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CHEMOSELECTIVE SYNTHESIS OF NEW DIBENZO[*d,f*]-1,3-DIOXEPINES AND 12*H*-DIBENZO[*d,g*]-1,3-DIOXOCINES†

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Abstract – A new series of dibenzodioxepine and dibenzodioxocine derivatives was prepared starting from aliphatic and aromatic aldehydes, underlining the chemoselectivity of both the catalyst and the biphenol, also confirming the importance of the hydrogen atom in α position to the carbonyl group.

INTRODUCTION

The biaryl scaffold has received improved attention as a privileged structure by pharmaceutical industry and this is justified by its presence in many biologically active compounds.[1]

In this context, it is important to remember the dibenzo[*d,f*]-1,3-dioxepine and 12*H*-dibenzo[*d,g*]-1,3-dioxocine derivatives, a well known class of heterocyclic compounds whose biological activity is associated to the presence of a methylenedioxy group related to the biaryl unit.[2]

Since 1957, when some dibenzo[*d,f*]-1,3-dioxepines analogous compounds were isolated from *Cercospora Kikuchii,*[3] some efforts have been made to synthesize new derivatives.[4]

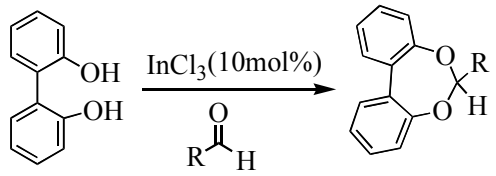
Recently we reported a simple method to prepare some new dibenzo[*d,f*]-1,3-dioxepines and 12*H*-dibenzo[*d,g*]-1,3-dioxocine, starting from the opportune biphenol and a ketone or a β-ketoester, using indium (III) chloride as a catalyst. The key of the entire process showed to be the presence of at least one hydrogen atom in α position to the carbonyl group of the ketone.[5]

We have also studied and discussed in details their mass spectrometric behaviour, with the aid of labelled compounds and of collisionally induced dissociation experiments performed using an ion trap.[6]

RESULTS AND DISCUSSION

Pursuing our research in this field, some other reactions have been carried out by using aliphatic and aromatic aldehydes, with the aim of investigating the importance of the α hydrogen, trying to improve the yields of the reactions, too (Scheme 1). To date, many examples of the use of indium (III) chloride are

reported in literature;[5] this is because it can provide high products yields when used in catalytic amount. In particular, it has been recently used as chemoselective reagent in some aldol-like[7] or acetalization[8] reactions. The advantages of the use of that reagent are related to the fact that it is a mild and water stable Lewis acid that can be easily used in the presence of acid-sensitive substrates also avoiding possible side reactions in the presence of enolizable ketones such as β-ketoesters.[5]



1 **2 a-v** **3 a-v**

a: R=—CH_2CH_3
b: R=—$(CH_2)_2CH_3$
c: R=—$(CH_2)_4CH_3$
d: R=—$(CH_2)_5CH_3$
e: R=—$(CH_2)_{10}CH_3$
f: R=—C_6H_5
g: R=—2-MeC_6H_5
h: R=—3-MeC_6H_5
i: R=—4-MeC_6H_5
j: R=—2-$OMeC_6H_5$
k: R=—3-$OMeC_6H_5$
l: R=—4-$OMeC_6H_5$
m: R= —3,4-$(OMe)_2C_6H_5$
n: R= —2-$NO_2C_6H_5$
o: R=—3-$NO_2C_6H_5$
p: R=—4-$NO_2C_6H_5$
q: R= —2-ClC_6H_5
r: R= —3-ClC_6H_5
s: R= —4-ClC_6H_5
t: R=
u: R=
v: R=

Scheme 1

As expected, the aldehydes possessing hydrogens in α position, also showed to be very reactive at rt, proceeding with good yields if compared to the ketones[5] (Table 1).

Table 1. $InCl_3$-catalyzed synthesis of some dibenzo[*d*,*f*]-1,3-dioxepines from aliphatic aldehydes.

Substrate (2)	Catalyst (%)	Temperature (°C)	Time (h)	Product (3)	Yield (%)
propanal (**2a**)	10	60	0.3	**3a**	43
propanal (**2a**)	10	rt	0.3	**3a**	36
butanal (**2b**)	10	60	0.3	**3b**	40
butanal (**2b**)	10	rt	0.3	**3b**	30
hexanal (**2c**)	10	60	0.3	**3c**	45
hexanal (**2c**)	10	rt	0.3	**3c**	33
heptanal (**2d**)	10	60	0.3	**3d**	60
heptanal (**2d**)	10	rt	0.3	**3d**	44
heptanal (**2d**)	-	rt	1.5	**-**	-
dodecanal (**2e**)	10	60	0.3	**3e**	42
dodecanal (**2e**)	10	rt	0.3	**3e**	40

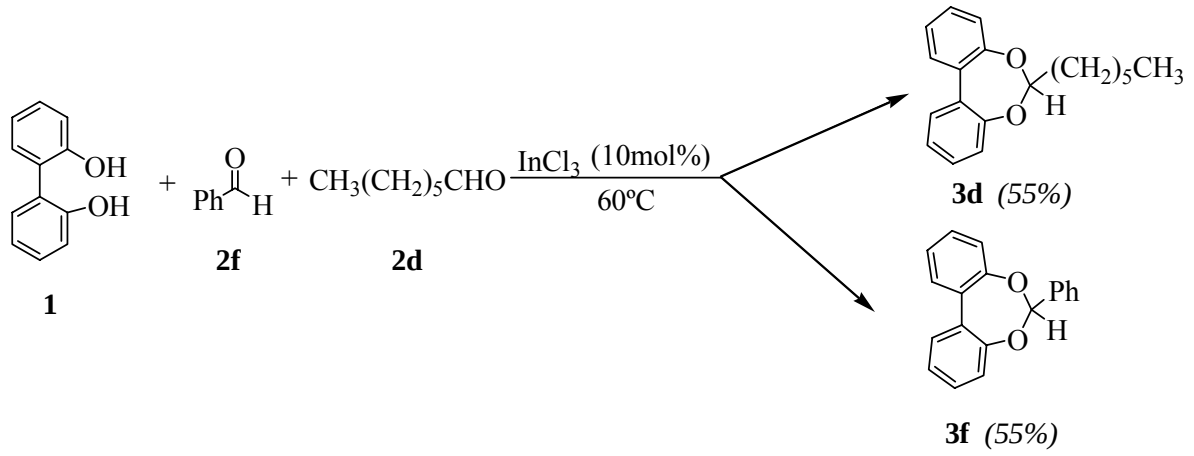
Conversely, the aromatic aldehydes exhibited a minimum of reactivity only at high temperature, giving rise to the final products in very low yields (Table 2). This fact is also probably related to the steric hindrance of both the 2,2'-dihydroxybiphenyl (**1**) and the carbonyl substrates (**2**). Further evidence was provided by the experiment reported in Scheme 2, where the dibenzodioxepine derived from the aliphatic

aldehyde was the one obtained in higher yields. No yield improvement was obtained for higher reaction times[8b] or when the experiments were carried out in the presence of dehydrating agents such as $MgSO_4$. Moreover, all the reactions showed to be irreversible, even when an excess of catalyst was used.[9]

Table 2. $InCl_3$-catalyzed synthesis of some dibenzo[*d,f*]-1,3-dioxepines from aromatic aldehydes.

Substrate (2)	Catalyst (%)	Temperature (°C)	Time (h)	Product (3)	Yield (%)
benzaldehyde (**2f**)	10	60	0.5	**3f**	15
o-methylbenzaldehyde (**2g**)	10	60	0.5	**3g**	9
o-methylbenzaldehyde **(2g)**	10	rt	1.5	-	-
m-methylbenzaldehyde **(2h)**	10	60	0.5	**3h**	13
m-methylbenzaldehyde (**2h**)	10	rt	1.5	-	-
p-methylbenzaldehyde (**2i**)	10	60	0.5	**3i**	8
o-methoxybenzaldehyde (**2j**)	10	60	0.5	**3j**	5
m-methoxybenzaldehyde (**2k**)	10	60	0.5	**3k**	6
p-methoxybenzaldehyde (**2l**)	10	60	0.5	**3l**	6
3,4-dimethoxybenzaldehyde (**2m**)	10	40[a]	0.5	**3m**	< 5
o-nitrobenzaldehyde (**2n**)	10	60	0.5	**3n**	15
m-nitrobenzaldehyde (**2o**)	10	60	0.5	**3o**	10
p-nitrobenzaldehyde (**2p**)	10	60	0.5	**3p**	20
o-chlorobenzaldehyde (**2q**)	10	60	0.5	**3q**	19
m-chlorobenzaldehyde (**2r**)	10	60	0.5	**3r**	10
p-chlorobenzaldehyde (**2s**)	10	60	0.5	**3s**	18
2-furfural (**2t**)	10	60	0.5	**3t**	< 5
2-furfural (**2t**)	10	rt	1.5	-	-
2-thiophenaldehyde (**2u**)	10	60	0.5	**3u**	6
piperonal (**2v**)	10	60	0.5	**3v**	10

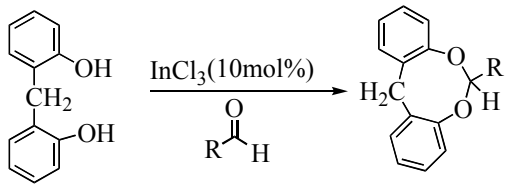
[a]*Dichloromethane was used as solvent.*



Scheme 2

Analogous experiments have been performed starting from bis(2-hydroxyphenyl)methane (**4**) to obtain the dibenzodioxocine derivatives (**5**) (Scheme 3).

Unfortunately, all the reactions proceeded with very poor yields (Table 3).



4 **2 a, d-h, l, o, t-v** **5 a, d-h, l, o, t-v**

a: R=—CH_2CH_3 **f:** 26) R= —Ph **l:** 29) R= —4-$OMeC_6H_5$ **u:** 32) R=

d: R=—$(CH_2)_5CH_3$ **g:** 27) R= —2-MeC_6H_5 **o:** 30) R= —3-$NO_2C_6H_5$

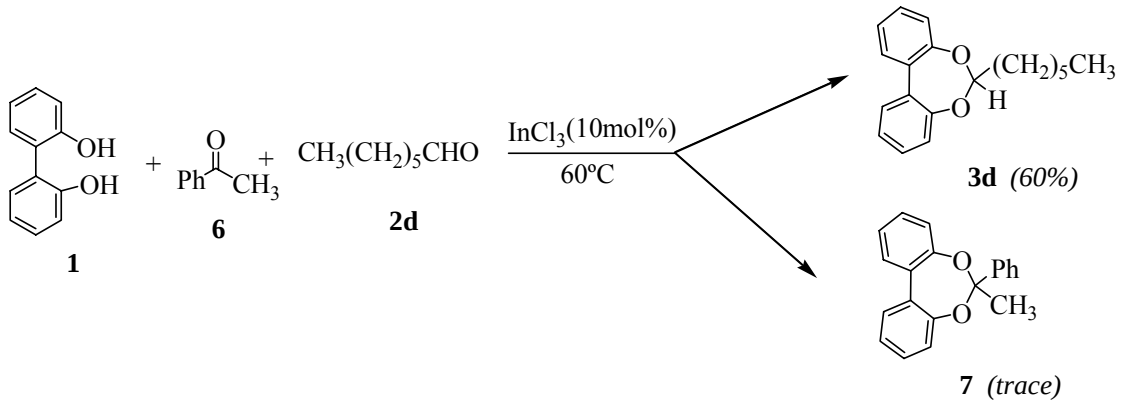
e: R=—$(CH_2)_{10}CH_3$ **h:** 28) R=—3-MeC_6H_5 **t:** 31) R= **v:** 33) R=

Scheme 3

Table 3. $InCl_3$-catalyzed synthesis of some 12*H*-dibenzo[*d*,*g*]-1,3-dioxocines.

Entry	Substrate (2)	Catalyst (%)	Temperature (°C)	Time (h)	Product (5)	Yield (%)
1	propanal (**2a**)	10	60	0.3	**5a**	12
2	heptanal (**2d**)	10	60	0.3	**5d**	10
3	heptanal (**2d**)	10	rt	0.3	-	-
4	dodecanal (**2e**)	10	60	0.3	**5e**	12
5	benzaldehyde (**2f**)	10	60	1.5	-	-
6	o-methylbenzaldehyde **(2g)**	10	60	0.3	**5g**	< 5
7	m-methylbenzaldehyde (**2h**)	10	60	0.3	**5h**	7
8	p-methoxybenzaldehyde (**2l**)	10	60	0.3	**5l**	< 5
9	m-nitrobenzaldehyde (**2o**)	10	60	0.3	**5o**	6
10	2-furfural (**2t**)	10	60	1.5	-	-
11	2-thiophenaldehyde (**2u**)	10	60	1.5	-	-
12	piperonal (**2v**)	10	60	1.5	-	-

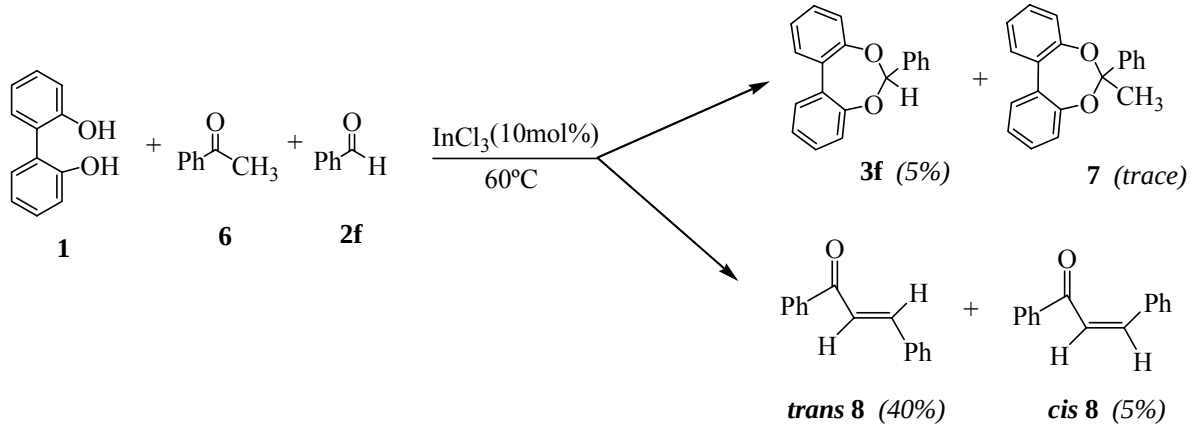
The chemoselectivity of indium (III) chloride in the reaction of 2,2'-dihydroxybiphenyl (**1**) with aldehydes and ketones was also investigated. To this aim, we carried out the reaction using a mixture of heptanal (**2d**) and acetophenone (**6**) in a 1:1 ratio, isolating almost totally the 6-hexyl- (**3d**) instead of the 6-methyl-6-phenyl-dibenzo[*d*,*f*]-1,3-dioxepine (**7**) (Scheme 4).



1 **6** **2d** **3d** *(60%)* **7** *(trace)*

Scheme 4

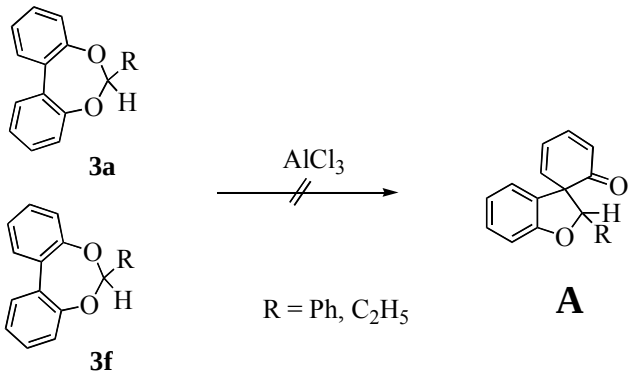
A further experiment, performed by using benzaldehyde (**2f**) and acetophenone (**6**), evidenced that, when hindered carbonyl substrates are used, the predominant reaction is not the formation of the dioxepine derivatives, but the Claisen-Schmidt condensation, which gives rise to *cis*/*trans* chalcone isomers in an approximately 5/95 ratio (Scheme 5).



Scheme 5

Dibenzodioxepines (**3a)** and (**3f)** were also treated with $AlCl_3$, but no conversion to **A** was observed (Scheme 6), pointing out that substituents in C-6 position are not influent for the spirocyclization.[10]

A detailed investigation of the mass spectrometric behaviour of all the synthesized compounds was also performed, by using gas chromatography ion trap tandem mass spectrometry, observing that, contrary to what happens in solution, in gas-phase the electron ionization promotes the conversion of dioxepines into a spirocyclic product. In particular, we observed that the spirocyclization size is strictly related to the nature of the C-6 substituents: it depends on the length of the aliphatic chains, while it is always observable when aromatic groups are present.[11]



Scheme 6

In conclusion, we succeeded in synthesizing new dibenzodioxepine and dibenzodioxocine derivatives, evidencing the chemoselectivity of both the catalyst[8b] and the biphenol for the aldehydes, also underlining the importance of the hydrogen in α position to carbonyl group to bring the reaction to a successful conclusion.

It was also evidenced that, when 2,2'-dihydroxybiphenyl (**1**) is used instead of an alcohol[9] and hindered carbonyl substrates are employed, indium (III) chloride promotes *aldol-like* reactions instead of dibenzodioxepine formation.

EXPERIMENTAL

Typical synthetic procedure.

A mixture of 2,2'-dihydroxybiphenyl (**1**) or bis(2-hydroxyphenyl)methane (**4**) (5.37 mmol) and the appropriate aldehyde (**2**) (21.48 mmol) was stirred under nitrogen for the period indicated (TLC) at 60°C, in the presence of indium (III) chloride (0.54 mmol). After reaction, the crude mixture was separated by flash-column chromatography (hexane/CH_2Cl_2 4/1) on silica gel, obtaining the desired product. Solid compounds were recrystallized from hexane/CH_2Cl_2 8/1.

Analytical details for *cis* and *trans* chalcones.

GC-MS: Low resolution mass spectrometric experiments were carried out on a Saturn 2000 ion-trap coupled with a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA) operating under EI conditions (electron energy 70 eV, emission current 20μA, ion-trap temperature 200°C, manifold temperature 80 °C, automatic gain control (AGC) target 21,000) with the ion trap operating in scan mode (scan range from *m/z* 40-400 at a scan rate of 1 scan sec^{-1}). Aliquot of 1 μL of solutions 1.0 X 10^{-5} M in chloroform have been introduced into the gas chromatograph inlet.A CIP Sil-8 CB Lowbleed/MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used. The oven temperature was programmed from 150 °C (held for 2 min) to 310 °C at 30 °C/min (held for 2 min). The temperature was then ramped to 350 at 20 °C/min. The transfer line was maintained at 250 °C and the injector port 30/1 split) at 270 °C. *cis* isomer retention time: 12.04 min.; *trans* isomer retention time: 12.98 min. The structure of the isolated compounds has been determined by ^{1}H NMR analysis.

6-Ethyldibenzo[*d,f*]-1,3-dioxepine (3a): oil. Yield: 43%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.30 (m, 8H), 6.40 (t, 1H), 1.93 (q, 2H), 1.04 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 156.68, 133.09, 127.00, 124.09, 118.08, 108.7, 30.66, 7.78 ppm. EI-MS: m/z: 226 [$M^{+\cdot}$]. Anal. Calcd for $C_{15}H_{14}O_2$: C 79.65, H 6.19. Found: C 79.48, H 6.08.

6-Propyldibenzo[*d,f*]-1,3-dioxepine (3b): oil. Yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90-7.25 (m, 8H), 5.30 (t, 1H), 1.75 (m, 2H), 1.58 (m, 2H), 0.90 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.52, 133.12, 125.26, 119.50, 105.84, 40.44, 15.86, 13.46 ppm. EI-MS: m/z: 240 [$M^{+\cdot}$]. Anal. Calcd for $C_{16}H_{16}O_2$: C 80.00, H 6.67. Found: C 79.35, H 6.57.

6-Pentyldibenzo[*d,f*]-1,3-dioxepine (3c): pale yellow oil. Yield: 45%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.20 (m, 8H), 5.90 (t, 1H), 1.58 (m, 4H), 1.30 (m, 2H), 0.85 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.16, 132.36, 127.55, 108.53, 110.05, 37.54, 30.73, 14.01 ppm. EI-MS: m/z: 254 [$M^{+\cdot}$]. Anal. Calcd for $C_{17}H_{18}O_2$: C 80.31, H 7.09. Found: C 80.36, H 7.00.

6-Hexyldibenzo[*d,f*]-1,3-dioxepine (3d): pale yellow oil. Yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94-7.30 (m, 8H), 5.54 (t, 1H), 1.45-1.60 (m, 4H), 1.25-1.33 (m, 6H), 0.78 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.26, 133.24, 127.43, 119.57, 111.43, 108.65, 37.30, 29.04, 22.80, 14.10 ppm. EI-MS: m/z: 268 [$M^{+\cdot}$]. Anal. Calcd for $C_{18}H_{20}O_2$: C 80.60, H 7.46. Found: C 80.45, H 7.50.

6-Undecyldibenzo[*d,f*]-1,3-dioxepine (3e):white crystals (mp 32-35°C). Yield: 42%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85-7.20 (m, 8H), 5.90 (t, 1H), 1.30-1.54 (m, 4H), 1.15-1.22 (m, 16H), 0.87 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 1155.38, 133.28, 127.55, 119.57, 111.67, 108.62, 36.96, 29.60, 27.44, 14.04 ppm. EI-MS: m/z: 352 [$M^{+\cdot}$]. Anal. Calcd for $C_{24}H_{32}O_2$: C 81.82, H 9.09. Found: C 81.76, H 9.00.

6-Phenyldibenzo[*d,f*]-1,3-dioxepine (3f): sticky oil. Yield: 15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33- 7.74 (m, 5H), 6.90-7.15 (m, 8H), 6.60 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.48, 134.87, 133.75, 128.22, 125.14, 119.33, 109.35, 102.84 ppm. EI-MS: m/z: 274 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{14}O_2$: C 83.21, H 5.11. Found: C 83.14, H 5.00.

6-(2-Methylphenyl)dibenzo[*d,f*]-1,3-dioxepine (3g): sticky oil. Yield: 9%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87-7.60 (m, 4H), 6.98-7.35 (m, 8H), 6.83 (s, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.68, 137.89, 133.74, 128.02, 119.36, 109.54, 99.56, 19.89 ppm. EI-MS: m/z: 288 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{16}O_2$: C 83.33. H 5.55. Found: C 83.24, H 5.48.

6-(3-Methylphenyl)dibenzo[*d,f*]-1,3-dioxepine (3h): sticky oil. Yield: 13%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35- 7.80 (m, 4H), 7.32-7.07 (m, 8H), 6.69 (s, 1H), 2.28 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.49, 138.64, 133.75, 129.08, 119.25, 109.42, 21.40 ppm. EI-MS: m/z: 288 [$M^{+\cdot}$]. Anal. Calcd. for $C_{20}H_{16}O_2$: C 83.33. H 5.55. Found: C 83.37, H 5.60.

6-(4-Methylphenyl)dibenzo[*d,f*]-1,3-dioxepine (3i): sticky oil. Yield: 8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 - 7.01 (dd, 4H, ^{3}J 8.10 Hz), 7.30-6.95 (m, 8H), 6.61(s, 1H), 2.15 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.36, 137.61, 129.86, 126.50, 119.03, 109.35, 102.84, 21.13 ppm. EI-MS: m/z: 288 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{16}O_2$: C 83.33. H 5.55. Found: C 83.28, H 5.47.

6-(2-Metoxyphenyl)dibenzo[*d,f*]-1,3-dioxepine (3j): white crystals (77-80°C). Yield: 5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70- 8.03 (m, 4H), 7.42-6.82 (m, 8H), 5.97 (s, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 157.57, 150.66, 133.75, 128.26, 126.43, 119.00, 110.85, 99.01, 54.54 ppm. EI-MS: m/z: 304 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{16}O_3$: C 78.95. H 5.26. Found: C 78.87, H 5.20.

6-(3-Metoxyphenyl)dibenzo[*d,f*]-1,3-dioxepine (3k): sticky oil. Yield: 6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.66 (m, 4H), 7.34-6.75 (m, 8H), 6.45 (s, 1H), 3.75 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.52, 155.37, 135.15, 125.14, 113.31, 109.00, 103.83, 55.20 ppm. EI-MS: m/z: 304 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{16}O_3$: C 78.95. H 5.26. Found: C 78.69, H 5.00.

6-(4-Metoxyphenyl)dibenzo[*d,f*]-1,3-dioxepine (3l): sticky oil. Yield: 6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.54 (m, 4H), 7.29-6.54 (m, 8H), 6.45 (s, 1H), 3.75 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.70, 155.48, 131.74, 128.62, 119.32, 114.64, 109.58, 120.84, 55.15 ppm. EI-MS: m/z: 304 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{16}O_3$: C 78.95. H 5.26. Found: C 78.69, H 5.00.

6-(3,4-Dimetoxyphenyl)dibenzo[*d,f*]-1,3-dioxepine (3m): white crystals (mp 98-100°C). Yield: <5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 1H), 7.32-7.00 (m, 8H), 6.38 (m, 2H), 5.97 (s, 1H), 3.82 (s, 6H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.78, 149.11, 133.71, 128.03, 125.00, 120.26, 113.69, 109.43, 103.28, 55.87 ppm. EI-MS: m/z: 334 [$M^{+\cdot}$]. Anal. Calcd for $C_{21}H_{18}O_4$: C 75.45. H 5.39. Found: C 75.38, H 5.34.

6-(2-Nitrophenyl)dibenzo[*d,f*]-1,3-dioxepine (3n): pale yellow crystals (mp 75-77°C). Yield: 15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, 1H), 7.72 (d, 1H), 7.56 (m, 1H), 7.43 (m, 1H), 7.27-6.98 (m, 8H), 5.78 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 157.78, 149.11, 142.33, 132.84, 128.42, 125.07, 122.51, 106.91, 98.12 ppm. EI-MS: m/z: 319 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{13}NO_4$: C 71.47. H 4.07. Found: C 71.50, H 3.99.

6-(3-Nitrophenyl)dibenzo[*d,f*]-1,3-dioxepine (3o): pale yellow crystals (mp 77-80°C). Yield: 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (m, 2H), 7.98 (d, 1H), 7.69 (m, 1H), 7.43 (m, 1H), 7.31-7.07 (m, 8H), 6.99 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.13, 148.76,135.33, 131.64, 128.03, 124.47, 118.20, 109.53, 103.33 ppm. EI-MS: m/z: 319 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{13}NO_4$: C 71.47. H 4.07. Found: C 71.38, H 4.03.

6-(4-Nitrophenyl)dibenzo[*d,f*]-1,3-dioxepine (3p): pale yellow crystals (111-113°C). Yield: 20%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22-8.13 (dd, 4H), 7.29-6.94 (m, 8H), 6.60 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.48, 147.59, 139.08, 133.89, 127.85, 124.74, 118.96, 109.75, 102.84 ppm. EI-MS: m/z: 319 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{13}NO_4$: C 71.47. H 4.07. Found: C 71.43, H 4.05.

6-(2-Chlorophenyl)dibenzo[*d,f*]-1,3-dioxepine (3q): oil. Yield: 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66-7.29 (m, 4H), 7.19 (s, 1H), 7.10-6.95 (m, 8H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.51, 131.17, 130.69, 128.04, 124.91, 119.75, 109.31, 99.52 ppm. EI-MS: m/z: 319 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{13}NO_4$: C 71.47. H 4.07. Found: C 71.38, H 4.03.

6-(3-Chlorophenyl)dibenzo[*d,f*]-1,3-dioxepine (3r): oil. Yield: 19%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.35 (m, 4H), 7.25-6.94 (m, 8H), 6.60 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.25,

135.62, 133.75, 130.55, 128.02, 125.14, 119.25, 109.53, 103.60 ppm. EI-MS: m/z: 308 [$M^{+\cdot}$]. Anal. Calcd. for $C_{19}H_{13}ClO_2$: C 74.02. H 4.22. Found: C 73.98, H 4.18.

6-(4-Chlorophenyl)dibenzo[*d,f*]-1,3-dioxepine (3s): white crystals (mp 68-72°C). Yield: 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.66 (dd, 4H), 7.35-6.96 (m, 8H), 6.48 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.48, 135.33, 133.80, 129.47, 125.04, 118.93, 110.57, 102.84 ppm. EI-MS: m/z: 308 [$M^{+\cdot}$]. Anal. Calcd for $C_{19}H_{13}ClO_2$: C 74.02. H 4.22. Found: C 74.00, H 4.24.

6-(Furan-2-yl)dibenzo[*d,f*]-1,3-dioxepine (3t): sticky oil. Yield: <5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.05 (m, 8H), 6.85 (d, 1H), 6.24 (s, 1H), 5.80 (m, 1H), 5.66 (d, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 156.23, 151.75, 151.00, 133.48, 127.81, 124.97, 119.58, 114.75, 113.04, 108.09 ppm. EI-MS: m/z: 252 [$M^{+\cdot}$]. Anal. Calcd for $C_{16}H_{12}O_3$: C 76.19. H 4.76. Found: C 76.03, H 4.69.

6-(Thiophen-2-yl)dibenzo[*d,f*]-1,3-dioxepine (3u): sticky oil. Yield: 6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.02 (m, 8H), 6.54 (s, 1H), 6.42 (m, 2H), 6.27 (m, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 157.56, 148.80, 132.85, 127.26, 119.59, 109.33, 106.75 ppm. EI-MS: m/z: 268 [$M^{+\cdot}$]. Anal. Calcd. for $C_{16}H_{12}SO_2$: C 71.64. H 4.48, Found: C 71.60, H 4.49.

6-(Benzo[*d*][1,3]dioxol-5-yl)dibenzo[*d,f*]-1,3-dioxepine (3v): white crystals (mp 114-116°C). Yield: 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.33 (m, 3H), 7.24-6.85 (m, 8H), 6.65 (s, 1H), 6.00 (s, 2H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.37, 141.12, 133.75, 129.41, 128.02, 125.14, 119.61, 110.46, 106.71, 103.83, 101.08 ppm. EI-MS: m/z: 318 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{14}O_4$: C 75.47. H 4.40. Found: C 75.42, H 4.37.

6-Ethyl-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5a): oil. Yield: 12%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85-7.15 (m, 8H), 6.25 (t, 1H), 2.80 (s, 2H), 1.90 (q, 2H), 1.01 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.70, 130.16, 128.50, 125.64, 118.83, 112.9, 31.22, 30.45, 7.81 ppm. EI-MS: m/z: 240 [$M^{+\cdot}$]. Anal. Calcd for $C_{16}H_{16}O_2$: C 80.00, H 6.67. Found: C 79.77, H 6.45.

6-Hexyl-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5d): oil. Yield: 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91-6.72 (m, 8H), 5.37 (t, 1H), 2.81 (s, 2H), 1.58-1.23 (m, 10H), 0.84 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.23, 130.35, 128.87, 119.64, 37.30, 31.20, 29.04, 24.20 ppm. EI-MS: m/z: 296 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{24}O_2$: C 81.08, H 8.11. Found: C 81.00, H 8.03.

6-Undecyl-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5e): white crystals (mp 42-44°C). Yield: 12%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75-6.91 (m, 8H), 5.76 (t, 1H), 2.81 (s, 2H), 1.52-1.29 (m, 20 H), 0.89 (t, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.46, 130.15, 127.83, 118.95, 36.96, 29.62, 27.44 ppm. EI-MS: m/z: 366 [$M^{+\cdot}$]. Anal. Calcd for $C_{25}H_{34}O_2$: C 81.97, H 9.29. Found: C 81.89, H 9.25.

6-(2-Methylphenyl)-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5g): sticky oil. Yield: <5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.34 (m, 2H), 6.94-6.61 (m, 8H), 6.66 (s, 1H), 2.85 (s, 2H), 2.33 (s, 3H)

ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 153.85, 137.56, 132.56, 134.89, 129.40, 124.34, 112.76, 104.24, 31.27, 19.89 ppm. EI-MS: m/z: 302 [$M^{+\cdot}$]. Anal. Calcd for $C_{21}H_{18}O_2$: C 83.44, 5.96. Found: C 83.39, H 5.90.

6-(3-Methylphenyl)-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5h): sticky oil. Yield: 7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.17 (m, 2H), 6.94-6.80 (m, 8H), 6.48 (s, 1H), 2.79 (s, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.58, 137.61, 130.82, 119.36, 107.68, 31.22, 21.13 ppm. EI-MS: m/z: 302 [$M^{+\cdot}$]. Anal. Calcd for $C_{21}H_{18}O_2$: C 83.44, 5.96. Found: C 83.48, H 5.91.

6-(4-Metoxyphenyl)-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5l): white crystals (65-68°C). Yield: <5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, 2H), 6.80-7.07 (m, 8H), 6.58 (dd, 2H), 6.43 (s, 1H), 3.54 (s, 3H), 2.84 (s, 2H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.90, 154.02, 130.61, 128.78, 114.64, 112.08, 107.98, 54.99, 31.11 ppm. EI-MS: m/z: 318 [$M^{+\cdot}$]. Anal. Calcd for $C_{21}H_{18}O_3$: C 79.24, 5.66. Found: C 79.21, H 5.59.

6-(3-Nitrophenyl)-12*H*-dibenzo[*d,g*]-1,3-dioxocine (5o):pale yellow crystals (mp 80-82°C). Yield: 6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31-8.04 (m, 4H), 6.96-6.70 (m, 8H), 6.82 (s, 1H), 2.81 (s, 2H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 154.58, 147.59, 129.80, 124.65, 119.83, 112.83, 107.09, 31.03 ppm. EI-MS: m/z: 333 [$M^{+\cdot}$]. Anal. Calcd for $C_{20}H_{15}NO_4$: C 75.23, 4.70. Found: C 75.13, H 4.72.

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