The Catalytic Fries Rearrangement and *o*-Acylation Reactions Using Group 3 and 4 Metal Triflates as Catalysts

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Group 3 and 4 metal triflates ($Sc(OTf)_3$, $TiCl(OTf)_3$, $Zr(OTf)_4$, and $Hf(OTf)_4$) were found to be efficient catalysts in the Fries rearrangement of phenyl or 1-naphthyl acylates. It was also found that the *o*-acylation (direct acylation) reactions of phenols and 1-naphthols with acid chlorides proceeded smoothly in the presence of the triflates. Both reactions were successfully carried out using small amounts of the triflates (catalytically), and comparison of catalytic activities of these metal triflates in these reactions is discussed.

The Fries rearrangement of phenyl or naphthyl acylates provides useful routes to hydroxyaryl ketones,[1,2] which are versatile intermediates in the synthesis of biologically active naphthoquinones,[3] phenols or naphthalenes containing LC (Liquid Crystal) polymers, low molecular weight mesogens,[4] etc. In this rearrangement, however, more than a stoichiometric amount of $AlCl_3$ is required because the acid is trapped by the products.[1,5,6] On the other hand, an alternative method is direct acylation of phenols and naphthols using $AlCl_3$[7] or $HClO_4$[8] as a promoter.[9] However, in this case also, the requirement of more than stoichiometric amounts of the acids has caused some severe side reactions. Therefore, development of new catalysts which promote the above mentioned reactions catalytically is strongly desired.

Recently, we have focused on group 3 and 4 metal triflates. Metal triflates have high Lewis acidity compared to the corresponding metal halides because of the strong electronwithdrawing trifluoromethanesulfonyl groups. While several metal triflates have already been used in organic synthesis,[10] we recently found group 3 metal triflates, especially lanthanide triflates ($Ln(OTf)_3$), are stable Lewis acids in water and can be successfully applied as catalysts to several carbon-carbon bond forming reactions.[11] We also found unique activity of $Sc(OTf)_3$ in organic synthesis, and several $Sc(OTf)_3$-catalyzed reactions have been developed in both aqueous and organic solvents.[11,12] On the other hand, group 4 metals, especially Zr and Hf, have similar ionic radii to lanthanides, and are expected high catalytic activities as Lewis acids. We first prepared $Hf(OTf)_4$ and have shown that it is a very effective catalyst in the Friedel–Crafts acylation reactions.[13,14]

We thus examined use of group 3 and 4 metal triflates as catalysts in the Fries rearrangement and *o*-acylation reactions. In this paper, we describe full details on the catalytic Fries rearrangement of phenyl of 1-naphthyl acylates and also on the catalytic direct acylation of phenols of 1-naphthols with acid chlorides using group 3 and 4 metal triflates as catalysts.[15] Comparison of catalyst activities of these metal triflates in these reactions is also reported.

Results and Discussion

The Fries Rearrangement. First, catalytic activity of Lewis acids was examined in the Fries rearrangement. A 1 mol dm^{-3} toluene solution of 1-naphthyl acetate was treated with 0.1 molar amount of Lewis acids at 100 °C; effects of Lewis acids are summarized in Table 1. While

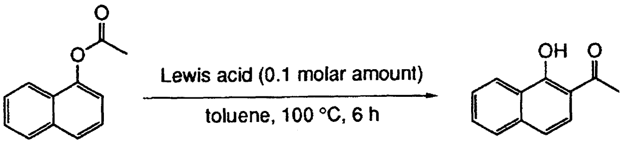


Table 1. Effects of Lewis Acids (1)[a]

Entry	Lewis acid	Yield (%)
1	$AlCl_3$	0
2	$TiCl_4$	7
3	$SnCl_4$	Trace
4	$BF_3\cdot OEt_2$	Trace
5	$Al(OTf)_3$	34
6	$Yb(OTf)_3$	2
7	$Sc(OTf)_3$	75 (85)[b]
8	$TiCl(OTf)_3$	66
9	$Zr(OTf)_4$	71
10	$Hf(OTf)_4$	76
11	$AlCl_3$ (140 molar amount)	61[c]
12	(photo)	38[d]

a) The reaction was carried out in 1 mol dm^{-3} toluene. b) In 0.5 mol dm^{-3} toluene using 5 molar amount $Sc(OTf)_3$. c) Ref. 2a. d) Ref. 3.

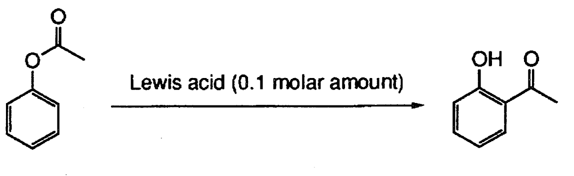
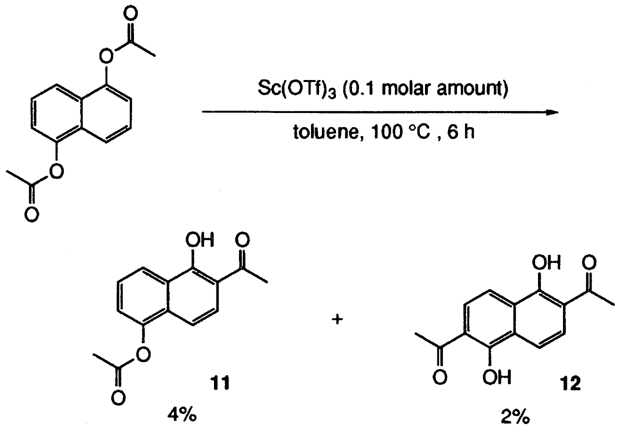


Table 2. Effects of Lewis Acids (2)[a)]

Entry	Lewis acid	Yield (%)
1	$Sc(OTf)_3$	16
2	$TiCl(OTf)_3$	39[b)]
3	$Zr(OTf)_4$	41[c)]
4	$Hf(OTf)_4$	57[d)]

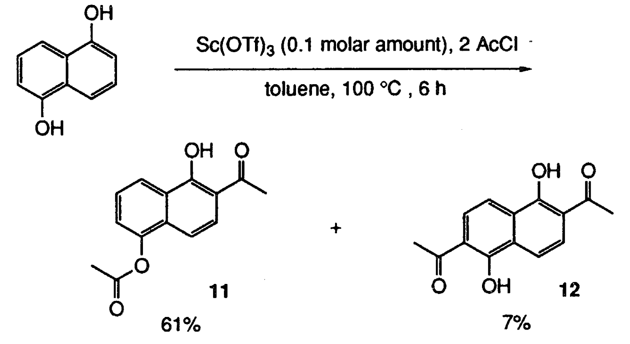
a) The reactions were carried out in 12 mol dm^{-3} $LiClO_4$–$MeNO_2$ media at 50 °C for 6 h. b) Ortho = 2% yield. Para = 37% yield. c) Ortho = 2% yield. Para = 39% yield. d) Ortho = 5% yield. Para = 52% yield.

the reaction proceeded sluggishly when catalytic amounts of typical Lewis acids were used, remarkably high yields were obtained when group 3 and 4 metal triflates, $Sc(OTf)_3$, $TiCl(OTf)_3$,[16)] $Zr(OTf)_4$, and $Hf(OTf)_4$, were used. Judging from the results, both group 3 or 4 element and triflate anion are essential for the high yields. It should be noted that the yields were much higher than that in the stoichiometic $AlCl_3$-promoted reactions[2a)] or that in the photo reaction.[3)] On the other hand, $Hf(OTf)_4$ gave the best result in the Fries rearrangement of phenyl acetate (Table 2). In the reactions using $Hf(OTf)_4$, $Zr(OTf)_4$, or $TiCl(OTf)_3$ as a catalyst, the major products were 4-hydroxyphenyl methyl ketone (para) and a small amount of 2-hydroxyphenyl methyl ketone (ortho) was obtained, while only 4-hydroxyphenyl methyl ketone was produced using $Sc(OTf)_3$ as a catalyst though the yield was lower.

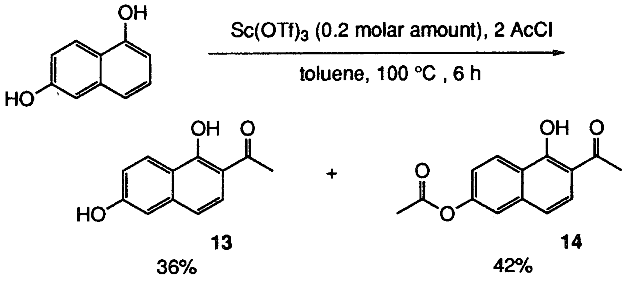


(1)

Several examples of the catalytic Fries rearrangement are shown in Table 3. In the rearrangement of most phenyl acylates, $Hf(OTf)_4$ was the best catalyst and 2-acylated phenols were obtained regioselectively, except for the reaction of phenyl acetate. $Sc(OTf)_3$ gave a better yield in the rearrangement of 3-methoxyphenyl acetate. Although migration or loss of a *t*-butyl group was observed in $AlCl_3$-promoted Fries rearrangement,[17)] no such side reactions occurred under the conditions in the rearrangement of 3-*t*-butylphenyl acetate. On the other hand, the rearrangement of 1-naphthyl acylates proceeded smoothly in the presence of $Sc(OTf)_3$ as a catalyst at a lower concentration (0.5 mol dm^{-3}). In general, the rearrangement of 1-naphthyl acylates gave higher yields than the rearrangement of phenyl acylates. The rearrangement proceeded smoothly in every case, using 0.05 molar amounts of $Sc(OTf)_3$ to afford 1-hydroxy-2-naphthyl ketones in high yields.



(2)



(3)

The *o*-Acylation Reactions. We then examined the direct acylation of phenols and 1-naphthols. First, 1-naphthol was treated with acetyl chloride in the presence of 0.05 molar amount of group 3 and 4 metal triflates: $Sc(OTf)_3$, $TiCl(OTf)_3$, $Zr(OTf)_4$, $Hf(OTf)_4$. The reactions proceeded smoothly in all cases to afford 1-hydroxy-2-naphthyl methyl ketone in high yields (Table 4). It is noted that the yields are much improved compared to those of the Fries rearrangements, especially using $Sc(OTf)_3$, $Zr(OTf)_4$, and $Hf(OTf)_4$ as catalysts. Similarly, it was found that the direct acylations of phenol proceeded rapidly to afford 2-hydroxyphenyl methyl ketone in good yields, although the yields are still lower compared to those of the direct acylations of 1-naphthol. It is noteworthy that the efficient catalytic reactions have been successfully carried out using these group 3 and 4 metal triflates, even in the presence of free hydroxy groups of the starting materials, phenol and 1-naphthol, and the products, 1-hydroxy-2-naphthyl methyl ketone and 2-hydroxyphenyl methyl ketone.

Several examples of the direct acylation reactions of phenols or 1-naphthols with acid chlorides are shown in Table 5. In this case also, phenols was less reactive than 1-naphthols; however, higher yields were obtained in all cases than those obtained in the corresponding Fries rearrangements. The direct acylation of 1-naphthols were successfully carried out using a small amount of $Sc(OTf)_3$ (0.05 molar amount) to

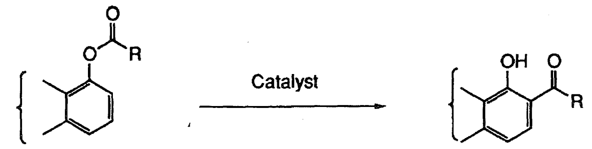
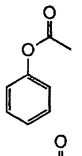
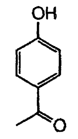
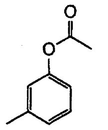
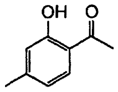
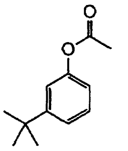
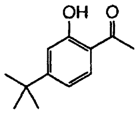
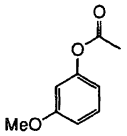
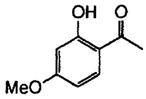
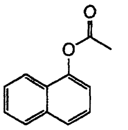
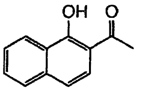
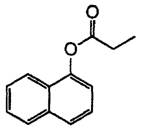
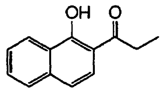
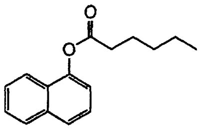
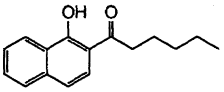
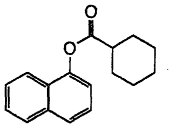
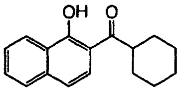
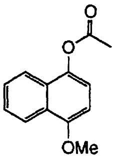
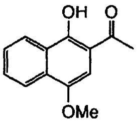
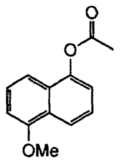
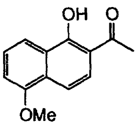


Table 3. Sc(OTf)$_3$ or Hf(OTf)$_4$-Catalyzed Fries Rearrangement of Phenyl or 1-Naphthyl Acylates

Entry	Catalyst (molar amount)	Phenyl or 1-Naphthyl acylates	Major product	Yield (%)	
1	Hf(OTf)$_4$ (0.1)			**1**	57$^{a,b)}$
2	Hf(OTf)$_4$ (0.2)			**2**	64
3	Hf(OTf)$_4$ (0.1)			**3**	60$^{a)}$
4	Sc(OTf)$_3$ (0.2)			**4**	65$^{c)}$
5	Hf(OTf)$_4$ (0.2)				53
6	Sc(OTf)$_3$ (0.05)			**5**	85
7	Sc(OTf)$_3$ (0.05)			**6**	89
8	Sc(OTf)$_3$ (0.05)			**7**	85
9	Sc(OTf)$_3$ (0.05)			**8**	78
10	Sc(OTf)$_3$ (0.05)			**9**	80
11	Sc(OTf)$_3$ (0.05)			**10**	66

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a) The reactions were carried out in 12 mol dm^{-3} LiClO$_4$–MeNO$_2$ media at 50 °C for 6 h. b) Containing 2-hydroxyphenyl methyl ketone (yield 5%). c) Containing 4-hydroxy-2-methoxyphenyl methyl ketone (yield 7%).

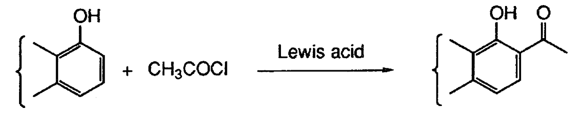


Table 4. Effect of Lewis Acids in *o*-Acylation Reactions

Lewis acid	Yield (%)	
	Phenol[a)]	1-Naphthol[b)]
$Sc(OTf)_3$	41[c)]	90
$TiCl(OTf)_3$	42[d)]	56
$Zr(OTf)_4$	51[e)]	97
$Hf(OTf)_4$	64[f)]	90

a) The reactions were carried out using 0.1 molar amount of Lewis acids in 12 mol dm^{-3} $LiClO_4$–$MeNO_2$ media. b) The reactions were carried out using 0.05 molar amount of Lewis acids. c) Ortho=2% yield. Para=39% yield. d) Ortho=2% yield. Para=40% yield. e) Ortho=3% yield. Para=48% yield. f) Ortho=3% yield. Para=61% yield.

give several acylated adducts in excellent yields.

As mentioned above, the yields of the direct acylation were higher than those of the Fries rearrangement in most cases. By-products of the Fries rearrangement were deacylated phenols and 1-naphthols (yield 10—30%). Synthetic advantages of the direct acylation over the Fries rearrangement were demonstrated not only by process shortening but also by the following experiments, as shown in Eqs. 1 and 2. While only 4 and 2% of mono- (**11**) and di-rearranged (**12**) products were obtained, respectively, in the Fries rearrangement of 1,5-naphthalenediyl diacetate, the direct acylation of 1,5-naphthalenediol with acetyl chloride gave the mono- and di-rearranged products in 61 and 7% yields, respectively, using $Sc(OTf)_3$ as a catalyst. Similarly, 1,6-naphthalenediol reacted with acetyl chloride in the presence of $Sc(OTf)_3$ to afford the corresponding acylated adducts, **13** and **14**, in 36 and 42% yields, respectively (Eq. 3).

Mechanism. While $AlCl_3$ or other typical Lewis acids form rather strong complexes with carbonyl compounds (for example, hydroxyaryl ketones), group 3 and 4 metal triflates, carbonyl compounds, and their complexes would exist under equilibrium conditions. This is a key to show that the catalytic Fries rearrangements and the catalytic *o*-acylation reactions have been successfully carried out.

The following cross-over experiments showed that the Fries rearrangement proceeded not via intramolecular fashion but via intermolecular fashion (Eq. 4, Chart 1). Namely, equimolar amounts of 1-naphthyl cyclohexanecarboxylate and 4-methoxy-1-naphthyl acetate were treated with 0.1 molar amount of $Sc(OTf)_3$ in toluene at 100 °C. After 6 h, four cross-over 1-hydroxy-2-naphthyl ketones, **5**, **8**, **9**, and **15** were isolated in 18, 15, 19, 8% yields, respectively. In addition, it is suggested in the reactions of phenols or naphthols with acid chlorides that both a direct acylation pathway and formation of esters[18)] followed by the Fries rearrangement are included.

Conclusions.

We have developed the catalytic Fries rearrangement and catalytic *o*-acylation reactions. Use of group 3 and 4 metal triflates is essential for the reactions. The reactions proceeded smoothly in all cases by using small amounts of the catalysts. In the reactions of 1-naphthols, $Sc(OTf)_3$ has been concluded to be the best catalyst, judging from the facts that it gave high yields and it is reusable. On the other hand, $Hf(OTf)_4$ has been quite effective in the reactions of phenols. The *o*-acylation reactions are superior to the Fries rearrangements in yields, and we are currently investigating use of free carboxylic acids as acylating agents instead of acid chlorides.[19)]

Experimental

General. Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNR-EX270L spectrometer, and tetramethylsilane (TMS) served as internal standard. Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F.

$Sc(OTf)_3$,[20)] $TiCl(OTf)_3$,[16a)] $Zr(OTf)_4$,[16a)] and $Hf(OTf)_4$[13)] were prepared by the literature methods.

A Typical Procedure of the Fries Rearrangement. To $Sc(OTf)_3$ (0.05 mmol, 0.05 molar amount) and 1-naphthyl acetate (1.0 mmol) was added toluene (2.0 ml) at room temperature. The mixture was stirred for 6 h at 100 °C and was then cooled to room temperature. Water was added to quench the reaction and CH_2Cl_2

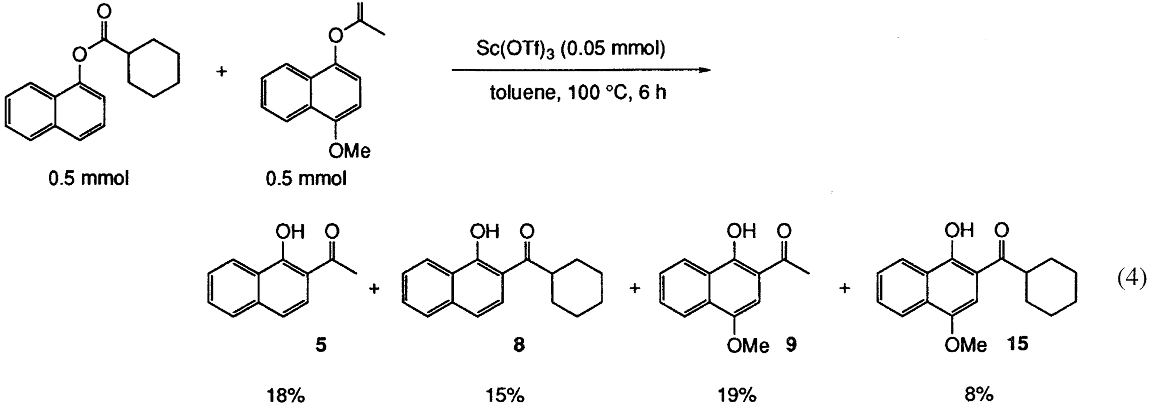


Chart 1.

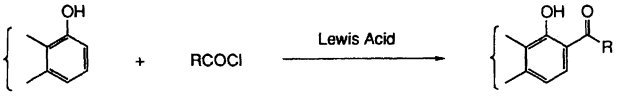
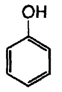
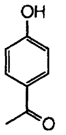
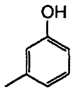
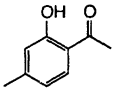
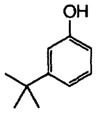
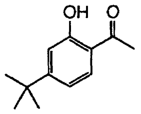
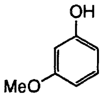
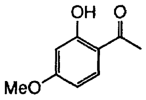
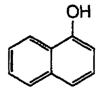
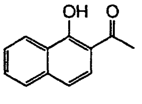
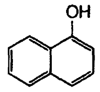
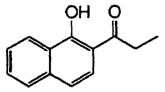
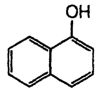
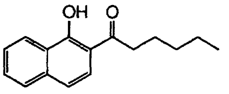
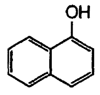
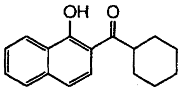
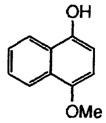
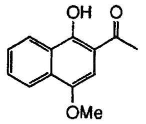
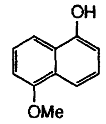
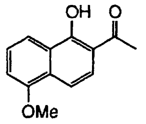


Table 5. Sc(OTf)$_3$ and Hf(OTf)$_4$-Catalyzed *o*-Acylation Reactions of Phenols or 1-Naphthol Derivatives

Entry	Catalyst (molar amount)	Phenol or 1-Naphthol derivative	Acid chloride	Major product		Yield (%)
1	Hf(OTf)$_4$ (0.1)		CH_3COCl		**1**	64$^{a,b)}$
2	Sc(OTf)$_3$ (0.2)		CH_3COCl		**2**	62
3	Hf(OTf)$_4$ (0.1)		CH_3COCl		**3**	76$^{a)}$
4	Sc(OTf)$_3$ (0.2)		CH_3COCl		**4**	80$^{c)}$
5	Sc(OTf)$_3$ (0.05)		CH_3COCl		**5**	93
6	Sc(OTf)$_3$ (0.05)		CH_3CH_2COCl		**6**	Quant.
7	Sc(OTf)$_3$ (0.05)		$CH_3(CH_2)_4COCl$		**7**	90
8	Sc(OTf)$_3$ (0.05)		*c*-$C_6H_{11}COCl$		**8**	92
9	Sc(OTf)$_3$ (0.05)		CH_3COCl		**9**	93
10	Sc(OTf)$_3$ (0.05)		CH_3COCl		**10**	73

a) The reactions were carried out in 12 mol dm^{-3} $LiClO_4$–$MeNO_2$ media at 50 °C for 6 h. b) Containing 2-hydroxyphenyl methyl ketone (yield 3%). c) Containing 4-hydroxy-2-methoxyphenyl methyl ketone (yield 6%).

was then added. After separation of the organic layer, the aqueous layer was extracted twice with CH_2Cl_2 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 1-hydroxy-2-naphthyl methy ketone (yield 85%).

A Typical Procedure of the 2-Acylation Reaction. Sc(OTf)$_3$ (0.05 mmol, 0.05 molar amount) and 1-naphthol (1.0 mmol), and acetyl chloride (1.1 mmol) were combined in toluene (2.0 ml) and nitromethane (0.3 ml) for 6 h at 100 °C. Water was added to quench the reaction and CH_2Cl_2 was then added. After separation of the organic layer, the aqueous layer was extracted twice with CH_2Cl_2 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 1-hydroxy-2-naphthyl methyl ketone (yield 93%).

4-Hydroxyphenyl Methyl Ketone (1): Mp 107—109 °C.

IR (KBr) 3340, 1664 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.59 (s, 3H), 6.81 (brs, 1H), 6.93 (d, 2H, *J*=8.91 Hz), 7.92 (d, 2H, *J*=8.91 Hz); ^{13}C NMR (CDCl$_3$) δ=26.3, 115.4, 130.0, 131.1, 160.7, 197.9.

2-Hydroxy-4-methylphenyl Methyl Ketone (2): IR (neat) 2956, 1637 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.34 (s, 3H), 2.59 (s, 3H), 6.70 (d, 1H, *J*=8.25 Hz), 6.78 (d, 1H), 7.60 (d, *J*=8.25 Hz), 12.29 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=21.9, 26.4, 117.5, 118.3, 120.1, 148.0, 162.4, 203.8. HRMS Calcd for $C_9H_{10}O_2$: (M$^+$), 150.0681. Found: *m*/*z* 150.0715.

4-*t*-Butyl-2-hydroxyphenyl Methyl Ketone (3): IR (neat) 2964, 1641, 1203 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=1.30 (s, 9H), 1.60 (s, 3H), 6.93 (dd, 1H, *J*=1.65, 8.24 Hz), 6.98 (d, 1H, *J*=1.65 Hz), 7.66 (d, 1H, *J*=8.24 Hz), 12.25 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=26.4, 30.7, 35.3, 115.0, 116.6, 117.4, 130.4, 161.0, 162.2, 203.8. HRMS Calcd for $C_{12}H_{16}O_2$: (M$^+$), 192.1150. Found: *m*/*z* 192.1139.

2-Hydroxy-4-methoxyphenyl Methyl Ketone (4): IR (neat) 2974, 1633, 1259, 1024 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.54 (s, 3H), 3.83 (s, 3H), 6.41 (s, 1H), 6.44 (d, 1H, *J*=8.58 Hz), 7.62 (d, 1H, *J*=8.58 Hz), 12.75 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=26.1, 55.5, 100.7, 107.5, 113.8, 132.2, 165.1, 166.0, 202.5. HRMS Calcd for $C_9H_{10}O_3$: (M$^+$), 166.0630. Found: *m*/*z* 166.0591.

4-Hydroxy-2-methoxyphenyl Methyl Ketone: ^{1}H NMR (CDCl$_3$) δ=1.73 (brs, 1H), 2.59 (s, 3H), 3.87 (s, 3H), 6.47 (d, 2H, *J*=5.60 Hz), 7.77 (d, 1H, *J*=8.91 Hz).

1-Hydroxy-2-naphthyl Methyl Ketone (5): Mp 98—100 °C (lit,$^{2a)}$ Mp 98—99 °C). IR (KBr) 1626, 1572 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.66 (s, 3H), 7.23 (d, 1H, *J*=8.58 Hz), 7.47—7.63 (m, 3H), 7.73 (d, 1H, *J*=8.92 Hz), 8.42—8.45 (m, 1H), 14.00 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=26.9, 113.2, 118.3, 124.4, 124.9, 125.2, 125.9, 127.4, 130.0, 137.3, 162.4, 204.3.

Ethyl 1-Hydroxy-2-naphthyl Ketone (6): Mp 84—85 °C. IR (KBr) 1620, 1572 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=1.28 (t, 3H, *J*=7.26 Hz), 3.09 (q, 2H, *J*=7.26 Hz), 7.25 (d, 1H, *J*=8.90 Hz), 7.48—7.67 (m, 3H), 7.74 (d, 1H, *J*=7.59 Hz), 8.45 (t, 1H, *J*=8.66 Hz), 14.08 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=8.3, 31.9, 112.7, 118.2, 124.2, 124.4, 125.4, 125.9, 127.4, 129.9, 137.2, 162.3, 206.9. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. Found: C, 78.10; H, 6.00%.

1-Hydroxy-2-naphthyl Pentyl Ketone (7): Mp 64—65 °C. IR (KBr) 1624, 1576 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=0.92 (t, 3H, *J*=6.93 Hz), 1.31—1.45 (m, 4H), 1.71—1.82 (m, 2H), 2.99 (t, 2H, *J*=7.42 Hz), 7.22 (d, 1H, *J*=8.90 Hz), 7.46—7.63 (m, 3H), 7.72 (d, 1H, *J*=8.25 Hz), 8.44 (d, 1H, *J*=8.57 Hz), 14.15 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=13.9, 22.5, 24.3, 31.5, 38.6, 112.8, 118.1, 124.3, 125.4, 125.8, 127.3, 129.9, 137.2, 162.5, 206.7. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%. Found: C, 79.27; H, 7.55%.

Cyclohexyl 1-Hydroxy-2-naphthyl Ketone (8): Mp 101—102 °C (lit,$^{3)}$ Mp99—101 °C). IR (KBr) 1622, 1570 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=1.26—1.66 (m, 5H), 1.76—1.96 (m, 5H), 3.29—3.39 (m, 1H), 7.25 (d, 1H, *J*=8.90 Hz), 7.47—7.75 (m, 5H), 8.46 (d, 1H, *J*=8.90 Hz), 14.38 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=25.8, 25.9, 29.5, 45.4, 111.8, 124.2, 124.4, 125.6, 125.8, 127.3, 129.9, 137.2, 163.3, 209.8.

1-Hydroxy-4-methoxy-2-naphthyl Methyl Ketone (9): Mp 120—122 °C. IR (KBr) 1631, 1572, 1234, 980 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.60 (s, 3H), 3.91 (s, 3H), 6.70 (s, 1H), 7.50—7.65 (m, 2H), 8.13 (d, 1H, *J*=7.58 Hz), 8.38—8.41 (m, 1H), 13.72 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=26.9, 55.5, 100.7, 111.8, 121.8, 124.3, 125.8, 126.5, 129.6, 130.2, 147.2, 157.3, 203.6. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%. Found: C, 72.27; H, 5.75%.

1-Hydroxy-5-methoxy-2-naphthyl Methyl Ketone (10): Mp 119—120 °C (lit,$^{3)}$ Mp 119—120 °C). IR (KBr) 1624, 1255, 1061 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.70 (s, 3H), 4.00 (s, 3H), 6.99 (d, 1H, *J*=7.59 Hz), 7.44 (t, 1H, *J*=8.09 Hz), 7.65 (q, 2H, *J*=8.90 Hz), 8.03 (d, 1H, *J*=8.25 Hz), 13.90 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=26.9, 55.6, 108.1, 112.4, 113.6, 116.2, 124.6, 126.0, 126.2, 129.2, 155.0, 161.9, 204.5.

5-Acetoxy-1-hydroxy-2-naphthyl Methyl Ketone (11): Mp 141—143 °C. IR (KBr) 1761, 1618, 1572, 1207 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.45 (s, 3H), 2.67 (s, 3H), 7.26 (d, 1H, *J*=9.24 Hz), 7.39 (dd, 1H, *J*=1.32, 7.58 Hz), 7.51 (t, 1H, *J*=7.92 Hz), 7.65 (d, 1H, *J*=8.91 Hz), 8.36 (d, 1H, *J*=8.58 Hz), 14.00 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=20.9, 26.9, 111.5, 113.4, 122.4, 122.5, 125.6, 126.6, 130.5, 146.2, 162.3, 169.3, 204.3. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95%. Found: C, 68.97; H, 4.75%.

2,6-Diacetyl-1,5-naphthalenediol (12): Mp 234—236 °C. IR (KBr) 1633, 1591 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.74 (s, 6H), 7.73 (d, 2H, *J*=8.91 Hz), 7.90 (d, 2H, *J*=8.58 Hz), 13.71 (s, 2H).

1,6-Dihydroxy-2-naphthyl Methyl Ketone (13): Mp 217—219 °C. IR (KBr) 3325, 1633, 1591 cm^{-1}. ^{1}H NMR (*d*^{6}-DMSO) δ=2.63 (s, 3H), 7.03—7.14 (m, 3H), 7.53 (d, 1H, *J*=8.90 Hz), 8.29 (d, 1H, *J*=8.90 Hz), 9.58 (d, 1H, *J*=2.64 Hz), 14.13 (s, 1H); ^{13}C NMR (*d*^{6}-DMSO) δ=26.3, 109.5, 111.2, 116.7, 117.7, 118.6, 125.3, 126.1, 139.6, 159.1, 162.6, 203.3.

6-Acetoxy-1-hydroxy-2-naphthyl Methyl Ketone (14): Mp 105—106 °C. IR (KBr) 1759, 1624, 1576, 1203 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=2.40 (s, 3H), 2.71 (s, 3H), 7.21—7.31 (m, 2H), 7.51 (d, 1H, *J*=2.31 Hz), 7.66 (d, 1H, *J*=8.88 Hz), 8.49 (d, 1H, *J*=9.24 Hz), 14.05 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=21.2, 26.8, 113.1, 117.9, 118.4, 120.8, 125.9, 126.4, 138.3, 151.8, 162.3, 169.2, 204.2. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95%. Found: C, 68.76; H, 5.01%.

Cyclohexyl 1-Hydroxy-4-methoxy-2-naphthyl Ketone (15): Mp 89—91 °C. IR (KBr) 1616, 1576, 1238, 993 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=1.21—1.59 (m, 5H), 1.63—2.02 (m, 5H), 3.20—3.23 (m, 1H), 3.92 (s, 3H), 6.81 (s, 1H), 7.48—7.63 (m, 2H), 8.13 (d, 1H, *J*=8.57 Hz), 8.39—8.42 (m, 1H), 14.1 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=25.7, 25.8, 29.3, 45.4, 55.5, 100.2, 110.4, 121.7, 124.2, 126.1, 126.3, 129.5, 130.0, 147.2, 158.1, 209.0.

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