Hafnium(IV) Trifluoromethanesulfonate, An Efficient Catalyst for the Friedel–Crafts Acylation and Alkylation Reactions

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Hafnium(IV) trifluoromethanesulfonate (hafnium(IV) triflate, $Hf(OTf)_4$) was synthesized from hafnium tetrachloride and trifluoromethanesulfonic acid. The triflate thus prepared was found to be effective in the catalytic Friedel–Crafts acylation reactions of various substituted benzenes with acid anhydrides in lithium perchlorate–nitromethane ($LiClO_4$–$MeNO_2$). Lithium perchlorate–nitromethane is an excellent solvent system, and the catalytic activity of the Lewis acid was much improved in this medium. The product was obtained in up to 250000% molar amounts based on the catalyst. Hafnium(IV) triflate was also found to be quite effective in the catalytic Friedel–Crafts alkylation reactions of aromatic compounds with alkyl chlorides. The reactions proceeded smoothly in the presence of 5% molar amount of $Hf(OTf)_4$ and 50% molar amount of $LiClO_4$ by using a slow addition procedure.

Synthetic reactions using Lewis acids as promoters are among the most important processes in organic synthesis. Many kinds of Lewis acid-promoted reactions have been developed to realize unique reactivities and selectivities, and some of them have been applied in industrial processes.[1] In most of these reactions, however, more than a stoichiometric amount of a Lewis acid is required and it is desired to decrease the amount of the acid by developing an efficient catalyst and catalytic processes.

Recently, we have studied the chemistry of metal trifluoromethanesulfonates (triflates), which have stronger Lewis acidity than the corresponding metal halides because of the electron-withdrawing trifluoromethanesulfonyl group. Lanthanide(III) triflates ($Ln(OTf)_3$) and scandium(III) triflate ($Sc(OTf)_3$) were found to work as Lewis acids even in aqueous solution, and they effectively catalyzed the aldol,[2] Michael, Diels–Alder,[3] and allylation reactions.[2c,4] Now we focused on group 4 elements (Ti, Zr, Hf) since they were expected to be stronger Lewis acids and four trifluoromethanesulfonyl groups (OTf) might be potentially introduced into the metal centers. In this paper, we would like to report a novel catalyst, hafnium(IV) triflate ($Hf(OTf)_4$), which was successfully used in the Friedel–Crafts acylation and alkylation reactions.[5]

Results and Discussion

Synthesis of Hafnium(IV) Triflate. We expected that metal(IV) triflates would have stronger Lewis acidity. In the literature, it was reported that titanium has up to three OTf ligands, probably due to its small ionic radius.[6] On the other hand, zirconium(IV) triflate ($Zr(OTf)_4$) was reported to be prepared from $ZrCl_4$ and trifluoromethanesulfonic acid (TfOH).[6a] As for $Hf(OTf)_4$, there was no report to the best of our knowledge. Since its large radius attracted us,[2f] we synthesized $Hf(OTf)_4$ from hafnium tetrachloride ($HfCl_4$) and TfOH, according to the similar standard procedure for the preparation of metal triflates.[6,7] $Hf(OTf)_4$ thus prepared is a white powder and was found to be stable even at 300 °C.

Catalytic Friedel–Crafts Acylation Reactions Using Hafnium(IV) Triflate as a Catalyst in Lithium Perchlorate–Nitromethane. The Friedel–Crafts acylation reactions, which are one of the most important processes in organic synthesis, are generally done by using aluminum trichloride ($AlCl_3$) as a Lewis acid.[8] The $AlCl_3$-promoted reactions have some disadvantages such as the requirement of more than a stoichiometric amount of the Lewis acid and of treatment of the $AlCl_3$ residue after the reactions. Although several catalytic Friedel–Crafts acylation reactions have been reported so far, they are not satisfactory in terms of yield, scope of the substrates, and turnover of the catalyst.[9,10]

In the course of our investigations to search for efficient catalysts in the Friedel–Crafts reactions, we got two important findings. 1) Turnover of Lewis acid catalysts in Friedel–Crafts acylation reactions is 5—20 times improved in lithium perchlorate–nitromethane ($LiClO_4$–$MeNO_2$). 2) Hafnium(IV) triflate (Hf-

(OTf)$_4$) is the most effective catalyst we have tested in the Friedel–Crafts acylation reactions.

The effects of Lewis acids in 4 M LiClO$_4$ solution (1 M=1 mol dm^{-3}) in MeNO$_2$ (4 M LiClO$_4$–MeNO$_2$) in the model reaction of acetic anhydride with *m*-xylene are shown in Table 1. Among the Lewis acids screened, Hf(OTf)$_4$ was found to be the most effective, and 2,4-dimethylphenyl methyl ketone was obtained in a high yield. It is noted that the turnover of all the catalysts tested was 5—20 times improved in 4 M LiClO$_4$–MeNO$_2$.[11] We also examined the effects of solvents in this reaction. While the reaction proceeded smoothly in LiClO$_4$–MeNO$_2$, *i*-PrNO$_2$, or CH$_2$Cl$_2$, only a trace of the product was detected in Et$_2$O or CS$_2$. Several examples of the Friedel–Crafts acylation reactions of substituted benzenes with acid anhydrides using a catalytic amount of Hf(OTf)$_4$ in LiClO$_4$–MeNO$_2$ are shown in Table 2. The features of these Friedel–Crafts acylation reactions are as follows. In all cases (except for Entry 8), the reactions proceeded smoothly using a catalytic amount of Hf(OTf)$_4$ in LiClO$_4$–MeNO$_2$ to give the corresponding aromatic ketones in high yields. Various substituted benzenes could be used, and not only acetic anhydride but also propionic anyhdride and benzoic anhydride reacted with substituted benzenes to afford the corresponding aromatic ketones in high yields. Even sterically hindered acid anhydrides such as

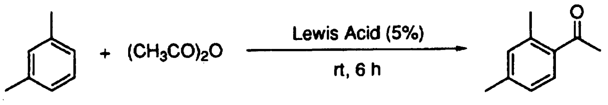

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Table 1. Effect of Lewis Acids in MeNO$_2$ and LiClO$_4$–MeNO$_2$ Media

		Yield (%)	
Entry	Lewis acid	MeNO$_2$	4 M LiClO$_4$–MeNO$_2$
1	BF$_3$·OEt$_2$	1	25
2	SnCl$_4$	5	50
3	Sc(OTf)$_3$	5	40
4	SbCl$_5$	6	59
5	Zr(OTf)$_4$	18	68
6	Hf(OTf)$_4$	16	76 (91)[a]

a) The reaction was carried out in 12 M LiClO$_4$–MeNO$_2$.

Table 2. Hf(OTf)$_4$-Catalyzed Friedel–Crafts Acylation Reactions in LiClO$_4$–MeNO$_2$ Media[a]

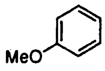
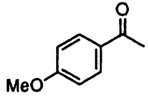
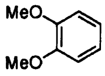
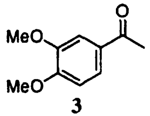
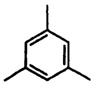
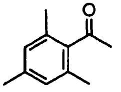
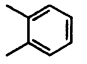
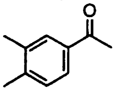
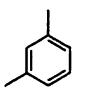
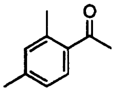
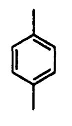
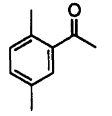
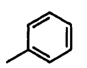
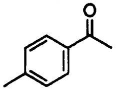
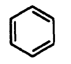
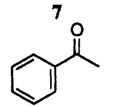
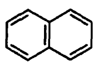
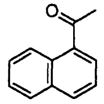
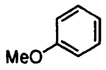
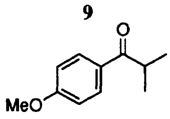
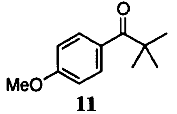
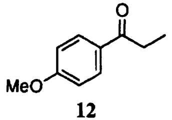
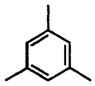
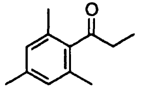
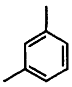
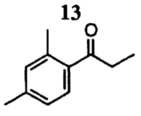
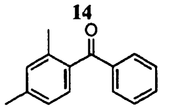
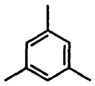
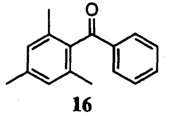
Entry	Aromatic compound	Acid anhydride	Major product	Yield (%)
1		(CH$_3$CO)$_2$O	 **2**	95
2			 **3**	90
3			 **4**	92
4			 **5**	90
5			 **1**	91
6			 **6**	66
7			 **7**	85[b]
8			 **8**	17

Table 2. (Continued)

Entry	Aromatic compound	Acid anhydride	Major product	Yield (%)
9			 **9**	$99^{c)}$
10		$(^{i}PrCO)_2O$	 **10**	Quant.
11		$(^{t}BuCO)_2O$	 **11**	91
12		$(CH_3CH_2CO)_2O$	 **12**	93
13			 **13**	84
14			 **14**	83
15		$(PhCO)_2O$	 **15**	88
16			 **16**	94

a) The reactions were carried out using 5% molar amount of $Hf(OTf)_4$ except for Entry 3 (1%) and Entries 6, 7, and 8 (10%). The reactions were carried out at room temperature except for Entry 2 (0 °C) and Entry 15 (50 °C). b) Ortho/para=3/97. c) Methyl 1-naphthyl ketonre/methyl 2-naphthyl ketonre=52/48.

Table 3. Wavenumbers of the Key Intermediate

$LiClO_4$ (molar amount)	$Hf(OTf)_4$ (molar amount)	Wavenumber cm^{-1}
—	—	1826, 1757
1	—	1824, 1801, 1726
1	0.025	1807, 1724
2	0.025	1803, 1724

Acetic anhydride (1 molar amount).

isobutyric anhydride and pivalic anyhdride worked well. The product in the Friedel–Crafts reaction of mesitylene with acetic anhydride was obtained in up to 250000% molar amounts based on the catalyst.

It is assumed that in these Friedel–Crafts acylations an active species is generated from acetic anhydride and $LiClO_4$ in the presence of catalytic amount of $Hf(OTf)_4$. Although the precise structure is not yet clear, IR data supported the existence of this species. The absorption of the carbonyl groups of acetic anhydride in nitromethane was measured at 1826 and 1757 cm^{-1}, while absorptions were observed in lower wavenumbers in the presence of $Hf(OTf)_4$ in accordance with the amount of $LiClO_4$ (Table 3).

Catalytic Friedel–Crafts Alkylation Reactions Using Hafnium(IV) Triflate as a Catalyst in Lithium Perchlorate–Nitromethane. Next, we examined the use of hafnium triflate in the Friedel–Crafts alkylation reactions.

Friedel–Crafts alkylation reactions are very important methods for introducing alkyl substituents on aromatic rings.[12)] Although several Friedel–Crafts alkylation catalysts were reported, yields and regioselectivities were not high in some cases and rather drastic reaction conditions sometimes lead to severe environmental problems. The new catalyst system, $Hf(OTf)_4$ in $LiClO_4$–$MeNO_2$, was then applied to the Friedel–Crafts alkylation reactions of aromatic compounds with alkyl chlorides.

First, the reaction of benzene with benzyl chloride was chosen as a model, and a mixture of benzene (2.0 mmol) and benzyl chloride (0.5 mmol) in $MeNO_2$ (1.0 ml) was added to $Hf(OTf)_4$ (0.025 mmol, 5%) and $LiClO_4$ (1.0 mmol, 200%) at room temperature. After the mixture was stirred for 20 h at this temperature, the desired alkylated product, diphenylmethane, was obtained in a 39% yield along with dibenzylbenzene as a by-product in a 29% yield. In order to decrease the formation of dibenzylbenzene, we then examined the addition order of the substrates. When benzyl chloride in $MeNO_2$ was added to $Hf(OTf)_4$ and $LiClO_4$ in an excess of benzene, the yield of dibenzylbenzene was only 4%, and the desired product, diphenylmethane, was obtained in an 85% yield.

We also found that the amount of $LiClO_4$ influenced the yield strongly. The effects of the amount of $LiClO_4$ are shown in Table 4. While the reaction did not proceed in the absence of $LiClO_4$, the yield increased in proportion to the amount of $LiClO_4$, and the best yield was obtained when 400% molar amounts of $LiClO_4$ was used. Several examples of the Friedel–Crafts alkylation reactions of aromatic compounds with alkyl chlorides using $Hf(OTf)_4$ as a catalyst in $LiClO_4$–$MeNO_2$ are shown in Table 5. In every case, the reactions proceeded smoothly by using a catalytic amount of $Hf(OTf)_4$ to give the desired mono-alkylated adducts in high yields. Not only benzyl chloride but also 2-chloro-2-methylpropane worked well. On the other hand, ethyl bromide and 2-chloropropane did not react under these conditions. In the reaction of toluene with 1-chloroadamantane, (1-adamantyl)toluene was obtained in a 92% yield with a high regioselectivity.

From Table 4, it was suggested that an active alkylating reagent was generated from benzyl chloride and $LiClO_4$, and that a ratio of $LiClO_4$ to the alkyl chloride was crucial in the reactions. To increase the ratio of $LiClO_4$ to the alkyl chloride, the alkyl chloride was slowly added to benzene–$MeNO_2$ solution in the presence of $LiClO_4$. The effects of the addition time in the presence of a 50% molar amount of $LiClO_4$ is shown in Table 6 (benzene (4 ml)–$MeNO_2$ (1 ml)). The adduct was obtained in an 80% yield when benzyl chloride was added over 18 h.

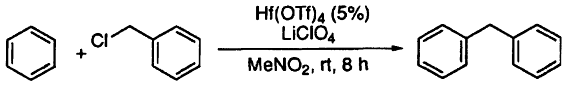


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Table 4. Effect of $LiClO_4$

Entry	$LiClO_4$ (molar amount (%))	Yield (%)
1	0	0
2	50	6
3	100	9
4	150	72
5	200	79
6	400	85
7	600	77

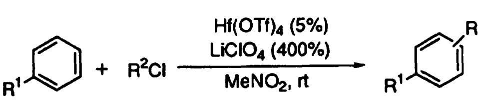
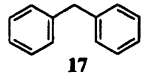
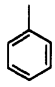
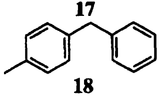
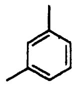
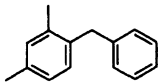
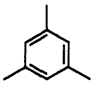
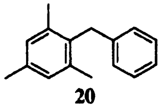
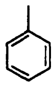
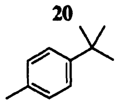
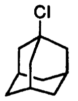
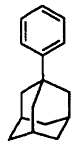
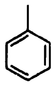
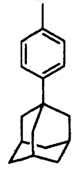
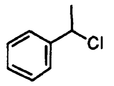
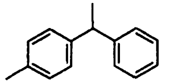
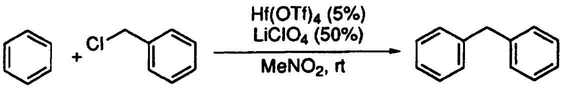


Table 5. $Hf(OTf)_4$-Catalyzed Friedel–Crafts Alkylation Reactions

Aromatic compound	R^2Cl	Major product	Yield (%)
	BnCl	 **17**	85
		 **18**	93[a]
		 **19**	91[b]
		 **20**	84
	*t*-BuCl	 **21**	76
		 **22**	66
		 **23**	92[c]
		 **24**	93[d]

a) Ortho/para=41/59.[14,15] b) Containing 19% of (2,6-dimethylphenyl)phenylmethane. c) Meta/para=6/94.[16] d) Ortho/para=12/88.[14]



17

Table 6. Effect of Addition Time

Entry	Addition time (h)	Yield (%)
1	4	46
2	8	78
3	13	67
4	18	80

This slow addition procedure was successfully applied to other examples of the Friedel–Crafts alkylations (Table 7). In all cases, alkylated benzenes were obtained in good to high yields in the presence of

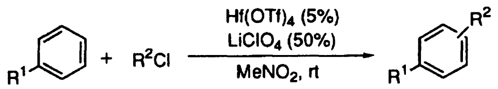
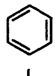
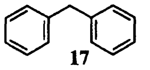
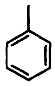
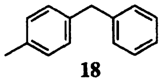
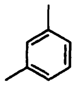
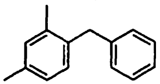
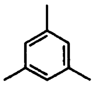
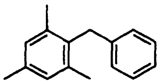
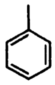
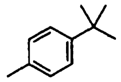
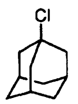
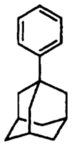
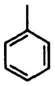
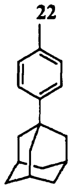
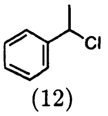
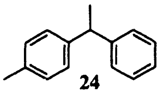


Table 7. $Hf(OTf)_4$-Catalyzed Friedel–Crafts Alkylation Reactions Using a Slow Addition Procedure[a)]

Aromatic compound	R^2Cl (addition time (h))	Major product	Yield (%)
	BnCl (18)	 **17**	80
	(3.5)	 **18**	$82^{b)}$
	(4)	 **19**	$86^{c)}$
	(4)	 **20**	87
	*t*-BuCl (7)	 **21**	71
	 (9)	 **22**	63
	(12)	 **23**	$75^{d)}$
	 (12)	 **24**	$83^{e)}$

a) See text. b) Ortho/para = 40/60.[14,15)] c) Containing 18% of (2, 6- dimethylphenyl)phenylmethane. d) Meta/para = 7/93.[16)] e) Ortho/para=12/88.[14)]

a 5% molar amount of $Hf(OTf)_4$ and a 50% molar amount of $LiClO_4$. It was reported that $LiClO_4$ accelerated some glycosylation,[11e,11f,13)] Diels–Alder,[11a)] Michael reactions,[11c)] etc. In these reactions, however, a large excess of $LiClO_4$ was required in order to achieve high yields. It is noted that these Friedel–Crafts alkylation reactions require only a 50% molar amount of $LiClO_4$ by using the slow addition procedure and that this may be applicable to other synthetic reactions which require a large amount of $LiClO_4$.

In summary, the catalytic Friedel–Crafts acylation and alkylation reactions of aromatic compounds with acid anhydrides or alkyl chlorides were successfully done under mild conditions by using $Hf(OTf)_4$ in lithium perchlorate-nitromethane ($LiClO_4$–$MeNO_2$). Lithium perchlorate-nitromethane ($LiClO_4$–$MeNO_2$) was an excellent solvent system and it was found that the turnover of Lewis acid catalysts in the Friedel–Crafts acylation was 5—20 times improved in this specific media. In the alkylation reaction, the slow addition procedure was effective and the reactions were done in the presence of a 5% molar amount of $Hf(OTf)_4$ and a 50% molar amount of $LiClO_4$.

Further investigations to develop other synthetic reactions using $Hf(OTf)_4$ as a catalyst as well as to clarify the origin of high efficiency in $LiClO_4$–$MeNO_2$ media are now in progress.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 LFT-NMR system (270

MHz). Tetramethylsilane (TMS) served as an internal standard. Column chromatography was done on silica gel 60 (Merck) or Wacogel B5F. All reagents and solvents were used after purification according to the usual methods.

Preparation or Hafnium(IV) Triflate (Hf(OTf)$_4$). Trifluoromethanesulfonic acid 22.1 ml (250 mmol) was added to hafnium tetrachloride 8.61 g (26.9 mmol) and the mixture was heated at 50 °C for 68 h under argon. The excess trifluoromethanesulfonic acid was removed and then the residue was washed with petroleum ether. White powder was dried for 8 h (100 °C/0.5 mmHg, 1 mmHg=133.322 Pa) to give Hf(OTf)$_4$ 20.9 g (100%). Mp>300°C; IR (KBr) 1637, 1350, 1311, 1267, 1209, 1161, 1030, 985, 715, 675, 638, 573, 534, 513, 463, 426 cm^{-1}; ^{13}C NMR (CD_3CN) δ=120.1 (q, J=316.6 Hz). Found: C, 6.23; S, 16.02%. Calcd for $C_4F_{12}HfO_{12}S_4$: C, 6.19; S, 16.55%.

A Typical Procedure of the Friedel–Crafts Acylation Reaction. To Hf(OTf)$_4$ (0.1 mmol, 5%) and $LiClO_4$ (12 mmol) was added a mixture of *m*-xylene (2 mmol) and acetic anhydride (4 mmol) in nitromethane (1 ml) at room temperature. The mixture was stirred for 6 h at this temperature and then aqueous saturated sodium hydrogencarbonate was added. After separation of the organic layer, the aqueous layer was extracted with dichloromethane (twice) and the organic solvents were dried (Na_2SO_4). The solvents were removed under reduced pressure, and the crude product was chromatographed on silica gel to afford 2,4-dimethylphenyl methyl ketone (91%).

2,4-Dimethylphenyl Methyl Ketone (1):[17] IR (neat) 2924, 1682, 1610, 1444, 1354, 1294, 1255, 966, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33 (s, 3H), 2.51 (s, 3H), 2.54 (s, 3H), 7.03 (s, 1H), 7.05 (d, 1H, J=8.58 Hz), 7.62 (d, 1H, J=8.58 Hz); ^{13}C NMR ($CDCl_3$) δ=21.4, 21.7, 29.2, 126.2, 129.9, 132.8, 134.5, 138.9, 142.1, 200.9.

4-Methoxyphenyl Methyl Ketone (2):[9h] IR (neat) 2964, 1674, 1601, 1360, 1311, 1257, 1176, 1026, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.51 (s, 3H), 3.82 (s, 3H), 6.87—6.92 (m, 2H), 7.87—7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=26.2, 55.3, 113.5, 130.1, 130.4, 163.3, 196.6.

3,4-Dimethoxyphenyl Methyl Ketone (3):[18] IR (neat) 2962, 2935, 1672, 1591, 1514, 1417, 1269, 1223, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.58 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 6.89 (d, 1H, J=8.58 Hz), 7.53 (d, 1H, J=1.98 Hz), 7.58 (dd, 1H, J=8.58, 1.98 Hz); ^{13}C NMR ($CDCl_3$) δ=26.1, 55.9, 55.9, 109.8, 109.9, 123.2, 130.4, 148.9, 153.2, 196.6.

2,4,6-Trimethylphenyl Methyl Ketone (4):[17] IR (neat) 2920, 1699, 1610, 1425, 1352, 1252, 1059, 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.21 (s, 6H), 2.27 (s, 3H), 2.45 (s, 3H), 6.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=19.0, 20.9, 32.1, 128.4, 132.2, 138.2, 139.8, 208.5.

3,4-Dimethylphenyl Methyl Ketone (5):[19] IR (neat) 2924, 1680, 1606, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 6H), 2.56 (s, 3H), 7.20 (d, 1H, J=7.92 Hz), 7.66—7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=19.7, 19.9, 26.4, 126.0, 129.3, 129.7, 135.0, 136.8, 142.5, 198.1.

2,5-Dimethylphenyl Methyl Ketone (6):[17] IR (neat) 2925, 1684, 1441, 1356, 1294, 1257, 1190, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (s, 3H), 2.47 (s, 3H), 2.55 (s, 3H), 7.10 (d, 1H, J=7.59 Hz), 7.17 (d, 1H, J=7.59 Hz), 7.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=20.7, 21.0, 29.4, 129.8, 131.8, 132.1, 135.0, 135.0, 137.4, 201.7.

Methyl *p*-Tolyl Ketone (7) and Methyl *o*-Tolyl Ketone:[17] Ortho/para=3/97; IR (neat) 1682, 1606 1358, 1267, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 2.91H), 2.53 (s, 0.09H), 2.57 (s, 3H), 7.24—7.28 (m, 2H), 7.34—7.40 (m, 0.03H), 7.69 (d, 0.03H, J=7.58 Hz), 7.84—7.87 (m, 1.94H); ^{13}C NMR ($CDCl_3$) δ=21.4, 26.3, 128.3, 129.0, 134.5, 143.7, 197.6.

Acetophenone (8):[20] IR (neat) 1685, 1360, 1265, 760, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.60 (s, 3H), 7.43—7.49 (m, 2H), 7.54—7.60 (m, 1H), 7.95—7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=26.5, 128.2, 128.5, 133.0, 137.0, 198.1.

Methyl 1-Naphthyl Ketone (9) and Methyl 2-Naphtyl Ketone:[21] Methyl 1-naphthyl ketone/methyl 2-naphthyl ketone=52/48; IR (neat) 1678, 1360, 1279, 1238 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.69 (s, 1.44H), 2.71 (s, 1.56H), 7.43—7.61 (m, 2.52H), 7.82—8.03 (m, 3.48H), 8.43 (s, 0.48H), 8.75 (d, 0.52H, J=8.57 Hz); ^{13}C NMR ($CDCl_3$) δ=26.6 (methyl 2-naphthyl ketone), 29.8 (methyl 1-naphthyl ketone), 123.8, 124.2, 125.9, 126.3, 126.7, 127.7, 127.9, 128.3, 128.4, 128.6, 129.4 130.1, 132.4, 132.9, 133.9, 134.3, 135.3, 135.5, 198.0 (methyl 2-naphthyl ketone), 201.7 (methyl 1-naphthyl ketone).

Isopropyl 4-Methoxyphenyl Ketone (10):[17] IR (neat) 2972, 1674, 1603, 1259, 1230, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.21 (d, 6H, J=6.60 Hz), 3.52 (sept, 1H, J=6.60 Hz), 3.87 (s, 3H), 6.92—6.97 (m, 2H), 7.93—7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) 19.2, 34.8, 55.3, 113.8, 129.0, 130.4, 163.1, 203.0.

***t*-Butyl 4-Methoxyphenyl Ketone (11):**[22] IR (neat) 2970, 1672, 1601, 1263, 1175, 1032, 958 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.37 (s, 9H), 3.86 (s, 3H), 6.87—6.93 (m, 2H), 7.83—7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=28.3, 43.8, 55.2, 113.1, 129.9, 130.9, 161.9, 206.1.

Ethyl 4-Methoxyphenyl Ketone (12):[23] IR (neat) 2973, 1678, 1603, 1510, 1460, 1354, 1313, 1259, 1228, 1174, 1026, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.21 (t, 3H, J=7.26 Hz), 2.95 (q, 2H, J=7.26 Hz), 3.86 (s, 3H), 6.90—6.95 (m, 2H), 7.92—7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.4, 31.3, 55.4, 113.6, 129.9, 130.1, 163.2, 199.4.

Ethyl 2,4,6-Trimethylphenyl Ketone (13):[24] IR (neat) 2974, 2931, 1699, 1610, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.19 (t, 3H, J=7.26 Hz), 2.17 (s, 6H), 2.27 (s, 3H), 2.70 (q, 2H, J=7.26 Hz), 6.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=7.6, 19.0, 21.0, 37.9, 128.4, 132.4, 138.1, 139.8, 211.5.

2,4-Dimethylphenyl Ethyl Ketone (14):[25] IR (neat) 2976, 2929, 1684, 1612, 1217 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.17 (t, 3H, J=7.26 Hz), 2.33 (s, 3H), 2.48 (s, 3H), 2.89 (q, 2H, J=7.26 Hz), 7.04 (d, 2H, J=2.97 Hz), 7.55—7.58 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=8.3, 21.1, 21.4, 34.1, 126.1, 128.8, 132.7, 134.8, 138.3, 141.5, 204.0.

2,4-Dimethylbenzophenone (15):[17] IR (neat) 1662, 1606, 1448, 1271, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33 (s, 3H), 2.37 (s, 3H), 7.02—7.10 (m, 2H), 7.21—7.24 (m, 1H), 7.39—7.45 (m, 2H), 7.52—7.58 (m, 1H), 7.77—7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=20.0, 21.3, 125.7, 129.2, 130.0, 131.8, 132.8, 135.5, 137.2, 138.1, 140.6, 198.4.

2,4,6-Trimethylbenzophenone (16):[17] IR (neat) 2920, 1668, 1604, 1448, 1267, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.08 (s, 6H), 2.33 (s, 3H), 6.90 (s, 2H), 7.41—7.47 (m, 2H), 7.54—7.61 (m, 1H), 7.79—7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=19.3, 21.1, 128.3, 128.8, 129.3, 133.5, 134.1, 136.8, 137.3, 138.4, 200.7.

A Typical Procedure of the Friedel–Crafts Alkyl-

ation Reaction. To $Hf(OTf)_4$ (0.05 mmol, 5%) and $LiClO_4$ (4 mmol, 400%) in mesitylene (3.0 ml) was added benzyl chloride (1.0 mmol) in nitromethane (1.0 ml) and mesitylene (1.0 ml) at room temperature. The mixture was stirred for 8 h at this temperature and then aqueous saturated sodium hydrogencarbonate was added to quench the reaction. After separation of organic layer, the aqueous layer was extracted with dichloromethane (twice) and the combined organic solvents were dried (Na_2SO_4). The solvents were removed under reduced pressure, and the crude product was chromatographed on silica gel to afford phenyl(2,4,6-trimethylphenyl)methane (84%).

A Typical Slow Addition Procedure of the Friedel–Crafts Alkylation Reaction. To $Hf(OTf)_4$ (0.05 mmol, 5%) and $LiClO_4$ (0.5 mmol, 50%) in mesitylene (3.0 ml) and nitromethane (1.0 ml) was added slowly benzyl chloride (1.0 mmol) in mesitylene (1.0 ml) for 4 h at room temperature and then the mixture was stirred for 16 h at this temperature. Aqueous saturated sodium hydrogencarbonate was added to quench the reaction. After separation of organic layer, the aqueous layer was extracted with dichloromethane (twice) and the combined organic solvents were dried (Na_2SO_4). The solvents were removed under reduced pressure, and the crude product was chromatographed on silica gel to afford phenyl(2,4,6-trimethylphenyl)methane (87%).

Diphenylmethane (17):[26] IR (neat) 3062, 3026, 2916, 1599, 1493, 1448, 1076, 733, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.98 (s, 2H), 7.17—7.31 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=41.9, 126.0, 128.4, 128.9, 141.1.

Phenyl *p*-Tolyl Methane (18) and Phenyl *o*-Tolyl Methane:[14,15] Ortho/para=41/59; IR (neat) 3062, 3024, 2916, 1600, 1495, 1450, 1109, 1032, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.23 (s, 1.23H), 2.30 (s, 1.77H), 3.93 (s, 1.18H), 3.98 (s, 0.82H), 7.08—7.35 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=19.7 (ortho), 21.0 (para), 39.4 (ortho), 41.5 (para), 125.9, 125.9, 126.4, 128.3, 128.4, 128.4, 128.7, 128.8, 128.8, 129.1, 129.9, 130.2, 135.5, 136.6, 138.0, 138.9, 140.3, 141.4.

(2,4-Dimethylphenyl)phenylmethane (19) and (2,6-Dimethylphenyl)phenylmethane:[26] 2,6-(Dimethylphenyl)phenylmethane/2,4-(dimethylphenyl)phenylmethane=21/79; IR (neat) 3022, 2916, 1603, 1496, 1448, 1030, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.19—2.30 (m, 6H), 3.94 (s, 1.58H), 4.05 (s, 0.42H), 6.98—7.28 (m, 8H); ^{13}C NMR ($CDCl_3$) δ=19.6, 20.2, 20.9, 35.0, 39.0, 125.7, 125.8, 126.3, 126.6, 127.8, 128.1, 128.3, 128.6, 129.9, 131.1, 135.8, 136.4, 136.8, 137.1, 140.6.

Phenyl(2,4,6-trimethylphenyl)methane (20):[27] IR (neat) 3020, 2922, 1606, 1489, 1450, 1030, 852, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.20 (s, 6H), 2.29 (s, 3H), 4.02 (s, 2H), 6.89 (s, 2H), 7.01 (d, 2H, J=6.97 Hz), 7.13—7.25 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=20.1, 20.9, 34.7, 125.6, 127.8, 128.3, 128.9, 133.7, 135.6, 137.0, 140.1.

4-*t*-Butyltoluene (21):[14] IR (neat) 2962, 1516, 1462, 1365, 1113, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (s, 9H), 2.32 (s, 3H), 7.12 (d, 2H, J=8.25 Hz), 7.29 (d, 2H, J=8.25 Hz); ^{13}C NMR ($CDCl_3$) δ=20.8, 31.4, 34.3, 125.1, 128.7, 134.8, 148.1.

1-Adamantylbenzene (22):[16] IR (KBr) 2906, 2846, 1489, 1442, 1344, 1105, 750, 694, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.75 (t, 6H, J=14.0 Hz), 1.91 (d, 6H, J=2.3 Hz), 2.08 (s, 3H), 7.09—7.18 (m, 1H), 7.25—7.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=28.9, 36.1, 36.8, 43.1, 124.8, 125.4, 128.0, 151.2.

4-(1-Adamantyl)toluene (23) and 3-(1-Adamantyl)toluene:[16] Metha/para=7/93; IR (KBr) 3005, 2912, 2852, 1509, 1444, 1338, 1107, 1034, 791, 532 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.74 (t, 6H, J=14.0 Hz), 1.88 (d, 6H, J=2.3 Hz), 2.06 (s, 3H), 2.29 (s, 2.79H), 2.33 (s, 0.21H), 6.98—7.19 (m, 2H), 7.21—7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) **Meta:** δ=21.7, 29.1, 36.0, 36.8, 43.2, 121.8, 125.5, 126.2, 127.9, 137.3, 151.2. **Para:** δ=20.8, 29.0, 35.7, 36.8, 43.2, 124.6, 128.7, 134.7, 148.3.

1-(4-Methylphenyl)-1-phenylethane (24) and 1-(2-Methylphenyl)-1-phenylethane:[14] Ortho/para=12/88; IR (neat) 3026, 2970, 1601, 1504, 1450, 1375, 1115, 1030, 822, 766, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.59—1.64 (m, 3H), 2.23 (s, 0.36H), 2.30 (s, 2.64H), 4.11 (q, 0.88H, J=7.26 Hz), 4.31 (q, 0.12H, J=7.26 Hz), 7.06—7.30 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=19.7 (ortho), 21.0 (para), 21.9 (para), 22.1 (ortho), 41.0 (ortho), 44.3 (para), 125.8, 125.9, 126.1, 126.6, 127.5, 127.5, 127.6, 128.3, 129.0, 130.4, 135.5, 143.4, 146.6.

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