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ARTICLE TYPE

NHC-Gold(I) catalysed [4+2] cycloaddition/ acyclic addition of dialkyl substituted propargylic esters with 1,3-diphenylisobenzofuran: Synthesis of novel benzo[*c*]fluorenols and substituted dienes

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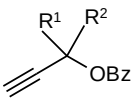
A gold carbene complex [IPrAuCl/$AgSbF_6$] catalysed novel cycloaddition of propargylic esters with 1,3-diphenylisobenzofuran. A [4+2] cycloaddition followed by sequential aromatic allylation leading to pentannulation with the expulsion of benzoic acid, then 1,2-phenyl migration coupled with ring opening and aromatisation leading to a new class of benzofluorenols, is discovered. This process involves facile multiple C-C bond formation. An accompanying second pathway involving the attack of benzoyloxy anion on the central allenic carbon affording substituted dienes is also observed. Key products are characterised by X-ray structure determination.

Introduction

Gold catalysis has emerged as an important area in modern organic synthesis during the last decade.[1] The catalytic activity of gold salts finds enormous applications in recent methodologies for the construction of new C-C and C-X bonds[1c-f, 2] leading to a wide range of heterocycles and carbocycles.[3] Due to the alkynophilicity of gold catalysts, propargylic esters can undergo inter-/intra-molecular cycloaddition reactions.[4] In addition to [4+2] cycloaddition,[5] [4+3] cycloaddition of propargylic esters with α,β-unsaturated imines and furan leading to azepines[4a, 4e] and trienes[4c, 4d] respectively has been reported. Pioneering studies of Hashmi's group on gold catalysed intramolecular cyclisation of alkynes and furans has led to a new methodology for the synthesis of various phenol derivatives.[6] Very recently, formation of phenols *via* cyclisation of acetylenes and furans has been reported by Echavarren's group.[7] In continuation of our work on the reactions of propargylic alcohol/ ester /and alkyne chemistry,[8] we report herein NHC-gold(I) catalysed [4+2] cycloaddition and acyclic addition of dialkyl substituted propargylic esters with 1,3-diphenylisobenzofuran (IBF) leading to benzo[*c*]fluorenols and substituted dienes. Benzofluorene derivatives are organic electroluminescent compounds and used as key components in organic light emitting diodes.[9] They are the core structures for kinamycins which are strongly active natural products against gram positive bacteria.[10] They are also potent anticancer and antimicrobial agents.[10] Natural products seongomycin[11a], cysfluretin[11b], shikometabolins[11c] and fluostatins[11d] also comprise benzofluorene core structure.

Results and Discussion

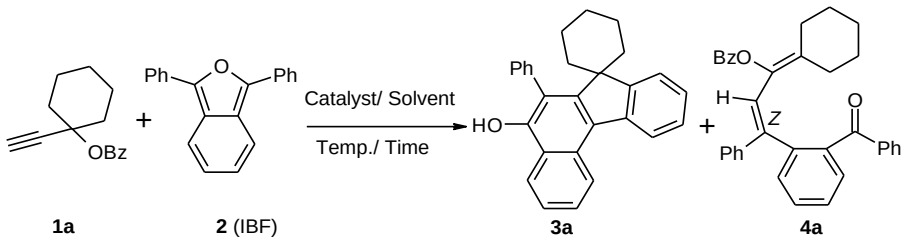
The propargylic esters **1a-l** used in the present study were synthesised from the corresponding silyl substituted propargylic esters (see Supplementary Information; species **I-V**) or propargylic alcohols.



$(R^1R^2) = (CH_2)_5$	(**1a**)	R^1 = Me, R^2 = *n*-pentyl	(**1g**)
(R^1R^2) = 4-*t*-butylcyclohexyl	(**1b**)	R^1 = Me, R^2 = *n*-hexyl	(**1h**)
$R^1 = R^2$ = Me	(**1c**)	R^1 = Et, R^2 = Et	(**1i**)
R^1 = Me, R^2 = Et	(**1d**)	R^1 = Et, R^2 = *n*-propyl	(**1j**)
R^1 = Me, R^2 = *n*-propyl	(**1e**)	$R^1 = R^2$ = *n*-propyl	(**1k**)
R^1 = Me, R^2 = *n*-butyl	(**1f**)	R^1 = H, R^2 = *p*-anisyl	(**1l**)

For optimisation, we chose cycloaddition of propargylic ester **1a** with IBF **2** (Scheme 1). First it was confirmed that **1a** did not react with 1,3-diphenylisobenzofuran (IBF, 1:1.5 molar ratio) in dichloromethane at rt under catalyst-free condition (Table 1, entry 1). Then, gold carbene complex was employed as the catalyst. To our delight, we found that 2 mol% each of IPrAuCl[12] and $AgSbF_6$ in CH_2Cl_2 worked well to lead to benzofluorenols **3a** and substituted diene **4a** in 36% and 54% yields respectively (Table 1, entry 2) based on **1a**. The combined yield (**3a** + **4a**; after isolation) is excellent (90%). An additional important point is that the R_f values of the two products are significantly different, and hence the benzofluorenols can be very easily isolated. Hence our trials were directed towards improving the yield of benzofluorenol derivatives rather than dienes. Thus when the quantity of IBF was reduced to 1.2 mmol equivalents, the yield of benzofluorenol was increased to 52% whereas yield of diene was 34% [combined yield 86%; Table 1, entry 3]. Equimolar ratio of substrates led to benzofluorenol and diene in 57% and 33% respectively (entry 4) whereas as 1.2:1 ratio of alkyne and IBF afforded improved yield of benzofluorenol (58%) with a

combined yield of 91% (entry 5). Use of 2:1 ratio of alkyne and IBF led to decrease in the yield of benzofluorenol to 48% (entry 6). At 55 °C, the reaction afforded 32% of benzofluorenol only (entry 7). Use of 1-ethynylcyclohexyl acetate did not improve the yield of benzofluorenol (53%, entry 8). Silver-free IPrAu(NCMe)SbF_6[13] led to 42% of benzofluorenol with overall yield of 82% (entry 9). Interestingly, use of 2 mol % IPrAuCl/AgOTf gave only the diene product in 48% yield (Table 1, entry 10). Changing the silver salt to $AgNTf_2$ or $AgBF_4$ led to benzofluorenol in lower yields (entries 11 and 12); 2 mol% IMesAuCl/$AgSbF_6$ could drive the reaction to obtain benzofluorenol in 50% of yield (entry 13). $PicAuCl_2$, IPrAuCl or $AgSbF_6$ individually were not effective to form benzofluorenol (entries 14, 15 and 16). Use of 2 mol % Ph_3PAuCl/ $AgSbF_6$ led to diene product only (entry 17). Solvents like CH_3CN, THF and dioxane (entries 18, 19 and 20) in the presence of 2 mol% IPrAuCl/ $AgSbF_6$ did not perform well in forming the benzofluorenol; it should be noted that the catalytic system in entry 18 can be treated as AgCl+[IPrAu(NCMe)SbF_6].[13] Hence it is concluded that 2 mol% IPrAuCl/ $AgSbF_6$ in dichloromethane at rt is the best choice for the formation of the benzofluorenol (entry 5). Details on the optimisation of the products using various screening conditions are presented in Table 1.



1a **2** (IBF) **3a** **4a**

Scheme 1: Reaction of propargylic ester **1a** and 1,3-diphenylisobenzofuran **2**

Table 1. Screening for the optimisation of the yields of benzofluorenol **3a** and diene **4a**

Entry[a]	Alkyne/ IBF	Catalyst	Solvent	Time (h)	Combined yield (%)[b] (**3a**+ **4a**)
1	1/ 1	No Catalyst	DCM	12	0[c]
2	1/ 1.5	2% IPrAuCl/ $AgSbF_6$	DCM	4	90 (36 + 54)[d]
3	1/ 1.2	2% IPrAuCl/ $AgSbF_6$	DCM	4	86 (52 + 34)
4	1/ 1	2% IPrAuCl/ $AgSbF_6$	DCM	4	90 (57 + 33)
5	**1.2/ 1**	**2% IPrAuCl/ $AgSbF_6$**	**DCM**	**4**	**91 (58 + 33)**
6	2/1	2% IPrAuCl/ $AgSbF_6$	DCM	4	84 (48 + 36)
7	1.2/ 1	2% IPrAuCl/ $AgSbF_6$	DCM	4 (at 55 °C[e])	74 (32 + 42)
8	1.2/ 1	2% IPrAuCl/ $AgSbF_6$	DCM	4	80 (60 + 20[f])
9	1.2/1	2% IPrAu(NCMe)SbF_6	DCM	4	82 (42 +40)
10	1.2/ 1	2% IPrAuCl/ AgOTf	DCM	12	48 (0 + 48)[c]
11	1.2/ 1	2% IPrAuCl/ $AgNTf_2$	DCM	12	62 (26 + 36)[c]
12	1.2/ 1	2% IPrAuCl/ $AgBF_4$	DCM	4	85 (38 + 47)
13	1.2/ 1	2% IMesAuCl/ $AgSbF_6$	DCM	4	88 (50 + 38)
14	1.2/ 1	3% $PicAuCl_2$	DCM	12	54 (0 + 54)[c]
15	1.2/ 1	3% IPrAuCl	DCM	12	15 (0 + 15)[c]
16	1.2/ 1	3% $AgSbF_6$	DCM	12	68 (0 + 68)[c]
17	1.2/ 1	2% Ph_3PAuCl/ $AgSbF_6$	DCM	12	65 (0 + 65)[c]
18	1.2/ 1	2% IPrAuCl/ $AgSbF_6$	CH_3CN	12	~32 (trace + 32)
19	1.2/ 1	2% IPrAuCl/ $AgSbF_6$	THF	12	38 (10 + 28)[c]
20	1.2/ 1	2% IPrAuCl/ $AgSbF_6$	dioxane	12	36 (6 + 30)[c]

[a] All reactions were performed at room temperature.

[b] Isolated yield.

[c] Starting material remained.

[d] A diketone[14] which is a dimeric form of IBF was also formed.

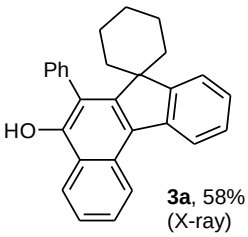
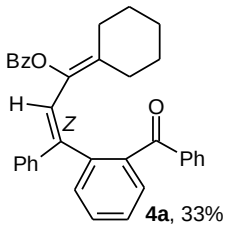
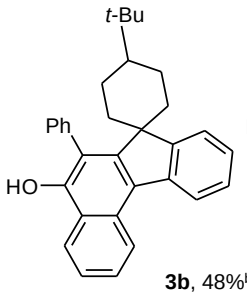
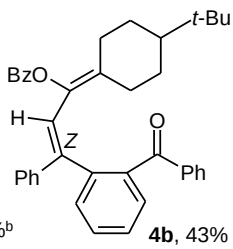
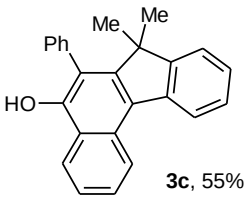
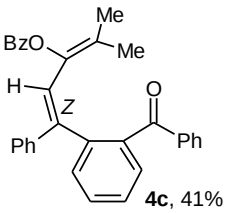
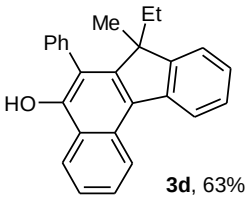
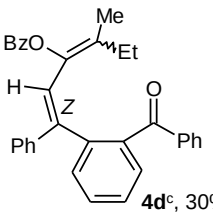
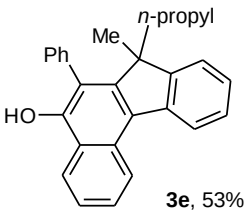
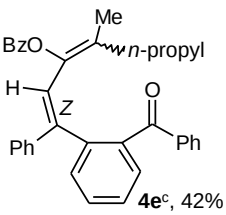
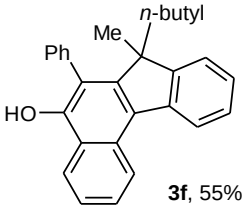
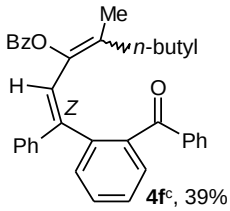
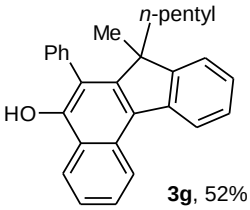
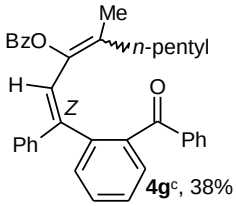
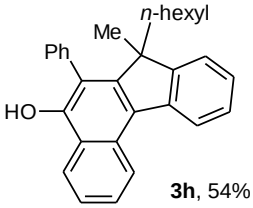
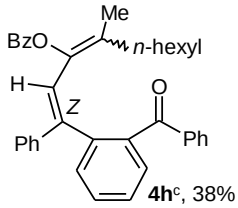
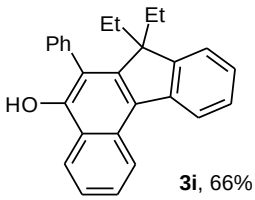
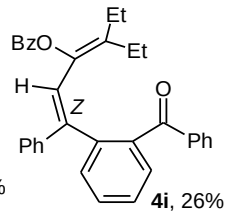
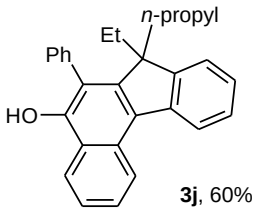
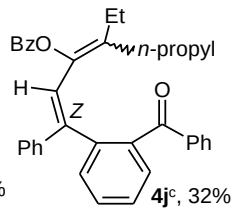
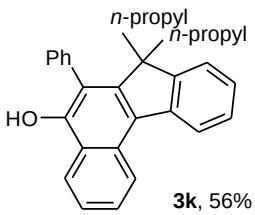
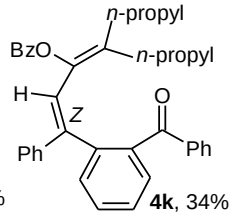
[e] Oil bath temperature.

[f] 1-Ethynylcyclohexyl acetate was used. The diene product, although present (ca 20%; tlc), could not be isolated.

To ascertain the efficacy and generality of the above catalytic system, various propargylic benzoates **1b-1k** were treated with IBF (Scheme 1). These reactions afforded products **3(b-k)-4(b-k)** (benzofluorenols and dienes) in combined yields of 90-96% with benzofluorenols as predominant and *readily isolatable* products. The structure of benzofluorenol **3a** was confirmed by X-ray crystallography (Figure 1). The substituents were varied in terms of alkyl groups. The configuration at one of the double bonds in the diene product is *Z* and the other double bond exhibits (*E*+*Z*) isomeric mixture (~1:1) if the alkyl groups are unsymmetrically substituted (Table 2, entries 4-8 and 10). The R_f values of the two diene isomers were very close to each other and hence they were not separated. However, in the case of mono-substituted

propargyl benzoate **1l** under similar conditions, isomeric dienes **4l** and **4l'** were formed (via acyclic addition; Scheme 2). These were separated and the structure of **4l** was confirmed by X-ray crystallography (Figure 2). Use of the terminally substituted ester 1-(phenylethynyl)cyclohexyl benzoate led to a mixture with much of the starting material unreacted.

Table 2. Synthesis of benzofluorenols **3a-k** and dienes **4a-k**.

Entry	Alkyne	Benzofluorenol[a]	Substituted diene[a]
1	**1a**	 **3a**, 58% (X-ray)	 **4a**, 33%
2	**1b**	 **3b**, 48%[b]	 **4b**, 43%
3	**1c**	 **3c**, 55%	 **4c**, 41%
4	**1d**	 **3d**, 63%	 **4d**[c], 30%
5	**1e**	 **3e**, 53%	 **4e**[c], 42%
6	**1f**	 **3f**, 55%	 **4f**[c], 39%
7	**1g**	 **3g**, 52%	 **4g**[c], 38%
8	**1h**	 **3h**, 54%	 **4h**[c], 38%
9	**1i**	 **3i**, 66%	 **4i**, 26%
10	**1j**	 **3j**, 60%	 **4j**[c], 32%
11	**1k**	 **3k**, 56%	 **4k**, 34%

[a] Yields of the isolated products
[b] Diastereomeric mixture [dr ~ 1:1]
[c] *E*+*Z* (*ca* 1:1) isomers

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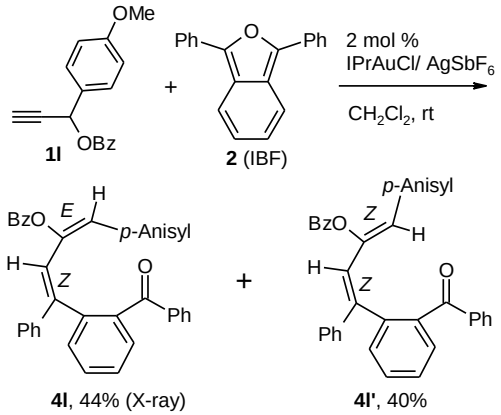


Scheme 2: Formation of diene products **4l** and **4l'**

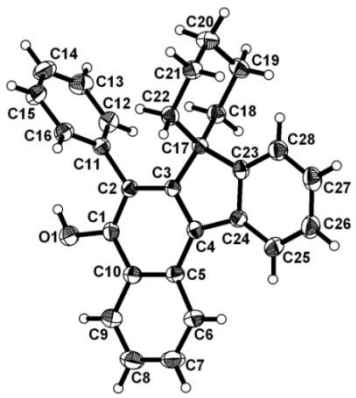


Figure 1. ORTEP diagram for compound **3a**. Selected bond lengths with esd's in parentheses: C2-C1 1.377(4), C3-C2 1.422(4), C4-C3 1.389(3), C17-C23 1.518(4), C11-C2 1.485(3).

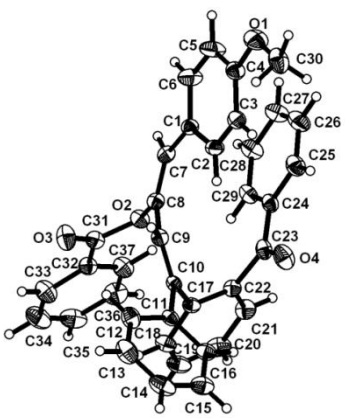
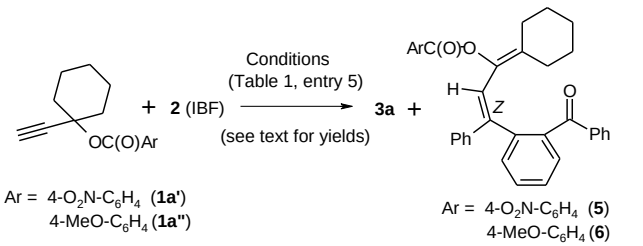


Figure 2. ORTEP diagram for compound **4l**. Selected bond lengths with esd's in parentheses: C7-C8 1.320(3), C8-C9 1.445(3), C9-C10 1.328(3), O4-C23 1.218(2).

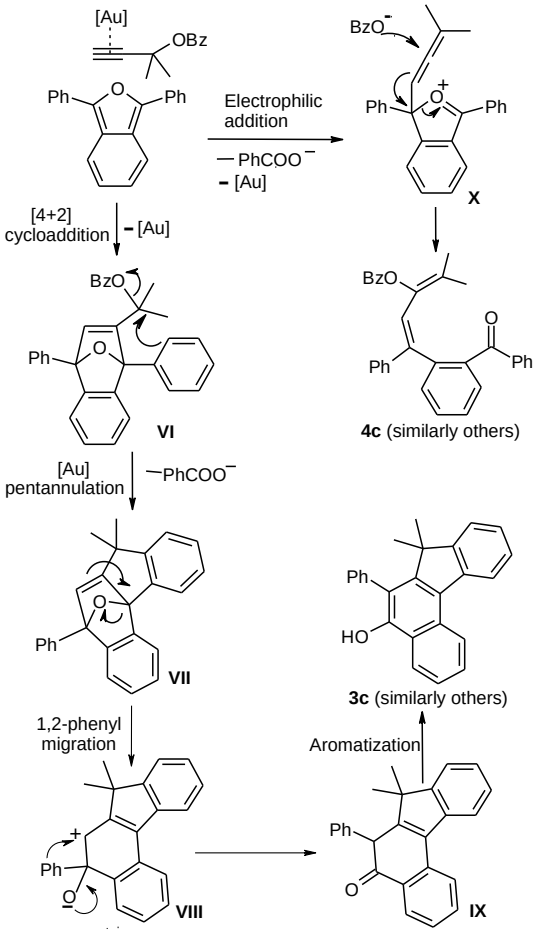
We have also performed the above reaction by using 4-nitrobenzoate (**1a'**) and 4-methoxybenzoate (**1a"**)[15] in place of unsubstituted benzoate **1a** (Scheme 3). It was found that the yield of the isolated fluorenol product **3a** was increased to 66% in the former while it decreased to 23% in the case of latter. The yield of the diene **5** (29%) or **6** (26%) was low in both the cases.



Scheme 3: Reaction of 4-nitro- and 4-methoxy-benzoate propargylic esters with **2**

The variation in the ester moiety having electron withdrawing -NO_2 and electron donating –OMe substrates in the cycloaddition favours a gold-alkyne pathway. The propargylic ester having the -NO_2 group resulted in higher yield. This suggests that 1,2- or 1,3-benzyloxy group migration[16, 17] is less favourable. Based on these results, a plausible mechanism for the above reaction is shown in Scheme 4. Initially, alkyne coordinates to [Au], and undergoes [4+2] cycloaddition with 1,3-diphenylisobenzofuran to form **VI**. This intermediate undergoes elimination of benzoyl group to generate a five membered ring forming the polycycle **VII** with bridged oxygen between two phenyl rings. A new C-C bond is formed and benzoic acid is eliminated at this stage. Then the ring containing bridged oxygen is opened by the attack of the double bond to form allylic cationic intermediate **VIII**. The other phenyl group migrates to the adjacent carbocation followed by ketone formation to lead to the intermediate **IX**. Species **IX** aromatises to the benzofluorenol product. In the case of monoaryl substituted propargyl ester **1l**, 1,2-benzoyloxy group migration is only observed which can be in line with the literature.[17d, 18]

For the diene product as shown on the right of the Scheme 4, the allenic intermediate **X** is formed first; attack of the benzoyloxy anion on the central allenic carbon of followed by reorganization of bonds leads to the diene product.



Scheme 4. Proposed reaction pathway for the formation of benzofluorenols and substituted dienes

Conclusions

In summary, a new type of cycloaddition involving propargylic esters with the aid of N-heterocyclic carbene-gold complex under very mild conditions is discovered. The products are novel benzo[*c*]fluorenols and substituted dienes that are very conveniently isolated. While the former product involves sequential cycloaddition, carbocyclisation, 1,2-phenyl migration, ring opening and aromatisation, the latter involves attack of benzoyloxy anion on central allenic carbon followed by rearrangement. The structures of two such products have been unambiguously established by X-ray structure determination.

Experimental Section

General procedure for the synthesis of benzofluorenols ***3a-k,*** *dienes* ***4a-l, 4l'*** *and* ***5-6****.* To a mixture of IPrAuCl [IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene] (0.006 g, 0.01 mmol) and $AgSbF_6$ (0.003 g, 0.01) in DCM (2 mL) was added the corresponding propargyl benzoate **1a-l** (0.6 mmol) and 1,3-diphenylisobenzofuran **2** (0.5 mmol). The contents were stirred at rt (25 ^oC) for 4 h. The solvent was removed under vacuum. Products **3a-k** were separated from the reaction mixture by column chromatography by using acetone/hexane (1:100) mixture whereas **4a-l**, **4l'** and **5-6** (**1a'** and **1a"** were used for these) were isolated by using acetone/hexane (1:50) mixture.

Compound 3a. White solid [R_f 0.5 in acetone-hexane (1:50) mixture]; Yield 0.109 g (58%) using **1a**, 0.124 g (66%) using **1a'** and 0.056 g (23%) using **1a"**; Mp 230-232 ^oC; IR υ_{max}(KBr): 3534, 3052, 2953, 2932, 2843, 1622, 1563, 1439, 1391, 1343, 1219, 1065, 1024, 752, 710, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.75-0.79, 1.32-1.54, 1.76-2.00 and 2.21-2.28 (m, 10H, cyclohexyl-*H*), 5.10 (s, 1H, Ar-O*H*), 7.23-7.96, 8.36-8.42 and 8.86-8.88 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 25.1, 32.6 and 52.4 (cyclohexyl-*C*H_2), 120.3, 122.2, 123.6, 123.7, 124.3, 124.8, 125.2, 126.7, 126.8, 127.4, 129.0, 129.2, 129.6, 130.5, 132.8, 134.2, 140.8, 149.4, 149.8 and 153.6 (Ar-*C*); HRMS (ESI): Calcd. for $C_{28}H_{25}O$ [M^++H]: *m/z* 377.1906. Found: 377.1904. X-ray structure has been determined for this compound after crystallisation from CH_2Cl_2-hexane mixture. CCDC No. 952109.

Compound 4a. Gummy liquid [R_f 0.3 in acetone-hexane (1:50) mixture]; Yield 0.82 g (33%,); IR υ_{max}(neat) 3063, 2926, 2854, 1726, 1671, 1599, 1452, 1276, 1068, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.31-1.53 and 1.87-2.10 (m, 10H, cyclohexyl-*H*), 6.73 (s, 1H, PhC=C*H*), 7.10-7.76 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2, 26.6, 27.0, 28.1, 29.4 (cyclohexyl-*C*), 121.1, 126.3, 127.5, 128.0$_0$, 128.0$_2$, 129.1, 129.3, 129.4, 129.7, 130.1, 130.2, 131.3, 132.6, 132.9, 134.1, 136.4, 137.2, 139.2, 140.4, 141.0, 142.6 (alkenyl-C + Ar-*C*), 164.3 (O*C*OPh), 196.3 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{35}H_{30}O_3$ [M^++H]: *m/z* 499.2274. Found: 499.2274.

Compound 3b. White solid; Yield 0.104 g (48%); Mp 260-262 ^oC; IR υ_{max}(KBr) 3523, 3058, 3036, 2948, 2866, 1584, 1556, 1441, 1397, 1211, 1063, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.73 and 0.89 (2 s, 18H, *t*-Bu-*H*), 1.28-2.30 (m, 18H, cyclohexyl-*H*), 5.10 and 5.11 (2 s, 2H, Ar-O*H*), 7.24-7.69 and 8.33-8.85 (m, 26H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 23.3, 26.8, 27.7, 31.6, 32.6, 33.3, 33.6, 42.9 and 47.0 (*t*-Bu-*C* + cyclohexyl-*C*), 120.2, 120.2, 122.1, 122.2, 123.6, 124.4, 124.7, 124.8, 125.0, 126.2, 126.6, 126.8, 127.4, 128.8, 129.0, 129.1, 129.5, 129.6, 130.5, 132.5, 132.8, 134.1, 140.2, 140.8, 149.4 and 149.7 (Ar-*C*); HRMS (ESI): Calcd. for $C_{32}H_{33}O$ [M^++H]: *m/z* 433.2532. Found: 433.2530.

Compound 4b. Gummy liquid; Yield 0.119 g (43%); IR υ_{max}(neat): 3057, 2953, 2860, 1731, 1665, 1599, 1457, 1260, 1101, 1024, 772, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.80-1.03, 1.22-1.72 and 2.37-2.60 (m, 18H, cyclohexyl-*H* + *t*-Bu-*H*), 6.73 (s, 1H, PhC=C*H*), 6.94-7.75 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 28.1, 29.3, 32.4 and 47.9 (cyclohexyl-*C* + *t*-Bu-*C*), 121.2, 126.3, 127.4, 127.4, 128.0, 129.3, 129.5129.8, 130.1, 130.2, 131.3, 132.5, 132.8, 133.8, 136.4, 137.3, 139.3, 140.4, 141.5 and 142.6 (Alkenyl-*C* + Ar-*C*), 164.3 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{39}H_{39}O_3$ [M^++H]: *m/z* 555.2900. Found: 555.2903.

Compound 3c. White solid; Yield 0.093 g (55%); Mp 150-152 ^oC; IR υ_{max}(KBr): 3507, 3057, 2981, 2959, 2860, 1578, 1441, 1391, 1216, 1057, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 6H, C(CH_3)$_2$), 5.16 (s, 1H, Ar-O*H*), 7.28-7.60, 8.30-8.35 and 8.80-8.82 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6 (C(*C*H_3)$_2$), 48.6 (*C*(CH$_3$)$_2$), 120.4, 121.9, 122.2, 123.5, 123.8, 124.8, 125.4, 126.5, 127.0, 127.2, 127.3, 127.9, 129.0, 129.9,

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132.4, 134.0, 140.0, 149.1, 149.8 and 154.9 (Ar-*C*); HRMS (ESI): Calcd. for $C_{25}H_{20}O$ [M^++H]: *m/z* 337.1593. Found: 337.1592.

Compound 4c. Gummy liquid; Yield : 0.094 g (41%,); IR υ_{max}(neat): 3063, 2915, 2854, 1726, 1665, 1599, 1457, 1309, 1287, 1117, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 and 1.62 (2 s, 6H, =C(CH_3)$_2$), 6.69 (s, 1H, PhC=C*H*), 7.10-7.74 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5 and 19.2 (=C(*C*H$_3$)$_2$), 121.6, 126.4, 127.0, 127.5, 127.9, 128.5, 129.2, 129.3, 129.8, 130.0, 130.2, 130.6, 131.3, 132.6, 132.9, 137.1, 139.1, 139.3, 140.2, 140.7, 142.4 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{32}H_{26}O_3$ [M^++H]: *m/z* 459.1961. Found: 459.1964.

Compound 3d. White solid; Yield 0.110 g (63%); Mp 118-120 ^oC; IR υ_{max}(KBr) 3436, 3063, 2970, 2920, 2860, 1660, 1594, 1452, 1277, 1069, 932 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (t, ^3J(H-H) = 7.2 Hz, 3H, C*H*$_3$CH$_2$), 1.31 (s, 3H, C*H*$_3$CAr), 1.69-1.72 and 1.78-1.82 (m, 2H, C*H*$_2$CH$_3$), 5.14 (s, 1H, Ar-O*H*), 7.28-7.71 and 8.29-8.80 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.7 (*C*H$_3$CH$_2$), 26.6 and 31.8 (CH$_3$*C*H$_2$ + *C*H$_3$CAr), 53.1 (Ar*C*(Me)Et), 120.2, 121.7, 121.9, 123.5, 123.7, 124.8, 125.3, 126.9, 127.2, 128.0, 129.1, 129.8, 131.1, 132.3, 134.0, 141.3, 147.4, 149.0 and 152.8 (Ar-*C*); HRMS (ESI): Calcd. for $C_{26}H_{23}O$ [M^++H]: *m/z* 351.1750. Found: 351.1749.

Compound 4d. Gummy liquid; Yield 0.071 g (30%); IR υ_{max}(neat): 3057, 2964, 2931, 1732, 1660, 1595, 1452, 1310, 1277, 1063, 773, 707 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.75 and 0.85 (2 t, ^3J(H-H) = 6.4 Hz each, 6H, C*H*$_3$CH$_2$), 1.41 and 1.60 (2 s, 6H, C*H*$_3$C=C), 1.65 and 2.04 (2 br s, 4H, C*H*$_2$CH$_3$), 6.67 and 6.73 (2 s, 2H, PhC=C*H*), 7.07-7.77 (m, 38H, Ar-*H*). In the assignment, the proton numbers are doubled to show the presence of both the isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.7 and 12.0 (2 *C*H$_3$CH$_2$), 15.8, 16.5, 25.2 and 26.2 (2 CH$_3$C*H*$_2$ and 2 *C*H$_3$C=C), 120.6, 121.8, 126.3, 126.5, 127.5, 127.9, 128.1, 129.1, 129.4, 129.7, 129.8, 129.9, 130.1, 130.2, 131.1, 131.3, 132.5, 132.6, 132.9, 137.2, 137.3, 138.7, 139.0, 139.4, 140.0, 140.6, 140.9, 142.4, 142.5 (Ar-*C*), 163.9, 164.3 (O*C*OPh), 196.5 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{33}H_{28}NaO_3$ [M^++Na]: *m/z* 495.1936. Found: 495.1938.

Compound 3e. White solid; Yield 0.097 g (53%); Mp 120-122 ^oC; IR υ_{max}(KBr) 3518, 2959, 2926, 2860, 1578, 1441, 1397, 1238, 1222, 1069, 795, 751, 707, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (t, ^3J(H-H) = 6.4 Hz, 3H, C*H*$_3$CH$_2$), 1.31 (s, 3H, C*H*$_3$CAr), 1.62-1.75 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 5.13 (s, 1H, Ar-O*H*), 7.27-7.70 and 8.28-8.81 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 17.5, 27.0, 41.2 (*C*H$_3$ + propyl-*C*), 52.7 (Ar*C*(Me)propyl), 120.2, 121.6, 121.9, 123.6, 124.8, 125.3, 126.9, 127.2, 127.7, 128.4, 129.1, 129.6, 129.8, 131.1, 132.3, 134.0, 141.0, 147.9, 149.0 and 153.3 (Ar-*C*); HRMS (ESI): Calcd. for $C_{26}H_{23}O$ [M^++H]: *m/z* 351.1750. Found: 351.1749.

Compound 4e. Gummy liquid; Yield 0.102 g (42%,); IR υ_{max}(neat): 3058, 2955, 2929, 2872, 1728, 1666, 1599, 1444, 1314, 1278, 1071, 931, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77 and 0.83 (2 t, ^3J(H-H) = 7.4 Hz and 7.2 Hz respectively, 6H, C*H*$_3$CH$_2$), 0.86-0.97, 1.22-1.65 (m, 14H, C*H*$_3$ + C*H*$_2$C*H*$_2$CH$_3$), 6.68 and 6.73 (2 s, 2H, PhC=C*H*), 6.81-7.74 (m, 38H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 14.2, 16.4, 17.1, 20.5, 21.0, 34.3 and 35.1 (propyl-*C* + *C*H$_3$), 121.1, 121.9, 126.3, 126.5, 127.5, 127.9, 128.1, 129.1, 129.5, 129.8, 129.9, 130.2, 130.3, 130.6, 131.2, 131.3, 132.4, 132.6, 132.8, 137.3$_0$, 137.3$_4$, 139.3, 139.7, 139.9, 140.1, 140.6, 140.9, 142.4 and 142.6 (Ar-*C*), 163.9, 164.3 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{34}H_{31}O_3$ [M^++H]: *m/z* 487.2274. Found: 487.2273.

Compound 3f. White solid; Yield 0.105 g (55%); Mp 110-112 ^oC; IR υ_{max}(KBr): 3534, 3057, 2959, 2931, 2860, 1599, 1572, 1441, 1353, 1057, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.45 (br s, 1H, butyl-*H*), 0.66 (t, ^3J(H-H) = 7.2 Hz, 3H, C*H*$_3$CH$_2$), 0.90-1.06 and 1.27-1.74 (m, 8H, C*H*$_3$ and butyl-*H*), 5.14 (s, 1H, Ar-O*H*), 7.27-7.69 and 8.30-8.82 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.9, 26.3, 27.0 and 38.8 (*C*H$_3$ + butyl-*C*), 52.6 (*C*(Me)*n*-butyl), 120.2, 121.6, 122.0, 123.6, 124.8, 125.3, 126.9, 127.2, 127.7, 129.1, 129.9, 131.2, 132.3, 134.0, 141.1, 147.9, 149.0 and 153.3 (Ar-*C*); HRMS (ESI): Calcd. for $C_{28}H_{26}NaO$ [M^++Na]: *m/z* 401.1882. Found: 401.1883.

Compound 4f. Gummy liquid; Yield 0.097 g (39%); IR υ_{max}(neat): 3057, 2953, 2926, 2860, 1731, 1660, 1599, 1446, 1320, 1282, 1172, 1095, 1030, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80-0.96, 1.15-1.24 and 1.35-2.04 (m, 24H, C*H*$_3$ + butyl-*H*), 6.67 and 6.73 (2 s, 2H, PhC=C*H*), 7.05-7.75 (m, 38H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.9, 16.4, 17.0, 22.6$_0$, 22.6$_2$, 29.3, 29.9, 31.8 and 32.9 (*C*H$_3$ + butyl-*C*), 121.0, 121.8, 126.3, 126.4, 127.4, 127.9, 128.0$_0$, 128.0$_2$, 129.0, 129.3, 129.5, 129.7, 129.9, 130.1, 130.2, 130.7, 131.1, 131.3, 131.4, 132.4, 132.5, 132.8, 137.3, 139.1, 139.2, 140.0, 140.9, 142.4, 142.6, (Alkenyl-*C* + Ar-*C*), 163.9 and 164.3 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{35}H_{33}O_3$ [M^++H]: *m/z* 501.2430. Found: 501.2432.

Compound 3g. White solid; Yield 0.102 g (52%); Mp 116-118 ^oC; IR υ_{max}(KBr): 3496, 2948, 2931, 2855, 1584, 1386, 1222, 1069, 751, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.44 (br s, 1H, pentyl-*H*), 0.71 (t, ^3J(H-H) = 6.0 Hz, 3H, C*H*$_3$CH$_2$), 0.95-1.04 (m, 5H, pentyl-*H*), 1.05 (s, 3H, C*H*$_3$), 1.59-1.75 (m, 2H, pentyl-*H*), 5.13 (s, 1H, Ar-O*H*), 7.29-7.71 and 8.28-8.82 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.4, 23.8, 27.0, 32.1, 38.9 (*C*H$_3$ + pentyl-*C*), 52.5 (Ar-*C*(Me)*n*-pentyl), 120.3, 122.0, 123.5, 124.7, 125.3, 126.7, 127.1, 128.3, 129.1, 129.6, 131.1, 132.3, 133.9, 141.0, 147.9 and 153.2 (Ar*C*); HRMS (ESI): Calcd. for $C_{29}H_{29}O$ [M^++H]: *m/z* 393.2219. Found: 393.2217.

Compound 4g. Gummy liquid; Yield 0.098 g (38%); IR υ_{max}(neat): 3047, 2959, 2931, 2855, 1732, 1666, 1595, 1452, 1315, 1266, 1244, 1156, 767, 740, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 and 0.86 (2 t, ^3J(H-H) = 7.0 Hz and 6.8 Hz respectively, 6H, C*H*$_3$CH$_2$), 1.13-1.31 (m, 12H, pentyl-*H*), 1.43 and 1.66 (2 br s, 10H, pentyl-*H* + C*H*$_3$), 6.69 and 6.72 (2 s, 2H, PhC=C*H*), 6.74-7.79 (m, 38H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 16.4, 17.1, 22.4, 22.6, 26.8, 27.0, 27.4, 31.8, 32.1

and 33.2 (*n*-pentyl-*C* + CH_3), 121.0, 121.9, 126.3, 126.5, 126.7, 127.5, 127.9, 128.1, 128.4, 129.1, 129.4, 129.8, 130.2, 130.8, 131.2, 131.4, 132.4, 132.6, 132.8, 137.4, 139.2, 139.3, 139.5, 139.8, 140.1, 140.7, 142.5 and 142.6 (Alkenyl-*C* + Ar-*C*), 164.3 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{36}H_{35}O_3$ [M^++H]: *m/z* 515.2587. Found: 515.2589.

Compound 3h. White solid; Yield 0.110 g (54%); Mp 114-116 ^oC; IR υ_{max}(KBr): 3534, 3063, 2955, 2924, 2851, 1625, 1583, 1459, 1438, 1392, 1350, 1273, 1221, 1061, 760, 703, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.49 and 0.72 (2 br s, 2H, hexyl-*H*), 0.80 (t, ^3J(H-H) = 7.4 Hz, 3H, CH_3CH$_2$), 1.03-1.78 (m, 11H, CH_3 + hexyl-*H*), 5.18 (s, 1H, Ar-O*H*), 7.31-7.73 and 8.32-8.86 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 24.1, 27.1, 29.5, 31.6, 39.0 (*C*H$_3$ + hexyl-*C*), 52.6 (Ar*C*(Me)hexyl), 120.2, 121.6, 121.9, 123.5, 123.8, 124.7, 125.3, 126.9, 127.2, 127.7, 128.3, 129.1, 129.6, 129.8, 131.2, 132.3, 141.0, 147.9, 148.9 and 153.3 (Ar-*C*); HRMS (ESI): Calcd. for $C_{30}H_{31}O$ [M^++H]: *m/z* 407.2376. Found: 407.2373.

Compound 4h. Gummy liquid; Yield 0.100 g (38%); IR υ_{max}(neat): 3053, 3022, 2924, 2856, 1733, 1661, 1599, 1449, 1268, 926 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.80 and 0.86 (2 t, ^3J(H-H) = 7.0 Hz and 7.4 each, 6H, CH_3CH$_2$), 1.15-1.27 (m, 16H, hexyl-*H*), 1.43-1.66 (2 s, 6H, CH_3), 1.71-1.74 and 2.00-2.04 (m, 2H, hexyl-*H*), 6.69 and 6.74 (2 s, 2H, PhC=C*H*), 7.05-7.20, 7.27-7.37, 7.44-7.49, 7.54-7.76 (m, 38H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 14.2, 16.4, 17.1, 22.6, 24.7, 27.1, 27.7, 29.2, 31.6, 31.8, 32.1, 33.2, 36.7 (*n*-C_6H_{13} + *C*H$_3$), 121.0, 121.8, 126.3, 126.5, 127.1, 127.5, 127.9, 128.0$_0$, 128.0$_4$, 129.0, 129.4, 129.7, 129.9, 130.2, 130.9, 131.1, 131.3, 131.5, 132.5, 132.6, 132.8, 132.9, 137.2, 137.3, 139.1, 139.2, 139.4, 139.8, 140.0, 140.6, 140.9, 142.4, 142.6 (Alkenyl-*C* + Ar-*C*), 163.9 and 164.2 (O*C*OPh), 196.5 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{37}H_{37}O_3$ [M^++H]: *m/z* 529.2743. Found: 529.2742.

Compound 3i. White solid; Yield 0.120 g (66%); Mp 126-128 ^oC; IR υ_{max}(KBr): 3490, 2953, 2857, 1584, 1562, 1392, 1211, 1058, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (t, ^3J(H-H) = 7.2 Hz, 6H, CH_3CH$_2$), 1.67-1.82 (m, 4H, CH$_3$CH_2), 5.12 (s, 1H, Ar-O*H*), 7.27-7.69 and 8.27-8.82 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.3 (*C*H$_3$CH$_2$), 31.8 (CH$_3$*C*H$_2$), 58.3 (Ar*C*(Et)$_2$), 120.1, 121.7, 123.7, 124.7, 125.3, 126.9, 127.1, 128.4, 129.3, 129.6, 131.0, 134.0, 142.7, 145.1, 148.8 and 150.9 (Ar-*C*); HRMS (ESI): Calcd. for $C_{27}H_{24}O$ [M^++H]: *m/z* 365.1906. Found: 365.1903.

Compound 4i. Gummy liquid; Yield 0.063 g (26%); IR υ_{max}(neat): 3063, 2970, 2871, 1726, 1665, 1599, 1452, 1271, 1090, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.75 and 0.83 (2 t, ^3J(H-H) = 7.4 Hz each, 6H, CH_3CH$_2$), 1.98 and 2.13 (2 br s, 4H, CH$_3$CH_2), 6.72 (s, 1H, PhC=C*H*), 7.00-7.72 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1 and 12.6 (CH$_2$*C*H$_3$), 22.8 and 23.6 (*C*H$_2$CH$_3$), 121.2, 126.4, 127.5, 127.9, 128.1, 128.4, 129.1, 129.4, 129.7, 129.9, 130.1, 130.2, 131.1, 132.6, 132.9, 137.3, 137.8, 139.0, 139.5, 139.8, 140.8, 142.6 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{34}H_{30}O_3$ [M^++H]: *m/z* 487.2274. Found: 487.2272.

Compound 3j. White solid; Yield 0.113 g (60%); Mp 106-108 ^oC; IR υ_{max}(KBr): 3534, 3057, 3041, 2959, 2926, 2870, 1583, 1462, 1391, 1227, 1068, 876 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.25 (t, ^3J(H-H) = 7.4 Hz, 3H, CH_3CH$_2$), 0.50-0.55 (m, 1H, alkyl-*H*), 0.62 (t, ^3J(H-H) = 6.8 Hz, 3H, CH_3CH$_2$), 0.67-0.91 and 1.55-1.82 (m, 5H, alkyl-*H*), 5.14 (s, 1H, Ar-O*H*), 7.29-7.71 and 8.28-8.83 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.1, 14.2, 17.1, 32.1 and 41.4 (ethyl-*C* + propyl-*C*), 57.8 (*C*(Et)*n*-propyl), 120.1, 121.4, 121.7, 123.5, 123.7, 124.7, 125.3, 126.9, 127.2, 129.1, 129.3, 129.8, 131.1, 134.0, 142.4, 145.6, 148.9 and 151.4 (Ar-*C*); HRMS (ESI): Calcd. for $C_{28}H_{26}NaO$ [M^++Na]: *m/z* 401.1882. Found: 401.1883.

Compound 4j. Gummy liquid; Yield 0.080 g (32%,); IR υ_{max}(neat): 3063, 2965, 2932, 2871, 1731, 1671, 1595, 1452, 1321, 1271, 1069, 932, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.76 and 0.93 (m, 12H, CH_3CH$_2$), 1.19-1.32 (m, 6H, alkyl-*H*), 1.64 and 2.09 (2 br s, 6H, alkyl-*H*), 6.73 (br s, 2H, PhC=C*H*), 7.02-7.72 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 12.7, 14.2, 14.4, 20.9, 21.5, 23.4, 24.1, 32.0 and 32.7 (Ethyl-*C* + propyl-*C*), 121.2, 121.3, 126.4, 127.4, 127.9$_0$, 127.9$_6$, 128.1, 128.6, 129.2, 129.6, 129.7, 130.0, 130.1, 130.4, 131.1, 132.5, 132.8, 136.5, 136.6, 137.4, 139.5, 139.7, 139.8, 140.8, 142.6 and 142.7 (Alkenyl-*C* + Ar-*C*), 164.2 (O*C*OPh), 196.5 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{35}H_{33}O_3$ [M^++H]: *m/z* 501.2430. Found: 501.2431.

Compound 3k. White solid; Yield 0.110 g (54%) Mp 112-114 ^oC; IR υ_{max}(KBr): 3529, 3036, 2953, 2926, 2871, 1578, 1463, 1436, 1392, 1222, 1145, 767, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.23 (t, ^3J(H-H) = 7.2 Hz, 6H, CH_3CH$_2$), 1.60-1.74 (m, 8H, CH$_3$CH$_2$CH_2), 5.14 (s, 1H, Ar-O*H*), 7.29-7.71 and 8.27-8.82 (m, 13H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 16.9, 41.6 (*C*$_3$H$_7$), 57.3 (Ar-*C*(*n*-propyl)$_2$), 120.0, 121.4, 121.7, 123.5, 123.7, 124.7, 125.2, 126.8, 127.2, 128.8, 129.3, 131.1, 134.0, 142.1, 146.1, 148.8 and 151.8 (Ar*C*); HRMS (ESI): Calcd. for $C_{29}H_{29}O$ [M^++H]: *m/z* 393.2219. Found: 393.2217.

Compound 4k. Gummy liquid; Yield 0.088 g (34%); IR υ_{max}(neat): 3063, 2959, 2931, 2866, 1732, 1666, 1600, 1452, 1315, 1266, 1063, 762, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.79 and 0.86 (2 t, ^3J(H-H) = 7.4 Hz and 7.2 Hz respectively, 6H, CH_3CH$_2$), 1.22-1.45 and 1.74-2.14 (m, 8H, CH$_3$CH_2CH_2), 6.76 (s, 1H, PhC=C*H*), 6.81-6.83, 6.98-7.54 and 7.60-7.71 (m, 19H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.4, 20.9, 21.5, 32.4 and 33.0 (propyl-*C*), 126.3, 127.1, 127.4, 127.6, 127.8, 127.9, 128.0, 129.2, 129.5, 129.6, 130.0, 130.1, 131.1, 131.6, 131.8, 132.5, 132.7, 135.2, 137.3, 139.0, 139.3, 139.5, 140.0, 140.7, 142.6 and 144.7 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.5 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{36}H_{35}O_3$ [M^++H]: *m/z* 515.2587. Found: 515.2585.

Compound 4l. White solid; Yield 0.118 g (44%) Mp 94-96 ^oC; IR υ_{max}(KBr): 3057, 3030, 2838, 1726, 1660, 1594, 1501, 1265, 1249, 1139, 1024, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H, OCH_3), 6.22 (s, 1H, BzO-C=C*H*), 6.76-6.83 and 7.12-7.73 (m, 23H, PhC=C*H* + Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3 (O*C*H$_3$), 113.8, 121.6, 124.1, 126.8, 127.3, 127.9, 128.1$_0$, 128.1$_4$, 129.3, 129.5, 129.8, 130.1, 130.3, 130.5, 131.2, 132.7, 133.0, 136.9, 139.3, 140.5, 142.0, 142.9, 143.9, 159.2 (Alkenyl-C + Ar-*C*), 164.5 (O*C*OPh), 196.6 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{37}H_{28}NaO_4$ [M^++Na]: *m/z* . 559.1886 Found: 559.1886. X-ray structure was determined for this compound after crystallisation from CH_2Cl_2-hexane mixture. CCDC No. 952110.

Compound 4l'. White solid; Yield 0.107 g (40%) Mp 116-118 ^oC; IR υ_{max} (KBr): 3057, 3014, 2937, 2838, 1732, 1666, 1595,

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1507, 1255, 1238, 1184, 1063, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H, OCH_3), 6.22 (s, 1H, BzO-C=C*H*), 6.59-6.73 and 7.06-7.73 (m, 23H, PhC=C*H* + Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2 (OCH_3), 114.0, 123.1, 124.8, 126.7, 127.1, 127.6, 127.7, 127.8, 128.0, 129.1, 129.3, 129.7, 130.1, 130.2, 131.4, 132.5, 133.2, 137.5, 139.4, 139.6, 140.0, 141.8, 143.9, 159.1 (Alkenyl-C + Ar-*C*), 163.5 (O*C*OPh), 197.2 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{37}H_{28}NaO_4$ [M^++Na]: *m/z* . 559.1886 Found: 559.1886.

Compound 5. Yellow solid; Yield 0.080 g (29%,) Mp 64-66 ^oC; IR υ_{max}(KBr): 3058, 2926, 2855, 1737, 1666, 1534, 1348, 1277, 1090, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.35-1.55 (m, 6H, cyclohexyl-*H*), 1.90-1.94 (m, 2H, cyclohexyl-*H*), 2.20-2.24 (m, 2H, cyclohexyl-*H*), 6.74 (s, 1H, PhC=C*H*), 7.13-7.18 (m, 8H, Ar-*H*), 7.29-7.32 (m, 3H, Ar-*H*), 7.46 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 7.64 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.70 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.10 (d, *J* = 8.4 Hz, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.1, 26.7, 27.1, 28.2, 29.5 (cyclohexyl-*C*), 120.6, 123.0, 126.5, 127.6, 128.0, 129.2, 129.9, 130.1, 130.8, 131.3, 132.7, 134.6, 134.8, 136.3, 136.9, 139.4, 140.5, 141.0, 142.2 150.3 (alkenyl-*C* + Ar-*C*), 162.3 (O*C*OPh), 196.2 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{35}H_{29}NO_5Na$ [M^++Na]: *m/z* 566.1944. Found: 566.1947.

Compound 6 (other unidentified products were also present in the reaction mixture). Gummy liquid; Yield 0.086 g (26%,); IR υ_{max}(neat): 3063, 2926, 2855, 1721, 1671, 1606, 1507, 1441, 1321, 1249, 1162, 1080, 1025, 849, 767, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.29-1.43 (m, 6H, cyclohexyl-*H*), 1.84-1.87 (m, 2H, cyclohexyl-*H*), 2.05-2.15 (m, 2H, cyclohexyl-*H*), 3.84 (s, 3H, OCH_3), 6.72 (s, 1H, PhC=C*H*), 6.75-6.78 (m, *J* ~ 8.8 Hz, 2H, Ar-*H*), 7.13-7.19 (m, 8H, Ar-*H*), 7.33-7.39 (m, 3H, Ar-*H*), 7.47-7.51 (m, *J* ~ 8.8 Hz, 3H, Ar-*H*), 7.75 (d, *J* = 8.4 Hz, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2, 26.6, 27.0, 28.1, 29.4 (cyclohexyl-*C*), 55.4 (OCH_3), 113.1, 121.4, 121.9, 126.3, 127.4, 127.9, 128.0, 129.2, 130.1, 130.2, 131.3, 131.8, 132.5, 134.0, 136.3, 137.2, 139.2, 140.2, 141.0, 142.6, 163.3 (alkenyl-*C* + Ar-*C*) 164.0 (O*C*OPh), 196.4 (Ar*C*OPh); HRMS (ESI): Calcd. for $C_{36}H_{32}O_4Na$ [M^++Na]: *m/z* 551.2199. Found: 551.2199.

Single crystal X-ray data for compounds **3a**, and **4l** were collected on an OXFORD diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by full-matrix least squares method using standard procedures.[19] Absorption corrections were done using SADABS program, where applicable. In general, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier map and refined isotropically.

3a: colourless block, $C_{28}H_{24}O$, *M* = 376.47, Monoclinic, Space group $P2_1/c$, *a* = 8.8110(8), *b* = 20.9480(13), *c* = 10.5926(7) Å, *β* = 90.386(7), *V* = 1955.1(3) $Å^3$, *Z* = 4, *μ* = 0.076 mm^{-1}, data/restraints/parameters: 3176/0/263, R indices (I> 2σ(I)): R1 = 0.0616, *w*R2 (all data) = 0.1025. CCDC No. 952109.

4l: colourless block, $C_{40}H_{28}O_2$, *M* = 540.62, Monoclinic, Space group $P2_1/n$, *a* = 11.8178(5), *b* = 11.1901(4), *c* = 23.1887(9) Å, *β* = 103.940(4), *V* = 2976.2(2) $Å^3$, *Z* = 4, *μ* = 0.073 mm^{-1}, data/restraints/parameters: 4271/0/379, R indices (I> 2σ(I)): R1 = 0.0368, *w*R2 (all data) = 0.0841, CCDC No. 952110.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details on the synthesis of precursors **1b, 1f** and **1h-j**,^1H and ^{13}C NMR spectra and CIF files]. See DOI: 10.1039/b000000x/

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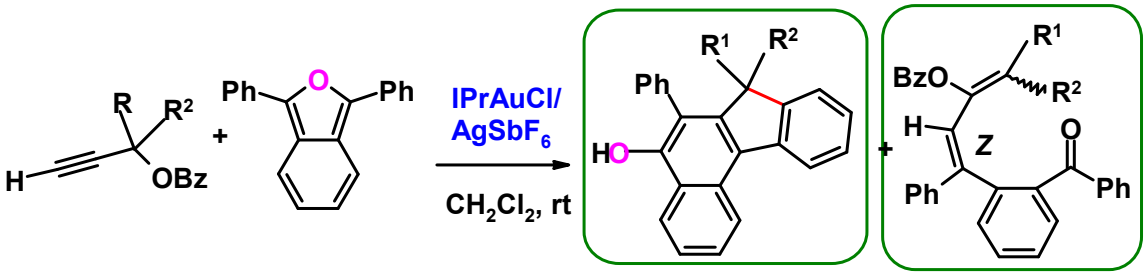
A new class of benzofluorenols is generated via a novel gold carbene complex [IPrAuCl/$AgSbF_6$] catalysed cycloaddition of propargylic esters with 1,3-diphenylisobenzofuran.



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