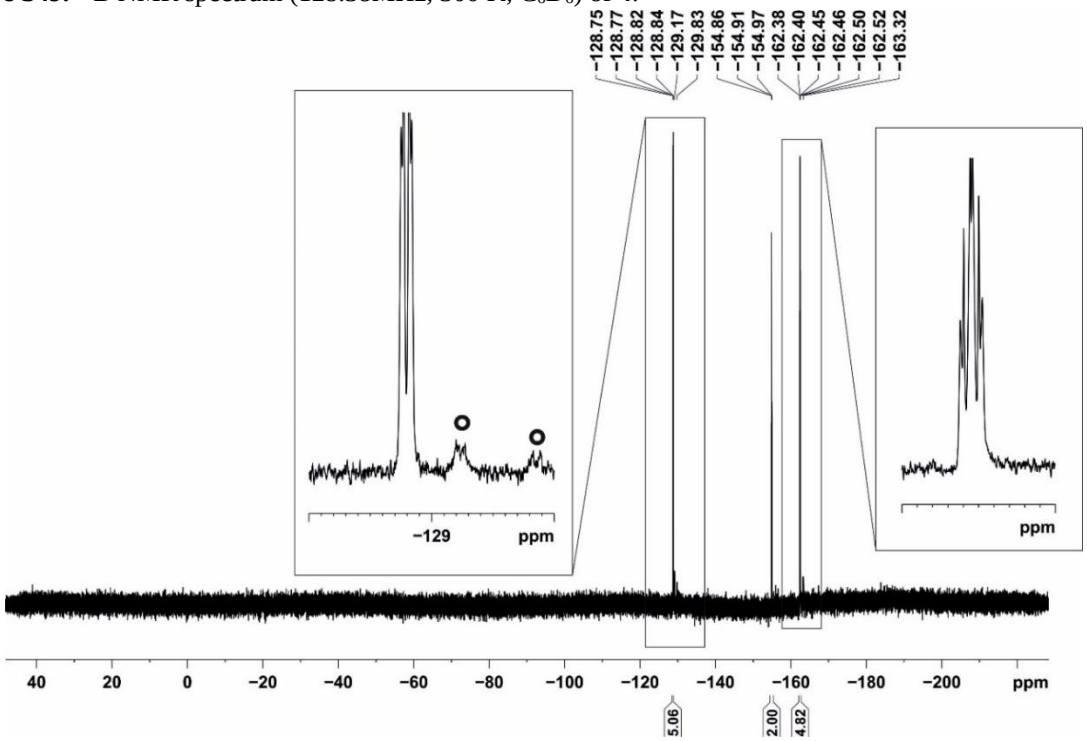


Figure S50. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **4**; ° impurities. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5c**. The integrals for the $^{19}F\{^1H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.8 NMR Spectra of 5a

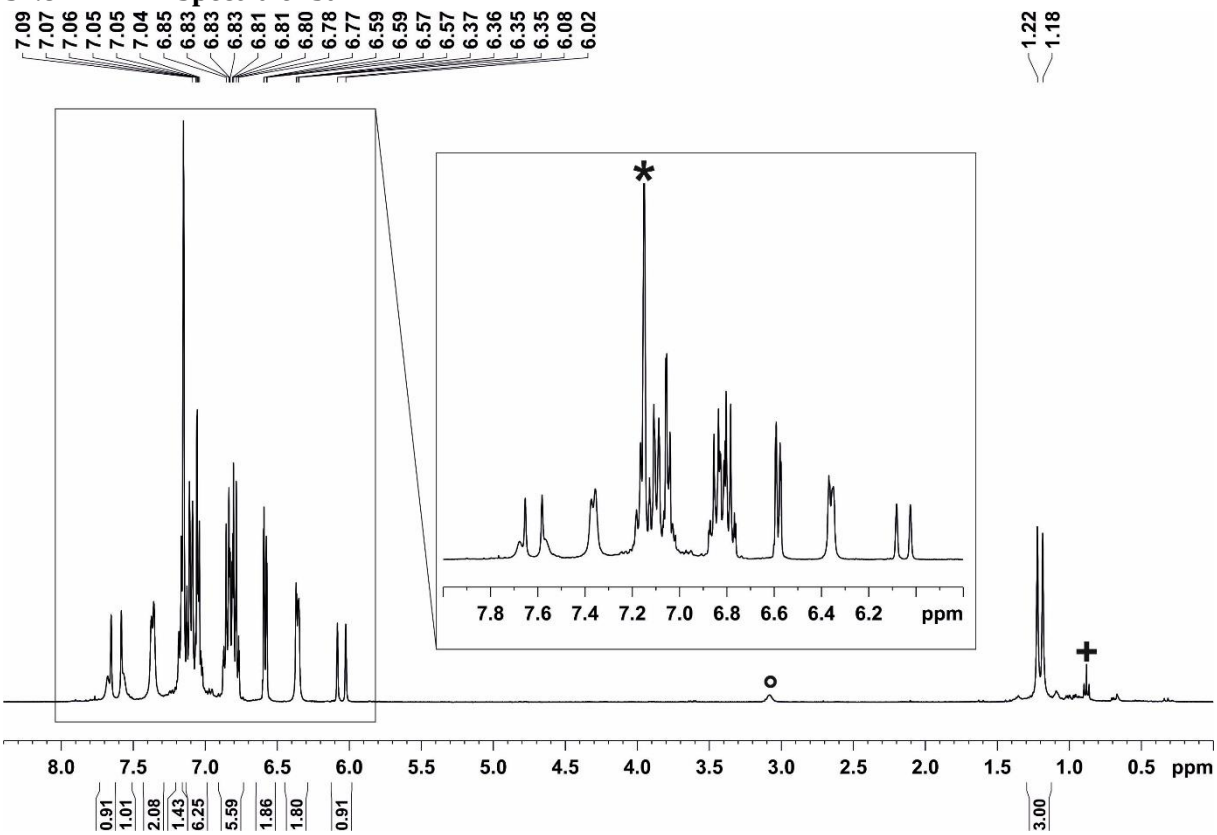


Figure S51. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **5a**; * C_6D_6; °impurity; + *n*-hexane.

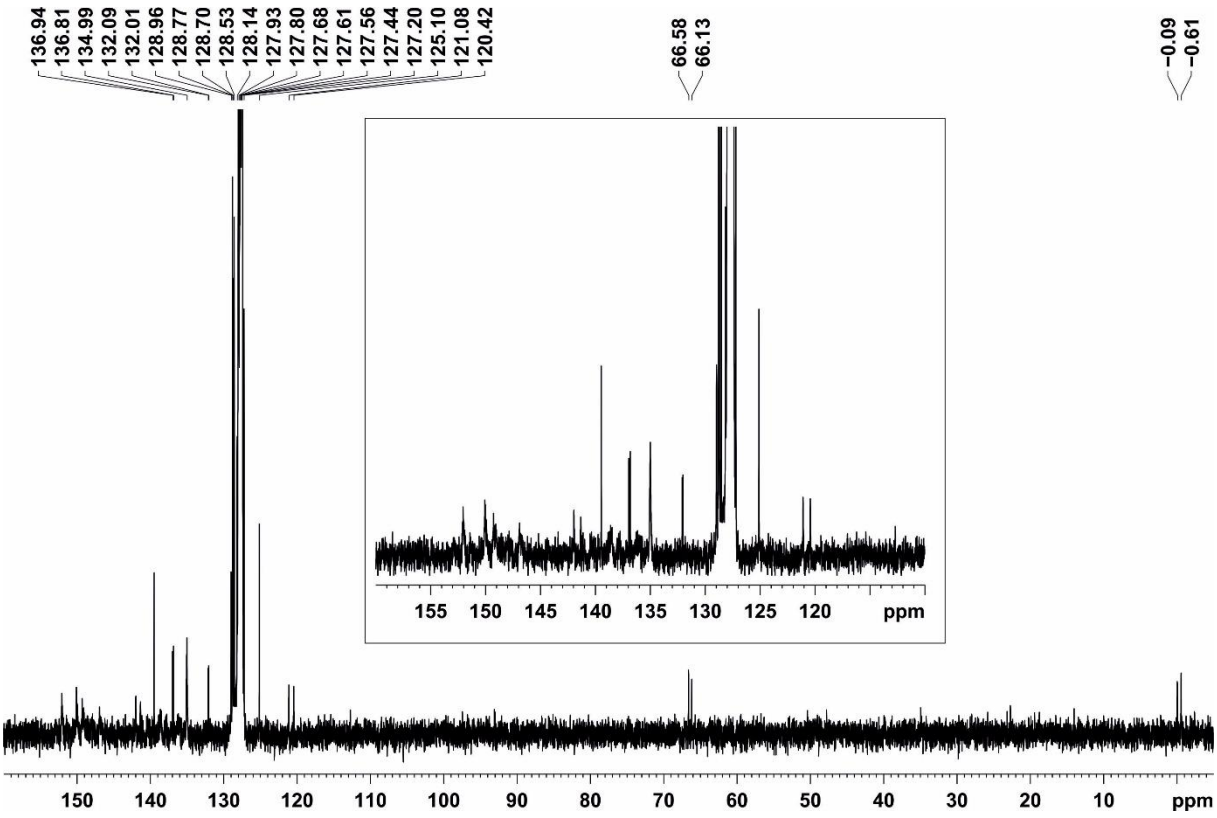


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **5a**.

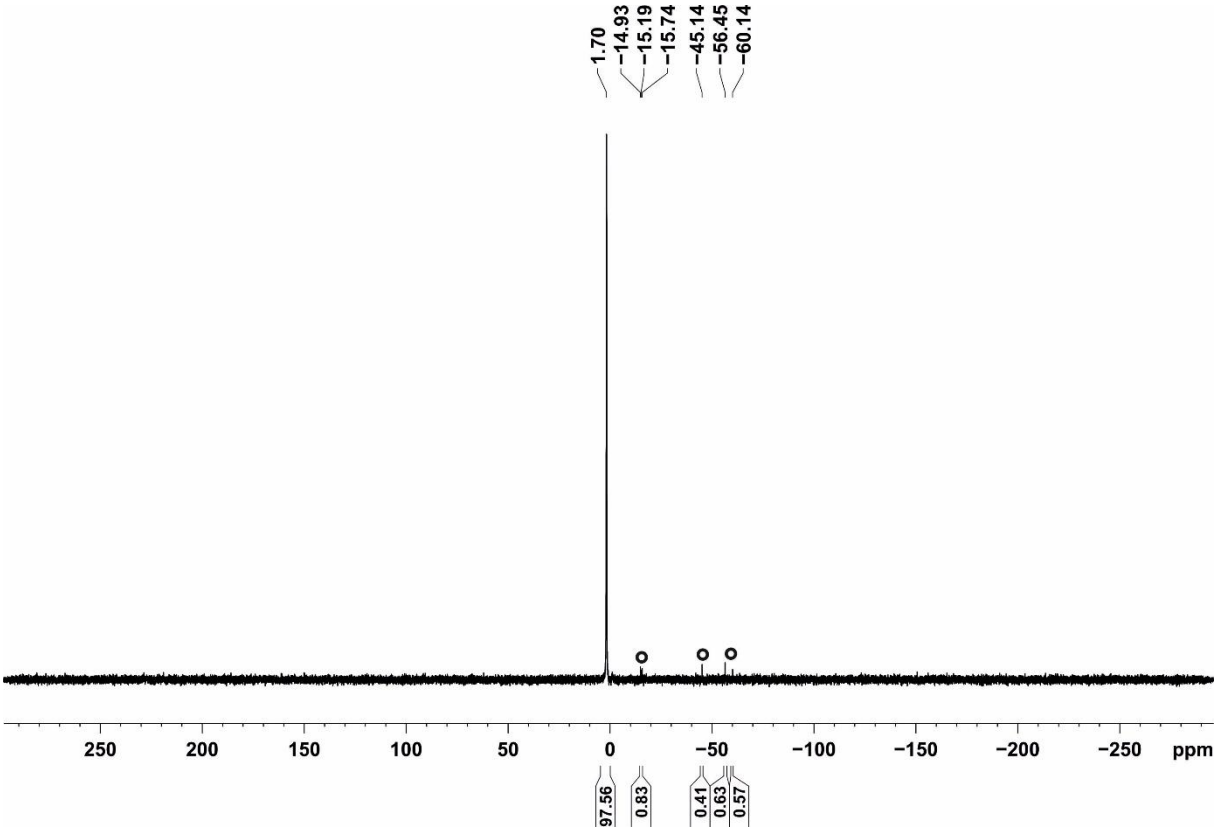


Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5a**; ° impurities.

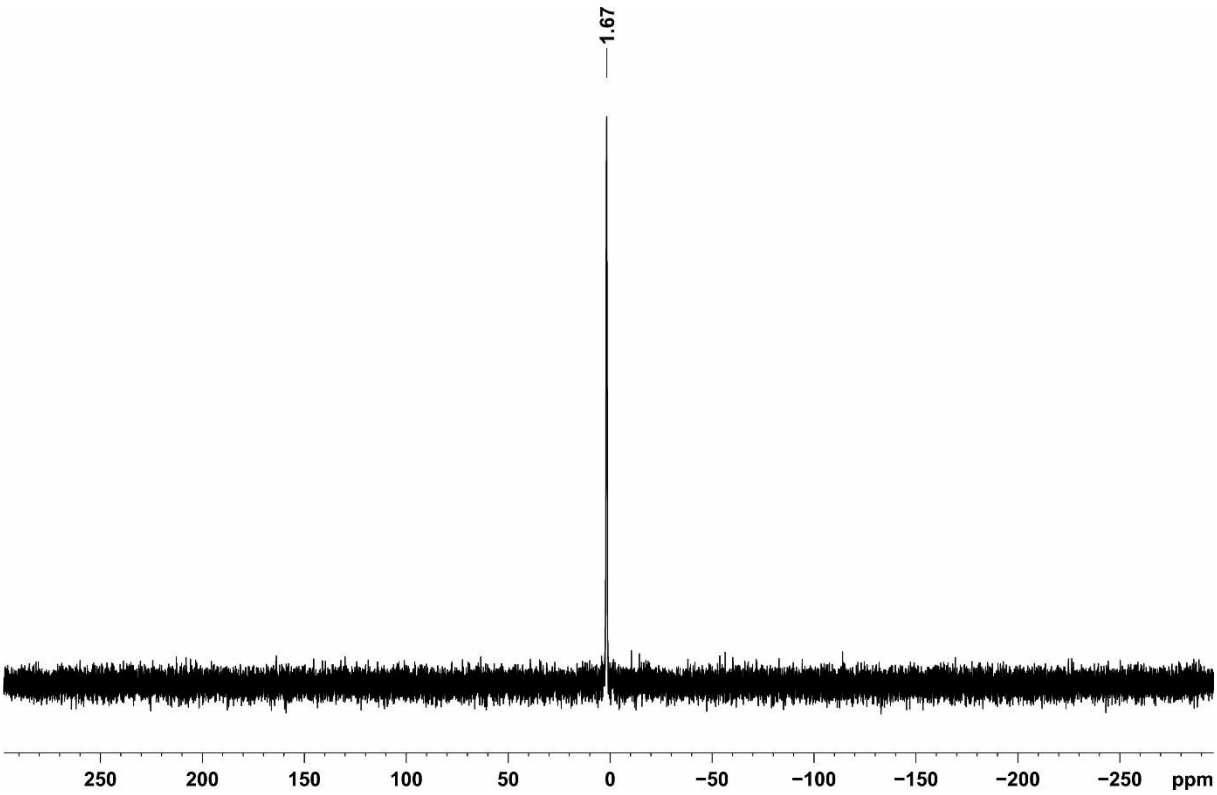


Figure S54. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5a**.

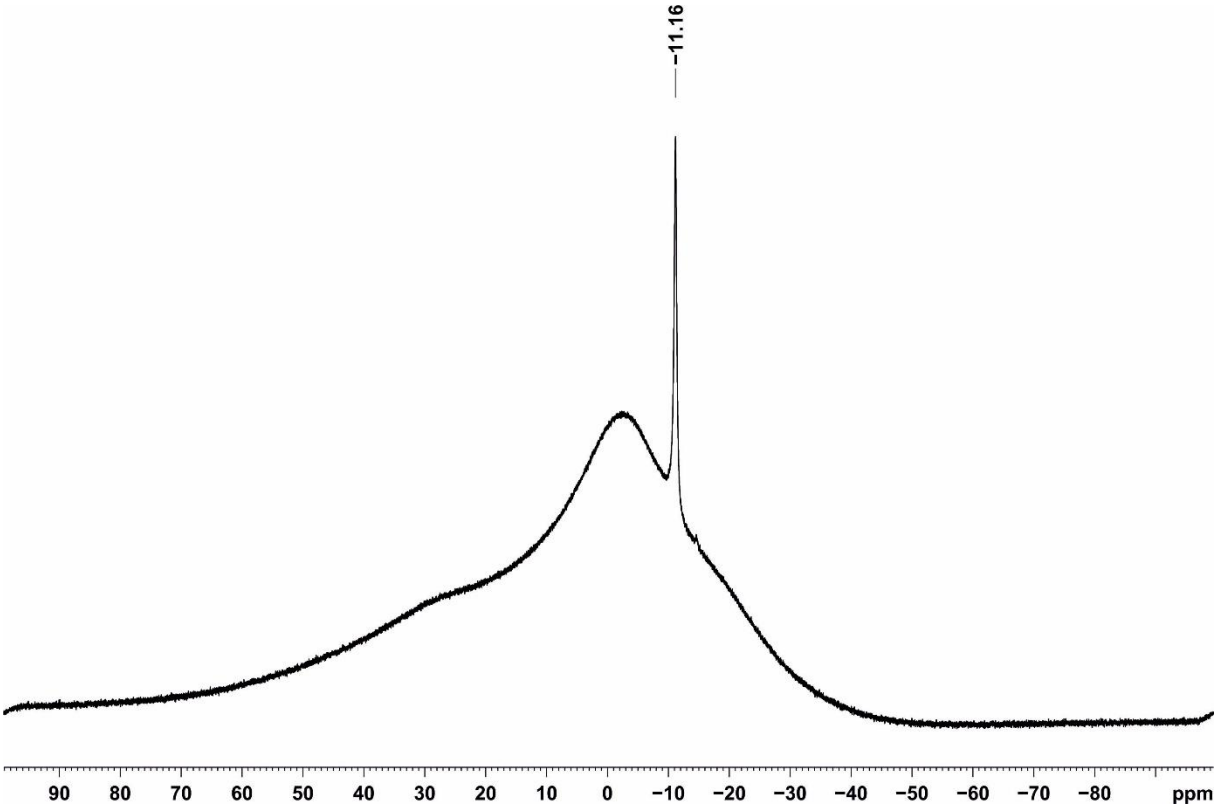


Figure S55. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5a**.

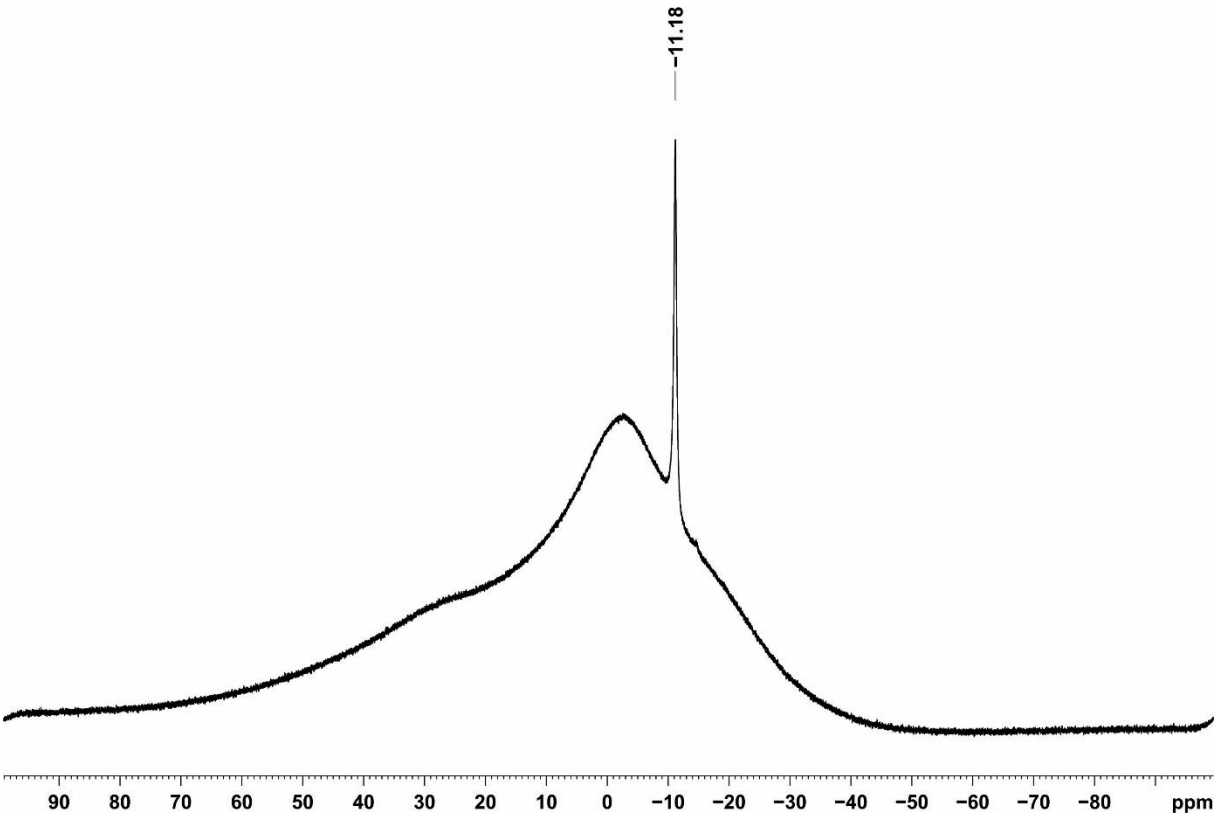


Figure S56. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5a**.

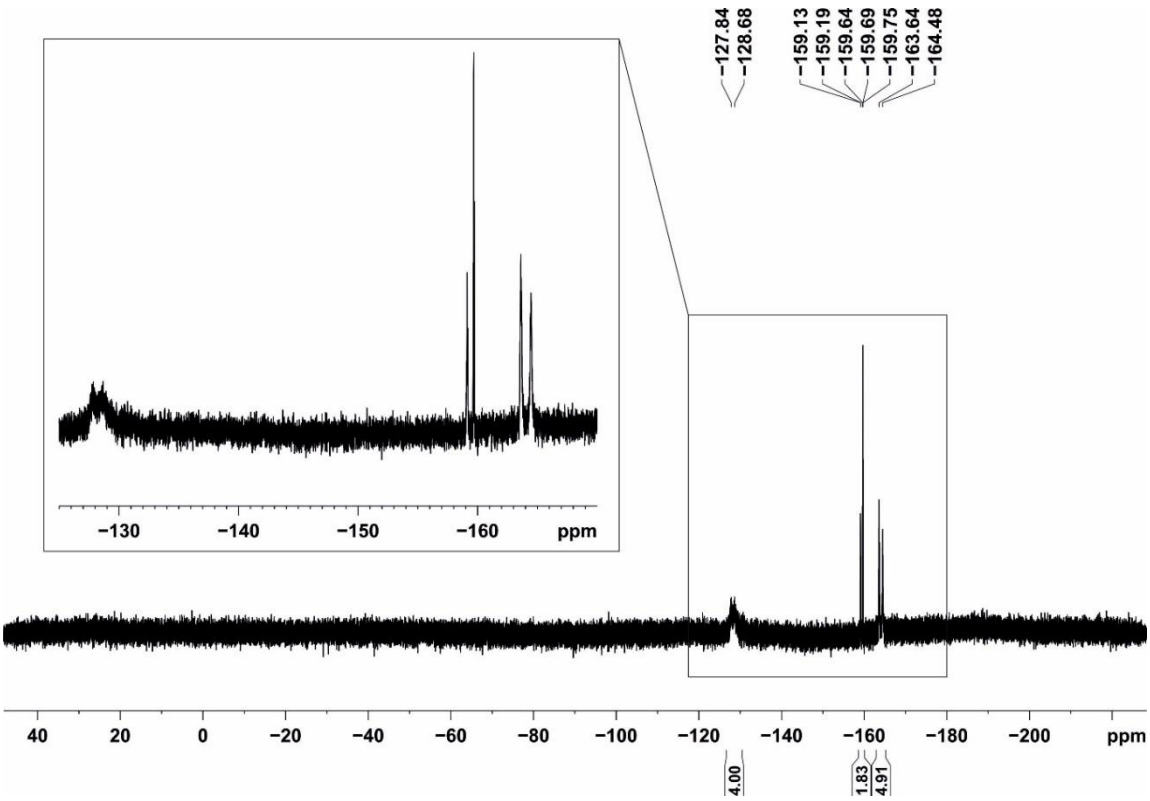


Figure S57. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5a**. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5c**. The integrals for the $^{19}F\{^{1}H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.9 NMR Spectra of 5b

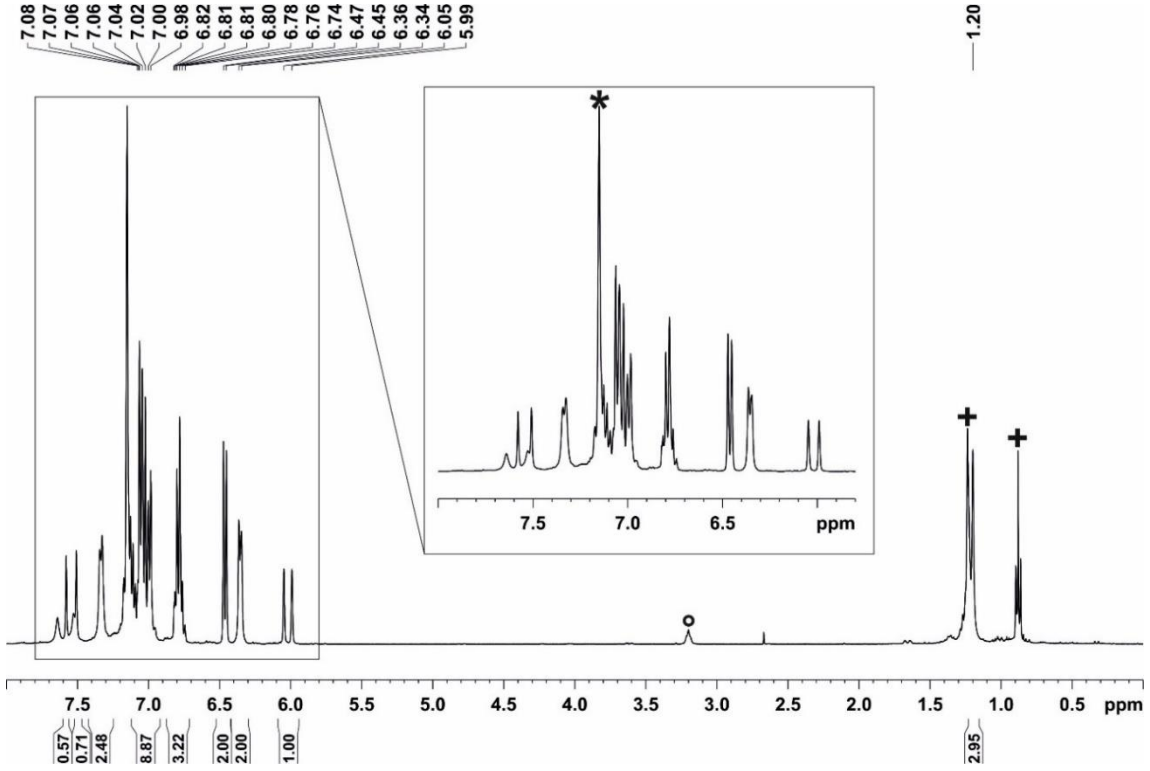


Figure S58. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **5b**; * C_6D_6; °impurity; +*n*-hexane .

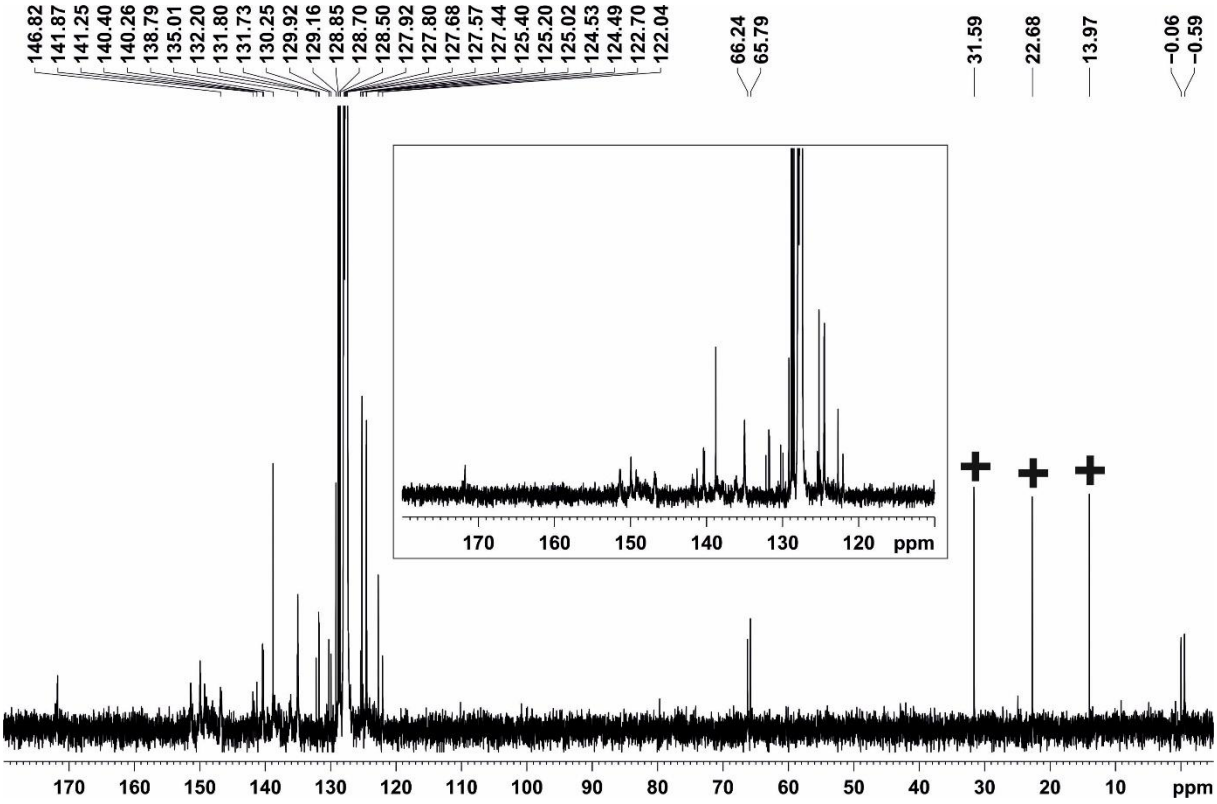


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **5b**; +*n*-hexane.

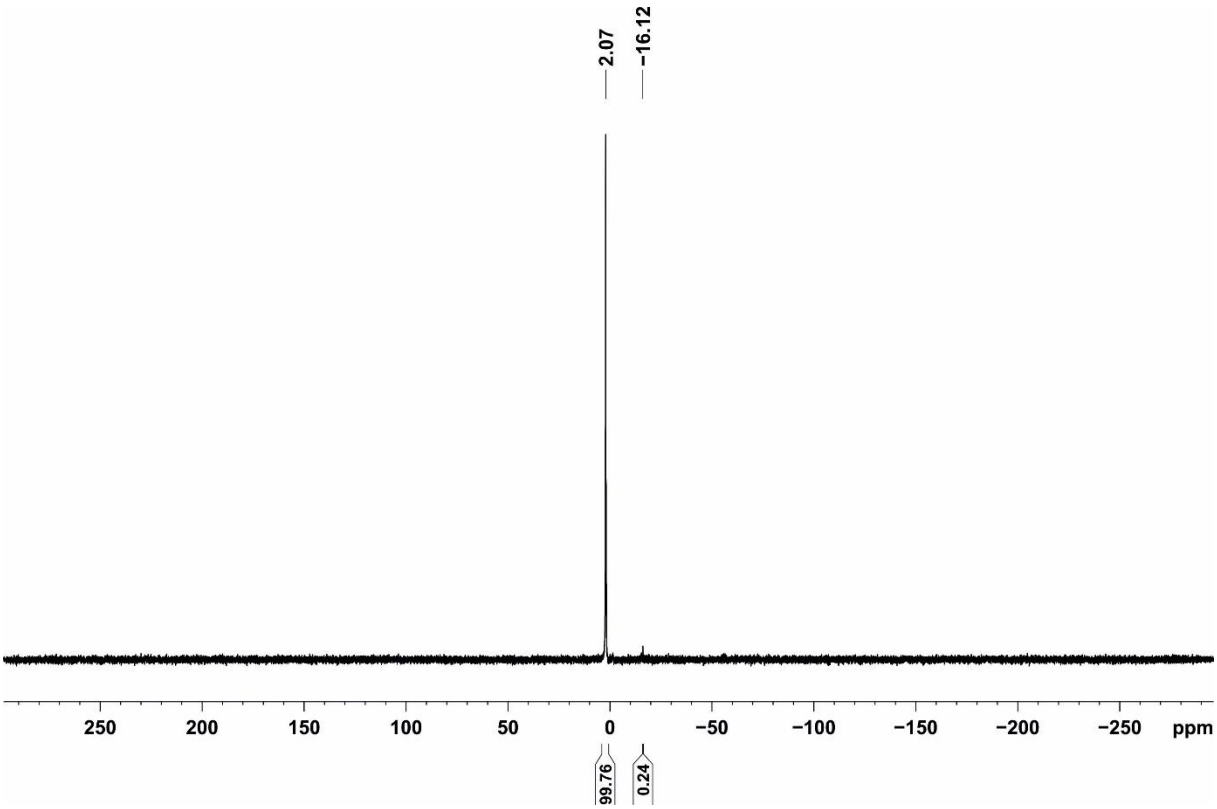


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5b**.

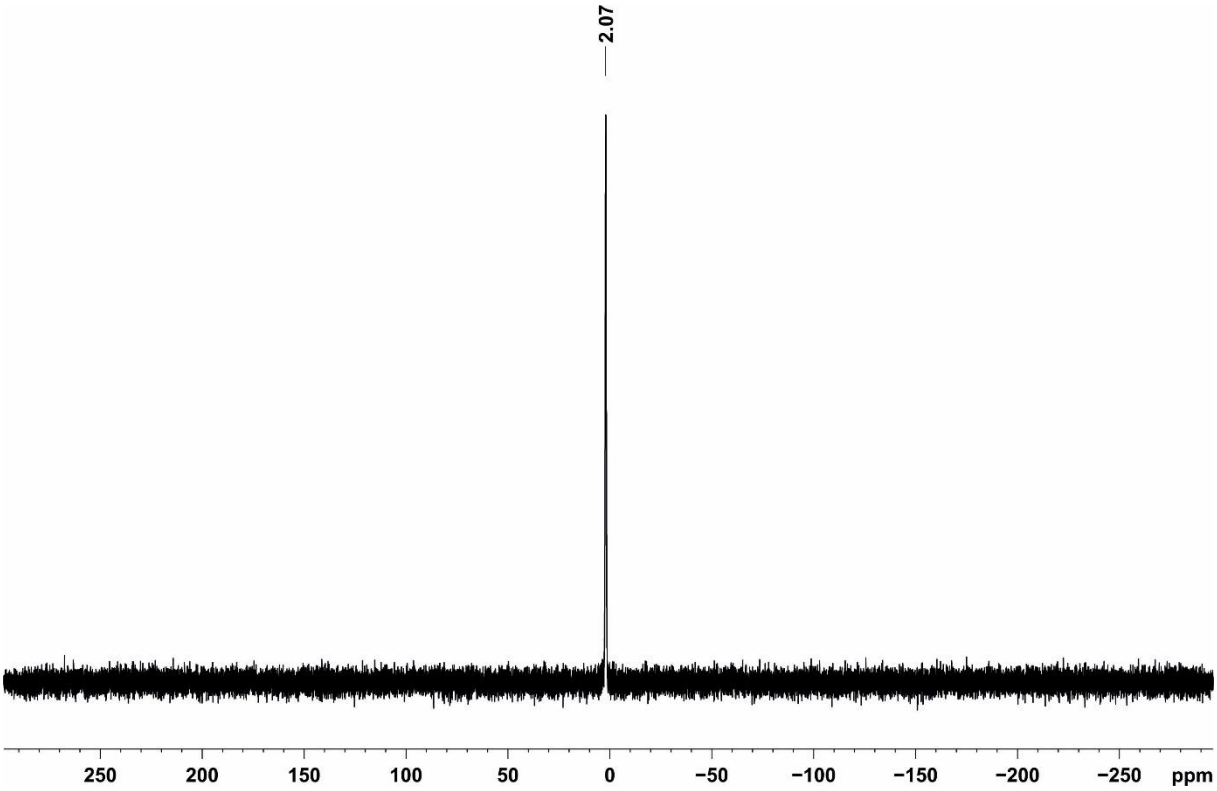


Figure S61. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5b**.

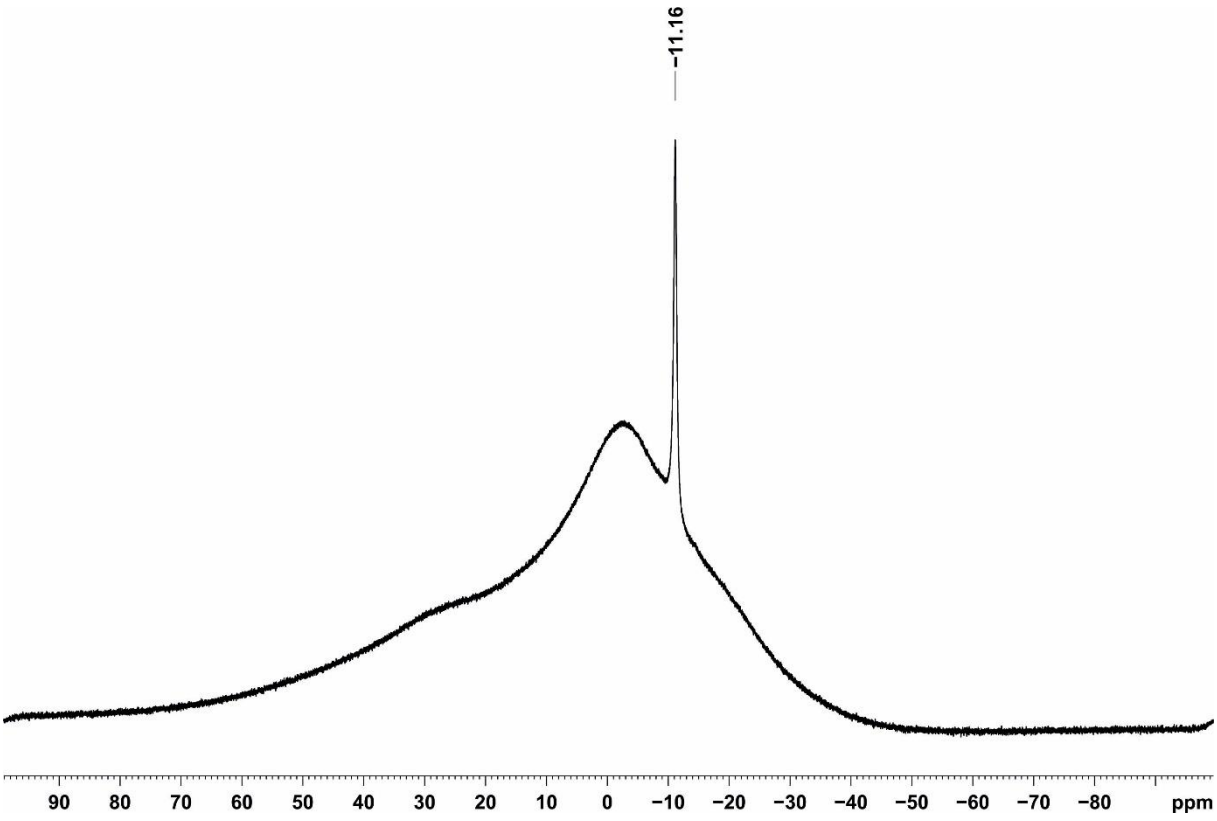


Figure S62. $^{11}B\{^1H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5b**.

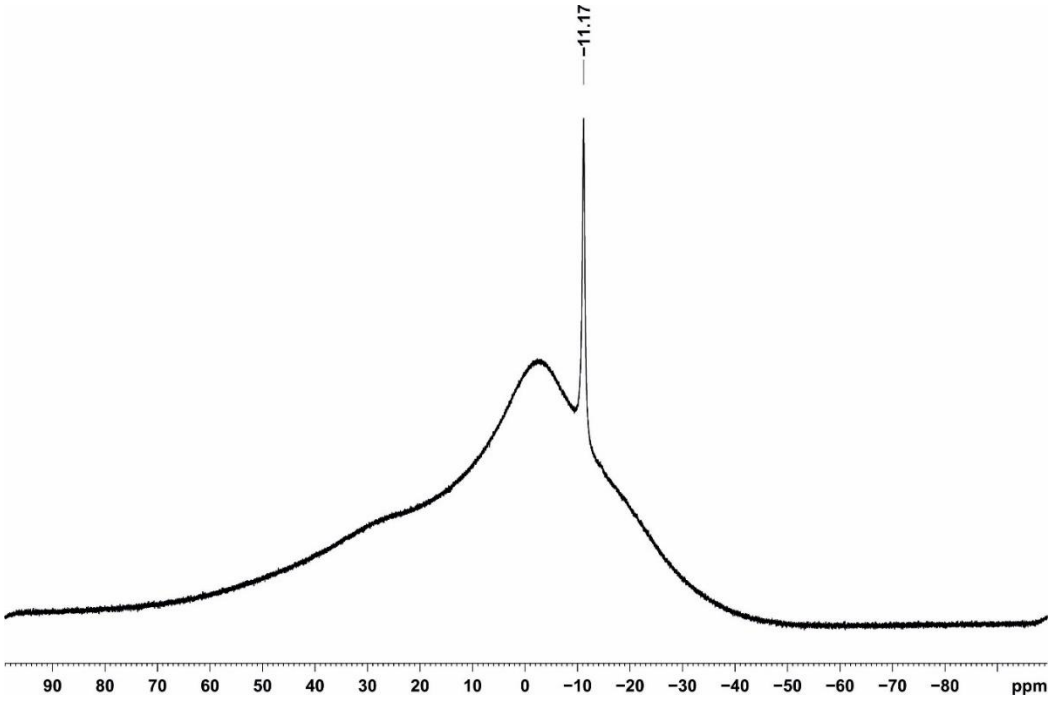


Figure S63. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5b**.

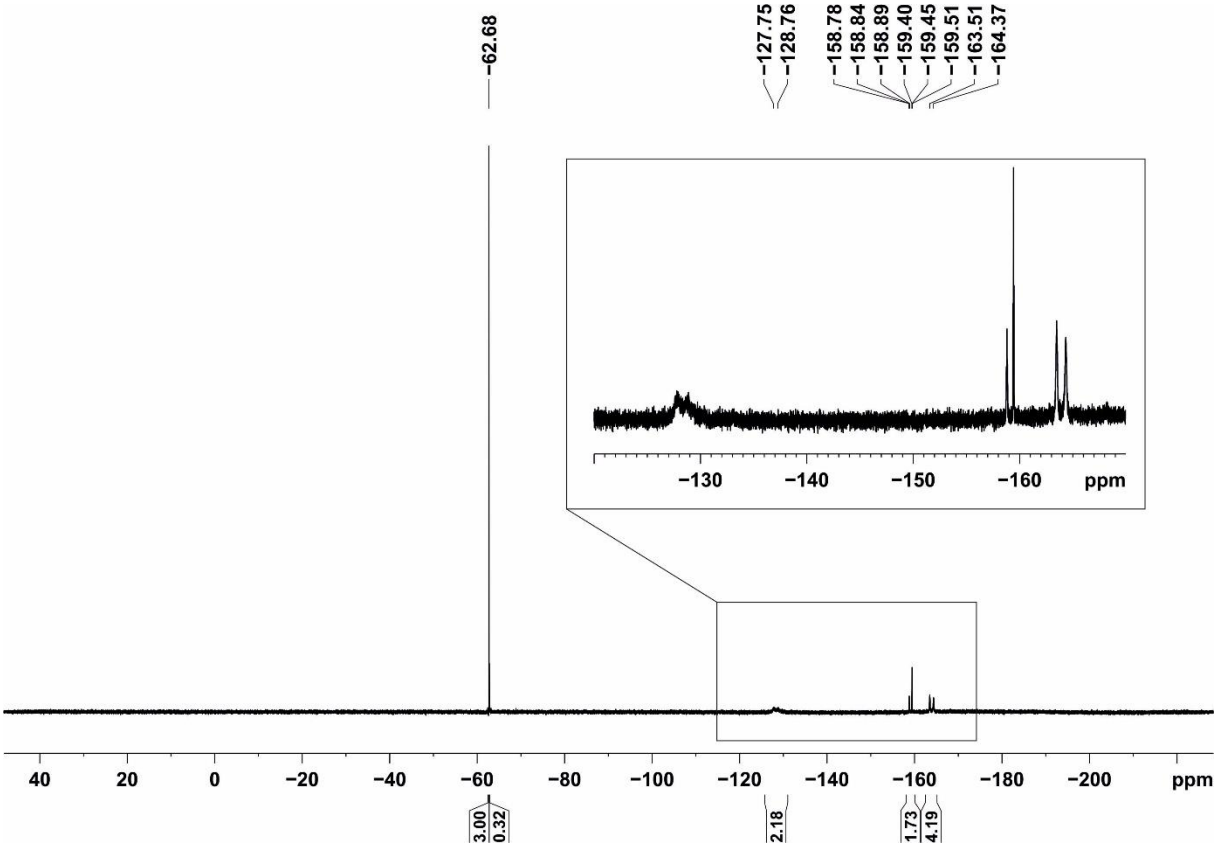


Figure S64. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5b**. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5c**. The integrals for the $^{19}F\{^1H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S2.10 NMR Spectra of 5c

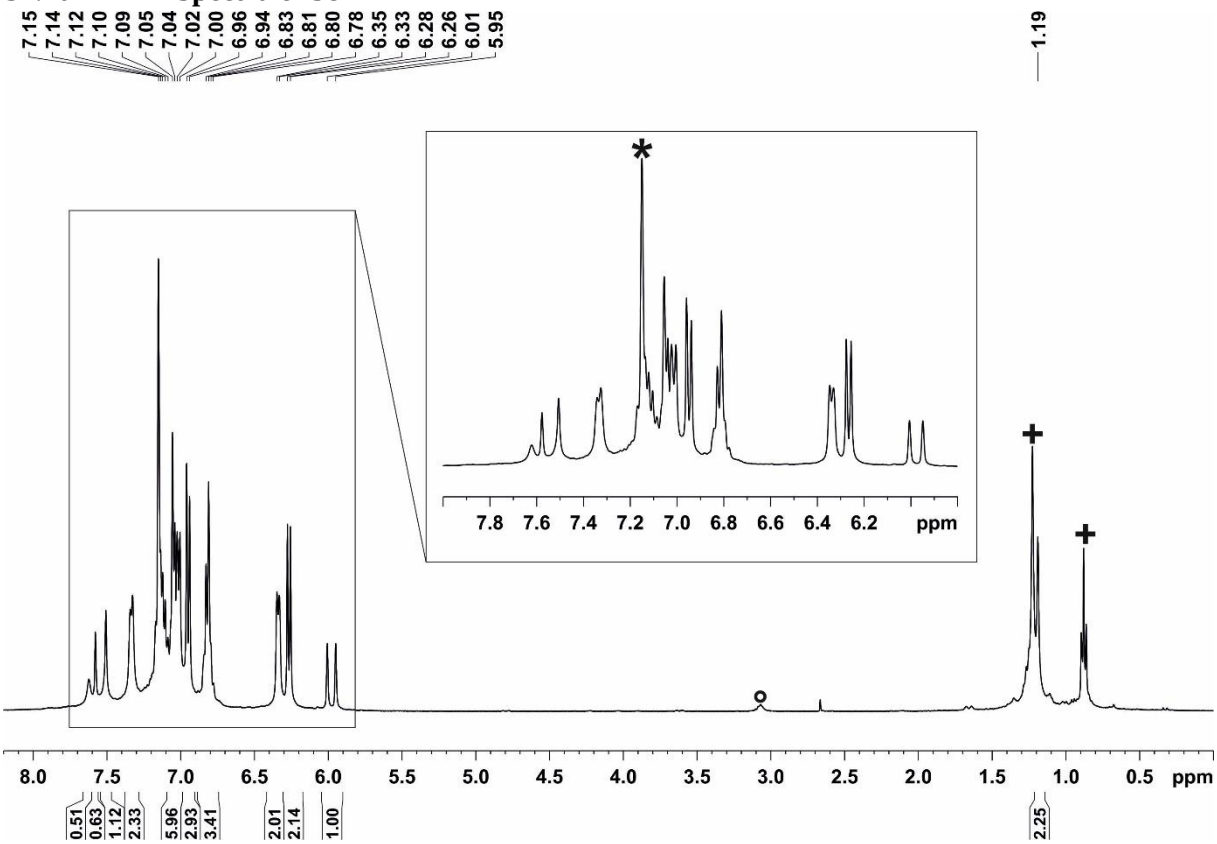


Figure S65. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **5c**; * C_6D_6; °impurity; +*n*-hexane.

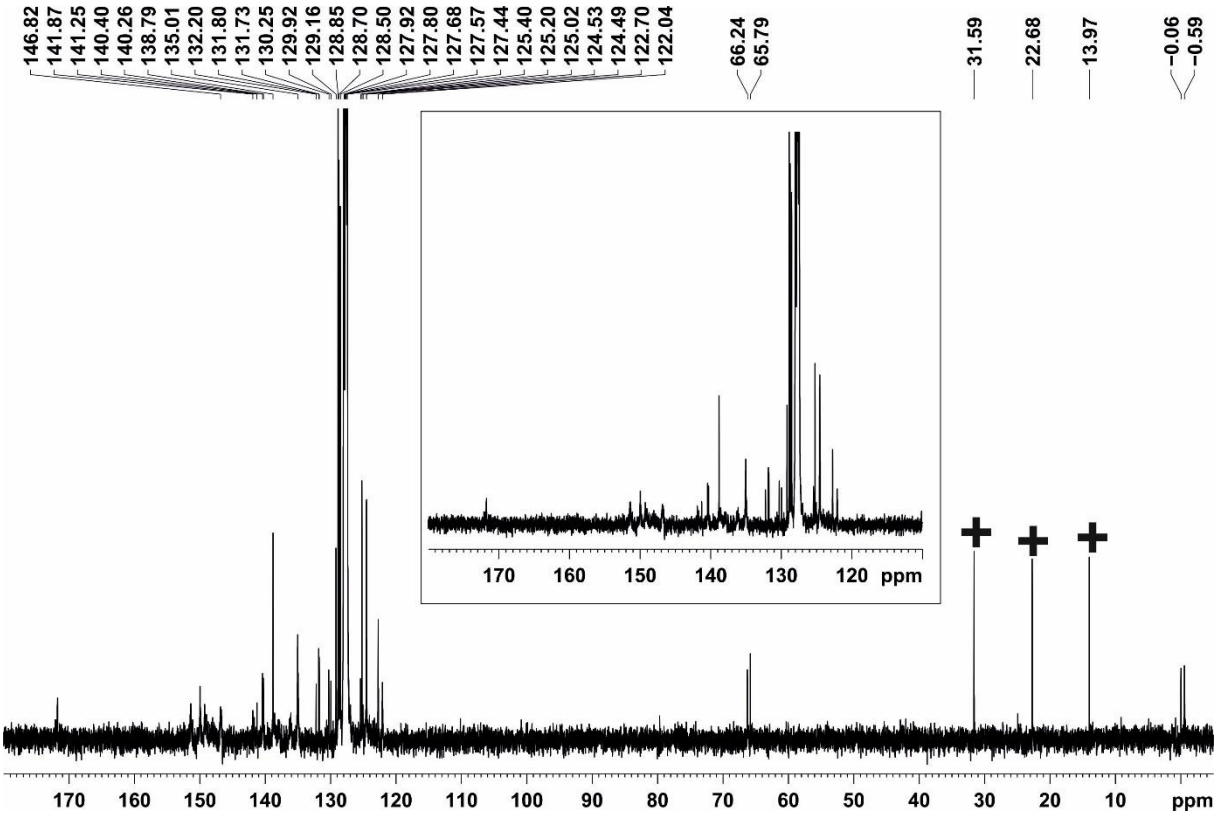


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **5c**; +*n*-hexane.

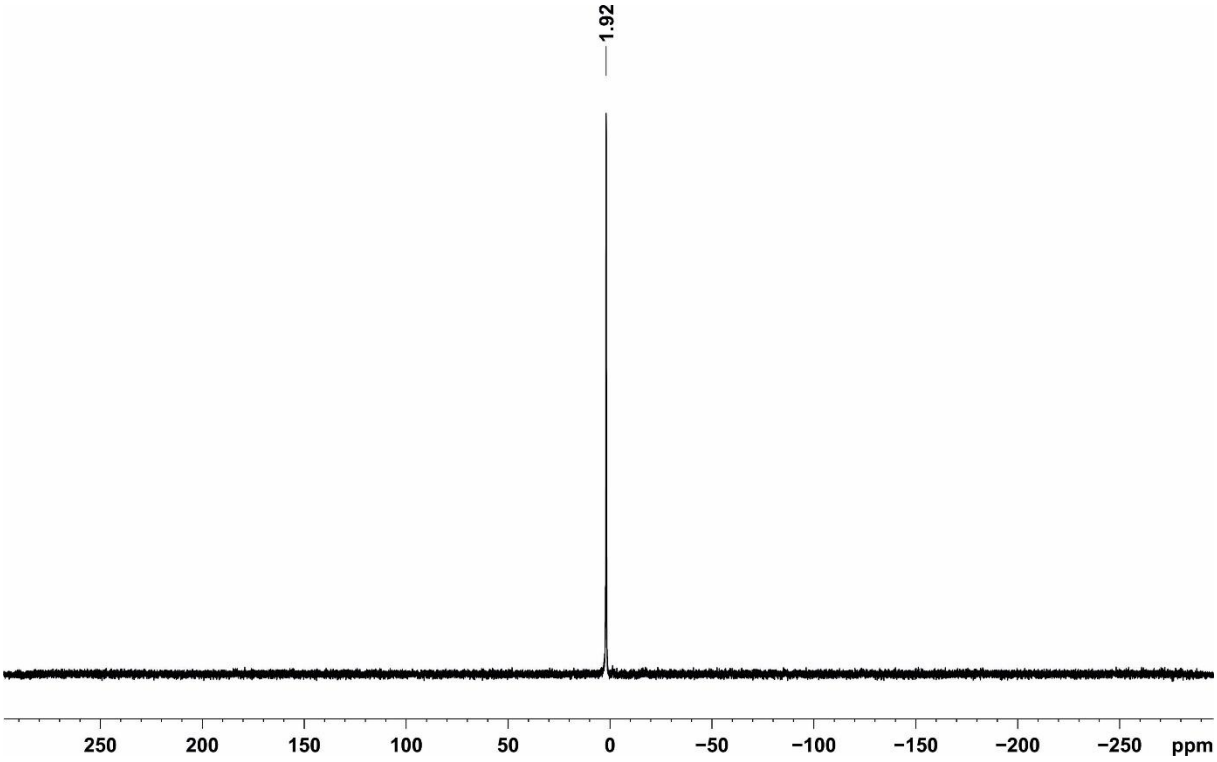


Figure S67. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5c**.

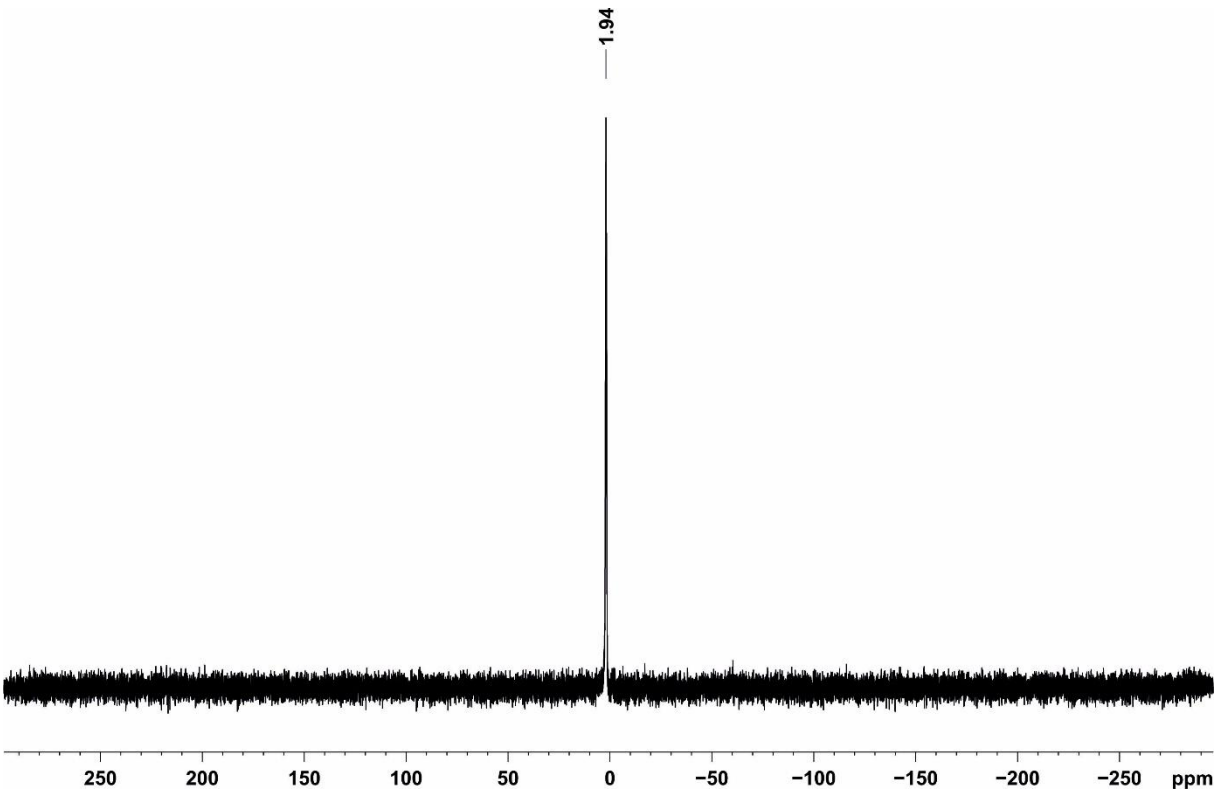


Figure S68. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5c**.

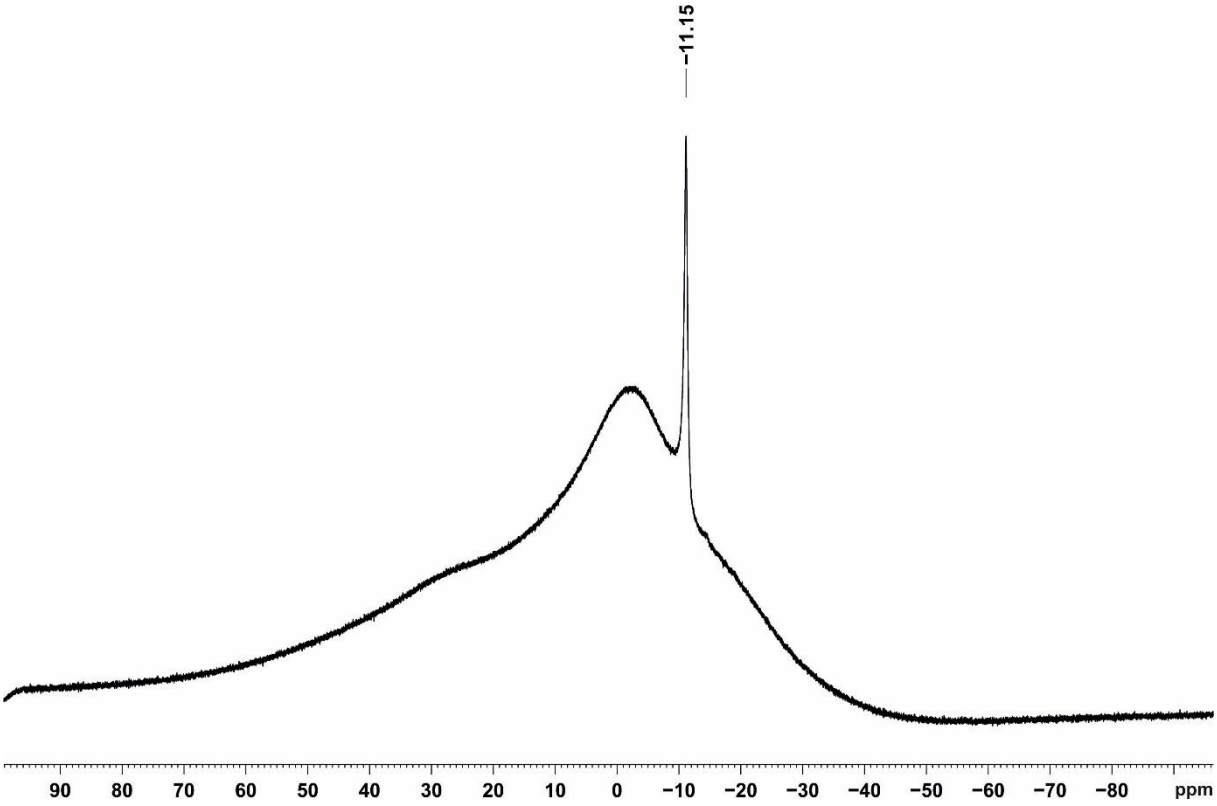


Figure S69. $^{11}B\{^{1}H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5c**.

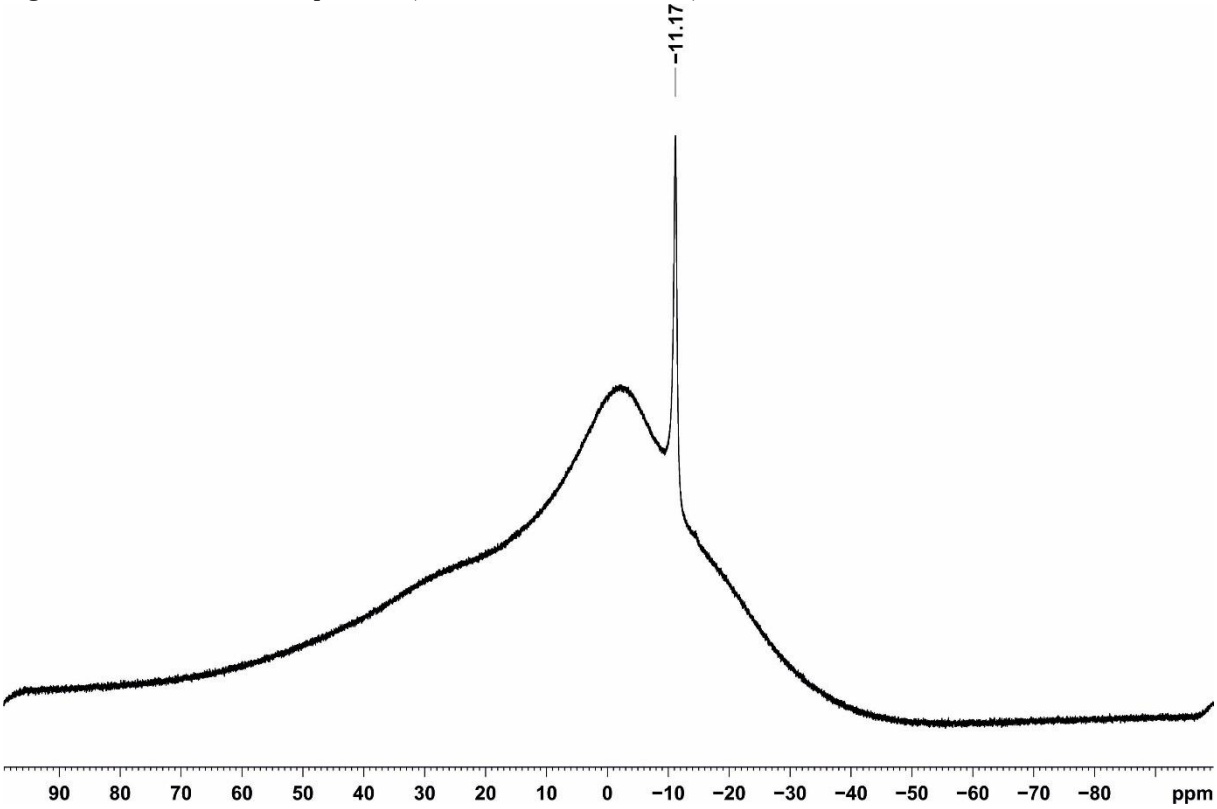


Figure S70. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **5c**.

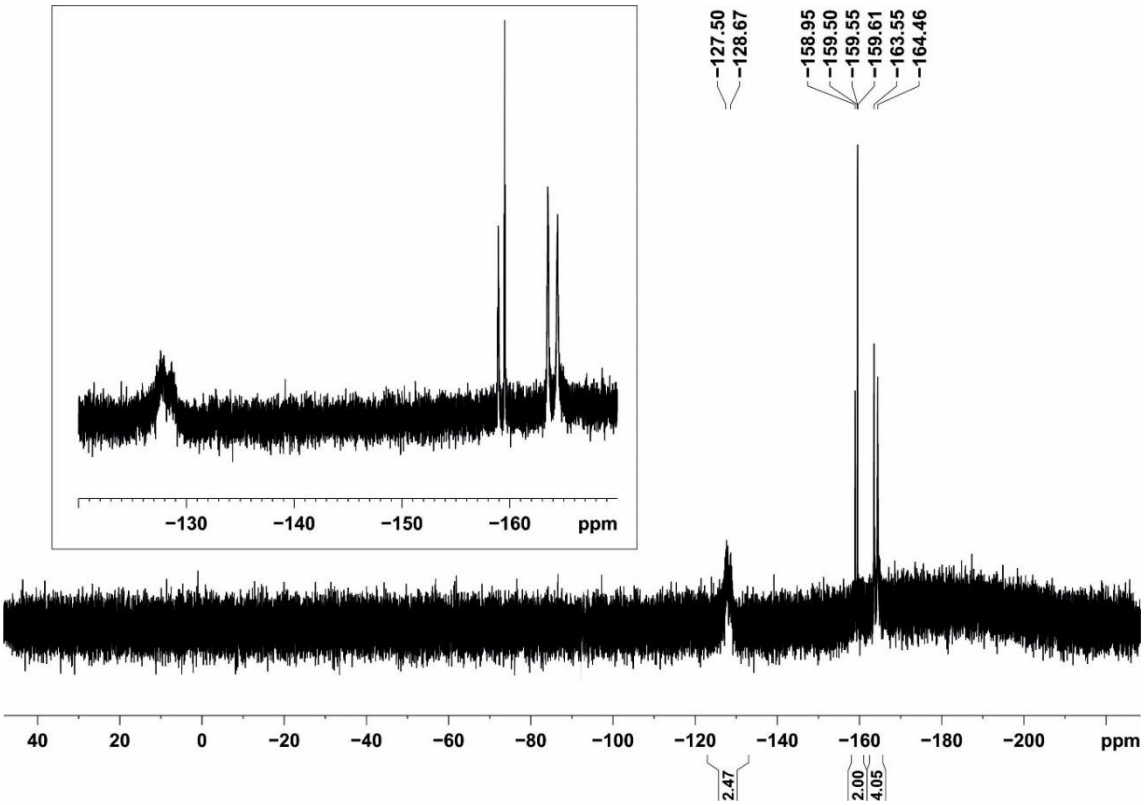


Figure S71. $^{19}F\{^{1}H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **5c**. The integrals for the $^{19}F\{^{1}H\}$ signals do not fit perfectly to the expected integration values due to the high noise level of the spectrum or/and the difference signal enhancement in the proton decoupled fluorine spectra, due to the different coupling constants of ortho, meta and para fluorine atoms. The integrals can be improved by changing the processing parameters and manual baseline corrections (for example see **3d**).

S1.11 NMR Spectra of 6

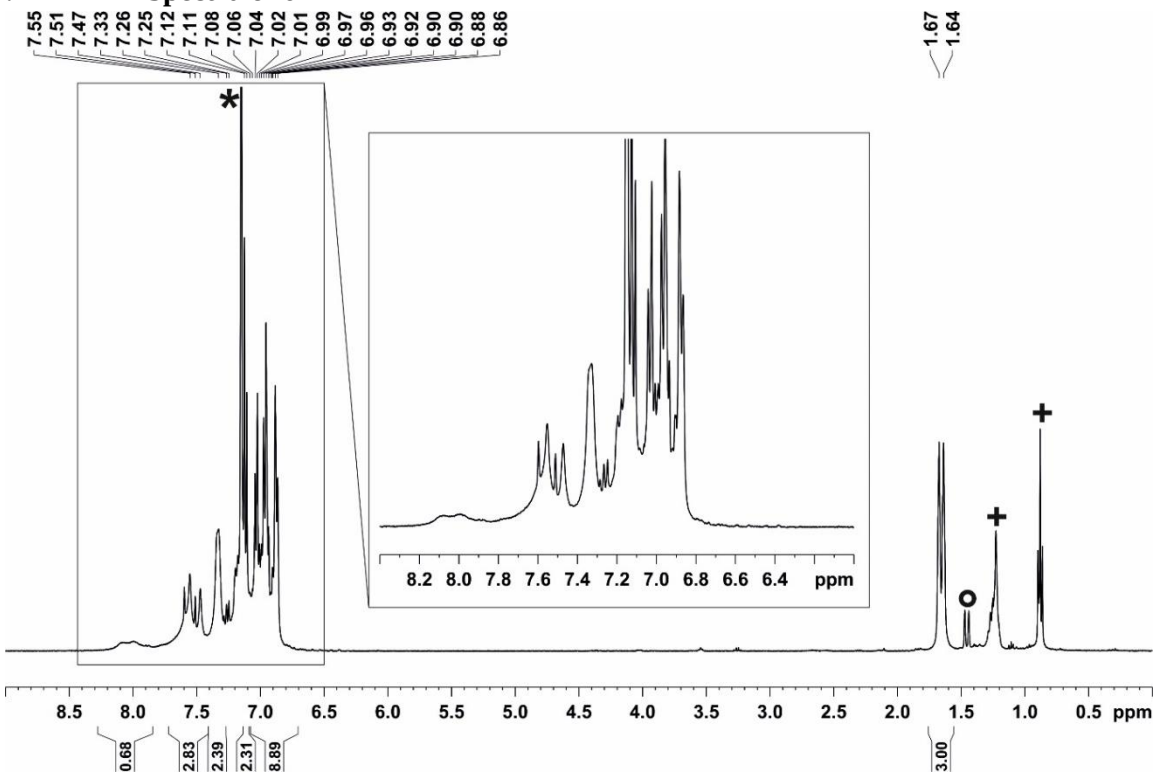


Figure S72. ^{1}H NMR spectrum (400.13 MHz, 300 K,C_6D_6) of **6**; * C_6D_6; °compound **2**; +*n*-hexane.

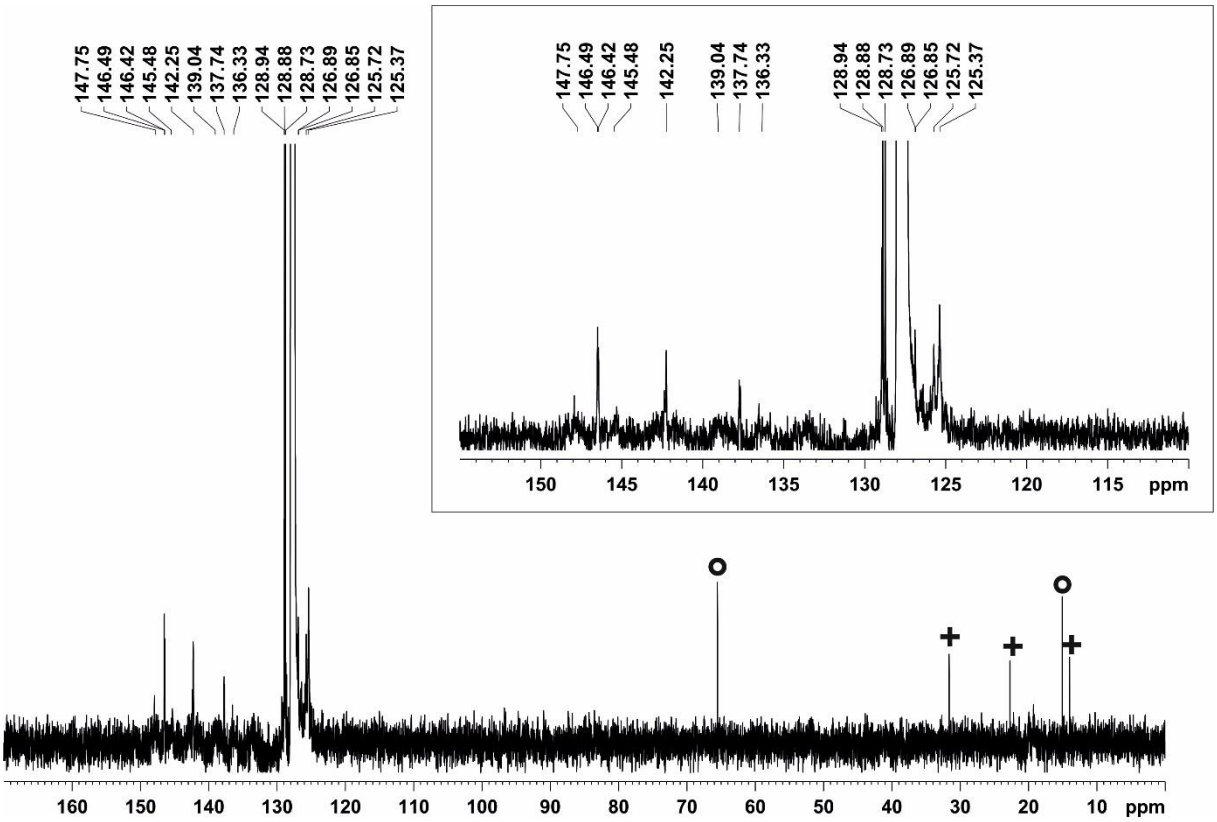


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **6**; °diethylether, +*n*-hexane.

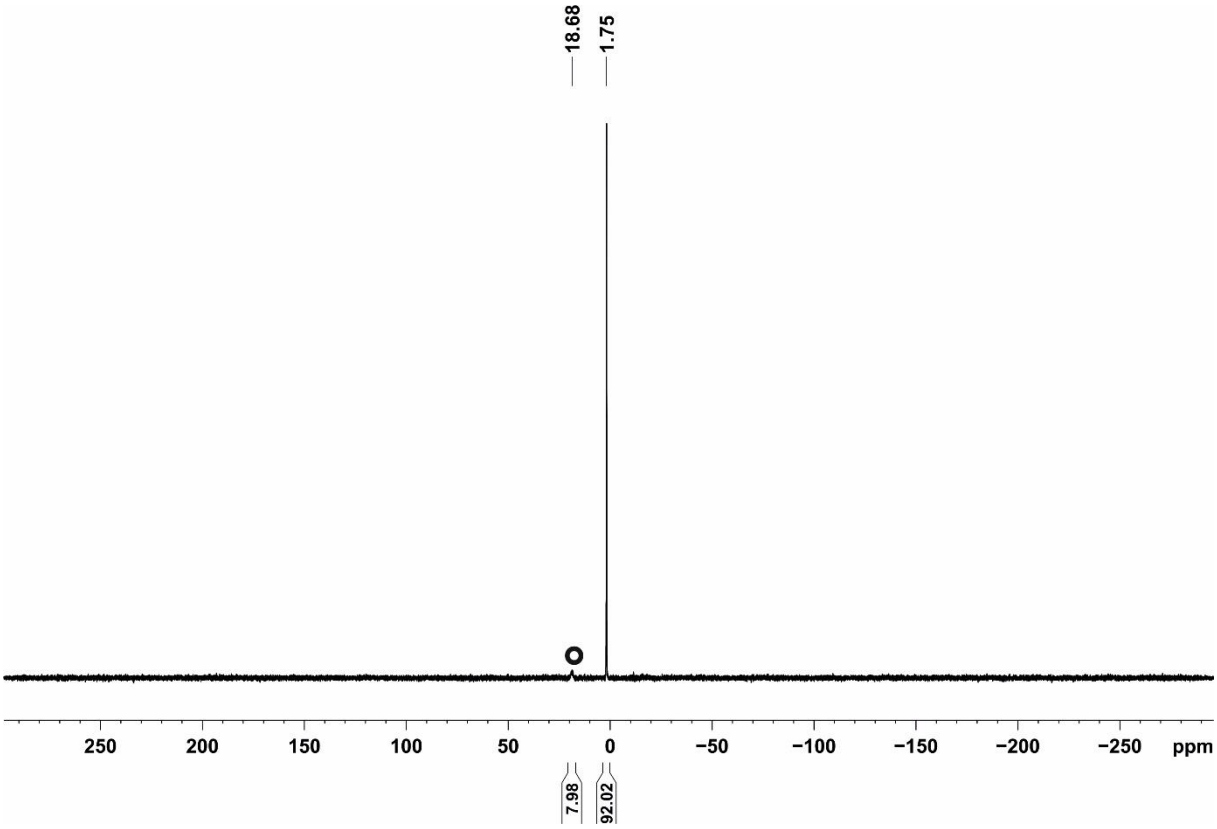


Figure S74. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **6**, °compound **2**.

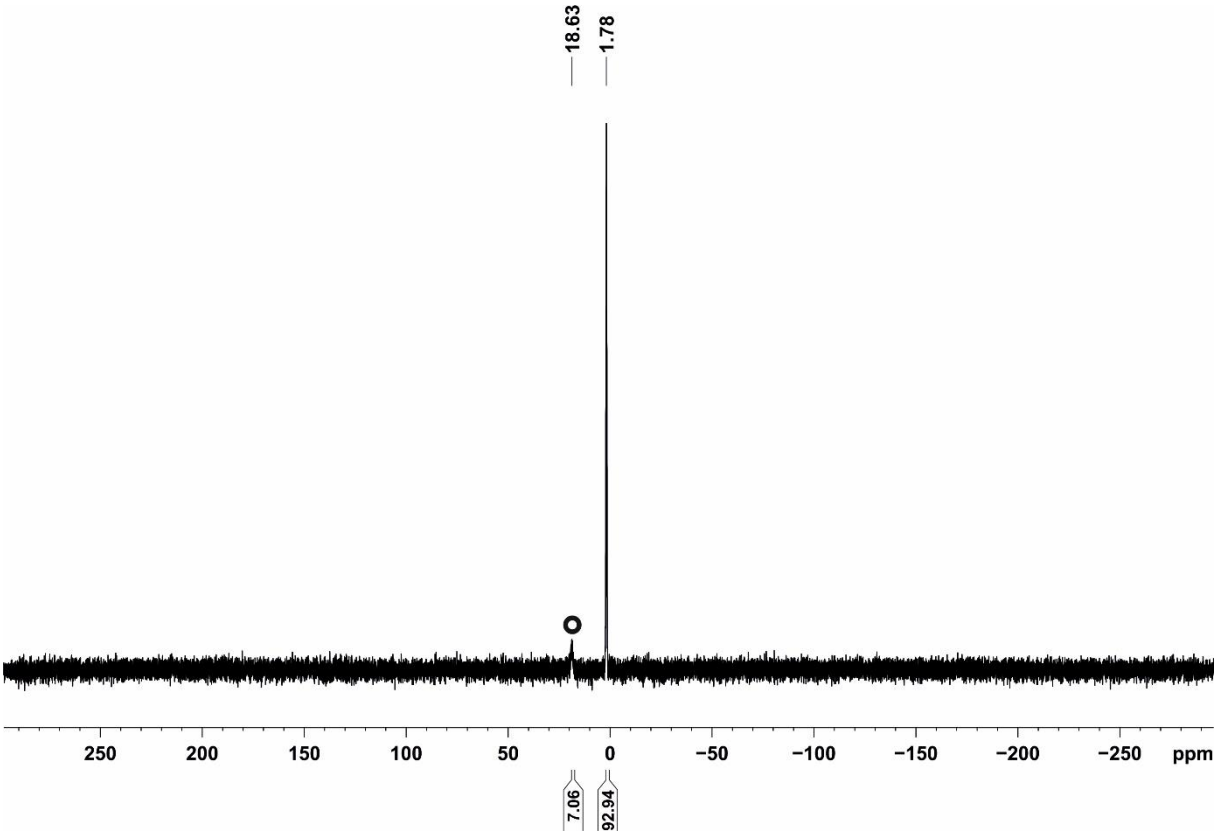


Figure S75. ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **6**, °compound **2**.

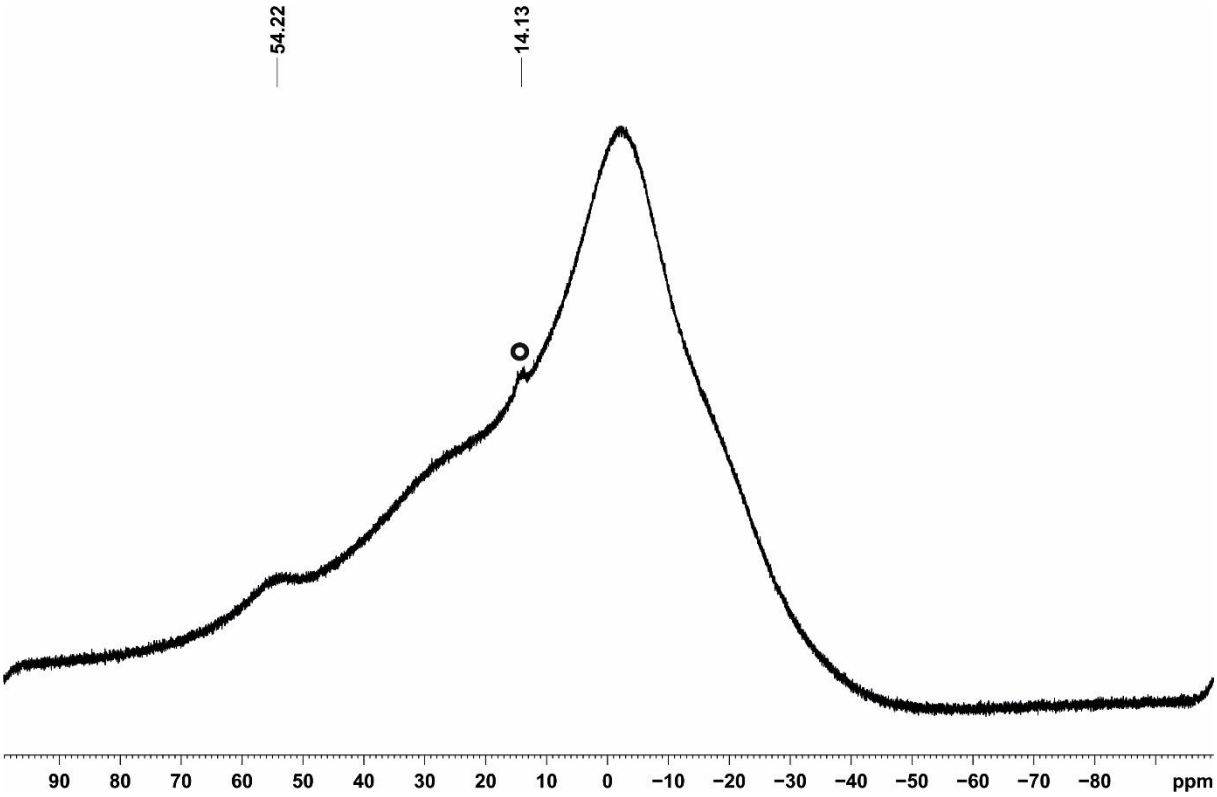


Figure S76. $^{11}B\{^1H\}$ NMR spectrum (128.38MHz, 300 K, C_6D_6) of **6**, °compound **2**.

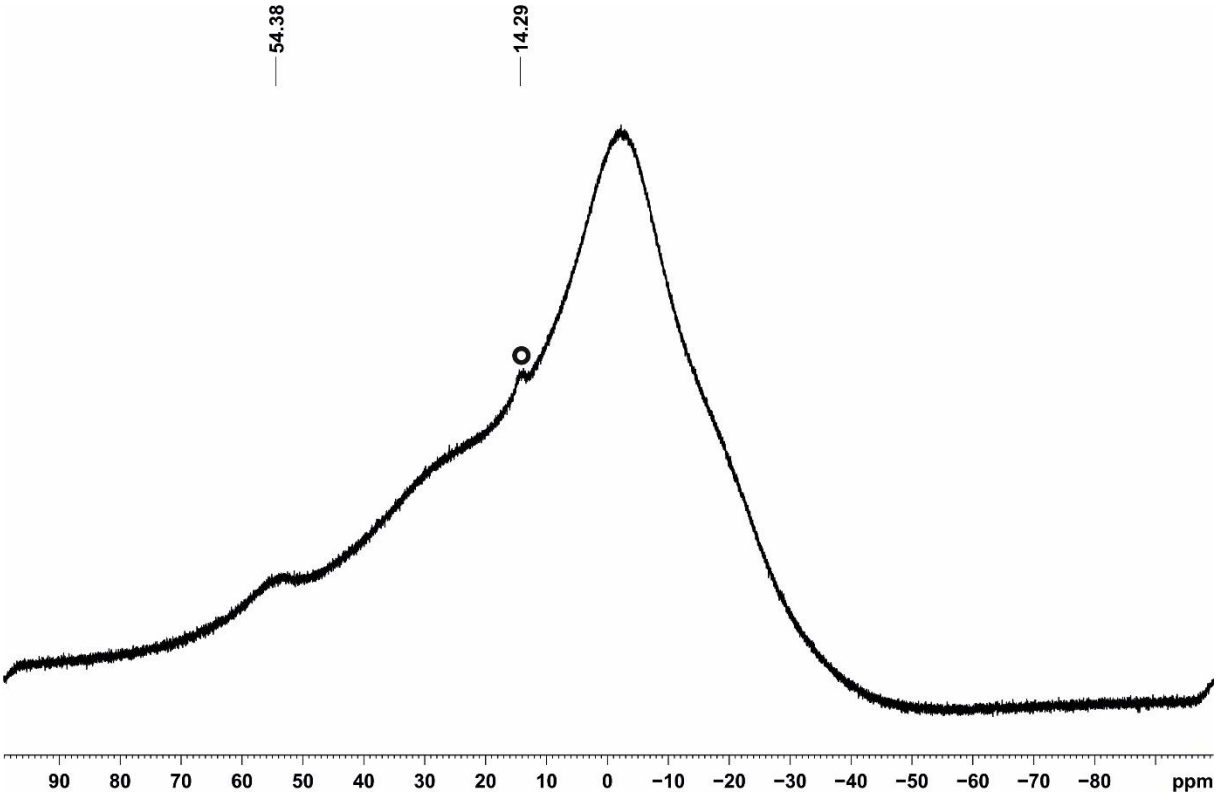


Figure S77. ^{11}B NMR spectrum (128.38MHz, 300 K, C_6D_6) of **6**, °compound **2**.

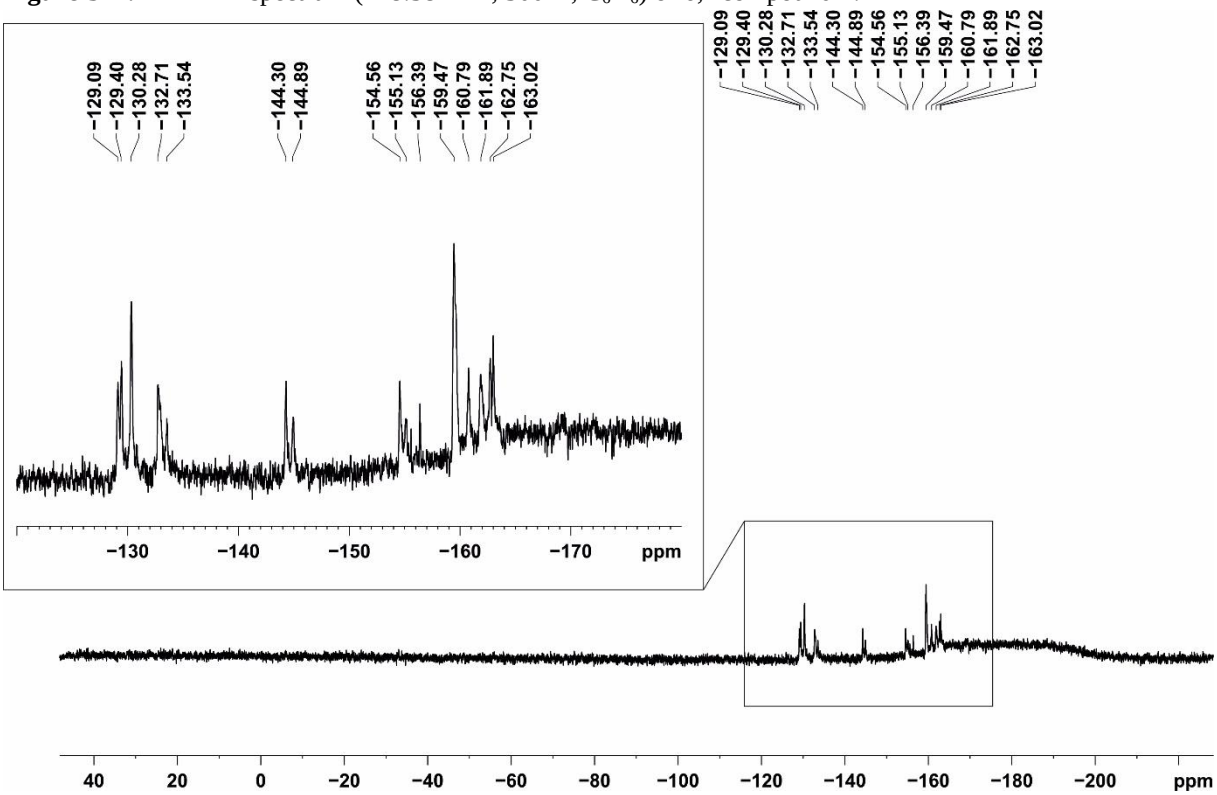


Figure S78. $^{19}F\{^1H\}$ NMR spectrum (376.50 MHz, 300 K, C_6D_6) of **6**.

S1.12 Variable temperature NMR monitoring – formation of 2

For the $^{31}P\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR monitoring, **1** (30 mg, 0.067 mmol, 1 equiv.) and $(C_6F_5)_2BCl$ (25 mg, 0.067 mmol, 1 equiv.) were dissolved in toluene-d_8 (0.5 mL) and loaded in a J. Young NMR tube. The sample was immediately cooled to 193 K and quickly loaded into the NMR device. $^{31}P\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra were recorded from 193 K to 300 K in a 30 minutes interval.

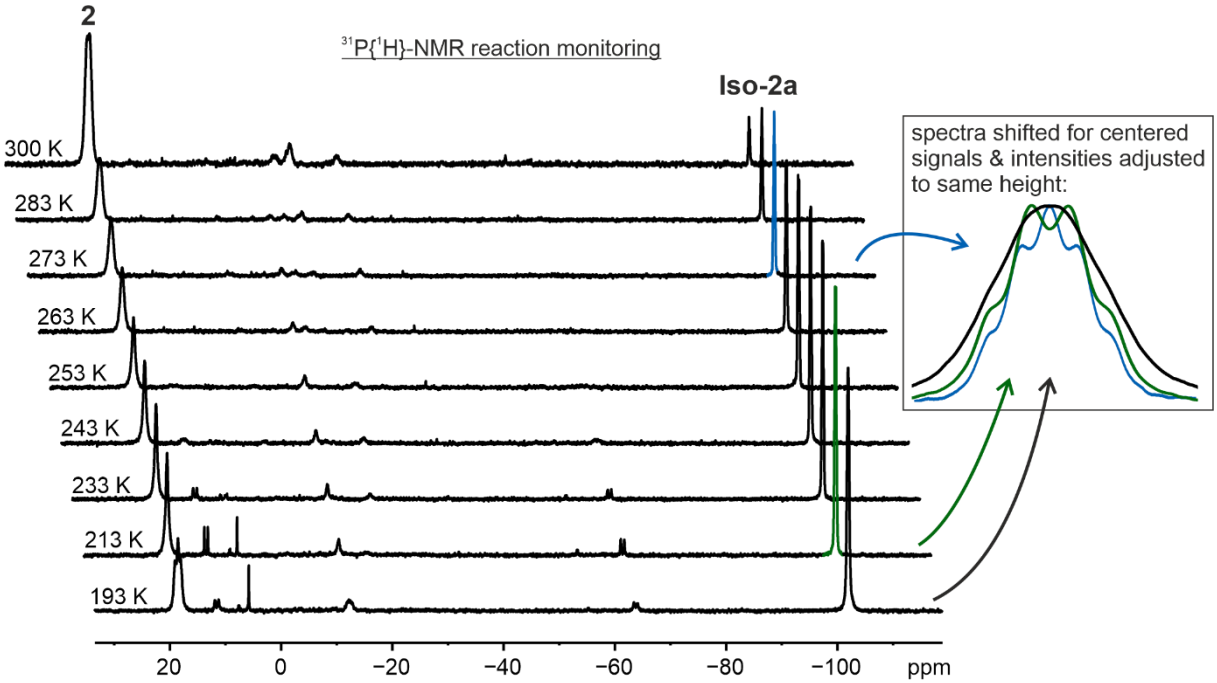


Figure S79. $^{31}P\{^{1}H\}$ NMR temperature monitoring of the reaction of **1** with $(C_6F_5)_2BCl$ (161.98 MHz, toluene-d_8, 256 scans recorded) starting from 193 K and warming up to 300 K. Formation of **2** at ca. δ = +18 ppm and formation of **Iso-2a** at ca. δ = −101 ppm. The spectra of 193 K, 213K and 273 K were selected and overlayed seperately in a way that the signals of **Iso-2a** are centered and adjusted in heigth to show that the overall signal width decreses with increasing temperature.

The shape of the ^{31}P signals of **2** and **Iso-2a** change upon temperature increase. At a temperature of 273 K, several ^{1}H and ^{19}F decoupling experiments were performed to investigate the line widths and the origin of the signal splitting (see Figure S80). For compound **2** no change in line width was observed upon ^{1}H and/or ^{19}F decoupling. This indicates a strong line broadening caused by the direct interaction with the quadrupolar isotopes ^{10}B and ^{11}B. Compound **Iso-2a** showed a quintet like splitting of its ^{31}P signal when ^{1}H decoupling was applied. Further ^{19}F decoupling parallel to ^{1}H decoupling led to an increase in signal intensity and a decrease in line width.

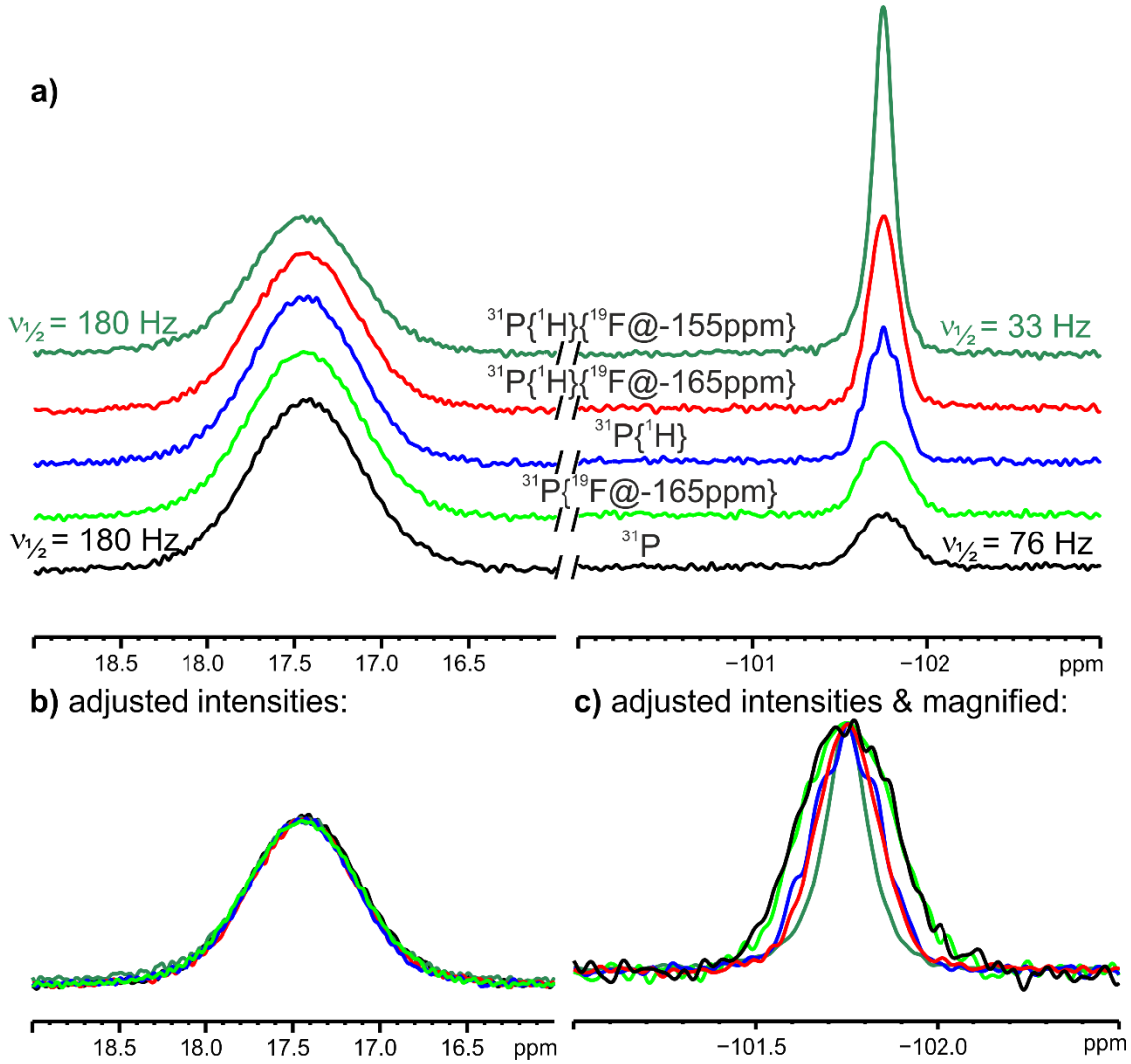


Figure S80. ^{31}P NMR decoupling experiments (zgigf2igf3) of the reaction of **1** with $(C_6F_5)_2BCl$ (242.87 MHz, TBI-F, 273 K, toluene-d_8): no decoupling (black), ^{19}F decoupling at -165 ppm (light green), ^{1}H decoupling (blue), simultaneous ^{1}H and ^{19}F decoupling at a fluorine frequency of -165 ppm (red) and simultaneous ^{1}H and ^{19}F decoupling at a fluorine frequency of -155 ppm (dark green). Waltz16 was used for ^{1}H and ^{19}F decoupling and 512 scans were recorded for each spectrum. A) stacked spectra, no intensity adjustment; b) overlayed spectra of the ^{31}P signal of compound **2**; the intensities were adjusted to the same hight to show that the line width doesn't change upon decoupling; c) overlayed spectra of the ^{31}P signal of compound **Iso-2a**; the intensities were adjusted to the same hight to show that the line width decreases upon decoupling.

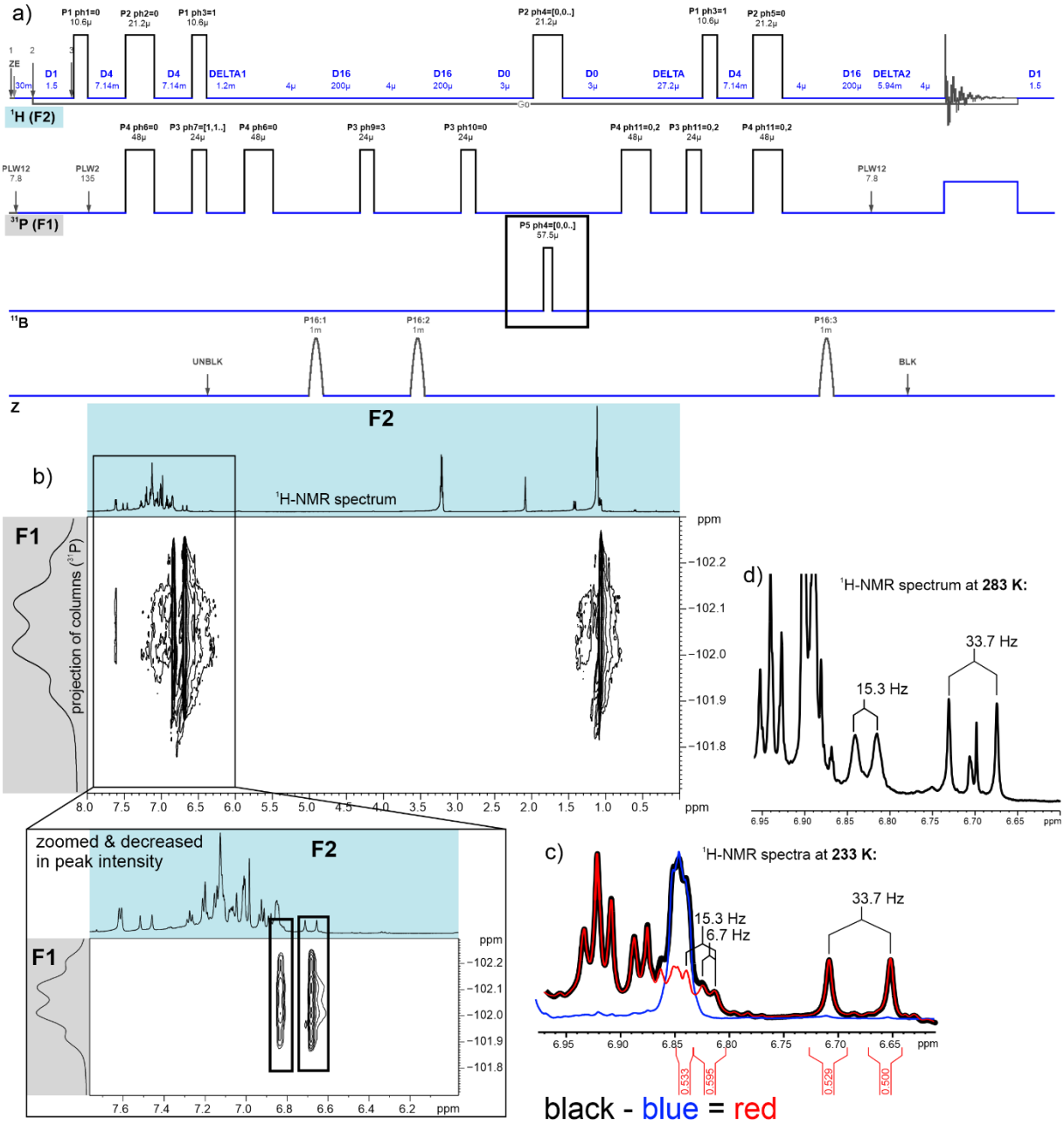


Figure S81. a) Pulse program of ^{1}H-^{31}P-HSQC{^{11}B & ^{1}H in F1 (indirect dimension); ^{31}P in F2 (direct dimension)} based on a standard HSQC (hsqcgpph) with an additional third channel (^{11}B) containing a 180° hard pulse (framed) to enable ^{11}B decoupling in the F1 dimension (^{31}P). b) ^{1}H-^{31}P-HSQC{^{11}B & ^{1}H in F1; ^{31}P in F2} during the reaction of **1** with $(C_6F_5)_2BCl$ (600 MHz spectrometer, toluene-d_8, cnst2=35 Hz) at 233 K. A stronger coupling of 33.7 Hz is observed to a proton at 6.68 ppm and a smaller coupling of 15.3 Hz to the proton at 6.83 ppm. c) Overlaid ^{1}H-NMR spectra of the reaction of **1** with $(C_6F_5)_2BCl$ (600.03 MHz, toluene-d_8) at 233 K (black), compound **2** in toluene-d_8 at 233 K (blue) and their difference (red). For the difference, the blue spectrum was shifted and adjusted in intensity so that the big signals at 6.85 ppm overlap as good as possible. The proton at 6.68 ppm shows next to the coupling of 15.3 Hz to ^{31}P another coupling of 6.7 Hz which disappears during temperature increase (see d) at 283 K). This coupling could be a $^6J_{HF}$ coupling being only observable at low temperature probably due to matching geometry between the coupling partners which may be disturbed upon temperature increase.

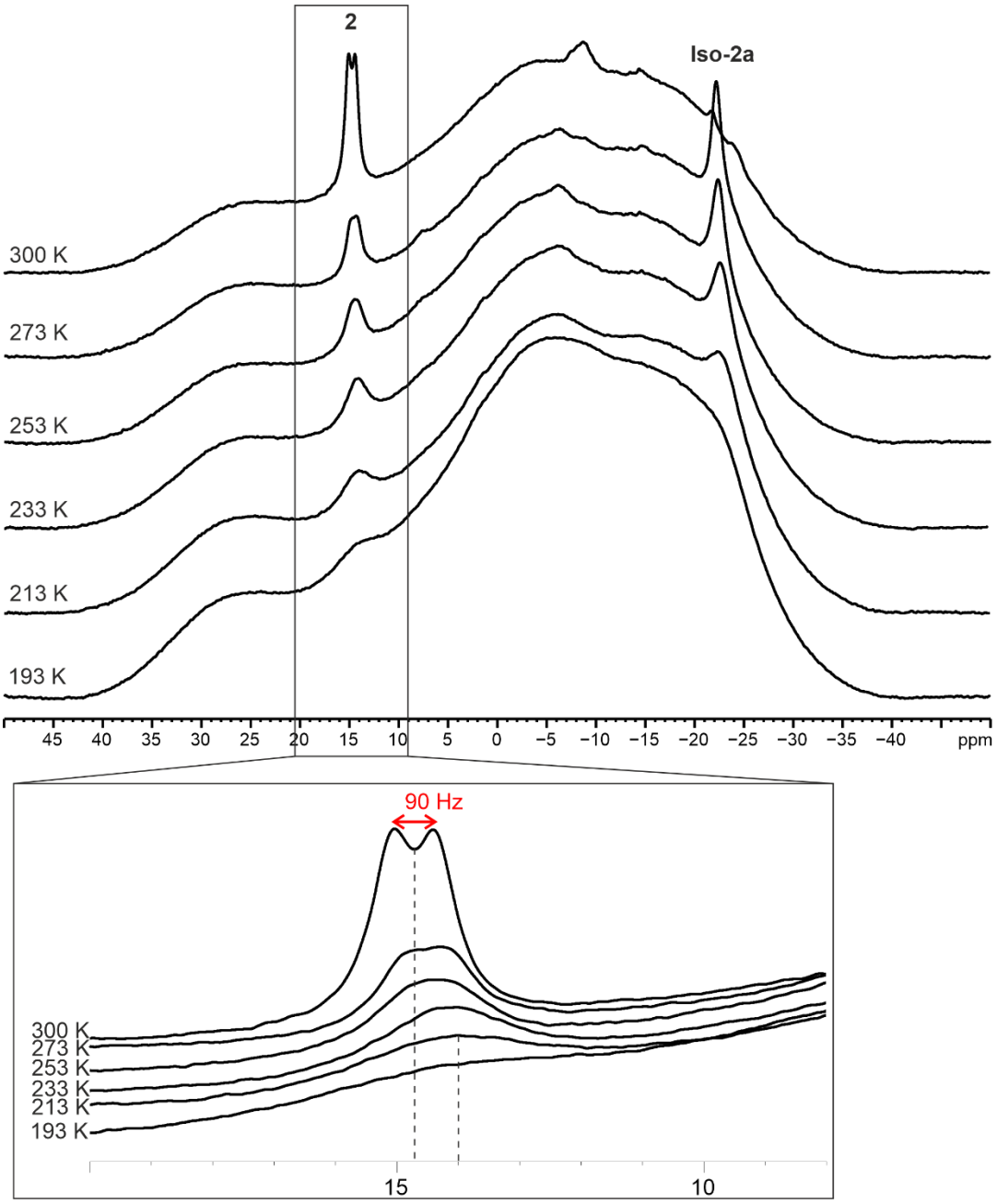


Figure S82. ^{11}B {^{1}H} VT NMR monitoring of the reaction of **1** with $(C_6F_5)_2BCl$ (128.38 MHz, 193 K to 300 K, toluene-d_8). The ^{11}B {^{1}H} NMR signal of **2** arises as a doublet at δ = +14.7 ppm with a coupling constant of $^{1}J_{PB}$ = 90 Hz probably to phosphorus at 300 K. indicating a small shift of the signal belonging to **2**. ^{11}B spectra were processed with WDW = EM and LB = 100 Hz and baseline corrected to remove the extremely broad overlapping peak of the NMR-tube.

S1.13 Variable temperature NMR monitoring of 2

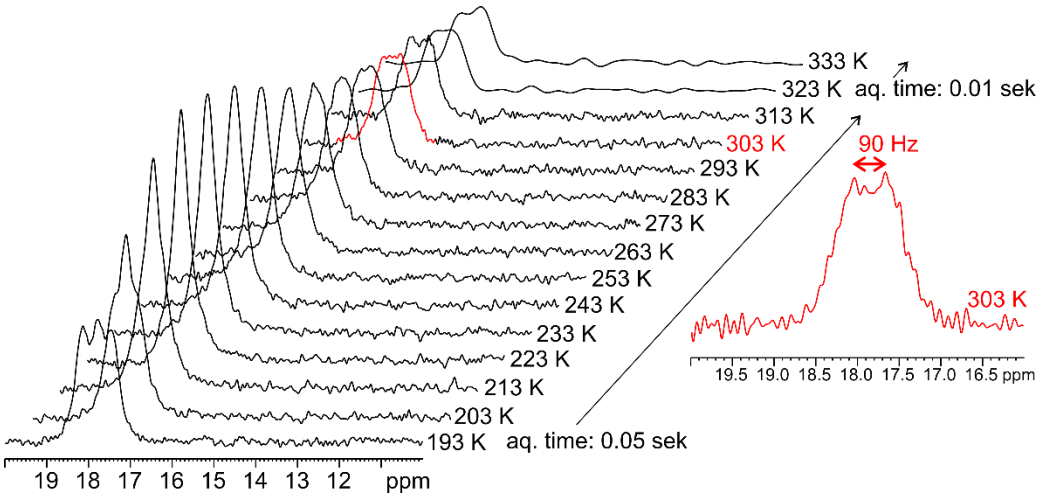


Figure S83. $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, toluene-d_8, 16 scans recorded) of **2** at different temperatures. Spectra were processed with an exponential function (EM), a linebroadening factor (LB) of 10 Hz. The red, zoomed spectrum was recorded at 303 K with 128 scans and processed with a gauss function (GM), LB = -10, GB = 0.6 and shows a big coupling constant of 90 Hz probably to boron (see Figure S82 for $^{11}B\{^{1}H\}$ spectrum at 300K with a similar coupling of 90 Hz).

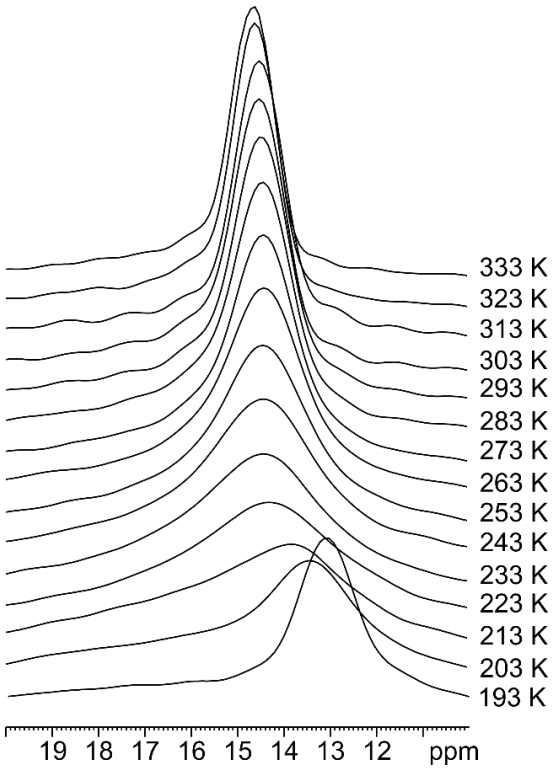


Figure S84. ^{11}B NMR monitoring (192.51 MHz, toluene-d_8) of **2** at different temperatures. Spectra were processed with an exponential function (EM), a line broadening factor (LB) of 10 Hz. An acquisition time of 0.006 seconds was adjusted, which is probably the reason why there is no splitting of the ^{11}B signal at 303K in this case. Upon temperature increase the signal first broadens and then narrows again, both accompanied by a downfield shift. A total downfield shift of around 1.4 ppm was observed between 193 K and 303 K. Under the assumption, that this is the result of a chemical exchange with **Iso-2d** (calculated shift of 48 ppm, see chapter S5), around 4% of **Iso-2d** would cause a downfield shift of 1.4 ppm of **2** ((1 – x)×13.13 ppm (**2** @193K) + x×48 ppm (**Iso-2d**) = 14.54 ppm (**2** @303K); → x=4%).

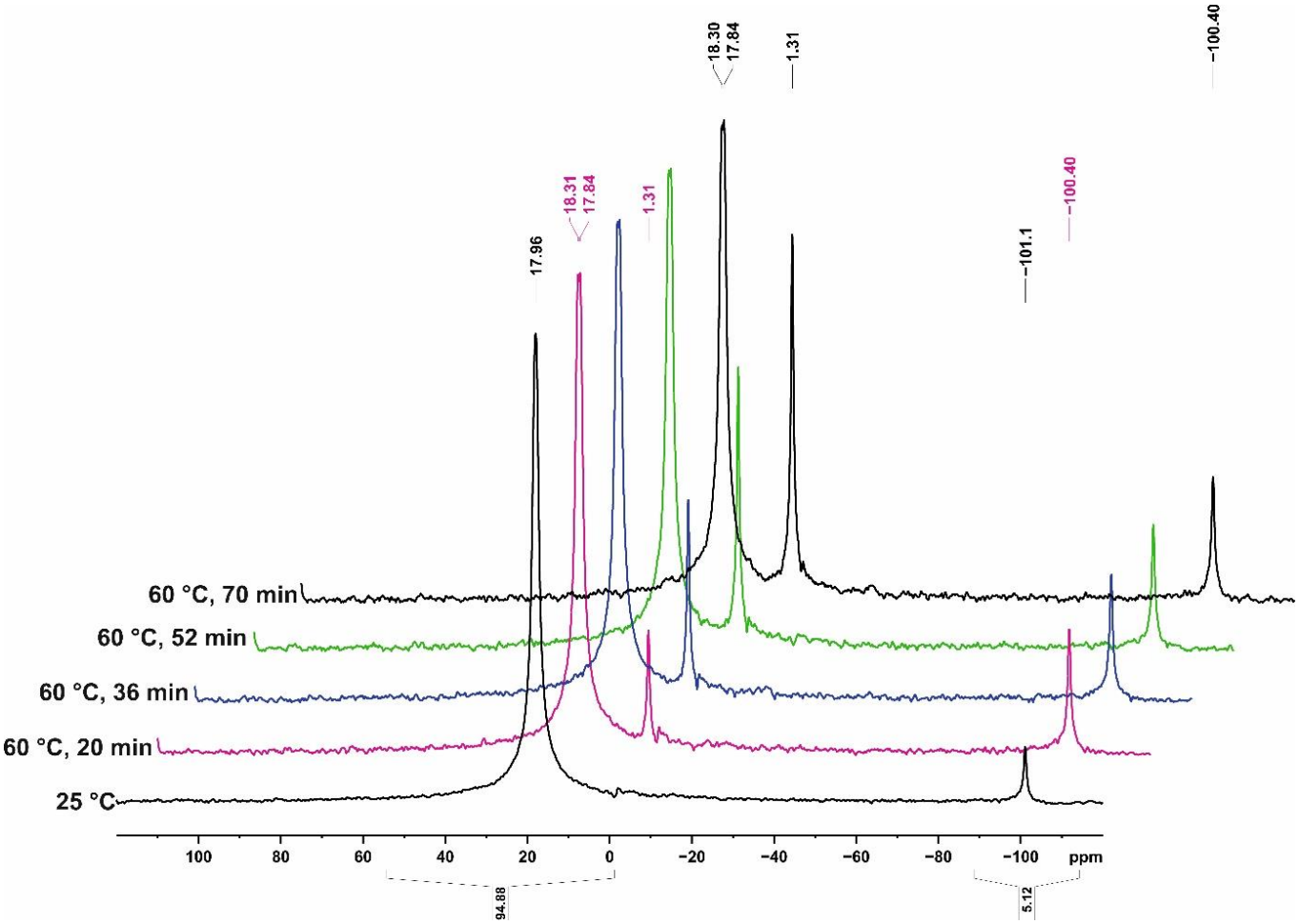


Figure S85. $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, 333 K, C_6D_6) of **2** at 60 °C. Spectra were processed with an exponential function (EM), a line broadening factor (LB) of 100 Hz and magnitude calculation (mc).

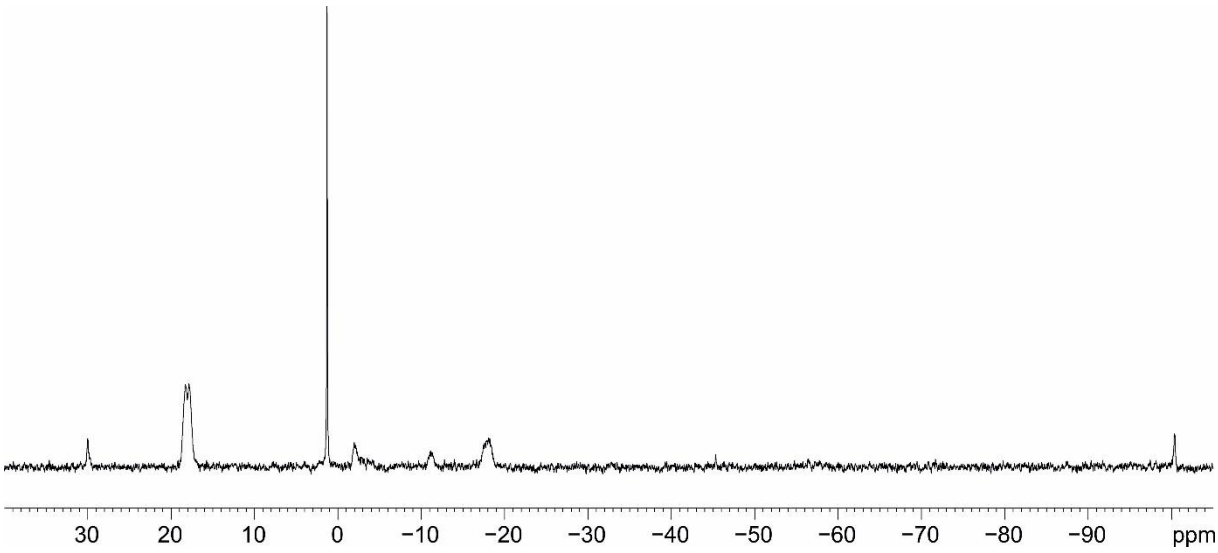


Figure S86. $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, 333 K, C_6D_6) of **2** at 60 °C after 21 h. It is noteworthy that additional species can be observed upon heating for longer time.

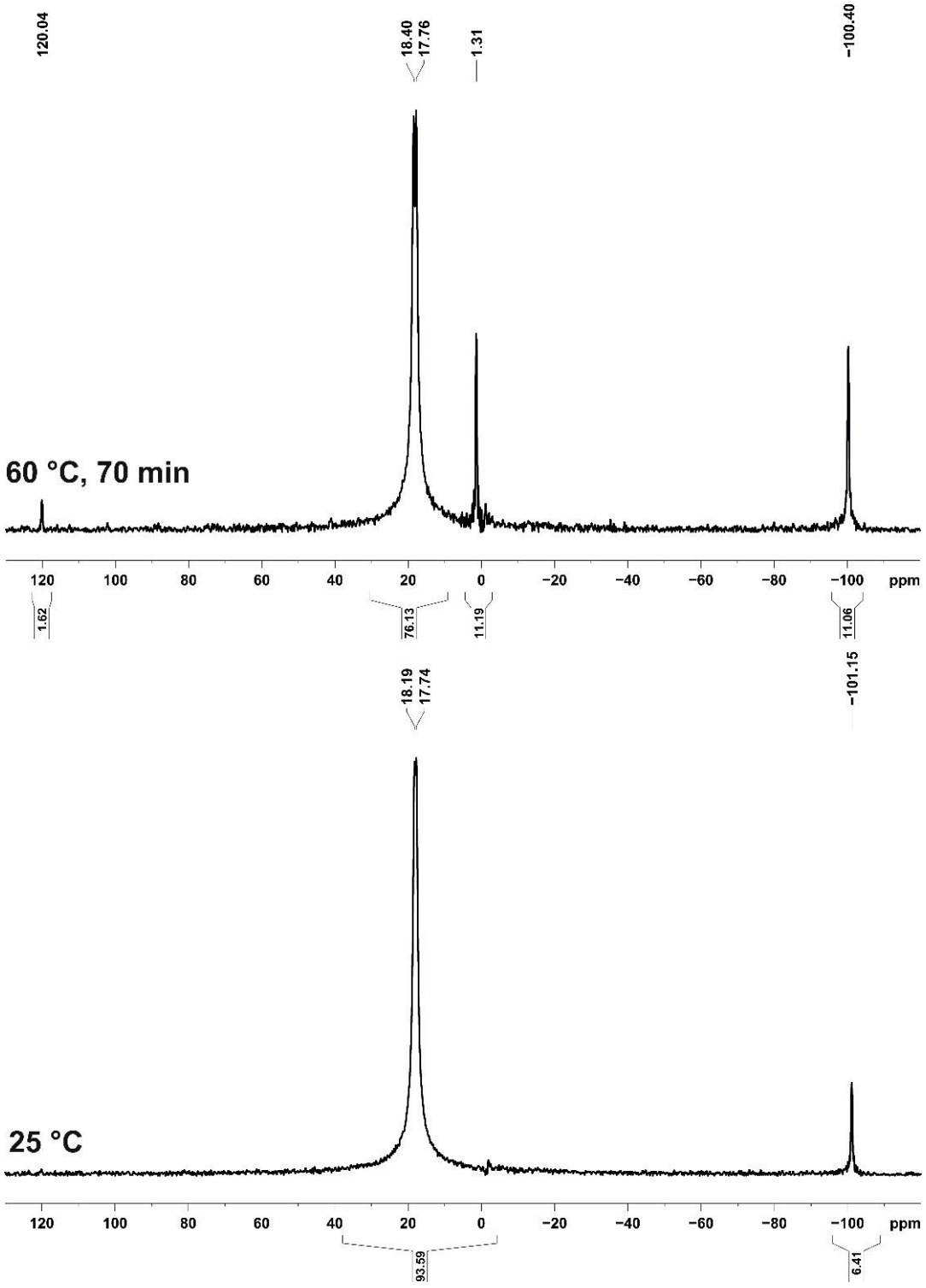


Figure S87. $^{31}P\{^{1}H\}$ NMR spectrum (242.87 MHz, 300 K (bottom) and 333 K (top), C_6D_6) of **2** for comparison.

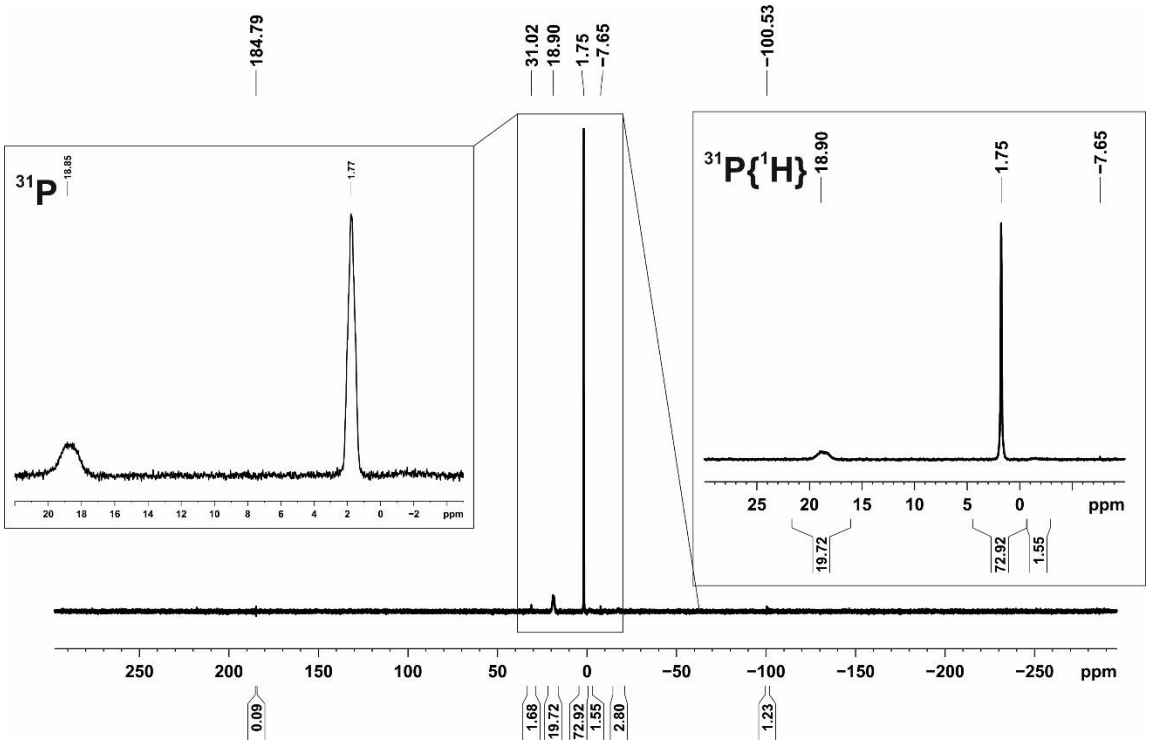


Figure S88. $^{31}P\{^{1}H\}$ NMR spectrum (242.87 MHz, 300 K, C_6D_6) of **2** after heating to 60 °C overnight; the spectrum was recorded at room temperature.

S1.14 Variable temperature NMR monitoring – formation of 5c

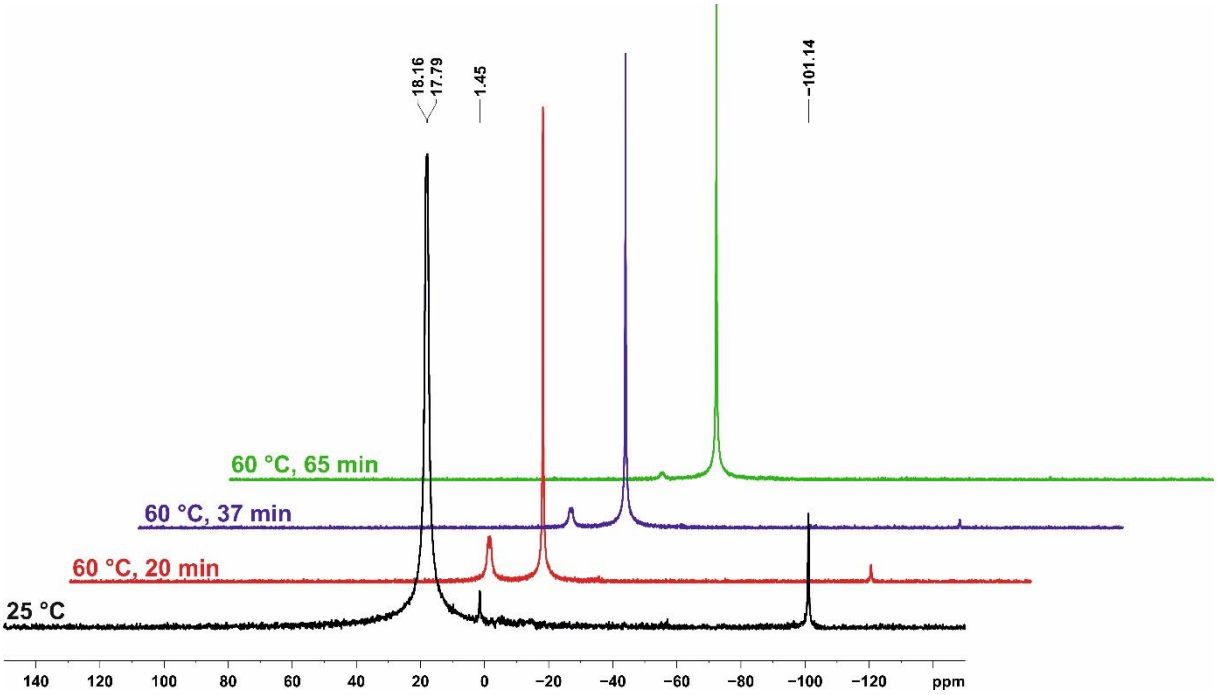


Figure S89. $^{31}P\{^{1}H\}$ VT NMR monitoring (242.87 MHz, 300 K and 333 K, C_6D_6 (0.5 mL)) of the reaction of **2** (50 mg, 0.073 mmol, 1 equiv.) with 4-(trifluoromethyl)phenylacetylene (24 µL, 0.073 mmol, 1 equiv.).

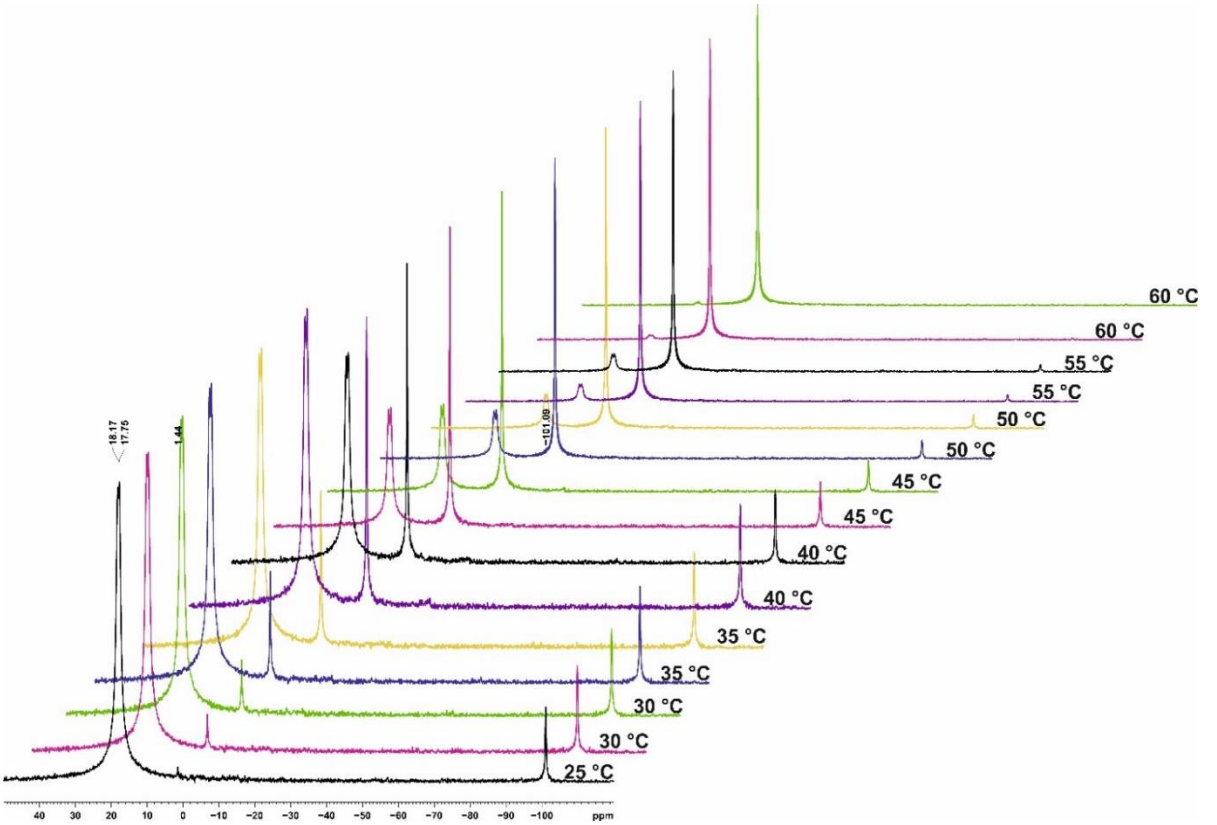


Figure S90. $^{31}P\{^{1}H\}$ VT NMR monitoring (242.87 MHz, 300 K to 333 K, C_6D_6 (0.5 mL)) of the reaction of **2** (50 mg, 0.073 mmol, 1 equiv.) with 4-(trifluoromethyl)phenylacetylene (24 µL, 0.073 mmol, 1 equiv.) in 5 °C steps (the reaction was kept at the certain temperature for 30 min each).

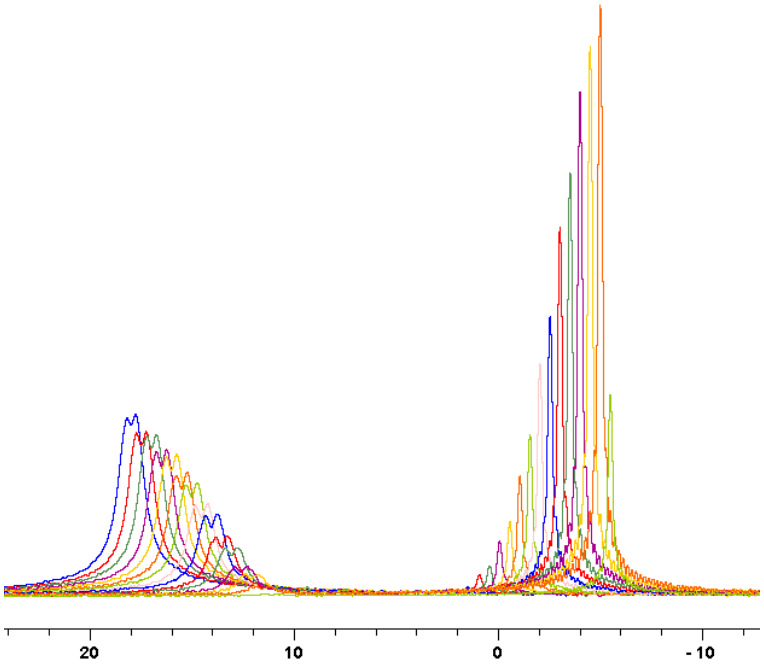


Figure S91. $^{31}P\{^{1}H\}$ VT NMR monitoring (242.87 MHz, 300 K to 333 K, C_6D_6 (0.5 L)) of the reaction of **2** (50 mg, 0.073 mmol, 1 equiv.) with 4-(trifluoromethyl)phenylacetylene (24 µL, 0.073 mmol, 1 equiv.) with 5 °C steps (reaction was kept 30 minutes at the certain temperature); decrease of starting material **2** (left) and increase of product **5b** (right). Spectra are overlaid with a horizontal offset and no vertical offset.

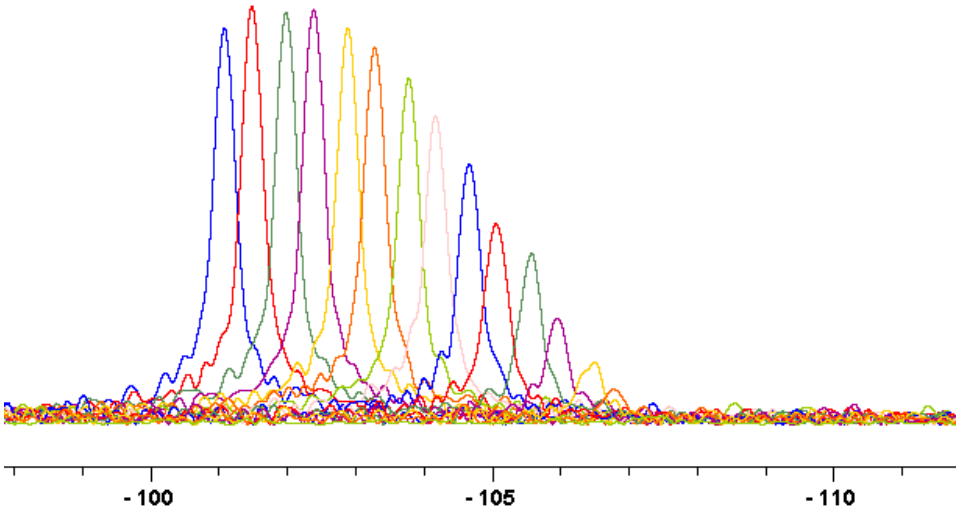


Figure S92. $^{31}P\{^{1}H\}$ VT NMR monitoring (242.87 MHz, 300 K to 333 K, C_6D_6 (0.5 mL)) of the reaction of **2** (50 mg, 0.073 mmol, 1 equiv.) with 4-(trifluoromethyl)phenylacetylene (24 µL, 0.073 mmol, 1 equiv.) with 5 °C steps (reaction was kept 30 minutes at the certain temperature); decrease of compund **Iso-2a**. Spectra are overlaid with a horizontal offset and no vertical offset.

S1.15 Reaction of 6 with 4-(trifluoromethyl)phenylacetylene

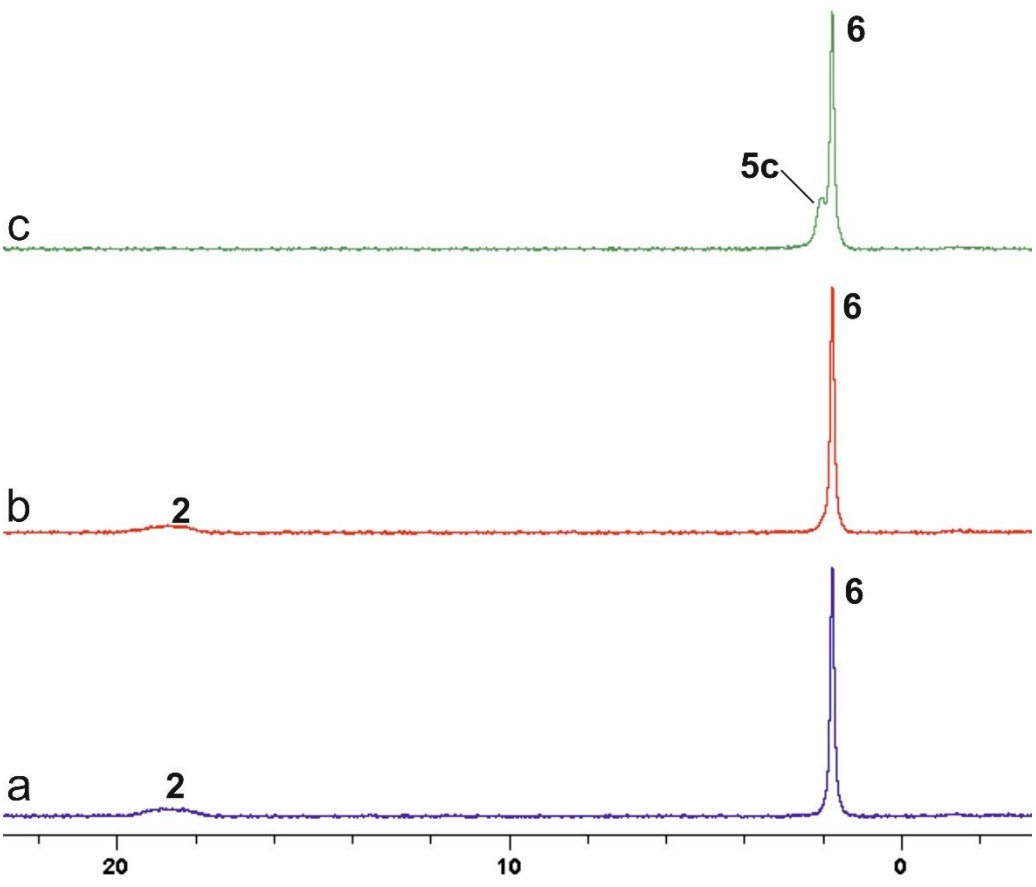


Figure S93. $^{31}P\{^{1}H\}$ NMR monitoring (161.98 MHz, 300 K, C_6D_6 (0.5 mL)) of the reaction of **6** with 4-(trifluoromethyl)phenylacetylene. a) **2** (50 mg, 0.073 mmol, 1 equiv.) was heated to 60 °C overnight to form **6**; b) 4-(trifluoromethyl)phenylacetylene (24 µL, 0.073 mmol, 1 equiv.) was added to the reaction mixture of a) at room temperature – no reaction observed; c) the mixture of b) was heated to 60 °C – reaction of **2** with alkyne leading to the formation of **5c**; no change for **6** observable.

S2 UV-vis Spectra

S2.1 UV-Vis spectrum of **2**

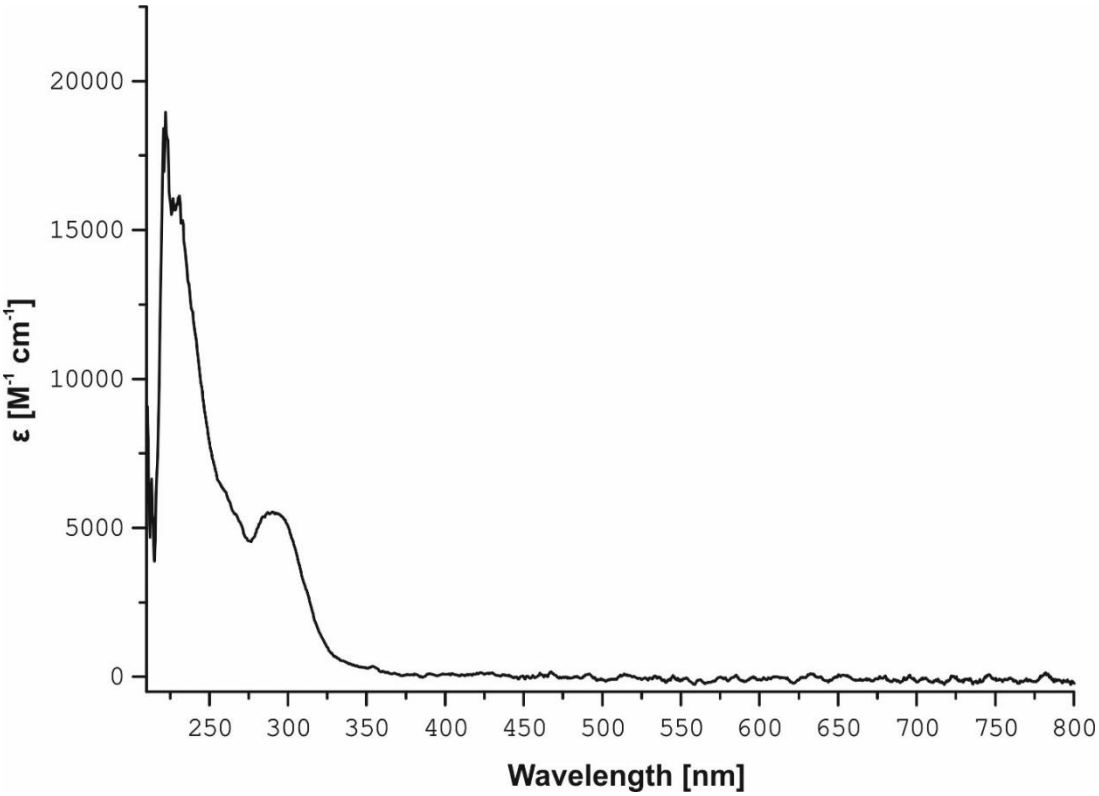


Figure S94. UV/vis spectrum of **2** in *n*-hexane.

S2.2 UV-Vis spectra of **3a – 3e**

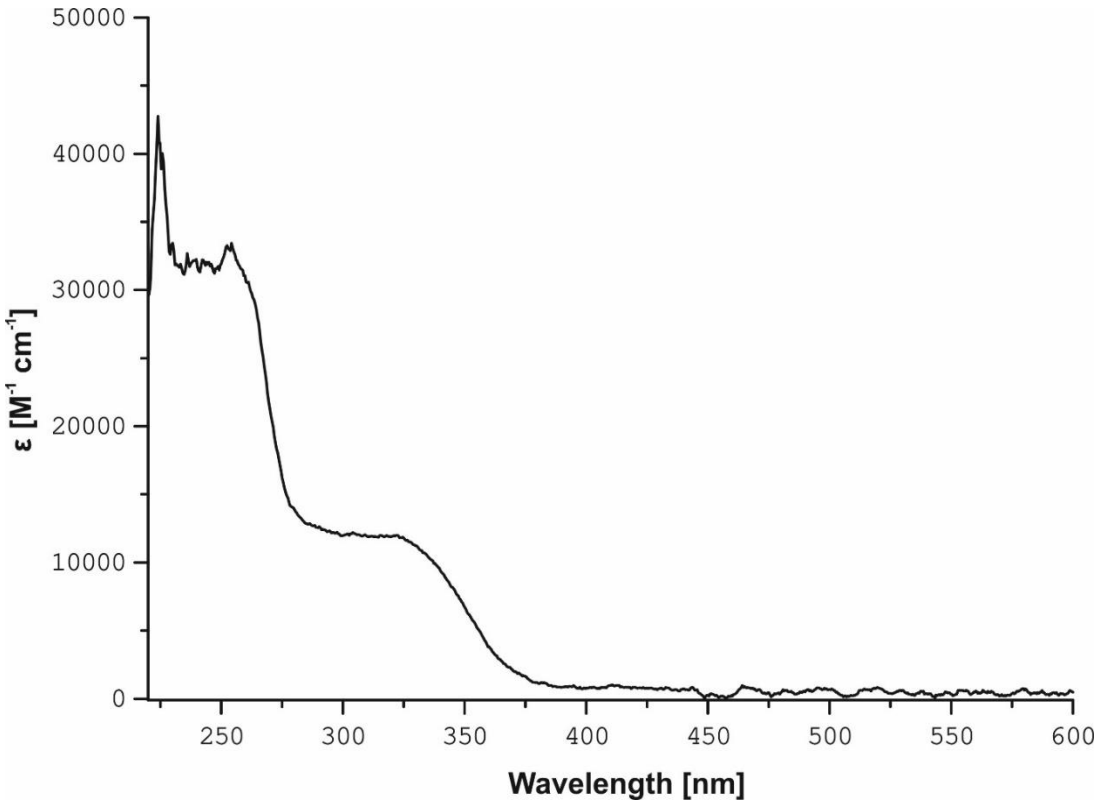


Figure S95. UV/vis spectrum of **3a** in *n*-hexane.

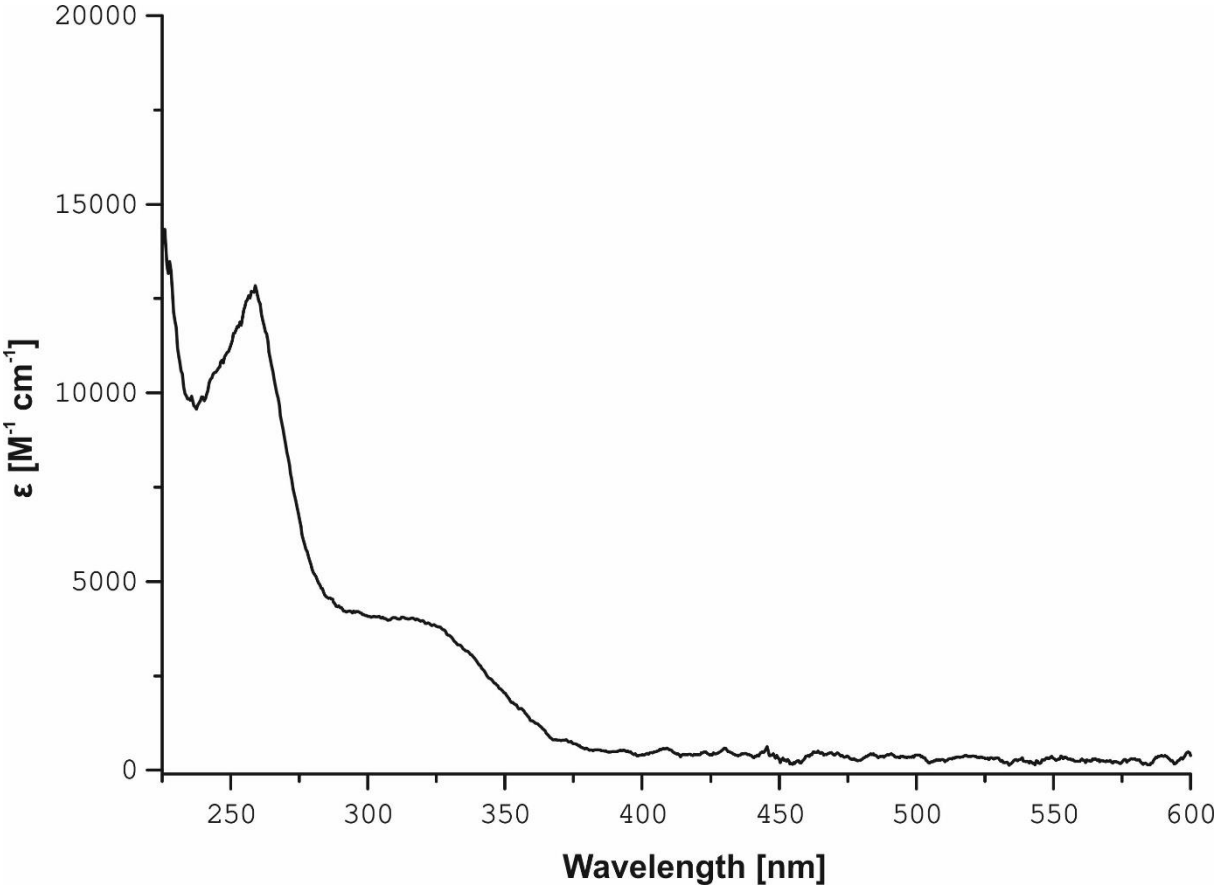


Figure S96. UV/vis spectrum of **3b** in *n*-hexane.

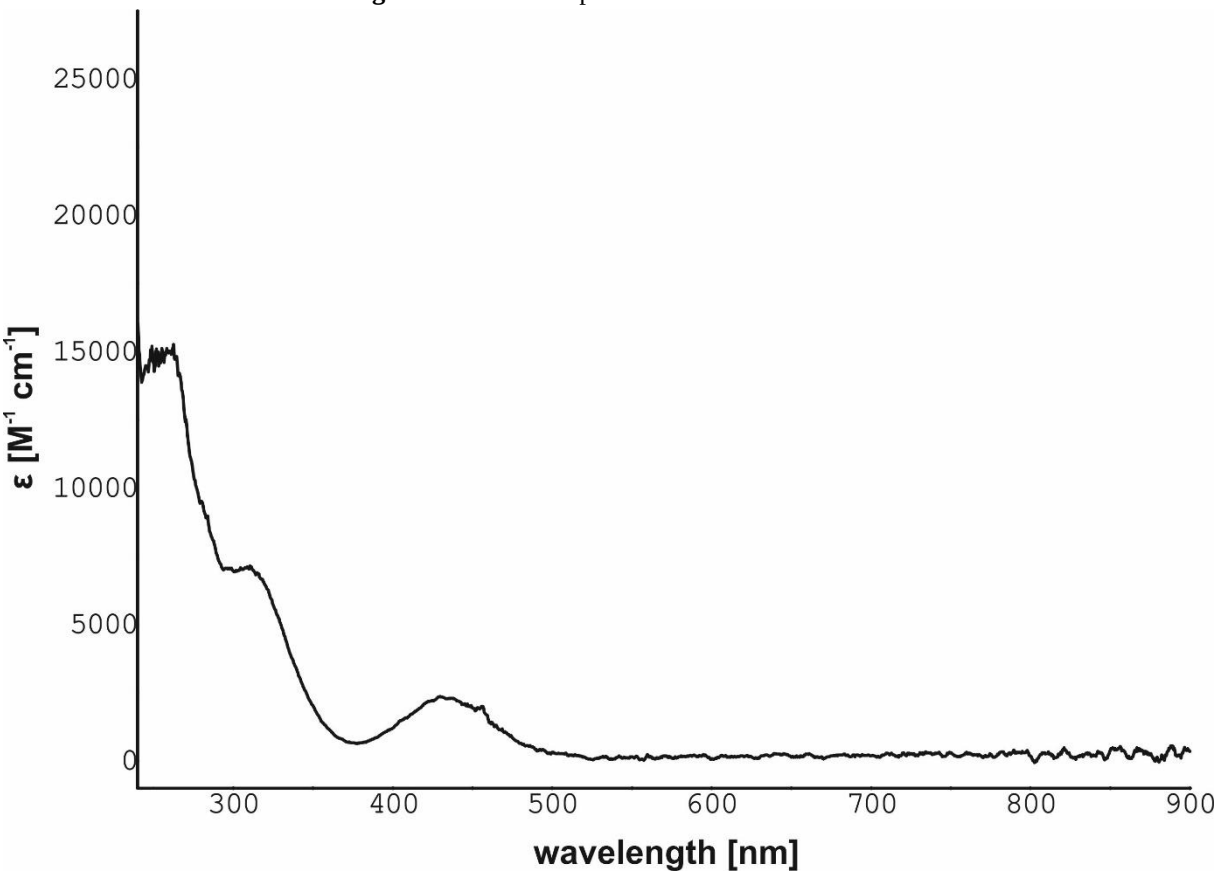


Figure S97. UV/vis spectrum of **3c** in *n*-hexane.

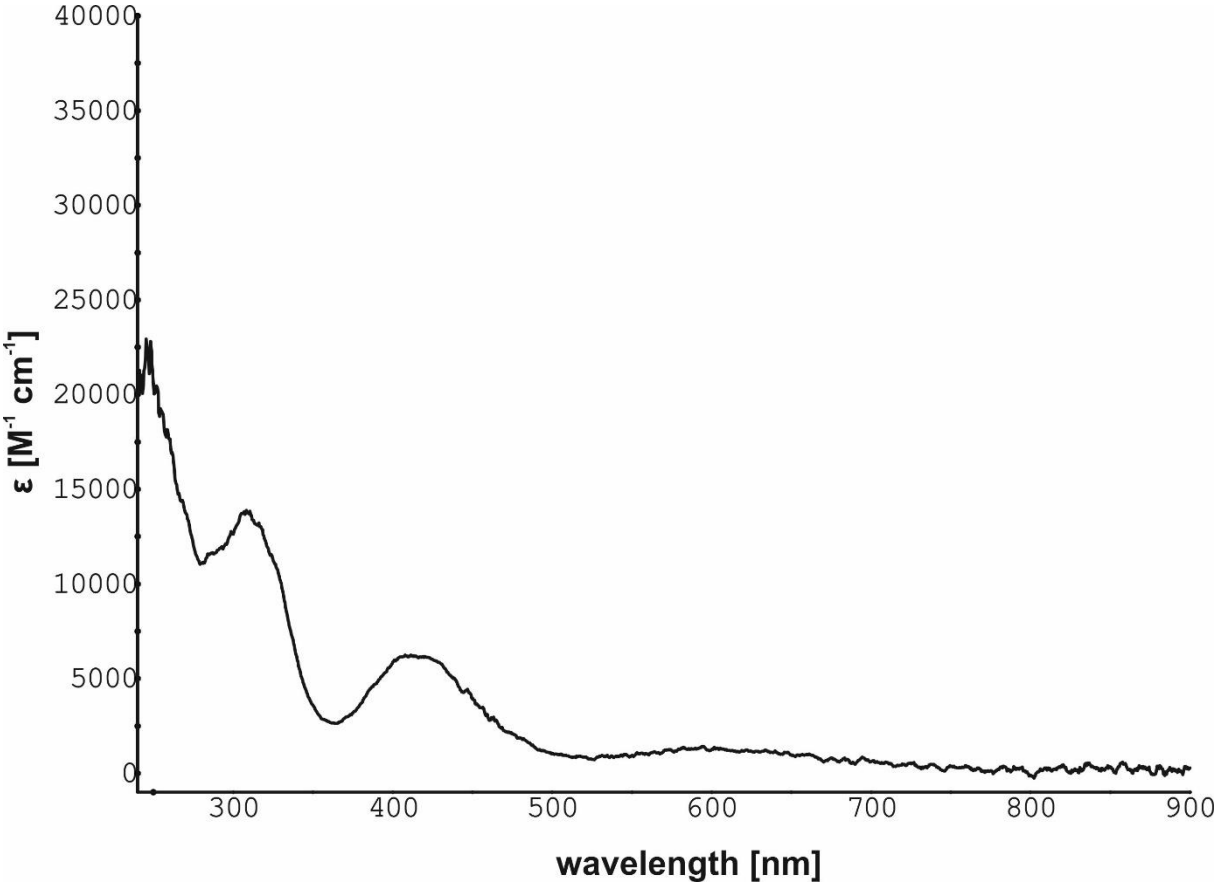


Figure S98. UV/vis spectrum of **3d** in *n*-hexane.

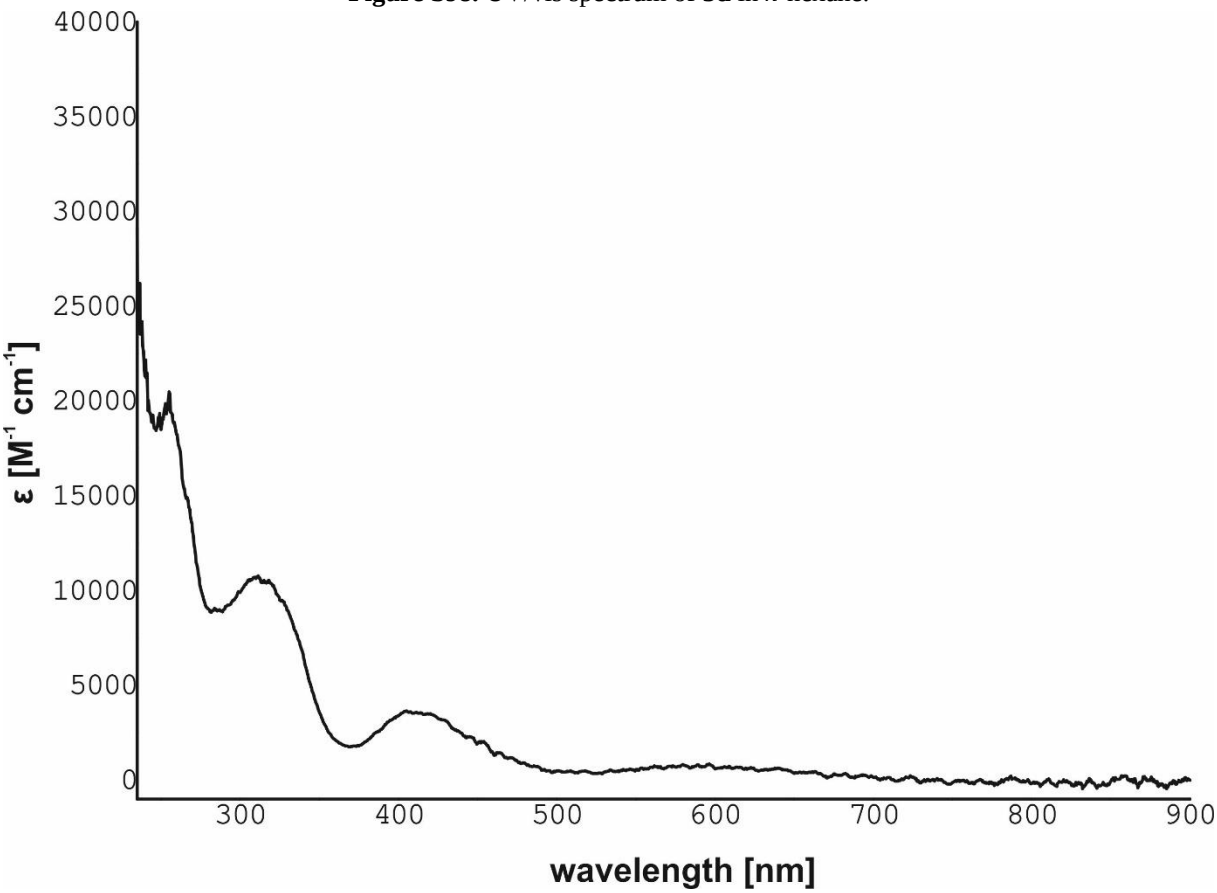


Figure S99. UV/vis spectrum of **3e** in *n*-hexane.

S2.3 UV-Vis spectrum of **4**

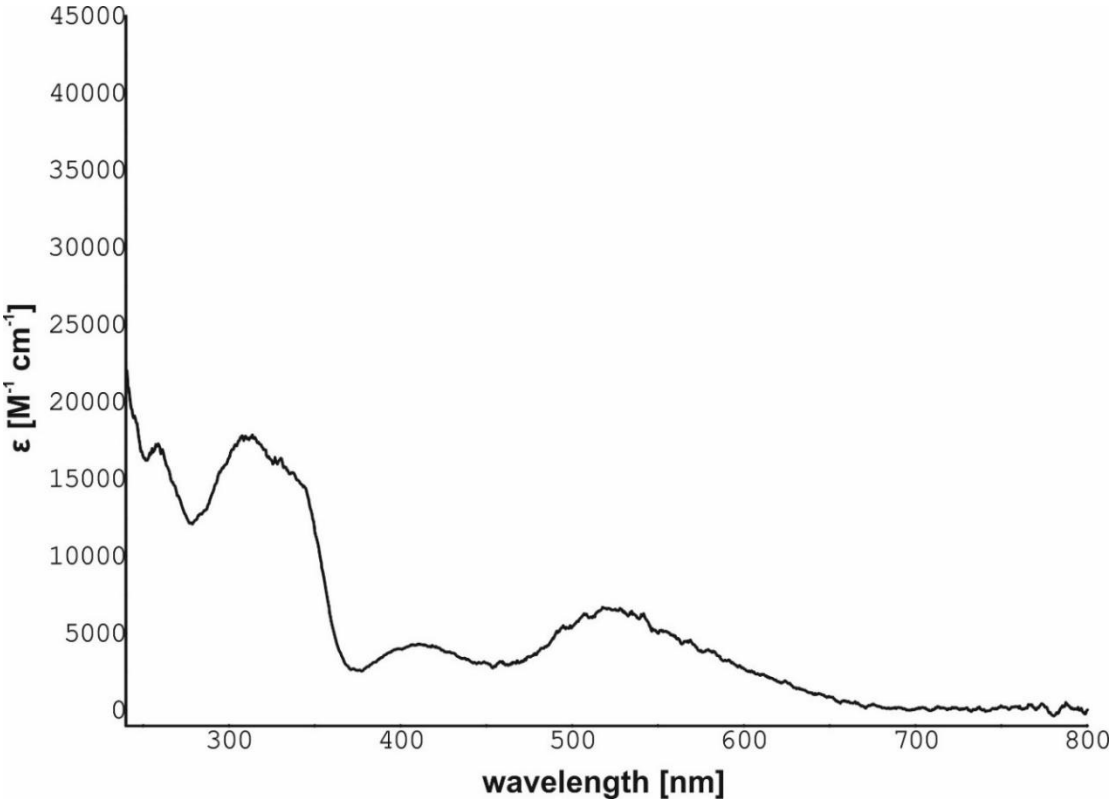


Figure S100. UV/vis spectrum of **4** in diethyl ether.

S2.4 UV-Vis spectra of **5a – 5c**

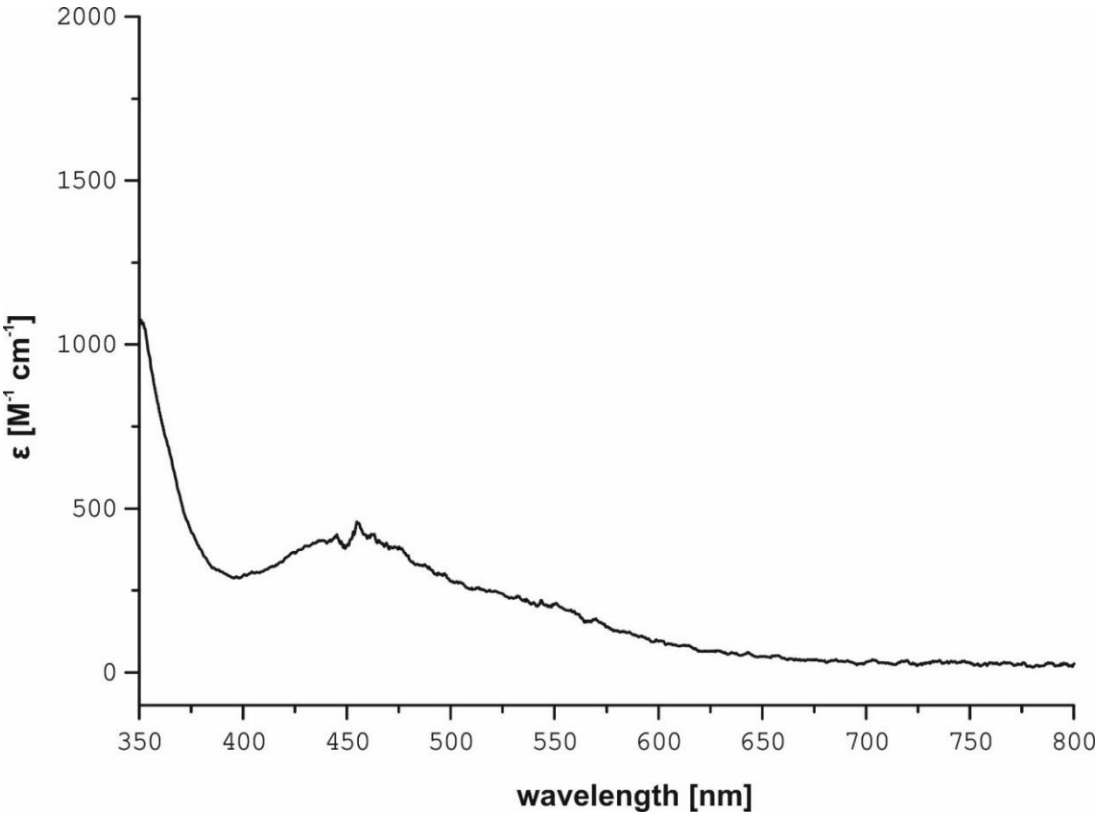


Figure S101. UV/vis spectrum of **5a** in diethyl ether.

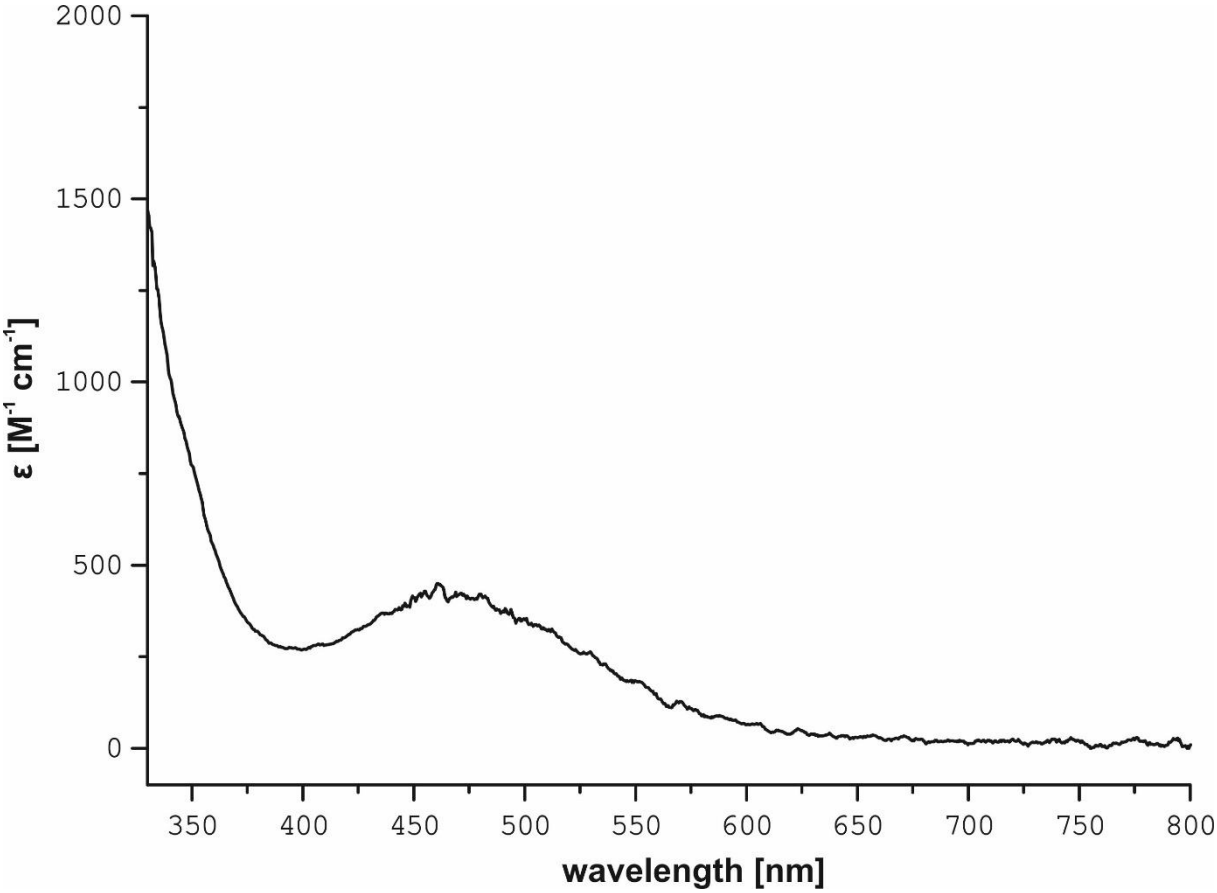


Figure S102. UV/vis spectrum of **5b** in diethyl ether.

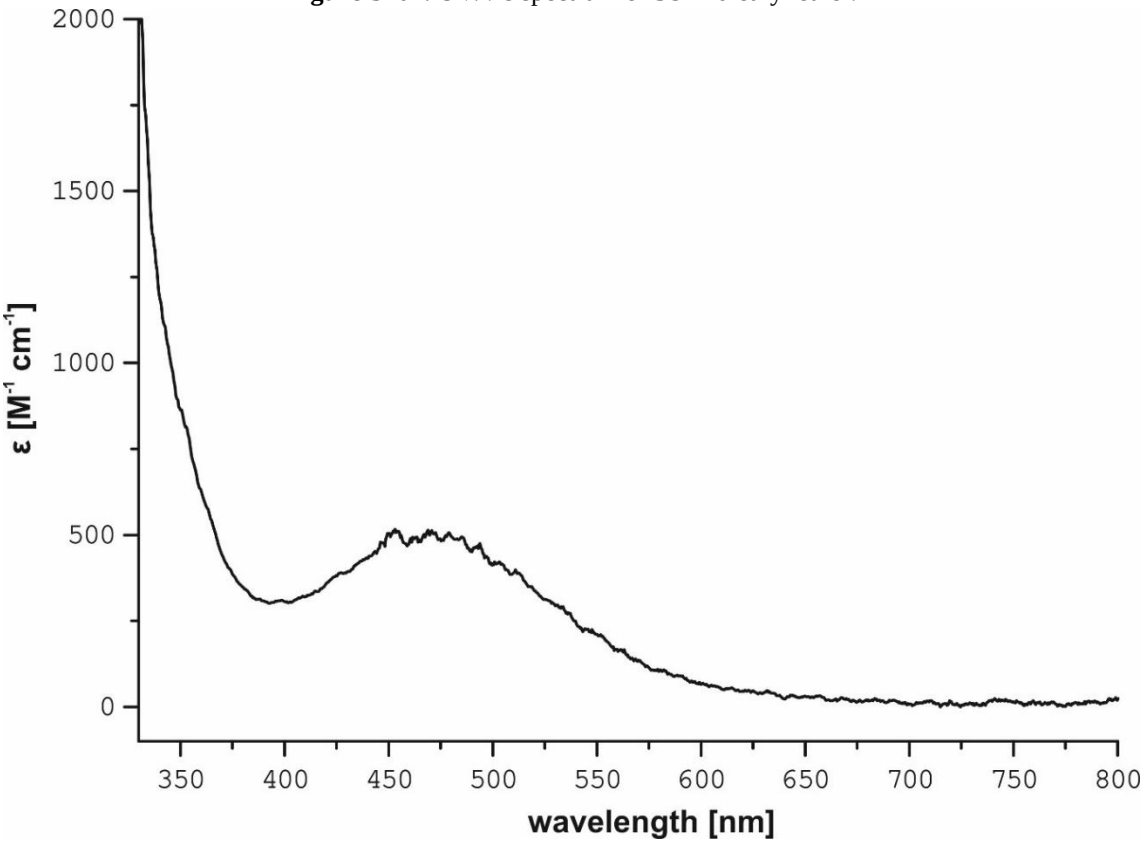


Figure S103. UV/vis spectrum of **5c** in diethyl ether.

S2.5 UV-Vis spectrum of **6**

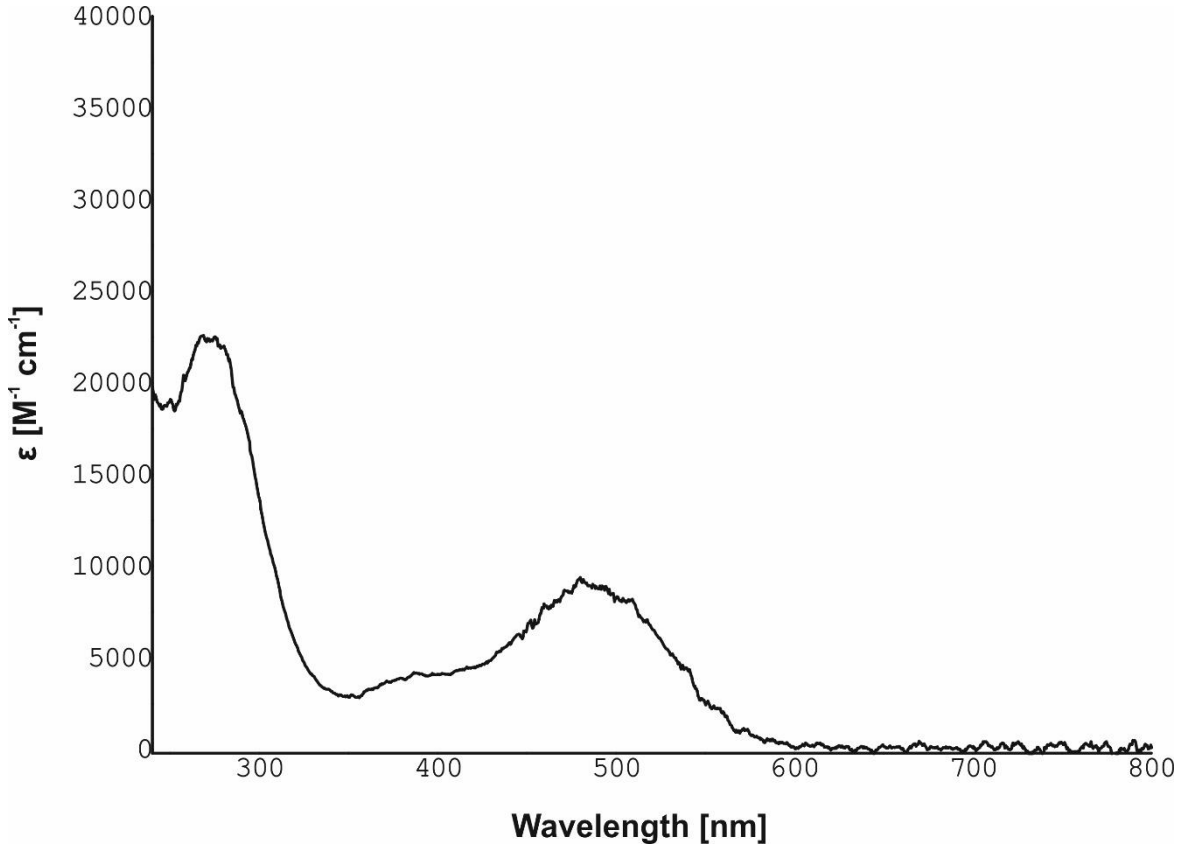


Figure S104. UV/vis spectrum of **6** in diethyl ether.

S3 X-ray crystallography

Table S1. Crystallographic data and structure refinement of **2**, **3a**, **3b** and **3c**.

	2	**3a**	**3b**	**3c**
Empirical formula	$C_{36}H_{20}BF_{10}P$	$C_{38}H_{23}BF_{10}NP$	$C_{43}H_{25}BF_{10}NP$	$C_{43}H_{23}BBr_2F_{10}NP$
Formula weight / g·mol^{-1}	684.30	725.35	787.42	945.22
Temperature / K	122.99(10)	123.01(10)	123.01(10)	123.01(10)
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic
Space group	$P2_1/n$	$P4_2/n$	P21/c	I2/a
a / Å	11.5536(3)	29.89394(10)	18.0931(2)	30.7174(4)
b / Å	15.1768(3)	29.89394(10)	14.00200(10)	10.06220(10)
c / Å	17.4069(4)	7.14392(5)	15.5885(2)	27.2799(3)
α /°	90	90	90	90
β /°	100.549(2)	90	115.278(2)	90.1630(10)
γ /°	90	90	90	90
V / Å^3	3000.66(12)	6384.15(6)	3571.03(8)	8431.76(17)
Z	4	8	4	8
ρ_{calc} / g cm^{-1}	1.515	1.509	1.465	1.489
μ / mm^{-1}	1.620	1.567	1.451	3.468
F(000)	1384.0	2944.0	1600.0	3744.0
Crystal size / mm^3	0.261 × 0.083 × 0.069	0.156 × 0.092 × 0.08	0.382 × 0.235 × 0.107	0.434 × 0.177 × 0.122
Radiation / Å	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection /°	7.786 to 147.71	8.366 to 147.282	8.312 to 152.648	8.658 to 147.448
Diffractometer	SuperNova	GV1000, TitanS2	GV1000, TitanS2	SuperNova
Index ranges	-10 ≤ h ≤ 14, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	-37 ≤ h ≤ 36, -37 ≤ k ≤ 36, -8 ≤ l ≤ 8	-22 ≤ h ≤ 22, -17 ≤ k ≤ 17, -16 ≤ l ≤ 19	-35 ≤ h ≤ 37, -9 ≤ k ≤ 12, -33 ≤ l ≤ 33
Reflections collected	22315	135858	48454	30607
Independent reflections	5997 [R_{int} = 0.0582, R_{sigma} = 0.0484]	6424 [R_{int} = 0.0309, R_{sigma} = 0.0087]	7428 [Rint = 0.0236, Rsigma = 0.0133]	8414 [Rint = 0.0193, Rsigma = 0.0151]
Data/restraints/parameters	5997/0/434	6424/384/493	7428/0/506	8414/0/525
Goodness-of-fit on F^2	1.039	1.100	1.173	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1220	R_1 = 0.0405, wR_2 = 0.1023	R1 = 0.0493, wR2 = 0.1208	R1 = 0.0332, wR2 = 0.0851
Final R indexes [all data]	R_1 = 0.0576, wR_2 = 0.1305	R_1 = 0.0413, wR_2 = 0.1030	R1 = 0.0499, wR2 = 0.1210	R1 = 0.0345, wR2 = 0.0861
Largest diff. peak/hole / e Å^{-3}	0.69/-0.55	0.90/-0.49	0.34/-0.27	1.14/-0.82

Table S2. Crystallographic data and structure refinement of **4**, **5b** and **5c**.

	4	**5b**	**5c**
Empirical formula	$C_{40}H_{28}BF_{10}N_2P$	$C_{48}H_{32}BF_{13}P$	$C_{47}H_{32}BBrF_{10}P$
Formula weight	768.42	897.51	908.41
Temperature/K	123.01(10)	123.00(10)	123.01(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	$P2_1/c$	P-1
a/Å	31.7032(5)	20.6272(9)	10.4317(4)
b/Å	11.20500(10)	10.2314(3)	19.8207(9)
c/Å	19.2458(3)	21.1124(8)	21.0457(7)
α/°	90	90	108.346(4)
β/°	103.612(2)	110.769(4)	90.030(3)
γ/°	90	90	100.828(3)
Volume/Å^3	6644.74(17)	4166.1(3)	4048.5(3)
Z	8	4	4
ρ_{calc}g/cm^3	1.536	1.431	1.490
μ/mm^{-1}	1.549	1.414	2.465
F(000)	3136.0	1828.0	1836.0
Crystal size/mm^3	0.28 × 0.219 × 0.189	0.19 × 0.125 × 0.039	0.157 × 0.069 × 0.057
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.396 to 147.074	8.494 to 151.654	7.502 to 147.466
Diffractometer	SuperNova	SuperNova	SuperNova
Index ranges	-39 ≤ h ≤ 37, -13 ≤ k ≤ 11, -19 ≤ l ≤ 23	-25 ≤ h ≤ 25, -8 ≤ k ≤ 12, -25 ≤ l ≤ 26	-12 ≤ h ≤ 12, -24 ≤ k ≤ 20, -23 ≤ l ≤ 26
Reflections collected	13708	17907	31902
Independent reflections	6496 [R_{int} = 0.0141, R_{sigma} = 0.0175]	8469 [R_{int} = 0.0401, R_{sigma} = 0.0515]	15939 [R_{int} = 0.0826, R_{sigma} = 0.0943]
Data/restraints/parameters	6496/0/490	8469/75/598	15939/0/1085
Goodness-of-fit on F^2	1.016	1.121	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0790	R_1 = 0.0768, wR_2 = 0.1919	R_1 = 0.1508, wR_2 = 0.4075
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0803	R_1 = 0.0948, wR_2 = 0.2017	R_1 = 0.1726, wR_2 = 0.4221
Largest diff. peak/hole / e Å^{-3}	0.34/-0.27	0.53/-0.49	2.45/-1.29

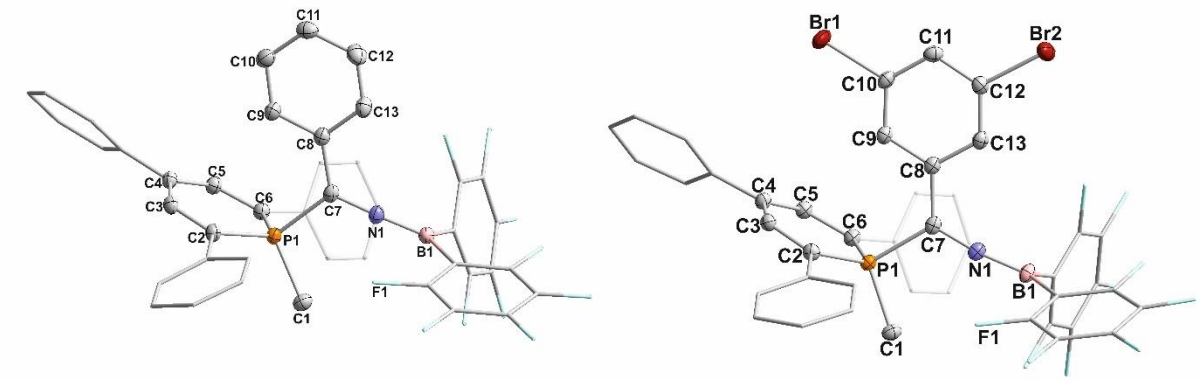


Figure S105. Solid state molecular structures of **3b** and **3c**. Ellipsoids are drawn at the 40% probability level; H atoms are omitted for clarity; phenyl and C_6F_5 groups were shown in wireframe for clarity.

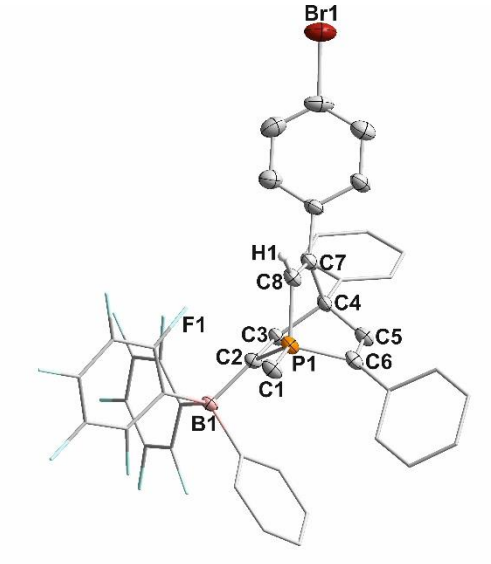


Figure S106. Solid state molecular structure of **5c**. Ellipsoids are drawn at the 40% probability level; H atoms are omitted for clarity; phenyl and C_6F_5 groups were shown in wireframe for clarity; *n*-hexane molecule was omitted for clarity; the crystal of **5c** contained two second crystallographically independent molecules with very similar structural parameters; only one of these molecules is shown. It has to be mentioned that the structure of **5c** exhibits high R_1 = 15.08 % and wR_2 = 42.2 1% due to the bad crystal quality. The solid state molecular structure of **5c** represents an additional proof for the formation of the phosphabarrelene architecture in the reaction of **2** with phenylacetylene derivatives.

S4 DFT calculations

S4.1 General Information

Electronic structure calculations, including geometry optimizations and frequency calculations, were performed using Gaussian 09[5] at the ωB97X-D/6-311+G** level of theory using an ultrafine grid.[6] Frequency calculations were carried out on all optimized structures, and intermediates and transition states were confirmed by the presence of 0 and 1 imaginary frequencies, respectively, unless otherwise stated. Each transition state was verified by inspection of displacement vector of the single imaginary frequency. All thermodynamic data below are given in terms of the thermally corrected Gibbs free energy in units of kcal/mol.

S4.2 Possible products of the reaction of 1 with $(C_6F_5)_2BCl$

Five different products for the reaction of the *P*-methyl-triphenylphosphinine anion with the bis(pentafluorophenyl)chloroborane were optimized (**2**, **Iso-2a** – **Iso-2d**), and the relative electronic energies and Gibbs free energies compared (relative to the norbornadiene structure **2**, Figure S107). The first three structures, with three-coordinate boron centres, are all higher in energy than the two bridging structures. There is very little energetic difference between the three-membered bridging ring and the norbornadiene bridged structure at this level of theory.

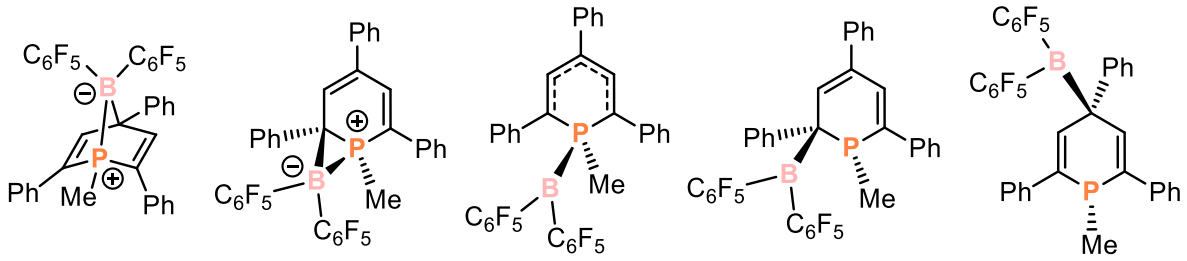


Figure S107. Relative electronic and Gibbs free energies of possible products **2** and **Iso-2a** - **Iso-2d**.

S4.3 Reaction of 2 with nitriles

Simplified system:

Initial calculations exploring the mechansim of formation of the observed product **3a** were carried out on a simplified molecule with the three phenyl groups removed (denoted by ' labels on all simplified structure names). **2'$_{closed}$** has the norbornadiene structure confirmed by X-ray crystallography (the simplified analogue of **2** above). This molecule can be described as an intramolecular frustrated Lewis pair (FLP), by analogy with Erker's P/B 4-membered heterocycle that can act as an ethylene-bridged FLP (Figure S108) for the activation of H_2, CO_2 and other small molecules.[7] **2'$_{open}$** is only 5.9 kcal/mol higher in energy than **2'$_{closed}$**, which is comparable to the energy difference in Erker's system (between 7-10 kcal/mol, depending on the computational method used).[11]

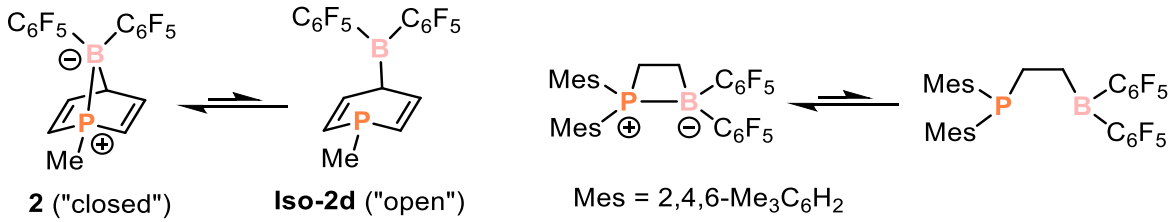


Figure S108. "Closed" and "open" forms of frustrated Lewis pairs; left: the compound under investigation herein; right: Erker's intramolecular P/B FLP.[7]

Iso-2d' can then act as an FLP for the activation of nitriles, modelled here using acetonitrile. The nitrile first binds to the Lewis acidic boron centre to give adduct (**Int-A'**). The rate-determining step (although over a small energy barrier of only 15.4 kcal/mol, which is rapid at room temperature) is the cyclisation to give the FLP activated

product **Int-B'**. This tricyclic cage structure featuring two 7-membered rings is unstable, and very rapidly rearranges with breaking of the B–C bond and concomitant planarization of the 6-membered phosphorus-containing ring (**Int-C'**). This is the connectivity in the final product, although the single-crystal X-ray structure showed the molecule with a rotation around the P–C single bond (**3a'**). In the case of this simplified molecule **3a'** is actually slightly higher in energy than **Int-C'**, so the experimental observation of **3a'** in the solid-state could be due to packing effects, or more likely because of the steric clash of the C_6F_5 groups on boron with the phenyl groups on the λ^5-phosphinine ring that were not modelled in this simplified system.

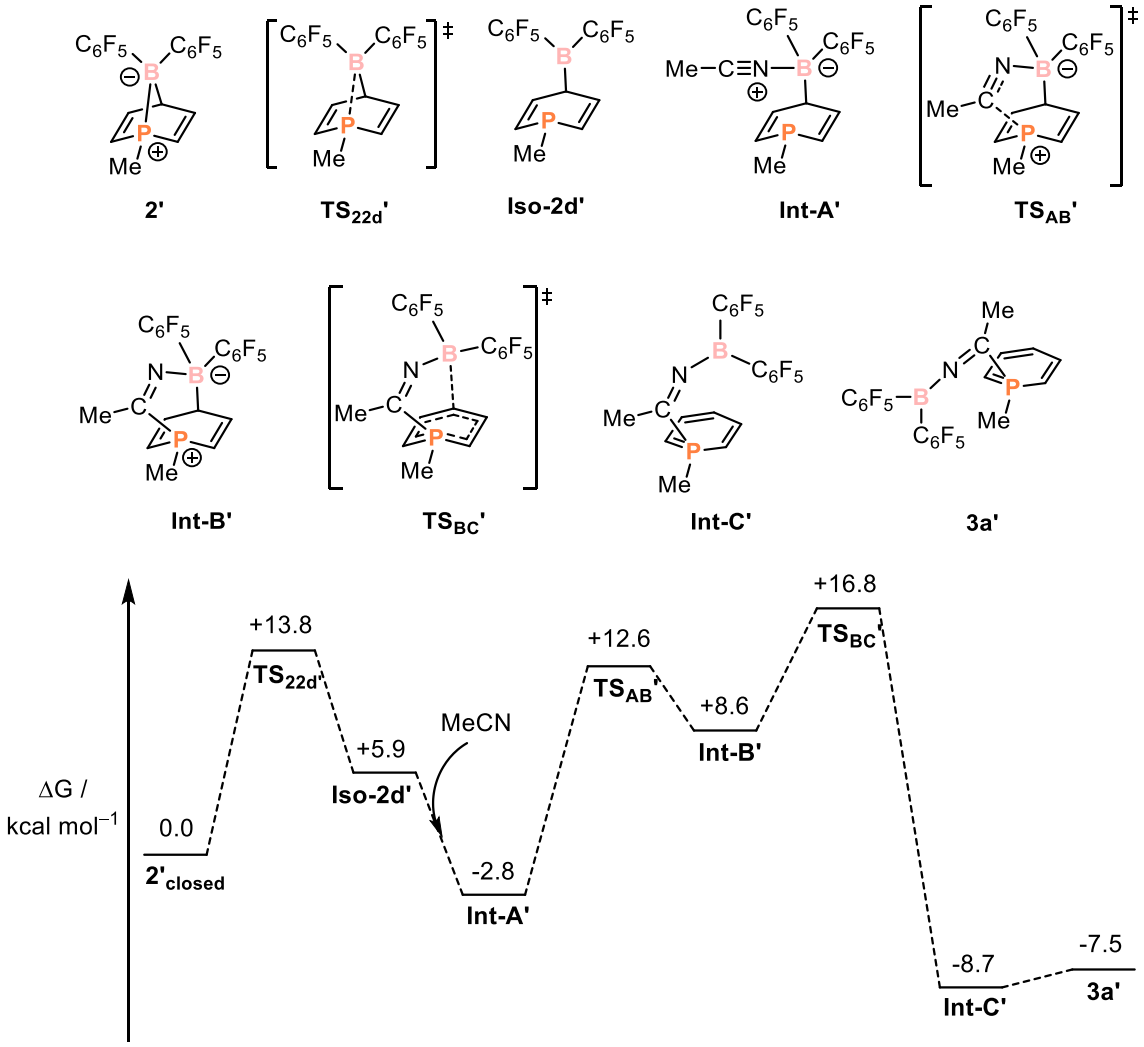


Figure S109. Reaction profile for activation of acetonitrile by the simplified P/B-norbornadiene system.

Full system:

The analogous calculations on the full system with the three phenyl groups present were subsequently carried out (Figure S110). In this case the open form of the starting material (**Iso-2d**, the structure **Iso-2d** above) is only +3.9 kcal/mol higher in energy than the closed P–B compound (**2**$_{\mathbf{closed}}$, the structure **2** above), although the barrier to form the open species is slightly higher than before. The formation of the MeCN adduct (**Int-A**) is slightly unfavourable, presumably due to the steric clash of the C_6F_5 groups with the Ph on the ring. The ring closing step is once again rate-determining, with a barrier of 17.1 kcal mol^{-1}, which is still rapid at room temperature. In this case the ring structure **Int-B** is highly unstable, as the transition state with the breaking of the B–C bond is (**TS$_{78}$**) is only 0.6 kcal/mol higher in energy. This affords product **Int-C** in a process that is exothermic by 28.3 kcal/mol. In this case **3a** is actually the thermodynamically more stable product, consistent with the obtained single crystal X-ray structure of **3a**.

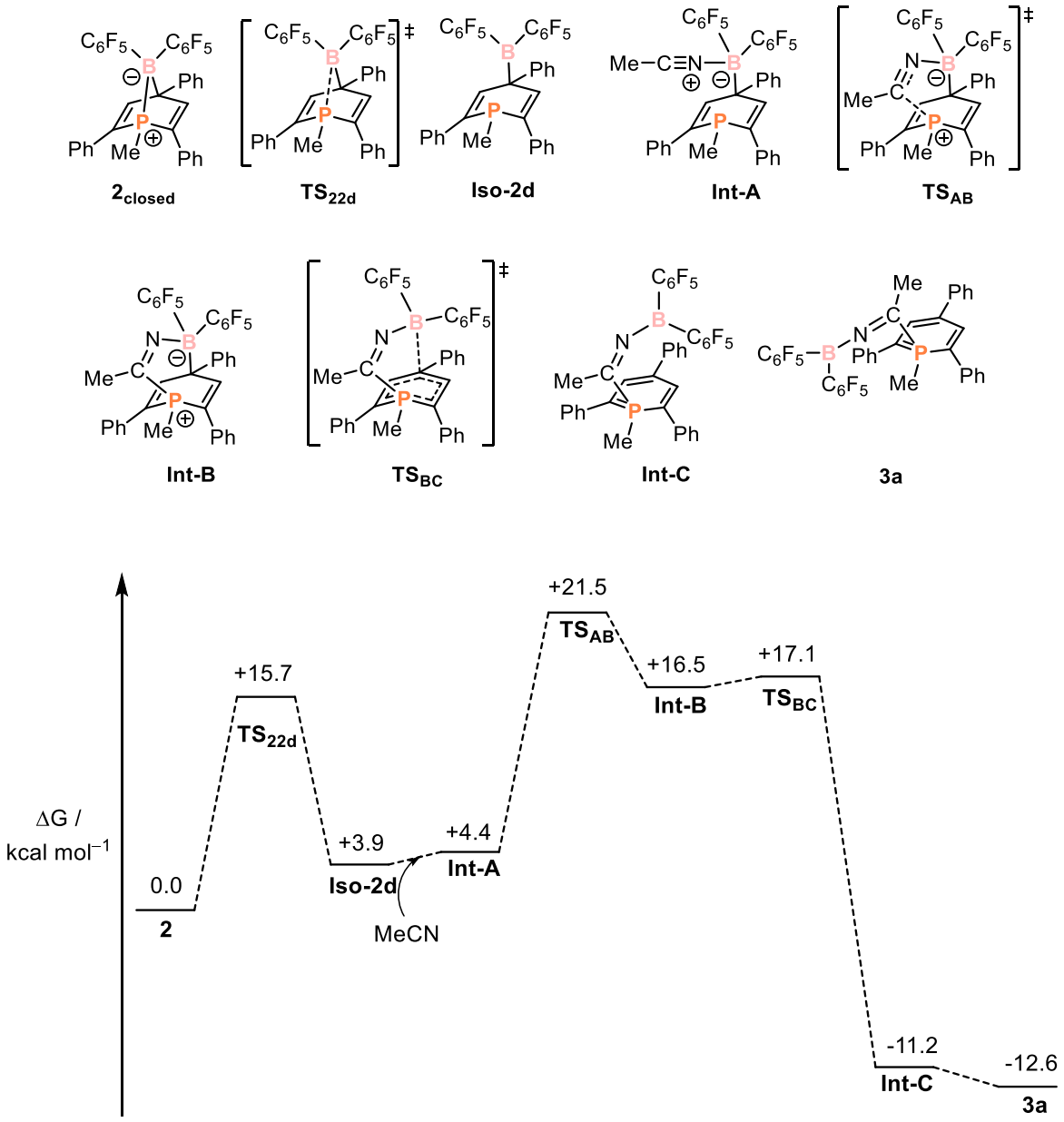
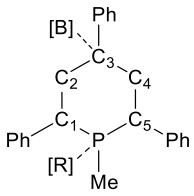


Figure S110. Reaction profile for activation of acetonitrile by the P/B-norbornadiene system.

Note that the 6-membered phosphorus-containing ring alternately flattens and puckers during the transformation from **Iso-2d** to **Int-B**, but the C–C bond distances in the ring remain as localised single and double bonds (see Table S3 below). It is only in **Int-C** and **3a** (and to a lesser extent in **TS$_{AB}$**) where delocalisation is observed (highlighted in green in Table S3).

Table S3. C–C bond distances in structures **2$_{closed}$** to **3a**, with labelling as shown (the dashed lines are due to the fact that P and C3 vary in their coordination number during the reaction).



	C1–C2 (Å)	C2–C3 (Å)	C3–C4 (Å)	C4–C5 (Å)
2_{closed}	1.339	1.523	1.533	1.335
TS_{22d}	1.333	1.520	1.528	1.331
Iso-2d	1.343	1.522	1.509	1.334
Int-A	1.336	1.506	1.511	1.335
TS_{AB}	1.336	1.511	1.513	1.335
Int-B	1.339	1.502	1.511	1.337
TS_{BC}	1.351	1.459	1.461	1.350
Int-C	1.381	1.402	1.395	1.391
3a	1.385	1.400	1.398	1.387

An alternative possible mechanism could feature the initial breaking of the B-C bond from **2_{closed}** to give the λ^5-phosphinine intermediate featuring a P–B bond (which was previously examined as **Iso-2b** from Figure S107). **Iso-2b** could feasibly be attacked by MeCN followed by a rearrangement to give the product. This mechanism can be ruled out, however, as the breaking of the B–C bond (pathway highlighted in red) is significantly higher in energy (both kinetically and thermodynamically) than the breaking of the P–B bond (shown in black):

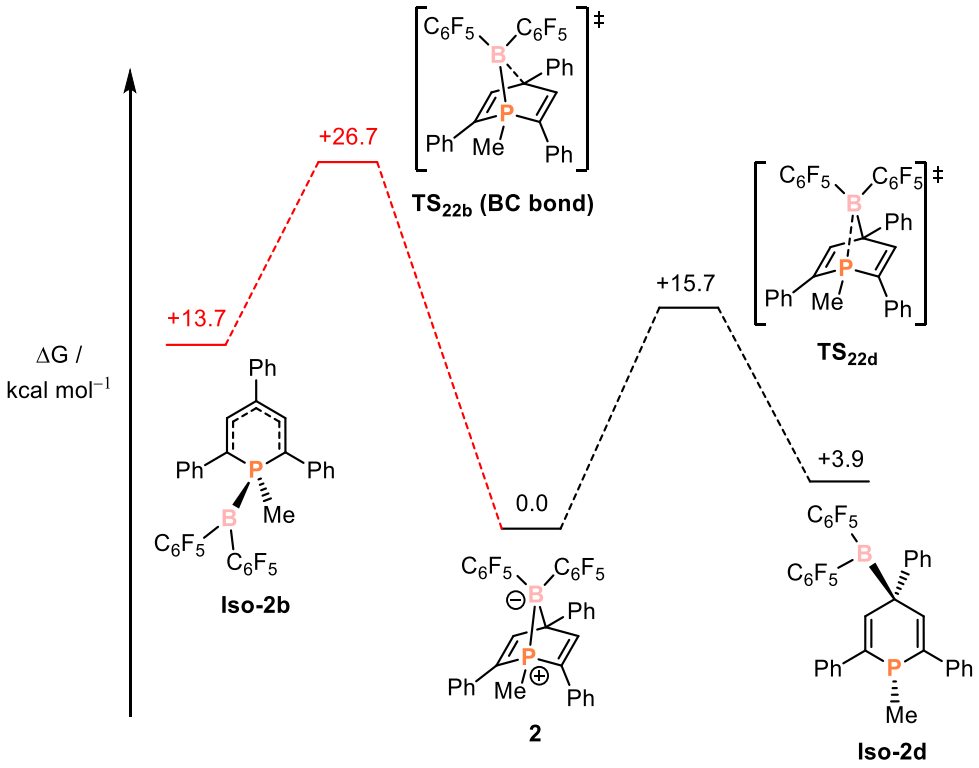


Figure S111 Reaction profile for alternative "opening" pathways of the P/B-norbornadiene system.

S4.4 Reaction of 2 with alkynes

The acetonitrile reactivity data above showed that the full system is required for accurate modelling of the chemistry, so this was used from the start for the alkyne case. First we analysed the analogous route as seen for the nitrile reactivity, as shown in Figure S110. This reaction, i.e. 1,2-addition of the triple bond by the B/P moieties,

is more thermodynamically favourable for the alkyne than the nitrile, as shown by the lower relative value of **Int-F** compared to **Int-B**. This is consistent with a previous report studying a methylene-linked B/P FLP and its reactivity towards alkynes and nitriles.[8] However, this reaction does not occur in solution (see manuscript for full details), and nor does any of the following rearrangement (from **Int-F** to **Int-H**) that was observed for the nitrile reactions. All attempts at trying to locate the transition state that would lead to this intermediate failed. The conjectured concerted transition state is shown below as **TS_{2dF}**, and the step-wise pathways were also tried, but all attempts led to unstable structures that collapsed during the optimization process. This leads us to postulate that this transition state is therefore unstable and high in energy, consistent with experimental observations, but we are unable to quantify this barrier.

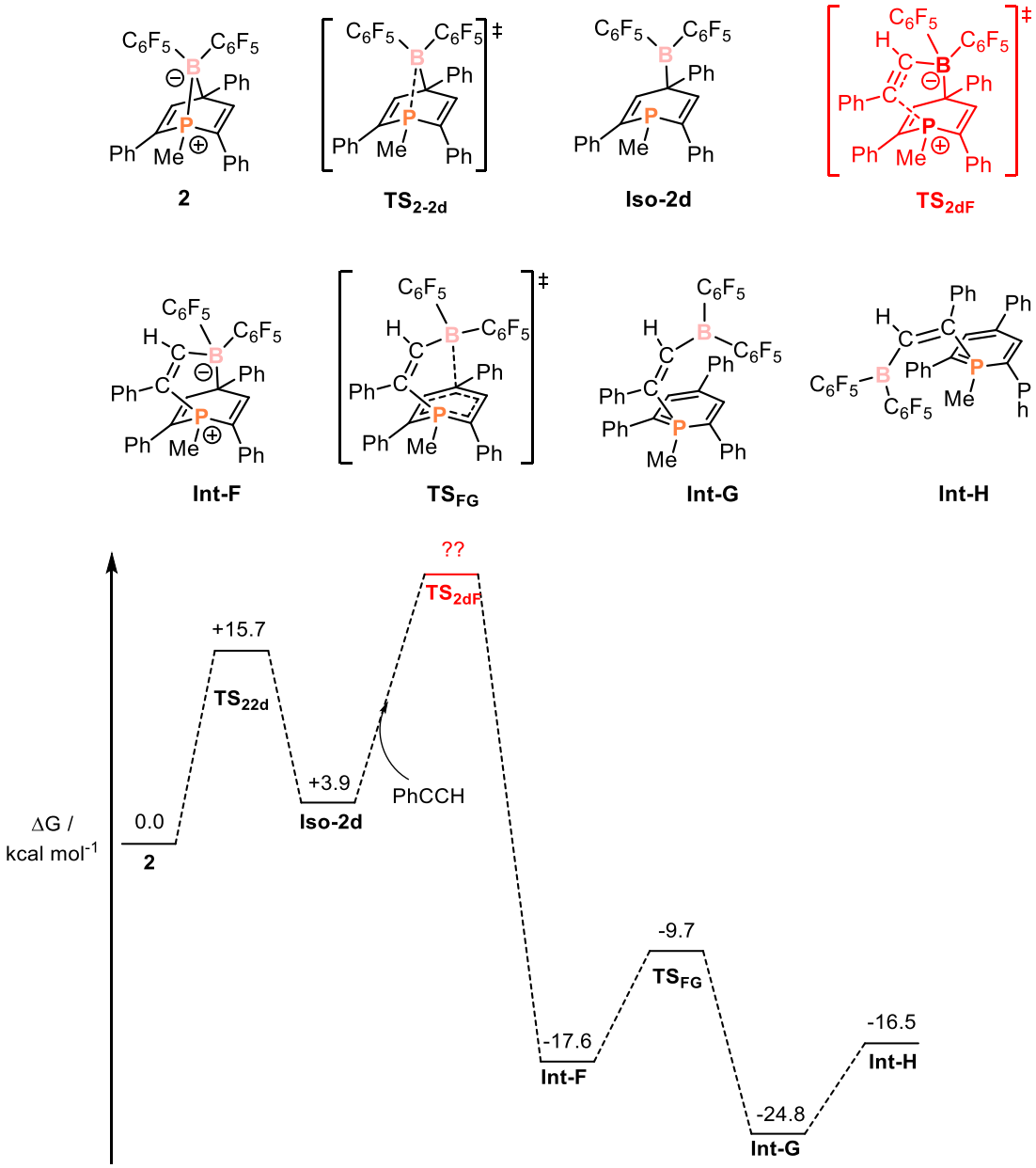


Figure S112 Hypothetical reaction profile for activation of phenylacetylene by the P/B-norbornadiene system by analogy with the nitrile pathway. The barrier **TS_{2dF}** could not be calculated, see text for details.

To explain the observed reactivity, we explored another possible pathway. We have already shown that the three-membered ring **Iso-2a** (from Figure S107) is almost isoenergetic with the norbornadiene derivative, and is present in small quantities by NMR spectroscopy. This species is in equilibrium with its open form, the *ortho*-borylated species **Iso-2c**. At elevated temperatures, a subsequent 1,2-phenyl migration can occur, as evidenced by the relatively large but accessible energy barrier in Figure S108. This results in a zwitterionic methylphosphinium

borate species, **Int-D**. Alkynes have previously been shown to add in a 1,4 manner across methylphosphinium salts,[9] and this is what we observe here as well to afford the observed product **5a**.

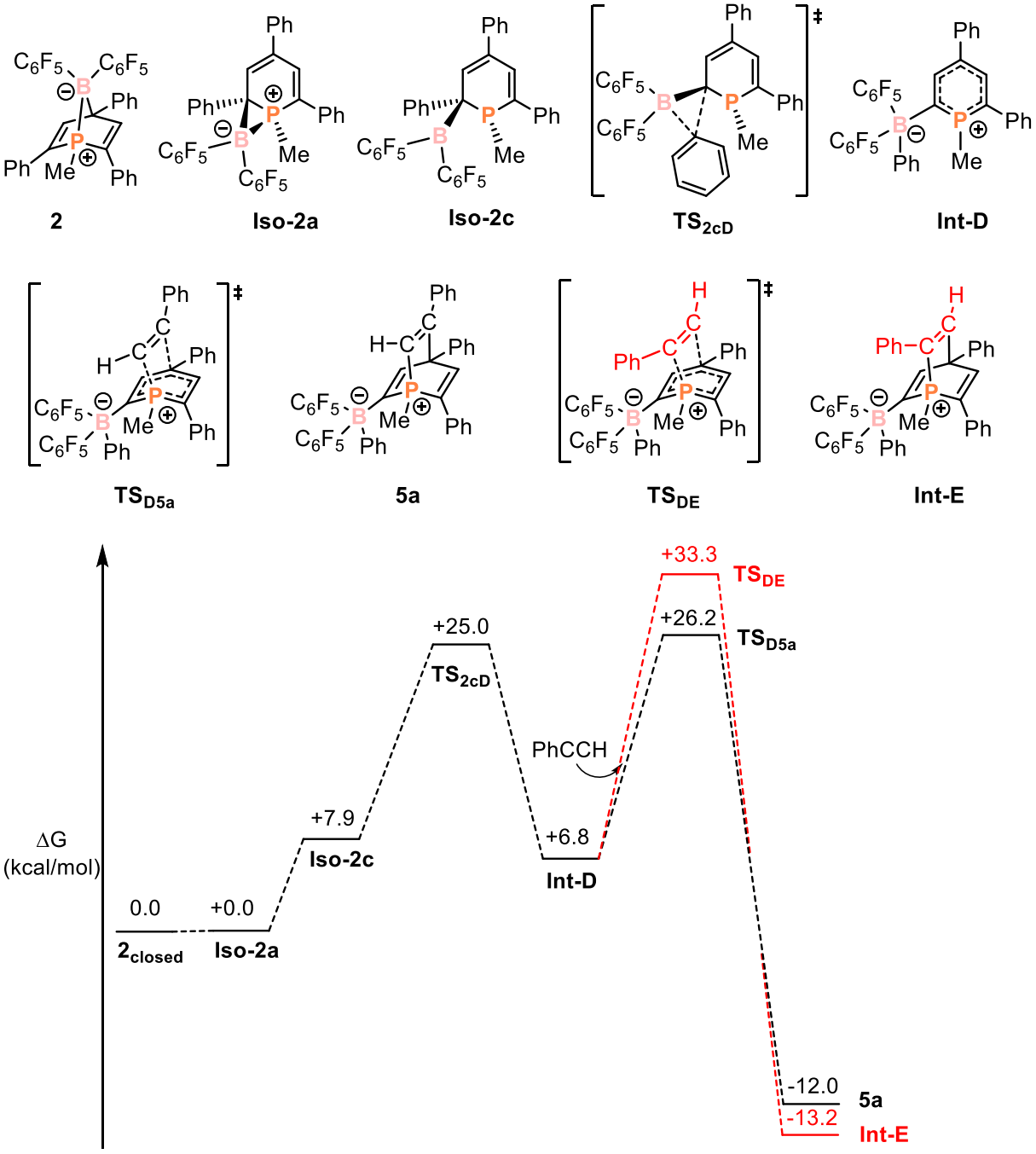


Figure S113 Proposed reaction profile for activation of phenylacetylene by the P/B-norbornadiene system.

Interestingly this chemistry is also the concerted addition of a Lewis acid and a Lewis base to an unsaturated centre, as in the aforementioned FLP nitrile activation. It has previously been shown that the regiochemistry for the FLP addition to an aryl-alkyne, such as phenylacetylene, results in the aryl-substituted carbon bound to the Lewis basic fragment, and the terminal carbon of the alkyne bound to the Lewis acid.[10] This is due to the better stabilisation of the positive charge on the aryl-bound carbon during the interaction of the alkyne with the Lewis acidic centre. Indeed, we calculated the reactivity of **Int-D** towards phenylacetylene to generate the other regioisomer, **Int-E**, and although **Int-E** is thermodynamically slightly lower in energy than **5a**, the barrier the energy of the transition state $\mathbf{TS_{DE}}$ is significantly higher in energy than $\mathbf{TS_{D5a}}$ (see Figure S113).

This implies that the phosphorus centre is the Lewis acidic site, and the *para*-carbon is the Lewis basic site, which is consistent with the activation of dihydrogen by triphosphabenzene derivatives.[11] This means that the phenyl

migration to form the phosphinium borate results in an *umpolung* effect, where the phosphorus centre changes from a nucleophilic centre in the P/B FLP system for the activation of nitriles to an electrophilic centre in the activation of alkynes.

During the heating of compound **2** at 60 °, another rearrangement also occurred, leading to the formation of **6** (Figure S114), which is a thermodynamic sink in the absence of alkyne. Two possible transition states involving intramolecular phenyl migration were considered, but their energies are prohibitively high. Transition states involving intermolecular migration have not been considered.

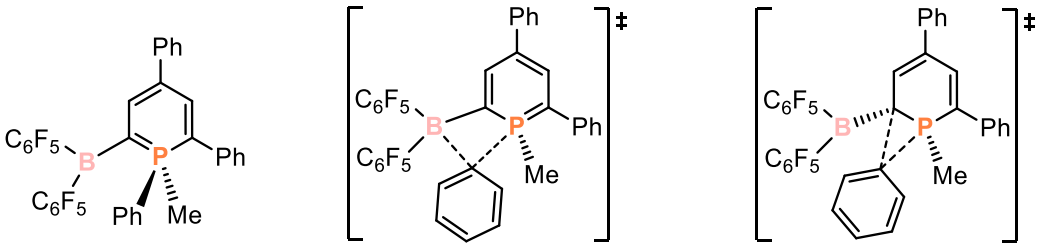


Figure S114 Energies of **6** and two possible transition states accounting for its formation (ΔG values relative to $\mathbf{2}_{\mathbf{closed}}$, by analogy with Figure S113).

S4.5 Computed NMR data

The ^{31}P NMR chemical shifts of selected compounds were calculated at the ωB97X-D/6-311+G** level of theory using an ultrafine grid. PPh_3 was used as the reference compound (^{31}P NMR chemical shift at -6 ppm).

Table S4. Computed ^{31}P NMR chemical shifts (in ppm) at the ωB97X-D/6-311+G** level of theory.

Compound	Computed ^{31}P chemical shift
Iso-2b	-33
Iso-2c	-43
Iso-2d	-53
Iso-2a	-115
2	+10
Int-D	+151
6	+0.4

To verify the results, additional calculations of the ^{11}B and ^{31}P chemical shifts for **2**, **6** and **Iso-2a** to **Int-D** were carried out at the TPSS/IGLO-III CPCM(THF)[12] level of theory using the ORCA program package. Thereby, **2** was used as the reference compound. Furthermore, the ^{11}B–^{31}P coupling constants as well as the quadrupole tensor eigenvalues of the boron atoms were calculated in **2** and **Iso-2a** at the same level of theory.

Table S5. Computed ^{31}P and ^{11}B NMR chemical shifts (in ppm) at the TPSS/IGLO-III CPCM(THF) level of theory.

Compound	Computed ^{31}P chemical shift	Computed ^{11}B chemical shift
Iso-2b	−16	+32
Iso-2c	−38	+66
Iso-2d	−43	+47
Iso-2a	−98	−26
Int-D	+132	−13
6	+5	43

Table S6. Computed coupling constants and quadrupole tensor eigenvalues (C_Q = quadrupolar coupling constant) for **2** and **Iso-2a** at the TPSS/IGLO-III CPCM(THF) level of theory.

Compound	J(^{11}B–^{31}P) [Hz]	C_Q [MHz]	η
2	+87	1.449	0.230
Iso-2a	+6	1.471	0.291

S4.6 TDDFT calculations on 6

In order to further characterise **6**, TDDFT calculations at the CAM-B3LYP/def2-TZVP CPCM(THF) level of theory have been conducted. The calculated spectrum is blue-shifted compared to the experimental spectrum. This observation is typical for range-separated functionals. Looking at the difference density of the first transition ($\lambda_{max, calc.}$ = 400 nm, $\lambda_{max, obs.}$ = 489 nm) can be assigned to a π- π* excitation based on its calculated difference density:

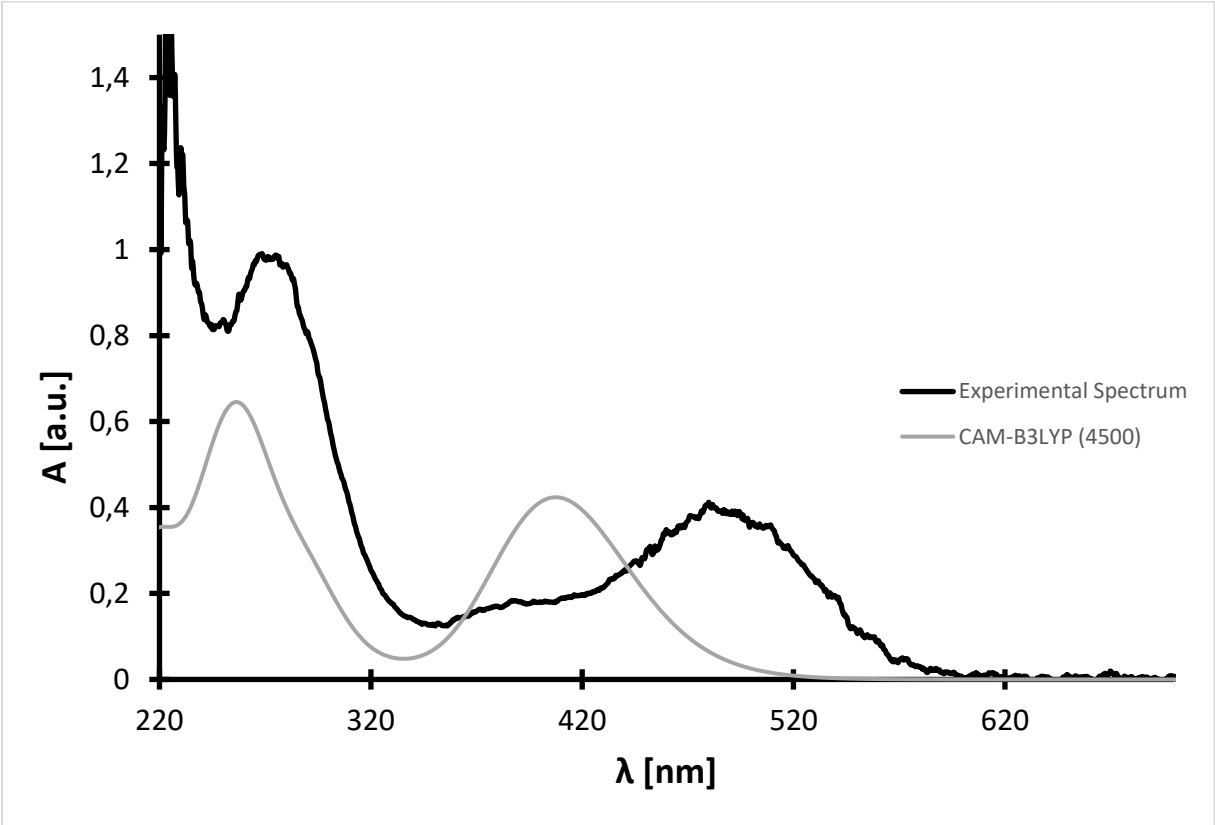


Figure S115. Experimental and calculated UV-Vis spectrum of **6**.

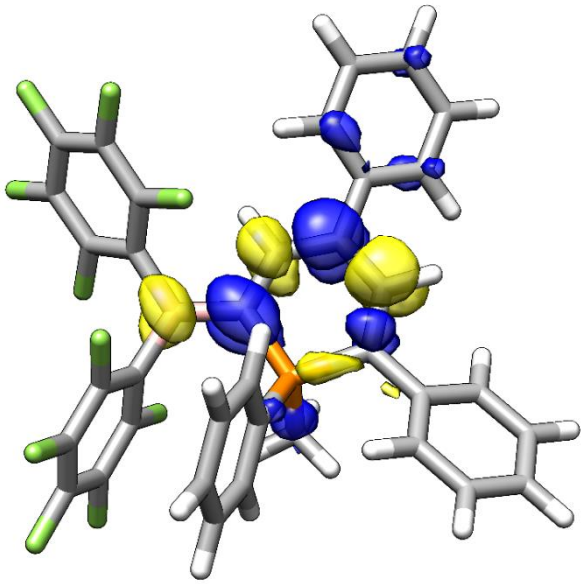


Figure S116. Difference density of the first transition in **6**. Isosurface value = 0.002, transition proceed from blue to yellow.

S4.7 Tables of optimized Cartesian coordinates

Table S7. Cartesian coordinates of the optimized structure of **Iso-2b**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.206997	-0.502739	1.492800
2	9	0	1.087048	0.024444	-1.804769
3	9	0	-1.275056	3.345420	0.554870
4	9	0	2.510475	1.924753	-3.048207
5	9	0	2.072807	4.539500	-2.494553
6	9	0	0.163555	5.252873	-0.702376
7	9	0	-2.935330	0.513372	2.404024
8	9	0	-2.094938	0.061033	-2.213633
9	9	0	-5.500632	-0.156712	1.992683
10	9	0	-6.357774	-0.762355	-0.505646
11	9	0	-4.647556	-0.649861	-2.600278
12	6	0	0.840778	1.299508	-1.504122
13	6	0	0.376997	3.970379	-0.972902
14	6	0	1.576901	2.267577	-2.165966
15	6	0	-0.353452	2.978099	-0.345373
16	6	0	1.351638	3.606454	-1.888829
17	6	0	3.911365	-2.869237	0.137721
18	6	0	-1.042678	-2.647913	0.117764
19	6	0	-0.130492	1.626333	-0.567292
20	6	0	0.218865	-2.039047	0.614868
21	6	0	1.442735	-2.595575	0.271277
22	1	0	1.390756	-3.544195	-0.259092
23	6	0	1.870910	0.104745	1.385940
24	6	0	2.868432	-0.768863	0.999301
25	1	0	3.885709	-0.390939	1.066958
26	6	0	2.716327	-2.072874	0.504563
27	6	0	-2.411119	0.296951	0.114584
28	6	0	2.130301	1.534853	1.631910
29	6	0	3.974634	-4.236810	0.425193
30	1	0	3.150091	-4.707727	0.950465
31	6	0	-3.328858	0.231038	1.157610
32	6	0	5.003606	-2.285260	-0.513572
33	1	0	4.968206	-1.234258	-0.780915
34	6	0	-1.179639	-2.928207	-1.247141
35	1	0	-0.364132	-2.680919	-1.917530
36	6	0	-2.119761	-2.946226	0.958500
37	1	0	-2.032041	-2.784205	2.026250
38	6	0	3.166156	2.193043	0.946535
39	1	0	3.781582	1.637059	0.248211
40	6	0	1.321969	2.314427	2.469715
41	1	0	0.517415	1.859557	3.033074
42	6	0	2.558331	4.310348	1.928493
43	1	0	2.715983	5.377433	2.031295
44	6	0	1.526738	3.682610	2.609692
45	1	0	0.872045	4.255911	3.256149
46	6	0	5.085168	-4.993259	0.073078
47	1	0	5.111298	-6.051104	0.310952
48	6	0	-0.364516	-0.729915	3.219357
49	1	0	-1.330890	-1.231900	3.232965
50	1	0	-0.459917	0.217968	3.748228
51	1	0	0.383432	-1.355314	3.712516
52	6	0	-2.905880	0.020738	-1.159217
53	6	0	6.165360	-4.396554	-0.566168
54	1	0	7.034627	-4.984774	-0.837307
55	6	0	6.119165	-3.037419	-0.856004
56	1	0	6.950323	-2.562506	-1.365810
57	6	0	-3.300645	-3.474898	0.451412
58	1	0	-4.122514	-3.694428	1.124365
59	6	0	-3.423975	-3.736566	-0.907891
60	1	0	-4.345510	-4.147272	-1.304496
61	6	0	3.382159	3.552233	1.099953
62	1	0	4.182269	4.030928	0.545899
63	6	0	-4.656133	-0.103995	0.968901
64	6	0	-2.352465	-3.471443	-1.753594
65	1	0	-2.437727	-3.666887	-2.816599
66	6	0	-5.098508	-0.408031	-0.309756
67	6	0	-4.221382	-0.347743	-1.381144
68	5	0	-0.894705	0.593896	0.335802

Table S8. Cartesian coordinates of the optimized structure of **Iso-2c**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.750272	1.351553	1.025076
2	6	0	0.071546	0.118434	1.271702
3	6	0	2.119046	1.938173	0.431632
4	6	0	1.072594	2.640430	-0.031423
5	6	0	-0.322515	2.435706	0.361392
6	1	0	-1.809371	1.293528	1.254867
7	1	0	1.263151	3.477118	-0.699208
8	6	0	3.513154	2.340036	0.134475
9	6	0	3.868846	3.694176	0.123220
10	6	0	4.507675	1.390242	-0.122516
11	6	0	5.168893	4.086445	-0.163407
12	1	0	3.121394	4.442074	0.364184
13	6	0	5.807823	1.783989	-0.409917
14	1	0	4.254489	0.337294	-0.115023
15	6	0	6.143462	3.132351	-0.434084
16	1	0	5.424413	5.140249	-0.163376
17	1	0	6.560748	1.032482	-0.619469
18	1	0	7.159851	3.438085	-0.655060
19	6	0	-0.375820	-0.694142	2.501247
20	6	0	0.227688	-1.926335	2.779228
21	6	0	-1.359708	-0.230276	3.376991
22	6	0	-0.158949	-2.680285	3.878876
23	1	0	1.026680	-2.292184	2.144685
24	6	0	-1.739559	-0.981212	4.480638
25	1	0	-1.826401	0.732620	3.215219
26	6	0	-1.149407	-2.213635	4.731943
27	1	0	0.319755	-3.634303	4.067473
28	1	0	-2.502517	-0.597992	5.148842
29	1	0	-1.454228	-2.801231	5.590125
30	6	0	-1.305416	3.483247	-0.024809
31	6	0	-1.376908	3.923256	-1.348669
32	6	0	-2.198613	4.012906	0.907686
33	6	0	-2.330102	4.857372	-1.732543
34	1	0	-0.699022	3.510743	-2.088591
35	6	0	-3.150177	4.949968	0.524377
36	1	0	-2.134413	3.696266	1.943482
37	6	0	-3.220431	5.373381	-0.797498
38	1	0	-2.382223	5.177308	-2.767139
39	1	0	-3.833728	5.355465	1.262034
40	1	0	-3.962995	6.103970	-1.097383
41	6	0	1.857081	1.390357	3.140684
42	15	0	1.902632	0.481484	1.529512
43	5	0	-0.297178	-0.913868	0.116303
44	6	0	0.676753	-1.982863	-0.522366
45	6	0	0.404280	-3.343404	-0.430356
46	6	0	1.808473	-1.631876	-1.246548
47	6	0	1.231829	-4.311148	-0.973973
48	6	0	2.652676	-2.570747	-1.816703
49	6	0	2.364574	-3.918660	-1.671771
50	6	0	-1.769913	-0.854471	-0.479800
51	6	0	-1.926268	-0.149557	-1.664716
52	6	0	-2.923057	-1.367108	0.093452
53	6	0	-3.156083	0.065570	-2.259255
54	6	0	-4.173413	-1.181681	-0.479818
55	6	0	-4.289886	-0.458663	-1.656489
56	9	0	-0.838060	0.366058	-2.254064
57	9	0	3.723550	-2.191885	-2.503941
58	9	0	3.162958	-4.829761	-2.205964
59	9	0	-0.680236	-3.755076	0.229733
60	9	0	0.950260	-5.601804	-0.840477
61	9	0	2.093076	-0.346358	-1.451044
62	9	0	-3.260021	0.758333	-3.386903
63	9	0	-5.481386	-0.272175	-2.206654
64	9	0	-5.260213	-1.687525	0.092770
65	9	0	-2.866102	-2.062426	1.229089
66	1	0	1.669081	0.691541	3.957603
67	1	0	2.840304	1.843156	3.288454
68	1	0	1.097612	2.175262	3.145447

Table S9. Cartesian coordinates of the optimized structure of **Iso-2d**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.531034	1.018229	0.328822
2	9	0	-0.736017	-2.777050	-0.679576
3	9	0	0.546764	0.259730	2.677323
4	9	0	-2.530187	-3.873456	1.002737
5	9	0	-2.785010	-2.913961	3.524249
6	9	0	-1.229270	-0.852881	4.361676
7	9	0	2.139225	-2.875210	0.710430
8	9	0	3.065201	1.643471	-0.375708
9	9	0	4.730485	-3.296324	1.066065
10	9	0	6.513846	-1.281319	0.705994
11	9	0	5.637652	1.180959	-0.014855
12	6	0	-0.869671	-2.258995	0.544677
13	6	0	-1.109022	-1.318122	3.122100
14	6	0	-1.782548	-2.849353	1.400256
15	6	0	-0.201326	-0.758798	2.238132
16	6	0	-1.907332	-2.366146	2.694969
17	6	0	-0.074136	-1.187830	0.925948
18	6	0	-0.976094	1.982328	0.311632
19	6	0	0.109887	1.629541	-0.394587
20	1	0	0.992310	2.251146	-0.310368
21	6	0	-2.280444	0.077783	-1.221221
22	6	0	-1.079691	-0.121157	-1.766778
23	1	0	-1.012293	-0.758229	-2.644472
24	6	0	0.250343	0.396991	-1.276318
25	6	0	2.450657	-0.587644	0.160043
26	6	0	2.957779	-1.832850	0.541716
27	6	0	-3.723780	2.314568	-0.239777
28	1	0	-3.863713	3.046066	0.558015
29	1	0	-4.682614	1.833603	-0.443098
30	1	0	-3.375368	2.820418	-1.142110
31	6	0	3.413532	0.404959	-0.027005
32	6	0	4.307659	-2.085865	0.721555
33	6	0	5.220695	-1.062378	0.533527
34	6	0	4.768849	0.192798	0.160634
35	5	0	0.891622	-0.446773	-0.085499
36	6	0	1.156255	0.629298	-2.476398
37	6	0	1.239117	1.875864	-3.091274
38	6	0	1.869075	-0.435427	-3.027180
39	6	0	2.038448	2.062749	-4.212573
40	1	0	0.674590	2.710048	-2.688286
41	6	0	2.665576	-0.254850	-4.150433
42	1	0	1.798832	-1.420495	-2.574583
43	6	0	2.758192	0.999255	-4.743048
44	1	0	2.097988	3.042402	-4.673497
45	1	0	3.214987	-1.093995	-4.562237
46	1	0	3.384204	1.145117	-5.615937
47	6	0	-0.964142	3.208981	1.144052
48	6	0	-1.441176	3.179669	2.457635
49	6	0	-0.481056	4.414026	0.629115
50	6	0	-1.418470	4.325405	3.240916
51	1	0	-1.812615	2.249152	2.873630
52	6	0	-0.463204	5.560364	1.412669
53	1	0	-0.132180	4.452287	-0.397173
54	6	0	-0.930264	5.518964	2.721141
55	1	0	-1.778901	4.283950	4.262456
56	1	0	-0.088833	6.489476	0.997920
57	1	0	-0.916380	6.413855	3.332752
58	6	0	-3.496376	-0.535475	-1.812172
59	6	0	-4.395330	-1.247087	-1.012759
60	6	0	-3.761026	-0.417347	-3.178161
61	6	0	-5.520091	-1.840926	-1.569604
62	1	0	-4.203492	-1.349376	0.050628
63	6	0	-4.887035	-1.010875	-3.734279
64	1	0	-3.081739	0.154249	-3.801355
65	6	0	-5.769500	-1.725366	-2.932395
66	1	0	-6.199997	-2.400836	-0.937441
67	1	0	-5.078921	-0.908926	-4.796623
68	1	0	-6.648783	-2.187436	-3.366563

Table S10. Cartesian coordinates of the optimized structure of **Iso-2a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.087675	1.365168	0.987427
2	9	0	0.475197	-2.671095	-0.692707
3	9	0	-0.161344	1.747217	-2.239418
4	9	0	2.152383	-3.123042	-2.709644
5	9	0	2.703775	-1.166608	-4.505942
6	9	0	1.519964	1.267448	-4.259467
7	9	0	-2.771937	2.257275	-0.057477
8	9	0	-2.293900	-2.365272	-0.921820
9	9	0	-5.324378	2.105165	-0.726876
10	9	0	-6.420258	-0.255927	-1.506884
11	9	0	-4.869587	-2.488121	-1.603252
12	6	0	0.720934	-1.661144	-1.529902
13	6	0	1.267714	0.310141	-3.369974
14	6	0	1.591012	-1.925072	-2.576859
15	6	0	0.403493	0.532361	-2.310822
16	6	0	1.871733	-0.929751	-3.498506
17	6	0	3.403951	-1.645301	1.207430
18	6	0	-1.223023	-0.815882	2.526879
19	6	0	0.117450	-0.421727	-1.341881
20	6	0	-0.267652	-0.445000	1.418104
21	6	0	1.023810	-1.150892	1.545481
22	1	0	0.932896	-2.170044	1.909239
23	6	0	1.659604	1.704905	0.830931
24	6	0	2.534182	0.679972	0.863516
25	1	0	3.581342	0.920648	0.695749
26	6	0	2.250275	-0.706140	1.205922
27	6	0	-2.405897	-0.063271	-0.418151
28	6	0	2.072343	3.118169	0.675998
29	6	0	3.644805	-2.509243	2.276372
30	1	0	3.003509	-2.468061	3.150462
31	6	0	-3.237465	1.049295	-0.410162
32	6	0	4.254670	-1.693843	0.100750
33	1	0	4.070723	-1.039109	-0.745782
34	6	0	-2.174593	-1.818763	2.344282
35	1	0	-2.244501	-2.320873	1.388538
36	6	0	-1.100051	-0.238797	3.792382
37	1	0	-0.332146	0.508004	3.965341
38	6	0	3.172956	3.614220	1.380415
39	1	0	3.706515	2.961523	2.062826
40	6	0	1.370100	3.980825	-0.171298
41	1	0	0.526394	3.606200	-0.742033
42	6	0	2.869860	5.783445	0.378441
43	1	0	3.179279	6.815812	0.262589
44	6	0	1.767341	5.302687	-0.318911
45	1	0	1.219409	5.955745	-0.988465
46	6	0	4.704853	-3.405948	2.235658
47	1	0	4.880973	-4.068072	3.076070
48	6	0	-0.896649	2.565771	2.088401
49	1	0	-1.849108	2.150768	2.415995
50	1	0	-1.076519	3.490412	1.541431
51	1	0	-0.257350	2.760325	2.950068
52	6	0	-3.014416	-1.238413	-0.850613
53	6	0	5.542118	-3.450474	1.126859
54	1	0	6.368357	-4.151442	1.095309
55	6	0	5.313748	-2.591002	0.058693
56	1	0	5.955368	-2.624940	-0.814519
57	6	0	-1.935935	-0.617104	4.835308
58	1	0	-1.828783	-0.151142	5.808478
59	6	0	-2.899447	-1.597930	4.632504
60	1	0	-3.553937	-1.895687	5.443759
61	6	0	3.572104	4.935227	1.226990
62	1	0	4.427677	5.305787	1.780165
63	6	0	-4.578431	1.004304	-0.764656
64	6	0	-3.007056	-2.205644	3.387545
65	1	0	-3.739180	-2.988800	3.225816
66	6	0	-5.139719	-0.194299	-1.166425
67	6	0	-4.346601	-1.329516	-1.213576
68	5	0	-0.831552	-0.078984	-0.092757

Table S11. Cartesian coordinates of the optimized structure of **2 (2_{closed})**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.444478	-1.518041	-0.423279
2	9	0	-1.125755	2.947952	0.524590
3	9	0	-2.137389	-1.050321	-1.782625
4	9	0	-3.508371	3.935923	-0.169883
5	9	0	-5.229733	2.443874	-1.651468
6	9	0	-4.507031	-0.051234	-2.447883
7	9	0	0.426948	0.753316	-2.738867
8	9	0	1.959828	2.039075	1.543287
9	9	0	2.318793	2.261786	-3.850745
10	9	0	4.060762	3.656423	-2.289068
11	9	0	3.844820	3.506335	0.416132
12	6	0	-1.944022	2.166045	-0.187377
13	6	0	-3.680224	0.674506	-1.697789
14	6	0	-3.169193	2.705866	-0.543857
15	6	0	-2.444434	0.174695	-1.318076
16	6	0	-4.048933	1.948688	-1.300165
17	6	0	-0.693645	0.723341	2.675625
18	6	0	3.158021	-1.954104	0.654384
19	6	0	-1.543195	0.878904	-0.533654
20	6	0	1.790014	-1.434944	0.795416
21	6	0	1.278527	-0.723544	1.808537
22	1	0	1.844956	-0.510095	2.707889
23	6	0	-0.878781	-2.304695	0.520813
24	6	0	-1.059398	-1.472747	1.549349
25	1	0	-1.765620	-1.672938	2.348768
26	6	0	-0.154505	-0.237701	1.633294
27	6	0	1.086150	1.317838	-0.537186
28	6	0	-1.573241	-3.566275	0.226189
29	6	0	0.103789	1.379699	3.611364
30	1	0	1.175073	1.233845	3.620740
31	6	0	1.245423	1.435507	-1.916088
32	6	0	-2.072201	0.959472	2.718474
33	1	0	-2.723601	0.462393	2.007091
34	6	0	4.245170	-1.131389	0.963655
35	1	0	4.062597	-0.113619	1.291310
36	6	0	3.405391	-3.252615	0.202437
37	1	0	2.573015	-3.909693	-0.027642
38	6	0	-0.857885	-4.734193	-0.047973
39	1	0	0.227220	-4.717994	-0.023281
40	6	0	-2.968620	-3.613264	0.220462
41	1	0	-3.529301	-2.704231	0.406996
42	6	0	-2.911346	-5.961872	-0.312255
43	1	0	-3.430463	-6.889784	-0.522818
44	6	0	-3.632102	-4.804253	-0.042229
45	1	0	-4.715911	-4.825671	-0.046433
46	6	0	-0.451558	2.250240	4.541886
47	1	0	0.195319	2.749059	5.255016
48	6	0	0.883703	-2.291615	-1.996004
49	1	0	1.774998	-1.799441	-2.388195
50	1	0	0.055219	-2.149027	-2.689201
51	1	0	1.080884	-3.355978	-1.872263
52	6	0	1.998326	2.051870	0.206575
53	6	0	-1.819049	2.486794	4.559331
54	1	0	-2.248583	3.172046	5.281021
55	6	0	-2.630162	1.832948	3.640356
56	1	0	-3.701102	2.002964	3.638573
57	6	0	4.705430	-3.722437	0.074053
58	1	0	4.880855	-4.735481	-0.269948
59	6	0	5.779355	-2.898461	0.391983
60	1	0	6.794540	-3.264001	0.289114
61	6	0	-1.521502	-5.924272	-0.313678
62	1	0	-0.953248	-6.825126	-0.515906
63	6	0	2.222239	2.204909	-2.524908
64	6	0	5.545129	-1.602983	0.838768
65	1	0	6.377850	-0.952727	1.081607
66	6	0	3.110524	2.914267	-1.734257
67	6	0	2.995828	2.833975	-0.357896
68	5	0	-0.112366	0.347749	-0.004365

Table S12. Cartesian coordinates of the optimized structure of **2'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.013747	2.674350	0.283058
2	9	0	-0.674332	-1.476595	-2.008420
3	9	0	-2.186289	1.183306	1.589268
4	9	0	-2.797618	-3.078648	-1.699692
5	9	0	-4.623550	-2.568604	0.248375
6	9	0	-4.285081	-0.423180	1.881515
7	9	0	0.725797	0.114576	2.191955
8	9	0	2.137785	-0.261660	-2.299731
9	9	0	2.853531	-1.316454	2.967119
10	9	0	4.632282	-2.228068	1.122019
11	9	0	4.243131	-1.680324	-1.507800
12	6	0	-1.550532	-1.184713	-1.036305
13	6	0	-3.395810	-0.679531	0.925237
14	6	0	-2.638951	-2.030223	-0.897185
15	6	0	-2.291151	0.138705	0.746356
16	6	0	-3.571672	-1.773583	0.095236
17	6	0	-1.332010	-0.072826	-0.231393
18	6	0	1.390298	3.181593	-0.732865
19	6	0	1.234952	2.525529	-1.885757
20	1	0	1.922764	2.591884	-2.720988
21	6	0	-1.419955	3.177185	-0.733305
22	6	0	-1.257176	2.514590	-1.880960
23	1	0	-1.946515	2.576759	-2.715927
24	6	0	-0.006130	1.651710	-1.959088
25	6	0	1.332234	-0.005774	-0.085552
26	6	0	1.577359	-0.320608	1.245113
27	6	0	0.029401	3.359396	1.956738
28	1	0	0.916157	2.980981	2.466761
29	1	0	-0.854879	3.033409	2.502114
30	1	0	0.065299	4.449164	1.918726
31	6	0	2.267932	-0.494394	-0.987074
32	6	0	2.668426	-1.055814	1.675405
33	6	0	3.577032	-1.520353	0.737848
34	6	0	3.374924	-1.237469	-0.602547
35	5	0	-0.003520	0.819812	-0.478316
36	1	0	2.173047	3.879970	-0.472239
37	1	0	-2.213912	3.861288	-0.470107
38	1	0	-0.004068	0.992589	-2.823516

Table S13. Cartesian coordinates of the optimized structure of **TS_{22d}'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.436147	3.052377	0.427029
2	9	0	-0.991830	-1.713674	-1.997810
3	9	0	-1.999773	1.249488	1.528576
4	9	0	-3.352520	-2.957789	-1.612815
5	9	0	-5.034784	-2.089745	0.341700
6	9	0	-4.326814	0.015208	1.893195
7	9	0	0.494347	-0.375090	2.085506
8	9	0	2.231324	-0.503092	-2.301008
9	9	0	2.653151	-1.689022	2.967089
10	9	0	4.606101	-2.413948	1.232920
11	9	0	4.376979	-1.815485	-1.401498
12	6	0	-1.807530	-1.271293	-1.025540
13	6	0	-3.506052	-0.406023	0.936660
14	6	0	-3.014014	-1.925482	-0.848394
15	6	0	-2.289052	0.226654	0.725520
16	6	0	-3.871650	-1.483942	0.146497
17	6	0	-1.403903	-0.185496	-0.260291
18	6	0	1.698730	3.049233	-0.878967
19	6	0	1.399520	2.238165	-1.891684
20	1	0	2.052712	2.093155	-2.743805
21	6	0	-1.016874	3.324536	-0.637593
22	6	0	-1.073716	2.493003	-1.674393

23	1	0	-1.883683	2.501451	-2.395255
24	6	0	0.071220	1.504081	-1.838692
25	6	0	1.288156	-0.349413	-0.137132
26	6	0	1.433101	-0.708812	1.200317
27	6	0	0.667008	4.620611	1.355596
28	1	0	1.604177	4.573041	1.913158
29	1	0	-0.146892	4.731029	2.074483
30	1	0	0.684323	5.486140	0.691003
31	6	0	2.312046	-0.748903	-0.989904
32	6	0	2.541471	-1.386906	1.678517
33	6	0	3.543531	-1.757023	0.794166
34	6	0	3.426762	-1.443861	-0.550832
35	5	0	0.015452	0.429656	-0.646018
36	1	0	2.618222	3.618916	-0.808676
37	1	0	-1.776016	4.062719	-0.406372
38	1	0	-0.070468	0.903181	-2.745696

Table S14. Cartesian coordinates of the optimized structure of **Iso-2'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.098342	1.920212	-0.483040
2	9	0	1.218790	-0.721246	2.513686
3	9	0	0.336805	-0.465868	-2.099015
4	9	0	3.235957	-2.444640	2.030074
5	9	0	3.800468	-3.187014	-0.516341
6	9	0	2.339893	-2.199183	-2.577875
7	9	0	-1.474774	-2.078327	0.390338
8	9	0	-2.571557	2.530334	0.106164
9	9	0	-4.020707	-2.679275	0.041295
10	9	0	-5.865901	-0.723253	-0.284810
11	9	0	-5.105662	1.877354	-0.247821
12	6	0	1.506332	-1.042509	1.246111
13	6	0	2.068969	-1.825452	-1.332397
14	6	0	2.531600	-1.943838	1.020501
15	6	0	1.047484	-0.931034	-1.064373
16	6	0	2.817569	-2.329492	-0.280585
17	6	0	0.751322	-0.499078	0.219246
18	6	0	1.549681	2.582974	-1.172180
19	6	0	0.378152	2.593900	-0.532517
20	1	0	-0.498219	2.997297	-1.027880
21	6	0	2.658500	2.115369	1.273077
22	6	0	1.406951	2.135993	1.726070
23	1	0	1.233449	2.208340	2.795960
24	6	0	0.166021	2.059920	0.879065
25	6	0	-1.863692	0.264858	0.255406
26	6	0	-2.316733	-1.061231	0.224357
27	6	0	4.214404	3.378624	-0.731345
28	1	0	4.430126	3.486498	-1.796935
29	1	0	5.160992	3.189520	-0.219721
30	1	0	3.776499	4.303838	-0.352504
31	6	0	-2.866543	1.228730	0.099333
32	6	0	-3.647036	-1.406779	0.050812
33	6	0	-4.594841	-0.410096	-0.112624
34	6	0	-4.201833	0.918697	-0.090473
35	5	0	-0.343185	0.609981	0.485980
36	1	0	1.603324	2.990997	-2.178213
37	1	0	3.483888	2.172449	1.977440
38	1	0	-0.626899	2.640721	1.351379

Table S15. Cartesian coordinates of the optimized structure of **Int-A'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	4.239610	-1.750713	-0.019835
2	9	0	-1.155600	1.062629	-2.082242
3	9	0	1.259917	1.954632	1.889536
4	9	0	-1.648256	3.669055	-2.345996
5	9	0	-0.699385	5.439293	-0.511530

6	9	0	0.754268	4.533154	1.597530
7	9	0	-1.453154	-0.163756	2.239278
8	9	0	-1.125259	-1.916022	-2.145745
9	9	0	-3.860749	-1.275679	2.483117
10	9	0	-4.927632	-2.706672	0.429556
11	9	0	-3.519790	-2.999334	-1.873859
12	6	0	-0.671598	1.887969	-1.142310
13	6	0	0.282165	3.674972	0.696484
14	6	0	-0.939154	3.236900	-1.307644
15	6	0	0.526772	2.314802	0.822381
16	6	0	-0.457647	4.141337	-0.375595
17	6	0	0.062458	1.367781	-0.081002
18	6	0	2.838237	-2.719699	-0.655364
19	6	0	1.700896	-2.194025	-1.116322
20	1	0	0.921976	-2.872116	-1.452771
21	6	0	3.793136	-0.147629	-0.752513
22	6	0	2.576656	0.158543	-1.205637
23	1	0	2.412534	1.159877	-1.598339
24	6	0	1.369489	-0.734491	-1.207850
25	6	0	-1.141586	-1.011976	0.051621
26	6	0	-1.918239	-0.878022	1.199308
27	6	0	5.601106	-2.300025	-1.146965
28	1	0	5.867566	-3.333773	-0.914097
29	1	0	6.484095	-1.679930	-0.974868
30	1	0	5.304913	-2.228212	-2.195132
31	6	0	-1.740994	-1.737944	-0.970213
32	6	0	-3.176270	-1.435236	1.353174
33	6	0	-3.723490	-2.162482	0.309237
34	6	0	-3.000746	-2.311123	-0.861164
35	5	0	0.306576	-0.248575	-0.029092
36	1	0	2.950447	-3.800921	-0.627356
37	1	0	4.579555	0.602034	-0.786549
38	1	0	0.830080	-0.566795	-2.145103
39	7	0	1.051772	-0.625905	1.301239
40	6	0	1.697640	-0.976772	2.171982
41	6	0	2.537180	-1.390083	3.270247
42	1	0	2.686135	-0.543430	3.942328
43	1	0	2.062372	-2.212231	3.807168
44	1	0	3.495606	-1.712062	2.851109

Table S16. Cartesian coordinates of the optimized structure of **TS_{AB}'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.156521	-2.463743	-0.103185
2	9	0	-1.083078	1.475888	-1.929878
3	9	0	2.060608	1.357380	1.611622
4	9	0	-0.929537	4.134578	-1.949879
5	9	0	0.706929	5.431062	-0.204102
6	9	0	2.187572	3.993963	1.562584
7	9	0	-1.174457	0.106448	2.229657
8	9	0	-1.765832	-1.511031	-2.184103
9	9	0	-3.729882	-0.406440	2.738237
10	9	0	-5.333937	-1.465514	0.814668
11	9	0	-4.303903	-2.001548	-1.643539
12	6	0	-0.269893	2.058510	-1.034075
13	6	0	1.376005	3.368180	0.711362
14	6	0	-0.206469	3.441818	-1.073162
15	6	0	1.281662	1.983105	0.715882
16	6	0	0.625291	4.105193	-0.186880
17	6	0	0.454719	1.271446	-0.144600
18	6	0	1.853595	-3.227717	-1.081577
19	6	0	0.957282	-2.430197	-1.666275
20	1	0	0.133864	-2.878244	-2.212059
21	6	0	3.435223	-0.949687	-1.037546
22	6	0	2.388597	-0.384043	-1.639798
23	1	0	2.530457	0.558470	-2.161837
24	6	0	0.984760	-0.928463	-1.613708
25	6	0	-1.310348	-0.723552	0.012901
26	6	0	-1.898520	-0.445619	1.245442
27	6	0	4.656622	-3.503412	-0.269846
28	1	0	4.484887	-4.472613	0.202005
29	1	0	5.496924	-3.017784	0.229534

30	1	0	4.895744	-3.650417	-1.325352
31	6	0	-2.182164	-1.239978	-0.935697
32	6	0	-3.231158	-0.688453	1.535948
33	6	0	-4.053055	-1.224121	0.558550
34	6	0	-3.523484	-1.497808	-0.689131
35	5	0	0.279408	-0.362337	-0.212169
36	1	0	1.786853	-4.308953	-1.129814
37	1	0	4.423434	-0.504076	-1.046669
38	1	0	0.429156	-0.530188	-2.463154
39	6	0	1.861677	-1.672505	1.504592
40	7	0	1.019474	-1.011042	0.998081
41	6	0	2.298328	-2.105111	2.851418
42	1	0	2.331555	-3.195270	2.899929
43	1	0	3.301748	-1.719879	3.044200
44	1	0	1.601826	-1.714501	3.595068

Table S17. Cartesian coordinates of the optimized structure of **Int-B'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.599945	-2.748338	-0.161171
2	9	0	-0.925743	1.615486	-1.821481
3	9	0	2.425815	0.899704	1.451747
4	9	0	-0.326045	4.206570	-1.837249
5	9	0	1.638109	5.176605	-0.221929
6	9	0	2.990742	3.476564	1.409052
7	9	0	-1.149772	0.509259	2.151619
8	9	0	-2.020510	-1.438313	-2.084699
9	9	0	-3.738469	0.439141	2.690425
10	9	0	-5.505212	-0.554960	0.879594
11	9	0	-4.590599	-1.484503	-1.509796
12	6	0	0.035462	2.033397	-0.980256
13	6	0	2.013928	3.013529	0.629406
14	6	0	0.331629	3.386559	-1.020024
15	6	0	1.683904	1.665262	0.637755
16	6	0	1.330763	3.883875	-0.201079
17	6	0	0.676540	1.119728	-0.149698
18	6	0	1.333043	-3.468345	-1.179336
19	6	0	0.552997	-2.559326	-1.777185
20	1	0	-0.303666	-2.894005	-2.350134
21	6	0	3.188090	-1.367377	-1.119549
22	6	0	2.213979	-0.701287	-1.747833
23	1	0	2.459067	0.202850	-2.297425
24	6	0	0.770266	-1.086030	-1.685436
25	6	0	-1.416935	-0.529339	0.032058
26	6	0	-1.945859	-0.037303	1.226860
27	6	0	3.916800	-3.914463	0.257935
28	1	0	3.501400	-4.752270	0.819926
29	1	0	4.668680	-3.414237	0.870293
30	1	0	4.379726	-4.283906	-0.658811
31	6	0	-2.371467	-0.990816	-0.862334
32	6	0	-3.298759	-0.041652	1.528347
33	6	0	-4.204198	-0.541272	0.607795
34	6	0	-3.734403	-1.015177	-0.602127
35	5	0	0.221490	-0.468144	-0.178729
36	1	0	1.174504	-4.537765	-1.229111
37	1	0	4.229299	-1.073088	-1.115605
38	1	0	0.211428	-0.578487	-2.469069
39	6	0	1.663337	-2.037598	1.292827
40	7	0	0.789425	-1.181829	1.061822
41	6	0	2.018117	-2.549625	2.663760
42	1	0	1.892167	-3.635563	2.732316
43	1	0	3.059909	-2.315998	2.908210
44	1	0	1.366638	-2.065348	3.391014

Table S18. Cartesian coordinates of the optimized structure of **TS_{BC}'**

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

1	15	0	-1.719047	3.250409	-0.318994
2	9	0	0.456848	-1.988965	-1.573201
3	9	0	-2.551199	-0.195863	1.616821
4	9	0	-0.971595	-4.231519	-1.629366
5	9	0	-3.195705	-4.482525	-0.087561
6	9	0	-3.951739	-2.435682	1.526323
7	9	0	1.284463	-0.369254	2.394742
8	9	0	2.111278	0.393893	-2.213078
9	9	0	3.874280	-0.780114	2.765642
10	9	0	5.611511	-0.608654	0.679649
11	9	0	4.670416	-0.017812	-1.798728
12	6	0	-0.614121	-2.059946	-0.774982
13	6	0	-2.860732	-2.319491	0.772916
14	6	0	-1.344927	-3.235274	-0.831635
15	6	0	-2.104443	-1.157021	0.802258
16	6	0	-2.479426	-3.366701	-0.048046
17	6	0	-0.956473	-0.979461	0.034063
18	6	0	-0.354639	3.479268	-1.393807
19	6	0	0.051609	2.353641	-2.049976
20	1	0	0.971353	2.408729	-2.622336
21	6	0	-2.727192	2.041280	-1.101669
22	6	0	-2.046549	1.097321	-1.808677
23	1	0	-2.613138	0.260734	-2.209815
24	6	0	-0.638630	1.104500	-2.054024
25	6	0	1.549917	0.113889	0.086018
26	6	0	2.083024	-0.225041	1.331682
27	6	0	-2.597577	4.774648	0.103959
28	1	0	-1.915779	5.476922	0.586558
29	1	0	-3.421823	4.552923	0.784044
30	1	0	-2.989844	5.218434	-0.812147
31	6	0	2.476045	0.149138	-0.949316
32	6	0	3.430049	-0.465131	1.551499
33	6	0	4.316929	-0.384948	0.492457
34	6	0	3.832721	-0.080308	-0.766207
35	5	0	-0.055681	0.349704	0.062753
36	1	0	0.186465	4.415047	-1.427920
37	1	0	-3.794881	2.005301	-0.933470
38	1	0	-0.252181	0.335926	-2.708910
39	6	0	-1.036549	2.452103	1.198631
40	7	0	-0.452551	1.360893	0.999234
41	6	0	-1.191970	3.058917	2.565493
42	1	0	-0.758911	4.063883	2.600783
43	1	0	-2.252315	3.147066	2.824412
44	1	0	-0.696398	2.424287	3.300292

Table S19. Cartesian coordinates of the optimized structure of **Int-C'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.257848	2.866514	-0.437305
2	9	0	-1.751625	-2.355253	1.190523
3	9	0	-2.253359	2.094606	-0.322934
4	9	0	-4.333255	-2.808419	0.668275
5	9	0	-5.886999	-0.833326	-0.351759
6	9	0	-4.823157	1.615060	-0.837821
7	9	0	2.116490	-0.121354	2.326626
8	9	0	-0.309582	-1.814163	-1.364093
9	9	0	4.125693	-1.758375	1.735493
10	9	0	3.948418	-3.447300	-0.380112
11	9	0	1.710463	-3.460115	-1.916725
12	6	0	-2.472439	-1.356282	0.675809
13	6	0	-4.060854	0.644047	-0.343985
14	6	0	-3.809170	-1.613850	0.419792
15	6	0	-2.721792	0.864186	-0.066952
16	6	0	-4.606916	-0.605659	-0.098118
17	6	0	-1.879461	-0.121111	0.435798
18	6	0	2.980085	2.653762	-0.403194
19	6	0	3.560914	1.600976	-1.085080
20	1	0	4.634330	1.478822	-0.963880
21	6	0	0.673510	1.749870	-1.626275
22	6	0	1.544742	0.845379	-2.218326
23	1	0	1.112767	0.178048	-2.959820
24	6	0	2.901927	0.714185	-1.943388

25	6	0	0.793123	-0.906882	0.522843
26	6	0	1.965867	-0.928085	1.272395
27	6	0	0.720228	4.591433	-0.654785
28	1	0	1.163206	5.223842	0.118231
29	1	0	-0.368819	4.644723	-0.581542
30	1	0	1.041372	4.940891	-1.636112
31	6	0	0.752931	-1.791997	-0.550810
32	6	0	3.025455	-1.775080	0.988594
33	6	0	2.937120	-2.641375	-0.087132
34	6	0	1.791683	-2.649390	-0.865770
35	5	0	-0.352230	0.156918	0.754921
36	1	0	3.582172	3.312988	0.210779
37	1	0	-0.360766	1.807847	-1.938058
38	1	0	3.474274	-0.050054	-2.452783
39	6	0	0.557982	2.446821	1.274181
40	7	0	-0.021996	1.348851	1.382293
41	6	0	0.857671	3.355836	2.428646
42	1	0	1.907577	3.663472	2.404653
43	1	0	0.245596	4.260520	2.362258
44	1	0	0.652264	2.851697	3.372498

Table S20. Cartesian coordinates of the optimized structure of **3a'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-3.396386	-0.568374	-0.482558
2	9	0	-1.133259	2.265173	-0.713697
3	9	0	2.908597	0.923690	1.328397
4	9	0	-0.216576	4.769633	-0.855787
5	9	0	2.255088	5.378185	0.081607
6	9	0	2.159630	-0.196613	-1.821099
7	9	0	0.507600	-2.453631	1.979489
8	9	0	3.807431	3.440767	1.172914
9	9	0	2.118709	-4.522062	1.439269
10	9	0	3.755054	-4.450875	-0.720291
11	9	0	3.765429	-2.280798	-2.347607
12	7	0	-0.961131	-0.250490	0.736679
13	6	0	-5.748193	0.755708	-0.218217
14	1	0	-6.300408	1.692293	-0.205039
15	6	0	-6.467516	-0.421639	-0.011672
16	6	0	-4.387627	0.852448	-0.461112
17	6	0	0.852227	1.487559	0.314722
18	6	0	1.276388	-1.239693	0.102109
19	6	0	-2.160038	-0.510208	0.951280
20	6	0	0.542984	3.821262	-0.319210
21	6	0	0.090326	2.515582	-0.227407
22	6	0	-5.842505	-1.667643	-0.070022
23	1	0	-6.466392	-2.549943	0.050945
24	6	0	1.294169	-2.376215	0.901764
25	6	0	2.113608	1.845903	0.777472
26	6	0	2.122233	-3.457366	0.644934
27	6	0	2.132533	-1.246586	-0.992042
28	6	0	2.599542	3.141374	0.710931
29	6	0	-4.493466	-1.896569	-0.285797
30	6	0	2.962802	-3.422606	-0.457143
31	6	0	1.807221	4.134439	0.155861
32	6	0	2.968424	-2.310965	-1.285933
33	6	0	-2.737807	-0.735866	2.314717
34	1	0	-3.557620	-0.030702	2.481633
35	1	0	-1.974835	-0.621159	3.083359
36	1	0	-3.172804	-1.738384	2.361312
37	6	0	-2.277808	-0.708789	-1.911407
38	1	0	-2.901097	-0.831826	-2.797146
39	1	0	-1.618389	-1.572572	-1.799469
40	1	0	-1.675078	0.194645	-2.009621
41	5	0	0.332480	-0.004413	0.403515
42	1	0	-4.105899	-2.907454	-0.332691
43	1	0	-7.534056	-0.369737	0.161217
44	1	0	-3.916444	1.813954	-0.622181

Table S21. Cartesian coordinates of the optimized structure of **TS_{22d}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.139857	1.552029	-0.784604
2	9	0	2.010247	-2.750817	0.773178
3	9	0	2.072692	1.270233	-1.693701
4	9	0	4.586694	-3.166859	0.138404
5	9	0	5.911567	-1.361978	-1.402324
6	9	0	4.622622	0.843844	-2.308917
7	9	0	0.161280	-1.139256	-2.654730
8	9	0	-1.402640	-2.408495	1.620107
9	9	0	-1.586984	-2.805912	-3.770812
10	9	0	-3.268654	-4.267832	-2.221592
11	9	0	-3.146266	-4.049485	0.481881
12	6	0	2.635598	-1.844186	0.012688
13	6	0	3.980724	-0.029072	-1.538893
14	6	0	3.962662	-2.079483	-0.300544
15	6	0	2.653336	0.178882	-1.193642
16	6	0	4.640693	-1.158812	-1.083576
17	6	0	0.946497	-0.242914	2.571049
18	6	0	-3.591983	0.935466	0.636061
19	6	0	1.943767	-0.710587	-0.399863
20	6	0	-2.115059	0.954042	0.648475
21	6	0	-1.360928	0.444273	1.622899
22	1	0	-1.813603	0.038172	2.518776
23	6	0	0.088152	2.519823	0.165599
24	6	0	0.626229	1.810704	1.155597
25	1	0	1.363624	2.242059	1.824098
26	6	0	0.144403	0.385749	1.421747
27	6	0	-0.560075	-1.657938	-0.460076
28	6	0	0.425559	3.923044	-0.144472
29	6	0	0.369737	-1.051714	3.549734
30	1	0	-0.688973	-1.265124	3.536389
31	6	0	-0.631512	-1.840150	-1.842093
32	6	0	2.328027	-0.024685	2.640133
33	1	0	2.816104	0.588564	1.891098
34	6	0	-4.267577	0.205326	-0.346591
35	1	0	-3.696439	-0.341936	-1.091633
36	6	0	-4.334674	1.620488	1.597502
37	1	0	-3.815707	2.196394	2.355862
38	6	0	0.370426	4.896116	0.855898
39	1	0	0.060014	4.610290	1.854929
40	6	0	0.804035	4.304812	-1.434603
41	1	0	0.870425	3.556460	-2.216860
42	6	0	1.074285	6.586529	-0.709561
43	1	0	1.326218	7.617776	-0.929068
44	6	0	1.128111	5.625158	-1.713351
45	1	0	1.430818	5.903554	-2.716550
46	6	0	1.140672	-1.614504	4.560682
47	1	0	0.662203	-2.237730	5.307729
48	6	0	-2.227184	2.782274	-1.607960
49	1	0	-3.104638	2.267849	-2.002451
50	1	0	-1.689774	3.243023	-2.437026
51	1	0	-2.547259	3.558052	-0.910362
52	6	0	-1.429172	-2.444427	0.287313
53	6	0	2.508613	-1.390628	4.612735
54	1	0	3.108597	-1.836360	5.397700
55	6	0	3.100417	-0.589428	3.644030
56	1	0	4.168238	-0.402907	3.666488
57	6	0	-5.724108	1.569827	1.581519
58	1	0	-6.289797	2.105238	2.335865
59	6	0	-6.387161	0.840466	0.602265
60	1	0	-7.470395	0.802611	0.590814
61	6	0	0.695624	6.217849	0.575392
62	1	0	0.647349	6.961827	1.362733
63	6	0	-1.536568	-2.694753	-2.447214
64	6	0	-5.654505	0.156749	-0.362670
65	1	0	-6.164852	-0.421249	-1.124925
66	6	0	-2.399419	-3.440982	-1.659387
67	6	0	-2.339161	-3.321582	-0.281869
68	5	0	0.445961	-0.573674	0.122457

Table S22. Cartesian coordinates of the optimized structure of MeCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-1.175372
2	1	0	0.000000	1.025422	-1.547512
3	1	0	0.888042	-0.512711	-1.547512
4	1	0	-0.888042	-0.512711	-1.547512
5	6	0	0.000000	0.000000	0.280640
6	7	0	0.000000	0.000000	1.430133

Table S23. Cartesian coordinates of the optimized structure of **Int-A**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-3.362629	-0.848353	-0.622037
2	9	0	3.201640	1.036931	1.054736
3	9	0	-0.325243	2.578087	-1.713358
4	9	0	4.263985	3.460435	1.013311
5	9	0	3.062799	5.475984	-0.357630
6	9	0	0.758359	4.984865	-1.714600
7	9	0	2.466631	-0.126157	-2.602084
8	9	0	1.845977	-1.897177	1.744950
9	9	0	4.489586	-1.793624	-2.969643
10	9	0	5.223386	-3.534427	-1.008285
11	9	0	3.858997	-3.546056	1.342569
12	6	0	2.567971	1.967674	0.333506
13	6	0	1.356534	4.006969	-1.039219
14	6	0	3.140782	3.229504	0.340443
15	6	0	0.815168	2.729942	-1.018800
16	6	0	2.530511	4.260715	-0.353408
17	6	0	1.387297	1.658825	-0.339785
18	6	0	-2.077827	-1.959247	0.053184
19	6	0	-0.944745	-1.525946	0.613950
20	1	0	-0.233699	-2.286952	0.920466
21	6	0	-2.762028	0.746233	0.030881
22	6	0	-1.549061	0.913945	0.562646
23	1	0	-1.277156	1.926346	0.851998
24	6	0	-0.472749	-0.112301	0.829146
25	6	0	1.995497	-0.953914	-0.425915
26	6	0	2.750770	-0.976909	-1.597370
27	6	0	-4.774468	-1.201698	0.516392
28	1	0	-5.143629	-2.211227	0.324031
29	1	0	-5.578863	-0.491200	0.315124
30	1	0	-4.467261	-1.117497	1.560515
31	6	0	2.431979	-1.845679	0.545841
32	6	0	3.823005	-1.824798	-1.817646
33	6	0	4.201099	-2.709110	-0.822735
34	6	0	3.500291	-2.713714	0.369270
35	5	0	0.769328	0.140166	-0.300362
36	7	0	-0.009413	-0.062579	-1.666848
37	6	0	-0.640137	-0.232419	-2.599883
38	6	0	-1.455799	-0.419839	-3.776121
39	1	0	-1.500428	0.519869	-4.329172
40	1	0	-1.023474	-1.200542	-4.403347
41	1	0	-2.458101	-0.707215	-3.445965
42	6	0	-0.085795	0.108311	2.307380
43	6	0	-0.402157	-0.838052	3.283361
44	6	0	0.483440	1.307862	2.740432
45	6	0	-0.111417	-0.621846	4.624281
46	1	0	-0.883950	-1.765639	3.000865
47	6	0	0.777420	1.530334	4.079064
48	1	0	0.694099	2.097656	2.031998
49	6	0	0.489871	0.561265	5.030854
50	1	0	-0.361169	-1.384646	5.353650
51	1	0	1.230563	2.469762	4.376127
52	1	0	0.721304	0.730744	6.076228
53	6	0	-2.339454	-3.416526	-0.089514
54	6	0	-2.066100	-4.293336	0.964338
55	6	0	-2.865205	-3.946760	-1.271722
56	6	0	-2.284729	-5.658102	0.831447
57	1	0	-1.689560	-3.897242	1.900976
58	6	0	-3.086561	-5.311578	-1.404919

59	1	0	-3.097962	-3.283129	-2.098221
60	6	0	-2.794403	-6.173569	-0.354657
61	1	0	-2.065080	-6.320010	1.661673
62	1	0	-3.487336	-5.703143	-2.333385
63	1	0	-2.969058	-7.238480	-0.457039
64	6	0	-3.692247	1.897770	-0.097007
65	6	0	-4.407232	2.127342	-1.276050
66	6	0	-3.873164	2.778606	0.972902
67	6	0	-5.258661	3.218533	-1.390429
68	1	0	-4.287322	1.449651	-2.115163
69	6	0	-4.722765	3.871178	0.857908
70	1	0	-3.350641	2.591898	1.904988
71	6	0	-5.417770	4.096546	-0.324601
72	1	0	-5.797208	3.385864	-2.316695
73	1	0	-4.849713	4.543268	1.699322
74	1	0	-6.083663	4.947376	-0.413064

Table S24. Cartesian coordinates of the optimized structure of **TS_{AB}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.720269	2.793908	-0.689263
2	9	0	-0.058456	-3.042537	1.219353
3	9	0	2.149972	-0.582599	-2.181373
4	9	0	2.110431	-4.529771	1.518557
5	9	0	4.312142	-4.090710	-0.017482
6	9	0	4.266433	-2.104801	-1.877740
7	9	0	-0.917458	-3.533946	-1.297881
8	9	0	-3.011496	0.625777	-0.419214
9	9	0	-3.265820	-4.602760	-1.718387
10	9	0	-5.539399	-3.126302	-1.520843
11	9	0	-5.356606	-0.483245	-0.879920
12	6	0	0.997799	-2.739421	0.457718
13	6	0	3.203794	-2.320065	-1.103014
14	6	0	2.111336	-3.544791	0.623722
15	6	0	2.066318	-1.535358	-1.235324
16	6	0	3.231974	-3.330168	-0.160921
17	6	0	0.924622	-1.689525	-0.456635
18	6	0	-0.736388	2.711060	0.379462
19	6	0	-0.988575	1.558927	1.006857
20	1	0	-1.902667	1.505307	1.587978
21	6	0	1.843797	1.689675	0.202240
22	6	0	1.317950	0.672477	0.887768
23	1	0	2.022197	-0.029408	1.319880
24	6	0	-0.145360	0.305554	1.001780
25	6	0	-1.814432	-1.401976	-0.704968
26	6	0	-1.968616	-2.730169	-1.102001
27	6	0	1.409434	4.485019	-0.528749
28	1	0	0.724305	5.205303	-0.976867
29	1	0	2.372809	4.530708	-1.038218
30	1	0	1.545403	4.725943	0.527780
31	6	0	-3.012029	-0.690691	-0.687548
32	6	0	-3.198011	-3.322504	-1.361614
33	6	0	-4.357267	-2.575912	-1.271416
34	6	0	-4.259517	-1.236735	-0.940444
35	5	0	-0.360718	-0.654332	-0.432505
36	6	0	-0.042156	1.333769	-2.218941
37	7	0	-0.246767	0.323775	-1.643391
38	6	0	-0.114566	1.939168	-3.564919
39	1	0	-0.736773	2.835241	-3.535167
40	1	0	0.889414	2.227976	-3.881554
41	1	0	-0.533620	1.214604	-4.265284
42	6	0	-0.447832	-0.451176	2.299516
43	6	0	-1.751743	-0.892942	2.548386
44	6	0	0.510119	-0.701954	3.281270
45	6	0	-2.076344	-1.584747	3.703807
46	1	0	-2.532517	-0.706917	1.822063
47	6	0	0.190802	-1.400769	4.442379
48	1	0	1.528266	-0.352691	3.168017
49	6	0	-1.100972	-1.852715	4.658108
50	1	0	-3.095510	-1.922418	3.856091
51	1	0	0.963488	-1.586892	5.180211
52	1	0	-1.349103	-2.401656	5.559214

53	6	0	-1.646985	3.876841	0.454073
54	6	0	-2.070612	4.535798	-0.703166
55	6	0	-2.110306	4.334423	1.689221
56	6	0	-2.940014	5.615431	-0.630860
57	1	0	-1.735111	4.184928	-1.674945
58	6	0	-2.985282	5.411072	1.762621
59	1	0	-1.772268	3.843593	2.595301
60	6	0	-3.401323	6.056522	0.604388
61	1	0	-3.266266	6.107228	-1.540403
62	1	0	-3.336893	5.751559	2.730045
63	1	0	-4.081143	6.898669	0.662940
64	6	0	3.306157	1.877345	0.056473
65	6	0	4.133643	1.880435	1.180810
66	6	0	3.886487	2.030149	-1.205119
67	6	0	5.509722	2.016125	1.045163
68	1	0	3.688873	1.784187	2.165478
69	6	0	5.260621	2.170185	-1.340466
70	1	0	3.259854	2.002274	-2.091046
71	6	0	6.077006	2.162464	-0.214899
72	1	0	6.139526	2.013461	1.927647
73	1	0	5.696948	2.270540	-2.327760
74	1	0	7.150550	2.268183	-0.320375

Table S25. Cartesian coordinates of the optimized structure of **Int-B**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.652685	-0.027534	-0.794130
2	9	0	3.217895	0.197813	0.995769
3	9	0	0.155965	2.497694	-1.796238
4	9	0	4.616933	2.426699	1.262718
5	9	0	3.826419	4.717600	0.025640
6	9	0	1.574393	4.697760	-1.508852
7	9	0	2.964625	-0.254287	-2.098729
8	9	0	0.286743	-3.083523	0.618004
9	9	0	4.528791	-2.289444	-2.624955
10	9	0	4.048802	-4.742085	-1.545702
11	9	0	1.885192	-5.070090	0.081964
12	6	0	2.746082	1.288151	0.380229
13	6	0	1.969666	3.587250	-0.881317
14	6	0	3.510187	2.435010	0.522659
15	6	0	1.239843	2.413828	-1.001508
16	6	0	3.114802	3.602205	-0.106988
17	6	0	1.570840	1.226003	-0.364047
18	6	0	-2.396815	-1.325500	0.402268
19	6	0	-1.322431	-1.126812	1.176491
20	1	0	-1.130841	-1.867133	1.941688
21	6	0	-2.229251	1.452704	0.123206
22	6	0	-1.132047	1.299450	0.871787
23	1	0	-0.781361	2.186554	1.383523
24	6	0	-0.356510	0.018573	1.075095
25	6	0	1.572508	-1.490865	-0.610351
26	6	0	2.661919	-1.405193	-1.485216
27	6	0	-4.337545	-0.005764	-1.445371
28	1	0	-4.475629	-0.844203	-2.128343
29	1	0	-4.506788	0.934987	-1.971373
30	1	0	-5.047525	-0.098124	-0.622490
31	6	0	1.354598	-2.780259	-0.146139
32	6	0	3.499382	-2.462707	-1.797883
33	6	0	3.258734	-3.713328	-1.257117
34	6	0	2.167087	-3.870780	-0.429039
35	5	0	0.628901	-0.128936	-0.410938
36	6	0	-1.337413	-0.178232	-2.099290
37	7	0	-0.144279	-0.157516	-1.737697
38	6	0	-1.789557	-0.265383	-3.533443
39	1	0	-2.409674	-1.152089	-3.704487
40	1	0	-2.381072	0.613258	-3.811854
41	1	0	-0.906994	-0.318117	-4.170713
42	6	0	0.546542	0.088930	2.312998
43	6	0	1.037649	-1.081495	2.901855
44	6	0	0.980832	1.298177	2.865474
45	6	0	1.900891	-1.047989	3.987537
46	1	0	0.772826	-2.049565	2.501332

47	6	0	1.848671	1.337011	3.950525
48	1	0	0.682559	2.249586	2.445606
49	6	0	2.312919	0.163732	4.524195
50	1	0	2.261940	-1.981121	4.405518
51	1	0	2.166864	2.298116	4.338921
52	1	0	2.993370	0.192763	5.367184
53	6	0	-3.321396	-2.475703	0.504792
54	6	0	-3.595987	-3.267571	-0.613094
55	6	0	-3.923849	-2.795520	1.722370
56	6	0	-4.452976	-4.355137	-0.516129
57	1	0	-3.106094	-3.051227	-1.558332
58	6	0	-4.775155	-3.889458	1.820943
59	1	0	-3.723392	-2.178479	2.591553
60	6	0	-5.045390	-4.668499	0.702459
61	1	0	-4.647139	-4.968211	-1.388826
62	1	0	-5.232707	-4.129819	2.773889
63	1	0	-5.711530	-5.519945	0.779985
64	6	0	-3.004513	2.710677	-0.016548
65	6	0	-4.331045	2.765469	0.422131
66	6	0	-2.425251	3.858069	-0.560045
67	6	0	-5.063043	3.940033	0.317273
68	1	0	-4.782598	1.889394	0.876596
69	6	0	-3.158424	5.035363	-0.658116
70	1	0	-1.404081	3.821923	-0.915822
71	6	0	-4.477542	5.079121	-0.225304
72	1	0	-6.087352	3.969990	0.671169
73	1	0	-2.693721	5.919326	-1.079715
74	1	0	-5.047237	5.997848	-0.305114

Table S26. Cartesian coordinates of the optimized structure of **TS_{BC}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.580069	2.627271	-0.499647
2	9	0	-0.089967	-3.088920	0.840398
3	9	0	2.323413	-0.316634	-2.154064
4	9	0	2.111749	-4.484921	1.286095
5	9	0	4.437070	-3.837040	0.036058
6	9	0	4.482701	-1.747996	-1.705333
7	9	0	-0.863694	-3.345915	-1.693685
8	9	0	-2.955618	0.679814	-0.347958
9	9	0	-3.227824	-4.460566	-1.968800
10	9	0	-5.499889	-3.061004	-1.451298
11	9	0	-5.312182	-0.462517	-0.653915
12	6	0	1.021139	-2.682713	0.223506
13	6	0	3.358268	-2.055993	-1.060965
14	6	0	2.154112	-3.442941	0.459992
15	6	0	2.202250	-1.318369	-1.270215
16	6	0	3.339065	-3.121660	-0.180397
17	6	0	0.997764	-1.570229	-0.618572
18	6	0	-0.823092	2.631832	0.580358
19	6	0	-1.004154	1.468579	1.243046
20	1	0	-1.904606	1.390789	1.843842
21	6	0	1.807435	1.672779	0.366646
22	6	0	1.293919	0.642668	1.072666
23	1	0	2.020099	-0.042390	1.496447
24	6	0	-0.118068	0.309121	1.241288
25	6	0	-1.758383	-1.302130	-0.860308
26	6	0	-1.916946	-2.602266	-1.339302
27	6	0	1.135317	4.294984	-0.916658
28	1	0	0.321462	4.845209	-1.389748
29	1	0	1.996157	4.250684	-1.583315
30	1	0	1.420185	4.799022	0.008669
31	6	0	-2.956566	-0.616747	-0.693569
32	6	0	-3.150894	-3.207932	-1.526820
33	6	0	-4.310638	-2.497673	-1.275897
34	6	0	-4.210167	-1.180928	-0.866005
35	5	0	-0.296808	-0.591391	-0.711823
36	6	0	0.097721	1.629178	-1.975006
37	7	0	-0.191916	0.425932	-1.780633
38	6	0	0.092539	2.271408	-3.335807
39	1	0	-0.554704	3.154525	-3.358411
40	1	0	1.101804	2.599081	-3.608343

41	1	0	-0.257675	1.546624	-4.070635
42	6	0	-0.452467	-0.687314	2.319362
43	6	0	-1.779800	-1.096874	2.498314
44	6	0	0.504953	-1.242538	3.173208
45	6	0	-2.129769	-2.030829	3.460131
46	1	0	-2.558590	-0.697291	1.860523
47	6	0	0.158931	-2.186902	4.133393
48	1	0	1.544854	-0.946865	3.113062
49	6	0	-1.158754	-2.591859	4.281698
50	1	0	-3.167207	-2.330853	3.559189
51	1	0	0.931401	-2.603369	4.770491
52	1	0	-1.427591	-3.331446	5.026873
53	6	0	-1.762280	3.773677	0.627489
54	6	0	-2.334499	4.283576	-0.541613
55	6	0	-2.111307	4.350539	1.850051
56	6	0	-3.226532	5.345876	-0.491356
57	1	0	-2.108923	3.817902	-1.496770
58	6	0	-3.013769	5.406020	1.902175
59	1	0	-1.664002	3.968354	2.761179
60	6	0	-3.568897	5.910638	0.732499
61	1	0	-3.669273	5.722041	-1.406751
62	1	0	-3.277643	5.840205	2.859929
63	1	0	-4.269182	6.736905	0.773627
64	6	0	3.255872	1.928352	0.217286
65	6	0	4.085076	1.923212	1.342065
66	6	0	3.833086	2.145576	-1.037048
67	6	0	5.455114	2.111658	1.213276
68	1	0	3.645146	1.779734	2.323153
69	6	0	5.200334	2.345662	-1.164726
70	1	0	3.215965	2.107637	-1.928938
71	6	0	6.016576	2.327183	-0.039532
72	1	0	6.084305	2.099225	2.096066
73	1	0	5.632301	2.495540	-2.147569
74	1	0	7.085355	2.476676	-0.139719

Table S27. Cartesian coordinates of the optimized structure of **Int-C**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.860746	-2.269979	0.751684
2	9	0	-2.609622	2.239738	-2.093239
3	9	0	-2.973781	-2.163915	-0.401718
4	9	0	-5.237359	2.542427	-1.814662
5	9	0	-6.754689	0.517150	-0.839446
6	9	0	-5.596032	-1.837654	-0.158287
7	9	0	1.290014	-0.039344	-3.001905
8	9	0	-1.165315	2.311852	0.285119
9	9	0	3.090702	1.920691	-3.033291
10	9	0	2.764114	4.115079	-1.476859
11	9	0	0.629095	4.277785	0.201299
12	6	0	-3.297130	1.219785	-1.574535
13	6	0	-4.849543	-0.838938	-0.617947
14	6	0	-4.665450	1.398218	-1.454339
15	6	0	-3.478730	-0.980653	-0.749338
16	6	0	-5.444631	0.362733	-0.964111
17	6	0	-2.647562	0.043361	-1.205099
18	6	0	2.500519	-1.685839	0.577700
19	6	0	2.812264	-0.406190	0.992167
20	1	0	3.837800	-0.099018	0.801046
21	6	0	0.027317	-1.086353	1.734226
22	6	0	0.688575	0.102058	2.026561
23	1	0	0.102056	0.811536	2.603996
24	6	0	1.984316	0.489581	1.682933
25	6	0	-0.040453	1.059323	-1.375187
26	6	0	1.084731	1.006130	-2.189993
27	6	0	0.773800	-4.019136	1.260522
28	1	0	1.436662	-4.603500	0.619423
29	1	0	-0.247566	-4.386747	1.145505
30	1	0	1.095127	-4.117438	2.297885
31	6	0	-0.140361	2.187609	-0.568366
32	6	0	2.031073	2.016785	-2.231547
33	6	0	1.871219	3.136710	-1.432960
34	6	0	0.779746	3.220970	-0.584512

35	5	0	-1.080014	-0.136048	-1.295551
36	6	0	0.134566	-2.367197	-1.000241
37	7	0	-0.552732	-1.402918	-1.379138
38	6	0	0.552024	-3.493428	-1.902318
39	1	0	1.627345	-3.675950	-1.824363
40	1	0	0.036091	-4.411394	-1.604379
41	1	0	0.295993	-3.257583	-2.934959
42	6	0	2.506313	1.814160	2.096061
43	6	0	3.452569	2.491361	1.317228
44	6	0	2.071464	2.439825	3.270633
45	6	0	3.935280	3.739105	1.687171
46	1	0	3.805306	2.046662	0.392699
47	6	0	2.544142	3.692779	3.636563
48	1	0	1.370142	1.932836	3.924172
49	6	0	3.478695	4.351883	2.847252
50	1	0	4.657659	4.241033	1.053351
51	1	0	2.186541	4.151420	4.552029
52	1	0	3.846618	5.330604	3.132664
53	6	0	-1.368309	-1.289979	2.204369
54	6	0	-1.808185	-2.496812	2.759307
55	6	0	-2.287146	-0.234967	2.138517
56	6	0	-3.118251	-2.655069	3.193230
57	1	0	-1.115687	-3.317997	2.892190
58	6	0	-3.590308	-0.385656	2.590556
59	1	0	-1.983368	0.708772	1.703777
60	6	0	-4.019634	-1.602135	3.107169
61	1	0	-3.430558	-3.604066	3.614864
62	1	0	-4.278171	0.450307	2.520804
63	1	0	-5.042574	-1.726288	3.442641
64	6	0	3.484852	-2.493464	-0.192345
65	6	0	3.996200	-3.699017	0.296401
66	6	0	3.919283	-2.045188	-1.444172
67	6	0	4.900272	-4.444135	-0.451627
68	1	0	3.703087	-4.040451	1.283358
69	6	0	4.830605	-2.783868	-2.187988
70	1	0	3.521146	-1.117338	-1.840113
71	6	0	5.317718	-3.990319	-1.697532
72	1	0	5.290438	-5.374241	-0.053482
73	1	0	5.153953	-2.419100	-3.156451
74	1	0	6.024741	-4.570200	-2.279740

Table S28. Cartesian coordinates of the optimized structure of **3a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.688055	0.557511	0.548967
2	9	0	-1.530616	2.892293	0.332042
3	9	0	-4.840807	-0.107958	-1.216462
4	9	0	-3.356093	4.825057	0.448061
5	9	0	-5.929819	4.324219	-0.253318
6	9	0	-3.464891	-0.896073	1.774566
7	9	0	-1.425883	-2.064096	-2.310604
8	9	0	-6.648202	1.845008	-1.085136
9	9	0	-2.189238	-4.612146	-1.955303
10	9	0	-3.587806	-5.320313	0.252967
11	9	0	-4.210983	-3.459732	2.125788
12	7	0	-0.722898	0.396452	-0.747132
13	6	0	4.286323	1.112772	0.049430
14	1	0	5.077264	1.839441	-0.122944
15	6	0	6.049966	-0.614121	-0.308049
16	6	0	2.808307	3.107871	0.397469
17	6	0	6.698685	-1.642872	0.384470
18	1	0	6.180757	-2.154783	1.188872
19	6	0	4.652543	-0.236016	0.008160
20	6	0	3.032717	1.647442	0.308297
21	6	0	-3.102053	1.294108	-0.432606
22	6	0	-2.435853	-1.387376	-0.286734
23	6	0	0.500911	0.534404	-0.923994
24	6	0	-3.712493	3.609957	0.045497
25	6	0	-2.783217	2.586092	-0.025790
26	6	0	8.006126	-1.999163	0.080455
27	1	0	8.486599	-2.797719	0.635325
28	6	0	3.775053	3.945481	0.968694

29	1	0	4.680704	3.512189	1.378601
30	6	0	3.704741	-1.225616	0.295638
31	1	0	4.044379	-2.259353	0.274760
32	6	0	1.630397	3.700157	-0.073280
33	1	0	0.853015	3.092641	-0.525120
34	6	0	6.764893	0.049014	-1.312080
35	1	0	6.277836	0.831415	-1.885099
36	6	0	8.704717	-1.325555	-0.914936
37	1	0	9.727104	-1.599879	-1.148513
38	6	0	8.077394	-0.296231	-1.607092
39	1	0	8.607221	0.232050	-2.392358
40	6	0	1.425315	5.070691	0.016756
41	1	0	0.499149	5.497471	-0.351572
42	6	0	-2.116580	-2.373461	-1.208592
43	6	0	-4.433943	1.088425	-0.785401
44	6	0	-2.513173	-3.691156	-1.053226
45	6	0	-3.148641	-1.794179	0.831211
46	6	0	-5.391937	2.088321	-0.732283
47	6	0	2.366764	-1.052332	0.608101
48	6	0	-3.233092	-4.054500	0.072377
49	6	0	-5.027884	3.357185	-0.310580
50	6	0	3.579073	5.317247	1.042498
51	1	0	4.343974	5.942521	1.489706
52	6	0	2.402273	5.888512	0.569971
53	1	0	2.245818	6.958654	0.640141
54	6	0	-3.550033	-3.102894	1.028598
55	6	0	1.165109	0.542328	-2.267894
56	1	0	1.703180	1.485810	-2.402135
57	1	0	0.432347	0.406072	-3.061913
58	1	0	1.912176	-0.256242	-2.306769
59	6	0	0.610163	1.038360	1.929506
60	1	0	1.184149	0.928041	2.849963
61	1	0	-0.277683	0.406983	1.961456
62	1	0	0.307574	2.078350	1.807139
63	6	0	1.468000	-2.219747	0.795317
64	6	0	1.441260	-3.238775	-0.164239
65	1	0	2.046321	-3.137870	-1.058980
66	6	0	0.657807	-4.370802	0.015351
67	1	0	0.659576	-5.150833	-0.737637
68	6	0	-0.138294	-4.497356	1.147781
69	1	0	-0.749438	-5.381752	1.289367
70	6	0	-0.144316	-3.482373	2.096851
71	1	0	-0.757620	-3.574012	2.986702
72	6	0	0.656001	-2.359718	1.925847
73	1	0	0.681557	-1.604556	2.702943
74	5	0	-2.033124	0.129290	-0.499783

Table S29. Cartesian coordinates of the optimized structure of **TS_{22b} (BC bond)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.212617	1.583289	0.272422
2	9	0	0.368663	-2.902925	-0.750033
3	9	0	1.907492	1.346432	-2.071178
4	9	0	2.772519	-3.945857	-1.316972
5	9	0	4.761785	-2.350888	-2.218712
6	9	0	4.330530	0.294086	-2.605520
7	9	0	-1.649419	0.944799	-3.013352
8	9	0	-1.896305	-2.114641	0.554420
9	9	0	-4.221406	0.398304	-3.648405
10	9	0	-5.627513	-1.387089	-2.157515
11	9	0	-4.441021	-2.633723	-0.064186
12	6	0	1.320099	-2.092043	-1.193823
13	6	0	3.359201	-0.472735	-2.124655
14	6	0	2.556074	-2.648659	-1.478853
15	6	0	2.119325	0.052776	-1.816941
16	6	0	3.577832	-1.832106	-1.939531
17	6	0	1.568709	-1.558221	2.545260
18	6	0	-2.580433	1.245552	1.868859
19	6	0	1.073627	-0.726432	-1.322499
20	6	0	-1.158659	0.958464	1.624007
21	6	0	-0.432315	-0.061302	2.216497
22	1	0	-0.975632	-0.717609	2.890586

23	6	0	1.413806	1.840774	0.898150
24	6	0	1.809317	0.741015	1.620507
25	1	0	2.846981	0.700332	1.946544
26	6	0	0.955319	-0.302618	2.065901
27	6	0	-1.691387	-0.553913	-1.206373
28	6	0	2.264440	3.015110	0.626688
29	6	0	1.017737	-2.347682	3.563460
30	1	0	0.120407	-2.023516	4.078390
31	6	0	-2.333794	0.052805	-2.276514
32	6	0	2.747629	-2.019361	1.942296
33	1	0	3.191316	-1.441347	1.137619
34	6	0	-3.488274	0.215660	2.158210
35	1	0	-3.136472	-0.807518	2.218905
36	6	0	-3.083758	2.551737	1.805738
37	1	0	-2.402708	3.379239	1.642399
38	6	0	1.819410	4.317786	0.873455
39	1	0	0.841864	4.471853	1.318053
40	6	0	3.559884	2.846715	0.125213
41	1	0	3.923176	1.845337	-0.079256
42	6	0	3.912291	5.229946	0.102981
43	1	0	4.547233	6.084236	-0.101670
44	6	0	4.376789	3.939481	-0.126796
45	1	0	5.376154	3.782581	-0.517196
46	6	0	1.614699	-3.537923	3.952266
47	1	0	1.165557	-4.124192	4.746656
48	6	0	-0.906954	2.967279	-0.663754
49	1	0	-1.930278	2.725494	-0.952469
50	1	0	-0.296589	3.120731	-1.554327
51	1	0	-0.903851	3.875616	-0.064558
52	6	0	-2.433119	-1.476790	-0.483002
53	6	0	2.785443	-3.977436	3.342493
54	1	0	3.247335	-4.909167	3.647751
55	6	0	3.351735	-3.206146	2.336393
56	1	0	4.260945	-3.534560	1.844324
57	6	0	-4.434950	2.814428	1.990003
58	1	0	-4.792710	3.836906	1.936552
59	6	0	-5.321659	1.779988	2.261936
60	1	0	-6.375883	1.984124	2.408290
61	6	0	2.629793	5.413827	0.605224
62	1	0	2.263971	6.414355	0.808206
63	6	0	-3.648004	-0.209659	-2.617400
64	6	0	-4.835725	0.480172	2.355174
65	1	0	-5.512374	-0.339163	2.572177
66	6	0	-4.365278	-1.122544	-1.858148
67	6	0	-3.754670	-1.761005	-0.790688
68	5	0	-0.240441	-0.050235	-0.856129

Table S30. Cartesian coordinates of the optimized structure of **Int-F**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.660908	-0.045650	-0.734995
2	9	0	3.155824	0.418878	1.140380
3	9	0	0.038302	2.527698	-1.738356
4	9	0	4.328468	2.753859	1.548418
5	9	0	3.409286	5.000309	0.320527
6	9	0	1.257773	4.829278	-1.339733
7	9	0	3.224333	0.021779	-1.809263
8	9	0	0.293113	-3.076839	0.261881
9	9	0	4.900141	-1.930332	-2.299888
10	9	0	4.346587	-4.483486	-1.531233
11	9	0	1.993074	-4.995093	-0.248360
12	6	0	2.609736	1.484687	0.543535
13	6	0	1.705482	3.742508	-0.709924
14	6	0	3.260995	2.688650	0.755222
15	6	0	1.084477	2.515235	-0.891063
16	6	0	2.801094	3.833708	0.128226
17	6	0	1.482359	1.340682	-0.263116
18	6	0	-2.427018	-1.359879	0.443510
19	6	0	-1.308906	-1.233375	1.166327
20	1	0	-1.080022	-2.030155	1.863106
21	6	0	-2.164667	1.411631	0.175330
22	6	0	-1.089633	1.215185	0.946091

23	1	0	-0.671077	2.097262	1.412874
24	6	0	-0.343125	-0.081230	1.111148
25	6	0	1.697286	-1.363807	-0.611227
26	6	0	2.883829	-1.184259	-1.329225
27	6	0	-4.364997	0.062796	-1.310384
28	1	0	-4.708768	-0.924355	-1.619939
29	1	0	-4.425304	0.750629	-2.153527
30	1	0	-4.985075	0.429391	-0.491086
31	6	0	1.449765	-2.698867	-0.318332
32	6	0	3.780867	-2.196779	-1.630884
33	6	0	3.502823	-3.497025	-1.250245
34	6	0	2.314177	-3.748062	-0.594702
35	5	0	0.650152	-0.086466	-0.370170
36	6	0	-1.494392	-0.240052	-2.088381
37	6	0	0.545318	-0.092568	2.362293
38	6	0	1.150335	-1.286328	2.771433
39	6	0	0.828818	1.047628	3.117289
40	6	0	1.998652	-1.338755	3.866445
41	1	0	0.975893	-2.200542	2.221539
42	6	0	1.684045	1.001943	4.213728
43	1	0	0.404179	2.010604	2.868799
44	6	0	2.276494	-0.190430	4.596599
45	1	0	2.452964	-2.284064	4.141733
46	1	0	1.885472	1.913296	4.765770
47	1	0	2.946743	-0.225415	5.447547
48	6	0	-3.336232	-2.532697	0.444596
49	6	0	-2.926716	-3.732851	-0.139431
50	6	0	-4.618638	-2.445866	0.991132
51	6	0	-3.783395	-4.827604	-0.168599
52	1	0	-1.930388	-3.802844	-0.559779
53	6	0	-5.473641	-3.539656	0.959248
54	1	0	-4.937780	-1.520141	1.459028
55	6	0	-5.057844	-4.732591	0.377003
56	1	0	-3.451370	-5.756969	-0.617317
57	1	0	-6.463040	-3.463583	1.395965
58	1	0	-5.724580	-5.587036	0.354131
59	6	0	-2.820023	2.719241	-0.038872
60	6	0	-3.196206	3.503988	1.052406
61	6	0	-3.051831	3.200414	-1.330358
62	6	0	-3.780192	4.749614	0.856579
63	1	0	-3.035122	3.127701	2.056960
64	6	0	-3.641725	4.441030	-1.524185
65	1	0	-2.732543	2.618030	-2.189527
66	6	0	-4.007037	5.219618	-0.431034
67	1	0	-4.064292	5.350660	1.712919
68	1	0	-3.802745	4.807955	-2.531402
69	1	0	-4.464324	6.190417	-0.583538
70	6	0	-0.193519	-0.151056	-1.768158
71	6	0	-2.015421	-0.339876	-3.475358
72	6	0	-2.838334	-1.400094	-3.863592
73	6	0	-1.683897	0.638492	-4.414726
74	6	0	-3.317840	-1.481251	-5.164064
75	1	0	-3.083627	-2.179380	-3.147193
76	6	0	-2.161777	0.554399	-5.717435
77	1	0	-1.047194	1.463928	-4.114444
78	6	0	-2.981958	-0.502462	-6.093835
79	1	0	-3.946590	-2.315034	-5.455641
80	1	0	-1.893914	1.318301	-6.438680
81	1	0	-3.355378	-0.566748	-7.109449
82	1	0	0.465950	-0.189931	-2.639894

Table S31. Cartesian coordinates of the optimized structure of **TS_{FG}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.891939	-1.262844	0.873073
2	9	0	-3.208288	0.459836	0.817992
3	9	0	-0.761625	-2.022195	-2.383794
4	9	0	-5.018752	-1.466736	0.898126
5	9	0	-4.721413	-3.703586	-0.621639
6	9	0	-2.566469	-3.915273	-2.273287

7	9	0	-3.248045	1.607871	-1.602012
8	9	0	1.352579	2.485949	-0.883229
9	9	0	-3.594313	4.116748	-2.310205
10	9	0	-1.506863	5.851159	-2.364518
11	9	0	0.976508	4.984270	-1.666063
12	6	0	-2.997036	-0.606142	0.043731
13	6	0	-2.714965	-2.843672	-1.497221
14	6	0	-3.958487	-1.597479	0.104291
15	6	0	-1.767183	-1.829224	-1.515578
16	6	0	-3.811989	-2.739294	-0.667085
17	6	0	-1.834376	-0.686991	-0.721696
18	6	0	2.289530	0.299666	1.614520
19	6	0	1.225295	1.129594	1.724424
20	1	0	1.437503	2.160141	1.994925
21	6	0	0.302083	-1.687974	1.515968
22	6	0	-0.498283	-0.619932	1.774681
23	1	0	-1.519463	-0.848445	2.056276
24	6	0	-0.176237	0.773116	1.605438
25	6	0	-0.930439	1.902799	-1.149320
26	6	0	-2.172331	2.394947	-1.549403
27	6	0	3.113349	-2.561872	1.157702
28	1	0	4.114446	-2.182529	0.955481
29	1	0	2.908414	-3.402418	0.494633
30	1	0	3.036715	-2.887785	2.195733
31	6	0	0.106206	2.832765	-1.238428
32	6	0	-2.382551	3.708100	-1.947957
33	6	0	-1.321464	4.593921	-1.986455
34	6	0	-0.058590	4.147118	-1.635764
35	5	0	-0.627627	0.403972	-0.661540
36	6	0	1.776550	-0.893395	-0.889123
37	6	0	-1.093455	1.795115	2.214477
38	6	0	-0.989615	3.142684	1.856948
39	6	0	-2.030505	1.465263	3.197714
40	6	0	-1.814377	4.109733	2.415110
41	1	0	-0.248437	3.452222	1.131474
42	6	0	-2.859864	2.427149	3.757778
43	1	0	-2.122401	0.442538	3.543991
44	6	0	-2.765182	3.755595	3.363323
45	1	0	-1.710374	5.143946	2.105500
46	1	0	-3.580870	2.134207	4.512938
47	1	0	-3.415253	4.506124	3.797942
48	6	0	3.694246	0.748231	1.743710
49	6	0	4.144811	1.858929	1.023400
50	6	0	4.599615	0.072622	2.567484
51	6	0	5.464358	2.281347	1.126481
52	1	0	3.456357	2.377150	0.366314
53	6	0	5.920696	0.489871	2.662168
54	1	0	4.258845	-0.771713	3.157212
55	6	0	6.358067	1.595085	1.940202
56	1	0	5.796159	3.143925	0.559599
57	1	0	6.607525	-0.042269	3.310804
58	1	0	7.388949	1.921641	2.015583
59	6	0	-0.233039	-3.064084	1.452443
60	6	0	-1.123236	-3.524839	2.427243
61	6	0	0.049159	-3.898321	0.365093
62	6	0	-1.735144	-4.764645	2.301938
63	1	0	-1.335842	-2.902026	3.289755
64	6	0	-0.551213	-5.144636	0.247724
65	1	0	0.700143	-3.551731	-0.432295
66	6	0	-1.452518	-5.579947	1.211642
67	1	0	-2.432075	-5.097889	3.062734
68	1	0	-0.334737	-5.764180	-0.614932
69	1	0	-1.933052	-6.546250	1.112828
70	6	0	0.731477	-0.159696	-1.301471
71	6	0	2.887742	-1.296784	-1.791554
72	6	0	4.207554	-0.905670	-1.547984
73	6	0	2.613616	-2.087513	-2.909319
74	6	0	5.227631	-1.295888	-2.405268
75	1	0	4.438118	-0.269853	-0.698464
76	6	0	3.636593	-2.475965	-3.766734
77	1	0	1.592406	-2.395867	-3.101524
78	6	0	4.945869	-2.084217	-3.515963
79	1	0	6.244445	-0.974584	-2.209069
80	1	0	3.408197	-3.088690	-4.631632
81	1	0	5.743351	-2.388153	-4.184424
82	1	0	0.795925	0.120078	-2.357972

Table S32. Cartesian coordinates of the optimized structure of **Int-G**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.705228	0.826310	-0.899051
2	9	0	-3.061832	0.407543	-0.418664
3	9	0	-0.779258	2.690059	3.045676
4	9	0	-4.779114	2.409918	-0.584853
5	9	0	-4.535412	4.575092	1.036150
6	9	0	-2.526560	4.668935	2.862361
7	9	0	-3.330343	-0.952808	1.749685
8	9	0	1.309859	-1.818645	1.329616
9	9	0	-3.800144	-3.538631	1.612260
10	9	0	-1.753852	-5.301629	1.369011
11	9	0	0.803440	-4.394225	1.264207
12	6	0	-2.888210	1.429794	0.421216
13	6	0	-2.652318	3.613997	2.060791
14	6	0	-3.798077	2.464921	0.308469
15	6	0	-1.750942	2.565118	2.128997
16	6	0	-3.677343	3.570369	1.133192
17	6	0	-1.818960	1.435466	1.316809
18	6	0	2.309331	-0.761916	-1.394618
19	6	0	1.420130	-1.735611	-1.760214
20	1	0	1.866662	-2.698588	-1.997343
21	6	0	0.006997	0.831797	-1.368683
22	6	0	-0.575179	-0.372744	-1.795064
23	1	0	-1.634497	-0.309372	-2.007583
24	6	0	0.016943	-1.616418	-1.918359
25	6	0	-0.989093	-1.207458	1.401762
26	6	0	-2.278757	-1.740863	1.533541
27	6	0	2.666493	2.170647	-1.661028
28	1	0	3.712731	2.085935	-1.365797
29	1	0	2.283962	3.134328	-1.325603
30	1	0	2.571486	2.096201	-2.744735
31	6	0	0.025521	-2.172225	1.344880
32	6	0	-2.552464	-3.097570	1.501774
33	6	0	-1.511174	-4.003252	1.387251
34	6	0	-0.211411	-3.534535	1.332813
35	5	0	-0.669513	0.332845	1.320027
36	6	0	1.839874	1.153398	0.904469
37	6	0	-0.801175	-2.813726	-2.231245
38	6	0	-0.391494	-4.092260	-1.831002
39	6	0	-2.026285	-2.717767	-2.905153
40	6	0	-1.171266	-5.215684	-2.075246
41	1	0	0.544612	-4.220135	-1.299655
42	6	0	-2.812637	-3.836463	-3.139448
43	1	0	-2.371595	-1.756590	-3.268659
44	6	0	-2.393421	-5.095136	-2.722902
45	1	0	-0.825185	-6.187231	-1.740094
46	1	0	-3.757204	-3.723922	-3.660433
47	1	0	-3.009126	-5.968363	-2.904504
48	6	0	3.758612	-1.071781	-1.277431
49	6	0	4.186550	-2.034783	-0.357754
50	6	0	4.720609	-0.423350	-2.057254
51	6	0	5.537144	-2.325017	-0.208401
52	1	0	3.450114	-2.538002	0.257651
53	6	0	6.071761	-0.705216	-1.900368
54	1	0	4.407423	0.294951	-2.806070
55	6	0	6.485424	-1.652641	-0.970526
56	1	0	5.848913	-3.070894	0.514175
57	1	0	6.802775	-0.191270	-2.514577
58	1	0	7.539976	-1.872226	-0.848099
59	6	0	-0.664261	2.132858	-1.600174
60	6	0	-1.621466	2.270312	-2.614146
61	6	0	-0.387918	3.266268	-0.820527
62	6	0	-2.301298	3.465093	-2.807907
63	1	0	-1.835599	1.431854	-3.266271
64	6	0	-1.052313	4.466140	-1.026038
65	1	0	0.328037	3.201608	-0.008406
66	6	0	-2.024168	4.571425	-2.014567
67	1	0	-3.048395	3.531853	-3.590731
68	1	0	-0.822202	5.318397	-0.395713
69	1	0	-2.554549	5.504148	-2.166833
70	6	0	0.776915	0.853202	1.657118
71	6	0	3.061296	1.789154	1.467321
72	6	0	4.340070	1.265098	1.264972

73	6	0	2.927820	2.964636	2.212460
74	6	0	5.454605	1.898873	1.798962
75	1	0	4.469946	0.347449	0.704217
76	6	0	4.043428	3.596806	2.746591
77	1	0	1.939390	3.383201	2.370065
78	6	0	5.311425	3.066897	2.539048
79	1	0	6.437802	1.471258	1.637909
80	1	0	3.920687	4.507321	3.322317
81	1	0	6.183124	3.560988	2.952872
82	1	0	0.907421	1.043156	2.725627

Table S33. Cartesian coordinates of the optimized structure of **Int-H**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.830144	-2.129712	-0.416573
2	9	0	-4.918642	0.729237	-0.988937
3	9	0	-1.878356	-0.695830	2.341339
4	9	0	-6.773138	1.082250	0.881757
5	9	0	-6.219558	0.547641	3.478287
6	9	0	-4.043804	-2.347823	-1.168365
7	9	0	-1.236723	1.002620	-2.956258
8	9	0	-3.758253	-0.342156	4.188747
9	9	0	-2.129384	0.427016	-5.406028
10	9	0	-3.922324	-1.567226	-5.769135
11	9	0	-4.854109	-2.969735	-3.649497
12	6	0	3.397989	-2.602256	0.226131
13	1	0	4.171705	-2.784625	0.969411
14	6	0	5.267512	-2.285972	-1.390645
15	6	0	1.781627	-2.965486	2.095123
16	6	0	5.857911	-2.927911	-2.485202
17	1	0	5.252684	-3.565646	-3.121301
18	6	0	3.823381	-2.409046	-1.093603
19	6	0	2.095098	-2.622557	0.693671
20	6	0	-3.306156	-0.017281	0.582431
21	6	0	-2.605015	-0.650372	-1.959564
22	6	0	0.464976	-0.319925	-0.216890
23	6	0	-5.572297	0.636447	1.225013
24	6	0	-4.590956	0.434494	0.269763
25	6	0	7.213225	-2.786778	-2.753026
26	1	0	7.647523	-3.299025	-3.604954
27	6	0	2.455690	-4.012330	2.737488
28	1	0	3.182417	-4.593999	2.180774
29	6	0	2.881725	-2.388489	-2.126893
30	1	0	3.264965	-2.390987	-3.145402
31	6	0	0.821394	-2.260764	2.829718
32	1	0	0.296577	-1.430785	2.371248
33	6	0	6.087574	-1.499875	-0.572744
34	1	0	5.642067	-0.962058	0.257990
35	6	0	8.016689	-2.010156	-1.925120
36	1	0	9.075834	-1.904939	-2.131526
37	6	0	7.446257	-1.370360	-0.830726
38	1	0	8.059433	-0.753592	-0.182176
39	6	0	0.539997	-2.586293	4.150120
40	1	0	-0.210650	-2.021259	4.691858
41	6	0	-2.118232	0.011270	-3.085398
42	6	0	-3.068925	-0.252377	1.935909
43	6	0	-2.573776	-0.262147	-4.363907
44	6	0	-3.545647	-1.650502	-2.196713
45	6	0	-4.030629	-0.081643	2.916750
46	6	0	1.499291	-2.398428	-2.013067
47	6	0	-3.503865	-1.270450	-4.550451
48	6	0	-5.290920	0.368950	2.556312
49	6	0	2.189030	-4.326966	4.062792
50	1	0	2.725218	-5.141638	4.537299
51	6	0	1.226412	-3.619700	4.775940
52	1	0	1.012057	-3.874387	5.807521
53	6	0	-3.985639	-1.982819	-3.462163
54	6	0	-0.737126	-2.987674	-0.082688
55	1	0	-0.523442	-4.052658	0.013460
56	1	0	-1.429568	-2.837647	-0.909579
57	1	0	-1.175490	-2.628489	0.848507
58	6	0	0.657243	-2.444679	-3.232041

59	6	0	0.908733	-1.566907	-4.294333
60	1	0	1.659890	-0.794084	-4.171267
61	6	0	0.232034	-1.686195	-5.501015
62	1	0	0.454740	-1.001519	-6.311449
63	6	0	-0.736275	-2.669392	-5.667078
64	1	0	-1.265410	-2.763360	-6.608398
65	6	0	-1.024312	-3.526693	-4.611177
66	1	0	-1.772405	-4.303304	-4.731050
67	6	0	-0.333185	-3.418491	-3.410877
68	1	0	-0.519361	-4.141582	-2.624731
69	5	0	-2.189157	-0.205180	-0.513345
70	6	0	-0.735556	0.266959	-0.235001
71	1	0	-0.710681	1.353771	-0.081169
72	6	0	1.725302	0.471666	-0.111913
73	6	0	2.280564	1.011567	-1.272269
74	6	0	2.399488	0.617468	1.099764
75	6	0	3.492678	1.687652	-1.221918
76	1	0	1.761060	0.884181	-2.215660
77	6	0	3.605804	1.303772	1.149885
78	1	0	1.987749	0.182111	2.003217
79	6	0	4.158083	1.833020	-0.010982
80	1	0	3.922043	2.092759	-2.131016
81	1	0	4.121055	1.413855	2.097546
82	1	0	5.108557	2.353135	0.026831

Table S34. Cartesian coordinates of the optimized structure of **TS_{2bA}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.598055	-1.214827	-1.241664
2	9	0	2.202556	1.259812	2.444798
3	9	0	1.726324	1.246727	-2.255071
4	9	0	1.141264	-1.703090	-2.445556
5	9	0	2.792613	-1.443410	1.967494
6	9	0	3.737486	3.415646	2.271609
7	9	0	4.300268	4.525788	-0.139775
8	9	0	3.281333	3.419689	-2.404512
9	9	0	4.412867	-3.505965	1.470821
10	9	0	4.425743	-4.677124	-0.979228
11	9	0	2.777116	-3.745947	-2.927092
12	6	0	-0.172559	-0.332659	1.415080
13	6	0	-2.804611	3.016491	-0.619113
14	6	0	1.871711	-1.488583	-0.204683
15	6	0	-4.242745	-1.731430	-0.308075
16	6	0	-2.379429	1.598892	-0.507665
17	6	0	-0.485671	-0.055493	-0.411064
18	6	0	-3.394921	0.589263	-0.267861
19	1	0	-4.384726	0.917511	0.034412
20	6	0	2.429488	1.751535	1.223919
21	6	0	-3.181113	-0.719972	-0.506240
22	6	0	1.874307	1.157338	0.097159
23	6	0	3.238412	2.878779	1.161158
24	6	0	-0.243935	-1.611484	1.989394
25	1	0	0.112084	-2.470505	1.439283
26	6	0	2.751196	-1.990438	0.749958
27	6	0	-0.597495	0.753471	2.191909
28	1	0	-0.576077	1.752205	1.773147
29	6	0	2.204495	1.758996	-1.113783
30	6	0	-1.062767	1.294684	-0.590060
31	1	0	-0.363808	2.117872	-0.686068
32	6	0	-3.717792	3.561881	0.286768
33	1	0	-4.132012	2.943622	1.076206
34	6	0	-4.824365	-1.883875	0.952020
35	1	0	-4.480043	-1.262785	1.772000
36	6	0	-4.668019	-2.553928	-1.354557
37	1	0	-4.230689	-2.436026	-2.341044
38	6	0	1.929286	-2.112878	-1.445274
39	6	0	3.528211	3.448558	-0.066209
40	6	0	-2.274027	3.837592	-1.616771
41	1	0	-1.584947	3.417153	-2.341106
42	6	0	3.007199	2.882373	-1.218699
43	6	0	-0.701626	-1.792463	3.284659
44	1	0	-0.724465	-2.788091	3.712234

45	6	0	-2.640946	5.174208	-1.700697
46	1	0	-2.226195	5.796542	-2.485484
47	6	0	-1.054587	0.578880	3.485662
48	1	0	-1.364143	1.439062	4.067642
49	6	0	-1.113911	-0.697795	4.034531
50	1	0	-1.474570	-0.837955	5.047485
51	6	0	-1.377557	-2.938909	-0.645101
52	1	0	-1.965095	-3.585178	-1.298605
53	1	0	-1.721598	-3.072264	0.380578
54	1	0	-0.331676	-3.231736	-0.733900
55	6	0	-5.662073	-3.499944	-1.146214
56	1	0	-5.990960	-4.124009	-1.969460
57	6	0	-3.542606	5.710098	-0.788698
58	1	0	-3.829142	6.753436	-0.854530
59	6	0	-4.079133	4.900118	0.205677
60	1	0	-4.779785	5.312166	0.923115
61	6	0	3.604292	-3.056592	0.515426
62	6	0	3.614323	-3.656611	-0.734010
63	6	0	-5.818094	-2.833417	1.158641
64	1	0	-6.260056	-2.943367	2.142606
65	6	0	-6.239308	-3.643367	0.111292
66	1	0	-7.013722	-4.384386	0.272975
67	6	0	2.772635	-3.179388	-1.723880
68	5	0	0.967343	-0.180714	0.058897

Table S35. Cartesian coordinates of the optimized structure of **Int-D**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.146021	7.306265	13.580248
2	9	0	4.293818	9.096893	8.625706
3	9	0	0.045947	7.697060	10.190272
4	9	0	1.170109	5.421216	12.462522
5	9	0	3.134870	5.956059	8.181444
6	9	0	3.108898	10.609366	6.820532
7	9	0	0.401247	10.708907	6.640146
8	9	0	-1.111396	9.224830	8.352614
9	9	0	2.141906	3.605065	7.456378
10	9	0	0.671707	2.126121	9.203250
11	9	0	0.214443	3.086313	11.709176
12	6	0	4.506938	7.248242	10.752138
13	6	0	0.270885	10.706838	13.640515
14	6	0	2.229296	5.825731	10.365703
15	6	0	3.148563	7.655641	16.343152
16	6	0	1.227563	9.570335	13.645369
17	6	0	2.416418	7.916074	12.172367
18	6	0	1.732680	9.117002	14.863284
19	1	0	1.398897	9.608040	15.772660
20	6	0	2.958107	9.094579	8.627456
21	6	0	2.648829	8.074275	15.012393
22	6	0	2.237726	8.323552	9.533305
23	6	0	2.362152	9.893196	7.658927
24	6	0	5.250070	6.101834	10.461893
25	1	0	4.752709	5.214035	10.086870
26	6	0	2.421867	5.283335	9.094906
27	6	0	5.230952	8.347250	11.242096
28	1	0	4.705430	9.271646	11.467435
29	6	0	0.855586	8.404379	9.376829
30	6	0	1.584228	9.004077	12.408827
31	1	0	1.165131	9.487279	11.533531
32	6	0	0.479949	11.825391	14.450168
33	1	0	1.365216	11.880864	15.074911
34	6	0	4.518126	7.550740	16.594871
35	1	0	5.230388	7.801146	15.815072
36	6	0	2.242687	7.364528	17.365430
37	1	0	1.177572	7.427588	17.171213
38	6	0	1.464335	5.027342	11.204291
39	6	0	0.983780	9.945164	7.558626
40	6	0	-0.856165	10.671532	12.814829
41	1	0	-1.042645	9.801860	12.193656
42	6	0	0.219171	9.188371	8.429351
43	6	0	6.628360	6.041430	10.658089
44	1	0	7.165354	5.129201	10.419897

45	6	0	-1.753686	11.730439	12.803093
46	1	0	-2.626642	11.685745	12.162229
47	6	0	6.603069	8.303965	11.444588
48	1	0	7.123146	9.180322	11.817446
49	6	0	7.312222	7.140252	11.158333
50	1	0	8.384690	7.097583	11.313849
51	6	0	4.200440	5.849759	13.644251
52	1	0	4.161837	5.445631	14.656876
53	1	0	5.221433	6.116605	13.368104
54	1	0	3.817409	5.121825	12.929701
55	6	0	2.701390	6.974428	18.616307
56	1	0	1.989939	6.745268	19.401168
57	6	0	-1.536830	12.839681	13.612431
58	1	0	-2.236374	13.667537	13.599715
59	6	0	-0.417374	12.884912	14.435064
60	1	0	-0.235922	13.752052	15.059762
61	6	0	1.914630	4.060605	8.685847
62	6	0	1.164714	3.303929	9.570891
63	6	0	4.973381	7.158699	17.846994
64	1	0	6.038733	7.088103	18.033243
65	6	0	4.066348	6.868893	18.859334
66	1	0	4.422132	6.562884	19.836241
67	6	0	0.937581	3.795056	10.842555
68	5	0	2.866809	7.320734	10.685725

Table S36. Cartesian coordinates of the optimized structure of **TS_{D5a}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.064517	1.736113	0.449657
2	9	0	2.765821	0.152132	-3.193683
3	9	0	1.332180	-2.095443	0.723241
4	9	0	0.743677	0.637103	2.577593
5	9	0	4.412688	0.513757	-0.409039
6	9	0	3.436044	-2.169097	-4.256789
7	9	0	3.085865	-4.486267	-2.884764
8	9	0	2.025504	-4.412264	-0.375331
9	9	0	6.072509	0.491322	1.660543
10	9	0	5.113350	0.549042	4.205448
11	9	0	2.419084	0.622358	4.614630
12	6	0	1.705141	1.946173	-1.253433
13	6	0	-1.963502	0.911627	2.279740
14	1	0	-1.759030	1.691737	2.992170
15	6	0	-3.018297	-1.804637	-1.098896
16	6	0	2.480366	0.588707	0.958885
17	6	0	-3.291457	3.167510	-0.461191
18	6	0	-2.338296	-0.526746	-0.809271
19	6	0	-0.104745	0.448389	-0.181857
20	6	0	-3.051234	0.686160	-0.832851
21	1	0	-4.078172	0.681540	-1.183316
22	6	0	2.542398	-0.934270	-2.450004
23	6	0	-2.492295	-0.204550	2.212482
24	6	0	-2.534082	1.900495	-0.430333
25	6	0	1.990892	-0.837235	-1.177894
26	6	0	2.912418	-2.140981	-3.032246
27	6	0	-3.024552	-1.509577	2.248232
28	6	0	2.549002	2.992586	-0.872795
29	1	0	3.220305	2.867263	-0.029984
30	6	0	3.867424	0.545066	0.813648
31	6	0	0.860792	2.199800	-2.346559
32	1	0	0.186823	1.419239	-2.688337
33	6	0	1.854191	-2.057307	-0.519713
34	6	0	-0.917900	-0.542375	-0.672717
35	1	0	-0.430864	-1.427947	-1.064712
36	6	0	-4.258469	-1.872124	-1.748651
37	1	0	-4.732017	-0.972998	-2.124492
38	6	0	-2.717308	4.314869	-1.016983
39	1	0	-1.720934	4.260082	-1.445256
40	6	0	-4.586377	3.239347	0.059165
41	1	0	-5.029091	2.357359	0.509774
42	6	0	2.060493	0.609558	2.277546
43	6	0	2.740751	-3.324396	-2.337543
44	6	0	-2.438884	-3.005701	-0.669230

45	1	0	-1.498467	-2.990864	-0.132271
46	6	0	2.204638	-3.281842	-1.062059
47	6	0	2.547973	4.223815	-1.526728
48	1	0	3.219587	5.008937	-1.195031
49	6	0	-3.069668	-4.222371	-0.880465
50	1	0	-2.601243	-5.134069	-0.528249
51	6	0	0.846640	3.419162	-3.008501
52	1	0	0.180994	3.568067	-3.852777
53	6	0	1.689960	4.447502	-2.593956
54	1	0	1.684136	5.404117	-3.105199
55	6	0	-0.289413	3.257153	1.015021
56	1	0	-1.055008	3.896764	1.457735
57	1	0	0.189565	3.761571	0.175675
58	1	0	0.466526	3.001990	1.757705
59	6	0	-5.294354	4.433609	0.020280
60	1	0	-6.297064	4.478825	0.429942
61	6	0	-4.300278	-4.270258	-1.520998
62	1	0	-4.795861	-5.220365	-1.685019
63	6	0	-4.889915	-3.088195	-1.957654
64	1	0	-5.843477	-3.114499	-2.472976
65	6	0	4.759225	0.530394	1.874225
66	6	0	-4.356639	-1.764983	1.883126
67	1	0	-4.976374	-0.949495	1.529524
68	6	0	4.276676	0.558873	3.172496
69	6	0	-3.426678	5.507748	-1.051843
70	1	0	-2.974451	6.388573	-1.493092
71	6	0	-4.715696	5.570121	-0.533316
72	1	0	-5.268405	6.502149	-0.561688
73	6	0	2.910328	0.597847	3.374339
74	6	0	-2.208312	-2.570716	2.674690
75	1	0	-1.175499	-2.372073	2.935416
76	6	0	-4.056906	-4.091680	2.417076
77	6	0	-4.864852	-3.048453	1.973273
78	1	0	-5.891492	-3.241065	1.685585
79	5	0	1.538879	0.549567	-0.400430
80	6	0	-2.730751	-3.850993	2.761705
81	1	0	-2.098434	-4.665228	3.095924
82	1	0	-4.459881	-5.095653	2.484144

Table S37. Cartesian coordinates of the optimized structure of **5a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.802713	6.783899	13.889783
2	9	0	4.403882	8.851417	9.178244
3	9	0	-0.119181	7.704967	10.012695
4	9	0	0.328333	5.280045	11.922870
5	9	0	3.768785	5.865046	8.720998
6	9	0	3.616491	10.474933	7.256926
7	9	0	0.981321	10.765618	6.665673
8	9	0	-0.871944	9.351436	8.074076
9	9	0	3.126132	3.526914	7.632038
10	9	0	1.095395	2.037928	8.658512
11	9	0	-0.283716	2.965665	10.817552
12	6	0	4.114265	7.232024	11.490212
13	6	0	0.101036	6.839693	14.442169
14	1	0	-0.468774	5.954144	14.687569
15	6	0	-0.081155	10.570617	13.903076
16	6	0	2.124390	5.688009	10.411146
17	6	0	3.697247	7.780995	15.862876
18	6	0	0.606051	9.212141	13.968435
19	6	0	1.728797	7.653522	12.306196
20	6	0	1.821842	9.151277	14.899139
21	1	0	2.119015	10.037617	15.444527
22	6	0	3.086338	8.947659	8.981503
23	6	0	-0.385992	8.079211	14.403956
24	6	0	2.534597	8.029234	14.993271
25	6	0	2.183204	8.222769	9.752725
26	6	0	2.702349	9.800988	7.953507
27	6	0	-1.815567	8.362143	14.663668
28	6	0	4.972906	6.129295	11.524072
29	1	0	4.629444	5.166372	11.157033
30	6	0	2.776703	5.172354	9.291595

31	6	0	4.631446	8.436694	11.990350
32	1	0	3.995124	9.317317	12.005090
33	6	0	0.850759	8.390057	9.378714
34	6	0	1.126778	8.811324	12.556528
35	1	0	1.009103	9.565462	11.787084
36	6	0	0.107425	11.573967	14.848557
37	1	0	0.790779	11.440259	15.678027
38	6	0	4.833203	7.132018	15.373456
39	1	0	4.880943	6.821729	14.335964
40	6	0	3.677200	8.204903	17.194544
41	1	0	2.786961	8.683192	17.588469
42	6	0	1.084011	4.893841	10.866949
43	6	0	1.363083	9.950425	7.644543
44	6	0	-1.002578	10.795167	12.876687
45	1	0	-1.189351	10.019144	12.141636
46	6	0	0.424789	9.231262	8.364544
47	6	0	6.282620	6.224121	11.993048
48	1	0	6.920933	5.346522	11.987651
49	6	0	-1.708904	11.984670	12.795375
50	1	0	-2.421468	12.130417	11.991862
51	6	0	5.937350	8.552384	12.443054
52	1	0	6.303105	9.508525	12.801794
53	6	0	6.775065	7.440979	12.444460
54	1	0	7.797487	7.524250	12.796630
55	6	0	2.551323	5.152994	13.995664
56	1	0	2.826291	4.959455	15.033572
57	1	0	3.441719	5.125367	13.367720
58	1	0	1.830950	4.412804	13.650464
59	6	0	4.778781	7.998940	18.014319
60	1	0	4.751278	8.331499	19.045751
61	6	0	-1.506957	12.981958	13.743073
62	1	0	-2.056407	13.914232	13.681830
63	6	0	-0.597375	12.771481	14.768453
64	1	0	-0.431919	13.538974	15.516109
65	6	0	2.455616	3.963071	8.695533
66	6	0	-2.219691	9.212914	15.693625
67	1	0	-1.477740	9.685183	16.326594
68	6	0	1.419092	3.202136	9.211612
69	6	0	5.931819	6.926764	16.195776
70	1	0	6.811655	6.437671	15.793682
71	6	0	5.908482	7.358756	17.517072
72	1	0	6.767185	7.196032	18.158326
73	6	0	0.723925	3.676102	10.308275
74	6	0	-2.779130	7.762923	13.852566
75	1	0	-2.462968	7.115198	13.042019
76	6	0	-4.524989	8.865625	15.090003
77	6	0	-3.567538	9.457867	15.907921
78	1	0	-3.872416	10.117059	16.712551
79	5	0	2.555138	7.178670	10.978776
80	6	0	-4.129087	8.017984	14.063646
81	1	0	-4.869851	7.556064	13.421114
82	1	0	-5.577595	9.066797	15.253341

Table S38. Cartesian coordinates of the optimized structure of **TS_{DE}**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.696245	-0.185888	0.242691
2	9	0	3.045164	0.943234	2.865441
3	9	0	2.317603	0.495652	-1.795039
4	9	0	-0.013384	-1.731081	-1.670927
5	9	0	3.543848	-1.984666	1.430143
6	9	0	5.106609	2.513350	2.373348
7	9	0	5.829989	3.111377	-0.174737
8	9	0	4.405079	2.074146	-2.251940
9	9	0	4.399992	-4.201901	0.239594
10	9	0	3.070972	-5.222787	-1.902259

11	9	0	0.850143	-3.940585	-2.833394
12	6	0	0.792990	-0.662957	2.295544
13	6	0	-2.426021	-0.060616	-1.970121
14	6	0	-1.071385	3.784980	-1.304497
15	6	0	1.690926	-1.756150	-0.024879
16	6	0	-4.017064	0.811918	1.488975
17	6	0	-1.281608	2.488489	-0.604418
18	6	0	-0.076406	0.418227	0.120253
19	6	0	-2.463163	2.274618	0.156847
20	1	0	-3.188373	3.078914	0.226576
21	6	0	3.311798	1.195002	1.581204
22	6	0	-2.134408	1.069552	-2.375682
23	6	0	-2.766069	1.078622	0.750971
24	6	0	2.541272	0.647285	0.561464
25	6	0	4.408679	2.017341	1.352749
26	6	0	0.824124	-1.927052	2.890169
27	1	0	1.252998	-2.766795	2.354251
28	6	0	2.831874	-2.440285	0.391481
29	6	0	0.204567	0.361876	3.053801
30	1	0	0.156806	1.365899	2.641143
31	6	0	2.975021	0.975396	-0.721346
32	6	0	-0.107625	1.694841	-0.360667
33	1	0	0.834746	2.197457	-0.550940
34	6	0	-1.696276	4.967362	-0.900576
35	1	0	-2.348345	4.975768	-0.035059
36	6	0	-3.978773	0.151657	2.720086
37	1	0	-3.022173	-0.138548	3.144298
38	6	0	-5.250336	1.212651	0.968002
39	1	0	-5.286882	1.710186	0.004310
40	6	0	1.075850	-2.315140	-1.131103
41	6	0	4.785157	2.322453	0.057583
42	6	0	-0.199868	3.832525	-2.398626
43	1	0	0.294760	2.924085	-2.728751
44	6	0	4.058858	1.792546	-0.994880
45	6	0	0.296593	-2.164799	4.158422
46	1	0	0.342633	-3.163329	4.580609
47	6	0	0.035249	5.023193	-3.071545
48	1	0	0.713026	5.036567	-3.917207
49	6	0	-0.324493	0.142847	4.317797
50	1	0	-0.762624	0.967727	4.870672
51	6	0	-0.287431	-1.131749	4.877656
52	1	0	-0.698802	-1.311616	5.865033
53	6	0	-1.994759	-1.831555	0.902901
54	1	0	-3.069350	-2.009321	0.937573
55	1	0	-1.552468	-1.912495	1.896599
56	1	0	-1.529637	-2.553420	0.231033
57	6	0	-6.423717	0.956617	1.665249
58	1	0	-7.375525	1.267946	1.250133
59	6	0	-0.595640	6.191537	-2.661189
60	1	0	-0.411619	7.123261	-3.183405
61	6	0	-1.458368	6.159182	-1.572356
62	1	0	-1.942521	7.068760	-1.235704
63	6	0	3.306618	-3.593155	-0.214400
64	6	0	2.634965	-4.116620	-1.307607
65	6	0	-5.154098	-0.103262	3.413923
66	1	0	-5.112253	-0.609396	4.371545
67	6	0	-6.377919	0.296140	2.888039
68	1	0	-7.294270	0.094801	3.430948
69	6	0	1.507597	-3.466182	-1.772485
70	5	0	1.248884	-0.365842	0.743713
71	1	0	-2.023303	1.916047	-3.016461
72	6	0	-3.093705	-1.342514	-2.186281
73	6	0	-2.542834	-2.301335	-3.036354
74	6	0	-4.307237	-1.603485	-1.544077
75	6	0	-3.198696	-3.509436	-3.233394
76	1	0	-1.600168	-2.103063	-3.528324
77	6	0	-4.960384	-2.810147	-1.752138
78	1	0	-4.739126	-0.858298	-0.883992
79	6	0	-4.404989	-3.768324	-2.593159
80	1	0	-2.759684	-4.251779	-3.889789
81	1	0	-5.904239	-3.001383	-1.254407
82	1	0	-4.911675	-4.713651	-2.749692

Table S39. Cartesian coordinates of the optimized structure of **Int-E**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	1.545971	7.353187	15.364749
2	9	0	6.985171	8.500304	13.854307
3	9	0	3.683781	5.776921	11.816647
4	9	0	2.257680	4.735260	14.392692
5	9	0	6.871349	5.620062	14.971782
6	9	0	8.194773	8.741028	11.525664
7	9	0	7.202564	7.533444	9.303923
8	9	0	4.928238	6.046448	9.489630
9	9	0	7.288517	3.036004	15.439493
10	9	0	5.218429	1.273640	15.394802
11	9	0	2.704164	2.176920	14.859711
12	6	0	4.850707	7.901110	15.617873
13	6	0	0.086103	6.830870	14.420235
14	6	0	0.585957	9.533129	11.881040
15	6	0	4.538473	5.336846	14.705867
16	6	0	1.093857	9.757347	16.944922
17	6	0	0.934334	8.802235	13.170326
18	6	0	2.840679	7.431981	14.101750
19	6	0	0.887534	9.666374	14.439069
20	1	0	0.683996	10.726650	14.352661
21	6	0	6.405114	7.892567	12.816061
22	6	0	-0.050024	7.635281	13.370757
23	6	0	1.146459	9.110663	15.622676
24	6	0	5.225862	7.169205	12.964885
25	6	0	7.072891	8.026650	11.604187
26	6	0	5.280217	7.423323	16.859534
27	1	0	5.353026	6.352970	17.029874
28	6	0	5.804910	4.811887	14.960012
29	6	0	4.778657	9.295649	15.481359
30	1	0	4.431161	9.715659	14.541437
31	6	0	4.786629	6.547969	11.796792
32	6	0	2.363619	8.199784	13.127273
33	1	0	2.976324	8.481997	12.278727
34	6	0	-0.182716	10.694449	11.858704
35	1	0	-0.534983	11.144439	12.779194
36	6	0	2.098541	9.543695	17.891593
37	1	0	2.947526	8.913007	17.653994
38	6	0	0.028377	10.604156	17.263775
39	1	0	-0.769250	10.751513	16.543665
40	6	0	3.533610	4.383017	14.670343
41	6	0	6.575729	7.411257	10.470422
42	6	0	0.968905	8.967210	10.662522
43	1	0	1.538688	8.043596	10.650116
44	6	0	5.418576	6.658111	10.569508
45	6	0	5.652052	8.279857	17.894939
46	1	0	5.994846	7.866713	18.838043
47	6	0	0.621439	9.563327	9.458327
48	1	0	0.935539	9.108841	8.525718
49	6	0	5.161598	10.161582	16.494840
50	1	0	5.109581	11.233840	16.339030
51	6	0	5.605142	9.655206	17.712854
52	1	0	5.906561	10.326376	18.509706
53	6	0	1.829473	6.403252	16.864253
54	1	0	1.201561	6.798510	17.663319
55	1	0	2.879159	6.492376	17.144027
56	1	0	1.575565	5.362100	16.668187
57	6	0	-0.020692	11.238030	18.498128
58	1	0	-0.852022	11.892633	18.733892
59	6	0	-0.125011	10.735858	9.449175
60	1	0	-0.393400	11.205809	8.510129
61	6	0	-0.530950	11.294526	10.652806
62	1	0	-1.124870	12.201442	10.659212
63	6	0	6.053813	3.468941	15.195218
64	6	0	5.003320	2.565828	15.169545
65	6	0	2.045459	10.177579	19.124766
66	1	0	2.843433	10.014563	19.840057
67	6	0	0.987435	11.025613	19.431886
68	1	0	0.947450	11.519005	20.396280
69	6	0	3.728942	3.029027	14.900588
70	5	0	4.380570	6.945294	14.367970
71	6	0	-0.730965	5.651585	14.762318
72	6	0	-0.905180	4.627931	13.830548
73	6	0	-1.336193	5.543734	16.016135
74	6	0	-1.681040	3.520306	14.145407

75	1	0	-0.407642	4.694688	12.870004
76	6	0	-2.110546	4.434857	16.329027
77	1	0	-1.218801	6.341587	16.743034
78	6	0	-2.283461	3.420457	15.393865
79	1	0	-1.803983	2.726989	13.417283
80	1	0	-2.582136	4.364237	17.302493
81	1	0	-2.883100	2.551764	15.640033
82	1	0	-0.837202	7.506350	12.635682

Table S40. Cartesian coordinates of the optimized structure of PhCCH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.209057	0.012385	0.000065
2	6	0	0.178508	0.008471	0.000573
3	6	0	0.884553	1.215979	0.000054
4	6	0	0.178584	2.423548	-0.000975
5	6	0	-1.208969	2.419729	-0.001478
6	6	0	-1.905621	1.216075	-0.000960
7	1	0	-1.748533	-0.927858	0.000471
8	1	0	0.726497	-0.926284	0.001370
9	1	0	0.726654	3.358256	-0.001377
10	1	0	-1.748395	3.360000	-0.002279
11	1	0	-2.989693	1.216120	-0.001354
12	6	0	2.316874	1.215948	0.000556
13	6	0	3.518300	1.215928	0.001067
14	1	0	4.581795	1.215909	0.002387

Table S41. Cartesian coordinates of the optimized structure of **6**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	3.573210	10.017962	9.406654
2	15	0	2.650026	7.443729	14.018415
3	9	0	-0.538293	8.116813	10.718725
4	1	0	0.684637	5.690099	12.920018
5	1	0	4.834887	5.405305	14.003235
6	9	0	2.327366	11.306466	7.403215
7	9	0	-0.346981	11.005603	7.050609
8	9	0	-1.763630	9.404024	8.719940
9	1	0	4.871249	3.068348	13.241684
10	1	0	2.821409	2.023970	12.329255
11	1	0	0.723346	3.333555	12.183800
12	6	0	3.440482	7.217117	10.825606
13	6	0	-0.790358	10.455594	14.523829
14	6	0	2.752284	5.699822	13.518103
15	6	0	1.915982	6.867569	16.680826
16	6	0	0.296624	9.463289	14.329770
17	6	0	1.952021	8.431153	12.737550
18	6	0	0.642567	8.596740	15.424837
19	1	0	0.052310	8.705021	16.333150
20	6	0	2.253827	9.847918	9.260941
21	6	0	1.602116	7.637840	15.448885
22	6	0	1.568517	9.031168	10.150411
23	6	0	1.633538	10.521850	8.221816
24	6	0	3.054862	6.036172	10.206354
25	9	0	1.757531	5.817428	9.960709
26	6	0	3.928782	4.959756	13.610809
27	6	0	4.800755	7.382272	11.025610
28	9	0	5.263830	8.509697	11.584545
29	6	0	0.202601	8.903577	9.929981
30	6	0	0.920103	9.350766	13.122829
31	1	0	0.594693	10.031707	12.341313
32	6	0	-0.867765	11.221269	15.690959
33	1	0	-0.114513	11.099299	16.463045
34	6	0	1.905177	5.469435	16.710149
35	1	0	1.641202	4.912438	15.819471
36	6	0	2.238174	7.556281	17.854886
37	1	0	2.266152	8.640707	17.839583

38	6	0	1.595243	5.107185	13.010352
39	6	0	0.267303	10.371151	8.040438
40	6	0	-1.764078	10.651744	13.539438
41	1	0	-1.744383	10.041526	12.642582
42	6	0	-0.453996	9.555153	8.897391
43	6	0	3.950569	5.039969	9.859243
44	9	0	3.534565	3.905732	9.304251
45	6	0	-2.769879	11.594240	13.708962
46	1	0	-3.516229	11.727152	12.933534
47	6	0	5.732958	6.414041	10.684928
48	9	0	7.029815	6.603703	10.916314
49	6	0	5.301130	5.231280	10.107631
50	9	0	6.176528	4.283772	9.794056
51	6	0	4.319095	7.921573	14.555599
52	1	0	4.587268	7.359567	15.453211
53	1	0	4.280503	8.985216	14.795386
54	1	0	5.058886	7.765781	13.771994
55	6	0	2.531622	6.870429	19.026479
56	1	0	2.777007	7.423290	19.926328
57	6	0	-2.832825	12.350684	14.873609
58	1	0	-3.621039	13.082595	15.008347
59	6	0	-1.878771	12.157503	15.865961
60	1	0	-1.915121	12.745536	16.776472
61	6	0	3.950770	3.637543	13.183012
62	6	0	2.798777	3.051583	12.673067
63	6	0	2.205764	4.784513	17.880776
64	1	0	2.183971	3.700518	17.886269
65	6	0	2.520171	5.480757	19.041959
66	1	0	2.753089	4.943365	19.954129
67	6	0	1.619547	3.785321	12.591843
68	5	0	2.332020	8.255822	11.311723

Table S42. Cartesian coordinates of the optimized structure of **$TS_{Ph\text{-}PB}$**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	3.633473	1.465189	0.390126
2	15	0	-1.095646	-1.360022	0.105959
3	9	0	-0.691770	2.035559	-1.515274
4	1	0	-0.972446	0.153969	-2.339902
5	1	0	1.703172	-2.848642	-0.831488
6	9	0	4.334123	3.769120	-0.596829
7	9	0	2.592455	5.267160	-2.052094
8	9	0	0.069149	4.336992	-2.467284
9	1	0	2.065255	-3.659438	-3.097696
10	1	0	0.985102	-2.525237	-5.019327
11	1	0	-0.522204	-0.593824	-4.624552
12	6	0	2.094673	-0.719958	0.899198
13	6	0	-3.618945	2.159174	1.501587
14	6	0	0.375888	-1.223671	-1.374025
15	6	0	-3.593433	-2.396743	-0.534915
16	6	0	-2.796026	0.999872	1.072103
17	6	0	-0.520405	0.127466	0.712382
18	6	0	-3.416718	-0.102170	0.511622
19	1	0	-4.496784	-0.049484	0.393226
20	6	0	2.707640	2.080458	-0.352932
21	6	0	-2.809741	-1.294350	0.052063
22	6	0	1.443655	1.519678	-0.569563
23	6	0	3.108982	3.315863	-0.842959
24	6	0	3.261729	-1.179812	0.291898
25	9	0	3.499803	-0.888597	-0.992248
26	6	0	1.201850	-2.342148	-1.648075
27	6	0	1.976542	-1.038951	2.248171
28	9	0	0.920700	-0.635008	2.962362
29	6	0	0.586164	2.367556	-1.280115
30	6	0	-1.377311	1.103377	1.121180
31	1	0	-0.958835	2.067216	1.405579
32	6	0	-4.752425	1.972602	2.297403
33	1	0	-5.012506	0.971245	2.624622
34	6	0	-3.117159	-3.110720	-1.641574
35	1	0	-2.184774	-2.813978	-2.115300
36	6	0	-4.822441	-2.777448	0.017555
37	1	0	-5.200950	-2.254447	0.889038

38	6	0	-0.256053	-0.640375	-2.498941
39	6	0	2.227365	4.085601	-1.576279
40	6	0	-3.285412	3.461252	1.117068
41	1	0	-2.426932	3.626907	0.474788
42	6	0	0.948690	3.604544	-1.788178
43	6	0	4.224414	-1.928865	0.942145
44	9	0	5.312929	-2.347531	0.302090
45	6	0	-4.060282	4.541967	1.517191
46	1	0	-3.788851	5.543148	1.201193
47	6	0	2.923874	-1.782299	2.941899
48	9	0	2.753657	-2.060096	4.231675
49	6	0	4.052667	-2.234964	2.283970
50	9	0	4.965536	-2.948614	2.929146
51	6	0	-0.565368	-2.978157	0.752906
52	1	0	-0.720981	-3.744549	-0.006939
53	1	0	-1.176685	-3.190504	1.630247
54	1	0	0.485675	-2.943794	1.033514
55	6	0	-5.546679	-3.832178	-0.519155
56	1	0	-6.494699	-4.111985	-0.073291
57	6	0	-5.186781	4.342197	2.307018
58	1	0	-5.791827	5.185944	2.618759
59	6	0	-5.530995	3.052340	2.693967
60	1	0	-6.402998	2.886348	3.316940
61	6	0	1.415964	-2.807708	-2.930705
62	6	0	0.811527	-2.166727	-4.010579
63	6	0	-3.837759	-4.174008	-2.170112
64	1	0	-3.450301	-4.709216	-3.029934
65	6	0	-5.057059	-4.538794	-1.612817
66	1	0	-5.622826	-5.365009	-2.027496
67	6	0	-0.027779	-1.080205	-3.791715
68	5	0	0.962496	0.105181	0.086298

Table S43. Cartesian coordinates of the optimized structure of **$TS_{Ph\text{-}PC}$**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-3.236230	1.048590	-2.060084
2	15	0	1.423332	-1.280399	-0.945947
3	9	0	-0.741496	1.906938	1.847315
4	1	0	1.731730	0.420184	1.843828
5	1	0	-0.317625	-3.169837	0.655662
6	9	0	-4.676273	3.271852	-1.618531
7	9	0	-4.155704	4.821108	0.548214
8	9	0	-2.179992	4.123893	2.271521
9	1	0	-0.536350	-3.822481	3.020154
10	1	0	0.444607	-2.400788	4.805399
11	1	0	1.601043	-0.292502	4.194898
12	6	0	-1.993001	-1.248930	-0.491926
13	6	0	2.888024	3.055182	-0.486810
14	6	0	0.708118	-1.331695	1.124005
15	6	0	4.117207	-1.756149	-0.165386
16	6	0	2.376384	1.663232	-0.504795
17	6	0	0.395905	0.142859	-0.594977
18	6	0	3.353505	0.590507	-0.327135
19	1	0	4.349288	0.901149	-0.018812
20	6	0	-2.958058	1.783119	-0.976258
21	6	0	3.088169	-0.722656	-0.411492
22	6	0	-1.930196	1.392159	-0.127965
23	6	0	-3.711643	2.927776	-0.772027
24	6	0	-2.789853	-1.605955	0.591200
25	9	0	-2.786389	-0.847683	1.691266
26	6	0	0.066115	-2.523994	1.433319
27	6	0	-2.051246	-2.089685	-1.592116
28	9	0	-1.377417	-1.784671	-2.706755
29	6	0	-1.697968	2.216366	0.965552
30	6	0	1.040384	1.437597	-0.613643
31	1	0	0.400219	2.311175	-0.694560
32	6	0	4.057536	3.389280	-1.175735
33	1	0	4.589211	2.624155	-1.731985
34	6	0	3.806002	-2.929424	0.531100
35	1	0	2.798588	-3.084915	0.901212
36	6	0	5.425251	-1.580541	-0.627774
37	1	0	5.672570	-0.694450	-1.202334

38	6	0	1.264068	-0.523111	2.094364
39	6	0	-3.446014	3.722228	0.332370
40	6	0	2.215771	4.060477	0.214977
41	1	0	1.330145	3.810260	0.789081
42	6	0	-2.433695	3.364661	1.209467
43	6	0	-3.563117	-2.752713	0.610264
44	9	0	-4.281361	-3.077240	1.680353
45	6	0	2.690397	5.365011	0.212926
46	1	0	2.160610	6.129779	0.769571
47	6	0	-2.820565	-3.243860	-1.617227
48	9	0	-2.848523	-4.021062	-2.694970
49	6	0	-3.574020	-3.579388	-0.504453
50	9	0	-4.309005	-4.682797	-0.505867
51	6	0	1.744983	-1.344790	-2.780813
52	1	0	1.926430	-0.322738	-3.127867
53	1	0	0.892399	-1.769398	-3.307002
54	1	0	2.631124	-1.959036	-2.958371
55	6	0	6.400034	-2.538654	-0.382889
56	1	0	7.407260	-2.387858	-0.754839
57	6	0	3.847214	5.687519	-0.487537
58	1	0	4.218192	6.706061	-0.487774
59	6	0	4.529846	4.694959	-1.181245
60	1	0	5.431522	4.938638	-1.731795
61	6	0	-0.037988	-2.892741	2.768618
62	6	0	0.519591	-2.100406	3.767073
63	6	0	4.782924	-3.883276	0.779154
64	1	0	4.527226	-4.779728	1.332710
65	6	0	6.083081	-3.692344	0.324139
66	1	0	6.842869	-4.442050	0.513313
67	6	0	1.174138	-0.926109	3.425631
68	5	0	-1.104645	0.060195	-0.413044

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Supporting Information

Chapter 5

Facile C=O Bind Splitting of Carbon Dioxide Induced by Metal-Ligand Cooperativity in a Phosphinine Iron(0) Complex

S1 NMR Spectra

S1.1 NMR spectra of compounds 1-σ and 1-π

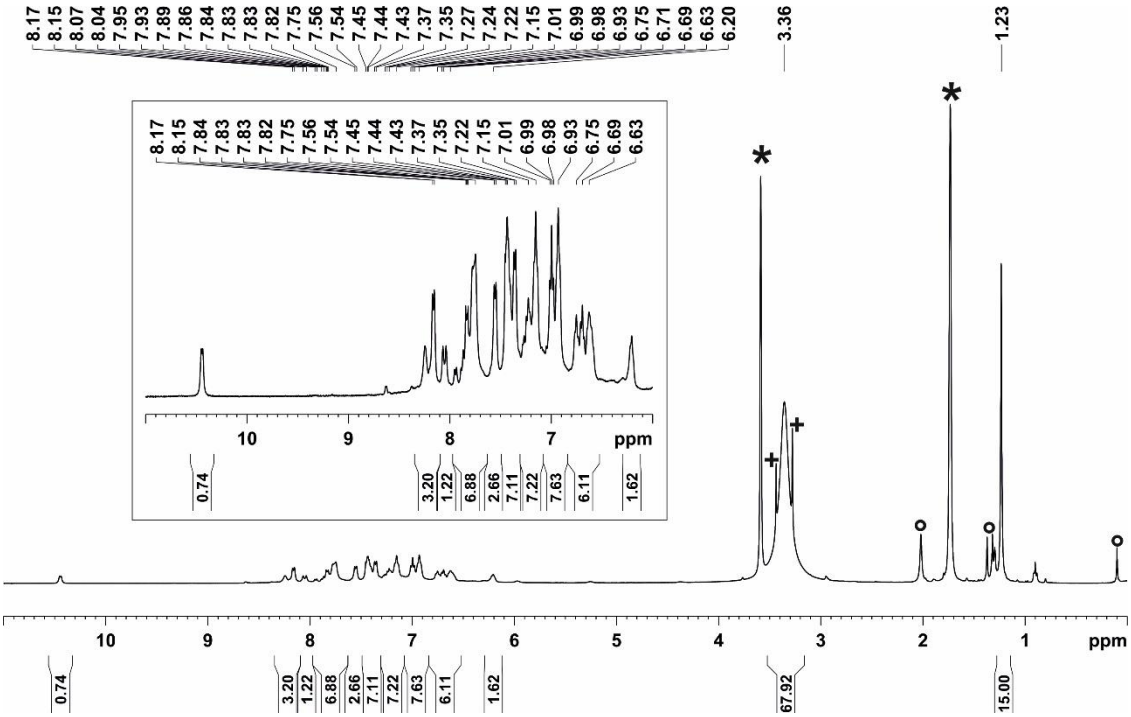


Figure S1 - ^{1}H NMR spectrum (400.13 MHz, 300 K, $[D_8]THF$) of **1-σ** and **1-π** (* = $[D_8]THF$, + = 1,2-dimethoxy ethane, ° = unidentified impurities).

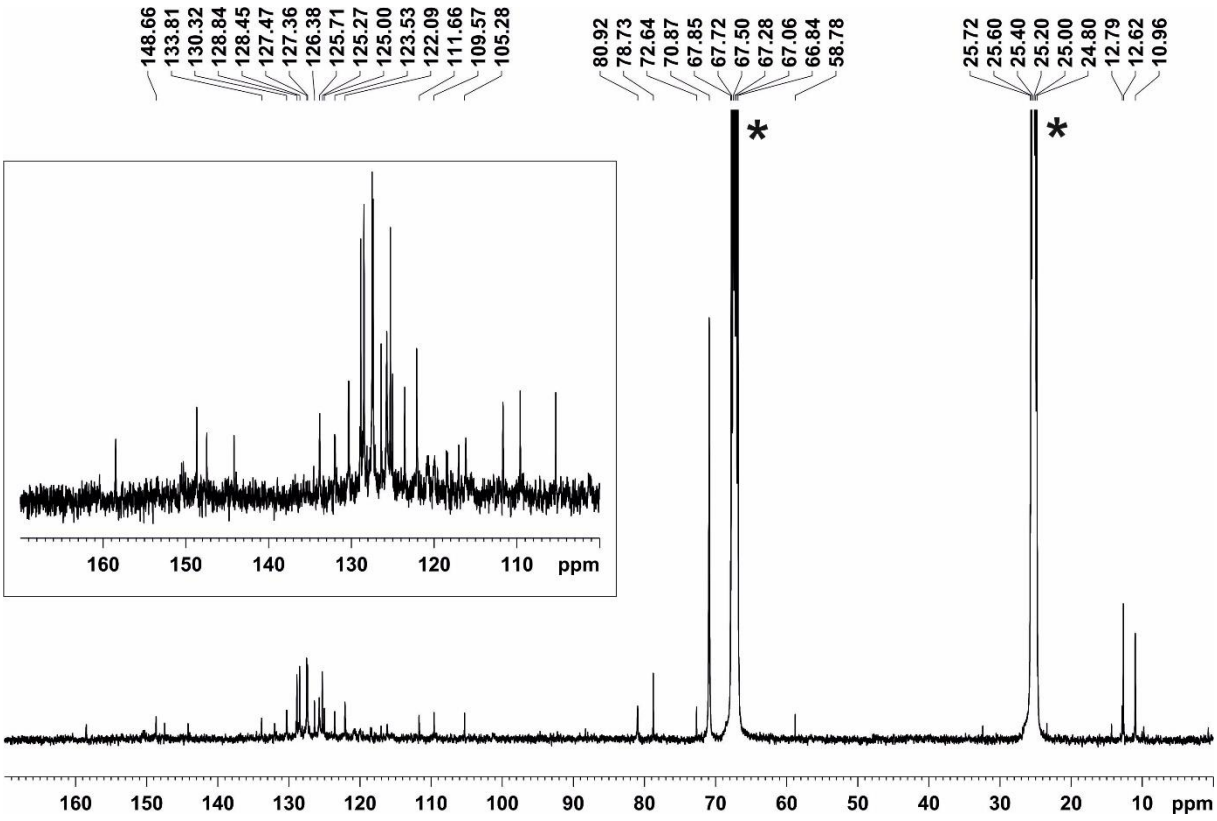


Figure S2 - $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, $[D_8]THF$) of **1-σ** and **1-π** (* = $[D_8]THF$).

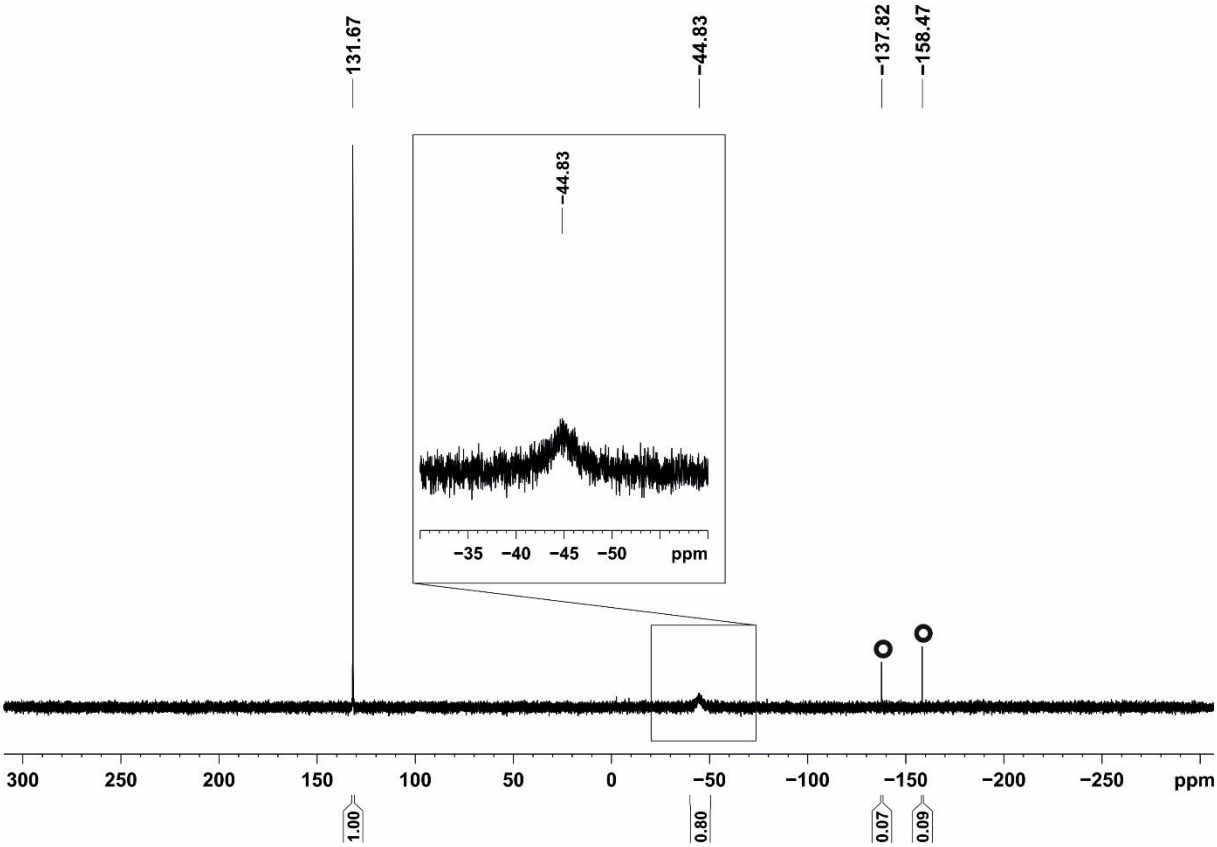


Figure S3 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **1-σ** and **1-π** (° = hydrophosphinine iron complexes **endo-4** and **exo-4**).

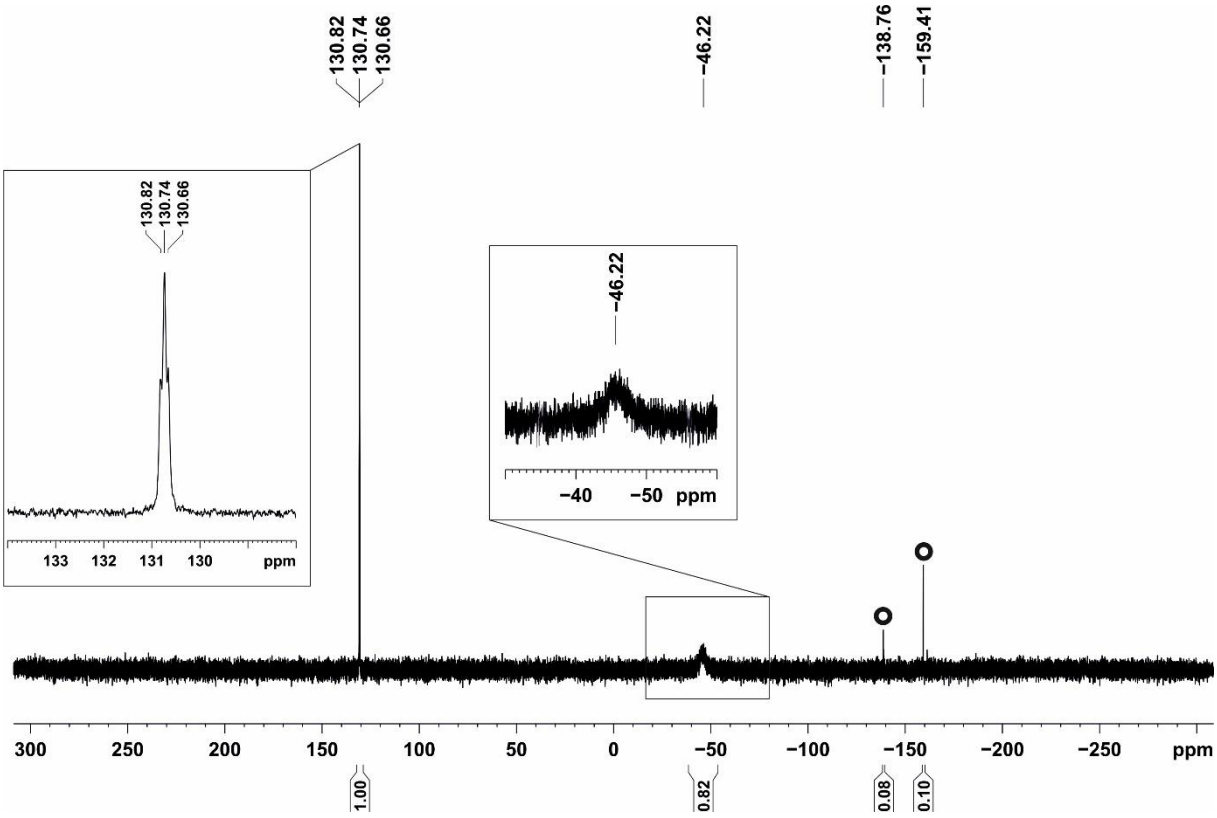


Figure S4 - ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **1-σ** and **1-π** (° = hydrophosphinine iron complexes **endo-4** and **exo-4**).

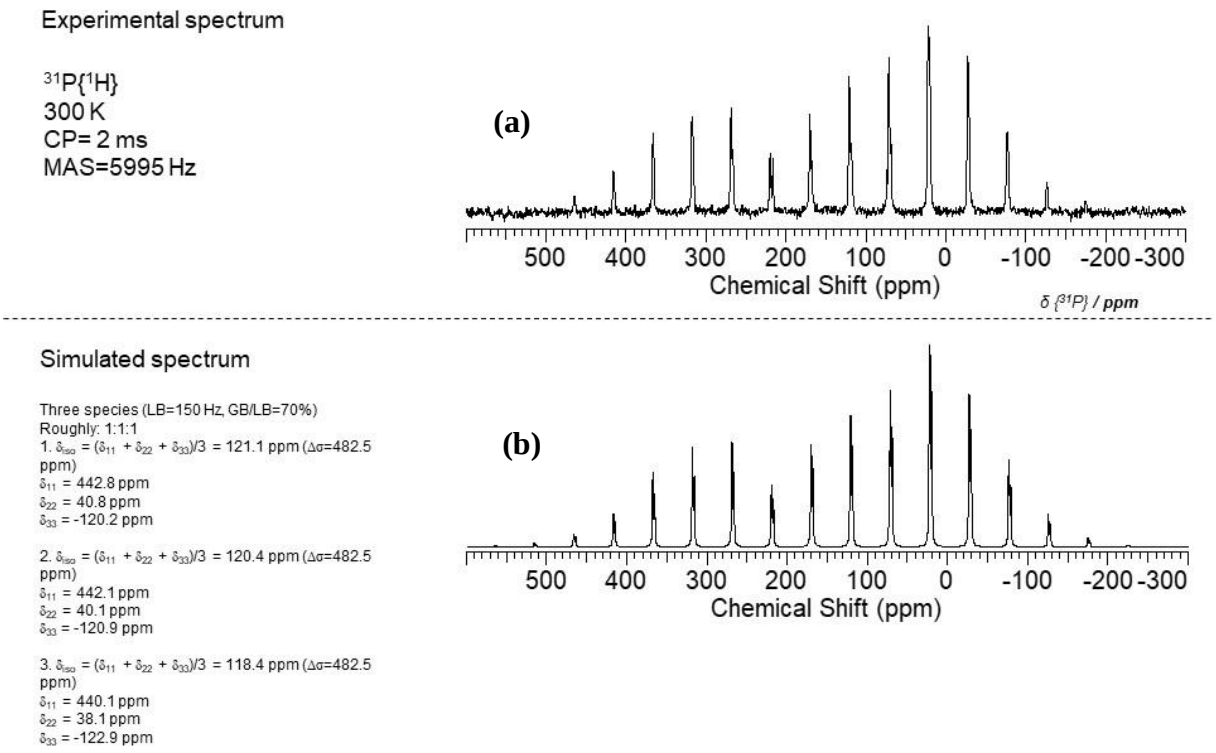


Figure S5 - ^{31}P CP MAS spectrum (6 kHz, 300 K) of **1-σ**; a) experimental spectrum (δ_{iso} = 121.1 ppm), b) simulated spectrum. The spectrum of **1-σ** indicates that there are two structurally similar species. They can belong to crystallographically different molecules.

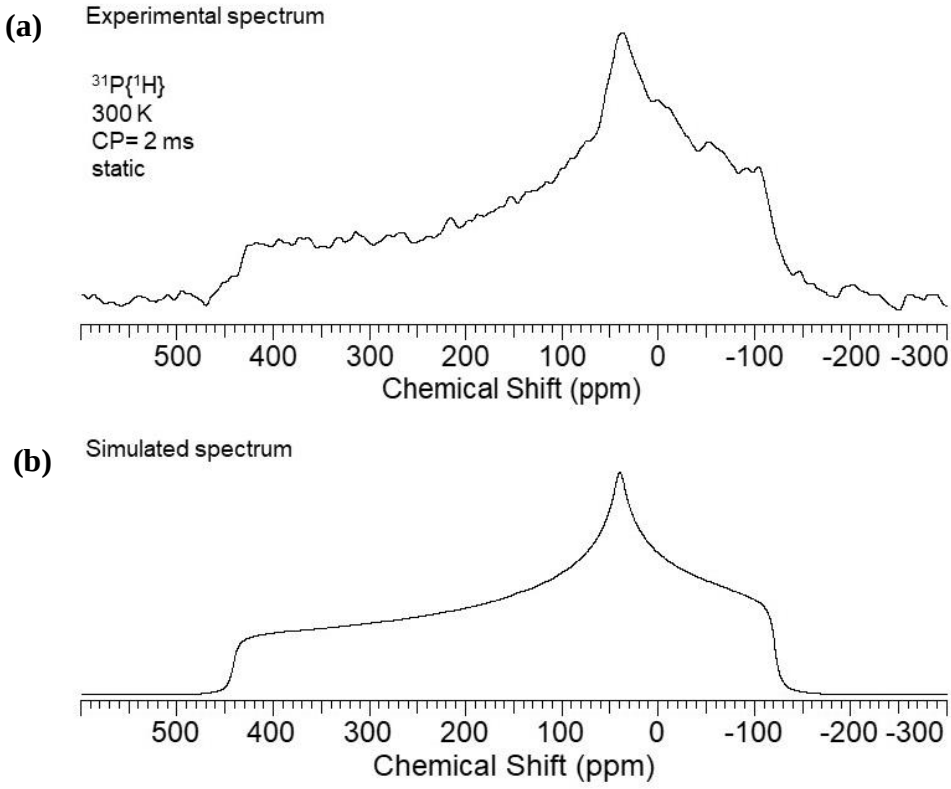


Figure S6 - ^{31}P CP MAS static spectrum (6 kHz, 300 K) of **1-σ**; a) experimental spectrum, b) simulated spectrum.

S1.2 NMR spectra of compound 2

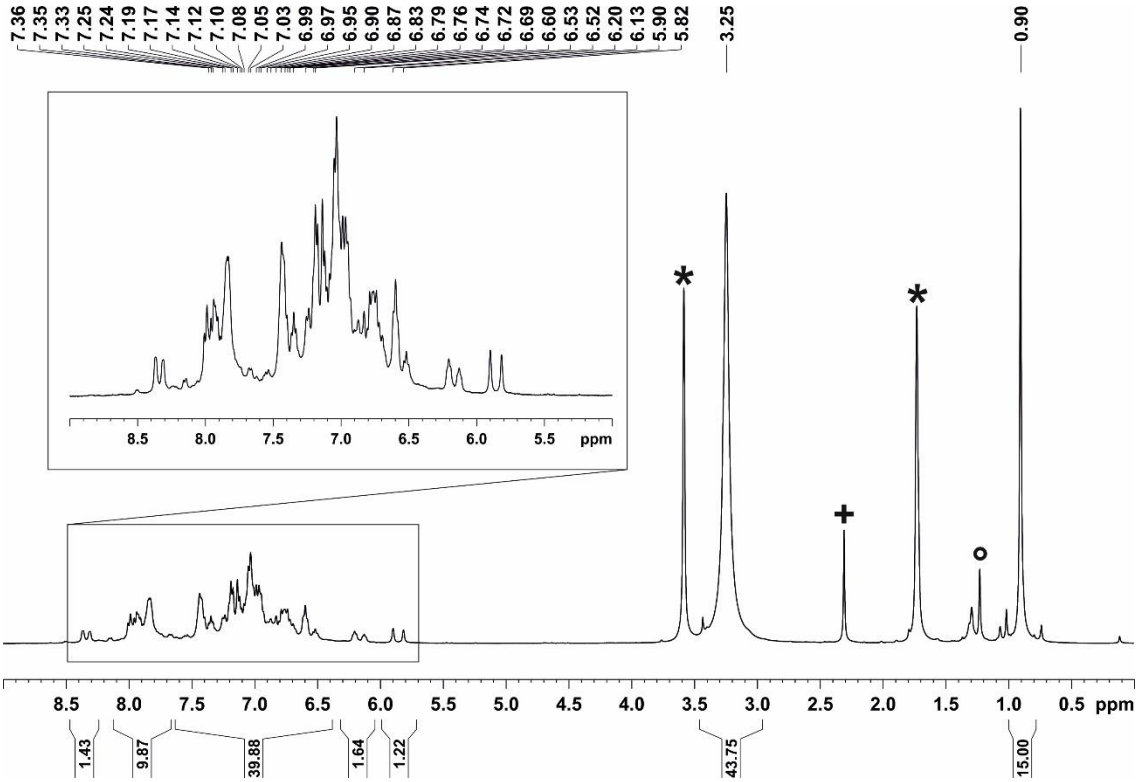


Figure S7 - ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **2** (* = [D_8]THF, + = toluene, ° = unidentified impurity).

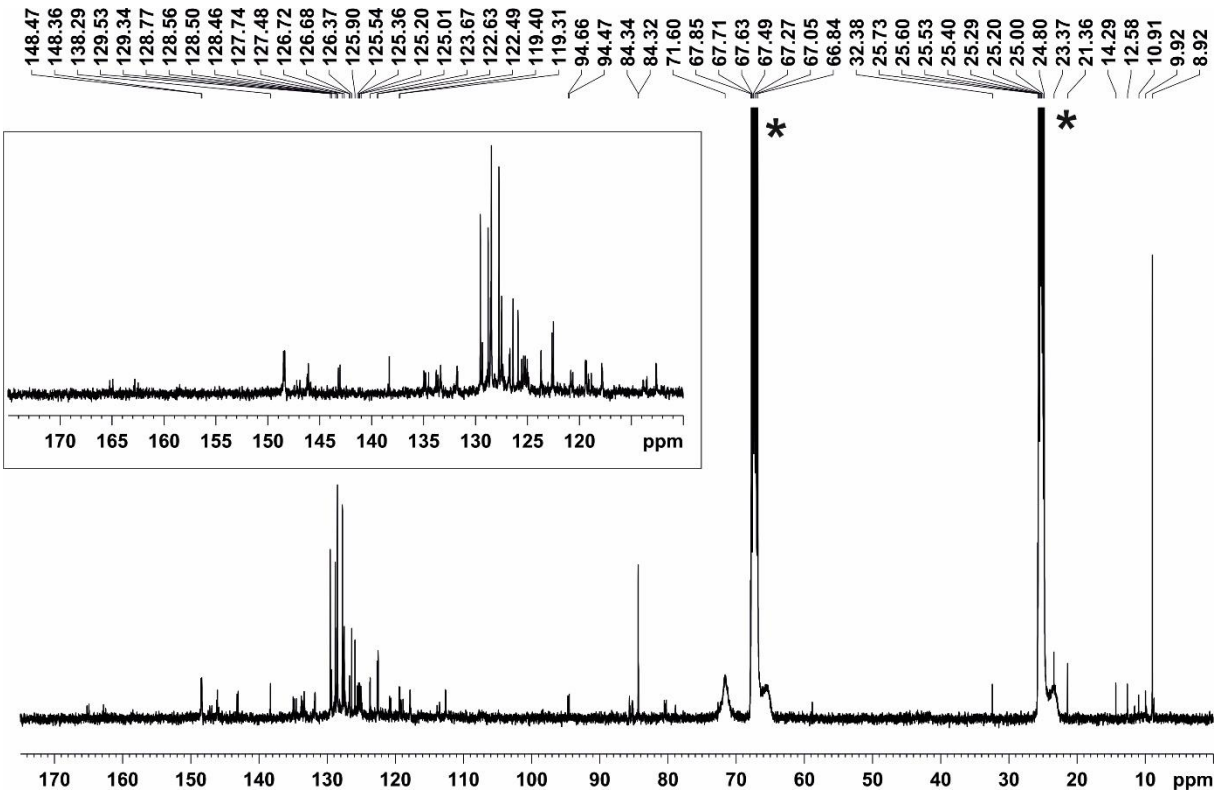


Figure S8 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **2** (* = [D_8]THF).

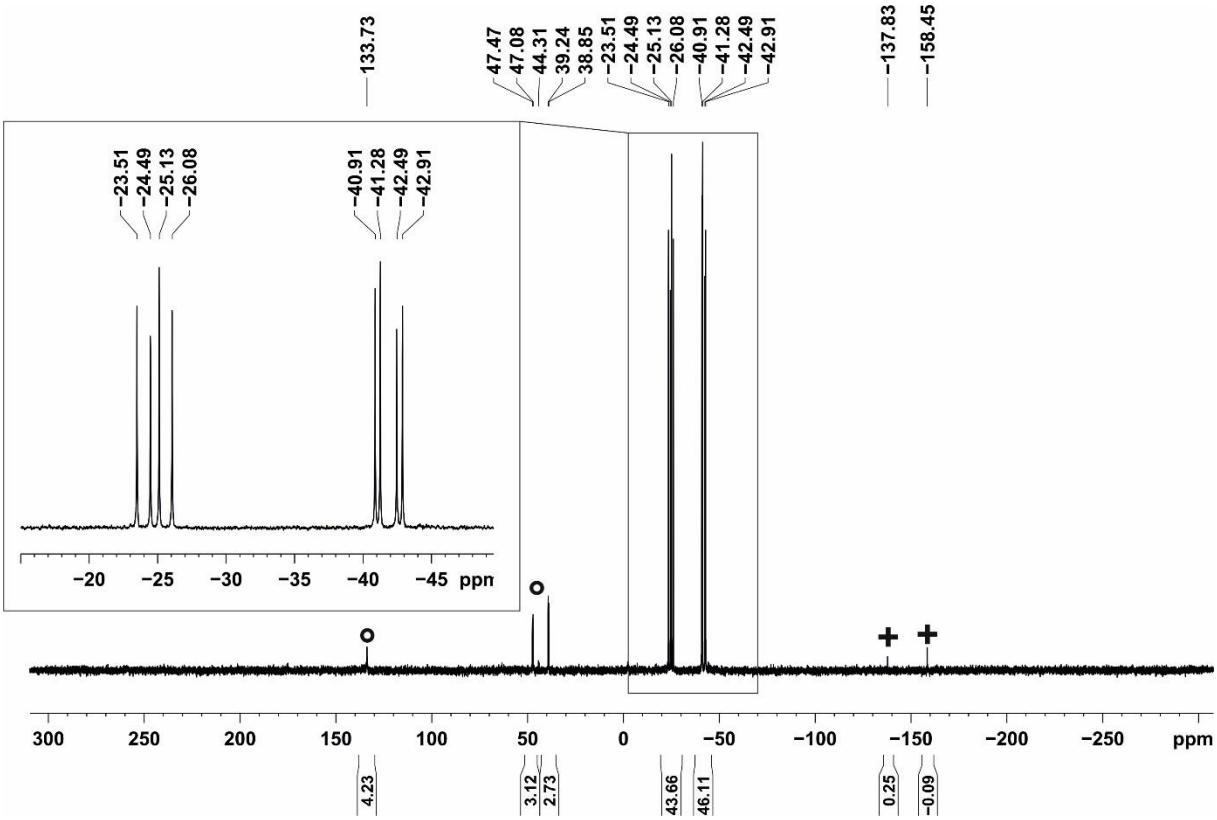


Figure S9 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **2** (° = unidentified impurities, + = hydrophosphinines **endo-4** and **exo-4**).

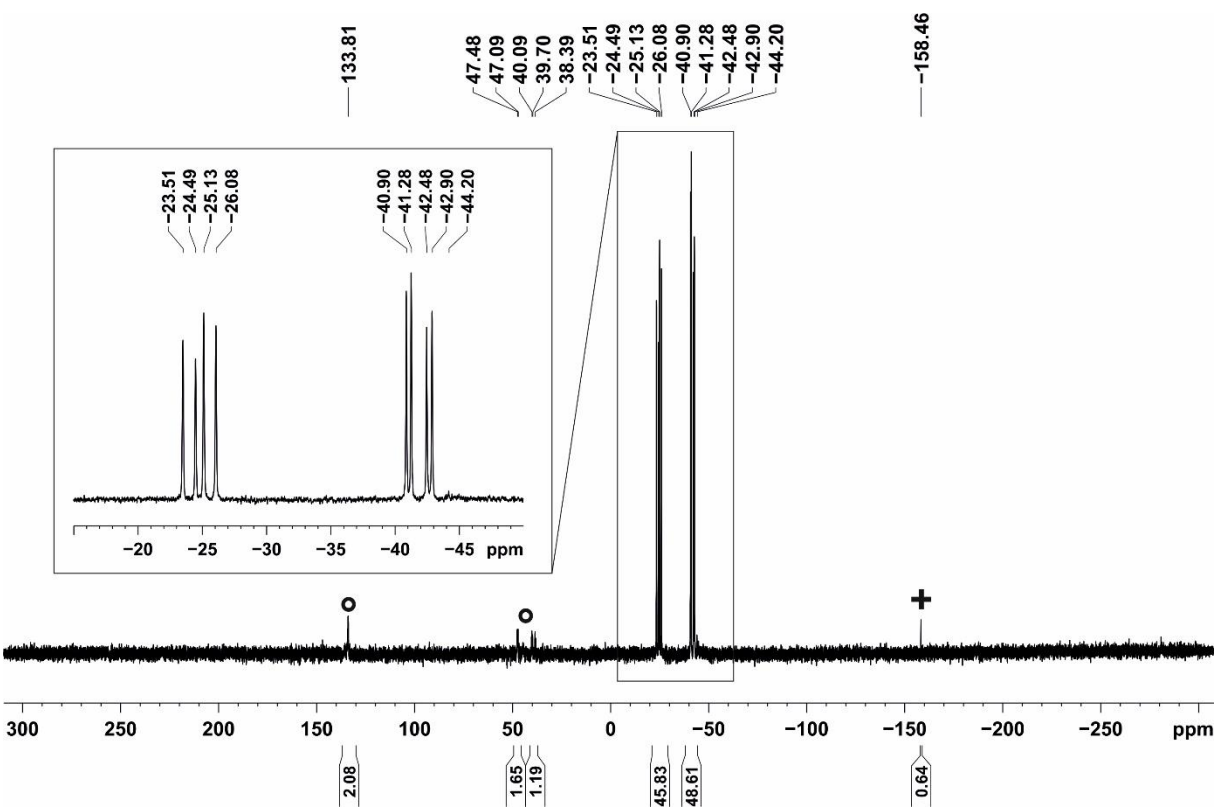


Figure S10 - ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **2** (° = impurities, + = hydrophosphinines **endo-4** and **exo-4**).

S1.3 NMR spectra of compound 3-σ

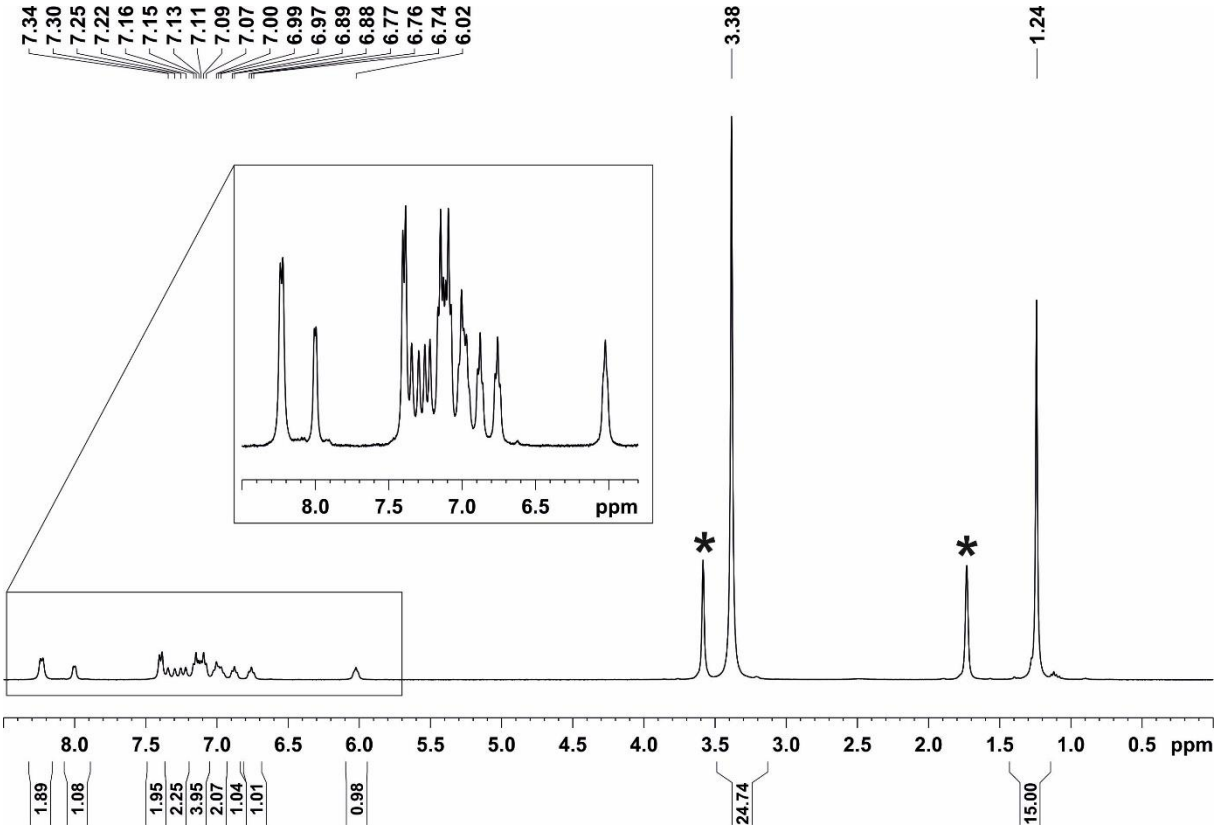


Figure S11 - ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **3-σ** (* = [D_8]THF).

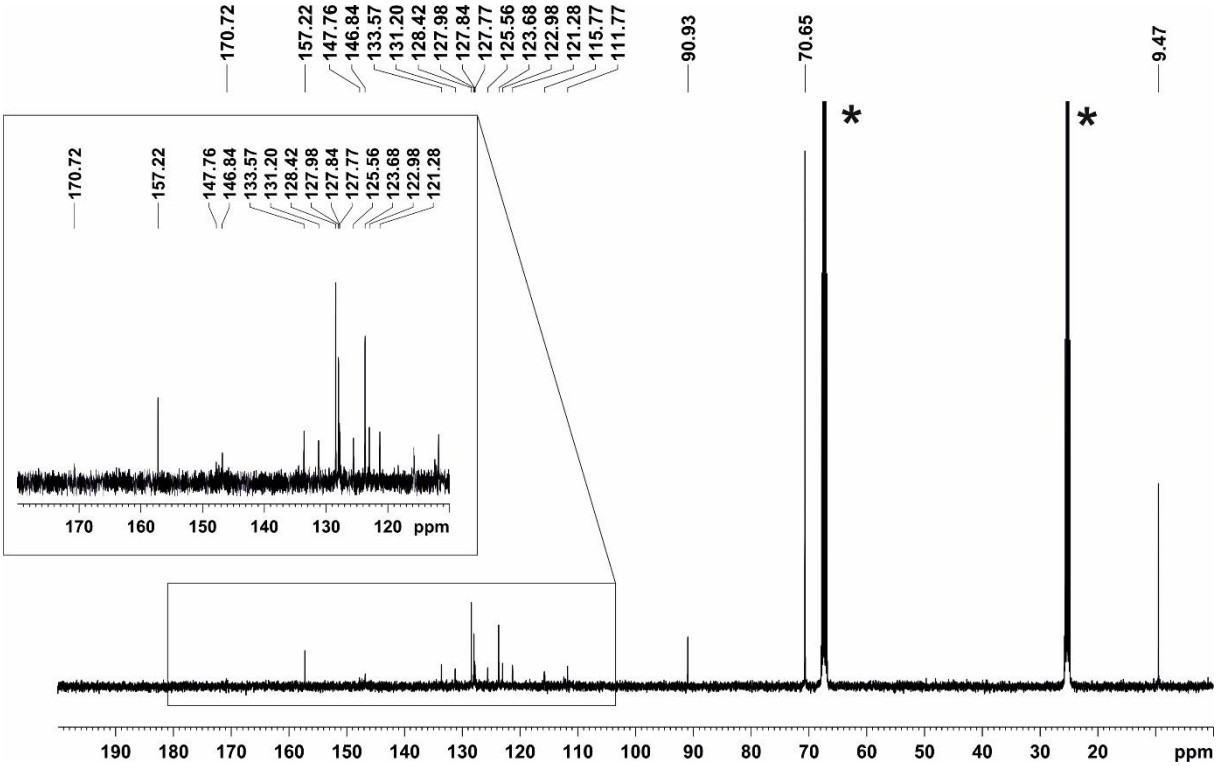


Figure S12 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **3-σ** (* = [D_8]THF).

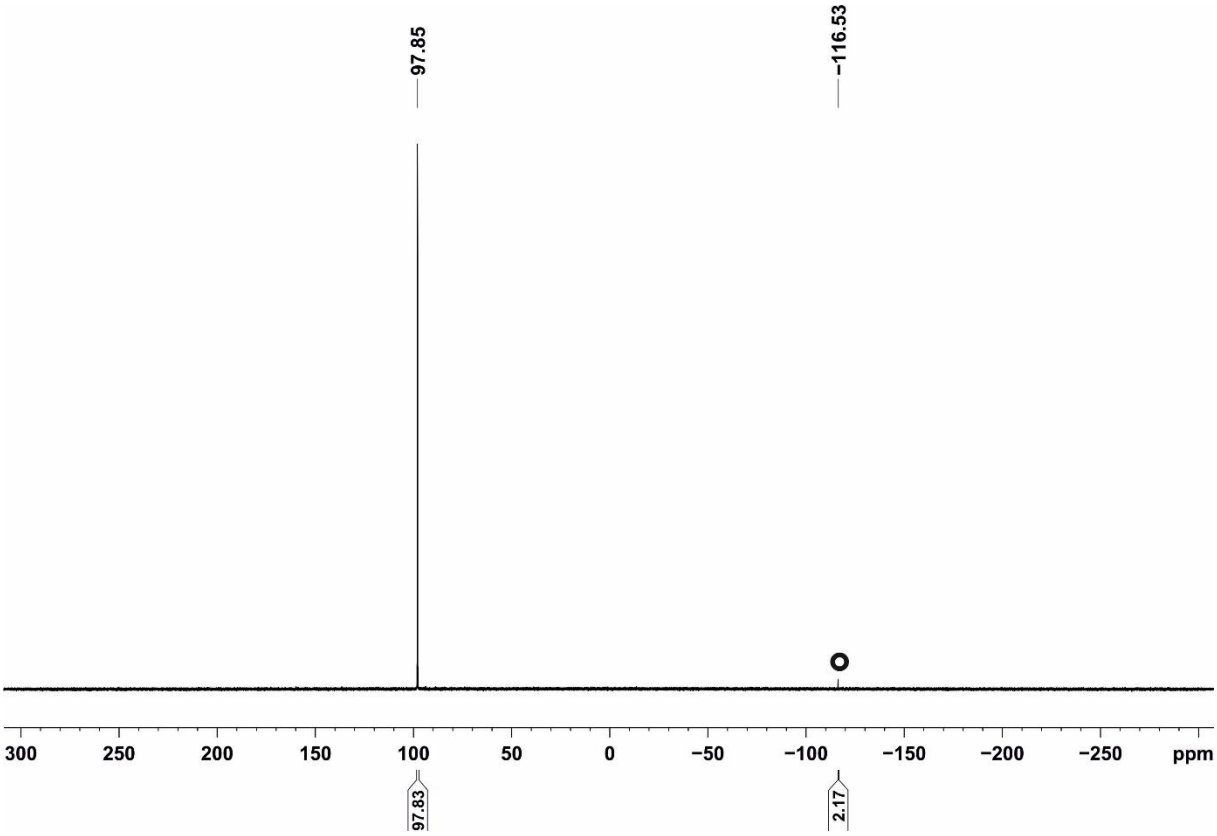


Figure S13 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **3-σ** (° = **3-π**).

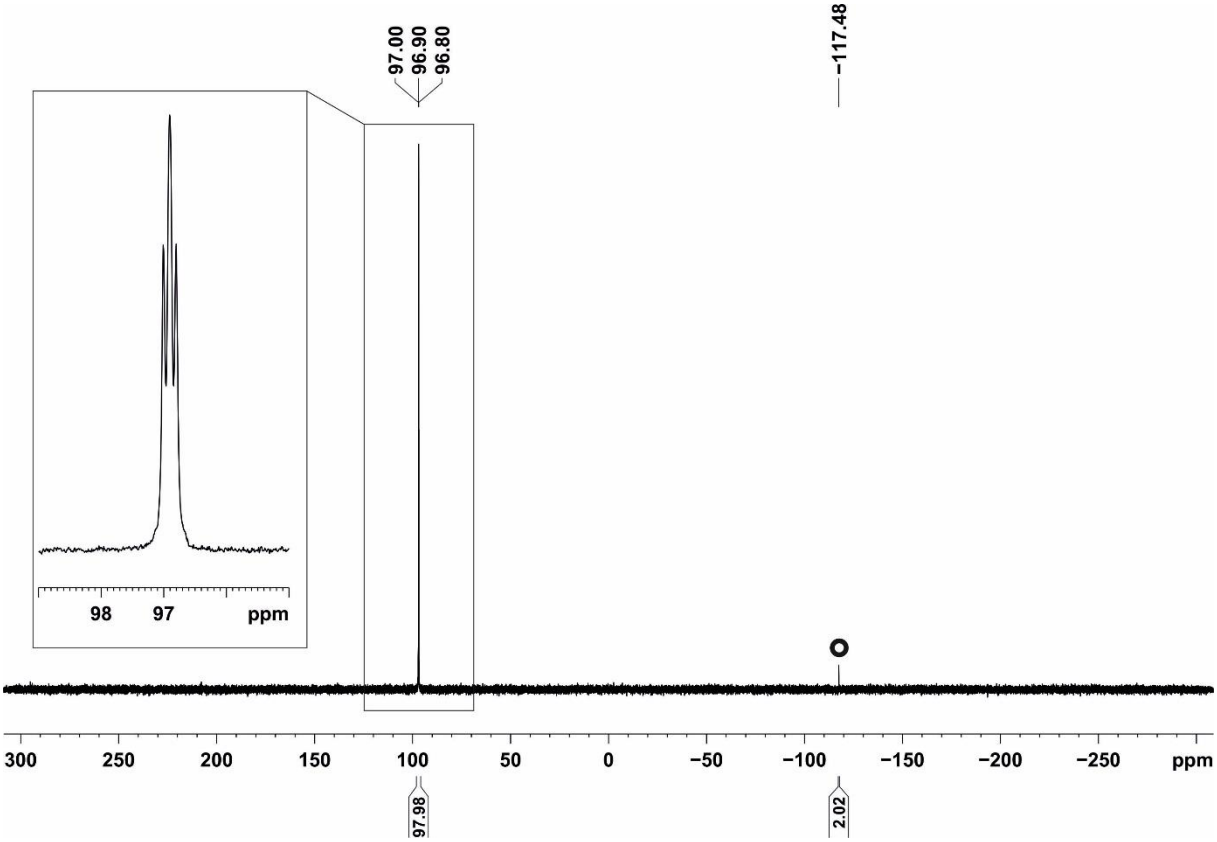


Figure S14 - ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **3-σ** (° = **3-π**).

S1.4 NMR Spectra of compound 3-π

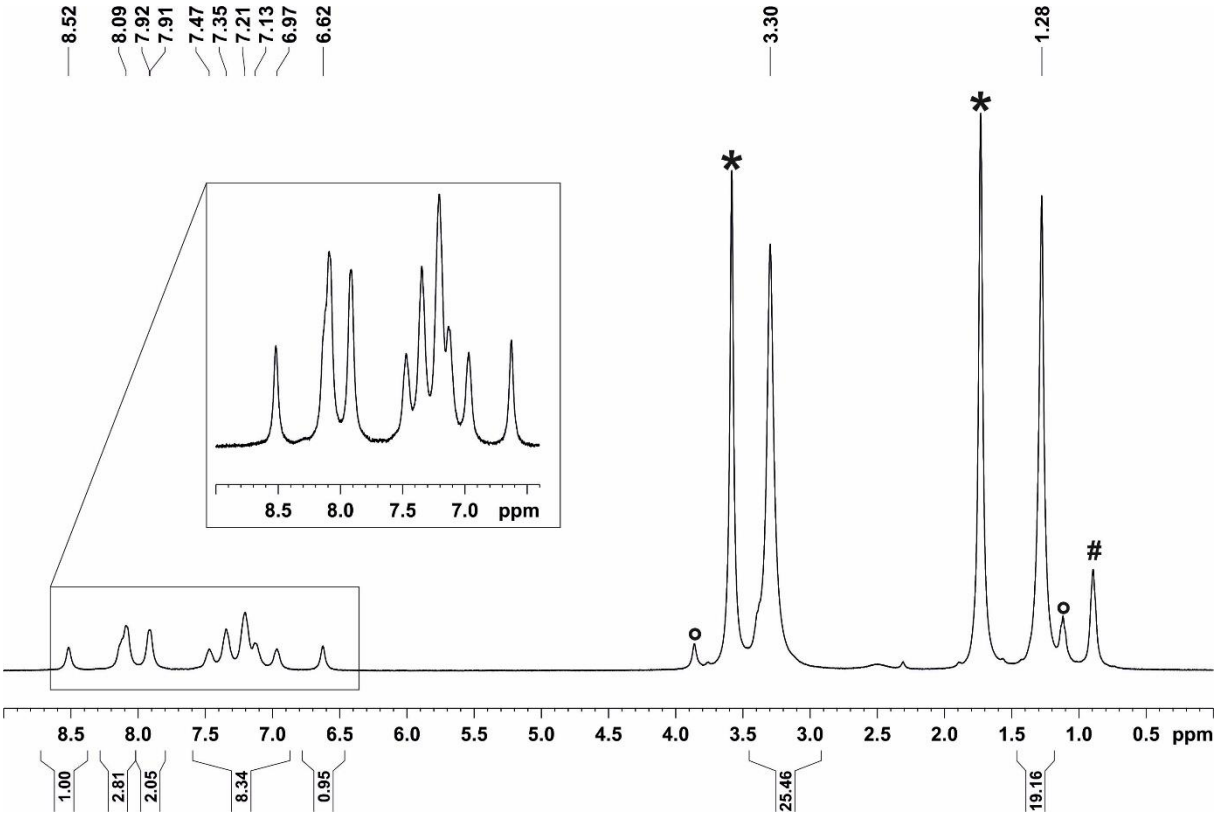


Figure S15 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **3-π** (* = [D_8]THF, # = *n*-hexane, ° = unidentified impurities).

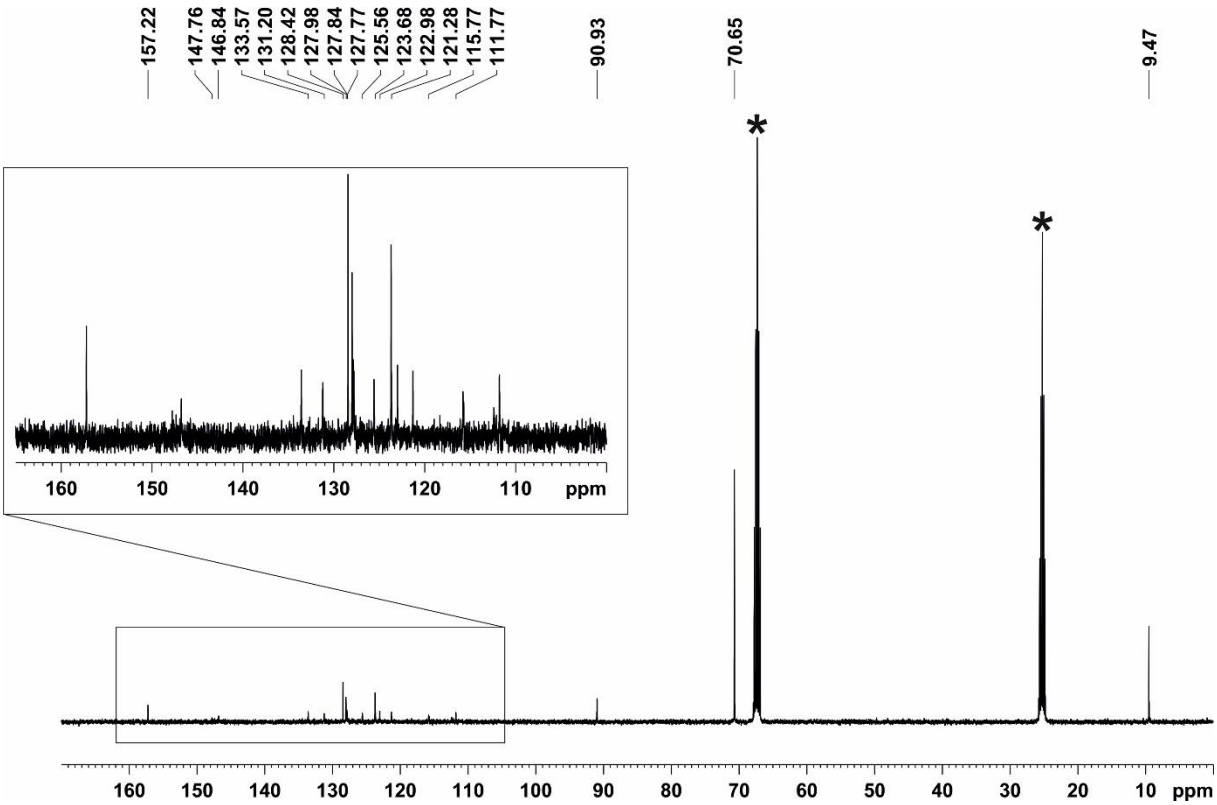


Figure S16 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **3-π** (* = [D_8]THF).

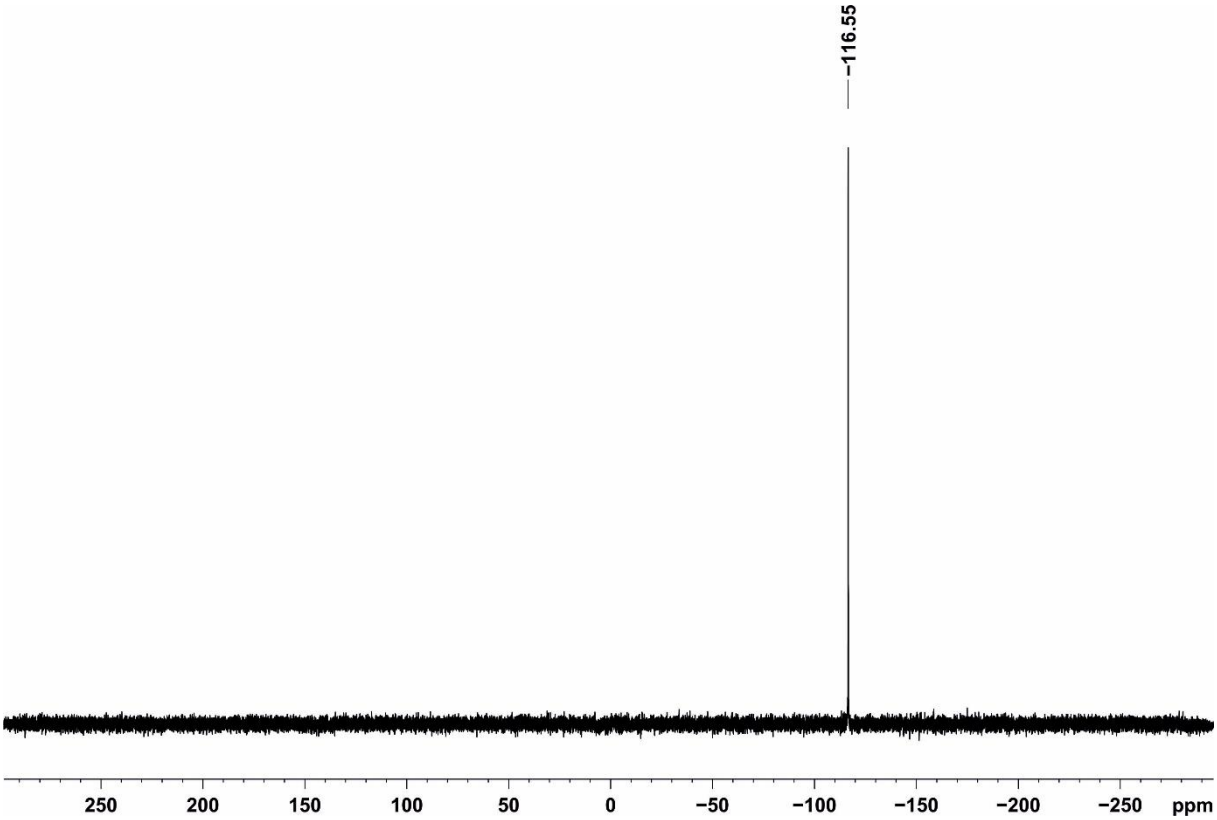


Figure S17 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **3-π**.

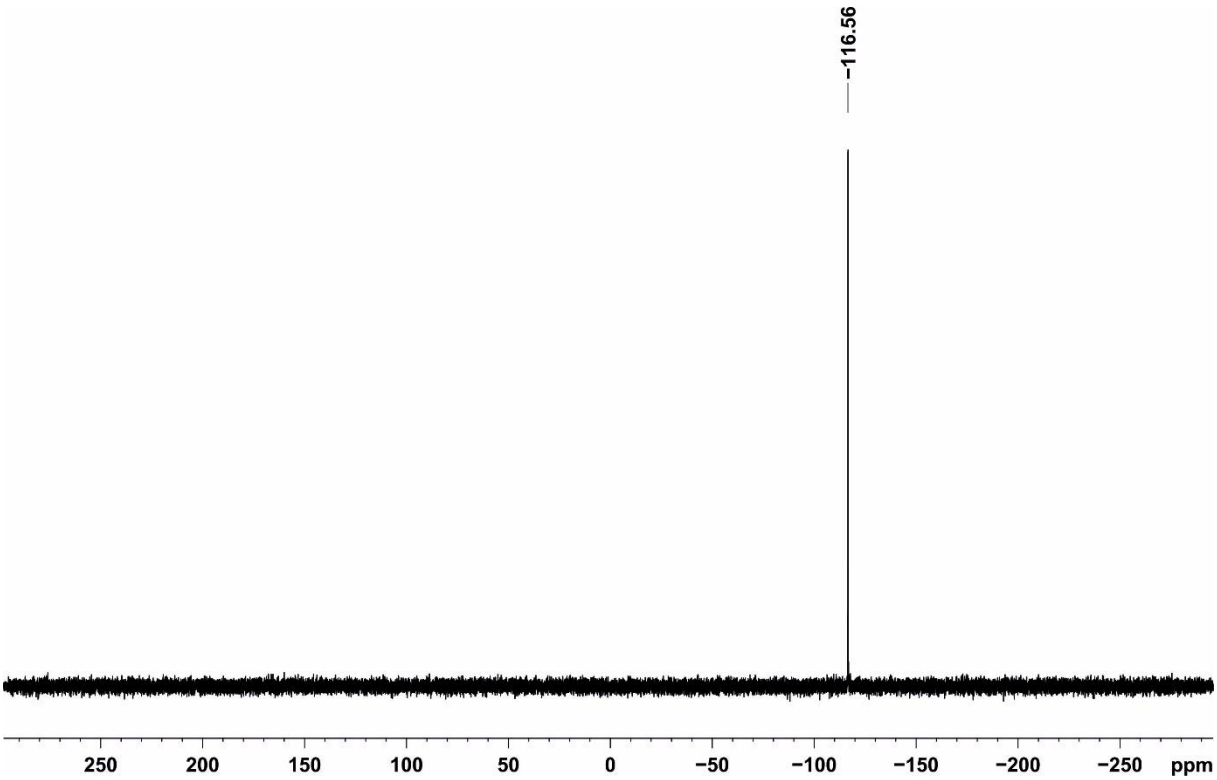


Figure S18 - ^{31}P NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **3-π**.

S1.5 Variable temperature $^{31}P\{^1H\}$ NMR spectra of compounds 1-σ and 1-π

[K([18]crown-6)][Cp*Fe($C_{10}H_8$)] (38 mg, 0.061 mmol) and **L** (20 mg, 0.061 mmol) were dissolved in [D_8]THF (0.5 mL) at room temperature. $^{31}P\{^1H\}$ NMR spectra were recorded at 300 K, 243 K and 333 K.

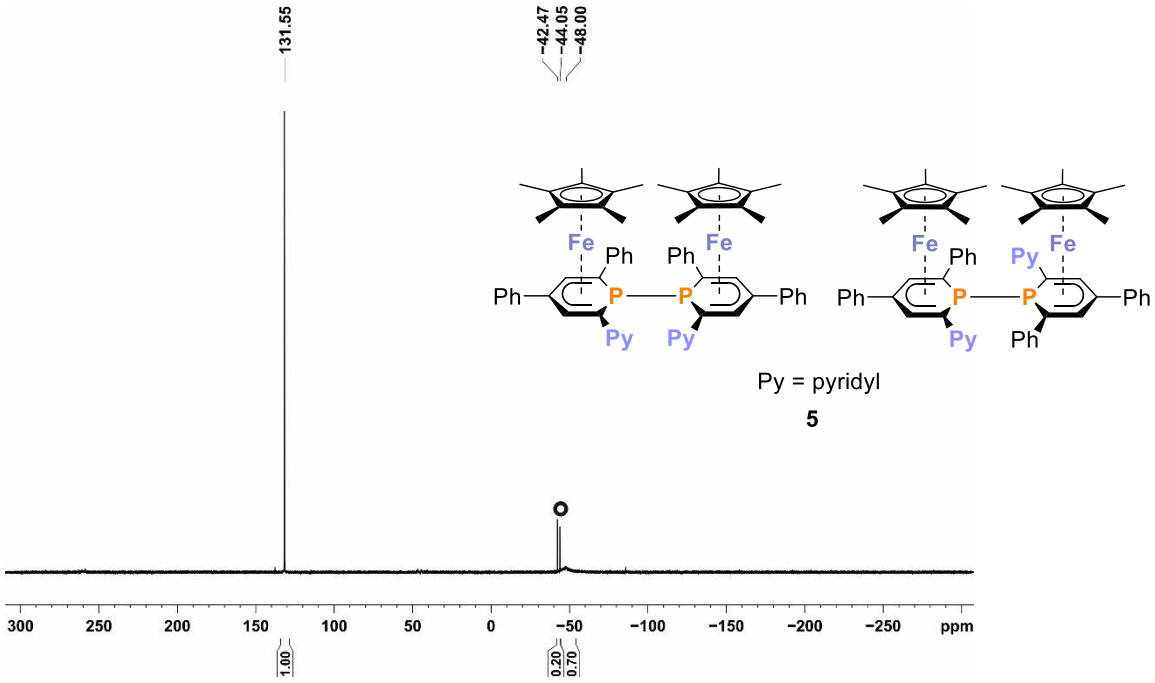


Figure S19 - $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, [D_8]THF) at 300 K (° = phosphinine iron dimers **5**).[8]

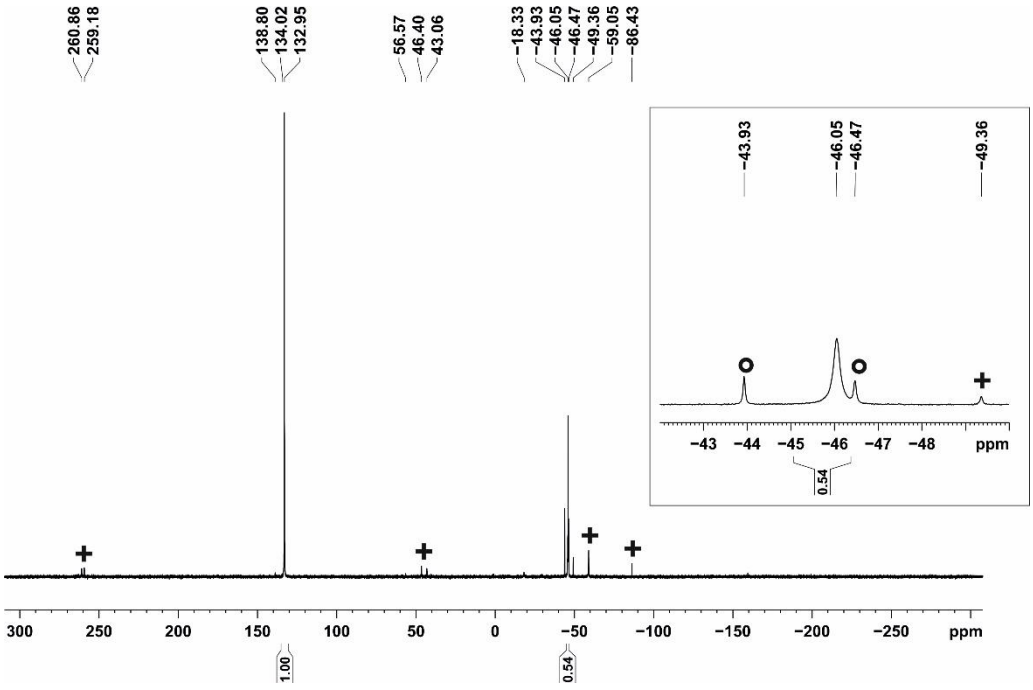


Figure S20 - $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, [D_8]THF) at 243 K (° = phosphinine iron dimers **5**, + = unidentified impurities).

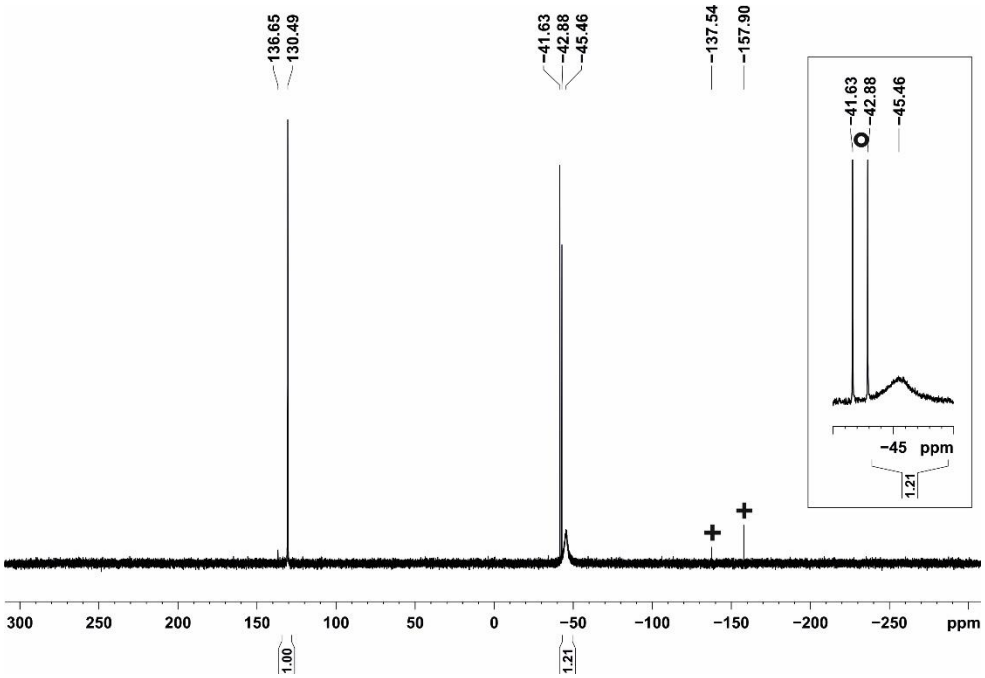


Figure S21 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, $[D_8]$THF) at 333 K (° = phosphinine iron dimers **5**, + = hydrophosphinine iron complexes **endo-4** and **exo-4**).

S1.6 $^{31}P\{^1H\}$ NMR monitoring of the formation of 1-σ and 1-π at 273 K

[K([18]crown-6)][Cp*Fe($C_{10}H_8$)] (38 mg, 0.061 mmol) and **L** (20 mg, 0.061 mmol) were dissolved in [D_8]THF (0.8 mL) cooled to −35 °C inside an NMR tube fitted with a screw cap. $^{31}P\{^1H\}$ NMR spectra were immediately recorded at a controlled temperature of 273 K, and recorded periodically while being maintained at the same temperature.

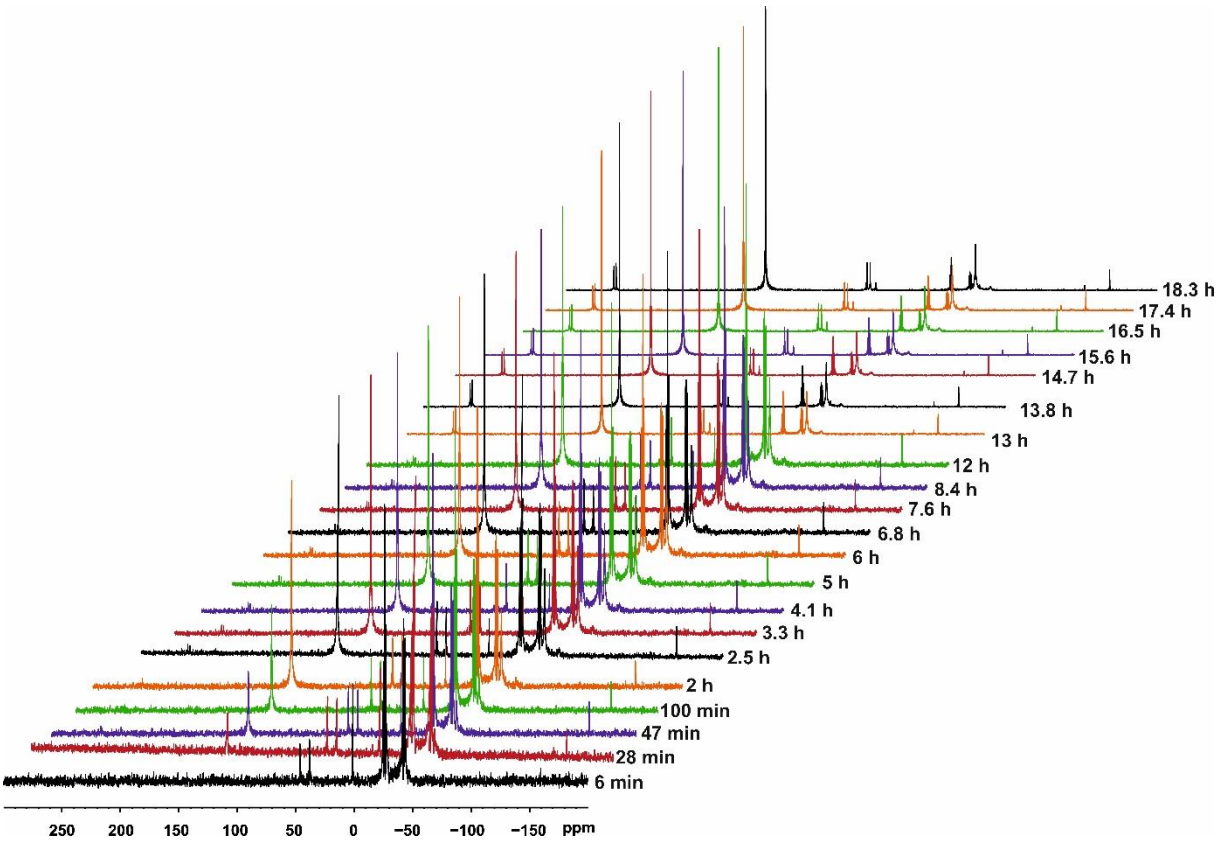


Figure S22 - $^{31}P\{^1H\}$ NMR monitoring (242.87 MHz, [D_8]THF) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 300 ppm ≥ δ ≥ −200 ppm.

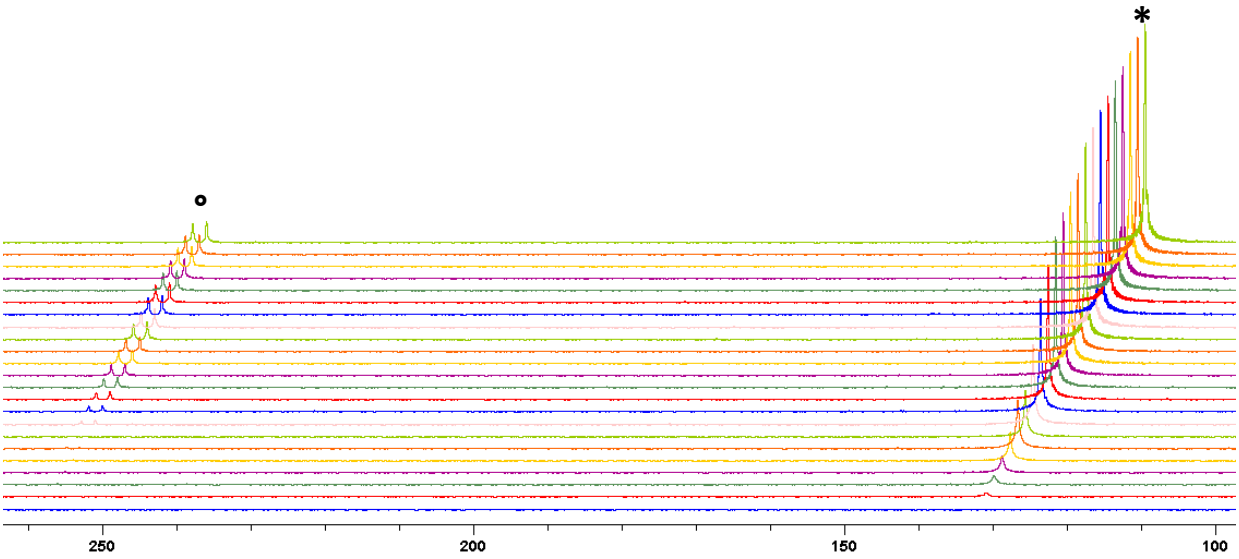


Figure S23 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 260 ppm ≥ δ ≥ 130 ppm. * = **1-σ**, ° = unknown species.

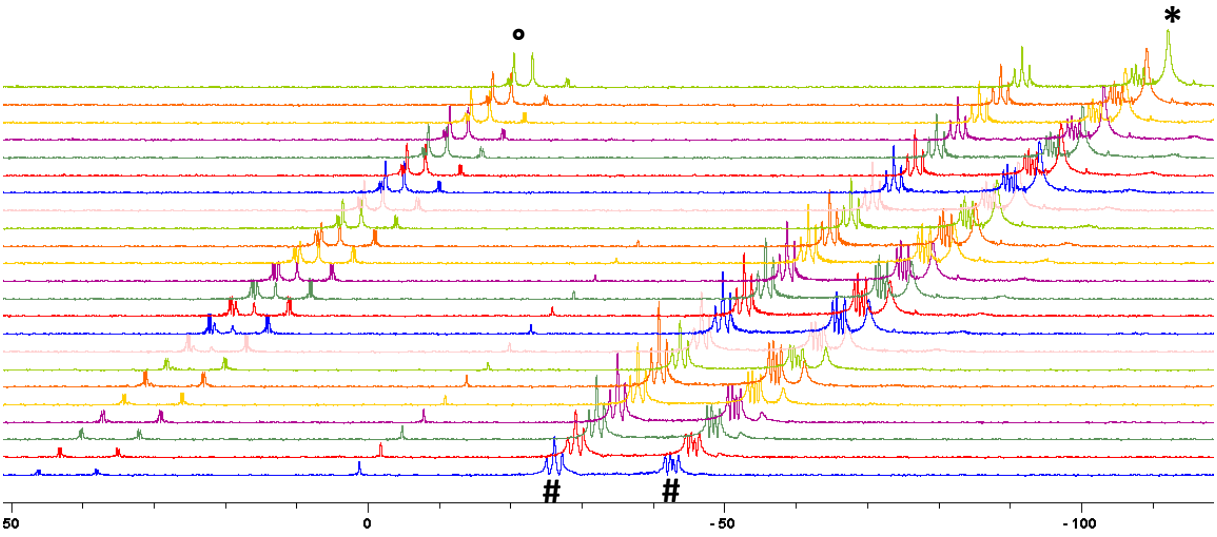


Figure S24 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 50 ppm ≥ δ ≥ −50 ppm. * = **1-π**, ° = unknown species, # = **2**.

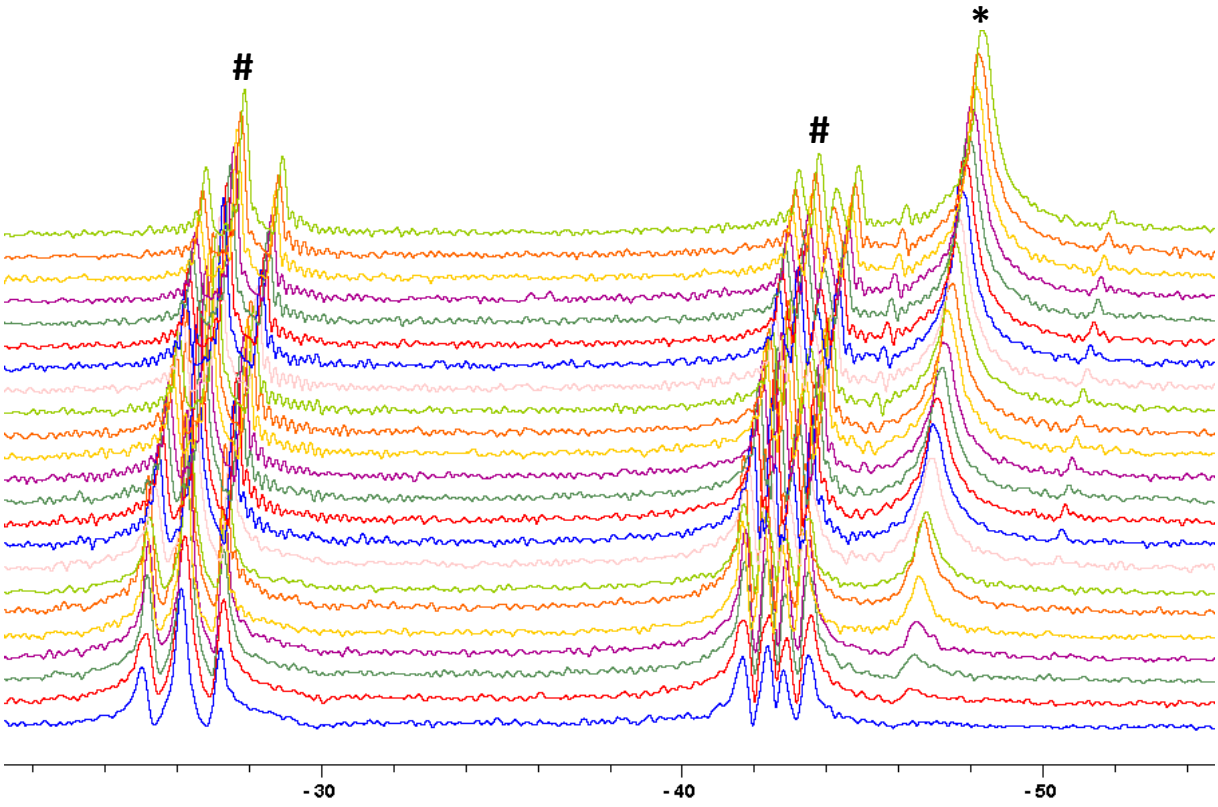


Figure S25 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of −20 ppm ≥ δ ≥ −50 ppm. * = **1-*π***, # = **2**.

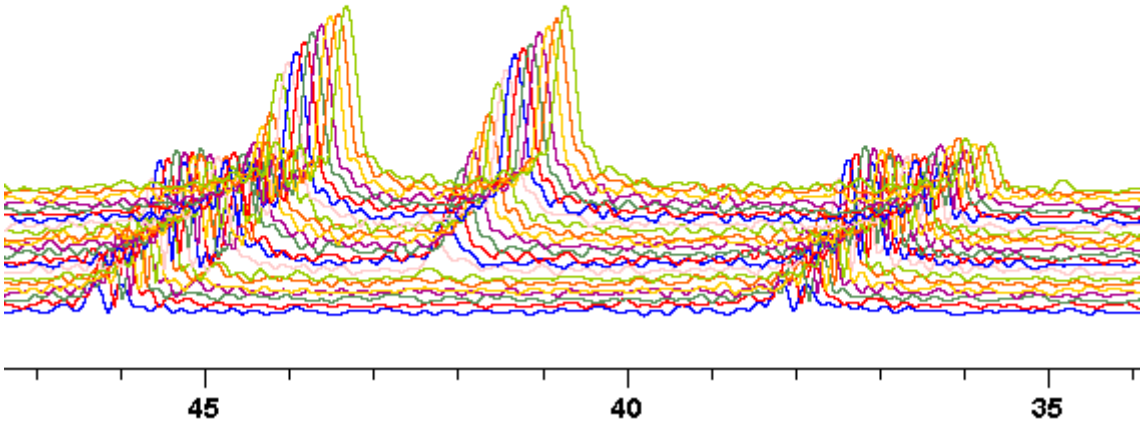


Figure S26 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 50 ppm ≥ δ ≥ 35 ppm; unknown species.

S2 UV-vis Spectra

S2.1 UV-vis spectrum of 1-σ and 1-π

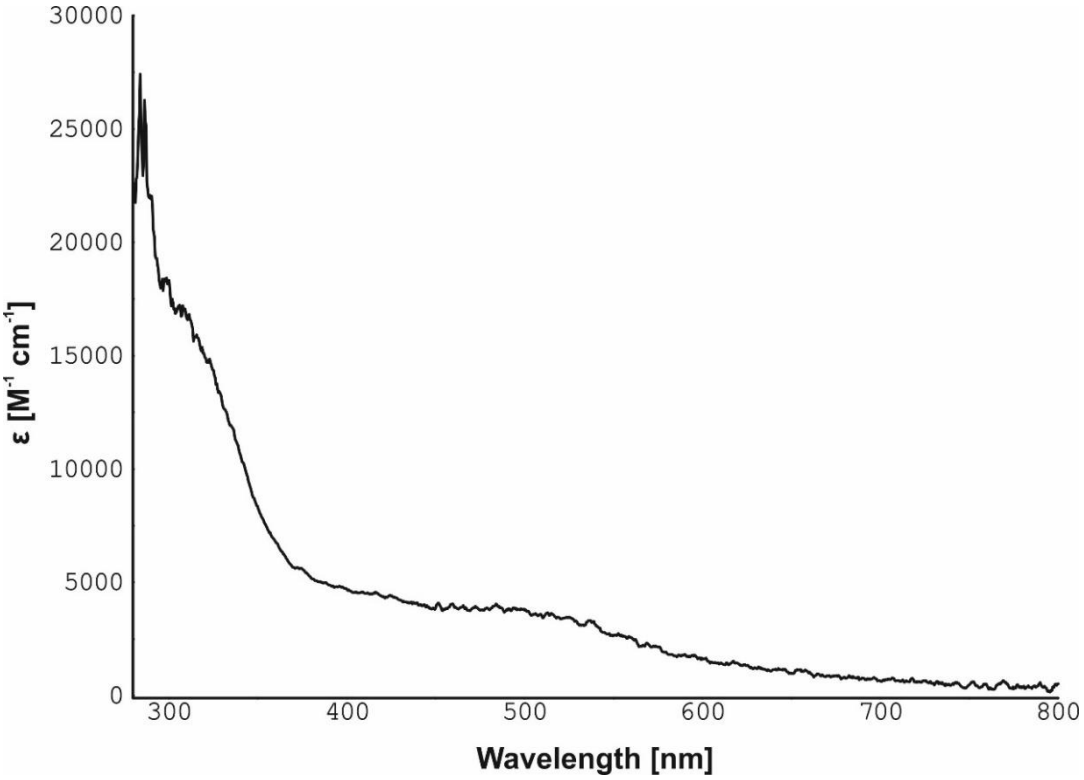


Figure S27 - UV/vis spectrum of **1-σ** and **1-π** in THF.

S2.2 UV-vis spectrum of 2

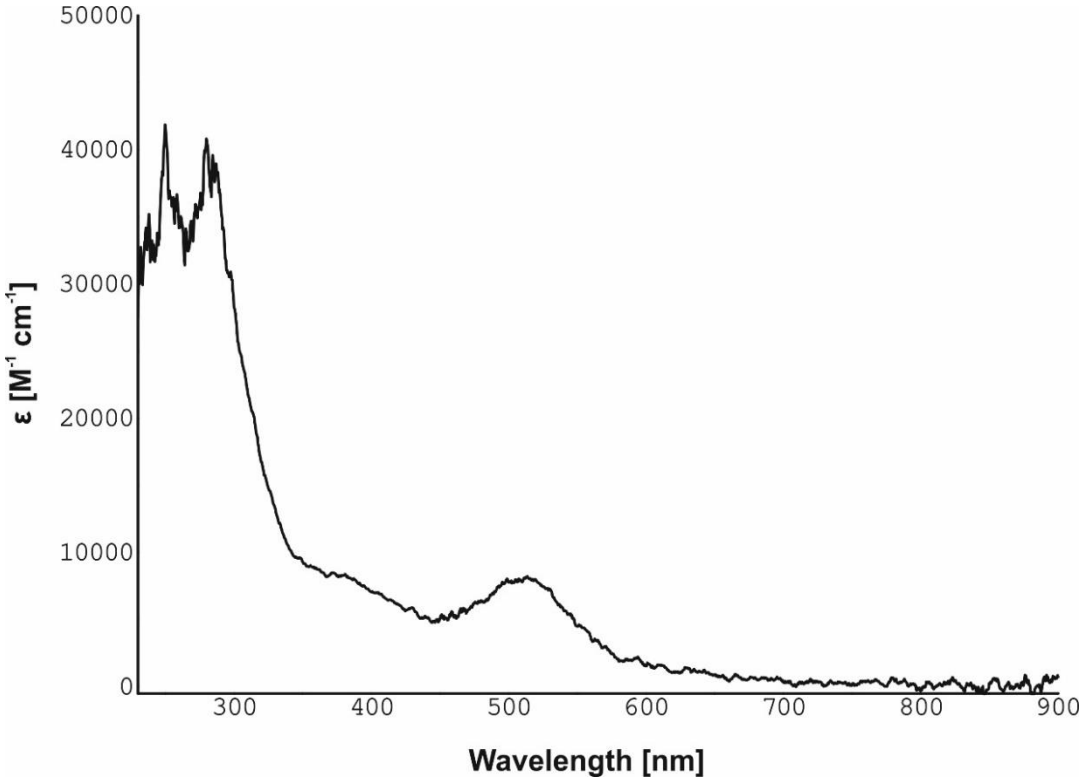


Figure S28 - UV/vis spectrum of **2** in THF.

S2.3 UV-vis spectrum of 3-σ

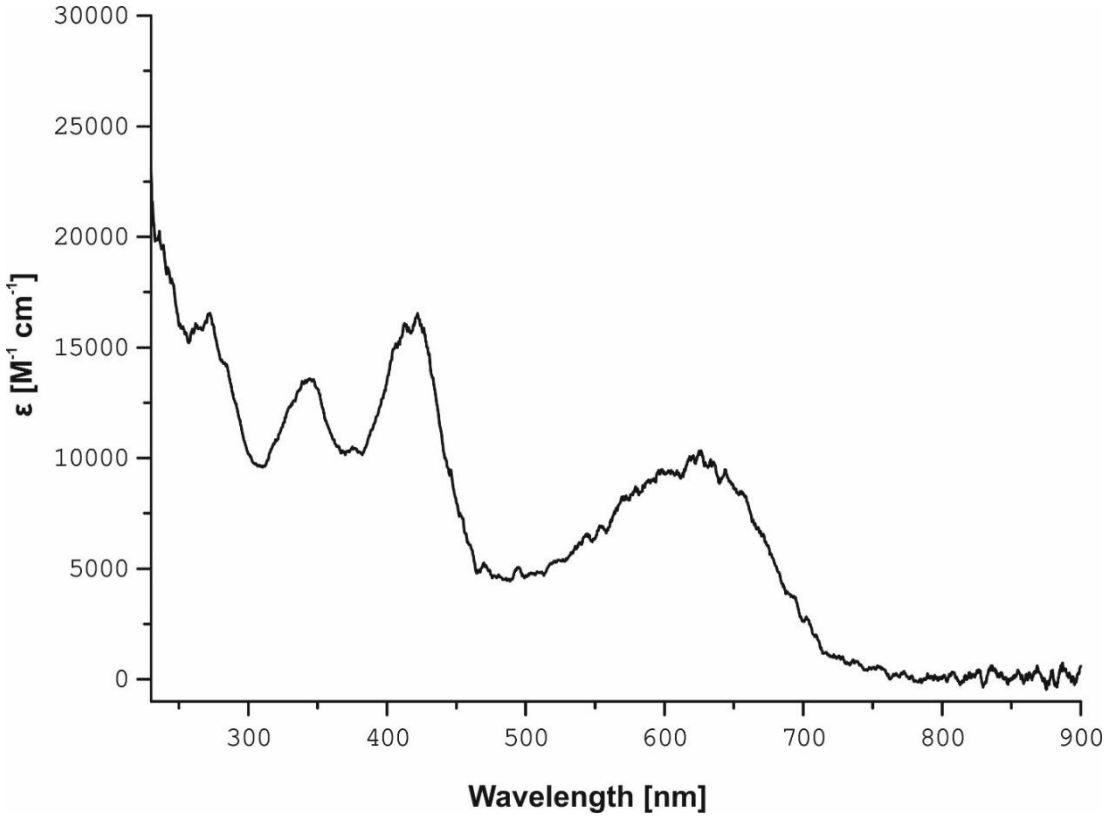


Figure S29 - UV/vis spectrum of **3-σ** in THF.

S2.4 UV-vis spectrum of 3-π

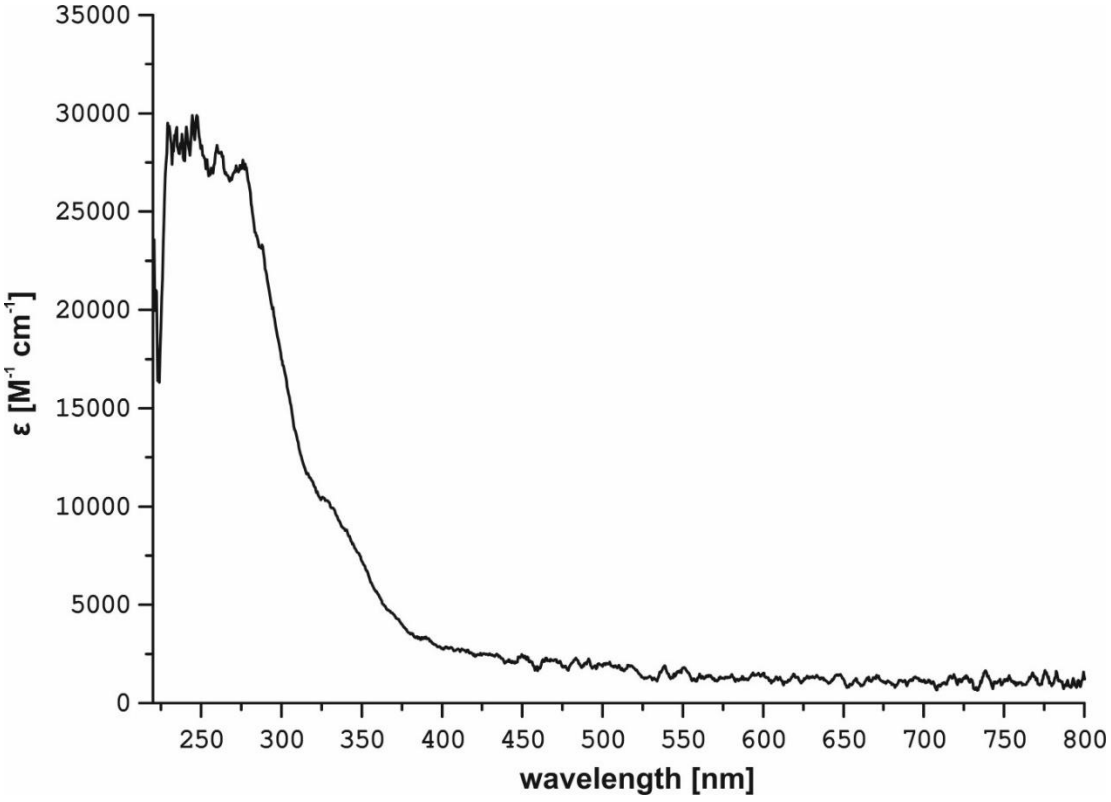


Figure S30 UV/vis spectrum of **3-π** in THF.

S3 IR Spectra

S3.1 IR spectrum of 3-σ

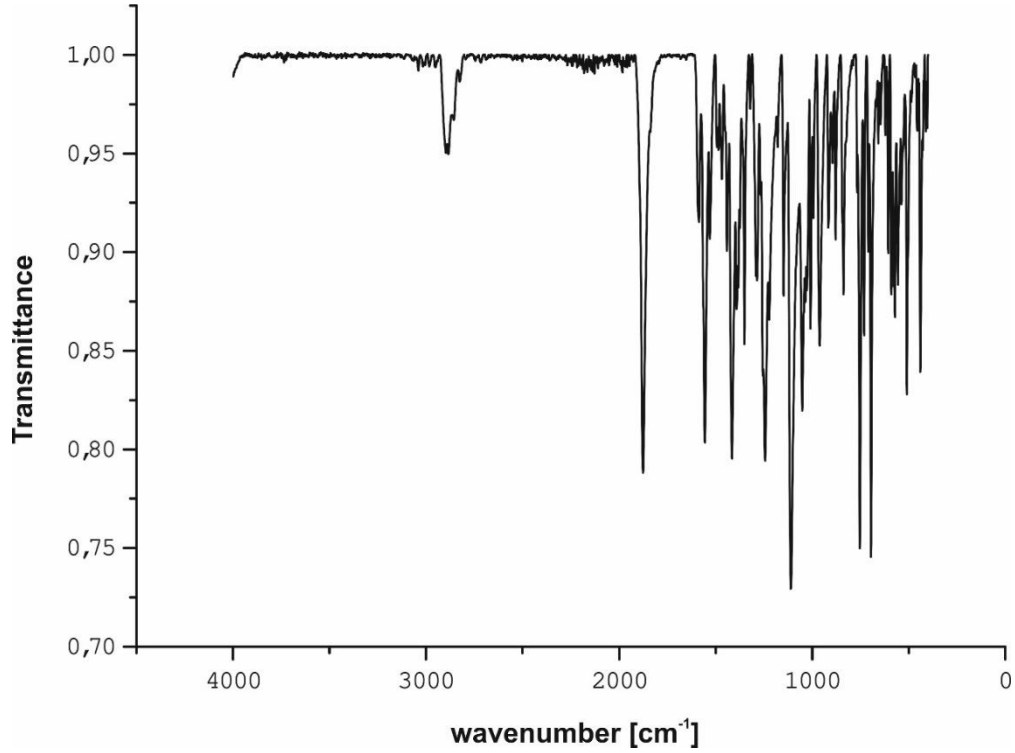


Figure S31 Solid state IR spectrum of **3-σ**.

S3.2 IR spectrum of 3-π

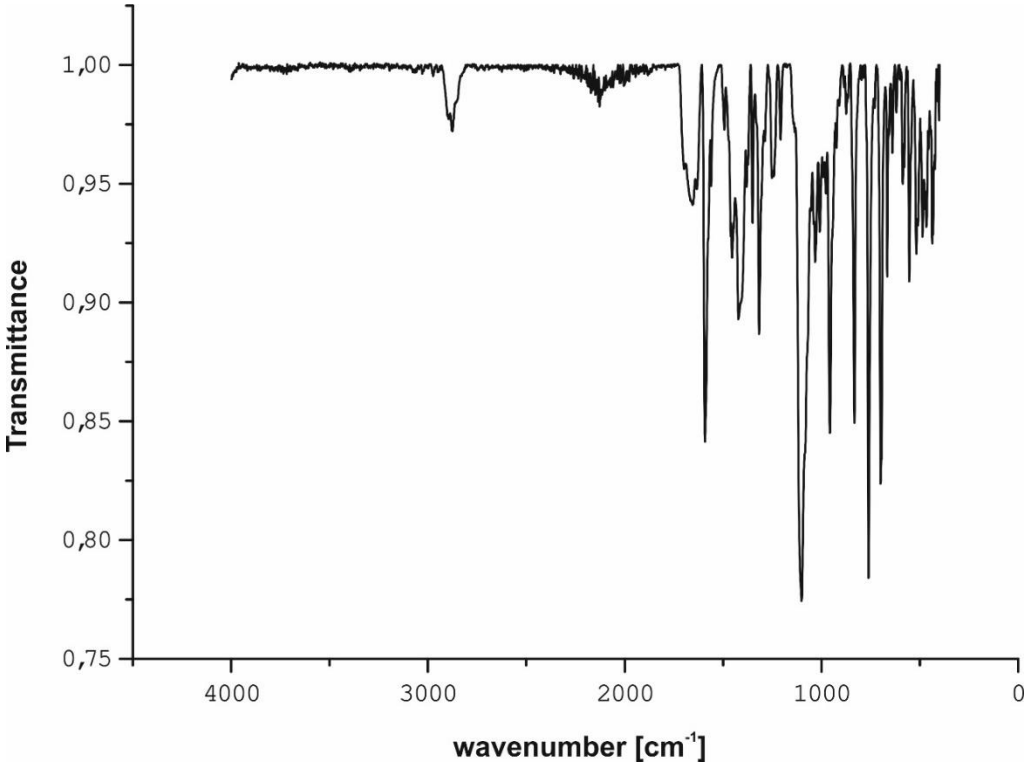


Figure S32 Solid state IR spectrum spectrum of **3-π**.

S4 X-ray Crystallographic Data

Table S1. Crystallographic data and structure refinement of **1-σ**, **2**, **3-σ** and **3-π**.

	1-σ	**2**	**3-σ**	**3-π**
Empirical formula	$C_{44}H_{55}FeKNO_6P$	$C_{66}H_{71}FeKN_2O_6P_2$	$C_{45}H_{55}FeKNO_8P$	$C_{45}H_{55}FeKNO_8P$
Formula weight / g·mol^{-1}	819.81	1145.13	863.82	863.82
Temperature / K	123.01(10)	123.00(10)	123.00(10)	123.00(10)
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	Pbcn	P-1	P21/n
a / Å	15.3111(2)	13.8522(4)	12.0465(4)	16.9137(3)
b / Å	17.0781(2)	38.2033(10)	12.2446(5)	11.6932(2)
c / Å	16.7872(3)	23.0082(6)	15.7693(5)	21.2321(4)
α /°	90	90	108.340(3)	90
β /°	106.967(2)	90	95.737(3)	99.828(2)
γ /°	90	90	92.223(3)	90
V / Å^3	4198.53(11)	12175.9(6)	2190.75(14)	4137.56(13)
Z	4	8	2	4
ρ_{calc} / g cm^{-1}	1.297	1.249	1.310	1.387
μ / mm^{-1}	4.503	3.503	4.379	4.637
F(000)	1736.0	4832.0	912.0	1824.0
Crystal size / mm^3	0.369 × 0.172 × 0.122	0.376 × 0.305 × 0.186	0.385 × 0.243 × 0.125	0.739 × 0.222 × 0.072
Radiation / Å	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2*Θ* range for data collection /°	7.558 to 147.676	6.788 to 147.266	7.396 to 147.044	7.324 to 152.886
Diffractometer	SuperNova	SuperNova	SuperNova	SuperNova
Index ranges	-19 ≤ h ≤ 18, -20 ≤ k ≤ 21, -20 ≤ l ≤ 19	-15 ≤ h ≤ 16, -38 ≤ k ≤ 46, -19 ≤ l ≤ 28	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -19 ≤ l ≤ 17	-21 ≤ h ≤ 21, -12 ≤ k ≤ 14, -26 ≤ l ≤ 24
Reflections collected	33166	32483	16728	27823
Independent reflections	8388 [R_{int} = 0.0402, R_{sigma} = 0.0289]	11993 [R_{int} = 0.0520, R_{sigma} = 0.0493]	8612 [R_{int} = 0.0404, R_{sigma} = 0.0481]	8583 [Rint = 0.0310, Rsigma = 0.0267]
Data/restraints/parameters	8388/390/655	11993/1623/1076	8612/0/519	8583/46/538
Goodness-of-fit on F^2	1.029	1.052	1.037	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0796	R_1 = 0.0850, wR_2 = 0.2172	R_1 = 0.0411, wR_2 = 0.1034	R1 = 0.0782, wR2 = 0.1713
Final R indexes [all data]	R_1 = 0.0322, wR_2 = 0.0812	R_1 = 0.0998, wR_2 = 0.2290	R_1 = 0.0427, wR_2 = 0.1051	R1 = 0.0799, wR2 = 0.1722
Largest diff. peak/hole / e Å^{-3}	0.46/-0.40	0.78/-0.54	0.87/-0.51	1.23/-0.49

S5 DFT Calculations

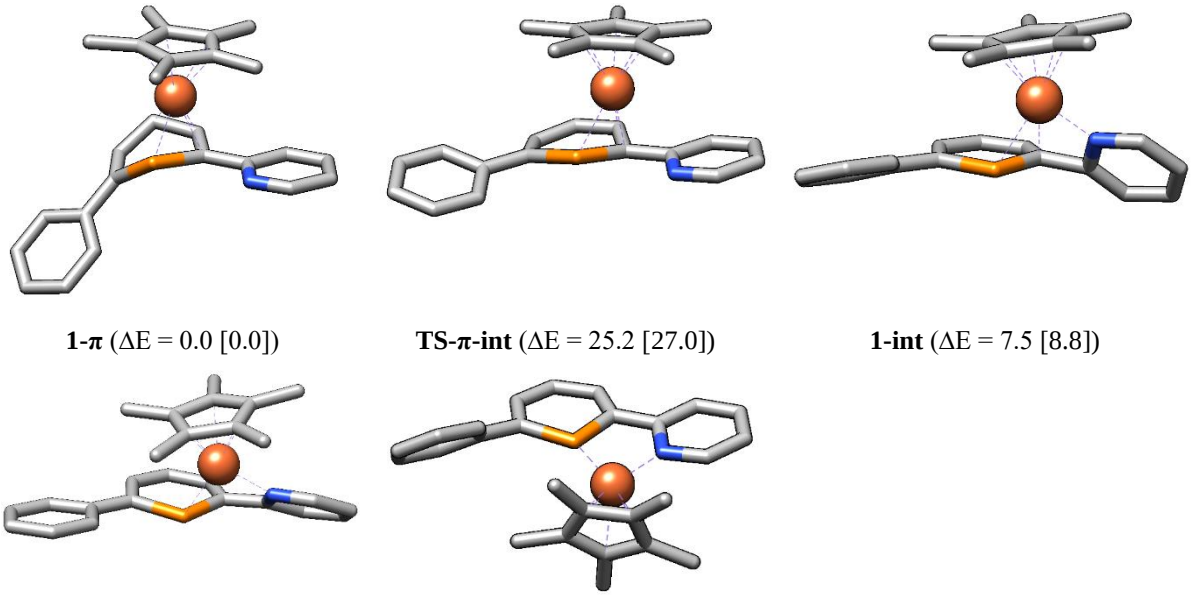
S5.1 General methods

All calculations were carried out with the ORCA program package.[9,10] All geometry optimisations were performed at the BP86-D3BJ/def2-TZVP[11–15] level of theory in the gas phase. Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimisations. Density fitting techniques, also called resolution-of-identity approximation (RI),[16] were used for GGA calculations, whereas the RIJCOSX[17] approximation was used for TPSSh calculations. To save computational cost the phenyl groups at the 4-position of the phosphinine moiety of ligand **L** were replaced by hydrogen atoms, and $[K([18]crown-6)]^+$ countercations were omitted. Approximate transition states were generated using the nudged elastic band (NEB) method implemented in ORCA, followed by a saddle-point optimisation.

S5.2 Isomerisation of complex 1

Final single-point calculations on the BP86 geometries were conducted at the TPSSh-D3BJ/def2-TZVP level of theory and zero-point energies and thermal corrections at 298 K were added from the BP86 calculations. Additionally, final single-point calculations of the calculated minima and transition states were carried out with the CPCM[19] model for THF at the TPSSh-D3BJ/def2-TZVP level.

The isomerisation of **1-π** to **1-σ** proceeds *via* a two-step mechanism. First, the intermediate **1-int** is formed, in which the Cp*Fe moiety 'slips' from η^4 to η^2 coordination to the phosphinine moiety, with concomitant formation of a new Fe—N interaction. Subsequent reorientation of the phosphinine switches it from a π- to a σ-coordination mode, providing the final isomerised complex (Figure S33).



1-π (ΔE = 0.0 [0.0]) **TS-π-int** (ΔE = 25.2 [27.0]) **1-int** (ΔE = 7.5 [8.8])

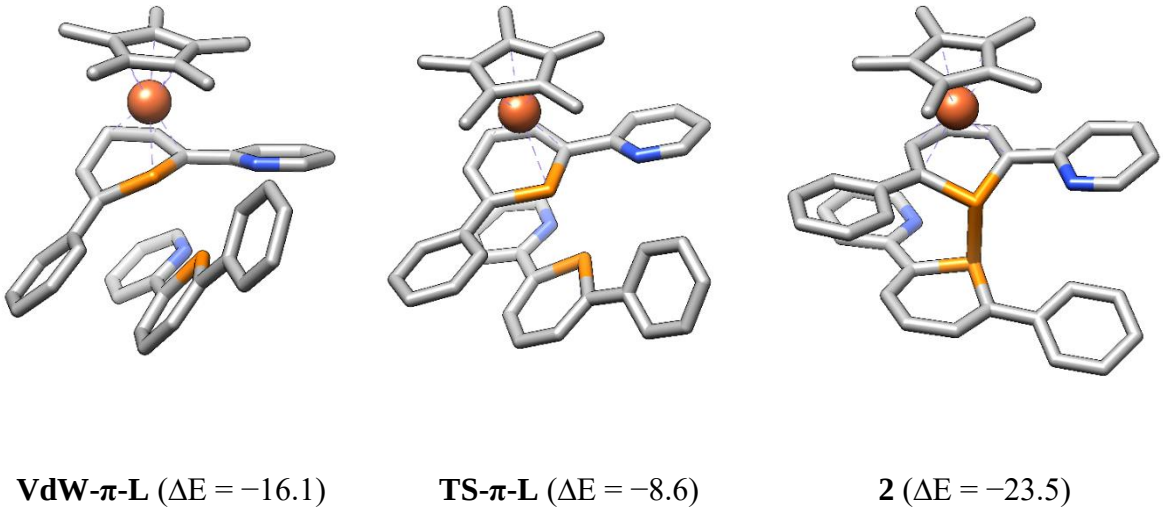
TS-σ-int (ΔE = 20.2 [23.0]) **1-σ** (ΔE = −1.4 [−0.9])

Figure S33 - Optimised structures for the isomerisation of **1-π to 1-σ**. Energies are given in kcal·mol^{-1} relative to the optimised structure of **1-π**. Energies in brackets correspond to electronic energies with solvent correction (TPSSh-D3BJ/def2-TZVP CPCM(THF)).

S5.3 Formation and electronic structure of compound 2

The reaction between **1-π** and **L** in the gas phase involves two steps (energies were obtained at the TPSSh-D3BJ/def2-TZVP[18] level of theory): the activation barrier-free formation of the Van-der-Waals complex **VdW-π-L**, and subsequent P−P bond formation yielding **2**. The respective transition state **TS-π-L** has a low energy (Figure S35), consistent with the experimental observation of rapid formation of **2** at room temperature.

The highest occupied molecular orbital (HOMO) of **2** strongly resembles the HOMO of the phosphacyclohexadienyl anion (Figure S35). Additionally, inspection of the molecular orbitals of **2** (Figure S36) revealed a $3d^6$ configuration at the iron center. Therefore, **2** can be described as an iron(II) complex with an η^6-coordinating, dianionic di(phosphacyclohexadienyl) ligand. Thus, the formation of **2** could formally be regarded as a redox reaction.



VdW-π-L (ΔE = −16.1) **TS-π-L** (ΔE = −8.6) **2** (ΔE = −23.5)

Figure S34 - Optimised key structures for the formation of **2** from **1-π** and **L**. Energies are given in kcal·mol^{-1} relative to the sum of the electronic energies of **1-π** and **L**.

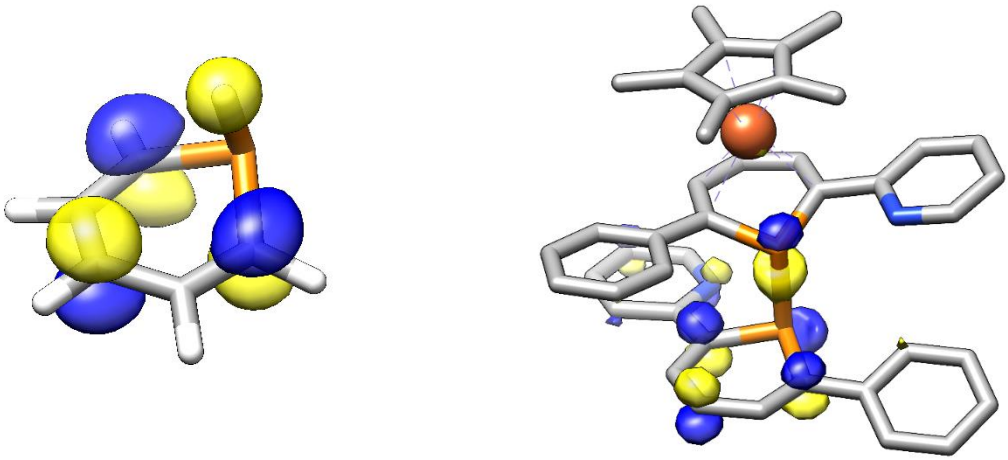
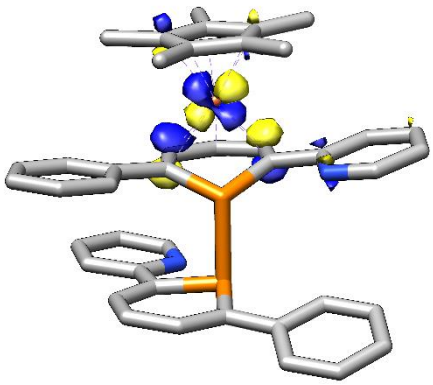
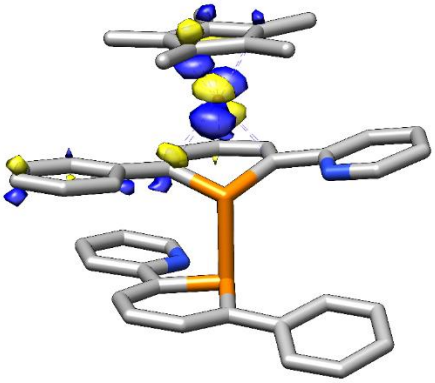


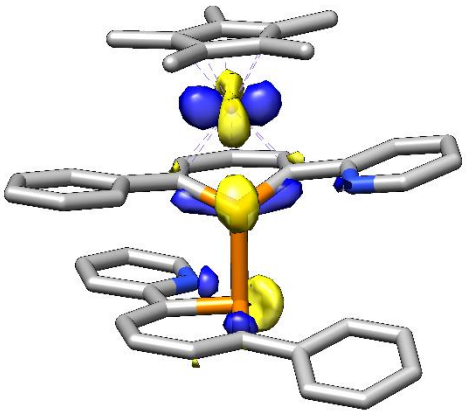
Figure S35 - Comparison of the HOMOs of the phosphacyclohexadienyl anion (left) and **2** (right), obtained at the BP86-D3BJ/def2-TZVP level. Hydrogen atoms of **2** have been omitted for claritiy. Surface isovalue = 0.06.



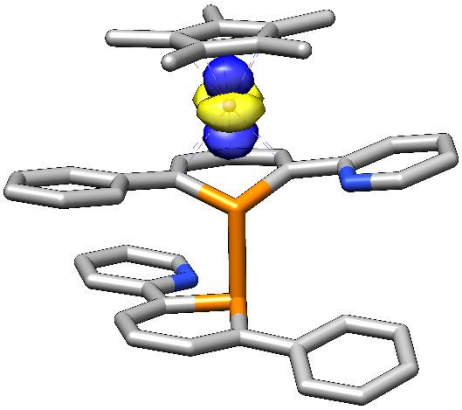
LUMO+3



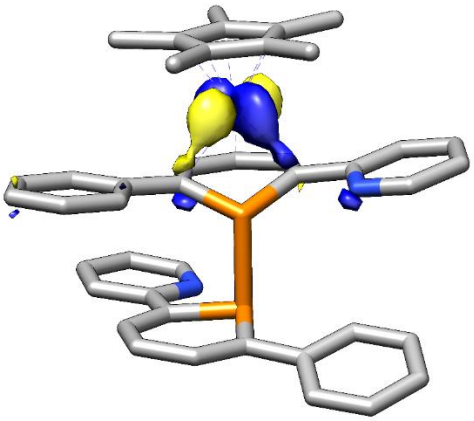
LUMO+1



HOMO−2



HOMO−3



HOMO−6

Figure S36 - Kohn-Sham orbitals of **2** with significant 3d character at iron (BP86-D3BJ/def2-TZVP level). Hydrogen atoms have been omitted for claritiy. Surface isovalue = 0.06.

S5.4 Reactions of 1-π and 1-σ with CO_2

To account for solvent effects, final single point calculations of the calculated minima and transition states were carried out with the CPCM[19] model for THF at the TPSSh-D3BJ/def2-TZVP level.

In the case of **1-π**, the first step of the mechanism involves the activation barrier-free formation of the van-der-Waals complex **VdW-π-CO₂**, followed by the exothermic formation of **3-π** *via* an energetically low-lying transition state **TS-π-CO₂** (+5.5 kcal·mol^{-1}, Figure S37). Note that for these calculations the [K([18]crown-6)]$^+$ countercation has been omitted for the sake of computational efficiency; they therefore do not account for any addition electrostatic stabilisation as a result of K···O—C interactions (as observed in the solid state for **3-π**).

In the case of **1-σ**, the first step involves the activation barrier-free coordination of CO_2 at the iron atom forming intermediate **VdW-σ-CO₂**. Subsequently, **VdW-σ-CO₂** undergoes CO_2 cleavage *via* transition state **TS-σ-CO₂** to form **3-σ** in a very strongly exothermic reaction. As for **1-π**, the activation barrier for this process is very small (+3.5 kcal·mol^{-1}, Figure S37), in agreement with the instantaneous reaction observed experimentally.

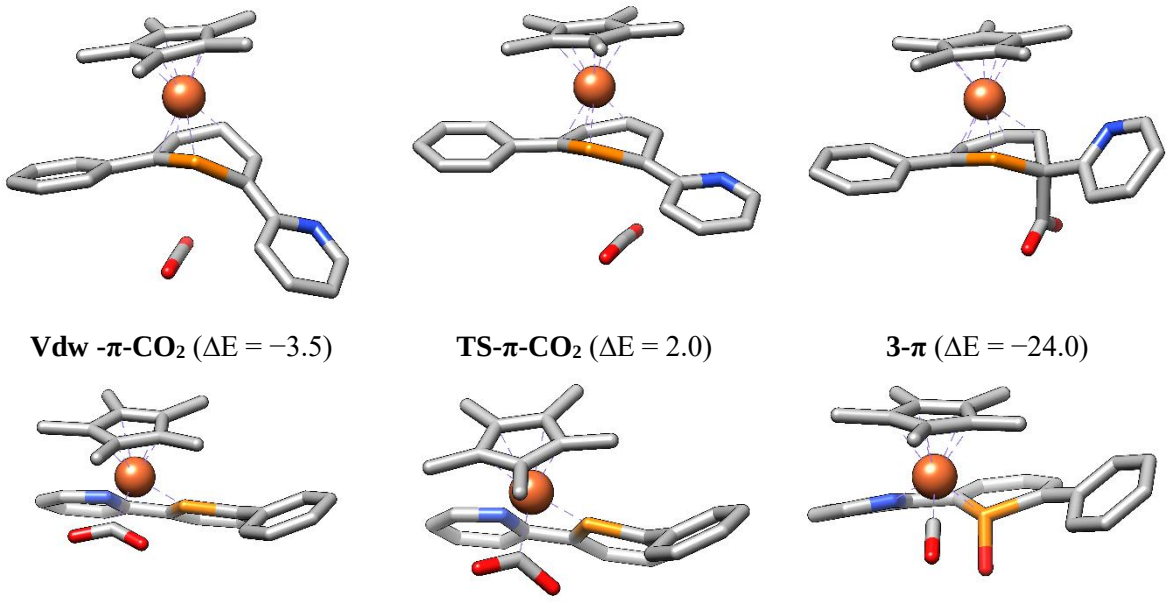


Figure S37 - Optimised key structures for the activation of CO_2 by **1-π** (top) and **1-σ** (bottom). Energies are given in kcal·mol^{-1} relative to the sum of the electronic energies of CO_2 and the relevant isomer of **1**.

S5.5 Electronic structure of 3-σ

Because the analysis of the Kohn-Sham orbitals of **3-σ** was not as straightforward as for **2**, CASSCF/def2-TZVP calculations with ten electrons in seven orbitals were carried out in order to obtain an insight into the electronic structure and bonding in **3-σ**. To aid convergence, the CASSCF calculation was carried out including six roots. The ground-state of **3-σ** is of dominant single-reference character (94% contribution of the ground-state configuration state function). Inspection of the natural orbitals of the active space reveals three lone pairs of electrons at the iron center (HOMO, HOMO−1 and HOMO−2, Figure S39) accounting for a $3d^6$ configuration and two metal-ligand bonding orbitals (HOMO−3 and HOMO−4) and their respective antibonding counterparts

(LUMO and LUMO+1). Additionally, the HOMO−5 resembles the HOMO of the phosphacyclohexadienyl anion, thus indicating the presence of a negative charge within the C_5P ring in **3-σ**. The bonding situation can therefore be described as an interaction of a cationic $[Fe^{II}(CO)(Cp^*)]^+$ fragment with a dianionic oxo-phosphacyclohexadiene ligand.

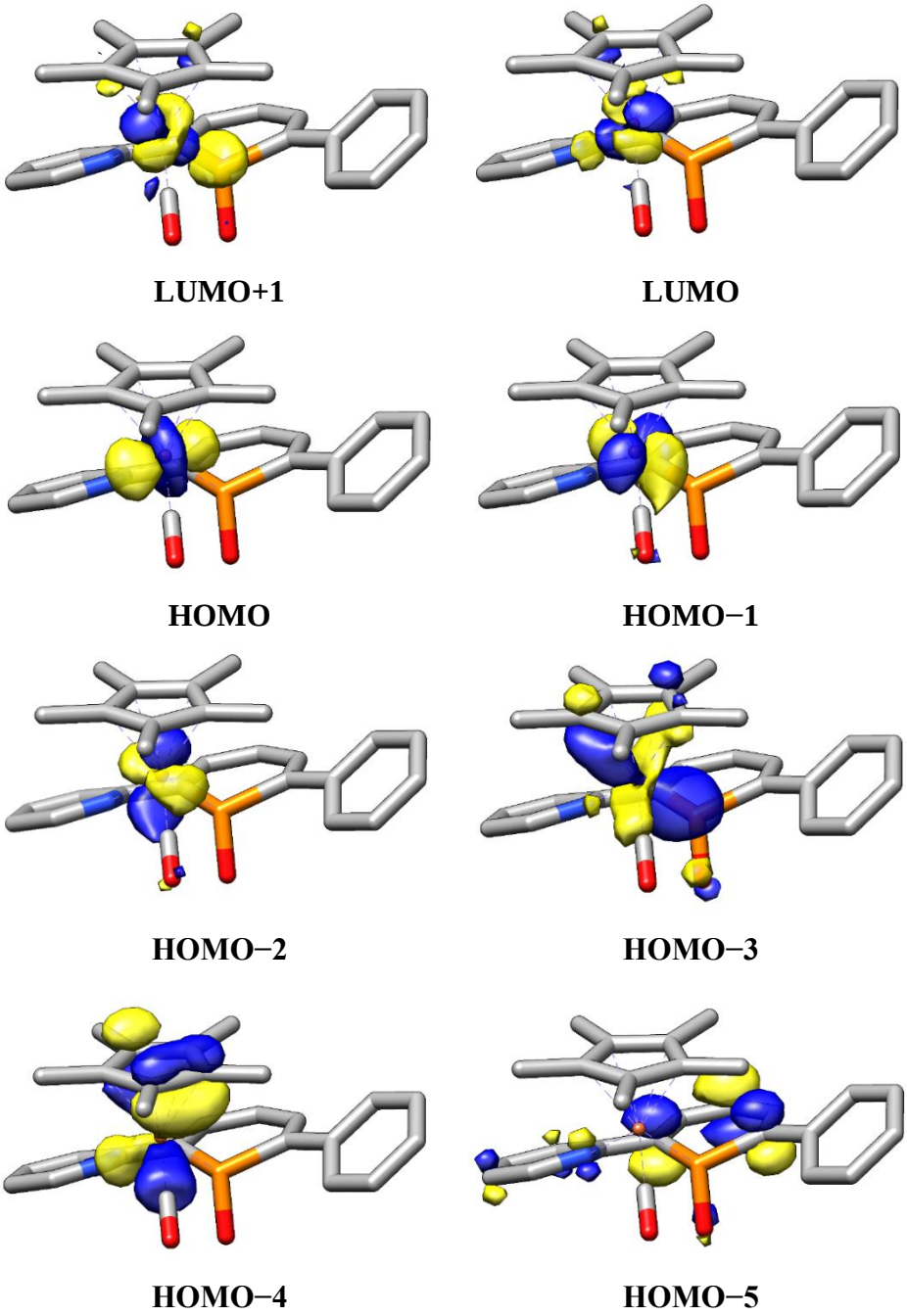


Figure S38 Selected molecular orbitals of 4-σ (CASSCF(10/7)/def2-TZVP level). Hydrogen atoms of the 4-σ have been omitted for claritiy. Surface isovalue = 0.06.

S5.6 Cartesian coordinates of optimised structures

$[C_5H_5P]^-$

C	-7.61943319559269	1.22409425547681	0.13533784859837
C	-7.64465161413261	2.59587319386719	0.30655806150595
C	-6.46424418962032	0.47009145181158	-0.19230249875865
C	-5.17738486014462	1.04326799732260	-0.03165911543904
C	-4.92836447320168	2.39473921664987	0.12075910803984
P	-6.23079634688711	3.61428255628433	-0.18313646659172
H	-8.53726116116016	0.65629539320926	0.35526367967173
H	-8.52398638132399	3.07923019770116	0.74215399853911
H	-4.33148673543528	0.34486561603294	0.06765676734310
H	-6.55098221652423	-0.61550683348109	-0.28501854811743
H	-3.93687915667162	2.73953775574318	0.42846629093591
H	-6.34139966930567	3.47491919938217	-1.64968912572718

L

P	6.04122337926595	24.63408168499444	10.97933198060370
C	6.08960118303451	26.38102873225077	10.75022889366670
C	5.86394350235381	27.01786074063859	9.52198000089409
H	5.94173500748529	28.10846159769303	9.48776660296668
C	5.58319435084327	26.34316947281555	8.33494039956308
C	5.49794456569007	24.95320382160534	8.25123074122980
H	5.30488939279188	24.51332433392341	7.26873401066420
C	5.68871142267727	24.09357247778719	9.33797204441012
C	5.57916845761728	22.62759068525408	9.15123071191018
C	4.72646922398813	22.05698178249720	8.18793551438395
H	4.09772039713966	22.69146888071547	7.56349075890103
C	4.67201228383245	20.67090387157797	8.06514324487574
H	4.01602743110801	20.20974644533032	7.32525654825285
C	5.45558524081305	19.88503800485405	8.91149915598559
H	5.44375709874828	18.79671836851895	8.85008926594723
C	6.25604186692401	20.53456912567334	9.85513931531024
C	6.36810393266843	27.20464479007647	11.95036446841172
H	5.44717675621914	26.92807203796902	7.42378818398789
C	5.66160778644344	28.39942471765804	12.18383860842483
C	5.91647771486721	29.17118253374181	13.31686695234687
C	6.88192929376833	28.76510071451661	14.24259996517816
C	7.58856340350576	27.57932192690138	14.02585573436544
C	7.33467792257424	26.80721372213552	12.89250019850521
H	7.90164320401353	25.89157814763470	12.71613940404032
N	6.32603590454227	21.86411741452478	9.97879964270533
H	6.87779545221354	19.95805821272706	10.54645969983165
H	4.88436086533311	28.70664610395373	11.48235146563765
H	5.35129726149673	30.08954095601434	13.48311094968027
H	7.08159905106075	29.36934419713680	15.12843577416666
H	8.34813664698058	27.25666449888003	14.73934976315279

1-σ

Fe	3.72592401196239	13.42136286396835	13.05841048003086
P	5.50741856996626	12.40791601565484	12.77336220237265
N	4.45241524290449	14.58019982644907	11.69500525801739
C	7.96462190229615	11.14102547354741	12.95606485756925
H	8.56915206010328	10.28075232362786	13.26636731763079
C	5.80641481923798	14.54496225852838	11.26442046771582
C	6.30886722935948	15.51378447711643	10.37749995200805
H	7.36328550097966	15.45172990411800	10.10107369759245
C	8.61257994180999	12.14895602150099	12.21596825323474
C	7.94006245125282	13.23602191264865	11.64947452229262
H	8.53515965993015	13.95662339415390	11.07573608031956
C	6.04969205736462	9.90197877564039	13.92441084653583
C	5.50499492078208	16.50825541721105	9.84398734262572
H	5.90390161046380	17.24814981645005	9.14910467590880
C	6.60301295011311	11.08955062401833	13.26070281068218
C	2.06852235235543	12.38475414999738	13.72796025904286
C	6.56911992103160	13.45528404035571	11.78893669337016
C	2.98081276905463	12.65666820618897	14.81297457402019
C	3.15405039715675	14.08461905644085	14.90286003940619
C	4.83456319370247	9.33506960098914	13.48305128108727
H	4.31361889190257	9.81972260698764	12.65523824027235
C	3.67656117724735	15.53917517058476	11.08757962846528
H	2.62314082720625	15.50252095239016	11.34565220829595
C	4.31144986189041	8.18986829728283	14.07885684681174
H	3.37135936815636	7.77312205640991	13.71040867036698
C	2.30985713851632	14.68902834537661	13.90626746829831
C	1.64324555980373	13.64169246323483	13.17061768004312
C	4.13596313835306	16.49196859562335	10.20490336036189
H	3.42638997780370	17.20825812544575	9.78736340357240
C	6.71017006174308	9.26860520477863	14.99909926502537
H	7.63453278865358	9.70764137059168	15.37903089264052
C	4.97964493548110	7.57430956223483	15.14498562727098
H	4.56431678037425	6.68346009548213	15.61936254361677
C	2.11383635004085	16.16705541338921	13.76137267678583
H	3.06235146947623	16.69551462891634	13.57668379258487
H	1.67072971472238	16.59054152389485	14.67931428666458
H	1.43629224333642	16.41405881993866	12.93252660351801
C	3.58157681527615	11.66108258655962	15.75583659653268
H	3.58984112836042	10.64899607456343	15.33469526972583
H	3.01723092338621	11.62411800589632	16.70577162028925
H	4.62376025244625	11.91323213049187	15.99862602858001
C	6.18396301654359	8.12388323293657	15.59808025445408
H	6.71052148874602	7.66448735273890	16.43799462637624
C	3.96119197469626	14.81723702801862	15.92748433455901
H	4.82076387435136	14.21610210308666	16.25397150416272
H	3.36429959773181	15.06391193851799	16.82811354696823
H	4.35593206491193	15.76005496209445	15.52276601974220
C	1.55142316545978	11.03854484229403	13.32953550274087
H	1.40274959551542	10.97051456401285	12.24164636164965
H	0.58195927042286	10.81344541188779	13.81368058140783
H	2.25163750959263	10.24466763738927	13.61942752165738
C	0.59863817538809	13.81063038573668	12.11381759495715
H	0.72122631804818	14.74995394836136	11.55356499138391
H	-0.42320135351064	13.82443949026823	12.53957132469791
H	0.63885161773648	12.99147387278839	11.38086274489048
H	9.68525271836241	12.04756704118894	12.03925876916626

1-π

C	3.61125486582820	9.03918688569993	27.68565513128886
C	3.83569963790186	8.87868373420748	29.08701205164057
H	4.35892737111890	9.63073639780870	29.68484927774780
C	3.33951778876598	7.66820746531041	29.73171538270757
C	2.01123064442944	7.16390603046133	29.44649065062213
H	1.37111885610258	6.82209476473519	30.26988569633945
C	1.52754999379959	7.17775317644029	28.17129466438196
C	4.17902427921395	10.15283487453821	26.91445660588487
C	5.02441339761459	11.12580525431114	27.49721257345247
H	5.25112062903747	11.06634353469987	28.56183789207276
C	5.59210805828843	12.14880232204174	26.73905450222963
H	6.24256599877326	12.87961647420594	27.22629102557377
C	5.34549844340157	12.24055611051254	25.36472125392829
H	5.79402174755969	13.03927165067001	24.77100295255508
C	4.50652497248837	11.29132287965869	24.76932659912789
H	4.29422308329745	11.34653506996670	23.69877312596449
C	3.92881866711998	10.27674669202870	25.53031800571930
C	6.54766619613959	7.46215079102878	27.18740790679346
C	6.73795837305055	7.48257915239320	28.60905806482385
C	6.11753747310611	6.30206654385060	29.15339893734285
C	5.54262332482801	5.53801189059696	28.06762681125098
C	5.81417722031901	6.26948349037433	26.85023331323779
C	7.03710614385524	8.48850287239565	26.21658359188551
H	8.05012209039953	8.24760598430484	25.84677669819766
H	7.07369096780055	9.48937141961007	26.66900135096448
C	7.46280776687605	8.53905577966933	29.38269506232281
H	8.53754908268238	8.30604903309117	29.49888790276883
H	7.04253638759369	8.65575111006754	30.39247800415420
H	7.38916909389704	9.51422521220043	28.88020554911778
C	6.10592904099172	5.90988662883733	30.59728703427114
H	7.00417208568400	5.32519869017604	30.86707633123483
H	5.22495570132331	5.29726937819093	30.83407650044078
H	6.07877557447794	6.79190017745350	31.25423151992198
C	4.88130900455148	4.20019045518585	28.17308792384076
H	5.60597610873259	3.36596765559566	28.09878201867071
H	4.13575358924854	4.06741353625465	27.37710731727004
H	4.34968992661270	4.09609969295551	29.12938847738430
C	5.45035460796757	5.83503312990096	25.46534088571024
H	6.26559421160988	5.25344051034710	24.99754909052807
H	5.23737000792554	6.69833934739815	24.81957089840732
H	4.54612710791980	5.21184322149256	25.47176895626531
H	6.37206990346448	8.56253381860202	25.34513433630705
C	0.15859846923210	6.84249591547721	27.82732610656442
C	-0.33036561042876	7.04136039754358	26.50864320510524
H	0.34767287327893	7.45727753802423	25.76133313959421
C	-1.63978230579314	6.70894145656353	26.19428100153755
H	-2.01830178088633	6.87010222160379	25.18163495944226
C	-1.90690740604016	5.99110774914719	28.45828744993659
H	-2.51660911748483	5.56411306885656	29.26518925950920
N	-0.65614129971411	6.31218111901965	28.79003554541147
Fe	4.69824576616723	7.38199706574192	28.15876673419968
C	-2.46629510269177	6.16476894236064	27.18654775284141
H	-3.50155532690195	5.88416064880012	26.98708225360933
P	2.81682056658736	7.58708804890620	26.89683759769819
H	3.69136504792863	7.52454772404499	30.75869674819384
H	3.26651580094814	9.54155526464030	25.06805637200694

VdW-π-L

P	0.49711555235886	10.61636542853112	26.83776075559199
P	2.16936279076416	8.60449430257576	27.60384033314439
C	3.44522299724362	9.78465068401888	28.20132369517420
C	4.07112283755185	9.43143034559252	29.42985968453436
H	4.91077633138880	10.00635606338555	29.83097961070587
C	3.61510570885541	8.22531789208598	30.08692908139276
C	2.19991346672340	7.90211025678621	30.20142623606057
H	1.85424001015765	7.42605767368927	31.12935495477637
C	1.32706604503570	8.11480211909985	29.18081744191446
C	3.88252965857899	10.89328807011530	27.36549741267833
C	4.64776674935856	11.96910245222644	27.86907133079094
H	4.89888000465057	12.00322604135567	28.92893241149860
C	5.07109273504993	12.97567681978939	27.00971693401019
H	5.66728294538504	13.80795113975535	27.39094458617448
C	4.71375097339717	12.91774478915427	25.65851997086862
H	5.01641890555527	13.69048545382692	24.95092266954224
C	3.93869914509011	11.83165682071324	25.24357803932552
H	3.61475441871584	11.74422314393263	24.20049010756221
N	3.54236137207733	10.84774512919366	26.05297971046353
C	6.02877319928328	8.07685539513139	26.96394175119096
C	6.32343172231325	7.44700217507229	28.22260524354126
C	5.47850646922049	6.28156891473190	28.34680085555718
C	4.66009013150021	6.18731109238386	27.17397400717873
C	4.99740781579732	7.30673793382676	26.31340132001462
C	6.69735200790049	9.29311086055484	26.40612630240128
H	7.61021115239678	9.03321894594030	25.84040526874349
H	6.98794019626113	9.99577209193131	27.20080126009962
C	7.33046615577773	7.90913763059800	29.22731796478942
H	8.31143217038343	7.41873690679997	29.08916449225793
H	6.99964254173955	7.69343222462345	30.25410110848010
H	7.49225748177251	8.99440776128242	29.15442853950052
C	5.47733317969230	5.32007876170581	29.49380735798895
H	6.20413071039328	4.50271790370325	29.33501552524084
H	4.48613987886918	4.86620224306927	29.62956408917092
H	5.74325948166598	5.81830674066527	30.43682089351860
C	3.67195874282299	5.10631830442801	26.86720175688858
H	4.14485441577168	4.25202751638427	26.34742266681351
H	2.86449174229678	5.48320110882488	26.22539827874690
H	3.20401122849227	4.72372243336558	27.78496306378821
C	4.40508685926055	7.59553639923325	24.97073646234446
H	4.99672903469775	7.14329971491825	24.15427691522955
H	4.34803654358461	8.67897939976458	24.79762055213735
H	3.37960525123744	7.20939077024882	24.89759223157736
H	6.02702405929022	9.83527529843775	25.72679339435221
C	-0.07684108570116	7.72432190879349	29.22287023451090
C	-0.74100222027560	7.31459642233350	28.04715360490012
H	-0.20613132073534	7.36722140256427	27.09733301563153
C	-2.05654249420576	6.86119934137657	28.07899631495702
H	-2.54171415077694	6.56261676908487	27.14782560215425
C	-2.12353944732911	7.21724678506520	30.46311207184397
H	-2.66478432914089	7.19567749479491	31.41243462176050
C	-0.80691602083796	7.67303747992098	30.43277666880154
H	-0.32864248573077	8.02171391719255	31.34894782047629
Fe	4.32336391909208	7.97448519765756	28.11788649659384
C	-2.76019697124184	6.80348288898467	29.28679356382442
H	-3.79507425609783	6.45709319756016	29.30970151838014
H	4.24546827154862	7.87266825803716	30.90921190171951
C	-0.66211839641078	9.97115691985447	25.63199573007212
C	-2.00203620201338	9.70769338182312	25.91442432849794

H	-2.62237570606283	9.28238964744869	25.11825935556124
C	-2.61807362991814	9.92023999969356	27.15215953587048
C	-1.92559061208095	10.39100148615935	28.26335984281686
H	-2.49185370983128	10.50445928578196	29.19197797638945
C	-0.56646966485557	10.71621891613624	28.26784943945103
C	0.10815622475899	11.12215196194840	29.50681632709908
C	-0.44169607009093	10.89769731727144	30.78992787985946
H	-1.41708592973719	10.42594070939499	30.89247322538149
C	0.30132593517683	11.21766155591457	31.91868001285393
H	-0.10376244962782	11.02191035352115	32.91402266171674
C	1.58031097081056	11.76211193341840	31.76509629929887
H	2.20552074988386	12.00925701115052	32.62393980503279
C	2.03846427944343	11.97584879022394	30.46320683211315
C	-0.12224476371229	9.71552741169307	24.28410213274723
H	-3.67393815726708	9.66910187596279	27.26153064770476
C	-0.94571608084070	9.67582113829348	23.13685265155387
C	-0.41831535887895	9.41771145100083	21.87316650613745
C	0.95459383472104	9.19653355072379	21.70996022938171
C	1.78690466116713	9.24693323488604	22.83157356349077
C	1.26233722700487	9.50346868375518	24.09859063086513
H	1.93801097872776	9.54792786022563	24.95620416381893
N	1.33770327948838	11.67715873632031	29.36967324267267
H	3.03045373753518	12.40475621000643	30.28798559974700
H	-2.01358854707542	9.87774411042299	23.23499538570116
H	-1.08194725031173	9.40053168241650	21.00548345817030
H	1.36814071713186	8.99544108067765	20.71977100038582
H	2.86032970393816	9.07674548705494	22.72726083229182

TS-π-L

P	-1.84025253592688	1.89966658445788	-0.64937669915608
P	-0.17810638971946	0.02296333809118	-0.32689675623801
C	1.22614304770461	1.01147888682122	0.30510774825981
C	1.71019996524247	0.95585298288477	1.64190424342553
H	2.55008962468559	1.57688714007989	1.95756408448759
C	1.19290392038820	0.00016364172709	2.55442386251500
C	-0.02949236931069	-0.70937949464310	2.36511963088646
H	-0.30070547574936	-1.39513510617964	3.17580212477697
C	-0.85692101134675	-0.66516340703832	1.25557985202312
C	1.82784734521874	1.91637540760485	-0.67433102914526
C	2.73641880820380	2.93789273984320	-0.31904458986509
H	2.99767886721995	3.09849585285796	0.72580635320839
C	3.27863208315214	3.75092574570667	-1.30625008560980
H	3.97999974730203	4.54397366172556	-1.03807721134293
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H	3.29164061594340	4.17988721710608	-3.44378539489234
C	1.97683023813809	2.54402839523621	-2.90460457059005
H	1.62168366687610	2.37013266916243	-3.92546299566279
N	1.45686762079382	1.74730217414327	-1.96709538662369
C	3.66372875932722	-1.13230121979826	-0.24752754483301
C	3.79676046181040	-1.57178722966353	1.12004458941577
C	2.82056623229272	-2.61102597676736	1.35200871369227
C	2.07123901356108	-2.79656507385008	0.14345057892906
C	2.59472973893957	-1.88432096751311	-0.85344081956950
C	4.50908720978601	-0.10738381070053	-0.93318187816255
H	5.42613585663187	-0.55725127103572	-1.35344355310999
H	4.81686825796444	0.69157684851898	-0.24333102124774
C	4.79695575530129	-1.06969752966020	2.11212288026164

H	5.71803722475090	-1.67986920620723	2.10984515831253
H	4.39252472425322	-1.08995685706595	3.13444886933246
H	5.08766240935270	-0.03301059448576	1.89077378812172
C	2.62548607183115	-3.36278015432289	2.63122765245574
H	3.25239359338121	-4.27197965353302	2.66529981347660
H	1.57957234117302	-3.67585018307939	2.75233852709372
H	2.89007578959846	-2.74686333737452	3.50220495755292
C	0.92754595983517	-3.74215219686597	-0.04739251789096
H	1.27295837597618	-4.73608053909739	-0.38450415436767
H	0.21900926430040	-3.35791618274989	-0.79211380838577
H	0.36182098604990	-3.88040459010008	0.88401902497657
C	2.12105724026222	-1.74512411687076	-2.26431400300757
H	2.77264199087238	-2.29803423503092	-2.96358710742642
H	2.09546247117041	-0.68954148645239	-2.57050843761744
H	1.09777954423565	-2.12478620069294	-2.37678645421374
H	3.96347369828061	0.36927055331820	-1.75798997398898
C	-2.04822082056521	-1.48918498846527	1.18964302966862
C	-2.61034337169049	-1.87853812080885	-0.05027795062624
H	-2.15814020820951	-1.51168533436097	-0.97296282516187
C	-3.72811571696103	-2.70560936736857	-0.11561301929010
H	-4.12955960897185	-2.97868196710248	-1.09399763624387
C	-3.83213684598372	-2.76335398823616	2.29022865128432
H	-4.32215213869709	-3.08157902129616	3.21402131307615
C	-2.71232964278108	-1.94262840916992	2.36132845086167
H	-2.35686895039074	-1.60808483207132	3.33733040086235
Fe	1.91794693866444	-0.84752349103311	0.77802635335870
C	-4.34763019462065	-3.16944161561181	1.04967778779078
H	-5.23315509722659	-3.80489009983582	0.99605425529605
H	1.70496598442521	-0.12354921570229	3.50988535898126
C	-3.04635403851182	1.20472181686447	-1.81275329167802
C	-4.26656452983946	0.67599250308431	-1.42311785253698
H	-4.91765846200895	0.26484855293403	-2.20264746022139
C	-4.71360527417937	0.56527011512823	-0.09365634090532
C	-3.96832594812503	1.00825672186765	0.99191378473848
H	-4.40959140102715	0.86728404880305	1.98251192119644
C	-2.70478650782430	1.60464393045225	0.91124874413548
C	-1.99192081366354	2.04454180018972	2.10166247149668
C	-2.37199797158421	1.69242125545472	3.42375553897772
H	-3.22173523902207	1.03061054852049	3.58985215964470
C	-1.63033653706320	2.15218143937866	4.49932405309679
H	-1.91114290962333	1.87022965835204	5.51687821053843
C	-0.50798856305367	2.96631325912040	4.26812921586939
H	0.10599084190963	3.34515795167522	5.08619841575707
C	-0.19256392496717	3.25389917764177	2.94055412040329
C	-2.68366446668895	1.22272615249953	-3.23764863841371
H	-5.67417573400061	0.08449034661940	0.09474754406395
C	-3.65744746336042	1.36082318611870	-4.25312631301453
C	-3.30895307358275	1.34224356924698	-5.60218990766841
C	-1.97084260719827	1.19192450928089	-5.98664286964511
C	-0.99251251803042	1.07007804637826	-4.99473894101357
C	-1.33662047826472	1.09046564159638	-3.64289129238327
H	-0.55361362600450	0.97974643931641	-2.88998168640168
N	-0.89332263953295	2.82231331224185	1.88967396794577
H	0.68620313802967	3.86543729666940	2.70317669355667
H	-4.70059813816776	1.51151466740943	-3.96966093096495
H	-4.08583531968528	1.45935145460788	-6.36161450297663
H	-1.69656217631557	1.17755908744389	-7.04330860287386
H	0.05554949889052	0.94187018295010	-5.27562919742235

2

Fe	10.21225277107162	22.22869978882484	10.63094430610991
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C	8.73218054493100	23.61855385968920	9.77896359991731
C	8.63325830377453	22.29124847807736	9.29763145640670
H	8.70968060544747	22.08962753262971	8.22847892943161
C	8.52679224012926	21.15366274607740	10.13368376178608
C	8.65214652063285	21.24658668462587	11.53984182121186
H	8.74007945166115	20.30577929780162	12.08754441004464
C	8.80026934894637	22.49115672241850	12.21436965672426
C	8.93329644774081	24.72215921658984	8.82082616399602
C	9.08585543145161	26.05196332221342	9.27564577854108
H	9.05463484811524	26.23943868563548	10.34952516837905
C	9.25479909512739	27.11324634129383	8.39038048209008
H	9.36568432023122	28.12437858493951	8.78687973824632
C	9.25283234640063	26.89671418943704	7.00947937689258
H	9.36944117632271	27.72994539282321	6.31412105415316
C	9.06702752781027	25.59269161941697	6.53387575033555
H	9.03428510708204	25.40149348641463	5.45883015105550
C	8.91536157205639	24.52834696204324	7.41925645497677
H	8.75093851563316	23.53494435097977	7.00666601286090
C	9.07053840795360	22.50389496568550	13.66133072530653
C	9.26405880986509	21.33842273903535	14.43791051161527
H	9.22423091557399	20.35210581970403	13.97813426800092
C	9.50716661033480	21.44873061872756	15.80238693584608
H	9.66350218640004	20.55099412687363	16.40434864932149
C	9.54052376745691	22.71850610927545	16.39176957799339
H	9.71737669099700	22.85024190181528	17.45997322078617
C	9.30928405101337	23.81763053449816	15.56308718854112
H	9.28312955837372	24.83089609704156	15.97656576579391
N	9.08574416150338	23.72519934893959	14.24981422064261
C	11.96382221311670	22.64999516665483	11.67175019960462
C	11.85434571735393	21.23996080932407	11.38362654275908
C	11.76598598038297	21.08582538893437	9.95436653932992
C	11.81432002948907	22.39785929279085	9.36284811562439
C	11.93804749192795	23.36339854664834	10.43109081399851
C	12.11659577631018	23.28234677325228	13.01630693345565
H	13.16629739926072	23.57462527733222	13.19005311076951
H	11.81938036766481	22.60165511759273	13.82390820361410
H	11.49100387833699	24.18136668329550	13.10422429034861
C	11.91475567046268	20.13042037271973	12.38470045949007
H	11.58292605482239	20.46885196651073	13.37419719331796
H	12.94499439414535	19.74750588748704	12.48969600762222
H	11.27852422966795	19.28391020684581	12.08922211522126
C	11.68579441205569	19.78985899239584	9.21102500000490
H	11.19200213236942	19.01387105508910	9.81212492936632
H	12.68951728052344	19.41483881263131	8.94458689162407
H	11.11596180040122	19.90068360285624	8.27825534319063
C	11.82895103312372	22.70850949731388	7.90107731512687
H	11.27798344518522	21.95438508973933	7.32227439520180
H	12.86334147240442	22.73178395954218	7.51572027009964
H	11.37023192108382	23.68272414878007	7.69161973506697
C	12.06598730059051	24.84320385676144	10.28640162296955
H	13.12485599933686	25.15096583747630	10.33699516797297
H	11.52191664381611	25.36369312842289	11.08692148960892
H	11.65405037156468	25.19596609621826	9.33351300505838
C	5.76031473847259	25.76931639411443	12.15731436626220
C	5.83103905166302	26.91050760419562	11.37846706707288
H	5.81847492310239	27.88243490239997	11.88541910286908

C	5.92756756994553	26.94094648390844	9.97104105223004
C	5.86719241108673	25.79683405381315	9.17960602511351
H	5.86367880238836	25.95586605071662	8.09673700985306
C	5.80529625145249	24.48153214934067	9.65139459196476
C	5.64017942925432	25.84120982270031	13.61281437491146
C	5.95635627529247	24.72324640739773	14.42467215274081
H	6.26913861065388	23.79652221429527	13.94343255710898
C	5.88917935432005	24.78041771756591	15.81497111892917
H	6.15841758105518	23.89612808496447	16.39724204544693
C	5.50188340306142	25.95694199877469	16.46390278788694
H	5.45259067950195	26.00438843287855	17.55351042856136
C	5.16529925560141	27.07305817223115	15.68339967370428
H	4.83869721544852	27.99738439281107	16.16709969760085
C	5.22609218123100	27.01453165757917	14.29455543929988
H	4.92739584096762	27.89011271546727	13.71624316823920
C	5.71897787900715	23.34716612478292	8.76465021682519
C	5.82541693096659	23.44758213698386	7.34336432663197
H	5.94589147249910	24.42135310563240	6.87110031921298
C	5.81378816022658	22.30542096748010	6.56269985015036
H	5.91806113439616	22.38892878311615	5.47761649445213
C	5.67289796489128	21.04464966051523	7.17107340596703
H	5.65643552583169	20.12063656192512	6.59155763914159
C	5.54532657648237	21.02943452750353	8.56340552928381
H	5.42355003471721	20.07405671439476	9.09043024927284
N	5.57506815290018	22.11109840712871	9.33991694908458
H	6.00307432620971	27.91049205424665	9.47622171251203
H	8.48649797216979	20.16775383299674	9.66867288427009

CO_2

O	-6.60332940005156	1.90052897740132	-0.00000000264688
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VdW-σ-CO_2

Fe	2.91506937427901	12.03761676589542	11.71132815048738
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N	3.58101392353033	13.84104903516326	11.43908047222587
C	6.97384006045567	11.18768610200906	14.06755982454969
H	7.62842545684727	10.45741996695445	14.55623618101538
C	4.69185285488964	14.35965477588063	12.11218145065662
C	4.95400152694683	15.73745226523233	12.11167264842955
H	5.81913485359461	16.10233045040087	12.66730357574632
C	7.29613567266747	12.54467393568061	14.23035921630320
C	6.59651928730910	13.58156191744265	13.60299593533825
H	6.92002652444875	14.61011190536132	13.79911359286915
C	5.75415859857014	9.22142107951128	13.12328098317932
C	4.14141257870896	16.61977018906468	11.40923073710652
H	4.34279337611113	17.69194285421748	11.41424537622335
C	5.92965125458595	10.67428815012657	13.29075367436407
C	1.05051977710566	10.98932335395474	11.24600178807244
C	5.50333157296352	13.36272850201147	12.76733416541198
C	1.74658988421250	10.36213155422557	12.32588957670813
C	1.90091119181636	11.33402280850994	13.38400474222862

C	5.32527428530807	8.69456298135441	11.88626712304251
H	5.05815094490507	9.37151911694905	11.06756449656322
C	2.86568241249067	14.71082415048875	10.67050766612572
H	2.13609236398676	14.23850113657486	10.02059737949864
C	5.20424020007035	7.31792064038975	11.70643573855699
H	4.87101184284879	6.93895608290193	10.73845198480673
C	1.32544436924973	12.56812927947231	12.93165456402186
C	0.79551016943479	12.34978271029655	11.60255177332506
C	3.08826165244912	16.07761320174674	10.65141791618134
H	2.46128665598992	16.70629876494466	10.01756232954228
C	6.02193914603173	8.31811686614762	14.17295062813469
H	6.31120977075130	8.70904197492446	15.15048013516069
C	5.48948482514096	6.43086039480131	12.75014660950437
H	5.38536688744098	5.35374543548549	12.60556280811654
C	1.26478887981874	13.85226976550800	13.69603597977122
H	2.07767461124135	13.91141481686829	14.43329471350814
H	0.30872769218668	13.96246314877646	14.23845027269546
H	1.36792594935871	14.71924684482256	13.02665086445770
C	2.10790719256539	8.91469132761268	12.38526270679506
H	2.50420731980277	8.57509377145833	11.41967654577394
H	1.22649211035141	8.29467672417743	12.63095517546906
H	2.87771052483301	8.71626716294510	13.14116515142021
C	5.89293058573302	6.94128307666253	13.98852471217716
H	6.09641890102428	6.26309506362679	14.82049197655864
C	2.47695132691017	11.06329137309089	14.73947466750421
H	3.27358617158084	10.30781736879777	14.69357077144267
H	1.70289524277102	10.69114422009256	15.43441880753673
H	2.91511985255239	11.97052953510036	15.17827121507038
C	0.52502915135889	10.29692591394056	10.02835285493803
H	0.47299142138064	10.98332128441680	9.17391258160363
H	-0.48947588754974	9.90089553105803	10.21881318528188
H	1.17454906987997	9.46176641535396	9.73991560655683
C	-0.04075989678452	13.29562421371610	10.80104085311612
H	0.07076762371514	14.33153038219108	11.14742259228973
H	-1.11211957380265	13.03446049382925	10.87616006351614
H	0.23405671082369	13.25987837825828	9.73619977226587
H	8.15253505360587	12.79729971192003	14.85825359188132
C	3.20091851853001	11.47585559730916	9.66862498558332
O	2.80957746600907	12.35079709671019	8.88345476598036
O	3.68264249928746	10.34064242437345	9.54261506235651

TS-σ-CO2

Fe	-0.49718521136388	0.69118464090412	-0.26414529953450
P	1.13854470183591	-0.53977611292608	-0.49746368646056
N	0.45092743437057	1.80029275998367	-1.51930426620480
C	3.31993290291312	-2.19470182124939	-0.33911590426194
H	3.76313794323342	-3.14936353085290	-0.03407265910560
C	1.79240843694679	1.60213566993688	-1.86715908135270
C	2.46747965307120	2.52832039114831	-2.67025331514226
H	3.51927457929676	2.34884076130426	-2.89732375639593
C	4.14240336443287	-1.29209626796975	-1.02736385618489
C	3.67956038816052	-0.07363186362813	-1.53533697195728
H	4.38980136175576	0.55463297663249	-2.08447375090246
C	1.18655977134097	-3.11162987100933	0.57785931435764
C	1.81300423500351	3.64005178481300	-3.19528443348794
H	2.34204446297256	4.35613009890647	-3.82523294186827
C	1.96014254589585	-2.02336047618367	-0.04914480985311

C	-1.30973551125895	0.03621988379673	1.56969608474623
C	2.36978426922292	0.37098924079153	-1.36370832894926
C	-0.60655067618633	1.27885434460138	1.77930034813482
C	-1.23483281932159	2.27268412462745	0.96837974526377
C	-0.07285057442954	-3.47111959651078	0.05584898595611
H	-0.45311075537625	-2.91850596193579	-0.80915692120890
C	-0.19296852553633	2.83612729848063	-2.13247988556071
H	-1.26790868301084	2.85987987038839	-1.97958332531031
C	-0.80141155792306	-4.51367815764939	0.62790517332397
H	-1.77297966620491	-4.78039652742913	0.20649987937261
C	-2.32908444273281	1.66186689309975	0.25674032372367
C	-2.36509002488708	0.27094670505321	0.63005283414118
C	0.43987041178136	3.76962777448572	-2.93629756781297
H	-0.15079891259065	4.57359044727612	-3.37725172048806
C	1.68234554904233	-3.82511609437339	1.68531680411797
H	2.64482109018478	-3.53689501856240	2.11339939500082
C	-0.30202381502390	-5.21338509595002	1.73219661032194
H	-0.88100870653248	-6.02248491689699	2.18184872564400
C	-3.32455579410074	2.33708777868992	-0.63167724987470
H	-3.07686386932608	3.39858317915003	-0.77972971260638
H	-4.33976327502274	2.29866570297354	-0.19929637986542
H	-3.35120159015558	1.83524048536542	-1.61291037807434
C	0.54437541971835	1.48228511923889	2.71542505293360
H	1.13178545230088	0.56030908669787	2.82358981712371
H	0.20687598824767	1.78249210433105	3.72523901159996
H	1.22799133225480	2.26143738048757	2.34958541010425
C	0.94570062072724	-4.86364441452023	2.25775556740760
H	1.34230371823344	-5.39466758621399	3.12607792288743
C	-0.84826280238523	3.71599429956680	0.91998735964102
H	0.19498237091940	3.85721725603096	1.23441446591797
H	-1.48523515068378	4.32163838151033	1.58766886096318
H	-0.94009454316783	4.13597803591509	-0.09221663570264
C	-1.08419987365704	-1.21487760054279	2.35723278220987
H	-1.47698308485021	-2.09806036375177	1.84177429167790
H	-1.58627506893313	-1.14571862468210	3.33910115506432
H	-0.01796910976802	-1.40041879201622	2.54451685680522
C	-3.41201447427355	-0.71144640757476	0.20991814800905
H	-3.68190549167174	-0.55612893158281	-0.84266884851722
H	-4.32283080945922	-0.61074435895732	0.82828233735307
H	-3.04949854470611	-1.74320506431044	0.31255179456719
H	5.18218479063719	-1.57298430839313	-1.20325040267385
C	-1.13158937659014	-0.30191754921172	-1.94780934038847
O	-2.10425781362463	0.15304401214593	-2.57086873018150
O	-0.40720323974578	-1.31239517344901	-2.27358689844305

3-σ

Fe	3.06224880227793	13.63376368863445	12.66633579472992
P	4.94417997565082	12.48778618024030	12.19039644091891
N	3.90823031315052	14.85062955239089	11.33300552702012
C	7.15483730206376	11.86800649548408	13.75274340719305
H	7.71307768007056	11.15668818613633	14.37562039354153
C	5.29238168967496	14.99924972658188	11.37824305124658
C	5.87743848021579	16.10838759194239	10.71261786295936
H	6.95763255864843	16.24172112526299	10.77845858906782
C	7.86287345357895	13.02365260857137	13.34140035306659
C	7.29099596545121	14.03545877092082	12.57028327362768

H	7.88984569594440	14.93687383399069	12.38248470808490
C	5.20094615236106	10.35875635312195	14.02819330663885
C	5.10151263895140	16.97179136314238	9.96312508401464
H	5.56350665377522	17.81459695776789	9.44408799546864
C	5.84320597444965	11.53438708613444	13.45015612012388
C	2.42078339400496	13.08474123651810	14.59824317225480
C	5.97945458812168	13.97952814459456	12.08924533937765
C	3.55145142847345	13.95850317301839	14.75023703738949
C	3.23533510665128	15.20042533054524	14.12721659403768
C	4.17762700289758	9.66916951901130	13.33115807648762
H	3.92670601465927	10.00194026460454	12.32205051203635
C	3.17996098423776	15.66137673543455	10.54834765529707
H	2.11407332562768	15.43727622731211	10.51549269642594
C	3.52309758471230	8.58207356504359	13.90336294486907
H	2.73519896340214	8.07721530490018	13.33957851614477
C	1.88541189471500	15.13589737282319	13.61669981555304
C	1.38909254336086	13.82778256173248	13.90924656761846
C	3.71778880798917	16.73412951285123	9.84572633408725
H	3.07374745767908	17.36038481535809	9.22991610680531
C	5.53225134699276	9.88559872305070	15.32063548478155
H	6.28925506327262	10.41868187577341	15.89934868019718
C	3.86374569150206	8.13035374168871	15.18498698676991
H	3.34426546911585	7.28061474423624	15.63195839970229
C	1.11662923914606	16.27263632662169	13.02429012257877
H	1.77039349092114	16.95004442080966	12.45742405624767
H	0.62096019715547	16.87611464722479	13.80663405443931
H	0.33339157879523	15.91671851356124	12.33955708047649
C	4.80334286907281	13.68251474648200	15.51654761159176
H	4.90227014695567	12.61695107193268	15.74897511345753
H	4.79484027076293	14.24209309985050	16.46817922289731
H	5.69997534696981	13.97826857137563	14.95446495283383
C	4.87975596250675	8.79050081740472	15.88561614596367
H	5.15015584080190	8.46294544053321	16.89265829941275
C	4.14557142763844	16.38376721304843	14.05861761977828
H	5.19437096831770	16.06506671012024	13.99377908799813
H	4.03784208467519	17.01717063437719	14.95601230697821
H	3.93329390307226	17.01031679205638	13.18132182023270
C	2.23700056914072	11.74072916169182	15.22641242114314
H	1.66755032562286	11.06385898990139	14.57697521841057
H	1.68912628885111	11.83039576851574	16.18184095212951
H	3.19584020654315	11.25225773034084	15.43168992406067
C	-0.00080431825000	13.33607852588430	13.64940136176853
H	-0.43920885637432	13.81350258707559	12.76242163899170
H	-0.65812743785497	13.55223955404557	14.50910531151301
H	-0.01643558700861	12.25153496712694	13.48184018290999
H	8.89776174758339	13.13403090910028	13.67063553012828
C	2.19652886969382	12.60992434683899	11.57714154353527
O	4.92752045555454	11.70069550165734	10.88475990118654
O	1.52795440602684	11.92449058360323	10.89960569179834

VdW-π-CO_2

Fe	8.21324871075741	15.39579092730344	2.44799070725311
P	6.15870594528159	15.53124944418308	3.38179717801195
N	5.66337265380671	18.68303068680170	6.04985374551191
C	5.37199293708823	17.56371648694024	5.32031950120531
C	7.39456167688561	14.29378654294266	3.94813854390813
C	8.66253610118560	14.86519517568269	4.27848573335317
H	9.52693208906475	14.25018285615237	4.54284829632373
C	8.79538409688032	16.31503818978434	4.24710000119612

C	7.77057122619762	17.16313943133458	4.82093955446203
H	8.05868560644397	18.01154116078325	5.45430025854195
C	6.45043404612386	16.86709520222377	4.64250349131202
C	9.44598947631420	16.37673568550193	1.11810737229672
C	9.90837764815151	15.02122483823605	1.28870139642626
C	8.83407667044040	14.13999527945552	0.92859743836150
C	7.70725194551038	14.95035259099240	0.52874242457481
C	8.09200279438448	16.34387278834999	0.64007504492593
C	10.25221568252530	17.61259563421427	1.36973673747905
H	10.98852244235395	17.45500489944506	2.17050747861228
H	10.80719844495043	17.92432554358539	0.46603086728387
H	9.60919189573338	18.44931358825163	1.67526329319270
C	11.26387441821921	14.61140446409650	1.77138877636149
H	11.23017309930708	13.62190465488152	2.25001761086077
H	12.00090924747056	14.55557947750771	0.94902440768869
H	11.65694198082586	15.32197187688133	2.51377754727984
C	8.87833851631261	12.64495726166723	0.93133009054407
H	7.89052615738573	12.21518759779928	1.14617858271414
H	9.21616463136558	12.24471394220894	-0.04183228924401
H	9.56101464698289	12.26410926661003	1.70422061529175
C	6.39435504417096	14.43687203653835	0.02656413386393
H	5.57152718084803	15.10513286544642	0.31660977499422
H	6.38495333193445	14.34066168242148	-1.07469925915390
H	6.17111532982112	13.44748294473111	0.45000151582308
C	7.25368117267027	17.52434001313465	0.26226971010291
H	7.49478536492524	18.39787358069686	0.88392799693982
H	7.39788672956007	17.81351819738133	-0.79644541426853
H	6.18674106211096	17.30871946779488	0.40908344816180
C	4.03268894165827	17.10359956969381	5.21967007574792
H	3.83464145079649	16.20778310458543	4.62926763476776
C	3.01405943368218	17.78257558471170	5.87145754377966
H	1.98450628539934	17.42232430928397	5.80411234642605
C	3.32129284859198	18.93033612737707	6.61431826214974
H	2.55462454124975	19.49948112805925	7.14223212043469
C	4.66388601686235	19.32423655838865	6.65630182143519
H	4.95012817991247	20.21920396115014	7.22376129108510
C	7.17387946956917	12.84461020504298	3.86361407299068
C	8.14073634190495	11.90425022301838	4.28470372843340
H	9.07390164855380	12.25726159189223	4.72423156465710
C	7.93064531370477	10.53167069933266	4.14670022693215
H	8.70344660098011	9.83464452133185	4.48034772761041
C	6.74669977121450	10.04363300825196	3.58627752387055
H	6.58433100606161	8.96978216748255	3.47667994229877
C	5.76669262261597	10.96002968897164	3.18223986530764
H	4.82801119396161	10.60082807328079	2.75350167968148
C	5.97307015078134	12.32880589226570	3.32775803876490
H	5.20342628425424	13.04323348229278	3.02769802285861
H	9.82352139730059	16.68064322225909	4.33861745866367
O	7.38261720536468	14.67688085597441	7.30016100379112
O	5.21802973894519	14.17086383532841	6.56215648121860
C	6.30826155264433	14.43713990806245	6.89818725490211

TS-π-CO_2

Fe	0.79670071538316	0.01363206184289	-0.35012124231664
P	-1.30882085468482	0.06836820215528	0.57259868252842
N	-0.88445350799970	3.59287339157328	2.59286288090859
C	-1.52318644707243	2.46417188149576	2.11606683105039
C	-0.18264451841186	-1.31337798520023	0.89949004555332
C	1.14501678172539	-1.02123097141445	1.35057175255440

H	1.87447468851811	-1.82283705028734	1.48460944392848
C	1.56542829553060	0.32595386099750	1.56622082603012
C	0.69108988054554	1.43183171193418	1.60865089252885
H	1.14946104272063	2.42250759013272	1.71980641420759
C	-0.73035436357867	1.35339361722305	1.71535026164621
C	1.40966147562153	1.46747412181189	-1.69051944554577
C	2.44809917236379	0.47391376472313	-1.50446222386920
C	1.92774518289239	-0.80359950904994	-1.90686744691515
C	0.55973679951466	-0.61063659845339	-2.31027997311843
C	0.25107724010922	0.79817826024688	-2.19335509138705
C	1.53290665053038	2.93884036310102	-1.44681373560877
H	2.29800956604064	3.15579416345424	-0.68952746050326
H	1.81376640269623	3.47901597715106	-2.36989990469263
H	0.58787534184030	3.36256049866645	-1.08176058543732
C	3.84209647744093	0.74419352010321	-1.03371925814582
H	4.26303743630457	-0.12692310136152	-0.51061021923073
H	4.51846181420612	0.98408185466404	-1.87367632440188
H	3.87160525409873	1.59334862161483	-0.33620265331519
C	2.69792345619854	-2.08520715172896	-1.97711138809506
H	2.02850540826095	-2.95362799673464	-1.92295571760917
H	3.26833519444935	-2.16442047621018	-2.92060446093089
H	3.41972198335663	-2.16843334328070	-1.15108583286617
C	-0.37612717812908	-1.66538266325988	-2.80894731324272
H	-1.40912811740590	-1.45265099928308	-2.49963016911467
H	-0.36265423136718	-1.73339906910709	-3.91129746268530
H	-0.11958152062619	-2.65470673289943	-2.40616414986626
C	-1.03430483879538	1.45202094633795	-2.59232345900941
H	-1.23958866876389	2.33752905907884	-1.97594896409550
H	-1.00496231616927	1.77244913680255	-3.64964356091818
H	-1.88281893692428	0.76733500187608	-2.46641844288533
C	-2.95397862696901	2.44372306910137	2.03247968020750
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3-π

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H	10.08890774139760	15.33737036028270	5.03512113423429

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Supporting Information

Chapter 6

Phosphorus-Analogues of [Ni(bpy)$_2$]: Synthesis and Application in Carbon-Halogen Bond Activation

S1 Experimental Section

S1.1 Determination of consumption of PhX (X = Br, I) *via* GC-FID

General procedure: **1** (0.042 mmol, 30 mg) was dissolved in benzene (0.5 mL) and PhX (X = Br, I; 1 or 2 equiv.; 0.042 mmol or 0.084 mmol) and the internal standard *n*-pentadecane (0.072 mmol, 20 µL) were added with a Hamilton syringe and the mixture was heated to 60 °C overnight. Control reactions in the absence of **1** were also performed in parallel. After cooling down to room temperature, the reaction mixtures were layered with *n*-hexane (1 mL) in order to precipitate compound [**1**]Br (for PhBr) or **3** (for PhI) overnight. The neon orange-pink solution was separated from the precipitated solid and quenched with $NH_4Cl_{(aq)}$ in order to remove leftover [Ni] particles. The organic solutions were filtered through Whatman filters (to remove moisture) and directly taken for GC-FID analysis.

Table S1 Amounts of substrates used for the determination of the consumption of phenyl halides.

Entry	equivalents of PhX	**1** / mg	PhBr / µL	PhI / µL
1	1	0	4.5	-
2	2	0	9	-
3	1	30	4.5	-
4	2	30	9	-
5	1	0	-	5
6	2	0	-	10
7	1	30	-	5
8	2	30	-	10

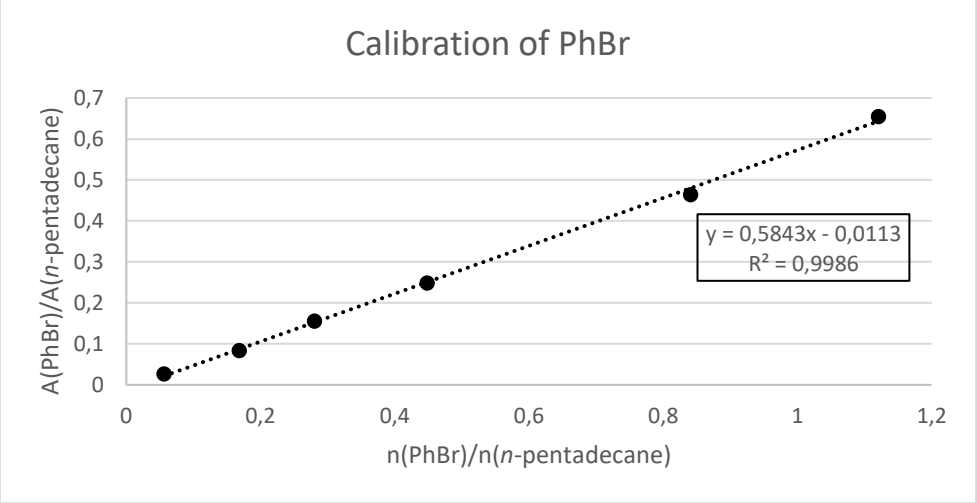

Figure S1 Calibration curve for bromobenzene.

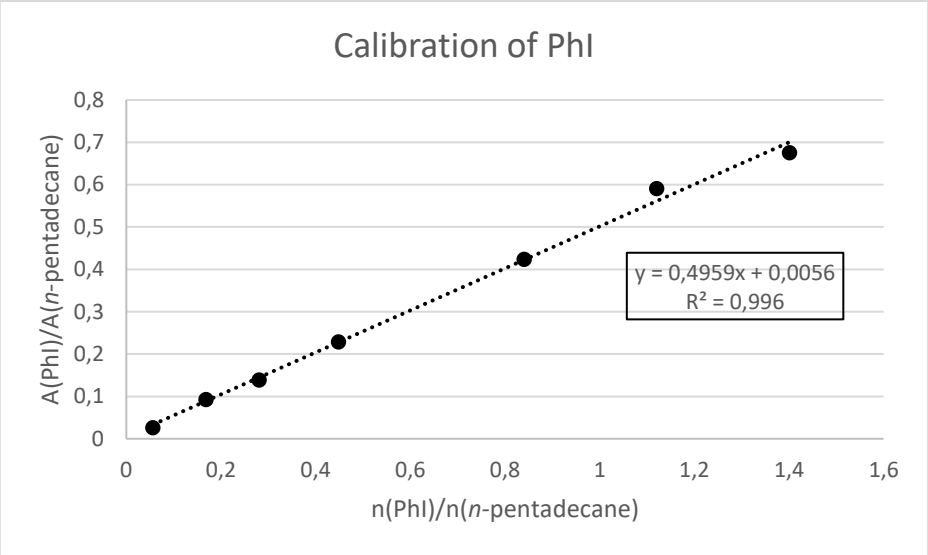

Figure S2 Calibration curve for iodobenzene.

Table S2 Conversions of PhX (X = Br, I) during reactions with **1**.

Entry	equivalents of PhX	Conversion [%]
1	1	0
2	2	0
3	1	69.9
4	2	39.6
5	1	0
6	2	0
7	1	99
8	2	80.1

S2 NMR Spectra

S2.1 NMR spectra of compound 1

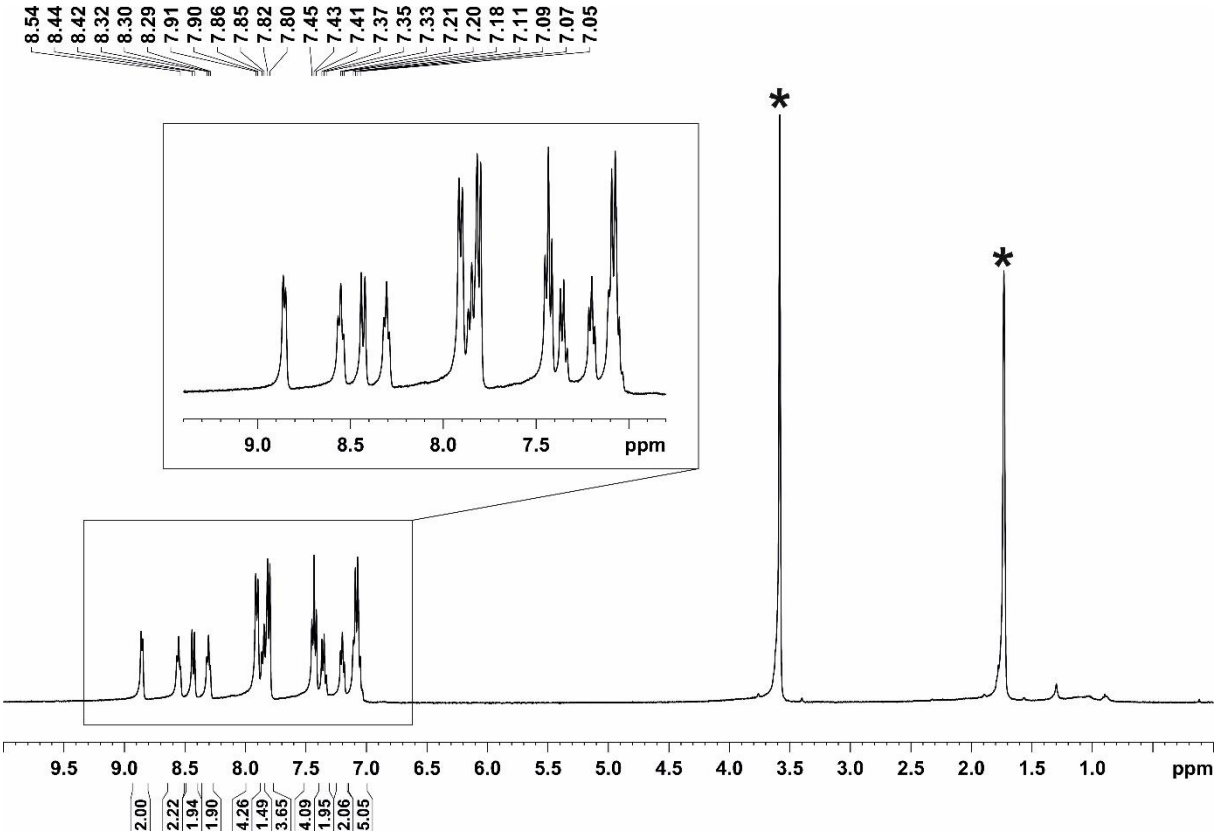

Figure S3 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **1**; * [D_8]THF.

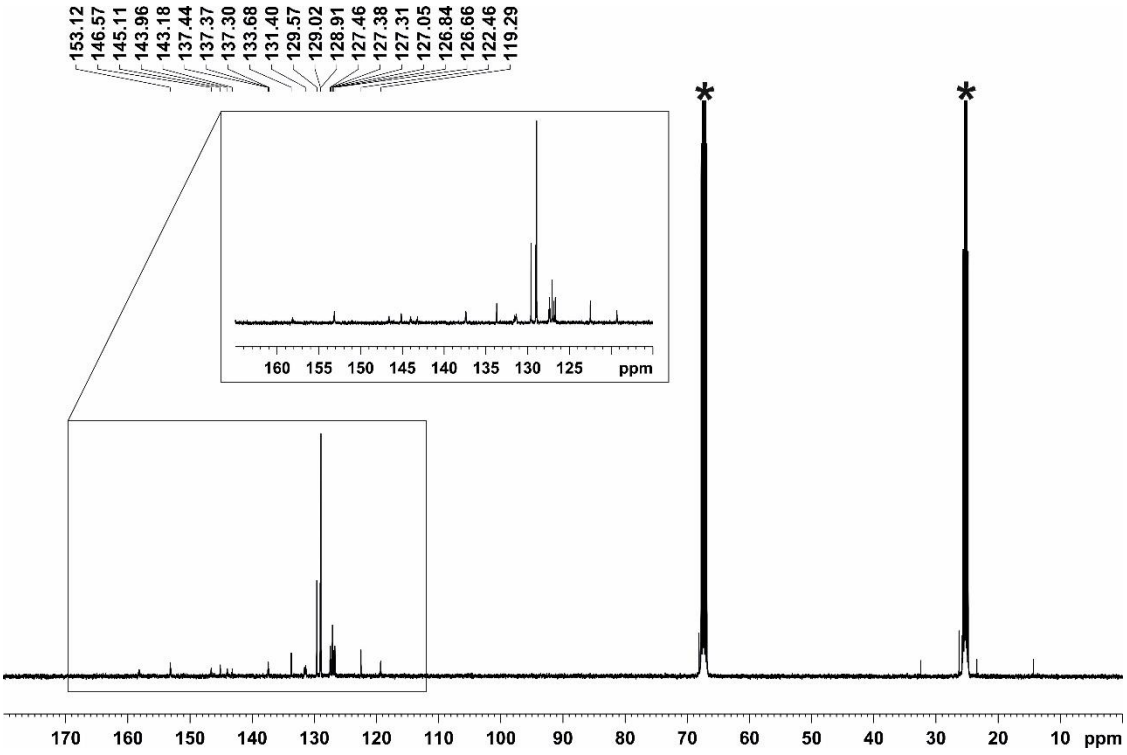

Figure S4 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **1**; *[D_8]THF.

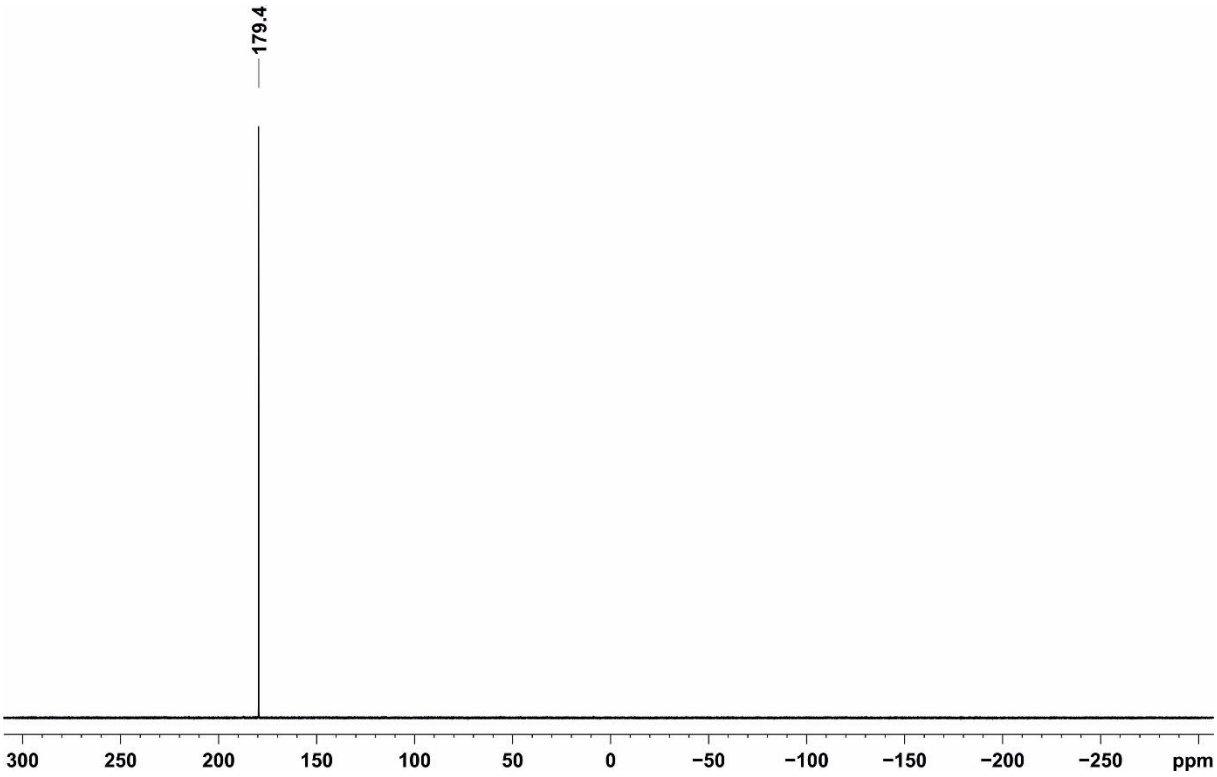

Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **1**.

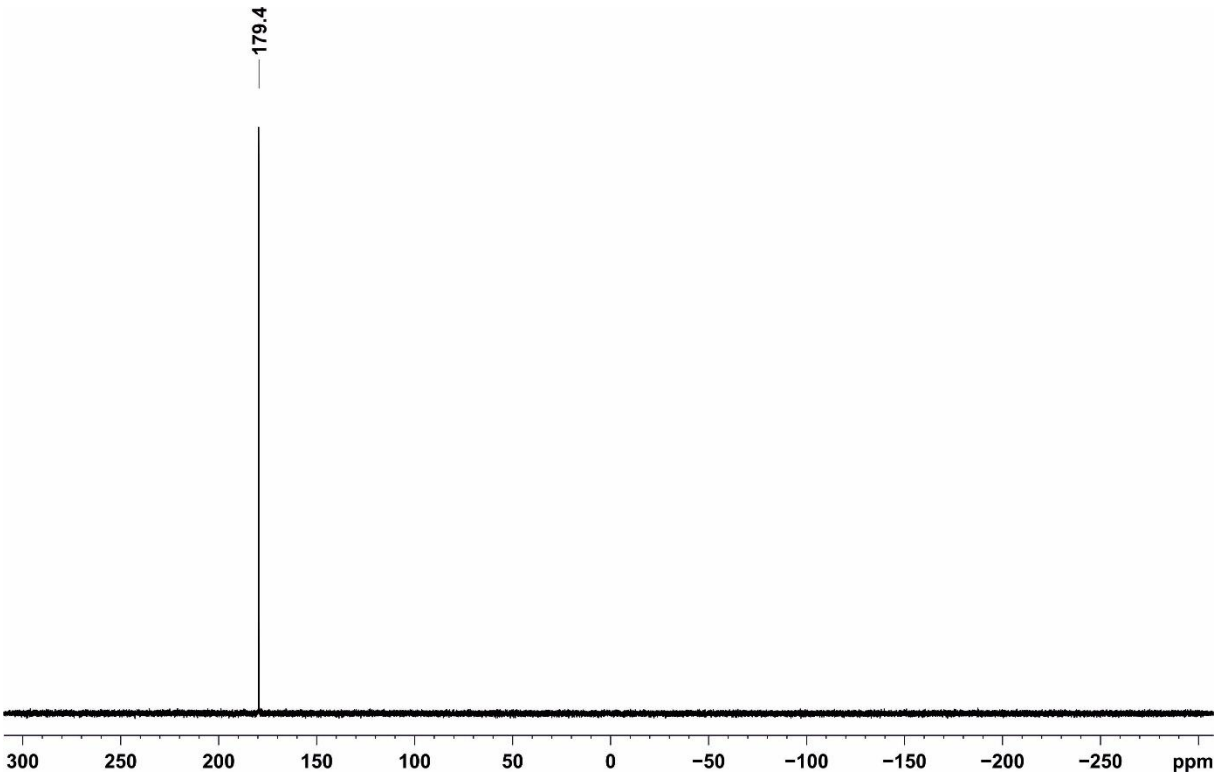

Figure S6 ^{31}P NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **1**.

S2.2 NMR spectra of compound 2

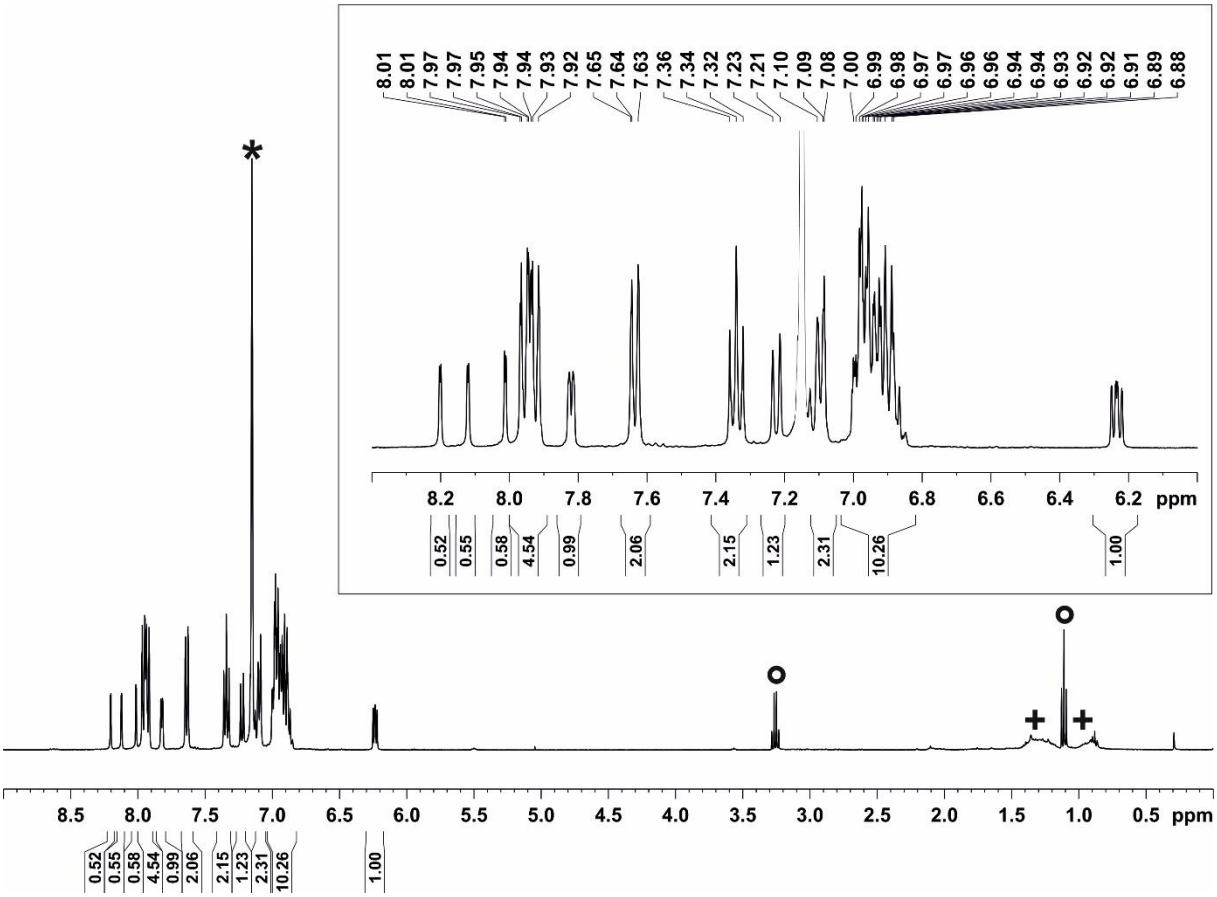

Figure S7 ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **2**; * C_6D_6, ° diethyl ether, + *n*-hexane.

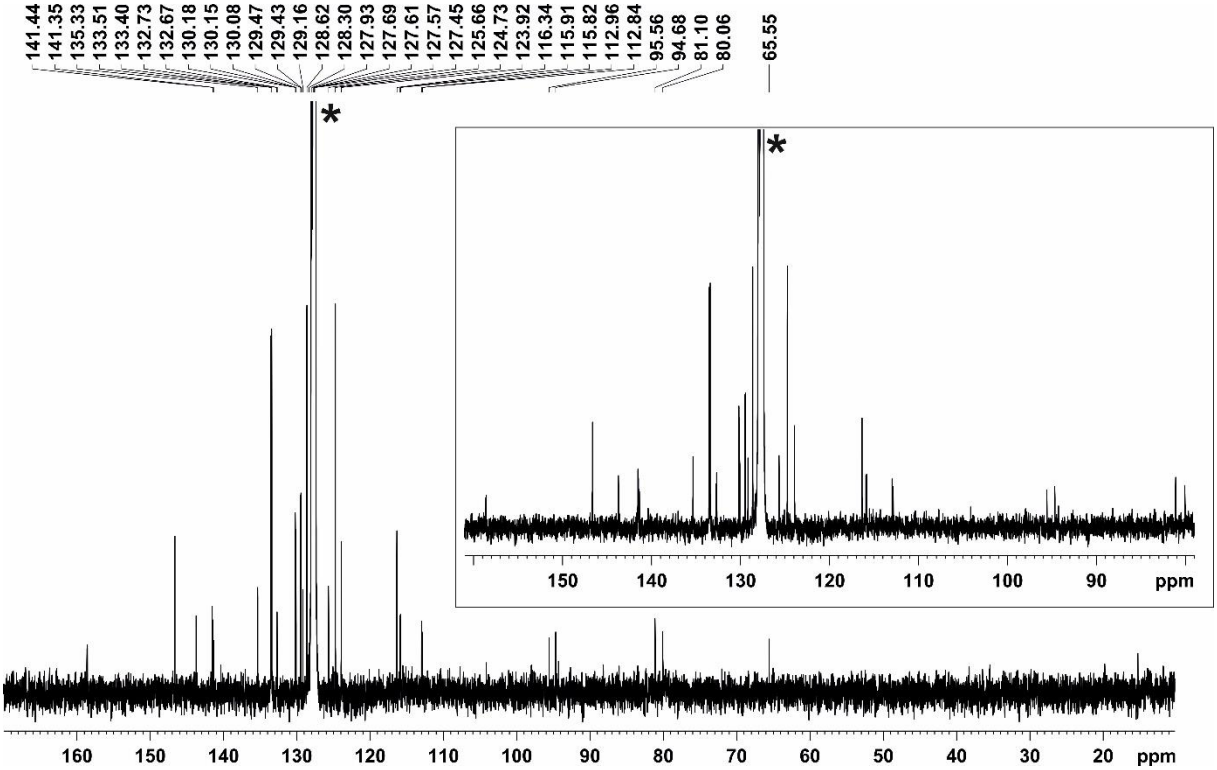

Figure S8 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **2**; * C_6D_6.

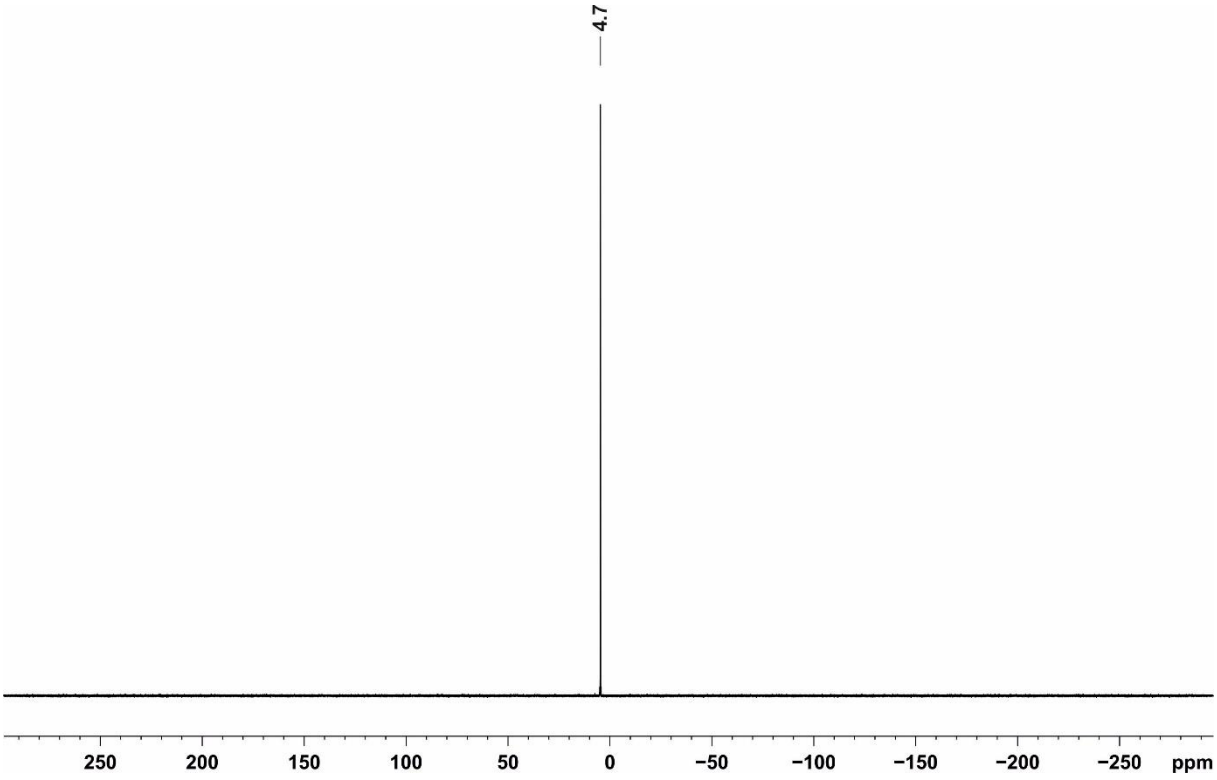

Figure S9 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **2**.

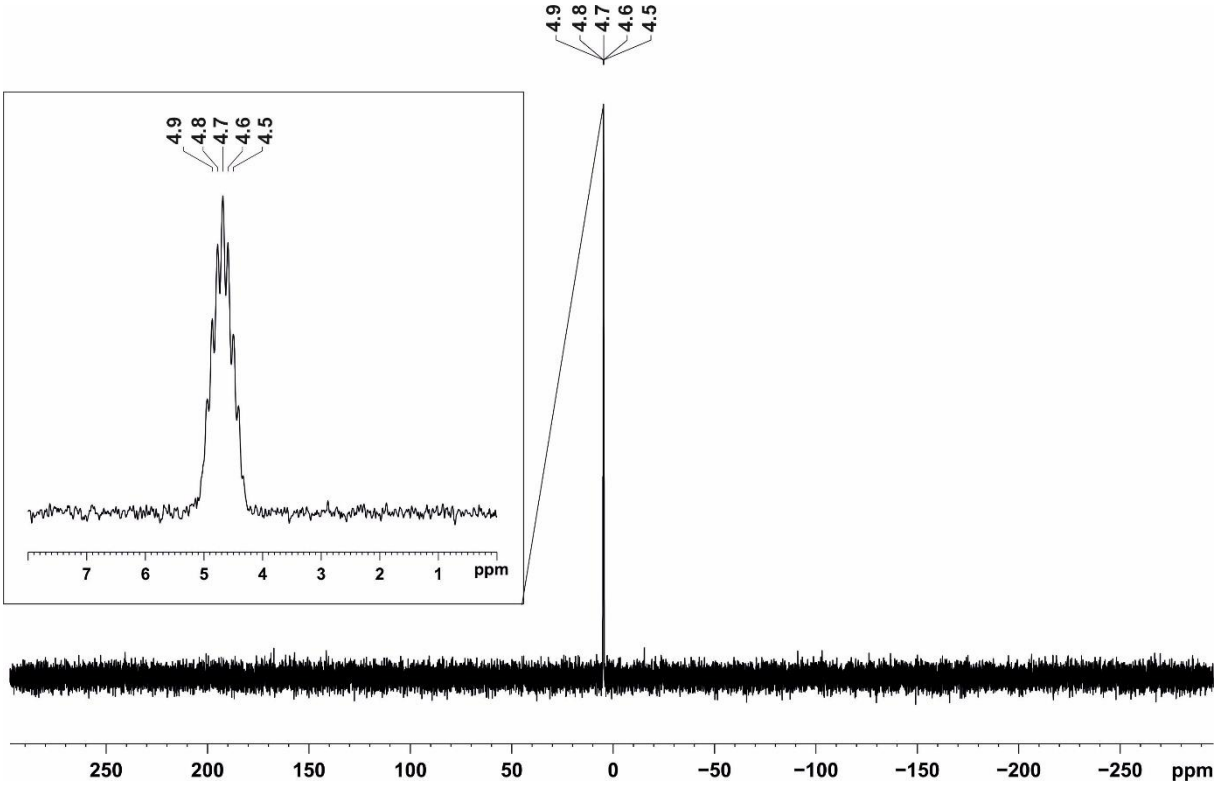

Figure S10 ^{31}P NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **2**.

S.2.3 $^{31}P\{^1H\}$ NMR spectrum of the reaction of D with one equivalent of L

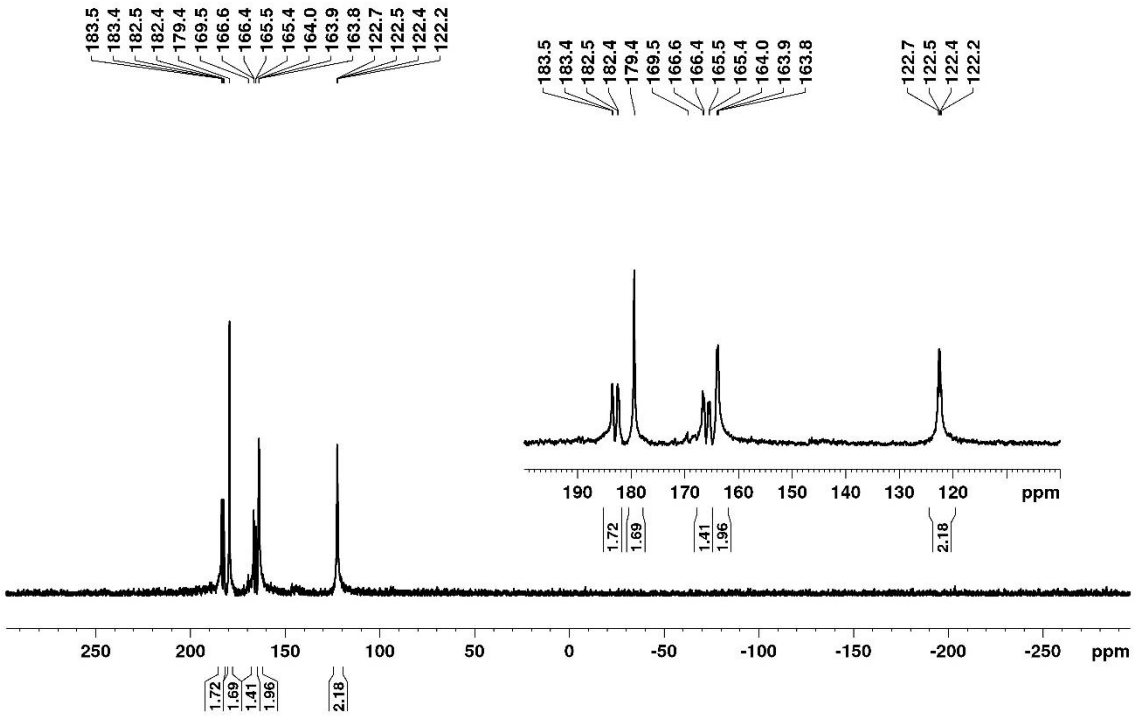

Figure S11 $^{31}P\{^1H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(IPr)Ni(H_2C=CHSiMe_3)$_2$] **D** with one equivalent of **L**.

3 UV-vis Spectra

S3.1 UV-vis spectrum of 1

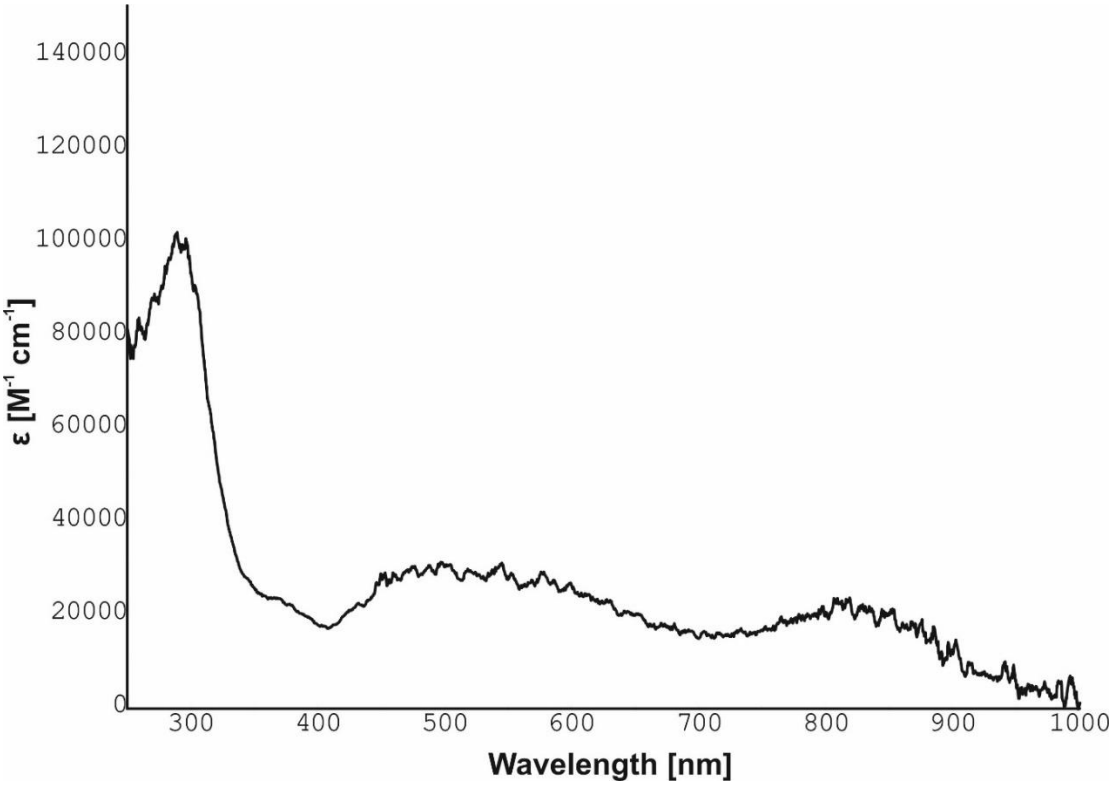

Figure S12 UV/vis spectrum of **1** in THF.

S3.2 UV-vis spectrum of [1]BF$_4$

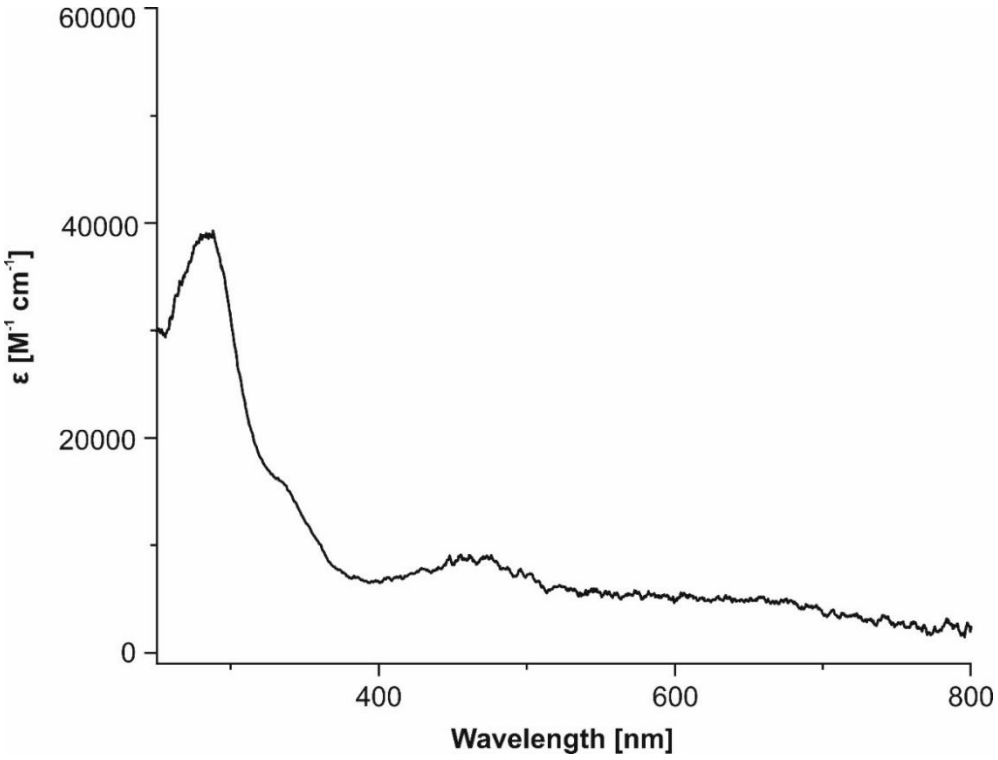

Figure S13 UV-Vis spectrum of [**1**]BF$_4$ in THF.

S3.3 UV-vis spectrum of [1(THF)]PF$_6$

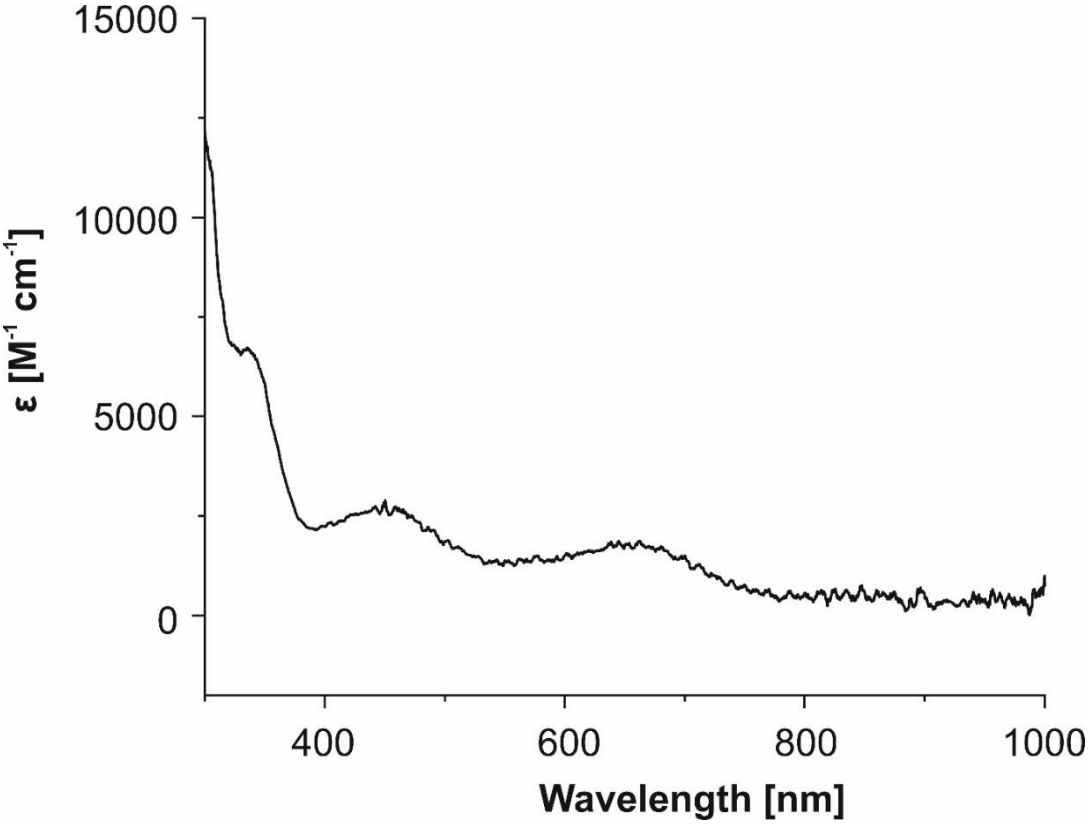

Figure S14 UV-Vis spectrum of [**1**(THF)]PF_6 in toluene.

S3.4 UV-vis spectrum of [1_2](BAr$^F{}_4$)$_2$

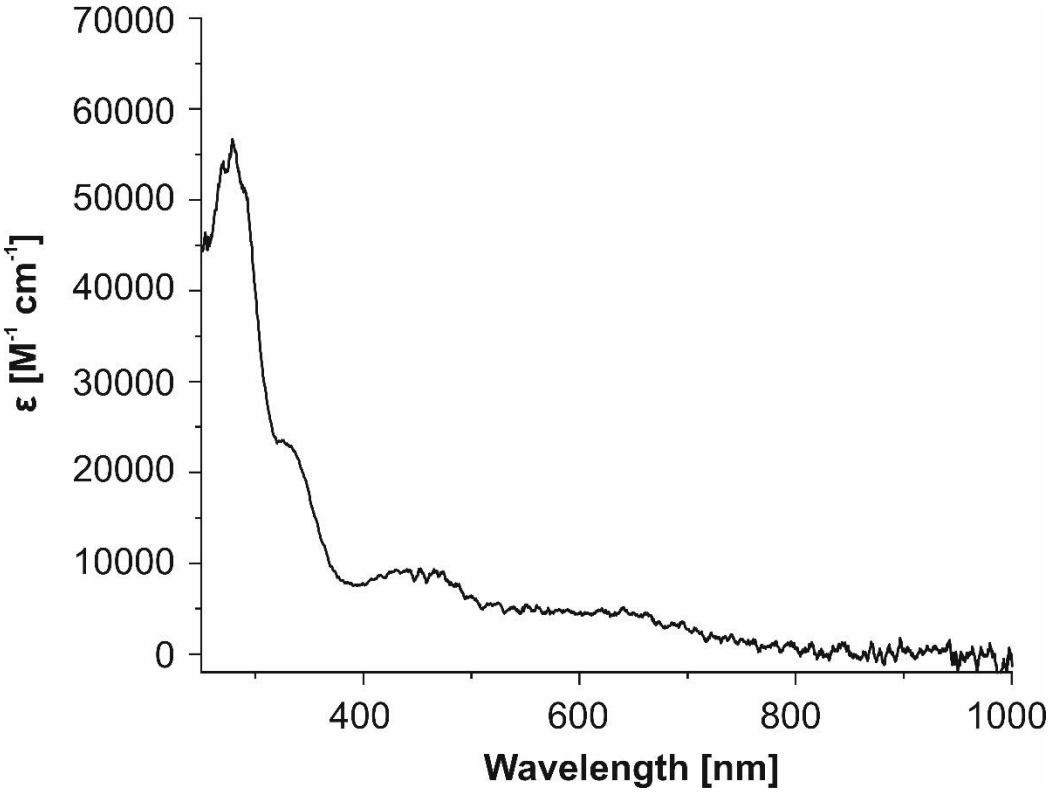

Figure S15 UV-Vis spectrum of [$\mathbf{1}_2$](BAr$^F{}_4$)$_2$ in diethyl ether.

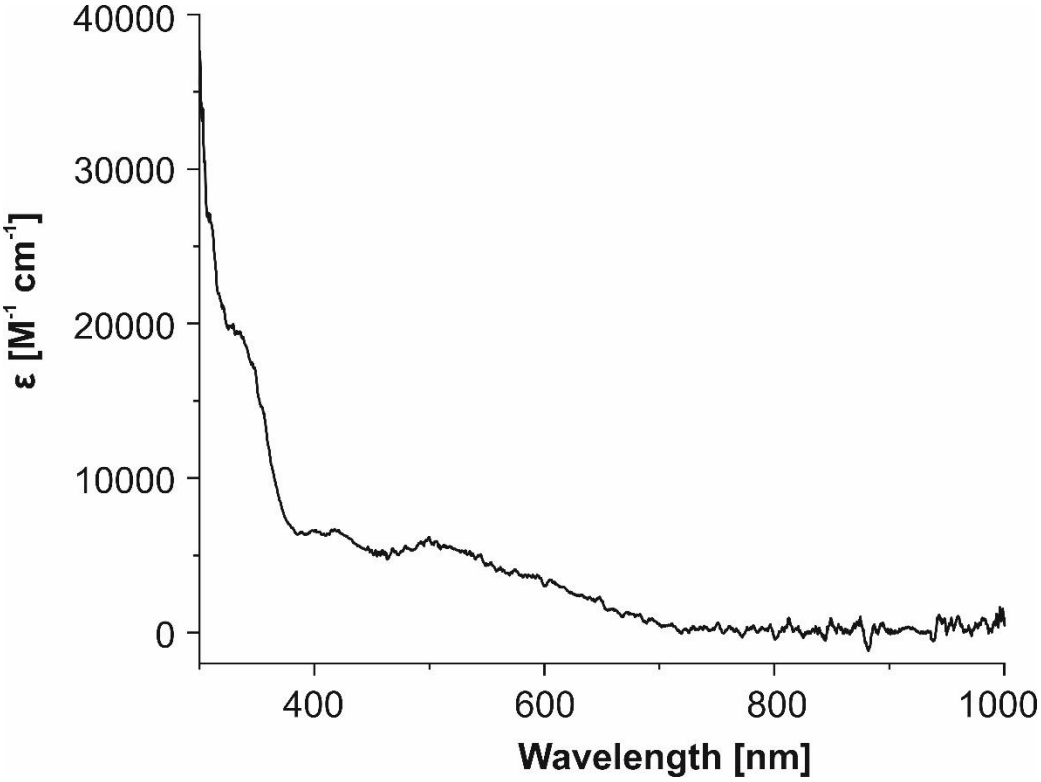

Figure S16 UV-Vis spectrum of [**1**$_2$](BAr$^F{}_4$)$_2$ in toluene.

S3.5 UV-vis spectrum of 2

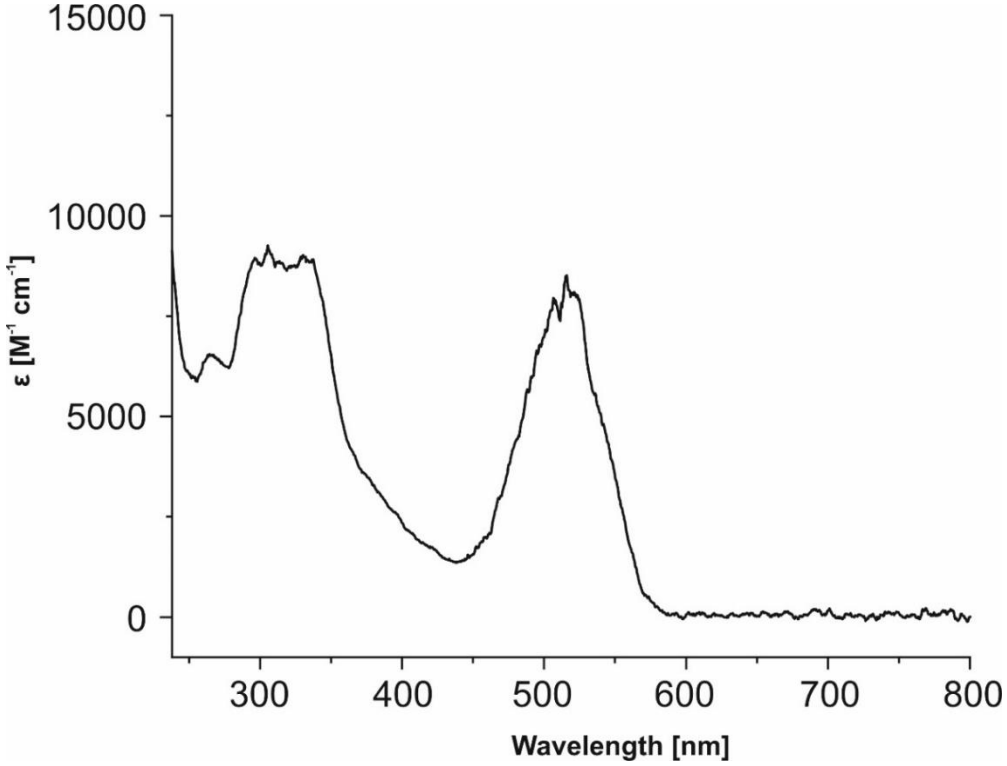

Figure S17 UV-Vis spectrum of **2** in *n*-hexane.

S3.6 UV-vis spectrum of [1]Br

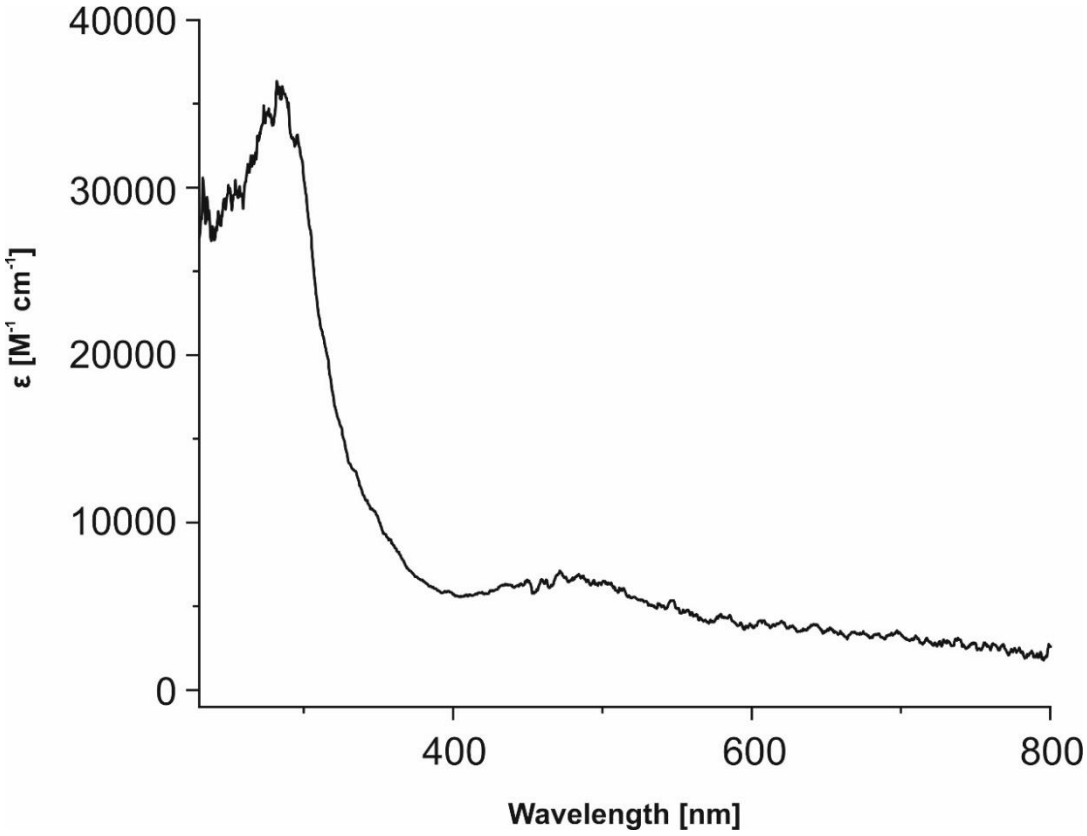

Figure S18 UV-Vis spectrum of [**1**]Br in THF.

S3.7 UV-vis spectrum of 3

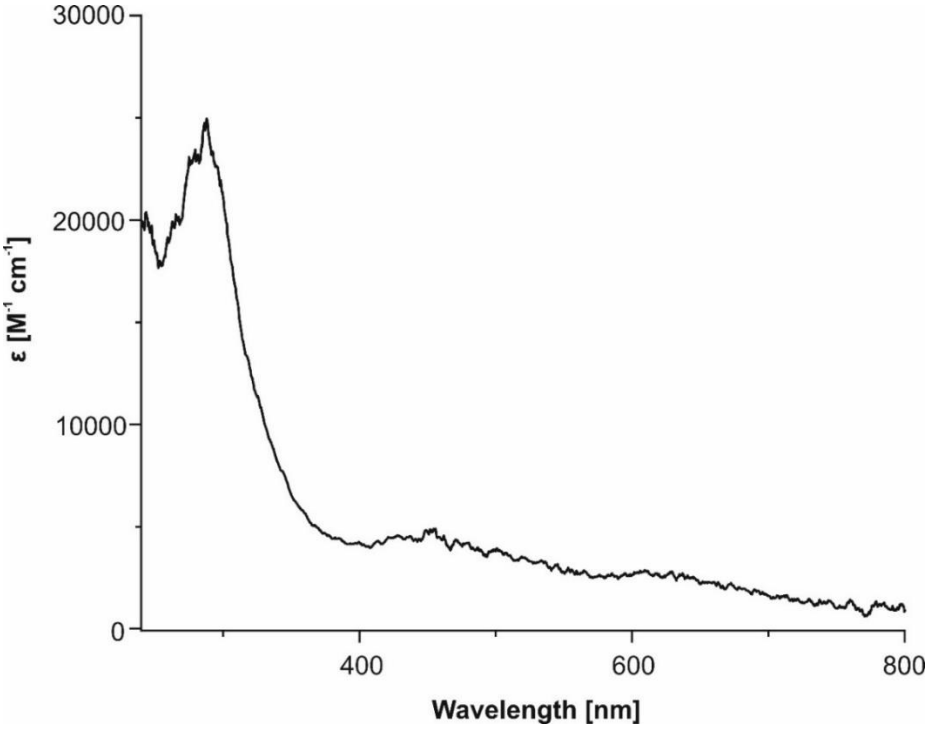

Figure S19 UV-Vis spectrum of **3** in THF.

S4 EPR Spectra

S4.1 EPR spectrum of [1]BF_4

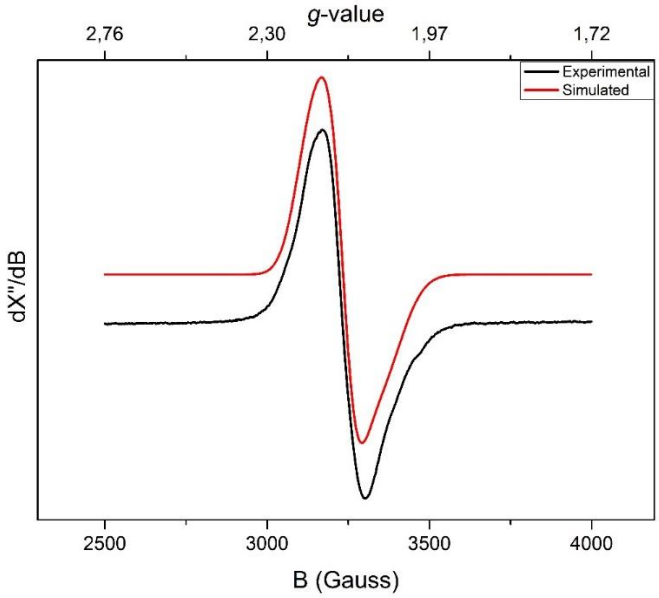

Figure S20 Experimental and simulated EPR spectra of [**1**]BF_4 recorded at 20 K in a toluene glass; simulation parameters: g_{11} = 2.195, g_{22} = 2.127, g_{33} = 2.060, W_{11} = 60, W_{22} = 45, W_{33} = 80; experimental conditions: microwave frequency 9.645282 GHz; power 6.325 mW; modulation amplitude 4.000 G.

S4.2 EPR spectrum of [1(THF)]PF_6

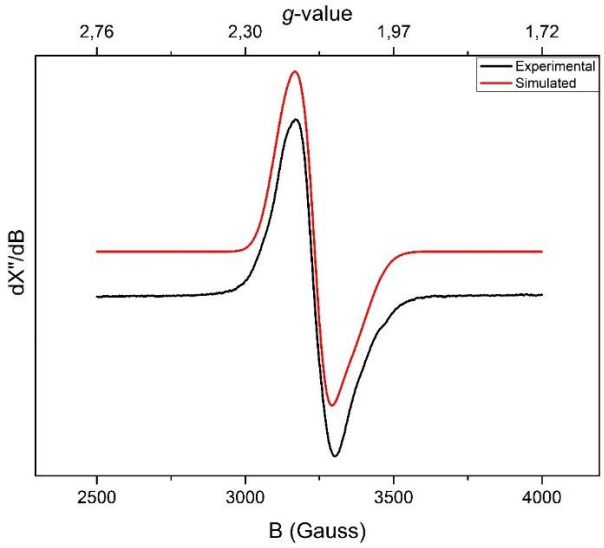

Figure S21 Experimental and simulated EPR spectra of [**1**(THF)]PF_6 recorded at 40 K in a toluene glass; simulation parameters: g_{11} = 2.200, g_{22} = 2.129, g_{33} = 2.035. W_{11} = 50, W_{22} = 28, W_{33} = 70. $A^{P1}{}_{11} = A^{P2}{}_{11}$ = 150 MHz, $A^{P1}{}_{22} = A^{P2}{}_{22}$ = 135 MHz, $A^{P1}{}_{33} = A^{P2}{}_{33}$ = 150 MHz; experimental conditions: microwave frequency 9.643394 GHz; power 6.325 mW; modulation amplitude 4.000 G.

S4.3 EPR spectrum of [$\mathbf{1}_2$](BAr$^F{}_4$)$_2$

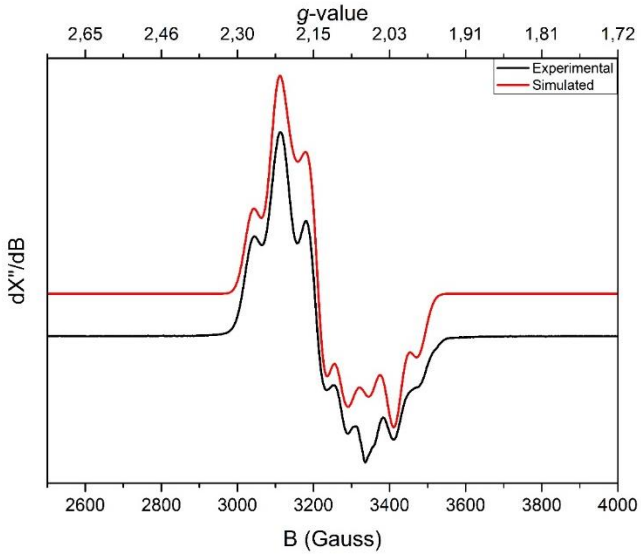

Figure S22 Experimental and simulated EPR spectra of [$\mathbf{1}_2$](BAr$^F{}_4$)$_2$ recorded at 30 K in a toluene glass; simulation parameters: g_{11} = 2.2170, g_{22} = 2.1450, g_{33} = 2.0195, W_{11} = 25, W_{22} = 25, W_{33} = 25, $A^{P1}{}_{11}$ = $A^{P2}{}_{11}$ = 205 MHz, $A^{P1}{}_{22}$ = $A^{P2}{}_{22}$ = 170 MHz, $A^{P1}{}_{33}$ = $A^{P2}{}_{33}$ = 175 MHz; experimental conditions: microwave frequency 9.644919 GHz; power 2.000 mW; modulation amplitude 2.000 G.

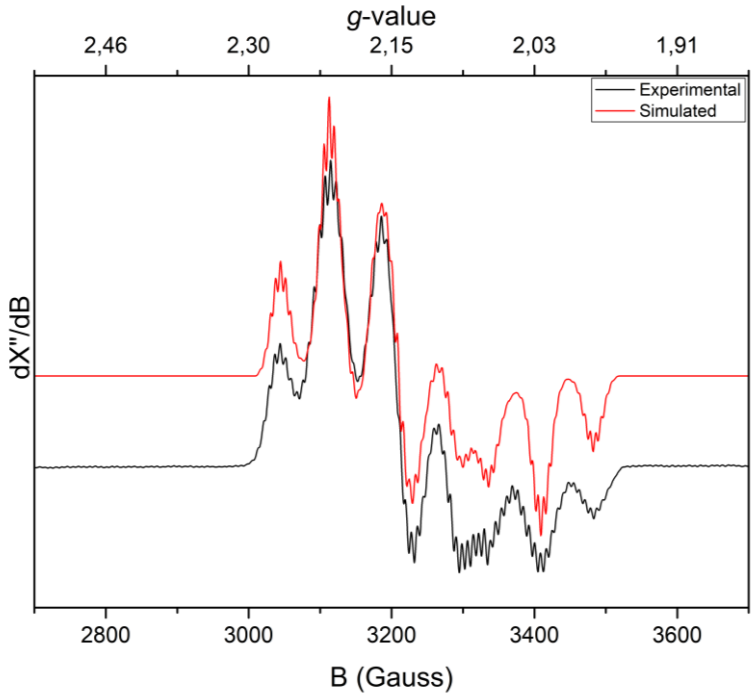

Figure S23 Experimental and simulated EPR spectra of [$\mathbf{1}_2$](BAr$^F{}_4$)$_2$ recorded at 20 K in a 2-methyl-tetrahydrofuran glass; simulation parameters: g_{11} = 2.2135, g_{22} = 2.1460, g_{33} = 2.0212, W_{11} = 3.0, W_{22} = 2.5, W_{33} = 3.2, $A^{P1}{}_{11}$ = $A^{P2}{}_{11}$ = 210 MHz, $A^{P1}{}_{22}$ = $A^{P2}{}_{22}$ = 212 MHz, $A^{P1}{}_{33}$ = $A^{P2}{}_{33}$ = 207 MHz. $A^{N1}{}_{11}$ = $A^{N}{}_{11}$ = 23 MHz, $A^{N1}{}_{22}$ = $A^{N2}{}_{22}$ = 28 MHz, $A^{N1}{}_{33}$ = $A^{N2}{}_{33}$ = 21 MHz, $A^{H1}{}_{11}$ = $A^{H2}{}_{11}$ = 20 MHz, $A^{H1}{}_{22}$ = $A^{H2}{}_{22}$ = 20 MHz, $A^{H1}{}_{33}$ = $A^{H2}{}_{33}$ = 19 MHz; experimental conditions: microwave frequency 9.64567 GHz; power 1.589 mW; modulation amplitude 4.000 G.

S4.4 EPR spectrum of [1]Br

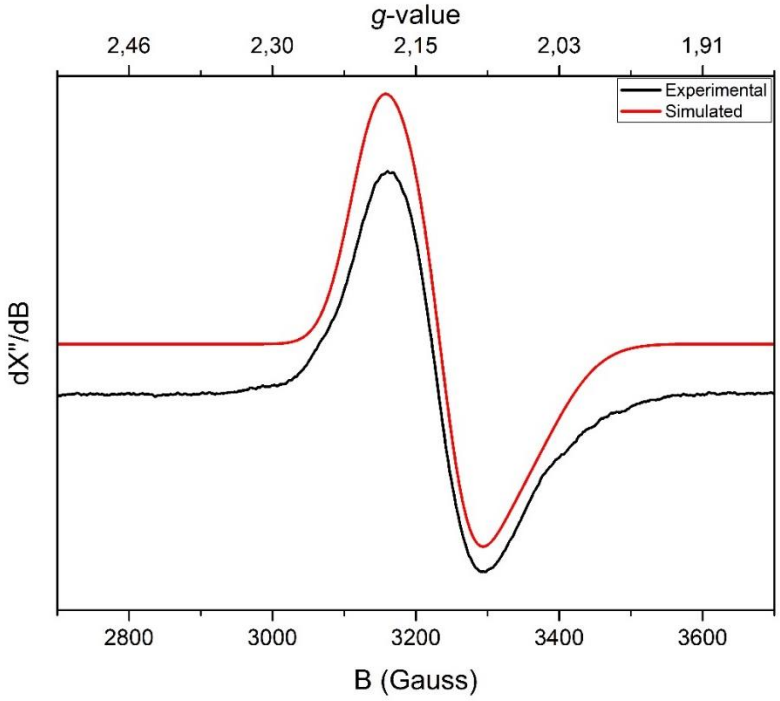

Figure S24 Experimental and simulated EPR spectra of [**1**]Br recorded at 20 K in a toluene glass; simulation parameters: g_{11} = 2.190, g_{22} = 2.125, g_{33} = 2.060, W_{11} = 45, W_{22} = 45, W_{33} = 75; experimental conditions: microwave frequency 9.646523 GHz; power 0.6325 mW; modulation amplitude 4.000 G.

S4.5 EPR spectrum of 3

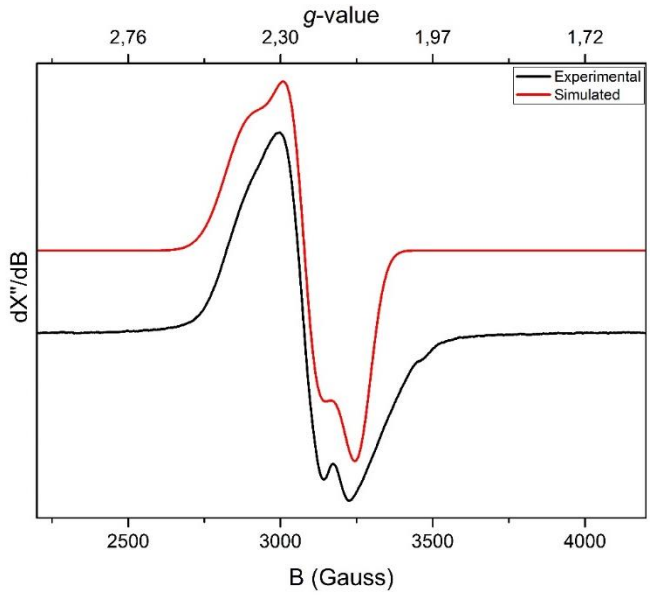

Figure S25 Experimental and simulated EPR spectra of **3** recorded at 20 K in a toluene glass; simulation parameters: g_{11} = 2.390, g_{22} = 2.242, g_{33} = 2.120, W_{11} = 90, W_{22} = 55, W_{33} = 55; experimental conditions: microwave frequency 9.644902 GHz; power 0.6325 mW; modulation amplitude 2.000 G.

S5 X-ray Crystallographic Data

S5.1 Crystallographic data and structure refinement of **1**, [**1**]BF_4, [**1**(THF)]PF_6 and [$\mathbf{1_2}$]$(BAr^F{}_4)_2$

Table S3 Crystallographic data and structure refinement of **1**, [**1**]BF_4, [**1**(THF)]PF_6 and [$\mathbf{1_2}$]$(BAr^F{}_4)_2$.

	1	[**1**]BF_4	[**1**(THF)]PF_6	[$\mathbf{1_2}$]$(BAr^F{}_4)_2$
Empirical formula	$C_{44}H_{32}N_2NiP_2$	$C_{51}H_{40}BF_4N_2NiP_2$	$C_{52}H_{48}F_6N_2NiO_2P_3$	$C_{307}H_{183}B_4F_{96}N_8Ni_4P_8O_{0.5}$
Formula weight / g·mol^{-1}	709.36	888.31	998.54	6341.44
Temperature / K	123(1)	123.01(10)	123.01(10)	123.01(10)
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	P-1	P-1	$P2_1/n$	P-1
a / Å	10.3221(6)	10.2588(3)	10.2472(2)	23.6833(4)
b / Å	11.0536(7)	15.4329(5)	15.9999(3)	24.1591(4)
c / Å	15.6845(6)	15.5298(6)	29.0867(5)	25.1043(4)
α /°	97.161(4)	115.755(3)	90	93.5980(10)
β /°	92.453(4)	103.667(3)	95.462(2)	96.9240(10)
γ /°	107.791(5)	96.193(2)	90	95.2700(10)
V / Å^3	1684.47(16)	2088.57(13)	4747.23(15)	14159.2(4)
Z	2	2	4	2
ρ_{calc} / g cm^{-1}	1.399	1.413	1.397	1.487
μ / mm^{-1}	2.000	1.868	2.111	1.798
F(000)	736.0	918.0	2068.0	6402.0
Crystal size / mm^3	0.152 × 0.109 × 0.076	0.146 × 0.089 × 0.071	0.249 × 0.119 × 0.062	0.234 × 0.16 × 0.088
Radiation / Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection /°	8.49 to 147.416	6.552 to 147.742	8.236 to 147.966	6.976 to 145.81
Diffractometer	SuperNova	SuperNova	SuperNova	SuperNova
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 11, -19 ≤ l ≤ 18	-12 ≤ h ≤ 12, -13 ≤ k ≤ 19, -19 ≤ l ≤ 18	-12 ≤ h ≤ 11, -16 ≤ k ≤ 19, -36 ≤ l ≤ 24	-26 ≤ h ≤ 29, -29 ≤ k ≤ 28, -29 ≤ l ≤ 31
Reflections collected	10781	16711	21561	122308
Independent reflections	6500 [R_{int} = 0.0288, R_{sigma} = 0.0359]	8256 [R_{int} = 0.0216, R_{sigma} = 0.0294]	9386 [R_{int} = 0.0199, R_{sigma} = 0.0239]	54323 [R_{int} = 0.0413, R_{sigma} = 0.0530]
Data/restraints/parameters	6500/0/442	8256/0/551	9386/0/595	54323/746/4059
Goodness-of-fit on F^2	1.147	1.032	1.055	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0885, wR_2 = 0.2779	R_1 = 0.0309, wR_2 = 0.0766	R_1 = 0.0412, wR_2 = 0.1040	R_1 = 0.0710, wR_2 = 0.1971
Final R indexes [all data]	R_1 = 0.0921, wR_2 = 0.2793	R_1 = 0.0359, wR_2 = 0.0801	R_1 = 0.0467, wR_2 = 0.1080	R_1 = 0.0903, wR_2 = 0.2155
Largest diff. peak/hole / e Å^{-3}	2.15/-0.74	0.38/-0.22	0.51/-0.45	1.40/-0.66

S5.2 Crystallographic data and structure refinement of **2**, [**1**]Br and **3**.

Table S4 Crystallographic data and structure refinement of **2**, [**1**]Br and **3**.

	2	[**1**]Br	**3**
Empirical formula	$C_{34}H_{26}NP$	$C_{48}H_{40}BrN_2NiOP_2$	$C_{70}H_{58}I_4N_2Ni_2P_2$
Formula weight / g·mol^{-1}	479.57	861.38	1614.206
Temperature / K	123.01(10)	123.01(10)	123.01(10)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a / Å	10.2550(4)	10.7332(4)	9.0557(2)
b / Å	10.4958(5)	13.0693(5)	13.2167(3)
c / Å	12.4245(5)	15.6703(4)	13.9415(4)
α /°	101.719(4)	97.800(3)	104.895(2)
β /°	97.635(4)	104.377(2)	96.912(2)
γ /°	102.229(4)	99.310(3)	101.037(2)
V / Å^3	1257.91(10)	2065.39(13)	1557.22(7)
Z	2	2	1
ρ_{calc} / g cm^{-1}	1.2660	1.385	1.721
μ / mm^{-1}	1.133	2.838	17.133
F(000)	505.9	886.0	787.0
Crystal size / mm^3	0.561 × 0.344 × 0.327	0.614 × 0.163 × 0.096	0.191 × 0.158 × 0.093
Radiation / Å	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection /°	7.4 to 147.88	8.28 to 148.212	6.66 to 152.56
Diffractometer	SuperNova	SuperNova	SuperNova
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 12, -15 ≤ l ≤ 15	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 19	-11 ≤ h ≤ 11, -16 ≤ k ≤ 15, -15 ≤ l ≤ 17
Reflections collected	9332	15598	11865
Independent reflections	4949 [R_{int} = 0.0139, R_{sigma} = 0.0145]	8130 [R_{int} = 0.0144, R_{sigma} = 0.0167]	6337 [R_{int} = 0.0200, R_{sigma} = 0.0221]
Data/restraints/parameters	4949/0/325	8130/41/505	6337/0/362
Goodness-of-fit on F^2	1.051	1.029	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0973	R_1 = 0.0251, wR_2 = 0.0653	R_1 = 0.0264, wR_2 = 0.0682
Final R indexes [all data]	R_1 = 0.0382, wR_2 = 0.0980	R_1 = 0.0262, wR_2 = 0.0661	R_1 = 0.0269, wR_2 = 0.0685
Largest diff. peak/hole / e Å^{-3}	0.35/-0.29	0.58/-0.38	1.13/-0.80

S6 Cyclic Voltammetry

Cyclic voltammogram (CV) was recorded with a CH Instruments potentiometer and software from CH Instruments. CV was measured with an electrode cell equipped with a Pt-working electrode, Pt-counter electrode and an Ag/$AgNO_3$-reference electrode. The Ag/$AgNO_3$ reference electrode was referenced against ferrocene in tetrahydrofuran. **1** (0.02 mmol) and the conducting salt [nBu$_4$N]PF_6 (1 mmol) were dissolved in tetrahydrofuran (10 mL) for the CV measurement.

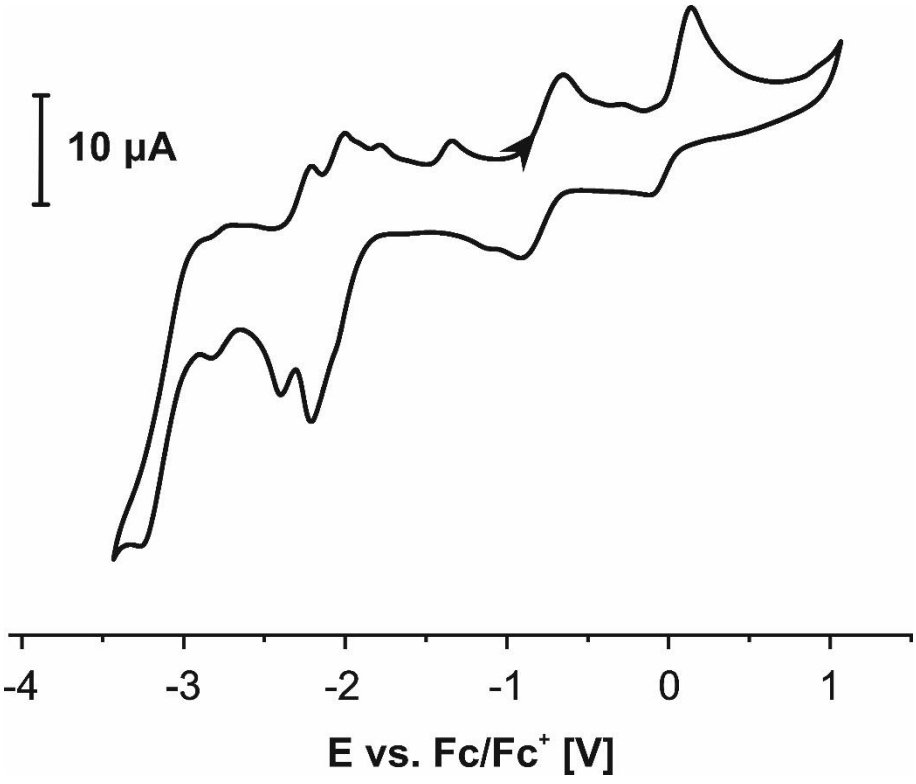

Figure S26 Cyclic voltammogram of **1**, scan rate 100 mV, range from E (V) = −3.4 − +1.1, E *vs.* Fc/Fc$^+$: quasi reversible process at E (V) = −0.6 and irreversible oxidation at E (V) = +0.139.

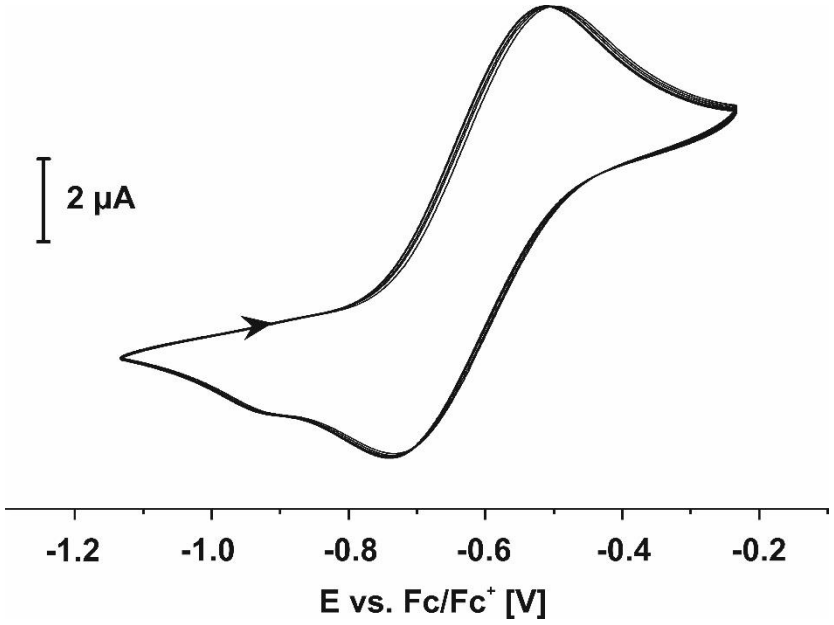

Figure S27 Cyclic voltammogram of **1**, scan rate 100 mV, range from E (V) = −1.1 − −0.2, E *vs.* Fc/Fc$^+$: quasi-reversible oxidation at E (V) = −0.506, ΔE (V)= −0.235.

S7 Quantum chemical calculations

S7.1 General Methods

All calculations were performed with the ORCA program package.[1,2] Geometry optimisations were carried out at the BP86-D3BJ/def2-TZVP[3–7] level of theory using a truncated geometry of the complexes (replacing the *para*-phenyl groups by a hydrogen atom). Unless stated otherwise, all calculations were carried out in the gas phase. DFT orbitals served as initial guess for the CASSCF calculations. The RIJCOSX[8] approximation was used for CASSCF calculations and DFT calculations of EPR parameters. Orbital pictures were rendered with the software Avogadro.[9]

S7.2 Calculations of EPR parameters

EPR parameters (g-tensor and A-tensor) were calculated using the TPSSh[10] functional, the IGLO-III[11] basis on C, H, B, F, N and P, the CP(PPP)[12] basis on Ni and the Partridge-2[13] basis on Br. In the case of **3**, the DKH-def2-TZVP basis set was used in order to treat relativistic effects with a DKH Hamiltonian. The results are summarised in Table S5. In addition, the Mulliken spin density on the nickel atom is given for each compound. These values prove the presence of nickel-centered radicals. Furthermore, for [**1**]Br, [**1**]BF_4 and the **NiL$_2$** cation (L = 2-(2′-pyridyl)-4,6-diphenylphosphinine), the calculated g-tensors are in good agreement with the experimental data. For **3** the agreement between experiment and theory is less good and the large calculated spin-density on Ni (1.23) indicates a more complex electronic structure. Therefore, we conducted further calculations on that species including broken-symmetry DFT (BS-DFT) and CASSCF calculations (*vide infra*).

Table S5 Summary of calculated EPR parameters and spin densities.

compound	g_x, g_y, g_z	spin density at Ni
[**1**]Br	2.033, 2.090, 2.109	0.82
[**1**]BF_4	2.027, 2.096, 2.100	0.85
NiL$_2$ cation	2.015, 2.116, 2.123	0.91
3	2.117, 2.216, 2.247	1.23

In addition, we calculated the hyperfine interactions for the [Ni(I)**L**$_2$]$^+$ cation. The results are in qualitative agreement with the values extracted from the experimental spectrum (see Table S6). Due to the deviation of the cation from ideal C_2 symmetry in the gas phase, two sets of hyperfine couplings are observed for the phosphorus, nitrogen and hydrogen atoms.

Table S6 Comparison of experimental and calculated hyperfine couplings in **[Ni(I)L$_2$]$^+$**. Coupling constants are given in MHz.

coupling nucleus	A^{11}, A^{22}, A^{33} (exp.)	A^{11}, A^{22}, A^{33} (calc.)
^{31}P	210, 212, 207	261, 231, 223
		236, 209, 200
^{14}N	23, 28, 21	21, 14 14
		16, 11, 11
^{1}H (*ortho* in pyridyl group)	20, 20, 19	4, 2, 12
		2, 3, 11

S7.3 Calculations on 3

CASSCF calculations were conducted in order to get an insight into the electronic structure of **3**. In particular, state-averaged (SA) CASSCF-NEVPT2 calculations with an active space of 13 electrons in 12 orbitals (13/12) and a spin-multiplicity of 2 were carried out. This allowed for the calculation of the g-tensor of **3** (*vide supra*). Thereby, the all-electron scalar-relativistic Douglas-Kroll-Hess (DKH) Hamiltonian and the DKH-def2-SVP basis on C and H and the DKH-def2-TZVP basis on N, P, I, Ni were used to account for relativistic effects. The orbitals comprising the active space are depicted in Figure S28. Here, 146 and 147 are metal-ligand bonding orbitals. Orbitals 148 to 152 are essentially 3d orbitals on nickel as can be derived from Loewdin population analysis (Figure S28). Orbital 153 is a ligand-centered orbital with dominant contributions from the phosphacyclohexadienyl backbone. Finally, 154 to 157 are four 4d orbitals on Ni, accounting for radial correlation. The ground-state of **3** is mainly composed of the following configuration state functions (CSF): 222221200000 (36%), 222221110000 (34%), 222222100000 (11%), 222221020000 (10%). Here, the orbitals are ordered from 146 to 157. The first and third CSF constitute a low-spin $3d^9$ configuration at the Ni atom with the ligand-centered orbital 153 being empty (**3-I**). The second CSF can be interpreted as an intermediate-spin (S = 1) Ni $3d^8$ center being antiferromagnetically coupled with a ligand-centered radical (**3-II**). Finally, the fourth CSF describes a low-spin Ni $3d^7$ center and a doubly occupied ligand-centered orbital (**3-III**). Thus, **3** exhibits significant multi-reference character which makes an assignment of the oxidation-state of the nickel atom somewhat ambiguous. An additional broken-symmetry DFT calculation at the TPPS0/def2-TZVP[7,10] level (def2-ECP[14] on I) reveals a similar situation as described with the second CSF, namely an Ni $3d^8$ center being anti-ferromagnetically coupled with a ligand-centered radical (J = −1276 cm^{-1}, see Figure S29 of a depiction of the respective corresponding orbitals). Thus, both methods clearly show the redox-active behavior of the phosphacyclohexadienyl ligand in **3**.

Having the SA-CASSCF wavefunction in hand, we were able to calculate the g-tensor in **3**. By inclusion of dynamic correlation effects by means of the NEVPT2 approach, we were able to calculate the following g-tensor: g_x = 2.173, g_y = 2.227, g_z = 2.562 (measured: g_x = 2.12, g_y = 2.242, g_z = 2.39). Here, g_z is somewhat larger than the experimental value whilst g_x and g_y are in good agreement. This might be due to use of perturbative dynamic correlation corrections in conjunction with medium-sized basis sets which potentially leads to unconverged results. Attempts to use larger basis sets (e.g. DKH-def2-QZVP on Ni) led to convergence issues and an enormous increase in calculation time. Still, the calculations are in qualitative agreement with the experiment and reproduce the observed significant anisotropy of the g-tensor.

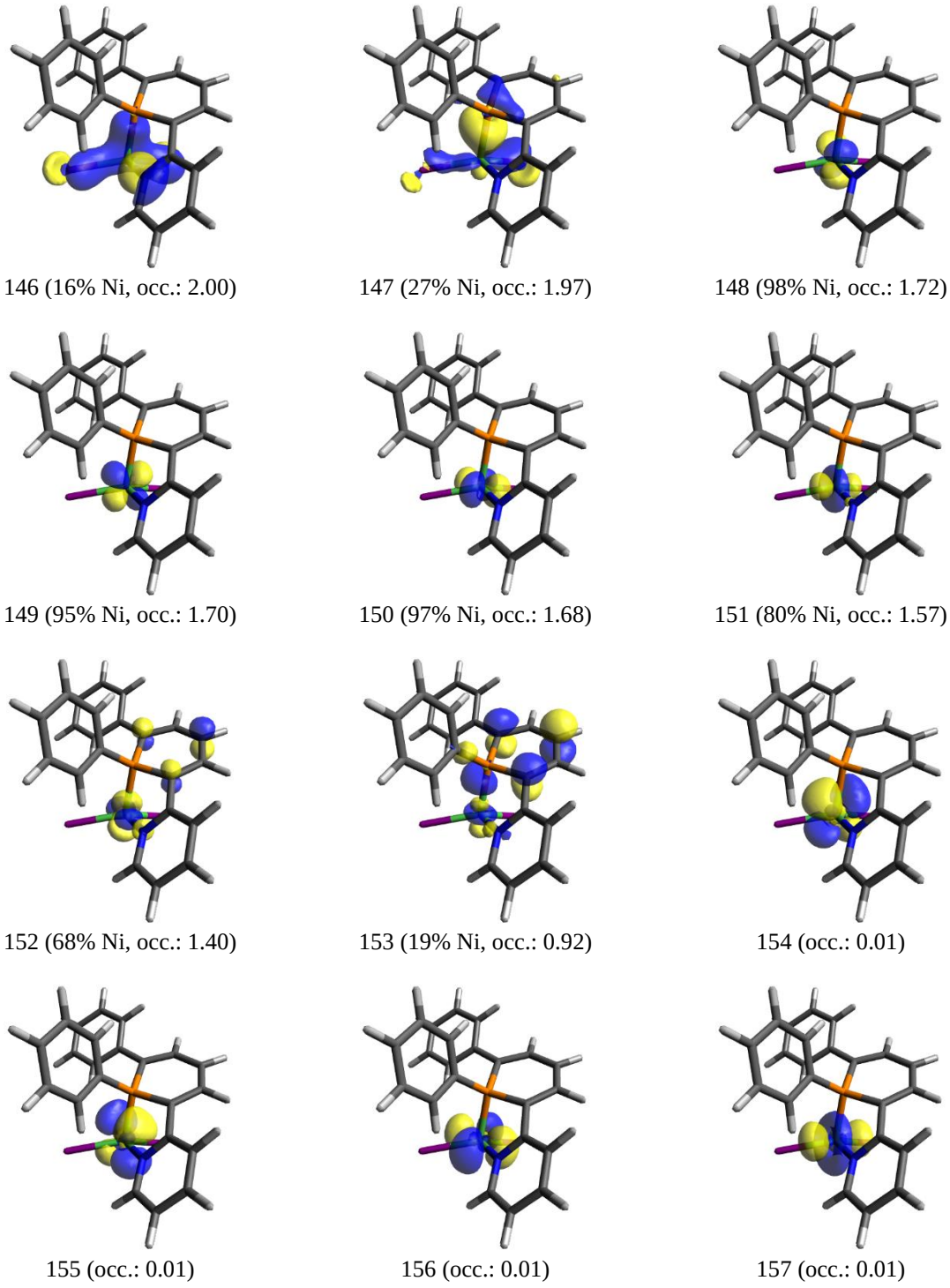

Figure S28 Natural orbitals of the active space of a SA-CASSCF(13/12) calculation on **3** including 13 roots. The contribution of 3d orbitals on Ni (determined from Loewdin population analysis) together with the occupation of each orbital is given in parentheses. Surface isovalue = 0.05.

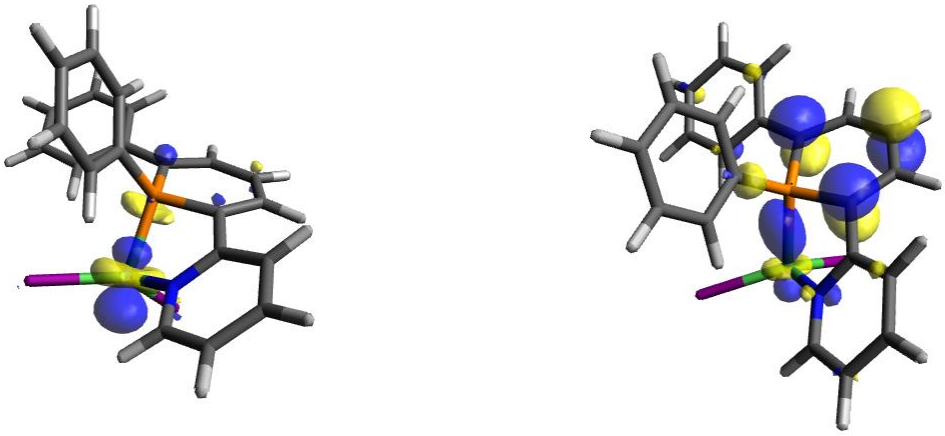

Figure S29 Unrestricted corresponding orbitals of **3** (left: α (spin-up), right: β (spin-down), overlap = 0.54).

S7.4 Cartesian coordinates of optimised structures

[**1**]Br

Br	4.17369523021368	3.61654514150453	3.61457572633797
Ni	2.94919801011276	5.73775590985170	3.58927783076741
P	1.28512850807729	6.65797576996317	2.41814453448017
P	3.11218440721368	7.36808697907393	5.09111982870227
N	1.62114321689731	4.96985783731505	4.94332966330204
N	4.09190682673379	6.45409673367392	2.02628965418930
C	3.54636499847621	7.31789029273417	1.11387797368640
C	-0.24896184348918	8.96764009855282	2.49689844919089
H	-1.13991105338875	9.49817193207339	2.84645896908081
C	-1.02020707185623	7.07195253731644	3.91408532714854
C	2.19990471110583	7.78925671977732	1.42249114059909
C	0.59652634209809	9.63927056554817	1.60555106739270
C	1.16272983690131	8.00375916343621	6.98154606075649
H	0.28883618296559	7.72355214489653	7.57384920263207
C	2.69290257169792	9.80805798293548	6.33005488860421
H	2.97080098128551	10.85766508049249	6.46603242813523
C	4.28651301719446	7.75055960846861	0.00058423246945
H	3.80785470542218	8.39111678937820	-0.73932300348583
C	5.60791621866170	7.35016941473243	-0.14688720813531
H	6.19291535960685	7.68346703477235	-1.00513529623718
C	1.77308638149074	9.07940439966664	1.10609185300540
H	2.42919248305618	9.71393383166656	0.50319177436299
C	1.20881165849191	5.68858047897130	6.02661402127300
C	1.73154740016775	7.05025952056926	6.13492339058250
C	3.43125248013031	9.07369978716076	5.39559629890655
C	1.61907853377632	9.31699382739128	7.07707920537215
C	1.16141677705545	3.71700209716216	4.76395852551765
H	1.54028198389874	3.20393003566537	3.88163439928110
C	5.37548547706148	6.07168924765429	1.87318518118025
H	5.74439968685300	5.38010251385217	2.62975238583206
C	6.16925129353819	6.51131745298570	0.82024421106090
H	7.20760665159226	6.18807236776602	0.76139229111989
C	4.57131863990526	9.70562962668906	4.70035317310044

C	-1.44099799779443	5.73477372515926	3.79272830179125
H	-1.05452199255586	5.13106169219714	2.96966101575138
C	-0.06492993635446	7.66195624894842	2.95698272068042
C	0.28683410768495	3.10820402471108	5.65515441426717
H	-0.05832408239104	2.09358534642647	5.46112616147689
C	4.77334466464432	9.49620539867324	3.32771083644252
H	4.04936749394592	8.89909363613108	2.78076906071116
C	0.34794109227968	5.11008897873482	6.97431385552488
H	0.05848979042420	5.67963595155435	7.85519216159167
C	-0.11519536807464	3.81563498903101	6.79032785705348
H	-0.78582621819988	3.36333426821662	7.52156790597859
C	-2.85891695753788	5.96293285574578	5.74026574748554
H	-3.57176758028028	5.53407633339010	6.44569405889239
C	-2.35558145305401	5.18942404121505	4.69073166454896
H	-2.67543700531131	4.15377983894625	4.57158511248798
C	5.85566249744777	10.07010316708754	2.66381174946579
H	5.98690320299334	9.88973766881688	1.59615176015857
C	5.48700933015533	10.51688396181880	5.39559539726058
H	5.36333522094685	10.66674438175738	6.46938922345388
C	-1.52903443844337	7.83781348405812	4.97998526864500
H	-1.17541668842179	8.86062824767494	5.11485627630096
C	6.76036878777559	10.87209359602527	3.36459200835813
H	7.61172218110416	11.32011652436585	2.85054676368433
C	6.56946041819492	11.09462340253969	4.73214282058644
H	7.27652709987356	11.71168082416690	5.28863436192133
C	-2.43742107458746	7.28782257291393	5.88329718359215
H	-2.81445848213862	7.89531008654591	6.70779387251167
H	1.10340594949697	10.00022821099659	7.75296527985020
H	0.34292683522985	10.66080361845411	1.32110897931511

[1]BF_4

Ni	3.41111953196818	8.89200901578479	3.94377101232159
P	2.84780088699047	6.76486584234240	3.67194081709707
P	4.96839557699381	8.54324330988271	5.48608126031847
F	2.88506892355093	11.82524212776272	1.42188398608432
F	1.35095688196868	12.12245951087747	3.13703036482762
F	3.44151853213992	11.19709804382114	3.58803330303456
F	1.88921014538388	9.97748382416215	2.43352962269260
N	4.58480346776290	8.53859745178517	2.34946087942220
N	2.24150609885514	9.24405098325309	5.54080798639382
C	5.33487101155729	6.26373218277637	7.62826922800599
C	4.43721974862797	4.07441718539717	4.04630458716698
C	6.22321122143575	7.30582109803485	5.55460222487095
C	5.08330867909580	9.55526249068116	1.62033506359165
H	4.78085255069441	10.55489850960906	1.92484504828070
C	2.61545397176845	8.76736575204148	6.76953251813886
C	4.30996457188024	6.21566957608771	2.85827275926820
C	1.48696363084355	5.71565885739008	5.83993522309337
C	3.36169040352060	4.34350120383642	4.89968541809926
H	3.09585649610498	3.57455234406465	5.63075703007873
C	2.57975615339900	5.50230042977477	4.87254449368999
C	4.19882792799936	7.06981416838017	7.72488757267204
H	3.47378201886645	6.84784822542882	8.51137885037934
C	3.90261367876475	8.07771414923382	6.80984510523466
C	7.23188052610765	7.30958114316939	4.47856931610516
C	4.89949180324717	4.97336682743010	3.08288689947021

H	5.80893201788553	4.71713443487716	2.53433038460959
C	5.77628957898123	6.98693855511075	0.94850002401947
H	6.01501215414266	5.95495493214596	0.69711806126597
C	1.07958791024169	9.91299466706064	5.41454351234201
H	0.83858712782267	10.27252679466309	4.41611535781219
C	-0.56251968269887	6.19880852147126	7.72018581801466
H	-1.35225809871493	6.38900916310488	8.44785039675363
C	6.26659569431120	6.36619747541151	6.58971426114090
H	7.11078993139284	5.67081868730042	6.60313948879354
C	1.56678741636237	5.19957992299639	7.14767988120691
H	2.45072503504233	4.63454041425159	7.44400178844729
C	4.91370117771683	7.24964781124131	2.02158391964485
C	-0.65894295762106	6.71425964736568	6.42492679926912
H	-1.52601619594420	7.30749371538781	6.13345599100965
C	0.55474568484838	5.43803666268473	8.07564099555723
H	0.64234947362968	5.03539925954376	9.08593888424981
C	0.22693045765679	10.12677007952994	6.49147282684278
H	-0.70273812135354	10.67172192449981	6.33485984499229
C	5.93933773517053	9.34694278997118	0.54519435455371
H	6.31490464784491	10.20466014879217	-0.01049368807074
C	8.75249040511458	6.10951715034341	2.99776624330391
H	9.19520379327131	5.16735645976675	2.67064655276727
C	7.59584572393388	8.50485786844960	3.82810228431775
H	7.15084144000346	9.44610433313379	4.15619921855434
C	1.78826159702798	8.95277881894039	7.88575833107779
H	2.10935943808726	8.57517671696103	8.85494582735472
C	7.82921082242312	6.11121123397888	4.04180658425490
H	7.53626344903972	5.16941509151098	4.50589797631678
C	6.29717454069510	8.03968816579257	0.20805359308441
H	6.96986257866568	7.84378848894187	-0.62731164752005
C	0.58452508410551	9.63091069279688	7.74726890014240
H	-0.06547047921029	9.77780884758606	8.61015874232962
C	0.35334105859052	6.47891706713467	5.49821542230850
H	0.26674927091681	6.87994392690074	4.48644879098658
C	9.10351193030709	7.30513123410883	2.36476801049953
H	9.82526034648011	7.30293831043469	1.54725582596707
C	8.52140306902007	8.50297039163027	2.78791192231698
H	8.78852685757334	9.44302644551109	2.30458335605066
B	2.36688962112726	11.33061229234267	2.61311844648538
H	5.48856578942730	5.49019378408065	8.38194855043945
H	4.96166823715585	3.12559281923642	4.16450759616883

NiL$_2$ cation

Ni	2.83169587379897	5.83953454871524	3.52436418395869
P	1.34723182749208	6.92355912217428	2.34122048323092
P	2.98880168794484	7.18255387851981	5.26186451846503
N	1.81670203360040	4.66200499762463	4.77126173212186
N	4.04863034328455	6.20228158295645	1.98023536012779
C	3.66240490410658	7.05091274524621	0.97211980068903
C	0.08818033925569	9.34184290094228	2.05097641939073
H	-0.71546308205653	10.03370910030973	2.31697647913685
C	-0.70498283290639	7.84666059097348	3.91766170684307
C	2.38311213539963	7.73362273527593	1.17847556003025
C	0.95946530604527	9.72518229772985	1.02449154470351
C	1.08112378866077	7.27551381211746	7.27134302607245
H	0.28921190073389	6.81198845259959	7.86234612383442

C	2.27467233424384	9.36776762888787	6.75337929125374
H	2.37301173506484	10.43047672341593	6.99039495374275
C	4.48848587546346	7.24296795935904	-0.14468591892340
H	4.15833747496901	7.90389985845244	-0.94495757882281
C	5.70455500069747	6.57617868919548	-0.23291170131871
H	6.34945931716536	6.72092192308833	-1.09966739093504
C	2.07067578054683	8.97859892064701	0.62717012155997
H	2.75917571385507	9.43033648293716	-0.09134027510676
C	1.37067623712801	5.13823788625112	5.97402399204608
C	1.71735760288651	6.52755006333291	6.28050423179091
C	3.04566080260361	8.87954894056012	5.68875945937219
C	1.36222622354770	8.62242305907030	7.50301568799498
C	1.52491123803941	3.39612488263415	4.40501107344622
H	1.89014485985891	3.08530993114270	3.42515515388624
C	5.23221658912384	5.55884240412543	1.88459203169646
H	5.49696700663643	4.91790875826631	2.72667485039684
C	6.08568503310126	5.71441123881752	0.80108857141070
H	7.03226362843053	5.17712999622037	0.77588780406234
C	3.96404524910703	9.75422027827182	4.93817172490099
C	-1.13710105878466	6.53420270944847	4.18748061155643
H	-0.88528387984006	5.73318169034733	3.48958253841601
C	0.16330535597156	8.13968742827126	2.76365149217845
C	0.78538406976735	2.53638377713616	5.20509207356199
H	0.57431489992058	1.52425440159219	4.86408309727584
C	4.17053526373939	9.53925056773223	3.56420335773619
H	3.61555486370520	8.74684716926110	3.06533906663694
C	0.62418871436854	4.30771204395126	6.82353956140954
H	0.28947640172546	4.68909254026186	7.78638270218422
C	0.32637982509279	3.00644315659592	6.44039974447901
H	-0.25466306461246	2.35948774945686	7.09776409785495
C	-2.26570138595961	7.28357580218193	6.19080373334499
H	-2.87904549916360	7.06899037481287	7.06657823882546
C	-1.91083352238527	6.25617127250507	5.31211308431951
H	-2.24953351540617	5.23614764364288	5.49572001960385
C	5.03440975078884	10.35041473768570	2.83358683485889
H	5.17251384275394	10.17150221097067	1.76625745053775
C	4.65576039022132	10.80769846054713	5.56486282044799
H	4.53894121125117	10.97195070618135	6.63678713985492
C	-1.06670546697128	8.87146552191471	4.81106504903289
H	-0.70551460924890	9.88611284882859	4.64072506303604
C	5.71395167922566	11.39547596033410	3.46579969053835
H	6.39223407389504	12.03317210317627	2.89834203338896
C	5.52106993148036	11.61928287742664	4.83295172002549
H	6.05704962379419	12.42587461521521	5.33399138246443
C	-1.84156964820891	8.59116725630140	5.93443562985795
H	-2.10970335967853	9.39614046011111	6.61934431714129
H	0.80589218564276	9.13592999671799	8.28734865182667
H	0.78999576887275	10.68945638602629	0.54511005020869

3

I	0.57983113854676	-2.41200876680676	8.39544025384048
I	0.63245157779244	0.49357116093142	11.91231741925053
Ni	1.39168757762293	-0.47355428749505	9.74066986083760
P	1.49125355544253	1.11794117112775	8.24066345875673
N	3.39422550654513	-0.38127611531221	9.63594850312452
C	2.91819484161817	0.40680294574295	7.45297283296146

C	-0.95698680383626	2.01768284115244	7.28924662570600
C	1.76718987854961	0.20595647987734	5.29193323743988
C	2.87970079456565	0.01691959561384	6.12392768127220
C	1.60683273455964	3.90291284538146	8.22089244337704
C	0.31099986409326	1.36243069259318	6.95580084113916
C	0.57321014954435	0.81624010913095	5.69971431580640
C	5.29286277006837	-0.13449278471131	8.18290841371764
C	-1.45398608009332	1.99415071196304	8.60786912117140
C	1.93109660808868	2.74302770126559	8.94190517340162
C	2.64924292219541	2.84337938180445	10.14008870297771
C	6.13037652225072	-0.56493849627089	9.20723033970443
H	1.81675729477187	-0.18547923723416	4.27614808870400
C	3.91467500250816	-0.03922845438441	8.41605913152266
C	5.58419178475460	-0.87836024951828	10.45720251271523
C	4.20958088173540	-0.76745289141519	10.63342321373340
C	3.04565915641764	4.09586920432877	10.60948484139009
C	-2.63713924106047	2.65002494535574	8.93588688254139
C	1.98761372762144	5.15264390704281	8.70898869011696
C	-3.35537539877122	3.34021171089283	7.95530636384437
C	2.71056959828459	5.25174343622828	9.90082393010558
C	-1.68983077456419	2.72031373665671	6.31031363714283
C	-2.87618969358581	3.37036469308049	6.64129680111299
H	2.87298248660824	1.94979307128697	10.71856604775317
H	3.60149087206609	4.16576492463240	11.54522060590731
H	3.00763454396799	6.23080322154927	10.27944130183008
H	1.71880193161605	6.05122456560988	8.15205027776197
H	1.05195675573688	3.82812953140093	7.28656407284621
H	-1.30533526018371	2.78359736318371	5.29123333322632
H	-3.42569859811104	3.91471277874820	5.87177251587340
H	-4.28345150368393	3.85247124429466	8.21208409906458
H	-3.00304115805222	2.61065855065197	9.96255867479784
H	-0.92344753793046	1.43364174538994	9.38201620033798
H	3.71685611622719	-1.00295784427904	11.57786105723866
H	6.21043420924135	-1.21116386740948	11.28366678405361
H	7.20545557227365	-0.63949497690601	9.04065195210665
H	5.69162240846286	0.15814246583086	7.21200956835079
H	3.72922276754289	-0.54832745550321	5.73055583174494
H	-0.23658950144793	0.86380869449716	4.96667435969219

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