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SUPPORTING INFORMATION

Salalen vs. thiolen: in the ring(-opening of epoxide and cyclic carbonate formation)

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General considerations

All chemicals were commercially obtained from Sigma-Aldrich. Cyclohexene oxide (CHO) was stirred with $MgSO_4$, cannula filtered and distilled before use. Propylene oxide (PO), styrene oxide (SO), epichlorohydrin (ECH), phenyl glycidyl ether (PGE) and allyl glycidyl ether (AGE) were stirred with CaH_2, cannula filtered and distilled before use. For anhydrous conditions and CO_2 / epoxide coupling reaction preparation, an MBraun LABmaster dp glovebox, standard Schlenk line techniques and oven-dried glassware were used. The Fe(III) complexes and all reagents used for CO_2 / epoxide coupling reactions were stored in the MBraun LABmaster dp glovebox.

NMR spectroscopy of the crude cyclic carbonate reaction mixtures and Evans method were recorded on a Bruker 400 II MHz Spectrometer instrument and referenced to residual solvent signals. Ligands and complexes were prepared and characterised following previously reported literature.[1–8] All Fe(III) complexes were characterised by electrospray ionisation-mass spectrometry (ESI-MS) using a MicroToF electrospray quadrupole time-of-flight mass spectrometer, with the sample dissolved in acetonitrile at approximately 1 μgmL^{-1} concentration. Mass spectra were recorded in positive loop injection mode set for a range of 50 – 1500 m/z. Elemental analysis was performed by Elemental Microanalysis Ltd. The pressurised CO_2 / epoxide coupling reactions were performed using a Parr 5500 Series Compact Reactor with mechanical stirring and a Parr 4848 Reactor Controller for temperature control. Evans' NMR spectroscopic method was conducted in $CDCl_3$ solvent using a capillary of pure $CDCl_3$, Bruker 400 II MHz Spectrometer at 298 K and taking into account the mass susceptibility of $CDCl_3$ and diamagnetic contribution of all atoms.

Materials characterization (GPC, ESI-MS) facilities were provided through MC^2 at the University of Bath.

Single crystallographic data was collected on an Excalibur EOS detector diffractometer using Mo-Kα (λ = 0.71073 Å) radiation. Data was recorded at 150(2) K. Structure was solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model, all refinement details are given in the .cif file. CCDC number 1980459 contains the necessary crystallographic data.

Complex Characterisation

Fe(**A**-**G**): Reported and used in previous literature. [1]

Fe(**1**-**5**): Reported and used in previous literature.[2]

Fe(6): Prepared following previously reported procedure.[9] Yield = 0.44 g, 70%. ESI-MS (MeCN): Calcd *m/z* $[C_{32}H_{47}FeNO_2S]^+$ = 565.2677, found *m/z* = 565.2745. Elemental analysis: Calcd for $C_{35}H_{52}FeNO_4SCl_2$ (found): C, 59.24 (57.28), H, 7.39 (7.52), N, 1.97 (3.80). Effective magnetic moment = 5.22 μ_B at 298 K in $CDCl_3$.

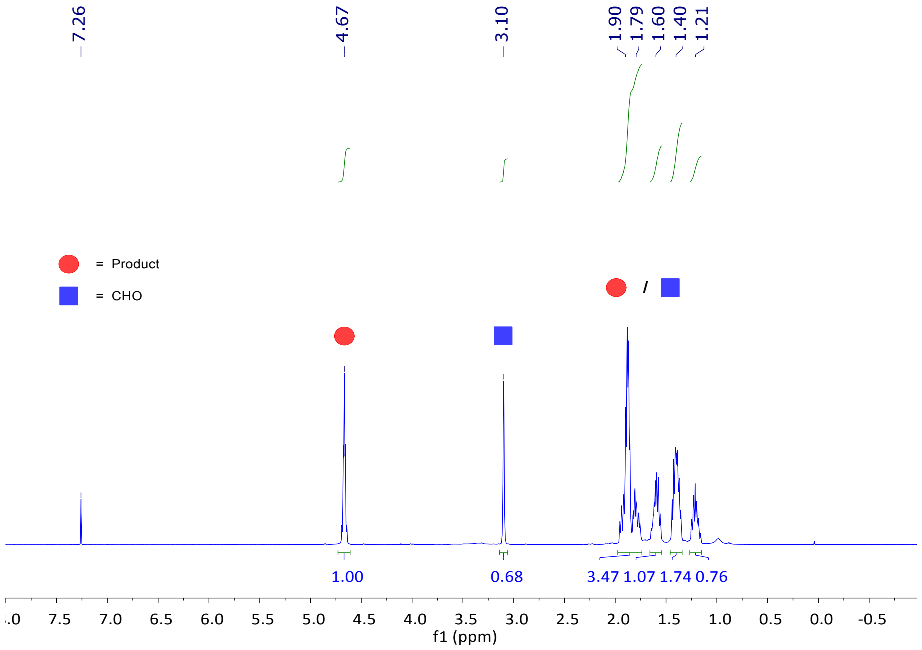
General CO_2 / epoxide coupling reaction method and procedure

All CO_2 / epoxide coupling reactions were carried out in a ratio of 1:8:1200 [catalyst (0.08 mol%)]:[co-catalyst (0.64 mol%)]:[epoxide] where tetrabutylammonium chloride (TBAC) was the co-catalyst and cyclohexene (CHO) was generally the epoxide.

The catalyst (4.21×10^{-5} mol) and TBAC (0.094 g, 3.37×10^{-4} mol) were added as solids to a glass reactor vial in a glovebox. CHO (5 mL) was added to the vial *via* syringe to form a dark purple mixture. The vial was transferred out of the glovebox and placed in the autoclave under a flow of argon. The autoclave was cycled five times with CO_2 and finally left pressurised at 10 bar. The temperature was ramped to 80 °C and left for 24 hours with mechanical stirring. After this time, the autoclave was cooled in an ice bath before bleeding to the air. An aliquot was taken of the crude dark red product mixture and analysed *via* ^1H NMR spectroscopy to determine conversion and selectivity. Electrospray ionisation-mass spectrometry (ESI-MS) was used to confirm the cyclic carbonate product was present in the mixture and gel permeation chromatography (GPC) analysis to confirm no polymer was present. GPC was carried out at 1 mL min^{-1} at 35 °C with a THF eluent using a PLgel 5 µm MIXED-D 300 × 7.5 mm column.

Crude ^{1}H NMR spectra of CO_2 / epoxide coupling reaction mixtures

Table 1. *Entry 14*, Epoxide = Cyclohexene oxide (CHO)



^{1}H NMR spectroscopy consistent with literature.[9–12] ESI-MS (MeCN): Calcd *m/z* $[C_7H_{11}O_3]^+$ = 143.0703, found *m/z* = 143.0741, calcd *m/z* $[C_7H_{10}O_3Na]^+$ = 165.0522, found *m/z* = 165.0597.

Table 1. *Entry 15*, Epoxide = Cyclohexene oxide (CHO)

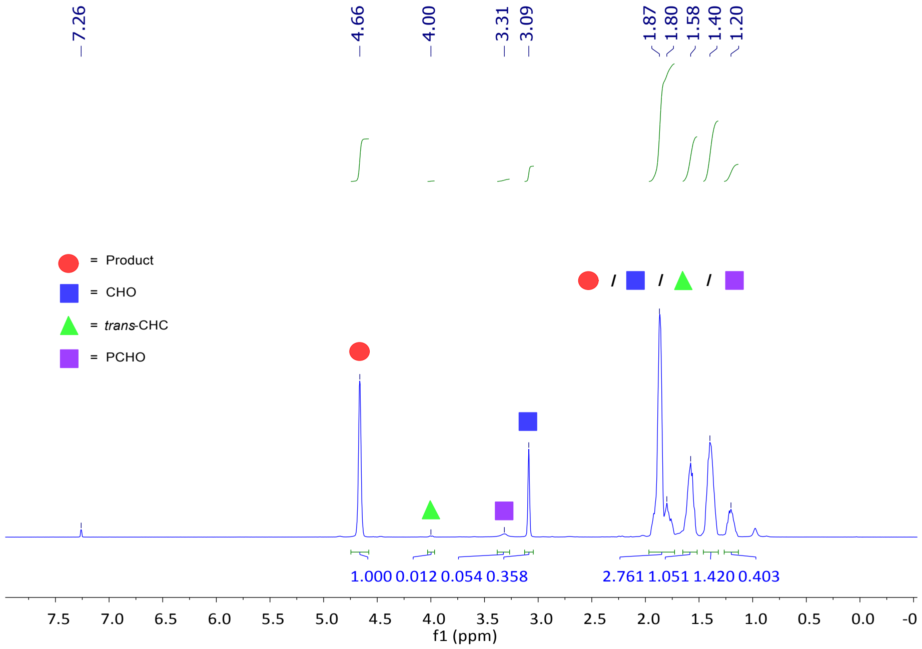
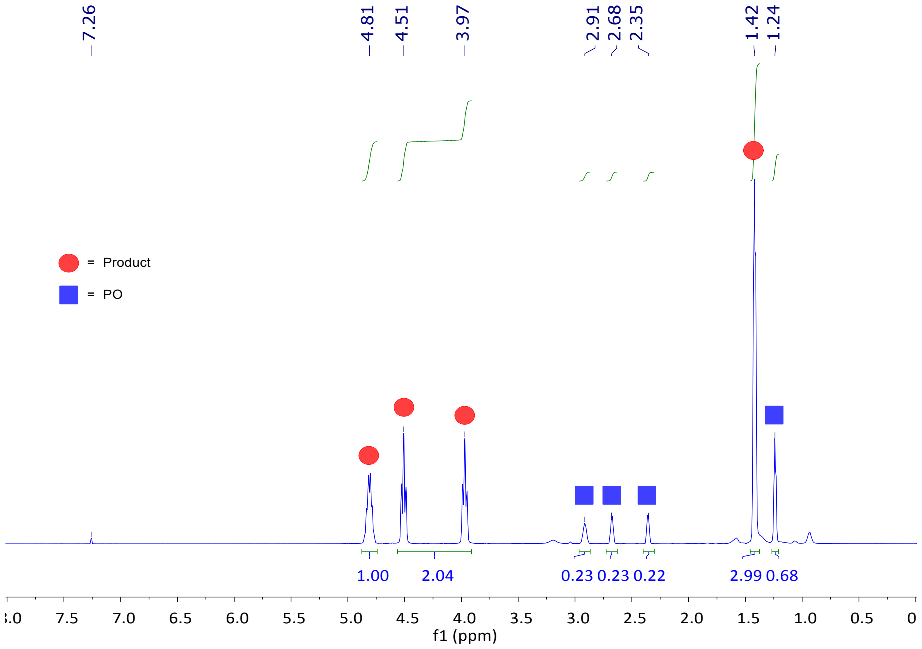
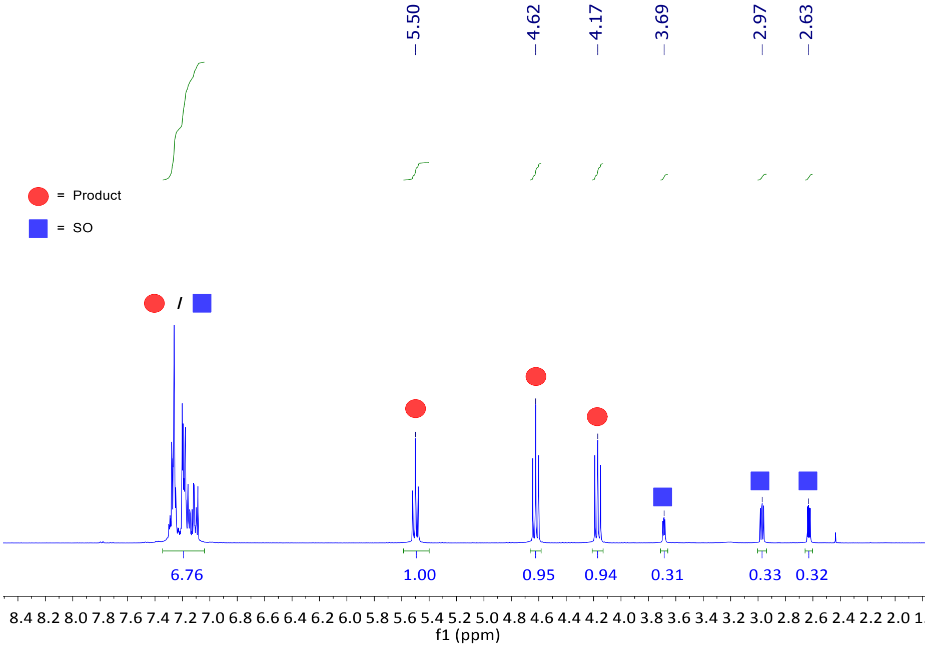


Table 3. *Entry 1*, Epoxide = Propylene oxide (PO)



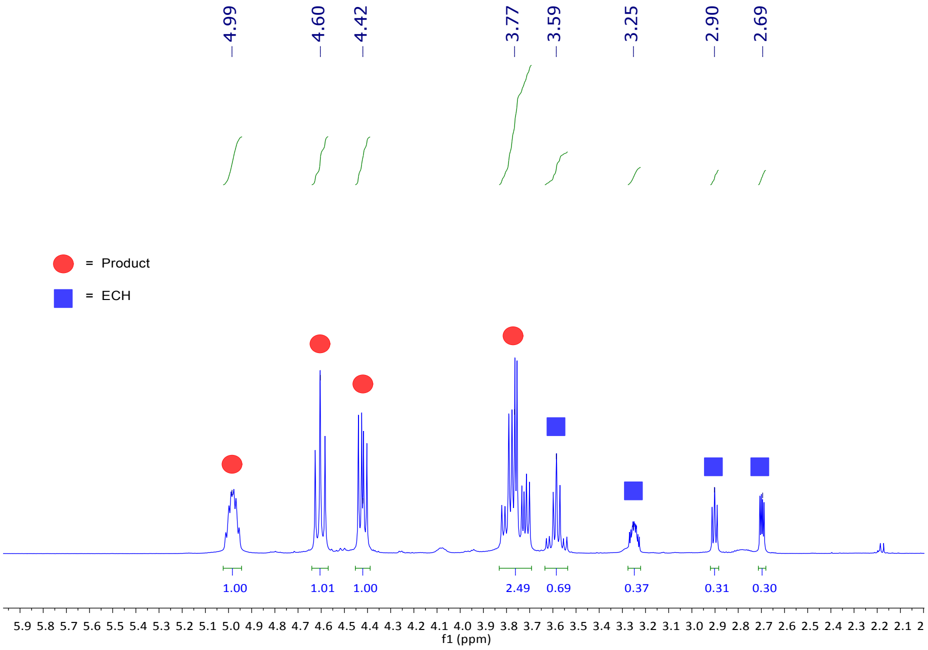
^{1}H NMR spectroscopy consistent with literature.[9–12] ESI-MS (MeCN): Calcd *m/z* [$C_4H_6O_3Na$]$^+$ = 125.0209, found *m/z* = 125.0226.

Table 3. *Entry 2*, Epoxide = Styrene oxide (SO)



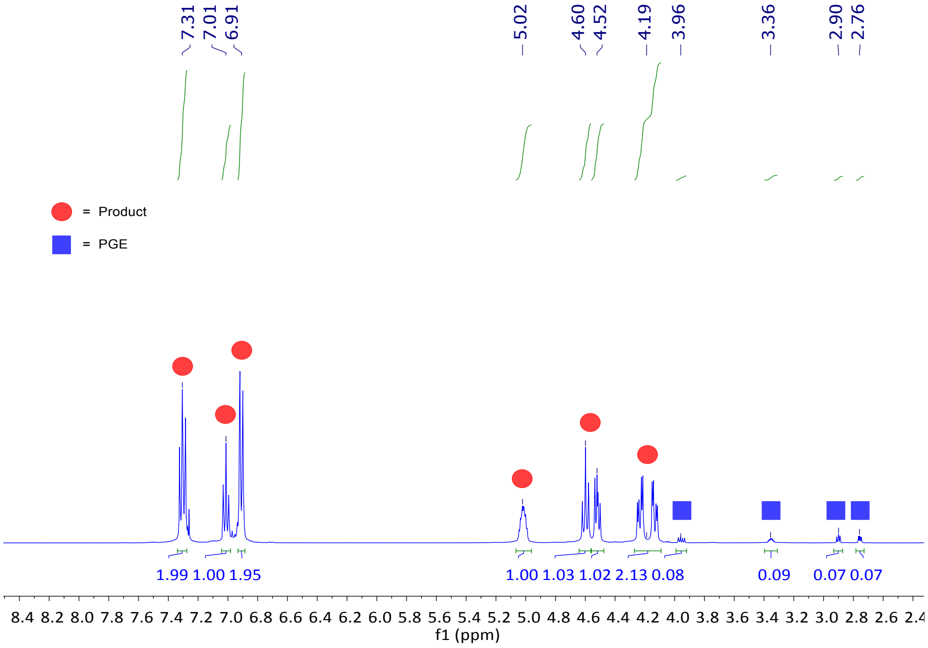
^{1}H NMR spectroscopy consistent with literature.[9–12] ESI-MS (MeCN): Calcd *m/z* [$C_9H_8O_3Na$]$^+$ = 187.0366, found *m/z* = 187.0377.

Table 3. *Entry 3*, Epoxide = Epichlorohydrin (ECH)



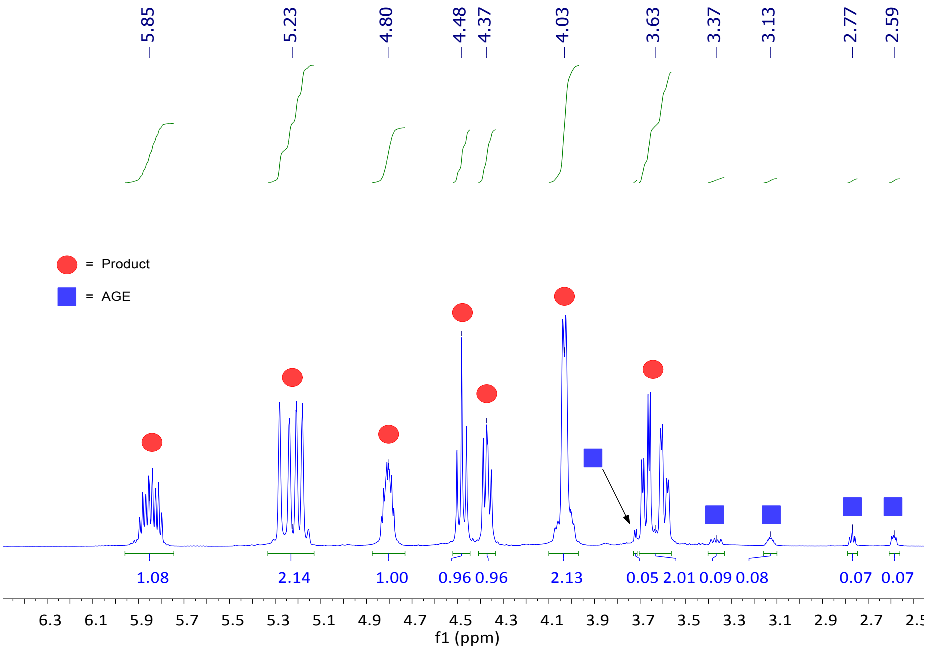
^{1}H NMR spectroscopy consistent with literature.[9–12] ESI-MS (MeCN): Calcd *m/z* $[C_4H_5ClO_3Na]^+$ = 158.9819, found *m/z* = 158.9845.

Table 3. *Entry 4*, Epoxide = Phenyl glycidyl ether (PGE)



^{1}H NMR spectroscopy consistent with literature.[9–11] ESI-MS (MeCN): Calcd *m/z* $[C_{10}H_{11}O_4]^+$ = 195.0652, found *m/z* = 195.0659, calcd *m/z* $[C_{10}H_{10}O_4Na]^+$ = 217.0471, found *m/z* = 217.0469.

Table 3. *Entry 5*, Epoxide = Allyl glycidyl ether (AGE)



^{1}H NMR spectroscopy consistent with literature.[9,11,12] ESI-MS (MeCN): Calcd *m/z* $[C_7H_{11}O_4]^+$ = 159.0652, found *m/z* = 159.0661, calcd *m/z* $[C_7H_{10}O_4Na]^+$ = 181.0471, found *m/z* = 181.0481.

Crystallographic data

Fe(**B**/**C**/**E**/**F**): Reported in previous literature. [1]

Fe(**2**): Reported in previous literature.[2]

Fe(6):

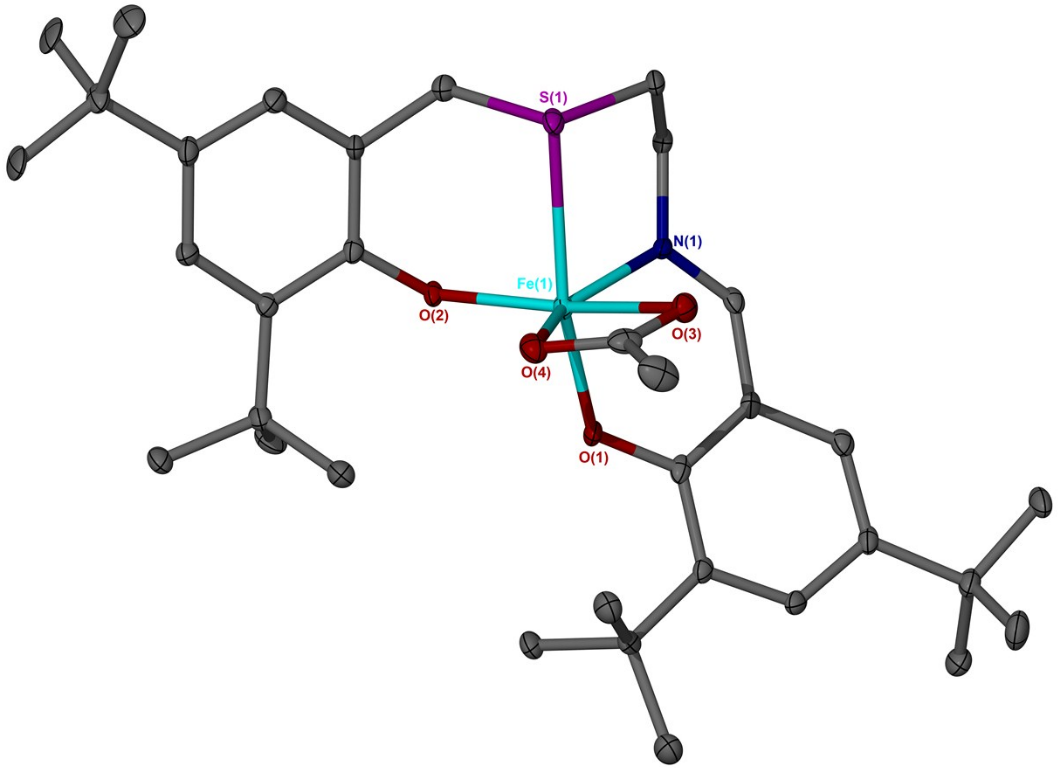


Figure 1. Solid-state structure of Fe(**6**). Ellipsoids shown at 30% probability level and all hydrogen atoms have been omitted for clarity. Disorder in recrystallisation solvent, CH_2Cl_2, Cl atoms split over two positions, 70:30. Methyl groups of one ^{t}Bu (C29) disordered over two positions, 60:40. Bond constraints applied in both cases.

Table 1. Crystal data and structure refinement for Fe(**6**).

Empirical formula	C35 H52 Cl2 Fe N O4 S	
Formula weight	709.58	
Temperature	150.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 14.777(4) Å	α= 90°.
	b = 14.448(7) Å	β= 112.01(2)°.
	c = 18.990(3) Å	γ = 90°.
Volume	3759(2) $Å^3$	
Z	4	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.635 mm^{-1}	
F(000)	1508	
Crystal size	0.3 x 0.2 x 0.05 mm^3	
Theta range for data collection	3.484 to 25.027°.	
Index ranges	-17<=h<=17, -12<=k<=17, -22<=l<=20	
Reflections collected	15364	
Independent reflections	6631 [R(int) = 0.0651]	
Completeness to theta = 25.027°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.31759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6631 / 8 / 459	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0669, wR2 = 0.1544	
R indices (all data)	R1 = 0.1263, wR2 = 0.1975	
Largest diff. peak and hole	0.798 and -0.541 e.$Å^{-3}$	

References

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