Supplementary Material (ESI) for Chemical Communications

Supplemental Information

Do ion tethered functional groups affect IL solvent properties? The case of sulfoxides and sulfones

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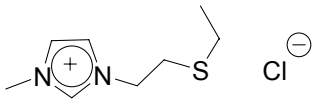
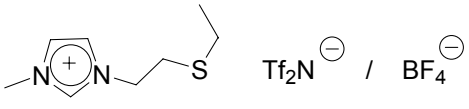
I. Synthesis of TSILs and TSIL precursors

(a) 

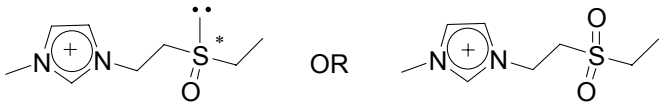
A 250 mL single-neck flask is charged with a magnetic stirbar and 100 mL of reagent grade toluene. To the toluene is added in turn 16.53g (0.20 mole) of distilled 1-methyl imidazole and 25.09g (0.20 mole) of 2-chloroethyl ethyl sulfide (hemisulfur mustard; Aldrich 98%). The flask is fitted with a water cooled condenser topped with a drying tube, and the solution then heated to reflux. Overnight a second, denser liquid phase is formed which is isolated by decantation of the toluene after cooling to room temperature. The toluene is decanted and the viscous yellow liquid maintained in vacuum overnight to remove residual volatiles. A ^{1}H-NMR of this material at this juncture typically shows the product to be devoid of residual starting materials or solvent. Product meeting this standard is used without further purification in the next phase of the synthesis.

Notes: If residual starting materials are found in the product, they are readily removed by washing the product several times with fresh toluene followed again by evacuation overnight.

(b) 

In a 250 mL single-neck flask charged with a magnetic stirbar, 41.29g (0.20 moles) of the [imidazolium thioether] Cl^- salt from Part (a) [above] is dissolved in 100 mL of de-ionized water. To the stirred solution is added in one portion 63.57g (0.22 mol) of lithium bis(trifluoromethane)sulfonyl amide [$LiTf_2N$]. Dissolution of the later is accompanied by the separation from the water of a second (denser) liquid phase. After stirring for 3-4 h, the product is isolated the addition of chloroform (into which the IL phase dissolves) followed by decantation. The chloroform product phase is washed with water to remove any residual starting salt, then dried with anhydrous $MgSO_4$. After filtration, the supernatant is evaporated to remove the chloroform, leaving the desired product as a mobile, colorless to pale yellow liquid.

Notes: The completeness of the anion exchange may be ascertained by the use of a silver ion test and/or by quantitative evaluation using a chloride sensitive electrode. With Tf_2N^- salts of this cation, Cl^- levels below silver ion detection limits are routinely achieved using the standard synthetic procedure. Very low Cl^- contents (routinely 0-15 ppm; ISE) are achieved by carrying out the anion metathesis using $AgTf_2N$, followed by chromatography of the product on silica gel, eluting with a chloroform/acetonitrile gradient. All Abraham parameter and enzyme activity studies reported in the present paper were conducted using ILs prepared in the latter fashion. In the case of the BF_4^- salts, very low chloride materials were also prepared by using $AgBF_4$ to accomplish the anion metathesis. It should also be noted that the BF_4^- salt of the imidazolium thioether cation does not completely phase separate from water. Consequently, regardless of which BF_4^- salt is being used to do the anion metathesis, the complete removal of product from the aqueous phase is only accomplished by chloroform extraction.

(c) 

Sulfoxide. In a 1L two-neck flask charged with a magnetic stirbar and fitted with a dropping funnel, 90.20g (0.20 moles) of the [imidazolium thioether] Tf_2N^- salt from Part (b) [above] is dissolved in 400 mL of dichloromethane. The solution is cooled to 5^o C by immersion in an ice/water bath. To the stirred solution is added dropwise 48.45g (0.20 mol) of m-chloroperoxybenzoic acid [m-CPBA; Aldrich; Assayed activity of 71.7% peroxyacid content] dissolved in 200 mL of dichloromethane. After a brief period a white precipitate (m-chlorobenzoic acid) begins to form. Stirring is continued overnight, after which time the solvent is removed by rotary evacuation. The white solid residue is extracted with multiple portions of ether until a well-defined liquid phase is form that, when checked by ^{1}H-NMR, shows no remaining m-chlorobenzoic acid. In cases where residual byproduct is not removed by washing, the product may be chromatographed on silica using a dichloromethane/acetonitrile gradient eluting phase.

Notes: The above procedure is also used to prepare the corresponding sulfone, the single alteration being the use of two molar equivalents of m-CPBA. In the sulfone synthesis, occasional under-oxidation occurs (especially when a somewhat older source of mCPBA is used), as evidenced by the observation or residual sulfoxide in the NMR. This is readily remedied by reaction of the mixture with additional mCPBA followed by repeat work-up. When using commercial m-CPBA, it is VITAL to ascertain the peroxyacid titre of the particular lot being used, and NOT to rely upon the label-listed maximum peroxyacid content; Failing to do so may lead to under- or overoxidation (when sulfoxide is being prepared), and it should be noted that the resulting mixtures are exceedingly difficult to separate!

Other oxidants (including NaOCl) have been investigated and give product. However, in our hands mixtures (see above) of sulfoxide, sulfone and unoxidized thioether were commonly the result. We have also found that results are highly variable when this oxidation step is conducted *before* the anion exchange step [Part (b)], although the TSIL chloride salts may be prepared and isolated. Finally, these procedures are used without modification for oxidations of the [imidazolium thioether] BF_4^- salt.

II. TSIL / co-solvent & (putative) clathrate data

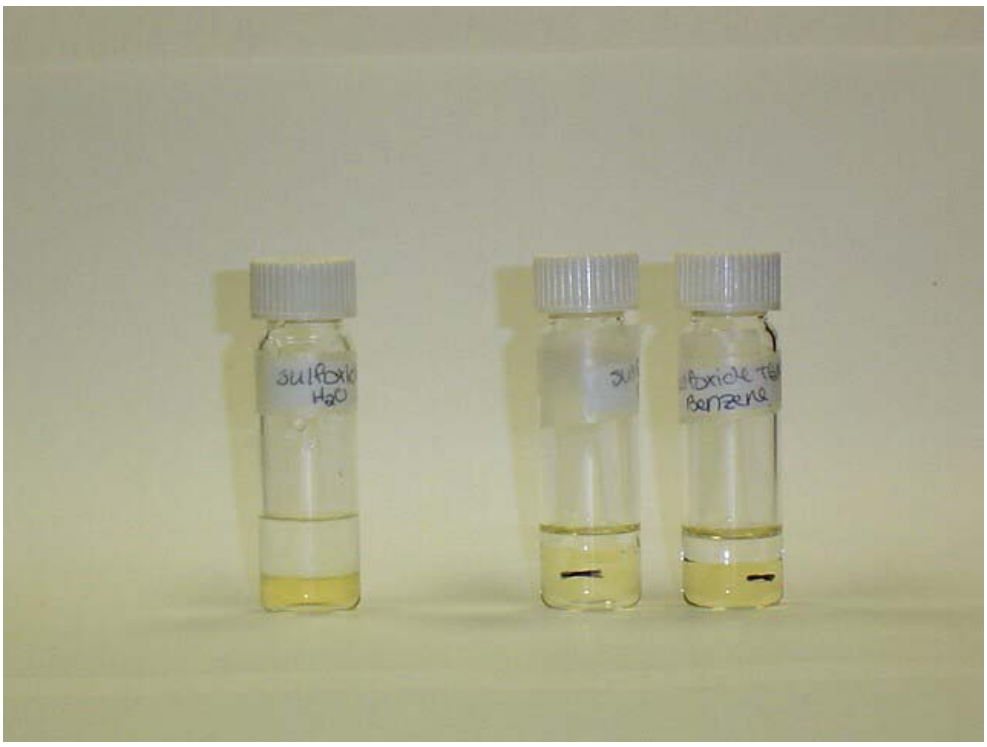
	2·Tf_2N	**2·BF_4**	**3·Tf_2N**	**3·BF_4**
benzene	1:1.8	Y	Y	Y
chloroform	1:4.3	1:4.8	1:2.4	1:3.2
dichloromethane	no clathrate	1:3.1	no clathrate	1:2.4

TSIL clathrate formation (TSIL:solvent); gravimetric determination. No clathrate = no clathrate formation was observed over a wide IL:solvent composition range. Y = likely clathrate formation, not yet quantified. In all clathrate experiments, > ~1 ppt IL was observed in any molecular solvent excess volume. In all cases, these compositions are (within experimental error) reproducible, and in each case the viscosity of the clathrate phase is visibly less than that of the pure IL. The one-phase nature of the clathrate phase is maintained on removal of the excess molecular solvent. These characteristics all comport with those outlined by Holbrey, et al. in the below reference.

* From: Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C. And Rogers, R. D. *Chem. Commun*. 2003, 476.

In the photo below, the two-phase system formed by **2·Tf_2N** and water is shown (left). On the right (l to r) are shown the clathrate systems formed by **2·Tf_2N** and chloroform

and benzene. The mark shows the original volume of TSIL in each instance. Note the larger volume in each case of the clathrate phase versus the pure IL. Also note the greater volume of the resulting clathrate phase involving chloroform compared to that involving benzene (equal quantities of TSIL were used for each experiment).



II. Determination of Abraham solvation parameters.

(a) Experimental

All probe molecules (Table 1) were purchased from Aldrich (Milwaukee, WI) and were used as received.

Untreated fused silica capillary tubing (0.25-mm i.d.) was purchased from Supelco (Bellefonte, PA). Five-meter capillary columns were coated at 40 °C by the static coating method using a 0.26% (w/v) solution of each RTIL in dichloromethane.[2] Following the coating process, the columns were flushed with dry helium gas and conditioned overnight from 30 – 120°C at 1°C per minute. The column efficiency was tested with naphthalene at 100°C and averaged nearly 2175 plates/meter for all columns. The retention time and peak efficiency of naphthalene at 100°C was monitored for each column daily to ensure that the coated layer of the RTIL had not changed during the chromatographic characterization process.

Supplementary Material (ESI) for Chemical Communications

Mixtures of probe molecules were dissolved in dichloromethane. Some probe molecules with very low boiling points (e.g. ethyl acetate, benzene, 1-hexyne) eluted with the void volume of the column at 100°C. Therefore, we opted to carry out the characterization at lower temperatures, namely 70, 50, and 30°C.

Chromatographic retention factors (*k*) are obtained for each solute used in the model at a specific temperature. Gas chromatographic measurements were made using a Hewlett-Packard model 5890 gas chromatograph and a Hewlett-Packard 3391 series II integrator. Helium was used as the carrier gas at a column inlet pressure of 3.1 psi and a flow rate of 1.0 mL/min. Split injection and flame ionization detection were utilized with injection and detection temperatures of 250°C. Methane was used to determine the dead volume of each column at the respective temperature.

Multiple linear regression analysis (MLRA) and statistical calculations were performed using the program Analyze-it (Microsoft, USA).

Bibliography relevent to this section:

[1] Abraham, M.H. *Chem. Soc. Rev.* **1993**, *22*, 73.
[2] Anderson, J.L.; Ding, J.; Welton, T.; Armstrong, D.W. *J. Am. Chem. Soc.* **2002**, *124,* 14247-14254
[3]Joesten, M.D.; Drago, R.S. *J. Amer. Chem. Soc.* **84**, 2037, 2696, 3817, (1962).

Table 1 (this section)**: List of Probe Molecules and Solute Descriptors used in the Abraham Solvation Parameter Model**

Probe Molecule	R_2	π_2^H	α_2^H	β_2^H	log L^{16}
Phenol	0.805	0.890	0.600	0.310	3.766
Octyl Aldehyde	0.160	0.650	0.000	0.450	4.360
Valeraldehyde	0.163	0.650	0.000	0.450	2.851
O-Xylene	0.663	0.560	0.000	0.160	3.939
P-Xylene	0.613	0.520	0.000	0.160	3.839
Cyclohexanol	0.460	0.540	0.320	0.570	3.758
Nitrobenzene	0.871	1.110	0.000	0.280	4.511
N,N-dimethylformamide	0.367	1.310	0.000	0.740	3.173
M-Xylene	0.623	0.520	0.000	0.160	3.839
2-Pentanone	0.143	0.680	0.000	0.510	2.755
1-Nitropropane	0.242	0.950	0.000	0.310	2.894
Toluene	0.601	0.520	0.000	0.140	3.325
Benzaldehyde	0.820	1.000	0.000	0.390	4.008
Pyridine	0.794	0.870	0.000	0.620	3.003
Aniline	0.955	0.960	0.260	0.530	3.993
Butanol	0.224	0.420	0.370	0.480	2.601
Acetic Acid	0.265	0.650	0.610	0.440	1.750
1-Octanol	0.199	0.420	0.370	0.480	4.619
Acetophenone	0.818	1.010	0.000	0.490	4.501
2-Chloroaniline	1.033	0.920	0.250	0.310	4.674
Methyl Caproate	0.080	0.600	0.000	0.450	3.874

Benzene	0.610	0.520	0.000	0.140	2.786
1-Hexyne	0.166	0.230	0.130	0.100	2.510
Pyrrole	0.613	0.730	0.410	0.290	2.865
Benzonitrile	0.742	1.110	0.000	0.330	4.039
Proprionitrile	0.162	0.900	0.020	0.360	2.082
1-chlorohexane	0.201	0.400	0.000	0.100	3.777
Ethyl acetate	0.106	0.620	0.000	0.450	2.314
p-Cresol	0.820	0.870	0.570	0.310	4.312
Ethylphenylether	0.681	0.700	0.000	0.320	4.242
Naphthalene	1.340	0.920	0.000	0.200	5.161
Dioxane	0.329	0.750	0.000	0.640	2.892
Cyclohexanone	0.403	0.860	0.000	0.560	3.792
Biphenyl	1.360	0.990	0.000	0.220	6.014
2-Fluorophenol	0.660	0.690	0.610	0.260	3.453
Benzylamine	0.829	0.880	0.100	0.720	4.319
Benzylalcohol	0.803	0.870	0.330	0.560	4.221

Table 2 (this section): Abraham Parameters at all measured temperatures.

	r	*s*	*a*	*b*	*l*
[bmim]BF_4					
40° C	0	1.647	2.219	-0.102	0.644
70° C	0	1.456	1.967	-0.127	0.569
2·BF_4					
30° C	0	2.23	4.13	0	0.56
50° C	0	2.07	3.73	0	0.49
70° C	0	1.90	3.36	0	0.45
3·BF_4					
30° C	0.22	2.43	3.79	0.50	0.56
50° C	0.21	2.34	3.38	0.49	0.44
70° C	0.17	1.83	3.21	0.21	0.42
[bmim]Tf_2N					
40° C	0	1.889	2.016	0.362	0.634
70° C	0	1.671	1.752	0.378	0.557
1·Tf_2N					
30° C	0	1.93	2.25	0.62	0.67
50° C	0	1.75	1.95	0.55	0.62
70° C	0	1.70	1.75	0.42	0.55
2·Tf_2N					
30° C	0	1.78	2.61	0.41	0.58
50° C	0	1.67	2.30	0.30	0.52
70° C	0	1.49	1.95	0.36	0.45
3·Tf_2N					
30° C	0.08	2.24	2.35	0.55	0.56
50° C	0.10	2.09	2.08	0.48	0.48
70° C	0.10	2.01	1.93	0.49	0.44
[bmim]PF_6					
40° C	0	1.914	1.887	0	0.620
70° C	0	1.695	1.579	0	0.515
[bmim]Cl					
40° C	0.237	2.247	7.030	-0.358	0.627
70° C	0.291	2.007	5.230	-0.320	0.445

IV. Experimental Procedures, Comments, and References, Lipase-catalyzed Transesterification of methyl methacrylate and 2-ethylhexanol

(a) *Materials and Methods*

Candida rugosa lipase (previously known as *Candida cylindracea*, L-1754) and porcine pancreatic lipase (PPL) were purchased from Sigma Chemicals (St. Louis, MO). Lipase AK 'Amano' and Lipase PS-C 'Amano' were generous gift from Amanoenzymes, USA. Lipase PC 'CLEC', Chiro 'CLEC'-BL, Pepti 'CLEC'-TR, Pepti 'CLEC'-BL were purchased from Altus Biologics Inc. (Cambridge, MA). All enzymes were used as such without any further purification or treatment. The [bmim][PF_6] used in transesterification reactions was synthesized and purified by SACHEM Inc. (Austin, TX) following the procedure described by Huddleston and co-workers[1] and used as supplied. All other reagents were purchased from Aldrich chemicals (St. Louis, MO) and of highest purity available. Water content in the TSIL **2-Tf_2N** was routinely determined to be 70-80 ppm (Karl Fischer method) after drying overnight under high vacuum.

(b) *General Procedure for Lipase-Catalyzed Transesterification of Methyl Methacrylate and 2-Ethylhexanol*

Both the substrates methyl methacrylate and 2-ethylhexanol were dissolved in the solvent at a concentration of 200 mM. All transesterification reactions were performed through the addition of solvent containing methyl methacrylate (1 ml, 200 mM) and 2-ethylhexanol (1ml, 200 mM) to enzyme (lipase) in a 5 ml Kimble glass vial. The enzyme and substrate suspension was sonicated for 1 min. The reaction vials were then immediately placed in constant temperature shaker pre-set at 35 °C and 300 rpm.

While performing reactions in organic solvents, aliquots (1.0 μl) were removed from reaction mixture using 1.0 μl Hamilton syringe. When performing reactions in ionic liquids, 2-ethylhexyl methacrylate was recovered via liquid-liquid extraction using hexane. In both cases samples were withdrawn at specified time intervals for measurement of initial reaction rate.

The formation of 2-ethylhexylmethacrylate was monitored and analyzed using a Perkin-Elmer Auto system Gas Chromatograph (GC). The GC was fitted with an Alltech EC 1000 capillary column (30 m X 0.53 mm X 1.0 μm) and was operated with a 1:4 split ratio using helium as carrier gas. The injector and detector temperature were set to 300 °C. The oven program consisted of an initial temperature of 100 °C that was maintained for 2 min after which the temperature was increased at a rate of 25 °C /min to a final temperature of 160 °C and maintained for 3 min. The retention time of 2-ethylhexyl methacrylate was 5.4 min. A calibration curve of peak area versus the concentration of 2-ethylhexyl methacrylate in presence of substrates was created for each ionic

liquid and organic solvent[2, 3]. No internal standard was used; however GC was calibrated daily.

(c) *Results, Enzyme activity in Ionic liquid*

Most of the enzyme-mediated reactions performed to date are in dialkylimidazolium based ionic liquids with hexafluorophosphate and tetrafluoroborate anions. Only recently have other cations and anions begin to be studied [4-7]. Our interest is in expanding the portfolio of potential biocatalytic solvents by studying a variety of ionic liquids. Initial reaction rates of the lipase-catalyzed transesterification of methyl methacrylate and 2-ethylhexanol were measured in the ionic liquids and organic solvents to determine the effect of ionic liquid on enzyme specificity and activity **(Figure 1)**. Our experience with this reaction system, combined with an extensive data set, makes this an ideal model system. The selection of lipases for these experiments was based on prior work[8-10] in which several lipases were screened for activity in hexane via the lipase-catalyzed transesterification of methyl methacrylate with 2-ethylhexanol performed under identical reaction conditions. Result of lipase screen indicated that *Candida rugosa* lipase exhibited the highest activity and was therefore chosen as the model enzyme for this study. It would appear that although there is much enthusiasm about biocatalysis in ionic liquids, only one such ionic liquid supports significant activity with lipases. Having demonstrated that lipase maintains a high level of activity in [bmim][PF_6], a natural extension was to screen newer ionic liquids with lipases. While screening *Candida rugosa* in this new ionic liquid we did not observe any transesterification under similar reaction conditions as well as higher concentrations of enzyme **(Table 1)**. As a part of ongoing biocatalysis in ionic liquid we have screened other lipases in this ionic liquid. As a result of this lipase screen in **3·Tf_2N**, we observed that Lipase PC 'CLEC'[11] has shown significant transesterification. However, Lipase PC 'CLEC' was not active in [bmim] [PF_6]. In **3·Tf_2N,** 'CLEC' lipase (*Pseudomonas cepacia*) catalyzed the transesterification at an initial rate of 95.4 μM /*hr*/mg **(Figure 2)**. This transesterification reaction did not proceed in the more polar organic solvents. Based on these results we believe this enzyme initially showed significant transesterification however after 15 hours the enzyme appears to slightly deactivate. Further stability studies must be done for practical applications and in order to understand enzyme activity as a function of water activity.

(d) *Conclusions*

We have shown that an enzymatic synthesis[10] in a functionalized ionic liquid is possible, adding to the variety of environments in which a biocatalytic synthesis can be considered. We are now exploring the design of other novel ionic liquids which activate enzymes and aid, rather than complicate product separation.

(e) *Section-specific references*

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2. Kamat, S.: Critchley, G.; Beckman, E.J.; Russell, A.J. *Biotechnol. Bioeng.* 1995, **46**, 610-620.
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10. Erbeldinger, M.; Mesiano, A.J.; Russell, A.J. *Biotechnol. Prog*. 2000, **16**, 1129-1131.
11. CLECs are cross linked enzyme crystals. They offer a combination of features associated with either enzymes (high activity and selectivity, ability to function under mild reaction condition, ease of disposal) or heterogeneous catalysts (stability in different environments, recycling).

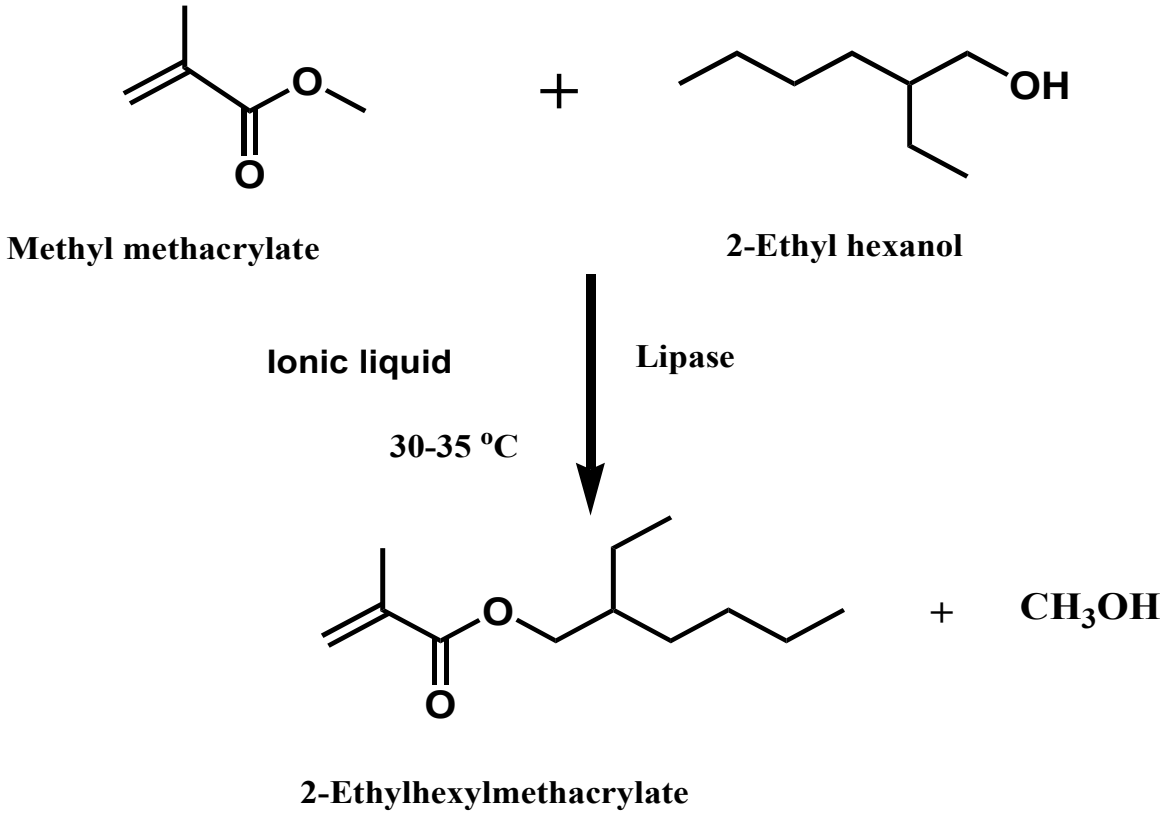


Figure 1 [Part II of Supplemental information]. Lipase-catalyzed transesterification of methyl methacrylate with 2-ethylhexanol to 2-ethylhexyl methacrylate

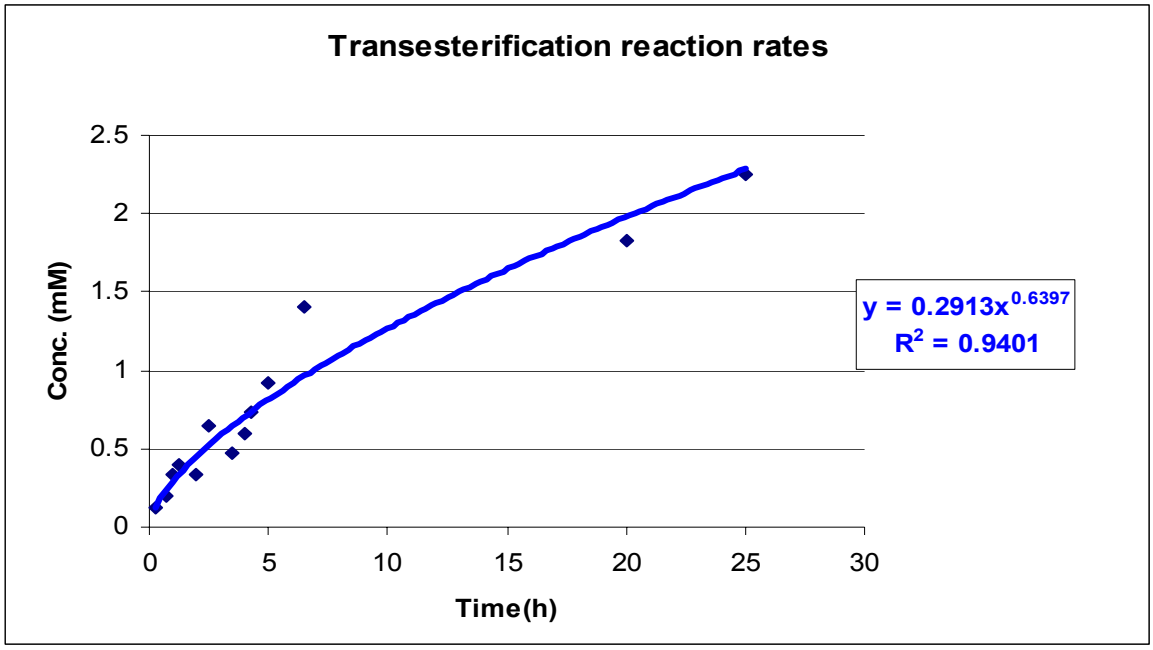


Figure 2 [Part II of Supplemental information]. Initial reaction rates of lipase-catalyzed transesterification of methyl methacrylate and 2-ethylhexanol

Table 1 [Part II of Supplemental Information]. Summary of lipase screening in **3·Tf_2N** and other reaction media

Lipase & Temperature (100mM of MMA and 2-Ethyl hexanol)	**Ionic Liquid or Solvent**	**Initial Rate μM/hr/mg**
Candida rugosa, 30 °C	3-Tf_2N	No reaction
Candida rugosa, 30 °C	3-Tf_2N	No reaction
Candida rugosa, 45 °C	3-Tf_2N	No reaction
Porcine Panreatic Lipase, 35 °C	3-Tf_2N	No reaction
Lipase AK "Amano", 35 °C	3-Tf_2N	No reaction
Lipase PS-C "Amano", 35 °C	3-Tf_2N	No initial reaction[a]
Lipase PC "CLEC", 35°C	3-Tf_2N	95.4
Lipase PC "CLEC", 35°C	[bmim] [PF_6]	No reaction
Chiro "CLEC"-BL, 35 °C	[bmim] [PF_6]	No reaction
Pepti "CLEC"-TR, 35 °C	[bmim] [PF_6]	No reaction
Pepti "CLEC"-TR, 35 °C	[bmim] [PF_6]	No reaction
Lipase PC "CLEC", 35 °C	Hexane	No initial reaction[b]
Lipase PC "CLEC", 35 °C	Tetrahydrofuran	No reaction
Lipase PC "CLEC", 35 °C	Acetonitrile	No initial reaction[c]

No initial reaction was detected but after 28 hours, 3.5 hours and 3 hours, 0.19 mM, 0.09 mM and 0.08 mM was detected in 3-Tf_2N[a], hexane[b] and acetonitrile[c] respectively.

V. Spectra/Spectroscopic studies [Grouped by compound; ^{1}H-NMR, ^{13}C-NMR; ^{19}F-NMR; IR spectra grouped separately at end.

(a) **2·BF4**

^{1}H-NMR (300 mHz, 0.5 M acetone-d^6) δ: 1.27 (t, 3H, CH_3); 2.7-3.0 (overlapping m, 2H, CH_2); 3.29 (m, 1H, C*H*H); 3.43 (m, 1H, CH*H*); 4.01, (s, 3H, N-CH_3); 4.78 (m, 2H, CH_2); 7.67 (d, 1H, CH); 7.79 (d, 1H, CH); 9.03 (s, 1H, CH).
^{13}C-NMR (75.56 mHz, ^{1}H-decoupled 0.5 M acetone-d^6) δ: 6.09 (CH_3), 36.20 (CH_2), 43.84 (CH_2), 45.54 (CH_2), 49.78 (CH_3), 122.99 (CH), 124.02 (CH), 137.54(CH).

^{19}F-NMR (282.78 mHz, 0.5 M acetone-d^6) δ: -150.34, -150.28 (^{10}B and ^{11}B isotopes)

(b) **2·Tf_2N**

^{1}H-NMR (300 mHz, 0.5 M acetone-d^{6}) δ: 1.26 (t, 3H, CH_3); 2.7-2.9 (overlapping m, 2H, CH_2); 3.30 (m, 1H, C*H*H); 3.43 (m, 1H, CH*H*); 4.07, (s, 3H, N-CH_3); 4.84 (m, 2H, CH_2); 7.73 (d, 1H, CH); 7.84 (d, 1H, CH); 9.11 (s, 1H, CH).
^{13}C-NMR (75.56 mHz, ^{1}H-decoupled) 0.5 M acetone-d^{6}) δ: 6.01 (CH_3), 36.22 (CH_2), 43.92 (CH_2), 45.64 (CH_2), 49.76 (CH_3), 120.1 (quartet, CF_3) 123.03 (CH), 124.17 (CH), 137.43(CH).

^{19}F-NMR (282.78 mHz, 0.5 M acetone-d^{6}) δ: -79.75

(c) **3·BF_4**

^{1}H-NMR (300 mHz, 0.5 M acetone-d^{6}) δ: 1.33 (t, 3H, CH_3); 3.17 (q, 2H, CH_2); 3.80 (t, 2H, CH*H*); 4.02, (s, 3H, N-CH_3); 4.81 (t, 2H, CH_2); 7.67 (d, 1H, CH); 7.80 (d, 1H, CH); 9.10 (s, 1H, CH).
^{13}C-NMR (75.56 mHz, ^{1}H-decoupled 0.5 M acetone-d^{6}) δ: 5.71 (CH_3), 36.35 (CH_2), 47.67 (CH_2), 50.58 (CH_2), 49.78 (CH_3), 122.99 (CH), 123.94 (CH), 137.66(CH).

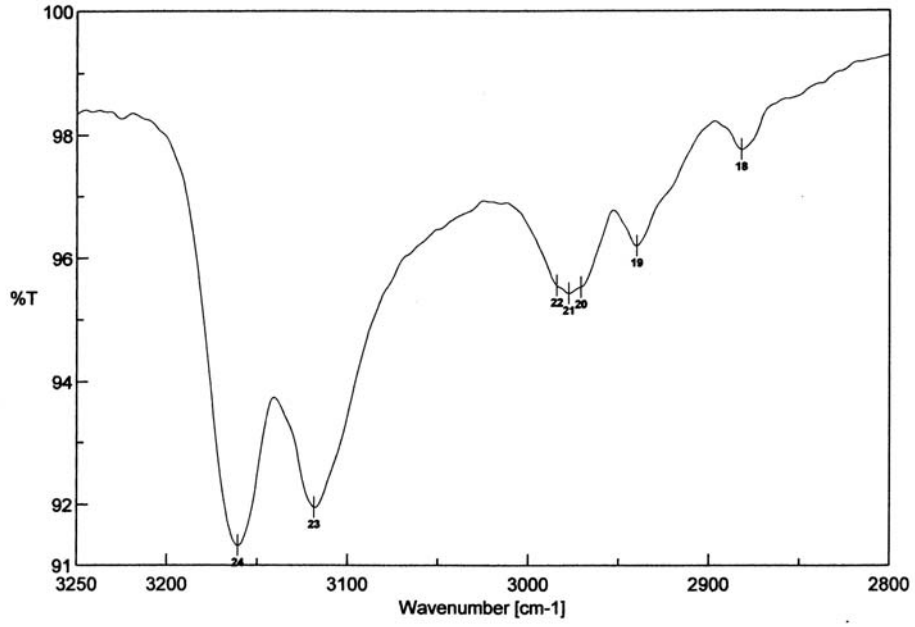
^{19}F-NMR (282.78 mHz, 0.5 M acetone-d^{6}) δ: -150.37, -150.31 (^{10}B and ^{11}B isotopes)

(d) **3·Tf_2N**

^{1}H-NMR (300 mHz, 0.5 M acetone-d^{6}) δ: 1.31 (t, 3H, CH_3); 3.17 (q, 2H, CH_2); 3.78 (t, 2H, CH*H*); 4.01, (s, 3H, N-CH_3); 4.83 (t, 2H, CH_2); 7.65 (d, 1H, CH); 7.79 (d, 1H, CH); 8.96 (s, 1H, CH).
^{13}C-NMR (75.56 mHz, ^{1}H-decoupled 0.5 M acetone-d^{6}) δ: 5.72 (CH_3), 36.40 (CH_2), 42.96 (CH_2), 47.92 (CH_2), 50.55 (CH_3), 121.38 (quartet, CF_3), 123.06 (CH), 124.09 (CH), 137.55(CH).

^{19}F-NMR (282.78 mHz, 0.5 M acetone-d^6) δ: -79.76

(e) IR, **2·BF$_4$**, aromatic & aliphatic CH fingerprint region.

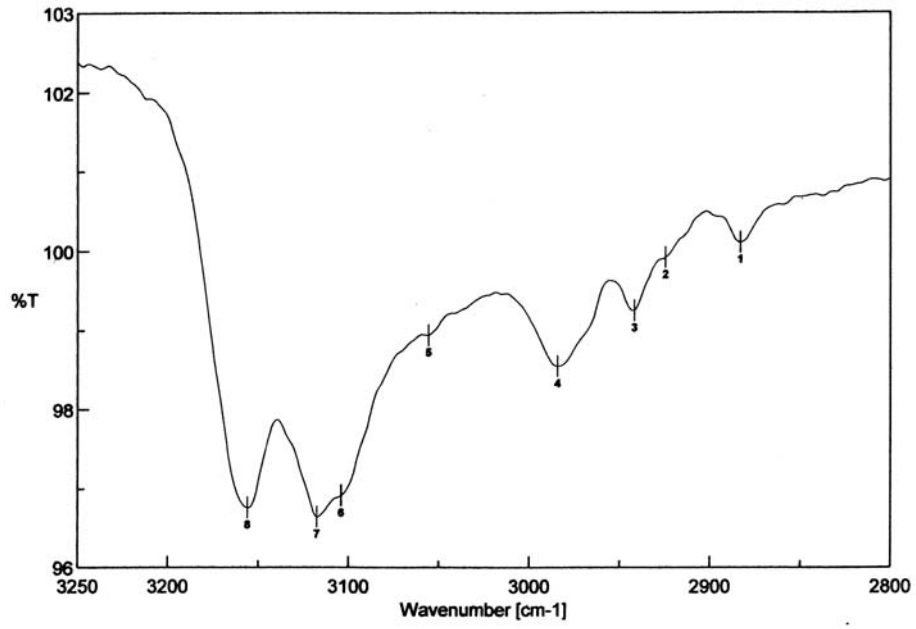


Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity
1	754.995	71.391	2	845.633	75.8218
3	1014.37	17.6383	4	1028.84	21.215
5	1045.23	23.8095	6	1173.47	74.6303
7	1262.18	95.7308	8	1286.29	93.0484
9	1338.36	94.3095	10	1363.43	93.9751
11	1380.78	94.0917	12	1423.21	91.7347
13	1456.96	87.7264	14	1565.92	84.8924
15	1577.49	84.2282	16	1636.3	95.2231
17	1706.69	97.494	18	2882.09	97.7563
19	2939.95	96.1946	20	2970.8	95.5199
21	2977.55	95.4184	22	2984.3	95.5517
23	3118.33	91.9528	24	3160.76	91.3243

[Comment]	
Sample Name	sulfoxide - BF_4
Comment	
User	
Division	
Company	University of South Alabama
[Measurement Information]	
Model Name	FT/IR-4100typeA
Serial Number	B013761016
Light Source	Source #1
Detector	Detector #1
Accumulation	8
Resolution	4 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (4)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

(f) IR, **2·TF$_2$N**, aromatic & aliphatic CH fingerprint region.



Result of Peak Picking

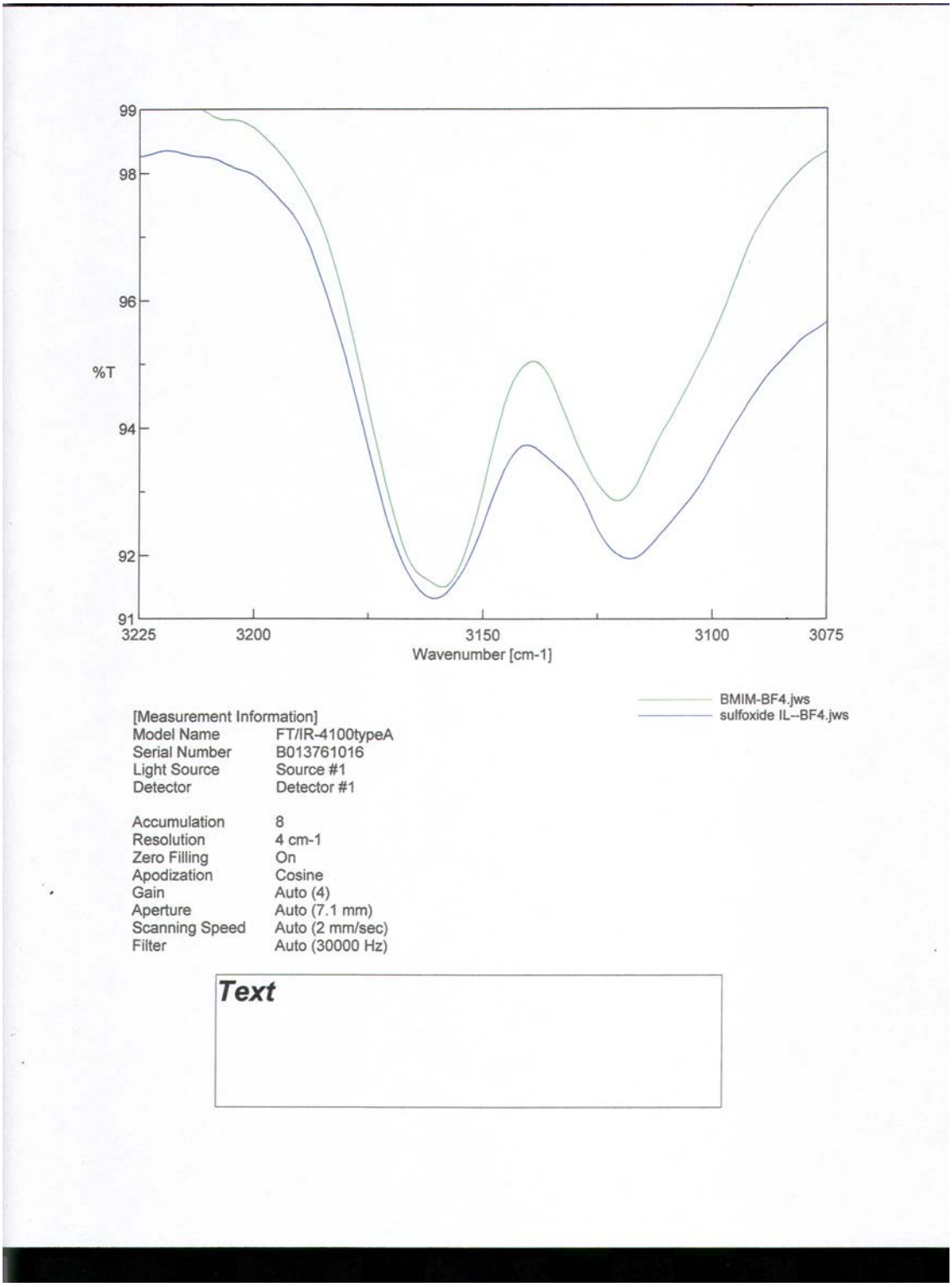
No.	Position	Intensity	No.	Position	Intensity
1	2883.06	100.112	2	2924.52	99.9159
3	2941.88	99.246	4	2984.3	98.5453
5	3055.66	98.9365	6	3103.87	96.9132
7	3117.37	96.6454	8	3155.94	96.7599

[Comment]	Sulfoxide TFN
Sample Name	
Comment	
User	
Division	
Company	University of South Alabama

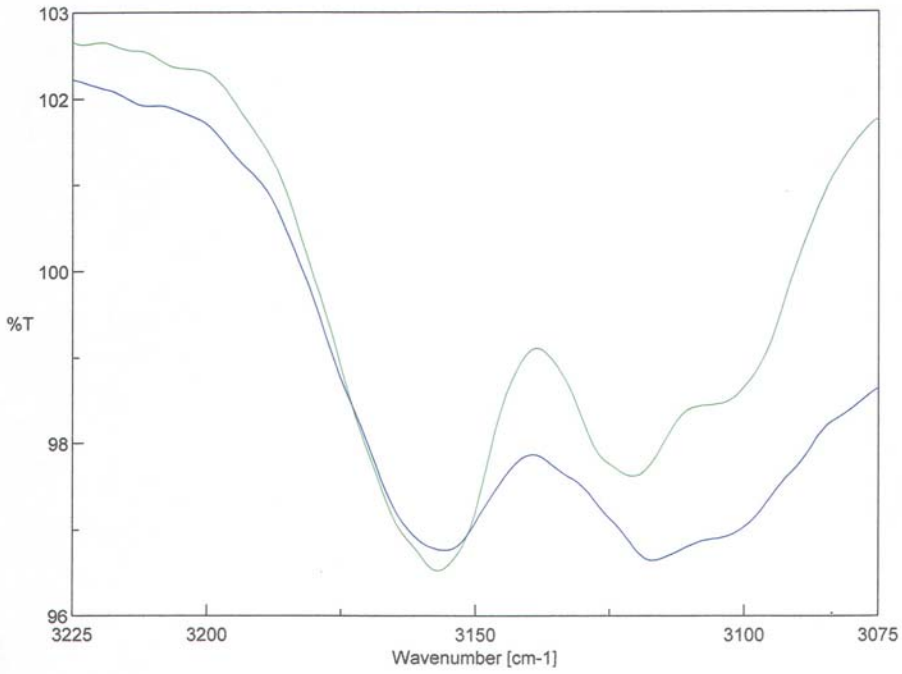
[Measurement Information]

Model Name	FT/IR-4100typeA
Serial Number	B013761016
Light Source	Source #1
Detector	Detector #1
Accumulation	8
Resolution	4 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (4)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

(g) IR overlay, **2·BF_4** (lower trace) and [BMIM]BF_4 (upper trace) aromatic fingerprint region.



(h) IR overlay, **2·TF_2N** (lower trace) and [BMIM]TF_2N (upper trace) aromatic fingerprint region.



[Measurement Information]

Model Name	FT/IR-4100typeA
Serial Number	B013761016
Light Source	Source #1
Detector	Detector #1
Accumulation	8
Resolution	4 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (4)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

Text

Supplementary Material (ESI) for Chemical Communications