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Imidazolium Based Fluorous N-Heterocyclic Carbenes as Effective and Recyclable Organocatalysts for Redox Esterification

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Abstract: A series of new highly fluorophilic ionic liquids (*f* > 110) was synthetized from 3-iodopropyltris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane and N-alkyl imidazoles, followed by anion exchange. N-heterocyclic carbenes generated *in situ* from obtained imidazolium salts were employed to catalyze redox esterification (*umpolung*) of cinnamaldehyde with alcohols. The most effective N-methyl derivative with iodide as a counter anion was studied in detail with respect to the optimization of reaction conditions, substrate scope and recyclability. Recovery of the precatalyst was achieved using either fluorous extraction or performing the reaction in suitable fluorous biphase system with direct recycling of the fluorinated precatalyst phase. For both tested options, the catalytic activity did not significantly decrease within 5 subsequent cycles. The redox esterification was shown to proceed also in supercritical carbon dioxide ($scCO_2$) as an alternative solvent where the activity of the fluorinated catalyst was also superior to the nonfluorinated model, while retaining the benefit of easy recycling.

Introduction

N-heterocyclic carbenes (NHCs) have rapidly gained interest in many areas of chemical research,[1] particularly as excellent ligands in metal-based catalytic reactions[2] but also as efficient organocatalysts for a wide range of chemical transformations and processes.[3] The ability of NHCs to induce the inversion of polarity (*umpolung*) in the structure of aldehydes, described first by Breslow,[4] was later utilized in several transformations e.g. benzoin condensation[5] or Stetter reaction.[6] In the case of α,β-unsaturated aldehydes, homoenolates are formed on the reaction with NHCs *via* transfer of the nucleophilic character to β-position, which was initially exploited for the synthesis of γ-butyrolactones[7] and redox esterification of enals producing saturated esters.[8] Further research was focused on the reactivity of homoenolates towards different nucleophiles[9] and on targeting the observed byproducts such as unsaturates esters[10] or γ-lactones[11] as main products by modification of reaction conditions and NHC type. Steric demands of the substituent on nitrogen were identified as a key factor controlling the reversibility of formation of the reactive species (Breslow intermediate) and thus affecting the NHC performance.[12]

Although many aspects of NHC catalyzed umpolung reactions were studied and optimized, the methodology of catalyst separation stayed somewhat aside. Increasing the sustainability of organocatalytic processes and overcoming the major drawback of organocatalysis, i. e. high catalyst loading, by means of catalyst separation and recycling is still a challenge. Inesi et al. applied electrogenerated NHCs as catalysts for the redox esterification of enals, thus avoiding the use of any base and lowering the number of reaction components.[13] Up to now, the effort focused on the application of separable (pre)catalysts was limited to benzoin condensation or Stetter reaction. Chen et al. published benzoin self-coupling of furfural catalyzed by polystyrene[14] or inorganic silica[15] supported azolium salts paired with an acetate counterion. Poly(ionic liquid)s based on imidazolium hydrogen carbonate were studied as precatalysts for benzoin condensation of benzaldehyde.[16] Active NHCs released from Ag(I)-crosslinked single-chain nanoparticles were tested in the same benchmark reaction.[17] Products of parallel Stetter reactions catalyzed by gel-supported thiazolium iodide prepared via ROMPolymerization were obtained in high yields and excellent purities after minimal purification.[18]

The use of supercritical CO_2 ($scCO_2$) as an alternative green solvent in different reactions is receiving considerable attention due to its numerous advantageous properties.[19] Surprisingly, in contrast to many reports on transition metal catalysis in $scCO_2$, studies dealing with organocatalysis in this environmentally friendly medium are extremely rare.[20] This is probably due to low solubility of polar organocatalysts in nonpolar $scCO_2$.

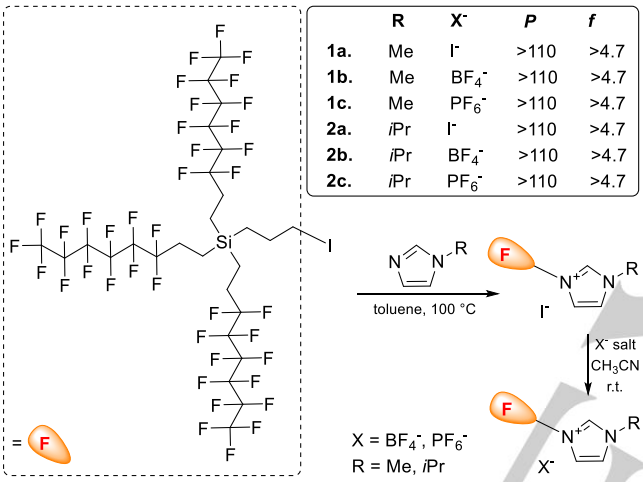
In the course of our ongoing studies focused on tagging of organic and organometallic compounds by fluorous chains[21] we have recently synthesized a new type of fluorinated imidazolium ionic liquid.[22] Here we report the synthesis, properties and catalytic activity of several new organocatalysts bearing large fluorous substituent in the redox esterification of cinnamaldehyde, together with a suitable recycling procedure, which is, in contrast to recyclable polymer supported catalyst systems, based on a unique behavior of highly fluorinated substances.[23] As a second benefit, the large fluorophilic domain should also increase the solubility of the tagged organocatalysts in $scCO_2$,[24] so their performance was tested also in this nonconventional solvent. To our best knowledge, this is the first use of flourous NHCs as catalysts for umpolung reaction.

10.1002/ejoc.202000273

FULL PAPER

Results and Discussion

Unsymmetrically substituted imidazolium salts containing fluorous moiety and methyl or isopropyl substituent were prepared analogously to recently described butyl derivative.[22] As shown in Scheme 1, this procedure involved quarternization of imidazoles with silicon-branched fluorous tag containing iodopropyl group. Compounds **1a** and **2a** were obtained as waxy solids soluble in fluorinated as well as in polar protic (MeOH, EtOH) and aprotic (DMSO, MeCN) solvents. Compounds **1b, c** and **2b, c** were prepared by anion exchange. The reaction of **1a** with $NaBF_4$ did not proceed to completion so $AgBF_4$ was used to obtain tetrafluoroborates. Hexafluorophosphate anion was introduced by the reaction of **1a** or **2a** with NH_4PF_6. The new ionic liquids **1a-c** and **2a-c** show the highest fluorophilicity compared to literature data[25] even though they contain only cca 60 % of fluorine. This fact makes them ideal candidates for application in fluorous biphasic catalysis.



	R	X⁻	*P*	*f*
1a.	Me	I⁻	>110	>4.7
1b.	Me	BF_4^-	>110	>4.7
1c.	Me	PF_6^-	>110	>4.7
2a.	*i*Pr	I⁻	>110	>4.7
2b.	*i*Pr	BF_4^-	>110	>4.7
2c.	*i*Pr	PF_6^-	>110	>4.7

Scheme 1. Synthesis, fluorous partition coefficient *P* and fluorophilicity *f* of fluorous imidazolium salts.

Catalytic activity of newly prepared compounds was tested in redox esterification of cinnamaldehyde (Table 1). Preliminary experiments were performed in inert atmosphere with toluene as a solvent and benzyl alcohol as a nucleophile. First, we examined the effect of anion on catalytic activity using rather high loading (20 mol %). After 1 hour the conversion of aldehyde was 77, 28 and 36 % for **1a**, **1b** and **1c**, respectively (Table 1, Entries 1-3), which corresponds quite well to the trend of carbene stability as a function of the anion observed by Feroci et al. for electrogenerated carbenes.[26] When comparing the iodides, methyl substituted fluorinated carbene proved to be more active than carbene generated from a nonfluorinated model 1-ethyl-3-methylimidazolium iodide ($[EMIM]^+I^-$; Table 1, Entry 7; Figure 1a), which in turn was much more efficient than isopropyl derivative **2a**. The addition of excess phenol as a source of protons for the catalytic cycle, previously shown to improve the outcome of this reaction[8a] led in our case only to a slight increase in the reaction rate when sterically hindered 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used, whereas the addition of 2 equiv of PhOH actually resulted in its decrease (Figure 1b). Since the presence of phenols did not improve the final yield of the target ester, next experiments were done without any additive unless otherwise stated.

As the precatalyst **1a** showed the highest activity in preliminary tests, it was used for further optimization, recycling tests and substrate screening. We found that decreasing the precatalyst loading from 20 to 10 mol % had a negligible effect on the reaction rate while the yield of **3a** increased; further decrease of the precatalyst loading to 5 mol % led to slight decrease in the reaction rate (Figure 1c). Presumably, at higher concentrations NHCs are stabilized due to intermolecular interactions and so the concentration of catalytically active species is lower than it would correspond to precatalyst loading.[27]

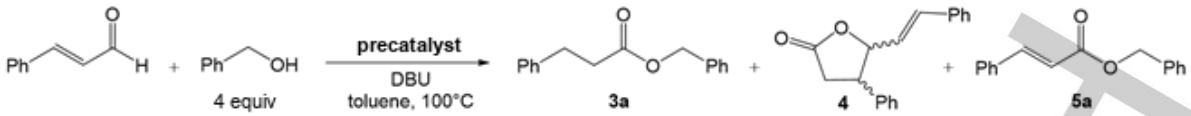
As depicted in scheme in Table 1, the saturated ester **3a** is not the sole product of the studied reaction. The formation of lactone **4**, a product of aldehyde dimerization, was associated with the onset of the reaction. Precatalysts of similar structure were recently shown to yield predominantly γ-lactones.[8b,10a] The second type of side product was identified as an unsaturated ester **5a**. Its emergence was ascribed to the presence of oxygen in the reaction mixture and this hypothesis was later confirmed by an experiment in oxygen atmosphere, where nearly equal amount of both **3a** and **5a** was observed, together with lower reaction rate (Table 1, Entry 13). This particularly interesting behavior is likely caused by high affinity of fluorous chains to oxygen[28] and it will be the subject of further experiments as this type of reaction was described to proceed with unsaturated aldehydes only in the presence of cocatalysts that are easily oxidized by molecular oxygen.[29]

To explore the scope of the catalyst, we employed several types of alcohols as substrates in the redox esterification of cinnamaldehyde with **1a** as the precatalyst (Figure 2; Table 2). All reactions were let to proceed for 5 h with 10 mol % of **1a** and 20 mol % of DBU, the products were identified by GC-MS and their amount and the conversion of cinnamaldehyde were determined by CG-FID with respect to the internal standard. Quantitative conversions and yields comparable to benzyl alcohol were obtained in case of all tested primary monofunctional alcohols, allyl alcohol proved to be an excellent substrate giving 91 % yield. The only detected side products were the lactone **4** (4 – 7 %) and unsaturated esters (1 – 5 %); however, the difference between the conversion and overall yield points to the presence of higher molecular weight impurities (presumably oligomers of cinnamaldehyde) which could not be isolated and identified. Secondary alcohols were slightly less reactive while tertiary alcohol did not react at all; cyclic alcohols gave better yields than acyclic ones. The amount of detected side products was lower than in case of primary alcohols, however the discrepancy between the conversion and overall yield increased which points to greater extent of aldehyde oligomerization. The sensitivity of the reaction to steric characteristics of the substrates was well demonstrated in the reaction with borneol; whereas the starting *endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol contained 11 % of *exo*-isomer according to GC-FID, the amount of *exo*- ester in the product mixture was only 3 %. Concerning halogenated alcohols, their use as substrates is limited by their reactivity towards DBU, which rules out iodides and bromides. 4-chloro-1-butanol gave no product and aldehyde was recovered almost quantitatively. The absence of any reaction implies the quarternization of the base which in turn cannot deprotonate the imidazolium salt and form the active catalyst. On the other hand, dichloroethanol and tetrafluoropropanol provided the target esters in moderate yield, in spite of lower reaction rate; the selectivity was comparable to the reaction with primary alcohols.

10.1002/ejoc.202000273

FULL PAPER

Table 1. Screening of precatalysts and reaction conditions for model redox esterification of cinnamaldehyde with benzyl alcohol.



Entry	Precatalyst	Loading [mol %]	Solvent	Time [h]	Conversion [%][a]	Yield **3a** / **4** / **5a** [%][a]
1	**1a**	20	toluene	1	77	54 / 7 / 3
2	**1b**	20	toluene	1	28	20 / 3 / 3
3	**1c**	20	toluene	1	36	27 / 3 / 1
4	**2a**	20	toluene	1	12	9 / 3 / 0.5
5	**2b**	20	toluene	1	6	4 / 2 / 0.3
6	**2c**	20	toluene	1	12	8 / 2 / 0.5
7	$[EMIM]^+I^-$	20	toluene	1	44	27 / 9 / 4
8	**1a**[b]	20	toluene	1	53	41 / 6 / 2
9	**1a**[c]	20	toluene	1	87	64 / 9 / 2
10	**1a**	10	toluene	1	77	54 / 8 / 2
11	**1a**	5	toluene	1	54	41 / 5 / 1
12	**1a**	20	toluene	5	100	77 / 9 / 10
13	**1a**[d]	20	toluene	5	62	28 / 0 / 34
14	**1a**	20	toluene/PFMC (4:1)	5	0	0 / 0 / 0
15	**1a**	20	toluene/$(C_4F_9)_3N$ (4:1)	5	53	25 / 5 / 4
16	**1a**	20	toluene/FC-770 (4:1)	5	80	39 / 10 / 2
17	**1a**[e]	20	toluene/FC-770 (4:1)	5	88	53 / 10 / 2

[a] determined by GC; [b] 2 equiv of PhOH were added; [c] 2 equiv of BHT were added; [d] 0.11 MPa O_2; [e] recycled precatalyst from Entry 16.

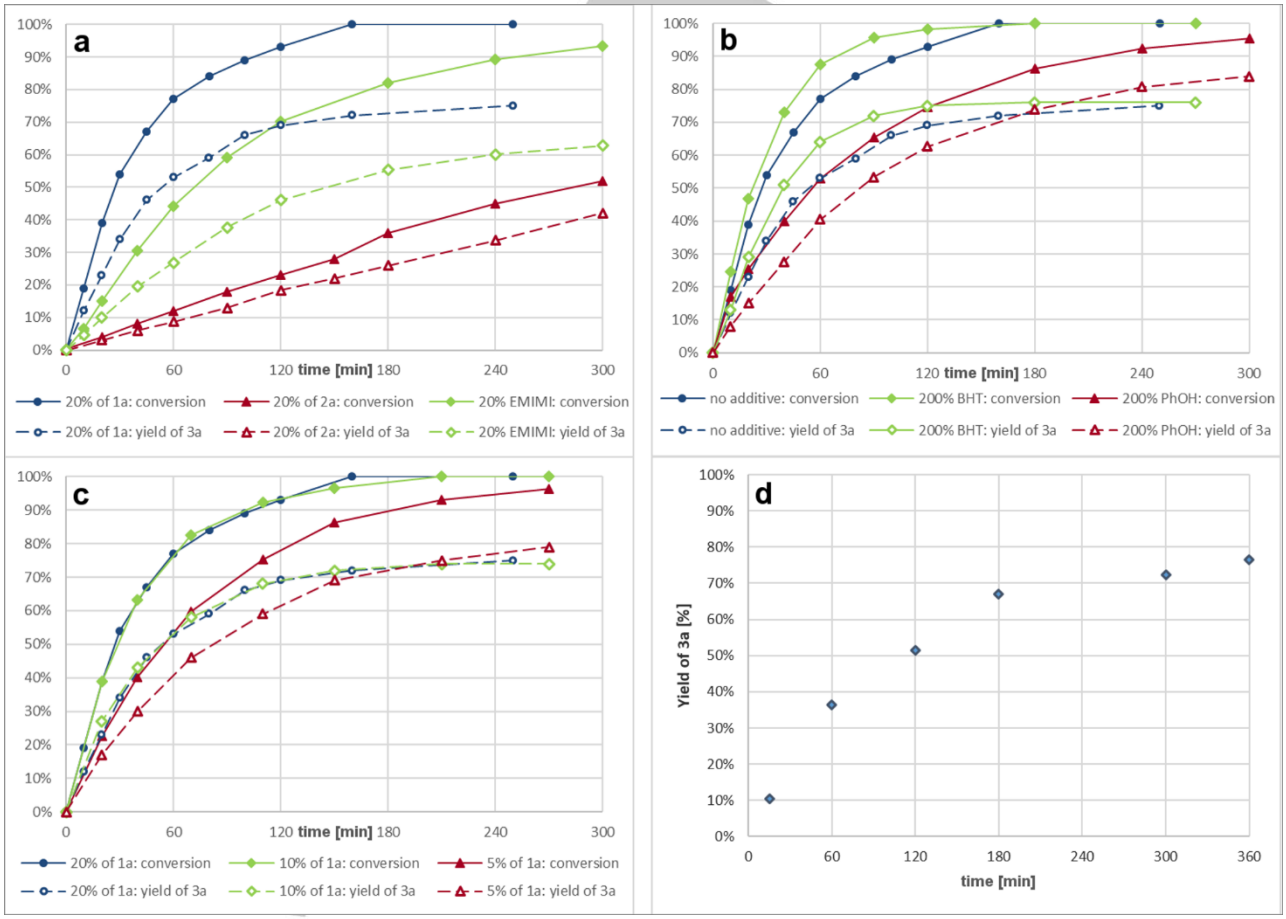


Figure 1. Time-course of redox esterification of cinnamaldehyde with benzyl alcohol; (a) influence of catalyst structure: comparison of catalysts **1a**, **2a** and $[EMIM]^+I$; (b) impact of additional proton source on performance of catalyst **1a** (no additive, BHT, PhOH); (c) influence of catalyst loading (20, 10 and 5 mol % of **1a**); (d) progress of reaction catalyzed by **1a** in $scCO_2$ (data points from separate experiments).

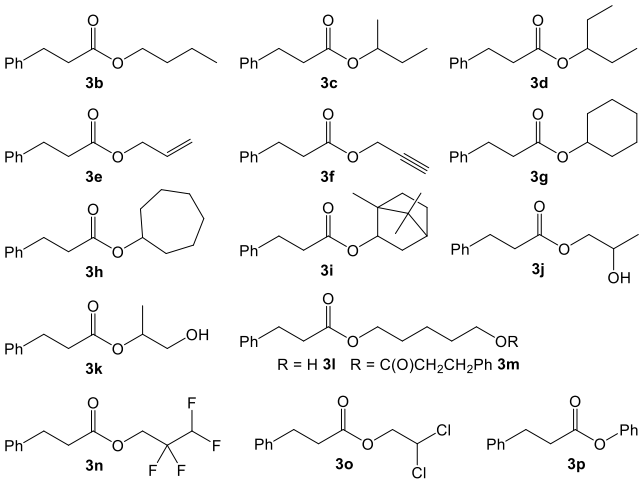


Figure 2. Target products of redox esterification of cinnamaldehyde with different alcohols.

Table 2. Redox esterification of cinnamaldehyde with different alcohols.[a]

Entry	Substrate	Conversion [%][b]	Satur. ester	Yield **3** / **4** / **5** [%][b]
1	1-butanol	100	**3b**	78 / 5 / 3
2	2-butanol	100	**3c**	60 / 0 / 0
3	3-pentanol	99	**3d**	55 / 0 / 1
4	*t*-butanol	0	-	0 / 0 / 0
5	allyl alcohol	100	**3e**	91 / 5 / 1
6	propargyl alcohol	100	**3f**	78 / 7 / 6
7	cyclohexanol	100	**3g**	64 / 3 / 2
8	cycloheptanol	89	**3h**	68 / 3 / 3
9	borneol	100	**3i**	71 / 2 / 1
10	borneol[c,d]	79	**3i**	26 / 1 / 1
11	borneol[d]	91	**3i**	41 / 0 / 0
12	borneol[d,e]	92	**3i** + **3p**	4 + 72 / 7 / 0
13	1,2-propandiol	69	**3j** + **3k**	26 + 11 / 5 / 0
14	1,2-propandiol[c]	78	**3j** + **3k**	27 + 12 / 6 / 0
15	1,5-pentandiol[c,f]	100	**3l** + **3m**	16 + 50 / 3 / 3[g]
16	1,5-pentandiol	92	**3l** + **3m**	39 + 2 / 17 / 0
17	1,5-pentandiol[c]	93	**3l** + **3m**	37 + 1 / 11 / 0
18	2,2,3,3-tetrafluoro-1-propanol	65	**3n**	44 / 8 / 4
19	2,2-dichloro-1-ethanol	70	**3o**	49 / 6 / 8
20	phenol	66	**3p**	56 / 5 / 1

[a] Conditions: 10 mol % of **1a**, 20 mol % of DBU, 4 equiv of alcohol, 100 °C, 5h. [b] Determined by GC. [c] 2 equiv of BHT were added. [d] 1 equiv of alcohol. [e] 2 equiv of PhOH were added. [f] 0.5 equiv of alcohol. [g] Yield of **5m** (monounsaturated diester).

The reaction with excess diols gives predominantly the monoesters while the decrease of amount of 1,5-pentandiol to 0.5 equiv relative to the aldehyde in the presence of BHT leads to the preferential formation of diester **3m**. In case of unsymmetrical 1,2-propandiol we were not able to distinguish between the regioisomers **3j** and **3k** from the mass spectra but we assume on the basis of general reactivity of primary and secondary alcohols that the primary isomer **3j** would be the more abundant one. The attempt to add BHT to the reaction mixture so as to promote the reaction with less reactive substrates was unsuccessful, the yields were at best the same as without this additive. Phenol itself cannot be used as such additive because in our system its reactivity is similar to that of aliphatic secondary alcohols (Table 2, Entry 20) and formation of a mixture of products can be expected. In fact, it seems that by contrast the secondary alcohol promotes the reactivity of phenol when both of them are present in the reaction mixture, as apparent from Entry 12. The addition of 2 equiv of phenol to the reaction of cinnamaldehyde and borneol in 1:1 ratio did increase the conversion and yield only with respect to the reaction with phenol, while the target ester **3i** was obtained in much lower yield (cf. Entry 11, 12 and 20 in Table 2).

We were particularly interested in the proposal of suitable protocol for catalyst recycling and its reuse in next reaction cycles under the conditions of fluorous biphase catalysis (FBC). Commonly used solvent system consisting of toluene and perfluoromethylcyclohexane (PFMC) proved to be unsuitable in our case because of low boiling point of PFMC (76 °C). On the other hand, PFMC can be used to quantitatively separate the precatalyst from the reaction mixture. By extraction with PFMC, **1a** was recycled and reused five times without the loss of activity.

From other tested FBC systems with suitable boiling point and miscibility properties, the smallest decrease of catalytic activity was found for the solvent system toluene:FC-770 (Table 1, Entry 16). Although the reaction proceeds at slightly lower temperature (declared b.p. of FC-770 is 90-98 °C) and the two phases are not fully miscible at the reflux temperature of the mixture, the conversion of the benchmark reaction was 80 % after 5 h. The fluorinated phase containing precatalyst was separated and reused in the subsequent cycle with even better outcome (Table 1, Entry 17). The slightly lower yield compared to the experiments in pure toluene can be due to lower availability of alcohol reagent in the fluorinated phase and thus higher propensity for formation of aldehyde oligomers. Lowering of the reaction temperature to 75 °C while extending the reaction time led to decrease of both yield and selectivity. The following set of recycling experiments was therefore conducted at FC-770 reflux temperature and the reaction time was set so as not to reach the full conversion to allow a straightforward comparison of the catalyst performance in particular runs. The yield of **3a** in the second and following cycles was again higher than in the first cycle and the conversion over 90 % was reached in 6 h with overall outcome 70 – 80 % according to GC (Table 3). No substrates or products are retained in the fluorinated catalytic phase after its separation, as it was demonstrated by changing the substrate from benzyl alcohol to cycloheptanol in the 6th catalytic cycle (Table 3, Entry 6). No contamination of the product mixture with benzyl alcohol or benzyl ester was observed; moreover the yield of cycloheptyl ester was similar to that obtained in pure toluene (cf. Table 2, Entry 8).

Table 3. Recycling of **1a** in the redox esterification of cinnamaldehyde in FBC system.[a]

Run	Substrate	Conversion [%][b]	Yield of **3a** / **4** / **5a** [%][b]
1	benzyl alcohol	94	53 / 13 / 3
2[c]	benzyl alcohol	100	64 / 9 / 7
3	benzyl alcohol	90	61 / 8 / 4
4	benzyl alcohol	92	62 / 9 / 3
5	benzyl alcohol	95	64 / 9 / 3
6	cycloheptanol	100	65[d]/ 4 / 2[e]

[a] Conditions: 20 mol % of **1a**, 20 mol % of DBU, 4 equiv of alcohol, 95 °C, toluene:FC-770 4:1, 6 h. [b] Determined by GC. [c] reaction time 7 h. [d] Yield of **3h**. [e] Yield of **5h**.

Since high fluorine content is known to increase the solubility of a substance in $scCO_2$, the prepared imidazolium salts should be good candidates for the application in this medium. The catalytic activity of **1a** in the redox esterification of cinnamaldehyde with benzyl alcohol was tested under various conditions and compared to that of nonfluorinated analog, $[BMIM]^+I^-$ (Table 4). As preliminary experiments showed lower reaction rate in $scCO_2$ than in conventional solvent, the catalyst loading was increased to 15 mol %. The effect of temperature on the reaction outcome was more pronounced in the case of $[BMIM]^+I^-$ than with **1a**, which is likely due to poor solubility of this nonfluorinated ionic liquid in $scCO_2$. Thus, both Eyring-type and solubility contributions can participate. At higher temperature, the ratio between the performance of $[BMIM]^+I^-$ and **1a** and also the purity of the obtained product is similar to the results obtained in toluene; relative activity of **2a** is low but somewhat higher than in organic solvents. The pressure also influences the reaction rate through changes in the solvation power (Entry 7). Interestingly, the reaction in $scCO_2$ is very sensitive to the type and structure of the base; except DBU the desired product was in much lower yield obtained only with potassium *tert*-butoxide (Entry 8), whereas in the presence of triethylamine, DIPEA or sodium ethanolate the reaction did not proceed. The progress of the reaction under optimized conditions (15 mol % of **1a**, 130 °C, 17 – 18 MPa) is shown in Figure 1d. The supercritical reaction setup did not allow for taking samples in the course of experiment, so each point represents a separate run under identical conditions, let to proceed for a specified time.

Table 4. Redox esterification of cinnamaldehyde in $scCO_2$.[a]

Entry	Precatalyst	Loading [mol %]	Temperature [°C]	Yield of **3a** [%][b]
1	**1a**	8	130	54
2	**1a**	10	130	60
3	**1a**	20	130	79
4	**1a**	15	100	19
5	**1a**	15	110	37
6	**1a**	15	130	72
7	**1a**[c]	15	130	61
8	**1a**[d]	15	130	14
9	$[BMIM]^+I^-$	15	100	5
10	$[BMIM]^+I^-$	15	110	30
11	$[BMIM]^+I^-$	15	130	52
12	**2a**	15	130	21

[a] Conditions: DBU (equimolar to precatalyst), 4 equiv of BnOH, 17 – 18 MPa, 5 h. [b] Determined by GC. [c] 13 MPa. [d] *t*-BuOK instead of DBU.

As apparent from Table 5, the redox esterification in $scCO_2$ is more substrate sensitive than when carried out in toluene (*cf*. Table 2); the addition of BHT leads to a slight increase of the reaction rate and yield. Clearly, physical properties, especially the polarity of substrates, play an important role in the supercritical reaction medium.

The stability of **1a** under supercritical conditions and its recyclability were evaluated in a series of consecutive experiments (Table 6). Similarly to the results in FBC system, slightly lower activity was observed in the first run. Although some fluctuations in conversion and yield were observed, there is no decreasing trend which would point to catalyst loss or degradation.

Table 5. Redox esterification of cinnamaldehyde with different alcohols in $scCO_2$, catalyzed by **1a**.[a]

Entry	Substrate	Product	Yield [%][b]
1	1-butanol	**3b**	30
2	1-butanol[c]	**3b**	40
3	1-butanol[d]	**3b**	46
4	cyclohexanol	**3g**	19
5	cyclohexanol[c]	**3g**	21

[a] Conditions: 15 mol % of **1a**, 15 mol % of DBU, 4 equiv of alcohol, 130 °C, 17 – 18 MPa, 5 h. [b] Determined by GC. [c] 1.5 equiv of BHT was added. [d] reaction time 12 h.

Table 6. Recycling of **1a** in the redox esterification of cinnamaldehyde with benzyl alcohol in $scCO_2$.[a]

Entry	Conversion [%][b]	Yield **3a** / **4** / **5a** [%][b]
1	76	60 / 5 / 8
2	83	71 / 3 / 5
3	92	78 / 4 / 7
4	96	51 / 3 / 7
5	97	65 / 3 / 6
6	86	72 / 3 / 14

[a] Conditions: 15 mol % of **1a**, 15 mol % of DBU, 4 equiv of alcohol, 130 °C, 17 – 18 MPa, 5 h. [b] Determined by GC.

Conclusion

We have shown a great potential of our fluorous tag for the synthesis of highly fluorophilic catalytically active ionic liquids. The introduced fluorinated domain increased the activity of NHCs generated from the corresponding imidazolium salts in the redox esterification of cinnamaldehyde with respect to nonfluorinated analog while at the same time it enabled facile separation of the precatalyst from the reaction mixture by means of fluorous extraction and its recycling without the loss of activity. The redox esterification employing the prepared fluorinated catalysts can also be carried out in fluorous biphase system or in $scCO_2$ with only a slight decrease of the reaction rate. Also in these systems the precatalyst is readily recovered and when reused, it preserves its activity for at least 5 cycles. The presented concept can be easily applied to the synthesis of other classes of ionic liquids to make them fluorophilic and recyclable. Beside this, the unexpected formation of considerable quantity of unsaturated ester under aerobic conditions opens up a question, whether it would be possible to exploit the known high affinity of the fluorinated materials to oxygen for the purpose of catalytic oxidative esterification of α,β-unsaturated aldehydes with molecular oxygen as the sole oxidant.

Experimental Section

General. All experiments were carried out in anhydrous conditions under an inert atmosphere of argon or nitrogen, using standard Schlenk or glove box techniques, unless otherwise stated. Solvents were dried by usual procedures, then distilled and kept under argon. $CDCl_3$, $CF_2ClCFCl_2$ and FC-84 (commercially available fluorocarbon liquid with average molecular weight 388 $g.mol^{-1}$ and b.p. 80 °C) were dried over molecular sieves and stored under argon. FC-770 (commercially

available fluorocarbon liquid with average molecular weight 399 g.mol^{-1} and b.p. 90 – 98 °C) was obtained as a kindly gift from 3M and used as received. (3-Iodopropyl)tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane was prepared as previously described.[21] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Acros Organics. Dioctyl phthalate, propargyl alcohol and 2,2-dichloro-1-ethanol were purchased from Sigma-Aldrich. Fluorinated chemicals were purchased from Apollo Scientific. Other chemicals were from laboratory stock and their purity was checked before use by GC-MS.

NMR spectroscopy. NMR spectra were measured on Bruker Avance 400 or Varian Inova 500 (^{1}H at 400.1/499.9 MHz; ^{13}C at 100.6/125.7 MHz; ^{29}Si {^{1}H} (inept technique) at 79.5 MHz; ^{19}F at 376.4 MHz) and ^{31}P at 361.95 MHz at 25°C. ^{1}H and ^{13}C chemical shifts (δ/ppm) are given relative to solvent signals (δ_H/δ_C: $CDCl_3$ 7.26/77.16; CD_3OD 3.31/49.00). ^{29}Si and ^{19}F spectra were referenced to external standards.

Mass spectrometry. HRMS spectra were measured on Bruker MicrOTOF-QIII instrument in ESI$^+$/ESI$^-$ (80 – 2000/30 – 1000 *m*/*z*, calibrated by sodium formate) or APCI$^+$ mode (50 – 2000 *m*/*z*, calibrated by Tuning mix APCITOF (Fluka)).

Gas chromatography. GC/FID and GC/MS analyses were performed on Agilent 6890 gas chromatograph equipped with DB-5MS column (30 m_0.2 mm_0.25 mm). Injector and detector temperatures were set at 260 °C and 300 °C, respectively. Helium was used as a carrier gas at a flow rate 1.61 mL/min. Oven temperature was set at 50 °C for 3 min and then programmed to 290 °C at a rate 10 °C/min. Quantitative data were calculated using Agilent MSD Chemstation D.02 from the FID peak areas assuming a linear response for the analytes and the internal standard dioctyl phthalate and applying relative response factors calculated from the molecular formula according to previously published method.[30] For cinnamaldehyde, benzyl 3-phenylpropanoate and benzyl cinnamate the results were corrected with respect to experimentally determined calibration curve relative to dioctyl phthalate.

1-Methyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium iodide (**1a**). (3-iodopropyl)tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (2.00 g, 1.62 mmol) was dissolved in toluene (12 mL), then *N*-methylimidazole (0.14 g, 1.70 mmol) was added and the mixture was stirred at 100 °C for 2 days. The reaction mixture was then cooled to 4 °C, organic layer was separated and the product layer was washed with toluene. Residual solvent was evaporated in vacuum. Yield 1.90 g (1.44 mmol, 89 %) of a honey-like compound. Compound **1a** was also prepared in a similar manner without a solvent; unreacted *N*-methylimidazole was evaporated in vacuum at 90 °C. Yield 2.10 g (1.59 mmol, 98 %). HRMS (ESI$^+$): Calcd. for $[C_{31}H_{24}F_{39}N_2Si]^+$ 1193.1080, found 1193.1082, (ESI$^-$): Calcd. for $[I]^-$ 126.9050, found 126.9054. NMR (CD_3OD): ^{1}H (499.9 MHz): 0.75 – 0.79 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.97 – 1.01 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.89 – 1.99 (m, 2H, CH$_2$*CH*$_2$CH$_2$); 2.14 – 2.25 (m, 6H, C*H*$_2$CF$_2$); 3.94 (s, 3H, C*H*$_3$); 4.24 (t, 2H, ^3J = 7.1 Hz, C*H*$_2$N); 7.59, 7.66 (2 × t, ^3J = 1.9 Hz, 2 × 1H, C*H*); 8.96 (br s, 1H, C*H*). ^{13}C (125.7 MHz): 1.8 (s, *C*H$_2$CH$_2$CF$_2$); 8.8 (s, Si*C*H$_2$CH$_2$CH$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.5 Hz, *C*H$_2$CF$_2$); 36.5 (s, *C*H$_3$); 53.3 (s, *C*H$_2$N); 106 – 121 (m, *C*F$_3$, *C*F$_2$); 123.5, 125.1 (2 × s, 2 × *C*H); not detected (s, *C*H). ^{29}Si (79.5 MHz): 7.23. ^{19}F (376.5 MHz): -127.44 – -127.36 (m, 6F); -124.30 – -124.27 (m, 6F); -123.95 (br s, 6F); -122.96 (br s, 6F); -117.02 – -116.88 (m, 6F); -82.50 (t, 9F, *J* = 10.2 Hz).

1-Methyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium tetrafluoroborate (**1b**). Iodide **1a** (200 mg, 0.15 mmol) and $AgBF_4$ (33 mg, 0.17 mmol) were dissolved in acetonitrile (1 mL) and the mixture was stirred at room temperature for 18 hours. The reaction mixture was washed with aqueous solution of $Na_2S_2O_3$ (1 M), extracted into ethyl acetate and filtered through a pad of silica gel. The solvent was evaporated and the product was dried in vacuum. Yield 163 mg (0.11 mmol, 71 %) of a caramel-like compound. HRMS (ESI$^+$): Calcd. for $[C_{31}H_{24}F_{39}N_2Si]^+$ 1193.1080, found 1193.1082, (ESI$^-$): Calcd. for $[BF_4]^-$ 87.0024 (100%), found 87.0018. NMR (CD_3OD): ^{1}H (400.1 MHz): 0.74 – 0.78 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.96 – 1.00 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.89 – 1.93 (m, 2H, CH$_2$*CH*$_2$CH$_2$); 2.12 – 2.25 (m, 6H, C*H*$_2$CF$_2$); 3.93 (s, 3H, C*H*$_3$); 4.22 (t, ^3J = 7.1 Hz, 2H, C*H*$_2$N); 7.58, 7.64 (2 × t, ^3J = 1.8 Hz, 2 × 1H, C*H*); 8.88 (br s, 1H, C*H*). ^{13}C (100.6 MHz): 1.7 (s, *C*H$_2$CH$_2$CF$_2$); 8.6 (s, Si*C*H$_2$CH$_2$CH$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.6 Hz, *C*H$_2$CF$_2$); 36.4 (s, *C*H$_3$); 53.3 (s, *C*H$_2$N); 109.0 – 122.6 (m, *C*F$_3$, *C*F$_2$); 123.5, 125.0, 137.8 (3 × s, 3 × *C*H). ^{29}Si (79.5 MHz): 7.25. ^{19}F (376.5 MHz): -154.38 (s, $^{10}BF_4$); -154.33 (s, $^{11}BF_4$); -127.41 (m, 6F); -124.32 (bs, 6F); -123.95 (m, 6F); -122.99 (m, 6F); -117.00 (m, 6F); -82.49 (t, 9F, *J* = 10.1 Hz).

1-Methyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium hexafluorophosphate (**1c**). Iodide **1a** (411 mg, 0.31 mmol) and NH_4PF_6 (56 mg, 0.34 mmol) were dissolved in acetonitrile (2 mL) and the mixture was stirred at room temperature for 2 days. The reaction mixture was extracted between water and ethyl acetate and filtered through a pad of silica gel. The solvent was evaporated and the product was dried in vacuum. Yield 300 mg (0.22 mmol, 72 %) of orange solid. HRMS (ESI$^+$): Calcd. for $[C_{31}H_{24}F_{39}N_2Si]^+$ 1193.1080, found 1193.1081, (ESI$^-$): Calcd. for $[PF_6]^-$ 144.9647, found 144.9644. NMR (CD_3OD): ^{1}H (499.9 MHz): 0.74 – 0.77 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.97 – 1.00 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.88 – 1.95 (m, 2H, CH$_2$*CH*$_2$CH$_2$); 2.13 – 2.24 (m, 6H, C*H*$_2$CF$_2$); 3.93 (s, 3H, C*H*$_3$); 4.22 (t, 2H, ^3J = 7.1 Hz, C*H*$_2$N); 7.58, 7.64 (2 × t, ^3J = 1.9 Hz, 2 × 1H, C*H*); 8.90 (br s, 1H, C*H*). ^{13}C (125.7 MHz): 1.7 (s, *C*H$_2$CH$_2$CF$_2$); 8.7 (s, Si*C*H$_2$CH$_2$CH$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.5 Hz, *C*H$_2$CF$_2$); 36.4 (s, *C*H$_3$); 53.3 (s, *C*H$_2$N); 106 – 121 (m, *C*F$_3$, *C*F$_2$); 123.6, 125.1, 138.0 (3 × s, 3 × *C*H). ^{29}Si (79.5 MHz): 7.26. ^{19}F (376.5 MHz): -127.40 (m, 6F), -124.32 (bs, 6F), -123.94 (br s, 6F), -122.96 (br s, 6F), -116.98 (m, 6F), -82.47 (t, 9F, $^2J_{FF}$ = 10.1 Hz), -74.71 (d, 6F, $^1J_{PF}$ = 707.8 Hz, PF_6). ^{31}P (161.95 MHz): -144.62 (hept, $^1J_{FP}$ = 707.7 Hz, *P*F$_6$).

1-Isopropyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium iodide (**2a**). This compound was synthetized according to a protocol for the synthesis of **1a**, starting from (3-iodopropyl)tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane and *N*-isopropylimidazole. HRMS (ESI$^+$): Calcd. for $[C_{33}H_{28}F_{39}N_2Si]^+$ 1221.1393, found 1221.1389, (ESI$^-$): Calcd. for $[I]^-$ 126.9036, found 126.9042. NMR (CD_3OD): ^{1}H (400.1MHz): 0.75 – 0.78 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.97 – 1.01 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.59 (d, ^3J = 6.7 Hz, 6H, CH*Me*$_2$), 1.92 – 1.98 (m, 2H, CH$_2$*CH*$_2$CH$_2$); 2.13 – 2.26 (m, 6H, C*H*$_2$CF$_2$); 4.24 (t, ^3J = 7.2 Hz, 2H, C*H*$_2$N); 4.68 (hept, ^3J = 6.7 Hz, 1H, C*H*Me$_2$); 7.69, 7.77, 9.12 (3 × t, ^3J = 1.7 Hz, 3 × 1H, 3 × C*H*). ^{13}C (100.6 MHz): 1.8 (s, *C*H$_2$CH$_2$CF$_2$); 8.8 (s, Si*C*H$_2$CH$_2$CH$_2$); 23.0 (s, CH*Me*$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.6 Hz, *C*H$_2$CF$_2$); 53.4 (s, *C*H$_2$N); 54.6 (s, *C*HMe$_2$); 107 – 122 (m, *C*F$_3$, *C*F$_2$); 122.0, 123.8 (2 × s, 2 × *C*H); 136.3 (from HMBC, *C*H). ^{29}Si (79.5 MHz): 7.25. ^{19}F (376.5 MHz): -127.37 (m, 6F); -124.29 (bs, 6F); -123.94 (m, 6F); -122.94 (m, 6F); -116.91 (m, 6F); -82.47 (m, 9F).

1-Isopropyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium tetrafluoroborate (**2b**). This compound was synthetized according to a protocol for the synthesis of **1b**, starting from **2a**. HRMS (ESI$^+$): Calcd. for $[C_{33}H_{28}F_{39}N_2Si]^+$ 1221.1393, found 1221.1398, (ESI$^-$): Calcd. for $[BF_4]^-$ 87.0024 (100%), found 87.0020. NMR (CD_3OD): ^{1}H (400.1 MHz): 0.74 – 0.78 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.96 – 1.01 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.58 (d, ^3J = 6.7 Hz, 6H, CH*Me*$_2$), 1.89 – 1.97 (m, 2H, CH$_2$*CH*$_2$CH$_2$); 2.12 – 2.25 (m, 6H, C*H*$_2$CF$_2$); 4.23 (t, ^3J = 7.2 Hz, 2H, C*H*$_2$N); 4.67 (hept, ^3J = 6.7 Hz, 1H, C*H*Me$_2$); 7.66, 7.75, 9.03 (3 × t, ^3J = 1.7 Hz, 3 × 1H, 3 × C*H*). ^{13}C (100.6 MHz): 1.7 (s, *C*H$_2$CH$_2$CF$_2$); 8.7 (s, Si*C*H$_2$CH$_2$CH$_2$); 22.9 (s, CH*Me*$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.7 Hz, *C*H$_2$CF$_2$); 53.4 (s, *C*H$_2$N); 54.6 (s, *C*HMe$_2$); 107 – 122 (m, *C*F$_3$, *C*F$_2$); 122.0, 123.8, 136.0 (3 × s, 3 × *C*H). ^{29}Si (79.5 MHz): 7.23. ^{19}F (376.5 MHz): -154.28 (s, $^{10}BF_4$); -154.33 (s, $^{11}BF_4$); -127.40 (m, 6F); -124.33 (bs, 6F); -123.95 (m, 6F); -122.96 (m, 6F); -116.97 (m, 6F); -82.50 (t, 9F, *J* = 10.2 Hz).

1-Isopropyl-3-(3-(tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)propyl)imidazolium hexafluorophosphate (**2c**). This compound was synthetized according to a protocol for the synthesis of **1c**, starting from **2a**. HRMS (ESI^+): Calcd. for $[C_{33}H_{28}F_{39}N_2Si]^+$ 1221.1393, found 1221.1408, (ESI^-): Calcd. for $[PF_6]^-$ 144.9647, found 144.9641. NMR (CD_3OD): ^1H (400.1MHz): 0.73 – 0.78 (m, 2H, Si*CH*$_2$CH$_2$CH$_2$); 0.96 – 1.00 (m, 6H, C*H*$_2$CH$_2$CF$_2$); 1.58 (d, ^3J = 6.7 Hz, 6H, CH*Me*$_2$), 1.88 – 1.96 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 2.11 – 2.24 (m, 6H, C*H*$_2$CF$_2$); 4.22 (t, ^3J = 7.2 Hz, 2H, C*H*$_2$N); 4.65 (hept, ^3J = 6.7 Hz, 1H, C*H*Me$_2$); 7.64, 7.73, 8.97 (3 × t, ^3J = 1.7 Hz, 3 × 1H, 3 × C*H*). ^{13}C (100.6 MHz): 1.7 (s, *C*H$_2$CH$_2$CF$_2$); 8.7 (s, Si*C*H$_2$CH$_2$CH$_2$); 22.9 (s, CH*Me*$_2$); 25.5 (s, CH$_2$*C*H$_2$CH$_2$); 26.3 (t, $^2J_{CF}$ = 23.8 Hz, *C*H$_2$CF$_2$); 53.4 (s, *C*H$_2$N); 54.6 (s, *C*HMe$_2$); 107 – 122 (m, *C*F$_3$, *C*F$_2$); 122.0, 123.7, 135.9 (3 × s, 3 × *C*H). ^{29}Si (79.5 MHz): 7.23. ^{19}F (376.5 MHz): -127.40 (m, 6F); -124.33 (bs, 6F); -123.95 (m, 6F); -122.98 (m, 6F); -116.96 (m, 6F); -82.51 (t, 9F, J = 10.2 Hz); -74.40 (d, $^1J_{FP}$ = 708.0 Hz, PF_6). ^{31}P (161.95 MHz): -144.58 (hept, $^1J_{FP}$ = 700.0 Hz, *P*F$_6$).

Determination of partition coefficients *P*. 50 mg of a sample was vigorously stirred with 1 mL of PFMC and 1 mL of toluene for 5 h at room temperature. The mixture was left to stand for 18 h to ensure phase separation and from each layer 0.5 mL was taken. ^{19}F NMR spectra were measured using a capillary with D_2O and the solution of internal standard trifluoromethylbenzene was added. Integration of CF_3 fluorine signals of products versus CF_3 fluorine signals of the internal standard was used to determine the partition coefficients.

Catalysis in organic/fluorinated solvents. In a typical experiment, 13 mg (0.01 mmol) of **1a** was weighed in a glovebox and introduced in a Schlenk flask, then aldehyde (0.10 mmol), alcohol (0.40 mmol), DBU (0.02 mmol) and dioctyl phthalate (0.03 mmol) followed by 1 mL of toluene were added under the flow of argon. All components were thoroughly mixed, 30 μl sample was withdrawn for GC analysis and the reaction mixture was heated for a specified time in the oil bath of constant temperature (100 °C unless otherwise noted). Then the mixture was let to cool down, 0.2 mL of PFMC or FC-770 was added, the catalyst was extracted to the fluorous phase and separated and the organic phase was analyzed by GC. The fluorous phase containing precatalyst was washed twice with 0.1 mL of toluene and either stored for subsequent **1a** recovery or used again in recycling experiments. In case that samples were taken in the course of experiment, 30 μl of the reaction mixture was withdrawn *via* syringe under the flow of argon, dissolved in cold DCM and stored in refrigerator till analysis.

Catalysis in $scCO_2$. Catalytic experiments in $scCO_2$ were performed in 17 cm^3 cylindrical batch reactor. The precatalyst (0.02 mmol), substrates (cinnamaldehyde (0.10 mmol), alcohol (0.30 mmol), DBU (0.02 mmol)) and standard (dioctyl- or dibutyl phthalate (0.04 mmol)) were weighted in a glovebox and introduced into the reactor in a glass vial. The reactor was slowly (15 min) pressurized from the gas cylinder to the initial pressure 51 bar at r.t. The reactor was then immersed in the oil bath of constant temperature and let to temperate for 15 min, then it was slowly (15 min) pressurized to 170-180 bar and the pressure and temperature were kept constant for a specified time. Then the reactor was cooled down to -70 °C and slowly (3 h) depressurized at r.t. The reactor was washed by DCM and a sample for the analysis was taken. In recycling experiments the mixture was evaporated to dryness and extracted between toluene and FC-84. Fluorous phase was washed with toluene, evaporated under vacuum and obtained material was used in subsequent cycle. Between particular runs the reaction arrangement was washed by DCM at 80 °C and flushed three times with $scCO_2$.

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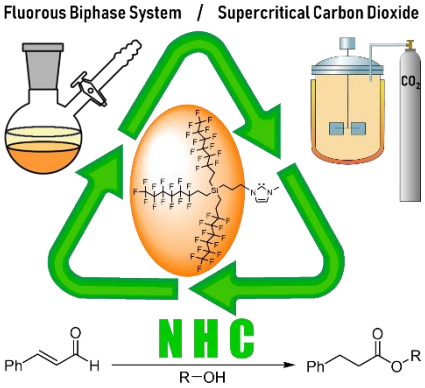
Entry for the Table of Contents



Let's get fluorophilic! Tagging the imidazolium ionic liquids catalytically active in redox esterification with large fluorous substituent enables their facile recovery from reaction mixtures and multiple reuse without loss of activity. It also allows for their application as catalysts in fluorous biphase catalysis and supercritical CO_2.