Supporting Information for:

Protonation of Nickel-Iron Hydrogenase Models Proceeds after Isomerization at Nickel

Mioy T. Huynh, David Schilter, Sharon Hammes-Schiffer, and Thomas B. Rauchfuss

Department of Chemistry, University of Illinois at Urbana-Champaign,
Urbana, IL 61801, USA

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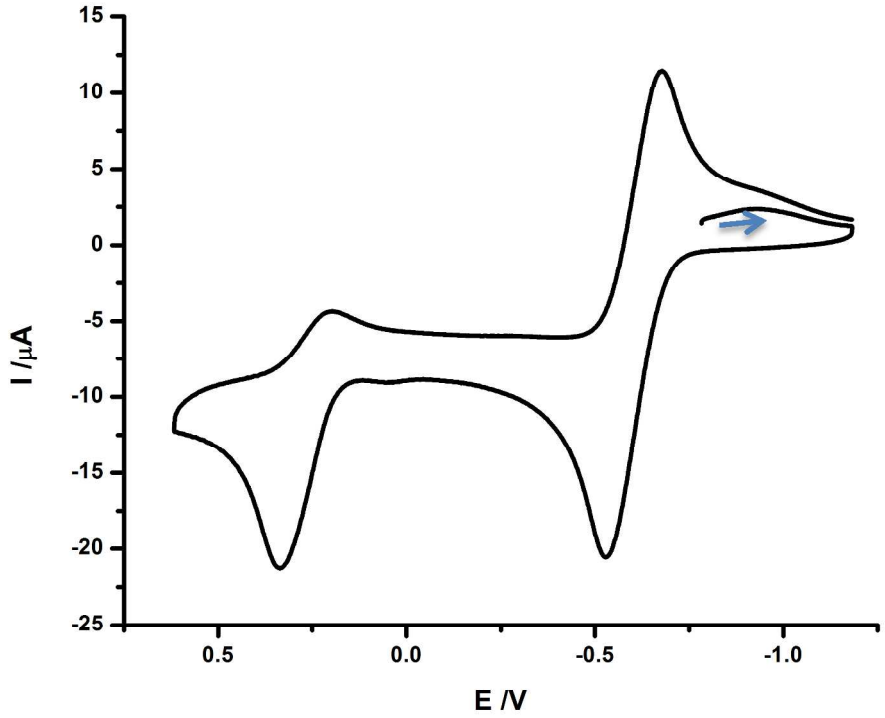

Figure S1. Cyclic voltammogram of **1**. *Conditions*: see Experimental.

The barrier to Ni(dppe) rotation in **1** (tetrahedral ↔ square planar) was determined according to the Gutowsky-Holm relation, using previously reported data:

T_C = –30°C = 243 K
$\Delta\nu$ = (82 ppm – 46 ppm)(202 MHz) = 7272 s^{-1}
k_C = $\pi\Delta\nu)/2^{0.5}$
= 16200 s^{-1}

$\Delta G^{\dagger}$ = $4.58(T_C)\{10.32 + \log_{10}(T_C/k_C)\}$cal/mol
= $4.58(243)(10.32 + \log_{10}(243/16200))$ cal/mol
≈ 9.5 kcal/mol

Since the Pd(dppe) fragment in **2** was found to be dynamic even at –85 °C, we could estimate only an upper bound for $\Delta G^{\dagger}$. Since we could not determine $\Delta\nu$ (difference in resonant frequency for the two decoalesced ^{31}P signals) for **2**, we employed the value 7272 s^{-1} found for **1**.

T_C < –85°C = 188 K
$\Delta G^{\dagger}$ < $4.58(188)(10.32 + \log_{10}(188/16200))$ cal/mol
< 7.2 kcal/mol

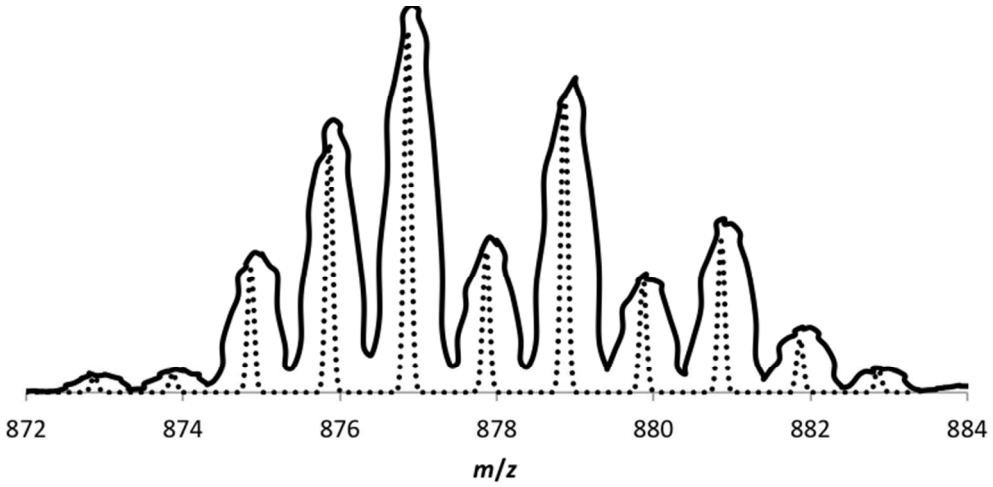

Figure S2. Positive ion ESI mass spectrum of [**2**I]$^+$. The simulated spectrum is presented as a dotted trace.

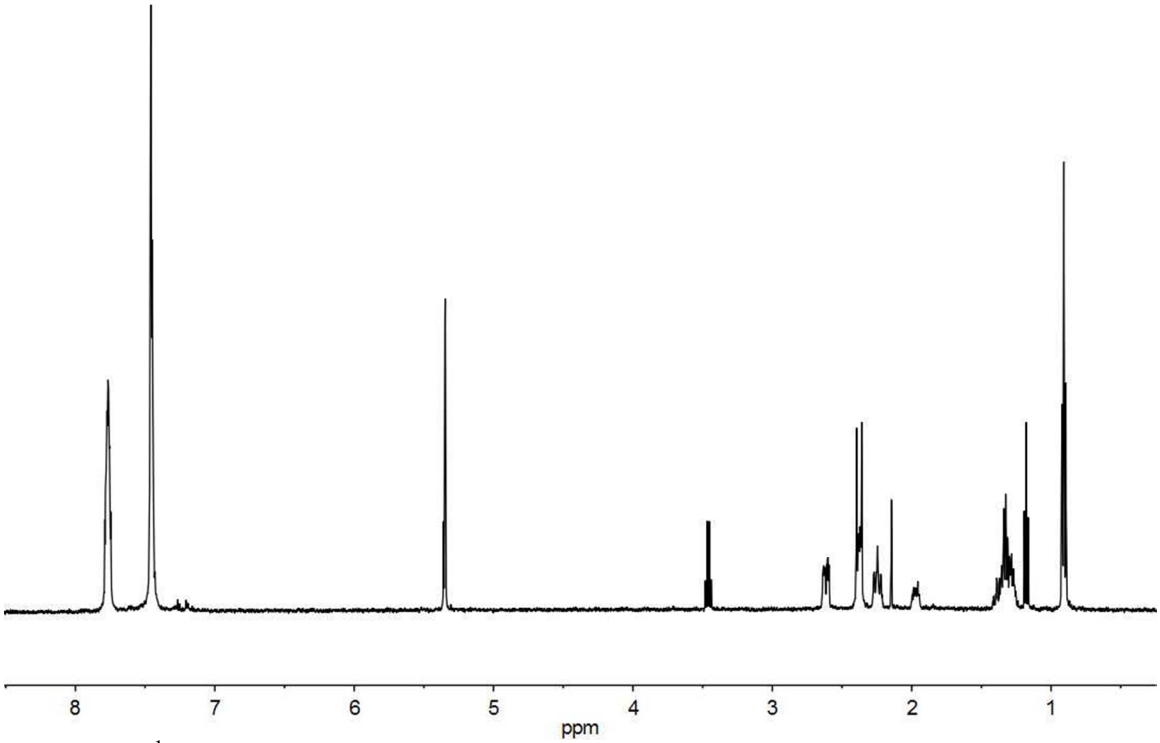

Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of **2**. Resonances at 3.43 (Et_2O), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

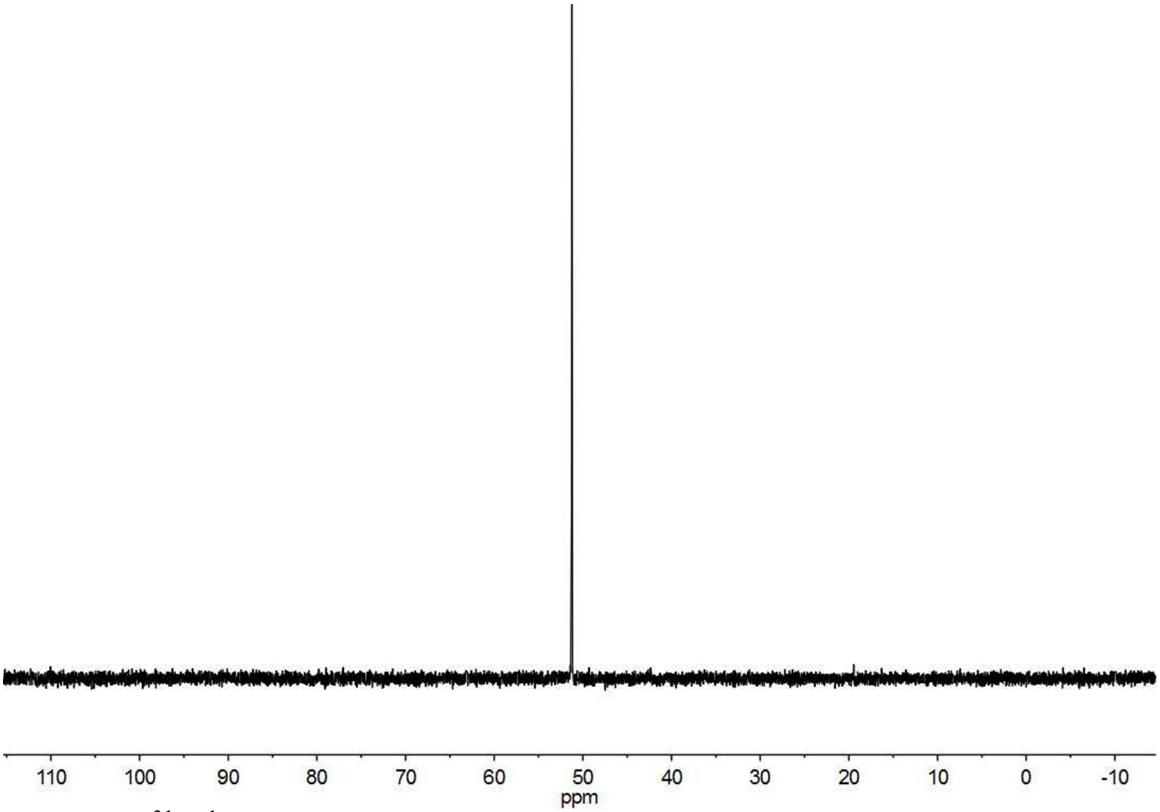

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of **2** acquired at room temperature.

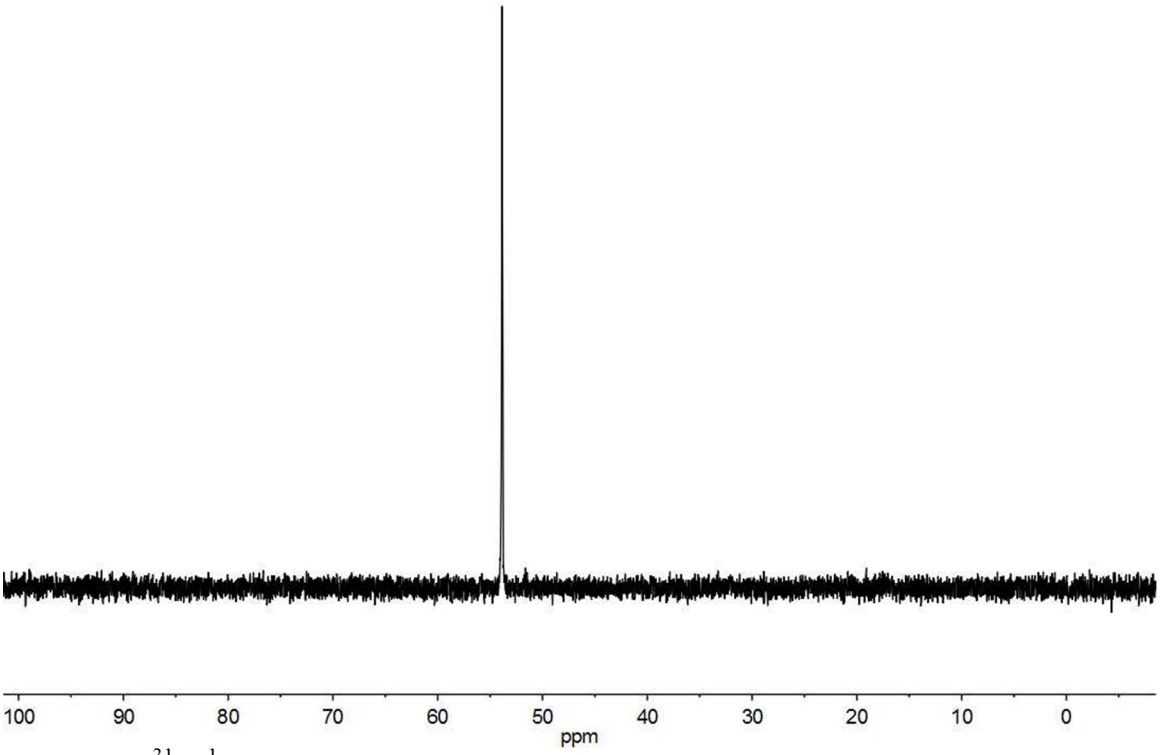

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of **2** acquired at –85 °C.

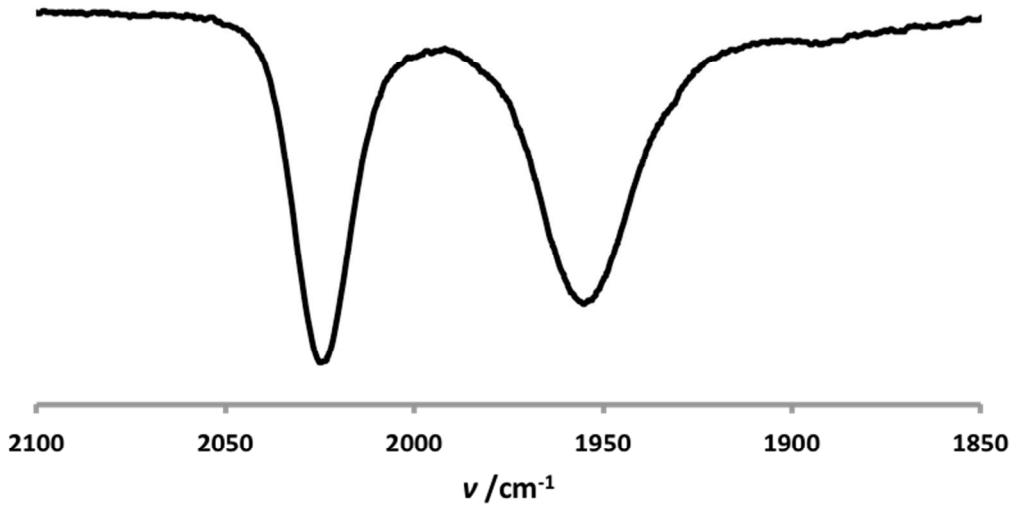

Figure S6. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of **2**.

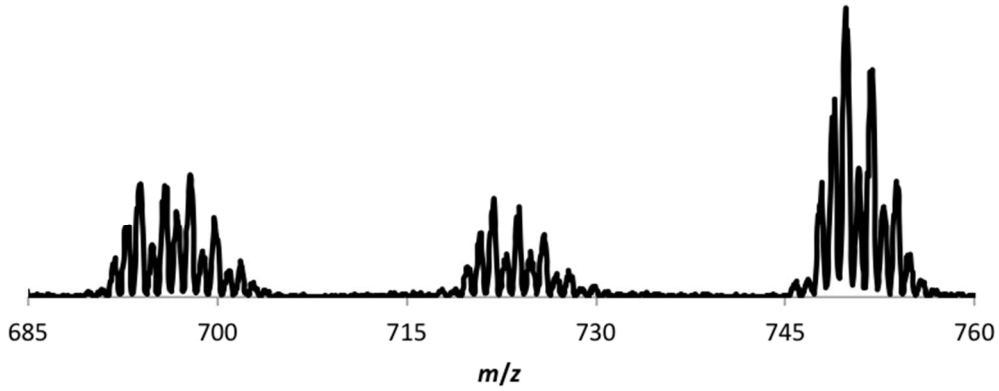

Figure S7. Positive ion ESI mass spectrum of **2** revealing decarbonylation.

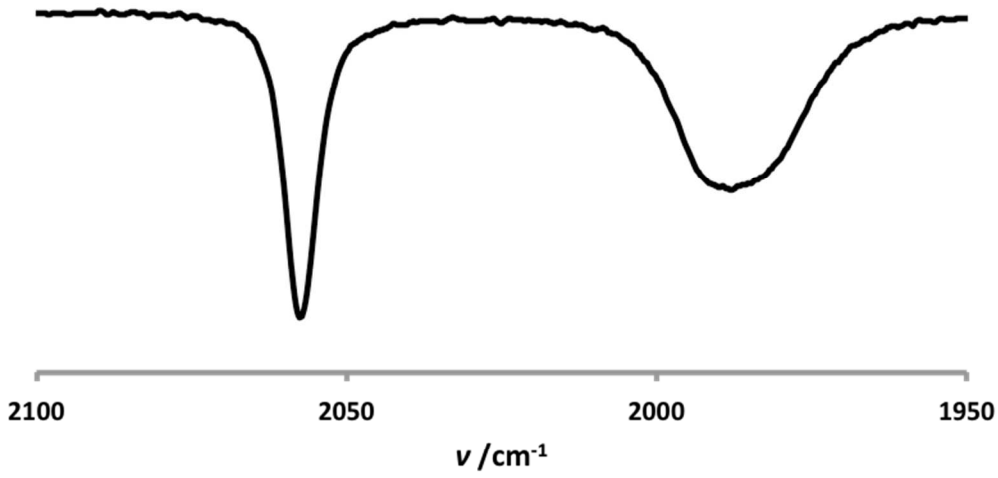

Figure S8. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**2**]BF_4.

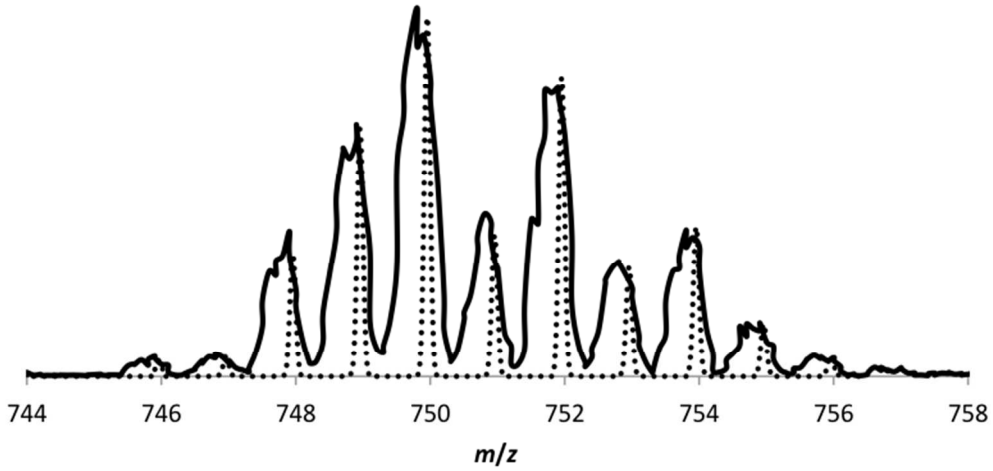

Figure S9. Positive ion ESI mass spectrum of [**2**]BF_4. The simulated spectrum is presented as a dotted trace.

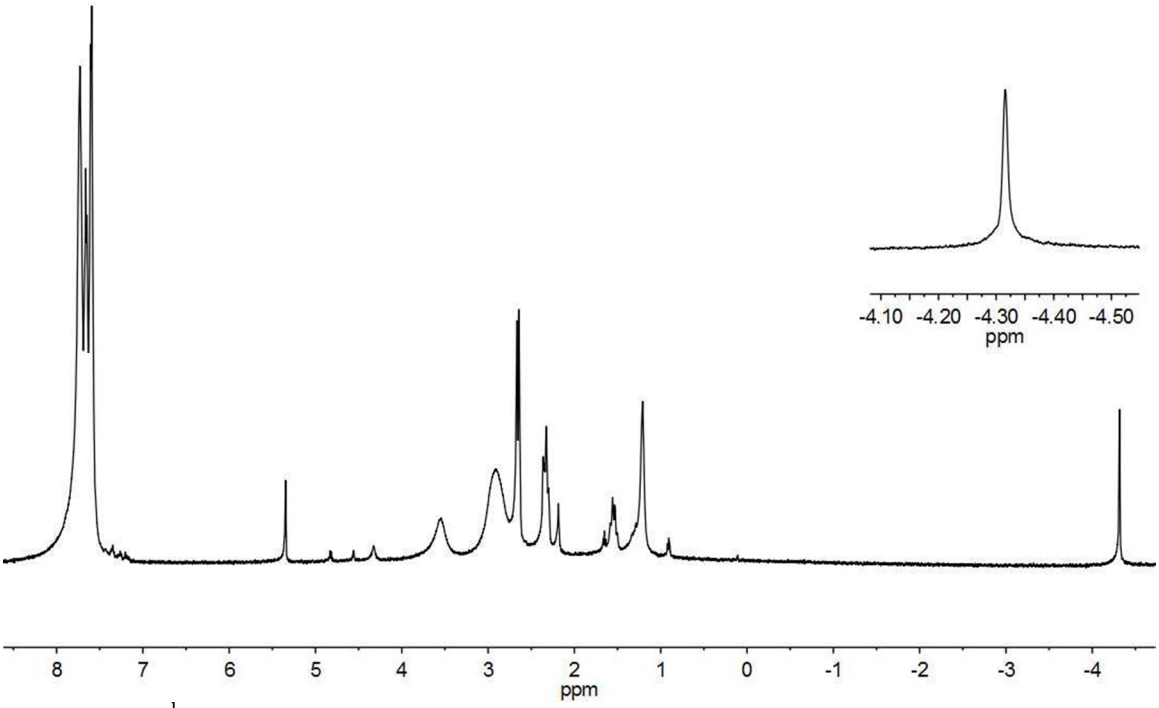

Figure S10. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of [**2**H]BF_4. Resonances at 3.52 (Et_2O), 1.31 (pentane), 1.18 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

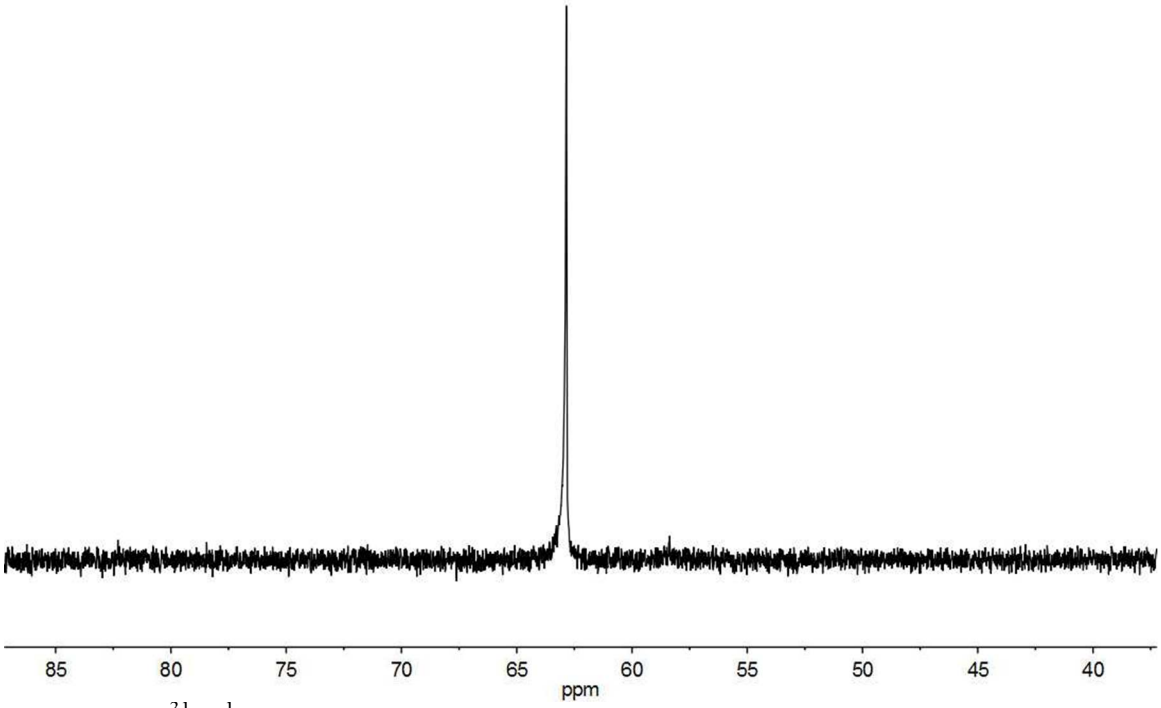

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [**2**H]BF_4.

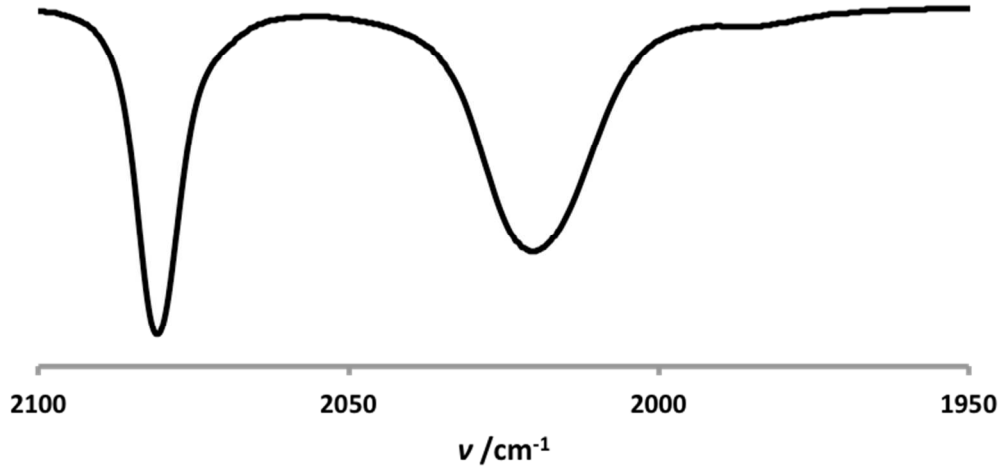

Figure S12. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**2**H]BF_4.

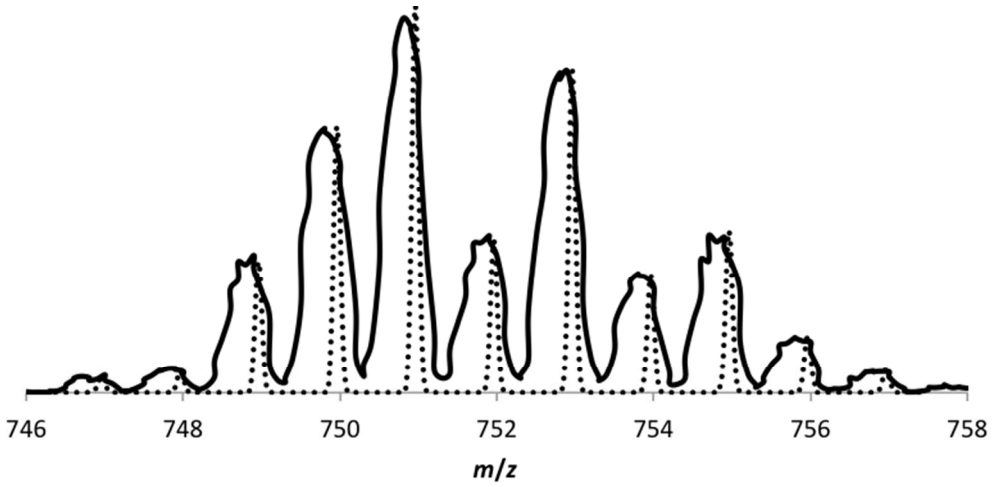

Figure S13. Positive ion ESI mass spectrum of [**2**H]BF_4. The simulated spectrum is presented as a dotted trace. In solution, moisture/air induces degradation of [**2**H]BF_4 to **2** and [(dppe)Pd(pdt)Pd(dppe)]$(BF_4)_2$ (*m*/*z* 1203.7 $[M - BF_4^-]^+$, 558.8 $[M - 2BF_4^-]^{2+}$ see **Figure S15**) and [(dppe)Pd(pdt)Pd(pdt)Pd(dppe)]$(BF_4)_2$ (*m*/*z* 663.8.7 $[M - 2BF_4^-]^{2+}$).

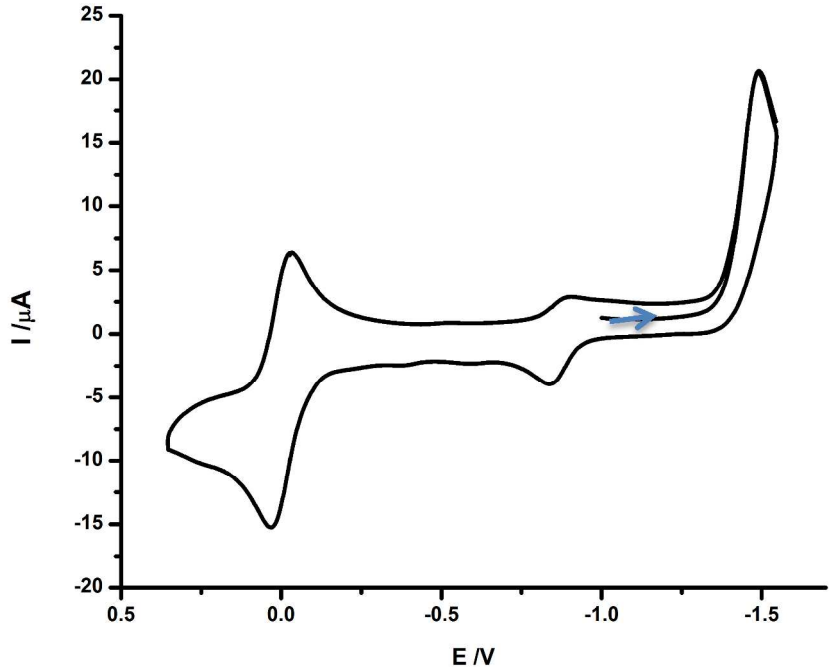

Figure S14. Cyclic voltammogram of [**2**H]BF_4. The wave at 0 V is due to internal $Fc^{0/+}$. The electrochemistry of [**2**H]BF_4 is complicated, an irreversible wave at –1.49 V being ascribed to a metal-centered. This event is followed by decomposition of the $1e^-$ reduced species [**2**H] (perhaps by interaction with $[\mathbf{2}H]^+$) to liberate H_2 and 2. The presence of the latter is evidenced by the appearance of a reversible wave at –0.87 V (assigned to the $[\mathbf{2}]^{0/+}$ couple) on the return scan. *Conditions*: see Experimental.

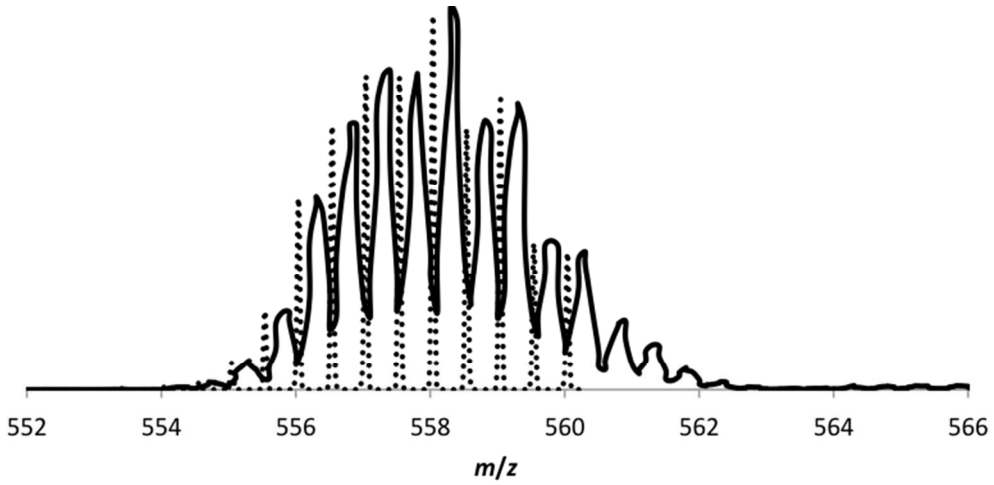

Figure S15. Positive ion ESI mass spectrum of residue dissolved in CH_3CN after [**2**H]BF_4 was left for 2 d in CH_2Cl_2/air.

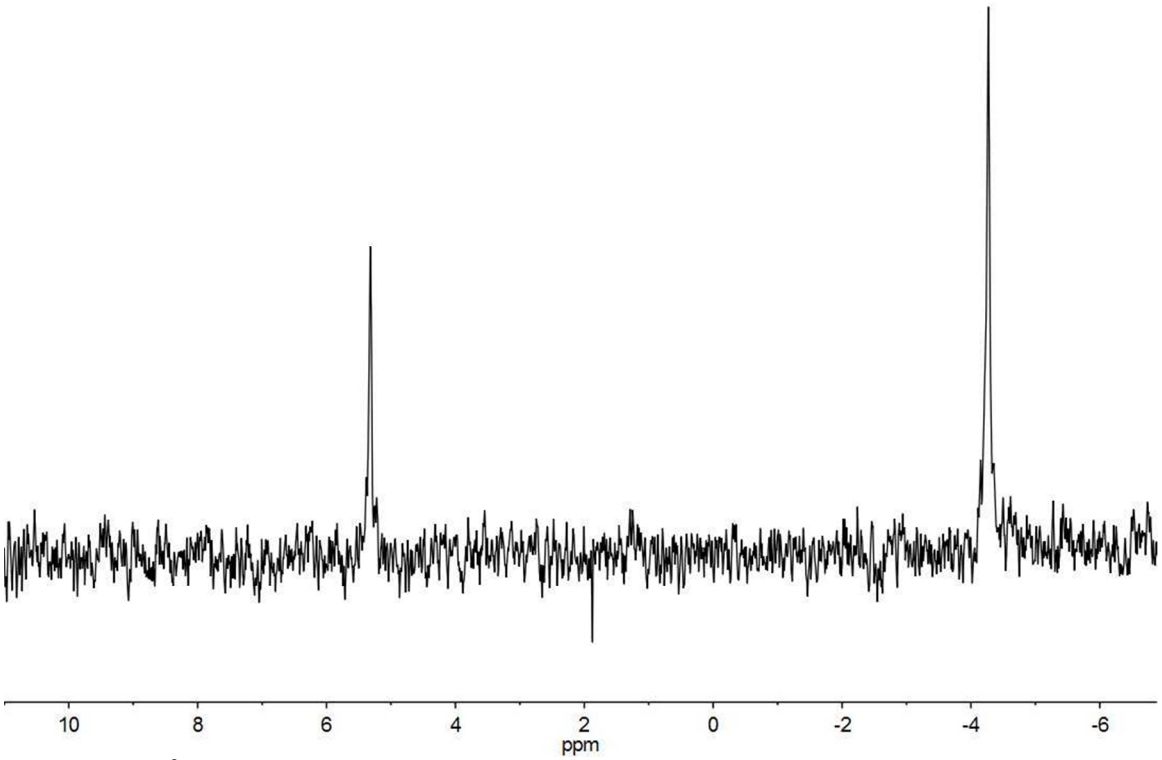

Figure S16. ^2H NMR spectrum (CH_2Cl_2, 77 MHz) of [**2**D]BF_4. The resonance at 5.3 ppm is from residual $CHDCl_2$.

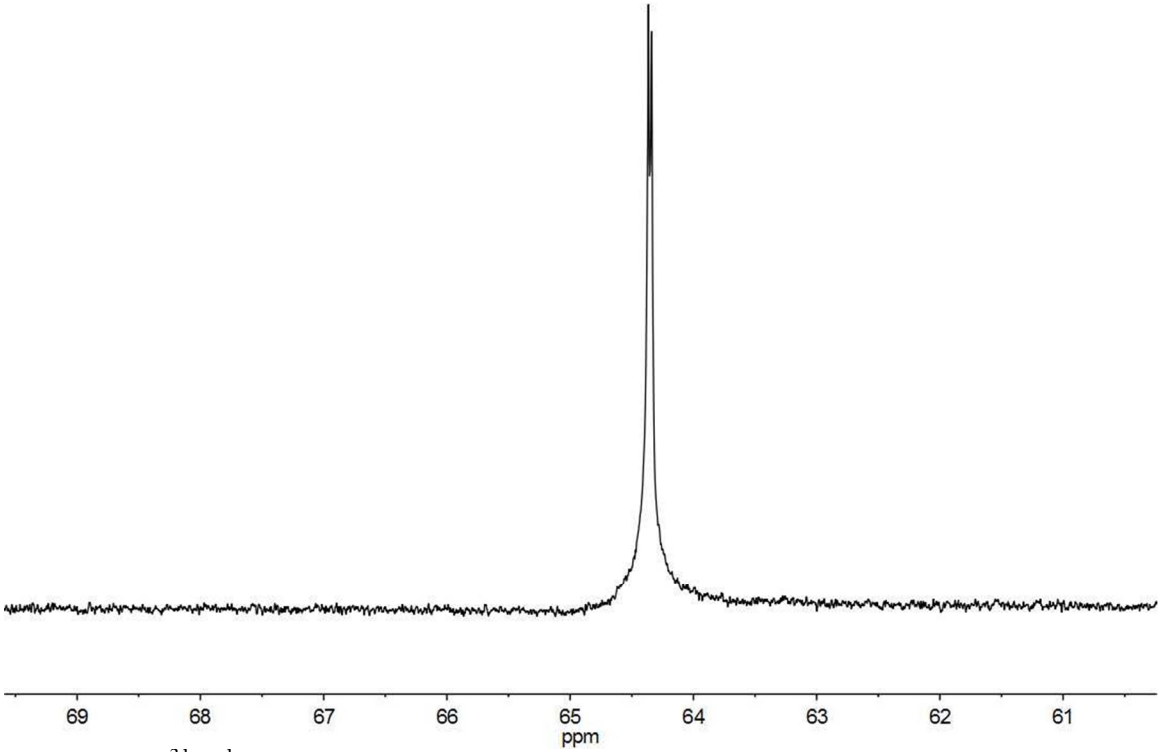

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (CH_2Cl_2, 202 MHz) of [**2**D]BF_4.

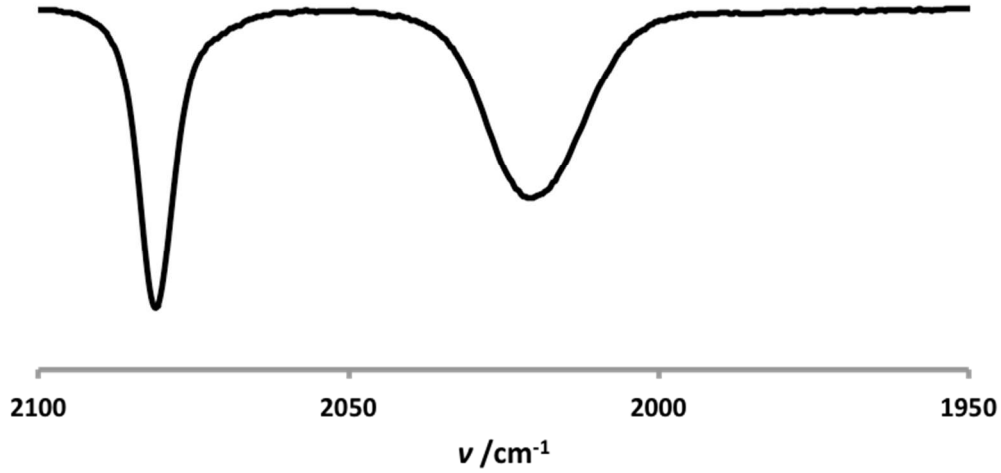

Figure S18. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**2**D]BF_4.

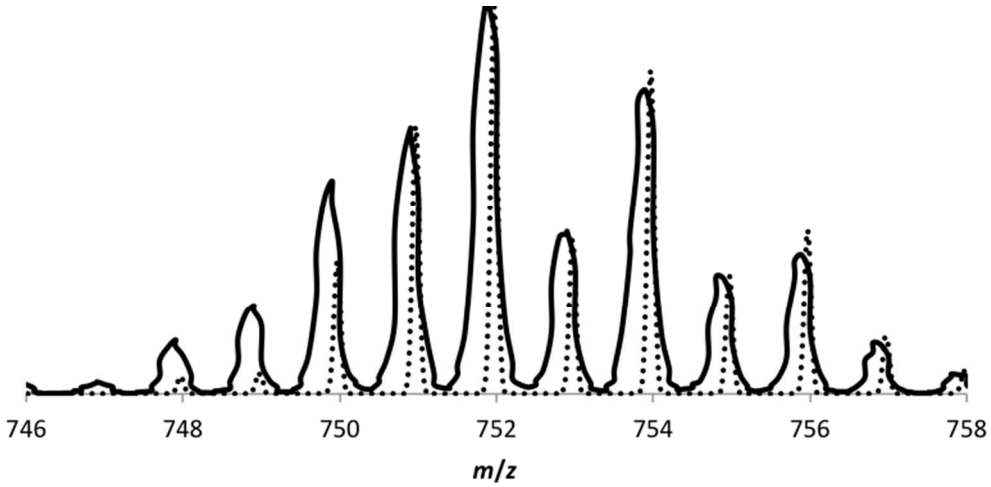

Figure S19. Positive ion ESI mass spectrum of [**2**D]BF_4. The simulated spectrum is presented as a dotted trace.

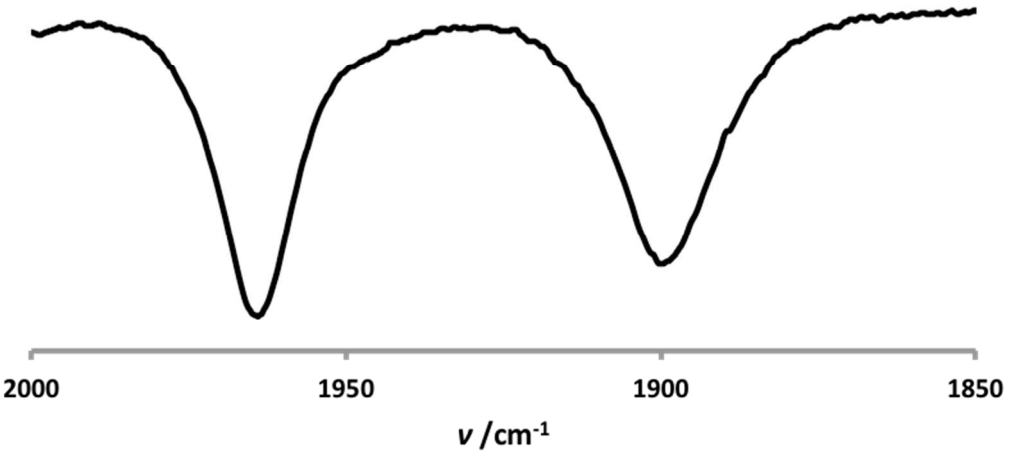

Figure S20. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**2′**]BF_4.

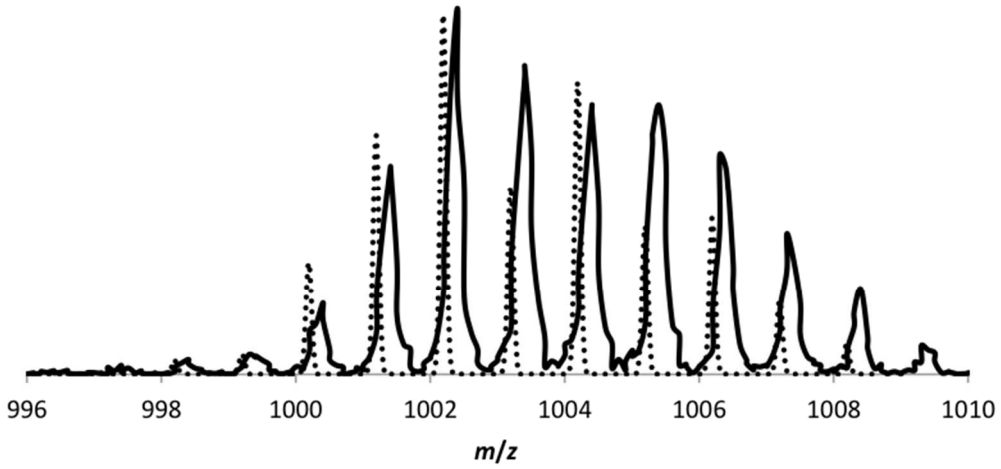

Figure S21. Positive ion ESI mass spectrum of [**2′**]BF_4. The simulated spectrum is presented as a dotted trace.

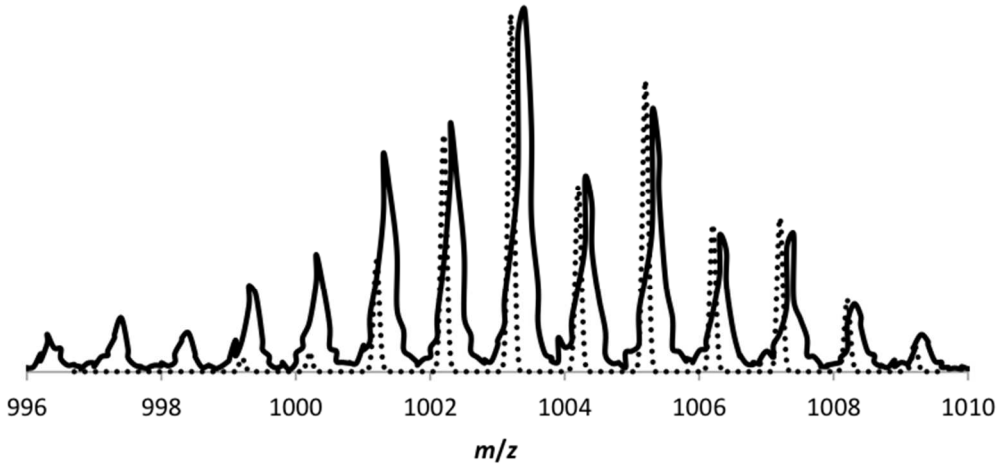

Figure S22. Positive ion ESI mass spectrum of [**2′**]BF_4 after 2 d in CH_2Cl_2. The simulated spectrum is presented as a dotted trace.

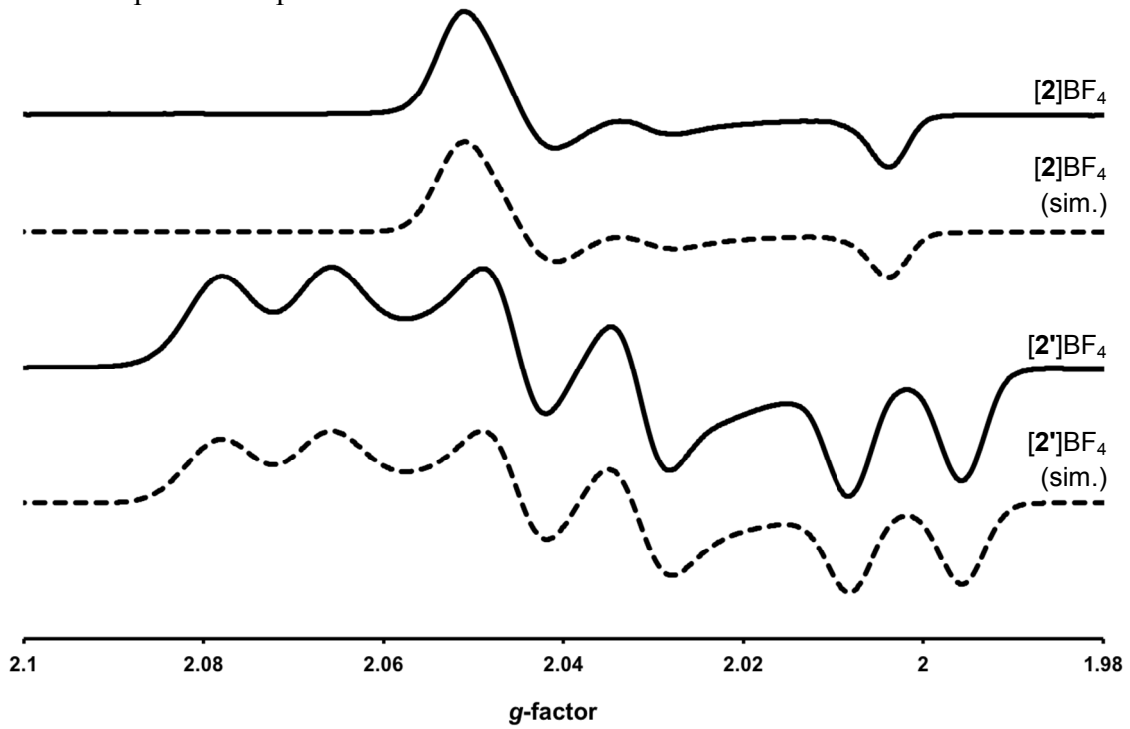

Figure S23. X-band EPR spectra (CH_2Cl_2/PhMe, 110 K) of [**2**]BF_4 and [**2′**]BF_4. The simulated spectra are presented as dotted traces.

Table S1. EPR Simulation Parameters for [**2**]BF_4 (Two Conformers) and [**2′**]BF_4.

	***g*-factor**	***A*(^{31}P) /MHz**	**line width /G**	**relative abundance**
[**2**]BF_4	2.053, 2.046, 2.005	–	10, 8, 6	0.74
	2.050, 2.032, 2.006	–	15, 10, 9	0.26
[**2′**]BF_4	2.072, 2.038, 2.002	54, 61, 57	11, 9, 8	1.00

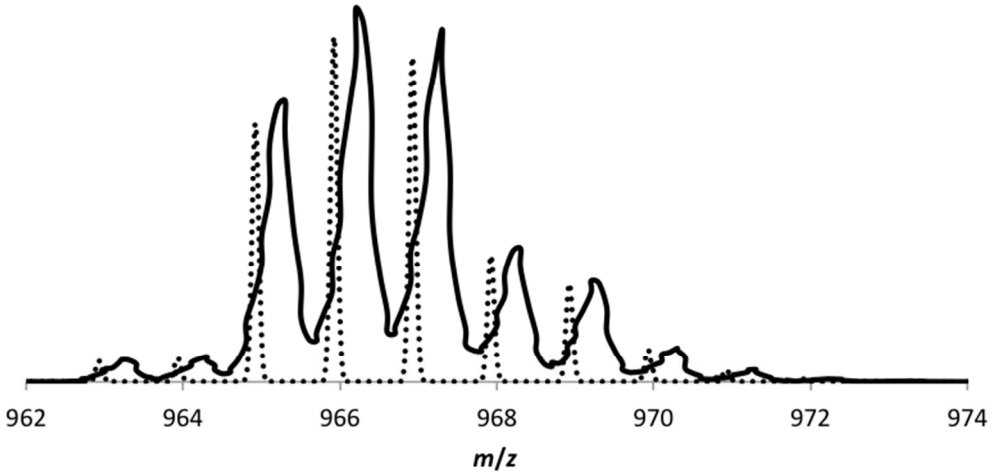

Figure S24: Positive ion ESI mass spectrum of [**3**I]$^+$ generated from (pdt)Pt(dppe) and $FeI_2(CO)_4$. The simulated spectrum is presented as a dotted trace.

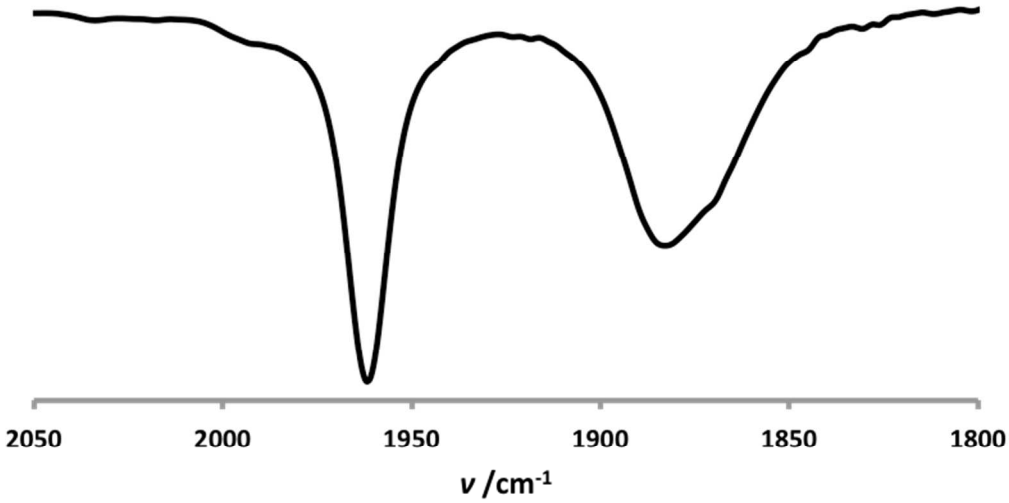

Figure S25. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of **3**.

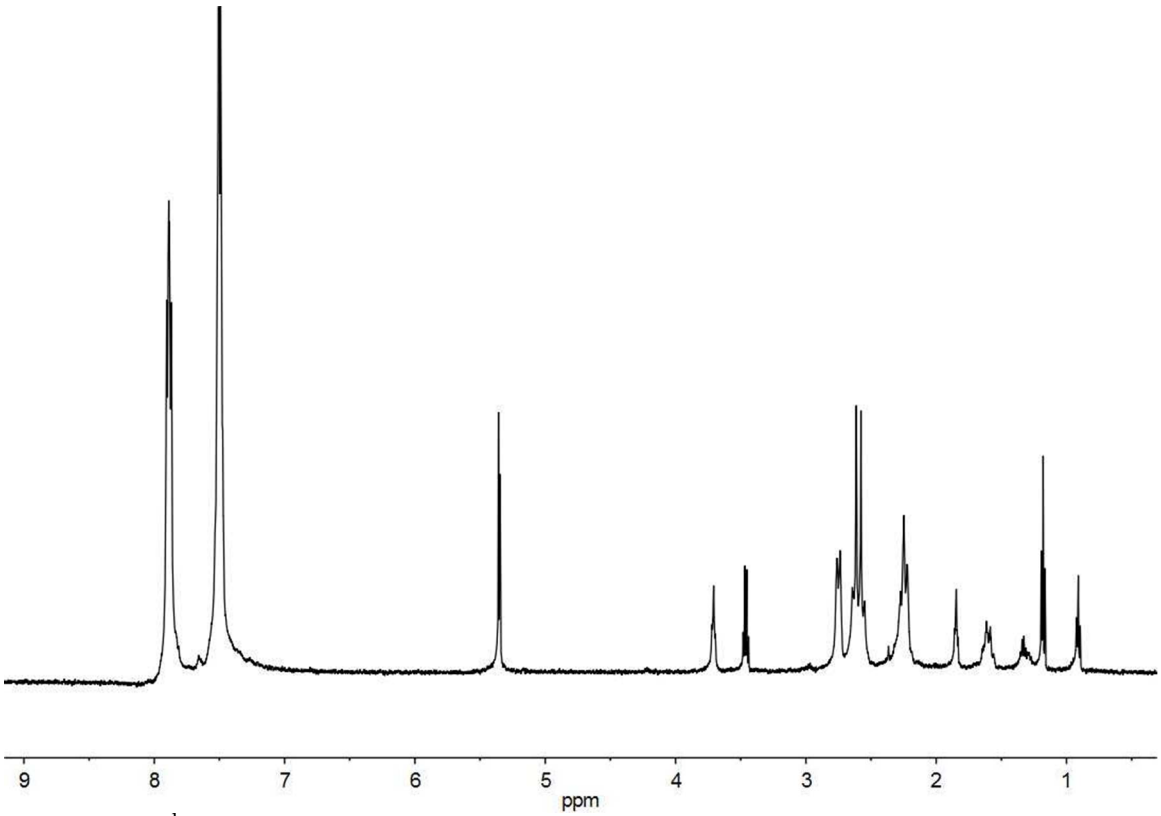

Figure S26. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of **3**. Resonances at 3.68 (THF), 3.43 (Et_2O), 1.83 (THF), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from impurities.

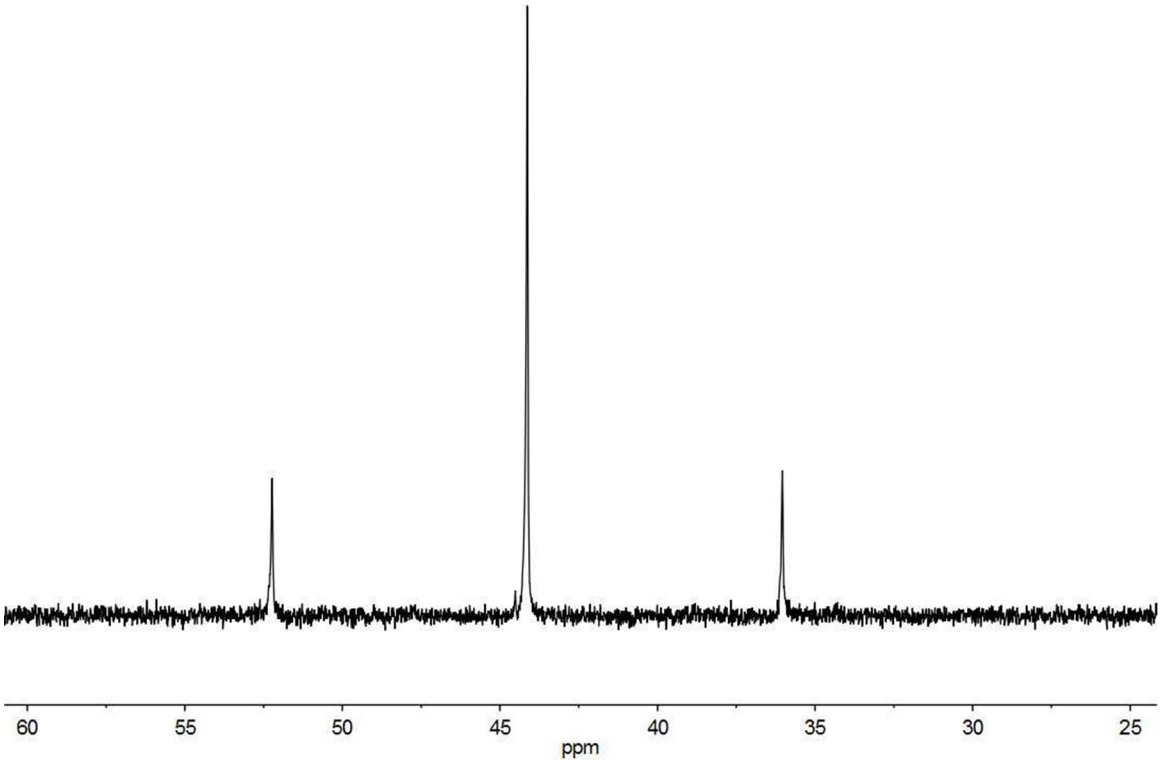

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of **3**.

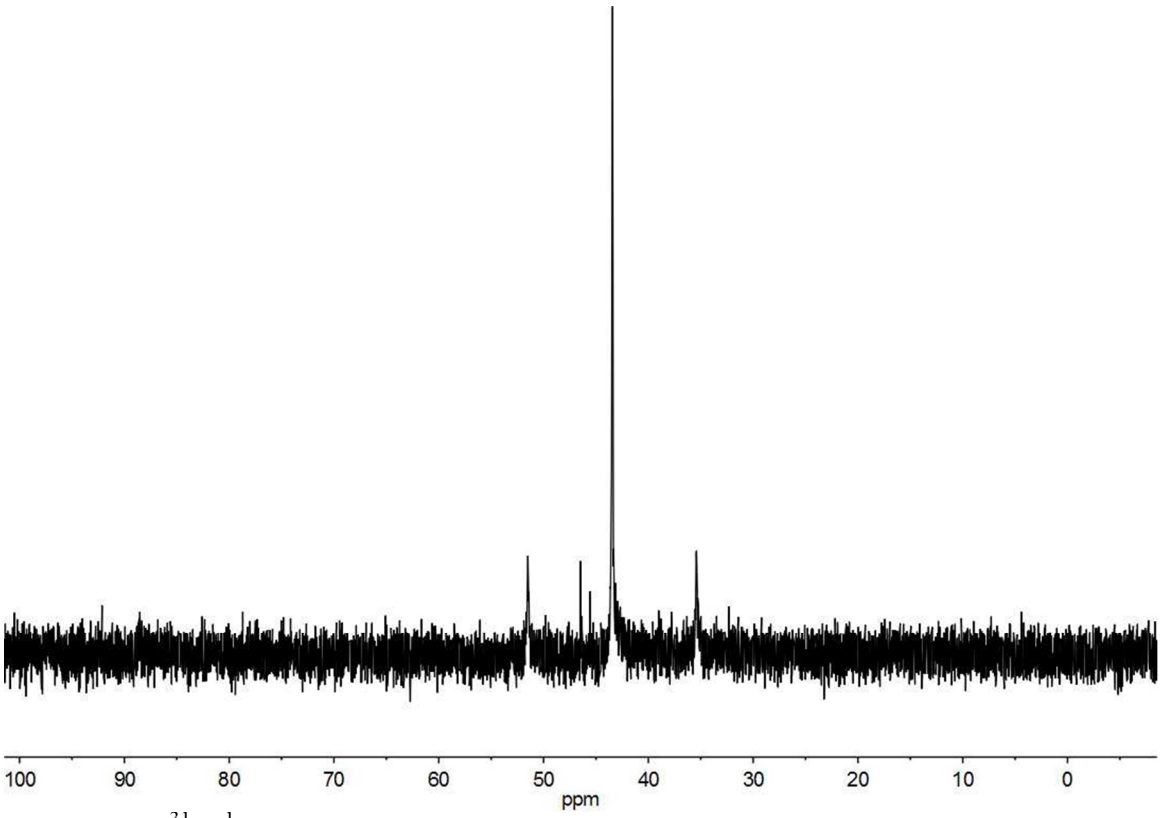

Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of **3** acquired at –85 °C.

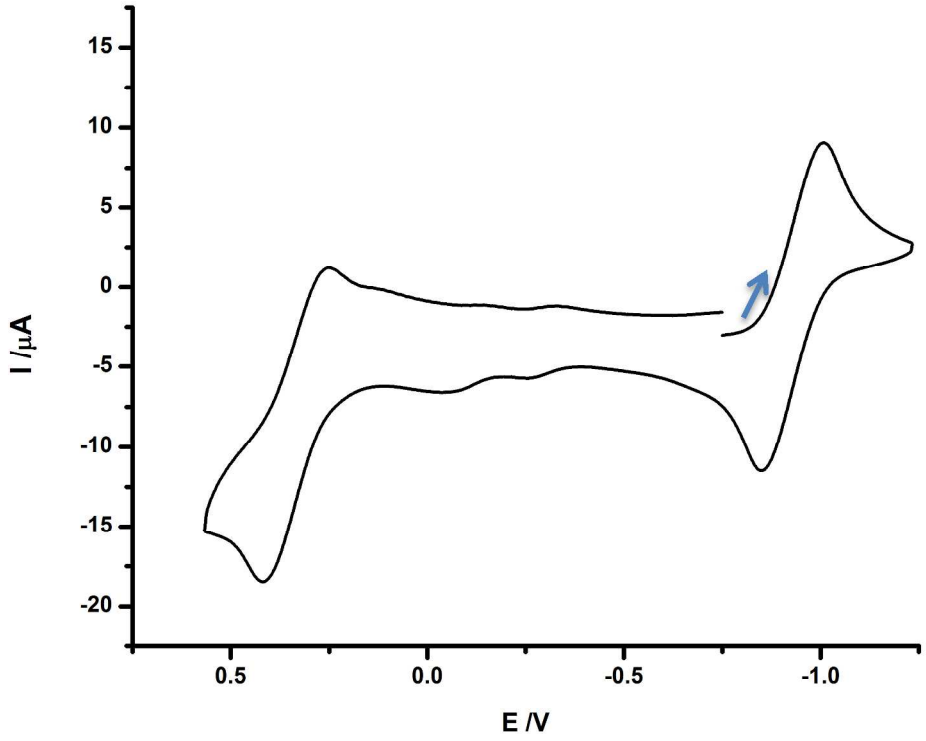

Figure S29. Cyclic voltammogram of **3**. *Conditions*: see Experimental.

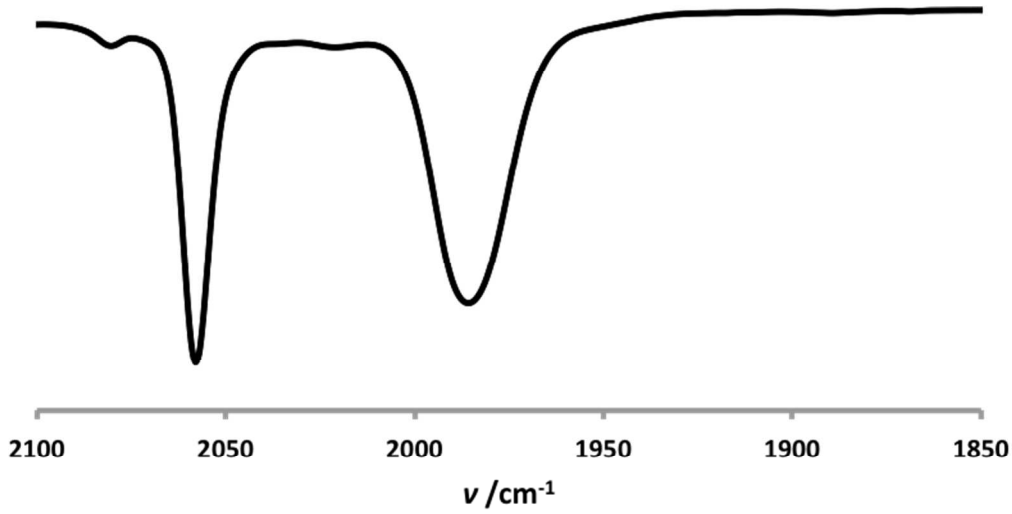

Figure S30. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**3**]BF_4. Manipulation of this compound should be performed quickly in order to avoid H atom abstraction to form [**3**H]BF_4 (ν_{CO} = 2081, 2022 cm^{-1}).

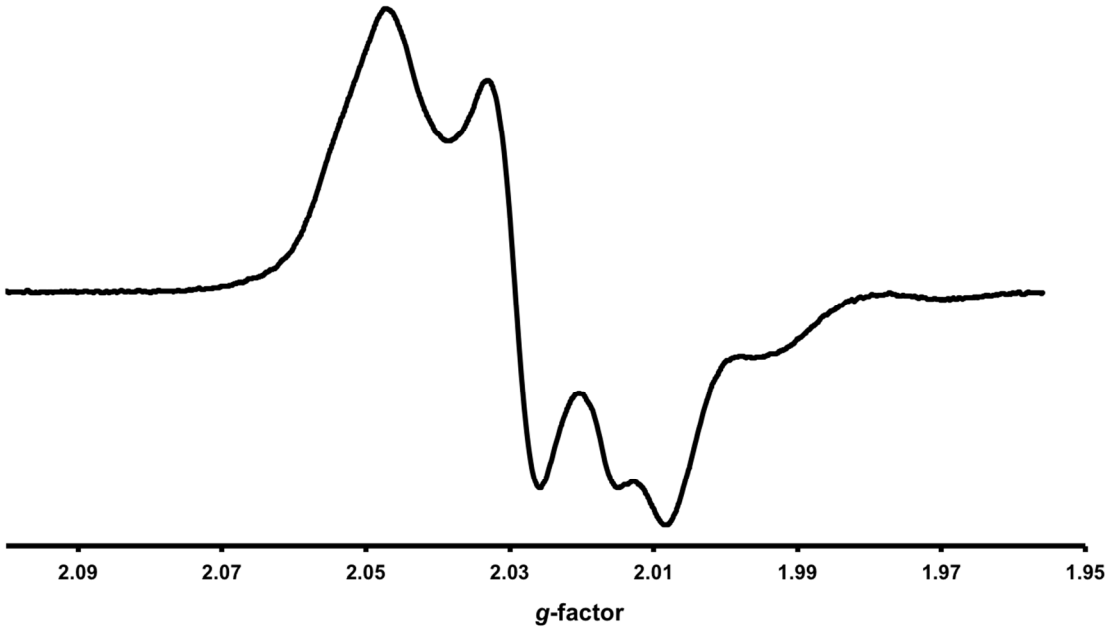

Figure S31. X-band EPR spectrum (CH_2Cl_2/PhMe, 120 K) of [**3**]BF_4.

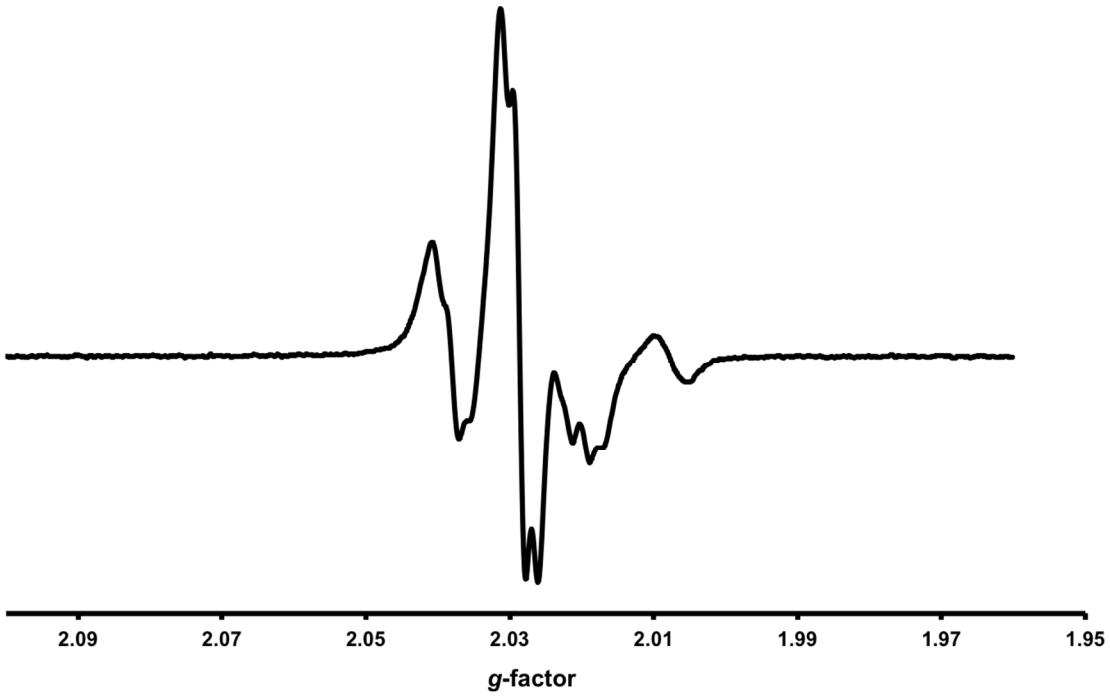

Figure S32. X-band EPR spectrum (CH_2Cl_2/PhMe, RT) of [**3**]BF_4.

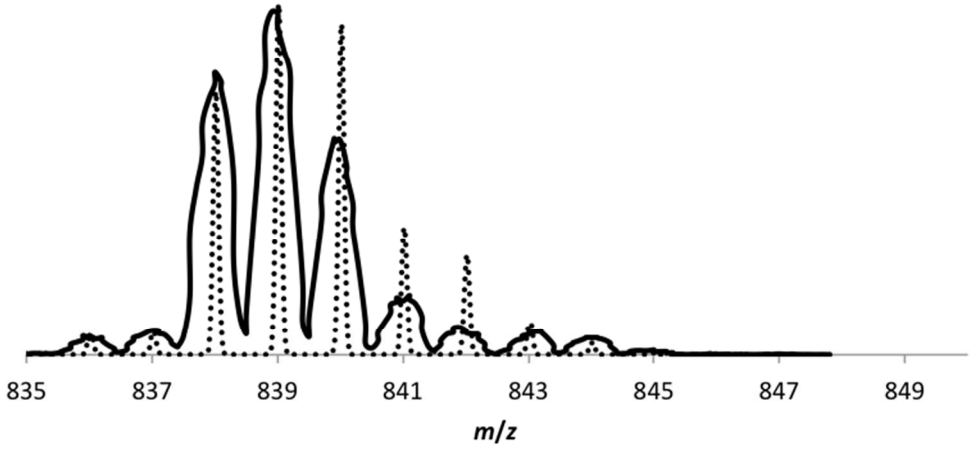

Figure S33. Positive ion ESI mass spectrum of [**3**]BF_4. The simulated spectrum is presented as a dotted trace.

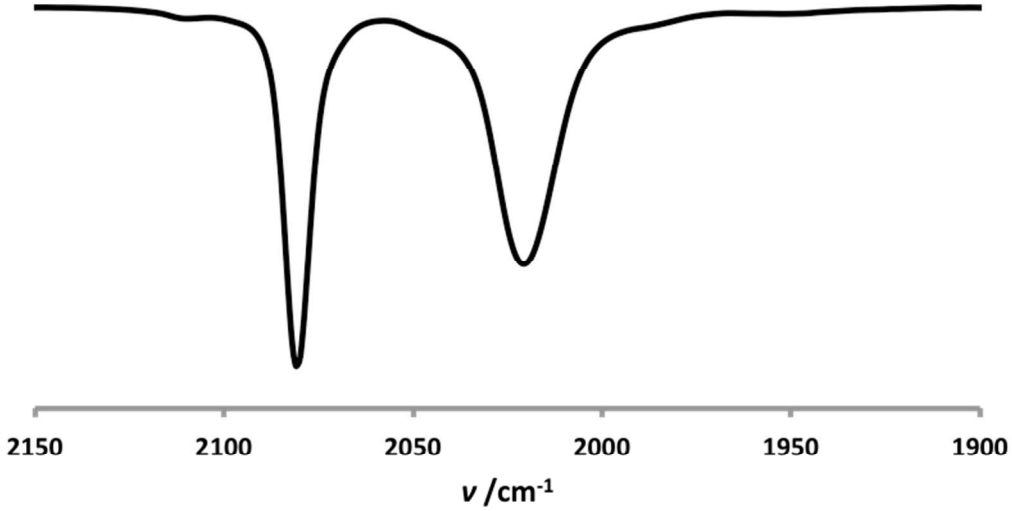

Figure S34. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**3**H]BF_4.

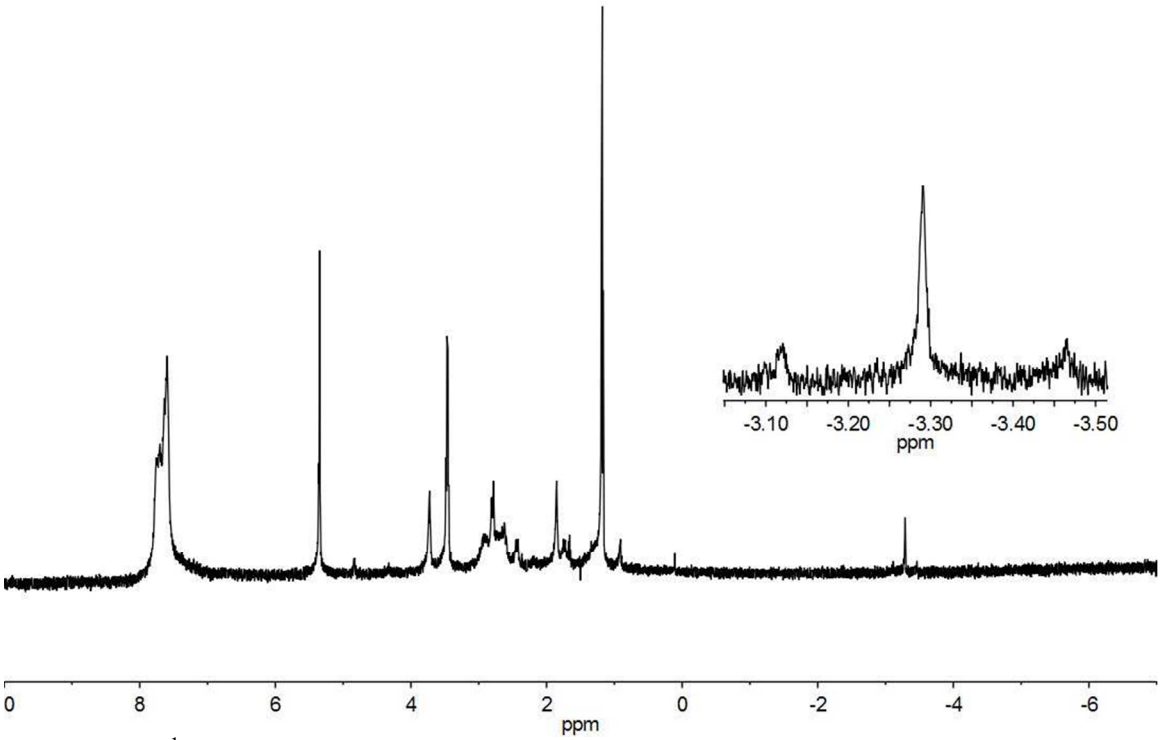

Figure S35. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of [**3**H]BF_4. Resonances at 3.70 (THF), 3.43 (Et_2O), 1.83 (THF), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

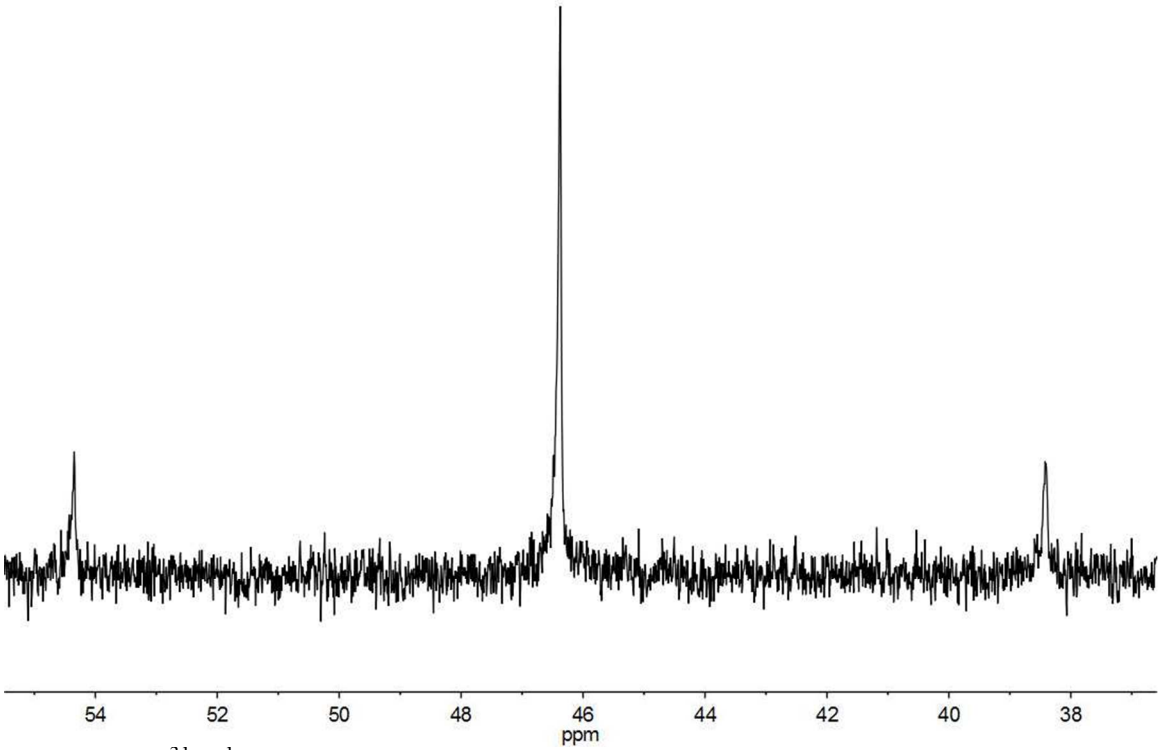

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [**3**H]BF_4.

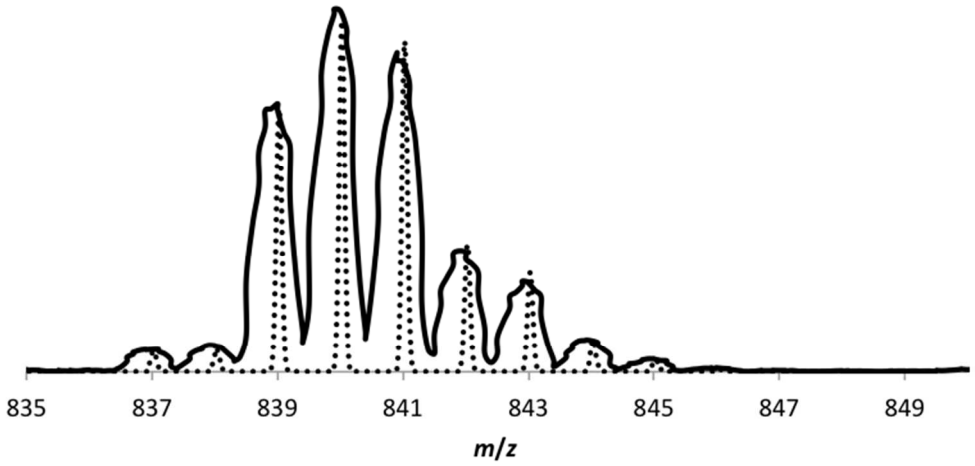

Figure S37. Positive ion ESI mass spectrum of [**3**H]BF_4. The simulated spectrum is presented as a dotted trace.

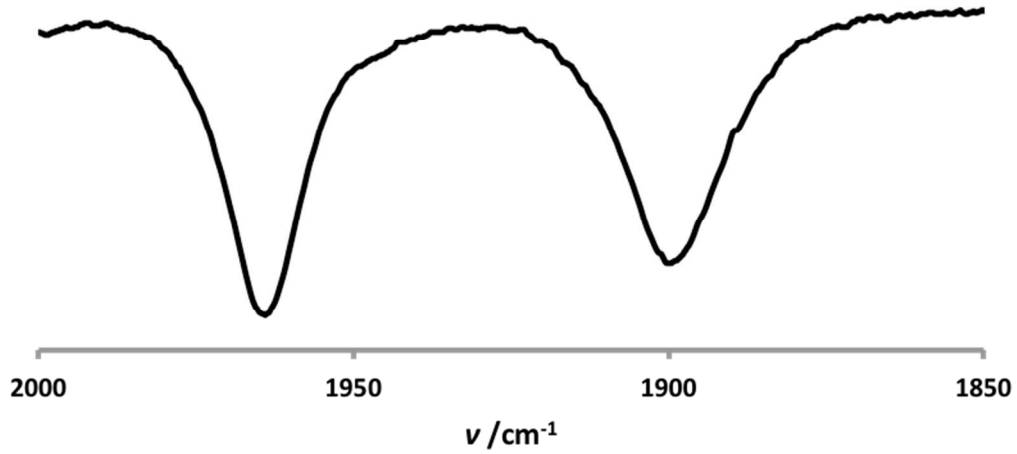

Figure S38. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of [**3′**]BF_4.

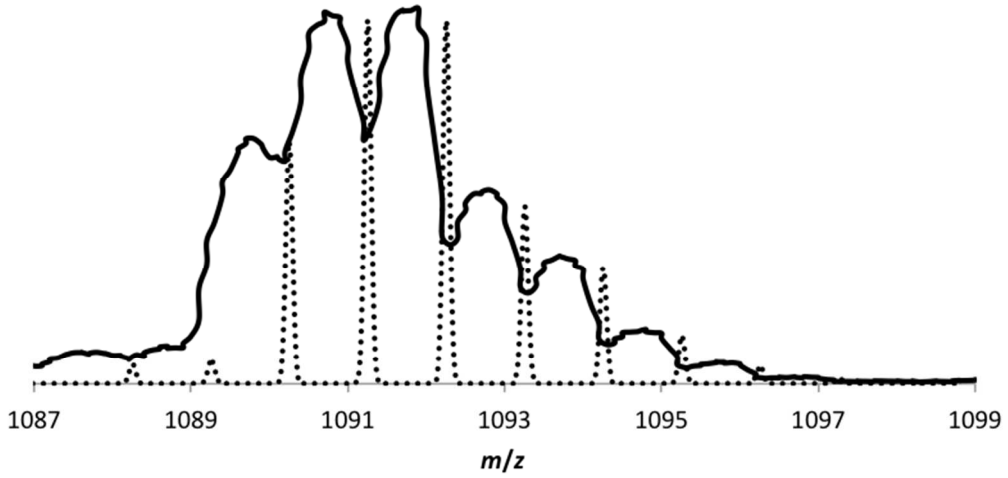

Figure S39. Positive ion ESI mass spectrum of [**3′**]BF_4. The simulated spectrum is presented as a dotted trace.

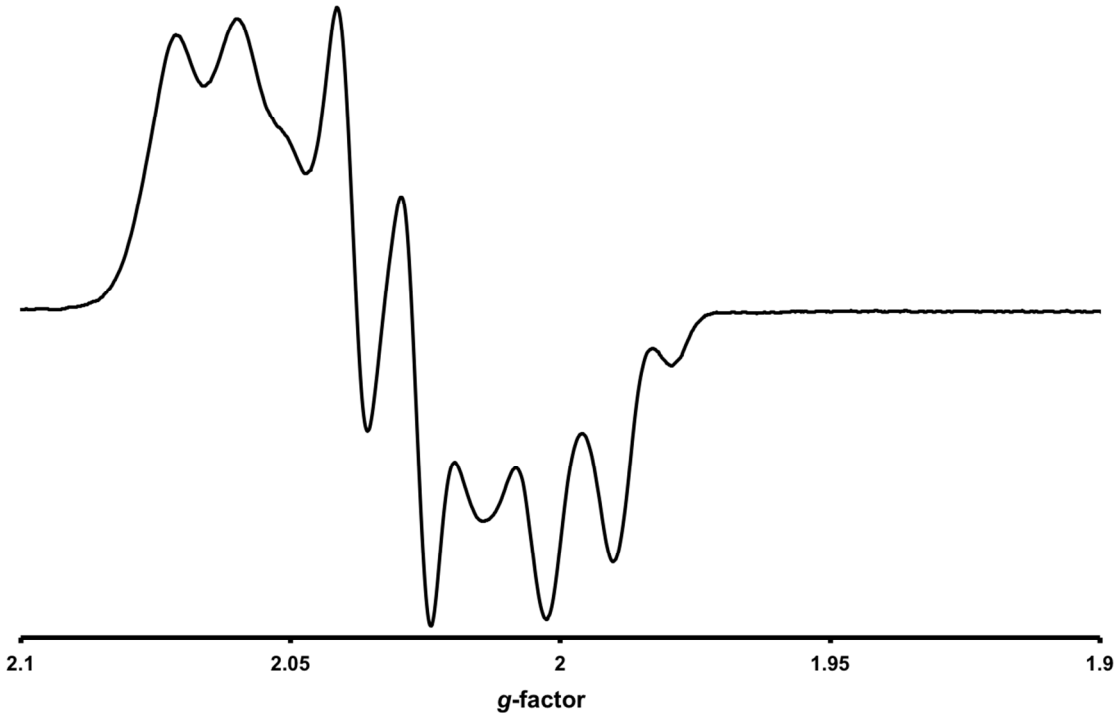

Figure S40. X-band EPR spectrum (CH_2Cl_2/PhMe, 120 K) of [**3′**]BF_4.

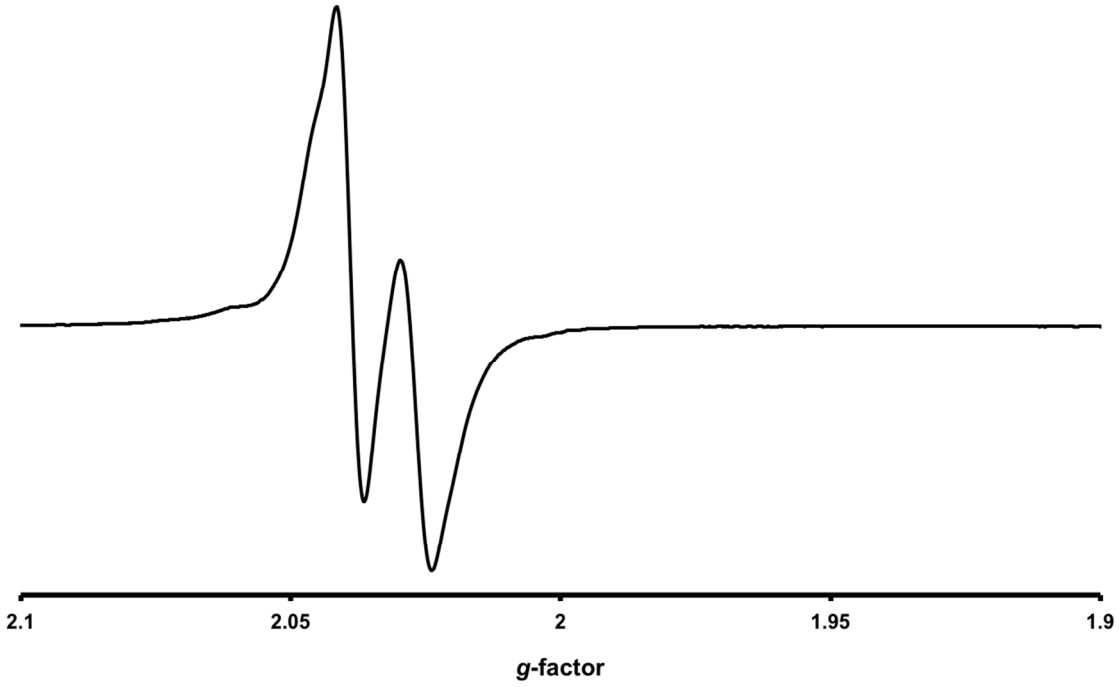

Figure S41. X-band EPR spectrum (CH_2Cl_2/PhMe, 290 K) of [**3′**]BF_4.

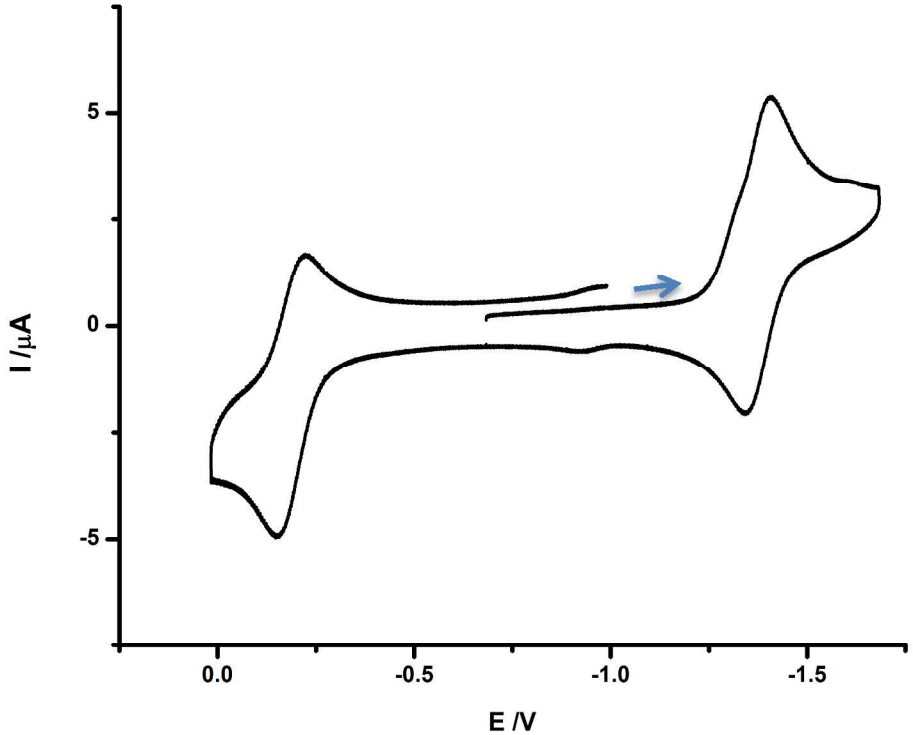

Figure S42. Cyclic voltammogram of [**3′**]BF_4. *Conditions*: see Experimental.

Table S2. Reversibility of the $[\mathbf{3'}]^{2+/+}$ Couple is Unaffected by Scan Rate.

v /mVs^{-1}	$\lvert i_{pa}/i_{pc}\rvert$
100	0.50
200	0.51
300	0.49
400	0.46
500	0.46
1000	0.43

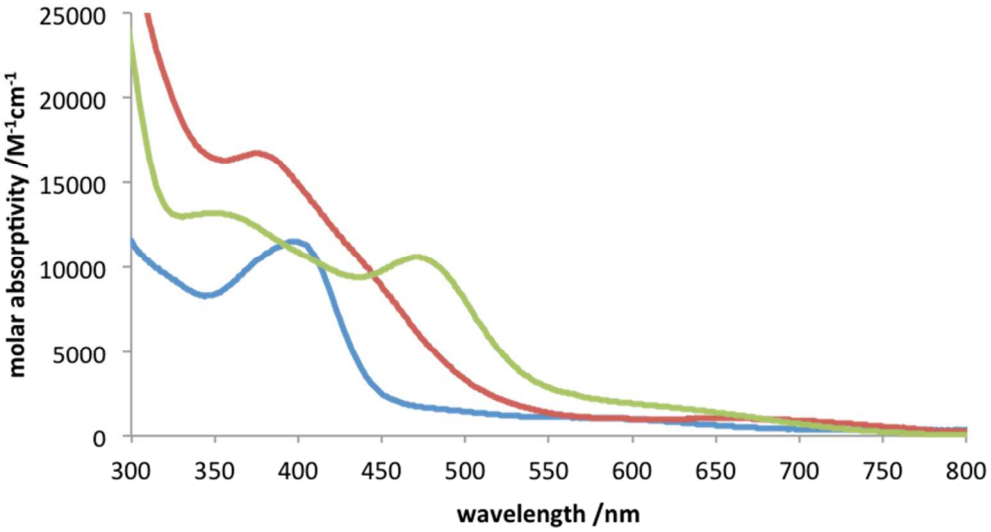

Figure S43. UV-vis spectra of **1** (blue), **2** (red) and **3** (green trace) (0.1 mM in CH_2Cl_2)

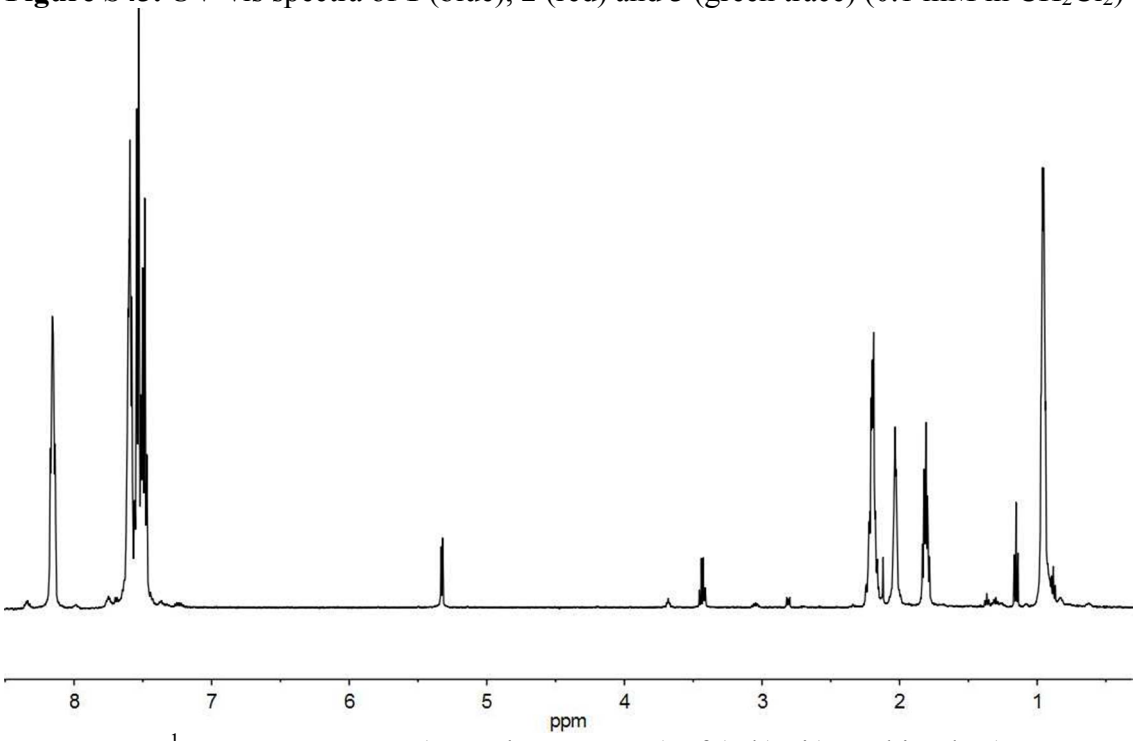

Figure S44. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of (pdt)Ni(*S*,*S*-chiraphos). Resonances at 3.69 (THF), 3.43 (Et_2O), 1.82 (THF), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

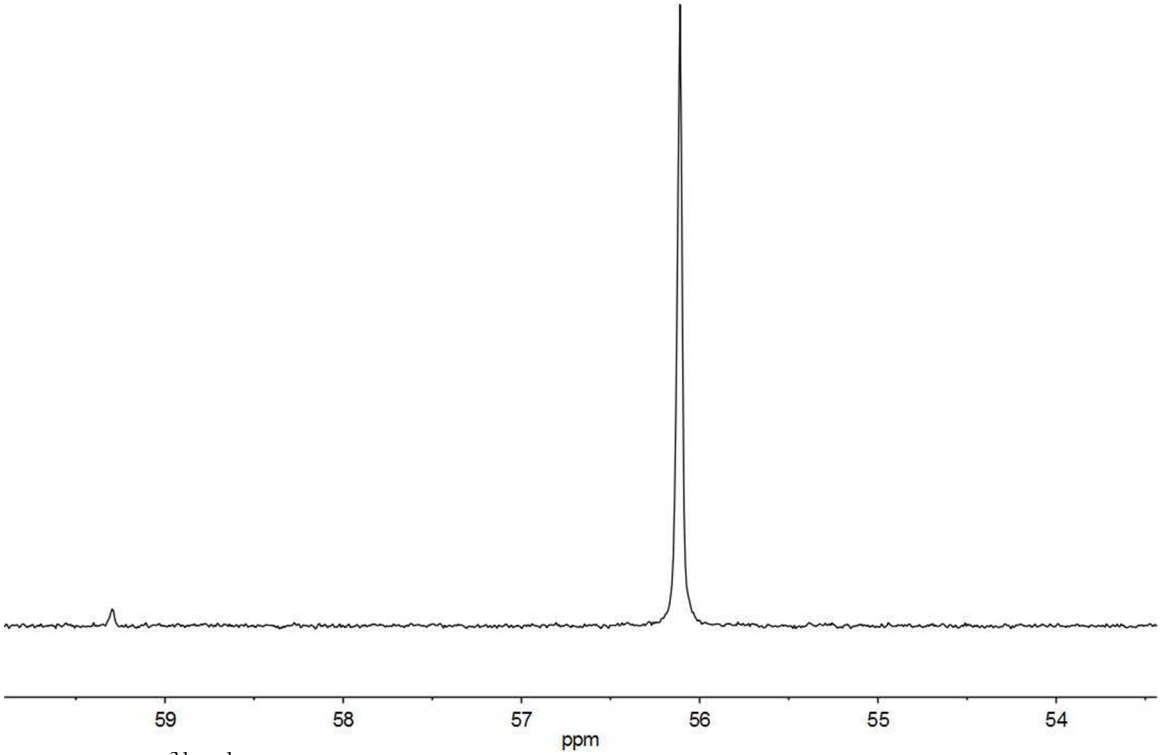

Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of (pdt)Ni(*S*,*S*-chiraphos). The narrow linewidth (~6 Hz) indicates conformational dynamics that equivalence the otherwise distinct ^{31}P sites.

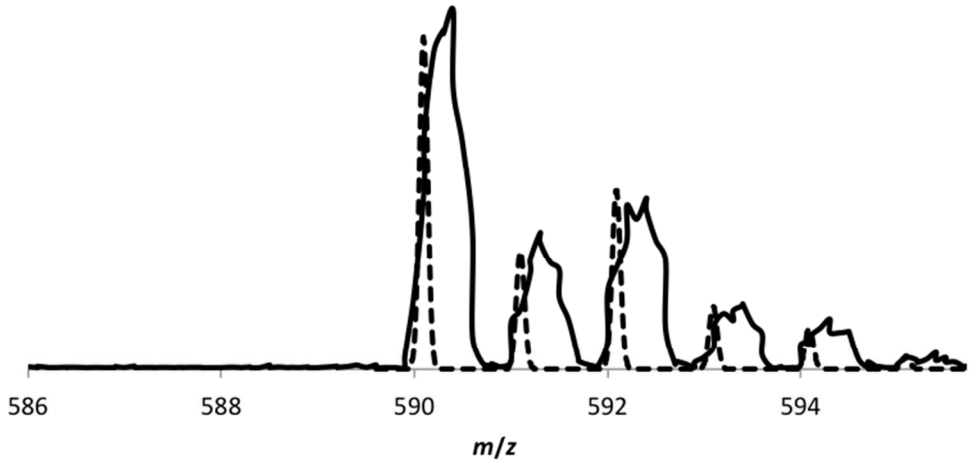

Figure S46. Positive ion ESI mass spectrum of (pdt)Ni(*S*,*S*-chiraphos). The simulated spectrum is presented as a dotted trace.

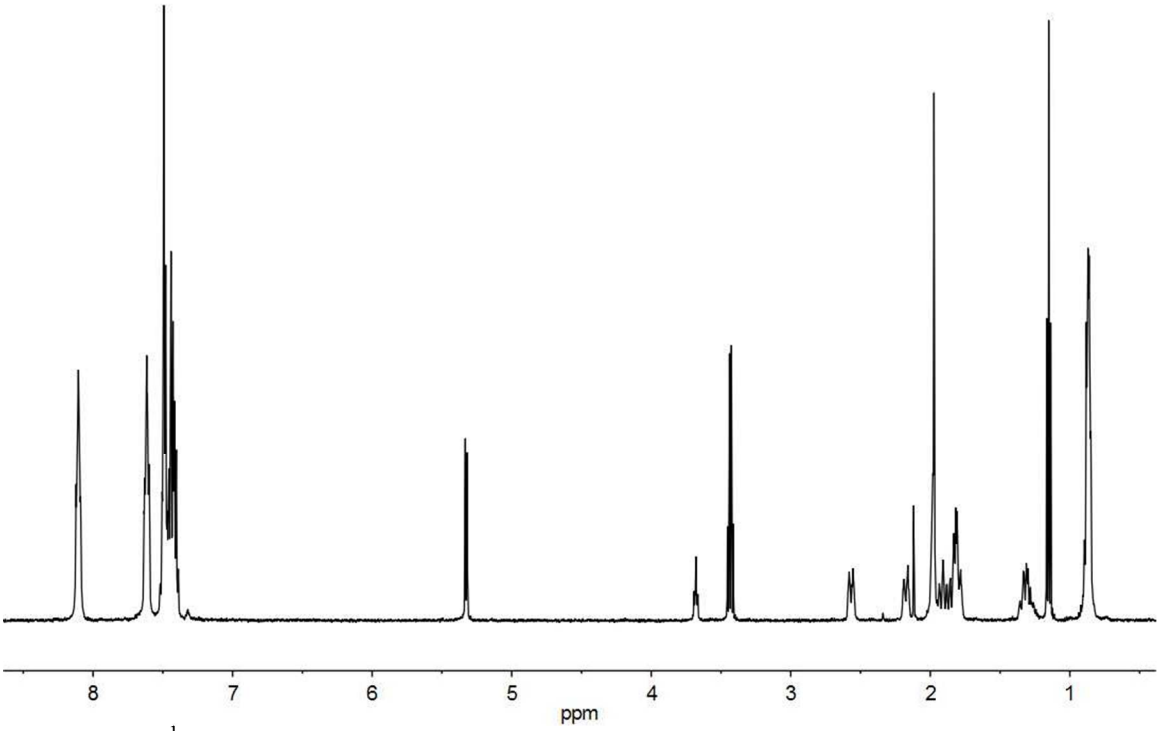

Figure S47. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of $(CO)_3$Fe(pdt)Ni(*S*,*S*-chiraphos). Resonances at 3.69 (THF), 3.43 (Et_2O), 1.82 (THF), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

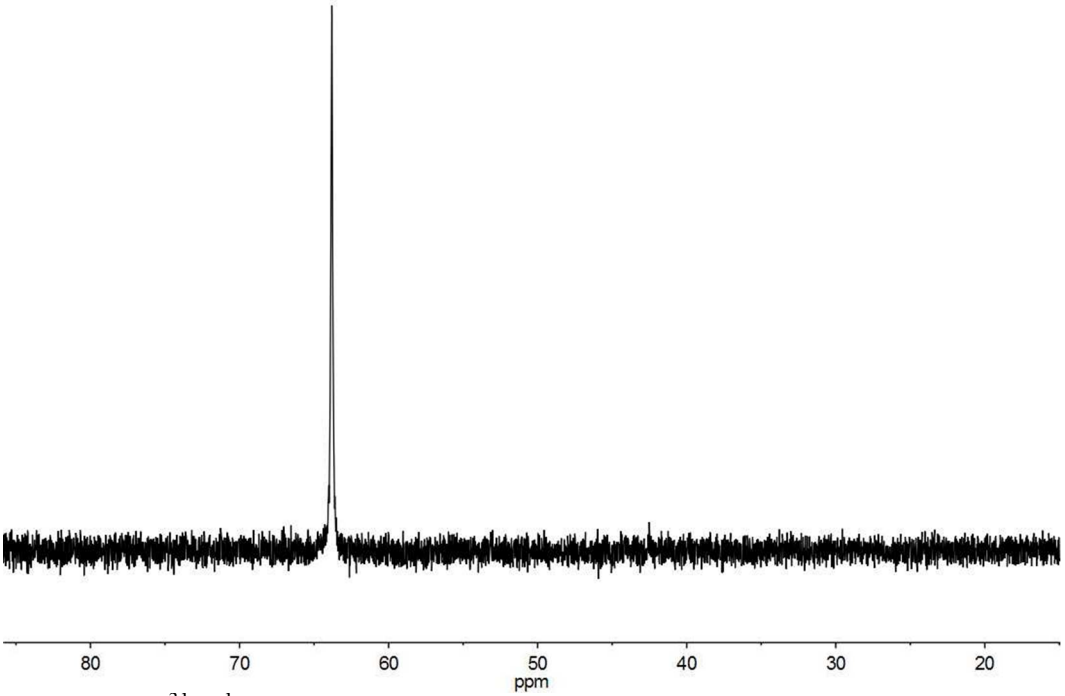

Figure S48. ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, 202 MHz) of $(CO)_3$Fe(pdt)Ni(*S*,*S*-chiraphos). If recrystallization is not performed correctly, an orange $(CO)_2$Ni(*S*,*S*-chiraphos) impurity is observed (53.0 ppm, ν_{CO} = 2001 cm^{-1}). This is easily removed by recrystallization until a pale olive filtrate is obtained.

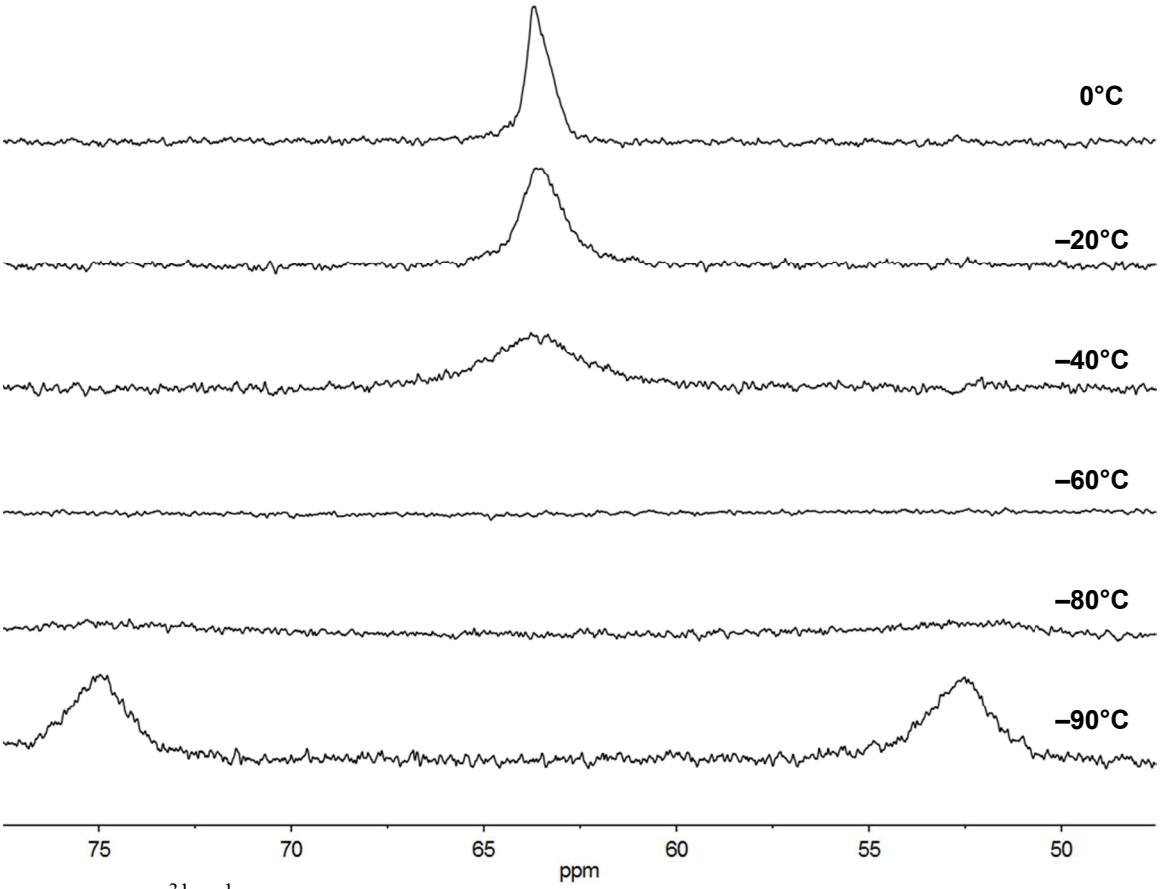

Figure S49. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2, 202 MHz) of $(CO)_3Fe(pdt)Ni(S,S\text{-chiraphos})$ acquired at different temperatures.

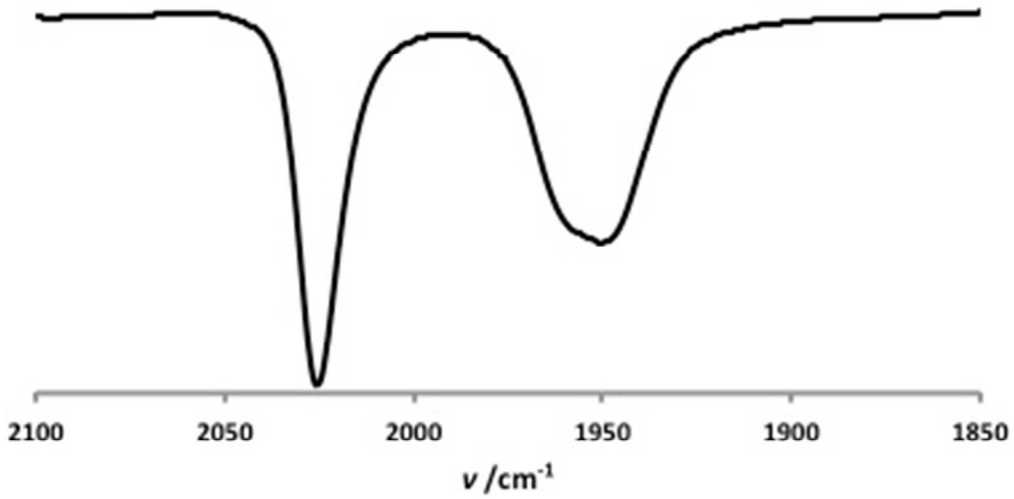

Figure S50. FT-IR spectrum (ν_{CO} region, CH_2Cl_2) of $(CO)_3Fe(pdt)Ni(S,S\text{-chiraphos})$.

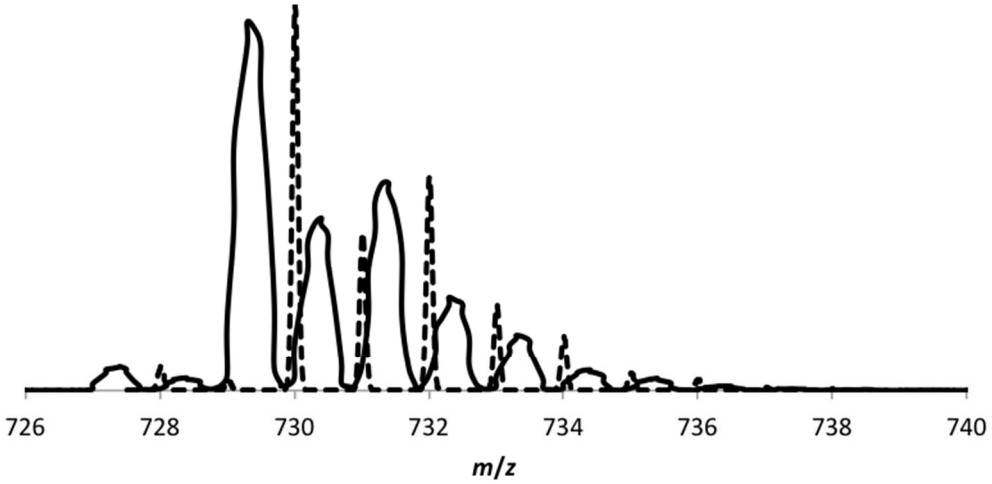

Figure S51. Positive ion ESI mass spectrum of $(CO)_3Fe(pdt)Ni(S,S\text{-chiraphos})$. The simulated spectrum is presented as a dotted trace.

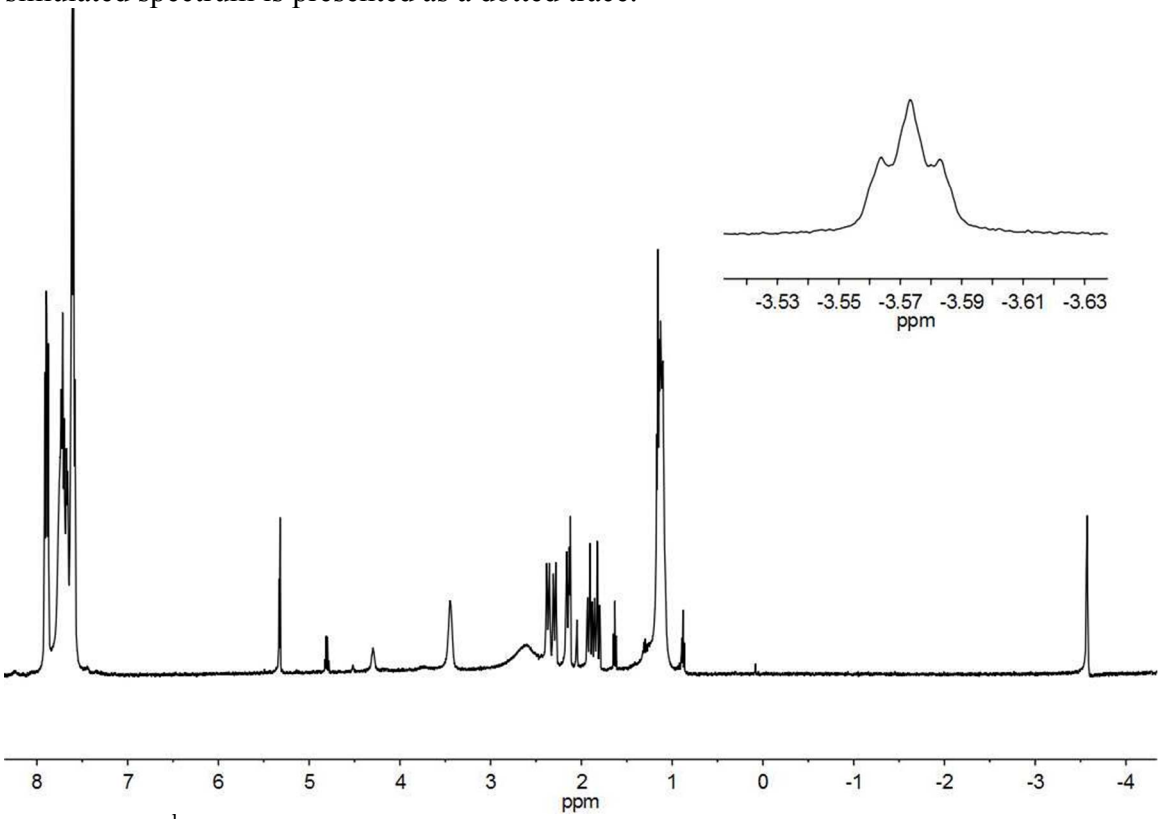

Figure S52. ^1H NMR (CD_2Cl_2, 500 MHz) spectrum of $[(CO)_3FeH(pdt)Ni(S,S\text{-chiraphos})]BF_4$. Resonances at 3.43 ($Et_2O$), 1.31 (pentane), 1.12 (Et_2O) and 0.89 ppm (pentane) are from solvent impurities.

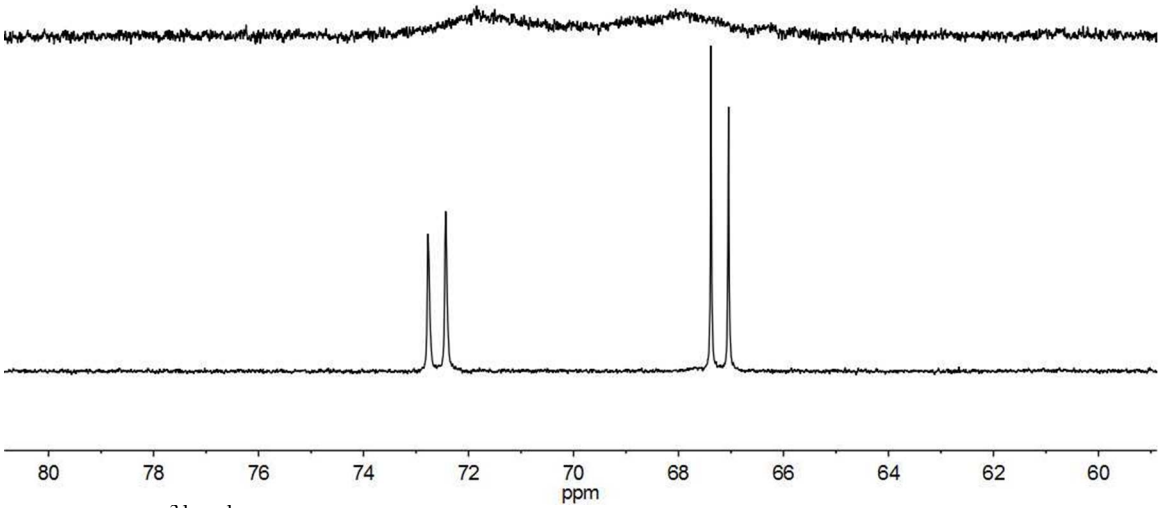

Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202 MHz) of [$(CO)_3FeH(pdt)Ni(S,S$-chiraphos)]BF_4 acquired at room temperature (top trace) and –70°C (bottom trace).

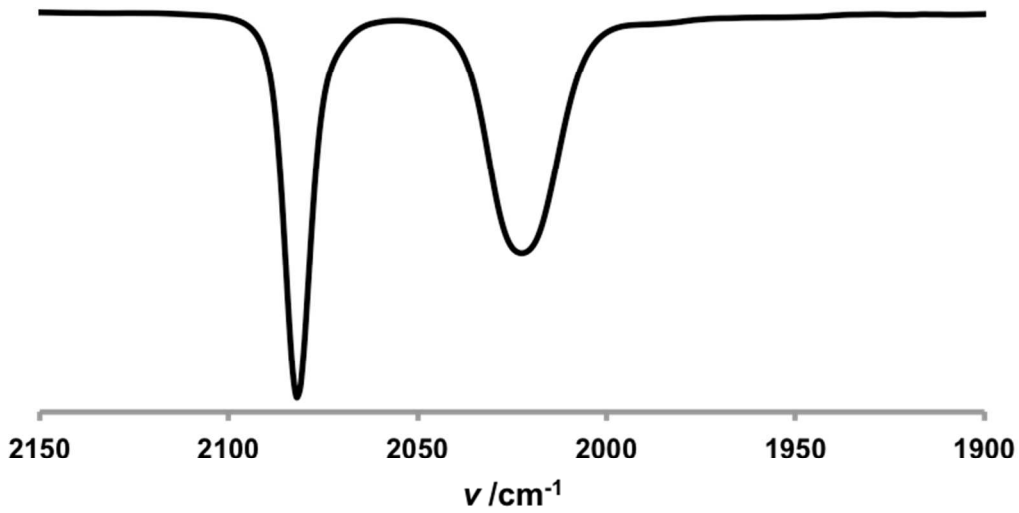

Figure S54. FT-IR (ν_{CO} region, CH_2Cl_2) of [$(CO)_3FeH(pdt)Ni(S,S$-chiraphos)]BF_4.

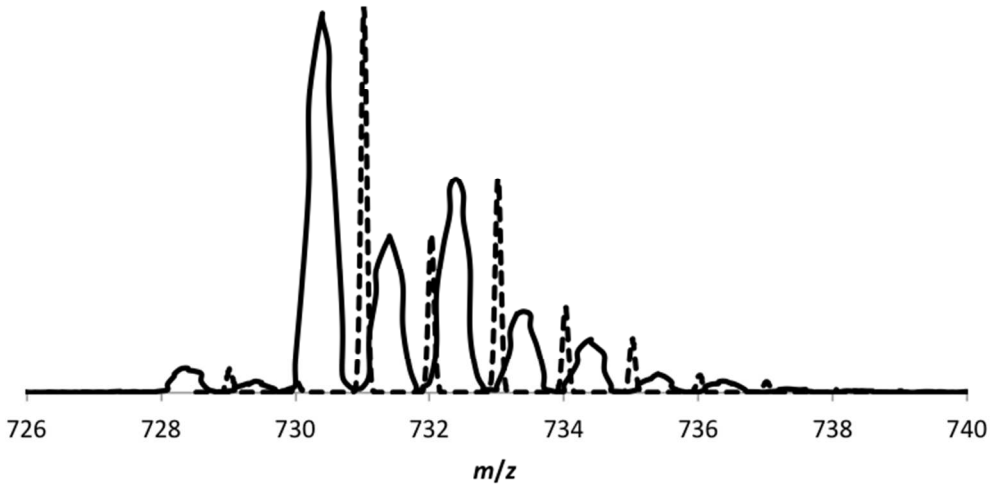

Figure S55. Positive ion ESI mass spectrum of $[(CO)_3FeH(pdt)Ni(S,S\text{-chiraphos})]BF_4$. The simulated spectrum is presented as a dotted trace.

Table S3. Selected Bond Lengths (Å) and Angles (°) for **1**-**3**, Determined Experimentally (X-ray Crystallography) and Computationally (DFT).

	$(OC)_3Fe(pdt)Ni(dppe)$ (**1**)		$(OC)_3Fe(pdt)Pd(dppe)$ (**2**)		$(OC)_3Fe(pdt)Pt(dppe)$ (**3**)	
	expt	calc	expt	calc	expt	calc
M-Fe	2.47	2.42	2.56	2.56	n/a	2.87
M-P[a]	2.15	2.16	2.26	2.26	n/a	2.28
M-S[a]	2.25	2.30	2.49	2.49	n/a	2.38
Fe-S[a]	2.28	2.29	2.29	2.30	n/a	2.36
Fe-C[a]	1.80	1.80	1.80	1.77	n/a	1.75
P-M-S[a]	117.06	114.50	128.85	135.12	n/a	176.89
S-Fe-C[a,b]	161.65	161.27	162.66	161.07	n/a	153.12

[a]These bond distances/angles are average values. [b]Values for S-Fe-CO_{trans}.

Table S4. Selected Bond Lengths (Å) and Angles (°) for [**1**-**3**H]$^+$, Determined Experimentally (X-ray Crystallography) and Computationally (DFT).

	[**1**H]$^+$		[**2**H]$^+$		[**3**H]$^+$	
	expt	calc	expt	calc	expt	calc
M-Fe	2.61	2.64	2.85	2.92	n/a	2.97
M-H	1.64	1.87	2.17	2.19	n/a	2.23
Fe-H	1.46	1.56	1.47	1.54	n/a	1.54
M-P[a]	2.17	2.19	2.26	2.30	n/a	2.29
M-S[a]	2.21	2.23	2.37	2.39	n/a	2.41
Fe-S[a]	2.32	2.34	2.34	2.35	n/a	2.36
Fe-C[a]	1.80	1.79	1.80	1.79	n/a	1.79
M-H-Fe	114.94	100.12	101.18	101.24	n/a	102.25
P-M-S[a]	176.73	178.73	177.39	176.56	n/a	176.17
S-Fe-C[a,b]	166.35	165.99	166.53	165.75	n/a	165.24

[a]These bond distances/angles are average values. [b]Values for S-Fe-CO_{trans}.

Table S5. Selected Bond Lengths (Å) and Angles (°) for Isomers of FeM Complexes **1**-**3**, with Tetrahedral or Square Planar M.

	$(OC)_3Fe(pdt)Ni(dppe)$ (**1**)		$(OC)_3Fe(pdt)Pd(dppe)$ (**2**)		$(OC)_3Fe(pdt)Pt(dppe)$ (**3**)	
	Tetrahedral	Square Planar	Tetrahedral	Square Planar	Tetrahedral	Square Planar
M-Fe	2.42	2.55	2.56	2.84	2.57	2.87
M-P[a]	2.16	2.18	2.26	2.30	2.27	2.28
M-S[a]	2.30	2.22	2.49	2.36	2.64	2.38
Fe-S[a]	2.29	2.34	2.30	2.35	2.31	2.36
Fe-C[a]	1.80	1.75	1.77	1.75	1.77	1.75
P-M-S[a]	114.50	166.46	135.12	176.10	140.21	176.89
S-Fe-C[a,b]	161.27	150.87	161.07	152.602	160.23	153.12

[a]These bond distances/angles are average values. [b]Values for S-Fe-CO_{trans}.

Table S6. Calculated Reaction Free Energies ($\Delta G°$)[a] for Rotation from Tetrahedral to Square Planar Geometry at the Ni(dppe) Site in $(CO)_3Fe(pdt)Ni(dppe)$ using Different Functionals.[b]

Functional	Gas-opt w/ solvation[c]	Sol-opt w/ solvation[d]
B3P86	–0.67	–1.28
BP86	nf[e]	–1.80
BP86-D2	nf[e]	+3.88
B3LYP	–1.10	–2.77
BLYP	nf[e]	+0.82
TPSSh	nf[e]	+1.11
M06L	nf[e]	+0.93
M11L	nf[e]	+2.71
ωB97xD	–1.28	–2.88

[a]Values given in kcal/mol for the square planar geometry relative to the tetrahedral geometry. [b]All calculations were performed using the SDD pseudopotential and associated basis set for the Fe and Ni centers, and the 6-31G* basis set for all other atoms. [c]Structures were optimized in the gas phase, and solvation free energies were calculated in CH_2Cl_2 using C-PCM. [d]Structures were optimized in CH_2Cl_2 solvent using C-PCM. [e]Minimum for the square planar geometry not found (nf).

Table S7. Calculated Reaction Free Energies ($\Delta G°$)[a] for Rotation from Tetrahedral to Square Planar Geometry at the Ni(dppe) Site in $(CO)_3Fe(pdt)Ni(dppe)$ using Different Basis Sets with the BP86 Functional.

For Ni,Fe	For other atoms	Sol-opt w/ solvation[b]
SDD[c]	6-31G*	–1.80
SDD[c]	D95*	+0.29
TZVP[d]	6-31G*	+4.20
TZVP[d]	D95*	+1.28
TZVP[d]	TZVP	+1.22

[a]Values given in kcal/mol for the square planar geometry relative to the tetrahedral geometry. [b]Structures were optimized in CH_2Cl_2 solvent using C-PCM. When optimizations were performed in the gas phase, a minimum was not found for the square planar geometry. [c]SDD pseudopotential and associated basis set used for Fe and Ni. [d]No pseudopotentials were used for Fe and Ni.

Table S8. Calculated Reaction Free Energies ($\Delta G°$)[a] for Rotation from Tetrahedral to Square Planar Geometry at the M(dppe) Site in **2** and **3** using Different Functionals.[b]

	$(OC)_3Fe(pdt)Pd(dppe)$ (**2**)		$(OC)_3Fe(pdt)Pt(dppe)$ (**3**)
Functional	Gas-opt w/ solvation[c]	Sol-opt w/ solvation[d]	Gas-opt w/ solvation[c]
B3P86	+0.99	+2.96	–30.42
BP86	nf[e]	+1.21	–3.04[f]
BP86-D2	–1.86	–0.48	–31.45
M06L	+0.96	+5.22	–39.11
ωB97xD	+1.10	+1.63	–30.83

[a]Values given in kcal/mol for the square planar geometry relative to the tetrahedral geometry. [b]All calculations were done using the SDD pseudopotential and associated basis set for the Fe, Pd, and Pt centers, and the 6-31G* basis set for all other atoms. [c]Structures were optimized in the gas phase, and solvation free energies were calculated in CH_2Cl_2 using C-PCM. [d]Structures were optimized in CH_2Cl_2 solvent using C-PCM. [e]Minimum for the square planar geometry not found (nf). [f]When the structures are optimized in solution, $\Delta G° = –26.81$ kcal/mol.

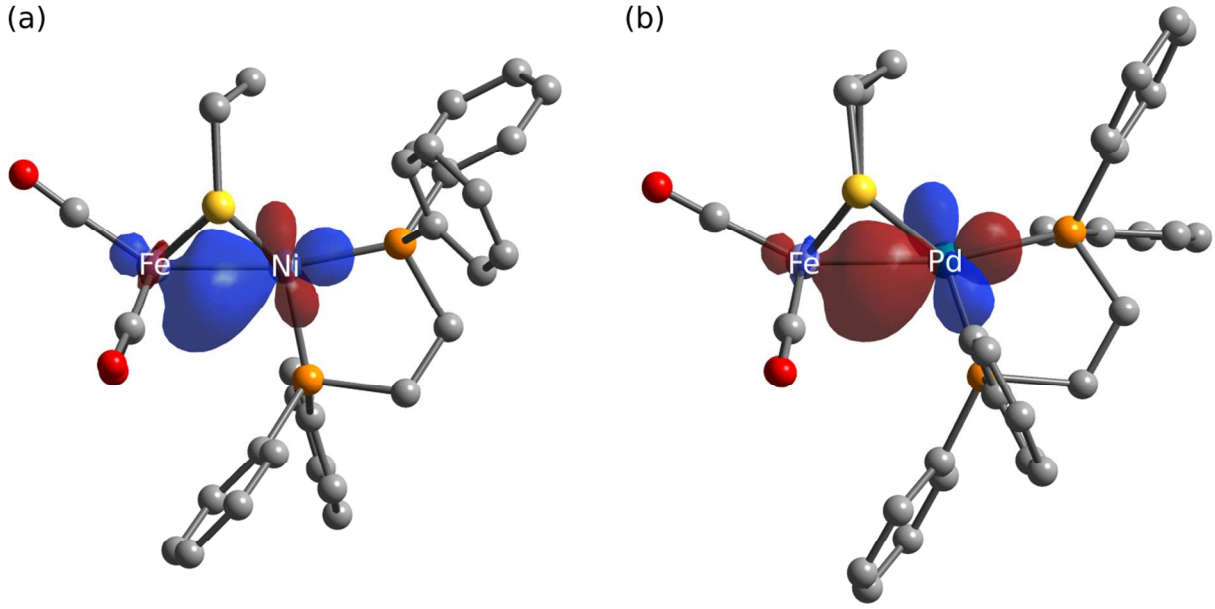

Figure S56. Depiction of natural bonding orbitals (NBO) for (a) the Ni–Fe bond in **1** and (b) the Pd–Fe bond in **2**.

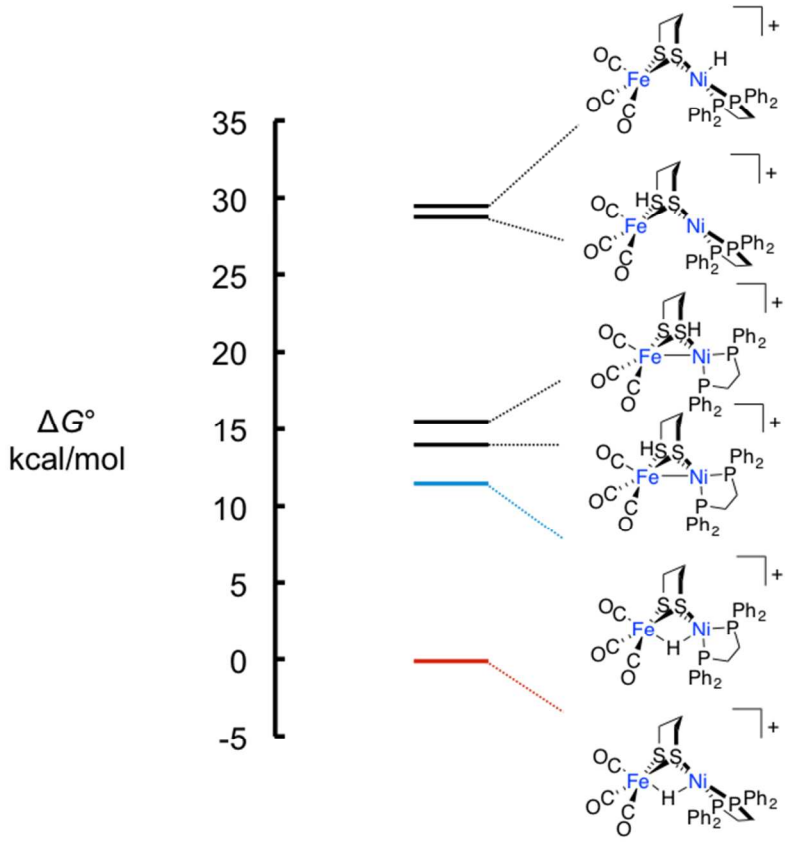

Figure S57. Isomeric forms of [**1**H]$^+$ and their free energies relative to the square-planar μ-hydride (red line). Note the high energy of the twisted Ni form (~11 kcal/mol, blue line). Even higher in energy are species in which H^+ has attacked S (~15 – 27 kcal/mol) or Ni (~30 kcal/mol). Despite their relative instabilities, these tautomers (in particular the S-protonated species) cannot be ruled out as intermediates in [**1**H]$^+$-catalyzed H^+ reduction. This is of relevance to the [NiFe]-H_2ase catalytic cycle, in which some redox states feature protonated (terminal) Cys residues bonded to Ni.

Table S9. Calculated Free Energy Barriers ($\Delta G^{\ddagger}$) and Imaginary Frequencies of Transition States for Tetrahedral to Square Planar Rotation at the Ni(dppe) Site in $(CO)_3$Fe(pdt)Ni(dppe)

	$\Delta G^{\ddagger}$ [a]	ν [b]
TS[c]	6.66	–13
TS1	4.79	–23
TS2	4.06	–52
TS3	3.18	–33

[a]Values given in kcal/mol relative to the tetrahedral geometry at 298.15 K. [b]Values given in cm^{-1}, where the negative sign indicates a negative force constant or imaginary frequency. [c]The potential energy surface was found to be extremely flat along the isomerization pathway. As a result, the single imaginary frequencies for the TSs are very small. Each TS was verified to lead to the relevant tetrahedral and square planar geometries by following the intrinsic reaction coordinate (IRC) for 4 or 5 steps in both directions and subsequently optimizing the geometries. As the imaginary frequencies may be below the numerical accuracy of the methodology, and the complete IRC was not obtained, the free energy barriers should be viewed with caution. Moreover, the observation of multiple TSs suggests a ruffled potential energy surface connecting the two isomers. Only the highest free energy barrier is reported in the main text.

In the following tables are the Cartesian coordinates of all species studied herein. The geometries were optimized in the gas phase using the B3P86 functional. The SDD psuedopotential and associated basis set were used for the Fe, Ni, Pd, and Pt centers, the 6-31G** basis set was used for the μ-H, and the 6-31G* basis set was used for all other atoms.

Table S10. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Ni(dppe)$ in Tetrahedral Geometry (**1**, –3243.63774874 E_h).

atom	x	y	z
Ni	8.847687	10.159493	2.956441
Fe	6.811047	11.448540	3.150529
P	9.873822	10.726983	4.768762
S	8.287077	11.847037	1.434691
O	5.618119	10.553429	5.674070
C	11.233549	9.462947	5.015494
H	11.998572	9.845556	5.699808
H	10.786082	8.575265	5.475655
P	10.428130	8.758622	2.469669
S	6.814672	9.236791	2.608478
C	11.816904	9.127506	3.647629
H	12.555146	8.318421	3.685126
H	12.326340	10.003656	3.228324
O	7.645944	14.023923	4.265177
O	4.384647	12.289245	1.771591
C	7.611007	11.143346	-0.116273
H	6.648811	11.628292	-0.316916
H	8.302058	11.463664	-0.903973
C	7.470826	9.631258	-0.154382
H	8.452877	9.177562	0.026233
H	7.169030	9.341802	-1.172587
C	6.454036	9.054554	0.815604
H	6.360111	7.974582	0.651988
H	5.462488	9.486806	0.639529
C	6.114081	10.906079	4.697399
C	7.335754	13.004232	3.824793
C	5.338715	11.968354	2.335833
C	10.875263	12.273307	4.792626
C	10.909057	13.086014	3.656181
H	10.300240	12.825258	2.794403
C	11.717411	14.222055	3.622433
H	11.728500	14.846504	2.733612
C	12.500015	14.555799	4.723113

H	13.128047	15.442098	4.697873
C	12.475504	13.750366	5.861912
H	13.083429	14.007256	6.725167
C	11.670781	12.616705	5.895788
H	11.650190	12.002378	6.792650
C	9.042581	10.714477	6.406956
C	8.758741	11.891012	7.110490
H	9.077337	12.850512	6.714895
C	8.065991	11.842536	8.318291
H	7.853991	12.765544	8.850898
C	7.647346	10.621783	8.840176
H	7.108373	10.586023	9.782600
C	7.910273	9.447018	8.138699
H	7.571630	8.491008	8.528063
C	8.593670	9.493619	6.928179
H	8.755201	8.571777	6.374780
C	11.289022	8.788837	0.845562
C	11.960129	7.673423	0.330734
H	11.938197	6.730456	0.869801
C	12.650897	7.764500	-0.874891
H	13.165143	6.891738	-1.268012
C	12.682742	8.968926	-1.574863
H	13.221168	9.036875	-2.516136
C	12.017299	10.083321	-1.068495
H	12.034016	11.023325	-1.613198
C	11.317996	9.993224	0.132375
H	10.774897	10.852157	0.521713
C	10.067551	6.973898	2.716228
C	10.729370	6.177122	3.656541
H	11.516937	6.593924	4.276566
C	10.389201	4.834083	3.816652
H	10.911380	4.232697	4.555717
C	9.390129	4.266775	3.032513
H	9.125856	3.220538	3.156948
C	8.726654	5.049932	2.088646
H	7.942932	4.616263	1.473986
C	9.056789	6.391537	1.939066
H	8.523518	6.998530	1.213197

Table S11. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Ni(dppe)$ in Square Planar Geometry (**1**, –3243.62931132 E_h).

atom	x	y	z
Ni	11.771907	8.828739	14.674505
Fe	10.494872	9.632165	12.624243
S	12.279380	8.172914	12.645290
S	9.635970	8.229166	14.328885
P	13.867523	9.006801	15.268319
P	11.225085	9.970070	16.448227
O	8.129190	11.285588	12.987394
O	9.779559	8.944817	9.889227
O	12.225289	11.983574	12.688701
C	14.995089	9.887248	14.128952
C	15.242305	11.257973	14.261942
H	14.789020	11.824970	15.069320
C	16.064127	11.919997	13.354465
H	16.243794	12.984815	13.470358
C	16.645075	11.221536	12.299801
H	17.283154	11.739335	11.589473
C	16.400254	9.857838	12.155113
H	16.846331	9.307291	11.331917
C	15.578951	9.193405	13.060207
H	15.392784	8.131453	12.938814
C	14.795886	7.483202	15.686926
C	16.177745	7.504491	15.915596
H	16.735828	8.427618	15.784383
C	16.842843	6.342378	16.293711
H	17.915101	6.366697	16.466961
C	16.136946	5.149253	16.445001
H	16.659711	4.242520	16.736286
C	14.763812	5.119957	16.216755
H	14.211498	4.191012	16.327491
C	14.096578	6.282924	15.837881
H	13.026125	6.271847	15.648588
C	10.887965	8.977581	17.954495
C	10.725605	7.593445	17.848761
H	10.759798	7.137796	16.862891
C	10.504087	6.820490	18.987416
H	10.376195	5.745782	18.893273
C	10.442934	7.424378	20.239921
H	10.271427	6.822026	21.127670
C	10.595836	8.806030	20.354425

H	10.540123	9.282195	21.329320
C	10.814916	9.578850	19.218896
H	10.911695	10.657099	19.317743
C	9.889353	11.212079	16.411229
C	10.074607	12.399959	15.690569
H	10.995015	12.572931	15.140368
C	9.063381	13.352173	15.639078
H	9.217354	14.267656	15.075663
C	7.851164	13.123078	16.287975
H	7.059032	13.864536	16.237304
C	7.652386	11.935649	16.985337
H	6.704312	11.744196	17.479695
C	8.666043	10.982395	17.049686
H	8.502947	10.059104	17.596123
C	11.659108	6.486793	12.267666
H	11.134304	6.562309	11.308561
H	12.551338	5.870673	12.112525
C	10.764162	5.837277	13.309233
H	10.530085	4.819264	12.962654
H	11.315600	5.734321	14.252716
C	9.460757	6.570856	13.569507
H	8.844618	5.985482	14.261849
H	8.898047	6.694466	12.637349
C	9.083884	10.644900	12.857115
C	10.026047	9.176997	11.001409
C	11.579542	11.011725	12.714878
C	13.935609	9.981361	16.857065
H	13.882368	9.243912	17.666053
H	14.891385	10.507231	16.956139
C	12.740197	10.927512	16.935598
H	12.839187	11.752352	16.221628
H	12.633753	11.363317	17.934828

Table S12. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Ni(dppe)$ Transition State (**1**, –3243.62855419 E_h).

atom	x	y	z
Ni	-0.192720	0.214282	-0.321409
Fe	-2.499788	0.903913	0.081258
S	-0.985012	2.155929	-1.028222
S	-2.028064	-0.833463	-1.408868
P	1.944031	0.564200	-0.541729
P	0.248716	-1.152352	1.326836
O	-4.017273	-1.086063	1.590026
O	-4.843105	2.276285	-0.969305
O	-1.733089	2.477054	2.428853
C	2.436279	2.326417	-0.390999
C	3.155435	3.015741	-1.374494
H	3.455074	2.509564	-2.291441
C	3.464589	4.364667	-1.206364
H	4.003993	4.889867	-1.993415
C	3.059880	5.040007	-0.057143
H	3.293562	6.093915	0.063016
C	2.330273	4.364286	0.923424
H	2.006341	4.882888	1.826434
C	2.013954	3.021054	0.754396
H	1.418977	2.511729	1.515816
C	2.928805	-0.084094	-1.949198
C	2.278030	-0.817209	-2.948012
H	1.213428	-0.945979	-2.876695
C	2.993926	-1.382694	-4.005282
H	2.490145	-1.903297	-4.779613
C	4.373949	-1.209848	-4.071912
H	4.930402	-1.641046	-4.901529
C	5.039931	-0.483233	-3.072211
H	6.122951	-0.324160	-3.126939
C	4.325000	0.072730	-2.013621
H	4.860511	0.690705	-1.252790
C	0.766203	-2.849781	0.833512
C	1.415445	-3.703136	1.738033
H	1.581873	-3.386561	2.764885
C	1.841385	-4.964405	1.336161
H	2.349793	-5.614203	2.043431
C	1.615805	-5.393579	0.027569
H	1.939626	-6.383267	-0.283138
C	0.961045	-4.558626	-0.872714

H	0.758175	-4.898741	-1.885393
C	0.540261	-3.290125	-0.473722
H	0.007264	-2.639075	-1.162790
C	-0.773827	-1.465085	2.817037
C	-0.889133	-0.479754	3.806960
H	-0.379699	0.472645	3.696552
C	-1.678978	-0.696462	4.931158
H	-1.755196	0.077408	5.689817
C	-2.374528	-1.895289	5.078867
H	-2.991434	-2.062543	5.957258
C	-2.277770	-2.873459	4.093786
H	-2.820182	-3.808850	4.198608
C	-1.482971	-2.662025	2.969998
H	-1.412124	-3.436067	2.212288
C	-1.373595	2.182320	-2.821260
H	-2.372130	2.626738	-2.911113
H	-0.660622	2.897192	-3.247612
C	-1.290990	0.861234	-3.562548
H	-1.450822	1.067019	-4.632507
H	-0.267274	0.474782	-3.464951
C	-2.283903	-0.197462	-3.107228
H	-2.190004	-1.070840	-3.765038
H	-3.311675	0.175463	-3.197366
C	-3.389626	-0.310613	1.012570
C	-3.926306	1.700613	-0.562817
C	-2.026139	1.836876	1.509226
C	2.815969	-0.247826	0.909819
H	3.209770	-1.202669	0.544531
H	3.664804	0.363694	1.233548
C	1.833788	-0.494813	2.049635
H	2.246194	-1.188013	2.791316
H	1.594302	0.438170	2.570323

Table S13. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Ni(dppe)]^+$ ($[\mathbf{1}]^+$, –3243.44266981 E_h).

atom	x	y	z
Ni	11.771907	8.828739	14.674505
Fe	10.494872	9.632165	12.624243
S	12.279380	8.172914	12.645290
S	9.635970	8.229166	14.328885
P	13.867523	9.006801	15.268319
P	11.225085	9.970070	16.448227
O	8.129190	11.285588	12.987394
O	9.779559	8.944817	9.889227
O	12.225289	11.983574	12.688701
C	14.995089	9.887248	14.128952
C	15.242305	11.257973	14.261942
H	14.789020	11.824970	15.069320
C	16.064127	11.919997	13.354465
H	16.243794	12.984815	13.470358
C	16.645075	11.221536	12.299801
H	17.283154	11.739335	11.589473
C	16.400254	9.857838	12.155113
H	16.846331	9.307291	11.331917
C	15.578951	9.193405	13.060207
H	15.392784	8.131453	12.938814
C	14.795886	7.483202	15.686926
C	16.177745	7.504491	15.915596
H	16.735828	8.427618	15.784383
C	16.842843	6.342378	16.293711
H	17.915101	6.366697	16.466961
C	16.136946	5.149253	16.445001
H	16.659711	4.242520	16.736286
C	14.763812	5.119957	16.216755
H	14.211498	4.191012	16.327491
C	14.096578	6.282924	15.837881
H	13.026125	6.271847	15.648588
C	10.887965	8.977581	17.954495
C	10.725605	7.593445	17.848761
H	10.759798	7.137796	16.862891
C	10.504087	6.820490	18.987416
H	10.376195	5.745782	18.893273
C	10.442934	7.424378	20.239921
H	10.271427	6.822026	21.127670
C	10.595836	8.806030	20.354425

H	10.540123	9.282195	21.329320
C	10.814916	9.578850	19.218896
H	10.911695	10.657099	19.317743
C	9.889353	11.212079	16.411229
C	10.074607	12.399959	15.690569
H	10.995015	12.572931	15.140368
C	9.063381	13.352173	15.639078
H	9.217354	14.267656	15.075663
C	7.851164	13.123078	16.287975
H	7.059032	13.864536	16.237304
C	7.652386	11.935649	16.985337
H	6.704312	11.744196	17.479695
C	8.666043	10.982395	17.049686
H	8.502947	10.059104	17.596123
C	11.659108	6.486793	12.267666
H	11.134304	6.562309	11.308561
H	12.551338	5.870673	12.112525
C	10.764162	5.837277	13.309233
H	10.530085	4.819264	12.962654
H	11.315600	5.734321	14.252716
C	9.460757	6.570856	13.569507
H	8.844618	5.985482	14.261849
H	8.898047	6.694466	12.637349
C	9.083884	10.644900	12.857115
C	10.026047	9.176997	11.001409
C	11.579542	11.011725	12.714878
C	13.935609	9.981361	16.857065
H	13.882368	9.243912	17.666053
H	14.891385	10.507231	16.956139
C	12.740197	10.927512	16.935598
H	12.839187	11.752352	16.221628
H	12.633753	11.363317	17.934828

Table S14. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Ni(dppe)]^{2+}$ ($[\mathbf{1}]^{2+}$, –3243.09204890 E_h).

atom	x	y	z
Ni	11.852384	8.688197	14.881823
Fe	10.636173	9.283715	12.642104
S	12.320934	7.811054	12.859634
S	9.666981	8.313423	14.413524
P	13.997513	9.009863	15.416213
P	11.322068	9.875076	16.676056
O	8.609106	11.459123	12.852209
O	9.222800	7.860138	10.538905
O	12.350212	10.896349	10.817829
C	14.829733	10.269627	14.409011
C	15.280183	11.471871	14.974354
H	15.158929	11.674841	16.033212
C	15.925070	12.419525	14.183833
H	16.279690	13.341182	14.634498
C	16.129766	12.178858	12.827376
H	16.639876	12.916547	12.215878
C	15.692036	10.983118	12.258804
H	15.867343	10.784323	11.206041
C	15.040481	10.033984	13.039484
H	14.726234	9.097279	12.588705
C	14.959394	7.476708	15.371777
C	16.220086	7.400002	14.768310
H	16.653628	8.268627	14.283457
C	16.930114	6.202275	14.804924
H	17.911134	6.147259	14.343660
C	16.391340	5.083776	15.436859
H	16.952257	4.154814	15.465032
C	15.136104	5.156527	16.042298
H	14.723068	4.288195	16.546345
C	14.419382	6.347036	16.008300
H	13.448564	6.402937	16.498743
C	10.582223	8.896199	18.006557
C	10.500907	7.502700	17.896970
H	10.833363	7.011149	16.985101
C	9.996646	6.744408	18.950115
H	9.936716	5.663909	18.863417
C	9.568263	7.376014	20.115605
H	9.172649	6.786384	20.936675
C	9.645894	8.764156	20.231610

H	9.310256	9.254421	21.139998
C	10.153695	9.526292	19.184962
H	10.203823	10.607565	19.284526
C	10.230559	11.266074	16.276505
C	10.757335	12.392586	15.620282
H	11.812890	12.448112	15.365849
C	9.928894	13.464002	15.303263
H	10.343852	14.341095	14.816311
C	8.571420	13.415368	15.620913
H	7.928499	14.256292	15.380259
C	8.039972	12.290617	16.250451
H	6.984006	12.253517	16.499183
C	8.861524	11.214709	16.575936
H	8.442151	10.348899	17.078733
C	11.738487	6.066982	12.954685
H	11.243150	5.856863	12.001014
H	12.661177	5.480341	12.979731
C	10.860677	5.716641	14.140563
H	10.612803	4.648926	14.065638
H	11.436770	5.833417	15.066761
C	9.554086	6.481625	14.235353
H	8.990044	6.164535	15.117464
H	8.915735	6.302450	13.363834
C	9.405128	10.649564	12.802900
C	9.771641	8.457729	11.340374
C	11.705457	10.281898	11.524619
C	14.007998	9.593437	17.169304
H	13.862079	8.698493	17.785668
H	14.988777	10.000787	17.437233
C	12.876303	10.590902	17.385640
H	13.077724	11.543700	16.887397
H	12.721745	10.802757	18.448750

Table S15. Cartesian Coordinates of the Optimized Structure of $[(OC)_3FeH(pdt)Ni(dppe)]^+$ in Square Planar Geometry ($[\mathbf{1}H]^+$, –3244.06263786 E_h).

atom	x	y	z
Ni	8.783654	10.028306	2.863227
Fe	6.508034	10.917070	3.148014
S	7.873013	11.419506	1.411648
S	6.893654	8.655974	2.695546
P	10.856432	9.789358	2.274304
P	9.373793	9.662305	4.928506
O	7.031578	13.615650	4.152528
O	3.976136	11.275722	1.752155
O	5.281309	10.046259	5.654561
C	11.865046	11.212898	1.701478
C	11.303043	12.489978	1.624685
H	10.248589	12.621295	1.846944
C	12.083867	13.581187	1.244864
H	11.633596	14.567866	1.182673
C	13.431113	13.406151	0.944005
H	14.038943	14.257072	0.649012
C	14.000335	12.134784	1.017403
H	15.051104	11.992729	0.780134
C	13.222386	11.044446	1.391346
H	13.670169	10.054666	1.431939
C	11.207570	8.522592	0.988527
C	11.246810	7.163417	1.324269
H	11.129280	6.853577	2.359369
C	11.426548	6.193706	0.342275
H	11.461042	5.144416	0.622212
C	11.559488	6.566506	-0.993697
H	11.698009	5.809696	-1.760475
C	11.512819	7.914903	-1.340005
H	11.617070	8.214902	-2.379115
C	11.337628	8.886333	-0.357829
H	11.312914	9.935719	-0.638220
C	8.354747	8.704443	6.111618
C	7.986794	7.397168	5.762143
H	8.289743	6.985052	4.804145
C	7.205182	6.630468	6.620337
H	6.926600	5.620304	6.333940
C	6.772217	7.159438	7.834124
H	6.159504	6.561034	8.502439
C	7.116751	8.462932	8.180367

H	6.770049	8.888770	9.117721
C	7.899661	9.233124	7.324574
H	8.151080	10.251754	7.602420
C	10.053599	11.058556	5.913232
C	9.989939	12.353043	5.392348
H	9.496958	12.510583	4.438238
C	10.550897	13.425532	6.084234
H	10.487135	14.426528	5.667803
C	11.185492	13.211544	7.303778
H	11.622397	14.046052	7.845210
C	11.260155	11.922328	7.831632
H	11.754557	11.750676	8.783864
C	10.700267	10.852635	7.141061
H	10.753944	9.854522	7.568410
C	7.347904	10.524574	-0.107683
H	6.336132	10.875981	-0.340772
H	8.009956	10.896776	-0.897036
C	7.398340	9.007195	-0.067839
H	7.132450	8.641494	-1.071534
H	8.425697	8.680055	0.130240
C	6.464355	8.361890	0.942298
H	6.493886	7.273406	0.817710
H	5.428543	8.679948	0.774519
C	5.810259	10.374161	4.684373
C	4.972214	11.123426	2.317094
C	6.851447	12.539128	3.771476
C	11.828041	9.201195	3.760238
H	12.623547	8.513064	3.454527
H	12.306048	10.092385	4.182060
C	10.890178	8.581124	4.789009
H	10.541800	7.593674	4.466229
H	11.382505	8.458393	5.760124
Ni	8.783654	10.028306	2.863227

Table S16. Cartesian Coordinates of the Optimized Structure of $[(OC)_3FeH(pdt)Ni(dppe)]^+$ in Tetrahedral Geometry ($[\mathbf{1}H]^+$, –3244.04345183 E_h).

atom	x	y	z
Ni	11.827170	9.006419	14.641203
Fe	10.561795	9.145075	12.443890
H	11.141137	10.097806	13.604115
S	12.779336	8.411936	12.415058
S	10.194505	7.622578	14.128212
P	12.300885	8.275118	16.640506
P	12.759428	10.897652	15.213863
O	8.179873	10.675389	13.218181
O	8.937312	7.438715	10.691307
O	11.566774	11.067552	10.459587
C	13.232191	6.705859	16.630779
C	14.585494	6.701181	16.267687
H	15.095507	7.630803	16.029590
C	15.290938	5.503754	16.203395
H	16.341671	5.511164	15.929606
C	14.650487	4.299684	16.492204
H	15.202210	3.365857	16.443040
C	13.303895	4.296710	16.849141
H	12.803866	3.361455	17.082539
C	12.594049	5.492983	16.917850
H	11.548003	5.483271	17.209671
C	10.972841	8.027475	17.863917
C	11.311939	7.608851	19.160068
H	12.344482	7.380525	19.411208
C	10.325183	7.469161	20.129273
H	10.594839	7.143468	21.129354
C	8.993841	7.742525	19.815590
H	8.224499	7.629371	20.573487
C	8.651347	8.156221	18.531696
H	7.614918	8.363881	18.283426
C	9.637019	8.301463	17.557356
H	9.365677	8.612558	16.554455
C	11.662558	12.047552	16.100899
C	10.286741	11.806921	16.167027
H	9.872590	10.930830	15.677455
C	9.452175	12.682792	16.857852
H	8.384675	12.490016	16.901123
C	9.988139	13.801440	17.489388
H	9.338351	14.484026	18.028697

C	11.359730	14.049108	17.428622
H	11.778238	14.923550	17.917582
C	12.195411	13.178872	16.737559
H	13.259643	13.392539	16.681003
C	13.590172	11.859007	13.913972
C	14.697317	11.296326	13.262346
H	15.052293	10.306740	13.535277
C	15.335798	11.993871	12.242780
H	16.194628	11.553332	11.745881
C	14.867868	13.247942	11.854131
H	15.365746	13.789135	11.055322
C	13.757802	13.803617	12.485556
H	13.387871	14.778081	12.181515
C	13.117268	13.114328	13.511871
H	12.255722	13.557715	14.001264
C	12.724305	6.618278	12.073431
H	12.141899	6.453447	11.160176
H	13.759107	6.338193	11.849579
C	12.212983	5.768170	13.222399
H	12.339392	4.709692	12.953522
H	12.833263	5.944829	14.106323
C	10.749002	5.955782	13.578544
H	10.482632	5.298692	14.412122
H	10.097803	5.687596	12.738908
C	9.092211	10.064718	12.892996
C	9.631438	8.091993	11.326649
C	11.168725	10.328844	11.235823
C	13.430710	9.512938	17.470515
H	12.796915	10.077818	18.162221
H	14.184260	8.987683	18.065824
C	14.061856	10.454628	16.450236
H	14.874992	9.969641	15.899434
H	14.475262	11.348796	16.928445

Table S17. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Pd(dppe)$ in Tetrahedral Geometry (**2**, –3200.63063206 E_h).

atom	x	y	z
Pd	11.760100	8.959800	14.585700
Fe	10.734400	9.333100	12.291000
P	11.739700	11.003200	15.608000
P	12.809600	8.122000	16.459300
S	9.284900	8.219700	13.721900
S	12.339400	7.752100	12.581300
O	9.007700	11.635700	12.820200
O	9.525200	8.386100	9.814300
O	12.927500	10.998200	11.277000
C	12.351000	12.506900	14.757100
C	13.691200	12.553000	14.348300
H	14.353600	11.716700	14.557600
C	14.180800	13.650500	13.649200
H	15.223000	13.671400	13.343100
C	13.334800	14.710700	13.328200
H	13.715900	15.564800	12.775700
C	11.996300	14.662200	13.707100
H	11.326100	15.477700	13.449700
C	11.504500	13.568900	14.417100
H	10.457800	13.542600	14.702700
C	10.215100	11.549800	16.473200
C	10.203700	12.690000	17.290300
H	11.094700	13.307000	17.377200
C	9.050700	13.052800	17.978000
H	9.052400	13.939800	18.605500
C	7.894400	12.281000	17.859000
H	6.993700	12.566700	18.395300
C	7.896600	11.149100	17.050000
H	6.997900	10.547600	16.947200
C	9.052000	10.782700	16.359600
H	9.052900	9.897200	15.727900
C	12.922500	10.832600	17.044600
H	13.942100	10.902700	16.649100
H	12.782900	11.659300	17.749900
C	12.710700	9.484600	17.726700
H	11.709500	9.435300	18.171300
H	13.436400	9.328300	18.532200
C	12.122500	6.675200	17.352300
C	10.764600	6.716700	17.702100

H	10.165900	7.586800	17.441300
C	10.169100	5.642000	18.352600
H	9.117800	5.691700	18.622100
C	10.914000	4.499200	18.642900
H	10.446600	3.656400	19.144100
C	12.255400	4.439500	18.276800
H	12.839700	3.548500	18.489800
C	12.858900	5.520300	17.635900
H	13.906200	5.461100	17.356400
C	14.612500	7.805100	16.342800
C	15.413200	7.637700	17.482200
H	14.965200	7.654600	18.472600
C	16.783800	7.432100	17.358300
H	17.393300	7.303100	18.248500
C	17.372100	7.391700	16.094500
H	18.442800	7.233200	15.999000
C	16.585800	7.555500	14.957800
H	17.038600	7.525600	13.970700
C	15.212600	7.763100	15.079600
H	14.595000	7.898400	14.194800
C	9.262900	6.444800	13.297700
H	8.476200	6.014900	13.927700
H	8.939500	6.327600	12.256300
C	10.566500	5.701300	13.540700
H	10.904700	5.886100	14.567400
H	10.373300	4.621100	13.453600
C	11.679800	6.041300	12.566600
H	11.365800	5.840500	11.535400
H	12.552000	5.408800	12.765500
C	9.691600	10.731100	12.614500
C	10.003200	8.775300	10.788500
C	12.065600	10.349600	11.679400

Table S18. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Pd(dppe)$ in Square Planar Geometry (**2**, –3200.61739333 E_h).

atom	x	y	z
Pd	11.781700	8.815800	14.693900
Fe	10.669800	9.373900	12.138700
P	11.197000	9.938900	16.606800
P	13.965200	9.097600	15.352900
S	9.548200	8.414200	14.003700
S	12.359900	7.847400	12.637100
O	8.558800	11.367000	12.001300
O	9.981600	8.130000	9.593400
O	12.670600	11.446800	11.682100
C	14.956100	7.591300	15.652200
C	14.291100	6.381200	15.876000
H	13.206500	6.351400	15.799900
C	15.012800	5.229200	16.178400
H	14.488700	4.292800	16.347600
C	16.402900	5.277000	16.251900
H	16.966800	4.376900	16.480200
C	17.071700	6.478800	16.024800
H	18.156100	6.517300	16.076000
C	16.353500	7.633100	15.726400
H	16.880100	8.564600	15.538400
C	15.020600	10.137100	14.290700
C	15.482900	9.606100	13.077900
H	15.236200	8.584700	12.804500
C	16.242400	10.389000	12.215800
H	16.589600	9.968500	11.276800
C	16.544700	11.708000	12.547100
H	17.131900	12.319300	11.868000
C	16.083600	12.244000	13.745800
H	16.310600	13.273400	14.007700
C	15.323800	11.464300	14.613700
H	14.968100	11.905000	15.540400
C	13.940800	9.923700	17.021500
H	13.885700	9.106500	17.749900
H	14.881000	10.455900	17.204700
C	12.724400	10.836800	17.154900
H	12.800400	11.698600	16.481500
H	12.617900	11.235700	18.170100
C	9.909500	11.227000	16.548900
C	9.651900	11.857400	15.327400

H	10.178600	11.529900	14.433700
C	8.705700	12.876200	15.254800
H	8.497800	13.342100	14.296600
C	8.015700	13.268800	16.398800
H	7.272000	14.058700	16.340200
C	8.267000	12.640100	17.618000
H	7.722600	12.940100	18.509000
C	9.207800	11.618100	17.695900
H	9.387400	11.118500	18.644000
C	10.723600	8.861100	18.007300
C	9.714600	7.914100	17.781700
H	9.265400	7.843200	16.793600
C	9.298200	7.073700	18.808100
H	8.510700	6.348700	18.622900
C	9.893000	7.154500	20.066900
H	9.572400	6.491300	20.865200
C	10.900400	8.086600	20.297300
H	11.368200	8.155400	21.275400
C	11.311500	8.940200	19.274500
H	12.092800	9.666100	19.479400
C	9.344000	6.646200	13.556800
H	8.620500	6.232600	14.268700
H	8.892300	6.622800	12.558500
C	10.609600	5.804500	13.584800
H	11.065700	5.874600	14.581700
H	10.326200	4.752100	13.431700
C	11.644000	6.164300	12.529600
H	11.209100	6.081600	11.526700
H	12.488200	5.469200	12.591700
C	9.406900	10.575700	12.053400
C	10.216300	8.567200	10.645800
C	11.889500	10.619500	11.934100

Table S19. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Pd(dppe)$ Transition State (**2**, –3200.61680041 E_h).

atom	x	y	z
Pd	11.497455	8.606819	14.929156
Fe	10.879576	8.985757	12.273784
P	13.485564	8.541377	16.075957
P	10.855196	10.263067	16.381954
S	9.307436	8.366440	13.962921
S	12.202461	7.300807	13.124546
O	9.129261	11.247573	11.734958
O	10.345938	7.667185	9.732455
O	13.225320	10.699588	11.966480
C	10.052027	11.770660	15.742048
C	10.701112	12.473293	14.717169
H	11.632514	12.095837	14.302241
C	10.134048	13.629139	14.193868
H	10.641698	14.161556	13.395284
C	8.906202	14.084445	14.672521
H	8.457967	14.980234	14.252451
C	8.246638	13.378151	15.673602
H	7.281835	13.719398	16.037927
C	8.814940	12.224283	16.209583
H	8.290609	11.677353	16.986551
C	9.852098	9.724742	17.815450
C	9.720949	10.522457	18.961245
H	10.189549	11.502230	19.005165
C	8.973825	10.077267	20.047282
H	8.879584	10.702958	20.930334
C	8.345584	8.833264	19.999674
H	7.762964	8.486943	20.848705
C	8.463235	8.039162	18.862441
H	7.969748	7.072406	18.818657
C	9.214385	8.480649	17.774979
H	9.309546	7.872979	16.878827
C	12.423418	10.880985	17.165620
H	12.909781	11.524414	16.423641
H	12.206074	11.498585	18.043849
C	13.303310	9.687804	17.528287
H	12.823335	9.092318	18.313858
H	14.282608	9.995287	17.912093
C	14.013556	6.970992	16.853607
C	13.052015	5.983952	17.093078

H	12.030909	6.150134	16.756738
C	13.403447	4.802217	17.740715
H	12.650683	4.039702	17.919814
C	14.719935	4.595247	18.145855
H	14.996783	3.670436	18.644160
C	15.684659	5.572127	17.904375
H	16.713243	5.410501	18.214488
C	15.335674	6.755995	17.261047
H	16.093711	7.509267	17.065172
C	14.971256	9.112559	15.180132
C	15.485903	8.304064	14.156008
H	15.011906	7.354619	13.926744
C	16.589366	8.720585	13.419841
H	16.974010	8.086409	12.626579
H	17.144522	11.719605	14.913323
C	15.579779	10.345365	15.441528
H	15.200589	10.996463	16.223407
C	8.926412	6.611579	13.603961
H	8.034156	6.369887	14.193251
H	8.662038	6.543146	12.542208
C	10.030491	5.621616	13.938409
H	10.318373	5.745224	14.991186
H	9.629507	4.602350	13.830209
C	11.269092	5.723169	13.062841
H	11.003080	5.575575	12.009591
H	11.982147	4.940382	13.342866
C	9.836072	10.357286	11.955488
C	10.504566	8.151036	10.777608
C	12.304715	10.010247	12.152188

Table S20. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Pd(dppe)]^+$ ($[\mathbf{2}]^+$, –3200.43767846 E_h).

atom	x	y	z
Pd	11.854982	8.736043	14.815498
Fe	10.777786	9.068406	12.064401
S	12.425307	7.598521	12.799867
S	9.625973	8.470910	13.999975
P	14.040055	9.089183	15.468396
P	11.237858	9.891102	16.713456
O	9.045323	11.434872	11.855920
O	9.408649	7.290846	10.092489
O	12.797508	10.276257	10.299961
C	14.895033	10.344663	14.470937
C	15.285161	11.582917	14.994634
H	15.118212	11.825224	16.039603
C	15.906894	12.524049	14.177046
H	16.209026	13.480271	14.593240
C	16.144413	12.237396	12.835609
H	16.629443	12.972697	12.200918
C	15.761754	11.004520	12.308319
H	15.946407	10.776075	11.263345
C	15.136887	10.062295	13.117500
H	14.844970	9.101879	12.700381
C	15.119701	7.630092	15.527871
C	16.495562	7.724784	15.291357
H	16.938827	8.675585	15.010991
C	17.298053	6.592898	15.408462
H	18.364773	6.669332	15.221195
C	16.736206	5.368377	15.762558
H	17.365976	4.488252	15.850462
C	15.365825	5.269860	15.999656
H	14.926596	4.314885	16.272125
C	14.557589	6.395375	15.878084
H	13.485996	6.317068	16.049452
C	10.525043	8.808034	17.988538
C	9.269577	8.232066	17.739395
H	8.740765	8.464623	16.818478
C	8.693367	7.380654	18.675249
H	7.715861	6.949673	18.480674
C	9.365300	7.084371	19.861061
H	8.914105	6.417644	20.589545
C	10.612202	7.649419	20.112732

H	11.135632	7.427935	21.037839
C	11.191431	8.510321	19.182638
H	12.159082	8.949006	19.405908
C	10.089002	11.278550	16.498073
C	10.135924	12.004375	15.300989
H	10.810408	11.694588	14.505560
C	9.313966	13.112703	15.124545
H	9.346640	13.665584	14.191011
C	8.439451	13.497923	16.139032
H	7.792544	14.358544	15.998362
C	8.387795	12.777012	17.330468
H	7.704382	13.076201	18.119332
C	9.208551	11.668004	17.514433
H	9.158722	11.106046	18.442344
C	11.650156	5.939290	12.960028
H	11.224426	5.694893	11.980737
H	12.482286	5.251848	13.138781
C	10.610965	5.786002	14.057813
H	10.286165	4.735476	14.063305
H	11.074669	5.980470	15.033892
C	9.370140	6.650081	13.911083
H	8.667109	6.419738	14.717131
H	8.860295	6.447581	12.963038
C	9.725631	10.514075	11.945242
C	9.930075	8.008184	10.819933
C	12.010691	9.814646	10.997422
C	13.979130	9.713049	17.212909
H	13.896052	8.813935	17.834109
H	14.924516	10.196206	17.483609
C	12.781494	10.636156	17.420806
H	12.915128	11.580259	16.880500
H	12.637293	10.893792	18.475984

Table S21. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Pd(dppe)]^{2+}$ ($[\mathbf{2}]^{2+}$, –3200.09088385 E_h).

atom	x	y	z
Pd	11.833087	8.753169	14.802254
Fe	10.807468	9.161728	12.316504
S	12.405285	7.632314	12.737285
S	9.573492	8.370425	14.014806
P	14.039770	9.135241	15.446048
P	11.226139	9.924011	16.718636
O	8.952692	11.493561	12.248211
O	9.500865	7.706593	10.164916
O	12.775390	10.567436	10.577873
C	14.882298	10.344930	14.396305
C	15.184767	11.634208	14.856043
H	14.943775	11.939799	15.869318
C	15.829221	12.539896	14.017396
H	16.071387	13.532331	14.384381
C	16.176273	12.168833	12.720271
H	16.686460	12.874949	12.072617
C	15.879978	10.886619	12.257405
H	16.164529	10.591158	11.252297
C	15.230212	9.977650	13.085408
H	15.021330	8.974306	12.723277
C	15.030431	7.623365	15.511610
C	16.382246	7.609495	15.146098
H	16.860291	8.505536	14.763206
C	17.120180	6.436207	15.281808
H	18.168729	6.427585	15.001382
C	16.519906	5.281487	15.779038
H	17.101624	4.370902	15.883222
C	15.174245	5.292684	16.148218
H	14.710094	4.394125	16.542959
C	14.428880	6.458463	16.013533
H	13.381025	6.466261	16.310523
C	10.564130	8.793486	17.968291
C	9.346938	8.138844	17.712043
H	8.799905	8.342082	16.794695
C	8.816262	7.260628	18.650116
H	7.865302	6.773902	18.456559
C	9.497573	7.014579	19.842498
H	9.081019	6.328956	20.573721
C	10.706241	7.656753	20.100526

H	11.231851	7.476336	21.032912
C	11.240588	8.544847	19.170389
H	12.174627	9.046064	19.403236
C	10.062853	11.283120	16.454196
C	10.360762	12.216405	15.447780
H	11.246796	12.090859	14.826843
C	9.534115	13.316790	15.253636
H	9.770790	14.044518	14.483545
C	8.402247	13.486687	16.052350
H	7.756844	14.346033	15.899663
C	8.102287	12.560403	17.048264
H	7.226280	12.697943	17.674222
C	8.928334	11.457995	17.255298
H	8.694616	10.750100	18.043942
C	11.730759	5.938043	12.971263
H	11.311936	5.639735	12.004162
H	12.618068	5.321951	13.144163
C	10.734606	5.748906	14.101191
H	10.469123	4.683182	14.129236
H	11.213410	5.974339	15.062113
C	9.441633	6.534501	13.978624
H	8.779887	6.296931	14.816489
H	8.899093	6.287542	13.059841
C	9.670664	10.613724	12.293923
C	10.011408	8.314770	10.983064
C	12.034188	10.032375	11.253736
C	13.977082	9.794566	17.173734
H	13.927454	8.909734	17.818220
H	14.918239	10.303017	17.411490
C	12.768637	10.699069	17.380432
H	12.875993	11.642101	16.833211
H	12.628107	10.966506	18.433770

Table S22. Cartesian Coordinates of the Optimized Structure of $[(OC)_3FeH(pdt)Pd(dppe)]^+$ ($[\mathbf{2}H]^+$, –3201.05077293 E_h).

atom	x	y	z
Pd	6.095431	7.186811	2.688546
Fe	8.509967	6.581939	1.171311
H	8.285184	7.195985	2.565487
S	6.812839	5.083952	1.817382
S	6.735260	7.987850	0.534187
P	5.657809	6.343251	4.776299
P	5.482312	9.237899	3.537457
O	10.404242	4.925468	2.659786
O	8.942553	5.408074	-1.512579
O	10.294243	8.881756	0.916214
C	9.675240	5.568008	2.054044
C	8.756095	5.859529	-0.475858
C	9.611063	7.965641	0.996975
C	5.823327	4.727509	0.313356
H	6.511186	4.353604	-0.452986
H	5.169220	3.896333	0.594800
C	4.983116	5.874926	-0.225314
H	4.275038	6.199072	0.548769
H	4.385862	5.488315	-1.063252
C	5.756770	7.083969	-0.726277
H	5.058862	7.824212	-1.129279
H	6.440352	6.804761	-1.535558
C	4.061714	5.489638	4.947747
C	3.259760	5.271695	3.822663
H	3.615401	5.592830	2.847218
C	2.020528	4.648706	3.953396
H	1.403094	4.482683	3.075756
C	1.576609	4.239696	5.207821
H	0.610934	3.753979	5.310395
C	2.371734	4.450751	6.334485
H	2.027803	4.128248	7.312511
C	3.608905	5.073012	6.208595
H	4.226216	5.218947	7.091412
C	6.938108	5.260111	5.473125
C	8.205092	5.799000	5.741604
H	8.410463	6.849735	5.551340
C	9.218062	4.987432	6.239471
H	10.194430	5.412631	6.450628
C	8.981556	3.630903	6.459375

H	9.774666	2.998054	6.845698
C	7.731763	3.087203	6.175653
H	7.547299	2.029649	6.337872
C	6.710856	3.895048	5.681068
H	5.740269	3.462145	5.461229
C	5.534954	7.797021	5.922035
H	5.040966	7.499212	6.853020
H	6.555762	8.103661	6.174142
C	4.775002	8.919393	5.221364
H	4.753057	9.839835	5.814846
H	3.732193	8.626440	5.051532
C	4.192711	10.149715	2.639543
C	4.085687	11.542051	2.740187
H	4.816087	12.107447	3.311453
C	3.044769	12.205598	2.097052
H	2.966710	13.285749	2.174786
C	2.108970	11.488331	1.354382
H	1.300411	12.010762	0.852060
C	2.212426	10.102348	1.250623
H	1.486414	9.543629	0.667577
C	3.253304	9.433822	1.887532
H	3.347172	8.354140	1.797978
C	6.870059	10.394169	3.754245
C	7.336756	10.780799	5.016189
H	6.856064	10.425085	5.922302
C	8.424687	11.644151	5.127069
H	8.775460	11.942043	6.110562
C	9.053087	12.128107	3.983132
H	9.899773	12.801889	4.072239
C	8.591248	11.750104	2.722893
H	9.075859	12.128171	1.828045
C	7.508503	10.885849	2.605327
H	7.153875	10.597018	1.619517

Table S23. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Pt(dppe)$ in Tetrahedral Geometry (**3**, –3192.11918792 E_h).

atom	x	y	z
Pt	8.738200	10.001500	3.030000
Fe	6.486600	11.248700	2.958400
P	10.467000	8.570300	2.596300
P	9.885500	10.704400	4.848700
S	6.779700	9.244800	1.915400
S	7.945600	12.308100	1.466800
O	5.377300	9.683000	5.171900
O	4.067900	12.278200	1.684100
O	7.161700	13.503100	4.687100
C	10.872500	12.245700	4.758900
C	10.761500	13.066200	3.632800
H	10.063900	12.799600	2.841300
C	11.538100	14.219700	3.526200
H	11.436900	14.852700	2.649200
C	12.430600	14.559600	4.538100
H	13.034400	15.459000	4.453900
C	12.547700	13.745400	5.664900
H	13.240800	14.008600	6.459100
C	11.774100	12.594900	5.775400
H	11.862200	11.976000	6.665100
C	9.022700	10.765600	6.461200
C	8.889900	11.942800	7.204700
H	9.326500	12.867900	6.843300
C	8.186800	11.936900	8.408100
H	8.086900	12.859300	8.973300
C	7.612500	10.760900	8.881000
H	7.065100	10.759700	9.819200
C	7.728600	9.586900	8.137600
H	7.266300	8.669300	8.489800
C	8.419500	9.590700	6.931700
H	8.466700	8.681700	6.336800
C	11.208600	9.418200	5.128200
H	11.969900	9.797700	5.818200
H	10.731800	8.552900	5.602400
C	11.823200	9.023100	3.789400
H	12.536200	8.199800	3.904900
H	12.364600	9.870400	3.352200
C	10.179300	6.793600	2.940000
C	8.872400	6.343900	3.156500

H	8.052100	7.054500	3.097500
C	8.629000	5.002700	3.448600
H	7.609500	4.666500	3.614400
C	9.686400	4.101300	3.531600
H	9.496000	3.057000	3.763100
C	10.992700	4.540300	3.318200
H	11.821200	3.840200	3.380800
C	11.238400	5.878000	3.024200
H	12.260200	6.204900	2.847900
C	11.301400	8.624700	0.965600
C	11.460600	7.506300	0.141100
H	11.107100	6.533700	0.469100
C	12.071100	7.632700	-1.105800
H	12.186900	6.756000	-1.737000
C	12.530400	8.872300	-1.540500
H	13.007700	8.967600	-2.511700
C	12.364400	9.994700	-0.729400
H	12.706500	10.968700	-1.067700
C	11.744000	9.875100	0.508900
H	11.577300	10.761700	1.116800
C	6.853900	9.342000	0.084600
H	7.112300	8.326800	-0.236200
H	5.822300	9.530200	-0.236800
C	7.801900	10.341400	-0.550800
H	8.833200	10.109100	-0.260400
H	7.733200	10.201200	-1.640500
C	7.502400	11.797100	-0.225800
H	6.446700	12.026300	-0.416600
H	8.094600	12.443800	-0.883000
C	5.817600	10.298800	4.302100
C	5.018000	11.869200	2.194100
C	6.893900	12.607700	4.010500

Table S24. Cartesian Coordinates of the Optimized Structure of $(OC)_3Fe(pdt)Pt(dppe)$ in Square Planar Geometry (**3**, –3192.15744694 E_h).

atom	x	y	z
Pt	8.834100	9.939500	2.856100
Fe	6.332300	11.335800	2.985400
P	9.272400	7.981900	3.931600
P	10.852600	10.676800	3.621300
S	6.735200	9.224600	1.979000
S	8.267600	12.012600	1.849700
O	4.233500	10.087200	4.562100
O	4.523300	13.019000	1.436900
O	7.182900	12.857200	5.323100
C	12.090300	11.144600	2.360500
C	11.950700	10.646500	1.061000
H	11.072400	10.053200	0.818600
C	12.917900	10.921800	0.098000
H	12.801100	10.534800	-0.909700
C	14.026000	11.699800	0.425100
H	14.776800	11.920400	-0.327900
C	14.168300	12.201200	1.717400
H	15.028700	12.812300	1.973100
C	13.205600	11.925900	2.684100
H	13.314800	12.329200	3.686500
C	10.846200	12.075500	4.791900
C	10.584400	13.362100	4.300300
H	10.422100	13.513400	3.237500
C	10.513800	14.442600	5.171800
H	10.304300	15.433100	4.780600
C	10.697100	14.254500	6.540000
H	10.635000	15.099500	7.218700
C	10.950500	12.979300	7.036000
H	11.088800	12.825100	8.101700
C	11.023600	11.893600	6.167600
H	11.215600	10.906100	6.575900
C	11.665800	9.258600	4.507800
H	12.221200	8.715700	3.735600
H	12.397600	9.627600	5.233400
C	10.619200	8.352000	5.148600
H	10.112500	8.854800	5.979400
H	11.057900	7.433900	5.552300
C	7.959300	7.211200	4.932600
C	6.949100	8.029000	5.448800

H	6.934600	9.085900	5.191800
C	5.956900	7.482300	6.257800
H	5.164200	8.121300	6.632800
C	5.971300	6.122000	6.555100
H	5.192600	5.695000	7.180200
C	6.975600	5.303700	6.040300
H	6.981900	4.241200	6.264800
C	7.967200	5.842700	5.226900
H	8.737900	5.198900	4.813000
C	9.903800	6.635300	2.866700
C	9.152400	6.300500	1.731700
H	8.242400	6.855200	1.516600
C	9.571200	5.276400	0.890300
H	8.977300	5.020900	0.018100
C	10.752500	4.585500	1.159100
H	11.082900	3.792200	0.495500
C	11.508000	4.916800	2.279200
H	12.428900	4.383300	2.494500
C	11.083800	5.933500	3.133800
H	11.684100	6.169400	4.007000
C	6.684500	9.545100	0.170700
H	6.625900	8.562800	-0.309500
H	5.745100	10.074700	-0.019900
C	7.860400	10.316300	-0.403900
H	8.788800	9.784000	-0.160600
H	7.764300	10.320100	-1.499300
C	7.975300	11.759400	0.057900
H	7.061600	12.314700	-0.180700
H	8.811200	12.244300	-0.455900
C	5.074400	10.588600	3.938500
C	5.249200	12.297900	1.989700
C	6.895200	12.207700	4.400600

Table S25. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Pt(dppe)]^+$ ($[\mathbf{3}]^+$, –3191.97670157 E_h).

atom	x	y	z
Pt	11.863461	8.743407	14.836427
Fe	10.766466	9.085595	12.071662
S	12.422215	7.610947	12.796310
S	9.624758	8.456885	14.010101
P	14.041834	9.102312	15.470268
P	11.242029	9.887200	16.726569
O	9.009464	11.434779	11.877478
O	9.415015	7.319646	10.077916
O	12.777940	10.333251	10.324910
C	14.905411	10.344611	14.463995
C	15.285654	11.590259	14.976124
H	15.105002	11.845497	16.015317
C	15.913423	12.522663	14.153308
H	16.207478	13.485067	14.559629
C	16.166967	12.218765	12.818996
H	16.656993	12.946659	12.180377
C	15.794065	10.978044	12.303645
H	15.991970	10.736836	11.264440
C	15.163119	10.044487	13.117710
H	14.878395	9.078206	12.710224
C	15.108712	7.634832	15.530625
C	16.487425	7.724210	15.310297
H	16.937915	8.673441	15.037555
C	17.282996	6.588268	15.432427
H	18.351605	6.659771	15.257119
C	16.711179	5.365636	15.775998
H	17.335471	4.482559	15.867982
C	15.338068	5.272935	15.997841
H	14.891819	4.319609	16.262712
C	14.536246	6.402453	15.871785
H	13.462934	6.332475	16.031406
C	10.529708	8.808128	18.004955
C	9.275541	8.229506	17.757606
H	8.745945	8.457760	16.836483
C	8.701992	7.379660	18.696271
H	7.725853	6.945825	18.503820
C	9.375069	7.088953	19.882618
H	8.925763	6.423769	20.613017
C	10.620515	7.657254	20.132283

H	11.144484	7.439464	21.057385
C	11.197337	8.516502	19.199301
H	12.164279	8.957276	19.419635
C	10.088690	11.268752	16.502533
C	10.133765	11.988862	15.302132
H	10.808426	11.673527	14.509799
C	9.310323	13.095429	15.122730
H	9.340575	13.644296	14.187284
C	8.438002	13.484627	16.137361
H	7.790644	14.343967	15.994271
C	8.389479	12.769734	17.332229
H	7.707592	13.072060	18.120559
C	9.211252	11.662265	17.519516
H	9.163715	11.104318	18.449546
C	11.652298	5.945611	12.928522
H	11.234742	5.718296	11.942578
H	12.487319	5.261020	13.098978
C	10.611443	5.771617	14.020427
H	10.287612	4.721976	14.005264
H	11.074905	5.949393	14.998445
C	9.370000	6.636453	13.893968
H	8.672019	6.395298	14.700022
H	8.853246	6.454130	12.946544
C	9.700263	10.521538	11.961951
C	9.929148	8.031319	10.816087
C	11.994468	9.855787	11.015063
C	13.987589	9.731714	17.210900
H	13.921084	8.833328	17.833626
H	14.929544	10.225839	17.468834
C	12.781585	10.641842	17.427294
H	12.901197	11.588773	16.890399
H	12.637675	10.892784	18.482951

Table S26. Cartesian Coordinates of the Optimized Structure of $[(OC)_3Fe(pdt)Pt(dppe)]^{2+}$ ($[\mathbf{3}]^{2+}$, –3191.58941051 E_h).

atom	x	y	z
Pt	11.816103	8.719779	14.817908
Fe	10.716523	9.376754	12.453897
S	12.262769	7.734196	12.647644
S	9.511846	8.426952	14.108502
P	14.050086	9.033625	15.404095
P	11.280344	9.943206	16.714104
O	8.951676	11.760526	12.722386
O	9.288697	8.246361	10.182101
O	12.688235	10.922353	10.846741
C	14.939080	10.184049	14.325481
C	15.309713	11.463647	14.761262
H	15.089283	11.798753	15.769872
C	15.999864	12.318656	13.905681
H	16.294755	13.303514	14.254024
C	16.325836	11.905234	12.616106
H	16.871521	12.571239	11.955035
C	15.964295	10.630958	12.178430
H	16.233364	10.301357	11.179707
C	15.269755	9.772398	13.023656
H	15.011704	8.774064	12.680699
C	14.985324	7.489227	15.488863
C	16.355094	7.451581	15.198632
H	16.872227	8.342751	14.856948
C	17.059134	6.260141	15.352018
H	18.120978	6.232632	15.128785
C	16.407093	5.110211	15.792166
H	16.962238	4.184846	15.910150
C	15.043513	5.144481	16.084908
H	14.538631	4.248626	16.432912
C	14.332283	6.329447	15.933136
H	13.269875	6.356986	16.169998
C	10.694990	8.910261	18.078119
C	10.581620	7.523013	17.923756
H	10.810066	7.067258	16.962085
C	10.172046	6.730996	18.993241
H	10.084351	5.655856	18.871469
C	9.872171	7.322018	20.218492
H	9.551270	6.705733	21.052514
C	9.978546	8.704271	20.377395

H	9.739347	9.162735	21.331710
C	10.388427	9.500639	19.313859
H	10.453686	10.577720	19.445649
C	10.084791	11.273668	16.441500
C	10.488602	12.485267	15.857595
H	11.524932	12.655442	15.579038
C	9.557928	13.495639	15.639948
H	9.877494	14.438374	15.206826
C	8.220822	13.301627	15.986194
H	7.498325	14.094693	15.820466
C	7.812116	12.093998	16.549370
H	6.772387	11.943829	16.822502
C	8.736910	11.079057	16.777228
H	8.413311	10.147854	17.232118
C	11.505855	6.058315	12.676961
H	11.030793	5.919993	11.699902
H	12.362765	5.379704	12.719742
C	10.550557	5.766068	13.818793
H	10.234147	4.718445	13.723443
H	11.086308	5.843169	14.772662
C	9.293610	6.615388	13.862963
H	8.660113	6.307941	14.700279
H	8.696699	6.505686	12.951203
C	9.638613	10.858585	12.643741
C	9.846612	8.729604	11.051005
C	11.945578	10.328316	11.469549
C	14.010408	9.736476	17.113751
H	13.891288	8.876500	17.783605
H	14.977855	10.190560	17.354540
C	12.857526	10.719659	17.288697
H	13.020614	11.633019	16.708795
H	12.745801	11.014027	18.337790

Table S27. Cartesian Coordinates of the Optimized Structure of $[(OC)_3FeH(pdt)Pt(dppe)]^+$ ($[\mathbf{3}H]^+$, –3192.54469861 E_h).

atom	x	y	z
Pt	11.834508	8.781878	14.817795
Fe	10.689583	9.345467	12.140051
H	11.464302	10.214107	13.153090
S	12.297473	7.722497	12.707935
S	9.561309	8.574193	14.059110
P	14.022670	9.039734	15.446924
P	11.276640	9.906334	16.726502
O	8.911424	11.666102	12.135742
O	9.210437	7.661298	10.204367
O	12.641080	10.506653	10.300964
C	14.964209	10.213792	14.423773
C	15.393289	11.454946	14.907906
H	15.206440	11.747688	15.936543
C	16.080430	12.333954	14.073059
H	16.412747	13.292593	14.459808
C	16.345655	11.981219	12.753042
H	16.882712	12.666940	12.104837
C	15.924995	10.744367	12.265294
H	16.133835	10.463417	11.237655
C	15.235652	9.864530	13.092140
H	14.913482	8.901616	12.704625
C	15.024897	7.527987	15.538492
C	16.419946	7.579761	15.432764
H	16.919525	8.522093	15.227773
C	17.169964	6.416510	15.580218
H	18.251432	6.459764	15.494200
C	16.536400	5.201615	15.833692
H	17.125544	4.296341	15.945284
C	15.147801	5.145763	15.939307
H	14.653573	4.198345	16.132654
C	14.391945	6.304370	15.789035
H	13.307469	6.267989	15.857518
C	10.701638	8.870913	18.105387
C	10.492434	7.501157	17.914967
H	10.657246	7.074316	16.929380
C	10.082208	6.699646	18.978045
H	9.921905	5.636853	18.823615
C	9.879549	7.261457	20.235606
H	9.560536	6.636924	21.064570

C	10.084663	8.627032	20.433029
H	9.923878	9.066425	21.412772
C	10.494254	9.430930	19.374794
H	10.636784	10.496313	19.537691
C	10.079207	11.256421	16.516141
C	10.426773	12.337547	15.692874
H	11.396143	12.366793	15.200852
C	9.524279	13.373821	15.483205
H	9.801613	14.210203	14.848962
C	8.264317	13.333888	16.079733
H	7.559547	14.142625	15.912228
C	7.907887	12.253950	16.882271
H	6.924434	12.215861	17.340677
C	8.809241	11.214742	17.101288
H	8.521875	10.375750	17.726799
C	11.449250	6.094900	12.692434
H	10.997732	5.974080	11.701779
H	12.251300	5.355428	12.777731
C	10.428129	5.866181	13.794560
H	10.060243	4.834673	13.700652
H	10.932439	5.939324	14.766751
C	9.220645	6.789730	13.789594
H	8.540782	6.505409	14.598809
H	8.661289	6.703665	12.851736
C	9.596978	10.749095	12.113318
C	9.783017	8.298277	10.965896
C	11.857184	10.047769	10.999224
C	13.994979	9.718385	17.170324
H	13.867204	8.849428	17.826507
H	14.959725	10.169572	17.425414
C	12.835303	10.694635	17.348523
H	12.992309	11.611712	16.770418
H	12.714522	10.983079	18.397900