Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for

Ammonium Halide Selective Ion Pair Recognition and Extraction with a Chalcogen Bonding Heteroditopic Receptor

Andrew Docker,[b] Yuen Cheong Tse, Hui Min Tay, Zongyao Zhang, Paul D. Beer* [a]

[a] *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, U. K.*

[b] Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW U.K.

Contents

1. Materials and Methods

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was de-ionized and micro filtered using a Milli-Q ® Millipore machine. Routine NMR spectra were recorded on either a Varian Mercury 300, a Bruker AVIII 400 or a Bruker AVIII 500 spectrometer with ^1H NMR titrations recorded on a Bruker AVIII 500 spectrometer. Tetrabutylammonium (TBA) salts were stored in a vacuum desiccator containing phosphorus pentoxide prior to use. Where mixtures of solvents were used, ratios are reported by volume. Chemical shifts are quoted in parts per million relative to the residual solvent peak.

2. ^1H NMR Anion Recognition Studies

Titration Protocol: In a typical ^1H NMR anion titration experiment, aliquots of anion were added as their TBA salts to 0.5 ml of 1 mM solution of **1·ChB^{PFP}** precomplexed with an equimolar quantity of NH_4PF_6 in a $CD_3CN/CDCl_3$ 1:1 (v/v) solvent mixture and the spectrum recorded.

Spectra were recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents.

[**1·ChB^{PFP}**] = 1.0 mM

[TBAX] = 50 mM, X =Cl^-, Br^-, I^-, NO_3^- and SCN^-

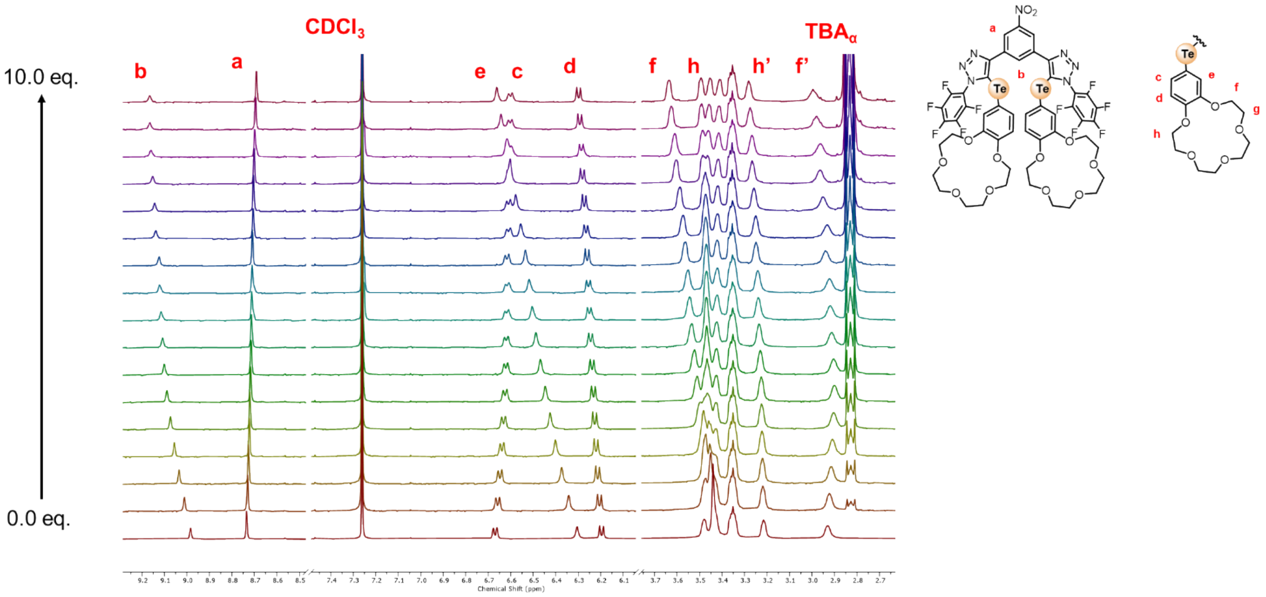

Figure S1. Stacked ^{1}H NMR titration spectra of **1·ChB^{PFP}** (1 mM) with TBACl (50 mM) in the presence of one equivalent of NH_4PF_6 (1:1 CD_3CN:$CDCl_3$ (v/v), 500 MHz, 298K).

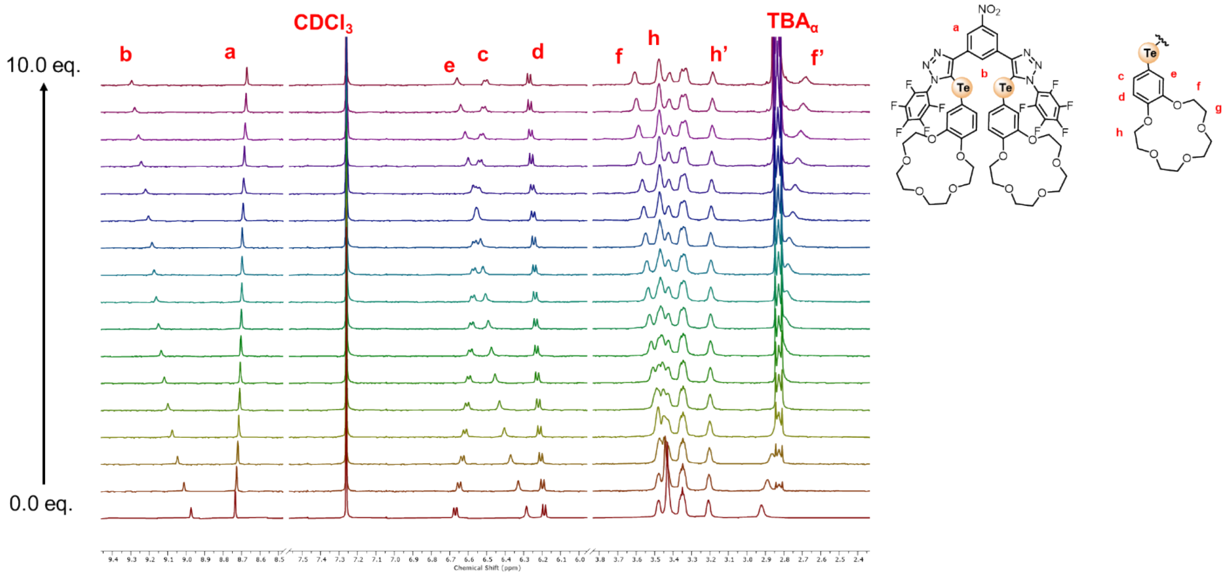

Figure S2. Stacked ^{1}H NMR titration spectra of **1·ChB^{PFP}** (1 mM) with TBABr (50 mM) in the presence of one equivalent of NH_4PF_6 (1:1 CD_3CN:$CDCl_3$ (v/v), 500 MHz, 298K).

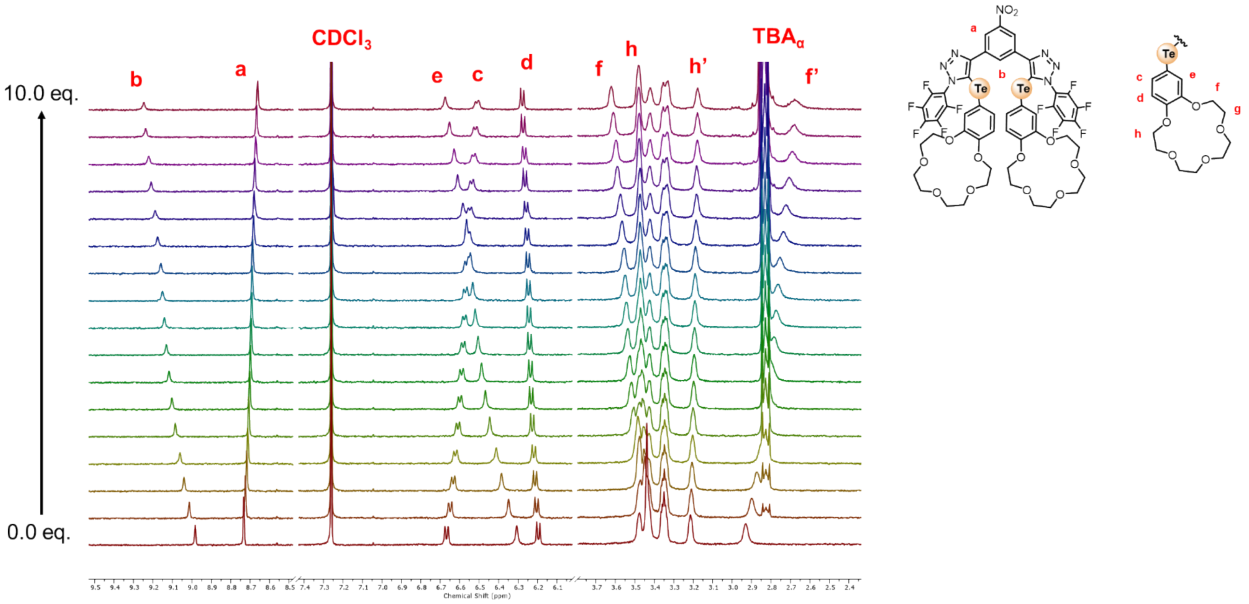

Figure S3. Stacked ^{1}H NMR titration spectra of **1·ChB^{PFP}** (1 mM) with TBAI (50 mM) in the presence of one equivalent of NH_4PF_6 (1:1 CD_3CN:$CDCl_3$ (v/v), 500 MHz, 298K).

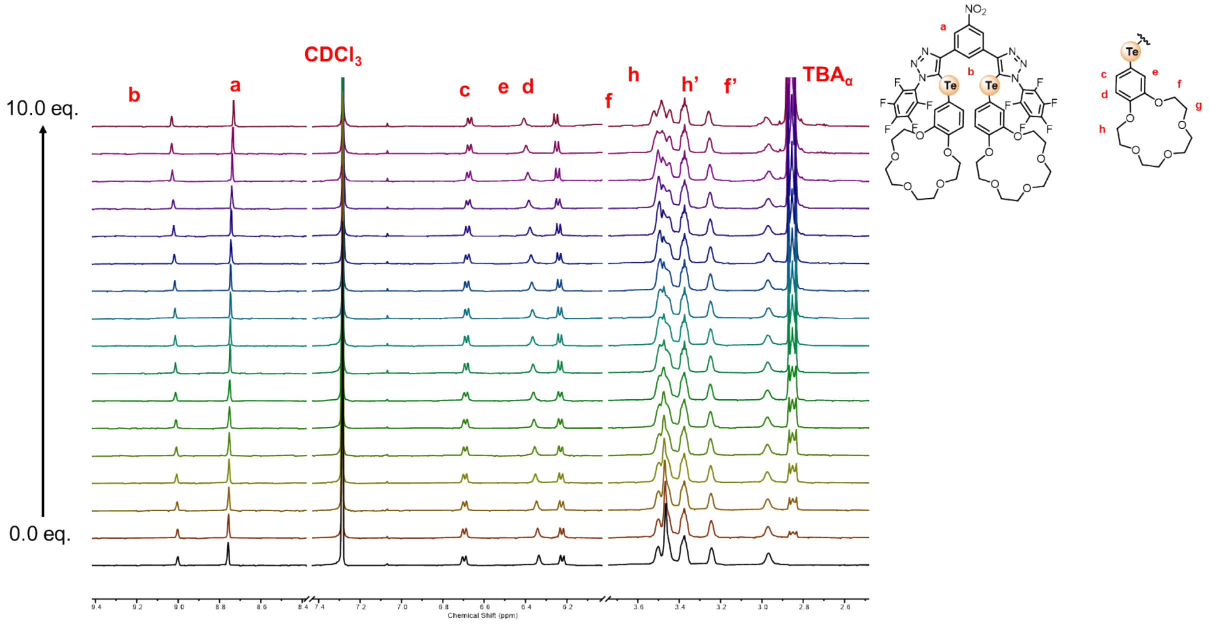

Figure S4. Stacked ^{1}H NMR titration spectra of **1·ChB^{PFP}** (1 mM) with $TBANO_3$ (50 mM) in the presence of one equivalent of NH_4PF_6 (1:1 CD_3CN:$CDCl_3$ (v/v), 500 MHz, 298K).

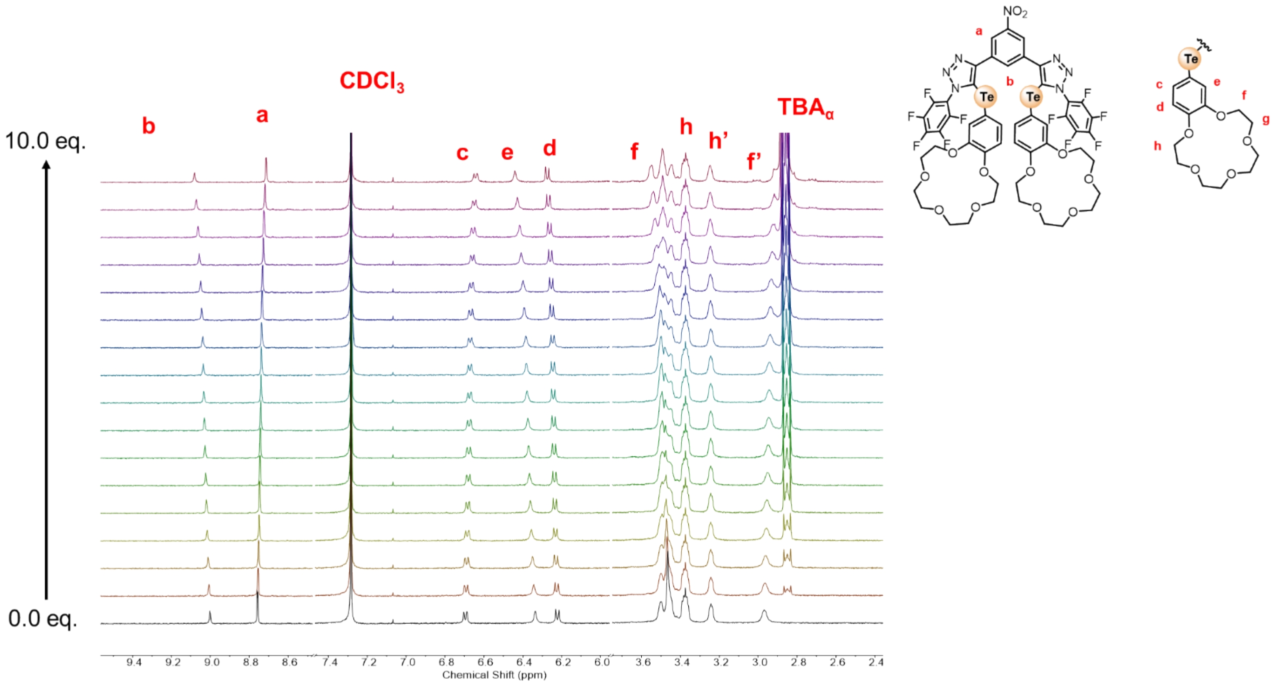

Figure S5. Stacked ^{1}H NMR titration spectra of **1·ChB^{PFP}** (1 mM) with TBASCN (50 mM) in the presence of one equivalent of NH_4PF_6 (1:1 CD_3CN:$CDCl_3$ (v/v), 500 MHz, 298K).

3. Solid Liquid Extraction (SLE) Studies

A 2 mM solution of **1·ChB**$^{\mathbf{PFP}}$ in $CDCl_3$ (0.7 ml) was exposed to an excess (ca. 5 equivalents) of a microcrystalline sample of NH_4X ($X = Cl^-$, Br^-, I^-, NO_3^-, SCN^-). The mixture was sonicated for 10 minutes, after which the solution was removed and passed through a syringe filter and the ^1H NMR spectrum recorded.

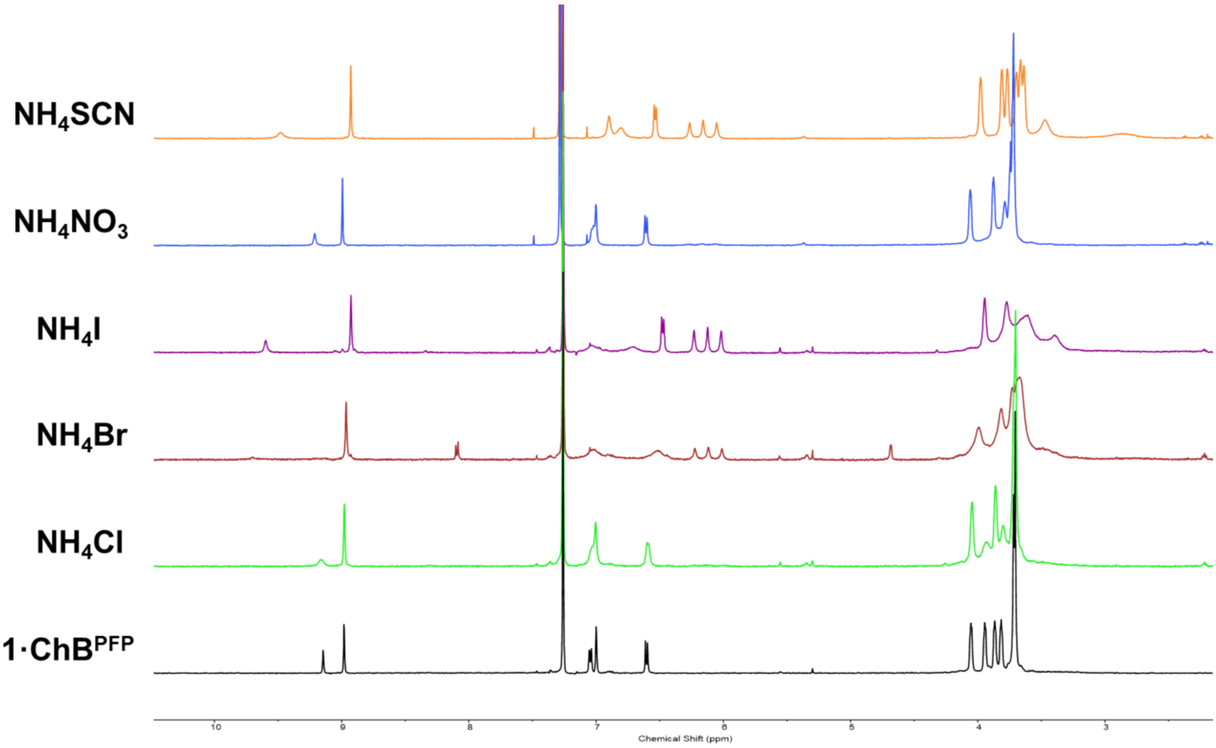

Figure S6. ^1H NMR spectrum from SLE extraction experiment of **1·ChB**^{PFP} ($CDCl_3$, 500 MHz, 298K).

4. Liquid Liquid Extraction (LLE) Studies

In a typical experiment a $CDCl_3$ solution of the receptor (0.7 ml) was added to a D_2O solution of the NH_4X ($X = Cl^-$, Br^-, I^-, NO_3^-, SCN^-) (4 M, 0.7 ml), to which was added a stirrer bar and the mixture was stirred vigorously for 30 mins. After which time the biphasic mixture was allowed to settle, the organic phase removed and the ^1H NMR spectrum recorded.

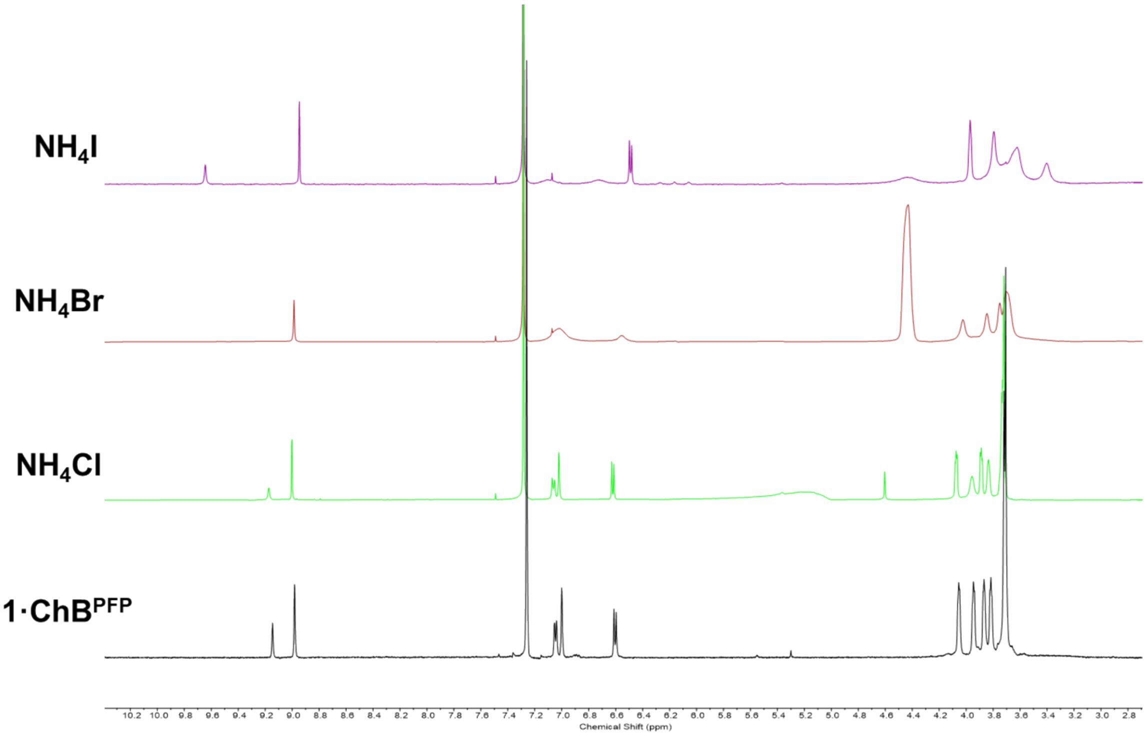

Figure S7. ^1H NMR spectrum from LLE extraction experiment of **$1{\cdot}ChB^{PFP}$** ($CDCl_3$, 500 MHz, 298K).

5. Crystal Structure Determination

Single crystals of **1·ChB**^{PFP}·NH_4Br suitable for X-ray analysis were each coated with Paratone-N oil, suspended on a 200 µm MiTeGen loop, and placed in a cold gaseous nitrogen stream on an Oxford Diffraction Supernova X-ray diffractometer performing φ- and ω-scans at 150(2) K. Diffraction16 intensities were measured using graphite monochromated Cu K_α radiation (1.54184 Å). Data collection, indexing, initial cell refinements, frame integration, final cell refinements and absorption corrections were accomplished using the program CrysAlisPro.† Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography. All structures were solved by direct methods and refined against F2. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. Details of the data quality and a summary of the residual values for the refinements are listed in Table S1. Figures of the crystal structures have been created using the open-source PyMOL Molecular Graphics System.

Deposition Number 2155965 (for **1·ChB**^{PFP}·NH_4Br) contains the supplementary crystallographic data for this paper. This data is provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

† CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.

Table S1. Crystal data and structure refinement for **1·ChB**^{PFP}.

Identification code	001zy21_sq	
Empirical formula	$C_{54} H_{49} Br Cl_{12} F_{10} N_8 O_{12} Te_2$	
Formula weight	1952.52	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 17.2868(4) Å	a= 85.749(2)°.
	b = 20.8341(5) Å	b= 89.525(2)°.
	c = 25.0337(5) Å	g = 68.431(2)°.
Volume	8359.9(3) Å^3	
Z	4	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	10.267 mm^{-1}	
F(000)	3832	
Crystal size	0.400 x 0.400 x 0.400 mm^3	
Theta range for data collection	3.542 to 76.468°.	
Index ranges	-21<=h<=21, -26<=k<=26, -31<=l<=30	
Reflections collected	191943	
Independent reflections	34679 [R(int) = 0.0633]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Sphere	
Max. and min. transmission	0.13143 and 0.03628	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	34679 / 20 / 1783	
Goodness-of-fit on F^2	0.862	
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1837	
R indices (all data)	R1 = 0.0658, wR2 = 0.2026	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.989 and -1.377 e.Å^{-3}	