Supporting Information for the Paper Entitled:

Probing for Four-Coordinate Zero-Valent Iron in a π-Acidic Ligand Field: A Functional Source of FeL_4 Enabled by Labile Dinitrogen Binding

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Contents:

S1. Representative NMR Spectra

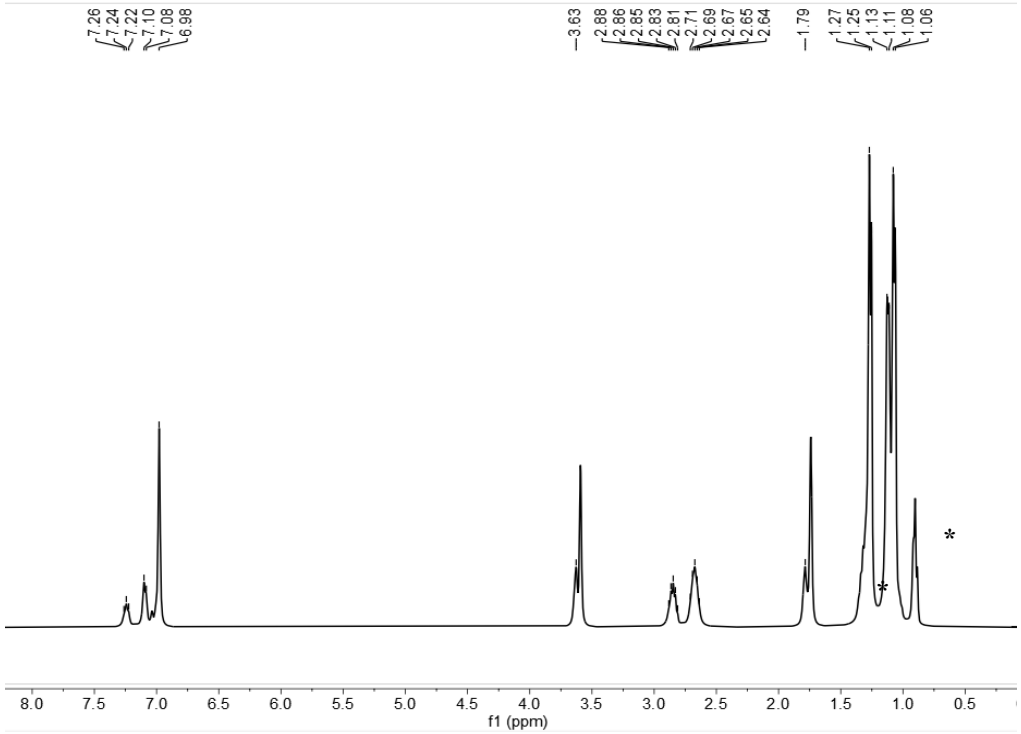

Figure S1.1. ^{1}H NMR spectrum (499.8 MHz, d_8-THF, 20 ˚C) of Fe(THF)(CO)$_2$(CNAr^{Tripp2})$_2$ (**2**). *n*-pentane (*) present in sample.

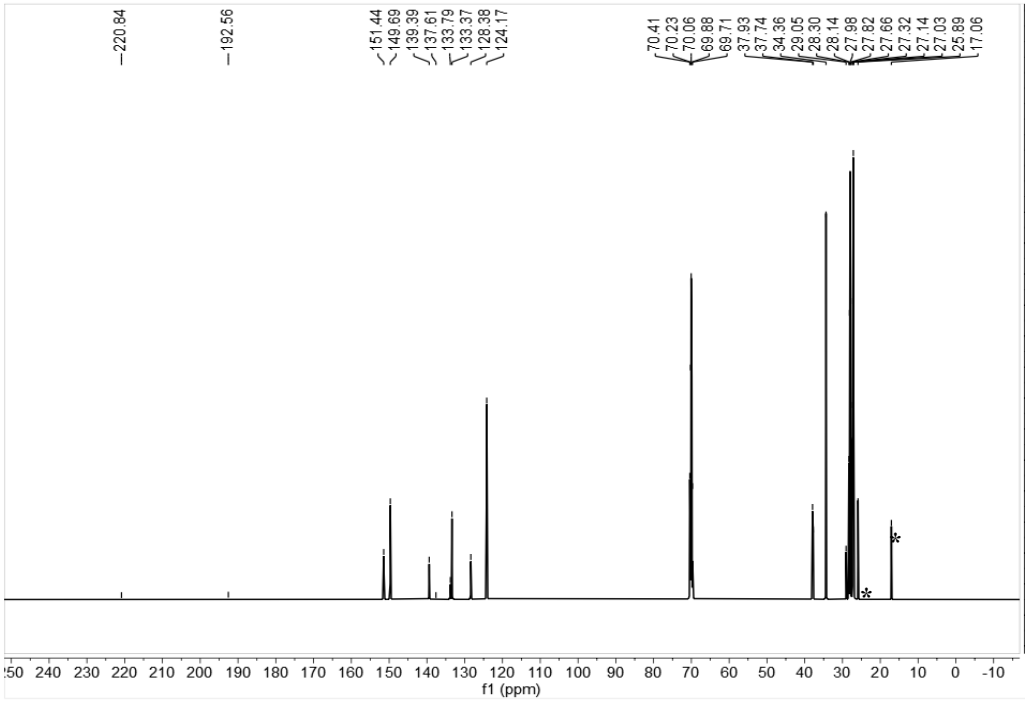

Figure S1.2. ^{13}C NMR spectrum (125.7 MHz, d_8-THF, 20 ˚C) of Fe(THF)(CO)$_2$(CNAr^{Tripp2})$_2$ (**2**). *n*-pentane (*) present in sample.

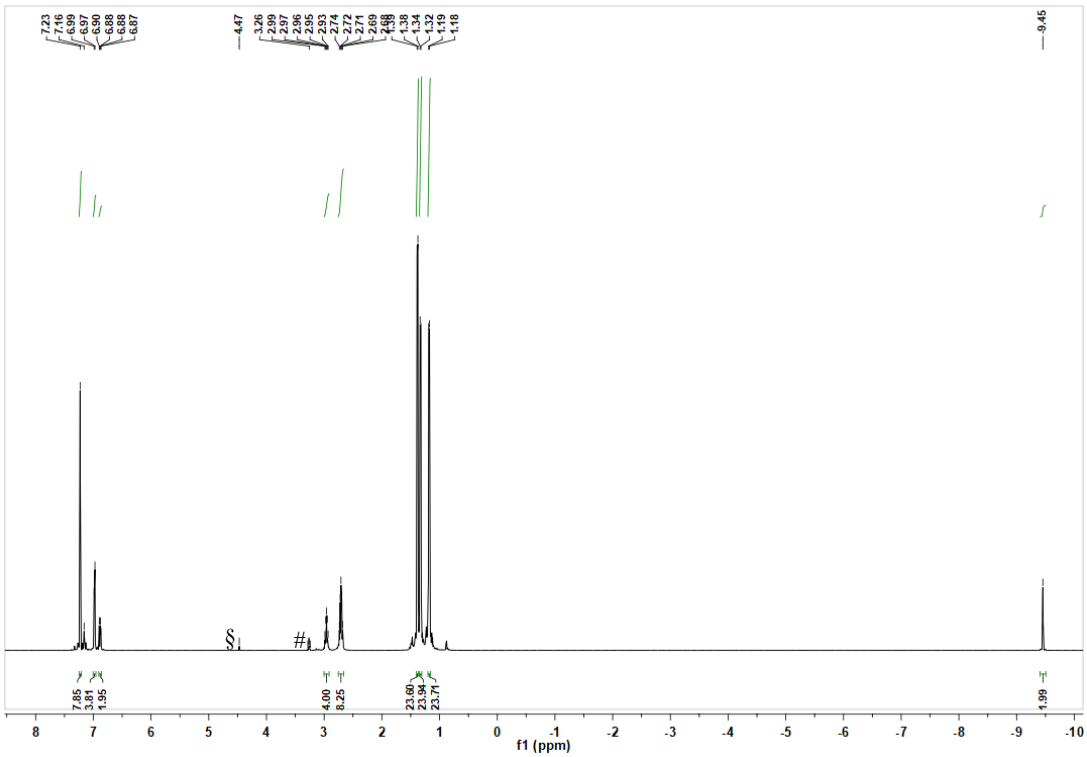

Figure S1.3. ^{1}H NMR spectrum (499.8 MHz, C_6D_6, 20 ˚C) of $H_2Fe(CO)_2(CNAr^{Tripp2})_2$ (**3**). Et_2O (#) and residual H_2 (§) present in sample.

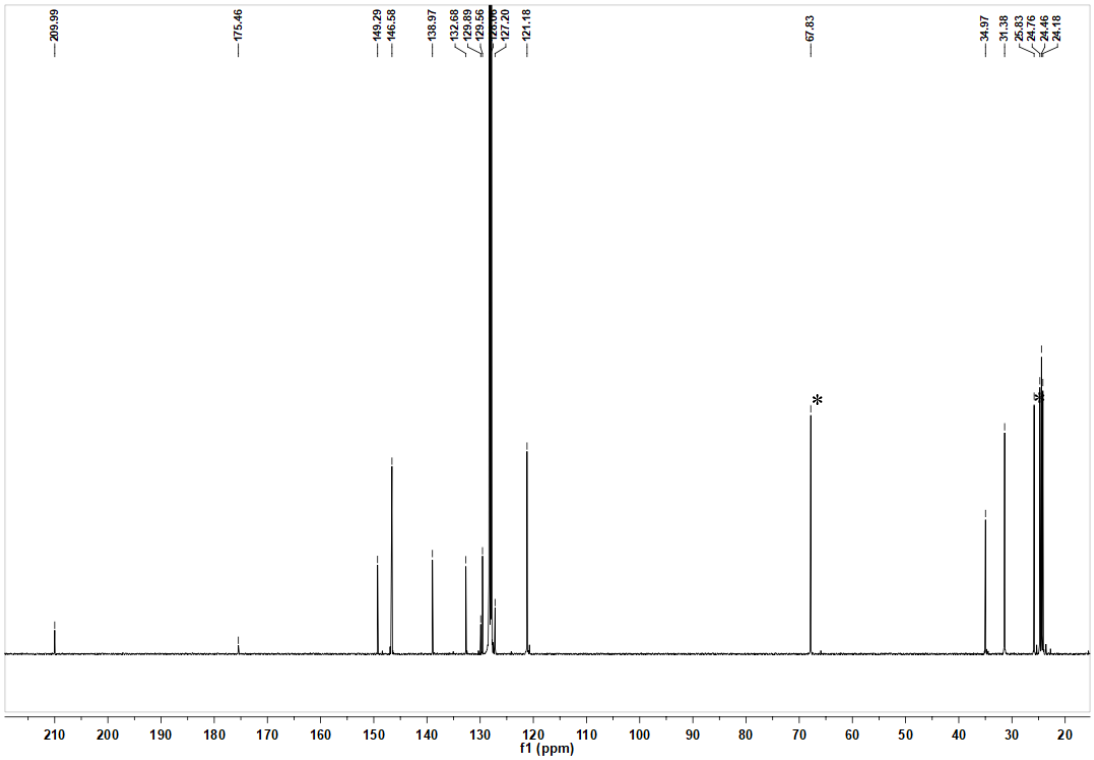

Figure S1.4. ^{13}C NMR spectrum (125.7 MHz, C_6D_6, 20 ˚C) of $H_2Fe(CO)_2(CNAr^{Tripp2})_2$ (**3**). THF (*) present in sample.

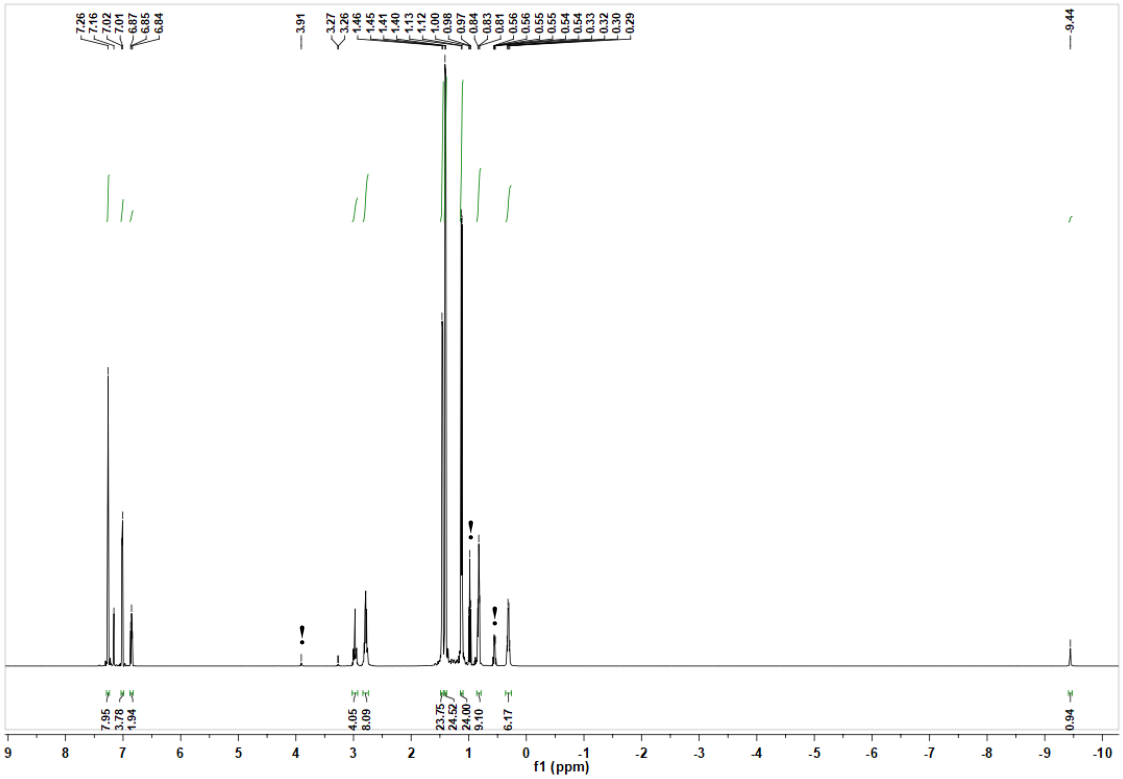

Figure S1.5. ^{1}H NMR spectrum (499.8 MHz, C_6D_6, 20 ˚C) of $HFe(SiEt_3)(CO)_2(CNAr^{Tripp2})_2$ (**4**). Residual $HSiEt_3$ (!) present in sample.

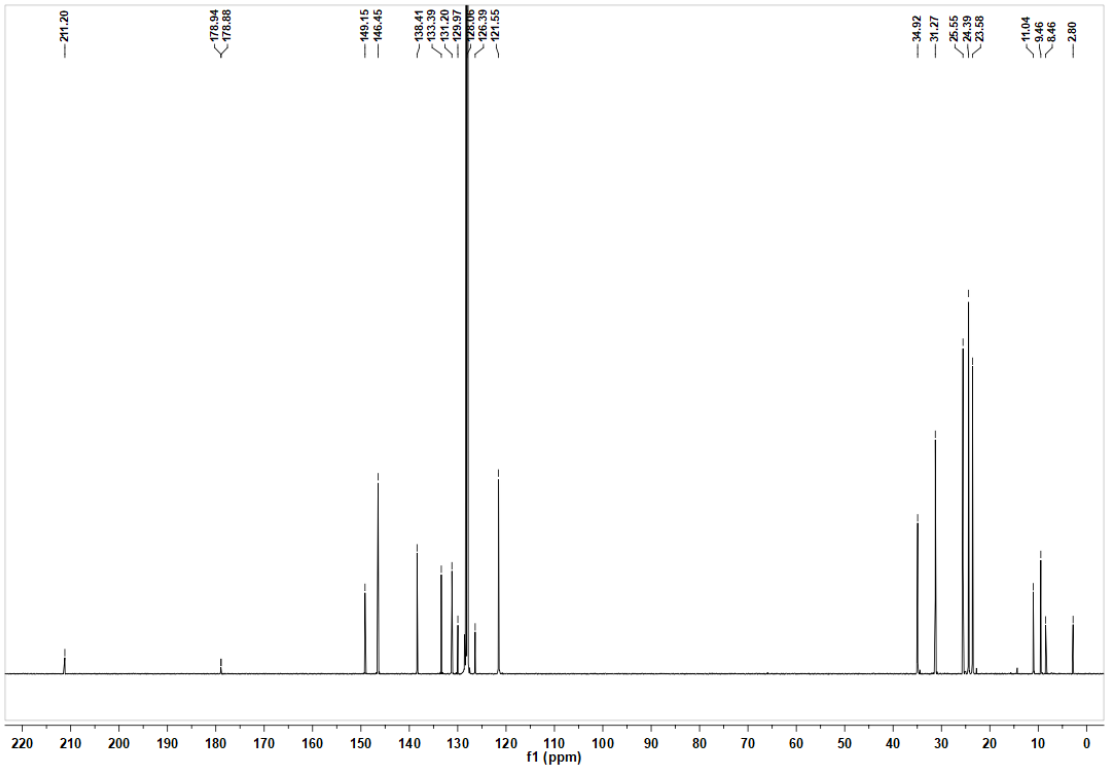

Figure S1.6. ^{13}C NMR spectrum (125.7 MHz, C_6D_6, 20 ˚C) of $HFe(SiEt_3)(CO)_2(CNAr^{Tripp2})_2$ (**4**).

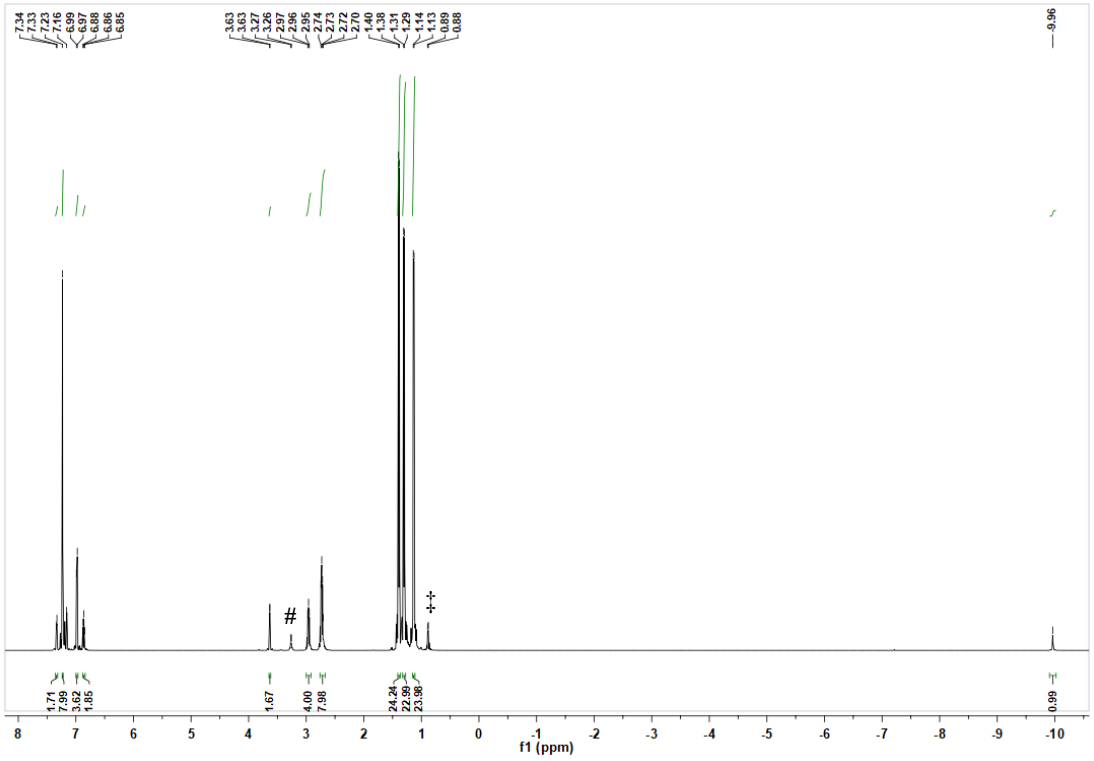

Figure S1.7. ^{1}H NMR spectrum (499.8 MHz, C_6D_6, 20 ˚C) of $HFe(SiH_2Ph)(CO)_2(CNAr^{Tripp2})_2$ (**5**). Et_2O (#) and *n*-hexane (‡) present in sample.

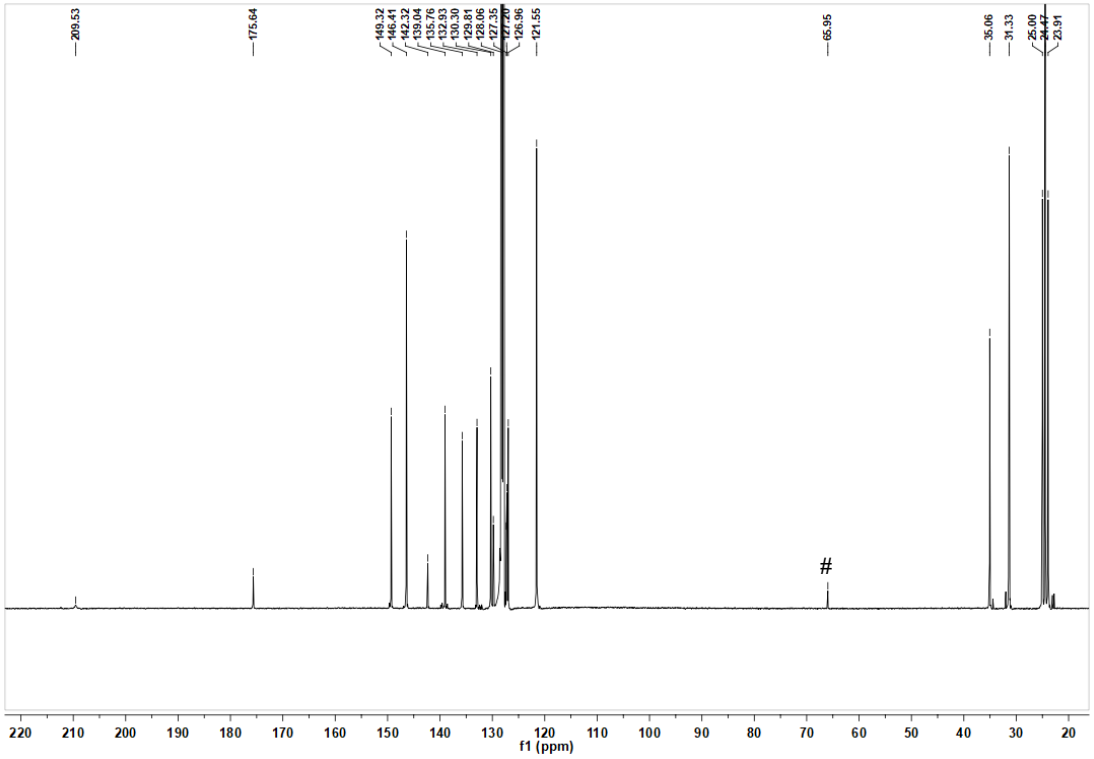

Figure S1.8. ^{13}C NMR spectrum (125.7 MHz, C_6D_6, 20 ˚C) of $HFe(SiH_2Ph)(CO)_2(CNAr^{Tripp2})_2$ (**5**). Et_2O (#) present in sample.

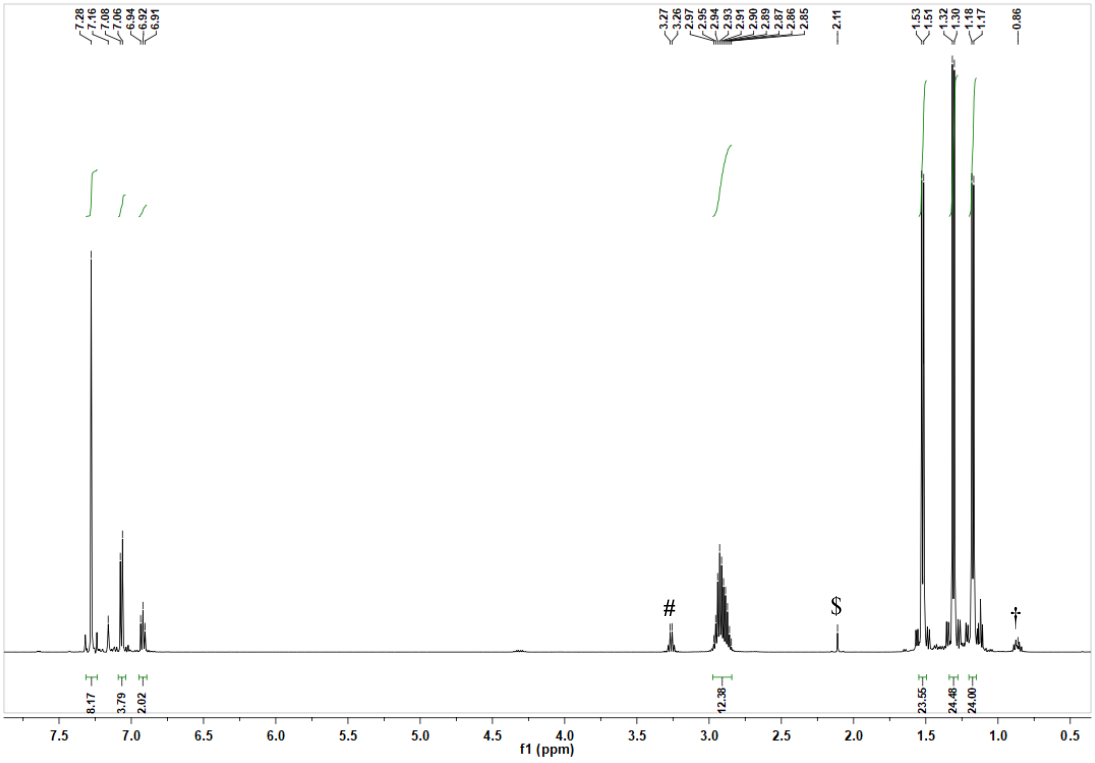

Figure S1.9. ^{1}H NMR spectrum (499.8 MHz, C_6D_6, 20 ˚C) of Fe(κ^2-P$_4$)(CO)$_2$(CNAr^{Tripp2})$_2$ (**6**). Et_2O (#), toluene ($), and *n*-pentane (†) present in sample.

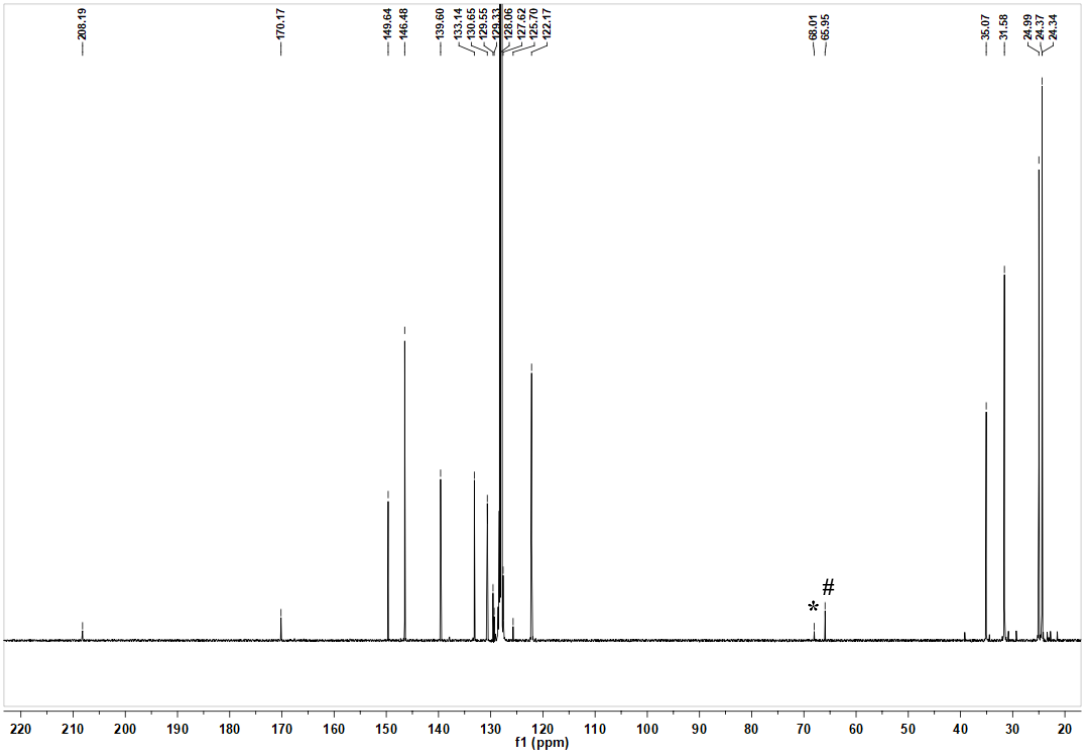

Figure S1.10. ^{13}C NMR spectrum (125.7 MHz, C_6D_6, 20 ˚C) of Fe(κ^2-P$_4$)(CO)$_2$(CNAr^{Tripp2})$_2$ (**6**). THF (*) and Et_2O (#) present in sample.

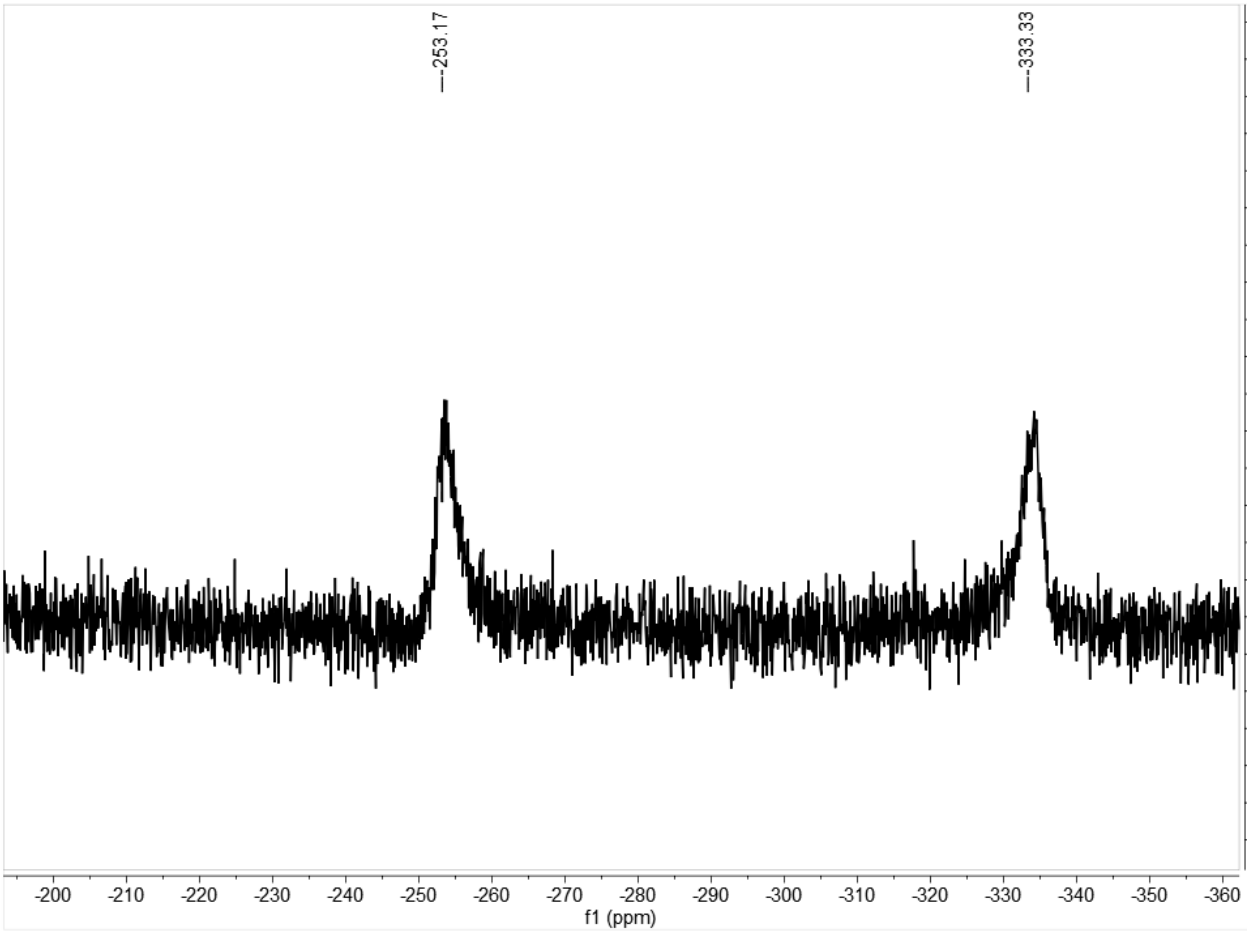

Figure S1.11. $^{31}P\{^{1}H\}$ NMR spectrum NMR (202.7 MHz, C_6D_6, 20 ˚C) of Fe(κ²-P_4)$(CO)_2(CNAr^{Tripp2})_2$ (**6**). Additional scanning did not lead to resolution of ^{1}J or ^{2}J P-P coupling.

S2. Crystallographic Structure Determinations

S2.1. General. Single X-ray structure determinations were performed at 100 K on Bruker Kappa diffractometers equipped with a Mo radiation source and an APEX-II CCD area detector. All structures were solved via direct methods with SHELXS[1] and refined by full-matrix least-squares procedures using SHELXL[1] within the Olex2[2] software. The PLATON routine SQUEEZE[3] was used to account for residual electron density in solvent accessible voids for compounds **2**, and **6**. Disordered components and co-crystallized solvent molecules are not shown for clarity. Nonetheless, the following molecules possessed positional disorder that was successfully modeled and refined anisotropically:

$H_2Fe(CO)_2(CNAr^{Tripp2})_2$ (3) contains positional disorder in two isopropyl groups of the flanking arenes.

HFe(SiEt$_3$)(CO)$_2$(CNAr^{Tripp2})$_2$ (4) contains positional disorder of the iron atom that affects the entire triethylsilyl ligand. Additional disorder in three isopropyl groups of the flanking arenes was also modeled.

S2.2. CCDC Deposition. All crystal structures have been deposited with the Cambridge Crystallographic Data Center (CCDC) and have been assigned the following CCDC deposition numbers:

- Fe(THF)(CO)$_2$(CNAr^{Tripp2})$_2$ (**2**): 2016082
- H$_2$Fe(CO)$_2$(CNAr^{Tripp2})$_2$ (**3**): 2016083
- HFe(SiEt$_3$)(CO)$_2$(CNAr^{Tripp2})$_2$ (**4**): 2016084
- HFe(SiH$_2$Ph)(CO)$_2$(CNAr^{Tripp2})$_2$ (**5**): 2016085
- Fe(κ^2-P$_4$)(CO)$_2$(CNAr^{Tripp2})$_2$ (**6**): 2016086

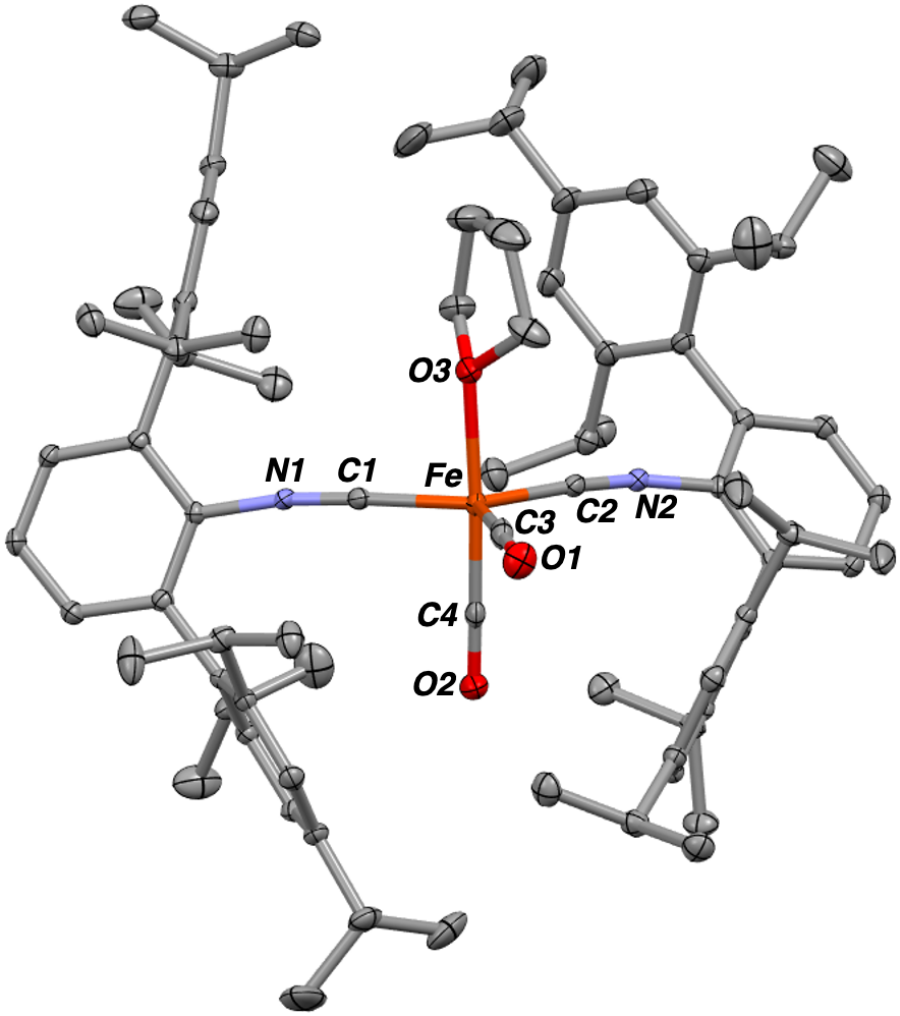

Figure 2.1. Molecular structure of Fe(THF)(CO)$_2$(CNAr^{Tripp2})$_2$ (**2**).

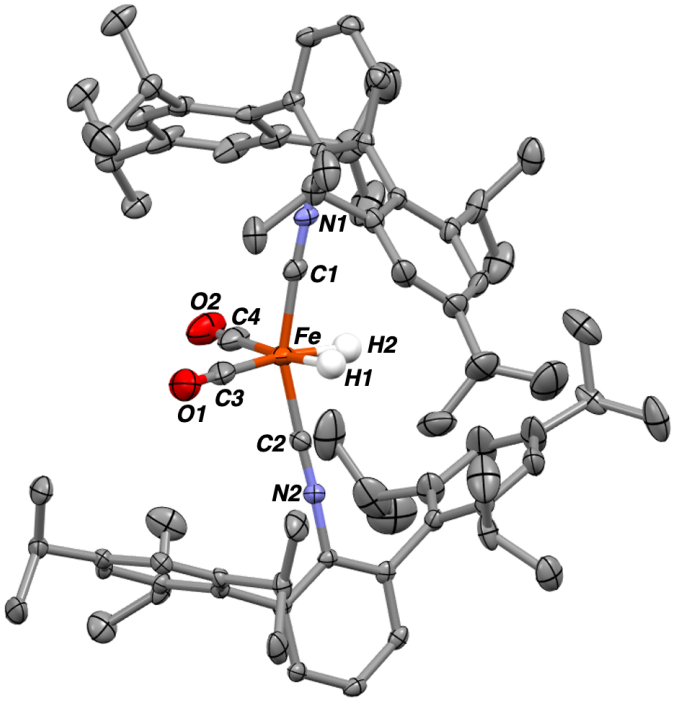

Figure 2.2. Molecular structure of $H_2Fe(CO)_2(CNAr^{Tripp2})_2$ (**4**).

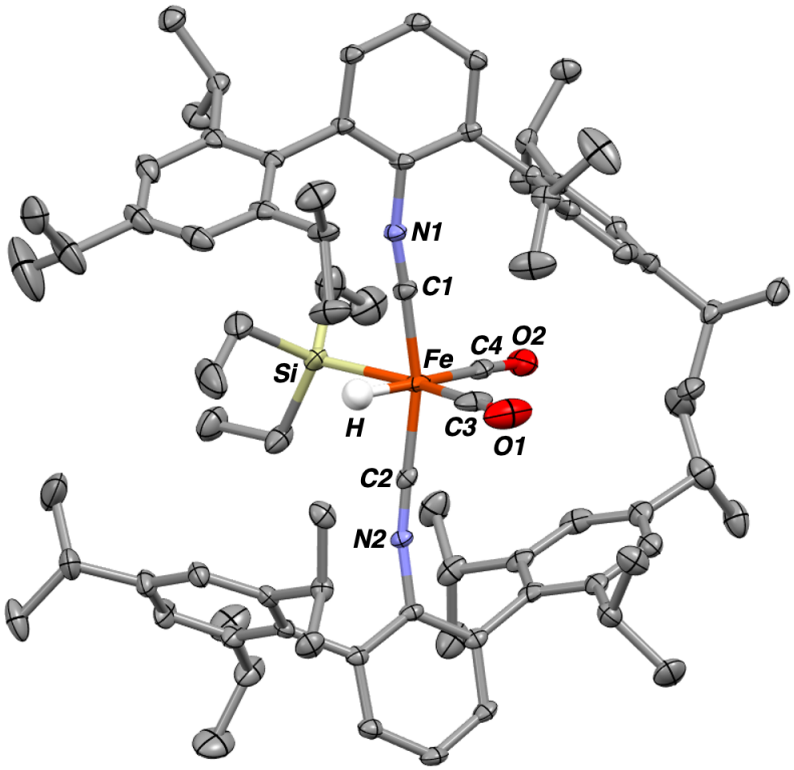

Figure 2.3. Molecular structure of $HFe(SiEt_3)(CO)_2(CNAr^{Tripp2})_2$ (**4**).

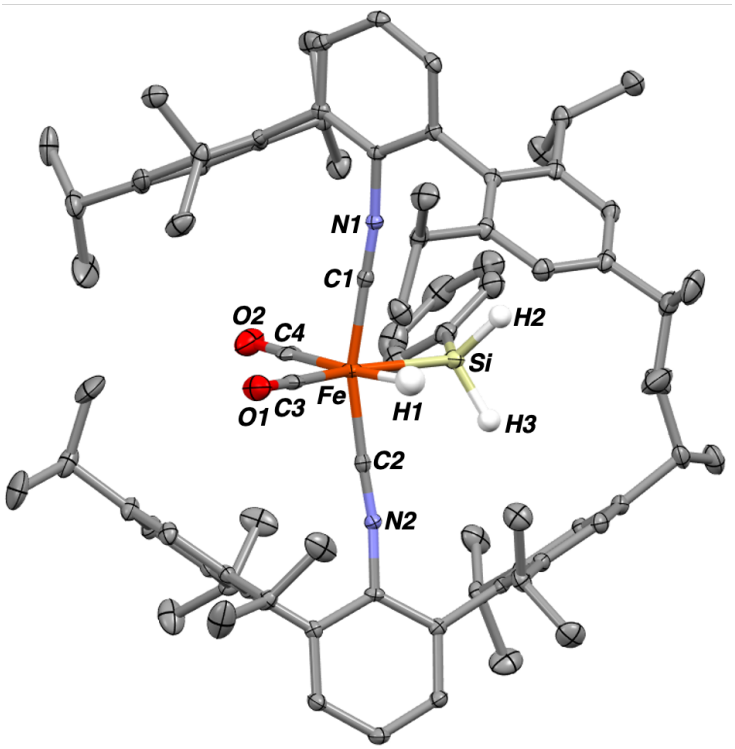

Figure 2.4. Molecualr structure of $HFe(H_2SiPh)(CO)_2(CNAr^{Tripp2})_2$ (**5**).

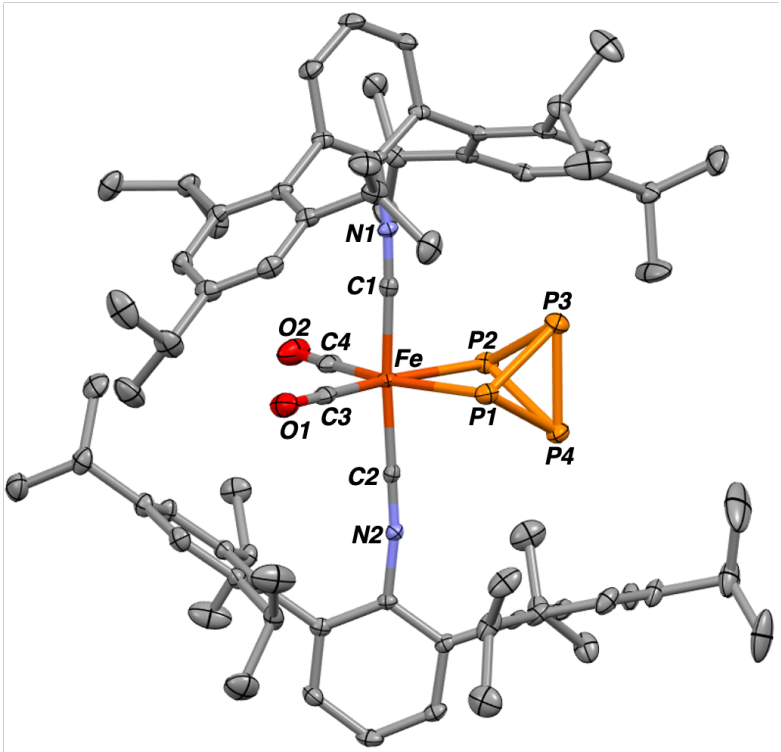

Figure 2.5. Molecular structure of $Fe(\kappa^2\text{-}P_4)(CO)_2(CNAr^{Tripp2})_2$ (**6**).

Table S2.1. Crystallographic Data Collection and Refinement Information.

Name	$Fe(THF)(CO)_2(CNAr^{Tripp2})_2$ (**2**)	$H_2Fe(CO)_2(CNAr^{Tripp2})_2$ (**3**)	$HFe(SiEt_3)(CO)_2(CNAr^{Tripp2})_2$ (**4**)
Formula	$C_{80}H_{106}FeN_2O_3$	$C_{76}H_{100}FeN_2O_2$	$C_{85}H_{121}FeN_2O_2Si$
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	*P*–1	*P*–1	*C*2/c
a, Å	13.6542(8)	14.5092(10)	47.693(3)
b, Å	15.8001(9)	14.6438(10)	13.2656(7)
c, Å	20.3384(11)	18.6823(12)	25.4285(13)
α, deg	87.3360(10)	101.541(2)	90
β, deg	73.0710(10)	91.979(2)	102.304(2)
γ, deg	69.8070(10)	116.759(2)	90
V, $Å^3$	3932.5(4)	3437.3(4)	15718.3(15)
Z	2	2	8
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), Mg/m^3	1.013	1.091	1.088
μ (Mo Kα), mm^{-1}	0.235	0.264	0.252
Temp, K	100	100	100
θ max, deg	26.022	25.707	25.512
data/ parameters	15485/799	13048/792	14603/979
R_1	0.0449	0.0750	0.0486
wR_2	0.1163	0.1806	0.1160
GOF	1.040	1.027	1.020

Table S2.1. cont'd.

Name	$HFe(H_2SiPh)(CO)_2(CNAr^{Tripp2})_2$ (**5**)	$Fe(\kappa^2\text{-}P_4)(CO)_2(CNAr^{Tripp2})_2$ (**6**)
Formula	$C_{82}H_{106}FeN_2O_2Si$	$C_{76}H_{98}FeN_2O_2P_4$
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a, Å	23.2688(19)	17.7725(7)
b, Å	14.4185(11)	15.6997(7)
c, Å	25.0312(18)	28.0844(13)
α, deg	90	90
β, deg	113.066(2)	101.538(2)
γ, deg	90	90
V, Å^3	7726.6(10)	7677.8(6)
Z	4	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), Mg/m^3	1.062	1.082
μ (Mo Kα), mm^{-1}	0.252	0.321
Temp, K	100	100
θ max, deg	25.35	25.385
data/ parameters	14153/827	14073/790
R_1	0.0468	0.0541
wR_2	0.1077	0.1267
GOF	1.022	1.071

S3. References

(1) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C72*, 3-8.
(2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
(3) Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Cryst.* **2015**, *C71*, 9-18.