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Supplementary Material

Gold extraction using novel ionic thiourea derivatives

Megan L. Himmelman[A], *Amir Joorab-Doozha*[A], *Christa L. Brosseau*[A] and *Robert D. Singer*[A,*]

[A]Department of Chemistry, Saint Mary's University, Halifax, NS B3H 3C3, Canada

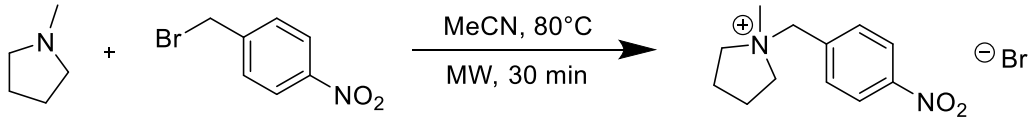
*Correspondence to: Email: robert.singer@smu.ca

Electronic Supplementary Information

Reagents

The chemicals used for ionic liquid synthesis, *N*-methylpyrrolidine, 1-methylimidazole, 1-butylimidazole, *p*-nitrobenzyl bromide, sodium borohydride, sodium citrate, iron (II) sulphate helptahydrate, nickel (II) chloride hexahydrate, potassium hexafluorophosphate, sodium dodecylsulphate, and 4-methoxyphenyl isothiocyanate, were purchased from Sigma Aldrich and used as received. Hydrogen tetrachloroaurate (III) hydrate (99.8% Au) (min. 49% Au) was purchased from Strem Chemicals Inc. Copper nitrate (99.999% trace metals basis) and zinc nitrate salt (99.999% trace metals basis), as well as silver nitrate solution (2.5 % w/v in H_2O) and iron nitrate solution (*Trace***Cert**®, 1000mg/L Fe in nitric acid) were purchased from Sigma Aldrich. All solvents were purchased from ThermoFisher Scientific.

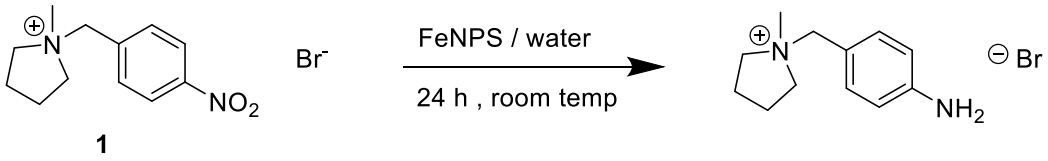
1-methyl-1-(4-nitrobenzyl)pyrrolidin-1-ium bromide



Following a previously reported synthesis with slight modification,[47] 2.16 g (10.0 mmol) of *p*-nitrobenzyl bromide was added to a 35 mL microwave reaction tube with 10 mL of acetonitrile.

Then, 1.14 mL (11.0 mmol) of *N*-methyl pyrrolidine was added and the reaction tube was placed in the microwave reactor for 30 minutes at 80°C and 30 W power. The solution was transferred to a beaker and approximately 40 mL of ethyl acetate was added which produced a precipitate that was isolated and dried under vacuum to afford 2.88 g (9.6mmol, 95.7%) of white powder. No further purification was required. MP 168.3-168.5 °C, ^{1}H NMR (300 MHz, DMSO-D_6) 8.35 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 4.77 (s, 2H), 3.69-3.54 (m, 2H), 3.51-3.38 (m, 2H), 2.93 (s, 3H), 2.22-2.06 (m, 4H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 148.4, 136.0, 134.0, 123.7, 63.6, 63.0, 47.2, 20.6. ESI-MS: Positive mode found: m/z 221.1 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1; Negative mode: m/z 80.9 [97.3%, Br^-]; Calc.80.9; ESI-HRMS: Positive mode found: m/z 221.1285 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1285; Negative mode: m/z 78.9186[100%, Br^-]; Calc. 78.9188, m/z 80.9165[97.3%, Br^-]; Calc. 80.9168.

1-(4-aminobenzyl)-1-methylpyrrolidin-1-ium bromide

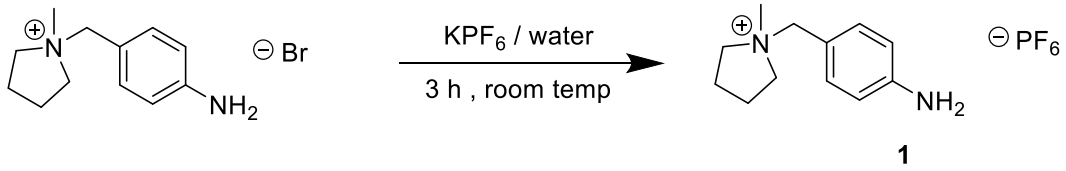


1

In a 250 mL beaker, 7.97 g (28.7 mmol) of iron (II) sulphate heptahydrate and 0.70 g (2.4 mmol) of sodium citrate were dissolved in 150 mL of deionized water. Slowly, 1.80 g (47.6 mmol) of sodium borohydride was added to reduce the iron (II) sulphate to iron (0), followed by rinsing with 50 mL of water and decanting. The iron (0) nanoparticles were rinsed three times with water before being added to 2.85 g (9.5 mmol) of 1-methyl-1-(4-nitrobenzyl)pyrrolidin-1-ium bromide , **1** dissolved in 10 mL of water, which was then stirred at room temperature for 24 hours under an inert atmosphere. The mixture was filtered through 2 cm of diatomaceous earth

and the reduced bromide salt was left in the aqueous solution for the following metathesis. ^{1}H NMR (300 MHz, DMSO-D_6) 7.15 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 5.48 (s, 2H), 4.30 (s, 2H), 3.53-3.38 (m, 2H), 3.36-3.23 (m, 2H), 2.83 (s, 3H), 2.17-2.01 (m, 4H). ^{13}C (75.7 MHz, DMSO-D_6) 150.4, 133.4, 114.9, 113.5, 65.6, 61.8, 46.9, 20.8. ESI-MS: Positive mode found: m/z 191.2 [100%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.2; ESI-HRMS: Positive mode found: m/z 191.1549 [100%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.1543, m/z 192.1581 [13%, $C_{12}H_{19}N_2)^+$]; Calc. 192.1577.

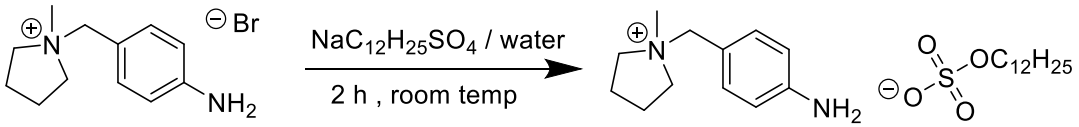
1-(4-aminobenzyl)-1-methylpyrrolidin-1-ium hexafluorophosphate (**1**)



1

To the aqueous solution containing 2.58 g (9.5 mmol) of 1-(4-aminobenzyl)-1-methyl pyrrolidine-1-ium bromide, 2.21 g (12.0 mmol) of potassium hexafluorophosphate was added and stirred at room temperature for 3 hours. The resulting precipitate was filtered and washed with additional water to remove any impurities. The precipitate was dried to afford 2.73 g (85.6%) of product, which did not require further purification. The ^{1}H and ^{13}C NMR data is the same as the previous bromide salt. MP 148.9-149.1 °C, ^{31}P (121.5 MHz, DMSO-D_6) -144.2 (septet, ^{1}J = 711.5 Hz). ^{19}F (282.5 MHz, DMSO-D_6) -70.1 (d, ^{1}J = 711.5 Hz). ESI-MS: Negative Mode Found: m/z 145.0 [100%, $(PF_6)^-$]; Calc. 145.0. ESI-HRMS: Negative Mode Found: m/z 144.9650 [100%, $(PF_6)^-$]; Calc. 144.9647.

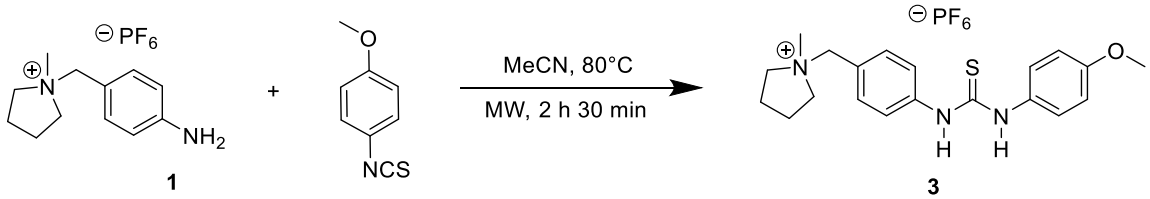
1-(4-aminobenzyl)-1-methylpyrrolidin-1-ium dodecyl sulphate (**2**)



2

After the reduction of **1**, 3.42 g (11.9 mmol) of sodium dodecyl sulphate was added to the aqueous solution containing 2.58 g (9.5 mmol) of 1-(4-aminobenzyl)-1-methylpyrrolidin-1-ium bromide. The solution was stirred for 2 hours at room temperature and the precipitate formed was filtered and dried to yield 3.42 g (79.1%) of white powder with no further purification step. MP 126.1-126.3 °C, ^{1}H NMR (300 MHz, DMSO-D_6) 7.16 (d, *J* = 8.3, 2H), 6.60 (d, *J* = 8.3, 2H), 5.49 (s, 2H), 4.31 (s, 2H), 3.67 (t, *J* = 6.8, 2H), 3.55-3.40 (m, 2H), 3.37-3.23 (m, 2H), 2.84 (s, 3H), 2.18-2.01 (m, 4H), 1.55-1.40 (m, 2H), 1.24 (s, 18H), 0.91-0.79 (m, 3H). ^{13}C NMR (75.7 MHz, DMSO-D_6) 150.5, 133.3, 114.8, 113.5, 65.6, 65.5, 61.8, 46.9, 31.3, 29.1, 29.0, 28.8, 28.7, 25.5, 22.1, 20.8, 14.0. ESI-MS Positive mode found: m/z 191.2 (100%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.2; Negative mode found: m/z 265.1 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.2; ESI-HRMS Positive mode found: m/z 191.1545 [100%, $C_{12}H_{19}N_2)^+$]; Calc. 191.1543, m/z 192.1571 [13%, $C_{12}H_{19}N_2)^+$]; Calc. 192.1577; Negative mode found: m/z 265.1482 [100%, $C_{12}H_{25}O_4S)^-$]; m/z 266.1509 [14.2%,($C_{12}H_{25}O_4S)^-$]; Calc. 266.15, m/z 267.1462 [4.5%,($C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

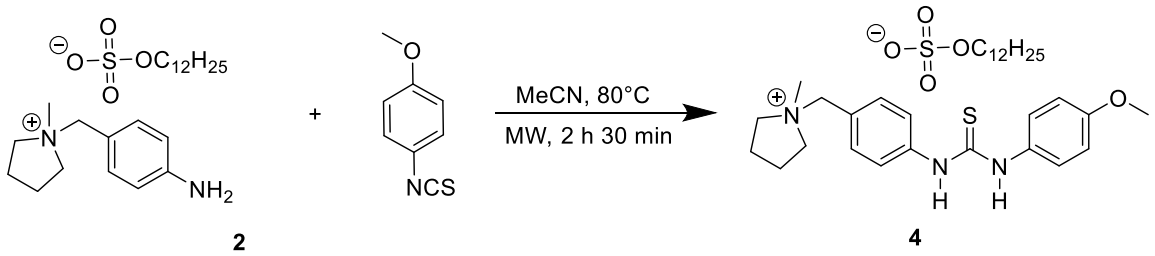
<u>1-(4-(3-(4-methoxy)phenyl)thioureido)benzyl-1-methylpyrrolidin-1-ium hexafluorophosphate **(3)**</u>



1 **3**

In a 35 mL microwave reaction vessel, 2.70 g (8.0 mmol) of compound **2** was added and the vessel was capped with a septum. The reaction vessel was flushed with argon, and a syringe was then used to add 5 mL of dry acetonitrile, and the vessel was stirred until complete dissolution. Using a glass syringe, 1.22 mL (8.8 mmol) of 4-methoxy isothiocyanate was added to the solution, and the reaction vessel was placed in a microwave reactor for 2 hours and 30 minutes at 80°C and 30 W. The solution was then allowed to cool to room temperature before refrigeration for 24 hours. The contents of the vessel were then filtered, and the filtrate was transferred to a separatory funnel to be washed with 5 x 10 mL of hexanes. The acetonitrile was then removed by rotary evaporation and dried fully under vacuum to afford a light yellow solid. (3.64 g, 91%) ^{1}H NMR (300 MHz, $[CD_3]_2CO$) 9.14(s, 1H), 7.84-7.75 (m, 2H), 7.64-7.56 (m, 2H), 7.40-7.32 (m, 2H), 6.97-6.86 (m, 2H), 4.69 (s, 2H), 3.87-3.71 (m, 2H), 3.80 (s, 3H), 3.66-3.54 (m, 2H),3.14 (s, 3H), 2.39-2.29 (m, 4H). ^{13}C NMR (75.5 MHz, $[CD_3]_2CO$) 181.3, 158.7, 142.7, 133.5, 132.1, 127.5, 125.1, 124.4, 114.8, 66.9, 64.1, 55.7, 48.5, 21.9. ESI-MS Positive mode found: m/z 356.2 [100%, $(C_{20}H_{26}N_3OS)^+$]; Calc. 356.2; Negative mode found: m/z 145.0 [100%, $(PF_6)^-$]; Calc. 145.0; ESI-HRMS Positive mode found: m/z 356.1796 [100%, $(C_{20}H_{26}N_3OS)^+$]; Calc. 356.18, 357.1812 [23.6%, $(C_{20}H_{26}N_3OS)^+$]; Negative mode found: m/z 144.9651 [100%, $(PF_6)^-$]; Calc. 144.9647.

1-(4-(3-(4-methoxy)phenyl)thioureido)benzyl-1-methylpyrrolidin-1-ium dodecyl sulphate (**4**)

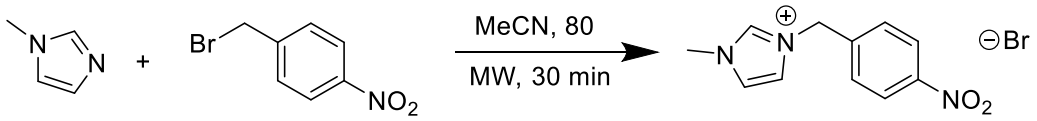


2 **4**

Following a similar procedure as for the synthesis of compound **4**, 3.38 g (7.4 mmol) of compound 3 was added to a 35 mL reaction vessel and capped with a septum. The vessel was flushed with argon and maintained under positive pressure of argon before the addition of 10 mL of dry acetonitrile. The vessel was then stirred and gently heated by a sand bath to facilitate dissolution, at which point 1.15 mL (8.4 mmol, 1.1 eq) of 4-methoxyphenyl isothiocyanate was added using a glass syringe. The vessel was then placed in a microwave reactor for 2 hours and 30 minutes at 80°C and 30 W power. The vessel was cooled to room temperature and the precipitate was filtered before washing with 5 x 10 mL of hexanes. The acetonitrile was removed by rotary evaporation and the product was dried fully under vacuum to afford a light yellow solid. (4.86 g, 66%) 1H NMR (300MHz, DMSO-D_6) 9.86 (s, 1H), 9.77 (s, 1H), 7.71-7.64 (m, 2H), 7.54-7.46 (m, 2H), 7.36-7.29 (m, 2H), 6.95-6.87 (m, 2H), 4.50 (s, (2H), 3.75 (s, 2H), 3.67 (t, J = 6.5, 2H), 3.61-3.47 (m, 2H), 3.43-3.31 (m, 2H), 2.89 (s, 3H), 2.19-2.08 (m, 4H), 1.54-1.41 (m, 2H), 1.33-1.89 (m, 24H), 0.90-0.81 (m, 2H). NMR^{13}C NMR (75.7 MHz, DMSO-D_6) 179.5, 156.5, 141.3, 132.4, 131.8, 125.8, 123.9, 122.6, 113.6, 65.3, 64.7, 62.4, 55.1, 54.8, 47.1, 31.1, 28.92, 28.90, 28.86, 28.62, 28.55, 25.4, 22.6, 21.9, 20.7, 13.8. ESI-MS Positive mode found: m/z 356.2 [100%, $(C_{20}H_{26}N_3OS)^+$]; Calc. 356.2; Negative mode found: m/z 265.1 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.2; ESI-HRMS Positive mode found: m/z 356.1784 [100%, $C_{20}H_{26}N_3OS)^+$]; Calc. 356.1792, m/z 357.1806 [21.6%, $C_{20}H_{26}N_3OS)^+$]; Calc. 357.1825;

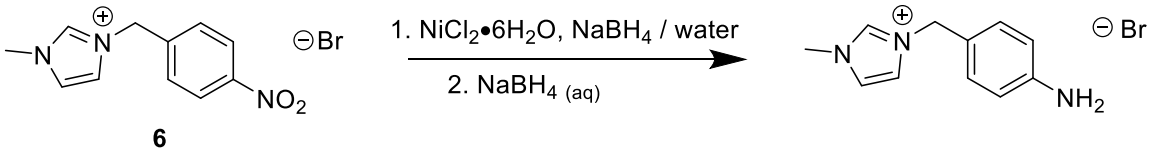
Negative mode found: m/z 265.1478 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.1479, m/z 266.1508 [13%, $(C_{12}H_{25}O_4S)^-$]; Calc. 266.1512, m/z 267.1459 [4.5%, $(C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

1-(4-nitrobenzyl)-3-methylimidazol-1-ium bromide



In a 35 mL microwave reaction vessel, 2.17 g (10.0 mmol) of p-nitrobenzyl bromide was dissolved in 10 mL acetonitrile. Slowly, 0.88 mL (11.0 mmol) of 1-methyl imidazole was added and the vessel was capped and placed in the microwave reactor for 30 minutes at 80°C and 30W power. The solution was then transferred immediately to a beaker, where upon cooling there is the formation of a white precipitate. The precipitate was washed with 50 mL of ethyl acetate and filtered to obtain 2.84 g (95.2%) of product. No further purification was needed. MP 169.4-170.7 °C, ^{1}H NMR (300 MHz, DMSO-D_6) 9.31 (s, 1H), 8.28 (d, *J* = 8.8, 2H), 7.84 (s, 1H), 7.77 (s, 1H), 7.68 (d, *J* = 8.8, 2H), 5.63 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 147.5, 142.2, 137.1, 129.5, 124.1, 123.9, 122.4, 50.7, 35.9. ESI-MS Positive mode found: m/z 218.1 [100%, $(C_{11}H_{12}N_3O_2)^+$]; Calc. 218.1; Negative mode found: m/z 78.9 [100%, Br^-]; Calc. 78.9, m/z 80.9 [97.3%, Br^-]; Calc. 80.9; ESI-HRMS Positive mode found: m/z 218.0932 [100%, $(C_{11}H_{12}N_3O_2)^+$]; Calc. 218.0925, m/z 219.0956 [11.9%, $(C_{11}H_{12}N_3O_2)^+$]; Calc. 219.0958; Negative mode found: 78.9186 [100%, Br^-]; Calc. 78.9188, m/z 80.9167 [97.3%, Br^-]; Calc. 80.9168.

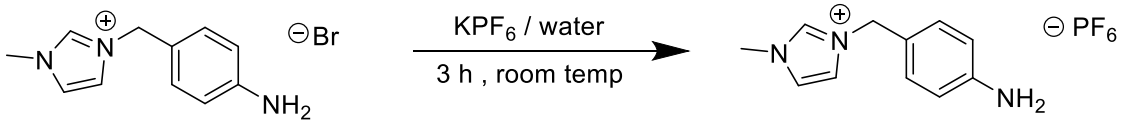
1-(4-aminobenzyl)-3-methylimidazol-1-ium bromide



6

In a 50 mL beaker, 0.44 g (18.6 mmol) of nickel (II) chloride hexahydrate was dissolved in 10 mL of water. Slowly, 0.18 g (4.8 mmol) of sodium borohydride was added to the aqueous nickel (II) chloride solution, and the resulting black catalyst was transferred to a 250 mL round bottomed flask containing **6** dissolved in 40 mL of water. An additional 0.88 g (23.2 mmol) of sodium borohydride was dissolved in 10 mL of water and then added dropwise to the flask. The mixture was stirred at room temperature for 20 minutes and then filtered through a 2 cm of diatomaceous earth. The product was left in the aqueous solution for the next step. ^{1}H NMR (300 MHz, DMSO-D_6) 9.07 (s, 1H), 7.68 (d, *J* = 12.0, 2H), 7.10 (d, *J* = 8.4, 2H), 6.56 (d, *J* = 8.4, 2H), 5.27 (s, 2H), 5.16 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 149.4, 136.1, 129.8, 123.8, 122.1, 121.0, 113.9, 52.1, 35.8. ESI-MS Positive mode found: m/z 188.1 [100%, $(C_{11}H_{14}N_3)^+$]; Calc. 188.1 ; ESI-HRMS Positive mode found: m/z 188.1175 [100%, $(C_{11}H_{14}N_3)^+$]; Calc. 188.1183, m/z 189.1211 [11.9%, $(C_{11}H_{14}N_3)^+$]; Calc. 189.1216.

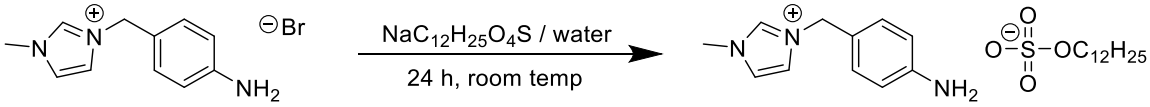
1-(4-aminobenzyl)-3-methylimidazol-1-ium hexafluorophosphate



Following the same procedure as described for **2**, 2.14 g (11.6 mmol) of potassium hexafluorophosphate was added to the aqueous solution containing the imidazolium bromide salt described previously. After stirring for 3 hours at room temperature, the precipitate was isolated

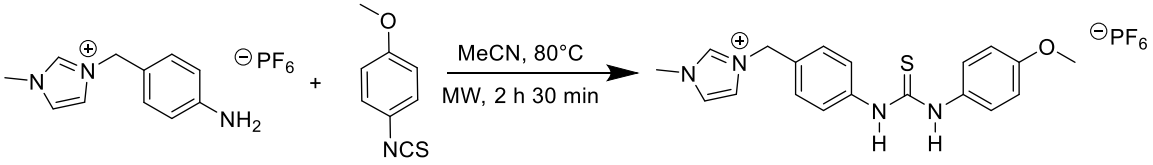
by filtration and dried to afford 2.44 g (78.8%) of white powder. The ^{1}H and ^{13}C NMR spectra data match the previously reported imidazolium bromide salt. ^{31}P (121.5 MHz, DMSO-D_6) -144.2 (septet, ^{1}J = 711.5 Hz). ^{19}F (282.5 MHz, DMSO-D_6) -70.1 (d, ^{1}J = 711.5 Hz). MP 123.4-124.0 °C, ESI-MS Negative mode found: m/z 145.0 [100%, $(PF_6)^-$]; Calc. 145.0; ESI-HRMS Negative mode found: m/z 144.9651 [100%, $(PF_6)^-$]; Calc. 144.9647.

1-(4-aminobenzyl)-3-methylimidazol-1-ium dodecyl sulphate



After the reduction of 0.14 g (4.8 mmol) of **6**, 1.45 g (5.0 mmol) of sodium dodecyl sulphate was added to the aqueous solution and stirred at room temperature for 24 hours. The solution was extracted with 50 mL dichloromethane three times and the organic layers were combined and dried with magnesium sulphate. The mixture was filtered, and the organic layer was concentrated and dried under vacuum to afford 2.05 g (91%) of a white solid. No further purification was needed. MP 106.4-107.3 °C, ^{1}H NMR (300 MHz, DMSO-D_6) 9.10 (s, 1H), 7.73-7.69 (m, 1H), 7.68-7.64 (m, 1H), 7.11 (d, 2H), 6.55 (d, 2H), 5.26 (s, 2H), 5.16 (s, 2H), 3.83 (s, 3H), 3.68 (t, *J* = 6.7 ,2H), 1.48 (m, 2H), 1.24 (s, 23H), 0.89-0.81 (m, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 148.3, 136.8, 130.3, 123.7, 122.0, 121.9, 115.2, 67.9, 53.1, 36.3, 32.0, 29.79, 29.75, 29.70, 29.53, 29.46, 26.0, 22.8, 14.2, 0.09. Negative mode found: m/z 265.1 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.2; ESI-HRMS Positive mode found: m/z 188.1185 [100%, $(C_{11}H_{14}N_3)^+$]; Calc. 188.1183; Negative mode found: m/z 265.1485 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.1479, m/z 266.1510 [13%, $(C_{12}H_{25}O_4S)^-$]; Calc. 266.1512, m/z 267.1460 [4.5%, $(C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

1-(4-(3-(4-methoxy)phenyl)thioureido)benzyl-3-methylimidazol-1-ium hexafluorophosphate (**5**)

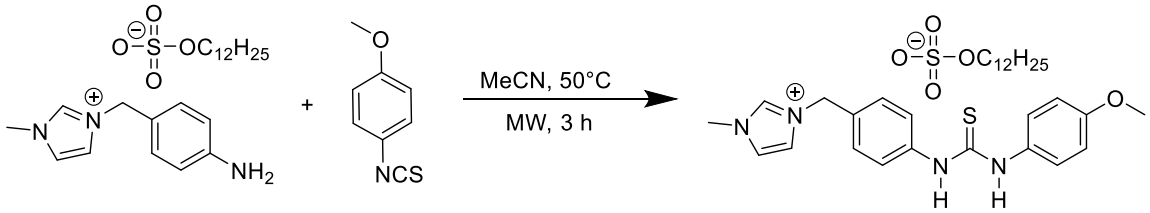


5

Following a similar procedure as the synthesis of compound **4**, 2.40 g (7.2 mmol) of compound **7** was added to a 35 mL microwave reactor vessel and capped with a septum. The vessel was filled with argon, and 5 mL of dry acetonitrile was added. The vessel was gently stirred until **7** was completely dissolved, and 1.10 mL (8.0 mmol, 1.1 eq) of 4-methoxyphenyl isothiocyanate was added using a glass syringe. The reaction vessel was then placed in the microwave reactor for 2 hours and 30 minutes at 80°C and 30 W power. The reaction vessel was then cooled to room temperature before refrigeration for 24 hours. The resulting precipitate was removed by filtration, and the filtrate was washed with 5 x 10 mL of hexanes. The acetonitrile was removed by rotary evaporation and dried completely under vacuum to afford a light yellow solid. (3.56 g, 65%) ^{1}H NMR (300 MHz, DMSO-D_6) 9.93 (s, 0.3H), 9.68 (s, 1H), 9.42 (s, 0.3H), 9.19 (s, 1H), 7.82-7.73 (m, 1H), 7.73-7.65 (m, 1H), 7.58-7.46 (m, 2H), 7.42-7.25 (m, 4H), 7.02-6.94 (m, 1H), 6.93-6.83 (m, 1H), 5.36 (s, 2H), 3.84 (s, 3H), 3.75-3.69 (m, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 156.6, 136.5, 131.9, 128.6, 128.5, 126.1, 126.0, 124.0, 123.8, 122.3, 113.7, 113.6, 55.2, 51.5, 35.9. ^{31}P (121.5 MHz, DMSO-D_6) -144.2 (septet, ^{1}J = 711.5 Hz). ^{19}F (282.5 MHz, DMSO-D_6) -70.1 (d, ^{1}J = 711.5 Hz). ESI-MS Positive mode found: m/z 353.1 [100%, $(C_{19}H_{21}N_4OS)^+$]; Calc. 353.1; Negative mode found: m/z 145.0 [100%, $(PF_6)^-$]; Calc. 145.0; ESI-HRMS Positive mode found: m/z 353.1424 [100%, $(C_{19}H_{21}N_4OS)^+$]; Calc. 353.1431, m/z 354.1436 [20.5%,

$(C_{19}H_{21}N_4OS)^+$]; Calc. 354.1465, m/z 355.1412 [4.5%, $(C_{19}H_{21}N_4OS)^+$]; Calc. 355.1389; Negative mode found: m/z 144.9643 [100%, $(PF_6)^-$]; Calc. 144.9647.

1-(4-(3-(4-methoxyphenyl)thioureido)benzyl-3-methylimidazol-1-ium dodecyl sulphate (**6**)

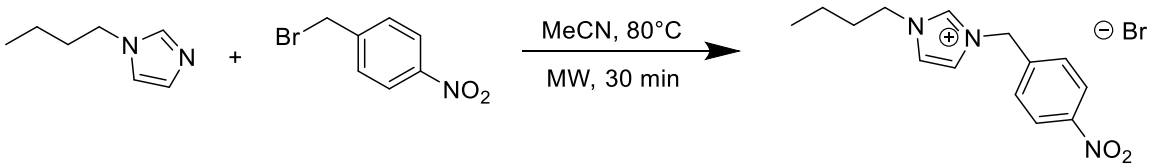


6

In a 35 mL microwave reaction vessel, 0.91 g (2.0 mmol) of **8** was suspended in 10 mL of acetonitrile and 0.28 mL (2.0 mmol) of 4-methoxyphenyl isothiocyanate was added. The vessel was flushed with nitrogen gas and heated to 50°C by microwave irradiation at 30 W for 3 hours. The reaction was cooled to room temperature before concentrating under vacuum. The resulting viscous liquid was then left at room temperature for 48 hours before being re-dissolved in dichloromethane and filtered to remove any precipitate. The final product was dried under vacuum to produce 1.27 g (99%) of a light yellow solid, compound **10,** with no additional purification needed. ^{1}H NMR (300 MHz, DMSO-D_6) 9.73 (s, 2H), 9.22 (s, 1H), 7.87-7.76 (m, 1H), 7.76-7.67 (m, 1H), 7.57 (d, *J* = 8.3, 2H), 7.45-7.28 (m, 4H), 6.90 (d, *J* = 8.3, 2H), 5.37 (s, 2H), 3.86 (s, 3H), 3.80-3.64 (m, 6H), 1.56-1.39 (m, 3H), 1.38-1.09 (s, 22H), 0.92-0.77 (m, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 179.7, 158.6, 156.5, 140.2, 136.5, 132.0, 130.3, 128.5, 127.3, 125.8, 123.9, 123.6, 122.2, 115.1, 113.6, 65.6, 55.5, 55.2, 51.5, 35.8, 31.3, 29.05, 29.01, 28.7, 25.5, 22.1, 13.9. ESI-MS Positive mode found: m/z 353.2 [100%, $(C_{19}H_{21}N_4OS)^+$] ; Calc. 353.1; Negative mode found: 265.1 [100%, $(C_{12}H_{25}O_4S)^-$] ; Calc. 265.2; ESI-HRMS Positive mode found: 353.1437 [100%, $(C_{19}H_{21}N_4OS)^+$]; Calc. 353.1431, m/z 354.1426 [20.5%, $(C_{19}H_{21}N_4OS)^+$]; Calc. 354.1465; Negative mode found: m/z 265.1489 [100%, $(C_{12}H_{25}O_4S)^-$];

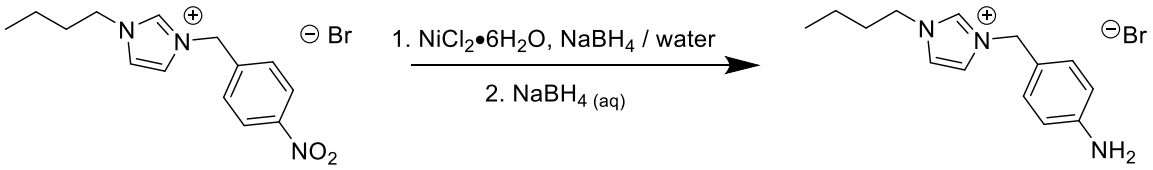
Calc. 265.1479, m/z 266.1512 [13%, $(C_{12}H_{25}O_4S)^-$]; Calc. 266.1512, m/z 267.1461 [4.5%, $(C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

1-(4-nitrobenzyl)-3-butylimidazol-1-ium bromide



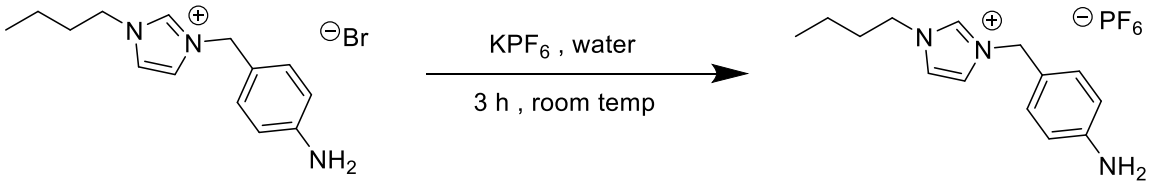
Following the same procedure as for **1** and **6**, 2.19 g (10.2 mmol) of p-nitrobenzyl bromide was dissolved in 10 mL of acetonitrile in a 35 mL microwave reactor tube followed by 1.45 mL (11.0 mmol) of 1-butyl imidazole. The reaction tube was capped and placed in the microwave reactor for 30 minutes at 80°C and 30 W power. The solution was then transferred to a beaker and washed with 3 mL aliquots of ethyl acetate until a precipitate formed. The precipitate was washed with an additional 30 mL of ethyl acetate and then isolated by filtration and dried to produce 3.29 g (95.1%) of white product. MP 124.9-125.9 °C, ^{1}H NMR (300 MHz, DMSO-D_6) 9.42 (s, 1H), 8.29 (d. *J* = 8.7, 2H), 7.88 (d, *J* = 1.5, 2H), 7.68 (d, *J* = 8.7, 2H), 5.63 (s, 2H), 4.20 (t, *J* = 7.2, 2H), 1.86-1.72 (m, 2H), 1.35-1.19 (m, 2H), 0.90 (t, *J* = 7.4, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 147.7, 142.3, 136.7, 129.6, 124.1, 123.1, 122.8, 51.0, 48.9, 31.3, 18.9, 13.4. ESI-MS Positive mode found: m/z 260.1 [100%, $(C_{14}H_{18}N_3O_2)^-$]; Calc. 260.1; Negative mode found: m/z 80.9 [100%, Br^-]; Calc. 80.9; ESI-HRMS Positive mode found: m/z 260.1388 [100%, $(C_{14}H_{18}N_3O_2)^-$]; Calc. 260.1394, m/z 261.1394 [15.1%, $(C_{14}H_{18}N_3O_2)^-$]; Calc. 261.1428; Negative mode found: 78.9186 [100%, Br^-]; Calc. 78.9188, m/z 80.9166 [97.3%, Br^-]; Calc. 80.9168.

1-(4-aminobenzyl)-3-butylimidazol-1-ium bromide



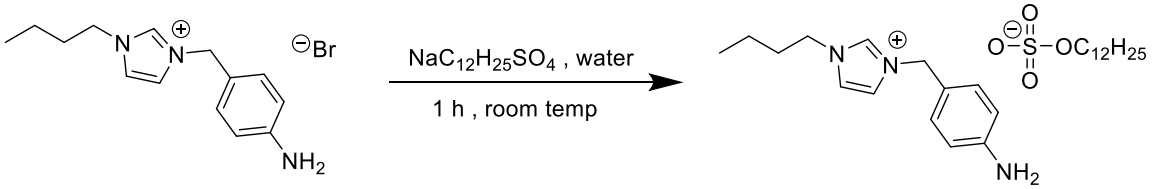
Following the reduction procedure described for compound **6**, 0.46 g (1.9 mmol) of nickel (II) chloride hexahydrate was dissolved in 10 mL water and 0.18 g (4.9 mmol) of sodium borohydride was slowly added to the aqueous solution. The nickel boride catalyst was transferred to the 250 mL round bottomed flask containing **11,** which was dissolved in 40 mL of water. In a separate beaker, sodium borohydride, 0.91 g (24.1 mmol), was dissolved in 10 mL of water and added to the round bottomed flask dropwise. The mixture was stirred at room temperature for 20 minutes and then filtered through 2 cm of diatomaceous earth. The product was left in the aqueous solution for the following procedure. ^{1}H NMR (300 MHz, DMSO-D_6) 9.17 (s, 1H), 7.74 (d, *J* = 10.0, 2H), 7.10 (d, *J* = 8.2, 2H), 6.56 (d, *J* = 8.2, 2H), 5.27 (s, 2H), 5.16 (s, 2H), 4.15 (t, *J* = 6.9, 2H), 1.83-1.68 (m, 2H), 1.32-1.15 (m, 2H), 0.89 (t, *J* = 6.9, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 149.4, 135.5, 129.8, 122.6, 122.3, 121.0, 113.9, 52.2, 48.6, 31.3, 18.9, 13.3. ESI-MS Positive mode found: m/z 230.2 [100%, $(C_{14}H_{20}N_3)^+$]; Calc. 230.2; ESI-HRMS Positive mode found: 230.1644 [100%, $(C_{14}H_{20}N_3)^+$]; Calc. 230.1652.

1-(4-aminobenzyl)-3-butylimidazol-1-ium hexafluorophosphate



To the aqueous solution containing the butylimidazolium bromide salt, 2.20 g (11.9 mmol) of potassium hexafluorophosphate was added and stirred for 3 hours at room temperature. The resulting precipitate was isolated by filtration and dried to yield 3.49 g (97.3%) of white powder. ^{1}H and ^{13}C NMR spectra data are the same as the bromide salt reported previously. ^{31}P (121.5 MHz, DMSO-D_6) -144.2 (septet, ^{1}J = 711.5 Hz). ^{19}F (282.5 MHz, DMSO-D_6) -70.1 (d, ^{1}J = 711.5 Hz). MP 86.9-87.5 °C, ESI-MS Negative mode found: 145.0 [100%, $(PF_6)^-$]; Calc. 145.0; ESI-HRMS Negative mode found: 144.9649 [100%, $(PF_6)^-$]; Calc. 144.9647.

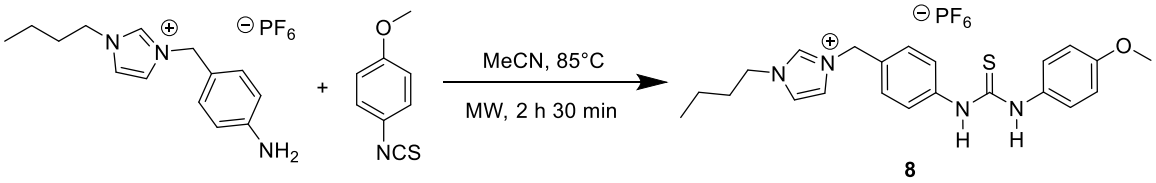
1-(4-aminobenzyl)-3-butylimidazol-1-ium dodecyl sulphate



To an aqueous solution containing the butylimidazolium bromide salt, 1.36 g (4.0 mmol) of sodium dodecyl sulphate was added and stirred for 1 hour at room temperature. The resulting precipitate was isolated by filtration and dried under vacuum to product 1.37g (69%) of white solid. MP 102.5-102.9 °C, ^{1}H NMR (300MHz, DMSO-D_6) 9.19 (s, 1H), 7.80-7.75 (m, 1H), 7.75-7.70 (m, 1H), 7.10 (d, J = 8.4, 2H), 6.55 (d, J = 8.4, 2H), 5.27 (s, 2H), 5.17 (s, 2H), 4.15 (t, J = 7.2, 2H), 3.67 (t, J = 6.6, 2H), 1.82-1.69 (m, 2H), 1.53-1.41 (m, 2H), 1.33-1.16 (m, 20H), 0.94-0.80 (m, 6H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 149.3, 135.5, 129.6, 122.6, 122.2, 120.9, 113.8, 65.4, 52.1, 48.6, 31.28, 31.26, 29.05, 29.02, 28.98, 28.75, 28.68, 25.5, 22.1, 18.8, 13.9,

13.2. ESI-MS Negative mode found: m/z 265.1 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.2; ESI-HRMS Negative mode found: m/z 265.1478 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.1479, m/z 266.1509 [13%, $(C_{12}H_{25}O_4S)^-$]; Calc. 266.1512, m/z 267.1463 [4.5%, $(C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

1-(4-(3-(4-methoxy)phenyl)thioureido)benzyl-3-butylimidazol-1-ium hexafluorophosphate (**8**)

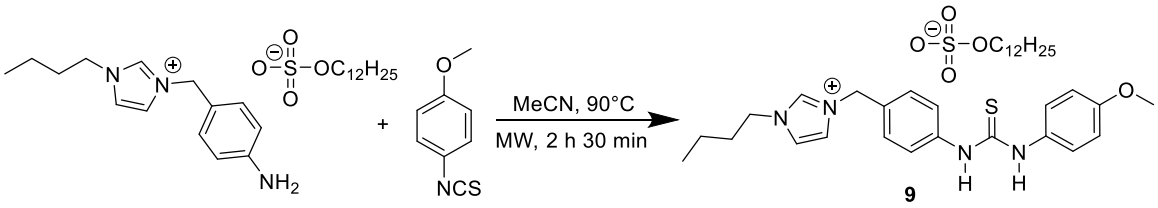


8

Following a similar procedure for the synthesis of compound **4**, 2.04 g (5.4 mmol) of compound **12** was added to a 35 mL microwave reactor vessel and capped with a septum. The vessel was filled with argon, followed by 5 mL of dry acetonitrile. The vessel was gently stirred to promote dissolution, and 0.90 mL (6.5 mmol) of 4-methoxyphenyl isothiocyanate was added by glass syringe. The vessel was then placed in a microwave reactor for 2 hours and 30 minutes at 85°C and 30 W power. The vessel was then cooled to room temperature before refrigeration for 24 hours, after which a white precipitate was removed by filtration. The filtrate was then washed with 5 aliquots of 10 mL of hexanes, and then the solvent was removed by rotary evaporation and dried fully under vacuum to afford 0.91 g (88%) of product. ^{1}H NMR (300 MHz, DMSO-D_6) 9.71 (s, 1H), 9.30 (s, 1H), 7.84-7.77 (m, 2H), 7.55 (d, *J* = 8.3, 2H), 7.42-7.27 (m, 4H), 6.94-6.85 (m, 2H), 5.37 (s, 2H), 4.17 (t, *J* = 7.1, 2H), 3.74 (s, 2H), 1.84-1.71 (m, 2H), 1.34-1.18 (m, 2H), 0.896 (t, *J* = 7.1, 3H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 179.9, 158.6, 156.7, 140.2, 136.0, 132.2, 132.0, 130.3, 129.9, 128.6, 128.5, 127.4, 126.6, 126.1, 123.8, 122.8, 122.5, 122.2, 115.1, 113.7, 113.6, 55.6, 55.2, 51.6, 48.7, 31.3, 18.8, 13.3, 1.2. ESI-MS Positive mode found: m/z

395.2 [100%, $(C_{22}H_{27}N_4OS)^+$]; Calc. 395.2; Negative mode found: m/z 145.0 [100%, $(PF_6)^-$]; Calc. 145.0; ESI-HRMS Positive mode found: m/z 395. 1903 [100%, $(C_{22}H_{27}N_4OS)^+$]; Calc. 395.1901, m/z 396.1961 [23.8%, $(C_{22}H_{27}N_4OS)^+$]; Calc. 396.1934; Negative mode found: m/z 144.9642 [100%, $(PF_6)^-$]; Calc. 144.9647.

1-(4-(3-(4-methoxy)phenyl)thioureido)benzyl-3-butylimidazol-1-ium dodecyl sulphate (**9**)



Following a similar procedure to the synthesis of **4**, 0.99 g (2.0 mmol) of compound **13** was added to a 35 mL microwave reactor vessel and dissolved in 6 mL of acetonitrile. Then, 0.28 mL (2.0 mmol) of 4-methoxyphenyl isothiocyanate was added and the vessel was degassed with nitrogen and placed in the microwave reactor for 3 hours at 90°C and 30 W. The solution was concentrated by rotary evaporation and left for 48 hours at room temperature under nitrogen gas. The viscous liquid was then re-dissolved in dichloromethane and filtered to remove any impurities or byproducts, and then dried under vacuum to produce 1.02 g (77%) of to afford a white solid. ^{1}H NMR (300 MHz, DMSO-D_6) 9.73-9.63 (m, 2H), 9.31 (s, 1H), 7.84-7.78 (m, 2H), 7.56 (d, *J* = 8.8, 2H), 7.42-7.28 (m, 4H), 6.90 (d, *J* = 8.8, 2H), 5.37 (s, 2H), 4.17 (t, *J* = 7.2, 2H), 3.74 (s, 3H), 3.68 (t, *J* = 7.2, 2H), 1.85-1.71 (m, 2H), 1.54-1.40 (m, 2H), 1.31-1.19 (m, 21H), 0.95-0.78 (m, 6H). ^{13}C NMR (75.5 MHz, DMSO-D_6) 179.8, 156.6, 140.1, 135.9, 131.9, 130.2, 128.4, 125.9, 123.7, 122.8, 122.5, 113.7, 65.5, 55.2, 51.6, 48.7, 31.3, 31.2, 29.03, 28.98, 28.74, 28.68, 25.5, 22.1, 18.8, 13.9, 13.2. ESI-MS Positive mode found: m/z 395.2 [100%, $(C_{22}H_{27}N_4OS)^+$]; Calc. 395.2; Negative mode found: m/z 265.1 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc.

265.2; ESI-HRMS Positive mode found: m/z 395.1901 [100%, $(C_{22}H_{27}N_4OS)^+$]; Calc. 395.1901; Negative mode found: m/z 265.1483 [100%, $(C_{12}H_{25}O_4S)^-$]; Calc. 265.1479, m/z 266.1510 [13%, $(C_{12}H_{25}O_4S)^-$]; Calc. 266.1512, m/z 267.1459 [4.5%, $(C_{12}H_{25}O_4S)^-$]; Calc. 267.1437.

A total of 6 ionic liquids were synthesized using three different starting materials, which became the cationic core of the ionic liquid. *N*-methyl pyrrolidine was chosen for its higher thermal stability and high conductivity, and two imidazolium derivatives which have increased stability due to resonance, and varying solubilities depending on the length of the alkyl chain. Additional considerations for the ligand design include using a different isothiocyanate derivative to create a chemical modifier, 4-methoxyl phenyl, when forming the thiourea in order to donate electron density toward the sulphur atom in order to enhance the 'softness' of the coordination site.

The final consideration for the ionic liquids was the choice of anion. The hexafluorophosphate anion was used previously for the synthesis of thiourea-containing ionic liquids by members of the Singer group. This anion was chosen because it facilitates easy synthesis of the ionic liquid intermediates due to its hydrophobicity, which allow it to be isolated by separation from aqueous solutions. The hydrophobicity of the resulting ionic liquid was also ideal for performing liquid-liquid extraction experiments for gold recovery. The second anion that was explored was dodecyl sulphate, which is amphiphilic in nature, and more environmentally friendly than fluorine-containing anions. The sulphate moiety also considered to aid in the extraction of gold.

Nuclear Magnetic Resonance spectra were acquired using a Bruker 300 MHz Ultrashield spectrometer. Spectral data were processed using Bruker Topspin 4.1.1. The deuterated solvent,

DMSO-D_6 and $(CD_3)_2CO$, were supplied from Cambridge Isotope Laboratories. Residual internal $OS(CD_3)(CD_2H)$ and $OC(CD_3)(CD_2H)$ appear in the ^1H NMR spectra at δ 2.5 and 2.05 for DMSO-D_6 and acetone-D_6, respectively. Residual internal DMSO-D_6 and acetone-D_6 in the ^{13}C NMR spectra appear at δ 39.52 and 29.84, respectively.

A CEM Discover and Discover 2.0 Microwave Synthesizer were used in the synthesis of the ionic ligands. The instrument operates at a frequency of 2450 MHz and reactions were performed as closed systems, using 30 W of power and maximum stirring.

Melting points of solid products were determined using an Electrothermal Mel-Temp 3.0 instrument.

Electrospray ionization mass spectrometry was performed by Xiao Feng at the Mass Spectrometry Laboratory at Dalhousie University. A Bruker microTOF Focus Mass Spectrometer and Bruker Compact QTOF Mass Spectrometer were used for positive and negative ion masses, respectively.

The optimized molar ratio of ionic liquid to gold and shaking time was then compared to liquid-liquid extraction using a separatory funnel. Using compound **8**, [Thbim][PF_6], gold (III) extraction was performed with the mixing machine set to a frequency of 6 Hz and shaking time of 120 seconds in 20 mL scintillation vials without the addition of the milling balls typically used for this instrument. These results were compared to manual shaking of a separatory funnel for 120 seconds. As seen in **Figure 7**, the extraction results were comparable for both methods, but the extraction with the separatory funnel resulted in a much larger standard deviation. It was found that by using the mixing machine, which provides constant shaking frequency and precise timing, and does not require frequent venting, the extraction efficiency was more precise and

therefore more reproducible. Hence, the mixing machine was used for the rest of the experiments.

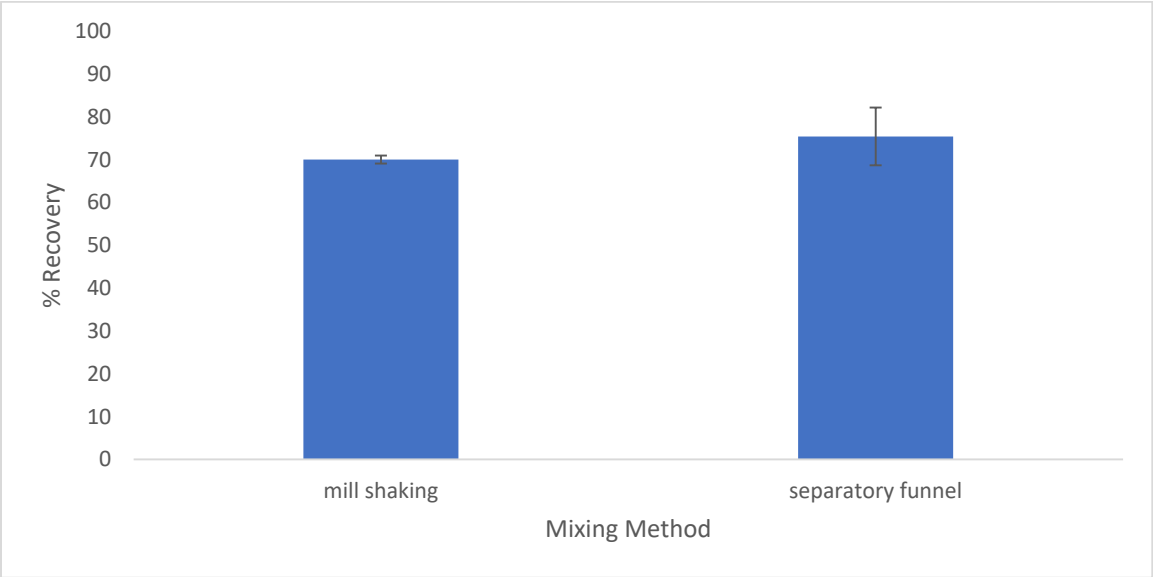


Figure 7: Comparison of the extraction efficiency and precision of ball mill shaking versus manual shaking in a separatory funnel. Error bars reflect the standard deviation of the measurement from triplicate analysis.

Solutions of each thiourea-functionalized ionic liquid were prepared in dichloromethane (DCM), a water-immiscible organic solvent, with a concentration of 3.9 $x10^{-3}$ mmol/mL. Each ionic liquid was weighed into a test tube and quantitatively transferred to a 100 mL volumetric flask. The solutions were inverted 30 times. Using the previously made solutions, 50.00 mL was transferred to a 100 mL volumetric flask and diluted with dichloromethane to obtain ionic liquid solutions with a concentration of $2.0x10^{-4}$ mmol/mL.

The gold (III) solution was made by dissolving hydrogen tetrachloroaurate (III) hydrate in Milli-Q ultra-pure water (>18.2 MΩ·cm) to obtain a solution with a concentration of $1.17x10^{-3}$ mmol/mL (20 ppm). A gold (I) solution was made by dissolving the hydrogen tetrachloroaurate

(III) hydrate salt in 500 mL of water and reducing with sodium citrate. The solution was stirred for 20 minutes at room temperature, and complete reduction of gold (III) to gold (I) was confirmed by UV-vis spectroscopy, where the absorbance at 385 nm for gold (III) is absent prior to reduction. The solution was used immediately after preparation. The leachate solution was made by dissolving appropriate amounts of hydrogen tetrachloroaurate (III) hydrate, copper nitrate, and zinc nitrate salts in Milli-Q ultra-pure water. The standard silver solution and iron solution were added to obtain concentrations of 20 ppm for all metals.

Gold recovery experiments were performed by transferring 10.00 mL of one of the three metal-containing aqueous solutions to a 20 mL scintillation vial and adding 3.00 mL of the desired ionic liquid solution. Gold extraction was carried out using a Retsch Mixer Mill 200 set to 6 Hz for 120 seconds. After mixing, the aqueous and organic layers were allowed to fully separate for 1 hour prior to analysis of the aqueous layer.

Metal recovery percentage was determined by a ThermoScientific iCE3000 Series AA Spectrometer using an air/acetylene flame, a burner slot of 50 nm, and a slit width of 0.5 nm. The software used to collect the data was SOLAAR software for Thermo Scientific iCE 3000 Series AA Spectrometers.

The concentration of each metal was analyzed using their respective hollow cathode lamp, and a calibration curve was made for each metal prior to analysis using analytical standards. The unique wavelengths were chosen based on the manufacturer specifications for each hollow cathode lamp. The primary wavelength was chosen for Au, Ag, Cu, and Zn, as 267.6, 328.1, 324.8, and 213.9 nm, respectively. The secondary wavelength, 372.0 nm, was chosen for Fe in order to mitigate interference. Background interference was corrected using a deuterium lamp. Each extraction experiment was performed in triplicate.