Supporting Information

1,2-Diaza-4-phosphaferrocenes: Synthesis, Structural Characterization, ^{57}Fe Mössbauer Spectrum Analysis, and DFT Calculation

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S1. Crystal data and structure refinements for **3–4**

Table S1-1. Crystal structural analysis data for **3**

Table S1-1-1. Crystal data and structure refinement for **3**

Identification code	081801
Empirical formula	$C_{20}H_{33}N_2FeP$
Formula weight	388.30
Temperature/K	296(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	19.2288(7)
b/Å	8.6506(3)
c/Å	26.1206(9)
α/°	90
β/°	100.554(3)
γ/°	90
Volume/Å^3	4271.4(2)
Z	8
ρ_{calc}g/cm^3	1.208
μ/mm^{-1}	0.785
F(000)	1664
Crystal size/mm^3	0.152 x 0.101 x 0.108
Radiation	MoKα (λ = 0.71073)
2*Θ* range for data collection/°	2.90 to 26.50
Index ranges	–23 ≤ h ≤ 24, –10 ≤ k ≤ 10, –32 ≤ l ≤ 32
Reflections collected	14394
Independent reflections	4429 [R_{int} = 0.0260, R_{sigma} = 0.0292]
Data/restraints/parameters	4429 / 0 / 228
Goodness-of-fit on F^2	1.038
Final *R* indexes [I>=2*σ* (I)]	R_1 = 0. 0352, wR_2 = 0.0941
Final *R* indexes [all data]	R_1 = 0. 0488, wR_2 = 0.0917
Largest diff. peak/hole / e Å^{-3}	0.239 and –0.218

Table S1-1-2. Bond Lengths for compound

3

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N2	2.0119(16)	C7	C9	1.526(3)
Fe1	N1	2.0167(16)	C7	C8	1.527(3)
Fe1	C13	2.070(2)	C7	C10	1.539(3)
Fe1	C14	2.071(2)	C8	H8A	0.9600
Fe1	C11	2.071(2)	C8	H8B	0.9600
Fe1	C15	2.072(2)	C8	H8C	0.9600
Fe1	C12	2.090(2)	C9	H9A	0.9600
Fe1	C2	2.0921(19)	C9	H9B	0.9600
Fe1	C1	2.1048(19)	C9	H9C	0.9600
Fe1	P1	2.3228(6)	C10	H10A	0.9600
N1	C1	1.371(2)	C10	H10B	0.9600
N1	N2	1.392(2)	C10	H10C	0.9600
N2	C2	1.369(2)	C11	C12	1.414(3)
P1	C1	1.777(2)	C11	C15	1.426(3)
P1	C2	1.777(2)	C11	C17	1.497(3)
C1	C7	1.520(3)	C12	C13	1.417(3)
C2	C3	1.522(3)	C12	C18	1.508(3)
C3	C5	1.517(3)	C13	C14	1.422(3)
C3	C6	1.524(3)	C13	C19	1.506(3)
C3	C4	1.533(3)	C14	C15	1.418(3)
C4	H4A	0.9600	C14	C20	1.503(3)
C4	H4B	0.9600	C15	C16	1.499(3)
C4	H4C	0.9600	C16	H16A	0.9600
C5	H5A	0.9600	C17	H17B	0.9600
C5	H5B	0.9600	C18	H18C	0.9600
C5	H5C	0.9600	C19	H19A	0.9600
C6	H6A	0.9600	C19	H19B	0.9600
C6	H6B	0.9600	C20	H20A	0.9600
C6	H6C	0.9600	C20	H20C	0.9600

[1]1-X,+Y,1/2-Z

Table S1-1-3. Bond Angles for compound **3**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(2)	Fe(1)	N(1)	40.44(7)	C(6)	C(3)	C(4)	108.4(2)
N(2)	Fe(1)	C(13)	157.83(8)	C(3)	C(4)	H(4A)	109.5
N(1)	Fe(1)	C(13)	161.60(8)	C(3)	C(4)	H(4B)	109.5
N(2)	Fe(1)	C(14)	156.20(8)	H(4A)	C(4)	H(4B)	109.5
N(1)	Fe(1)	C(14)	122.47(8)	C(3)	C(4)	H(4C)	109.5
C(13)	Fe(1)	C(14)	40.18(8)	H(4A)	C(4)	H(4C)	109.5
N(2)	Fe(1)	C(11)	102.86(8)	H(4B)	C(4)	H(4C)	109.5
N(1)	Fe(1)	C(11)	115.86(8)	C(3)	C(5)	H(5A)	109.5
C(13)	Fe(1)	C(11)	67.27(9)	C(3)	C(5)	H(5B)	109.5
C(14)	Fe(1)	C(11)	67.35(9)	H(5A)	C(5)	H(5B)	109.5
N(2)	Fe(1)	C(15)	118.67(8)	C(3)	C(5)	H(5C)	109.5
N(1)	Fe(1)	C(15)	102.61(8)	H(5A)	C(5)	H(5C)	109.5
C(13)	Fe(1)	C(15)	67.44(8)	H(5B)	C(5)	H(5C)	109.5
C(14)	Fe(1)	C(15)	40.03(9)	C(3)	C(6)	H(6A)	109.5
C(11)	Fe(1)	C(15)	40.27(9)	C(3)	C(6)	H(6B)	109.5
N(2)	Fe(1)	C(12)	120.17(8)	H(6A)	C(6)	H(6B)	109.5
N(1)	Fe(1)	C(12)	152.28(8)	C(3)	C(6)	H(6C)	109.5
C(13)	Fe(1)	C(12)	39.82(8)	H(6A)	C(6)	H(6C)	109.5
C(14)	Fe(1)	C(12)	66.95(9)	H(6B)	C(6)	H(6C)	109.5
C(11)	Fe(1)	C(12)	39.73(9)	C(1)	C(7)	C(9)	112.31(18)
C(15)	Fe(1)	C(12)	67.02(9)	C(1)	C(7)	C(8)	111.39(18)
N(2)	Fe(1)	C(2)	38.90(7)	C(9)	C(7)	C(8)	110.3(2)
N(1)	Fe(1)	C(2)	67.68(7)	C(1)	C(7)	C(10)	105.56(18)
C(13)	Fe(1)	C(2)	127.80(8)	C(9)	C(7)	C(10)	108.7(2)
C(14)	Fe(1)	C(2)	164.59(8)	C(8)	C(7)	C(10)	108.4(2)
C(11)	Fe(1)	C(2)	120.79(8)	C(7)	C(8)	H(8A)	109.5
C(15)	Fe(1)	C(2)	154.37(8)	C(12)	C(11)	C(15)	108.03(19)
C(12)	Fe(1)	C(2)	110.02(8)	C(12)	C(11)	C(17)	127.7(2)
N(2)	Fe(1)	C(1)	67.68(7)	C(15)	C(11)	C(17)	124.2(2)
N(1)	Fe(1)	C(1)	38.80(7)	C(12)	C(11)	Fe(1)	70.87(12)
C(13)	Fe(1)	C(1)	130.65(8)	C(15)	C(11)	Fe(1)	69.91(12)
C(14)	Fe(1)	C(1)	109.39(8)	C(17)	C(11)	Fe(1)	126.97(16)
C(11)	Fe(1)	C(1)	150.08(9)	C(11)	C(12)	C(13)	108.25(19)
C(15)	Fe(1)	C(1)	117.59(8)	C(11)	C(12)	C(18)	126.5(2)

C(12)	Fe(1)	C(1)	168.81(9)	C(13)	C(12)	C(18)	124.5(2)
C(2)	Fe(1)	C(1)	70.52(7)	C(11)	C(12)	Fe(1)	69.40(12)
N(2)	Fe(1)	P(1)	75.39(5)	C(13)	C(12)	Fe(1)	69.33(12)
N(1)	Fe(1)	P(1)	75.26(5)	C(18)	C(12)	Fe(1)	134.77(17)
C(13)	Fe(1)	P(1)	107.32(6)	C(12)	C(13)	C(14)	107.9(2)
C(14)	Fe(1)	P(1)	121.00(6)	C(12)	C(13)	C(19)	126.5(2)
C(15)	Fe(1)	P(1)	161.23(7)	C(14)	C(13)	C(19)	125.4(2)
C(12)	Fe(1)	P(1)	156.27(7)	C(12)	C(13)	Fe(1)	70.85(12)
C(2)	Fe(1)	P(1)	124.76(7)	C(14)	C(13)	Fe(1)	69.92(11)
C(1)	Fe(1)	P(1)	47.12(5)	C(19)	C(13)	Fe(1)	129.26(16)
C(1)	N(1)	N(2)	47.00(5)	C(15)	C(14)	C(13)	108.12(19)
C(1)	N(1)	Fe(1)	112.19(16)	C(15)	C(14)	C(20)	127.4(2)
N(2)	N(1)	Fe(1)	74.07(10)	C(13)	C(14)	C(20)	123.9(2)
C(2)	N(2)	N(1)	69.59(9)	C(15)	C(14)	Fe(1)	70.05(12)
C(2)	N(2)	Fe(1)	112.00(16)	C(13)	C(14)	Fe(1)	69.90(11)
N(1)	N(2)	Fe(1)	73.72(10)	C(20)	C(14)	Fe(1)	132.39(16)
C(1)	P(1)	C(2)	69.97(9)	C(14)	C(15)	C(11)	107.7(2)
C(1)	P(1)	Fe(1)	85.96(9)	C(14)	C(15)	C(16)	127.1(2)
C(2)	P(1)	Fe(1)	60.04(6)	C(11)	C(15)	C(16)	125.1(2)
N(1)	C(1)	C(7)	59.61(6)	C(14)	C(15)	Fe(1)	69.93(12)
N(1)	C(1)	P(1)	118.23(17)	C(11)	C(15)	Fe(1)	69.82(12)
C(7)	C(1)	P(1)	126.04(15)	C(16)	C(15)	Fe(1)	127.90(16)
N(1)	C(1)	Fe(1)	67.13(10)	C(15)	C(16)	H(16A)	109.5
C(7)	C(1)	Fe(1)	138.02(14)	C(15)	C(16)	H(16B)	109.5
P(1)	C(1)	Fe(1)	72.96(7)	H(16A)	C(16)	H(16B)	109.5
N(2)	C(2)	C(3)	118.61(18)	C(15)	C(16)	H(16C)	109.5
N(2)	C(2)	P(1)	114.98(14)	H(16A)	C(16)	H(16C)	109.5
C(3)	C(2)	P(1)	125.63(16)	H(16B)	C(16)	H(16C)	109.5
N(2)	C(2)	Fe(1)	67.38(10)	C(11)	C(17)	H(17A)	109.5
C(3)	C(2)	Fe(1)	136.64(14)	C(11)	C(17)	H(17B)	109.5
P(1)	C(2)	Fe(1)	73.27(7)	H(17A)	C(17)	H(17B)	109.5
C(5)	C(3)	C(2)	110.93(18)	C(11)	C(17)	H(17C)	109.5
C(5)	C(3)	C(6)	110.9(2)	H(17A)	C(17)	H(17C)	109.5
C(2)	C(3)	C(6)	111.37(19)	H(17B)	C(17)	H(17C)	109.5
C(5)	C(3)	C(4)	109.1(2)	C(12)	C(18)	H(18A)	109.5
C(2)	C(3)	C(4)	105.99(18)	C(12)	C(18)	H(18B)	109.5

[1]1-X,+Y,1/2-Z

Table S1-1-4. Torsion Angles for compound **3**

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N(2)	Fe(1)	N(1)	C(1)	121.68(16)	C(12)	Fe(1)	C(11)	C(15)	-118.40(18)
C(13)	Fe(1)	N(1)	C(1)	-63.6(3)	C(2)	Fe(1)	C(11)	C(15)	156.97(12)
C(14)	Fe(1)	N(1)	C(1)	-80.59(14)	C(1)	Fe(1)	C(11)	C(15)	52.1(2)
C(11)	Fe(1)	N(1)	C(1)	-159.12(12)	P(1)	Fe(1)	C(11)	C(15)	-158.15(16)
C(15)	Fe(1)	N(1)	C(1)	-118.62(12)	N(2)	Fe(1)	C(11)	C(17)	1.2(3)
C(12)	Fe(1)	N(1)	C(1)	177.11(16)	N(1)	Fe(1)	C(11)	C(17)	-39.6(3)
C(2)	Fe(1)	N(1)	C(1)	86.30(12)	C(13)	Fe(1)	C(11)	C(17)	160.3(3)
P(1)	Fe(1)	N(1)	C(1)	37.04(10)	C(14)	Fe(1)	C(11)	C(17)	-156.0(3)
C(13)	Fe(1)	N(1)	N(2)	174.8(2)	C(15)	Fe(1)	C(11)	C(17)	-118.3(3)
C(14)	Fe(1)	N(1)	N(2)	157.73(11)	C(12)	Fe(1)	C(11)	C(17)	123.3(3)
C(11)	Fe(1)	N(1)	N(2)	79.19(13)	C(2)	Fe(1)	C(11)	C(17)	38.7(3)
C(15)	Fe(1)	N(1)	N(2)	119.69(12)	C(1)	Fe(1)	C(11)	C(17)	-66.2(3)
C(12)	Fe(1)	N(1)	N(2)	55.4(2)	P(1)	Fe(1)	C(11)	C(17)	83.6(3)
C(2)	Fe(1)	N(1)	N(2)	-35.38(10)	C(15)	C(11)	C(12)	C(13)	1.7(2)
C(1)	Fe(1)	N(1)	N(2)	-121.68(16)	C(17)	C(11)	C(12)	C(13)	179.0(2)
P(1)	Fe(1)	N(1)	N(2)	-84.64(10)	Fe(1)	C(11)	C(12)	C(13)	-58.59(15)
C(1)	N(1)	N(2)	C(2)	-0.1(2)	C(15)	C(11)	C(12)	C(18)	-168.5(2)
Fe(1)	N(1)	N(2)	C(2)	62.02(13)	C(17)	C(11)	C(12)	C(18)	8.7(4)
C(1)	N(1)	N(2)	Fe(1)	-62.10(13)	Fe(1)	C(11)	C(12)	C(18)	131.1(2)
N(1)	Fe(1)	N(2)	C(2)	-121.46(15)	C(15)	C(11)	C(12)	Fe(1)	60.32(14)
C(13)	Fe(1)	N(2)	C(2)	62.9(2)	C(17)	C(11)	C(12)	Fe(1)	-122.4(2)
C(14)	Fe(1)	N(2)	C(2)	-173.88(18)	N(2)	Fe(1)	C(12)	C(11)	72.73(15)
C(11)	Fe(1)	N(2)	C(2)	123.59(13)	N(1)	Fe(1)	C(12)	C(11)	34.6(2)
C(15)	Fe(1)	N(2)	C(2)	163.49(12)	C(13)	Fe(1)	C(12)	C(11)	-119.97(19)
C(12)	Fe(1)	N(2)	C(2)	84.83(13)	C(14)	Fe(1)	C(12)	C(11)	-81.80(14)
C(1)	Fe(1)	N(2)	C(2)	-86.26(12)	C(15)	Fe(1)	C(12)	C(11)	-38.14(13)
P(1)	Fe(1)	N(2)	C(2)	-37.17(10)	C(2)	Fe(1)	C(12)	C(11)	114.46(13)
C(13)	Fe(1)	N(2)	N(1)	-175.61(19)	C(1)	Fe(1)	C(12)	C(11)	-154.8(4)
C(14)	Fe(1)	N(2)	N(1)	-52.4(2)	P(1)	Fe(1)	C(12)	C(11)	165.50(11)
C(11)	Fe(1)	N(2)	N(1)	-114.95(12)	N(2)	Fe(1)	C(12)	C(13)	-167.30(12)
C(15)	Fe(1)	N(2)	N(1)	-75.05(13)	N(1)	Fe(1)	C(12)	C(13)	154.54(15)
C(12)	Fe(1)	N(2)	N(1)	-153.71(12)	C(14)	Fe(1)	C(12)	C(13)	38.17(13)
C(2)	Fe(1)	N(2)	N(1)	121.46(15)	C(11)	Fe(1)	C(12)	C(13)	119.97(19)
C(1)	Fe(1)	N(2)	N(1)	35.19(10)	C(15)	Fe(1)	C(12)	C(13)	81.82(14)
P(1)	Fe(1)	N(2)	N(1)	84.29(10)	C(2)	Fe(1)	C(12)	C(13)	-125.58(13)

N(2)	Fe(1)	P(1)	C(1)	-72.93(9)	C(1)	Fe(1)	C(12)	C(13)	-34.8(5)
N(1)	Fe(1)	P(1)	C(1)	-31.07(9)	P(1)	Fe(1)	C(12)	C(13)	-74.53(13)
C(13)	Fe(1)	P(1)	C(1)	129.97(10)	N(2)	Fe(1)	C(12)	C(18)	-48.7(3)
C(14)	Fe(1)	P(1)	C(1)	88.24(10)	N(1)	Fe(1)	C(12)	C(18)	-86.8(3)
C(11)	Fe(1)	P(1)	C(1)	-159.9(2)	C(13)	Fe(1)	C(12)	C(18)	118.6(3)
C(15)	Fe(1)	P(1)	C(1)	56.79(17)	C(14)	Fe(1)	C(12)	C(18)	156.8(3)
C(12)	Fe(1)	P(1)	C(1)	170.24(10)	C(11)	Fe(1)	C(12)	C(18)	-121.4(3)
C(2)	Fe(1)	P(1)	C(1)	-104.11(10)	C(15)	Fe(1)	C(12)	C(18)	-159.6(3)
N(2)	Fe(1)	P(1)	C(2)	31.18(9)	C(2)	Fe(1)	C(12)	C(18)	-7.0(3)
N(1)	Fe(1)	P(1)	C(2)	73.04(9)	C(1)	Fe(1)	C(12)	C(18)	83.8(5)
C(13)	Fe(1)	P(1)	C(2)	-125.92(10)	P(1)	Fe(1)	C(12)	C(18)	44.1(3)
C(14)	Fe(1)	P(1)	C(2)	-167.65(10)	C(11)	C(12)	C(13)	C(14)	-1.8(2)
C(11)	Fe(1)	P(1)	C(2)	-55.8(2)	C(18)	C(12)	C(13)	C(14)	168.7(2)
C(15)	Fe(1)	P(1)	C(2)	160.90(17)	Fe(1)	C(12)	C(13)	C(14)	-60.42(14)
C(12)	Fe(1)	P(1)	C(2)	-85.65(11)	C(11)	C(12)	C(13)	C(19)	-176.2(2)
C(1)	Fe(1)	P(1)	C(2)	104.11(10)	C(18)	C(12)	C(13)	C(19)	-5.7(4)
N(2)	N(1)	C(1)	C(7)	-166.96(16)	Fe(1)	C(12)	C(13)	C(19)	125.2(2)
Fe(1)	N(1)	C(1)	C(7)	133.57(17)	C(11)	C(12)	C(13)	Fe(1)	58.64(15)
N(2)	N(1)	C(1)	P(1)	2.5(2)	C(18)	C(12)	C(13)	Fe(1)	-130.9(2)
Fe(1)	N(1)	C(1)	P(1)	-56.99(11)	N(2)	Fe(1)	C(13)	C(12)	30.2(3)
N(2)	N(1)	C(1)	Fe(1)	59.47(12)	N(1)	Fe(1)	C(13)	C(12)	-140.7(2)
C(2)	P(1)	C(1)	N(1)	-3.08(15)	C(14)	Fe(1)	C(13)	C(12)	-118.20(19)
Fe(1)	P(1)	C(1)	N(1)	53.92(13)	C(11)	Fe(1)	C(13)	C(12)	-36.89(14)
C(2)	P(1)	C(1)	C(7)	165.40(18)	C(15)	Fe(1)	C(13)	C(12)	-80.69(15)
Fe(1)	P(1)	C(1)	C(7)	-137.61(19)	C(2)	Fe(1)	C(13)	C(12)	75.28(16)
C(2)	P(1)	C(1)	Fe(1)	-57.00(7)	C(1)	Fe(1)	C(13)	C(12)	171.60(13)
N(2)	Fe(1)	C(1)	N(1)	-36.63(11)	P(1)	Fe(1)	C(13)	C(12)	123.96(12)
C(13)	Fe(1)	C(1)	N(1)	158.12(11)	N(2)	Fe(1)	C(13)	C(14)	148.44(19)
C(14)	Fe(1)	C(1)	N(1)	118.07(12)	N(1)	Fe(1)	C(13)	C(14)	-22.5(3)
C(11)	Fe(1)	C(1)	N(1)	40.0(2)	C(11)	Fe(1)	C(13)	C(14)	81.31(14)
C(15)	Fe(1)	C(1)	N(1)	75.13(13)	C(15)	Fe(1)	C(13)	C(14)	37.51(13)
C(12)	Fe(1)	C(1)	N(1)	-173.1(4)	C(12)	Fe(1)	C(13)	C(14)	118.20(19)
C(2)	Fe(1)	C(1)	N(1)	-78.28(12)	C(2)	Fe(1)	C(13)	C(14)	-166.51(12)
P(1)	Fe(1)	C(1)	N(1)	-127.20(13)	C(1)	Fe(1)	C(13)	C(14)	-70.20(16)
N(2)	Fe(1)	C(1)	C(7)	-144.0(2)	P(1)	Fe(1)	C(13)	C(14)	-117.83(12)
N(1)	Fe(1)	C(1)	C(7)	-107.4(2)	N(2)	Fe(1)	C(13)	C(19)	-91.7(3)
C(13)	Fe(1)	C(1)	C(7)	50.7(2)	N(1)	Fe(1)	C(13)	C(19)	97.3(3)
C(14)	Fe(1)	C(1)	C(7)	10.7(2)	C(14)	Fe(1)	C(13)	C(19)	119.8(3)
C(11)	Fe(1)	C(1)	C(7)	-67.4(3)	C(11)	Fe(1)	C(13)	C(19)	-158.8(2)
C(15)	Fe(1)	C(1)	C(7)	-32.3(2)	C(15)	Fe(1)	C(13)	C(19)	157.4(2)

C(12)	Fe(1)	C(1)	C(7)	79.6(5)		C(12)	Fe(1)	C(13)	C(19)	-121.9(3)	
C(2)	Fe(1)	C(1)	C(7)	174.3(2)		C(2)	Fe(1)	C(13)	C(19)	-46.7(2)	
P(1)	Fe(1)	C(1)	C(7)	125.4(2)		C(1)	Fe(1)	C(13)	C(19)	49.7(3)	
N(2)	Fe(1)	C(1)	P(1)	90.57(8)		P(1)	Fe(1)	C(13)	C(19)	2.0(2)	
N(1)	Fe(1)	C(1)	P(1)	127.20(13)		C(12)	C(13)	C(14)	C(15)	1.2(2)	
C(13)	Fe(1)	C(1)	P(1)	-74.67(11)		C(19)	C(13)	C(14)	C(15)	175.6(2)	
C(14)	Fe(1)	C(1)	P(1)	-114.73(8)		Fe(1)	C(13)	C(14)	C(15)	-59.86(14)	
C(11)	Fe(1)	C(1)	P(1)	167.21(13)		C(12)	C(13)	C(14)	C(20)	-170.7(2)	
C(15)	Fe(1)	C(1)	P(1)	-157.67(8)		C(19)	C(13)	C(14)	C(20)	3.7(3)	
C(12)	Fe(1)	C(1)	P(1)	-45.9(4)		Fe(1)	C(13)	C(14)	C(20)	128.2(2)	
C(2)	Fe(1)	C(1)	P(1)	48.92(7)		C(12)	C(13)	C(14)	Fe(1)	61.01(15)	
N(1)	N(2)	C(2)	C(3)	168.13(16)		C(19)	C(13)	C(14)	Fe(1)	-124.5(2)	
Fe(1)	N(2)	C(2)	C(3)	-132.06(17)		N(2)	Fe(1)	C(14)	C(15)	-31.7(3)	
N(1)	N(2)	C(2)	P(1)	-2.4(2)		N(1)	Fe(1)	C(14)	C(15)	-69.20(15)	
Fe(1)	N(2)	C(2)	P(1)	57.45(11)		C(13)	Fe(1)	C(14)	C(15)	119.03(19)	
N(1)	N(2)	C(2)	Fe(1)	-59.81(12)		C(11)	Fe(1)	C(14)	C(15)	37.93(13)	
C(1)	P(1)	C(2)	N(2)	3.04(15)		C(12)	Fe(1)	C(14)	C(15)	81.20(14)	
Fe(1)	P(1)	C(2)	N(2)	-54.34(12)		C(2)	Fe(1)	C(14)	C(15)	162.9(3)	
C(1)	P(1)	C(2)	C(3)	-166.67(18)		C(1)	Fe(1)	C(14)	C(15)	-110.14(13)	
Fe(1)	P(1)	C(2)	C(3)	135.94(19)		P(1)	Fe(1)	C(14)	C(15)	-160.95(11)	
C(1)	P(1)	C(2)	Fe(1)	57.38(7)		N(2)	Fe(1)	C(14)	C(13)	-150.70(17)	
N(1)	Fe(1)	C(2)	N(2)	36.73(10)		N(1)	Fe(1)	C(14)	C(13)	171.77(12)	
C(13)	Fe(1)	C(2)	N(2)	-154.83(11)		C(11)	Fe(1)	C(14)	C(13)	-81.10(14)	
C(14)	Fe(1)	C(2)	N(2)	170.7(3)		C(15)	Fe(1)	C(14)	C(13)	-119.03(19)	
C(11)	Fe(1)	C(2)	N(2)	-70.97(14)		C(12)	Fe(1)	C(14)	C(13)	-37.83(13)	
C(15)	Fe(1)	C(2)	N(2)	-35.2(2)		C(2)	Fe(1)	C(14)	C(13)	43.9(4)	
C(12)	Fe(1)	C(2)	N(2)	-113.60(12)		C(1)	Fe(1)	C(14)	C(13)	130.83(13)	
C(1)	Fe(1)	C(2)	N(2)	78.28(11)		P(1)	Fe(1)	C(14)	C(13)	80.02(13)	
P(1)	Fe(1)	C(2)	N(2)	127.07(13)		N(2)	Fe(1)	C(14)	C(20)	91.3(3)	
N(2)	Fe(1)	C(2)	C(3)	108.3(2)		N(1)	Fe(1)	C(14)	C(20)	53.8(3)	
N(1)	Fe(1)	C(2)	C(3)	145.1(2)		C(13)	Fe(1)	C(14)	C(20)	-118.0(3)	
C(13)	Fe(1)	C(2)	C(3)	-46.5(2)		C(11)	Fe(1)	C(14)	C(20)	160.9(3)	
C(14)	Fe(1)	C(2)	C(3)	-81.0(4)		C(15)	Fe(1)	C(14)	C(20)	123.0(3)	
C(11)	Fe(1)	C(2)	C(3)	37.4(2)		C(12)	Fe(1)	C(14)	C(20)	-155.8(3)	
C(15)	Fe(1)	C(2)	C(3)	73.1(3)		C(2)	Fe(1)	C(14)	C(20)	-74.1(4)	
C(12)	Fe(1)	C(2)	C(3)	-5.3(2)		C(1)	Fe(1)	C(14)	C(20)	12.8(3)	
C(1)	Fe(1)	C(2)	C(3)	-173.4(2)		P(1)	Fe(1)	C(14)	C(20)	-38.0(3)	
P(1)	Fe(1)	C(2)	C(3)	-124.6(2)		C(13)	C(14)	C(15)	C(11)	-0.1(2)	
N(2)	Fe(1)	C(2)	P(1)	-127.07(13)		C(20)	C(14)	C(15)	C(11)	171.4(2)	
N(1)	Fe(1)	C(2)	P(1)	-90.34(8)		Fe(1)	C(14)	C(15)	C(11)	-59.85(14)	

C(13)	Fe(1)	C(2)	P(1)	78.09(11)	C(13)	C(14)	C(15)	C(16)	-177.3(2)
C(14)	Fe(1)	C(2)	P(1)	43.6(3)	C(20)	C(14)	C(15)	C(16)	-5.8(4)
C(11)	Fe(1)	C(2)	P(1)	161.95(9)	Fe(1)	C(14)	C(15)	C(16)	122.9(2)
C(15)	Fe(1)	C(2)	P(1)	-162.28(16)	C(13)	C(14)	C(15)	Fe(1)	59.76(14)
C(12)	Fe(1)	C(2)	P(1)	119.33(9)	C(20)	C(14)	C(15)	Fe(1)	-128.7(2)
C(1)	Fe(1)	C(2)	P(1)	-48.80(7)	C(12)	C(11)	C(15)	C(14)	-1.0(2)
N(2)	C(2)	C(3)	C(5)	155.8(2)	C(17)	C(11)	C(15)	C(14)	-178.4(2)
P(1)	C(2)	C(3)	C(5)	-34.8(3)	Fe(1)	C(11)	C(15)	C(14)	59.92(14)
Fe(1)	C(2)	C(3)	C(5)	69.3(3)	C(12)	C(11)	C(15)	C(16)	176.3(2)
N(2)	C(2)	C(3)	C(6)	31.8(3)	C(17)	C(11)	C(15)	C(16)	-1.1(3)
P(1)	C(2)	C(3)	C(6)	-158.84(17)	Fe(1)	C(11)	C(15)	C(16)	-122.8(2)
Fe(1)	C(2)	C(3)	C(6)	-54.8(3)	C(12)	C(11)	C(15)	Fe(1)	-60.93(15)
N(2)	C(2)	C(3)	C(4)	-85.9(2)	C(17)	C(11)	C(15)	Fe(1)	121.7(2)
P(1)	C(2)	C(3)	C(4)	83.5(2)	N(2)	Fe(1)	C(15)	C(14)	166.03(11)
Fe(1)	C(2)	C(3)	C(4)	-172.40(19)	N(1)	Fe(1)	C(15)	C(14)	126.07(12)
N(1)	C(1)	C(7)	C(9)	-34.6(3)	C(13)	Fe(1)	C(15)	C(14)	-37.65(12)
P(1)	C(1)	C(7)	C(9)	157.29(16)	C(11)	Fe(1)	C(15)	C(14)	-118.63(18)
Fe(1)	C(1)	C(7)	C(9)	51.8(3)	C(12)	Fe(1)	C(15)	C(14)	-80.99(14)
N(1)	C(1)	C(7)	C(8)	-158.85(19)	C(2)	Fe(1)	C(15)	C(14)	-169.60(17)
P(1)	C(1)	C(7)	C(8)	33.0(3)	C(1)	Fe(1)	C(15)	C(14)	87.72(14)
Fe(1)	C(1)	C(7)	C(8)	-72.4(3)	P(1)	Fe(1)	C(15)	C(14)	44.1(2)
N(1)	C(1)	C(7)	C(10)	83.7(2)	N(2)	Fe(1)	C(15)	C(11)	-75.34(14)
P(1)	C(1)	C(7)	C(10)	-84.5(2)	N(1)	Fe(1)	C(15)	C(11)	-115.29(13)
Fe(1)	C(1)	C(7)	C(10)	170.06(19)	C(13)	Fe(1)	C(15)	C(11)	80.98(14)
N(2)	Fe(1)	C(11)	C(12)	-122.14(13)	C(14)	Fe(1)	C(15)	C(11)	118.63(18)
N(1)	Fe(1)	C(11)	C(12)	-162.94(12)	C(12)	Fe(1)	C(15)	C(11)	37.64(13)
C(13)	Fe(1)	C(11)	C(12)	36.97(12)	C(2)	Fe(1)	C(15)	C(11)	-51.0(2)
C(14)	Fe(1)	C(11)	C(12)	80.69(14)	C(1)	Fe(1)	C(15)	C(11)	-153.65(13)
C(15)	Fe(1)	C(11)	C(12)	118.40(18)	P(1)	Fe(1)	C(15)	C(11)	162.69(13)
C(2)	Fe(1)	C(11)	C(12)	-84.63(14)	N(2)	Fe(1)	C(15)	C(16)	44.1(3)
C(1)	Fe(1)	C(11)	C(12)	170.46(15)	N(1)	Fe(1)	C(15)	C(16)	4.1(2)
P(1)	Fe(1)	C(11)	C(12)	-39.8(3)	C(13)	Fe(1)	C(15)	C(16)	-159.6(3)
N(2)	Fe(1)	C(11)	C(15)	119.47(13)	C(14)	Fe(1)	C(15)	C(16)	-122.0(3)
N(1)	Fe(1)	C(11)	C(15)	78.66(14)	C(11)	Fe(1)	C(15)	C(16)	119.4(3)
C(13)	Fe(1)	C(11)	C(15)	-81.42(13)	C(12)	Fe(1)	C(15)	C(16)	157.0(3)
C(14)	Fe(1)	C(11)	C(15)	-37.71(12)	P(1)	Fe(1)	C(15)	C(16)	-77.9(3)

[1]1-X,+Y,1/2-Z

Table S1-2. Crystal structural analysis data for **4**

Table S1-2-1. Crystal data and structure refinement for compound **4**

Identification code	Exp_1677
Empirical formula	$C_{24}H_{25}N_2FeP$
Formula weight	428.28
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	*C c*
a/Å	15.7621(4)
b/Å	7.4818(2)
c/Å	17.8088(4)
α/°	90.00
β/°	95.917(2)
γ/°	90.00
Volume/Å^3	2088.98(9)
Z	4
ρ_{calc}g/cm^3	1.362
μ/mm^{-1}	6.587
F(000)	896.0
Crystal size/mm^3	0.250 × 0.160 × 0.070
Radiation	Mo Kα (λ = 0.71073)
2*Θ* range for data collection/°	6.56 to 67.05
Index ranges	−17 ≤ h ≤ 18, −8 ≤ k ≤ 8, −14 ≤ l ≤ 21
Reflections collected	3581
Independent reflections	2238 [R_{int} = 0.0277, R_{sigma} = 0.0261]
Data/restraints/parameters	2238/50/258
Goodness-of-fit on F^2	1.064
Final *R* indexes [I>=2*σ* (I)]	R_1 = 0.0673, wR_2 = 0.1808
Final *R* indexes [all data]	R_1 = 0.0694, wR_2 = 0.1841
Largest diff. peak/hole / e Å^{-3}	0.795/–0.976

Table S1-2-2. Bond Lengths for compound **4**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1)	C(6)	1.383(11)	C(15)	H(15B)	0.9600
C(1)	C(2)	1.405(10)	C(15)	H(15C)	0.9600
C(1)	H(1)	0.9300	C(16)	C(17)	1.415(12)
C(2)	C(3)	1.377(11)	C(16)	C(23)	1.444(9)
C(2)	H(2)	0.9300	C(16)	Fe(1)	2.065(7)
C(3)	C(4)	1.381(11)	C(17)	C(19)	1.421(12)
C(3)	H(3)	0.9300	C(17)	C(18)	1.539(13)
C(4)	C(5)	1.401(11)	C(17)	Fe(1)	2.053(8)
C(4)	H(4)	0.9300	C(18)	H(18A)	0.9600
C(5)	C(6)	1.383(10)	C(18)	H(18B)	0.9600
C(5)	H(5)	0.9300	C(18)	H(18C)	0.9600
C(6)	C(7)	1.479(9)	C(19)	C(21)	1.431(11)
C(7)	N(1)	1.376(9)	C(19)	C(20)	1.494(11)
C(7)	P(1)	1.790(7)	C(19)	Fe(1)	2.065(7)
C(7)	Fe(1)	2.078(8)	C(20)	H(20A)	0.9600
C(8)	N(2)	1.380(9)	C(20)	H(20B)	0.9600
C(8)	C(9)	1.479(9)	C(20)	H(20C)	0.9600
C(8)	P(1)	1.791(7)	C(21)	C(23)	1.414(11)
C(8)	Fe(1)	2.084(7)	C(21)	C(22)	1.506(10)
C(9)	C(14)	1.384(11)	C(21)	Fe(1)	2.062(7)
C(9)	C(10)	1.392(11)	C(22)	H(22A)	0.9600
C(10)	C(11)	1.396(11)	C(22)	H(22B)	0.9600
C(10)	H(10)	0.9300	C(22)	H(22C)	0.9600
C(11)	C(12)	1.367(13)	C(23)	C(24)	1.490(11)
C(11)	H(11)	0.9300	C(23)	Fe(1)	2.071(7)
C(12)	C(13)	1.397(13)	C(24)	H(24A)	0.9600
C(12)	H(12)	0.9300	C(24)	H(24B)	0.9600
C(13)	C(14)	1.401(12)	C(24)	H(24C)	0.9600
C(13)	H(13)	0.9300	Fe(1)	N(1)	1.989(6)
C(14)	H(14)	0.9300	Fe(1)	N(2)	2.015(6)
C(15)	C(16)	1.487(10)	Fe(1)	P(1)	2.304(2)
C(15)	H(15A)	0.9600	N(1)	N(2)	1.377(8)

1- X,+Y,1/2-Z

Table S1-2-3. Bond Angles for compound **4**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C(6)	C(1)	C(2)	119.8(7)	H(20A)	C(20)	H(20C)	109.5
C(6)	C(1)	H(1)	120.1	H(20B)	C(20)	H(20C)	109.5
C(2)	C(1)	H(1)	120.1	C(23)	C(21)	C(19)	108.7(6)
C(3)	C(2)	C(1)	119.7(7)	C(23)	C(21)	C(22)	126.8(7)
C(3)	C(2)	H(2)	120.1	C(19)	C(21)	C(22)	124.5(7)
C(1)	C(2)	H(2)	120.1	C(23)	C(21)	Fe(1)	70.4(4)
C(2)	C(3)	C(4)	121.0(7)	C(19)	C(21)	Fe(1)	69.8(4)
C(2)	C(3)	H(3)	119.5	C(22)	C(21)	Fe(1)	127.7(6)
C(4)	C(3)	H(3)	119.5	C(21)	C(22)	H(22A)	109.5
C(3)	C(4)	C(5)	119.1(7)	C(21)	C(22)	H(22B)	109.5
C(3)	C(4)	H(4)	120.4	H(22A)	C(22)	H(22B)	109.5
C(5)	C(4)	H(4)	120.4	C(21)	C(22)	H(22C)	109.5
C(6)	C(5)	C(4)	120.4(7)	H(22A)	C(22)	H(22C)	109.5
C(6)	C(5)	H(5)	119.8	H(22B)	C(22)	H(22C)	109.5
C(4)	C(5)	H(5)	119.8	C(21)	C(23)	C(16)	107.9(6)
C(5)	C(6)	C(1)	120.0(6)	C(21)	C(23)	C(24)	127.8(7)
C(5)	C(6)	C(7)	121.1(6)	C(16)	C(23)	C(24)	124.3(7)
C(1)	C(6)	C(7)	118.9(6)	C(21)	C(23)	Fe(1)	69.6(4)
N(1)	C(7)	C(6)	119.0(6)	C(16)	C(23)	Fe(1)	69.3(4)
N(1)	C(7)	P(1)	114.2(5)	C(24)	C(23)	Fe(1)	125.3(5)
C(6)	C(7)	P(1)	126.6(5)	C(23)	C(24)	H(24A)	109.5
N(1)	C(7)	Fe(1)	66.8(4)	C(23)	C(24)	H(24B)	109.5
C(6)	C(7)	Fe(1)	125.1(5)	H(24A)	C(24)	H(24B)	109.5
P(1)	C(7)	Fe(1)	72.7(3)	C(23)	C(24)	H(24C)	109.5
N(2)	C(8)	C(9)	118.2(6)	H(24A)	C(24)	H(24C)	109.5
N(2)	C(8)	P(1)	114.5(5)	H(24B)	C(24)	H(24C)	109.5
C(9)	C(8)	P(1)	127.2(5)	N(1)	Fe(1)	N(2)	40.2(2)
N(2)	C(8)	Fe(1)	67.7(4)	N(1)	Fe(1)	C(17)	156.5(3)
C(9)	C(8)	Fe(1)	126.4(5)	N(2)	Fe(1)	C(17)	123.1(3)
P(1)	C(8)	Fe(1)	72.5(3)	N(1)	Fe(1)	C(21)	120.7(3)
C(14)	C(9)	C(10)	119.6(7)	N(2)	Fe(1)	C(21)	154.8(3)
C(14)	C(9)	C(8)	119.7(7)	C(17)	Fe(1)	C(21)	67.7(3)
C(10)	C(9)	C(8)	120.7(7)	N(1)	Fe(1)	C(19)	158.7(3)
C(9)	C(10)	C(11)	120.3(7)	N(2)	Fe(1)	C(19)	161.0(3)

C(9)	C(10)	H(10)	119.8	C(17)	Fe(1)	C(19)	40.4(3)
C(11)	C(10)	H(10)	119.8	C(21)	Fe(1)	C(19)	40.6(3)
C(12)	C(11)	C(10)	119.7(8)	N(1)	Fe(1)	C(16)	119.1(3)
C(12)	C(11)	H(11)	120.1	N(2)	Fe(1)	C(16)	104.5(3)
C(10)	C(11)	H(11)	120.1	C(17)	Fe(1)	C(16)	40.2(3)
C(11)	C(12)	C(13)	121.0(8)	C(21)	Fe(1)	C(16)	68.1(3)
C(11)	C(12)	H(12)	119.5	C(19)	Fe(1)	C(16)	68.2(3)
C(13)	C(12)	H(12)	119.5	N(1)	Fe(1)	C(23)	103.7(3)
C(12)	C(13)	C(14)	118.9(8)	N(2)	Fe(1)	C(23)	118.8(3)
C(12)	C(13)	H(13)	120.5	C(17)	Fe(1)	C(23)	67.7(3)
C(14)	C(13)	H(13)	120.5	C(21)	Fe(1)	C(23)	40.0(3)
C(9)	C(14)	C(13)	120.4(8)	C(19)	Fe(1)	C(23)	67.9(3)
C(9)	C(14)	H(14)	119.8	C(16)	Fe(1)	C(23)	40.9(3)
C(13)	C(14)	H(14)	119.8	N(1)	Fe(1)	C(7)	39.5(3)
C(16)	C(15)	H(15A)	109.5	N(2)	Fe(1)	C(7)	68.3(3)
C(16)	C(15)	H(15B)	109.5	C(17)	Fe(1)	C(7)	163.9(3)
H(15A)	C(15)	H(15B)	109.5	C(21)	Fe(1)	C(7)	107.2(3)
C(16)	C(15)	H(15C)	109.5	C(19)	Fe(1)	C(7)	125.9(3)
H(15A)	C(15)	H(15C)	109.5	C(16)	Fe(1)	C(7)	153.9(3)
H(15B)	C(15)	H(15C)	109.5	C(23)	Fe(1)	C(7)	119.0(3)
C(17)	C(16)	C(23)	106.9(7)	N(1)	Fe(1)	C(8)	68.4(2)
C(17)	C(16)	C(15)	128.5(7)	N(2)	Fe(1)	C(8)	39.3(3)
C(23)	C(16)	C(15)	124.6(7)	C(17)	Fe(1)	C(8)	109.1(3)
C(17)	C(16)	Fe(1)	69.4(4)	C(21)	Fe(1)	C(8)	165.2(3)
C(23)	C(16)	Fe(1)	69.8(4)	C(19)	Fe(1)	C(8)	127.7(3)
C(15)	C(16)	Fe(1)	126.9(5)	C(16)	Fe(1)	C(8)	119.4(3)
C(16)	C(17)	C(19)	109.6(8)	C(23)	Fe(1)	C(8)	153.6(3)
C(16)	C(17)	C(18)	127.0(9)	C(7)	Fe(1)	C(8)	71.8(3)
C(19)	C(17)	C(18)	123.4(8)	N(1)	Fe(1)	P(1)	76.45(18)
C(16)	C(17)	Fe(1)	70.4(5)	N(2)	Fe(1)	P(1)	76.22(18)
C(19)	C(17)	Fe(1)	70.3(5)	C(17)	Fe(1)	P(1)	120.2(2)
C(18)	C(17)	Fe(1)	127.4(6)	C(21)	Fe(1)	P(1)	120.2(2)
C(17)	C(18)	H(18A)	109.5	C(19)	Fe(1)	P(1)	103.6(2)
C(17)	C(18)	H(18B)	109.5	C(16)	Fe(1)	P(1)	157.3(2)
H(18A)	C(18)	H(18B)	109.5	C(23)	Fe(1)	P(1)	157.4(2)
C(17)	C(18)	H(18C)	109.5	C(7)	Fe(1)	P(1)	47.9(2)
H(18A)	C(18)	H(18C)	109.5	C(8)	Fe(1)	P(1)	47.9(2)
H(18B)	C(18)	H(18C)	109.5	C(7)	N(1)	N(2)	113.0(6)
C(17)	C(19)	C(21)	106.9(7)	C(7)	N(1)	Fe(1)	73.7(4)
C(17)	C(19)	C(20)	127.4(8)	N(2)	N(1)	Fe(1)	70.9(3)

C(21)	C(19)	C(20)	125.7(7)		N(1)	N(2)	C(8)	112.3(6)
C(17)	C(19)	Fe(1)	69.4(4)		N(1)	N(2)	Fe(1)	68.8(3)
C(21)	C(19)	Fe(1)	69.6(4)		C(8)	N(2)	Fe(1)	73.0(4)
C(20)	C(19)	Fe(1)	127.7(5)		C(7)	P(1)	C(8)	85.9(3)
C(19)	C(20)	H(20A)	109.5		C(7)	P(1)	Fe(1)	59.4(3)
C(19)	C(20)	H(20B)	109.5		C(8)	P(1)	Fe(1)	59.6(2)
H(20A)	C(20)	H(20B)	109.5					

-X,+Y,1/2-Z

Table S1-2-4. Torsion Angles for compound **4**

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C(6)	C(1)	C(2)	C(3)	-0.4(11)	C(15)	C(16)	Fe(1)	C(7)	-71.3(10)
C(1)	C(2)	C(3)	C(4)	0.2(12)	C(17)	C(16)	Fe(1)	C(8)	-85.0(5)
C(2)	C(3)	C(4)	C(5)	-1.1(12)	C(23)	C(16)	Fe(1)	C(8)	157.0(4)
C(3)	C(4)	C(5)	C(6)	2.2(11)	C(15)	C(16)	Fe(1)	C(8)	38.3(8)
C(4)	C(5)	C(6)	C(1)	-2.4(11)	C(17)	C(16)	Fe(1)	P(1)	-35.5(9)
C(4)	C(5)	C(6)	C(7)	-180.0(7)	C(23)	C(16)	Fe(1)	P(1)	-153.5(5)
C(2)	C(1)	C(6)	C(5)	1.5(11)	C(15)	C(16)	Fe(1)	P(1)	87.8(9)
C(2)	C(1)	C(6)	C(7)	179.1(7)	C(21)	C(23)	Fe(1)	N(1)	121.7(4)
C(5)	C(6)	C(7)	N(1)	176.2(6)	C(16)	C(23)	Fe(1)	N(1)	-118.9(4)
C(1)	C(6)	C(7)	N(1)	-1.3(10)	C(24)	C(23)	Fe(1)	N(1)	-0.8(7)
C(5)	C(6)	C(7)	P(1)	-9.1(11)	C(21)	C(23)	Fe(1)	N(2)	162.0(4)
C(1)	C(6)	C(7)	P(1)	173.4(6)	C(16)	C(23)	Fe(1)	N(2)	-78.6(5)
C(5)	C(6)	C(7)	Fe(1)	-103.1(8)	C(24)	C(23)	Fe(1)	N(2)	39.5(8)
C(1)	C(6)	C(7)	Fe(1)	79.4(8)	C(21)	C(23)	Fe(1)	C(17)	-81.4(5)
N(2)	C(8)	C(9)	C(14)	18.1(10)	C(16)	C(23)	Fe(1)	C(17)	38.0(5)
P(1)	C(8)	C(9)	C(14)	-159.1(6)	C(24)	C(23)	Fe(1)	C(17)	156.1(8)
Fe(1)	C(8)	C(9)	C(14)	-63.9(9)	C(16)	C(23)	Fe(1)	C(21)	119.4(6)
N(2)	C(8)	C(9)	C(10)	-160.7(7)	C(24)	C(23)	Fe(1)	C(21)	-122.6(8)
P(1)	C(8)	C(9)	C(10)	22.1(10)	C(21)	C(23)	Fe(1)	C(19)	-37.6(4)
Fe(1)	C(8)	C(9)	C(10)	117.4(7)	C(16)	C(23)	Fe(1)	C(19)	81.8(4)
C(14)	C(9)	C(10)	C(11)	2.0(11)	C(24)	C(23)	Fe(1)	C(19)	-160.2(7)
C(8)	C(9)	C(10)	C(11)	-179.2(7)	C(21)	C(23)	Fe(1)	C(16)	-119.4(6)
C(9)	C(10)	C(11)	C(12)	-0.6(12)	C(24)	C(23)	Fe(1)	C(16)	118.0(8)
C(10)	C(11)	C(12)	C(13)	-1.0(13)	C(21)	C(23)	Fe(1)	C(7)	82.3(5)
C(11)	C(12)	C(13)	C(14)	1.1(13)	C(16)	C(23)	Fe(1)	C(7)	-158.3(4)
C(10)	C(9)	C(14)	C(13)	-2.0(12)	C(24)	C(23)	Fe(1)	C(7)	-40.2(8)

C(8)	C(9)	C(14)	C(13)	179.2(7)	C(21)	C(23)	Fe(1)	C(8)	-169.4(6)
C(12)	C(13)	C(14)	C(9)	0.5(12)	C(16)	C(23)	Fe(1)	C(8)	-50.0(8)
C(23)	C(16)	C(17)	C(19)	0.5(8)	C(24)	C(23)	Fe(1)	C(8)	68.0(10)
C(15)	C(16)	C(17)	C(19)	179.1(7)	C(21)	C(23)	Fe(1)	P(1)	34.0(8)
Fe(1)	C(16)	C(17)	C(19)	-59.5(5)	C(16)	C(23)	Fe(1)	P(1)	153.4(5)
C(23)	C(16)	C(17)	C(18)	-177.4(7)	C(24)	C(23)	Fe(1)	P(1)	-88.6(8)
C(15)	C(16)	C(17)	C(18)	1.3(13)	C(6)	C(7)	Fe(1)	N(1)	-110.1(7)
Fe(1)	C(16)	C(17)	C(18)	122.6(8)	P(1)	C(7)	Fe(1)	N(1)	126.9(4)
C(23)	C(16)	C(17)	Fe(1)	60.0(5)	N(1)	C(7)	Fe(1)	N(2)	-36.1(4)
C(15)	C(16)	C(17)	Fe(1)	-121.3(8)	C(6)	C(7)	Fe(1)	N(2)	-146.1(7)
C(16)	C(17)	C(19)	C(21)	-0.2(8)	P(1)	C(7)	Fe(1)	N(2)	90.9(3)
C(18)	C(17)	C(19)	C(21)	177.8(7)	N(1)	C(7)	Fe(1)	C(17)	-173.5(9)
Fe(1)	C(17)	C(19)	C(21)	-59.8(5)	C(6)	C(7)	Fe(1)	C(17)	76.4(12)
C(16)	C(17)	C(19)	C(20)	-178.1(7)	P(1)	C(7)	Fe(1)	C(17)	-46.6(11)
C(18)	C(17)	C(19)	C(20)	-0.1(12)	N(1)	C(7)	Fe(1)	C(21)	117.6(4)
Fe(1)	C(17)	C(19)	C(20)	122.3(8)	C(6)	C(7)	Fe(1)	C(21)	7.6(7)
C(16)	C(17)	C(19)	Fe(1)	59.6(5)	P(1)	C(7)	Fe(1)	C(21)	-115.4(3)
C(18)	C(17)	C(19)	Fe(1)	-122.5(8)	N(1)	C(7)	Fe(1)	C(19)	158.4(4)
C(17)	C(19)	C(21)	C(23)	-0.3(8)	C(6)	C(7)	Fe(1)	C(19)	48.3(7)
C(20)	C(19)	C(21)	C(23)	177.7(7)	P(1)	C(7)	Fe(1)	C(19)	-74.7(4)
Fe(1)	C(19)	C(21)	C(23)	-59.9(5)	N(1)	C(7)	Fe(1)	C(16)	42.4(8)
C(17)	C(19)	C(21)	C(22)	-177.9(7)	C(6)	C(7)	Fe(1)	C(16)	-67.7(10)
C(20)	C(19)	C(21)	C(22)	0.1(12)	P(1)	C(7)	Fe(1)	C(16)	169.3(5)
Fe(1)	C(19)	C(21)	C(22)	122.5(8)	N(1)	C(7)	Fe(1)	C(23)	75.8(4)
C(17)	C(19)	C(21)	Fe(1)	59.6(5)	C(6)	C(7)	Fe(1)	C(23)	-34.3(7)
C(20)	C(19)	C(21)	Fe(1)	-122.4(8)	P(1)	C(7)	Fe(1)	C(23)	-157.3(3)
C(19)	C(21)	C(23)	C(16)	0.6(8)	N(1)	C(7)	Fe(1)	C(8)	-77.8(4)
C(22)	C(21)	C(23)	C(16)	178.1(7)	C(6)	C(7)	Fe(1)	C(8)	172.1(7)
Fe(1)	C(21)	C(23)	C(16)	-59.0(5)	P(1)	C(7)	Fe(1)	C(8)	49.1(3)
C(19)	C(21)	C(23)	C(24)	179.0(7)	N(1)	C(7)	Fe(1)	P(1)	-126.9(4)
C(22)	C(21)	C(23)	C(24)	-3.4(13)	C(6)	C(7)	Fe(1)	P(1)	123.0(7)
Fe(1)	C(21)	C(23)	C(24)	119.5(8)	N(2)	C(8)	Fe(1)	N(1)	35.7(4)
C(19)	C(21)	C(23)	Fe(1)	59.5(5)	C(9)	C(8)	Fe(1)	N(1)	145.1(7)
C(22)	C(21)	C(23)	Fe(1)	-122.9(8)	P(1)	C(8)	Fe(1)	N(1)	-91.1(3)
C(17)	C(16)	C(23)	C(21)	-0.7(8)	C(9)	C(8)	Fe(1)	N(2)	109.4(8)
C(15)	C(16)	C(23)	C(21)	-179.4(7)	P(1)	C(8)	Fe(1)	N(2)	-126.8(5)
Fe(1)	C(16)	C(23)	C(21)	59.1(5)	N(2)	C(8)	Fe(1)	C(17)	-119.3(4)
C(17)	C(16)	C(23)	C(24)	-179.2(7)	C(9)	C(8)	Fe(1)	C(17)	-9.9(7)
C(15)	C(16)	C(23)	C(24)	2.1(12)	P(1)	C(8)	Fe(1)	C(17)	113.9(3)
Fe(1)	C(16)	C(23)	C(24)	-119.4(7)	N(2)	C(8)	Fe(1)	C(21)	166.2(10)

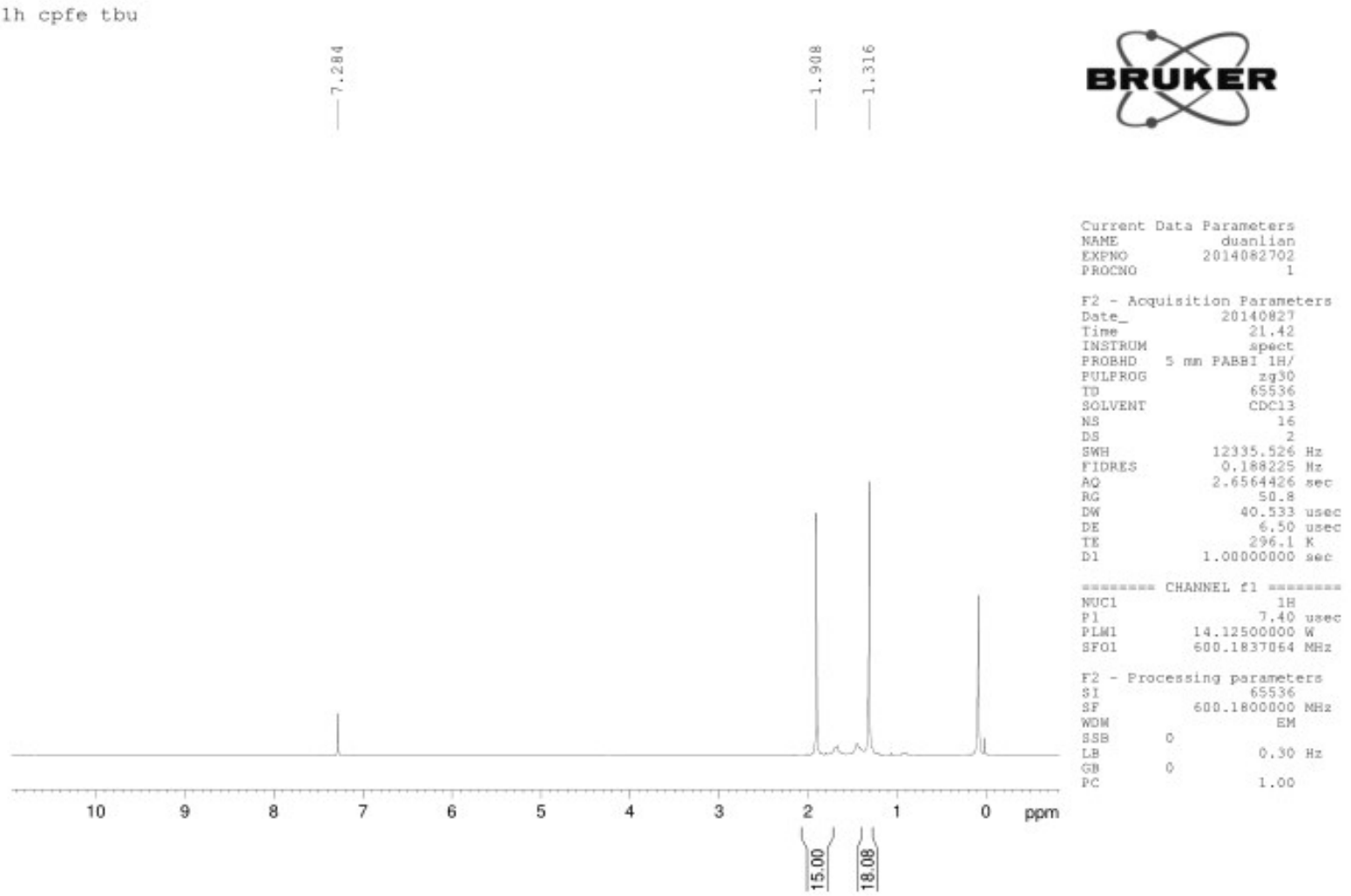
C(17)	C(16)	C(23)	Fe(1)	-59.8(5)	C(9)	C(8)	Fe(1)	C(21)	-84.4(13)
C(15)	C(16)	C(23)	Fe(1)	121.5(7)	P(1)	C(8)	Fe(1)	C(21)	39.4(12)
C(16)	C(17)	Fe(1)	N(1)	33.9(9)	N(2)	C(8)	Fe(1)	C(19)	-160.6(4)
C(19)	C(17)	Fe(1)	N(1)	154.3(6)	C(9)	C(8)	Fe(1)	C(19)	-51.2(8)
C(18)	C(17)	Fe(1)	N(1)	-88.1(10)	P(1)	C(8)	Fe(1)	C(19)	32.9(7)
C(16)	C(17)	Fe(1)	N(2)	72.1(5)	N(2)	C(8)	Fe(1)	C(16)	156.7(3)
C(19)	C(17)	Fe(1)	N(2)	-167.5(4)	C(9)	C(8)	Fe(1)	C(16)	-41.4(8)
C(18)	C(17)	Fe(1)	N(2)	-49.9(9)	P(1)	C(8)	Fe(1)	C(16)	68.1(9)
C(16)	C(17)	Fe(1)	C(21)	-82.1(5)	N(2)	C(8)	Fe(1)	C(23)	32.9(7)
C(19)	C(17)	Fe(1)	C(21)	38.3(4)	C(9)	C(8)	Fe(1)	C(23)	156.7(3)
C(18)	C(17)	Fe(1)	C(21)	155.9(10)	P(1)	C(8)	Fe(1)	C(23)	-168.1(6)
C(16)	C(17)	Fe(1)	C(19)	-120.4(7)	N(2)	C(8)	Fe(1)	C(7)	-168.1(6)
C(18)	C(17)	Fe(1)	C(19)	117.5(10)	C(9)	C(8)	Fe(1)	C(7)	77.7(4)
C(19)	C(17)	Fe(1)	C(16)	120.4(7)	P(1)	C(8)	Fe(1)	C(7)	-172.9(7)
C(18)	C(17)	Fe(1)	C(16)	-122.1(11)	N(2)	C(8)	Fe(1)	P(1)	-49.1(3)
C(16)	C(17)	Fe(1)	C(23)	-38.7(4)	C(9)	C(8)	Fe(1)	P(1)	126.8(5)
C(19)	C(17)	Fe(1)	C(23)	81.7(5)	C(6)	C(7)	N(1)	N(2)	-123.8(7)
C(18)	C(17)	Fe(1)	C(23)	-160.7(10)	P(1)	C(7)	N(1)	N(2)	178.9(6)
C(16)	C(17)	Fe(1)	C(7)	-156.5(9)	Fe(1)	C(7)	N(1)	N(2)	3.6(8)
C(19)	C(17)	Fe(1)	C(7)	-36.0(12)	C(6)	C(7)	N(1)	Fe(1)	60.4(5)
C(18)	C(17)	Fe(1)	C(7)	81.5(13)	P(1)	C(7)	N(1)	Fe(1)	118.6(6)
C(16)	C(17)	Fe(1)	C(8)	113.3(5)	N(2)	Fe(1)	N(1)	C(7)	-56.8(4)
C(19)	C(17)	Fe(1)	C(8)	-126.3(5)	C(17)	Fe(1)	N(1)	C(7)	122.2(5)
C(18)	C(17)	Fe(1)	C(8)	-8.7(9)	C(21)	Fe(1)	N(1)	C(7)	175.5(6)
C(16)	C(17)	Fe(1)	P(1)	165.0(4)	C(19)	Fe(1)	N(1)	C(7)	-79.7(5)
C(19)	C(17)	Fe(1)	P(1)	-74.6(5)	C(16)	Fe(1)	N(1)	C(7)	-55.0(9)
C(18)	C(17)	Fe(1)	P(1)	42.9(9)	C(23)	Fe(1)	N(1)	C(7)	-160.2(4)
C(23)	C(21)	Fe(1)	N(1)	-73.9(5)	C(8)	Fe(1)	N(1)	C(7)	87.3(4)
C(19)	C(21)	Fe(1)	N(1)	166.5(4)	P(1)	Fe(1)	N(1)	C(7)	37.6(3)
C(22)	C(21)	Fe(1)	N(1)	48.0(9)	C(17)	Fe(1)	N(1)	N(2)	53.3(8)
C(23)	C(21)	Fe(1)	N(2)	-39.5(8)	C(21)	Fe(1)	N(1)	N(2)	158.1(4)
C(19)	C(21)	Fe(1)	N(2)	-159.0(6)	C(19)	Fe(1)	N(1)	N(2)	-177.2(7)
C(22)	C(21)	Fe(1)	N(2)	82.4(10)	C(16)	Fe(1)	N(1)	N(2)	77.7(4)
C(23)	C(21)	Fe(1)	C(17)	81.4(5)	C(23)	Fe(1)	N(1)	N(2)	118.6(4)
C(19)	C(21)	Fe(1)	C(17)	-38.1(5)	C(7)	Fe(1)	N(1)	N(2)	-122.2(5)
C(22)	C(21)	Fe(1)	C(17)	-156.7(9)	C(8)	Fe(1)	N(1)	N(2)	-34.9(4)
C(23)	C(21)	Fe(1)	C(19)	119.6(6)	P(1)	Fe(1)	N(1)	N(2)	-84.6(3)
C(22)	C(21)	Fe(1)	C(19)	-118.5(9)	C(7)	N(1)	N(2)	C(8)	-1.8(8)
C(23)	C(21)	Fe(1)	C(16)	37.9(4)	Fe(1)	N(1)	N(2)	C(8)	60.2(5)
C(19)	C(21)	Fe(1)	C(16)	-81.7(5)	C(7)	N(1)	N(2)	Fe(1)	-62.0(5)

C(22)	C(21)	Fe(1)	C(16)	159.8(8)	C(9)	C(8)	N(2)	N(1)	-178.3(6)
C(19)	C(21)	Fe(1)	C(23)	-119.6(6)	P(1)	C(8)	N(2)	N(1)	-0.8(7)
C(22)	C(21)	Fe(1)	C(23)	121.9(9)	Fe(1)	C(8)	N(2)	N(1)	-57.8(4)
C(23)	C(21)	Fe(1)	C(7)	-114.8(4)	C(9)	C(8)	N(2)	Fe(1)	-120.5(6)
C(19)	C(21)	Fe(1)	C(7)	125.6(4)	P(1)	C(8)	N(2)	Fe(1)	57.1(4)
C(22)	C(21)	Fe(1)	C(7)	7.1(8)	C(17)	Fe(1)	N(2)	N(1)	-157.5(4)
C(23)	C(21)	Fe(1)	C(8)	161.4(11)	C(21)	Fe(1)	N(2)	N(1)	-48.9(8)
C(19)	C(21)	Fe(1)	C(8)	41.8(13)	C(19)	Fe(1)	N(2)	N(1)	176.9(8)
C(22)	C(21)	Fe(1)	C(8)	-76.8(14)	C(16)	Fe(1)	N(2)	N(1)	-118.2(4)
C(23)	C(21)	Fe(1)	P(1)	-165.6(4)	C(23)	Fe(1)	N(2)	N(1)	176.9(8)
C(19)	C(21)	Fe(1)	P(1)	74.8(4)	C(7)	Fe(1)	N(2)	N(1)	100.9(0)
C(22)	C(21)	Fe(1)	P(1)	-43.8(8)	C(8)	Fe(1)	N(2)	N(1)	116.9(8)
C(17)	C(19)	Fe(1)	N(1)	-151.6(7)	P(1)	Fe(1)	N(2)	N(1)	85.2(3)
C(21)	C(19)	Fe(1)	N(1)	-33.5(10)	N(1)	Fe(1)	N(2)	C(8)	-122.9(6)
C(20)	C(19)	Fe(1)	N(1)	86.5(11)	C(17)	Fe(1)	N(2)	C(8)	79.6(5)
C(17)	C(19)	Fe(1)	N(2)	34.0(11)	C(21)	Fe(1)	N(2)	C(8)	-171.8(6)
C(21)	C(19)	Fe(1)	N(2)	152.1(8)	C(19)	Fe(1)	N(2)	C(8)	179.5(7)
C(20)	C(19)	Fe(1)	N(2)	-88.0(11)	C(16)	Fe(1)	N(2)	C(8)	56.7(3)
C(21)	C(19)	Fe(1)	C(17)	118.1(7)	C(23)	Fe(1)	N(2)	C(8)	-54.5(4)
C(20)	C(19)	Fe(1)	C(17)	-121.9(10)	C(7)	Fe(1)	N(2)	C(8)	122.8(7)
C(17)	C(19)	Fe(1)	C(21)	-118.1(7)	P(1)	Fe(1)	N(2)	C(8)	-31.5(3)
C(20)	C(19)	Fe(1)	C(21)	120.0(9)	N(1)	C(7)	P(1)	C(8)	-73.0(3)
C(17)	C(19)	Fe(1)	C(16)	-36.8(5)	C(6)	C(7)	P(1)	C(8)	-178.2(7)
C(21)	C(19)	Fe(1)	C(16)	81.3(5)	Fe(1)	C(7)	P(1)	C(8)	-56.9(3)
C(20)	C(19)	Fe(1)	C(16)	-158.7(8)	N(1)	C(7)	P(1)	Fe(1)	53.6(5)
C(17)	C(19)	Fe(1)	C(23)	-81.0(5)	C(6)	C(7)	P(1)	Fe(1)	-121.3(7)
C(21)	C(19)	Fe(1)	C(23)	37.1(4)	N(2)	C(8)	P(1)	C(7)	2.2(5)
C(20)	C(19)	Fe(1)	C(23)	157.1(8)	C(9)	C(8)	P(1)	C(7)	179.5(7)
C(17)	C(19)	Fe(1)	C(7)	168.4(4)	Fe(1)	C(8)	P(1)	C(7)	56.7(3)
C(21)	C(19)	Fe(1)	C(7)	-73.5(5)	N(2)	C(8)	P(1)	Fe(1)	-54.5(4)
C(20)	C(19)	Fe(1)	C(7)	46.4(9)	C(9)	C(8)	P(1)	Fe(1)	122.8(7)
C(17)	C(19)	Fe(1)	C(8)	74.3(6)	N(1)	Fe(1)	P(1)	C(7)	-31.5(3)
C(21)	C(19)	Fe(1)	C(8)	-167.6(4)	N(2)	Fe(1)	P(1)	C(7)	-73.0(3)
C(20)	C(19)	Fe(1)	C(8)	-47.7(9)	C(17)	Fe(1)	P(1)	C(7)	166.5(4)
C(17)	C(19)	Fe(1)	P(1)	121.0(4)	C(21)	Fe(1)	P(1)	C(7)	86.3(4)
C(21)	C(19)	Fe(1)	P(1)	-120.9(4)	C(19)	Fe(1)	P(1)	C(7)	126.5(4)
C(20)	C(19)	Fe(1)	P(1)	-1.0(8)	C(16)	Fe(1)	P(1)	C(7)	-167.8(6)
C(17)	C(16)	Fe(1)	N(1)	-165.2(4)	C(23)	Fe(1)	P(1)	C(7)	61.8(6)
C(23)	C(16)	Fe(1)	N(1)	76.8(5)	C(8)	Fe(1)	P(1)	C(7)	-104.5(4)
C(15)	C(16)	Fe(1)	N(1)	-41.9(8)	N(1)	Fe(1)	P(1)	C(8)	72.9(3)

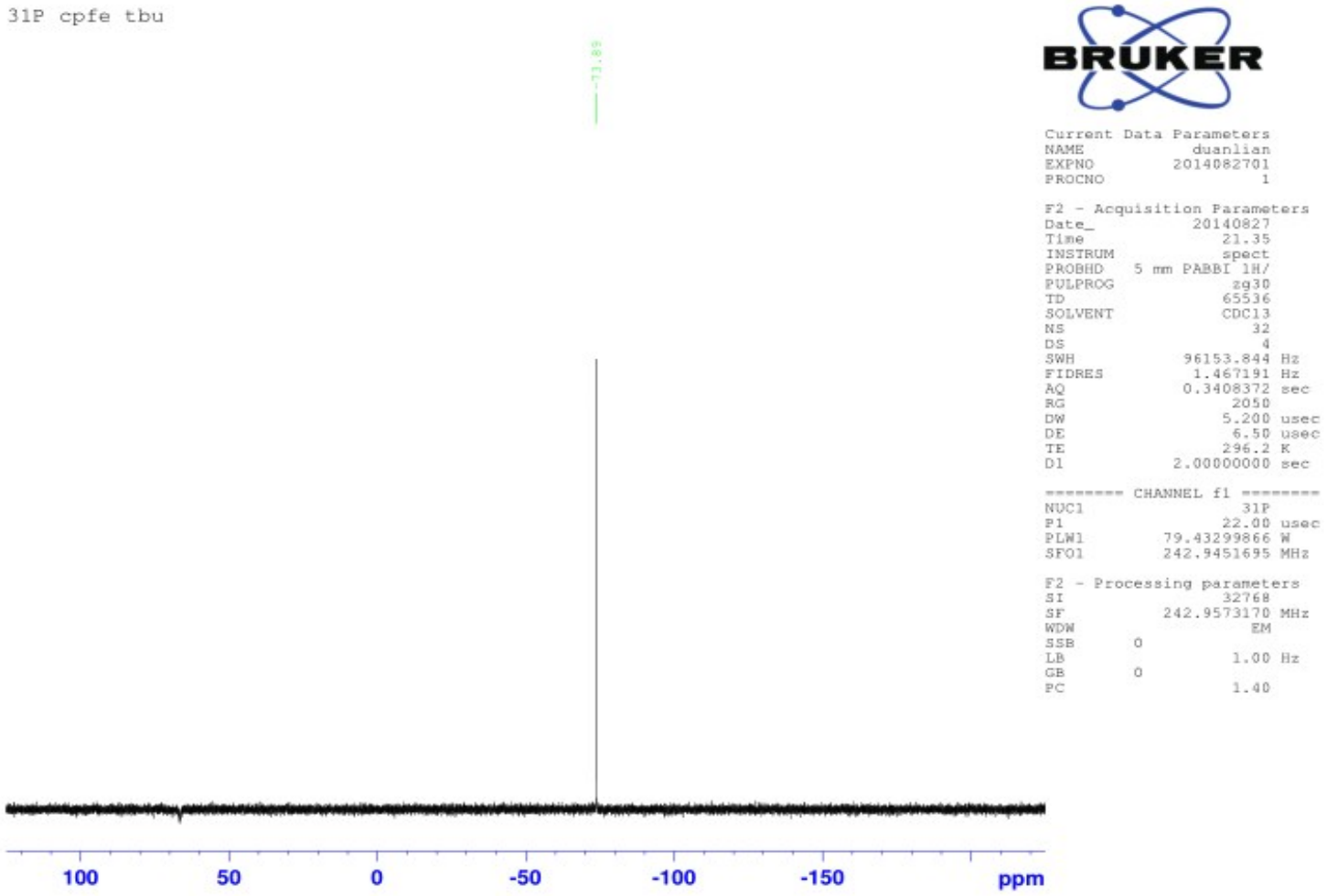
C(17)	C(16)	Fe(1)	N(2)	-124.5(5)		N(2)	Fe(1)	P(1)	C(8)	31.5(3)
C(23)	C(16)	Fe(1)	N(2)	117.5(4)		C(17)	Fe(1)	P(1)	C(8)	-89.0(4)
C(15)	C(16)	Fe(1)	N(2)	-1.2(7)		C(21)	Fe(1)	P(1)	C(8)	-169.2(4)
C(23)	C(16)	Fe(1)	C(17)	-118.0(6)		C(19)	Fe(1)	P(1)	C(8)	-129.0(3)
C(15)	C(16)	Fe(1)	C(17)	123.3(9)		C(16)	Fe(1)	P(1)	C(8)	-63.3(6)
C(17)	C(16)	Fe(1)	C(21)	80.8(5)		C(23)	Fe(1)	P(1)	C(8)	166.2(6)
C(23)	C(16)	Fe(1)	C(21)	-37.1(4)		C(7)	Fe(1)	P(1)	C(8)	104.5(4)
C(15)	C(16)	Fe(1)	C(21)	-155.8(8)						

[1]-X,+Y,1/2-Z

S2-1-2. The ^{1}H spectrum of **3**



S2-1-2. The $^{31}P\{^{1}H\}$ spectrum of **3**

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PROCNO                    1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       4
SWH               96153.844 Hz
FIDRES             1.467191 Hz
AQ                 0.3408372 sec
RG                    2050
DW                   5.200 usec
DE                    6.50 usec
TE                   296.2 K
D1              2.00000000 sec

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P1                   22.00 usec
PLW1          79.43299866 W
SFO1         242.9451695 MHz

F2 - Processing parameters
SI                    32768
SF           242.9573170 MHz
WDW                      EM
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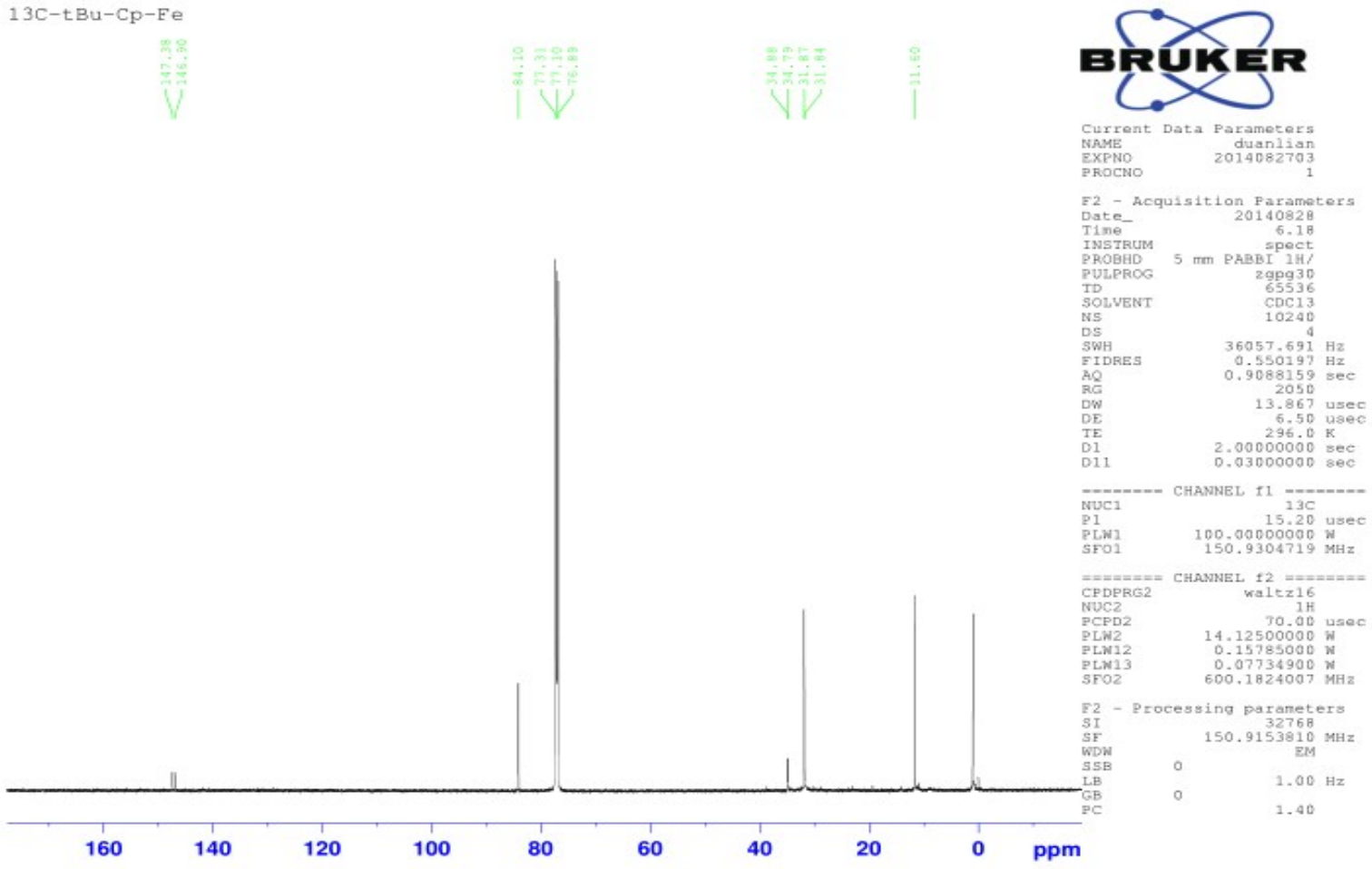
S2-1-3. The $^{13}C\{^{1}H\}$ spectrum of **3**

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PULPROG                zgpg30
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SOLVENT                 CDCl3
NS                      10240
DS                          4
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FIDRES              0.550197 Hz
AQ                  0.9088159 sec
RG                       2050
DW                     13.867 usec
DE                      6.50 usec
TE                     296.0 K
D1                 2.00000000 sec
D11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                       15.20 usec
PLW1              100.00000000 W
SFO1               150.9304719 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    70.00 usec
PLW2              14.12500000 W
PLW12              0.15785000 W
PLW13              0.07734900 W
SFO2              600.1824007 MHz

F2 - Processing parameters
SI                        32768
SF                 150.9153810 MHz
WDW                          EM
SSB           0
LB                        1.00 Hz
GB            0
PC                        1.40
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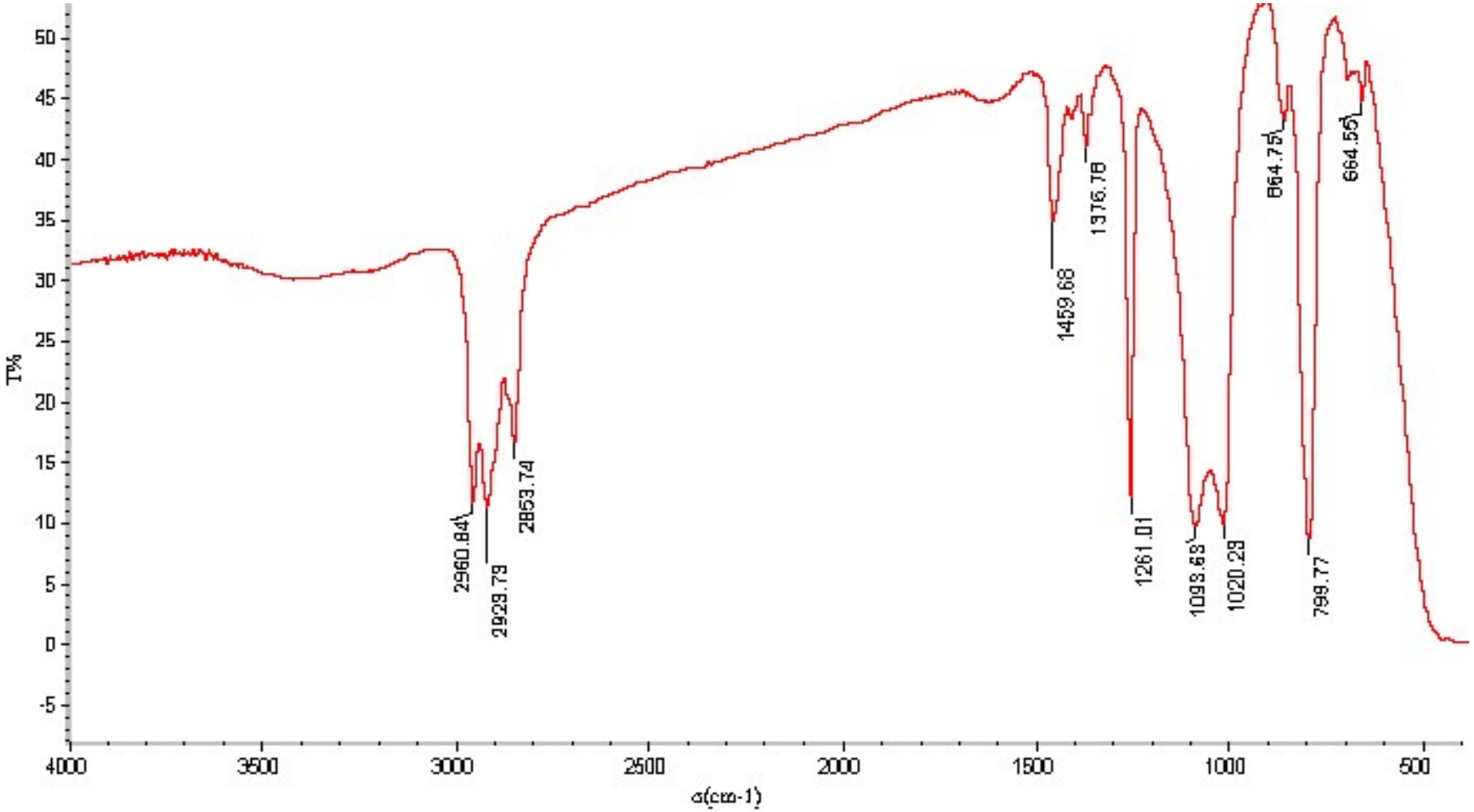
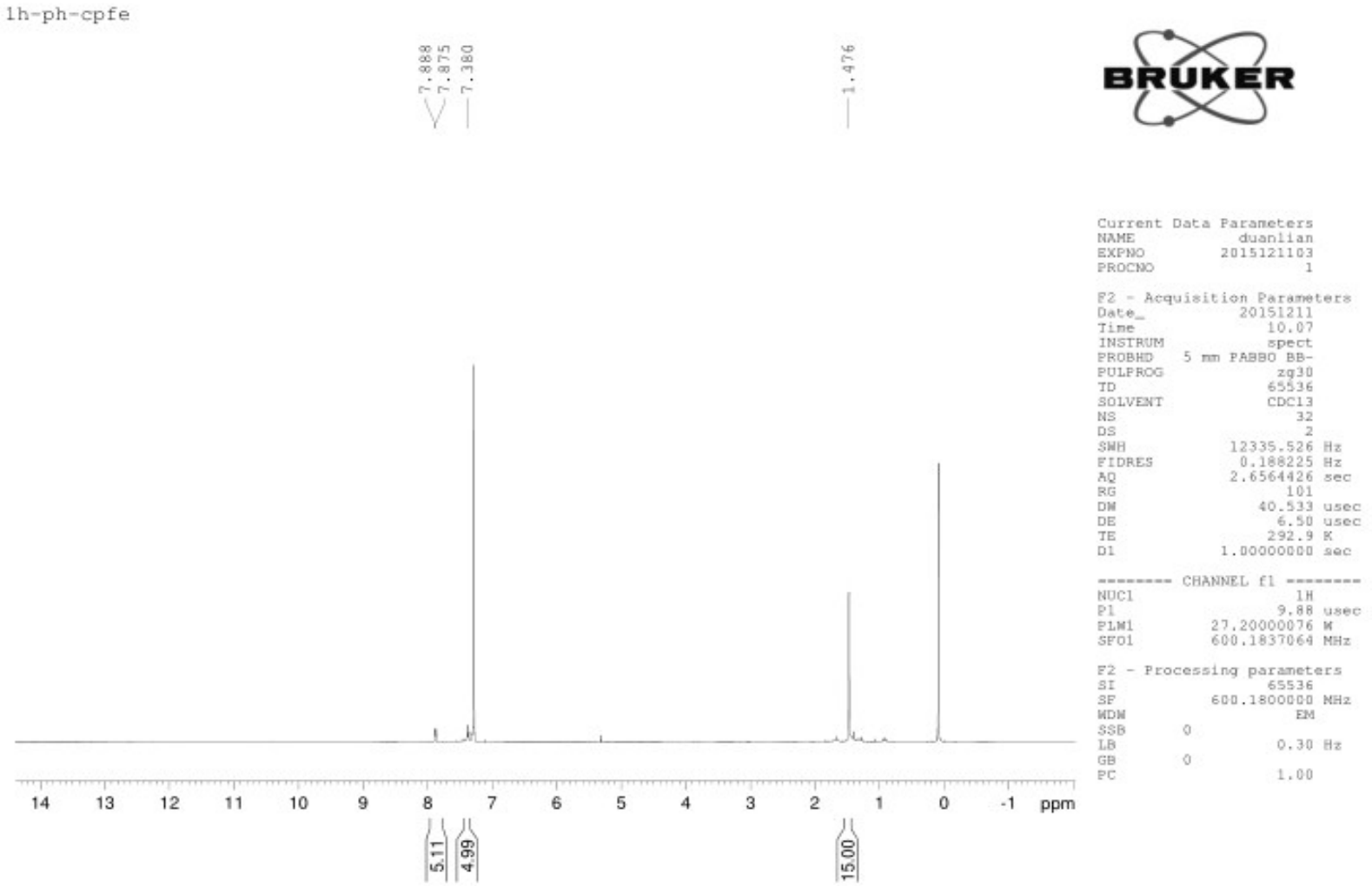
S2-1-4. The IR spectrum of **3**



S2-2-1. The ^{1}H NMR spectrum of **4**

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EXPNO              2015121103
PROCNO                     1

F2 - Acquisition Parameters
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PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                12335.526 Hz
FIDRES              0.188225 Hz
AQ                  2.6564426 sec
RG                       101
DW                    40.533 usec
DE                     6.50 usec
TE                    292.9 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.88 usec
PLW1              27.20000076 W
SFO1              600.1837064 MHz

F2 - Processing parameters
SI                         65536
SF                600.1800000 MHz
WDW                        EM
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LB                       0.30 Hz
GB           0
PC                       1.00
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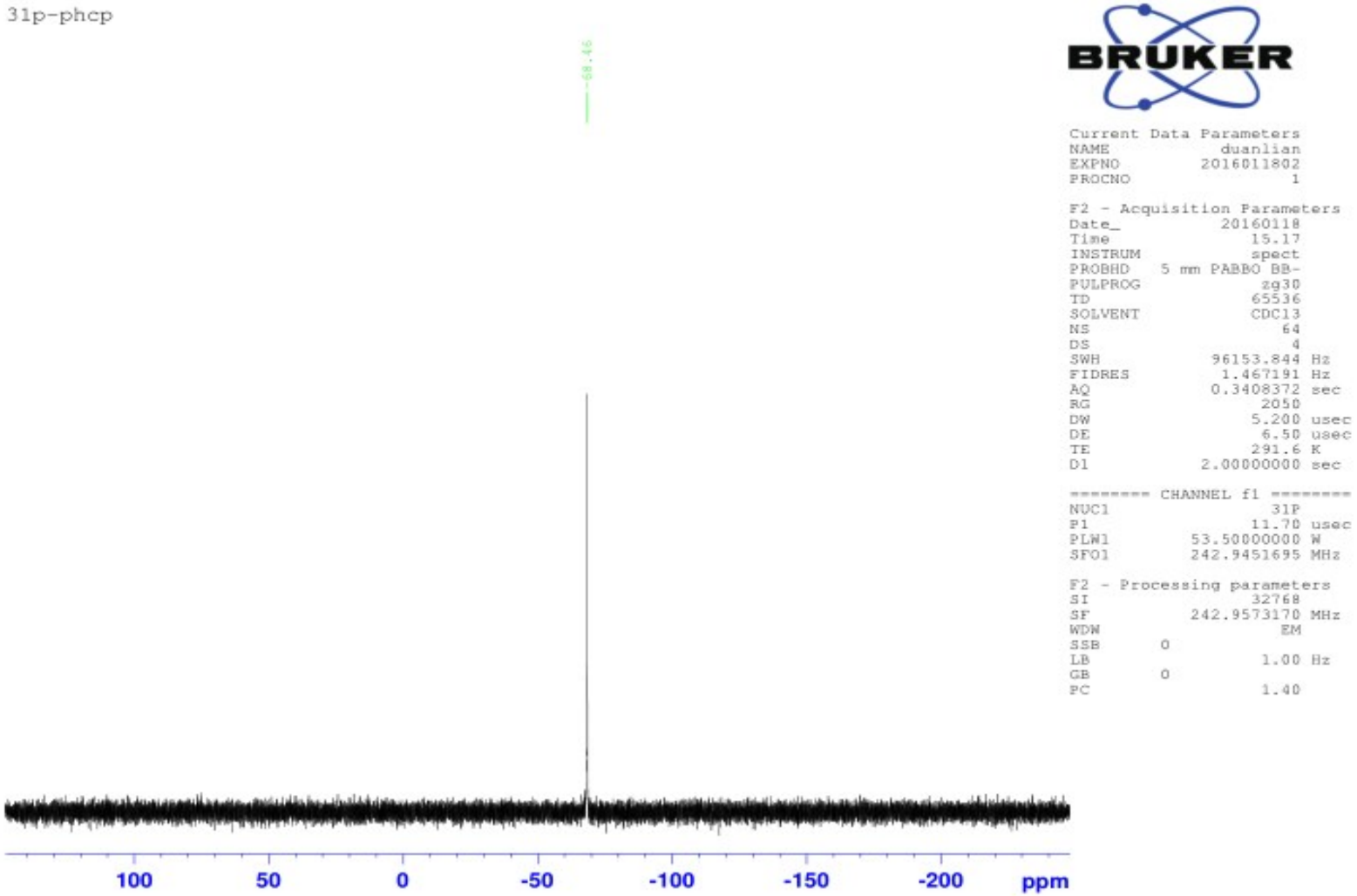
S2-2-2. The $^{31}P\{^{1}H\}$ spectrum of **4**

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Current Data Parameters
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EXPNO              2016011802
PROCNO                      1

F2 - Acquisition Parameters
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Time                   15.17
INSTRUM                spect
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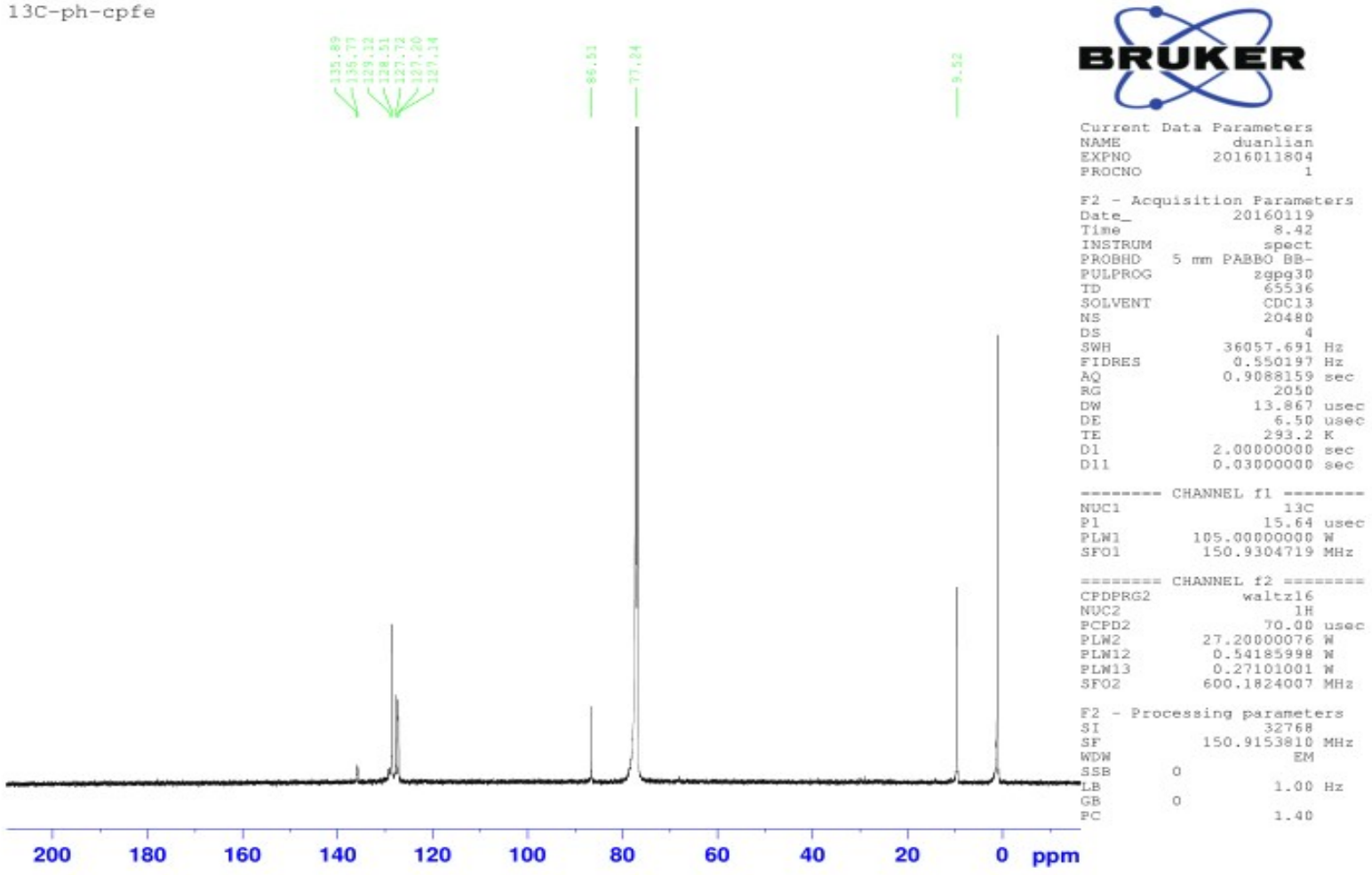
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         4
SWH                96153.844 Hz
FIDRES             1.467191 Hz
AQ                 0.3408372 sec
RG                      2050
DW                     5.200 usec
DE                     6.50 usec
TE                    291.6 K
D1                 2.00000000 sec

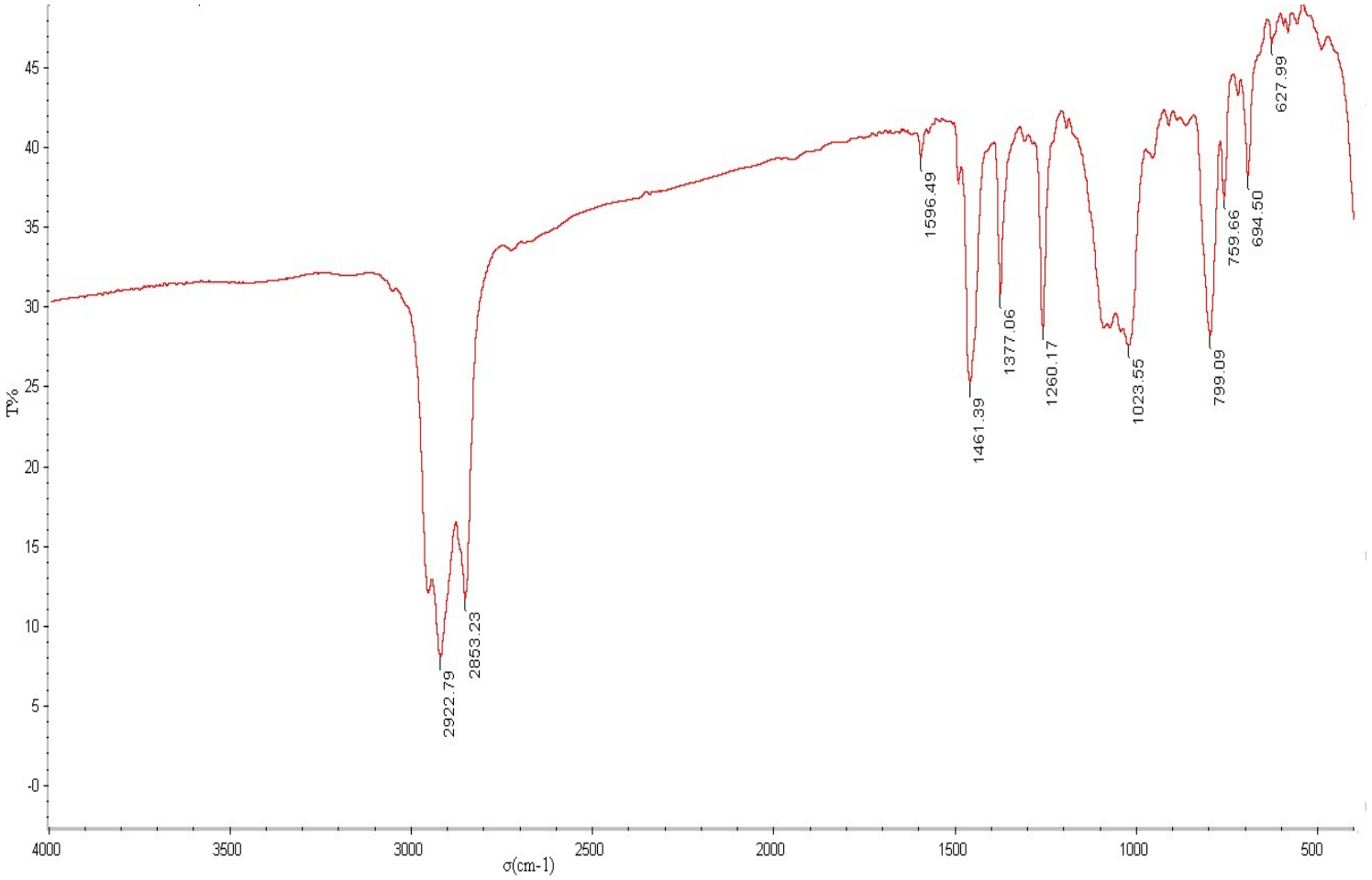
======== CHANNEL f1 ========
NUC1                     31P
P1                     11.70 usec
PLW1           53.50000000 W
SFO1           242.9451695 MHz

F2 - Processing parameters
SI                     32768
SF             242.9573170 MHz
WDW                       EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

S2-2-3. The $^{13}C\{^{1}H\}$ spectrum of **4**



S2-2-4. The IR spectrum of **4**



S3. The procedure for the preparation of complexes **3**–**4**

3: To a solution of **1** (0.24 g, 1.0 mmol) in tetrahydrofuran (20 mL) at –40°C, was slowly added a suspension of $FeCl_2$(DME) (0.217 g, 1.0 mmol) in tetrahydrofuran (20 mL) at –40°C via syringe. The deep-red suspension was stirred for 2 h and the suspension of $CpMe_5Li$ (0.143 g, 1.0 mmol) in tetrahydrofuran (20 mL) was then slowly added via syringe at –40°C. The solution was stirred at room temperature for 48 h and refluxed for another 48 h. After the volatile components were removed under reduced pressure, the resultant residue was extracted with *n*-hexane (3 × 10 mL). The solution was filtered through Celite and the filtrate was concentrated to give **3** as red crystals at –15°C (0.10 g, 25%). Alternatively, **3** can be sublimed at 100°C in high vacuum (0.01 mmHg). M.p. = 105°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): δ = 1.91 (s, 15 H, CH_3 for CpCH_3), 1.32 (s, 18 H, CH_3) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 23°C): δ = 147.14 (d, $^1J_{C–P}$ = 72.0 Hz, P*C*N), 84.1 (s, *C*CH_3 for $CpMe_5$ ring), 34.84 (d, $^2J_{C–P}$ = 13.5 Hz, *C*CH_3 for *t*Bu groups), 31.86 (d, $^3J_{C–P}$ = 4.5 Hz, C*C*H_3), 11.60 (s, Cp*C*H_3); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 23°C): δ = –73.89(s) ppm; IR (KBr, Nujol mull, cm^{-1}): 3422(m), 2960(s), 2923(s), 2853(s), 1459(s), 1261(vs), 799(vs); Anal. calcd. for $C_{20}H_{33}N_2PFe$: C 61.81, H 8.50, N 7.21; Found: C 61.73, H 8.56, N 7.15.

4: In a fashion similar to that for the preparation of **3**, complex **4** was obtained by the use of **2** as starting material.
To a solution of [**2**·0.67(THF)] (0.32 g, 1.0 mmol) in tetrahydrofuran (20 mL) at –40°C, was slowly added a suspension of $FeCl_2$(DME) (0.217 g, 1.0 mmol) in tetrahydrofuran (20 mL) at –40°C via syringe. The deep-red suspension was stirred for 2 h and the suspension of $CpMe_5Li$ (0.143 g, 1.0 mmol) in tetrahydrofuran (20 mL) was then slowly added via syringe at –40°C. The solution was stirred at room temperature for 48 h and refluxed for another 48 h. After the volatile components were removed under reduced pressure, the resultant residue was extracted with *n*-hexane (3 × 10 mL). The solution was filtered through Celite and the filtrate was concentrated to give **4** as red crystals at –15°C (0.08 g, 15%). M.p. = 190°C. ^{1}H NMR (600 MHz, $CDCl_3$, 23°C): δ = 1.48 (s, 15 H, CH_3 for CpCH_3), 7.38 (s, 5 H, C*H* on the pheny rings), 7.88 (d, 5 H, C*H* on the pheny rings) ppm; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 23°C): δ = ~160 ppm (d, $^1J_{C–P,}$ P*C*N, not observed after 20480 scans), 135.88 (d, $^2J_{C–P}$ = 18.0 Hz, *ipso-C* on the phenyl rings), 129.12–127.14 (m, *C* on the phenyl rings), 86.51 (s, *C*CH_3 for $CpMe_5$ ring), 9.52 (s, Cp*C*H_3); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 23°C): δ = –68.46(s) ppm; IR (KBr, Nujol mull, cm^{-1}): 3422(m), 2960(s), 2853(s), 1459(s), 1261(vs), 799(vs); Anal. calcd. for $C_{24}H_{25}N_2PFe$: C 67.29, H 5.84, N 6.54; Found: C 67.20, H 5.75, N 6.60.

S4. The DFT Calculation

S4-1. Calculated and experimental bond lengths in model complexes **5** and **7**

From the data given in Table 1 we can see that, PBE1PBE method with BS+diffuse functions gives best geometry for 5 and 7. Adding diffuse functions for all the heaver atoms (C, N, P and Fe) slightly improves the optimized geometry of **5**.

Table 1. Calculated and experimental measured bond lengths in **5** and **7**

Species	Bond lengths in 5 (Å)				
	M11/BS	B3LYP/BS	PBE1PBE/BS	PBE1PBE/BS_d	Experimental
Fe–N1, Fe–N2	2.098	2.046	2.030	2.008	(2.012, 2.017)

Fe–C6, Fe–C7	2.188	2.158	2.121	2.111	(2.092, 2.105)
Fe–P	2.435	2.389	2.357	2.342	(2.323)
N1-N2	1.358	1.375	1.361	1.362	(1.392)
N1–C6, N2–C7	1.349	1.363	1.360	1.361	(1.368, 1.371)
C6-P, C7-P	1.777	1.791	1.784	1.781	(1.777, 1.777)

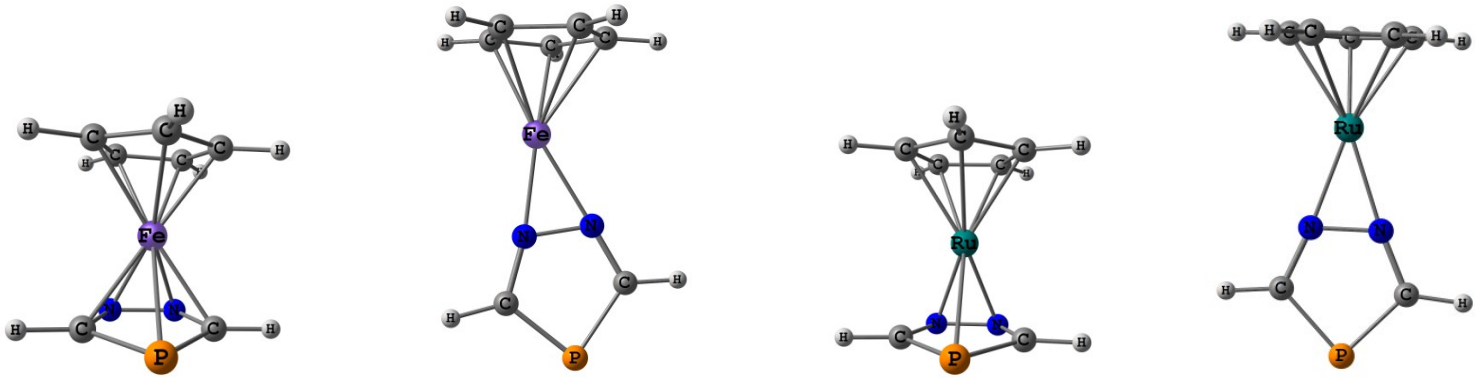
Bond lengths in 7 (Å)

	M11/BS	B3LYP/BS	PBE1PBE/BS	PBE1PBE/BS_d	Experimental

Ru-N1, Ru-N2	2.269	2.256	2.215	2.181	(2.165, 2.166)
Ru-C6, Ru-C7	2.314	2.323	2.270	2.252	(2.213, 2.225)
Ru-P	2.519	2.529	2.480	2.456	(2.431)
N1-N2	1.355	1.371	1.359	1.361	(1.395)
N1-C6, N2-C7	1.354	1.365	1.364	1.365	(1.368, 1.372)
C6-P, C7-P	1.784	1.797	1.789	1.787	(1.777,1.780)

BS: basis set combination of 6-311G(d,p) for H, C, N and P atoms, and LANL2DZ for Fe and Ru atoms; BS_d: BS plus additional aug-cc-pVTZ diffuse functions for C, N, P and Fe atoms, and aug-cc-pVTZ-DK diffuse functions for Ru atom.

S4-2. Relative stabilities of model complexes **5H**, **6H**, **7H** and **8H**



5H **6H** **7H** **8H**

Table 2. Relative energies of model complexes **5H**, **6H**, **7H** and **8H** calculated at the PBE1PBE/BS_d level

Species	Relative energies(kcal/mol)
5H(S)/**7H**(S)	0.00/0.00
6H(S)/**8H**(S)	9.58/15.25
6H(T)/**8H**(T)	17.79/34.47
6H(Q)/**8H**(Q)	-19.16/48.96

From Table 2, we can see than theoretical results suggested that **6H** (**Q**) is the most stable from among the four Fe complexes while **7H** is the most stable form among the four Ru complexes.

S4-3. Steric effect of bulky substituents

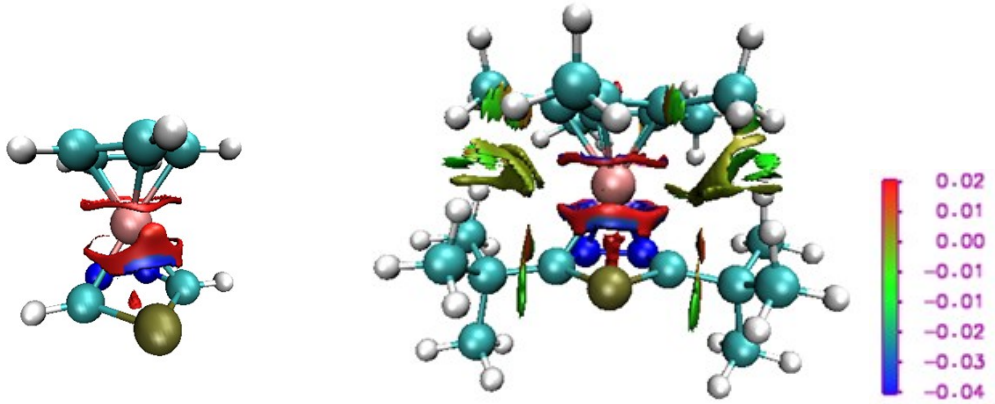


Figure 1. Reduced density gradient(RDG)[1] isosurface (s=0.5 au) calculated at the PBE1PBE/BS_d level. The surfaces are colored on a blue-green-red sacle according to the values of sing(λ_2)ρ ranging from -0.04 to 0.02 au. Blue indicates strong attractive interactions and red indicates strong nonbonded overlap. The green regions have weak Van der Waals (vdw) attraction, the breen regions have weak steric repulsion. The scatters of RDG versus sign(λ_2)ρ were calculated with Multiwfn [2] and visualized by VMD software [3].

$$\mathrm{RDG}(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}$$

λ_2(r): the second largest eigenvalue of Hessian matrix of electron density.

ρ(r): electron density

From Figure 1, we can see that bulky substituents in pentamethylcyclopentadienyl (Methyl), and 1,2,4-diazaphospholide (*t*Bu) induce both vdw attraction and steric repulsion between each pair of two closely-located groups, and the steric repulsion is stronger than the vdw attraction. As the results, all the bulky groups in the two rings deviate to the outside of the ring plane.

References:

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2. T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer *J. Comput. Chem.* **2012**, *33*, 580–592.
3. W. Hurnphrey, A. Dalke, K. Schulten, VMD: visual molecular dynamics, *J. Mol. Graph.* **1996**, *14*, 33–38.

S4-3. Optimized Coordinates of **5**, **6S**, **6T** and **6Q** At the PBE1PBE/BS_d level.

5(S):

Fe	-0.000047000	-0.418874000	-0.072252000
C	0.712775000	-2.170985000	-0.877333000
P	0.000247000	1.592473000	1.127883000
C	-0.713824000	-2.170721000	-0.877070000
C	1.155671000	-2.051980000	0.475517000
C	-1.156189000	-2.051495000	0.475936000
C	-0.000084000	-1.952987000	1.308544000
C	-1.212018000	1.307441000	-0.145973000
C	1.212460000	1.307133000	-0.145952000
N	-0.680865000	0.969599000	-1.353117000
N	0.681246000	0.969402000	-1.353098000
C	0.000194000	-1.879566000	2.799778000
H	0.881478000	-1.356387000	3.176665000
H	-0.880553000	-1.355702000	3.176968000

H	-0.000121000	-2.886251000	3.235762000
C	-2.554827000	-2.211648000	0.971545000
H	-2.714582000	-1.694934000	1.919681000
H	-3.300697000	-1.854155000	0.260554000
H	-2.760508000	-3.275092000	1.146260000
C	2.554401000	-2.212847000	0.970624000
H	3.300205000	-1.855954000	0.259270000
H	2.714842000	-1.696066000	1.918604000
H	2.759512000	-3.276381000	1.145461000
C	1.570483000	-2.337660000	-2.086771000
H	1.171460000	-1.783343000	-2.939414000
H	2.589493000	-1.988733000	-1.913056000
H	1.625897000	-3.394577000	-2.373917000
C	-1.572024000	-2.337078000	-2.086206000
H	-2.591081000	-1.988625000	-1.911823000
H	-1.173611000	-1.782158000	-2.938745000

H	-1.627181000	-3.393863000	-2.373878000
C	2.686669000	1.659727000	-0.057535000
C	-2.686153000	1.660295000	-0.057541000
C	3.227685000	1.443999000	1.355468000
H	4.269074000	1.777267000	1.409544000
H	2.656356000	2.017252000	2.092796000
H	3.193181000	0.391331000	1.641834000
C	3.527928000	0.887503000	-1.073291000
H	3.503001000	-0.185443000	-0.878136000
H	3.166532000	1.052601000	-2.090099000
H	4.569555000	1.219276000	-1.015535000
C	2.778848000	3.159828000	-0.393994000
H	3.823846000	3.485543000	-0.361619000
H	2.387425000	3.359663000	-1.395689000
H	2.209936000	3.759855000	0.322733000
C	-3.227138000	1.444667000	1.355490000

H	-2.655732000	2.017898000	2.092774000
H	-4.268495000	1.778029000	1.409587000
H	-3.192712000	0.391998000	1.641896000
C	-3.527537000	0.888083000	-1.073199000
H	-4.569120000	1.219993000	-1.015450000
H	-3.166141000	1.053033000	-2.090032000
H	-3.502733000	-0.184853000	-0.877941000
C	-2.778121000	3.160395000	-0.394088000
H	-3.823065000	3.486273000	-0.361659000
H	-2.209067000	3.760379000	0.322563000
H	-2.386737000	3.360112000	-1.395822000

6(S):

Fe	1.020387000	-0.002584000	-0.018373000
C	2.604432000	0.572569000	1.084546000
P	-3.229332000	0.008334000	0.004393000

C	2.647209000	1.196509000	-0.198064000
C	2.612947000	-0.850533000	0.892401000
C	2.650416000	0.159169000	-1.183400000
C	2.648858000	-1.106228000	-0.508359000
C	-1.958998000	1.229857000	-0.011070000
C	-1.966388000	-1.220882000	-0.011680000
N	-0.753019000	0.675363000	-0.027912000
N	-0.756959000	-0.673738000	-0.027921000
C	2.568132000	1.266767000	2.405924000
H	1.975183000	0.710999000	3.136988000
H	3.579223000	1.372427000	2.817857000
H	2.141586000	2.269408000	2.325442000
C	2.588829000	-1.871497000	1.981496000
H	2.199730000	-2.829080000	1.627950000
H	3.598485000	-2.050857000	2.370480000
H	1.968077000	-1.550764000	2.822181000

C	2.677626000	-2.446844000	-1.165538000
H	2.158050000	-2.436501000	-2.127169000
H	3.709085000	-2.767305000	-1.355827000
H	2.206967000	-3.212136000	-0.543495000
C	2.665301000	0.356316000	-2.663249000
H	3.694330000	0.379638000	-3.042285000
H	2.143924000	-0.451316000	-3.183099000
H	2.189488000	1.297421000	-2.949281000
C	2.683811000	2.665016000	-0.465673000
H	3.717581000	3.028582000	-0.509832000
H	2.211035000	2.913911000	-1.419008000
H	2.172037000	3.232383000	0.315631000
C	-2.099859000	2.737037000	-0.007310000
C	-2.117421000	-2.727104000	-0.007483000
C	-1.419609000	-3.302673000	1.232558000
H	-1.870814000	-2.913394000	2.150435000

H	-1.510681000	-4.393958000	1.243134000
H	-0.357283000	-3.044765000	1.240069000
C	-3.596295000	-3.112347000	0.022184000
H	-4.126801000	-2.725725000	-0.853689000
H	-3.697438000	-4.202103000	0.025185000
H	-4.091867000	-2.724042000	0.917550000
C	-1.469879000	-3.304744000	-1.273527000
H	-0.407901000	-3.050606000	-1.321633000
H	-1.564668000	-4.395742000	-1.280217000
H	-1.955665000	-2.914352000	-2.173107000
C	-1.380694000	3.309263000	1.221873000
H	-1.824037000	2.927394000	2.146635000
H	-0.321311000	3.039278000	1.216095000
H	-1.459437000	4.401474000	1.230238000
C	-3.575503000	3.132281000	0.042010000
H	-4.120421000	2.747783000	-0.825925000

H	-4.061113000	2.748387000	0.944686000
H	-3.669613000	4.222675000	0.044599000
C	-1.466110000	3.307697000	-1.283572000
H	-0.406858000	3.045214000	-1.346058000
H	-1.967630000	2.919342000	-2.175328000
H	-1.552324000	4.399370000	-1.290973000

6(T):

Fe	-0.961760000	0.000045000	-0.033895000
C	-2.710695000	0.708004000	-0.993270000
P	3.317791000	0.000255000	0.022668000
C	-2.719723000	1.143549000	0.383034000
C	-2.710378000	-0.709505000	-0.992534000
C	-2.798428000	0.000290000	1.221952000
C	-2.719420000	-1.143747000	0.384230000
C	2.044618000	1.224760000	0.001236000

C	2.044774000	-1.224429000	0.001318000
N	0.841107000	0.670605000	-0.021203000
N	0.841175000	-0.670451000	-0.021155000
C	-2.776758000	1.604564000	-2.188266000
H	-2.345288000	1.130207000	-3.073124000
H	-3.814468000	1.866149000	-2.430264000
H	-2.239051000	2.541676000	-2.021302000
C	-2.775613000	-1.607294000	-2.186663000
H	-2.237682000	-2.544047000	-2.018440000
H	-3.813111000	-1.869478000	-2.428925000
H	-2.343829000	-1.133708000	-3.071780000
C	-2.761510000	-2.567669000	0.835733000
H	-2.350928000	-2.685642000	1.841439000
H	-3.793484000	-2.938996000	0.857953000
H	-2.197561000	-3.221284000	0.165648000
C	-2.877459000	0.001293000	2.714364000

H	-3.920305000	0.004606000	3.054750000
H	-2.399889000	-0.882031000	3.146167000
H	-2.394630000	0.882183000	3.145358000
C	-2.762336000	2.567808000	0.833412000
H	-3.794507000	2.938577000	0.855984000
H	-2.351254000	2.686739000	1.838810000
H	-2.199121000	3.221220000	0.162511000
C	2.186233000	2.732085000	0.008282000
C	2.186688000	-2.731726000	0.008393000
C	1.515110000	-3.312159000	-1.243710000
H	1.985714000	-2.927005000	-2.153477000
H	1.605691000	-4.403523000	-1.247686000
H	0.452901000	-3.054775000	-1.274822000
C	3.663672000	-3.125429000	0.015482000
H	4.175540000	-2.735935000	0.901033000
H	3.758950000	-4.215748000	0.021462000

H	4.181747000	-2.744646000	-0.870201000
C	1.506726000	-3.298867000	1.262330000
H	0.443796000	-3.043569000	1.282276000
H	1.599319000	-4.389992000	1.279788000
H	1.970262000	-2.902319000	2.170875000
C	1.513819000	3.312479000	-1.243375000
H	1.984031000	2.927582000	-2.153455000
H	0.451664000	3.054799000	-1.273953000
H	1.604089000	4.403869000	-1.247258000
C	3.663137000	3.126094000	0.014597000
H	4.175567000	2.736650000	0.899846000
H	4.180807000	2.745469000	-0.871390000
H	3.758196000	4.216432000	0.020604000
C	1.506824000	3.298975000	1.262651000
H	0.443940000	3.043515000	1.283065000
H	1.970877000	2.902375000	2.170906000

H	1.599261000	4.390112000	1.280197000

6(Q):

Fe	1.042256000	-0.152687000	-0.000370000
C	3.100267000	-0.524700000	-0.708709000
P	-3.404342000	-0.491406000	-0.000035000
C	3.095506000	-0.515847000	0.724130000
C	2.758758000	0.791406000	-1.155231000
C	2.750707000	0.805702000	1.151925000
C	2.551748000	1.608306000	-0.007415000
C	-1.932578000	-1.447796000	0.002878000
C	-2.370730000	0.946584000	-0.005449000
N	-0.845495000	-0.678516000	-0.000381000
N	-1.080544000	0.653831000	-0.004852000
C	3.507658000	-1.673099000	-1.578658000
H	3.015681000	-1.638731000	-2.554354000
H	4.589324000	-1.668331000	-1.762205000

H	3.264145000	-2.636309000	-1.121983000
C	2.695392000	1.244607000	-2.579987000
H	1.964651000	2.045825000	-2.719020000
H	3.665501000	1.629784000	-2.917665000
H	2.421477000	0.428563000	-3.253851000
C	2.198134000	3.060909000	-0.017536000
H	1.608864000	3.340635000	0.859741000
H	3.097475000	3.689100000	-0.016831000
H	1.617588000	3.330223000	-0.903807000
C	2.676672000	1.276744000	2.570393000
H	3.642879000	1.670547000	2.909315000
H	1.941545000	2.076426000	2.694620000
H	2.401954000	0.468134000	3.252863000
C	3.498173000	-1.652588000	1.611397000
H	4.578035000	-1.642071000	1.805057000
H	2.996856000	-1.608169000	2.581913000

H	3.262135000	-2.622029000	1.164124000
C	-1.781484000	-2.955512000	0.000044000
C	-2.803520000	2.400428000	-0.001244000
C	-2.205220000	3.113977000	-1.220564000
H	-2.557969000	2.658571000	-2.151261000
H	-2.498853000	4.169216000	-1.223684000
H	-1.113637000	3.059119000	-1.207090000
C	-4.327540000	2.506589000	-0.055233000
H	-4.791802000	2.015212000	0.805640000
H	-4.630036000	3.558716000	-0.047538000
H	-4.726993000	2.045583000	-0.963987000
C	-2.298136000	3.073563000	1.282106000
H	-1.208264000	3.018225000	1.347605000
H	-2.592853000	4.128442000	1.298304000
H	-2.718167000	2.587936000	2.168566000
C	-1.061684000	-3.394100000	-1.283099000

H	-1.629107000	-3.095849000	-2.169903000
H	-0.065338000	-2.947054000	-1.350746000
H	-0.947907000	-4.483211000	-1.299896000
C	-3.154410000	-3.626024000	0.055448000
H	-3.696236000	-3.346557000	0.964217000
H	-3.768849000	-3.343966000	-0.805075000
H	-3.039982000	-4.714645000	0.048605000
C	-0.960014000	-3.394268000	1.219965000
H	0.041878000	-2.954679000	1.203342000
H	-1.449110000	-3.090216000	2.150416000
H	-0.852339000	-4.483986000	1.230385000

Optimized Coordinates of 7, 8S,8T and 8Q At the PBE1PBE/BS level.

7(S):

Ru	0.000118000	-0.392687000	-0.083623000
C	0.717105000	-2.298874000	-0.871667000

P	-0.000392000	1.765662000	1.138122000
C	-0.716748000	-2.299142000	-0.871229000
C	1.161973000	-2.162581000	0.485965000
C	-1.160870000	-2.163026000	0.486624000
C	0.000774000	-2.058268000	1.321657000
C	-1.214001000	1.523692000	-0.153312000
C	1.213337000	1.524169000	-0.153256000
N	-0.679909000	1.268474000	-1.382130000
N	0.679369000	1.268761000	-1.382132000
C	0.001165000	-1.996214000	2.812284000
H	0.881656000	-1.472508000	3.188480000
H	-0.879031000	-1.472353000	3.188938000
H	0.001189000	-3.006422000	3.238976000
C	-2.563928000	-2.303414000	0.972441000
H	-2.716391000	-1.786153000	1.921198000
H	-3.291477000	-1.917613000	0.256810000

H	-2.794725000	-3.363028000	1.136266000
C	2.565308000	-2.302807000	0.971011000
H	3.292446000	-1.916775000	0.255090000
H	2.718192000	-1.785699000	1.919784000
H	2.796348000	-3.362415000	1.134529000
C	1.582462000	-2.519009000	-2.066080000
H	1.157784000	-2.053105000	-2.957471000
H	2.582230000	-2.107176000	-1.919740000
H	1.690686000	-3.591437000	-2.267505000
C	-1.582544000	-2.519309000	-2.065326000
H	-2.582929000	-2.109404000	-1.917799000
H	-1.159264000	-2.051506000	-2.956388000
H	-1.689067000	-3.591670000	-2.268010000
C	2.700233000	1.796638000	-0.046076000
C	-2.701013000	1.795513000	-0.046074000
C	3.203855000	1.496816000	1.365701000

H	4.269220000	1.735601000	1.441780000
H	2.673839000	2.094808000	2.113885000
H	3.069012000	0.442069000	1.615824000
C	3.493195000	0.984996000	-1.070777000
H	3.358298000	-0.086609000	-0.909415000
H	3.170814000	1.214191000	-2.087938000
H	4.559239000	1.215717000	-0.980078000
C	2.892004000	3.294041000	-0.341110000
H	3.954197000	3.554048000	-0.286356000
H	2.527371000	3.540604000	-1.342098000
H	2.350493000	3.910535000	0.382545000
C	-3.204415000	1.495598000	1.365756000
H	-2.674714000	2.093987000	2.113845000
H	-4.269912000	1.733790000	1.441838000
H	-3.068953000	0.440964000	1.616002000
C	-3.493701000	0.983450000	-1.070654000

H	-4.559806000	1.213929000	-0.980056000
H	-3.171327000	1.212530000	-2.087845000
H	-3.358566000	-0.088093000	-0.909085000
C	-2.893445000	3.292808000	-0.341241000
H	-3.955746000	3.552368000	-0.286437000
H	-2.352146000	3.909608000	0.382311000
H	-2.528994000	3.539438000	-1.342280000

8(S):

Ru	-0.981716000	0.007811000	0.011963000
C	-2.713568000	0.614003000	-1.068509000
P	3.491532000	-0.015025000	-0.002788000
C	-2.748270000	1.211527000	0.231057000
C	-2.720920000	-0.824288000	-0.907487000
C	-2.734718000	0.144959000	1.196389000
C	-2.747620000	-1.113265000	0.490396000

C	2.228512000	1.215853000	0.006746000
C	2.213030000	-1.229488000	0.008531000
N	1.018541000	0.672941000	0.018569000
N	1.010364000	-0.670552000	0.019230000
C	-2.741000000	1.337415000	-2.371432000
H	-2.183073000	0.797108000	-3.139235000
H	-3.772702000	1.449903000	-2.726314000
H	-2.308216000	2.336054000	-2.284073000
C	-2.759499000	-1.819119000	-2.016857000
H	-2.316317000	-2.770434000	-1.715950000
H	-3.794418000	-2.014193000	-2.322987000
H	-2.216495000	-1.460528000	-2.893911000
C	-2.823901000	-2.465470000	1.115163000
H	-2.296346000	-2.495143000	2.071155000
H	-3.867210000	-2.746844000	1.302070000
H	-2.384599000	-3.228924000	0.469653000

C	-2.789528000	0.309332000	2.676453000
H	-3.830934000	0.335526000	3.019913000
H	-2.291245000	-0.516386000	3.188694000
H	-2.311152000	1.238593000	2.992544000
C	-2.834204000	2.669490000	0.533582000
H	-3.880802000	2.986363000	0.616634000
H	-2.339257000	2.912076000	1.476479000
H	-2.367813000	3.269810000	-0.250464000
C	2.374880000	2.722961000	0.002757000
C	2.339247000	-2.738470000	0.003235000
C	1.664200000	-3.293227000	-1.258685000
H	2.146107000	-2.904701000	-2.160830000
H	1.735115000	-4.385900000	-1.275408000
H	0.607997000	-3.013568000	-1.289072000
C	3.811172000	-3.150316000	0.012073000
H	4.324216000	-2.776763000	0.903567000

H	3.893363000	-4.241500000	0.006614000
H	4.337665000	-2.767327000	-0.867548000
C	1.644813000	-3.306358000	1.248431000
H	0.587890000	-3.028263000	1.265349000
H	1.716726000	-4.399069000	1.254872000
H	2.112299000	-2.926903000	2.161971000
C	1.682428000	3.290804000	-1.243689000
H	2.143281000	2.901291000	-2.156367000
H	0.622904000	3.022271000	-1.255836000
H	1.764874000	4.382701000	-1.256858000
C	3.852027000	3.115351000	-0.015591000
H	4.377354000	2.731752000	0.864455000
H	4.356227000	2.728830000	-0.906634000
H	3.948443000	4.205362000	-0.018528000
C	1.712979000	3.295104000	1.263689000
H	0.653272000	3.030128000	1.300469000

H	2.193800000	2.906062000	2.166209000
H	1.798870000	4.386764000	1.272726000

8(T):

Ru	-0.938992000	0.000084000	0.036080000
C	-2.812826000	0.710616000	-1.029775000
P	3.560744000	-0.001586000	-0.011812000
C	-2.804438000	1.142065000	0.357578000
C	-2.813970000	-0.701691000	-1.034711000
C	-2.905735000	-0.002823000	1.206379000
C	-2.804991000	-1.142155000	0.349604000
C	2.283536000	1.220450000	0.010160000
C	2.282112000	-1.222069000	0.010106000
N	1.080778000	0.668080000	0.032713000
N	1.080060000	-0.668165000	0.032718000
C	-2.868815000	1.610788000	-2.218178000

H	-2.449433000	1.131312000	-3.105131000
H	-3.905255000	1.887783000	-2.447646000
H	-2.315569000	2.537545000	-2.048658000
C	-2.872383000	-1.593706000	-2.229101000
H	-2.318192000	-2.521330000	-2.067531000
H	-3.909254000	-1.869727000	-2.457856000
H	-2.455695000	-1.107801000	-3.113810000
C	-2.841337000	-2.568146000	0.792472000
H	-2.410501000	-2.689486000	1.788671000
H	-3.875046000	-2.932059000	0.830183000
H	-2.291298000	-3.218039000	0.108079000
C	-3.105449000	-0.007975000	2.683892000
H	-4.174100000	-0.011086000	2.934639000
H	-2.658697000	-0.890022000	3.148072000
H	-2.662505000	0.873105000	3.153489000
C	-2.840224000	2.565088000	0.809928000

H	-3.873908000	2.928607000	0.851849000
H	-2.407568000	2.679895000	1.806110000
H	-2.291535000	3.219603000	0.128889000
C	2.414240000	2.729171000	0.006329000
C	2.410762000	-2.730967000	0.006358000
C	1.691784000	-3.295331000	-1.226286000
H	2.136571000	-2.908494000	-2.147908000
H	1.767441000	-4.387697000	-1.240746000
H	0.632858000	-3.022781000	-1.219862000
C	3.883397000	-3.138843000	-0.036937000
H	4.427677000	-2.757180000	0.832201000
H	3.968884000	-4.229787000	-0.037765000
H	4.374894000	-2.759855000	-0.938090000
C	1.765811000	-3.293650000	1.280073000
H	0.709356000	-3.017940000	1.336949000
H	1.839408000	-4.386197000	1.290200000

H	2.266727000	-2.907939000	2.172919000
C	1.696293000	3.294438000	-1.226496000
H	2.140632000	2.906811000	-2.148003000
H	0.636970000	3.023478000	-1.220168000
H	1.773598000	4.386687000	-1.241093000
C	3.887439000	3.135050000	-0.036735000
H	4.431054000	2.752763000	0.832545000
H	4.378601000	2.755312000	-0.937756000
H	3.974374000	4.225877000	-0.037676000
C	1.769825000	3.292844000	1.279875000
H	0.712972000	3.018627000	1.336562000
H	2.270023000	2.906492000	2.172847000
H	1.844968000	4.385286000	1.289939000

8(Q):

Ru	-0.916862000	0.000789000	-0.076149000
C	-2.836367000	0.713093000	-0.960955000

P	3.565947000	-0.001529000	0.050520000
C	-2.813048000	1.148696000	0.415912000
C	-2.835795000	-0.713467000	-0.959829000
C	-2.909882000	0.001638000	1.256135000
C	-2.812199000	-1.146753000	0.417775000
C	2.290781000	1.222279000	-0.006087000
C	2.289099000	-1.223578000	-0.006173000
N	1.090054000	0.668668000	-0.065445000
N	1.089170000	-0.668241000	-0.065471000
C	-2.975681000	1.605173000	-2.150948000
H	-2.563390000	1.143566000	-3.050840000
H	-4.031424000	1.828731000	-2.349163000
H	-2.462082000	2.557658000	-2.001625000
C	-2.974817000	-1.607483000	-2.148407000
H	-2.461345000	-2.559769000	-1.997352000
H	-4.030525000	-1.831238000	-2.346555000

H	-2.562173000	-1.147411000	-3.048924000
C	-2.886491000	-2.567314000	0.871267000
H	-2.427763000	-2.701831000	1.853347000
H	-3.930850000	-2.893583000	0.946255000
H	-2.382518000	-3.237597000	0.172123000
C	-2.976460000	0.002264000	2.745577000
H	-4.018372000	-0.005181000	3.089663000
H	-2.488431000	-0.876989000	3.172830000
H	-2.501340000	0.889149000	3.171433000
C	-2.888033000	2.570165000	0.866441000
H	-3.932455000	2.896985000	0.938033000
H	-2.431745000	2.706598000	1.849375000
H	-2.381996000	3.238831000	0.167230000
C	2.425499000	2.730563000	0.008939000
C	2.421709000	-2.732055000	0.008660000
C	1.785156000	-3.306340000	-1.264100000

H	2.291778000	-2.928165000	-2.157043000
H	1.860266000	-4.398833000	-1.264053000
H	0.729192000	-3.031427000	-1.329310000
C	3.894602000	-3.137050000	0.064435000
H	4.380078000	-2.750131000	0.965580000
H	3.981701000	-4.227855000	0.075070000
H	4.443860000	-2.761731000	-0.804343000
C	1.695831000	-3.287474000	1.241692000
H	0.636960000	-3.016226000	1.225317000
H	1.773481000	-4.379596000	1.265779000
H	2.135046000	-2.892463000	2.162668000
C	1.789906000	3.305900000	-1.263826000
H	2.296062000	2.927074000	-2.156758000
H	0.733546000	3.032547000	-1.329166000
H	1.866617000	4.398281000	-1.263662000
C	3.898940000	3.133526000	0.064968000

H	4.383782000	2.745773000	0.966096000
H	4.447795000	2.757635000	-0.803819000
H	3.987516000	4.224208000	0.075832000
C	1.700215000	3.286790000	1.241958000
H	0.641024000	3.016806000	1.225484000
H	2.138878000	2.891166000	2.162935000
H	1.779211000	4.378812000	1.266130000

S5. The cyclic voltammograms of Fc/Fc^{+} (left), 2.0×10^{-3} M in acetonitrile containing 0.08 M $Bu_4N{\cdot}PF_6$, were measured at 100 mVs^{-1} at 23°C vs. AgCl/Ag