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Supporting Information

Solvent-free Transformation of Protic Ionic Liquids into Zwitterions†

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1. General Information

[HNEt$_3$][TVA] (**2**) and K[TVA] were synthesized according to the method in the literature.[S1] K[TVA] was recrystalized from a acetonitrile–dichloromethane mixture by slow cooling to −40°C for further purification. [HEtPyr]Cl and [HBuIm]Cl were prepared through the reaction of EtPyr or BuIm and hydrochloric acid, respectively.[S2] Basic alumina was purchased from Kokusan Chemical Co., Ltd. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. FT-IR spectra were acquired via attenuated total reflectance spectroscopy using a Thermo Scientific Nicolet iS5 spectrometer. DSC measurements were performed using a TA Instrument Q100 differential scanning calorimeter at a scan rate of 10 °C min^{-1}. The UCST behavior of the aqueous solutions of ILs (1:1 v/v) was examined by using an SRS melting point apparatus (MPA100). The aqueous solution of each salt was injected into a capillary (1 mm o.d), and a clear point was observed upon heating the sample at 3 °C min^{-1} to 90 °C. Ionic conductivity was measured using a Solartron 1260 impedance analyzer. Each sample was sandwiched between a gold interdigitated electrode (gap dimension: 200 μm, Metrohm) and a quartz glass plate, with Kapton tape as a spacer.

2. Experimental Procedures

Synthesis of ILs. 1 was prepared as follows: an aqueous solution (2 mL) of [HEtPyr]Cl (112 mg, 0.82 mmol) was added to an aqueous solution (2 mL) of K[TVA] (247 mg, 0.89 mmol) and stirred for 1 h. The mixture was then extracted five times with dichloromethane. The organic layers were combined, washed with water, and dried over anhydrous magnesium sulfate. After solvent evaporation, the residue was dried under vacuum for 7 h at room temperature to provide **1** in the form of a pale-yellowish liquid (185 mg, yield 66%). ^{1}H NMR (400 MHz, CDCl$_3$: δ = 1.45 (t, 3H, CH$_2$CH_3, J =7.3 Hz), 2.10 (m ,2H, pyrrolidinium ring), 2.23 (m, 2H, pyrrolidinium ring), 2.85 (m, 2H, pyrrolidinium ring), 3.22 (m, 2H, CH_2CH$_3$), 3.92 (m, 2H, pyrrolidinium ring), 5.83 (d, 1H, *cis*-C*H*, J = 10.0 Hz), 6.23 (d, 1H, *trans*-C*H*, J = 16.4 Hz), 6.81 (dd, 1H, CH_2CHSO_2, J = 10.0, 16.6 Hz), 9.09 (br, 1H, N*H*). The synthesis of **1** as described for **2** using trifluoromethanesulfonamide, EtPyr, and 2-chloroethanesulfonyl chloride was also attempted, but this method produced high amounts of **1zw** and resulted in a low yield of **1**.

The preparation of **3** was done as described for **1** with [HBuIm]Cl (146 mg, 0.91 mmol) and K[TVA] (260 mg, 0.94 mmol). The product was obtained as a colorless liquid (239 mg, yield 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.99 (t, 3H, CH_2CH_3, J =7.2 Hz), 1.40 (td, 2H, CH_2CH_3, J = 7.5, 22.7 Hz), 1.89 (m, 2H, $CH_2CH_2CH_3$), 4.17 (t, 2H, $CH_2CH_2CH_2$, J =7.4 Hz), 5.82 (d, 1H, *cis*-C*H*, J = 10.0 Hz), 6.25 (d, 1H, *trans*-C*H*, J = 16.6 Hz), 6.82 (dd, 1H, CH_2CHSO_2, J = 10.0, 16.6 Hz), 7.16 (t, 1H, imidazolium ring, J = 1.7, 2.1 Hz), 7.41 (t, 1H, imidazolium ring, J = 1.5, 2.1 Hz), 8.63 (s, 1H, imidazolium ring). Anal. Calcd. for $C_{10}H_{16}F_3N_3O_4S_2$: C, 33.05; H, 4.44; N, 11.56. Found: C, 32.61; H, 4.71; N, 11.31.

Transformation of ILs into ZIs. EtPyr (2.3 mg, 0.023 mmol, 14 mol%) was added to **1** (56.4 mg, 0.17 mmol), and the mixture was left for 1 day at room temperature. The mixture gradually solidified to form colorless crystals of **1zw** (99% conversion). The product was washed with chloroform to remove excess amine and unreacted IL and vacuum dried for 2 h (39.2 mg, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 3.59–3.49 (m, 8H), 3.36 (t, J = 7.2 Hz, 2H), 2.07–2.04 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6): δ = –77.30 (s, 3F, CF_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 119.8 (q, $J_{C–F}$ = 323 Hz), 61.9, 54.2, 52.8, 48.0, 21.1, 8.1. Anal. Calcd. for $C_9H_{17}F_3N_2O_4S_2$: C, 31.95; H, 5.06; N, 8.28. Found: C, 32.13; H, 5.06; N, 8.13.

The reaction of **2** was performed as described for **1** using NEt_3 (2.3 mg, 0.023 mmol, 15 mol%) and **2** (50 mg, 0.15 mmol). A conversion of 97% was achieved after 4 days at room temperature, yielding **2zw** in the form of colorless crystals (33 mg, 60% yield after washing with chloroform). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 3.52–3.45 (m, 4H), 3.31 (q, J = 7.2 Hz, 6H), 1.18 (t, J = 7.2 Hz, 9H). ^{19}F NMR (376 MHz, DMSO-d_6): δ = –77.25 (s, 3F, CF_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 119.8 (q, $J_{C–F}$ = 320 Hz), 52.2, 50.9, 46.8, 7.0. ESI-MS Calcd. for [$C_9H_{19}F_3N_2O_4S_2$+H]: 341.08221. Found 341.0803. FT-IR (cm^{-1}): 2992 (C–H), 2954 (C–H), 1439, 1396, 1326, 1298, 1131, 1047, 831, 624, 595. Anal. Calcd. for $C_9H_{19}F_3N_2O_4S_2$: C, 31.76; H, 5.63; N, 8.23. Found: C, 31.72; H, 5.76; N, 8.05.

The reaction of **3** was performed using BuIm (2.9 mg, 0.023 mmol, 15 mol%) and **3** (56.7 mg, 0.16 mmol). The mixture was held at 80 °C for 7 days. A highly viscous liquid was formed (92% conversion), added to chloroform, and stirred to extract excess amine and unreacted IL. After removing the chloroform layer, the residue was dried under vacuum for 3 h and recrystallized from dichroloethane–diethyl ether at −40 °C to obtain **3zw** in the form of colorless crystals (13.6 mg, 24% isolated yield). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 9.21 (s, 1H), 7.83 (t, J = 1.6 Hz, 1H), 7.76 (t, J = 1.6 Hz, 1H), 4.54 (t, J = 6.4 Hz, 2H), 4.15 (t, J = 7.2 Hz, 2H), 3.59 (t, J = 6.4 Hz, 2H), 1.78–1.71 (m, 2H), 1.31–1.21 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6): δ = –77.51 (s, 3F, CF_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 136.7, 122.5, 122.1, 119.9 (q, $J_{C–F}$ = 323 Hz), 53.2, 48.4, 44.4, 31.2, 18.6, 13.2. FT-IR (cm^{-1}): 3148, 3110, 2964, 2879, 1562, 1463, 1314, 1176, 1121, 1051, 838, 751, 768, 691, 615, 594. Anal. Calcd. for $C_{10}H_{16}F_3N_3O_4S_2$: C, 33.05; H, 4.44; N, 11.56. Found: C, 32.92; H, 4.48; N, 11.48.

The use of alumina that was vacuum dried at 180 °C for 4 h as a catalyst for the formation of **1zw** was also investigated (Table S1). Leaving the mixture of alumina (2.4 mg) and **1** (21.4 mg, 0.063 mmol) resulted in 8%, 81% and 97% conversions, after 2 h, 4 days and 11 days, respectively. The product was dissolved in acetonitrile and filtrated to remove alumina. After solvent evaporation and vacuum drying at room temperature for 2 h, the residue was washed with chloroform to remove the unreacted IL and vacuum dried to obtain crystals of **1zw** (13.0

mg, 61% yield).

The effect of the amount and pretreatment of alumina was examined. Leaving the mixture of alumina (23.4 mg, dried under vacuum at 180 °C for 4 h) and **1** (14.7 mg, 0.043 mmol) resulted in 40% and 98% conversions after 2 h and 1 day, respectively. This result demonstrates that the use of an excess amount of alumina leads to higher conversion. Leaving the mixture of alumina (23.6 mg, dried under vacuum at room temperature for 1 h) and **1** (14.6 mg, 0.043 mmol) resulted in 27% and 98% conversions, after 2 h and 1 day, respectively. This result demonstrates that the use of preheated, vacuum-dried alumina leads to a higher reaction rate.

The reaction of **2** was performed similarly with basic alumina (31.6 mg) and **2** (23.7 mg, 0.070 mmol). The alumina was vacuum dried for 1 h at room temperature before use. Leaving the mixture for 1 day at 25 °C resulted in 8% conversion. Subsequent heating of the mixture at 50 °C for 4 days resulted in 34% conversion, and further heating at 80 °C for 4 days increased the conversion to 90%. **2zw** was obtaied as colorless crystals (14.3 mg, 60% yield).

X-ray crystallography. Single crystals of **1zw** and **2zw** were collected from the reaction products, whereas those of **3zw** were prepared by recrystallization from dichloromethane–diethyl ether (−40 °C). X-ray diffraction data were collected at −183 °C using a Bruker APEX II Ultra diffractometer (X-ray source: Mo Kα), and calculations were performed using SHELXL.[S3] Crystallographic parameters are listed in **Tables S1**. CCDC-2280235 (**1zw**), 2249355 (**2zw**), and 2297749 (**3zw**) contain the crystallographic data.

References

S1 H. T. Ho, M. Rollet, T. N. T. Phan and D. Gigmes, *Eur. Polym. J.*, 2018, **107**, 74–81.

S2 A. Sun, J. Zhang, C. Li and H. Meng, *Chin. J. Chem.*, 2009, **27**, 1741–1748.

S3 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.

3. Figures and Tables

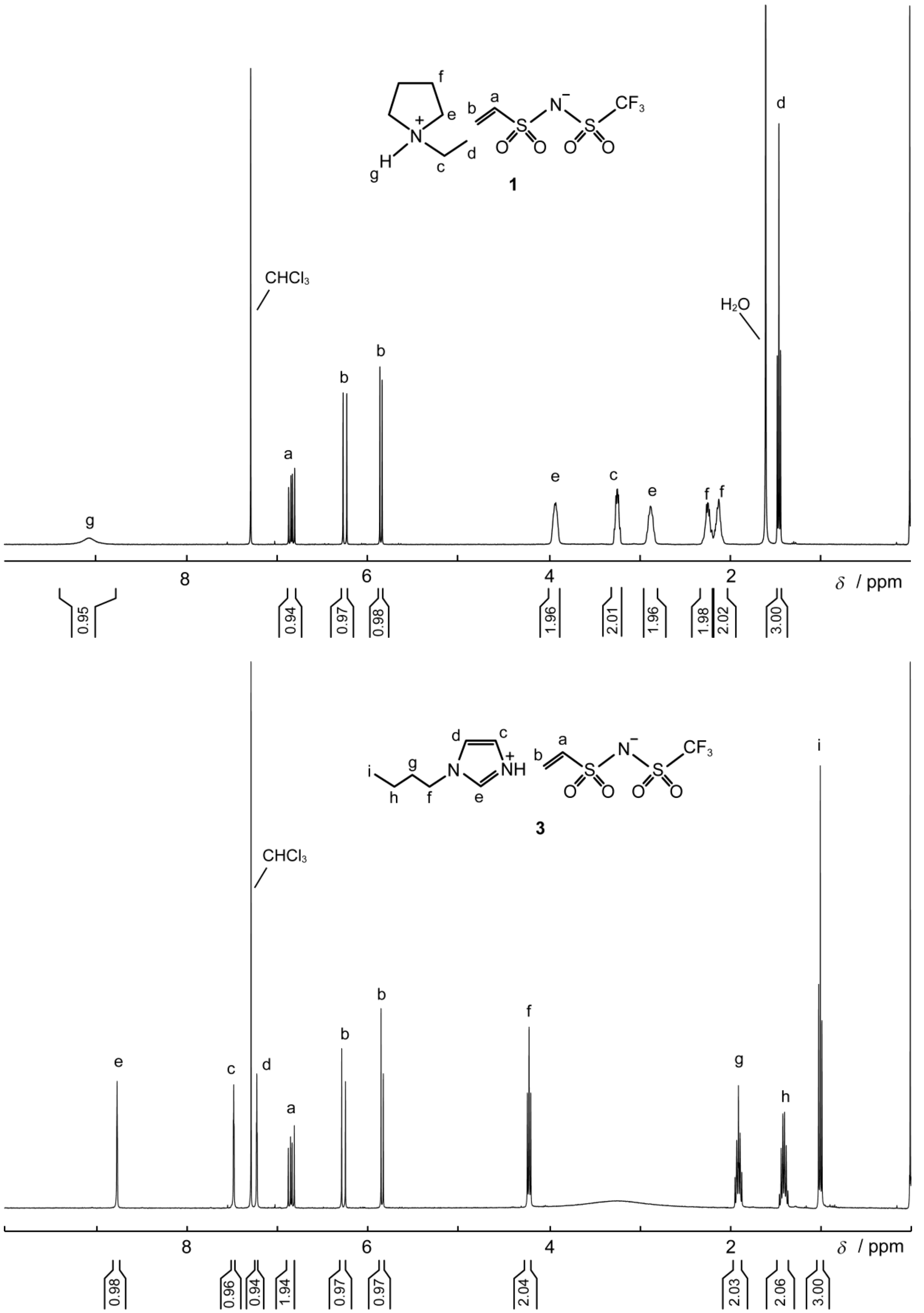

Fig. S1 ^{1}H NMR spectra of **1** and **3** in $CDCl_3$.

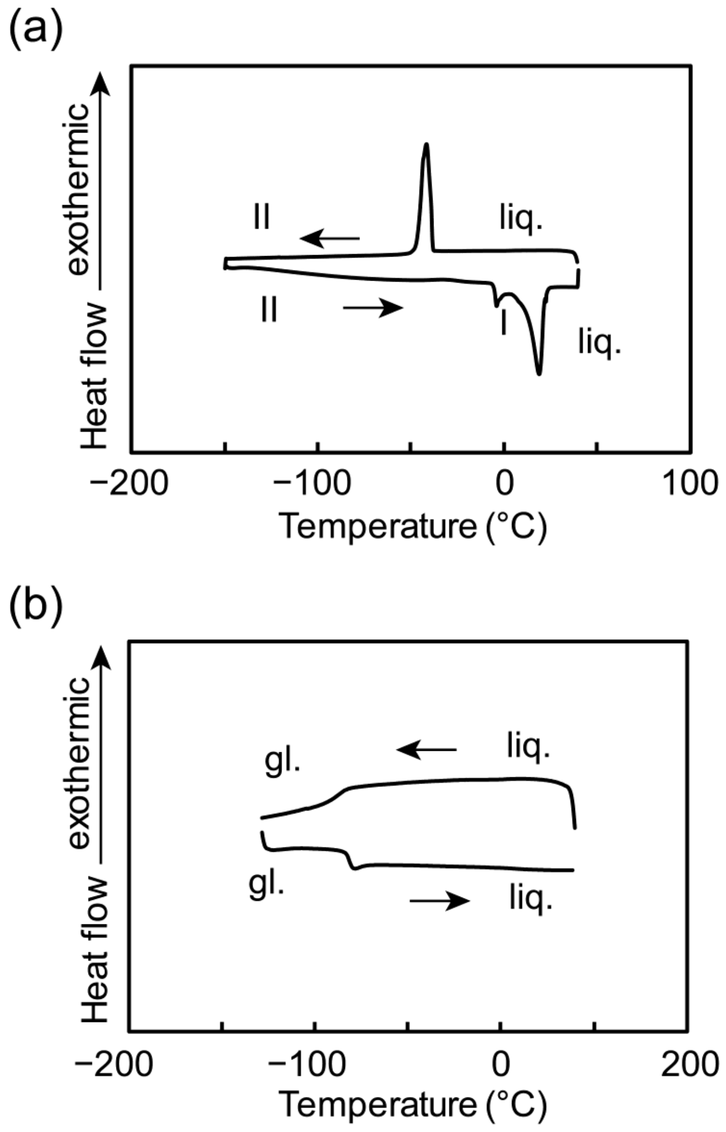

Fig. S2 DSC traces of (a) **1** and (b) **3** where liq. and gl. are the liquid and glassy states, respectively.

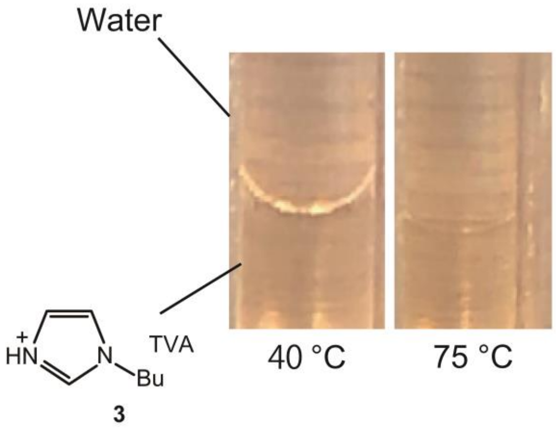

Fig. S3 Photographs of mixtures of **3** and water (1:1 w/w) in glass capillaries taken at 40 °C and 75 °C.

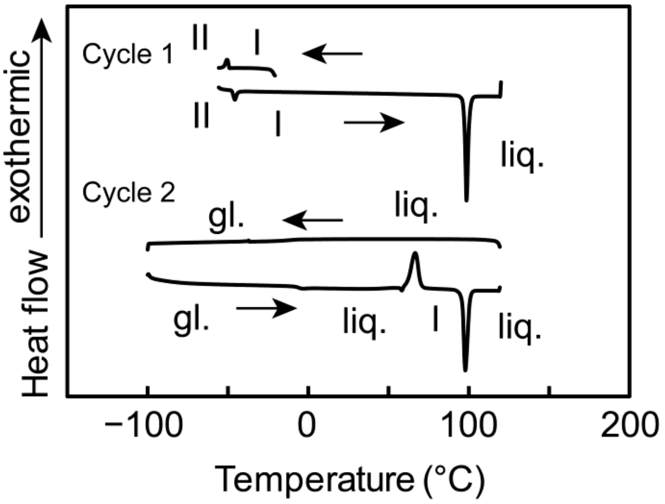

Fig. S4 DSC traces of **3zw** where liq. and gl. are the liquid and glassy states, respectively.

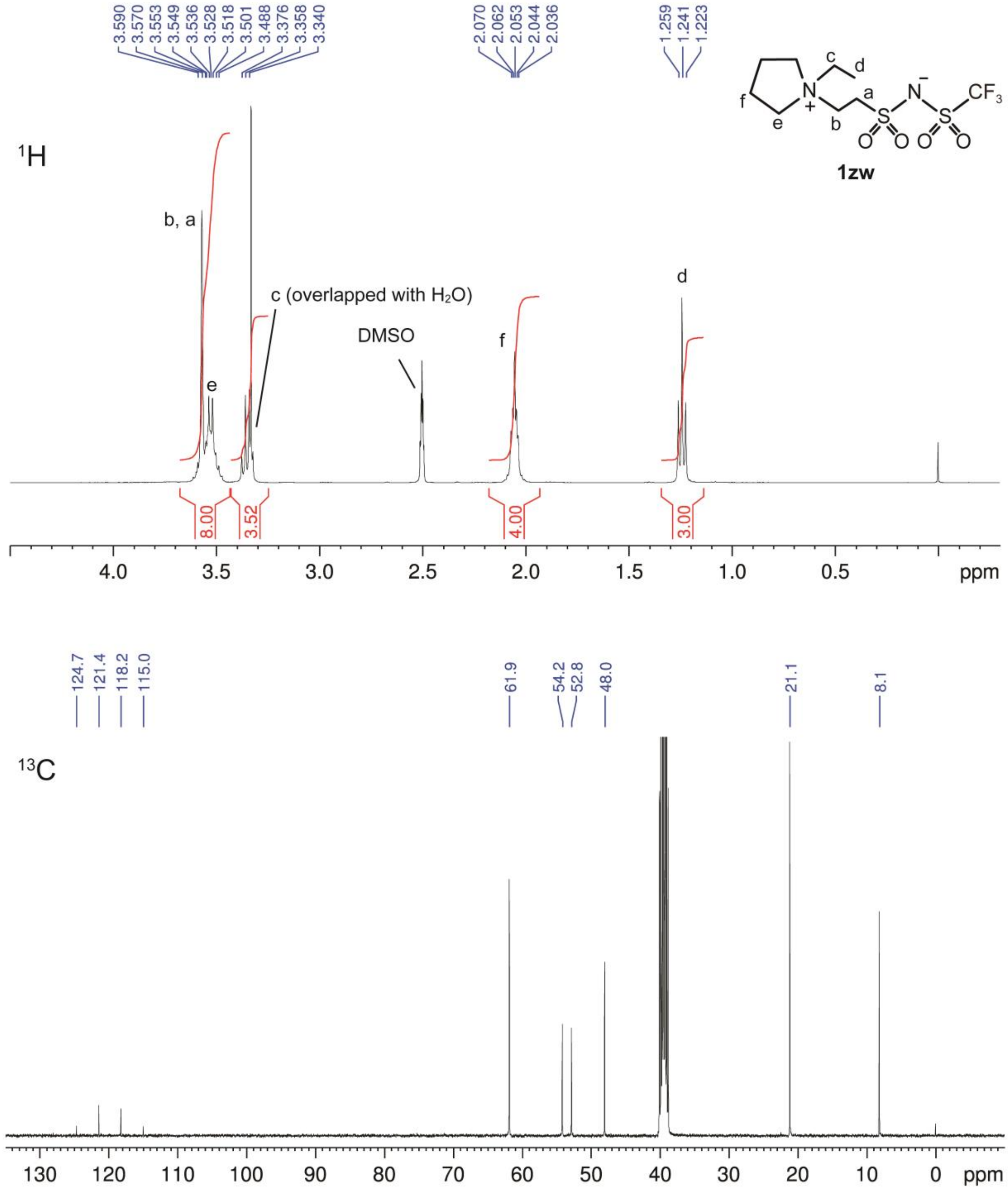

Fig. S5 (a) ^{1}H and ^{13}C NMR spectra of **1zw** in dmso-*d*$_6$.

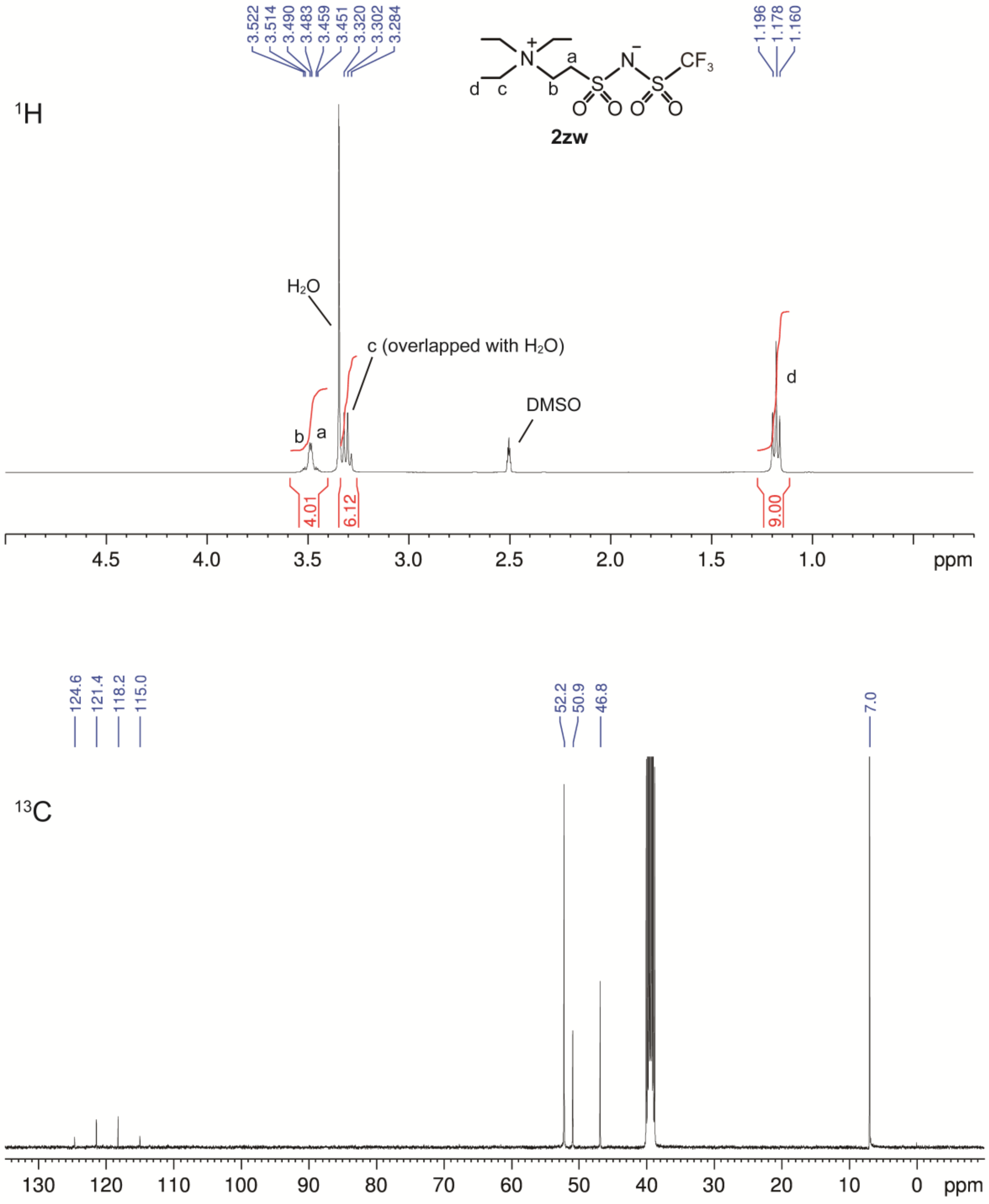

Fig. S5 (b) ^{1}H and ^{13}C NMR spectra of **2zw** in dmso-d_6.

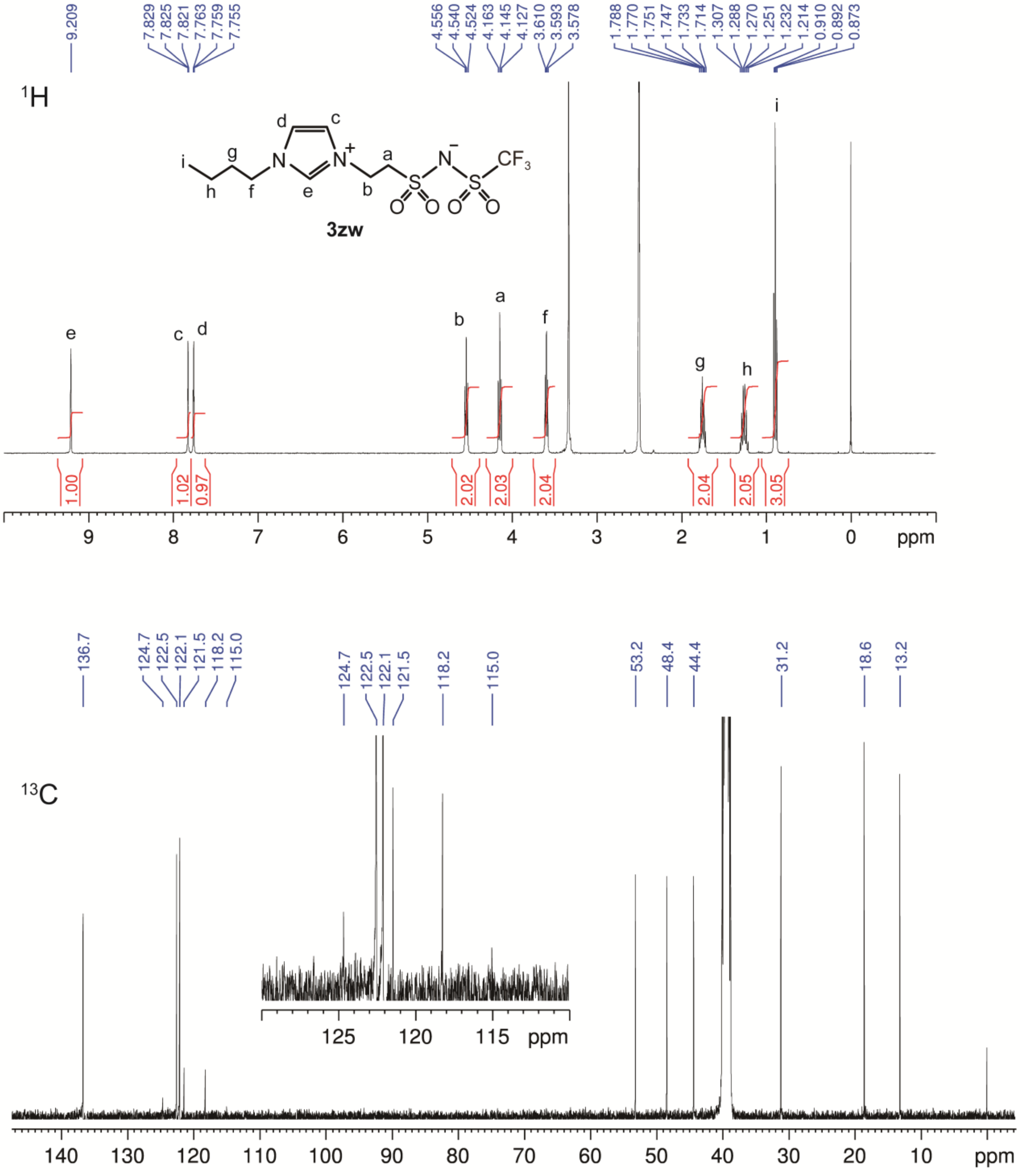

Fig. S5 (c) ^{1}H and ^{13}C NMR spectra of **3zw** in dmso-d_6.

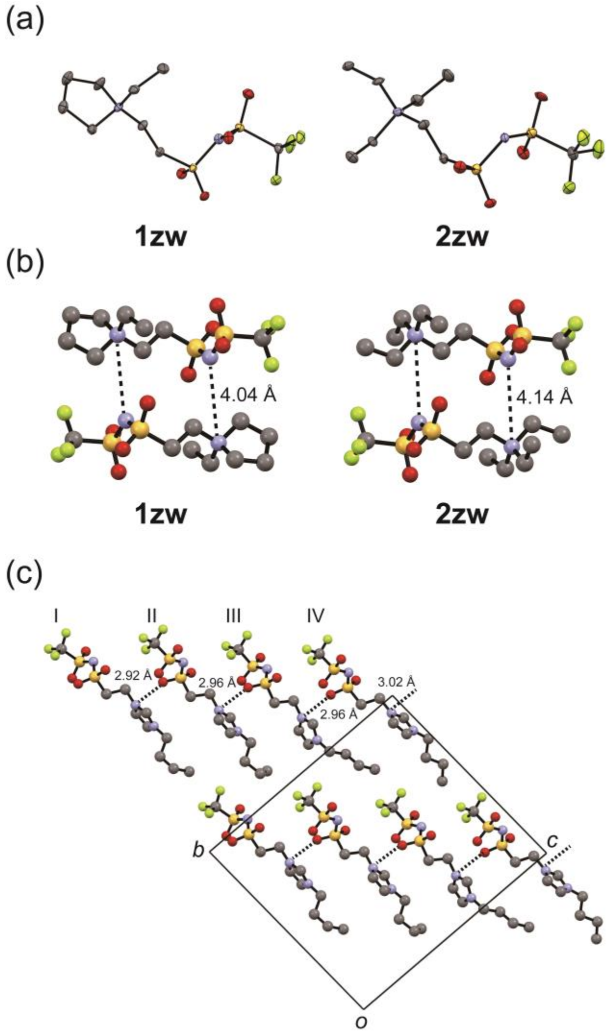

Fig. S6 (a) Molecular structures (ORTEP drawings) and (b) dimer arrangements of **1zw** and **2zw** in crystals. (c) Packing diagram of **3zw** (*a*-axis projection). Dotted lines in (b) indicate the intermolecular distances between cationic and anionic centers, whereas those in (c) indicate the shortest intermolecular distances between cationic N and anionic O atoms. Hydrogen atoms have been omitted.

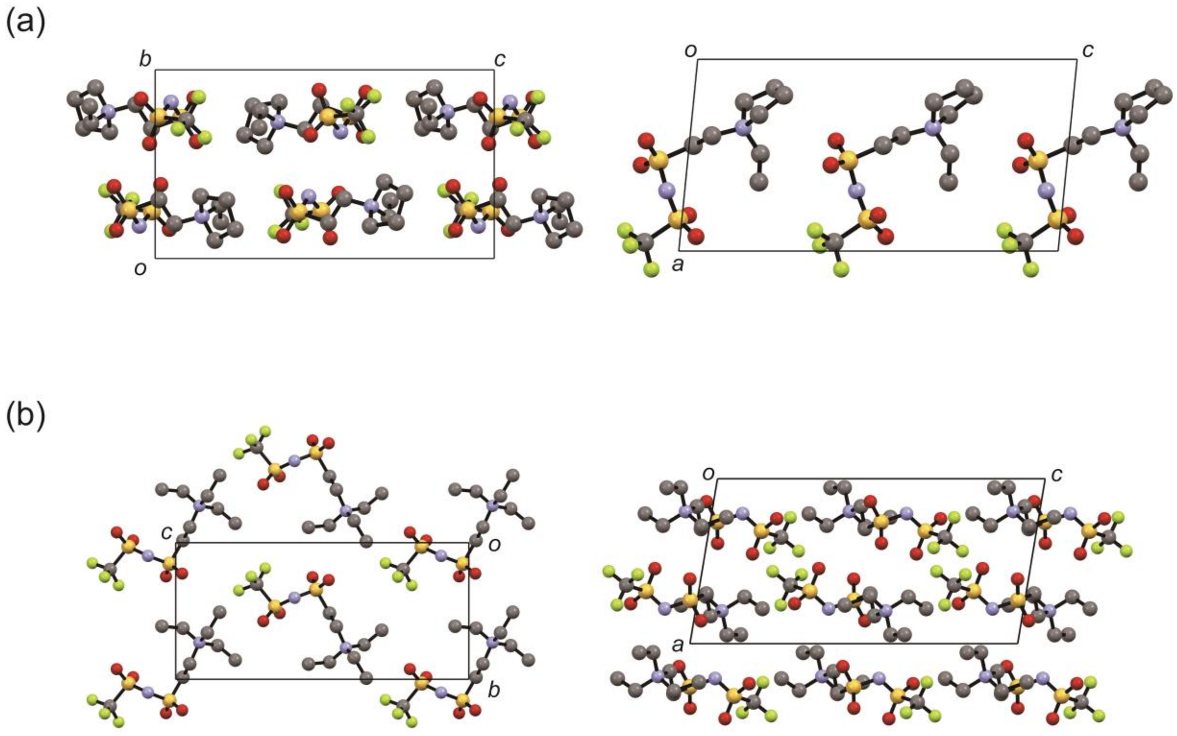

Fig. S7 Packing diagrams of (a) **1zw** and (b) **2zw** at −183 °C. *a*-Axis (left) and *b*-axis (right) projection. Hydrogen atoms have been omitted.

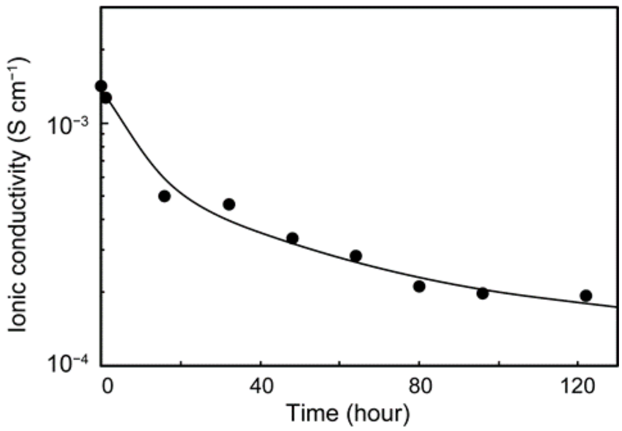

Fig. S8 Time course of the ionic conductivity of **3** after the addition of BuIm (11 mol%). The reaction was performed at 50 °C, and the values were measured at 25 °C. The line is provided as a guide. The conversion after 122 h was 30%, and the remaining amount of amine was 9 mol%.

Table S1 Added bases, reaction conditions, and conversions in the transformation of **1–3** into ZIs

IL	Added base	Reaction	Conv.	Product distribution [a]		
	(amount)	condition	(%)[a]	**1zw**	**2zw**	**3zw**
1	NEt_3 (23 mol%)	25 °C, 2 h	86	77	9	
		1 d	99	89	10	
	BuIm (15 mol%)	80 °C, 2 h	89	86		3
		1 d	99	93		6
	Al_2O_3 (11 wt%) [b]	25 °C, 2 h	8	8		
		4 d	81	81		
		11 d	97	97		
	Al_2O_3 (159 wt%) [b]	25 °C, 2 h	40	40		
		1 d	98	98		
	Al_2O_3 (162 wt%)	25 °C, 2 h	27	27		
		1 d	98	98		
2	EtPyr (27 mol%)	25 °C, 2 h	40	30	10	
		1 d	59	33	26	
		4 d	95	29	66	
	BuIm (12 mol%)	80 °C, 2 h	10		6	4
		1 d	60		45	15
	Al_2O_3 (133 wt%)	25 °C, 1 d	8		8	
		50 °C, 4 d	34		34	
		80 °C, 4 d	90		90	
3	EtPyr (15 mol%)	80 °C, 2 h	8	0.2		8
		1 d	65	5		60
		4 d	87	7		80
	NEt_3 (18 mol%)	80 °C, 2 h	17		0.7	16
		1 d	66		0.7	65

[a] Determined by ^{19}F NMR.

[b] Vacuum-dried at 180 °C for 4 h.

Table S2 Crystallographic parameters

	1zw	**2zw**	**3zw**
Empirical formula	$C_9H_{17}F_3N_2O_4S_2$	$C_9H_{19}F_3N_2O_4S_2$	$C_{10}H_{16}F_3N_3O_4S_2$
Formula weight	338.36	340.38	363.38
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a / Å	8.664(3)	9.520(2)	9.869(6)
b / Å	9.443(3)	8.588(2)	17.149(11)
c / Å	17.044(7)	18.645(5)	18.682(12)
α / °			93.615(7)
β / °	95.637(4)	99.465(4)	92.206(8)
γ / °			94.036(7)
V / Å^3	1387.7(8)	1503.6(6)	3145.0(3)
Z	4	4	8
ρ_{calkd} / g cm^{-3}	1.62	1.504	1.535
Temperature / K	90	90	90
F (000)	704	712	1504
Reflns collected	7928	8263	11577
Independent reflns	3175	3271	11577
Parameters	182	184	798
R(int)	0.0588	0.113	0.0544
$R_1{}^a$, $R_w{}^b$ ($I > 2\sigma(I)$)	0.0494, 0.0987	0.0443, 0.0435	0.0509, 0.1239
$R_1{}^a$, $R_w{}^b$ (all data)	0.0854, 0.1119	0.1521, 0.0558	0.0717, 0.1377
Goodness of fit	1.037	0.686	1.028
$\Delta\rho_{\text{max,min}}$ [e Å^{-3}]	0.426, −0.372	0.413, −0.426	0.983, −0.539

${}^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ${}^bR_w = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2}$.