

Supporting Information

Effects of Spiro-Cyclohexane Substitution of Nitroxyl Biradicals on Dynamic Nuclear Polarization

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X-ray crystallography

XRD data were obtained at room temperature on a Bruker Kappa Apex II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Absorption corrections were applied empirically using *SADABS* programs [1]. The structures were solved by direct methods using the *SHELX-97* [2] programs set and refined by full-matrix least-squares method against all F^2 in anisotropic (beside the atoms H) approximation using the *SHELXL2014/7* programs set [3]. The H atoms positions were calculated with the riding model. The asymmetric unit contains also molecule of chloroform. The obtained crystal structure geometry and short contacts between non-bonded atoms were analyzed using the *PLATON* program [4].

Crystal solvate of diradical **4** is triclinic, space group P-1, a 12.4262(5), b 13.3902(5), c 13.7759(6) Å, α 67.121(2), β 67.676(2), γ 77.066(2)°, V 1945.7(1) Å³, Z 2, C₄₁H₅₁C₁₃N₆O₂Fe, D_c 1.333 g/cm³, μ 0.638 mm⁻¹, $F(000)$ 864, crystal size 0.20 \times 0.06 \times 0.05 mm³, independent reflections 8868, R 0.0973, R_2 0.2002 for, S 1.028 for all reflections (R 0.0657, wR_2 0.1767 for 6296 $I > 2\sigma$), largest difference peak and hole 1.769 and -1.412 e.Å⁻³.

CCDC 2168987 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk

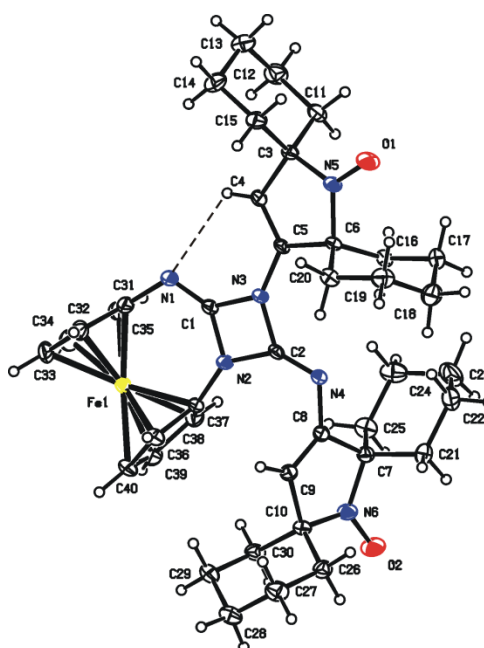


Figure S1. Molecular structure of diradical **4** with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Intermolecular short contact Cl3...O2 equaling to 3.067(3) Å is observed in solvate of **4** (sum of VDW radii [5] is 3.34 Å) (Figure S2). Solvates are bound through H-bond C1S-H...N1 (Table 3) between chloroform and 2,4-diimino-1,3-diazetidino moiety into chains directed along the (*b*-*c*). The chains, in turn, are formally bound *via* C40-H...O1 h-bond in (*b*, *c*) plain and then *via* C32-H...O1 and C38-H...O2 h-bonds along axis *a* into 3D-structure.

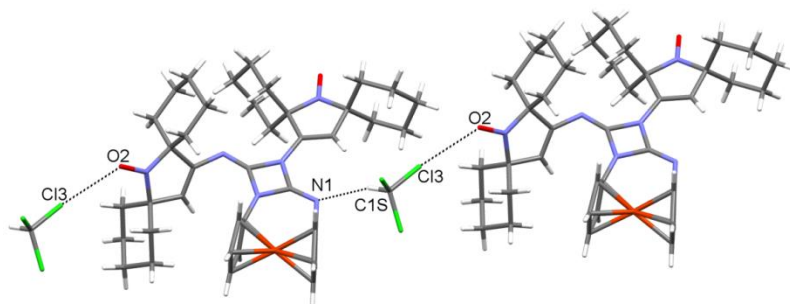


Figure S2. Fragment of molecular chain directed along (*b*-*c*).

Table S1. Intermolecular hydrogen bonds in crystals of diradical **4** solvate.

	H...O, Å	C...O, Å	C-H...O, °
C1S-H...N1	2.59	3.536(6)	161
C32-H...O1	2.59	3.485(6)	163
C40-H...O1	2.51	3.274(5)	140
C38-H...O2	2.61	3.403(5)	144

References

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