Electronic supplementary information
(ESI)
for the paper

Grid–double-helicate interconversion

Complex $[Cu_2\mathbf{1}_2](CF_3SO_3)_2$

Synthesis. The solution of complex $[Cu_2\mathbf{1}_2](CF_3SO_3)_2$ was obtained by mixing a suspension made of ligand **1** (2.11 mg, 0.005 mmol) and 0.5 mL of CD_3NO_2 with 1 equivalent of $Cu(CD_3CN)_4CF_3SO_3$ contained in 45 µL of CD_3CN solution. The solution was red.

The solution of $Cu(CD_3CN)_4CF_3SO_3$ was prepared by reaction of $Cu(CF_3SO_3)_2$ (100 mg, 0.277 mmol) with an excess (3 equivalents) of Cu powder in CD_3CN (2 mL) at 40-45°C overnight, under stirring in a screw-cap vial (the final solution was colorless). See also: J. Irangu, M. J. Ferguson and R. B. Jordan, *Inorg. Chem*., 2005, **44**, 1619-1625. After cooling, the suspension was filtered and the filtrate was collected in a 5 mL volumetric flask. The unreacted Cu and the filter were washed 5 times with 0.5 mL of CD_3CN that was also collected in the volumetric flask. Then, the solution from the flask was brought to the final volume of 5 mL with CD_3CN. Its concentration was determined by gravimetric analysis (precipitation of Cu^I as CuSCN); one equivalent of $Cu(MeCN)_4CF_3SO_3$ that corresponds to 2.11 mg ligand **1** is contained in 45 µL solution.

^{1}H NMR (400 MHz, CD_3NO_2/CD_3CN 10/0.9 v/v; reference C***H***D_2NO_2 peak, δ_{ref} = 4.34 ppm): 8.35 (s, 4H, H_E), 8.31-8.25 (m, 4H, H_H), 7.97-7.87 (m, 8H, H_A+H_C), 7.87-7.80 (m, 4H, H_D), 7.63-7.53 (m, 6H, H_I+H_J), 7.08 (s, 2H, H_G), 7.07-7.02 (m, 4H, H_B), 3.75 (s, 12H, H_F) ppm.

^{13}C NMR (100 MHz, CD_3NO_2/CD_3CN 10/0.9; reference ***C***D_3NO_2 peak, δ_{ref} = 62.9 ppm): 164.1, 162.9, 152.4, 150.6, 140.2, 140.0, 138.8, 132.4, 129.9, 129.5, 127.4, 126.6, 93.7, 33.2 ppm.

HR-ESI-MS, m/z: $[Cu_2\mathbf{1}_2CF_3SO_3]^+$ = $C_{49}H_{44}Cu_2F_3N_{16}O_3S^+$, found 1121.208 (100%), calcd. 1121.203 (the sample for ESI-MS was prepared using CH_3NO_2 as a solvent).

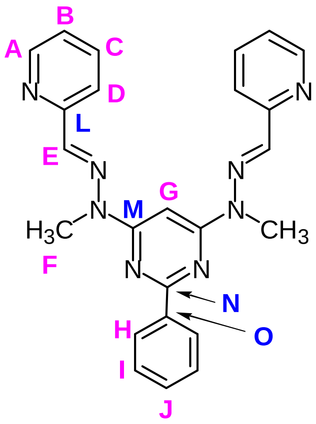

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Figure S1. ROESY spectrum of complex $[Cu_2\mathbf{1}_2](CF_3SO_3)_2$ (400 MHz, solvent CD_3NO_2/CD_3CN 10/0.9 v/v; ^1H-^1H interactions corresponding to key cross peaks are shown on the structural formula of the complex).

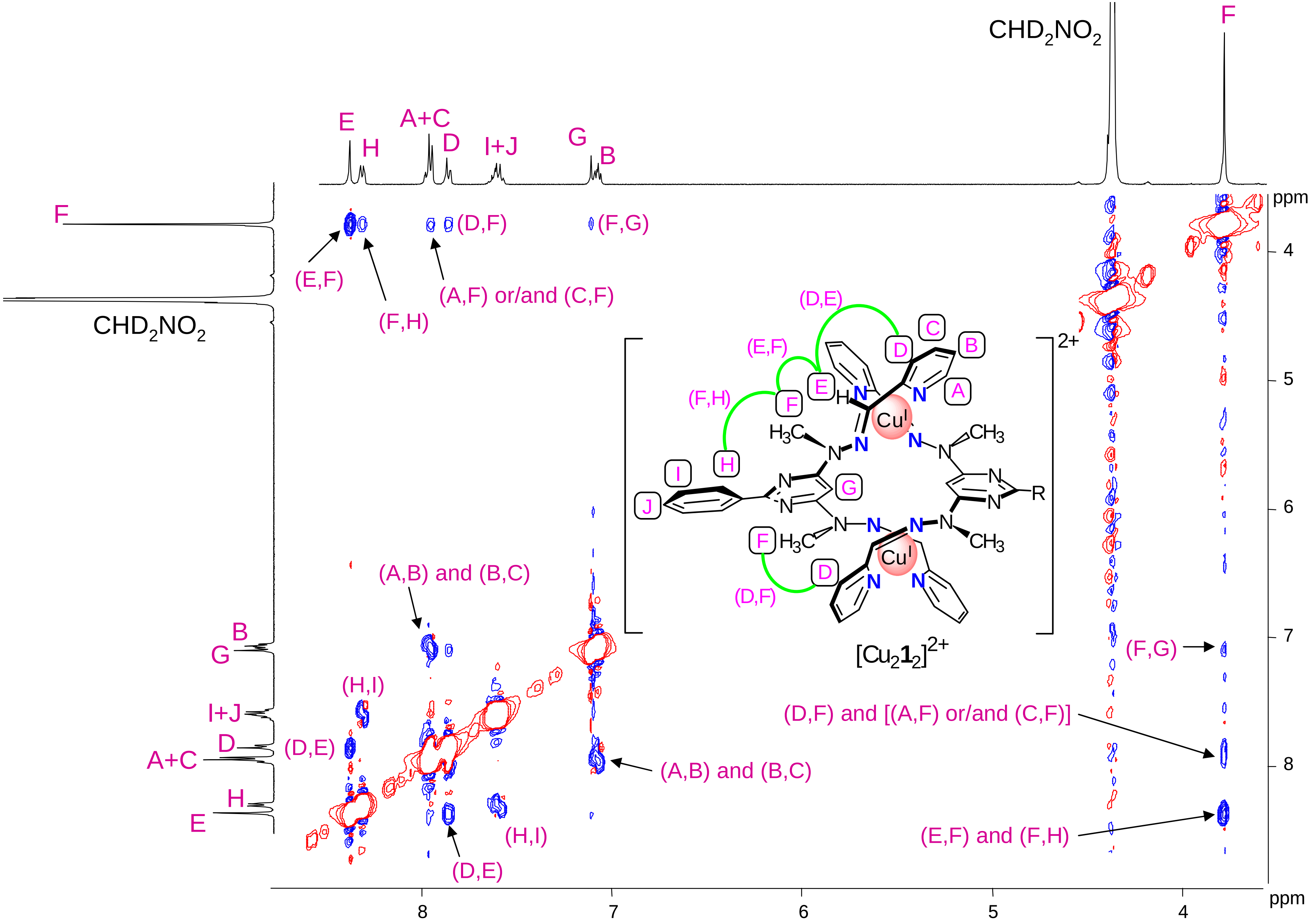
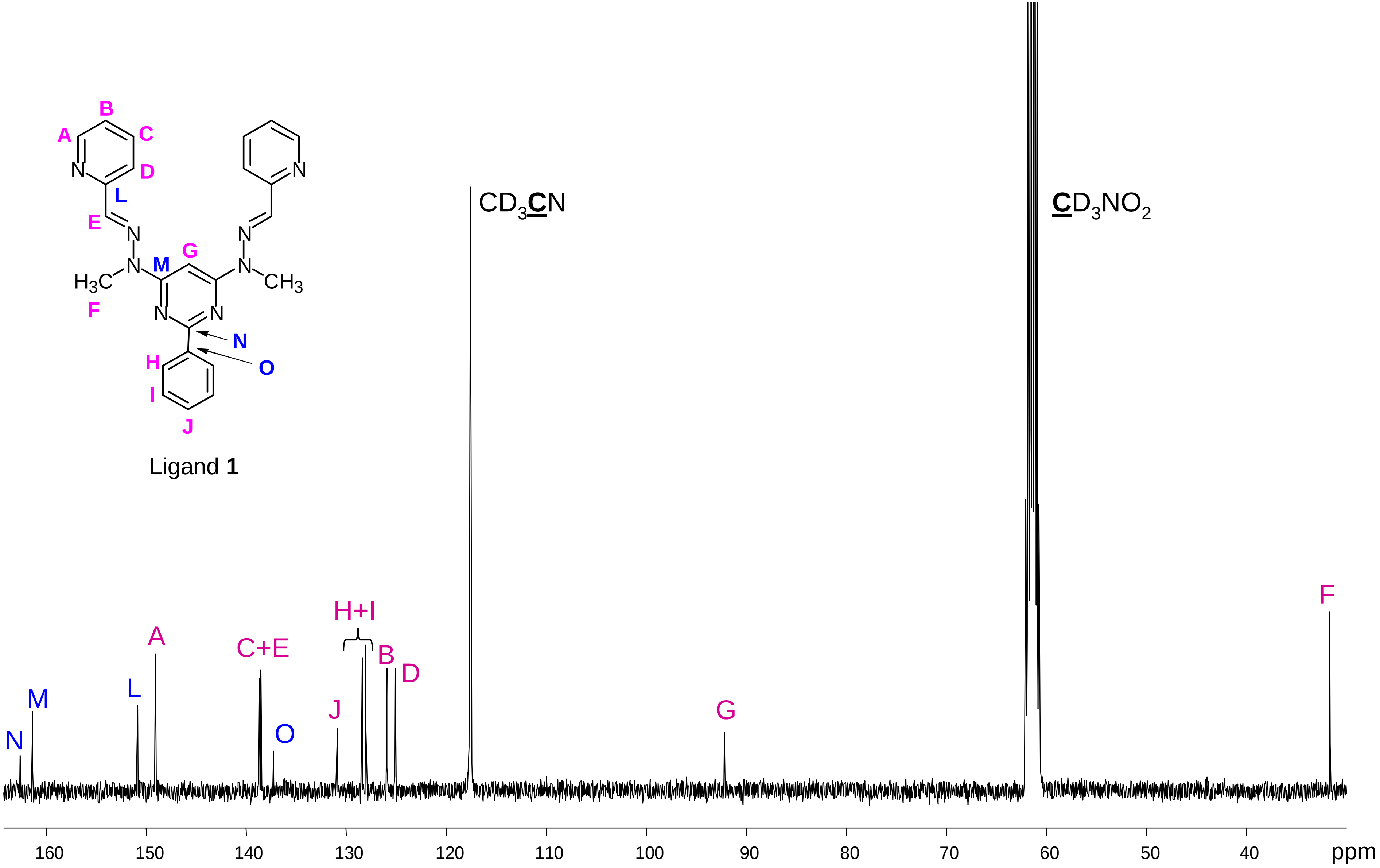


Figure S2. ^{13}C NMR spectrum of complex [Cu$_2$**1**$_2$](CF$_3$SO$_3$)$_2$ (100 MHz, CD$_3$NO$_2$/CD$_3$CN 10/0.9 v/v)



Complex $[Cu_4\mathbf{1}_4](CF_3SO_3)_8$

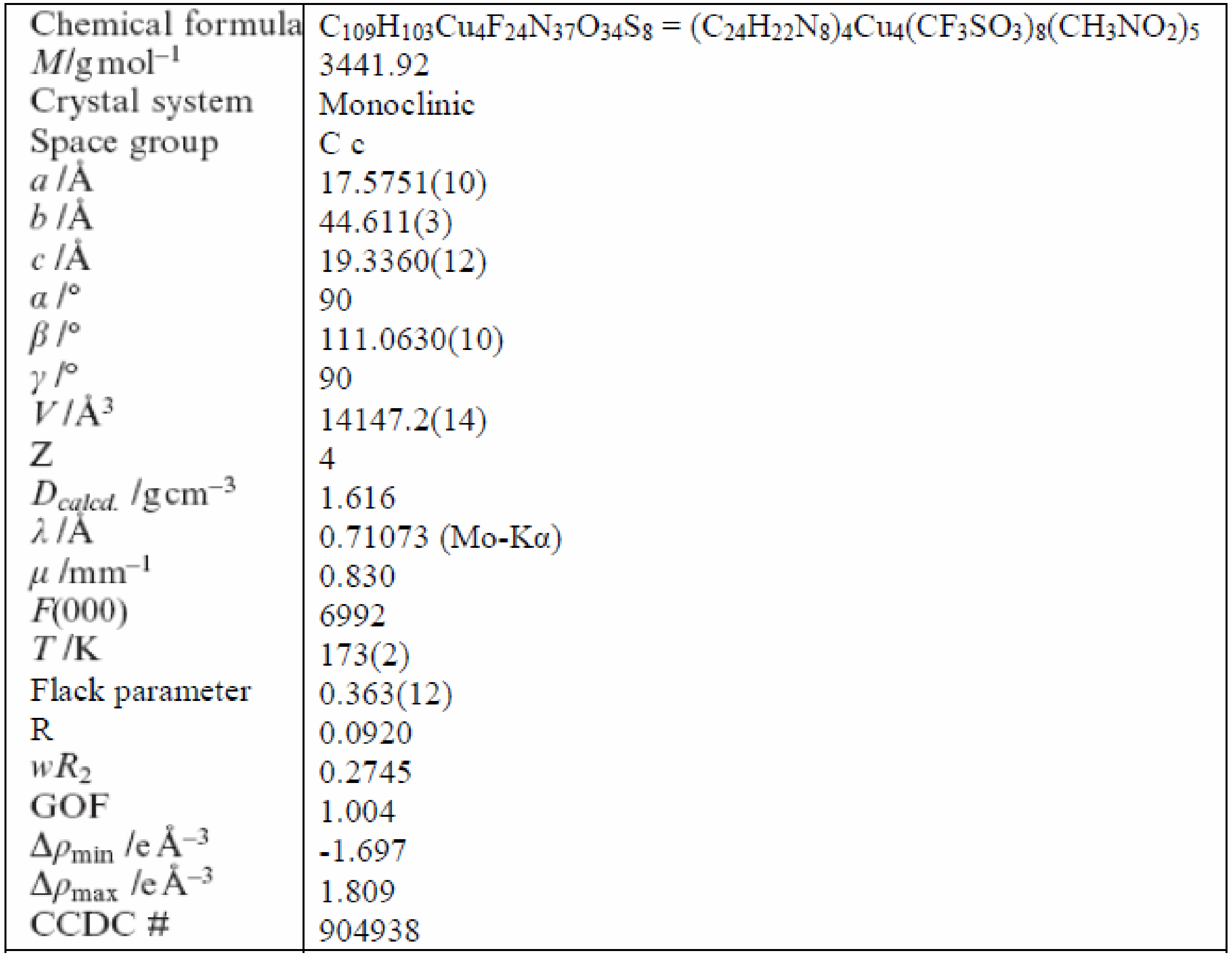
Synthesis. The solution of complex [Cu_4**1**$_4$]$(CF_3SO_3)_8$ was obtained by mixing a suspension made of ligand **1** (2.11 mg, 0.005 mmol) and 0.5 mL of CD_3NO_2 with 1 equivalent of $Cu(CF_3SO_3)_2$. The mixture was stirred for 10 min at r.t. The solution was brown.

HR-ESI-MS, m/z: [Cu_4**1**$_4(CF_3SO_3)_6]^{2+}$ = $C_{102}H_{88}Cu_4F_{18}N_{32}O_{18}S_6{}^{2+}$, found 1419.108 (100%), calcd. 1419.108 (the sample for ESI-MS was prepared using CH_3NO_2 as a solvent).

Crystallization. Single crystals of [Cu_4**1**$_4$]$(CF_3SO_3)_8$ suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether (non solvent) into the nitromethane solution of the complex, as follows: the nitromethane solution was placed in a small glass vial equipped with a cap with a small hole; this vial was placed inside a bigger vial with the appropriate amount of ether, and the bigger vial was sealed with a cap.

Attempts to grow crystals of [Cu_2**1**$_2$]$(CF_3SO_3)_2$ following the above procedure with chloroform as a non solvent resulted in crystals of [Cu_4**1**$_4$]$(CF_3SO_3)_8$.

Crystal data:



Chemical formula	$C_{109}H_{103}Cu_4F_{24}N_{37}O_{34}S_8 = (C_{24}H_{22}N_8)_4Cu_4(CF_3SO_3)_8(CH_3NO_2)_5$
M/g mol^{-1}	3441.92
Crystal system	Monoclinic
Space group	C c
a /Å	17.5751(10)
b /Å	44.611(3)
c /Å	19.3360(12)
α /°	90
β /°	111.0630(10)
γ /°	90
V /Å^3	14147.2(14)
Z	4
$D_{calcd.}$ /g cm^{-3}	1.616
λ /Å	0.71073 (Mo-Kα)
μ /mm^{-1}	0.830
F(000)	6992
T /K	173(2)
Flack parameter	0.363(12)
R	0.0920
wR_2	0.2745
GOF	1.004
$\Delta\rho_{min}$ /e Å^{-3}	-1.697
$\Delta\rho_{max}$ /e Å^{-3}	1.809
CCDC #	904938