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[Pd]-Catalyzed Intermolecular Coupling and Acid Mediated Intramolecular Cyclodehydration: One-Pot Synthesis of Indenes

Pedireddi Niharika[a] and Gedu Satyanarayana*[a]

Abstract: An efficient one-pot synthesis of indenes from simple starting materials is presented. This process involves a dual C-C bond formation via intermolecular Heck coupling followed by acid mediated intramolecular cyclodehydration. The strategy is amenable on varied substituted aromatics to give indenes. Alongside, the regioselective synthesis of benzyl styrenes in a single column purification technique, via *in-situ* reduction of Heck products (ketones) followed by acid mediated dehydration of crude reaction mixture is also presented.

Introduction

Domino one-pot approaches enable the synthesis of highly functionalized or annulated products from simple precursor molecules. Domino processes are also an added advantage for their high productivity, minimum individual reaction steps for purification, and with reduced waste generation. Indene scaffold forms an integral part of an important class of organic compounds depicting many synthetic and pharmaceutical applications. Substituted indene derivatives are reported to be antitubercular agents,[1] antihistamine drugs,[2] aldosterone synthase inhibitors,[3] anti-inflammatory drugs[4] and hence are very significant in medicinal chemistry. Some indenes have been employed as active ligands in organometallics.[5] Due to existence of free *pi*-electrons, they have also found a place of utility in functional materials[6] (Figure 1).

Hence, indenes have emerged as attractive synthetic targets. Various groups have approached the synthesis of indenes via transition metal and Lewis acid catalysis. In the recent past, many transition metal catalyzed synthetic approaches have been established for carboannulations from olefinic/alcohol compounds.[7] Very recently, a number of reports have appeared in the domain of Lewis acid catalysis.[8] Among them most prominent route involves ring expansion of substituted cyclopropanes and cyclopropenes aided by various Lewis catalysts.[9] However, synthesis of indenes by acid mediated approaches, particularly; using carbonyl precursors have been scarcely explored.[10]

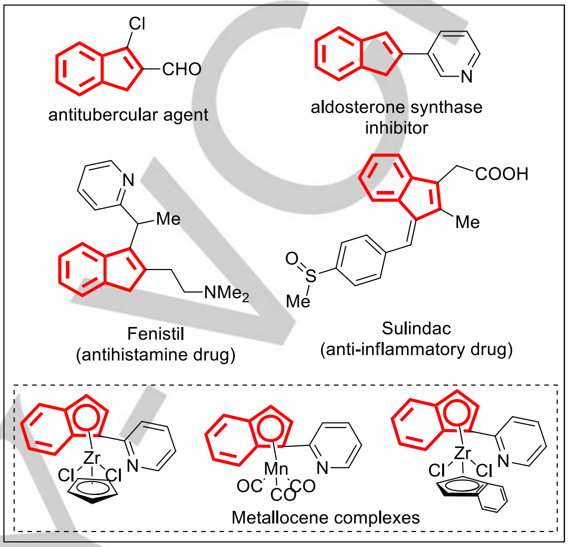

Figure 1: Representative examples of indene core utility.

Initially, Koo et al synthesized indenes under polyphosphoric acid medium,[11] albeit, the study suffered from various drawbacks related to the scope, numerous steps involved, excess of regents and low yields. Later, Shudo et al described intramolecular cyclodehydration of 1,3-diphenyl-1-propanones in a mixture of TFA and TFSA, to produce 1*H*-indenes, however, the method had limited substrate scope and required very high equivalence of acid (100 equiv).[12] Xu et al studied the synthesis of substituted indenes via aluminum chloride promoted Friedel-Crafts alkylation of arenes on cinnamaldehydes. It is important to mention that although this methodology was studied on a wide scope, but the tandem Friedel-Crafts reaction was ineffective to deliver 3-aryl-1*H*-indene exclusively.[13] Klumpp et al described an effective protocol for the synthesis of heterocyclic indenes via cyclodehydration.[14] A few other indene synthesis protocols and reviews have also been reported.[15] Hence, in view with the background, in particular, for the synthesis of 1*H*-indenes in a single pot, from easily accessible starting materials still remains a challenge. To the best of our knowledge, there is no general strategy for the one-pot synthesis of indenes by the combination of transition metal catalyzed carbonyl formation followed by acid induced intramolecular condensation. In continuation to our interest in developing one-pot domino processes,[16] herein, we present an efficient one-pot synthetic strategy for the formation of 3-aryl indenes via Heck coupling followed by acid mediated cyclodehydration starting from simple allylic alcohols.

Results and Discussion

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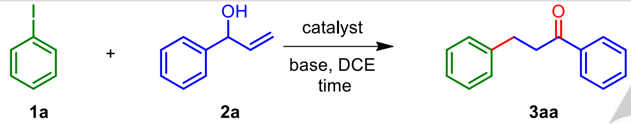
In continuation of our research interest in transition metal catalysis as well as acid (Brønsted/Lewis) promoted transformations,[17] we speculated the indene synthesis in a one-pot operation. Thus, it was contemplated that [Pd]-catalyzed intermolecular C-C bond formation via Heck coupling between iodoarenes and allylic alcohols, followed by subsequent acid mediated intramolecular condensation would afford indenes. DMF and CH_3CN are commonly used solvents for Heck coupling, while, most of the acid mediated transformations, particularly under strong acids, employ chlorinated solvents. Thus, firstly, it was realized to optimize only Heck reaction in 1, 2-dichloroethane (DCE). In our laboratory, we have extensively used Heck coupling[18] between iodoarenes and allylic alcohols. Accordingly, iodoarene **1a** and allylic alcohol **2a** were chosen as the model substrates for Heck coupling in DCE solvent, and the results are as illustrated in Table 1. Thus, the reaction was performed under our established conditions i.e in the presence of $Pd(OAc)_2$ (3 mol%), $NaHCO_3$ (3 equiv), TEBAC (1 equiv), DCE (1 mL) at 50 °C for 24 h. However, no progress was noticed (Table 1, entry 1). Upon increasing the temperature to 80 °C, very less conversion was noticed towards product formation, as large amount of unreacted allylic alcohol **2a** remained (Table 1, entry 2).

Table 1: Optimization of Heck reaction in chlorinated solvent to give **3aa**.[a]



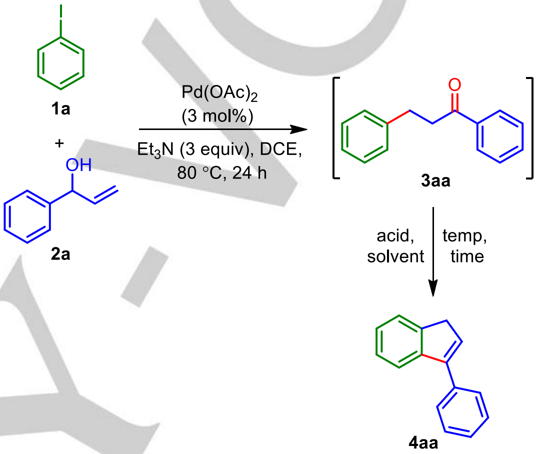
Entry	Catalyst	Base (3 equiv)	Time (h)	Yield **3aa** (%)[b]
1[c]	$Pd(OAc)_2$	$NaHCO_3$	24	-[e]
2[d]	$Pd(OAc)_2$	$NaHCO_3$	24	15
3	$Pd(OAc)_2$	Na_2CO_3	24	10[f]
4	$Pd(OAc)_2$	K_2CO_3	24	17[f]
5	$Pd(OAc)_2$	$^iPr_2NEt$	24	34[f]
6	$Pd(OAc)_2$	$^iPr_2NEt$	48	54[f]
7	$PdCl_2$	$^iPr_2NEt$	24	25[f]
8	**$Pd(OAc)_2$**	**Et_3N**	**24**	**83**
9[g]	$Pd(OAc)_2$	Et_3N	24	84
10	$PdCl_2$	Et_3N	24	44[f]

[a]Reactions were tried on 0.5 mmol scale of iodoarene **1a** and alcohol **2a** with 3 mol% catalyst and 1 mL DCE and at 80 °C. [b]Yields represented are of chromatographically purified product. [c]Benzyltriethylammonium chloride (TEBAC) (1 equiv) was used as additive and reaction was performed at 50 °C. [d]Benzyltriethylammonium chloride (TEBAC) (1 equiv) was used as additive and reaction was performed at 80 °C. [e]Only starting materials were recovered. [f]Starting material was present but not recovered. [g]5 mol% of $Pd(OAc)_2$ was used.

With base Na_2CO_3, very poor yield of the desire ketone **3aa** was obtained (Table 1, entry 3). While in the presence of K_2CO_3, the yield was slightly improved (Table 1, entry 4). The reaction with Hünig's base (*N*,*N*-diisopropylethylamine), gave the product **3aa**, in 34% and 54% yields, for 24 h and 48 h, respectively (Table 1, entries 5 & 6). While the reaction with catalyst $PdCl_2$ with Hünig's base, furnished the ketone **3aa**, in poor yield (Table 1, entry 7). Gratifyingly, the reaction with the base triethylamine, afforded the product **3aa**, in very good yield (Table 1, entry 8). Not much improvement was noted in the yield when the reaction was carried out with 5 mol% of $Pd(OAc)_2$ instead of 3 mol% (Table 1, entry 9). On the other hand, moderate yield of the product **3aa** was obtained with $PdCl_2$ (Table 1, entry 10).

With these optimized conditions in hand (Table 1, entry 8), for the formation of ketones **3**, next, we planned to optimize the acid mediated intramolecular condensation to give indene **4** in one-pot. Thus, it was aimed for one-pot Heck reaction followed by acid induced intramolecular condensation. Therefore, *in-situ* formed

Table 2: Optimization for the one-pot synthesis of indenes **4aa**.[a]



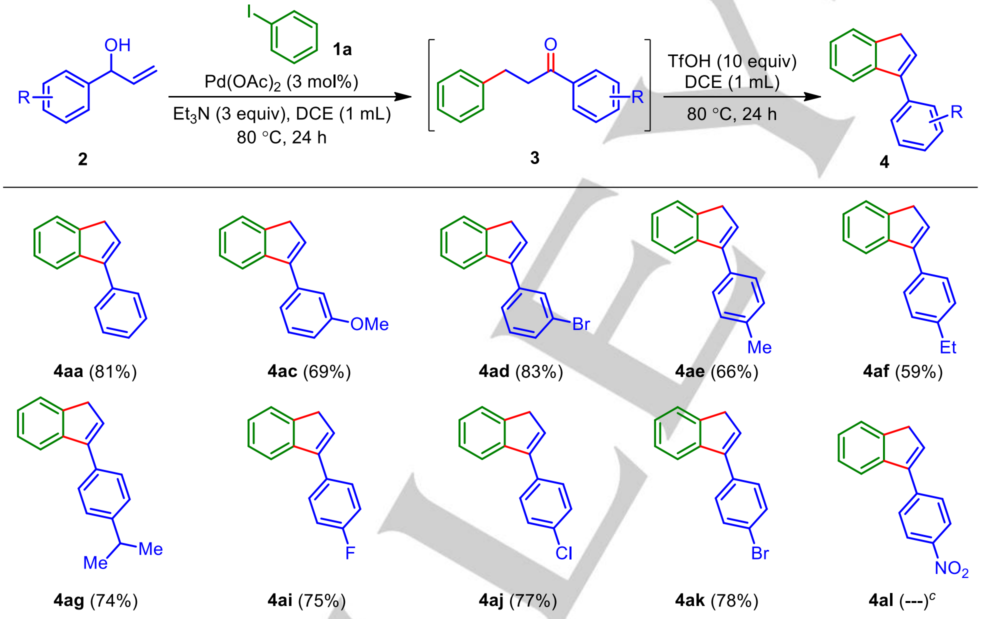
Entry	Acid (equiv)	Temp (°C)	Time (h)	Yield **4aa** (%)[b]
1	$Sc(OTf)_3$ (0.5)	80	24	-[c]
2	$Cu(OTf)_3$ (0.5)	80	24	-[c]
3	$FeCl_3$ (3)	80	12	-[c]
4	$FeCl_3$ (3)	80	24	-[c]
5	$ZnCl_2$ (3)	80	24	-[c]
6	H_2SO_4 (3)	80	1	-[d]
7	H_2SO_4 (3)	rt	12	-[e]
8	TFA (3)	80	24	-[c]
9	TfOH (3)	80	12	35%[f]
10	TfOH (3)	80	28	45%[f]
11	TfOH (5)	80	28	65%[f]
12	**TfOH (10)**	**80**	**24**	**81%**

[a]Reactions were performed on 0.5 mmol scale of alcohol **2a**. [b]Yields represented are of chromatographically purified product. [c]Only starting material **2a** was recovered. [d]Decomposition of intermediate **3aa**. [e]TLC showed multiple spots. [f]Not complete conversion.

ketone **3aa** was treated with different acids with an additional amount of DCE solvent to generate indene **4aa** and the results are illustrated in Table 2. The additional amount of solvent is necessary to avoid the slurry formation, which prevents proper mixing of the reaction mixture. Initially, the *in-situ* formed ketone **3aa** was treated under catalytic amount of Lewis acid Sc(OTf)$_3$, however, no progress was noted (Table 2, entry 1). Similar results were observed with other Lewis acids (Table 2, entries 2 to 5). Complete decomposition of intermediate ketone **3aa**, was noticed with conc. H_2SO_4 at 80 °C after 1 h (Table 2, entry 6), while multiple spots were seen on TLC when the reaction was conducted at room temperature for longer reaction times (Table 2, entry 7). On the other hand, trifluoroacetic acid could not drive the reaction (Table 2, entry 8). Interestingly, the reaction with 3 equiv of trifluoromethanesulfonic acid (TfOH) at 80 °C for 12 h, afforded the product indene **4aa**, albeit in 35% yield (Table 2, entry 9). Notably, increasing the reaction time from 12 to 28 h, slightly improved the yield to 45% (Table 2, entry 10). Further increase in TfOH to 5 equiv raised the yield to 65% (Table 2, entry 11). It is quite possible that the *in-situ* present triethylamine might have neutralized the TfOH. Gratifyingly, the reaction with 10 equiv of TfOH at 80 °C for 24 h, afforded the indene **4aa**, in very good overall yield (Table 2, entry 12).

After establishing the one-pot synthetic conditions for indene **4aa** [(Table 1, entry 8) & (Table 2, entry 12)], to check the scope and applicability of the method, the reaction was performed between different iodobenzenes **1** and allylic alcohols **2**. The *in-situ* formed ketones **3** were reacted with 10 equiv of TfOH in DCE and results are as summarized in Table 3. The reaction was amenable on a wide range of substrates and furnished the indenes **4**, in fair to very good yields (Table 3). Notably, the reaction was suitable to simple as well as electron rich aromatic allylic alcohols [i.e. phenyl, alkylphenyl and anisyl moieties; (Table 3, **4aa-4ak**)]. Significantly, reaction was also compatible with electron deactivating groups, such as F, Cl and Br substituents on the aromatic ring of the allylic alcohols **2** (Table 3; **4ad** & **4ai-4ak**). These indene systems are of synthetic importance, particularly, the bromoindenes (**4ad** & **4ak**) would serve as useful synthons for further elaborations under transition-metal catalysis. However, the nitro substituted allylic alcohol **2l** was unsuccessful to produce the indene **4al**, where even, the corresponding Heck ketone **3al** formation was not clear from TLC.

Table 3: Synthesis of indenes **4** from the allylic alcohols **2** with iodobenzene **1a**.^{a,b}



^{a}Reactions were performed on 0.5 mmol scale of iodoarene **1** and allylic alcohol **2**. ^{b}Yields represented are of chromatographically purified products **4**. ^{c}Product **4al** was not formed, as *in-situ* ketone **3al** was not clean by TLC.

Further to check the utility of the method, it was explored with various iodoarenes **1** and allylic alcohols **2**, under standard reaction conditions. Gratifyingly, the strategy was found feasible and afforded the corresponding indenes **4**, in moderate to good yields (Table 4). The reaction was compatible to *ortho*-iodotoluene **1b** and furnished the indene **4ba**. Significantly, the reaction showed very good tolerance with regards to highly electron rich iodoarenes (Table 4, **4ga**-**4hc**). The moderate yield of indene **4gc** could be due to the formation of undesired allylic alcohol along with the usual ketone **3gb**, via simple Mizoroki-Heck coupling of sterically constrained allylic alcohol **2b**.[18c] On the other hand, as seen above (cf. Table 3), in addition to the electronically neutral simple phenyl allylic alcohol, the process was smooth with electron deactivating groups (F, Cl & Br) as well as with electron rich OMe functional group on the aromatic ring of the allylic alcohol **2** (Table 4, **4gi**, **4gj** & **4gk**). Also, as mentioned previously, the indene **4gk** with bromo substituent (Table 4), would permit further functionalization under transition metal catalysis. However, the reactions with the deactivating F and Cl groups on iodoarene were unsuccessful (Table 4, **4ea** & **4fa**). This could be due to the fact that these haloarenes are less nucleophilic in nature to cyclize with the carbonyl group.

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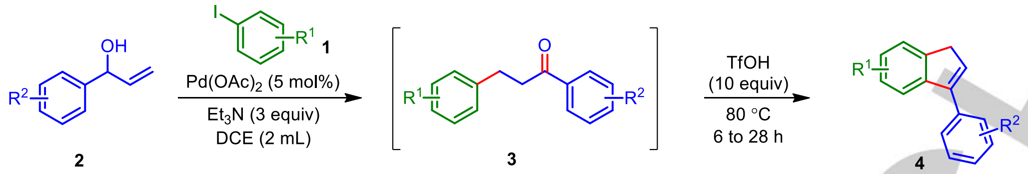
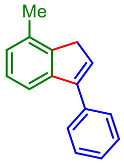
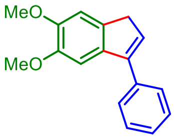
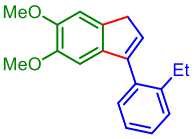
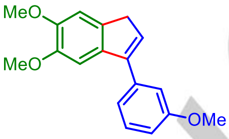
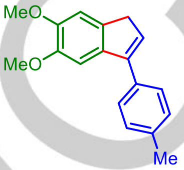
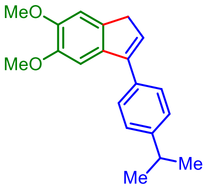
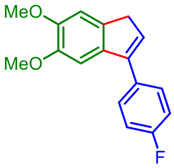
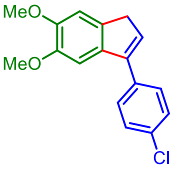
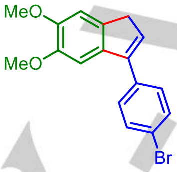
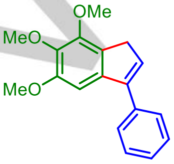
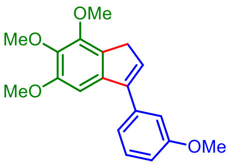
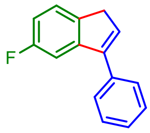
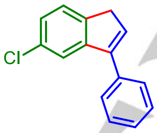
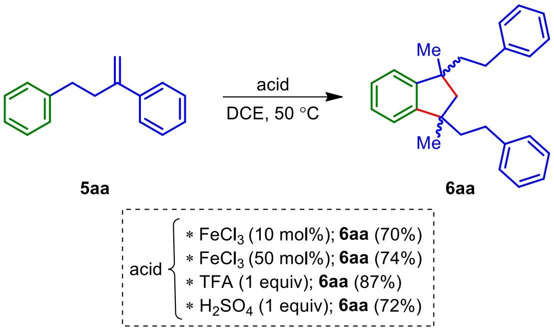
Table 4: Synthesis of indenes **4** from the allylic alcohols **2**.[a,b]



 **4ba** (71%)	 **4ga** (75%)	 **4gb** (49%)	 **4gc** (69%)	 **4ge** (57%)
 **4gg** (76%)	 **4gi** (79%)	 **4gj** (70%)	 **4gk** (73%)	 **4ha** (61%)
 **4hc** (58%)	 **4ea** (---)[c]	 **4fa** (---)[c]		

[a]Reactions were performed on 0.5 mmol scale of allylic alcohol **2**. [b]Yields represented are of chromatographically purified products **4**. [c]Products **4ea** & **4fa** were not formed, although the corresponding ketones were confirmed by TLC.

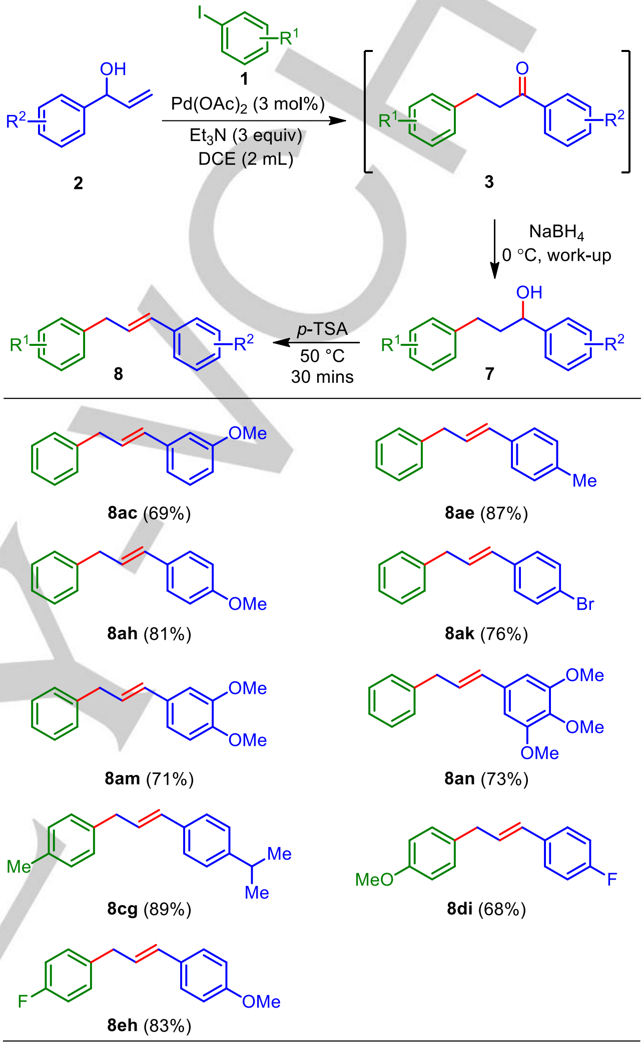
On the other hand, investigations have been carried out on 2,4-diphenylbut-1-ene **5aa** in the presence of different acids in their catalytic or stoichiometric amounts. However, surprisingly, none of the trials could produce the expected indane via intramolecular cyclization, rather, afforded a stereoisomeric mixture of indane **6aa** through homodimerization (Scheme 1). Though, it looks like an exception, this may be attributed to the fact that olefin is relatively more nucleophilic than aromatic ring. Hence, prefers intermolecular homodimerization over intramolecular cyclization.



Scheme 1: Formation of isomeric indane mixture **6aa**.

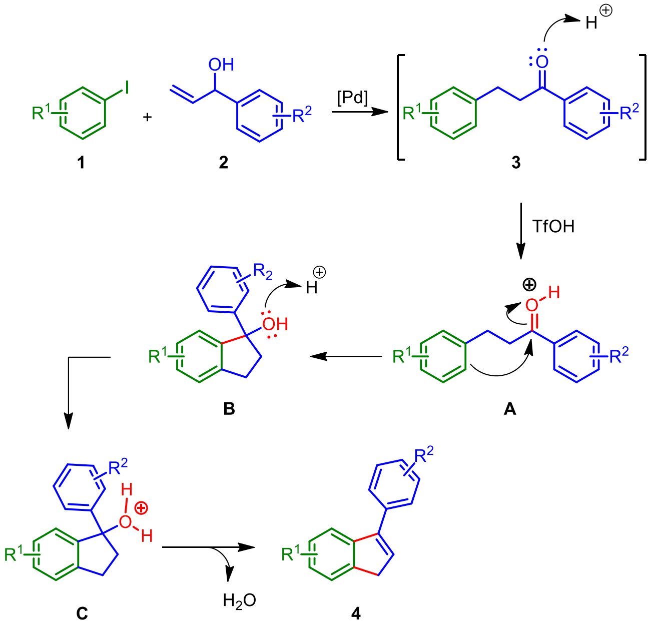
To further demonstrate the applicability of the strategy, it was presumed that the indanes could be accomplished by using intramolecular Friedel-Crafts alkylation of secondary alcohols. In turn, these secondary alcohols can be easily accessed by reducing the *in-situ* formed ketone **3**, by Heck coupling.[18b] Thus, *in-situ* formed ketones **3** were reduced by NaBH$_4$ in one-pot operation. The resultant crude reaction mixture after work-up, was concentrated under vacuum and the crude mass was initially reacted with TfOH (10 to 50 mol%). However, it led to the decomposition at ice temperature itself. Similar results were obtained with conc. H$_2$SO$_4$, while no progress was noted with stoichiometric amounts of TFA (3 equiv). In the presence of *p*-TSA, it led to the formation of benzyl styrenes **5**, in a highly regioslective manner instead of indane formation. The retardation of this chemical reaction to give indane after forming the benzyl styrene can be explained based on Thorpe–Ingold (or gem-dimethyl) effect. As the carbon tether is devoid of gem-dialkyl group and could not push the olefin to come close to the aromatic ring to facilitate the cyclization to give indane. Indeed, these results are in good agreement with that reported by Stokes et al.[19] that signifies the impact of gem-dialkyl moiety on the synthesis of indanes. Gratifyingly, this protocol is advantageous, as it facilitates the synthesis of benzyl styrenes, in a highly regioselective manner (i.e. with regards to the position of double bond) when compared to some of the earlier reports, wherein, a mixture regioisomeric products have been formed.[20] The present strategy allowed the synthesis of simple to highly electron rich benzyl styrenes (Table 5; **8ac-8eh**). The coupling of iodobenzene **1a** with different allylic alcohols (**2c**, **2e**, **2h**, **2k**, **2m** & **2n**) containing Me, OMe and Br substituents on the aromatic ring resulted in the corresponding products with ease (Table 5; **8ac**, **8ae**, **8ah**, **8ak**, **8am** & **8an**). The method was also amenable to substituted iodoarenes (**1c**, **1d** & **1e**) and furnished the respective products, in good to very good yields (Table 5, **8cg, 8di** & **8eh**). Particularly, the product **8ak** with bromo substituent, would expand the scope of the present strategy towards transition metal catalysis.

Table 5: Synthesis of benzyl styrenes **5** from the allylic alcohols **2**.[a,b]



[a]Reactions were performed on 0.5 mmol scale of allylic alcohol **2** and iodoarene **1**. [b]Yields represented are of chromatographically purified products **8ae-8dh**.

A plausible reaction mechanism is as depicted in Scheme 2. The initial Heck coupling between iodoarene **1** and allylic alcohol **2**, generates the ketone **3**. Protonation of the resulted ketone **3** leads to the formation of activated oxonium ion species **A**. Intramolecular Friedel-Crafts alkylation of **A**, furnishes the indanol **B**. Further protonation of labile tertiary hydroxyl group of indanol **B**, gives the corresponding oxonium ion intermediate **C**. Finally, dehydration of **C**, affords the indene **4**.



Scheme 2: Plausible reaction mechanism for the formation of indene **4** from iodoarene **1** and allylic alcohol **2**.

Conclusions

In conclusion, we have presented a one-pot method for the synthesis of indenes starting from simple starting materials. The strategy proceeds through the formation of a dual C-C bond via intermolecular Heck coupling and intramolecular condensation. The strategy was compatible to varied functional groups present on either aromatic rings. In addition, we demonstrated the regioselective formation of benzyl styrenes using *in-situ* reduction of the resulting Heck ketones followed by the reaction of the crude reaction mixture with an acid.

Experimental Section

Experimental:

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using Schlenk tubes under inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. TfOH was purchased from local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

GP-1 (General procedure for the synthesis of 3-aryl-1*H*-indenes 4): In an oven dried Schlenk tube, were added alcohol **2** (67–106.5 mg, 0.5 mmol), iodoarene **1** (122.4–176.4 mg, 0.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%) and trimethylamine (0.2 mL, 1.5 mmol) followed by DCE (1.0 mL) at room temperature under nitrogen atmosphere and allowed the reaction mixture to stir at 80 °C for 24 h. Progress of the ketone **3** formation was monitored by TLC till the reaction is completed. To the cooled reaction mixture at room temperature, was added trifluoromethanesulfonicacid (0.44 mL, 5 mmol) under nitrogen atmosphere. The stirred reaction mixture was then heated in an oil bath at 80 °C for 6 to 24 h and monitored by TLC. Then, the mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the 3-aryl-1*H*-indene **4** (49–83%) as viscous liquid/semi-solid/solid.

3-(3-Bromophenyl)-1*H*-indene (4ad): GP-1 was carried out with alcohol **2d** (106.5 mg, 0.5 mmol), iodoarene **1a** (122.4 mg, 0.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3ad** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene **4ad** at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indene **4ad** (112.6 mg, 83%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2d**)=0.90, R_f(**4ad**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2909, 2808, 1564, 1477, 1264, 1200, 1080, 828, 757 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.74 (s, 1H, ArH), 7.60–7.45 (m, 4H, ArH), 7.38–7.20 (m, 3H, ArH), 6.59 (s, 1H, C=CH), 3.50 (s, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=144.6 (s, C_q), 143.8 (s, C_q), 143.3 (s, C_q), 138.2 (s, C_q), 131.9 (d, ArCH), 130.6 (d, ArCH), 130.5 (d, ArCH), 130.1 (d, ArCH), 126.3 (d, 2C, 2 × ArCH), 125.1 (d, ArCH), 124.2 (d, ArCH), 122.7 (s, ArC), 120.1 (d, C=CH), 38.2 (t, CH_2) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{15}H_{12}Br]^+$=$[M+H]^+$: 271.0122; found: 271.0120.

3-(4-Ethyl)-1*H*-indene (4af): GP-1 was carried out with alcohol **2f** (81 mg, 0.5 mmol), iodoarene **1a** (122.4 mg, 0.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3af** at 80 °C for 24 h and then with TfOH (0.44 mL, 5 mmol) for indene at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indene **4af** (65.1 mg, 59%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2f**)=0.90, R_f(**4af**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2900, 2929, 1645, 1571, 1472, 1258, 1079, 1003, 817, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.60 (d, 1H, *J*=7.3 Hz, ArH), 7.53 (d, 2H, *J*=8.3 Hz, ArH), 7.37–7.20 (m, 5H, ArH), 7.38–7.20 (m, 3H, ArH), 6.55 (t, 1H, *J*=2.4 Hz, C=CH), 3.49 (d, 2H, *J*=2.4 Hz, CH_2), 2.71 (q, 1H, *J*=7.3 Hz, CH_2CH_3), 1.29 (t, 3H, *J*=7.3 Hz, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=145.0 (s, C_q), 144.8 (s, C_q), 144.0 (s, C_q), 143.6 (s, C_q), 133.5 (s, ArC), 130.4 (d, ArCH), 128.0 (d, 2C, 2 × ArCH), 127.6 (d, 3C, 3 × ArCH), 126.1 (d, ArCH), 124.7 (d, ArCH), 124.1 (d, ArCH), 120.3 (d, C=CH), 38.1 (t, CH_2), 28.7 (t, CH_2CH_3), 15.6 (q, CH_2CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{17}]^+$=$[M+H]^+$: 221.1330; found: 221.1329.

3-(4-Isopropylphenyl)-1H-indene (4ag): GP-1 was carried out with alcohol **2g** (88.1 mg, 0.5 mmol), iodoarene **1a** (122.4 mg, 0.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE

(1.0 mL) for ketone **3ag** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at 80 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1) furnished the indene **4ag** (86.6 mg, 74%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2g**)=0.10, R_f(**4ag**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3031, 2858, 1643, 1468, 1377, 1261, 1058, 821, 758 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.61 (d, 1H, *J*=7.8 Hz, ArH), 7.57–7.47 (m, 1H, ArH), 7.54 (d, 2H, *J*=7.8 Hz, ArH), 7.38–7.28 (m, 1H, ArH), 7.31 (d, 2H, *J*=7.8 Hz, ArH), 7.24 (ddd, 1H, *J*=7.8, 7.3 and 1.0 Hz, ArH), 6.59 (t, 1H, *J*=2.4 Hz, C=CH), 3.49 (d, 2H, *J*=2.4 Hz, CH$_2$), 2.97 [sept, 1H, *J*=7.3 Hz, C*H*(CH$_3$)$_2$], 1.30 [d, 6H, *J*=7.3 Hz, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=148.2 (s, C$_q$), 145.0 (s, C$_q$), 144.8 (s, C$_q$), 144.0 (s, C$_q$), 133.6 (s, C$_q$), 130.4 (d, ArCH), 127.6 (d, 2C, 2 × ArCH), 126.6 (d, 2C, 2 × ArCH), 126.1 (d, ArCH), 124.7 (d, ArCH), 124.0 (d, ArCH), 120.4 (d, C=CH), 38.1 (t, CH$_2$), 33.9 [d, *C*H(CH$_3$)$_2$], 24.0 [q, 2C, CH(*C*H$_3$)$_2$] ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{18}$H$_{19}$]$^+$=[M+H]$^+$: 235.1487; found 235.1487.

3-(2-Ethylphenyl)-5,6-dimethoxy-1H-indene (4gb): GP-1 was carried out with alcohol **2b** (81 mg, 0.5 mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gb** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4gb** (68.6 mg, 49%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2b**)=0.40, R_f(**4gb**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2906, 1650, 1561, 1328, 1104, 830, 786 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.40–7.30 (m, 2H, ArH), 7.27–7.20 (m, 2H, ArH), 7.13 (s, 1H, ArH), 6.63 (s, 1H, ArH), 6.32 (t, 1H, *J*=2.0 Hz, C=CH), 3.92 (s, 3H, ArOCH$_3$), 3.79 (s, 3H, ArOCH$_3$), 3.47 (d, 2H, *J*=2.0 Hz, CH$_2$), 2.61 (q, 2H, *J*=7.3 Hz, C*H*$_2$CH$_3$), 1.12 (t, 3H, *J*=7.3 Hz, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=148.2 (s, C$_q$), 147.2 (s, C$_q$), 144.5 (s, C$_q$), 142.6 (s, C$_q$), 138.5 (s, C$_q$), 136.1 (s, C$_q$), 135.3 (s, C$_q$), 130.1 (d, ArCH), 129.6 (d, ArCH), 128.5 (d, ArCH), 127.7 (d, ArCH), 125.6 (d, C=CH), 107.9 (d, ArCH), 103.9 (d, ArCH), 56.2 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 38.2 (t, CH$_2$), 26.3 (t, *C*H$_2$CH$_3$), 15.8 (q, CH$_2$*C*H$_3$) ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{19}$H$_{21}$O$_2$]$^+$=[M+H]$^+$: 281.1542; found: 281.1540.

3-(3-Methoxyphenyl)-5,6-dimethoxy-1H-indene (4gc): GP-1 was carried out with alcohol **2c** (82 mg, 0.5 mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gc** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the indene **4gc** (97.4 mg, 69%) as colour less semisolid. [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**2c**)=0.35, R_f(**4gc**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2967, 1639, 1584, 1477, 1329, 1262, 1198, 843 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.38 (dd, 1H, *J*=8.3 and 7.8 Hz, ArH), 7.22–7.05 (m, 4H, ArH), 6.93 (dd, 1H, *J*=8.3, 2.4 and 1.0 Hz, ArH), 6.47 (t, 1H, *J*=2.0 Hz, C=CH), 3.93 (s, 3H, ArOCH$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 3.44 (d, 2H, *J*=2.0 Hz, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=159.8 (s, C$_q$), 148.0 (s, C$_q$), 147.4 (s, C$_q$), 144.8 (s, C$_q$), 137.7 (s, C$_q$), 137.1 (s, C$_q$), 136.5 (s, C$_q$), 129.7 (d, C=CH), 119.9 (d, ArCH), 113.1 (d, ArCH), 108.1 (d, ArCH), 104.0 (d, ArCH), 56.2 (q, 2C, 2 × ArOCH$_3$), 55.2 (q, ArOCH$_3$), 38.0 (t, CH$_2$) ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{18}$H$_{19}$O$_3$]$^+$=[M+H]$^+$: 283.1334; found: 283.1334.

3-(4-Isopropylphenyl)-5,6-dimethoxy-1H-indene (4gg): GP-1 was carried out with alcohol **2g** (88 mg, 0.5 mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gg** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4gg** (111.8 mg, 76%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2g**)=0.40, R_f(**4gg**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2927, 1665, 1586, 1481, 1328, 1258, 1197, 825 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53 (d, 2H, *J*=8.3 Hz, ArH), 7.33 (d, 2H, *J*=8.3 Hz, ArH), 7.14 (s, 1H, ArH), 7.13 (s, 1H, ArH), 6.44 (t, 1H, *J*=1.9 Hz, C=CH), 3.93 (s, 3H, ArOCH$_3$), 3.90 (s, 3H, ArOCH$_3$), 3.43 (d, 2H, *J*=1.9 Hz, CH$_2$), 2.97 [sept, 1H, *J*=6.8 Hz, C*H*(CH$_3$)$_2$], 1.31 [d, 6H, *J*=6.8 Hz, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=148.2 (s, C$_q$), 148.0 (s, C$_q$), 147.3 (s, C$_q$), 144.8 (s, C$_q$), 137.2 (s, C$_q$), 136.7 (s, C$_q$), 133.8 (s, C$_q$), 129.1 (d, C=CH), 127.4 (d, 2C, 2 × ArCH), 126.7 (d, 2C, 2 × ArCH), 108.1 (d, ArCH), 104.1 (d, ArCH), 56.2 (q, 2C, 2 × ArOCH$_3$), 38.0 (t, CH$_2$), 33.9 [d, *C*H(CH$_3$)$_2$], 24.0 [q, 2C, CH(*C*H$_3$)$_2$] ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{20}$H$_{23}$O$_2$]$^+$=[M+H]$^+$: 295.1698; found 295.1699.

3-(4-Fluorophenyl)-5,6-dimethoxy-1H-indene (4gi): GP-1 was carried out with alcohol **2i** (76 mg, 0.5 mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gi** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4gi** (106.6 mg, 79%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2i**)=0.40, R_f(**4gi**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3032, 2893, 1647, 1548, 1455, 1400, 1254, 760 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53 (dd, 2H, *J*=8.8 and 5.3 Hz, ArH), 7.15 (d, 2H, *J*=8.8 Hz, ArH), 7.13 (s, 1H, ArH), 7.04 (s, 1H, ArH), 6.42 (t, 1H, *J*=2.0 Hz, C=CH), 3.93 (s, 3H, ArOCH$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.43 (d, 2H, *J*=2.0 Hz, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=162.2 (d, *J*=246.5 Hz, C$_q$), 148.1 (s, C$_q$), 147.5 (s, C$_q$), 143.9 (s, C$_q$), 137.1 (s, C$_q$), 136.5 (s, C$_q$), 132.3 (d, *J*=3.7 Hz, C$_q$), 129.5 (d, C=CH), 129.0 (d, 2C, *J*=8.1 Hz, 2 × ArCH), 115.5 (d, 2C, *J*=21.3 Hz, 2 × ArCH), 108.1 (d, ArCH), 103.8 (d, ArCH), 56.2 (q, 2C, 2 × ArOCH$_3$), 38.0 (t, CH$_2$) ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{17}$H$_{16}$FO$_2$]$^+$=[M+H]$^+$: 271.1134; found: 271.1133.

3-(4-Chlorophenyl)-5,6-dimethoxy-1H-indene (4gj): GP-1 was carried out with alcohol **2j** (84 mg, 0.5 mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gj** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4gj** (100.3 mg, 70%) as colour less semisolid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2j**)=0.45, R_f(**4gj**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3034, 2896, 1696, 1578, 1462, 1267, 1029, 866, 747 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.50 (d, 2H, *J*=8.3 Hz, ArH), 7.42 (d, 2H, *J*=8.3 Hz, ArH), 7.12 (s, 1H, ArH), 7.03 (s, 1H, ArH), 6.45 (t, 1H, *J*=2.0 Hz, C=CH), 3.92 (s, 3H, ArOCH$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.43 (d, 2H, *J*=2.0 Hz, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=148.1 (s, C$_q$), 147.5 (s, C$_q$), 143.8 (s, C$_q$), 137.1 (s, C$_q$), 136.3 (s, C$_q$), 134.8 (s, C$_q$), 133.2 (s, C$_q$), 129.9 (d, C=CH), 128.8 (d, 4C, 4 × ArCH), 108.2 (d, ArCH), 103.8 (d, ArCH), 56.2 (q, 2C, 2 × ArOCH$_3$), 38.1 (t, CH$_2$) ppm. HR-MS (ESI$^+$) m/z calculated for [C$_{17}$H$_{16}$ClO$_2$]$^+$=[M+H]$^+$: 287.0839; found: 287.0840.

3-(4-Bromophenyl)-5,6-dimethoxy-1H-indene (4gk): GP-1 was carried out with alcohol **2k** (106.5 mg, 0.5` mmol), iodoarene **1g** (158.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3gk** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4gk** (120.8 mg, 73%) as colour less semisolid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2k**)=0.45, R_f(**4gk**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3034, 2912, 1639, 1577, 1475, 1264, 845, 786 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.57 (d, 2H, *J*=8.3 Hz, ArH), 7.44 (d, 2H, *J*=8.3 Hz, ArH), 7.12 (s, 1H, ArH), 7.03 (s, 1H, ArH), 6.45 (t, 1H, *J*=2.0 Hz, C=CH), 3.92 (s, 3H, ArOCH$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.42 (d, 2H, *J*=2.0 Hz, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=148.1 (s, C_q), 147.5 (s, C_q), 143.9 (s, C_q), 137.1 (s, C_q), 136.2 (s, C_q), 135.2 (s, C_q), 131.7 (d, 2C, 2 × ArCH), 130.0 (d, C=CH), 129.1 (d, 2C, 2 × ArCH), 121.3 (s, C_q), 108.2 (d, ArCH), 103.7 (d, ArCH), 56.2 (q, 2C, 2 × ArOCH$_3$), 38.1 (t, CH$_2$) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{16}BrO_2]^+$=[M+H]$^+$: 331.0334; found: 331.0331.

5,6,7-Trimethoxy-3-phenyl-1H-indene (4ha): GP-1 was carried out with alcohol **2a** (67 mg, 0.5 mmol), iodoarene **1h** (176.4 mg, 0.5 mmol), Pd(OAc)$_2$ (3.4 mg, 3 mol%), triethylamine (0.2 mL, 1.5 mmol), and DCE (1.0 mL) for ketone **3ha** at 80 °C for 24 h, and then with TfOH (0.44 mL, 5 mmol) for indene at rt for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the indene **4ha** (86.1 mg, 61%) as colour less viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2a**)=0.40, R_f(**4ha**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2907, 1640, 1581, 1488, 1392, 1267, 1149, 834 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.55 (d, 2H, J=8.3 Hz, ArH), 7.46 (dd, 2H, J=8.3 and 7.8 Hz, ArH), 7.38 (t, 1H, J=7.8 Hz, ArH), 6.88 (s, 1H, ArH), 6.52 (t, 1H, J=2.0 Hz, C=CH), 4.03 (s, 3H, ArOCH$_3$), 3.90 (s, 3H, ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 3.49 (d, 2H, J=2.0 Hz, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=153.1 (s, C_q), 149.5 (s, C_q), 144.9 (s, C_q), 140.0 (s, C_q), 139.6 (s, C_q), 136.0 (s, C_q), 131.0 (d, C=CH), 128.6 (d, 2C, 2 × ArCH), 128.0 (s, C_q), 127.6 (d, 2C, 2 × ArCH), 127.5 (d, ArCH), 100.1 (d, ArCH), 61.2 (q, ArOCH$_3$), 60.3 (q, ArOCH$_3$), 56.4 (q, ArOCH$_3$), 35.7 (t, CH$_2$) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{18}H_{19}O_3]^+$=[M+H]$^+$: 283.1334; found: 283.1333.

1,3-Dimethyl-1,3-bis(2-phenylethyl)indane (6aa): [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**5aa**)=0.90, R_f(**xx**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2899, 1635, 1579, 1525, 1470, 1354, 1230, 1146, 943, 912, 810 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz; peaks due to major isomer of **6aa**): δ=7.42–7.00 (m, 13H, ArH), 6.77 (d, 1H, J=7.3 Hz, ArH), 2.80–1.80 (m, 10H, 5 × CH$_2$), 1.42 (s, 3H, CH$_3$), 1.00 (s, 3H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=152.3 (s, C_q), 149.2 (s, C_q), 145.9 (s, C_q), 142.7 (s, C_q), 128.4 (d, ArCH), 128.3 (2 × d, 4C, 4 × ArCH), 128.2 (2 × d, 4C, 4 × ArCH), 128.2 (d, ArCH), 128.1 (d, ArCH), 126.9 (d, ArCH), 126.8 (d, ArCH), 125.7 (d, ArCH), 54.9 (s, C_q), 54.8 (s, C_q), 52.0 (t, CH$_2$), 45.1 (t, CH$_2$), 44.5 (t, CH$_2$), 32.1 (t, CH$_2$), 31.8 (t, CH$_2$), 28.6 (q, CH$_3$), 27.6 (q, ArCH$_3$) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{27}H_{31}]^+$=[M+H]$^+$: 355.2426; found: 355.2429.

1-Isopropyl-4-[(2E)-3-(4-methylphenyl)prop-2-enyl]benzene (8cg): GP-2 was carried out with alcohol **2g** (0.50 mmol), iodoarene **1c** (0.50 mmol), Pd(OAc)$_2$ (3 mol%), triethylamine (1.5 mmol), and DCE (1.0 mL) for ketone **3cg** at 80 °C for 24 h. In-situ NaBH$_4$ (2 equiv) was added at 0 ºC and worked up and extracted in ethyl acetate. The solvent was removed under vacuo. *p*-TSA was added (2 equiv) for olefin **8cg** formation at 50 °C for 30 min. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the olefin **8cg** (111.2 mg, 89%) as colour less liquid. [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2g**)=0.10, R_f(**8cg**)=0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3018, 2960, 1694, 1514, 1461, 966, 807 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.31 (d, 2H, J=8.3 Hz, ArH), 7.22–7.10 (m, 6H, ArH), 6.45 (d, 2H, J=15.6 Hz, CH$_2$C*H*=CHAr), 6.31 (td, 1H, J=15.6 and 6.8 Hz, CH$_2$C*H*=CHAr), 3.52 (d, 2H, J=6.8 Hz, CH$_2$), 2.90 [sept, 1H, J=6.8 Hz, C*H*(CH$_3$)$_2$], 2.35 (s, 3H, ArCH$_3$), 1.26 [d, 6H, J=6.8 Hz, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=147.8 (s, C_q), 137.2 (s, C_q), 135.6 (s, C_q), 135.2 (s, C_q), 130.7 (d, CH), 129.1 (d, 2C, 2 × ArCH), 128.5 (2 × d, 3C, CH and 2 × ArCH), 126.5 (d, 2C, 2 × ArCH), 126.1 (d, 2C, 2 × ArCH), 38.9 (t, CH$_2$), 33.8 [d, *C*H(CH$_3$)$_2$], 23.9 [q, 2C, CH(*C*H$_3$)$_2$], 21.0 (q, ArCH$_3$) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{19}H_{23}]^+$=[M+H]$^+$: 251.1800; found: 251.1801.

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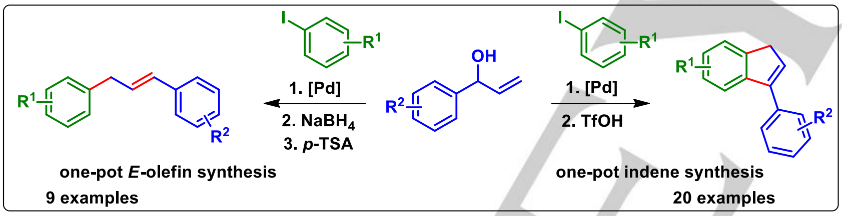

An efficient one-pot synthesis of indenes from simple starting materials is presented. This process involves a dual C-C bond formation via intermolecular Heck coupling followed by acid mediated intramolecular cyclodehydration. Alongside, the regioselective synthesis of benzyl styrenes in a single column purification technique, via in-situ reduction of Heck products (ketones) followed by acid mediated dehydration is also presented.