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Lanthanide catalysts with tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide ponytails: recyclable Lewis acid catalysts in fluorous phases or as solids☆

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Abstract—Lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide complexes are shown to be immobilized and continuously recycled in fluorous phases or as solids. The lanthanide complexes are thus extremely efficient Lewis acid catalysts for carbon–carbon bond forming (CCF) reactions. The CCF reactions such as the Friedel–Crafts acylation, Diels–Alder, and Mukaiyama aldol reaction are effectively catalyzed by the lanthanide complexes by virtue of the highly electron-withdrawing effect of tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide ponytails without any hydrocarbon spacer. © 2002 Published by Elsevier Science Ltd.

1. Introduction

A wide variety of Lewis acid catalysts have been developed for carbon–carbon bond forming (CCF) reactions, on the basis of the Lewis acid–base complexation in aprotic polar solvents.[1] However, the Lewis acid complexes have often been employed and then wasted after the reactions in more than a stoichiometric amount. Therefore, it is desirable to decrease the amount of a Lewis acid complex in catalytic reactions by developing a stronger Lewis acid catalyst and the recycle process thereof. Quite recently, the concept of fluorous bi-phasic catalysis (FBC) was introduced as an environmentally benign recyclable process.[2] Phosphine or phosphite ligands with fluorous ponytails and hydrocarbon spacers have been developed to immobilize late transition metal catalysts for hydroformylation,[3] hydrogenation,[4] alkene epoxidation[5] and hydroboration[6] in the non-polar fluorous media. The design and immobilization of strong Lewis acid catalysts are challenging in this unorthodox non-polar media for Lewis acid catalysis.[7] Numerous (nine) and long-enough (perfluorooctyl, C_8F_{17}) fluorous ponytails can be attached directly without any hydrocarbon spacer for increasing the Lewis acidity of lanthanide catalysts and for fluorous phase immobilization (Fig. 1). The key to the success is the powerful electron-withdrawing effect of perfluoroalkanesulfonyl-methide or -amide group[8] without any hydrocarbon spacer. Further to our preliminary communication, we report the 'super' Lewis acidities and the completely recyclable use of lanthanide(III) tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide complexes in the fluorous phases or as solids.[9]

2. Results and discussion

The solubility of the scandium and ytterbium complexes with perfluorooctyl (C_8F_{17}) fluorous ponytails was first examined in fluorous and/or non-fluorous solvents. The lanthanide(III) tris(perfluorooctanesulfonyl)methide complexes were soluble in aromatic and aliphatic fluorocarbons. However, fluoroaromatic solvents were miscible in non-fluorous solvents. Therefore, we examined the aliphatic fluorocarbon/non-fluorous solvent systems with or without fluoroaromatics, in order to check the catalytic activities of the lanthanide complexes for alcohol acylation as a probe reaction; in the bi-phases or a homogeneous phase with fluoroaromatics at higher temperature. The ester formation of cyclohexanol (2 mmol) with acetic anhydride (2 mmol) in perfluoromethylcyclohexane (5 ml), toluene (5 ml) and perfluorobenzene (3 ml) was completed within 15 min in the homogeneous phase at 40°C, with 1 mol% of scandium and ytterbium complexes

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☆ See Ref. 17.

Keywords: carbon–carbon bond forming reactions; environmental benignity; fluorous phase; lanthanide; Lewis acid catalysis; tris(perfluoroalkanesulfonyl)methide; bis(perfluorooctanesulfonyl)amide.

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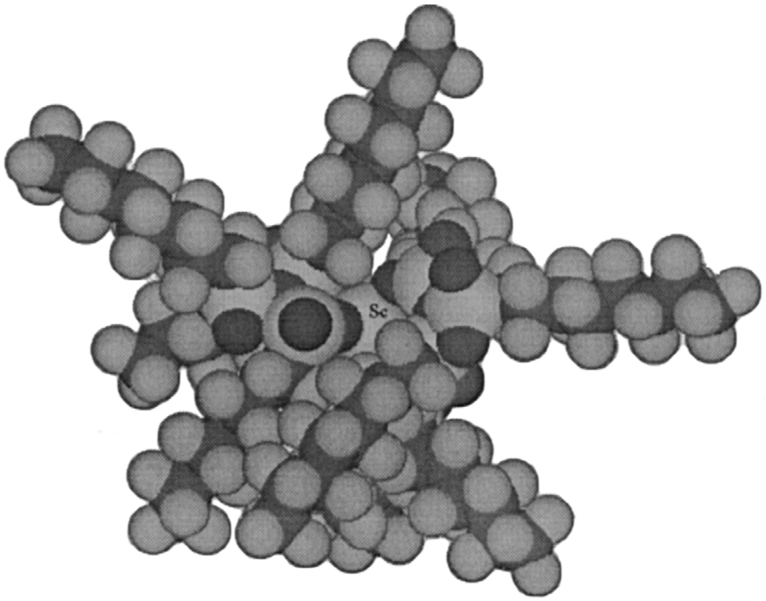
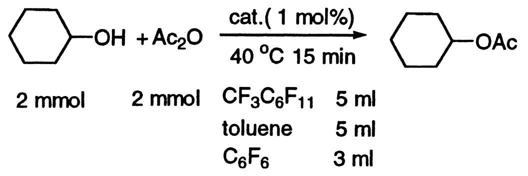


Figure 1. ScL′3, L′=$C(SO_2C_8F_{17})_3$. The core structure of ScL_3, L=$C(SO_2CF_3)_3$ is optimized at the Hartree–Fock level with 6-31 G basis set for C, F, S, O and with CEP-31G pseudo potential and basis set for Sc. Then the CF_3 group in the core structure is replaced with C_8F_{17} and those chains are optimized using UFF force field.[10]

(Scheme 1). Then, the reaction mixture was allowed to stand at 15°C for 3 min, so that the reaction mixture could be separated into the upper phase (19.9% $CF_3C_6F_{11}$, 52.5% toluene, 27.6% C_6F_6) and the lower phase (69.9% $CF_3C_6F_{11}$, 13.8% toluene, 16.3% C_6F_6) (Photo 1). Cyclohexyl acetate was obtained in quantitative yield as calculated by GC analysis (Table 1). Scandium and ytterbium complexes were completely (>99%) recovered in the lower phase as determined by atomic emission spectrometry.

We then conducted the reaction and separation in the bi-phase (FBC) mode of perfluoromethylcyclohexane/toluene. The reaction of cyclohexanol (2 mmol) with acetic anhydride (2 mmol) in perfluoromethylcyclohexane (5 ml) and toluene (5 ml) was carried out at 30°C for 20 min, in the presence of 1 mol% of lanthanide complexes (Scheme 2). Then, the heterogeneous two phases were separated within just 10 s into the upper toluene composition and the lower



Scheme 1.

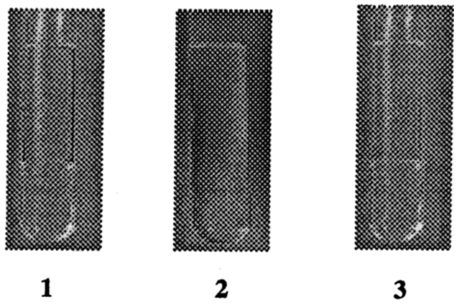


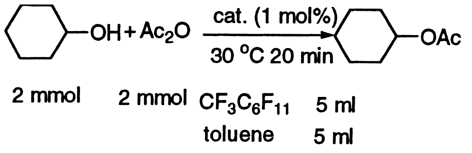
Photo 1. (1) Before (15°C). (2) During (40°C). (3) After (3 min, 15°C) the reaction.

Table 1. Esterification in homogeneous phase catalyzed by $Ln[C(SO_2C_8F_{17})_3]_3$

Yield[a] (%)	
$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
100	100 (95)[b]

[a] Calculated by GC analysis using *n*-nonane as an internal standard.

[b] Values in parenthesis refer to the isolated yields.



Scheme 2.

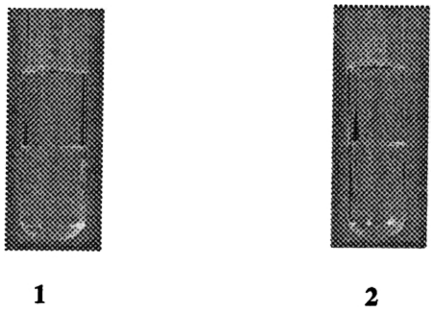


Photo 2. (1) Before (25°C). (2) After (10 s, 25°C) the reaction.

Table 2. Esterification in two phases catalyzed by $Ln[C(SO_2C_8F_{17})_3]_3$

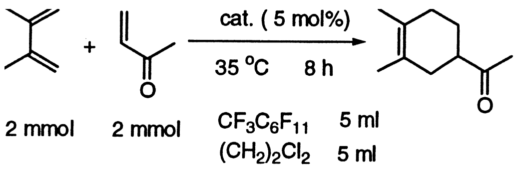
Cycle[a]	Yield[b] (%)	
	$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	99	99 (98)[c]
2	99 (96)[c]	100 (98)[c]
3	98	99
4	99	99
5	99 (96)[c]	100 (98)[c]

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-nonane as an internal standard.
[c] Values in parenthesis refer to the isolated yields.

fluorous layers (Photo 2). Cyclohexyl acetate was obtained in good isolated yield. Scandium and ytterbium complexes were completely (>99%) recovered and reused in the fluorous phase without isolation (Table 2).

Then, the catalytic activities and recyclable use of the lanthanide complexes were examined for CCF reactions. The Diels–Alder (D–A) reaction constitutes one of the most efficient construction processes of six-membered rings.[11] The D–A reaction of 2,3-dimethyl-1,3-butadiene (2 mmol) with methyl vinyl ketone (2 mmol) in perfluoromethylcyclohexane (5 ml) and 1,2-dichloroethane (5 ml) was carried out at 35°C for 8 h, in the presence of a catalytic amount (5 mol%) of scandium complexes. Then, the heterogeneous two phases were separated to give acetylcyclohexene in good isolated yield (Scheme 3). Scandium methide and amide complexes were completely (>99.9%) recovered and reused in the recyclable fluorous immobilized phase (Table 3).

The Friedel–Crafts (F–C) reaction also constitutes one of the most useful CCF processes in organic synthesis.[12] The F–C acylation reaction of anisole (2 mmol) with acetic anhydride (4 mmol) was also carried out in the presence of a catalytic amount (10 mol%) of the lanthanide complexes in perfluoromethylcyclohexane (6 ml) and 1,2-dichloroethane (6 ml) at 70°C for 6 h. The aromatic ketone product was obtained in good isolated yields (Scheme 4). Scandium complex was completely (99.8%) recovered and reused in the fluorous phase (Table 4).

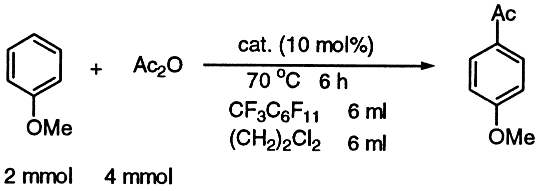


Scheme 3.

Table 3. Diels–Alder reaction catalyzed by $Sc[C(SO_2C_8F_{17})_3]_3$ and $Sc[N(SO_2C_8F_{17})_2]_3$

Cycle[a]	Yield[b] (%)	
	$Sc[C(SO_2C_8F_{17})_3]_3$	$Sc[N(SO_2C_8F_{17})_2]_3$
1	95 (92)[c]	91 (89)[c]
2	94 (91)[c]	92
3	95	91
4	95 (92)[c]	91 (88)[c]

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-nonane as an internal standard.
[c] Values in parenthesis refer to the isolated yields.



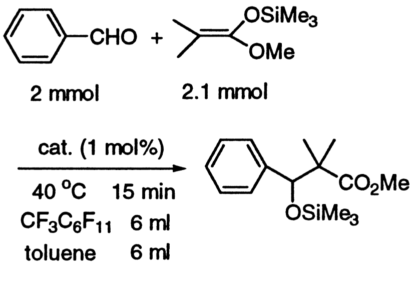
Scheme 4.

Table 4. Friedel–Crafts acylation reaction catalyzed by $Sc[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	Yield[b] (%)
1	94 (87)[c]
2	93
3	93
4	92

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-decane as an internal standard.
[c] Values in parenthesis refer to the isolated yields.

The Mukaiyama aldol reaction is a synthetically and biologically important CCF process.[13] The aldol reaction of benzaldehyde (2 mmol) with trimethylsilyl enol ether derived from methyl 2-methylpropanoate (2.1 mmol) was completed within 15 min even in the presence of only 1 mol% of the lanthanide complexes in perfluoromethylcyclohexane (6 ml) and toluene (6 ml) at 40°C (Scheme 5). The aldol product was obtained in good isolated yields. Lanthanide methide complex was completely (99.8%) recovered and reused (Table 5).

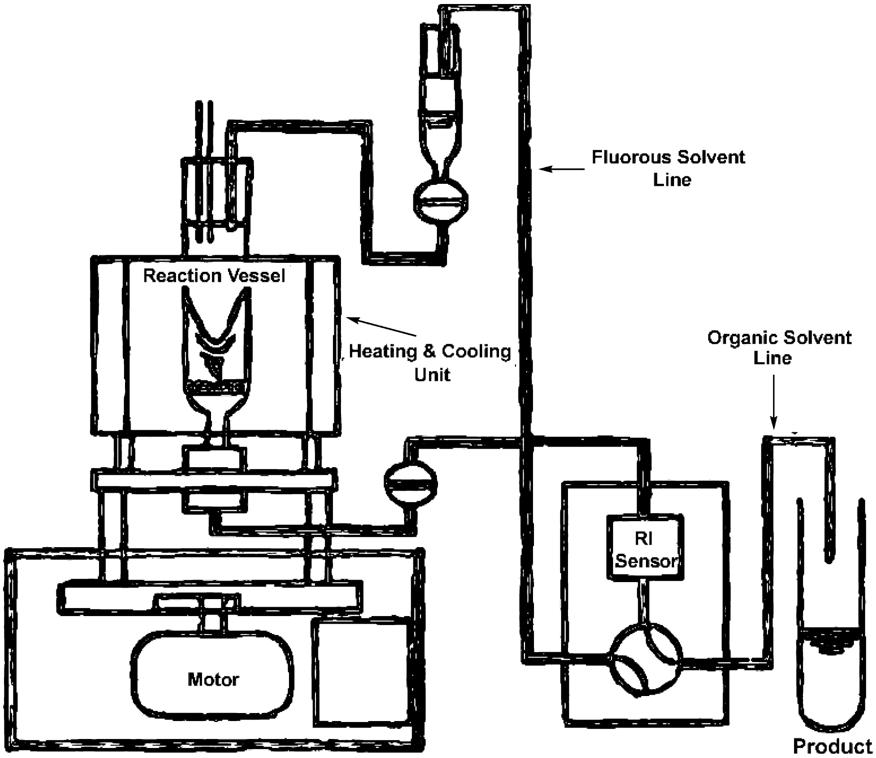


Scheme 5.

Table 5. Mukaiyama aldol reaction catalyzed by $Ln[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	Yield[b] (%)	
	$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	84	88 (84)[c]
2	85	88
3	83	86

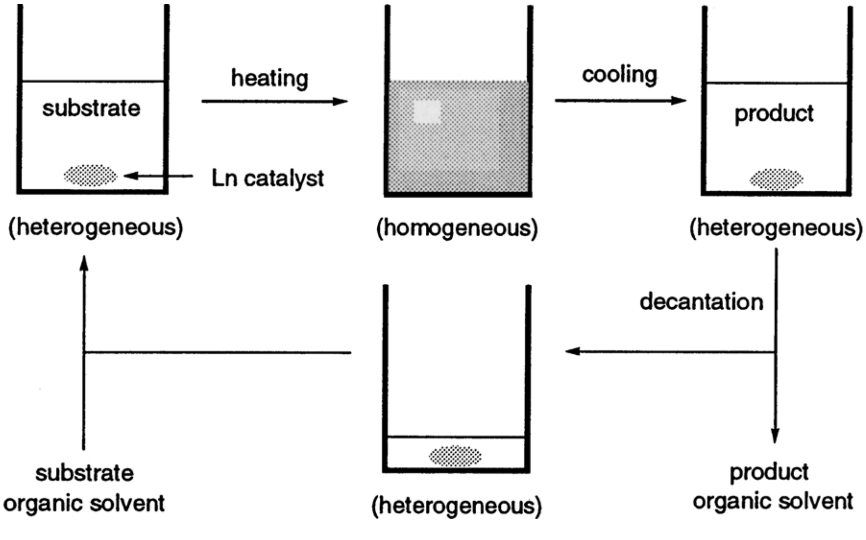
[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-nonane as an internal standard.
[c] Values in parenthesis refer to the isolated yields.



Scheme 6.

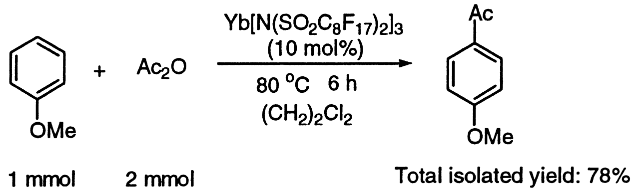
Continuous recycling was then conducted in the F–C acylation reaction (Schemes 4 and 6). *p*-Acetylanisole was obtained in good yield (87%) in the organic phase, which was automatically separated from the fluorous phase using a refractive index (RI) sensor. Substantially, the same reaction was repeated using the catalyst in the fluorous phase (perfluoromethylcyclohexane). To the fluorous phase containing the catalyst were added 1,2-dichloroethane, anisole and acetic anhydride, followed by stirring at 60°C for 2 h. The resultant reaction mixture was allowed to stand still at room temperature (20°C) for 15 s, so that the reaction mixture separated into the organic upper phase and the lower fluorous phase. The Sc C_8-methide complex was recovered and reused in a continuous manner (yields: 1st run: 87%; 2nd run: 85%; 3rd run: 86%).

The lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide complexes were insoluble in organic solvent such as toluene and 1,2-dichloroethane at room temperature or below even in the presence of reaction substrates. However, these complexes were soluble in organic solvent at high temperature to be a low melting point. To demonstrate this advantage of the lanthanide complexes with respect to temperature-dependent solubility, we examined to reuse these complexes for the F–C acylation reaction without fluorous solvent



Scheme 7. Recovery and reuse of Ln catalyst.

Table 6. Reuse of $Yb[N(SO_2C_8F_{17})_2]_3$ as a solid



Use of catalyst	1	2	3
% Conversion[a]	>85	>85	>85

[a] Determined by GC analysis.

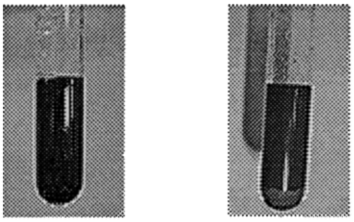

1 2

Photo 3. (1) During (80°C). (2) After standing at −20°C for 30 min.

(Scheme 7 and Table 6).[14] After heating the reaction mixture at 80°C for 6 h, the mixture was allowed to stand at −20°C for 30 min to precipitate the ytterbium bis(perfluorooctanesulfonyl)amide complex (Photo 3). The liquid phase was decanted and the residual lanthanide complex was reused without isolation. No loss of activity was observed for the catalyst recovered. The total isolated yield of the product, which was combined from the three runs, was 78%.

In summary, we have disclosed lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide complexes[15] as efficient immobilized Lewis acid catalysts with or without fluorous media by virtue of the powerful electron-withdrawing effect of the tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide ponytails without any hydrocarbon spacer.[16]

3. Experimental

3.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-EX400 (400 MHz) spectrometers. Chemical shifts of ^1H NMR were expressed in parts per million relative to chloroform (δ 7.26) or tetramethylsilane (δ 0.00) as an internal standard in chloroform-*d*. Chemical shifts of ^{13}C NMR were expressed in parts per million relative to chloroform-*d* (δ 77.0) as an internal standard. GC analysis was carried out on SHIMADZU GC-1700AF and GC–MS analysis was taken by Hewlett–Packard G1800A GLS. Atomic emission spectrometer is of IRIS/AP Nippon Jarrell Ash Co. 1,2-Dichoroethane and toluene were freshly distilled from calcium hydride. Perfluoromethylcyclohexane and perfluorobenzene were distilled from phosphorous pentaoxide.

3.2. Typical procedure for fluorous biphase system

3.2.1. Ester formation of cyclohexanol with acetic anhydride. Cyclohexanol (0.21 ml, 0.20 g, 2 mmol) and acetic anhydride (0.19 ml, 0.20 g, 2 mmol) were added to a mixture of perfluoromethylcyclohexane (5 ml) and toluene (5 ml). To the resultant mixture was added 1 mol% of scandium tris(perfluorooctanesulfonyl)methide (89 mg, 0.02 mmol). The solution was stirred at 30°C for 20 min. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of toluene and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. Cyclohexyl acetate was obtained from the upper phase after evaporation under reduced pressure and silica gel chromatography (0.279 g, 98% isolated yield). To the lower phase containing the catalyst were again added toluene (5 ml), cyclohexanol (0.21 ml, 0.20 g, 2 mmol) and acetic anhydride (0.19 ml, 0.20 g, 2 mmol), followed by stirring at 30°C for 20 min. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of toluene and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. The overall yield of cyclohexyl acetate in the upper phase and lower phase was 100%. Substantially, the same procedure as mentioned above was repeated further three times. The overall yields of cyclohexyl acetate were 99, 99, 100% in the three times repeated reactions, respectively. ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.44 (m, 5H), 1.52–1.58 (m, 1H), 1.70–1.74 (m, 2H), 1.84–1.87 (m, 2H), 2.03 (s, 3H), 4.71–4.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.45, 23.81, 25.37, 31.65, 72.61, 170.40; MS (EI, 70 eV): *m/z* 127 ($C_6H_{11}CO_2^+$), 99 ($C_6H_{11}O^+$), 82 ($C_6H_{10}^+$), 67, 43 (CH_3CO^+). Elemental analysis (%) calcd for $C_8H_{14}O_2$: C 67.57, H 9.92, found: C 67.41, H 9.96.

3.2.2. The Diels–Alder reaction of 2,3-dimethyl-1,3-butadiene with methyl vinyl ketone. 2,3-Dimethyl-1,3-butadiene (0.23 ml, 0.16 g, 2 mmol) and methyl vinyl ketone (0.17 ml, 0.14 g, 2 mmol) were added to a mixture of perfluoromethylcyclohexane (5 ml) and 1,2-dichloroethane (5 ml). To the resultant mixture was added 5 mol% of scandium tris(perfluorooctanesulfonyl)methide (0.44 g, 0.1 mmol). The solution was stirred at 35°C for 8 h. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of 1,2-dichloroethane and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. Acetylcyclohexene was obtained from the upper phase after evaporation under reduced pressure and silica gel chromatography (0.280 g, 92% isolated yield). To the lower phase containing the catalyst were again added 1,2-dichloroethane (5 ml), 2,3-dimethyl-1,3-butadiene (0.23 ml, 0.16 g, 2 mmol) and methyl vinyl ketone (0.17 ml, 0.14 g, 2 mmol), followed by stirring at 35°C for 8 h. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of 1,2-dichloroethane and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. The overall yield of acetylcyclohexene in the upper phase and lower phase was 94%. Substantially, the same procedure as mentioned above was repeated further two times. The overall yields of acetylcyclohexene were 95, 95% in the two times repeated reactions, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18–1.58 (m, 1H), 1.61 (s, 3H), 1.63 (s, 3H), 1.90–2.14 (m, 5H), 2.17 (s, 3H), 2.52–2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.82, 19.02, 25.32, 27.93, 31.22, 33.08, 48.25, 123.81, 125.25, 211.60; MS (EI, 70 eV): *m/z* 152 (M^+), 137 ($C_8H_{13}CO^+$), 119, 109 ($C_8H_{13}{}^+$), 91, 79, 67, 43 (CH_3CO^+). Elemental analysis (%) calcd for $C_{10}H_{16}O$: C 78.90, H 10.59, found: C 78.99, H 10.51.

3.2.3. The Friedel–Crafts acylation of anisole with acetic anhydride. Anisol (0.22 ml, 0.22 g, 2 mmol) and acetic anhydride (0.38 ml, 0.41 g, 4 mmol) were added to a mixture of perfluoromethylcyclohexane (6 ml) and 1,2-dichloroethane (6 ml). To the resultant mixture was added 10 mol% of scandium tris(perfluorooctanesulfonyl)methide (0.89 g, 0.2 mmol). The solution was stirred at 70°C for 6 h. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of 1,2-dichloroethane and the lower phase of perfluoromethylcyclohexane. Each of the upper and lower phases was individually analyzed by GC. *p*-Methoxyacetophenone was obtained from the upper phase after evaporation under reduced pressure and silica gel chromatography (0.261 g, 87% isolated yield). To the lower phase containing the catalyst were again added 1,2-dichloroethane (6 ml), anisol (0.22 ml, 0.22 g, 2 mmol) and acetic anhydride (0.38 ml, 0.41 g, 4 mmol) followed by stirring at 70°C for 6 h. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of 1,2-dichloroethane and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. The overall yield of *p*-methoxyacetophenone in the upper phase and lower phase was 93%. Substantially the same procedure as mentioned above was repeated further two times. The overall yields of *p*-methoxyacetophenone were 93, 92% in the two times repeated reactions, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 3.87 (s, 3H), 6.93 (d, 2H, J=9.8 Hz), 7.94 (d, 2H, J=9.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.36, 55.44, 113.57, 130.22, 130.46, 163.31, 196.55; MS (EI, 70 eV): *m/z* 150 (M^+), 135 ($MeOPhCO^+$), 107 ($MeOPh^+$), 92, 77, 64, 63, 43 (CH_3CO^+). Elemental analysis (%) calcd for $C_9H_{10}O_2$: C 71.98, H 6.71, found: C 72.10, H 6.69.

3.2.4. The Mukaiyama aldol reaction of benzaldehyde with trimethylsilyl enol ether of methyl 2-methylpropanoate. Benzaldehyde (0.20 ml, 0.21 g, 2 mmol) and trimethylsilyl enol ether derived from methyl 2-methylpropanoate (0.37 g, 2.1 mmol) were added to a mixture of perfluoromethylcyclohexane (6 ml) and toluene (6 ml). To the resultant mixture was added 1 mol% of scandium tris(perfluorooctanesulfonyl)methide (89 mg, 0.02 mmol). The solution was stirred at 40°C for 15 min. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of toluene and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. The aldol product from the upper phase was obtained (0.391 g, 84% isolated yield). To the lower phase containing the catalyst were again added toluene (6 ml), benzaldehyde (0.20 ml, 0.21 g, 2 mmol) and trimethylsilyl enol ether derived from methyl 2-methylpropanoate (0.37 g, 2.1 mmol) followed by stirring at 40°C for15 min. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture separated into the upper phase of toluene and the lower phase of perfluoromethylcyclohexane. Each of the upper phase and lower phase was individually analyzed by GC. The overall yield of the aldol product in the upper phase and lower phase was 88%. Substantially, the same procedure as mentioned above was repeated. The overall yield of the aldol product was 86%. MS (EI, 70 eV): *m/z* 281 (M^++1), 265, 179 ($Me_3SiOPhCH^+$), 163, 115, 89, 73 (Me_3Si^+). Elemental analysis (%) calcd for $C_{15}H_{24}O_3Si$: C 64.25, H 8.62, found: C 64.45, H 8.67.

3.3. Continuous recycling via automatic separation using a refractive index sensor

The same F–C reaction was repeated using the catalyst contained in the lower phase. Anisol (0.22 ml, 0.22 g, 2 mmol) and acetic anhydride (0.38 ml, 0.41 g, 4 mmol) were added to a mixture of perfluoromethylcyclohexane (6 ml) and 1,2-dichloroethane (6 ml). To the resultant mixture was added 10 mol% of scandium tris(perfluorooctanesulfonyl)methide (0.89 g, 0.2 mmol). The solution was stirred at 60°C for 2 h. The resultant mixture was allowed to stand still at room temperature (20°C), so that the reaction mixture was separated into the upper phase of 1,2-dichloroethane and the lower phase of perfluoromethylcyclohexane. The upper phase containing *p*-methoxyacetophenone was separated from the lower phase containing the catalyst. *p*-Methoxyacetophenone was obtained from the upper phase after evaporation under reduced pressure and silica gel chromatography (0.260 g, 87% isolated yield). To the lower phase containing the catalyst were again added 1,2-dichloroethane (6 ml), anisole (0.22 ml, 0.22 g, 2 mmol) and acetic anhydride (0.38 ml, 0.41 g, 4 mmol), followed by stirring at 60°C for 2 h.

3.4. The Friedel–Crafts acylation catalyzed by ytterbium bis(perfluorooctanesulfonyl)amide as a solid

10 mol% of ytterbium bis(perfluorooctanesulfonyl)amide (0.31 g, 0.1 mmol), anisol (0.11 ml, 0.11 g, 1 mmol) and acetic anhydride (0.19 ml, 0.20 g, 2 mmol) were added to 1,2-dichloroethane (5 ml). The solution was stirred at 80°C for 6 h. The resultant mixture was allowed to stand still in a convenient freezer (−20°C) to precipitate the ytterbium complex. After 30 min, the liquid phase of the resultant mixture was decanted and the residual solid catalyst was reused without isolation. Catalyst remained in the vessel in the third reaction. Liquid phases, which were obtained in each reaction, were combined, concentrated under reduced pressure. *p*-Methoxyacetophenone was purified by silica gel chromatography (0.354 g, 78% isolated yield).

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