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Electronic Supplementary Information

Reactions of a 2,4,6-triphenylphosphinine ferrate anion with electrophiles: a new route to phosphacyclohexadienyl complexes

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The supplementary information contains:

(S1) NMR Spectra

[Cp*Fe(2-*endo*-H-$PC_5Ph_3H_2$)] (endo-3)

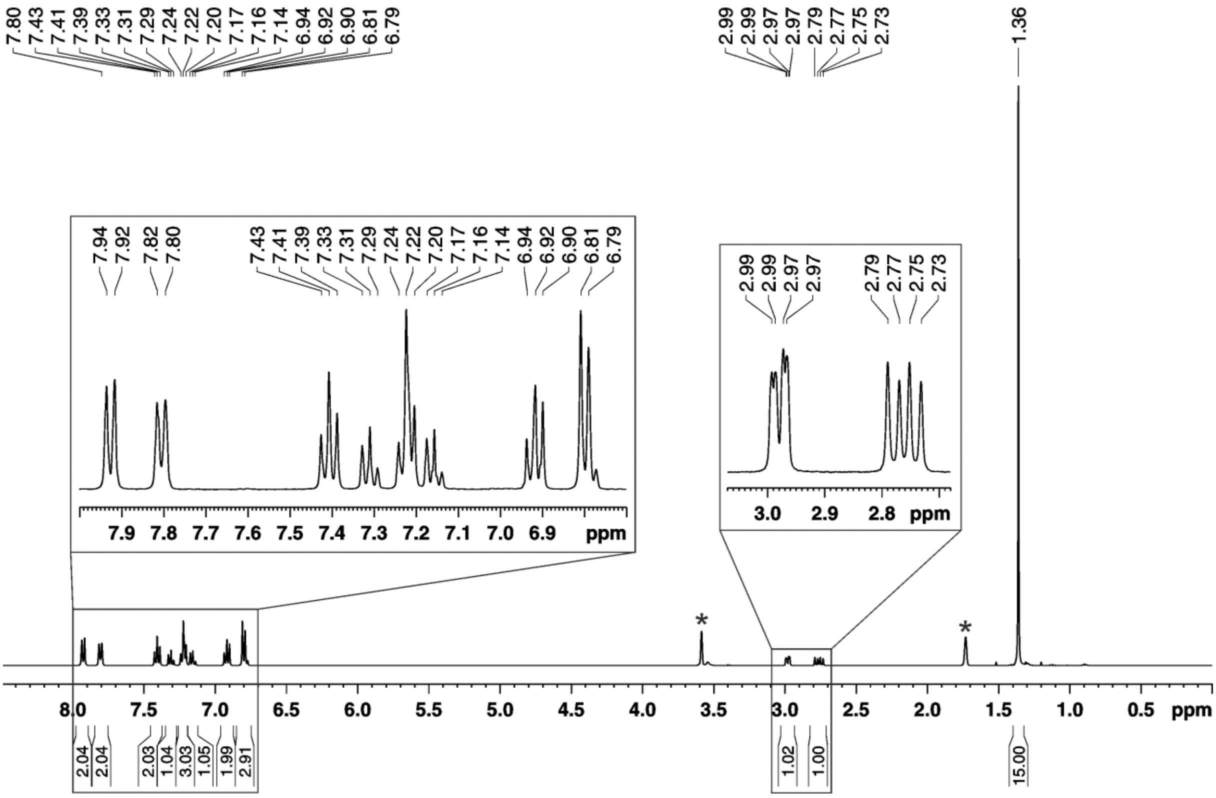

Figure S1 [1]H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of [Cp*Fe(2-*endo*-H-$PC_5Ph_3H_2$)] (**endo-3**); * [D_8]THF.

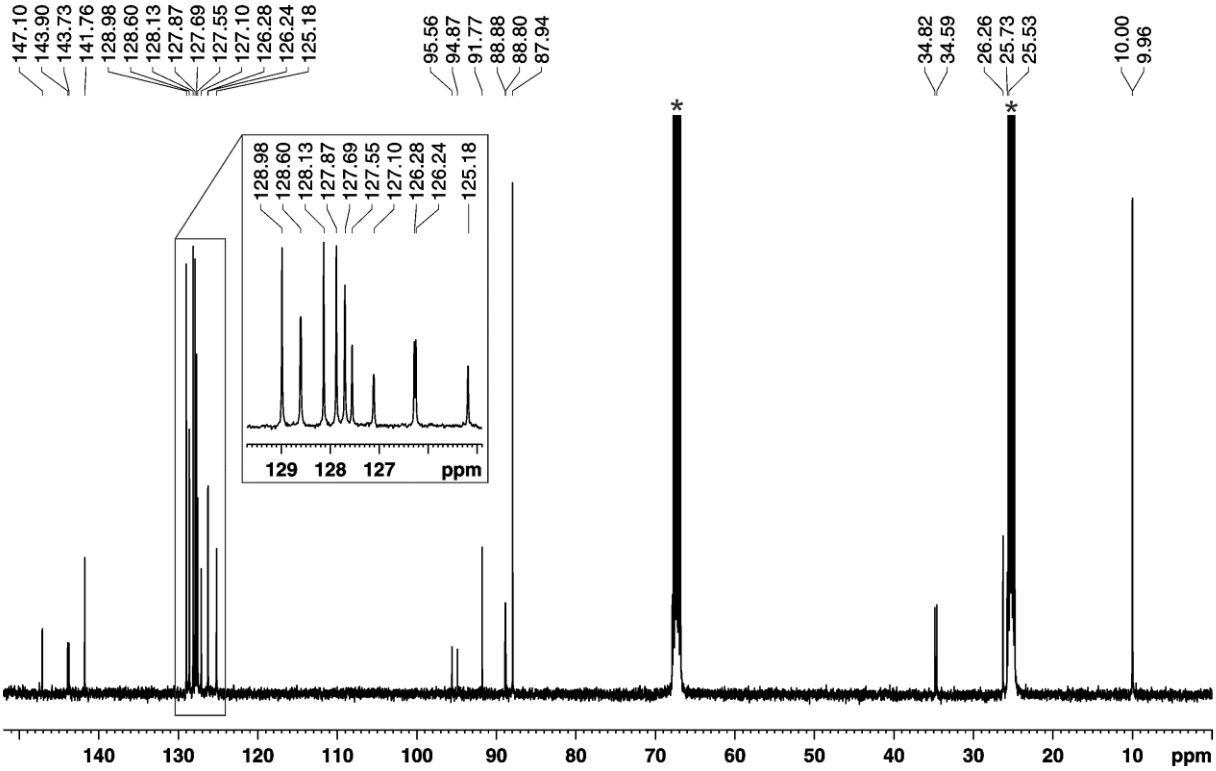

Figure S2 [13]C{[1]H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of [Cp*Fe(2-*endo*-H-$PC_5Ph_3H_2$)] (**endo-3**); * [D_8]THF.

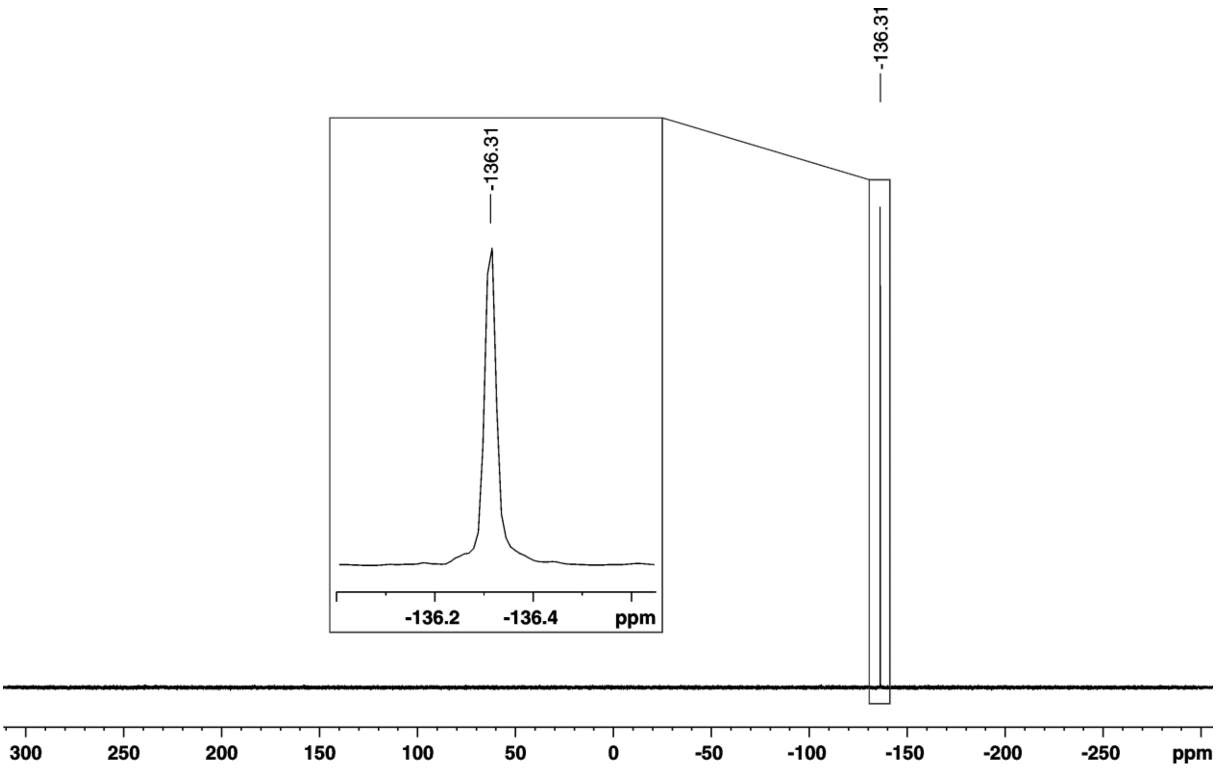

Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-*endo*-H-PC$_5$Ph$_3$H$_2$)] (**endo-3**).

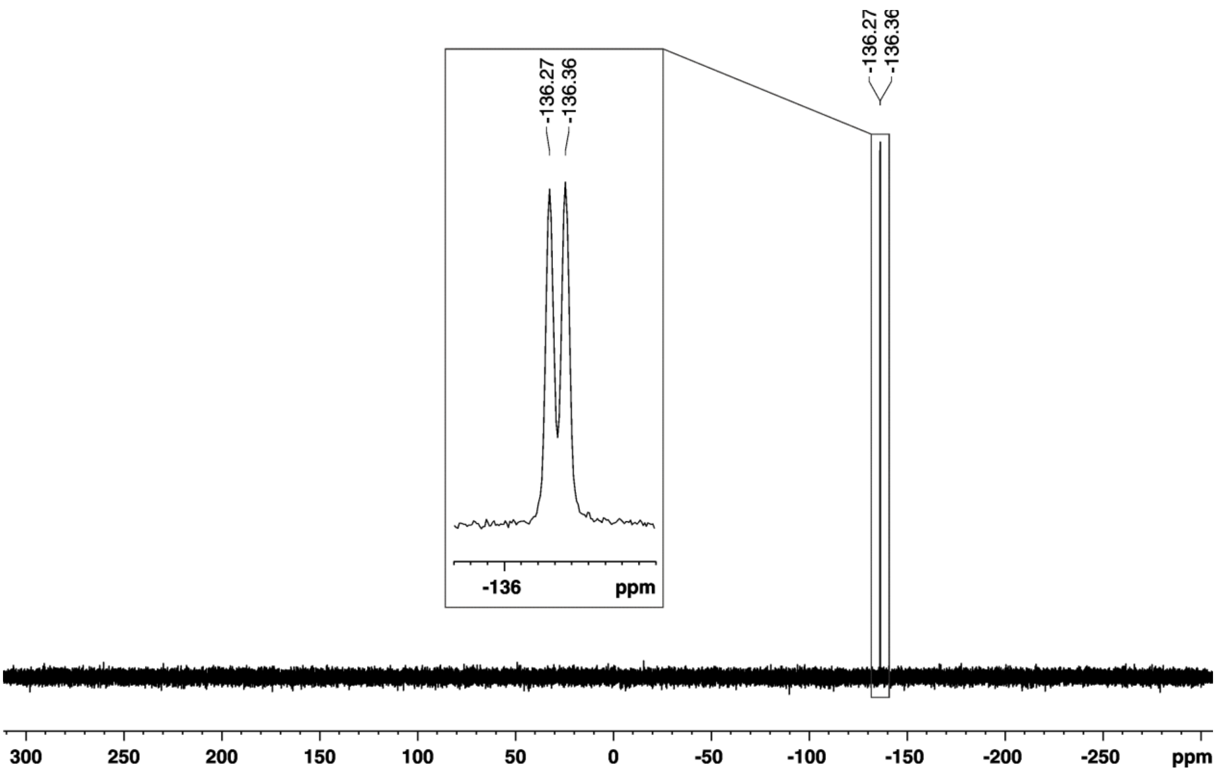

Figure S4 ^{31}P NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-*endo*-H-PC$_5$Ph$_3$H$_2$)] (**endo-3**).

[Cp*Fe(2-*exo*-H-PC$_5$Ph$_3$H$_2$)] (exo-3)

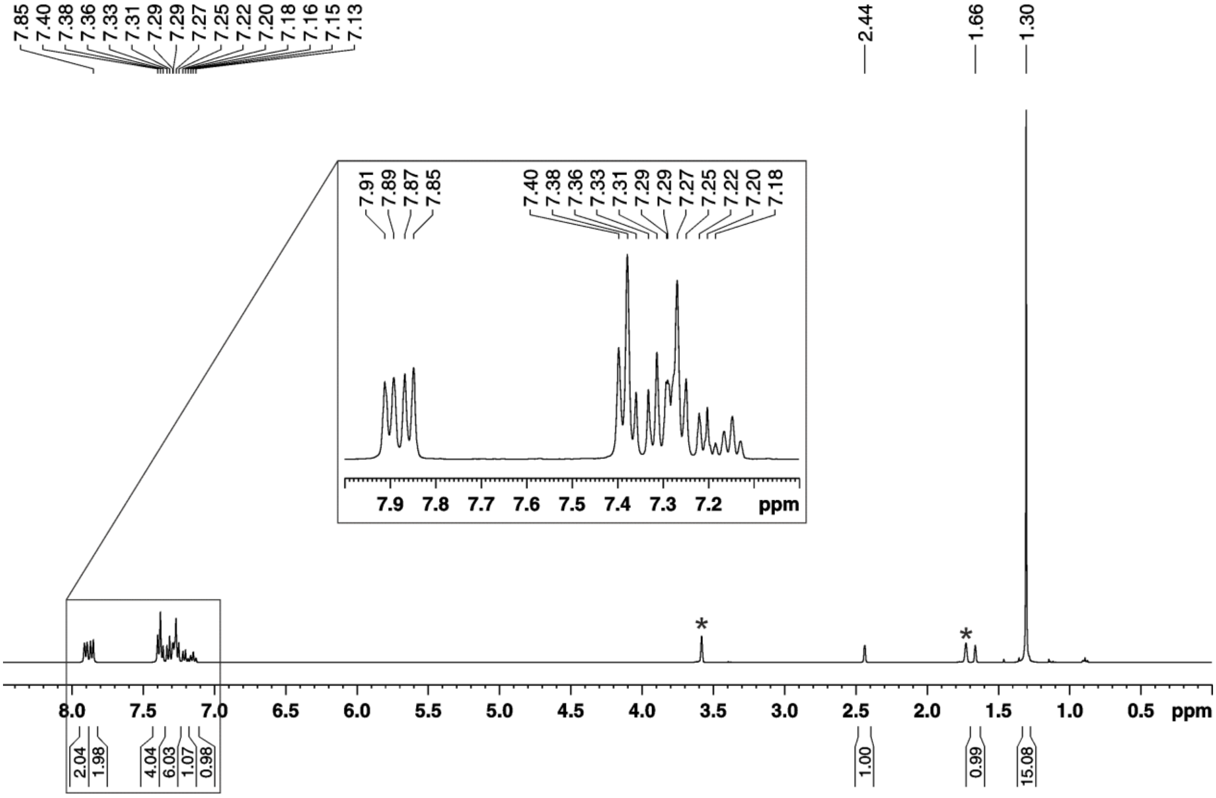

Figure S5 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-*exo*-H-PC$_5$Ph$_3$H$_2$)] (**exo-3**); * [D$_8$]THF.

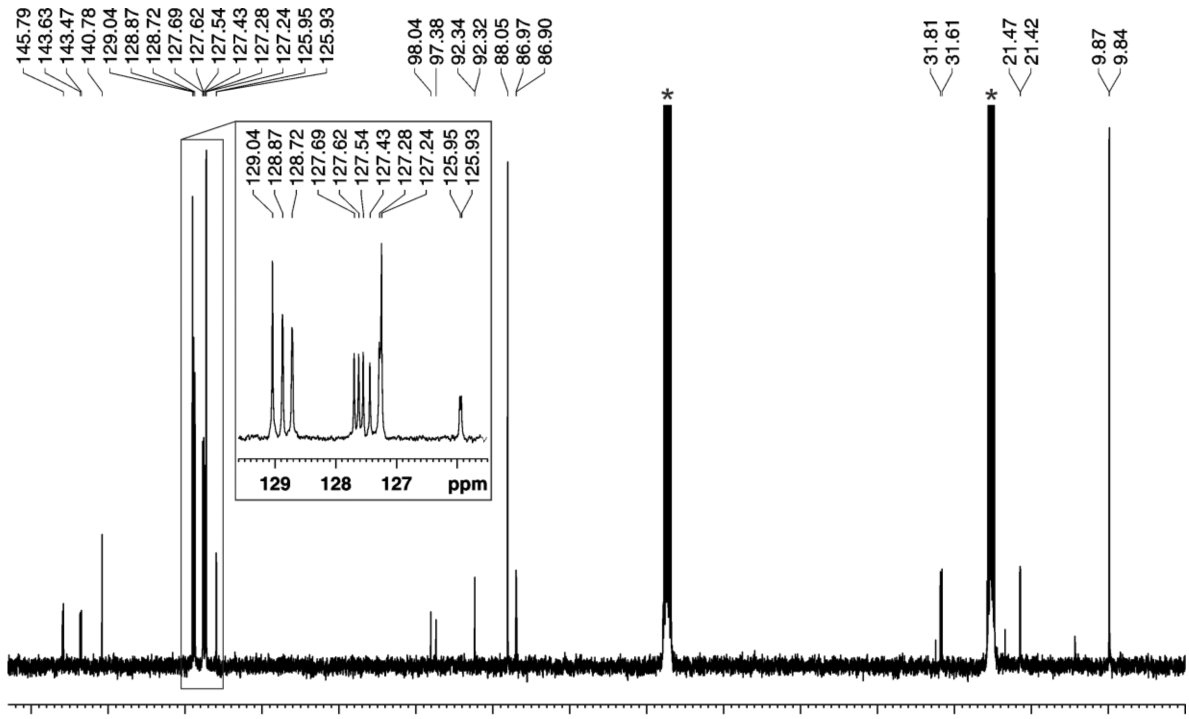

Figure S6 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-*exo*-H-PC$_5$Ph$_3$H$_2$)] (**exo-3**); * [D$_8$]THF.

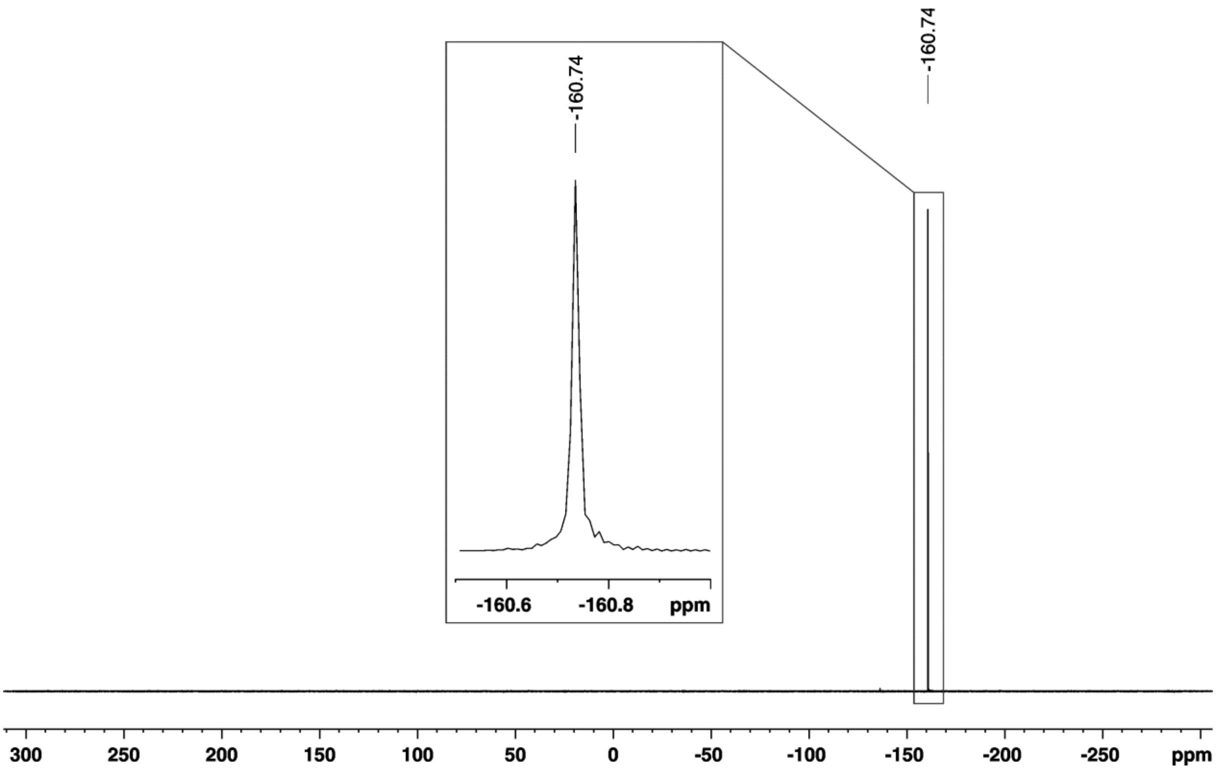

Figure S7 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-*exo*-H-PC$_5$Ph$_3$H$_2$)] (**exo-3**).

[Cp*Fe(1-Me-PC$_5$Ph$_3$H$_2$)] (4)

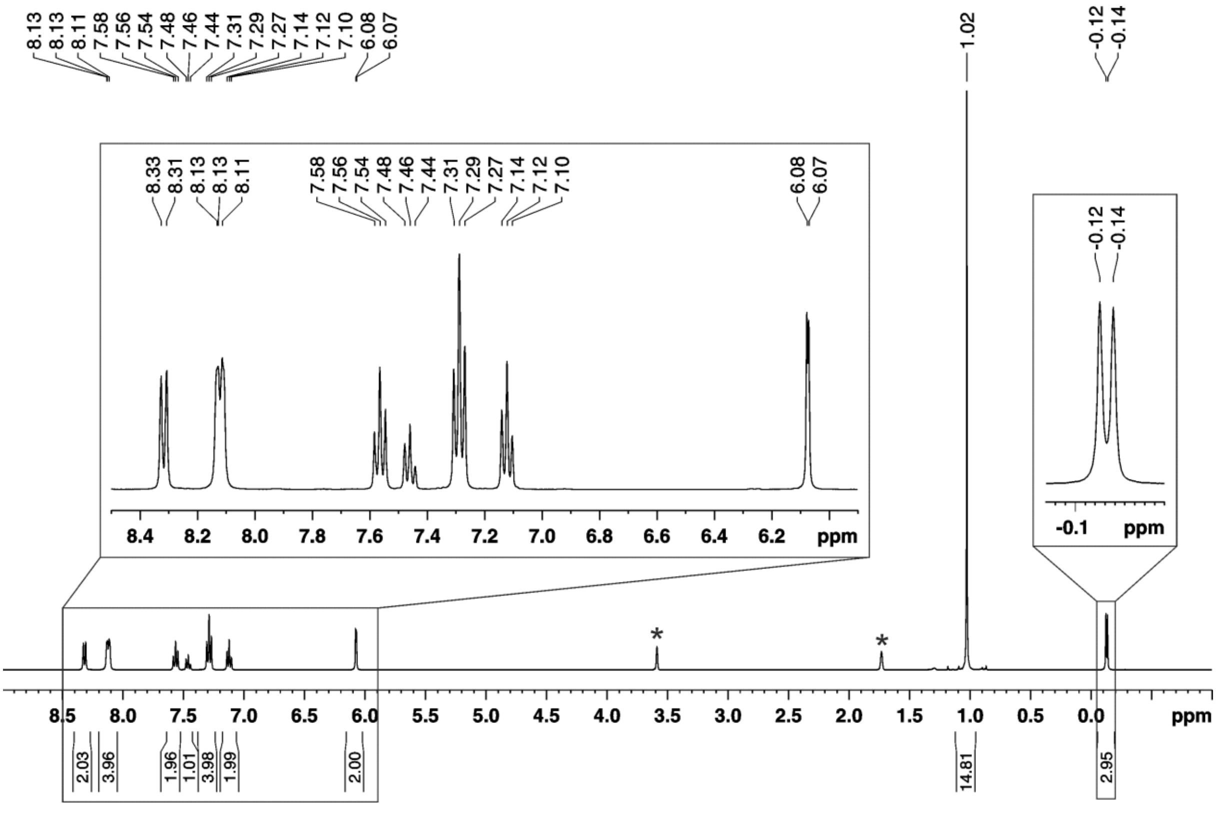

Figure S8 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Me-PC$_5$Ph$_3$H$_2$)] (**4**); * [D$_8$]THF.

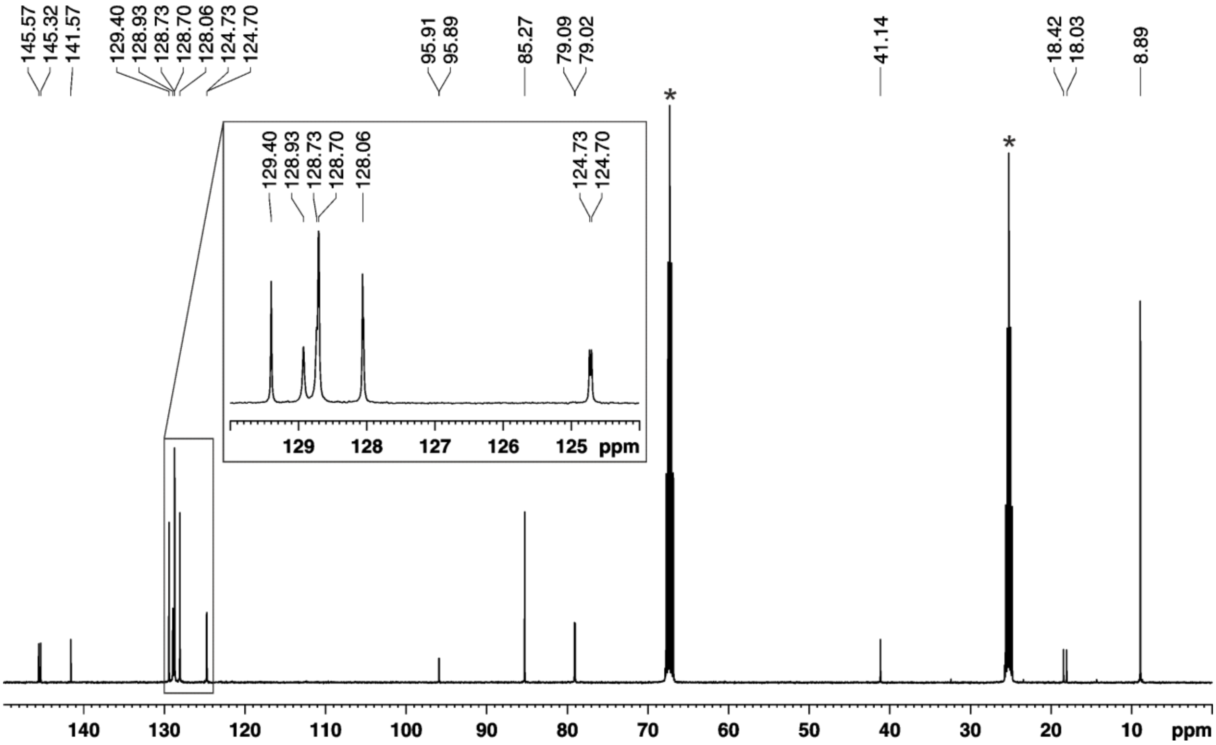

Figure S9 $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Me-PC$_5$Ph$_3$H$_2$)] (**4**); * [D$_8$]THF.

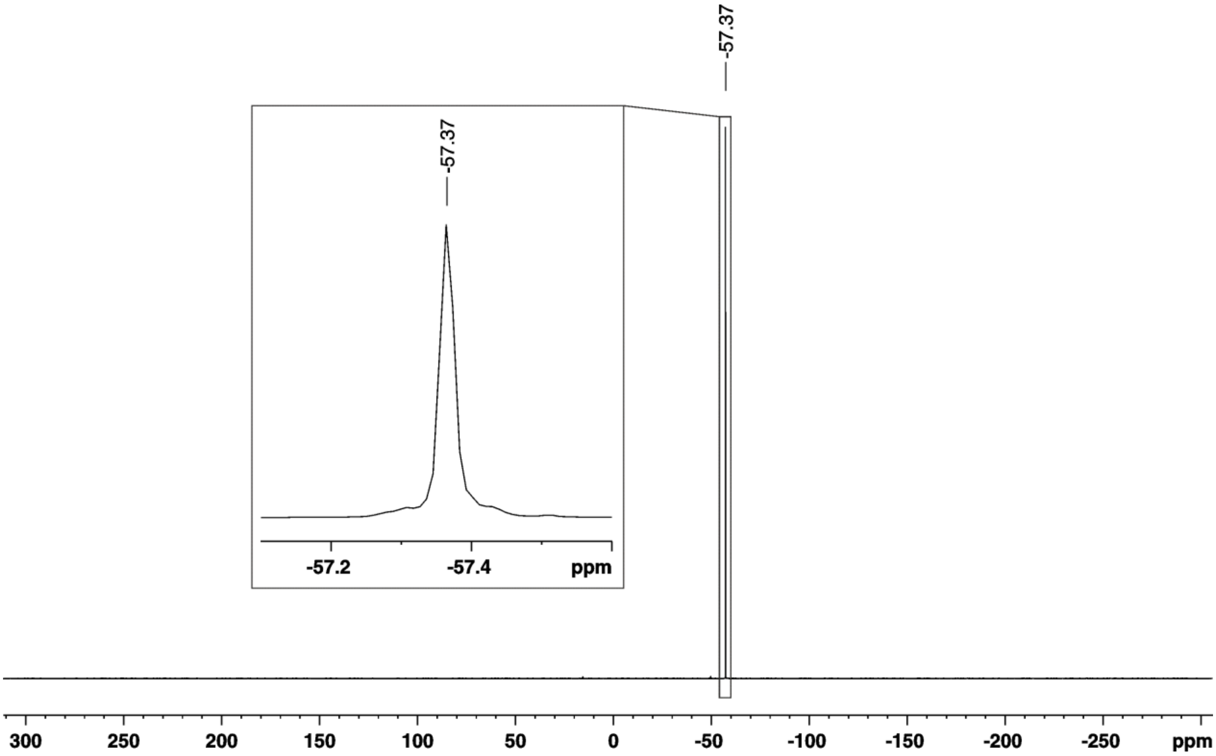

Figure S10 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Me-PC$_5$Ph$_3$H$_2$)] (**4**).

[Cp*Fe(1-Me3Si-PC5Ph3H2)] (5)

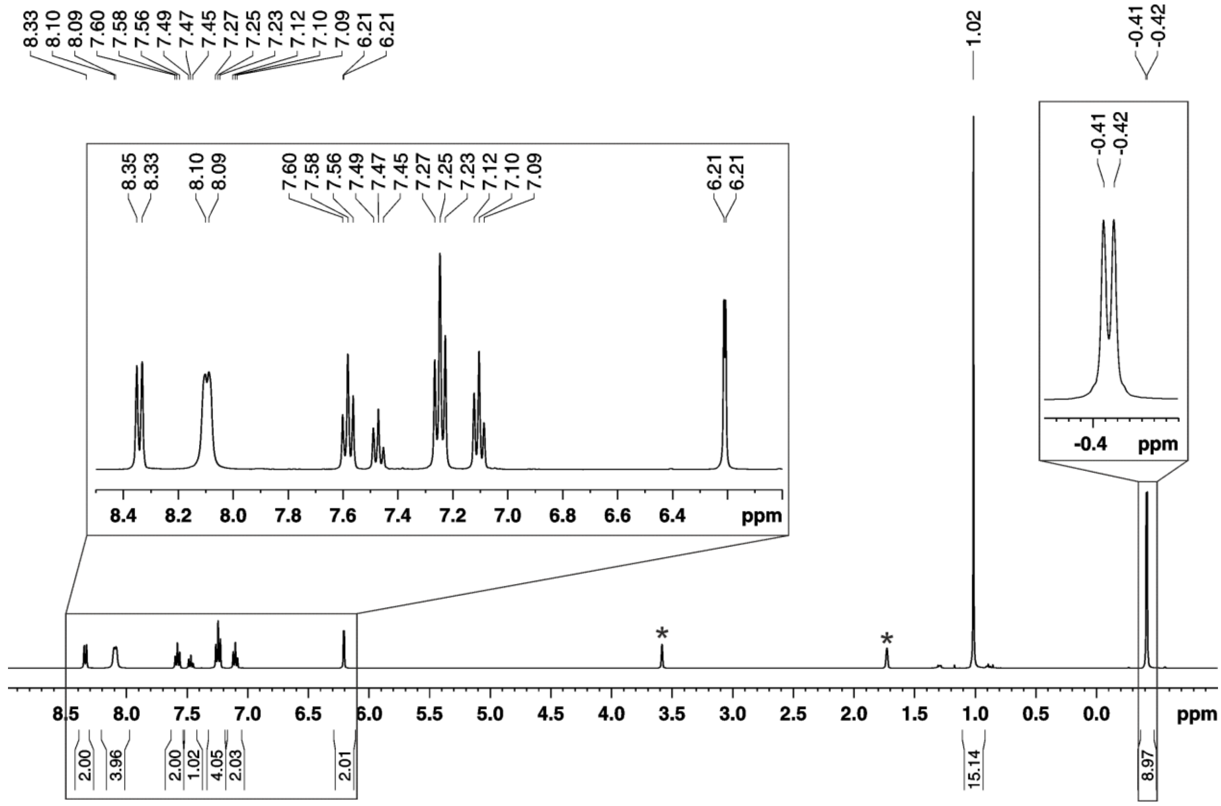

Figure S11 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Me$_3$Si-PC$_5$Ph$_3$H$_2$)] (**5**); * [D$_8$]THF.

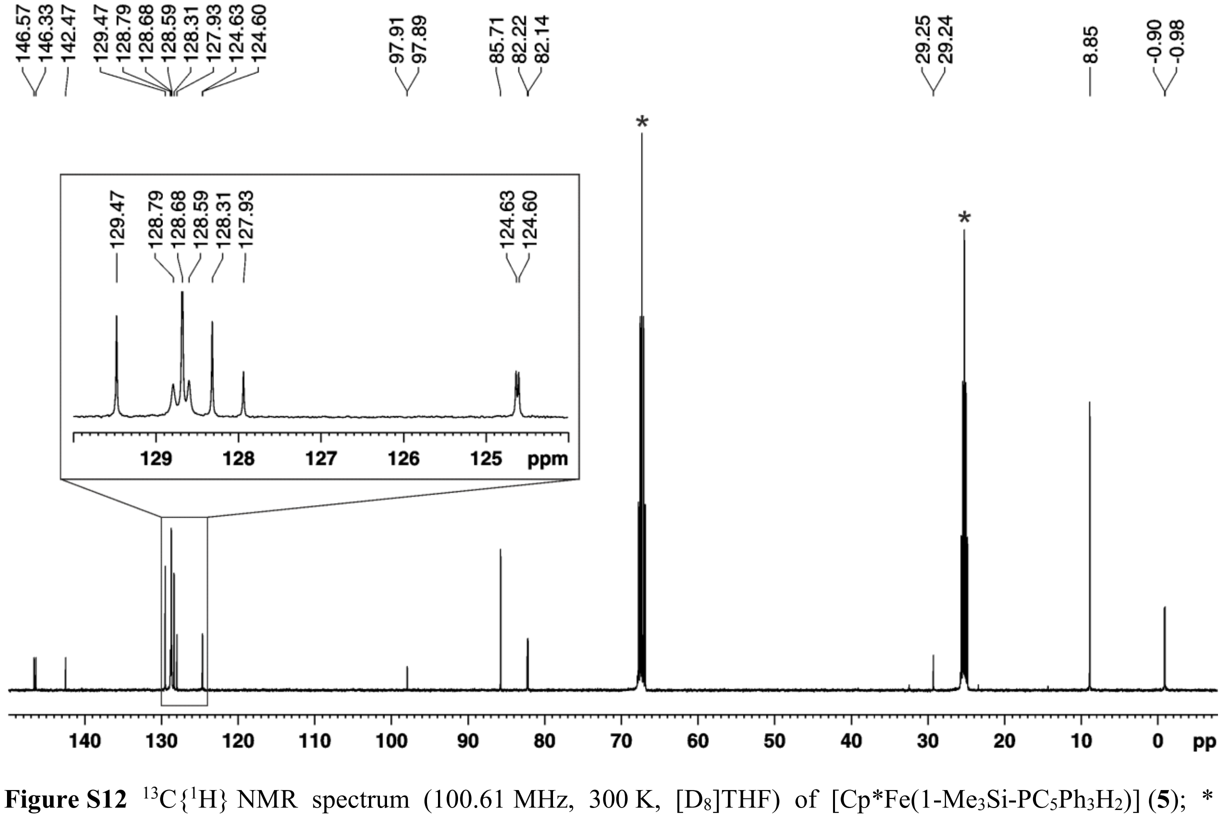

Figure S12 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-Me$_3$Si-PC$_5$Ph$_3$H$_2$)] (**5**); * [D$_8$]THF.

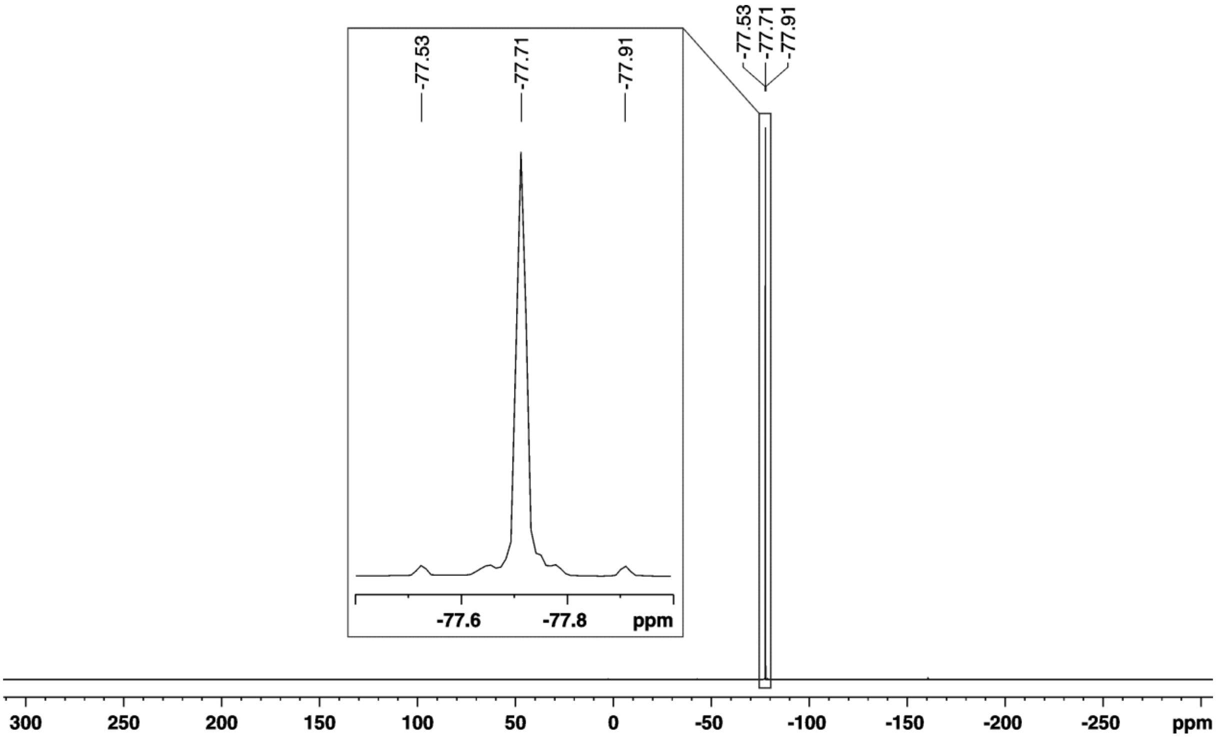

Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of [Cp*Fe(1-Me_3Si-$PC_5Ph_3H_2$)] (**5**).

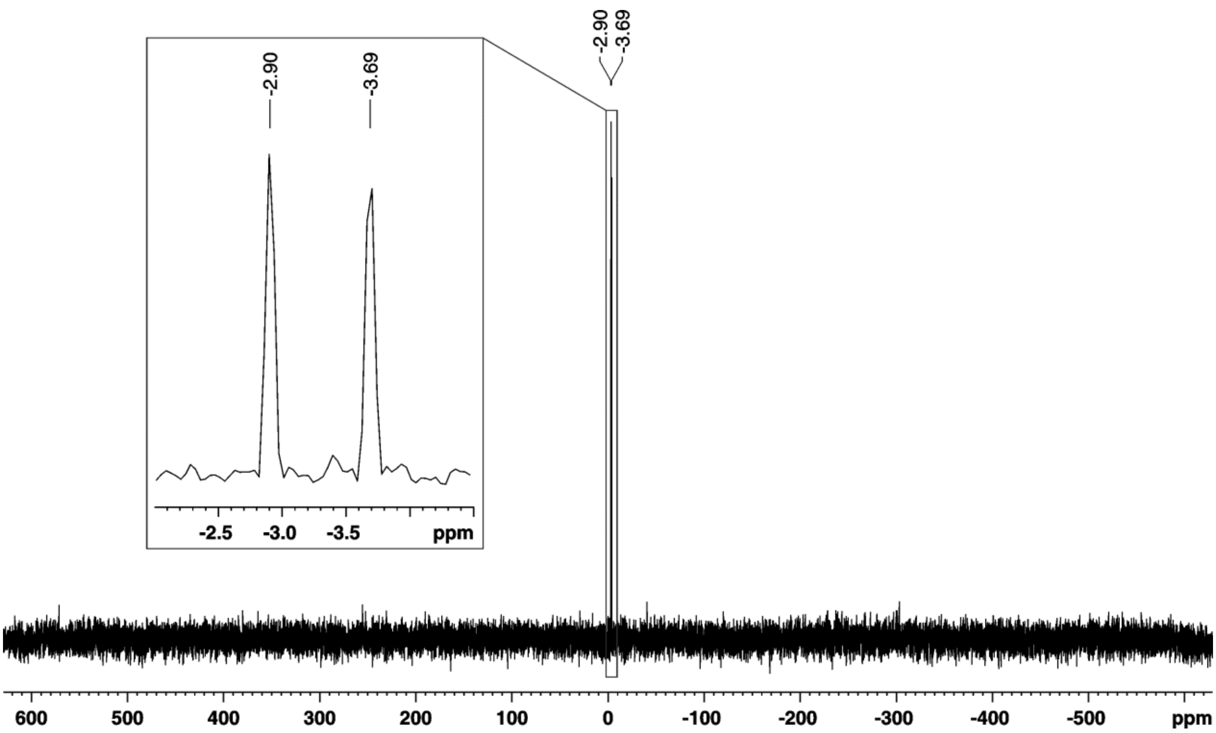

Figure S14 ^{29}Si DEPT NMR spectrum (79.49 MHz, 300 K, [D_8]THF) of [Cp*Fe(1-Me_3Si-$PC_5Ph_3H_2$)] (**5**).

[Cp*Fe(1-PPh2-PC5Ph3H2)] (6)

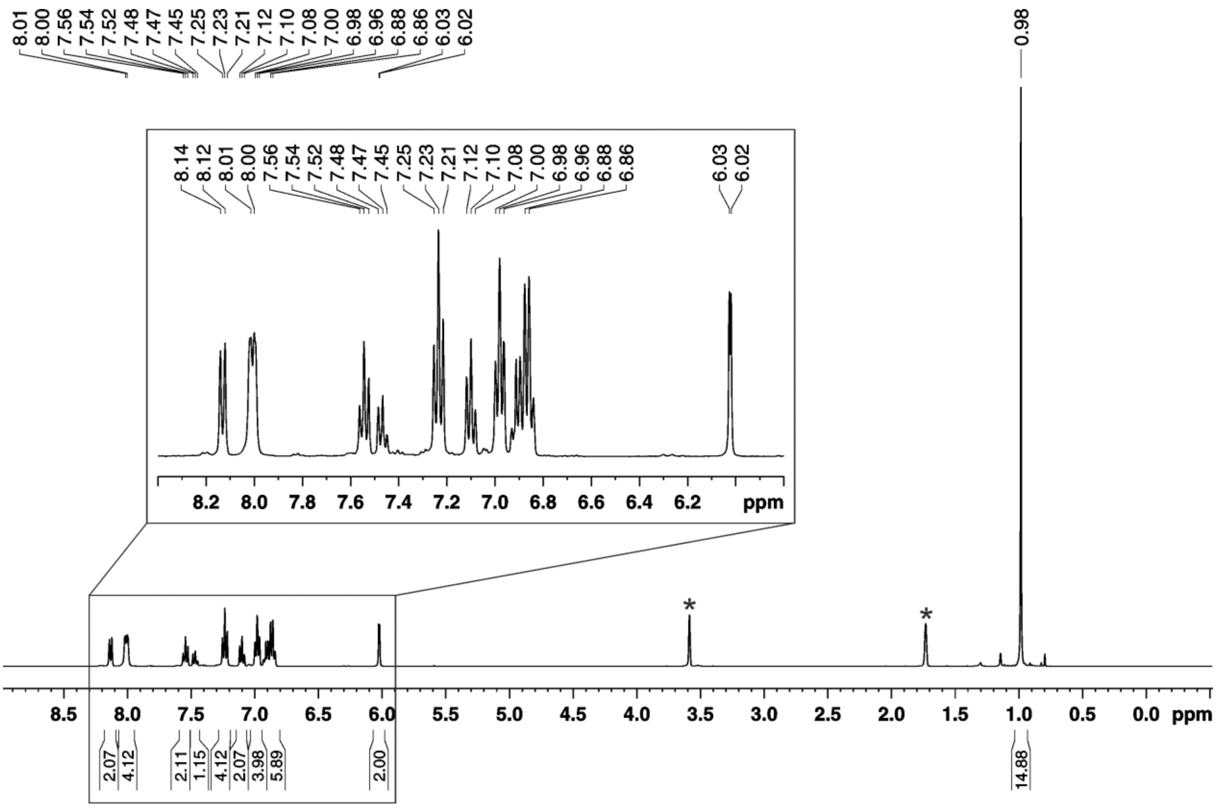

Figure S15 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-PPh$_2$-PC$_5$Ph$_3$H$_2$)] (**6**); * [D$_8$]THF.

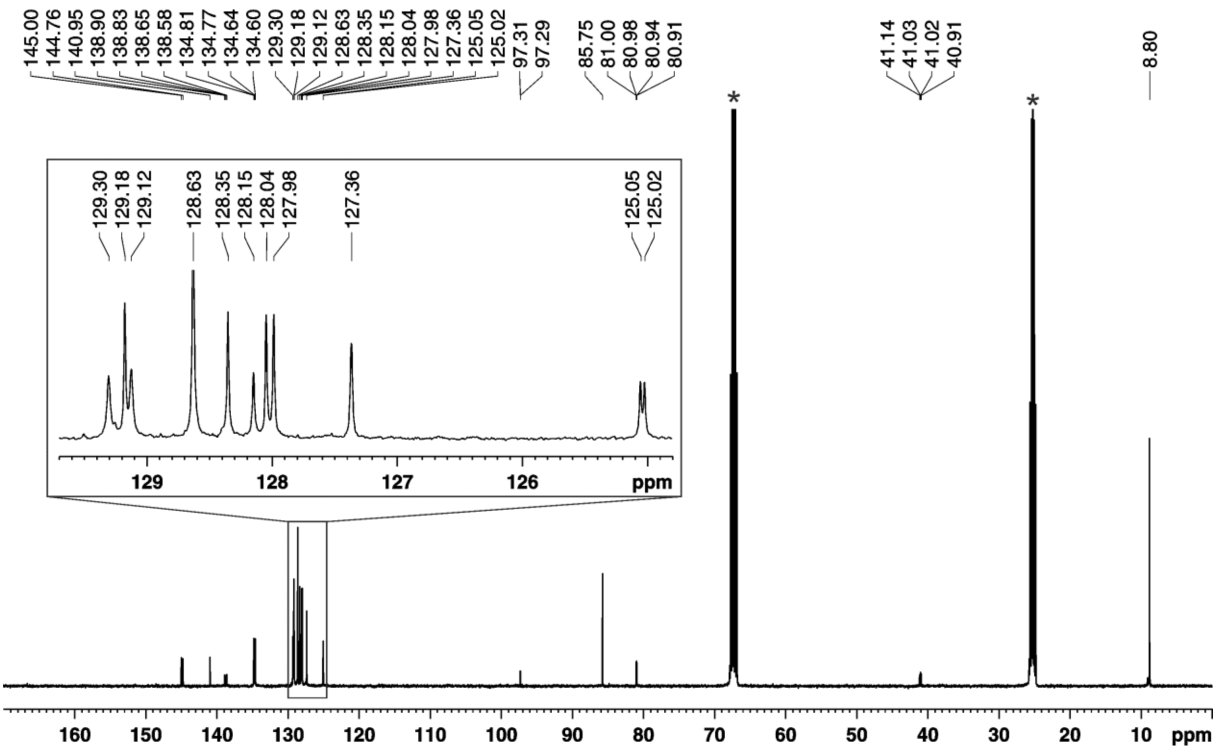

Figure S16 ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(1-PPh$_2$-PC$_5$Ph$_3$H$_2$)] (**6**); * [D$_8$]THF.

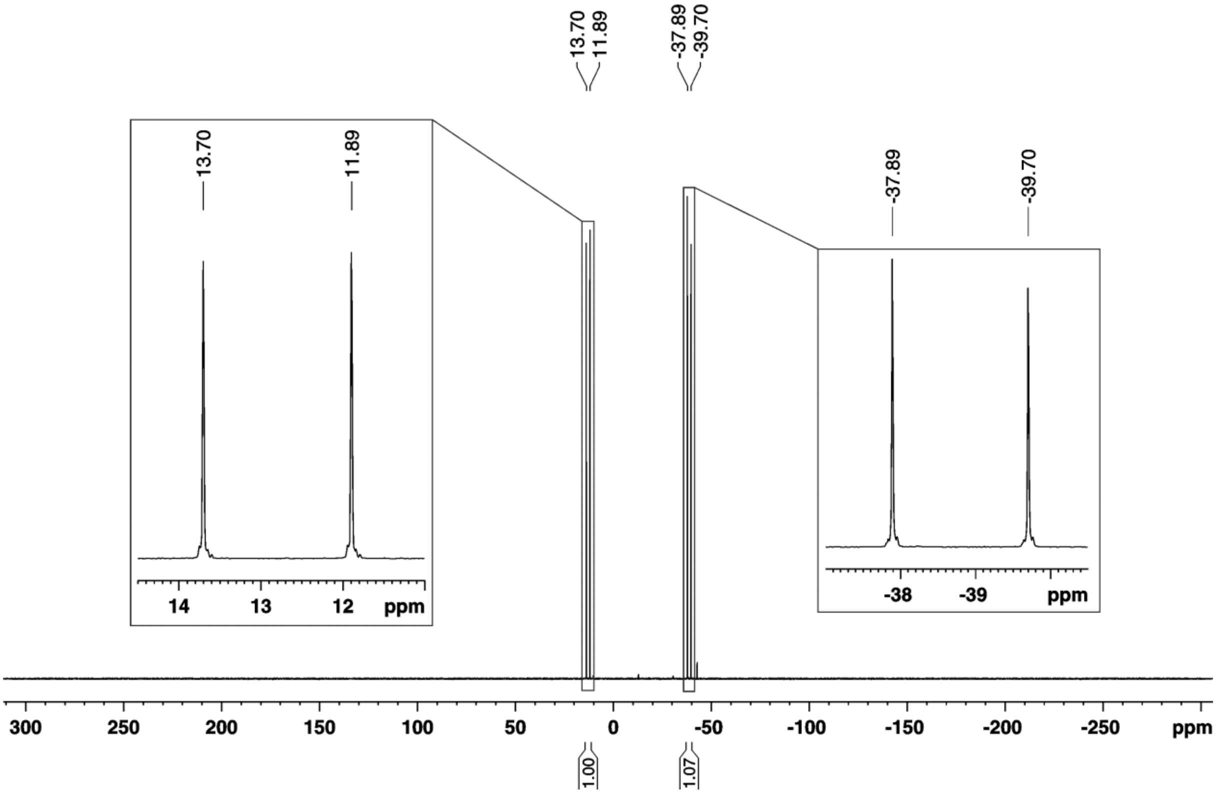

Figure S17 ^{31}P{^{1}H} NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of [Cp*Fe(1-PPh_2-$PC_5Ph_3H_2$)] (**6**).

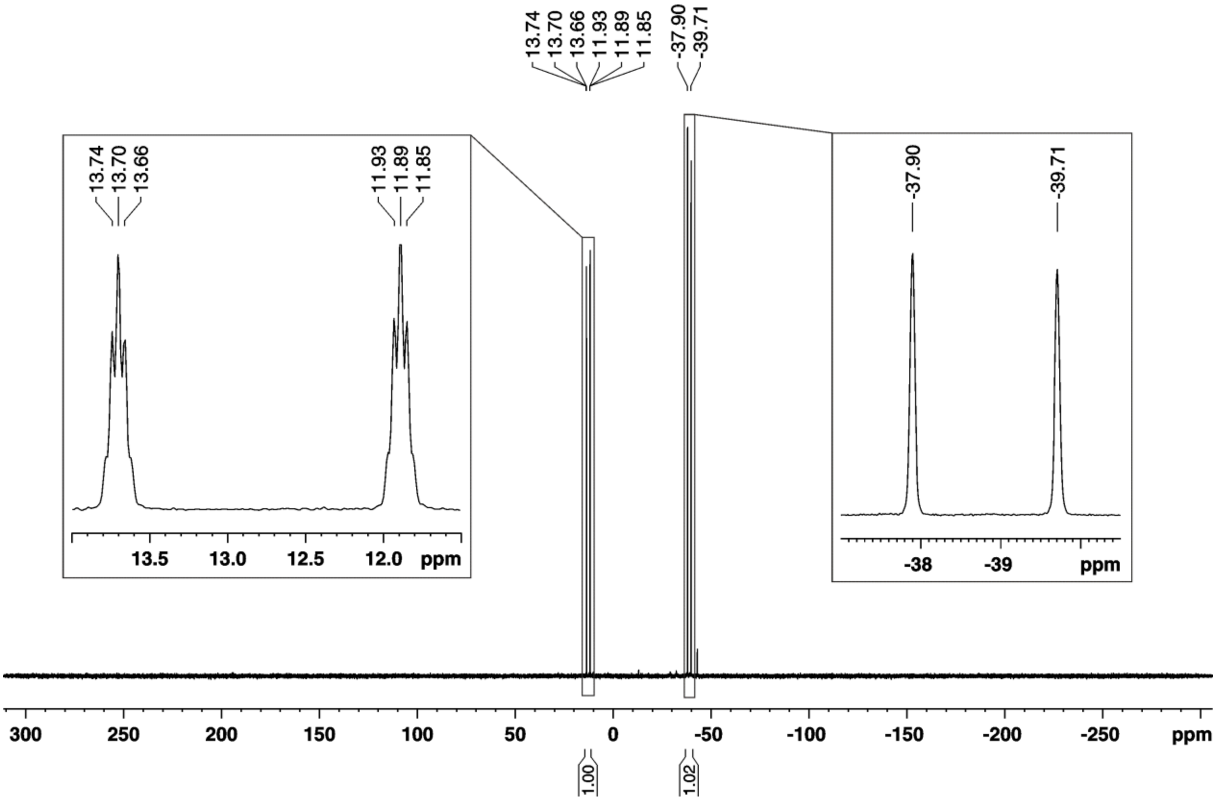

Figure S18 ^{31}P NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of [Cp*Fe(1-PPh_2-$PC_5Ph_3H_2$)] (**6**).

[Cp*Fe(2-BCat-$PC_5Ph_3H_2$)] (BCat = 2-benzo[*d*][1,3,2]dioxaborol-2-yl) (7)

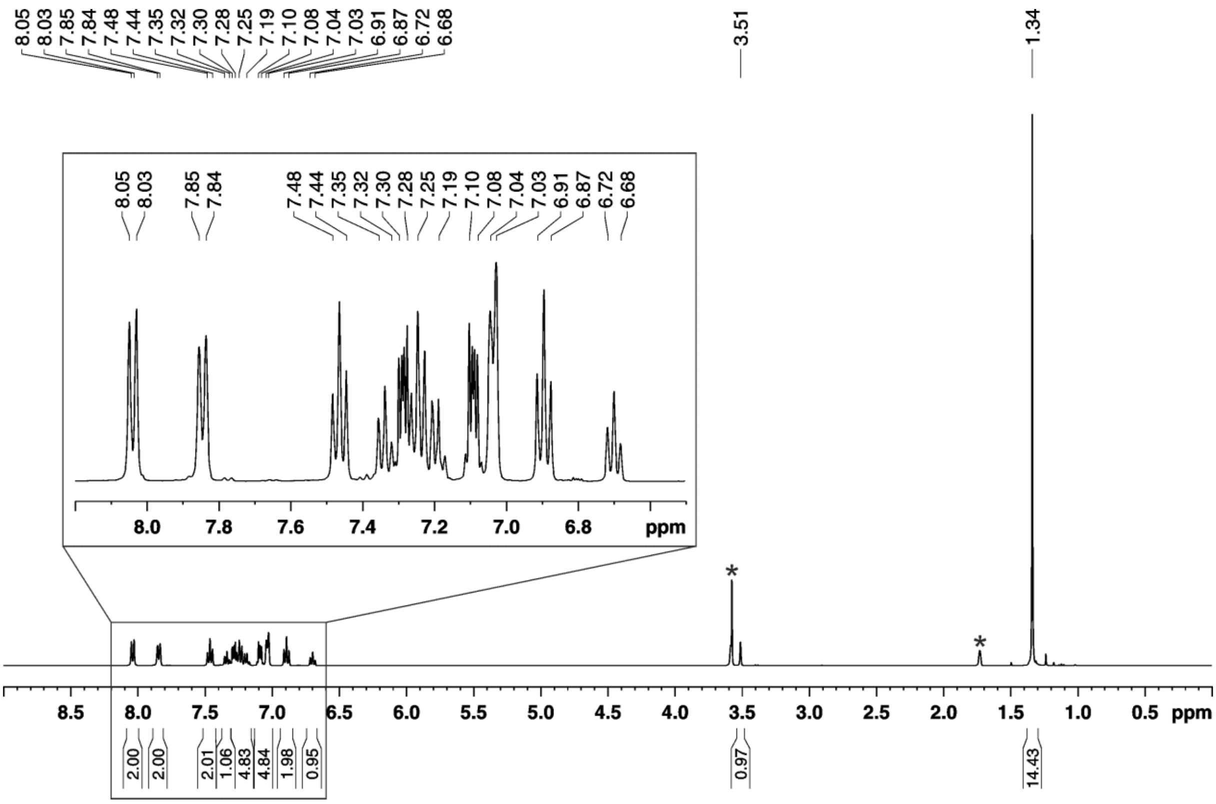

Figure S19 ^{1}H NMR spectrum (400.13 MHz, 300 K, $[D_8]$THF) of [Cp*Fe(2-BCat-$PC_5Ph_3H_2$)] (**7**); * $[D_8]$THF and [18]crown-6.

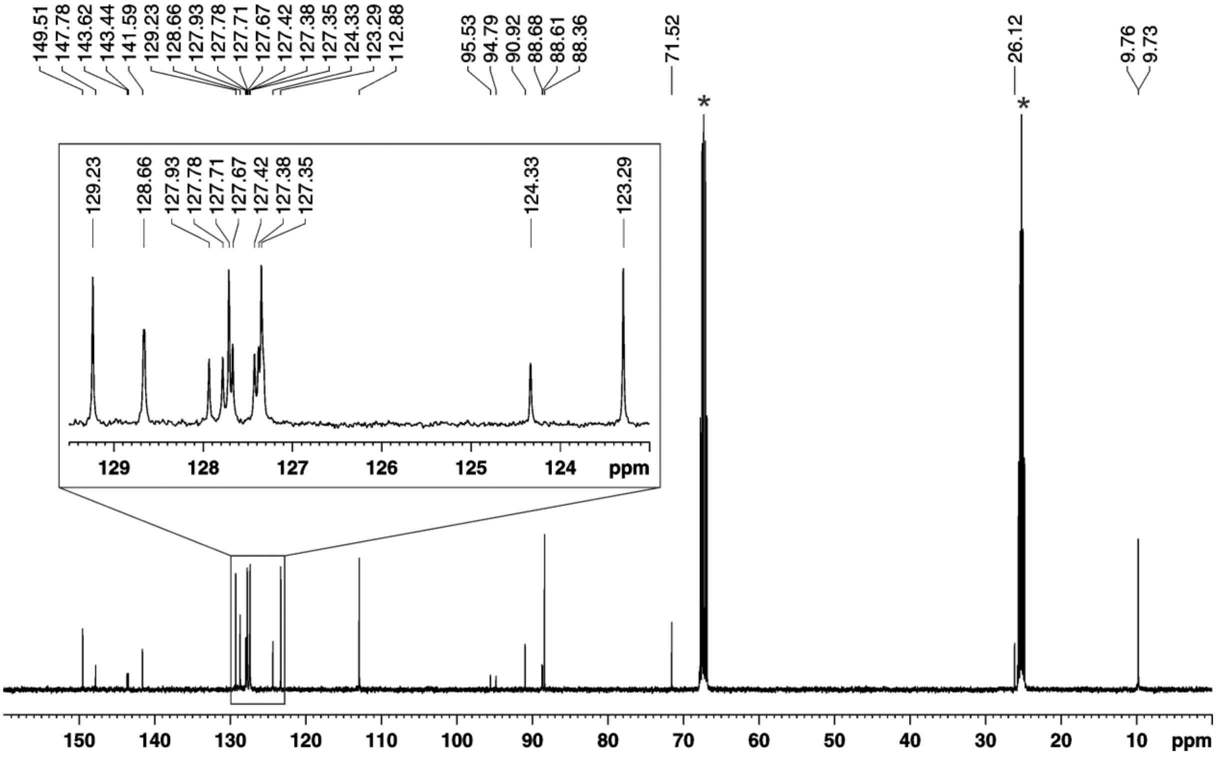

Figure S20 $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, $[D_8]$THF) of [Cp*Fe(2-BCat-$PC_5Ph_3H_2$)] (**7**); * $[D_8]$THF.

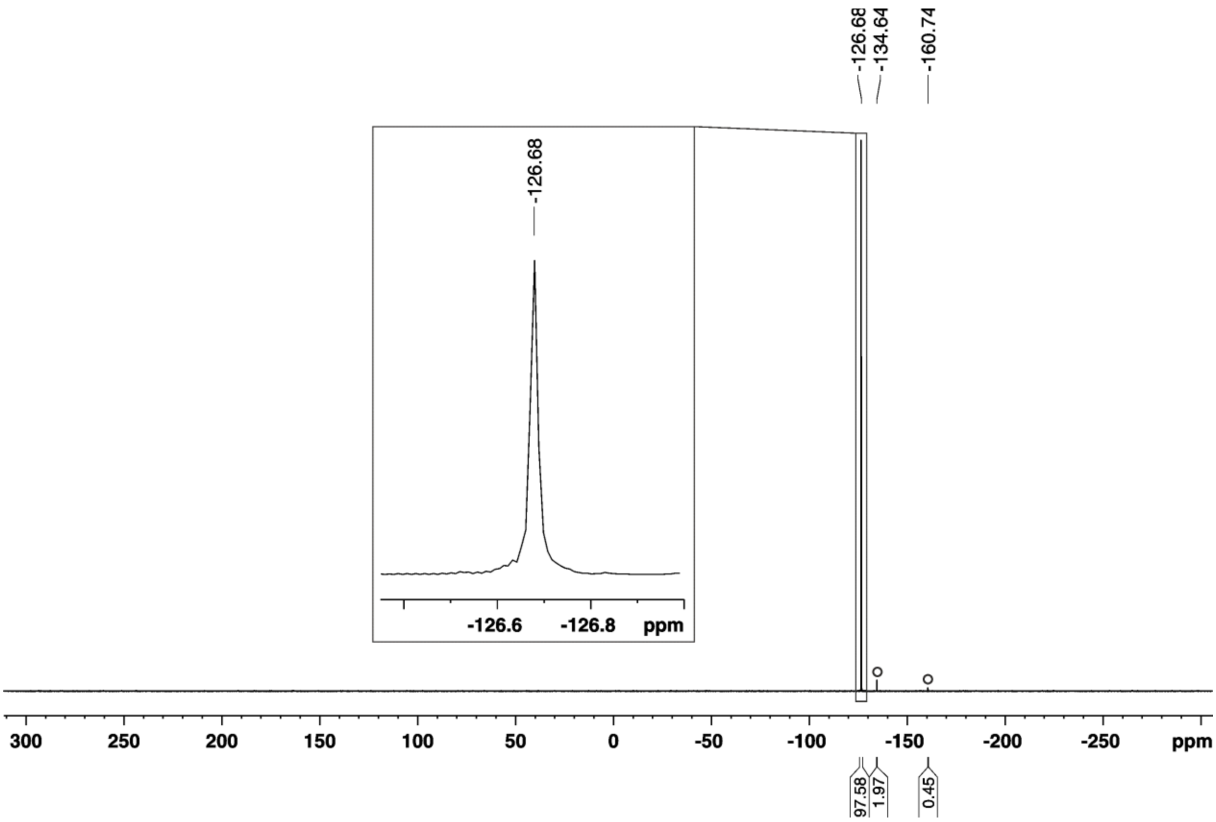

Figure S21 $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-BCat-PC$_5$Ph$_3$H$_2$)] (**7**); ○ minor impurities.

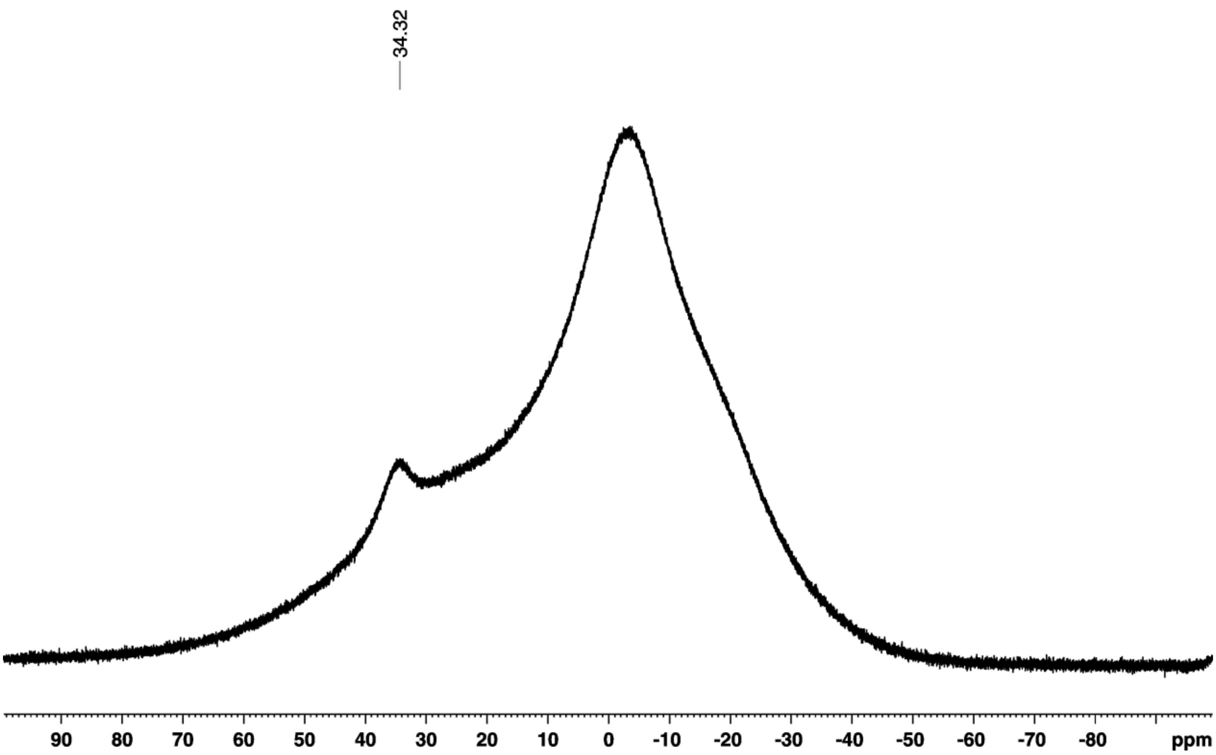

Figure S22 $^{11}B\{^{1}H\}$ NMR spectrum (128.38 MHz, 300 K, [D$_8$]THF) of [Cp*Fe(2-BCat-PC$_5$Ph$_3$H$_2$)] (**7**). The large background signal is caused by the borosilicate glass of the NMR tube.

(S5) NMR Monitoring of the reaction of 1 with chlorocatecholborane

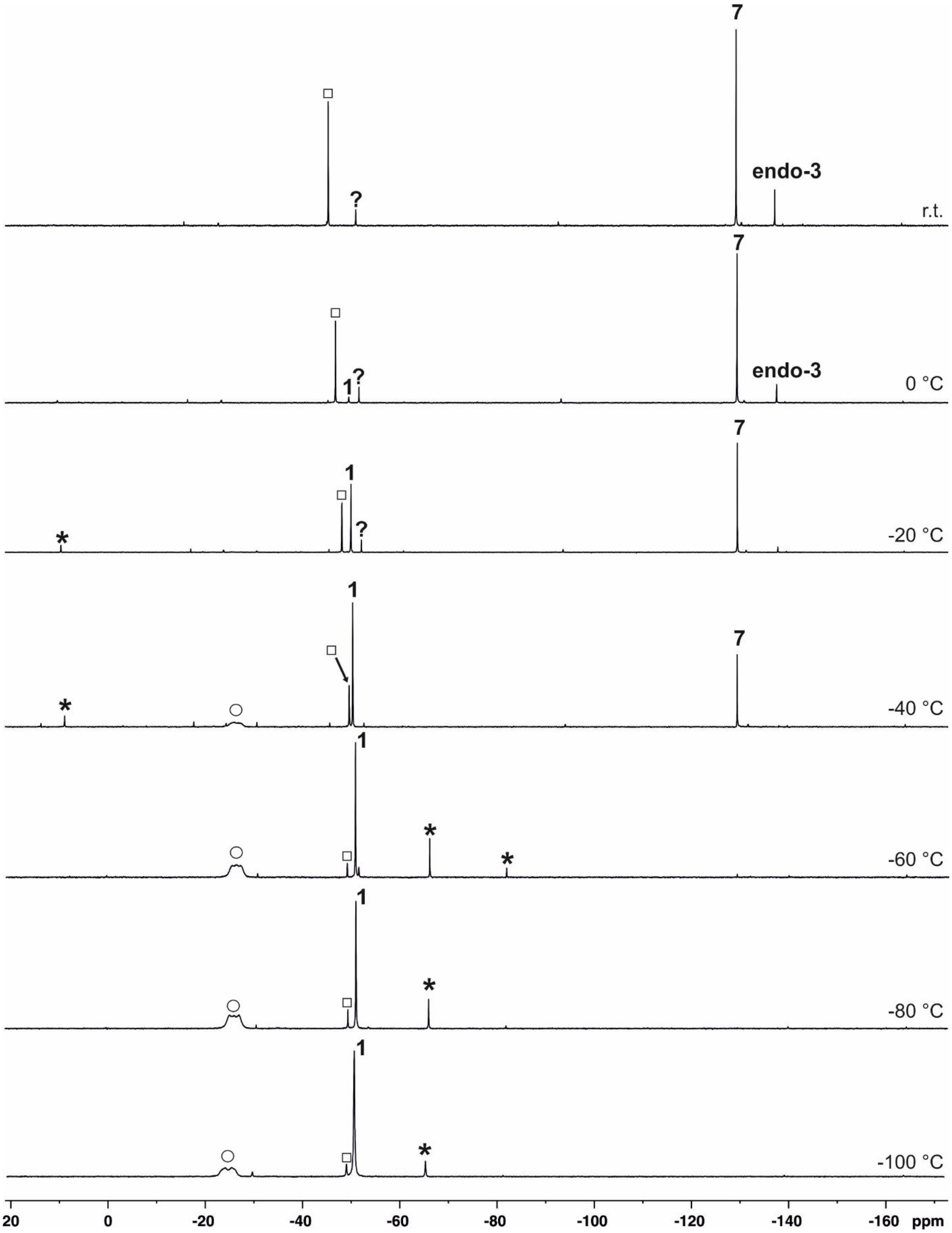

Figure S23 $^{31}P\{^1H\}$ NMR Monitoring of the reaciton of **1** with chlorocatecholborane in [D$_8$]THF. * designates unknown intermediates and **?** and unidentified by-products formed below room temperature, □ diphosphinine complex [Cp*$_2$Fe$_2$(μ-{PC$_5$Ph$_3$H$_2$}$_2$)], ○ presumably P−B functionalised complex [Cp*Fe(1-BCat-PC$_5$Ph$_3$H$_2$)] (BCat = 2-benzo[*d*][1,3,2]dioxaborol-2-yl).

(S3) UV-vis Spectra

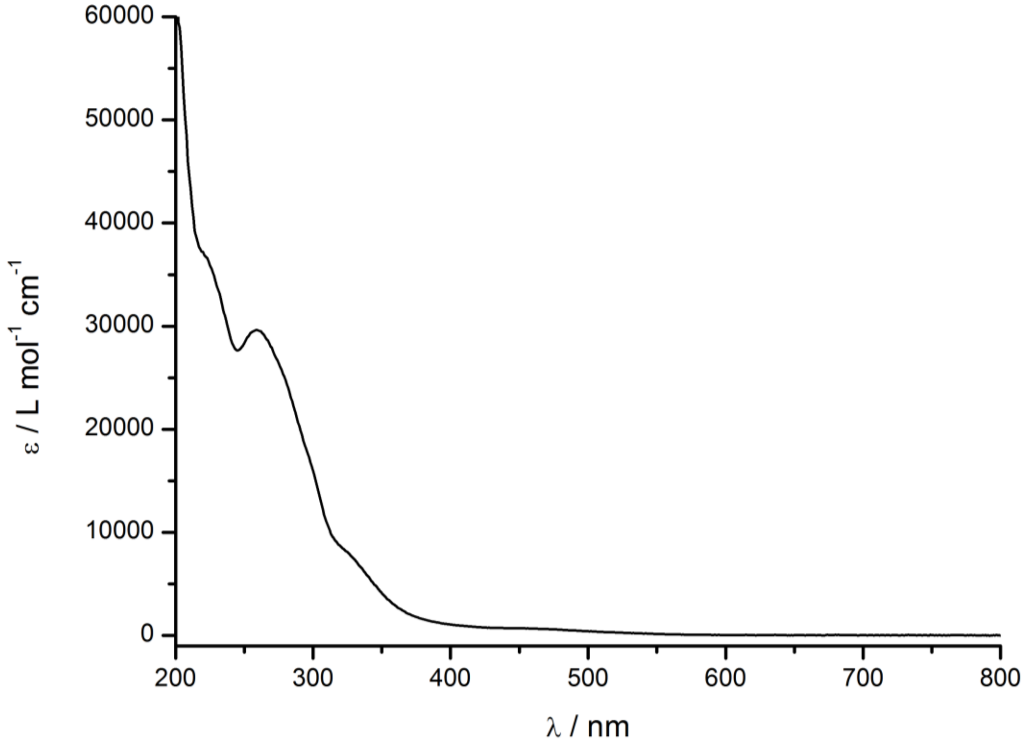

Figure S24 UV/vis spectrum of [Cp*Fe(2-*endo*-H-$PC_5Ph_3H_2$)] (**endo-3**) in *n*-hexane.

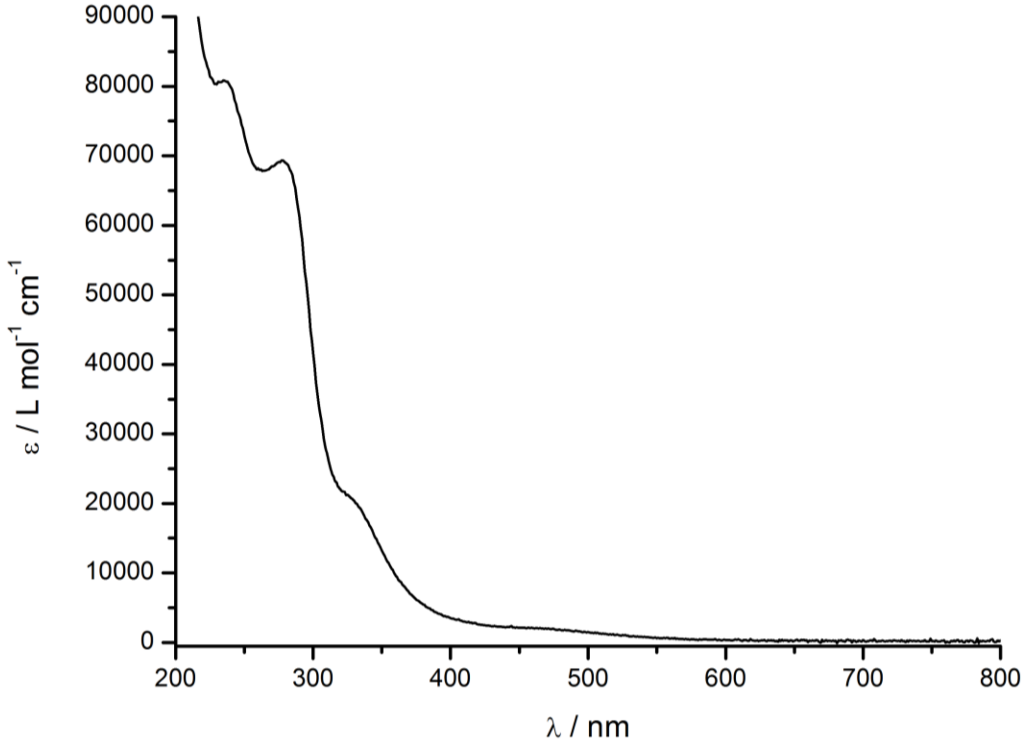

Figure S25 UV/vis spectrum of [Cp*Fe(2-*exo*-H-$PC_5Ph_3H_2$)] (**exo-3**) in *n*-hexane.

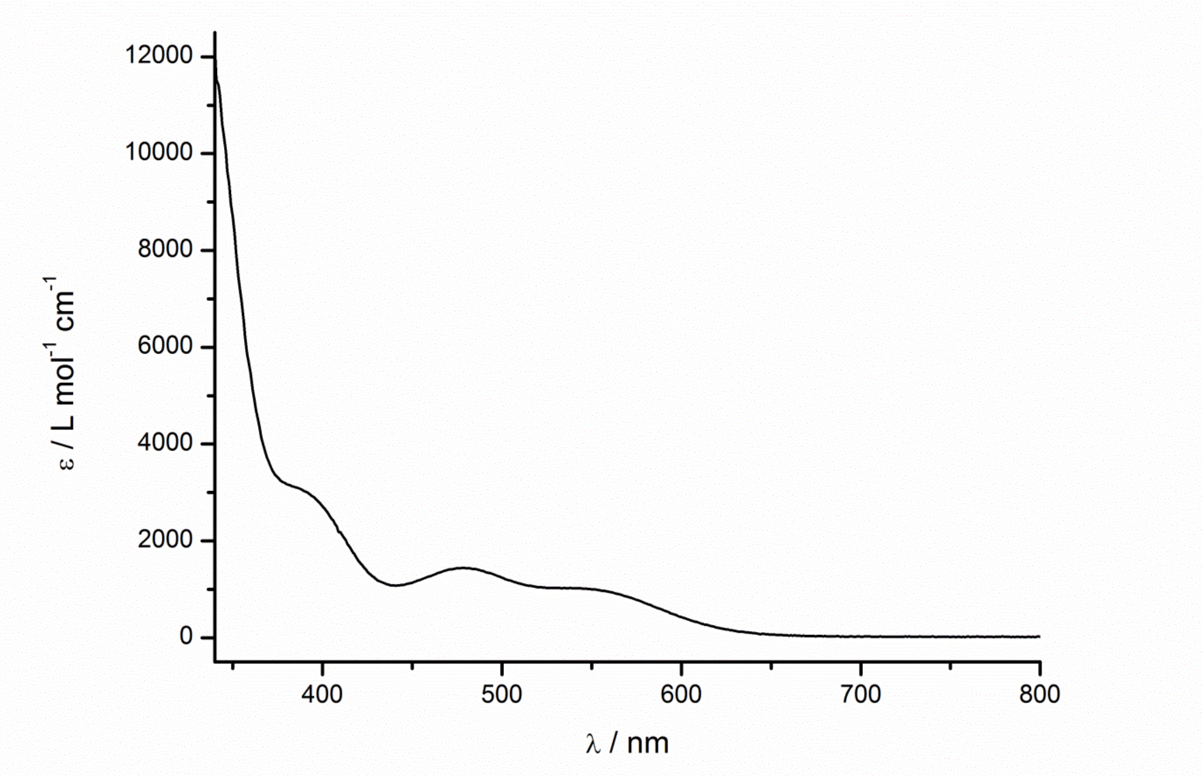

Figure S26 UV/vis spectrum of [Cp*Fe(1-Me-$PC_5Ph_3H_2$)] (**4**) in *n*-hexane.

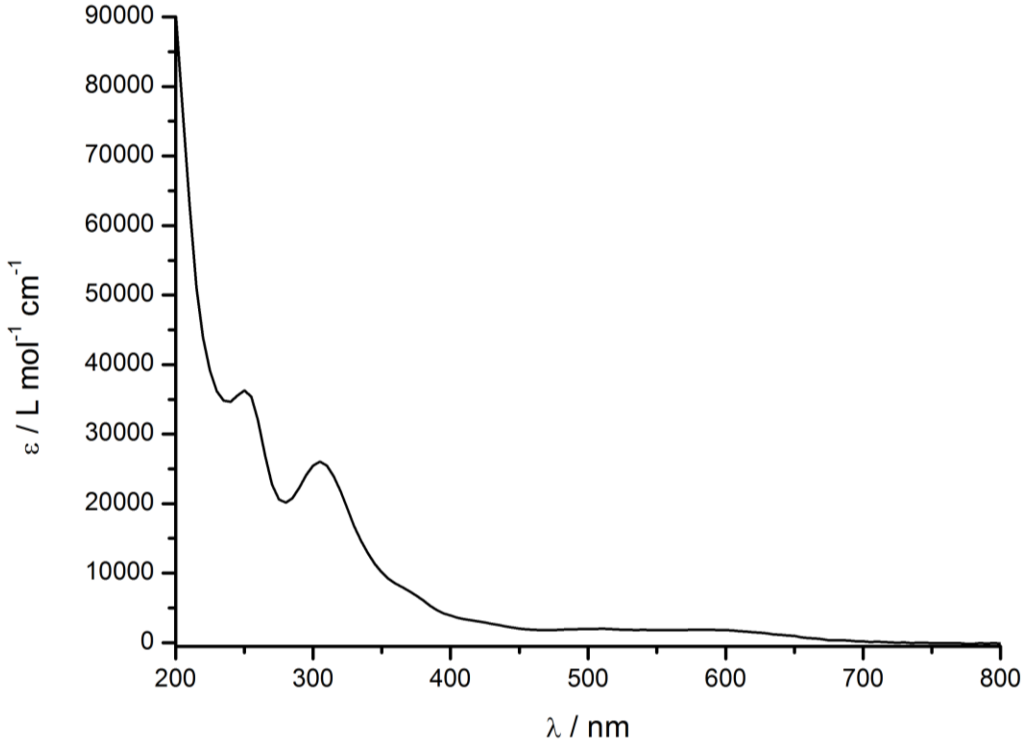

Figure S27. UV/vis spectrum of [Cp*Fe(1-Me_3Si-$PC_5Ph_3H_2$)] (**5**) in *n*-hexane.

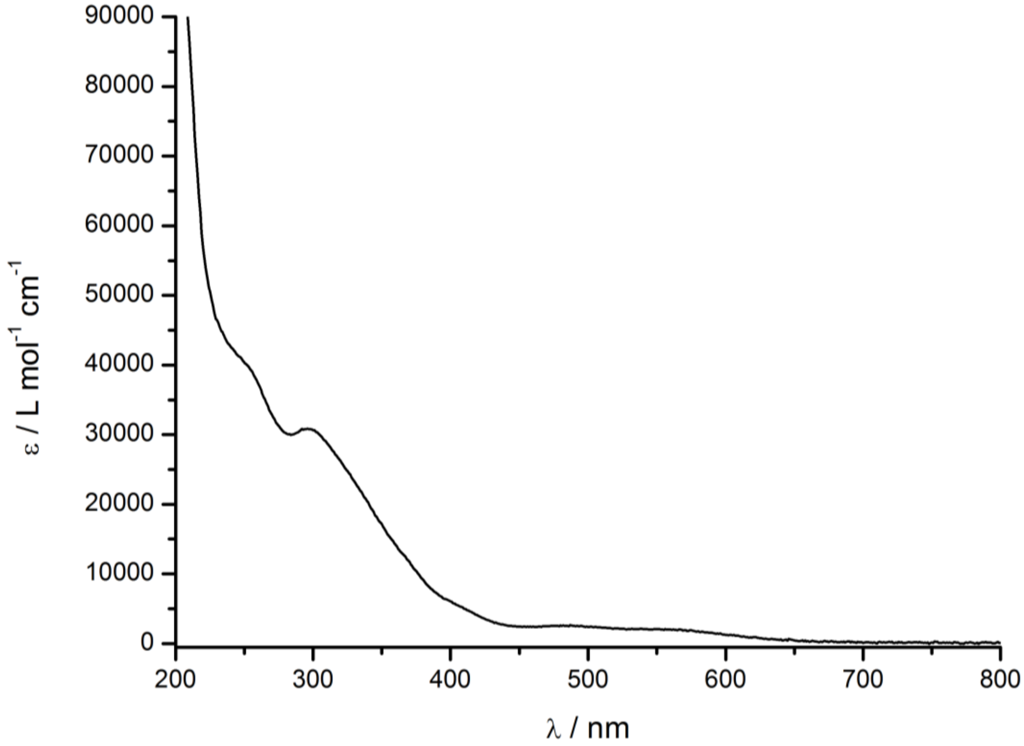

Figure S28 UV/vis spectrum of [Cp*Fe(1-PPh_2-$PC_5Ph_3H_2$)] (**6**) in *n*-hexane.

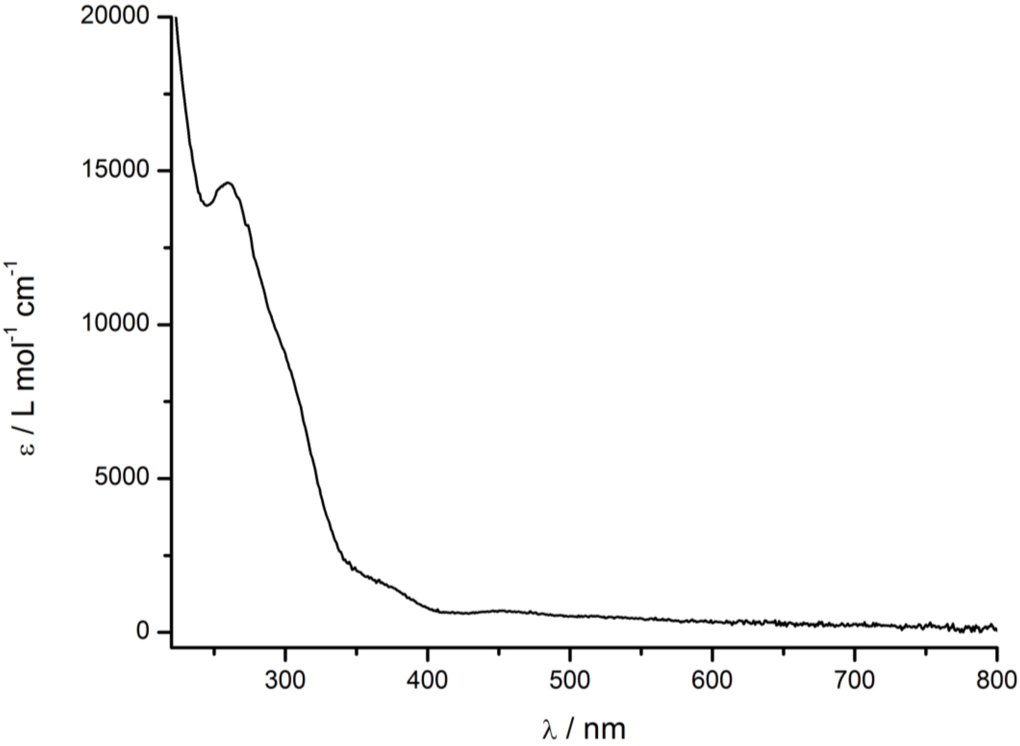

Figure S29 UV/vis spectrum of [Cp*Fe(2-BCat-$PC_5Ph_3H_2$)] (**7**) in *n*-hexane.

(S4) X-ray crystallography

Table S1. Crystallographic data and structure refinement of **endo-3**, **exo-3** and **4**.

	endo-3	**exo-3**	**4**
Empirical formula	$C_{33}H_{33}FeP$	$C_{33}H_{33}FeP$	$C_{34}H_{35}FeP$
Formula weight / g·mol^{-1}	516.41	516.41	530.44
Temperature / K	123.0(1)	123.(1)	123.(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a / Å	10.6858(1)	8.5501(1)	9.89052(5)
b / Å	12.90255(8)	19.9687(3)	16.24733(7)
c / Å	19.4099(2)	15.1620(2)	17.1954(1)
α /°	90	90	90
β /°	103.8168(8)	91.561(1)	99.3153(5)
γ /°	90	90	90
V / Å^3	2598.69(4)	2587.71(5)	2587.71(5)
Z	4	4	4
ρ_{calc} / g cm^{-1}	1.320	1.326	1.292
μ / mm^{-1}	5.367	5.390	5.128
F(000)	1088.0	1088.0	1120.0
Crystal size / mm^3	0.24 × 0.12 × 0.12	0.17 × 0.11 × 0.11	0.40 × 0.28 × 0.13
Radiation / Å	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)
2Θ range for data collection /°	8.304 − 147.364	7.322 − 133.446	7.534 − 147.134
Diffractometer	Agilent Technologies SuperNova	Agilent Technologies Gemini Ultra R	Agilent Technologies SuperNova
Index ranges	$-12 \leq h \leq 13$ $-15 \leq k \leq 16$ $-23 \leq l \leq 24$	$-10 \leq h \leq 9$ $-23 \leq k \leq 21$ $-18 \leq l \leq 17$	$-12 \leq h \leq 12$ $-20 \leq k \leq 20$ $-19 \leq l \leq 21$
Reflections collected	38029	16543	78382
Independent reflections	5187 [R_{int} = 0.0286, R_{sigma} = 0.0142]	4548 [R_{int} = 0.0318, R_{sigma} = 0.0270]	5489 [R_{int} = 0.0357, R_{sigma} = 0.0133]
Data/restraints/parameters	5187/0/321	4548/0/321	5489/0/331
Goodness-of-fit on F^2	1.071	1.074	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0767	R_1 = 0.0332, wR_2 = 0.0803	R_1 = 0.0291, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0785	R_1 = 0.0363, wR_2 = 0.0856	R_1 = 0.0302, wR_2 = 0.0774
Largest diff. peak/hole / e Å^{-3}	0.47/−0.44	0.65/−0.40	0.45/−0.35

Table S2 Crystallographic data and structure refinement of **5**, **6** and **7**.

	5	**6**	**7**
Empirical formula	$C_{36}H_{41}FePSi$	$C_{45}H_{42}FeP_2$	$C_{45}H_{48}BFeO_5P$
Formula weight / g·mol^{-1}	588.60	700.57	766.46
Temperature / K	123.(1)	123.(1)	123.(1)
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a / Å	10.6876(2)	20.8847(5)	11.4433(3)
b / Å	16.4330(3)	8.5330(2)	12.5938(3)
c / Å	17.8191(3)	22.0647(5)	15.2161(5)
α /°	90	90	99.662(3)
β /°	90	116.708(3)	105.624(3)
γ /°	90	90	108.818(3)
V / Å^3	3129.5(1)	3512.6(2)	1919.3(1)
Z	4	4	2
ρ_{calc} / g cm^{-1}	1.249	1.325	1.326
μ / mm^{-1}	4.871	4.536	3.910
F(000)	1248.0	1472.0	808.0
Crystal size / mm^3	0.50 × 0.48 × 0.32	0.16 × 0.13 × 0.10	0.38 × 0.35 × 0.18
Radiation / Å	CuK$_\alpha$ (λ = 1.54184)	CuK$_\alpha$ (λ = 1.54184)	CuK$_\alpha$ (λ = 1.54184)
2Θ range for data collection /°	7.318 − 133.654	8.046 − 147.074	7.725 − 147.152
Diffractometer	Agilent Technologies Gemini Ultra R	Agilent Technologies SuperNova	Agilent Technologies SuperNova
Index ranges	$-12 \le h \le 8$ $-19 \le k \le 16$ $-21 \le l \le 20$	$-25 \le h \le 25$ $-10 \le k \le 10$ $-27 \le l \le 27$	$-13 \le h \le 14$ $-15 \le k \le 10$ $-18 \le l \le 18$
Reflections collected	9237	29452	14471
Independent reflections	5044 [R_{int} = 0.0352, R_{sigma} = 0.0468]	6984 [R_{int} = 0.0329, R_{sigma} = 0.0252]	7382 [R_{int} = 0.0224, R_{sigma} = 0.0272]
Data/restraints/parameters	5044/0/360	6984/0/438	7382/0/483
Goodness-of-fit on F^2	1.109	1.105	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1159	R_1 = 0.0358, wR_2 = 0.0974	R_1 = 0.0337, wR_2 = 0.0904
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.1177	R_1 = 0.0396, wR_2 = 0.1037	R_1 = 0.0347, wR_2 = 0.0931
Largest diff. peak/hole / e Å^{-3}	0.38/−0.62	0.44/−0.41	0.50/−0.35
Flack parameter	−0.005(5)	-	-

(S5) DFT calculations

Table S3 Electronic energies, thermal and free enthalpies of the isomeric species **2**, **endo-3** and **exo-3** calculated at the BP86/def2-TZVP level.

	2	**endo-3**	**exo-3**
electronic energy *E* / au	−2883.41927769	−2883.43186157	−2883.43046884
relative electronic energy Δ*E* / kcal mol^{-1}	7.9	0	0.9
thermal enthalpy *H* / au	−2882.84216634	−2882.85329522	−2882.85102802
relative thermal enthalpy Δ*H* / kcal mol^{-1}	7.0	0	1.4
total entropy S / au	0.09064251	0.08895247	0.09097113
298 K·S / kcal mol^{-1}	56.88	55.82	57.09
total free enthalpy *G* at 298 K / au	−2882.93280885	−2882.94224769	−2882.94199915
relative free enthalpy Δ*G* at 298 K / kcal mol^{-1}	5.9	0	0.2

Table S4 Electronic energies of the isomeric species **2**, **endo-3** and **exo-3** obtained from single-point calculations at the BP86/def2-QZVPP level on the BP86/def2-TZVP-optimized geometries.

	2	**endo-3**	**exo-3**
Electronic energy *E* / au	−2883.5476119020	−2883.5599928575	−2883.5586834141
Relative electronic energy Δ*E* / kcal mol^{-1}	7.8	0	0.8

Cartesian Coordinates of **endo-3** (optimized at the BP86/def2-TZVP level of theory)

```
Fe  4.09995155189956    6.47983273568826    14.09909805283014
P   2.00931386778806    7.36888656655403    13.70684176306973
C   4.61130078127577    7.17244586281327    15.99325005265338
C   3.70836909673193    6.42872930999598    12.05355027374068
H   4.50588804601077    6.78020747643810    11.39472376108430
C   3.86056519738851    5.11211822308561    12.59301305174481
C   1.53192835703696    5.34913235701857    15.62899613928145
C   4.78601883552313    8.21806786631848    15.01801938399994
C   6.16279018523045    6.44250326798925    14.41734098305162
C   5.45859654729511    6.07144045099255    15.61801858821391
C   3.01808102954719    4.75607595797262    13.69123447421717
H   3.10132804138977    3.75361351826409    14.10972669549537
C   5.73027493752127    7.76017116169034    14.03980405094191
```

C	4.88373051459334	4.16587584771818	12.09680599365715
C	2.16786797811237	5.69620046668888	14.33585130165980
C	6.84225916105361	2.38062756178449	11.10591534904246
H	7.59882996851218	1.69315748956314	10.72606600394071
C	6.28396710799163	2.18703875864059	12.37380305431309
H	6.60848865772686	1.34771304151852	12.99102236069530
C	5.43806548104565	4.33209037946920	10.81542963734052
H	5.08639357129958	5.14902776530591	10.18503497773874
C	5.32314448484192	3.06886271153908	12.86182649688361
H	4.92589287204966	2.91700386285447	13.86539042199570
C	2.00669248257820	4.29853040024032	16.43845588474699
H	2.86956751556959	3.71605207196763	16.11687435410543
C	1.27143382201288	6.35704313273470	11.10701973203625
C	1.43857712103459	5.07783942481022	10.56059490658586
H	2.39283704131685	4.56444820048314	10.67026605809937
C	2.35261016204332	7.06317193245322	11.88089009786201
H	2.48733204943048	8.07683147481224	11.47181811819499
C	0.02826314998932	6.99342530221256	10.94558959538986
H	-0.11859788054818	7.98926867419410	11.37131850274404
C	6.24417160606572	8.54464706488676	12.87628628617486
H	6.53727015624264	7.88598716474500	12.04788193639467
H	7.13359157360182	9.13110558052337	13.16063383451703
H	5.48956029721956	9.24712164381316	12.49892817912331
C	6.41180820630345	3.45758606295695	10.32940480114144
H	6.82583439628881	3.61321425439785	9.33198248437696
C	0.39373001691541	4.45207678338916	9.87425482510038
H	0.54627892450697	3.45583833621540	9.45544700793358
C	3.75368079698786	7.26731931714288	17.21287366374392
H	2.82572557108603	7.81893870090642	17.00911974695571
H	4.28495296288650	7.79460375349206	18.02232718670001
H	3.46638003424557	6.27759149894401	17.58780662757024
C	1.41282776180488	4.00583745407773	17.66414750311914
H	1.80392574971526	3.18721218104742	18.27079898581610
C	4.18058638549368	9.58313169293472	15.08203448362469
H	4.06814374339098	10.02323434034182	14.08266592287581
H	4.82272894900672	10.25575540882326	15.67505977537890
H	3.18800652133192	9.56365478047415	15.54850738912199
C	0.42917476854575	6.08529823791542	16.09754315592521
H	0.03013911670141	6.88499100822586	15.47161005464294
C	0.33089835189560	4.76365970046771	18.12443263671916
H	-0.12943023930629	4.53869051441353	19.08725644578190
C	7.24914902350093	5.66744886275057	13.74683431578167
H	7.19542216882476	4.59806129479346	13.98063059946967
H	8.23500758771195	6.03381339438991	14.07817399174345
H	7.21086731887115	5.76300952487058	12.65324245324188
C	-1.01519740628307	6.37090350604172	10.26331320365816
H	-1.97202236300013	6.88370144561993	10.15100376313583
C	5.67854183025541	4.82043923412619	16.40808576652648
H	4.80366280270439	4.57576750950345	17.02277338484855
H	6.53813232147541	4.93560269457208	17.08939931343717
H	5.89110090839957	3.96267496638211	15.75638315530365
C	-0.15724183963513	5.80457227032964	17.33236836670369
H	-1.00879531519207	6.39669089787435	17.67122046210197
C	-0.83742412625116	5.09195192938739	9.72453808307116
H	-1.65312029760457	4.60095373541225	9.19214009088239

Cartesian Coordinates of **exo-3** (optimized at the BP86/def2-TZVP level of theory)

Fe	3.56429677835077	13.52768985019901	3.21258481866156
P	4.05394041153101	14.65623450379708	5.16000990916878
C	5.75858968453556	13.83497199615664	5.12700177050026
H	6.56675722230293	14.57274999386489	5.01107965019011
C	5.48089085849410	13.04048446813532	3.87384285319743
H	5.71570460805039	11.97401923777180	3.90801865967041
C	5.51231436294011	13.67806352919899	2.59209197758335

C	4.88154508582531	14.96023593421344	2.50438097794953
H	4.88891411978896	15.48159743416325	1.54838655822351
C	4.12175708826076	15.50926988584353	3.57712757539395
C	1.94048181908606	12.50792075502730	4.01446527419284
C	2.72732121929953	11.61469897258899	3.21228870491233
C	2.75771060433350	12.12405674654365	1.87174280473885
C	2.00445077672182	13.34826614426428	1.84254670757163
C	1.49220683260627	13.58532911271389	3.16603494550324
C	1.55545654913095	12.30326449301765	5.44425329032262
H	2.33422279593823	11.76953480242615	6.00382178107261
H	0.62539710521306	11.71440864718486	5.51090655533433
H	1.38862447524981	13.26005640896530	5.95403650802480
C	3.32163552329840	10.31311994727374	3.64268345627395
H	4.32751727268221	10.16439387908087	3.22515311683146
H	2.69813078887687	9.47277956582756	3.29550649180636
H	3.39016797675026	10.23672499649025	4.73470997094562
C	3.34937943749452	11.41915095333231	0.69672247897905
H	3.58120822918389	12.10972118728646	-0.12216911395985
H	2.63900570798195	10.66909060004708	0.31036331353060
H	4.27889594509198	10.89472148884392	0.95496229651871
C	1.69587891435957	14.14942669976624	0.61806962314231
H	1.44163966095405	15.18600909312433	0.86938283006432
H	0.83624753836441	13.71844381968447	0.07808142102840
H	2.54471821405633	14.16538018121165	-0.07937007649916
C	0.59450485099692	14.70311521993375	3.58673436979798
H	0.81622334991831	15.03077056003350	4.61144923803135
H	-0.46123504394889	14.38679966052885	3.55919157833554
H	0.70068140974297	15.57842096849703	2.93432542544912
C	5.96247938647714	13.04538068903465	6.38143597684839
C	6.75282563320180	13.56687843740689	7.41828441549583
H	7.24681143208597	14.53059969216311	7.27561304486622
C	6.91548124252533	12.87245870375978	8.61720171001025
H	7.53952737686816	13.29471872944696	9.40652547416949
C	6.28582874777573	11.63856431729888	8.80766241029805
H	6.41374428642423	11.09398360920812	9.74398190980418
C	5.49468001035586	11.10922718968037	7.78566936092628
H	4.99836594396011	10.14665406031317	7.92140889705391
C	5.33526950487451	11.80649451330519	6.58665260410884
H	4.71290088093555	11.39042969384304	5.79570627475549
C	6.08822091104021	13.03023613946056	1.39346807937040
C	6.94283849714526	11.92104675356433	1.52911911764493
H	7.19964941111263	11.56474886945719	2.52665992408906
C	7.48510903079217	11.28265343538870	0.41285604952110
H	8.14096099779146	10.42170833014092	0.55129296512000
C	7.20747214499698	11.75190486539973	-0.87237897780091
H	7.63627451751148	11.25921566718529	-1.74566123892490
C	6.38074148277542	12.86916342955673	-1.02499298692583
H	6.15699743941901	13.25054870536569	-2.02260997695717
C	5.82613471927365	13.49342631066797	0.08962818760344
H	5.15841084731902	14.34157757703034	-0.06135755873355
C	3.25866894909860	16.69373719253625	3.35473997761609
C	2.91008450616595	17.14097565829230	2.06486461787222
H	3.28488109276570	16.61494717871969	1.18796083702961
C	2.06544961352099	18.23392601759435	1.88220328191487
H	1.81126594506601	18.55443290001189	0.87039601053923
C	1.53556390823971	18.91164211452982	2.98509108915595
H	0.86938728038586	19.76307108444816	2.84112472462170
C	1.87992946906524	18.49087985681872	4.27108018777346
H	1.48671897132522	19.01648277639790	5.14265194404694
C	2.73796870479710	17.40576169707623	4.45108732571186
H	3.01829494144503	17.09331206785892	5.45848659888666

Cartesian Coordinates of **2** (optimized at the BP86/def2-TZVP level of theory)

C	0.75969921956477	1.48292236164413	7.58725384541971
C	-0.47620044855918	1.62917752956912	8.27377146538595
H	-1.21313679722227	0.82892928251549	8.22440186837259

C	-0.78837070653940	2.72747440339980	9.13242902415829
C	0.23788215818491	3.66967479110450	9.45723805576180
H	0.05274914973110	4.30466864591519	10.32421289465678
C	1.51057961133072	3.70453372457801	8.83111420827776
C	1.06980249408882	0.21909635069739	6.88202887961869
C	0.17200502464912	-0.86908782921545	6.84162025643020
H	-0.80710146524148	-0.79134209728838	7.31269016488164
C	0.50074218538112	-2.06233438880729	6.19943398099180
H	-0.22121553808790	-2.88084274463295	6.18820993626079
C	1.73994055191858	-2.21402002998545	5.57155226881683
H	1.99736062020186	-3.14880950207331	5.07250931881688
C	2.63695780213489	-1.14289300417476	5.58445530081936
H	3.60664876238184	-1.23584424558023	5.09240115652857
C	2.30516204504554	0.05020190972836	6.22321372048076
H	3.01656555339447	0.87735701564308	6.22891851785480
C	2.72434997707897	1.22618722102566	10.69515049389858
C	1.81158018441144	1.91277667769419	11.57883875292760
C	0.58864791545465	1.15867781609208	11.62892985943993
C	0.73832578531389	0.01833473048445	10.76540947923838
C	2.06337699340017	0.05470767873148	10.20696024550665
C	4.14702748757452	1.59331453282475	10.43652530768413
H	4.31018803370038	2.67386687033922	10.52417847991895
H	4.46350177104734	1.28730600761335	9.43050309630388
H	4.81120376401158	1.09391175530364	11.16185501984772
C	2.12931826341646	3.11829164617926	12.40174783859828
H	2.88417345437450	3.75204380850895	11.92240215687101
H	2.52032391500305	2.81645947379397	13.38779350935830
H	1.23839527440169	3.73601476562443	12.57772480166199
C	-0.58436084045434	1.47550201940864	12.49772623507186
H	-1.50306350083139	0.99802701825577	12.13765218303284
H	-0.77608428866936	2.55627880164511	12.54411877578688
H	-0.40447329213379	1.12564063202805	13.52767760050171
C	-0.25811979476414	-1.07733254069407	10.56102406461568
H	-0.16506276707830	-1.52018050642026	9.56115365015453
H	-1.28700728752042	-0.71497407173464	10.68349633320020
H	-0.10620942651280	-1.88474514966970	11.29656832098303
C	2.68713604824397	-1.00311105696738	9.36153784367738
H	1.94686794709450	-1.54768640986185	8.76358358823730
H	3.20351036436733	-1.73381746765046	10.00618522485461
H	3.42830941286440	-0.58790093344411	8.66812697558604
C	-2.09781224525644	2.80216297776256	9.82179372938210
C	-2.55526099751679	4.02827022587863	10.33722239368026
H	-1.95491601385662	4.92684585464179	10.19380182797344
C	-3.77911107355985	4.12460788025260	11.00056969301958
H	-4.10699369030761	5.09064052356093	11.38733250473716
C	-4.58737082531668	2.99712774072313	11.15631426140765
H	-5.54502567784592	3.07058627760661	11.67271758123062
C	-4.15887487018014	1.77465319300970	10.63104198197600
H	-4.78078179748662	0.88475205940734	10.73964733269099
C	-2.93351154247299	1.68036012902920	9.97493885876471
H	-2.61528323228089	0.71046439806787	9.59419510758987
C	2.54555146497351	4.64967211388410	9.30645410582572
C	2.24608915580900	5.71764175085676	10.17792745302653
H	1.22200751991218	5.87524493606095	10.51536135153068
C	3.23392813426136	6.59971473411238	10.61366535171491
H	2.96504054581085	7.41654933265455	11.28562178042139
C	4.55672832732199	6.44994174354399	10.18897270189422
H	5.32879861387277	7.14046015128421	10.53015271040410
C	4.87051806415503	5.41316387391720	9.30567232575156
H	5.89517420790494	5.28702574904571	8.95195127948699
C	3.88138790662497	4.53421514351956	8.86892155177933
H	4.13409613245827	3.73364256935383	8.17315967300913
P	1.75529241763175	2.96013969398973	7.18411925292591
Fe	0.98635822890466	1.78885822608308	9.69660916470817
H	0.80105863028744	3.72202722960581	6.40363132457831

(S6) Preparation and structural data of [Cp*Fe(1-Ph_3Sn-$PC_5Ph_3H_2$)] (8)

A suspension of triphenyltin chloride (15 mg, 0.04 mmol) in THF (1 mL) was slowly added to a dark orange solution of **1** (39 mg, 0.04 mmol) in THF (1 mL) and stirred at room temperature for 17 h. The resulting dark greenish brown mixture was dried in *vacuo* and the residue was extracted with *n*-hexane (4 x 0.5 mL). The red brown extracts were combined and concentrated to 2 mL. X-ray quality crystals of **8** were isolated as dark red rods after storage at room temperature for two weeks. The yield was not determined and no further characterization was performed, because the isolation of **8** as a pure compound was not successful.

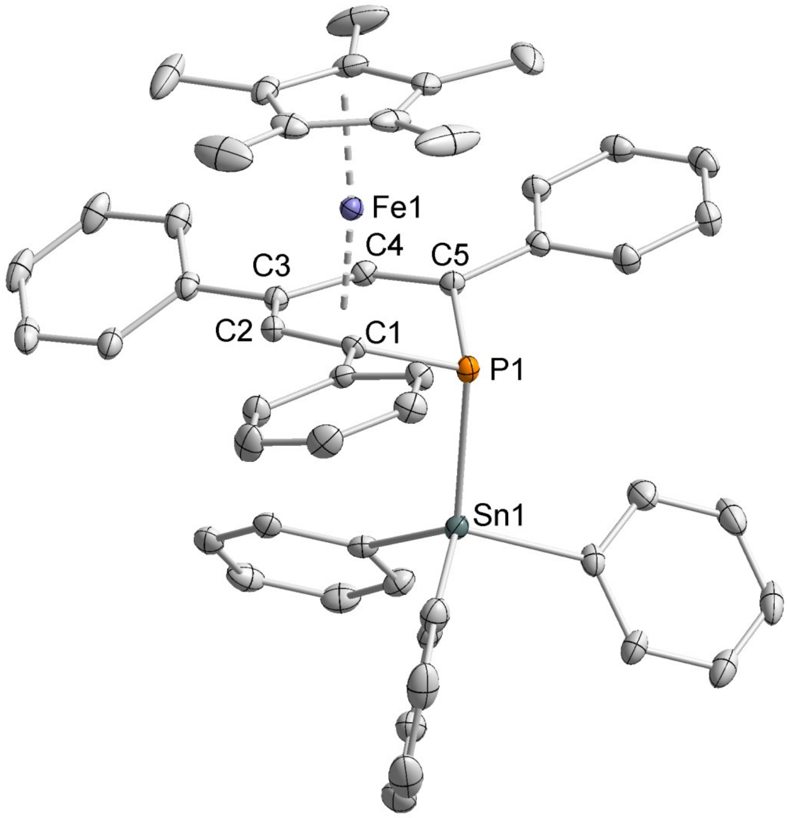

Figure S30 Solid-state molecular structure of [Cp*Fe(1-Ph_3Sn-$PC_5Ph_3H_2$)] (**8**). Displacement ellipsoids are drawn at the 40% probability level. H-atoms are omitted for clarity.

Table S5 Selected bond lenghts [Å] and angles [°] of [Cp*Fe(1-Ph_3Sn-$PC_5Ph_3H_2$)] (**8**).

Fe1−C1	2.170(2)	P1−C5	1.812(2)
Fe1−C2	2.052(2)	P1−Sn1	2.5610(7)
Fe1−C3	2.084(3)	C2−C1−P1	121.8(2)
Fe1−C4	2.058(3)	C1−C2−C3	123.7(2)
Fe1−C5	2.133(2)	C4−C3−C2	120.1(2)

Fe1−Cp*(c)	1.700(1)	C5−C4−C3	123.5(2)
P1−C1	1.815(2)	C4−C5−P1	120.8(2)
C1−C2	1.411(4)	C5−P1−C1	94.3(1)
C2−C3	1.425(4)	C1−P1−Sn1	107.08(8)
C3−C4	1.424(3)	C5−P1−Sn1	104.21(8)
C4−C5	1.422(3)		

Table S6 Crystallographic data and structure refinement of [Cp*Fe(1-Ph_3Sn-$PC_5Ph_3H_2$)] (**8**).

Empirical formula	$C_{51}H_{47}FePSn$
Formula weight / g·mol^{-1}	865.39
Temperature / K	123.(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	13.8770(1)
b / Å	20.7905(2)
c / Å	14.6865(2)
α /°	90
β /°	105.530(1)
γ /°	90
V / Å^3	4082.50(8)
Z	4
ρ_{calc} / g cm^{-1}	1.408
μ / mm^{-1}	8.338
F(000)	1776.0
Crystal size / mm^3	0.44 × 0.26 × 0.13
Radiation / Å	CuK_α (λ = 1.54184)
2Θ range for data collection /°	7.558 − 146.882
Diffractometer	Agilent Technologies SuperNova
Index ranges	$-17 \leq h \leq 15$ $-25 \leq k \leq 25$ $-17 \leq l \leq 18$
Reflections collected	24280
Independent reflections	7980 [R_{int} = 0.0319, R_{sigma} = 0.0282]
Data/restraints/parameters	7980/0/492
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0898
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0912
Largest diff. peak/hole / e Å^{-3}	1.40/−1.28
Flack parameter	-