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The Catalytic Friedel–Crafts Acylation Reaction Starting from Aromatic Compounds and Free Carboxylic Acids (or Their Trimethylsilyl Esters) by Promotion of Silicon(IV) Cationic Species via Mixed Anhydrides

Kaoru SUZUKI,* Hideo KITAGAWA, and Teruaki MUKAIYAMA*
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162

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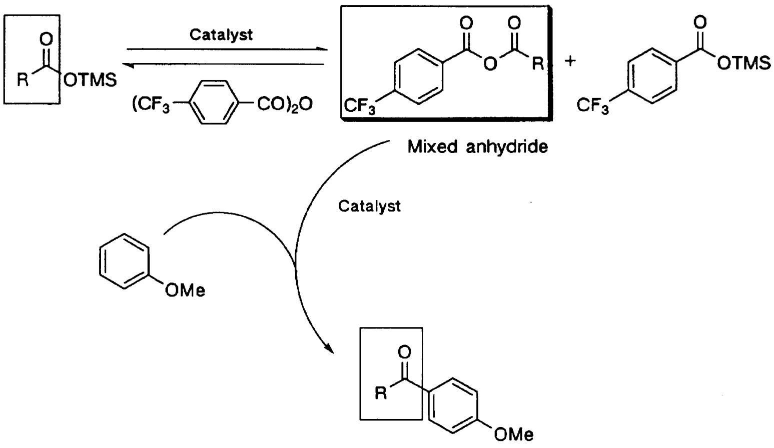
In the presence of active cationic species generated from silicon(IV) chloride and silver perchlorate, carboxylic acids or their trimethylsilyl esters react with *p*-trifluoromethylbenzoic anhydride to form corresponding mixed anhydrides in situ. Then the catalytic Friedel–Crafts acylation reaction between initially formed mixed anhydrides and coexisted aromatic compounds smoothly proceeds at room temperature to afford the corresponding aromatic ketones in high yields. The above two sequential reactions are effectively promoted by the active silicon(IV) catalyst under mild conditions.

The Friedel–Crafts acylation reaction is a very useful tool for the synthesis of aromatic ketones even in industrial chemistry[1)] and the reaction is generally carried out with acylating reagents such as carboxylic acid anhydrides or acyl chlorides by using a stoichiometric amount of Lewis acid due to the consumption by the coordination to the produced aromatic ketons. Concerning the catalytic Friedel–Crafts acylation reaction of aromatic compounds with carboxylic acid anhydrides or acyl chlorides, activated iron sulfates,[2)] iron oxides,[3)] heteropoly acids,[4)] trifluoromethanesulfonic acid,[5)] diphenylboryl hexachloroantimonate,[6)] or iron(III) chloride,[7)] has been used as active promoters. Aromatic ketones are also prepared from free carboxylic acids and aromatic compounds by using methanesulfonic acid,[8)] zeolites,[9)] trimethylsilyl polyphosphate,[10)] or Nafion-H[11)] as the catalyst, under rather drastic conditions. Therefore, further development of more efficient catalysts is still desired to promote the reaction under mild conditions. Recently, we focused our attention on the utilization of unique characters of some active cationic species generated from Lewis acids and lithium perchlorate ($LiClO_4$) or silver salts of superacids such as silver perchlorate ($AgClO_4$), silver hexafluoroantimonate ($AgSbF_6$), silver trifluoromethanesulfonate (AgOTf), etc., and reported the catalytic Beckmann[12)] and pinacol[13)] rearrangements, the catalytic and highly stereoselective glycosylation[14)] and the catalytic sulfenylation.[15)] The above results led us to investigate the catalytic Friedel–Crafts acylation reaction of carboxylic acid anhydrides (2 mol) and aromatic compounds (1 mol) by using gallium(III)chloride($GaCl_3$)–$AgClO_4$,[16)] or antimony(V)chloride($SbCl_5$)–$LiClO_4$[17)] catalyst systems, and the corresponding aromatic ketones were obtained in high yields. Further, it was found that the above active cationic species efficiently promote esterification reaction between equimolar amounts of carboxylic acid trimethylsilyl esters and alkyl silyl ethers in coexistence of *p*-trifluoromethylbenzoic anhydride.[18)] These results prompted us to study on the development of a convenient method for the catalytic Friedel–Crafts acylation reaction starting from carboxylic acid trimethylsilyl esters, aromatic compounds and a co-reagent, *p*-trifluoromethylbenzoic anhydride, via mixed anhydrides (Scheme 1).[19)] In this paper, we would like to describe the catalytic Friedel–Crafts acylation reaction between equimolar amounts of carboxylic acid trimethylsilyl esters and aromatic compounds by the promotion of silicon(IV)chloride ($SiCl_4$)–$AgClO_4$ catalyst system. Further, one pot synthesis of aromatic ketones just starting from free carboxylic acids according to the above procedure will be described in detail.

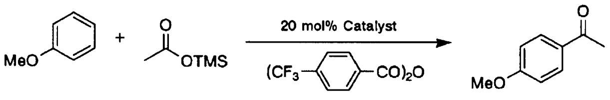
Results and Discussion

Synthesis of Aromatic Ketones from Aromatic Compounds and Free Carboxylic Acids (or Their Trimethylsilyl Esters) via Mixed Anhydrides. Active Cationic Species Generated from $SiCl_4$–$AgClO_4$ Promotes Two Sequential Reactions of Forming Mixed Anhydrides and the Subsequent Acylation of Aromatic Compounds. In the first place, several reaction conditions were examined. As shown in Table 1, when tin triflate ($Sn(OTf)_2$) was employed by taking the reaction of anisole (methoxybenzene) with trimethylsilyl acetate as a model, no desired aromatic ketone was obtained (Table 1, Entry 1). Tin triflate which had been an efficient catalyst for the formation of mixed anhydrides from carboxylic acid trimethylsilyl esters and *p*-trifluoromethylbenzoic anhydride shown in the previously reported catalytic esterification reaction[18)] could not promote an acylation reaction between an initially formed mixed anhydride and anisole because of its weak Lewis acidity. Therefore, other catalyst systems were screened; an active cationic catalyst generated from $SiCl_4$–$AgClO_4$ promoted the above two sequential reactions to afford 4-methoxyacetophenone (**1**) in 68% yield (Table 1, Entry 13). In addition, effects of solvents were examined and the results were shown in Table 2. Dichloromethane was suitable as a solvent for this reaction (Table 2, Entry 1) and when acetonitrile was used, the yield of **1** was low



Scheme 1.

Table 1. Effect of Lewis Acid



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Entry	Catalyst	Yield/%	Entry	Catalyst	Yield/%
1	$\mathrm{Sn(OTf)_2}$	0	8	$\mathrm{BiCl_3+2AgClO_4}$	54
2	$\mathrm{TiCl_4+2AgClO_4}$	28	9	$\mathrm{HfCl_4+2AgClO_4}$	53
3	$\mathrm{SbCl_5+2AgClO_4}$	48	10	$\mathrm{MeSiCl_3+2AgClO_4}$	60
4	$\mathrm{GaCl_3+2AgClO_4}$	40	11	$\mathrm{MeSiCl_3+3AgClO_4}$	61
5	$\mathrm{AlCl_3+2AgClO_4}$	59	12	$\mathrm{SiCl_4+2AgClO_4}$	60
6	$\mathrm{GeCl_4+2AgClO_4}$	58	13	$\mathrm{SiCl_4+3AgClO_4}$	68
7	$\mathrm{ZrCl_4+2AgClO_4}$	56	14	$\mathrm{SiCl_4+4AgClO_4}$	67

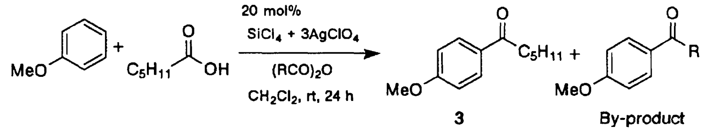
Table 2. Effect of Solvent on the Acylation of Anisole with Trimethylsilyl Acetate

Entry	Solvent	Yield/%
1	$\mathrm{CH_2Cl_2}$	68
2	$\mathrm{CH_2ClCH_2Cl}$	66
3	$\mathrm{CHCl_3}$	36
4	$\mathrm{CH_3CN}$	26
5	THF	0

(Table 2, Entry 4) probably due to the deactivation of the cationic catalyst by coordination. When the present reaction was carried out in tetrahydrofuran, no desired ketone **1** was obtained and only polymerization of tetrahydrofuran took place.

Next, several co-reagents were examined by taking the reaction of anisole with hexanoic acid as a model. As shown in Table 3, the desired aromatic ketone, 1-(4-methoxyphenyl)-1-hexanone (**3**), was obtained in 47% yield along with **1** (23%) when the reaction was carried out in the coexistence of acetic anhydride which has been frequently used in the common Friedel–Crafts acylation reaction (Table 3, Entry 1). This result indicated that hexanoic acid reacted with acetic anhydride to form the initial mixed anhydride, which in turn reacted with coexisting anisole to give the corresponding ketone **2**. In the above procedure, desired aromatic ketone **3** was obtained in 67% yield (Table 3, Entry 2) without accompanying any by-product when benzoic anhydride was used. After screening the effect of substituents in benzoic anhydride derivatives, benzoic anhydrides with electron withdrawing groups were proved to be preferable to this reaction (Table 3, Entries 7—10) and the best yield (80%) was obtained by employing *o*-fluorobenzoic anhydride (**20**) or *p*-trifluoromethylbenzoic anhydride (**22**) (Table 3, Entries 8 and 10). Furthermore, effects of kinds of silver salts and mole ratio of $\mathrm{SiCl_4}$ to $\mathrm{AgClO_4}$ were examined by taking the reaction of anisole with hexanoic acid as a model (Tables 4 and 5). Among several silver salts screened, the desired aromatic ketone **3** was obtained in good yield when $\mathrm{SiCl_4}$ was treated with $\mathrm{AgClO_4}$, AgOTf or $\mathrm{AgSbF_6}$ (Table 4, Entries 1—3), while the acylation reaction did not proceed smoothly when the catalyst generated from $\mathrm{SiCl_4}$ and silver hexafluorophosphate ($\mathrm{AgPF_6}$) was used (Table 4, Entry 4). It should be noted that the acylation reaction proceeds only when $\mathrm{SiCl_4}$ and silver salts such as $\mathrm{AgClO_4}$, AgOTf or $\mathrm{AgSbF_6}$ are combined, but not $\mathrm{SiCl_4}$ alone. The effect of ratio of $\mathrm{SiCl_4 : AgClO_4}$ was examined by using *o*-fluorobenzoic anhydride or *p*-trifluoromethylbenzoic anhydride as co-reagents (see Table 5) and it was made clear that the yield of ketone **3** was influenced by the amount of $\mathrm{AgClO_4}$. When the ratio of $\mathrm{SiCl_4}$ to $\mathrm{AgClO_4}$ was 1 : 4 in the above exper-

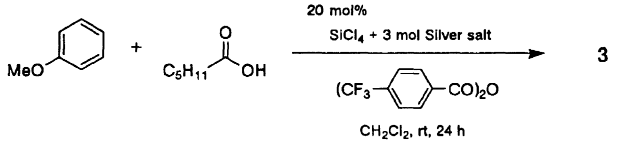
Table 3. Effect of Co-Reagent



Entry	Co-reagent		Yield/%[a)		
	R		**3**	By-product	
1	Me	**13**	47	23	**1**
2	C_6H_5	**14**	67	0	
3	*o*-MeO–C_6H_4	**15**	43	24	**23**
4	*p*-MeO–C_6H_4	**16**	60	7	**24**
5	*o*-Me–C_6H_4	**17**	64	11	**25**
6	*p*-Me–C_6H_4	**18**	71	2	**26**
7	*p*-Cl–C_6H_4	**19**	75	0	
8	*o*-F–C_6H_4	**20**	80	0	
9	*p*-F–C_6H_4	**21**	74	0	
10	*p*-CF_3–C_6H_4	**22**	80	0	

a) Isolated yields.

Table 4. Effect of Silver Salt



Entry	Silver salt	Yield/%	Entry	Silver salt	Yield/%
1	$AgClO_4$	80	4	$AgPF_6$	6
2	AgOTf	65	5	$AgBF_4$	NR
3	$AgSbF_6$	52	6	—	NR

Table 5. Effect of the Ratio of $SiCl_4 : AgClO_4$ on the Acylation of Anisole with Hexanoic Acid[a)

Entry	$SiCl_4$: $AgClO_4$ (mole ratio)	Co-reagent	Yield/%[b)
1	1 : 1	**20**	56 (56)
2	1 : 2	**20**	66 (60)
3	1 : 3	**20**	80 (84)
4	1 : 4	**20**	86 (85)
5	1 : 1	**22**	64 (67)
6	1 : 2	**22**	78 (81)
7	1 : 3	**22**	80 (86)
8	1 : 4	**22**	89 (89)
9	1 : 5	**22**	92

a) $SiCl_4$, 20 mol%; solvent, CH_2Cl_2; r. t.; 24 h. b) Yield by using trimethylsilyl hexanoate in parentheses.

iment, the desired aromatic ketone **3** was obtained in 86 and 89% yields (Table 5, Entries 4 and 8). Further addition of 5 equivalents of $AgClO_4$ to $SiCl_4$ was not effective any more concerning the increase in the yield of the ketone **3** (Table 5, Entry 9). Similarly, when trimethylsilyl hexanoate was used instead of free hexanoic acid, the desired ketone **3** was afforded in the best yield by the use of 3 equivalents of $AgClO_4$ to $SiCl_4$. The use of 4 equivalents of $AgClO_4$ to $SiCl_4$, however, had no influence on the yield of ketone **3**.

Several examples of the present reaction of aromatic compound with free carboxylic acids or their trimethylsilyl esters via mixed anhydrides are demonstrated in Table 6. In every case, the desired aromatic ketones were obtained in good to high yields even when the reaction was carried out at room temperature. In these reactions, the other isomers (*o*-, and *m*-) were not observed by ^1H and ^{13}C NMR. The intramolecular Friedel–Crafts acylation reaction of free 4-phenylbutanoic acid or its trimethylsilyl ester smoothly proceeded at room temperature to give 3,4-dihydro-1(2*H*)-naphthalenone (**12**) in quantitative or 86% yields, respectively (Table 7, Entries 1 and 2).

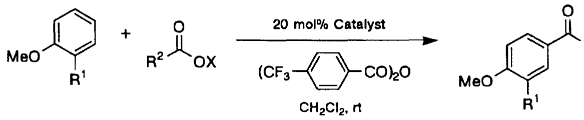
Concerning the catalyst cycle of the present Friedel–Crafts acylation reaction, it is assumed that the active cationic catalyst **23** is initially generated from $SiCl_4$ and $AgClO_4$ as shown in Scheme 2. This active cationic catalyst **23** promotes the formation of mixed anhydride **24** which is converted to the intermediate **25** by the influence of **23**. The intermediate **25** immediately reacts with the aromatic compound to give the desired aromatic ketone along with $HClO_4$, which in turn reacts with $ArCO_2SiCl_m(ClO_4)_{n-1}$ (**26**) to regenerate the catalyst **23**. Thus, the active cationic species generated from $SiCl_4$ and $AgClO_4$ effectively promotes the above two sequential reactions.

It is concluded that the catalytic Friedel–Crafts acylation reaction of aromatic ketones was established by just starting from free carboxylic acids or their trimethylsilyl esters and aromatic compounds under mild reaction conditions.

Experimental

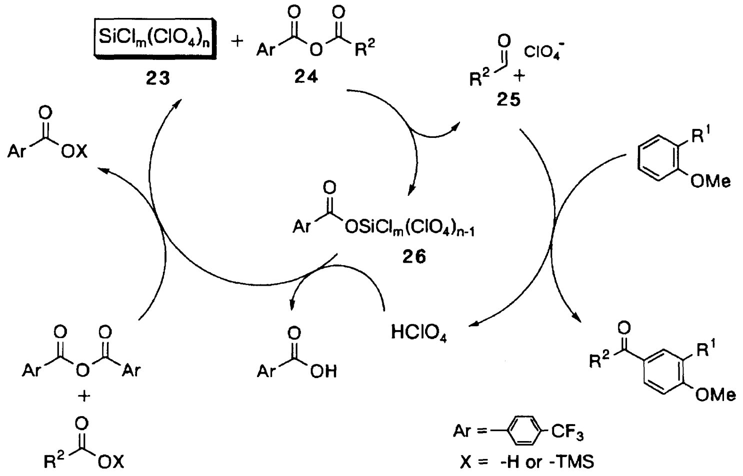
IR spectra were recorded on a Hobita FT-300 infrared spectrometer. ^1H NMR spectra were recorded on a

Table 6. The Catalytic Friedel–Crafts Acylation Reaction via Mixed Anhydrides



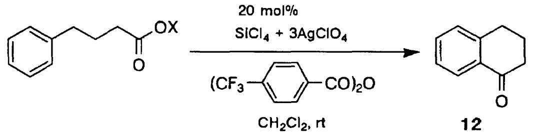
Entry	R^1	R^2	X	Catalyst[a)]	Time/h	Product	Yield/%
1	H	C_4H_9	TMS	A	22	**2**	68
2	H	C_4H_9	H	B	23		86
3	H	C_5H_{11}	TMS	A	76	**3**	84
4	H	C_5H_{11}	H	B	24		89
5	H	$Ph(CH_2)_2$	TMS	A	63	**4**	Quant.
6	H	$Ph(CH_2)_2$	H	B	42		93
7	H	Ph	H	B	47	**5**	76
8	Me	C_4H_9	TMS	A	19	**6**	Quant.
9	Me	C_4H_9	H	B	24		88
10	Me	C_5H_{11}	TMS	A	23	**7**	Quant.
11	Me	C_5H_{11}	H	A	24		Quant.
12	Me	$Ph(CH_2)_2$	TMS	A	24	**8**	88
13	Me	$Ph(CH_2)_2$	H	A	22		93
14	Me	Ph	TMS	A	42	**9**	76
15	Me	Ph	H	B	40		78
16	MeO	C_4H_9	TMS	A	20	**10**	Quant.
17	MeO	C_4H_9	H	B	24		94
18	MeO	C_5H_{11}	TMS	A	19	**11**	89
19	MeO	C_5H_{11}	H	A	19		86

a) A; $SiCl_4+3AgClO_4$, B; $SiCl_4+4AgClO_4$.



Scheme 2. The catalytic cycle.

Table 7. The Intramolecular Friedel–Crafts Acylation Reaction



Entry	X	Time/h	Yield/%
1	H	24	Quant.
2	TMS	12	86

Hitachi R-1100, R-1200, or JEOL JNR-EX270L spectrometer, and tetramethylsilane (TMS) served as internal standard. ^{13}C NMR spectra were recorded on a JEOL JNR-EX270L spectrometer, and TMS served as internal standard. Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F. All reactions were carried out under argon atmosphere in dried glassware.

Silicon(IV)chloride ($SiCl_4$) was distilled from CaH_2 before use. Silver perchlorate ($AgClO_4$) was refluxed with benzene in a flask fitted with a Dean and Stark distilling receiver until all the water was removed azeotropically, then purified by recrystallization from dry benzene. Dichloromethane wad distilled from P_2O_5, then CaH_2, and dried over MS4A. Anisole, 1-methoxy-2-methylbenzene, 1,2-dimethoxybenzene and carboxylic acids were distilled or recrystallized before use.

Trimethylsilyl acetate was purchased from Aldrich Chemical Company, Lnc. Other trimethylsilye esters were prepared from the corresponding carboxylic acids by the treatment with trimethylsilyl chloride and pyridine in dichloromethane, and were purified by distillation. *p*-Trifluoromethylbenzoic acid and *p*-trifluoromethylbenzoyl chloride were purchased from Tokyo Kasei Co., Ltd. and were used without further purification.

Preparation of *p*-Trifluoromethylbenzoic Anhydride (22). To the mixture of *p*-trifluoromethylbenzoic acid (13.69 g, 72 mmol) and *p*-trifluoromethylbenzoyl chloride (15.02 g, 72 mmol) in dichloromethane (144 ml), pyridine (6.11 ml, 75.6 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 21 h at room temperature and then quenched with cold water (50 ml). After usual work up, the crude product was purified by recrystallization from dichloromethane to afford *p*-trifluoromethylbenzoic anhydride (23.2 g, 89% yield). Mp 132—133 °C; IR (KBr) 1732, 1795 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ=7.80 (4H, d, J=9 Hz), 8.26 (4H, d, J=9 Hz). Found: C, 53.09; H, 2.04%. Calcd for $C_{16}H_8F_6O_3$: C, 53.05; H, 2.23%.

Typical Experimental Procedure for the Catalytic Friedel–Crafts Acylation Reaction via Mixed Anhydrides. A typical experimental procedure is described for the reaction of methoxybenzene with hexanoic acid; $SiCl_4$ (0.08 mmol) and $AgClO_4$ (0.32 mmol) were stirred for 1 h in dichloromethane (2.0 ml) at room temperature, and then a mixture of hexanoic acid (0.4 mmol) and *p*-trifluoromethylbenzoic anhydride (0.4 mmol) in dichloromethane (3 ml) and a solution of anisole (0.4 mmol) in dichloromethane (1.0 ml) were successively added and the reaction mixture was stirred for 24 h at room temperature. Then aqueous sodium hydrogencarbonate was added and the aqueous layer was extracted with dichloromethane. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the crude product was purified by preparative TLC on silica gel to afford 1-(4-methoxyphenyl)-1-hexanone (89% yield).

Spectral data are presented below.

4-Methoxyacetophenoene (1).[20] IR (KBr) 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.55 (s, 3H), 3.87 (s, 3H), 6.91—6.96 (m, 2H), and 7.91—7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=26.34, 55.45, 113.67, 130.31, 130.58, 163.48, and 196.78.

1-(4-Methoxyphenyl)-1-pentanone (2).[20] IR (KBr) 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (t, 3H, J=7.3 Hz), 1.36—1.44 (m, 2H), 1.65—1.76 (m, 2H), 2.91 (t, 2H, J=7.6 Hz), 3.85 (s, 3H), 6.91—6.95 (m, 2H), and 7.92—7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.96, 22.55, 26.74, 38.01, 55.44, 113.66, 130.19, 130.31, 163.30, and 199.21.

1-(4-Methoxyphenyl)-1-hexanone (3).[20] IR (KBr) 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, 3H, J=6.9 Hz), 1.32—1.39 (m, 4H), 1.7—1.75 (m, 2H), 2.87—2.93 (m, 2H), 3.86 (s, 3H), 6.91—6.95 (m, 2H), and 7.91—7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.89, 22.48, 24.24, 31.54, 38.17, 55.35, 113.57, 130.1, 130.23, 163.22, and 199.17.

1-(4-Methoxyphenyl)-3-phenyl-1-propanone (4). Mp 97 °C; IR (KBr) 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.01—3.06 (m, 2H); 3.2—3.26 (m, 2H), 3.83 (s, 3H), 6.79—6.82 (m, 2H), 7.25—7.29 (m, 5H), and 7.77—7.79 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=30.21, 39.98, 113.62, 125.98, 128.32, 128.39, 129.87, and 130.19. Found: C, 80.01; H, 6.79%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

4-Methoxybenzophenone (5).[20] IR (KBr) 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.88 (s, 3H), 6.94—6.99 (m, 2H), 7.44—7.59 (m, 3H), 7.73—7.77 (m, 2H), and 7.81—7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=55.49, 113.55, 128.19, 129.72, 130.11, 131.89, 132.56, 138.25, 163.21, and 195.58.

1-(4-Methoxy-3-methylphenyl)-1-pentanone (6).[20] IR (KBr) 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (t, 3H, J=7.3 Hz), 1.36—1.47 (m, 2H), 1.65—1.76 (m, 2H), 2.24 (s, 3H), 2.9 (t, 2H, J=7.6 Hz), 3.88 (s, 3H), 6.82—6.85 (m, 1H), and 7.78—7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.98, 16.28, 22.57, 26.85, 37.97, 55.47, 109.14, 126.68, 128.14, 129.68, 130.69, 161.58, and 199.55.

1-(4-Methoxy-3-methylphenyl)-1-hexanone (7). Mp 34 °C; IR (KBr) 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, 3H, J=6.9 Hz), 1.32—1.39 (m, 4H), 1.69—1.76 (m, 2H), 2.25 (s, 3H), 2.9 (t, 2H, J=7.6 Hz), 3.89 (s, 3H), 6.82—6.85 (m, 1H), and 7.77—7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14, 16.28, 22.57, 24.44, 31.64, 38.24, 55.49, 109.14, 126.68, 130.71, 161.58, and 199.62. Found: C, 76.04; H, 8.84%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

1-(4-Methoxy-3-methylphenyl)-3-phenyl-1-propanone (8). Mp 77 °C; IR (KBr) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.22 (s, 3H), 3.01—3.07 (m, 2H), 3.2—3.26 (m, 2H), 3.86 (s, 3H), 6.79—6.82 (m, 1H), 7.17—7.32 (m, 5H), and 7.77—7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=16.26, 30.37, 40.07, 55.47, 109.18, 126.04, 126.74, 128.1, 128.43, 128.48, 129.41, 130.67, 141.54, 161.7, and 198.07. Found: C, 80.25; H, 7.11%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

4-Methoxy-3-methylbenzophenone (9). IR (neat) 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.25 (s, 3H), 3.9 (s, 3H), 6.84—6.88 (m, 1H), 7.43—7.57 (m, 3H), and 7.66—7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=16.26, 55.53, 108.97, 126.63, 126.72, 128.14, 129.74, 130.62, 131.79, 132.72, 138.45, 161.52, and 195.9. Found: C, 79.70; H, 6.26%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

1-(3,4-Dimethoxyphenyl)-1-pentanone (10).[20] IR (KBr) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (t, 3H, J=7.3 Hz), 1.37—1.45 (m, 2H), 1.66—1.77 (m, 2H), 2.92 (t, 2H, J=7.6 Hz), 3.94 (s, 3H), 3.95 (s, 3H), 6.87—6.90 (m, 1H), and 7.53—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.98, 22.55, 26.90, 37.86, 55.96, 56.05, 109.94, 110.13, 122.69, 130.35, 149.00, 153.08, and 199.26.

1-(3,4-Dimethoxyphenyl)-1-hexanone (11).[20] IR (KBr) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, 3H, J=6.93 Hz), 1.33—1.4 (m, 4H), 1.71—1.76 (m, 2H), 2.92 (t, 2H, J=7.59 Hz), 3.94 (s, 3H), 3.95 (s, 3H), 6.87—6.90 (m, 1H), and 7.28—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14, 22.57, 31.63, 38.13, 55.96, 56.05, 109.94, 110.15, 122.68, 130.35, 149.00, 153.08, and 199.33.

3,4-Dihydro-1(2*H*)-naphthalenone (12).[21] IR (neat) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.09—2.18 (m, 2H), 2.63—2.68 (m, 2H), 2.94—2.99 (m, 2H), 7.23—7.33 (m, 2H), 7.43—7.47 (m, 1H), and 8.01—8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=23.27, 29.69, 39.16, 126.61, 127.13, 128.77, 132.58, 133.39, 144.49, and 198.42.

2,4′-Dimethoxybenzophenone (23). Mp 73 °C; IR (KBr) 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.73 (s, 3H), 3.85 (s, 3H), 6.87—6.96 (m, 2H), 6.99—7.05 (m, 2H), 7.29—7.41 (m, 1H), 7.43—7.47 (m, 1H), and 7.77—7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=55.53, 55.37, 111.27, 113.39, 120.34, 129.09, 130.55, 131.32, 132.2, 156.91, 163.47, and 195. Found: C, 74.48; H, 6.05%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%.

4,4′-Dimethoxybenzophenone (24). Mp 139 °C; IR (KBr) 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.88 (s, 6H), 6.93—6.98 (m, 4H), and 7.76—7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ= 55.38, 113.37, 130.64, 132.13, 162.75, and 194.36. Found: C, 74.15; H, 5.84%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%.

4-Methoxy-2′-methylbenzophenone (25). IR (neat) 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.3 (s, 3H), 3.87 (s, 3H), 6.7—6.95 (m, 2H), and 7.21—7.4 (m, 4H), and 7.76—7.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=19.78, 55.51, 113.69, 125.17, 127.92, 129.79, 130.49, 130.82, 132.5, 136.15, 139.19, 163.7, and 197.37. Found: C, 79.43; H, 6.32%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

4-Methoxy-4′-methylbenzophenone (26). Mp 105—107 °C; IR (KBr) 1644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 2.43 (s, 3H), 3.87 (s, 3H), 6.93—6.97 (m, 2H), 7.25—7.28 (m, 2H), 7.66—7.69 (m, 2H), and 7.97—7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=21.6, 55.45, 113.48, 128.88, 129.99, 130.44, 135.49, 142.6, 163.02, and 195.34. Found: C, 79.86; H, 6.27%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

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