Organic & Biomolecular Chemistry

Accepted Manuscript

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C8OB01496E

Journal Name

ARTICLE

Synthesis of medium-sized (6-7-6) ring compounds by iron-catalyzed dehydrogenative C-H activation/annulation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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In this report, we have described a $FeCl_3$-catalyzed process involving intramolecular annulation of *o*-phenoxy diarylacetylenes via hydroarylation to afford a series of the biologically potent fused seven-membered (6-7-6) ring compounds under mild reaction conditions. This reaction believed to proceeds through Friedel-Crafts type sequential carbometallation followed by protonation to produce phenyldibenz[*b,f*]oxepines. This method was also extended to synthesize seven-membered rings that are fused with coumarins.

Introduction

Medium sized (7-11 membered) ring motif with one or more heteroatom(s) is the key structural component of numerous biologically active compounds as well as natural products.[1] As a result, synthetic access to such unit is receiving a great deal of attention. Dibenzo[*b,f*]oxepine structural scaffold, having a (6-7-6) ring system is present in numerous natural products that show a wide spectrum of biological activities[2] (Figure 1). For instance, pacharin and bauhiniastatins possess inhibitory activity in cancer cell growth.[3] *Artocarpol* ***A***, isolated from the root bark of *Artocarpus rigida* shows anti-inflammatory activity.[4] Other synthetic derivatives of dibenzo[*b,f*]oxepine including bermoprofen (Dibenon)[@], CGP3466, Fluradoline, etc. also exhibit excellent biological properties, such as antipsychotic,[5] antidepressant,[6] antihypertensive,[7] antiestrogenic,[8] anti-inflammatory,[9] and insecticidal activities.[10] Nevertheless, fewer synthetic methods involving the cyclization of acyclic precursors have been reported for their preparation as compared to the annulation methods delineated for five- and six-membered rings. This is probably due to the unfavourable enthalpic (transannular interactions) and entropic (difficulty in closing a relatively large ring) factors, which tend to raise the cyclization activation energy.[11] Evidently, the intramolecular Friedel-Crafts annulation of the preformed functionalized diaryl ether intermediates, and Wagneer-Meerwein rearrangement of xanthene-10-methoxycarbonyl are two classical approaches to access dibenzo[*b,f*]oxepines (Scheme 1a).[12] However, both these methods require harsh reaction conditions.[13] Besides, multi-step access to starting material and substituent dependent annulation are some other limitations of these methods. Therefore, development of a general method which precedes under mild reaction conditions with wide substrate scope seems to be desirable.

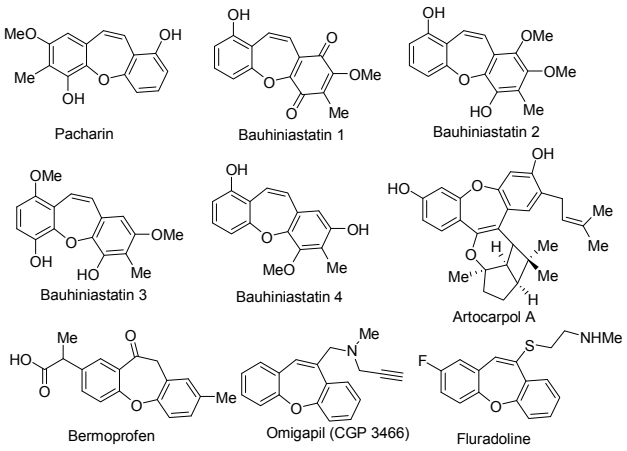

Figure 1. Selected biologically potent benzoxepines

In 1992, Kitamura and Taniguchi reported the acid-mediated annulation of *o*-(aryloxy)diarylacetylene which proceeds through the initial 1,2-addition of the electrophile (i.e., H^+) to the alkyne by generating the vinyl cation and subsequent intramolecular arylation to afford the desired 7-membered heterocycle (Scheme 1b).[14] Unfortunately, this protocol was successful only with 1-(*p*-methoxyphenyl)-2-(*o*-phenoxyphenyl)ethyne (one example only), where the resulting carbocation was stabilized; and failed with any other substrate. Other alternative approaches including the intramolecular annulation of 2-styryl phenols through Ullmann type

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Electronic Supplementary Information (ESI) available: [experimental details, copies of NMR spectra and crystal structure data of **3b**]. See DOI: 10.1039/x0xx00000x

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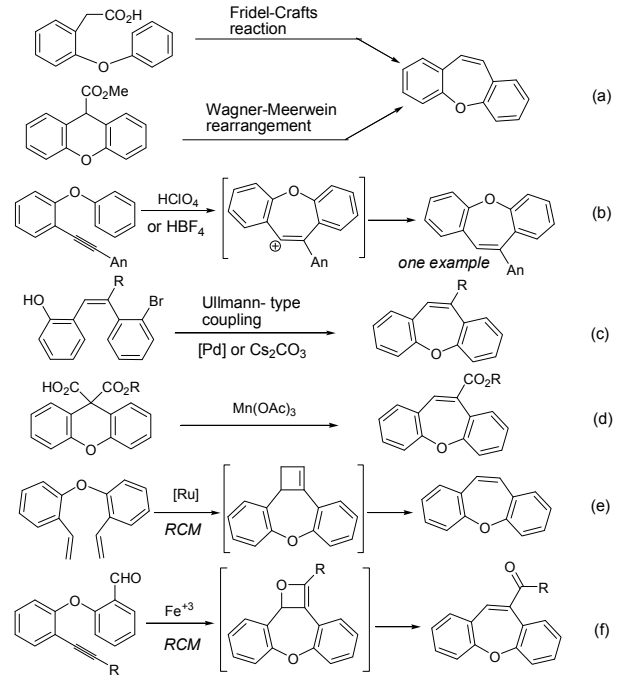
DOI: 10.1039/C8OB01496E

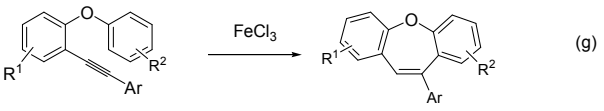
C-O bond formation (Scheme 1c)[15] and Mn-catalyzed oxidative radical rearrangement of monoalkyl 2-(9*H*-xanthenyl)malonates (Scheme 1d)[13] are promising methods to achieve dibenzo[*b,f*]oxepines. Moreover, ring closing metathesis has also been practiced to construct such medium-sized ring compounds. Mohapatra et al. used RCM of 2,2'-oxybis(vinylbenzene) in the presence of Grubb's catalyst to get dibenzo[*b,f*]oxepines in good to excellent yield (Scheme 1e).[16] Jana and co-workers employed $FeCl_3$-catalyzed alkyne–aldehyde metathesis reaction to achieve acylated dibenzo[*b,f*]oxepines (Scheme 1f) with acclaimed regio- and chemoselectivity under mild conditions.[17] In continuation of our recent research interest on transition metal-mediated heterocycle synthesis, here we report an efficient iron-catalyzed method for the construction of dibenzo[*b,f*]oxepines from *o*-(aryloxy)phenyl alkynes via intramolecular hydroarylation of alkynes under mild reaction conditions (Scheme 1g).

Scheme 1. Synthetic approaches to dibenzo[*b,f*]oxepines

Earlier Methods



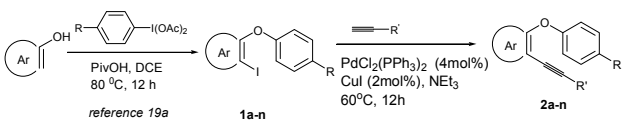
Present work

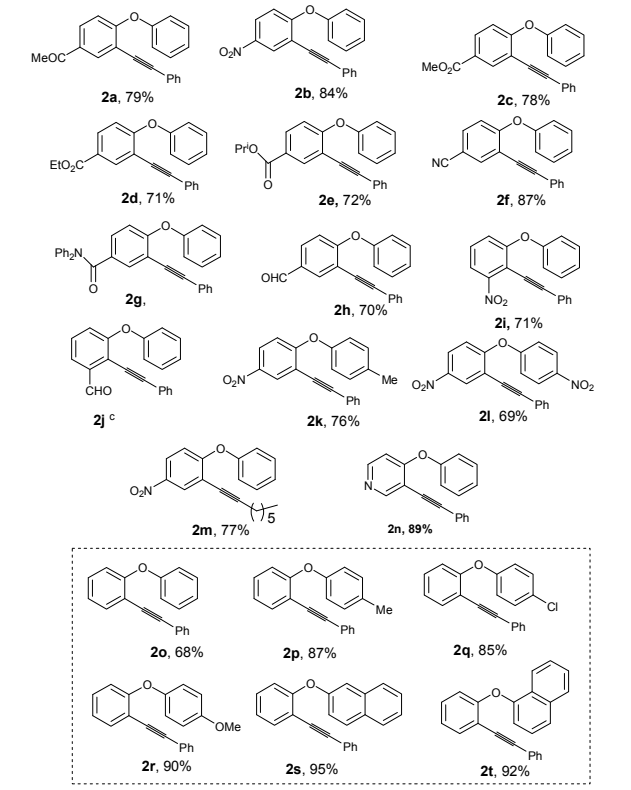


Results and Discussion

Our strategy to dibenzo[*b,f*]oxepines was originated from the seminal work of Perumal on cyclization reaction of aryl propargyl ethers in the presence of $Pd(OAc)_2$ to generate benzopyrans.[18] We hypothesized that the 2-phenoxy diarylacetylenes would undergo transition metal-catalyzed intramolecular C-H hydroarylation of internal alkynes to produce dibenzo[*b,f*]oxepines through 7-*endo-dig* annulation. Thus, our investigation commenced with the synthesis of *o*-(aryloxy)diarylacetylene (**1**). Recently, the phenyl iododiacetate (PIDA)-mediated synthesis of varieties *o*-iododiaryl ethers (e.g., **1**) directly from the electronically deficient phenols in the presence of pivalic acid was reported by us.[19a] Sonogashira coupling[20] reaction of terminal acetylenes and **1** in the presence of $PdCl_2(PPh_3)_2$ (4 mol %) and CuI (2 mol%) in triethyl amine afforded the *o*-(aryloxy)diarylacetylenes (**2**) in appreciable yield (Scheme 2). Notably, 2-iodo diarylethers **1a-m** were prepared from the reaction of phenol with an electron withdrawing group and hypervalent iodine derivatives, while **1n** was prepared from the reaction of 4-hydroxy pyridine and PIDA following the similar procedure. **1o-u** were prepared classically from the reaction of phenol and *o*-chloro nitrobenzene, followed by reduction, diazotization and iodination.[21]

Scheme 2. Synthesis of *o*-(aryloxy)diarylacetylene[a-c]





[a]Reaction conditions: **1** (0.29 mmol), $PdCl_2(PPh_3)_2$ (4 mol%), CuI (2 mol%), alkyne (0.42 mmol, 1.5 equiv.) in 3 mL of triethyl amine was stirred at 60°C. [b] Isolated yield. [c]Contaminated with some inseparable impurity having the same R_f, hence, subsequent reaction was carried out with the contaminated one.

Next, we prompted for the intramolecular annulation of *o*-(aryloxy)diarylacetylene to dibenzo[*b,f*]oxepine using $Pd(OAc)_2$ catalyst. Unfortunately, no reaction took place with the recovery of the starting material (Table 1, entry 1). Careful screening of other transition-metal catalysts such as $Cu(OAc)_2$, $Ag(OAc)_2$, $ZnCl_2$ or

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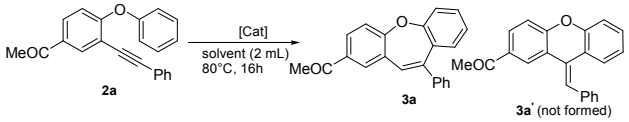
$Ni(OAc)_2$ for cyclization was unsuccessful (entries 2-5). Owing to the low-cost, non-toxicity and proven potential of iron-catalyst for intramolecular hydroarylation;[22, 23] Fe-salts were then employed for the annulation reaction. Pleasingly, when $FeCl_3$ (anhydrous) (100 mol%), was employed, the *endo-dig* cyclization occurred partially with the formation of the desired dibenzo[*b,f*]oxepines (**3a**) in 62% yield at room temperature in DCE over a period of 24h (entry 6). However, rising the reaction temperature to 80°C resulted in **3a** with complete conversion of starting material (entry 7). A further rise in temperature to 100°C causes decomposition of the starting material with the appearance of additional spots in TLC (70% yield). Formation of the medium-sized ring was anticipated from the ^1H and ^{13}C NMR spectra. Though there is a possibility for the formation of 6-6-6 tricyclic compound **3a'** by the 6-*exo-dig* reaction, we could not identify the same from the crude reaction mixture (^1H NMR). Noteworthy that in TLC, there is no difference in R_f value of the starting material and product. By decreasing the $FeCl_3$ concentration from 100 to 50 to 30 mol%, did not affect the yield of **3a** appreciably (entries 7-9), while the reaction time increases from 3h to 8h to 16h respectively**.** However, further lowering of the catalyst concentration to 20 mol% causes incomplete conversion with reduced yield (72%, entry 10) even after 24h. Next, we investigated the effect of solvent polarity in the annulation process. We observed that among the tested solvents (i.e., DCE, toluene, 1,4-dioxane, water, DMF), DCE produces the best yield of **3a**. However, in polar solvents (e.g., 1,4-dioxane, acetonitrile), the reaction did not proceed with recovery of starting material. Although the exact reason for such observation is not known at this time, but we may presume that polar solvents would serve as ligands with the displacement of halogen from $FeCl_3$;[24] as a result the catalytic activity of the Fe-catalyst for the initial co-ordination with alkyne get diminished. Notably**,** the reaction does not require any inert atmosphere or dry solvent or additional acid to afford the annulated product.

Table 1. Optimization of *endo-dig* cyclization[a]

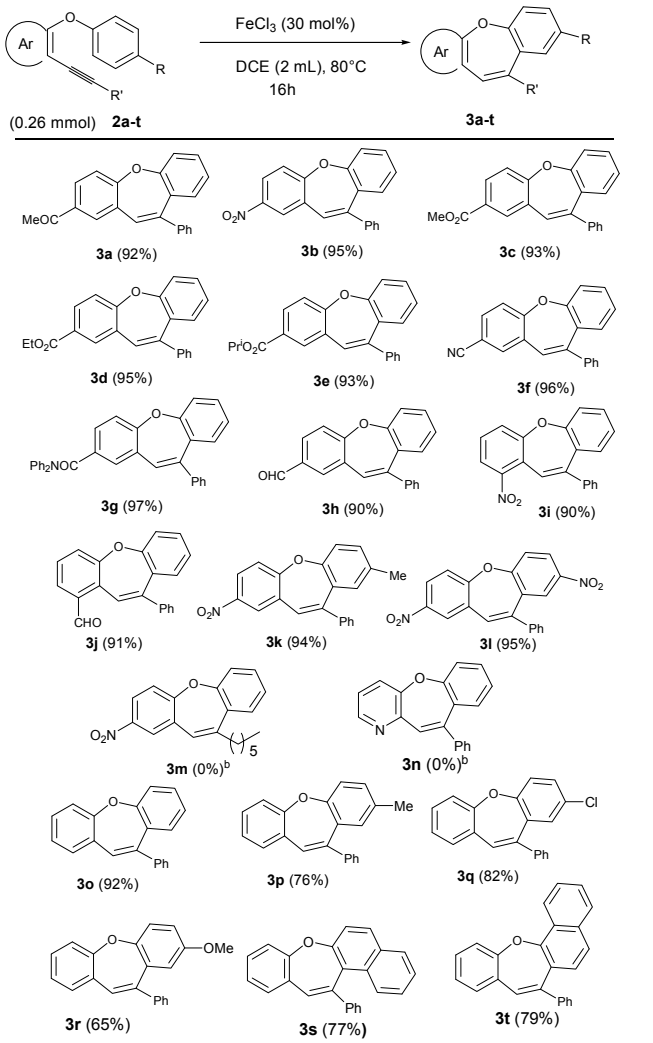


Entry	catalyst (mol%)	solvent	GC yield of **3a** (%)
1	$Pd(OAc)_2$ (10)	DCE	nr
2	CuI (30)	DCE	nr
3	AgOAc (100)	DCE	nr
4	$ZnCl_2$ (100)	DCE	nr
5	$Ni(OAc)_2$ (30)	DCE	nr
6	$FeCl_3$ (100)	DCE	62[b]
7	$FeCl_3$ (100)	DCE	91[c]
8	$FeCl_3$ (50)	DCE	92[d]
9	$FeCl_3$ (30)	DCE	92
10	$FeCl_3$ (20)	DCE	72
11	$Fe(NO_2)_3$ (30)	DCE	10
12	$Fe(acac)_3$(30)	DCE	nr
13	$FeSO_4$ (30)	DCE	nr
14	$FeCl_3$ (30)	toluene	30
15	$FeCl_3$ (30)	1,4-dioxane	nr
16	$FeCl_3$ (30)	CH_3CN	nr
17	$FeCl_3$ (30)	water	nr

[a]Reaction conditions: **2a** (0.26 mmol), catalyst in 3mL of solvent, 80°C. [b] Reaction was carried at room temperature. [c] Heated for 3h. [d] Heated for 8h.

With the optimum reaction conditions in hand, we sought to probe the scope and generality of this protocol for dibenzo[*b,f*]oxepines synthesis (Table 2). It may be mentioned here that the *ortho*-substituted diaryl ethers with various electron-donating and –withdrawing substituents are compatible to the $FeCl_3$-catalyzed cyclization to enable a series of tricyclic dibenzo[*b,f*]oxepines in good to excellent yield with complete consumption of starting material (Scheme 3). Crystallization of 2-nitro-9-phenyl dibenzo[*b,f*]oxepines (**3b**) in CH_2Cl_2 gave a crystal whose molecular structure was confirmed by X-ray single-crystal diffraction (Figure 2).[25] Unfortunately, the reaction of **2m** and **2t** did not afford any tricyclic product even at a higher temperature (110°C) with the recovery of starting material quantitatively.

Scheme 3. Synthesis of dibenzo[*b,f*]oxepines[a]



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[a]Reaction conditions: A mixture of 2 (0.26 mmol) and 13 mg (30 mol %) of $FeCl_3$ in DCE (3 mL), was heated at 80°C for 16 h.

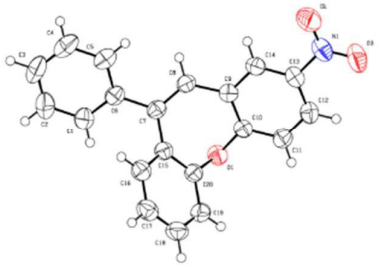
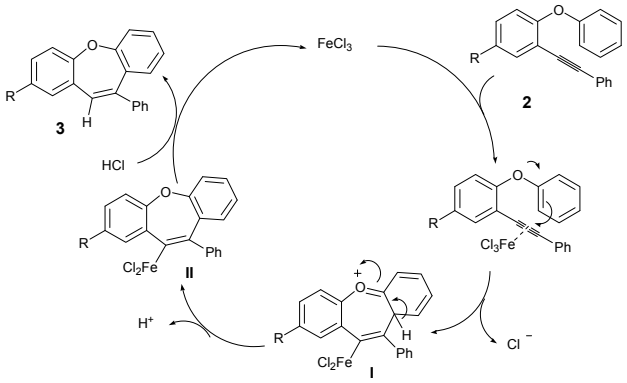


Figure 2. ORTEP diagram of **3b**.[25]

A plausible mechanism for the intramolecular annulation reaction was shown in Scheme 4. It may be believed that the reaction proceeds with initial carbometalation to afford the vinyl carbocationic intermediate **I**, which subsequently undergo oxygen-induced intramolecular Friedel-crafts type *7-endo-dig* annulation to afford the intermediate **II**. Finally, protonation by the in-situ generated HCl led to the annulated product and the catalyst for the subsequent cycle.

Scheme 4. Plausible mechanism

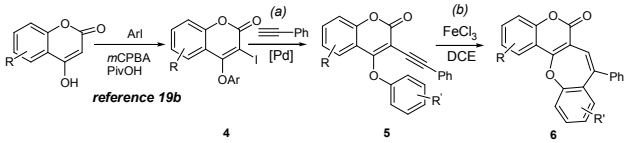


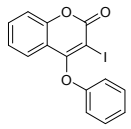
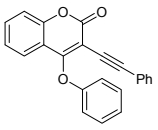
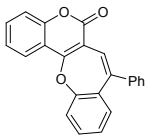
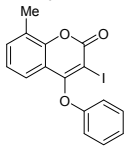
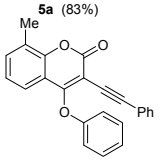
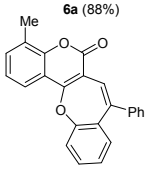
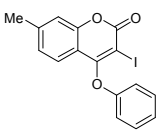
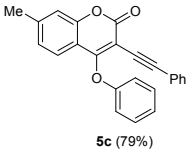
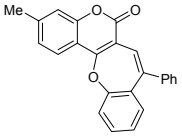
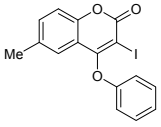
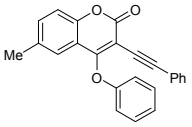
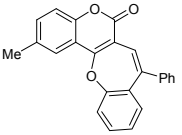
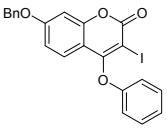
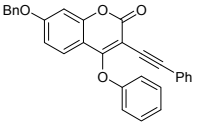
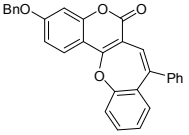
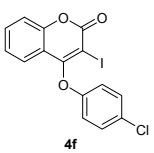
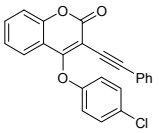
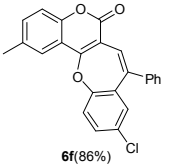
Next, we turned our attention for the synthesis of seven-membered rings fused with coumarin. Notably the coumarins are plant products and exhibit interesting biological properties. As can be seen from Table 2, several coumarin 3-iodophenoxy coumarins (**4**) were prepared following the procedure reported earlier by us from the reaction of 4-hydroxy coumarins and aryl iodide in the presence of mCPBA and PivOH.[19b] Further, Sonogashira coupling of phenyl acetylene with **4** led to the phenoxyacetylene derivatives **5** in appreciable yield (70-83%). Unlike, Kitamura and Taniguchi's report the acid-mediated annulation of **5** did not afford the desired product with complete decomposition of starting material. To our delight, our iron-catalyzed hydroarylation procedure was found to be effective to afford coumarin fused seven-membered rings in good yield from **5** at 80°C in DCE over a period of 12h.

Conclusions

In summary, we have developed a simple strategy for the *7-endo-dig* intramolecular annulation of *o*-phenoxy diarylacetylenes in the presence of commercially viable, cheap and environmentally benign iron catalyst under mild reaction conditions. This reaction believed to proceeds with sequential carbometallation followed by protonation to afford a series of phenyldibenz[*b,f*]oxepines. The scope of this intramolecular annulation through Friedel-Crafts type reaction was extended to coumarin-fused seven-membered rings.

Table 2. Synthesis of coumarin-fused oxepines



Entry	4	5 (% yield)	6 (% yield)
1		 **5a** (83%)	 **6a** (88%)
2	 **4b**	 **5b** (82%)	 **6b** (86%)
3	 **4c**	 **5c** (79%)	 **6c** (83%)
4	 **4d**	 **5d** (80%)	 **6d** (87%)
5	 **4e**	 **5e** (70%)	 **6e**(90%)
6	 **4f**	 **5f** (75%)	 **6f**(86%)

Reaction conditions: a) **1** (0.29 mmol), $PdCl_2(PPh_3)_2$ (4 mol%), CuI (2 mol%), alkyne (0.42 mmol, 1.5 equiv.) in 3 mL of triethyl amine was stirred at 60°C. b) A mixture of **5** (0.26 mmol) and 13 mg (30 mol %) of $FeCl_3$ in DCE (3 mL), was heated at 80°C for 16 h.

Experimental

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General information

Unless otherwise noted, the reagents (chemicals) were purchased from commercial sources and used without further purification. The reactions were monitored by TLC, and the residue was chromatographed on silica gel (Ranchem, India), using an ethyl acetate–petroleum ether (60–80°C) mixture as eluent. All NMR spectra were recorded on a 400 MHz (for ^{1}H NMR) and 100 MHz (for ^{13}C NMR) NMR spectrometer, and chemical shifts were expressed in δ units relative to the TMS signal as an internal reference in $CDCl_3$. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet, when multiplicity is complex) for ^{1}H NMR. Coupling constants, *J* were reported in Hz. High-resolution mass spectrometry (ESI-HRMS) (Agilent 6520 Q-TOF) was used to determine the elemental composition.

General procedure for the synthesis of phenoxy(phenylethynyl) benzene (2 & 5)

A mixture of *ortho*-iododiaryl ether **1** (0.29 mmol), $PdCl_2(PPh_3)_2$ (4 mol%), CuI (2 mol%), phenyl acetylene (0.42 mmol, 1.5 equiv.) in 3 mL of triethyl amine was stirred at 60°C. The progress of the reaction was monitored by TLC. After 12 h, the reaction mixture was quenched with water (20 mL) and then extracted with dichloromethane (3 × 15 mL). The combined organic layer was washed with dilute HCl (10%) solution (2 × 10 mL). Then, the solvent was removed under reduced pressure, and the crude reaction mixture was purified by column chromatography over silica gel (60-120 mesh) using mixture of ethyl acetate and petroleum ether as eluent to get the desired alkynes (**1a-n**)

General procedure for the $FeCl_3$-catalyzed synthesis of oxepines (3 & 6)

To a mixture of *phenoxy(phenylethynyl) benzene* (**2**) (0.26 mmol) in DCE (3 mL), 13 mg (30 mol%) of $FeCl_3$ was added and the reaction mixture was heated at 80°C for 16 h. After completion of the reaction (monitored by GC), it was cooled to room temperature and poured into water (10 mL). Then the product was extracted with dichloromethane (3 × 15 mL) and dried over anhydrous sodium sulfate. Then, solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography over silica gel (60-120 mesh) using a mixture of ethyl acetate and petroleum ether as eluent to afford the oxepines (**3**) in 80-97% yield.

1-(4-Phenoxy-3-(phenylethynyl)phenyl)ethanone (2a)

Colourless crystal (79% yield), m. p. 78-80°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, 1H, *J* = 2.1 Hz), 7.88 (dd, 1H, J_1=8.7 Hz, J_2=2.2 Hz), 7.47-7.38 (m, 4H), 7.37 – 7.31 (m, 3H), 7.22 (t, 1H, *J* = 7.4 Hz), 7.13 (d, 2H, *J* = 7.8 Hz), 6.92 (d, 1H, *J* = 8.7 Hz), 2.62 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 161.5, 155.7, 134.3, 131.9, 131.6, 129.9, 129.7, 128.4, 128.2, 124.3, 122.7, 119.5, 117.1, 114.9, 94.8, 84.1, 26.4. HRMS (ESI) calcd. for $C_{22}H_{17}O_2$ $[M+H]^+$ 313.1229; found 313.1225.

4-Nitro-1-phenoxy-2-(phenylethynyl)benzene (2b)

White solid (84% yield), m. p. 74-76°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51-8.46 (m, 1H), 8.14-8.07 (m, 1H), 7.55-7.49 (m, 2H), 7.51-7.43 (m, 2H), 7.40-7.34 (m, 3H), 7.32-7.26 (m, 1H), 7.19-7.12 (m, 2H), 6.91-6.85 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.0, 142.4, 137.4, 131.8, 130.2, 129.2, 129.0, 128.4, 125.3, 124.9, 122.3, 120.2, 116.3, 115.3, 96.1, 83.0. HRMS (ESI) calcd. for $C_{20}H_{14}NO_3^+$ $[M+H]^+$ 316.0974; found 316.0967.

Methyl 4-phenoxy-3-(phenylethynyl)benzoate (2c)

Colourless oil (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, 1H, *J* = 2.1 Hz), 7.95 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.2 Hz), 7.49 – 7.38 (m, 4H), 7.37-7.30 (m, 3H), 7.21 (t, 1H, *J* = 7.4 Hz), 7.15 – 7.10 (m, 2H), 6.92 (d, 1H , *J* = 8.7 Hz,), 3.95 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 161.3, 155.8, 135.3, 131.5, 130.9, 129.8, 128.3, 128.1, 124.8, 124.1, 122.8, 119.4, 117.2, 115.0, 94.7, 84.1, 52.0. HRMS (ESI) calcd. for $C_{22}H_{17}O_3^+$ $[M+H]^+$ 329.1178; found 329.1173.

Ethyl 4-phenoxy-3-(phenylethynyl)benzoate (2d)

Colourless oil (71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.95 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2 Hz), 7.49 – 7.38 (m, 4H), 7.36-7.27 (m, 3H), 7.21 (t, 1H, *J* = 6.8 Hz), 7.14 – 7.08 (m, 2H), 6.91 (d, 1H , *J* = 8.4 Hz,), 4.45 - 4.35 (m, 2H) , 1.42 (t, 3H , *J* = 7.2 Hz,), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.3, 156.0, 135.3, 131.7, 131.0, 129.9, 128.5, 128.2, 125.2, 124.2, 122.9, 119.5, 117.3, 115.0, 94.8, 84.3, 61.1, 14.3. HRMS (ESI) calcd. for $C_{23}H_{19}O_3^+$ $[M+H]^+$ 343.1334; found 343.1329.

Isopropyl 4-phenoxy-3-(phenylethynyl)benzoate (2e)

Colourless oil (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, 1H, *J* = 1.9 Hz), 7.96 (dd,1H, J_1 = 8.7 Hz, J_2 = 2.0 Hz), 7.45 – 7.32 (m, 7H), 7.20 (t, 1H, *J* = 7.3 Hz), 7.13 (d,2H, *J* = 13.9 Hz), 6.93 (d, 1H, *J* = 8.7 Hz), 5.33-5.23 (m, 1H), 1.41 (s, 3H), 1.40 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 161.1, 156.0, 135.1, 131.5, 130.9, 129.8, 128.3, 128.1, 125.6, 124.0, 122.8, 119.2, 117.4, 114.9, 94.7, 84.2, 68.4, 21.8. HRMS (ESI) calcd. for $C_{24}H_{21}O_3^+$ $[M+H]^+$ 357.1491; found 357.1495.

4-Phenoxy-3-(phenylethynyl)benzonitrile (2f)

White solid (87% yield), m. p. 82-84°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 1H, *J*=2 Hz), 7.55-7.41 (m, 5H), 7.39-7.33 (m, 3H), 7.30-7.22 (m, 1H), 7.16-7.10 (m, 2H), 6.91-6.87 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 155.1, 137.4, 133.1, 131.8, 130.2, 128.9, 128.3, 125.0, 122.4, 120.0, 118.3, 117.5, 116.1, 106.4, 96.2, 82.9. HRMS (ESI) calcd. for $C_{21}H_{14}NO^+$ $[M+H]^+$ 296.1075; found 296.1069.

4-phenoxy-N,N-diphenyl-3-(phenylethynyl)benzamide (2g)

White powder (78% yield) , m. p. 86-88°C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 1H, *J* = 2.1 Hz), 7.42 – 7.28 (m, 12H), 7.28 – 7.13 (m, 7H), 7.02 (d, 2H, *J* = 8.2 Hz), 6.73 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 158.7, 156.2, 143.7, 134.9, 131.5, 130.9, 130.5, 129.7, 129.1, 128.3, 128.1, 127.3, 126.4, 123.7, 122.8, 118.9, 117.3, 115.0, 94.6, 84.2. HRMS (ESI) calcd. for $C_{33}H_{24}NO_2^+$ $[M+H]^+$ 466.1807; found 466.1802.

4-Phenoxy-3-(phenylethynyl)benzaldehyde (2h)

Colourless oil (70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.13 (d, 1H, *J* = 2.0 Hz), 7.79 (dd, 1H, J_1 = 8.6 Hz, J_2=2.0 Hz), 7.52 – 7.40 (m, 4H), 7.39 – 7.32 (m, 3H), 7.26 (t, 1H, *J* = 6.5 Hz), 7.15 (d, 2H, *J* = 7.9 Hz), 6.96 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 162.7, 155.3, 135.7, 131.6, 131.2, 130.6, 129.9, 128.5, 128.2, 124.6, 122.6, 119.8, 117.1, 115.4, 95.2, 83.7. HRMS (ESI) calcd. for $C_{21}H_{15}O_2^+$ $[M+H]^+$ 299.1072; found 299.1080.

1-Nitro-3-phenoxy-2-(phenylethynyl)benzene (2i)

White crystalline solid (71% yield), m. p. 108-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, 1H, *J* = 2.7 Hz), 8.63 (d, 1H, *J* = 2.8 Hz), 7.42 – 7.32 (m, 4H), 7.32 - 7.28 (m, 2H), 7.22 - 7.11 (m, 3H), 7.04 – 6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.0, 144.0, 143.1, 131.7, 131.6, 129.7, 129.6, 128.2, 123.8, 122.1, 120.8, 119.8, 116.2, 100.9, 81.3. HRMS (ESI) calcd. for $C_{20}H_{14}NO_3^+$ $[M+H]^+$ 316.0968; found 316.0965.

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DOI: 10.1039/C8OB01496E

4-Nitro-2-(phenylethynyl)-1-(p-tolyloxy)benzene (2k)

Gummy oil (76 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, 1H, *J* = 2.7 Hz), 8.09 (dd, 1H, J_1 = 9.1 Hz, J_2 = 2.7 Hz), 7.58 - 7.51 (m, 2H), 7.40 – 7.35 (m, 4H), 7.27 (d, 2H, *J* = 8.4 Hz), 7.05 (d, 2H, *J* = 8.4 Hz), 6.84 (d, 1H, *J* = 9.2 Hz), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 152.5, 142.0, 135.1, 131.7, 130.6, 129.1, 128.8, 128.2, 124.8, 122.3, 120.1, 115.5, 114.8, 95.8, 83.0, 20.7. HRMS (ESI) calcd. for $C_{21}H_{15}NNaO_3^+$ $[M+Na]^+$ 352.0950; found 352.0960.

4-Nitro-1-(4-nitrophenoxy)-2-(phenylethynyl)benzene (2l)

Brown solid (69 % yield), m. p. 98-100°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, 1H, *J* = 2.3 Hz), 8.30 (d, 2H, *J* = 9.1 Hz), 8.25 (dd, 1H, J_1=9.0 Hz, J_2=2.7 Hz), 7.41 – 7.30 (m, 5H), 7.22 (d, 1H, *J* = 9.0 Hz), 7.17 (dd, 2H, J_1=9.8 Hz, J_2=2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 159.7, 144.3, 143.7, 131.5, 129.3, 129.2, 128.3, 126.0, 124.9, 121.5, 120.3, 118.0, 117.6, 97.7, 82.0. HRMS (ESI) calcd. for $C_{20}H_{13}N_2O_5^+$ $[M+H]^+$ 361.0824; found 361.0818.

1-(3-(Oct-1-yn-1-yl)-4-phenoxyphenyl)ethanone (2m)

Red oil (77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, 1H, *J* = 2.2 Hz), 7.81 (dd, 1H, J_1=8.7 Hz, J_2=2.2 Hz), 7.42-7.34 (m, 2H), 7.18 (t, 1H *J* = 7.4 Hz), 7.11 – 7.02 (m, 2H), 6.86 (d, 1H, *J* = 8.7 Hz), 2.58 (s, 3H), 2.41 (t, 2H, *J* = 7.0 Hz), 1.59-1.51 (m, 2H), 1.46 – 1.38 (m, 2H), 1.32 - 1.26 (m, 4H), 0.89 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 161.6, 155.8, 134.3, 131.8, 129.7, 128.9, 124.1, 119.4, 117.1, 115.7, 96.4, 75.2, 51.4, 31.2, 28.3, 26.3, 22.4, 19.5, 13.9. HRMS (ESI) calcd. for $C_{20}H_{22}NO_3^+$ $[M+H]^+$ 324.1600; found 324.1606..

4-phenoxy-3-(2-phenylethynyl)pyridine (2n)

White crystalline solid (89% yield), m. p. 77°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.36 (d, 1H, *J* = 5.6 Hz), 7.56 - 7.52 (m, 2H), 7.47 (t, 2H, *J* = 8 Hz), 7.38 – 7.35 (m, 3H), 7.31 – 7.27 (m, 1H), 7.18-7.7.16 (m, 2H), 6.66 (d, 1H, *J* = 6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 154.4, 154.2, 150.1, 131.7, 130.2, 128.7, 128.3, 125.5, 122.7, 120.7, 111.3, 110.4, 96.5. HRMS (ESI) calcd. for $C_{19}H_{14}NO^+$ $[M+H]^+$ 272.1072; found 272.1075.

1-Phenoxy-2-(phenylethynyl)benzene (2o)

White crystalline solid (68% yield), m. p. 82-84°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.41 – 7.27 (m, 8H), 7.20-7.07 (m, 2H), 7.09 – 7.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.0, 133.5, 132.4, 131.4, 129.6, 129.5, 128.3, 128.1, 128.0, 123.5, 122.8, 119.6, 118.0, 94.3, 85.0. HRMS (ESI) calcd. for $C_{20}H_{15}O^+$ $[M+H]^+$ 271.1123; found 271.1125.

1-(*p*-Tolyloxy)-2-(2-phenylethynyl)benzene (2p)

Gummy liquid (87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.45 – 7.41 (m, 2H), 7.34-7.29 (m, 4H), 7.19 – 7.09 (m, 3H), 6.99-6.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.0, 133.6, 132.7, 131.6, 130.1, 129.6, 128.2, 123.3, 123.2, 118.8, 118.5, 115.5, 94.1, 85.3, 20.7. HRMS (ESI) calcd. for $C_{21}H_{17}O^+$ $[M+H]^+$ 285.1274; found 285.1279.

1-(4-Chlorophenoxy)-2-(2-phenylethynyl)benzene (2q)

Gummy liquid (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.38 – 7.29 (m, 8H), 7.21 - 7.18 (m, 1H), 7.05 – 7.01 (m, 1H), 6.99-6.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 156.2, 133.7, 131.5, 129.8, 129.6, 128.4, 128.2, 127.8, 124.2, 123.0, 119.9, 119.1, 116.2, 94.7, 84.8. HRMS (ESI) calcd. for $C_{20}H_{14}ClO^+$ $[M+H]^+$ 305.0728; found 305.0725.

1-(4-Methoxyphenoxy)-2-(2-phenylethynyl)benzene (2r)

Gummy liquid (90 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.49-7.44 (m, 2H), 7.34-7.30 (m, 3H), 7.29 – 7.24 (m, 1H), 7.12-7.01 (m, 3H), 6.94-6.87 (m, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.1, 152.4, 142.2, 142.0, 132.6, 130.5, 129.6, 129.5, 128.9, 128.5, 128.4, 127.8, 124.7, 122.0, 120.6, 115.3, 115.1, 55.6. HRMS (ESI) calcd. for $C_{21}H_{17}O_2^+$ $[M+H]^+$ 31.1223; found 301.1227.

2-(2-(2-Phenylethynyl)phenoxy)naphthalene (2s)

Gummy liquid (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, 2H, *J* = 8.8 Hz), 7.72 (d, 1H, *J* = 7.6 Hz), 7.65 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.48 – 7.41 (m, 2H), 7.39-7.18 (m, 10H), 7.08 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.3, 134.3, 133.7, 131.5, 130.0, 129.7, 128.2, 127.7, 127.1, 126.5, 124.5, 123.8, 123.1, 119.9, 119.5, 116.2, 113.2, 94.4, 85.0. HRMS (ESI) calcd. for $C_{24}H_{17}O^+$ $[M+H]^+$ 321.1274; found 321.1278.

1-(2-(2-phenylethynyl)phenoxy)naphthalene (2t)

Gummy liquid (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, 1H, J = 7.2 Hz), 7.93 (d, 1H, *J* = 7.6 Hz), 7.69 - 7.63 (m, 2H), 7.61-7.58 (m, 2H), 7.41 (t, 1H, *J* = 7.6 Hz), 7.36 - 7.32 (m, 1H), 7.27-7.11 (m, 6H), 7.04 (d, *J* = 8 Hz), 6.93 (d, 1H, 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.4, 134.9, 133.6, 131.5, 129.7, 128.2, 128.1, 127.7, 126.6, 126.5, 126.0, 125.8, 123.6, 123.0, 122.3, 119.4, 115.8, 112.3, 94.4, 85.0. HRMS (ESI) calcd. for $C_{24}H_{17}O^+$ $[M+H]^+$ 321.1274; found 321.1278.

1-(10-Phenyldibenzo[*b,f*]oxepin-2-yl)ethanone (3a)

White solid (92% yield), m. p. 96-98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.52-7.46 (m, 2H), 7.48-7.42 (m, 3H), 7.44-7.34 (m, 1H), 7.34-7.27 (m, 2H), 7.13-7.05 (m, 1H), 7.03-6.97 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 161.4, 157.8, 143.1, 141.9, 133.9, 131.6, 130.7, 130.5, 130.4, 130.0, 129.6, 128.7, 128.3, 127.9, 127.3, 124.9, 121.4, 121.1, 26.5. HRMS (ESI) calcd. for $C_{22}H_{17}O_2^+$ $[M+H]^+$ 313.1229; found 313.1232.

2-Nitro-10-phenyldibenzo[*b,f*]oxepine (3b)

Colourless crystal (95 % yield), m. p. 122-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.14 (m, 2H), 7.51-7.39 (m, 6H), 7.41 - 7.27 (m, 2H), 7.16 - 6.98 (m, 2H), 6.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 157.6, 144.8, 144.6, 141.5, 131.7, 131.4, 130.9, 130.8, 128.8, 128.5, 128.4, 126.1, 125.4, 125.0, 124.6, 121.8, 121.5. HRMS (ESI) calcd. for $C_{20}H_{14}NO_3^+$ $[M+H]^+$ 316.0974; found 316.0969.

Methyl 10-phenyldibenzo[*b,f*]oxepine-2-carboxylate (3c)

Colourless oil (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.56 – 7.34 (m, 6H), 7.33 – 7.26 (m, 2H), 7.12 – 7.05 (m, 1H), 7.04 – 6.94 (m, 2H), 3.94 (s, 3H); 166.2, 161.3, 157.8, 142.9, 141.9, 131.3, 130.8, 130.6, 130.5, 130.3, 128.8, 128.3, 127.9, 127.3, 126.8, 124.8, 121.4, 120.9, 120.2, 52.1. HRMS (ESI) calcd. for $C_{22}H_{17}O_3^+$ $[M+H]^+$ 329.1178; found 329.1175.

Ethyl 10-phenyldibenzo[*b,f*]oxepine-2-carboxylate (3d)

Colourless oil (95 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.55 – 7.25 (m, 8H), 7.14 – 7.06 (m, 1H), 7.03-6.98 (m, 2H), 4.45-4.36 (m, 2H), 1.43 (t, 3H, *J* = 7.1 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 161.2,

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DOI: 10.1039/C8OB01496E

157.9, 142.9, 142.0, 131.6, 131.2, 130.8, 130.6, 130.5, 130.3, 128.8, 128.3, 127.9, 127.4, 127.1, 124.8, 121.4, 120.9, 61.0, 14.2. HRMS (ESI) calcd. for $C_{23}H_{19}O_3^+$ $[M+H]^+$ 343.1334; found 343.1330.

Isopropyl 10-phenyldibenzo[*b,f*]oxepine-2-carboxylate (3e)

Gummy liquid (93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.53-7.33(m, 6H), 7.34 - 7.26 (m, 2H), 7.12-7.04 (m, 1H,), 7.03-6.98 (m, 2H), 5.33-5.22 (m, 1H), 1.40 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 161.2, 157.9, 142.8, 142.0, 131.6,131.1, 130.8, 130.5, 130.5, 130.3, 128.8, 128.3, 127.9, 127.5, 127.4, 124.8, 121.4, 120.8, 68.4, 21.8. HRMS (ESI) calcd. for $C_{24}H_{21}O_3^+$ $[M+H]^+$ 357.1491; found 357.1495.

10-Phenyldibenzo[*b,f*]oxepine-2-carbonitrile (3f)

White crystalline solid (96% yield), m. p. 140 - 142°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2H), 7.48 - 7.37 (m, 5H), 7.40 - 7.36 (m, 1H), 7.36 - 7.28 (m, 2H), 7.15 - 7.09 (m, 1H), 7.11 - 6.99 (m, 1H), 7.01 - 6.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 157.8, 144.5, 141.6, 133.5, 133.0, 132.1, 131.4, 130.8, 130.8, 128.8, 128.5, 128.3, 125.9, 125.3, 122.2, 121.5, 118.3, 108.9. HRMS (ESI) calcd. for $C_{21}H_{14}NO^+$ $[M+H]^+$ 296.1075; found 296.1071.

N,N, 10-triphenyldibenzo[*b,f*]oxepine-2-carboxamide (3g)

Red solid (97% yield), m. p. 138-140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 1H, *J* = 2.0 Hz), 7.47 – 7.39 (m, 5H), 7.37 – 7.30 (m, 6H), 7.23-7.15 (m, 7H), 7.11 – 7.01 (m, 2H), 6.97 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.5 Hz), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 159.0, 158.0, 143.9, 142.8, 142.2, 132.7, 131.8, 131.2, 130.5, 130.4, 130.3, 129.2, 128.9, 128.4, 127.9, 127.4, 126.4, 124.8, 121.5, 120.3. HRMS (ESI) calcd. for $C_{33}H_{24}NO_2^+$ $[M+H]^+$ 466.1807; found 466.1805.

10-Phenyldibenzo[*b,f*]oxepine-2-carbaldehyde (3h)

White powder (90% yield), m. p. 130-132°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.88-7.82 (m, 2H), 7.52-7.43 (m, 5H), 7.45-7.35 (m, 2H), 7.34 -7.28 (m, 1H), 7.14-7.06 (m, 1H), 7.04-6.96 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 162.4, 157.6, 143.5, 141.7, 133.5, 131.5, 131.4, 131.3, 130.8, 130.6, 130.5, 128.7, 128.4, 128.0, 126.8, 125.0, 121.7, 121.5. HRMS (ESI) calcd. for $C_{21}H_{15}O_2^+$ $[M+H]^+$ 299.1072; found 299.1080.

1-Nitro-10-phenyldibenzo[*b,f*]oxepine (3i)

Yellow crystalline solid (90% yield), m. p. 156-158°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, 1H, *J* = 2.7 Hz), 8.36 (d, 1H, *J* = 2.6 Hz), 7.55 – 7.43 (m, 8H), 7.21 – 7.13 (m, 1H), 7.02 – 6.97 (m, 1H), 6.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 146.8, 140.7, 135.0, 131.6, 130.9, 130.7, 129.7, 128.8, 128.6, 128.5, 128.2, 127.4, 126.1, 124.6, 122.1, 118.8, 116.2. HRMS (ESI) calcd. for $C_{20}H_{14}NO_3^+$ $[M+H]^+$ 316.0968; found 316.0964.

10-Phenyldibenzo[*b,f*]oxepine-1-carbaldehyde (3j)

Pale yellow oil (91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.84 (s, 1H), 7.70-7.58 (m, 1H), 7.56-7.49 (m, 2H), 7.51-7.44 (m, 6H), 7.46-7.29 (m, 1H), 7.16-7.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 159.7, 158.7, 143.9, 142.0, 134.0, 131.8, 131.2, 130.5, 130.4, 130.3, 129.0, 129.0, 128.3, 128.1, 126.1, 125.0, 124.9, 120.9. HRMS (ESI) calcd. for $C_{21}H_{15}O_2^+$ $[M+H]^+$ 299.1072; found 299.1067.

8-Methyl-2-nitro-10-phenyldibenzo[*b,f*]oxepine (3k)

White crystalline solid (94% yield), m. p. 94 - 96°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.13 (m, 2H), 7.50-7.41 (m, 5H), 7.34 (d, 1H, *J* = 8.4 Hz,), 7.19 (s, 2H), 6.92 (s, 1H), 6.79 (s, 1H,), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 155.4, 144.6, 144.6, 141.4, 134.9, 131.6, 131.5, 130.8, 128.7, 128.4, 128.2, 125.9, 124.9, 124.4, 121.6, 121.1, 20.6. HRMS (ESI) calcd. for $C_{21}H_{15}NNaO_3^+$ $[M+Na]^+$ 352.0950; found 352.0961.

2,8-Dinitro-10-phenyldibenzo[*b,f*]oxepine (3l)

White crystalline solid (95% yield), m. p. 152-154°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.18 (m, 3H), 7.89 (d, 1H, *J* = 2.7 Hz), 7.45-7.34 (m, 7H), 7.38 (d, 1H, *J* = 9.6 Hz), 7.05 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.1, 145.3, 142.8, 140.1, 132.6, 130.9, 129.0, 128.9, 128.4, 127.8, 126.1, 125.7, 125.1, 125.0, 123.1, 122.6, 121.8. HRMS (ESI) calcd. for $C_{20}H_{13}N_2O_5^+$ $[M+H]^+$ 361.0824; found 361.08120.

10-Phenyldibenzo[*b,f*]oxepine (3o)[12b]

Colourless oil (92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.45 – 7.29 (m, 8H), 7.21 – 7.15 (m, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 157.8, 142.3, 142.1, 132.4, 130.3, 130.0, 129.4, 129.1, 128.8, 128.3, 128.2, 128.1, 127.6, 124.7, 124.5, 121.4, 120.7.

2-Methyl-10-phenyldibenzo[*b,f*]oxepine (3p)

White crystalline solid (76% yield), m. p. 102°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.48 (m, 2H), 7.47-7.39 (m, 3H), 7.33-7.29 (m, 3H), 7.26-7.23 (m, 1H), 7.21-7.12 m, 3H), 6.95 (s, 1H), 6.77 (s, 1H, 2.2 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.5, 142.5, 142.2, 134.1, 131.5, 130.8, 130.7, 130.6, 129.5, 129.4, 128.9, 128.3, 128.2, 127.7, 124.7, 121.1, 120.7, 20.7); HRMS (ESI) calcd. for $C_{21}H_{17}O^+$ $[M+H]^+$ 285.1274; found 285.1279.

2-Chloro-10-phenyldibenzo[*b,f*]oxepine (3q)

White crystalline solid (82% yield), m. p. 105 - 106°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 5H), 7.37-7.29 (m, 3H), 7.26-7.16 (m, 3H), 7.00 (s, 1H), 6.95 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.9, 141.7, 141.1, 133.6, 130.3, 130.0, 129.9, 129.8, 129.7, 129.2, 128.8, 128.6, 125.1, 122.8, 120.7. HRMS (ESI) calcd. for $C_{20}H_{14}ClO^+$ $[M+H]^+$ 305.0728; found 305.0725.

2-Methoxy-10-phenyldibenzo[*b,f*]oxepine (3r)

White crystalline solid (65% yield), m. p. 110 - 112°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.46-7.39 (m, 3H), 7.33 - 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 - 7.15 (m 1H), 6.98 (s, 1H), 6.91- 6.86 (m, 1H), 6.49 (d, 1H, *J* = 2.8 Hz), 3.64 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 158.1, 156.1, 152.4, 142.2, 142.0, 132.6, 130.5, 129.6, 129.5, 128.9, 128.5, 128.4, 127.8, 124.7, 122.0, 120.6, 115.3, 115.1, 55.6. HRMS (ESI) calcd. for $C_{21}H_{17}O_2^+$ $[M+H]^+$ 31.1223; found 301.1229.

11-Phenyl benzo[*b*]naphth[1,2-*f*]oxepin (3s)

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DOI: 10.1039/C8OB01496E

White solid (77% yield), m.p. 96 - 97°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, 1H, *J* = 8.8 Hz), 7.77 (d, 1H, *J* = 8 Hz), 7.51 (d, 1H, *J* = 8 Hz),7.43-7.26 (m, 11H), 7.20 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 159.1, 143.5, 141.5, 132.0, 131.9, 131.1, 131.0, 130.4, 129.3, 129.2, 128.7, 128.1, 127.45, 127.40, 127.0, 125.5, 124.97, 124.92, 124.5, 121.0, 120.5. HRMS (ESI) calcd. for $C_{24}H_{17}O^+$ $[M+H]^+$ 321.1274; found 321.1279.

12-Phenyl benzo[*b*]naphth[2,1-*f*]oxepin (3t)

Gummy liquid (79% yield); 8.74 (d, 1H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 8.0 Hz), 7.67 (t, 1H, *J* = 7.6 Hz), 7.59-7.47 (m, 4H), 7.46-7.7.34 (m, 6H), 7.20-7.16 (m, 2H), 7.07 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 153.4, 142.7, 142.3, 134.9, 131.2, 129.7, 129.5, 128.9, 128.7, 128.4, 127.8, 127.6, 127.5, 127.3, 126.8, 126.7, 126.6, 124.9, 123.8, 122.8, 121.1. HRMS (ESI) calcd. for $C_{24}H_{17}O^+$ $[M+H]^+$ 321.1274; found 321.1278.

4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5a)

White crystalline solid (83% yield), m. p. 84-86°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.67-7.59 (m, 1H), 7.46 - 7.31 (m, 4H), 7.29-7.18 (m, 4H), 7.20-7.13 (m, 2H), 7.11 - 7.05 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.1, 155.2, 152.2, 132.9, 131.5, 129.6, 128.5, 127.8, 124.5, 124.3, 123.6, 122.1, 117.9, 116.7, 116.5, 103.0, 99.1, 79.6. HRMS (ESI) calcd. for $C_{23}H_{15}O_3^+$ $[M+H]^+$ 339.1021; found 339.1015.

8-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5b)

White crystalline solid (82% yield), m. p. 128-130°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 1H, *J* = 8.0 Hz), 7.47 (d, 1H, *J* = 7.3 Hz), 7.43-7.35 (m, 2H), 7.28 – 7.12 (m, 7H), 7.10 (dd, 2H, J_1=8.1 Hz, J_2=1.4 Hz), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.1, 155.4, 150.6, 134.3, 131.6, 129.6, 128.5, 127.8, 126.2, 124.1, 124.0, 122.2, 121.3, 117.7, 116.3, 102.8, 99.1, 79.8, 15.5. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1172.

7-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5c)

White crystalline solid (79% yield), m. p. 94-96°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, *J* = 6.9 Hz), 7.46 (d, 1H, *J* = 6.7 Hz), 7.39-7.35 (m, 3H), 7.27 – 7.02 (m, 13H), 2.69 (s, 1H), 2.50 (s, 3H). ; ^{13}C NMR (100 MHz, $CDCl_3$) δ13C NMR (101 MHz, CDCl3) δ 163.5, 162.2, 155.3, 154.7, 153.7, 152.3, 144.5, 136.9, 132.2, 131.5, 131.5, 129.7, 129.6, 128.6, 128.4, 128.2, 127.8, 127.8, 125.8, 124.2, 123.7, 123.3, 122.3, 117.8, 116.8, 116.8, 115.2, 114.0, 105.0, 102.8, 102.5, 98.0, 79.8, 77.2, 76.9, 76.6, 22.8, 21.7. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1170.

6-methyl-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5d)

White crystalline solid (80% yield), m. p. 102-104°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.45 – 7.36 (m, 3H), 7.33 – 7.19 (m, 5H), 7.16 (d, 2H, *J* = 7.9 Hz), 7.07 (d, 2H, *J* = 6.8 Hz), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.2, 155.2, 150.4, 134.4, 134.0, 131.5, 129.6, 128.5, 127.8, 124.3, 123.2, 122.2, 117.8, 116.4, 116.2, 103.0, 99.0, 79.8, 20.8. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1172.

7-(benzyloxy)-4-phenoxy-3-(phenylethynyl)-2H-chromen-2-one (5e)

White crystalline solid (70% yield), m. p. 138-140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 1H, *J* = 8.5 Hz), 7.50 – 7.35 (m, 7H), 7.27 – 7.11 (m, 6H), 7.09 – 7.04 (m, 2H), 7.01 – 6.95 (m, 2H), 5.19 (s, 2H). ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 162.8, 161.7, 155.2, 154.1, 135.4, 131.4, 129.6, 128.7, 128.3, 128.3, 127.8, 127.4, 124.9, 124.2, 122.3, 117.8, 113.6, 110.0, 102.0, 101.5, 79.7, 70.5. HRMS (ESI) calcd. for $C_{30}H_{21}O_4^+$ $[M+H]^+$ 445.1440; found 445.1434.

4-(4-chlorophenoxy)-3-(2-phenylethynyl)-2H-chromen-2-one (5f)

White crystalline solid (75% yield), m. p. 144-146°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, 1H, J_1=8.0 Hz, J_2=1.4 Hz), 7.68 – 7.60 (m, 1H), 7.43 (d, 1H, *J* = 8.0 Hz), 7.38 – 7.26 (m, 6H), 7.15 – 7.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.8, 153.6, 152.1, 133.0, 131.4, 129.8, 129.5, 128.7, 128.0, 124.6, 123.4, 121.9, 119.5, 116.7, 116.2, 103.4, 98.8, 79.4. HRMS (ESI) calcd. for $C_{23}H_{14}ClO_3^+$ $[M+H]^+$ 373.0631; found 373.0626.

8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6a)

Pale yellow crystal (88% yield), m. p. 130-132°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.46 (d, 1H, *J* = 8.4 Hz), 7.33 – 7.17 (m, 6H), 7.16 – 7.06 (m, 3H), 6.80 – 6.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 160.0, 155.2, 153.2, 135.1, 134.5, 133.1, 129.4, 128.4, 128.0, 127.9, 127.8, 124.8, 124.6, 124.3, 124.2, 121.9, 117.2, 116.9, 116.0, 112.6. HRMS (ESI) calcd. for $C_{23}H_{15}O_3^+$ $[M+H]^+$ 339.1021; found 339.1017.

4-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6b)

Pale yellow crystal (86% yield), m. p. 128-130°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, 2H, *J* = 6.9 Hz), 7.25 – 7.19 (m, 4H), 7.16 – 7.04 (m, 4H), 6.81 (s, 1H), 6.77 (d, 2H, *J* = 7.7 Hz), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 160.3, 155.4, 151.6, 135.1, 134.5, 134.4, 129.3, 129.1, 128.7, 128.4, 127.9, 127.8, 126.4, 124.0, 123.9, 122.4, 122.1, 117.1, 115.8, 112.6, 15.6. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1171.

3-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6c)

Pale yellow crystal (83% yield), m. p. 158-160°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 1H, *J* = 8.1 Hz), 7.29-7.18 (m, 6H), 7.14-7.02 (m, 4H), 6.82 – 6.74 (m, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 160.3, 155.4, 153.4, 144.8, 135.0, 134.6, 129.4, 128.4, 127.9, 127.8, 127.7, 125.6, 124.5, 124.1, 123.8, 122.2, 117.1, 117.0, 116.7, 113.4, 21.7. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1172.

2-methyl-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6d)

Pale yellow crystal (87% yield) , m. p. 120-122°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, 2H, J_1=11.6 Hz, J_2=3.0 Hz), 7.35 (d, 1H, *J* = 8.4 Hz), 7.25 – 7.21 (m, 4H), 7.16 – 7.05 (m, 3H), 6.79 (d, 2H, *J* = 7.8 Hz), 6.75 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 160.0, 155.2, 151.4, 135.1, 134.5, 134.3, 130.9, 129.3, 128.7, 128.4, 128.0, 127.8, 124.3, 124.2, 122.1, 117.2, 116.6, 116.4, 115.8, 112.2, 20.7. HRMS (ESI) calcd. for $C_{24}H_{17}O_3^+$ $[M+H]^+$ 353.1178; found 353.1173.

3-(benzyloxy)-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6e)

Pale yellow powder (90% yield), m. p. 128-130°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J* = 8.9 Hz), 7.48 – 7.42 (m, 4H), 7.25 – 7.18 (m, 5H), 7.13 – 7.04 (m, 3H), 6.98 (d, 1H, *J* = 2.4 Hz), 6.87 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.4 Hz), 6.83-6.74 (m, 3H), 5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.4, 159.4, 155.4, 155.1, 135.4, 134.9, 134.6, 133.3, 129.7, 129.3, 128.7, 128.4, 128.3, 127.8, 127.8, 127.4, 126.0, 124.0, 122.4, 117.1, 113.4, 112.6, 109.3, 101.6, 70.5. HRMS (ESI) calcd. for $C_{30}H_{21}O_4^+$ $[M+H]^+$ 445.1440; found 445.1435.

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DOI: 10.1039/C8OB01496E

10-chloro-8-phenyl-6H-benzo[6,7]oxepino[3,2-c]chromen-6-one (6f)

Pale yellow solid (86% yield), m. p. 122-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.46 (d, 1H, *J* = 8.1 Hz), 7.27 – 7.21 (m, 3H), 7.19 – 7.12 (m, 2H), 7.11 – 7.03 (m, 2H), 6.82 (s, 1H), 6.75 – 6.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.6, 153.7, 153.2, 135.4, 134.3, 133.3, 130.8, 129.4, 129.3, 128.6, 128.5, 128.1, 127.7, 124.6, 124.5, 121.6, 118.4, 117.0, 115.7, 112.9. HRMS (ESI) calcd. for $C_{23}H_{14}ClO_3^+$ $[M+H]^+$ 373.0631; found 373.0627.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

We are thankful to CSIR (Ref. No. 02(0278)/16/EMR-II), Government of India for financial support.

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