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Synthesis of 2-bromo-1-aryl-1*H*-indenes via a Ag(I) promoted domino 2π-electrocyclic ring-opening/4π-electrocyclization reaction of 1,2-diaryl substituted *gem*-dibromocyclopropanes

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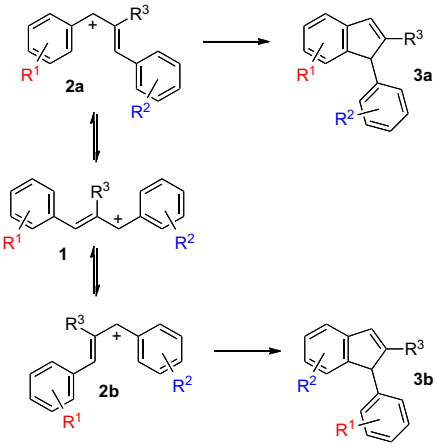
ABSTRACT

2-Bromo-1-aryl substituted indenes can be synthesized from 1,2-diaryl substituted *gem*-dibromocyclopropanes via a domino reaction sequence. The cascade reaction involves silver(I) promoted ionization and 2π-disrotatory electrocyclic ring-opening, followed by a 4π-conrotatory electrocyclic ring closing reaction of the allylic carbocation intermediate. Reaction conditions utilize silver tetrafluoroborate ($AgBF_4$) in dichloroethane at 65 °C. Selectivity effects for the electrocyclization were also studied. The 2-bromoindenes can be further functionalized using cross-coupling reactions, such as the Suzuki–Miyaura protocol. The alkene π-bond of the indenes can also be isomerized to give the thermodynamically more stable 2-bromo-3-aryl-1*H*-indene isomers using triethylamine in dichloromethane at room temperature.

1. Introduction

Indenes are important structural motifs that are found in a variety of biologically active molecules,[1] in ligands useful for catalysis, and as precursors for many chemical products.[2] There are numerous strategies that can be used to synthesize indenes, and related indanes, most commonly involving either cyclization or annulation to form the five-membered ring of the indene using cationic or transition metal catalyzed reactions.[3] Another method that has been utilized is the ionization of 1,3-biphenyl allyl alcohols in acidic media[4] originally reported by Pittman[5] and Olah.[6] In this approach allylic cations are generated, which then undergo cyclization in a process, which can be viewed as an intramolecular Friedel–Crafts reaction,[7] but which is perhaps more accurately described as an electrocyclization reaction. In the case of a 1,3-diaryl substituted allylic cation cyclization must occur via initial isomerization of the 'W' shaped cation **1** into an 'U'-shaped shaped cation **2** followed by cyclization and proton loss to give the indenes **3** (Scheme 1). For differentially substituted 1,3-biaryl systems the issues that control from which ring electrocyclization occurs, to give either **3a** or **3b** have recently been elaborated.[8] The allylic carbocations were generated from the corresponding alcohols and boron trifluoride diethyl etherate in dichloromethane at room temperature. Selectivity outcomes reflect the inductive and mesomeric effects of the substituents for an electrophilic aromatic substitution mechanism, while a computational study supports a 4π-conrotatory electrocyclization pathway.



Scheme 1. Synthesis of substituted indenes via cationic cascade cyclization pathway.

In the previous study the presence of a substituent was found to be essential for the electrocyclization of the allylic cations, since in

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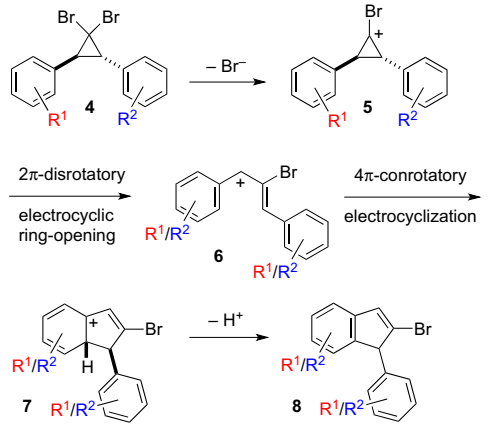
its absence the 'W'-cation is favored from which cyclization cannot occur.[8] As an extension of these studies we envisaged an analogous approach to the synthesis of 2-bromo-1-aryl substituted indenes. In principle, as for the previous study an approach based upon the ionization of appropriately substituted allylic alcohols (i.e., 2-bromo-1,3-biaryl substituent pattern) could be used. However, a more expeditious route was suggested by the known 2π-electrocyclic ring-opening reactions of *gem*-dihalocyclopropanes to give products resulting from reaction of intermediate 2-bromo allylic cations. The use of *gem*-dihalocyclopropanes in organic synthesis has been documented by many researchers,[9] including thermal openings.[10] West has reported the domino ring-opening of *gem*-dichlorocyclopropanes followed by conrotatory Nazarov cyclization to give chlorocyclopentenones, as well as subsequent Friedel–Crafts reaction to generate benzohydrindenones.[11] The thermal reactions (139 °C, *m*-xylenes) of some monophenyl-substituted dibromocyclopropanes have been reported to give mixtures of indenes and dienes.[12] In addition, *gem*-dicyanoethanes in the presence of samarium have also been used to synthesize indenes as reported by Zhang.[13] Banwell and co-workers have utilized ring-opening of *gem*-dihalocyclopropanes followed by nucleophilic trapping of the allylic cations for natural product synthesis.[14]

Accordingly, we were interested in investigating a pathway based upon a domino 2π-electrocyclic ring-opening of cyclopropanes **4** followed by a 4π-electrocyclic ring-closure to give the product indenes **8** (Scheme 2). Of particular interest were whether similar substituent effects would be observed to those of our previous study. The overall synthetic approach would allow for rapid formation of highly substituted indenes in a two-step protocol, involving dibromocyclopropanation of readily accessible stilbenes, followed by the subsequent domino cascade reaction.[15] The resultant C–Br functionality of the product indenes could then serve as a valuable synthetic handle for late stage diversification through reactions, such as transition metal catalyzed couplings. We now report the results of this study and briefly demonstrate the synthetic utility of the products.

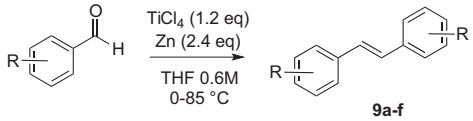


Scheme 2. Synthesis of 2-bromoindenes **8** via cascade electrocyclic ring-opening/cyclization pathway.

2. Results and discussion

The synthesis of symmetric and unsymmetric 1,2-diaryl *gem*-dihalocyclopropanes was accomplished using a two-step protocol involving olefination followed by cyclopropanation. The requisite stilbenes were synthesized using three different methods. For symmetrically substituted stilbenes **9a**–**f** McMurry reaction of aryl aldehydes in refluxing THF with Zn metal and $TiCl_4$ was employed (Table 1). The stilbenes were obtained with excellent trans-selectivity (≥98:2 dr) consistent with previous reports using the McMurry coupling reaction.[16]

Table 1
Symmetrical stilbene synthesis using the McMurry coupling reaction

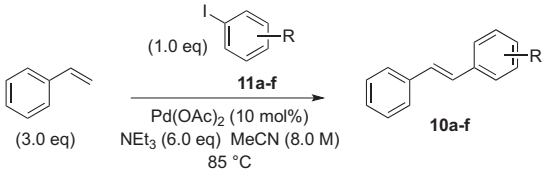


Entry	R	Time[a] (h)	*E*/*Z*[b]	Yield (%)	Stilbene
1	*o*-Me	2	≥98:2	87	**9a**
2	*p*-Me	2.5	≥98:2	85	**9b**
3	*o*-Cl	2	≥98:2	77	**9c**
4	*p*-Cl	1.5	≥98:2	81	**9d**
5	*m*-OMe	20	≥98:2	84	**9e**
6	3,4-OMe	2	≥98:2	88	**9f**

[a] Reaction was stirred at 0 °C during addition of $TiCl_4$ and aldehyde for 30 min prior to reflux.
[b] *E*/*Z* ratio determined by ^{1}H NMR integration of purified products.

Unsymmetrical stilbenes **10** were synthesized either using Heck or Wittig–Horner reactions. Heck reaction of styrene and aryl iodides **11** using palladium acetate and triethylamine in acetonitrile afforded stilbenes **10a**–**g** in generally high yields and isolated dr's favoring the trans-isomers (Table 2). Alternatively, a more convenient Wittig–Horner reaction using benzyl phosphonate ester and aryl aldehydes could also be used affording the stilbenes in high yields and isolated dr's (Table 3).

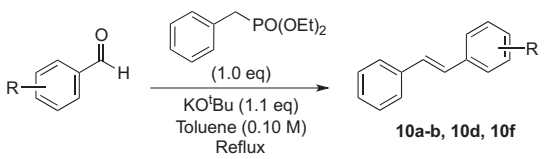
Table 2
Unsymmetrical stilbene synthesis using the Heck reaction



Entry	Aryl iodide	R	Time (h)	*E*/*Z*[a]	Yield (%)	Stilbene
1	**11a**	*o*-Me	24	95:5	63	**10a**
2	**11b**	*p*-Me	20	85:15	24	**10b**
3	**11c**	3,5-Me	24	95:5	53	**10c**
4	**11d**	*m*-NO_2	22	≥98:2	99	**10d**
5	**11e**	*p*-NO_2	46	≥98:2	87	**10e**
6	**11f**	*m*-OMe	72	≥98:2	97	**10f**

[a] *E*/*Z* ratio determined by ^{1}H NMR integration of purified products.

Table 3
Unsymmetrical stilbene synthesis using the Wittig–Horner reaction

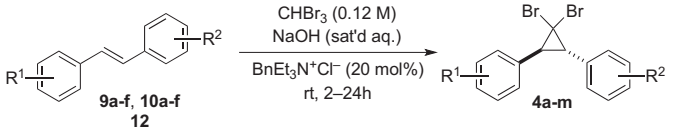


Entry	R	Time (h)	*E*/*Z*[a]	Yield (%)	Stilbene
1	*o*-Me	7	≥98:2	64	**10a**
2	*p*-Me	24	≥98:2	58	**10b**
3	*m*-NO_2	6	≥98:2	quant	**10d**
4	*m*-OMe	6	≥98:2	69	**10f**

[a] *E*/*Z* ratio determined by ^{1}H NMR integration of purified products.

There are various reports in the literature of procedures that can be applied for dihalocyclopropanation reactions.[9,17] The use of a modified procedure based on a method reported by West was found to be the most efficient for the formation of the *gem*-dibromocyclopropanes **4** in moderate to excellent yields.[11] West's method utilizes benzyltriethylammonium bromide and benzyltriethylammonium chloride in solvent with the corresponding haloform and stilbene. Our modification involved more concentrated conditions of the stilbene with bromoform as the solvent (0.12 M) to give the *gem*-dibromocyclopropanes **4a**–**m** (Table 4). Reaction of the unsubstituted stilbene **12** provided the *gem*-dibromocyclopropane **4a** in 77% yield (Table 4, entry 1). A similar reaction using chloroform as solvent afforded the corresponding *gem*-dichlorocyclopropane in 81% yield. In general, reaction of alkyl-substituted stilbenes led to moderate to good product yields, while symmetrical *ortho*- and *para*-chloro substituted compounds were obtained in moderate yields. Reaction of the more electron deficient *m*-NO_2 and *p*-NO_2 substituted stilbenes **10d** and **10e**, provided the cyclopropanated products in 75% and 95% yields, respectively (Table 4, entries 11 and 12). Reaction of the more electron-rich methoxy substituted symmetrical stilbenes occurred in lower yields, perhaps reflecting the instability of the products (Table 4, entries 6 and 7).

Table 4
Cyclopropanation of stilbenes to *gem*-dihalocyclopropanes **4**

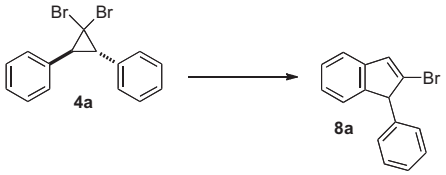


Entry	Stilbene	R^1	R^2	Time (h)	dr[a] (*trans*:*cis*)	Yield (%)	Product
1	**12**	H	H	19	≥98:2	77	**4a**
2	**9a**	*m*-Me	*m*-Me	6	≥98:2	91	**4b**
3	**9b**	*p*-Me	*p*-Me	6	≥98:2	78	**4c**
4	**9c**	*o*-Cl	*o*-Cl	24	≥98:2	60	**4d**
5	**9d**	*p*-Cl	*p*-Cl	4	≥98:2	66	**4e**
6	**9e**	*m*-OMe	*m*-OMe	5	90:10	73	**4f**
7	**9f**	3,4-OMe	3,4-OMe	2–24	—	≤2[b]	**4g**
8	**10a**	*o*-Me	H	3	≥98:2	61	**4h**
9	**10b**	*p*-Me	H	24	≥98:2	42	**4i**
10	**10c**	3,5-Me	H	7	≥98:2	55	**4j**
11	**10d**	*m*-NO_2	H	18	≥98:2	75	**4k**
12	**10e**	*p*-NO_2	H	4	≥98:2	95	**4l**
13	**10f**	*m*-OMe	H	19	≥98:2	73	**4m**

[a] dr determined by ^{1}H NMR integration of purified product.
[b] Minor amounts obtained as determined by ^{1}H NMR and MS analysis.

Optimization of reaction conditions suitable for the ring-opening/closure cascade were evaluated using the 1,2-diphenyl substrate **4a** (Table 5). Whereas thermal conditions failed to give product (Table 5, entry 1), the use of silver salts, and in particular silver tetrafluoroborate ($AgBF_4$) to initiate carbocation formation and subsequent reaction to give **8a** was more successful (Table 5, entries 2–7). Reaction in THF afforded a low 17% yield of **8a** after 3 days at room temperature, while similar reaction at 60 °C afforded an improved 77% yield. The use of toluene as solvent was less successful, whereas 1,2-dichloroethane solvent gave the product in excellent yields after 2.5 h using just 2.0 equiv of $AgBF_4$ at 60 °C (Table 5, entry 7). These conditions were optimal providing the indene **8a** in 95% yield on a one hundred milligram scale and 85% on a four-gram scale.

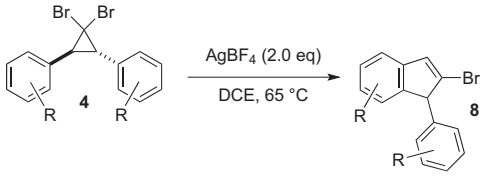
Table 5
Optimization of conditions suitable for the 2π–4π electrocyclic cascade reaction of **4a** into **8a**



Entry	Solvent	Additive	Temp (°C)	Time (h)	Isolated yield (%)
1	Toluene (0.07 M)	—	Reflux	48	N.R.
2	THF (0.07 M)	$AgBF_4$ (4.0 equiv)	rt	72	17
3	THF (0.07 M)	$AgBF_4$ (4.0 equiv)	60	72	77
4	Toluene (0.07 M)	$AgBF_4$ (4.0 equiv)	60	120	55
5	DCE (0.07 M)	$AgBF_4$ (2.0 equiv)	rt	24	<5
6	DCE (0.07 M)	$AgBF_4$ (2.0 equiv)	60	1	73
7	DCE (0.07 M)	$AgBF_4$ (2.0 equiv)	60	2.5	95

The optimized conditions were then applied to the domino indene formation reaction using the symmetrical *gem*-dibromocyclopropanes and reaction times of 4–48 h (Table 6). Reaction of the *m*-Me substrate **4b** was accomplished with poor conversion under these conditions. However, reaction for 48 h afforded the product as an inseparable 1:1 mixture of the 5-methyl and 7-methyl substituted indenes **8b-A** and **8b-B**, respectively, in 90% yield (Table 6, entry 1 and Fig. 1). Reaction of the *p*-Me substrate **4c** occurred in good yields after 4 h (Table 6, entry 2). Interestingly, reaction of the chloro-substituted precursors **4d** and **4e** required the use of more silver tetrafluoroborate salt (4.0–5.0 equiv) to achieve full conversion (Table 6, entries 3–4). Reaction of the more electron-rich *m*-OMe substrate **4f** led to inseparable product mixtures.

Table 6
2π–4π Electrocyclic cascade reaction of symmetric *gem*-dibromocyclopropanes **4** into 2-bromoindenes **8**



Entry	R	Substrate	$AgBF_4$ (equiv)	Time (h)	Yield (%)	Indene
1	*m*-Me	**4b**	2	48	quant	**8b**[a]
2	*p*-Me	**4c**	2	4	86	**8c**
3	*o*-Cl	**4d**	5	48	93	**8d**
4	*p*-Cl	**4e**	4	5	91	**8e**

[a] Product **8b** was obtained as a 1:1 mixture of the **8b-A** and **8b-B** regioisomers (See Fig. 1).

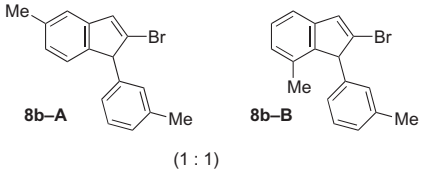
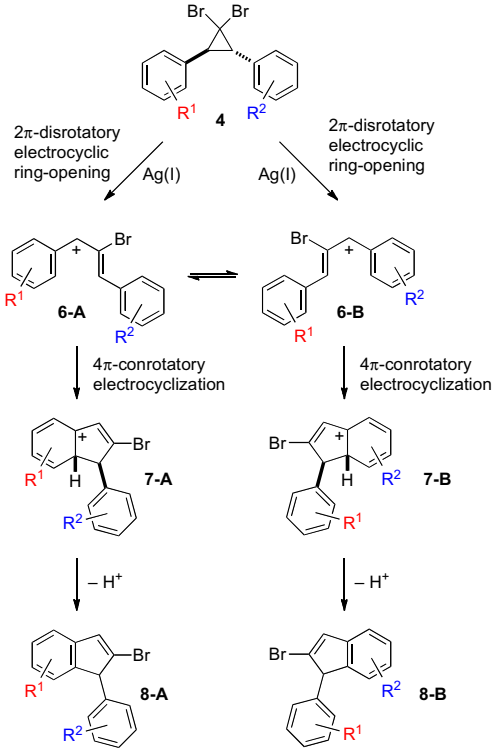


Fig. 1. The two *m*-Me substituted indene isomers **8b-A** and **8b-B** obtained in the electrocyclic cascade reaction of **4b**.

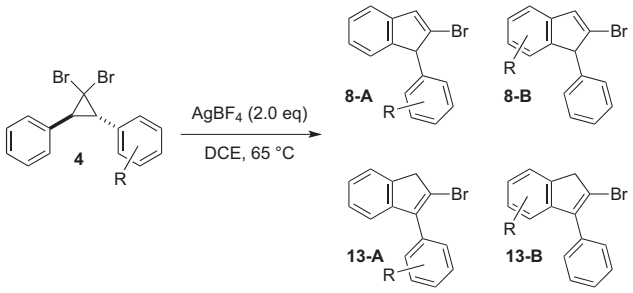
In the case of cyclization of the unsymmetrical dibromocyclopropane substrates **4** a selectivity issue arises for which aryl ring participates in the electrocyclization reaction (Scheme 3). Thus, 2π-disrotatory electrocyclic opening of **4** can lead to the 'U'-shaped cations **6-A** and **6-B**, which under the reaction conditions could equilibrate with each other. 4π-Conrotatory electrocyclization of **6-A** can lead to **8-A**, whereas electrocyclization of **6-B** can lead to the isomeric indene **8-B**, which differs in the positioning of the R^1 and R^2 substituents on the indene ring or the 1-aryl ring.



Scheme 3. Electrocyclization cascade mechanism leading to the formation of isomeric indenes **8-A** and **8-B**.

Reaction of the unsymmetrical *gem*-dibromocyclopropane substrates **4h**–**m** led to the formation of the anticipated 2-bromo-1-aryl-1*H*-indenes **8-A** and **8-B**, and for reaction of the more electron-deficient substrates the corresponding 2-bromo-3-aryl-1*H*-indenes **13-A** and **13-B** were also formed (Table 7). Reaction of the *o*-Me substrate **4h** gave a 3:1 ratio of indenes **8h-A** and **8h-B** with a product yield of 74% (Table 7, entry 1). Reaction of the *p*-Me substrate **4i** yielded a 55:45 ratio of indene **8i-A** and **8i-B** in a combined yield of 97% (Table 7, entry 2). Reaction of the 3,5-dimethyl substrate **4j** afforded a 1:3 mixture of indene products **8j-A** and **8j-B** in 92% yield (Table 7, entry 3). The selectivities obtained for each of these reactions are consistent with previous results on electrocyclization selectivities.[8] Reaction of both the *m*-NO_2 and *p*-NO_2 substrates **4k** and **4l** resulted in exclusive electrocyclization occurring through the more electron-rich phenyl ring to give mixtures of the indenes and isomerized indenes **8k-A**/**13k-A** and **8l-A**/**13l-A**, respectively (Table 7, entries 4 and 5). The formation of isomerized products and the highly selective initial electrocyclization through the phenyl ring are consistent with previous studies.[8] Reaction of **4m** led to an inseparable mixture of isomers (predominantly compound **8m-B**) in 90% yield. While the selectivities obtained in these examples are consistent with equilibration between cations **6-A** and **6-B** occurring prior to cyclization, the alternative possibility of reaction selectivity reflecting the initial ring-opening of **4** cannot be ruled-out.

Table 7
2π–4π Electrocyclic cascade reaction of unsymmetrical *gem*-dibromocyclopropanes

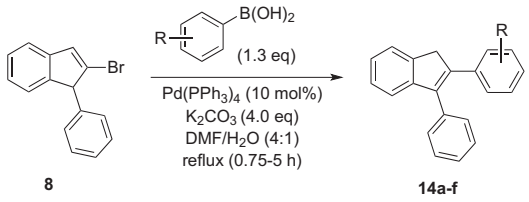


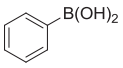
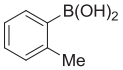
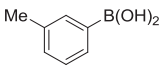
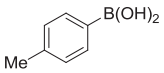
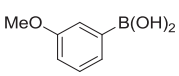
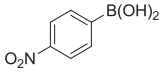
Entry	Substrate	R	Time (h)	Ratio (**8-A**:**8-B**:**13-A**:**13-B**)[a]	Yield (%)
1	**4h**	*o*-Me	6	75:25:0:0	74
2	**4i**	*p*-Me	21	55:45:0:0	97
3	**4j**	3,5-di-Me	16	25:75:0:0	92
4	**4k**	*m*-NO_2	22	90:0:10:0	75
5	**4l**	*p*-NO_2	12	90:0:10:0	93

[a] Determined by ^{1}H NMR analysis of the crude products.

We next set out to develop derivatization methods based upon reactions of the C–Br bond of the indenes. 2-Bromo-1-phenyl-1*H*-indene **8a** was evaluated as a model substrate. Several Suzuki–Miyaura cross coupling protocols were attempted for **8a** and phenylboronic acid. A modification of the procedure reported by O'Shea and Kurata[18] using 0.01 mol % $Pd(PPh_3)_4$, 1.0 equiv of the boronic acid, and 4.0 equiv of K_2CO_3 in a refluxing 4:1 DME/H_2O solvent mixture led to an 80% yield of the isomerized indene **14a** (Table 8, entry 1). Several different arylboronic acids were reacted with **8a** under the same conditions to give the cross-coupled

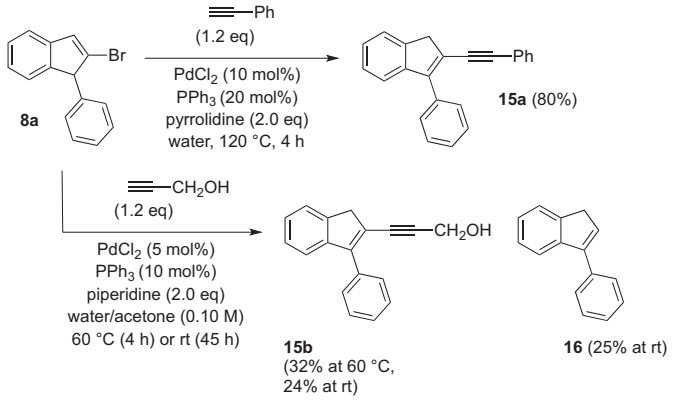
Table 8
Suzuki–Miyaura cross coupling reactions of **8a**



Entry	$ArB(OH)_2$ (1.1–1.3 equiv)	Time (h)	Yield (%)	Indene
1		4	82	**14a**
2		5	72	**14b**
3		4	79	**14c**
4		1	87	**14d**
5		0.75	90	**14e**
6		2	78	**14f**

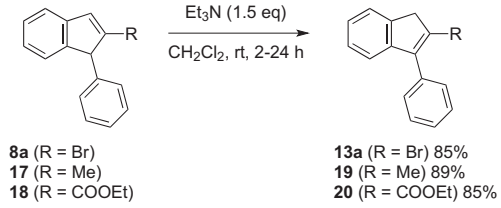
indene products **14** (Table 8, entries 2–7). In each of the examples the cross-coupled products were obtained solely as the isomerized species **14**. The formation of the isomerized compounds **14** reflects both the greater thermodynamic stability of these products, which incorporate a tetra-substituted and more highly conjugated alkene, as well as the ease with which base catalyzed isomerization occurs under the reaction conditions. The yields were generally very high using both electron-rich and electron-deficient arylboronic acids.

Cross-coupling of phenyl acetylene with 2-bromo-1-phenyl indene **8a** gave unsatisfactory results using several literature protocols,[19] but reaction using phenyl acetylene (1.2 equiv), $PdCl_2$ (10 mol %), and PPh_3 (20 mol %) in refluxing water, with pyrrolidine (for 4 h) afforded the isomerized cross-coupled indene **15a** in 80% yield under copper-free conditions (Scheme 4). Reaction of **8a** and propargyl alcohol was unsuccessful under similar conditions. However, reaction using piperidine (2.0 equiv) in an acetone/water mixture at 60 °C for 4 h afforded **15b** in 32% yield. Reaction at room temperature for 45 h using piperidine afforded a mixture of **15b** in 24% yield and the reduced product 1-phenylindene **16** in 25% yield.



Scheme 4. Alkyne cross-coupling reaction of **8a**.

The observation of isomerized indenes **13** as side products and the formation of the cross-coupled products in isomerized form (Tables 7 and 8 and Scheme 4) suggested that a general set of conditions could be established for isomerization of the indenes. Various base catalyzed conditions were evaluated using substrate **8a** to form **13a**. Reactions using potassium phosphate (1.4 equiv) in DMA solvent for 72 h at room temperature afforded **13a** in 68% yield. Reaction of **8a** with triethylamine (1.5 equiv) in dichloromethane at room temperature for 2 h afforded the isomerized product **13a** in 85% isolated yield (Scheme 5). Similar reaction of the indenes **17**[8] and **18**[8] for 24 h afforded the corresponding isomerized products **19** and **20** in 89% and 85% isolated, respectively. Application of the same conditions to the isomerizations of **4d**, **4e**, **4k**, and **4l** led to the formation of the indenes **13d**, **13e**, **13k-A**, and **13l-A** in good to excellent yields (Fig. 2). The ester substituted compound **21** was formed in a similar manner in 78% yield.



Scheme 5. Base promoted isomerization of indenes.

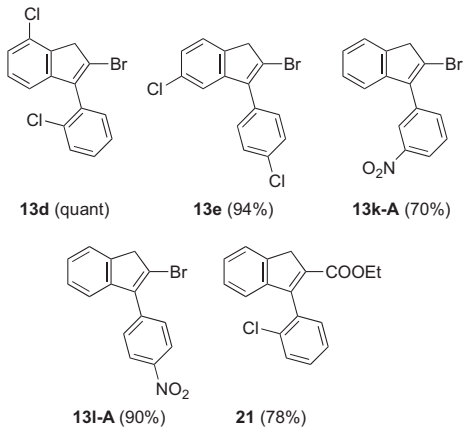
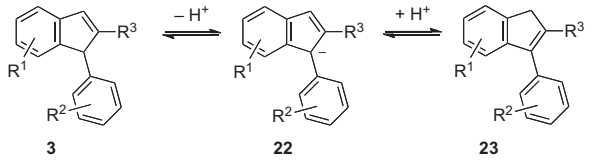


Fig. 2. Products resulting from base-catalyzed isomerization using triethylamine.

While there are various mechanisms that are known for the isomerization of indenes, the base promoted reaction conditions and substituent effects for isomerization are consistent with a deprotonation/protonation mechanism. Deprotonation of the acidic hydrogen at the 1-position of the indene **3** to give the aromatic indenyl anion **22** is then followed by protonation to give the more thermodynamically stable isomerized indene **23** (Scheme 6).



Scheme 6. Mechanism of base catalyzed indene isomerization.

3. Conclusions

In summary, 2-bromo-substituted indenes have been synthesized via a domino electrocyclic cascade reaction of *gem*-dibromocyclopropanes. The reaction is promoted by silver tetrafluoroborate facilitating initial 2π-disrotatory electrocyclic ring-opening to form an allylic carbocation. This species then undergoes a 4π-conrotatory electrocyclization to form the indene ring. Selectivity for the electrocyclization parallel those of our previous study, which in general can be rationalized based upon substituent effects for electrophilic aromatic substitution. The product indenes are useful intermediates, and the C–Br functionality can be used as a synthetic handle for cross-coupling and isomerization reactions.

4. Experimental section

4.1. General

The following general experimental applies for all experiments described in this paper. Unless otherwise stated, all reactions were performed under nitrogen. All reagents, unless otherwise stated were used as received. Reaction solvents were distilled under an inert atmosphere before use and transferred via syringe using standard techniques unless otherwise stated. Dichloromethane was distilled from CaH_2 under nitrogen. All other solvents were obtained as ACS grade (or better). All reagents, unless otherwise stated, were used as received (Aldrich, Fischer Scientific Ltd., or Lancaster). FT-IR spectra were obtained on a Perkin–Elmer Spectrum 1000, with samples loaded as films on NaCl plates. ^1H and ^{13}C

NMR spectra were obtained on Varian Mercury 300 or Unity 400 spectrometers as solutions in deuterated solvents ($CDCl_3$ were obtained from Cambridge Isotope Labs) and referenced to their corresponding solvent peaks (i.e., $CHCl_3$ 7.26 ppm for proton resonances, and $CHCl_3$, 77.23 ppm for carbon resonances). Chemical Shifts are expressed in parts per million values. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet; *J*, coupling constant in Hertz. Low and high-resolution electron ionization (EI) mass spectra were measured using a GCT Premier time-of-flight mass spectrometer (Waters Corporation, Milford, MA). Calculated exact masses and molecular formula determinations were generated using the data processing software Mass Lynx version 4.1 (Waters). Waters software does not consider the mass of the electron at any point in the calibration of the instrument, measurement of high-resolution masses or calculation of exact masses; therefore, all measured and calculated HRMS masses are given as neutral species (M) and not ions (M^+). Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Flash column chromatography on silica gel (60 Å, 230–400 mesh, low acidity, obtained from Silicycle Inc.) Analytical thin-layer chromatography (TLC) was performed on pre-coated aluminum-backed silica gel plates (Alugram SIL/G/UV254 purchased from Silicycle Inc.), visualized with a UV lamp (254 nm), potassium permanganate, phosphomolybdic acid, and vanillin. Spectral data are provided for all new compounds and for compounds that lack full characterization in the literature.

4.2. McMurry reaction general procedure for stilbene 9 synthesis

To a stirred suspension of Zn powder (4.70 g, 71.9 mmol) in THF (50.0 mL, 0.60 M) in a flame dried sealed tube at 0 °C was added $TiCl_4$ (3.93 mL, 35.9 mmol) dropwise. The mixture was stirred at 0 °C for 30 min and then aldehyde (29.9 mmol) was added. The mixture was then refluxed for 24 h and then slowly quenched with water (25 mL) at 0 °C. The mixture was then extracted with CH_2Cl_2 (3×75 mL), and the combined organic extracts dried over sodium sulfate, filtered, and evaporated in vacuo. Purification using flash column chromatography (ethyl acetate/hexanes) afforded the product stilbene **9**.

4.3. Heck reaction general procedure for stilbene 10 synthesis

To a flame dried round bottom flask was added styrene (4.43 mL, 38.8 mmol), aryl iodide **11** (12.9 mmol), freshly distilled triethylamine (10.7 mL, 77.5 mmol), $Pd(OAc)_2$ (289 mg, 1.29 mmol), and acetonitrile (2.0 mL). The mixture was heated at reflux under a nitrogen atmosphere until reaction was complete as monitored by TLC analysis. The mixture was quenched with water (20 mL) and HCl (25.0 mL, 1 M), extracted with CH_2Cl_2 (3×25 mL), dried over sodium sulfate, and evaporated in vacuo. Purification using flash column chromatography (ethyl acetate/hexanes) afforded the product stilbene **10**.

4.4. Wittig–Horner general procedure for stilbene 10 synthesis

To a flame dried round flask was added aryl aldehyde (8.32 mmol) and toluene (83 mL), followed by diethylbenzylphosphonate (1.73 mL, 8.32 mmol). The reaction was stirred at room temperature for 20 min, and KO^tBu (980 mg, 8.73 mmol) was added. The reaction was heated to reflux for 7 h monitoring for the disappearance of the aryl aldehyde. The reaction was quenched with water (50.0 mL) and ethyl acetate (75.0 mL) and washed with water (3×75 mL) and brine (3×50 mL). The organic layer was dried over Na_2SO_4 gravity filtered, and evaporated in vacuo. Purification using flash column chromatography (ethyl acetate/hexanes) afforded the product stilbene **10**.

4.5. General dibromocyclopropanation procedure for synthesis of 4

To a stirred solution of stilbene **9**/**10b** (2.40 mmol) in bromoform (20.0 mL, 0.12 M) was added triethylbenzylammonium chloride (109 mg, 0.480 mmol). An equal volume of a saturated aqueous solution of concentrated sodium hydroxide was added dropwise. The reaction was stirred at room temperature until full reaction conversion was achieved (as monitored by ^1H NMR analysis). The reaction mixture was quenched with water (150.0 mL) and stirred at room temperature for 15 min. The reaction mixture was washed with water (5×100 mL) and dichloromethane (3×75 mL). The organic phase was evaporated under high vacuum to remove bromoform. Purification using flash column chromatography (hexanes) afforded cyclopropane **4**.

4.6. General procedure for indene synthesis 8

To a stirred solution of *gem*-dibromocyclopropane **4** (7.50 mmol) in 1,2-dichloroethane (120.0 mL) at 65 °C was added silver tetrafluoroborate (2.91 g, 15.0 mmol). The reaction was heated for 4–48 h and then quenched with water (100 mL) and ethyl acetate (100 mL). The reaction mixture was washed with water (3×75 mL), brine (3×75 mL). The organic layer was dried over sodium sulfate, filtered, and evacuated. Purification using flash column chromatography (ethyl acetate/hexanes) was necessary in some cases.

4.7. General procedure for Suzuki–Miyaura cross coupling for synthesis of 14

A solution of 2-bromo-1-phenyl indene **8a** (150.0 mg, 0.555 mmol), arylboronic acid (0.833 mmol), and potassium carbonate (574 mg, 4.16 mmol) in dimethoxyethane (14.0 mL) was stirred at room temperature for 10 min. Water (5.5 mL) was then added, followed by palladium tetrakistriphenylphosphine (6.4 mg, 10 mol %), and the mixture was refluxed until the reaction was complete as monitored by TLC analysis (0.75–5 h). The reaction mixture was cooled to room temperature and quenched with water (30 mL), ethyl acetate (100 mL) and washed with 1 M HCl (3×25 mL), water (3×75 mL), and brine (3×50 mL). The organic phase was dried with sodium sulfate, filtered, and evaporated in vacuo. Purification using flash column chromatography (ethyl acetate/hexanes) afforded the product indene **14**.

4.8. General procedure for alkyne trapping method for synthesis of 15

A solution of 2-bromo-1-phenyl indene **8a** (100.0 mg, 0.369 mmol), propargyl alcohol (25.7 μL, 0.443 mmol), triphenylphosphine (9.7 mg, 0.036 mmol), palladium chloride (3.5 mg, 0.020 mmol), and piperidine (73 μL, 0.738 mmol) in acetone (3.8 mL) was stirred at room temperature for 10 min. Water (3.0 mL) was added dropwise, and the reaction mixture heated at 60 °C until reaction was complete as monitored by TLC analysis. The reaction mixture quenched with water (3.0 mL), allowed to cool to room temperature, and extracted with diethyl ether (3×25 mL). The organic phase was dried with sodium sulfate, filtered, and evaporated in vacuo. Purification using flash column chromatography (ethyl acetate/hexanes) afforded the product indene **15**.

4.9. General procedure for base promoted isomerization

To a solution of 2-bromo-1-aryl indene (0.555 mmol) in dichloromethane (5.50 mL) at room temperature was added triethylamine (0.101 mL, 0.723 mmol) dropwise and the reaction stirred for 2–24 h until reaction was complete as monitored by ^{1}H NMR analysis. Water (25.0 mL) was added and the reaction mixture stirred for 10 min, extracted with dichloromethane (3×25 mL), dried over Na_2SO_4, and evaporated in vacuo to give the indene products. Purification using flash column chromatography (ethyl acetate/hexanes) was necessary in some cases.

4.10. Characterization data

4.10.1. (3,3-Dibromocyclopropane-1,2-diyl)dibenzene ***4a***.[12] Isolated by flash column chromatography (5–10% EtOAc in hexanes) as a light yellow opaque waxy solid in 77% yield. Mp=52–54 °C. IR (Thin Film): 3064, 3028, 2904, 1602, 1496, 1446, 1086, 1041, 837, 753, 693 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (10H, m), 3.27 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 129.2, 128.7, 128.1, 40.3. LRMS (EI$^+$): *m*/*z*=274 (8), 271 (26), 195 (47), 191 (100), 189 (27), 165 (21), 115 (14), 94 (11), 63 (9).

4.10.2. 3,3′-(3,3-Dibromocyclopropane-1,2-diyl)bis(methylbenzene) ***4b***. Isolated by flash column chromatography (5% EtOAc in hexanes) as a tan oil in 91% yield IR (Thin Film): 3031, 2995, 3917, 1519, 1447, 1413, 1377, 1220, 1178, 1124, 1065, 1018, 907, 856, 817, 708 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (2H, dd, *J*=7.5, 7.5 Hz), 7.20–7.14 (6H, m), 3.25 (2H, s), 2.38 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 136.1, 129.9, 128.8, 128.5, 126.1, 40.2, 37.2, 21.7. LRMS (EI$^+$): *m*/*z*=302 (2), 299 (14), 220 (48), 219 (100), 205 (34), 203 (18), 189 (8), 165 (3), 128 (5), 86 (7), 77 (3). HRMS (EI$^+$) *m*/*z* calcd for $C_{17}H_{16}Br$ [M−Br] 299.0435, found 299.0443.

4.10.3. 4,4′-(3,3-Dibromocyclopropane-1,2-diyl)bis(methylbenzene) ***4c***. Isolated by flash column chromatography (5% EtOAc in hexanes) as a white crystalline solid in 78% yield. Mp=137–139 °C. IR (Thin Film): 3041, 3005, 2917, 1517, 1450, 1377, 1119, 102, 1021, 905, 863, 807, 696 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (4H, d, *J*=8.0 Hz), 7.20 (4H, d, *J*=8.0 Hz), 3.19 (2H, s), 2.37 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 133.2, 129.3, 129.0, 40.0, 37.7, 21.4. LRMS (EI$^+$): *m*/*z*=302 (2), 299 (14), 298 (6), 220 (48), 219 (100), 205 (34), 202 (18), 189 (8), 165 (3), 128 (5), 89 (4), 77 (3). HRMS (EI$^+$) *m*/*z* calcd for $C_{17}H_{16}Br$ [M−Br] 299.0435, found 299.0449.

4.10.4. 2,2′-(3,3-Dibromocyclopropane-1,2-diyl)bis(chlorobenzene) ***4d***. Isolated by flash column chromatography (10–20% EtOAc in hexanes) as a white crystalline solid in 60% yield. Mp=124–125 °C. IR (Thin Film): 3072, 2995, 3015, 1592, 1568, 1475, 1434, 1279, 1264, 1212, 1132, 1065, 1057, 1034, 954, 874, 838, 752, 727, 706 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (2H, dd, *J*=7.5, 1.5 Hz), 7.32 (2H, ddd, *J*=7.5, 7.5, 2.0 Hz), 7.27 (2H, ddd, *J*=7.5, 7.5, 1.5 Hz), 7.22 (2H, dd, *J*=7.5, 1.5 Hz), 3.32 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 134.9, 129.8, 129.7, 129.5, 127.1, 39.5, 35.2. LRMS (EI$^+$): *m*/*z*=344 (2), 340 (39), 338 (12), 262 (61), 260 (100), 259 (26), 227 (24), 225 (93), 189 (46), 178 (4), 125 (4), 94 (19). HRMS (EI$^+$): *m*/*z* calcd for $C_{15}H_{10}Cl_2Br$ [M−Br] 338.9343, found=338.9340.

4.10.5. 4,4′-(3,3-Dibromocyclopropane-1,2-diyl)bis(chlorobenzene) ***4e***. Isolated by flash column chromatography (0–5% EtOAc in hexanes) as a white crystalline solid in 66% yield. Mp=185 °C. IR (Thin Film): 3046, 3005, 2927, 2834, 1648, 1594, 1573, 1493, 1403, 1367, 1308, 1287, 1238, 1178, 1091, 1060, 1016, 907, 858, 814, 755, 729, 701, 652 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (4H, ddd, *J*=8.5, 2.0, 2.0 Hz), 7.29 (4H, ddd, *J*=8.5, 2.0, 2.0 Hz), 3.16 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 134.1, 130.4, 128.9, 39.8, 35.7. LRMS (EI$^+$): *m*/*z*=342 (4), 340 (7), 261 (8), 228 (31), 225 (100), 199 (3), 189 (53), 178 (3), 149 (3), 113 (3), 94 (8). HRMS (EI$^+$): *m*/*z* calcd for $C_{15}H_{10}Cl_2Br$ [M−Br] 338.9343, found=338.9349.

4.10.6. 3,3′-(3,3-Dibromocyclopropane-1,2-diyl)bis(methoxybenzene) ***4f***. Isolated by flash column chromatography (10–20% EtOAc in hexanes) as a tan oil in 73% yield as a 90:10 mixture of cis and trans isomers. IR (Thin Film): 3001, 2939, 2833, 1927, 1720, 1612, 1489, 1458, 1433, 1319, 1259, 1196, 1158, 1087, 1045, 995, 960, 870, 784, 733 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (2H, t, *J*=8.0 Hz), 7.26 (2H, t, *J*=8.0 Hz), 7.11 (2H, m), 7.04 (2H, m), 3.84 (6H, s), 3.82 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 137.6, 129.7, 129.1, 121.4, 114.9, 55.4, 40.4, 36.6. LRMS (EI$^+$): *m*/*z*=252 (8), 240 (100), 225 (18), 224 (12), 209 (48), 197 (16), 182 (20), 177 (11), 165 (93), 153 (41), 102 (4), 77 (5). HRMS (EI$^+$): *m*/*z* calcd for $C_{17}H_{16}O_2Br$ [M−Br] 331.0334, found=331.0331.

4.10.7. 1-(2,2-Dibromo-3-phenylcyclopropyl)-2-methylbenzene ***4h***. Isolated by flash column chromatography (0–5% EtOAc in hexanes) as a white crystalline solid in 61% yield. Mp=62–63 °C. IR (Thin Film): 3062, 3028, 2944, 2920, 1584, 1602, 1496, 1458, 1447, 1110, 1083, 1057, 1029, 914, 841, 790, 740, 713 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (5H, m), 7.30–7.25 (2H, m), 7.20–7.12 (2H, m), 3.27 (1H, d, *J*=7.0 Hz), 3.12 (1H, d, *J*=7.0 Hz), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 136.4, 135.7, 130.3, 129.2, 128.8, 128.3, 128.1, 128.1, 126.3, 40.2, 40.0, 37.1, 20.6. LRMS (EI$^+$): *m*/*z*=288 (9), 285 (58), 209 (74), 206 (100), 191 (45), 189 (21), 165 (14), 128 (22), 102 (9), 91 (16), 77 (11), 63 (9). HRMS (EI$^+$): *m*/*z* calcd for $C_{16}H_{14}Br$ [M−Br] 285.0279, found=285.0282.

4.10.8. 1-(2,2-Dibromo-3-phenylcyclopropyl)-4-methylbenzene ***4i***.[20] Isolated by flash column chromatography (0–5% EtOAc in hexanes) as a light yellow oil in 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.35 (5H, m), 7.27 (2H, d, *J*=8.0 Hz), 7.21 (2H, d, *J*=8.0 Hz), 3.21 (2H, s), 2.29 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 136.2, 133.1, 129.3, 129.1, 128.9, 128.6, 128.0, 40.2, 40.0, 37.3, 21.4.

4.10.9. 1-(2,2-Dibromo-3-phenylcyclopropyl)-3,5-dimethylbenzene ***4j***. Isolated by flash column chromatography (10–20% EtOAc in hexanes) as a clear oil in 55% yield. IR (Thin Film): 3086, 3060, 3028, 2916, 2946, 2862, 1603, 1497, 1447, 1376, 1334, 1156, 1107, 1083, 1056, 1030, 1001, 953, 908, 830, 850, 771, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (5H, m), 6.99 (3H, s), 3.23 (1H, d, *J*=9.0 Hz), 3.19 (1H, d, *J*=9.0 Hz), 2.35 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 136.3, 135.9, 129.7, 129.1, 128.6, 128.0, 126.9, 40.2, 40.2, 37.1, 21.5. LRMS (EI$^+$): *m*/*z*=302 (8), 299 (61), 243 (4), 220 (100), 219 (92), 205 (53), 195 (58), 189 (19), 178 (17), 165 (12), 128 (8), 115 (18), 84 (23), 63 (8). HRMS (EI$^+$): *m*/*z* calcd for $C_{17}H_{16}Br$ [M−Br] 299.0435, found=299.0431.

4.10.10. 1-(2,2-Dibromo-3-phenylcyclopropyl)-3-nitrobenzene ***4k***. Isolated by flash column chromatography (0–10% EtOAc in hexanes) as a light yellow oil in 75% yield. IR (Thin Film): 3063, 3030, 1724, 1603, 1581, 1496, 1449, 1349, 1219, 1145, 1095, 963, 904, 826, 803, 748 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (1H, d, *J*=1.5 Hz), 8.22 (1H, m), 7.60 (1H, ddd, *J*=8.0, 1.0, 1.0 Hz), 7.62–7.58 (1H, m), 7.46–7.36 (5H, m), 3.28 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 138.3, 135.4, 135.2, 129.7, 129.0, 128.8, 128.4, 124.0, 123.1, 40.8, 39.5, 35.3. LRMS (EI$^+$): *m*/*z*=316 (8), 236 (35), 191 (51), 189 (100), 165 (35), 152 (20), 126 (4), 115 (32), 89 (25). HRMS (EI$^+$): *m*/*z* calcd for $C_{15}H_{11}NO_2Br$ [M−Br] 315.9973, found=315.9973.

4.10.11. 1-(2,2-Dibromo-3-phenylcyclopropyl)-4-nitrobenzene ***4l***. Isolated by flash column chromatography (20% EtOAc in hexanes) as a light yellow oil in 95% yield. IR (Thin Film): 3085, 3078,

3065, 3060, 3061, 1596, 1512, 1447, 1412, 1401, 1110, 1073, 970, 872, 853, 832, 763, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (2H, dd, J=8.0, 1.5 Hz), 7.59 (2H, dd, J=8.0, 1.5 Hz), 7.40 (5H, m), 3.35 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 143.4, 135.2, 130.1, 129.0, 128.9, 128.4, 123.9, 41.0, 39.8, 35.1. LRMS (EI^+): m/z=319 (4), 316 (13), 272 (4), 237 (48), 191 (100), 189 (58), 178 (11), 165 (12), 149 (8), 131 (8), 115 (6), 69 (43). HRMS (EI^+): m/z calcd for $C_{15}H_{11}NO_2Br$ [M−Br] 315.9973, found=315.9975.

4.10.12. 1-(2,2-Dibromo-3-phenylcyclopropyl)-3-methoxybenzene ***4m***. Isolated by flash column chromatography (0–10% EtOAc in hexanes) as a light yellow oil in 73% yield. IR (Thin Film): 3058, 2939, 2337, 1945, 1491, 1451, 1431, 1318, 1273, 1244, 1157, 1072, 1047, 961, 866, 836, 777, 749, 717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.34 (5H, m), 7.33–7.28 (1H, dd, J=8.5, 8.0 Hz), 6.96 (1H, d, J=8.0 Hz), 6.89 (2H, m), 3.82 (3H, s), 3.21 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 137.7, 136.2, 129.7, 129.1, 128.7, 128.1, 121.4, 114.9, 113.5, 55.5, 40.4, 40.3, 36.8. LRMS (EI^+): m/z=301 (4), 221 (25), 210 (100), 194 (29), 179 (63), 178 (84), 165 (95), 152 (51), 115 (17), 89 (6). HRMS (EI^+): m/z calcd for $C_{16}H_{14}OBr$ [M−Br] 301.0228, found=301.0233.

4.10.13. 2-Bromo-1-phenyl-1H-indene ***8a***. Isolated by flash column chromatography (20% EtOAc in hexanes) as a white solid in 95% yield. Mp=74–76 °C. IR (Thin Film): 3062, 2981, 1951, 1599, 1548, 1491, 1451, 1419, 1335, 1263, 1187, 1152, 1093, 1072, 1029, 908, 876, 851, 693, 647 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.22 (5H, m), 7.15–7.06 (4H, m), 7.00 (1H, d, J=1.5 Hz), 4.58 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 143.2, 137.8, 133.3, 131.8, 129.2, 128.8, 127.8, 127.5, 125.9, 124.2, 120.7, 61.4. LRMS (EI^+): m/z=273 (3), 272 (6), 191 (100), 189 (29), 165 (15), 163 (4), 95 (1), 63 (1). HRMS (EI^+): m/z calcd for $C_{15}H_{11}Br$ [M] 270.0044, found=270.0037.

4.10.14. 2-Bromo-5-methyl-1-(m-tolyl)-1H-indene ***8b-A*** *and 2-bromo-7-methyl-1-(m-tolyl)-1H-indene* ***8b-B***. Isolated by flash column chromatography (hexanes) to provide the indene isomers **8b-A** and **8b-B** in a 1:1 ratio as a clear oil in quantitative yield. IR (Thin Film): 3041, 3015, 2963, 2906, 2855, 1605, 1558, 1491, 1466, 1455, 1419, 1385, 1258, 1168, 1096, 1034, 1016, 913, 887, 845, 771, 745, 732, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–6.80 (8H, m), 4.45 (0.5H, s), 4.43 (0.5H, s), 2.36 (1.5H, s), 2.30 (1.5H, s), 2.28 (1.5H, s), 1.97 (1.5H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 144.9, 143.5, 143.1, 138.5, 138.4, 137.7, 137.0, 136.5, 133.8, 133.0, 132.5, 132.3, 131.7, 129.1, 129.1, 128.8, 128.6, 128.4, 128.3, 127.7, 127.3, 126.4, 125.9, 125.6, 123.7, 121.2, 118.1, 60.9, 60.9, 21.6, 21.6, 18.8 (missing 1 aliphatic signal). LRMS (EI^+): m/z=298 (5), 220 (4), 219 (100), 202 (3). HRMS (EI^+): m/z calcd for $C_{17}H_{15}Br$ [M] 298.0357, found 298.0364.

4.10.15. 2-Bromo-6-methyl-1-(p-tolyl)-1H-indene ***8c***. Isolated as a tan oil in 86% yield. IR (Thin Film): 3015, 2912, 2855, 1594, 1548, 1509, 1470, 1450, 1382, 1258, 1189, 1132, 1111, 1021, 863, 812, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (1H, d, J=7.5 Hz), 7.12 (2H, d, J=7.5 Hz), 7.06 (1H, d, J=7.5 Hz), 6.99–6.96 (3H, m), 6.94 (1H, s), 4.49 (1H, s), 2.33 (3H, s), 2.23 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 140.3, 137.2, 135.5, 134.8, 132.8, 130.4, 129.7, 128.5, 127.9, 124.8, 120.1, 60.8, 21.6, 21.4. LRMS (EI^+): m/z=298 (5), 220 (4), 219 (100), 204 (3), 203 (4), 189 (3), 128 (2), 86 (4), 84 (7). HRMS (EI^+): m/z calcd for $C_{17}H_{15}Br$ [M] 298.0357, found=298.0358.

4.10.16. 2-Bromo-4-chloro-1-(2-chlorophenyl)-1H-indene ***8d***. Isolated as a white solid in 93% yield. Mp=69 °C. IR (Thin Film): 3066, 3010, 2896, 1581, 1550, 1441, 1474, 1453, 1427, 1257, 1184, 1168, 1134, 1052, 1035, 917, 862, 837, 771, 756, 652, 640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (1H, dd, J=8.0, 1.0 Hz), 7.23 (3H, m), 7.12 (2H, ddd, J=8.0, 1.0, 1.0 Hz), 7.06 (m, 1H), 6.67 (1H, dd, J=8.0, 1.0 Hz), 5.41 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 141.3, 135.2, 134.8, 131.7, 131.4, 130.0, 129.1, 128.4, 127.8, 127.7, 127.1, 125.8, 122.2, 57.9. LRMS (EI^+): m/z=339 (11), 263 (4), 261 (54), 259 (100), 223 (4) 189 (18), 187 (4). HRMS (EI^+): m/z calcd for $C_{15}H_9Cl_2Br$ [M] 337.9265, found=337.9274.

4.10.17. 2-Bromo-6-chloro-1-(4-chlorophenyl)-1H-indene ***8e***. Isolated as a white solid in 91% yield. Mp=69–71 °C. IR (Thin Film): 3066, 3010, 2896, 2958, 1583, 1449, 1454, 1408, 1330, 1261, 1192, 1176, 1092, 1064, 1015, 913, 835, 807, 785, 744, 682, 618 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, m), 7.23 (2H, m), 7.09 (1H, m), 6.99 (2H, m), 6.98 (1H, s), 4.56 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 141.4, 135.3, 133.8, 132.6, 132.0, 131.3, 129.9, 129.4, 127.9, 124.5, 121.4, 60.5. LRMS (EI^+): m/z=341 (6), 339 (11), 337 (8), 263 (4), 261 (48), 259 (100), 223 (4) 189.5 (13), 129 (3). HRMS (EI^+): m/z calcd for $C_{15}H_9Cl_2Br$ [M] 337.9265, found=337.9274.

4.10.18. 2-Bromo-1-(o-tolyl)-1H-indene ***8h-A*** *and 2-bromo-4-methyl-1-phenyl-1H-indene* ***8h-B***. Isolated as a mixture of **8h-A** and **8h-B** in a 3:1 ratio as a pale tan oil in 74% yield. IR (Thin Film): 3072, 3031, 2932, 2849, 1597, 1555, 1496, 1450, 1382, 1331, 1258, 1191, 1160, 1073, 1026, 998, 949, 910, 876, 861, 765, 747, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–6.94 (8.75H, m), 6.50 (0.25H, d, J=8.0 Hz), 4.88 (0.25H, d, J=2.0 Hz), 4.48 (0.75H, s), 2.64 (0.75H, s), 2.42 (2.25H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 141.9, 137.8, 133.4, 133.1, 132.5, 132.0, 131.6, 131.5, 131.4, 130.9, 130.8, 129.8, 129.0, 128.6, 128.5, 127.6, 127.5, 127.2, 126.9, 126.8, 125.8, 125.6, 123.8, 121.5, 120.6, 61.5, 56.7, 20.5, 18.7. LRMS (EI^+): m/z=286 (7), 205 (100), 203 (10), 202 (11), 190 (6), 189 (5), 178 (4), 102 (2), 77 (1) HRMS (EI^+): m/z calcd for $C_{16}H_{13}Br$ [M] 284.0201, found=284.0209.

4.10.19. 2-Bromo-1-(p-tolyl)-1H-indene ***8i-A*** *and 2-bromo-6-methyl-1-phenyl-1H-indene* ***8i-B***. Isolated as a mixture of **8i-A** and **8i-B** in a 55:45 ratio as a tan oil in 97% yield. IR (Thin Film): 3025, 2920, 1602, 1551, 1512, 1494, 1473, 1334, 1256, 1189, 1109, 1072, 1023, 935.7, 863.8, 808.5, 772.4, 746.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–6.94 (9H, m), 4.53 (1H, s), 2.32 (1.35H, s), 2.27 (1.65H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 147.6, 142.8, 140.1, 137.7, 137.1, 135.3, 134.2, 132.7, 132.7, 131.6, 130.0, 129.5, 128.7, 128.4, 128.2, 127.8, 127.3, 127.0, 125.4, 124.6, 123.7, 120.2, 119.9, 60.8, 60.7, 21.4, 21.1. LRMS (EI^+) m/z=286 (5), 205 (100), 189 (27), 178 (19), 165 (6), 128 (19), 77 (15). HRMS (EI^+) m/z calcd $C_{16}H_{13}Br$ [M] 284.0201, found 284.0198.

4.10.20. 2-Bromo-1-(3,5-dimethylphenyl)-1H-indene ***8j-A*** *and 2-bromo-5,7-dimethyl-1-phenyl-1H-indene* ***8j-B***. Isolated as a mixture of **8j-A** and **8j-B** in a 25:75 ratio as a light yellow solid in 92% yield. Mp=73–76 °C. IR (Thin Film): 3026, 2916, 1610, 1563, 1492, 1454, 1379, 1230, 1173, 1073, 1029, 883, 861, 748, 726, 648, 628 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.00 (5.75H, m), 6.91 (0.25H, s), 6.87 (0.75H, d, J=2.0 Hz), 6.75 (0.75H, s), 6.68 (0.5H, s), 4.48 (0.25H, s), 4.46 (0.75H, s), 2.35 (2.25H, s), 2.27 (1.5H, s), 1.92 (2.25H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 143.4, 142.4, 138.2, 137.3, 137.0, 136.8, 133.2, 132.7, 132.2, 132.1, 131.5, 129.2, 128.9, 128.6, 128.4, 127.9, 127.2, 127.0, 126.0, 125.4, 123.8, 120.2, 118.7, 61.0, 60.4, 21.3, 21.2, 18.4. LRMS (EI^+): m/z=298 (10), 220 (4), 219 (100), 204 (3), 203 (9), 189 (3), 115 (4), 101 (3). HRMS (EI^+): m/z calcd for $C_{17}H_{15}Br$ [M] 298.0357, found=298.0349.

4.10.21. 2-Bromo-1-(3-nitrophenyl)-1H-indene ***8k-A*** *and 2-bromo-3-(3-nitrophenyl)-1H-indene* ***13k-A***. Isolated by flash column chromatography (10–20% EtOAc in hexanes) as indenes **8k-A** and **13k-A** in a 9:1 ratio as a white solid in 75% yield. Mp=142–143 °C. IR (Thin Film): 3070, 2902, 1604, 1531, 1473, 1457, 1355, 1256, 1195, 1095, 1080, 1025, 934, 908, 887, 821, 184, 757, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, ddd, J=8.0, 2.0, 1.0 Hz), 7.97 (1H, dd, J=2.0, 2.0 Hz), 7.37 (1H, dd, J=8.0, 8.0 Hz), 7.38 (2H, m), 7.28 (1H, ddd, J=7.5, 7.5, 1.0 Hz), 7.19–6.95 (3H, m), 4.66 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 142.8, 139.9, 134.5, 133.9, 129.7, 129.6, 127.8, 125.9, 123.7,

123.5, 122.6, 120.8, 60.2 (1 aromatic C missing). LRMS (EI^+): m/z=315 (8), 285 (5), 236 (100), 189 (96), 163 (11), 94.5 (6). HRMS (EI^+): m/z calcd for $C_{15}H_{10}NO_2Br$ [M] 314.9895, found 314.9892.

4.10.22. 2-Bromo-1-(4-nitrophenyl)-1H-indene ***8l-A*** *and 2-bromo-3-(4-nitrophenyl)-1H-indene* ***13l-A***. Obtained as a mixture of indenes **8l-A** and **13l-A** in a 9:1 ratio (crude NMR). Compounds **8l-A** and **13l-A** were isolated by flash column chromatography in a combined 93% yield (0–10% EtOAc in hexanes). Compound **8l-A** was obtained as yellow oil. IR (Thin Film): 3062, 2941, 2868, 1731, 1697, 1533, 1455, 1356, 1257, 1182, 1148, 1095, 1078, 1027, 1010, 933, 882, 848, 816, 807, 749, 729, 679 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19–8.16 (2H, m), 7.35 (1H, d, J=7.5 Hz), 7.31–7.23 (3H, m), 7.15 (1H, ddd, J=7.5, 7.5, 1.0 Hz), 7.11–7.08 (2H, m), 4.67 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 146.4, 145.6, 143.0, 134.2, 129.7, 129.4, 128.0, 126.2, 124.3, 124.0, 121.0, 60.6. LRMS (EI^+): m/z=317 (6), 315 (6), 236 (100), 190 (21), 189 (51), 187 (3), 94 (4). HRMS (EI^+): m/z calcd for $C_{15}H_{10}BrNO_2$ [M] 314.9895, found=314.9896. Compound **13l-A** was obtained as a light yellow oil. IR (Thin film): 3070, 2947, 2857, 1714, 1597, 1513, 1457, 1339, 1311, 1104, 1012, 942, 849, 771, 721, 690, 620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (2H, dd, J=7.0, 2.0 Hz), 7.72 (2H, dd, J=7.0, 2.0 Hz), 7.23–7.20 (4H, m), 3.82 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 142.0, 140.8, 140.4, 135.1, 130.0, 129.6, 126.9, 126.9, 125.7, 123.8, 119.4, 45.9. LRMS (EI^+): m/z=317 (5), 315 (5), 236 (100), 206 (18), 189 (41), 177 (1), 94 (4). HRMS (EI^+): m/z calcd for $C_{15}H_{10}NO_2Br$ [M] 314.9895, found=314.9892.

4.10.23. 2,3-Diphenyl-1H-indene ***14a***. Isolated by flash column chromatography (20% EtOAc in hexanes) as a tan oil in 82% yield. IR (Thin Film): 3056, 3024, 2882, 1948, 1808, 1600, 1490, 1458, 1442, 1389, 1357, 1242, 1210, 1173, 1156, 1074, 1026, 941, 917, 841, 810 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (1H, d, J=6.60 Hz), 7.38 (5H, m), 7.30–7.16 (9H, m), 3.93 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 142.3, 141.0, 139.9, 136.5, 136.0, 129.3, 128.8, 128.2, 128.1, 127.3, 126.9, 125.0, 123.5, 120.3, 104.7, 41.1. LRMS (EI^+): m/z=268 (100), 267 (27), 265 (18), 263 (5), 252 (4), 191 (12), 189 (10), 165 (8), 134 (3), 131 (4), 126 (8), 119 (5), 113 (4). HRMS (EI^+): m/z calcd for $C_{21}H_{16}$ [M] 268.1252, found=268.1251.

4.10.24. 3-Phenyl-2-(o-tolyl)-1H-indene ***14b***. Isolated by flash column chromatography (20% EtOAc in hexanes) as yellow needle crystals in 72% yield. Mp=118–120 °C. IR (Thin Film) 3062, 3024, 2916, 2943, 2873, 2334, 1951, 1908, 1884, 1803, 1706, 1604, 1575, 1486, 1454, 1386, 1354, 1171, 1120, 1077, 1026, 905, 755, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (2H, m), 7.28–7.06 (11H, m), 3.80 (2H, s), 1.97 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 143.1, 143.1, 140.3, 137.2, 136.0, 135.4, 130.1, 129.8, 128.8, 128.2, 127.1, 127.0, 126.4, 125.4, 124.8, 123.7, 120.3, 43.5, 20.2. LRMS (EI^+): m/z=297 (2), 296 (8), 282 (100), 282 (29), 265 (5), 252 (3), 239 (2). HRMS (EI^+): m/z calcd for $C_{22}H_{18}$ [M] 282.1409, found=282.1408.

4.10.25. 3-Phenyl-2-(m-tolyl)-1H-indene ***14c***. Isolated by flash column chromatography (0–5% EtOAc in hexanes) as yellow crystals in 79% yield. Mp=118–120 °C. IR (Thin Film): 3029, 2927, 2878, 1948, 1873, 1806, 1604, 1494, 1389, 1327, 1292, 1260, 1212, 1174, 1152, 1075, 1015, 878, 773, 720, 701, 601, cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55–7.52 (1H, m), 7.44–7.32 (6H, m), 7.28–7.19 (3H, m), 7.15–6.88 (3H, m), 3.91 (2H, s), 2.24 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 142.5, 140.5, 139.9, 138.8, 138.1, 130.9, 130.5, 130.4, 130.1, 129.9, 129.8, 128.9, 127.5, 126.5, 124.5, 123.9, 120.1, 41.5, 21.5. LRMS (EI^+): m/z=283 (5), 282 (100), 267 (12), 265 (7), 239 (3), 252 (3), 265 (8), 189 (3), 133 (1). HRMS (EI^+): m/z calcd for $C_{22}H_{18}$ [M] 282.1409, found=282.1412.

4.10.26. 3-Phenyl-2-(p-tolyl)-1H-indene ***14d***. Isolated by flash column chromatography (20% EtOAc in hexanes) as yellow needle crystals in 87% yield. Mp=118–120 °C. IR (Thin Film): 3046, 3015, 2917, 1604, 1576, 1511, 1491, 1465, 1442, 1390, 1238, 1191, 1176, 1158, 1073, 1026, 1116, 938, 820, 770, 724, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, d, J=6.0 Hz), 7.38 (3H, m), 7.26–7.15 (6H, m), 7.05 (2H, d), 3.9 (2H, s), 3.9 (1H, s), 2.23 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 142.3, 141.1, 139.2, 136.7, 136.3, 133.6, 129.3, 128.9, 128.7, 128.1, 127.3, 126.4, 124.8, 123.5, 120.2, 41.1, 21.1. LRMS (EI^+): m/z=282 (100), 267 (13), 265 (8), 252 (28), 239 (3), 205 (3), 189 (4), 165 (4), 126 (3). HRMS (EI^+): m/z calcd for $C_{22}H_{18}$ [M] 282.1409, found=282.1403.

4.10.27. 2-(3-Methoxyphenyl)-3-phenyl-1H-indene ***14e***. Isolated by flash column chromatography (10% EtOAc in hexanes) as a light yellow oil in 90% yield. IR (Thin Film): 3067, 3015, 2958, 2829, 1607, 1486, 1462, 1429, 1393, 1323, 1292, 1264, 1217, 1173, 1034, 910, 866, 773, 727, 701, 600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (1H, m), 7.46–7.42 (2H, m), 7.39–7.34 (3H, m), 7.28–7.19 (3H, m), 7.14 (1H, t, J=8.0 Hz), 6.92 (1H, ddd, J=8.0, 1.5, 1.0 Hz), 6.80 (1H, dd, J=2.5, 1.5 Hz), 6.72 (1H, ddd, J=8.0, 2.5, 1.0), 3.92 (2H,s), 3.55 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 147.1, 142.5, 141.1, 140.5, 138.0, 136.4, 129.6, 129.4, 129.0, 127.7, 126.8, 125.4, 123.8, 120.9, 120.6, 113.5, 113.4, 55.1, 41.3. LRMS (EI^+): m/z=299 (9), 298 (100), 283 (7), 267 (5), 252 (5), 239 (4), 191 (4), 165 (3), 126 (3), 86 (4). HRMS (EI^+): m/z calcd for $C_{22}H_{18}O$ [M] 298.1358, found=298.1353.

4.10.28. 2-(4-Nitrophenyl)-3-phenyl-1H-indene ***14f***. Isolated by flash column chromatography (10% EtOAc in hexanes) as an orange crystalline solid in 78% yield. Mp=149–151 °C. IR (Thin Film): 3062, 2360, 2341, 1589, 1509, 1459, 1443, 1391, 1296, 1243, 1191, 1108, 909, 848, 775, 752, 725, 701, 667, 617 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, m), 7.59–7.55 (1H, m), 7.48–7.42 (3H, m), 7.39 (2H, m), 7.36–7.30 (4H, m), 7.28–7.24 (1H, m), 3.96 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 144.1, 143.2, 142.5, 138.3, 135.1, 129.3, 129.2, 129.0, 128.6, 128.1, 126.8, 126.2, 123.7, 123.5, 121.2, 40.9. LRMS (EI^+): m/z=225 (4), 208 (7), 193 (63), 165 (54), 139 (19), 105 (28), 92 (100), 91 (71), 77 (54), 63 (57), 51 (56). HRMS (EI^+): m/z calcd for $C_{21}H_{15}NO_2$ [M] 313.1103, found=313.1095.

4.10.29. 3-Phenyl-2-(phenylethynyl)-1H-indene ***15a***. Isolated by flash column chromatography (hexanes) as a light yellow oil in 80% yield. IR (Thin Film): 3047, 3019, 2930, 2347, 2190, 1967, 1599, 1487, 1459, 1443, 1387, 1361, 1333, 1177, 1154, 1126, 1065, 1020, 942, 903, 754, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, dt, J=7.0, 1.5 Hz), 7.56–7.47 (4H, m), 7.46–7.38 (3H, m), 7.34–7.26 (5H, m), 3.76 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 144.0, 143.2, 134.7, 131.6, 129.0, 128.5, 128.5, 128.3, 128.2, 126.8, 126.2, 124.0, 123.7, 122.8, 121.2, 95.8, 87.5, 42.6. LRMS (EI^+): m/z=293 (8), 292 (100), 291 (46), 289 (26), 276 (4), 215 (14), 144 (3), 131 (1). HRMS (EI^+): m/z calcd for $C_{23}H_{16}$ [M] 292.1252, found=292.1251.

4.10.30. 3-(3-Phenyl-1H-inden-2-yl)prop-2-yn-1-ol ***15b***. Isolated by flash column chromatography (10% EtOAc in hexanes) as a light yellow oil in 32% yield. IR (Thin Film): 3053, 2914, 2837, 1592, 1488, 1435, 1387, 1323, 1173, 1064, 1036, 920, 881, 851, 782, 699, 658, 614 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.66 (2H, m), 7.51–7.46 (4H, m), 7.42–7.38 (1H, m), 7.33–7.26 (2H, m), 4.44 (2H, s), 3.66 (2H, s), 1.62 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 143.9, 143.0, 134.5, 128.9, 128.6, 128.3, 126.9, 126.4, 124.1, 121.3, 93.5, 83.2, 52.1, 42.7 (1 carbon missing). LRMS (EI^+): m/z=252 (100), 251 (7), 237 (4), 215, (39), 202 (53), 189 (8), 187 (4), 187 (4), 139 (2), 128 (2), 94 (4), 86 (33), 84 (53). HRMS (EI^+): m/z calcd for $C_{18}H_{14}O$ [M] 246.1045, found=246.1042.

4.10.31. 2-Bromo-3-phenyl-1H-indene ***13a***. Isolated as a light yellow oil in 85% yield. IR (Thin Film): 3067, 3013, 2884, 1948, 1881, 1798, 1696, 1604, 1569, 1486, 1451, 1386, 1338, 1292, 1166, 1075,

1023, 940, 854, 789, 744, 720, 639, 615 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, dt, J=7.0, 1.5 Hz), 7.47 (2H, tt, J=8.0, 1.0 Hz), 7.40 (2H, m), 7.28–7.18 (3H, m), 3.74 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 142.7, 142.4, 133.8, 129.2, 128.7, 128.3, 126.9, 125.4, 123.6, 122.0, 120.1, 45.8. LRMS (EI^+): m/z=265 (4), 264 (21), 235 (1), 219 (2), 218 (2), 205 (1), 192 (11), 191 (45), 189 (10), 165 (2), 163 (1). HRMS (EI^+): m/z calcd for $C_{18}H_{16}O_2$ [M] 246.1150, found=246.1147.

4.10.32. 2-Methyl-3-phenyl-1H-indene ***19***.[21] Isolated by flash column chromatography (20% EtOAc in hexanes) as a clear oil in 89% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.31 (6H, m), 7.26–7.20 (2H, m), 7.18–7.12 (1H, m), 3.46 (2H, s), 2.14 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 142.6, 140.8, 138.8, 135.7, 129.4, 128.6, 127.2, 126.4, 124.2, 123.6, 119.5, 43.3, 15.1.

4.10.33. Ethyl 3-phenyl-1H-indene-2-carboxylate ***20***. Isolated as a light yellow oil in 85% yield. IR (Thin Film): 3051, 2970, 2889, 1698, 1615, 1572, 1459, 1440, 1389, 1373, 1298, 1263, 1239, 1190, 1112, 1091, 1150, 1021, 945, 862, 833, 776, 755, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, dt, J=8.5, 1.0 Hz), 7.45–7.38 (5H, m), 7.36 (1H, td, J=7.5, 2.0 Hz), 7.30–7.25 (2H, m), 4.25 (2H, q, J=7.0 Hz), 3.58 (2H, s), 1.25 (3H, t, J=7.0). ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.3, 153.3, 145.2, 143.7, 134.7, 131.3, 129.1, 128.2, 128.1, 127.9, 126.9, 124.3, 123.0, 60.3, 39.6, 14.2. LRMS (EI^+): m/z=265 (4), 264 (21), 235 (1), 219 (4), 191 (100), 189 (22), 165 (5), 163 (1). HRMS (EI^+): m/z calcd for $C_{18}H_{16}O_2$ [M] 264.1150, found=264.1147.

4.10.34. 2-Bromo-7-chloro-3-(2-chlorophenyl)-1H-indene ***13d***. Isolated as a light yellow oil in quantitative yield. IR (Nujol thin film): 3053, 2907, 2851, 1594, 1487, 1445, 1387, 1289, 1258, 1168, 1090, 1017, 944, 908, 802, 735, 690, 620, 528 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.40 (4H, m), 7.36–7.30 (1H, m), 7.22–7.16 (2H, m), 3.73 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 141.7, 139.7, 133.7, 132.8, 131.5, 130.1, 130.0, 129.6, 128.6, 127.1, 125.6, 125.0, 118.8, 45.1. LRMS (EI^+): m/z=341 (8), 339 (31), 337 (14), 261 (91), 260 (11), 259 (100), 223 (11), 189 (51), 187 (16), 111 (3), 93 (3). HRMS (EI^+): m/z calcd for $C_{15}H_9Cl_2Br$ [M] 337.9265, found=337.9273.

4.10.35. 2-Bromo-5-chloro-3-(4-chlorophenyl)-1H-indene ***13e***. Isolated as a clear oil in 94% yield. IR (Nujol): 2907 (Nujol thin film), 2722, 2678, 2358, 1451, 1370, 1294, 1258, 1163, 1093, 1073, 1014, 956, 869, 833, 799, 729, 670, 555 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.50 (1H, m), 7.42–7.29 (3H, m), 7.21–7.16 (2H, m), 6.92–6.86 (1H, m), 3.92–3.74 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 141.1, 140.4, 134.5, 133.2, 131.6, 130.7, 130.4, 125.4, 124.6, 124.1, 120.1, 45.4. LRMS (EI^+): m/z=341 (2), 339 (9), 261 (42), 259 (100), 189 (15), 187 (4), 129 (2). HRMS (EI^+): m/z calcd for $C_{15}H_9Cl_2Br$ [M] 337.9265, found=337.9260.

4.10.36. 2-Bromo-3-(3-nitrophenyl)-1H-indene ***13k-A***. Isolated as a light yellow oil in 70% yield. IR (Thin Film): 3070, 2902, 1604, 1531, 1473, 1457, 1355, 1256, 1195, 1095, 1080, 1025, 934, 908, 887, 821, 184, 757, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (1H, s), 8.30 (1H, d, J=8.0 Hz), 7.89 (1H, d, J=8.0 Hz), 7.68 (1H, dd, J=8.0, 1.0 Hz), 7.48 (1H, d, J=8.0 Hz), 7.30–7.20 (3H, m), 3.83 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 146.2, 142.8, 139.9, 134.5, 133.9, 129.6, 127.8, 125.9, 124.0, 123.7, 123.5, 122.6, 120.8, 60.2. LRMS (EI^+): m/z=315 (8), 237 (12), 236 (100), 190 (34), 189 (66), 163 (7), 131 (12) 94.5 (6), 69 (38). HRMS (EI^+): m/z calcd for $C_{15}H_{10}NO_2Br$ [M] 314.9895, found=314.9882.

4.10.37. Ethyl 3-(2-chlorophenyl)-1H-indene-2-carboxylate ***21***. Isolated as a light yellow oil in 78% yield. IR (Thin Film): 3062, 2986, 2895, 2366, 1736, 1704, 1610, 1577, 1464, 1392, 1368, 1343, 1249, 1193, 1109, 1093, 1058, 1018, 951, 919, 865, 76, 749, 717 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (1H, m), 7.51–7.48 (1H, m), 7.42–7.26 (5H, m), 7.12–7.09 (1H, m), 4.18–4.05 (2H, m), 3.94 (1H, d, J=24.0 Hz), 3.85 (1H, d, J=24.0 Hz) 1.05 (3H, t, J=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 150.1, 144.2, 143.3, 134.3, 133.2, 132.8, 130.0, 129.4, 129.1, 127.7, 126.8, 126.3, 124.1, 122.5, 60.1, 39.1, 13.8. LRMS (EI^+): m/z=298 (1), 263 (59), 249 (100), 235 (43), 225 (51), 189 (46), 176 (50), 163 (6), 88 (1). HRMS (EI^+): m/z calcd for $C_{18}H_{15}O_2Cl$ [M] 298.0761, found=298.0768.

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