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Article

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Synthesis of Functionalized 1*H*-Indenes and Benzofulvenes through Iodocyclization of *ortho*-(Alkynyl)styrenes

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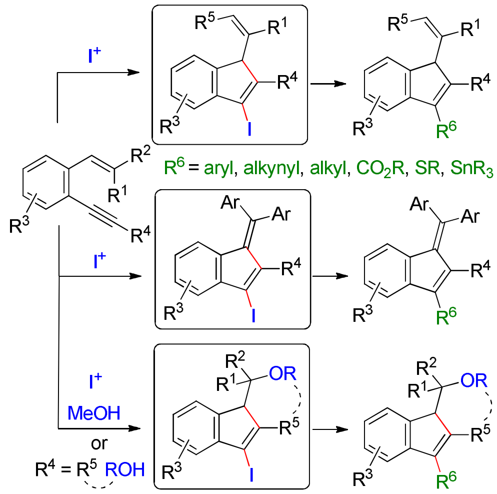


ABSTRACT:

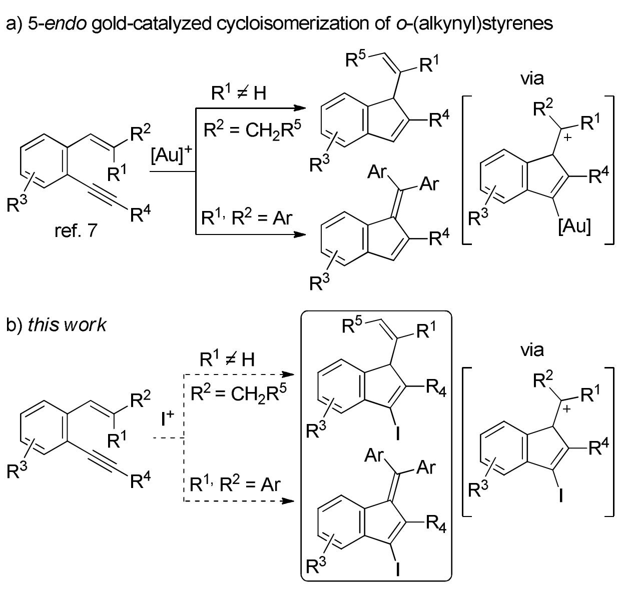
A convenient method for the preparation of synthetically useful 3-iodoindene derivatives has been developed. This protocol, based on the 5-*endo* iodocyclization reaction of *o*-(alkynyl)styrenes, represents one of the scarce examples of halocyclizations using olefins as nucleophilic counterparts, and allows the synthesis of both 3-iodo-1*H*-indenes (from β-alkyl-β-alkyl/aryl *o*-(alkynyl)styrenes) and 3-iodobenzofulvenes (from β,β-diaryl *o*-(alkynyl)styrenes) in good yields under mild reaction conditions. Besides, related alkoxyiodocyclization processes are described, which are particularly interesting in their intramolecular version because they allow the synthesis of heteropolycyclic structures containing the indene core. Finally, the usefulness of the prepared 3-iodoindenes has been demonstrated by the synthesis of several polysubstituted indene derivatives through conventional palladium–catalyzed cross-coupling reactions and iodine–lithium exchange processes.

INTRODUCTION

Indene derivatives, including methyleneindenes (benzofulvenes), are privileged scaffolds in organic chemistry. These molecules are present in the structure of many biologically active compounds[1-4] and they have also found application in material chemistry[5-9] and as ligands in metal catalysis.[10-11] Therefore, several approaches for the synthesis of 1*H*-indenes and benzofulvenes have been described.[12] In particular, haloindenes are highly attractive building blocks, as they provide opportunity for subsequent functionalization. Therefore, the search for new simple, efficient, and general methods for the synthesis of haloindenes is an active field in organic chemistry.[13]

On the course of our studies on gold-catalyzed cyclizations of 1,3-dien-5-ynes,[14-19] we have reported practical methods for the synthesis of 1*H*-indenes[17-19] and benzofulvenes[16] by cycloisomerization of appropriately substituted *o*-(alkynyl)styrenes (Scheme 1a). The reaction is in both cases based on the nucleophilic attack of the olefin unit to the gold-coordinated triple bond. Taking into account these results and considering the known ability of iodonium species to activate alkynes,[20,21] we thought that the 5-*endo* iodocyclization of *o*-(alkynyl)styrenes could provide a useful method for the synthesis of 3-iodo-1*H*-indenes and 3-iodobenzofulvenes (Scheme 1b).[22]

SCHEME 1. Reported gold-catalyzed cycloisomerizations of *o*-(alkynyl)styrenes, and proposed synthesis of 3-iodo-1*H*-indenes and 3-iodobenzofulvenes.



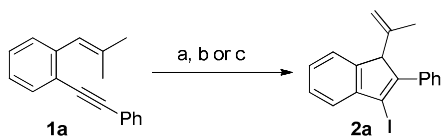
Although it is well known that iodocyclizations involving alkynes are valuable transformations for the synthesis of a variety of functionalized cyclic structures,[20,21] it should be noted that iodocyclization processes involving the addition of carbon-centered nucleophiles to alkynes are an underdeveloped area.[23] Particularly, the iodocyclization of enyne derivatives (and related compounds such as *o*-(alkynyl)styrenes) has received very little attention. The work of S. F. Kirsch and co-workers on the 6-*endo* iodocyclization of 1,5-enynes[24-27] and 5- and 6-*exo* iodocyclization of 1,6-enynes[26,28] should be remarked upon at this point. In this context, we have recently reported pioneering preliminary results regarding the 5-*endo* iodocyclization reaction proposed in Scheme 1b for the synthesis of 1*H*-indenes.[29,30] Herein we provide a detailed investigation on this area, including its application for the preparation of benzofulvenes.[31]

RESULTS AND DISCUSSION

Initial results:

At the beginning of the project we thought that the best way to get the desired 5-*endo* iodocyclization reaction could be the use of β,β-disubstituted *o*-(alkynyl)styrenes, because upon the intramolecular addition of the alkene to the activated alkyne a relatively stable tertiary carbocation would be formed (Scheme 1b). With this idea in mind, we initially selected β,β-dimethyl *o*-(alkynyl)styrene **1a** as model substrate to check the viability of our proposal. Gratifyingly, **1a** cleanly afforded the iodoindene **2a** (71% yield) when stirred with *N*-iodosuccinimide (NIS) in dichloromethane at room temperature for 24 h (Scheme 2, conditions a). The yield could be improved (85%) and the reaction time reduced (3 h) by performing the process at reflux (Scheme 2, conditions b). Interestingly, we also observed that the reaction could be done with molecular iodine in the presence of a base (K_3PO_4) instead of NIS (Scheme 2, conditions c). However, under these conditions compound **2a** was isolated in slightly lower yield (74%). These results demonstrated the feasibility of our proposed synthesis of 3-iodo-1*H*-indenes through a 5-*endo* halocyclization reaction of enyne derivatives.

SCHEME 2. Proof of concept and initial experiments.

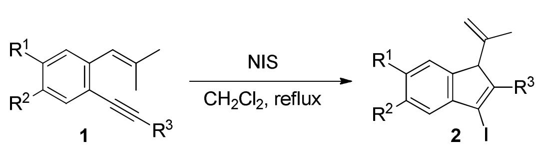


a) NIS (3 equiv.), CH_2Cl_2, RT, 24 h 71%
b) NIS (3 equiv.), CH_2Cl_2, reflux, 3 h 85%
c) I_2/K_3PO_4 (3 equiv.), CH_2Cl_2, RT, 1 h 74%

Synthesis of 3-iodo-1*H*-indenes 2 by iodocyclization of *o*-(alkynyl)styrenes 1:

Once the potential of *o*-(alkynyl)styrenes as precursors of 3-iodo-1*H*-indenes had been demonstrated, we explored the scope and limitations of this transformation. We initially tested the iodocyclization of diverse β,β-dimethyl *o*-(alkynyl)styrenes **1** with NIS as the iodinating agent (Table 1). Gratifyingly, 3-iodo-1*H*-indenes with various substituents at the aromatic ring, including electron-withdrawing (entries 2−3) or electron-donating groups (entry 4) could be efficiently synthesized. Moreover, 3-iodo-1*H*-indenes with aromatic (entries 1−5), heteroaromatic (entry 6), aliphatic (entries 7−9), and heteroatomic (entry 10) groups at C-2 could be easily obtained by using as substrate the *o*-(alkynyl)styrene appropriately substituted at the terminal position of the alkyne. Nevertheless, decomposition was observed for an *o*-(alkynyl)styrene having an iodine at this position, whereas the corresponding terminal or TMS-substituted alkynes were not reactive in the presence of NIS. The iodocyclization of β,β-dimethyl *o*-(alkynyl)styrenes **1** is also possible using as halogen source molecular iodine in the presence of a base, as previously shown for **1a** and further illustrated in entries 4 and 5.

TABLE 1. Synthesis of 3-iodo-1*H*-indenes 2 by iodocyclization of *o*-(alkynyl)styrenes 1.[a]



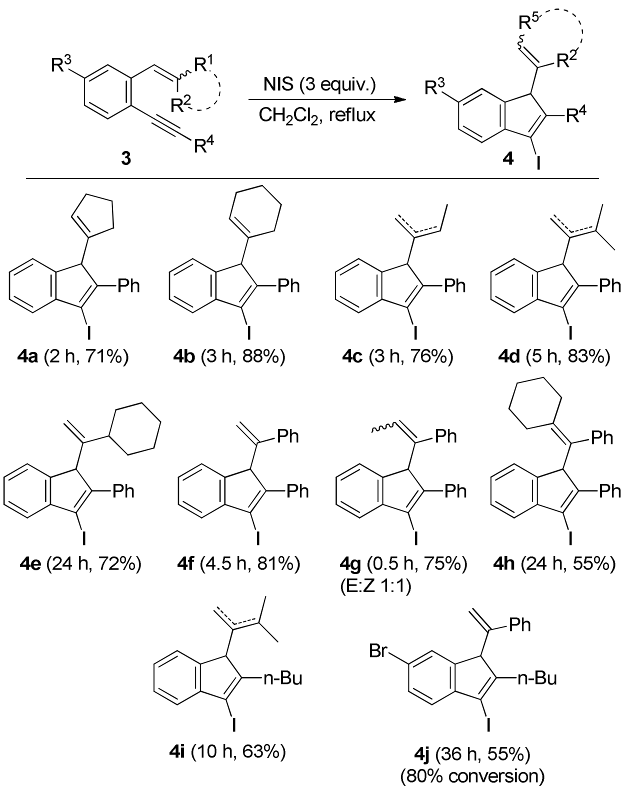
entry	**1**	R^1	R^2	R^3	**2**	t (h)	yield [%][b]
1	**1a**	H	H	Ph	**2a**	3	85(74)[c]
2	**1b**	F	H	Ph	**2b**	17	79

3	**1c**	Br	H	Ph	**2c**	7	84
4	**1d**	–OCH$_2$O–		Ph	**2d**	1	78(67)[c]
5	**1e**	H	H	4-MeOC$_6$H$_4$	**2e**	1	92(71)[c]
6	**1f**	H	H	3-Th[c]	**2f**	2.5	87
7	**1g**	H	H	*n*-Bu	**2g**	2	81
8	**1h**	Br	H	*n*-Bu	**2h**	16	82
9	**1i**	H	H	(CH$_2$)$_3$CN	**2i**	15	71
10	**1j**	H	H	SPh	**2j**	1	80

[a] Reactions conducted using 0.5 mmol of *o*-(alkynyl)styrene derivative **1** and 1.5 mmol of NIS in CH$_2$Cl$_2$ (2 mL) at reflux. These reactions can also be performed at RT although with prolonged reaction times and slightly lower yields. [b] Yield of product based on starting material **1**. [c] Performed with I$_2$/K$_3$PO$_4$ (3 equiv.) as electrophilic source at RT. [d] 3-Thienyl.

Next, we explored the halocyclization of several *o*-(alkynyl)styrenes **3** possessing different aliphatic and aromatic groups at the olefin (Scheme 3). Thus, substrates **3a** and **3b** having a cycloalkane as R^1–R^2 substituent provided the corresponding iodoindenes with high yields in short reaction times (2–3 h). *o*-(Alkynyl)styrenes **3c** and **3d**, which have two different alkyl groups in the alkene, furnished iodoindenes **4c**,**d** in high yields as mixtures of isomers that differ in the position of the external double bond (1:1.5 for **4c**, 4:1 for **4d**). The formation of isomeric products can be explained from a common carbocationic intermediate that experiences proton elimination from either of the two different aliphatic groups. Conversely, in the halocyclization of **3e** to give **4e**, only the indene coming from the elimination of the proton from the methyl group was observed (the cyclohexyl group remained unaffected). Moreover, substrates **3f-h**, having both an aliphatic and an aromatic substituent at the olefin, efficiently provided the corresponding 3-iodo-1*H*-indenes **4f-h**. *o*-(Alkynyl)styrenes with an aliphatic substituent at the alkyne and two different groups at the olefin, either alkyl/alkyl (**3i**) or alkyl/aryl (**3j**), were also useful starting materials for the synthesis of iodoindenes via iodocyclization in the presence of NIS. In the case of **4i** a 2:1 mixture of olefin isomers was obtained. On the other hand, an *o*-(alkynyl)styrene lacking substituents at the double bond (R^1=R^2=H) turned out to be unreactive, whereas *o*-(alkynyl)styrene derivatives monosubstituted at the terminal position of the alkene (β-methyl or β-phenyl *o*-(alkynyl)styrenes) decomposed under the optimal reaction conditions. These results demonstrate the requirement of a starting material with a β,β-disubstituted olefin as a prerequisite for an efficient iodocyclization that leads to 3-iodoindenes.

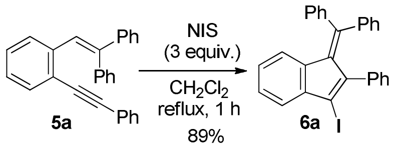
SCHEME 3. Iodocyclization of *o*-(alkynyl)styrenes 3 bearing different substituents at the olefin.



Synthesis of 3-iodobenzofulvenes 6 from *o*-(alkynyl)styrenes 5:

Next, we studied the reaction with starting materials where the olefin was substituted with aryl groups. Considering the cationic intermediate of this process (see Scheme 1), it should be noted that in these cases the final elimination process would involve the hydrogen at C1 of the indene. Thus, these reactions should deliver fulvene derivatives instead of the previously observed indenes. In fact, when *o*-(alkynyl)styrene **5a** having two phenyl groups as substituents of the olefin was used as starting material under the previous optimal conditions, 3-iodobenzofulvene **6a** was obtained as only product in good yield (Scheme 4).

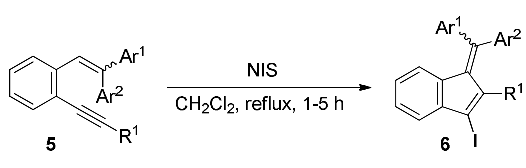
SCHEME 4. Synthesis of 3-iodobenzofulvenes: proof of concept.



The structure of **6a** was confirmed by X-ray diffraction analysis (Scheme 4).[32] A significant twist of the three aryl substituents with respect to the benzofulvene plane is observed, with the phenyl in C-2 and one of the phenyls linked to the external olefin adopting an almost face-to-face arrangement, which suggests that π-π-interactions are established between both rings. These observations are in full agreement with those previously reported for related aryl-substituted benzofulvenes.[33]

To further assess the usefulness of our methodology, the scope of the iodocyclization of β,β-diaryl *o*-(alkynyl)styrenes **5** was analyzed (Table 2). Gratifyingly, a variety of 3-iodobenzofulvenes with substituents of different nature at C-2 could be obtained in good to excellent yields, as either aromatic, heteroaromatic, alkenyl, alkyl, and heteroatomic groups were well tolerated as substituents of the triple bond in the starting material (entries 1−8). Moreover, variability in the aromatic rings of the double bond was also possible, including phenyl rings with either electron-donating (entries 9−12) or electron-withdrawing (entry 14) substituents and also heteroaromatic rings (entry 13). When an *o*-(alkynyl)styrene with two different aryl rings in the olefin was used as starting material (entries 11−14), the corresponding 3-iodobenzofulvene was obtained as a ~1:1 mixture of *E*/*Z* isomers, regardless of the *E*/*Z* ratio of the starting material.

TABLE 2. Synthesis of 3-iodobenzofulvenes 6 by iodocyclization of β,β-diaryl-substituted *o*-(alkynyl)styrenes 5.[a]



entry	5	Ar[1]	Ar[2]	R[1]	6	yield [%][b]
1	**5a**	Ph	Ph	Ph	**6a**	89
2	**5b**	Ph	Ph	4-MeC_6H_4	**6b**	90
3	**5c**	Ph	Ph	4-$MeOC_6H_4$	**6c**	91
4	**5d**	Ph	Ph	3-FC_6H_4	**6d**	92

5	**5e**	Ph	Ph	3-Th[c]	**6e**	84
6	**5f**	Ph	Ph	*c*-C_6H_9[d]	**6f**	69
7	**5g**	Ph	Ph	*n*-Bu	**6g**	59
8	**5h**	Ph	Ph	SPh	**6h**	95
9	**5i**	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4	**6i**	90
10	**5j**	4-MeC_6H_4	4-MeC_6H_4	*n*-Bu	**6j**	70
11	**5k**	Ph	3,4,5-$MeOC_6H_4$	*n*-Bu	**6k**	54[e]
12	**5l**	Ph	4-$MeOC_6H_4$	*n*-Bu	**6l**	75[e]
13	**5m**	Ph	2-Th[c]	*n*-Bu	**6m**	59[e]
14	**5n**	4-FC_6H_4	4-$MeOC_6H_4$	*n*-Bu	**6n**	72[e]

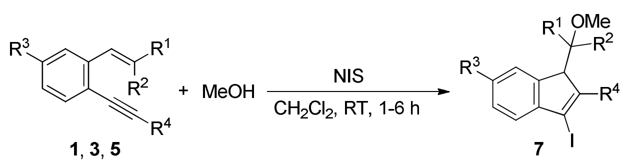
[a] Reactions conducted using 0.2 mmol of *o*-(alkynyl)styrene derivative **5** and 0.6 mmol of NIS in CH_2Cl_2 (0.8 mL) at reflux. [b] Yield of product based on starting material **5**. [c] 3-Thienyl. [d] Cyclohexenyl. [e] Obtained as a ~1:1 mixture of geometrical isomers.

Synthesis of oxygen-functionalized 3-iodo-1*H*-indenes:

Considering the carbocationic nature of the intermediate proposed in the halocyclization mechanism (see Scheme 1b), we decided to explore the possibility of trapping this intermediate with a nucleophile before the proton elimination occurred.[34] In this way, indenes having additional functionalization at the C-1 substituent could be easily obtained. First assays were performed with *o*-(alkynyl)styrene **1a** and methanol as nucleophile in the presence of NIS as iodinating agent. We were glad to observe the formation of the corresponding new indene derivative **7a**, incorporating the methoxy group in the C1-substituent, when performing the reaction in a 2:1 mixture of dichloromethane and methanol at room temperature.[35] The scope of the methoxyiodocyclization of *o*-(alkynyl)styrenes **1**, **3**, and **5** was then evaluated (Table 3). Different groups in the triple bond were tolerated including phenyl (entries 1–3, 6, 8–10), functionalized aryl (entry 4) as well as heteroatomic groups (entry 5). In the case of *o*-(alkynyl)styrenes having two different substituents in the olefin, the corresponding alkoxyiodocyclization products **7** were obtained as mixtures of diastereoisomers, ranging from 1:1 to 3:1 (entries 6, 8 and 9). Finally, β,β-diphenyl *o*-(alkynyl)styrene **5a** efficiently led to indene **7i** under the optimized methoxyiodocyclization conditions.

It should be noted that along with the alkoxyiodocyclization products **7** we detected in most of the cases the formation of small amounts of the corresponding products **2**, **4**, or **6**, derived from the competitive elimination process. In this sense, we observed that the amount of the corresponding elimination product was increased when the olefin of the starting material was substituted with sterically hindered groups. A limit situation was found when the alkoxyiodocyclization reaction was attempted with *o*-(alkynyl)styrene **3d** having a bulky isopropyl group. In this particular case, we only observed the formation of the elimination product **4d** (entry 7).

TABLE 3. Synthesis of oxygen-functionalized 3-iodo-1*H*-indenes 7.[a]



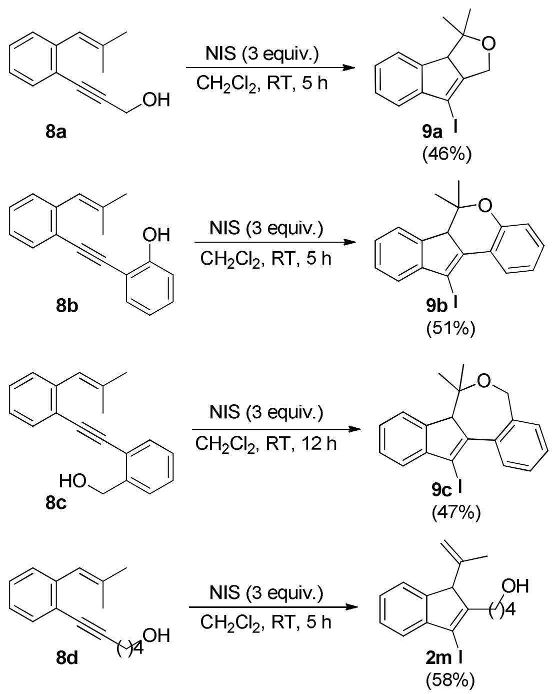
entry	**1,3,5**	R^1	R^2	R^3	R^4	**7**	yield [%][b]
1	**1a**	Me	Me	H	Ph	**7a**	66(58)[c]
2	**1b**	Me	Me	F	Ph	**7b**	78
3	**1c**	Me	Me	Br	Ph	**7c**	72
4	**1e**	Me	Me	H	4-MeOC_6H_4	**7d**	70
5	**1j**	Me	Me	H	SPh	**7e**	58
6	**3c**	Me	Et	H	Ph	**7f**	45[d]
7	**3d**	Me	*i*-Pr	H	Ph	–	–[e]
8	**3f**	Me	Ph	H	Ph	**7g**	81[d]
9	**3g**	Et	Ph	H	Ph	**7h**	60[d]
10	**5a**	Ph	Ph	H	Ph	**7i**	66

[a] Reactions conducted using 0.5 mmol of *o*-(alkynyl)styrene derivative **1**, **3**, or **5**, and 1.5 mmol of NIS in a mixture of MeOH (1 mL) and CH_2Cl_2 (2 mL) at RT. [b] Yield of product based on starting material **1**, **3** or **5**. [c] Performed with I_2/K_3PO_4 (3 equiv.) as electrophilic source. [d] Obtained as a mixture of diasteroisomers: 3:1 (entry 6), 2:1 (entry 8), 1:1 (entry 9). [e] Only **4d** is formed, no incorporation of MeOH is observed.

With the aim of accessing polycyclic compounds, the alkoxyiodocyclization reaction was also tried in an intramolecular fashion. Thus, several *o*-(alkynyl)styrenes **8** with a pendant hydroxyl group were prepared and their reactivity tested under the standard conditions (Scheme 5). Pleasantly, iodoindenes fused to 5-, 6- and 7-membered oxygen–containing heterocyclic rings could be obtained in this way.[36]

However, the corresponding iodoindene fused to an 8-membered heterocycle could not be synthesized following this methodology since indene **2m** was the only product observed in the reaction of **8d** with NIS.

SCHEME 5. Synthesis of polycyclic compounds 9 by intramolecular alkoxyiodocyclization of *o*-(alkynyl)styrenes 8.



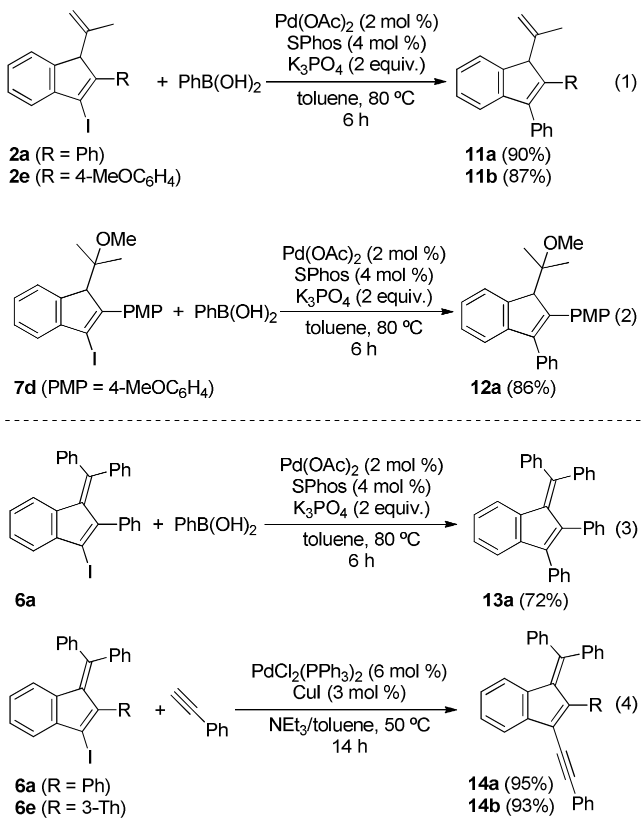
Derivatization of 3-iodoindenes:

An appealing issue of the reported method for the synthesis of indenes and benzofulvenes from *o*-(alkynyl)styrenes is that it provides indene derivatives containing a carbon–iodine bond. The rich reactivity of this bond can be exploited to get indenes and benzofulvenes with a variety of substituents at C-3. For example, palladium–catalyzed Suzuki cross-coupling of indenes **2a** and **2e** with phenylboronic acid afforded 3-phenylindenes in excellent yields (Scheme 6, eq 1). Indenes **7** were also suitable partners for this coupling, as illustrated in the reaction of **7d** with phenylboronic acid (Scheme 6, eq 2).

3-Phenylbenzofulvene **13a** could also be easily obtained by Suzuki coupling of the corresponding 3-iodobenzofulvene **6a**, (Scheme 6, eq 3). Moreover, the synthesis of 3-alkynylbenzofulvenes **14a** and

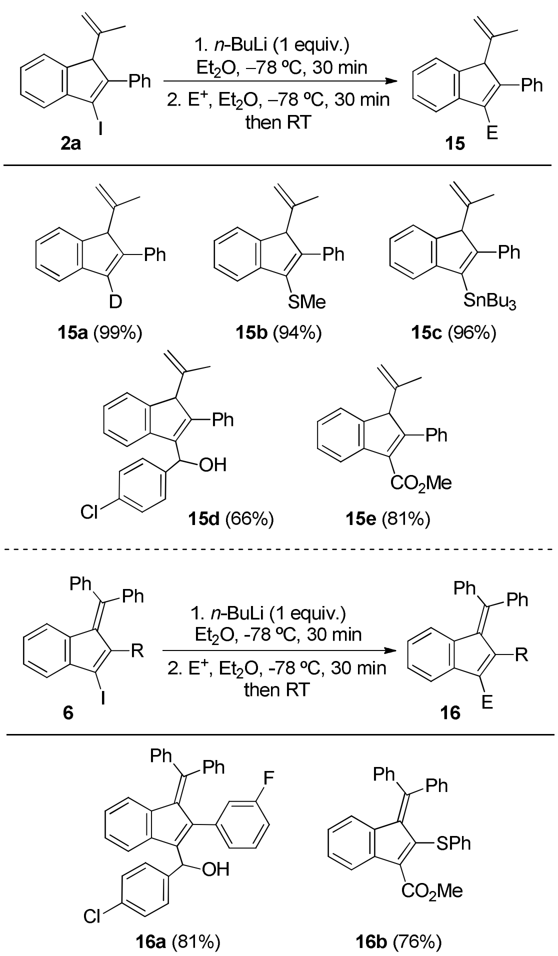
14b was efficiently achieved by means of a Sonogashira reaction between the corresponding iodobenzofulvene **6** and phenylacetylene (Scheme 6, eq 4).

SCHEME 6. Palladium-catalyzed cross-coupling reactions of 3-iodo-1*H*-indenes 2 and 7, and 3-iodobenzofulvenes 6.



Besides these typical palladium–catalyzed cross-coupling reactions that allow the introduction of aryl and alkynyl groups at C-3 we also tried other type of reactions. Thus, iodo-1*H*-indenes **2** and iodobenzofulvenes **6** could be alternatively functionalized by iodine–lithium exchange followed by treatment with selected electrophiles (Scheme 7). Accordingly, treatment of **2a** in Et_2O with 1 equivalent of butyllithium at −78 ºC followed by addition of MeOD quantitatively led to deuterated derivative **15a**, thus confirming that the halogen–lithium exchange had efficiently occurred. We were glad to find that other electrophiles, such as disulfides, chlorostannanes, aldehydes, and chloroformates, also reacted with the in situ formed organolithium compound. Moreover, 3-iodobenzofulvenes **7** bearing substituents of varied nature at C-2 were also efficiently functionalized at C-3 position following an analogous iodine–lithium exchange protocol. Therefore, a variety of 1*H*-indenes and benzofulvenes with either heteroatom or carbon substituents in C-3, complementary to the ones obtained by palladium–catalyzed cross-coupling reactions, were synthesized in good to excellent yields.

SCHEME 7. Derivatization of 3-iodoindenes 2 and 6 via I–Li exchange.



CONCLUSIONS

Polysubstituted indene derivatives can be conveniently prepared from easily available *o*-(alkynyl)styrene derivatives by a 5-*endo* iodocyclization process. The presence of a new C–I bond in the final products allows for subsequent functionalization through conventional palladium–catalyzed cross-coupling processes and iodine–lithium exchange reactions followed by coupling with appropriate electrophiles.

It was found that the reaction of β,β-dialkyl or β-alkyl,β-aryl *o*-(alkynyl)styrenes with a source of electrophilic iodine efficiently leads to 3-iodo-1*H*-indenes, whereas the reaction of β,β-diaryl *o*-(alkynyl)styrenes gives rise to 3-iodobenzofulvenes in high yields. Moreover, alkoxyiodocyclizations are achieved when the reactions are performed in the presence of an alcohol. These reactions allow the introduction of an oxygenated functionality at C-1 of the indene. Particularly interesting is the intramolecular version of these alkoxyiodocyclization reactions as complex polycyclic compounds containing the indene core are easily available.

Overall, the current methodology provides an appealing alternative for the synthesis of polysubstitued indene derivatives.

EXPERIMENTAL SECTION

General Experimental Methods: All reactions involving air-sensitive compounds were carried out under a N_2 atmosphere in oven-dried glassware with magnetic stirring. Temperatures are reported as bath temperatures. Solvents used in extraction and purification were distilled prior to use. TLC was performed on alumina-backed plates coated with silica gel 60 with F254 indicator; the chromatograms were visualized by UV light (254 nm) and/or by staining with a Ce/Mo reagent solution and subsequent heating. R_f values refer to silica gel. Flash column chromatography was carried out on silica gel 60, 230-400 mesh. ^{1}H NMR spectra were recorded at 300 or 500 MHz. Chemical shifts are reported in ppm with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublets, ddd: doublet of doublet of doublets, td: triplet of doublets, t: triplet, dq: doublet of quartets, sex: sextet, sep: septet, m: multiplet), coupling constants (*J* in Hz) and integration. ^{13}C NMR spectra were recorded at 75.4 or 100 MHz using broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. Gas chromatography–mass spectra (GC-MS) were recorded on an instrument equipped with a 30 m × 0.25 mm capillary apolar column (stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm). Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV and only the molecular ions and/or base peaks as well as significant peaks in MS are given. High-resolution mass spectra

(HRMS) were recorded on an instrument equipped with a magnetic sector ion analyzer using EI at 70 eV or on an instrument equipped with a QTOF analyzer using ESI (+). Melting points were measured on a microscopic apparatus using open capillary tubes and are uncorrected. All commercially available reagents were used without purification unless otherwise indicated and were purchased from standard chemical suppliers. *o*-(Alkynyl)styrenes **1**, **3**, **5**, **8** have been previously reported and were prepared following two step protocols that involve an olefination reaction of a carbonyl derivative and a Sonogashira coupling.[29, 16-19]

Synthesis of 3-iodo-1*H*-indenes 2 and 4 by iodocyclization of *o*-(alkynyl)styrenes 1 and 3:

Method A: *N*-Iodosuccinimide (338 mg, 1.5 mmol) was added to a solution of the corresponding starting *o*-(alkynyl)styrene **1** or **3** (0.5 mmol) in CH_2Cl_2 (2 mL). The reaction vial was sealed and protected from light. The resulting mixture was heated at reflux until complete consumption of the starting material as determined by TLC or GC-MS (1-48 h). The mixture was quenched by addition of saturated aq $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 3-iodo-1*H*-indenes **2** or **4** in the yields reported in Table 1 and Scheme 3.

Method B: Iodine (381 mg, 1.5 mmol) was added to a solution of the corresponding starting *o*-(alkynyl)styrene **1** (0.5 mmol) and K_3PO_4 (318 mg, 1.5 mmol) in CH_2Cl_2 (2 mL). The reaction vial was sealed and protected from light. The resulting mixture was stirred at RT until complete consumption of the starting material as determined by TLC (1-3 h). The mixture was quenched by addition of saturated aq $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 3-iodo-1*H*-indenes **2** in the yields reported in Table 1.

The characterization data of **2a-j** and **4a**,**b**,**f**,**j** have been previously reported.[29]

The characterization data of novel compounds obtained by method A are reported below:

*3-Iodo-1-[(E)-1-methyl-1-propenyl]-2-phenyl-1H-indene and 1-(1-ethylvinyl)-3-iodo-2-phenyl-1H-indene (***4c***).* Pale yellow oil; R*f* = 0.51 (hexane); 76% yield (141 mg); Obtained as a 1.5:1 mixture: major isomer (maj) 3-iodo-1-[(*E*)-1-methyl-1-propenyl]-2-phenyl-1*H*-indene; minor isomer (min) 1-(1-ethylvinyl)-3-iodo-2-phenyl-

1*H*-indene; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.73 (t, *J* = 7.4 Hz, 3H, min), 0.99 (s, 3H, maj), 1.30–1.62 (m, 2H, min), 1.60 (d, *J* = 6.7 Hz, 3H, maj), 4.48 (s, 1 H, maj), 4.65 (s, 1H, min), 4.98 (m, 1H, min), 5.24 (bs, 1H, min), 5.73 (m, 1H, maj), 7.21–7.49 (m, 14H), 7.54–7.65 (m, 4H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 11.1 (CH_3), 11.9 (CH_3), 13.8 (CH_3), 22.9 (CH_2), 62.3 (CH), 63.5 (CH), 94.4 (C), 94.7 (C), 113.4 (CH_2), 122.8 (CH), 122.9 (CH), 123.08 (CH), 123. 10 (CH), 124.9 (CH), 126.5 (CH), 126.6 (CH), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.1 (2 x CH), 128.2 (2 x CH), 129.0 (4 x CH), 133.1 (C), 135.9 (C), 136.0 (C), 144.3 (C), 145.5 (C), 146.1 (C), 146.0 (C), 148.5 (C), 152.3 (C), 152.7 (C) ppm; HRMS (EI): calcd for $C_{19}H_{17}I^+$: 372.0369, found: 372.0374.

3-Iodo-1-(1-isopropylvinyl)-2-phenyl-1H-indene ***(4d)***. Colourless oil; R*f* = 0.44 (hexane); 66% yield (127 mg). Isolated from a *ca.* 4:1 crude mixture of isomers; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.60 (t, *J* = 6.8 Hz, 3H), 0.67 (t, *J* = 6.8 Hz, 3H), 1.52 (sep, *J* = 6.8 Hz, 1H), 4.62 (s, 1H), 5.01 (s, 1H), 5.17 (s, 1H), 7.24–7.45 (m, 7H), 7.59–7.64 (m, 2H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 23.1 (CH_3), 24.7 (CH_3), 29.7 (CH), 62.3 (CH), 94.8 (C), 113.2 (CH_2), 123.0 (CH), 123.5 (CH), 126.5 (CH), 127.7 (CH), 128.0 (CH), 128.1 (2 x CH), 129.2 (2 x CH), 136.0 (C), 144.5 (C), 146.1 (C), 152.4 (C), 153.8 (C) ppm; LRMS (EI): *m/z* (%): 386 (M^+, 26), 259 (86), 217 (100), 202 (71); HRMS (EI): calcd for $C_{20}H_{19}I^+$: 386.0526; found: 386.0533.

1-(1-Cyclohexylvinyl)-3-iodo-2-phenyl-1H-indene ***(4e)***. Pale yellow oil. R*f* = 0.53 (hexane). 72% yield (153 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.84–1.29 (m, 7H), 1.41–1.55 (m, 4H), 4.60 (s, 1H), 4.98 (s, 1H), 5.16 (s, 1H), 7.25–7.45 (m, 7H), 7.55–7.63 (m, 2H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 26.2 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 33.5 (CH_2), 35.2 (CH_2), 40.4 (CH), 62.2 (CH), 94.7 (C), 113.6 (CH_2), 123.0 (CH), 123.5 (CH), 126.4 (CH), 127.7 (CH), 128.0 (CH), 128.07 (CH), 128.11 (2 x CH), 129.2 (2 x CH), 136.1 (C), 144.5 (C), 146.0 (C), 152.5 (C), 152.7 (C) ppm; LRMS (EI): *m/z* (%): 426 (M^+, 6), 300 (31), 217 (100), 202 (35); HRMS (EI): calcd for $C_{23}H_{23}I^+$: 426.0839; found: 426.0846.

3-Iodo-2-phenyl-1-(1-phenyl-1-propenyl)-1H-indene ***(4g)***. Pale yellow solid; R*f* = 0.47 (hexane:CH_2Cl_2 20:1). Mp = 95–97 ºC; 75% yield (163 mg); Obtained as a ~1:1 mixture of *E*:*Z* diastereoisomers; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ = 1.50 (d, *J* = 6.8 Hz, 3H), 2.14 (d, *J* = 6.8 Hz, 3H), 4.80 (s, 1H), 5.31 (bs, 1H), 5.91–5.97 (m, 2H), 6.39–6.44 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 2H), 6.97–7.01 (m, 2H), 7.04–7.08 (m, 1H), 7.25–7.50 (m, 18H) ppm; $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$, 25 ºC): δ = 14.8 (CH_3), 15.0 (CH_3), 54.4 (CH), 62.4 (CH), 94.0 (C), 94.5 (C), 123.0 (CH), 123.1 (CH), 123.4 (CH), 123.5 (CH), 126.37 (2 x CH), 126.4 (CH), 126.65 (CH), 126.70 (CH), 126.72 (CH), 127.35 (CH), 127.44 (2 x CH), 127.5 (2 x CH), 127.65 (CH), 127.68 (CH), 127.80 (CH), 127.84 (CH), 127.9 (2 x CH), 128.0 (2 x CH), 128.5 (2 x CH), 128.8 (2 x CH), 129.3 (2 x CH), 136.1 (C), 136.2 (C), 137.6 (C), 138.6 (C), 138.9 (C), 141.2 (C), 144.6 (2 x C), 145.9 (C), 146.2 (C), 152.2 (C), 153.2 (C) ppm; one aromatic CH signal is not observed probably due to overlaping with other signals. HRMS (EI): calcd for $C_{24}H_{19}I^+$: 434.0526, found: 434.0530.

*1-[Cyclohexylidene(phenyl)methyl]-3-iodo-2-phenyl-1H-indene (**4h**).* Colourless solid; Mp = 43–45 ºC; 55% yield (122 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.32–1.48 (m, 2H), 1.62–1.70 (m, 2H), 1.80–1.91 (m, 4H), 2.77 (t, J = 6.0 Hz, 2H), 5.40 (s, 1H), 6.09 (dd, J = 8.2, 1.3 Hz, 2H), 6.84 (t, J = 7.6 Hz, 2H), 6.90–7.03 (m, 1H), 7.26–7.47 (m, 9H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 27.1 (CH_2), 28.6 (CH_2), 29.2 (CH_2), 31.4 (CH_2), 32.7 (CH_2), 55.3 (CH), 93.5 (C), 123.0 (CH), 123.5 (CH), 126.2 (CH), 126.3 (CH), 126.9 (2 x CH), 127.4 (CH), 127.8 (CH), 127.9 (4 x CH), 129.15 (C), 129.23 (2 x CH), 136.2 (C), 138.8 (C), 140.8 (C), 144.6 (C), 146.6 (C), 152.4 (C) ppm; LRMS (EI): *m/z* (%): 488 (M^+, 90), 406 (76), 279 (100), 215 (40); HRMS (EI): calcd for $C_{28}H_{25}I^+$: 488.0996; found: 488.1004.

*2-Butyl-3-iodo-1-(1-isopropylvinyl)-1H-indene (**4i**).* Colourless oil. R*f* = 0.68 (hexane); 42% yield (77 mg); Isolated along with traces of the isomer having an internal olefin from a *ca.* 2:1 crude mixture; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.78 (d, J = 6.8 Hz, 3H), 0.91–0.96 (m, 6H), 1.32–1.44 (m, 2H), 1.45–1.60 (m, 3H), 2.28–2.33 (m, 1H), 2.52–2.63 (m, 1H), 4.10 (s, 1H), 5.11 (s, 1H), 5.13 (s, 1H), 7.12–7.27 (m, 3H), 7.30–7.36 (m, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 14.1 (CH_3), 22.7 (CH_2), 23.6 (CH_3), 24.5 (CH_3), 29.9 (CH), 31.2 (CH_2), 31.7 (CH_2), 60.8 (CH), 94.7 (C), 112.9 (CH_2), 121.7 (CH), 123.4 (CH), 125.6 (CH), 127.4 (CH), 144.8 (C), 145.8 (C), 154.1 (C), 155.8 (C) ppm; LRMS (EI): *m/z* (%): 366 (M^+, 39), 239 (100), 197 (64); HRMS (EI): calcd for $C_{18}H_{23}I^+$: 366.0839; found: 366.0846.

Synthesis of 3-iodobenzofulvenes 6 by iodocyclization of β,β-diaryl-substituted *o*-(alkynyl)styrenes 5: *N*-Iodosuccinimide (338 mg, 1.5 mmol) was added to a solution of the corresponding starting *o*-(alkynyl)styrene **5** (0.5 mmol) in CH_2Cl_2 (2 mL). The reaction vial was sealed and protected from light. The resulting mixture was heated at reflux until complete consumption of the starting material as determined by TLC or GC-MS (1-6 h). The mixture was quenched by addition of saturated aq $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 3-iodobenzofulvenes **6** in the yields reported in Table 2.

*3-Iodo-1a,1a,2-triphenylbenzofulvene (**6a**).* Orange solid. R*f* = 0.55 (hexane); Mp = 170–171 ºC; 89% yield (215 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 6.31 (d, *J* = 7.9 Hz, 1H), 6.81–7.02 (m, 9H), 7.05–7.10 (m, 2H), 7.237.28 (m, 1H), 7.33–7.54 (m, 6H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 104.3 (C), 122.7 (CH), 123.2 (CH), 126.2 (CH), 126.4 (CH), 127.1 (2 × CH), 127.2 (2 × CH), 127.5 (CH), 128.1 (CH), 128.8 (2 × CH), 129.1 (CH), 130.6 (2 × CH), 130.9 (2 × CH), 132.2 (2 × CH), 137.0 (C), 137.7 (C), 137.9 (C), 141.1 (C), 142.9 (C), 143.3 (C), 146.5 (C), 149.4 (C) ppm; LRMS (EI): *m/z* (%): 482 (M^+, 100), 355 (38), 276 (45); HRMS (EI): calcd for $C_{28}H_{19}I^+$: 482.0526, found: 482.0537.

*3-Iodo-2-(4-methylphenyl)-1a,1a-diphenylbenzofulvene (**6b**).* Orange solid; R*f* = 0.23 (hexane); Mp = 175–177 ºC; 90% yield (223 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 2.21 (s, 3H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 2H), 6.83–7.02 (m, 8H), 7.23–7.31 (m, 1H), 7.33–7.57 (m, 6H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 21.2 (CH_3), 103.8 (C), 122.6 (CH), 123.2 (CH), 126.1 (CH) 127.1 (2 × CH), 127.4 (CH), 127.7 (CH), 127.9 (2 × CH), 128.7 (2 × CH), 129.1 (CH), 130.5 (2 × CH), 130.9 (2 × CH), 132.1 (2 × CH), 134.8 (C), 135.9 (C), 137.0 (C), 137.8 (C), 141.2 (C), 143.0 (C), 143.4 (C), 146.7 (C), 149.3 (C) ppm; LRMS (EI): *m/z* (%): 496 (M^+, 100), 369 (36), 354 (23); HRMS (EI): calcd for $C_{29}H_{21}I^+$: 496.0683; found: 496.0669.

*3-Iodo-2-(4-methoxyphenyl)-1a,1a-diphenylbenzofulvene (**6c**).* Orange solid; R*f* = 0.37 (hexane:EtOAc, 9:1); Mp = 180–182 ºC; 91% yield (233 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 3.71 (s, 3H), 6.29 (d, *J* = 7.8 Hz, 1H), 6.51–6.54 (m, 2H), 6.84–6.91 (m, 5H), 6.93–7.01 (m, 3H), 7.22–7.27 (m, 1H), 7.33–7.39 (m, 3H), 7.41–7.46 (m, 2H), 7.47–7.51 (m, 1H) ppm; ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 55.3 (CH_3), 103.9 (C), 112.9 (2 × CH), 122.6 (CH), 123.2 (CH), 126.1 (CH), 127.2 (2 × CH), 127.5 (CH), 127.9 (CH), 128.8 (2 × CH), 129.1 (CH), 130.3 (C), 130.9 (2 × CH), 131.8 (2 × CH), 132.1 (2 × CH), 137.0 (C), 137.8 (C), 141.2 (C), 143.0 (C), 143.4 (C), 146.3 (C), 149.3 (C), 158.0 (C) ppm; LRMS (EI): *m/z* (%): 512 (M^+, 13), 167 (100), 105 (49); HRMS (EI): calcd for $C_{29}H_{21}OI^+$: 512.0632; found: 512.0637.

2-(3-Fluorophenyl)-3-iodo-1a,1a-diphenylbenzofulvene ***(6d)***. Orange solid; R*f* = 0.25 (hexane); Mp = 179–181 ºC; 92% yield (230 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 6.37 (d, *J* = 7.8 Hz, 1H), 6.64–6.68 (m, 1H), 6.75 (ddd, *J* = 10.0, 2.5, 1.5 Hz, 1H), 6.86–7.03 (m, 8H), 7.28 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.36–7.41 (m, 3H), 7.44–7.48 (m, 2H), 7.49–7.53 (m, 1H) ppm; ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 104.5 (C), 113.3 (d, *J* = 21.1 Hz, CH), 117.6 (d, *J* = 21.9 Hz, CH), 123.0 (CH), 123.2 (CH), 126.5 (CH), 126.6 (d, *J* = 2.8 Hz, CH), 127.3 (2 x CH), 127.6 (CH), 128.4 (CH), 128.8 (d, *J* = 8.6 Hz, CH), 128.81 (2 x CH), 129.3 (CH), 130.9 (2 x CH), 132.0 (2 x CH), 136.9 (C), 137.6 (C), 140.2 (d, *J* = 8.2 Hz, C), 141.2 (C), 142.6 (C), 143.1 (C), 145.2 (d, *J* = 1.9 Hz, C), 149.6 (C), 161.8 (d, *J* = 244.9 Hz, C) ppm; LRMS (EI): *m/z* (%): 500 (M^+, 100), 373 (28), 86 (31); HRMS (EI): calcd for $C_{28}H_{18}IF^+$: 500.0432; found: 500.0427.

3-Iodo-1a,1a-diphenyl-2-thienylbenzofulvene ***(6e)***. Orange solid; R*f* = 0.24 (hexane); Mp = 161–163 ºC; 84% yield (205 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 6.32 (d, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.86 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.89–7.11 (m, 7H), 7.24–7.31 (m, 1H), 7.33–7.56 (m, 6H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 104.2 (C), 122.8 (CH), 123.0 (CH), 123.7 (CH), 124.8 (CH), 126.2 (CH), 127.2 (2 x CH), 127.5 (CH), 128.2 (CH), 128.8 (2 x CH), 129.1 (CH), 129.5 (CH), 130.9 (2 x CH), 131.9 (2 x CH), 137.0 (C), 137.78 (C), 137.82 (C), 141.1 (C), 141.8 (C), 142.8 (C), 143.2 (C), 149.3 (C) ppm; LRMS (EI): *m/z* (%): 488 (M^+, 100), 361 (27), 284 (34); HRMS (ESI): calcd for $C_{26}H_{18}IS^+$ [$(M+H)^+$]: 489.0168; found: 489.0165.

2-(Cyclohex-1-en-1-yl)-3-iodo-1a,1a-diphenylbenzofulvene ***(6f)***. Orange solid; R*f* = 0.19 (hexane); Mp = 117–119 ºC; 69% yield (168 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.63–0.84 (m, 1H), 1.08–1.43 (m, 3H), 1.60–2.12 (m, 4H), 5.46–5.61 (m, 1H), 6.19–6.35 (m, 1H), 6.85 (ddd, *J* = 7.8, 7.2, 1.4 Hz, 1H), 7.01–7.64 (m, 12H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 21.8 (CH_2), 22.2 (CH_2), 25.4 (CH_2), 29.5 (CH_2), 102.1 (C), 122.4 (CH), 123.1 (CH), 125.7 (CH), 127.2 (bs, 2 x CH), 127.4 (CH), 128.4 (CH), 128.7 (bs, 2 x CH), 128.9 (CH), 130.4 (bs, 2 x CH), 131.1 (bs, 2 x CH), 131.6 (CH), 135.2 (C), 136.8 (C), 137.2 (C), 141.7 (C), 142.9 (C), 143.4 (C), 148.5 (C), 149.3 (C) ppm; LRMS (EI): *m/z* (%): 486 (M^+, 60), 359 (77), 281 (57), 252 (48); HRMS (ESI): calcd for $C_{28}H_{24}I^+$ [$(M+H)^+$]: 487.0917; found: 487.0917.

2-Butyl-3-iodo-1a,1a-diphenyl-benzofulvene ***(6g)***. Orange oil; R*f* = 0.31 (hexane); 59% yield (136 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.71 (t, *J* = 7.1 Hz, 3H), 0.93 (sex, *J* = 7.1 Hz, 2H), 1.16–1.34 (m, 2H), 2.03–2.23 (m, 2H), 6.26 (d, J = 7.8 Hz, 1H), 6.82 (ddd, J = 7.9, 6.5, 2.2 Hz, 1H), 7.05–7.71 (m, 12H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 13.9 (CH_3), 22.8 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 103.1 (C), 121.6 (CH), 123.1 (CH), 125.4 (CH), 127.3 (CH), 128.1 (2 x CH), 128.6 (CH), 128.7 (2 x CH), 128.9 (CH), 130.5 (2 x CH), 130.9 (2 x CH), 137.07 (C), 137.09 (C), 142.6 (C), 143.0 (C), 143.5 (C), 146.7 (C), 147.7 (C) ppm; LRMS (EI): m/z (%): 462 (M^+, 100), 292 (95), 215 (50); HRMS (EI): calcd for $C_{26}H_{23}I^+$: 462.0840; found: 462.0846.

*3-Iodo-1a,1a-diphenyl-2-phenylsulfanylbenzofulvene (**6h**)*. Orange solid; R*f* = 0.50 (hexane:EtOAc, 10:1); Mp = 71–73 ºC; 95% yield (244 mg); ^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 6.39 (d, J = 7.9 Hz, 1H), 6.80–6.87 (m, 2H), 6.94–6.99 (m, 1H), 7.01–7.08 (m, 3H), 7.09–7.15 (m, 2H), 7.17–7.22 (m, 2H), 7.25–7.32 (m, 3H), 7.32–7.36 (m, 1H), 7.36–7.43 (m, 3H), 7.45–7.50 (m, 1H) ppm; $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 117.4 (C), 123.1 (CH), 125.1 (CH), 127.0 (CH), 127.2 (2 × CH), 127.5 (CH), 127.6 (2 x CH), 128.6 (2 × CH), 128.7 (3 x CH), 128.9 (CH), 129.4 (CH), 131.0 (2 x CH), 131.9 (2 x CH), 136.4 (C), 137.3 (C), 137.5 (C), 138.1 (C), 142.1 (C), 142.5 (C), 142.9 (C), 150.7 (C) ppm; LRMS (ESI): m/z (%): 515 [$(M+H)^+$, 73], 457 (43), 388 (100); HRMS (ESI): calcd for $C_{28}H_{20}IS^+$ [$(M+H)^+$]: 515.0325; found: 515.0324.

*3-Iodo-1a,1a,2-tri-(4-methylphenyl)benzofulvene (**6i**)*. Orange solid; R*f* = 0.13 (hexane); Mp = 197–199 ºC; 90% yield (236 mg); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 2.20 (s, 3H), 2.26 (s, 3H), 2.51 (s, 3H), 6.48 (d, J = 7.8 Hz, 1H), 6.88 (d, J = 8.0 Hz, 2H), 6.73–6.87 (m, 4H), 6.92–6.99 (m, 3H), 7.24–7.34 (m, 5H), 7.41 (d, J = 7.6 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 21.2 (2 x CH_3), 21.6 (CH_3), 102.7 (C), 122.5 (CH), 123.1 (CH), 125.9 (CH), 127.1 (CH), 127.7 (2 x CH), 127.8 (2 x CH), 129.4 (2 x CH), 130.6 (2 x CH), 131.1 (2 x CH), 132.2 (2 x CH), 135.0 (C), 135.7 (C), 137.1 (C), 137.2 (C), 138.1 (C), 138.6 (C), 139.2 (C), 140.0 (C), 143.2 (C), 146.7 (C), 149.9 (C) ppm; LRMS (EI): m/z (%): 524 (M^+, 100), 382 (24), 211 (33); HRMS (EI): calcd for $C_{31}H_{25}I^+$: 524.0996; found: 524.1011.

*2-Butyl-3-iodo-1a,1a-di-(4-methylphenyl)benzofulvene (**6j**)*. Orange oil; R*f* = 0.29 (hexane); 70% yield (172 mg); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.72 (t, J = 7.3 Hz, 3H), 0.90–1.02 (m, 2H), 1.18–1.30 (m, 2H), 2.13–2.23 (m, 2H), 2.42 (s, 3H), 2.46 (s, 3H), 6.34–6.43 (m, 1H), 6.85 (ddd, J = 7.8, 6.9, 1.7 Hz ,1H), 7.13–7.32 (m, 10H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 13.9 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 22.7 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 102.2 (C), 121.5 (CH), 123.0 (CH), 125.2 (CH), 127.0 (CH), 128.7 (2 x CH), 129.4 (2 x CH), 130.8 (2 x CH), 131.2 (2 x CH), 136.6 (C), 137.4 (C), 138.7 (C), 139.0 (C), 140.0 (C), 140.2 (C), 143.3 (C), 146.8 (C), 148.4 (C) ppm; LRMS (EI): *m/z* (%): 490 (M^+, 100), 320 (76), 305 (47); HRMS (EI): calcd for $C_{28}H_{27}I^+$: 490.1153; found: 490.1154.

*2-Butyl-3-iodo-1a-(3,4,5-trimethoxyphenyl)-1a-phenylbenzofulvene (**6k**).* Orange oil; R*f* = 0.37 (hexane:EtOAc, 5:1); 54% yield (149 mg); Obtained as a 1:1 mixture of *E*/*Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.70 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H), 0.83–1.08 (m, 6H), 1.17–1.34 (m, 4H), 2.05–2.21 (m, 2H), 3.75 (s, 2 x 3H), 3.81 (s, 2 x 3H), 3.91 (s, 3H), 3.95 (s, 3H), 6.26 (dd, *J* = 7.8, 0.6 Hz,1H), 6.44 (dd, *J* = 7.8, 0.6 Hz,1H), 6.48 (s, 2H), 6.52 (s, 2H), 6.76–6.93 (m, 2H), 7.10–7.54 (m, 14H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 13.8 (CH_3), 13.9 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 31.5 (2 x CH_2), 32.2 (CH_2), 32.7 (CH_2), 56.3 (2 x CH3), 56.4 (2 x CH3), 61.1 (CH_3), 61.2 (CH_3), 102.9 (C), 103.0 (C), 107.8 (2 x CH), 108.2 (2 x CH), 121.6 (2 x CH), 123.1 (CH), 123.2 (CH), 125.4 (CH), 125.6 (CH), 127.28 (CH), 127.31 (CH), 128.0 (2 x CH), 128.7 (3 x CH), 129.1 (CH), 130.5 (2 x CH), 130.8 (2 x CH), 136.9 (2 x C), 137.0 (C), 137.1 (C), 138.0 (C), 138.1 (C), 138.7 (C), 138.9 (C), 142.3 (C), 142.5 (C), 143.3 (C), 143.5 (C), 146.6 (C), 146.7 (C), 147.5 (C), 147.6 (C), 152.9 (2 x C), 153.4 (2 x C) ppm; HRMS (ESI): calcd for $C_{29}H_{30}IO_3^+$ [$(M+H)^+$]: 553.1234; found: 553.1237.

*2-Butyl-3-iodo-1a-(4-methoxyphenyl)-1a-phenylbenzofulvene (**6l**).* Red oil; R*f* = 0.29 (hexane:EtOAc, 20:1); 75% yield (185 mg); Obtained as a 1:1 mixture of *E*/*Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.71 (t, *J* = 7.1 Hz, 3H), 0.73 (t, *J* = 7.1 Hz, 3H), 0.85–1.08 (m, 4H), 1.17–1.32 (m, 4H), 2.07–2.17 (m, 2H), 2.21–2.30 (m, 2H), 3.87 (s, 3H), 3.89 (s, 3H), 6.27 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.79–6.96 (m, 6H), 7.14–7.51 (m, 18H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 13.88 (CH_3), 13.94 (CH_3), 22.7 (CH_2), 22.8 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 32.3 (CH_2), 55.46 (CH_3), 55.50 (CH_3), 102.3 (C), 102.4 (C), 113.5 (2 x CH), 114.0 (2 x CH), 121.52 (CH), 121.54 (CH), 122.9 (2 x CH), 125.2 (CH), 125.3 (CH), 126.96 (CH), 127.01 (CH), 128.0 (2 x CH), 128.6 (2 x CH), 128.7 (CH), 129.0 (CH), 131.0 (2 x CH), 131.3 (2 x CH), 132.6 (2 x CH), 132.9 (2 x CH), 135.0 (C), 135.3 (C), 136.6 (C), 136.7 (C), 137.4 (2 x C),142.9 (C), 143.2 (C), 143.3 (2 x C), 146.7 (C), 146.8 (C),147.8 (C), 147.9 (C), 160.3 (C), 160.5 (C) ppm; HRMS (EI): calcd for $C_{27}H_{25}IO^+$: 492.0945; found: 492.0943.

*2-Butyl-3-iodo-1a-phenyl-1a-(2-thienyl)benzofulvene (**6m**).* Red oil; R*f* = 0.60 (hexane); 59% yield (130 mg); Obtained as a 1:1 mixture of *E*/*Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.70 (t, *J* = 7.2 Hz, 3H), 0.77

(t, J = 7.3 Hz, 3H), 0.85–1.42 (m, 8H), 2.04–2.10 (m, 2H), 2.35–2.40 (m, 2H), 6.21 (d, J = 7.8 Hz, 1H), 6.69–6.88 (m, 3H), 6.88–7.02 (m, 2H), 7.04–7.61 (m, 18H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 13.9 (CH_3), 14.0 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 32.2 (CH_2), 32.7 (CH_2), 103.6 (2 x C), 121.6 (CH), 121.7 (CH), 122.8 (CH), 123.0 (CH), 125.5 (CH), 125.6 (CH), 127.1 (CH), 127.4 (CH), 127.5 (CH), 127.7 (CH), 128.1 (2 x CH), 128.7 (2 x CH), 129.2 (CH), 129.5 (CH), 129.6 (CH), 129.7 (CH), 130.7 (CH), 130.8 (2 x CH), 131.1 (2 x CH), 131.7 (CH), 137.0 (C), 137.1 (C), 138.3 (C), 138.5 (C), 139.4 (C), 139.6 (C), 142.5 (C), 142.6 (C), 143.3 (C), 143.4 (C), 144.7 (C), 145.0 (C), 146.5 (C), 146.6 (C) ppm; HRMS (EI): calcd for $C_{24}H_{21}IS^+$: 468.0403; found: 468.0395.

2-Butyl-1a-(4-fluorophenyl)-3-iodo-1a-(4-methoxyphenyl)benzofulvene ***(6n)***. Red oil; R*f* = 0.23 (hexane:EtOAc, 20:1); 72% yield (184 mg); Obtained as a ~1:1 mixture of *E*/*Z* isomers; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 0.71 (t, J = 7.3 Hz, 3H), 0.72 (t, J = 7.4 Hz, 3H), 0.93–1.02 (m, 4H), 1.17–1.26 (m, 4H), 2.10–2.18 (m, 2H), 2.20–2.24 (m, 2H), 3.87 (s, 3H), 3.89 (s, 3H), 6.30 (d, J = 7.8 Hz, 1H), 6.44 (d, J = 7.8 Hz, 1H), 6.82–6.88 (m, 2H), 6.89–6.96 (m, 4H), 7.04–7.12 (m, 4H), 7.14–7.18 (m, 2H), 7.18–7.26 (m, 8H), 7.27–7.31 (m, 2H) ppm; $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 13.89 (CH_3), 13.92 (CH_3), 22.74 (CH_2), 22.76(CH_2), 31.5 (2 x CH_2), 32.25 (CH_2), 32.28 (CH_2), 55.50 (CH_3), 55.53 (CH_3), 102.5 (C), 102.7 (C), 113.6 (2 x CH), 114.1 (2 x CH), 115.1 (d, J = 21.5 Hz, 2 x CH), 115.8 (d, J = 21.5 Hz, 2 x CH), 121.6 (CH), 121.7 (CH), 122.7 (CH), 122.8 (CH), 125.3 (CH), 125.4 (CH), 127.09 (CH), 127.11 (CH), 132.7 (2 x CH), 133.02 (d, J = 8.2 Hz, 2 x CH), 133.03 (2 x CH), 133.3 (d, J = 8.2 Hz, 2 x CH), 134.9 (C), 135.1 (C), 136.9 (2 x C), 137.2 (C), 137.4 (C), 138.9 (d, J = 3.3 Hz, C), 139.1 (d, J = 3.4 Hz, C), 143.3 (C), 143.4 (C), 146.39 (C), 146.41 (C), 146.5 (C), 146.7 (C), 160.5 (C), 160.7 (C), 163.2 (d, J = 249.6 Hz, C), 163.4 (d, J = 249.8 Hz, C) ppm; ; HRMS (EI): calcd for $C_{27}H_{24}FIO^+$: 510.0850; found: 510.0846.

Synthesis of oxygen-functionalized 3-iodo-1*H*-indenes 7 by iodocyclization of *o*-(alkynyl)styrenes 1, 3 or 5:

N-Iodosuccinimide (338 mg, 1.5 mmol) was added to a solution of the corresponding starting *o*-(alkynyl)styrene **1**, **3** or **5** (0.5 mmol) in a 2/1 mixture CH_2Cl_2/MeOH (3 mL). The reaction vial was sealed and protected from light. The resulting mixture was stirred at room temperature until completed consumption of the starting material as determined by TLC (1-6 h). The mixture was quenched by addition of saturated aq $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 1-methoxymethyl-3-iodo-1*H*-indenes **7** in the yields reported in Table 3. The characterization data of **7a**-**e**,**g** have been previously reported.[29]

*3-Iodo-1-(2-methoxybutan-2-yl)-2-phenyl-1H-indene (7**f**).* Yellow oil. R*f* = 0.45 (hexane:CH_2Cl_2, 9:1). 45% yield (91 mg). Obtained as a 3:1 mixture of isomers. Data of the major isomer from an enriched 5:1 mixture are reported; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.69 (t, *J* = 7.4 Hz, 3H), 0.78 (s, 3H), 1.12-1.34 (m, 2H), 3.30 (s, 3H), 4.36 (s, 1H), 7.21-7.30 (m, 1H), 7.30-7.48 (m, 7H), 7.53 (d, *J* = 7.5 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, CDCl3, 25 ºC): δ = 7.6 (CH_3), 21.7 (CH_3), 28.0 (CH_2), 49.4 (CH), 59.7 (CH_3), 79.6 (C), 97.9 (C), 123.0 (CH), 125.5 (CH), 126.2 (CH), 127.5 (CH), 127.7 (CH), 128.1 (2 x CH), 129.3 (2 x CH), 139.1 (C), 142.8 (C), 146.1 (C), 152.8 (C) ppm; LRMS (EI): *m/z* (%): 404 (M^+, 1), 317 (15), 189 (45), 87(100); HRMS (EI): calcd for $C_{20}H_{21}IO^+$: 404.0632, found: 404.0629.

*3-Iodo-1-(1-methoxy-1-phenylpropyl)-2-phenyl-1H-indene (7**h**).* 60 % yield (140 mg); Obtained as a 1:1 mixture of isomers that were separated by flash column chromatography; *Isomer A:* Colourless oil. R*f* = 0.30 (hexane:CH_2Cl_2, 9:1). 29% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.82 (t, *J* = 7.2 Hz, 3H), 1.60-1.77 (m, 2H), 3.21 (s, 3H), 4.52 (s, 1H), 6.73-6.84 (m, 2H), 6.94-7.12 (m, 4H), 7.20-7.34 (m, 2H), 7.36-7.52 (m, 5H), 7.73-7.83 (m, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 7.6 (CH_3), 25.9 (CH_2), 49.5 (CH), 58.5 (CH_3), 83.5 (C), 99.6 (C), 122.5 (CH), 125.7 (CH), 126.57 (2 x CH), 126.59 (2 x CH), 126.87 (CH), 126.90 (CH), 127.3 (CH), 127.9 (CH), 128.0 (2 x CH), 129.4 (2 x CH), 138.5 (C), 139.5 (C), 142.9 (C), 146.0 (C), 150.4 (C) ppm; LRMS (EI): *m/z* (%): 466 (M^+, 1), 317 (18), 189 (31), 149(100); HRMS (EI): calcd for $C_{25}H_{23}IO^+$: 466.0789, found: 466.0789. *Isomer B:* Colourless oil; R*f* = 0.40 (hexane:CH_2Cl_2, 9:1); 31% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.54 (t, *J* = 7.4 Hz, 3H), 1.92 (dq, *J* = 14.9, 7.5 Hz, 1H), 2.14 (dq, *J* = 14.5, 7.1 Hz, 1H), 2.96 (s, 3H), 4.52 (s, 1H), 6.90 (d, *J* = 6.9 Hz, 2H), 6.95-7.10 (m, 5H), 7.11-7.20 (m, 5H),7.21-7.30 (m, 2H), 7.32-7.41 (m, 1H), 7.72 (d, *J* = 7.5 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, CDCl3, 25 ºC): δ = 8.2 (CH_3), 26.0 (CH_2), 49.7 (CH), 61.8 (CH3), 83.6 (C), 98.3 (C), 122.8 (CH), 125.8 (CH), 126.1 (CH), 126.6 (CH), 126.88 (CH), 126.94 (2 x CH), 127.3 (2 x CH), 127.4 (2 x CH), 127.5 (CH), 129.2 (2 x CH), 138.0 (C), 142.5 (C), 143.2 (C), 146.0 (C), 152.4 (C) ppm; LRMS (EI): *m/z* (%): 466 (M^+, <1), 317 (4), 189 (9), 149(100); HRMS (EI): calcd for $C_{25}H_{23}IO^+$: 466.0789, found: 466.0799.

*3-Iodo-1-(methoxydiphenylmethyl)-2-phenyl-1H-indene (**7i**)*. Colourless solid; Mp = 163–165 ºC; R*f* = 0.42 (hexane:CH_2Cl_2, 9:1); 66% yield (170 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 2.65 (d, *J* = 1.1 Hz, 3H), 5.20 (s, 1H), 6.73-6.78 (m, 3H), 6.97-7.10 (m, 3H), 7.13-7.21 (m, 2H), 7.24-7.51 (m, 9H), 7.60-7.76 (m, 2H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 51.9 (CH), 62.1 (CH_3), 87.9 (C), 98.6 (C), 122.7 (CH), 125.0 (CH), 125.7 (CH), 126.4 (2 x CH), 126.9 (2 x CH), 127.0 (CH), 127.2 (CH), 127.7 (CH), 127.9 (2 x CH), 128.1 (CH), 128.4 (2 x CH), 129.7 (2 x CH), 130.1 (2 x CH), 136.0 (C), 138.5 (C), 139.0 (C), 141.3 (C), 146.9 (C), 152.4 (C) ppm; LRMS/HRMS (EI): Decomposition.

Synthesis of polycyclic compounds 9 by intramolecular alkoxyiodocyclization of *o*-(alkynyl)styrenes 8: *N*-Iodosuccinimide (338 mg, 1.5 mmol) was added to a solution of the corresponding starting *o*-(alkynyl)styrene **8** (0.5 mmol) in CH_2Cl_2 (2 mL). The reaction vial was sealed and protected from light. The resulting mixture was stirred at room temperature until completed consumption of the starting material as determined by TLC or GC-MS (5-12 h). The mixture was quenched by addition of saturated aq $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding adducts **9** in the yields depicted in Scheme 5.

*8-Iodo-3,3-dimethyl-3,3a-dihydro-1H-indeno[1,2-c]furan (**9a**)*. White solid; Mp = 92–94 ºC; R*f* = 0.34 (hexane:EtOAc 20:1); 46% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 0.68 (s, 3H), 1.65 (s, 3H), 3.96 (s, 1H), 4.34 (dd, *J* = 13.9, 1.0 Hz, 1H), 4.70 (d, *J* = 13.9 Hz, 1H), 7.19–7.25 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H) ppm; ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 20.9 (CH_3), 29.1 (CH_3), 65.4 (CH), 67.5 (CH_2), 81.4 (C), 86.8 (C), 122.4 (CH), 123.3 (CH), 126.5 (CH), 128.3 (CH), 140.8 (C), 150.2 (C), 161.0 (C) ppm; LRMS (ESI): *m/z* (%): 313 [$(M+H)^+$, 100]; HRMS (ESI): calcd for $C_{13}H_{14}IO^+$ [$(M+H)^+$]: 313.0084; found: 313.0088.

*11-Iodo-6,6-dimethyl-6,6a-dihydroindeno[1,2-c]chromene (**9b**)*. Yellow oil; R*f* = 0.17 (hexane); 51% yield (95 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.80 (s, 3H), 1.88 (s, 3H), 3.81 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.17–7.32 (m, 2H), 7.36–7.52 (m, 3H), 8.48 (d, *J* = 7.6 Hz, 1H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 19.0 (CH_3), 29.0 (CH_3), 57.1 (CH), 81.0 (C), 87.4 (C), 117.2 (CH), 118.8 (C), 119.8 (CH), 122.5 (CH), 123.2 (CH), 124.9 (CH), 126.1 (CH), 127.9 (CH), 130.2 (CH), 139.5 (C), 142.0 (C), 147.2 (C), 155.4 (C) ppm; LRMS (ESI): *m/z* (%): 375 [(M+H)$^+$, 100]; HRMS (ESI): calcd for $C_{18}H_{16}IO^+$ [(M+H)$^+$]: 375.0240; found: 375.0230.

12-Iodo-7,7-dimethyl-7,7a-dihydro-5H-benzo[c]indeno[2,1-e]oxepine ***(9c)***. Colourless oil; R*f* = 0.40 (hexane:CH_2Cl_2, 3:2); 47% yield (91 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.82 (s, 3H), 1.72 (s, 3H), 3.96 (s, 1H), 4.46 (d, *J* = 14.6 Hz, 1H), 4.89 (d, *J* = 14.6 Hz, 1H), 7.19–7.48 (m, 7H), 7.65 (d, *J* = 7.4 Hz, 1H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 19.1 (CH_3), 30.6 (CH_3), 63.9 (CH), 66.4 (CH_2), 80.4 (C), 96.6 (C), 123.4 (CH), 123.8 (CH), 126.3 (CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 128.1 (CH), 131.1 (CH), 137.4 (C), 138.8 (C), 143.5 (C), 146.7 (C), 151.3 (C) ppm; LRMS (EI): *m/z* (%): 388 (M$^+$, 3), 330 (28), 203 (100), 101 (21); HRMS (EI): calcd for $C_{19}H_{17}IO^+$: 388.0319; found: 388.0327.

12-Iodo-7-(iodomethyl)-7-methyl-7,7a-dihydro -5H-benzo[c]indeno[2,1-e]oxepine ***(10c)***. Colourless solid, Mp = 119–121 ºC, R*f* = 0.50 (hexane:CH_2Cl_2, 3:2), 19% yield (49 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.94 (s, 3H), 3.79 (s, 2H), 4.27 (s, 1H), 4.49 (d, *J* = 14.6 Hz, 1H), 4.89 (d, *J* = 14.6 Hz, 1H), 7.18–7.49 (m, 7H), 7.61 (d, *J* = 7.3 Hz, 1H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.3 (CH_3), 20.7 (CH_2), 61.6 (CH), 67.0 (CH_2), 79.3 (C), 97.2 (C), 123.0 (CH), 124.1 (CH), 126.8 (CH), 127.7 (CH), 128.08 (CH), 128.12 (CH), 128.3 (CH), 131.4 (CH), 137.2 (C), 138.1 (C), 142.4 (C), 146.7 (C), 151.0 (C) ppm; LRMS (EI): *m/z* (%): 514 (M$^+$, 2), 330 (49), 203 (100); HRMS (EI): calcd for $C_{19}H_{16}I_2O^+$: 513.9286, found: 513.9291.

2-(4-Hydroxybutyl)-3-iodo-1-(prop-1-en-2-yl)-1H-indene ***(2m)***. Colourless oil; R*f* = 0.14 (hexane:EtOAc, 5:1); 58% yield (103 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.15 (s, 3H), 1.50–1.75 (m, 4H), 2.29–2.38 (m, 1H), 2.55–2.64 (m, 1H), 3.68 (t, *J* = 6.1 Hz, 2H), 4.10 (s, 1H), 5.03–5.10 (m, 1H), 5.20 (bs, 1H), 7.18–7.27 (m, 3H), 7.31–7.37 (m, 1H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 16.9 (CH_3), 25.2 (CH_2), 30.8 (CH_2), 32.4 (CH_2), 60.5 (CH), 62.6 (CH_2), 94.9 (C), 115.7 (CH_2), 121.4 (CH), 122.7 (CH), 125.7 (CH), 127.2 (CH), 143.0 (C), 143.6 (C), 145.3 (C), 154.1 (C) ppm; HRMS (ESI): calcd for $C_{16}H_{19}IONa^+$ [(M+Na)$^+$]: 377.0373; found: 377.0372.

Palladium-catalyzed Suzuki cross-coupling reactions of 3-iodoindenes: These reactions were conducted following the methodology described by Wu et al.[37] The corresponding 3-iodoindene (0.2 mmol) was added to a mixture of arylboronic acid (1.5 equiv., 0.3 mmol), $Pd(OAc)_2$ (0.9 mg, 2 mol%), S-Phos (3.3 mg, 4 mol%) and K_3PO_4 (84 mg, 2 equiv., 0.4 mmol) in toluene (1 mL) and the solution stirred at 80 ºC until full conversion was observed by TLC or GC-MS (6 h). The solvent was evaporated and the residue was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 2,3-diaryl-1*H*-indenes **11-12** or the 2,3-diarylbenzofulvene **13a** in the yields depicted in Scheme 6. The characterization data of **11a**,**b**[29] and **13a**[33] have been previously reported.

*2-(4-Methoxyphenyl)-1-(2-methoxypropan-2-yl)-3-phenyl-1H-indene **(12a)***. White solid; Mp = 138–140 ºC; R*f* = 0.23 (hexane:EtOAc, 20:1); 86% yield (64 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 0.86 (s, 3H), 0.93 (s, 3H), 3.40 (s, 3H), 3.79 (s, 3H), 4.35 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.20–7.31 (m, 6H), 7.32–7.36 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 21.3 (CH_3), 25.4 (CH_3), 49.1 (CH), 55.0 (CH_3), 58.4 (CH_3), 113.2 (2 x CH), 119.8 (CH), 124.7 (CH), 126.0 (CH), 126.6 (CH), 126.6 (CH), 128.1 (2 x CH), 129.6 (2 x CH), 130.3 (C), 130.6 (2 x CH), 135.4 (C), 141.2 (C), 144.1 (C), 144.4 (C), 145.8 (C), 158.2 (C) ppm; LRMS (ESI): *m/z* (%): 393 [$(M+Na)^+$, 100], 339 (49); HRMS (ESI): calcd for $C_{26}H_{26}O_2Na^+$ [$(M+Na)^+$]: 393.1825, found: 393.1827.

Palladium-catalyzed Sonogashira cross-coupling reaction of 3-iodobenzofulvenes: Synthesis of 2-(aryl)-1a,1a-diphenyl-3-(phenylethynyl)benzofulvenes 14a,b: These reactions were conducted following the methodology described by Michelet, Toullec et al.[13a] The corresponding 3-iodobenzofulvene **6** (0.2 mmol) was dissolved in a 3:1 mixture of NEt_3 and toluene (0.1 M) under argon. Then phenylacetylene (33 µL, 0.3 mmol, 1.5 equiv.), $PdCl_2(PPh_3)_2$ (8.6 mg, 6 mol %), and CuI (1.2 mg, 3 mol %) were added and the reaction mixture was stirred at 50 ºC overnight. The resulting mixture was washed with a saturated solution of NH_4Cl, the layers were separated and the aqueous one was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The solvent was evaporated and the residue was purified by flash chromatography on silica gel using hexane:EtOAc (50:1) as eluent to obtain the corresponding 2-(aryl)-1a,1a-diphenyl-3-(phenylethynyl)benzofulvenes **14** in the yields depicted in Scheme 6.

*1a,1a,2-Triphenyl-3-(phenylethynyl)benzofulvene **(14a)***. Red solid; Mp = 173–175 ºC; R*f* = 0.27 (hexane:EtOAc, 50:1); 95% yield (87 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 6.45 (d, *J* = 7.9 Hz, 1H), 6.85–7.11 (m, 9H), 7.19–7.43 (m, 6H), 7.44–7.59 (m, 7H), 7.65 (d, *J* = 7.5 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 85.3 (C), 98.9 (C), 119.7 (CH), 122.9 (CH), 123.4 (C), 125.5 (CH), 125.6 (C), 125.8 (CH), 126.76 (2 x CH), 126.81 (2 x CH), 127.0 (CH), 128.0 (CH), 128.10 (3 x CH), 128.4 (2 x CH), 128.9 (CH), 129.8 (2 x CH), 131.0 (2 x CH), 131.5 (2 x CH), 132.4 (2 x CH), 136.1 (C), 137.1 (C), 137.3 (C), 141.1

(C), 141.4 (C), 142.8 (C), 145.5 (C), 150.5 (C) ppm; LRMS (ESI): *m/z* (%): 457 [$(M+H)^+$, 100]; HRMS (ESI): calcd for $C_{36}H_{25}^+$ [$(M+H)^+$]: 457.1951; found: 457.1951.

1a,1a-Diphenyl-3-(phenylethynyl)-2-thienylbenzofulvene (***14b***). Red solid; Mp = 162–164 ºC; R*f* = 0.23 (hexane:EtOAc, 50:1); 93% yield (86 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 6.39 (d, *J* = 7.8 Hz, 1H), 6.75–6.87 (m, 2H), 6.87–7.12 (m, 6H), 7.17–7.30 (m, 2H), 7.30–7.56 (m, 10H), 7.60 (d, *J* = 7.4 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 85.3 (C), 99.6 (C), 119.7 (CH), 122.8 (CH), 122.9 (CH), 123.4 (C), 123.6 (CH), 125.2 (C), 125.5 (CH), 126.7 (2 x CH), 127.1 (CH), 128.2 (4 x CH), 128.4 (2 x CH), 128.9 (CH), 129.0 (CH), 131.0 (2 x CH), 131.5 (2 x CH), 132.3 (2 x CH), 136.3 (C), 137.0 (C), 137.5 (C), 140.2 (C), 141.0 (C), 141.3 (C), 142.7 (C), 150.4 (C) ppm; LRMS (ESI): *m/z* (%): 463 [$(M+H)^+$, 100]; HRMS (ESI): calcd for $C_{34}H_{23}S^+$ [$(M+H)^+$]: 463.1515; found: 463.1516.

Derivatization of iodoindene 2a via I/Li exchange: Synthesis of 3-functionalized-1*H*-indenes 15: *n*-BuLi (1.0 equiv., 0.5 mmol, 0.31 mL 1.6 M) was added to a solution of iodoindene **2a** (1.0 equiv., 0.5 mmol, 179 mg) in Et_2O (5 mL) at −78 ºC and stirred at this temperature for 30 min. Then the appropriate electrophile (1.0-1.5 equiv., 0.5-0.75 mmol) was added and the resulting mixture stirred at −78 ºC for 30 min and then allowed to reach room temperature. Water was added, the layers were separated and the aqueous one was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 3-functionalized-1*H*-indenes **15** in the yields depicted in Scheme 7.

3-Deutero-1-isopropenyl-2-phenyl-1H-indene (***15a***). Synthesized following the general procedure using MeOD in excess (0.25 mL/mmol, ~12 equiv.) as electrophile. White solid; Mp = 103–105 ºC; R*f* = 0.43 (hexane); 99% yield (115 mg, > 99%-D at C3); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.19 (bs, 3H), 4.59 (s, 1H), 5.07–5.14 (m, 1H), 5.34–5.41 (m, 1H), 7.21–7.46 (m, 7H), 7.64–7.77 (m, 2H) ppm; $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.1 (CH_3), 58.8 (CH), 115.1 (CH_2), 120.9 (CH), 123.3 (CH), 125.3 (CH), 126.4 (2 x CH), 127.3 (CH), 127.6 (CH), 128.6 (2 x CH), 135.7 (C), 144.3 (C), 145.1 (C), 146.4 (C), 148.6 (C) ppm. The signal corresponding to the carbon bonded to deuterium is not observed; LRMS (EI): *m/z* (%): 233 (M^+, 58), 218 (100), 190 (56); HRMS (EI): calcd for $C_{18}H_{15}D^+$: 233.1310, found: 233.1316.

*1-Isopropenyl-3-methylsulfanyl-2-phenyl-1H-indene (**15b**)*. Synthesized following the general procedure using dimethyl disulfide (1.5 equiv.) as electrophile. Colourless solid; Mp = 98–100 ºC; R*f* = 0.45 (hexane:CH_2Cl_2, 9:1); 94% yield (131 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.14 (bs, 3H), 2.34 (s, 3H), 4.69 (s, 1H), 5.01 (bs, 1H), 5.25 (bs, 1H), 7.29–7.41 (m, 2H), 7.41–7.51 (m, 4H), 7.65–7.75 (m, 3H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.0 (CH_3), 17.3 (CH_3), 60.9 (CH), 115.7 (CH_2), 120.4 (CH), 123.3 (CH), 125.9 (CH), 127.4 (CH), 127.7 (CH), 128.1 (2 x CH), 129.3 (2 x CH), 133.7 (C), 135.3 (C), 143.9 (C), 144.4 (C), 145.0 (C), 149.7 (C) ppm; LRMS (EI): *m/z* (%): 278 (M^+, 13), 263 (41), 215 (100), 77 (16); HRMS (EI): calcd for $C_{19}H_{18}S^+$: 278.1124, found: 278.1128.

*1-Isopropenyl-2-phenyl-3-tributylstannyl-1H-indene (**15c**)*. Synthesized following the general procedure using $ClSnBu_3$ (1.0 equiv.) as electrophile. Pale yellow oil; R*f* = 0.42 (hexane:CH_2Cl_2, 9:1); 96% yield (250 mg); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.77–1.08 (m, 15H), 1.14 (bs, 3H), 1.18–1.55 (m, 12H), 4.57 (s, 1H), 4.93 (bs, 1H), 5.12 (bs, 1H), 7.18–7.27 (m, 1H), 7.28–7.49 (m, 8H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 10.8 (3 x CH_2), 13.8 (3 x CH_3), 17.0 (CH_3), 27.7 (3 x CH_2), 29.4 (3 x CH_2), 63.7 (CH), 115.3 (CH_2), 122.4 (CH), 123.3 (CH), 124.6 (CH), 127.1 (CH), 127.5 (CH), 128.0 (2 x CH), 128,6 (2 x CH), 139.4 (C), 142.6 (C), 144.1 (C), 146.3 (C), 151.0 (C), 161.2 (C) ppm; LRMS (EI)/HRMS (EI): Decomposition.

*1-Isopropenyl-3-(1-(4-chlorophenyl)-1-hydroxylmethyl)-2-phenyl-1H-indene (**15d**)*. Synthesized following the general procedure using *p*-chlorobenzaldehyde (1.0 equiv.) as electrophile. Colourless oil; R*f* = 0.43 (hexane:EtOAc, 9:1); 66% yield (123 mg); Obtained as a ~1:1 mixture of diastereoisomers; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.17 (s, 6H), 4.57 (s, 1H), 4.67 (s, 1H), 4.94 (bs, 1H), 4.96 (bs, 1 H), 5.14 (bs, 1H), 5.20 (bs, 1 H), 6.10 (s, 1H), 6.12 (s, 1H), 7.14–7.55 (m, 26H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.2 (CH_3), 17.4 (CH_3), 60.9 (CH), 61.3 (CH), 68.9 (CH), 69.4 (CH), 116.0 (2 x CH_2), 121.8 (CH), 122.6 (CH), 123.5 (2 x CH), 125.55 (CH), 125.62 (CH), 127.02 (CH), 127.04 (CH), 127.2 (2 x CH), 127.89 (CH), 127.92 (CH), 128.0 (2 x CH), 128.5 (2 x CH), 128.6 (2 x CH), 128.7 (2 x CH), 128.8 (2 x CH), 128.9 (2 x CH), 129.0 (2 x CH), 132.9 (C), 133.4 (C), 135.0 (C), 135.5 (C), 139.7 (C), 140.0 (C), 140.3 (C), 140.7 (C), 142.4 (C), 142.5 (C), 143.1 (C), 143.3 (C), 145.6 (C), 145.7 (C), 147.5 (C), 148.0 (C) ppm; HRMS (EI): calcd for $C_{25}H_{21}ClO^+$: 372.1275, found: 372.1261.

1-Isopropenyl-3-methoxycarbonyl-2-phenyl-1H-indene ***(15e)***. Synthesized following the general procedure using methyl chloroformate (1.0 equiv.) as electrophile. Colourless solid; Mp= 77–79 ºC; R*f* = 0.35 (hexane:CH_2Cl_2, 3:2); 81% yield (118 mg). Traces of the isomeric indene were detected; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 1.13 (bs, 3H), 3.82 (s, 3H), 4.65 (s, 1H), 4.97 (bs, 1H), 5.18 (bs, 1H), 7.25–7.45 (m, 8H), 7.75–7.82 (m, 1H) ppm; ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 17.3 (CH_3), 51.8 (CH_3), 61.9 (CH), 116.5 (CH_2), 121.8 (CH), 123.4 (CH), 126.2 (CH), 127.6 (CH), 128.1 (2 x CH), 128.5 (CH), 128.9 (2 x CH), 131.2 (C), 135.0 (C), 141.8 (C), 142.8 (C), 144.6 (C), 155.9 (C), 166.1 (C) ppm; LRMS (EI): *m/z* (%): 290 (M^+, 26), 230 (48), 215 (100); HRMS (EI): calcd for $C_{20}H_{18}O_2^+$: 290.1302, found: 290.1310.

Derivatization of iodobenzofulvenes 6 via I/Li exchange: Synthesis of 3-functionalized benzofulvenes 16: These reactions were conducted following the same methodology described for iodoindene **2a**, although in a 0.2 mmol scale, to obtain the corresponding 3-functionalized benzofulvenes **16** in the yields depicted in Scheme 7.

1-(Diphenylmethylene)-3-(1-(4-chlorophenyl)-1-hydroxylmethyl)-2-(3-fluorophenyl)-1H-indene ***(16a)*** Synthesized following the general procedure using *p*-chlorobenzaldehyde (1.0 equiv.) as electrophile. Orange solid; Mp= 103–105 ºC; R*f* = 0.21 (hexane:EtOAc, 20:1); 81% yield (83 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 2.28 (bs, 1H), 5.88 (s, 1H), 6.45 (d, *J* = 7.9 Hz, 1H), 6.57–6.81 (m, 3H), 6.83–6.95 (m, 7H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.30–7.51 (m, 9H) ppm; ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 69.5 (CH), 113.3 (d, *J* = 20.7 Hz, CH), 117.3 (bs, CH), 122.0 (CH), 123.9 (CH), 125.5 (CH), 126.1 (bs, CH), 127.0 (CH), 127.3 (2 x CH), 127.6 (bs, 2 x CH), 128.3 (CH), 128.7 (2 x CH), 128.8 (d, *J* = 8.5 Hz, CH), 129.1 (3 x CH), 130.8 (bs, 2 x CH), 131.0 (bs, 2 x CH), 133.1 (C), 137.9 (C), 138.0 (C), 138.6 (d, *J* = 7.9 Hz, C), 139.6 (d, *J* = 2.0 Hz, C), 139.7 (C), 140.7 (C), 141.7 (C), 142.9 (C), 143.0 (C), 150.8 (C), 162.0 (d, *J* = 245.8 Hz, C) ppm; LRMS (ESI): *m/z* (%): 537 [$(M+Na)^+$, 38], 497 (100); HRMS (ESI): calcd for $C_{35}H_{24}ClFONa^+$ [$(M+Na)^+$]: 537.1392; found: 537.1397.

1-(Diphenylmethylene)-3-methoxycarbonyl-2-phenylsulfanyl-1H-indene ***(16b)***. Synthesized following the general procedure using methyl chloroformate (1.0 equiv.) as electrophile. Red oil; R*f* = 0.41 (hexane:EtOAc, 5:1); 76% yield (68 mg); ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ = 3.62 (s, 3H), 6.44 (d, *J* = 7.9 Hz, 1H), 6.88 (td, *J* = 7.9, 1.1 Hz, 1H), 6.97–7.01 (m, 2H), 7.03–7.07 (m, 1H), 7.08–7.14 (m, 4H), 7.18 (td, *J* = 7.6, 0.9 Hz, 1H), 7.29–7.33 (m, 4H), 7.93–7.45 (m, 3H), 7.47–7.52 (m, 1H), 7.64 (d, J = 7.6 Hz, 1H) ppm; $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$, 25 ºC): δ = 51.6 (CH_3), 121.0 (CH), 123.2 (CH), 125.8 (CH), 126.0 (CH), 127.5 (CH), 128.1 (2 x CH), 128.6 (2 x CH), 128.8 (2 x CH), 129.1 (2 x CH), 129.8 (CH), 129.9 (CH), 131.4 (2 x CH), 132.6 (2 x CH), 137.03 (C), 137.04 (C), 138.4 (C), 138.5 (C), 139.7 (C), 140.1 (C), 142.1 (C), 142.4 (C), 155.2 (C), 165.3 (C) ppm; LRMS (ESI): *m/z* (%): 469 [$(M+Na)^+$, 100], 447 [$(M+H)^+$, 26], 415 (62); HRMS (ESI): calcd for $C_{30}H_{23}O_2S^+$ [$(M+H)^+$]: 447.1413; found: 447.1407.

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Supporting Information. ^1H and $^{13}C\{^1H\}$NMR spectra for all new compounds (spectra of iodoindenes **2** and **4** correspond to samples obtained by method A). Crystallographic data for **6a**.

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