Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of Iron(II) complexes supported by an Iminophosphorane ligand: Synthesis and Reactivity

Thibault Tannoux, Louis Mazaud, Thibault Cheisson, Nicolas Casaretto, Audrey Auffrant*

Laboratoire de Chimie Moléculaire (LCM), CNRS, École Polytechnique, Institut Polytechnique de Paris, Route de Saclay, 91120 Palaiseau, France.

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1. X-ray data

Table S1. X-ray data for **[LFeCl$_2$]**, **[LFe(CH$_3$CN)$_3$](OTf)$_2$**, **[LFe(OTf)$_2$]**

Compound	**[LFeCl$_2$]**	**[LFe(OTf)$_2$]**	**[LFe(CH$_3$CN)$_3$](OTf)$_2$**
Molecular formula	$C_{37}H_{32}Cl_2FeN_2P_2$, C_4H_8O	$C_{39}H_{32}F_6FeN_2O_6P_2S_2$	$C_{47}H_{44}F_6FeN_6O_6P_2S_2$
Molecular weight	765.44	920.57	1084.79
Space group	$P2_1/c$	$P2_1/n$	Cc
V(Å^3)	3746.6(8)	4067.6(6)	4943.0(9)
a (Å)	15.4950(18)	11.8695(10)	10.2743(12)
b (Å)	15.9446(19)	23.485(2)	25.414(3)
c (Å)	16.3447(18)	14.6125(12)	18.9605(17)
α (°)	90	90	90
β (°)	111.904(3)	93.038(3)	93.233(4)
γ (°)	90	90	90
Z	4	4	4
d(g-cm^{-3})	1.357	1.503	1.458
F(000)	1592	1880	2232.0
Θ_{max}	27.482	27.537	28.282
Rflns measd	56231	87342	46864
Unique data	8576	9361	12064
Rint	0.1033	0.0505	0.0787
wR2	0.1268	0.0881	0.1131
R1	0.0547	0.0332	0.0515
GoF	1.030	1.096	1.046
CCDC number	2227071	2227072	2227073

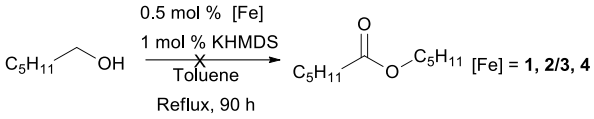
Table S2. X-ray data for **[LFe(NC^{t}Bu)$_3$Cl$_2$**, **[L*FeCl(pyr)]**

Compound	**[LFe(NC^{t}Bu)$_3$Cl$_2$**	**[L*FeCl(pyr)]**
Molecular formula	$C_{53}H_{61}Cl_4FeN_5P_2$	$C_{42}H_{36}ClFeN_3P_2$
Molecular weight	1027.65	735.98
Space group	$P2_1/n$	$P2_1/c$
V(Å^3)	5546(3)	3519.0(5)
a (Å)	13.298(5)	12.9480(10)
b (Å)	17.214(5)	10.1740(10)
c (Å)	25.028(10)	26.9910(10)
α (°)	90	90
β (°)	104.507(13)	98.2320(10)
γ (°)	90	90
Z	4	4
d(g-cm^{-3})	1.231	1.389
F(000)	2152.0	1528
Θ_{max}	26.029	25.025
Rflns measd	154394	20627
Unique data	10914	6153
Rint	0.0745	0.0576
wR2	0.1352	0.1123
R1	0.0511	0.0595
GoF	1.073	1.117
CCDC number	2227074	2227075

Table S3. Comparison of bond lengths between [Fe(PPyNP)(CH_3CN)$_3$](OTf)$_2$**,** [Fe(PPyNP)(OTf)$_2$] , and [LFe($CNtBu$)$_3$](Cl)$_2$

Bond lengths (Å	**2**	[Fe(PPyNP)(OTf)$_2$] **3**	[Fe(NPyNP)($CNtBu$)$_3$]Cl_2 **4'**
Fe1-N2	1.972(4)	2.1972(14)	1.992(2)
Fe1-P2	2.2338(15)	2.4733(5)	2.2035(8))
Fe1-N1	2.060(4)	2.0499(15)	2.055(2)
P1-N1		1.6097(15)	1.604(2)

2. X-ray data



Scheme S1: Catalytic attempts of dehydrogenative coupling of hexan-1-ol

3. NMR spectra

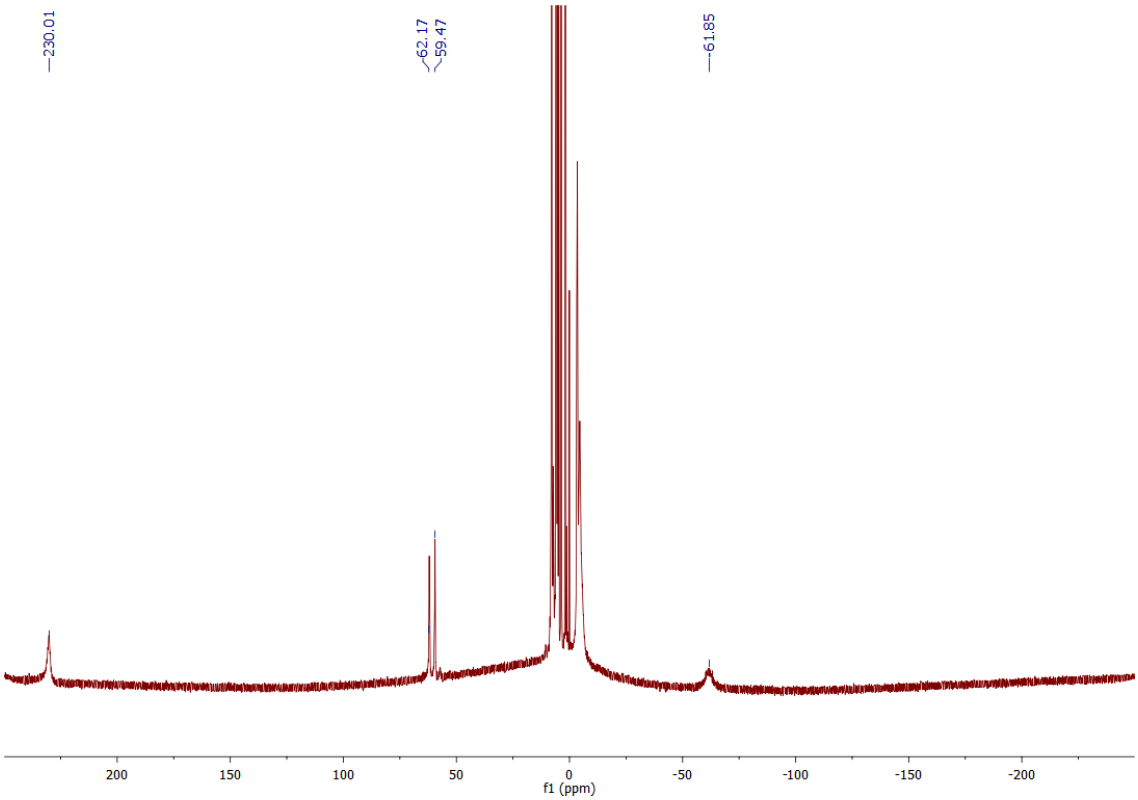


Figure S1: ^{1}H NMR spectrum of **[Fe(PPyNP)Cl$_2$]** in CD_2Cl_2.

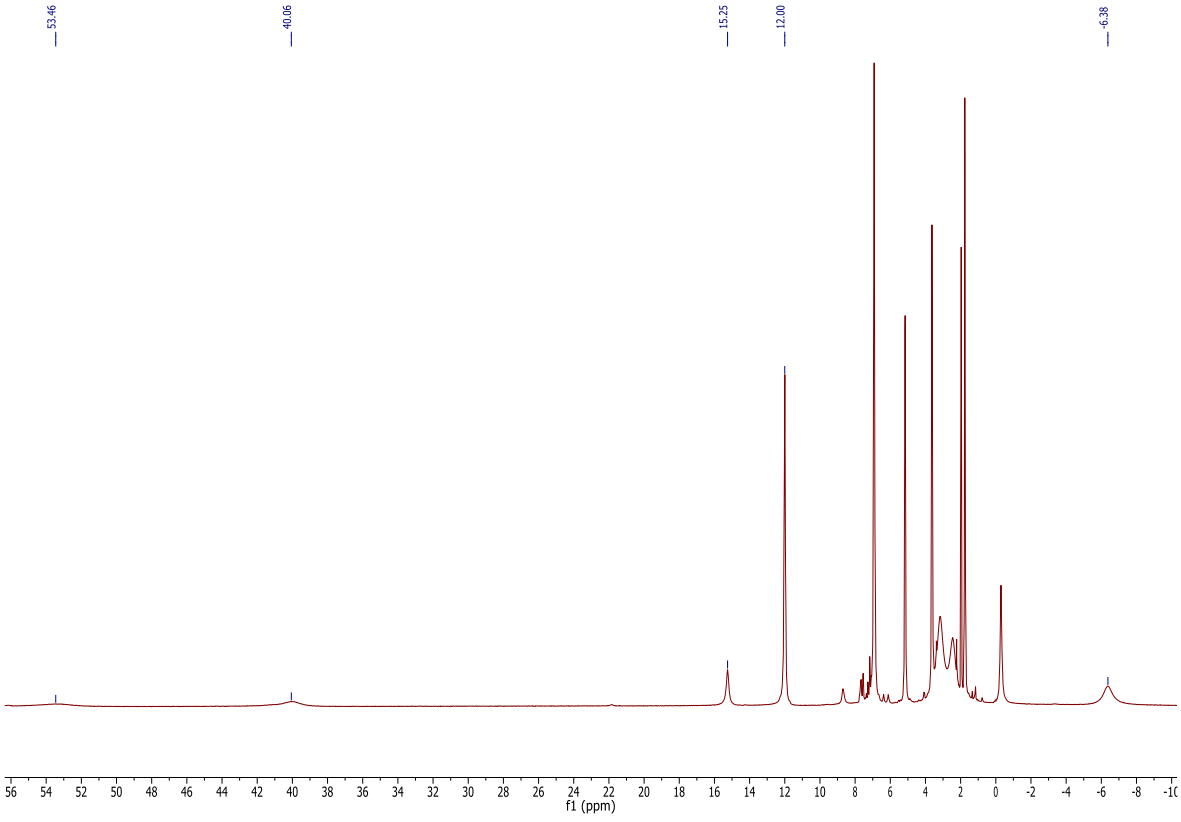


Figure S2: ^{1}H NMR spectrum of **[Fe(PPyNP)(OTf)$_2$]/[Fe(PPyNP) (CH$_3$CN)$_3$](OTf)$_2$** in CD_3CN.

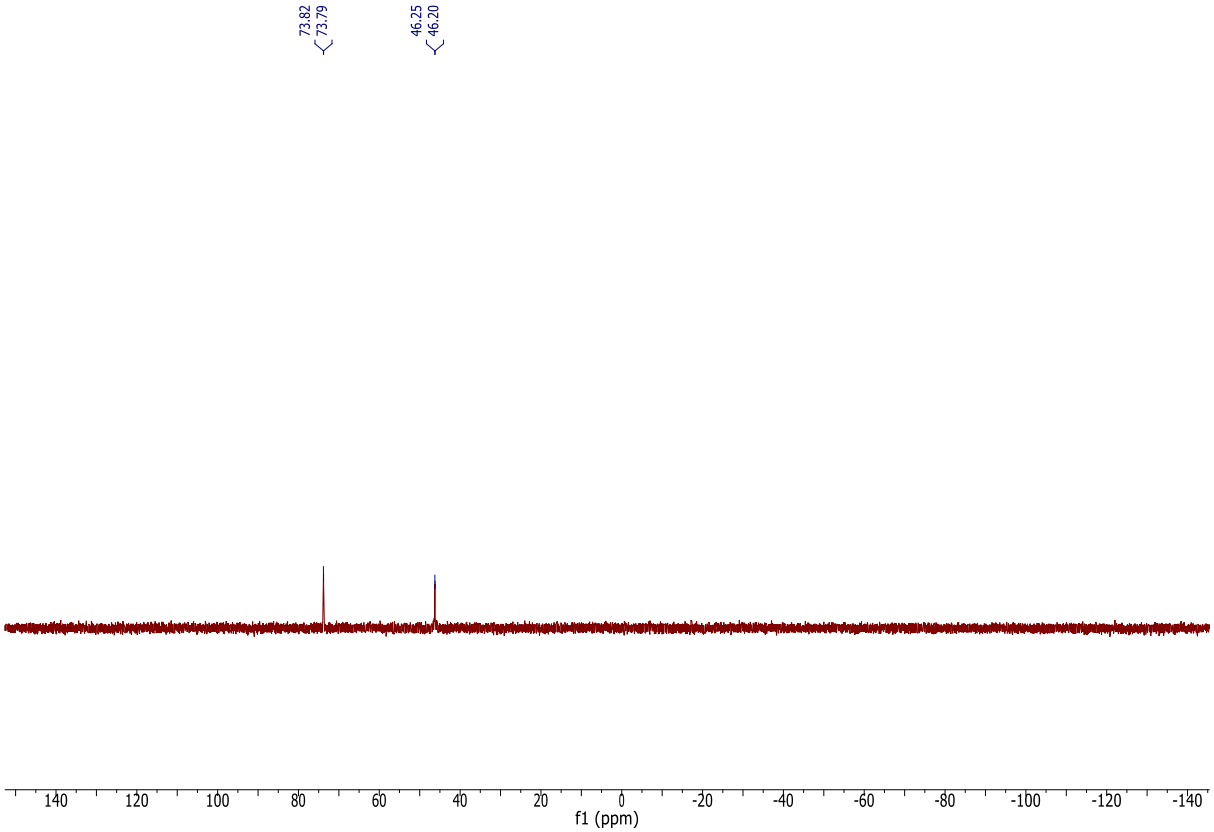


Figure S3: $^{13}P\{^{1}H\}$ NMR spectrum of **[Fe(PPyNP)(NC^{t}Bu)$_3$](OTf)$_2$** in CD_2Cl_2

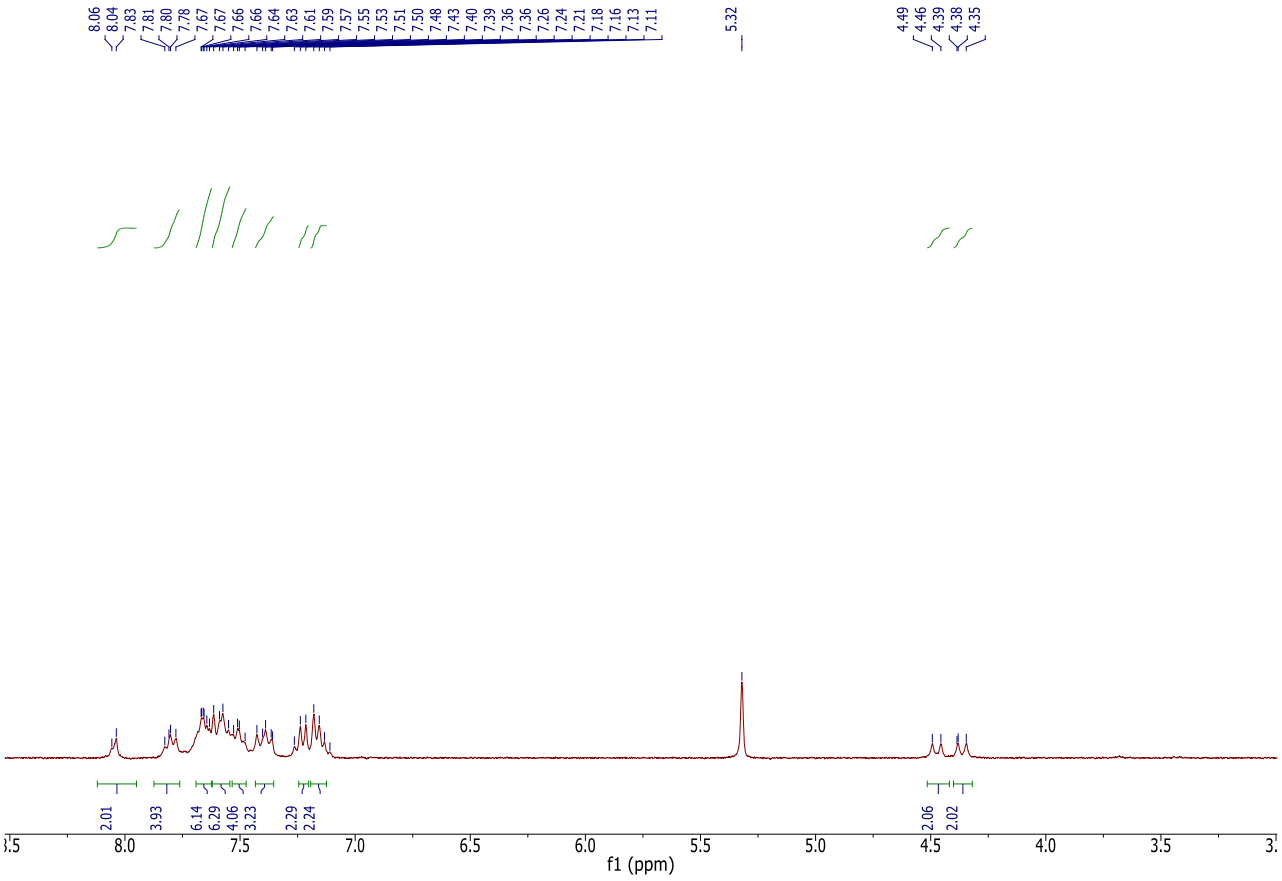


Figure S4: ^{1}H NMR spectrum of **[Fe(PPyNP)(NC^{t}Bu)$_3$](OTf)$_2$** in CD_2Cl_2

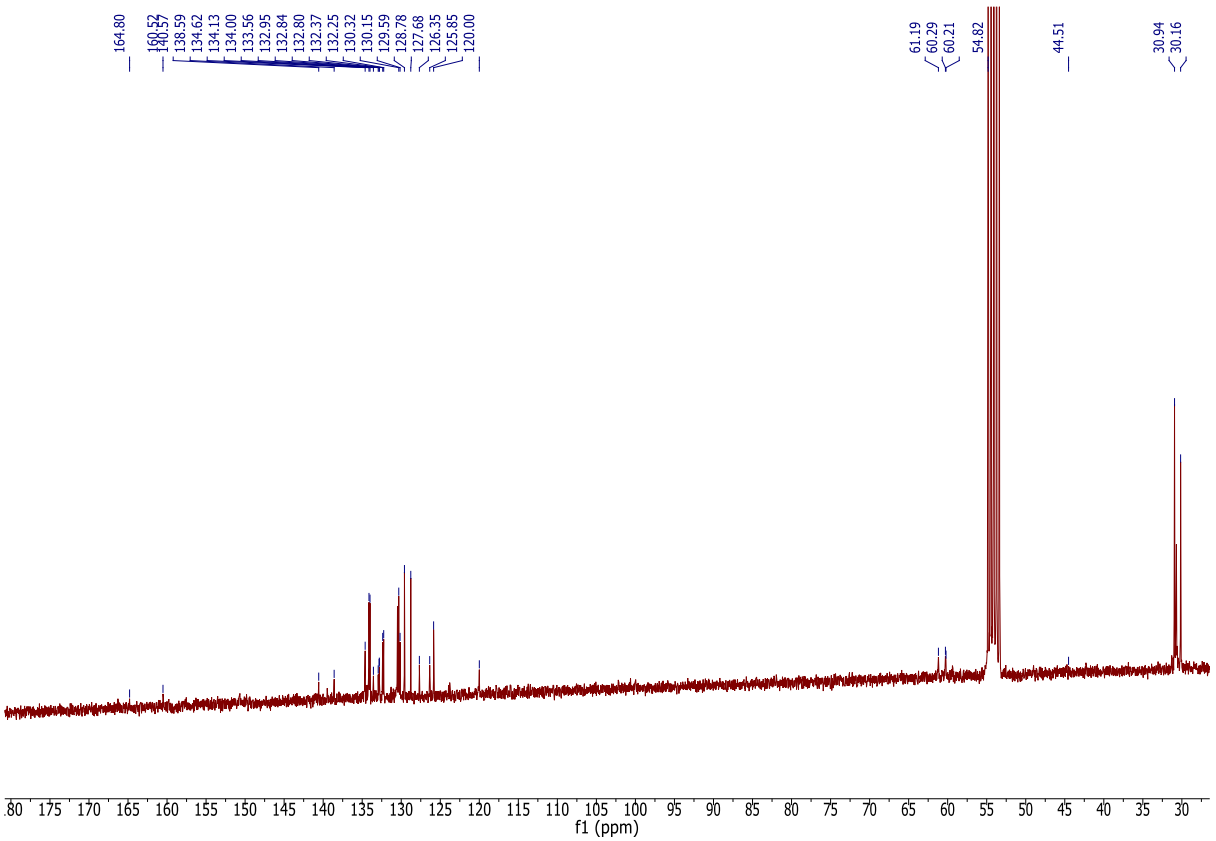


Figure S5: ^{13}C NMR spectrum of **[Fe(PPyNP)(NC^{t}Bu)$_3$](OTf)$_2$** in CD_2Cl_2

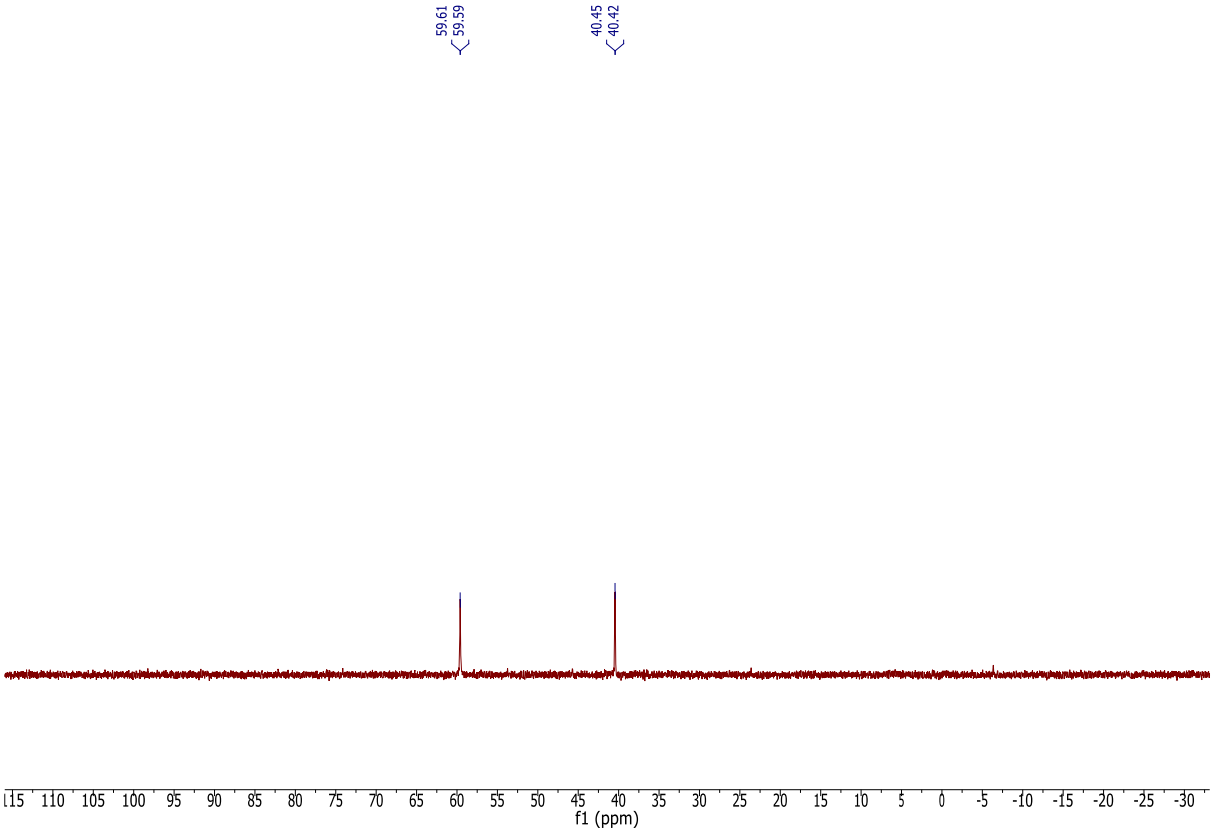


Figure S6: $^{31}P\{^1H\}$ NMR spectrum of **[Fe(PPyNP)*(NC^{t}Bu)$_3$](OTf)** in THF-d_8

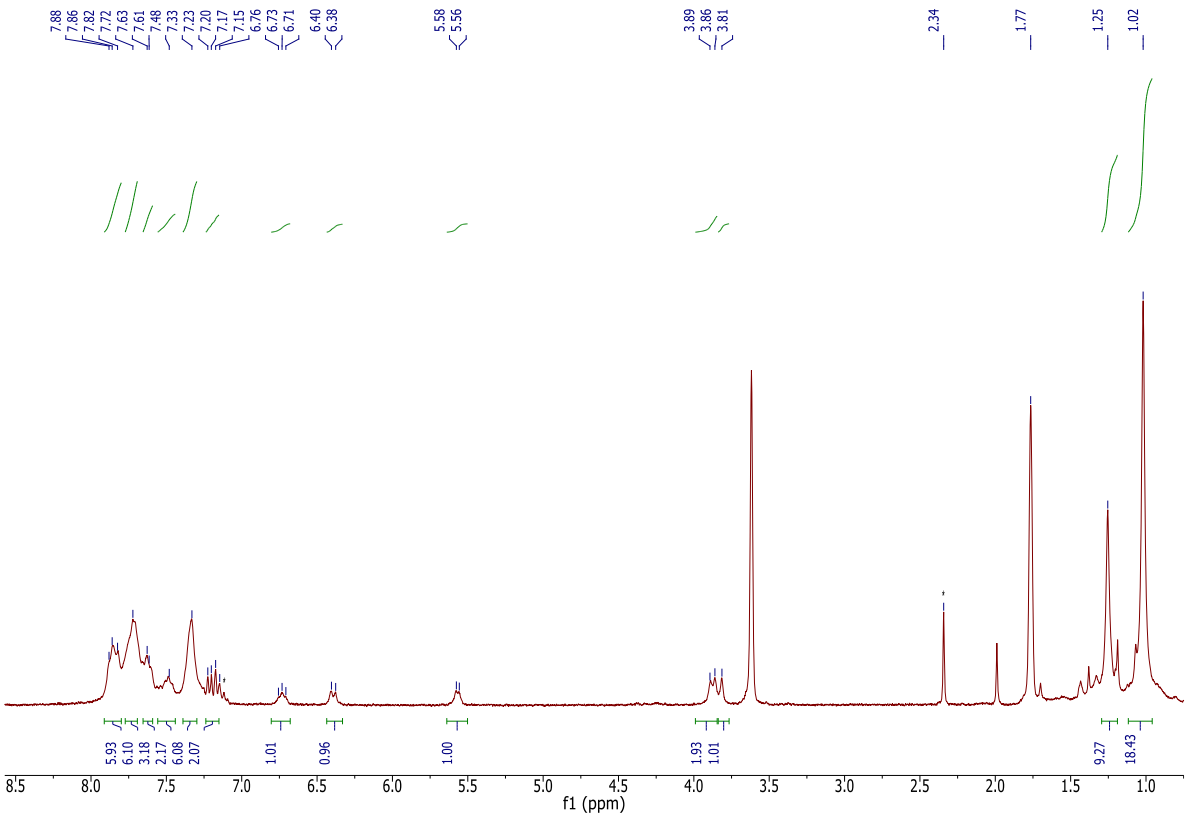


Figure S7: ^{1}H NMR spectrum of **[Fe(PPyNP)*(NC^{t}Bu)$_3$](OTf)** in THF-d$_8$

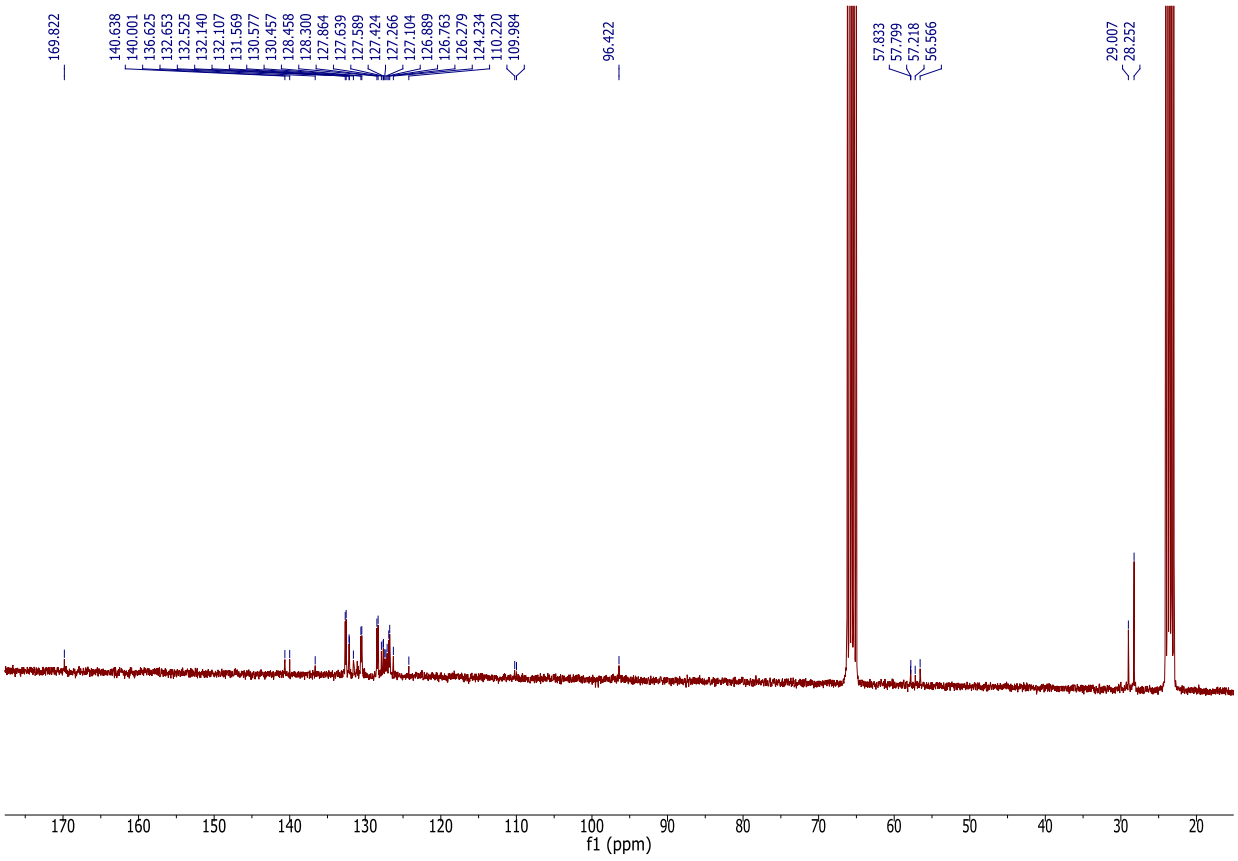


Figure S8: ^{13}C NMR spectrum of **[Fe(PPyNP)*(NC^{t}Bu)$_3$](OTf)** in THF-d$_8$

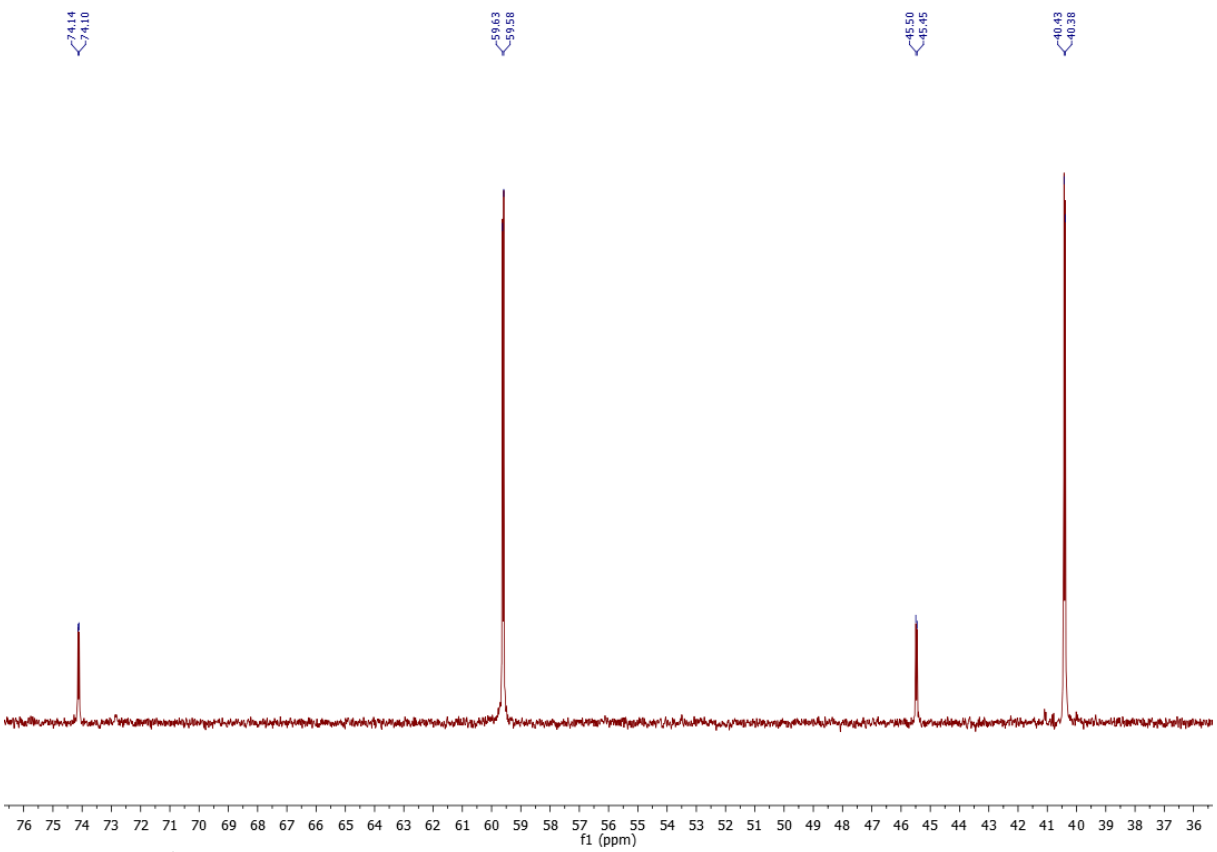


Figure S9: $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **[Fe(PPyNP)*(NC^{t}Bu)$_3$](OTf)** and **[Fe(PPyNP)*(NC^{t}Bu)$_3$](OTf)** in THF-d_8 after removal of volatiles.