Contents

1. Experimental

1.1 General Requirements

Experimental conditions: All experiments with water and/or oxygen sensitive compounds were carried out in heat-dried glassware using standard high vacuum (up to $1 \cdot 10^{-3}$ mbar) and *Schlenk* techniques, unless otherwise noted.

Storage, weighing and sample preparation for analytical purposes of water and/or oxygen sensitive compounds as well as ruthenium nanoparticle synthesis were carried out using glove box technique (glove box type: MB 150B-G-II by M-BRAUN).

All commercial chemicals and solvents were purchased form SIGMA-ALDRICH, MERCK or ACROS and used as received or purified by standard methods when needed.[1]

1.2 Analytical Methods

Nuclear magnetic resonance spectroscopy was performed at 293.5K using an Oxford Mercury AS 400 spectrometer or an Oxford Mercury AS 200 spectrometer by VARIAN. All measurements, if not otherwise indicated, were proton broad band decoupled. The chemical shift δ is referenced relative to the remaining signal of the deuterated solvent for ^{1}H, to TMS for ^{13}C spectra and to trifluoromethane (δ = 0 ppm) for ^{19}F spectra respectively. All chemical shifts are given in *parts per million* (ppm).

When possible, the multiplicity of each proton spectrum was assigned using the following abbreviations: s: singlet, d: doublet, t: triplet, q: quartet quint: quintet, sext: sextet, sept: septet, m: multiplet, br: broad signal and mc: multiplet, centered. Possible coupling between nuclei *A* and *A'* via *n* bonds is referenced by the coupling constant $^{n}J_{AA}$ = x Hz. The assignment for carbon spectra is noted as: p: primary, s: secondary, t: tertiary and q: quaternary. The atom numbering does not follow the IUPAC nomenclature.

Single Crystal X-Ray Diffractometry (XRD) was performed on a D8 Ventrue by BRUKER an conducted by *Mu-Chieh Chang* from research group of *Otten.* Structure refinement was accomplished *Mu-Chieh Chang* and *Dr. Edwin Otten* by Suitable crystals of (**I2**) and (**IL-H^{+}1**) were mounted on a cryo-loop under glove box conditions and transferred, using inert-atmosphere handling techniques. Intensity data were corrected for Lorentz and polarisation effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS).[3] The structures were solved by direct methods using the program SHELXS.[4] The hydrogen atoms were generated by geometrical considerations and constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure refinement was performed with the program package SHELXL.[4] Crystal data and details on data collection and refinement are presented in the Section 5 of this SI.

Generally, if *yields* are shown for a given conversion under catalytic conditions, these relate to calibrated products using the mentioned analytic system, and if not otherwise noted. Octadecane (IS 1, GC) or 4-ethoxyphenol (IS 2, HPLC) were used as internal standards (IS). Also, if extraction was performed, the listed yields for guaiacol (**3**) and 2-phenylacetaldehyde (**2**) were corrected for the extraction efficiency, which was previously determined through extraction experiments.

Gas Chromatography with Flame Ionization Detector (GC-FID) was performed on a GC-system by AGILENT using the 6890 series and a 19091J-433 HP5 column by AGILENT with a 0.25 μm film, a length of 30 m and 0.25 mm in diameter. The phase composition is 5% phenylpolysiloxan and 95% methylpolysiloxane (non-polar). Nitrogen was used as a carrier gas. The inlet temperature was 250 °C with an injection volume of 1 μL, a split ratio of 50:1 and an N_2 flow of 1.0 $^{mL}/_{s}$ or otherwise indicated. The used temperature program had a starting temperature of 60 °C held for 5 min, followed by a ramp of 10 $^{°C}/_{min}$ for 20 min, ending at 260 °C held for 5 min. Signal detection was carried out on the integrated FID of the AGILENT series 6890N GC-system via flame ionization using H_2 as a carrier gas.

Gas Chromatography-Mass Spectrometry (GC-MS) was performed on a GC-system by AGILENT using the 6890 series and 19091S-933 HP1 column by AGILENT with a 0.25 μm film, a length of 30 m and 0.25 mm in diameter. The phase composition is methylpolysiloxane (non-polar). Nitrogen was used as a carrier gas. The inlet temperature was 250 °C with an injection volume of 1 μL, a split ratio of 50:1 and an N_2 flow of 1.0 $^{mL}/_{s}$ (or otherwise indicated). The used temperature program had a starting temperature of 60 °C held for 5 min, followed by a ramp of 10 $^{°C}/_{min}$ for 20 min, ending at 260 °C held for 5 min. Mass detection was carried out on an Agilent 5973 Network Mass Selective Detector by AGILENT. Ionization was achieved by electron impact ionization (EI) with an ionization potential of 70 eV.

Gas Chromatography-Mass Spectrometry with Flame Ionization Detector (GC-MS/FID) was performed on a GC-system by AGILENT using the 5890 series II plus with a with a QUADRUPOLE HEWLETT PACKARD 5972 MSD and a FID System. A RTX-1701 capillary column by RESTEK with a 0.25 μm film, a length of 60 m and 0.25 mm in diameter was used as stationary phase The phase composition is crossbonded 14% cyanopropylphenyl, 86% dimethylpolysiloxane (mid-polarity). Helium was used as a carrier gas. The inlet temperature was 250 °C with an injection volume of 1 μl, a split ratio of 1:1 and a He flow of 2.0 $^{mL}/_{s}$. The used temperature program had a starting temperature of 40 °C , a ramp of 10 $^{°C}/_{min}$ and a final temperature of 250 °C. Mass detection was carried out on an Agilent 597 Network Mass Selective Detector by AGILENT. Ionization was achieved by electron impact ionization (EI) with an ionization potential of 70 eV.

High Performance Liquid Chromatography (HPLC) was performed on a Prominence HPLC-system by SHIMADZU, a SIL-HTA auto sampler by SHIMADZU and a ZORBAX Eclipse XDB-C18 reversed phase column by AGILENT with a particle size of 5 μm, a length of 150 mm and 4.6 mm in diameter. Acetonitrile and water with 0.1 % TFA were used as eluents with a flow rate of 1.0 $^{mL}/_{min}$. Chromatography was performed at 35 °C with a gradient eluent flow staring at a water concentration of 95% for 5 min, going to a water concentration of 10% within 25 min and holding this concentration for 15 min. The injection volume varied from 3 μL to 15 μL, depending on sample concentration. Signal detection was conducted on a photodiode array detector SPD-M10A by SHIMADZU using a deuterium lamp for UV and a tungsten lamp for VIS light radiation. If performed, fraction collection was achieved using the FRC-10A by SHIMADZU.

Column Chromatography was conducted using silica gel SiliaFlash® by SILICYLE with a particle size of 40-63 μm (230-400 mesh) as stationary phase.

Analytical thin-layer chromatography (TLC) was performed with 0.2 mm coated commercial silica gel plates (MERCK, TLC Silica gel 60, fluorescence indicator F_{254}).The UV light source was a "Utraviolettstrahler" by BENDA.

Gel Permeation Chromatography (GPC) was performed on a Hewlett Packard 1100 system equipped with three PL-gel 3 lm MIXED-E columns in series as THF as a solvent. The columns were operated at 42 °C with a flow-rate of 1 mL/min. Detection was accomplished at 35 °C using a GBC LC 1240 RI detector. The apparent molecular weights and dispersities were determined using polystyrene standards and WinGPC software.

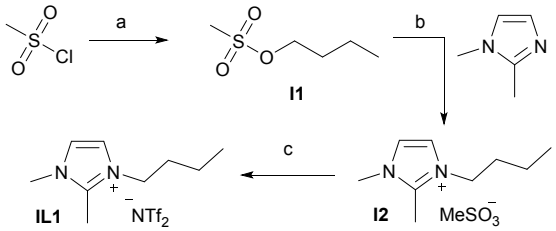
High Resolution Mass Spectrometry (HR-MS) was performed by *Theodora Tiemersma-Wegman* from the Stratingh Institute of Chemistry (Rijksuniversiteit Groningen) using an Orbitrap XL System by THERMO FISHER SCIENTIFIC and positive atmospheric-pressure chemical ionisation (+APCI) as ionisation method.

2. Synthesis Section

2.1 Synthesis of Ionic Liquids

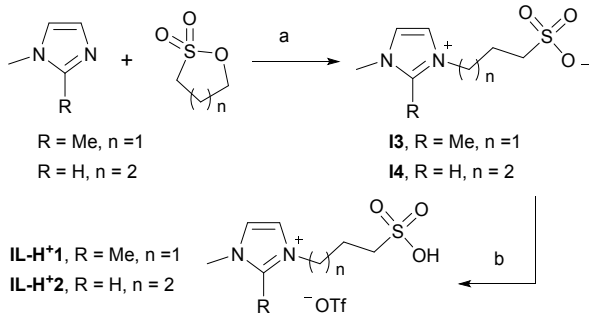
2.1.1 Overview

The ionic liquid, 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imidate ([BM_2Im][NTf_2]) **IL1**, was synthesized in high yield according to a reported procedure for similar ionic liquids (Scheme S1).[5-7] Crystals suitable for single crystal X-ray diffraction were obtained of **I2** (SI section 5).



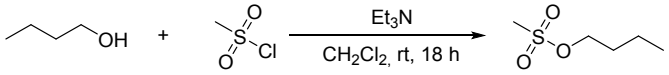
Scheme S1. Synthesis of **IL1**; Conditions: a) 1 eq. 1-butanol, Et_3N/DCM, 20 °C, 18 h (93%, **I1**)[5,7]; b) 1 eq. 1,2-dimethylimidazole, rt, 3 days (92%, **I2**)[5]; c) 1 eq. Li[NTf_2], H_2O, rt, 30 min (98%, **IL1**).[6]

Brønsted-acidic ionic liquid **IL-H$^+$2** was synthesized according to an excellent high-yielding literature procedure (Scheme S2).[8-11] Accordingly, **IL-H$^+$1** was synthesized using a similar procedures and was obtained in excellent yield. Crystals suitable for single crystal X-ray diffraction were obtained, confirming the annotated structure (SI section 5).



Scheme S2. Synthesis of **IL-H$^+$1** and **IL-H$^+$2**; conditions: a) For **I3**, 90 °C, 2 hours (97%); For **I4**, 60 °C, 2 hours (97%)[8,9]; b) For **IL-H$^+$1**, 1 eq HOTf, 80 °C, 18 hours (97%); For **IL-H$^+$2**, 1 eq HOTf, 50 °C, 18 hours (99%).[8,11]

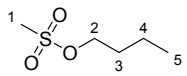
2.1.2 Synthesis of Butyl Methanesulfonate (I1)



I1

The reactions was performed under inert atmosphere. Under vigorous stirring, 77.7 mL (115.0 g, 1.00 mol, 1.0 eq) methanesulfonyl chloride was added drop wise to a solution of 95 mL (77.0 g, 1.03 mol 1.0 eq) butanol and 145 mL Et_3N in 800 mL DCM, within 45 min. During this time, the temperature was kept at 20 °C using a water bath. After complete addition, the reaction mixture was stirred at rt. overnight, followed by addition of 200 mL demin. water. The phases were separated and the aq. phase was extracted 3x with 150 mL DCM. The combined org. phases were washed once with 200 mL water, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The obtained pale yellow, clear oil was purified by vacuum distillation at an oil bath temperature of 125 °C, a head temperature of 97 °C and a pressure of 15 mbar.

Yield: 141.2 g (0.93 mol, 93%)

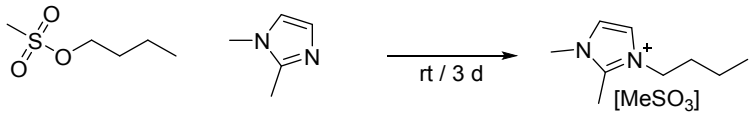


^{1}H-NMR: (400 MHz, $CDCl_3$) δ [ppm] = 4.22 (t, $^3J_{HH}$= 6.5 Hz, 2H, *H*2), 2.99 (s, 3H, *H*1), 1.78 – 1.66 (m, 2H, *H*3), 1.50 – 1.35 (m, 2H, *H*4), 0.94 (t, J = 7.4 Hz, 3H, *H5*)

^{13}C-NMR: (50 MHz, $CDCl_3$) δ [ppm] = 70.0 (s, *C2*), 37.4 (t, *C*1), 31.13 (s, *C*3), 18.73 (s, *C*4), 13.52 (t, *C*5).

Analytical data corresponded to literature data.

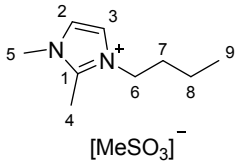
2.1.3 Synthesis of 1-Butyl-2,3-dimethylimidazolium Methanesulfonate [BM_2Im][$MeSO_3$] (I2)



I1 **I2**

The reactions was performed under inert atmosphere. 50.0 g (520 mmol, 1.0 eq) 1,2-dimethylimidazole was dissolved in 79.2 g (520 mmol, 1.0 eq) butyl methanesulfonate (**I1**) and the mixture was kept at rt for 3 d without stirring. The resulting pale yellow solid was recrystallized twice from 1000 mL acetone to yield the desired product as colorless crystals. The solvent was removed by decantation, the crystals were rinsed 3x with 50 mL cold acetone and dried under high vacuum.

Yield: 119.4 g (206 mmol, 92%)

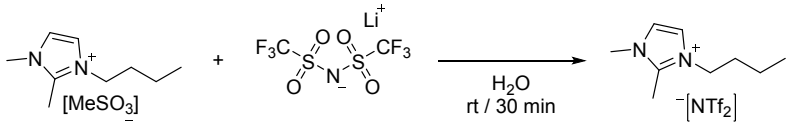


^{1}H- NMR: (200 MHz, D_2O) δ [ppm] = 7.33 (d, $^3J_{HH}$ = 5.9 Hz, 2H, *H*2, *H*3), 4.11 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *H*6), 3.77 (s, 3H, *H*5), 2.82 (s, 3H, $H_{Me\text{-}anion}$), 2.59 (s, 3H, *H*4), 1.83(quint, $^3J_{HH}$ = 7.3 Hz, 2H, *H*7), 1.34 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, *H*8), 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 3H, *H*9).

^{13}C-NMR: (50 MHz, D_2O) δ [ppm] = 121.9 (p) and 120.6 (p) *C*2 and *C*3, 47.8 (s, *C*6), 38.4 (t, $C_{Me\text{-}anion}$), 34.4 (t, *C*5), 30.9 (s, *C*7), 18.79 (s, *C*8), 12.65 (t, *C*9), 8.65 (t, *C*4), *C*1 was not observed.

Analytical data corresponded to literature data.

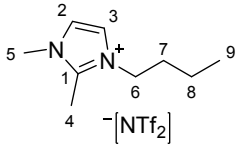
2.1.4 Synthesis of 1-Butyl-2,3-dimethylimidazolium Bis(trifluoromethanesulfoylnimide) [BM_2Im][NTf_2] (IL1)



I2 **IL1**

The reactions was performed under inert atmosphere. 19.8 g (79.7 mmol, 1.0 eq) [BM_2Im][$MeSO_3$] (**I2**) was dissolved in 50 mL demin. water and a solution of 23.0 g (80.1 mmol, 1.0 eq) Li[NTf_2] in 50 mL demin. water was added. The immediate formation of two phases was observed. The mixture was stirred vigorously for 30 min followed by addition of 100 mL DCM. The phases were separated and the aq. phase was extracted 2x with 50 mL DCM. The combined org. fractions were washed 2x with 50 mL demin. water and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product, obtained as colorless oily liquid, was dried under high vacuum.

Yield: 34.0 g (78.4 mmol, 98%)



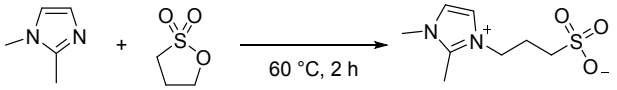
^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm] 7.18 (m, 2H, *H*2, *H*3), 4.03 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *H*6), 3.78 (s, 3H, *H*5), 2.59 (s, 3H, *H*4), 1.77 (quint, $^3J_{HH}$ = 7.6 Hz, 2H, *H*7), 1.37 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, *H*8), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H, *H*9).

^{13}C-NMR: (101 MHz, $CDCl_3$) δ [ppm] = 143.8 (q, *C*1), 122.6 (p) and 120.9 (p) *C*2 and *C*3, 119.9 (q, quartet, $^1J_{CF}$ = 321 Hz, C_{anion}), 48.7 (s, *C*6), 35.4 (t, *C*5), 31.6 (s, *C*7), 19.6 (s, *C*8), 13.5 (t, *C*9), 9.7 (t, *C*4).

^{19}F-NMR: (376 MHz, $CDCl_3$) δ [ppm] = -79.1 (s).

Analytical data corresponded to literature data.

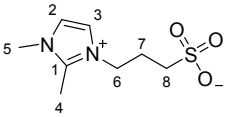
2.1.5 Synthesis of 1-Propanesulfonate-2,3-dimethylimidazolium PSO_3M_2Im (I3)



I3

The reactions was performed under inert atmosphere. A round bottom flask was charged with 8.90 g (92.6 mmol, 1.0 eq) 1,2-dimethylimidazol and 10.9 g (89.2 mmol, 1.0 eq) 1,3-propane sultone was added at once. An immediate strong exothermic reaction was observed resulting in the precipitation of a white solid. No additional cooling was applied. After 10 min. the reaction mixture had solidified. The obtained white product was washed with 3x 50 mL toluene, with 3x 50 mL Et_2O and dried under high vacuum.

Yield: 19.0 g (87.0 mmol, 97%)

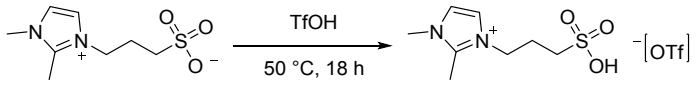


^{1}H NMR: (400 MHz, D_2O) [ppm] = δ 7.38 (d, $^3J_{HH}$ = 2.1 Hz, 1H, *H*3), 7.31 (d, $^3J_{HH}$ = 2.1 Hz, 1H, *H*2) 4.26 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *H*6), 3.75 (s, 3H, *H5*), 2.92 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *H*8), 2.58 (s, 3H, *H*4), 2.23 (quint, *J* = 7.4 Hz, 2H, *H*7).

^{13}C-NMR: (101 MHz, D_2O) δ [ppm] = 144.4 (q, *C*1), 122.2 (p) and 120.5 (p) *C*2 and *C*3, 47.1 (s, *C*6), 46.2 (s, *C*8), 34.4 (t, *C*5), 24.5 (s, *C*7), 8.7 (t, *C*4).

Analytical data corresponded to literature data.

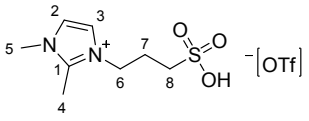
2.1.6 Synthesis of 1-Propanesulfonic acid-2,3-dimethylimidazolium Triflate [PSO_3HM_2Im][OTf] (IL-H^+1)



I3 **IL-H^+1**

A heat dried *Schlenk* flask was charged with 4.93 g (22.6 mmol, 1.0 eq) dried PSO_3M_2Im (**I3**). 2.0 mL (3.39 g, 22.6 mmol, 1.0 eq) TfOH were added via syringe resulting in vapor formation. The reaction mixture was stirred for 18 h at 50 °C forming a pale rosé oil. After cooling, the obtained product was washed under air with 3x 50 mL toluene, with 3x 50 mL Et_2O and dried under high vacuum.

Yield: 8.25 g (22.4 mmol, 99%)



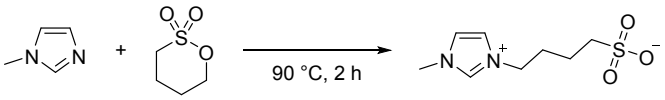
^{1}H NMR: (400 MHz, D_2O) δ [ppm] = 7.30 (d, $^3J_{HH}$ = 1.7 Hz, 1H, *H*3), 7.24 (d, $^3J_{HH}$ = 1.8 Hz, 1H, *H*2), 4.19 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *H*6), 3.68 (s, 3H, *H*5), 2.85 (t, $^3J_{HH}$ = 7.4 Hz, 2H, *H*8), 2.51 (s, 3H, *H*4), 2.16 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, *H*7).

^{13}C-NMR: (50 MHz, D_2O) δ [ppm] = 146.9 (q, *C*1), 124.8 (p) and 123.0 (p) *C*2 and *C*3, 122.1 (q, quartet, $^1J_{CF}$ = 318 Hz, C_{anion}), 49.7 (s, *C*6), 48.7 (s, *C*8), 37.0 (t, *C*5), 27.0 (s, *C*7), 11.2 (t *C*4).

^{19}F-NMR: (376 MHz, $CDCl_3$) δ [ppm] = -79.0 (s).

Analytical data corresponded to literature data.

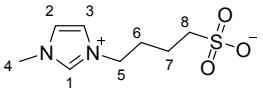
2.1.7 Synthesis of 1-Butanesulfonate-3-methylimidazolium BSO_3MIm (I4)



I4

The reactions was performed under atmosphere. A round bottom flask was charged with 3.11 g (37.9 mmol, 1.0 eq) 1-methylimidazol under nitrogen atmosphere. 5.22 g (38.3 mmol, 1.0 eq) 1,4-butane sultone was added via syringe. The reaction mixture was stirred and slowly heated to 90 °C, till the precipitation of a white solid was observed. After 2 h at this temperature the reaction mixture had solidified. The obtained white product was washed under air with 3x 50 mL toluene, with 3x 50 mL Et_2O and dried under high vacuum.

Yield: 8.02 g (36.7 mmol, 97%)

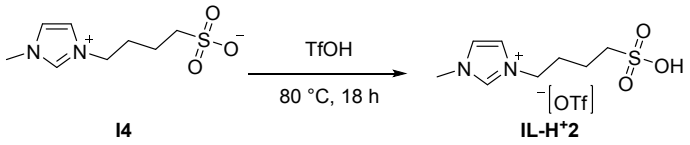


^{1}H NMR: (400 MHz, D_2O) δ [ppm] = 8.75 (s, 1H, *H*1), 7.51-7.45 (m, 2H, *H*2, *H3*), 4.26 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *H*5), 3.90 (s, 3H, *H*4), 2.96 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *H*8), 2.04 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, *H*6), 1.83 – 1.61 (m, 2H, *H*7).

^{13}C-NMR: (101 MHz, D_2O) δ [ppm] = 123.4 (p) and 122.0 (p) *C*2 and *C*3, 49.9 (s, *C*5), 48.7 (s, *C*8), 35.5 (t, *C*4), 27.9 (s, *C*6), 20.8 (s, *C*7), *C*1 was not observed.

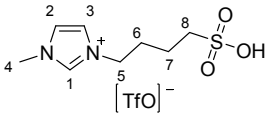
Analytical data corresponded to literature data.

2.1.8 Synthesis of 3-Methyl-1-butanesulfonic acid imidazolium Triflate [BSO_3HMIm][OTf] (IL-H^+2)



A heat dried *Schlenk* flask was charged with 8.02 g (36.7 mmol, 1.0 eq) high vacuum dried BSO_3MIm (**I4**). 3.3 mL (5.59 g, 37.3 mmol, 1.0 eq) TfOH were added via syringe resulting in vapor formation. The reaction mixture was stirred for 18 h at 80 C forming a pale rosé oil. After cooling, the obtained product was washed under atmosphere with 3x 50 mL toluene, with 3x 50 mL Et_2O and dried under high vacuum. The product was stored under glove box conditions, slowly crystalizing to a pale rosé solid within a week.

Yield: 13.2 g (22.4 mmol, 97%)



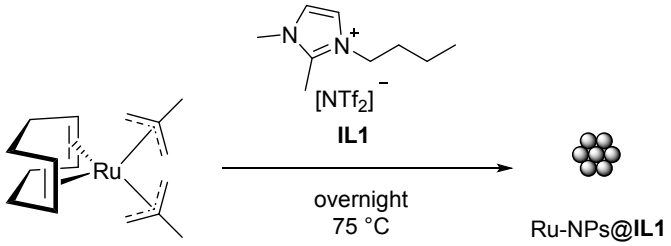
^{1}H NMR: (400 MHz, D_2O) [ppm] = δ 8.71 (s, 1H, *H*1), 7.47-7.41 (m, 2H, H*2, H3*), 7.41 (s, 1H, *H*2), 4.22 (t, *J* = 7.1 Hz, 2H, *H*5), 3.87 (s, 3H, *H*4), 2.92 (t, *J* = 7.6 Hz, 2H, *H*8), 2.00 (m, 2H, *H*6), 1.79 – 1.65 (m, 2H, *H*7).

^{13}C-NMR: (101 MHz, D_2O) δ 135.7 (p, *C*3), 123.5 (p) and 122.0 (p) *C*2 and *C*3, 119.5 (q, quartet, $^1J_{CF}$ = 318 Hz, C_{anion}), 49.9 (s, *C*5), 48.7 (s, *C*8), 35.5 (t, *C*4), 27.9 (s, *C*6), 20.7 (s, *C*7), *C*1 was not observed.

^{19}F-NMR: (376 MHz, $CDCl_3$) δ [ppm] = -78.9 (s).

Analytical data corresponded to literature data.

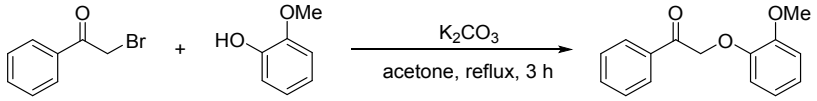
2.1.9 Synthesis of Ruthenium NP in [BM_2Im][NTf_2] (Ru-NPs@IL1)



The literature reported procedure by *Prechtl et al.* was adapted for the course of this work.[12] Under glove box conditions, a screw neck vial was loaded with 10 to 20 mg of ruthenium precursor bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II) and 1.4 to 2.8 g of ionic liquid (**IL1**) and sealed. The reaction mixture was stirred for 18 h at 75 °C to yield a brown to dark brown, yet clear liquid.

2.2 Synthesis of Model Compound (1)

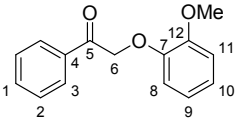
2.2.1 Synthesis of 2-(2-methoxyphenoxy)-1-phenylethanone (I5)



I5

I5 was synthesized according to a literature procedure.[13] A round bottom flask was loaded with 12.1 g (60.8 mmol, 1.0 eq) 2-bromoacetophenone 12.5 g (90.4 mmol, 1.5 eq) K_2CO_3 and 250 mL acetone. After stirring the mixture for 5 min 8.5 mL (9.60 g, 77.3 mmol, 1.3 eq) guaiacol were added, and the reaction mixture was refluxed for 3 h. The resulting orange solution was filtered over celite and the solvent was removed *in vacuo*. The resulting orange solid was recrystallized twice from ethanol. It is important to notify, that the oil bath temp. was kept at exact 55 °C for optimal crystallization, yielding the product as colorless needles. The product was dried under high vacuum.

Yield: 13.6 g (55.0 mmol, 90%)

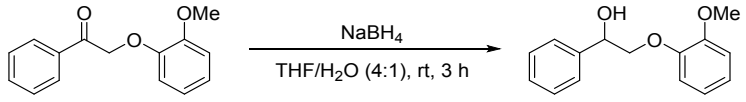


^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm] = 8.01 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *H*3), 7.61 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *H*1), 7.49 (m, *H*2), 7.03 – 6.70 (m, 4H, *H8-H11*), 5.35 (s, 2H, *H6*), 3.89 (s, 3H, H_{Me}).

^{13}C-NMR: (101 MHz, $CDCl_3$) δ [ppm] = 194.7 (q, *C*5), 149.9 (q) and 147.6 (q) (*C*7 and *C*12), 134.7 (q, *C*4), 133.9 (p, *C*1), 128.9 (p) and 128.2 (p) *C*2 and *C*3, 122.6 (p) and 120.9 (p) and 115.0 (p) and 112.3 (p) *C*8 to *C*11, 72.2 (s, *C*6), 56.2 (t, C_{OMe}).

Analytical data corresponded to literature data.

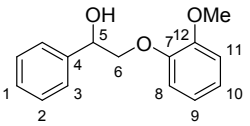
2.2.2 Synthesis of 2-(2-methoxyphenoxy)-1-phenylethanol (1)



I5 **1**

1 was synthesized according to a literature procedure.[13] 12.6 g (52.0 mmol, 1.0 eq) 2-(2-methoxyphenoxy)-1-phenylethanone (**I5**) was dissolved in 250 mL THF and 63 mL demin. water was added. After addition of 3.90 g (103 mmol, 2.0 eq) sodium borohydride within 5 min reduction was observed after 3 h monitored by TLC and NMR. Remaining $NaBH_4$ was quenched by adding sat. aq.NH_4Cl solution, till no gas formation was observed. The solution was diluted with 200 mL demin. water, followed by extraction with 3x150 mL Et_2O. The combined organic fractions were washed with brine, dried over Na_2SO_4 and the solvent was removed *in vacuo*, yielding the product as a white solid. The product was dried under high vacuum.

Yield: 12.65 g (51.8 mmol, 99.6%)

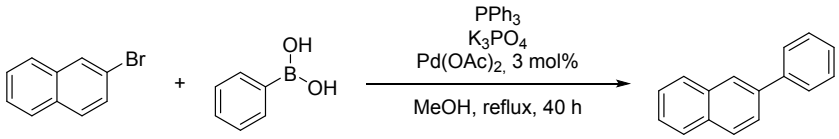


^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm] = 7.44 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *H*3), 7.38 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *H*2), 7.31 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *H*1), 7.05 – 6.86 (m, 4H, *H8-H11*), 5.11 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ =2.7 Hz, 1H, H*5*), 4.19 (dd, $^2J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, H*6*), 3.98 (t, $^2J_{HH}$ = 9.8 Hz, 1H H*6*), 2.91 (br, s, 1H, H_{OH}).

^{13}C-NMR: (101 MHz, $CDCl_3$) δ [ppm] = 150.0 (p) and 148.0 (p) *C*7 and *C*12, 139.7 (q, *C*4), 128.5 (p) and 126.4 (p) *C*2 and *C*3, 128.0 (p, *C*1), 122.5 (p) and 121.1 (p) and 115.7 (p) and 112.0 (p) *C*8 to *C*11, 76.2 (s, *C*5), 72.4 (s, *C*6), 55.9 (t, C_{OMe}).

Analytical data corresponded to literature data.

2.3 Synthesis of 2-Phenylnaphthalene (7)

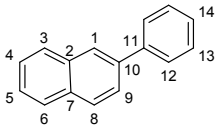


7

7 was synthesized according to a literature procedure.[14] The reaction was performed under atmosphere. A round bottom flask was loaded with 497.3 mg (2.40 mmol, 1.0 eq) 2-bromonaphthalene, 444.1 mg (3.64 mmol, 1.5 eq) phenylboronic acid, 15.0 mg (66.8 µmol, 3 mol%) palladium(II)acetate, 54.0 mg (206 µmol, 9 mol%) triphenylphosphine and 1.03 g (7.45 mmol, 2.0 eq) K_3PO_4 as well as 45 mL methanol. The reaction mixture was refluxed for 18 h and conversion was monitored by GC-MS. After incomplete conversion was observed, 100 mg (82 µmol, 0.3 eq) phenylboronic acid were added. Refluxing was maintained for 22 h and complete conversion was observed. The solvent was removed *in vacuo* from the cooled reaction mixture and 50 mL demin. water as well as 50 ml pentane were added. The mixture was stirred, till complete solubilization was observed. The phases were separated, the aq. phase was extracted with 3x 50 mL pentane, the combined organic phases were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The obtained crude white product was purified by column chromatography.

R_f: 0.47 (Pentane)

Yield: 375 mg (1.84 mmol, 77%)



^{1}H NMR: (400 MHz, $CDCl_3$) δ [ppm] = 8.05 (s, 1H, *H*1), 7.95 – 7.85 (m, 3H, *H*3, *H*6, *H*8), 7.79 – 7.70 (m, 3H, *H*9, *H*12), 7.55 – 7.45 (m, 4H, *H*4, *H*5, *H*13), 7.38 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *H*14).

^{13}C-NMR: (101 MHz, $CDCl_3$) δ [ppm] = 141.3 (q, C*11)*, 138.7 (q, C*10*), 133.8 (q, C*2*), 132.8 (q, C*7*), 129.0 (t, C*13*), 128.6 (t, C*8*), 128.3 (t, C*3*), 127.8 (t, C*6*), 127.6 (t, C*12*) 127.5 (t, C*14*), 126.4 (t, C*4*), 126.1 (t, C*5*) 125.9 (t, C*1*), 125.7 (t, C*9*).

Analytical data corresponded to literature data.

3. Catalytic Reactions

If not otherwise noted hydrogenation was performed in a Millireactor by MANONTHE MOONTECH[15] using a 2 mL GC vial or in a custom made, up-scaled replica manufactured by the mechanical department of the University of Groningen using a 4 mL glass vial as reaction vessel (Figure S1).

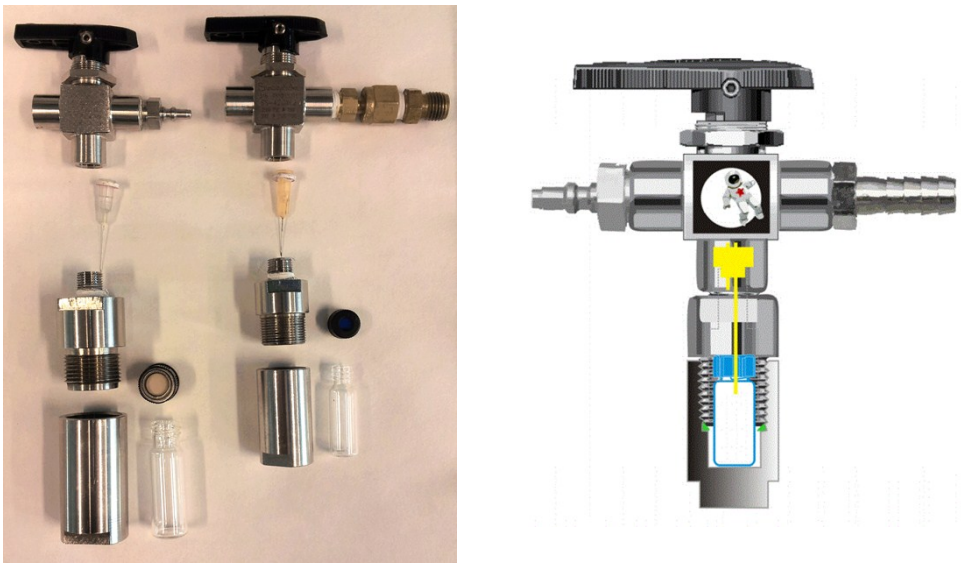
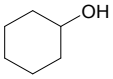
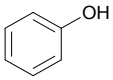
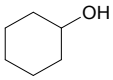


Figure S1**.** Autoclave by MANONTHEMOONTECH (2 mL, right), larger replica (4 mL left) and mechanical drawing by MANONTHEMOONTECH.[15]

3.1 Verification of the activity of Ru-NP@IL1 and IL-H$^+$1

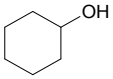
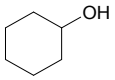
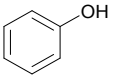
3.1.1 Overview of control reactions with Ru-NP@IL1 and IL-H$^+$1

Table S1. Hydrogenation reaction using Ru-NP@**IL1**.[a]

Substrate/conversion[b]	T (°C)	t (h)	H_2 (bar)	Product/selectivity[b]
 97%[c]	75	24	5	 100%
 99%	110	4	40	 95%
 99%	130	24	40	 100%

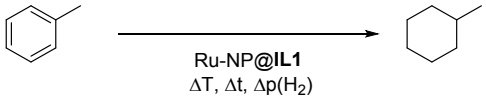
[a] Conditions: 1 mmol substrate, Ru-NP@**IL1** 1.5 mol% [Ru], 1.4 mg **IL1**, [b] GC-FID [c] 1 ml substrate, Ru-NP@**IL1** 0.3 mol% [Ru].

Table S2. Dehydration reactions using **IL-H$^+$1** and hydrogenation/dehydration reactions by a combination of Ru-NP@**IL1** and **IL-H$^+$1**.[a]

Substrate/conversion[b]	T (°C)	t (h)	Product/selectivity[b]
 88%	110	2	 95%
 19%[c]	110	4	 91%[d]
 8%[c]	130	24	 15%  85%

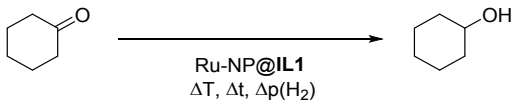
[a] Conditions: 1 mmol substrate, 10 mol% **IL-H$^+$1**, 1.4 mg **IL1** [b] GC-FID [c] Ru-NP@**IL1**, 1.5 mol% [Ru], 40 bar H_2 [d] 9% dicyclohexane,

3.1.2 Conversion of toluene



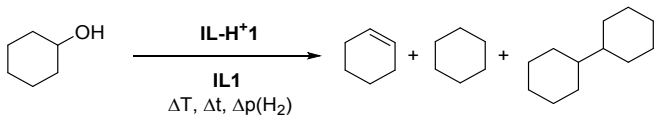
The literature reported procedure by *Prechtl et al.* was adapted for the course of this work.[16] A screw neck vial was loaded with a stirrer, Ru-NP@**IL1** and a defined amount of toluene. The vial was sealed with a septum screw cap, the septum was punctured 3x using a needle, the vial was placed in an autoclave, purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling and pressure release, the mixture was analyzed by the given method. The reaction mixture was extracted with 3x 1 mL Et_2O. The combined organic fractions were centrifuged for 3 min. at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed GC-FID and GCMS.

3.1.3 Conversion of Cyclohexanone



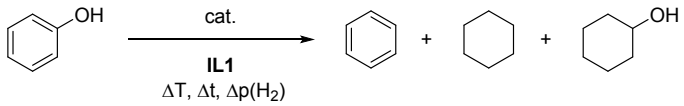
A screw neck vial was loaded with a stirrer, Ru-NP@**IL1** and a defined amount of cyclohexanone. The vial was sealed with a septum screw cap, the septum was punctured 3x using a needle, the vial was placed in an autoclave, purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling and pressure release, the reaction mixture was extracted with 3x 1 mL Et_2O. The combined organic fractions were centrifuged for 3 min. at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed GC-FID and GCMS.

3.1.4 Conversion of Cyclohexanol



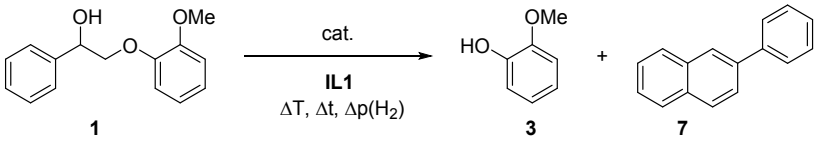
A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of cyclohexanol and defined amount of catalyst (**IL-H1**$^+$). The vial was sealed with a septum screw cap. If hydrogenation was performed, the septum was punctured 3x using a needle, the vial was placed in an autoclave, purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling (and pressure release by hydrogenation), the reaction mixture was extracted with 3x 1 ml Et_2O. The combined organic fractions were centrifuged for 3 min. at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed GC-FID and GCMS.

3.1.5 Conversion of Phenol



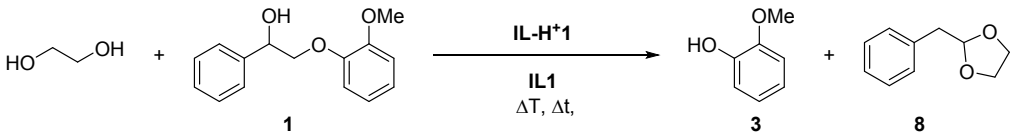
A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of phenol and defined amount of catalyst (**IL-H**$^+$ and/or Ru-NPs@**IL1**). The vial was sealed with a septum screw cap. If hydrogenation was performed, the septum was punctured 3x using a needle, the vial was placed in an autoclave, purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling (and pressure release by hydrogenation), the reaction mixture was extracted with 3x 1 mL Et_2O. The combined organic fractions were centrifuged for 3 min. at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed GC-FID and GCMS.

3.1.6 Cleavage of Lignin β-O-4 Model Compound (1)



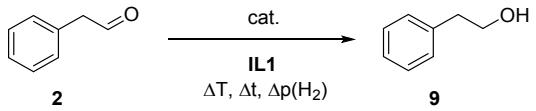
A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of model compound (**1**), a defined amount of catalyst (**IL-H**$^+$) and if used, a defined amount of additive. The vial was sealed with a septum screw cap. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling, 4-ethoxyphenol was added as IS and diluted with 1 mL MeCN. A sample was taken and analyzed by HPLC in MeCN/H_2O (60:40).

3.1.7 β-O-4 Cleavage of Model Compound (1) with Acetal (8) Formation



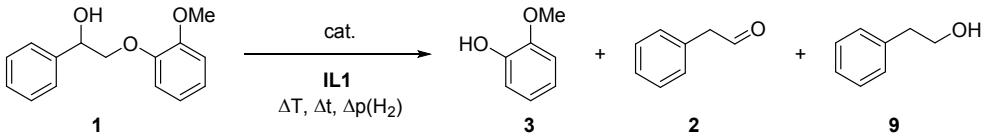
A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of model compound (**1**), a defined amount of acid (**IL-H$^+$1**) and a defined amount of ethylene glycol. The vial was sealed with a septum screw cap. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling, 4-ethoxyphenol was added as IS and diluted with 1 mL MeCN. A sample was taken and analyzed by HPLC in MeCN/H_2O (60:40).

3.1.8 Conversion of 2-Phenylacetaldehyde (2) in Ionic Liquid



A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of 2-phenylacetaldehyde (**2**) and a defined amount of catalyst (**IL-H$^+$** and/or Ru-NPs@**IL1**). The vial was sealed with a septum screw cap, the septum was punctured 3x using a needle and the vial was placed in an autoclave. The autoclave was purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling, n-octadecane was added as IS. Subsequently the reaction mixture was extracted with 3x 1 mL Et_2O. The combined organic fractions were centrifuged for 3 min at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed by GC-FID.

3.1.9 One Pot Conversion of Model Compound (1) in Ionic Liquid



A screw neck vial was loaded with a stirrer, a defined amount of **IL1**, a defined amount of model compound (**1**), a defined amount of catalyst (**IL-H$^+$** and Ru-NPs@I**L1**) and if used, a defined amount of additive. The vial was sealed with a septum screw cap, the septum was punctured 3x using a needle and the vial was placed in an autoclave. The autoclave was purged gently with 3x 5 bar H_2 and then set to the desired pressure. The reaction mixture was stirred at 1000 rpm at the desired temperature for the given time. After cooling, n-octadecane was added as IS. Subsequently the reaction mixture was extracted with 3x 1 mL Et_2O. The combined organic fractions were centrifuged for 3 min at 13400 rpm to ensure phase separation. A sample of the organic layer was analyzed by GC-FID.

4. Partition of the substrate and products in IL/dioxane biphasic mixtures

Experiments were carried out to determine the amount of 2-phenylacetaldehyde (**2**), guaiacol (**3**) and β-O-4 model compound (**1**) residing in the organic phase, when 1,4-dioxane/**IL1** mixtures are used for catalysis. These measurements were carried out using a 4 : 1 mixture of 1,4-dioxane : **IL1**. The 4 : 1 (1,4-dioxane : **IL1**) ratio was chosen because IL1 and 1,4-dioxane form a single phase at (<3 : 1) mixtures. Even when mixing 4 : 1 of 1,4-dioxane : **IL1** (1 mL : 250 µL), most of the 1,4-dioxane is absorbed into the **IL1** layer leaving a 1,4-dioxane layer of 250-300 µL.

In the following experiment, compounds **1-3** were added to a 1.25 mL 4 : 1 mixture of 1,4-dioxane : **IL1** (1 mL : 250 µL). The mixtures were vortexed for 5 minutes, centrifuged and separated. The concentrations of **1**-**3** in the 250-300 µL 1,4-dioxane layer were determined by GC(FID) against n-octadecane as internal standard (Table S3).

Table S3. Partition of compounds **1**-**3** in a 4 : 1 mixture of 1,4-dioxane : **IL1**

Entry	Substrate	$Conc_{initial}$ (µmol)	$Conc_{1,4\text{-dioxane}}$ (µmol)[a]	%[b]	Vol. Corr. %[c]
1	**1**	12.5	5.8 ±1.5	46 ±12	77 ±20
2	**2**	15	7.8 ±2.2	52 ±15	81 ±23
3	**3**	15	3.6 ±0.9	24 ±6	56 ±14

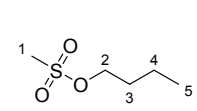
[a] Amount of **1**-**3** measured in the resulted 1,4-dioxane layer of 250-300 µL as determined by GC(FID) using n-octadecane as internal standard.

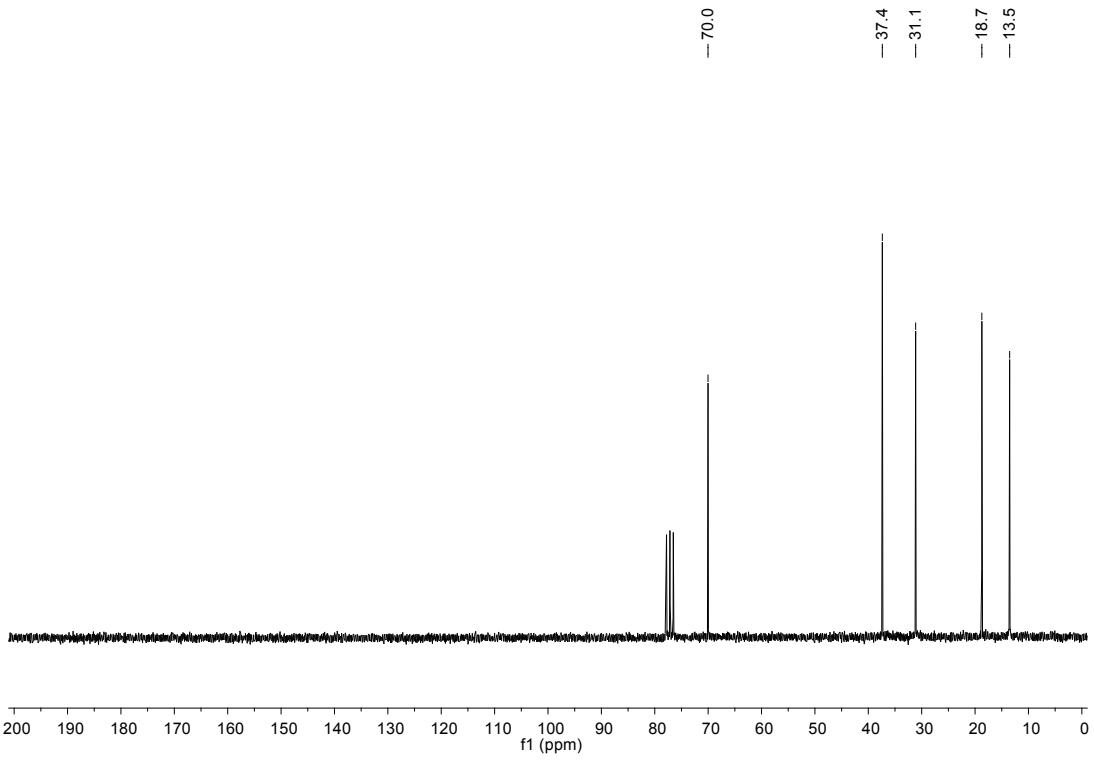
[b] Amount of **1**-**3** measured in the resulted 1,4-dioxane layer of 250-300 µL as a percentage of the total amount of **1**-**3** added to the solvent mixture.

[c] Corrected for the 1 : 4 (1,4-dioxane : **IL1)** volume ratio between these layers assuming a volume of the 1,4-dioxane layer of 250 µL.

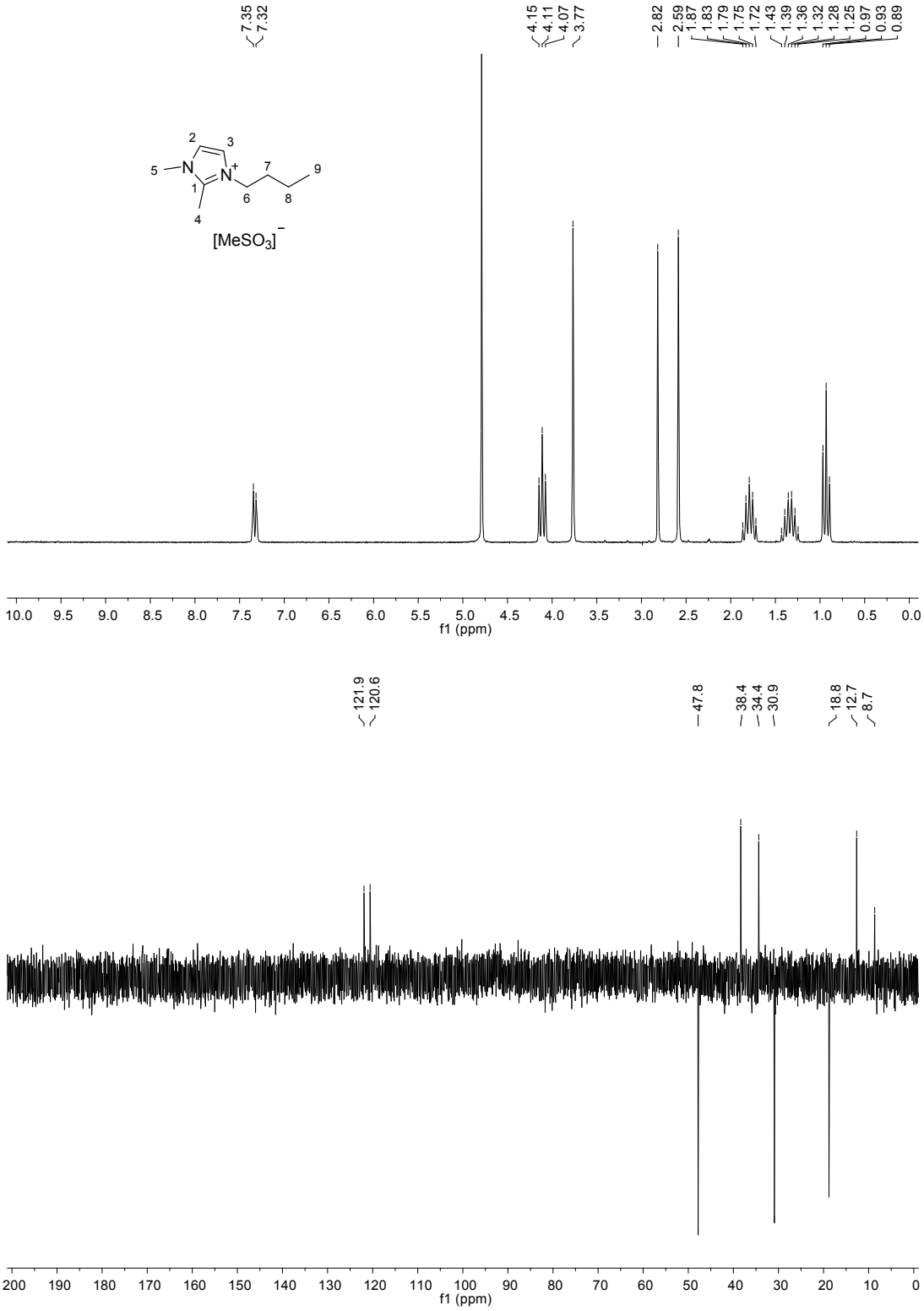
5. Spectra

5.1.1 Butyl Methanesulfonate (I1)

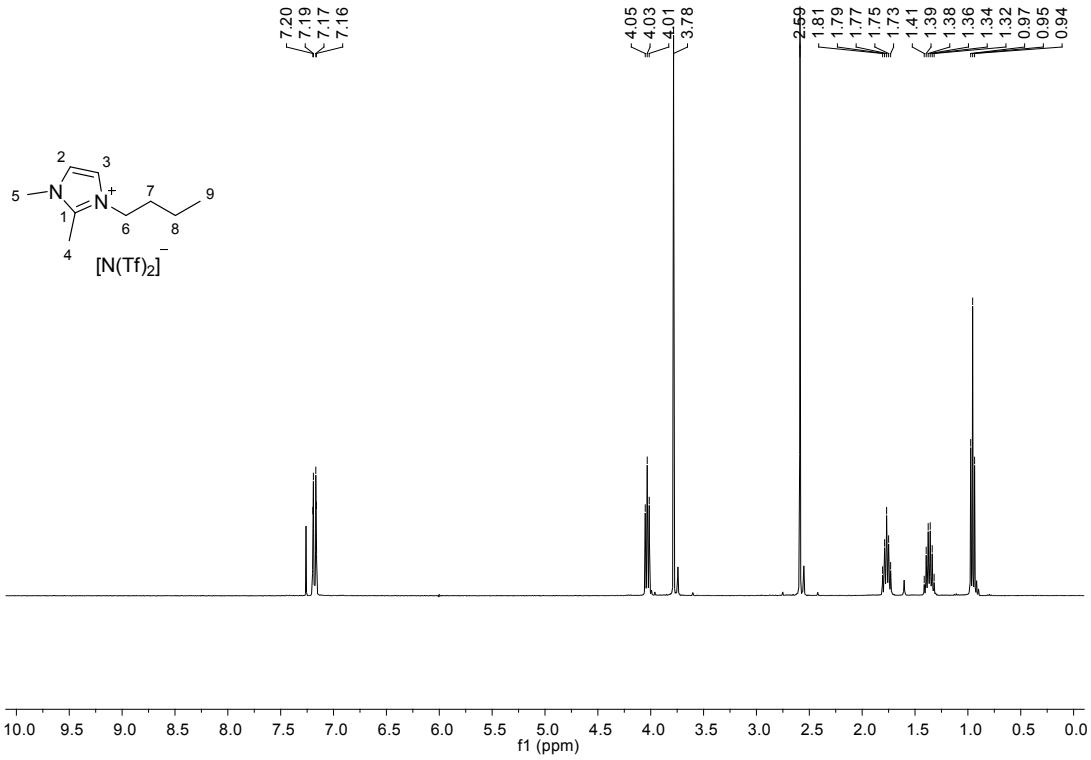


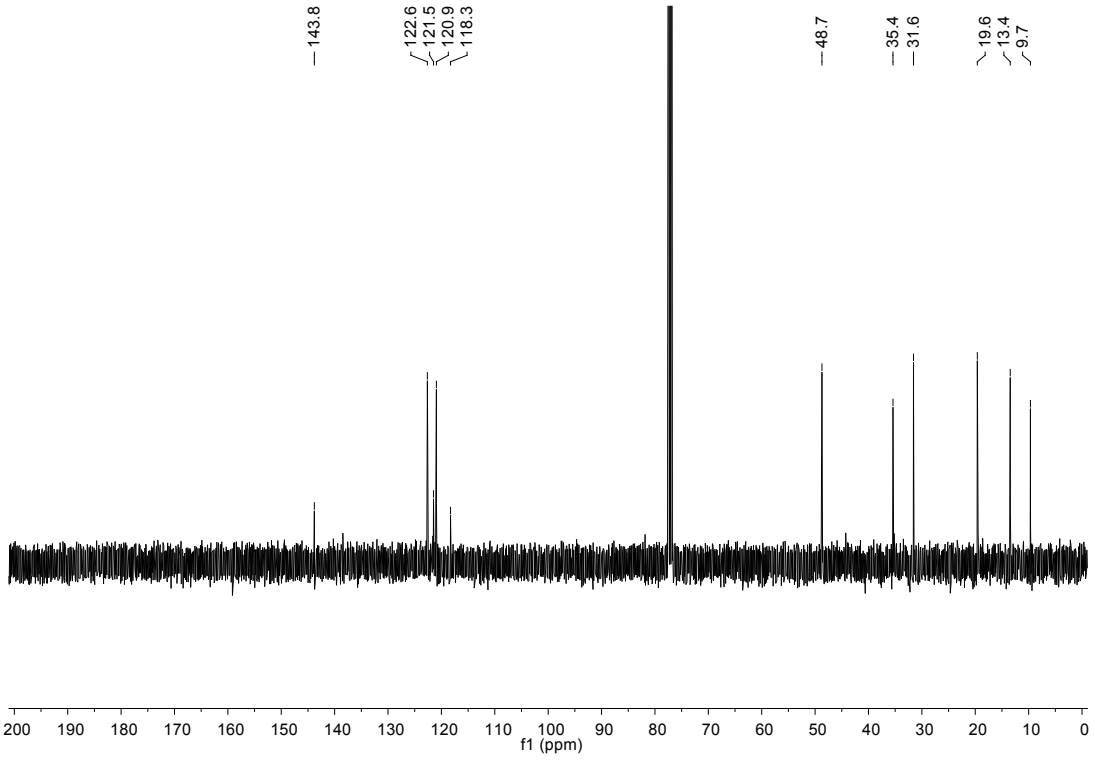


5.1.2 [BM_2Im][$MeSO_3$] (I2)

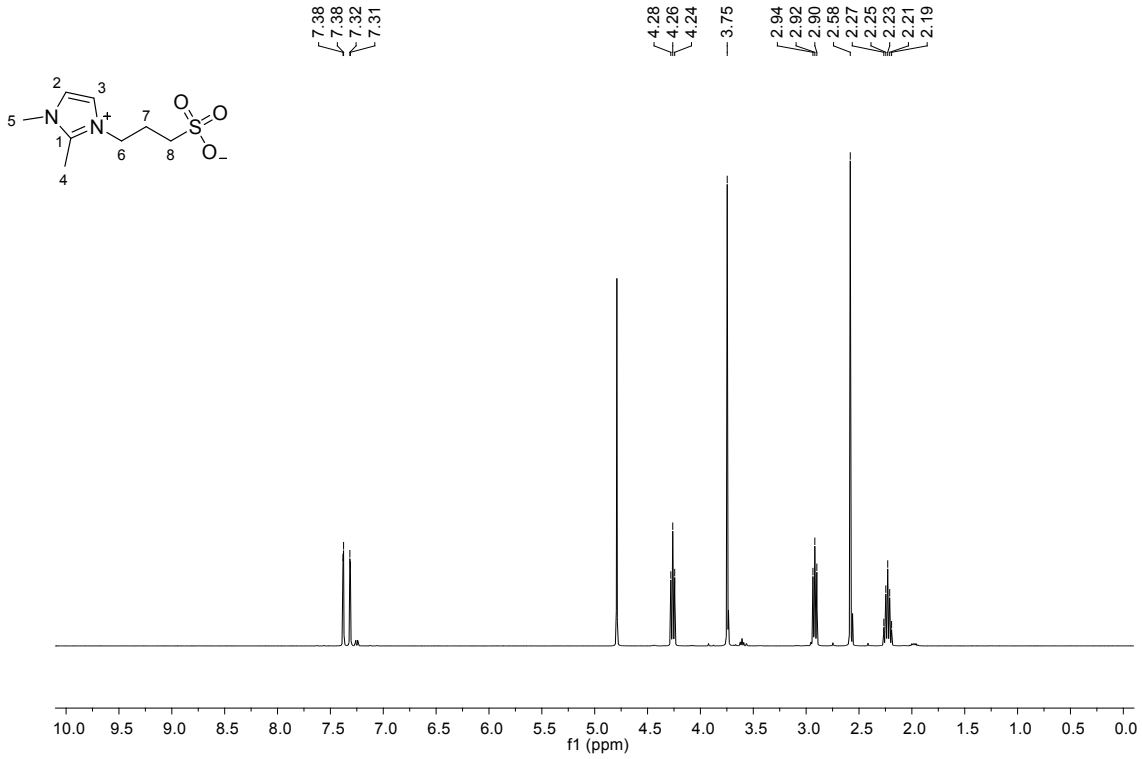


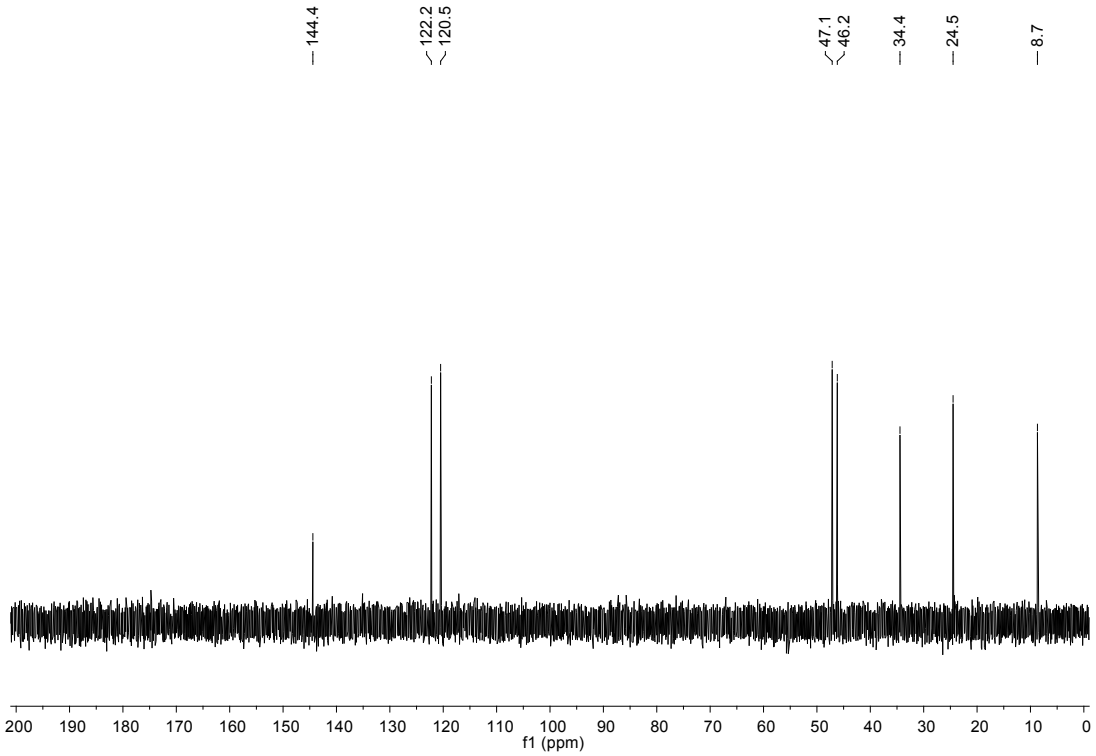
5.1.3 [BM_2Im][NTf_2] (IL1)



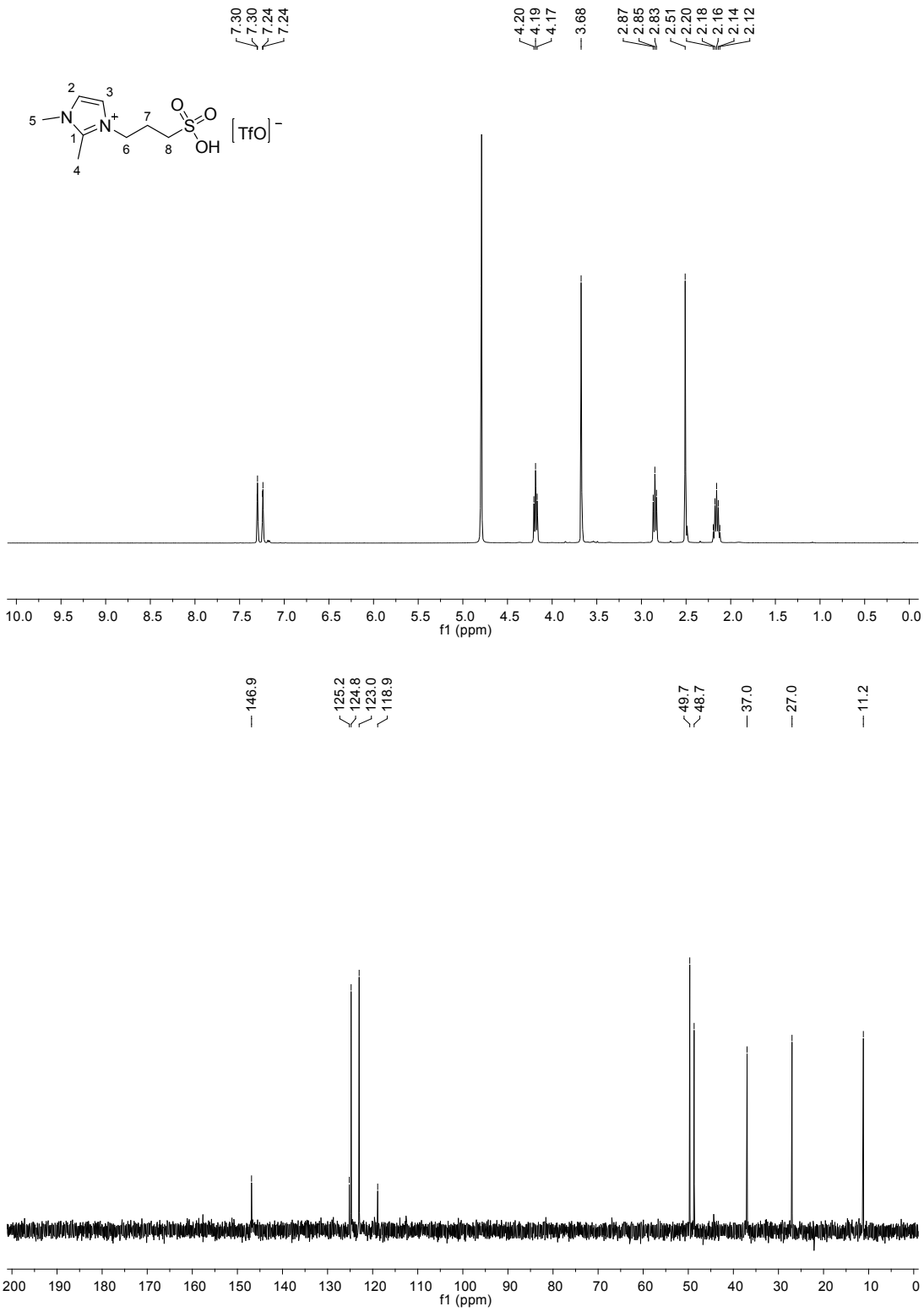


5.1.4 PSO_3M_2Im (I3)

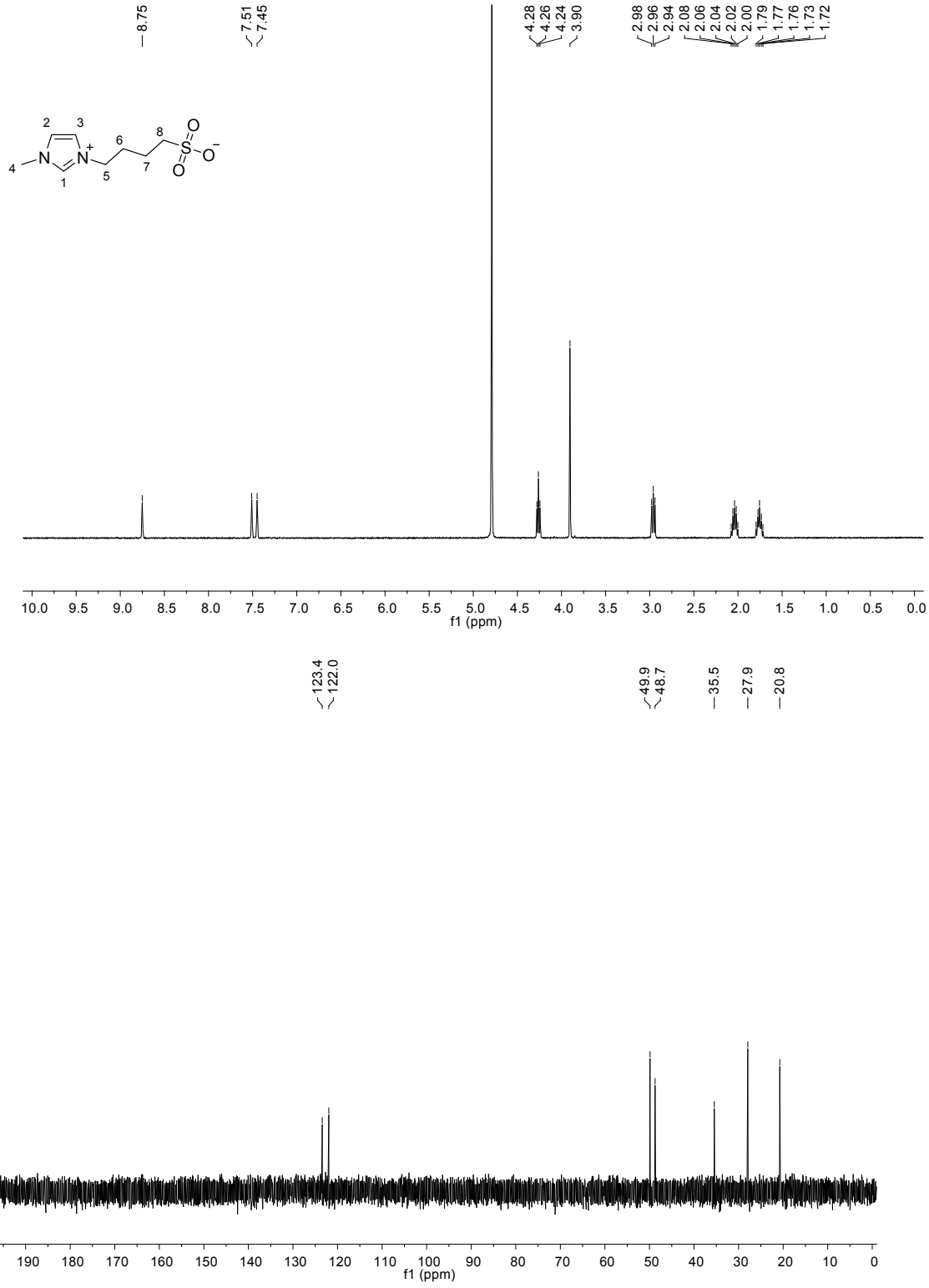




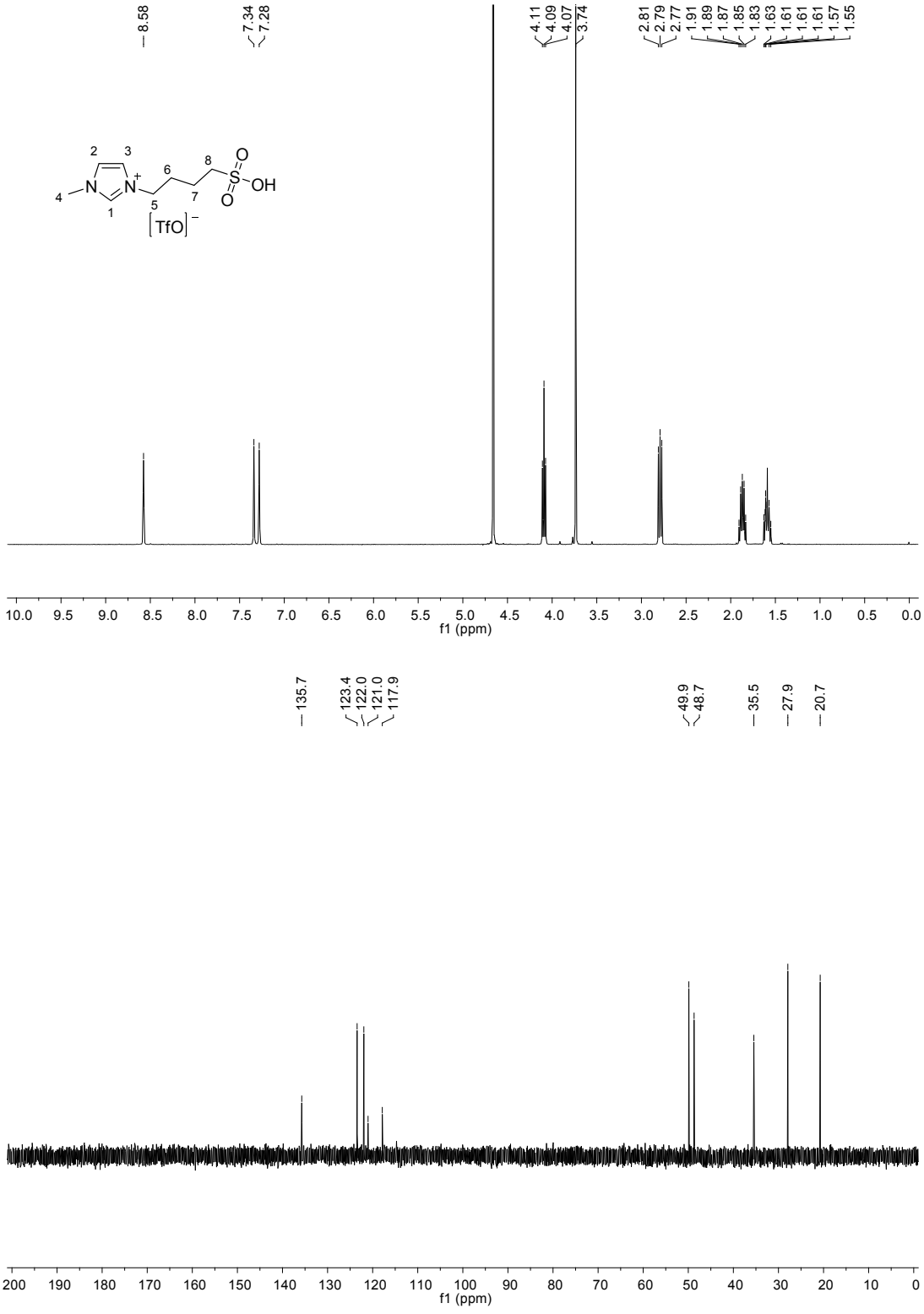
5.1.5 [PSO$_3$HM$_2$Im][OTf] (IL-H$^+$1)



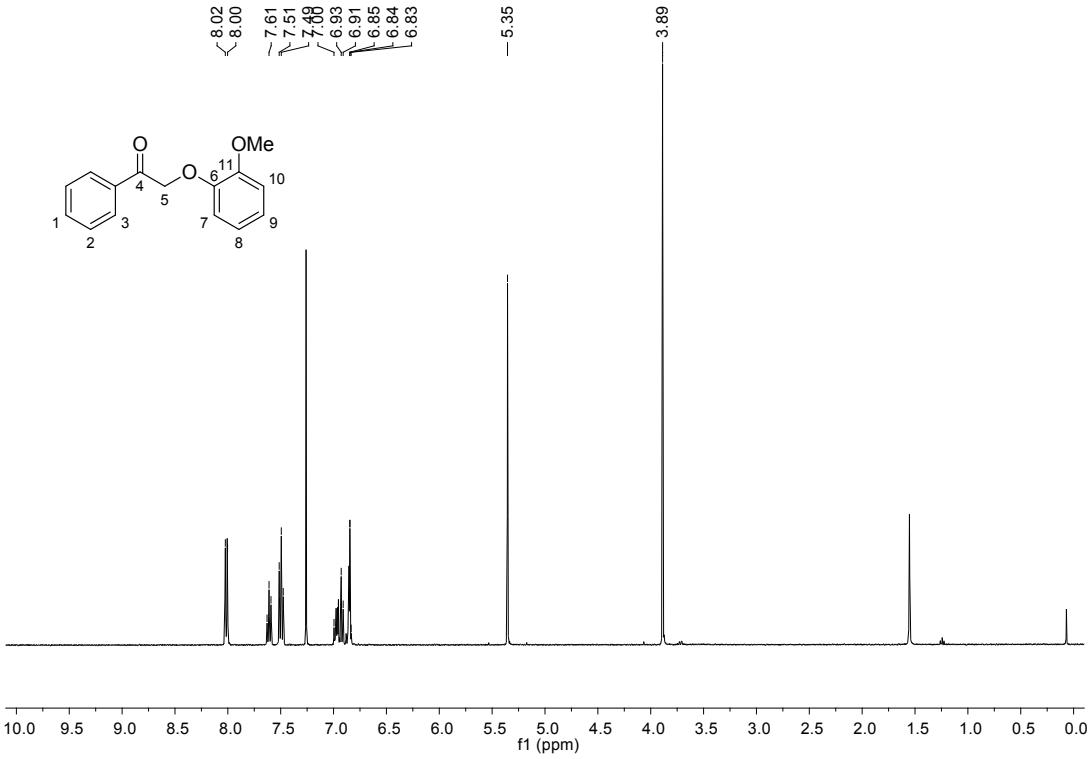
5.1.6 BSO_3MIm (I4)

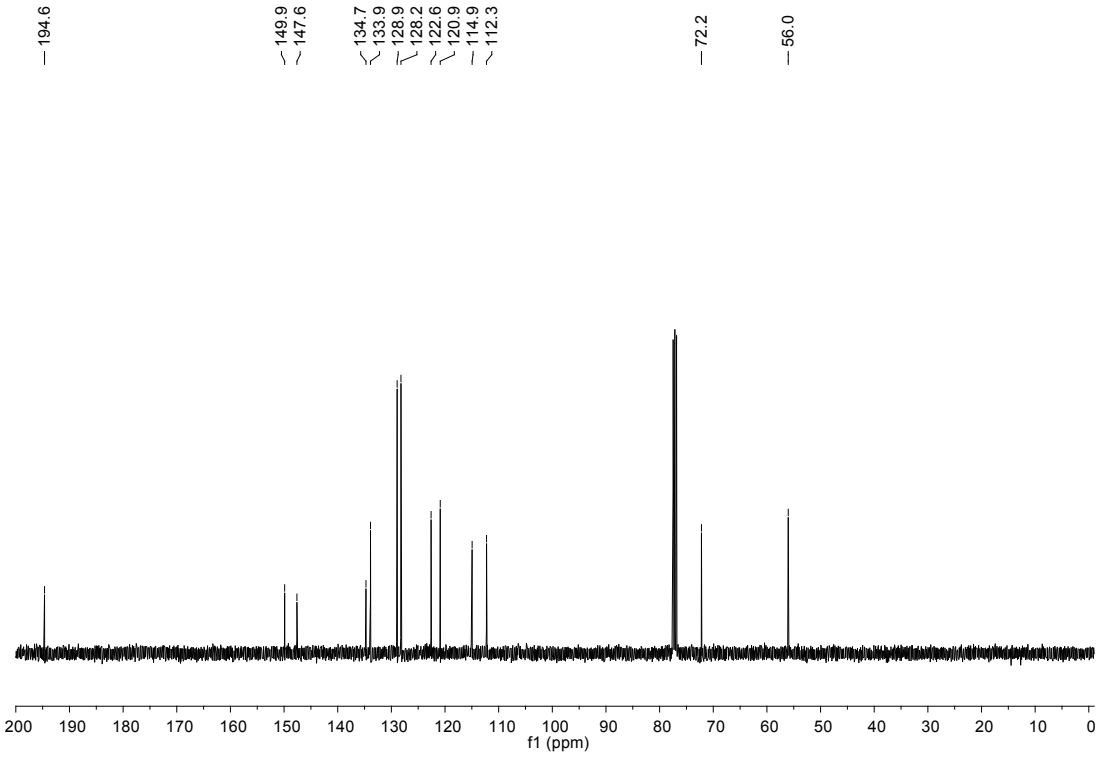


5.1.7 [BSO_3HMIm][OTf] (IL-H^+2)

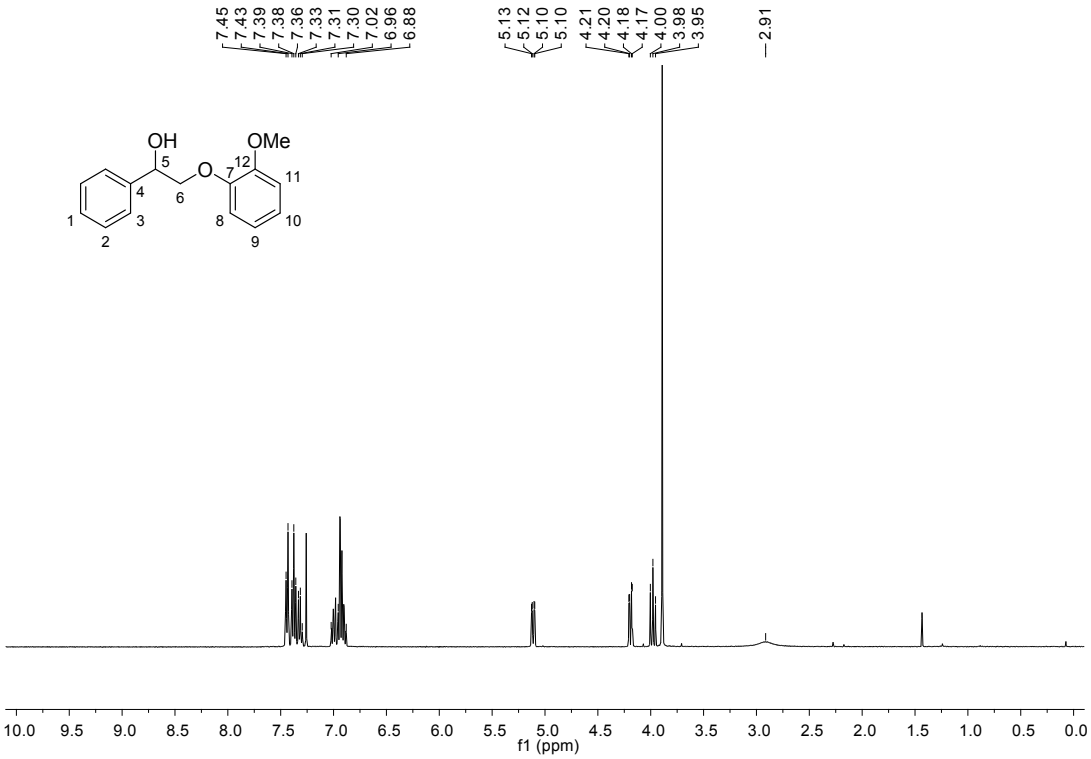


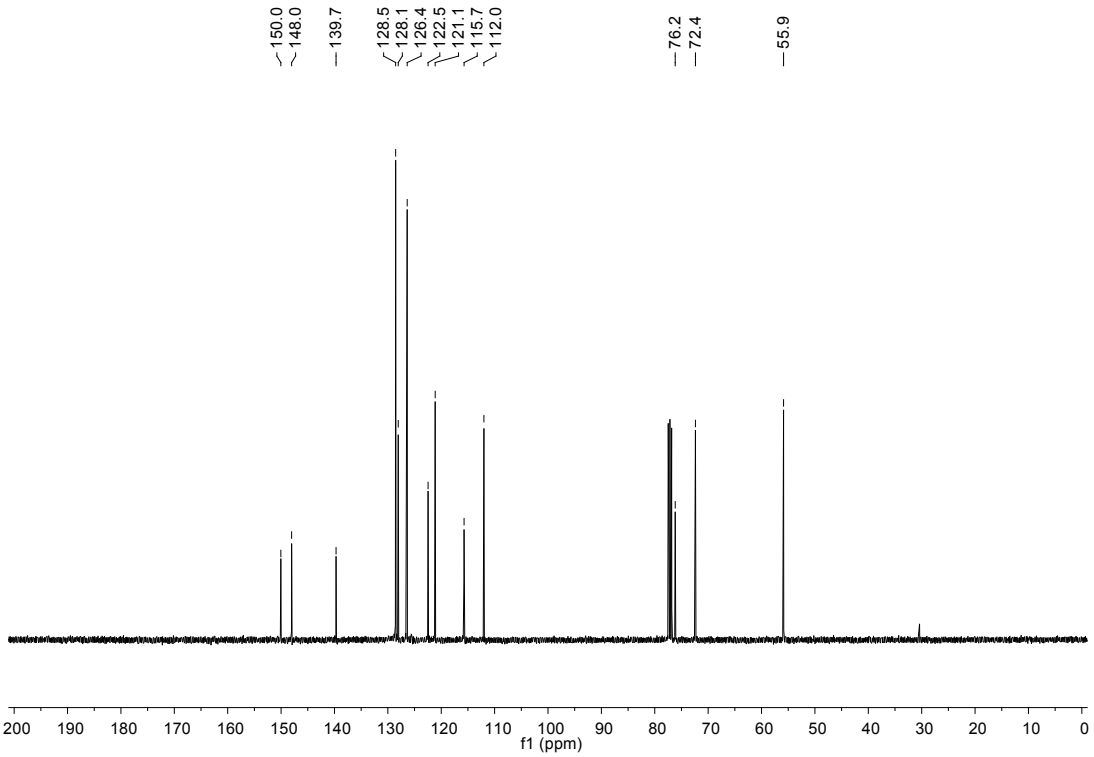
5.1.8 2-(2-methoxyphenoxy)-1-phenylethanone (I5)



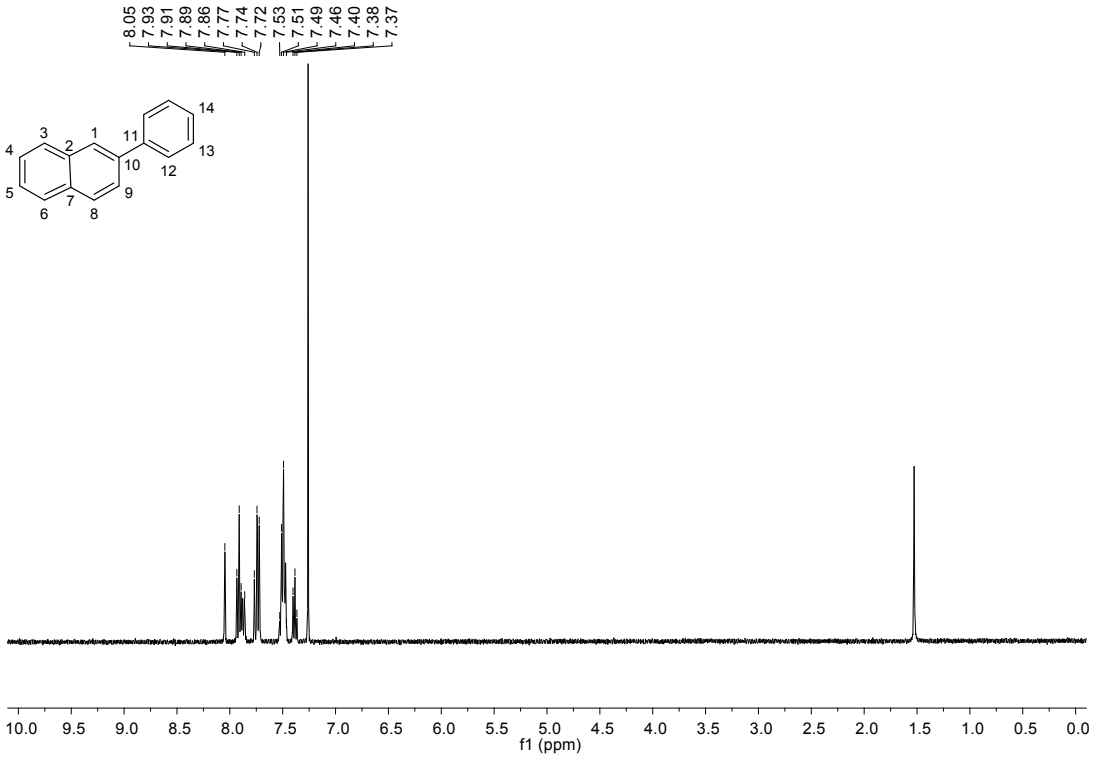


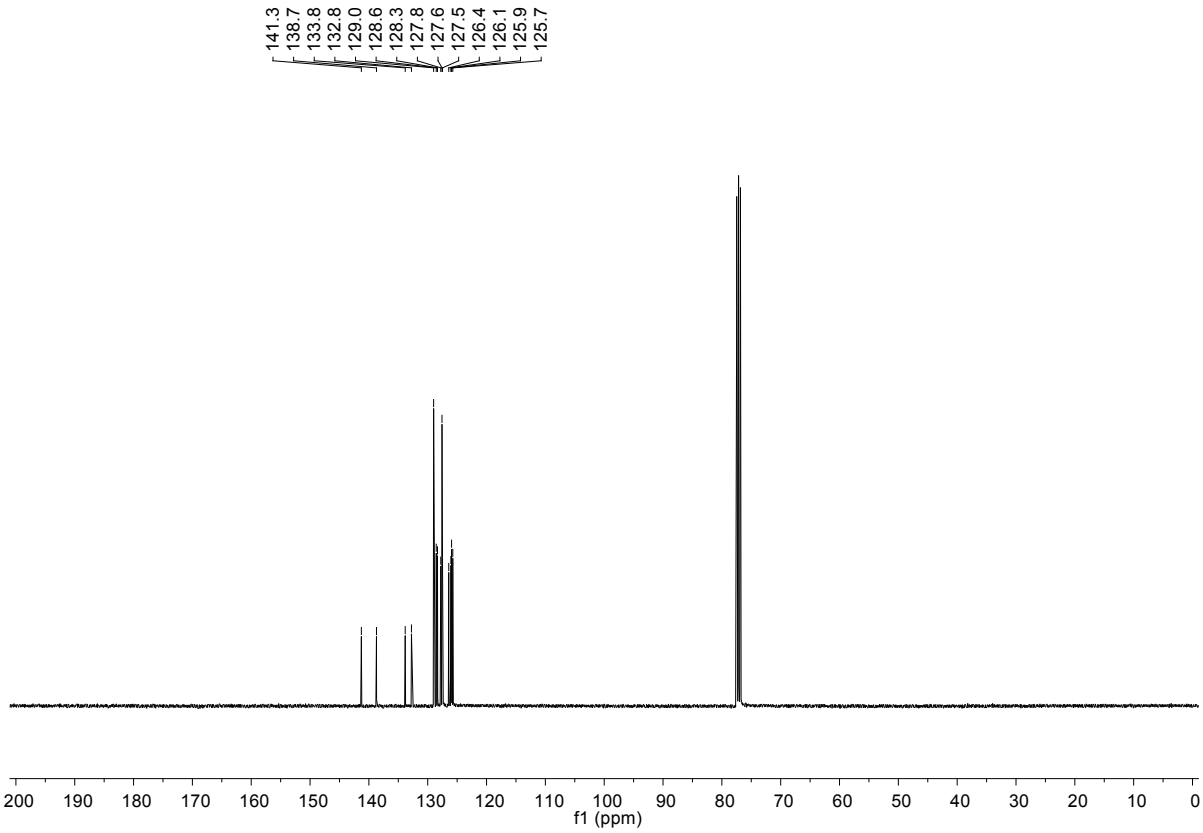
5.1.9 2-(2-methoxyphenoxy)-1-phenylethanol (1)





5.1.10 2-Phenylnaphthalene (7)





6. Crystallographic Data

Crystal structure solved and refined by Mu-Chieh Chang, Dr. Edwin Otten (RUG)

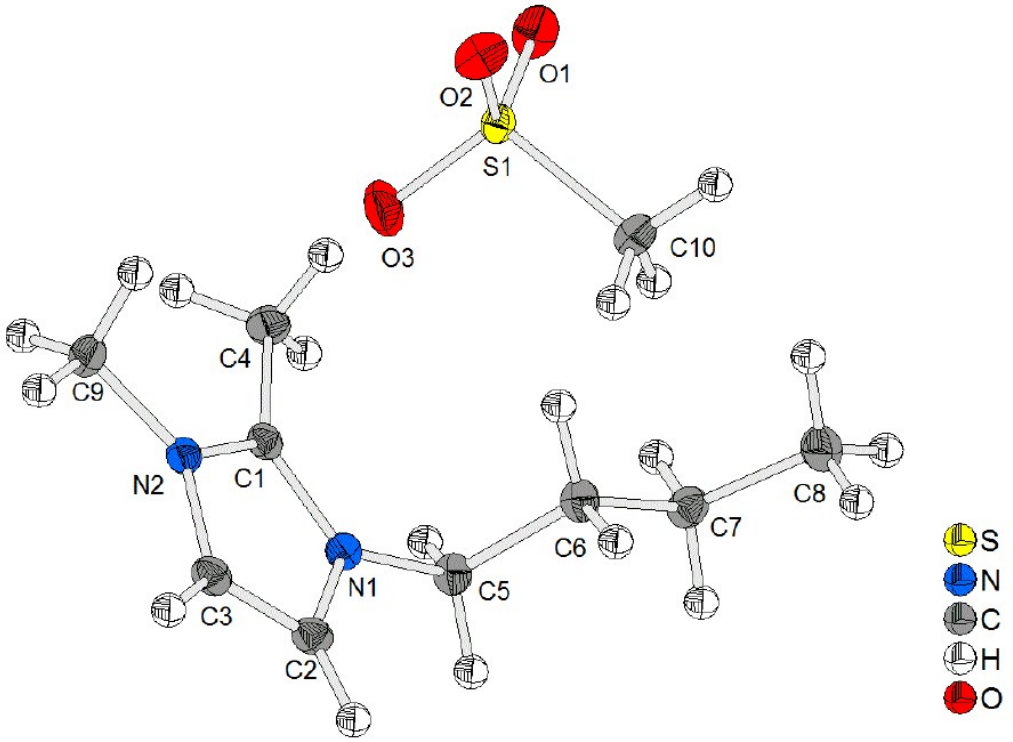


Figure S2. Crystal structure of **I2**.

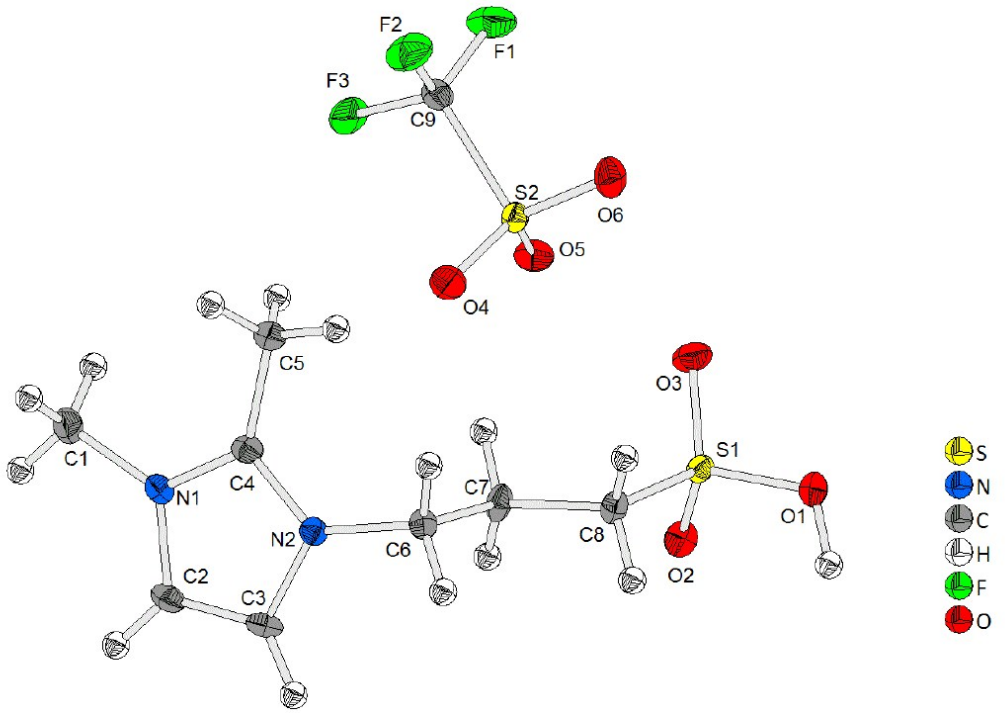


Figure S3. Crystal structure of **IL-H$^+$1**.

Crystal Data:

	[BM_2Im][MeSO3] (**I2**)	[PSO3HM_2Im][OTf] (**IL-H^+1**)
Formula	$C_{10}H_{20}N_2O_3S$	$C_9H_{15}F_3N_2O_6S_2$
M[g·mol^{-1}]	248.34	368.35
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	C2/c
Absorption coefficient [mm^{-1}]	0.252	0.425
a [Å]	7.5791(3)	25.831(2)
b [Å]	8.5101(3)	6.3322(6)
c [Å]	11.2041(4)	18.3070(15)
α [°]	71.3773(12)	90.000
β [°]	67.6333(11)	100.142(3)
γ [°]	85.2013(13)	90.000
V [$Å^3$]	632.70(4)	2947.7(4)
Z	2	8
μ(MoKα) [mm^{-1}]	0.71073	0.71073
F(000)	268	1520
2θ Area [°]	3.154 - 28.377	2.992-27.169
Reflections collected	25351	27962
Independent reflections	3141	3240
Indep. refl. with $(I > 2\theta(I))$	2985	2996
restraints / parameters	149/0	3240/206
R_1 (I > 2θ(I))	0.0293	0.0401
wR_2 (all data)	0.0306	0.0978
GooF (all data)	1.056	1.095
Absorption correction	multi-scan	multi-scan
completeness	0.998	0.995

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