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Synthetic Method of Chiral Iron-based Ionic Liquids: Modelling Stable Hybrid Materials

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1. NMR SPECTRA

Fig. S1 ^{1}H NMR spectrum of **[*S*-methylBMMIm]Cl** (**1**) in $CDCl_3$ (400 MHz, R.T.).

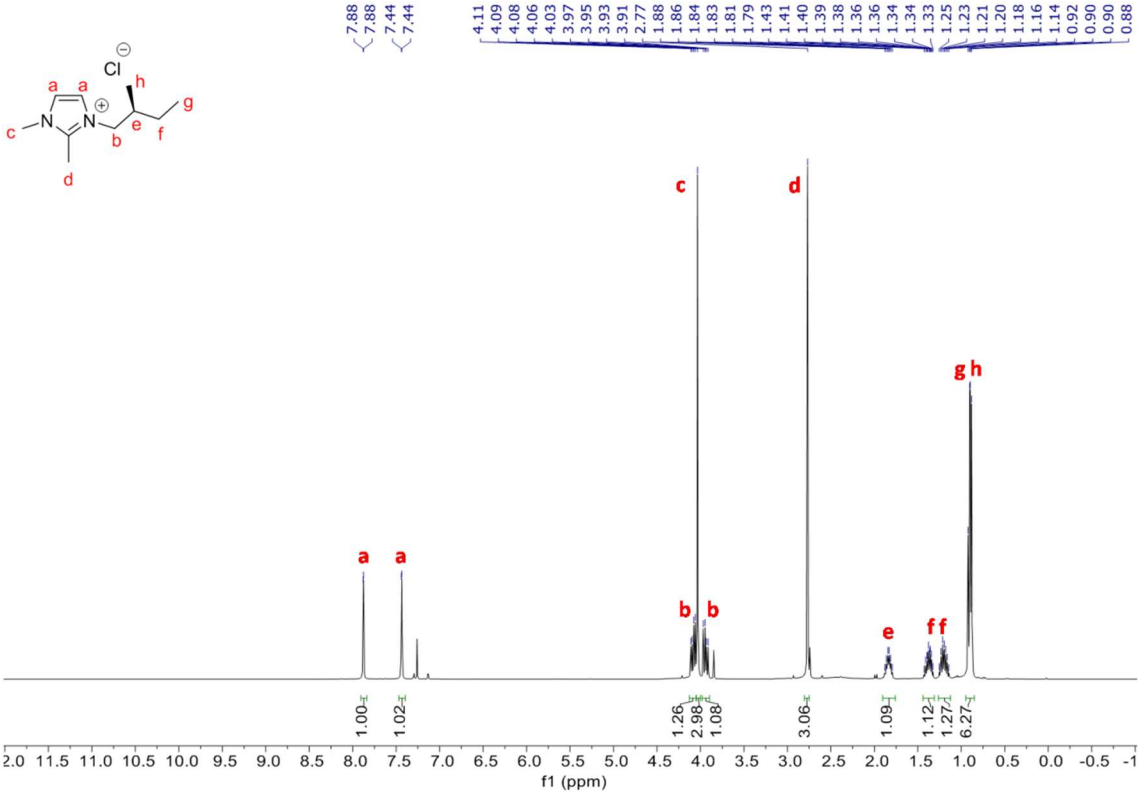


Fig. S2 ^{13}C NMR spectrum of of **[*S*-methylBMMIm]Cl** (**1**) in $CDCl_3$ (101 MHz, R.T.).

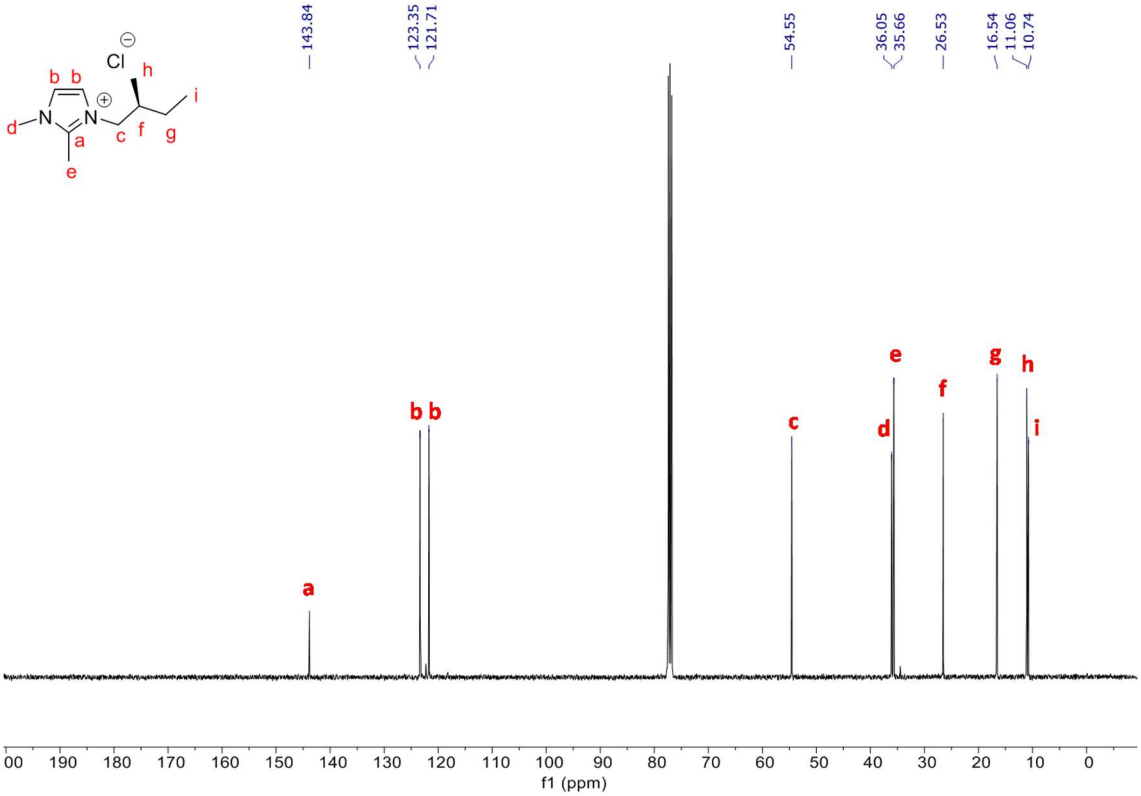


Fig. S3 ^{1}H NMR spectrum of [***R*-diOHPrMIm]Cl** (**2**) in D_2O (400 MHz, R.T.).*

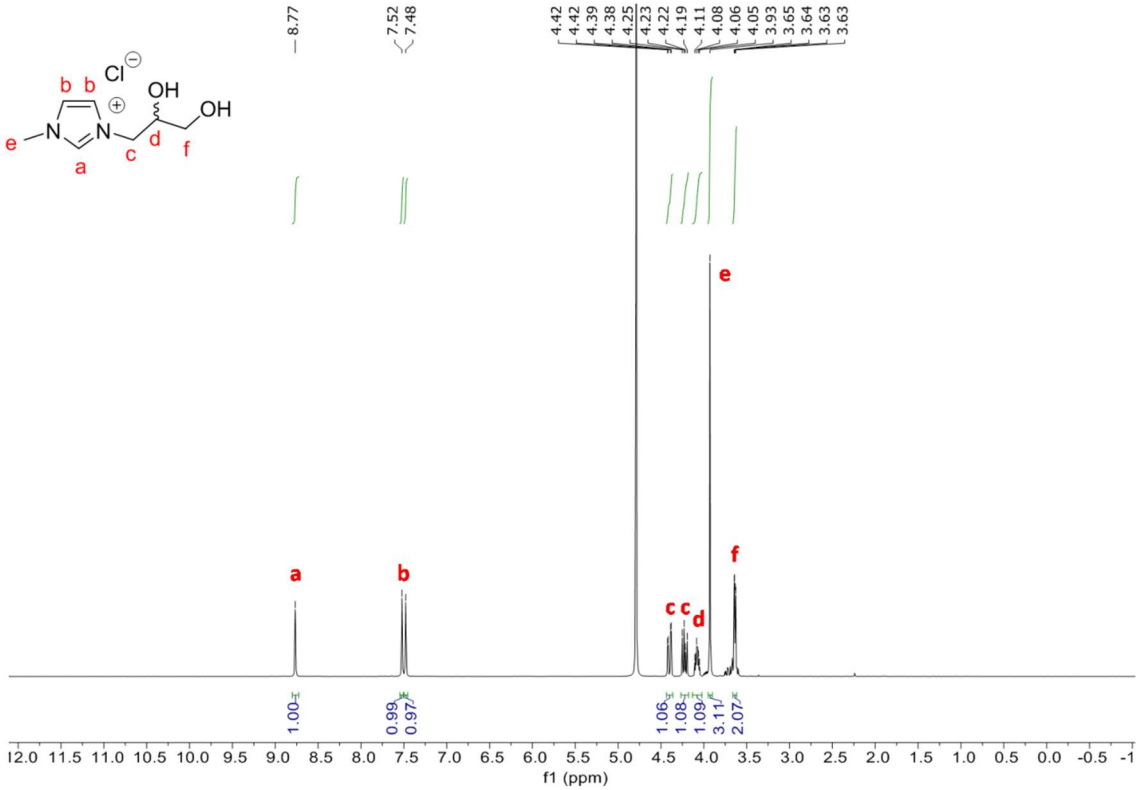
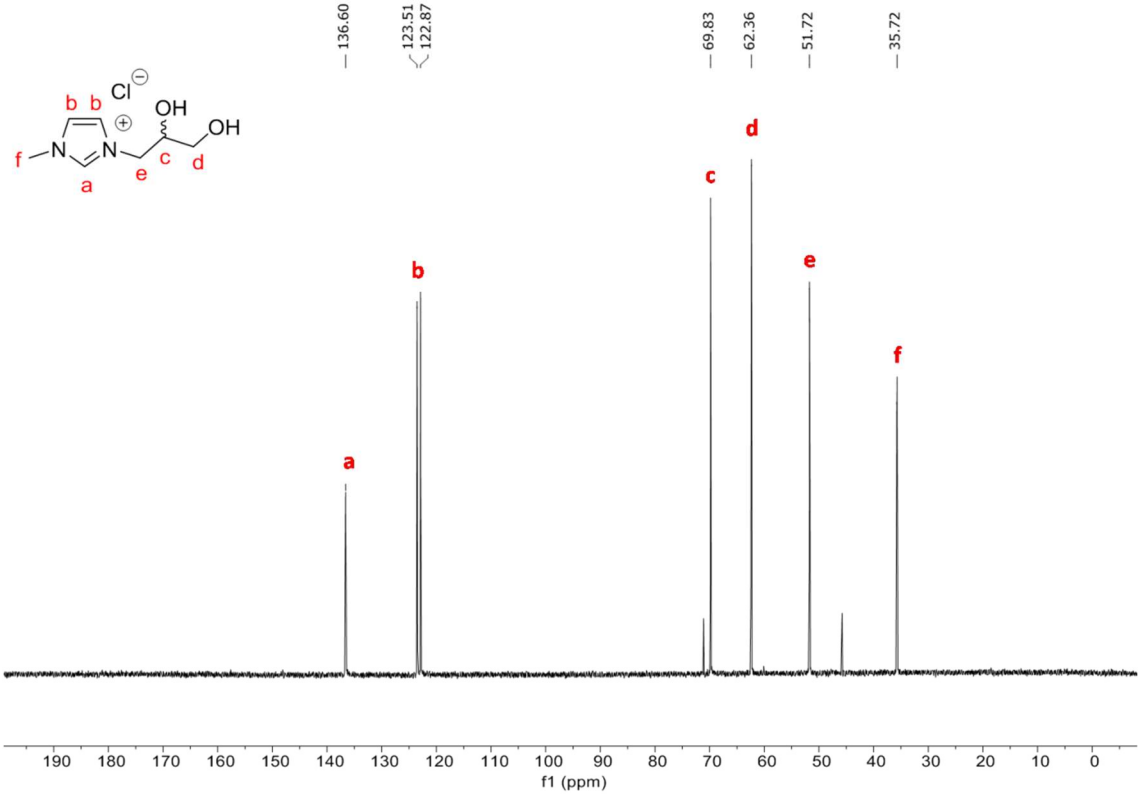


Fig. S4 ^{13}C NMR spectrum of of [***R*-diOHPrMIm]Cl** (**2**) in D_2O (101 MHz, R.T.).*



*Note that ^{1}H and ^{13}C NMR spectra of [***S*-diOHPrMIm]Cl** (**3**) are the same as those shown in figures S3 and S4.

Fig. S5 ^{1}H NMR spectrum of **[*R*-menthylMMIm]Cl** (**4**) in $CDCl_3$ (400 MHz, R.T.).

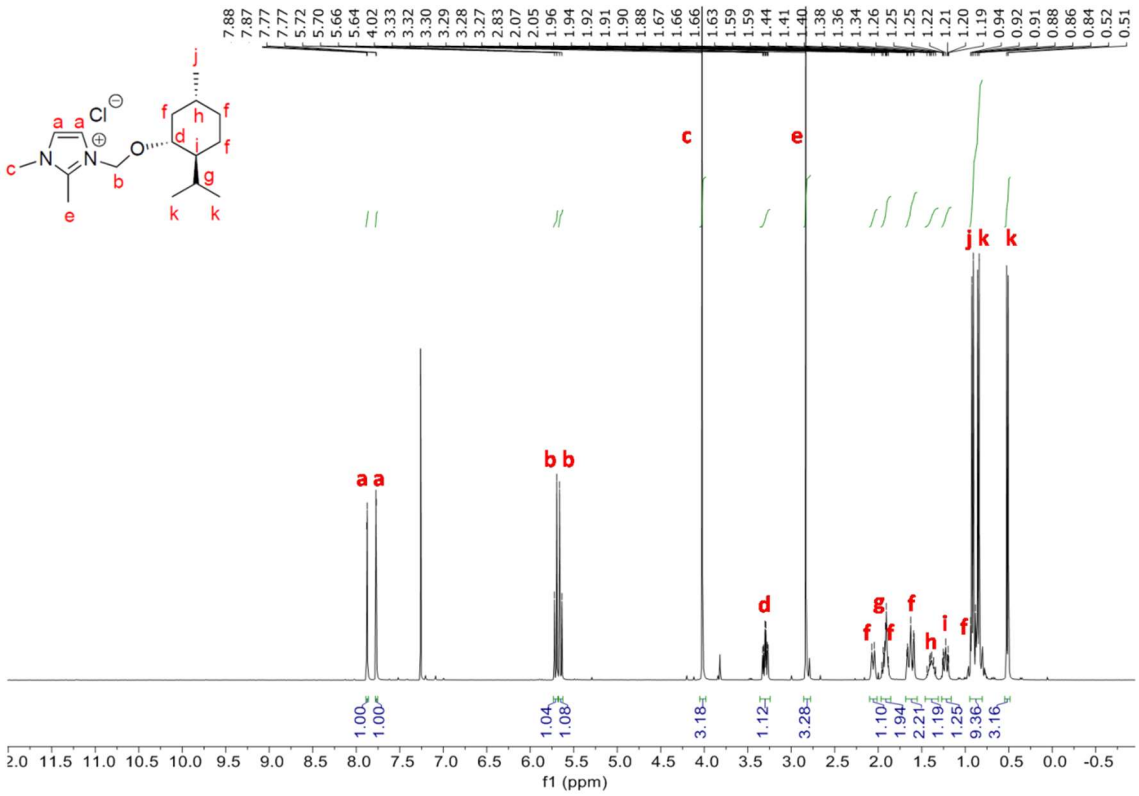
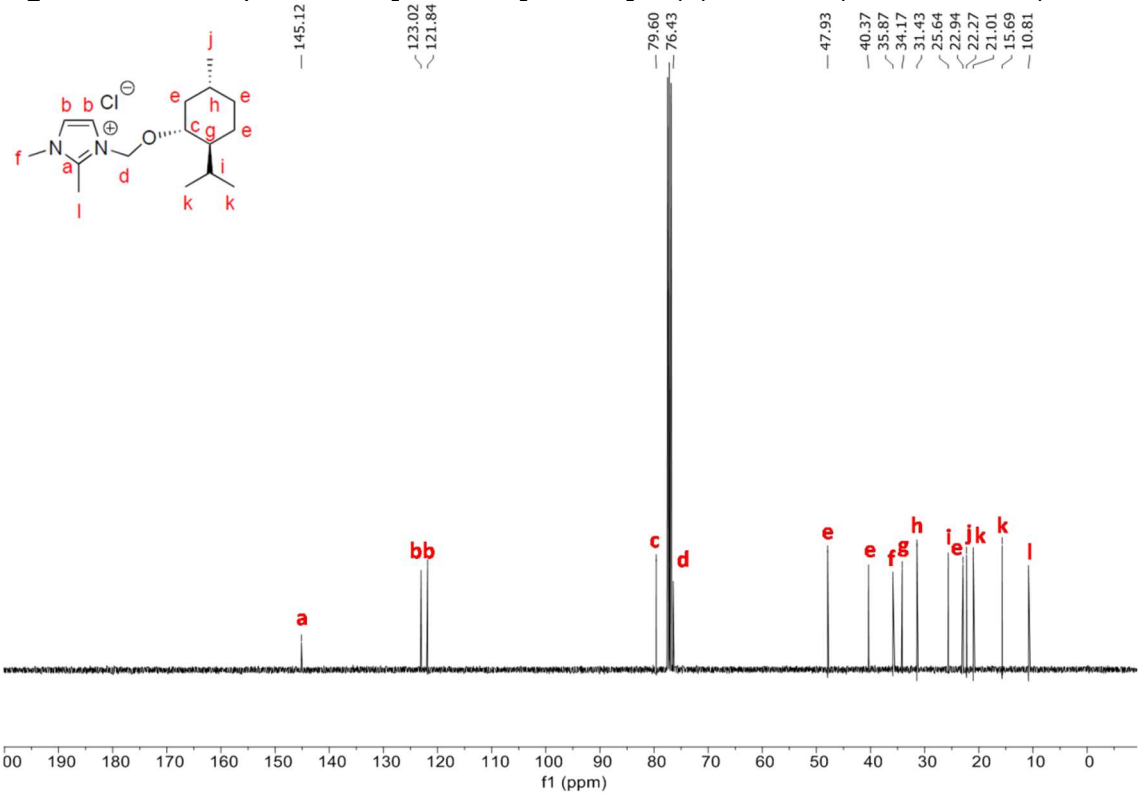


Fig. S6 ^{13}C NMR spectrum of **[*R*-menthylMMIm]Cl** (**4**) in $CDCl_3$ (101 MHz, R.T.).



2. MS SPECTRA

Fig. S7 ESI-MASS spectrum of **[*S*-methylBMMIm]Cl** (**1**) in the region 60-300.

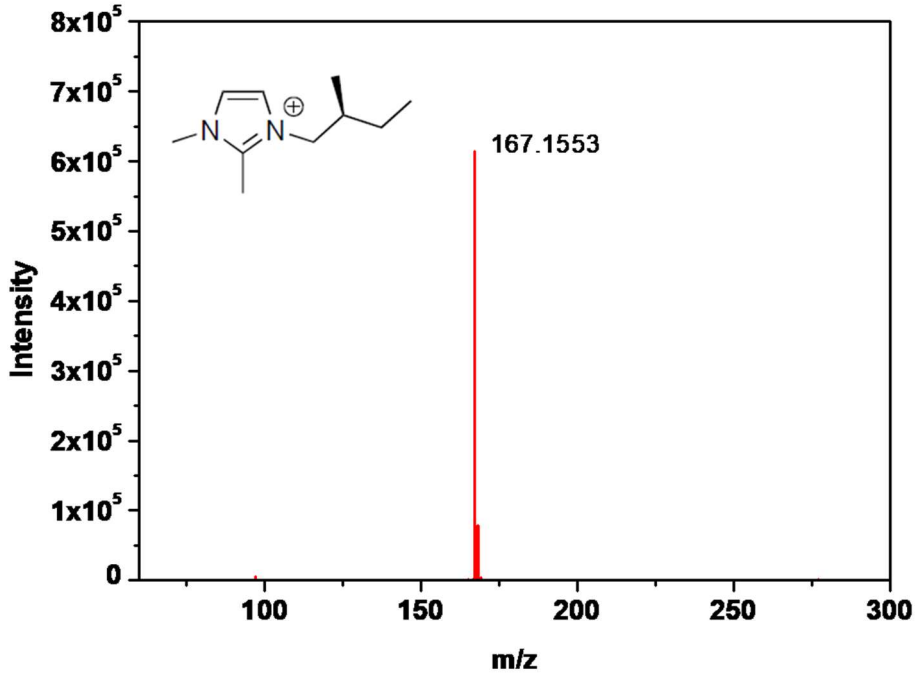
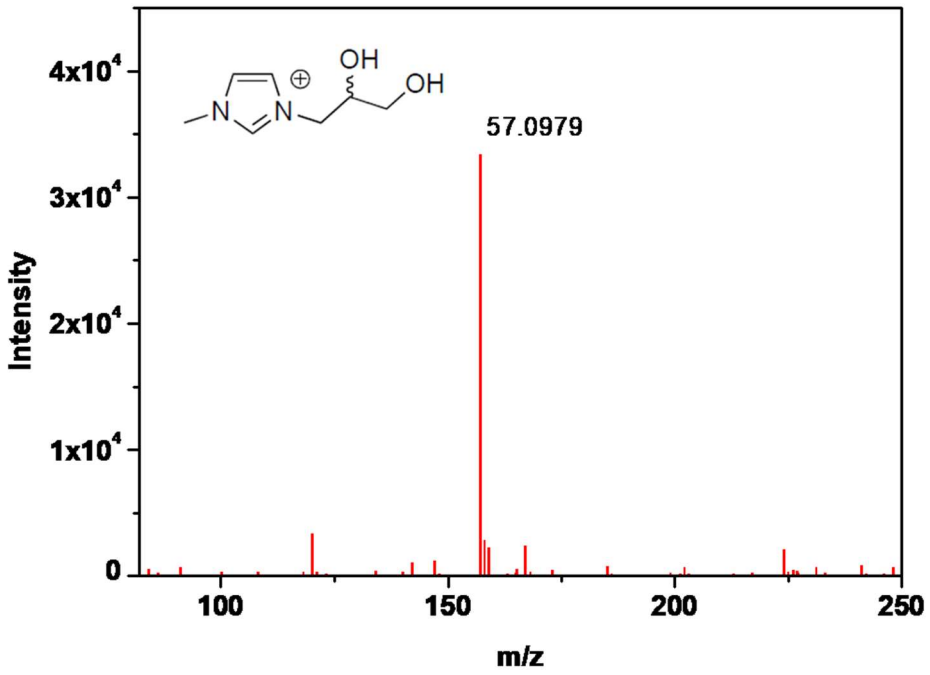


Fig. S8 ESI-MASS spectrum of [***R*-diOHPrMIm]Cl** (**2**) in the region 80-250.**



Note that the ESI-MASS spectrum of **[*S*-diOHPrMIm]Cl (**3**) is same as that shown in Figure S8.

Fig. S9 ESI-MASS spectrum of **[*R*-menthylMMIm]Cl** (**4**) in the region 150-400.

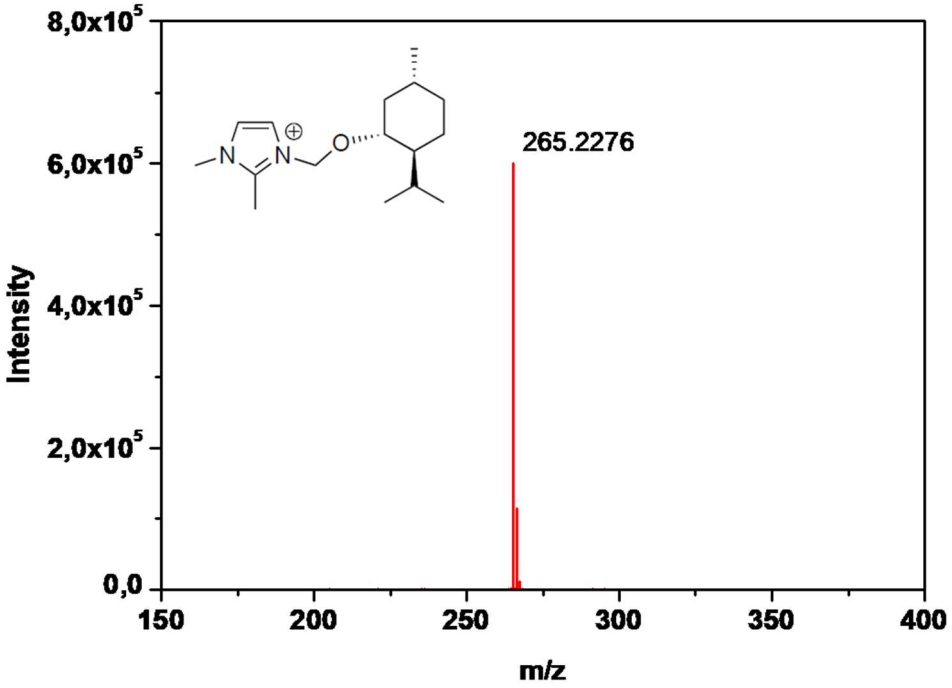


Fig. S10 ESI-MASS + spectrum of **[*S*-methylBMMIm]$FeCl_4$** (**5**) in the region 175-900.

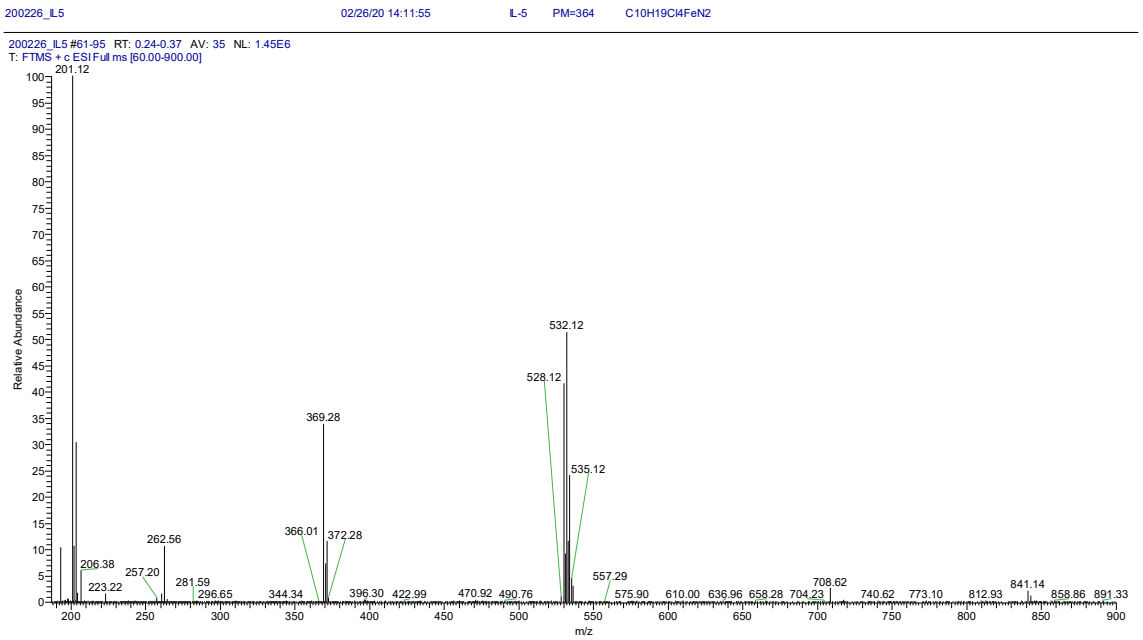


Fig. S11 ESI-MASS - spectrum of **[*S*-methylBMMIm]$FeCl_4$** (**5**) in the region 60-500.

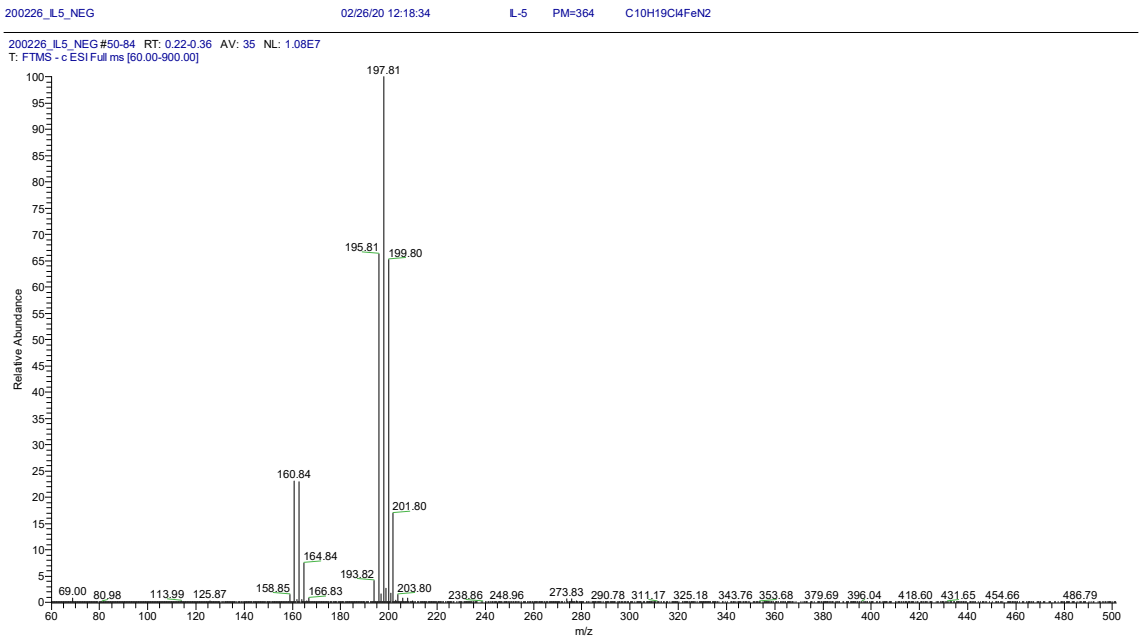
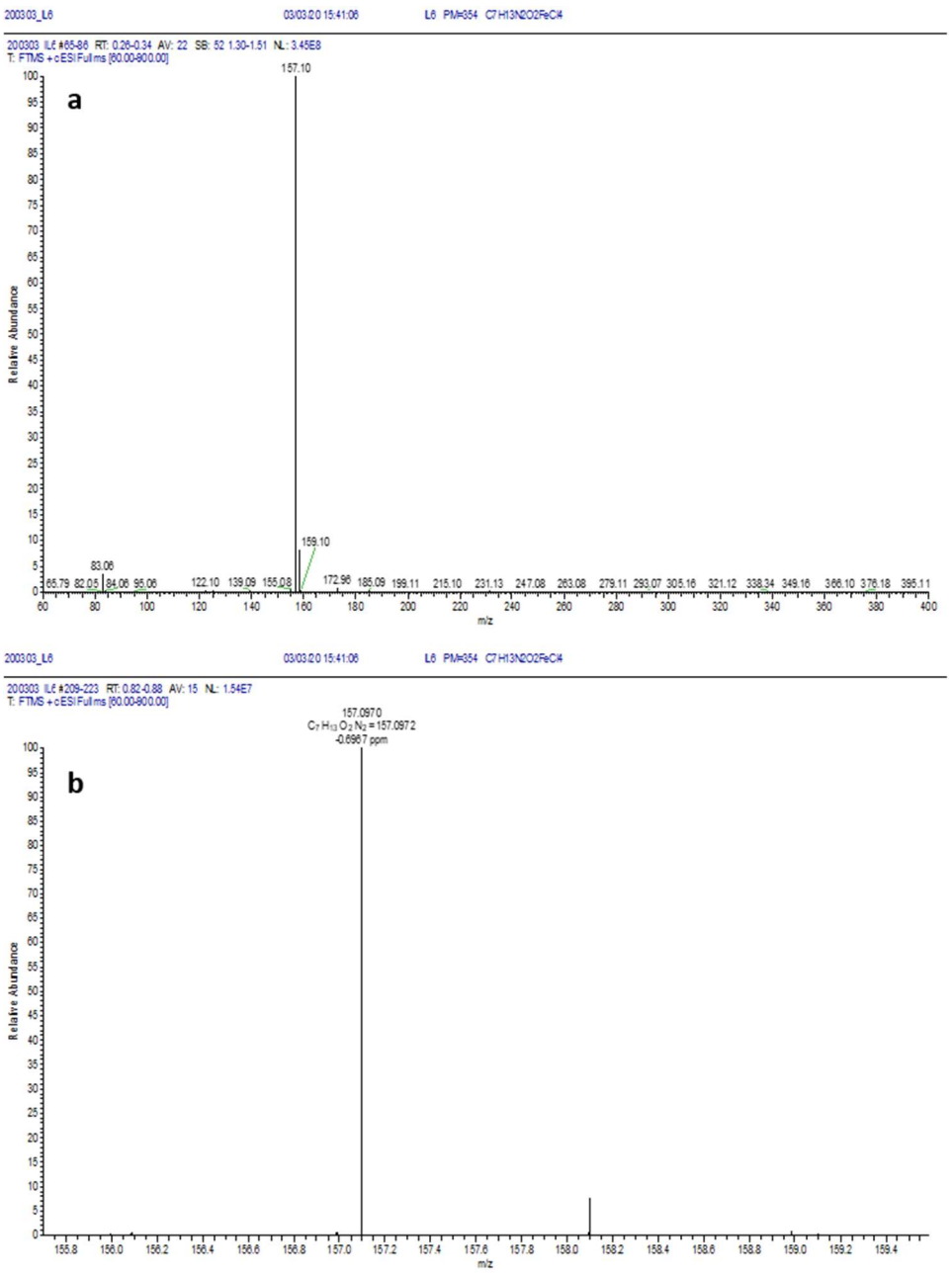
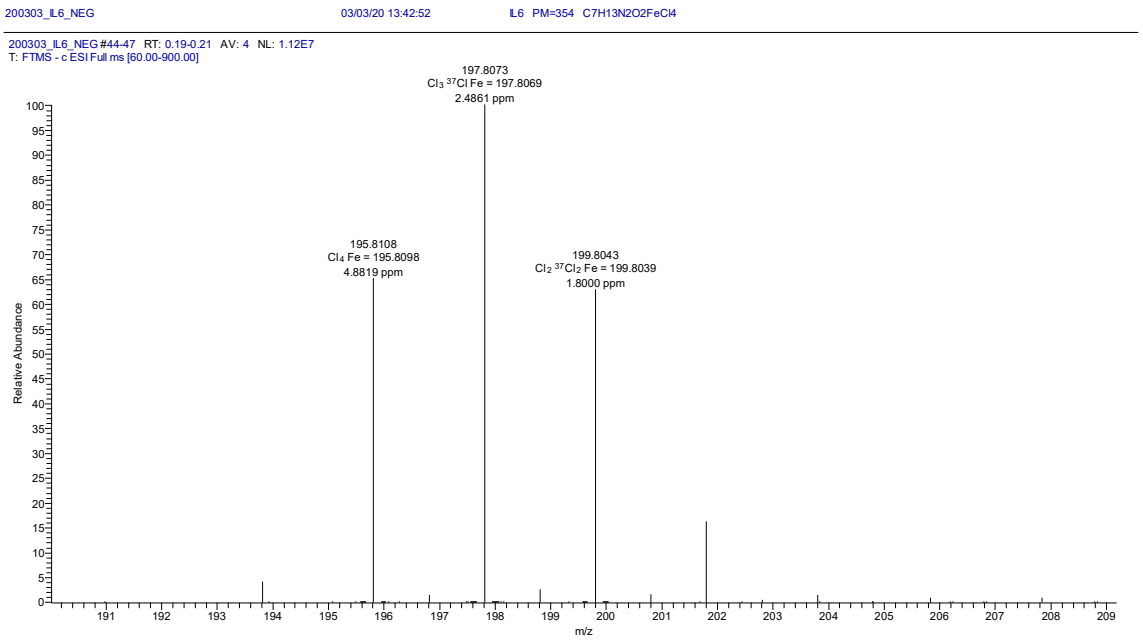


Fig. S12 ESI-MASS + spectrum of [***R*-diOHPrMIm] $FeCl_4$** (**6**): a) Low resolution in the region 60-400. b) Hight resolution in the region 155-160.



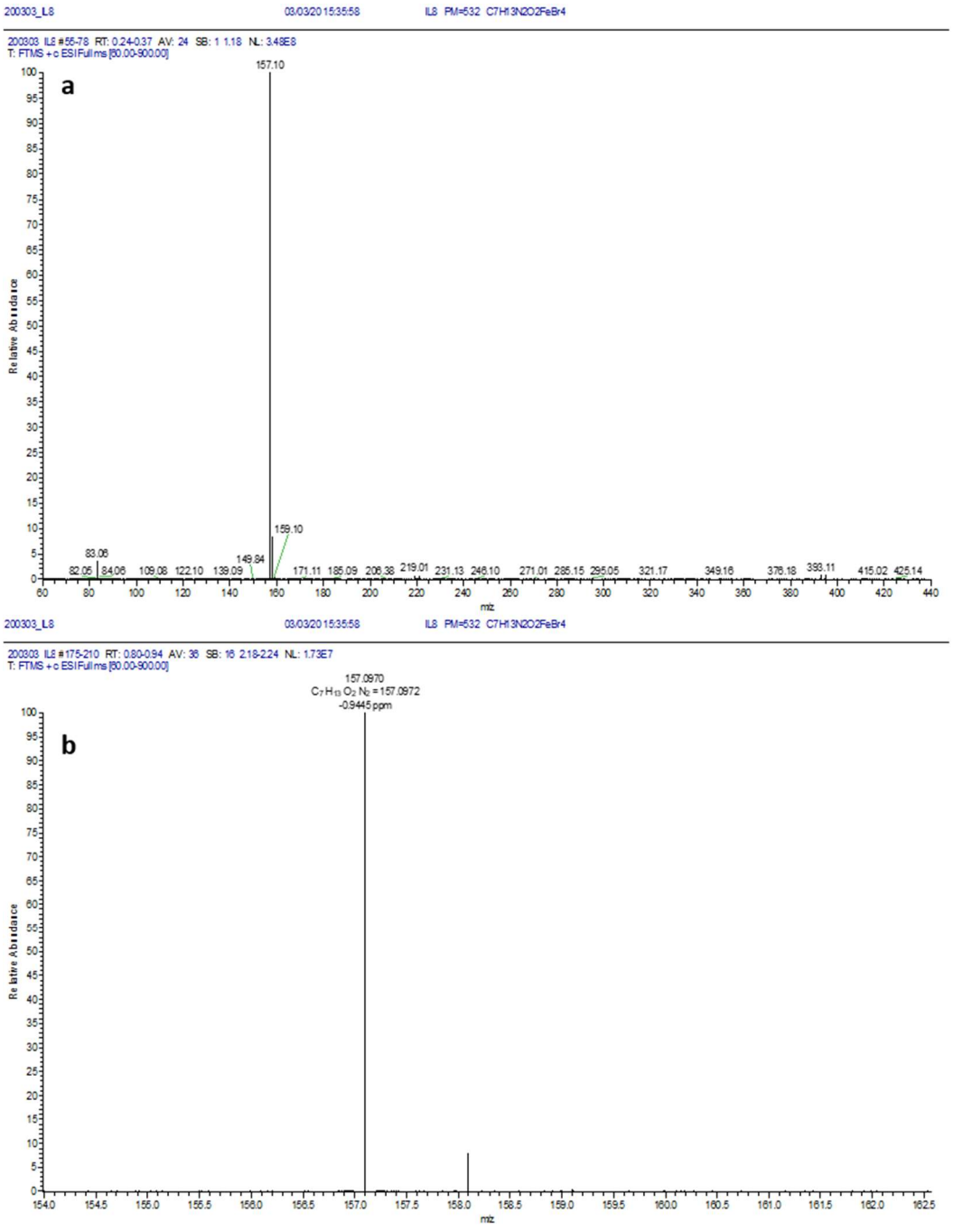
Note that the ESI-MASS + spectrum of **[*S*-diOHPrMIm]$FeCl_4$ (**7**) is same as that shown in Figure S12.

Fig. S13 ESI-MASS - spectrum of [***R*-diOHPrMIm] $FeCl_4$** (**6**) in the region 190-209.



Note that the ESI-MASS - spectrum of **[*S*-diOHPrMIm]$FeCl_4$ (**7**) is same as that shown in Figure S13.

Fig. S14 ESI-MASS + spectrum of **[*S*-diOHPrMIm]FeBr$_4$** (**8**): a) Low resolution in the region 60-440. b) Hight resolution in the region 154-163.



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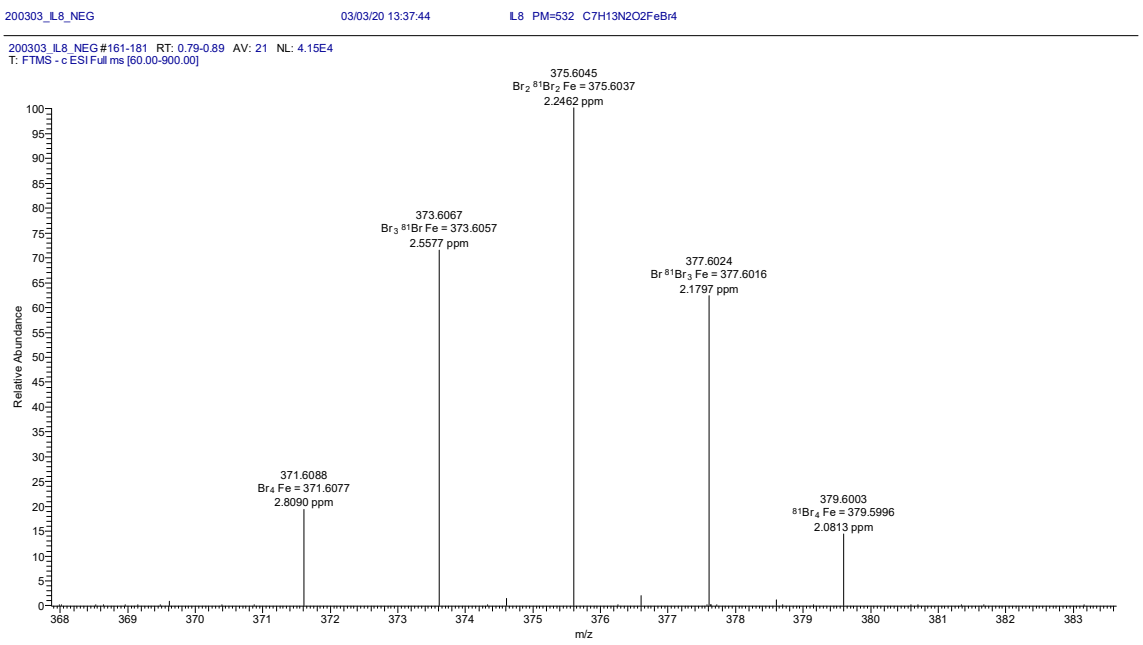

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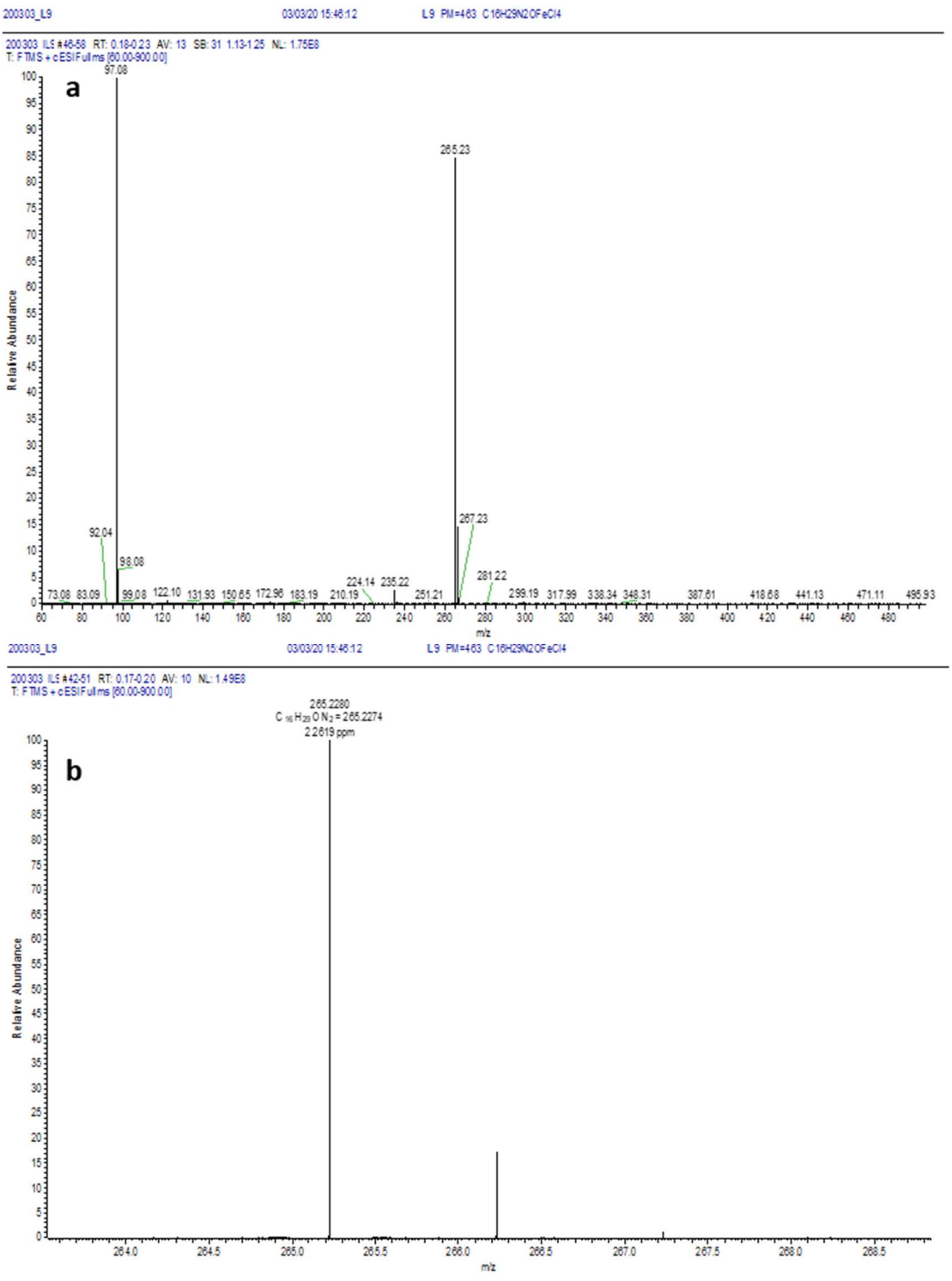

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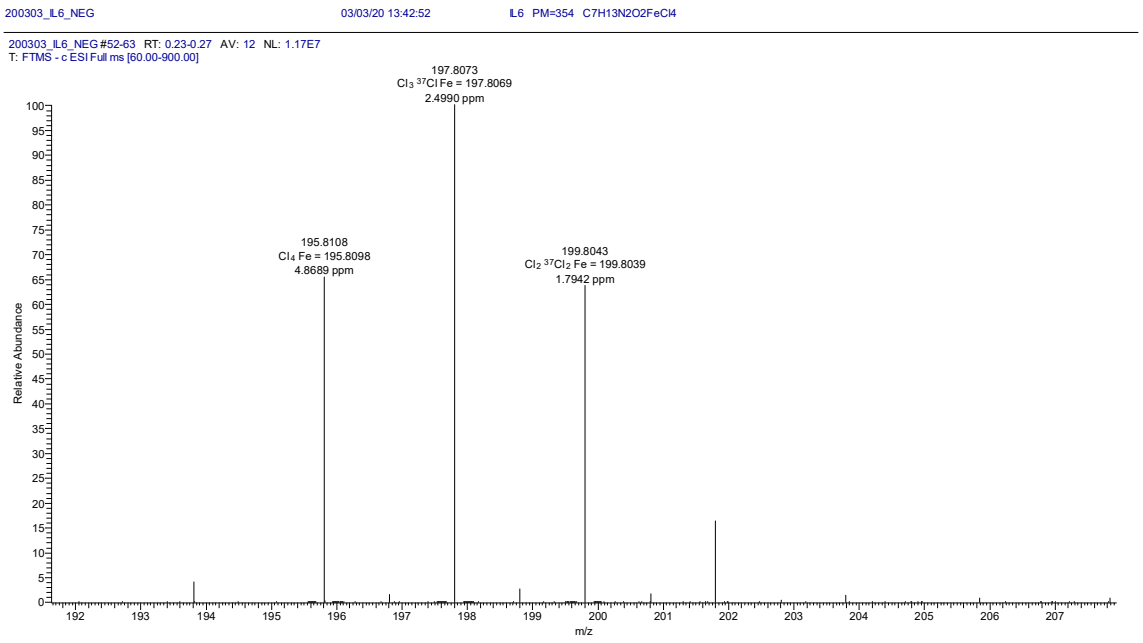


3. IR SPECTRA

Fig. S18 IR spectrum of **[*S*-methylBMMIm]Cl** (**1**).

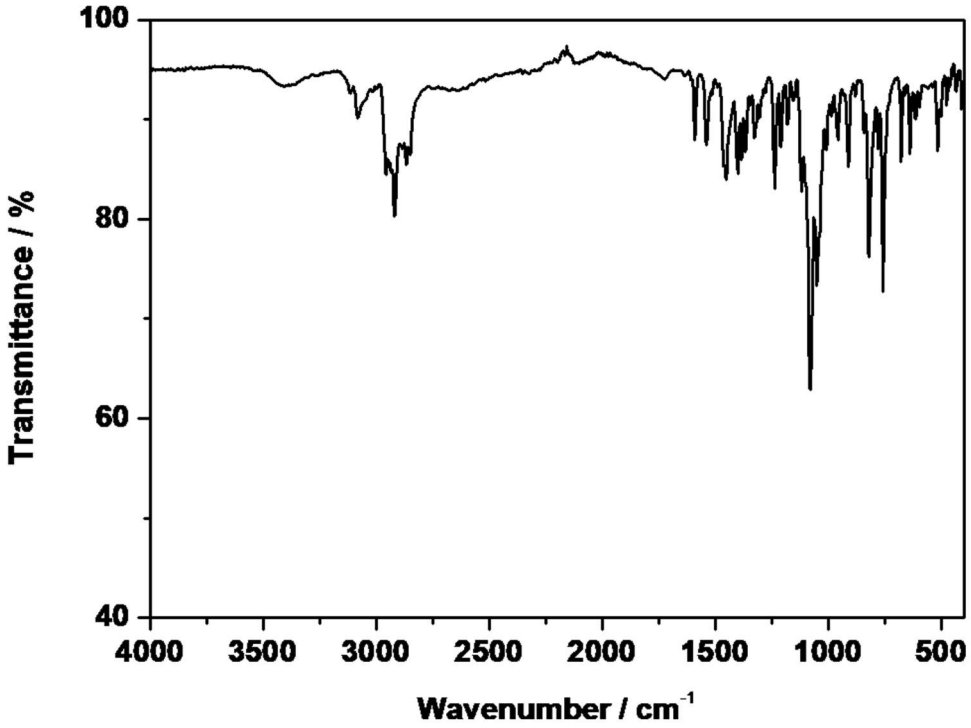
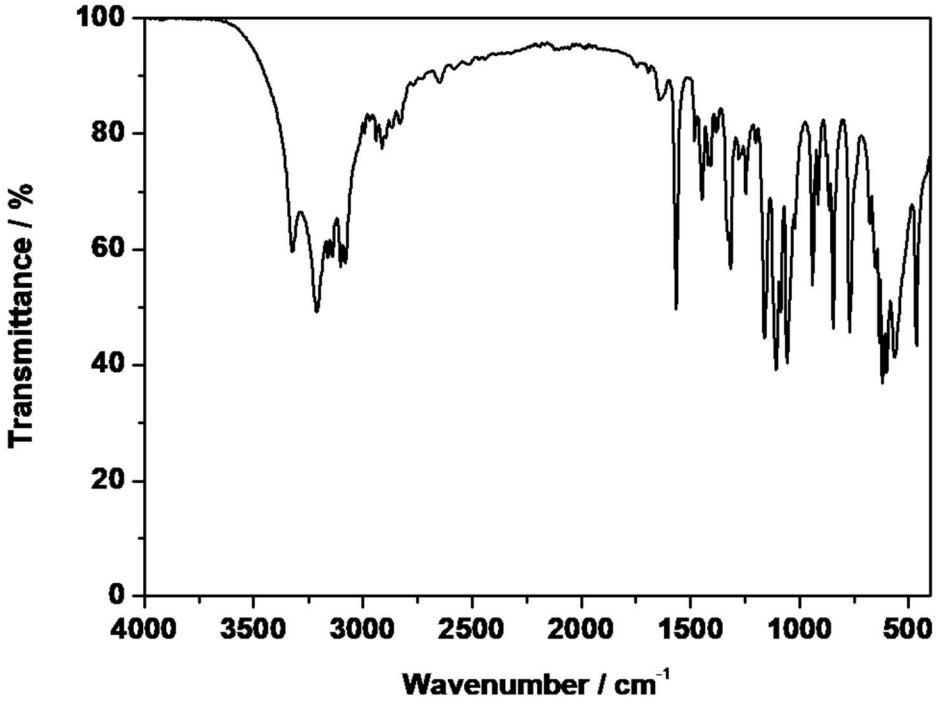


Fig. S19 IR spectrum of [***R*-diOHPrMIm]Cl** (**2**).***



***Note that IR spectrum of **[*S*-diOHPrMIm]Cl** (**3**) is same as that shown in Figure S11.

Fig. S20 IR spectrum of **[*R*-menthylMMIm]Cl** (**4**).

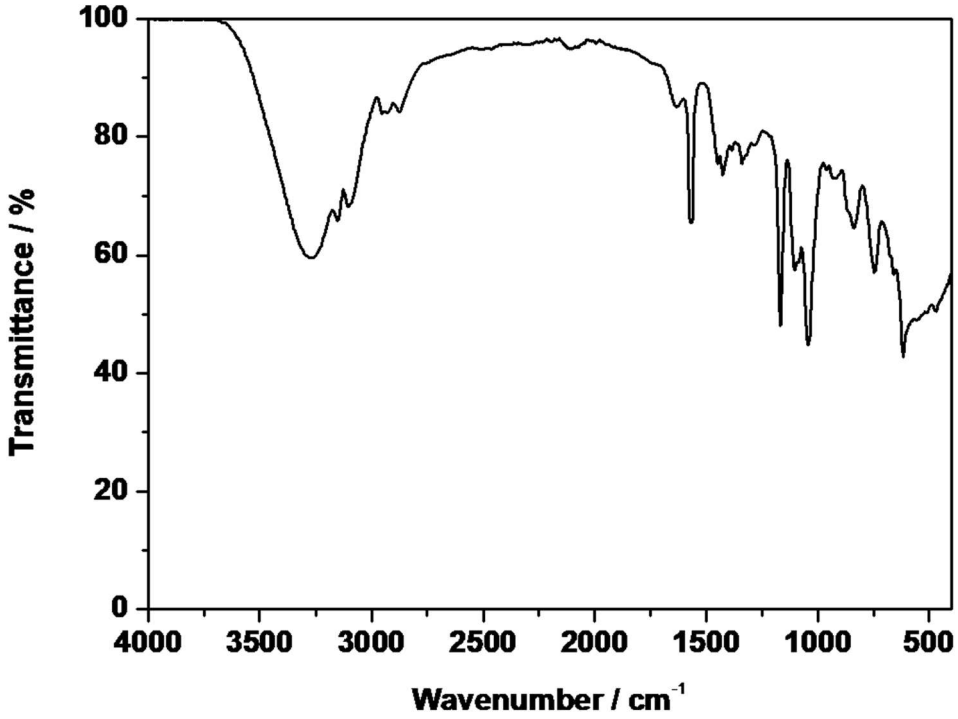


Fig. S21 IR spectrum of **[*S*-methylBMMIm]$FeCl_4$** (**5**).

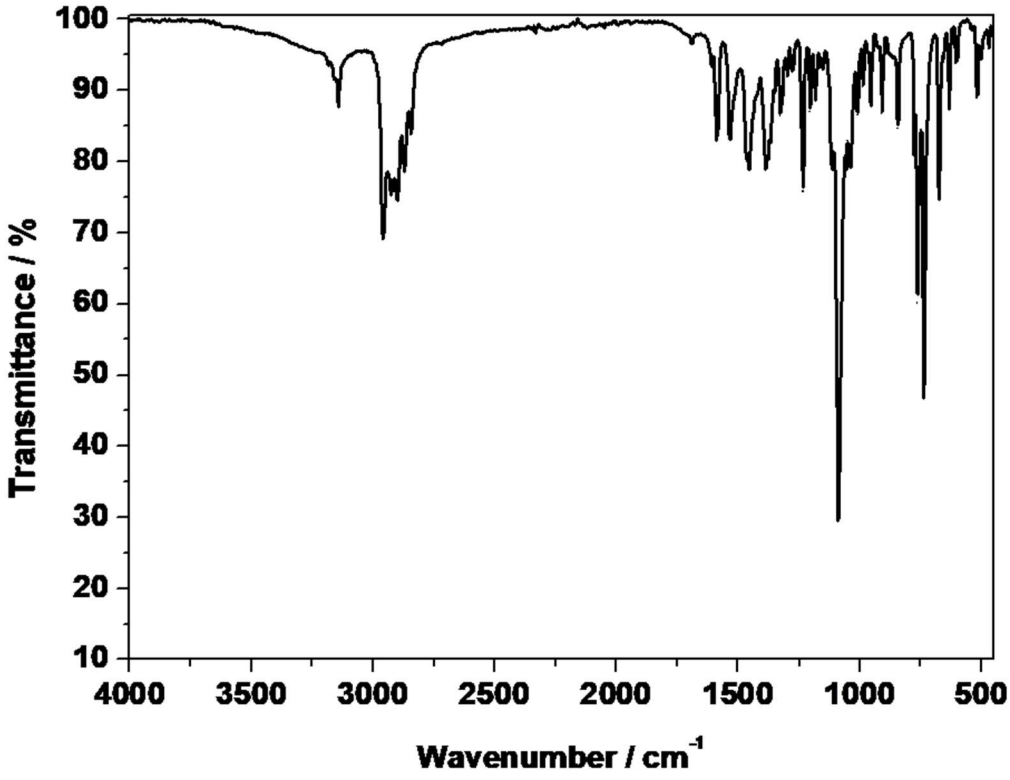


Fig. S22 IR spectrum of [***R*-diOHPrMIm]$FeCl_4$** (**6**).

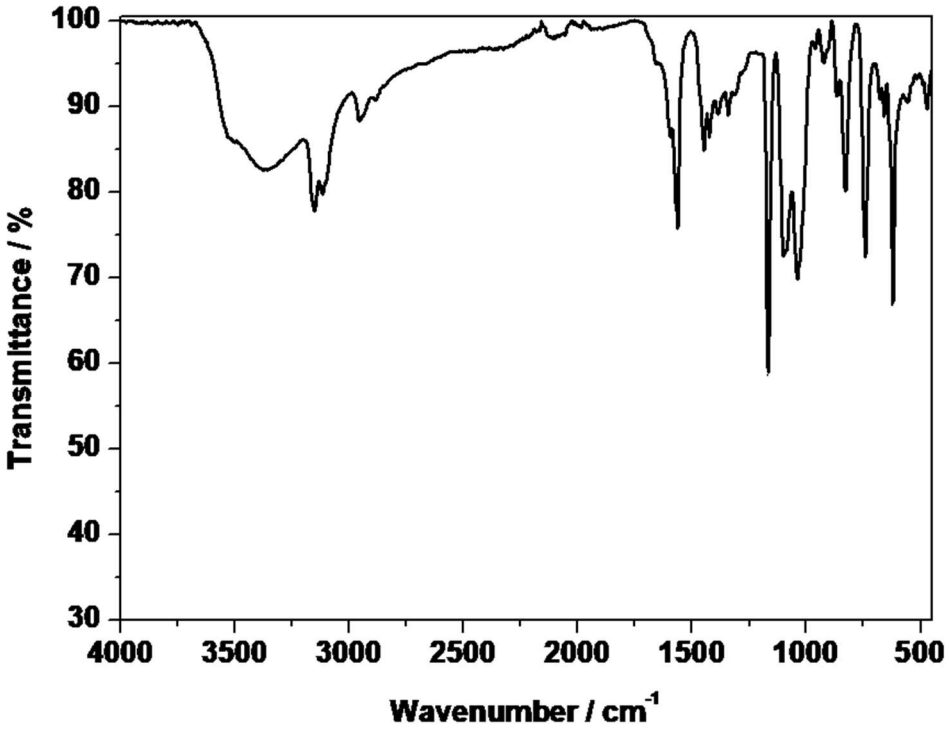


Fig. S23 IR spectrum of **[*S*-methylBMMIm]$FeCl_4$** (**7**).

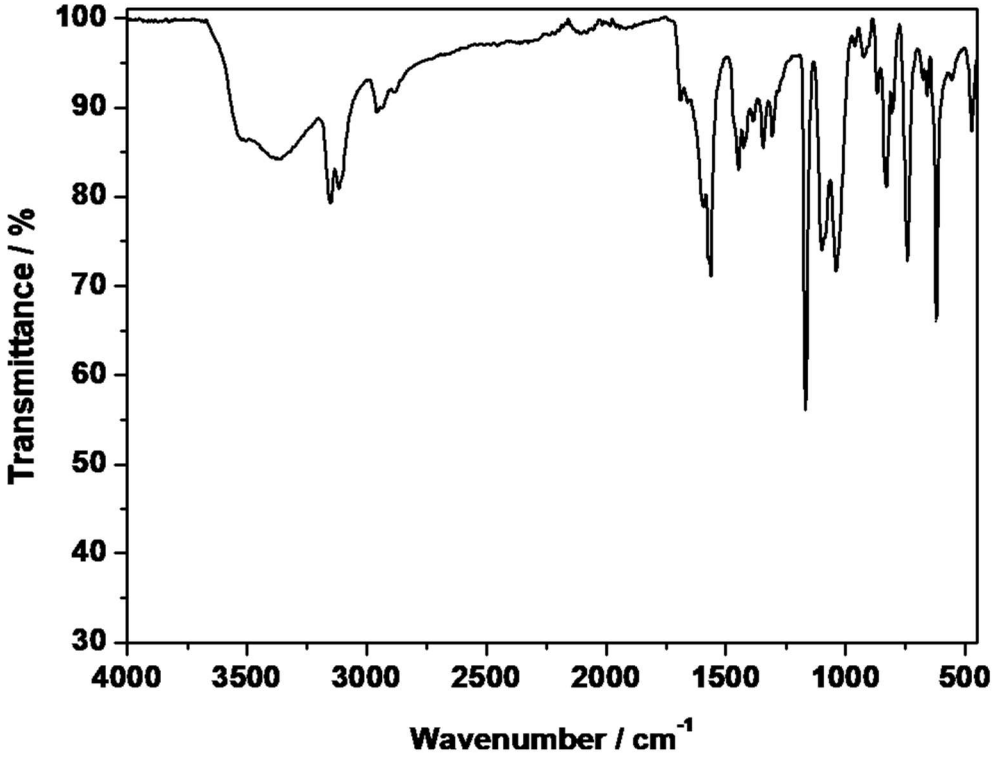


Fig. S24 IR spectrum of [***S*-diOHPrMIm]$FeBr_4$** (**8**).

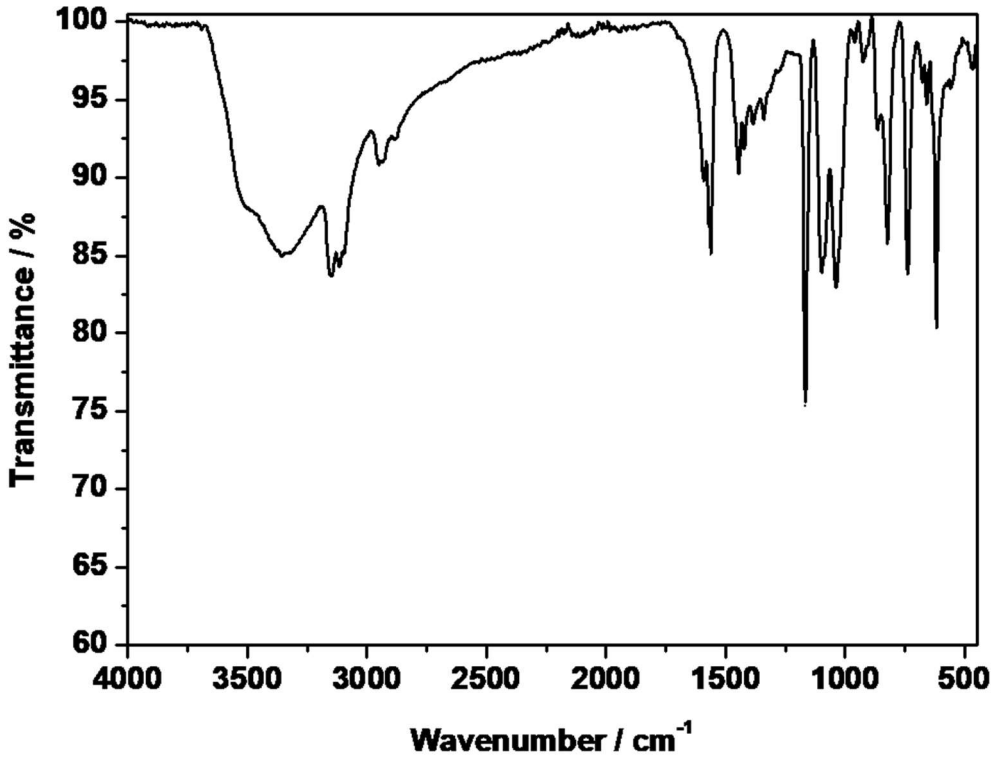
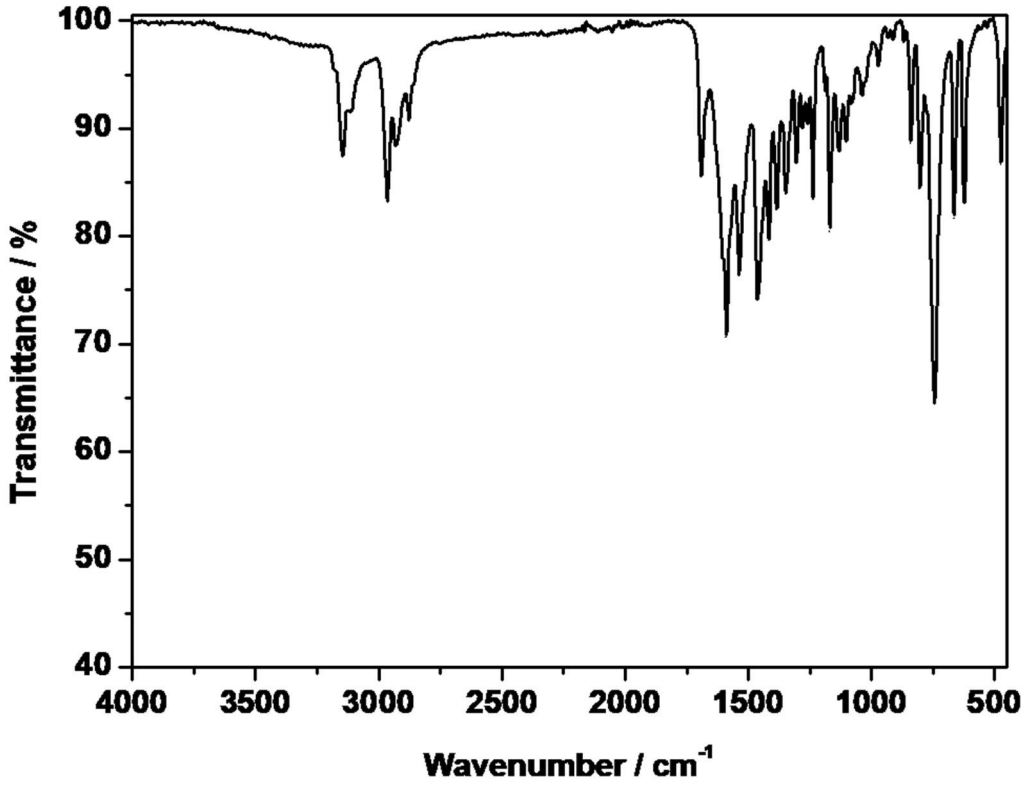


Fig. S25 IR spectrum of **[*R*-menthylMMIm]$FeCl_4$** (**9**).



4. THERMAL ANALYSIS (DSC & TGA)

Fig. S26 TGA of **[*S*-methylBMMIm]Cl** (**1**). T_d= 250 ºC at 10 % weight loss of material.

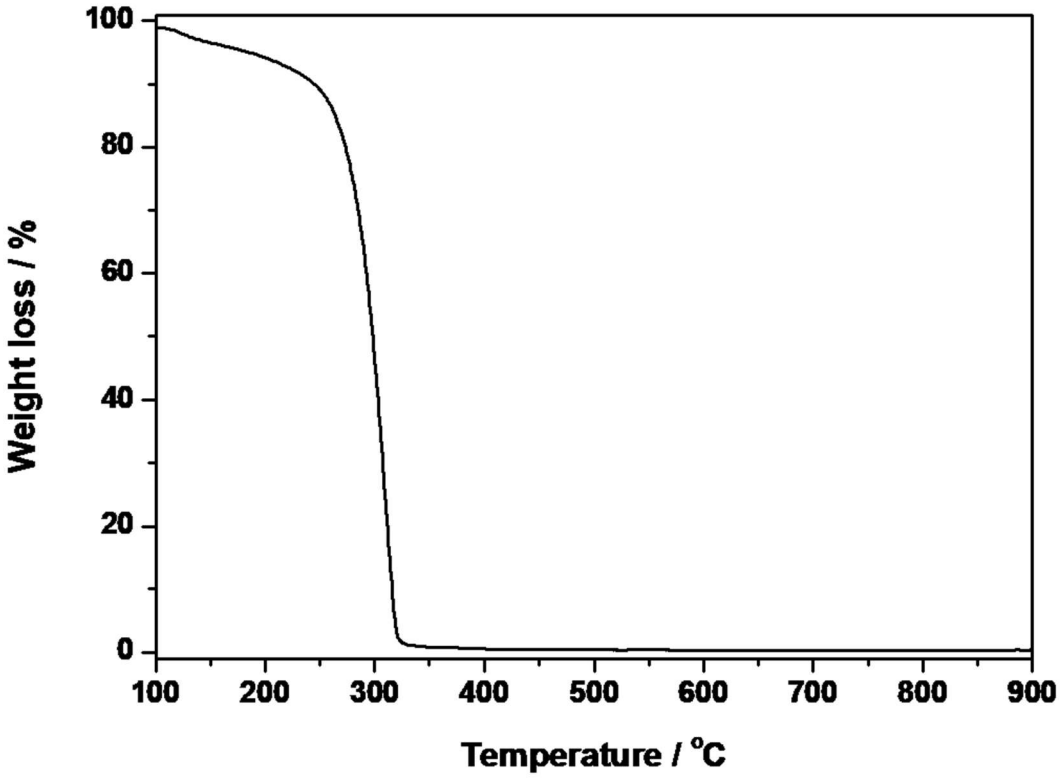


Fig. S27 TGA of [***R*-diOHPrMIm]Cl** (**2**). T_d= 300 ºC at 10 % weight loss of material.

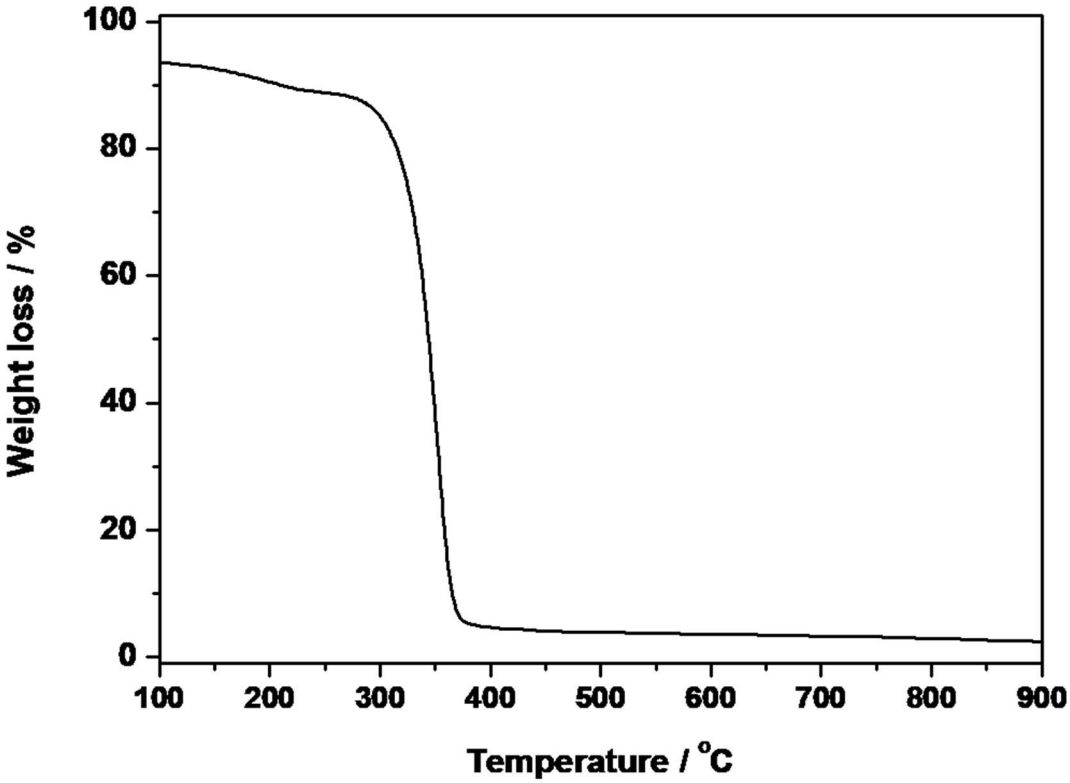


Fig. S28 TGA of [***S*-diOHPrMIm]Cl** (**3**). T_d= 280 ºC at 10 % weight loss of material.

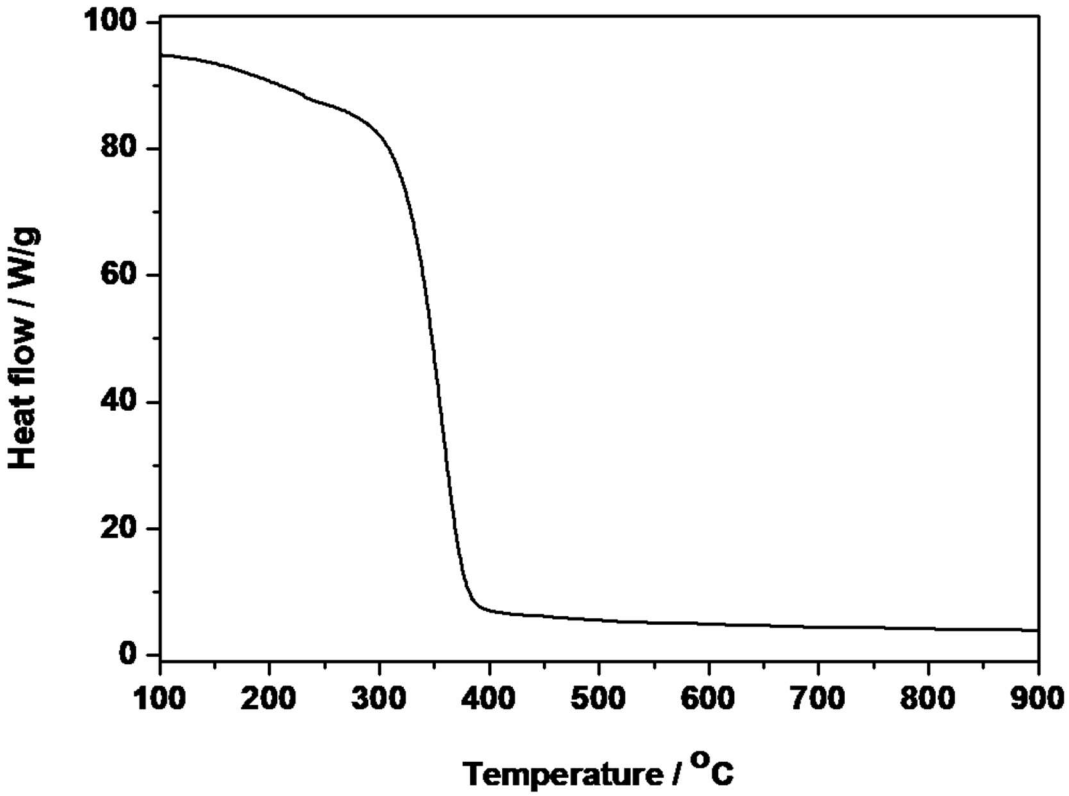


Fig. S29 TGA of **[*R*-menthylMMIm]Cl** (**4**). T_d= 212 ºC at 10 % weight loss of material.

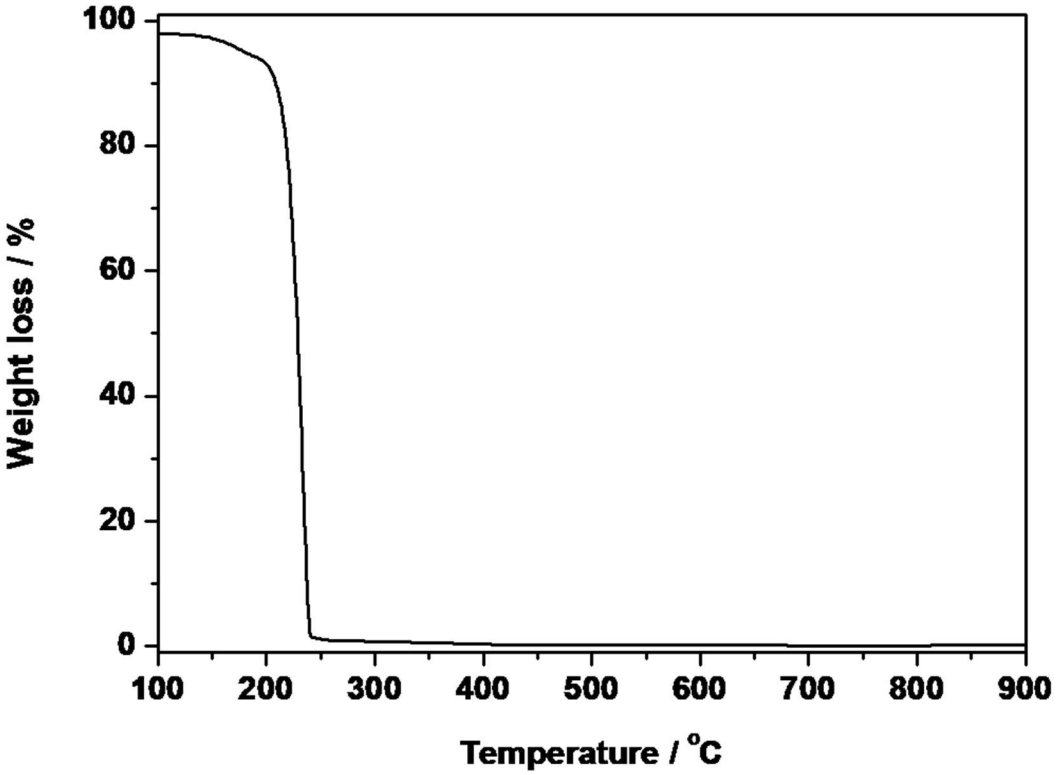


Fig. S30 TGA of **[*S*-methylBMMIm]$FeCl_4$** (**5**). T_d= 334 ºC at 10 % weight loss of material.

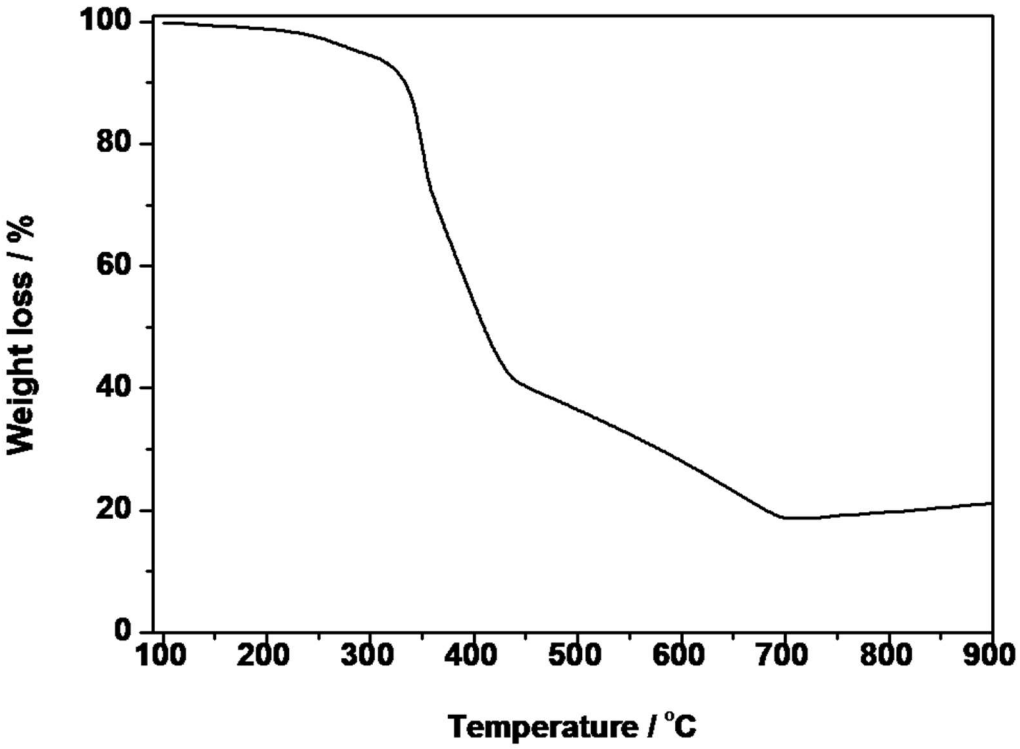


Fig. S31 DSC analysis of **[*S*-methylBMMIm]$FeCl_4$** (**5**). Traces after a first, second and third cycle. (T_g: -63.3, -63.3 and -62.7 ºC, respectively).

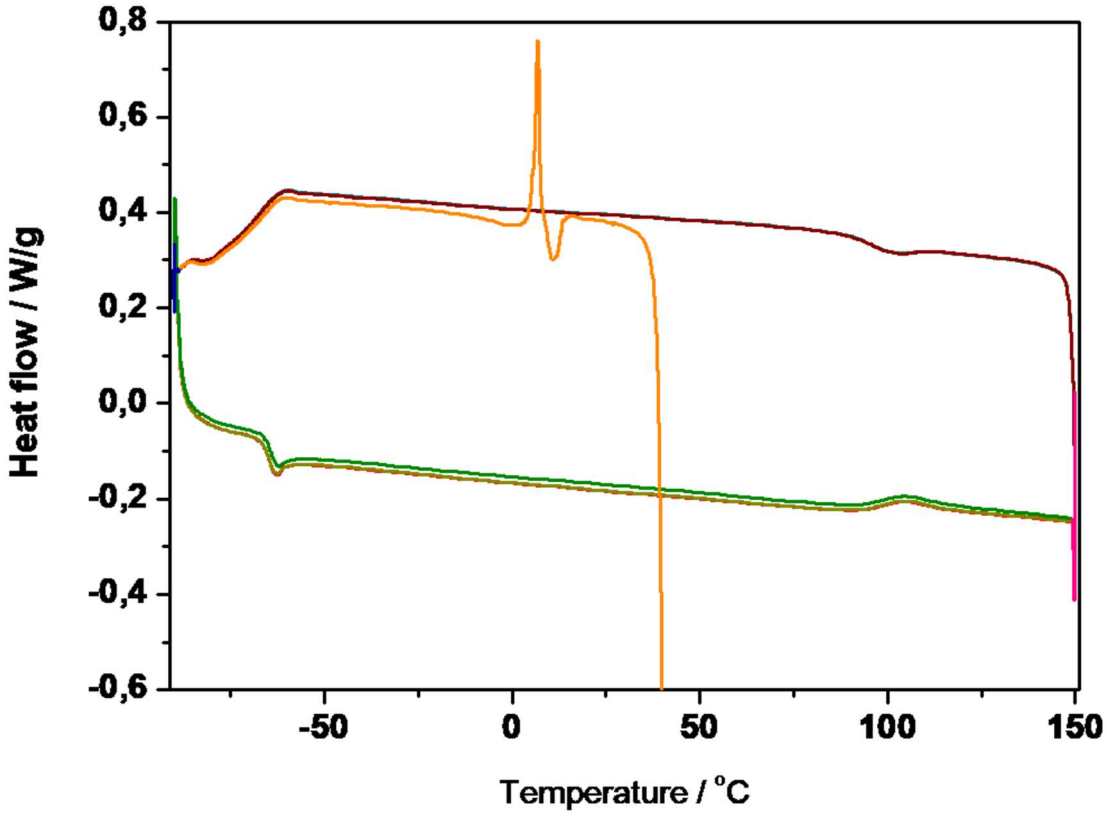


Fig. S32 TGA of [***R*-diOHPrMIm]$FeCl_4$** (**6**). T_d= 259 ºC at 10 % weight loss of material.

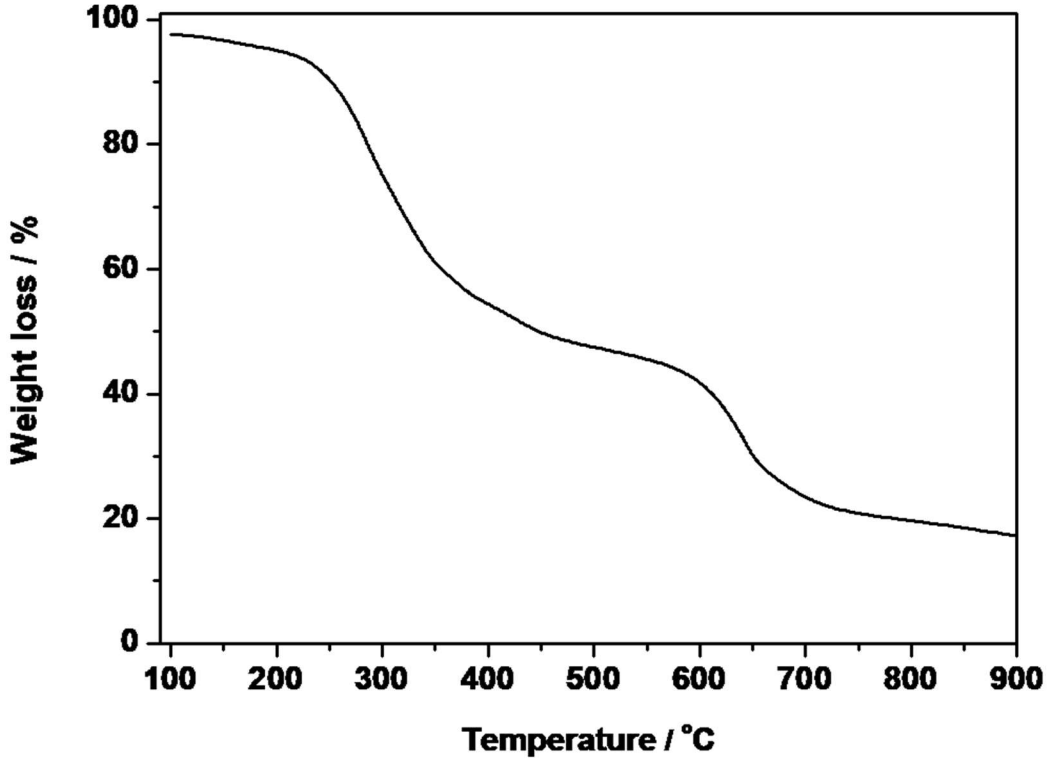


Fig. S33 DSC analysis of [***R*-diOHPrMIm]$FeCl_4$** (**6**). Traces after a first, second and third cycle. (T_g: -35.0, -34.9 and -34.8 ºC, respectively).

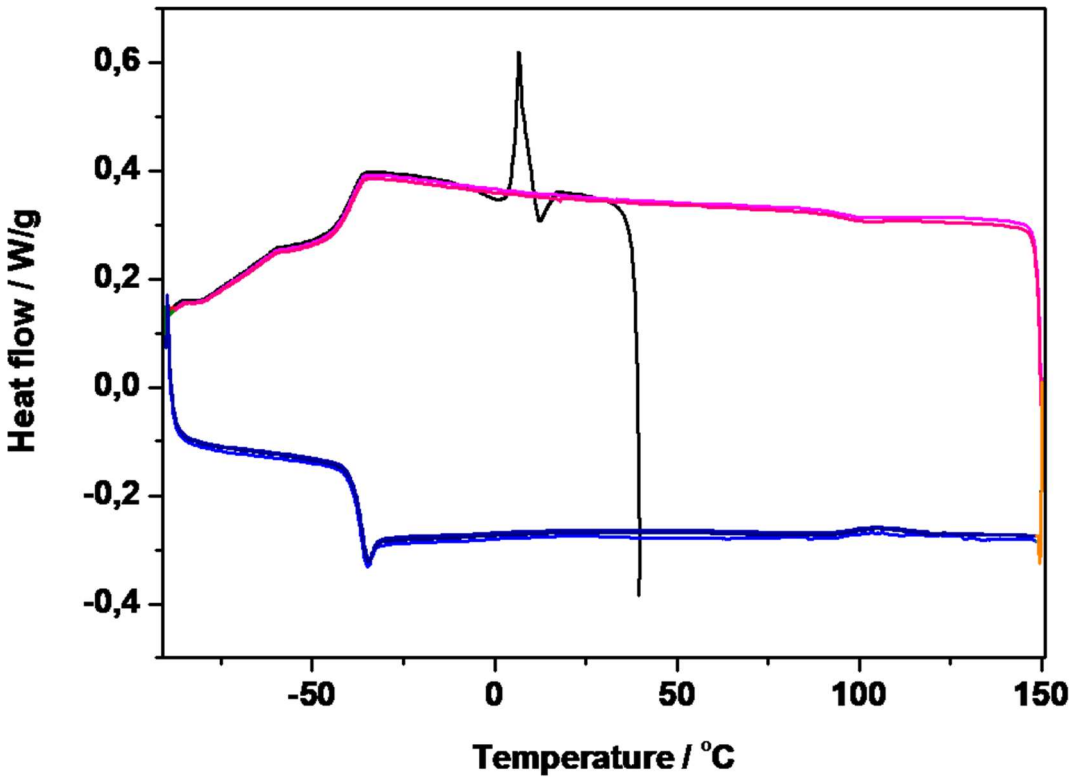


Fig. S34 TGA of [***S*-diOHPrMIm]FeCl$_4$** (**7**). T_d= 257 ºC at 10 % weight loss of material.

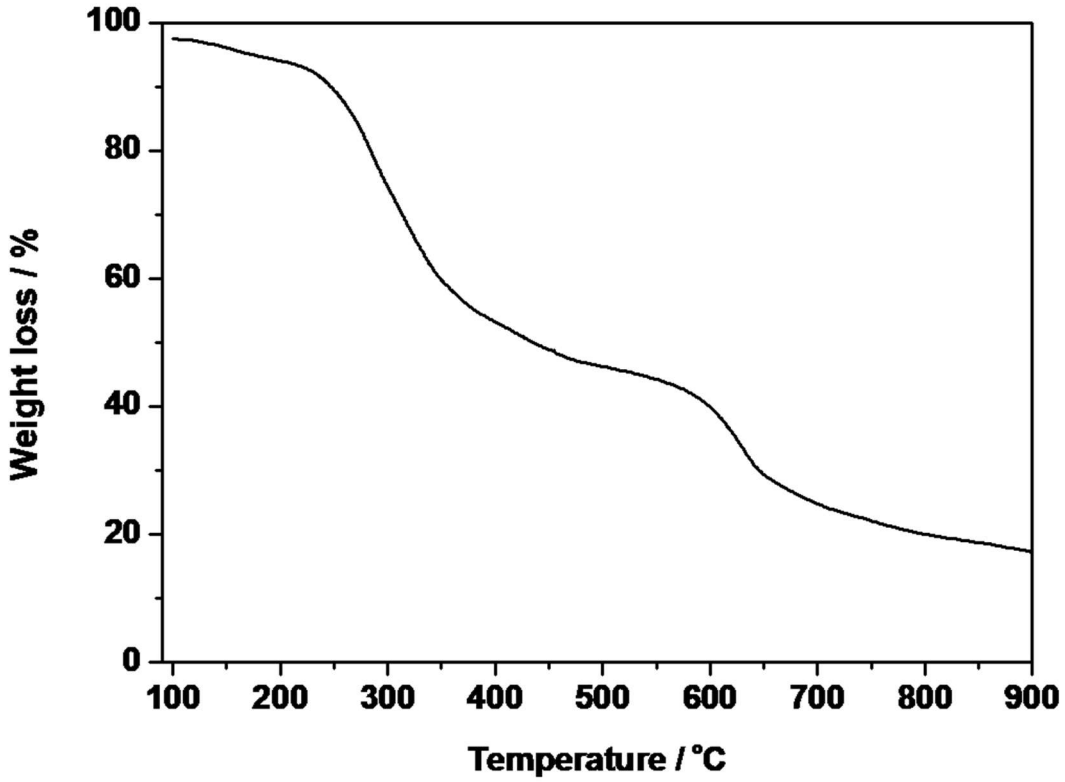


Fig. S35 DSC analysis of [***S*-diOHPrMIm]FeCl$_4$** (**7**). Traces after a first, second and third cycle. (T_g: -36.0, -33.8 and -33.7 ºC, respectively).

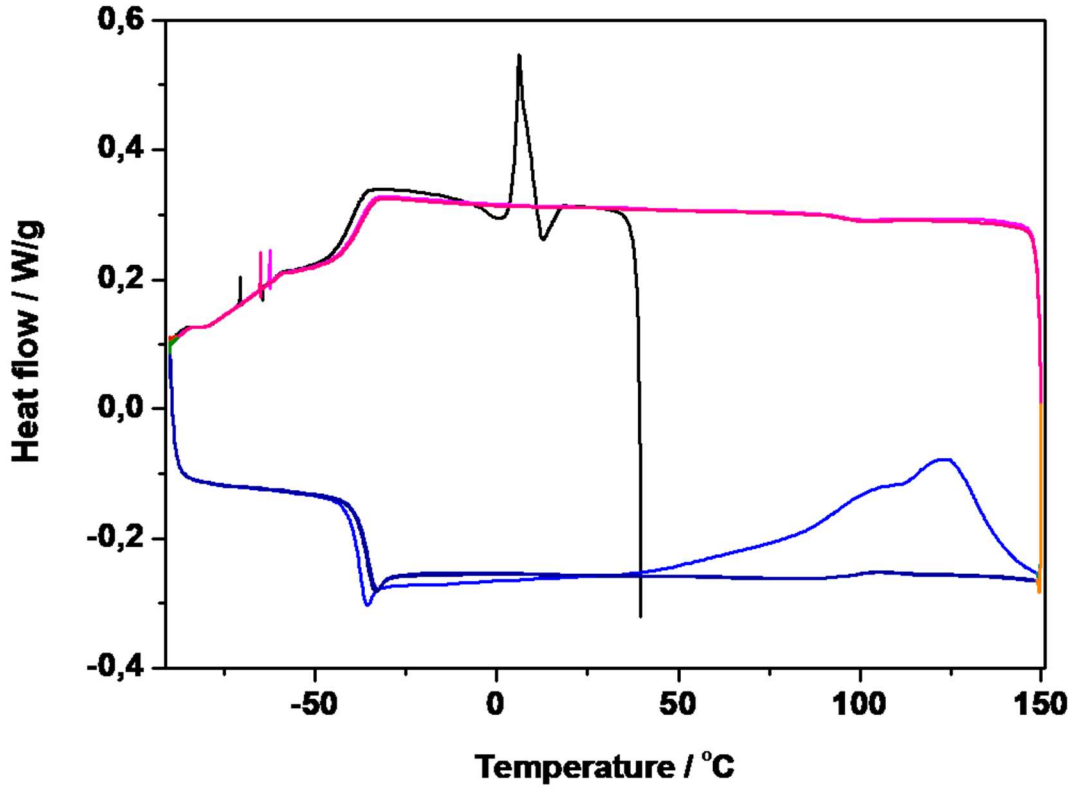


Fig. S36 TGA of [***S*-diOHPrMIm]FeBr$_4$** (**8**). T_d= 275 ºC at 10 % weight loss of material.

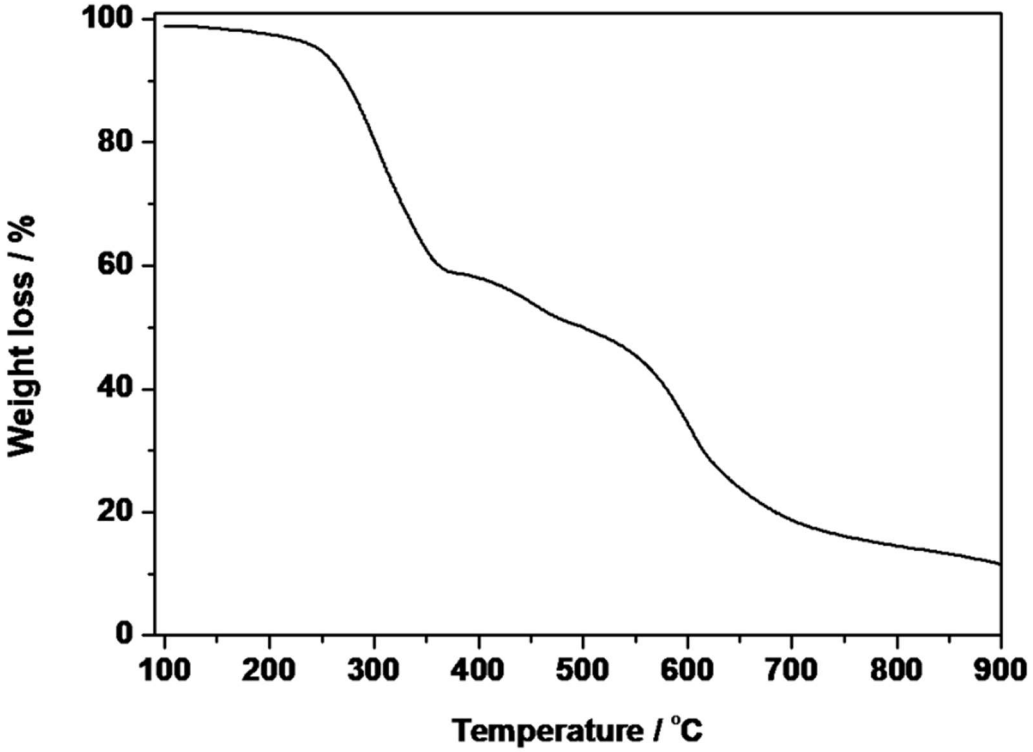


Fig. S37 DSC analysis of [***S*-diOHPrMIm]FeBr$_4$** (**8**). Traces after a first, second and third cycle. (T_g: loss of solvent, -31.7 and -30.7 ºC, respectively).

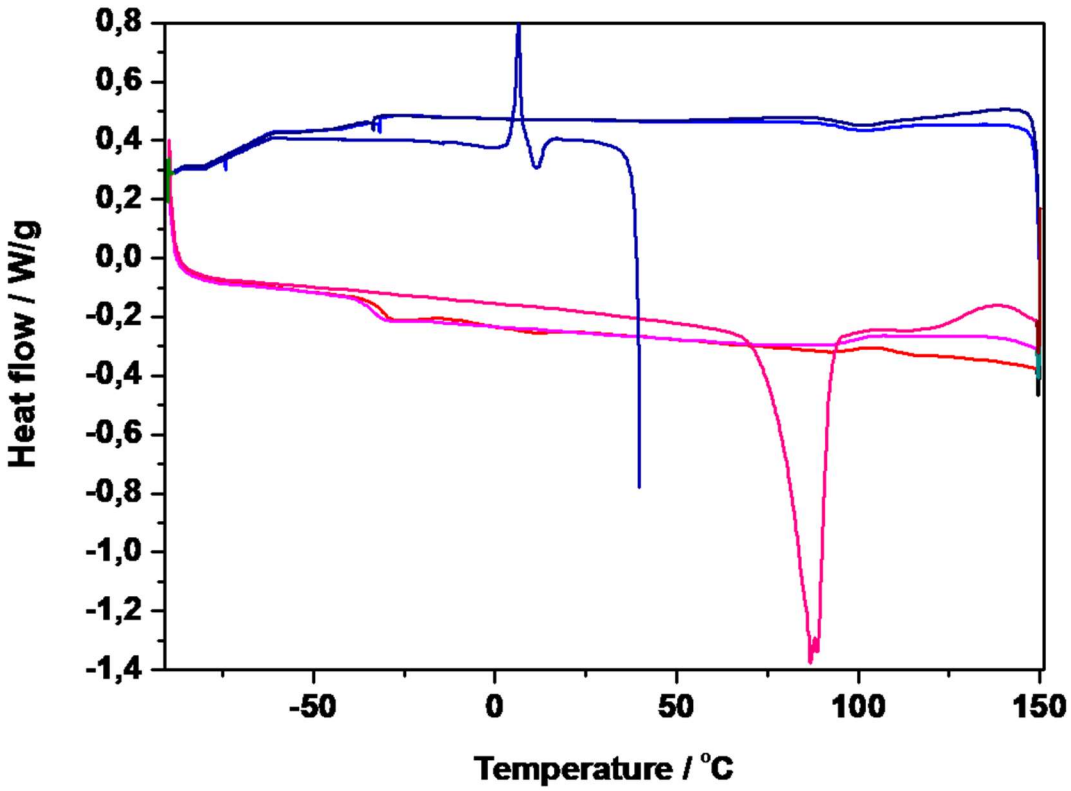


Fig. S38 TGA of **[*R*-menthylMMIm]$FeCl_4$** (**9**). T_d= 210 ºC at 10 % weight loss of material.

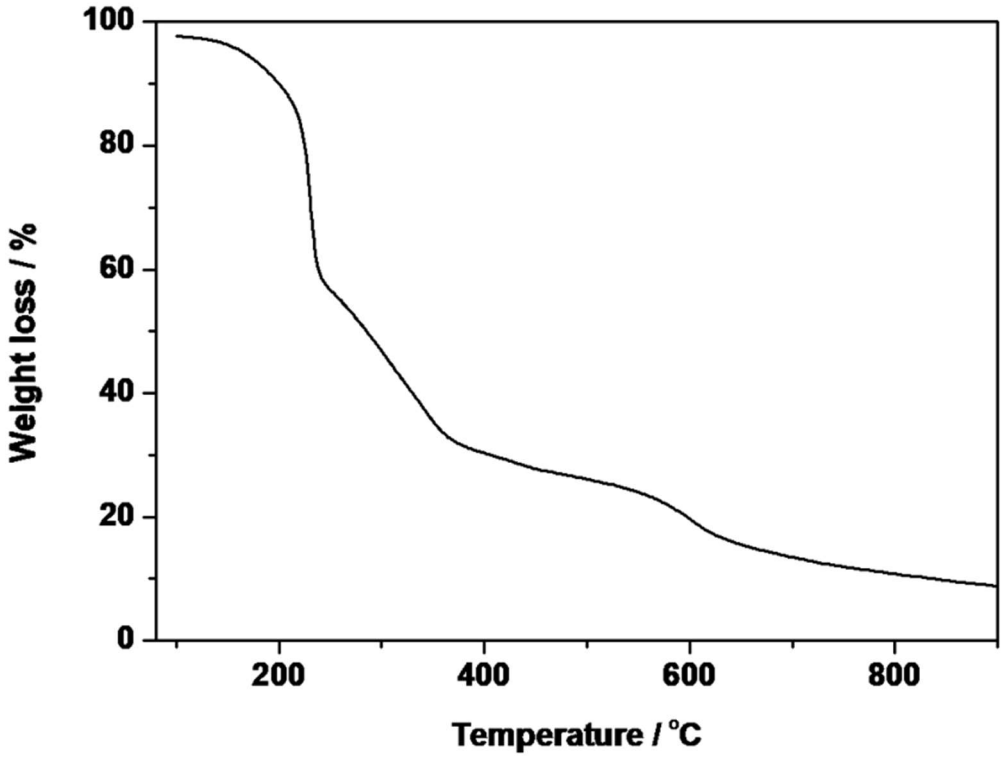
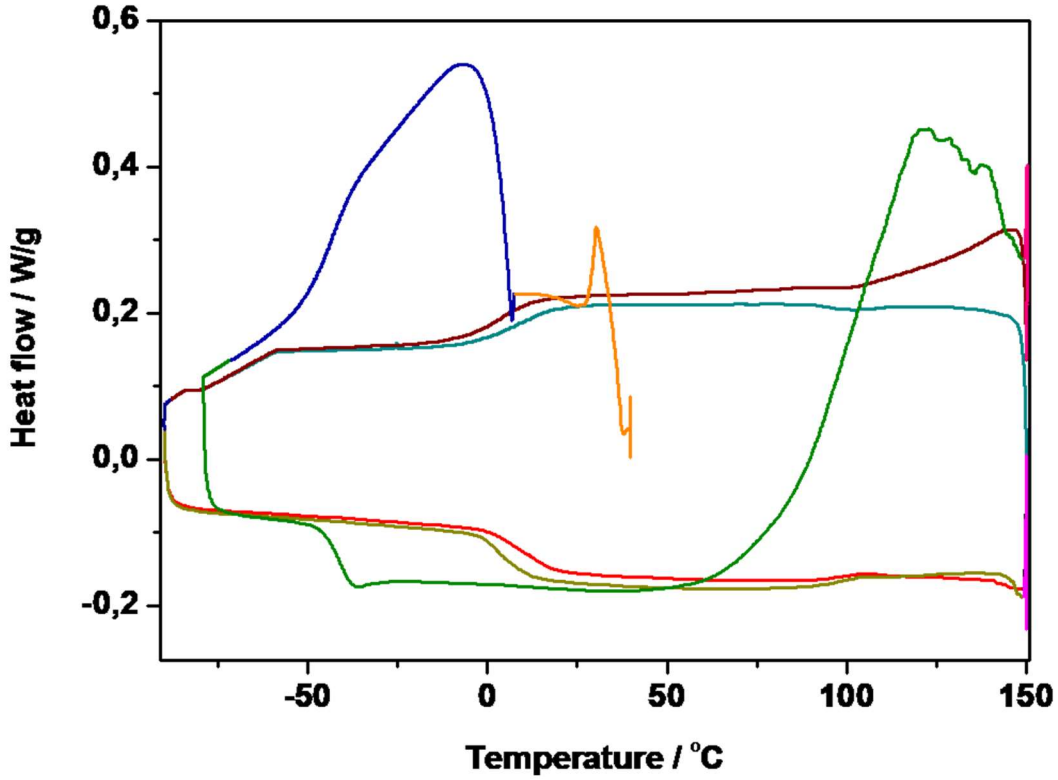


Fig. S39 DSC analysis of **[*R*-menthylMMIm]$FeCl_4$** (**9**). Traces after a first, second and third cycle. (T_g: -37.5, 8.0 and 8.0 ºC, respectively).



5. UV-VIS SPECTRA

Fig. S40 UV-Vis spectrum of **[*S*-methylBMMIm]$FeCl_4$** (**5**) in DMF at 25 ºC. [**5**] = 0.07 mM.

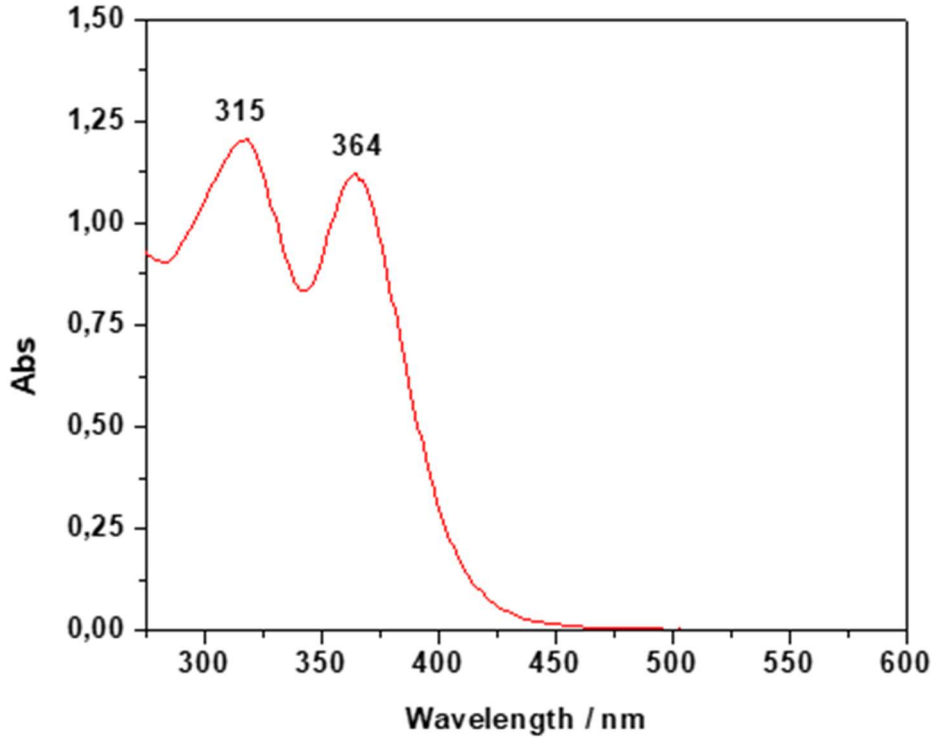


Fig. S41 UV-Vis spectrum of [***R*-diOHPrMIm]$FeCl_4$** (**6**) in DMF at 25 ºC. [**6**] = 0.01 mM.

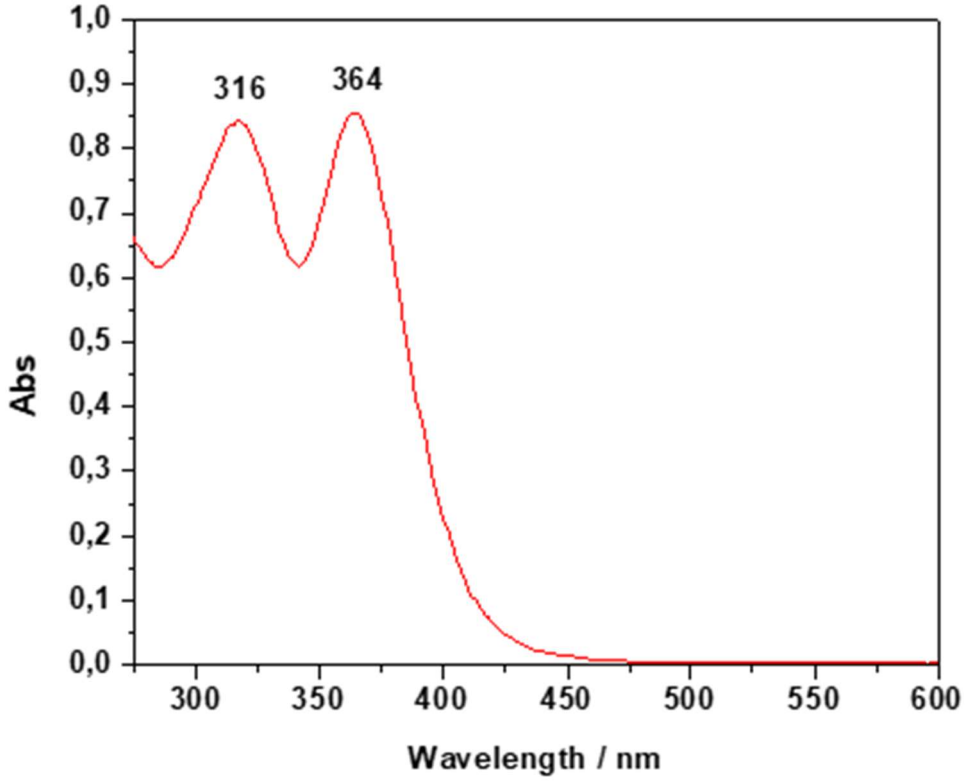


Fig. S42 UV-Vis spectrum of [***S*-diOHPrMIm]$FeCl_4$** (**7**) in DMF at 25 ºC. [**7**] = 0.04 mM.

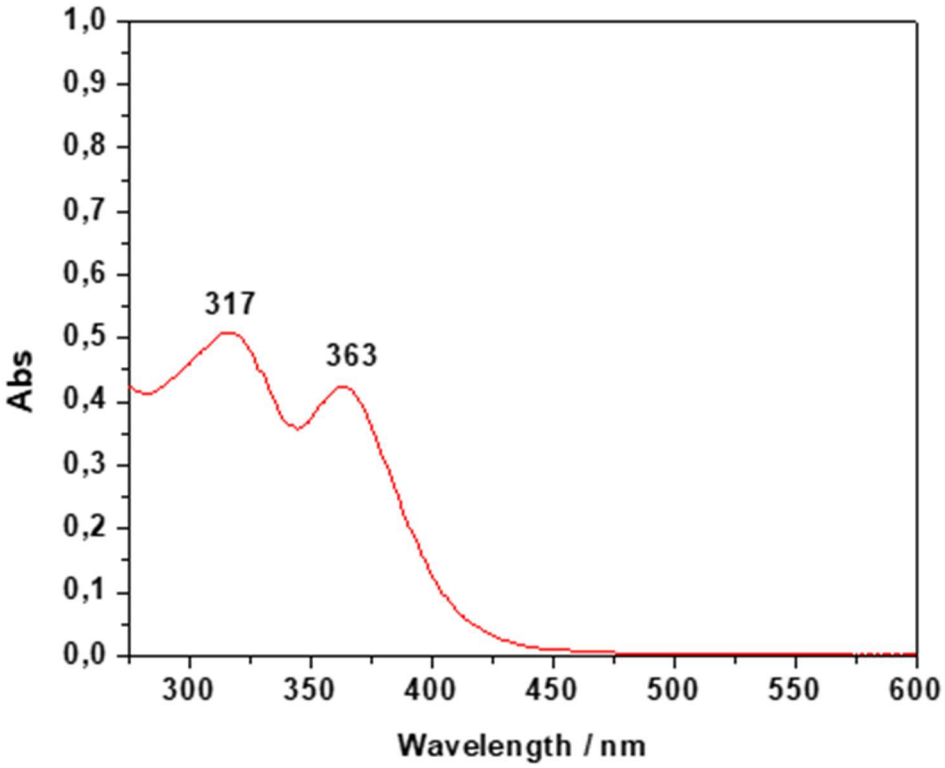


Fig. S43 UV-Vis spectrum of [***S*-diOHPrMIm]$FeBr_4$** (**8**) in DMF at 25 ºC. [**8**] = 0.21 mM.

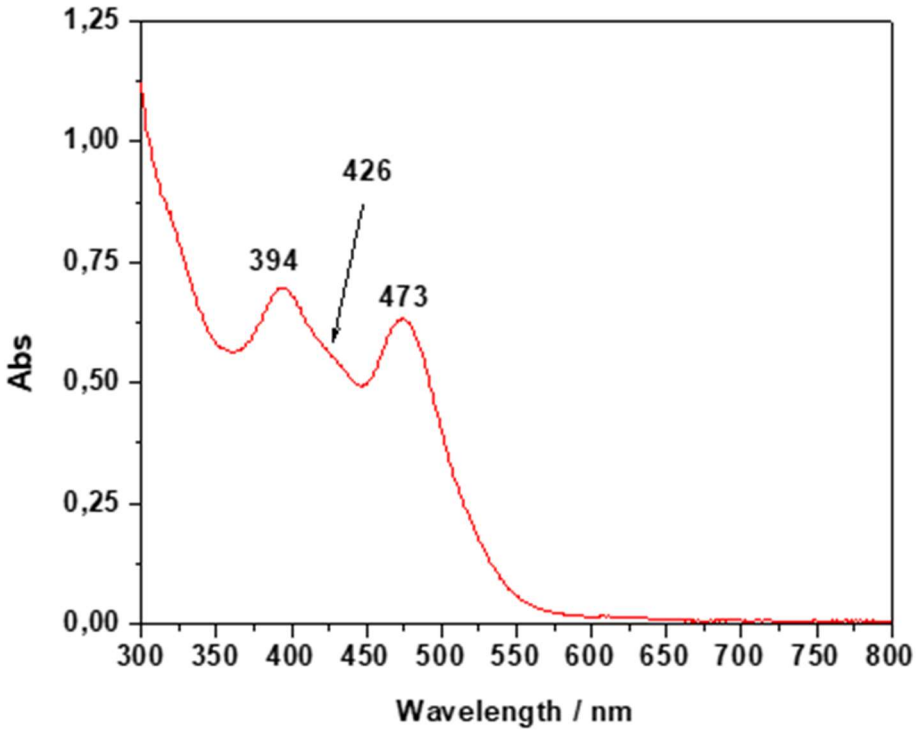
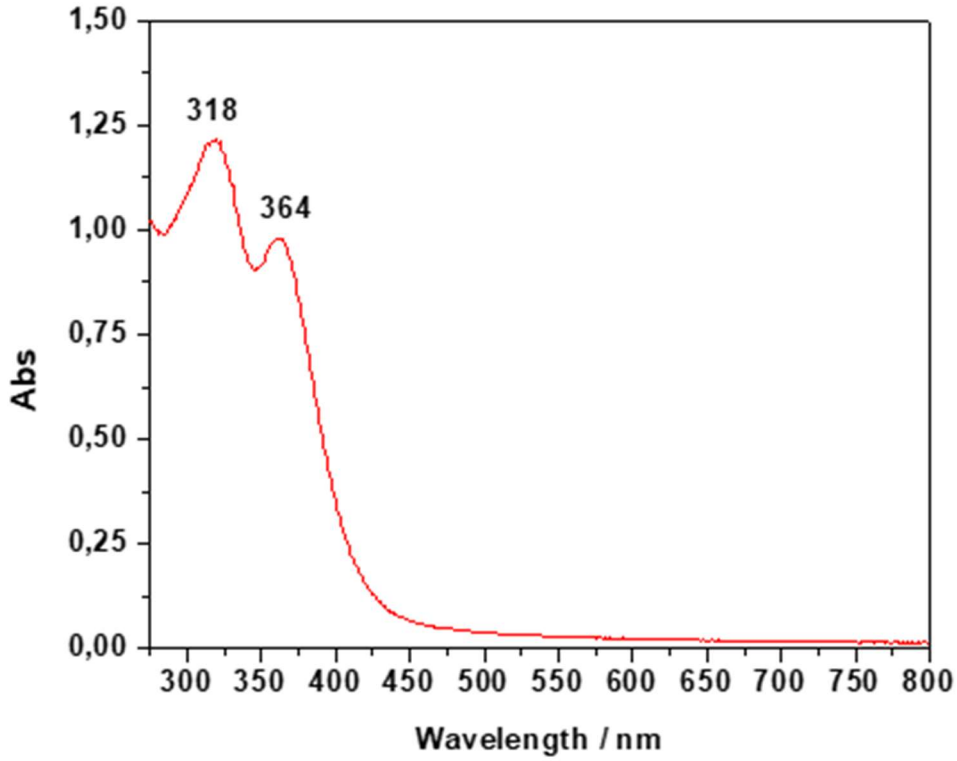


Fig. S44 UV-Vis spectrum of **[*R*-menthylMMIm]$FeCl_4$** (**9**) in DMF at 25 ºC. [**6**] = 0.06 mM.



6. MAGNETIC DATA

Fig. S45 Magnetic data of **5**: a) Temperature dependence of χ_m and $\chi_m T$ measured under 10 kOe. b) Field dependence of the magnetization M(H), collected at 2 K.

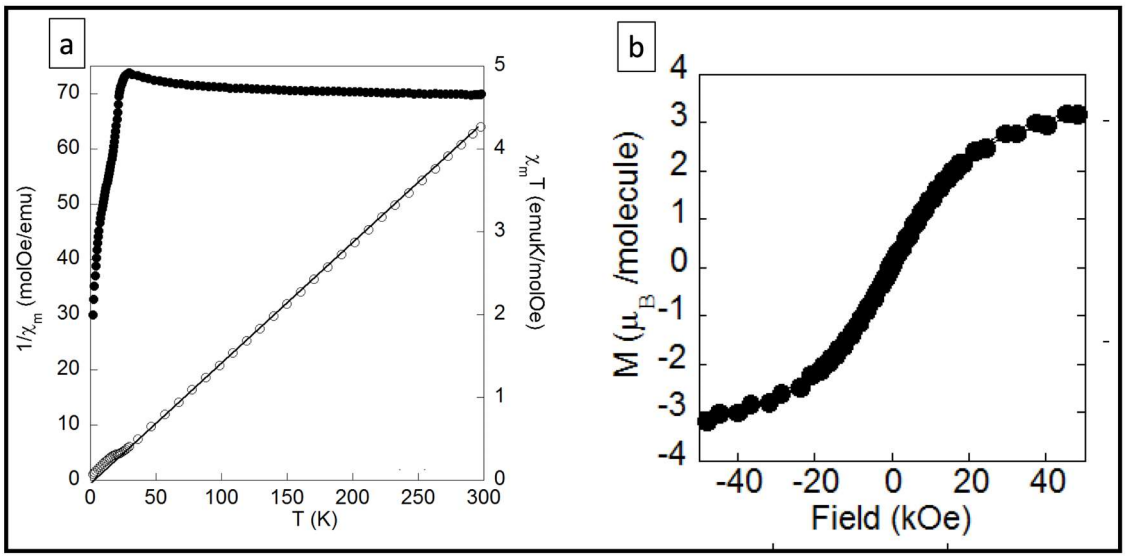


Fig. S46 Magnetic data of **6**: a) Temperature dependence of χ_m and $\chi_m T$ measured under 10 kOe. b) Field dependence of the magnetization M(H), collected at 2 K.

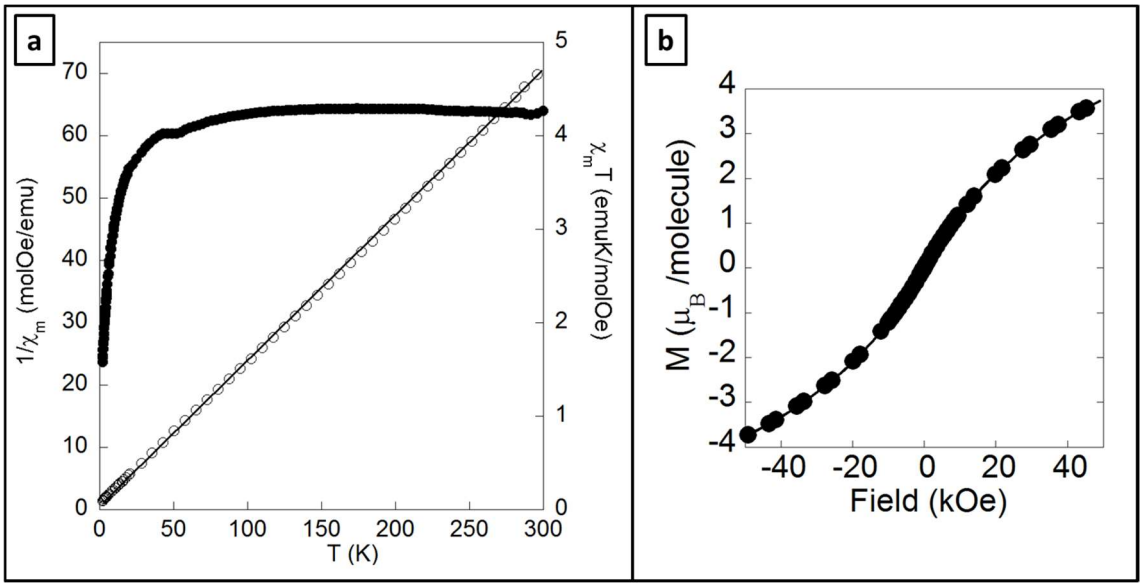


Fig. S47 Magnetic data of **7**: a) Temperature dependence of χ_m and $\chi_m T$ measured under 10 kOe. b) Field dependence of the magnetization M(H), collected at 2 K.

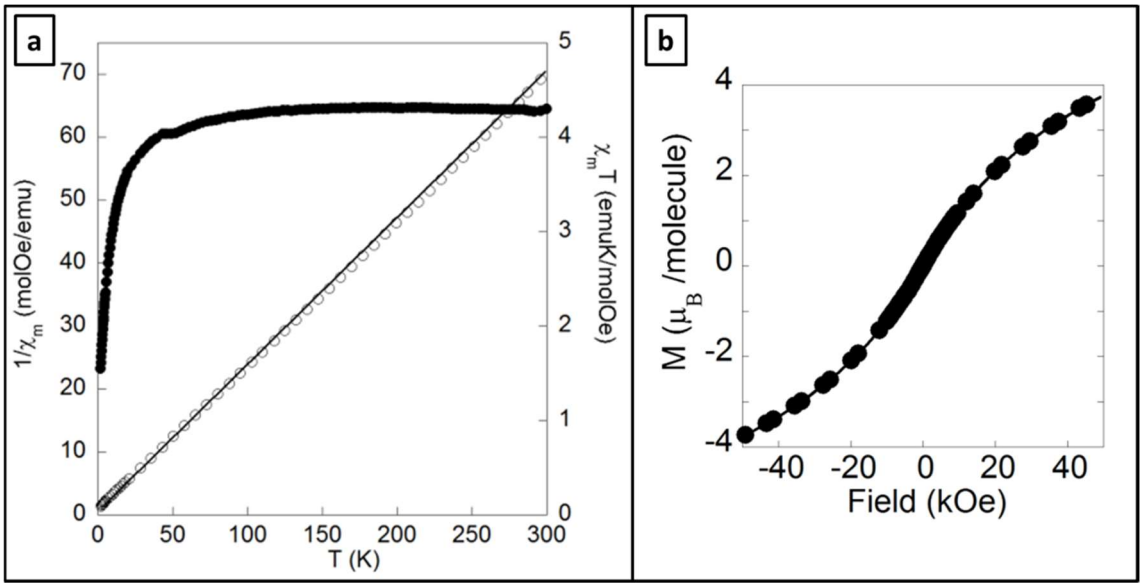


Fig. S48 Magnetic data of **8**: a) Temperature dependence of χ_m and $\chi_m T$ measured under 10 kOe. b) Field dependence of the magnetization M(H), collected at 2 K.

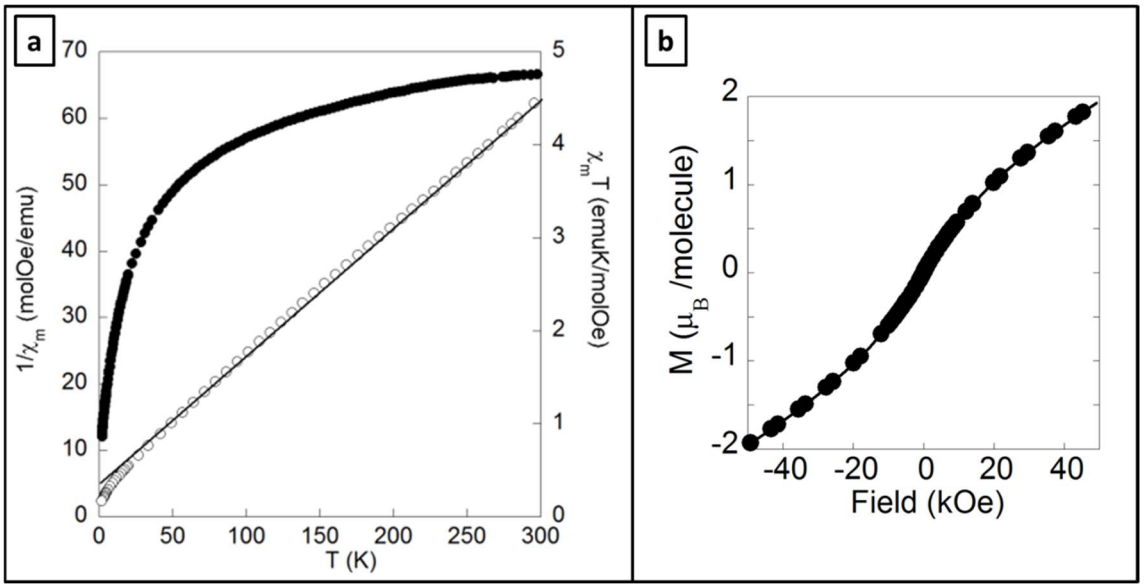
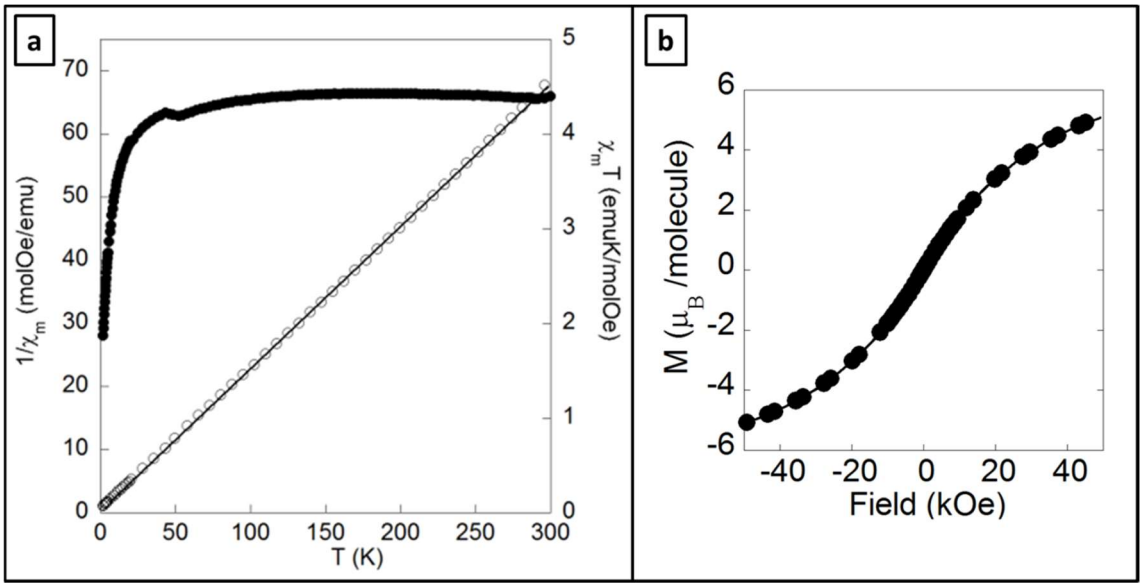


Fig. S49 Magnetic data of **9**: a) Temperature dependence of χ_m and $\chi_m T$ measured under 10 kOe. b) Field dependence of the magnetization M(H), collected at 2 K.



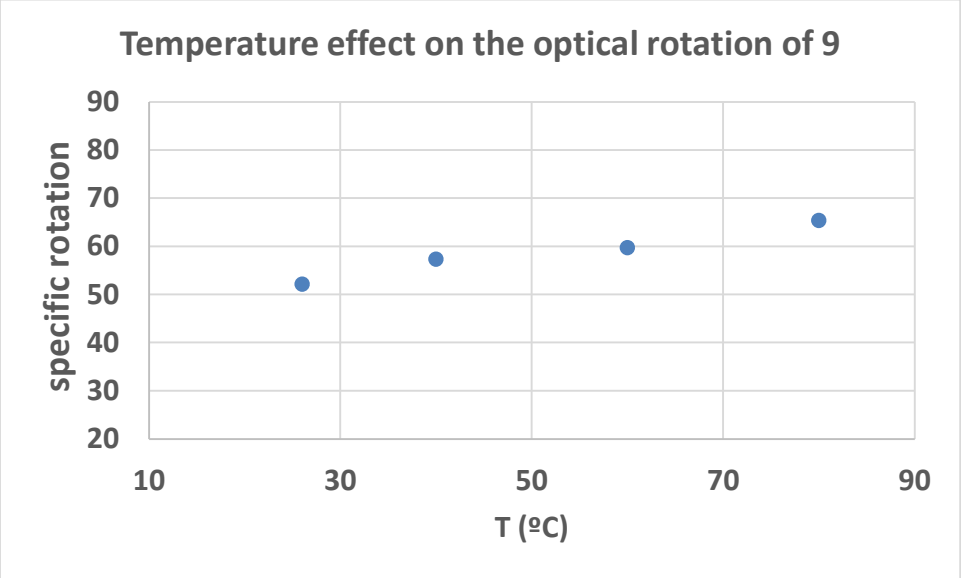
7. SPECIFIC ROTATION DATA

Table S1 Specific rotations of ACMILs **9**.[a]

Entry	T (ºC)	Solvent	$[\alpha]_D^x$
1	25	CH_3CN	44.9
2	25	DCM	51.4
3	25	MeOH	52.2
4	40	MeOH	57.4
5	60	MeOH	59.8
6	80	MeOH	65.4

[a] c = 5 mg/mL.

Fig. S50 Temperature effect on the optical rotation of **9**.



8. X-RAY CRYSTALLOGRAPHIC ANALYSIS

Fig. S51 Part of the packing diagram for **1**. Color codes: C = brown, Cl = green, H = white, N = blue.

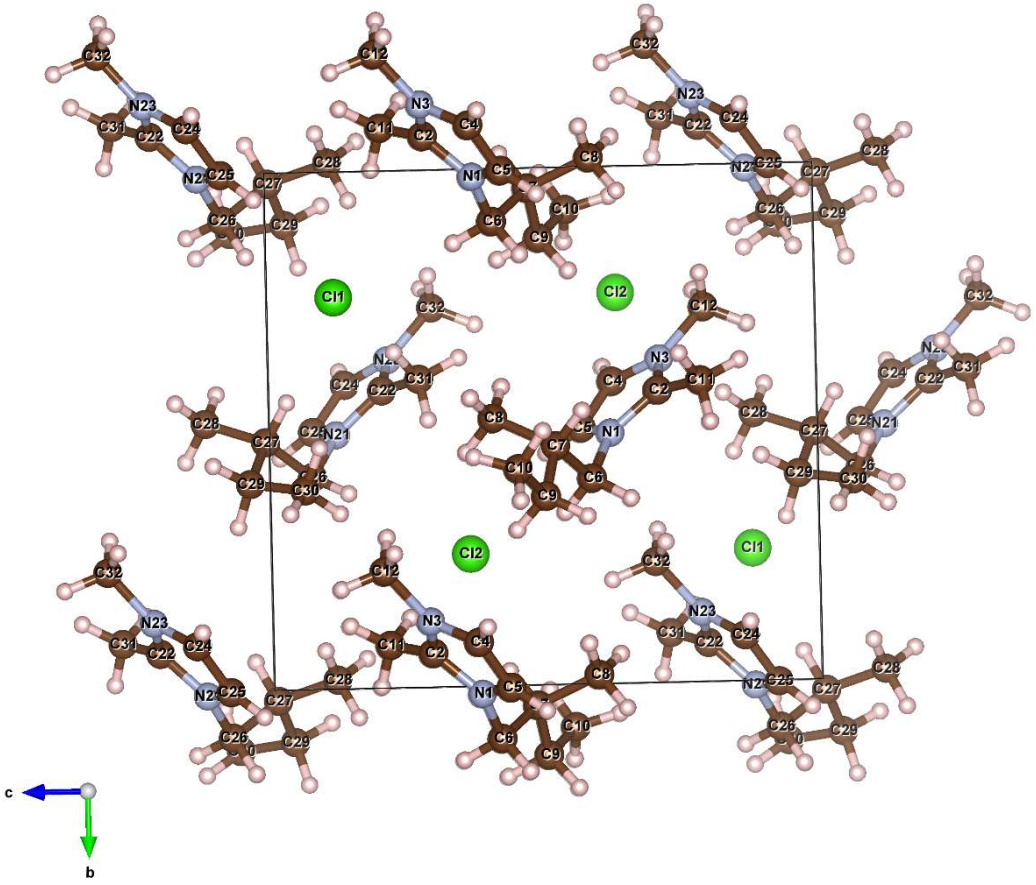


Table S2 Crystal data and structure refinement for **1**.

Empirical formula	$C_{10}H_{19}ClN_2$
Formula weight	202.72
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.0742(3)
b/Å	10.8811(4)
c/Å	11.8127(4)
α/°	90
β/°	102.664(3)
γ/°	90
Volume/Å^3	1137.98(7)
Z	4
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	2.635
F(000)	440.0
Crystal size/mm^3	0.856 × 0.794 × 0.38
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.67 to 147.732
Index ranges	-11 ≤ h ≤ 7, -13 ≤ k ≤ 12, -10 ≤ l ≤ 14
Reflections collected	7067
Independent reflections	3541 [R_{int} = 0.0290, R_{sigma} = 0.0322]
Data/restraints/parameters	3541/1/245
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0886
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.30/-0.32
Flack parameter	0.033(14)

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	1286(2)	5152.0(18)	3780.8(14)	14.1(4)
C2	943(2)	4348(2)	2904.2(18)	15.4(4)
N3	2210(2)	3734.8(18)	2863.3(15)	16.0(4)
C4	3378(2)	4156(2)	3733.4(18)	16.4(4)
C5	2805(2)	5046(2)	4307.3(18)	15.5(4)
C6	221(2)	6023(2)	4131.0(18)	17.2(4)
C7	-840(2)	5389(2)	4791(2)	18.7(5)
C8	39(3)	4829(3)	5923(2)	28.3(6)
C9	-1993(3)	6357(3)	4981(2)	28.0(6)
C10	-3260(3)	5818(3)	5480(3)	36.2(6)
C11	-563(2)	4174(2)	2126(2)	22.4(5)
C12	2339(3)	2751(2)	2038(2)	24.4(5)
N21	6038.1(18)	5082.3(19)	8773.5(14)	14.5(4)
C22	5621(2)	4247(2)	7931.7(17)	16.1(4)
N23	6868(2)	3653.6(19)	7818.1(16)	18.5(4)
C24	8104(2)	4119(2)	8601.7(19)	19.3(4)
C25	7591(2)	5020(2)	9201.2(19)	17.8(4)
C26	5000(2)	5895(2)	9226.4(18)	17.8(4)
C27	4220(2)	5202(2)	10067.6(19)	19.6(5)
C28	5374(3)	4821(3)	11160(2)	33.7(6)
C29	2980(3)	6005(3)	10364(2)	29.1(6)
C30	1612(3)	6154(3)	9374(3)	39.6(7)
C31	4065(3)	4038(3)	7253(2)	24.1(5)
C32	6945(3)	2662(2)	6998(2)	27.9(6)
Cl1	8560.8(5)	7429.5(5)	1217.4(4)	20.99(16)
Cl2	3346.0(5)	7439.1(5)	6373.9(4)	19.83(16)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	13.3(7)	12.7(10)	17.5(8)	0.7(7)	5.7(6)	-0.3(7)
C2	18.1(9)	12.0(11)	17.7(9)	-0.4(8)	7.1(7)	-0.6(8)
N3	19.4(8)	13.2(9)	17.1(8)	-1.2(7)	7.6(6)	0.5(7)
C4	16.3(9)	13.9(11)	20.8(10)	0.4(9)	7.9(7)	-0.6(8)
C5	14.6(8)	15.3(11)	16.7(9)	1.6(8)	3.6(7)	-1.0(8)
C6	18.5(9)	12.8(11)	21.4(10)	-2.3(9)	7.0(8)	2.5(8)
C7	15.4(9)	17.7(12)	25(1)	-3.1(9)	8.4(8)	-1.5(8)
C8	23.2(11)	35.1(15)	29.5(11)	9.6(11)	11.7(9)	1.4(11)
C9	22.8(10)	27.4(14)	36.4(13)	-2.3(11)	12.4(9)	5.4(10)
C10	21.8(11)	36.4(16)	54.8(17)	-12.2(13)	18.5(11)	-1.0(11)
C11	20.4(10)	21.4(12)	23(1)	-4.2(9)	-0.4(8)	1.0(9)
C12	29.2(11)	19.8(13)	25.6(11)	-8.7(9)	9.2(9)	3.8(9)
N21	14.7(8)	12(1)	18.2(9)	0.9(7)	6.5(7)	-0.6(7)
C22	21.3(10)	13.8(11)	15.2(9)	0.9(8)	8.1(8)	-2.2(9)
N23	24.6(9)	13.5(9)	20.4(8)	-0.7(7)	11.6(7)	1.4(8)
C24	17.7(9)	17.6(11)	24.6(10)	3.3(9)	8.7(8)	-0.3(9)
C25	15.8(9)	17.6(12)	20.4(10)	3.4(9)	5.1(7)	-1.7(9)
C26	19.5(9)	14.6(11)	20.9(10)	-1.3(9)	7.9(8)	2.7(9)
C27	17.0(9)	20.7(12)	22.4(10)	-0.2(9)	7.4(8)	0.4(9)
C28	26.1(11)	50.0(18)	26.7(11)	14.2(13)	9.2(9)	-1.3(12)
C29	25.5(11)	29.8(15)	37.0(13)	-5.9(11)	17.3(10)	-0.4(11)
C30	25.7(12)	40.0(17)	55.2(17)	2.6(14)	13.8(11)	11.5(12)
C31	22.4(11)	27.2(13)	22.6(10)	-2.9(10)	4.7(8)	-4.3(10)
C32	44.7(14)	15.7(13)	27.5(11)	-5.7(9)	17.4(10)	2.0(11)
Cl1	22.1(2)	16.7(3)	24.5(3)	-1.8(3)	5.83(17)	-2.7(3)
Cl2	19.1(2)	17.3(3)	24.0(2)	-3.7(3)	6.83(17)	-2.7(3)

Table S5 Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C2	1.339(3)	N21	C22	1.339(3)
N1	C5	1.387(3)	N21	C25	1.390(3)
N1	C6	1.476(3)	N21	C26	1.475(3)
C2	N3	1.339(3)	C22	N23	1.335(3)
C2	C11	1.483(3)	C22	C31	1.481(3)
N3	C4	1.383(3)	N23	C24	1.385(3)
N3	C12	1.469(3)	N23	C32	1.462(3)
C4	C5	1.351(3)	C24	C25	1.350(3)
C6	C7	1.529(3)	C26	C27	1.538(3)
C7	C8	1.526(3)	C27	C28	1.530(3)
C7	C9	1.535(3)	C27	C29	1.525(3)
C9	C10	1.519(4)	C29	C30	1.516(4)

Table S6 Bond Angles for **1**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	N1	C5	109.37(19)	C22	N21	C25	109.59(19)
C2	N1	C6	125.54(18)	C22	N21	C26	125.27(18)
C5	N1	C6	125.08(18)	C25	N21	C26	125.05(19)
N1	C2	C11	126.1(2)	N21	C22	C31	125.9(2)
N3	C2	N1	107.34(18)	N23	C22	N21	107.19(18)
N3	C2	C11	126.6(2)	N23	C22	C31	126.9(2)
C2	N3	C4	109.42(19)	C22	N23	C24	109.6(2)
C2	N3	C12	125.51(18)	C22	N23	C32	126.0(2)
C4	N3	C12	125.07(19)	C24	N23	C32	124.3(2)
C5	C4	N3	107.08(19)	C25	C24	N23	107.09(19)
C4	C5	N1	106.79(19)	C24	C25	N21	106.5(2)
N1	C6	C7	112.19(19)	N21	C26	C27	111.16(19)
C6	C7	C9	106.9(2)	C28	C27	C26	110.52(18)
C8	C7	C6	111.13(18)	C29	C27	C26	109.5(2)
C8	C7	C9	112.8(2)	C29	C27	C28	111.4(2)
C10	C9	C7	113.0(2)	C30	C29	C27	113.9(2)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1**.

Atom	*x*	*y*	*z*	U(eq)
H4	4393.02	3871.96	3896.68	20
H5	3338.86	5510.86	4948.08	19
H6A	-386.02	6425.33	3430.63	21
H6B	799.26	6669.17	4628.48	21
H7	-1389.38	4716.96	4294.68	22
H8A	590.16	5478.22	6416.13	42
H8B	756.38	4220.5	5753	42
H8C	-665.65	4428.83	6327.54	42
H9A	-1465.66	6996.85	5515.42	34
H9B	-2434.02	6757.27	4230.58	34
H10A	-2861.8	5573.18	6287.03	54
H10B	-3682.15	5097.99	5023.82	54
H10C	-4053.38	6436.29	5449.41	54
H11A	-1182.38	3645.8	2508.01	34
H11B	-445.23	3787.45	1402.07	34
H11C	-1058.02	4973.96	1954.55	34
H12A	3368.07	2419.26	2220.8	37
H12B	2116.04	3083.38	1247.99	37
H12C	1619.56	2095.01	2096.05	37
H24	9122.47	3855.43	8699.15	23
H25	8175.19	5513.23	9797.84	21
H26A	4225.38	6221.53	8571.66	21
H26B	5572.48	6599.73	9634.27	21
H27	3743.83	4441.8	9671.93	23
H28A	5901.37	5552.43	11529.52	51
H28B	6107.84	4253.22	10948.5	51
H28C	4853.57	4415.19	11701.33	51
H29A	2651.92	5641.5	11036.64	35
H29B	3404.4	6828.1	10599.2	35
H30A	822.25	6604.63	9648.13	59

H30B	1230.76	5341.8	9093.64	59
H30C	1898.87	6611.77	8741.22	59
H31A	4103.52	3637.08	6517.35	36
H31B	3540.67	4827.64	7096.89	36
H31C	3520.91	3510.63	7696.39	36
H32A	7948.96	2283.65	7189.67	42
H32B	6758.72	2995.64	6208.54	42
H32C	6177.94	2040.94	7044.83	42

Fig. S52 Part of the packing diagram for **4**. Color codes: C = brown, Cl = green, H = white, N = blue, O = red.

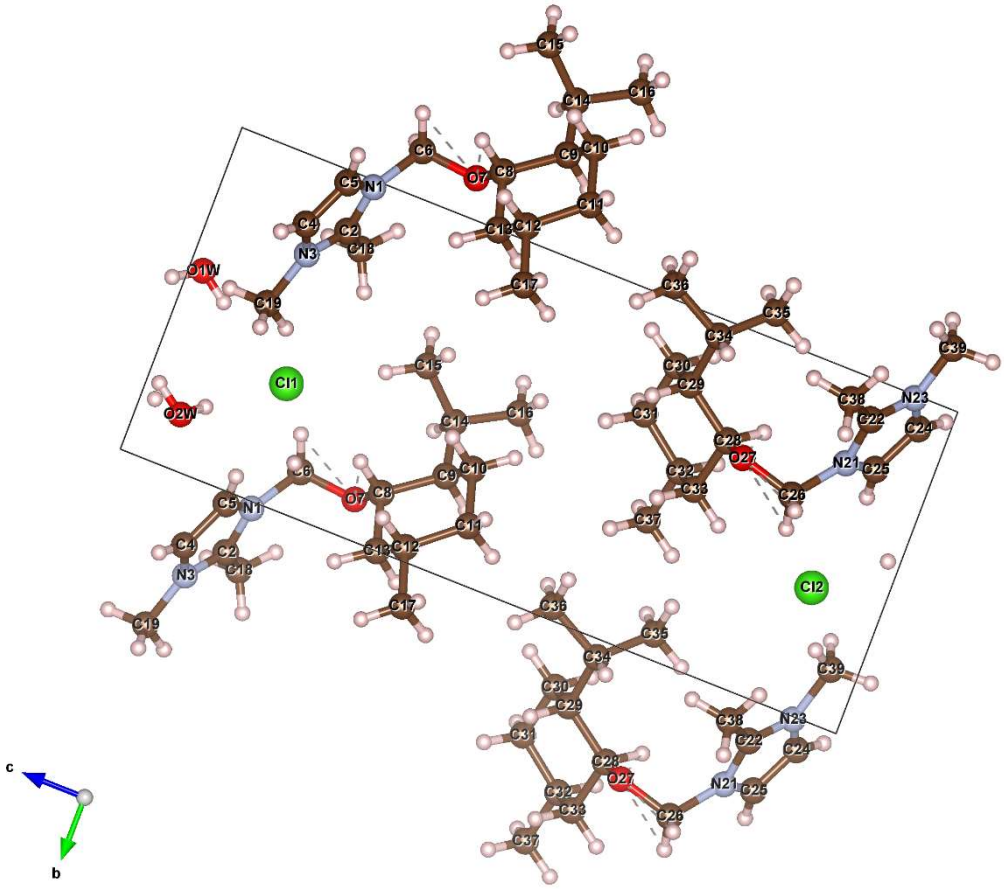


Table S8 Crystal data and structure refinement for **4**.

Empirical formula	$C_{16}H_{31}N_2O_2Cl$
Formula weight	318.88
Temperature/K	120(2)
Crystal system	triclinic
Space group	P1
a/Å	6.6283(2)
b/Å	7.8369(3)
c/Å	17.6060(5)
α/°	90.888(3)
β/°	94.947(3)
γ/°	91.100(3)
Volume/Å^3	910.84(6)
Z	2
ρ_{calc}g/cm^3	1.163
μ/mm^{-1}	1.900
F(000)	348.0
Crystal size/mm^3	0.505 × 0.258 × 0.058
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.088 to 147.888
Index ranges	-7 ≤ h ≤ 8, -9 ≤ k ≤ 9, -21 ≤ l ≤ 21
Reflections collected	49890
Independent reflections	6939 [R_{int} = 0.0466, R_{sigma} = 0.0234]
Data/restraints/parameters	6939/7/401
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1109
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.1119
Largest diff. peak/hole / e Å^{-3}	0.29/-0.33
Flack parameter	0.000(13)

Table S9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	8470(4)	10203(3)	8131.3(14)	23.5(5)
C2	9532(5)	11668(4)	8242.0(16)	24.0(6)
N3	8446(4)	12733(3)	8632.3(14)	23.7(5)
C4	6654(5)	11919(4)	8778.3(18)	28.5(7)
C5	6658(5)	10349(4)	8463.5(17)	26.7(7)
C6	9075(5)	8686(4)	7703.1(17)	27.3(7)
O7	8664(3)	8852(3)	6921.5(11)	24.9(4)
C8	6617(4)	8391(3)	6626.1(14)	20.4(5)
C9	6705(4)	7237(3)	5923.4(15)	23.2(6)
C10	4516(5)	6756(4)	5624.5(18)	31.1(7)
C11	3293(5)	8336(4)	5419.0(17)	32.7(7)
C12	3284(5)	9595(4)	6092.0(17)	29.9(7)
C13	5455(5)	10001(4)	6419.2(16)	24.1(6)
C14	8085(5)	5690(4)	6064.1(17)	28.8(6)
C15	7348(7)	4454(4)	6648(2)	41.8(8)
C16	8378(6)	4751(5)	5315(2)	42.9(9)
C17	2172(6)	11212(5)	5857(2)	41.0(8)
C18	11581(6)	12018(5)	8001(2)	42.6(9)
C19	9033(5)	14485(4)	8883.1(18)	27.8(7)
N21	7239(4)	2583(3)	1126.2(13)	23.1(5)
C22	6117(5)	1140(4)	1026.7(17)	25.8(7)
N23	7102(4)	86(3)	588.9(14)	25.8(6)
C24	8869(5)	876(4)	405.5(17)	27.6(7)
C25	8958(5)	2439(4)	738.6(17)	25.8(7)
C26	6858(5)	4028(4)	1638.6(17)	25.0(6)
O27	7147(3)	3548(3)	2403.6(11)	23.0(4)
C28	9243(4)	3255(3)	2668.0(14)	19.1(5)
C29	9279(4)	2133(3)	3371.8(15)	22.3(6)
C30	11504(5)	1778(4)	3625.0(17)	29.0(6)
C31	12750(5)	3421(4)	3789.6(17)	30.5(6)

C32	12621(5)	4596(4)	3104.2(16)	27.1(6)
C33	10397(5)	4921(4)	2847.5(15)	23.3(6)
C34	7928(5)	515(4)	3255.3(17)	30.0(7)
C35	8619(6)	-724(4)	2662.4(19)	36.8(8)
C36	7757(7)	-386(5)	4018(2)	47.9(10)
C37	13804(6)	6258(5)	3272(2)	38.5(7)
C38	4168(5)	803(5)	1354(2)	37.4(8)
C39	6488(6)	-1672(4)	359(2)	34.0(8)
Cl1	3937.9(9)	6447.3(8)	8282.0(4)	30.07(18)
Cl2	1733.4(10)	6315.4(8)	10968.0(4)	34.3(2)
O2W	1387(5)	8416(4)	9432.8(16)	50.3(8)
O1W	4197(6)	4291(4)	9813.5(16)	55.2(9)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	24.1(14)	21.0(12)	24.5(11)	3.0(9)	-4.1(10)	2.9(10)
C2	23.2(16)	25.6(15)	22.3(13)	4.1(11)	-3.9(11)	0.8(12)
N3	25.1(14)	20.8(12)	24.3(11)	2.6(9)	-3.7(10)	1.4(10)
C4	21.6(17)	32.8(17)	31.4(15)	3.2(12)	3.6(12)	-2.2(13)
C5	24.8(17)	28.5(16)	26.5(15)	3.3(12)	0.2(12)	-5.5(13)
C6	30.4(17)	20.8(14)	28.9(14)	-1.7(11)	-7.9(12)	5.9(13)
O7	22.0(11)	26.5(10)	25.6(10)	1.1(8)	-1.0(8)	-0.9(8)
C8	18.2(14)	21.1(13)	21.8(12)	5.7(10)	0.2(10)	-0.3(11)
C9	25.9(16)	21.8(13)	21.8(12)	4.1(10)	-0.4(10)	2.9(11)
C10	32.1(17)	24.7(14)	34.4(15)	1.9(11)	-8.5(12)	0.9(13)
C11	29.5(17)	35.0(17)	31.8(15)	4.0(12)	-9.4(12)	4.7(14)
C12	26.9(16)	34.4(17)	28.4(14)	8.8(12)	-0.1(11)	7.3(13)
C13	28.7(16)	20.6(13)	23.2(12)	5.2(10)	2(1)	3.4(12)
C14	33.4(17)	21.4(13)	30.4(14)	1.5(11)	-4.3(12)	6.1(12)
C15	62(2)	21.1(14)	41.2(17)	8.6(13)	-2.1(16)	9.8(15)
C16	55(2)	35.6(18)	37.5(17)	-2.6(13)	-0.5(15)	21.9(17)
C17	41(2)	43.5(19)	38.3(17)	4.2(14)	-4.8(14)	20.8(17)
C18	29(2)	47(2)	53(2)	-10.6(17)	10.1(16)	-5.7(17)
C19	30.9(18)	19.3(14)	32.5(15)	1.2(12)	-1.6(13)	-1.8(13)
N21	22.3(13)	23.8(12)	22.5(11)	6.3(9)	-3.5(9)	2(1)
C22	22.6(16)	28.1(15)	25.6(14)	5.9(11)	-5.7(12)	0.0(13)
N23	24.5(14)	26.3(13)	25.6(12)	3.4(10)	-4(1)	-2.1(11)
C24	27.0(17)	32.0(16)	23.8(14)	3.8(12)	1.5(11)	0.8(14)
C25	24.2(16)	29.1(15)	23.9(14)	8.4(11)	0.0(11)	-2.7(13)
C26	24.9(16)	23.1(14)	26.5(14)	6.2(11)	-2.7(11)	4.7(12)
O27	19.0(11)	27.6(10)	22.5(9)	6.2(7)	0.8(7)	3.2(8)
C28	18.2(14)	18.9(13)	20.2(11)	5.4(9)	1.0(9)	2(1)
C29	26.1(15)	19.8(13)	20.6(12)	6.3(10)	-0.5(10)	-3.2(11)
C30	30.8(17)	26.7(14)	27.8(14)	7.1(11)	-7.7(12)	-2.3(12)
C31	27.8(16)	32.5(16)	29.5(14)	2.9(12)	-6.5(11)	-4.5(13)
C32	24.1(16)	28.9(15)	28.2(13)	1.4(11)	2.7(11)	-6.8(12)

C33	25.9(15)	19.5(12)	25.0(13)	5.5(10)	4.0(11)	-1.0(11)
C34	34.7(17)	26.3(14)	27.7(14)	9.7(11)	-4.5(12)	-9.1(13)
C35	48(2)	21.8(14)	38.6(16)	4.1(12)	-9.6(14)	-4.6(14)
C36	61(3)	45(2)	35.8(17)	18.9(15)	-5.3(16)	-30.0(19)
C37	33.0(19)	37.8(18)	44.0(17)	1.6(14)	2.1(14)	-14.1(15)
C38	20.5(17)	45(2)	46.2(19)	-1.9(16)	2.2(14)	-4.3(15)
C39	35.1(19)	30.3(17)	35.9(17)	-1.2(13)	0.1(14)	-5.8(15)
Cl1	27.2(4)	29.8(4)	34.0(4)	6.1(3)	7.0(3)	-3.7(3)
Cl2	36.4(5)	36.5(4)	30.8(4)	4.6(3)	8.8(3)	-9.4(3)
O2W	69(2)	48.3(16)	35.3(13)	9.6(11)	8.0(13)	31.2(15)
O1W	77(2)	53.3(17)	38.4(14)	14.1(12)	12.0(14)	34.1(17)

Table S11 Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C2	1.337(4)	N21	C22	1.343(4)
N1	C5	1.386(4)	N21	C25	1.383(4)
N1	C6	1.478(4)	N21	C26	1.476(4)
C2	N3	1.334(4)	C22	N23	1.338(4)
C2	C18	1.479(5)	C22	C38	1.480(5)
N3	C4	1.383(5)	N23	C24	1.379(5)
N3	C19	1.470(4)	N23	C39	1.470(4)
C4	C5	1.341(5)	C24	C25	1.348(5)
C6	O7	1.388(4)	C26	O27	1.402(3)
O7	C8	1.448(3)	O27	C28	1.450(3)
C8	C9	1.527(4)	C28	C29	1.529(3)
C8	C13	1.523(3)	C28	C33	1.516(4)
C9	C10	1.538(4)	C29	C30	1.536(4)
C9	C14	1.543(4)	C29	C34	1.539(4)
C10	C11	1.524(4)	C30	C31	1.527(4)
C11	C12	1.531(4)	C31	C32	1.527(4)
C12	C13	1.529(4)	C32	C33	1.532(4)
C12	C17	1.523(4)	C32	C37	1.520(4)
C14	C15	1.528(5)	C34	C35	1.520(5)
C14	C16	1.529(4)	C34	C36	1.539(4)

Table S12 Bond Angles for **4**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	N1	C5	108.9(3)	C22	N21	C25	109.3(3)
C2	N1	C6	126.1(3)	C22	N21	C26	126.1(3)
C5	N1	C6	124.9(3)	C25	N21	C26	124.2(3)
N1	C2	C18	126.1(3)	N21	C22	C38	125.5(3)
N3	C2	N1	107.8(3)	N23	C22	N21	107.2(3)
N3	C2	C18	126.1(3)	N23	C22	C38	127.3(3)
C2	N3	C4	109.0(3)	C22	N23	C24	109.4(3)
C2	N3	C19	126.5(3)	C22	N23	C39	126.5(3)
C4	N3	C19	124.5(3)	C24	N23	C39	124.1(3)
C5	C4	N3	107.4(3)	C25	C24	N23	107.3(3)
C4	C5	N1	106.9(3)	C24	C25	N21	106.8(3)
O7	C6	N1	112.1(2)	O27	C26	N21	110.7(2)
C6	O7	C8	115.3(2)	C26	O27	C28	114.0(2)
O7	C8	C9	108.8(2)	O27	C28	C29	108.3(2)
O7	C8	C13	109.5(2)	O27	C28	C33	111.4(2)
C13	C8	C9	110.4(2)	C33	C28	C29	111.0(2)
C8	C9	C10	107.7(2)	C28	C29	C30	107.6(2)
C8	C9	C14	113.4(2)	C28	C29	C34	113.6(2)
C10	C9	C14	114.0(2)	C30	C29	C34	113.9(2)
C11	C10	C9	111.4(3)	C31	C30	C29	112.0(2)
C10	C11	C12	112.1(2)	C32	C31	C30	111.7(2)
C13	C12	C11	110.0(2)	C31	C32	C33	109.7(2)
C17	C12	C11	111.0(2)	C37	C32	C31	112.0(3)
C17	C12	C13	111.4(3)	C37	C32	C33	111.4(3)
C8	C13	C12	112.0(2)	C28	C33	C32	110.8(2)
C15	C14	C9	113.5(3)	C29	C34	C36	110.6(2)
C15	C14	C16	110.6(3)	C35	C34	C29	113.5(3)
C16	C14	C9	110.8(2)	C35	C34	C36	110.5(3)

Table S13 Hydrogen Bonds for **4**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2W	H2WA	Cl1	0.88(3)	2.29(3)	3.153(3)	166(5)
O2W	H2WB	Cl2	0.86(3)	2.32(3)	3.180(3)	172(6)
O1W	H1WA	Cl1	0.86(3)	2.34(3)	3.198(3)	175(6)
O1W	H1WB	Cl2	0.87(3)	2.28(3)	3.144(3)	174(6)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4**.

Atom	*x*	*y*	*z*	U(eq)
H4	5612.87	12385.39	9051.33	34
H5	5617.1	9499.89	8467.46	32
H6A	10543.01	8510.31	7819.88	33
H6B	8341.69	7666.7	7871.82	33
H8	5926.94	7762.24	7023.87	24
H9	7291.77	7937.48	5523.28	28
H10A	4531.47	6004.52	5168	37
H10B	3860.41	6114.78	6019.52	37
H11A	1881.15	7982.74	5249.86	39
H11B	3872.1	8912.56	4988.55	39
H12	2550.22	9038.6	6498.3	36
H13A	6169.43	10643.16	6039.56	29
H13B	5425.53	10736.36	6880.18	29
H14	9444.87	6143.8	6272.74	35
H15A	7184.05	5074.99	7125.72	63
H15B	8342.06	3555.62	6742.73	63
H15C	6044.57	3939.39	6450.81	63
H16A	7097.06	4197.44	5117.15	64
H16B	9415.61	3886.23	5404.29	64
H16C	8808.2	5569.5	4942.28	64
H17A	2825.07	11746.42	5439.11	62
H17B	2216.67	12008.36	6292.63	62
H17C	758.71	10921.43	5686.39	62
H18A	11611.13	13135.13	7759.19	64
H18B	11917.48	11132.26	7636.27	64
H18C	12571.64	12018.36	8447.51	64
H19A	7827.29	15192.48	8863.52	42
H19B	9997.43	14956.84	8546.14	42
H19C	9666.18	14473.04	9406.99	42
H24	9842.69	405.5	101	33

H25	10000.39	3279.04	712.3	31
H26A	7789.71	4992.31	1548.65	30
H26B	5452.48	4414.43	1525.78	30
H28	9898.51	2630.1	2258.35	23
H29	8738.51	2827.79	3787.23	27
H30A	11571.29	1078.8	4089.78	35
H30B	12097.62	1112.68	3219.59	35
H31A	12251.07	4026.33	4231.98	37
H31B	14183.24	3134.27	3924.48	37
H32	13229.15	3993.25	2676.97	33
H33A	9768.97	5547.72	3256.02	28
H33B	10316.99	5639.27	2388.55	28
H34	6539.31	886.16	3069.59	36
H35A	8748.93	-125.29	2183.9	55
H35B	7621.37	-1660.73	2575.19	55
H35C	9933.23	-1184.71	2845.87	55
H36A	9049.65	-911.72	4180.4	72
H36B	6686.99	-1269.7	3955.15	72
H36C	7425.34	450.52	4405.82	72
H37A	13733.62	6953.45	2813.17	58
H37B	15221.9	6009.6	3428.11	58
H37C	13220.58	6884.36	3684.02	58
H38A	3507.94	-216.61	1108.83	56
H38B	3287.49	1784.46	1267.65	56
H38C	4417.81	619.48	1903.42	56
H39A	5323.05	-2027.06	630.03	51
H39B	7616.63	-2436.09	485.9	51
H39C	6114.85	-1725.73	-191.71	51
H2WA	2280(70)	7940(70)	9160(30)	75
H2WB	1570(90)	7790(70)	9830(20)	75
H1WA	4180(100)	4920(70)	9420(30)	83
H1WB	3540(90)	4790(80)	10160(30)	83