Supporting Information

Cyclopentadienyl Iron(II) Complexes of N-heterocyclic Carbenes Bearing a Malonate or Imidate Backbone: Synthesis, Structure and Catalytic Potential in Hydrosilylation

Vincent César,[†,‡] Luis C. Misal Castro,[§] Thomas Dombray,[§] Jean-Baptiste Sortais,*[§] Christophe Darcel,[§] Stéphane Labat,[⊥] Karinne Miqueu,[⊥] Jean-Marc Sotiropoulos,[⊥] Rémy Brousses,[†,‡] Noël Lugan,*[†,‡] Guy Lavigne[†,‡]*

Contents

Characterization of the products of catalysis **S3**

Normal resolution and high resolution XRD studies **S8**

- **Table S1.** Crystal data and structures refinements for complexes $\mathbf{3_{tBu}}$, $\mathbf{3_{Me}}$, **4**, and **[6^{Me}](OTf)** **S8**
- **Table S2.** Multipolar parameters for complex $\mathbf{3_{Me}}$ **S9**
- **Table S3.** Values of the experimental and theoretical (italic) orthodox parameters at bond critical points within complex $\mathbf{3_{Me}}$ **S15**
- **Figure S1**. Residual electron density maps for $\mathbf{3_{Me}}$ after the multipolar refinement **S17**
- **Figure S2**. Laplacian of the experimental (left) and theoretical (right, M06-2X/6-31G**) electron density for $\mathbf{3_{Me}}$ in various planes **S18**

Computational studies **S19**

- **Table S4.** Main geometrical parameters (bond lengths in Å and bond angles in deg) for the complex $\mathbf{3_{Me}}$ at different levels of theory **S21**

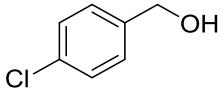
- **Table S5.** Experimental X-Ray data for complexes $\mathbf{3_{Me}}$, **4**, $\mathbf{6^{Me}}$ **(OTf)**. Calculated geometrical parameters for compounds $\mathbf{3_{Me}}$, **4**, $\mathbf{6^{Me}}$**(OTf)**, **7** and **8** at the M06-2X/6-31G** level of theory **S22**
- **Table S6.** Experimental and theoretical topological analysis of complex $\mathbf{3_{Me}}$ **S23**
- **Table S7.** AIM analysis for complex **4** **S25**
- **Table S8.** AIM analysis for complex $\mathbf{6^{Me}}$**(OTf)** **S27**
- **Table S9.** AIM analysis for complex **7** **S29**
- **Table S10.** AIM analysis for complex **8** **S31**
- *Analysis of the influence of the electronic properties of the carbene and of the N-substituents on the interligand interaction* **S33**
- *Analysis of the bonding situation of the Fe-$C_{carbene}$ bond in 3_{Me}, 4 and 6^{Me}(OTf)* **S34**
- **Table S11.** NBO analysis of the C→Fe interaction in the three complexes $\mathbf{3_{Me}}$, **4** and $\mathbf{6^{Me}}$**(OTf)** **S35**
- **Table S12.** Topological analysis of the C(aryl)…C(≡O) bond critical points **S37**
- **Table S13.** NBO analysis of the C(aryl)…C(≡O) non-covalent weak interactions for compounds $\mathbf{3_{Me}}$, **4**, $\mathbf{6_{Me}}$**(OTf)**, **7** and **8** at the M06-2X/6-31G** level of theory. **S38**
- **Figure S3.** Contour plot of the Laplacien $\nabla^2\rho$(BCP) with charge accumulation ($\nabla^2\rho(r)<0$) printed in blue and charge depletion ($\nabla^2\rho(r)>0$) printed in red for the complexes $\mathbf{3_{Me}}$, **4** and $\mathbf{6^{Me}}$**(OTf)** **S39**
- **Figure S4.** Molekel plot (cutoff : 0.05) for the NLMO associated with the C→Fe interaction in complex $\mathbf{3_{Me}}$ **S39**
- **Figure S5.** Electronic delocalization and density $\rho(\mathbf{r}_b)$ in $e^{-}Å^{-3}$ for the carbene skeleton in the complexes $\mathbf{3_{Me}}$, **4** and $\mathbf{6^{Me}}$**(OTf)** **S39**

Z-Matrices **S39**

NMR Spectra **S45**

Characterizations of the products of catalysis

4-Chlorobenzyl alcohol

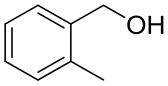


According to the general procedure A, 4-chlorobenzaldehyde (141 mg, 1 mmol) gave 4-chlorophenylmethanol (118 mg, 83%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, *J* = 8.7 Hz), 7.26 (d, 2H, *J* = 8.7 Hz), 4.62 (s, 2H), 2.19 (br s, 1H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 139.4, 133.5, 128.8, 128.4, 64.6.

o-Tolylmethanol

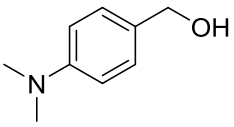


According to the general procedure A, *o*-tolualdehyde (116 μL, 1 mmol) gave *o*-tolylmethanol (88 mg, 72%) as a light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.32 (m, 1H), 7.25-7.15 (m, 3H), 4.68 (s, 2H), 2.36 (s, 3H), 1.87 (br s, 1H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.9, 136.3, 130.5, 127.8, 127.7, 126.2, 63.6, 18.8.

4-(*N,N*-dimethylaminophenyl)methanol

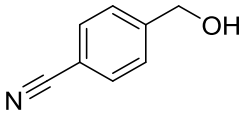


A flame dried Schlenk flask was charged with the iron complex $\mathbf{3}_{t\mathbf{Bu}}$ (5.8 mg, 10 μmol, 1 mol%), 4-(*N,N*-dimethylamino)benzaldehyde (149 mg, 1.0 mmol), phenylsilane (113 μL, 1.2 mmol) and anhydrous toluene (0.2 mL). The reaction was stirred in a 30 °C pre-heated oil bath under light irradiation for 3 hours. The reaction was then hydrolyzed with methanol (2 mL) and a 2M aqueous solution of sodium hydroxide (2 mL). The product was extracted with diethylether (3×10 mL). The combined organic layers were washed with brine, dried with sodium sulfate and evaporated. The crude residue was purified by silica gel chromatography using a petroleum ether/diethyl ether mixture (7:3) as the eluent to give 4-(*N,N*-dimethylaminophenyl)methanol (124 mg, 82%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 8.4 Hz), 6.73 (d, 2H, *J* = 8.4 Hz), 4.57 (s, 2H), 2.95 (s, 6H), 1.61 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.5, 129.1, 128.8, 112.8, 65.6, 40.9.

4-Cyanobenzyl alcohol

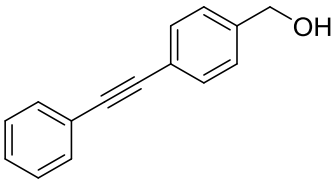


A flame-dried Schlenk tube was charged with the iron complex **3**$_{t\mathbf{Bu}}$ (5.8 mg, 10 μmol, 1 mol%), 4-cyanobenzaldehyde (131.1 mg, 1 mmol), phenylsilane (113 μL, 1.2 mmol) and anhydrous toluene (0.2 mL). The reaction was stirred in a 30 °C pre-heated oil bath under light irradiation for 3 hours. The reaction was hydrolyzed with methanol (2 mL) and 2M aqueous solution of sodium hydroxide (2 mL). The product was extracted with diethylether (3×10 mL). The combined organic layer was washed with brine, dried with sodium sulfate and evaporated. The crude residue was purified by silica gel chromatography using a petroleum ether/diethyl ether mixture (6:4) as the eluent to give 4-cyanophenylmethanol (129 mg, 95%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 2H, *J* = 8.3 Hz), 4.66 (s, 2H), 3.48 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 146.7, 132.2, 127.0, 118.9, 110.5, 63.7.

[4-(Phenylethynyl)phenyl]methanol

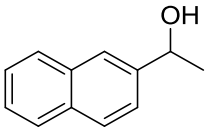


According to the general procedure A, 4-(phenylethynyl)benzaldehyde (103 mg, 0.5 mmol) gave [4-(phenylethynyl)phenyl]methanol (100 mg, 96%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.45 (m, 4H), 7.42-7.28 (m, 5H), 4.68 (s, 2H), 2.13 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.2, 131.9, 131.8, 128.5, 128.4, 127.0, 123.4, 122.6, 89.6, 89.4, 65.1.

1-(Naphthalen-2-yl)ethanol

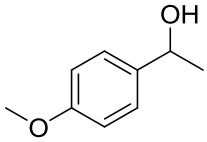


According to the general procedure B, 2-acetonaphtone (85 mg, 0.5 mmol) gave 1-(naphthalen-2-yl)ethanol (60 mg, 70%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-7.73 (m, 4H), 7.54-7.43 (m, 3H), 5.05 (q, 1H, *J* = 6.5 Hz), 2.20 (br s, 1H), 1.58 (d, 3H, *J* = 6.5 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.2, 133.4, 132.9, 128.3, 128.0, 127.7, 126.2, 125.8, 123.9, 123.8, 70.5, 25.2.

1-(4-Methoxyphenyl)ethanol

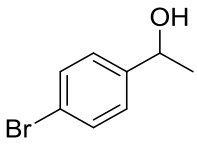


According to the general procedure B, 4-methoxyacetophenone (75 mg, 0.5 mmol) gave 1-(4-methoxyphenyl)ethanol (23 mg, 30%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 4.85 (q, 1H, *J* = 6.5 Hz), 3.80 (s, 3H), 1.88 (br s, 1H), 1.48 (d, 3H, *J* = 6.5 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.2, 138.2, 126.9, 114.0, 70.2, 55.5, 25.2.

1-(4-Bromophenyl)ethanol

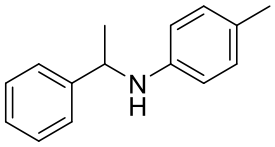


According to the general procedure B, 4-bromoacetophenone (199 mg, 1 mmol) gave 1-(4-bromophenyl)ethanol (94 mg, 47%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 2H, *J* = 8.4Hz), 7.24 (d, 2H, *J* = 8.4Hz), 4.85 (q, 1H, *J* = 6.4 Hz), 1.97 (br s, 1H), 1.46 (d, 3H, *J* = 6.4 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.9, 131.7, 127.3, 121.3, 70.0, 25.4.

4-Methyl-*N*-(1-phenylethyl)aniline

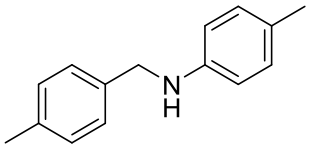


A flame dried Schlenk flask was charged with the iron complex **3**$_{t\mathbf{Bu}}$ (14.5 mg, 25 μmol, 5 mol%), 4-methyl-*N*-(1-phenylethylidene)aniline (105 mg, 0.5 mmol), phenylsilane (250 μL, 2 mmol) and anhydrous toluene (0.2 mL). The reaction was stirred in a 100 °C pre-heated oil bath under light irradiation for 24 hours. The reaction was hydrolyzed with methanol (2 mL) and a 2M aqueous solution of sodium hydroxide (2 mL). The product was extracted with diethylether (3×10 mL). The combined organic layer was washed with brine, dried with sodium sulfate and evaporated. The crude residue was purified by silica gel chromatography using a petroleum ether/diethyl ether mixture (95:5) as the eluent to give 4-methyl-*N*-(1-phenylethyl)aniline (98 mg, 93%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.30 (m, 5H), 6.99 (d, 2H, *J* = 8.3Hz), 6.48 (d, 2H, *J* = 8.7Hz), 4.49 (q, 1H, *J* = 6.8 Hz), 3.90 (br s, 1H), 2.27 (s, 3H), 1.54 (d, 3H, *J* = 6.8 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.9, 144.2, 132.5, 129.8, 128.9, 127.4, 126.8, 113.6, 53.3, 25.2, 20.5.

4-Methyl-*N*-(4-methylbenzyl)aniline



A flame dried Schlenk flask was charged with the iron complex **3**$_{t\mathbf{Bu}}$ (14.5 mg, 25 μmol, 5 mol%), 4-methyl-*N*-(4-methylbenzylidene)aniline (105 mg, 0.5 mmol), phenylsilane (250 μL, 2 mmol) and anhydrous toluene (0.2 mL). The reaction was stirred in a 30 °C pre-heated oil bath under light irradiation for 30 hours. The reaction was hydrolysed with methanol (2 mL) and 2M aqueous solution of sodium hydroxide (2 mL). The product was extracted with diethylether (3×10 mL). The combined organic layer was washed with brine, dried with sodium sulfate and evaporated. The crude residue was purified by silica gel chromatography using a petroleum ether/diethyl ether mixture (98:2) as the eluent to give 4-methyl-*N*-(4-methylbenzyl)aniline (55 mg, 52%) as a yellow solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.32 (d, 2H, J = 7.9 Hz), 7.21 (d, 2H, J = 7.9 Hz), 7.05 (d, 2H, J = 8.3 Hz), 6.62 (d, 2H, J = 8.3 Hz), 4.32 (s, 2H), 3.93 (br s, 1H), 2.41 (s, 3H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 146.0, 136.9, 136.7, 129.9, 129.4, 127.7, 126.9, 113.2, 48.6, 21.3, 20.6.

Normal resolution and high resolution XRD studies

Table S1. Crystal data and structure refinements for complexes $\mathbf{3_{tBu}}$, $\mathbf{3_{Me}}$, **4**, and $\mathbf{[6^{Me}](OTf)}$

SHELX Refinment				
complex	$\mathbf{3_{tBu}}$	$\mathbf{3_{Me}}$	**4**	$\mathbf{[6^{Me}](OTf)}$
empirical formula	$C_{33}H_{36}FeN_2O$,CH_2Cl_2	$C_{30}H_{30}FeN_2O_4$	$C_{28}H_{27}FeN_3O_4$	$C_{29}H_{30}FeN_3O_4$, CF_3O_3S
molecular weight (g)	612.42	538.39	525.38	689.48
temperature (K)	180	100	180	180
crystal system	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_12_12_1$ (#19)	P 1 (bar) (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	13.079(3)	9.6895(8)	9.5746(3)	12.5292(5)
b (Å)	15.663(3)	9.9041(8)	15.8303(5)	15.1526(6)
c (Å)	15.731(3)	14.4926(12)	16.3931(6)	16.9812(6)
α (°)		109.600(3)		
β (°)		104.051(15)	93.601(1)	109.835(2)
γ (°)		107.503(2)		
volume ($Å^3$)	3222.6(11)	1259.82(18)	2479.78(14)	3032.6(2)
Z	4	2	4	4
$D_{calcd.}$ ($g.cm^{-3}$)	1.372	1.419	1.407	1.510
μ (mm^{-1})	0.674	0.634	0.634	0.637
F_{000}	1392	564	1096	1424
θ_{max} (°)	30.5	26.4	26.4	26. 4
completeness to θ_{max}	99	99	99	99
index range	-18<h<18	-12<h<11	-11<h<11	-15<h<15
	-22<k<22	-12<l<11	-19<k<19	-18<k<18
	-22<l<22	-18<l<18	-20<l<20	-21<l<21
reflections collected	1013470	312535	97705	182350
independant reflections	9802	5144	6196	6203
data/restraints/parameters	9802 / 0 / 397	5144/ 0 / 341	6196 / 0 / 417	6203 / 0 / 363
g.o.f.	1.08	1.067	1.04	1.03
R, Rw [I>2σ(I)]	R1 = 0.0222	R1 = 0.0255	R1 = 0.0278	R1 = 0.0278
	wR2 = 0.0588	wR2 = 0.0767	wR2 = 0.0741	wR2 = 0.0741
R , Rw (all data)	R1 = 0.0230	R1 = 0.0257	R1 = 0.0321	R1 = 0.0332
	wR2 = 0.0594	wR2 = 0.0770	wR2 = 0.0780	wR2 = 0.0780
resid. electr. dens. ($e.Å^{-3}$)	0.44 / -0.31	0.35 / -0.39	0.35 / -0.33	0.35 / -0.31
MoPro Refinment (S < 1.1 $Å^{-1}$)				
θ_{max}		53.2		
Completeness to θ_{max} (%)		99		
index range		-23<h<23		
		-23<l<23		
		-34<l<34		
Independent reflections		23392		
Parameters / restraints		965 / 84		
g.o.f.		1.05		
R [I>3σ(I)] (calculated against F)		0.0132		
R_w [I>3σ(I)] (calculated against F)		0.0169		

Table S2. Multipolar parameters for complex $\mathbf{3_{Me}}$

atom:	Fe1							
system coord		D0 X Fe1 C3 Y						
κ, κ'	**0.962746**	**0.798890**						
Pv	5.8753							
P00	0.0000							
P1m±	0.0270	0.0630	-0.0840					
P2m±	0.0170	0.0750	0.0110	-0.0050	-0.0040			
P3m±	-0.0320	-0.0710	0.0390	-0.0370	-0.0730	0.0200	-0.0120	
P4m±	-0.0310	-0.1150	-0.3060	-0.0180	0.0020	-0.0350	-0.1000	-0.0180
	0.0870							
atom:	O1							
system coord		C1 Z O1 Fe1 Y						
κ, κ'	1.003132	0.998316						
Pv	5.7827							
P00	0.0000							
P1m±	-0.0120	-0.0260	-0.1160					
P2m±	0.0110	-0.0090	0.0730	-0.0690	-0.0140			
P3m±	0.0230	0.0100	0.0110	-0.0190	0.0130	0.0420	-0.0090	
atom:	O2							
system coord		C2 Z O2 Fe1 Y						
κ, κ'	1.003132	0.998316						
Pv	5.9365							
P00	0.0000							
P1m±	0.0110	0.0530	-0.0420					
P2m±	0.0180	0.0620	0.1060	0.0470	-0.0400			
P3m±	0.0380	-0.0370	0.0000	0.0050	0.0390	0.0210	0.0210	
atom:	O3							
system coord		C4 X O3 N1 Y						
κ, κ'	0.980041	0.963376						
Pv	6.3211							
P00	0.0000							
P1m±	-0.0200	0.0060	-0.0450					
P2m±	-0.0010	-0.0120	-0.0200	0.0040	-0.0640			
P3m±	-0.0070	-0.0100	-0.0130	0.0030	-0.0010	0.0050	0.0380	
atom:	O4							
system coord		C6 X O4 N2 Y						
κ, κ'	0.980041	0.963376						
Pv	6.2653							
P00	0.0000							
P1m±	0.0410	-0.0070	-0.0700					
P2m±	0.0200	-0.0150	-0.0180	0.0090	-0.0510			
P3m±	-0.0030	-0.0010	0.0320	-0.0170	0.0120	-0.0050	0.0350	
atom:	N1							
system coord		C6 X N1 C3 Y						
κ, κ'	1.001363	0.960001						
Pv	5.0636							
P00	0.0000							
P1m±	-0.0340	0.0290	0.0550					
P2m±	-0.0090	-0.0040	-0.0210	0.0050	0.0130			
P3m±	0.0450	0.0030	0.0150	-0.0010	0.0190	0.0040	-0.2170	
atom:	N2							
system coord		C4 X N2 C3 Y						
κ, κ'	1.001363	0.960001						
Pv	5.0603							
P00	0.0000							
P1m±	-0.0420	0.0100	0.0160					
P2m±	0.0230	0.0060	-0.0240	-0.0040	-0.0130			
P3m±	0.0370	-0.0280	0.0270	0.0170	0.0100	-0.0230	-0.2220	
atom:	C1							
system coord		O1 Z C1 Fe1 Y						
κ, κ'	0.980570	0.926660						
Pv	4.2149							
P00	0.0000							
P1m±	0.0400	-0.0020	0.0850					
P2m±	-0.0280	-0.0250	0.4540	-0.0350	0.0210			
P3m±	0.0360	0.0230	0.0180	0.1260	-0.0280	0.0220	0.0380	
atom:	C2							
system coord		O2 Z C2 Fe1 Y						
κ, κ'	0.980570	0.926660						
Pv	4.2658							
P00	0.0000							
P1m±	-0.0150	-0.0790	0.0140					
P2m±	-0.0100	-0.0250	0.4000	0.0520	-0.0170			
P3m±	0.0230	-0.0420	-0.0190	0.0250	0.0500	0.0200	-0.0310	
atom:	C3							
system coord		N1 X C3 N2 Y						
κ, κ'	0.977123	0.931556						
Pv	4.2024							
P00	0.0000							
P1m±	-0.0650	0.0310	-0.0680					
P2m±	0.0360	0.0210	-0.2360	-0.0030	-0.0480			
P3m±	0.0390	0.0140	-0.0260	0.0130	-0.0210	0.0050	0.2660	

Table S2 (continued)

atom:	C4						
system coord		N2 X C4 C5 Y					
κ, κ'	1.016601	1.002564					
Pv	3.9252						
P00	0.0000						
P1m±	0.1130	-0.0060	-0.0540				
P2m±	0.0990	-0.0080	-0.1970	0.0020	0.0330		
P3m±	0.0380	0.0250	0.0050	0.0150	0.0160	0.0090	-0.2520
atom:	C5						
system coord		C3 X C5 C6 Y					
κ, κ'	1.008238	1.001011					
Pv	4.0630						
P00	0.0000						
P1m±	0.0420	0.0240	0.0440				
P2m±	-0.0150	-0.0120	-0.0650	-0.0070	0.0020		
P3m±	0.0070	-0.0130	0.0280	-0.0160	0.0470	-0.0290	-0.2600
atom:	C6						
system coord		N1 X C6 C5 Y					
κ, κ'	1.016601	1.002564					
Pv	3.8622						
P00	0.0000						
P1m±	0.0840	0.0020	-0.0650				
P2m±	0.1240	0.0010	-0.2270	-0.0020	0.0900		
P3m±	0.0700	-0.0060	-0.0060	-0.0020	0.0300	-0.0310	-0.2560
atom:	C7						
system coord		C5 Z C7 H71 X					
κ, κ'	0.973579	0.921152					
Pv	4.4084						
P00	0.0000						
P1m±	0.0000	-0.0620	-0.0450				
P2m±	0.0000	0.0000	-0.0370	0.0000	0.0000		
P3m±	-0.0540	0.0000	0.0000	0.3500	0.0000	0.0000	0.0390
atom:	C11						
system coord		D0 X C11 Fe1 Z					
κ, κ'	0.975475	0.916847					
Pv	4.2047						
P00	0.0000						
P1m±	0.0000	0.0330	-0.0220				
P2m±	0.0000	0.0000	-0.2600	-0.0180	0.0670		
P3m±	0.0000	0.0000	0.0000	0.0090	0.0440	0.0430	-0.3300
atom:	C12						
system coord		D0 X C12 Fe1 Z					
κ, κ'	0.975475	0.916847					
Pv	4.2269						
P00	0.0000						
P1m±	0.0000	0.0410	-0.0410				
P2m±	0.0000	0.0000	-0.2160	-0.0070	0.0530		
P3m±	0.0000	0.0000	0.0000	0.0330	0.0330	0.0360	-0.2790
atom:	C13						
system coord		D0 X C13 Fe1 Z					
κ, κ'	0.975475	0.916847					
Pv	4.1486						
P00	0.0000						
P1m±	0.0000	0.0360	-0.0570				
P2m±	0.0000	0.0000	-0.1890	-0.0050	0.0580		
P3m±	0.0000	0.0000	0.0000	0.0530	0.0640	0.0200	-0.2750
atom:	C14						
system coord		D0 X C14 Fe1 Z					
κ, κ'	0.975475	0.916847					
Pv	4.2428						
P00	0.0000						
P1m±	0.0000	0.0280	0.0210				
P2m±	0.0000	0.0000	-0.2380	0.0110	0.0500		
P3m±	0.0000	0.0000	0.0000	0.0720	0.0580	-0.0060	-0.3340
atom:	C15						
system coord		D0 X C15 Fe1 Z					
κ, κ'	0.975475	0.916847					
Pv	4.3017						
P00	0.0000						
P1m±	0.0000	0.0310	0.0000				
P2m±	0.0000	0.0000	-0.1980	0.0440	0.1210		
P3m±	0.0000	0.0000	0.0000	0.0200	0.0370	0.0150	-0.2680
atom:	C21						
system coord		C24 X C21 C22 Y					
κ, κ'	1.002619	0.958249					
Pv	4.0339						
P00	0.0000						
P1m±	0.0170	-0.0140	0.0880				
P2m±	-0.0030	-0.0280	-0.1400	-0.0210	-0.0900		
P3m±	-0.0070	0.0040	-0.0200	-0.0410	0.0330	0.0150	-0.2930
atom:	C22						
system coord		C25 X C22 C23 Y					
κ, κ'	1.002619	0.958249					
Pv	3.9882						
P00	0.0000						
P1m±	0.0140	-0.0240	0.0370				
P2m±	0.0240	0.0080	-0.1800	-0.0070	-0.0270		
P3m±	-0.0070	0.0010	-0.0040	-0.0200	0.0300	0.0220	-0.2270

Table S2 (continued)

atom:	C23						
system coord		C26 X C23 C24 Y					
κ, κ'	1.002619	0.958249					
Pv	4.2313						
P00	0.0000						
P1m±	-0.0500	-0.0080	-0.0220				
P2m±	-0.0410	-0.0120	-0.1930	0.0010	0.0210		
P3m±	-0.0270	-0.0210	0.0020	-0.0020	0.0430	-0.0030	-0.2610
atom:	C24						
system coord		C21 X C24 C25 Y					
κ, κ'	1.002619	0.958249					
Pv	3.9847						
P00	0.0000						
P1m±	-0.0420	-0.0250	0.0770				
P2m±	0.0240	0.0000	-0.2180	-0.0240	-0.0300		
P3m±	-0.0150	0.0040	0.0120	0.0150	0.0200	-0.0080	-0.2610
atom:	C25						
system coord		C22 X C25 C26 Y					
κ, κ'	1.002619	0.958249					
Pv	4.1730						
P00	0.0000						
P1m±	-0.0080	-0.0160	-0.0200				
P2m±	0.0070	0.0100	-0.1760	-0.0260	-0.0160		
P3m±	-0.0010	-0.0190	0.0280	-0.0120	0.0310	0.0260	-0.2850
atom:	C26						
system coord		C23 X C26 C25 Y					
κ, κ'	1.002619	0.958249					
Pv	3.9909						
P00	0.0000						
P1m±	-0.0170	0.0200	0.0640				
P2m±	-0.0110	0.0120	-0.1870	0.0110	-0.0280		
P3m±	0.0060	-0.0100	0.0190	-0.0070	0.0140	-0.0020	-0.2480
atom:	C27						
system coord		C22 Z C27 H271 X					
κ, κ'	0.973579	0.921152					
Pv	4.4549						
P00	0.0000						
P1m±	0.0000	-0.0540	0.0000				
P2m±	0.0000	0.0000	-0.0450	0.0000	0.0000		
P3m±	0.0060	0.0000	0.0000	0.3230	0.0000	0.0000	0.1990
atom:	C28						
system coord		C24 Z C28 H281 X					
κ, κ'	0.973579	0.921152					
Pv	4.4745						
P00	0.0000						
P1m±	0.0000	-0.0540	0.0000				
P2m±	0.0000	0.0000	-0.0450	0.0000	0.0000		
P3m±	0.0060	0.0000	0.0000	0.3230	0.0000	0.0000	0.1990
atom:	C29						
system coord		C26 Z C29 H291 X					
κ, κ'	0.973579	0.921152					
Pv	4.4109						
P00	0.0000						
P1m±	0.0000	-0.0540	0.0000				
P2m±	0.0000	0.0000	-0.0450	0.0000	0.0000		
P3m±	0.0060	0.0000	0.0000	0.3230	0.0000	0.0000	0.1990
atom:	C31						
system coord		C33 X C31 C32 Y					
κ, κ'	1.002619	0.958249					
Pv	4.0394						
P00	0.0000						
P1m±	-0.0570	-0.0080	0.1120				
P2m±	0.1180	0.0240	-0.1460	0.0020	-0.0220		
P3m±	-0.2840	-0.0020	-0.0120	-0.0120	0.0130	0.0070	0.0290
atom:	C32						
system coord		C35 X C32 C33 Y					
κ, κ'	1.002619	0.958249					
Pv	4.0102						
P00	0.0000						
P1m±	-0.0170	0.0160	0.0220				
P2m±	0.0260	0.0060	-0.1810	0.0220	0.0030		
P3m±	-0.0320	-0.0150	-0.0030	0.0280	0.0120	-0.0030	-0.2230
atom:	C33						
system coord		C36 X C33 C34 Y					
κ, κ'	1.002619	0.958249					
Pv	4.1531						
P00	0.0000						
P1m±	-0.0230	-0.0140	-0.0150				
P2m±	0.0240	-0.0100	-0.1800	-0.0240	-0.0050		
P3m±	-0.0350	-0.0230	-0.0330	-0.0010	0.0220	-0.0160	-0.2860
atom:	C34						
system coord		C31 X C34 C35 Y					
κ, κ'	1.002619	0.958249					
Pv	4.0465						
P00	0.0000						
P1m±	0.0190	-0.0040	0.0490				
P2m±	0.0210	-0.0170	-0.2110	0.0150	-0.0870		
P3m±	-0.0430	0.0030	0.0040	0.0090	0.0220	0.0070	-0.2660

Table S2 (continued)

atom: C35
system coord C32 X C35 C36 Y
κ, κ' 1.002619 0.958249
Pv 4.0275
P00 0.0000
P1m± 0.0000 -0.0060 -0.0340
P2m± 0.0110 -0.0200 -0.1600 0.0000 0.0340
P3m± -0.0240 -0.0070 0.0150 0.0100 0.0420 -0.0100 -0.2550
atom: C36
system coord C33 X C36 C35 Y
κ, κ' 1.002619 0.958249
Pv 4.0154
P00 0.0000
P1m± 0.0060 -0.0010 0.0570
P2m± -0.0040 0.0140 -0.1830 -0.0170 -0.0210
P3m± 0.0430 -0.0080 -0.0120 0.0110 -0.0080 0.0230 -0.2880
atom: C37
system coord C32 Z C37 H371 X
κ, κ' 0.973579 0.921152
Pv 4.4327
P00 0.0000
P1m± 0.0000 -0.0740 0.0000
P2m± 0.0000 0.0000 -0.0570 0.0000 0.0000
P3m± -0.0050 0.0000 0.0000 0.3210 0.0000 0.0000 0.1440
atom: C38
system coord C34 Z C38 H381 X
κ, κ' 0.973579 0.921152
Pv 4.5581
P00 0.0000
P1m± 0.0000 -0.0740 0.0000
P2m± 0.0000 0.0000 -0.0570 0.0000 0.0000
P3m± -0.0050 0.0000 0.0000 0.3210 0.0000 0.0000 0.1440
atom: C39
system coord C36 Z C39 H391 X
κ, κ' 0.973579 0.921152
Pv 4.3658
P00 0.0000
P1m± 0.0000 -0.0740 0.0000
P2m± 0.0000 0.0000 -0.0570 0.0000 0.0000
P3m± -0.0050 0.0000 0.0000 0.3210 0.0000 0.0000 0.1440

atom: H71
system coord C7 Z H71 C5 X
κ, κ' 1.142921 1.200000
Pv 0.7630
P00 0.0000
P1m± 0.0000 0.1570 0.0000
atom: H72
system coord C7 Z H72 C5
κ, κ' 1.142921 1.200000
Pv 0.7630
P00 0.0000
P1m± 0.0000 0.1970 0.0000
atom: H73
system coord C7 Z H73 C5 X
κ, κ' 1.142921 1.200000
Pv 0.7630
P00 0.0000
P1m± 0.0000 0.1670 0.0000
atom: H11
system coord C11 Z H11 C12 X
κ, κ' 1.207180 1.200000
Pv 0.7172
P00 0.0000
P1m± 0.0000 0.1020 0.0000
atom: H12
system coord C12 Z H12 C11 X
κ, κ' 1.207180 1.200000
Pv 0.7172
P00 0.0000
P1m± 0.0000 0.1240 0.0000
atom: H13
system coord C13 Z H13 C12 X
κ, κ' 1.207180 1.200000
Pv 0.7172
P00 0.0000
P1m± 0.0000 0.1400 0.0000
atom: H14
system coord C14 Z H14 C13 X
κ, κ' 1.207180 1.200000
Pv 0.7172
P00 0.0000
P1m± 0.0000 0.1600 0.0000
atom: H15
system coord C15 Z H15 C11 X
κ, κ' 1.207180 1.200000
Pv 0.7172
P00 0.0000
P1m± 0.0000 0.1170 0.0000

Table S2 (continued)

atom: H23
system coord C23 Z H23 C22 X
κ, κ' 1.265170 1.200000
Pv 0.7943
P00 0.0000
P1m± 0.0000 0.0820 0.0000
atom: H25
system coord C25 Z H25 C24 X/
κ, κ' 1.265170 1.200000
Pv 0.7943
P00 0.0000
P1m± 0.0000 0.1160 0.0000
atom: H271
system coord C27 Z H271 C22 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1640 0.0000
atom: H272
system coord C27 Z H272 C22 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1840 0.0000
atom: H273
system coord C27 Z H273 C22 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1320 0.0000
atom: H281
system coord C28 Z H281 C24 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1730 0.0000
atom: H282
system coord C28 Z H282 C24 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1040 0.0000
atom: H283
system coord C28 Z H283 C24 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1650 0.0000
atom: H291
system coord C29 Z H291 C26 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000

P1m± 0.0000 0.1410 0.0000
atom: H292
system coord C29 Z H292 C26 X
κ, κ' 1.142921 1.200000

Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1230 0.0000
atom: H293
system coord C29 Z H293 C26 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1470 0.0000
atom: H33
system coord C33 Z H33 C32 X
κ, κ' 1.265170 1.200000
Pv 0.7943
P00 0.0000
P1m± 0.0000 0.1440 0.0000
atom: H35
system coord C35 Z H35 C34 X
κ, κ' 1.265170 1.200000
Pv 0.7943
P00 0.0000
P1m± 0.0000 0.1310 0.0000
atom: H371
system coord C37 Z H371 C32 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1620 0.0000

Table S2 (continued)

atom: H372
system coord C37 Z H372 C32 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1630 0.0000
atom: H373
system coord C37 Z H373 C32 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1700 0.0000
atom: H381
system coord C38 Z H381 C34 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1000 0.0000
atom: H382
system coord C38 Z H382 C34 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1030 0.0000
atom: H383
system coord C38 Z H383 C34 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1280 0.0000
atom: H391
system coord C39 Z H391 C36 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1660 0.0000
atom: H392
system coord C39 Z H392 C36 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1440 0.0000

atom: H39
system coord C39 Z H393 C36 X
κ, κ' 1.142921 1.200000
Pv 0.8437
P00 0.0000
P1m± 0.0000 0.1180 0.0000

Table S3. Values of experimental and theoretical (italic) orthodox parameters at bond critical points within complex $\mathbf{3_{Me}}^{a,b}$

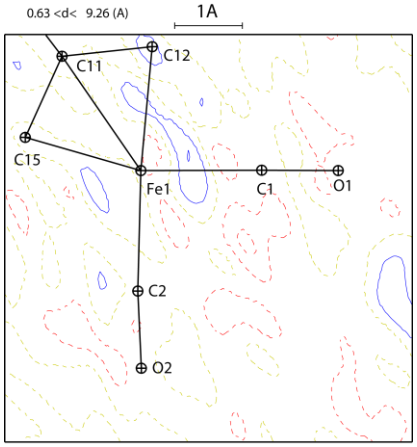
bond	R_b	$d1$	$d2$	$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	λ_1	λ_2	λ_3	ε	$G\rho(\mathbf{r}_b)$	$G\rho(\mathbf{r}_b)/\rho(\mathbf{r}_b)$	$V\rho(\mathbf{r}_b)$	$H\rho(\mathbf{r}_b)$	δ(A/B)	E_{int}
Interatomic bonds															
Fe1-C1	1.793	0.908	0.893	0.95	13.42	-4.29	-3.74	21.46	0.15	1.36	1.44	-1.79	-0.42		
	1.889	*0.971*	*0.926*	*0.75*	*11.89*	*-3.30*	*-2.31*	*17.48*	*0.44*	*1.05*	*1.40*	*-1.27*	*-0.27*	*0.74*	
Fe1-C2	1.782	0.907	0.875	1.09	13.48	-5.18	-4.91	23.56	0.06	1.55	1.43	-2.16	-0.61		
	1.876	*0.970*	*0.913*	*0.76*	*13.31*	*-2.75*	*-2.45*	*18.19*	*0.30*	*1.14*	*1.50*	*-1.35*	*-0.21*	*0.78*	
Fe1-C3	2.044	0.967	1.079	0.62	8.03	-2.09	-1.87	11.99	0.11	0.74	1.19	-0.91	-0.17		
	2.075	*0.966*	*1.111*	*0.60*	*6.72*	*-2.01*	*-1.58*	*10.52*	*0.12*	*0.64*	*1.07*	*-0.81*	*-0.17*	*0.61*	
Fe1-C11	2.141	1.097	1.055	0.53	6.14	-1.79	-0.19	8.12	8.41	0.57	1.07	-0.71	-0.14		
	2.170	*1.103*	*1.068*	*0.47*	*4.55*	*-1.54*	*-0.67*	*6.76*	*1.29*	*0.46*	*0.99*	*-0.60*	*-0.14*	*0.30*	
Fe1-C12	*not observed experimentally*														
	2.159	*1.123*	*1.057*	*0.46*	*5.06*	*-1.61*	*-0.28*	*6.95*	*4.74*	*0.48*	*1.04*	*-0.61*	*-0.13*	*0.33*	
Fe1-C13	2.103	1.056	1.07	*0.53*	*6.10*	*-1.41*	*-0.41*	*7.93*	*2.40*	*0.57*	*1.06*	*-0.71*	*-0.14*		
	2.167	*1.118*	*1.065*	*0.47*	*4.77*	*-1.53*	*-0.45*	*6.75*	*2.43*	*0.47*	*1.01*	*-0.61*	*-0.14*	*0.31*	
Fe1-C14	2.111	1.062	1.06	*0.54*	*6.18*	*-1.59*	*-0.51*	*8.27*	*2.13*	*0.58*	*1.07*	*-0.73*	*-0.15*		
	2.177	*1.110*	*1.072*	*0.46*	*4.53*	*-1.48*	*-0.62*	*6.62*	*1.39*	*0.46*	*0.99*	*-0.60*	*-0.14*	*0.30*	
Fe1-C15	*not observed experimentally*														
	2.170	*1.125*	*1.057*	*0.45*	*5.17*	*-1.74*	*-0.11*	*7.02*	*14.95*	*0.48*	*1.07*	*-0.60*	*-0.12*	*0.33*	
O1-C1	1.145	0.749	0.395	3.23	-11.26	-35.07	-32.74	56.55	0.07	5.16	1.60	-11.11	-5.95		
	1.133	*0.757*	*0.376*	*3.18*	*33.04*	*-34.91*	*-18.92*	*102.83*	*0.00*	*7.55*	*2.38*	*-12.79*	*-5.23*	*1.55*	
O2-C2	1.142	0.756	0.387	3.12	10.39	-32.41	-30.55	73.35	0.06	5.83	1.87	-10.93	-5.10		
	1.133	*0.756*	*0.376*	*3.18*	*32.82*	*-35.08*	*-18.93*	*102.90*	*0.00*	*7.55*	*2.37*	*-12.79*	*-5.24*	*1.55*	
O3-C4	1.241	0.767	0.474	2.76	-31.45	-25.25	-22.54	16.34	0.12	2.89	1.05	-7.99	-5.09		
	1,227	0,821	0,406	2,66	2,33	-24,37	-13,35	49,09	0,09	4,65	1,75	-9,14	-4,49	*1.18*	
O4-C6	1.236	0.747	0.489	2.90	-36.11	-27.56	-24.89	16.35	0.11	3.06	1.05	-8.64	-5.58	-	
	1,227	0,822	0,406	2,66	2,04	-24,30	-13,34	48,78	0,08	4,63	1,74	-9,12	-4,49	*1.17*	
N1-C3	1.355	0.823	0.532	2.18	-23.80	-16.84	-14.97	8.01	0.13	1.83	0.84	-5.34	-3.51		
	1.349	*0.891*	*0.458*	*2.16*	*-17.34*	*-15.62*	*-8.78*	*13.56*	*0.02*	*2.30*	*1.06*	*-5.81*	*-3.51*	*1.09*	
N1-C4	1.455	0.837	0.618	1.80	-11.31	-14.09	-11.88	14.66	0.19	1.61	0.90	-4.02	-2.41		
	1.476	*0.891*	*0.561*	*1.67*	*-15.24*	*-11.41*	*-5.19*	*7.05*	*0.05*	*0.92*	*0.55*	*-2.90*	*-1.99*	*0.79*	
N1-C21	1.446	0.822	0.624	1.87	-13.19	-13.88	-13.39	14.08	0.04	1.67	0.89	-4.26	-2.59		
	1.439	*0.911*	*0.529*	*1.82*	*-18.64*	*-12.40*	*-6.12*	*5.78*	*0.03*	*1.13*	*0.62*	*-3.56*	*-2.44*	*0.89*	
N2-C3	1.362	0.804	0.558	2.27	-23.58	-18.20	-15.54	10.16	0.17	2.04	0.90	-5.74	-3.70		
	1.347	*0.890*	*0.457*	*2.16*	*-17.29*	*-15.59*	*-8.85*	*13.73*	*0.01*	*2.31*	*1.07*	*-5.84*	*-3.53*	*1.10*	
N2-C6	1.462	0.843	0.620	1.75	-10.70	-13.54	-11.43	14.27	0.18	1.54	0.88	-3.82	-2.28		
	1.480	*0.915*	*0.565*	*1.66*	*-15.00*	*-11.33*	*-5.13*	*7.14*	*0.05*	*0.90*	*0.54*	*-2.84*	*-1.95*	*0.79*	
N2-C31	1.448	0.837	0.611	1.79	-12.29	-13.16	-12.33	13.20	0.07	1.55	0.87	-3.97	-2.42		
	1.441	*0.913*	*0.529*	*1.81*	*-18.41*	*-12.29*	*-11.93*	*5.81*	*0.03*	*1.12*	*0.62*	*-3.55*	*-2.42*	*0.08*	

C4-C5	1.396	0.736	0.660	2.17	-19.65	-17.95	-13.84	12.14	0.30	2.02	0.93	-5.41	-5.01		
	1.401	*0.743*	*0.658*	*2.07*	*-20.12*	*-15.43*	*-5.49*	*7.43*	*0.27*	*0.70*	*0.34*	*-2.80*	*-2.11*	*1.20*	
C5-C6	1.401	0.673	0.728	2.14	-17.99	-17.54	-12.99	12.53	0.35	2.01	0.94	-5.28	-3.27		
	1.401	*0.659*	*0.743*	*2.06*	*-19.93*	*-15.37*	*-5.47*	*7.44*	*0.28*	*0.70*	*0.34*	*-2.79*	*-2.10*	*1.21*	
C5-C7	1.498	0.767	0.731	1.78	-13.47	-12.61	-11.44	10.59	0.10	1.46	0.82	-3.87	-2.41		
	1.500	*0.765*	*0.735*	*1.69*	*-13.77*	*-11.16*	*-4.04*	*8.02*	*0.05*	*0.42*	*0.25*	*-1.80*	*-1.39*	*1.01*	
C-C (Cp)	1.424	0.716	0.709	2.02	-16.64	-14.450	-11.65	9.50	0.24	1.82	0.90	-4.80	-2.98		
	1.418	*0.713*	*0.705*	*1.98*	*-17.49*	*-14.00*	*-11.35*	*7.86*	*0.23*	*0.67*	*0.34*	*-2.58*	*-1.90*	*1.27*	
C-H (Cp)	*1.083*	0.76	0.32	1.76	-16.64	-17.47	-16.62	17.46	0.05	1.28	0.73	-3.73	-2.45		
	1.081	*0.683*	*0.398*	*1.91*	*-24.91*	*-18.14*	*-17.85*	*11.07*	*0.02*	*0.26*	*0.14*	*-2.27*	*-2.01*	*0.95*	
C-C (aryl)	1.40	0.70	0.70	2.14	-18.69	-16.60	-13.43	11.33	0.23	1.99	0.93	-5.28	-3.29		
	1.396	*0.704*	*0.692*	*2.08*	*-19.94*	*-15.26*	*-12.56*	*7.88*	*0.22*	*0.67*	*0.32*	*-2.75*	*-2.07*	*1.33*	
C-H (aryl)	1.083	0.73	0.36	1.78	-14.10	-17.38	-16.40	19.71	0.06	1.45	0.81	-3.88	-2.43		
	1.088	*0.677*	*0.411*	*1.88*	*-23.50*	*-17.40*	*-17.06*	*10.96*	*0.02*	*0.29*	*0.15*	*-2.23*	*-1.94*	*0.95*	
C-C(sp^3)	1.502	0.76	0.74	1.71	-11.86	-11.54	-10.80	10.48	0.07	1.41	0.83	-3.65	-2.24		
	1.505	*0.765*	*0.740*	*1.70*	*-14.24*	*-11.34*	*-11.02*	*8.12*	*0.03*	*0.40*	*0.23*	*-1.80*	*-1.40*	*1.01*	
C(sp^3)-H	1.093	0.75	0.35	1.68	-14.11	-15.32	-14.16	15.37	0.08	1.24	0.74	-3.47	-2.23		
	1.094	*0.682*	*0.412*	*1.85*	*-22.52*	*-16.15*	*-16.65*	*10.93*	*0.01*	*0.30*	*0.16*	*-2.19*	*-1.88*	*0.94*	
Intramolecular interligand weak interactions															
C1…C21	2.720	1.337	1.388	0.13	1.15	-0.30	-0.24	1.69	0.28	0.08	0.61	-0.08	0.00		3.9
	2.811	*1.357*	*1.455*	*0.11*	*1.16*	*-0.28*	*-0.17*	*1.62*	*0.62*	*0.07*	*0.65*	*-0.06*	*0.01*	*0.05*	3.1
C2…C36	not observed experimentally														
	2.908	*1.516*	*1.409*	*0.08*	*0.95*	*-0.19*	*-0.05*	*1.19*	*2.67*	*0.05*	*0.72*	*-0.04*	*0.01*	*0.02*	2.0
C32…H15	2.39	1.44	0.999	0.09	1.08	-0.22	-0.18	1.48	0.25	0.06	0.67	-0.05	0.01		2.5
	2.489	*1.485*	*1.010*	*0.07*	*0.91*	*-0.19*	*-0.17*	*1.26*	*0.12*	*0.05*	*0.72*	*-0.04*	*0.01*	*0.03*	*2.0*
H11…H372	1.992	1.924	1.145	0.05	0.99	-0.18	-0.15	1.32	0.18	0.05	1.0	-0.04	0.02		1.7
	2.155	*1.101*	*1.072*	*0.05*	*0.73*	*-0.19*	*-0.15*	*1.07*	*0.22*	*0.04*	*0.73*	*-0.03*	*0.01*	*0.02*	*1.4*
O3…H48	not observed experimentally														
	2.525	*1.476*	*1.075*	*0.07*	*0.92*	*-0.21*	*-0.15*	*1.28*	*0.46*	*0.06*	*0.82*	*-0.05*	*0.01*	*0.03*	*1.9*
O4…H61	not observed experimentally														
	2.623	*1.522*	*1.151*	*0.06*	*0.83*	*-0.15*	*-0.08*	*1.06*	*0.87*	*0.05*	*0.83*	*-0.04*	*0.01*	*0.02*	*1.6*

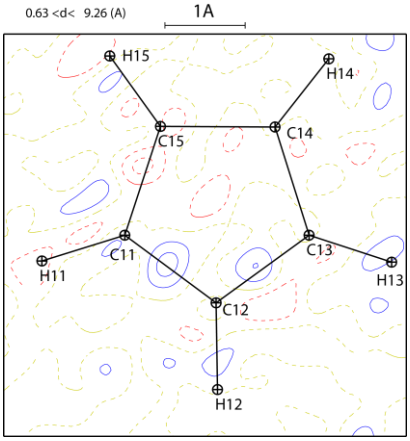
[a]Top line experimental values, second line (italic) theoretical values from isolated molecule DFT calculation. [b]R_b is the interatomic distance (Å); *d*1 and *d*2 are the distances of the bcp from the two atoms (Å); $\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); $\lambda_{1\text{-}3}$ are the curvatures of the bond (e.Å^{-5}); ε is the ellipcity of the bond; $G\rho(\mathbf{r}_b)$, $V\rho(\mathbf{r}_b)$, and $H\rho(\mathbf{r}_b)$ are the kinetic, potential, and total electron energy densities estimated using the approximation of Abramov (hartree.Å^{-3}).[f] δ(C…C) are the delocalization indices; [f] E_{int} is the interaction energy estimated using Espinoza correlation scheme (kcal.mol^{-1}).

Figure S1. Residual electron density maps for $\mathbf{3_{Me}}$ after the multipolar refinement (0.1 e.Å^{-3} isocontours; positive: full lines; negative: dashed lines; zero contour: yellow dashed line).

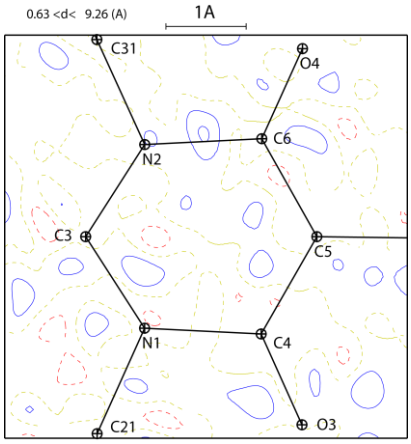
In the Fe1 / C1 / O1 plane



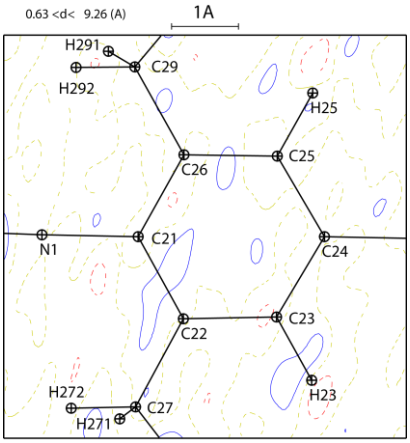
In the C11 / C13 / C15 plane



In the C3 / N1 / N2 plane



In the C21 / C23/C25 plane



In the C31 / C33 / C35 plane

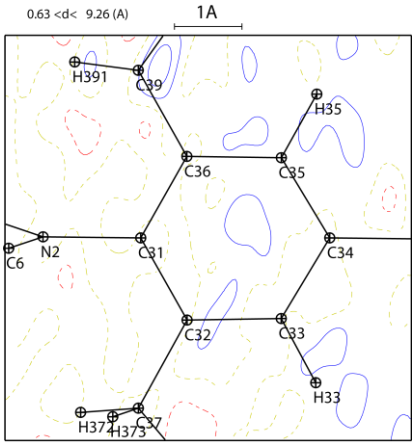
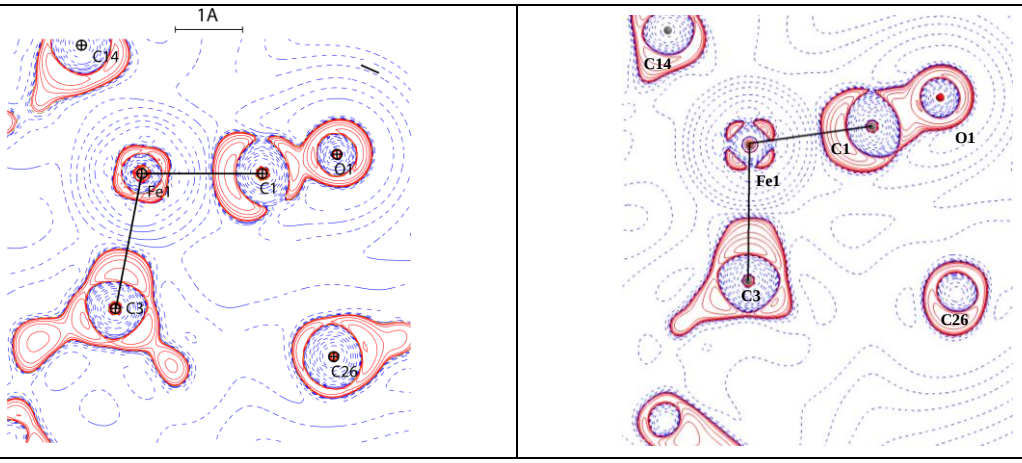
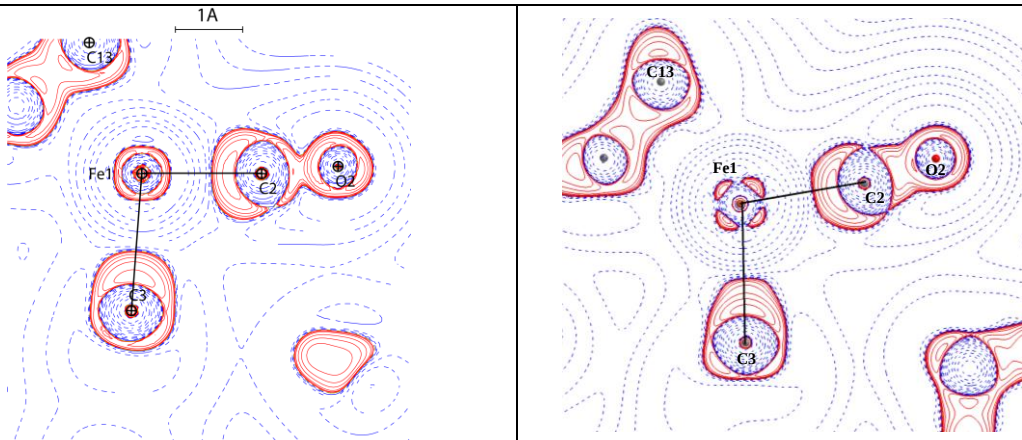


Figure S2. Laplacian of the experimental (left) and theoretical (right, M06-2X/6-31G**) electron density for $\mathbf{3_{Me}}$ in various planes. Contours are drawn at 0.000, ±2.0 x 10n, ±4.0 x 10n, ±8.0 x 10n e.Å^{-5} levels, where n = 0, -3, ±2, ±1; positive: solid (red) lines, negative: dashed (blue) lines.

In the Fe1 / C1 / C3 plane



In the Fe1 / C2 / C3 plane



In the C3 / N1 / N2 plane

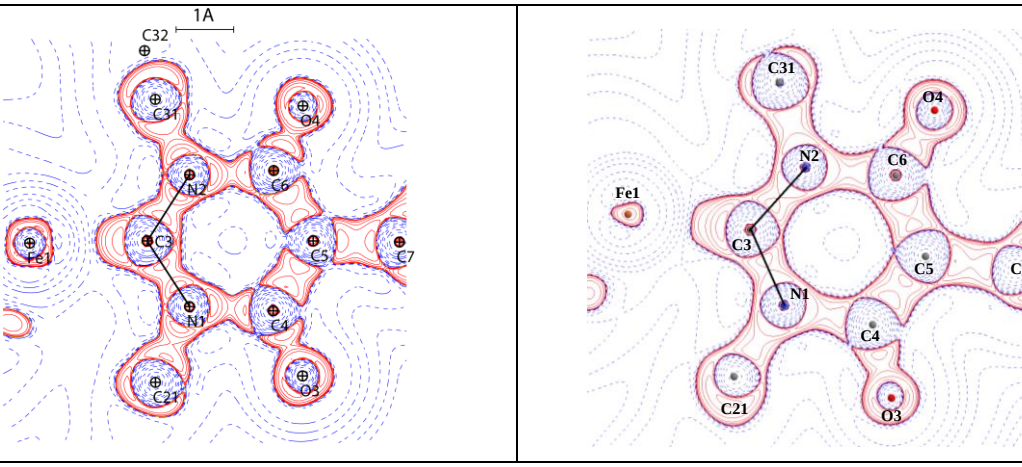
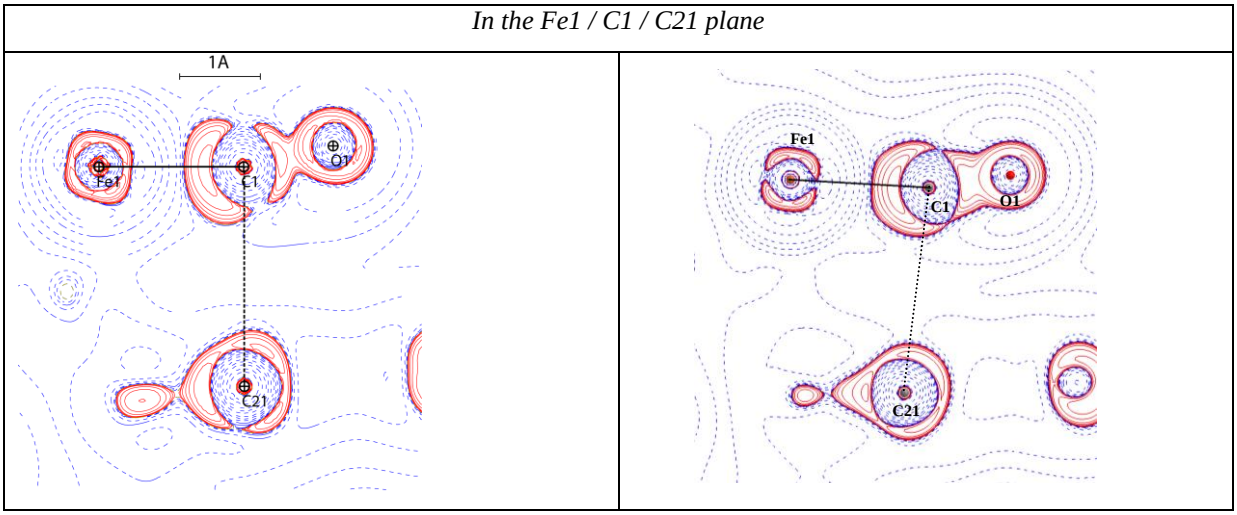


Figure S2 (continued)



Computational studies

Calculations were carried out with the Gaussian 09 program[1] at the DFT level of theory using the M06-2X functional.[2] All the atoms (C, N, H, O, Fe) were described with a 6-31G(d,p) double-ζ basis set.[3] Geometry optimizations were carried out without any symmetry restrictions, the nature of the *minima* was verified with analytical frequency calculations. All total energies and Gibbs free energies were zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies. The electronic structure of the different complexes was studied using Natural Bond Orbital analysis

[1] *Gaussian 09. Revision C.01* Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[2] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

[3] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(NBO-5 program).[4] The electron density of the optimized structures was subject to an Atoms-In Molecules analysis (QTAIM analysis).[5] The Natural Localized Molecular Orbital associated with the Fe-$C_{carbene}$ bond was plotted by using the molecular graphic package Molekel.[6]

In order to choose the better level of theory (M06-2X), geometry optimizations of $\mathbf{3_{Me}}$ were carried out with different functionals like B3LYP,[7] BPW91,[11a-b,8] M06,[6] M06-L,[9] B97D[10] and WB97XD.[11] Diffuse functions were also been added in some cases on the different atoms except hydrogens and iron.

[4] (a) *NBO 5.0.* Glendening, E. D.; Badenhoop, J, K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**; (b) Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899; (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211; (d) Reed A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.

[5] (a) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New-York Ed., **1990**; (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893; (c) AIMAll (Version 10.10.11), Keith, T. A. **2010** (aim.tkgristmill.com).

[6] (a) Molekel 4.3, Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. Swiss Center for Scientific Computing, Manno, Switzerland, **2000-2002**; (b) Portmann, S.; Lüthi, H. P. *Chimica* **2000**, *54*, 766.

[7] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098; (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev*. **1988**, *B37*, 785.

[8] Perdew, J. P. in *Electronic Structure of Solids '91*, Ed. P. Ziesche and H. Eschrig (Akademie Verlag, Berlin), **1991**, 11.

[9] Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.*, **2006**, *125*, 1.

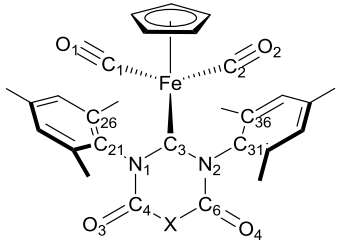
[10] (a) Becke, A. D. *J. Chem. Phys.*, **1997**, *107*, 8554; (b) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.*, **1998**, *108*, 9624; (c) Grimme, S. *J. Comp. Chem.*, **2006**, *27*, 1787.

[11] Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615.

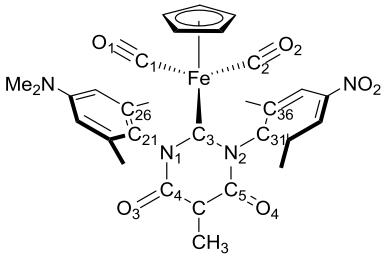
Table S4. Main geometrical parameters (Interatomic distances, in Å, and bond angles, in°) for the complex $\mathbf{3_{Me}}$ at different level of theory.

Bond or angle	B3LYP/6-31+G** SDD(Fe)	B3LYP/6-31G** SDD (Fe)	B3LYP/6-31+G**	B3LYP/6-31G**	B97D/6-31+G**	BPW91/6-31+G**	BPW91/6-31G**	WB97XD/6-31+G**	M06/6-31+G**	M06L/6-31+G**	M062X/6-31+G**	M062X/6-31G**	RX
$d_{(N1-C3)}$	1.357	1.356	1.357	1.356	1.356	1.364	1.361	1.350	1.350	1.351	1.350	**1.349**	**1.363**
$d_{(C1-N2)}$	1.357	1.355	1.357	1.355	1.356	1.362	1.362	1.350	1.350	1.351	1.349	**1.349**	**1.356**
$\angle_{N1-C3-N2\ (deg)}$	115.09	114.92	115.15	114.83	115.70	115.21	114.93	114.89	115.25	115.57	114.79	**114.59**	**114.49**
$d_{(N1-C4)}$	1.491	1.499	1.495	1.500	1.513	1.510	1.517	1.474	1.485	1.495	1.471	**1.476**	**1.462**
$d_{(C4-C5)}$	1.402	1.401	1.403	1.401	1.410	1.409	1.408	1.399	1.400	1.400	1.402	**1.401**	**1.400**
$d_{(C5-C6)}$	1.403	1.401	1.402	1.401	1.410	1.409	1.408	1.399	1.400	1.400	1.403	**1.401**	**1.396**
$d_{(C6-N2)}$	1.495	1.497	1.492	1.498	1.511	1.510	1.516	1.474	1.490	1.495	1.476	**1.480**	**1.454**
$\angle_{N1-C4-C5\ (deg)}$	115.96	115.63	115.96	115.58	115.436	115.758	115.686	116.088	116.030	115.528	115.974	**115.477**	**116.409**
$\angle_{N1-C4-C5-C6\ (deg)}$	-2.38	-3.07	-3.02	-2.82	-1.62	-3.94	0.86	-1.46	4.69	2.04	1.62	**-0.04**	**6.65**
$d_{(Fe-C2)}$	1.789	1.785	1.780	1.773	1.756	1.753	1.748	1.784	1.782	1.767	1.894	**1.876**	**1.782**
$d_{(C2-O)}$	1.150	1.150	1.151	1.151	1.166	1.169	1.169	1.144	1.149	1.158	1.133	**1.133**	**1.143**
$\angle_{(Fe-C2-O2)\ (deg)}$	168.32	168.62	167.67	167.92	167.82	167.89	167.52	167.68	168.22	168.36	170.22	**169.77**	**173.95**
$d_{(Fe-C1)}$	1.79	1.79	1.780	1.775	1.756	1.755	1.749	1.784	1.782	1.767	1.90	**1.89**	**1.793**
$d_{(C1-O1)}$	1.150	1.149	1.151	1.151	1.166	1.169	1.169	1.144	1.149	1.158	1.133	**1.133**	**1.146**
$\angle_{(Fe-C1-O1)\ (deg)}$	168.33	168.91	167.68	167.18	167.77	166.57	166.70	167.72	168.21	168.35	167.03	**165.49**	**165.45**
$d_{(C3-Fe)}$	2.07	2.07	2.067	2.059	2.047	2.054	2.046	2.041	2.047	2.053	2.089	**2.075**	**2.044**
$d_{(N2-C31)}$	1.45	1.45	1.453	1.450	1.447	1.453	1.451	1.442	1.442	1.442	1.443	**1.441**	**1.448**
$d_{(C31-C2)}$	2.996	3.045	2.989	3.033	2.979	3.076	3.056	2.959	2.927	2.968	3.085	**3.105**	**3.183**
$d_{(C31-O2)}$	3.509	3.574	3.506	3.573	3.512	3.634	3.619	3.480	3.407	3.474	3.629	**3.666**	**3.687**
$\angle_{(N2-C31-C2)\ (deg)}$	90.54	88.84	90.40	88.64	91.33	87.03	86.12	91.54	92.14	91.77	92.11	**90.32**	**84.03**
$d_{(N1-C21)}$	1.45	1.45	1.453	1.450	1.447	1.453	1.451	1.442	1.441	1.442	1.442	**1.439**	**1.446**
$d_{(C21-C1)}$	3.00	2.96	2.991	2.964	2.968	2.946	2.980	2.954	2.925	2.955	2.863	**2.811**	**2.720**
$d_{(C21-O1)}$	3.51	3.47	3.508	3.483	3.497	3.467	3.520	3.474	3.404	3.453	3.352	**3.296**	**3.178**
$\angle_{(N1-C21-C1)\ (deg)}$	90.43	91.00	90.23	89.97	91.57	90.37	88.34	91.60	92.04	92.09	97.77	**98.15**	**97.04**

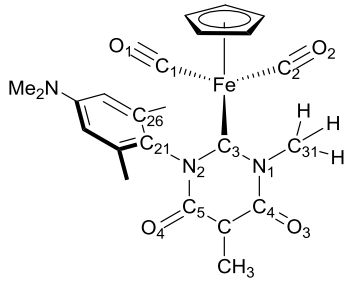
Table S5. Experimental and/or optimized (M06-2X/6-31G** level of theory) geometrical parameters for complexes $\mathbf{3_{Me}}$, **4**, $\mathbf{6^{Me}(OTf)}$, **7**, and **8**.



$\mathbf{3_{Me}}$, **4,** and $\mathbf{[6^{Me}](OTf)}$



7



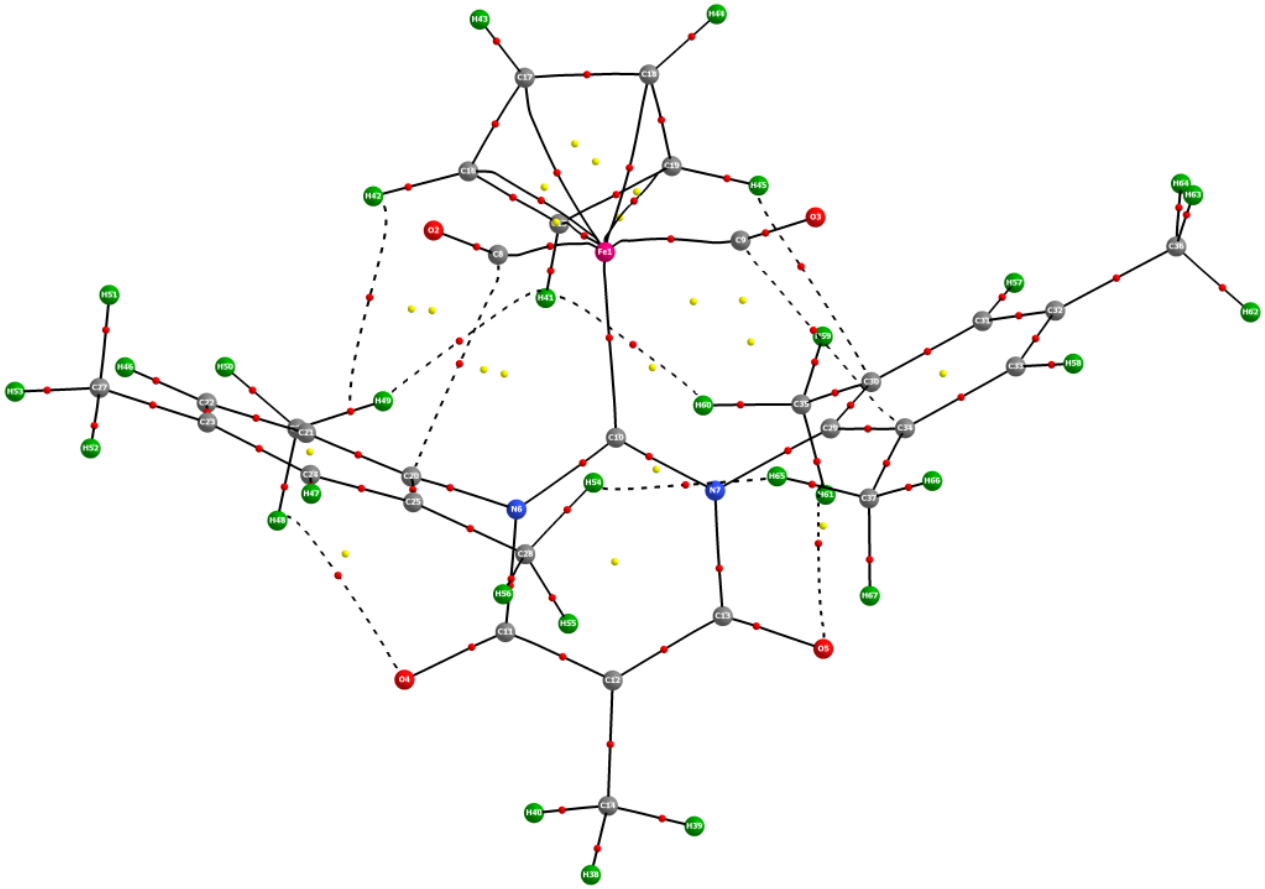
8

bond or angle[a]	$\mathbf{3_{Me}}$(exp)	$\mathbf{3_{Me}}$(theo)	**4**(exp)	**4**(theo)	$\mathbf{[6^{Me}](OTf)}$(exp)	$\mathbf{[6^{Me}](OTf)}$(theo)[b]	**7**	**8**
Fe-C3	2.044	2.075	2.031	2.065	2.003	2.079	2.074	2.061
N1-C4	1.463	1.480	1.464	1.495	1.423	1.431	1.480	1.477
N2-C5	1.455	1.476	1.464	1.494	1.423	1.428	1.479	1.474
C4-O3	1.236	1.227	1.219	1.215	1.198	1.203	1.229	1.229
C5-O4	1.241	1.227	1.221	1.214	1.205	1.204	1.225	1.228
C4-X	1.401	1.401	1.333	1.331	1.373	1.374	1.399	1.401
C5-X	1.396	1.401	1.330	1.330	1.365	1.372	1.403	1.401
C1-C21	2.720	2.811	2.867	2.816	2.856	2.856	2.755	2.663
C1-C26	2.922	2.896	2.924	2.908	3.020	2.939	2.878	2.909
C2-C31	3.180	3.105	3.095	3.119	3.042	3.070	3.142	3.243
C2-C36	3.052	2.908	3.001	2.923	2.930	2.955	2.935	/
Fe-C1-O1	174.00	169.77	171.84	170.22	171.96	166.65	164.906	163.15
Fe-C2-O2	165.48	165.49	168.73	165.31	171.29	169.76	171.047	178.77

[a] bond lengths in Å and bond angles in deg; [b] for $\mathbf{6^{Me}}$, the geometry optimization was carried out by taking into account the counter-anion.

Table S6. Experimental and theoretical topological analysis of complex $\mathbf{3_{Me}}^{a}$

Molecular grap including bcp's (red dots), rcp's (yellow dots), and bp's (black lines) within or close to that plane.



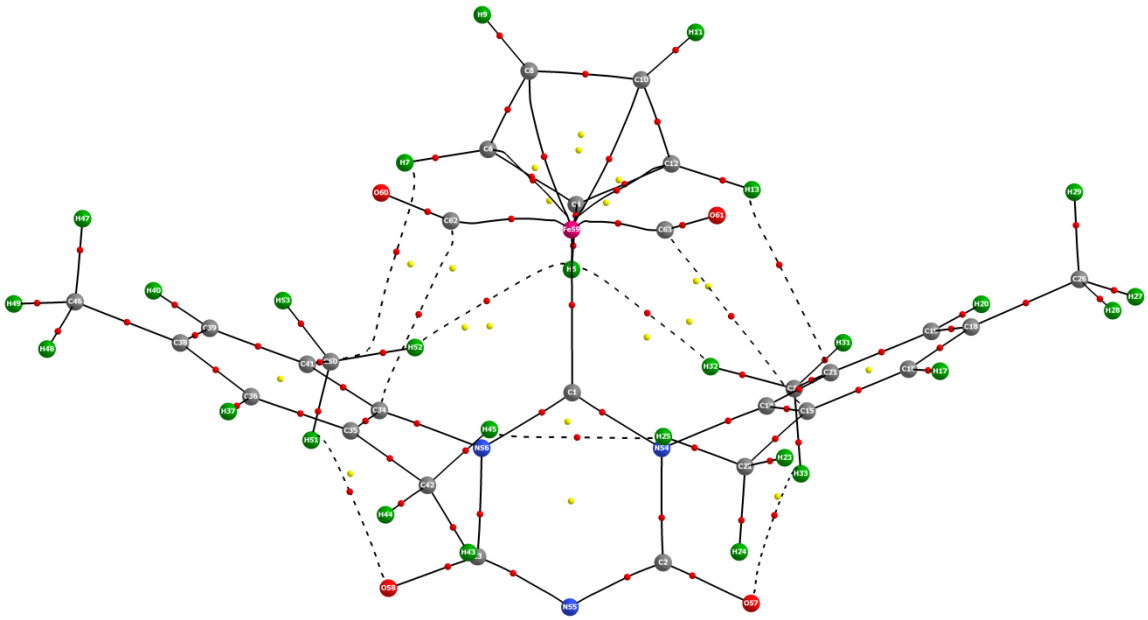
bond	R_b[b]	*d*1	*d*2	$\rho(r_b)$[c]	$\nabla^2\rho(r_b)$[d]	λ_1[e]	λ_2[e]	λ_3[e]	ε[f]	$G\rho(r_b)$[g]	$G\rho(r_b)/\rho(r_b)$	$V\rho(r_b)$[g]	$H\rho(r_b)$[g]
Fe1-C1	1.793	0.908	0.893	0.95	13.42	-4.29	-3.74	21.46	0.15	1.36	1.44	-1.79	-0.43
	1.889	*0.971*	*0.926*	*0.75*	*11.89*	*-3.30*	*-2.31*	*17.48*	*0.44*	*1.05*	*1.40*	*-1.27*	*-0.22*
Fe1-C2	1.782	0.907	0.875	1.09	13.48	-5.18	-4.91	23.56	0.06	1.55	1.43	-2.16	-0.61
	1.876	*0.970*	*0.913*	*0.76*	*13.31*	*-2.75*	*-2.45*	*18.19*	*0.30*	*1.14*	*1.50*	*-1.35*	*-0.21*
Fe1-C3	2.044	0.967	1.079	0.62	8.03	-2.09	-1.87	11.99	0.11	0.74	1.19	-0.91	-0.17
	2.075	*0.966*	*1.111*	*0.60*	*6.72*	*-2.01*	*-1.58*	*10.52*	*0.12*	*0.64*	*1.07*	*-0.81*	*-0.17*
O1-C1	1.145	0.749	0.395	3.23	-11.26	-35.07	-32.74	56.55	0.07	5.16	1.60	-11.11	-5.95
	1.133	*0.757*	*0.376*	*3.18*	*33.04*	*-34.91*	*-18.92*	*102.83*	*0.00*	*7.55*	*2.38*	*-12.79*	*-5.23*
O2-C2	1.142	0.756	0.387	3.12	10.39	-32.41	-30.55	73.35	0.06	5.83	1.87	-10.93	-5.10
	1.133	*0.756*	*0.376*	*3.18*	*32.82*	*-35.08*	*-18.93*	*102.90*	*0.00*	*7.55*	*2.37*	*-12.79*	*-5.24*
N1-C3	1.355	0.823	0.532	2.18	-23.80	-16.84	-14.97	8.01	0.13	1.83	0.84	-5.34	-3.51
	1.349	*0.891*	*0.458*	*2.16*	*-17.34*	*-15.62*	*-8.78*	*13.56*	*0.02*	*2.30*	*1.06*	*-5.81*	*-3.51*
N1-C4	1.455	0.837	0.618	1.80	-11.31	-14.09	-11.88	14.66	0.19	1.61	0.90	-4.02	-2.41
	1.476	*0.891*	*0.561*	*1.67*	*-15.24*	*-11.41*	*-5.19*	*7.05*	*0.05*	*0.92*	*0.55*	*-2.90*	*-1.99*
N1-C21	1.446	0.822	0.624	1.87	-13.19	-13.88	-13.39	14.08	0.04	1.67	0.89	-4.26	-2.59
	1.439	*0.911*	*0.529*	*1.82*	*-18.64*	*-12.40*	*-6.12*	*5.78*	*0.03*	*1.13*	*0.62*	*-3.56*	*-2.44*
N2-C3	1.362	0.804	0.558	2.27	-23.58	-18.20	-15.54	10.16	0.17	2.04	0.90	-5.74	-3.70
	1.347	*0.890*	*0.457*	*2.16*	*-17.29*	*-15.59*	*-8.85*	*13.73*	*0.01*	*2.31*	*1.07*	*-5.84*	*-3.53*
N2-C6	1.462	0.843	0.620	1.75	-10.70	-13.54	-11.43	14.27	0.18	1.54	0.88	-3.82	-2.28
	1.480	*0.915*	*0.565*	*1.66*	*-15.00*	*-11.33*	*-5.13*	*7.14*	*0.05*	*0.90*	*0.54*	*-2.84*	*-1.95*
N2-C31	1.448	0.837	0.611	1.79	-12.29	-13.16	-12.33	13.20	0.07	1.55	0.87	-3.97	-2.42
	1.441	*0.913*	*0.529*	*1.81*	*-18.41*	*-12.29*	*-11.93*	*5.81*	*0.03*	*1.12*	*0.62*	*-3.55*	*-2.42*
C4-C5	1.396	0.736	0.660	2.17	-19.65	-17.95	-13.84	12.14	0.30	2.02	0.93	-5.41	-5.01
	1.401	*0.743*	*0.658*	*2.07*	*-20.12*	*-15.43*	*-5.49*	*7.43*	*0.27*	*0.70*	*0.34*	*-2.80*	*-2.11*
C5-C6	1.401	0.673	0.728	2.14	-17.99	-17.54	-12.99	12.53	0.35	2.01	0.94	-5.28	-3.27
	1.401	*0.659*	*0.743*	*2.06*	*-19.93*	*-15.37*	*-5.47*	*7.44*	*0.28*	*0.70*	*0.34*	*-2.79*	*-2.10*
C5-C7	1.498	0.767	0.731	1.78	-13.47	-12.61	-11.44	10.59	0.10	1.46	0.82	-3.87	-2.41
	1.500	*0.765*	*0.735*	*1.69*	*-13.77*	*-11.16*	*-4.04*	*8.02*	*0.05*	*0.42*	*0.25*	*-1.80*	*-1.39*

[a]Top line experimental values, second line (italic) theoretical values from isolated molecule DFT calculation. [b]R_b is the interatomic distance (Å); *d*1 and *d*2 are the distances of the bcp from the two atoms (Å); [c]$\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); [d]$\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); [e]$\lambda_{1\text{-}3}$ are the curvatures of the bond (e.Å^{-5}); [f]ε is the ellipcity of the bond; [g] $G\rho(\mathbf{r}_b)$, $V\rho(\mathbf{r}_b)$, and $H\rho(\mathbf{r}_b)$ are the kinetic, potential, and total electron energy densities estimated using the approximation of Abramov (hartree.Å^{-3}).[12]

[12] Abramov, Y. A. *Acta Crystallogr.*, *Sect A.* **1997**, *53*, 264.

Table S7. AIM analysis for complex **4**.

Molecular graph including bcp's (red dots), rcp's (yellow dots), and bp's (black lines).



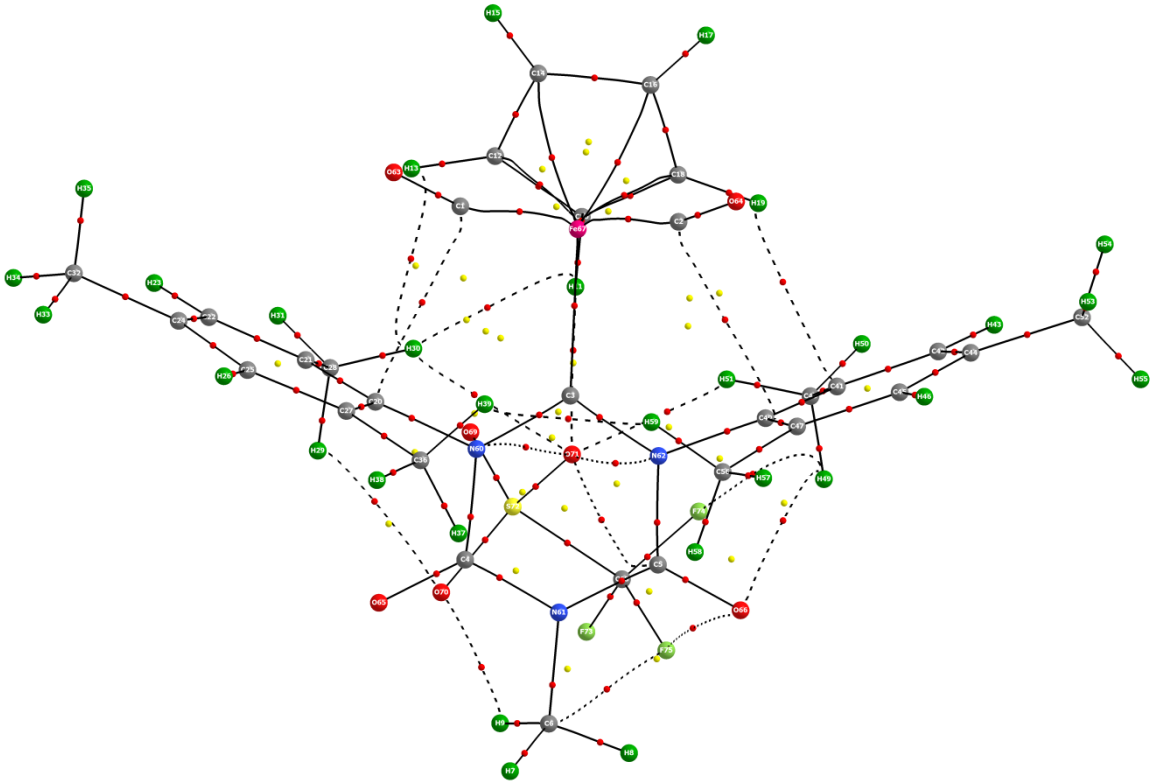
bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
C1 - N54	2.19	-18.29	0.01	-3.58	1.10
C2 - N55	2.36	-29.34	0.14	-3.70	1.08
C1 - N56	2.19	-18.13	0.03	-3.58	1.09
C3 - N55	2.36	-29.35	0.14	-3.71	1.08
C1 - Fe59	0.61	6.93	0.12	-0.17	0.62
C4 - H5	1.92	-25.09	0.01	-2.02	0.93
C4 - C6	2.00	-17.76	0.25	-1.94	1.30
C6 - H7	1.91	-24.88	0.02	-2.01	0.94
C6 - Fe59	0.47	5.08	4.35	-0.13	0.33
C4 - Fe59	0.47	4.57	1.29	-0.14	0.30
C6 - C8	1.94	-16.88	0.21	-1.83	1.22
C8 - Fe59	0.47	4.79	2.57	-0.14	0.32
C8 - H9	1.90	-24.57	0.02	-1.99	0.96
C12 - Fe59	0.45	5.22	12.40	-0.12	0.33
C4 - C12	1.98	-17.45	0.23	-1.90	1.27
C8 - C10	2.01	-18.02	0.25	-1.97	1.32
C10 - C12	1.97	-17.31	0.22	-1.87	1.25
C10 - Fe59	0.46	4.54	1.44	-0.14	0.30
C10 - H11	1.91	-24.67	0.01	-1.99	0.96
C12 - H13	1.92	-25.37	0.02	-2.04	0.93
C14 - N54	1.81	-18.19	0.03	-2.45	0.89
C2 - N54	1.63	-14.00	0.06	-1.78	0.74
H13 - C21	0.07	0.86	0.12	0.01	0.03
C14 - C15	2.09	-19.95	0.24	-2.08	1.30
C15 - C16	2.08	-19.83	0.21	-2.07	1.35
C16 - H17	1.88	-23.57	0.02	-1.94	0.95
C16 - C18	2.09	-20.07	0.21	-2.09	1.37
C18 - C19	2.08	-19.88	0.20	-2.06	1.35
C19 - C21	2.09	-19.97	0.21	-2.08	1.36
C19 - H20	1.88	-23.49	0.02	-1.94	0.95
C14 - C21	0.06	0.77	0.25	0.01	0.02
C15 - C22	2.08	-19.93	0.23	-2.07	1.28
C22 - H25	1.70	-14.16	0.03	-1.40	1.00
C22 - H23	1.84	-22.11	0.01	-1.87	0.93
C22 - H24	1.86	-22.75	0.01	-1.90	0.95
C18 - C26	1.85	-22.70	0.01	-1.88	0.93
C26 - H27	1.70	-14.26	0.03	-1.39	1.01
C26 - H28	1.85	-22.60	0.01	-1.89	0.96
C26 - H29	1.86	-22.67	0.01	-1.90	0.96
H33 - O57	1.83	-22.07	0.01	-1.86	0.95

bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
H5 - H32	0.05	0.75	0.46	0.01	0.02
C21 - C30	1.70	-14.26	0.03	-1.41	1.01
C30 - H31	1.85	-22.57	0.01	-1.89	0.96
C30 - H32	1.85	-22.34	0.01	-1.88	0.93
C30 - H33	1.85	-22.94	0.01	-1.89	0.93
C34 - N56	1.83	-18.48	0.03	-2.48	0.89
C3 - N56	1.62	-13.92	0.06	-1.77	0.74
C34 - C35	2.07	-19.61	0.24	-2.05	1.29
C35 - C36	2.09	-20.00	0.21	-2.08	1.35
C36 - H37	1.88	-23.59	0.02	-1.94	0.95
C36 - C38	2.09	-20.10	0.20	-2.09	1.36
C34 - C62	0.11	1.15	0.60	0.01	0.05
C38 - C39	2.08	-19.90	0.20	-2.06	1.35
C39 - C41	2.09	-20.04	0.21	-2.09	1.37
C39 - H40	1.88	-23.54	0.02	-1.94	0.95
H7 - C50	0.05	0.69	1.44	0.01	0.02
H5 - H52	0.05	0.71	0.50	0.01	0.02
C34 - C41	2.08	-19.87	0.22	-2.06	1.28
H25 - H45	0.05	0.58	0.07	0.01	0.02
C35 - C42	1.70	-14.15	0.03	-1.39	1.01
C42 - H43	1.86	-22.95	0.01	-1.90	0.94
C42 - H45	1.81	-21.33	0.01	-1.82	0.93
C42 - H44	1.86	-22.90	0.01	-1.91	0.95
C38 - C46	1.70	-14.30	0.03	-1.40	1.01
C46 - H47	1.83	-22.08	0.01	-1.86	0.95
C46 - H48	1.86	-22.66	0.01	-1.90	0.96
C46 - H49	1.85	-22.63	0.01	-1.89	0.96
H51 - O58	0.07	0.91	0.52	0.01	0.03
C41 - C50	1.70	-14.29	0.03	-1.41	1.01
C50 - H51	1.86	-23.20	0.01	-1.91	0.92
C50 - H52	1.85	-22.50	0.01	-1.89	0.93
C50 - H53	1.85	-22.36	0.01	-1.88	0.96
C2 - O57	2.74	4.19	0.12	-4.66	1.13
C3 - O58	2.75	4.40	0.13	-4.66	1.14
C15 - C63	0.07	0.93	2.73	-0.08	0.02
Fe59 - C62	0.75	11.83	0.44	-2.54	0.74
Fe59 - C63	0.76	13.31	0.30	-2.70	0.78
O60 - C62	3.18	33.13	0.00	-25.60	1.55
O61 - C63	3.18	32.91	0.00	-25.61	1.56

Theoretical values from isolated molecule DFT calculation.
$\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); ε is the ellipcity of the bond; $H\rho(\mathbf{r}_b)$ is the total electron energy density. δ(A-B) is the delocalization index.

Table S8. AIM analysis for complex $\mathbf{6^{Me}(OTf)}$.

Molecular graph including bcp's (red dots), rcp's (yellow dots), and bp's (black lines).



bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
C3 - Fe67	0.56	7.13	0.19	-0.14	0.58
C4 - N60	1.90	-20.73	0.10	-2.41	0.82
C5 - N62	1.91	-21.00	0.09	-2.42	0.82
C4 - N61	2.14	-24.59	0.13	-3.27	0.89
C6 - N61	1.61	-12.15	0.03	-2.19	0.86
C5 - N61	2.13	-24.63	0.13	-3.23	0.89
C6 - H7	1.90	-24.07	0.04	-1.96	0.93
C6 - H8	1.93	-25.42	0.03	-2.04	0.91
C6 - H9	1.92	-25.82	0.03	-2.04	0.89
C14 - Fe67	0.47	4.70	2.39	-0.14	0.32
C12 - Fe67	0.47	5.03	3.79	-0.13	0.34
C16 - Fe67	0.47	4.55	1.66	-0.14	0.31
C18 - Fe67	0.46	5.16	6.73	-0.13	0.35
C10 - Fe67	0.47	4.44	1.73	-0.14	0.30
N62 - O71	0.09	1.19	2.15	0.01	0.05
H51 - O71	0.12	1.38	0.10	0.00	0.06
C10 - H11	1.93	-26.82	0.01	-2.09	0.88
C10 - C12	1.99	-17.70	0.23	-1.93	1.29
C12 - H13	1.91	-24.99	0.02	-2.01	0.94
C12 - C14	1.94	-16.87	0.21	-1.82	1.22
C14 - H15	1.90	-24.54	0.01	-1.99	0.96
C10 - C18	1.98	-17.48	0.22	-1.90	1.27
C14 - C16	2.02	-18.07	0.25	-1.97	1.32
C16 - C18	1.96	-17.20	0.21	-1.86	1.24
C16 - H17	1.90	-24.58	0.01	-1.99	0.96
C18 - H19	1.92	-25.25	0.02	-2.03	0.94
C1 - C20	0.10	1.07	0.62	0.01	0.05
C3 - N60	2.15	-17.70	0.06	-3.50	1.07
C20 - C21	2.08	-19.88	0.22	-2.06	1.29
H13 - H30	0.05	0.79	1.36	0.01	0.01
C22 - H23	1.89	-23.78	0.02	-1.95	0.95
C21 - C22	2.08	-19.87	0.20	-2.06	1.36
C22 - C24	2.08	-19.95	0.20	-2.07	1.36
C20 - C27	2.07	-19.58	0.25	-2.05	1.29
C24 - C32	1.70	-14.30	0.02	-1.40	1.01
C24 - C25	2.08	-20.03	0.20	-2.08	1.35
C25 - H26	1.88	-23.59	0.02	-1.94	0.95
C25 - C27	2.09	-19.95	0.21	-2.08	1.36
C20 - N60	1.74	-15.91	0.02	-2.35	0.86
H11 - H30	0.05	0.76	1.18	0.01	0.01
C21 - C28	1.70	-14.35	0.03	-1.43	1.01
N60 - O71	0.07	0.89	1.13	0.00	0.04
H30 - O71	0.08	0.94	0.11	0.00	0.04
C28 - H29	1.84	-22.94	0.01	-1.88	0.90
C28 - H30	1.87	-23.38	0.02	-1.94	0.90
C28 - H31	1.85	-22.52	0.01	-1.89	0.95
C32 - H34	1.86	-22.70	0.01	-1.90	0.96
C32 - H33	1.85	-22.63	0.01	-1.89	0.96
C32 - H35	1.83	-22.11	0.01	-1.86	0.95
C36 - H39	1.81	-21.47	0.01	-1.82	0.93
C27 - C36	1.70	-14.19	0.02	-1.40	1.01

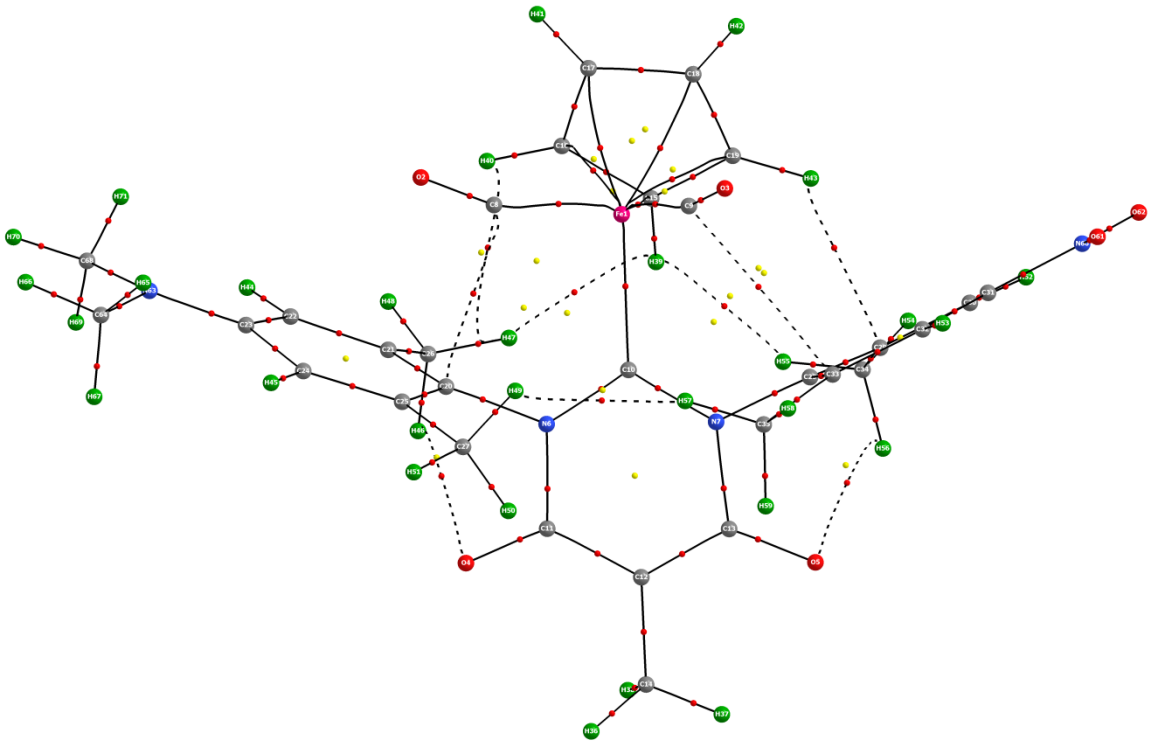
bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
C36 - H37	1.85	-22.56	0.01	-1.88	0.94
C36 - H39	1.81	-21.47	0.01	-1.82	0.93
C27 - C36	1.70	-14.19	0.02	-1.40	1.01
C36 - H37	1.85	-22.56	0.01	-1.88	0.94
C36 - H38	1.86	-23.00	0.01	-1.91	0.95
H39 - H59	0.06	0.70	0.10	0.01	0.02
C2 - C40	0.07	0.84	6.20	0.01	0.03
C3 - N62	2.14	-18.11	0.06	-3.47	1.06
H19 - C41	0.06	0.82	1.65	0.01	0.02
C40 - C41	2.07	-19.79	0.22	-2.05	1.29
C42 - H43	1.88	-23.65	0.02	-1.94	0.95
C41 - C42	2.08	-19.87	0.20	-2.07	1.36
C42 - C44	2.08	-19.94	0.20	-2.07	1.36
C40 - C47	2.08	-19.64	0.25	-2.06	1.30
C44 - C52	1.70	-14.26	0.03	-1.39	1.01
C44 - C45	2.09	-20.06	0.20	-2.08	1.36
C45 - H46	1.88	-23.61	0.02	-1.95	0.95
C45 - C47	2.08	-19.85	0.21	-2.07	1.35
C40 - N62	1.73	-15.92	0.02	-2.33	0.86
H49 - O66	0.06	0.81	0.74	0.01	0.02
C41 - C48	1.70	-14.29	0.03	-1.42	1.01
C48 - H49	1.84	-22.58	0.01	-1.87	0.92
C48 - H51	1.89	-24.09	0.01	-1.97	0.90
C48 - H50	1.84	-22.29	0.01	-1.88	0.95
H11 - O71	0.13	1.45	0.05	0.00	0.06
C52 - H53	1.86	-22.66	0.01	-1.90	0.96
C52 - H54	1.85	-22.50	0.01	-1.88	0.96
C52 - H55	1.84	-22.29	0.01	-1.87	0.95
C56 - H59	1.83	-21.97	0.01	-1.86	0.92
C47 - C56	1.69	-14.13	0.03	-1.39	1.00
C56 - H57	1.86	-22.96	0.01	-1.91	0.95
C56 - H58	1.84	-22.31	0.01	-1.86	0.94
O66 - F75	0.02	0.49	0.06	0.01	0.01
C5 - O71	0.09	1.26	9.89	0.01	0.02
C1 - O63	3.18	33.30	0.00	-5.24	1.56
C2 - O64	3.18	33.18	0.00	-5.25	1.56
C4 - O65	2.81	6.65	0.13	-4.80	1.17
C5 - O66	2.80	6.03	0.12	-4.78	1.16
C1 - Fe67	0.74	11.61	0.44	-0.21	0.73
C2 - Fe67	0.74	12.49	0.37	-0.20	0.75
C6 - F75	0.03	0.49	1.38	0.01	0.01
H49 - F74	0.02	0.36	1.11	0.01	0.01
H9 - O70	0.10	1.17	0.07	0.00	0.05
H29 - O70	0.06	0.73	0.24	0.01	0.03
O71 - S72	1.82	23.90	0.06	-2.03	0.89
C68 - S72	1.35	-10.85	0.00	-1.04	0.65
C68 - F73	1.88	-1.18	0.19	-2.78	0.67
O69 - S72	1.91	28.77	0.06	-2.16	1.00
O70 - S72	1.89	27.29	0.06	-2.12	0.97
C68 - F74	1.85	-1.49	0.20	-2.72	0.66
C68 - F75	1.83	0.00	0.21	2.58	0.66

Theoretical values from isolated molecule DFT calculation.

$\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); ε is the ellipcity of the bond; $H\rho(\mathbf{r}_b)$ is the total electron energy density. δ(A-B) is the delocalization index.

Table S9. AIM analysis for complex **7**.

Molecular graph including bcp's (red dots), rcp's (yellow dots), and bp's (black lines).



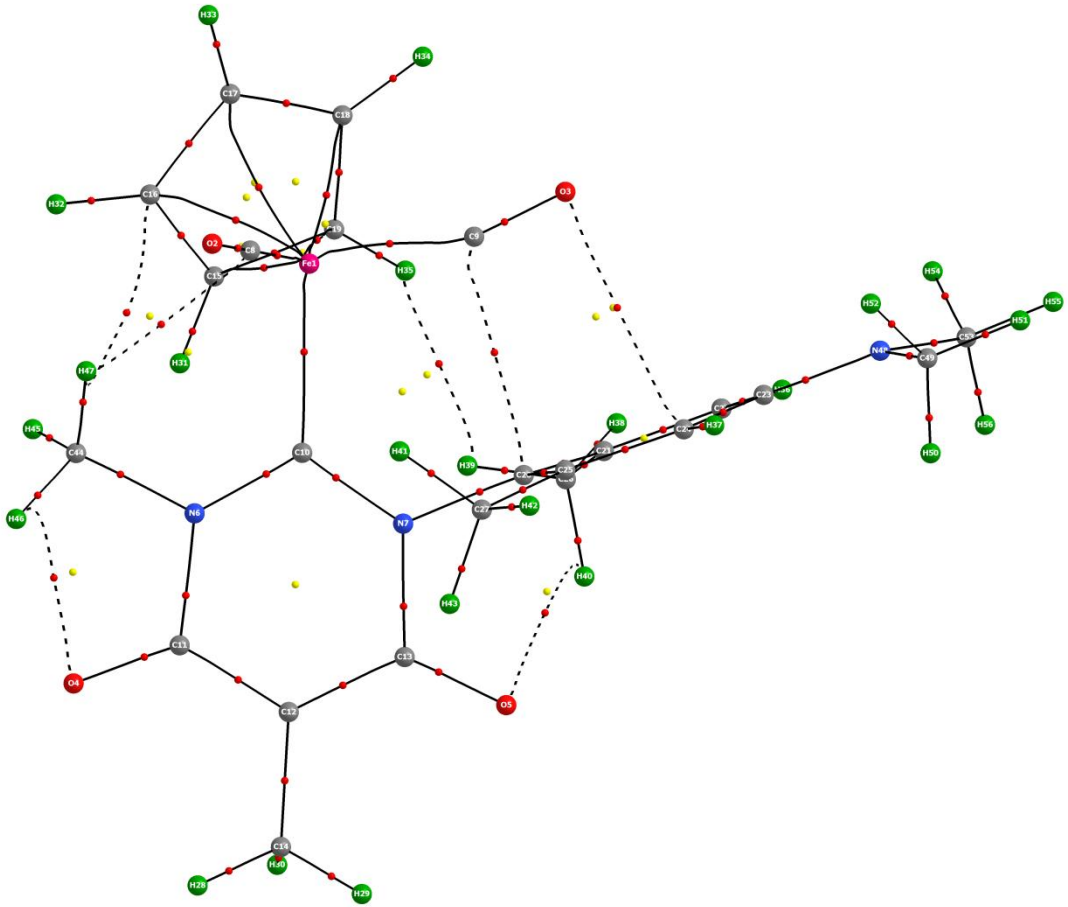
bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
Fe1 - C10	0.6	6.9	0.1	-0.2	0.6
Fe1 - C8	0.7	11.6	0.4	-0.2	0.7
Fe1 - C9	0.8	13.6	0.3	-0.2	0.8
C8 - C20	0.1	1.2	0.4	0.0	0.1
N6 - C10	2.2	-17.6	0.0	-3.6	1.1
N6 - C11	1.7	-15.1	0.1	-2.0	0.8
O4 - C11	2.7	2.8	0.1	-4.5	1.2
N7 - C10	2.1	-16.9	0.0	-3.5	1.1
C12 - C13	2.1	-20.1	0.3	-2.1	1.2
C9 - C33	0.1	0.9	2.4	0.0	0.0
C11 - C12	2.1	-20.0	0.3	-2.1	1.2
N7 - C13	1.7	-14.9	0.0	-2.0	0.8
O5 - C13	2.7	1.6	0.1	-4.5	1.2
O2 - C8	3.2	33.2	0.0	-5.2	1.6
O3 - C9	3.2	32.7	0.0	-5.2	1.6
C12 - C14	1.7	-13.8	0.0	-1.4	1.0
C14 - H37	1.9	-23.3	0.0	-1.9	0.9
Fe1 - C15	0.5	4.6	1.3	-0.1	0.3
Fe1 - C16	0.5	5.0	4.4	-0.1	0.3
Fe1 - C18	0.5	4.5	1.4	-0.1	0.3
Fe1 - C19	0.4	5.2	13.5	-0.1	0.3
C16 - C17	1.9	-16.9	0.2	-1.8	1.2
C15 - C16	2.0	-17.8	0.2	-1.9	1.3
Fe1 - C17	0.5	4.8	2.6	-0.1	0.3
C17 - C18	2.0	-18.1	0.2	-2.0	1.3
C18 - C19	2.0	-17.4	0.2	-1.9	1.3
C15 - C19	2.0	-17.4	0.2	-1.9	1.3
N6 - C20	1.8	-17.7	0.0	-2.5	0.9
H40 - H47	0.0	0.7	1.8	0.0	0.0
C20 - C21	2.1	-19.9	0.2	-2.1	1.3
C21 - C22	2.1	-20.0	0.2	-2.1	1.4
C22 - C23	2.0	-19.1	0.2	-2.0	1.3
C20 - C25	2.1	-19.6	0.2	-2.0	1.3
C23 - C24	2.0	-19.2	0.2	-2.0	1.3
C24 - C25	2.1	-20.0	0.2	-2.1	1.4
O4 - H46	0.1	0.9	0.5	0.0	0.0
H39 - H47	0.1	0.7	0.5	0.0	0.0
C21 - C26	1.7	-14.3	0.0	-1.4	1.0
C25 - C27	1.7	-14.2	0.0	-1.4	1.0
C24 - H45	1.9	-23.8	0.0	-2.0	0.9
N7 - C28	1.8	-19.6	0.1	-2.4	0.9
C29 - H43	0.1	0.9	0.1	0.0	0.0
C28 - C29	2.1	-20.0	0.2	-2.1	1.3
C29 - C30	2.1	-20.0	0.2	-2.1	1.4

bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
C30 - C31	2.1	-20.8	0.2	-2.2	1.3
C28 - C33	2.1	-19.9	0.2	-2.1	1.3
C31 - C32	2.1	-21.0	0.2	-2.2	1.3
C32 - C33	2.1	-19.9	0.2	-2.1	1.3
O5 - H56	0.1	0.9	0.7	0.0	0.0
H39 - H55	0.1	0.7	0.2	0.0	0.0
C29 - C34	1.7	-14.3	0.0	-1.4	1.0
H49 - H57	0.0	0.5	0.1	0.0	0.0
C33 - C35	1.7	-14.2	0.0	-1.4	1.0
C14 - H36	1.8	-22.3	0.0	-1.9	1.0
C14 - H38	1.8	-22.1	0.0	-1.9	1.0
C15 - H39	1.9	-25.1	0.0	-2.0	0.9
C16 - H40	1.9	-24.9	0.0	-2.0	0.9
C17 - H41	1.9	-24.6	0.0	-2.0	1.0
C18 - H42	1.9	-24.7	0.0	-2.0	1.0
C19 - H43	1.9	-25.3	0.0	-2.0	0.9
C22 - H44	1.9	-23.8	0.0	-2.0	0.9
C26 - H46	1.9	-23.1	0.0	-1.9	0.9
C26 - H47	1.9	-22.5	0.0	-1.9	0.9
C26 - H48	1.8	-22.4	0.0	-1.9	1.0
C27 - H49	1.8	-21.2	0.0	-1.8	0.9
C27 - H50	1.9	-23.0	0.0	-1.9	0.9
C27 - H51	1.9	-22.9	0.0	-1.9	1.0
C30 - H52	1.9	-25.1	0.0	-2.0	0.9
C32 - H53	1.9	-25.2	0.0	-2.0	0.9
C34 - H54	1.9	-22.6	0.0	-1.9	1.0
C34 - H55	1.9	-22.6	0.0	-1.9	0.9
C34 - H56	1.9	-23.1	0.0	-1.9	0.9
C35 - H57	1.8	-22.4	0.0	-1.9	0.9
C35 - H58	1.9	-22.9	0.0	-1.9	1.0
C35 - H59	1.8	-22.7	0.0	-1.9	0.9
C31 - N60	1.7	-17.3	0.1	-2.2	0.8
N60 - O61	3.4	-25.1	0.1	-4.4	1.7
N60 - O62	3.4	-25.1	0.1	-4.4	1.7
N63 - C68	1.8	-18.3	0.1	-2.3	0.9
C23 - N63	2.1	-21.1	0.1	-3.1	1.0
N63 - C64	1.8	-18.3	0.1	-2.3	0.9
C64 - H67	1.9	-22.9	0.0	-1.9	0.9
C64 - H66	1.9	-23.9	0.0	-2.0	0.9
C64 - H65	1.9	-23.4	0.0	-1.9	0.9
C68 - H69	1.9	-22.9	0.0	-1.9	0.9
C68 - H70	1.9	-23.9	0.0	-2.0	0.9
C68 - H71	1.9	-23.3	0.0	-1.9	0.9

Theoretical values from isolated molecule DFT calculation.
$\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); ε is the ellipcity of the bond; $H\rho(\mathbf{r}_b)$ is the total electron energy density.δ(A-B) is the delocalization index.

Table S10. AIM analysis for complex **8**.

Molecular grap including bcp's (red dots), rcp's (yellow dots), and bp's (black lines)



bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
Fe1 - C8	0.79	15.50	0.04	-0.20	0.82
Fe1 - C9	0.74	11.46	0.40	-0.21	0.72
Fe1 - C10	0.62	6.84	0.12	-0.18	0.62
N7 - C10	2.17	-17.62	0.02	-3.53	1.10
N6 - C11	1.68	-15.62	0.05	-2.03	0.80
N7 - C13	1.66	-15.15	0.05	-1.98	0.79
C12 - C14	1.69	-13.78	0.05	-1.39	1.01
C9 - C20	0.14	1.40	0.16	0.01	0.08
C11 - C12	2.07	-20.03	0.28	-2.10	1.21
N7 - C20	1.83	-18.18	0.02	-2.49	0.89
O5 - C13	2.66	2.08	0.08	-4.48	1.17
O2 - C8	3.17	32.28	0.00	-5.23	1.55
C8 - H47	0.09	1.10	0.45	0.01	0.03
O3 - C9	3.17	32.88	0.00	-5.22	1.55
N6 - C10	2.18	-16.82	0.03	-3.58	1.11
C12 - C13	2.07	-20.08	0.28	-2.11	1.21
N6 - C44	1.73	-16.84	0.04	-2.22	0.91
O4 - C11	2.65	2.12	0.08	-4.46	1.17
C14 - H29	1.86	-22.88	0.01	-1.91	0.95
C14 - H28	1.86	-22.88	0.01	-1.91	0.95
Fe1 - C15	0.47	4.61	1.28	-0.14	0.30
Fe1 - C16	0.47	5.06	3.19	-0.13	0.33
Fe1 - C19	0.45	5.44	12.54	-0.12	0.33
C16 - H47	0.06	0.74	0.68	0.01	0.02
Fe1 - C18	0.46	4.52	1.35	-0.14	0.30
C15 - C16	2.00	-17.65	0.25	-1.94	1.30
Fe1 - C17	0.46	4.84	3.83	-0.13	0.31
C16 - C17	1.94	-16.91	0.21	-1.83	1.22
C17 - C18	2.02	-18.08	0.25	-1.98	1.32
C15 - C19	1.98	-17.49	0.24	-1.90	1.27
C18 - C19	1.96	-17.16	0.22	-1.86	1.24
O3 - C24	0.06	0.75	3.65	0.01	0.03
O5 - H40	0.06	0.85	0.86	0.01	0.03
H35 - H39	0.05	0.64	0.18	0.01	0.02

bond	$\rho(r_b)$ (eÅ^{-3})	$\nabla^2\rho(r_b)$ (eÅ^{-5})	ε	H	δ(A/B)
C20 - C21	2.08	-19.86	0.23	-2.06	1.26
C21 - C22	2.09	-20.01	0.23	-2.10	1.38
C22 - C23	2.03	-19.15	0.20	-1.98	1.26
C20 - C25	2.07	-19.60	0.24	-2.04	1.26
C23 - C24	2.03	-19.13	0.20	-1.97	1.25
C24 - C25	2.10	-20.05	0.23	-2.11	1.38
C21 - C26	1.70	-14.30	0.03	-1.41	1.01
C25 - C27	1.70	-14.19	0.03	-1.39	1.01
C14 - H30	1.83	-21.79	0.01	-1.84	0.95
C15 - H31	1.91	-25.12	0.01	-2.01	0.94
C16 - H32	1.91	-24.68	0.02	-2.00	0.95
C17 - H33	1.90	-24.58	0.02	-1.99	0.96
C18 - H34	1.91	-24.69	0.01	-2.00	0.96
C19 - H35	1.91	-24.89	0.02	-2.01	0.95
C22 - H36	1.89	-23.76	0.03	-1.97	0.94
C53 - H56	1.86	-22.82	0.03	-1.88	0.93
C49 - H50	1.86	-22.82	0.03	-1.88	0.93
C24 - H37	1.90	-23.79	0.03	-1.98	0.94
C26 - H40	1.85	-23.03	0.01	-1.90	0.93
C26 - H38	1.84	-22.31	0.01	-1.88	0.96
C26 - H39	1.85	-22.50	0.01	-1.89	0.93
C27 - H42	1.86	-22.81	0.01	-1.91	0.96
C27 - H41	1.82	-21.70	0.01	-1.84	0.94
C27 - H43	1.85	-22.84	0.01	-1.89	0.94
O4 - H46	0.16	2.58	1.23	0.02	0.06
C44 - H46	1.94	-25.80	0.02	-2.06	0.90
C44 - H45	1.87	-23.23	0.03	-1.91	0.92
C44 - H47	1.91	-24.04	0.03	-1.99	0.91
C23 - N48	2.06	-21.13	0.08	-3.12	1.04
N48 - C49	1.79	-18.34	0.05	-2.26	0.94
N48 - C53	1.79	-18.34	0.05	-2.26	0.94
C49 - H51	1.89	-23.90	0.03	-1.96	0.93
C49 - H52	1.88	-23.35	0.03	-1.92	0.92

Theoretical values from isolated molecule DFT calculation.
$\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); ε is the ellipcity of the bond; $H\rho(\mathbf{r}_b)$ is the total electron energy density. δ(A-B) is the delocalization index.

Analysis of the influence of the electronic properties of the carbene and of the N-substituents on the interligand interaction

Both experimental and optimized geometries of complexes **4** and $\mathbf{6^{Me}}$ also exhibit a somewhat unsymmetrical geometry, one of the C_{ipso}(aryl)…C(≡O) distances being slightly shorter than the other one (Table S5). As a matter of fact, the variation of σ-donor effects along the series of free carbenes $\mathbf{1_{Me}^{-}.K^{+}}$, $\mathbf{2^{-}.K^{+}}$ and $\mathbf{2_{Me}}$ (n_C^{σ} : -6.40 eV for $\mathbf{1_{Me}^{-}.K^{+}}$, -6.60 eV for $\mathbf{2^{-}.K^{+}}$ and -7.3 eV for $\mathbf{2_{Me}}$), coherent with the IR observations (donor effect : $\mathbf{1_{Me}^{-}} > \mathbf{2^{-}}$), is not substantiated by important changes in the geometry of these complexes. As previously observed for $\mathbf{3^{Me}}$, the AIM analysis of the theoretical ED within these complexes in their optimized geometry also reveals the recurrence of bcp's between the C_{ipso} and C_{ortho} of each aryl ring, and their proximal CO ligand (Tables S7 and S8). Topological characteristics ($\rho(\mathbf{r}_b)$, $\nabla^2\rho(\mathbf{r}_b)$) and derived values (including E_{int}) as well as delocalization indices at these pairs of bcp's appear to be very similar to those appearing in the molecular graph of $\mathbf{3_{Me}}$ and do not reveal any clear trend between the electron donating properties of the *malo*- or *imid*NHC rings and the magnitude of the weak non-covalent interactions (Tables S7 and S8). In the same way, the calculated energies E_{int} and the NBO stabilizing energies ΔE(2) are only weakly modified and do not exceed respectively 3 and 5 kcal/mol. The strongest interaction, even if it remains weak, corresponds to the shortest $C_{Mes}…C_{C\equiv O}$ distance. As previously observed for $\mathbf{3_{Me}}$, the NLMO associated with the $\pi_{C=C}^{Mes}$ orbitals involved in the interaction with the $\pi^*_{C\equiv O}$ orbitals presents a weak CO participation. The latter is quasi similar for the three complexes $\mathbf{3_{Me}}$, **4** and $\mathbf{6^{Me}}$(OTf), the highest participation corresponding to the shortest $C_{Mes}…C_{CO}$ contact (Table S11). By contrast, the electron richness of the aryl ring appears to be more influential on these interligand interactions. In order to bring support to this hypothesis, DFT calculations were conducted on the unsymmetrical model complex **7** derived from $\mathbf{3_{Me}}$ by formal substitution of the *4*-Me groups of the two Mesityl substituents by an NMe_2 group and an NO_2 group respectively. These changes do not affect the steric hindrance of the aryl groups, remaining *a priori* constant. Very characteristically, the DFT geometry optimization carried out on **7** leads to a slightly more unsymmetrical structure than that previously observed for $\mathbf{3_{Me}}$. It is characterized by a shortening of the C_{ipso}(aryl)…C(≡O) distance involving the aryl

group bearing the *4*-NMe_2 donor substituent (C1…C21 = 2.755 Å, Table S5), and an increase in the C_{ortho}(aryl)…C(≡O) distance involving on the other side the aryl group bearing the *4*-NO_2 donor substituent (C2…C36: 2.935 Å). Beyond distance variations, the AIM and NBO analyses conducted as above (Table S12 and S13) indicate a strengthening of the C1…C21 interaction, concomitant with a weakening of the C2…C26 one, corroborating our previous demonstration that the magnitude of such interactions is sensitive to the electron-richness of the aryl ring,[13] favoring the $\pi(C_{ipso}=C_{ortho})$ to $\pi^*(C\equiv O)$ donation. For the shortest contact, the energy value E_{int} becomes higher than 3 kcal.mol^{-1}and the $\Delta E(2)$ NBO stabilizing energy becomes higher than 5 kcal.mol^{-1}.

It is noteworthy that the magnitude of such an interaction is even more strengthened in the case of a totally unsymmetrical structure such as **8**, in which the nitrogen substituents are a para-NMe_2-2,6-dimethylphenyl substituent on one side and a methyl group on the other side. Here, the stabilizing interaction on the aryl group side is maximised up to 6.9 kcal.mol^{-1}, leading to a significant shortening of the $C_{Mes}…C_{CO}$ bond (2.663 Å) and an even more bent carbonyl group, with a Fe-C-O bond angle of 163.15°. In the same way, the density $\rho(r_b)$ is 0.14 Å.bohr^{-3} with a delocalization index $\delta(C_{Mes},C_{CO})$ around 0.08 and the energy E_{int} is the highest calculated (3.8 kcal.mol^{-1}). All these results are corroborated by the NLMO analysis, associated with the $\pi_{C=C}$ orbital of the aryl group since the small participation of the $\pi^*_{C=O}$ orbital slightly increases from $\mathbf{3_{Me}}$ to **8** (Table S13 : %C : from 0.5 to 1.4; %O : from 0.2 to 0.5).

Analysis of the bonding situation of the Fe-$C_{carbene}$ bond in 3_{Me}, 4 and 6^{Me}(OTf)

An analysis of the bonding situation of the Fe-$C_{carbene}$ bond reveals the presence of a strong donor-acceptor interaction between the carbene unit and the $FeCp(CO)_2$ fragment. The sum of the stabilizing interaction [$\Delta E(2)$] at the second order perturbation theory between the carbene lone pair (hybridization : ~40%s, ~60%p) and an orbital involving the mixing of the s and d_{z2} orbitals of iron is strong around 140-150 kcal.mol^{-1}, which is in the range of a covalent bond (Table S11). The corresponding NLMO (Plot see Figure S2) presents a

[13] Valyaev, D. A.; Brousses, R.; Lugan, N.; Fernández, I.; Sierra, M. A. *Chem. Eur. J.* **2011**, *17*, 6602.

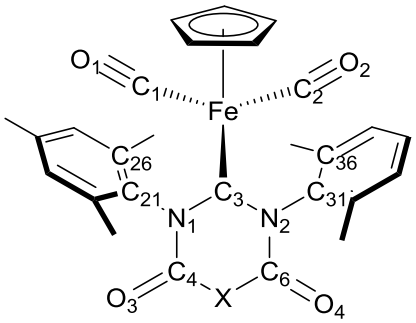
major contribution from the carbene center (~79-80 %) and a "delocalization tail" from the metal center (15-17%).

Table S11. NBO analysis of the C→Fe interaction in the three for the complexes $\mathbf{3_{Me}}$, **4** and $\mathbf{6^{Me}(OTf)}$.

NBO analysis		
	$\Delta E(2)^a$	NLMO[b]
	$n_C^{\sigma} \rightarrow$ Fe	n_C^{σ}
3_{Me}	$n_{C3}^{\sigma} \rightarrow s_{(Fe)}$: 74.45	C_3 : 79.2 %
	$n_{C3}^{\sigma} \rightarrow d_{(Fe)}$: 70.97	Fe : 17.0 %
4	$n_{C3}^{\sigma} \rightarrow s_{(Fe)}$: 74.78	C_3 : 79.2 %
	$n_{C3}^{\sigma} \rightarrow d_{(Fe)}$: 71.32	Fe : 17.2 %
$[6^{Me}](OTf)$	$n_{C3}^{\sigma} \rightarrow s_{(Fe)}$: 77.25	C_3 : 81.1 %
	$n_{C3}^{\sigma} \rightarrow d_{(Fe)}$: 45.66	Fe : 15.2 %

[a] Stabilizing energy in kcal/mol;
[b] Natural Localized Molecular Orbital associated with the n_c^{σ} orbital.

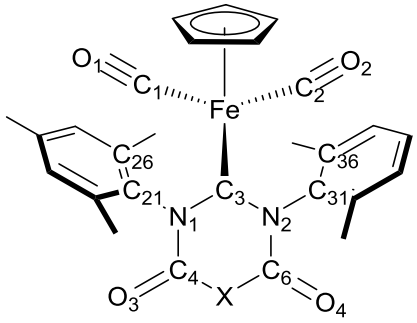
Table S12. Topological analysis of the C(aryl)…C(≡O) bond critical points[a]



complex	contact	R_b [b]	$\rho(\mathbf{r}_b)$ [c]	$\nabla^2\rho(\mathbf{r}_b)$ [d]	$G\rho(\mathbf{r}_b)$ [e]	$V\rho(\mathbf{r}_b)$ [e]	δ(C…C) [f]	E_{int} [g]
$\mathbf{3_{Me}}$ [a]	C1…C21	2.7197(4)	0.13	1.15	0.08	-0.08	*n/a*	3.9
		2.811	*0.11*	*1.16*			*0.05*	*2.7*
	C2…C36 [h]	3.0518(5)			bcp not observed experimentally			
		2.908	*0.08*	*0.95*	*0.05*	*-0.04*	*0.02*	*1.9*
4	C1…C21	*2.816*	*0.11*	*1.15*	*0.07*	*-0.06*	*0.05*	2.7
	C2…C36 [h]	*3.119*	*0.07*	*0.93*	*0.04*	*-0.04*	*0.02*	*2.0*
[6^{Me}]OTf	C1…C21	*2.856*	*0.10*	*1.07*	*0.06*	*-0.05*	*0.05*	2.4
	C2…C31 [h]	*3.070*	*0.07*	*0.84*	*0.05*	*-0.04*	*0.03*	*1.8*
7	C1…C21	*2.755*	*0.12*	*1.25*	*0.08*	*-0.07*	*0.06*	3.1
	C2…C36 [h]	*2.935*	*0.07*	*0.91*	*0.05*	*-0.04*	*0.02*	*1.9*
8	C2…C31	*2.663*	*0.014*	*1.40*	*0.09*	*-0.08*	*0.08*	*3.8*

[a] For $\mathbf{3_{Me}}$: top line experimental values, second line (italic) theoretical values from isolated molecule DFT calculation; for the other complexes: theoretical values from isolated molecule DFT calculation; [b] R_b is the interatomic distance (Å); [c] $\rho(\mathbf{r}_b)$ is the ED (e.Å^{-3}); [d] $\nabla^2\rho(\mathbf{r}_b)$ is the Laplacian of the ED (e.Å^{-5}); [e] $G\rho(\mathbf{r}_b)$, and $V\rho(\mathbf{r}_b)$ are the kinetic and potential electron energy densities, respectively, estimated using the approximation of Abramov[ref] (hartree.Å^{-3}); [f] δ(C…C) are the delocalization indices; [g] E_{int} is the interaction energy estimated using Espinoza correlation scheme (kcal.mol^{-1}). [h] for the weak interaction C(aryl)…C(≡O) either C_{ipso} (labeled C_{21}) or C_{ortho} (labeled C_{36}) carbon atom of the aryl group is involved.

Table S13. NBO analysis of the C(aryl)…C(≡O) non-covalent weak interactions for compounds **3_{Me}**, **4**, **6_{Me}(OTf)**, **7** and **8** at the M06-2X/6-31G** level of theory.

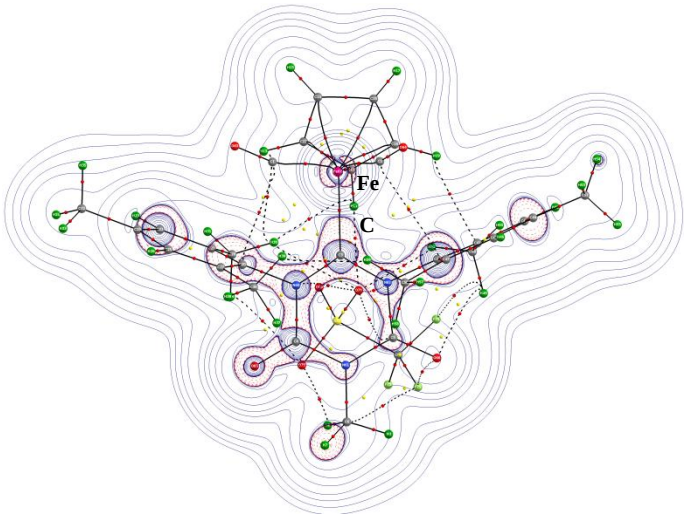


	NBO Analysis			
	$\pi_{C=C} \rightarrow \pi^*_{C=O}$ interaction involved in the major $C_{Mes}…C_{CO}$ contact		**$\pi_{C=C} \rightarrow \pi^*_{C=O}$ interaction involved in the minor $C_{Mes}…C_{CO}$ contact**	
	$\Delta E(2)^a$	**NLMO[b]**	**$\Delta E(2)^a$**	**NLMO[b]**
	$\pi_{C=C} \rightarrow \pi^*_{C=O}$	**$\pi_{C=C}$**	**$\pi_{C=C} \rightarrow \pi^*_{C=O}$**	**$\pi_{C=C}$**
3_{Me}	4.4	C_{21} : 43.8 % C_{26} : 38.8 % C_1 : 0.6% O_1 : 0.2 %	3.4	C_{31} : 43.5 % C_{36} : 39.1 % C_2 : 0.3% O_2 : 0.1 %
4	4.9	C_{21}: 43.8 % C_{26} : 38.9 % C_1: 0.6% O_1: 0.2 %	2.6	C_{31}: 43.9 % C_{36} : 39.0 % C_2: 0.3% O_2: 0.1 %
6^{Me}(OTf)	3.7	C_{21} : 45.6 % C_{26} : 38.1 % C_1: 0.5% O_1 : 0.2 %	3.4	C_{31} : 45.2 % C_{36} : 38.8 % C_1: 0.3% O_1 : 0.1 %
7	5.2	C_{21} : 48.8 % C_{26} : 33.7 % C_1 : 1.0% O_1 : 0.4 %	2.8	C_{31} : 42.8 % C_{36} : 38.0 % C_2 : 0.3% O_2 : 0.1 %
8	6.9	C_{21} : 48.8 % C_{26} : 32.4 % C_1 : 1.4% O_1 : 0.5 %	/	/

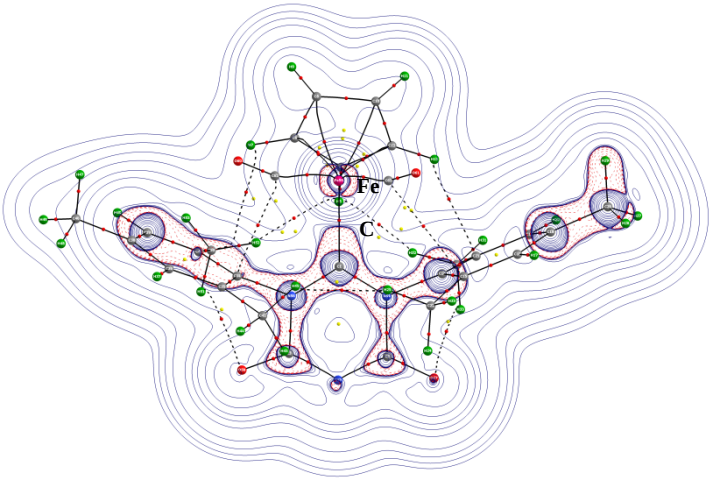
[a] Stabilizing energy in $kcal.mol^{-1}$; [b] Natural Localized Molecular Orbital associated with the $\pi_{C=C}^{aryl}$ orbital involved in the weak interaction $\pi_{C=C}^{aryl} \rightarrow \pi^*_{C\equiv O}$.

Figure S3. Contour plot of the Laplacien $\nabla^2\rho$(BCP) with charge accumulation ($\nabla^2\ \rho(r)<0$) printed in blue and charge deplection ($\nabla^2\ \rho(r)>0$) printed in red for the complexes **3_{Me}**, **4** and **6^{Me}(OTf)**.

3_{Me}



4



6^{Me}(OTf)

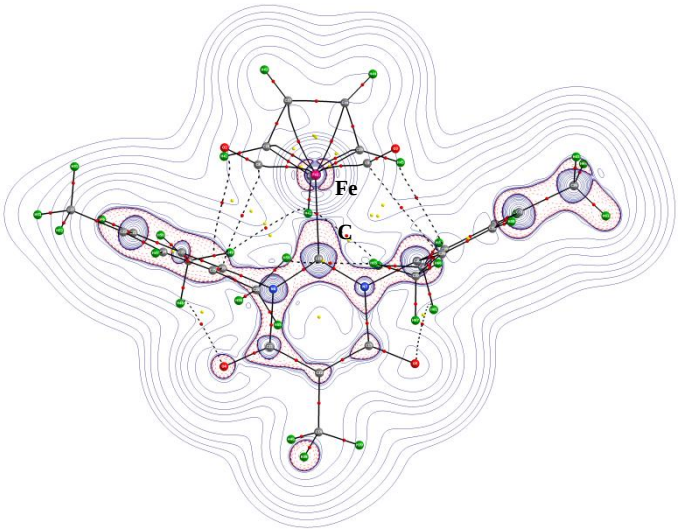
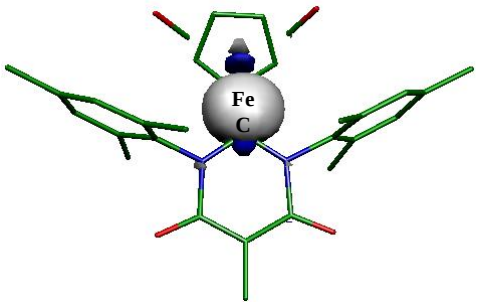


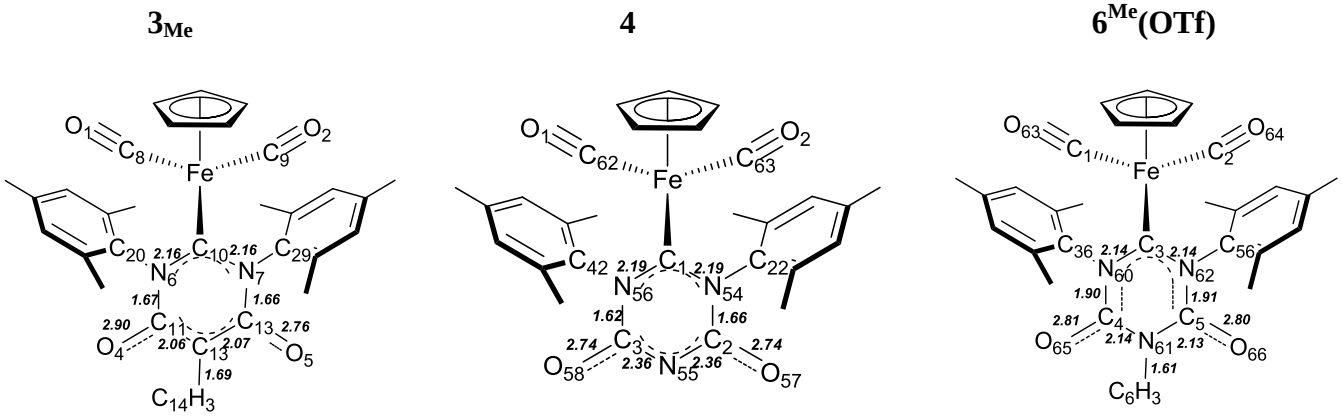
Figure S4. Molekel plot (cutoff : 0.05) for the NLMO associated with the C→Fe interaction in the complex **3_{Me}**.



Electronic delocalization in complexes 3_{Me}, 4 and 6^{Me}(OTf).

In agreement with the experimental description of the geometrical structure given in the main text, the calculated geometrical parameters and the AIM analysis carried out for the three complexes show that compounds **3_{Me}** and **4** can be described as the juxtaposition of two π-systems, namely, NCN NCN (4π e^- system) and O=CXC=O (6π e^- system) units whereas in **6^{Me}(OTf)** an electronic delocalization occurs between these two units. Indeed, a slight decrease of the central C-N bond lengths (1.46 to 1.48 Å *versus* 1.43Å) and a slight increase of the density $\rho(r_b)$ from 1.6-1.7 Å.bohr^{-3} in **3_{Me}** and **4** to 1.9 Å.bohr^{-3} in **6_{Me}(OTf**) are theoretically observed (Figure S3).

Figure S5. Electronic delocalization and density$\rho(\mathbf{r}_b)$ in e$^-$Å^{-3} for the carbene skeleton in the complexes **3_{Me}**, **4** and **6^{Me}(OTf)**.



Z-matrices

3_{Me}

Fe	-0.00507100	-1.55535200	-0.28001400
O	2.46071500	-2.49974100	1.14385600
O	-1.66354500	-2.43539800	2.05669900
O	2.33530800	3.15164600	-0.48730500
O	-2.34992800	3.18835100	0.04478900
N	1.12934800	1.22470800	-0.11219300
N	-1.13519900	1.23502100	0.01662200
C	1.56322900	-1.98431300	0.68245700
C	-1.08214100	-1.98685300	1.19400100
C	-0.00503000	0.50247700	-0.01194700
C	1.21400800	2.68484100	-0.31427400
C	-0.00713300	3.37050400	-0.27439700
C	-1.22421400	2.71036500	-0.05815000
C	0.01291700	4.86047300	-0.44644700
C	-0.20378400	-1.24211600	-2.41857000
C	0.92636400	-2.05054900	-2.16400100
C	0.46336700	-3.25228600	-1.54416800
C	-0.93638900	-3.16364000	-1.41475100

C	-1.35864800	-1.91021500	-1.93964100
C	2.42075800	0.63125800	0.11356200
C	3.26690600	0.34154700	-0.96252200
C	4.50798500	-0.22814400	-0.68378800
C	4.94703800	-0.43170100	0.62585000
C	4.11751600	-0.03414300	1.67329900
C	2.85126100	0.49666700	1.43832800
C	2.89509700	0.73814900	-2.36374900
C	6.28574900	-1.06486400	0.90205400
C	1.94827100	0.86888700	2.58428600
C	-2.42898400	0.62194400	0.18342100
C	-3.28332900	0.50338400	-0.91553400
C	-4.52210700	-0.10898000	-0.72578400
C	-4.94156400	-0.54093100	0.53245700
C	-4.10488000	-0.30994600	1.62368700
C	-2.85919000	0.29814800	1.47293200
C	-2.91816000	1.10071800	-2.24581700
C	-6.29466000	-1.17690100	0.72397200
C	-2.02223200	0.66279700	2.66973900
H	0.51022700	5.35551400	0.39466000
H	-1.00922200	5.23441900	-0.51758000
H	0.56750000	5.13779000	-1.34803300
H	-0.18446800	-0.26011800	-2.87060600
H	1.95309900	-1.81309500	-2.40539800
H	1.08064700	-4.08327700	-1.23020400
H	-1.58059100	-3.91049100	-0.96938300
H	-2.37615500	-1.55374000	-1.98438000
H	5.16835500	-0.47725700	-1.51169500
H	4.45922100	-0.15086800	2.69926000
H	3.10379200	1.80586500	-2.48138200
H	1.82895600	0.60248900	-2.55662000
H	3.46850500	0.17578500	-3.10502000
H	6.18735100	-2.15107300	1.00237000
H	6.71609300	-0.68564100	1.83191600
H	6.99216600	-0.86943900	0.09204900
H	1.20693500	0.07941800	2.77002400
H	1.39560100	1.79058600	2.38186700
H	2.52429400	0.99842000	3.50236900
H	-5.18674900	-0.22565800	-1.57940900
H	-4.43579200	-0.59226500	2.62081700
H	-3.45775100	0.61912200	-3.06499800
H	-1.84520200	1.04401900	-2.43996300
H	-3.17497500	2.16468800	-2.22453700
H	-7.01932800	-0.44112700	1.08717500
H	-6.25170400	-1.98509300	1.45868500
H	-6.67804800	-1.58527100	-0.21374800
H	-0.98878800	0.31618900	2.58084200
H	-2.44881600	0.24929400	3.58577000
H	-1.98087500	1.75354100	2.76117800

4

C	-0.00582600	0.62286800	-0.07797400
C	-1.16789500	2.84061400	-0.25862400
C	1.14140200	2.80686300	-0.55241100
C	-0.21190900	-1.30841600	-2.32201700
H	-0.20234700	-0.37044200	-2.85921500
C	0.92480400	-2.08670100	-2.01002200
H	1.94806900	-1.86417500	-2.27910000
C	0.47299500	-3.23505500	-1.28831200
H	1.09750600	-4.03383800	-0.91137100
C	-0.92630100	-3.14236200	-1.15462900
H	-1.56203300	-3.85274200	-0.64243500
C	-1.35950300	-1.93798800	-1.77713600
H	-2.37877300	-1.58814000	-1.84133900
C	-2.43427100	0.77575800	0.09310300
C	-2.86968700	0.55912100	1.40247200
C	-4.12654000	-0.01434700	1.59764500
H	-4.46486800	-0.20677400	2.61322400
C	-4.96453600	-0.31763800	0.52613100
C	-4.53976200	0.01617500	-0.76141700
H	-5.20944100	-0.14721700	-1.60332000
C	-3.29135000	0.58929200	-0.99591400
C	-2.03328600	1.01469800	2.56824300
H	-2.46737900	0.68491300	3.51418300
H	-1.98229900	2.10890600	2.56570700
H	-1.00301600	0.65052400	2.51532800
C	-6.30486900	-0.96919800	0.74915300
H	-7.04625300	-0.59849500	0.03715600
H	-6.67457600	-0.77772000	1.75898300
H	-6.23851100	-2.05475600	0.62043700
C	-2.91549700	1.08562200	-2.36437200
H	-3.48042700	0.57348400	-3.14670100
H	-1.84790700	0.97259800	-2.56292400
H	-3.13146600	2.15786900	-2.41705200
C	2.41889100	0.80233200	0.03979900
C	2.86813600	0.77945500	1.36563900
C	4.14035600	0.27528100	1.62617500
H	4.49642600	0.24570600	2.65335100
C	4.95744300	-0.20442600	0.60389100
C	4.49999900	-0.11099000	-0.71220200
H	5.15072900	-0.42557100	-1.52538500
C	3.25194500	0.42630900	-1.02066000
C	1.98091100	1.25025700	2.48766400
H	1.46890900	2.18294700	2.23468200
H	2.56253600	1.40796400	3.39763700
H	1.20527800	0.50710700	2.71729800
C	6.30301200	-0.80808200	0.91023000
H	6.22137900	-1.89325500	1.03394300
H	6.71691700	-0.40043900	1.83530600
H	7.01512200	-0.62004300	0.10331500
C	2.86088800	0.69756400	-2.44651800
H	3.08124500	1.74559800	-2.67052100
H	1.79032000	0.56027400	-2.61022500
H	3.41420900	0.06008800	-3.14085600
N	-1.13356500	1.35350700	-0.11638100
N	-0.01957400	3.45578300	-0.53031700
N	1.11634500	1.35091200	-0.21361500
O	-2.26765400	3.34191900	-0.13720000
O	2.23976100	3.25593500	-0.80990200
Fe	0.00553100	-1.44087400	-0.16823100
O	2.49655900	-2.24235000	1.30027300
O	-1.65702900	-2.10871300	2.23638100
C	1.58775100	-1.77376500	0.81234500
C	-1.06708400	-1.74280800	1.34132600

6^{Me}(OTf).

C	-2.95699300	1.66027200	-0.64749000
C	-0.81039800	3.34307300	-0.36586200
C	-0.35723900	0.47141500	0.42894300
C	-0.46846000	-1.57234300	1.81447400
C	1.60353300	-0.32457600	1.70741100
C	1.46243300	-2.41015000	3.00317000
H	0.91593300	-2.47814700	3.94486500
H	2.49618100	-2.12025500	3.17169100
H	1.40370700	-3.35603800	2.46209800
C	-0.09938700	0.34320400	-2.54281400
H	0.45456700	-0.53409800	-2.22245200
C	-1.48168700	0.38617100	-2.84339600
H	-2.15990900	-0.45578900	-2.84680500
C	-1.81553200	1.73738900	-3.17597200
H	-2.79391900	2.10241800	-3.46027500
C	-0.64678200	2.51495100	-3.05764300
H	-0.57729800	3.58214400	-3.22594600
C	0.41763700	1.66088300	-2.64467700
H	1.44030500	1.96406700	-2.47887900
C	-2.43796900	-0.80774400	0.69362600
C	-2.86382100	-1.70060300	-0.29591600
C	-4.24046500	-1.87625100	-0.45176000
H	-4.59289100	-2.55387000	-1.22631600
C	-5.16738200	-1.25584500	0.38818000
C	-4.69172000	-0.44700900	1.42090000
H	-5.39757900	0.01584600	2.10698700
C	-3.32952100	-0.20847500	1.59045900
C	-1.88574300	-2.51423400	-1.09244800
H	-1.47860800	-3.31691600	-0.46464300
H	-1.02971600	-1.92633500	-1.42516200
H	-2.36527900	-2.97133600	-1.96092400
C	-6.64681100	-1.45904700	0.18825200
H	-7.18911200	-1.36309700	1.13200800
H	-6.85637200	-2.44592100	-0.23136000
H	-7.04728100	-0.71081100	-0.50419100
C	-2.84869800	0.70589000	2.68499300
H	-1.96257400	0.31159600	3.19152300
H	-3.63193800	0.85416600	3.43062900
H	-2.58598500	1.69272200	2.28182800
C	1.65305800	1.85536200	0.70296600
C	2.70577800	1.92693100	-0.21729600
C	3.37305200	3.14752100	-0.33465300
H	4.17982300	3.22884100	-1.06053700
C	3.06950300	4.24561600	0.47313700
C	2.07776400	4.09922700	1.44219000
H	1.84886200	4.92923700	2.10659100
C	1.36894100	2.90593100	1.58201000
C	3.17845400	0.72880100	-0.99024500
H	3.83486500	0.13157800	-0.34734500
H	3.74575800	1.03304200	-1.87363200
H	2.36719800	0.06278700	-1.28379600
C	3.84405200	5.53154800	0.33919200
H	3.32426400	6.36105200	0.82387200
H	4.00105200	5.78950700	-0.71158900
H	4.83013900	5.43455200	0.80512800
C	0.33140500	2.75469100	2.66318500
H	0.30590700	3.64286500	3.29717100
H	0.54656600	1.88663700	3.29627600
H	-0.67110000	2.60671100	2.24823100
N	-1.01792000	-0.60136300	0.91621300
N	0.84192800	-1.37037700	2.16902800
N	0.90662200	0.62210300	0.89121700
O	-4.08207500	1.78098500	-0.60017100
O	-0.72299400	4.43340300	-0.07300500
O	-1.14636400	-2.46298400	2.25775300
O	2.75755400	-0.14555700	2.00700100
Fe	-1.11909600	1.63961900	-1.12645000
C	3.26862200	-3.33884400	-0.59954200
O	1.15778600	-3.68156200	-2.14557700
O	0.88887800	-3.91257900	0.32645700
O	1.27391700	-1.69825700	-0.67468000
S	1.44148200	-3.16761600	-0.80947500
F	3.65836700	-4.60780500	-0.70920300
F	3.92294900	-2.61694900	-1.51623800
F	3.63151000	-2.88947400	0.61061700

7

Fe	-0.08574600	-1.42991500	-0.41103900
O	2.43365600	-2.40512400	0.90718400
O	-1.67848000	-2.36172900	1.94770300
O	2.27683100	3.26949600	-0.42909800
O	-2.40721700	3.30884300	0.12273800
N	1.06376800	1.33043100	-0.13707300
N	-1.19832500	1.35965100	-0.00381900
C	1.52252300	-1.87415200	0.49244400
C	-1.11226200	-1.90753800	1.07768000
C	-0.07412700	0.61522500	-0.06842400
C	1.15620000	2.80049100	-0.26969000
C	-0.05910900	3.49619300	-0.18275600
C	-1.28001900	2.83697900	-0.00590300
C	-0.02372500	4.99325200	-0.26853700
C	-0.30860300	-1.05825500	-2.53908100
C	0.81279600	-1.88736000	-2.32081500
C	0.34228300	-3.09856000	-1.72415900
C	-1.05461700	-2.99619500	-1.57621400
C	-1.46654900	-1.72433700	-2.06192600
C	2.35247000	0.71269400	0.03310400
C	3.18103300	0.47229600	-1.06842000
C	4.43131700	-0.09621000	-0.85884000
C	4.91715700	-0.35461400	0.44002100
C	4.10368300	0.01426300	1.52960200
C	2.83475400	0.54413700	1.33590900
C	2.77376100	0.92350400	-2.44359100
C	1.96507400	0.87858900	2.51935800
C	-2.49491800	0.75781800	0.15137900
C	-3.35660600	0.69167400	-0.95126800
C	-4.59768700	0.08317200	-0.78407800
C	-4.95528700	-0.38317000	0.47220200
C	-4.15130400	-0.22095700	1.58789500
C	-2.90630200	0.38760500	1.43679000
C	-2.99064700	1.33557200	-2.25819500
C	-2.05394200	0.71192900	2.63343300
H	0.68118600	5.40819800	0.45826100
H	-1.01972200	5.39415700	-0.07680200
H	0.30862500	5.32796700	-1.25700500
H	-0.28175900	-0.06738200	-2.97059300

H	1.84001800	-1.65521000	-2.56668500
H	0.95226100	-3.94504400	-1.43894800
H	-1.70352000	-3.74677300	-1.14401100
H	-2.48111900	-1.35942100	-2.09673800
H	5.05724500	-0.28461700	-1.72313200
H	4.45464900	-0.11614600	2.54593500
H	2.98070800	1.99502900	-2.52451200
H	1.70269700	0.79531200	-2.61184200
H	3.32537900	0.39182400	-3.22288700
H	1.20994700	0.09669200	2.68100100
H	1.43005400	1.82115400	2.37227200
H	2.56105700	0.95117600	3.43079400
H	-5.29451500	-0.01421000	-1.60837300
H	-4.50492400	-0.55286700	2.55671400
H	-3.56642600	0.91561000	-3.08569400
H	-1.92505200	1.23954100	-2.47417500
H	-3.20153800	2.40688800	-2.17929800
H	-1.02056700	0.37599100	2.51401500
H	-2.46550200	0.26283600	3.53894600
H	-2.02080400	1.79923900	2.76078500
N	-6.25974800	-1.04647000	0.63186700
O	-6.56359300	-1.43254100	1.74554300
O	-6.95080200	-1.17455700	-0.36213300
N	6.15342500	-0.93269800	0.63469400
C	6.70178500	-0.98846200	1.97410000
H	6.05911200	-1.58372300	2.63116200
H	7.67765200	-1.47256500	1.93821900
H	6.82337600	0.00790900	2.42172000
C	7.05161900	-1.07435000	-0.49293700
H	7.29225700	-0.11020900	-0.96255800
H	7.97930200	-1.53403500	-0.15242000
H	6.61781900	-1.72843400	-1.25681900

8

Fe	1.11538200	-1.71552100	0.04690700
O	1.67056600	-2.05837100	2.96161000
O	-1.83741300	-2.16198500	0.38075500
O	4.20548200	2.51291000	0.26305700
O	-0.36324000	3.30303400	-0.58684600
N	2.63937600	0.83237000	0.38253300
N	0.44146500	1.21196200	-0.05357600
C	1.44602600	-1.93407000	1.85681500
C	-0.76746600	-1.79457900	0.30033600
C	1.40926300	0.31713900	0.22385500
C	3.01391000	2.23754200	0.14394900
C	1.96378300	3.09825800	-0.20213500
C	0.63989300	2.65345100	-0.30663200
C	2.26767300	4.54416300	-0.45947000
C	2.45239600	-1.69694800	-1.65518900
C	2.89424000	-2.66429900	-0.72559200
C	1.86473300	-3.64751100	-0.59673500
C	0.80371200	-3.27157900	-1.44160000
C	1.14905500	-2.04965300	-2.08719500
C	-0.94562100	0.84211400	-0.03116200
C	-1.65656100	0.68663800	-1.22600100
C	-3.00995800	0.37909700	-1.16771400
C	-3.69291200	0.28428500	0.06194700
C	-2.96690900	0.55161000	1.24129900
C	-1.60995000	0.83979300	1.20220600
C	-0.98684100	0.94288300	-2.54770400
C	-0.85272700	1.15836300	2.46459100
H	3.13188600	4.85263600	0.13266700
H	1.40059600	5.15629500	-0.20246300
H	2.50548700	4.73369500	-1.51283400
H	2.98929600	-0.80362500	-1.94658200
H	3.85176900	-2.68020900	-0.22570000
H	1.89736600	-4.52741800	0.03087300
H	-0.13303800	-3.80131700	-1.55455900
H	0.54232500	-1.51262800	-2.80124100
H	-3.54456900	0.25534100	-2.10186100
H	-3.46368600	0.54674700	2.20380400
H	-1.48226900	0.40601800	-3.36061000
H	0.07151100	0.67143000	-2.52437300
H	-1.02879800	2.01761300	-2.74973600
H	-0.06294600	0.42392600	2.66202100
H	-1.52185300	1.17650900	3.32650400
H	-0.36444200	2.13401700	2.37873300
C	3.79291500	0.02882200	0.78012600
H	4.37918000	-0.28323300	-0.08957200
H	4.43365500	0.66307800	1.38816200
H	3.48223300	-0.84229700	1.34764600
N	-5.03215400	-0.04348900	0.10989000
C	-5.74537500	0.09670800	1.36271900
H	-5.72093200	1.12556500	1.74906100
H	-6.78582700	-0.19158500	1.21316500
H	-5.32343500	-0.56592000	2.12559400
C	-5.79387300	-0.07514300	-1.12166900
H	-5.39405700	-0.83038100	-1.80622700
H	-6.82473000	-0.34708700	-0.89477200
H	-5.79504800	0.89325400	-1.64208500

$1_{Me}^{-}.K^{+}$

C	-0.21663100	-0.56548300	-0.10113000
C	-1.24653600	1.64812300	-0.63967400
C	1.20771800	1.41133000	-0.61850100
C	0.15572000	3.60921800	-1.30179800
H	-0.57670000	3.76372700	-2.09824900
H	1.15498200	3.80532300	-1.70351000
H	-0.09362600	4.37933800	-0.55015400
C	-2.57529100	-0.32945100	-0.07670400
C	-3.28964200	-0.02797400	1.08381600
C	-4.53215600	-0.63091000	1.27002300
H	-5.09869300	-0.40287200	2.17047700
C	-5.06373400	-1.51392700	0.33127400
C	-4.32466300	-1.78368200	-0.81950300
H	-4.72876400	-2.46459500	-1.56567900
C	-3.07875800	-1.20011000	-1.04478100
C	-2.72762500	0.93303800	2.09592100
H	-2.70499900	1.94230100	1.67240300
H	-1.70234700	0.65611900	2.36586500
H	-3.33512500	0.94324800	3.00350800
C	-6.39390300	-2.18398100	0.56572600
H	-6.92069700	-2.35566700	-0.37648900
H	-7.03524800	-1.57701900	1.20947100
H	-6.26291000	-3.15704700	1.05107900
C	-2.28806800	-1.49859100	-2.28973400
H	-2.01828000	-0.57404600	-2.81026400
H	-2.86417800	-2.12607100	-2.97293300

H	-1.35636600	-2.01222400	-2.03349900
C	2.15233900	-0.76834400	-0.05807700
C	2.45850900	-1.15754200	1.24830900
C	3.57872700	-1.96068900	1.45557600
H	3.82005700	-2.27907300	2.46783800
C	4.38960400	-2.37029600	0.39769500
C	4.05193500	-1.96313800	-0.89208000
H	4.66775800	-2.28197900	-1.73041300
C	2.93978200	-1.16092900	-1.14249200
C	1.57887200	-0.74558900	2.39938700
H	1.41225300	0.33960900	2.40783800
H	2.02490800	-1.03236700	3.35438400
H	0.59169400	-1.20790600	2.30639500
C	5.61252500	-3.21600200	0.64723400
H	5.88037000	-3.79455800	-0.24008600
H	5.44994500	-3.91410300	1.47247200
H	6.47497700	-2.59336700	0.90799200
C	2.58642000	-0.72644800	-2.53805600
H	3.18756100	-1.26154300	-3.27608700
H	2.76206600	0.34787200	-2.65027100
H	1.52862500	-0.91300500	-2.74755800
N	-1.27468400	0.26278800	-0.27490300
N	0.98549500	0.04641800	-0.28588200
O	-2.29445700	2.26865900	-0.78175500
C	0.06308800	2.19658000	-0.79096800
O	2.39730500	1.83431600	-0.65935000
K	1.93236300	3.51633900	1.09110600

$2^{\cdot}.K^{+}$

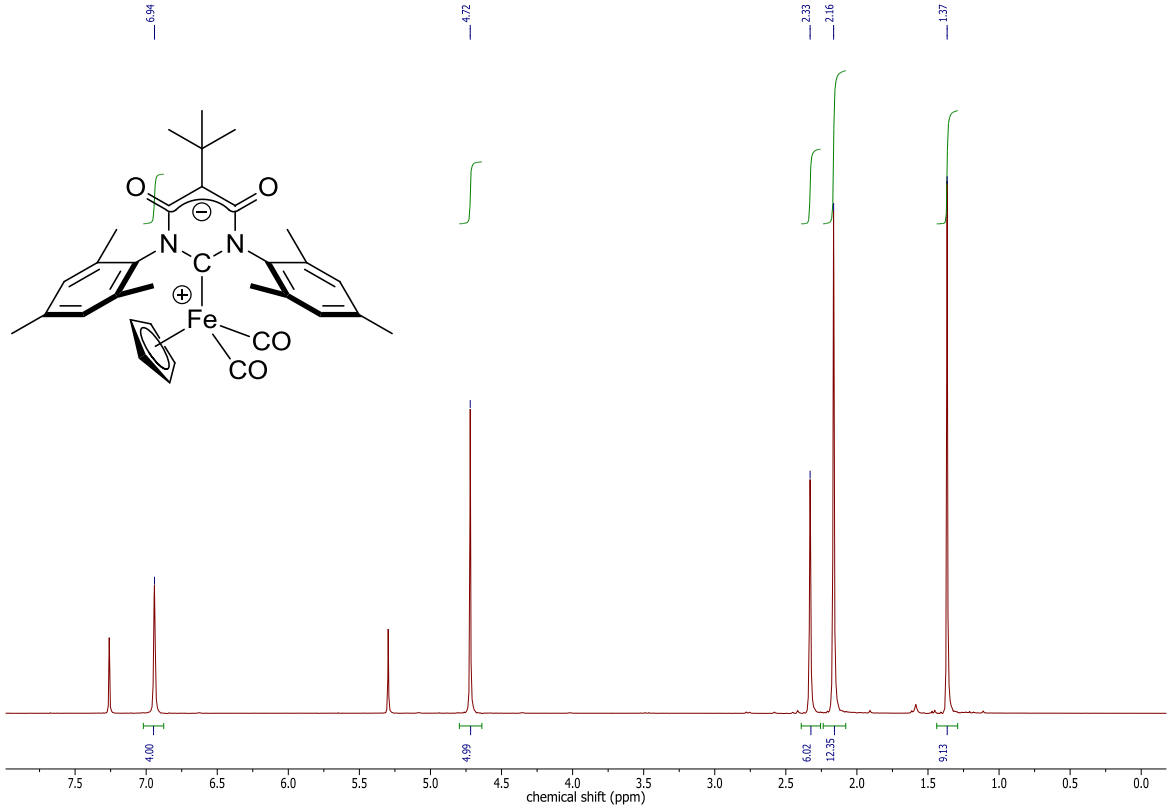
C	0.16771000	-0.53324000	0.04891200
C	1.15638600	1.74460100	-0.13626900
C	-1.18702900	1.50833600	-0.21670500
C	2.53405600	-0.27059900	0.05933700
C	3.10206300	-0.80596000	-1.09509500
C	4.36457800	-1.39152100	-0.99700500
H	4.81877700	-1.81563800	-1.88982700
C	5.05450100	-1.44102400	0.21195900
C	4.45917200	-0.87817000	1.34183200
H	4.99034000	-0.89871900	2.29127600
C	3.20037700	-0.28627400	1.28586400
C	2.36619600	-0.74281200	-2.40588200
H	2.96841800	-1.16957800	-3.21058400
H	2.12591500	0.29350400	-2.66589800
H	1.42131400	-1.29135200	-2.34723600
C	6.40584400	-2.10242500	0.30956300
H	7.08972300	-1.51362800	0.92700000
H	6.85848900	-2.22683300	-0.67691600
H	6.32380800	-3.09450900	0.76592000
C	2.56392800	0.33555500	2.49815800
H	3.18993200	0.19720500	3.38203900
H	1.58265000	-0.10891800	2.69287100
H	2.42094900	1.40872900	2.33514600
C	-2.22202700	-0.69207500	0.05042400
C	-2.53279000	-1.55036400	-1.00518800
C	-3.67598700	-2.34255100	-0.89630200
H	-3.92453600	-3.01824900	-1.71175900
C	-4.50024700	-2.29154300	0.22497500
C	-4.15373800	-1.42613200	1.26266300
H	-4.77806900	-1.38385700	2.15290900
C	-3.02140100	-0.61841700	1.19571800
C	-1.64212400	-1.65086000	-2.21365500
H	-1.36171300	-0.66133600	-2.58781200
H	-2.14024700	-2.19844700	-3.01657900
H	-0.71624400	-2.17129500	-1.95065800
C	-5.74689100	-3.13459400	0.31345500
H	-5.70061300	-3.98369800	-0.37232600
H	-6.63561700	-2.54839000	0.05704000
H	-5.89079200	-3.52174800	1.32573300
C	-2.65962700	0.30502100	2.32686900
H	-2.83121000	1.34475900	2.03143600
H	-1.60241100	0.20488100	2.59147000
H	-3.26021500	0.08775900	3.21256500
N	1.21761600	0.31561600	-0.01672300
N	-0.08771300	2.27609100	-0.25346800
N	-1.03129000	0.11689700	-0.03004100
O	2.18406600	2.39713800	-0.12799600
O	-2.33078900	1.98947800	-0.33399200
K	-1.50857100	4.40034100	-0.55368600

2_{Me}

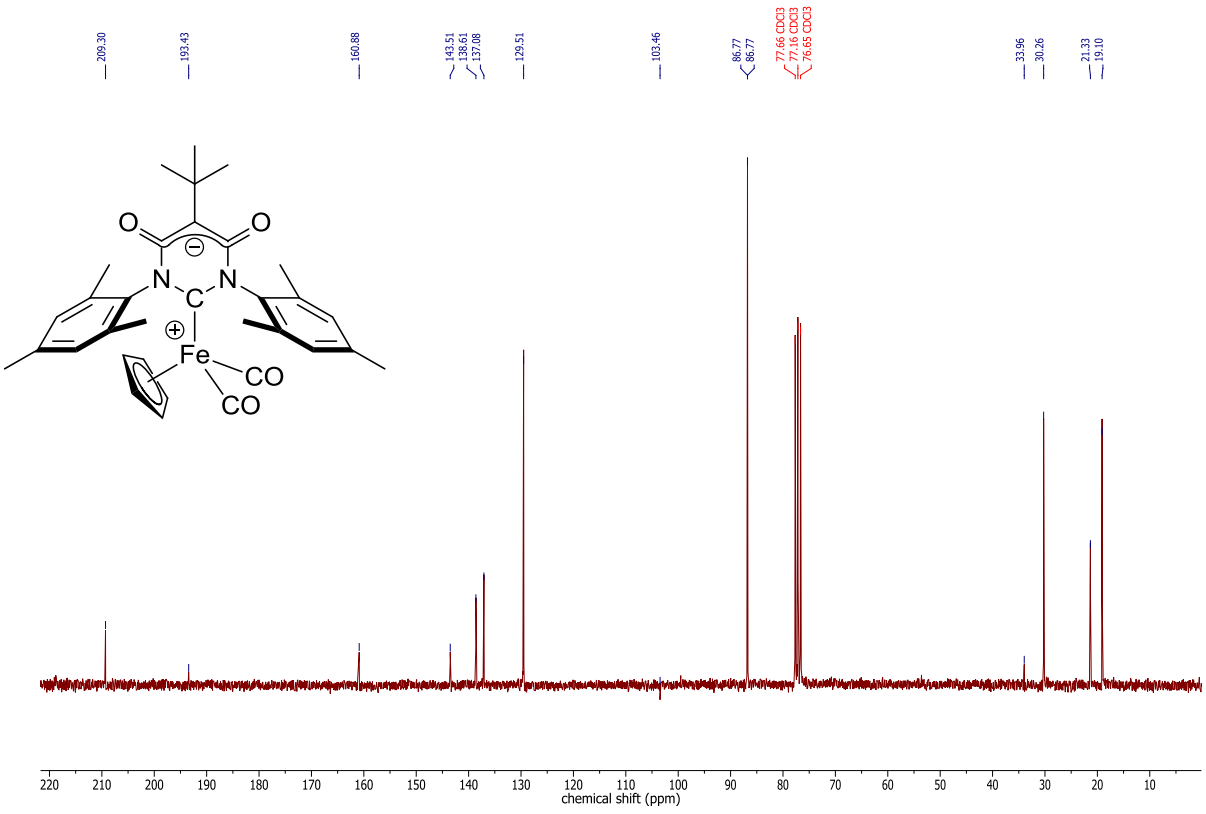
C	0.00258400	-0.25190200	-0.00199900
C	-1.22298200	1.89805800	-0.04593400
C	1.23154000	1.90429400	0.04013400
C	-0.03833100	4.00819300	-0.00309100
H	-0.53865200	4.35786000	-0.90702000
H	0.98709600	4.36522000	0.03475600
H	-0.60194700	4.35555600	0.86376000
C	-2.38741200	-0.22786500	-0.05869500
C	-3.16924600	-0.27770600	1.09547700
C	-4.36515300	-0.99165600	1.04021600
H	-4.98891500	-1.03942100	1.92979900
C	-4.77746500	-1.64170500	-0.12172800
C	-3.96478300	-1.56518000	-1.25271800
H	-4.27488600	-2.06434200	-2.16796000
C	-2.76248900	-0.86119700	-1.24451800
C	-2.73705000	0.42524200	2.35372400
H	-2.82597200	1.50996000	2.23589600
H	-1.69335100	0.19793200	2.59374400
H	-3.35671100	0.12066700	3.19900400
C	-6.05842800	-2.43551400	-0.14978500
H	-6.53669800	-2.37839400	-1.13072800
H	-6.76663500	-2.07085900	0.59777800
H	-5.86574500	-3.49224700	0.06242000
C	-1.88756600	-0.79084400	-2.46719600
H	-1.68063900	0.24793400	-2.74565600
H	-2.36898300	-1.28190700	-3.31469100
H	-0.92614400	-1.27814900	-2.27662700
C	2.39014800	-0.22356300	0.05669400
C	2.76495400	-0.85285300	1.24569600
C	3.96329400	-1.56185100	1.25496400
H	4.27066100	-2.06265200	2.17041500
C	4.77592600	-1.64427200	0.12327500
C	4.36177400	-1.00332900	-1.04196500
H	4.98036000	-1.06315500	-1.93431700
C	3.16785000	-0.28440900	-1.09847100
C	1.88927100	-0.77703200	2.46745300
H	1.68455600	0.26314300	2.74235000
H	2.36911200	-1.26630200	3.31687800

H	0.92687400	-1.26287400	2.27785400
C	6.07893700	-2.40004100	0.17479200
H	6.48819800	-2.55380300	-0.82598700
H	5.94857300	-3.37883500	0.64438600
H	6.82387200	-1.85183800	0.76038800
C	2.73203000	0.40724400	-2.36161300
H	3.35166300	0.09823900	-3.20531900
H	2.81786500	1.49312500	-2.25218300
H	1.68867300	0.17520600	-2.59860500
N	-1.13319300	0.49378000	-0.02595900
N	0.00147500	2.54599900	-0.00327400
N	1.13577900	0.49871000	0.02130900
O	-2.26796100	2.50298100	-0.08712500
O	2.28482700	2.49425000	0.08173200

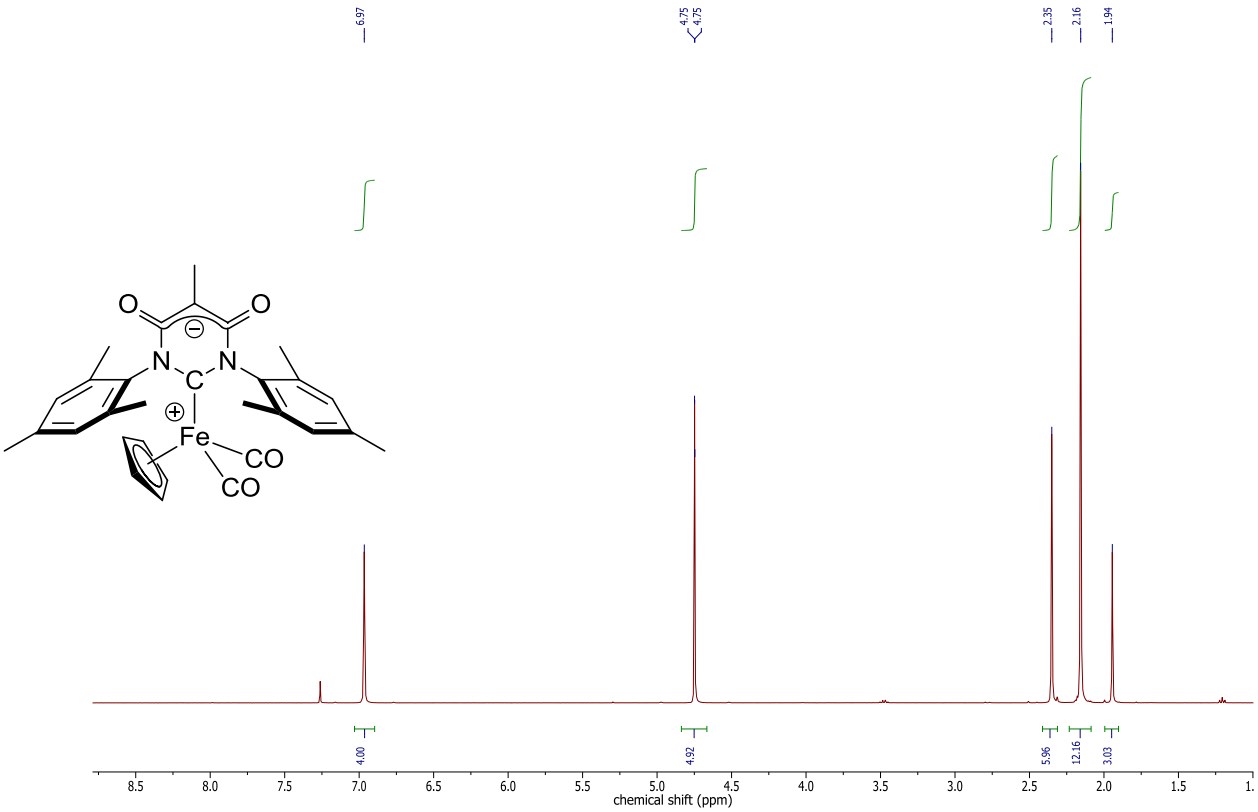
^{1}H NMR spectrum of $3_{t\mathrm{Bu}}$ (250 MHz, $CDCl_3$)



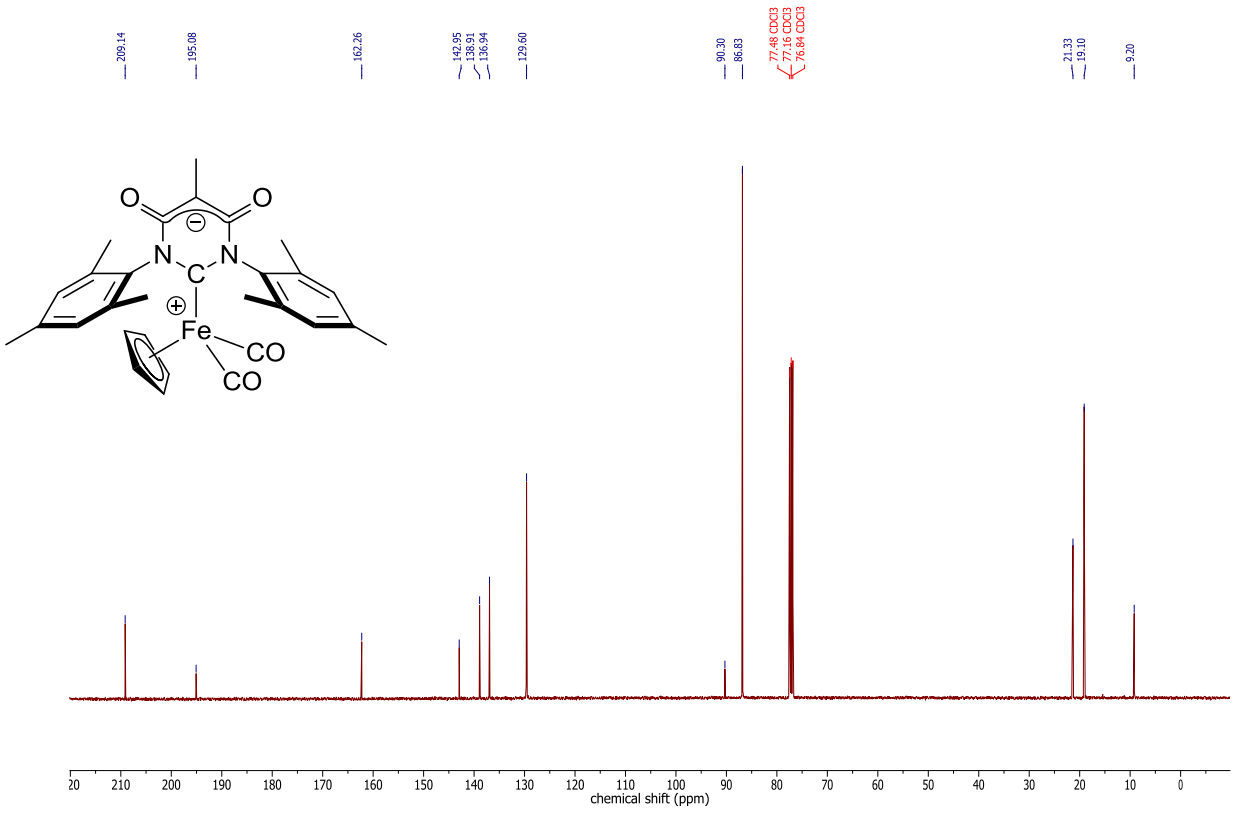
^{13}C {^{1}H} NMR spectrum of $3_{t\mathrm{Bu}}$ (63 MHz, $CDCl_3$)



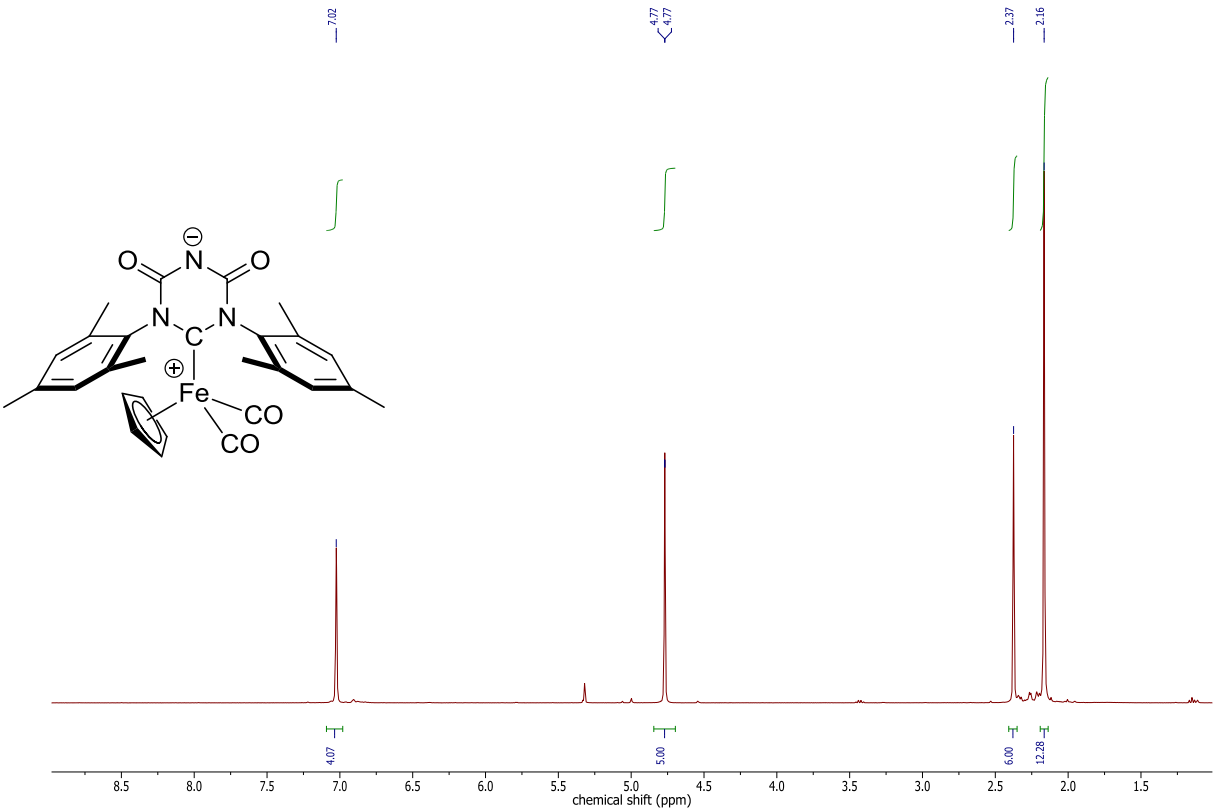
^{1}H NMR spectrum of 3_{Me} (400 MHz, $CDCl_3$)



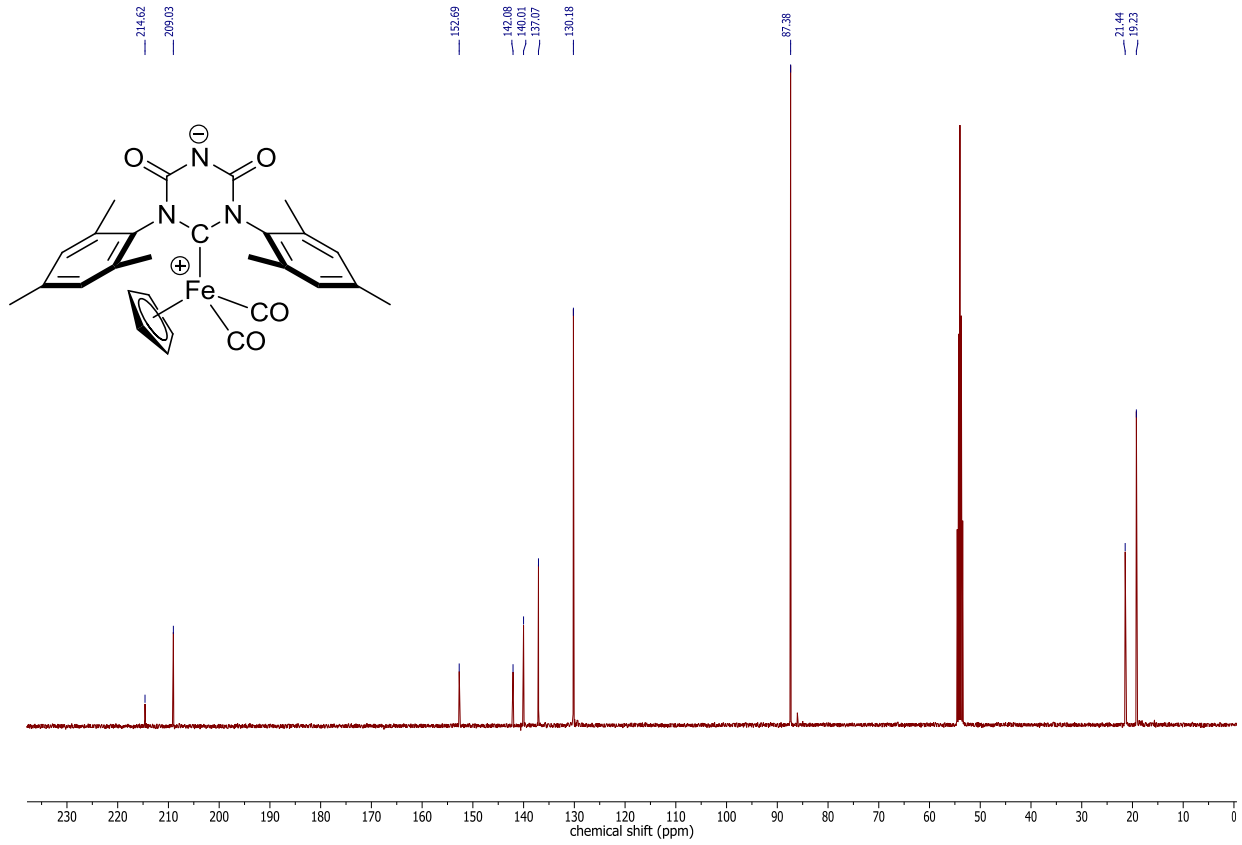
^{13}C {^{1}H} NMR spectrum of 3_{Me} (100.5 MHz, $CDCl_3$)



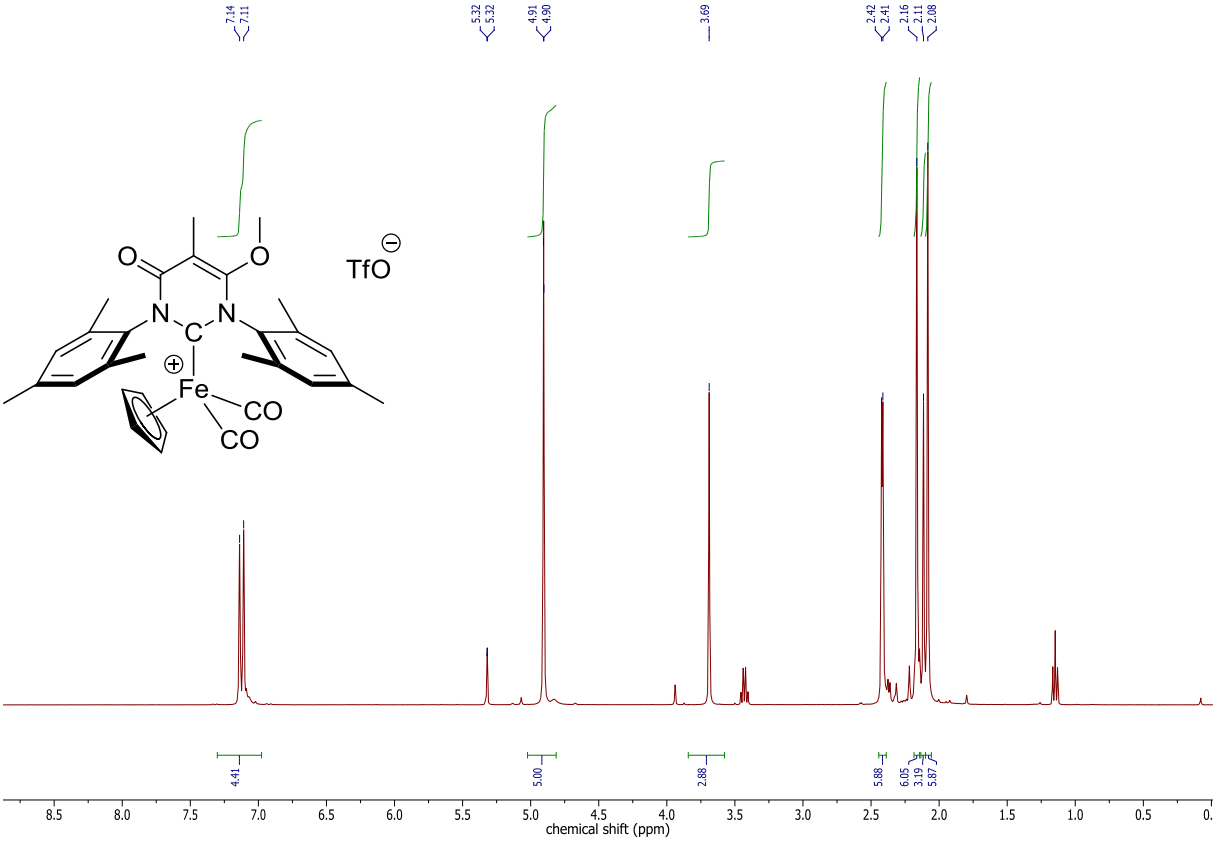
^{1}H NMR spectrum of 4 (400 MHz, CD_2Cl_2)



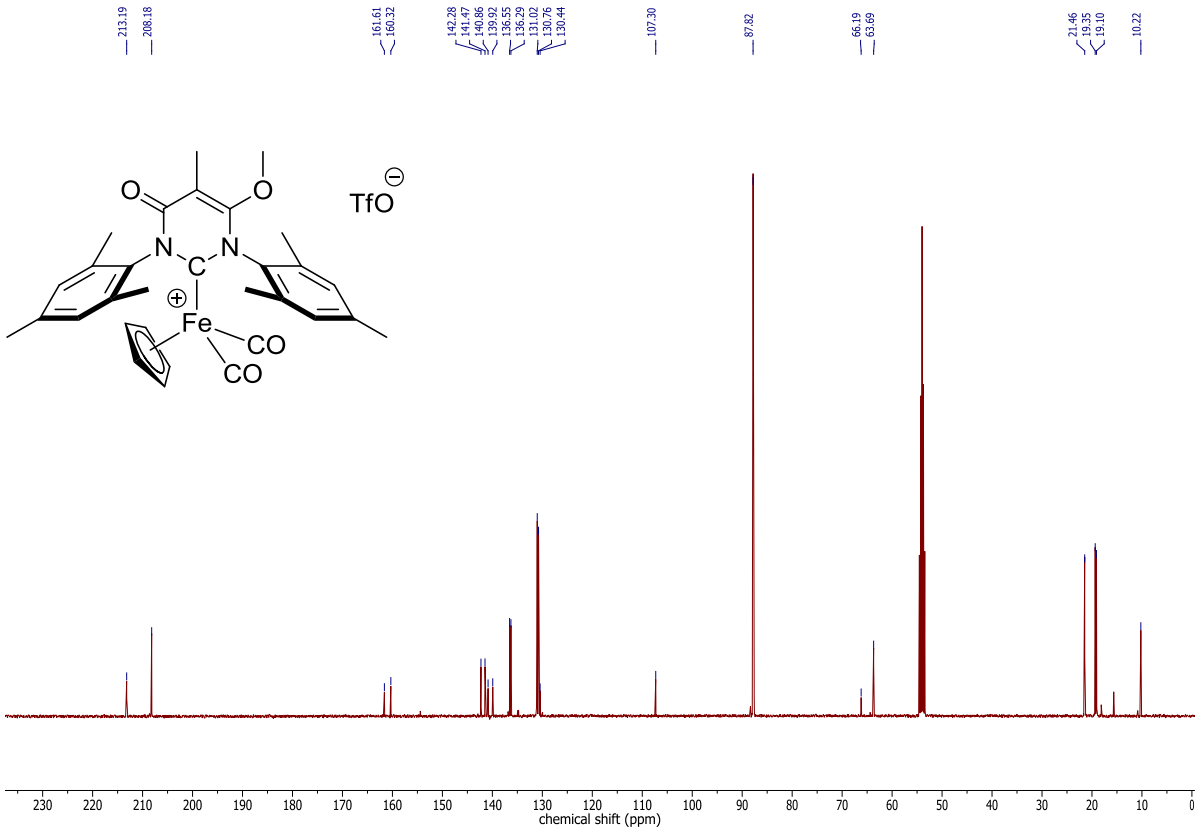
$^{13}C\{^{1}H\}$ NMR spectrum of 4 (100.5 MHz, CD_2Cl_2)



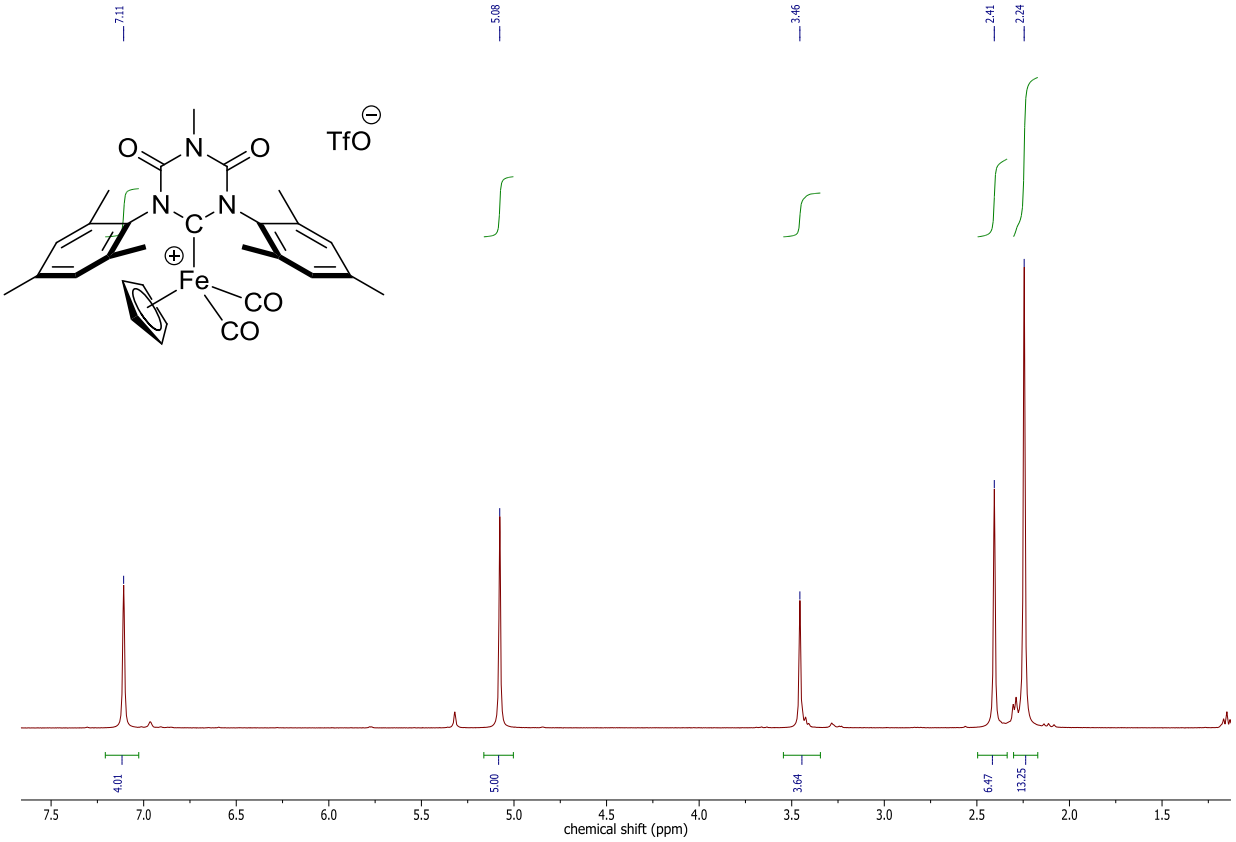
^{1}H NMR spectrum of [5_{Me}^{Me}](TfO) (400 MHz, CD_2Cl_2)



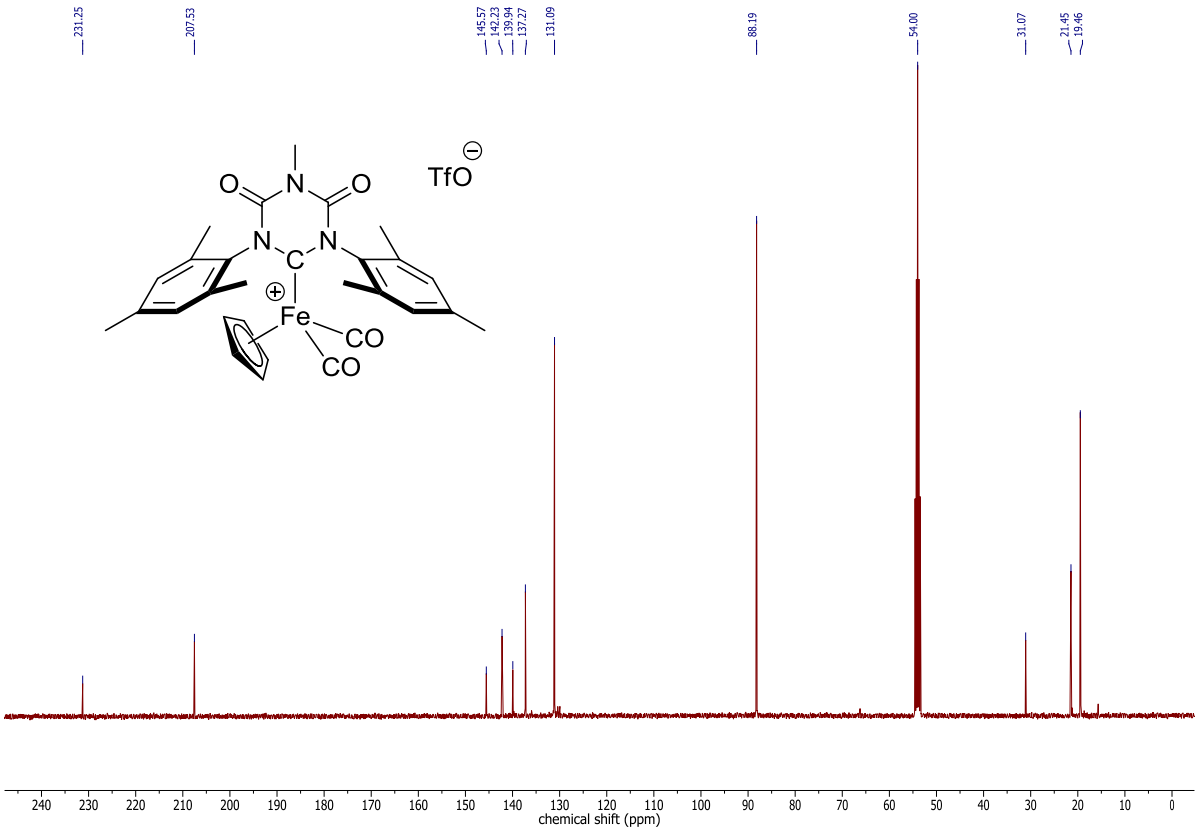
^{13}C{^{1}H} NMR spectrum of [5_{Me}^{Me}](TfO) (100.5 MHz, CD_2Cl_2)

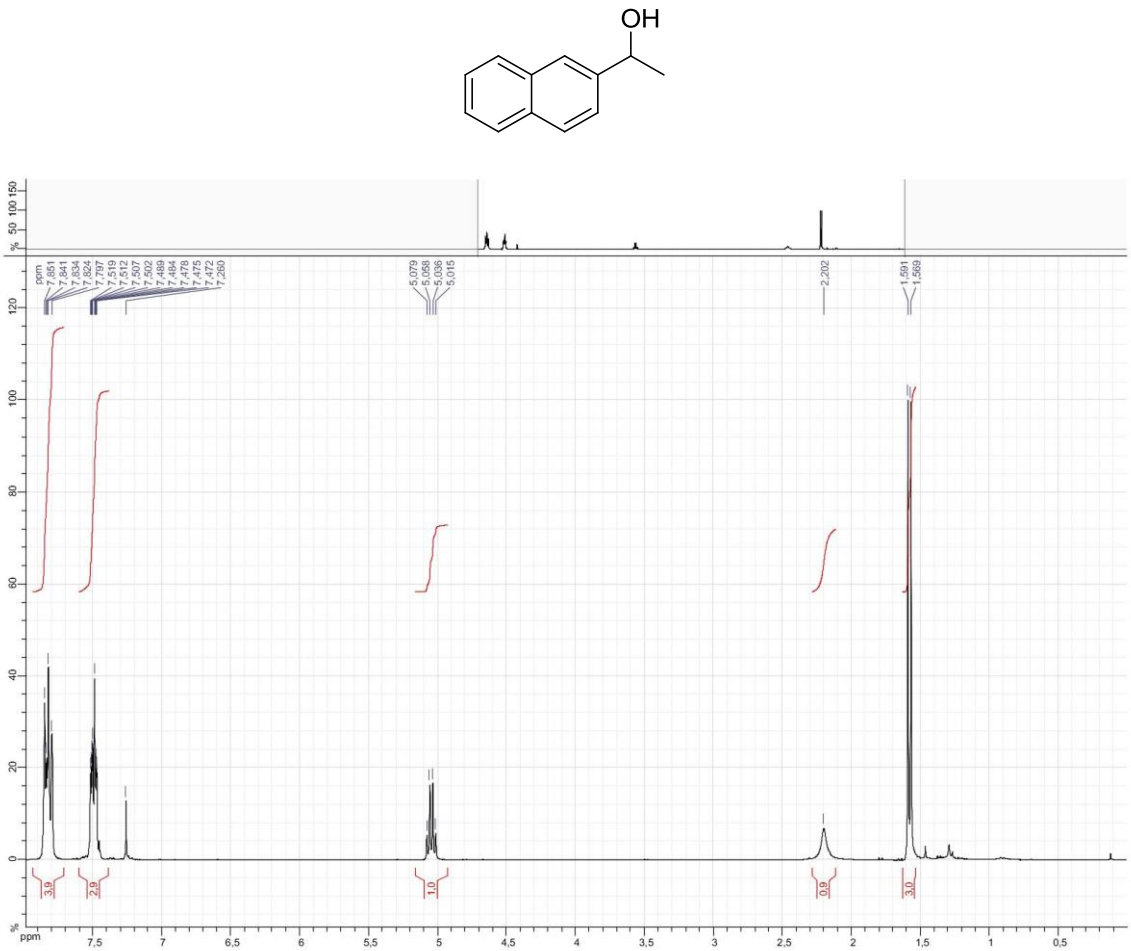


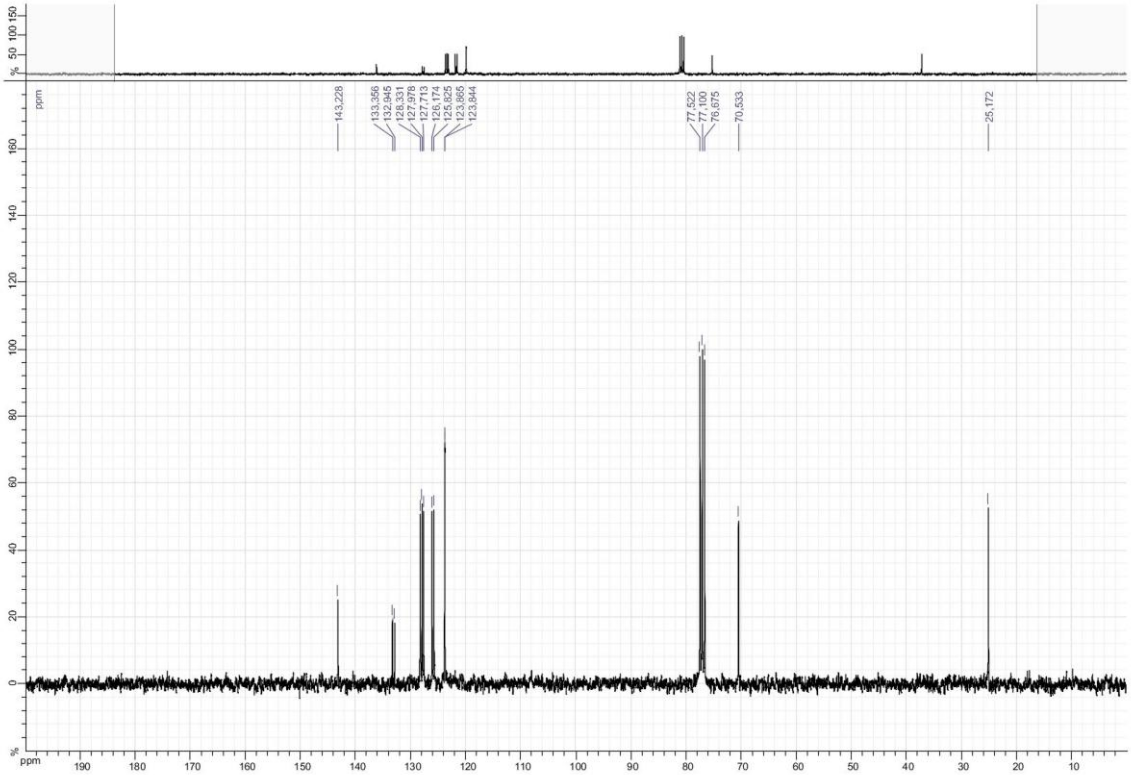
^{1}H NMR spectrum of [6^{Me}](TfO) (400 MHz, CD_2Cl_2)

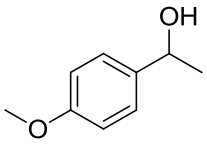


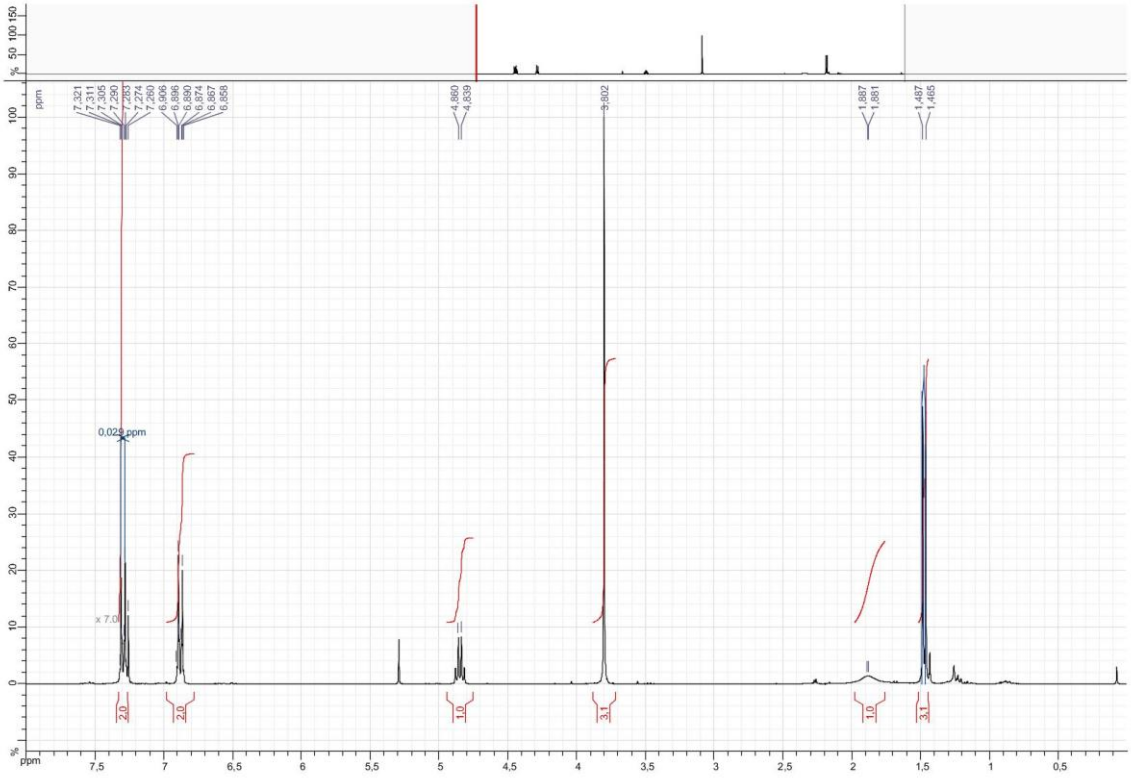
^{13}C{^{1}H} NMR spectrum of [6^{Me}](TfO) (100.5 MHz, CD_2Cl_2)

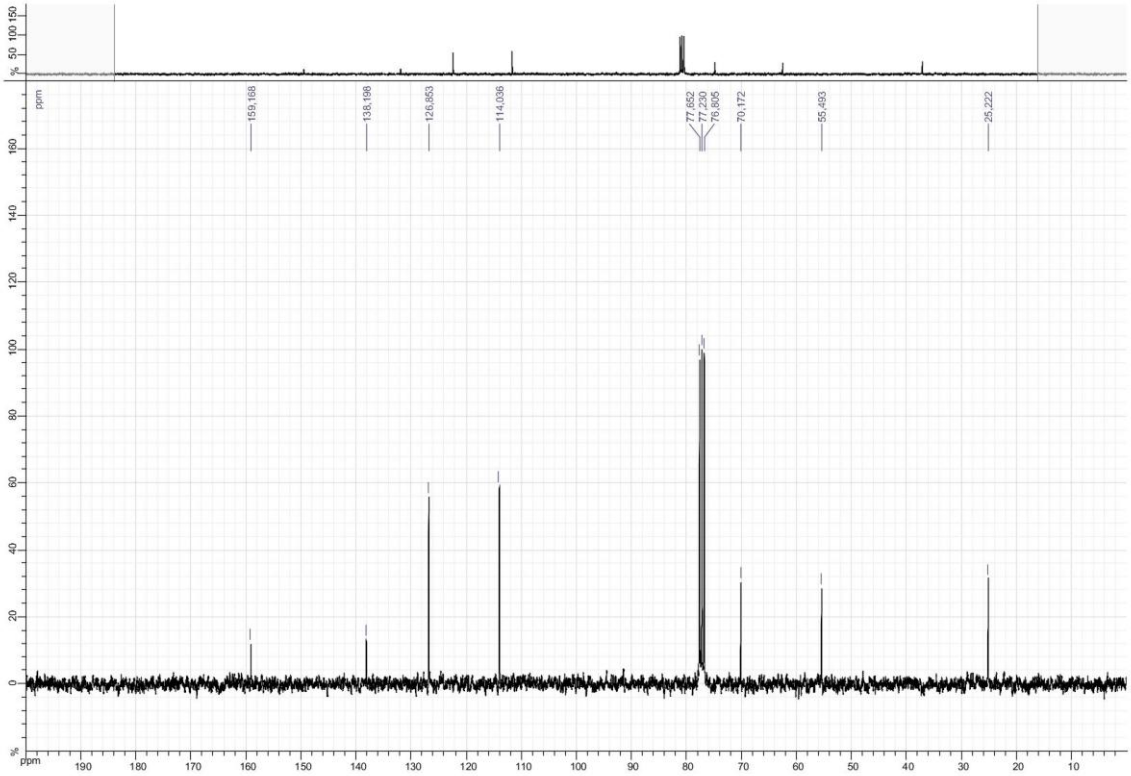


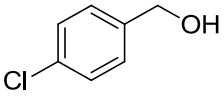

OH
ppm
7.851
7.841
7.834
7.824
7.797
7.519
7.512
7.507
7.502
7.489
7.484
7.478
7.475
7.472
7.260
5.079
5.068
5.058
5.046
5.016
2.202
1.591
1.569
3.0
2.9
1.0
0.9
3.0

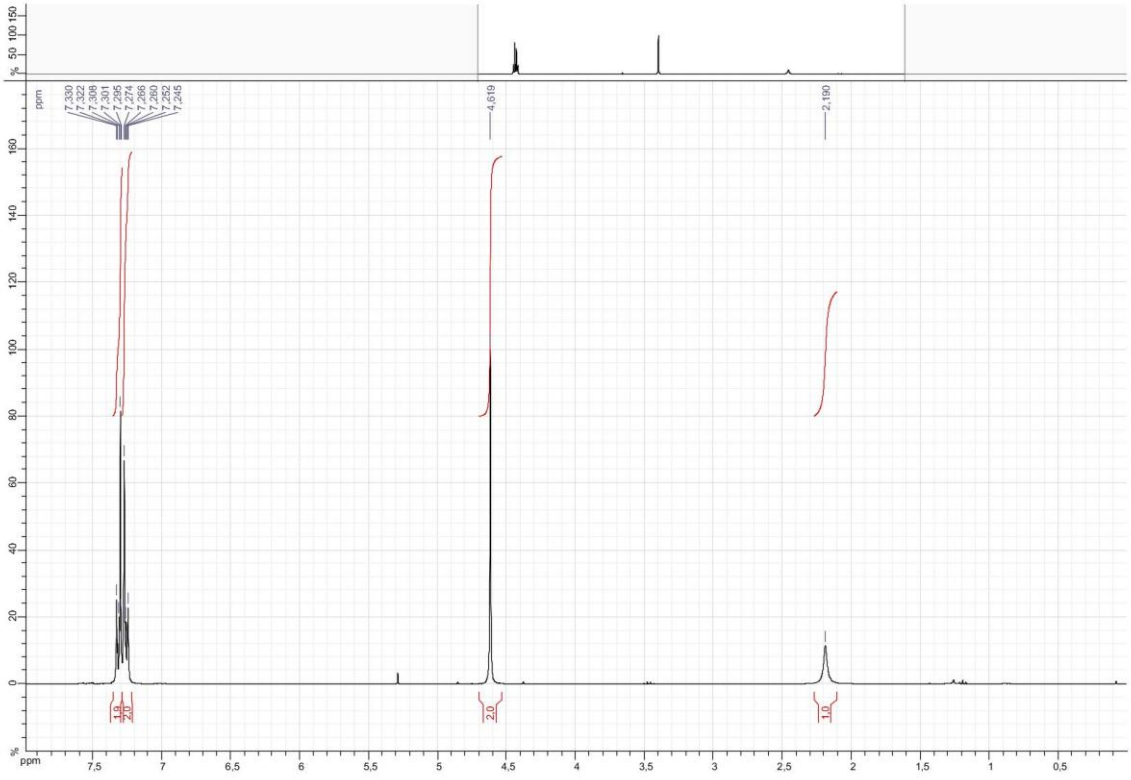

ppm
143.228
133.356
132.945
128.331
127.976
127.773
126.174
125.825
123.865
123.844
77.522
77.100
76.675
70.533
25.172

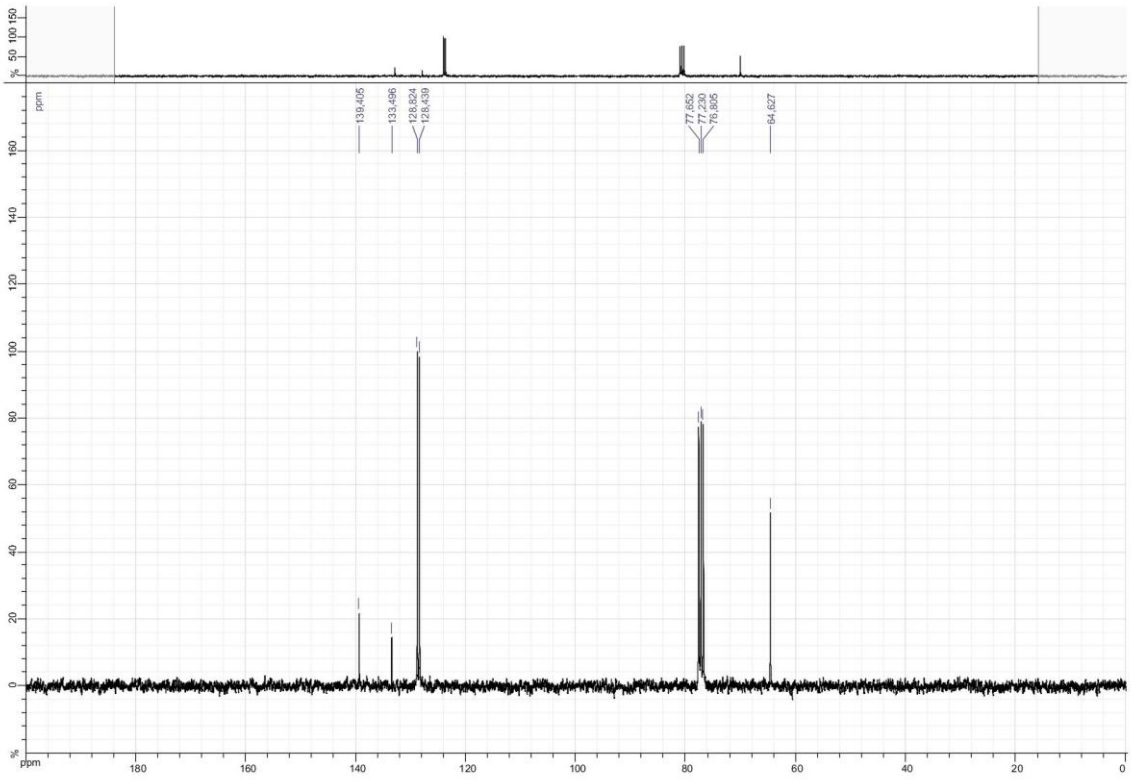

OH
O

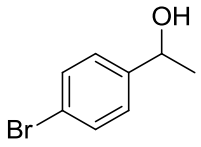

7,321
7,311
7,305
7,290
7,283
7,274
7,260
6,906
6,896
6,890
6,874
6,867
6,858
4,860
4,839
3,802
1,887
1,881
1,487
1,465
0,029 ppm
x 7,0
2,0
2,0
1,0
3,1
1,0
3,1
ppm

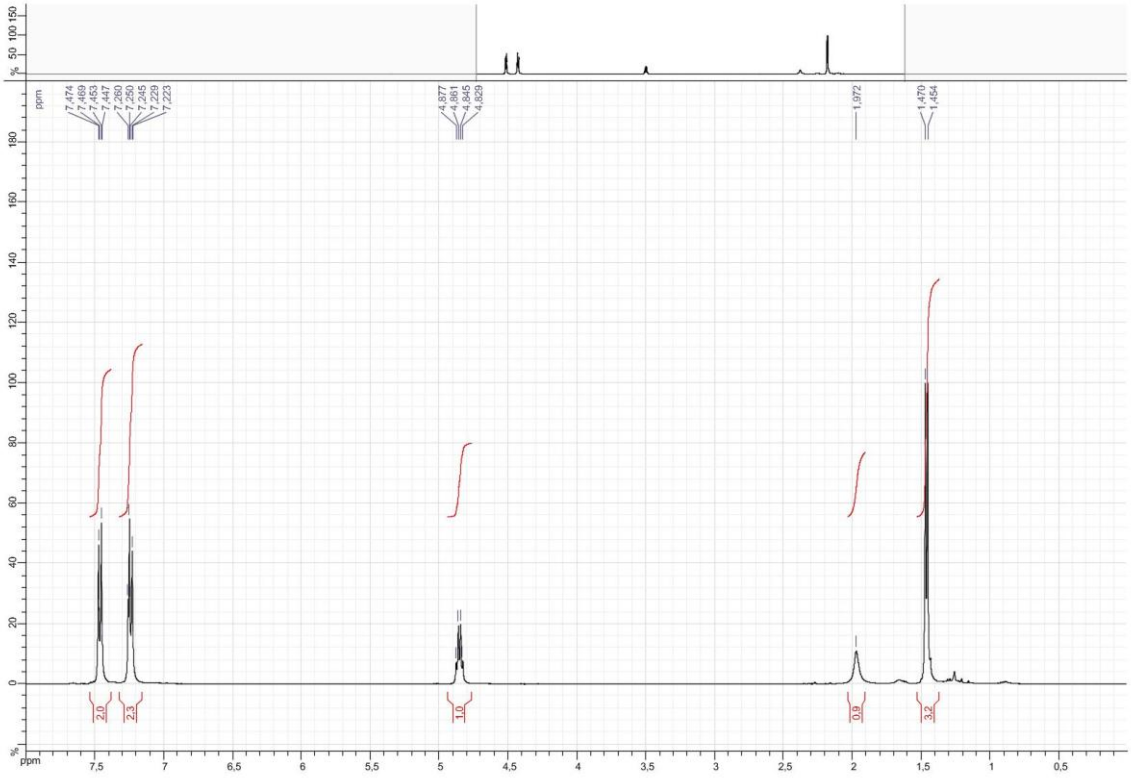

159,168
138,198
126,853
114,036
77,652
77,230
76,805
70,172
55,493
25,222
ppm

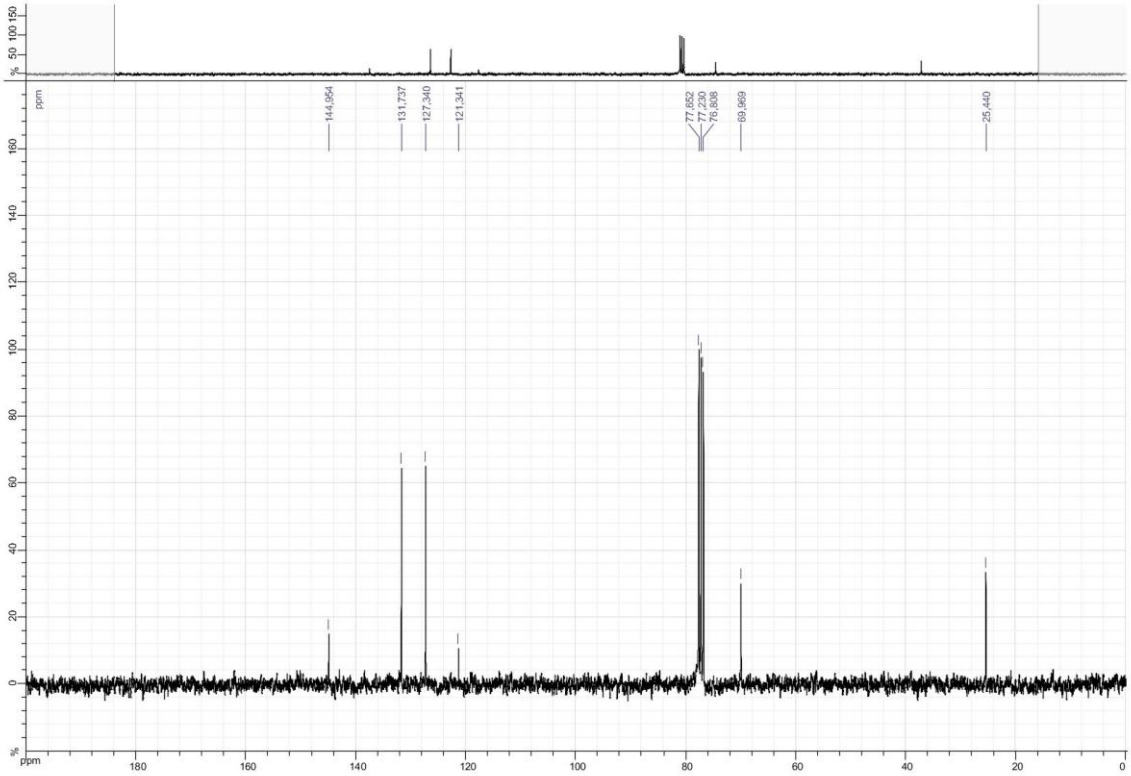

OH
Cl

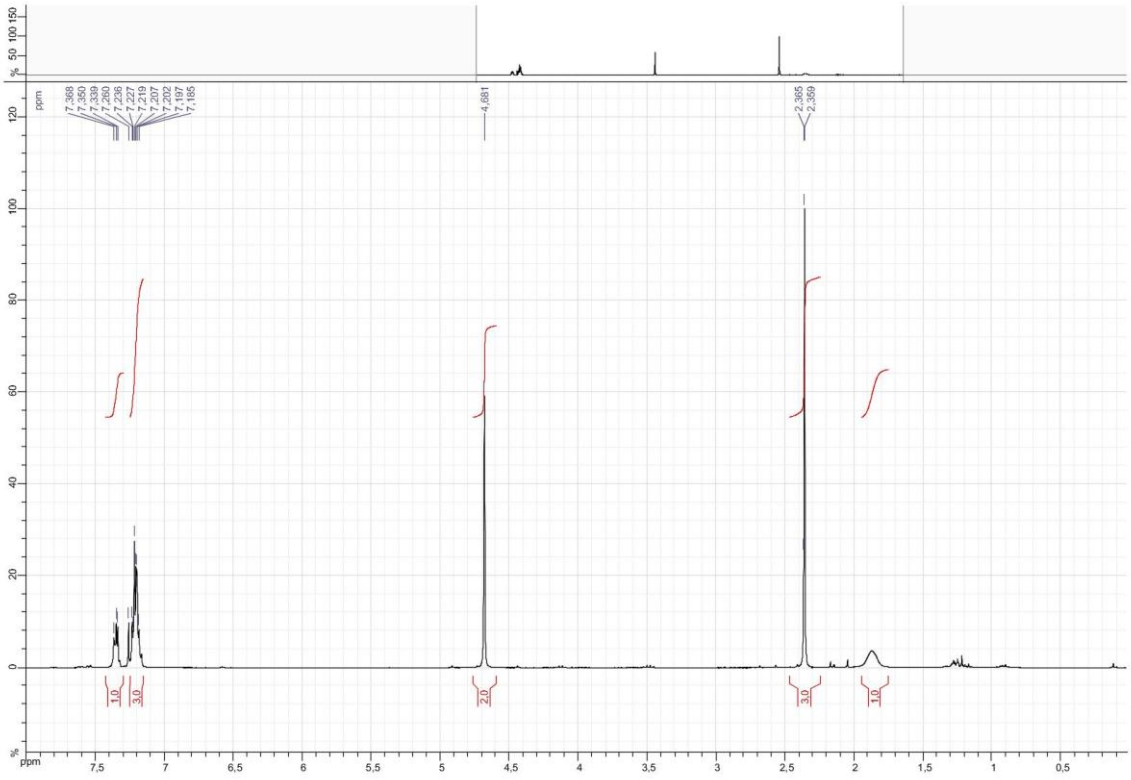

7,330
7,322
7,308
7,301
7,295
7,274
7,266
7,260
7,252
7,245
4,619
2,190
1,0
2,0
2,0
1,0
ppm

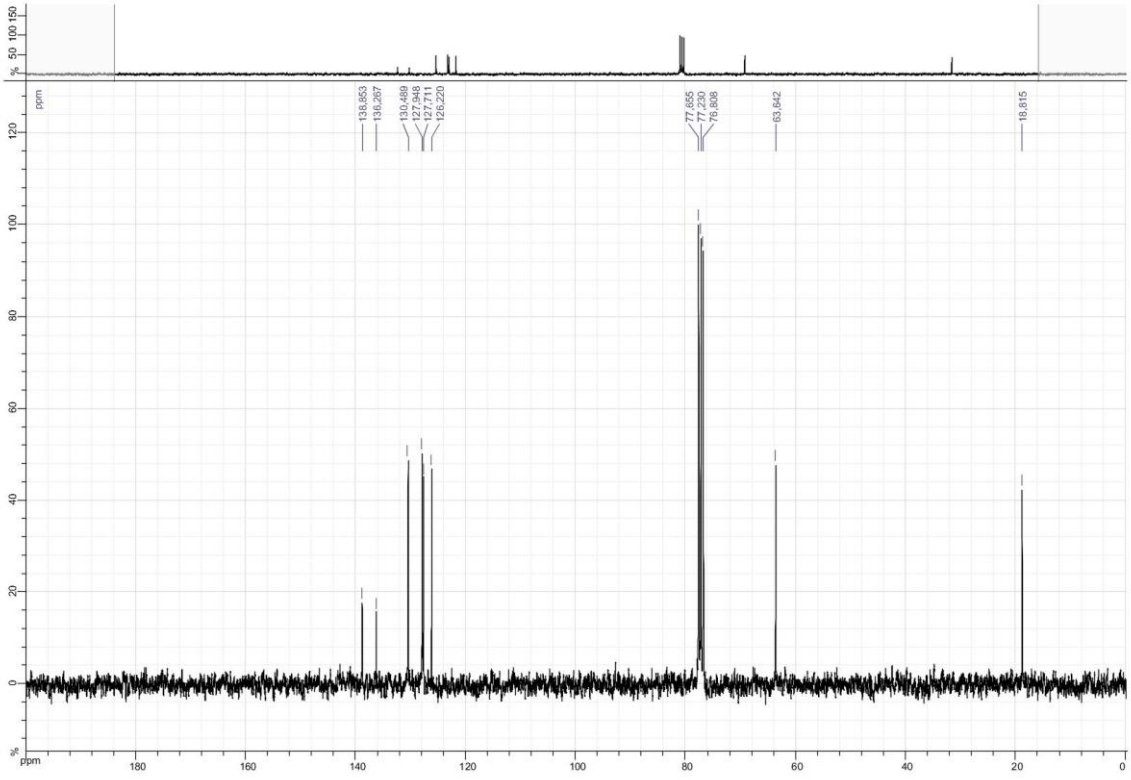

139,405
133,496
128,824
128,439
77,662
77,230
76,805
64,627
ppm

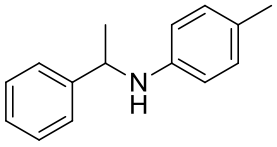

OH
Br

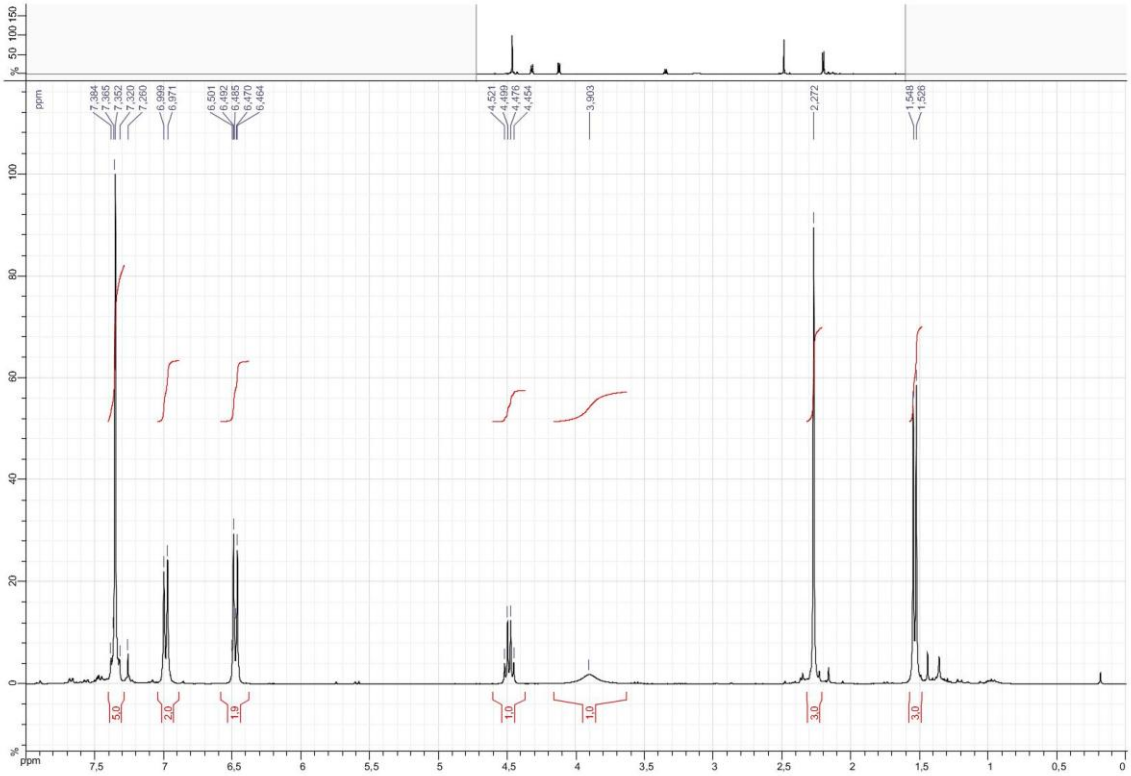

7.474
7.469
7.453
7.447
7.260
7.250
7.245
7.229
7.223
4.877
4.861
4.845
4.829
1.972
1.470
1.454
2.0
2.3
1.0
0.9
3.2
ppm

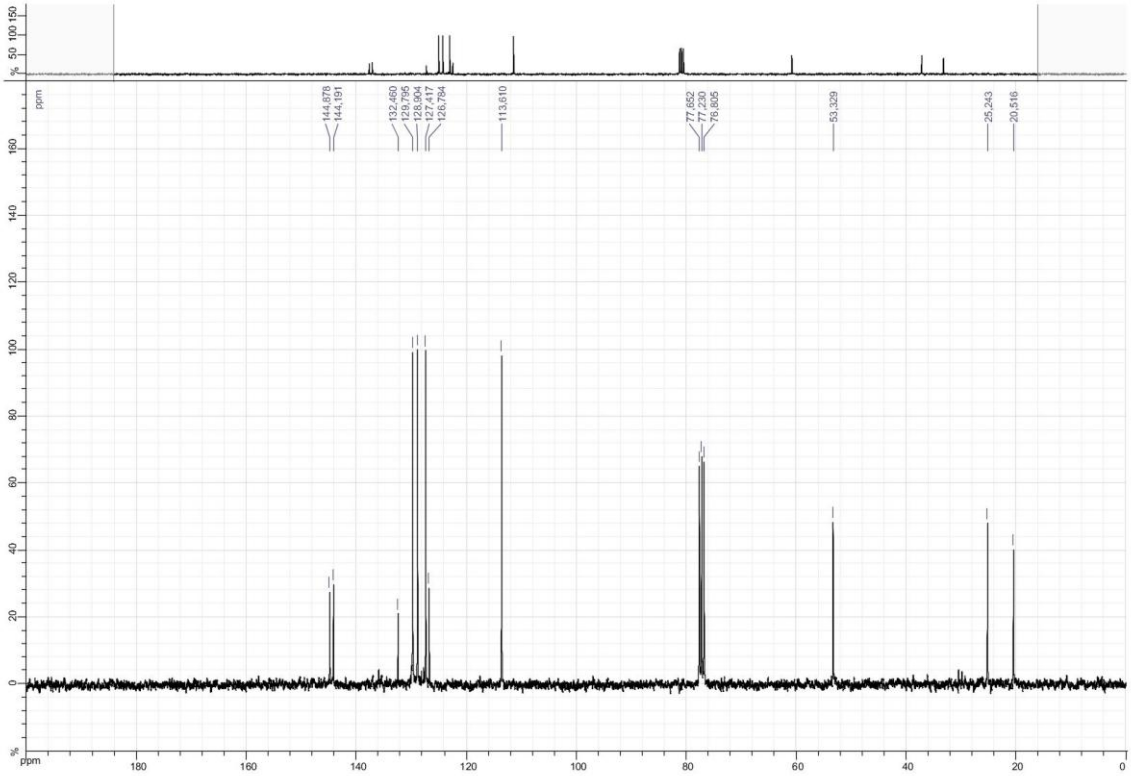

144.964
131.737
127.340
121.341
77.652
77.230
76.808
69.969
25.440
ppm

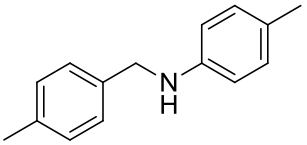

7,368
7,350
7,339
7,260
7,236
7,227
7,219
7,207
7,202
7,197
7,185
4,681
2,365
2,359
1,0
3,0
2,0
3,0
1,0
ppm

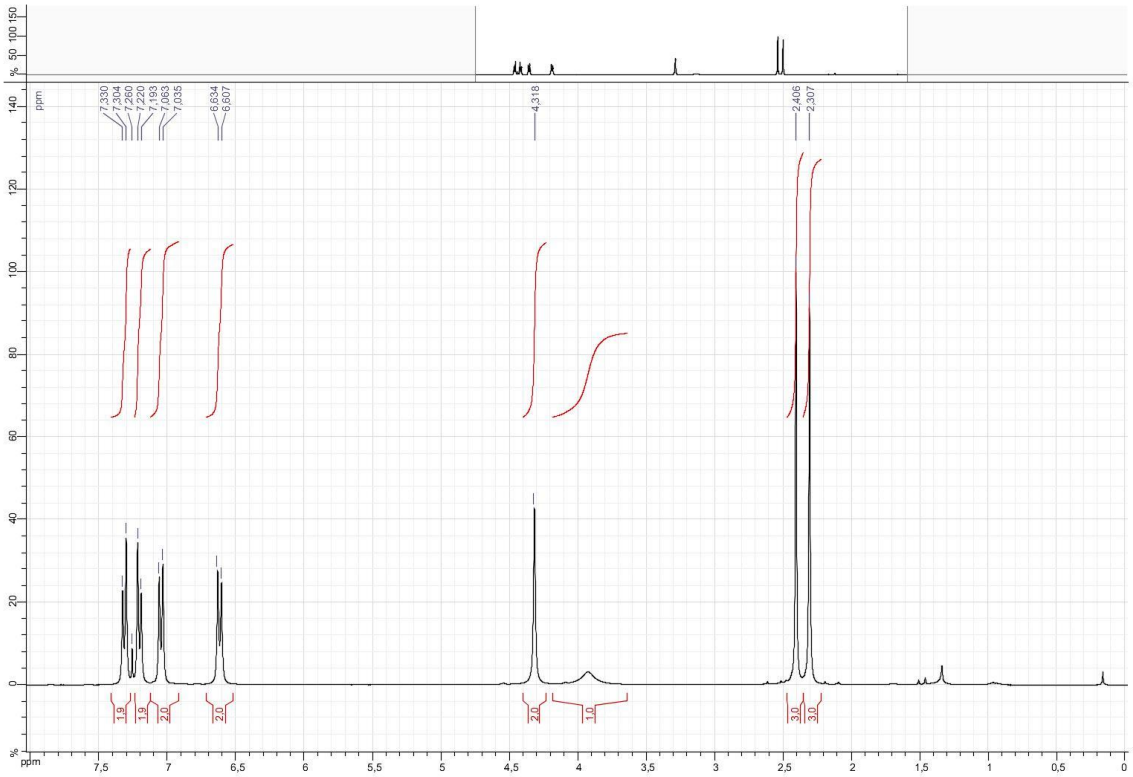

138,853
136,267
130,489
127,948
127,711
126,220
77,665
77,230
76,808
63,642
18,815
ppm

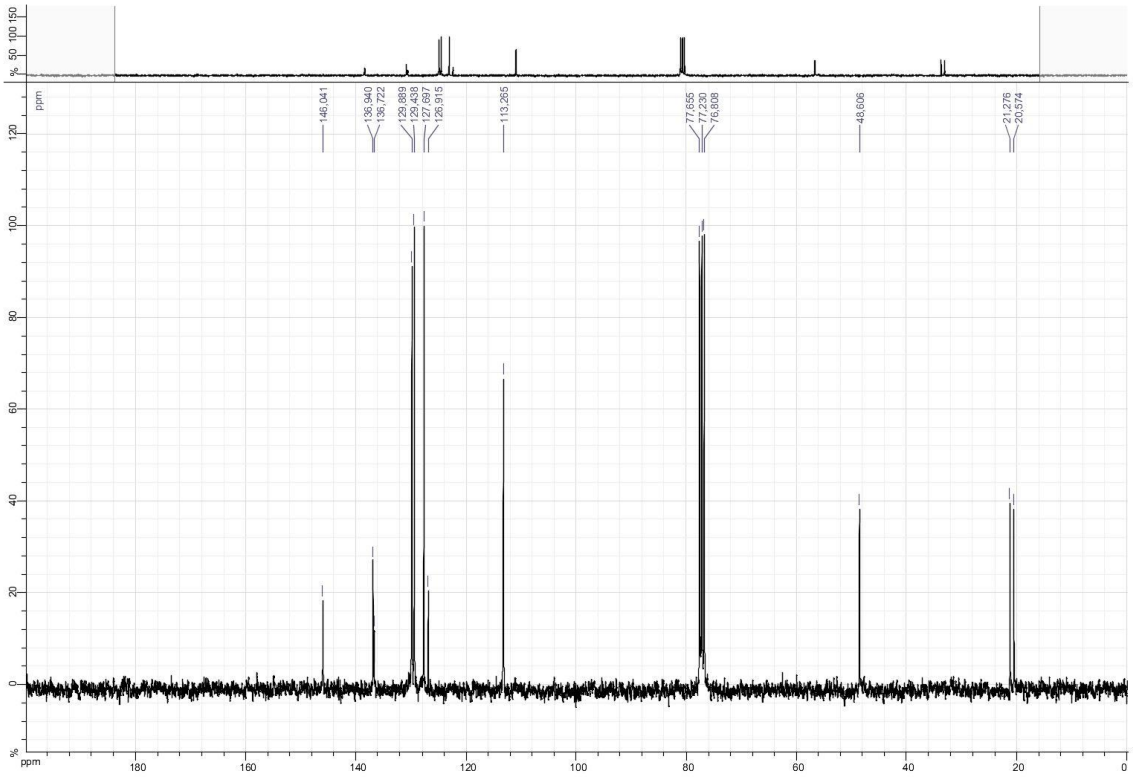

N
H

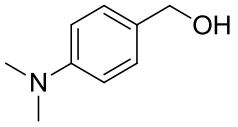

ppm
7,384
7,365
7,352
7,320
7,260
6,999
6,971
6,501
6,492
6,485
6,470
6,464
4,521
4,499
4,476
4,454
3,903
2,272
1,548
1,526
5,0
2,0
1,9
1,0
1,0
3,0
3,0

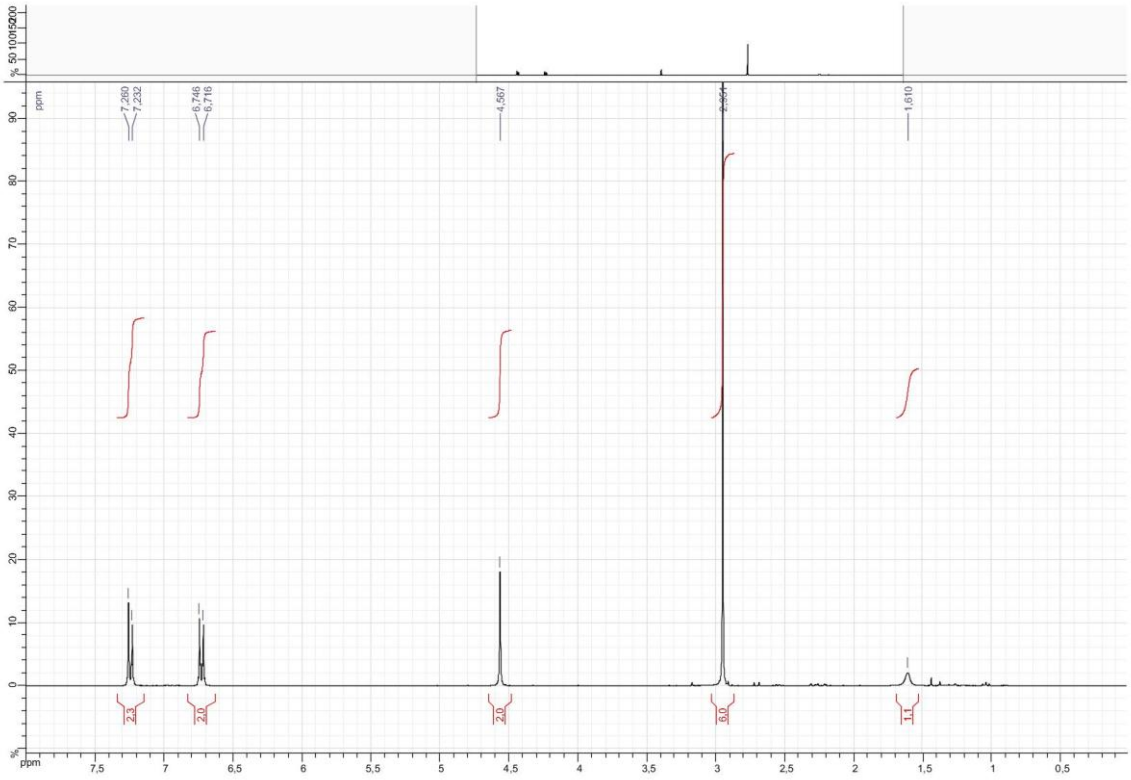

ppm
144,678
144,191
132,460
129,795
128,904
127,417
126,784
113,610
77,652
77,230
76,805
53,329
25,243
20,516

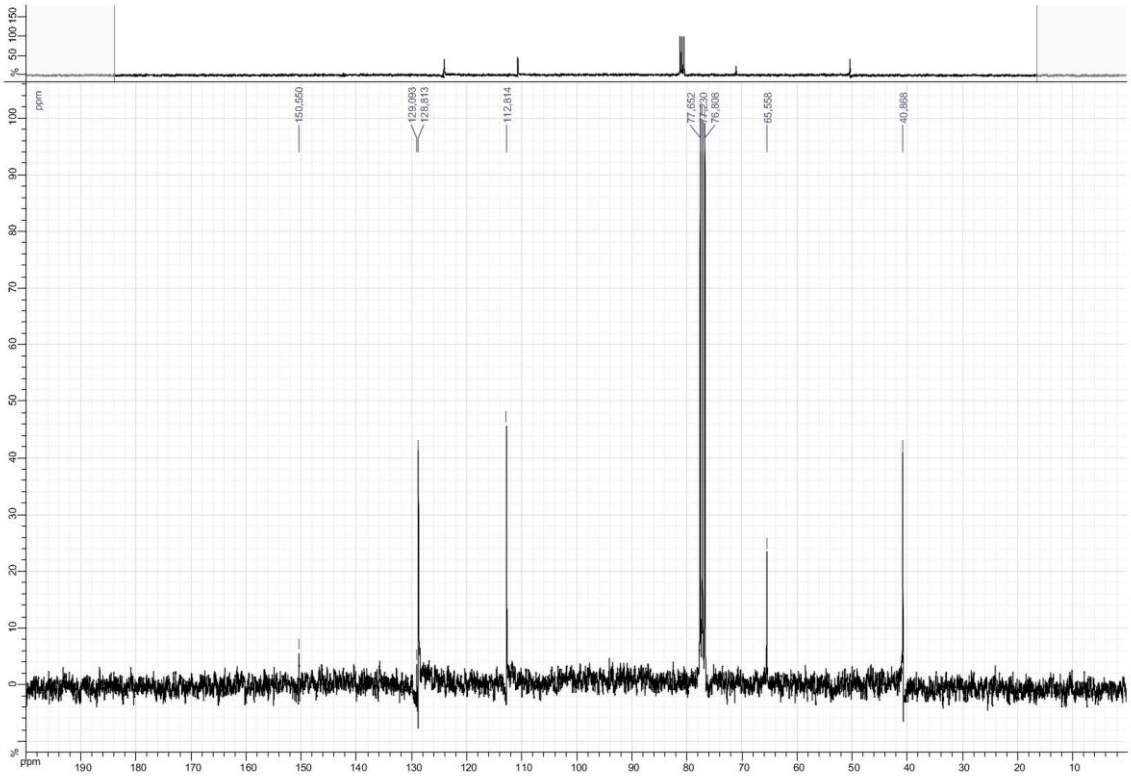

N
H

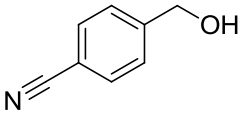

7,330
7,304
7,280
7,220
7,193
7,063
7,035
6,634
6,607
4,318
2,406
2,307
1,9
1,9
2,0
2,0
2,0
1,0
3,0
3,0
ppm

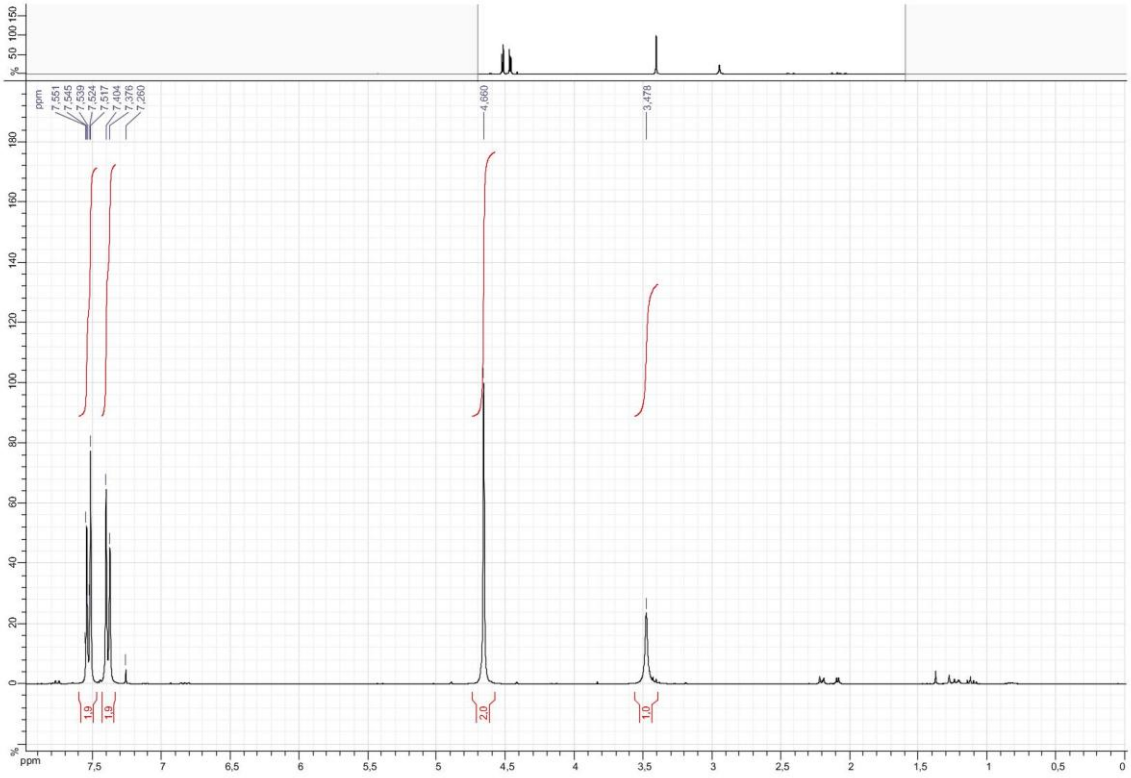

146,041
136,940
136,722
129,889
129,438
127,697
126,915
113,265
77,655
77,230
76,808
48,606
21,276
20,574
ppm

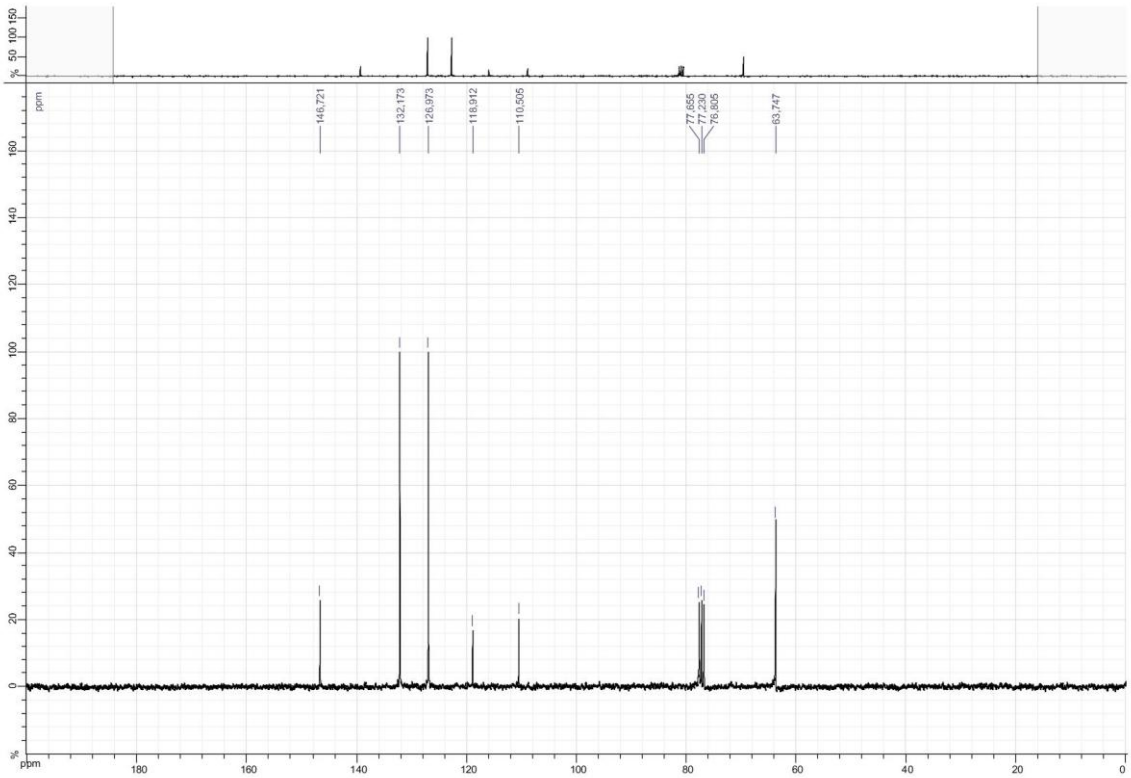

OH
N

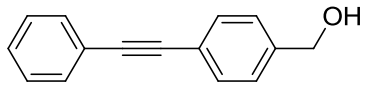

7,260
7,232
6,746
6,716
4,567
2,951
1,610
2,0
2,0
2,0
6,0
1,1
ppm

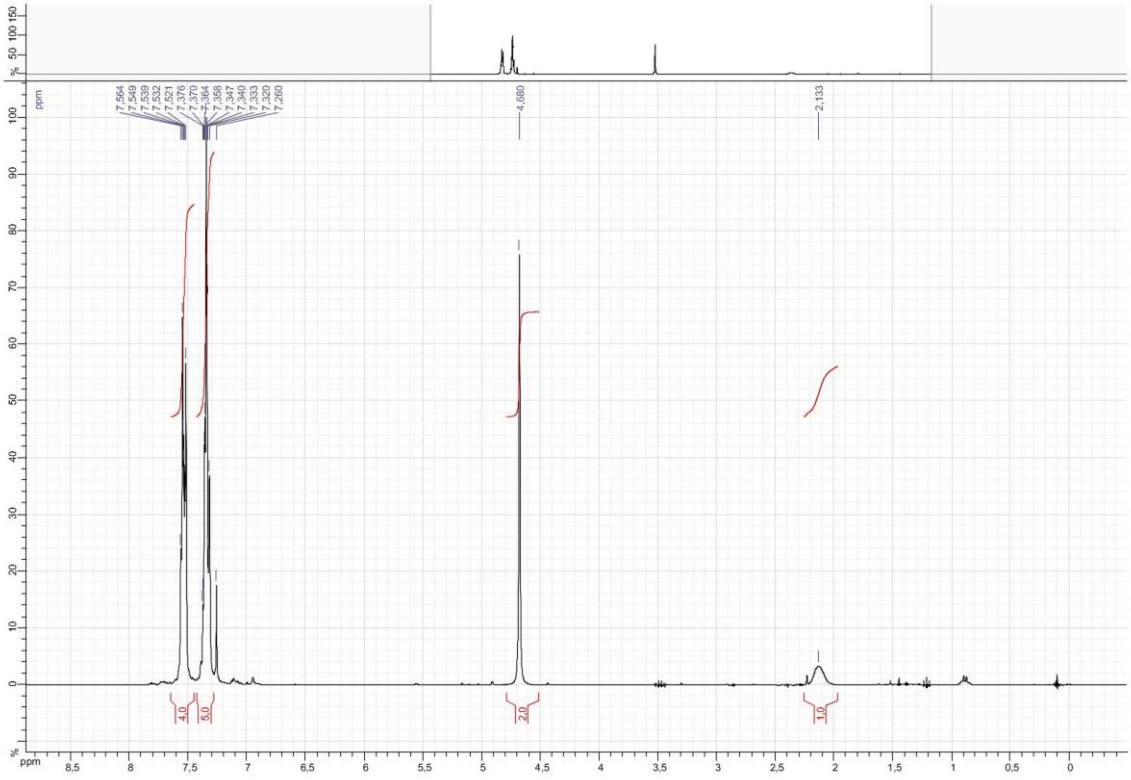

150,550
129,093
128,813
112,814
77,652
77,333
76,808
65,556
40,868
ppm

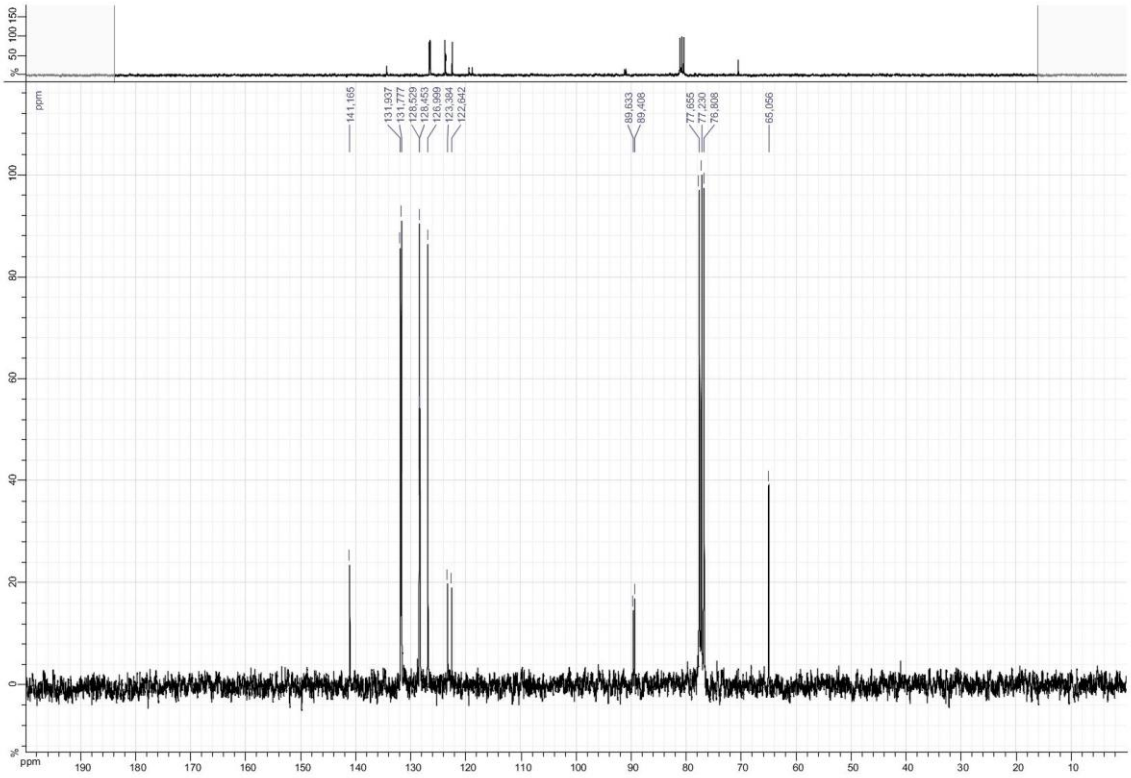

OH
N


ppm
7,551
7,545
7,539
7,524
7,517
7,404
7,376
7,260
4,660
3,478
1,9
1,9
2,0
1,0


ppm
146,721
132,173
126,973
118,912
110,505
77,655
77,230
76,805
63,747


OH


7.564
7.549
7.539
7.532
7.521
7.376
7.370
7.364
7.358
7.347
7.340
7.333
7.320
7.260
4.680
2.133
4.0
5.0
2.0
1.0
ppm


141.165
131.937
131.777
128.529
128.453
123.969
123.394
122.842
89.633
89.408
77.655
77.230
76.808
65.056
ppm