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Indium(III) chloride catalyzed one step synthesis of some new dibenzo(*d*,*f*)(1,3)dioxepines and 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives

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Abstract—In the presence of catalytic amount of indium(III) chloride (10 mol%), 2,2′-dihydroxybiphenyl and bis(2-hydroxyphenyl)methane react quickly, without using any solvent, with ketones or β-keto esters possessing at least one hydrogen atom in α to the ketone-carbonyl group, to afford some new dibenzo(*d*,*f*)(1,3)dioxepines and some 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives, respectively.

It has been proved that the presence of a methylenedioxy group related to one or two aromatic nuclei, as in 1,3-benzodioxoles and 12*H*-dibenzo(*d*,*f*)(1,3)dioxepines, respectively, is very important in pharmaceutical applications.[1] In fact it has been found that such a structure, which is probably related to their pharmacological activity, is present in many biologically active natural products.[2]

Some 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives, in particular the 2,10-dichloro-12H-dibenzo(*d*,*g*)(1,3)dioxocin-6-carboxylic acid and its esters,[3] have also been investigated for their interesting biological activity as potent hypolypidemic agents.[4]

To date, the only significant synthetic methods developed for the dibenzo(*d*,*f*)(1,3)dioxepines derivatives are the condensation of biphenols with the appropriate ketone using phosphorus pentoxide,[5] the condensation of phenol with a dibromoacetate in the presence of sodium hydride,[6] a *trans*-ketalization[7] or a double Michael addition.[8] The only example of the use of a Lewis acid as a catalyst is in the preparation of **3a** with boron trifluoride etherate.[9]

On the other hand, only a few examples of 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives have been reported in literature.[3,4,10]

Firstly, the 2,10-dichloro-12*H*-dibenzo(*d*,*g*)(1,3)dioxocin-6-carboxylic acid was prepared as an extension of some synthetic studies on *o*-phenylenedioxyacetic acids,[3] and then some other methods have been developed,[4,10] always using basic reaction condition.

In this letter we intend to describe a new synthetic strategy to approach these series of compounds. Its unique feature is that the reaction was carried out for the first time using indium(III) chloride as a catalyst.

Indium(III) chloride is a mild, water-stable Lewis acid that can also avoid the problem of side reactions in acid-sensitive substrates. It has been demonstrated that this commercially available salt could be used as an efficient catalyst for a wide variety of organic reactions, such as acylations of phenols, alcohols and amines,[11] reductive Friedel–Crafts alkylations,[12] Diels–Alder reactions,[13] Michael reactions,[14] Mukaiyama-aldol reactions,[15] cross-cyclizations between epoxides and homoallyl alcohols[16] and coumarin syntheses via a von Pechmann reaction.[17]

Keywords: Synthesis; Heterocycles; Indium trichloride; Dibenzo(*d*,*f*)(1,3)dioxepines; 12*H*-Dibenzo(*d*,*g*)(1,3)dioxocins.
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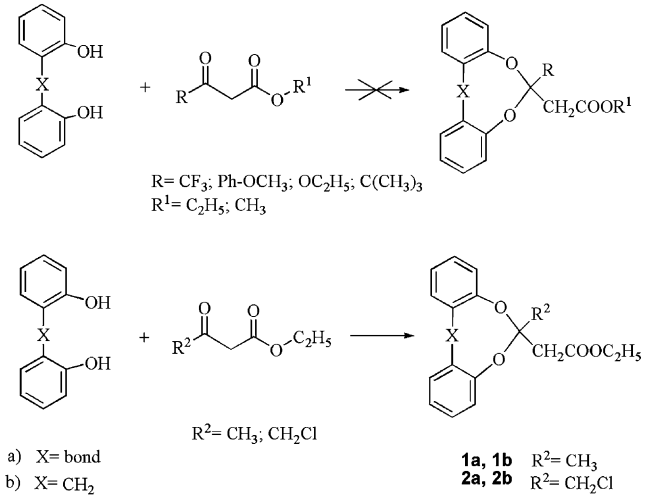
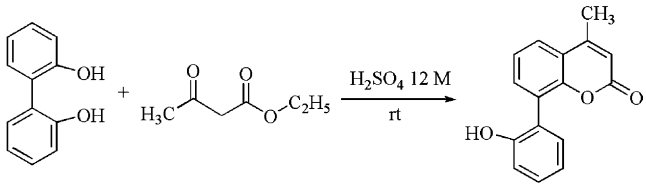
It is peculiar that historically some of the cited reactions have been carried out under basic conditions, while they are now allowed to happen in pseudo-acid conditions.[18]

The work we describe was focused on the synthesis of some new dibenzo(*d*,*f*)(1,3)dioxepines and 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives starting, respectively, from 2,2′-dihydroxybiphenyl or from bis-(2-hydroxyphenyl) methane and some ketones or β-keto esters using a catalytic amount (10 mol%) of indium(III) chloride without any solvent. The essential feature of these reactions consists of the presence of at least one hydrogen atom adjacent to the carbonyl group of the ketone. In particular, we observed that when ethyl 4,4,4-trifluoroacetoacetate (entry 3), ethyl 4-methoxybenzoyl acetate (entry 4), diethyl malonate (entry 5) or methyl 4,4-dimethyl-3-oxopentanoate (entry 13) were used as substrates, the reaction did not occur. The explanation could be that when a β-keto ester is used, the carbonyl group involved in the reaction mechanism must be the ketone group and that the α-hydrogens involved are those in position 4 (Scheme 1).

The exact mechanism of the reaction is now being investigated. This is probably the formation of a complex between indium(III) chloride and 2,2′-dihydroxy reagent. This could be also confirmed by the fact that when we used a protic acid as a catalyst (i.e., H_2SO_4 12 M), we



Scheme 1.



Scheme 2.

did not isolate a dibenzodioxepine unlike previous reports,[7] but a coumarin derivative, which was obviously obtained by a von Pechmann mechanism (Scheme 2).[19]

It is also noteworthy that if the substrate contains only one phenolic unit or if 4,4′-dihydroxybiphenyl is used,[15] the final product always consists of a coumarin derivative (Scheme 3).

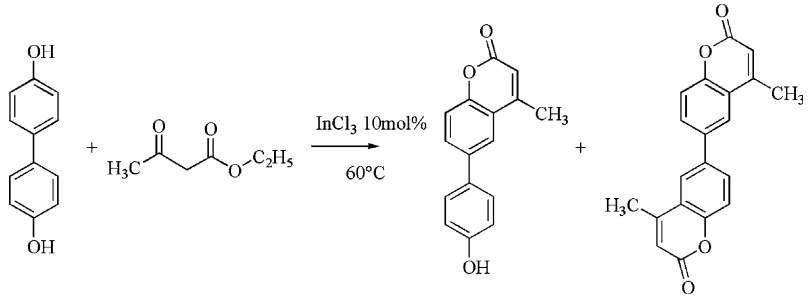
All this experimental evidence seems to give credit also to the hypothesis of a synergic interaction between the two reagents and the catalyst. As a matter of fact, yields drastically decrease when the components are added at different times.

All obtained derivatives proved to be very stable also under drastic conditions (i.e., high molecular ion peaks under EI-mass experiments). The reaction was carried out using a large variety of keto-substrates, as shown in Scheme 4.

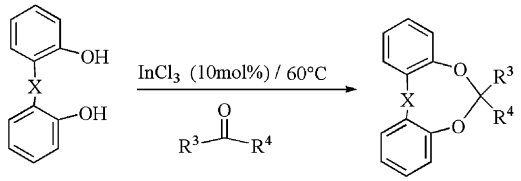
On analyzing the results reported in Table 1, it is important to underline that the maximum yield is obtained after no more than 20–30 min, and that apart from the reagents the only product isolated is the dibenzo-(*d*,*f*)(1,3)dioxepine or 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivative.[20,21] The operative temperature was fixed at 60 °C; increasing the temperature, in fact, yields did not improve.

All reactions were also carried out using stoichiometric amounts of indium(III) chloride, with no improvement in the yields. It was also observed that none of the reactions proceeded at room temperature or in absence of a catalyst.

The keto-substrates were used in excess in order to carry out the reactions under homogeneous conditions, avoiding the use of any solvent.



Scheme 3.



a) **X= bond**
b) **X= CH_2**

1a, 1b R^3=CH_3 R^4=$CH_2COOC_2H_5$
2a, 2b R^3=CH_2Cl R^4=$CH_2COOC_2H_5$
3a, 3b R^3=CH_3 R^4=CH_3
4a, 4b R^3=CH_3 R^4=$CH(CH_3)_2$
5a, 5b R^3=CH_3 R^4=Bz
6a, 6b R^3=CH_3 R^4= Ph
7a, 7b R^3=CH_3 R^4= Bu
8a R^3=CH_3 R^4= $CH(CH_2Ph)COOCH_2CH_3$

Scheme 4.

Table 1. $InCl_3$-catalyzed syntheses of some new dibenzo(*d*,*f*)(1,3)dioxepines and 12H-dibenzo(*d*,*g*)(1,3)dioxocin derivatives

Entry	Substrate	Catalyst (mol%)	Time (h)	Product	Yield[a] (%)	Lit. Yield (%)
1	Ethyl acetoacetate	10	0.33	**1a**	25	—
				1b	30	
2	Ethyl 4-chloroacetoacetate	10	0.5	**2a**	20	—
				2b	20	
3	Ethyl 4,4,4-trifluoroacetoacetate	10	3.5	—	—	—
4	Ethyl 4-methoxybenzoyl acetate	10	3.5	—	—	—
5	Diethyl malonate	10	3.5	—	—	—
6	Acetone	10	0.33	**3a**	30	20;[6] not reported[9]
				3b	30	—
7	3-Methyl-2-propanone	10	0.5	**4a**	20	—
				4b	25	
8	Methyl benzyl ketone	10	0.5	**5a**	25	—
				5b	25	
9	Acetophenone	10	0.5	**6a**	25	Not reported[5]
				6b	30	—
10	Butyl methyl ketone	10	0.5	**7a**	40	—
				7b	40	
11	2,2,2-Trifluoroacetophenone	10	2.0	—	—	—
12	Benzophenone	10	2.0	—	—	—
13	Methyl 4,4-dimethyl-3-oxopentanoate	10	2.0	—	—	—
14	Ethyl 2-benzylacetoacetate	10	0.5	**8a**	30	—
15	Ethyl acetoacetate	100	0.33	**1a**	25	—
				1b	30	
16	Ethyl acetoacetate	—	3.5	—	—	—

[a] Isolated yields.

In conclusion we demonstrated that indium(III) chloride is a versatile Lewis acid catalyst for the synthesis of new dibenzo(*d*,*f*)(1,3)dioxepine and 12*H*-dibenzo(*d*,*g*)(1,3)dioxocin derivatives. It is noteworthy that the developed procedure is very simple, it proceeds without using any solvent and it produces only dibenzodioxepine or dioxocin compounds.[22]

We are at present experimenting on the use of other substrates and different Lewis acids as catalysts.

Typical synthetic procedure. A mixture of 2,2′-dihydroxybiphenyl (1 g, 5.37 mmol) and ethyl acetoacetate (2.8 g, 21.48 mmol) was stirred under nitrogen for 20 min (TLC) at 60 °C, in the presence of indium(III) chloride (0.12 g, 0.54 mmol). After reaction, the crude mixture was separated by flash-column chromatography (hexane/dichloromethane 1/1) on silica gel, obtaining the desired product **1a** (0.4 g, 25 %).

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References and notes

1. Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*; Butterworths: London, 1963, p 549.
2. Wilkinson, C. F.; Murray, M.; Marcus, C. B. *Rev. Biochem. Toxicol* **1984**, *6*, 27.
3. Wenstrup, D.L. MS thesis, Xavier University, Cincinnati, Ohio, 1968.
4. Grisar, J. M.; Parker, R. A.; Kariya, T.; Blohm, T. R.; Fleming, R. W.; Petrow, V. *J. Med. Chem.* **1972**, *15*(12), 1273.

5. Silcox Yoder, C. M.; Zuckerman, J. J. *J. Heterocycl. Chem.* **1967**, *4*, 166.
6. Hewgill, F. R.; Hewitt, D. G. *J. Chem. Soc.*, **1965**, 1536.
7. Breslow, R.; Mohacsi, E. *J. Am. Chem. Soc.* **1963**, *85*, 431.
8. (a) Huang, W. Y.; Liu, Y. S.; Lu, L. *Chin. J. Chem.* **1994**, *12*, 79; (b) Johnson, R. E.; Bacon, E. R. *Tetrahedron Lett.* **1994**, *35*, 9327.
9. Orlando, M.; George, M.; Gross, M. L. *Org. Mass Spectrom.* **1993**, *28*, 1184.
10. Anonimova, I. V.; Il'yasov, K. A.; Yakubov, T. E.; Yarkova, E. G.; Safiullina, N. R., et al. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1991**, *61*, 153.
11. Chakraborti, A. K.; Gulhane, R. *Tetrahedron Lett.* **2003**, *44*, 6749.
12. Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 6291.
13. Loh, T. P.; Pei, J.; Lin, M. J. *Chem. Soc., Chem. Commun.*, **1996**, 2315.
14. Loh, T. P.; Wei, L. L. *Tetrahedron* **1998**, *54*, 7615.
15. (a) Loh, T. P.; Pei, J.; Cao, G. Q. *J. Chem. Soc., Chem. Commun.*, **1996**, 1819; (b) Loh, T. P.; Pei, J.; Ve Koh, K. S.; Cao, G. Q.; Li, X. R. *Tetrahedron Lett.* **1997**, *38*, 3465.
16. Li, J.; Li, C. J. *Tetrahedron Lett.* **2001**, *42*, 793.
17. Bose, D. S.; Rudradas, A. P.; Hari Babu, M. *Tetrahedron Lett.* **2002**, *43*, 9195.
18. (a) Ohki, H.; Wada, M.; Akiba, K. *Tetrahedron Lett.* **1998**, *29*, 4719; (b) Duhamel, P.; Dujardin, G.; Hennequin, L.; Poirier, J. M. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 387; (c) Heathcock, C. H.; Norman, M. H.; Uehiling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2797.
19. (a) von Pechmann, H.; Duisberg, C. *Chem. Ber.* **1884**, *17*, 929; (b) Russel, A.; Frye, J. R. *Org. Synth.* **1941**, *21*, 22.
20. *Dibenzo(d,f)(1,3)dioxepin-6-methyl-6-acetic acid ethyl ester* (**1a**): Yield: 0.42 g (25%). IR (NaCl): ν 3050, 1740, 1260, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55–7.2 (*m*, 8H), 4.30 (*q*, 2H), 3.06 (*s*, 2H,), 1.90 (*s*, 3H), 1.15 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.06, 151.10, 133.12, 128.75, 128.39, 125.45, 123.49, 114.39, 60.74, 43.24, 23.06, 14.23 ppm. EI-MS: *m/z* (%) 298 [$M^{+\cdot}$] (63). Anal. $C_{18}H_{18}O_4$. Calcd: C 72.48, H 6.04. Found: C 72.25, H 6.00. *Dibenzo(d,f)(1,3)dioxepin-6-chloromethyl-6-acetic acid ethyl ester* (**2a**): Yield: 0.36 g (20%). IR (NaCl): ν 3070, 1750, 1260, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–7.10 (*m*, 8H), 4.20 (*q*, 2H), 3.50 (*s*, 2H), 2.80 (*s*, 2H), 1.15 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 166.24, 150.02, 132.34, 128.88, 125.78, 122.91, 113.81, 61.43, 48.07, 45.98, 13.76 ppm. EI-MS: *m/z* (%) 332 [$M^{+\cdot}$] (51). Anal. $C_{18}H_{17}ClO_4$. Calcd: C 65.06, H 5.12. Found: C 64.98, O 5.05. *6-Isopropyl-6-methyl-dibenzo(d,f)(1,3)dioxepine* (**4a**): Yield: 0.27 g (20%). IR (NaCl): ν 3070, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–7.16 (*m*, 8H), 2.36 (*q*, 1H), 1.70 (*s*, 3H), 1.29 (*d*, 6H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.50, 132.84, 127.11, 125.00, 118.84, 109.81, 103.77, 33.53, 23.79, 18.37 ppm. EI-MS: *m/z* (%) 254 [$M^{+\cdot}$] (100). Anal. $C_{17}H_{18}O_2$. Calcd: C 80.31, O 7.09. Found: C 80.16, H 7.00. *6-Benzyl-6-methyl-dibenzo(d,f)(1,3)dioxepine* (**5a**): Yield: 0.40 g (25%). IR (NaCl): ν 3100, 1270 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.63 (*m*, 5H), 7.50–7.25 (*m*, 8H), 3.38 (*s*, 2H), 1.58 (*s*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.64, 136.60, 133.17, 130.45, 128.57, 128.34, 116.98, 44.80, 22.40 ppm. EI-MS: *m/z* (%) 302 [$M^{+\cdot}$] (82). Anal. $C_{21}H_{18}O_2$. Calcd: C 83.44, O 5.96. Found: C 83.36, H 5.85. *6-Butyl-6-methyl-dibenzo(d,f)(1,3)dioxepine* (**7a**): Yield: 0.57 g (40%). IR (NaCl): ν 3080, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60–7.20 (*m*, 8H), 1.63 (*d*, 2H), 1.53 (*m*, 2H), 1.45 (*s*, 3H), 1.30 (*dd*, 2H), 0.80 (*q*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.42, 132.84, 127.11, 124.09, 119.57,103.94, 42.89, 28.40, 23.88, 13.95 ppm. EI-MS: *m/z* (%): 268 [$M^{+\cdot}$] (75). Anal. $C_{18}H_{20}O_2$. Calcd: C 80.59, H 7.46. Found: C 79.96, H 7.25. *Dibenzo(d,f)(1,3)dioxepin-6-methyl-6-(2-benzyl)acetic acid ethyl ester* (**8a**): Yield: 0.62 g (30). IR (NaCl): ν 3050, 1740, 1260, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.10 (*m*, 13H), 4.53 (*q*, 2H), 3.20 (*t*, 1H), 2.30 (*d*, 2H), 1.80 (*s*, 3H), 1.05 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 170.50, 156.00, 142.73, 132.69, 130.97, 128.67, 126.96, 119.57, 109.61, 60.56, 40.59, 30.84, 23.29, 14.28 ppm. EI-MS: *m/z* (%) 388 [$M^{+\cdot}$] (49). Anal. $C_{25}H_{24}O_4$ Calcd: C 77.32, H 6.18. Found: C 77.00, H 6.05.
21. *12H-Dibenzo(d,g)(1,3)dioxocin-6-methyl-6-acetic acid ethyl ester* (**1b**): Yield: 0.50 g (30%). IR (NaCl): ν 3060, 1730, 1260, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.30–7.10 (*m*, 8H), 4.20 (*q*, 2H), 3.06 (*s*, 2H,), 2.81 (*s*, 2H), 1.90 (*s*, 3H) 1.15 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 165.96, 152.87, 129.77, 128.00, 119.63, 112.45, 60.60, 46.03, 31.22, 27.21, 14.20 ppm. EI-MS: *m/z* (%) 312 [$M^{+\cdot}$] (23). Anal. ($C_{19}H_{20}O_4$) C 73.08, H 6.41. Found: C 72.98, H 6.35. *12H-Dibenzo(d,g)(1,3)dioxocin-6-chloromethyl-6-acetic acid ethyl ester* (**2b**): Yield: 0.37 g (20%). IR (NaCl): ν 3070, 1750, 1260, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.10 (*m*, 8H), 4.25 (*q*, 2H), 3.60 (*s*, 2H), 2. 80 (*s*, 2H), 2.75 (*s*, 2H), 1.15 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.54, 151.00, 132.34, 128.88, 125.48, 122.79, 112.71, 61.43, 50.25, 45.98, 31.22, 13.76 ppm. EI-MS: *m/z* (%) 347 [$M^{+\cdot}$] (41). Anal. ($C_{19}H_{19}ClO_4$) C 65.71, H 5.47. Found: C 65.98, H 5.29. *6,6-Dimethyl-12H-dibenzo(d,g)(1,3)dioxocin* (**3b**): Yield: 0.39 g (30%). IR (NaCl): ν 3070, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.20–7.10 (*m*, 8H), 2.81 (*s*, 2H), 1.86 (*s*, 6H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.50, 130.01, 128.39, 126.02, 119.60, 112.20, 106.00, 31.22, 25.00 ppm. EI-MS: *m/z* (%) 180 [$M^{+\cdot}$] (50). Anal. ($C_{16}H_{16}O_2$) C 80.00, H 6.67. Found: C 79.71, H 6.59. *6-Isopropyl-6-methyl-12H-dibenzo(d,g)(1,3)dioxocin* (**4b**): Yield: 0.36 g (25%). IR (NaCl): ν 3090, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.20–7.05 (*m*, 8H), 2.75 (*s*, 2H), 1.91 (*m*, 1H), 1.62 (*s*, 3H), 1.05 (*d*, 6H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.00, 129.31, 127.35, 125.00, 119.60, 112.00, 108.65, 33.53, 31.18, 23.79, 18.37 ppm. EI-MS: *m/z* (%) 268 [$M^{+\cdot}$] (39). Anal. ($C_{18}H_{20}O_2$) C 80.59, H 7.46. Found: C 80.31, H 7.39. *6-Benzyl-6-methyl-12H-dibenzo(d,g)(1,3)dioxocin* (**5b**): Yield: 0.42g (25%). IR (NaCl): ν 3100, 1270 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.05 (*m*, 13H), 3.05 (*s*, 2H), 2.80 (*s*, 2H), 1.79 (*s*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.72, 144.17, 130.15, 128.39, 119.63, 11.35, 36.51,35.14, 31.22, 25.26, 17.67 ppm. EI-MS: *m/z* (%) 316 [$M^{+\cdot}$] (25). Anal. ($C_{22}H_{20}O_2$) C 83.54, H 6.33. Found: C 83.35, H 6.30. *6-Methyl-6-phenyl-12H-dibenzo(d,g)(1,3)dioxocin* (**6b**): Yield: 0.49 g (30%). IR (NaCl): ν 3080, 1260 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.05 (*m*, 13H), 2.81 (*s*, 2H), 1.89 (*s*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 153.16, 142.15, 130.15, 127.39, 119.58, 113.08, 31.19, 30.05 ppm. EI-MS: *m/z* (%) 316 [$M^{+\cdot}$] (30). Anal. ($C_{21}H_{18}O_2$) C 83.44, H 5.96. Found: C 83.27, H 5.80. *6-Butyl-6-methyl-12H-dibenzo(d,g)(1,3)dioxocin* (**7b**): Yield: 0.64 g (40%). IR (NaCl): ν 3080, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.15–7.00 (*m*, 8H), 2.79 (*s*, 2H), 1.60 (*d*, 2H), 1.50 (*s*, 3H), 1.30 (*m*, 4H), 0.87 (*t*, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.03, 130.02, 128.39, 125.90, 116.76, 111.18, 36.96, 31.11, 25.39, 16.16, 14.11 ppm. EI-MS: *m/z* (%) 282 [$M^{+\cdot}$] (34). Anal. ($C_{19}H_{22}O_2$) C 80.85, H 7.80. Found: C 80.67, H 7.70.
22. Purity determination. Electron impact (EI) experiments were performed by a Carlo Erba QMD mass spectrometer operating at 70 eV and 200 μA with an ion source

temperature of 200 °C. The samples were introduced directly into the ion source. IR spectra were recorded by a Perkin–Elmer 157 spectrometer. ^{1}H and ^{13}C NMR were recorded by a Varian 300 MHz using tetramethylsilane as internal standard. Microanalysis for CHN were performed by a Carlo Erba 1106 Elemental Analyzer.