Electronic Supplementary Material (ESI) for Green Chemistry

Separable fluorous ionic liquids for the dissolution and saccharification of cellulose

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Experimental

General

Cellulose (medium cotton linters, C6288) was from Sigma Chemical (St. Louis, MO). Other commercial chemicals were of reagent grade or better and were used without further purification. FluoroFlash® fluorous silica gel was from Aldrich Chemical (Milwaukee, WI).

The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator at water aspirator pressure (<20 torr) while maintaining the water-bath temperature below 50 °C unless noted otherwise. The term "high vacuum" refers to vacuum (<0.1 torr) achieved by a mechanical belt-drive oil pump.

NMR spectra were acquired with a Bruker DMX-400 Avance spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) at the National Magnetic Resonance Facility at Madison (NMRFAM). NMR spectra were acquired at ambient temperature unless indicated otherwise. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) in the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison.

Analytical methods

Reaction products were analyzed by HPLC and quantified using calibration curves generated from commercially available standards. Reaction mixtures were diluted with a known mass of deionized water, subjected to centrifugation at 12,000 rpm for 5 min to sediment insoluble products, and analyzed. Product concentrations were calculated from HPLC-peak integrations, which were then used to calculate yields. HPLC was performed using an Agilent 1200 system equipped with refractive index and photodiode array detectors. Sugars were analyzed by ion-exclusion chromatography with a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) using a 5 mM H_2SO_4 mobile phase at a flow rate of 0.6 mL/min at 65 °C.

3-Methyl-1-(3′,3′,4′,4’,5′,5′,6′,6′,6′-nonafluorohexyl)-imidazolium chloride (1)

Under Ar(g), toluene (15 mL) and 1,1,1,2,2,3,3,4,4-nonafluorohexyl iodide (5.0 g, 13.4 mmol) were combined in a round-bottom flask. The resulting solution was cooled to 0 °C, and 1-methylimidazole was added dropwise. The solution was stirred for 19 d, and separated into an orange lower layer and a colorless upper layer. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, 5:95–15:85 methanol/dichloromethane). Fractions containing the iodide salt were concentrated under reduced pressure.

Dowex 1-X8 resin (chloride form, 100–200 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (17 cm long, 20 mL volume, 24 meq). The resin bed was flushed extensively with 1:1 methanol/H_2O to remove contaminants. The iodide salt was dissolved in methanol (5 mL) and water (5 mL), and loaded onto the column. The column was eluted with 1:1 methanol/H_2O, and fractions were collected. The fractions containing ionic liquid were concentrated under reduced pressure to yield an orange oil contaminated with white solids. The oil and solids were dissolved in boiling methanol, and the solution was concentrated under reduced pressure until the white solids precipitated. The solids were removed by filtration and washed with tetrahydrofuran. Concentration of the filtrate under reduced pressure afforded **1** (0.7 g, 1.9 mmol, 14% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD) δ 9.25 (s, 1H), 7.87 (s, 1H), 7.71 (s, 1H), 4.72 (t, J = 7.3 Hz, 2H), 4.02 (s, 3H), 3.03 (m, 2H).

1-(2′,2′,3′,3′,4′,4′,4′-heptafluorobutyl)-3-methylimidazolium chloride (2)

A round-bottom flask was placed under Ar(g) to which trifluoroacetic anhydride (30.2 g, 143.9 mmol) was added. The flask was then cooled to –15 °C using a benzyl alcohol/dry ice bath before adding 50% v/v H_2O_2 (2.1 mL, 43.1 mmol) dropwise. 2,2,3,3,4,4,4-Heptafluoro-1-iodobutane (5.4 g, 17.4 mmol) was added to the round-bottom flask, which was protected from light with aluminum foil and allowed to warm to room temperature. The reaction mixture was stirred for 3 d. The reaction mixture was then concentrated under reduced pressure and left under high vacuum overnight to yield a white solid (5.3 g, 9.8 mmol). This solid was dissolved with trifluoroacetic anhydride (10 mL) in a round-bottom flask under Ar(g). Trifluoromethanesulfonimide (4.5 g, 15.9 mmol) was placed in another round-bottom flask under Ar(g), and the trifluoroacetic anhydride solution was transferred *via* cannula. The resulting solution was cooled to 0 °C in an ice-water bath and protected from light with aluminum foil. After stirring for 15 min, benzene (2.0 mL) was added. The reaction was allowed to warm to room temperature after 3 h and continued for another 15 h. A second portion of benzene (0.7 mL) was then added with stirring continued for an additional 5 h. The reaction mixture was then concentrated under reduced pressure and placed under high vacuum overnight to yield a brown oil (7.9 g). 1-Methylimidazole (0.7 mL, 9.1 mmol) and $NaHCO_3$ (0.9 g, 10.9 mmol) were dissolved in double deionized water (50

mL) in a round-bottom flask. The brown oil was then dissolved in dichloromethane (50 mL) and added to the aqueous mixture in one portion to give two layers. The mixture was stirred at room temperature for 4 h. The bottom, brown layer was then separated, concentrated under reduced pressure at 65 °C, and placed under high vacuum overnight to yield a brown oil (5.9 g). Purification was performed with flash chromatography (silica gel, 0:100–20:80 methanol/dichloromethane). Silica present in the residue was removed by dissolution in dichloromethane and filtration through a Millipore GVHP 0.22-µm membrane to yield an orange oil (1.5 g, 2.8 mmol).

Dowex 1-X8 resin (chloride form, 200–400 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (3 cm long, 37 mL volume, 16 meq). The resin bed was flushed extensively with methanol/H_2O to remove contaminants. The salt was dissolved in methanol (7.5 mL) and water (2.5 mL) and loaded on the column. The column was eluted with H_2O, 1:1 methanol/H_2O, and methanol, and fractions were collected. Fractions containing ionic liquid were concentrated under reduced pressure to yield **2** (0.90 g, 3.1 mmol, 34% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD) δ 9.09 (s, 1H), 7.69 (s, 1H), 7.64 (s, 1H), 5.24 (t, J = 15.7 Hz, 2H), 3.92 (s, 3H). HRMS (ESI) m/z 265.0573 [calculated for $C_8H_8N_2F_7$ $(M - Cl)^+$ 265.0571].

3-Methyl-1-(3′,4′,4′,4′-tetrafluoro-3′-trifluoromethyl-butyl)-imidazolium chloride (3)

Under Ar(g), anhydrous toluene (75 mL) and 1-methylimidazole (3.0 mL, 37.8 mmol) were added to a round-bottom flask equipped with a reflux condenser. 4-Iodo-2-(trifluoromethyl)-1,1,1,2-tetrafluorobutane (8.2 g, 25.2 mmol) was then added, and the reaction mixture was stirred at reflux for 16 h. The mixture was then allowed to cool to room temperature before the toluene was decanted to leave a brown oil. This oil was concentrated under reduced pressure before being placed under high vacuum overnight. Purification was attempted by flash chromatography (silica gel, 0:100–30:70 methanol/dichloromethane), but failed to yield the pure iodide salt. Hence, the compound was passed through a fluorous SPE cartridge according to the procedure by Fluorous Technologies, Inc.[1] to yield the pure iodide salt as an orange oil.

Dowex 1-X8 resin (chloride form, 200–400 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (4 cm long, 20 mL volume, 8 meq). The resin bed was flushed extensively with methanol/H_2O to remove contaminants. The salt was dissolved in methanol (7.5 mL) and water (2.5 mL), and loaded onto the column. The column was eluted with H_2O, 1:1 methanol/H_2O, and methanol, and fractions were collected. Fractions containing ionic liquid were concentrated under reduced pressure to yield **3** (1.2 g, 3.7 mmol, 15% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD) δ 9.08 (s, 1H), 7.74 (s, 1H), 7.59 (s, 1H), 4.56 (t, J = 7.8 Hz, 2H), 3.92 (s, 3H), 2.93 (m, 2H). HRMS (ESI) m/z 279.0742 [calculated for $C_9H_{10}N_2F_7$ $(M - Cl)^+$ 279.0727].

3-Methyl-1-(3′,3′,4′,4′,4′-pentafluorobutyl)-imidazolium chloride (4)

In a round-bottom flask equipped with a magnetic stirbar and a reflux condenser were placed 3,3,4,4,4-pentafluorobutyl iodide (5.7 g, 20.8 mmol), 1-methylimidazole (2.5 mL, 31.2 mmol), and toluene (50 mL). The resulting solution was stirred and maintained at 75 °C for 15 h. Then, the temperature was increased to 100 °C. After 8 h, a red layer had appeared beneath the upper toluene layer. The reaction mixture was then concentrated under reduced pressure to a red-orange residue.

Dowex 1-X8 resin (chloride form, 100-200 mesh) was mixed with water and poured into a glass column to create a resin bed (17 cm long, 20 mL volume, 24 meq). The resin bed was flushed extensively with water to remove contaminants. The red-orange residue was dissolved in water and loaded on the column. The column was eluted with water, and fractions were collected. Fractions containing ionic liquid were concentrated under high vacuum, yielding an orange oil. The major impurity was 1-methylimidazole. The residue was purified by flash chromatography (silica gel, 15:85–30:70 methanol/dichloromethane), and the fractions containing the chloride salt were concentrated under reduced pressure. To remove silica, the residue was dissolved partially in dichloromethane, and filtered through a Millipore GVHP 0.22-µm membrane. The filtrate was concentrated under high vacuum, yielding **4** (1.69 g, 6.39 mmol, 30.7% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.69 (s, 1H), 7.55 (s, 1H), 4.55 (t, J = 7.2 Hz, 2H), 3.88 (s, 3H), 2.84 (m, 2H). HRMS (ESI) m/z 229.0768 [calculated for $C_8H_{10}N_2F_5$ $(M - Cl)^+$ 229.0759].

3-Methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5)

A round-bottom flask was placed under Ar(g) to which trifluoroacetic anhydride (30.2 g, 143.9 mmol) was added. The flask was then cooled to –15 °C using a benzyl alcohol/dry ice bath before adding 50% H_2O_2 (2.1 mL, 43.1 mmol) dropwise. 1,1,1,2,2-Pentafluoro-3-iodopropane (5.1 g, 19.4 mmol) was then added to the round-bottom flask, which was protected from light with aluminum foil and allowed to warm to room temperature. The reaction mixture was stirred for 3 d. The reaction mixture was then concentrated under reduced pressure and left under high vacuum overnight to yield a brown oil (7.9 g). This oil was dissolved in trifluoroacetic anhydride (10 mL) in a round-bottom flask under Ar(g). Trifluoromethanesulfonimide (4.8 g, 17.1 mmol) was placed in a separate round-bottom flask under Ar(g), and the trifluoroacetic anhydride solution was transferred *via* cannula. The resulting solution was cooled to 0 °C in an ice-water bath and protected from light with aluminum foil. After stirring for 15 min, benzene (2.0 mL) was added. The reaction mixture was allowed to warm to room temperature after 3 h and continued for another 15 h. A second portion of benzene (0.7 mL) was then added with stirring continued for an additional 5 h. The reaction mixture was then concentrated under reduced pressure and placed under high vacuum overnight to yield a brown oil (8.5 g).

1-Methylimidazole (0.9 mL, 11.3 mmol) and $NaHCO_3$ (1.2 g, 13.6 mmol) were dissolved in double deionized water (50 mL) in a round-bottom flask. The brown oil was then dissolved in dichloromethane (50 mL) and added to the aqueous mixture in one portion to give two layers. The mixture was stirred at room temperature for 4 h. The bottom, brown layer was then separated, concentrated under reduced pressure at 70 °C, and placed under high vacuum overnight to yield a brown oil (5.6 g). Purification was performed with flash chromatography (silica gel, 0:100–20:80 methanol/dichloromethane). Silica present in the residue was removed by dissolution in dichloromethane and filtration through a Millipore GVHP 0.22-µm membrane to yield an orange oil, which formed a crystalline solid at room temperature (3.8 g, 7.8 mmol).

Dowex 1-X8 resin (chloride form, 200–400 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (4 cm long, 52 mL volume, 8 meq). The resin bed was flushed extensively with 1:1 methanol/H_2O to remove contaminants. The salt was dissolved in methanol (7.5 mL) and water (2.5 mL) and loaded on the column. The column was eluted with H_2O, 1:1 methanol/H_2O, and methanol, and fractions were collected. Fractions containg ionic liquid were concentrated under reduced pressure to yield **5** (1.6 g, 6.4 mmol, 33% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD) δ 9.19 (s, 1H), 7.72 (s, 1H), 7.68 (s, 1H), 5.27 (t, J = 15.5 Hz, 2H), 3.94 (s, 3H). HRMS (ESI) m/z 215.0600 [calculated for $C_7H_8N_2F_5$ $(M - Cl)^+$ 215.0603].

3-Methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium acetate. Lead(II) acetate trihydrate (1.5 g, 3.9 mmol) and 3-Methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (0.7 g, 2.6 mmol) were dissolved together in water (10 mL). Upon standing, a brown precipitate formed, which was filtered off. The filtrate was concentrated under reduced pressure, resulting in a mixture of ionic liquid and unreacted lead(II) acetate. This mixture was treated with acetone, precipitating white $Pb(OAc)_2$, which was filtered off. The filtrate was concentrated under reduced pressure. This process of treating the residue with acetone, filtering off lead(II) acetate, and concentrating the filtrate was repeated three more times, yielding 3-Methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium acetate (432 mg, 1.6 mmol, 60% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD): δ 9.22 (s, 1H), 7.76 (s, 1H), 7.72 (s, 1H), 5.31 (t, J = 15.5 Hz, 3H), 3.98 (s, 3H), 1.87 (s, 3H).

3-Methyl-1-(2′,2′,2′-trifluoroethyl)-imidazolium chloride (6)

A round-bottom flask was placed under Ar(g) to which trifluoroacetic anhydride (30.2 g, 143.9 mmol) was added. The flask was then cooled to –15 °C using a benzyl alcohol/dry ice bath before adding 50% H_2O_2 (2.1 mL, 43.1 mmol) dropwise. 2,2,2-Trifluoroiodoethane (5.7 g, 27.2 mmol) was then added to the round-bottom flask, which was protected from light with aluminum foil and allowed to warm to room temperature. The reaction mixture was stirred for 3 d. The reaction mixture was then concentrated under reduced pressure and left under high vacuum overnight to yield a brown oil (9.2 g). This oil was dissolved with trifluoroacetic anhydride (10 mL) in a round-bottom flask under Ar(g). Trifluoromethanesulfonimide (5.3 g, 18.9 mmol) was placed in a separate round-bottom flask under Ar(g), and the trifluoroacetic anhydride solution was tranferred *via* cannula. The resulting solution was cooled to 0 °C in an ice-water bath and protected from light with aluminum foil. After stirring for 15 min, benzene (2.0 mL) was added. The reaction was allowed to warm to room temperature after 3 h and continued for another 15 h. A second portion of benzene (0.7 mL) was then added with stirring continued for an additional 5 h. The reaction mixture was then concentrated under reduced pressure and placed under high vacuum overnight to yield a brown oil (7.0 g). 1-Methylimidazole (0.7 mL, 8.8 mmol) and $NaHCO_3$ (1.0 g, 12.0 mmol) were dissolved in double-deionized water (50 mL) in a round-bottom flask. The brown oil was then dissolved in dichloromethane (50 mL) and added to the aqueous mixture in one portion to give two layers. The mixture was stirred at room temperature for 4 h. The bottom, brown layer was then separated, concentrated under reduced pressure at 70 °C, and placed under high vacuum overnight to yield a brown oil (4.6 g, 10.4 mmol). Purification was performed with flash chromatography (silica gel, 0:100–20:80 methanol/dichloromethane). Silica present in the residue was removed by dissolution in dichloromethane and filtration through a Millipore GVHP 0.22-µm membrane to yield an orange oil (1.5 g, 3.4 mmol).

Dowex 1-X8 resin (chloride form, 200–400 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (3 cm long, 22 mL volume, 16 meq). The resin bed was flushed extensively with methanol/H_2O to remove contaminants. The salt was dissolved in methanol (7.5 mL) and water (2.5 mL) and loaded on the column. The column was eluted with H_2O, 1:1 methanol/H_2O, and methanol, and fractions were collected. Fractions containing ionic liquid were concentrated under reduced pressure to yield **6** (0.80 g, 4.0 mmol, 15% yield) as an orange oil. ^{1}H NMR (400 MHz, CD_3OD) δ 9.12 (s, 1H), 7.68 (s, 1H), 7.63 (s, 1H), 5.14 (q, J = 8.6 Hz, 2H), 3.90 (s, 3H). HRMS (ESI) m/z 165.0644 [calculated for $C_6H_8N_2F_3$ $(M - Cl)^+$ 165.0635].

3-Methyl-1-pentafluorophenylmethylimidazolium chloride (7)

To a round-bottom flask containing dichloromethane (125 mL) was added 1-methylimidazole (1.5 mL, 18.8 mmol) and 2,3,4,5,6-pentafluorobenzyl bromide (4.9 g, 18.8 mmol). The solution was stirred at room temperature for 20 h. The reaction mixture was then concentrated under reduced pressure and placed under high vacuum to afford a colorless oil (6.17 g). Purification was performed by flash chromatography (silica gel, 0:100–30:70 methane/dichloromethane). Silica present in the residue was

removed by dissolution in dichloromethane and filtration through a Millipore GVHP 0.22-μm membrane to yield a colorless solid (3.5 g, 10.2 mmol).

Dowex 1-X8 resin (chloride form, 200–400 mesh) was mixed with 1:1 methanol/H_2O and poured into a glass column to create a resin bed (5 cm long, 70 mL volume, 8 meq). The resin bed was flushed extensively with methanol/H_2O to remove contaminants. The salt was dissolved in methanol (7.5 mL) and water (2.5 mL) and loaded on the column. The column was eluted with H_2O, 1:1 methanol/H_2O, and methanol, and fractions were collected. Fractions containing ionic liquid were concentrated under reduced pressure to yield **7** (2.6 g, 8.7 mmol, 46% yield) as a white solid. ^{1}H NMR (400 MHz, CD_3OD) δ 9.02 (s, 1H), 7.60 (s, 1H), 7.54 (s, 1H), 5.55 (s, 2H), 3.84 (s, 3H). HRMS (ESI) *m*/*z* 263.0594 [calculated for $C_{11}H_8N_2F_5$ $(M - Cl)^+$ 263.0603].

Cellulose solubility in 3-methyl-1-(3′,3′,4′,4’,5′,5′,6′,6′,6′-nonafluorohexyl)-imidazolium chloride (1)

Cellulose (3.5 mg, 0.5 wt % relative to ionic liquid) was added to the fluorous ionic liquid (0.7 g) at 100 °C with stirring. After heating and stirring overnight, cellulose fibers remained visible in the ionic liquid. The temperature of the ionic liquid was raised to 140 °C. After 1 h, insoluble cellulose fibers were visible.

Cellulose solubility in 1-(2′,2′,3′,3′,4′,4′,4′-heptafluorobutyl)-3-methylimidazolium chloride (2)

Cellulose (1.4 mg, 1.0 wt % relative to ionic liquid) was added to the fluorous ionic liquid (145.6 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken and examined under a light microscope to reveal cellulose fibers.

Cellulose solubility in 3-methyl-1-(3′,4′,4′,4′-tetrafluoro-3′-trifluoromethyl-butyl)-imidazolium chloride (3)

Cellulose (1.7 mg, 3.0 wt % relative to ionic liquid) was added to the fluorous ionic liquid (56.2 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken and examined under a light microscope to reveal cellulose fibers.

Cellulose solubility in 3-methyl-1-(3′,3′,4′,4′,4′-pentafluorobutyl)-imidazolium chloride (4)

Cellulose (2.6 mg, 1.1 wt % relative to ionic liquid) was added to the fluorous ionic liquid (228.0 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken and examined under a light microscope to reveal cellulose fibers.

Cellulose solubility in 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5)

Cellulose (1.1 mg, 0.6 wt % relative to ionic liquid) was added to the fluorous ionic liquid (187.8 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken of the viscous solution and examined under a light microscope. No cellulose fibers were visible.

Cellulose solubility in 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium acetate. Cellulose (2.0 mg, 0.9 wt % relative to ionic liquid) was added to the fluorous ionic liquid (216.1 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken of the viscous solution and examined under a light microscope. No cellulose fibers were visible.

Cellulose solubility in 3-methyl-1-(2′,2′,2′-trifluoroethyl)-imidazolium chloride (6)

Cellulose (1.3 mg, 1.2 wt % relative to ionic liquid) was added to the fluorous ionic liquid (105.6 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, an aliquot was taken of the viscous solution and examined under a light microscope to reveal slight traces of cellulose fibers.

Cellulose solubility in 3-methyl-1-pentafluorophenylmethylimidazolium chloride (7)

Cellulose (1.4 mg, 1.4 wt % relative to ionic liquid) was added to the fluorous ionic liquid (97.6 mg), and the resulting mixture was heated at 140 °C with stirring. After 1 h, the ionic liquid had not melted, so the temperature was increased to 160 °C. After a 1 h, the ionic liquid had turned black due to decomposition. It was then tested using DMA–LiCl (10 wt%) as a co-solvent to solubilize the ionic liquid. Four concentrations of ionic liquid were tested: 1.0 mg cellulose (1.0 wt%), 79.7 mg ionic liquid, 20.3 mg DMA–LiCl; 1.2 mg cellulose (1.1 wt %), 65.9 mg ionic liquid, 45.2 mg DMA–LiCl; 1.4 mg cellulose (1.4 wt%), 35.3 mg ionic liquid, 65.4 mg DMA–LiCl; and 1.4 mg cellulose (1.3 wt%), 22.5 mg ionic liquid, 86.3 mg DMA–LiCl. An aliquot of each was taken and examined under a light microscope to reveal all contained visible cellulose fibers.

Attempted separation of 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5) from glucose with FluoroFlash SPE cartridge

The cartridge was washed with *N,N*-dimethylformamide (5 mL) and conditioned with 4:1 methanol/H_2O (30 mL) followed by H_2O (30 mL). Glucose (27.4 mg) and 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (24.1 mg) were dissolved in water (600 mg). This mixture was then loaded and eluted with ice-cold H_2O (40 mL), followed by methanol (40 mL). Fractions were collected for each elution, concentrated under reduced pressure, and analyzed by ^{1}H NMR spectroscopy.

Glucose eluted in the third and fourth fractions of the H_2O wash, and the ionic liquid eluted in the third, fourth, and fifth fractions. The majority of the ionic liquid eluted in the second and third fractions of the methanol wash. The breakthrough of the fluorous ionic liquid in the water wash revealed that the SPE cartridge did not obtain a clean separation.

Separation of 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5) from glucose in water

Glucose (25 mg) and 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (24 mg) were dissolved in water (511 mg). A slurry of FluoroFlash silica (10 g) in water and methanol was poured into a flash chromatography column (20 cm length × 1 cm diameter), and the silica was washed extensively with water. The ionic liquid solution was loaded onto the column and eluted with water while fractions were collected. Fractions were concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. Glucose eluted in the fourth fraction, fractions five and six had no solute, and fraction seven contained the ionic liquid, demonstrating a clean separation. 3-Methyl-1-(3′,3′,4′,4′,4′-pentafluorobutyl)-imidazolium chloride (**4**) was also separated from glucose in a similar manner.

Attempted separation of 1-butyl-3-methylimidazolium chloride from glucose in water

Glucose (25 mg) and 3-methyl-1-butylimidazolium chloride (25 mg) were dissolved in water (500 mg). A slurry of FluoroFlash silica (10 g) in water and methanol was poured into a flash chromatography column (20 cm length × 1 cm diameter), and the silica was washed extensively with water. The ionic liquid solution was loaded on the column and eluted with water while fractions were collected. Fractions were concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. Glucose eluted in the third, fourth, and fifth fractions, while the ionic liquid began to elute in the fourth and fifth fractions, demonstrating that a clean separation of glucose and the ionic liquid was not possible under these conditions.

Procedure for cellulose hydrolysis in 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5)

The reaction was performed in a 4-mL glass vial heated in a temperature-controlled VWR Mini Shaker at 600 rpm. Cellulose (5.0 mg, mmol) was dissolved in 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (254.2 mg) by stirring at 90 °C for 3 h. Hydrochloric acid (2.36 mg, 0.065 mmol) and $CrCl_2$ (2.2 mg, 0.018 mmol) were added, the vial was capped, and the mixture was heated at 105 °C for 4 h. At 1-h intervals, an aliquot of the reaction mixture was removed, quenched with deionized water, subjected to centrifugation to sediment insolubles, and analyzed by HPLC.

Separation of 3-methyl-1-(2′,2′,3′,3′,3′-pentafluoropropyl)-imidazolium chloride (5) from cellulose hydrolysis products

The cellulose hydrolysis reaction mixture (120.1 mg) was dissolved in 1 mL of water. This solution was then loaded on the FluoroFlash silica (10 g) column used previously. Fractions were concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. The cellulose hydrolysis products were detected in the first fraction, and fluorous ionic liquid **5** was recovered in the third, fourth, and fifth fractions. The column was then eluted with methanol to recover additional amounts of **5**. The fluorous ionic liquid containing fractions were combined to recover 115 mg of **5**, resulting in a >95% recovery.

Computational methodology

Hybrid density functional theory as implemented in Gaussian '03[2] was employed to determine the conformational preferences of compounds **1**–**7**. Gas-phase full-geometry optimizations and frequency calculations were performed at the B3LYP/6-311+G (2d,p) level of theory[3,4] employing Berny algorithm and a tight SCF convergence criteria.

Notes and references

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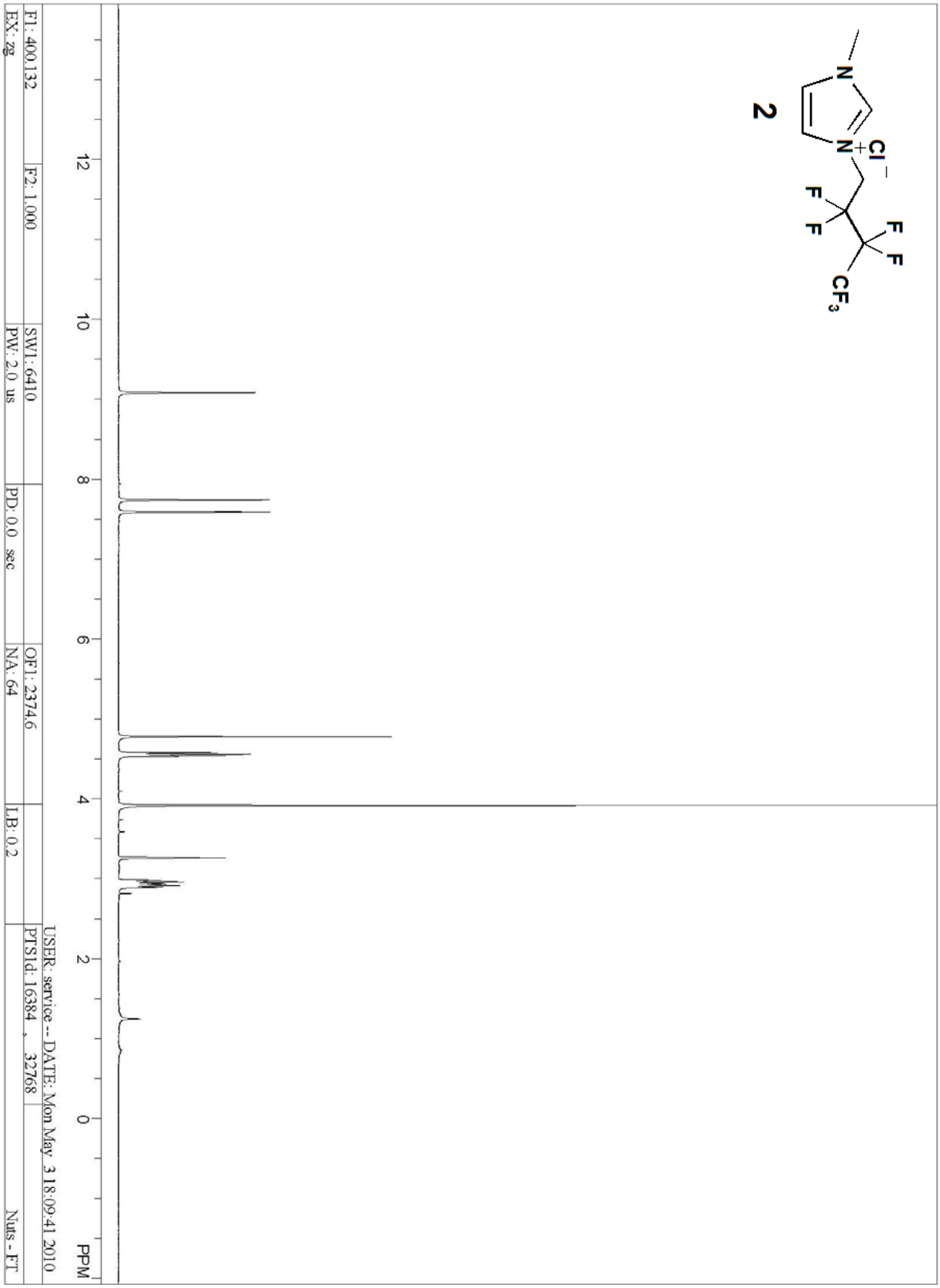
2
F1: 400.132
F2: 1.000
SW1: 6410
PW: 2.0 us
PD: 0.0 sec
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NA: 64
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USER: service -- DATE: Mon May 3 18:09:41 2010
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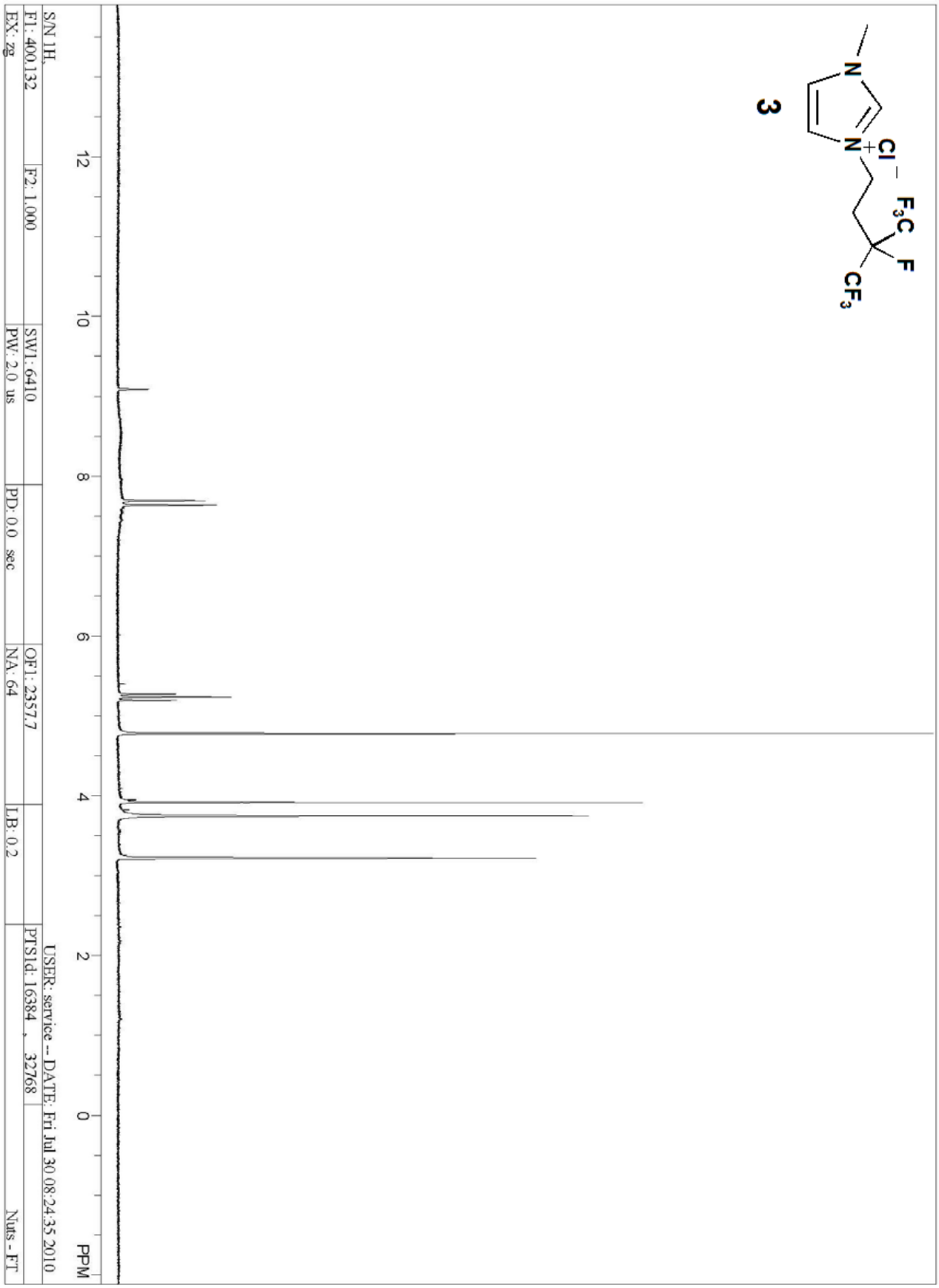
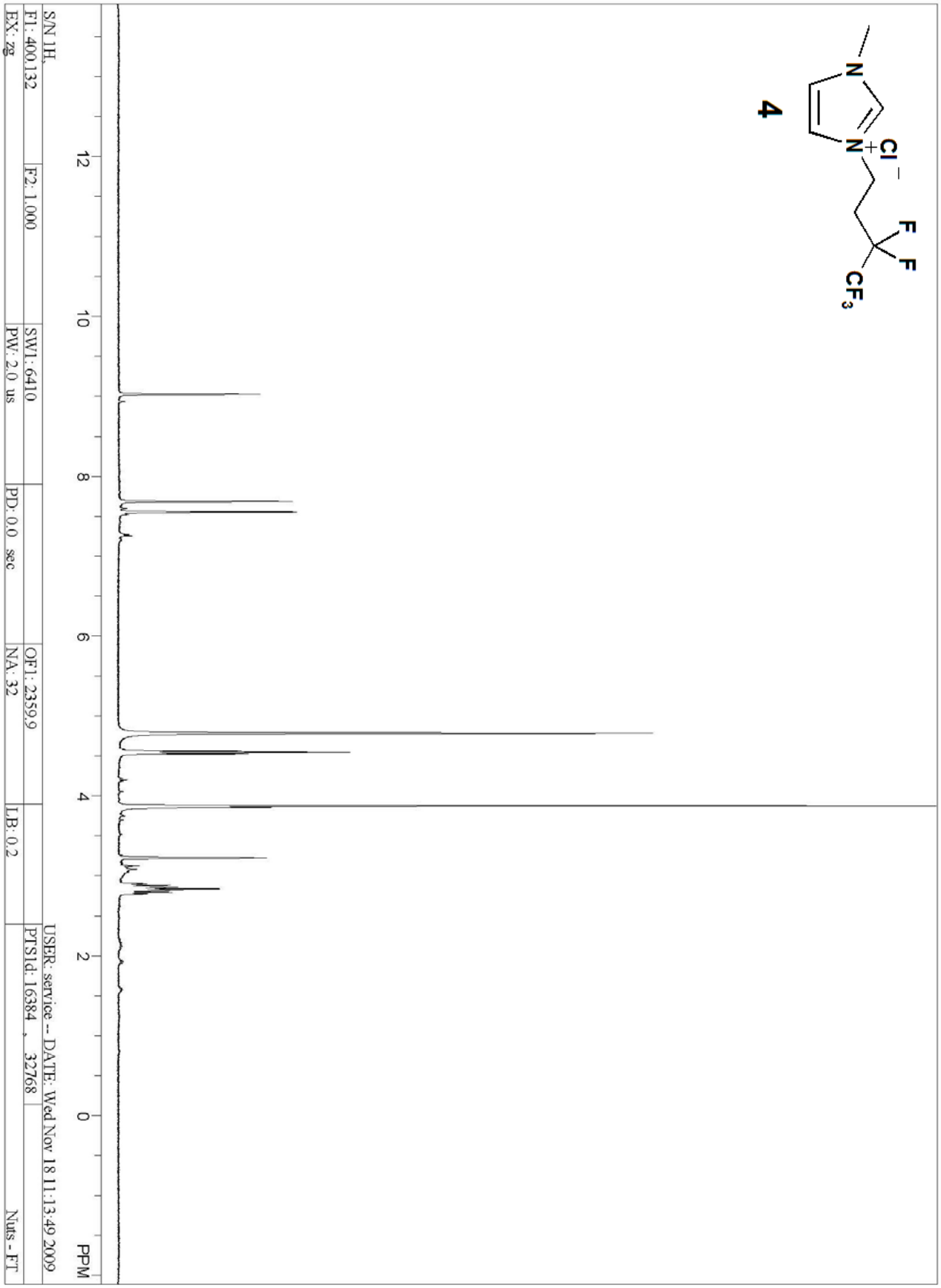
Nuts - FT
EX: zg
PPM
12
10
8
6
4
2
0




4
Cl⁻
F
F
CF3
12
10
8
6
4
2
0
PPM
S/N 1H,
F1: 400.132
F2: 1.000
SW1: 6410
OF1: 2359.9
PD: 0.0 sec
NA: 32
LB: 0.2
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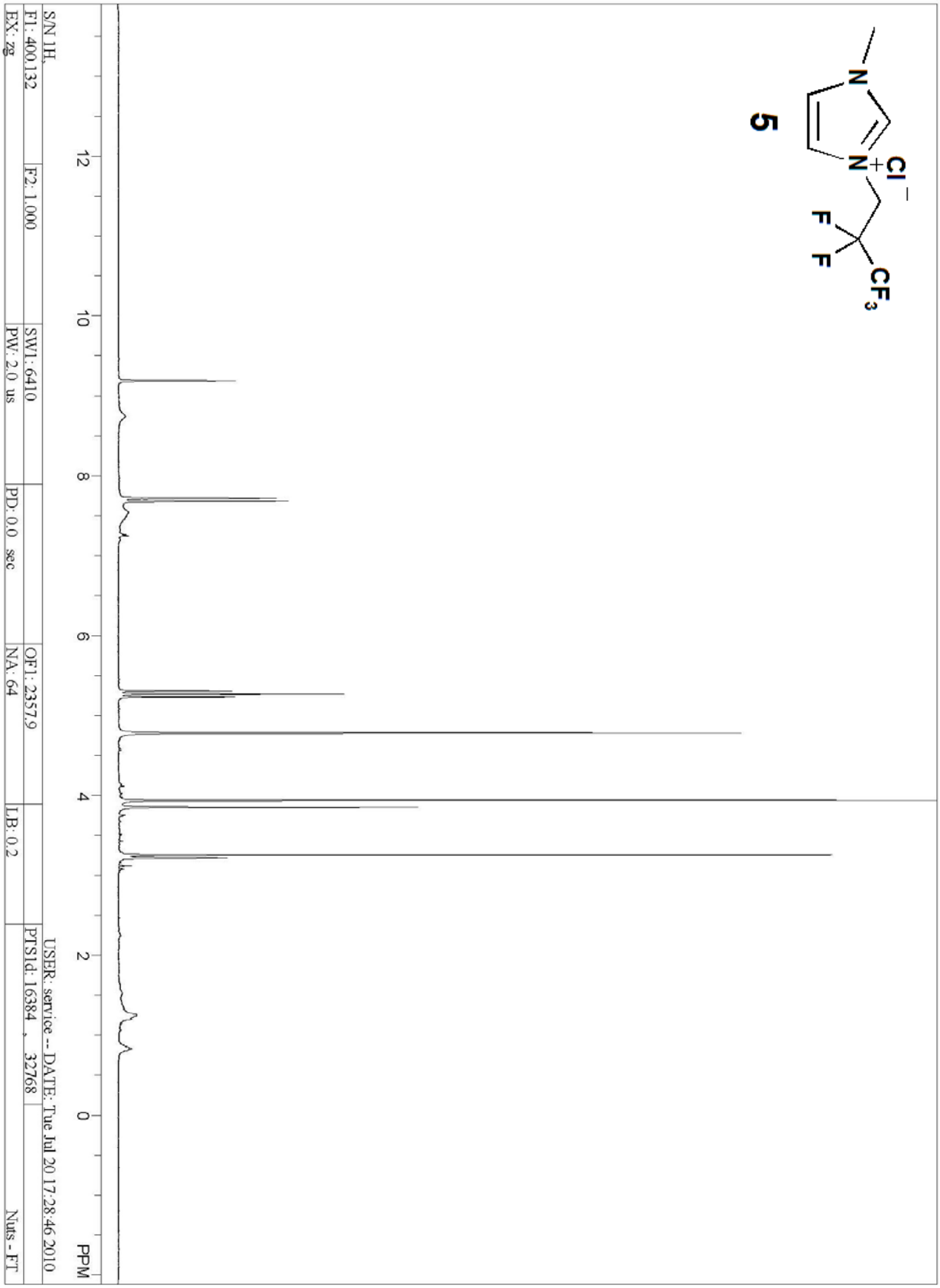
EX: zg
PW: 2.0 us
Nuts - FT


5
N
N+
Cl−
F
F
CF3
12
10
8
6
4
2
0
PPM
S/N 1H
F1: 400.132
F2: 1.000
SW1: 6410
OF1: 2357.9
EX: zg
PW: 2.0 us
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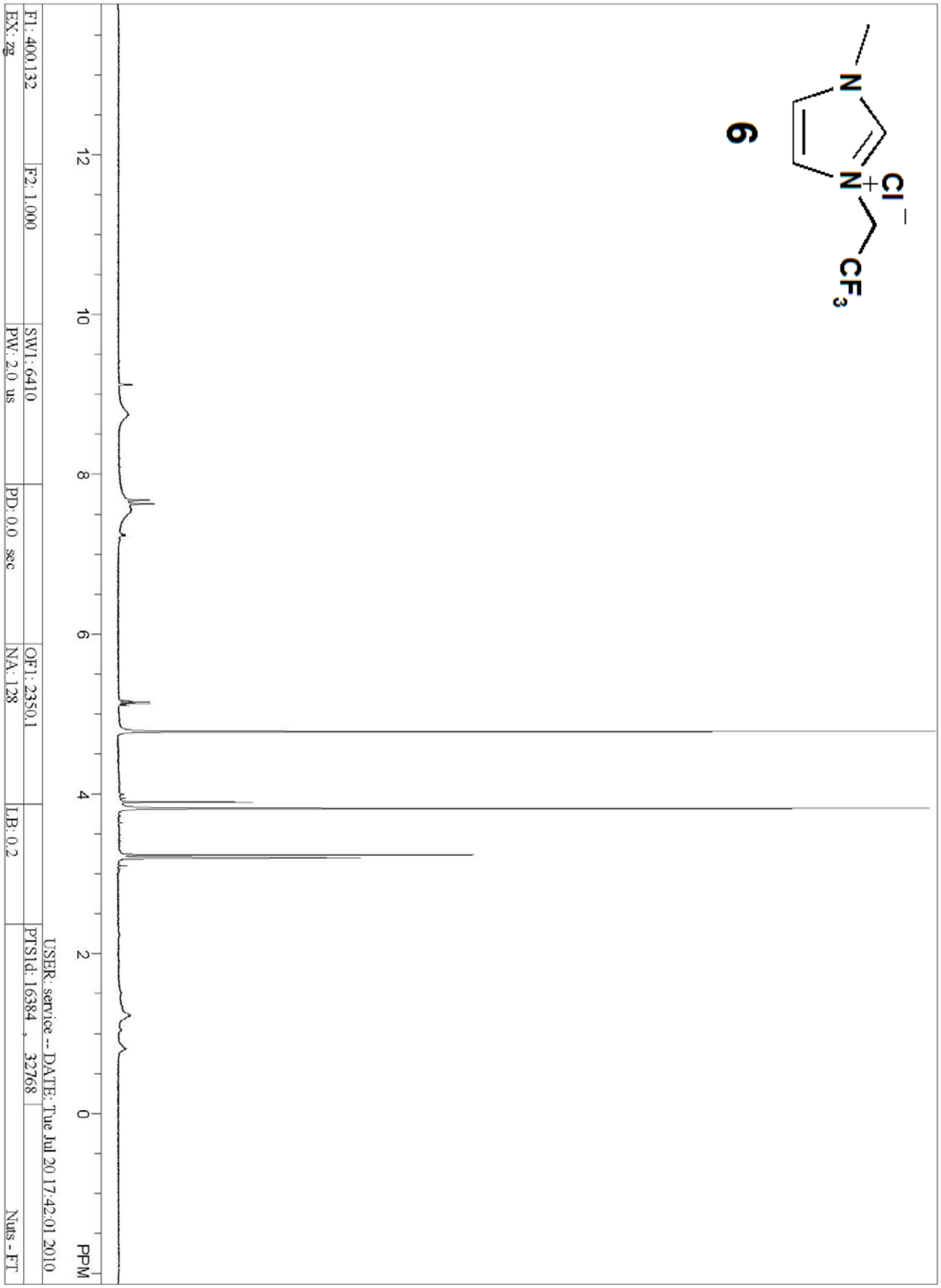
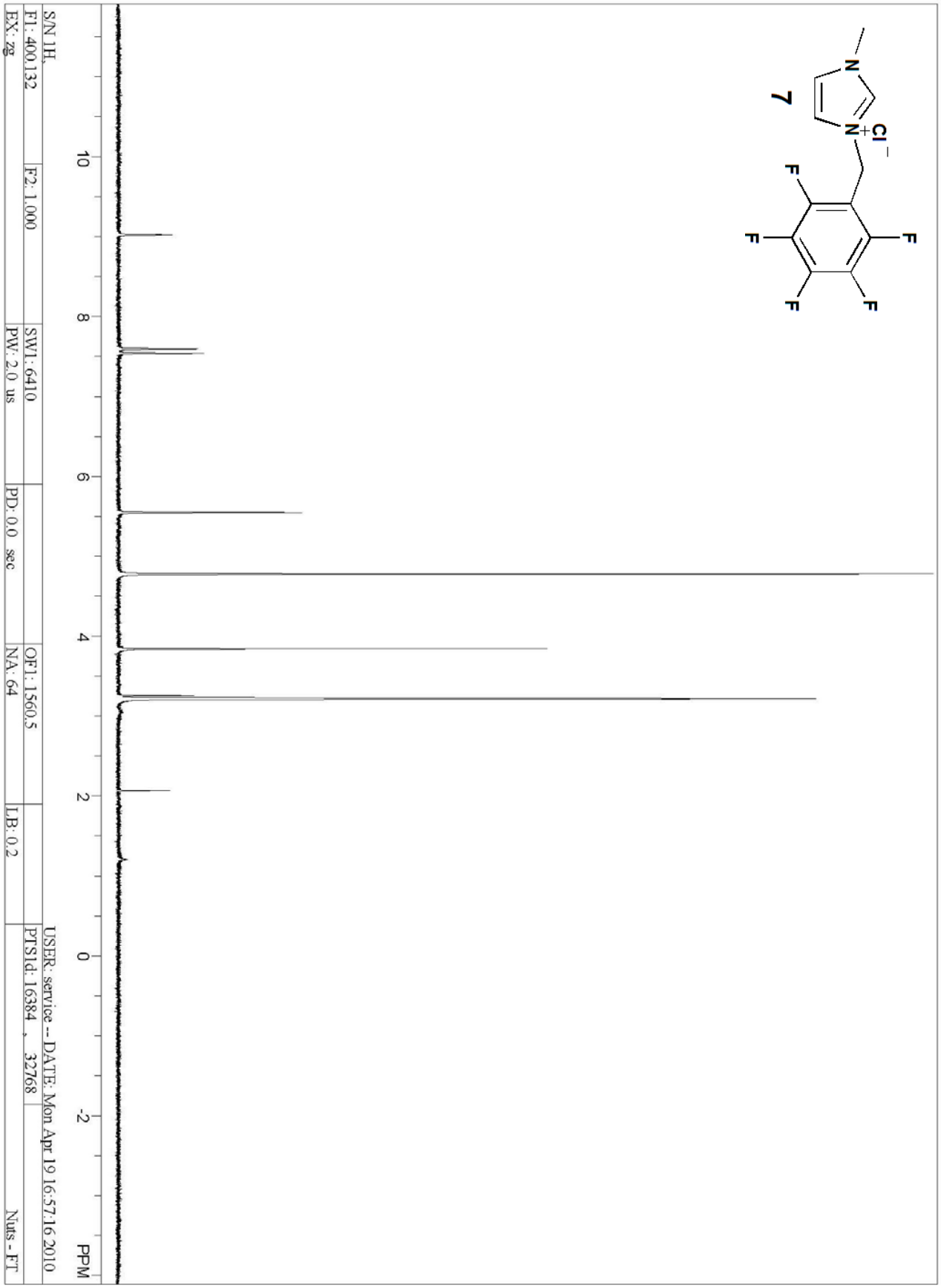
NA: 64
LB: 0.2
USER: service -- DATE: Tue Jul 20 17:28:46 2010
PTS1d: 16384 , 32768
Nuts - FT


6
N
N+
Cl−
CF3
12
10
8
6
4
2
0
PPM
F1: 400.132
F2: 1.000
SW1: 6410
OF1: 2350.1
PW: 2.0 us
PD: 0.0 sec
NA: 128
LB: 0.2
PTS1d: 16384 , 32768
EX: zg
USER: service -- DATE: Tue Jul 20 17:42:01 2010
Nuts - FT


7
N
N+
Cl−
F
F
F
F
F
10
8
6
4
2
0
-2
PPM
S/N 1H,
F1: 400.132
F2: 1.000
SW1: 6410
OF1: 1560.5
PD: 0.0 sec
NA: 64
LB: 0.2
PW: 2.0 us
EX: zg
USER: service -- DATE: Mon Apr 19 16:57:16 2010
PTS1d: 16384 , 32768
Nuts - FT