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Friedel–Crafts acylation reaction using carboxylic acids as acylating agents

Masato Kawamura, Dong-Mei Cui[†] and Shigeru Shimada[*]

*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5,
Tsukuba, Ibaraki 305-8565, Japan*

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Abstract—Dehydrative Friedel–Crafts acylation reaction of aromatic compounds with carboxylic acids as acylating agents was investigated in the presence of Lewis acid- or Brønsted acid-catalyst. Various metal triflates and bis(trifluoromethanesulfonyl)amides showed catalytic activity at high temperature, among which $Eu(NTf_2)_3$ proved to be the most effective and efficiently catalyzed the acylation reaction of alkyl- and alkoxybenzenes with aliphatic and aromatic carboxylic acids at 250 °C. $Bi(NTf_2)_3$ was more effective than $Eu(NTf_2)_3$ at lower temperature, but proved to be hydrolyzed in the presence of a small amount of water to give $HNTf_2$ and $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$. The structure of the latter compound was confirmed by a single crystal X-ray analysis. Among five Brønsted acids, HOTf, $HNTf_2$, $HCTf_3$, TsOH, and Nafion® SAC-13, $HNTf_2$ has proved to be the most efficient catalyst and more effective than $Eu(NTf_2)_3$ for the acylation of *p*-xylene with heptanoic acid at 220 °C or lower temperature. $HNTf_2$ catalyzed the acylation of anisole with carboxylic acids in high yields in refluxing toluene with azeotropic removal of water.

1. Introduction

The Friedel–Crafts acylation reaction is a useful method for the preparation of aromatic ketones and is widely used not only in laboratory scale but also in large scale in industry.[1] The most common procedure uses acid chlorides, which are usually prepared from the corresponding carboxylic acids and thionyl chloride, as acylating agents and a stoichiometric or an excess amount of $AlCl_3$ as a reaction promoter. This procedure suffers from severe corrosion and waste problems (stoichiometric amounts of SO_2 and HCl are formed as by-products and $AlCl_3$ is hydrolyzed to form a large amount of waste). Therefore, there are strong demands for a cleaner alternative that meets recent requirement for environmentally benign chemical processes.

Several new methods have been explored to overcome these disadvantages. One important direction is to substitute the stoichiometric reaction promoter by efficient catalysts, and another is to replace acid chlorides by cleaner alternatives such as acid anhydrides and esters. Recently a number of reports have described catalytic Friedel–Crafts acylation reaction using acid anhydrides as acylating agents.[2] However, the use of acid anhydrides necessarily yields 1 equiv of carboxylic acids as by-products. Methyl esters, which form methanol as a by-product, could be employed in the presence of excess amount of trifluoromethanesulfonic acid.[3] Meldrum's acids are also used as acylating agents in Lewis acid-catalyzed acylations.[4] However, the most desirable acylating agents are probably carboxylic acids, which are common precursors of acid chlorides and anhydrides, because the reaction produces water as the only by-product. Recently there are some reports on catalytic Friedel–Crafts acylation reactions using carboxylic acids as acylating agents; zeolites,[5,6] heteropoly acids and their salts,[5,7] clay,[5,8] Lewis acids,[9] and graphite/TsOH[10] have been used as catalysts.

Our approach to the catalytic Friedel–Crafts acylation reaction using carboxylic acids as acylating agents was started by using simple Lewis acid- and Brønsted acid-catalysts, since the potential of these catalysts for this reaction was not well explored at the time we started. We have reported that some Lewis acids are effective for the intramolecular Friedel–Crafts acylation of carboxylic acids to form cyclic aromatic ketones.[11] In this paper, we describe the details on the intermolecular Friedel–Crafts acylation reaction catalyzed by Lewis acid- and Brønsted acid-catalysts.[12]

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[*] Corresponding author. Tel.: +81 29 861 6257; fax: +81 29 861 4511; e-mail: s-shimada@aist.go.jp

[†] Present address: College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, PR China.

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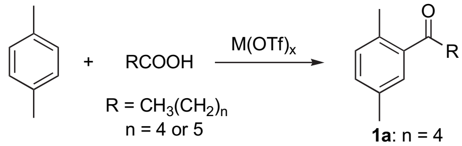
2. Results and discussion

2.1. Lewis acid-catalyzed Friedel–Crafts acylation reaction of *p*-xylene with hexanoic and heptanoic acids

The acylation of *p*-xylene with hexanoic and heptanoic acids was selected as a model reaction to examine catalytic performance of metal triflates, $M(OTf)_3$ and $M(OTf)_4$.[13] The results are summarized in Table 1. The reaction was carried out using a sealed glass tube with an excess of *p*-xylene (30–65 equiv to carboxylic acids) in an oil bath set at the temperature shown in tables. The reaction can take place at 180 °C with various Lewis acids, although the yields of desired ketone **1a** are low. At this temperature, $Sc(OTf)_3$ (Table 1, entry 1) afforded **1a** in the highest yield, 39%, among 14 metal triflates tested. $Bi(OTf)_3$, which has been utilized as a catalyst for Friedel–Crafts acylation using acid chlorides and anhydrides as acylating agents in recent years,[2d,14] also showed relatively good results under these conditions (Table 1, entry 32). As it can be seen from Table 1, considerable side reaction took place at 180 °C in many cases; for example, $Sc(OTf)_3$ afforded **1a** in 39% yield although the carboxylic acid was completely consumed (Table 1, entry 1). However, the reaction at higher temperature, 250 °C, unexpectedly proved to give the desired product in higher yields. In most cases, rare earth metal triflates gave ketone **1b** in moderate to high yields at 250 °C, among which $Yb(OTf)_3$ showed the highest performance (83% yield, Table 1, entry 24). Although $Hf(OTf)_4$ has high activity for the conversion of heptanoic acid, secondary reaction of ketone **1b** easily takes place under the reaction conditions to give uncharacterized side products and longer reaction time causes the disappearance of **1b** (Table 1, entries 28 and 29).

Table 1. Reaction of *p*-xylene with hexanoic and heptanoic acids[a]



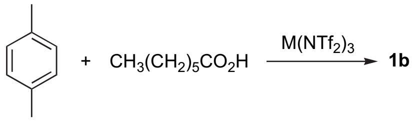
1a: n = 4
1b: n = 5

Entry	Catalyst (mol %)	*n*	Conditions	Conv. (%)[b]	Yield (%)[c]
1	$Sc(OTf)_3$ (20)	4	180 °C, 45 h	>99	39
2[d]	$Sc(OTf)_3$ (20)	5	250 °C, 12 h	>99	49
3	$Y(OTf)_3$ (20)	4	180 °C, 45 h	40	12
4	$Y(OTf)_3$ (15)	5	250 °C, 12 h	>99	65
5	$La(OTf)_3$ (15)	5	250 °C, 12 h	52	0
6	$Pr(OTf)_3$ (15)	5	250 °C, 12 h	66	23
7	$Nd(OTf)_3$ (20)	4	180 °C, 45 h	20	Trace
8	$Nd(OTf)_3$ (15)	5	250 °C, 12 h	72	29
9	$Sm(OTf)_3$ (20)	4	180 °C, 45 h	45	20
10	$Sm(OTf)_3$ (15)	5	250 °C, 12 h	97	64
11	$Eu(OTf)_3$ (20)	4	180 °C, 45 h	>99	29
12[d]	$Eu(OTf)_3$ (20)	5	250 °C, 12 h	83	52
13	$Gd(OTf)_3$ (15)	5	250 °C, 12 h	96	62
14	$Tb(OTf)_3$ (20)	4	180 °C, 45 h	21	1
15	$Dy(OTf)_3$ (20)	4	180 °C, 60 h	3	2
16[d]	$Dy(OTf)_3$ (15)	5	250 °C, 12 h	97	80
17	$Ho(OTf)_3$ (20)	4	180 °C, 45 h	30	3
18	$Ho(OTf)_3$ (15)	5	250 °C, 12 h	99	65
19	$Er(OTf)_3$ (20)	4	180 °C, 45 h	41	16
20	$Er(OTf)_3$ (15)	5	250 °C, 12 h	>99	66
21	$Tm(OTf)_3$ (20)	4	180 °C, 45 h	15	8
22	$Tm(OTf)_3$ (15)	5	250 °C, 12 h	>99	43
23	$Yb(OTf)_3$ (20)	4	180 °C, 45 h	76	14
24[d]	$Yb(OTf)_3$ (20)	5	250 °C, 12 h	>99	83
25	$Lu(OTf)_3$ (20)	4	180 °C, 45 h	51	28
26	$Lu(OTf)_3$ (15)	5	250 °C, 12 h	>99	63
27	$Hf(OTf)_4$ (20)	4	180 °C, 62 h	46	25
28[e]	$Hf(OTf)_4$ (20)	5	180 °C, 1.25 h	89	36
29[d]	$Hf(OTf)_4$ (20)	5	250 °C, 12 h	>99	0
30[d]	$Ga(OTf)_3$ (20)	5	250 °C, 12 h	94	22
31[d]	$In(OTf)_3$ (20)	5	250 °C, 12 h	>99	62
32	$Bi(OTf)_3$ (20)	4	180 °C, 45 h	75	33

[a] The ratio of *p*-xylene/carboxylic acid is 65/1 for the reaction of hexanoic acid and 50/1 for the reaction of heptanoic acid, unless otherwise noted.
[b] Conversion of carboxylic acids was determined by GC analysis using naphthalene (for hexanoic acid) or docosane (for heptanoic acid) as an internal standard.
[c] Yields are based on carboxylic acids and are determined by GC analysis using naphthalene (for hexanoic acid) or docosane (for heptanoic acid) as an internal standard.
[d] *p*-Xylene/carboxylic acid=65/1.
[e] *p*-Xylene/carboxylic acid=60/1.

Then we examined four bis(trifluoromethanesulfonyl)amide salts, $Sc(NTf_2)_3$,[15] $Yb(NTf_2)_3$,[16] $Eu(NTf_2)_3$,[17] and $Bi(NTf_2)_3$,[18] which are stronger Lewis acids than the corresponding triflates. $Sc(NTf_2)_3$ afforded **1b** in higher yield than $Sc(OTf)_3$ (Table 2, entry 1) while $Yb(NTf_2)_3$ showed poorer results than $Yb(OTf)_3$ (Table 2, entry 2). Considering their strong Lewis acidity, $Yb(NTf_2)_3$ and $Sc(NTf_2)_3$ were expected to give more promising results. However, their strong Lewis acidity seemed to promote undesirable side reaction at the same time. The best result was obtained by using $Eu(NTf_2)_3$ to give **1b** in excellent yields (Table 2, entries 3 and 5). The yield of **1b** decreased when the amount of catalyst or *p*-xylene was reduced (Table 2, entries 6–8). Figure 1 shows the effect of temperature on the yield of **1b** in $Eu(NTf_2)_3$-catalyzed reaction. At 240 °C or higher, more than 80% of **1b** is formed after 12 h, while the yield drastically decreases at 230 °C or lower. On the other hand, $Bi(NTf_2)_3$, which is less selective than $Eu(NTf_2)_3$ at 250 °C (Table 2, entry 4), proved to be more effective than $Eu(NTf_2)_3$ at 220 °C (Table 2, entry 9). Only 1 mol % of

Table 2. Reaction of *p*-xylene with heptanoic acid[a]



Entry	$M(NTf_2)_3$ (mol %)	Temp (°C)	Time (h)	Conv. (%)[b]	Yield (%)[c]
1	$Sc(NTf_2)_3$ (15)	250	12	98	75
2	$Yb(NTf_2)_3$ (15)	250	10	>99	64
3	$Eu(NTf_2)_3$ (15)	250	12	>99	91
4	$Bi(NTf_2)_3$ (15)	250	8	>99	80
5[d]	$Eu(NTf_2)_3$ (20)	250	12	>99	96
6[e]	$Eu(NTf_2)_3$ (20)	250	12	87	75
7	$Eu(NTf_2)_3$ (10)	250	12	>99	73
8[d]	$Eu(NTf_2)_3$ (5)	260	18	51	15
9	$Bi(NTf_2)_3$ (20)	220	9	80	53
10[d]	$Bi(NTf_2)_3$ (1)	220	48	92	66

[a] The ratio of *p*-xylene/carboxylic acid is 50/1 unless otherwise noted.
[b] Conversion of the carboxylic acid was determined by GC analysis using docosane as an internal standard.
[c] Yields are based on the carboxylic acid and are determined by GC analysis using docosane as an internal standard.
[d] *p*-Xylene/carboxylic acid=65/1.
[e] *p*-Xylene/carboxylic acid=30/1.

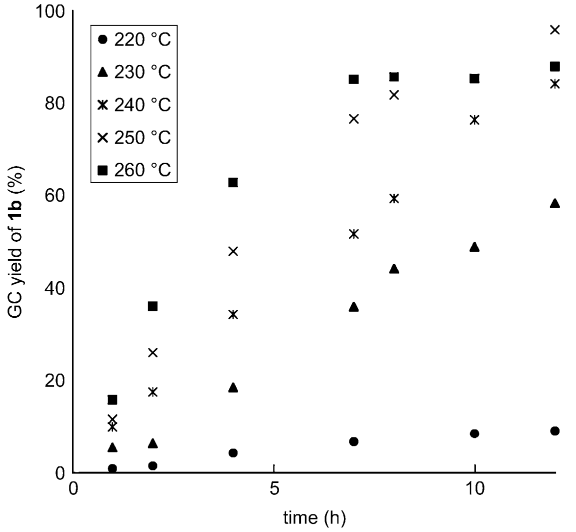
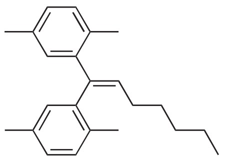


Figure 1. Temperature and time dependence of the yield of **1b** in the $Eu(NTf_2)_3$-catalyzed reaction of *p*-xylene with *n*-heptanoic acid.

$Bi(NTf_2)_3$ afforded **1b** in 66% yield after 48 h (Table 2, entry 10).

As mentioned above, considerable side reactions take place depending on the catalysts and reaction conditions. We tried to identify the structures of side products and succeeded to elucidate the structure of one of the major by-products, **2**. In the reaction of *p*-xylene with heptanoic acid using 20 mol % of $Yb(NTf_2)_3$ at 250 °C, **2** was isolated in 19% yield in addition to 51% of **1b**. The structure of **2** was confirmed by ^1H and ^{13}C NMR, IR, and HRMS spectroscopies. Compound **2** is probably derived from the dehydrative condensation of **1b** and *p*-xylene. Although other by-products were detected by TLC analysis, their structures could not be identified.

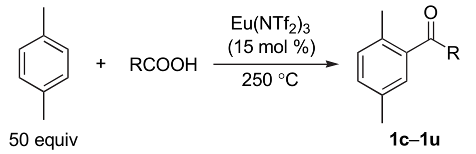


2

It is noteworthy that the acylation using aliphatic carboxylic acids is successful despite high reaction temperature because Friedel–Crafts acylation reaction of aliphatic acid chlorides with a catalytic amount of Lewis acids is often only successful for highly reactive aromatic compounds such as anisole.[19] At higher reaction temperature, side reactions of ketone products are suggested.[2d,e]

In order to clarify the scope and limitation of $Eu(NTf_2)_3$-catalyzed Friedel–Crafts acylation, reaction of *p*-xylene with various carboxylic acids (Table 3) as well as that of various aromatic compounds with aliphatic carboxylic acids (Table 4) was examined. In the reaction of *p*-xylene, straight chain carboxylic acids afforded ketones in good yields (Table 3, entries 5, 7, and 10–14) although the yields decreased to some extent in the cases of short chain carboxylic acids (Table 3, entries 1–3), whose boiling points are much lower than the reaction temperature and probably caused the decreased yields. The use of branched carboxylic acids, especially at the α-position, decreased the yields considerably (Table 3, entries 4, 6, 8, and 9), suggesting the high sensitivity of *p*-xylene to the steric hindrance around the carboxyl group. Acylation with aromatic carboxylic acids also successfully proceeded to give benzophenones (Table 3, entries 15–19).

Table 3. $Eu(NTf_2)_3$-catalyzed Friedel–Crafts acylation of *p*-xylene and anisole using various carboxylic acids

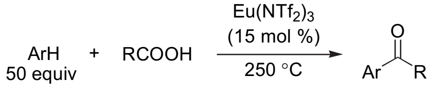


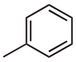
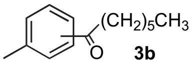
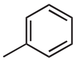
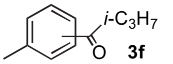
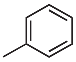
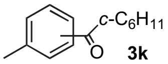
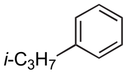
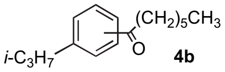
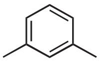
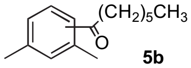
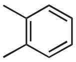
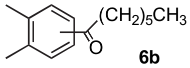
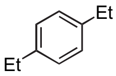
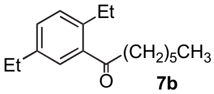
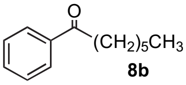
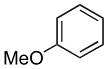
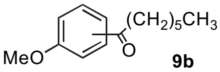
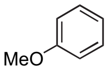
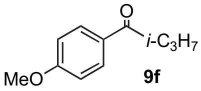
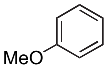
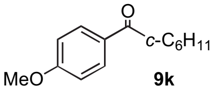
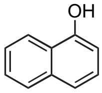
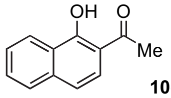
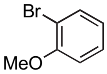
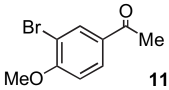
Entry	R	Time (h)	Conv. (%)[a]	Product	Yield (%)[b]
1	CH_3	8	94	**1c**	48
2	C_2H_5	8	>99	**1d**	56
3	*n*-C_3H_7	9	>99	**1e**	61
4	*i*-C_3H_7	16	91	**1f**	34
5	*n*-C_4H_9	9	98	**1g**	70
6	*i*-C_4H_9	11	>99	**1h**	55
7	*n*-C_5H_{11}	7	96	**1i**	65 (78)[c]
8	*i*-C_5H_{11}	10	>99	**1j**	61
9	*c*-C_6H_{11}	17	>99	**1k**	21
10	*n*-C_7H_{15}	12	>99	**1l**	80
11	*n*-C_8H_{17}	12	nd[d]	**1m**	86
12	*n*-C_9H_{19}	13	>99	**1n**	82
13	*n*-$C_{10}H_{21}$	13	>99	**1o**	76
14	*n*-$C_{11}H_{23}$	14	>99	**1p**	72
15	Ph	14	>99	**1q**	66
16	2-MeC_6H_4	14	>99	**1r**	59
17	4-MeC_6H_4	14	94	**1s**	76
18	2-FC_6H_4	13	>99	**1t**	76
19	4-FC_6H_4	16	60	**1u**	60

[a] Conversion of the carboxylic acid was determined by GC analysis using docosane as an internal standard.
[b] Isolated yield unless otherwise noted.
[c] The value in the parenthesis is GC yield.
[d] Not determined.

Acylation of toluene is less sensitive to the steric hindrance of carboxylic acids than that of *p*-xylene and afforded ketones in moderate to good yields with usual *p*-selectivity (Table 4, entries 1–3). Other alkylbenzenes such as cumene, *o*- and *m*-xylene, and *p*-diethylbenzene gave ketones in good yield (Table 4, entries 4–7), while benzene afforded **8b** only in 4% yield under the same reaction conditions (Table 4, entry 8). The acylation of anisole is more efficient than that of alkylbenzenes as expected and gave ketones in good yields with excellent *p*-selectivity (Table 4, entries 9–11). The reactions mentioned above were carried out by using large excess amount of aromatic compounds as reactants as well as solvents. Since chlorobenzene does not react with carboxylic acids under the present reaction conditions, it can be used as a solvent of this reaction. Acetylation of 1-naphthol was carried out using excess amount of acetic acid in chlorobenzene to give ketone **10c** in good yield (Table 4, entry 12). In the same way, 2-bromoanisole was acetylated to give **11c** as a single isomer although the yield was low (Table 4, entry 13). The reaction of 1-naphthol may proceed via naphthyl acetate (*O*-acylated product), which readily undergoes Fries rearrangement to form **10c**.[20]

Table 4. Reaction of various aromatic compounds with aliphatic carboxylic acids catalyzed by $Eu(NTf_2)_3$



Entry	ArH	Product	Time (h)	Yield (%)[a]	Isomer ratio[b]
1		 **3b**	17	78	*o-/m-/p-*=22/5/73
2		 **3f**	24	58	(*o-*+*m-*)/*p-*=14/86
3		 **3k**	24	58	(*o-*+*m-*)/*p-*=12/88
4		 **4b**	19	71	(*o-*+*m-*)/*p-*=15/85
5		 **5b**	12	74	96/4[c,d]
6		 **6b**	12	85	88/12[e,f]
7[g]		 **7b**	12	74	
8		 **8b**	24	4	
9		 **9b**	6	87	*o-/p-*=<3/>97[f]
10		 **9f**	16	77	
11		 **9k**	16	80	
12[h]		 **10c**	18	83	
13[h]		 **11c**	15	11	

[a] Isolated yields.

[b] The ratio of regioisomers was determined by GC analysis unless otherwise noted.

[c] The ratio of regioisomers was determined by GC–MS analysis.

[d] 1-(2,4-Dimethylphenyl)-1-heptanone/other regioisomers.

[e] 1-(3,4-Dimethylphenyl)-1-heptanone/1-(2,3-dimethylphenyl)-1-heptanone.

[f] The ratio of regioisomers was determined by ^1H NMR.

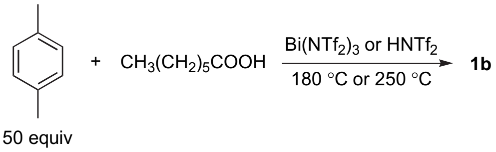
[g] $Eu(NTf_2)_3$ (10 mol %) was used.

[h] Reaction was carried out in chlorobenzene using 4 equiv of AcOH.

2.2. Evaluation of catalytic activity of $Bi(NTf_2)_3$ and $HNTf_2$

We had interest in the exceptional activity of $Bi(NTf_2)_3$, only 1 mol % of which catalyzed the reaction of *p*-xylene with heptanoic acid to give **1b** in 66% yield, as mentioned above (Table 2, entry 10). Since it has been reported that $Bi(NTf_2)_3$ is hydrolyzed by water[18b] and the present reaction produces water as a by-product, it is possible that $HNTf_2$, which will be produced by the hydrolysis of $Bi(NTf_2)_3$, is working as a catalyst at least partially in $Bi(NTf_2)_3$-catalyzed reactions. Since complete hydrolysis of $Bi(NTf_2)_3$ produces 3 equiv of

Table 5. Reaction of various aromatic compounds with aliphatic carboxylic acids catalyzed by Eu(NTf_2)$_3$



Entry	Catalyst (mol %)	Temp (°C)	Time (h)	Conv. (%)[a]	Yield (%)[a]
1	Bi(NTf_2)$_3$ (1)	180	50	46	12
2	Bi(NTf_2)$_3$ (1)	220	50	85	65
3	Bi(NTf_2)$_3$ (20)	180	48	41	27
4	Bi(NTf_2)$_3$ (20)	220	9	80	53
5	$HNTf_2$ (3)	180	50	57	18
6	$HNTf_2$ (3)	220	28	97	84
7	$HNTf_2$ (60)	180	48	56	25
8	$HNTf_2$ (60)	220	9	97	78

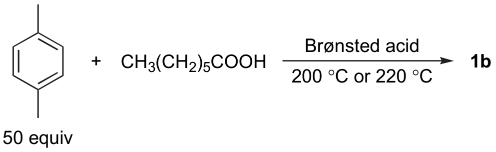
[a] The yields and the conversions were determined by GC analysis using docosane as an internal standard.

$HNTf_2$, catalytic activity of Bi(NTf_2)$_3$ was compared with that of 3 equiv of $HNTf_2$ (Table 5). At 180 °C, very similar results were obtained (Table 5, entries 1, 3, 5, and 7), while 3 equiv of $HNTf_2$ showed higher activity than Bi(NTf_2)$_3$ at 220 °C (Table 5, entries 2, 4, 6, and 8). Since we have confirmed partial hydrolysis of Bi(NTf_2)$_3$ (vide infra), the results in Table 5 probably suggest that $HNTf_2$ mainly catalyzes the reaction in Bi(NTf_2)$_3$-catalyzed dehydrative acylations, while Bi(NTf_2)$_3$ acts as a Lewis acid catalyst at the beginning stage of the reaction.

2.3. $HNTf_2$-catalyzed Friedel–Crafts acylation reaction using carboxylic acids as acylating agents

Based on the above results, we examined the catalytic activities of several Brønsted acids for the reaction of *p*-xylene with heptanoic acid (Table 6). Among five Brønsted acids tested, $HNTf_2$ showed the highest performance; 10 mol % of $HNTf_2$ at 200 or 220 °C afforded **1b** in high yields (Table 6, entries 2 and 3). HOTf is less efficient than $HNTf_2$ (Table 6, entry 5), while *p*-toluenesulfonic acid did not afford **1b** at all (Table 6, entry 4). The use of $HCTf_3$[21] and Nafion® SAC-13 afforded a complex mixture (Table 6, entries 6 and 7). In the latter case, the formation of *p*-xylene dimer (2,5,4′-trimethyldiphenylmethane) as a by-product was confirmed by GC–MS analysis of the reaction mixture.[22]

Table 6. Brønsted acid-catalyzed Friedel–Crafts acylation of *p*-xylene with heptanoic acid[a]



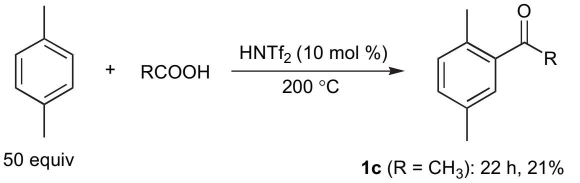
Entry	Brønsted acid (mol %)	Temp (°C)	Time (h)	Conv. (%)[a]	Yield (%)[a]
1	$HNTf_2$ (20)	220	15	>99	82
2	$HNTf_2$ (10)	220	16	98	89
3	$HNTf_2$ (10)	200	16	94	89
4	HOTs (10)	220	16	38[b]	0
5	HOTf (10)	220	24	98	70
6	$HCTf_3$ (10)	220	9	97	20
7	Nafion® SAC-13[c]	220	50	52	10

[a] Reactions were carried out in a sealed glass tube, and yields and conversions were determined by GC analysis using docosane as an internal standard unless otherwise noted.

[b] Determined by GC analysis using tetradecane as an internal standard.

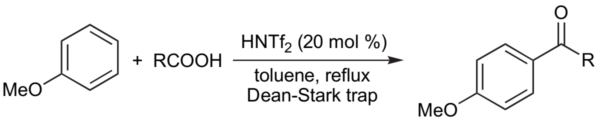
[c] 20 wt %.

To evaluate the generality of $HNTf_2$-catalyzed reaction, acylation of *p*-xylene and anisole with several carboxylic acids was examined (Schemes 1 and 2). Acetylation of *p*-xylene afforded ketone **1c** in a low yield probably because the boiling point of acetic acid is much lower than the reaction temperature, while dodecanoic acid and benzoic acid gave ketones in moderate to good yields. The acylation of anisole can be conducted in refluxing toluene with azeotropic removal of water. By using 20 mol % of $HNTf_2$, acylation of anisole efficiently took place to give ketones in good yields. Acylation products of toluene were not observed at all under these conditions.



1c (R = CH_3): 22 h, 21%
1p (R = $C_{11}H_{23}$): 22 h, 84%
1q (R = Ph): 28 h, 58%

Scheme 1. $HNTf_2$-catalyzed acylation of *p*-xylene with carboxylic acids.



9b (R = C_6H_{13}): 36 h, 89%
9d (R = C_2H_5): 24 h, 64%
9p (R = $C_{11}H_{23}$): 36 h, 84%

Scheme 2. $HNTf_2$-catalyzed acylation of anisole with carboxylic acids.

2.4. Structure of hydrolysis product of Bi(NTf_2)$_3$

Anhydrous Bi(NTf_2)$_3$ is highly moisture sensitive and fumes in air.[18b] It is reported that Bi(NTf_2)$_3$ is hydrolyzed in the presence of water,[18b] while no structural information is available on the bismuth-containing product by the hydrolysis. Therefore, we have tried the hydrolysis of Bi(NTf_2)$_3$ under various conditions and succeeded to isolate colorless single crystals of the hydrolysis product under the conditions similar to those of the catalytic acylation reaction, i.e., in *p*-xylene in the presence of *n*-$C_6H_{13}CO_2H$ or *c*-$C_6H_{11}CO_2H$ and a small amount of water.[23] The hydrolysis was attempted in the presence of 2.4, 3, and 6 equiv (to Bi) of water and gave crystals of the same hydrolysis product in all cases. The structure was identified by a single crystal X-ray analysis to be $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$ **12** (Fig. 2). Similar hexanuclear $[Bi_6O_4(OH)_4]$ structures were reported for $[Bi_6O_4(OH)_4](NO_3)_6\cdot(H_2O)_n$[24] and $[Bi_6O_4(OH)_4](ClO_4)_6\cdot(H_2O)_n$.[25] Each oxygen atom of $[Bi_6O_4(OH)_4]$ units disordered in two positions with nearly equal occupancies (showed in red and yellow in Fig. 2). This disorder is understood to show the positions of oxide and hydroxide oxygen

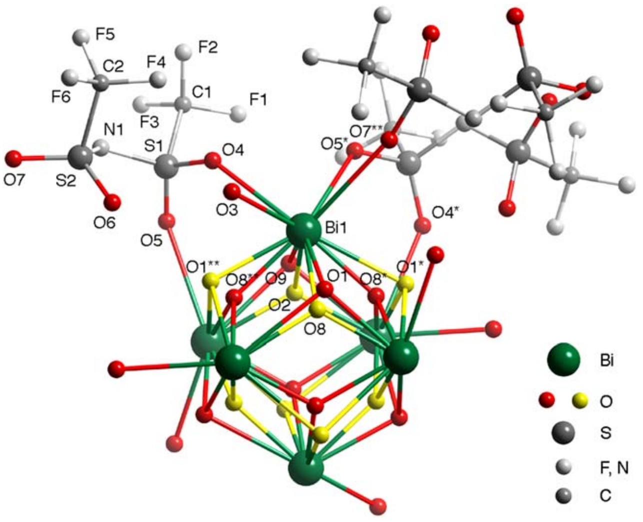


Figure 2. Structure of $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$. Only NTf_2^- anions bound to the top bismuth atom are shown for clarity. Oxygen atoms in yellow are one set of disordered oxygen atoms (see text).

atoms judging from Bi–O distances, which suggest O2 and O8 (Bi–O, 2.107(12)–2.204(13) Å) are oxide oxygens and O1 and O9 (Bi–O, 2.297(14)–2.557(16) Å) are hydroxide oxygens.[24,25] Each bismuth atom is coordinated by one water molecule (disordered in two positions; only one of the disordered water oxygen (O3) is shown in Fig. 2) and three oxygen atoms of NTf_2^- anions. Bi–O distances for water molecule is 2.59(2) and 2.65(3) Å and those for NTf_2^- anions ranges from 2.693(6) to 2.909(8) Å. The bismuth atoms, therefore, eight coordinate and their geometric arrangement can be described as a distorted square antiprism. Among four oxygen atoms of each NTf_2^- anion, three are used for the coordination to bismuth atoms and one is used for the hydrogen bonding. As shown in Figure 3, each $[Bi_6O_4(OH)_4(H_2O)_6]$ unit is coordinated by 12 NTf_2^- anions, every two of which are shared between two $[Bi_6O_4(OH)_4(H_2O)_6]$ units. Therefore, each $[Bi_6O_4(OH)_4(H_2O)_6]$ unit is connected to six other $[Bi_6O_4(OH)_4(H_2O)_6]$ units to form a 3D-network structure.

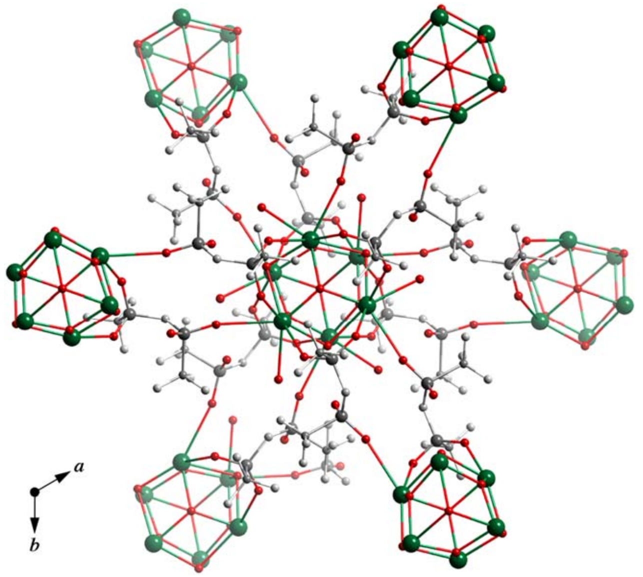


Figure 3. A view showing seven $[Bi_6O_4(OH)_4]$ units.

In order to evaluate the catalytic activity of **12**, Friedel–Crafts acylation reaction of *p*-xylene with hexanoic acid was carried out in the presence of **12** (Bi/hexanoic acid/*p*-xylene=0.2/1/65; 180 °C, 45 h). The yield of ketone (2%; 5% carboxylic acid conversion) was much lower than that (27%) obtained in the reaction carried out under the similar reaction conditions using $Bi(NTf_2)_3$ (Table 5, entry 3). This result supports our assumption that the main catalytically active species is $HNTf_2$ in the $Bi(NTf_2)_3$-catalyzed dehydrative acylations.

3. Conclusions

Dehydrative Friedel–Crafts acylation reaction of aromatic compounds with carboxylic acids as acylating agents can be catalyzed by simple Lewis acid- and Brønsted acid-catalysts. Lewis acid-catalyzed reaction of *p*-xylene with aliphatic carboxylic acids can take place at 180 °C with various metal triflates and bis(trifluoromethanesulfonyl)-amides, while higher reaction temperature generally affords desired ketones with higher selectivities. $Eu(NTf_2)_3$ shows the highest performance at 250 °C and efficiently catalyzes the acylation reaction of alkyl- and alkoxybenzenes with aliphatic and aromatic carboxylic acids. Brønsted acid-catalyst $HNTf_2$ has proved to be more efficient than $Eu(NTf_2)_3$ for the acylation of *p*-xylene with carboxylic acids at 200 °C. $HNTf_2$ catalyzes the acylation of anisole with carboxylic acids in high yields in refluxing toluene with azeotropic removal of water. These catalytic systems do not require any additives and can be applied to a wide range of carboxylic acids and aromatic compounds. Therefore, the present catalytic systems are superior to the reported counterparts in terms of simplicity and generality. These results suggest that Lewis acid- and Brønsted acid-catalysts have a great potential as catalysts for dehydrative Friedel–Crafts acylation using carboxylic acids as acylating agents.

4. Experimental

4.1. General

Reagents were purchased from Tokyo Kasei Kogyo, Junsei Chemical, Kanto Chemical, Aldrich, and Wako Pure Chemical Industries and used as received unless otherwise noted. Anisole, *m*-xylene, and cumene were distilled from CaH_2 prior to use. Preparative TLC was performed on Wakogel 60N (Wako Pure Chemical Industries). ^1H and ^{13}C NMR were recorded on a JEOL JMN-LA500 (499 MHz for ^1H, 125 MHz for ^{13}C) using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. IR spectra were measured using a JASCO FT/IR-610. GC analyses were performed on a Shimadzu GC-18A using an Ultra Alloy® FFAP capillary column (30 M×0.25 mm, Frontier Laboratories) or TC-FFAP capillary column (30 M×0.25 mm, GL Sciences Inc.). Low- and high-resolution GC–MS (EI) were measured on a Shimadzu QP-5000 spectrometer with a Shimadzu GC-17A and a DB-1 (25 M×0.32 mm, J&W Scientific), and JEOL JMS-GC MATE (BU20) spectrometer with a Hewlett

Packard HP6890 GC system and a NEUTRA BOND-1 capillary column (30 M×0.25 mm, GL Science).

4.2. A typical procedure for Friedel–Crafts acylation

A mixture of Eu$(NTf_2)_3$ (87.8 mg, 0.0885 mmol), octanoic acid (85.1 mg, 0.590 mmol), docosane (22.3 mg, an internal standard for GC analysis), and *p*-xylene (3.62 mL, 29.5 mmol) was stirred at 250 °C for 12 h with periodical monitoring of octanoic acid conversion by GC. After cooling to room temperature, water (3 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc=27/1) to give 1-(2,5-dimethylphenyl)-1-octanone **1l** as a pale yellow oil (109 mg, 80% yield).

Characterization data for the new compounds are shown below. All new compounds except for the by-product **2** were determined to be >95% pure by ^{1}H NMR spectroscopy. ^{1}H NMR spectrum of compound **2** showed some small unidentified signals in the aliphatic region.

4.2.1. 1-(2,5-Dimethylphenyl)-3-methyl-1-butanone (1h). The title compound was obtained by the reaction of isovaleric acid (51.1 mg, 0.500 mmol) and *p*-xylene (3.06 mL, 25.0 mmol) as described in the typical procedure in 55% yield (52.4 mg) as a pale yellow oil after the purification by preparative TLC (hexane/EtOAc=28/1). ^{1}H NMR δ 0.98 (d, 6H, J=6.8 Hz), 2.25 (nonet, 1H, J=6.8 Hz), 2.35 (s, 3H), 2.43 (s, 3H), 2.75 (d, 2H, J=6.8 Hz), 7.09–7.38 (m, 3H); ^{13}C NMR δ 20.51, 20.87, 22.65, 25.07, 50.65, 128.72, 131.58, 131.68, 134.37, 134.99, 138.68, 204.87; IR (neat) ν 1686 cm^{-1}; HRMS calcd for $C_{19}H_{30}O$ [M$^+$] 190.1358, found 190.1366.

4.2.2. 1-(2,5-Dimethylphenyl)-1-undecanone (1o). The title compound was obtained by the reaction of undecanoic acid (81.5 mg, 0.437 mmol) and *p*-xylene (2.68 mL, 21.9 mmol) as described in the typical procedure in 76% yield (90.9 mg) as a colorless oil after the purification by preparative TLC (hexane/EtOAc=30/1). ^{1}H NMR δ 0.88 (t, 3H, J=7.5 Hz), 1.39–1.20 (m, 14H), 1.68 (quintet, 2H, J=7.5 Hz), 2.35 (s, 3H), 2.43 (s, 3H), 2.86 (t, 2H, J=7.5 Hz), 7.08–7.41 (m, 3H); ^{13}C NMR δ 14.08, 20.61, 20.90, 22.65, 24.39, 29.29, 29.32, 29.45, 29.48, 29.55, 31.87, 41.67, 128.73, 131.61, 131.69, 134.46, 135.02, 138.40, 205.17; IR (neat) ν 1684 cm^{-1}; HRMS calcd for $C_{19}H_{30}O$ [M$^+$] 274.2297, found 274.2298.

4.2.3. 1,1-Bis(2,5-dimethylphenyl)-1-heptene (2). A mixture of Yb$(NTf_2)_3$ (101 mg, 0.100 mmol), heptanoic acid (65.1 mg, 0.500 mmol), and *p*-xylene (3.06 mL, 25.0 mmol) was stirred at 250 °C for 12 h. After cooling to room temperature, water (3 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc=30/1) to give **1b** (56.2 mg, 51% yield) and **2** (30.5 mg, 19% yield). Characterization data for **2**: ^{1}H NMR δ 0.85 (t, 3H, J=7.5 Hz), 1.21–1.30 (m, 4H), 1.41 (quintet, 2H, J=7.0 Hz), 2.00 (q, 2H, J=7.5 Hz), 2.10 (s, 3H), 2.24 (s, 6H), 2.29 (s, 3H), 5.70 (t, 1H, J=7.5 Hz), 6.85–6.94 (m, 3H), 6.97 (dd, 1H, J=7.5, 1.5 Hz), 7.03 (d, 1H, J=7.5 Hz), 7.05 (d, 1H, J=7.5 Hz); ^{13}C NMR δ 14.04, 19.58, 20.49, 20.96, 20.99, 22.49, 29.26, 29.60, 31.53, 127.17, 127.46, 129.92, 130.32, 130.60, 130.97, 132.26, 133.08, 133.79, 134.40, 134.65, 140.11, 140.16, 142.77; IR (neat) ν 2952, 2925, 2862, 1496, 1454, 808 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{26}O$ [M$^+$] 306.2348, found 306.2351.

4.2.4. 1-(4-Isopropylphenyl)-1-heptanone and its isomers (4b). The title compounds were obtained as a mixture of isomers (*p*-isomer:(*o*-+*m*-isomers)=85/15) by the reaction of heptanoic acid (50.8 mg, 0.390 mmol) and cumene (2.71 mL, 19.5 mmol) as described in the typical procedure in 71% yield (64.7 mg) as a pale yellow oil after the purification by preparative TLC (hexane/EtOAc=22/1). The minor isomers were only characterized by GC–MS that showed M$^+$ ion peaks and the similar fragment patterns as that of the major isomer. ^{1}H NMR (for *p*-isomer) δ 0.89 (t, 3H, J=7.2 Hz), 1.27 (d, 6H, J=7.0 Hz), 1.25–1.42 (m, 6H), 1.72 (quintet, 2H, J=7.5 Hz), 2.94 (t, 2H, J=7.5 Hz), 2.96 (septet, 1H, J=7.0 Hz), 7.31 (d, 2H, J=8.4 Hz), 7.90 (d, 2H, J=8.4 Hz); ^{13}C NMR (for *p*-isomer) δ 14.02, 22.52, 23.66, 24.45, 29.07, 31.66, 34.20, 38.52, 126.59, 128.29, 134.98, 154.27, 200.25; IR (neat) ν 1684 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}O$ [M$^+$] 232.1827, found 232.1820.

4.2.5. 1-(2,4-Dimethylphenyl)-1-heptanone (5b). The title compound was obtained by the reaction of heptanoic acid (75.7 mg, 0.582 mmol) and *m*-xylene (3.56 mL, 29.1 mmol) as described in the typical procedure in 74% yield (94.6 mg) as a colorless oil after the purification by preparative TLC (hexane/EtOAc=27/1). GC–MS analysis of the product showed the presence of a small amount of isomer (ca. 4% by the TIC integration). ^{1}H NMR δ 0.88 (t, 3H, J=7.0 Hz), 1.23–1.40 (m, 6H), 1.68 (quintet, 2H, J=7.5 Hz), 2.34 (s, 3H), 2.47 (s, 3H), 2.86 (t, 2H, J=7.5 Hz), 7.02–7.06 (m, 2H), 7.56 (d, 1H, J=8.5 Hz); ^{13}C NMR δ 13.97, 21.24, 21.35, 22.49, 24.52, 29.00, 31.63, 41.32, 126.16, 128.81, 132.73, 135.27, 138.31, 141.46, 204.13; IR (neat) ν 1684 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{22}O$ [M$^+$] 218.1671, found 218.1664.

4.2.6. 1-(3,4-Dimethylphenyl)-1-heptanone and 1-(2,3-dimethylphenyl)-1-heptanone (6b). The title compounds were obtained as a mixture (1-(3,4-dimethylphenyl)-1-heptanone/1-(2,3-dimethylphenyl)-1-heptanone=88/12) by the reaction of heptanoic acid (73.0 mg, 0.561 mmol) and *o*-xylene (3.42 mL, 28.0 mmol) as described in the typical procedure in 85% yield (104 mg) as a colorless oil after the purification by preparative TLC (hexane/EtOAc=20/1). ^{1}H NMR δ 0.86–0.92 (m, 3H), 1.27–1.42 (m, 6H), 1.66–1.75 (m, 2H), 2.27–2.34 (m, 6H), 2.83 (t, 0.24H, J=7.5 Hz, for the minor isomer), 2.92 (t, 1.76H, J=7.5 Hz, for the major isomer), 7.13 (t, 0.12H, J=7.5 Hz, for the minor isomer), 7.17–7.24 (m, 1H), 7.28 (d, 0.12H, J=7.5 Hz, for the minor isomer), 7.69 (dd, 0.88H, J=8.0, 2.0 Hz, for the major isomer), 7.73 (d, 0.88H, J=2.0 Hz, for the major isomer); ^{13}C NMR (for the major isomer) δ 14.39, 20.12, 20.32, 22.89, 24.90, 29.44, 32.04, 38.89, 126.17, 129.56, 130.10, 135.45, 137.18, 142.62, 200.93; IR (neat) ν 1681 cm^{-1}; HRMS calcd for $C_{15}H_{22}O$ [M$^+$] 218.1671, found 218.1664.

4.2.7. 1-(2,5-Diethylphenyl)-1-heptanone (7b). The title compound was obtained by the reaction of heptanoic acid (82.6 mg, 0.635 mmol) and *p*-diethylbenzene (4.94 mL, 31.8 mmol) as described in the typical procedure in 74% yield (115 mg) as a colorless oil after the purification by preparative TLC (hexane/EtOAc=20/1). ^{1}H NMR δ 0.89 (t, 3H, J=7.0 Hz), 1.20 (t, 3H, J=7.5 Hz), 1.24 (t, 3H, J=7.5 Hz), 1.28–1.42 (m, 6H), 1.70 (quintet, 2H, J=7.5 Hz), 2.65 (q, 2H, J=7.5 Hz), 2.76 (q, 2H, J=7.5 Hz), 2.87 (t, 2H, J=7.5 Hz), 7.18 (d, 1H, J=8.0 Hz), 7.22 (dd, 1H, J=2.0, 8.0 Hz), 7.33 (d, 1H, J=2.0 Hz); ^{13}C NMR δ 14.01, 15.51, 16.11, 22.51, 24.31, 26.43, 28.34, 28.97, 31.65, 42.19, 127.18, 130.16, 130.36, 138.85, 140.61, 141.40, 205.86; IR (neat) ν 1691 cm^{-1}; HRMS calcd for $C_{17}H_{26}O$ [M$^+$] 246.1984, found 246.1989.

4.3. A typical procedure for $HNTf_2$-catalyzed Friedel–Crafts acylation with azeotropic removal of H_2O

A mixture of $HNTf_2$ (141 mg, 0.500 mmol), heptanoic acid (325 mg, 2.50 mmol), anisole (13.5 g, 125 mmol), and toluene (30 mL) was refluxed for 36 h in 100 mL flask equipped with Dean–Stark apparatus. After cooling to room temperature, water was added to the mixture and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc=24/1) to give 1-(4-methoxyphenyl)-1-heptanone **9b** as a white solid (488 mg, 89% yield). Mp: 38–39 °C (lit.[26] mp 39–40 °C).

4.4. Hydrolysis of $Bi(NTf_2)_3$

4.4.1. Hydrolysis of $Bi(NTf_2)_3$ in *p*-xylene. $Bi(NTf_2)_3$ (105 mg, 0.10 mmol), *p*-xylene (4 mL), and carboxylic acid (heptanoic acid, 72 μL, 66 mg, 0.51 mmol or cyclohexanecarboxylic acid, 64 mg, 0.50 mmol) were mixed in a glass tube. Under these conditions, some $Bi(NTf_2)_3$ remained undissolved (the amount of $Bi(NTf_2)_3$ was too much for complete dissolution). Then 4.7, 5.4, or 10.4 μL of water was added. In some cases, the mixture was heated to reflux for a few minutes, while in other case the mixture was kept at room temperature. In all cases, colorless crystals of $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$ were formed within a few days.

4.4.2. X-ray crystallography. Crystals were covered by inert oil (Paratone 8236, Exxon) and mounted on a glass fiber under cold nitrogen flow. Data were collected on a Bruker Smart Apex CCD area detector diffractometer. Crystal data, data collection, and refinement parameters for $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$ are given in Table 7. Hydrogen atoms could not be located. The number of hydrogen in $[Bi_6O_4(OH)_4]$ was assumed to keep the charge balance as well as from the similar structures reported.[23,24] O3 atom was judged to be an oxygen atom of a water molecule from its position as well as the Bi–O distance. Disorder was observed for O1 (O8), O2 (O9), O3, S2, F4–F6, O6, O7, and C2 atoms (the atomic numberings refer to those in Fig. 2).

Table 7. Crystallographic data for $[Bi_6O_4(OH)_4(H_2O)_6](NTf_2)_6$

Formula	$C_{12}H_{16}Bi_6F_{36}N_6O_{38}S_{12}$
Formula weight	3174.82
Crystal size (mm)	0.14×0.13×0.11
Crystal system	Trigonal
Space group	*R*-3 (no. 148)
a (Å)	19.1789(8)
b (Å)	19.1789(8)
c (Å)	15.8377(13)
α (°)	90
β (°)	90
γ (°)	120
V (Å)	5045.1(5)
Z	3
D_{calc} (g cm^{-3})	3.135
F(000)	4344
μ(Mo Kα) (cm^{-1})	16.18
T (K)	153(2)
No. of rflns measd	7602
No. of unique rflns (R_{int})	2473
No. of variables	202
$R1$ ($I_0>2\sigma(I_0)$)	0.0319
$wR2$ (all data)	0.0859
GOF	1.05
Diff peak, hole (eÅ^{-3})	1.80, −1.64

5. Crystallographic data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 608158. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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