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N,N-Dimethylacrylamide-Triflic Anhydride Complex as a Novel Bifunctional Electrophile in Reaction with Electron-Rich Aromatics

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Abstract: The reaction of *N,N*-dimethylacrylamide/trifluoromethanesulfonic anhydride complex with alkoxybenzenes followed by hydrolysis leads to the corresponding indan-1-ones and 1,3-diarylpropan-1-ones. Substituted naphthalenes yield dihydrophenalen-1-ones. Fused ring aromatics afford aromatic amines. Copyright © 1996 Elsevier Science Ltd

Introduction

The reaction of *N,N*-disubstituted formamides/phosphorus oxychloride (or other chlorides such as $SOCl_2$, $COCl_2$) complexes with electron-rich aromatic compounds (Vilsmeier-Haack reaction) are well-known and widely used in organic synthesis as a method of preparing aromatic aldehydes.[1,2] Unfortunately, iminium salts produced from amides of higher carboxylic acids, beginning from dimethylacetamide, are far less active in most cases (except very reactive aromatics such as pyrrole, indole, phloroglucinol). Earlier it was shown[3] that the replacement of $POCl_3$ by triflic anhydride in a Vilsmeier-Haack reaction permits elevation of the reactivity of the corresponding iminium salts and application to a greater number of aromatic substrates.

Recently we have studied a novel aspect of the Vilsmeier-Haack reaction.[4] We have found that the complex of dimethylacrylamide with trifluoromethanesulfonic anhydride reacts with electron-rich aromatic compounds. This method was shown to be effective for one step preparation of aromatic ketones - various indan-1-ones and 1,3-diarylpropan-1-ones, which are widely used in metallocenic and natural compounds chemistry.[5-9]

Indan-1-ones are mainly prepared by cyclization of 3-arylpropionic acids.[5,10,11] Furthermore α- or β-substituted acrylic acids[12] and α,β-unsaturated N-acylureas[13] were found to react with aryl alkyl ethers in the presence of polyphosphoric acid to give 2- or 3-substituted indan-1-ones, but in the case of ordinary acrylic acid yields are very low (less than 4%). 1,3-

Diarylpropan-1-ones were obtained earlier, predominantly by hydrogenation of the corresponding chalcones.[9,13] The application of dimethylacrylamide in the Vilsmeier-Haack reaction for synthetic preparation of compounds cited above has not been previously described.

Study of the system dimethylacrylamide/triflic anhydride

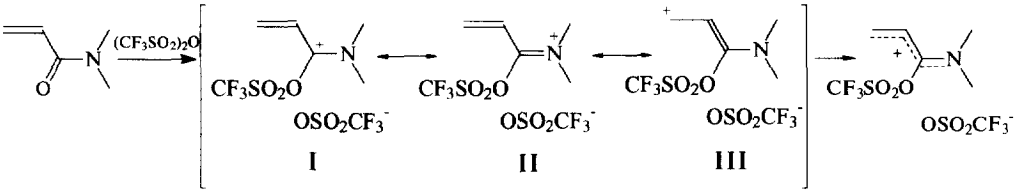
Addition of triflic anhydride to a solution of dimethylacrylamide in dichloroethane leads to formation of white amorphous precipitate, which does not decompose on boiling in dichloroethane and reacts with active aromatic compounds. We have recorded ^{1}H and ^{13}C spectra of the dimethylacrylamide/triflic anhydride complex in CD_3CN and have compared these data with ^{1}H and ^{13}C spectra of pure dimethylacrylamide in CD_3CN (Table 1). The signals of the carbonyl group and terminal olefinic carbon atom in the ^{13}C NMR spectrum of the complex are low-field shifted ($\Delta\delta$ = 3.2 ppm and 8.2 ppm correspondingly) compared with the same signals of pure dimethylacrylamide, that corresponds to a proposed additional polarisation of the C=O bond after complexation with triflic anhydride. Significant downfield shift of the terminal olefinic carbon atom indicates a considerable positive charge at this carbon atom.

Table 1. Comparison of ^{1}H, ^{13}C NMR for dimethylacrylamide/triflic anhydride complex and pure dimethylacrylamide

Position	^{1}H NMR, δ[ppm]		^{13}C NMR, δ[ppm]	
	dimethyl acrylamide	Complex	dimethyl acrylamide	Complex
=CH	6.64	6.70	126.88	122.38
$=CH_2$, *trans*	6.25	6.40	126.22	134.43
$=CH_2$, *cis*	5.66	6.30	126.22	134.43
$N(CH_3)_2$	3.12, 3.10	3.26, 3.22	36.27, 34.48	39.70, 38.03
CO			165.34	168.57

The structure of the complex can be rationalised by the resonance structures I-III depicted in Scheme 1. We propose that NMR studies allow us to conclude that the activation of dimethylacrylamide is achieved by coordination of triflic anhydride on its C=O bond. Delocalisation of the positive charge between C-1, C-3 carbon atoms and nitrogen atom occurs. The insignificant difference (0.1 ppm) between chemical shifts of *cis*-and *trans*-

hydrogen atoms in the complex (in the pure dimethylacrylamide this difference 0.59 ppm) allows the assumption about considerable contribution of structure III into the resonance.



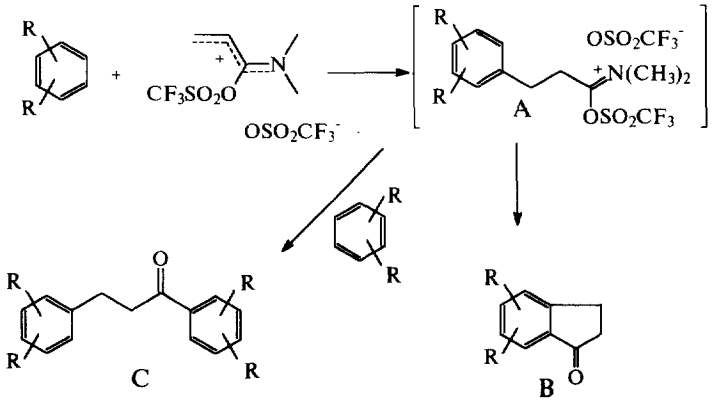
Scheme 1.

This complex may be assumed to possess two electrophilic reaction centers: the carbonyl carbon atom and the terminal olefinic carbon atom.

In order to study the scope and limitations of the reactions of dimethylacrylamide/triflic anhydride complex we have investigated the behaviour of different types of aromatics in this reaction. The results are summarised in Table 2.

Reaction of dimethylacrylamide/triflic anhydride complex with alkoxybenzenes and naphthalenes

This complex was found to react with various alkoxybenzenes yielding two types of compounds after hydrolysis (Scheme 2).[4] Phenols and N,N-dialkylanilines do not react, possibly because they decompose the reagent to yield a complex with triflic anhydride. Aromatic compounds which have no efficient electron-donating substituents such as benzene, toluene, mesitylene and naphthalene do not enter into the reaction; acenaphthene is the least reactive compound of aromatics which are able to react with the dimethylacrylamide/triflic anhydride complex (as in the classic Vilsmeier-Haack reaction[1]).



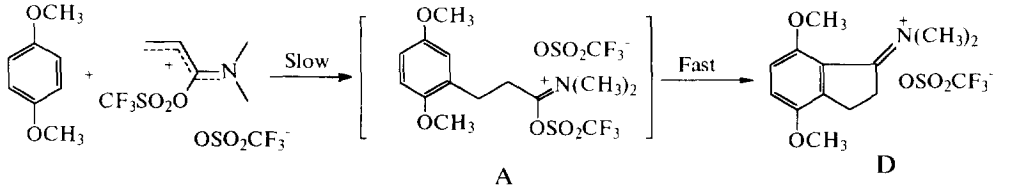
Scheme 2

The reactions with dialkoxybenzenes 1-4 lead mainly to the product of type B. In the cases of monoalkoxybenzenes 5-8 and resorcinol dimethyl ether 9 only the products of type C were obtained (Table 2).

The reaction was supposed to proceed in two step via iminium triflate A to give a cyclic product (for 1-4) or a acyclic iminium salt (for 5-9). The reaction path depends upon the difference in reactivity of adjacent positions of aromatic substrate.[4] If this difference is insignificant, predominantly the formation of products of type B occurs; otherwise, mainly the product of type C is formed.

Surprisingly, in the case of 1,2,3-trimethoxybenzene 4, mainly the corresponding indanone was obtained, although the position 4 in 1,2,3-trimethoxybenzene is far more active than position 5. Also unexpected was that benzodioxolane 3 reacted with the dimethylacrylamide/triflic anhydride complex to give 3b as the major product and 3a as the minor product while 1,2-dimethoxybenzene 2 gave only the product 2a. It is supposed that the first step of the reaction occurs at position 6 of benzodioxane 3, but that the cyclization proceeds either at the 7-position or at the 5-position, and the latter was preferable. In the case of 2, the steric hindrance of *ortho*-position is considerable and cyclization proceeds only at the 5-position.

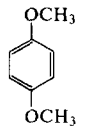
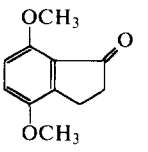
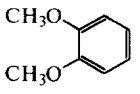
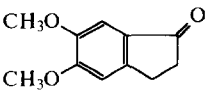
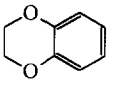
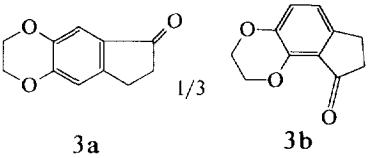
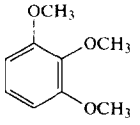
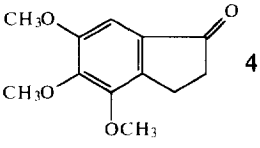
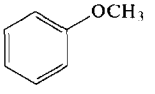
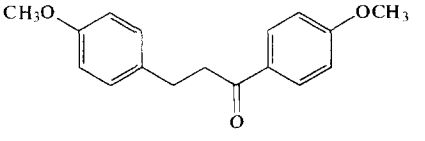
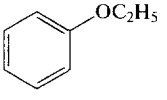
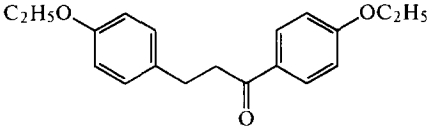
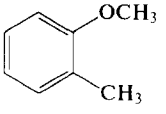
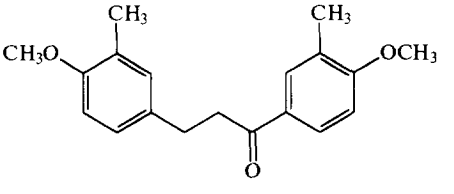
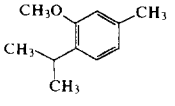
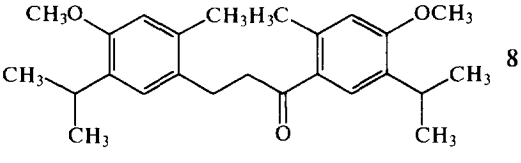
To study the mechanism of the reaction we have recorded ^{1}H and ^{13}C NMR for the reaction mixture of 1,4-dimethoxybenzene 1 before hydrolysis. Excepting the signals for both starting compounds (1 and reagent), signals of only one intermediate - the cyclic iminium salt D - were observed.[14] Since no signals of intermediate A were observed, we assume the second step of the reaction proceeds faster than the first one (Scheme 3).

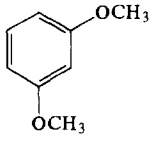
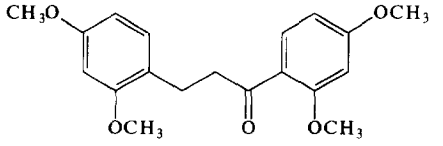
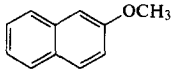
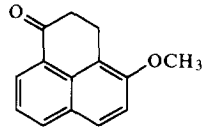
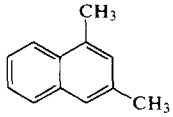
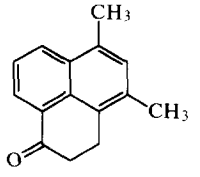
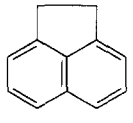
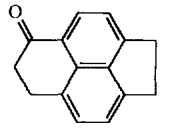
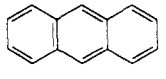
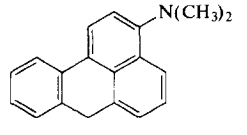
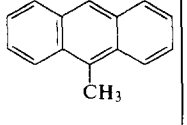
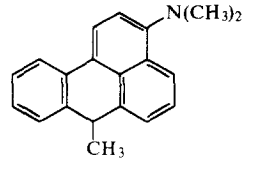
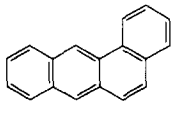
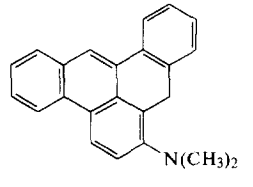
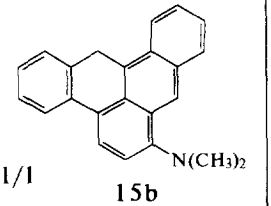
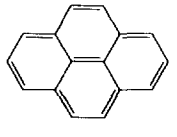
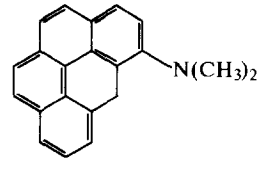


Scheme 3

We have also studied the reaction of dimethylacrylamide/triflic anhydride complex with substituted naphthalenes 10-12. The reactions proceed sluggishly and the corresponding dihydrophenalene-1-ones were isolated in low yields (Scheme 4). The first step of the reaction proceeds at the α-position of the naphthalene ring, the second being the cyclization into the *peri*-position to yield the iminium triflate which contains a dihydrophenalene fragment.

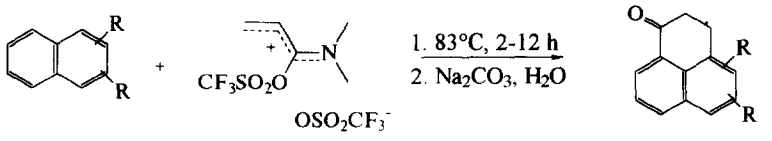
Table 2. Reaction of aromatic compounds with N,N-dimethylacrylamide/ trifluoromethanesulfonic anhydride complex

Entry	Substrate	Reaction time, h	Product	Yield, %
1		6	 1a	60 (75)[a]
2		6	 2a	42 (67)[a]
3		8	 1/3 3a 3b	48 (72)[a]
4		1	 4a	36 (53)[a]
5		3	 5a	56 (74)[a]
6		3	 6a	40 (64)[a]
7		3	 7a	35 (65)[a]
8		2	 8a	51 (81)[a]

9		0.5	 **9a**	46
10		3	 **10a**	18 (35) [a]
11		10	 **11a**	21 (59) [a]
12		12	 **12a**	11 (63) [a]
13		7	 **13a**	41 (79) [a]
14		5	 **14a**	38 (60) [a]
15		3	 **15a** 1/1  **15b**	47 (63) [a]
16		3	 **16a**	53 (75) [a]

[a] - yield based on conversion of substrate

In the case of 12 and 13 the activity of substrate is low and a considerable quantity of the starting compounds may be recovered (Table 2).

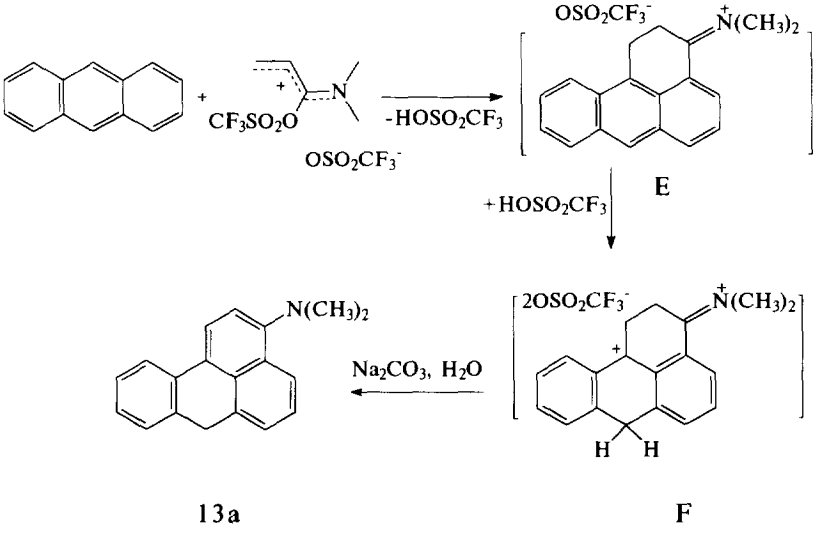


Scheme 4

Reaction of dimethylacrylamide/triflic anhydride complex with fused ring aromatics

Polyarenes and their derivatives represent a very interesting and important class of organic compounds, primarily due to the important role of the polycyclic aromatic hydrocarbons in the cause of cancer. Their chemical properties and methods of preparation are of continuing importance.

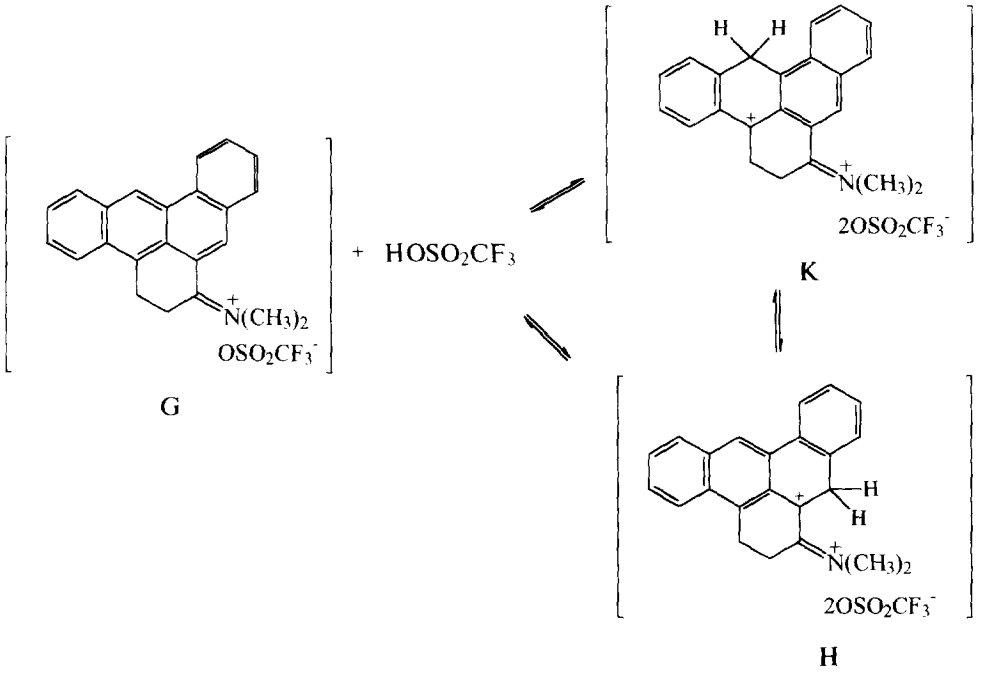
We have investigated the behaviour of some polycyclic aromatics in the reaction with dimethylacrylamide/triflic anhydride complex. It was found that the complex reacts with fused ring aromatics such as anthracene, 9-methylanthracene, benz[*a*]anthracene and pyrene (13-16), affording aromatic amines (13a-16a). Phenanthrene and benz[*b*]anthracene were found to be unreactive towards the iminium reagent. The proposed mechanism is shown in Scheme 5.



Scheme 5

We assume that the reaction path is similar for naphthalenes: initial attack at the most active position followed by cyclization at the *peri*-position to give the intermediate analogous to E. In contrast to the reaction with naphthalenes, intermediate E then undergoes isomerisation into F; the latter after quenching by aqueous K_2CO_3 leads to the aromatic amine 13a.

In the cases of hydrocarbons 13, 14 and 16 the reaction proceeds selectively to give in each case only a single product (besides starting compounds). Benz[*a*]anthracene 15 initially reacts[15] at the 5-position giving a 1:1 mixture of two isomers (15a and 15b) which could not be separated by column chromatography. We assume that one of them (15a) contains the phenanthrene aromatic system, having two *bay*-protons indicated in the ^1H NMR spectrum as two doublets near 8.60 ppm. Another isomer apparently contains the anthracene ring system with the *meso*-proton displayed as singlet at 8.33 ppm.



Scheme 6

Signals of CH_2-protons in 15a are low-field shifted ($\Delta\delta$ = 0.40 ppm) compared to the same signal 15b, that corresponds to a proposal about the strong interaction of methylene protons with the dimethylamino group in 15a (as in the case of 16).[16] The mechanism proposed for formation of 15a and 15b are represented in Scheme 6. Intermediate G which was generated from 15 by reaction with dimethylacrylamide/triflic anhydride complex then

protonated by triflic acid at the 8- or 13-position giving dications **H** and **K**. The latter is converted into **15a** and **15b** respectively when treated with base.

Conclusion

Thus, we have investigated a new electrophilic reagent produced by the reaction of the *N,N*-dimethylacrylamide with triflic anhydride. The activation of dimethylacrylamide is achieved by coordination of triflic anhydride to the C=O bond. This reagent possesses two electrophilic reaction centers (carbonyl carbon atom and terminal olefinic carbon atom) and reacts with electron-rich aromatic compounds, such as various alkoxybenzenes, substituted naphthalenes and polyarenes. We have found that this reagent afforded one-pot syntheses of various aromatic ketones - indan-1-ones, 1,3-diarylpropan-1-ones and dihydrophenalen-1-ones. Moreover, the complex allows aromatic amines to be obtained from fused ring aromatics in one step.

Experimental section

NMR spectra were recorded on Varian VXR-400 and Bruker AM 400C spectrometer with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer as films. Column chromatography was performed on silica gel (63-200 mesh, Merck). All solvents used were dried and distilled according to the standard procedure.

General procedure

A solution of 0.86 g (8.5 mmol) of *N,N*-dimethylacrylamide in 15 ml anhydrous dichloroethane was cooled to 0° C. Over a period of 10 min 2.4 g (8.5 mmol) of triflic anhydride in 10 ml of dichloroethane was added dropwise. Then 8.5 mmol of corresponding aromatic substrate[17] in 10 ml dichloroethane was added. The reaction mixture was heated at reflux 3-8 h and then was added to a mixture of ether and aqueous K_2CO_3 and stirred for an additional 1 h. The organic layer was separated, the aqueous layer was extracted with ether (2×50 ml). The organic solvents were removed *in vacuo*. The products were purified by column chromatography (silica gel, benzene).

4,7-Dimethoxy-1-indanone (1a), yield 63% (75%)[18]. mp 125-126 °C. (lit[11]. 125 °C). IR (ν,cm^{-1}): 1720 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 6.98 (d, 1H, CH-5, ^{3}J 8.73 Hz), 6.72 (d, 1H, CH-6, ^{3}J 8.73 Hz), 3.91, 3.86 (2s, 6H, $2CH_3O$), 3.00-2.91 (m, 2H, CH_2-2),

2.69-2.60 (m, 2H, CH_2-3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 204.63 (CO), 151.55, 150.23 (C-7, C-4), 145.75, 126.10 (C-7a, C-3a), 116.39 (C-5), 109.24 (C-6), 55.80, 55.63 ($2CH_3O$), 36.56 (C-2), 22.07 (C-3).

5,6-Dimethoxy-1-indanone (2a), yield 42% (67%)[18]. mp 117-118 °C. (lit[10]. 118 °C). IR (ν,cm^{-1}): 1710 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.19 (s, 1H, CH-7), 6.90 (s, 1H, CH-4), 3.97, 3.92 (2s, 6H, $2CH_3O$), 3.10-3.02 (m, 2H, CH_2-2), 2.72-2.64 (m, 2H, CH_2-3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 205.46 (CO), 155.31 (C-5), 150.33 (C-6), 149.29, 129.61 (C-7a, C-3a), 107.41, 104.08 (C-7, C-4), 56.13, 55.98 ($2CH_3O$), 36.42 (C-2), 25.48 (C-3).

2,3,7,8-Tetrahydro-6*H*-indeno[5,6-*b*][1,4]dioxin-6-one (3a), yield 12% (18%)[18]. mp 90-92 °C. IR (ν,cm^{-1}): 1715 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.20 (s, 1H, CH-5), 6.88 (s, 1H, CH-9), 4.33-4.27, 4.24-4.18 (2m, 4H, OCH_2CH_2O), 3.00-2.93 (m, 2H, CH_2-7), 2.66-2.60 (m, 2H, CH_2-8). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 212.78 (CO), 150.26, 149.35 (C-4a, C-9a), 130.82, 118.11 (C-5a, C-8a), 114.35, 111.73 (C-5, C-9), 64.88, 64.11 ($2CH_2O$), 36.83 (C-7), 25.35 (C-8). Elemental analysis: found (%): C, 69.13; H, 5.23; Calc. for $C_{11}H_{10}O_3$: C, 69.47; H, 5.26.

2,3,8,9-Tetrahydro-7*H*-indeno[4,5-*b*][1,4]dioxin-9-one (3b), yield 36% (54%)[18]. mp 113 °C. IR (ν,cm^{-1}): 1700 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.07 (d, 1H, CH-5, ^3J 8.10Hz), 6.87 (d, 1H, CH-6 ^3J 8.10Hz), 4.42-4.37, 4.27-4.22 (2m, 4H, OCH_2CH_2O), 3.02-2.96 (m, 2H, CH_2-8), 2.67-2.61 (m, 2H, CH_2-7). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 212.37 (CO), 149.92, 147.45 (C-4a, C-9b), 130.23, 125.66 (C-6a, C-9a), 124.61, 118.53 (C-5, C-6), 65.19, 64.24 ($2CH_2O$), 37.81 (C-8), 25.30 (C-7). Elemental analysis: found (%): C, 69.06; H, 5.42; Calc. for $C_{11}H_{10}O_3$: C, 69.47; H, 5.26.

4,5,6-Trimethoxy-1-indanone (4a), yield 36% (53%)[18]. mp 82 °C (lit[5]. 82-83 °C). IR (ν,cm^{-1}): 1720 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.02 (s, 1H, CH-7), 3.98, 3.95, 3.89 (3s, 9H, $3CH_3O$), 3.10-3.00 (m, 2H, CH_2-2), 2.69-2.60 (m, 2H, CH_2-3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 205.73 (CO), 154.03, 149.95, 147.40 (C-5, C-4, C-6), 141.34, 132.31 (C-7a, C-3a), 100.36 (C-7), 60.87, 60.39, 56.02 ($3CH_3O$), 35.93 (C-2), 22.21 (C-3). Elemental analysis: found (%): C, 64.83; H, 6.34; Calc. for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31.

1,3-Di(4-metoxyphenyl)propan-1-one (5a), yield 56% (74%)[18]. mp 39-40 °C. (lit[9]. 41-42 °C). IR (ν,cm^{-1}): 1685 (CO). ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.88 (d, 2H, CH-1,

CH-6, ^{3}J 8.1 Hz), 7.12 (d, 2H, CH-1', CH-6', ^{3}J 8.1 Hz), 6.85 (d, 2H, CH-3, CH-5, ^{3}J 8.1 Hz), 6.78 (d, 2H, CH-3', CH-5', ^{3}J 8.1 Hz), 3.77, 3.70 (2s, 6H, $2CH_3O$), 3.13 (m, 2H, CH_2-α), 2.97 (m, 2H, CH_2-β). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 197.40 (CO), 163.03, 157.60 (C-4, C-4'), 133.07, 129.59 (C-1, C-1'), 129.90, 128.98 (4C, C-2, C-2', C-6, C-6'), 113.52, 113.33 (4C, C-3, C-5, C-3', C-5'), 54.99, 54.76 ($2CH_3O$), 39.86 (CH_2-α), 29.06 (CH_2-β).

1,3-Di(4-ethoxyphenyl)propan-1-one (6a), yield 40% (64%)[18]. mp 79-80 °C. IR (ν,cm^{-1}): 1695 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.84 (d, 2H, CH-2, CH-6, ^{3}J 8.93 Hz), 7.06 (d, 2H, CH-2', CH-6', ^{3}J 8.55 Hz), 6.81 (d, 2H, CH-3, CH-5, ^{3}J 8.93 Hz), 6.74 (d, 2H, CH-3', CH-5', ^{3}J 8.55 Hz), 4.05-3.85 (m, 4H, $2CH_2O$), 3.17-3.07 (m, 2H, CH_2-α), 2.96-2.86 (m, 2H, CH_2-β), 1.40-1.20 (m, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 197.91 (CO), 162.73, 157.17 (C-4, C-4'), 133.24, 129.66 (C-1, C-1'), 130.21, 129.22 (4C, C-2, C-2', C-6, C-6'), 114.37, 114.01 (4C, C-3, C-3', C-5, C-5'), 63.62, 63.28 ($2CH_2O$), 40.26 (CH_2-α), 29.39 (CH_2-β), 14.80, 14.59 ($2CH_3$) Elemental analysis: found (%): C, 76.17; H, 7.60; Calc. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43.

1,3-Di(3-methyl-4-methoxyphenyl)propan-1-one (7a), yield 35% (65%)[18]. mp 76-77 °C. IR (ν,cm^{-1}): 1680 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.55 (m, 2H, CH-2, CH-6), 7.00 (m, 2H, CH-2', CH-6'), 6.70 (m, 2H, CH-5, CH-5'), 3.79, 3.73 (2s, 6H, $2CH_3O$), 3.22-3.10 (m, 2H, CH_2-α), 2.98-2.86 (m, 2H, CH_2-β), 2.20, 2.19 (2s, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 197.79 (CO), 161.30, 155.76 (C-4, C-4'), 132.79, 129.17 (C-1, C-1'), 130.44, 130.29, 127.81, 126.13 (C-2, C-2', C-6, C-6'), 126.30 (C-3, C-3'), 109.59, 108.84 (C-5, C-5'), 55.08, 54.90 ($2CH_3O$), 40.06 (CH_2-α), 29.22 (CH_2-β), 15.92, 15.60 ($2CH_3$). Elemental analysis: found (%): C 76.13; H 7.64; Calc. for $C_{19}H_{22}O_3$: C 76.48; H 7.43.

1,3-Di(5-isopropyl-2-methyl-4-methoxyphenyl)propan-1-one (8a), yield 51% (81%)[18]. mp 86-87 °C. IR (ν,cm^{-1}): 1690 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.55 (s, 1H, CH-6), 7.00 (s, 1H, CH-6'), 6.67 (s, 1H, CH-3), 6.65 (s, 1H, CH-3'), 3.87, 3.79 (2s, 6H, $2CH_3O$), 3.31-3.22 (m, 2H, 2CH), 3.17-3.11 (m, 2H, CH_2-α), 3.00-2.94 (m, 2H, CH_2-β), 2.55, 2.32 (2s, 6H, $2CH_3$), 1.21, 1.18 (2d, 12H, $4CH_3$ isopropyl, ^{3}J 3.11 Hz). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 201.82 (CO), 158.97, 155.04 (C-4, C-4'), 139.11, 134.56, 133.88, 131.26, 129.52, 128.27 (6C), 127.66, 126.69 (C-6, C-6'), 113.71, 112.56 (C-3, C-3'), 55.39, 55.31 ($2CH_3O$), 41.86 (CH_2-α), 27.96 (CH_2-β), 26.51, 26.46 (2CH), 22.74, 22.52 ($4CH_3$

isopropyl), 22.18, 19.28 ($2CH_3$). Elemental analysis: found (%): C, 77.83; H, 9.04; Calc. for $C_{25}H_{34}O_3$: C, 78.39; H, 8.96.

1,3-Di(2,4-dimethoxyphenyl)propan-1-one (9a), yield 46%, the compound was previously described[4].

4-Methoxy-2,3-dihydro-1*H*-phenalen-1-one (10a), yield 18% (35%)[18]. mp 65-67 °C. IR (ν,cm^{-1}): 1690 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 8.13 (dd, 1H, CH-9, ^{3}J 7.13 Hz, ^{4}J 1.38 Hz), 7.97 (dd, 1H, CH-7, ^{3}J 8.15 Hz, ^{4}J 1.38 Hz), 7.78 (d, 1H, CH-6, ^{3}J 9.05 Hz), 7.40 (dd, 1H, CH-8, ^{3}J 7.13Hz, ^{3}J 8.15Hz) 7.29 (d, 1H, CH-5, ^{3}J 7.15Hz), 3.96 (s, 3H, OCH_3), 3.40-3.30 (m, 2H, CH_2-2), 2.95-2.85 (m, 2H, CH_2-3). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 198.86 (CO), 154.72 (C-4), 132.90, 128.95, 128.60, 117.50 (C-3a, C-6a, C-9a, C-9b), 133.95, 127.11, 125.61, 123.04 (C-6, C-7, C-8, C-9), 113.13 (C-5), 56.08 (CH_3O), 37.81 (C-2), 21.46 (C-3). Elemental analysis: found (%): C, 79.31; H, 5.64; Calc. for $C_{14}H_{12}O_2$: C, 79.25; H, 5.66.

4,6-Dimethyl-2,3-dihydro-1*H*-phenalen-1-one (11a), yield 21% (59%)[18]. mp 103 °C. IR (ν,cm^{-1}): 1700 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 8.17 (d, 1H, CH-9, ^{3}J 7.17 Hz), 8.10 (d, 1H, CH-7, ^{3}J 8.30 Hz), 7.50 (dd, 1H, CH-8, ^{3}J 7.17Hz, ^{3}J 8.30Hz) 7.18 (s, 1H, CH-5), 3.30-3.20 (m, 2H, CH_2-2), 2.97-2.87 (m, 2H, CH_2-3), 2.62, 2.43 (2s, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 199.11 (CO), 133.39, 132.20, 132.00, 131.37, 129.67, 127.69 (C-3a, C-4, C-6, C-6a, C-9a, C-9b), 130.28, 130.35, 124.75, 124.19 (C-5, C-7, C-8, C-9), 38.02 (C-2), 24.93 (C-3), 19.60, 19.08 ($2CH_3$). Elemental analysis: found (%): C, 85.45; H, 6.76; Calc. for $C_{15}H_{14}O$: C, 85.71; H, 6.67.

4,7,8,9-Tetrahydro-3*H*-cyclopenta[*cd*]phenalen-7-one (12a), yield 11% (63%)[18]. mp 98-99 °C. IR (ν,cm^{-1}): 1690 (CO). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 8.07 (d, 1H, CH-6, ^{3}J 7.20 Hz), 7.30 (m, 3H, 3CH-arom), 3.42 (s, 4H, CH_2-3, CH_2-4), 3.40-3.33 (m, 2H, CH_2-8), 2.97-2.90 (m, 2H, CH_2-9). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 197.98 (CO), 153.40, 143.76, 139.16 (C-2a, C-2b, C-4a,), 130.09, 128.83, 128.30 (C-6a, C-9a, C-9b), 126.44, 126.37, 119.75, 119.41 (4CH-arom.), 39.04 (C-8), 31.39, 30.38 (C-3, C-4), 27.58 (C-9). Elemental analysis: found (%): C, 86.35; H, 5.82; Calc. for $C_{15}H_{12}O$: C, 86.54; H, 5.77

3-(N,N-Dimethylamino)-7*H*-benzo[*de*]anthracene (13a), yield 41% (79%)[18]. mp 102 °C. ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 8.14 (d, 1H, ^{3}J 8.40 Hz), 8.03 (d, 1H, ^{3}J 8.00 Hz), 8.00 (d, 1H, ^{3}J 8.00 Hz), 7.53-7.30 (m, 5H), 7.18 (s, 1H, CH-2, ^{3}J 8.00 Hz), 4.60 (s,

2H, CH_2), 2.98 (s, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 150.46 (C-3), 133.62, 133,52, 132.75, 130.07, 128.90, 125.90 (6C-q. arom.), 128.68, 126.90, 126.72, 125.20, 124.60, 122.75, 121.78, 118.85 (8CH-arom.), 114.10 (C-2), 44.97 ($2CH_3$), 34.74 (CH_2) Elemental analysis: found (%): C, 87.74; H, 6.64; N, 5.10; Calc. for $C_{19}H_{17}N$: C, 88.03; H, 6.56; N, 5.41.

3-(N,N-Dimethylamino)-7-methyl-7*H*-benzo[*de*]anthracene (14a), yield 38% (60%)[18]. mp 81-83 °C. ^1H NMR (400MHz, $CDCl_3$, δ ppm): 8.23 (d, 1H, ^3J 8.50 Hz), 8.10 (d, 1H, ^3J 7.90 Hz), 8.00 (d, 1H, CH-11, ^3J 8.00 Hz), 7.62-7.35 (m, 5H), 7.18 (d, 1H, CH-2, ^3J 8.00 Hz), 4.53 (q, 1H, CH-5, ^3J 7.30 Hz), 3.00 (s, 6H, $N(CH_3)_2$), 1.57 (d, 3H, CH_3, ^3J 7.30 Hz). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 150.50 (C-3), 139.82, 139.63, 131.60, 128.93, 128.66, 124.90 (6C-q. arom.), 128.40, 126.85, 126.53, 125.37, 124.82, 122.79, 121.81, 118.90 (8CH-arom.), 114.05 (C-2), 44.97 ($N(CH_3)_2$), 39.72 (CH-7), 31.06 (CH_3) Elemental analysis: found (%): C, 87.50; H, 6.95; N, 5.15; Calc. for $C_{20}H_{19}N$: C, 87.91; H, 6.96; N, 5.13.

7-(N,N-Dimethylamino)-8*H*-dibenzo[*a.de*]anthracene (15a) and 7-(N,N-Dimethylamino)-13*H*-dibenzo[*a.de*]anthracene (15b), yield 47% (63%)[18]. ^1H NMR (400MHz, $CDCl_3$, δ ppm): 8.60 (m, 3H), 8.32 (s, 1H), 8.23 (d, 1H, ^3J 7.90 Hz), 8.15 (m, 2H), 8.00 (d, 1H, ^3J 7.90 Hz), 7.95 (d, 1H, ^3J 7.90 Hz), 7.90 (d, 1H, ^3J 7.90 Hz), 7.83 (d, 1H, ^3J 7.90 Hz), 7.65-7.40 (m, 10H), 7.22 (d, 1H, ^3J 7.90 Hz), 4.98 (s, 2H, CH_2 for 15a), 4.60 (s, 2H, CH_2 for 15b), 3.00 (s, 6H, $2CH_3$), 2.85 (s, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 150.1, 149.2, 134.5, 133.2, 132.2, 131.7, 131.5, 131.2, 130.0, 129.6, 129.3, 128.9, 128.6, 128.3, 127.8, 126.7, 126.0, 125.0 (18C-q. arom.), 128.8, 128.4, 128.1, 127.4, 126.9, 126.4, 126.1, 126.0, 125.9 (2C), 125.1, 125.0 (2C), 123.1, 122.9, 122.0, 121.5, 120.9 (2C), 119.2, 118.8, 113.7 (22 CH-arom.) 44.6 ($2CH_3$), 44.3 ($2CH_3$), 31.3 (CH_2), 30.4 (CH_2). Elemental analysis: found (%): C, 88.99; H, 6.16; Calc. for $C_{23}H_{19}N$: C, 89.32; H, 6.15.

5-(N,N-Dimethylamino)-6*H*-benzo[*cd*]pyrene (16a), yield 53% (75%)[18]. mp 69-70 °C. ^1H NMR (400MHz, $CDCl_3$, δ ppm): 7.82-7.40 (m, 9H, 9CH-arom), 4.94 (s, 2H, CH_2), 2.85 (s, 6H, $2CH_3$). ^{13}C NMR (100MHz, $CDCl_3$, δ ppm): 148.96 (C-5), 134.38, 131.71, 128.72, 128.28, 128.02, 127.80, 127.29, 125.79 (8C-q. arom.), 126.71, 126.65, 126.58, 126.26, 126.15, 125.35, 125.24, 125.14, 119.36 (9CH-arom.), 44.34 ($2CH_3$), 30.81 (CH_2) Elemental analysis: found (%): C, 89.33; H, 6.24; N, 4.80; Calc. for $C_{21}H_{17}N$: C, 89.05; H, 6.00; N, 4.95.

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17. In the case of 6-11 two equivalents of substrate were used.
18. Yield based on conversion of substrate.

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