10.1071/CH19184_AC

Australian Journal of Chemistry 2021, 74(3), 204-210

Supplementary Material

Synthesis and Structures of 1,1′,2-Tribromoferrocene, 1,1′,2,2′-Tetrabromoferrocene, 1,1′,2,2′-Tetrabromoruthenocene: Expanding the Range of Precursors for the Metallocene Chemist's Toolkit

Ian R. Butler,[A,D] *Michael Beaumont*,[A] *Michael I. Bruce*,[B] *Natalia N. Zaitseva*,[B] *Jonathan A. Iggo*,[A] *Craig Robertson*,[A] *Peter N. Horton*,[C] *and Simon J. Coles*[C]

[A]Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK.

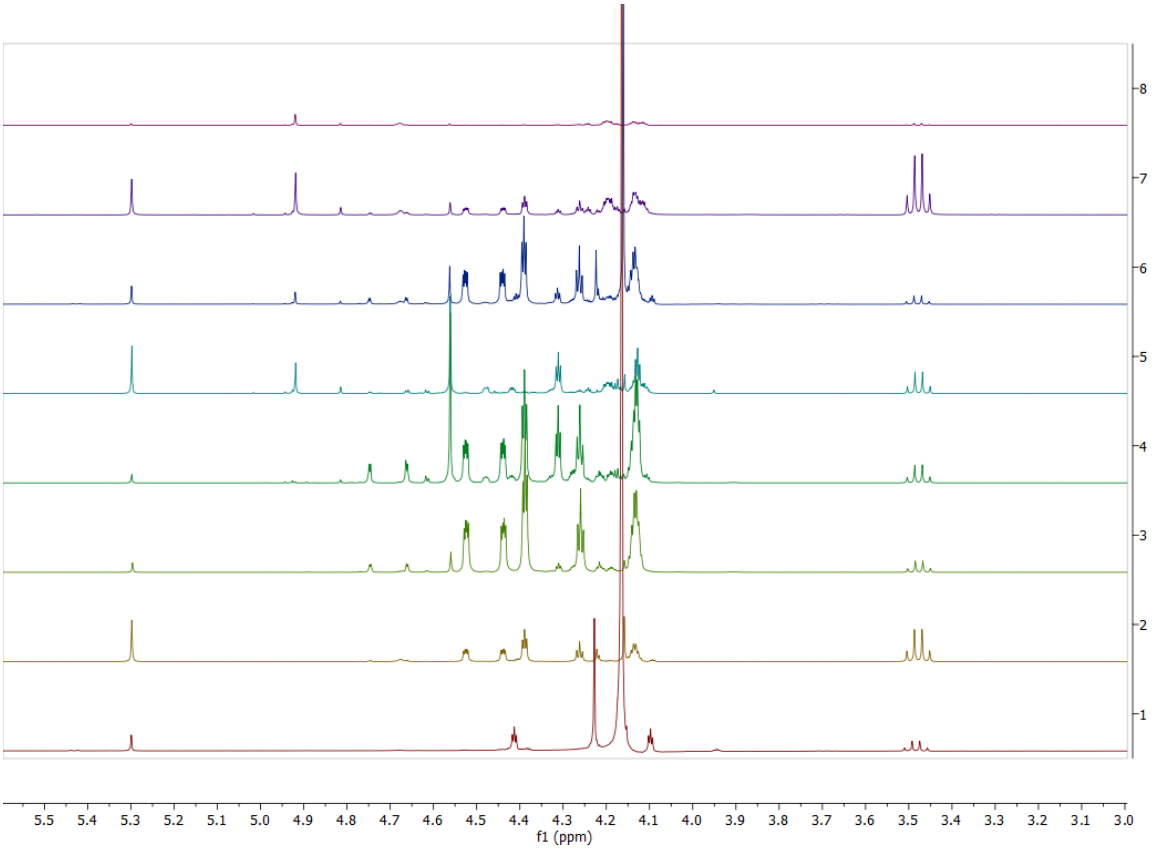
[B]Department of Chemistry, School of Physical Sciences, University of Adelaide, Adelaide, SA 5005, Australia.

[C]EPSRC National Crystallography Service, University of Southampton, Southampton, SO17 1BJ, UK.

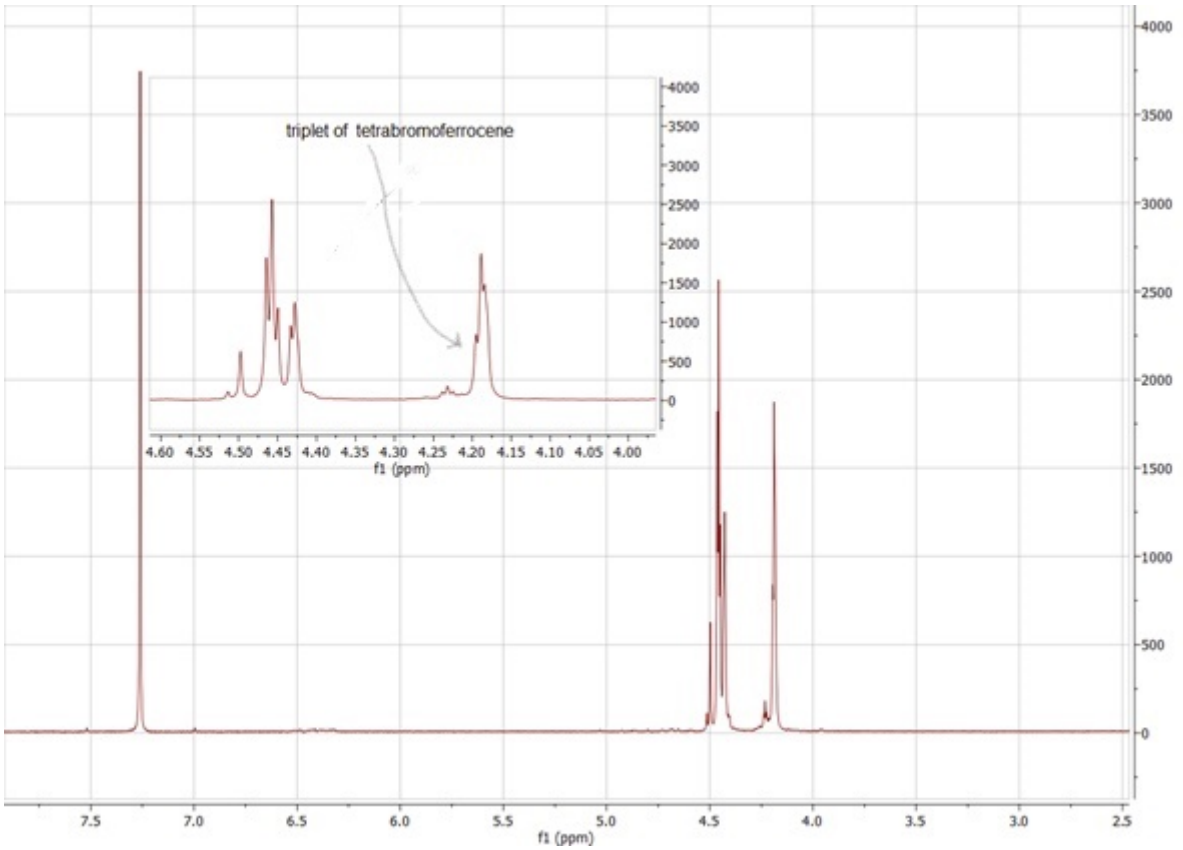
[D]Corresponding author. Email: irbutler@liverpool.ac.uk

List of Supplementary Data. (all data is raw)

Index		Page No.
1.	Stacked Spectra Crude Fractions proton NMR spectra.	2
2.	Typical fraction spectrum showing identification of 1,1',2,2'-tetrabromoferrocene.	3
3.	NMR Spectra and Mass Spectra of 1,1',2-Tribromoferrocene.	4
4.	NMR Spectra and Mass Spectra of 1,1',2,2'-Tetrabromoferrocene.	6
5.	NMR Spectra of 1,1'-Dibromoruthenocene	9
6.	NMR Spectra and Mass spectra of 1,1',2,2'-Tetrabromoruthenocene	11
7.	Additional NMR Data for Comparison (1,1´-dibromoferrocene)	15
8.	Spectra to show nature of pre-chromatography mixtures and by-products.	18
9.	Additional Crystallographic View Data	19
10.	Crystallographic Data: 1,1',2-Tribromoferrocene.	24
11.	Crystallographic Data: 1,1',2,2'-Tetrabromoferrocene.	32
12.	Crystallographic Data: 1,1'-Dibromoruthenocene	40
13.	Crystallographic Data: 1,1',2,2'-Tetrabromoruthenocene	48
14.	Crystallographic Data: 1,2-Dibromoferrocene (for comparisons only).	56
15.	Appendix: Additional Views of Structures.	67
16.	First single crystal structural determination data 1,1',2,2'-tetrabromoferrocene	71

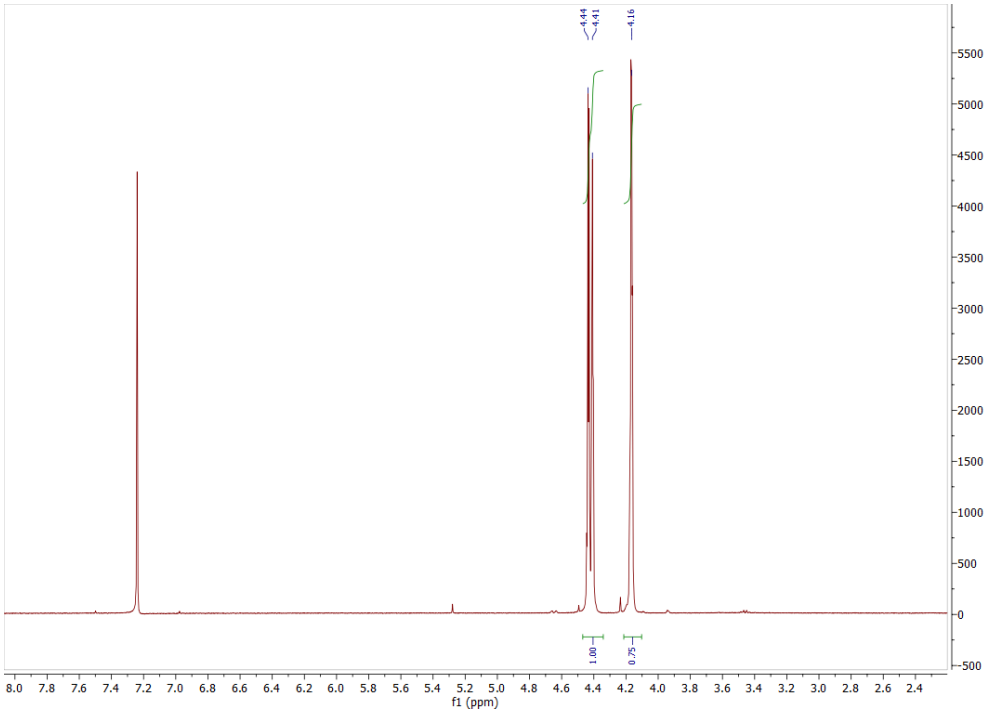


S1. Typical NMR spectra of crude column fractions observed from 1,1'-bromoferrocene lithiation, 1-7. (resonance δ, 5.3 = dichloromethane, δ, 3.5 quartet from reaction solvent)

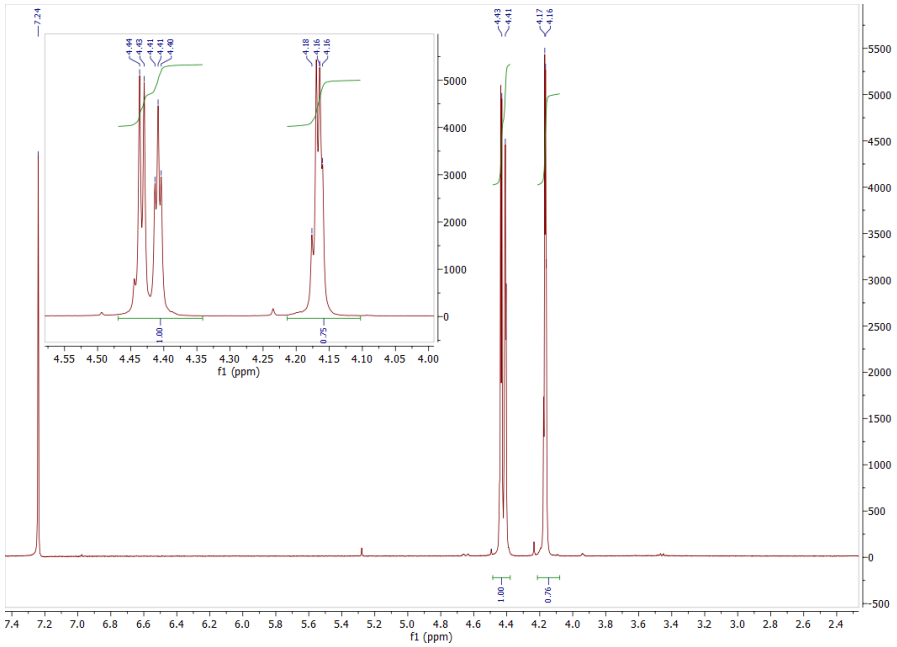


S2. Typical fraction containing 1,1’,2,2’-tetrabromoferrocene showing how identification is made.

S3. NMR Spectra of 1,1’,2-Tribromoferrocene.



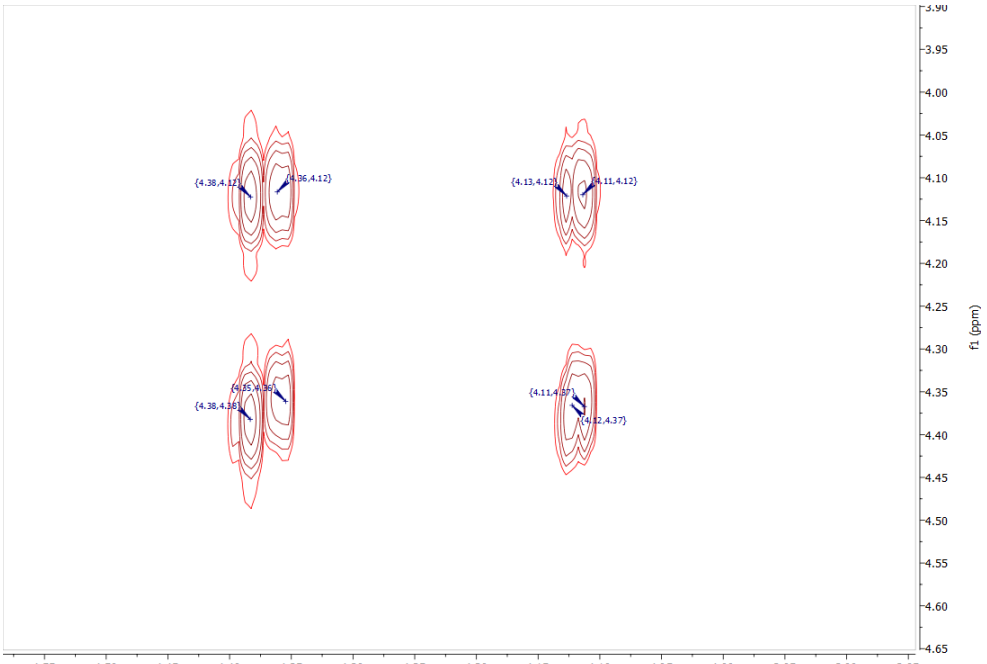
S4. 1,1’,2-Tribromoferrocene Data



1.

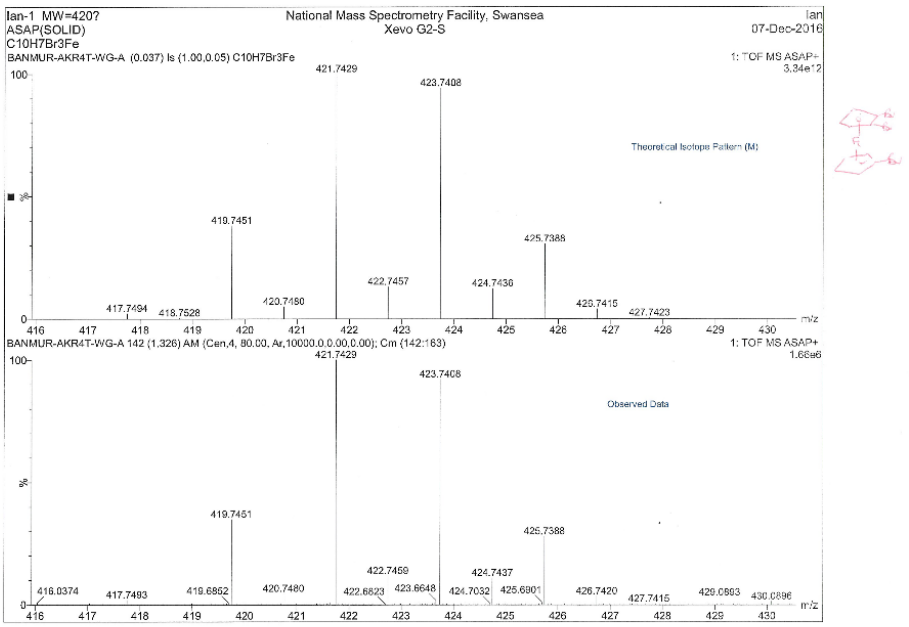
S5: Proton NMR 1,1’,2-tribromoferrocene.

5



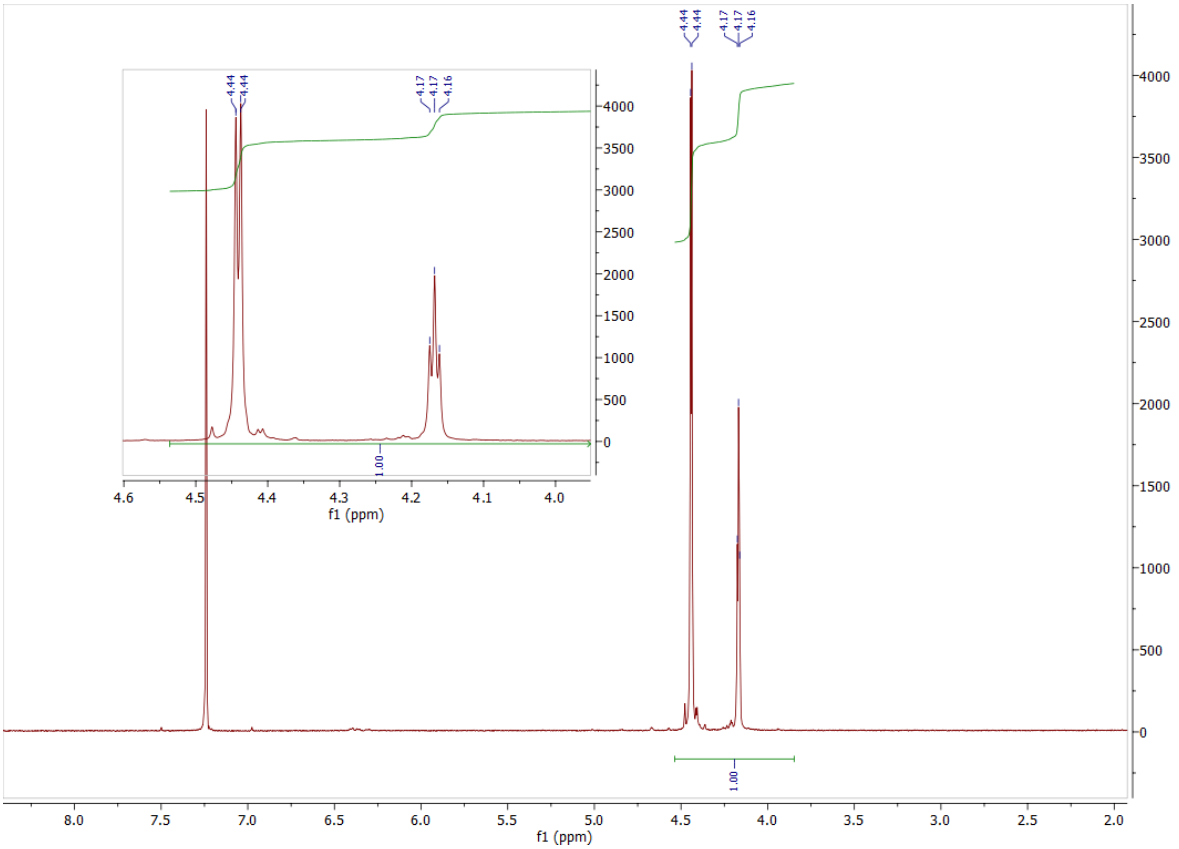
2.

S6: 1,1’,2-Tribromoferrocene: $^{1}H/^{1}H$ COSY NMR

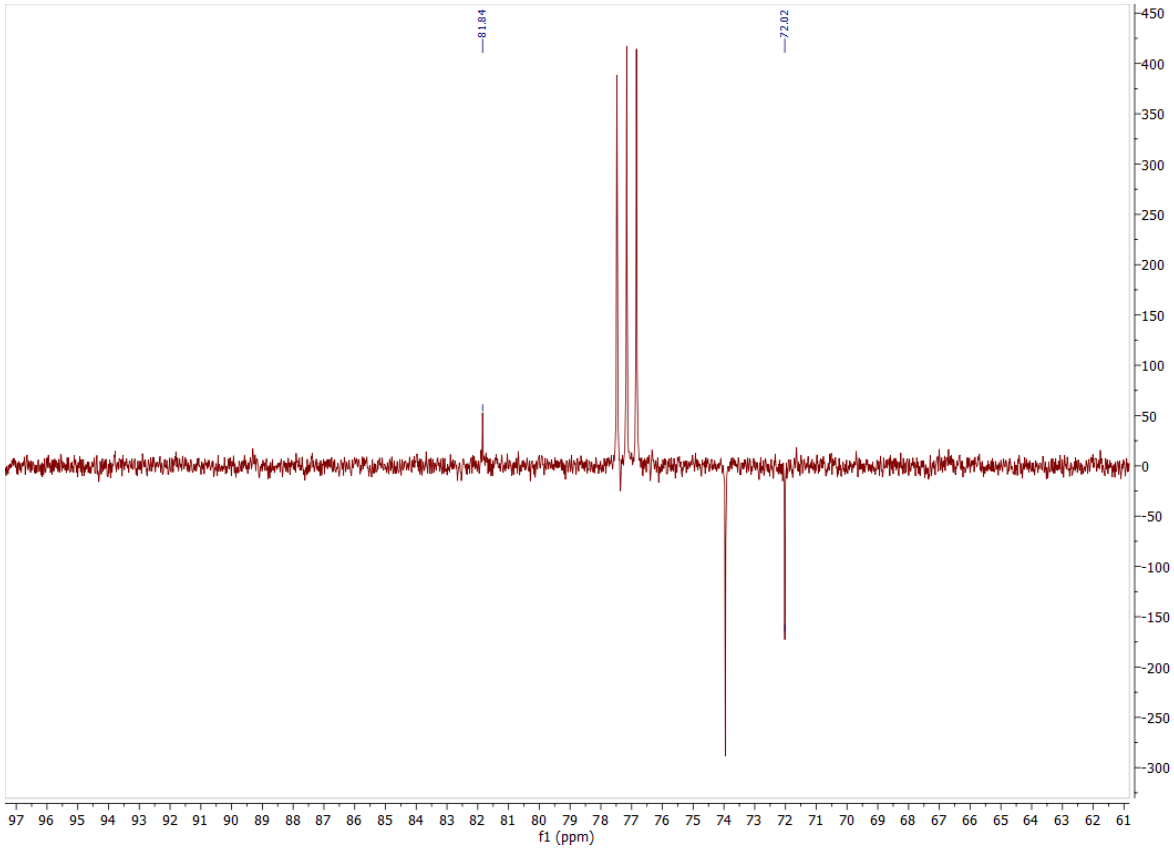


S7: 1,1’,2-Tribromoferrocene- mass spectrum parent ion

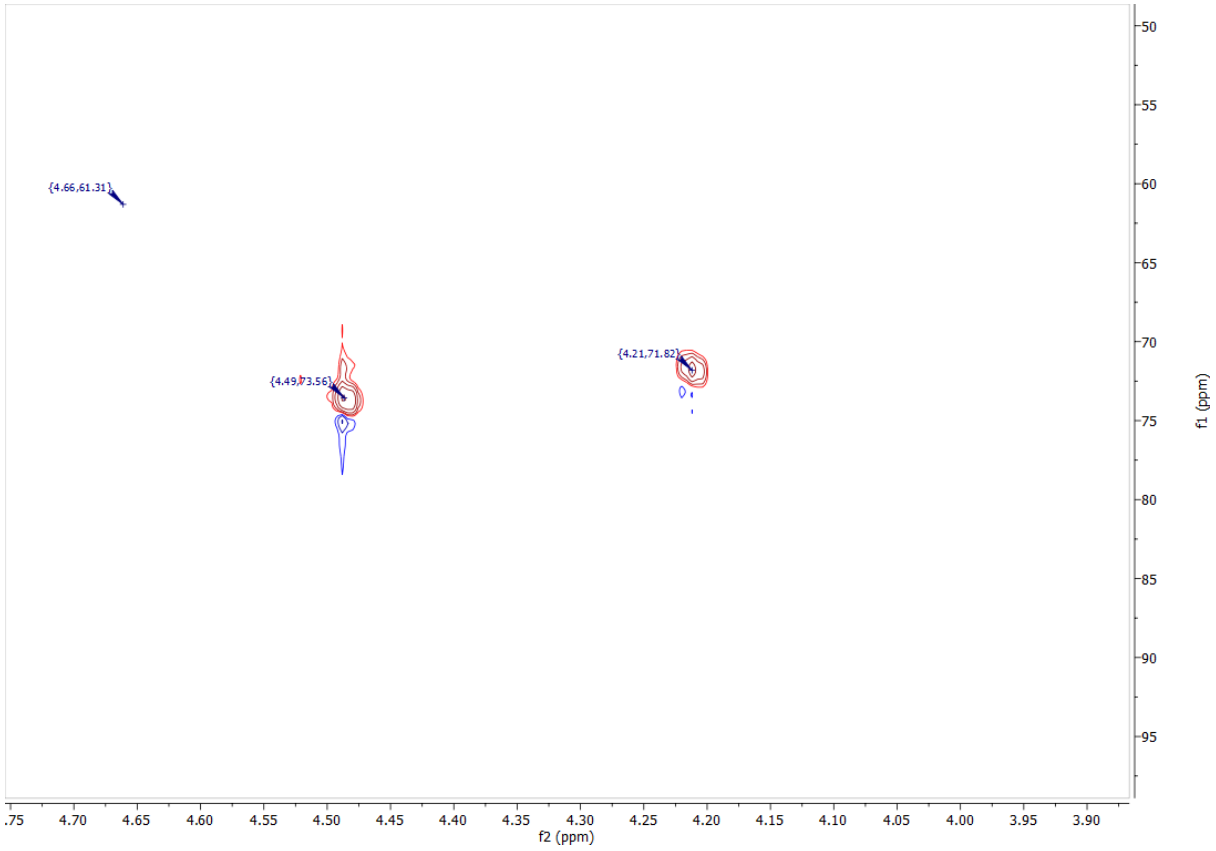
Spectra 1,1’,2,2’-tetrabromoferrocene.



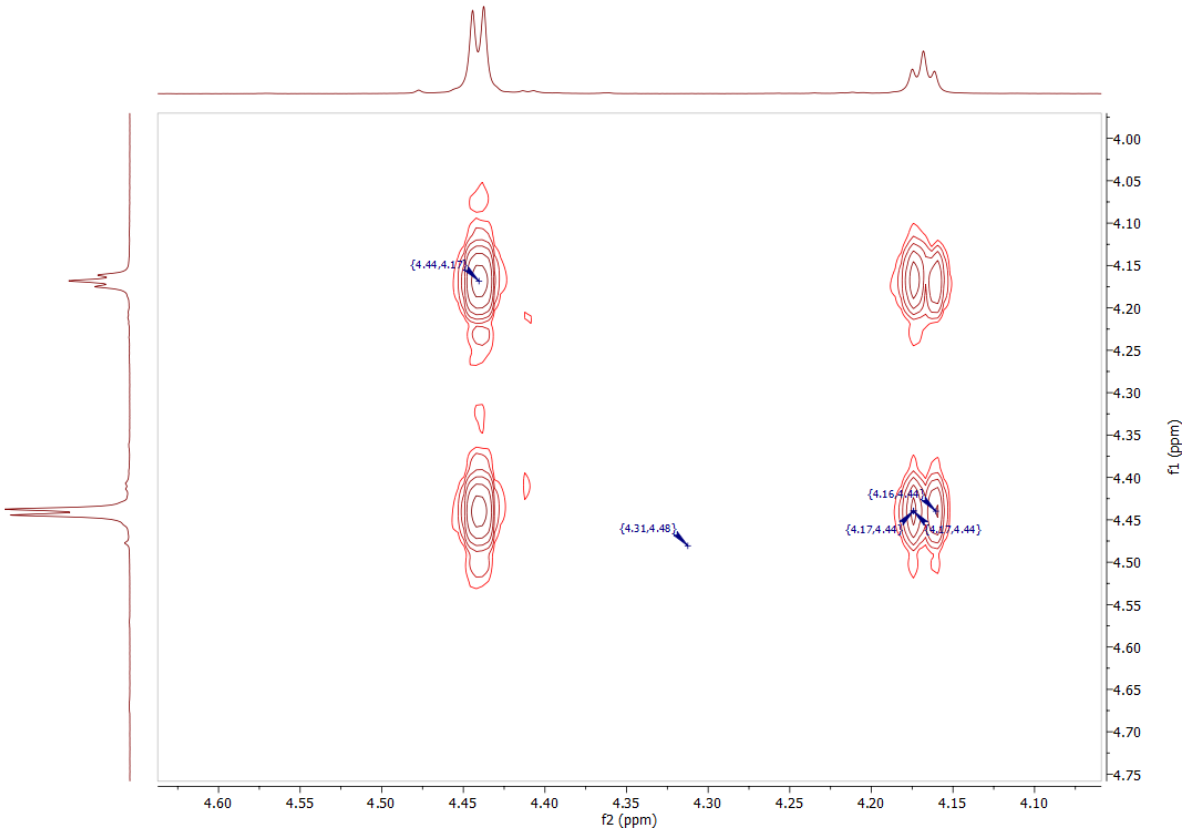
S8: NMR Spectrum of 1,1´,2,2´-Tetrabromoferrocene. (proton)



S9. ^{13}C DEPT NMR of 1,1´,2,2´-Tetrabromoferrocene

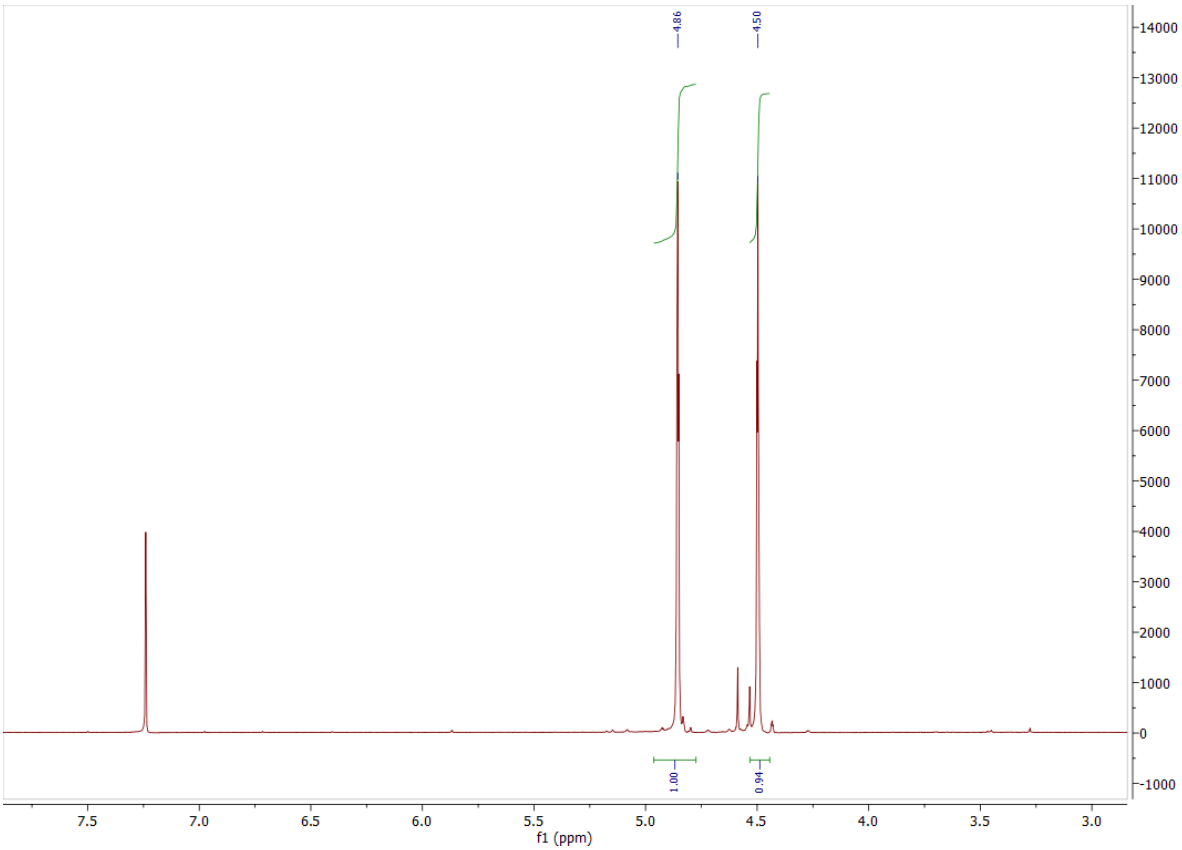


S10. Proton/carbon NMR correlation spectrum of 1,1’,2,2’-tetrabromoferrocene.

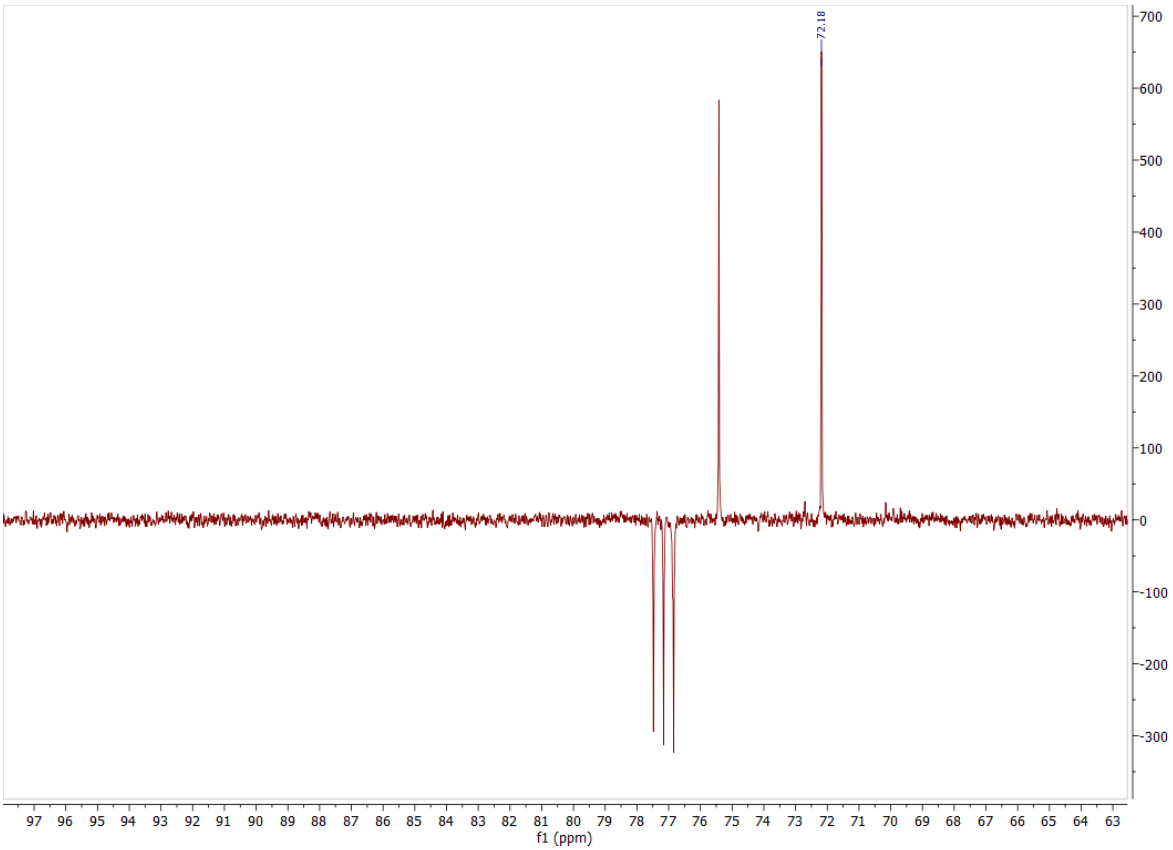


S11. 1,1´,2,2´-Tetrabromoferrocene H/H COSY NMR spectrum.

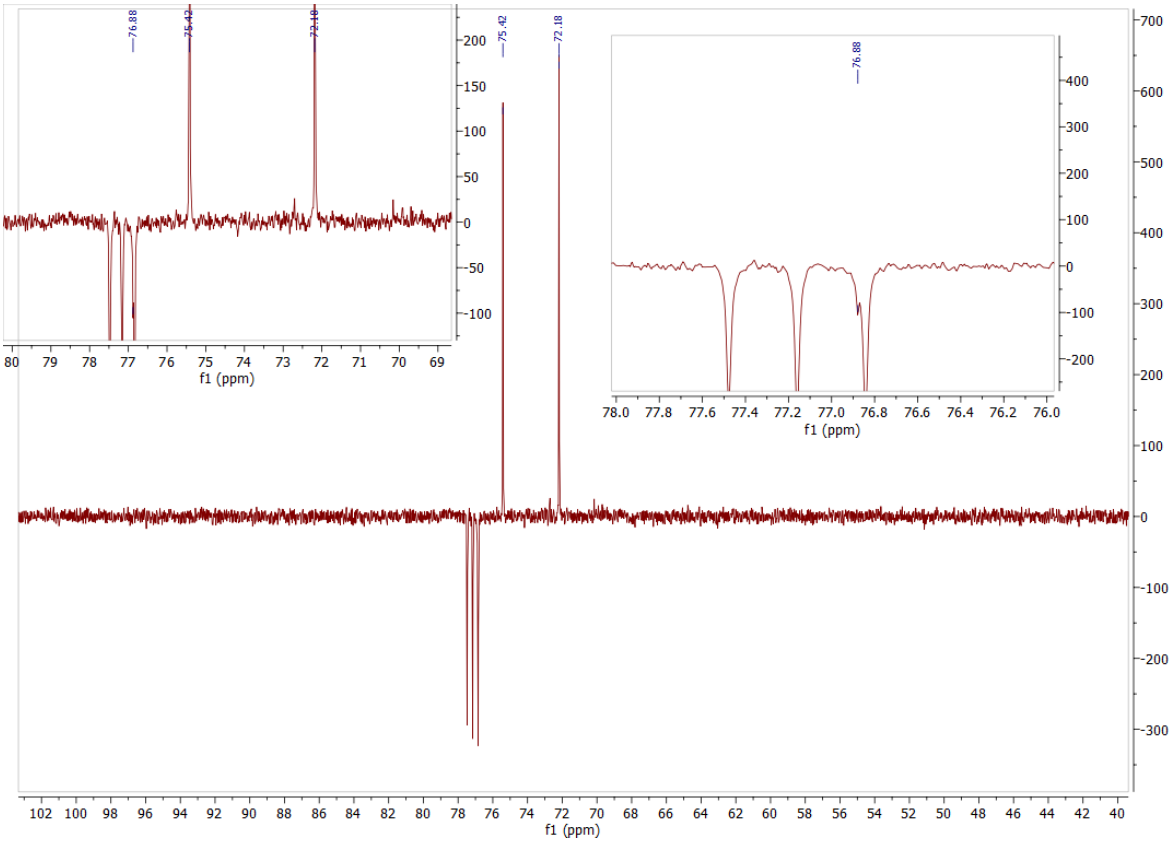
NMR Spectra of 1,1'-Dibromoruthenocene



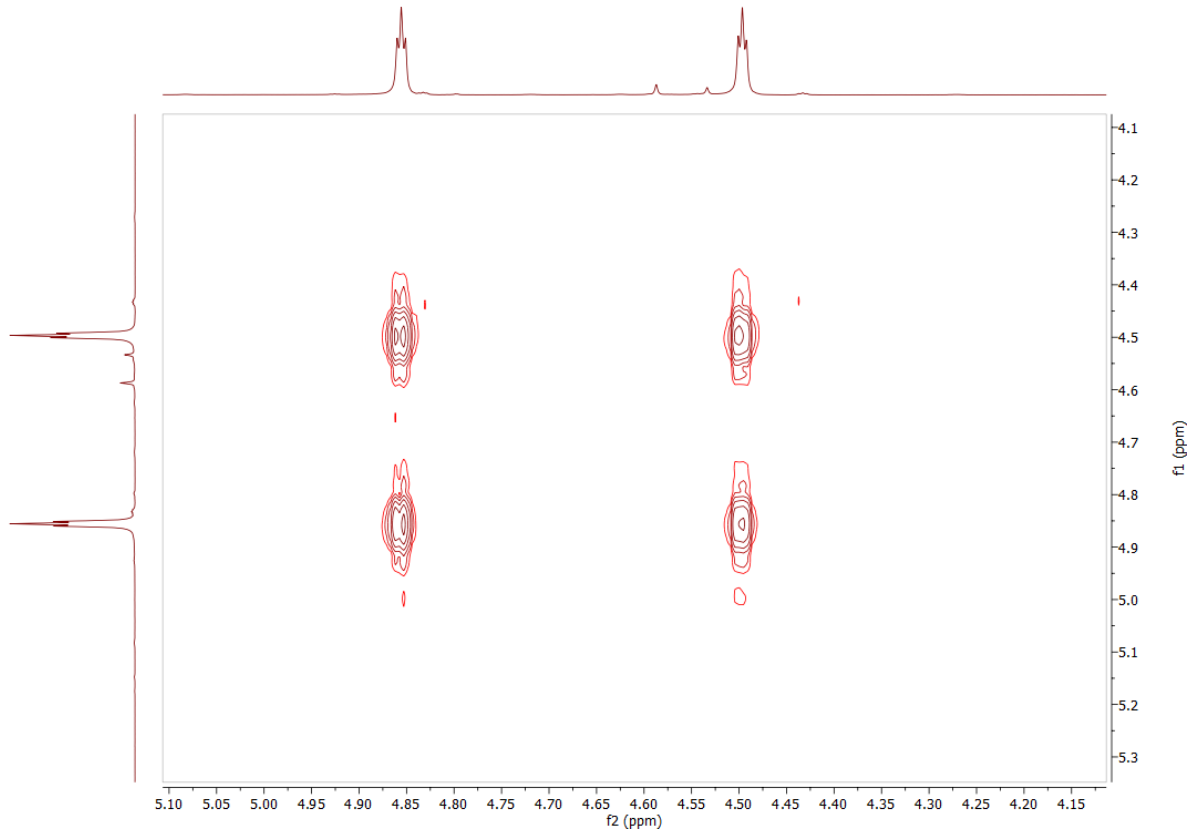
S12. 1,1'-Dibromoruthenocene: proton NMR



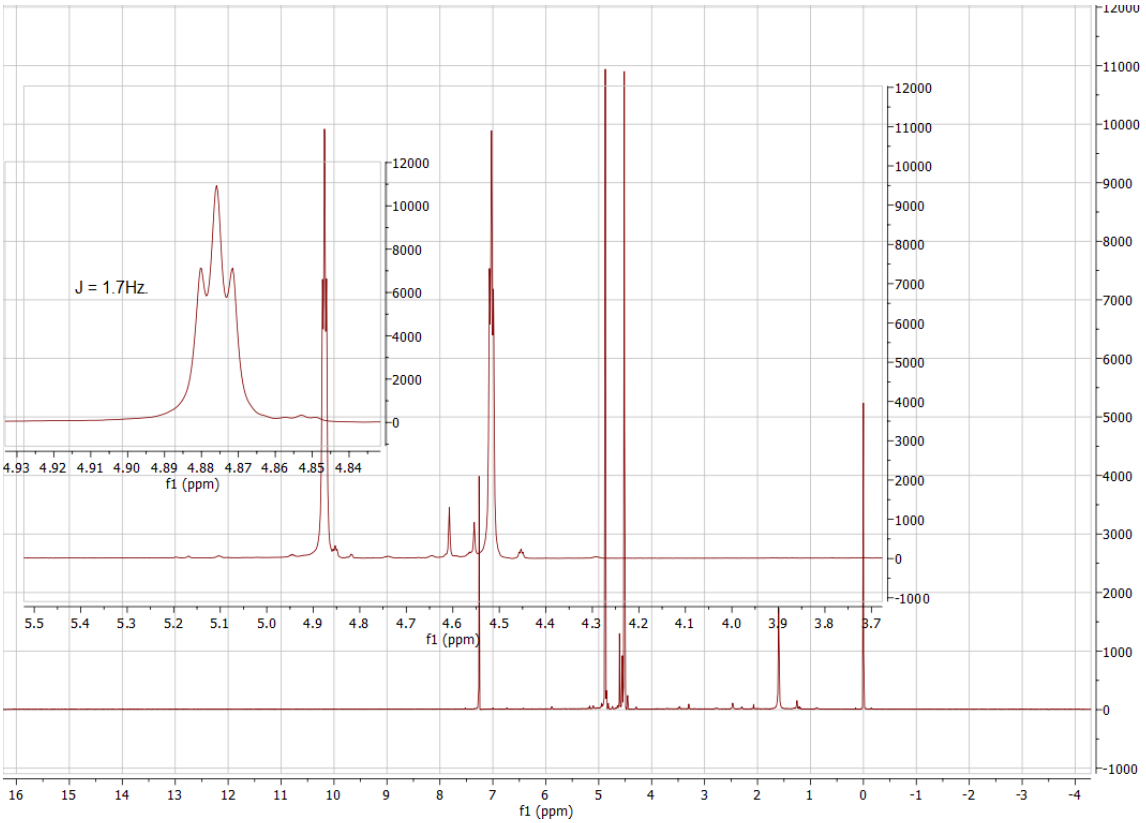
S13. 1,1´-Dibromoruthenocene ^{13}C (DEPT) NMR.



S14. Expanded spectrum (^{13}C) 1,1'-dibromoruthenocene.

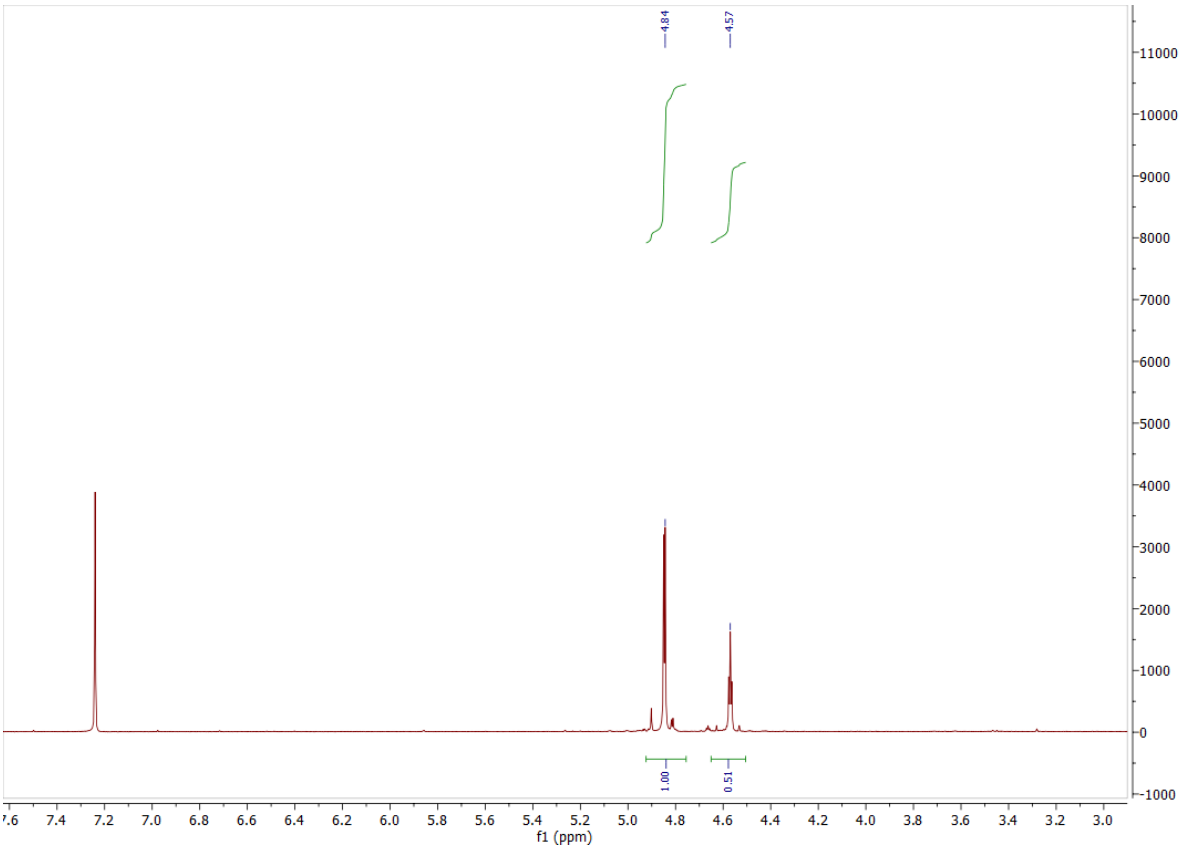


S15. 1,1'-Dibromoruthenocene H/H COSY NMR.

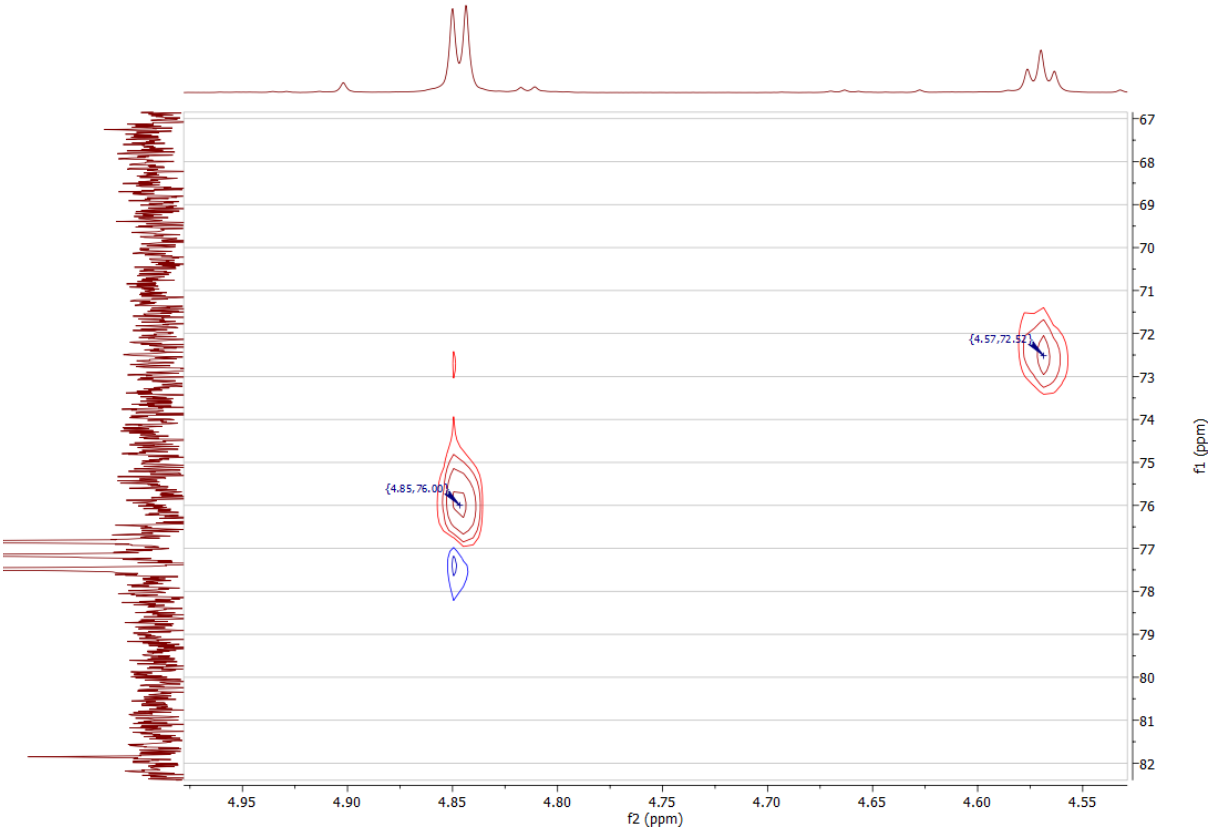


S15. ^{1}H NMR 1,1’-dibromoruthenocene for determination of J value

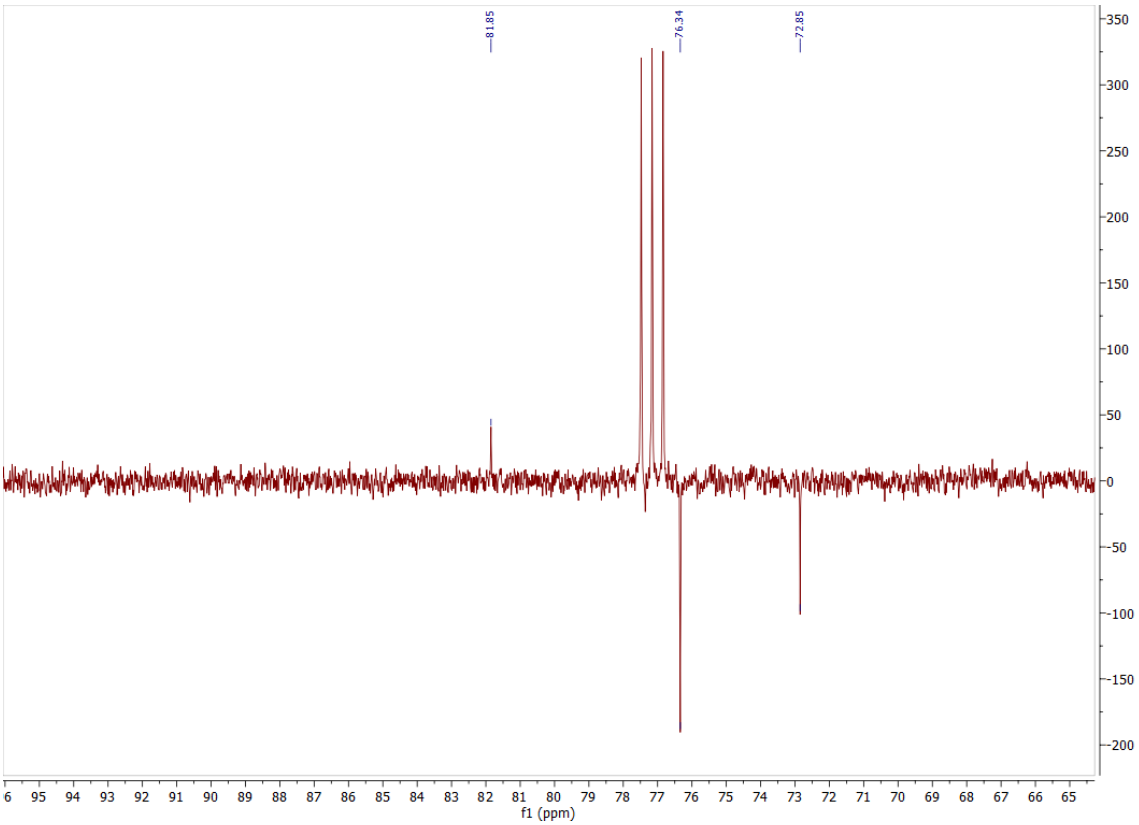
NMR Spectra: 1,1’,2,2’-Tetrabromoruthenocene.



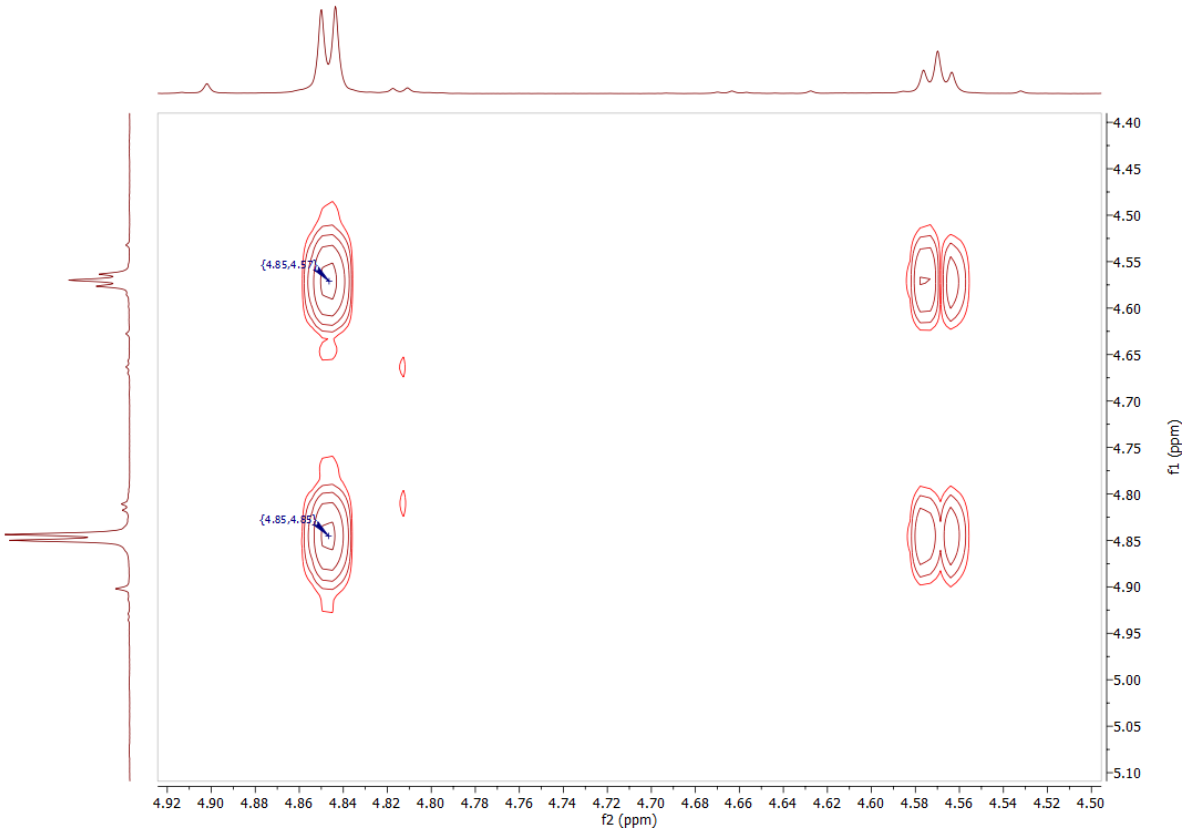
S16. ^{1}H NMR spectrum of 1,1’,2,2’-Tetrabromoruthenocene



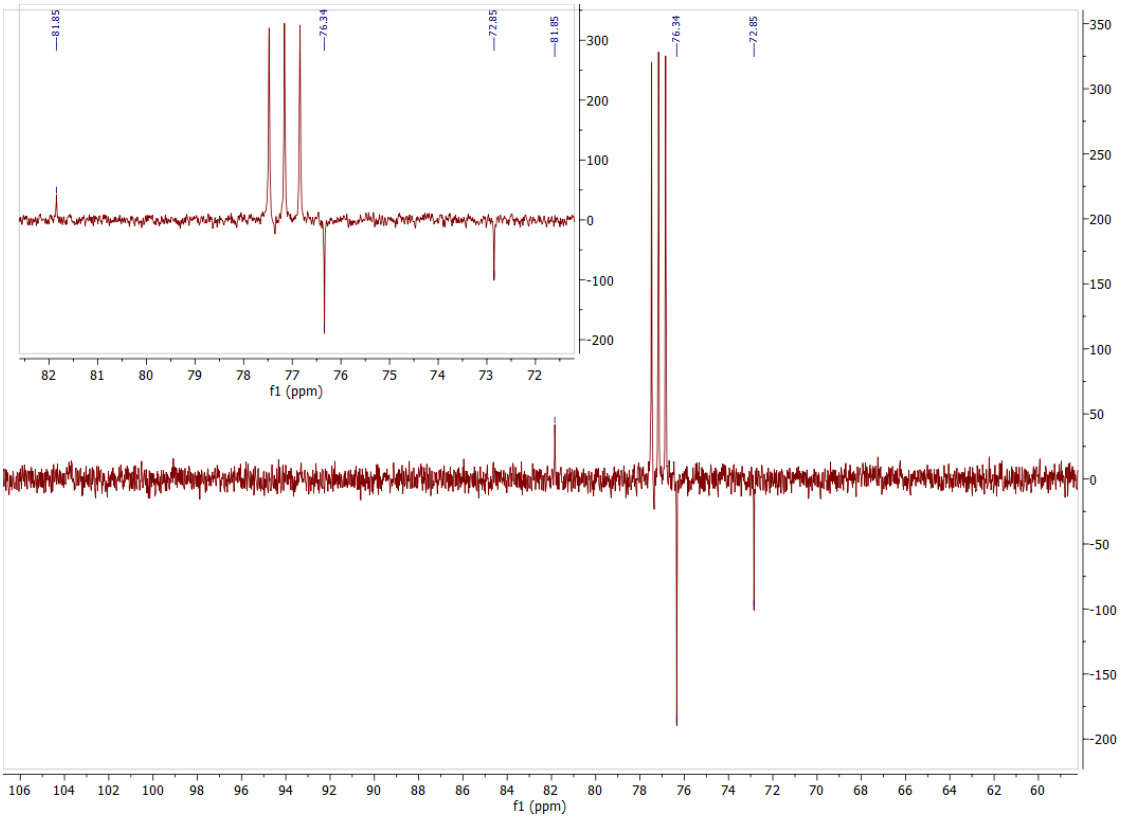
S17. 1,1’2,2´-tetrabromoruthenocene H/C COSY



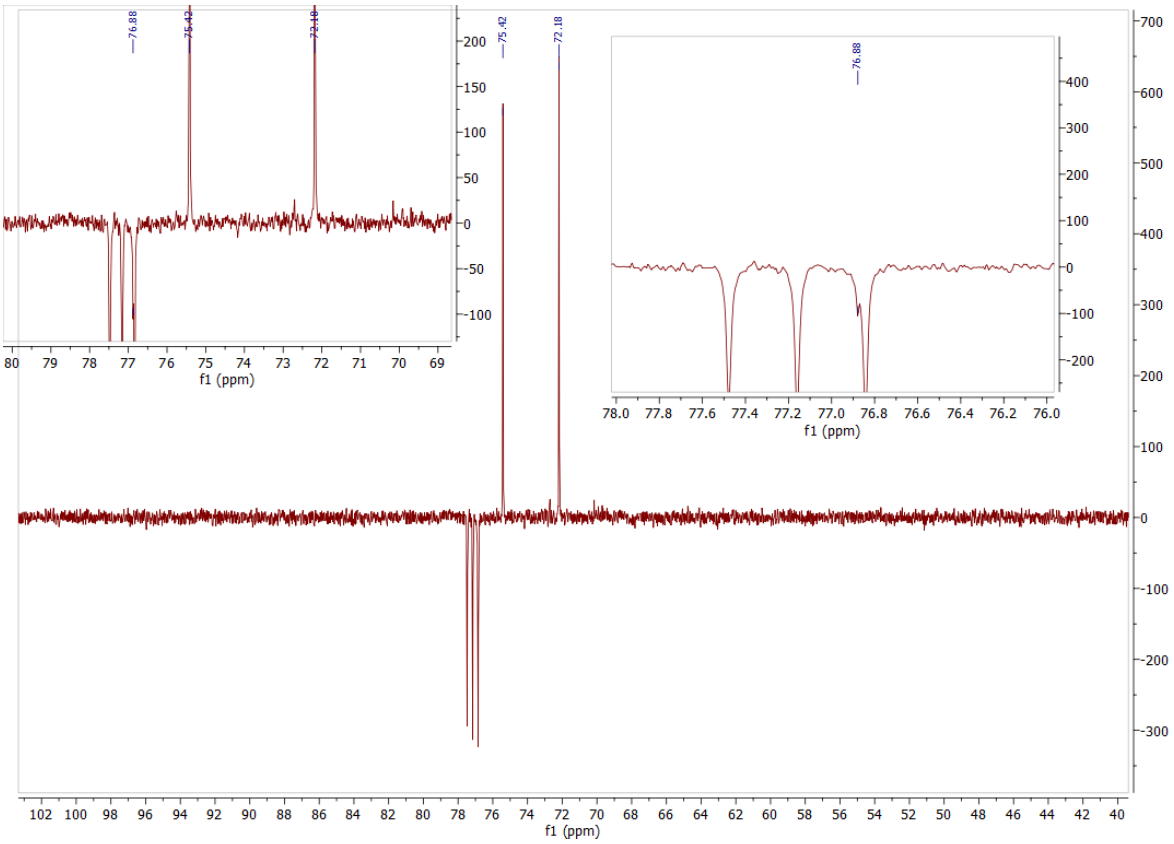
S18. 1,1’,2,2’-Tetrabromoruthenocene (DEPT) ^{13}C NMR.



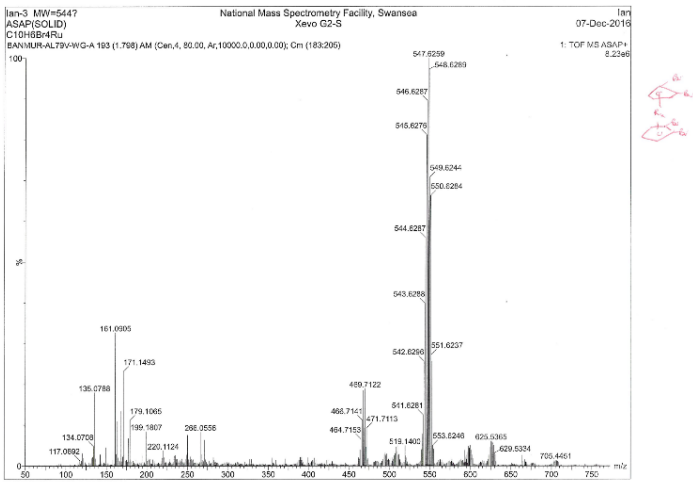
S19. 1,1’,2,2´-Tetrabromoruthenocene H/H COSY NMR



S20. (DEPT) ^{13}C NMR with expansion 1,1’,2,2´-Tetrabromoruthenocene



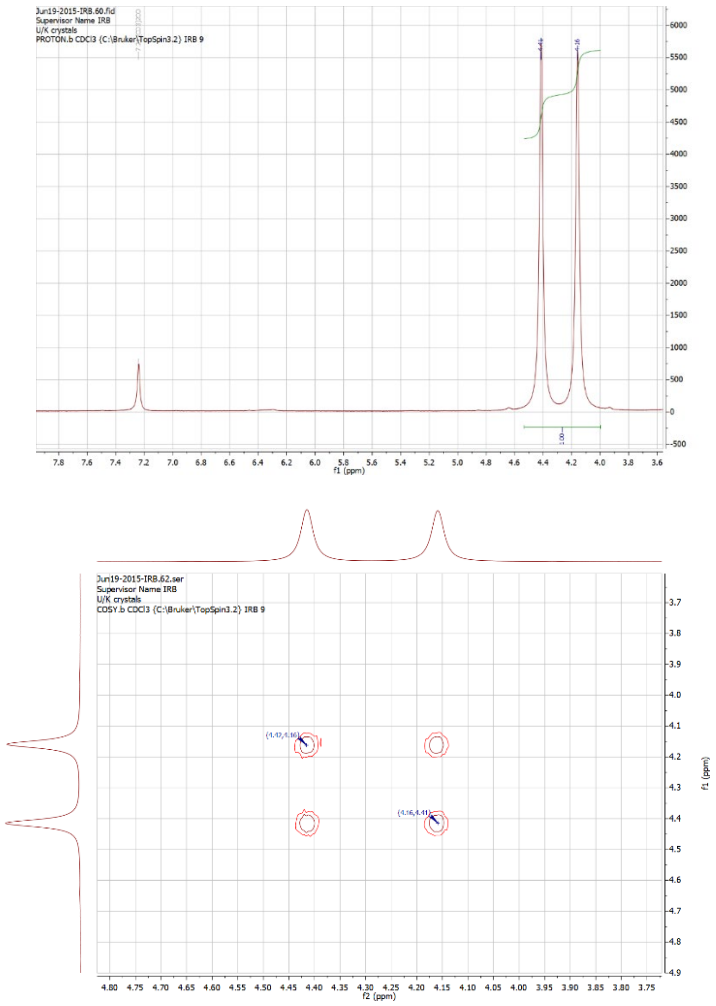
S21. DEPT 2: 1,1'2,2'-tetrabromoruthenocene Further expansions.



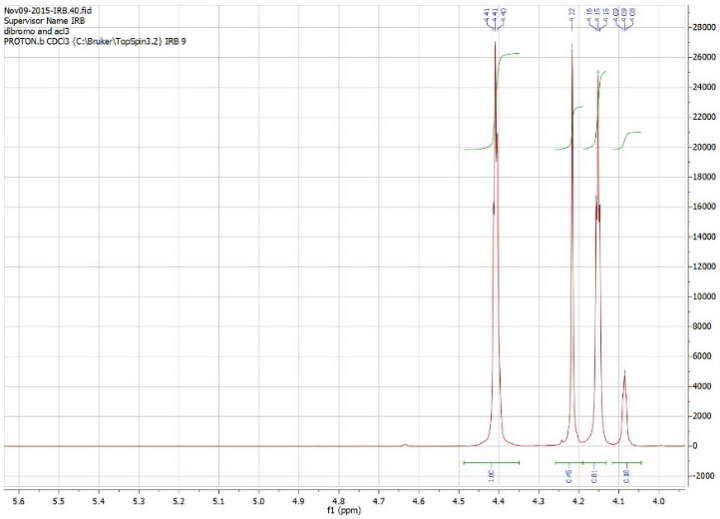
S22. 1,1',2,2´-tetrabromoruthenocene : mass spectrum, showing trace presence of higher substituted bromoruthenocenes.

Additional NMR Spectra for comparison:

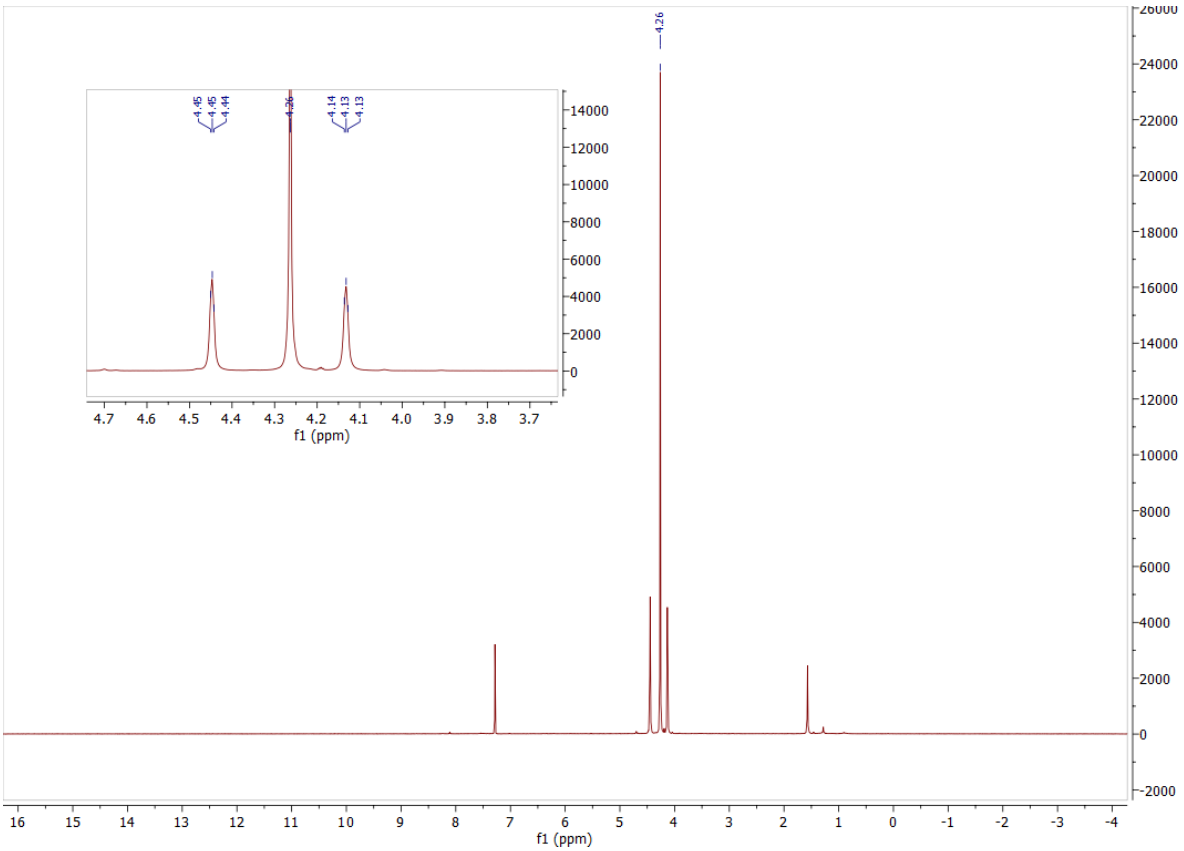
1,1´-dibromoferrocene spectra



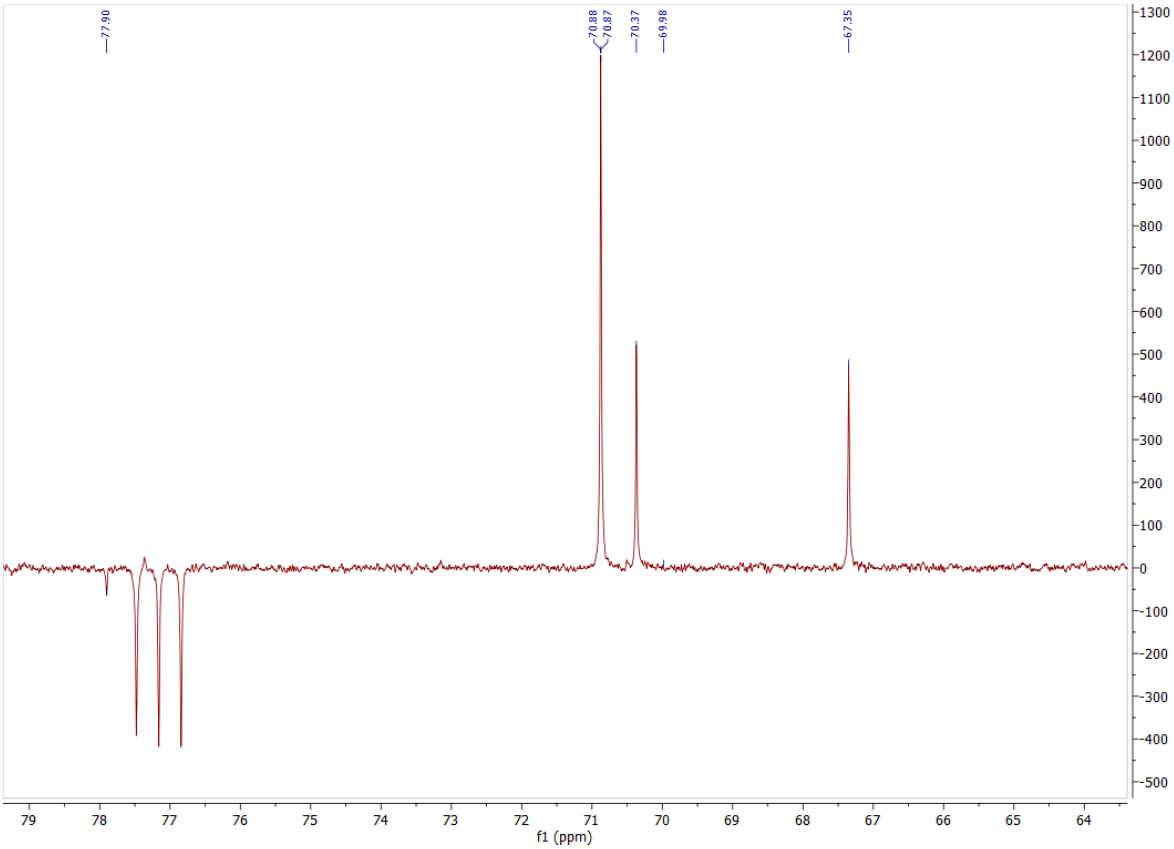
S23. 1,1’-Dibromoferrocene H/H COSY



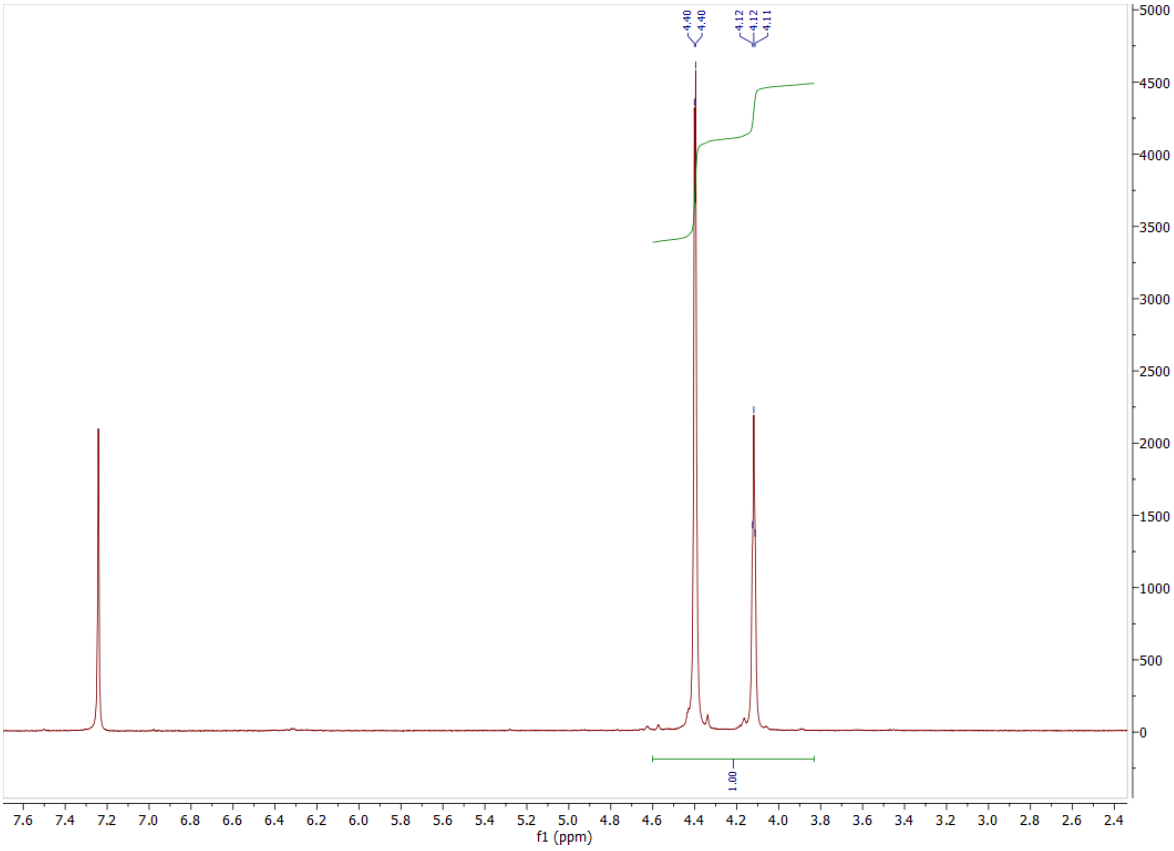
S24. ^{1}H NMR spectrum of mixture of 1,1'-Dibromo- with monobromoferrocene to show relationship of resonances.



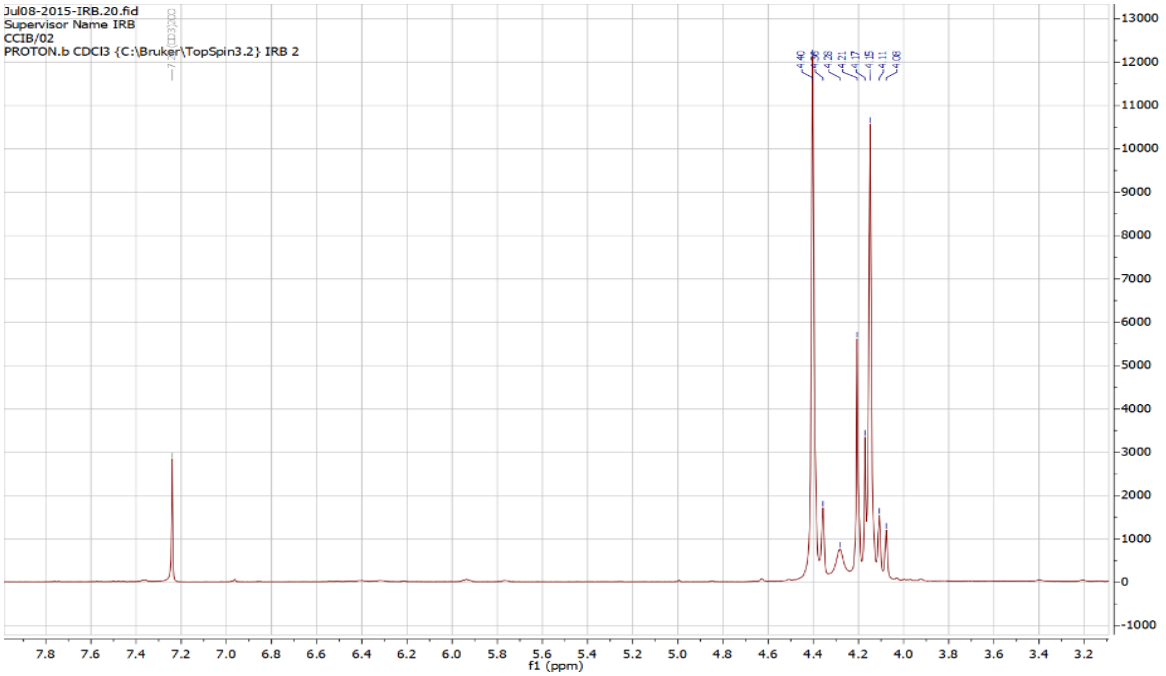
S25. ^{1}H NMR Monobromoferrocene



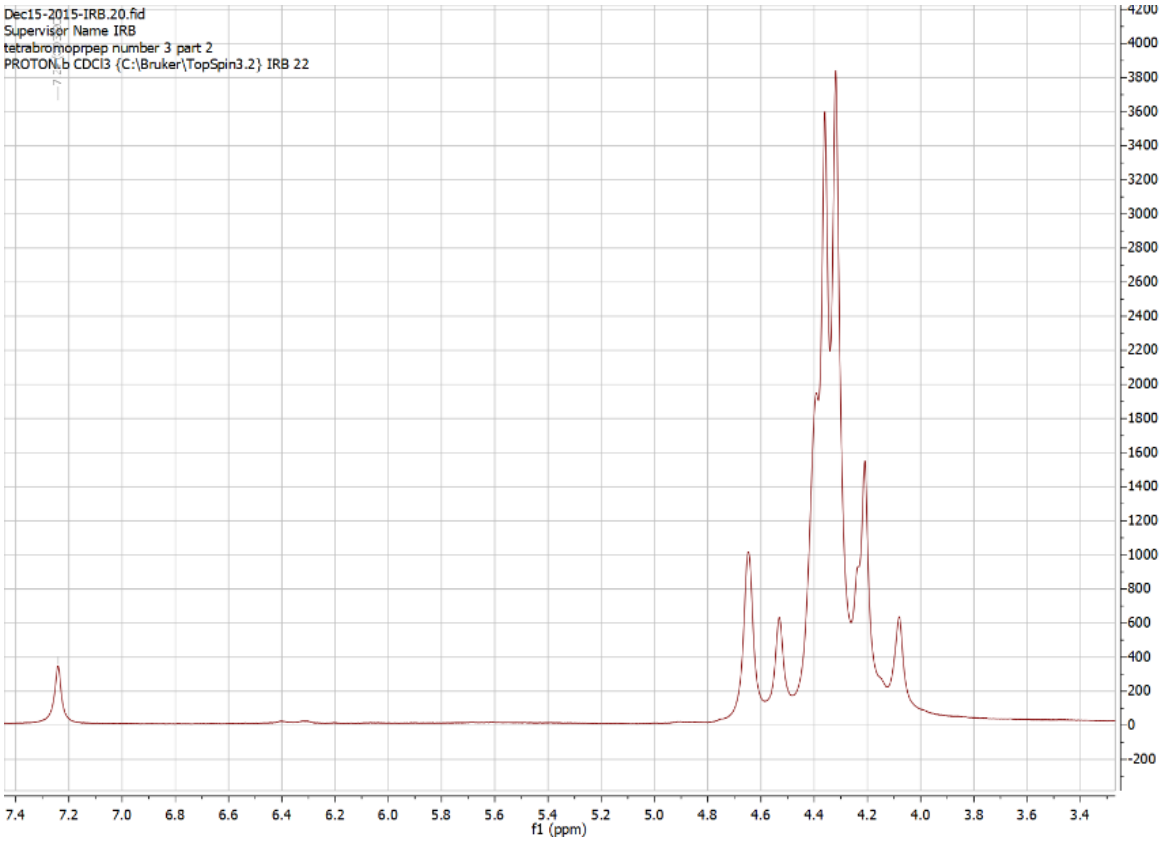
S26. Mono bromoferrocenes (DEPT) for comparison



S27. 1,1’,2,2’-Tetrachloroferrocene ^{1}H NMR for comparison with 1,1’2,2’-Tetrabromoferrocene.

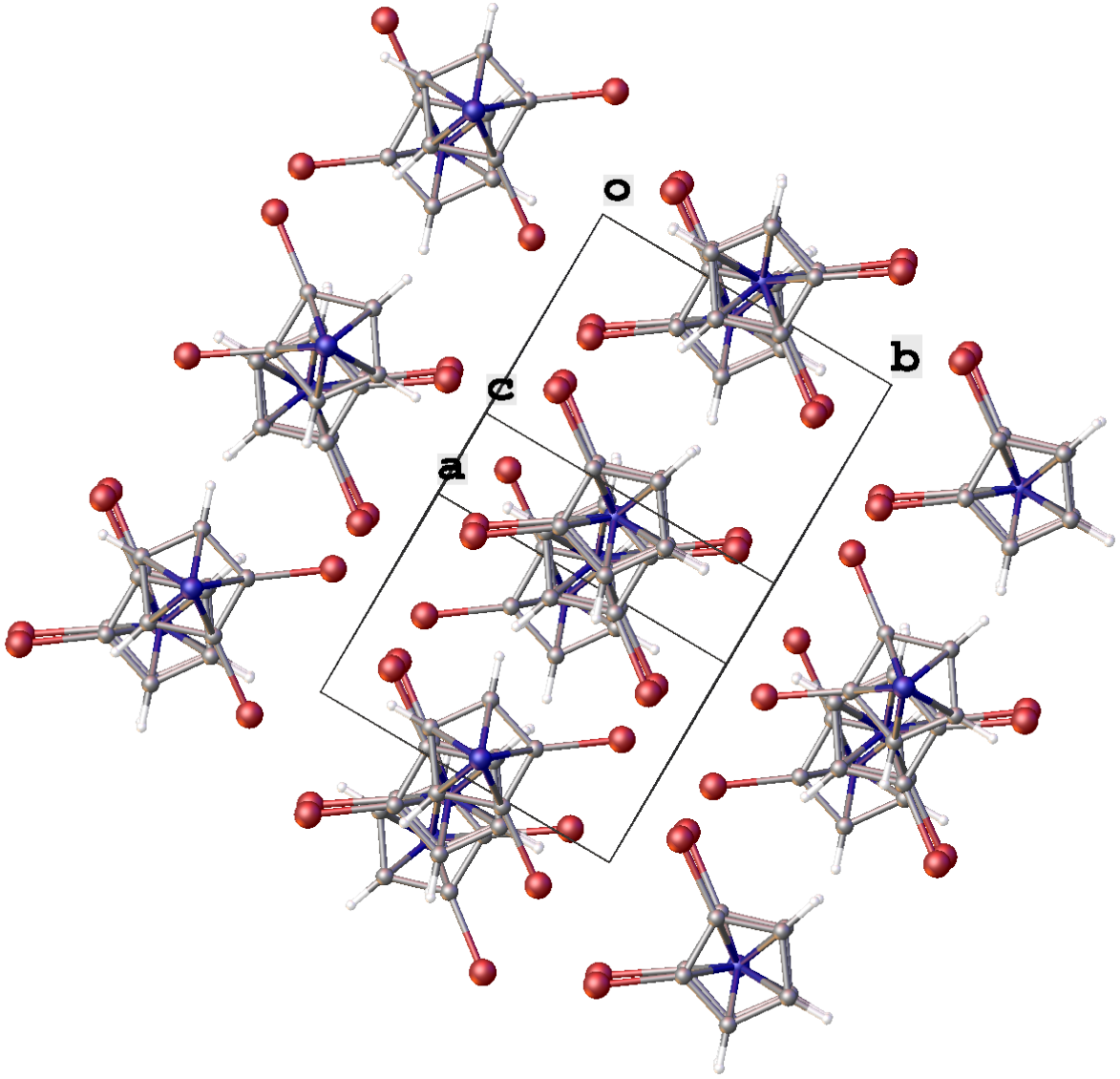


S28. Typical mixture obtained of bromoferrocenes before chromatography (2 examples) and mixture of mono and 1,1´-dibromoferrocene to show their relative chemical shifts:

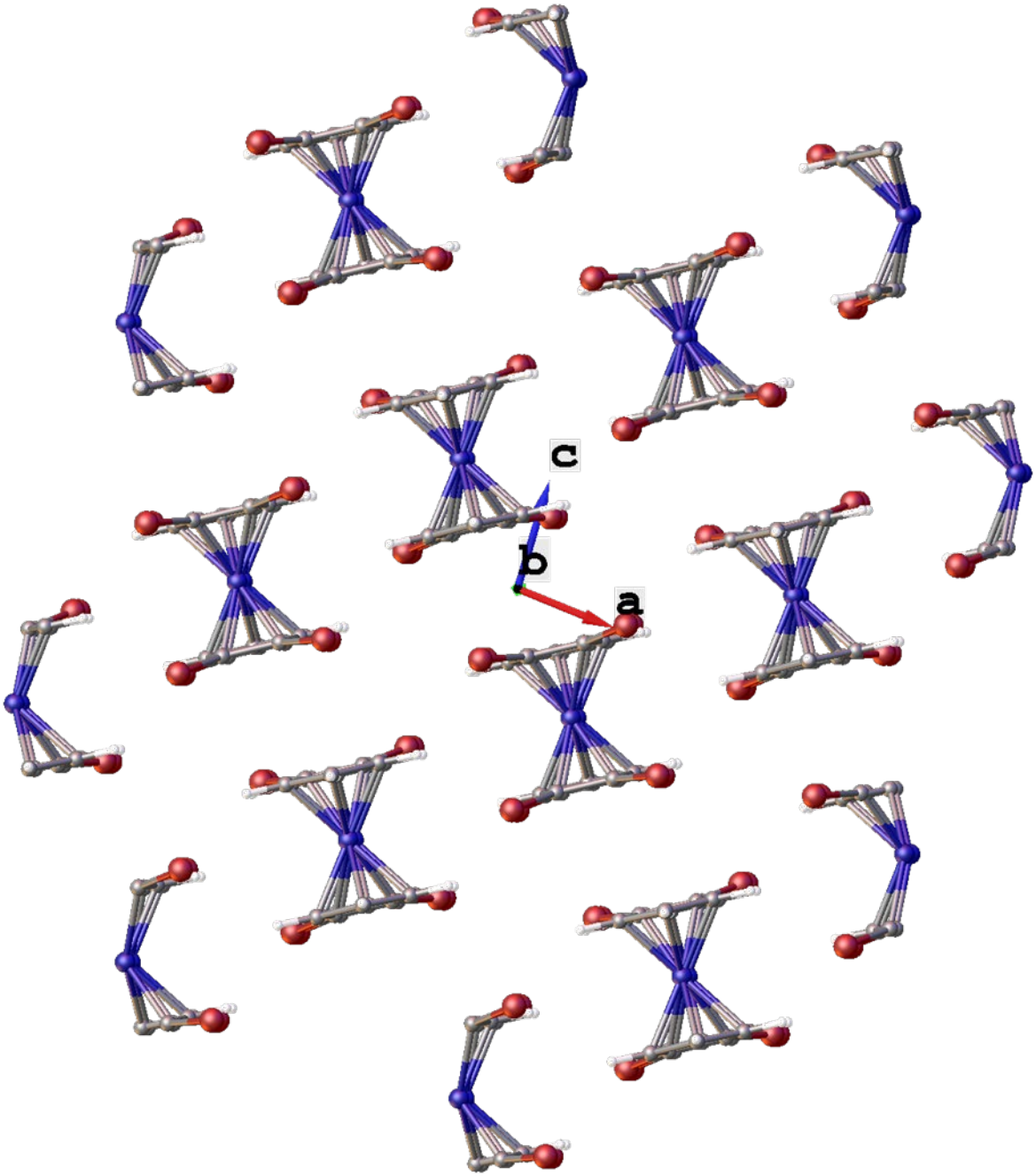


S29. Pre-chromatography spectrum of by-products obtained in 1,1’,2,2’-tetrabromoferrocene preparation.

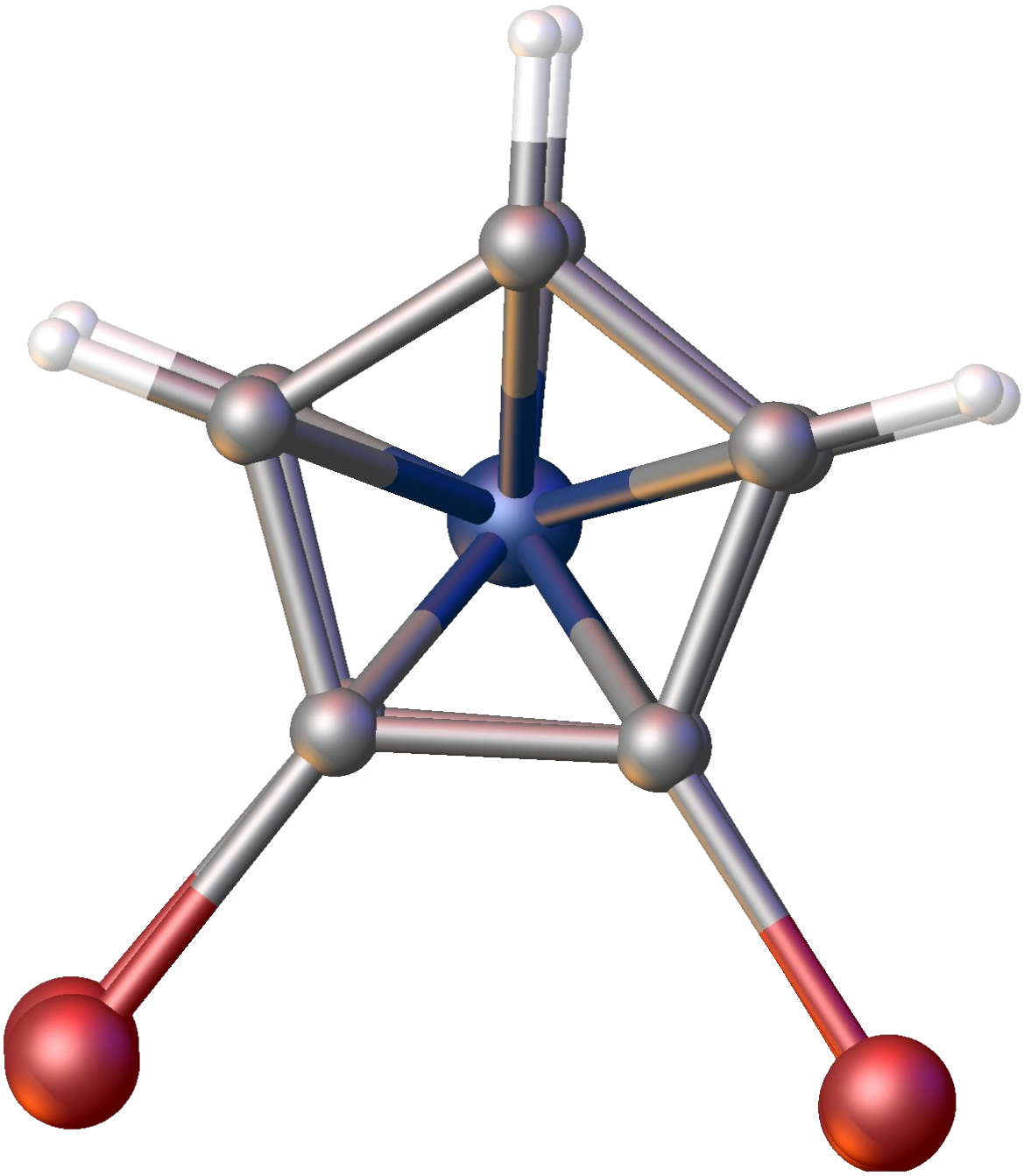
Additional Crystallographic Data. (figures)



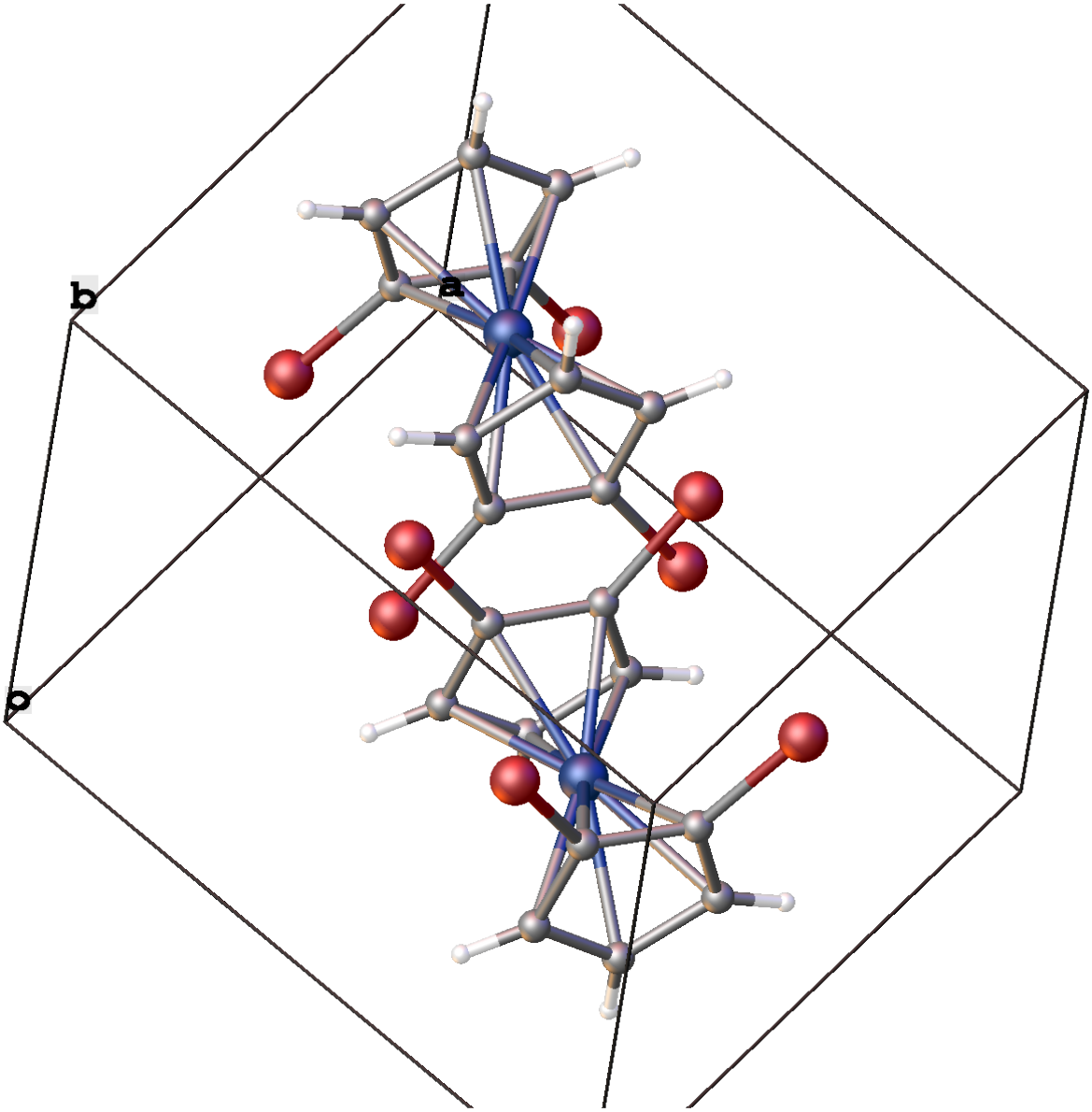
1,1’,2,2’-Tetrabromoferrocene packing 1



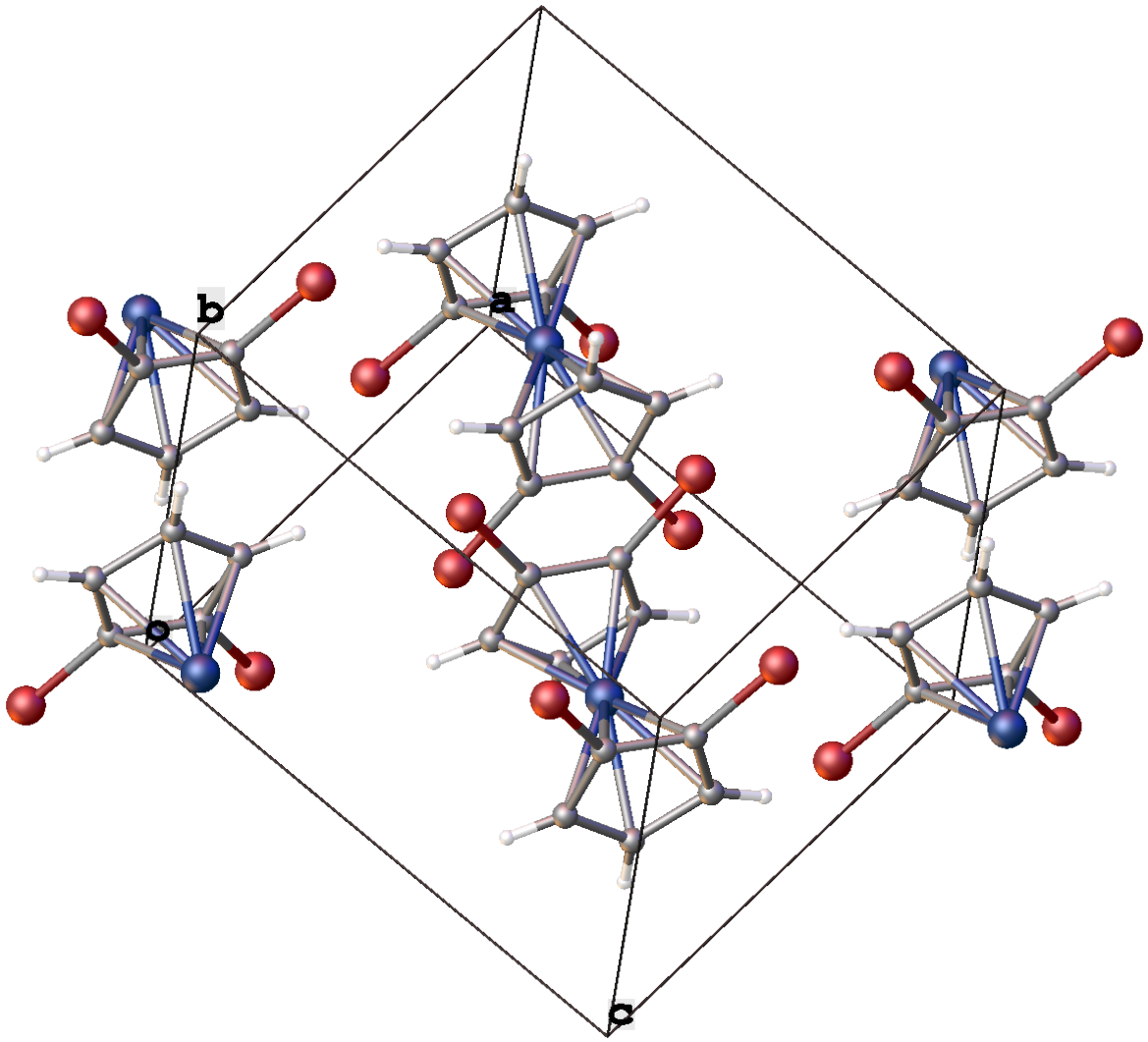
1,1’,2,2’-Tetrabromoferrocene packing 2, with unit cell axes.



1,1’,2,2’-Tetrabromoruthenocene top view

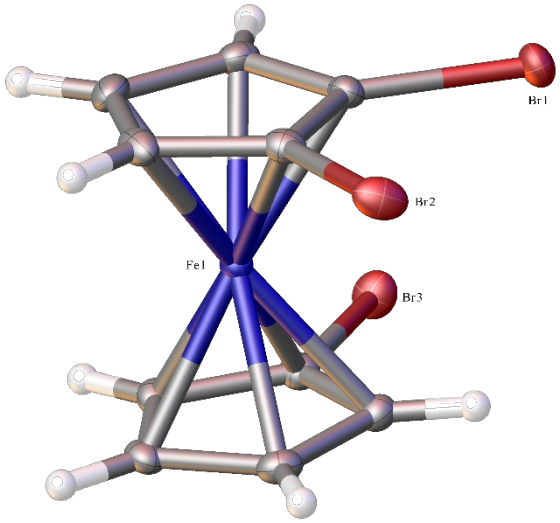


1,1’,2,2’-Tetrabromoruthenocene unit cell packing diagram



1,1’,2,2’-Tetrabromoruthenocene unit cell packing 2.

1,1',2-Tribromoferrocene Additional Crystal Data



Experimental. Single orange block-shaped crystals of (**2016ncs0648**) were recrystallised from hexane. A suitable crystal (0.170×0.070×0.045) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{10}H_7FeBr_3$, M_r = 422.74, monoclinic, $C2/c$ (No. 15), a = 12.6299(5) Å, b = 18.1045(6) Å, c = 10.4365(4) Å, β = 113.493(4)°, $\alpha = \gamma = 90°$, V = 2188.58(15) $Å^3$, T = 100(2) K, Z = 8, Z' = 1, $\mu(MoK_\alpha)$ = 12.285, 12440 reflections measured, 2521 unique (R_{int} = 0.0256) which were used in all calculations. The final wR_2 was 0.0468 (all data) and R_1 was 0.0180 (I > 2(I)).

Compound	**2016ncs0648**
Formula	$C_{10}H_7FeBr_3$
$D_{calc.}$/ g cm^{-3}	2.566
μ/mm^{-1}	12.285
Formula Weight	422.74
Colour	orange
Shape	block
Size/mm^3	0.170×0.070×0.045
T/K	100(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	12.6299(5)
b/Å	18.1045(6)
c/Å	10.4365(4)
α/°	90
β/°	113.493(4)
γ/°	90
V/Å^3	2188.58(15)
Z	8
Z'	1
Wavelength/Å	0.71075
Radiation type	MoK_α
Θ_{min}/°	2.250
Θ_{max}/°	27.485
Measured Refl.	12440
Independent Refl.	2521
Reflections Used	2411
R_{int}	0.0256
Parameters	127
Restraints	0
Largest Peak	0.880
Deepest Hole	-0.368
GooF	1.054
wR_2 (all data)	0.0468
wR_2	0.0461
R_1 (all data)	0.0193
R_1	0.0180

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 78.7	Rint 2.56%	complete 100% (IUCr) 100%
Refinement:	Shift 0.002	Max Peak 0.9	Min Peak -0.4	GooF 1.054

A orange block-shaped crystal with dimensions 0.170×0.070×0.045 mm^3 was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100(2) K.

Data were measured using profile data from ω-scans scans of 0.5 ° per frame for 2.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku).The maximum resolution achieved was Θ = 27.485°.

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.39.34b, 2017) software and refined using **CrysAlisPro** (Rigaku, V1.171.39.34b, 2017) on 9947 reflections, 80 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.39.34b, 2017) software which corrects for Lorentz polarisation. The final completeness is 99.90 % out to 27.485° in Θ.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.39.34b (Rigaku Oxford Diffraction, 2017) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 12.285 mm^{-1} at this wavelength (λ = 0.71075Å) and the minimum and maximum transmissions are 0.58435 and 1.00000..

The structure was solved in the space group $C2/c$ (# 15) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: CrysAlisPro 1.171.39.34b (Rigaku Oxford Diffraction, 2017) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

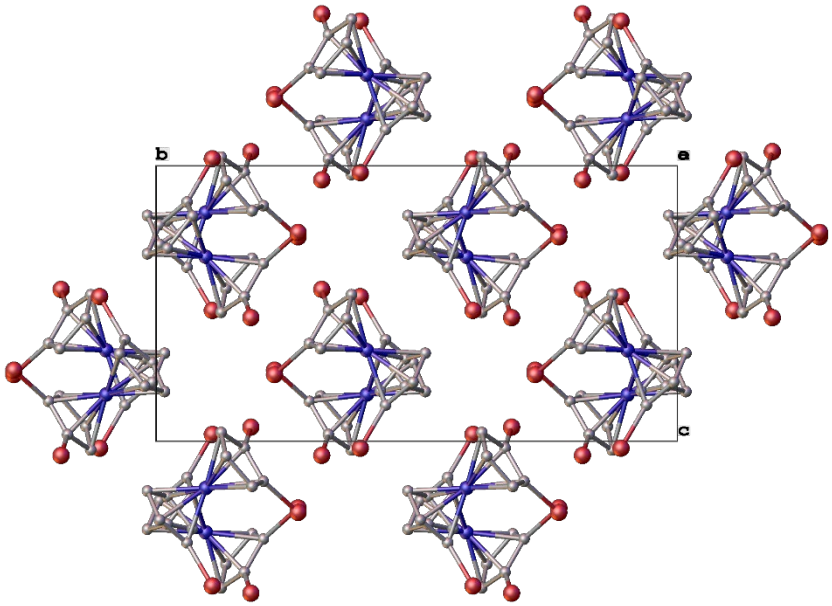
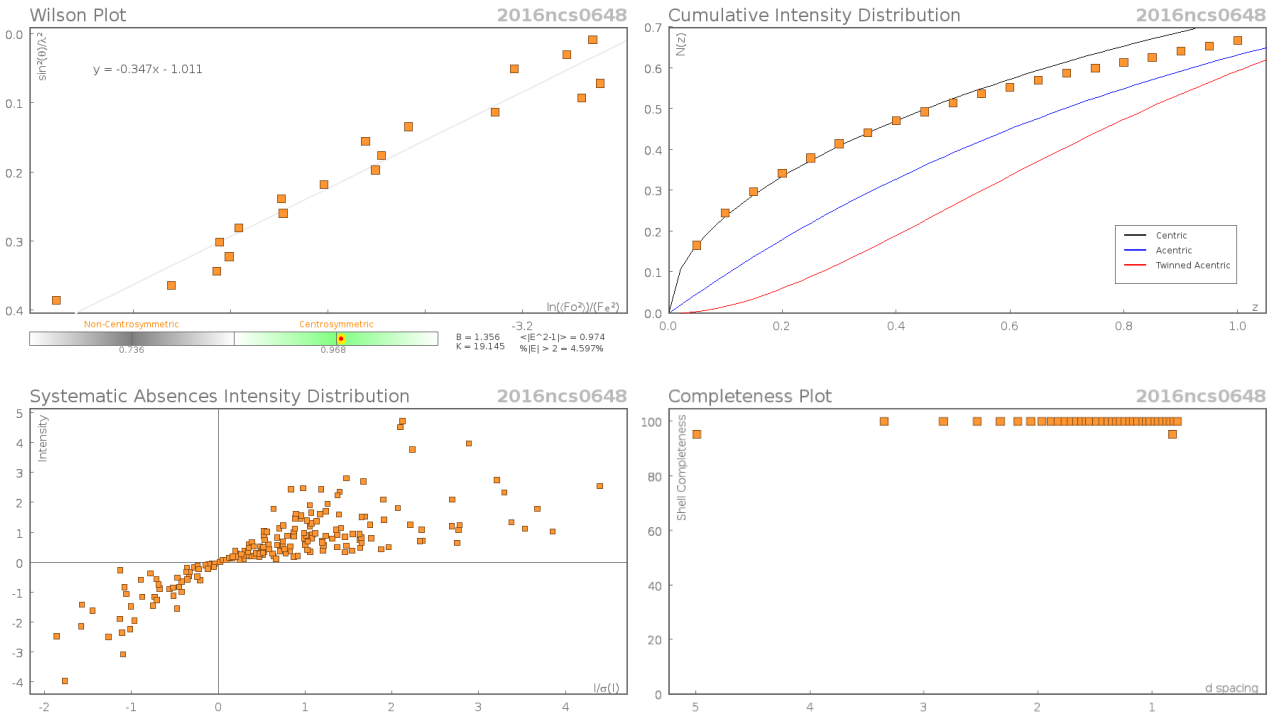
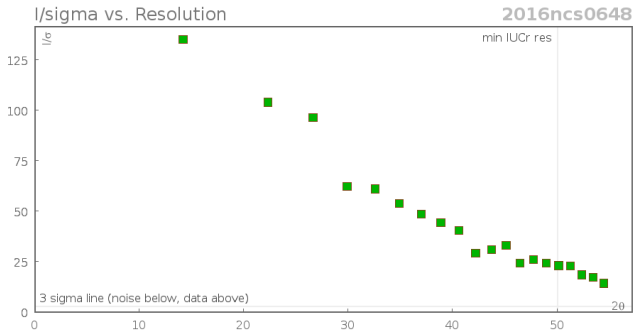


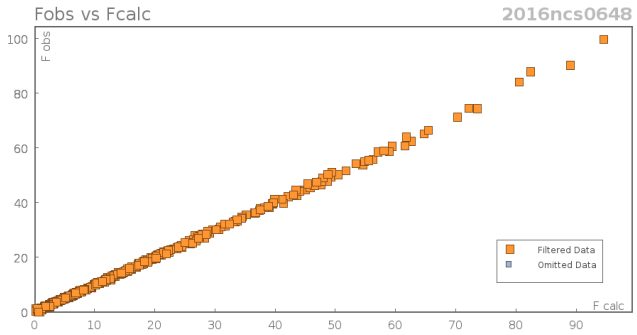
Figure S1: Packing diagram of 2016ncs0648.

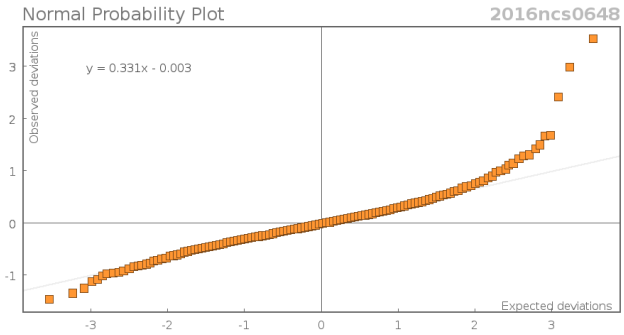
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	12705	Unique reflections	2521
Completeness	1.0	Mean I/σ	57.94
hkl_{max} collected	(16, 21, 13)	hkl_{min} collected	(-16, -23, -13)
hkl_{max} used	(15, 23, 13)	hkl_{min} used	(-16, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	9.05	d_{min} used	0.77
Friedel pairs	2544	Friedel pairs merged	1
Inconsistent equivalents	121	R_{int}	0.0256
R_{sigma}	0.0127	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3610, 2676, 911, 200, 36, 5)	Maximum multiplicity	15
Removed systematic absences	265	Filtered off (Shel/OMIT)	0

Table S1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2016ncs0648**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br1	6774.9(2)	7726.2(2)	7581.1(2)	17.97(6)
Br3	9018.6(2)	6080.9(2)	10251.6(2)	19.31(6)
Br2	4751.2(2)	6820.6(2)	4486.7(2)	20.92(7)
Fe1	7307.6(2)	5955.8(2)	6696.3(3)	11.44(7)
C6	7918.4(17)	5596.1(11)	8686.5(19)	14.6(4)
C2	6356.2(17)	6694.5(11)	5247(2)	15.0(4)
C3	6986.5(19)	6250.3(12)	4680(2)	18.1(4)
C7	6703.3(17)	5698.6(11)	8175(2)	14.9(4)
C1	7151.8(17)	7059.4(11)	6453(2)	13.7(4)
C10	8182.4(17)	5069.1(11)	7855(2)	15.9(4)
C5	8285.6(17)	6843.8(11)	6639(2)	16.4(4)
C9	7110.1(18)	4835.1(11)	6803(2)	16.4(4)
C8	6207.4(17)	5217.8(11)	7001(2)	16.4(4)
C4	8177.9(18)	6342.2(12)	5542(2)	18.8(4)

Table S2: Anisotropic Displacement Parameters (×10⁴) **2016ncs0648**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	20.83(11)	14.41(11)	19.04(11)	-3.95(7)	8.34(8)	0.66(7)
Br3	17.17(10)	24.81(12)	13.52(10)	-1.68(8)	3.55(8)	-0.90(8)
Br2	15.82(11)	18.87(12)	21.08(11)	4.59(8)	-0.03(8)	0.03(7)
Fe1	13.26(13)	10.60(14)	10.78(13)	0.82(10)	5.14(10)	0.50(10)
C6	16.3(9)	14.7(10)	11.6(8)	2.0(7)	4.2(7)	0.2(7)
C2	16.8(9)	13.4(9)	12.9(9)	2.4(7)	4.1(7)	-0.5(7)
C3	29.2(11)	13.6(10)	12.9(9)	0.8(7)	9.8(8)	-0.4(8)
C7	16.1(9)	15.6(9)	14.3(9)	1.5(7)	7.3(7)	0.4(7)
C1	17.0(9)	10.6(9)	14.3(8)	-0.5(7)	7.0(7)	-1.7(7)
C10	17.7(9)	14.0(9)	16.1(9)	3.5(7)	7.0(7)	3.3(8)
C5	15.9(9)	15.1(10)	19.5(9)	2.5(8)	8.4(8)	-1.7(7)
C9	22.6(10)	10.9(9)	16.6(9)	2.0(7)	8.8(8)	0.3(8)
C8	15.6(9)	17.0(10)	15.8(9)	3.3(8)	5.4(7)	-2.4(7)
C4	23.2(10)	17.7(10)	21.8(10)	2.4(8)	15.5(8)	0.6(8)

Table S3: Bond Lengths in Å for **2016ncs0648**.

Atom	Atom	Length/Å
Br1	C1	1.876(2)
Br3	C6	1.887(2)
Br2	C2	1.873(2)
Fe1	C6	2.0139(19)
Fe1	C2	2.0179(19)
Fe1	C3	2.049(2)
Fe1	C7	2.0296(19)
Fe1	C1	2.014(2)
Fe1	C10	2.048(2)
Fe1	C5	2.043(2)
Fe1	C9	2.053(2)
Fe1	C8	2.042(2)
Fe1	C4	2.050(2)
C6	C7	1.422(3)
C6	C10	1.416(3)
C2	C3	1.416(3)
C2	C1	1.422(3)
C3	C4	1.422(3)
C7	C8	1.428(3)
C1	C5	1.421(3)
C10	C9	1.426(3)
C5	C4	1.424(3)
C9	C8	1.418(3)

Table S4: Bond Angles in ° for **2016ncs0648**.

Atom	Atom	Atom	Angle/°
C6	Fe1	C2	148.91(8)
C6	Fe1	C3	168.86(9)
C6	Fe1	C7	41.17(8)
C6	Fe1	C10	40.80(8)
C6	Fe1	C5	107.29(8)
C6	Fe1	C9	68.23(8)
C6	Fe1	C8	68.44(8)
C6	Fe1	C4	129.90(8)
C2	Fe1	C3	40.75(8)
C2	Fe1	C7	115.48(8)
C2	Fe1	C10	169.10(8)
C2	Fe1	C5	69.06(8)
C2	Fe1	C9	130.31(8)
C2	Fe1	C8	108.16(8)
C2	Fe1	C4	68.40(8)
C3	Fe1	C9	109.54(8)
C3	Fe1	C4	40.60(8)
C7	Fe1	C3	149.35(8)
C7	Fe1	C10	69.46(8)
C7	Fe1	C5	128.17(8)
C7	Fe1	C9	68.97(8)
C7	Fe1	C8	41.06(8)
C7	Fe1	C4	167.70(9)
C1	Fe1	C6	115.41(8)
C1	Fe1	C2	41.30(8)
C1	Fe1	C3	69.06(8)
C1	Fe1	C7	106.04(8)
C1	Fe1	C10	148.74(8)
C1	Fe1	C5	41.00(8)
C1	Fe1	C9	168.43(8)
C1	Fe1	C8	129.10(8)
C1	Fe1	C4	68.63(8)
C10	Fe1	C3	130.52(8)
C10	Fe1	C9	40.69(8)
C10	Fe1	C4	108.95(8)
C5	Fe1	C3	68.86(8)
C5	Fe1	C10	116.36(8)
C5	Fe1	C9	150.17(8)
C5	Fe1	C4	40.73(8)
C8	Fe1	C3	117.51(8)
C8	Fe1	C10	68.63(8)
C8	Fe1	C5	167.56(8)
C8	Fe1	C9	40.52(8)
C8	Fe1	C4	150.71(8)

Atom	Atom	Atom	Angle/°
C4	Fe1	C9	118.32(8)
Br3	C6	Fe1	126.12(10)
C7	C6	Br3	125.21(15)
C7	C6	Fe1	70.01(11)
C10	C6	Br3	124.89(15)
C10	C6	Fe1	70.90(11)
C10	C6	C7	109.90(17)
Br2	C2	Fe1	128.22(10)
C3	C2	Br2	125.87(15)
C3	C2	Fe1	70.80(11)
C3	C2	C1	108.48(18)
C1	C2	Br2	125.58(15)
C1	C2	Fe1	69.20(11)
C2	C3	Fe1	68.45(11)
C2	C3	C4	107.36(18)
C4	C3	Fe1	69.76(11)
C6	C7	Fe1	68.82(11)
C6	C7	C8	106.34(17)
C8	C7	Fe1	69.93(11)
Br1	C1	Fe1	126.56(10)

Atom	Atom	Atom	Angle/°
C2	C1	Br1	126.02(15)
C2	C1	Fe1	69.50(11)
C5	C1	Br1	125.81(15)
C5	C1	Fe1	70.59(11)
C5	C1	C2	108.15(17)
C6	C10	Fe1	68.30(11)
C6	C10	C9	106.77(17)
C9	C10	Fe1	69.83(11)
C1	C5	Fe1	68.41(11)
C1	C5	C4	107.28(17)
C4	C5	Fe1	69.92(11)
C10	C9	Fe1	69.48(11)
C8	C9	Fe1	69.32(11)
C8	C9	C10	108.36(17)
C7	C8	Fe1	69.01(11)
C9	C8	Fe1	70.16(11)
C9	C8	C7	108.64(17)
C3	C4	Fe1	69.64(11)
C3	C4	C5	108.73(18)
C5	C4	Fe1	69.35(11)

Table S5: Torsion Angles in ° for **2016ncs0648**.

Atom	Atom	Atom	Atom	Angle/°
Br1	C1	C5	Fe1	121.64(15)
Br1	C1	C5	C4	-179.01(14)
Br3	C6	C7	Fe1	120.74(16)
Br3	C6	C7	C8	-179.07(14)
Br3	C6	C10	Fe1	-121.28(15)
Br3	C6	C10	C9	179.22(14)
Br2	C2	C3	Fe1	-123.82(16)
Br2	C2	C3	C4	177.05(15)
Br2	C2	C1	Br1	1.9(3)
Br2	C2	C1	Fe1	122.81(15)
Br2	C2	C1	C5	-176.91(14)
Fe1	C6	C7	C8	60.19(13)
Fe1	C6	C10	C9	-59.50(13)
Fe1	C2	C3	C4	-59.13(14)
Fe1	C2	C1	Br1	-120.96(15)
Fe1	C2	C1	C5	60.28(14)
Fe1	C3	C4	C5	-58.47(14)
Fe1	C7	C8	C9	59.13(14)
Fe1	C1	C5	C4	59.35(14)
Fe1	C10	C9	C8	-58.57(14)
Fe1	C5	C4	C3	58.65(14)
Fe1	C9	C8	C7	-58.43(14)
C6	C7	C8	Fe1	-59.48(13)
C6	C7	C8	C9	-0.3(2)
C6	C10	C9	Fe1	58.53(13)
C6	C10	C9	C8	0.0(2)
C2	C3	C4	Fe1	58.30(14)
C2	C3	C4	C5	-0.2(2)
C2	C1	C5	Fe1	-59.59(14)
C2	C1	C5	C4	-0.2(2)
C3	C2	C1	Br1	178.91(14)
C3	C2	C1	Fe1	-60.13(14)
C3	C2	C1	C5	0.1(2)
C7	C6	C10	Fe1	59.33(14)

Atom	Atom	Atom	Atom	Angle/°
C7	C6	C10	C9	-0.2(2)
C1	C2	C3	Fe1	59.14(13)
C1	C2	C3	C4	0.0(2)
C1	C5	C4	Fe1	-58.40(14)
C1	C5	C4	C3	0.3(2)
C10	C6	C7	Fe1	-59.87(14)
C10	C6	C7	C8	0.3(2)
C10	C9	C8	Fe1	58.67(14)
C10	C9	C8	C7	0.2(2)

Table S6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2016ncs0648**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
H3	6671	5947	3872	22
H7	6301	6022	8541	18
H10	8930	4903	7975	19
H5	8985	7004	7361	20
H9	7017	4483	6092	20
H8	5406	5164	6445	20
H4	8799	6108	5409	23

Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2017).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.


3BrFewithaxes.png


3BrFe.cif

Crystal Data and Experimental: 1,1´,2,2´-Tetrabromoferrocene

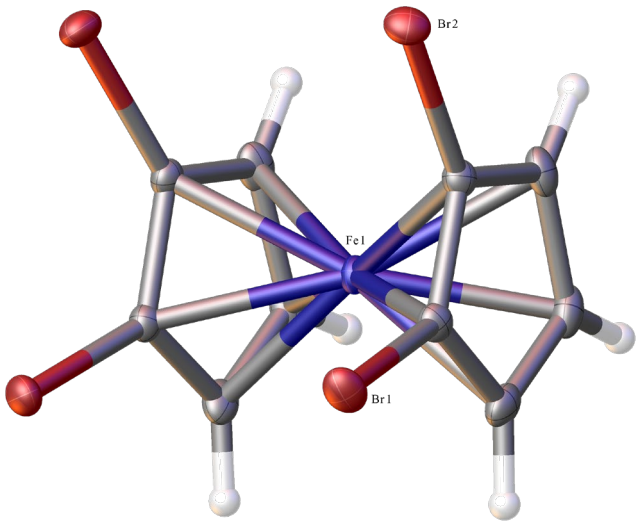


Figure S2: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single brown block-shaped crystals of (**2016ncs0636b**) were obtained by recrystallisation from petrol. A suitable crystal (0.070×0.050×0.035) mm^3 was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{10}H_6Br_4Fe$, M_r = 501.64, monoclinic, P2/n (No. 13), a = 8.7231(4) Å, b = 7.1951(3) Å, c = 9.5708(5) Å, β = 95.968(5)°, α = γ = 90°, V = 597.44(5) Å^3, T = 100(2) K, Z = 2, Z' = 0.5, μ(MoK$_\alpha$) = 14.598, 9360 reflections measured, 1372 unique (R_{int} = 0.0232) which were used in all calculations. The final wR_2 was 0.0393 (all data) and R_1 was 0.0156 (I > 2(I)).

Compound	**2016ncs0636b**
Formula	$C_{10}H_6Br_4Fe$
$D_{calc.}$/ g cm^{-3}	2.789
μ/mm^{-1}	14.598
Formula Weight	501.64
Colour	brown
Shape	block
Size/mm^3	0.070×0.050×0.035
T/K	100(2)
Crystal System	monoclinic
Space Group	P2/n
a/Å	8.7231(4)
b/Å	7.1951(3)
c/Å	9.5708(5)
α/°	90
β/°	95.968(5)
γ/°	90
V/Å^3	597.44(5)
Z	2
Z'	0.5
Wavelength/Å	0.71075
Radiation type	MoK_α
Θ_{min}/°	2.831
Θ_{max}/°	27.556
Measured Refl.	9360
Independent Refl.	1372
Reflections Used	1293
R_{int}	0.0232
Parameters	69
Restraints	0
Largest Peak	0.692
Deepest Hole	-0.378
GooF	1.034
wR_2 (all data)	0.0393
wR_2	0.0384
R_1 (all data)	0.0174
R_1	0.0156

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 66.1	Rint 2.32%	complete at 2θ=55° 99%
Refinement:	Shift 0.001	Max Peak 0.7	Min Peak -0.3	GooF 1.038

A brown block-shaped crystal with dimensions 0.070×0.050×0.035 was mounted on a MITIGEN holder in oil. Data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0° per frame for 4.0 s using MoK$_\alpha$ radiation (Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (70µm focus), 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku). The actually achieved resolution was Θ = 27.556°.

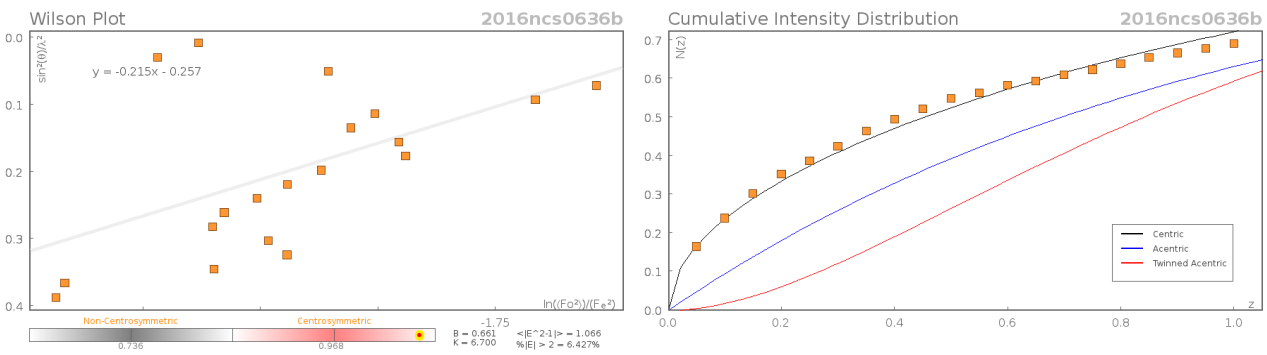
Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software and refined using **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) on 6943 reflections, 74% of the observed reflections.

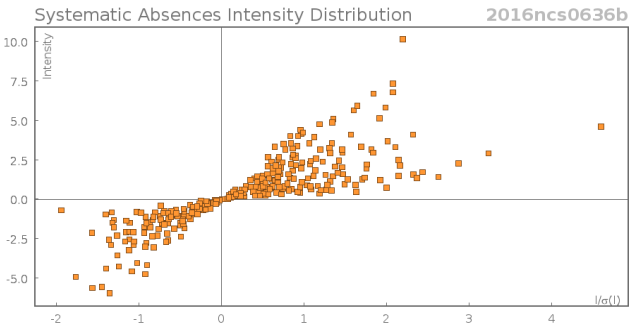
Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software which corrects for Lorentz polarisation. The final completeness is 98.80% out to 27.556° in Θ. The absorption coefficient μ of this material is 14.598 mm^{-1} at this wavelength (λ = 0.71075 Å) and the minimum and maximum transmissions are 0.70473 and 1.00000.

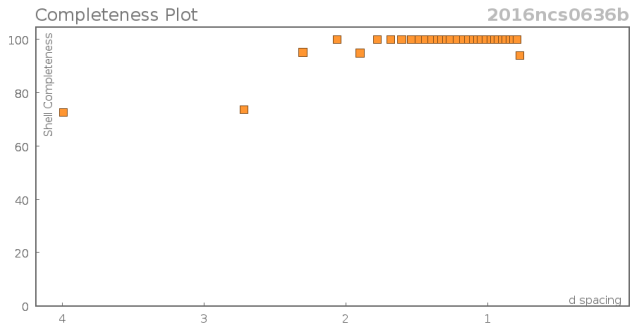
The structure was solved in the space group P2/n (# 13) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.?

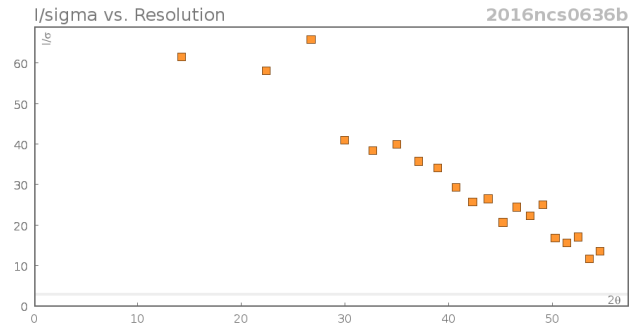
The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Data Plots: Diffraction Data

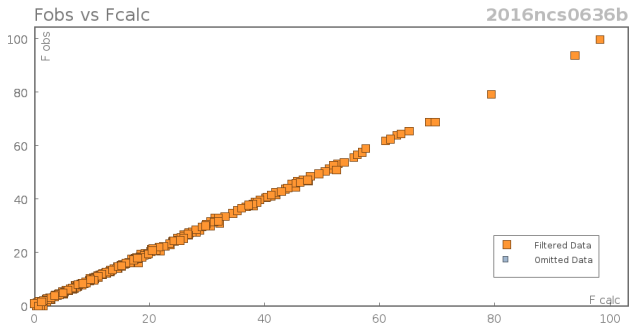


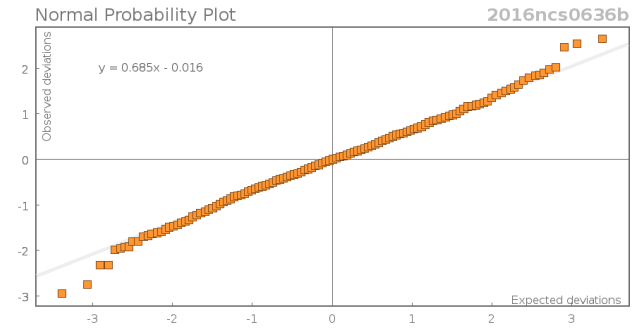






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	9780	Unique reflections	1372
Completeness	0.99	Mean I/σ	65.93
hkl_{max} collected	(11, 9, 12)	hkl_{min} collected	(-11, -9, -12)
hkl_{max} used	(11, 9, 12)	hkl_{min} used	(-11, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	9.52	d_{min} used	0.77
Friedel pairs	2123	Friedel pairs merged	1
Inconsistent equivalents	12	R_{int}	0.0232
R_{sigma}	0.0111	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(1402, 2074, 1255, 112, 1, 2)	Maximum multiplicity	12
Removed systematic absences	420	Filtered off (Shel/OMIT)	0

Table S7: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2016ncs0636b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br1	4682.7(2)	8521.9(3)	3020.7(2)	18.33(7)
Br2	8304.9(2)	8452.5(3)	5219.1(2)	16.88(7)
Fe1	7500	5109.2(5)	2500	11.52(9)
C1	5856(2)	6397(2)	3514.4(19)	13.4(4)
C2	7292(2)	6370(2)	4380.6(19)	12.9(4)
C3	7738(2)	4479(3)	4602.2(19)	17.0(4)
C4	6578(2)	3352(3)	3872(2)	18.9(4)
C5	5410(2)	4523(3)	3206(2)	17.4(4)

Table S8: Anisotropic Displacement Parameters (×10⁴) **2016ncs0636b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	15.29(11)	22.67(12)	17.22(11)	1.92(7)	2.60(7)	6.91(7)
Br2	17.82(11)	16.90(11)	15.49(11)	-4.71(6)	-0.28(7)	0.23(7)
Fe1	14.11(18)	10.78(18)	10.26(17)	0	4.02(13)	0
C1	13.0(9)	15.8(9)	11.9(8)	-0.3(6)	4.4(7)	1.3(7)
C2	13.9(9)	13.9(9)	11.3(8)	-0.6(6)	3.4(7)	0.4(6)
C3	23.7(10)	17.2(9)	11.0(8)	3.0(7)	5.8(7)	3.8(7)
C4	27.7(11)	14.7(10)	15.7(9)	0.8(7)	9.9(8)	-2.8(7)
C5	18.5(10)	20.4(10)	14.4(9)	-1.6(7)	7.5(7)	-5.9(8)

Table S9: Bond Lengths in Å for **2016ncs0636b**.

Atom	Atom	Length/Å
Br1	C1	1.8731(18)
Br2	C2	1.8768(18)
Fe1	C1[1]	2.0363(18)
Fe1	C1	2.0363(18)
Fe1	C2	2.0404(18)
Fe1	C2[1]	2.0403(18)
Fe1	C3	2.0518(18)
Fe1	C3[1]	2.0518(18)
Fe1	C4[1]	2.0471(19)
Fe1	C4	2.0471(19)
Fe1	C5	2.0529(19)
Fe1	C5[1]	2.0529(19)
C1	C2	1.429(3)
C1	C5	1.426(3)
C2	C3	1.425(3)
C3	C4	1.422(3)
C4	C5	1.422(3)

----

[1]3/2-X,+Y,1/2-Z

Table S10: Bond Angles in ° for **2016ncs0636b**.

Atom	Atom	Atom	Angle/°
C1	Fe1	C1[1]	125.87(10)
C1[1]	Fe1	C2	110.48(7)
C1	Fe1	C2	41.03(8)
C1[1]	Fe1	C2[1]	41.03(8)
C1	Fe1	C2[1]	110.48(7)
C1[1]	Fe1	C3	124.30(8)
C1[1]	Fe1	C3[1]	68.75(7)
C1	Fe1	C3	68.75(7)
C1	Fe1	C3[1]	124.30(8)
C1	Fe1	C4	68.41(8)
C1[1]	Fe1	C4	158.44(8)
C1	Fe1	C4[1]	158.44(8)
C1[1]	Fe1	C4[1]	68.41(8)
C1[1]	Fe1	C5	160.71(8)
C1	Fe1	C5[1]	160.71(8)
C1[1]	Fe1	C5[1]	40.81(7)
C1	Fe1	C5	40.81(7)
C2[1]	Fe1	C2	127.20(10)
C2[1]	Fe1	C3[1]	40.75(7)
C2	Fe1	C3[1]	162.56(8)
C2[1]	Fe1	C3	162.56(8)
C2	Fe1	C3	40.75(7)
C2[1]	Fe1	C4[1]	68.40(8)
C2[1]	Fe1	C4	156.56(8)
C2	Fe1	C4[1]	156.56(8)
C2	Fe1	C4	68.39(8)
C2[1]	Fe1	C5[1]	68.77(8)
C2	Fe1	C5[1]	123.02(8)
C2[1]	Fe1	C5	123.02(8)
C2	Fe1	C5	68.76(8)
C3	Fe1	C3[1]	154.47(11)
C3[1]	Fe1	C5	105.92(8)
C3[1]	Fe1	C5[1]	68.59(8)
C3	Fe1	C5	68.59(8)
C3	Fe1	C5[1]	105.92(8)
C4	Fe1	C3	40.61(8)
C4[1]	Fe1	C3	119.09(8)
C4	Fe1	C3[1]	119.09(8)
C4[1]	Fe1	C3[1]	40.61(8)
C4[1]	Fe1	C4	103.70(11)
C4[1]	Fe1	C5	120.38(8)
C4	Fe1	C5	40.57(8)
C4[1]	Fe1	C5[1]	40.57(8)
C4	Fe1	C5[1]	120.38(8)
C5[1]	Fe1	C5	156.28(11)
Br1	C1	Fe1	130.14(10)
C2	C1	Br1	125.50(13)
C2	C1	Fe1	69.64(10)
C5	C1	Br1	126.11(15)
C5	C1	Fe1	70.22(10)
C5	C1	C2	108.15(16)
Br2	C2	Fe1	130.63(10)
C1	C2	Br2	125.64(13)
C1	C2	Fe1	69.33(10)
C3	C2	Br2	126.13(15)
C3	C2	Fe1	70.06(10)
C3	C2	C1	107.98(16)
C2	C3	Fe1	69.19(11)
C4	C3	Fe1	69.52(11)
C4	C3	C2	107.59(18)
C3	C4	Fe1	69.87(11)
C5	C4	Fe1	69.93(11)
C5	C4	C3	108.82(18)
C1	C5	Fe1	68.97(10)
C4	C5	Fe1	69.49(11)
C4	C5	C1	107.45(17)

----

[1]3/2-X,+Y,1/2-Z

Table S11: Torsion Angles in ° for **2016ncs0636b**.

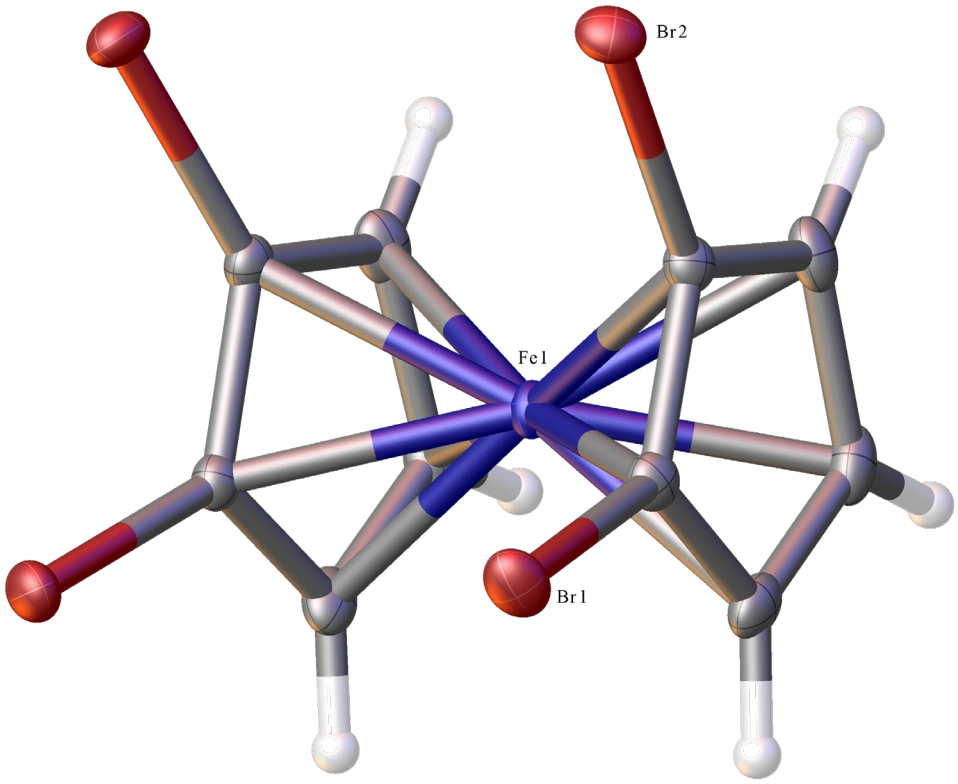
Atom	Atom	Atom	Atom	Angle/°
Br1	C1	C2	Br2	0.4(2)
Br1	C1	C2	Fe1	-125.44(14)
Br1	C1	C2	C3	174.94(13)
Br1	C1	C5	Fe1	125.84(15)
Br1	C1	C5	C4	-175.11(14)
Br2	C2	C3	Fe1	-126.35(15)
Br2	C2	C3	C4	174.52(14)
Fe1	C1	C2	Br2	125.87(14)
Fe1	C1	C2	C3	-59.62(13)
Fe1	C1	C5	C4	59.05(13)
Fe1	C2	C3	C4	-59.13(13)
Fe1	C3	C4	C5	-59.27(13)
Fe1	C4	C5	C1	-58.72(13)
C1	C2	C3	Fe1	59.17(13)
C1	C2	C3	C4	0.0(2)
C2	C1	C5	Fe1	-59.53(13)
C2	C1	C5	C4	-0.5(2)
C2	C3	C4	Fe1	58.92(13)
C2	C3	C4	C5	-0.3(2)
C3	C4	C5	Fe1	59.23(13)
C3	C4	C5	C1	0.5(2)
C5	C1	C2	Br2	-174.23(13)
C5	C1	C2	Fe1	59.90(13)
C5	C1	C2	C3	0.3(2)

Table S12: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2016ncs0636b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	8646	4049	5140	20
H4	6583	2032	3836	23
H5	4499	4129	2655	21


4BrFe.cif


4BrFewithaxes.png



Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, Yarnton, Oxford, UK (2015).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., Olex2: A complete structure solution, refinement and analysis program, J. Appl. Cryst., (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

Consensus

Crystal Data and Experimental: 1,1´-Dibromoruthenocene

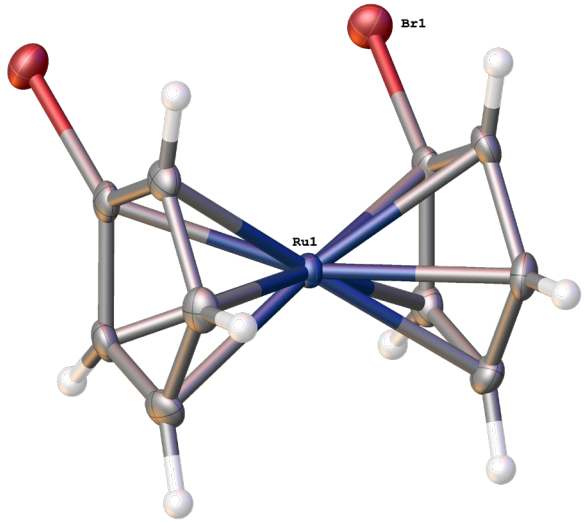


Figure S3: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single colourless needle-shaped crystals of (**2016ncs0630**) were obtained by recrystallisation from ether. A suitable crystal (0.280×0.020×0.015) mm^3 was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC10 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{10}H_8Br_2Ru$, M_r = 389.05, monoclinic, C2/c (No. 15), a = 14.0712(5) Å, b = 7.6052(2) Å, c = 9.6732(3) Å, β = 108.684(4)˚, α = γ = 90˚, V = 980.62(6) Å^3, T = 100(2) K, Z = 4, Z' = 0.5, μ(MoK$_\alpha$) = 9.692, 2009 reflections measured, 2009 unique (R_{int} = .) which were used in all calculations. The final wR_2 was 0.0690 (all data) and R_1 was 0.0251 (I > 2(I)).

Compound	**2016ncs0630**
Formula	$C_{10}H_8Br_2Ru$
$D_{calc.}$/ g cm^{-3}	2.635
μ/mm^{-1}	9.692
Formula Weight	389.05
Colour	colourless
Shape	needle
Size/mm^3	0.280×0.020×0.015
T/K	100(2)
Crystal System	monoclinic
Space Group	C2/c
a/Å	14.0712(5)
b/Å	7.6052(2)
c/Å	9.6732(3)
α/°	90
β/°	108.684(4)
γ/°	90
V/Å^3	980.62(6)
Z	4
Z'	0.5
Wavelength/Å	0.71075
Radiation type	MoK_α
Θ_{min}/°	3.084
Θ_{max}/°	27.480
Measured Refl.	2009
Independent Refl.	2009
Reflections Used	1993
R_{int}	.
Parameters	61
Restraints	0
Largest Peak	1.919
Deepest Hole	-0.724
GooF	1.085
wR_2 (all data)	0.0690
wR_2	0.0690
R_1 (all data)	0.0252
R_1	0.0251

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 55.4	Rint Merged!	complete 98%
Refinement:	Shift 0.001	Max Peak 1.9	Min Peak -0.7	GooF 1.085

A colourless needle-shaped crystal with dimensions 0.280×0.020×0.015 was mounted on a MITIGEN holder in oil. Data were collected using a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC10 goniometer and HG Saturn 724+ detector diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 0.5° per frame for 12.0 s using MoK_α radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku). The actually achieved resolution was Θ = 27.480°.

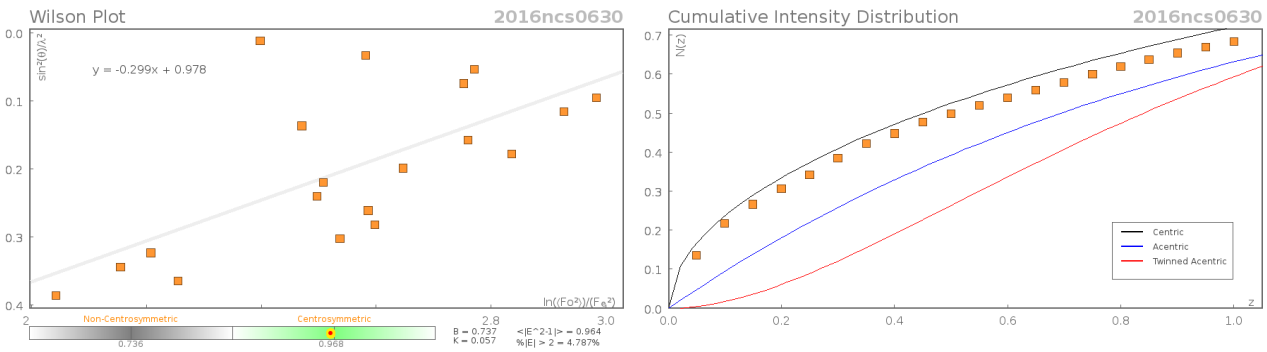
Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software and refined using **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) on 6349 reflections, 316% of the observed reflections.

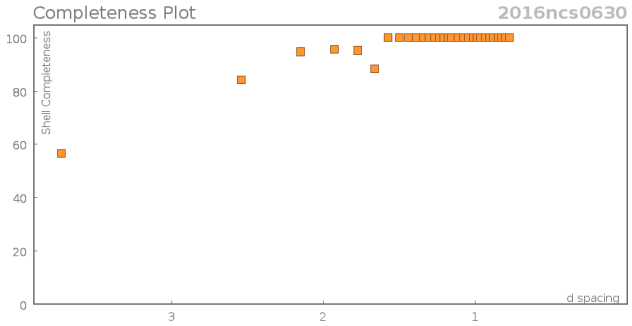
Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software which corrects for Lorentz polarisation. The final completeness is 98.00% out to 27.480° in Θ. The absorption coefficient μ of this material is 9.692 mm^{-1} at this wavelength (λ = 0.71075 Å) and the minimum and maximum transmissions are 0.74600 and 1.00000.

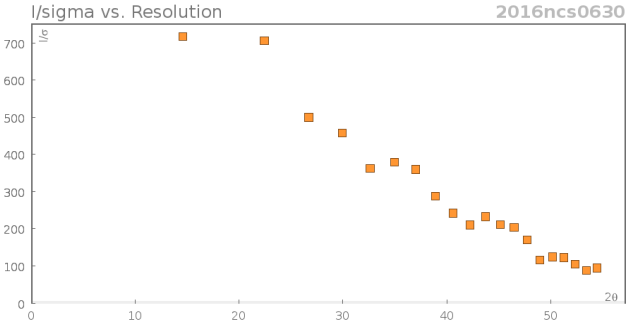
The structure was solved in the space group C2/c (# 15) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Refined as a 2-component twin. Component 2 rotated by 179.9779% around [-0.71 0.00 0.71] (reciprocal) or [-0.31 0.00 0.95] (direct)

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

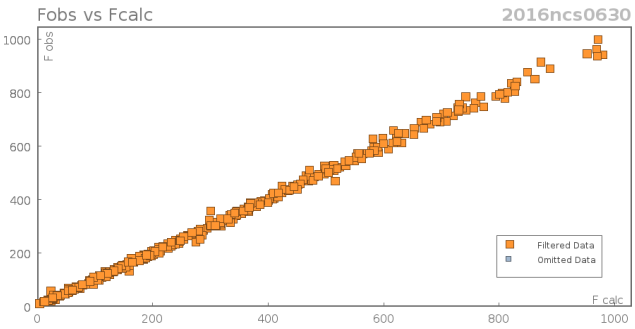
Data Plots: Diffraction Data

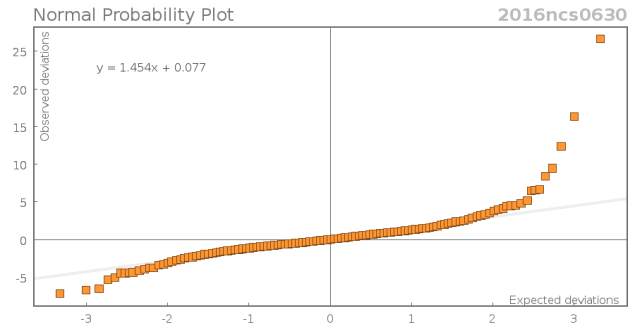






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	2300	Unique reflections	1108
Completeness	0.985	Mean I/σ	55.43
hkl_{max} collected	(18, 9, 12)	hkl_{min} collected	(-18, -9, -12)
hkl_{max} used	(17, 9, 12)	hkl_{min} used	(-18, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	6.61	d_{min} used	0.77
Friedel pairs	264	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0
R_{sigma}	0.003	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(1623, 190, 2)	Maximum multiplicity	0
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table S13: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2016ncs0630**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Ru1	5000	8043.6(4)	7500	11.72(13)
Br1	3660.6(2)	4016.7(4)	6159.8(3)	21.02(14)
C1	3747(2)	6495(5)	6228(3)	15.2(6)
C2	4064(3)	7546(4)	5254(4)	16.0(6)
C3	3938(3)	9333(4)	5612(4)	17.3(6)
C4	3541(3)	9339(5)	6802(4)	17.7(6)
C5	3422(3)	7563(4)	7182(4)	16.2(6)

Table S14: Anisotropic Displacement Parameters (×10⁴) **2016ncs0630**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	9.30(18)	13.43(19)	11.22(19)	0	1.57(12)	0
Br1	21.4(2)	16.6(2)	22.6(2)	-1.79(11)	3.55(15)	-2.93(11)
C1	8.4(13)	18.1(15)	16.0(17)	-0.8(11)	-0.6(11)	-1.5(11)
C2	11.4(15)	22.3(17)	11.9(19)	-0.5(11)	0.1(12)	0.4(11)
C3	14.4(14)	18.6(15)	15.9(15)	4.5(12)	0.5(12)	1.4(13)
C4	12.3(14)	19.7(15)	18.9(16)	0.5(13)	1.9(12)	6.1(13)
C5	7.7(14)	21.2(16)	19(2)	-0.4(12)	3.3(12)	-0.7(11)

Table S15: Bond Lengths in Å for **2016ncs0630**.

Atom	Atom	Length/Å
Ru1	C1[1]	2.149(3)
Ru1	C1	2.149(3)
Ru1	C2[1]	2.182(4)
Ru1	C2	2.182(4)
Ru1	C3	2.187(3)
Ru1	C3[1]	2.187(3)
Ru1	C4	2.180(3)
Ru1	C4[1]	2.179(3)
Ru1	C5	2.173(4)
Ru1	C5[1]	2.173(4)
Br1	C1	1.888(4)
C1	C2	1.413(4)
C1	C5	1.411(4)
C2	C3	1.428(5)
C3	C4	1.431(5)
C4	C5	1.423(5)

----

[1]1-X,+Y,3/2-Z

Table S16: Bond Angles in ° for **2016ncs0630**.

Atom	Atom	Atom	Angle/°
C1[1]	Ru1	C1	113.53(18)
C1	Ru1	C2	38.06(12)
C1	Ru1	C2[1]	126.67(12)
C1[1]	Ru1	C2	126.67(12)
C1[1]	Ru1	C2[1]	38.06(12)
C1	Ru1	C3[1]	159.99(12)
C1	Ru1	C3	63.38(13)
C1[1]	Ru1	C3	159.99(12)
C1[1]	Ru1	C3[1]	63.38(13)
C1[1]	Ru1	C4	160.61(12)
C1	Ru1	C4[1]	160.61(12)
C1[1]	Ru1	C4[1]	63.39(13)
C1	Ru1	C4	63.39(13)
C1[1]	Ru1	C5	127.06(13)
C1[1]	Ru1	C5[1]	38.11(12)
C1	Ru1	C5[1]	127.06(12)
C1	Ru1	C5	38.11(12)
C2	Ru1	C2[1]	160.02(17)
C2[1]	Ru1	C3[1]	38.15(12)
C2[1]	Ru1	C3	160.39(13)
C2	Ru1	C3[1]	160.39(13)
C2	Ru1	C3	38.15(12)
C3[1]	Ru1	C3	126.71(18)
C4[1]	Ru1	C2	126.48(12)
C4	Ru1	C2[1]	126.48(12)
C4	Ru1	C2	64.04(12)
C4[1]	Ru1	C2[1]	64.04(12)
C4	Ru1	C3	38.27(13)
C4	Ru1	C3[1]	112.32(13)
C4[1]	Ru1	C3	112.32(13)
C4[1]	Ru1	C3[1]	38.27(13)
C4[1]	Ru1	C4	126.27(19)
C5[1]	Ru1	C2[1]	64.32(13)
C5[1]	Ru1	C2	112.02(13)
C5	Ru1	C2[1]	112.02(13)
C5	Ru1	C2	64.32(13)
C5	Ru1	C3[1]	125.99(12)
C5[1]	Ru1	C3[1]	64.09(12)
C5	Ru1	C3	64.09(12)
C5[1]	Ru1	C3	125.99(12)
C5[1]	Ru1	C4	159.73(13)
C5	Ru1	C4[1]	159.73(13)
C5	Ru1	C4	38.17(13)
C5[1]	Ru1	C4[1]	38.17(13)
C5[1]	Ru1	C5	160.65(18)
Br1	C1	Ru1	126.79(15)
C2	C1	Ru1	72.2(2)
C2	C1	Br1	124.9(2)
C5	C1	Ru1	71.8(2)
C5	C1	Br1	124.5(2)
C5	C1	C2	110.4(3)
C1	C2	Ru1	69.71(19)
C1	C2	C3	106.7(3)
C3	C2	Ru1	71.10(19)
C2	C3	Ru1	70.75(19)
C2	C3	C4	108.0(3)
C4	C3	Ru1	70.6(2)
C3	C4	Ru1	71.1(2)
C5	C4	Ru1	70.66(19)
C5	C4	C3	108.3(3)
C1	C5	Ru1	70.04(18)
C1	C5	C4	106.7(3)
C4	C5	Ru1	71.16(19)

---

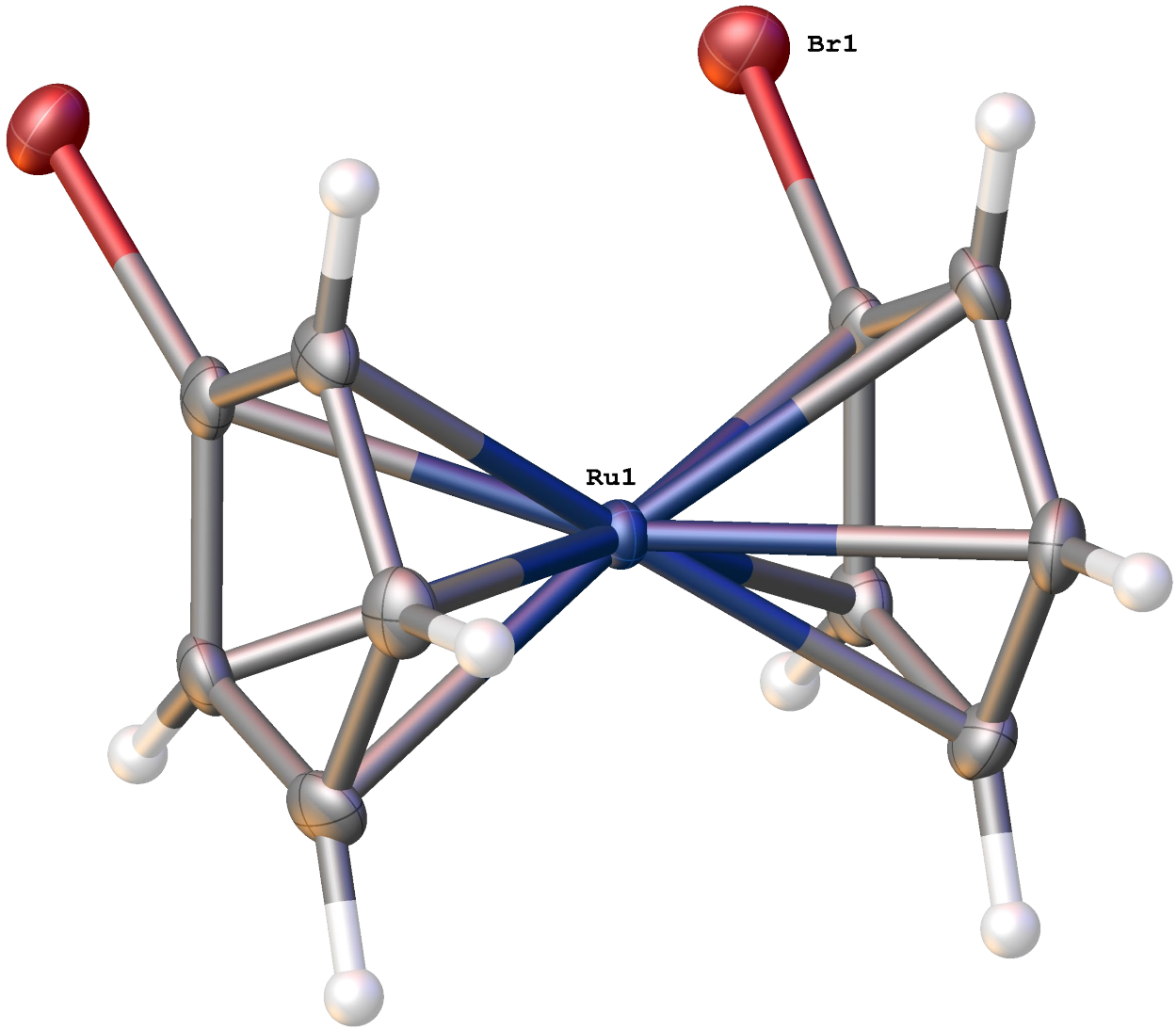
[1]1-X,+Y,3/2-Z

Table S17: Torsion Angles in ° for **2016ncs0630**.

Atom	Atom	Atom	Atom	Angle/°
Ru1	C1	C2	C3	-61.9(2)
Ru1	C1	C5	C4	62.1(2)
Ru1	C2	C3	C4	-61.1(3)
Ru1	C3	C4	C5	-61.2(2)
Ru1	C4	C5	C1	-61.4(2)
Br1	C1	C2	Ru1	-122.9(2)
Br1	C1	C2	C3	175.2(2)
Br1	C1	C5	Ru1	122.6(2)
Br1	C1	C5	C4	-175.2(2)
C1	C2	C3	Ru1	61.0(2)
C1	C2	C3	C4	-0.1(4)
C2	C1	C5	Ru1	-62.3(2)
C2	C1	C5	C4	-0.2(3)
C2	C3	C4	Ru1	61.2(2)
C2	C3	C4	C5	0.0(4)
C3	C4	C5	Ru1	61.5(3)
C3	C4	C5	C1	0.2(4)
C5	C1	C2	Ru1	62.1(2)
C5	C1	C2	C3	0.2(3)

Table 1: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2016ncs0630**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	4314	7142	4507	19
H3	4090	10342	5142	21
H4	3385	10353	7261	21
H5	3172	7173	7932	19



Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, Yarnton, Oxford, UK (2015).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., Olex2: A complete structure solution, refinement and analysis program, J. Appl. Cryst., (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, Acta Cryst., (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, Acta Cryst., (2015), **A71**, 3-8.

Crystal Data and Experimental: 1,1´,2,2´-Tetrabromoruthenocene

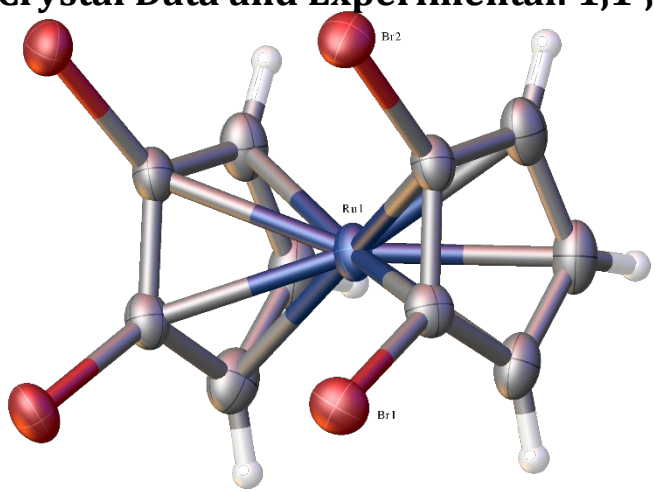


Figure S4: Thermal ellipsoids drawn at the 50% probability level.

Experimental. Single colourless plate-shaped crystals of (**2016ncs0637**) were obtained by recrystallisation from ether. A suitable crystal (0.150×0.050×0.010) mm^3 was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at T = 100(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{10}H_6Br_4Ru$, M_r = 546.86, monoclinic, P2/n (No. 13), a = 8.7802(2) Å, b = 7.1969(2) Å, c = 9.8857(3) Å, β = 99.066(2)°, α = γ = 90°, V = 616.88(3) Å^3, T = 100(2) K, Z = 2, Z' = 0.5, μ(MoK$_\alpha$) = 14.187, 9881 reflections measured, 1416 unique (R_{int} = 0.0415) which were used in all calculations. The final wR_2 was 0.0814 (all data) and R_1 was 0.0307 (I > 2(I)).

Compound	**2016ncs0637**
Formula	$C_{10}H_6Br_4Ru$
$D_{calc.}$/ g cm^{-3}	2.944
μ/mm^{-1}	14.187
Formula Weight	546.86
Colour	colourless
Shape	plate
Size/mm^3	0.150×0.050×0.010
T/K	100(2)
Crystal System	monoclinic
Space Group	P2/n
a/Å	8.7802(2)
b/Å	7.1969(2)
c/Å	9.8857(3)
α/°	90
β/°	99.066(2)
γ/°	90
V/Å^3	616.88(3)
Z	2
Z'	0.5
Wavelength/Å	0.71075
Radiation type	MoK_α
Θ_{min}/°	2.830
Θ_{max}/°	27.483
Measured Refl.	9881
Independent Refl.	1416
Reflections Used	1337
R_{int}	0.0415
Parameters	69
Restraints	0
Largest Peak	2.323
Deepest Hole	-0.846
GooF	1.072
wR_2 (all data)	0.0814
wR_2	0.0800
R_1 (all data)	0.0325
R_1	0.0307

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 40.9	Rint 4.15%	complete at 2θ=55° 99%
Refinement:	Shift 0.000	Max Peak 2.3	Min Peak -0.8	GooF 1.072

A colourless plate-shaped crystal with dimensions 0.150×0.050×0.010 was mounted on a MITIGEN holder in oil. Data were collected using a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T = 100(2) K.

Data were measured using profile data from ω-scans of 1.0° per frame for 7.0 s using MoK$_\alpha$ radiation (Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics (100µm focus), 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrystalClear** (Rigaku). The actually achieved resolution was Θ = 27.483°.

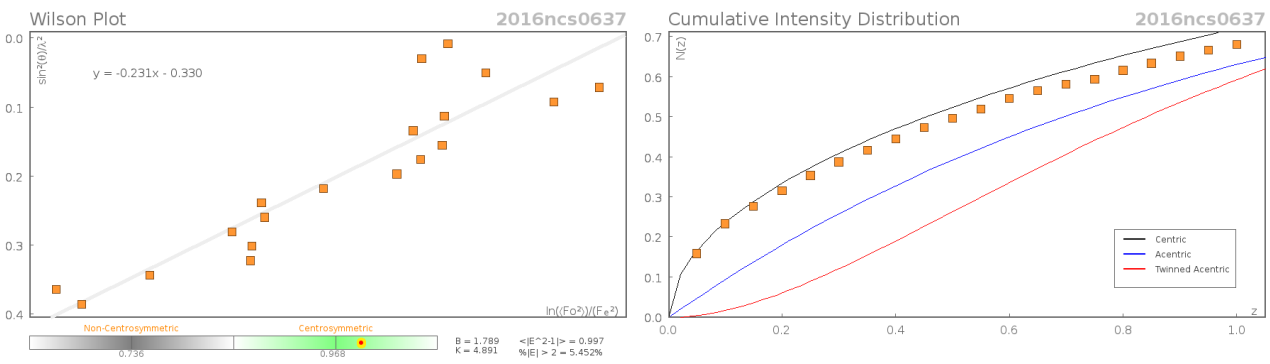
Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software and refined using **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) on 6367 reflections, 64% of the observed reflections.

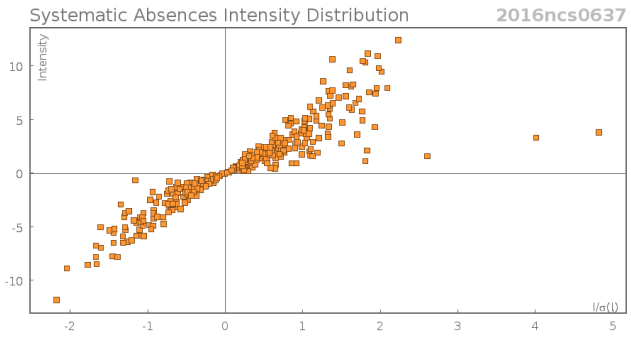
Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.38.43, 2015) software which corrects for Lorentz polarisation. The final completeness is 98.90% out to 27.483° in Θ. The absorption coefficient μ of this material is 14.187 mm^{-1} at this wavelength (λ = 0.71075 Å) and the minimum and maximum transmissions are 0.03094 and 0.05307.

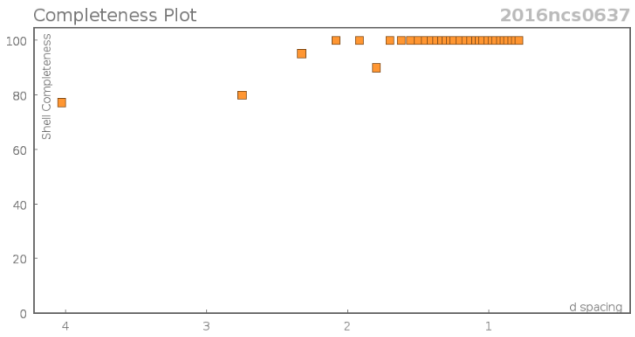
The structure was solved in the space group P2/n (# 13) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

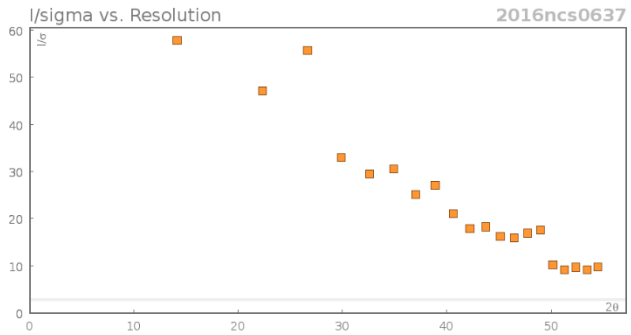
The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Data Plots: Diffraction Data

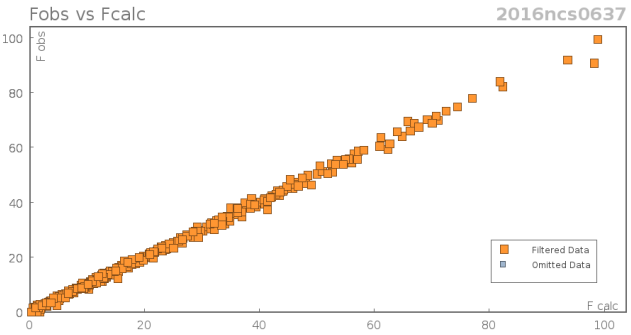


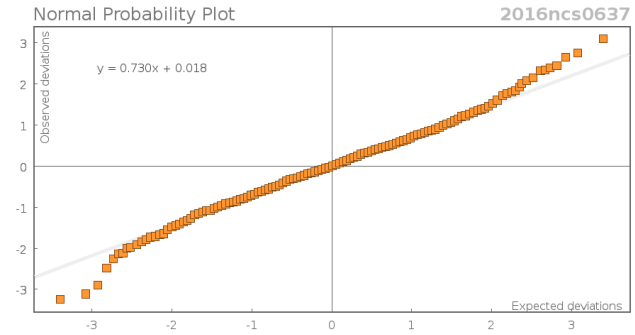






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	10392	Unique reflections	1416
Completeness	0.992	Mean I/σ	40.95
hkl_{max} collected	(11, 9, 12)	hkl_{min} collected	(-11, -9, -12)
hkl_{max} used	(11, 9, 12)	hkl_{min} used	(-11, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	9.76	d_{min} used	0.77
Friedel pairs	2184	Friedel pairs merged	1
Inconsistent equivalents	37	R_{int}	0.0415
R_{sigma}	0.0188	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(1658, 1751, 1091, 406, 61, 5)	Maximum multiplicity	15
Removed systematic absences	511	Filtered off (Shel/OMIT)	0

Table S2: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2016ncs0637**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Ru1	7500	4948.8(6)	2500	24.64(15)
Br1	8370.4(5)	1542.5(6)	5233.5(5)	31.89(15)
Br2	4676.1(5)	1474.3(6)	3026.1(5)	32.81(15)
C1	7309(5)	3626(5)	4438(4)	26.2(8)
C2	5834(5)	3598(5)	3567(4)	26.2(8)
C3	5359(6)	5473(7)	3302(5)	33.9(9)
C4	6546(6)	6646(6)	3996(5)	34.9(10)
C5	7736(6)	5518(6)	4694(5)	32.0(9)

Table S20: Anisotropic Displacement Parameters (×10⁴) **2016ncs0637**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	30.5(3)	17.6(2)	28.4(3)	0	12.78(18)	0
Br1	32.9(2)	27.9(2)	35.2(3)	6.12(16)	6.16(18)	-0.53(16)
Br2	30.0(2)	34.7(3)	35.3(3)	-2.99(17)	10.12(18)	-9.17(16)
C1	28.2(19)	24.6(19)	28(2)	2.6(15)	11.5(16)	-1.9(15)
C2	29(2)	22.6(19)	29(2)	-0.3(15)	13.1(16)	0.1(15)
C3	41(2)	33(2)	31(2)	1.8(18)	17.2(19)	7.4(19)
C4	51(3)	24(2)	34(2)	-1.0(17)	21(2)	2.2(18)
C5	43(2)	25.9(19)	30(2)	-4.4(17)	16.7(19)	-4.7(18)

Table S21: Bond Lengths in Å for **2016ncs0637**.

Atom	Atom	Length/Å
Ru1	C1[1]	2.170(4)
Ru1	C1	2.170(4)
Ru1	C2[1]	2.164(4)
Ru1	C2	2.164(4)
Ru1	C3[1]	2.185(4)
Ru1	C3	2.185(4)
Ru1	C4	2.185(4)
Ru1	C4[1]	2.185(4)
Ru1	C5[1]	2.185(4)
Ru1	C5	2.185(4)
Br1	C1	1.872(4)
Br2	C2	1.867(4)
C1	C2	1.438(6)
C1	C5	1.425(6)
C2	C3	1.424(6)
C3	C4	1.430(7)
C4	C5	1.414(7)

----

[1]3/2-X,+Y,1/2-Z

Table S22: Bond Angles in ° for **2016ncs0637**.

Atom	Atom	Atom	Angle/°
C1[1]	Ru1	C1	127.9(2)
C1	Ru1	C3[1]	125.94(17)
C1[1]	Ru1	C3[1]	64.20(17)
C1	Ru1	C3	64.19(17)
C1[1]	Ru1	C3	125.94(17)
C1[1]	Ru1	C4[1]	63.65(16)
C1	Ru1	C4	63.65(16)
C1[1]	Ru1	C4	159.17(17)
C1	Ru1	C4[1]	159.17(17)
C1[1]	Ru1	C5	161.90(18)
C1	Ru1	C5[1]	161.90(18)
C1[1]	Ru1	C5[1]	38.20(15)
C1	Ru1	C5	38.20(15)
C2	Ru1	C1	38.76(17)
C2[1]	Ru1	C1	112.68(15)
C2[1]	Ru1	C1[1]	38.76(17)
C2	Ru1	C1[1]	112.68(15)
C2[1]	Ru1	C2	126.6(2)
C2	Ru1	C3	38.23(15)
C2[1]	Ru1	C3[1]	38.23(15)
C2[1]	Ru1	C3	160.17(18)
C2	Ru1	C3[1]	160.17(18)
C2	Ru1	C4[1]	160.38(18)
C2[1]	Ru1	C4	160.38(18)
C2[1]	Ru1	C4[1]	63.92(16)
C2	Ru1	C4	63.92(16)
C2[1]	Ru1	C5[1]	64.29(16)
C2	Ru1	C5	64.29(16)
C2	Ru1	C5[1]	127.04(17)
C2[1]	Ru1	C5	127.04(17)
C3[1]	Ru1	C3	160.1(3)
C4	Ru1	C3[1]	126.35(18)
C4[1]	Ru1	C3	126.35(18)
C4	Ru1	C3	38.19(18)
C4[1]	Ru1	C3[1]	38.19(18)
C4[1]	Ru1	C4	112.0(2)
C5[1]	Ru1	C3	112.05(18)
C5	Ru1	C3	63.89(19)
C5	Ru1	C3[1]	112.05(18)
C5[1]	Ru1	C3[1]	63.88(19)
C5[1]	Ru1	C4[1]	37.77(18)
C5[1]	Ru1	C4	125.50(17)
C5	Ru1	C4[1]	125.50(17)
C5	Ru1	C4	37.77(18)
C5[1]	Ru1	C5	158.4(2)
Br1	C1	Ru1	128.3(2)
C2	C1	Ru1	70.4(2)
C2	C1	Br1	125.6(3)
C5	C1	Ru1	71.5(2)
C5	C1	Br1	126.3(3)
C5	C1	C2	107.8(4)
Br2	C2	Ru1	127.4(2)
C1	C2	Ru1	70.8(2)
C1	C2	Br2	125.5(3)
C3	C2	Ru1	71.7(2)
C3	C2	Br2	126.4(3)
C3	C2	C1	107.9(4)
C2	C3	Ru1	70.1(2)
C2	C3	C4	107.5(4)
C4	C3	Ru1	70.9(3)
C3	C4	Ru1	70.9(2)
C5	C4	Ru1	71.1(2)
C5	C4	C3	108.8(4)
C1	C5	Ru1	70.3(2)
C4	C5	Ru1	71.1(3)
C4	C5	C1	108.0(4)

----

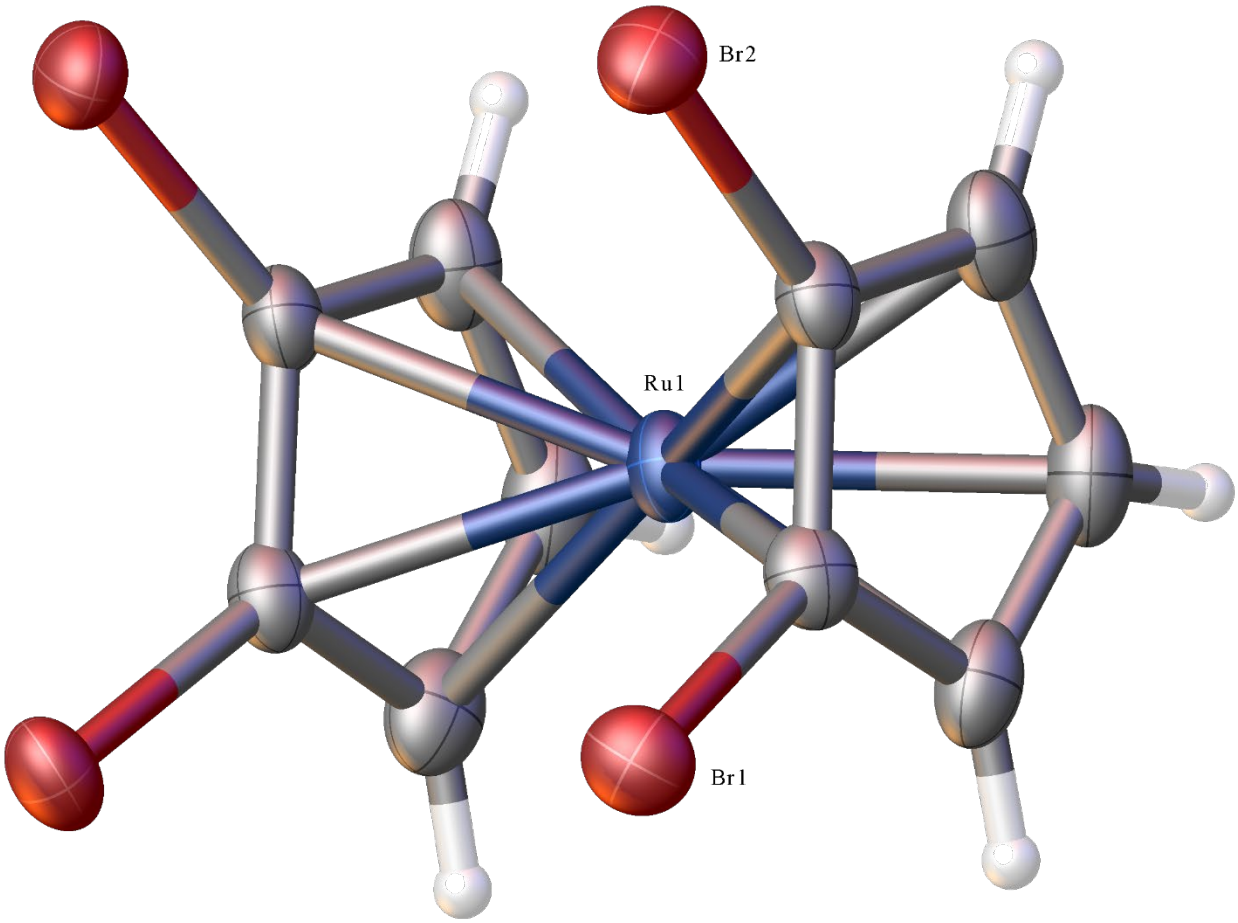
[1]3/2-X,+Y,1/2-Z

Table S23: Torsion Angles in ° for **2016ncs0637**.

Atom	Atom	Atom	Atom	Angle/°
Ru1	C1	C2	Br2	122.8(3)
Ru1	C1	C2	C3	-62.5(3)
Ru1	C1	C5	C4	61.5(3)
Ru1	C2	C3	C4	-61.3(3)
Ru1	C3	C4	C5	-61.4(3)
Ru1	C4	C5	C1	-61.0(3)
Br1	C1	C2	Ru1	-123.7(3)
Br1	C1	C2	Br2	-0.8(5)
Br1	C1	C2	C3	173.8(3)
Br1	C1	C5	Ru1	124.4(3)
Br1	C1	C5	C4	-174.1(3)
Br2	C2	C3	Ru1	-123.4(3)
Br2	C2	C3	C4	175.2(3)
C1	C2	C3	Ru1	61.9(3)
C1	C2	C3	C4	0.6(5)
C2	C1	C5	Ru1	-61.4(3)
C2	C1	C5	C4	0.1(5)
C2	C3	C4	Ru1	60.8(3)
C2	C3	C4	C5	-0.5(5)
C3	C4	C5	Ru1	61.2(3)
C3	C4	C5	C1	0.2(5)
C5	C1	C2	Ru1	62.0(3)
C5	C1	C2	Br2	-175.1(3)
C5	C1	C2	C3	-0.5(5)

Table S24: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2016ncs0637**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	X	y	z	
H3	4444	5864	2774	4
H4	6536	7938	3990	4
H5	8639	5938	5226	3



Citations

CrysAlisPro Software System, Rigaku Oxford Diffraction, Yarnton, Oxford, UK (2015).

CrystalClear, Rigaku Corporation, The Woodlands, Texas, U.S.A., (2008-2014).

Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., Olex2: A complete structure solution, refinement and analysis program, J. Appl. Cryst., (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C27**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

4BrRu.cif

Additional information for comparison: Crystal Data: 1,2-Dibromoferrocene

Table S25. Crystal data and structure refinement details.

Identification code	**2015ncs0397 / 1,2-DIBROMOFC from TRI BROMO Fe**	
Empirical formula	$C_{10}H_8Br_2Fe$	
Formula weight	343.83	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.3911(3) Å	α = 90°
	b = 10.1905(4) Å	β = 90°
	c = 10.3566(3) Å	γ = 90°
Volume	991.13(6) Å^3	
Z	4	
Density (calculated)	2.304 Mg / m^3	
Absorption coefficient	21.190 mm^{-1}	
F(000)	656	
Crystal	Blade; Orange	
Crystal size	0.210 × 0.080 × 0.030 mm^3	
θ range for data collection	6.092 – 67.258°	
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-12 \le l \le 12$	
Reflections collected	9001	
Independent reflections	1792 [R_{int} = 0.0368]	
Completeness to θ = 67.258°	99.8 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	1.00000 and 0.14883	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1792 / 0 / 120	

Goodness-of-fit on F^2	1.081
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0234, $wR2$ = 0.0636
R indices (all data)	$R1$ = 0.0241, $wR2$ = 0.0638
Absolute structure parameter	0.015(6)
Extinction coefficient	0.0008(2)
Largest diff. peak and hole	0.526 and –0.553 e Å^{-3}

Diffractometer: *Rigaku AFC11* quarter chi goniometer equipped with an enhanced sensitivity (HG) *Saturn944+* detector mounted at the window of *007 HF* copper rotating anode generator with *Varimax optics.* **Cell determination and data collection**: *CrystalClear-SM Expert 3.1 b27* (Rigaku, 2013). **Data reduction, cell refinement and absorption correction**: CrysAlisPro, Agilent Technologies,Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET)(compiled Aug 13 2014,18:06:01). S**tructure solution**: *SUPERFLIP* (Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.) S**tructure refinement**: *SHELXL-2014* (G Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.). **Graphics:** *ORTEP3 for Windows* (L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565

Special details:

Table S26. Atomic coordinates [× 10^4], equivalent isotropic displacement parameters [Å^2 × 10^3] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x* U_{eq}	*y* *S.o.f.*	*z*
Br1	5665(1) 26(1)	6618(1) 1	8168(1)
Br2	3093(1) 23(1)	8967(1) 1	9221(1)
Fe1	2168(1) 15(1)	6573(1) 1	6926(1)
C1	4169(5) 18(1)	7269(5) 1	7148(5)
C2	3151(5) 18(1)	8206(4) 1	7571(5)
C3	2253(5) 20(1)	8534(5) 1	6506(5)
C4	2729(5) 19(1)	7777(5) 1	5429(4)
C5	3914(5) 21(1)	6989(5) 1	5816(5)
C6	1988(6) 29(1)	4896(5) 1	7999(6)
C7	1012(6) 27(1)	5868(6) 1	8446(5)
C8	100(6) 28(1)	6201(5) 1	7404(6)
C9	493(6) 26(1)	5439(5) 1	6318(5)
C10	1666(6) 29(1)	4615(5) 1	6684(6)

Table S27. Bond lengths [Å] and angles [°].

Br1–C1	1.879(5)
Br2–C2	1.877(5)
Fe1–C2	2.017(5)
Fe1–C1	2.021(5)
Fe1–C8	2.040(6)
Fe1–C7	2.043(5)
Fe1–C6	2.046(5)
Fe1–C3	2.046(5)
Fe1–C4	2.047(5)
Fe1–C5	2.047(5)
Fe1–C9	2.051(5)
Fe1–C10	2.066(5)
C1–C2	1.420(7)
C1–C5	1.428(7)
C2–C3	1.428(7)
C3–C4	1.428(7)
C3–H3	0.9500
C4–C5	1.430(7)
C4–H4	0.9500
C5–H5	0.9500
C6–C10	1.425(8)
C6–C7	1.427(9)
C6–H6	0.9500
C7–C8	1.419(8)
C7–H7	0.9500
C8–C9	1.415(8)
C8–H8	0.9500
C9–C10	1.436(8)
C9–H9	0.9500
C10–H10	0.9500

C2–Fe1–C1	41.2(2)
C2–Fe1–C8	120.6(2)
C1–Fe1–C8	157.3(2)
C2–Fe1–C7	106.1(2)
C1–Fe1–C7	122.0(2)
C8–Fe1–C7	40.7(2)
C2–Fe1–C6	123.2(2)
C1–Fe1–C6	108.0(2)
C8–Fe1–C6	68.5(2)
C7–Fe1–C6	40.9(2)
C2–Fe1–C3	41.2(2)
C1–Fe1–C3	69.21(19)
C8–Fe1–C3	105.7(2)
C7–Fe1–C3	121.9(2)
C6–Fe1–C3	159.2(2)
C2–Fe1–C4	68.82(19)
C1–Fe1–C4	68.68(19)
C8–Fe1–C4	122.7(2)
C7–Fe1–C4	158.7(2)
C6–Fe1–C4	159.1(2)
C3–Fe1–C4	40.83(19)
C2–Fe1–C5	69.43(19)
C1–Fe1–C5	41.10(19)
C8–Fe1–C5	159.6(2)
C7–Fe1–C5	158.7(2)
C6–Fe1–C5	123.0(2)
C3–Fe1–C5	69.3(2)
C4–Fe1–C5	40.9(2)
C2–Fe1–C9	156.6(2)
C1–Fe1–C9	161.0(2)
C8–Fe1–C9	40.5(2)
C7–Fe1–C9	68.3(2)

C6–Fe1–C9	68.4(2)	C5–C4–Fe1	69.6(3)
C3–Fe1–C9	121.0(2)	C3–C4–H4	125.4
C4–Fe1–C9	107.6(2)	C5–C4–H4	125.4
C5–Fe1–C9	124.0(2)	Fe1–C4–H4	127.0
C2–Fe1–C10	160.4(2)	C1–C5–C4	106.8(4)
C1–Fe1–C10	124.4(2)	C1–C5–Fe1	68.5(3)
C8–Fe1–C10	68.4(2)	C4–C5–Fe1	69.5(3)
C7–Fe1–C10	68.4(2)	C1–C5–H5	126.6
C6–Fe1–C10	40.5(2)	C4–C5–H5	126.6
C3–Fe1–C10	157.8(2)	Fe1–C5–H5	126.9
C4–Fe1–C10	123.1(2)	C10–C6–C7	108.3(5)
C5–Fe1–C10	108.3(2)	C10–C6–Fe1	70.5(3)
C9–Fe1–C10	40.8(2)	C7–C6–Fe1	69.5(3)
C2–C1–C5	108.7(4)	C10–C6–H6	125.9
C2–C1–Br1	124.5(4)	C7–C6–H6	125.9
C5–C1–Br1	126.7(4)	Fe1–C6–H6	125.8
C2–C1–Fe1	69.2(3)	C8–C7–C6	107.8(5)
C5–C1–Fe1	70.4(3)	C8–C7–Fe1	69.5(3)
Br1–C1–Fe1	129.4(3)	C6–C7–Fe1	69.7(3)
C1–C2–C3	108.4(4)	C8–C7–H7	126.1
C1–C2–Br2	125.4(4)	C6–C7–H7	126.1
C3–C2–Br2	126.1(4)	Fe1–C7–H7	126.3
C1–C2–Fe1	69.6(3)	C9–C8–C7	108.5(5)
C3–C2–Fe1	70.5(3)	C9–C8–Fe1	70.2(3)
Br2–C2–Fe1	129.0(2)	C7–C8–Fe1	69.8(3)
C4–C3–C2	107.0(4)	C9–C8–H8	125.8
C4–C3–Fe1	69.6(3)	C7–C8–H8	125.8
C2–C3–Fe1	68.3(3)	Fe1–C8–H8	125.8
C4–C3–H3	126.5	C8–C9–C10	108.1(5)
C2–C3–H3	126.5	C8–C9–Fe1	69.3(3)
Fe1–C3–H3	127.2	C10–C9–Fe1	70.1(3)
C3–C4–C5	109.1(4)	C8–C9–H9	125.9
C3–C4–Fe1	69.6(3)	C10–C9–H9	125.9

Fe1–C9–H9	126.2
C6–C10–C9	107.3(5)
C6–C10–Fe1	69.0(3)
C9–C10–Fe1	69.0(3)
C6–C10–H10	126.4
C9–C10–H10	126.4
Fe1–C10–H10	127.2

Table S28. Anisotropic displacement parameters [Å^2× 10^3]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br1	20(1)	31(1)	28(1)	0(1)	−5(1)	5(1)
Br2	24(1)	25(1)	19(1)	−6(1)	1(1)	−1(1)
Fe1	15(1)	15(1)	15(1)	1(1)	0(1)	−2(1)
C1	14(2)	21(2)	20(2)	1(2)	1(2)	−2(2)
C2	19(2)	16(2)	18(2)	1(2)	1(2)	−6(2)
C3	21(3)	16(2)	23(2)	3(2)	−1(2)	−1(2)
C4	21(2)	19(2)	17(2)	2(2)	1(2)	−3(2)
C5	24(2)	21(2)	17(2)	1(2)	1(2)	−3(2)
C6	31(3)	24(3)	33(3)	13(2)	1(2)	−9(2)
C7	29(3)	29(3)	23(3)	3(2)	6(2)	−15(2)
C8	22(2)	26(3)	35(3)	1(2)	3(2)	−5(2)
C9	24(3)	24(2)	29(3)	2(2)	−1(2)	−5(2)
C10	31(3)	19(3)	37(3)	3(2)	7(2)	−4(2)

Table S29. Hydrogen coordinates [× 10^4] and isotropic displacement parameters [Å^2 × 10^3].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H3	1485	9140	6513	24	1
H4	2323	7795	4588	23	1
H5	4433	6393	5290	25	1
H6	2725	4503	8494	35	1
H7	978	6229	9292	32	1
H8	–647	6828	7430	33	1
H9	56	5469	5491	31	1
H10	2139	3997	6148	35	1

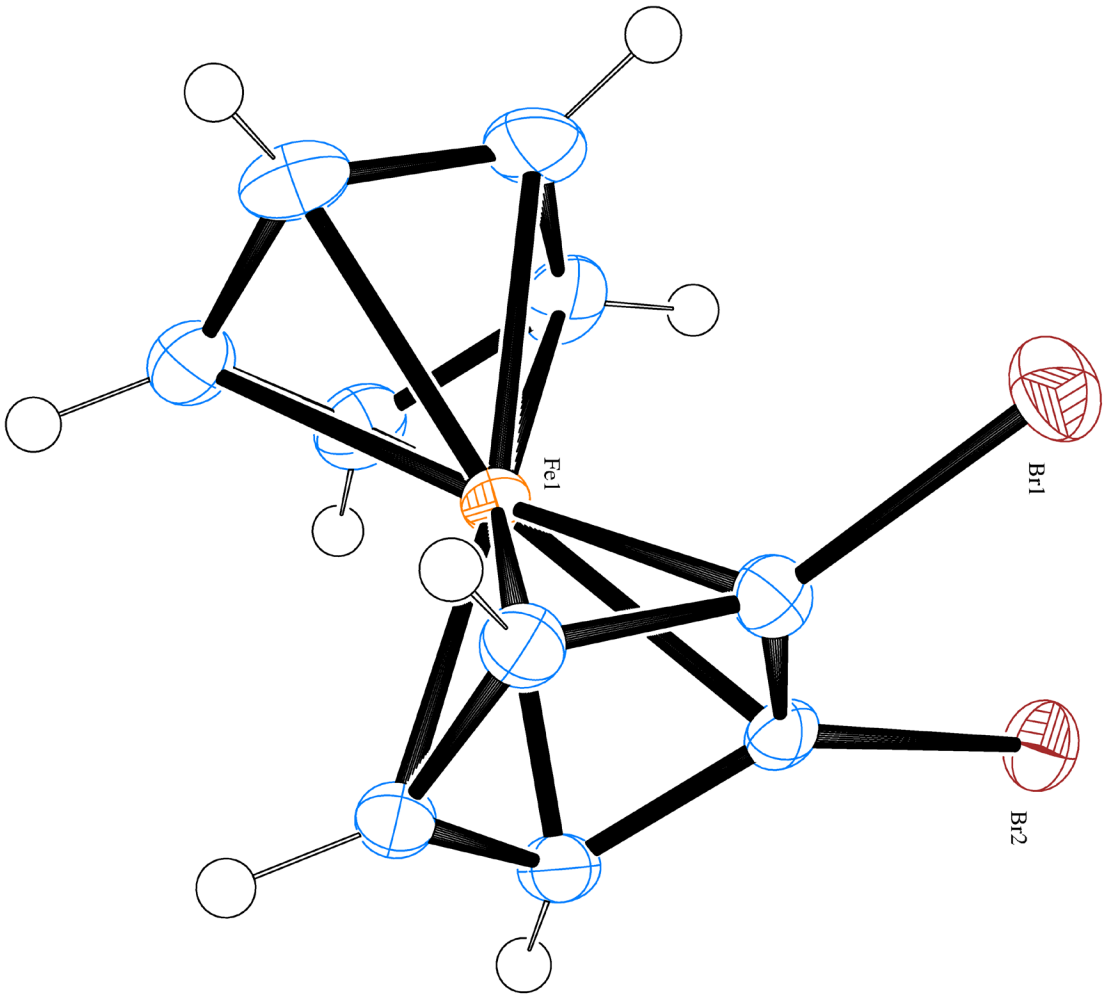
Table S30. Torsion angles [°].

C5–C1–C2–C3	–0.5(5)
Br1–C1–C2–C3	175.6(3)
Fe1–C1–C2–C3	–60.1(3)
C5–C1–C2–Br2	–176.4(3)
Br1–C1–C2–Br2	–0.2(6)
Fe1–C1–C2–Br2	124.0(4)
C5–C1–C2–Fe1	59.6(3)
Br1–C1–C2–Fe1	–124.2(4)
C1–C2–C3–C4	0.5(5)
Br2–C2–C3–C4	176.3(3)
Fe1–C2–C3–C4	–59.1(3)
C1–C2–C3–Fe1	59.5(3)
Br2–C2–C3–Fe1	–124.6(4)
C2–C3–C4–C5	–0.2(6)
Fe1–C3–C4–C5	–58.4(3)
C2–C3–C4–Fe1	58.2(3)
C2–C1–C5–C4	0.4(5)
Br1–C1–C5–C4	–175.7(4)
Fe1–C1–C5–C4	59.3(3)
C2–C1–C5–Fe1	–58.8(3)
Br1–C1–C5–Fe1	125.1(4)
C3–C4–C5–C1	–0.1(5)
Fe1–C4–C5–C1	–58.6(3)
C3–C4–C5–Fe1	58.4(3)
C10–C6–C7–C8	–0.8(6)
Fe1–C6–C7–C8	59.3(4)
C10–C6–C7–Fe1	–60.1(4)
C6–C7–C8–C9	0.4(6)
Fe1–C7–C8–C9	59.8(4)
C6–C7–C8–Fe1	–59.4(4)
C7–C8–C9–C10	0.1(6)
Fe1–C8–C9–C10	59.6(4)
C7–C8–C9–Fe1	–59.5(4)

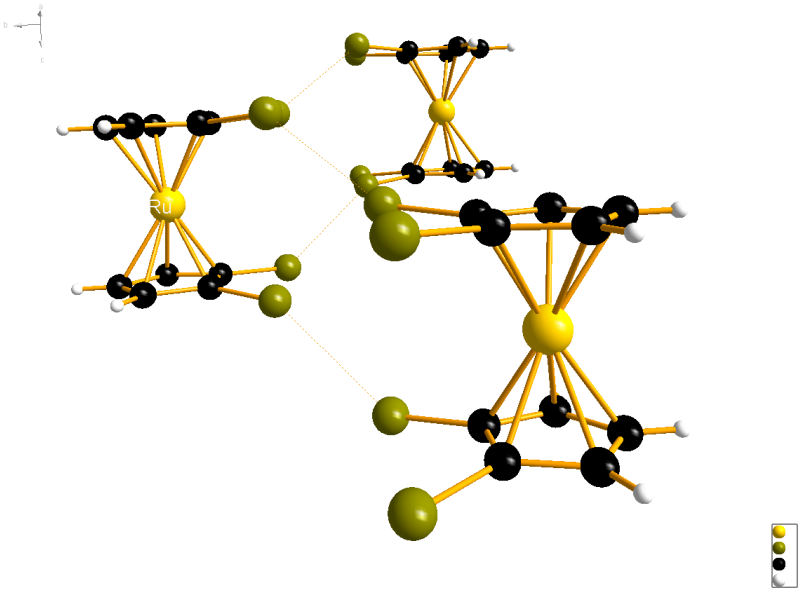
C7–C6–C10–C9	0.8(6)
Fe1–C6–C10–C9	–58.6(4)
C7–C6–C10–Fe1	59.4(4)
C8–C9–C10–C6	–0.6(6)
Fe1–C9–C10–C6	58.5(4)
C8–C9–C10–Fe1	–59.1(4)

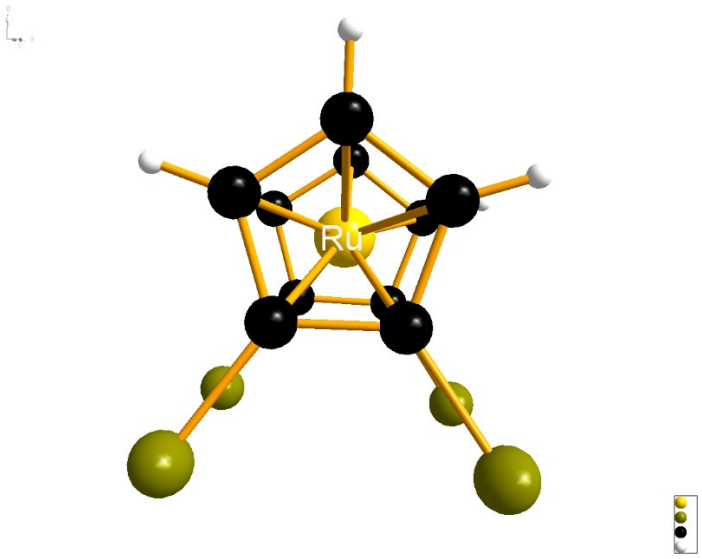
Symmetry transformations used to generate equivalent atoms:

2015ncs0397_ncs.cif

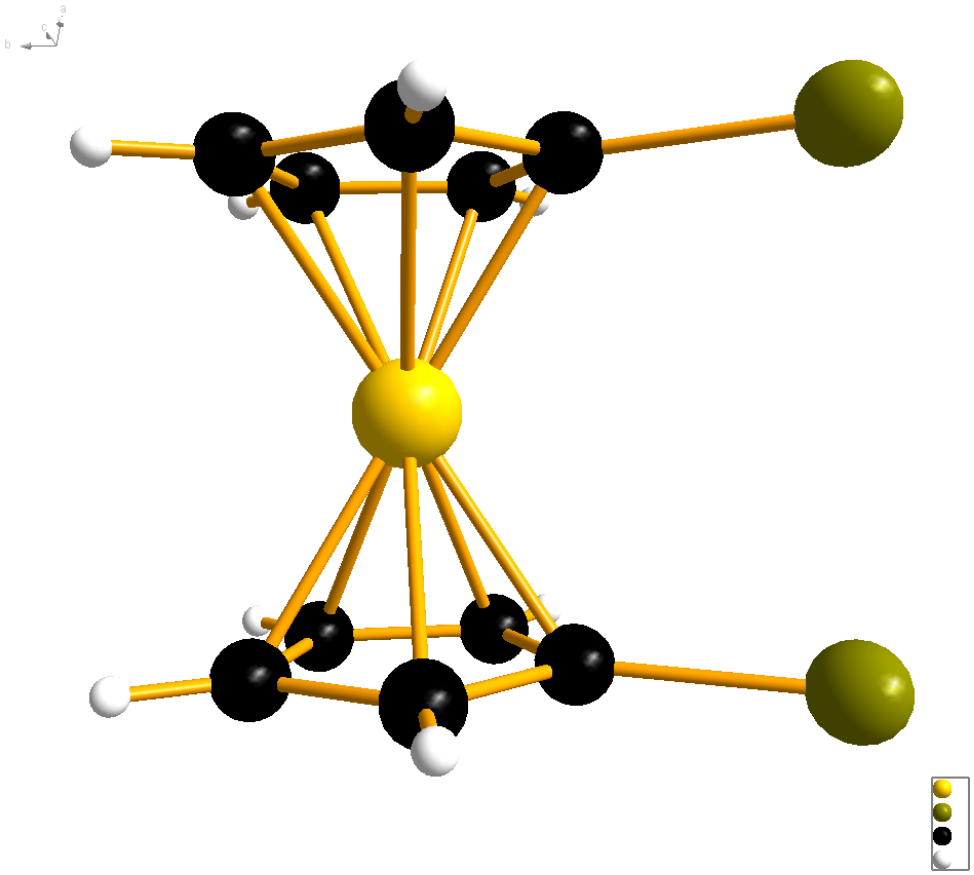

Fe1
Br1
Br2

Additional Views of Structures:

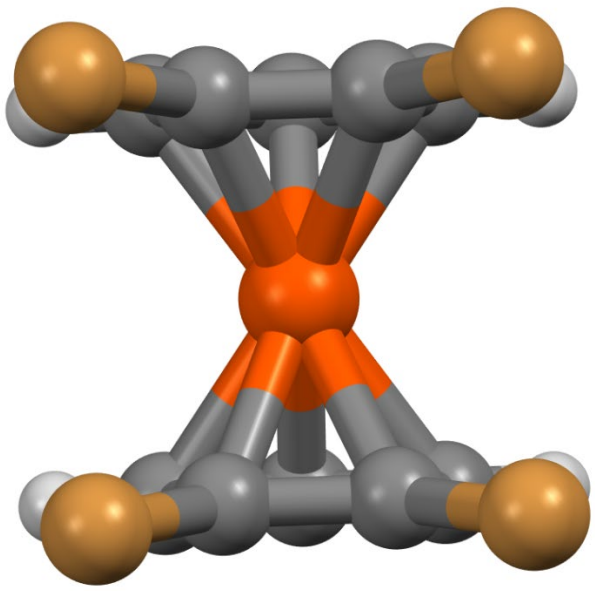




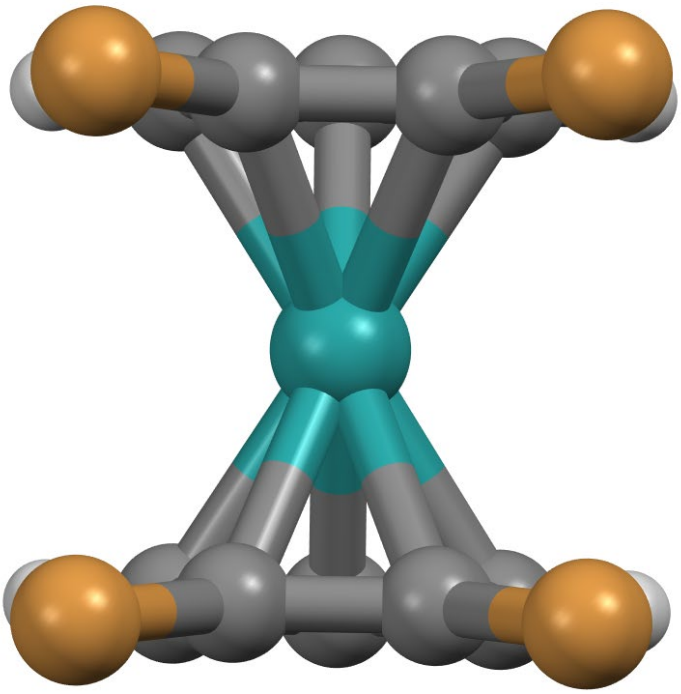
a) 1,1',2,2-Tetrabromoruthenocene: side and top view.



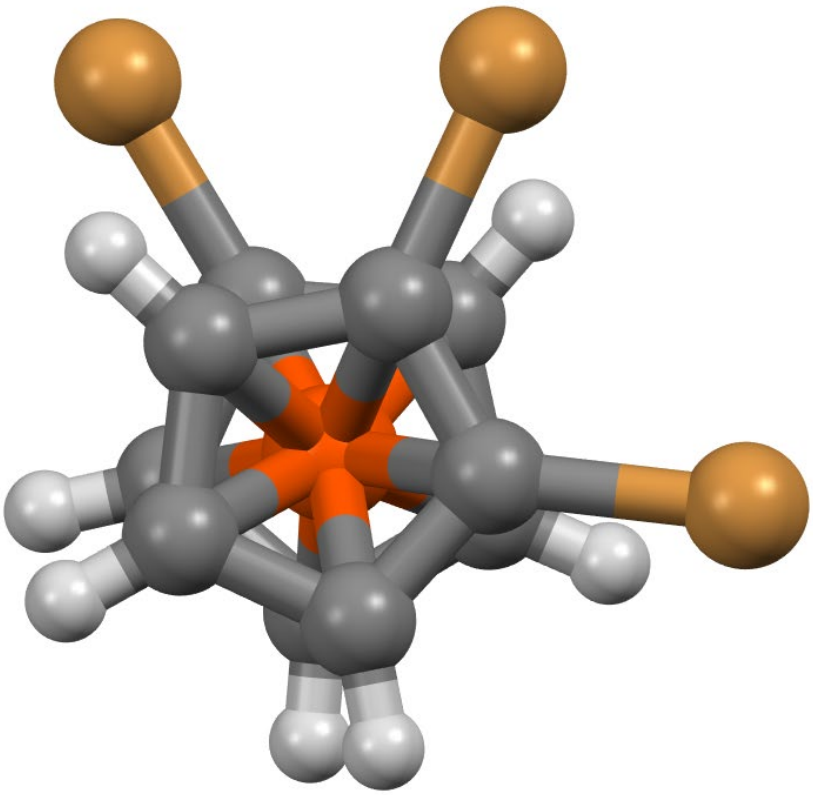
b) Side view 1,1'-Dibromoruthenocene.



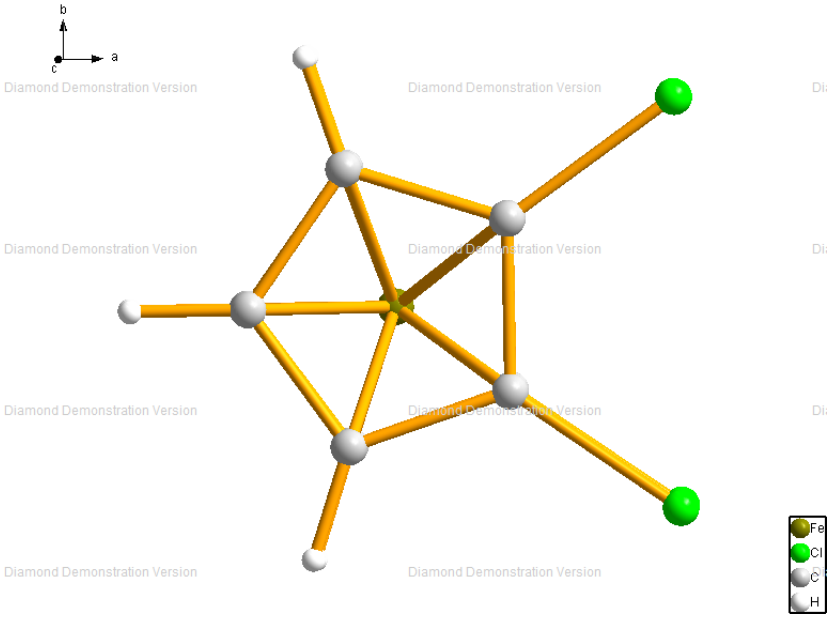
c) Front view 1,1',2,2'-Tetrabromoferrocene



d) Front View 1,1’,2,2’-Tetrabromoruthenocene



e) Top View 1,1’,2-Tribromoferrocene



f) 1,1’,2,2’-Tetrachloroferrocene top view showing eclipsed Cp-rings for comparisons.

Data from first crystal structure determination of 1,1′,2,2′-tetrabromoferrocene.

Table S31 Crystal data and structure refinement indicators.

Empirical formula	$C_{10}H_6FeBr_4$
Formula weight	501.64
Temperature/K	101.13
Crystal system	monoclinic
Space group	P2/n
a/Å	8.7101(9)
b/Å	7.1897(7)
c/Å	9.5894(10)
α/°	90
β/°	95.880(4)
γ/°	90
Volume/Å^3	597.36(11)
Z	2
ρ_{calc}g/cm^3	2.789
μ/mm^{-1}	14.601
F(000)	464.0
Crystal size/mm^3	0.19 × 0.095 × 0.039
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.666 to 52.906
Index ranges	$-10 \leq h \leq 10$, $-8 \leq k \leq 9$, $-11 \leq l \leq 11$
Reflections collected	3793
Independent reflections	1214 [R_{int} = 0.0496, R_{sigma} = 0.0474]
Data/restraints/parameters	1214/18/69
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1396
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1517
Largest diff. peak/hole / e Å^{-3}	2.05/-1.30

Table S32 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**

Br2	1701.2(8)	1546.8(8)	4789.2(8)	26.9(3)
Br1	-322.4(9)	1478.3(9)	8013.7(8)	29.8(3)
Fe1	2500	4895.0(17)	7500	21.3(4)
C5	2714(8)	3641(9)	5614(7)	25.1(12)
C3	864(9)	3617(8)	8520(8)	26.3(12)
C2	401(9)	5494(9)	8204(7)	28.2(11)
C1	1564(9)	6658(10)	8876(8)	29.1(12)
C4	2276(8)	5514(10)	5396(7)	26.6(12)

Table S33 Anisotropic Displacement Parameters ($Å^2×10^3$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br2	32.3(5)	16.2(4)	32.4(5)	-4.8(2)	3.7(3)	0.5(2)
Br1	31.1(5)	23.6(5)	35.6(5)	-2.2(2)	7.6(3)	-7.5(3)
Fe1	28.1(8)	9.0(6)	28.4(7)	0	10.1(5)	0
C5	29(3)	22(3)	26(3)	-2(2)	12(2)	1(2)
C3	34(3)	15(2)	32(2)	0.3(19)	13(2)	3.4(19)
C2	37(3)	16(2)	33(2)	0.3(17)	14(2)	4.5(18)
C1	39(3)	16(2)	34(2)	-0.8(19)	14(2)	5.4(19)
C4	31(3)	23(3)	27(3)	-2(2)	12(2)	1(2)

Table S34: Selected Bond Lengths.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br2	C5	1.878(7)	Fe1	$C4^1$	2.056(7)
Br1	C3	1.888(7)	Fe1	C4	2.056(7)
Fe1	C5	2.047(7)	C5	$C3^1$	1.419(11)
Fe1	$C5^1$	2.047(7)	C5	C4	1.410(9)
Fe1	$C3^1$	2.029(7)	C3	$C5^1$	1.419(11)
Fe1	C3	2.029(7)	C3	C2	1.431(9)
Fe1	$C2^1$	2.058(7)	C2	C1	1.417(11)
Fe1	C2	2.058(7)	C1	$C4^1$	1.428(10)
Fe1	$C1^1$	2.057(7)	C4	$C1^1$	1.428(10)
Fe1	C1	2.057(7)			

[1]1/2-X,+Y,3/2-Z

Table S35: Selected Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5[1]	Fe1	C5	127.7(4)	C1	Fe1	C2[1]	120.3(3)
C5	Fe1	C2	123.1(3)	C1[1]	Fe1	C2	120.3(3)
C5	Fe1	C2[1]	68.8(3)	C1[1]	Fe1	C1	103.9(4)
C5[1]	Fe1	C2[1]	123.1(3)	C4	Fe1	C2	106.2(3)
C5[1]	Fe1	C2	68.8(3)	C4	Fe1	C2[1]	68.3(3)
C5	Fe1	C1	156.4(3)	C4[1]	Fe1	C2[1]	106.2(3)
C5	Fe1	C1[1]	68.1(3)	C4[1]	Fe1	C2	68.3(3)
C5[1]	Fe1	C1	68.1(3)	C4[1]	Fe1	C1[1]	119.5(3)
C5[1]	Fe1	C1[1]	156.4(3)	C4	Fe1	C1[1]	40.6(3)
C5	Fe1	C4[1]	162.7(3)	C4	Fe1	C1	119.5(3)
C5	Fe1	C4	40.2(3)	C4[1]	Fe1	C1	40.6(3)
C5[1]	Fe1	C4[1]	40.2(3)	C4	Fe1	C4[1]	155.0(4)
C5[1]	Fe1	C4	162.7(3)	Br2	C5	Fe1	130.1(4)
C3	Fe1	C5[1]	40.7(3)	C3[1]	C5	Br2	125.6(5)
C3[1]	Fe1	C5[1]	111.0(3)	C3[1]	C5	Fe1	69.0(4)
C3	Fe1	C5	111.0(3)	C4	C5	Br2	126.5(6)
C3[1]	Fe1	C5	40.7(3)	C4	C5	Fe1	70.2(4)
C3	Fe1	C3[1]	126.2(4)	C4	C5	C3[1]	107.7(6)
C3	Fe1	C2	41.0(3)	Br1	C3	Fe1	129.6(4)
C3[1]	Fe1	C2[1]	41.0(3)	C5[1]	C3	Br1	125.6(5)
C3	Fe1	C2[1]	160.8(3)	C5[1]	C3	Fe1	70.3(4)
C3[1]	Fe1	C2	160.8(3)	C5[1]	C3	C2	108.8(6)
C3	Fe1	C1[1]	158.8(3)	C2	C3	Br1	125.3(6)
C3[1]	Fe1	C1[1]	68.0(3)	C2	C3	Fe1	70.6(4)
C3	Fe1	C1	68.0(3)	C3	C2	Fe1	68.4(4)
C3[1]	Fe1	C1	158.8(3)	C1	C2	Fe1	69.8(4)
C3[1]	Fe1	C4[1]	124.8(3)	C1	C2	C3	106.7(7)
C3	Fe1	C4[1]	68.0(3)	C2	C1	Fe1	69.9(4)
C3	Fe1	C4	124.8(3)	C2	C1	C4[1]	108.6(6)
C3[1]	Fe1	C4	68.0(3)	C4[1]	C1	Fe1	69.6(4)
C2	Fe1	C2[1]	155.9(4)	C5	C4	Fe1	69.5(4)
C1	Fe1	C2	40.3(3)	C5	C4	C1[1]	108.1(7)
C1[1]	Fe1	C2[1]	40.3(3)	C1[1]	C4	Fe1	69.7(4)

[1]1/2-X,+Y,3/2-Z

Table S36: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3).

Atom	*x*	*y*	*z*	U(eq)
H2	-557	5903	7621	34
H1	1578	8048	8835	35
H4	1316	5964	4836	32

Experimental

A single crystals of $C_{10}H_6FeBr_4$ was selected and mounted via fombilin oil on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination

Crystal Data for $C_{10}H_6FeBr_4$ (M =501.64 g/mol): monoclinic, space group P2/n (no. 13), a = 8.7101(9) Å, b = 7.1897(7) Å, c = 9.5894(10) Å, β = 95.880(4)°, V = 597.36(11) Å^3, Z = 2, T = 101.13 K, μ(MoKα) = 14.601 mm^{-1}, *Dcalc* = 2.789 g/cm^3, 3793 reflections measured (5.666° ≤ 2Θ ≤ 52.906°), 1214 unique (R_{int} = 0.0496, R_{sigma} = 0.0474) which were used in all calculations. The final R_1 was 0.0524 (I > 2σ(I)) and wR_2 was 0.1517 (all data).

Refinement model description

Number of restraints - 18, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2. Uiso/Uaniso restraints and constraints
All non-hydrogen atoms have similar U: within 1.7A with sigma of 0.002 and
sigma for terminal atoms of 0.004
3.a Ternary CH refined with riding coordinates:
 C2(H2), C1(H1), C4(H4)
```

This report has been created with Olex2, compiled on 2015.01.26 svn.r3150 for OlexSys.


new.cif


new.fcf