Supporting Information for

Reduction-Induced Hapticity Increase in a Silacycle-Bridged Biaryl-Based Ligand Coordinated to an Iron Center

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1. General

Manipulation of air and moisture sensitive compounds was carried out under a dry nitrogen atmosphere using Schlenk tube techniques associated with a high-vacuum line or in the glove box which was filled with dry nitrogen. All solvents were purchased from Kanto Chemical Co. Inc., and was dried over activated molecular sieves. ^{1}H NMR spectra were recorded on a JEOL Lambda 400 spectrometer at ambient temperature. ^{1}H NMR chemical shifts (δ values) were given in ppm relative to the solvent signals. Elemental analysis were performed by a Thermo Scientific FLASH 2000 Organic Elemental Analyzer. Fe($C_{20}H_{25}Si$)Br(tmeda) (**1**) was synthesized by the method reported in the literature[1]. All reagents were purchased from Tokyo Chemical Industries Co., Ltd., Kanto Chemical Co. Inc., or SigmaAldrich, and were used without further purification.

2. Synthesis of Compounds

Fe($C_{20}H_{25}Si$)Br(dcype) (2)

In a 100 mL J. Young tube was added THF solution of **1** (382 mg, 0.70 mmol) and THF solution of dcype (294 mg, 0.70 mmol) (total volume of solution: ca. 50 mL). The resultant red solution was stirred at 35 °C for 14 h. Volatiles were removed in vacuo, and the remaining solid was extracted with Et_2O (ca. 12 mL). The solution was concentrated *in vacuo* and cooled at −30 °C to give the product as red crystals (195 mg, 0.229 mmol, 33%). ^{1}H NMR (400 MHz, rt, C_6D_6): δ = 137.44 (brs, 1H), 95.56 (brs, 1H), 92.13 (brs, 1H), 89.11 (brs, 1H), 86.61 (brs, 1H), 58.04 (brs, 1H), 43.41 (brs, 1H), 33.02 (brs, 2H), 24.03 (brs, 3H), 19.19 (brs, 3H), 16.40 (brs, 1H), 11.37 (brs, 1H), 9.74 (brs, 1H), 9.01 (brs, 1H), 8.17 (brs, 1H), 7.88 (brs, 2H), 4.82 (brs, 2H), 4.17 (brs, 2H), 4.00 (brs, 2H), 3.14 (brs, 2H),

1.89 (brs, 1H), 1.76 (brs, 3H), 1.62 (brs, 1H), 0.45 (brs, 3H), 0.12 (brs, 2H), –0.57 (brs, 2H), –0.86 (brs, 2H), –1.04 (brs, 1H), –1.54 (brs, 2H), –1.68 (brs, 2H), –2.11 (brs, 2H), –2.82 (brs, 2H), –3.30 (brs, 2H), –3.59 (brs, 2H), –3.88 (brs, 2H), –5.61 (brs, 1H), –10.81 (brs, 2H), –13.01 (brs, 2H), –14.61 (brs, 2H), –16.61 (brs, 2H), –21.01 (brs, 3H), –61.69 (brs, 1H), –77.51 (brs, 1H). Magnetic susceptibility (Evans): μ_{eff} = 5.37 ± 0.02 μ_B (in C_6D_6, 21.4 °C). Anal. Calcd. for $C_{46}H_{73}P_2Si_1Fe_1Br_1$: C, 64.86; H, 8.64. Found: C, 64.87; H, 8.62.

Fe($C_{20}H_{25}Si$)(dcype) (3)

In a 20 mL vial were placed KC_8 (18.9 mg, 0.140 mmol), and THF (ca. 0.5 mL) was added. To this vial was added THF solution (ca. 5 mL) of **2** (66.0 mg, 0.078 mmol) at r.t., and stirred at this temperature for 14 h. The resultant blackish red suspension was filtered through cotton, and the solvents were removed *in vacuo*. The resultant dark red sticky solid was extracted with Et_2O and centrifuged to remove insoluble materials. The supernatant was cooled at –30 °C to give the product as brown crystals (22.5 mg, 0.029 mmol, 38%). ^{1}H NMR (400 MHz, rt, THF-d_8): δ = 34.57 (brs, 6H), 24.44 (brs, 3H), 15.68 (brs, 4H), 11.22 (brs, 1H), 5.24 (brs, 4H), 4.68 (brs, 4H), 2.26 (brs, 18H), 0.50 (brs, 12H), –0.42 (brs, 12H), –6.42 (brs, 1H), –12.67 (brs, 4H), –24.08 (brs, 1H), –42.07 (brs, 3H). Magnetic susceptibility (Evans): μ_{eff} = 1.86 ± 0.01 μ_B (in C_6D_6, 21.4 °C). Anal. Calcd. for $C_{46}H_{73}P_2Si_1Fe_1$: C, 71.57; H, 9.53. Found: C, 71.24; H, 9.64.

3. X-ray data collection and reduction

X-ray crystallography for **2** was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71075 Å). Single crystals of **3** suitable for X-ray crystallography were analyzed by synchrotron radiation at beam line BL02B1 (λ = 0.41440 Å) of Spring-8 (Hyogo, Japan) using PILATUS3 X CdTe 1M detector. The data were collected at 128(1) K for **2** and 100(1) K for **3** using ω scan to a maximum 2θ value of 62.2° for **2** and 43.6° for **3**. The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[2], and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 12724 observed reflections and 460 variable parameters for **2** and 20732 observed reflections and 456 variable parameters for **3**. Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[3] . Anomalous dispersion effects were included in Fcalc[4] ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[5] . The values for the mass attenuation coefficients are those of Creagh and Hubbell[6] . All calculations were performed using the CrystalStructure[7] crystallographic software package except for refinement, which was performed using SHELXL Version 2017/1[8] . Details of final refinement as well as the bond lengths and angles are summarized in Tables S1 and S2, and the numbering scheme employed is also shown in Figure S1 and S2 which were drawn with ORTEP at 50% probability ellipsoids. CCDC 2300419 (**2**) and 2300420 (**3**) contain the supplementary crystallographic data.

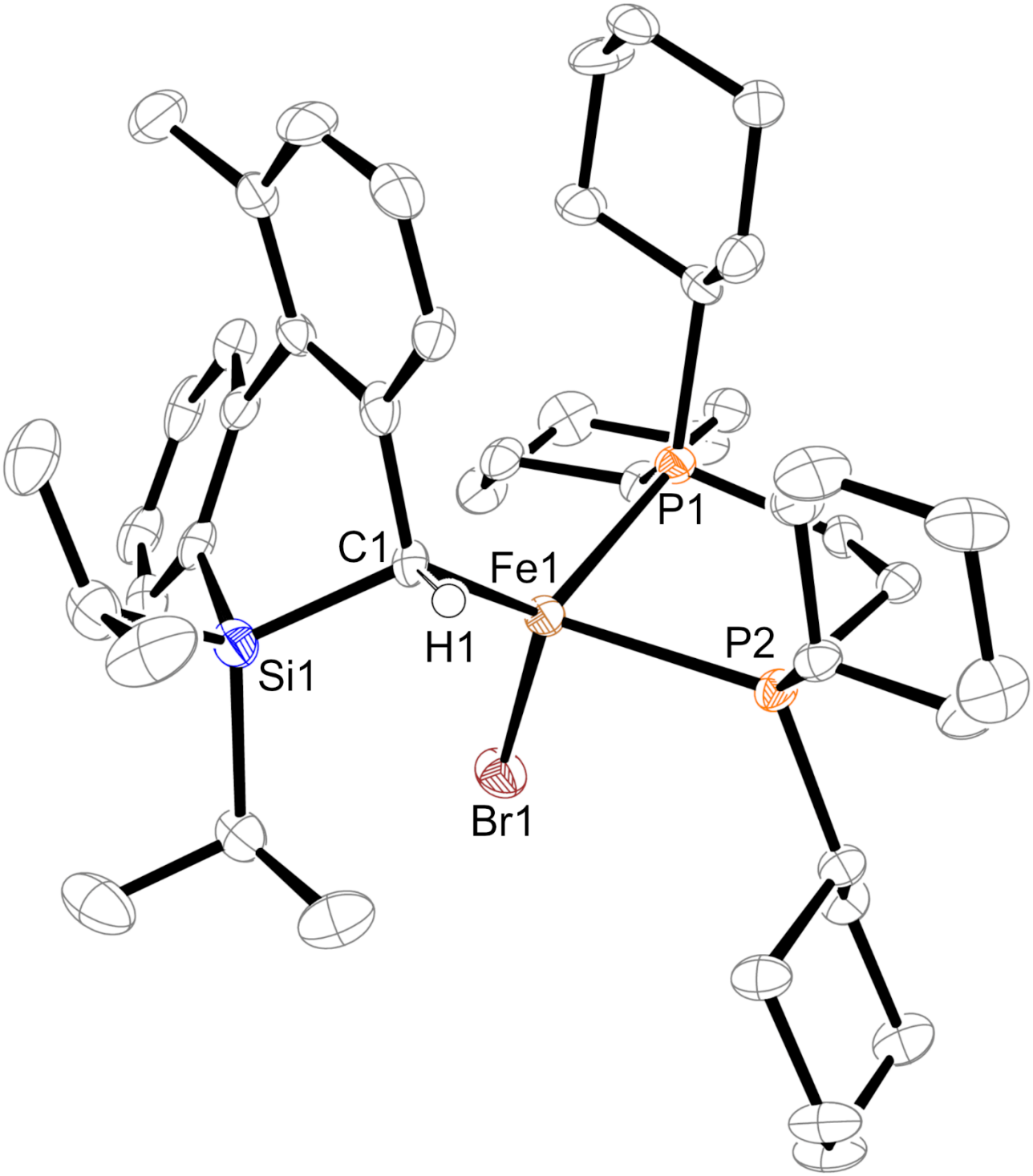

Figure S1-1. ORTEP drawing of **2** (50% probability of the thermal ellipsoids). H atoms except for H1 are omitted for clarity.

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

Empirical Formula	$C_{46}H_{73}BrFeP_2Si$
Formula Weight	851.87
Crystal Color, Habit	red, prism
Crystal Dimensions	0.020 X 0.020 X 0.010 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.3693(7) Å
	b = 22.8549(15) Å
	c = 18.8063(13) Å
	β = 94.720(6)°
	V = 4441.8(5) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.274 g/cm^3
F(000)	1816.00
Diffractometer	Saturn724
Radiation	Mo-$K\alpha$ (λ = 0.71073 Å)
	graphite monochromated
Voltage, Current	50 kV, 24 mA
Temperature	−145.0 °C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	–70.0 – 110.0°
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.00°
Detector Position	45.00 mm
Pixel Size	0.035 mm
No. of Reflections Measured	Total: 40562
	Unique: 12724 (R_{int} = 0.1535)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.548 − 0.986)
Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w\, (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\, \sigma^2(F_o^2) + (0.0306 \cdot P)^2 + 0.0000 \cdot P\,]$
	where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$

$2\theta_{max}$ cutoff	62.2°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	12724
No. Variables	460
Reflection/Parameter Ratio	27.66
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0794
Residuals: R (All reflections)	0.1961
Residuals: wR_2 (All reflections)	0.1558
Goodness of Fit Indicator	0.996
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.68 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.80 $e^-/Å^3$

Table S1-2. Atomic coordinates and B_{iso}/B_{eq} for **2**.

atom	*x*	*y*	*z*	B_{eq}
Br1	0.06504(5)	0.68183(2)	0.77542(3)	2.204(12)
Fe1	0.27787(6)	0.68151(3)	0.73083(3)	1.324(13)
P1	0.35377(11)	0.77108(5)	0.79600(6)	1.35(2)
P2	0.41462(11)	0.62888(5)	0.82619(6)	1.39(2)
Si1	0.17310(12)	0.63895(6)	0.57147(7)	1.71(3)
C1	0.3227(4)	0.65380(19)	0.6300(2)	1.20(8)
C2	0.3606(5)	0.8296(2)	0.4637(3)	2.86(11)
C3	0.3978(4)	0.6957(2)	0.5877(2)	1.71(9)
C4	0.5283(4)	0.6821(2)	0.5767(2)	1.72(8)
C5	0.5975(4)	0.7153(2)	0.5327(3)	2.17(10)
C6	0.5414(5)	0.7633(2)	0.4984(3)	2.25(10)
C7	0.4153(5)	0.7790(2)	0.5081(3)	1.93(9)
C8	0.3439(4)	0.7465(2)	0.5545(3)	1.51(8)
C9	0.2039(4)	0.7616(2)	0.5636(2)	1.67(9)
C10	0.1660(5)	0.8190(2)	0.5716(3)	2.06(9)
C11	0.0364(5)	0.8332(2)	0.5788(3)	2.26(10)
C12	-0.0553(5)	0.7891(2)	0.5783(3)	2.26(10)
C13	-0.0168(4)	0.7319(2)	0.5730(3)	1.99(9)
C14	0.1114(4)	0.7157(2)	0.5656(2)	1.59(9)
C15	0.0530(5)	0.5896(2)	0.6125(3)	1.98(9)
C16	0.1189(5)	0.5369(2)	0.6494(3)	3.15(12)
C17	-0.0596(5)	0.5707(3)	0.5610(3)	3.39(13)
C18	0.2040(5)	0.6091(2)	0.4796(3)	2.43(10)
C19	0.2963(6)	0.5566(2)	0.4864(3)	3.89(14)
C20	0.2538(5)	0.6533(3)	0.4276(3)	3.05(12)
C21	0.4133(4)	0.74240(19)	0.8841(2)	1.50(8)
C22	0.4923(4)	0.6862(2)	0.8840(2)	1.47(8)
C23	0.2250(4)	0.82088(19)	0.8224(2)	1.34(8)
C24	0.1353(4)	0.8426(2)	0.7598(3)	1.80(9)
C25	0.0222(4)	0.8771(2)	0.7857(3)	2.35(10)
C26	0.0692(5)	0.9275(2)	0.8337(3)	2.66(11)
C27	0.1566(5)	0.9049(2)	0.8967(3)	2.37(10)
C28	0.2709(4)	0.8709(2)	0.8714(3)	1.88(9)
C29	0.4886(4)	0.81735(19)	0.7684(2)	1.44(8)
C30	0.6001(4)	0.7785(2)	0.7486(3)	1.91(9)
C31	0.7116(4)	0.8138(2)	0.7224(3)	1.99(9)

C32	0.6668(4)	0.8535(2)	0.6613(3)	1.88(9)
C33	0.5589(4)	0.8926(2)	0.6820(3)	2.59(11)
C34	0.4455(4)	0.8572(2)	0.7062(3)	2.03(9)
C35	0.3447(4)	0.57924(19)	0.8902(2)	1.48(8)
C36	0.2448(4)	0.6088(2)	0.9337(2)	1.79(9)
C37	0.1964(5)	0.5653(2)	0.9877(3)	2.32(10)
C38	0.1419(5)	0.5102(2)	0.9519(3)	2.69(11)
C39	0.2405(5)	0.4817(2)	0.9075(3)	2.63(11)
C40	0.2884(5)	0.5247(2)	0.8533(3)	2.12(10)
C41	0.5510(4)	0.58529(19)	0.7960(2)	1.41(8)
C42	0.6320(4)	0.5518(2)	0.8538(3)	2.06(10)
C43	0.7363(5)	0.5153(2)	0.8212(3)	2.75(11)
C44	0.8209(5)	0.5521(2)	0.7767(3)	2.68(11)
C45	0.7407(5)	0.5854(2)	0.7199(3)	2.51(11)
C46	0.6394(4)	0.6229(2)	0.7539(3)	1.87(9)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S1-3. Anisotropic displacement parameters for **2**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.0226(3)	0.0362(3)	0.0257(3)	-0.0051(2)	0.0063(2)	-0.0044(2)
Fe1	0.0155(4)	0.0213(4)	0.0139(4)	-0.0015(3)	0.0037(3)	-0.0015(3)
P1	0.0174(7)	0.0192(7)	0.0153(7)	-0.0020(5)	0.0034(5)	-0.0001(5)
P2	0.0181(7)	0.0204(7)	0.0147(7)	0.0004(5)	0.0041(5)	0.0012(5)
Si1	0.0188(7)	0.0283(8)	0.0183(8)	-0.0023(6)	0.0032(6)	-0.0036(6)
C1	0.015(2)	0.021(3)	0.010(2)	0.0028(19)	0.0024(19)	-0.0028(19)
C2	0.034(3)	0.045(4)	0.030(3)	-0.001(3)	0.005(3)	0.015(3)
C3	0.019(3)	0.032(3)	0.014(3)	0.000(2)	0.001(2)	-0.005(2)
C4	0.020(3)	0.029(3)	0.016(3)	0.002(2)	0.001(2)	0.001(2)
C5	0.016(3)	0.043(3)	0.024(3)	-0.003(2)	0.007(2)	-0.008(3)
C6	0.029(3)	0.035(3)	0.023(3)	-0.007(2)	0.015(3)	0.001(2)
C7	0.022(3)	0.032(3)	0.019(3)	-0.008(2)	-0.001(2)	-0.001(2)
C8	0.012(2)	0.028(3)	0.017(3)	-0.004(2)	0.001(2)	-0.002(2)
C9	0.021(3)	0.029(3)	0.014(3)	0.001(2)	0.002(2)	0.005(2)
C10	0.030(3)	0.029(3)	0.019(3)	0.002(2)	-0.000(2)	0.002(2)
C11	0.038(3)	0.037(3)	0.011(3)	0.018(3)	0.003(2)	-0.002(2)
C12	0.025(3)	0.044(4)	0.018(3)	0.012(3)	0.007(2)	0.005(2)
C13	0.017(3)	0.042(3)	0.017(3)	0.003(2)	0.003(2)	-0.002(2)
C14	0.023(3)	0.028(3)	0.010(3)	0.005(2)	0.004(2)	0.002(2)
C15	0.024(3)	0.033(3)	0.019(3)	-0.005(2)	0.008(2)	-0.009(2)
C16	0.047(4)	0.035(3)	0.040(4)	0.001(3)	0.019(3)	0.006(3)
C17	0.036(3)	0.051(4)	0.045(4)	-0.017(3)	0.017(3)	-0.020(3)
C18	0.029(3)	0.040(3)	0.024(3)	-0.006(2)	0.006(2)	-0.009(2)
C19	0.086(5)	0.032(4)	0.035(4)	0.001(3)	0.034(4)	-0.007(3)
C20	0.043(4)	0.056(4)	0.018(3)	0.008(3)	0.008(3)	-0.002(3)
C21	0.016(2)	0.025(3)	0.016(3)	-0.001(2)	0.001(2)	-0.000(2)
C22	0.020(2)	0.022(3)	0.015(3)	-0.003(2)	0.005(2)	0.000(2)
C23	0.017(2)	0.019(2)	0.015(3)	0.005(2)	0.006(2)	0.000(2)
C24	0.019(3)	0.032(3)	0.019(3)	0.002(2)	0.006(2)	0.006(2)
C25	0.016(3)	0.039(3)	0.035(3)	0.008(2)	0.006(2)	0.011(3)
C26	0.035(3)	0.031(3)	0.037(4)	0.010(3)	0.013(3)	-0.002(3)
C27	0.033(3)	0.026(3)	0.033(3)	-0.004(2)	0.015(3)	-0.009(2)
C28	0.026(3)	0.025(3)	0.021(3)	-0.001(2)	0.004(2)	-0.002(2)
C29	0.015(2)	0.020(2)	0.020(3)	-0.003(2)	0.001(2)	-0.002(2)
C30	0.024(3)	0.025(3)	0.024(3)	0.004(2)	0.002(2)	0.005(2)
C31	0.016(3)	0.041(3)	0.020(3)	-0.001(2)	0.009(2)	0.001(2)

C32	0.017(3)	0.030(3)	0.025(3)	-0.007(2)	0.007(2)	-0.001(2)
C33	0.025(3)	0.036(3)	0.040(4)	-0.002(2)	0.016(3)	0.014(3)
C34	0.016(3)	0.030(3)	0.032(3)	-0.002(2)	0.004(2)	0.006(2)
C35	0.020(3)	0.019(3)	0.018(3)	0.001(2)	0.006(2)	0.001(2)
C36	0.023(3)	0.026(3)	0.020(3)	0.002(2)	0.010(2)	-0.004(2)
C37	0.035(3)	0.035(3)	0.021(3)	0.001(2)	0.018(3)	0.001(2)
C38	0.038(3)	0.034(3)	0.033(3)	-0.011(3)	0.024(3)	0.001(3)
C39	0.041(3)	0.022(3)	0.040(4)	-0.009(2)	0.015(3)	0.002(2)
C40	0.027(3)	0.027(3)	0.028(3)	-0.004(2)	0.011(2)	0.003(2)
C41	0.022(3)	0.016(2)	0.016(3)	-0.001(2)	0.005(2)	-0.0003(19)
C42	0.022(3)	0.031(3)	0.027(3)	0.005(2)	0.014(2)	0.006(2)
C43	0.030(3)	0.031(3)	0.044(4)	0.011(2)	0.009(3)	0.003(3)
C44	0.026(3)	0.027(3)	0.052(4)	0.003(2)	0.020(3)	0.002(3)
C45	0.026(3)	0.037(3)	0.036(4)	0.002(2)	0.022(3)	0.002(3)
C46	0.021(3)	0.025(3)	0.025(3)	0.001(2)	0.004(2)	0.005(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S1-4. Bond lengths (Å) for **2**.

atom	atom	distance	atom	atom	distance
Br1	Fe1	2.4245(8)	Fe1	P1	2.4806(13)
Fe1	P2	2.5010(13)	Fe1	C1	2.087(4)
P1	C21	1.841(4)	P1	C23	1.853(5)
P1	C29	1.861(4)	P2	C22	1.844(5)
P2	C35	1.845(5)	P2	C41	1.856(5)
Si1	C1	1.858(4)	Si1	C14	1.867(5)
Si1	C15	1.891(5)	Si1	C18	1.909(5)
C1	C3	1.503(6)	C2	C7	1.510(7)
C3	C4	1.420(6)	C3	C8	1.412(6)
C4	C5	1.368(7)	C5	C6	1.377(7)
C6	C7	1.383(7)	C7	C8	1.402(7)
C8	C9	1.515(6)	C9	C10	1.383(7)
C9	C14	1.424(7)	C10	C11	1.400(7)
C11	C12	1.384(7)	C12	C13	1.374(8)
C13	C14	1.397(6)	C15	C16	1.525(7)
C15	C17	1.517(7)	C18	C19	1.533(8)
C18	C20	1.525(8)	C21	C22	1.525(6)
C23	C24	1.523(6)	C23	C28	1.519(6)
C24	C25	1.526(7)	C25	C26	1.518(7)
C26	C27	1.521(7)	C27	C28	1.527(7)
C29	C30	1.527(6)	C29	C34	1.521(6)
C30	C31	1.524(7)	C31	C32	1.506(7)
C32	C33	1.509(7)	C33	C34	1.527(7)
C35	C36	1.530(6)	C35	C40	1.520(6)
C36	C37	1.534(7)	C37	C38	1.514(7)
C38	C39	1.518(8)	C39	C40	1.528(7)
C41	C42	1.523(6)	C41	C46	1.526(6)
C42	C43	1.534(7)	C43	C44	1.514(8)
C44	C45	1.505(7)	C45	C46	1.535(7)

Table S1-5. Bond angles (°) for **2**.

atom	atom	atom	angle	atom	atom	atom	angle
Br1	Fe1	P1	95.02(4)	Br1	Fe1	P2	103.41(4)
Br1	Fe1	C1	126.30(12)	P1	Fe1	P2	84.52(4)
P1	Fe1	C1	127.88(12)	P2	Fe1	C1	110.49(12)
Fe1	P1	C21	102.72(14)	Fe1	P1	C23	115.66(14)
Fe1	P1	C29	123.12(15)	C21	P1	C23	99.9(2)
C21	P1	C29	104.4(2)	C23	P1	C29	107.5(2)
Fe1	P2	C22	106.01(15)	Fe1	P2	C35	122.24(14)
Fe1	P2	C41	116.11(14)	C22	P2	C35	103.2(2)
C22	P2	C41	104.7(2)	C35	P2	C41	102.7(2)
C1	Si1	C14	97.4(2)	C1	Si1	C15	114.4(2)
C1	Si1	C18	114.0(2)	C14	Si1	C15	110.5(2)
C14	Si1	C18	111.4(2)	C15	Si1	C18	108.7(2)
Fe1	C1	Si1	110.9(2)	Fe1	C1	C3	116.8(3)
Si1	C1	C3	104.3(3)	C1	C3	C4	118.7(4)
C1	C3	C8	123.7(4)	C4	C3	C8	117.5(4)
C3	C4	C5	121.4(4)	C4	C5	C6	120.1(4)
C5	C6	C7	120.8(5)	C2	C7	C6	116.2(4)
C2	C7	C8	123.8(4)	C6	C7	C8	119.9(4)
C3	C8	C7	120.1(4)	C3	C8	C9	119.0(4)
C7	C8	C9	120.6(4)	C8	C9	C10	120.8(4)
C8	C9	C14	119.3(4)	C10	C9	C14	119.9(4)
C9	C10	C11	120.9(5)	C10	C11	C12	119.8(5)
C11	C12	C13	119.3(5)	C12	C13	C14	123.0(5)
Si1	C14	C9	117.7(3)	Si1	C14	C13	124.5(4)
C9	C14	C13	117.1(4)	Si1	C15	C16	111.9(3)
Si1	C15	C17	114.1(4)	C16	C15	C17	111.0(4)
Si1	C18	C19	110.8(3)	Si1	C18	C20	115.8(4)
C19	C18	C20	109.2(4)	P1	C21	C22	116.1(3)
P2	C22	C21	113.0(3)	P1	C23	C24	113.6(3)
P1	C23	C28	115.3(3)	C24	C23	C28	111.4(4)
C23	C24	C25	111.0(4)	C24	C25	C26	111.3(4)
C25	C26	C27	110.4(4)	C26	C27	C28	111.0(4)
C23	C28	C27	111.1(4)	P1	C29	C30	109.8(3)
P1	C29	C34	112.0(3)	C30	C29	C34	109.9(4)
C29	C30	C31	112.4(4)	C30	C31	C32	111.7(4)
C31	C32	C33	110.4(4)	C32	C33	C34	111.6(4)

C29	C34	C33	111.2(4)	P2	C35	C36	113.4(3)
P2	C35	C40	111.3(3)	C36	C35	C40	110.8(4)
C35	C36	C37	109.9(4)	C36	C37	C38	112.1(4)
C37	C38	C39	110.9(4)	C38	C39	C40	111.3(4)
C35	C40	C39	110.9(4)	P2	C41	C42	116.2(3)
P2	C41	C46	111.2(3)	C42	C41	C46	109.5(4)
C41	C42	C43	110.7(4)	C42	C43	C44	112.3(4)
C43	C44	C45	111.2(4)	C44	C45	C46	110.1(4)
C41	C46	C45	111.2(4)				

Table S1-6. Torsion Angles (°) for **2**.

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Br1	Fe1	P1	C21	85.13(5)	Br1	Fe1	P1	C23	-22.61(6)
Br1	Fe1	P1	C29	-157.95(6)	Br1	Fe1	P2	C22	-95.87(5)
Br1	Fe1	P2	C35	21.58(7)	Br1	Fe1	P2	C41	148.30(5)
Br1	Fe1	C1	Si1	8.5(3)	Br1	Fe1	C1	C3	127.74(19)
P1	Fe1	P2	C22	-2.01(5)	P1	Fe1	P2	C35	115.45(7)
P1	Fe1	P2	C41	-117.83(6)	P2	Fe1	P1	C21	-17.90(5)
P2	Fe1	P1	C23	-125.64(6)	P2	Fe1	P1	C29	99.01(7)
P1	Fe1	C1	Si1	-126.64(16)	P1	Fe1	C1	C3	-7.4(3)
C1	Fe1	P1	C21	-129.66(15)	C1	Fe1	P1	C23	122.59(15)
C1	Fe1	P1	C29	-12.75(17)	P2	Fe1	C1	Si1	134.07(16)
P2	Fe1	C1	C3	-106.7(2)	C1	Fe1	P2	C22	126.50(13)
C1	Fe1	P2	C35	-116.05(14)	C1	Fe1	P2	C41	10.68(14)
Fe1	P1	C21	C22	42.6(3)	Fe1	P1	C23	C24	-58.2(3)
Fe1	P1	C23	C28	171.47(19)	Fe1	P1	C29	C30	-43.7(3)
Fe1	P1	C29	C34	78.7(3)	C21	P1	C23	C24	-167.6(3)
C21	P1	C23	C28	62.1(3)	C23	P1	C21	C22	162.0(3)
C21	P1	C29	C30	72.4(3)	C21	P1	C29	C34	-165.2(2)
C29	P1	C21	C22	-86.9(3)	C23	P1	C29	C30	177.9(2)
C23	P1	C29	C34	-59.7(3)	C29	P1	C23	C24	83.7(3)
C29	P1	C23	C28	-46.6(3)	Fe1	P2	C22	C21	27.4(3)
Fe1	P2	C35	C36	-58.2(3)	Fe1	P2	C35	C40	67.6(3)
Fe1	P2	C41	C42	-178.29(18)	Fe1	P2	C41	C46	55.6(3)
C22	P2	C35	C36	60.7(3)	C22	P2	C35	C40	-173.6(2)
C35	P2	C22	C21	-102.1(3)	C22	P2	C41	C42	65.2(3)
C22	P2	C41	C46	-61.0(3)	C41	P2	C22	C21	150.7(3)
C35	P2	C41	C42	-42.3(3)	C35	P2	C41	C46	-168.5(2)
C41	P2	C35	C36	169.4(2)	C41	P2	C35	C40	-64.9(3)
C1	Si1	C14	C9	36.0(3)	C1	Si1	C14	C13	-134.6(3)
C14	Si1	C1	Fe1	65.9(2)	C14	Si1	C1	C3	-60.6(3)
C1	Si1	C15	C16	-44.7(4)	C1	Si1	C15	C17	-171.8(3)
C15	Si1	C1	Fe1	-50.6(3)	C15	Si1	C1	C3	-177.2(2)
C1	Si1	C18	C19	51.2(4)	C1	Si1	C18	C20	-73.9(3)
C18	Si1	C1	Fe1	-176.6(2)	C18	Si1	C1	C3	56.8(3)
C14	Si1	C15	C16	-153.4(3)	C14	Si1	C15	C17	79.6(3)
C15	Si1	C14	C9	155.6(3)	C15	Si1	C14	C13	-15.1(4)

C14	Si1	C18	C19	160.2(3)	C14	Si1	C18	C20	35.1(4)
C18	Si1	C14	C9	-83.5(3)	C18	Si1	C14	C13	105.9(3)
C15	Si1	C18	C19	-77.8(3)	C15	Si1	C18	C20	157.2(3)
C18	Si1	C15	C16	84.0(3)	C18	Si1	C15	C17	-43.0(4)
Fe1	C1	C3	C4	110.1(4)	Fe1	C1	C3	C8	-73.8(4)
Si1	C1	C3	C4	-127.2(3)	Si1	C1	C3	C8	49.0(5)
C1	C3	C4	C5	173.3(3)	C1	C3	C8	C7	-171.4(4)
C1	C3	C8	C9	2.3(6)	C4	C3	C8	C7	4.8(6)
C4	C3	C8	C9	178.5(4)	C8	C3	C4	C5	-3.1(6)
C3	C4	C5	C6	0.4(7)	C4	C5	C6	C7	0.6(7)
C5	C6	C7	C2	-175.6(4)	C5	C6	C7	C8	1.2(7)
C2	C7	C8	C3	172.6(4)	C2	C7	C8	C9	-1.0(7)
C6	C7	C8	C3	-4.0(7)	C6	C7	C8	C9	-177.5(4)
C3	C8	C9	C10	141.9(4)	C3	C8	C9	C14	-36.7(6)
C7	C8	C9	C10	-44.5(6)	C7	C8	C9	C14	137.0(4)
C8	C9	C10	C11	178.9(4)	C8	C9	C14	Si1	9.6(6)
C8	C9	C14	C13	-179.1(3)	C10	C9	C14	Si1	-169.0(3)
C10	C9	C14	C13	2.4(6)	C14	C9	C10	C11	-2.5(6)
C9	C10	C11	C12	0.3(7)	C10	C11	C12	C13	2.1(7)
C11	C12	C13	C14	-2.2(7)	C12	C13	C14	Si1	170.7(4)
C12	C13	C14	C9	-0.0(6)	P1	C21	C22	P2	-48.5(4)
P1	C23	C24	C25	173.0(2)	P1	C23	C28	C27	-173.5(2)
C24	C23	C28	C27	55.1(5)	C28	C23	C24	C25	-54.7(5)
C23	C24	C25	C26	55.8(5)	C24	C25	C26	C27	-56.9(5)
C25	C26	C27	C28	57.0(5)	C26	C27	C28	C23	-56.3(5)
P1	C29	C30	C31	177.6(2)	P1	C29	C34	C33	-177.3(2)
C30	C29	C34	C33	-54.9(4)	C34	C29	C30	C31	54.0(4)
C29	C30	C31	C32	-54.7(5)	C30	C31	C32	C33	55.1(5)
C31	C32	C33	C34	-56.8(5)	C32	C33	C34	C29	57.4(5)
P2	C35	C36	C37	-177.5(2)	P2	C35	C40	C39	175.5(2)
C36	C35	C40	C39	-57.3(4)	C40	C35	C36	C37	56.4(4)
C35	C36	C37	C38	-55.8(4)	C36	C37	C38	C39	55.3(5)
C37	C38	C39	C40	-55.1(5)	C38	C39	C40	C35	56.4(5)
P2	C41	C42	C43	177.1(2)	P2	C41	C46	C45	-171.9(2)
C42	C41	C46	C45	58.4(4)	C46	C41	C42	C43	-56.0(4)
C41	C42	C43	C44	55.0(5)	C42	C43	C44	C45	-55.0(5)
C43	C44	C45	C46	55.9(5)	C44	C45	C46	C41	-58.5(5)

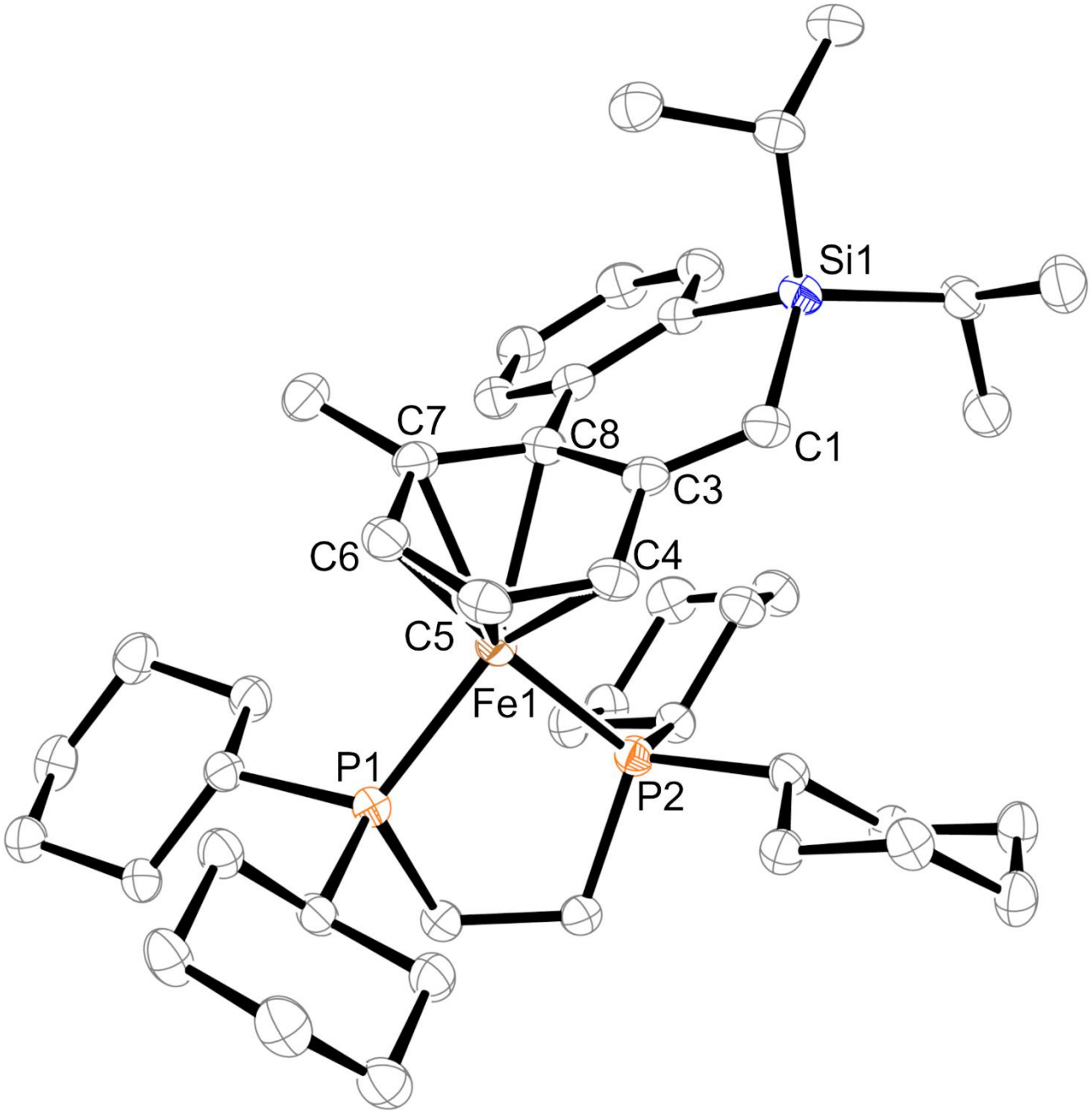

Figure S2. ORTEP drawing of **3** (50% probability of the thermal ellipsoids). H atoms are omitted for clarity.

Table S2-1. Crystal data and structure refinement for **3**.

Empirical Formula	$C_{46}H_{73}FeP_2Si$
Formula Weight	771.96
Crystal Color, Habit	brown, prism
Crystal Dimensions	0.010 X 0.005 X 0.002 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 12.3907(2) Å
	b = 17.3731(3) Å
	c = 19.8465(4) Å
	β = 96.6727(17)°
	V = 4243.31(13) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.208 g/cm^3
F(000)	1676.00
Diffractometer	R-AXIS IV
Radiation (λ = 0.414400 Å)	
Voltage, Current	8 kV, 100 mA
Temperature	−173.0 °C
Detector Aperture	300.0 x 300.0 mm
Data Images	1080 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	0.0 - 180.0°
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.00°
Detector Position	130.00 mm
Pixel Size	0.172 mm
No. of Reflections Measured	Total: 167094
	Unique: 20732 (R_{int} = 0.0600)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.472 − 1.000)
Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w\, (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\, \sigma^2(F_o^2) + (0.0316 \cdot P)^2 + 0.8296 \cdot P\,]$
	where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$
$2\theta_{max}$ cutoff	43.6°

Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	20732
No. Variables	456
Reflection/Parameter Ratio	45.46
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0464
Residuals: R (All reflections)	0.0758
Residuals: wR_2 (All reflections)	0.1164
Goodness of Fit Indicator	1.051
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.66 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.60 $e^-/Å^3$

Table S2-2. Atomic coordinates and B_{iso}/B_{eq} for **3**.

atom	*x*	*y*	*z*	B_{eq}
Fe1	0.57091(2)	0.40082(2)	0.74625(2)	1.282(3)
P1	0.45410(2)	0.32778(2)	0.79255(2)	1.291(5)
P2	0.69460(2)	0.31296(2)	0.78029(2)	1.254(5)
Si1	0.85908(3)	0.53302(2)	0.63086(2)	1.415(6)
C1	0.80781(10)	0.52669(7)	0.71327(6)	1.55(2)
C2	0.42397(11)	0.47506(9)	0.60578(7)	2.20(2)
C3	0.70233(10)	0.50383(6)	0.71821(6)	1.423(18)
C4	0.65889(10)	0.50508(7)	0.78350(6)	1.58(2)
C5	0.54785(11)	0.51180(7)	0.78856(6)	1.71(2)
C6	0.47369(10)	0.50055(7)	0.72893(7)	1.77(2)
C7	0.51095(10)	0.48023(7)	0.66622(6)	1.60(2)
C8	0.62615(9)	0.47010(6)	0.66278(6)	1.39(2)
C9	0.66744(10)	0.43982(7)	0.60017(6)	1.44(2)
C10	0.60734(10)	0.38276(7)	0.56127(6)	1.67(2)
C11	0.64402(11)	0.34996(8)	0.50416(7)	1.93(2)
C12	0.74411(12)	0.37183(8)	0.48435(7)	2.02(2)
C13	0.80547(11)	0.42669(8)	0.52265(6)	1.79(2)
C14	0.76964(10)	0.46191(7)	0.58003(6)	1.46(2)
C15	0.83812(11)	0.63177(7)	0.58958(6)	1.66(2)
C16	0.90318(12)	0.64435(8)	0.52901(7)	2.14(2)
C17	0.71608(11)	0.64575(8)	0.56775(7)	2.09(2)
C18	1.00978(10)	0.50961(7)	0.63435(7)	1.75(2)
C19	1.07668(12)	0.56869(9)	0.67903(9)	2.61(3)
C20	1.03919(12)	0.42772(8)	0.65938(8)	2.26(3)
C21	0.51490(9)	0.23306(7)	0.81979(6)	1.479(18)
C22	0.63867(9)	0.24124(7)	0.83692(6)	1.48(2)
C23	0.33083(9)	0.29954(7)	0.73470(6)	1.429(18)
C24	0.36345(10)	0.26665(8)	0.66795(6)	1.79(2)
C25	0.26262(11)	0.25305(9)	0.61681(7)	2.10(2)
C26	0.18321(11)	0.19788(8)	0.64578(7)	2.18(2)
C27	0.15122(10)	0.22769(8)	0.71317(7)	1.85(2)
C28	0.25149(10)	0.24426(7)	0.76426(6)	1.68(2)
C29	0.39400(9)	0.35541(7)	0.87112(6)	1.461(18)
C30	0.48194(10)	0.37118(8)	0.93108(6)	1.76(2)
C31	0.43026(12)	0.38538(9)	0.99672(7)	2.12(2)
C32	0.34812(12)	0.45152(9)	0.98820(7)	2.28(3)

C33	0.26254(11)	0.43722(8)	0.92782(7)	2.07(2)
C34	0.31350(10)	0.42276(8)	0.86194(6)	1.72(2)
C35	0.75219(9)	0.24484(7)	0.72119(6)	1.365(17)
C36	0.82385(10)	0.28394(7)	0.67324(6)	1.64(2)
C37	0.87416(11)	0.22441(8)	0.62892(7)	2.02(2)
C38	0.78676(12)	0.17478(8)	0.58905(7)	2.10(2)
C39	0.71345(11)	0.13704(8)	0.63638(7)	1.97(2)
C40	0.66314(10)	0.19690(7)	0.68013(7)	1.72(2)
C41	0.81855(9)	0.35060(7)	0.83259(6)	1.352(18)
C42	0.91506(10)	0.29517(7)	0.84836(6)	1.62(2)
C43	1.01302(10)	0.33739(8)	0.88634(7)	1.87(2)
C44	0.98468(10)	0.37618(9)	0.95137(7)	1.98(2)
C45	0.88664(10)	0.42969(7)	0.93616(6)	1.75(2)
C46	0.79003(10)	0.38468(7)	0.90043(6)	1.52(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2-3. Anisotropic displacement parameters for **3**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.01606(7)	0.01727(7)	0.01584(7)	0.00044(6)	0.00386(5)	0.00148(5)
P1	0.01477(11)	0.01802(12)	0.01651(12)	-0.00013(10)	0.00281(9)	0.00145(9)
P2	0.01541(12)	0.01676(12)	0.01566(12)	0.00023(10)	0.00257(9)	0.00007(9)
Si1	0.01955(14)	0.01718(14)	0.01781(14)	-0.00091(11)	0.00553(11)	0.00060(10)
C1	0.0214(5)	0.0206(5)	0.0170(5)	-0.0032(4)	0.0032(4)	0.0000(4)
C2	0.0223(5)	0.0348(7)	0.0257(6)	0.0052(5)	-0.0004(5)	0.0063(5)
C3	0.0215(5)	0.0160(4)	0.0171(5)	0.0010(4)	0.0045(4)	0.0012(3)
C4	0.0252(5)	0.0187(5)	0.0172(5)	-0.0021(4)	0.0063(4)	-0.0005(4)
C5	0.0260(5)	0.0188(5)	0.0218(5)	0.0016(4)	0.0099(4)	0.0003(4)
C6	0.0220(5)	0.0212(5)	0.0251(6)	0.0046(4)	0.0078(4)	0.0040(4)
C7	0.0201(5)	0.0208(5)	0.0204(5)	0.0029(4)	0.0042(4)	0.0048(4)
C8	0.0189(5)	0.0176(5)	0.0166(5)	0.0008(4)	0.0040(4)	0.0020(4)
C9	0.0202(5)	0.0186(5)	0.0159(5)	0.0011(4)	0.0026(4)	0.0014(4)
C10	0.0221(5)	0.0224(5)	0.0188(5)	-0.0020(4)	0.0018(4)	0.0001(4)
C11	0.0282(6)	0.0255(6)	0.0192(5)	-0.0018(5)	0.0007(4)	-0.0039(4)
C12	0.0306(6)	0.0278(6)	0.0192(5)	0.0000(5)	0.0057(5)	-0.0047(4)
C13	0.0251(5)	0.0240(5)	0.0201(5)	0.0000(5)	0.0071(4)	-0.0012(4)
C14	0.0207(5)	0.0181(5)	0.0174(5)	0.0002(4)	0.0045(4)	0.0012(4)
C15	0.0258(5)	0.0194(5)	0.0189(5)	0.0001(4)	0.0065(4)	0.0008(4)
C16	0.0327(6)	0.0264(6)	0.0237(6)	0.0011(5)	0.0094(5)	0.0061(5)
C17	0.0289(6)	0.0239(6)	0.0270(6)	0.0066(5)	0.0046(5)	0.0011(5)
C18	0.0202(5)	0.0214(5)	0.0255(6)	-0.0015(4)	0.0052(4)	0.0021(4)
C19	0.0260(6)	0.0266(6)	0.0457(9)	-0.0041(5)	-0.0003(6)	0.0001(6)
C20	0.0236(6)	0.0227(6)	0.0399(8)	0.0023(5)	0.0043(5)	0.0050(5)
C21	0.0172(4)	0.0189(5)	0.0203(5)	-0.0010(4)	0.0031(4)	0.0023(4)
C22	0.0178(5)	0.0206(5)	0.0179(5)	0.0003(4)	0.0023(4)	0.0034(4)
C23	0.0159(4)	0.0206(5)	0.0179(5)	0.0002(4)	0.0024(4)	0.0004(4)
C24	0.0207(5)	0.0290(6)	0.0187(5)	0.0021(5)	0.0034(4)	-0.0013(4)
C25	0.0237(5)	0.0365(7)	0.0188(5)	0.0047(5)	-0.0002(4)	-0.0037(5)
C26	0.0233(6)	0.0299(6)	0.0283(6)	0.0006(5)	-0.0023(5)	-0.0066(5)
C27	0.0182(5)	0.0258(6)	0.0256(6)	-0.0020(4)	-0.0001(4)	0.0005(4)
C28	0.0179(5)	0.0250(5)	0.0206(5)	-0.0030(4)	0.0016(4)	0.0015(4)
C29	0.0179(4)	0.0206(5)	0.0176(5)	-0.0019(4)	0.0045(4)	-0.0002(4)
C30	0.0201(5)	0.0279(6)	0.0189(5)	-0.0031(4)	0.0023(4)	-0.0005(4)
C31	0.0273(6)	0.0354(7)	0.0181(5)	-0.0056(5)	0.0044(4)	-0.0017(5)
C32	0.0283(6)	0.0342(7)	0.0254(6)	-0.0054(5)	0.0080(5)	-0.0101(5)

C33	0.0217(5)	0.0314(6)	0.0266(6)	-0.0028(5)	0.0080(5)	-0.0069(5)
C34	0.0194(5)	0.0248(5)	0.0219(5)	0.0007(4)	0.0053(4)	-0.0019(4)
C35	0.0178(4)	0.0174(4)	0.0169(5)	0.0001(4)	0.0030(4)	-0.0002(3)
C36	0.0224(5)	0.0201(5)	0.0207(5)	-0.0012(4)	0.0062(4)	-0.0001(4)
C37	0.0261(6)	0.0268(6)	0.0253(6)	0.0010(5)	0.0096(5)	-0.0038(5)
C38	0.0310(6)	0.0276(6)	0.0214(6)	0.0022(5)	0.0045(5)	-0.0054(4)
C39	0.0264(6)	0.0244(6)	0.0237(6)	-0.0026(5)	0.0019(5)	-0.0073(4)
C40	0.0190(5)	0.0239(5)	0.0223(5)	-0.0012(4)	0.0019(4)	-0.0043(4)
C41	0.0160(4)	0.0186(5)	0.0168(5)	-0.0003(4)	0.0021(4)	-0.0014(4)
C42	0.0174(5)	0.0215(5)	0.0223(5)	0.0016(4)	0.0004(4)	-0.0033(4)
C43	0.0167(5)	0.0290(6)	0.0253(6)	0.0005(4)	0.0015(4)	-0.0068(5)
C44	0.0191(5)	0.0336(6)	0.0221(6)	-0.0012(5)	0.0009(4)	-0.0068(5)
C45	0.0217(5)	0.0240(5)	0.0211(5)	-0.0013(4)	0.0042(4)	-0.0059(4)
C46	0.0177(5)	0.0229(5)	0.0176(5)	0.0005(4)	0.0032(4)	-0.0029(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S2-4. Bond lengths (Å) for **3**.

atom	atom	distance	atom	atom	distance
Fe1	P1	2.2042(5)	Fe1	P2	2.2124(4)
Fe1	C4	2.1974(12)	Fe1	C5	2.1354(13)
Fe1	C6	2.1154(13)	Fe1	C7	2.1688(12)
Fe1	C8	2.2192(12)	P1	C21	1.8636(12)
P1	C23	1.8666(11)	P1	C29	1.8672(13)
P2	C22	1.8647(13)	P2	C35	1.8655(13)
P2	C41	1.8690(11)	Si1	C1	1.8254(13)
Si1	C14	1.8741(12)	Si1	C15	1.9059(13)
Si1	C18	1.9044(13)	C1	C3	1.3803(18)
C2	C7	1.5192(17)	C3	C4	1.4599(18)
C3	C8	1.4843(16)	C4	C5	1.3960(19)
C5	C6	1.4249(17)	C6	C7	1.4214(19)
C7	C8	1.4477(17)	C8	C9	1.4934(17)
C9	C10	1.4141(17)	C9	C14	1.4242(18)
C10	C11	1.3913(19)	C11	C12	1.397(2)
C12	C13	1.3892(19)	C13	C14	1.4092(18)
C15	C16	1.539(2)	C15	C17	1.5431(19)
C18	C19	1.535(2)	C18	C20	1.5367(19)
C21	C22	1.5384(16)	C23	C24	1.5392(18)
C23	C28	1.5385(17)	C24	C25	1.5337(17)
C25	C26	1.533(2)	C26	C27	1.529(2)
C27	C28	1.5368(17)	C29	C30	1.5418(16)
C29	C34	1.5346(18)	C30	C31	1.5368(19)
C31	C32	1.531(2)	C32	C33	1.5254(19)
C33	C34	1.5373(19)	C35	C36	1.5336(18)
C35	C40	1.5383(17)	C36	C37	1.5360(19)
C37	C38	1.5307(19)	C38	C39	1.528(2)
C39	C40	1.5329(19)	C41	C42	1.5389(17)
C41	C46	1.5488(17)	C42	C43	1.5385(17)
C43	C44	1.532(2)	C44	C45	1.5316(18)
C45	C46	1.5330(17)			

Table S2-5. Bond angles (°) for **3**.

atom	atom	atom	angle	atom	atom	atom	angle
P1	Fe1	P2	86.597(17)	P1	Fe1	C4	131.18(4)
P1	Fe1	C5	103.39(4)	P1	Fe1	C6	98.64(4)
P1	Fe1	C7	119.07(4)	P1	Fe1	C8	153.88(3)
P2	Fe1	C4	99.61(3)	P2	Fe1	C5	128.50(4)
P2	Fe1	C6	167.40(4)	P2	Fe1	C7	145.97(4)
P2	Fe1	C8	109.84(3)	C4	Fe1	C5	37.56(5)
C4	Fe1	C6	68.31(5)	C4	Fe1	C7	80.58(5)
C4	Fe1	C8	67.67(4)	C5	Fe1	C6	39.17(5)
C5	Fe1	C7	70.34(5)	C5	Fe1	C8	82.58(5)
C6	Fe1	C7	38.73(5)	C6	Fe1	C8	69.74(5)
C7	Fe1	C8	38.51(4)	Fe1	P1	C21	111.49(4)
Fe1	P1	C23	115.14(4)	Fe1	P1	C29	123.03(4)
C21	P1	C23	102.75(5)	C21	P1	C29	99.89(6)
C23	P1	C29	101.77(5)	Fe1	P2	C22	110.63(4)
Fe1	P2	C35	123.21(4)	Fe1	P2	C41	115.06(4)
C22	P2	C35	98.69(6)	C22	P2	C41	103.77(5)
C35	P2	C41	102.79(5)	C1	Si1	C14	101.36(6)
C1	Si1	C15	113.28(6)	C1	Si1	C18	113.35(6)
C14	Si1	C15	108.63(5)	C14	Si1	C18	113.25(6)
C15	Si1	C18	106.97(6)	Si1	C1	C3	120.79(9)
C1	C3	C4	120.57(10)	C1	C3	C8	125.93(11)
C4	C3	C8	113.29(10)	Fe1	C4	C3	84.77(7)
Fe1	C4	C5	68.81(7)	C3	C4	C5	122.22(10)
Fe1	C5	C4	73.63(7)	Fe1	C5	C6	69.66(7)
C4	C5	C6	118.34(11)	Fe1	C6	C5	71.17(7)
Fe1	C6	C7	72.67(7)	C5	C6	C7	121.17(11)
Fe1	C7	C2	133.78(9)	Fe1	C7	C6	68.61(7)
Fe1	C7	C8	72.63(7)	C2	C7	C6	115.67(11)
C2	C7	C8	124.64(11)	C6	C7	C8	119.59(10)
Fe1	C8	C3	83.43(7)	Fe1	C8	C7	68.86(7)
Fe1	C8	C9	126.53(8)	C3	C8	C7	117.56(10)
C3	C8	C9	120.39(10)	C7	C8	C9	121.13(10)
C8	C9	C10	119.45(11)	C8	C9	C14	122.71(10)
C10	C9	C14	117.69(11)	C9	C10	C11	122.06(12)
C10	C11	C12	120.18(12)	C11	C12	C13	118.69(13)
C12	C13	C14	122.43(13)	Si1	C14	C9	121.07(9)

Si1	C14	C13	119.94(10)	C9	C14	C13	118.93(11)
Si1	C15	C16	113.96(9)	Si1	C15	C17	110.03(9)
C16	C15	C17	110.09(10)	Si1	C18	C19	109.85(9)
Si1	C18	C20	113.84(9)	C19	C18	C20	109.90(11)
P1	C21	C22	109.97(8)	P2	C22	C21	111.06(8)
P1	C23	C24	110.43(8)	P1	C23	C28	116.29(8)
C24	C23	C28	109.86(10)	C23	C24	C25	110.58(10)
C24	C25	C26	110.93(11)	C25	C26	C27	111.06(11)
C26	C27	C28	111.64(11)	C23	C28	C27	111.64(10)
P1	C29	C30	112.06(8)	P1	C29	C34	114.44(8)
C30	C29	C34	110.33(10)	C29	C30	C31	110.86(10)
C30	C31	C32	111.34(11)	C31	C32	C33	110.92(12)
C32	C33	C34	112.21(11)	C29	C34	C33	110.44(10)
P2	C35	C36	113.61(8)	P2	C35	C40	111.92(8)
C36	C35	C40	110.03(10)	C35	C36	C37	111.09(10)
C36	C37	C38	111.44(11)	C37	C38	C39	111.05(11)
C38	C39	C40	111.53(11)	C35	C40	C39	110.70(10)
P2	C41	C42	117.58(8)	P2	C41	C46	111.15(8)
C42	C41	C46	108.23(9)	C41	C42	C43	110.58(10)
C42	C43	C44	112.17(11)	C43	C44	C45	110.80(10)
C44	C45	C46	109.90(10)	C41	C46	C45	110.63(10)

Table S2-6. Torsion Angles (°) for **3**.

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
P1	Fe1	P2	C22	-8.86(2)	P1	Fe1	P2	C35	107.21(2)
P1	Fe1	P2	C41	-126.04(2)	P2	Fe1	P1	C21	-8.59(2)
P2	Fe1	P1	C23	-125.13(2)	P2	Fe1	P1	C29	109.84(2)
P1	Fe1	C4	C3	-178.29(3)	P1	Fe1	C4	C5	-50.72(6)
C4	Fe1	P1	C21	-108.40(5)	C4	Fe1	P1	C23	135.07(5)
C4	Fe1	P1	C29	10.04(5)	P1	Fe1	C5	C4	143.21(4)
P1	Fe1	C5	C6	-87.26(5)	C5	Fe1	P1	C21	-137.41(4)
C5	Fe1	P1	C23	106.05(4)	C5	Fe1	P1	C29	-18.98(4)
P1	Fe1	C6	C5	100.62(5)	P1	Fe1	C6	C7	-126.59(4)
C6	Fe1	P1	C21	-177.06(4)	C6	Fe1	P1	C23	66.40(4)
C6	Fe1	P1	C29	-58.63(4)	P1	Fe1	C7	C2	-40.35(12)
P1	Fe1	C7	C6	65.25(5)	P1	Fe1	C7	C8	-162.04(3)
C7	Fe1	P1	C21	147.86(4)	C7	Fe1	P1	C23	31.32(5)
C7	Fe1	P1	C29	-93.70(4)	P1	Fe1	C8	C3	160.70(5)
P1	Fe1	C8	C7	37.75(10)	P1	Fe1	C8	C9	-76.04(11)
C8	Fe1	P1	C21	122.01(8)	C8	Fe1	P1	C23	5.47(8)
C8	Fe1	P1	C29	-119.56(8)	P2	Fe1	C4	C3	87.80(5)
P2	Fe1	C4	C5	-144.63(4)	C4	Fe1	P2	C22	122.35(4)
C4	Fe1	P2	C35	-121.58(4)	C4	Fe1	P2	C41	5.17(4)
P2	Fe1	C5	C4	46.82(7)	P2	Fe1	C5	C6	176.35(3)
C5	Fe1	P2	C22	95.56(5)	C5	Fe1	P2	C35	-148.37(5)
C5	Fe1	P2	C41	-21.62(6)	P2	Fe1	C7	C2	94.21(11)
P2	Fe1	C7	C6	-160.18(4)	P2	Fe1	C7	C8	-27.47(9)
C7	Fe1	P2	C22	-150.27(6)	C7	Fe1	P2	C35	-34.20(7)
C7	Fe1	P2	C41	92.55(7)	P2	Fe1	C8	C3	-72.99(5)
P2	Fe1	C8	C7	164.07(3)	P2	Fe1	C8	C9	50.27(8)
C8	Fe1	P2	C22	-168.04(3)	C8	Fe1	P2	C35	-51.97(4)
C8	Fe1	P2	C41	74.78(4)	C4	Fe1	C5	C4	0.00(5)
C4	Fe1	C5	C6	129.53(9)	C5	Fe1	C4	C3	-127.57(9)
C5	Fe1	C4	C5	0.00(5)	C4	Fe1	C6	C5	-30.40(5)
C4	Fe1	C6	C7	102.39(6)	C6	Fe1	C4	C3	-95.95(6)
C6	Fe1	C4	C5	31.62(5)	C4	Fe1	C7	C2	-172.53(11)
C4	Fe1	C7	C6	-66.92(5)	C4	Fe1	C7	C8	65.79(5)
C7	Fe1	C4	C3	-57.68(5)	C7	Fe1	C4	C5	69.89(5)
C4	Fe1	C8	C3	19.52(5)	C4	Fe1	C8	C7	-103.42(5)

C4	Fe1	C8	C9	142.78(9)	C8	Fe1	C4	C3	-19.81(4)
C8	Fe1	C4	C5	107.76(5)	C5	Fe1	C6	C5	-0.00(6)
C5	Fe1	C6	C7	132.78(10)	C6	Fe1	C5	C4	-129.53(10)
C6	Fe1	C5	C6	0.00(6)	C5	Fe1	C7	C2	-135.09(12)
C5	Fe1	C7	C6	-29.49(5)	C5	Fe1	C7	C8	103.22(6)
C7	Fe1	C5	C4	-100.35(6)	C7	Fe1	C5	C6	29.18(5)
C5	Fe1	C8	C3	55.35(5)	C5	Fe1	C8	C7	-67.59(5)
C5	Fe1	C8	C9	178.61(8)	C8	Fe1	C5	C4	-62.67(5)
C8	Fe1	C5	C6	66.86(5)	C6	Fe1	C7	C2	-105.61(13)
C6	Fe1	C7	C6	-0.00(5)	C6	Fe1	C7	C8	132.71(9)
C7	Fe1	C6	C5	-132.78(9)	C7	Fe1	C6	C7	-0.00(5)
C6	Fe1	C8	C3	93.60(6)	C6	Fe1	C8	C7	-29.34(4)
C6	Fe1	C8	C9	-143.14(9)	C8	Fe1	C6	C5	-103.60(6)
C8	Fe1	C6	C7	29.19(4)	C7	Fe1	C8	C3	122.94(8)
C7	Fe1	C8	C7	-0.00(5)	C7	Fe1	C8	C9	-113.80(10)
C8	Fe1	C7	C2	121.68(13)	C8	Fe1	C7	C6	-132.71(9)
C8	Fe1	C7	C8	-0.00(5)	Fe1	P1	C21	C22	27.99(8)
Fe1	P1	C23	C24	50.10(8)	Fe1	P1	C23	C28	176.14(5)
Fe1	P1	C29	C30	-56.87(8)	Fe1	P1	C29	C34	69.71(7)
C21	P1	C23	C24	-71.31(8)	C21	P1	C23	C28	54.73(9)
C23	P1	C21	C22	151.86(7)	C21	P1	C29	C30	66.98(8)
C21	P1	C29	C34	-166.45(7)	C29	P1	C21	C22	-103.56(7)
C23	P1	C29	C30	172.35(7)	C23	P1	C29	C34	-61.07(8)
C29	P1	C23	C24	-174.43(7)	C29	P1	C23	C28	-48.39(8)
Fe1	P2	C22	C21	28.47(8)	Fe1	P2	C35	C36	68.26(7)
Fe1	P2	C35	C40	-57.11(8)	Fe1	P2	C41	C42	-170.57(6)
Fe1	P2	C41	C46	63.95(7)	C22	P2	C35	C36	-170.00(6)
C22	P2	C35	C40	64.63(7)	C35	P2	C22	C21	-102.04(7)
C22	P2	C41	C42	68.43(9)	C22	P2	C41	C46	-57.05(8)
C41	P2	C22	C21	152.40(7)	C35	P2	C41	C42	-34.00(9)
C35	P2	C41	C46	-159.48(7)	C41	P2	C35	C36	-63.64(8)
C41	P2	C35	C40	170.99(7)	C1	Si1	C14	C9	21.24(9)
C1	Si1	C14	C13	-155.77(8)	C14	Si1	C1	C3	-25.86(10)
C1	Si1	C15	C16	166.56(7)	C1	Si1	C15	C17	-69.23(8)
C15	Si1	C1	C3	90.32(9)	C1	Si1	C18	C19	-63.07(9)
C1	Si1	C18	C20	60.66(9)	C18	Si1	C1	C3	-147.55(8)
C14	Si1	C15	C16	-81.64(8)	C14	Si1	C15	C17	42.56(9)
C15	Si1	C14	C9	-98.30(9)	C15	Si1	C14	C13	84.69(9)

C14	Si1	C18	C19	-177.84(7)	C14	Si1	C18	C20	-54.11(10)
C18	Si1	C14	C9	143.01(8)	C18	Si1	C14	C13	-34.01(10)
C15	Si1	C18	C19	62.51(9)	C15	Si1	C18	C20	-173.76(7)
C18	Si1	C15	C16	40.94(9)	C18	Si1	C15	C17	165.14(7)
Si1	C1	C3	C4	-174.80(7)	Si1	C1	C3	C8	10.87(16)
C1	C3	C4	Fe1	-144.32(10)	C1	C3	C4	C5	154.81(10)
C1	C3	C8	Fe1	144.26(11)	C1	C3	C8	C7	-153.75(10)
C1	C3	C8	C9	15.42(16)	C4	C3	C8	Fe1	-30.43(9)
C4	C3	C8	C7	31.56(13)	C4	C3	C8	C9	-159.27(9)
C8	C3	C4	Fe1	30.69(9)	C8	C3	C4	C5	-30.19(14)
Fe1	C4	C5	Fe1	0.000(11)	Fe1	C4	C5	C6	-55.25(8)
C3	C4	C5	Fe1	68.90(11)	C3	C4	C5	C6	13.65(17)
Fe1	C5	C6	Fe1	0.0	Fe1	C5	C6	C7	-54.96(9)
C4	C5	C6	Fe1	57.22(10)	C4	C5	C6	C7	2.26(17)
Fe1	C6	C7	Fe1	0.0	Fe1	C6	C7	C2	129.50(9)
Fe1	C6	C7	C8	-53.76(9)	C5	C6	C7	Fe1	54.28(11)
C5	C6	C7	C2	-176.22(10)	C5	C6	C7	C8	0.52(17)
Fe1	C7	C8	Fe1	0.000(10)	Fe1	C7	C8	C3	-70.12(8)
Fe1	C7	C8	C9	120.80(8)	C2	C7	C8	Fe1	-131.68(13)
C2	C7	C8	C3	158.20(11)	C2	C7	C8	C9	-10.88(17)
C6	C7	C8	Fe1	51.89(10)	C6	C7	C8	C3	-18.23(15)
C6	C7	C8	C9	172.69(9)	Fe1	C8	C9	C10	49.57(13)
Fe1	C8	C9	C14	-125.79(9)	C3	C8	C9	C10	155.20(9)
C3	C8	C9	C14	-20.16(16)	C7	C8	C9	C10	-36.03(15)
C7	C8	C9	C14	148.61(10)	C8	C9	C10	C11	-177.14(9)
C8	C9	C14	Si1	-1.18(16)	C8	C9	C14	C13	175.86(9)
C10	C9	C14	Si1	-176.62(9)	C10	C9	C14	C13	0.42(16)
C14	C9	C10	C11	-1.55(16)	C9	C10	C11	C12	1.41(18)
C10	C11	C12	C13	-0.09(19)	C11	C12	C13	C14	-1.05(19)
C12	C13	C14	Si1	177.94(10)	C12	C13	C14	C9	0.87(18)
P1	C21	C22	P2	-34.64(10)	P1	C23	C24	C25	-172.74(7)
P1	C23	C28	C27	177.74(7)	C24	C23	C28	C27	-55.94(12)
C28	C23	C24	C25	57.68(12)	C23	C24	C25	C26	-58.22(14)
C24	C25	C26	C27	56.16(14)	C25	C26	C27	C28	-54.22(14)
C26	C27	C28	C23	54.62(13)	P1	C29	C30	C31	-174.02(7)
P1	C29	C34	C33	175.92(6)	C30	C29	C34	C33	-56.61(12)
C34	C29	C30	C31	57.21(13)	C29	C30	C31	C32	-56.33(14)
C30	C31	C32	C33	54.77(15)	C31	C32	C33	C34	-54.91(15)

C32	C33	C34	C29	56.09(14)	P2	C35	C36	C37	176.62(6)
P2	C35	C40	C39	-175.39(7)	C36	C35	C40	C39	57.29(12)
C40	C35	C36	C37	-57.01(11)	C35	C36	C37	C38	55.96(12)
C36	C37	C38	C39	-54.52(13)	C37	C38	C39	C40	55.08(14)
C38	C39	C40	C35	-56.73(13)	P2	C41	C42	C43	175.11(7)
P2	C41	C46	C45	-168.51(6)	C42	C41	C46	C45	60.95(11)
C46	C41	C42	C43	-57.98(12)	C41	C42	C43	C44	55.97(13)
C42	C43	C44	C45	-54.42(14)	C43	C44	C45	C46	55.99(13)
C44	C45	C46	C41	-60.26(12)					

4. NMR spectra of compounds

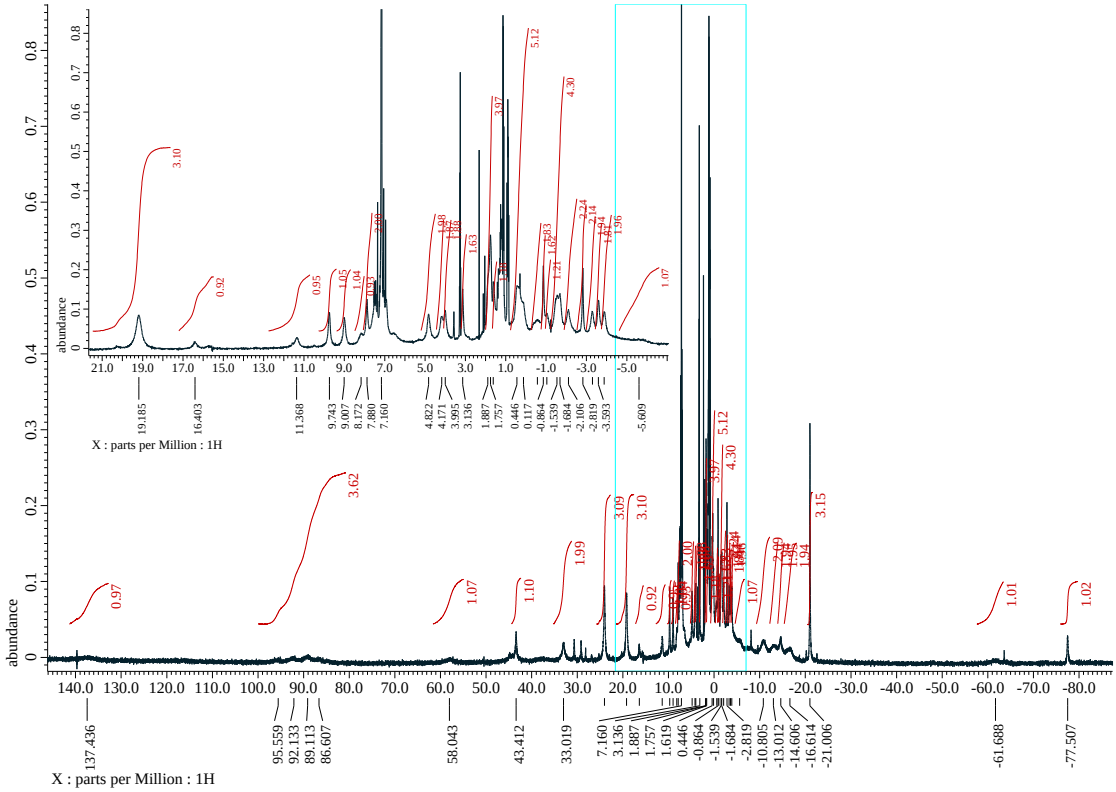

Figure S3. ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

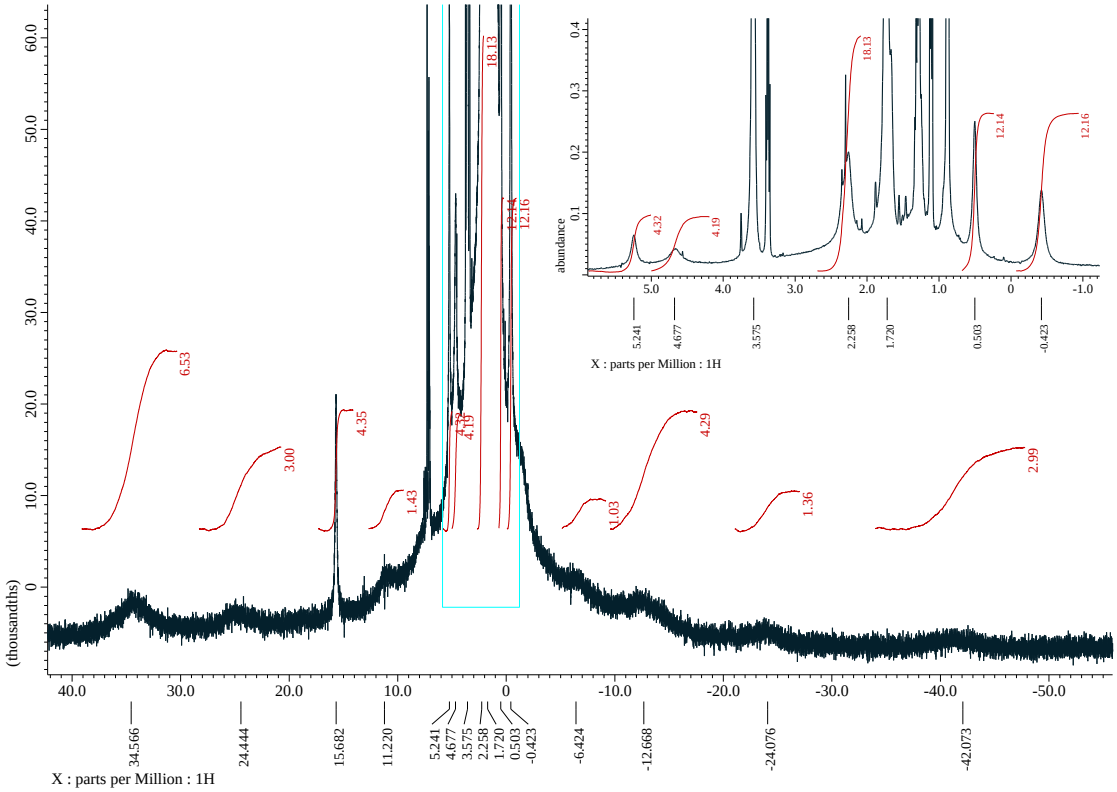

Figure S4. ^{1}H NMR spectrum of **3** in THF-d_8 at room temperature.

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