

Supporting Information

Post-Assembly Covalent Di- and Tetra-Capping of a Dinuclear $[\text{Fe}_2\text{L}_3]^{4+}$ Triple Helicate and two $[\text{Fe}_4\text{L}_6]^{8+}$ Tetrahedra using Sequential Reductive Aminations

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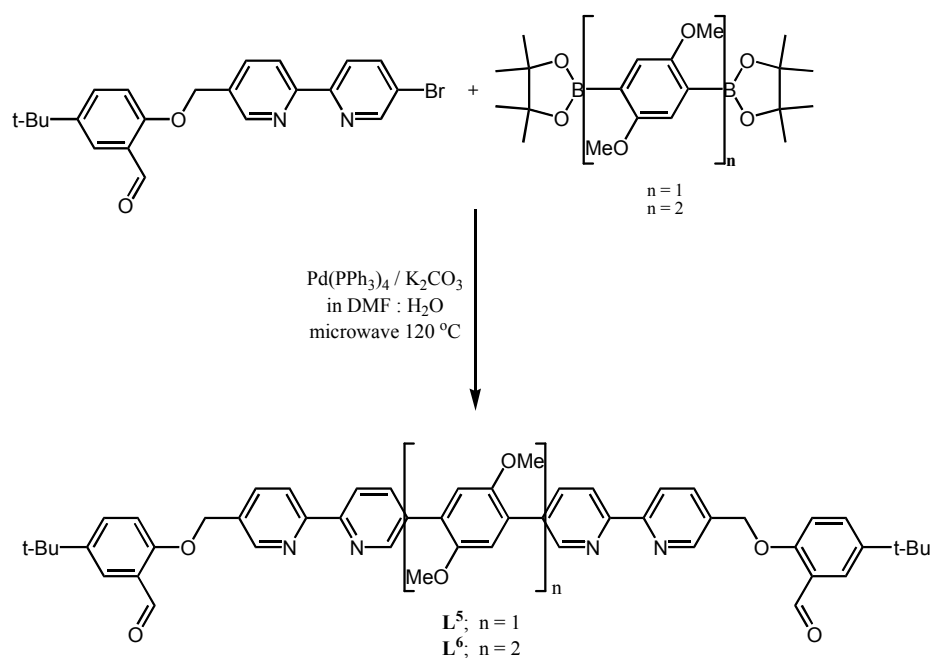
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<i>1. Ligand Synthesis</i>	<i>S2</i>
<i>2. NMR and HR-ESI-MS Spectra of Key Precursors and Capped Cages</i>	<i>S3</i>
<i>3. X-ray details for $[\text{Fe}_2\text{L}] \cdot 4\text{PF}_6 \cdot 30\text{DMSO}$</i>	<i>S9</i>
<i>4. References</i>	<i>S10</i>

1. Organic Synthesis

L⁵ and **L**⁶, were prepared by Suzuki coupling reactions of 2-(5'-bromo-[2,2']bipyridinyl-5-ylmethoxy)-5-*tert*-butyl-benzaldehyde to *bis*-boronic esters, 1,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene and 4,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-1,1'-(2,2',5,5'-tetramethoxy)biphenyl (Scheme S1).²



Scheme S1. Synthesis of **L**⁵ and **L**⁶ via Suzuki coupling.

2. Spectra of Key Precursors and the Capped Cages

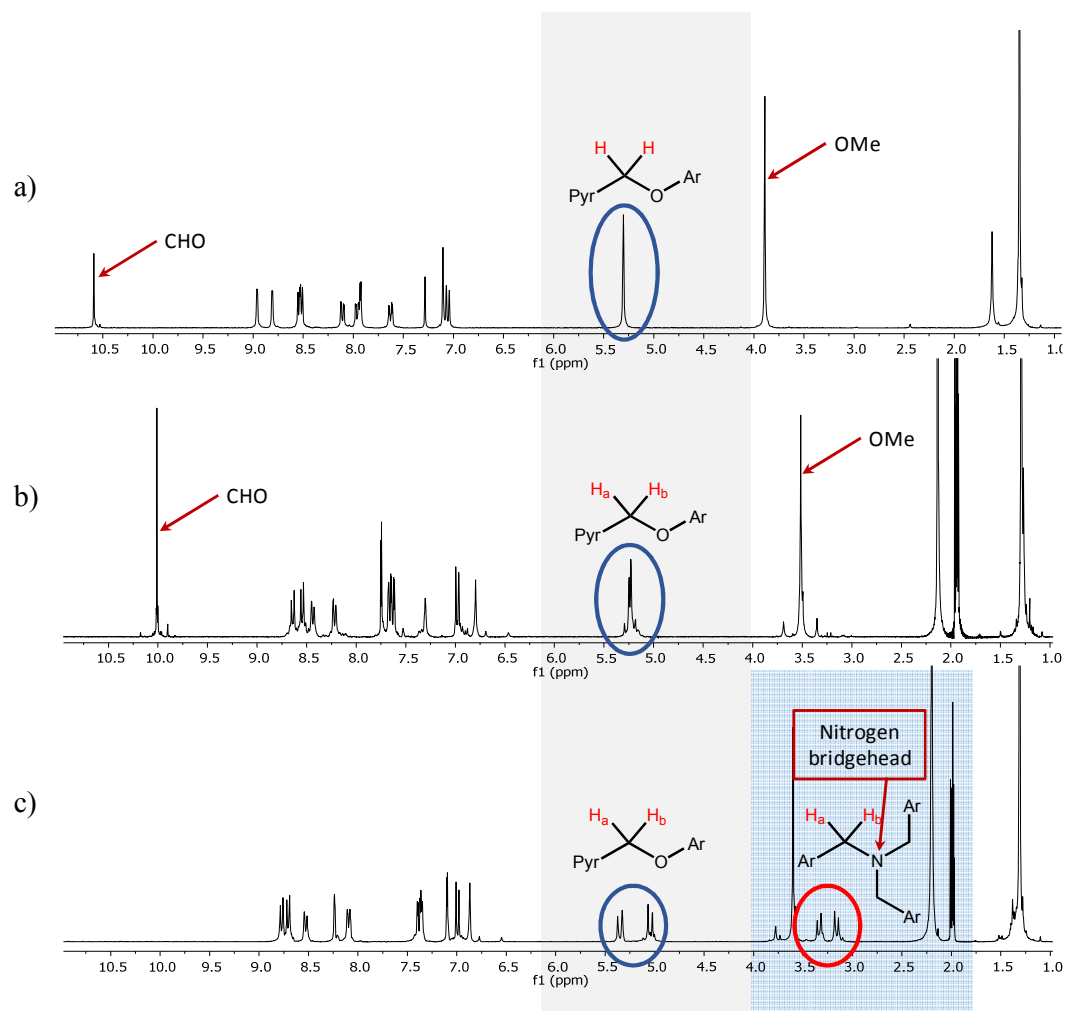


Figure S1. ^1H NMR spectra of a) L^5 in CDCl_3 , b) $[\text{Fe}_2(\text{L}^5)_3](\text{PF}_6)_4$ in CD_3CN , and c) $[\text{Fe}_2(\text{L}^7)](\text{PF}_6)_4$ in CD_3CN

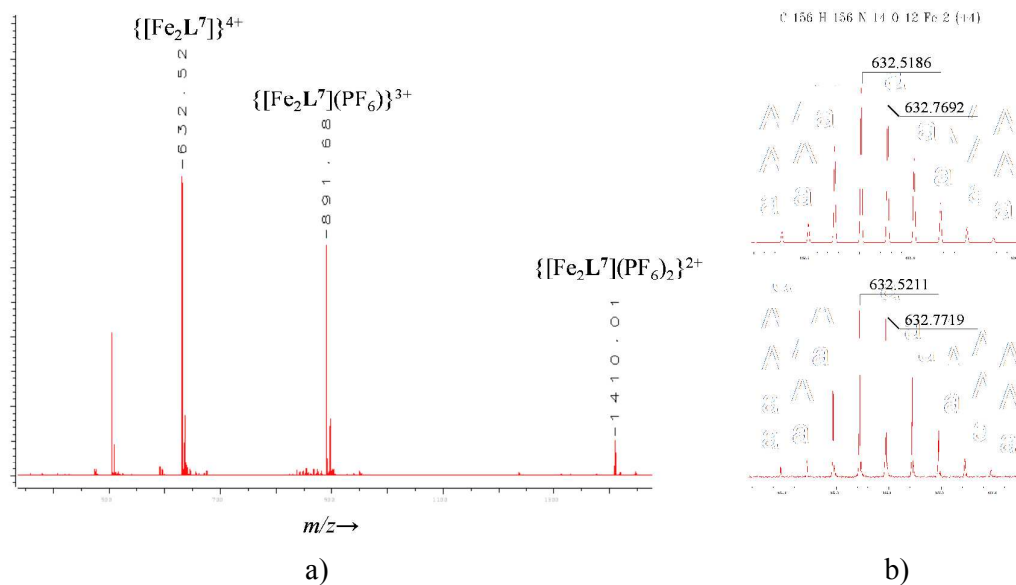


Figure S2. a) HR-ESI-MS of $[\text{Fe}_2(\text{L}^7)](\text{PF}_6)_4$, with b) the theoretical (top) and observed (bottom) isotopic distribution for its $+4$ ion

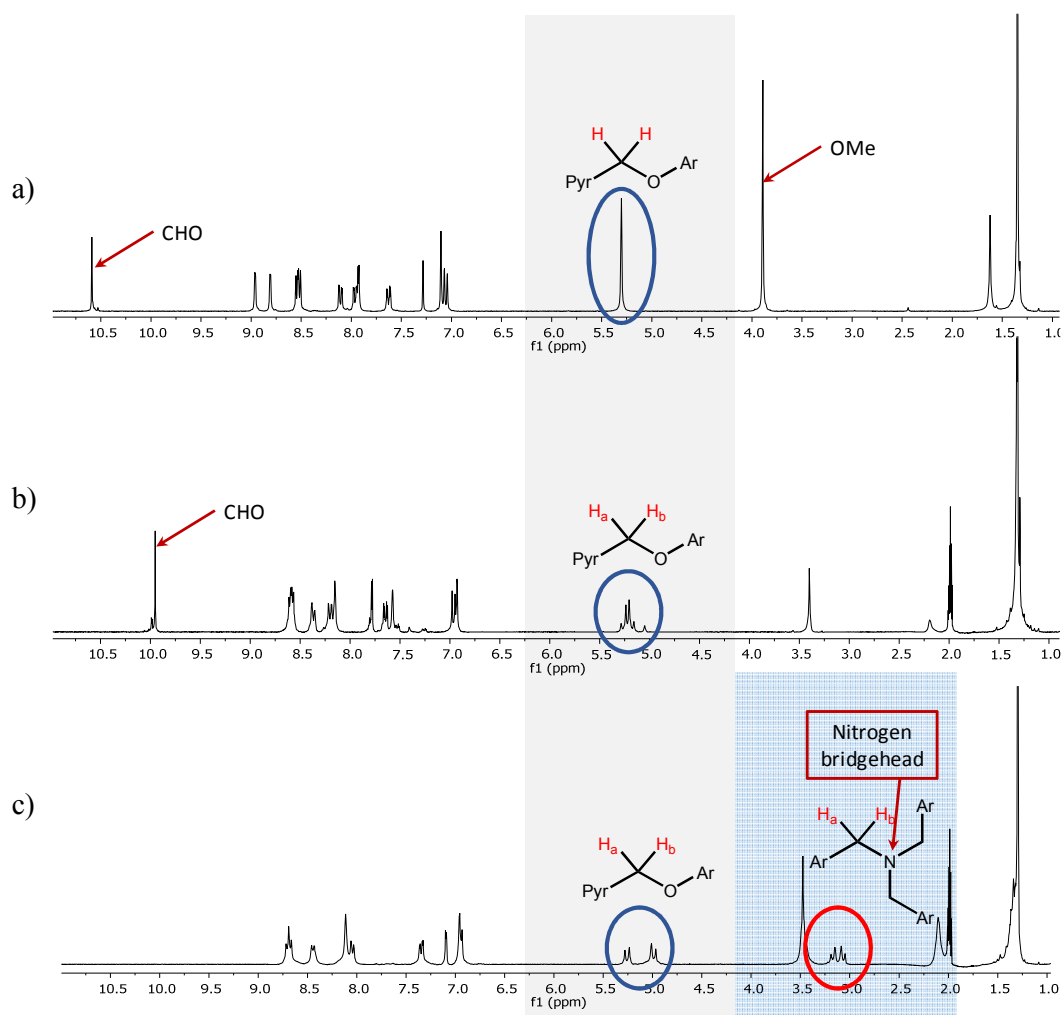


Figure S3. ^1H NMR spectra of a) L^5 , b) $[\text{Fe}_4(\text{L}^5)_6](\text{PF}_6)_8$, and c) $[\text{Fe}_4(\text{L}^8)](\text{PF}_6)_8$ in CD_3CN

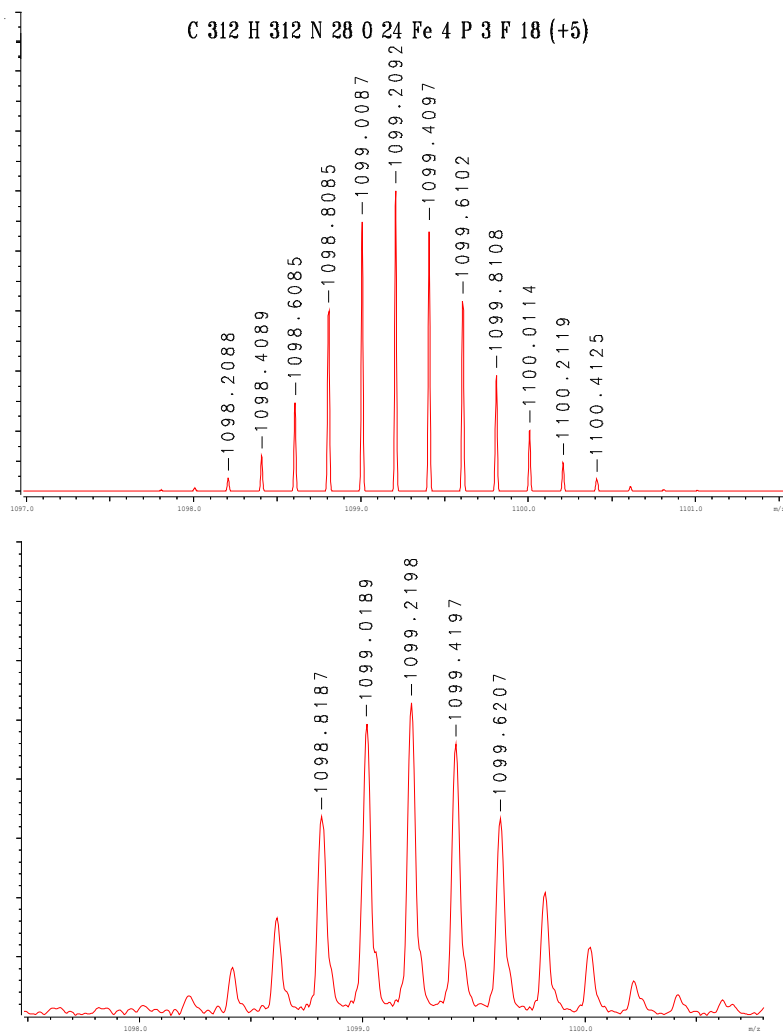


Figure S4. Theoretical (top) and observed HR-ESI-MS (bottom) isotopic distribution of the +5 ion arising from $[Fe_4(L^8)](PF_6)_8$

$[\text{Fe}_4(\text{L}^9)](\text{PF}_6)_8$:

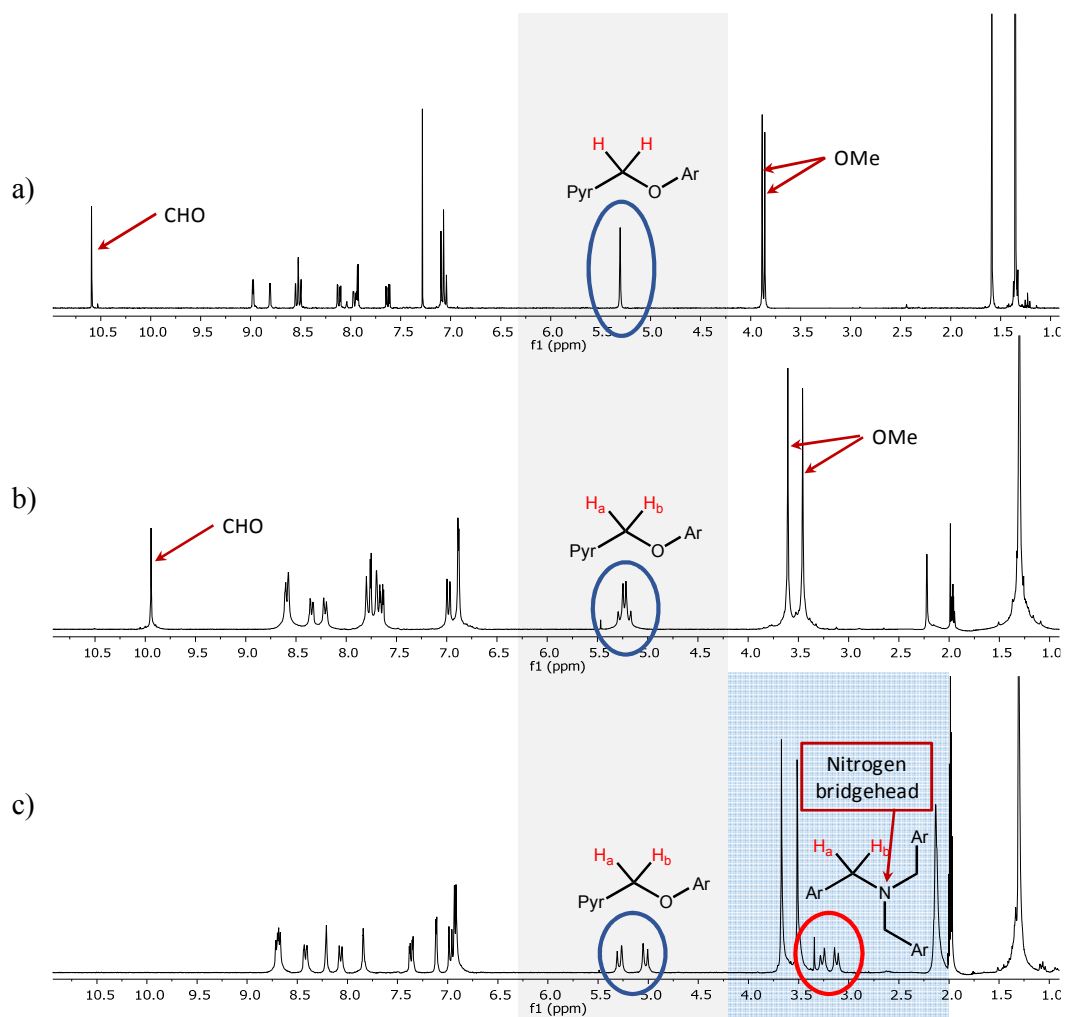


Figure S5. ^1H NMR spectra of a) L^6 , b) $[\text{Fe}_4(\text{L}^6)_6](\text{PF}_6)_8$, and c) $[\text{Fe}_4(\text{L}^9)](\text{PF}_6)_8$ in CD_3CN

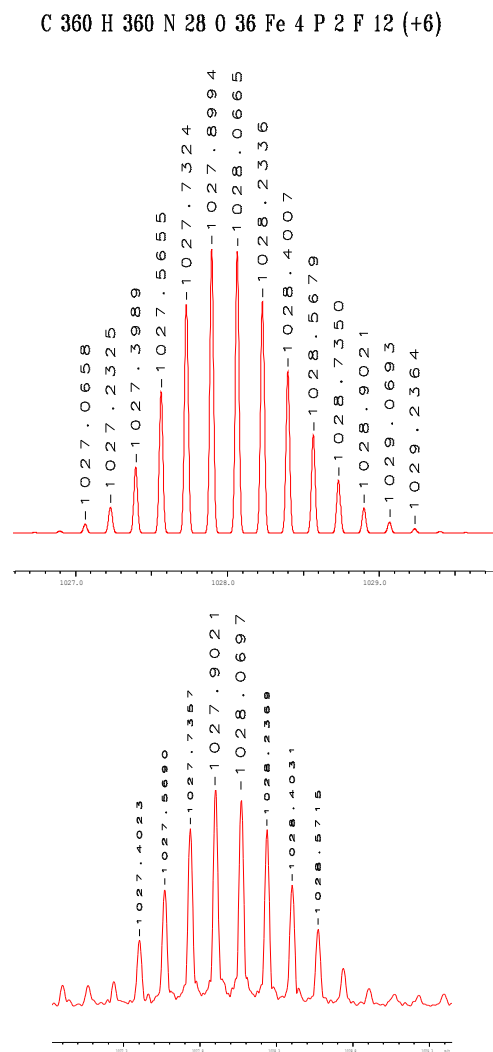


Figure S6. Theoretical (top) and observed (bottom) isotopic HR-ESI-MS distribution for the +5 ion derived from $[\text{Fe}_4(\text{L}^9)](\text{PF}_6)_8$

3. X-ray details for [Fe₂L]·4PF₆·30DMSO

Data were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-K α radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans to approximately 56° 2 θ at 150(2) K. Data integration and reduction were undertaken with SAINT and XPREP.¹ Subsequent computations were carried out using the WinGX-32 graphical user interface.² The structure was solved by direct methods using SIR97.³ Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.⁴ Data were refined and extended with SHELXL-97.⁵ All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included idealized over two positions. The *t*-butyl group is disordered and is modelled over three equal occupancy positions each with identical thermal parameters and a number of bond length restraints. One of the anions is modelled over two equal occupancy positions also with identical thermal parameters. The crystal employed in this study was small and even with the use of a high-powered laboratory source and long exposure times, very little reflection data was observed at greater than 40 ° 2 θ . In part this is due to a large void volume in the cell which contains disordered DMSO solvent molecules. This solvent could not be successfully modelled and the SQUEEZE⁶ function of PLATON⁷ was employed to account for this region of smeared electron density, which resulted in far more satisfactory residuals. CCDC 1020976.

Formula C₂₁₆H₃₃₆F₂₄Fe₂N₁₄O₄₂P₄S₃₀, M 5454.37, trigonal, space group R $\bar{3}c$ (#167), *a* 17.7579(17), *b* 17.7579(17), *c* 157.590(16) Å, γ 120.00°, V 43037(7) Å³, *D_c* 1.263 g cm⁻³, Z 6, crystal size 0.15 × 0.15 × 0.01 mm, colour orange, habit plate, temperature 150(2) K, λ (MoK α) 0.71073 Å, μ (MoK α) 0.420 mm⁻¹, T(SADABS)_{min,max} 0.2612, 0.4248, 2 θ _{max} 39.22, hkl range -16 16, -16 16, -148 148, *N* 131392, *N*_{ind} 4036(*R*_{merge} 0.0789), *N*_{obs} 2997(*I* > 2 σ (*I*)), *N*_{var} 325, residuals* *R*1(*F*) 0.1276, *wR*2(*F*2) 0.3567, GoF(all) 1.036, $\Delta\rho$ _{min,max} -0.514, 0.552 e⁻ Å⁻³.

* $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for $F_o > 2s(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (wF_c^2)^2)^{1/2}$ all reflections $w = 1 / [\sigma^2(F_o^2) + (0.3000P)^2 + 0.0500P]$ where $P = (F_o^2 + 2F_c^2) / 3$

4. References

- (1) Bruker-Nonius (2003). APEX v2.1, SAINT v.7 and XPREP v.6.14. Bruker AXS Inc. Madison, Wisconsin, USA.
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- (3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocavazzo, C.; Guagliardi, A.; Moliterni, A. G. C.; Polidori, G.; Spagna, S. *J. Appl. Cryst.* **1999**, 32, 115-119.
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