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# $InCl_3$ and $ZrCl_4$ catalyzed regioselective reaction of 2,2′-dihydroxybiphenyl with terminal alkynes: synthesis of new dibenzo[*d*,*f*][1,3]dioxepines

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ABSTRACT

The regioselective reaction of 2,2′-dihydroxybiphenyl with terminal alkynes was found to be rapidly catalyzed by $InCl_3$ and $ZrCl_4$. The chemoselectivity of catalysts and alkynes for biphenol over water, together with the reaction mechanism are discussed in details.



## 1. Introduction

Undoubtedly, the construction of new C–O bonds by addition of oxygen nucleophiles to a C–C triple bond represents one of the most useful methods to functionalize internal and terminal alkynes.

With this intention, several studies on the addition of water[1] to alkynes, also in the presence of alcohols,[2] have been recently reported in literature. As a consequence, a variety of catalysts for this reaction have been extensively studied. The dichloro (diphosphine) platinum(II) complex/silver salt system,[3] which led to ketones with dry alcohols, seemed to be particularly interesting. Another approach consists in the use of Pt(II)[4] or Ir[2b,5] complexes, useful for the preparation of acetals in dry conditions.

For these catalytic systems the presence of water is crucial in order to maintain an interesting catalytic efficiency.[2b] Moreover, these systems are almost chemoselective for water over alcohol,[4,5] which decreases the regioselective formation of acetals.

Other interesting approaches involve the Michael addition reaction, which is a versatile synthetic methodology for an efficient coupling of electron poor acetylenes with a vast array of nucleophiles. Among the many methods, we report, as particularly interesting, some recent works on: (1) the direct NaH-catalyzed transformation of arylsulfonylalkynes into the acetals or thioacetals of acetyl sulfones,[6] (2) the phosphine-catalyzed conjugate additions of electron-deficient olefins and acetylenes with alcohols or aminoacid-derived pronucleophiles[7] and (3) the amine-catalyzed hydroalkoxylation reactions of activated alkenes and alkynes.[8]

In the present study, we report the $InCl_3$ and $ZrCl_4$ catalyzed regioselective reaction of 2,2′-dihydroxybiphenyl with terminal alkynes, emphasizing the high chemoselectivity of the catalysts for biphenol over water.

## 2. Results and discussion

In recent years, we have focused our interest on the synthesis[9] and mass spectrometric behaviour[10] of dibenzo[*d*,*f*][1,3]dioxepines, obtained from biphenols and a variety of carbonyl compounds. In continuation of our research directed towards the development of new catalytic reactions using Lewis acids, we found that, in the presence of $InCl_3$ or $ZrCl_4$, terminal aliphatic and aromatic alkynes easily reacted with 2,2′-dihydroxybiphenyl (**1**), leading to 6,6-dialkyl or 6-alkyl-6-aryldibenzo dioxepine derivatives with exceptional regioselectivity.

In the beginning of our investigation, we studied the reactivity of both terminal and internal alkynes. However, no product was obtained using 3-hexyne (**2a**), dimethyl acetylenedicarboxylate (**2b**), diphenyl acetylene (**2c**) or ethyl 2-hexynoate (**2d**), even with higher temperatures, more catalyst or longer reaction times (Scheme 1).

Conversely, the reaction took place smoothly when terminal alkynes were employed (Scheme 2 and Tables 1 and 2).

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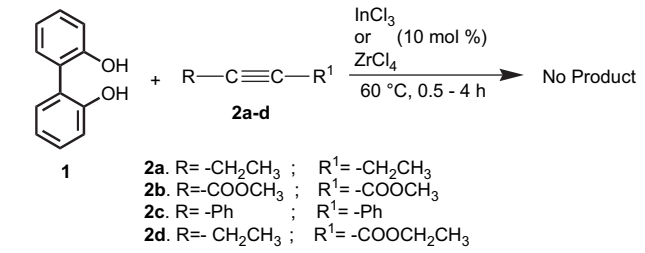
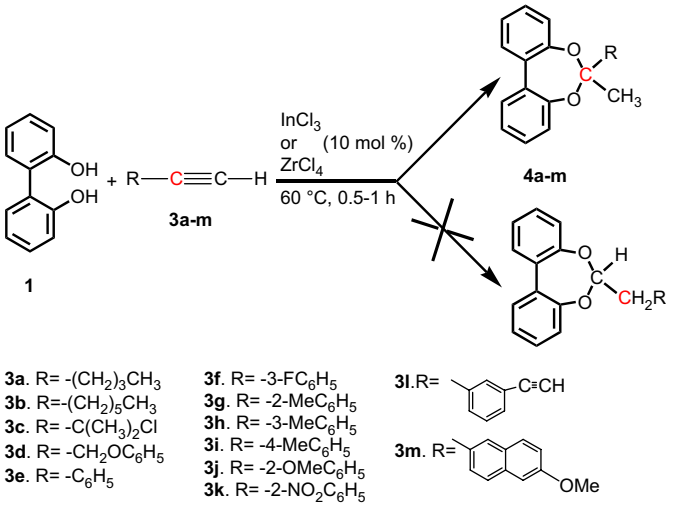



**Scheme 1.** Reaction of 2,2'-dihydroxybiphenyl with internal alkynes.




**Scheme 2.** Reaction of 2,2'-dihydroxybiphenyl with terminal alkynes.

In particular, the best results have been obtained with phenylacetylene (**3e**) and other electron rich aromatic alkynes such as (**3g–j**), (**3l**), (**3m**), as evidenced in Tables 1 and 2. Moreover, we observed that the maximum yields were isolated after not more than 35–60 min and, apart from the reagents, the only product obtained was the dibenzodioxepine derivative. The best results have been achieved at 60 °C; in fact, the reaction did not take place at all at room temperature or without catalyst. Besides, no yield enhancement was observed when the catalyst amount, the reaction times or the temperature were altered. Furthermore, while comparing the effect of catalysts, we found that, $InCl_3$ was slightly less efficient than $ZrCl_4$, in terms of isolated yields.

All the alkynes were used in excess in order to carry out the reactions under homogeneous conditions, avoiding, with the exception of entries 10 and 12 in Table 2, the use of any solvent.

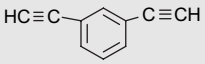
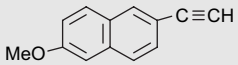
In order to better understand the regiochemistry of the reaction, we explored the reaction mechanism by means of GC–MS analysis. From the very beginning of the reaction, we observed the formation of a 2-chloroalkene, which rapidly disappeared in favour of the dibenzodioxepine. This was particularly evident when aromatic alkynes were used, due to a major stability of the α-chlorostyrene derivatives. Compounds (**5e**), (**5j**) and (**5m**) were isolated (entries 1, 8 and 12 in Table 2) and their structures elucidated in order to discern their role in the reaction mechanism (Scheme 3 and Fig. 1).

**Table 1**
Reaction of 2,2′-dihydroxybiphenyl with terminal aliphatic alkynes

| Entry | Alkyne | Cat. (mol %) | Temp (°C) | Time (min) | Prod. | Yield[a] (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | $InCl_3$ | $ZrCl_4$ |
| 1 | Bu–C≡CH | 10 | 60 | 50 | (**4a**)[b] | 30 | 40 |
| 2 | Bu–C≡CH | 10 | rt | 90 | (**4a**) | 0 | 0 |
| 3 | Bu–C≡CH | 0 | 60 | 90 | (**4a**) | 0 | 0 |
| 4 | Hex–C≡CH | 10 | 60 | 50 | (**4b**) | 35 | 38 |
| 5 | $ClCMe_2C$≡CH | 10 | 60 | 90 | (**4c**) | 0 | 0 |
| 6 | $PhOCH_2C$≡CH | 10 | 60 | 60 | (**4d**) | 10 | 10 |

[a] Isolated yields.
[b] Ref. 9a.

**Table 2**
Reaction of 2,2′-dihydroxybiphenyl with terminal aromatic alkynes

| Entry | Alkyne | Cat. (mol %) | Temp (°C) | Time (min) | Prod. | Yield[a] (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | $InCl_3$ | $ZrCl_4$ |
| 1 | PhC≡CH | 10 | 60 | 35 | (**4e**) | 60 | 73 |
| 2 | PhC≡CH | 10 | rt | 90 | (**4e**) | 0 | 0 |
| 3 | PhC≡CH | 0 | 60 | 90 | (**4e**) | 0 | 0 |
| 4 | 3-FPhC≡CH | 10 | 60 | 90 | (**4f**) | 15 | 13 |
| 5 | 2-MePhC≡CH | 10 | 60 | 45 | (**4g**) | 45 | 50 |
| 6 | 3-MePhC≡CH | 10 | 60 | 45 | (**4h**) | 37 | 36 |
| 7 | 4-MePhC≡CH | 10 | 60 | 45 | (**4i**) | 50 | 52 |
| 8 | 2-OMePhC≡CH | 10 | 60 | 45 | (**4j**) | 45 | 47 |
| 9 | 2-OMePhC≡CH | 10 | rt | 90 | (**4j**) | 0 | 0 |
| 10 | $2\text{-}NO_2PhC$≡CH | 10 | 40[b] | 90 | (**4k**) | 0 | 0 |
| 11 |  | 10 | 60 | 90 | (**4l**) | 13 | 10 |
| 12 |  | 10 | 40[b] | 40 | (**4m**) | 42 | 45 |

[a] Isolated yields.
[b] Dichloromethane was used as solvent.

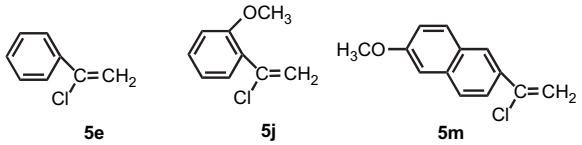
With this respect, 2,2′-dihydroxybiphenyl (**1**) was allowed to react with compound (**5m**), observing that, only in the presence of $InCl_3$ or $ZrCl_4$, it converted promptly into 6-methyl-6-(6-methoxynaphthyl)dibenzo[*d*,*f*][1,3]dioxepine (**4m**) (Scheme 4). Derivatives (**5e**) and (**5j**) exhibited the same behaviour.

These experimental data suggest that the reaction effectively proceeds successively through an α-chloroalkene intermediate. Moreover, it is evident that the Lewis acid is fundamental for the formation of the intermediate and for the proceeding of the reaction.

The experimental evidence seems to give credit also to the hypothesis of a synergic interaction between the biphenol (**1**), the alkynes (**3a–m**) and the catalyst. As a matter of fact, yields drastically decrease or the reaction did not take place at all, when the components are added at different times.

On the basis of these experiments, we postulate the mechanism presented in Scheme 5. The reaction presumably undergoes a concerted six-membered transition state[11] to form intermediates (**6**) and (**5**). The 2-chloroalkene intermediate (**5**) is formed by a Markovnikov addition of HCl derived from the nucleophilic interaction between biphenol (**1**) and $InCl_3$. The final product (**4**) is afforded by the nucleophilic addition of compound (**6**) at 2-chloroalkene (**5**), which is rapidly followed by an intramolecular cyclization, where an oxacarbenium ion represents the most likely reactive state. Otherwise, 2-chloroalkene (**5**) might generate a vinyl cation that could react with intermediate (**6**) to afford the final product (**4**).

Our hypothesis was also confirmed with the aid of phenylacetylene-*d*. The gas chromatogram reported in Figure 2 shows the rapid formation, after only few minutes, of the deuterated 2-chlorostyrene (*m*/*z* 139), which is rapidly transformed into the final 6-methyl-$d_1$-6-phenyl dibenzo[*d*,*f*][1,3]dioxepine (*m*/*z* 289).




**Scheme 3.** α-Chlorostyrene derivatives isolated from entries 1, 8 and 12.

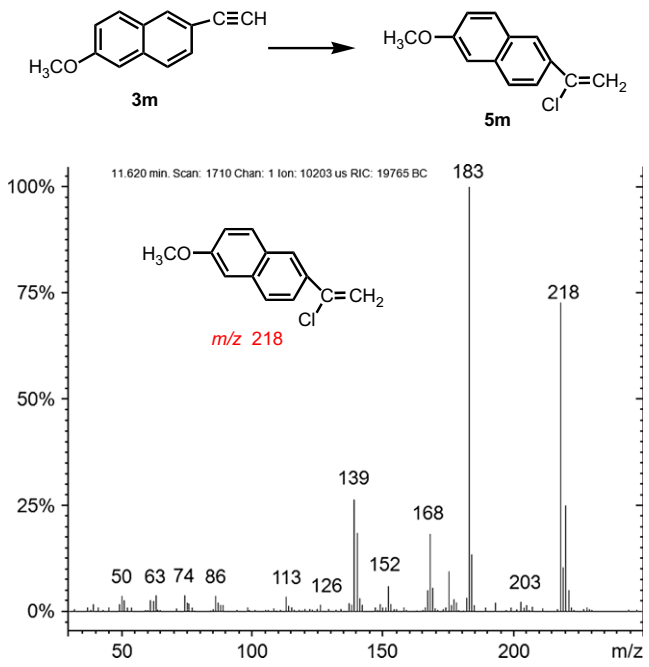
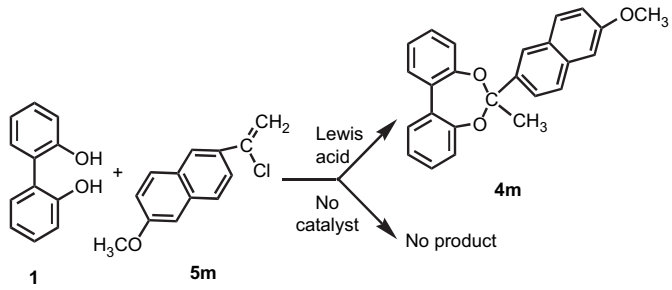
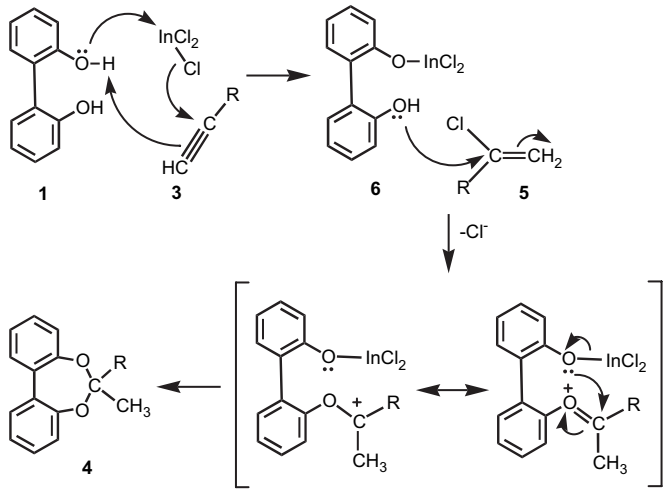



**Figure 1.** EIMS spectrum of 2-(1-chlorovinyl)-6-methoxynaphtalene (**5m**) obtained from 2-ethynyl-6-methoxynaphtalene (**3m**).




**Scheme 4.** Reaction between biphenol (**1**) and compound (**5m**).




**Scheme 5.** Proposed reaction mechanism.

We also studied the chemoselectivity of the catalysts. To this end, the reactions reported in Scheme 2 were carried out in the presence of water, observing that only the dibenzodioxepine derivative was obtained as a final product. No trace of ketone was evidenced, even when a stoichiometric amount of catalyst was used (Scheme 6).

In addition, we performed the reaction between phenylacetylene (**3e**) and water, evidencing that $InCl_3$ and $ZrCl_4$ did not catalyze, under our reaction conditions, the hydration of the alkynes.[1b]

It is also known that phenols usually undergo regioselective vinylation, especially with terminal alkynes, via C–H bond cleavage in the presence of transition-metals[12] or *poor metal* catalysts.[13] It is noteworthy that, during our experiments, we never found vinylbiphenol derivatives, which indicates that $InCl_3$ or $ZrCl_4$ did not catalyze the alkenylation of 2,2′-dihydroxybiphenyl (**1**).

Mass spectrometric studies on the gas-phase reactivity of aromatic alkynes towards 2,2′-dihydroxybiphenyl are currently in progress.

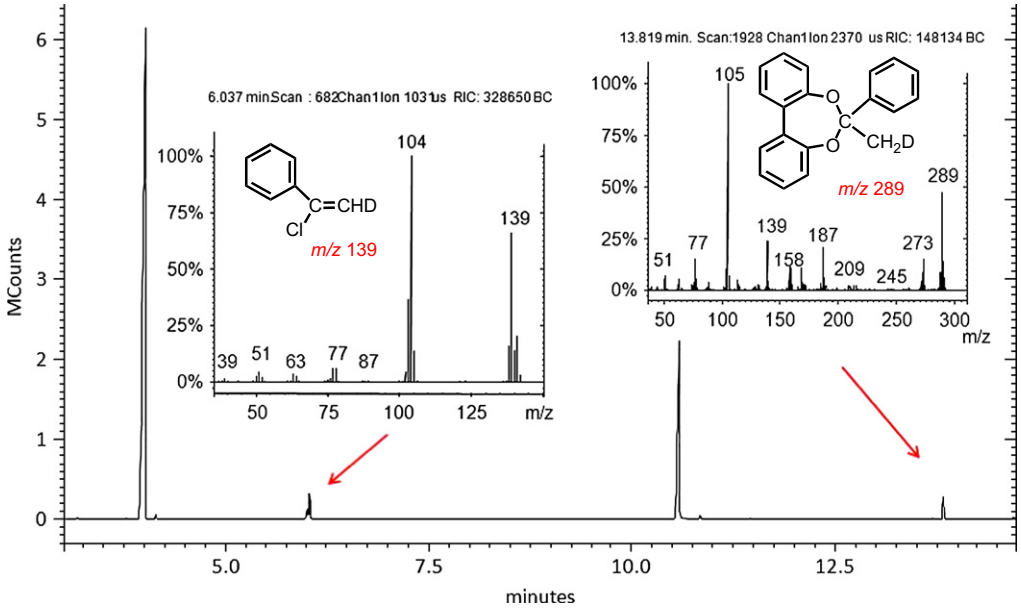
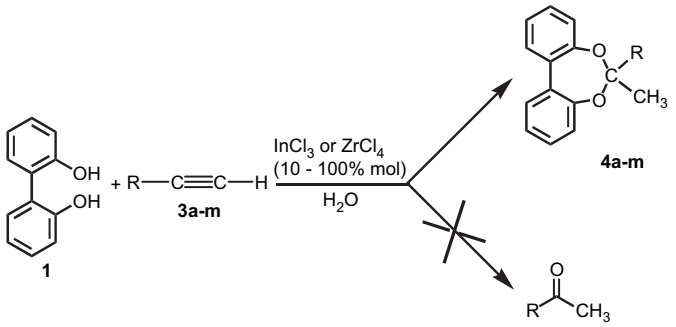



**Figure 2.** Gas chromatogram and mass spectra of deuterated 2-chlorostyrene intermediate and final 6-methyl-$d_1$-6-phenyldibenzo[$d_f$][1,3]dioxepine, in the reaction between compound (**1**) and labelled (**3e**).




**Scheme 6.** Chemoselectivity of $InCl_3$ and $ZrCl_4$ for 2,2'- dihydroxybiphenyl over water.

In conclusion, we succeeded in the high regioselective synthesis of new 6,6-disubstituted dibenzo[*d*,*f*][1,3]dioxepines, demonstrating that the reaction proceeds through a 2-chloroalkene intermediate or its related vinyl cation, whose formation represents the key of the reaction regiochemistry. The chemoselectivity of the catalysts for 2,2′-dihydroxybiphenyl over water was also investigated.

## 3. Experimental

### 3.1. General

$^1H$ 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. IR spectra were recorded by a Perkin Elmer 157 spectrometer.

*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 20 μA, 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 $s^{-1}$). Aliquot of 1 μL of solutions $1.0\times10^{-5}$ M in chloroform have been introduced into the gas chromatograph inlet. A CIP Sil-8 CB Low-bleed/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 $min^{-1}$ (held for 2 min). The temperature was then ramped to 350 at 20 °C $min^{-1}$. The transfer line was maintained at 250 °C and the injector port 30/1 split at 270 °C.

All starting materials and catalysts were purchased from commercial sources and used without further treatment.

### 3.2. Typical procedure to synthesize dibenzo[*d*,*f*][1,3]dioxepines

A mixture of 2,2′-dihydroxybiphenyl (**1**) (5.37 mmol) and the appropriate terminal alkyne (**3a**–**m**) (21.48 mmol) was stirred under nitrogen for the period indicated (TLC) at 60 °C, in the presence of indium(III) chloride or zirconium(IV) chloride (0.54 mmol). After reaction, the crude mixture was separated by flash-column chromatography (hexane/$CH_2Cl_2$ 4/1 or 1/1) on alumina, obtaining the desired product. Solid compounds were recrystallized from hexane/$CH_2Cl_2$ 6/1.

*3.2.1. 6-Butyl-6-methyldibenzo[d,f][1,3]dioxepine (**4a**)*

Pale yellow sticky oil. IR (NaCl): *ν* 3080, 1490, 1210 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.35–6.80 (m, 8H), 2.12 (t, 2H, $^3J$ 7.5 Hz), 1.85 (s, 3H), 1.63–1.26 (m, 4H), 1.02 (t, 3H, $^3J$ 7 Hz) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 154.9, 127.3, 125.0, 120.1, 115.1, 99.9, 40.1, 24.0, 15.4, 10.9 ppm. EIMS: *m*/*z*: 268 [$M^{+\bullet}$]. Anal. Calcd for $C_{18}H_{20}O_2$: C 80.60, H 7.46. Found: C 80.55, H 7.43.

*3.2.2. 6-Hexyl-6-methyldibenzo[d,f][1,3]dioxepine (**4b**)*

Yellow sticky oil. IR (NaCl): *ν* 3100, 1600, 1480, 1220 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 6.89–7.40 (m, 8H), 2.10 (t, 2H), 1.90 (s, 3H), 1.25–1.33 (m, 8H), 0.78 (t, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 155.3, 133.2, 127.4, 114.9, 100.4, 38.3, 31.0, 22.8, 23.6, 18.7, 13.0 ppm. EIMS: *m*/*z*: 296 [$M^{+\bullet}$]. Anal. Calcd for $C_{20}H_{24}O_2$: C 81.08, H 8.11. Found: C 81.03, H 8.01.

*3.2.3. 6-Methyl-6-(phenoxymethyl)dibenzo[d,f][1,3]dioxepine (**4d**)*

Yellow sticky oil. IR (NaCl): *ν* 3110, 1590, 1315, 1220, 1035 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.31–7.10 (m, 6H), 6.98–6.75 (m, 7H), 4.82 (s, 2H), 1.95 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 157.3, 154.5, 129.5, 126.1, 115.4, 100.8, 74.0, 19.9 ppm. EIMS: *m*/*z*: 318 [$M^{+\bullet}$]. Anal. Calcd for $C_{21}H_{18}O_3$: C 79.24, H 5.66. Found: C 79.32, H 5.59.

*3.2.4. 6-Methyl-6-phenyldibenzo[d,f][1,3]dioxepine (**4e**)*

Pale yellow crystals (mp 83–85 °C). IR (NaCl): *ν* 3080, 1600, 1450, 1260 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.42–7.38 (m, 5H), 7.35–6.80 (m, 8H), 2.35 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 154.4, 140.6, 129.2, 128.7, 127.0, 125.4, 115.1, 26.1 ppm. EIMS: *m*/*z*: 288 [$M^{+\bullet}$]. Anal. Calcd for $C_{20}H_{16}O_2$: C 83.33, H 5.55. Found: C 83.36, H 5.50.

*3.2.5. 6-Methyl-6-(3-fluorophenyl)dibenzo[d,f][1,3]dioxepine (**4f**)*

Yellow sticky oil. IR (NaCl): *ν* 3100, 1640, 1400, 1228 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.35–7.11 (m, 4H), 6.98–7.07 (m, 8H), 1.99 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 155.5, 142.7, 134.9, 133.7, 128.2, 125.1, 119.3, 109.3, 102.8 ppm. EIMS: *m*/*z*: 306 [$M^{+\bullet}$]. Anal. Calcd for $C_{20}H_{15}FO_2$: C 78.43, H 4.90. Found: C 78.39, H 4.93.

*3.2.6. 6-Methyl-6-(2-tolyl)dibenzo[d,f][1,3]dioxepine (**4g**)*

Yellow sticky oil. IR (NaCl): *ν* 3050, 1560, 1480, 1235 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.85–7.60 (m, 4H), 6.98–7.42 (m, 8H), 2.32 (s, 3H), 1.98 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 156.7, 140.9, 133.0, 126.0, 114.4, 109.5, 95.6, 19.9 ppm. EIMS: *m*/*z*: 302 [$M^{+\bullet}$]. Anal. Calcd for $C_{21}H_{18}O_2$: C 83.44, H 5.96. Found: C 83.21, H 6.00.

*3.2.7. 6-Methyl-6-(3-tolyl)dibenzo[d,f][1,3]dioxepine (**4h**)*

Yellow sticky oil. IR (NaCl): *ν* 3100, 1630, 1460, 1228 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.80–7.45 (m, 4H), 7.32–7.03 (m, 8H), 2.28 (s, 3H), 2.18 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 155.9, 138.3, 132.7, 127.0, 119.2, 101.3, 21.4 ppm. EIMS: *m*/*z*: 302 [$M^{+\bullet}$]. Anal. Calcd for $C_{21}H_{18}O_2$: C 83.44, H 5.96. Found: C 83.46, H 5.91.

*3.2.8. 6-Methyl-6-(4-tolyl)dibenzo[d,f][1,3]dioxepine (**4i**)*

Yellow sticky oil. IR (NaCl): *ν* 3120, 1550, 1450, 1210 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.78 (dd, 4H, $^3J$ 8.10 Hz, $^4J$ 2.61 Hz), 7.28–6.89 (m, 8H), 2.35 (s, 3H), 2.15 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 154.4, 137.6, 128.9, 126.5, 119.0, 109.3, 102.8, 21.1 ppm. EIMS: *m*/*z*: 302 [$M^{+\bullet}$]. Anal. Calcd for $C_{21}H_{18}O_2$: C 83.44, H 5.96. Found: C 83.41, H 5.93.

*3.2.9. 6-Methyl-6-(2-methoxyphenyl)dibenzo[d,f][1,3]-dioxepine (**4j**)*

Pale yellow crystals (mp 77–80 °C). IR (NaCl): *ν* 3110, 1660, 1480, 1310, 1220, 1050 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.50–7.03 (m, 4H), 7.28–6.82 (m, 8H), 3.68 (s, 3H), 2.20 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 157.6, 150.9, 130.7, 126.4, 113.0, 110.8, 99.0, 54.5 ppm. EIMS: *m*/*z*: 318 [$M^{+\bullet}$]. Anal. Calcd for $C_{21}H_{18}O_3$: C 79.24, H 5.66. Found: C 79.19, H 5.68.

*3.2.10. 6-Methyl-6-(3-ethynylphenyl)dibenzo[d,f][1,3]-dioxepine (**4l**)*

Brown oil. IR (NaCl): *ν* 3270, 3050, 1650 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): *δ* 7.45–7.37 (m, 6H), 7.22–6.87 (m, 6H), 3.12 (s, 1H), 2.04 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): *δ* 165.6, 134.2,

128.5, 126.2, 124.9, 122.7, 83.4, 27.3 ppm. EIMS: *m*/*z*: 312 [$M^{+\bullet}$]. Anal. Calcd for $C_{22}H_{16}O_2$: C 84.61, H 5.13. Found: C 84.59, H 5.12.

*3.2.11. 6-Methyl-6-(6-methoxynaphthyl)dibenzo[d,f][1,3]-dioxepine (**4m**)*

White crystals (mp 97–100 °C). IR (NaCl): $\nu$ 3120, 1600, 1480, 1240, 1035 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.98–7.25 (m, 9H), 6.95–6.60 (m, 5H), 3.36 (s, 3H), 2.18 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 156.1, 154.4, 141.6, 135.1, 128.2, 125.9, 126.9, 121.3, 119.1, 115.0, 113.23, 107.1, 101.1, 58.1, 26.0 ppm. EIMS: *m*/*z*: 368 [$M^{+\bullet}$]. Anal. Calcd for $C_{25}H_{20}O_3$: C 81.52, H 5.43. Found: C 81.48, H 5.39.

### 3.3. Reaction between 2,2′-dihydroxybiphenyl (1) and 2-(1-chlorovinyl)-6-methoxynaphtalene (5m)

A mixture of 2,2′-dihydroxybiphenyl (**1**) (0.54 mmol) and 2-(1-chlorovinyl)-6-methoxynaphtalene (**5m**) (0.65 mmol) in dichloromethane (5 ml) was stirred under nitrogen for 30 min at 40 °C, in the presence of indium(III) chloride or zirconium(IV) chloride (0.054 mmol). The reaction was monitored by GC–MS analysis, observing the total conversion of compound (**5m**) into dibenzodioxepine (**4m**) in the period indicated.

*3.3.1. 2-(1-Chlorovinyl)-6-methoxynaphtalene (**5m**)*

IR (NaCl): $\nu$ 3150, 1430, 1310, 1250 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.72–6.95 (m, 6H), 5.71 (d, 1H), 5.46 (d, 1H), 3.70 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 158.1, 134.3, 132.6, 127.0, 129.4, 124.1, 121.9, 111.3, 57.8 ppm. EIMS: *m*/*z*: 218 [$M^{+\bullet}$]. Anal. Calcd for $C_{13}H_{11}ClO$: C 71.56, H 5.04. Found: C 71.53, H 5.00.

*3.3.2. α-Chlorostyrene (**5e**)*

IR (NaCl): $\nu$ 3050, 1650, 1420 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.30–7.12 (m, 5H), 5.82 (d, 1H), 5.35 (d, 1H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 137.4, 128.0, 121.5, 110.1 ppm. EIMS: *m*/*z*: 138 [$M^{+\bullet}$]. Anal. Calcd for $C_8H_7Cl$: C 69.56, H 5.07. Found: C 69.51, H 5.00.

*3.3.3. 1-(1-Chlorovinyl)-2-methoxybenzene (**5j**)*

IR (NaCl): $\nu$ 3100, 1620, 1450, 1330 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.25–669 (m, 4H), 5.60 (d, 1H), 5.48 (d, 1H), 3.68 (s, 3H) ppm. $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 156.7, 128.1, 122.8, 11.7, 59.7 ppm. EIMS: *m*/*z*: 168 [$M^{+\bullet}$]. Anal. Calcd for $C_9H_9ClO$: C 64.28, H 5.35. Found: C 64.21, H 5.33.

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