Electronic Supporting Information for

"Correlating ionic liquid solvent effects with solvent parameters for a reaction that proceeds through a xanthylium intermediate"

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Synthesis of ionic liquid precursors

1-Butyl-3-methylimidazolium chloride ([bmim]Cl)[1]

N-Methylimidazole (192 mL, 2.41 mol) and *n*-chlorobutane (301 mL, 2.89 mol) were combined and stirred at 75 °C under a nitrogen atmosphere for 8 days. Ethyl acetate (200 mL) was added, and the mixture stirred at room temperature for 15 mins. During this time, a white solid formed. The solid was triturated with ethyl acetate (3 x 200 mL), then recrystallised from a 3:2 mixture of acetonitrile and ethyl acetate. The resultant solid was dried under reduced pressure to give the product as a white solid (316 g, 1.81 mol, 75%). MP: 64-66 °C (lit.[2] 65 °C). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.96 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.32-1.42 (m, 2H, $C\underline{H}_2CH_3$), 1.89-1.96 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.09 (s, 3H, $NC\underline{H}_3$), 4.33 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.79-7.86 (m, 2H, NC<u>H</u>C<u>H</u>N), 10.80 (s, 1H, NC<u>H</u>N).

1-Butyl-3-methylimidazolium bromide ([bmim]Br)[3]

N-Methylimidazole (61.8 g, 0.753 mol) and *n*-bromobutane (114 g, 0.832 mol) were combined and stirred at room temperature under a nitrogen atmosphere for 7 days, during which time a white solid formed. The solid was triturated with ethyl acetate (4 x 100 mL) and dried under reduced pressure to give the product as a white solid (156 g, 0.735 mol, 98%). MP: 71-73 °C (lit.[4] 70 °C). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.35-1.43 (m, 2H, $C\underline{H}_2CH_3$), 1.90-1.97 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.10 (s, 3H, $NC\underline{H}_3$), 4.45 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.83-7.91 (m, 2H, NC<u>H</u>C<u>H</u>N), 10.30(s, 1H, NC<u>H</u>N).

1-Butyl-2,3-dimethylimidazolium chloride ([bm$_2$im]Cl)[1]

1,2-Dimethylimidazole (47.1 g, 0.490 mol) and *n*-chlorobutane (54.3g, 0.587 mol) were combined and stirred at 75 °C under a nitrogen atmosphere for 7 days. During this time a white solid formed. The solid was dissolved in acetonitrile (100 mL) and the solution stirred at 75 °C under a nitrogen atmosphere for a further 28 days. The acetonitrile was removed under reduced pressure and the resultant solid was recrystallised from a 3:2 mixture of acetonitrile and ethyl acetate to give the product as a white solid (76.8 g, 0.406 mol, 83%). MP: 91-93 °C (lit.[5] 93 °C). ^{1}H NMR (400 MHz, acetone-d_6). δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.36-1.45 (m, 2H, $C\underline{H}_2CH_3$), 1.81-1.89 (m, 2H, $C\underline{H}_2CH_2CH_3$), 2.82 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 4.00 (s, 1H, $NC\underline{H}_3$), 4.36 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.83-7.84 (m, 2H, NC<u>H</u>C<u>H</u>N).

1-Butyl-2,3-dimethylimidazolium bromide ([bm$_2$im]Br)[6]

1,2-Dimethylimidazole (13.8 g, 0.143 mol) and *n*-bromobutane (23.6 g, 0.172 mol) were combined and stirred at room temperature under a nitrogen atmosphere for 4 days. During this time, a white solid formed. The solid was dissolved in acetonitrile (30 mL) and the solution was stirred at room temperature under a nitrogen atmosphere for a further 4 days. The acetonitrile was removed under reduced pressure. The resultant solid was triturated with ethyl acetate (4 x 50 mL) and dried under reduced pressure to give the product as a white solid (32.0 g, 0.138 mol, 96%). MP: 96-98 °C (lit.[6] 95-97 °C). ^{1}H NMR (400 MHz, acetone-d_6). δ 0.96 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.37-1.46 (m, 2H, $C\underline{H}_2CH_3$), 1.81-1.89 (m, 2H, $C\underline{H}_2CH_2CH_3$), 2.84 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 4.01 (s, 1H, $NC\underline{H}_3$), 4.37 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.82-7.83 (m, 2H, $NC\underline{H}C\underline{H}N$).

N-Butyl-*N*-methylpyrrolidinium bromide ([bmpyr]Br)[7]

N-Methylpyrrolidine (34.0 mL, 0.327 mol) and *n*-bromobutane (42.4 mL, 0.392 mol) were combined and stirred at room temperature under a nitrogen atmosphere for 24 hours. During this time a white solid formed. The solid was dissolved in acetonitrile (100 mL) and stirred at room temperature under a nitrogen atmosphere for a further 24 hours. The acetonitrile was removed under reduced pressure, and the solid recrystallised from a 1:1 mixture of acetonitrile and ethyl acetate to give the product as a white solid (59.2 g, 0.266 mol, 81%). MP: 213-215 °C (lit.[8] 216-217 °C). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.98 (t, J = 7.4 Hz, 3H, $C\underline{H}_3CH_2$), 1.39-1.48 (m, 2H, $C\underline{H}_2CH_3$), 1.84-1.92 (m, 2H, $C\underline{H}_2CH_2CH_3$), 2.28-2.30 (m, 4H, $NCH_2C\underline{H}_2C\underline{H}_2$), 3.31 (s, 3H, $NC\underline{H}_3$), 3.68-3.72 (m, 2H, $NC\underline{H}_2CH_2$), 3.82-3.85 (m, 4H, $C\underline{H}_2NC\underline{H}_2$).

Synthesis of ionic liquids 4-10

1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], **4**)[9]

1-Butyl-3-methylimidazolium chloride (51.8 g, 0.300 mol) and sodium tetrafluoroborate (38.3 g, 0.349 mol) were combined with acetone (200 mL) and stirred at room temperature for 40 hours. The sodium chloride that precipitated was removed by filtration and discarded. Acetone was removed under reduced pressure from the filtrate and dichloromethane (200 mL) was added to the residue. The solution was stored at -20 °C overnight to assist in precipitation of residual sodium chloride. The solution was filtered and the dichloromethane removed from the filtrate under reduced pressure. Dichloromethane (200 mL) was added to the residue and the process repeated 11 times to ensure complete removal of sodium chloride. The resultant solution was dried under reduced pressure to give the product **4** as a pale yellow, viscous liquid (39.3 g, 0.174 mol, 58%). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.33-1.42 (m, 2H, $C\underline{H}_2CH_3$), 1.87-1.95 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.03 (s, 3H, $NC\underline{H}_3$), 4.34 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.69-7.74 (m, 2H, NC$\underline{H}$C$\underline{H}$N), 8.97 (s, 1H, NC$\underline{H}$N).

1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6], **5**)[1]

1-Butyl-3-methylimidazolium bromide (19.0 g, 0.0867 mol) and potassium hexafluorophosphate (19.2 g, 0.104 mol) were each dissolved in water (100 mL each) and combined. The solution was stirred at room temperature for 16 hours. During this time, two immiscible layers formed. The aqueous layer was extracted with dichloromethane (3 x 75 mL) and the combined organic layers washed with water (10 x 100 mL). The dichloromethane was removed under reduced pressure and the resultant liquid dried to give the product **5** as a pale yellow, viscous liquid (15.0 g, 0.0528 mol, 61%). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.34-1.43 (m, 2H, $C\underline{H}_2CH_3$), 1.89-1.96 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.05 (s, 3H, $NC\underline{H}_3$), 4.36 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.69-7.75 (m, 2H, NC$\underline{H}$C$\underline{H}$N), 8.97 (s, 1H, NC$\underline{H}$N).

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf], **6**)[10]

1-Butyl-3-methylimidazolium chloride (17.6 g, 0.101 mol) was dissolved in dichloromethane (70 mL) and lithium trifluoromethanesulfonate (19.1 g, 0.122 mol) was added to the solution. The mixture was stirred at room temperature for 16 hours. The resultant lithium chloride was

removed by filtration and discarded. The dichloromethane was removed under reduced pressure. Dichloromethane (50 mL) was added to the residual liquid and the solution stored at -20 °C overnight to assist in further precipitation of residual lithium chloride. Again, residual lithium chloride was removed by filtration and discarded and the process of precipitating and discarding residual lithium chloride was repeated 12 times. Finally, the dichloromethane was removed under reduced pressure to give the product **6** as a colourless, viscous liquid (10.8 g, 0.0375 mol, 37%). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.34-1.43 (m, 2H, $C\underline{H}_2CH_3$), 1.89-1.96 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.06 (s, 3H, $NC\underline{H}_3$), 4.36 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.72-7.80 (m, 2H, $NC\underline{H}C\underline{H}N$), 9.11 (s, 1H, $NC\underline{H}N$).

1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([bmim][$N(SO_2CF_3)_2$], **7**)[9]

1-Butyl-3-methylimdazolium bromide and lithium *bis*(trifluoromethanesulfonyl)imide were each dissolved in water (200 mL each) and combined. The mixture was stirred at room temperature for 18 hours. During this time, two immiscible layers formed. The aqueous layer was extracted with dichloromethane (3 x 150 mL), the organic layers combined and washed with water (10 x 200 mL). The dichloromethane was removed under reduced pressure and the resultant liquid dried to give the product **7** as a colourless, viscous liquid (184 g, 0.439 mol, 90%). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.34-1.43 (m, 2H, $C\underline{H}_2CH_3$), 1.89-1.97 (m, 2H, $C\underline{H}_2CH_2CH_3$), 4.07 (s, 3H, $NC\underline{H}_3$), 4.37 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2$), 7.71-7.77 (m, 2H, $NC\underline{H}C\underline{H}N$), 9.03 (s, 1H, $NC\underline{H}N$).

1-Butyl-2,3-dimethylimidazolium tetrafluoroborate ([bm_2im][BF_4], **8**)[1]

1-Butyl-2,3-dimethylimidazolium chloride (33.0 g, 0.175 mol) and sodium tetrafluoroborate (21.9 g, 0.200 mol) were combined and acetone (100 mL) was added. The mixture was stirred at room temperature for 20 hours. The sodium chloride that precipitated was removed by filtration and discarded and the acetone was removed under reduced pressure. Dichloromethane (100 mL) was added to the residue and the solution was stored at -20 °C overnight to assist in precipitation of residual sodium chloride. The solution was filtered, the dichloromethane was removed under reduced pressure and dichloromethane (100 mL) was added and the solution again store at -20 °C overnight. This process was repeated ten times to ensure complete removal of sodium chloride. The dichloromethane was removed under reduced pressure to give the product **8** as a pale yellow, viscous liquid (19.5 g, 0.081 mol, 46%). ^{1}H NMR (400 MHz, acetone-d_6). δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.35-1.45 (m,

2H, C$\underline{H}_2$CH$_3$), 1.80-1.88 (m, 2H, C$\underline{H}_2$CH$_2$CH$_3$), 2.75 (s, 3H, NC(C$\underline{H}_3$)NCH$_3$), 3.91 (s, 1H, NC$\underline{H}_3$), 4.27 (t, *J* = 7.4 Hz, 2H, NC$\underline{H}_2$CH$_2$), 7.58-7.60 (m, 2H, NC$\underline{H}$C$\underline{H}$N).

N-Butyl-*N*-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide ([bmpyr][N(SO$_2$CF$_3$)$_2$], **9**)[9]

N-Butyl-*N*-methylpyrrolidinium bromide (23.0 g, 0.104 mol) and lithium *bis*(trifluoromethanesulfonyl)imide (36.1 g, 0.126 mol) were each dissolved in water (50 mL each) and combined. The solution was stirred at room temperature for 20 hours. During this time, two immiscible layers formed. The aqueous layer was extracted with dichloromethane (3 x 50 mL) and the combined organic layers were washed with water (10 x 100 mL). The organic layer was dried under reduced pressure to give the product **9** as a pale yellow, viscous liquid (35.8 g, 0.0848 mol, 82%). ^{1}H NMR (400 MHz, acetone-d_6) δ 0.98 (t, *J* = 7.4 Hz, 3H, C$\underline{H}_3$CH$_2$), 1.39-1.48 (m, 2H, C$\underline{H}_2$CH$_3$), 1.87-1.95 (m, 2H, C$\underline{H}_2$CH$_2$CH$_3$), 2.31-2.32 (m, 4H, NCH$_2$C$\underline{H}_2$C$\underline{H}_2$), 3.26 (s, 3H, NC$\underline{H}_3$), 3.52-3.56 (m, 2H, NC$\underline{H}_2$CH$_2$), 3.72-3.73 (m, 4H, C$\underline{H}_2$NC$\underline{H}_2$).

1-Butyl-2,3-dimethylimdazolium *bis*(trifluoromethanesulfonyl)imide ([bm$_2$im][N(SO$_2$CF$_3$)$_2$], **10**)[1]

1-Butyl-2,3-dimethylimidazolium bromide (11.0 g, 0.0472mol) and lithium *bis*(trifluoromethanesulfonyl)imide (15.6 g, 0.0543mol) were each dissolved in water (50 mL each) and combined. The solution was stirred at room temperature for 18 hours, during which time two immiscible layers formed. The aqueous layer was extracted with dichloromethane (3 x 25 mL). The combined organic layers were washed with water (10 x 50 mL) and dried with magnesium sulfate. The dichloromethane was removed under reduced pressure and the resultant liquid was dried to give the product **10** as a colourless, viscous liquid (14.9 g, 0.0344 mol, 73%). ^{1}H NMR (400 MHz, acetone-d_6). δ 0.95 (t, *J* = 7.4 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.38-1.44 (m, 2H, C$\underline{H}_2$CH$_3$), 1.83-1.90 (m, 2H, C$\underline{H}_2$CH$_2$CH$_3$), 2.80 (s, 3H, NC(C$\underline{H}_3$)NCH$_3$), 3.96 (s, 1H, NC$\underline{H}_3$), 4.30 (t, *J* = 7.4 Hz, 2H, NC$\underline{H}_2$CH$_2$), 7.60-7.64 (m, 2H, NC$\underline{H}$C$\underline{H}$N).

General experimental details for kinetic analyses

All kinetic analyses were performed in triplicate. All kinetic experiments were carried out on either a Bruker Avance III 400, Bruker Avance III 500 or Bruker Avance III 600 spectrometer with either a TBI or BBFO probe. Results were shown to be reproducible between probes and spectrometers, in cases where different spectrometers were used.

Experimental details for kinetic analyses – xanthene 1 system

Kinetic analyses were carried out in solutions containing the electrophile **1** (*ca.* 0.01 mol L^{-1}) and the nucleophile **2** (*ca.* 0.02 mol L^{-1}) and the desired solvent mixture containing acetonitrile and either [bmim][BF_4] **4** or [bmim][PF_6] **5**. An aliquot (*ca.* 0.5 mL) from each stock solution was placed in an NMR tube.

All cases were monitored using ^{1}H NMR spectroscopy following the depletion of the signal representing the benzylic proton of the electrophile **1** at *ca.* 6.0 ppm. For stock solutions containing acetonitrile as the solvent alone, the NMR tubes were placed in a water bath set to 73.8 °C and the reaction monitored intermittently. For stock solutions containing [bmim][BF_4] **4** the reaction was monitored *in situ* with the spectrometer set to 73.8 °C.

For both the acetonitrile only and [bmim][PF_6] **5** cases the reaction was monitored using initial rates by following the reaction to 10% consumption of the electrophile **1**. For the [bmim][BF_4] **4** cases, the reaction was monitored until more than 95% of the electrophile **1** was consumed.

NMR spectra used for kinetic analyses were processed using MestReNova 10.1 software. For the cases where initial rates methodology was used, the signals representing the starting material at *ca.* 6.0 ppm and the product at *ca.* 6.3 ppm were both integrated in order to calculate the extent of conversion. The LINEST function in Microsoft Excel 16.24 was used to determine the first order rate constant from a graph of extent of conversion *vs.* time. For cases where the reaction was monitored to completion, the first order rate constant was calculated by integration of the signal representing the starting material at *ca.* 6.0 ppm and

fitting the natural logarithm of the integrations to a linear function using the LINEST function.

Summary of effects of the ionic liquids 4 and 5 on the reaction between xanthydrol 1 and indole 2

Kinetic studies were carried out under much more dilute conditions than reported in literature[11] (*ca.* 0.01 mol L^{-1} compared to previously reported 0.4 mol L^{-1}) as the solubility of the xanthydrol **1** reported could not be reproduced. Even under these more dilute conditions, the reaction proceeded to a similar extent of conversion in the same time as had been reported[11] in each of the ionic liquids **4** and **5**. The rate constants observed for the reaction in each of [bmim][BF_4] **4** and [bmim][PF_6] **5** (χ = 0.99) were 1.3 x 10^{-4} s^{-1} and 4.7 x 10^{-6} s^{-1}, respectively; this difference represents an almost 30-fold increase when using ionic liquid **4** compared to salt **5** but also nearly three orders of magnitude greater than in acetonitrile. Importantly, the higher rate constant observed for [bmim][BF_4] **4** matches the higher extent of conversion observed for this ionic liquid compared to [bmim][PF_6] **5** (92% and 61%, respectively, after 24 h albeit at χ_{salt} *ca.* 0.5).

Mole fraction dependence studies were undertaken to understand how changing the amount of ionic liquid in the reaction mixture affected the rate constant for the process. [Bmim][BF_4] **4** was used as the ionic liquid for these studies as the largest increase in the rate constant was observed using this solvent in the initial studies. Acetonitrile was chosen as the molecular co-solvent; it has been widely used previously as a co-solvent with ionic liquids.[12-14] As shown in Figure S1, any amount of the ionic liquid **5** mixed with the molecular solvent resulted in a significant increase in the rate constant.

These studies were complicated by the enormous sensitivity of xanthydrol **1** to trace amounts of acid in the reaction mixture. Special care had to be taken to ensure that no acid was present (including pre-treatment of all reaction vessels). This problem was most notable for the molecular solvent case, which is perhaps surprising given known problems with the hydrolysis of the anions of both of the ionic liquids **4** and **5**.[15] However, in the case of this reaction, treatment of the ionic liquids to remove

acid gave reproducible data, suggesting the rate constant enhancement was a solvent effect, rather than due to the presence of acid.

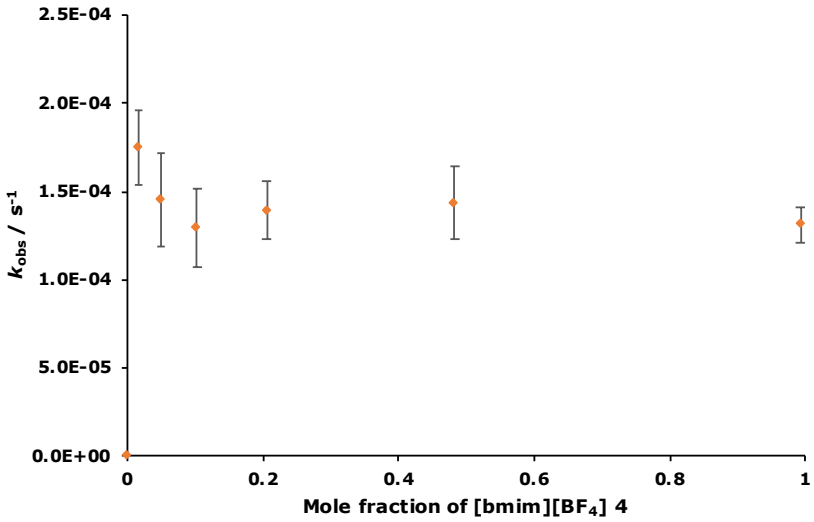


Figure S1. The dependence of the unimolecular rate constant (k_1) of the reaction between xanthydrol **1** and indole **2** on the mole fraction of [bmim][BF_4] **4** (♦) in acetonitrile. Uncertainties reported are obtained from the standard deviation of triplicate measurements.

Synthesis of xanthene substrates

Summary

Initially, a halogen leaving group was considered to increase the reactivity of the xanthene precursor **1**, not least because previous studies of ionic liquids as solvents on this reaction type have frequently used substrates with these leaving groups.[7, 13, 16-18] Unfortunately, due to the relative stability of the xanthylium carbocation, attempts to isolate the 9-chloroxanthene, 9-bromoxanthene and xanthene mesylate were unsuccessful and resulted exclusively in the decomposition products xanthene and xanthone. A potential mechanism involves xanthylium, which will form in the reaction mixture, acting as a hydride acceptor and resulting in the disproportionation (detailed below). It was decided that an acetate leaving group was more appropriate; the substrate **11** was shown to be both isolable and stable.

Synthesis of *9H*-xanthen-9-yl acetate **11**

Xanthydrol **1** (0.82 g, 4.1 mmol) and triethylamine (2.18 g, 21.5 mmol) were combined with dichloromethane (2 mL) and acetic anyhydride (1.73 g, 16.9 mmol) was added. The solution was stirred at room temperature for 16 hours. The solvent was removed under reduced pressure, and a resultant white solid formed. The solid was collected by vacuum filtration and dried under reduced pressure to give the product **11** as a white solid (0.50 g, 2.1 mmol, 50%) which was used without further purification. MP: 110-112 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.95 (s, 3H, C$\underline{H}_3$), 7.20-7.28 (m, 5H, Ar$\underline{H}$, COC$\underline{H}$), 7.45-7.48 (m, 2H, Ar$\underline{H}$), 7.57-7.60 (m, 2H, Ar$\underline{H}$). ^{13}C NMR (100MHz, acetone-d_6) δ 20.2 (CO$\underline{C}H_3$), 65.2 (ArH$\underline{C}$O), 116.6 (Ar$\underline{C}$H), 119.6 (Ar$\underline{C}$), 123.6 (Ar$\underline{C}$H), 130.3 (Ar$\underline{C}$H), 130.4 (Ar$\underline{C}$H), 152.1 (O$\underline{C}$OCH$_3$). HRMS (ESI) calculated for $C_{15}H_{12}O_3$ $[M+Na]^+$: 263.0679; found 263.0681.

Attempted synthesis of 9-chloro-*9H*-xanthene A

Xanthydrol **1** (0.49 g, 2.2 mmol) and pyridine (0.39 g, 5.0 mmol) were combined and dissolved in dry dichloromethane (20 mL) and cooled to 0 °C. Thionyl chloride (0.33 g, 2.8 mmol) was added dropwise over one minute and the solution was stirred at room temperature under a nitrogen atmosphere for 16 hours. ^{1}H NMR spectroscopy of the reaction mixture after this time confirmed formation of desired product [^{1}H NMR (400 MHz, CD_3CN) δ 6.83 (s, 1H), 7.23-7.27 (m, 4H), 7.45 (td, J = 8.0, 1.7 Hz, 2H), 7.62 (dd, J = 8.0, 1.7 Hz, 2H)]. Isolation was attempted using column chromatography (9:1 hexane/ethyl acetate), with two

white solids resulting after removal of solvent under reduced pressure. Product with $R_f = 0.78$ was confirmed as xanthene. ^{1}H NMR (CD_3CN, 400 MHz) δ 4.06 (s, 2H, C<u>H</u>$_2$), 7.02-7.08 (m, 4H, Ar<u>H</u>), 7.20-7.24 (m, 4H, Ar<u>H</u>). R_f 0.40 was confirmed as xanthone. ^{1}H NMR (CD_3CN, 400 MHz) δ 7.47 (ddd, J = 8.0, 7.1, 1.0 Hz, 2H, Ar<u>H</u>), 7.60 (ddd, J = 8.5, 1.0, 0.4 Hz, 2H, Ar<u>H</u>), 7.85 (ddd, J = 8.5, 7.1, 1.7 Hz, 2H, Ar<u>H</u>), 8.29 (dd, J = 8.0, 1.7, 0.4 Hz, 2H, Ar<u>H</u>).

<u>Attempted synthesis of 9-chloro-*9H*-xanthene B</u>

Xanthydrol **1** (1.09 g, 5.50 mmol) and triethylamine (1.38 g, 13.6 mmol) were combined in dichloromethane (20 mL). Thionyl chloride (3.26 g, 27.4 mmol) was added and the solution was stirred at room temperature for 16 h. ^{1}H NMR spectroscopy of the reaction mixture after this time confirmed formation of desired product as above. Isolation was attempted using Kugelrohr distillation, resulting in a brown liquid which showed no readily assignable resonances when analysed using NMR spectroscopy.

<u>Attempted synthesis of 9-chloro-*9H*-xanthene C</u>

Xanthydrol **1** (1.52 g, 7.67 mmol) and pyridine (0.91 g, 11 mmol) were combined in dichloromethane (20 mL) and the solution cooled to 0 °C. Thionyl chloride (1.37 g, 11.5 mmol) was added dropwise over 1 minute. The solution was stirred for 16 h at room temperature under a nitrogen atmosphere. ^{1}H NMR spectroscopy of the reaction mixture after this time confirmed formation of desired product as above. The reaction was quenched with water (20 mL). The aqueous layer was extracted with dichloromethane (3 x 20 mL) and the organic layers combined and washed with saturated aqueous sodium bicarbonate solution (3 x 50 mL) and water (3 x 50 mL). The organic layer was dried with magnesium sulfate and the solvent removed under reduced pressure to give an off-white powder (0.82 g). ^{1}H NMR spectroscopy confirmed a 1:1 mixture of disproportionation products xanthene and xanthone, consistent with the spectroscopic data reported above.

<u>Attempted synthesis of 9-bromo-*9H*-xanthene</u>

Xanthydrol **1** (0.54 g, 2.7 mmol) was dissolved in dry dichloromethane (20 mL) and cooled to 0 °C. Phosphorous tribromide in dichloromethane (1.00 M, 3.00 mL, 3.00 mmol) was added and the resultant orange solution was stirred at room temperature for 17 hours with a drying tube attached. ^{1}H NMR spectroscopy of the reaction mixture after this time indicated a mixture of the disproportionation products xanthene and xanthone and formation of desired

product **11b** due to appearance of a key singlet at δ 5.95. Water (20 mL) was added to quench the reaction. The aqueous layer was extracted with dichloromethane (3 x 20 mL), the organic layers were combined and washed with water (3 x 30 mL) and saturated aqueous sodium bicarbonate solution (3 x 30 mL) and dried over magnesium sulfate. Dichloromethane was removed under reduced pressure to give a brown solid (0.486 g). ^{1}H NMR spectroscopy confirmed a 1:1 mixture of disproportionation products xanthene and xanthone, consistent with the spectroscopic data reported above.

Attempted synthesis of *9H*-xanthen-9-yl methanesulfonate

Xanthydrol **1** (0.54 g, 2.7 mmol) was dissolved in dry tetrahydrofuran (20 mL) and methanesulfonyl chloride (0.62 g, 5.4 mmol) was added, followed by triethylamine (0.62 g, 6.2 mmol) at room temperature. The solution was stirred under a nitrogen atmosphere for 24 hours. Water (20 mL) was added to quench the reaction. The aqueous layer was extracted with ethyl acetate (3 x 20 mL) and combined organic layers were washed with aqueous ammonium chloride solution (3 x 30 mL), water (30 mL) and brine (30 mL) and dried over magnesium sulfate. Ethyl acetate was removed in vacuo to give a yellow-brown solid (0.34 g). ^{1}H NMR spectroscopy confirmed a 1:1 mixture of disproportionation products xanthene and xanthone, consistent with the spectroscopic data reported above.

Mechanism for the formation of xanthene and xanthone under conditions used for the synthesis of activated xanthene species

All calculations were performed using the *Gaussian09* suite of programs.[19] The M06-2X hybrid functional[20] in combination with a cc-pVDZ basis set[21] was used throughout. Solvation by dichloromethane was taken account of by employing a polarizable continuum model (scrf=pcm).[22, 23]

Xanthydrol **1** is present in the attempted syntheses of 9-chloroxanthene, 9-bromoxanthene and xantheyl mesylate; it may also form through their reaction with adventitious water. The conditions of the preparation of these activated xanthene derivatives are all acidic. Under these conditions, none of either the starting material **1** or the desired products are observed, only disproportionation into xanthene **S2** and xanthone **S4**.

The mechanism for this process is outlined in Figure S2; it likely initially involves protonation of xanthydrol to yield the xanthylium cation **S1** plus water; xanthylium **S1** may also form directly from species **11a-c**. Carbocation **S1** then abstracts a hydride from alcohol **1**, yielding xanthene **S2** and protonated xanthone **S3**. This step is significantly exergonic by ΔG = -13.4 kcal mol^{-1}, and (in CH_2Cl_2 solution) only has a very modest calculated free energy of activation of $\Delta G^{\ddagger}$ = 14.3 kcal mol^{-1}. Cation **S3** then transfers a proton to alcohol **1**, recovering the xanthylium cation **S1**. This step is predicted to be exergonic by ΔG = -8.0 kcal mol^{-1}. Overall, the catalytic cycle is thus calculated to be exergonic by ΔG = -21.4 kcal mol^{-1}.

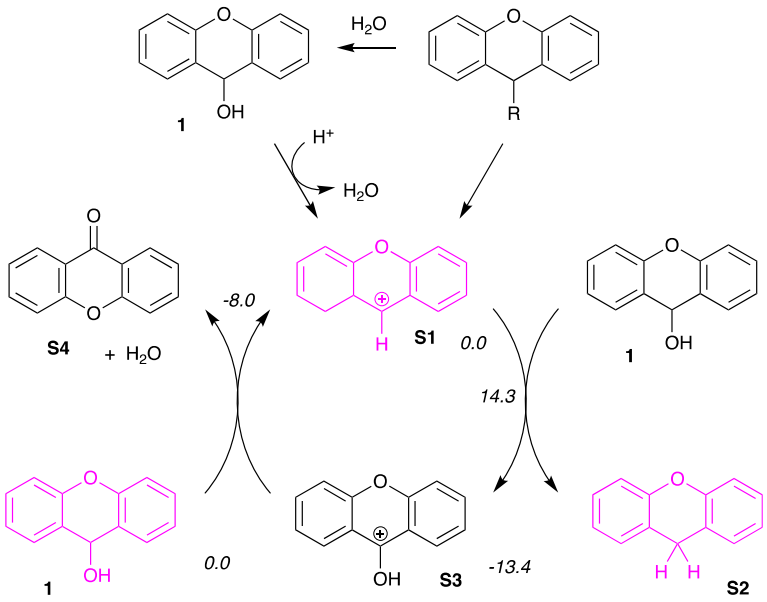
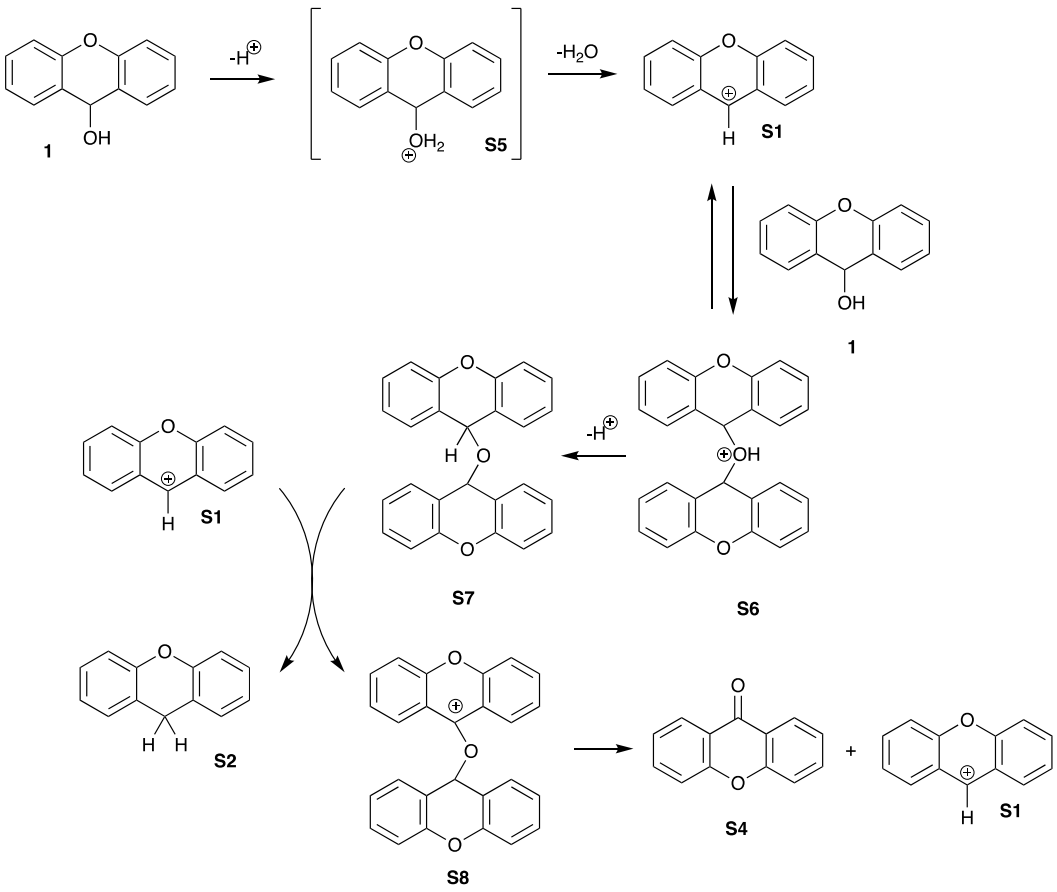


Figure S2. The mechanism of the formation of xanthene **S2** and xanthone **S3** through disproportionation under the conditions for the attempted synthesis of activated xanthene species. Free energies (in italics) in kcal mol^{-1}. Calculations at the M06-2X/cc-pVDZ (CH_2Cl_2) level of theory. Color coding black / magenta is used to facilitate tracking the fate of individual constituents of the catalytic cycle.

We note that OH-protonated xanthydrol **S5** is not a minimum structure at the DFT level used. Attempted geometry optimization of species **S5** results in formation of a complex of xanthylium cation **S1** with water. We cannot strictly rule out an alternative mechanism (Scheme S1) involving formation of di-xanthenylether **S7**, *via* its conjugated acid **S6**, followed by hydride abstraction from ether **S7** by xanthylium **2** and facile fragmentation of the resulting cation **S8**. However, we note that the energy of activation of the back reaction of cation **S6** into species **1** and **S1** is essentially zero (the free energy of the transition state for the reaction **S6** $\rightarrow$ **1** + **S1** is calculated to be even slightly below the free energy of **S6**, due to entropy contributions). The formation of cation **S6** from species **1** and **S1** is predicted to be endergonic by ΔG = 13.1 kcal mol^{-1}. Thus, cation **S6**, if formed, will likely be exceedingly short-lived, and in a dilute dichloromethane solution is unlikely to live long enough to encounter a reaction partner to transfer its excess proton to. Hence, based on both this fact and on Occam's razor, we have to discount this alternative mechanism.



Scheme S1. Alternative mechanism of formation of products **S2** and **S4** *via* ether **8**.

Importantly the mechanism outlined in Figure S1 is consistent with previous observations in the literature, particularly that the disproportionation of xanthydrol can proceed through an

ionic mechanism,[24] and the reaction rate in a series of similar disproportionation reactions depending on the basicity of the alcohol.[25] Hence, it is is considered that this mechanism reasonably explains the formation of xanthene **S2** and xanthone **S3** when the alcohol **1** is treated under acidic conditions in an attempt to form activated xanthene species.

Experimental details for kinetic analyses – acetate 11 system

Kinetic analyses were carried out in solutions containing the electrophile **11** (*ca.* 0.01 mol L^{-1}), the nucleophile **2** (*ca.* 0.02 mol L^{-1}), triethylamine (*ca.* 0.05 mol L^{-1}) and the desired solvent mixture containing acetonitrile and one of the ionic liquids **4-10**. An aliquot (*ca.* 0.5 mL) from each stock solution was placed in an NMR tube. All kinetic analyses were monitored using ^{1}H NMR spectroscopy *in situ* with the spectrometer set at the desired temperature (73.8 °C for mole fraction dependence studies; in the range of 46.9-73.8 °C for temperature dependence studies). All cases followed the formation of the signal representing the benzylic proton of the product at *ca.* 5.8 ppm.

NMR spectra used for kinetic analyses were processed using MestReNova 10.1 software. The first order rate constant was obtained by integrating the signal at 5.8 ppm over time and fitting the data to a three parameter exponential function.

Where applicable, the enthalpy and entropy of activation were calculated using the Eyring equation[26] (Equation 1).

$$ln\left(\frac{k_1 h}{k_B T}\right) = \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (1)$$

Nucleophile dependence plot

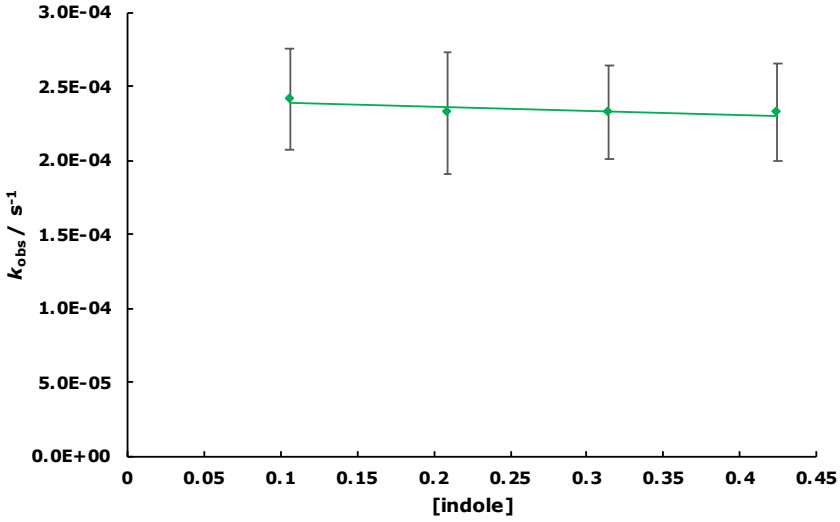


Figure S3. The nucleophile dependence plot for the reaction between the acetate **11** and indole **2** in acetonitrile, showing the lack of dependence on the concentration of indole, indicating the unimolecular substitution mechanism of the reaction (slope = -(2.55 ± 7.72) x 10^{-5} s^{-1}). The acetonitrile point for the mole fraction dependence studies between the acetate **11** and indole **2** is taken from the average of these data.

Eyring plot

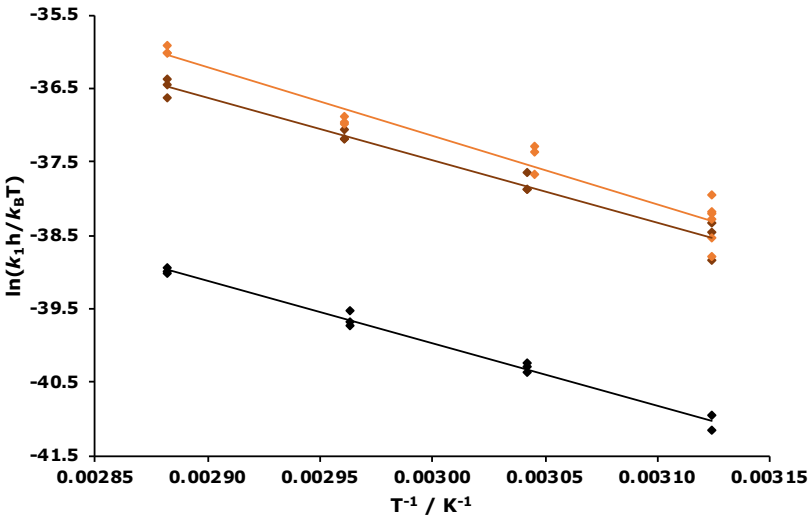


Figure S4. The Eyring plot from which the activation parameters were determined for the reaction between the acetate **11** and indole **2** in either acetonitrile (♦) or [bmim][BF_4] **4** at χ = 0.20 (♦) or χ = 0.96 (♦).

Mole fraction dependence plot with ionic liquids 4-10

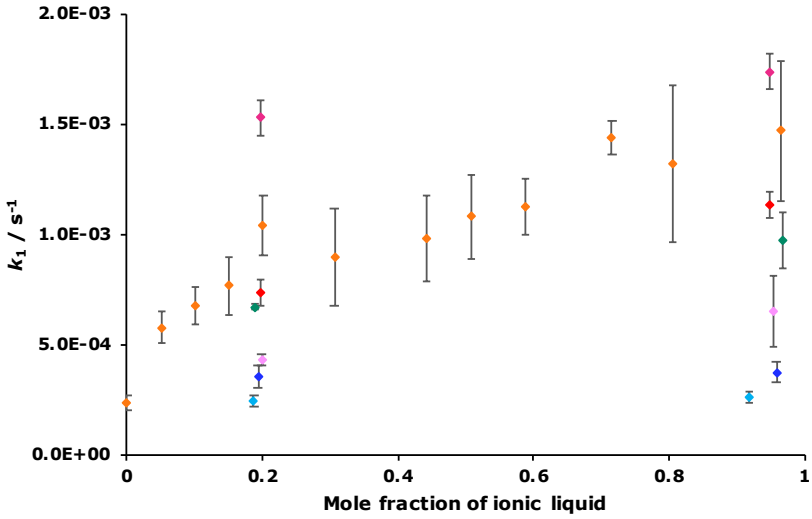


Figure S5. The dependence of the unimolecular rate constant (k_1) of the reaction between the acetate **11** and indole **2** on the mole fraction of either [bmim][BF_4] **4** (♦), [bmim][PF_6] **5** (♦), [bmim][OTf] **6** (♦), [bmim][$N(SO_2CF_3)_2$] **7** (♦), [bm_2im][BF_4] **8** (♦), [bmpyr][$N(SO_2CF_3)_2$] **9** (♦) or [bm_2im][$N(SO_2CF_3)_2$] **10** (♦) in acetonitrile. Uncertainties reported are obtained from the standard deviation of triplicate measurements.

Multivariate regression analyses for Kamlet–Taft correlations

These analyses, based on the work of Welton *et al.*,[27] have been performed using a combination of the Kamlet–Taft parameters as outlined below in each case. They are reported in the form $\ln(k_1)$ = intercept + aα + bβ + cπ^* with p-values in parentheses and italics after each coefficient.

χ = 0.20 for ionic liquids 4-10

Combination of α, β, and π^* with intercept

$\ln(k_1) = -9.74(\textit{0.00071}) + 4.11(\textit{0.00036})\alpha + 3.31(\textit{0.0017})\beta - 0.85(\textit{0.29})\pi^*$

Combination of α and π^* with intercept

$\ln(k_1) = -11.74(\textit{0.030}) + 4.67(\textit{0.018})\alpha + 1.82(\textit{0.62})\pi^*$

Combination of β and π^* with intercept

$\ln(k_1) = -6.77(\textit{0.32}) + 4.57(\textit{0.17})\beta - 2.01(\textit{0.76})\pi^*$

Combination of α and intercept

$\ln(k_1) = -9.89(\textit{1.59 x } 10^{-5}) + 4.67(\textit{0.0088})\alpha$

Combination of β and intercept

$\ln(k_1) = -8.72(\textit{7.33 x } 10^{-5}) + 4.25(\textit{0.12})\beta$

Combination of π^* and intercept

$\ln(k_1) = -9.10(\textit{0.24}) + 1.66(\textit{0.81})\pi^*$

Combination of α, β, and π^*

$\ln(k_1) = 3.32(\textit{0.11})\alpha + 4.51(\textit{0.10})\beta - 10.37(\textit{0.00045})\pi^*$

Combination of α and β

$\ln(k_1) = -9.22(\textit{0.14})\alpha - 7.10(\textit{0.46})\beta$

Combination of α and π^*

$\ln(k_1) = 3.90(0.12)\alpha - 9.31(0.00036)\pi^*$

Combination of β and π^*

$\ln(k_1) = 5.28(0.11)\beta - 8.87(0.00014)\pi^*$

χ = 0.96 for ionic liquids 4-10 with acetonitrile data

Combination of α, β, and π^* with intercept

$\ln(k_1) = -12.91(6.59 \times 10^{-5}) + 4.92(0.00065)\alpha + 2.52(0.020)\beta + 2.33(0.050)\pi^*$

Combination of α and β with intercept

$\ln(k_1) = -11.00(2.57 \times 10^{-6}) + 5.89(0.00017)\alpha + 2.24(0.080)\beta$

Combination of α and π^* with intercept

$\ln(k_1) = -11.65(0.00026) + 4.94(0.0039)\alpha + 1.85(0.29)\pi^*$

Combination of β and π^* with intercept

$\ln(k_1) = -15.79(0.0033) + 2.59(0.42)\beta + 7.68(0.036)\pi^*$

Combination of α and intercept

$\ln(k_1) = -10.21(1.76 \times 10^{-7}) + 5.72(0.00025)\alpha$

Combination of β and intercept

$\ln(k_1) = -7.71(0.0015) + 0.94(0.83)\beta$

Combination of π^* and intercept

$\ln(k_1) = -14.51(0.0013) + 7.21(0.033)\pi^*$

Combination of α, β, and π^*

$\ln(k_1) = 8.48(0.068)\alpha - 2.68(0.59)\beta - 10.80(0.0092)\pi^*$

Combination of α and β

$\ln(k_1) = -3.77(0.39)\alpha - 16.27(0.041)\beta$

Combination of α and π^*

$\ln(k_1) = 8.91(0.038)\alpha - 11.88(0.00049)\pi^*$

Combination of β and π^*

$\ln(k_1) = -4.93(0.44)\beta - 5.83(0.027)\pi^*$

χ = 0.96 for ionic liquids 4-10 without acetonitrile data

Combination of α, β, and π^* with intercept

$\ln(k_1) = -12.65(0.0075) + 4.88(0.0050)\alpha + 2.59(0.061)\beta + 2.08(0.37)\pi^*$

Combination of α and β with intercept

$\ln(k_1) = -10.61(1.17 \times 10^{-5}) + 4.81(0.0019)\alpha + 2.95(0.025)\beta$

Combination of α and π^* with intercept

$\ln(k_1) = -14.21(0.011) + 5.32(0.0081)\alpha + 4.17(0.25)\pi^*$

Combination of β and π^* with intercept

$\ln(k_1) = -9.13(0.28) + 4.09(0.28)\beta + 0.71(0.93)\pi^*$

Combination of α and intercept

$\ln(k_1) = -9.97(1.92 \times 10^{-5}) + 5.30(0.0063)\alpha$

Combination of β and intercept

$\ln(k_1) = -8.44(0.00020) + 4.20(0.19)\beta$

Combination of π^* and intercept

$\ln(k_1) = -11.21(0.19) + 3.99(0.61)\pi^*$

Combination of α, β, and π^*

$\ln(k_1) = 3.85(0.15)\alpha + 4.16(0.22)\beta - 10.28(0.0014)\pi^*$

Combination of α and β

$\ln(k_1) = -8.58(0.16)\alpha - 7.36(0.45)\beta$

Combination of α and π^*

$\ln(k_1) = 4.39(0.12)\alpha - 9.31(0.00066)\pi^*$

Combination of β and π^*

$\ln(k_1) = 5.05(0.20)\beta - 8.55(0.00047)\pi^*$

Natural logarithm of k_1 *vs* Kamlet–Taft solvent parameter plots

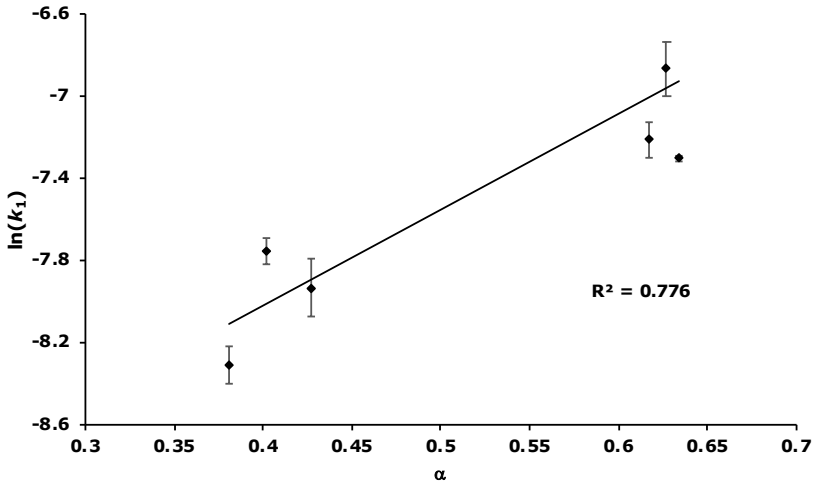


Figure S6. The relationship between the natural logarithm of k_1 and the Kamlet–Taft α parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.20$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

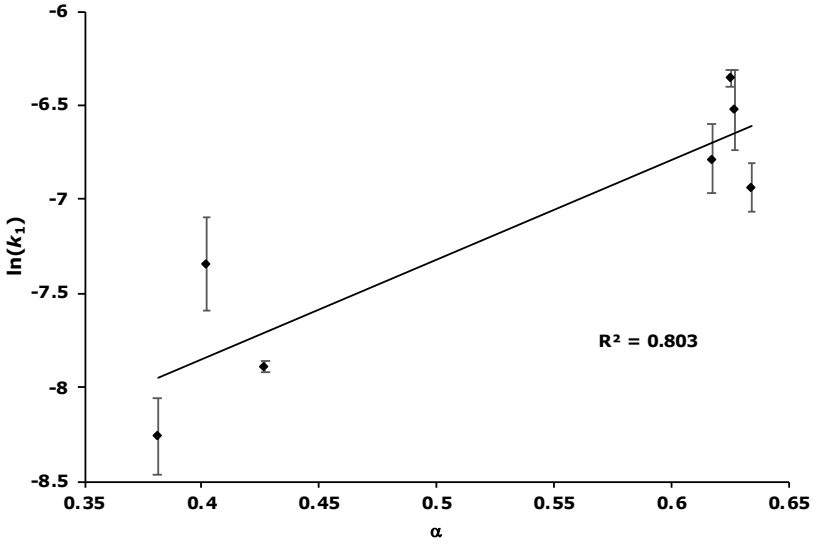


Figure S7. The relationship between the natural logarithm of k_1 and the Kamlet–Taft α parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.96$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

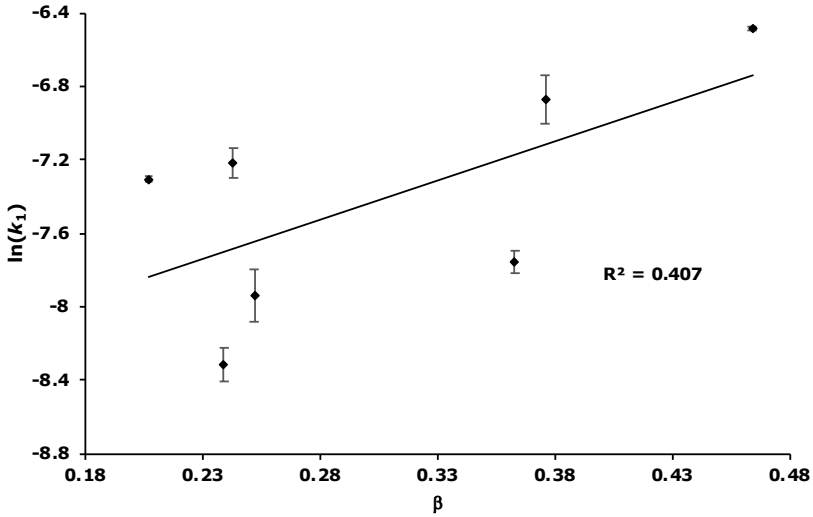


Figure S8. The relationship between the natural logarithm of k_1 and the Kamlet–Taft β parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.20$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

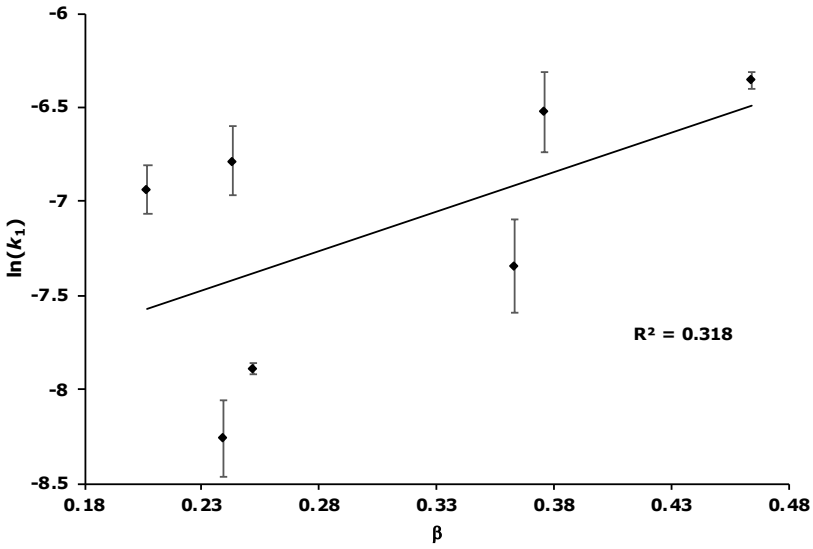


Figure S9. The relationship between the natural logarithm of k_1 and the Kamlet–Taft β parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.96$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

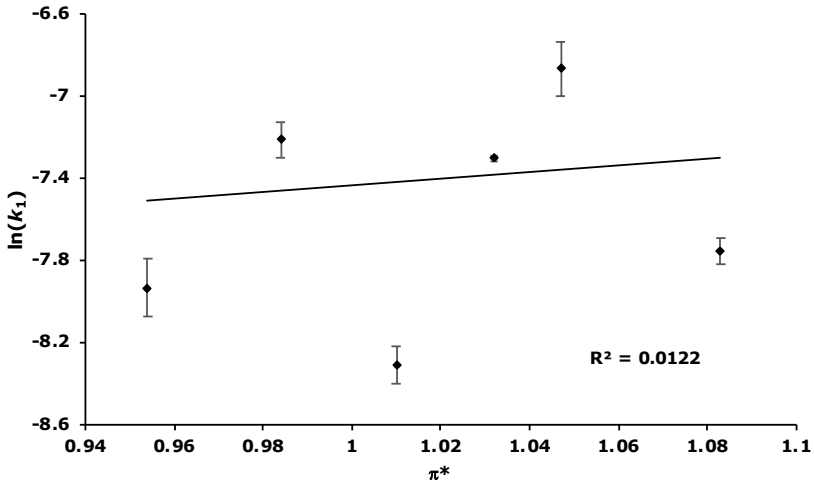


Figure S10. The relationship between the natural logarithm of k_1 and the Kamlet–Taft π^* parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.20$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

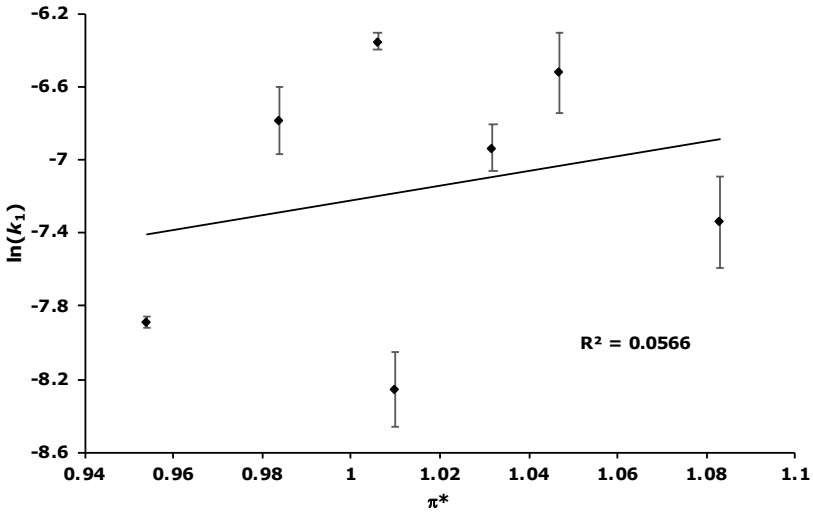


Figure S11. The relationship between the natural logarithm of k_1 and the Kamlet–Taft β parameter for the reaction between the acetate **11** and indole **2** in mixtures of each of the ionic liquids **4-10** in acetonitrile at $\chi = 0.96$. Uncertainties are calculated from the standard deviation of triplicate measurements and transformed on calculating the natural logarithm.

Rate data for the mole fraction dependence studies (xanthene 1 system)

Table S1. The mole fraction of [bmim][BF_4] **4**, the exact amounts of ionic liquid **4**, acetonitrile, the xanthene **1** and the nucleophile **2** and the observed rate constant (k_{obs}) for the process.

χ_4	Mass ionic liquid / g	Mass acetonitrile / g	Mass xanthene **1** / g	Mass indole **2** / g	k_{obs} / 10^{-4} s^{-1}
0.02	0.138	1.454	0.0051	0.0049	1.538
					1.758
					1.954
0.05	0.380	1.302	0.0053	0.0053	1.677
					1.157
					1.515
0.10	0.700	1.104	0.0049	0.0046	1.235
					1.110
					1.542
0.21	1.147	0.801	0.0056	0.0057	1.447
					1.520
					1.212
0.48	1.833	0.354	0.0049	0.0051	1.437
					1.646
					1.226
0.99	2.396	0	0.0047	0.0060	1.377
					1.358
					1.200

Table S2. The mole fraction of [bmim][PF_6] **5**, the exact amounts of ionic liquid **5**, acetonitrile, the xanthene **1** and the nucleophile **2** and the observed rate constant (k_{obs}) for the process.

χ_5	Mass ionic liquid / g	Mass acetonitrile / g	Mass xanthene **1** / g	Mass indole **2** / g	k_{obs} / 10^{-7} s^{-1}
0	0	1.542	0.0055	0.0052	1.532
					1.617
					4.292
0.99	2.751	0	0.0049	0.0057	49.07
					44.69
					46.93

Rate data for the nucleophile dependence studies (acetate 11 system)

Table S3. The exact amounts of acetonitrile, the xanthene **1**, the nucleophile **2** and triethylamine and the concentration of the nucleophile **2** and the observed rate constant (k_{obs}) for the process.

Mass acetonitrile / g	Mass xanthene **1** / g	Mass indole **2** / g	Mass NEt_3 / g	[Nu] **2** / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}
1.511	0.0034	0.0248	0.0108	0.106	2.722
					2.491
					2.047
1.490	0.0038	0.0490	0.0090	0.209	2.026
					2.159
					2.796
1.476	0.0045	0.0737	0.0117	0.315	2.426
					1.969
					2.589
1.464	0.0035	0.0995	0.0111	0.425	2.000
					2.662
					2.325

Rate data for the mole fraction dependence studies (acetate 11 system)

Table S4. The mole fraction of [bmim][BF_4] **4**, the exact amounts of ionic liquid **4**, acetonitrile, the acetate **11**, the nucleophile **2,** triethylamine and the first order rate constant (k_1) for the process.

χ_4	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.05	0.390	1.295	0.0046	0.0047	0.011	4.95
						6.02
						6.34
0.10	0.690	1.107	0.0038	0.0044	0.0109	6.44
						7.73
						6.07
0.15	0.930	0.952	0.0039	0.0044	0.0100	7.85
						6.29
						8.89
0.20	1.142	0.805	0.0040	0.0066	0.0099	11.5
						8.88
						10.8
0.31	1.476	0.601	0.0047	0.0053	0.0107	6.53
						10.7
						9.59
0.44	1.779	0.401	0.0041	0.0056	0.0106	9.47
						7.27
	1.761	0.401	0.0042	0.0045	0.0102	12.0
						10.5
0.51	1.876	0.324	0.0039	0.0058	0.0099	13.0
						9.42
						9.93
0.59	2.021	0.300	0.0039	0.0048	0.0110	10.6
						10.4
						12.7
0.72	2.147	0.149	0.0047	0.0049	0.0105	13.5

						14.1
						14.6
						15.7
						14.3
						14.1
0.81	2.226	0.091	0.0036	0.0055	0.0103	9.69
						9.81
						11.5
						14.1
						15.2
						18.8
0.96	2.368	0.010	0.0038	0.0048	0.0107	18.2
						16.6
						16.6
						15.0
						11.3
						10.2

Table S5. The mole fraction of [bmim][PF_6] **5**, the exact amounts of ionic liquid **5**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_5	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.19	1.302	0.801	0.0047	0.0051	0.0093	6.78
						6.74
						6.60
0.97	2.704	0.010	0.0038	0.0053	0.0094	8.39
						11.0
						9.88

Table S6. The mole fraction of [bmim][OTf] **6**, the exact amounts of ionic liquid **6**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_6	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.20	0.656	0.376	0.0019	0.0029	0.0054	15.2
						15.2
						15.5
0.95	2.514	0.013	0.0045	0.0050	0.0104	16.8
						17.0
						18.3

Table S7. The mole fraction of [bmim][$N(SO_2CF_3)_2$] **7**, the exact amounts of ionic liquid **7**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_7	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.20	1.657	0.654	0.0038	0.0045	0.0110	8.03
						7.19
						6.81
0.95	2.831	0.009	0.0036	0.0053	0.0092	13.0
						9.01
						11.9

Table S8. The mole fraction of [bm_2im][BF_4] **8**, the exact amounts of ionic liquid **8**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_8	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.20	1.168	0.800	0.0040	0.0051	0.0104	3.97
						4.44
						4.41
0.96	2.330	0.012	0.0035	0.0065	0.0115	8.68
						4.77
						5.05
						6.61
						7.27

Table S9. The mole fraction of [bmpyr][$N(SO_2CF_3)_2$] **9**, the exact amounts of ionic liquid **9**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_9	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.19	1.597	0.641	0.0046	0.0055	0.0099	3.20
						3.37
						4.14
0.96	2.750	0.005	0.0042	0.0052	0.0090	3.73
						3.87
						3.65

Table S10. The mole fraction of $[bm_2im][N(SO_2CF_3)_2]$ **10**, the exact amounts of ionic liquid **10**, acetonitrile, the acetate **11** and the nucleophile **2** and the first order rate constant (k_1) for the process.

χ_{10}	Mass ionic liquid / g	Mass acetonitrile / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0.19	1.617	0.660	0.0033	0.0048	0.0090	2.63
						2.19
						2.54
0.92	2.777	0.017	0.0039	0.0050	0.0099	1.98
						2.93
						2.86

Rate data for the temperature dependence studies (acetate 11 system)

Table S11. The mole fraction of [bmim][BF_4] **4**, the temperature, the exact amounts of ionic liquid **4**, acetonitrile, the acetate **11**, the nucleophile **2** and triethylamine, and the first order rate constant (k_1) for the process.

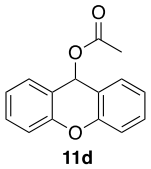
χ_4	Temp / °C	Mass ionic liquid / g	Mass CH_3CN / g	Mass acetate **11** / g	Mass indole **2** / g	Mass NEt_3 / g	k_1 / 10^{-4} s^{-1}
0	46.9	0	3.838	0.0093	0.0126	0.0253	0.09
							0.11
	55.6						0.23
							0.20
							0.22
	64.6						0.41
							0.39
							0.48
	73.8						0.81
							0.89
							0.85
0.20	46.9	2.827	2.025	0.0102	0.0120	0.0234	0.90
							1.33
							1.50
	55.6						3.09
							2.44
							2.44
	64.3						4.97
							4.94
							5.61
	73.8						11.5
							8.88
							10.8
0.96	46.9	2.359	0.01	0.0037	0.0049	0.0104	0.95
							2.19

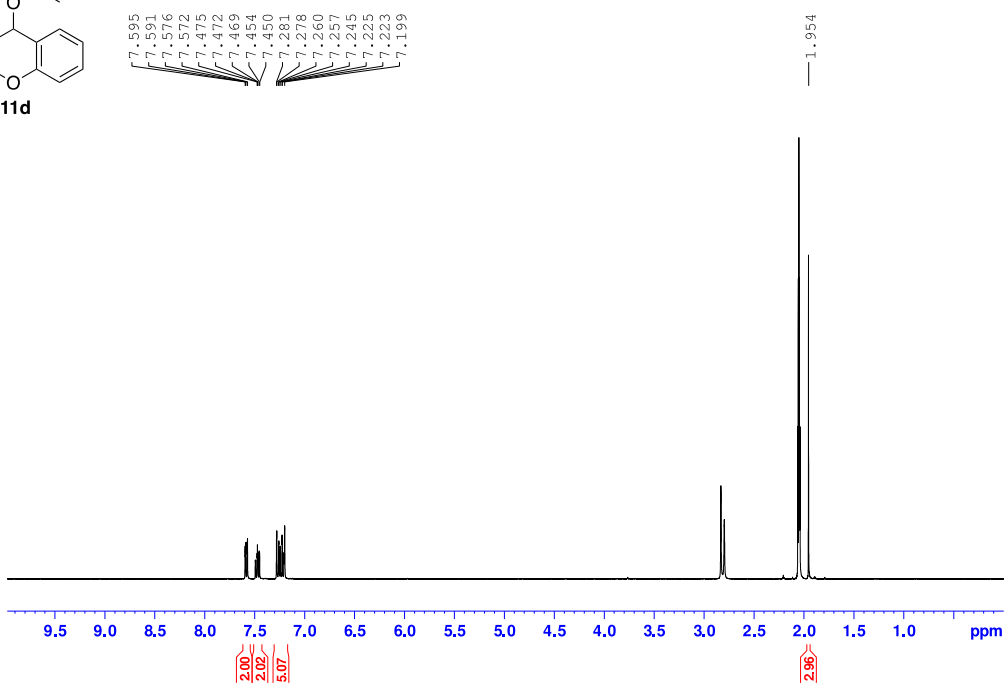
							1.23
	46.9	5.898	0.022	0.0105	0.0140	0.0246	1.71
							1.59
							1.76
	55.2						4.37
							3.02
							4.07
	64.6						6.78
							6.32
							6.04
	73.8						18.2
							16.6
							16.6

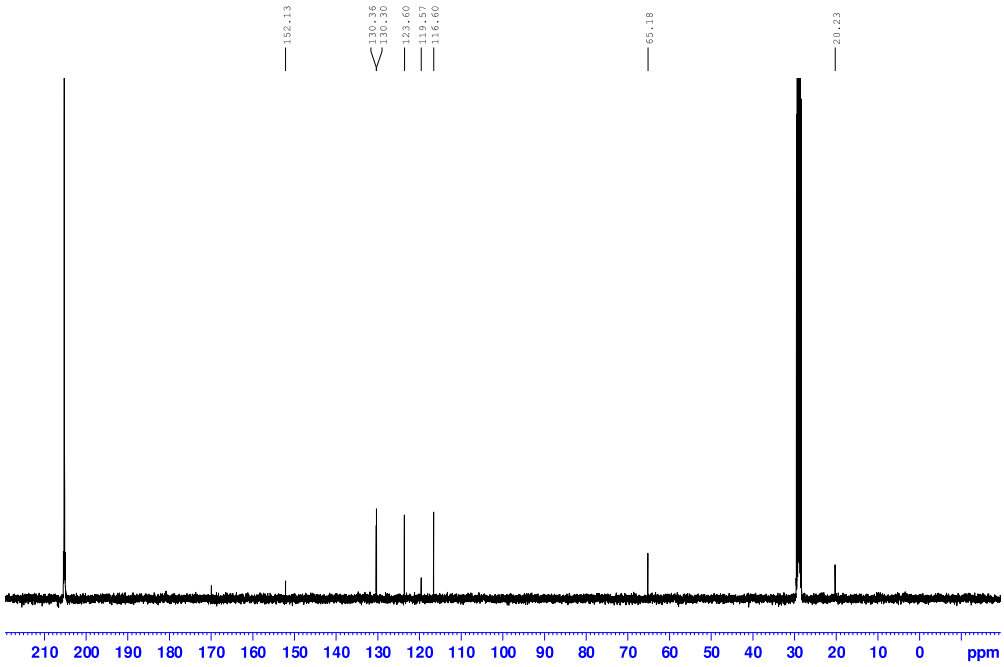
NMR spectra of synthesised compounds

All NMR spectra for characterisation of synthesised compounds were obtained using a Bruker Avance III spectrometer 400. Spectra were processed using the Bruker Topspin 4.0.6 software.

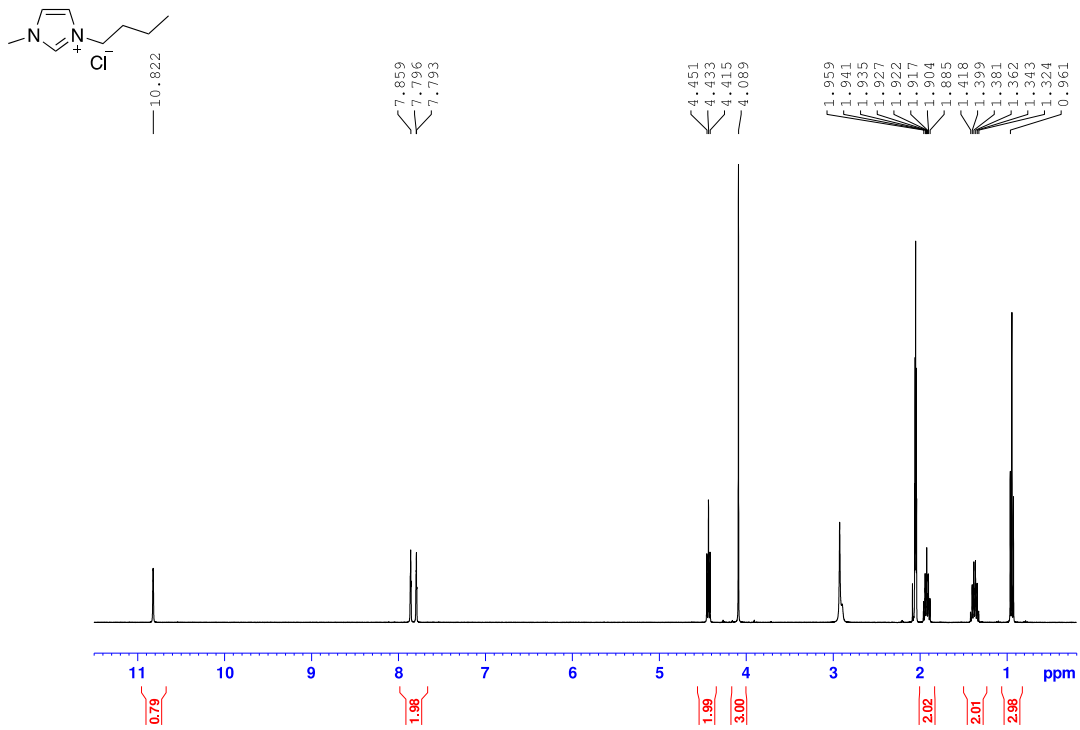
9H-Xanthen-9-yl acetate **11**



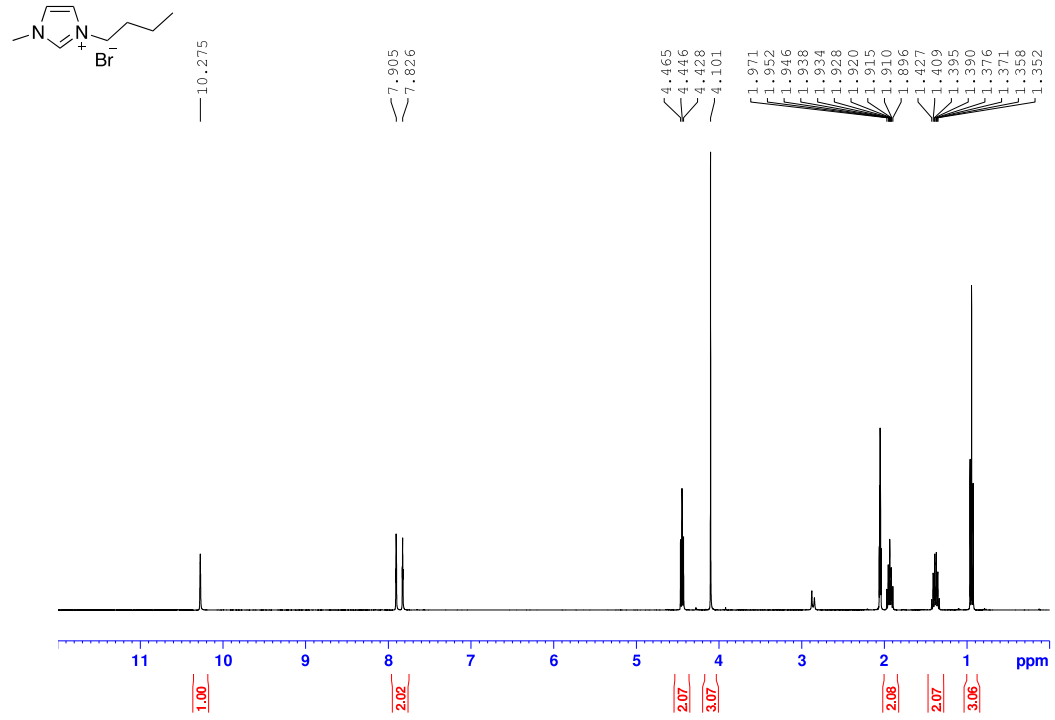




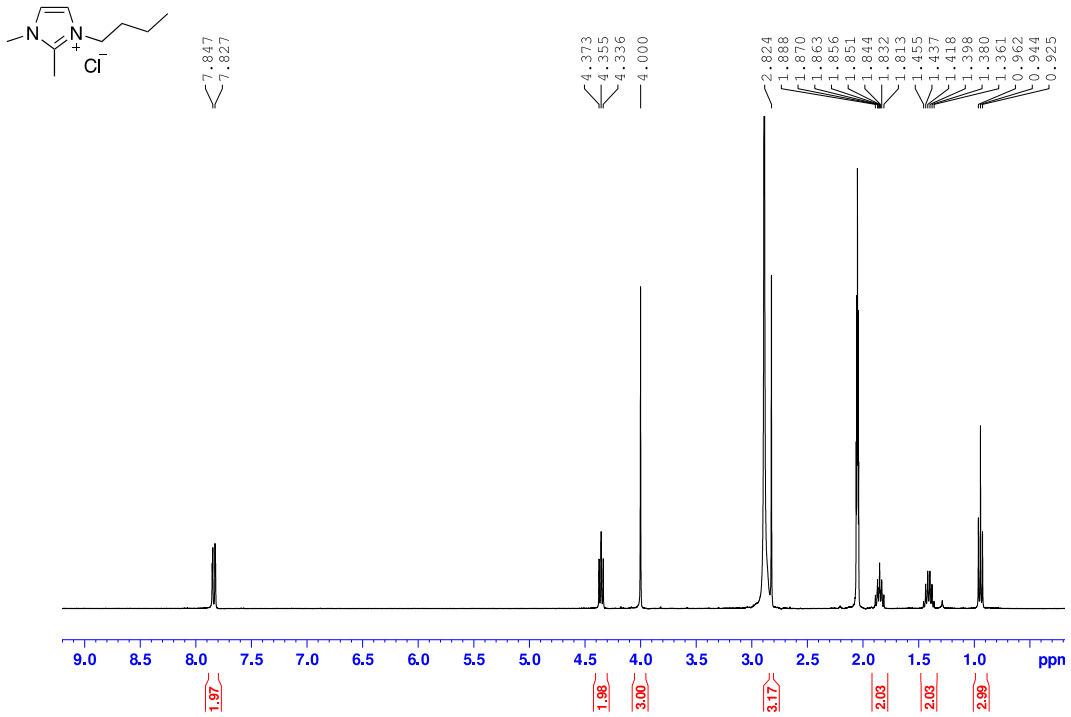
1-Butyl-3-methylimidazolium chloride ([bmim]Cl)



1-Butyl-3-methylimidazolium bromide ([bmim]Br)



1-Butyl-2,3-dimethylimidazolium chloride ([bm$_2$im]Cl)



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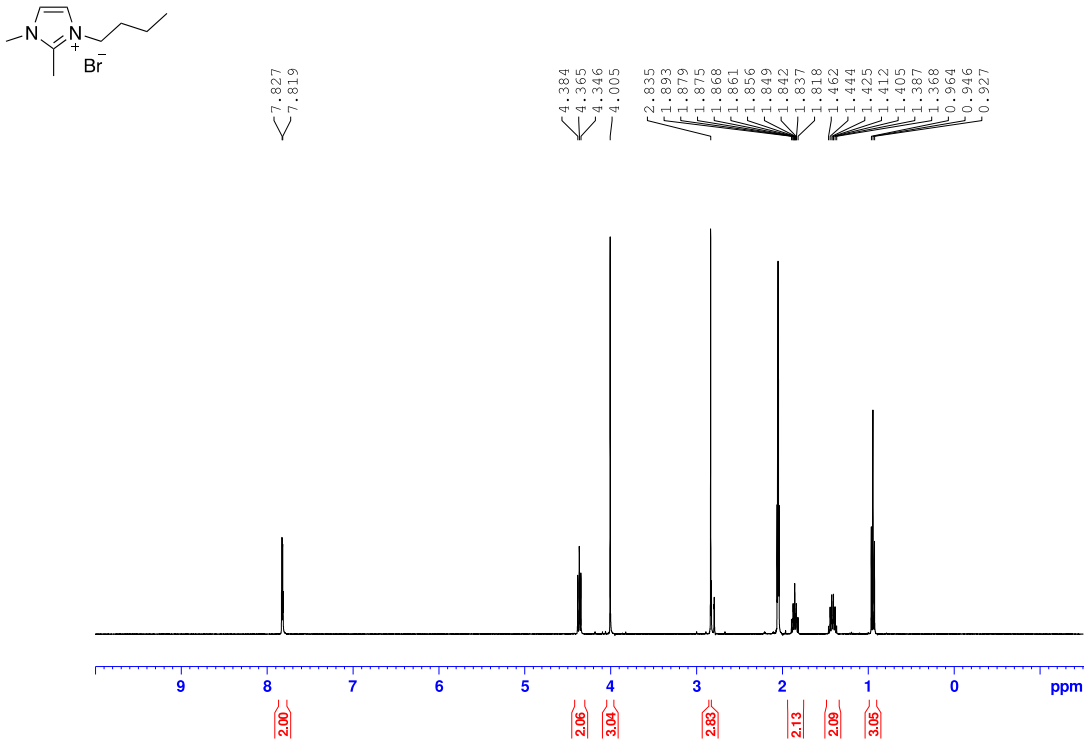
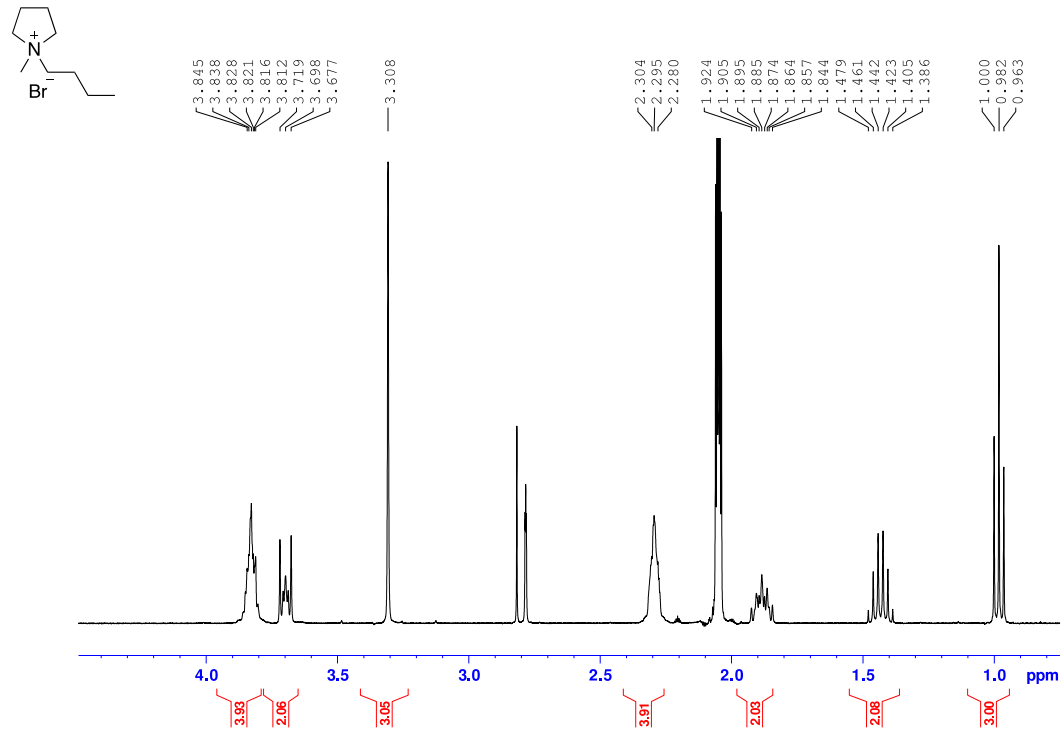
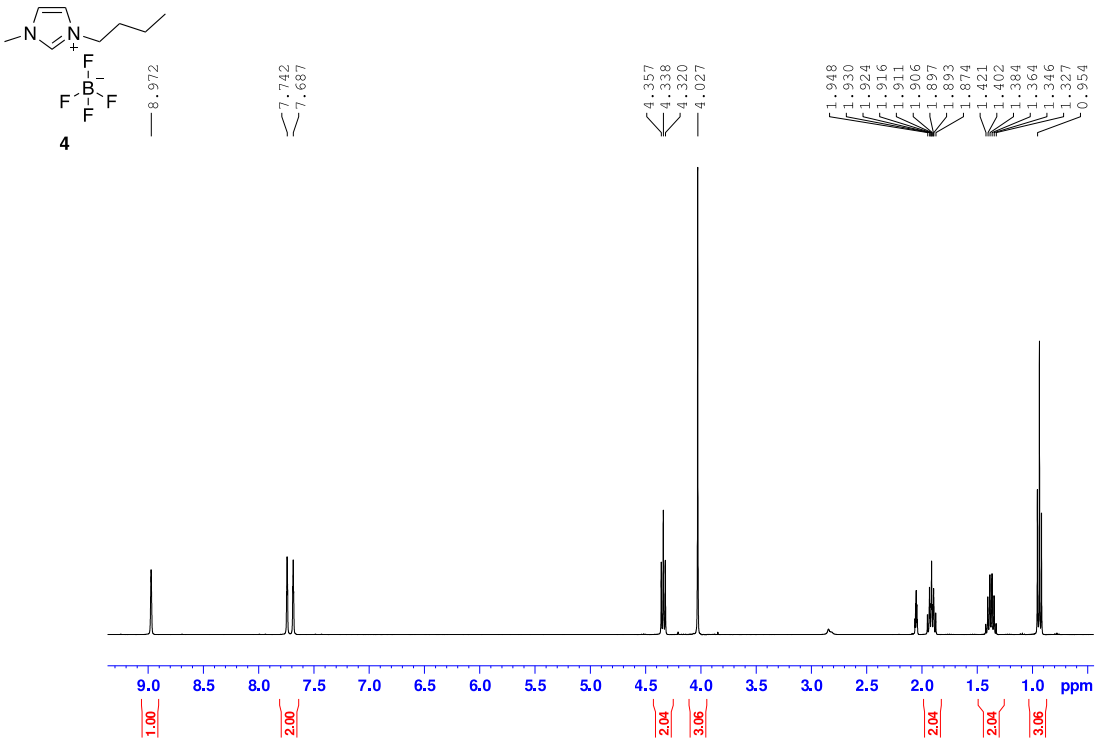


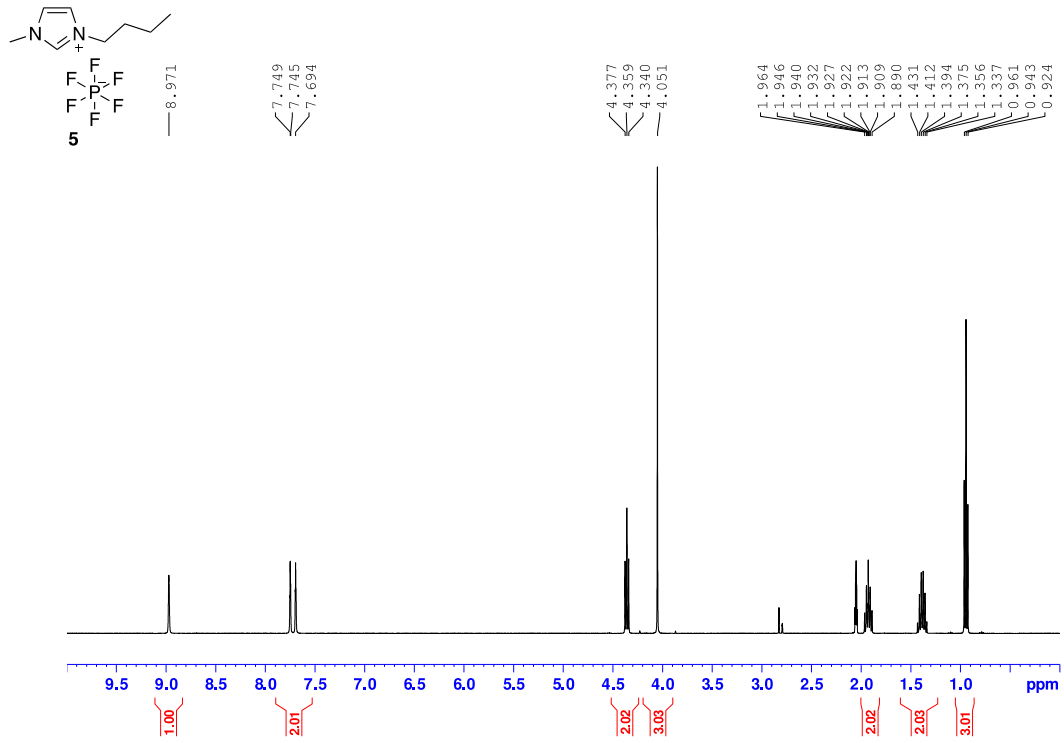
N-Butyl-*N*-methylpyrrolidinium bromide ([bmpyr]Br)



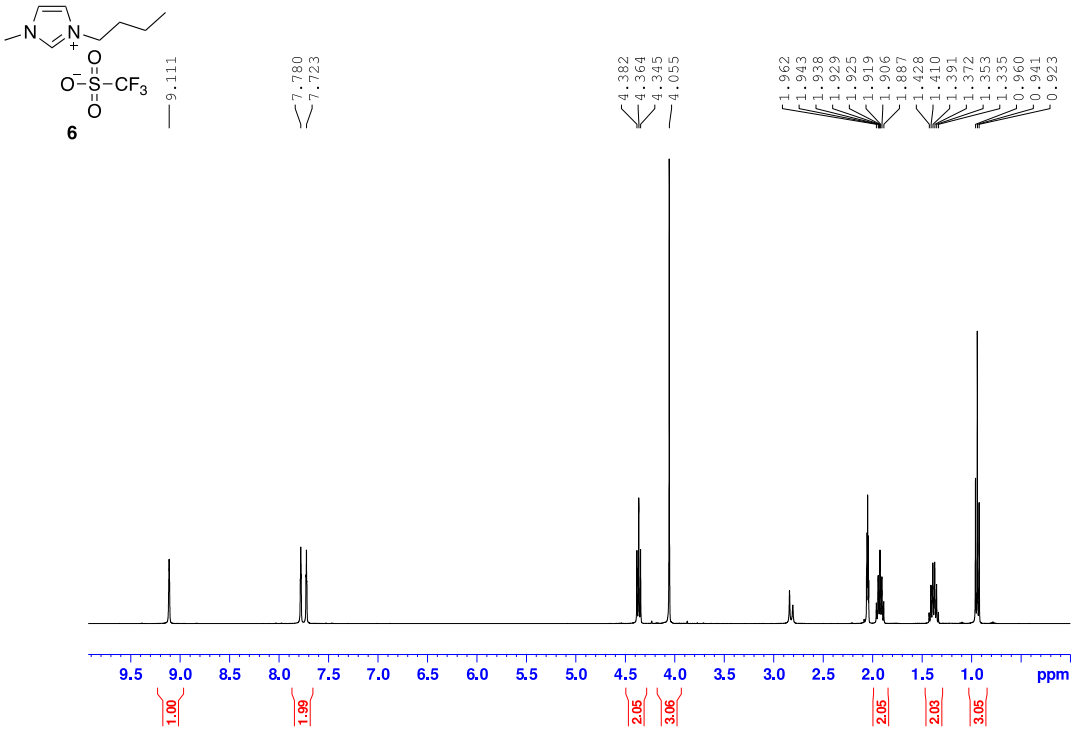
1-Butyl-3-methylimidazolium tetrafluoroborate **4**



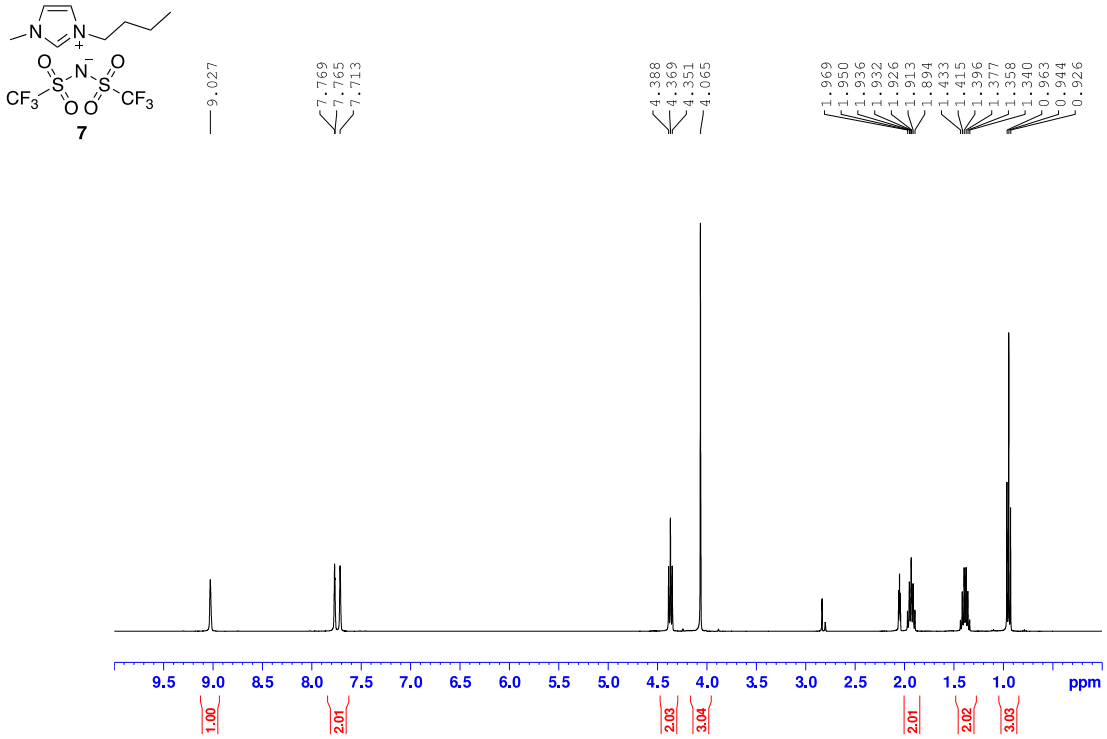
1-Butyl-3-methylimidazolium hexafluorophosphate **5**



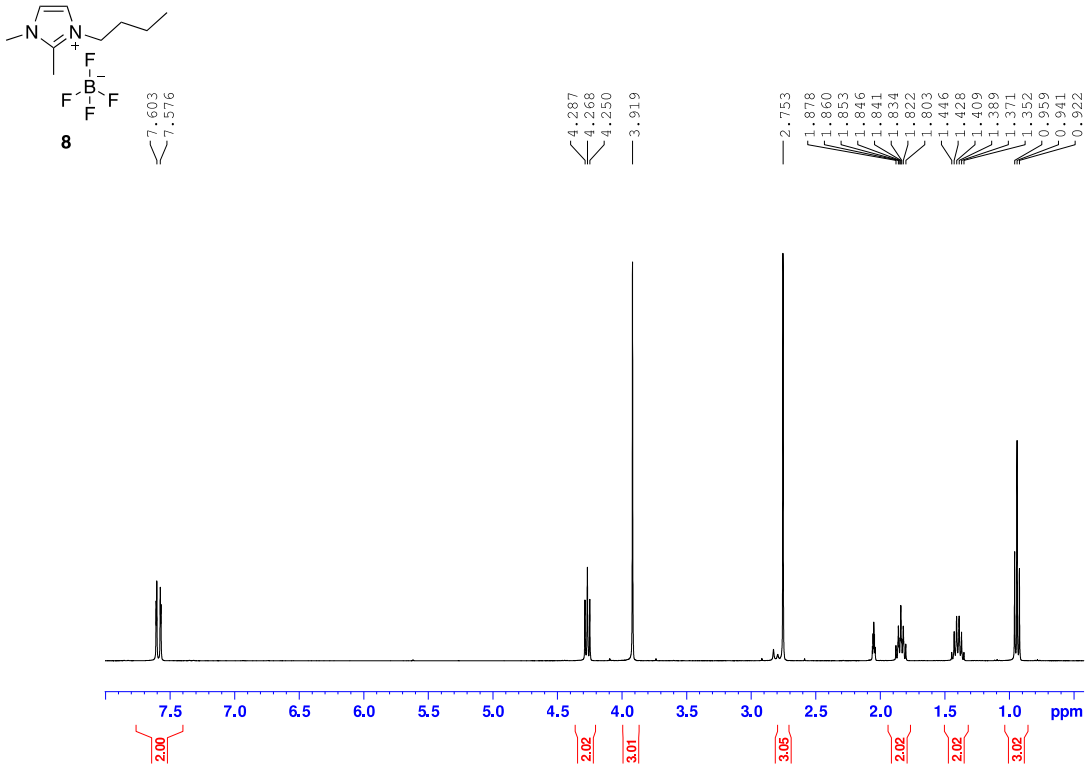
1-Butyl-3-methylimidazolium trifluoromethanesulfonate **6**



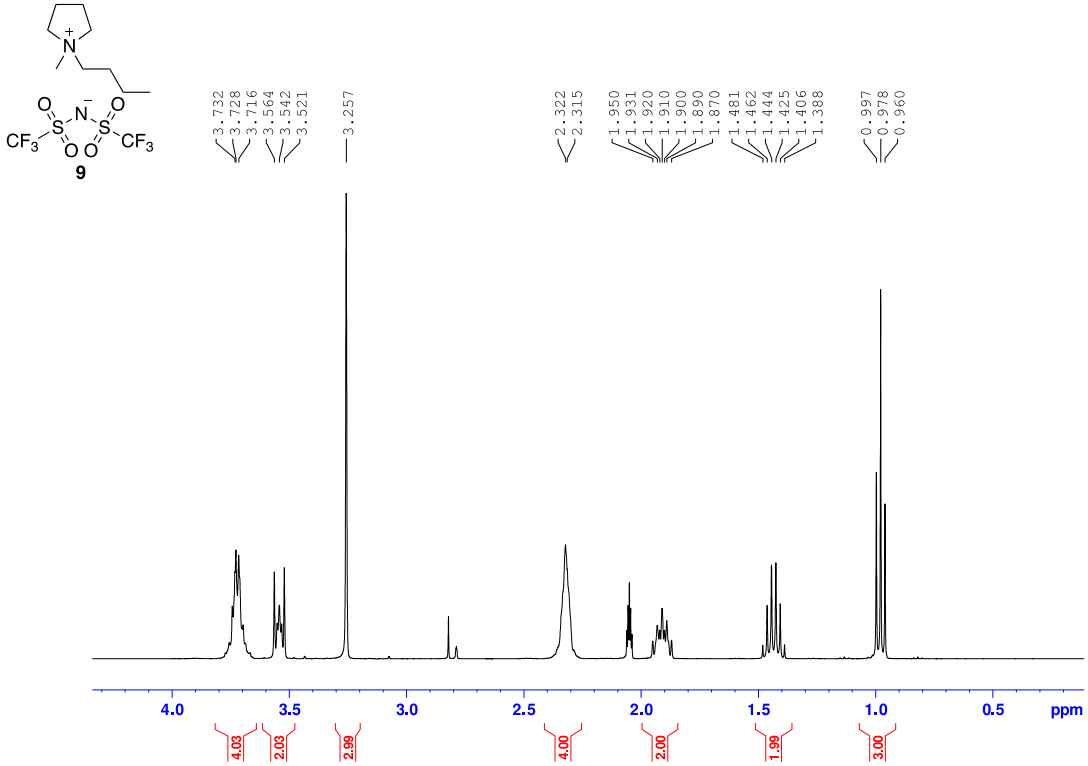
1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide **7**



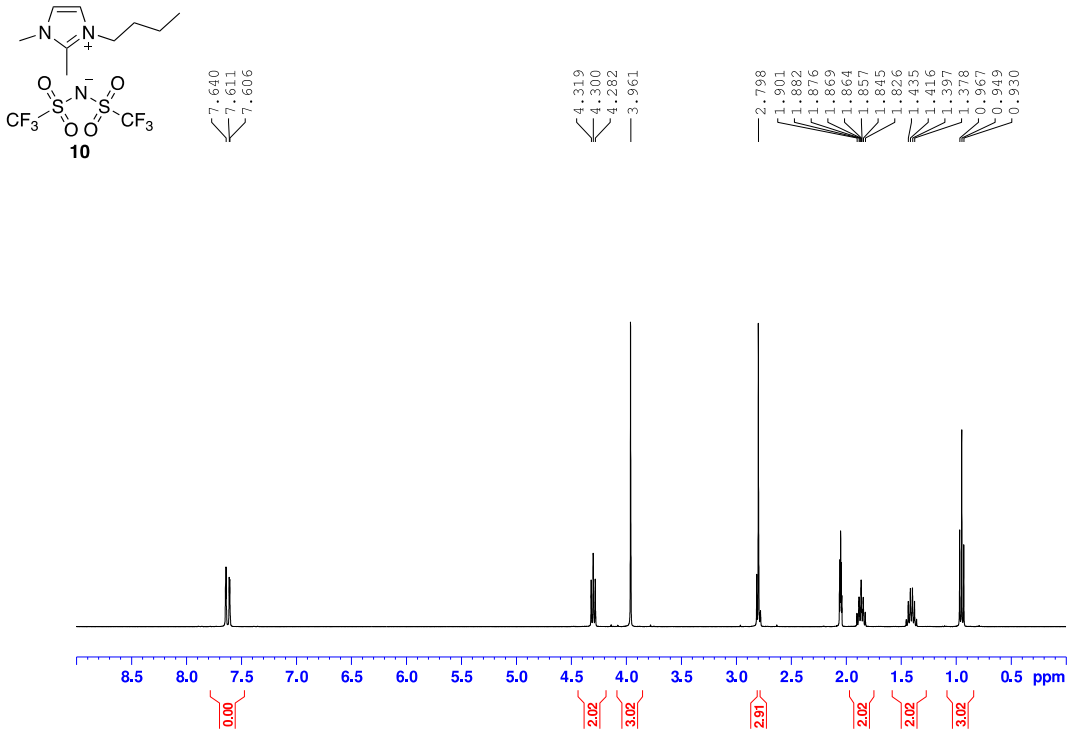
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate **8**



N-Butyl-*n*-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide **9**



1-Butyl-2,3-dimethylimdazolium *bis*(trifluoromethanesulfonyl) **10**



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