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Synthesis and characterization of light-fluorous NHC-ligands and their palladium complexes

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Highlights

- Light-fluorous olefins, iodides, and triflates containing *n*-C₃F₇, n-C₄F₉, and *t*-C₄F₉ groups were used to prepare light-fluorous alkyl imidazols and dialkyl imidazolium salts.
- The partition coefficients of the light-fluorous olefins, iodides, and triflates were measured in the perfluoro(methylcyclohexane)/toluene biphasic system.
- Two light-fluorous N,N'-dialkyl-imidazole-2-ylidene diiodo palladium(II) complexes were prepared and structurally characterized.

Dedicated to Professor László Kollár on the occasion of his 65th birthday.

Abstract

Light-fluorous ponytails containing perfluoro-*n*-propyl, perfluoro-*n*-butyl and perfluoro-*t*-butoxy groups were used to synthesize light-fluorous α -olefins, branched dialkyl iodides, alkyl triflates, alkyl imidazoles, and dialkyl imidazolium salts. The latter were used to prepare two light-fluorous N,N'-dialkyl-imidazole-2-ylidene diiodo palladium(II) complexes. The fluorous partition coefficients of the light-fluorous olefins, iodides, and triflates were measured in perfluoro(methylcyclohexane)/toluene biphasic system, which revealed that the shorter and environmentally friendlier perfluoroalkyl chains of the light-fluorous ponytails results in lower fluorous partition coefficients, especially as the number of methylene groups increases.

Graphical abstract

Keywords

Perfluoroalkyl groups, light-fluorous olefins, light-fluorous dialkyl iodides, light fluorous alkyl imidazols, light-fluorous dialkyl imidazolium salts, light-fluorous NHC ligands and their palladium complexes.

1. Introduction

N-heterocyclic carbenes (NHC) [1] can be used to replace carbonyl and phosphine ligands in organometallic chemistry and transition metal homogenous catalysis [2]. Fluorous NHC ligands [3] have been also developed to facilitate catalyst recycling and product(s) separation by using the fluorous biphasic concept (Scheme 1) [4]. In general, linear fluorous ponytails consisting of C_{6-10} -perfluoroalkyl chains and methylene spacers in appropriate number are attached to the N-atoms to achieve high fluorous partition and lower the strong electron-withdrawing effect of the perfluoroalkyl chains [4, 5].



Several fluorous NHC complexes of silver, ruthenium, and palladium have been synthesized and some of them successfully used in catalytic reactions including cyclization of diene, ring closing metathesis, Heck and Suzuki coupling, Mizoroki-Heck reactions, and Suzuki-Miyaura cross-coupling [1, 2].

The accidental release of fluorous compounds to the environment could result in light-assisted oxidation/hydrolysis of the hydrocarbon domain to form the corresponding perfluoroalkyl carboxylic acids (PFCAs), some of which are persistent, easily bioaccumulate, have long half-lives in human and animal species, and some of them are toxic [6].



Perfluorooctanoic acid (C₇F₁₅COOH, PFOA) is perhaps the best known and most studied PFCA. The health and ecologicals risks of perfluoroalkyl compounds have been also assessed [7, 8, 9, 10, 11, 12, 13].

The bioaccumulation and the cytotoxicity of perfluoroalkyl compounds have been shown to correlate with the length of the perfluoroalkyl chain [14, 15, 16, 17, 18]. Therefore, the replacement of long perfluoroalkyl chains with shorter ones was proposed to lower the toxicity with respect to PFOA and limit bioaccumulation [19]. For example, the perfluoro-*tert*-butyl group has been used to prepare fluorous compounds which could provide high fluorous solubility and minimise the adverse health and environmental effects [20]. To aid the further development of sustainable fluorous chemistry, we report the synthesis of novel fluorous olefins and iodides with perfluoro-*tert*-butoxy ponytails as well as novel alky imidazoles, dialkyl imidazolium salts and their palladium complexes, bearing shorter perfluoropropyl (C_3F_7 -) and perfluorobutyl (C_4F_9 -) groups.

2. Results and Discussions

Fluorous olefins **1a-c** were prepared by the reaction of the corresponding tosylates with sodium perfluoro-*tert*-butoxide in DMSO in good to high yields (Scheme 1). The starting precursor sodium perfluoro-*tert*-butoxide can be easily prepared from commercially available sodium perfluoro-*tert*-butanol by the reported literature procedure [20a].



Scheme 1. Synthesis of fluorous olefins 1a - c.

One of the possible applications of fluorous α -olefins is their radical reaction with perfluoroalkyl iodides to form the corresponding secondary fluorous iodides. The radical addition of perfluoro-*n*-butyl iodide to fluorous olefins **1a-c** in the presence of AIBN resulted in the formation of the corresponding branched fluorous iodides **2a-c** in moderate yields, which were isolated by fluorous extraction with perfluoro(methylcyclohexane) (Scheme 2).



Scheme 2. Synthesis of fluorous iodides 2a - c.

The synthesis of fluorous imidazoles and imidazolium salts by the reaction of imidazole with perfluoroalkyl iodide or triflate has been demonstrated [3a,d]. The used fluorous triflates **3a-c** were prepared from commercially available fluorous alcohols and triflic anhydride by published procedures with minor modifications in work-up (Scheme 3) [21].



Scheme 3. Synthesis of fluorous triflates 3a-c.

Fluorous triflates **3a** and **3c** were employed to prepare fluorous imidazoles **4a** and **4c** in good yields (Scheme 4). Commercially available 1,1,1,2,2,3,3-heptafluoro-5-iodopentane and 1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl iodide were used to prepare imidazole **4b** and **4d**. However, their reactivity were significantly lower than the similar reaction of imidazole and long-chain perfluorinated iodides [3]. Furthermore, approximately 20% of di-substituted imidazolium salts were formed as the by-product.



Scheme 4. Synthesis of fluorous imidazoles 4a-d.

The partition coefficients of fluorous olefins 1a-c, iodides 2a-c, triflates 3a-c were measured by dissolving a given compound in a fluorous biphasic system consisting of 2 mL perfluoro-(methylcyclohexane) and 2 mL toluene in a vial. The mixture was shaken vigorously for 3 minutes and kept in a 25°C water bath for 12 hours. The concentration of the given fluorous compound in the upper toluene-rich phase and the lower fluorous phase was established by ¹⁹F NMR analysis (Table 1). The partition coefficients of fluorous imidazoles 4a-d and imidazolium salts 5a-f in the toluene/perfluoro-(methylcyclohexane) solvents system are excluded as they could readily form insoluble materials. The formation of aggregates could be due to the intermolecular hydrogen bonding with nitrogen atoms [22, 23]. The fluorous partition coefficient ($P_{\rm F}$) of the tested compounds ranged from 0.10 to 4.59 by increasing fluorine content from 35.4% to 59.7%. It appears that the addition of methylene spacers and/or functional groups to a compound while keeping the perfluoroalkyl chain the same could cause dramatic change of $P_{\rm F}$, fluorous olefins **1a-c**, and triflates **3a-c** are in line with this trend. As illustrated in Table 1, the *P*_F of 2a resulted in higher fluorous partition than that of 2b-c. Similar observation was made for perfluoro-tert-butoxy diethers [20b], where the fluorous groups could aggregate or form a fluorous blanket to shield the hydrocarbon domain and limit the attractive interactions with the organic solvent.

Compound ^a	Fluorine content (%)	Fluorous Partition Coefficient (<i>P</i> _F) ^b
1 a	58.93	1.98
1b	56.22	1.22
1c	53.7	0.76
2a	53.8	3.00
2b	52.6	2.15
2c	51.5	1.93
3a	57.2	3.15
3b	52.8	0.65
30	59.7	4.59

Table 1. The fluorous partition coefficients (P_F) of some compounds in fluorous biphasic systems comprised of perfluoro(methylcyclohexane) and toluene.

^a 0.04-0.1 mmol of given compound was applied in biphasic solvent system.

^b $P_{\rm F}$ = the ratio of the equilibrium molar concentrations of the dissolved compound in the fluorous and the organic phases ($P_{\rm F}=c_{\rm fluorous}/c_{\rm organic}$) measured by ¹⁹F NMR.

Fluorous imidazolium salts **5a-f** were prepared by further alkylation with fluorous triflate or iodide of fluorous imidazoles **4a-d** to yield di-substituted

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imidazolium salts (Scheme 5). Symmetric imidazolium salts **5a-d** were yellow solid, and asymmetric imidazolium salts, which R₁ and R₂ have different fluorous ponytails, were viscous oil. Crystals of **5a**, **5c** and **5d** were obtained by vapor diffusion of acetone/n-hexane and their molecular structure were confirmed by X-ray diffraction characterisation. The imidazolium ring of the molecule's cation and ionic domains, i.e. iodide and triflate, appear well resolved, the perfluorinated part encountered greater anisotropy and disorders towards the end of the chain. Similar observations were reported for fluorous pyridinium ionic liquids [24]. All crystal structures and their crystallography data are available in supplementary document [25].



Scheme 5. Synthesis of imidazolium salts 5a-f.

Unfortunately, the reaction of fluorous secondary iodides **2a-c** and imidazole resulted in the elimination of HI and the formation of fluorous internal alkenes, probably due to the insufficient insulation of the electron-withdrawing effect of the n- C_4F_9 -group [26].

Nitrogen heterocyclic carbene (NHC) metal complexes can be easily prepared by the direct reaction of the imidazolium salts with metal compounds or traditionally by substitution reactions with free carbenes via deprotonation of corresponding imidazolium salts. The N-N'-disubstituted imidazole-2-ylidene palladium complexes **6a** and **6b** have been prepared by reacting palladium acetate with 2 equivalents of imidazolium salts **5b** and **5d**, respectively, in toluene for 2 hours. These complexes were both air- and water-stable and isolated as crystalline solids in good yields (Scheme 6).



Scheme 6. Synthesis of fluorous palladium complexes 6a-b.

Single crystals of complexes **6a** and **6b** were obtained by vapor diffusion of their solution in n-hexane:CH₂Cl₂(20:1) ν/ν %. X-ray crystal structural determination revealed the expected square-planar geometry of the palladium atom and transcoordination of the two fluorous NHC ligands as well as the two iodides [27]. The palladium-carbon bond lengths of 2.018(9)Å for **6a** and 2.025(5)° for **6b**, respectively (Figure 1 and 2), are comparable with values found for similar palladium complexes in the literature [3a,28,29].



Figure 1. ORTEP crystal structure of **6a** with partial atomic numberings, being omitted for clarity.



Figure 2. ORTEP crystal structure of **6b** with partial atomic numberings, being omitted for clarity.

3. Conclusions

Light-fluorous ponytails containing perfluoro-*t*-butoxy groups were used to synthesize light-fluorous olefins (**1a-c**), branched dialkyl iodides (**2a-c**), and alkyl triflates (**3a-c**). The fluorous partition coefficients of the light-fluorous olefins, iodides, and triflates were measured in perfluoro(methylcyclohexane)/toluene biphasic system, which revealed that the shorter and environmentally friendlier perfluoroalkyl chains of the light-fluorous ponytails results in lower fluorous partition coefficients, especially as the number of methylene groups increases. Light-fluorous ponytails with perfluoro-n-propyl and perfluoro-n-butyl groups were used to prepare alkyl imidazols (**4a-d**) and dialkyl imidazolium salts (**5a-f**). Two light-fluorous N,N'-dialkyl-imidazole-2-ylidene diiodo palladium(II) complexes (**6a-b**) were also isolated and structurally characterized – they exhibit the expected square-planar geometry of the palladium atom and trans-coordination of the two fluorous NHC ligands as well as the two iodides.

4. Experimental

4.1 Chemicals and General Procedures.

Perfluoro-*tert*-butanol, perfluoro(methyl-cyclohexane), 2,2,3,3,4,4,4-heptafluoro-1-butanol and 1,1,1,2,2,3,3-hepta-fluoro-5-iodopentane were products of FluoroChem. 1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl iodide was purchased from TCI. All purchased chemicals and solvents were used as received. Ethyl Acetate, toluene, acetonitrile and tetrahydrofuran were products of RCI LabScan., dried over calcium hydride and distilled prior to use. Sodium perfluoro-tert-butoxide was synthesized according to a literature method in 100% yield [30]. ¹H-, ¹³C-, ¹⁹F-NMR spectra were recorded on a Bruker 300 MHz ASCEND AVANCE III HD or Bruker 400 MHz AVANCE III or Bruker 600MHz ASCEND AVANCE III HD FT-NMR spectrometer at room temperature. Data were expressed as chemical shifts in ppm, relative to TMS (¹H NMR δ = 0.00 ppm, ¹³C(¹H) NMR δ = 0.00 ppm), residual chloroform (¹H-NMR δ = 7.26 ppm, ${}^{13}C{}^{1}H$ NMR δ = 77.2 ppm), d₆-acetone (${}^{1}H$ -NMR δ = 2.05 ppm, ${}^{13}C{}^{1}H$ NMR δ = 29.84 ppm) or an internal standard for ¹⁹F (hexafluorobenzene δ = -164.9 ppm). Infrared spectra were recorded in the range of 600-4000 cm⁻¹ using a Nujol matrix or KBr plates on a Thermo Fisher Model Nicolet iS50 FTIR spectrometer. X-

Ray crystallography of single crystal was recorded by Oxford Diffraction Gemini S Ultra diffractometer.

4.2 Synthesis and Characterization

4.2.1. But-3-en-1-yl 4-methylbenzenesulfonate

A solution of 3-buten-1-ol (10.20 g, 0.141 mol) in distilled pyridine (30 mL, 0.372 mol) in a round bottom flask was cooled with an ice-bath and then *p*-toluenesulfonate chloride (22.58 g, 0.118 mol) was added. After stirring the mixture at 0°C for 4 hours, iced water/concentrated HCl (45 mL, 4:1 *v/v*) was added to the mixture. 90 mL diethyl ether was added and the organic upper phase was separated. The organic phase was dried over anhydrous MgSO₄. The mixture was filtered and the diethyl ether was removed by rotary evaporator. The product was purified by silica column chromatography, using n-hexane/ethyl acetate (4:1, *v/v*) eluent to obtain a colourless liquid (20.44 g, 90.3 mmol, 76.5%). ¹H NMR (600 MHz, δ in TMS): 2.40 (qt, 2H, *J* = 6.7 Hz, CHC<u>H</u>₂), 2.46 (s, 3H, Me), 4.06 (t, 2H, *J* = 6.7 Hz, C<u>H</u>₂OTs), 5.07 (m, 2H, CH=C<u>H</u>₂), 5.67 (ddt, 1H, *J* = 17.1, 10.3, 6.7 Hz, C<u>H</u>=CH₂), 7.35 (d, 2H, *J* = 8.0Hz, 3,3'-Ar), 7.79 (d, 2H, *J* = 8.0 Hz, 2,2'-Ar); ¹³C{¹H} NMR (151 MHz, δ in TMS): 21.6 (s, Me), 33.1 (s, =CH<u>C</u>H₂), 69.4 (s, <u>C</u>H₂OTs), 118.1 (s, CH=<u>C</u>H₂), 127.9 (s, 2,2'-Ar), 129.8 (s, 3,3'-Ar), 132.3 (s, <u>C</u>H=CH2), 133.2 (s, 4-Ar), 144.7 (s, 1-Ar).

4.2.2. Pen-4-en-1-yl 4-methylbenzenesulfonate

A solution of 4-penten-1-ol (8.53 g, 0.99 mol) in distilled pyridine (20 mL, 0.248 mol) in a round bottom flask was cooled with an ice-bath and then *p*-toluenesulfonate chloride (17.17 g, 0.090 mol) was added. After stirring the mixture at 0°C for 4 hours, iced water/concentrated HCl (45 mL, 4:1 *v/v*) was added to the mixture. 90 mL diethyl ether was added and the organic upper phase was separated. The organic phase was dried over anhydrous MgSO₄. The mixture was filtered and the diethyl ether was removed by rotary evaporator. The product was purified by silica column chromatography, using n-hexane/ethyl acetate (4:1, *v/v*) eluent to obtain a colourless liquid (14.47 g, 60.1 mmol, 66.9%). ¹H NMR (600 MHz, δ in TMS): 1.74 (dq, 2H, *J* = 8.3, 6.5 Hz, C<u>H</u>₂CH₂OTs), 2.08 (tdd, 2H, 7.9, 6.1, 1.4 Hz, =CH<u>C</u>H₂), 2.45 (s, 3H, Me), 4.04 (t, 2H, *J* = 6.4 Hz, C<u>H</u>₂OTs), 4.96 (m, 2H, CH=C<u>H</u>₂), 5.69 (ddt, 1H, *J* = 16.2, 11.1, 6.7 Hz, C<u>H</u>=CH2), 7.35 (d, 2H, *J* = 8.0 Hz, 3,3'-Ar), 7.79 (d, 2H, *J* = 8.0 Hz, 2,2'-Ar); ¹³C{¹H} NMR (151 MHz, δ in TMS): 21.6 (s, Me), 28.0 (s,

<u>C</u>H₂CH₂OTs), 29.4 (s, =CH<u>C</u>H₂), 69.8 (s, <u>C</u>H₂OTs), 115.8 (s, CH=<u>C</u>H₂), 127.9 (s, 2,2'-Ar), 129.8 (s, 3,3'-Ar), 133.2 (s, 4-Ar), 136.6 (s, <u>C</u>H=CH₂), 144.7 (s, 1-Ar).

4.2.3. Hex-5-en-1-yl 4-methylbenzenesulfonate

A solution of 5-hexen-1-ol (12.51 g, 0.125 mmol) in distilled pyridine (20 mL, 0.248 mol) in a round bottom flask was cooled with an ice-bath and then ptoluenesulfonate chloride (21.65 g, 0.114 mol) was added. After stirring the mixture at 0°C for 4 hours, iced water/concentrated HCI (45 mL, 4:1 v/v) was added to the mixture. 90 mL diethyl ether was added and the organic upper phase was separated. The organic phase was dried over anhydrous MgSO₄. The mixture was filtered and the diethyl ether was removed by rotary evaporator. The product was purified by silica column chromatography, using n-hexane/ethyl acetate (4:1, v/v) eluent to obtain a colourless liquid (19.22 g, 75.6 mmol, 66.3%). ¹H NMR (600 MHz, δ in TMS): 1.41 (tt, 2H, J = 9.6, 6.6 Hz, CH_2CH_2OTs), 1.65 (m, 2H, =CHCH₂C H_2), 2.00 (qd, 2H, 7.3, 1.4 Hz, =CH<u>C</u>H₂), 2.45 (s, 3H, Me), 4.03 (t, 2H, J = 6.5 Hz, C<u>H₂</u>OTs), 4.95 (m, 2H, CH=C<u>H</u>₂), 5.72 (ddt, 1H, J = 16.9, 10.1, 6.7 Hz, C<u>H</u>=CH2), 7.34 (d, 2H, $J = 8.1 \text{ Hz}, 3,3'-\text{Ar}), 7.79 (d, 2H, J = 8.2 \text{ Hz}, 2,2'-\text{Ar}); {}^{13}\text{C}{}^{1}\text{H} \text{NMR}$ (151 MHz, δ in NMR): 21.6 (s, Me), 24.8 (s, =CHCH₂CH₂), 28.2 (s, <u>C</u>H₂CH₂OTs), 32.9 (s, =CH<u>C</u>H₂), 70.4 (s, <u>CH</u>₂OTs), 115.1 (s, CH=<u>C</u>H₂), 127.9 (s, 2,2'-Ar), 129.8 (s, 3,3'-Ar), 133.3 (s, 4-Ar), 137.9 (s, CH=CH₂), 144.7 (s, 1-Ar).

4.2.4 Nonafluoro-t-butoxy-1-butene (1a)

The sodium salt of perfluoro-*t*-butoxide (10.77 g, 41.7 mmol) was dissolved in DMSO (10 mL) in a round bottom flask. But-3-en-1-yl 4-methylbenzenesulfonate (10.38 g, 45 9 mmol) was added and the reaction mixture was stirred at 80 °C for 15 hours. The round bottom flask was cooled to room temperature, and water (30 mL) was added to the reaction mixture and the lower fluorous liquid phase was extracted. The fluorous phase was then washed with water (3 x 10 mL) and 1M sodium hydroxide solution (3 x 10 mL). The product was isolated by vacuum transfer to obtain a colourless liquid (8.69 g, 30.0 mmol, 71.8%). ¹H NMR (600 MHz, δ in TMS): 2.43 (qt, 2H, *J* = 6.7, 1.3 Hz, =CHC*H*₂), 4.04 (t, 2H, *J* = 6.6 Hz, OC*H*₂), 5.13 (m, 2H, CH=C*H*₂), 5.79 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz, C*H*=CH₂). ¹³C{¹H} NMR (151 MHz, δ in TMS): 34.1 (s, =CH<u>C</u>H₂), 69.1(s, <u>C</u>H₂OTs), 80.0 (m, *J* = 29.6, 59.3 Hz, (CF₃)₃<u>C</u>), 117.9 (s, CH=<u>C</u>H₂), 120.5 (m, ¹*J*_{C-F} = 292 Hz, <u>C</u>F₃), 131.6 (s, <u>C</u>H=CH₂); ¹⁹F NMR (282 MHz, δ in CDCl₃, C₆F₆ capillary): -68.79 (s, 9F, C<u>F₃</u>). IR (neat): v 3096 (w), 3012 (w, br), 2982 (w, br), 1649 (m), 1485 (m), 1253 (s), 1164 (s), 1015 (s).

4.2.5 Nonafluoro-t-butoxy-1-pentene (1b)

The sodium salt of perfluoro-t-butoxide (9.85 g, 38.2mmol) was dissolved in DMSO (10 mL) in a round bottom flask. Pen-4-en-1-yl 4-methylbenzenesulfonate (10.10 g, 42.0 mmol) was added and the reaction mixture was stirred at 80 °C for 15 hours. The round bottom flask was cooled to room temperature, and water (30 mL) was added to the reaction mixture and the lower fluorous liquid phase was extracted. The fluorous phase was further washed with water (3 x 10 mL) and 1M sodium hydroxide solution (3 x 10 mL). The crude product was isolated by vacuum transfer to obtain a colourless liquid (9.45 g, 31.1 mmol, 81.4%). ¹H NMR (600 MHz, δ in TMS): 1.79 (quint, 2H, *J*= 6.8 Hz, CH₂CH₂OTs), 2.16 (q, 2H, *J*= 6.7 Hz, =CHCH₂), 4.02 (t, 2H, *J*= 6.2 Hz, CH₂OTs), 5.03 (m, 2H, CH=CH₂), 5.79 (ddt, 1H, *J*= 16.9, 10.2, 6.7 Hz, CH=CH2). ¹³C{¹H} NMR (151 MHz, δ in TMS): 29.0 (s, =CHCH₂), 29.4 (s, CH₂CH₂OTs), 69.1(s, CH₂OTs). 80.0 (m, *J*= 29.5, 59.2 Hz, (CF₃)₃C), 115.7 (s, CH=CH₂), 119.9 (m, ¹*J*_{C-F} = 292 Hz, CF₃), 137.1 (s, CH=CH₂); ¹⁹F NMR (282 MHz, δ in CDCl3, C6F6 capillary): -68.81 (s, 9F, CF₃). IR (neat): v 2992 (w, br), 2934 (w, br), 2857 (w, br), 1647 (m), 1483 (m), 1270 (s), 1162 (s), 1011 (s).

4.2.6. Nonafluoro-t-butoxy-1-hexene (1c)

The sodium salt of perfluoro-*t*-butoxide (8.02 g, 31.1 mmol) was dissolved in DMSO (10 mL) in a round bottom flask. Hex-5-en-1-yl 4-methylbenzenesulfonate (11.84 g, 46.6 mmol) was added and the reaction mixture was stirred at 80 °C for 15 hours. The round bottom flask was cooled to room temperature, and ice-cold water (30 mL) was added to the reaction mixture and the lower fluorous liquid phase was extracted. The fluorous phase was further washed with ice-cold water (3 x 10 mL) and 1M sodium hydroxide solution (3 x 10 mL). The crude product was purified by vacuum transfer at 0°C to obtain a colourless liquid product (6.08 g, 19.1 mmol, 61.4%). ¹H NMR (600 MHz, δ in TMS): 1.49 (m, 2H, C<u>H</u>₂CH₂OTs), 1.69 (m, 2H, C<u>H</u>₂CH₂OTs), 2.09 (m, 2H, =CHC<u>H</u>₂), 4.01 (t, 2H, *J* = 6.7 Hz, C<u>H</u>₂OTs), 4.99 (m, 2H, CH=C<u>H</u>₂), 5.79 (ddt, 1H, *J* = 17.0, 10.2, 6.7 Hz, C<u>H</u>=CH₂). ¹³C{¹H} NMR (151 MHz, δ in TMS): 24.6 (s, <u>C</u>H₂CH₂CH₂OTs), 29.1 (s, <u>C</u>H₂CH₂OTs), 33.1 (s, =CH<u>C</u>H₂),

69.1(s, <u>C</u>H₂OTs), 80.0 (m, J = 29.6, 58.9 Hz, (CF₃)₃<u>C</u>), 114.9 (s, CH=<u>C</u>H₂), 119.9 (m, ${}^{1}J_{C-F} = 292$ Hz, <u>C</u>F₃), 138.1 (s, <u>C</u>H=CH₂); ¹⁹F NMR(282 MHz, δ in CDCI3, C₆F₆ capillary): -68.97 (s, 9F, C<u>F₃</u>). IR (neat): v 3012, 1650 (w), 1486 (w), 1283 (s), 1252 (s), 1160 (s), 1007 (s).

4.2.7. 1-(Nonafluoro-tert-butoxy)-3-iodo-4-perfluorobutyl-butane (2a)

Compound 1a (3.38 g, 11.6 mmol) and perfluoro-n-butyl iodide (4.25 g, 12.3 mmol) were added to the 10 mL pressure tube, and recrystallised AIBN (10 mol%) was added every 2 hours for 4 times, then the mixture was heated in 80°C oil bath for 15 hours. Perfluoro(methylcyclohexane) (10 mL) and methanol (10 mL) was added to the mixture, the lower fluorous phase was extracted. Solvent was removed by rotary evaporator to obtain a yellow oil (5.98 g, 9.40 mmol, 80.8%). ¹H NMR (600MHz, δ in CDCl₃): 2.21 (m, 2H, (CF₃)₃COCH₂C₁/₂), 2.92 (m, 2H, CH₂C₄F₉), 4.22 (m, 2H, (CF₃)₃COCH₂), 4.46 (tdd, 1H, CHICH₂C₄F₉), ¹³C{¹H} NMR (151 MHz, δ in CDCl₃): 14.24 (s, CHI), 40.23 (s, (CF₃)₃COCH₂CH₂), 41.94 (t, CH₂C₄F₉), 69.56 (s, (CF₃)₃COCH₂), 79,86 (m, (CF₃)₃CO, *J* = 29.7, 59.6 Hz), 108.70 (m, CF₂CF₂CF₂CF₃), 110.33 (m, CF₂CF₂CF₃CF₃), 117.74 (m, CF₂CF₂CF₂CF₂CF₃ and CF₂CF₂CF₂CF₃), 120.42 (q, CF₃, ¹J_{C-F} = 293.3 Hz); ¹⁹F NMR (δ in CDCl₃ and C₆F₆): -73.5 (s, (CF₃)₃), -84.2 (t, CF₂CF₂CF₂CF₃), -116.6 (m, CF₂CF₂CF₂CF₂CF₃), -127.7 (m, CF₂CF₂CF₂CF₃), 129.1 (m, CF₂CF₂CF₂CF₃). IR (neat): v 1477 (w), 1354 (m), 1285 (s), 1252(s), 1160 (s), 1136 (s), 1017 (s).

4.2.8. 1-(Nonafluoro-tert-butoxy)-4-iodo-5-perfluorobutyl-pentane (2b)

Compound **1b** (1.33 g, 4.36 mmol) and perfluoro-n-butyl iodide (1.71 g, 4.94 mmol) were added to the 10 mL pressure tube, and recrystallised AIBN (10 mol%) was added every 2 hours for 4 times, then the mixture was heated in 80°C oil bath for 15 hours. Perfluoro(methylcyclohexane) (10 mL) and methanol (10 mL) was added to the mixture, the lower fluorous phase was extracted. Solvent was removed by rotary evaporator to obtain a yellow oil (2.02 g, 3.11 mmol, 71.4%). ¹H NMR (600MHz, δ in CDCl₃): 1.92 (m, 4H, (CF₃)₃COCH₂CH₂CH₂), 2.86 (m, 2H, CH₂C₄F₉), 4.07 (t, 2H, (CF₃)₃COCH₂), 4.35 (tdd, 1H, CHICH₂C₄F₉); ¹³C{¹H} NMR (151 MHz, δ in CDCl₃): 19.3 (s, CHI), 30.1 (s, (CF₃)₃COCH₂CH₂), 36.3 (s, (CF₃)₃COCH₂CH₂CH₂), 41.9 (t, CH₂C₄F₉), 68.6 (s, (CF₃)₃COCH₂), 80.0 (m, (CF₃)₃CO, J = 29.5, 59.1 Hz),

108.6 (m, $CF_2CF_2CF_2CF_3$), 110.3 (m, $CF_2CF_2CF_3CF_3$), 117.6 (m, $CF_2CF_2CF_2CF_3$ and $CF_2CF_2CF_2CF_2CF_3$), 120.5 (q, CF_3 , ${}^1J_{C-F}$ = 293.7 Hz); ${}^{19}F$ NMR (δ in CDCI₃ and C_6F_6): -73.56 (s, (CF_3)₃), -84.20 (t, $CF_2CF_2CF_2CF_3$), -117.43 (m, $CF_2CF_2CF_2CF_3$), -127.68 (m, $CF_2CF_2CF_2CF_3$), -129.07 (m, $CF_2CF_2CF_2CF_3$). IR (neat): v 1358(m), 1285 (s), 1250 (s), 1160 (s), 1138 (s), 1026 (s).

4.2.9. 1-(Nonafluoro-tert-butoxy)-5-iodo-6-perfluorobutyl-hexane (2c)

Compound 1c (1.29 g, 4.06 mmol) and perfluoro-n-butyl iodide (1.61 g, 4.65 mmol) were added to the 10 mL pressure tube, and recrystallised AIBN (10 mol%) was added every 2 hours for 4 times, then the mixture was heated in 80°C oil bath for 15 hours. Perfluoro(methylcyclohexane) (10 mL) and methanol (10 mL) was added to the mixture, the lower fluorous phase was extracted. Solvent was removed by rotary evaporator to obtain a yellow oil (1.22 g, 1.84 mmol, 45.0%). ¹H NMR (600MHz, δ in CDCl₃): 1.79 (m, 6H, (CF₃)₃COCH₂CH₂CH₂CH₂), 2.88 (m, 2H, $CH_2C_4F_9$, 4.07 (t, 2H, (CF₃)₃COC H_2), 4.35 (tdd, 1H, $CH_1CH_2C_4F_9$); ¹³C{¹H} NMR (151 MHz, δ in TMS): 19.8 (s, <u>C</u>HI), 25.6 (s, (CF₃)₃COCH₂CH₂CH₂), 28.7 (s, (CF₃)₃COCH₂<u>C</u>H₂), 39.7 (s, (CF₃)₃COCH₂CH₂CH₂CH₂), 41.8 (s, <u>C</u>H₂C₄F₉), 69.4 (s, $(CF_3)_3CO_{CH_2}$, 79.9 (m, $(CF_3)_3CO_3$, J = 29.4, 59.7 Hz), 108.6 (m, $CF_2CF_2CF_2CF_3$), 110.3 (m, CF₂CF₂CF₂CF₃), 117.6 (m, <u>C</u>F₂CF₂CF₂CF₃ and CF₂CF₂CF₂CF₃), 120.6 (q, <u>C</u>F₃, ¹J_{C-F} = 292.7 Hz); ¹⁹F NMR (δ in CDCl₃ and C₆F₆): -73.42 (s, (C<u>F₃</u>)₃), -84.12 (tt, CF₂CF₂CF₂CF₂CF₃), -116.67 (m, CF₂CF₂CF₂CF₃), -127.59 (m, CF₂CF₂CF₂CF₃), -128.93 (m, CF₂CF₂CF₃), IR (neat): v 1354(m), 1284 (s), 1250 (s), 1162 (s), 1135 (s), 1024 (s).

4.2.10. 1,1,1,2,2,3,3-Heptafluoro-4-butyl triflate (**3a**)

A sample of,2,2,3,3,4,4,4-Heptafluoro-1-butanol (4.0 g, 20 mmol), distilled pyridine (1.8 mL, 22 mmol) and dichloromethane (10 mL) were added to 25 mL 2-neck round bottom flask in ice-bath under N₂ atmosphere. The mixture was stirred in ice-bath for 30 mins. Triflic anhydride (3.75 mL, 22 mmol) in dichloromethane (3 mL) was added dropwise to the mixture in ice-bath. After the addition of triflic anhydride, the mixture was continued to stir at room temperature for 18 h. The crude product was purified by flash alumina column, eluted with dichloromethane. The product was dried over anhydrous MgSO₄, filtered and solvent removed by rotary evaporator to

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yield a colourless liquid (4.29 g, 12.9 mmol, 64.5%). ¹H NMR (600MHz, δ in TMS): 4.82 (t, 2H, J = 12.2 Hz, C<u>H</u>₂Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 68.0 (t, J = 28.3 Hz, <u>C</u>H₂), 108.5 (tq, <u>C</u>F₂CF₂CF₃), 112.5 (tt, CF₂<u>C</u>F₂CF₃), 117.4 (qt, CF₂CF₂<u>C</u>F₃), 118.6 (q, ¹J_{C-F} = 286.4 Hz, -<u>C</u>F₃); ¹⁹F NMR (282MHz, δ in CDCI₃ and C₆F₆): -77.08 (s, C<u>F</u>₃), -83.83 (t, CF₂CF₂C<u>F</u>₃), -123.86 (m, CF₂<u>C</u>F₂CF₃), -130.34 (m, <u>C</u>F₂CF₂CF₃).). IR (neat): v 1434 (s), 1358 (m), 1304 (m), 1231 (s), 1145 (s), 1035 (s), 1007 (s).

4.2.11. 1,1,1,2,2,3,3-Heptafluoro-6-hexyl triflate (**3b**)

A sample of 4,4,5,5,6,6,6,-Heptafluorohexan-1-ol (0.895 g, 3.92 mmol), distilled pyridine (1.8 mL, 22 mmol) and dichloromethane (10 mL) were added to 25 mL 2-neck round bottom flask in ice-bath under N2 atmosphere. The mixture was stirred in ice-bath for 30 mins. Triflic anhydride (3.75 mL, 22 mmol) in dichloromethane (3 mL) was added dropwise to the mixture in ice-bath. After the addition of triflic anhydride, the mixture was continued to stir at room temperature for 18 h. The crude product was purified by flash alumina column, eluted with DCM. The product was dried over anhydrous MgSO4, filtered and solvent removed by rotary evaporator to yield a colourless liquid (0.841 g, 2.34 mmol, 59.6%). ¹H NMR (600 MHz, δ in TMS): 2.27-2.49 (m, 4H, C₃F₇C<u>H₂CH₂</u>), 4.65 (t, 2H, C<u>H₂OTf</u>); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 21.8 (t, <u>C</u>H₂CH₂OTf), 27.3 (t, C₃F₇<u>C</u>H₂), 49.5 (s, <u>C</u>H₂OTf), 108.5 (m, <u>C</u>F₂CF₂CF₃), 112.5 (m, CF₂<u>C</u>F₂CF₃), 117.4 (m, CF₂CF₂<u>C</u>F₃), 118.6 (q, ¹J_C-F = 286.5 Hz, -<u>C</u>F₃); ¹⁹F NMR (282MHz, δ in CDCl₃ and C₆F₆): -77.74 (s, -SO₂C<u>F₃</u>), -83.69 (t, C<u>F₃</u>), -118.48 (m, C<u>F₂CH₂), -130.87 (m, CF₃C<u>F₂</u>).). IR (neat): v 1431 (s), 1308 (m), 1231 (s), 1142 (s), 1024 (s).</u>

4.2.12. 1,1,1,2,2,3,3,4,4-Nonafluoro-5-pentyl triflate (**3c**)

A sample of,2,2,3,3,4,4,5,5,5-Nonafluoro-1-pentan-1-ol (1.345 g, 5.38 mmol), distilled pyridine (0.48 mL, 5.91 mmol) and dichloromethane (10 mL) were added to 25 mL 2-neck round bottom flask in ice-bath under N₂ atmosphere. The mixture was stirred in ice-bath for 30 mins. Triflic anhydride (1.00 mL, 5.91 mmol) in dichloromethane (3 mL) was added dropwise to the mixture in ice-bath. After the addition of triflic anhydride, the mixture was continued to stir at room temperature for 12 h. The crude product was purified by flash alumina column, eluted with dichloromethane. The product was dried over anhydrous MsgSO₄, filtered and

solvent removed by rotary evaporator to yield a colourless liquid (0.897 g, 2.26 mmol, 42%). ¹H NMR (300 MHz, δ in TMS): 4.85 (t, 2H, C<u>H</u>₂OTf); ¹³C{¹H} NMR (151 MHz, δ in TMS): 68.0 (t, <u>C</u>H₂OTf), 108.6 (m, <u>C</u>F₂CF₂CF₃), 110.3 (m, CF₂<u>C</u>F₂CF₃), 117.6 (m, CH₂<u>C</u>F₃ & CF₂CF₂<u>C</u>F₃), 118.5 (q, ¹J_{C-F} = 319.7 Hz, SO₂<u>C</u>F₃), ; ¹⁹F NMR (282 MHz, δ in CDCl₃ and C₆F₆): -77.0 (s, -SO₂C<u>F₃), -83.90 (t, CF₃), -122.96 (t, CF₂CH₂), -126.91 (m, CF₃C<u>F₂), -129.22 (m, CF₃CF₂C<u>F₂).</u>). IR (neat): v 1418 (s), 1360 (m), 1302 (m, br), 1225 (s), 1147 (s), 1121 (m), 1033 (w).</u></u>

4.2.13. 1-(1,1,1,2,2,3,3-Heptafluoro-4-butyl) imidazole (4a)

Under N₂ atmosphere, triflate **3a** (1.975 g, 5.95 mmol) was added to a 25 mL Schlenk flask. Imidazole (1.215 g, 17.8 mmol) in acetonitrile (10 mL) was added dropwise at room temperature. The mixture was stirred and heated in 80°C oil bath for 15 hrs. The solvent was removed by reduced pressure, followed by the addition of ethyl acetate (10 mL) and water (10 mL). The organic phase was separated and dried over anhydrous Mg₂SO₄ and filtered. The solvent was removed by rotary evaporator to obtain a yellow viscous liquid (0.833 g, 3.33 mmol, 56%).¹H NMR (600MHz, δ in TMS): 4.58 (t, 2H, C<u>H</u>₂Im), 7.01 (s, 1H, C₄-Im), 7.15 (s, 1H, C₅-Im), 7.56 (s, 1H, C₂-Im); ¹³C{¹H} NMR (151 MHz, δ in CDCl₃): 46.3 (t, ²J_{HF} = 24 Hz, C<u>H</u>₂Im), 108.8 (m, <u>C</u>F₂CF₂CF₃), 113.6 (m, CF₂<u>C</u>F₂CF₃), 116.5 (m, CF₂CF₂<u>C</u>F₃), 118.4 (m, <u>C</u>F₃), 120.5 (s, <u>C</u>₅-Im), 130.4 (s, <u>C</u>₄-Im), 138.5 (s, <u>C</u>₂-Im); ¹⁹F NMR (282 MHz, δ in CDCl₃ and C₆F₆): -83.70 (t, CF₃), -123.67 (m, C<u>F</u>₂CH₂), -130.46 (m, CF₃C<u>F</u>₂). IR (nujol): v 3371 (br), 1512 (m), 1229 (s), 1188 (s), 1115 (s).

4.2.14. 1-(1,1,1,2,2,3,3-Heptafluoro-5-pentyl) imidazole (4b)

Under N₂ atmosphere, 1,1,1,2,2,3,3-Heptafluoro-5-iodopentane (1.979 g, 6.11 mmol) in acetonitrile (5 mL) was added in 25 mL schlenk tube. Imidazole (1.264 g, 18.6 mmol) in acetonitrile (5 mL) was added dropwise to the tube at room temperature. The mixture was stirred and heated at 80°C for 24 h. Solvent removed by reduced pressure. Dark yellow crude product was purified by silica column chromatography, eluted with DCM/MeOH (10:1 ν/ν), to yield a yellow oil (0.259 g, 0.981 mmol, 16 %). ¹H NMR (600MHz, δ in TMS): 2.58 (m, 2H, C<u>H</u>₂CH₂Im), 4.58 (t,

2H, ${}^{3}J_{HF} = 8$ Hz, C<u>H</u>₂Im), 7.01 (s, 1H, C₄-Im), 7.15 (s, 1H, C₅-Im), 7.56 (s, 1H, C₂-Im); ${}^{13}C{}^{1}H{}$ NMR (151 MHz, δ in CDCl₃): 32.8 (t, ${}^{2}J_{CF} = 22$ Hz, <u>C</u>H₂CH₂Im), 38.9 (t, ${}^{3}J_{CF} = 5$ Hz, <u>C</u>H₂Im), 118.7 (s, <u>C</u>₅-Im), 130.3 (s, <u>C</u>₄-Im), 137.2 (s, <u>C</u>₂-Im); ${}^{19}F$ NMR (282MHz, δ in CDCl₃ and C₆F₆): -83.59 (t, J_{FF} = 10 Hz, C<u>F</u>₃), -118.42 (m, 2F), -130.88 (m, 2F). IR (nujol): v 3379 (br), 1511 (m), 1360(m), 1289 (m), 1235 (s), 1136 (s), 1110 (s), 1082 (s), 1011 (m).

4.2.15. 1-(1,1,1,2,2,3,3,4,4-Nonafluoro-5-pentyl) imidazole (4c)

In glove box, a 15 mL pressure tube was charged with triflate **3c** (0.593 g, 1.50 mmol), imidazole (0.317 g, 4.65 mmol) in ethyl acetate (10 mL). The pressure tube was closed and heated at 80°C oil bath for 24 h. White solid was formed. Crude product was purified by silica column chromatography, eluted with DCM/MeOH (10:1 v/v) to yield a yellow oil (0.224 g, 0.746 mmol, 50%). ¹H NMR (600 MHz, δ in TMS): 4.60 (t, ³*J*_{HF} = 15 Hz, C*H*₂Im), 7.01 (s, 1H, C₄-Im), 7.14 (s, 1H, C₅-Im), 7.56 (s, 1H, C₂-Im). ¹³C{¹H}-NMR (151 MHz, δ in TMS): 46.4 (t, ²*J*_{CF} = 24 Hz, *C*H₂Im), 120.6 (s, *C*₅-Im), 130.3 (s, *C*₄-Im), 138.6 (s, *C*₂-Im); ¹⁹F NMR (282MHz, δ in CDCl₃ and C₆F₆): -83.98 (t, *J*_{FF} = 10 Hz, C*F*₃), -120.77 (m, 2F), -126.99 (m, 2F), -129.05 (m, 2F)). IR (nujol): v 3372 (br), 1654 (w, br), 1507 (m), 1362 (m), 1293 (m), 1238 (s), 1140 (s), 1117 (m), 1082 (m), 1030 (m).

4.2.16. 1-(1,1,1,2,2,3,3,4,4-Nonafluoro-6-hexyl) imidazole (4d)

In glovebox, 1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl iodide (2.012 g, 5.38 mmol) and imidazole (1.178 g, 17.3 mmol) in toluene (10 mL) was added to 25 mL schlenk tube. The mixture was stirred and heated at 80°C for 24 h. Solvent removed by reduced pressure. Dark yellow crude product was purified by silica column chromatography, eluted with DCM/MeOH (10:1, *v/v*), to yield a yellow oil (0.784 g, 2.50 mmol, 46%). ¹H NMR (600 MHz, δ in TMS): 2.62 (tt, 2H, ³*J*_{HF} = 18 Hz, ³*J*_{HH} = 8 Hz, C*H*₂CH₂Im), 4.48 (t, 2H, ³*J*_{HH} = 8 Hz, CH₂Im), 6.97 (s, *C*₅-Im), 7.13 (s, *C*₄-Im), 7.55 (s, *C*₂-Im); ¹³C{¹H} NMR (151 MHz, δ in TMS): 33.2 (t, ²*J*_{CF} = 22 Hz, *C*H₂CH₂Im), 39.0 (t, ³*J*_{CF} = 6 Hz, *C*H₂Im), 118.7 (s, *C*₅-Im), 130.6 (s, *C*₄-Im), 137.3 (s, *C*₂-Im); ¹⁹F NMR (375 MHz, δ in CDCl₃ and C₆F₆): --84.15 (t, *J*_{FF} = 10 Hz, C*F*₃), -117.68 (m, 2F), -127.57 (m, 2F), -129.18 (m, 2F).). IR (nujol): v 3371 (br), 1511 (m), 1358 (m), 1235 (s), 1184 (s), 1121 (s), 1082 (m), 1031 (m).

4.2.17. 1,3-Bis(1,1,1,2,2,3,3-heptafluoro-4-butyl)imidazolium triflate (5a)

Under N₂ atmosphere, triflate **3a**, (0.311 g, 0.936 mmol) in acetonitrile (2 mL) was added to imidazole **4a** (0.134 g, 0.533 mmol) in acetonitrile (3 mL) in 25 mL schlenk flask. The mixture was stirred and heated at 80°C oil bath for 80 h. Solvent removed under reduced pressure, precipitated in CHCl₃ (10 mL). Crude product was filtered and recovered in acetone (10 mL). Solvent removed by rotary evaporator to yield white solid. Product was recrystallised in n-hexane/ethyl acetate (20:1, *v/v*) (90.7 mg, 0.156 mmol, 29%). ¹H NMR (600 MHz, δ in (CD₃)₂CO): 5.72 (t, 4H, ³*J*_{HF} = 16 Hz, C*H*₂), 8.22 (d, 2H, ³*J*_{HH} = 2 Hz, C₄- and C₅-proton Im), 9.83 (s, 1H, C₂-proton Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 49.1 (t, ²*J*_{CF} = 22 Hz, *C*H₂), 121.0 (q, ¹*J*_{CF} = 321 Hz, *C*F₃), 126.2 (s, *C*₄ and *C*₅-Im), 141.9 (s, *C*₂-Im); ¹⁹F NMR (282 MHz, δ in (CD₃)₂CO and C₆F₆): -79.41 (s, C*F*₃), -81.80 (t, *J*_{FF} = 10 Hz, C*F*₃), -118.92 (m, 2F), -128.08 (m, 2F).). IR (KBr): v 3451 (w, br), 3128 (w, br), 1628 (w, br), 1574 (w), 1357 (m), 1279 (s), 1249 (s), 1226 (s), 1192 (m), 1129 (m), 1033 (m). C₁₂H₇F₁₇N₂O₃S Calc. C 24.75, H 1.21, N 4.81; CHN analysis, C 24.96, H 1.193, N 4.91.

4.2.18. 1,3-Bis(1,1,1,2,2,3,3-heptafluoro-5-pentyl)imidazolium iodide (5b)

Under N₂ atmosphere, 1,1,1,2,2,3,3-Heptafluoro-5-iodopentane (0.485 g, 1.5 mmol) and imidazole **4b** (0.264 g, 1 mmol) in toluene (7 mL) were added into 10 mL pressure tube. The mixture was stirred and heated at 110°C for 144 h. The mixture was filtered and the solid recovered by dissolving in acetone. Solvent was removed by rotary evaporator to yield yellow solid (0.308 g, 0.524 mmol, 52%). ¹H NMR (600 MHz, δ in (CD₃)₂CO): 3.21 (m, 4H, C<u>H</u>₂C₄F₉), 4.92 (t, 2H, ³J_{HF} = 7 Hz), 8.11 (d, 2H, ³J_{HH} = 2 Hz, C₄- and C₅-proton Im), 9.97 (s, 1H, C₂-proton Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 31.8 (t, ²J_{CF} = 22 Hz, <u>C</u>H₂), 43.1 (t, ³J_{CF} = 5 Hz), 124.0 (s, <u>C</u>₄ and <u>C</u>₅-Im), 139.1 (s, <u>C</u>₂-Im); ¹⁹F NMR (282 MHz, δ in (CD₃)₂CO and C₆F₆): -81.66 (t, J_{FF} = 10 Hz, C<u>F</u>₃), -115.64 (m, 2F), -128.88 (m, 2F). IR (KBr): v 3455 (w, br), 3053 (w, br), 1626 (w, br), 1574 (w), 1355 (m), 1227 (s), 1174 (s), 1119 (s), 1045 (w), 1026 (w).

4.2.19. 1,3-Bis(1,1,1,2,2,3,3,4,4-nonafluoro-5-pentyl) imidazolium triflate (5c)

In glovebox, a 25 mL pressure tube was charged with triflate **3c** (0.223 g, 0.583 mmol) and imidazole **4c** (0.159 g, 0.530 mmol) in toluene (5 mL). The tube was sealed and heated in 110°C oil bath for 130 h. Crude product white solid was formed and filtered off. The crude product was further washed with toluene (3 x 10 mL) and filtered. Solvent was removed *in vacuo* to yield white solid (0.108 g, 0.158 mmol, 29.8%). ¹H NMR (600 MHz, δ in (CD₃)₂CO): 5.67 (t, 4H, ³*J*_{HF} = 16 Hz, C*H*₂lm), 8.16 (d, 2H, ³*J*_{HH} = 2 Hz, C₄- and C₅-proton Im), 9.80 (s, 1H, C₂-proton Im); ¹³C{¹H}-NMR (151 MHz, δ in (CD₃)₂CO): 46.9 (t, <u>C</u>H₂Im), 119.5 (q, ¹*J*_{CF} = 320 Hz, <u>C</u>F₃), 123.9 (s, <u>C</u>₄ and <u>C</u>₅-Im), 139.1 (s, <u>C</u>₂-Im). ¹⁹F NMR (282MHz, δ in (CD₃)₂CO and C₆F₆): -79.34 (s, C<u>F</u>₃), -82.08 (t, *J*_{FF} = 10 Hz, C<u>F</u>₃), -118.16 (m, 2F), -124.54 (m, 2F), -127.05 (m, 2F). IR (KBr): v 3451 (w, br), 3047 (w, br), 1603 (w, br), 1571 (w), 1360 (m), 1258 (s), 1227 (s), 1172 (m), 1137 (s), 1031 (m).

4.2.20. 1,3-Bis(1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl)imidazolium iodide (5d)

Under N₂ atmosphere, 1,1,1,2,2,3,3,4,4-ronafluoro-6-hexyl iodide (0.561 g, 1.5 mmol) and imidazole **4d** (0.314 g, 1 mmol) in toluene (8 mL) were added into 25 mL schlenk tube, the mixture was stirred and heated at 110°C for 200 h. White solid suspended in the solution and filtered off by canular filtration. The crude product was washed with toluene (3 x 10 mL), solvent was filtered off again. Residual solvent was removed *in vacuo* to yield yellow solid (0.337 g, 0.490 mmol, 49.0%). ¹H NMR (600MHz, δ in CD₃CN): 2.89 (m, 4H, C<u>H</u>₂C₄F₉), 4.59 (t, 4H, ³J_{HH} = 3 Hz, C<u>H</u>₂Im), 7.60 (d, 2H, ³J_{HH} = 2 Hz, C₄- and C₅-proton Im), 9.05 (s, 1H, C₂-proton Im); ¹³C{¹H} NMR (151 MHz, δ in CD₃CN): 31.9 (t, ²J_{CF} = 22 Hz, <u>C</u>H₂), 43.1 (t, ³J_{CF} = 5 Hz), 124.1 (s, <u>C</u>₄ and <u>C</u>₅-Im), 138.1 (s, <u>C</u>₂-Im); ¹⁹F NMR (δ in CD₃CN and C₆F₆): -82.28 (tt, ³J_{FF} = 10 Hz, ⁴J_{FF} = 3 Hz, C<u>F</u>₃), -115.07 (m, 2F), -125.48 (m, 2F), -127.04 (m, 2F). IR (KBr): v 3454 (w, br), 3047 (w, br), 1615 (w, br), 1570 (w), 1357 (m), 1225 (s), 1134 (s), 1014 (m).

4.2.21. 1-(1,1,1,2,2,3,3-Heptafluorobutyl)-3-(1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl) imidazolium triflate (**5e**)

Under N₂ atmosphere, triflate **3a** (0.273 g, 0.822 mmol) and imidazole **4d** (0.257 g, 0.818 mmol) in toluene (8 mL) were added into 25 mL schlenk tube. The mixture was stirred and heat at 110° C for 200 h. Yellow oily solid was formed and

filtered off by canular filtration. The crude product was washed with toluene (3 x 10 mL) and the solvent was filtered off again. Residual solvent was removed *in vacuo* to yield brown oil (0.125 g, 0.190 mmol, 23.6%). ¹H NMR (600 MHz, δ in (CD₃)₂CO): 3.18 (tt, 4H, ³*J*_{HH} = 7 Hz, ³*J*_{HF} = 19 Hz, C*H*₂C₄F₉), 4.95 (t, 4H, ³*J*_{HH} = 7 Hz, C*H*₂CH₂C4F₉), 5.58 (t, 4H, ³*J*_{HF} = 16 Hz), 8.04 (s, C₅-Im), 8.15 (s, C₄-Im), 9.61 (s, C₂-Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 31.0 (t, ²*J*_{CF} = 21 Hz, C*H*₂C₄F₉), 43.0 (t, ³*J*_{CF} = 5 Hz, C*H*₂CH₂C4F₉), 48.2 (t, ²*J*_{CF} = 22 Hz, C*H*₂C₃F₇), 121.6 (q, ¹*J*_{CF} = 321 Hz, SO₂C*F*₃), 124.2 (s, C₅-Im), 125.3 (s, C₄-Im), 139.9 (s, C₂-Im); ¹⁹F NMR (282 MHz, δ in (CD₃)₂CO) and C₆F₆): -79.42 (s, C*F*₃), -81.89 (t, *J*_{FF} = 10 Hz, Heptafluoro-C*F*₃), -82.28 (t, *J*_{FF} = 10 Hz, Nonafluoro-C*F*₃), -115.03 (m, 2F), -119.11 (m, 2F), -125.42 (m, 2F), -127.05 (m, 2F), -128.22 (m, 2F).

4.2.22. 1-(1,1,1,2,2,3,3-Heptafluoropentyl)-3-(1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl) imidazolium iodide (**5***f*)

Under N₂ atmosphere, imidazole (**4b**, 0.117 g, 0.442 mmol) and 1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl iodide (0.182 g, 0.486 mmol) in toluene (10 mL) were added into 15 mL pressure tube, the mixture was stirred and heated at 110°C for 72 h. Yellow oily solid was suspended in the solution and filtered off by canular filtration. The crude product was washed with toluene (3 x 10 mL) and the solvent was filtered off again. Residual solvent was removed *in vacuo* to yield brown oil (0.107 g, 0.168 mmol, 38%). ¹H NMR (600 MHz, δ in (CD₃)₂CO): 3.20 (m, 4H, C<u>H</u>₂CF₂), 4.91 (2 sets of t, 4H, ³J_{HF} = 7 Hz, C<u>H</u>₂Im), 8.13 (s, <u>C</u>₄ and <u>C</u>₅-Im), 9.95 (s, <u>C</u>₂-Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 31.5 (2 sets of t, ²J_{CF} = 21 Hz, <u>C</u>H₂CF₂), 42.7 (t, ³J_{CF} = 5 Hz, <u>C</u>H₂CH₂CF₂), 123.7 (s, <u>C</u>₄ and <u>C</u>₅-Im), 138.7 (s, <u>C</u>₂-Im); ¹⁹F NMR (282 MHz, δ in (CD₃)₂CO) and C₆F₆): -81.71 (t, J_{FF} = 10 Hz, Heptafluoro-C<u>F</u>₃), -82.22 (t, J_{FF} = 10 Hz, Nonafluoro-C<u>F</u>₃), -114.87 (m, 2F), -115.66 (m, 2F), -125.42 (m, 2F), -125.23 (m, 2F), -126.96 (m, 2F), -128.76 (m, 2F).

4.2.23. Bis-[1,3-bis(1,1,1,2,2,3,3-Heptafluoro-5-pentyl)imidazol-2-ylidene] diiodopalladium(II) (**6a**)

Under N₂ atmosphere, compound **5b** (0.111 g, 0.189 mmol), Pd(OAc)₂ (0.0202 g, 0.0898 mmol) and Cs₂CO₃ (0.0760 g, 0.233 mmol) in THF (10 mL) were stirred and heated at 65° C, in 25 mL schlenk tube for 15 h. The mixture was filtered

through a pad of alumina. Solvent removed and dried by rotary evaporator to yield yellow solid (0.0986 g, 0.0769 mmol, 85.1%). ¹H NMR (600MHz, δ in d-acetone): 3.13 (m, 4H, ${}^{3}J_{HH} = 8$ Hz, ${}^{3}J_{HF} = 19$ Hz, $C\underline{H}_{2}C_{3}F_{7}$), 4.85 (t, 4H, ${}^{3}J_{HF} = 8$ Hz), 7.54 (s, 2H, C₄- and C₅-proton Im); ${}^{13}C{}^{1}H$ NMR (151 MHz, δ in (CD₃)₂CO): 31.9 (t, ${}^{2}J_{CF} = 22$ Hz, $\underline{C}H_{2}C_{3}F_{7}$), 43.6 (t, ${}^{3}J_{CF} = 4$ Hz, $\underline{C}H_{2}$ Im), 123.6 (s, \underline{C}_{4} and \underline{C}_{5} -Im), 169.0 (s, \underline{C}_{2} -Im); ${}^{19}F$ NMR (376 MHz, δ in (CD₃)₂CO and C₆F₆): -81.67 (t, $J_{FF} = 10$ Hz, $C\underline{F}_{3}$), -115.67 (m, 2F), -128.88 (m, 2F). IR (KBr): v 3448 (w, br), 3120 (w, br), 1355 (m), 1222 (s), 1177 (s), 1115 (s). C₂₆H₂₂F₂₈I₂N₄Pd Calc. C 24.35, H 1.73, N 4.37; CHN analysis, C 25.51, H 1.77, N 3.82.

4.2.24. Bis-[1,3-bis(1,1,1,2,2,3,3,4,4-nonafluoro-6-hexyl)imidazol-2-ylidene] diiodo palladium(II) (**6b**)

Under N₂ atmosphere, compound **5d** (0.131 g, 0.190 mmol), Pd(OAc)₂ (0.0203 g, 0.0906 mmol) and Cs₂CO₃ (0.0738 g, 0.226 mmol) in THF (15 mL) were stirred and heated at 65°C, in 25 mL schlenk tube for 15 h. The mixture was filtered through a pad of alumina. Solvent removed and dried by rotary evaporator to yield yellow solid (0.123 g, 0.0830 mmol, 91.8%). ¹H NMR (600MHz, δ in (CD₃)₂CO): 3.15 (m, 4H, ³J_{HH} = 8 Hz, ³J_{HF} = 19 Hz, C<u>H</u>₂C₄F₉), 4.87 (t, 4H, ³J_{HF} = 8 Hz), 7.56 (s, 2H, C₄- and C₅-proton Im); ¹³C{¹H} NMR (151 MHz, δ in (CD₃)₂CO): 31.9 (t, ²J_{CF} = 22 Hz, <u>C</u>H₂C₃F₇), 43.4 (t, ³J_{CF} = 4 Hz, <u>C</u>H₂Im), 123.5 (s, <u>C</u>₄ and <u>C</u>₅-Im), 168.72 (s, <u>C</u>₂-Im); ¹⁹F NMR (376 MHz, δ in (CD₃)₂CO and C₆F₆): -82.30 (t, J_{FF} = 10 Hz, C<u>F</u>₃), -114.91(m, 2F), -125.34 (m, 2F), -127.02 (m, 2F). IR (KBr): v 3448 (w, br), 3103 (w, br), 1355 (m), 1227 (s), 1134 (s). C₃₀H₂₂F₃₆I₂N₄Pd Calc. C 24.30, H 1.50, N 3.78; CHN analysis, C 25.11, H 1.83, N 4.52.

4.3 Example of partition coefficient measurement

An 8 mL vial was charged with **2a** (0.0254 g, 0.04 mmol) and perfluoro(methylcyclohexane) (CF₃C₆F₁₁, 2.00 mL). Toluene (2.00 mL) was added and the mixture was vigorously shaken for 2 minutes. The vial was kept at 25°C for 12 hours. The aliquots (each phase 0.5 mL) were taken from both phases. The internal standard hexafluorobenzene (C₆F₆) was added to above aliquots (CF₃C₆F₁₁: 0.8674 g solution; 0.010 g, 0.0052 mmol C₆F₆; toluene: 0.4468 g solution; 0.009 g, 0.0048mmol C₆F₆). Then put in d⁶-DMSO capillary and the sample was analysed by

¹⁹F NMR (integration of CF₃ signal against C₆F₆). The procedure was triplicate and applied 2.0/0.5 scale factor gives an average partition coefficient of 25:75, a total mass recovery of 96%).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.