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$BeCl_2$ as a New Highly Selective Reagent for Dealkylation of Aryl-Methyl Ethers.

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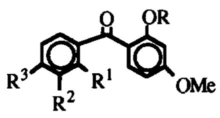
Abstract: An efficient and simple method is introduced for the selective removal of methyl group from poly aryl-methyl ethers, in some important derivatives of benzophenones, xanthones, anthraquinones, aryl esters, benzamides and nitroanisoles with $BeCl_2$.

Introduction

Ethers are among the most useful protective groups in synthetic organic chemistry.[1] Methylation of a hydroxyl moiety is regarded as one of the most effective protection methodologies, due to its very high stability under numerous reaction conditions. Variations in the structural environment of individual methyl ether groups can influence their lability. The relative lability of methoxy-groups to demethylating agents is found to be different when the structure of aryl-methyl ethers involves a carbonyl group for instance in ortho-methoxyketones, acids, esters, quinones, and xanthones.[2-4] Some reagents developed for demethylation of aromatic methyl ethers include Lewis acids, mixed mineral acids, oxidants, reductants as well as silica and aluminium compounds.[5a-c]

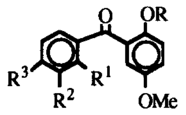
However, aryl-methyl ethers are difficult to dealkylate under mild reaction conditions,[5a] and rather drastic conditions are required which usually brings about other structural or stereochemical changes, in addition to the dealkylation reaction.[6,7] It is notable that very few methods are reported for selective demethylation of aryl-methyl ethers.[3,4,8] Selective demethylation has a key role in synthesis, especially, in the synthesis of benzophenones, as compounds with unique photo- and thermal behaviours[9] and hydroxyxanthones and anthraquinones as components of antitumor drugs.[10,11] In this paper we report a novel methodology for a simple, high-yielding and selective demethylation of methoxy substituted benzophenones, xanthones , anthraquinones, aryl esters, benzamides and nitroanisoles.

A series of methoxy substituted benzophenones were conveniently prepared by acylation of dimethoxy-benzene derivatives with either substituted benzoic acid in polyphosphoric acid[12] (**1,3a-g**), or substituted benzoyl chloride in dichloromethane in the presence of tintetrachloride ($SnCl_4$) at 0°C[13] (**2a-g**), (Scheme 1).



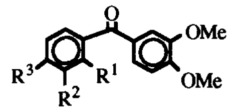
1 R=Me
6 R=H

a $R^1=R^2=R^3=H$
b $R^1=F$, $R^2=R^3=H$
c $R^1=Cl$, $R^2=R^3=H$
d $R^1=Br$, $R^2=R^3=H$
e $R^1=OMe$, $R^2=R^3=H$
f $R^2=OMe$, $R^1=R^3=H$
g $R^3=OMe$, $R^1=R^2=H$



2 R=Me

a $R^1=R^2=R^3=H$
b $R^1=F$, $R^2=R^3=H$
c $R^1=Cl$, $R^2=R^3=H$
d $R^1=Br$, $R^2=R^3=H$
e $R^1=OMe$, $R^2=R^3=H$
f $R^2=OMe$, $R^1=R^3=H$
g $R^3=OMe$, $R^1=R^2=H$



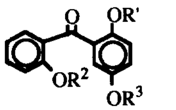
3

a $R^1=R^2=R^3=H$
b $R^1=F$, $R^2=R^3=H$
c $R^1=Cl$, $R^2=R^3=H$
d $R^1=Br$, $R^2=R^3=H$
e $R^1=OMe$, $R^2=R^3=H$
f $R^2=OMe$, $R^1=R^3=H$
g $R^3=OMe$, $R^1=R^2=H$
h $R^1=OH$, $R^2=R^3=H$

Scheme 1.

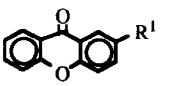
The results of our systematic studies showed that all these benzophenones (**1a-3g**) were found to be unreactive toward a variety of conditions even in the presence of excess reagents such as: Me_3SiBr/NaI, KBr/HOAc, $SnCl_2/CHCl_3$, $SnCl_2$/HOAc, $SnCl_4/CH_2Cl_2$ at 0°C, $SnCl_4/CHCl_3$/reflux, $Zn(OAc)_2$, $Zn(CrO_4)_2$, HgI_2, $TiCl_4$, $ZnBr_2$, LiF, NaI, ZnS and $Na_2S_2O_4$. Therefore, in order to find a suitable method for selective demethylation, benzophenone **2e** was chosen as a model compound and its reactions were studied under a variety of conditions via ^{1}H NMR spectroscopy.

Demethylation of **2e** with a powerful dealkylating agent such as pyridinum chloride gave only the cyclodehydration product of the resulting polyhydroxybenzophenone (**4a**), and 2-hydroxyxanthone **5a** was formed in 50% yield whereas, reaction of **2e** with hydrogen bromide in acetic acid as a less powerful demethylating agent, produced a mixture of **5a** and **4a** in 20 and 80% yields respectively.



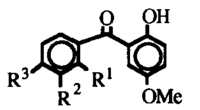
4

a $R^1=R^2=R^3=H$
b $R^1=R^2=H$, $R^3=Me$
c $R^1=H$, $R^2=R^3=Me$
d $R^2=H$, $R^1=R^3=Me$



5

a $R^1=OH$
b $R^1=OMe$



7

a $R^1=R^2=R^3=H$
b $R^1=F$, $R^2=R^3=H$
c $R^1=Cl$, $R^2=R^3=H$
d $R^1=Br$, $R^2=R^3=H$
e $R^2=OMe$, $R^1=R^3=H$
f $R^3=OMe$, $R^1=R^2=H$

Competitive structural change of the resulted benzophenone under these conditions led us to search for a milder method. Although, addition of boric acid, zinc chloride or zinc bromide to a mixture of hydrogen bromide and **2e** in acetic acid was not so promising for demethylation, but addition of zinc sulfide or ferrous sulfide in reaction mixture gave a good selectivity in demethylation reaction. Following the reaction in the presence of ZnS showed that after five hours 40% of **2e** remained unreactive and a mixture of monodeprotected products **4c** and **4d** were formed in 60% yield. Unfortunately, by extension of the reaction time, **5a**, **4a** and **4b** were also formed. Changing the amounts of the HBr and ZnS did not give better results.

Table 1. Reaction of methoxybenzophenone **2e** with some Lewis acids and $BeCl_2$.

Reagent	Solvent	Temperature °C	Time (h)	Ratio of products[a] **4a**	**4b**	**4c**	**4d**	**5a**	Yield %
$AlCl_3$	Benzene[b]	50	12	100	-	-	-	-	45
$AlCl_3$	$CHCl_3$[b]	60	10	100	-	-	-	-	50
BBr_3(1eq)	CH_2Cl_2[b]	0	1.5	-	-	50	50	-	80
BBr_3(3eq)	CH_2Cl_2[b]	0	3	100	-	-	-	-	88
BCl_3	CH_2Cl_2[b]	0	3	-	-	50	50	-	85
BF_3-etherate	Benzene[b]	reflux	6	-	-	60	40	-	60
BF_3-etherate	Toluene[b]	"	4	-	-	60	40	-	90
$BeCl_2$	Benzene	"	10	-	-	40	60	-	90
$BeCl_2$	Toluene	"	5	-	-	40	60	-	95

a. The products were isolated by recrystallization and characterized by physical and spectral data.
b. Reaction was carried out under N_2 atmosphere.

Reaction of **2e** with excess zinc bromide or zinc chloride and HCl in acetic acid, calcium formate in formic acid and ferric chloride in acetic acid were too mild and after 24 h. **4c** was formed in only 15-30% yield plus unreacted material.

However, the milder reagents aluminium trichloride[12] or boron tribromide[6], demethylated **2e** under N_2 atmosphere to give the trihydroxybenzophenone **4a** in 40-95% yield. Following the reactions by ^1H NMR in both cases confirmed that, initially the most sterically hindered methoxy group[2] undergoes cleavage and then further demethylation of other methoxy groups result in formation of the compeletly demethylated product **4a**. Use of 1 mole of boron tribromide did not increase selectivity of the demethylation reaction (Table 1).

Subsequently, reaction of trimethoxybenzophenone **2e** with boron trichloride which has been reported as a specific reagent for demethylation of *ortho*-methoxycarbonyl aryl ethers,[3,4] gave a mixture of 2-hydroxybenzophenones **4c**,**4d** in equal ratio in 85% yield. Cyclization of this mixture by refluxing in methanol and aqueous sodium hydroxide produced 2-methoxyxanthone **5b** in good yield.

Recently, selective dealkylation of methoxyanthraquinones has been reported in the presence of BF_3-etherate in benzene or toluene under N_2 atmosphere.[8] Under similar conditions, methoxybenzophenone **2e** was deprotected and again a mixture of **4c** and **4d** was obtained in 60-90% yields in ratio 60 to 40 respectively.

Since attempts at selective demethylation of **2e** were unsuccessful, our attention turned to beryllium chloride which has not yet been used for this purpose. Fortunately in the absence of an inert atmosphere, the reaction of **2e** with beryllium chloride in benzene produced an orange solution which after removal of the solvent and treatment of the resulting orange complex with 2N hydrochloric acid, a mixture of the monodeprotected products **4c** and **4d** were obtained in 95% yield in ratio 40:60 respectively. When toluene was used as solvent, the time of reaction is reduced and the same results were obtained. A comparision between results of deprotection reactions by BF_3-etherate[8] and $BeCl_2$ shows that the ratio of *ortho*-deprotected products is reversed (Table 1).

Similarly, as shown in Table 2 beryllium chloride demethylated selectively the other methoxybenzophenone derivatives (**1a-3g**) and the corresponding *ortho*-hydroxybenzophenones were formed in >90% yield.

Table 2. Demethylation of methoxybenzophenone derivatives **1a-3g** with excess $BeCl_2$ in refluxing benzene or toluene.

Entry	Solvent	Reaction Time(h)	Product[a]	Yield(%)
1a	Toluene	3	**6a**	90
1b	Toluene	3	**6b**	92
1c	Toluene	3	**6c**	90
1d	Toluene	3.5	**6d**	90
1e	Toluene	3	**6e**	90
1f	Toluene	3	**6f**	92
1g	Toluene	3	**6g**	90
2a	Toluene	3	**7a**	90
2b	Toluene	3.5	**7a**	90
2c	Toluene	3	**7c**	90
2d	Toluene	3.5	**7d**	90
2e	Benzene	8	**4c/4d(40/60)**	>95
2e	Toluene	3	**4c/4d(40/60)**	95
2f	Toluene	4	**7e**	90
2g	Toluene	3	**7f**	95
3a-3d,3f-g	Benzene	-	-[b]	-
3a-3d,3f-g	Toluene	-	-[b]	-
3e	Benzene	8	**3h**	~90
3e	Toluene	3.5	**3h**	92

a. All product were characterized by comparison of the R_f, mp, IR and ^1H NMR with authentic samples.
b. No product was isolated after 30 hours.

Use of the beryllium chloride is based on its Lewis acid property. Also $BeCl_2$ can be able to form an adduct with the oxygen of the methoxy group and selective formation of the beryllium chelate is the requirment of selective demethylation. The oxygen atom ortho to a ketone function is far less electron-rich than others and also has more necessary degree of coplanarity with carbonyl group[2], required for selective formation of beryllium chelate and consequently selective demethylation.

Furthermore this new selective methodology was successfully applied to demethylation of a series of methoxyxanthones and once again the specifity of $BeCl_2$ toward 2-methoxycarbonyl aryl ethers was shown. Therefore, the only 1-methoxyxanthone was reacted with $BeCl_2$ to produce an orange solution, which after work up 1-hydroxyxanthone was obtained in 90% yield (Table 3).

Table 3. Demethylation of methoxyxanthones with $BeCl_2$.

Entry	Solvent	Product	Time (h)	Yield(%)^a	^{1}H NMR OH/ppm
1-Methoxyxanthone	Benzene	1-Hydroxyxanthone	10	85	12.7
1-Methoxyxanthone	Toluene	1-Hydroxyxanthone	4	90	12.7
2-Methoxyxanthone	Benzene	-	24	-^{b}	-
3-Methoxyxanthone	Benzene	-	24	-^{b}	-

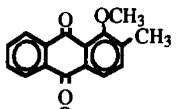
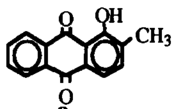
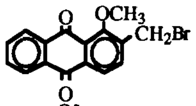
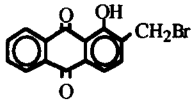
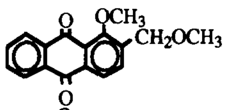
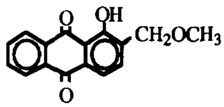
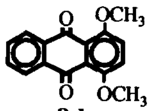
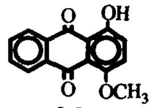
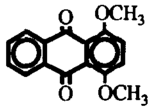
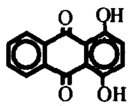
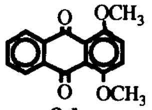
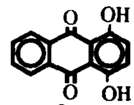
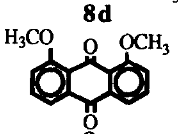
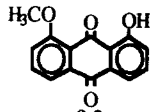
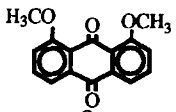
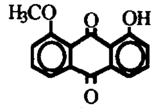
a. Yield of isolated product characterized by physical and spectral data (t.l.c, IR, ^{1}H NMR, mp.)
b. No product was detected even ofter 2 days in Toluene.

Extension of this new method to demethylation of methoxyanthraquinone derivatives was also successful. Thus, beryllium chloride demethylated selectively some methoxy anthraquinone derivatives into the more challenging compounds, hydroxyanthraquinones. In all cases, an intense color change from yellow to red was observed and the methoxy group adjacent to carbonyl function was selectively deprotected. This selectively is exhibited effectively in Table 4.

A similar selectivity for deprotection of ortho-methoxy carbonyl function were also found in the demethylation of some methoxysubstiuted esters and benzamides with $BeCl_2$ in toluene. Fortunately no Fries-rearrangement[12] or hydrolysis of esters and benzamides took place under these conditions. Though the 2-methoxysubstituted esters and benzamides gave a slurry solution in the reaction with $BeCl_2$, and produced 2-hydroxysubstituted esters and benzamides in excellent yields, but 3- or 4-methoxysubstituted esters and amides remained unreactive in the reaction with $BeCl_2$ in benzene or toluene (Table 5).

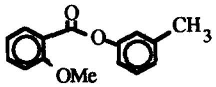
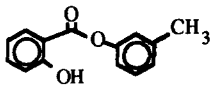
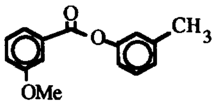
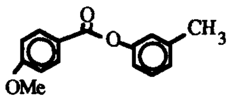
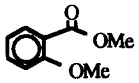
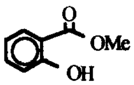
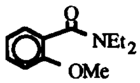
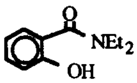
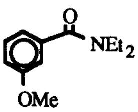
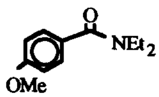
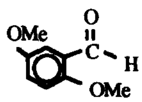
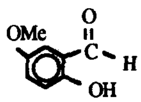
Subsequently, commercial 2,5-dimethoxybenzaldehyde was also demethylated with $BeCl_2$ in toluene to give an orange solution which after work up, the selective monodeprotected product 2-hydroxy-5-methoxy-benzaldehyde was obtained in 90% yield.

Table 4. Demethylation of methoxyanthraquinone derivatives with $BeCl_2$.

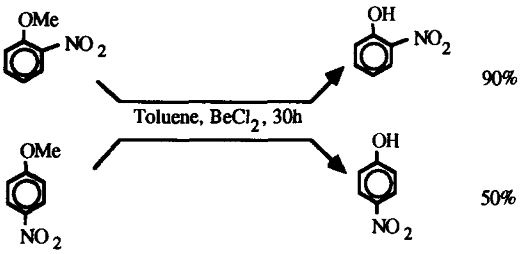
Entry	Solvent	Time	Product	Yield(%)
 **8a**	Benzene	3	 **9a**	92
 **8b**	Benzene	3	 **9b**	90
 **8c**	Benzene	3	 **9c**	>90
 **8d**	Benzene	3	 **9d**	30
 **8d**	Benzene	10	 **9e**	80
 **8d**	Toluene	5	 **9e**	>90
 **8e**	Benzene	8	 **9f**	60
 **8e**	Toluene	6	 **9f**	85

Finally, deprotection of nitroanisoles with $BeCl_2$ were also studied. However *ortho*-nitroanisole was completely deprotected by the reaction with $BeCl_2$ in toluene after 30 h. whereas, reaction of *para*-nitroanisole with beryllium chloride was not completed even after 30 hours (Scheme 2)

Table 5. Demethylation of methoxysubstituted esters, amides and benzaldehyde with $BeCl_2$

Entry	solvent	Reaction Time	Product	Yield(%)
	Toluene	4		95
10a	benzene	10	12	80
	Toluene	24	No Reaction	-
10b	benzene	24	No Reaction	-
	Toluene	24	No Reaction	-
10c	benzene	24	No Reaction	-
	Toluene	4		90
10d	benzene	10		80
	Toluene	5		92
11a	benzene	12	13	80
	Toluene	24	No Reaction	-
11b	benzene	24	No Reaction	-
	Toluene	24	No Reaction	-
11c	benzene	24	No Reaction	-
	Toluene	7		95
-[a]	benzene	12	14	80

a) 3-Methoxy-benzaldehyde remained unreactive under these reaction conditions.



Scheme 2

A comparison between given results, showes that the rate of deprotection reaction of nitroaryl-methyl ethers are much slower and non selective than aryl-methyl ethers with a *peri*-metoxy to carbonyl group. As a result it can be concluded that, in demethylation of all carbonyl containing aryl-methyl ethers (ketones, esters, amides and aldehyde) with $BeCl_2$, carbonyl group plays a critical role in the orientation of selectivity. This selectivity is also directed by electronegativity of the oxygen of methoxy adjacent to the carbonyl group and its coplanarity with the carbonyl function. Especially, in anthraquinones and xanthones these coplanarities gathered with the two benzene rings enforced by -CO- group and O- bridge.[14]

Therefore, coordination of the $BeCl_2$ to the carbonyl function is a key-prerequisite for the selectivity of deprotection which is rationalized in terms of chelation and the relative electronegativity of ether oxygenes for demethylation at the ortho position.

In conclusion our studies showed that $BeCl_2$ can be used as a very selective demethylating agent in the demethylation reaction of benzophenones, xanthones, anthraquinones, aryl esters, benzamides and nitro anisoles. In addition the generality of the method for *peri*-methoxy carbonyl aryl ethers, high selectivity, excellent yields, mild reaction conditions, purity and ease of conversion of the beryllium chelate to the corresponding hydroxy derivatives could make this method a very useful addition to the present methodologies. Further applications of this procedure in the synthesis are currently in progress.

Acknowledgement
We are thankful to Shiraz University Research Council for their financial support.

Experimental

Solvents, reagents, and chemical materials were obtained from Merck and Fluka chemical companies. Melting points were determined in open capillary tubes in a Buchi 510 circulating oil melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 781 spectrophotometers. ^1H NMR spectra were obtained on a Jeol-EX 90Q for solutions in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra (MS) were obtained by a GCMS-QP 1000 EX at 20 ev. UV spectra were recorded on a UV/Vis spectrometer PU 8750. TLC were carried out on silica gel 60F-254 analytical sheets obtained from Merck chemical company.

Preparation of methoxybenzophenones (1a-3g)

Methoxybenzophenones (**1,3a-g**) were prepared by the reaction of the corresponding benzoic acids (0.01 mol) and 1,3-dimethoxybenzene or veratrol (0.01 mol) in PPA at 90°C for 8 h. and methoxybenzophenones (**2a-g**) were prepared by the reaction between substituted benzoyl chlorides (0.012 mol) and 1,4-dimethoxybenzophenone (0.01 mol) in dry CH_2Cl_2 (150 ml) in the presence of $SnCl_4$[13] (0.012 mol) at 0°C. Analytical and spectroscopic data, as well as literature references for known benzophenones are followed;

2,4-dimethoxybenzophenone (**1a**) : 90% yield; white solid; m.p.=87°C (lit[15] 86-88°C); IR(KBr): 1645 (C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.6 (s,3H), 3.8(s,3H), 6.4(s,1H),6.5-7.6(m,7H).

2-Fluoro-2',4-dimethoxybenzophenone (**1b**) : 85% yield; white solid; m.p.=70°C; rf=0.6 (CCl_4/MeOH-90:10); IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.55(s,3H), 3.75(s,3H), 6.3-7.6(m,7H); UV(MeOH) λ 237(ε_{max}=18100), 282(ε=13600), 315 nm(ε=16300); MS:m/z=260(M^+,30), 243(54), 215(16), 165(100, basepeak), 150(5), 123(16),95(7),77(9). Found:C, 69.42; H, 4.8; $C_{15}H_{13}FO_3$ requires C, 69.23; H, 5.0%.

2-Chloro-2',4-dimethoxybenzophenone (**1c**)[16]: 90% yield; m.p.=60°C; IR(KBr): 1645 (C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.45(s,3H), 3.65(s,3H), 6.3(s,1H), 6.4-7.4(m,6H).

2-Bromo-2',4-dimethoxybenzophenone (**1d**) : 80% yield, m.p.=62°C; rf=0.64 (CCl_4/MeOH-90:10); IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H),3.7(s,3H),6.3(s,1H), 6.4-7.6(m,6H); UV(MeOH) λ 281(ε_{max}=18900), 315 nm(ε=12700); MS:m/z=322 (11), 320 (M^+,12), 303(10) 241(13), 165(100, base peak), 151(10), 122(8),107(5), 92(2). Found: C, 55.93; H, 4.2; $C_{15}H_{13}BrO_3$ requires C, 56.07; H, 4.05%.

2,2',4-Trimethoxybenzophenone (**1e**): 85% yield; m.p.=59-60°C (lit[2] 61-2); IR(KBr): 1650(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.7(s,3H), 3.85(s,6H), 6.6(s,1H), 6.7-7.5(m,6H).

2,3',4-Trimethoxybenzophenone (**1f**)[17]: 85% yield; m.p.=79-80°C; IR(KBr): 1650(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.75(s,6H), 6.4-7.4(m,7H)).

2,4',4-Trimethoxybenzophenone (**1g**)[18]: 85% yield; m.p.=145°C; IR(KBr): 1650(C=O), 1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.7(s,3H), 3.75(s,3H), 6.4-7.8 (m,7H).

2,5-Dimethoxybenzophenone (**2a**): 82% yield; m.p.=51°C (lit[15]49-50°C); IR(KBr): 1645(C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.7(s,3H), 6.8-7.8(m,9H).

2-Fluoro-2',5-dimethoxybenzophenone (**2b**): 83% yield; m.p.=50-1°C; rf=0.73(CCl_4/MeOH-90:10); IR(KBr): 1640(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.8(s,3H), 6.3-7.7(m,7H); UV(MeOH) λ 226(ε_{max}=18500), 347 nm(ε=5000); MS:m/z=360(M^+,35) ,243(55),215(20),165(100, base peak), 123(16), 95(7). Found: C, 68.98; H, 5.20; $C_{15}H_{13}FO_3$ requires C, 69.23; H, 5.00%.

2-Chloro-2',5-dimethoxybenzophenone (**2c**)[19]: 80% yield; m.p.=55°C; IR(KBr): 1640(C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.45(s,3H), 3.65(s,3H),3.65(s,3H), 6.3-7.7(m,7H).

2-Bromo-2',5-dimethoxybenzophenone (2d)[20]: 80% yield; m.p.=54°C; IR(KBr): 1640(C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 3.7(s,3H), 6.6-7.6(m,7H).

2,2',5-Trimethoxybenzophenone (2e)[21]: 82% yield; m.p.=48°C ; IR(KBr): 1650(C=O), 1595 cm^{-1} (C=O); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 3.6(s,3H), 3.7(s,3H), 6.8-7.8(m,7H).

2,3',5-Trimethoxybenzophenone (2f): 80% yield; white needles; m.p.=71-2°C; rf=0.68(CCl_4/MeOH-90:10); IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.55(s,3H), 3.65(s,3H), 3.7(s,3H), 6.8-7.4(m,7H); UV(MeOH) λ 218(ε_{max}=18800), 308 nm(ε=6000); MS:m/z=272(M^+,35), 258(35), 255(34),227(29), 165(100, base peak), 15(65), 135(30), 107(21), 92(25). Found: C, 70.50; H, 5.98; $C_{16}H_{16}O_4$ requires C, 70.58; H, 5.92%.

2,4',5-Trimethoxybenzophenone (2g)[22]: 80% yield; white solid; m.p.=70°C; IR(KBr): 1650(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.4(s,3H), 3.5(s,3H), 3.6(s,3H), 6.5-7.6(m,7H).

3,4-Dimethoxybenzophenone (3a) : 90% yield; m.p.=102°C (lit[15] 99-100 °C); IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.7(s,6H), 6.6-7.6(m,8H); UV(MeOH) λ 280(ε_{max}=18000), 314 nm(ε=15000).

2-Fluoro-3,4-dimethoxybenzophenone (3b)[23]: 85% yield; m.p.=76°C; rf=0.86(CCl_4/$CHCl_3$-97:3); IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,6H), 6.7-7.5(m,7H); UV(MeOH) λ 281(ε_{max}=18000), 312 nm(ε=16000).

2-Chloro-3,4-dimethoxybenzophenone (3c): 82% yield; m.p.=140°C (lit[16] 141-2°C); IR(KBr): 1645(C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,6H), 6.6-7.5(m,7H); UV(MeOH) λ 281(ε_{max}=13000), 313 nm(ε=9000).

2-Bromo-3,4-dimethoxybenzophenone (3d)[20]: 80% yield; m.p.=155°C; IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.85(s,6H), 6.6-7.4(m,7H); UV(MeOH) λ 282(ε_{max}=18000), 314 nm(ε=12000).

2',3,4-Trimethoxybenzophenone (3e): 82% yield; m.p.=78°C (lit[24] 80-82); IR(KBr): 1645(C=O), 1595 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.5 (s,3H),3.6 (s,3H), 3.7 (s,3H), 6.2-7.4(m,7H); UV(MeOH) λ 276(ε_{max}=17000), 310 nm (ε=13000).

3',3,4-Trimethoxybenzophenone (3f)[25]: 85% yield; white solid; m.p.=79-80°C; IR(KBr): 1645(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.7(s,3H), 3.8(s,6H), 6.7-7.4(m,7H); UV(MeOH) λ 281(ε=15000), 312 nm (ε_{max}=17000).

4',3,4-Trimethoxybenzophenone (3g)[25]: 80% yield; white solid; m.p.=96-7°C ; IR(KBr): 1650(C=O), 1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,9H), 6.6-7.6(m,7H); UV(MeOH) λ 250(ε_{max}=18000), 302 nm(ε=12000).

Preparation of Methoxyxanthones

1-Methoxyxanthone: 1-Methoxyxanthone was prepared by the refluxing a mixture of 0.001 mol of 1-

hydroxyxanthone (which was prepared from condenstion of 2-methoxybenzoic acid and resorcinol in PPA at 130°C)[12b], dimethylsulfate (0.002 mol) and K_2CO_3 (0.01 mol) in dry acetone (50 ml) within 24 h. Then water (100 ml) was added and the mixture was extracted with $CHCl_3$ (2x100 ml). The organic layer was washed with 10% NaOH (2x50 ml) and water (2x50 ml), dried (Na_2SO_4) and evaporated under reduced pressure, to give 1-methoxyxanthone in 75% yield; as pale yellow needles (CH_2Cl_2/n-hexane); m.p.=134-6°C(lit[12,26]136°C); IR(KBr): 1670(C=O),1595 cm^{-1} (Ar); ^1H NMR($CDCl_3$), δ 3.95(s,3H), 7.0-8.3(m,7H).

2-Methoxyxanthone (5b)

5b was prepared by the cyclization of **4c** and **4d** (0.01 mol) in a mixture of MeOH (30 ml), NaOH (2 g, 0.05 mol) and H_2O (20 ml) which was refluxed overnight. Then water (50 ml) was added and the product was isolated by filteration as white needles (MeOH); 70% yield; m.p.=130-1°C(lit 130°C[20,27]), IR(KBr):1665(C=O), 1600 cm^{-1}(Ar); ^1H NMR($CDCl_3$), δ 3.8(s,3H), 7.1-8.3(m,7H); UV($CHCl_3$)λ 250 (ε_{max}=25000), 290(ε=4000),360 nm(ε=6000).

3-Methoxyxanthone

3-Methoxyxanthone was obtained by the either cyclization of **6e** (as the same procedure of **5b**) or by the cyclization of **1b-1d** in refluxing 8% NaOH within 24 hours. Then water (50 ml) was added and the product was isolated by filtration, both in 65% yield as pale yellow needles; m.p.=128-130° (lit[19,20,26,27] 130-2°C); IR(KBr): 1665(C=O),1600 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 3.9 (s,3H), 6.8-8.4(m,7H); UV ($CHCl_3$) λ 240 (ε_{max}=35000), 270(ε=10000), 310 nm(ε=6000).

Methoxyanthraquinones (8a-e)

General Procedure: Methoxyanthraquinones **8a, 8d** and **8e** were prepared by refluxing a mixture of corresponding hydroxyanthraquinone (0.001 mol), dimethyl sulfate (0.003 mol) and K_2CO_3 (0.01 mol) in dry acetone (50 ml) within 24 h. Then water (100 ml) was added and the mixture was extracted with $CHCl_3$ (2x200 ml). The organic layer was washed with 10% NaOH (2x50 ml) and water (2x50 ml), dried (Na_2SO_4) and evaporated under reduced pressure to give the corresponding methoxyanthraquinone.

1-Methoxy-2-methyl-9,10-anthraquinone (8a)

8a was prepared by the methylation of **9a** (which was prepared from the reaction of 1-amino-2-methylanthraquinone and $NaNO_2$/HCl in H_2SO_4)[28] according to the general procedure as green-yellow needles (AcOH); m.p.=165°C (lit[28] 166-7°C); IR(KBr):1670 (C=O), 1585 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 2.34 (s,3H), 3.85(s,3H),7.3-8.3(m,6H); UV ($CHCl_3$) λ 257(ε_{max}=38900), 346 nm(3900).

1-Methoxy-2-bromomethyl-9,10-anthraquinone (8b)

8b was prepared by the bromination of **8a** (1.26 g, 5 mmol), by NBS (0.875 g, 5 mmol) in the presence of dibenzoyl peroxide (0.1 g) in dry CCl_4. Then the solvent was evaporated and the precipitate dissolved in chloroform (20 ml) and washed with water (3x20 ml), dried (Na_2SO_4) and the solvent was evaporated to give 1-methoxy-2-(bromomethyl)-9,10-anthraquinone (**8b**) in 93% yield as yellow needles (AcOH); m.p.=191°C (lit[28] 192); IR(KBr):1670(C=O),1585 cm^{-1} (Ar); ^1H NMR ($CDCl_3$), δ 4(s,3H), 4.57(s,2H),7.5-8.4(m,6H);

UV($CHCl_3$) λ 229(ε=31600), 258(ε_{max}=38900), 346 nm(ε=5000).

1-Methoxy-2-methoxymethyl-9,10-anthraquinone (8c)

8c was prepared by the reaction of **8b** (0.66 g, 2 mmol) and K_2CO_3 (0.25 g, 1.8 mmol) in methanol (100 ml) were refluxed for 3 h. Then the solvent was evaporated and the precipitate dissolved in chloroform (50 ml) and washed with water (3x20 ml), dried (Na_2SO_4) and the solvent was evaporated to give 1-methoxy-2-methoxymnethyl-9,10-anthraquinone (**8c**) in 90% yield, as yellow needles (n-hexane); m.p.=145°C (lit[28] 145°C); IR(KBr): 1680(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$),δ 3.4(s,3H), 3.84(s,3H),4.51(s,2H),7.5-8.3(m,6H); UV(chloroform) λ 231(ε=20000) 255(ε_{max}=39800) 344 nm(ε=6100).

1,4-Dimethoxyanthraquinene (8d)

8d was prepared by the methylation of quinizarine according to the general procedure as orange-yellow needles (acetone); m.p.=167-70°C(lit[29] 169-70°C); IR(KBr): 1670 (C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$),δ 3.99(s,6H), 7.3-8.1(m,6H); UV(MeOH) λ 315(ε=5700), 427 nm(ε_{max}=14500).

1,8-Dimethoxyanthraquinone (8e)

8e was prepared by the methylation of 1,8-dihydroxyanthraquinone according to the general procedure as yellow needles; m.p.=220-3°C(lit[30] 222-3°C); IR(KBr): 1660(C=O),1590 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 4(s,6H), 7.3-7.8(m,6H); UV(MeOH) λ 255(ε_{max}=20000), 385 nm(ε=6400).

Methoxyesters (10a-d)

General Procedure: Reaction of 0.01 mol of the corresponding benzoyl chloride and *m*-cresol or methanol in dry CH_2Cl_2 under vigorous stirring for 2 hours, was afforded the methoxyesters **10a-d**, which after extraction with CH_2Cl_2 (2x200 ml), the organic layer was washed with 10% NaOH (2x100 ml), and water (2x100 ml). Then the products were isolated by removing the solvent under reduced pressure.

m-Tollyl-2-methoxybenzoate (10a)

10a was prepared from 2-methoxybenzoylchloride and *m*-cresol following the general procedure in 90% yield; white needles; m.p.=49-50°C, rf=0.7(CCl_4/MeOH-90:10); IR(KBr): 1750(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 2.3(s,3H), 3.8(s,3H),6.7-7.9(m,8H); UV(MeOH) λ 238(ε_{max}=12300), 298 nm(ε=5300); MS:m/z=242(M^+,8), 136(10), 135(100, base peak), 107(21), 92(8), 77(18). Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found C, 74.52; H, 5.55%.

m-Tollyl-3-methoxybrenzoate (10b)

10b was prepared from 2-methoxybenzoylchloride and *m*-cresol following the general procedure in 89% yield; clear oil; rf=0.76(CCl_4/MeOH-90:10); IR(KBr): 1740(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 2(s,3H), 3.4(s,3H),6.7-7.5(m,8H); UV(MeOH) λ 240(ε_{max}=12600), 298 nm(ε=4400); MS:m/z=242(M^+,10), 135(100, base peak), 107(18), 92(7), 77(16). Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found C, 74.10; H, 5.800.

m-Tollyl-4-methoxybenzoate (10c)

10c was prepared from 4-methoxybenzoylchloride and *m*-cresol following the general procedure in 92% yield; white needles; m.p.=54-5°C; rf=0.72(CCl_4/MeOH-90:10); IR(KBr): 1735(C=O), 1605 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 2.3(s,3H), 3.8(s,3H),6.7-8.2(m,8H); UV(MeOH) λ 262(ε_{max}=14200); MS:m/z=242 (M^+,5), 136(9),135(100, base peak), 107(8), 92(13), 77(19). Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found C, 74.42; H, 5.58%.

2-Methoxy-methylsalicylate (10d)[31]

10d was prepared from 2-methoxybenzoylchloride and methanol following the general procedure in 85% yield, clear oil; rf=0.68(CCl_4/MeOH-90:10); IR(KBr): 1735(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.75(s,6H), 6.7-7.6(m,4H); UV(MeOH) λ 284(ε_{max}=13800), 295 nm(ε=7000).

Methoxyamides (11a-c): were prepared by the reaction of corresponding methoxybenzoyl chloride (0.01 mol) and diethylamine (0.05 mol) in CH_2Cl_2 (150 ml) at 0°C for 2 h, and were isolated as the same of esters **(10a-d)**.

N,N-Diethyl-*o*-anisamide (11a)

Colorless oil; b.p.=103°C(lit[32] 103-104°C); IR(KBr): 1640(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 1.1(t,6H), 3.3(q,4H), 3.7(s,3H), 6.7-7.5(m,4H).

N,N-Diethyl-*m*-anisamide (11b)

Clear oil, b.p.=177°C(lit[32] 177°C); IR(KBr): 1645(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 1.15(t,6H), 3.3(q,4H), 3.7(s,3H), 6.85-7.6(m,4H).

N,N-Diethyl-*p*-anisamide (11c)

White solid which was rapidly liquified; m.p.=45-7°C(lit[32] 48°C); IR(KBr): 1635(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 1.1(t,6H), 3.3(q,4H), 3.7(s,3H), 6.6-7.5(m,4H).

Deprotection of Aryl-methyl Ethers with $BeCl_2$

General Procedure: A mixture of substrate (1 mmoles) and beryllium chloride (3 mmol, 0.24 g) in dry benzene or toluene was refluxed for 3-8 hours. In the case of *peri*-carbonylarylmethyl ethers, an intense color change was observed, and evaporation of the solvent under reduced pressure yielded a red to yellow complexes. Treatment of the complexes with 2N hydrochloric acid and extraction with chloroform afforded the pure corresponding hydroxyderivatives in 85-92% Yield. During the reaction of esters and amides with $BeCl_2$ the color was not changed, but a slurry solution was given which after work up the pure corresponding hydroxyesters or benzamides were obtained. Analytical and spectroscopic data, as well as literature references for known demethylated products are followed;

2-Hydroxy-3',4'-dimethoxybenzophenone (3h): Colorless needles; m.p.=76-8°C; rf=0.7(CCl_4/MeOH-95:5); IR(KBr): 3400, 1625(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.65(s,3H), 3.7(s,3H), 6.1-7.5(m,7H), 12.7(s,1H); UV(MeOH) λ 282(ε_{max}=13850), 325c nm(ε=8000); MS:m/z=258(M^+,10), 228(16), 227(100, base peak), 184(4), 151(25), 135(15), 108(14), 95(9), 77(26). Found C, 69.48; H, 5.70; $C_{15}H_{14}O_4$ requires C, 69.77; H, 5.43%.

2-Hydroxy-4-methoxybenzophenone (6a) : Pale yellow needles; m.p.=63-5°C(lit[33] 63-4°C); rf=0.82(CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$,90 MHz), δ 3.6(s,3H), 6.2-7.4(m,8H), 12.6(s,1H); UV(MeOH) λ 240(ε=9600), 288(ε_{max}=13700), 325 nm(ε=8000).

2-Hydroxy-2'-fluoro-4-methoxybenzophenone (6b)[34]: Pale yellow plates; m.p.=149-50°C(d); rf=0.8 (CCl_4/MeOH-95:5); IR(KBr): 3410, 1630(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,3H), 6.3-7.6(m,7H), 12.6(s,1H); UV(MeOH) λ 237(ε=8400), 286(ε_{max}=14650), 324 nm(ε=7500).

2-Hydroxy-2'-chloro-4-methoxybenzophenone (6c)[35]: White needles; m.p.=74-5°C; rf=0.79 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.7(s,3H), 6.2-7.4(m,7H), 12.4(s,1H); UV(MeOH) λ 235(ε=7800), 285(ε_{max}=15300), 325 nm(ε=6700).

2-Hydroxy-2'-bromo-4-methoxybenzophenone (6d): Pale yellow needles; m.p.=96-8°C; rf=0.78 (CCl_4/MeOH-95:5); IR(KBr): 3380, 1630(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,3H), 6.2-7.6(m,7H), 12.45(s,1H); UV(MeOH) λ 286(ε_{max}=14650), 325(ε=8700); 324(ε=7500); MS:m/z=308(M^++1,8), 306(8), 227(45), 213(80), 185(5), 150(16), 137(18), 136(18), 81(100, base peak). Found C, 54.30; H, 3.62; $C_{14}H_{11}BrO_3$ requires C, 54.72; H, 3.58%.

2-Hydroxy-2',4-dimethoxybenzophenone (6e): Pale yellow needles; m.p.=92-3°C(lit[36] 88.5-9°C); rf=0.58 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,3H), 3.85(s,3H), 6.1-7.6(m,7H), 11.9(s,1H); UV(MeOH) λ 285(ε_{max}=14450), 325 nm(ε=9500).

2-Hydroxy-3',4-dimethoxybenzophenone (6f)[36]: Clear oil; rf=0.8(CCl_4/MeOH-95:5); IR(KBr): 1630(C=O), 1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.8(s,6H), 6.2-7.7(m,7H), 12.4(s,1H); UV(MeOH) λ 290(ε_{max}=19000), 328 nm(ε=6800).

2-Hydroxy-4',4-dimethoxybenzophenone (6g)[36]: Yellow needles; m.p.=110°C; rf=0.74 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.75(s,3H), 3.8(s,3H), 6.8-7.8(m,7H), ,12.45(s,1H); UV(MeOH) λ 290(ε_{max}=14600), 325 nm(ε=9000).

2-Hydroxy-5-dimethoxybenzophenone (7a): Pale yellow needles(hexane); m.p.=82-4°C(lit[37] 82°C); rf=0.86 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1630(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.55(s,3H), 6.9-7.5(m,8H), 11.6(s,1H); UV(MeOH) λ 253(ε_{max}=14300), 368 nm(ε=4200).

2-Hydroxy-2'-fluoro-5-methoxybenzophenone (7b): Pale yellow oil; rf=0.86 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1625(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 6.6-7.4(m,7H), 11.6(s,1H); UV(MeOH) λ 227(ε_{max}=14300), 375 nm(ε=4100); MS:m/z=246(M^+, 32), 150(100, base peak), 135(28), 123(88), 107(10), 95(20), 81(30). Found C, 68.40; H, 4.29; $C_{14}H_{11}FO_3$ requires C, 68.29; H, 4.47%.

2-Hydroxy-2'-chloro-5-methoxybenzophenone (7c): Pale yellow oil; rf=0.88 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 6.5-7.4(m,7H), 11.6(s,1H); UV(MeOH) λ 373 nm(ε_{max}=14600); MS:m/z=262(M^+, 8), 227(100, base peak), 151(16), 150(16). Anal. Calced. for $C_{14}H_{11}ClO_3$: C, 64.12; H, 4.20. Found C, 64.32; H, 4.05%.

2-Hydroxy-2'-bromo-5-methoxybenzophenone (7d): Pale yellow oil; rf=0.87 (CCl_4/MeOH-95:5); IR(KBr): 3380, 1630(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 6.45-7.6(m,7H), 11.65(s,1H); UV(MeOH) λ 263(ε_{max}=14700), 375 nm(ε=8000); MS:m/z=308(M^++1, 12), 306(10), 227(48), 213(85), 185(10), 150(26), 137(22), 136(28), 81(100, base peak). Found C, 54.89; H, 3.30; $C_{14}H_{11}BrO_3$ requires C, 54.72; H, 3.58%.

2-Hydroxy-2',5-dimethoxy and 2'-hydroxy-2,5-dimethoxybenzophenone (4c and 4d) 4c [2]: Pale yellow plates; m.p.=100-1°C; rf=0.89 (CCl_4/MeOH-95:5); IR(KBr): 3400, 1628(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.5(s,3H), 3.7(s,3H), 6.6-7.4(m,7H), 11.7(s,1H). Compound **4d**: Pale yellow plates; m.p.=98-100°C; IR(KBr): 3400, 1625(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.7(s,3H), 6.7-7.5(m,7H), 12.15(s,1H); UV(MeOH) λ 260(ε_{max}=15400), 365 nm(ε=15200); MS:m/z=258(M^+, 100), 227(50), 151(30), 150(41), 135(21), 107(21), 94(8), 77(10). Found C. 69.10; H, 5.62 $C_{15}H_{14}O_4$ requires C, 69.77; H, 5.43.

2-Hydroxy-3',5-dimethoxybenzophenone (7e) : Pale yellow oil; rf=0.84 (CCl_4/MeOH-95:5); IR(neat): 3410, 1625(C=O),1600 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.6, 3.75(each s,3H), 6.8-7.4(m,7H), 11.5(s,1H); UV(MeOH) λ 314(ε_{max}=15700), 368 nm(ε=14800); MS:m/z=258(M^+, 100), 227(42), 151(60), 150(56), 135(36), 107(38), 95(8), 77(30). Found C, 69.70; H, 5.50; $C_{15}H_{14}O_4$ requires C, 69.77; H, 5.43.

2-Hydroxy-4',5-dimethoxybenzophenone (7f) : Yellow needles; m.p.=66-8°C; rf=0.8 (CCl_4/MeOH-95:5); IR(KBr): 3380, 1630(C=O),1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 3.6(s,3H), 3.8(s,3H), 6.7-7.8(m,7H), 11.5(s,1H); UV(MeOH) λ 293(ε_{max}=15000), 367 nm(ε=5600); MS:m/z=258(M^+, 31), 151(11), 150(100, base peak), 135(25), 122(10), 107(18), 94(5), 77(10). Found C, 69.90; H, 5.30; $C_{15}H_{14}O_4$ requires C, 69.77; H, 5.43.

1-Hydroxyxanthone: Pale yellow needles; m.p.=148°C(lit[38] 148°C); IR(KBr): 1650(C=O),1605 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 6.8-8.2(m,7H), 12.7(s,1H); UV($CHCl_3$) λ 255(ε_{max}=18000), 289 nm(ε=8500), 298(ε=6000).

1-Hydroxy-2-methyl-9,10-anthraquinone (9a) : Yellow needles (ACOH); m.p.=180°C(lit[28] 180°C), IR(Nujol): 1670(C=O),1635 (H-bonded C=O), 1590 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 2.4(s,3H), 7.8-8.5(m,6H), 12.95(s,1H); UV($CHCl_3$) λ 255(ε_{max}=33800), 327(ε=5500), 414 nm(8900).

1-Hydroxy-2-bromomethyl-9,10-anthraquinone (9b) : Orange-yellow needles; m.p.=190-2°C(lit[28] 190-1°C), IR(KBr): 1670(C=O),1630 (H-bonded C=O), 1595 cm^{-1}(Ar); ^1H NMR ($CDCl_3$), δ 4.58(s,2H), 7.5-8.4(m,6H), 13.2(s,1H); UV($CHCl_3$) λ 253(ε_{max}=31600), 336(ε=3000), 412 nm(ε=7900).

1-Hydroxy-2-methoxymethyl-9,10-anthraquinone (9c) : Orange needles; m.p.=160-3°C(lit[28] 160-1°C); IR(KBr): 1675(C=O),1630 (H-bonded C=O), 1595 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 3.4(s,3H), 4.46(s,2H), 7.5-8.2(m,6H), 12.78(s,1H); UV($CHCl_3$) λ 252(ε_{max}=44600), 332(ε=6300), 406 nm(ε=7500).

1-Hydroxy-4-methoxy-9,10-anthraquinone (9d) : Orange needles; m.p.=168°C(lit[39] 167-8°C); IR(KBr): 1670(C=O),1620 (H-bonded C=O), 1595 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 3.95(s,3H), 7.4-8.5(m,6H), 12.95(s,1H).

1-Hydroxy-8-methoxy-9,10-anthraquinone (9e) : Yellow needles; m.p.=196-7°C(lit[8] 196°C); IR(KBr): 1670(C=O), 1618 (H-bonded C=O), 1595 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 3.90(s,3H), 7.3-8.6(m,6H), 13(s,1H).

m-Tolyl salicylate (12): White needles; m.p.=74-5°C(lit[40] 74°C); IR(KBr): 1685(C=O), 1605 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 2.35(s,3H), 6.7-8(m,8H), 10.6(s,1H), UV(MeOH) λ 240(ε_{max}=12000), 310 nm(ε=4800).

N,N-Diethyl salicylamide (13) : White solid; m.p.=100-1°C(lit[41] 101°C); IR(KBr): 3200, 1620(C=O), 1595 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 1.1(t,6H), 3.3(q,4H), 6.5-7.2(m,4H), 8.7(s,1H); UV(MeOH) λ 278 (ε_{max}=12300), 323 nm(ε=4000).

2-Hydroxy-5-methoxybenzaldehyde (14) : White oil; freezing point=2-3°C(lit[42] below 4°C); IR(KBr): 3200-2800, 1625(C=O), 1600 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 3.7(s,3H), 6.6-7.1(m,4H), 9.65(s,1H), 10.7(s,1H); UV(MeOH) λ 258 (ε_{max}=13000), 365(ε=6700).

2-Hydroxyxanthone (5a)

5a was obtained from the reaction of **2e** (0.01 mol) and pyridine hydrochloride (0.05 mol) at 200°C for 24 hours, which after usuall work up **5a** was isolated in 55% yield, as pale yellow needles; m.p.=240°C (lit[43] 241°C); IR(KBr): 3300, 1660(C=O), 1600 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 7.2-8.3(m,8H); UV($CHCl_3$) λ 250 (ε_{max}=33000), 300(ε=4200), 365 nm (ε=6600).

2,2'-Dihydroxy-5-methoxybenzophenone (4b)

4b was prepared from the reaction of **2e** (2.72 g, 0.01 mol) with $AlCl_3$ (0.02 mol) in dry benzene at 50°C under N_2 atmosphere for 12 hours. After usuall work up **4b** was obtained as yellow needles in 40% yield; m.p.=88-90°C; rf=0.81(CCl_4/MeOH-90:10); IR(KBr): 3350, 1620(C=O), 1600 cm^{-1}(Ar); ^{1}H NMR ($CDCl_3$), δ 3.7(s,3H), 6.7-7.2(m,7H), 10.1(s,1H), 10.7(s,1H); UV(MeOH) λ 260 (ε_{max}=15800), 340 nm(ε=6000); MS:m/z=244(M^+, 51), 227(24), 151(15), 150(100, base peak), 121(32), 107(40), 81(46), 71(45), 69(65). Found C, 68.95; H, 4.72 $C_{14}H_{12}O_4$ requires C, 68.85; H, 4.91%.

2,2',5-Trihydroxybenzophenone (4a)

4a was prepared from the reaction of **2e** (2.72 g, 0.01 mol) with BBr_3 (2.7 ml, 0.03 mol) in dry CH_2Cl_2 at 0°C under N_2 atmosphere for 3 hours, then 2N HCl (200 ml) was added and the product was extracted with CH_2Cl_2 (3x200 ml). The organic layer was washed with water (3x200 ml) and evaporated under reduced pressure. **4a** was obtained as orange needles in 85% yield; m.p.=149-50°C; rf=0.31(CCl_4/MeOH-90:10);

IR(KBr): 3380, 1620(C=O), 1595 cm^{-1}(Ar); ^1H NMR (DMSO-d_6), δ 6.6-7.6(m,8H), 10.2(s,1H), 10.6(s,1H); UV(MeOH), λ 257 (ε_{max}=13700), 344 nm(ε=4500); MS:m/z=230(M^+, 90), 229(80), 213(70), 138(100, base peak), 120(25), 93(20), 81(20). Found C, 68.13; H, 4.29; $C_{13}H_{10}O_4$ requires C, 67.82; H, 4.38%.

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