Electrophilic Aromatic Nitration Using a Mixed Catalyst of Lithium, Molybdenum, Ytterbium on Silica Gel

Min Shi,* Shi-Cong Cui

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Lu, Shanghai 200032, P.R. China
Fax: (+86)-21-64166128, e-mail: mshi@pub.sioc.ac.cn.

Received: August 6, 2003; Revised: October 31, 2003; Accepted: November 2, 2003

Abstract: A novel mixed catalyst of $LiClO_4$ (15% w/w), $Yb(OPf)_3$ (15% w/w, Pf = perfluorooctanesulfonyl), MoO_3 (15% w/w) on silica gel for electrophilic aromatic nitration reaction has been explored. The nitration reactions were accomplished by this mixed catalyst and nitric acid under solvent-free conditions. Moreover, the mixed catalyst can be easily recovered from the aqueous layer by heating in an oven and reused for the next nitration reaction.

Keywords: catalyst recycling; halogenated-solvent-free aromatic nitration; lithium; mixed catalyst; molybdenum, perfluorinated rare earth metal salt; silica gel; ytterbium

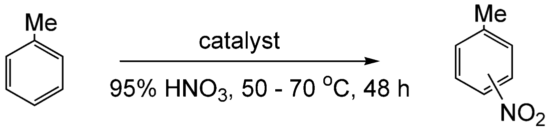
Introduction

Nitration of organic compounds has long been a very active and rewarding area of research and is the subject of a large body of literature. Ingold,[1] Olah,[2,3,6] Schofield,[4,5] and Ione[7] have published extensive and well documented reviews, among others. Nitration of aromatic compounds typically requires a mixture of concentrated or fuming nitric acid with sulfuric acid leading to excessive acid waste streams and added expense. The obvious disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, by using solid acid catalysts, other sources of NO_2^+, organic nitrating agents, other acids replacing sulfuric acid, etc. But none of them has practical value in industrial use. Recently, it was found that lanthanide triflates (1–10 mol %) [$Ln(OTf)_3$, Ln=Yb, Sc, Y. etc] can catalyze the nitration of a range of simple aromatic compounds in good to excellent yield using stoichiometric quantities of 69% nitric acid, the only by-product is water and the catalyst can be readily recycled by simple evaporation.[8] However, these nitrations were carried out in 1,2-dichloroethane, an environmentally hazardous solvent, under reflux. Previously, we reported two more eco-safer nitration processes: 1) using perfluorinated rare earth metal salts $Ln(OPf)_3$ [$Ln(OSO_2C_8F_{17})_3$] as catalysts without halogenated organic solvent and 2) electrophilic aromatic nitration using perfluorinated rare earth metal salts in the fluorous phase.[9,10] In order to seek a more efficient and eco-safer catalyst, we continuously pursued our research in this field. Herein, we report an unprecedented mixed catalyst system for electrophilic aromatic nitration reactions. Moreover, the mixed catalyst can be easily recovered from the aqueous layer by heating in an oven and can be reused for the next nitration reaction.

Results and Discussion

Recently, Skupinski and his co-workers reported the use of MoO_3/SiO_2, WO_3/SiO_2 or TiO_2/SiO_2 as a catalyst in the nitration reaction of *o*-xylene using 100% nitric acid. They found that MoO_3/SiO_2 is the most effective catalyst in this reaction.[11] The use of an MoO_3/SiO_2 catalyst containing 15% MoO_3 allows one to obtain as much as 99% yield in the nitration of *o*-xylene at 20 °C, although they used twice the amount of nitric acid in this reaction. Thus, we anticipated that the combination of the perfluorinated rare earth metal salts $Ln(OPf)_3$ [$Ln(OSO_2C_8F_{17})_3$] with MoO_3/SiO_2 would achieve a more affective and recyclable catalyst. As results, we synthesized two catalysts with $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (70% w/w) and $Yb(OPf)_3$ (30% w/w), MoO_3 (30% w/w) on SiO_2 (40% w/w), respectively, and utilized them in the catalytic nitration of electrophilic aromatic compounds (Scheme 1). The results are summarized in Table 1. As can be seen from Table 1, in the nitration reaction of toluene catalyzed by different catalysts, the mixed catalysts gave the better results than those of $Yb(OPf)_3$ or MoO_3 (15% w/w) on SiO_2, respectively (Table 1, entries 3, 4 and 1, 2). When using $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (70% w/w) as the catalyst, the yield reached 74%. The two different mixed catalysts have similar results (Table 1, entries 3, 4). It should be emphasized here that the results shown in Table 1 were repeated twice and the

DOI: 10.1002/adsc.200303129



Scheme 1.

Table 1. Nitration reaction of toluene catalyzed by different catalysts.

Entry	Catalyst	Yield [%][b]
1	$Yb(OPf)_3$[a]	67[d]
2	MoO_3 (15% w/w) in SiO_2	65[d]
3	$Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) in SiO_2[c]	74[d]
4	$Yb(OPf)_3$ (30% w/w), MoO_3 (30% w/w) in SiO_2[c]	74[d]

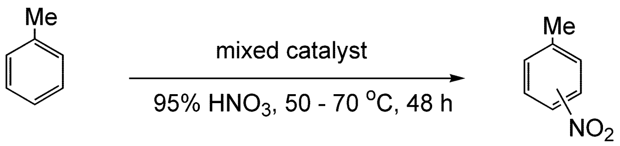
[a] $Yb(OPF)_3$ is $Yb(OSO_2C_8F_{17})_3$ and 10 mg were employed.
[b] Isolated yields.
[c] The amount of catalyst is 50 mg.
[d] *p*:*m*:*o* = 74:2:24.

mixed catalyst loaded on SiO_2 can be very easily recovered from reaction mixture just by heating the aqueous phase in an oven and the *ortho*, *meta* and *para* distribution is almost same with the ratio of *p*:*m*:*o*=74:2:24, which has been determined by ^{1}H NMR spectroscopy and checked by GLC analysis. The control experiment elucidates that only 10% of the nitrated product could be obtained in the absence of the metal catalyst but with 90% HNO_3.

Table 2. Nitration reaction catalyzed by mixed catalyst[a] in the presence of different metal salts.

Entry	Metal salt[b]	Yield [%][c,d]
1	$CrCl_2$	65
2	$CoCl_2$	67
3	$NaBF_4$	64
4	$NiCl_2$	67
5	LiCl	52
6	$LiClO_4$	77
7	$LiPF_6$	68
8	$Ni(OAc)_2$	70
9	$Cu(OAc)_2$	77
10	$Co(OAc)_2$	72
11	$Mn(OAc)_2$	67

[a] The mixed catalyst is $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) in SiO_2 and the amount is 50 mg.
[b] Amount of metal salt is 0.1 mmol.
[c] Isolated yields.
[d] *p*:*m*:*o* = 74:2:24.

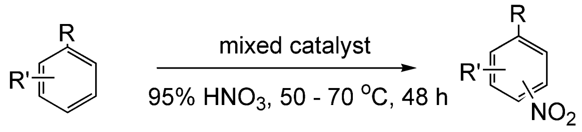


Scheme 2.

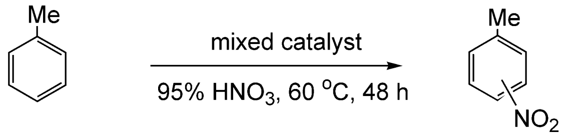
In order to further optimize this novel mixed catalyst, we examined many references about catalytic nitration and Friedel–Crafts reactions.[12] We noted the report of Kobayashi that in the Friedel–Crafts of activated aromatic compound with acetic anhydride catalyzed by $Ln(OTf)_3$, the addition of $LiClO_4$ can greatly accelerate the reaction rate.[13] Therefore, we hoped that the catalytic ability of the mixed catalyst could be further improved by the same means. In fact, we screened many metal salts combined with this mixed catalyst in the catalytic nitration reaction of toluene by 95% nitric acid. For this screening procedure the mixed catalyst [$Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (70% w/w)] (50 mg) and the metal salt (0.1 mmol) were added into toluene, then 95% nitric acid was dropped into this solution (Scheme 2). The reaction mixture was stirred at 60 °C for 48 h. The results are summarized in Table 2. Based on the results shown in Table 2, it is very clear that some metal salt additives such as $LiClO_4$, $Cu(OAc)_2$ or $Co(OAc)_2$ could afford higher yield of nitration products than that without metal salts under the same conditions (Table 2, entries 6, 9, 10). $LiClO_4$ is the best additive for the catalytic nitration by the mixed catalyst because although $Cu(OAc)_2$ is superior to $LiClO_4$ in terms of safety, it is more hazardous from an environmental standpoint.

By means of the optimized combination of the mixed catalyst [$LiClO_4$ (15% w/w), $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (55% w/w)], we next examined the nitration of other aromatic compounds (Scheme 3) The results are described in Table 3. The yields of the nitration products in general can reach 50–82% under very low catalyst loadings. The electrophilic aromatic nitration proceeded very well for many substrates. On the other hand, the mixed catalyst was easily recovered from aqueous layer just by heating the aqueous phase in an oven after extraction of the organic product with ether and can be reused for the next reaction. In our experiments, the recovered mixed catalyst was reused and recycled five times for nitration and we found that the same result was obtained in each catalyzed nitration (Table 4).

For solid aromatic compounds such as naphthalene (mp 80–81 °C), the nitration can also be carried out under the same conditions at 70–80 °C (Scheme 5). The corresponding 1-nitronaphthalene was obtained in 63% yield.



Scheme 3.



Scheme 4.

Table 3. Nitration reaction of different aromatic compounds using mixed catalyst.[a]

Entry	R	R'	Yield [%][b]
1	Me	H	80[c]
2	Cl	H	66[d]
3	Br	H	58[d]
4	H	H	74
5	Et	H	68[e]
6	*i*-Pr	H	65[f]
7	Me	Me	82

[a] The mixed catalyst is $LiClO_4$ (15% w/w), $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) in SiO_2 and the amount is 50 mg.
[b] Isolated yields.
[c] *p*:*m*:*o* = 74:2:24.
[d] *p*:*m*:*o* = 60:0:40.
[e] *p*:*m*:*o* = 53:0:47.
[f] *p*:*m*:*o* = 72:0:28.

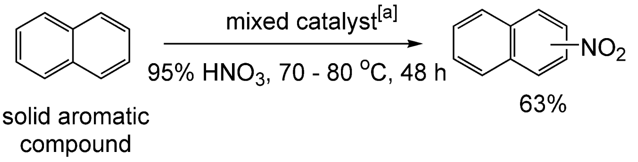
Conclusion

In conclusion, we have discovered a nitration process in the presence of a novel mixed catalyst using only nitric acid under mild reaction conditions. This new nitration process employs a mixed catalyst of rare earth metal salts and some other metal additives [$LiClO_4$ (15% w/w), $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (55% w/w)] by which the nitration of aromatic compound can be realized without using a halogenated organic solvent. Thus, we believe that this is a much eco-safer protocol for nitration. Efforts are underway to elucidate more mechanistic details of the nitration reaction catalyzed by this novel catalyst and to identify systems enabling the nitration of other aromatic compounds, and the subsequent transformations thereof.

Table 4. Isolated yields of nitration of toluene by recovered catalyst.[a]

Run	1	2	3	4	5
$Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2	74[b]	74	73	75	75
$Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w), $LiClO_4$ (15% w/w) on SiO_2	77[b]	80	80	79	80

[a] Isolated yields (%) based on the nitric acid.
[b] 95% HNO_3; *p*:*m*:*o* = 74:2:24.



[a] $LiClO_4$ (15% w/w), $Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (55% w/w)

Scheme 5.

Experimental Section

General

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured on a Finnigan MA+mass spectrometer. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification, All reactions were monitored by TLC on Huanghai GF_{254} silica gel coated plates. The orientation of nitration was determined by ^1H NMR spectroscopy and GLC analysis. Flash column chromatography was carried out using 200–300 mesh silica gel. $Yb(C_8F_{17}SO_3)_3$ was prepared by the reaction of perfluorooctanesulfonic acid ($C_8F_{17}SO_3H$) with Yb_2O_3 according to the literature.[14]

Preparation of the Mixed Catalysts

$Yb(OPf)_3$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (70% w/w): 1.83 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved in 15 mL of 3% H_2O_2 at room temperature. Then, 1.5 g $Yb(OPf)_3$ were added into this solution. 7.0 g of SiO_2 were poured into the resulting solution and the mixture was stirred at room temperature for 1 h. The obtained mixture was heated at 120 °C for 48 h in an oven.

$Yb(OPf)_3$ (15% w/w), $LiClO_4$ (15% w/w), MoO_3 (15% w/w) on SiO_2 (55% w/w): 1.83 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved in 15 mL of 3% H_2O_2 at room temperature. Then

1.5 g $Yb(OPf)_3$ and 1.5 g $LiClO_4$ were added into this solution. 7.0 g of SiO_2 were poured into the resulting solution and the mixture was stirred at room temperature for 1 h. The obtained mixture was dried at 120 °C for 48 h in an oven.

General Procedure for the Nitration of Aromatic Compounds in the Presence of a Mixed Catalyst

To a solution of toluene (2.1 mL, 20 mmol) and 95% nitric acid (0.5 mg, 12 mmol) were added 15% $LiClO_4$, 15% $Yb(OPf)_3$, 15% MoO_3 on SiO_2 (50 mg) and reaction mixture was stirred at 60 °C for 48 h. The reaction mixture was washed with water (l0 mL) and extracted with ether (Et_2O). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatograph (eluent: petroleum ether/EtOAc, 10/l) to give nitrotoluene as a yellow liquid. Total yield: 1.32 g (80%); *p*:*m*:*o* = 74:2:24; MS (EI): *m/z* = 137 (M^+) [HRMS calcd. for $C_7H_7NO_2$ (137.1360): 137.0477; found: 137.0464].

2-Nitrotoluene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.61$ (3H, s, CH_3), 7.20–7.45 (2H, m, Ar), 7.48 (1H, d, $J = 7.5$ Hz, Ar), 7.96 (1H, d, $J = 7.5$ Hz, Ar).

3-Nitrotoluene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.48$ (3H, s, CH_3), 7.40–7.51 (2H, m, Ar), 7.92–8.09 (2H, m, Ar).

4-Nitrotoluene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.48$ (3H, s, CH_3), 7.33 (2H, d, $J = 8.4$ Hz, Ar), 8.13 (2H, d, $J = 8.4$ Hz, Ar).

Nitration of *p*-Chlorobenzene

A yellow oil, yield: 194 mg (55%); *p*:*m*:*o* = 60:0:40; MS (EI): *m/z* = 158 (M^+) [HRMS: calcd. for $C_6H_5ClNO_2$ (l57.5542): 156.9931; found: 156.9915].

4-Nitrochlorobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7.62$ (2H, d, $J = 8.2$ Hz, Ar), 8.06 (2H, d, $J = 8.2$ Hz, Ar).

2-Nitrochlorobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7.30$–7.36 (3H, m, Ar), 7.75 (1H, d, $J = 7.8$ Hz, Ar).

Nitration of *p*-Bromobenzene

A yellow solid, mp 96–110 °C, yield: 1.09 g (58%); *p*:*m*:*o* = 60:0:40; MS (EI): *m/z* = 202 (M^+) [HRMS calcd. for $C_6H_5BrNO_2$ (202.0055): 200.9425; found: 200.9410].

4-Nitrobromobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7.59$ (2H, d, $J = 8.5$ Hz, Ar), 8.01 (2H, d, $J = 8.5$ Hz, Ar).

2-Nitrobromobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7.27$–7.33 (3H, m, Ar), 7.70 (1H, d, $J = 7.8$ Hz, Ar).

Nitration of Benzene

A yellow oil, yield: 1.10 g (74%); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7\ 31$ (2H, t, $J = 7.7$ Hz, Ar), 7.52–7.58 (1H, m, Ar), 8.24 (2H, d, $J = 7.8$ Hz, Ar); MS (EI): *m/z* = 123 (M^+) [HRMS calcd. for $C_6H_5NO_2$ (123.1094): 123.0320; found: 123.0333].

Nitration of Xylene

A yellow oil, yield: 1.48 g (82%); MS (EI): *m/z* = l51 (M^+) [HRMS calcd. for $C_8H_9NO_2$ (151.1626): 151.0633; found: 151.0630].

1,2-Dimethyl-4-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.38$ (6H, s, CH_3), 7.25 (1H, d, $J = 8.0$ Hz, Ar), 7.94–8.0 (2H, m, Ar).

l,3-Dimethyl-5-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.42$ (6H, s, CH_3), 7.30 (1H, s, Ar), 7.83 (2H, s, Ar).

l,4-Dimethyl-2-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2{,}40$ (3H, s, CH_3), 2.55 (3H, s, CH_3), 7.20–7.33 (2H, m, Ar), 7.78 (1H, s, Ar).

1,2-Dimethyl-6-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.37$ (6H, s, CH_3), 7.08–7.45 (2H, m, Ar), 7.58 (1H, d, $J = 7.8$ Hz, Ar).

1,3-Dimethyl-6-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.40$ (3H, s, CH_3), 2.60 (3H, s, CH_3), 7.11–7.16 (2H, m, Ar), 7.92 (1H, d, $J = 7.9$ Hz, Ar).

1,4-Dimethyl-6-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 2.30$ (6H, s, CH_3), 7.11–7.28 (3H, m, Ar).

Nitration of Ethylbenzene

A yellow oil, yield: 0.86 g (68%), *p*:*m*:*o* = 53:0:47; MS (EI): *m/z* = 151 (M^+) [Calcd. for $C_8H_9NO_2$ (151.1626): 151.0633, Found: 151.0623].

2-Nitroethylbenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 1.26$ (3H, t, $J = 7.2$ Hz, CH_3), 2.88 (2H, q, $J = 7.2$ Hz, CH_2), 7.10–7.60 (3H, m, Ar), 7.75 (1H, d, $J = 8.0$ Hz, Ar).

4-Nitroethylbenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 1.27$ (3H, t, $J = 7.2$ Hz, CH_3), 2.74 (2H, q, $J = 7.2$ Hz, CH_2), 7.30 (2H, d, $J = 8.0$ Hz, Ar), 8.03 (2H, d, $J = 8.0$ Hz, Ar).

Nitration of Isopropylbenzene

A yellow oil, yield: 0.94 g (65%); *p*:*m*:*o* = 72:0:28; MS (EI): *m/z* = 165 (M^+) [HRMS calcd. for $C_9H_{11}NO_2$ (165.1892): 165.0790; found: 165.0786].

1-Isopropyl-2-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 1.30$ (6H, d, $J = 7.8$ Hz, CH_3), 3.32–3.44 (1H, m, CH), 7.15–7.65 (4H, m, Ar).

1-Isopropyl-4-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 1.29$ (6H, d, $J = 7.8$ Hz, CH_3), 2.96–3.08 (1H, m, CH), 7.37 (2H, d, $J = 8.2$ Hz, Ar), 8.15 (2H, d, $J = 8.2$ Hz, Ar).

Nitration of Naphthalene

A yellow solid, mp 96–110 °C, yield: 63%.

1-Nitronaphthalene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 7.56$ (1H, t, $J = 7.8$ Hz, CH_3), 7.63 (1H, t, $J = 7.8$ Hz, Ar), 7.73 (1H, t, $J = 7.8$ Hz, Ar), 7.97 (1H, d, $J = 7.8$ Hz, Ar), 8.12 (1H, t, $J = 7.8$ Hz, Ar), 8.24 (1H, t, $J = 7.8$ Hz, Ar), 8.57 (1H, d, J = 7.8 Hz, Ar); MS (EI): *m/z* = 173 (M^+); anal. found: C 69.24, H 4.17, N 7.99%; $C_{10}H_7NO_2$ requires: C 69.36, H 4.07, N 8.09%.

Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China (20390050, 20025206 and 20272069) for financial support.

References and Notes

[1] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., Cornell University Press, Ithaca, New York, **1969**.

[2] G. A. Olah, S. J. Kuhn, in *Friedel–Crafts and Related Reactions*, (Ed.: G. A. Olah), Wiley-Interscience, New York, Vol. 2, **1964**.

[3] G. A. Olah, *ACS Symposium Series*, Vol. 22, (Ed.: F. Albright), American Chemical Society, Washington DC, **1967**, p. 1.

[4] J. G. Hoggett, R. B. Moodie, J. R. Penton, K. Schofield, *Nitration and Aromatic Reactivity*, Cambridge University Press, London, **1971**.

[5] K. Schofield, *Aromatic Nitration*, Cambridge University Press, London, **1980**.

[6] G. A. Olah, R. Malhotra, S. C. Narang, *Nitration: Methods and Mechanism*, (Ed.: H. Feuer), VCH Publishers, New York, **1989**.

[7] L. V. Malysheva, E. A. Paukshtis, K. G. Ione, *Catal. Rev. Sci. Eng*. **1995**, *37*, 179–226.

[8] a) F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramprasad, *Chem. Commun*. **1997**, 613–614; b) A. G. M. Barrett, D. C. Braddock, R. Ducray, R. M. McKinnell, F. I. Waller, *Synlett* **2001**, 57–60; c) F. J. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, D. Ramprasad, *J. Chem. Soc. Perkin Trans. 1* **1999**, 867–871; d) F. I. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, A. J. P. White, D. J. Williams R. Ducray, *J. Org. Chem*. **1999**, *64*, 2910–2913.

[9] a) M. Shi, S. C. Cui, *J. Fluorine Chem*. **2002**, *113*, 207–209; b) M. Shi, S. C. Cui, *Chem. Commun*. **2002**, 994–995.

[10] For a survey of the Kyodai nitration, see: a) M. Matsunaga, *Chimica Oggi* **1994**, *12*, 58–61; b) T. Mori, H. Suzuki, *Synlett* **1995**, 383–392; c) T. Suzuki, R. Noyori. *Chemtracts* **1997**, *10*, 813–817; d) J. H. Ridd, *Acta Chem. Scand.* **1998**, *52*, 11–22; e) N. Nonoyama, T. Mori, H. Suzuki, *Zh. Org. Khim.* **1998**, *34*, 1591–1594.

[11] T. Miłczak, J. Jacniacki, J. Zawadzki, M. Malesa, W. Skupinski, *Synth. Commun.* **2001**, *31*, 173–187.

[12] a) A. Cornelis, L.Delaude, A. Gertmans, P. Laszlo, *Tetrahedron Lett.* **1988**, *29*, 5657–5660; b) P. Laszlo, J. Vandormael, *Chem. Lett.* **1988**, *11*, 1843–1846; c) P. Laszlo, A. Cornelis, A. Germans, *Chem. Lett.* **l988**, *11*, l839–1842.

[13] S. Kobayashi, A. Kawada, S. Mitamura, J. Matsuo, T. Tsuchiya, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2325–2333.

[14] For the preparation of perfluorinated rare earth metal catalysts [$Ln(OSO_2C_8F_{17})_3$, Ln = La, Yb, Sc], see: J. H. Forsberg, V. T. Spasiano, T. M. Balasubramanian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown, J. L. Miller, *J. Org. Chem.* **1987**, *52*, 1017–1021; an excess amount of a lanthanide(III) oxide (99.9% purity) was added to an aqueous solution of $C_8F_{17}SO_3H$ (50% v/v) and the mixture heated at boiling for 30 min to 1 h. The mixture was filtered to remove the unreacted oxide. The water was then removed from the filtrate under reduced pressure. The resulting hydrate was dried by heating under vacuum at 180 to 200 °C for 48 h.