Synthesis of aryl-substituted indanones and indenes *via* a highly efficient ligand-free palladium-catalyzed Suzuki coupling process

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Abstract

Strategically substituted indene derivatives are useful building blocks for high efficiency olefin polymerization metallocene catalysts. In this paper, various 4-aryl-substituted 2-methyl-1*H*-indanones were prepared efficiently using a ligand-free palladium-catalysed Suzuki coupling procedure. Quantitative yields of indanone intermediates were achieved for most of the non-coordinative substrates with a loading of 0.005 mol% of palladium catalyst. The corresponding indene derivatives were obtained in high purity and multi-gram scale in excellent yields, following a simple sequential reduction and dehydration procedure.

Keywords: Suzuki coupling, ligand-free palladium catalysis, metallocenes, polymerization

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Introduction

Among numerous highly active homogeneous olefin polymerization catalysts, racemic dimethylsilyl-bridged bis-2-methyl-4-phenylindenyl $ZrCl_2$, (Figure1) reported by the Hoechst team in the early 1990s, acts as a cornerstone in isospecific propylene polymerization catalysis, producing isotactic polypropylene (iPP) with significantly high catalytic activity, high molecular mass, high iso-specificity, and high melting point for industrial applications. Known results have shown that methyl and phenyl substitutions are responsible for superior performance of the catalysts in respect of high molecular weight, isotacticity and activity.[1-3] Subsequent research found that the pre-catalyst **1** is also a versatile catalyst for the preparation of olefin copolymers[4-8] or heteroatom containing functionalized copolymers,[9-14] which could potentially be used for the substitution of

PS, PVC, polydiene and related copolymers or as specialty materials (for example coatings, blends, composites, or ion exchange membranes, etc.). Other metallocenes based on **1** have appeared since 1990, and intensive studies of substitution effects for all possible positions of the indene framework were carried out. Much better catalytic performances were achieved and the polymers or co-polymer materials so generated exhibit pronounced improvements of PP properties (melting temperature, molecular mass, uniform monomer distribution, comonomer incorporation, *et al.*).[2,3,15-18]

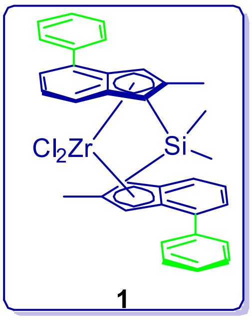

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Figure 1. The Hoechst catalyst.

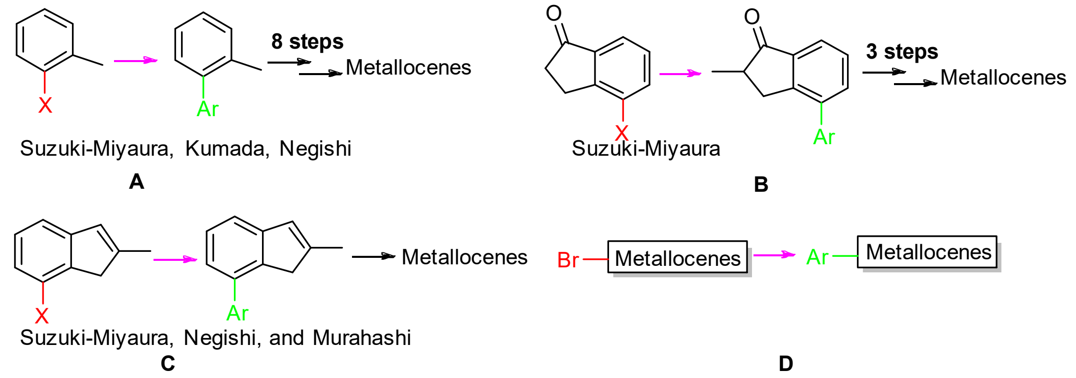
The critical dependence of the activity and selectivity of a metallocene on its ligand structure, especially the fact that some of the C_1 symmetric analogues exhibit boosted catalytic performances compared with their C_2 symmetric counterparts, have stimulated continuing efforts to develop fast and reliable ligand synthetic processes. Many research groups have developed diverse coupling procedures for the synthesis of substituted indenes, based on abundant starting materials and highly efficient organic transformations. There are several strategies applied according to different coupling precursors:

A) From the coupling of 2-functionalized toluenes with desired aryl partners, a reliable sequential procedure was established and a number of indene ligands were prepared. However, many repeated operations are needed to evaluate catalysts with various aryl substitutions. In addition, undesired side reactions may occur for some sensitive substrates during the tedious process. For example, an extremely low yield was observed during the preparation of 2-methyl-4-(l-naphthyl)indanone using the above mentioned procedure;[1,19]

B) As an important improvement, phosphine- or nitrogen-containing palladium complexes catalyzed Suzuki–Miyaura coupling of 4/7-halo indanones was widely applied in 4/7-aryl indene syntheses. Nevertheless, extra ligands used in these reactions caused additional limits such as inert atmosphere protection, more complex purification procedures or higher catalyst loadings.[7,18,20,21]

C) Alexander *et al.* reported an impressive procedure of catalyzed coupling of 4/7 functionalized indenes or indanes with arylboron, halogen, zinc, or magnesium reagents, using metal complexes, as the key step, affording 4-/7-aryl-substituted indenes in excellent yields. This method has been widely used in novel indene ligand synthesis. However, besides the above-mentioned limits with method **B**, the use of organometallic reagents greatly narrows the substrate scope.[22-24]

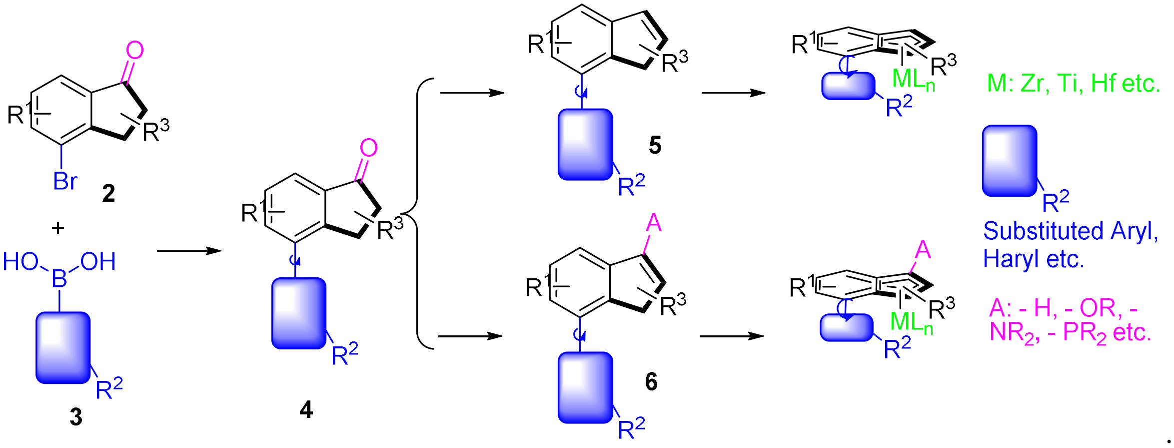
D) As the most straightforward strategy, bromo-substituted Group 4 metallocenes can be efficiently coupled with organo-zinc reagents following a Negishi coupling procedure. However, strikingly lower isolated yields were obtained for some of the substrates because of their sensitivity or isolation problems (Scheme 1).[25-27] Most of these methods need extra ligands to stabilize the palladium catalysts, relatively high noble metal catalyst loading (2-6 mol%) and some of the organometallic reagents utilized severely limit the reaction conditions and the substrate scope.



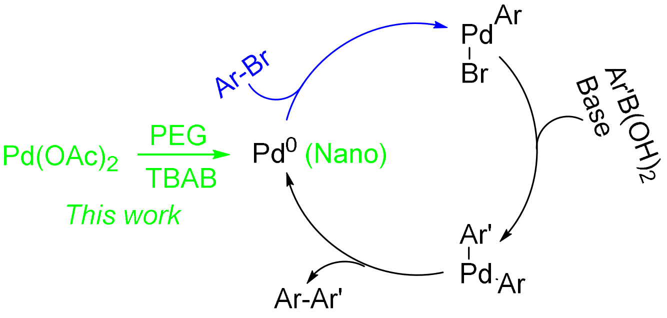
Scheme 1. General methods for Ar-Ar bond formation in metallocene synthesis.

In recent years, many computational studies have been reported aimed at understanding olefin polymerization mechanisms, which have stimulated the development of novel metallocenes useful for new plastic material production.[28-31] In our continuing efforts to develop highly efficient metallocene catalysts based on theoretical computation and high-throughput methods for specialty polyolefins, a simple and efficient synthesis of high purity 4/7-arylindene derivatives is, undoubtedly, of great importance. In this respect, special attention has been paid to 4-aryl-indanones **4**, which can easily be converted into substituted 7-arylindenes **5** and thence into electron-rich ligands **6** following known procedures (Scheme 2). Moreover, the brominated indanones **2** could easily be prepared from abundant commercially available materials. Also, the electron-withdrawing property of the ketone group facilitates the oxidative addition of aryl bromide to the palladium center, which in most cases is known as the rate determining step in the catalytic cycle (Scheme 3).[32-35] PEG-mediated ligand-free Suzuki coupling reactions are attractive because they avoid the use of a complex ligand, thus reducing the residue of harmful and costly noble metals in the final product and simplifying work-up procedures.[36-39]

We report here a highly efficient ligand-free catalytic system for the Suzuki coupling of 4-bromo-2-methyl-1*H*-indanone with aryl/heteroaryl boronic acids in a tetrabutylammonium bromide (TBAB)/Pd$(OAc)_2$/ PEG400 system. Most of the reactions were complete in one hour at 110 °C without inert gas protection. Following a prototype reduction and dehydration procedure, the final 7-aryl-2-methyl-1*H*-indene products could be prepared in excellent yields. Multi-gram scale reactions of 4-bromo-2-methyl-1*H*-indanone with 3,5-bis(trifluoromethyl)phenylboronic acid as the substrate proceeded smoothly, and the substituted indene was prepared in very high total yield for three steps without fractional distillation or column chromatography.



Scheme 2. Metallocenes prepared from 4-bromoindan-1-one.

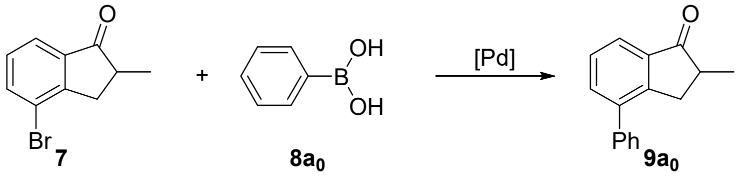


Scheme 3. General catalytic cycle of the Suzuki–Miyaura coupling.

Results and Discussion

The Suzuki coupling of 4-bromo-2-methylindan-1-one with phenylboronic acid (**8a$_0$**) in a PEG400/Pd(OAc)$_2$/TBAB system was chosen as the model reaction and various parameters were evaluated (Equation 1). The reaction yield improved from 17% to 98% in one hour at elevated temperatures (from 80 °C to 110 °C). *In situ* generated nano palladium particles, whose surface properties are unambiguously affected by reaction temperature, have been proved to be active catalysts (Table 1 entries 1, 2).[34] Of those tested, potassium carbonate was the base of choice, providing the highest product yields (Table 1, entries 2-5), while potassium hydroxide was a poor base for the coupling (Table 1, entry 3). Sodium carbonate and potassium phosphate also gave good yields (Table 1, entries 4, 5). In addition, the effect of TBAB on the reaction was examined under otherwise identical conditions; reactions without TBAB or decreasing its loading to 10 mol% furnished the coupled product in lower yields. Reported results showed that TBAB played a dual role for the reaction, as phase transfer catalyst and also as a nano-palladium stabilizer (Table 1, entries 6, 7). Surprisingly, on reducing the loading of the noble metal catalyst precursor $Pd(OAc)_2$ from 0.1 mol% to 0.01 mol%, or even to as low as 0.005 mol%, identical catalytic productivities were achieved under otherwise identical reaction conditions. Further decreasing the catalyst loading to 0.001 mol% resulted in a lowered yield of coupling product (53% in three hours). To the best of our knowledge, this is one of the most efficient methods for this kind of indanone synthesis to date (Table 1, entries 8, 9, 10). As a comparison, the same coupling was performed under the commonly used oxygen-free coupling conditions with 0.1 mol% of $Pd(PPh_3)_4$ as the catalyst, and 90% of coupling yield was obtained in five hours (Table 1, entry 11).

Table 1. Suzuki coupling of 4-bromo-2,3-dihydro-2-methyl-1*H*-inden-1-one **7** with phenylboronic acid **8a₀** [a]



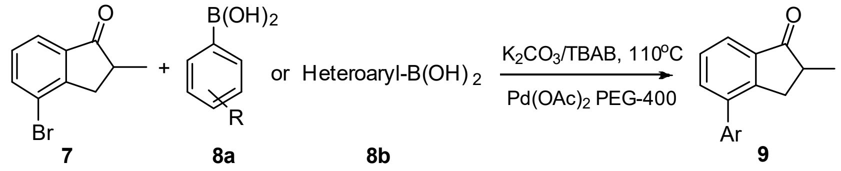
(1)

Entries	Catalyst	Base	TBAB	Temp (°C)	Time (h)	Yield (%) [b]
1	$Pd(OAc)_2$	K_2CO_3	1 eq.	80	1	17
2	$Pd(OAc)_2$	K_2CO_3	1 eq.	110	1	98
3	$Pd(OAc)_2$	KOH	1 eq.	110	1	27
4	$Pd(OAc)_2$	Na_2CO_3	1 eq.	110	1	74
5	$Pd(OAc)_2$	K_3PO_4	1 eq.	110	1	76
6	$Pd(OAc)_2$	K_2CO_3	none	110	12	34
7	$Pd(OAc)_2$	K_2CO_3	10 mol%	110	1	85
8 [c]	$Pd(OAc)_2$	K_2CO_3	1 eq.	110	1	95
9 [d]	$Pd(OAc)_2$	K_2CO_3	1 eq.	110	1	98
10 [e]	$Pd(OAc)_2$	K_2CO_3	1 eq.	110	3	53
11 [f]	$Pd(PPh_3)_4$	K_2CO_3	none	90	5	90

[a] **7** (0.2 mmol), **8a₀** (0.24 mmol), base, $Pd(OAc)_2$ (0.1 mol%), PEG400 (1 g); [b] GC-area normalization; [c] $Pd(OAc)_2$ (0.01 mol%); [d] $Pd(OAc)_2$ (0.005 mol%); [e] $Pd(OAc)_2$ (0.001 mol%); [f] $Pd(PPh_3)_4$ (0.1 mol%) in $EtOH-H_2O$.

With the process established, a variety of coupling reactions of 4-bromo-2-methylindan-1-one with substituted phenylboronic acids were investigated (Table 2, Equation 2).

Table 2. The Suzuki coupling of 4-bromo-2,3-dihydro-2-methyl-1*H*-inden-1-one **7** and arylboronic acids **8**[a]



(2)

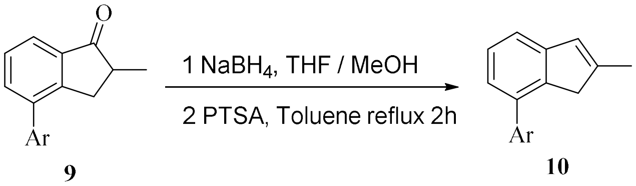
Entry	Boronic acid **8**	R or (Heteroaryl = Ar)	Cat. (mol%)	Time (h)	Product **9**	Isolated yield (%)
1	$\mathbf{8a_{1}}$	R = 2-CH_3	0.005	1	$\mathbf{9a_{1}}$	84
2	$\mathbf{8a_{2}}$	R = 3-CH_3	0.005	1	$\mathbf{9a_{2}}$	90
3	$\mathbf{8a_{3}}$	R = 2-OCH_3	0.005	1	$\mathbf{9a_{3}}$	89
4	$\mathbf{8a_{4}}$	R = 3-OCH_3	0.005	1	$\mathbf{9a_{4}}$	94
5	$\mathbf{8a_{5}}$	R = 4-OCH_3	0.005	1	$\mathbf{9a_{5}}$	91
6	$\mathbf{8a_{6}}$	R = 3,5-di-CH_3	0.005	1	$\mathbf{9a_{6}}$	98
7	$\mathbf{8a_{7}}$	R = 4-$C(CH_3)_3$	0.005	1	$\mathbf{9a_{7}}$	94
8	$\mathbf{8a_{8}}$	R = 4-OCF_3	0.005	1	$\mathbf{9a_{8}}$	90
9	$\mathbf{8a_{9}}$	R = 2-F	0.005	3	$\mathbf{9a_{9}}$	85
10	$\mathbf{8a_{10}}$	R = 3-F	0.005	1	$\mathbf{9a_{10}}$	95
11	$\mathbf{8a_{11}}$	R = 4-F	0.005	1	$\mathbf{9a_{11}}$	97
12	$\mathbf{8a_{12}}$	R = 4-Cl	0.005	0.5	$\mathbf{9a_{12}}$	90
13	$\mathbf{8a_{13}}$	R = 3-CF_3	0.005	1	$\mathbf{9a_{13}}$	87
14	$\mathbf{8a_{14}}$	R = 4-CF_3	0.005	1	$\mathbf{9a_{14}}$	90
15	$\mathbf{8a_{15}}$	R = 3,5-di-CF_3	0.005	1	$\mathbf{9a_{15}}$	98
16	$\mathbf{8a_{16}}$	R = 3-CN	0.005	1	$\mathbf{9a_{16}}$	90
17	$\mathbf{8a_{17}}$	R = 4-CN	0.005	1	$\mathbf{9a_{17}}$	96
18	$\mathbf{8a_{18}}$	R = 4-Ph	0.005	1	$\mathbf{9a_{18}}$	82
19	$\mathbf{8a_{19}}$	R = 2-Cl	0.01	2	$\mathbf{9a_{19}}$	90
20	$\mathbf{8a_{20}}$	R = 3-Cl	0.01	0.5	$\mathbf{9a_{20}}$	87
21	$\mathbf{8a_{21}}$	R = 3-NO_2	0.01	1	$\mathbf{9a_{21}}$	80
22	$\mathbf{8a_{22}}$	R = 2-CF_3	5	1	$\mathbf{9a_{22}}$	79
23	$\mathbf{8a_{23}}$	Ar = 2-naphthyl	1	1	$\mathbf{9a_{23}}$	85
24	$\mathbf{8b_{1}}$	(3-pyridinyl)	1	1	$\mathbf{9b_{1}}$	73
25	$\mathbf{8b_{2}}$	(4-pyridinyl)	1	1	$\mathbf{9b_{2}}$	84
26	$\mathbf{8b_{3}}$	(5-pyrimidinyl)	1	1	$\mathbf{9b_{3}}$	71
27	$\mathbf{8b_{4}}$	(3-quinolinyl)	1	1	$\mathbf{9b_{4}}$	59
28	$\mathbf{8b_{5}}$	(2-thienyl)	5	1	$\mathbf{9b_{5}}$	68
29	$\mathbf{8b_{6}}$	(2-furyl)	0.01	0.5	$\mathbf{9b_{6}}$	90

[a] **7** (0.2 mmol), **8** (0.24 mmol), K_2CO_3 (0.4 mmol), $Pd(OAc)_2$, PEG400 (1 g), 110 °C

To our satisfaction, all the coupling reactions proceeded smoothly with substituted phenylboronic acids containing either electron-withdrawing or -donating groups (CN, CF_3, *t*-Bu, OMe, *et al.*) with 0.005 mol% of catalyst loading in 84-97% isolated yields (Table 2, entries 1-18). For 2-Cl, 3-Cl or 3-NO_2 phenylboronic acid, slightly elevated $Pd(OAc)_2$ loading (0.01 mol%) is necessary for satisfactory coupling yields (80-90%, Table 2, entries 19-21). Generally, the *ortho* substituted phenylboronic acids produced a somewhat inferior result to their *meta* and *para* substituted congeners, thus the reaction of 2-trifluoromethylphenylboronic acid needed as high as 5 mol% of catalyst loading to deliver sufficient catalytic productivity (79% yield). We ascribed this to the stereo-hindrance effect of the substrates (Table 2 Entries 1,3,9,19,22). 2-Naphthaleneboronic acid and heteroaryl boronic acids proved to be good candidates for the current coupling with 1-5 mol% of catalyst precursor (Table 2, entries 23 - 28). The furan ring had much less effect on the reactivity than did N-containing heterocycles; thus with 0.01 mol% of catalyst loading, the reaction was complete within 30 minutes to give the desired product in 90% isolated yield (Table 2, entry 29).

7-Aryl-2-methyl-1*H*-indenes were prepared following a reduction/dehydration procedure (Equation 3) and the results are listed in Table 3.

Table 3. Preparation of 7-aryl-2-methyl-1*H*-indenes **10** from 4-aryl-2-methyl-1-indanones **9** [a,b]



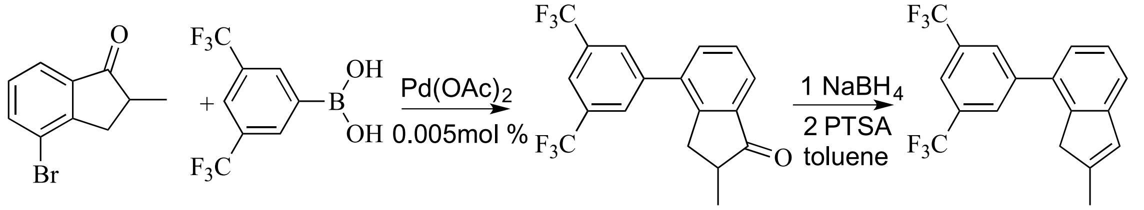
(3)

Entry	Substrate	Product	Yield[c] (%)	Entry	Substrate	Product	Yield[c] (%)
1	$\mathbf{9a}_{1}$	$\mathbf{10a}_{1}$	82	14	$\mathbf{9a}_{14}$	$\mathbf{10a}_{14}$	97
2	$\mathbf{9a}_{2}$	$\mathbf{10a}_{2}$	85	15	$\mathbf{9a}_{15}$	$\mathbf{10a}_{15}$	87
3	$\mathbf{9a}_{3}$	$\mathbf{10a}_{3}$	79	16	$\mathbf{9a}_{16}$	$\mathbf{10a}_{16}$	93
4	$\mathbf{9a}_{4}$	$\mathbf{10a}_{4}$	90	17	$\mathbf{9a}_{17}$	$\mathbf{10a}_{17}$	75
5	$\mathbf{9a}_{5}$	$\mathbf{10a}_{5}$	95	18	$\mathbf{9a}_{18}$	$\mathbf{10a}_{18}$	91
6	$\mathbf{9a}_{6}$	$\mathbf{10a}_{6}$	93	19	$\mathbf{9a}_{20}$	$\mathbf{10a}_{20}$	89
7	$\mathbf{9a}_{7}$	$\mathbf{10a}_{7}$	94	20	$\mathbf{9a}_{23}$	$\mathbf{10a}_{23}$	94
8	$\mathbf{9a}_{8}$	$\mathbf{10a}_{8}$	96	21	$\mathbf{9b}_{1}$	$\mathbf{10b}_{1}$	89
9	$\mathbf{9a}_{9}$	$\mathbf{10a}_{9}$	97	22	$\mathbf{9b}_{2}$	$\mathbf{10b}_{2}$	98
10	$\mathbf{9a}_{10}$	$\mathbf{10a}_{10}$	96	23	$\mathbf{9b}_{3}$	$\mathbf{10b}_{3}$	79
11	$\mathbf{9a}_{11}$	$\mathbf{10a}_{11}$	90	24	$\mathbf{9b}_{4}$	$\mathbf{10b}_{4}$	53
12	$\mathbf{9a}_{12}$	$\mathbf{10a}_{12}$	77	25	$\mathbf{9b}_{5}$	$\mathbf{10b}_{5}$	77
13	$\mathbf{9a}_{13}$	$\mathbf{10a}_{13}$	90	26	$\mathbf{9b}_{6}$	$\mathbf{10b}_{6}$	63

[a] Reduction: **9** (1.0 mmol), $NaBH_4$ (3.0 mmol), THF/MeOH (15 mL 2:1), 0 ºC~r.t, 4 h. [b] Dehydration: PTSA (100 mg), toluene (50 mL), reflux, 2 h. [c] Isolated yield.

Most of the reactions proceeded smoothly and produced the desired indene products in excellent yields. It is should be noted that higher concentrations in the dehydration step may promote undesirable side reactions, especially for some electron-rich substrates.

Considering the solubility differences of PEG400, $Pd(OAc)_2$, TBAB, arylboronic acids, substituted indanones and related indenes, developing a fast and highly efficient 7-aryl-2-alkyl-1*H*-indene synthetic procedure with simple purification operations is highly desirable. To this end, 3,5-bis(trifluoromethyl)phenylboronic acid was chosen as the model substrate for a multi-gram scale (4.5 g, 20 mmol) synthesis following the current procedure. According to previous results, the couplings were fast, clean and previously observed side reactions, such as debromination and/or de-boronation were, to our surprise, not observed; thus the aryl boronic acid was used in slight excess (1.05 eq.). As expected, the reaction proceeded smoothly at higher concentration and was accomplished with only 0.005 mol% of catalyst loading. After normal extraction and evaporation, complete removal of residual PEG400, $Pd(OAc)_2$, TBAB and aryl boronic acid was achieved by washing with cold methanol. After the reduction and dehydration protocol, the crude product was washed again with methanol to give 86% of pure indene derivative **$10a_{15}$** as a white crystalline material (Scheme 4).



7 **$8a_{15}$** **$9a_{15}$** **$10a_{15}$**

4.5 g (20 mmol) 5.4 g (21 mmol) 5.9 g (17 mmol) 86 %

Scheme 4 Multi-gram scale synthesis of **$10a_{15}$** from **$8a_{15}$**.

Conclusions

A ligand-free Suzuki coupling system consisting of PEG-400/$Pd(OAc)_2$/TBAB/K_2CO_3 in optimized ratio was employed for the Suzuki-Miyaura coupling reaction of 4-bromo-2,3-dihydro-2-methyl-1*H*-inden-1-one (**7**) with aryl and/or heteroarylboronic acids. Most of the substituted phenylboronic acids reacted smoothly with 0.005 mol% of catalyst loading, and all the reactions were accomplished within a period of 0.5–3 hours in excellent yields (82–98%). Some of the heteroarylboronic acids also reacted in good to excellent yield (59–90%) with controlled low catalyst loading (0.01–5 mol%). The intermediate indanones could be easily transformed into their indene derivatives in high purity and high productivity. Multi-gram scale reaction of **$8a_{15}$** was conducted following our typical Suzuki-Miyaura coupling, reducing and dehydrating procedures without fractional distillation or column chromatographic purification. Pure substituted indene **$10a_{15}$** was obtained in high yield. Coupling of more complex substituted indanones with arylboronic acids following the current procedure is in progress and the catalytic properties of newly prepared novel C1 and C2 symmetric metallocenes are under evaluation.

Experimental Section

General. Melting points were measured on a Novel X-5 melting point instrument. All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 Hz) spectra were measured in $CDCl_3$ and recorded on Bruker Avance II 400 (^{1}H NMR) spectrometer with chemical shifts reported as ppm (with TMS as an internal standard). Purification of the reaction products was carried out by flash chromatography (FC) on silica gel (200-300 mesh). HRMS were conducted on GCT mass spectrometer (EI). All reactions were carried out in air and using distilled solvents, without any precautions to exclude moisture unless otherwise noted. Commercial grade reagents and solvents were used without further purification; otherwise, where necessary, they were purified as recommended.

4-Bromo-2,3-dihydro-2-methyl-1*H*-inden-1-one 7 was prepared from 2-bromobenzyl bromide following a reported[22] procedure in 85% yield. Mp 40-42 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.74 (1H, d, $^3J_{HH}$ 7.8 Hz, ArH), 7.69 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.27 (1H, t, $^3J_{HH}$ 7.7 Hz, ArH), 3.31-3.38 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.6 Hz, CH_2CH), 2.71-2.81 (H, m, CH_2CH), 2.67 (1H, dd, $^3J_{HH}$ 4.0 Hz, $^2J_{HH}$ 17.6 Hz, CH_2CH), 1.32 (3H, d, $^3J_{HH}$ 7.4 Hz, $CHCH_3$).

General procedure for the Suzuki coupling reaction

Into a 10 mL vial, was filled with a mixture of 4-bromo-2,3-dihydro-2-methyl-1*H*-inden-1-one **7** (44.8 mg, 0.20 mmol, $PhB(OH)_2$ **8a₀** (26.8 mg, 0.22 mmol, 1.2 eq.), $Pd(OAc)_2$ (chloroform solution, 0.005 mol%), TBAB (75.7 mg, 0.20 mmol, 1.0 eq.), K_2CO_3 (55.3 mg, 0.40 mmol, 2.0 equiv) and PEG400 1.0 g. The vial was capped and the mixture was stirred at 110 °C till completion (TLC). 5 mL of water was added and the contents were extracted with EtOAc (10 mL × 3), the combined organic phases were washed with brine (10 mL × 3), dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography to obtain the desired product **9a₀** in 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.78 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.61 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.45-7.50 (5H, m, ArH), 7.40-7.43 (1H, m, ArH), 3.40-3.46 (1H, dd, $^3J_{HH}$ 7.6 Hz, ^2JHH 17.6 Hz, CH_2CH), 2.61-2.81 (2H, m, CH_2CH), 1.32 (3H, d, $^3J_{HH}$ 7.3 Hz, $CHCH_3$).

2-Methyl-4-(*o*-tolyl)-2,3-dihydro-1*H*-inden-1-one (9*a*₁). Yield: 84%, 198 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.75 (1H, m, ArH), 7.41-7.43 (2H, m, ArH), 7.28-7.30 (2H, m, ArH), 7.22-7.27 (1H, m, ArH), 7.14 (1H, d, $^3J_{HH}$ 7.1 Hz, ArH), 3.07 (1H, br, CH_2CH), 2.64-2.69 (1H, m, CH_2CH), 2.44 (1H, br, CH_2CH), 2.11 (3H, s, $ArCH_3$), 1.25 (3H, d, $^3J_{HH}$ 7.4 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.4, 151.7, 140.2, 138.5, 136.4, 135.4, 134.9, 130.2, 128.9, 127.8, 127.4, 125.7, 122.7, 41.9, 34.2, 19.2, 19.8, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1200.

2-Methyl-4-(*m*-tolyl)-2,3-dihydro-1*H*-inden-1-one (9a_2). Yield: 90%, 212 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.81 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.61-7.65 (1H, m, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.41 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.32 (1H, s, ArH), 7.28 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 3.44-3.51 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.60-2.82 (2H, m, CH_2CH), 2.49 (3H, s, $ArCH_3$), 1.36 (3H, d, $^3J_{HH}$ 7.4 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.4, 150.8, 140.3, 139.1, 138.2, 136.7, 134.7, 129.1, 128.4, 128.3, 127.9, 125.5, 122.8, 42.1, 34.8, 21.4, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1192

4-(2-Methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9a_3). Yield, 89%, 224 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.77 (1H, d, $^3J_{HH}$ 8.5 Hz, ArH), 7.53 (1H, dd, $^3J_{HH}$ 1.2 Hz, $^4J_{HH}$ 7.4 Hz, ArH), 7.44 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.37-7.42 (1H, m, ArH), 7.22 (1H, dd, ^4JHH 1.7 Hz, $^3J_{HH}$ 7.4 Hz, ArH), 7.06 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.02 (1H, d, $^3J_{HH}$ 8.3 Hz, ArH), 3.80 (3H, s, OCH_3), 3.19-3.26 (1H, dd, $^3J_{HH}$ 8.0 Hz, ^2JHH 17.2 Hz, CH_2CH), 2.67-2.71(1H, m, CH_2CH), 2.58 (1H, dd, $^3J_{HH}$ 4.0Hz, $^2J_{HH}$ 17.3, CH_2CH), 1.28 (3H, d, $^3J_{HH}$ 7.4 Hz, $CHCH_3$). ^{13}C NMR($CDCl_3$, 100 MHz) δ_C: 209.8, 156.4, 152.8, 137.5, 136.2, 135.8, 130.8, 129.4, 128.0, 127.4, 122.8, 120.6, 110.9, 55.4, 42.0, 34.4, 16.2. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1145.

4-(3-Methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9a_4). Yield 94%, 237 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δH: 7.77 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.60 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.46 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.39 (1H, t, $^3J_{HH}$ 7.9 Hz, ArH), 7.03 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.98 (1H, s, ArH), 6.95 (1H, dd, $^4J_{HH}$ 2.4 Hz, $^3J_{HH}$ 8.2 Hz, ArH), 3.86 (3H, s, OCH_3), 3.40-3.46 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.60-2.80 (2H, m, CH_2CH), 1.31 (3H, d, $^3J_{HH}$ 7.3 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.5, 159.6, 150.8, 140.5, 140.0, 136.8, 134.7, 129.6, 127.9, 123.0, 120.9, 114.4, 112.8, 55.3, 42.1, 34.8, 16.1. EI-HRMS (*m/z*): $[M+H]^+$ $C_{17}H_{16}O_2$, calculated 252.1150, found 252.1146

4-(4-Methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9a_5). Yeld, 91%, 229 mg, white solid Mp 85 - 87 °C. ^{1}H NMR ($CDCl_3$, 400MHz) δ_H: 7.73 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.55-7.57 (1H, m, ArH), 7.43 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.37-7.41 (2H, m, ArH), 6.98-7.02 (2H, m, ArH), 3.86 (3H, s, OCH_3), 3.38-3.44 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.63-2.78 (2H, m, CH_2CH), 1.30 (3H, d, $^3J_{HH}$ 7.3 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 158.6, 146.3, 146.1, 140.6, 136.9, 133.7, 129.4, 127.1, 126.9, 124.1, 118.5, 113.7, 55.1, 42.7, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1159

4-(3,5-Dimethylphenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9a_6). Yield 98%, 245 mg, pale yellow solid, Mp 104 – 106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.75 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.57-7.59 (1H, m, ArH), 7.44 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.07 (1H, s, ArH), 7.05 (1H, s, ArH), 3.40-3.46 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.65-2.80 (2H, m, CH_2CH), 2.40 (6H, s, $ArCH_3$), 1.31 (3H, d, $^3J_{HH}$ 7.3 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.5, 150.9, 140.6, 139.1, 138.1, 135.7, 134.7, 129.2, 127.8, 125.3, 122.7, 42.1, 34.9, 21.3, 16.1. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}O_2$ (M^+) 250.1358, found 250.1354.

4-(4-(tert-Butyl)phenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9a_7). Yield: 94%, 261 mg, white solid, Mp 102 – 104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.76 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.60 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 7.36-7.54 (5H, m, ArH), 3.43-3.49 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.80 (1H, dd, $^3J_{HH}$ 4.0 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.66-2.76 (H, m, CH$_2$CH), 1.38 (9H, s, C(CH$_3$)$_3$), 1.31 (3H, d, $^3J_{HH}$ 7.4 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ$_C$: 209.5, 150.9, 150.8, 140.1, 136.8, 136.2, 134.7, 128.1, 127.9, 125.5, 122.7, 42.2, 34.9, 34.6, 31.3, 16.1. EI-HRMS (*m/z*) calcd for $C_{20}H_{22}O$ (M$^+$) 278.1671, found 278.1661

2-Methyl-4-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1*H*-inden-1-one (9*a*$_8$). Yield, 90%, 275 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ$_H$: 7.79 (1H, d, $^3J_{HH}$ 8.5 Hz, ArH), 7.58 (1H, dd, $^4J_{HH}$ 1.2 Hz, $^3J_{HH}$ 7.5 Hz, ArH), 7.46-7.50 (3H, m, ArH), 7.33 (2H, d, $^3J_{HH}$ 8.7 Hz, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.6 Hz, CH$_2$CH), 2.70-2.78 (2H, m, CH$_2$CH), 1.32 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ$_C$: 209.1, 150.7, 148.8, 138.8, 137.8, 137.0, 134.7, 129.9, 128.1, 123.4, 121.1, 120.5 (q, $^1JFC = 255.9$ Hz) 42.2, 34.8, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}F_3O_2$ (M$^+$) 306.0868, found 306.0872

4-(2-Fluorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_9$). Yield: 85%, 204 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ$_H$: 7.80 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.56 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.44-7.48 (1H, m, ArH), 7.37-7.43 (1H, m, ArH), 7.31-7.35 (1H, m, ArH), 7.10-7.30 (2H, m, ArH), 3.25-3.31 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.60-2.80 (2H, m, CH$_2$CH), 1.29 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ$_C$: 209.3, 169.5 (d, ^1JFC 245.5 Hz), 152.3, 136.7, 135.7, 134.6, 131.2 (d, ^4JFC 3.6 Hz), 129.9 (d, ^3JFC 8.0 Hz), 127.7, 126.6 (d, ^2JFC 16.0 Hz), 124.3 (d, ^4JFC 3.7 Hz), 123.6, 115.9 (d, ^2JFC 22.2 Hz), 42.0, 34.2, 16.1. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}FO$ (M$^+$) 240.0950, found 240.0943

4-(3-Fluorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{10}$). Yield 95%, 228 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ$_H$: 7.78 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.58 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.40-7.48 (2H, m, ArH), 7.23 (1H, d, $^3J_{HH}$ 7.7 Hz, ArH), 7.13-7.17 (1H, m, ArH), 7.06-7.11 (1H, m, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 16.8 Hz, CH$_2$CH), 2.65-2.80 (2H, m, CH$_2$CH), 1.31 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ$_C$: 209.1, 162.8 (d, ^1JFC 245.1 Hz), 150.7, 141.3 (d, ^3JFC 7.6 Hz), 139.0, 137.0, 134.7, 130.2 (d, ^3JFC 8.4 Hz), 128.1, 124.3 (d, ^4JFC 2.9 Hz), 123.5, 115.5 (d, ^2JFC 21.6 Hz), 114.6 (d, 2*J*FC 20.9 Hz), 42.1, 34.8, 16.1. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}FO$ (M$^+$) 240.0950, found 240.0946

4-(4-Fluorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{11}$). Yield 97%, 232 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ$_H$: 7.76 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.56 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.40-7.46(3H, m, ArH), 7.15 (2H, t, $^3J_{HH}$ 8.7 Hz, ArH), 3.35-3.41 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 16.8 Hz, CH$_2$CH), 2.68-2.76 (2H, m, CH$_2$CH), 1.31 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ$_C$: 209.2, 162.4 (d, ^1JFC 245.6 Hz), 150.8, 139.2, 136.9, 135.2 (d, ^4JFC 3.4 Hz), 134.7, 130.1 (d, ^3JFC 8.1 Hz), 130.0, 128.0, 123.1, 115.6 (d, ^2JFC 21.3 Hz), 42.1, 34.8, 16.1. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}FO$ (M$^+$) 240.0950, found 240.0953

4-(4-Chlorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{12}$). Yield 90%, 230 mg, white solid, Mp 83 - 85 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ$_H$: 7.78 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.57 (1H, dd, $^4J_{HH}$ 1.1 Hz, $^3J_{HH}$ 7.4 Hz, ArH), 7.43-7.49 (3H, m, ArH), 7.37-7.40 (2H, m, ArH), 3.35-3.42 (1H, dd, $^3J_{HH}$ 8.4 Hz, $^2J_{HH}$ 17.6 Hz, CH$_2$CH), 2.69-2.77 (2H, m, CH$_2$CH), 1.31 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}CNMR (CDCl$_3$, 100 MHz) δ$_C$: 209.2, 150.7, 139.0, 137.6, 137.0, 134.6, 133.8, 129.8, 128.8, 128.1, 123.3, 42.2, 34.8, 16.1. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}ClO$ (M^+) 256.0655, found 256.0652.

2-Methyl-4-(3-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (9*a*$_{13}$). Yield 87%, 252 mg, white solid, Mp 114 -116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.82 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.72 (1H, s, ArH), 7.66 (2H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.59-7.62 (2H, m, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 3.37-3.44 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.4 Hz, CH_2CH), 2.70-2.81 (2H, m, CH_2CH), 1.32 (3H, d, $^3J_{HH}$ 7.2 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.2, 150.7, 139.9, 138.7, 137.0, 134.8, 131.8, 129.1, 128.2, 125.3 (q, ^4JFC = 3.7 Hz), 124.5 (q, ^4JFC = 3.9 Hz), 123.7, 42.2, 34.6, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}F_3O$ (M^+) 290.0918, found 290.0928

2-Methyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (6*a*$_{14}$). Yield 90%, 261 mg, white solid, Mp 93 - 95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.82 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.74 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.57-7.61 (3H, m, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 18.0 Hz, CH_2CH), 2.71-2.79 (2H, m, CH_2CH), 1.32 (3H, d, $^3J_{HH}$ 7.2 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 209.0, 150.7, 142.8, 138.8, 137.1, 134.7, 129.9 (q, ^2JFC 32.5 Hz), 128.9, 128.2, 125.6 (q, ^4JFC 3.6 Hz), 124.1 (q, ^1JFC 270.4 Hz), 123.8, 42.2, 34.7, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_3F_3O$ (M^+) 290.0918, found 290.0924

4-(3,5-bis(trifluoromethyl)phenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (**9*a*$_{15}$**). Yield 98%, 255 mg, white solid, Mp 115 - 117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.92 (3H, s, ArH), 7.86 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.63 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.54 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.71-2.79 (2H, m, CH_2CH), 1.33 (3H, d, $^3J_{HH}$ 7.6 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 208.5, 150.5, 141.3, 137.4, 137.2, 134.7, 132.2 (q ^2JFC 33.2 Hz), 128.6 (m), 128.5, 123.3 (q ^1JFC 271.0 Hz), 124.5, 121.5 (m), 42.2, 34.5, 16.1. EI-HRMS (*m/z*) calcd for $C_{18}H_{12}F_6O$ (M^+) 358.0792, found 358.0796

-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-4-yl)benzonitrile (9*a*$_{16}$). Yield 90%, 222 mg, white solid, Mp 160 - 162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.81 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.64-7.75 (5H, m, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.2 Hz, ArH), 3.34-3.41 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.0 Hz, CH_2CH), 2.72-2.77 (2H, m, CH_2CH), 1.31 (3H, d, $^3J_{HH}$ 7.2 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 208.8, 150.5, 140.5, 137.8, 137.2, 134.6, 132.9, 131.9, 131.2, 129.6, 128.3, 124.0, 118.5, 113.0, 42.2, 34.6, 16.1. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}NO$ (M^+) 247.0997, found 247.0996.

4-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-4-yl)benzonitrile (9*a*$_{17}$). Yield 96%, 237 mg, white solid, mp 112 - 114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.81 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.77 (2H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.57-7.60 (3H, m, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.2 Hz, ArH), 3.35-3.42 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.0 Hz, CH_2CH), 2.68-2.77 (2H, m, CH_2CH), 1.31 (3H, d, $^3J_{HH}$ 7.2 Hz, $CHCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 208.7, 150.4, 143.8, 138.2, 137.1, 134.5, 132.4, 129.2, 128.2, 124.0, 118.5, 111.5, 42.1, 34.6, 16.9. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}NO$ (M^+) 247.0997, found 247.0995.

4-([1,1'-Biphenyl]-4-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{18}$). Yield 82%, 244 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.81 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.71-7.74 (2H, m, ArH), 7.65-7.69 (3H, m, ArH), 7.55-7.57 (2H, m, ArH), 7.47-7.51 (3H, m, ArH), 7.37-7.42 (1H, m, ArH), 3.46-3.52 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.2 Hz, CH_2CH), 2.84 (1H, dd, $^3J_{HH}$ 4.1 Hz, $^2J_{HH}$

17.2 Hz, CH$_2$CH), 2.73-2.76 (2H, m, CH$_2$CH), 1.34 (3H, d, $^3J_{HH}$ 7.6 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.3, 150.8, 140.4, 140.4, 139.7, 138.0, 136.9, 134.7, 128.9, 128.8, 128.0, 127.5, 127.2, 127.0, 123.0, 42.1, 34.9, 16.1. EI-HRMS (*m/z*) calcd for C$_{22}$H$_{18}$O (M$^+$) 298.1358, found 298.1369

4-(2-Chlorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{19}$). Yield 90%, 230 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.75-7.82 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.44-7.58 (3H, m, ArH), 7.33-7.38 (2H, m, ArH), 7.26-7.30 (1H, m, ArH), 3.18-3.43 (H, br, CH$_2$CH), 2.65-2.80 (H, m, CH$_2$CH), 2.45-2.650 (H, br, CH$_2$CH), 1.28 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.3, 152.1, 137.9, 135.4, 133.2, 130.8, 129.8, 129.3, 127.5, 126.8, 123.5, 42.0, 34.1, 16.2. EI-HRMS (*m/z*) calcd for C$_{16}$H$_{13}$ClO (M$^+$) 256.0655, found 256.0652

4-(3-Chlorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*a*$_{20}$). Yield 87%, 222 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.79 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.57 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 7.32-7.49 (5H, m, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.0 Hz, CH$_2$CH), 2.68-2.78 (2H, m, CH$_2$CH), 1.31 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.1, 150.7, 140.9, 138.8, 137.0, 134.7, 134.5, 129.876, 128.6, 128.1, 127.8, 126.7, 123.5, 42.2, 34.7, 16.1 . EI-HRMS (*m/z*) calcd for C$_{16}$H$_{13}$ClO (M$^+$) 256.0655, found 256.0652

2-Methyl-4-(3-nitrophenyl)-2,3-dihydro-1*H*-inden-1-one (9*a*$_{21}$). Yield 80%, 213 mg, white solid, mp 111 - 113 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 8.35 (1H, t, $^3J_{HH}$ 2.0 Hz, ArH), 8.26-8.29 (1H, m, ArH), 7.85 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.80 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.61-7.74 (2H, m, ArH), 7.53 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 3.38-3.45 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.0 Hz, CH$_2$CH), 2.74-2.80 (2H, m, CH$_2$CH), 1.33 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR(CDCl$_3$, 100 MHz) δ_C: 208.7, 150.6, 140.8, 137.7, 137.3, 134.7, 134.5, 129.7, 128.4, 124.2, 123.4, 122.6, 42.2, 34.6, 16.1. EI-HRMS (*m/z*) calcd for C$_{16}$H$_{13}$NO$_3$ (M$^+$) 267.0895, found 267.0889.

2-Methyl-4-(2-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (9*a*$_{22}$ contains stereo isomers (1 : 1)). Yield 79%, 229 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.76-7.85 (2H, ArH), 7.58-7.65 (1H, ArH), 7.52-7.58 (1H, ArH), 7.41-7.48 (2H, m, ArH), 7.27-7.30 (1H, ArH), 3.97-3.11 (H, m, CH$_2$CH), 2.66-2.70 (H, m, CH$_2$CH), 2.33-2.64 (H, m, CH$_2$CH), 1.26 (3H, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.2, 151.9, 137.8, 137.7, 136.1, 135.0, 131.6, 131.2, 128.8 (m), 128.1, 127.0, 126.3 (m), 123.9 (q, ^1JFC = 270.8 Hz), 123.6, 42.0, 34.0, 16.1. EI-HRMS (*m/z*) calcd for C$_{17}$H$_{13}$F$_3$O (M$^+$) 290.0917, found 290.0918

2-Methyl-4-(naphthalen-2-yl)-2,3-dihydro-1*H*-inden-1-one (9*a*$_{23}$). Yield 85%, 231 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.95 (1H, d, $^3J_{HH}$ 8.5 Hz, ArH), 7.89-7.91 (3H, m, ArH), 7.82 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.69-7.71 (1H, m, ArH), 7.58-7.60 (1H, m, ArH), 7.49-7.56 (3H, m, ArH), 3.43-3.49 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.82 (1H, dd, $^3J_{HH}$ 4.1 Hz, $^2J_{HH}$ 17.3 Hz, CH$_2$CH), 2.71-2.75 (1H, m, CH$_2$CH), 1.33 (3H, d, $^3J_{HH}$ 7.6 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.4, 151.0, 140.1, 136.9, 136.6, 134.9, 133.3, 132.5, 128.2, 128.0, 128.0, 127.7, 127.4, 126.5, 126.4, 126.3, 123.0, 42.2, 34.9, 16.1. EI-HRMS (*m/z*) calcd for C$_{20}$H$_{16}$O (M$^+$) 272.1201, found 272.1200.

2-Methyl-4-(pyridin-3-yl)-2,3-dihydro-1*H*-inden-1-one (9*b*$_1$). Yield 73%, 162 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 8.73 (1H, s, ArH), 8.64 (1H, d, $^3J_{HH}$ 4.4 Hz, ArH), 7.77-7.82 (2H, m, ArH), 7.59 (1H, d, $^3J_{HH}$ 7.3 Hz, ArH), 7.50 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.41 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 4.8 Hz, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.69-2.82 (2H, m, CH$_2$CH), 1.31 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 208.8, 150.9, 149.1, 148.7, 137.1, 136.5, 135.7, 134.8, 134.7, 128.2, 123.7, 123.4, 42.1, 34.6, 16.0. EI-HRMS (*m/z*) calcd for $C_{15}H_{13}NO$ (M$^+$) 223.0997, found 223.0996.

2-Methyl-4-(pyridin-4-yl)-2,3-dihydro-1*H*-inden-1-one (9*b*$_2$). Yield 84%, 187 mg, white solid, mp 130-132 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 8.68 (1H, d, $^3J_{HH}$ 5.6 Hz, ArH), 7.80 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.60 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.48 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.37 (2H, d, $^3J_{HH}$ 6.0 Hz, ArH), 3.37-3.43 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.68-2.79 (2H, m, CH$_2$CH), 1.29 (3H, d, $^3J_{HH}$ 7.3 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 208.4, 150.3, 149.8, 146.7, 137.1, 137.0, 134.2, 128.1, 124.1, 123.1, 41.9, 34.5, 15.8. EI-HRMS (*m/z*) calcd for $C_{15}H_{13}NO$ (M$^+$) 223.0997, found 223.0993.

2-Methyl-4-(pyrimidin-5-yl)-2,3-dihydro-1*H*-inden-1-one (9*b*$_3$). Yield 71%, 159 mg, light yellow solid, Mp 187 - 189 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 9.27 (1H, s, ArH), 8.88 (2H, s, ArH), 7.88 (1H, d, $^3J_{HH}$ 7.4 Hz, ArH), 7.62 (1H, d, $^3J_{HH}$ 6.8 Hz, ArH), 7.55 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 3.39-3.46 (1H, dd, $^3J_{HH}$ 8.8 Hz, $^2J_{HH}$ 18.0 Hz, CH$_2$CH), 2.76-2.81 (2H, m, CH$_2$CH), 1.34 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100MHz) δ_C: 208.3, 157.8, 155.9, 150.8, 137.4, 134.6, 132.91, 132.8, 128.6, 124.66, 42.1, 34.5, 16.0. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}N_2O$ (M$^+$) 224.0950, found 224.0948.

2-Methyl-4-(quinolin-3-yl)-2,3-dihydro-*1H*-indan-1-one (9*b*$_4$). Yield 59%, 161 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 9.05 (1H, d, $^3J_{HH}$ 1.8 Hz, ArH), 8.24 (1H, s, ArH), 8.18 (1H, d, $^3J_{HH}$ 8.5 Hz, ArH), 7.90 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.87 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.78 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.72 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.63 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.56 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 3.44-3.50 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^2J_{HH}$ 16.8 Hz, CH$_2$CH), 2.70-2.90 (2H, m, CH$_2$CH), 1.33 (3H, d, $^3J_{HH}$ 7.2 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 208.9, 151.2, 150.2, 147.1, 137.2, 136.6, 135.2, 135.1, 132.1, 130.0, 129.1, 128.4, 127.9, 127.7, 127.3, 123.9, 42.2, 34.7, 16.1. EI-HRMS (*m/z*) calcd for (M$^+$) $C_{17}H_{13}NO$ 273.1155, found 273.1154

2-Methyl-4-(thien-2-yl)-2,3-dihydro-1*H*-inden-1-one (9*b*$_5$). Yield 68%, 155 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.76 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.68 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.36-7.40 (2H, m, ArH), 7.29 (1H, d, $^3J_{HH}$ 3.3 Hz, ArH), 7.11-7.13 (1H, m, ArH), 3.51-3.58 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.85 (1H, dd, $^3J_{HH}$ 3.9 Hz, $^2J_{HH}$ 17.2 Hz, CH$_2$CH), 2.69-2.74 (1H, m, CH$_2$CH), 1.32 (3H, d, $^3J_{HH}$ 7.4 Hz, CHCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 209.0, 149.7, 140.8, 137.1, 133.4, 132.6, 127.9, 127.6, 125.7, 125.6, 122.8, 41.8, 35.6, 16.1. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}OS$ (M$^+$) 228.0609, found 228.0609

4-(Furan-2-yl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (9*b*$_6$). Yield 90%, 190 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.93 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.64 (1H, d, $^3J_{HH}$ 7.5 Hz, ArH), 7.52 (1H, d, $^3J_{HH}$ 1.5 Hz, ArH), 7.38 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 6.64 (1H, d, $^3J_{HH}$ 3.4 Hz, ArH), 6.50-6.52 (1H, m, ArH), 3.50-3.56 (1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HH}$ 17.6 Hz, CH$_2$C), 2.87 (1H, dd, $^3J_{HH}$

3.6 Hz, ${}^2J_{HH}$ 17.6 Hz, CH_2C), 2.69-2.74 (1H, m, CH_2CH), 1.32 (3H, d, ${}^3J_{HH}$ 7.8 Hz, $CHCH_3$). ${}^{13}C$ NMR ($CDCl_3$, 100 MHz) δ_C: 209.1, 151.7, 148.4, 142.3, 137.0, 130.2, 128.7, 127.7, 122.5, 111.7, 108.3, 41.6, 35.8, 16.2. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}O_2$ (M^+) 212.0837, found 212.0831

Typical procedure for 7-aryl-2-methyl-1*H*-indene synthesis

To a solution of 2,3-dihydro-2-methyl-4-phenyl-1*H*-inden-1-one **9a₀** (222.3 mg, 1.0 mmol) in 15 mL of THF/MeOH (2:1), was added 114 mg (3.0 mmol, 3.0 eq.) of $NaBH_4$ in portions at 0 °C. The reaction mixture was warmed slowly to rt and stirred till completion (TLC). The solvent was evaporated and 10 mL of water was added. The mixture was extracted with EtOAc (10 mL X 2). The combined organic extracts were dried and evaporated. The residue was taken up in 50 mL of toluene and mixed with 100 mg of TsOH monohydrate. The formed mixture was refluxed with Dean-Stark head for 2 h. 30 mL of ethyl acetate was added and the resulting solution was washed with Na_2CO_3 (10%). The organic layer was separated and the aqueous layer was extracted with EtOAc (30 mL × 2). The combined organic extracts were dried and then filtered through a short pad of silica gel. The solvent was evaporated to give pure 2-methyl-7-phenyl-1*H*-indene **10a₀**. yield: 73 %, 151 mg, colorless oil. 1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.53 (2H, d, ${}^3J_{HH}$ 7.1 Hz, ArH), 7.44 (2H, t, ${}^3J_{HH}$ 7.5 Hz, ArH), 7.35 (H, t, ${}^3J_{HH}$ 7.4 Hz, ArH), 7.30 (H, d, ${}^3J_{HH}$ 7.4 Hz, ArH), 7.25 (H, d, ${}^3J_{HH}$ 5.8 Hz, ArH), 7.13 (1 H, t, ${}^3J_{HH}$ 7.5 Hz, ArH), 6.54 (1H, s, ArCH), 3.38 (2H, s, $ArCH_2$), 2.14 (3H, s, CCH_3).

2-Methyl-7-(o-tolyl)-1*H*-indene (10*a*₁). Yield 82%, 180 mg, colorless oil. ${}^1H$ NMR ($CDCl_3$, 400 MHz) δ_H: 7.15-7.30 (6H, m, ArH), 7.03 (1H, dd, ${}^3J_{HH}$ 6.7 Hz, ${}^4J_{HH}$ 1.8 Hz, ArH), 6.62 (1H, q, ${}^4J_{HH}$ 1.6 Hz, ArCH), 3.13 (2H, s, $ArCH_2$), 2.22 (3H, s, $ArCH_3$), 2.17 (3H, s, CCH_3).

2-Methyl-7-(m-tolyl)-1*H*-indene (10*a*₂). Yield 85%, 187 mg, colorless oil. ${}^1H$NMR ($CDCl_3$, 400 MHz) δ_H: 7.20-7.60 (7H, m, ArH), 6.67 (1H, s, ArCH), 3.51 (2H, s, $ArCH_2$), 2.55 (3H, s, $ArCH_3$), 2.27 (3H, s, CCH_3). ${}^{13}C$ NMR ($CDCl_3$, 100 MHz) δ_C: 146.4, 146.2, 141.30, 140.7, 137.8, 137.4, 129.2, 128.2, 127.7, 127.2, 126.9, 125.5, 124.2, 118.8, 42.7, 21.5, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}$ (M^+) 220.1252, found 220.1260

7-(2-Methoxyphenyl)-2-methyl-1*H*-indene (10*a*₃). Yield 79%, 186 mg, white solid, Mp 102 - 104 °C. ${}^1H$ NMR ($CDCl_3$, 400 MHz) δ_H: 7.20-7.40 (4H, m, ArH), 6.95-7.08 (3H, m, ArH), 6.50 (1H, q, ${}^4J_{HH}$ 1.6 Hz, ArCH), 3.75 (3H, s, OCH_3), 3.18 (2H, s, $ArCH_2$), 2.10 (3H, s, CCH_3).

7-(3-Methoxyphenyl)-2-methyl-*1H*-indene (10*a*₄). Yield 90%, 212 mg, white solid, Mp 82 - 84 °C. ${}^1H$ NMR ($CDCl_3$, 400 MHz) δ_H: 7.20-7.38 (3H, m, ArH), 7.02-7.15 (3H, m, ArH), 6.88 (1H, dd, ${}^3J_{HH}$ 8.4 Hz, ${}^4JHH$ 2.0 Hz, ArH), 6.60 (1H, q, ${}^4J_{HH}$ 1.2 Hz, ArCH), 3.91 (3H, s, OCH_3), 3.45 (2H, s, $ArCH_2$), 2.20 (3H, s, CCH_3). ${}^{13}C$ NMR ($CDCl_3$, 100 MHz) δ_C: 159.5, 146.4, 146.3, 142.8, 140.7, 137.2, 129.3, 127.1, 126.9, 124.1, 120.9, 118.9, 114.2, 112.4, 55.2, 42.7, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1210.

7-(4-Methoxyphenyl)-2-methyl-1*H*-indene (10*a*₅). Yield 95%, 224 mg, white solid, Mp 85 - 87 °C. ${}^1H$ NMR ($CDCl_3$, 400 MHz) δ_H: 7.43-7.46 (2H, m, ArH), 7.27-7.31 (1H, m, ArH), 7.20-7.22 (1H, m, ArH), 7.09-7.12 (1H, m, ArH), 7.94-7.97 (2H, m, ArH), 6.51 (1H, s, ArCH), 3.81 (3H, s, OCH_3), 3.34 (2H, s, $ArCH_2$), 2.11 (3H, s, CCH_3). ${}^{13}C$ NMR ($CDCl_3$, 100 MHz) δ_C: 158.6, 146.3, 146.1, 140.6, 136.9, 133.7, 129.4, 127.1, 126.9, 124.1, 118.5, 113.7, 55.1, 42.7, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1204.

7-(3,5-Dimethylphenyl)-2-methyl-1*H*-indene (10*a*$_6$). Yield 93%, 217 mg, white solid, Mp 57 - 59 °C. ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H: 7.25-7.50 (5H, m, ArH), 7.16 (1H, s, ArH), 6.69 (1H, s, ArCH), 3.54 (2H, s, $ArCH_2$), 2.55 (6H, s, $ArCH_3$), 2.29 (3H, s, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 146.3, 146.1, 141.3, 140.7, 137.7, 137.5, 128.6, 127.2, 126.8, 126.3, 124.2, 118.7, 42.7, 21.4, 16.6. EI-HRMS (*m/z*) calcd for $C_{18}H_{18}$ (M^+) 234.1409, found 234.1415

7-(4-(tert-Butyl)phenyl)-2-methyl-1*H*-indene (10*a*$_7$). Yield 94%, 246 mg, white solid, Mp 66 - 68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.51-7.54 (4H, m, ArH), 7.15-7.40 (3H, m, ArH), 6.60 (1H, s, ArCH), 3.47 (2H, s, $ArCH_2$), 2.20 (3H, s, CCH_3), 1.45 (9H, s, *t*Bu). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 149.9, 146.5, 146.3, 140.9, 138.4, 137.3, 128.2, 127.2, 127.0, 125.4, 124.3, 118.8, 42.9, 34.6, 31.5, 16.8. EI-HRMS (*m/z*) calcd for $C_{20}H_{22}$ (M^+) 262.1722, found 262.1713

2-Methyl-7-(4-(trifluoromethoxy)phenyl)-1*H*-indene (10*a*$_8$). Yield 96%, 278 mg, colorless oil. ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H: 7.59-7.63 (2H, m, ArH), 7.18-7.30 (4H, m, ArH), 7.03 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 6.65-6.66 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.43 (2H, s, $ArCH_2$), 2.25 (3H, s, CCH_3). ^{13}C NMR(CDCl3, 100 MHz) δC: 148.3, 146.6, 146.4, 140.7, 140.0, 135.9, 129.7, 127.2, 127.1, 124.1, 120.8, 120.7 (q, ^1JFC 255.5 Hz), 119.3, 42.6, 29.8, 16.5. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}F_3O$ (M^+) 290.0918, found 290.0923

7-(2-Fluorophenyl)-2-methyl-1*H*-indene (10*a*$_9$). Yield 97%, 217 mg, white solid, Mp 56 – 58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.35-7.55 (4H, m, ArH), 7.18-7.34 (3H, m, ArH), 6.66 (1H, s, ArCH), 3.38 (2H, s, $ArCH_2$), 2.24 (3H, s, CCH_3).

7-(3-Fluorophenyl)-2-methyl-1*H*-indene (10*a*$_{10}$). Yield 96%, 215 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.43-7.48 (1H, m, ArH), 7.30-7.38 (4H, m, ArH), 7.19 (1H, $^3J_{HH}$ 7.2 Hz, ArH), 7.09-7.14 (1H, m, ArH), 6.61 (1H, s, ArCH), 3.43 (2H, s, $ArCH_2$), 2.21 (3H, s, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 162.8 (d, ^1JFC 244.1 Hz), 146.6, 146.4, 143.6 (d, ^3JFC 7.6 Hz), 143.5, 140.7, 136.0, 129.8 (d, ^3JFC 8.4 Hz), 127.1 (d, ^4JFC 5.4 Hz), 124.1 (d, ^4JFC 2.7 Hz), 124.0, 119.4, 115.3 (d, ^2JFC 20.4 Hz), 113.9 (d, ^2JFC 21.0 Hz), 42.6, 16.6. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}F$ (M^+) 224.1001, found 224.0998.

7-(4-Fluorophenyl)-2-methyl-1*H*-indene (10*a*$_{11}$, contains indene double bond isomers (1:1.2)). Yield 90%, 201 mg, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.40-7.55 (2H, ArH), 7.05-7.39 (5H, ArH), 6.61 (0.55H, s ArCH), 6.53 (0.45H, m ArCH) 3.36 (1.1H, s, $ArCH_2$), 3.35 (0.9H, s, $ArCH_2$) , 2.14 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 162.0 (d, ^1JFC 241.8 Hz), 146.9, 146.5 (d, ^3JFC 11.2 Hz), 144.0, 143.5, 140.8,136.3, 132.8, 130.2 (d, ^3JFC 7.8 Hz), 130.0 (d, ^3JFC 7.9 Hz), 127.1 (d, ^3JFC 11.2 Hz), 126.6, 125.9, 124.1, 123.9, 122.4, 119.0, 115.2 (d, ^2JFC 21.1 Hz), 115.1 (d, ^2JFC 21.2 Hz), 42.9, 16.9. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}F$ (M^+) 224.1001, found 224.1009.

7-(4-Chlorophenyl)-2-methyl-1*H*-indene (10*a*$_{12}$ contains indene double bond isomers (1:1.4)). Yield 77%, 184 mg, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 7.17-7.53 (6.6H, m, ArH), 7.13 (0.41H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 6.61 (0.59H, s, ArCH), 6.53 (0.41H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.35 (1.22H, s, $ArCH_2$), 3.32 (0.87H, s, $ArCH_2$), 2.14 (1.79H, CCH_3), 2.13

(1.29H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 147.0, 144.1, 143.5, 139.6, 130.1, 128.5, 127.2, 126.5, 125.9, 123.9, 122.6, 119.2, 42.9, 16.8. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}Cl$ (M^+) 240.0706, found 240.0715

2-Methyl-7-(3-(trifluoromethyl)phenyl)-1*H*-indene (10*a*13). Yield 90%, 246 mg, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.86 (1H, s ArH), 7.75 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.67 (1H, d, $^3J_{HH}$ 7.8 Hz, ArH), 7.59 (1H, t, $^3J_{HH}$ 7.7 Hz, ArH), 7.39 (1H, t, $^3J_{HH}$ 7.4 Hz, ArH), 7.33 (1H, d, $^3J_{HH}$ 7.3 Hz, ArH), 7.17 (1H, d, $^3J_{HH}$ 7.3 Hz, ArH), 6.61 (1H, s ArCH), 3.40 (2H, s, $ArCH_2$), 2.20 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 146.7, 146.4, 142.1, 140.8, 135.9, 131.7, 130.8 (q, ^2JFC 31.9 Hz), 128.8, 127.2, 127.2, 125.3 (q, ^4JFC 3.7 Hz), 124.4 (q, ^1JFC 270.5 Hz), 124.1, 123.8 (q, ^4JFC 3.7 Hz), 119.6, 42.5, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}F_3$ (M^+) 274.0969, found 274.0978.

2-Methyl-7-(4-(trifluoromethyl)phenyl)-1*H*-indene (10*a*14 contains indene double bond isomers (1:3.6)**)**. Yield 97%, 265 mg, white solid, Mp 145-147 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.68 (2H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.62 (2.40H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.10 (0.78H, d, $^3J_{HH}$ 7.6 Hz, ArH), 6.62 (0.22H, s, ArCH), 6.54 (0.78H, s, ArCH), 3.37 (0.48H, s, $ArCH_2$), 3.34 (1.61H, s, $ArCH_2$), 2.14 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 146.7, 146.5, 140.8, 135.9, 129.2 (q, ^2JFC 32.7 Hz) 129.1, 128.7, 127.2, 127.2, 125.3 (q, ^4JFC 3.8 Hz), 124.4 (q, ^1JFC 266.1 Hz) , 124.1, 119.6, 42.6, 16.7. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}F_3$ (M^+) 274.0969, found 274.0979.

7-(3,5-Bis(trifluoromethyl)phenyl)-2-methyl-1*H*-indene (10*a*15). Yield 87%, 297 mg, white solid, Mp 65-67 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 8.01 (2H, s ArH), 7.91 (1H, s ArH), 7.33-7.40 (2H, m ArH), 7.14 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 6.59 (1H, s, ArCH), 3.35 (2H, s, $ArCH_2$), 2.19 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 147.0, 146.6, 143.5, 140.8, 134.4, 131.8 (q, ^2JFC 27.1 Hz), 128.5 (m), 127.5, 127.3, 123.9, 123.4 (q, ^1JFC 271.2 Hz), 120.8 (m), 120.3, 42.3, 16.6. EI-HRMS (*m/z*) calcd for $C_{18}H_{12}F_6$ (M^+) 342.0843, found 342.0835.

3-(2-Methyl-1*H*-inden-7-yl)benzonitrile (10*a*16). Yield 93%, 214 mg, white solid, Mp 91 - 93 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.82 (1H, t, $^4J_{HH}$ 1.4 Hz, ArH), 7.75 (1H, dt, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.65 (1H, dt, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.55 (1H, t, $^4J_{HH}$ 7.9 Hz, ArH), 7.29-7.36 (2H, m ArH), 7.09 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.4 Hz, ArH), 6.56 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.33 (2H, s, $ArCH_2$), 2.17 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 146.7, 146.4, 142.4, 140.6, 134.8, 132.7, 131.7, 130.5, 129.2, 127.3, 127.1, 123.8, 119.8, 118.8, 42.4, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}N$ (M^+) 231.1048, found 231.1053.

4-(2-Methyl-1*H*-inden-7-yl)benzonitrile (10*a*17 contains indene double bond isomers (1:3.3)). Yield 75%, 173 mg, white solid. (Major) ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.73 (2H, d, $^3J_{HH}$ 8.3 Hz, ArH), 7.62 (2H, d, $^3J_{HH}$ 7.2 Hz, ArH), 7.15-7.45 (2H, m, ArH), 7.10 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 6.55 (1H, q, 1.6 Hz, ArCH), 3.35 (2H, s, $ArCH_2$), 2.16 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 146.8, 146.5, 146.1, 140.7, 135.4, 132.2, 129.4, 129.1, 127.3, 127.1, 123.9, 120.0, 110.7, 42.6, 16.6. EI-HRMS (*m/z*) calcd for $C_{17}H_{13}N$ (M^+) 231.1048, found 231.1053.

7-([1,1'-Biphenyl]-4-yl)-2-methyl-1*H*-indene (10*a*18). Yield 91%, 256 mg, white solid, Mp 138-140 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.65 (5H, m, ArH), 7.47 (2H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.25-7.40 (3H, m, ArH), 7.19 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 6.56 (1H, s, ArCH), 3.44 (2H, s, $ArCH_2$), 2.16

(3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 146.5, 146.3, 140.8, 140.8, 140.3, 139.8, 136.9, 128.8, 128.8, 127.3, 127.2, 127.1, 127.0, 124.2, 119.0, 42.8, 16.7 EI-HRMS (*m/z*) calcd for $C_{22}H_{18}$ (M$^+$) 282.1409, found 282.1419.

7-(3-Chlorophenyl)-2-methyl-1*H*-indene (10*a*$_{20}$). Yield 89%, 213 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 7.46 (1H, s, ArH), 7.16-7.35 (5H, m, ArH), 7.04 (1H, dd, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 6.47-6.49 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.29 (2H, s, ArCH$_2$), 2.09 (3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 146.6, 146.4, 143.1, 140.7, 135.9, 134.2, 129.6, 128.5, 127.1, 127.1, 127.0, 126.6, 124.0, 119.4, 42.6, 16.6. EI-HRMS (*m/z*) calcd for $C_{16}H_{13}Cl$ (M$^+$) 240.0706, found 240.0717.

2-(2-Methyl-1*H*-inden-7-yl)naphthalene (10*a*$_{23}$). Yield 94%, 240 mg, light yellow solid, Mp 81 - 83 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 8.01 (1H, s, ArH), 7.90-7.95 (3H, m, ArH), 7.71 (1H, dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.8 Hz, ArH), 7.51-7.56 (2H, m, ArH), 7.39 (1H, t, $^3J_{HH}$ 7.5 Hz, ArH), 7.26-7.34 (2H, m, ArH), 6.60 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.46 (2H, s, ArCH$_2$), 2.18 (3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 146.5, 146.4, 141.0, 138.8, 137.3, 133.4, 132.4, 128.0, 127.9, 127.7, 127.2, 127.1, 127.1, 126.9, 126.2, 125.9, 124.5, 119.0, 42.8, 16.7. EI-HRMS (*m/z*) calcd for $C_{20}H_{16}$ (M$^+$), 256.1252, found 256.1258

3-(2-Methyl-1*H*-inden-7-yl)pyridine (10*b*$_1$ contains indene double bond isomers (1:5)**)**. Yield 89%, 184 mg, colorless oil. (Major) ^{1}HNMR (CDCl$_3$, 400 MHz) δ_H: 8.77 (1H, s, ArH), 8.56 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.81 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.8 Hz, ArH), 7.15-7.40 (3H, m, ArH), 7.09 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 0.8 Hz, ArH), 6.53 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.33 (2H, s, ArCH$_2$), 2.13 (3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 149.2, 148.1, 146.7, 146.5, 141.0, 135.6, 133.6, 127.2, 127.1, 124.0, 123.3, 119.6, 42.5, 16.6. EI-HRMS (*m/z*) calcd for $C_{15}H_{13}N$ (M$^+$) 207.1048, found 207.1057.

4-(2-Methyl-1*H*-inden-7-yl)pyridine (10*b*$_2$). Yield 98%, 202 mg, colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 8.66 (2H, d, $^3J_{HH}$ 6.0 Hz, ArH), 7.43-7.45 (2H, m, ArH), 7.29-7.36 (2H, m, ArH), 7.13 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 6.54 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.37 (2H, s, ArCH$_2$), 2.15 (3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 149.8, 148.9, 146.8, 146.5, 140.7, 134.3, 127.3, 127.1, 123.6, 123.2, 120.1, 42.5, 16.6. EI-HRMS (*m/z*) calcd for $C_{15}H_{13}N$ (M$^+$) 207.1048, found 207.1053.

5-(2-Methyl-1*H*-inden-7-yl)pyrimidine (10*b*$_3$). Yield 79%, 164 mg, light yellow solid, Mp 70-72 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 9.20 (1H, s, ArH), 8.90 (2H, s, ArH), 7.31-7.38 (2H, m, ArH), 7.09 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 0.8 Hz, ArH), 6.55 (1H, q, $^4J_{HH}$ 1.6 Hz, ArCH), 3.35 (2H, s, ArCH$_2$), 2.15 (3H, CCH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ_C: 157.2, 155.9, 147.0, 146.6, 141.1, 134.7, 129.9, 127.6, 127.1, 123.8, 120.4, 42.3, 16.6. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}N_2$ (M$^+$) 208.1000, found 208.1008.

3-(2-Methyl-1*H*-inden-7-yl)quinoline (10*b*$_4$). Yield 53%, 136 mg, white solid, Mp 190-192 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H: 9.12 (1H, d, $^4J_{HH}$ 2.0 Hz, ArH), 8.24 (1H, d, $^4J_{HH}$ 2.0 Hz, ArH), 8.16 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.85 (1H, d, $^3J_{HH}$ 8.4 Hz, ArH), 7.73 (1H, dt, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.6 Hz, ArH), 7.57 (1H, dt, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.2 Hz, ArH), 7.37 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.33 (1H, dd, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 0.8 Hz, ArH), 7.22 (1H, dd, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.0 Hz, ArH), 6.58 (1H, q,

$^4J_{HH}$ 1.6 Hz, ArCH), 3.41 (2H, s, $ArCH_2$), 2.16 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 150.8, 147.1, 146.8, 146.5, 141.3, 134.5, 134.1, 133.7, 129.3, 129.2, 127.9, 127.3, 127.1, 126.9, 124.4, 119.7, 42.6, 16.6. EI-HRMS (*m/z*) calcd for $C_{19}H_{15}N$ (M^+) 257.1204, found 257.1205.

2-(2-Methyl-1*H*-inden-7-yl)thiophene (10*b*₅). Yield 77%, 163 mg, brown oil. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.33-7.39 (2H, m, ArH), 7.29-7.32 (1H, m, ArH), 7.26 (1H, d, $^3J_{HH}$ 7.6 Hz, ArH), 7.19 (1H, d, $^3J_{HH}$ 8.0 Hz, ArH), 7.08-7.12 (1H, m, ArH), 6.57 (1H, s, ArCH), 3.37 (2H, s, $ArCH_2$), 2.17 (3H, CCH_3).

2-(2-Methyl-1*H*-inden-7-yl)furan (10*b*₆). Yield 63%, 123 mg, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 7.50 (1H, d, $^3J_{HH}$ 7.8 Hz, ArH), 7.47 (1H, d, $^4J_{HH}$ 1.3 Hz, ArH), 7.25 (1H, t, $^3J_{HH}$ 7.6 Hz, ArH), 7.16 (1H, d, $^3J_{HH}$ 7.2 Hz, ArH), 6.61 (1H, d, $^4J_{HH}$ 3.2 Hz, ArH), 6.46-6.48 (2H, m, ArH, ArCH), 3.44 (2H, s, $ArCH_2$), 2.12 (3H, CCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 153.7, 146.7, 146.2, 141.6, 137.9, 126.8, 126.7, 125.9, 120.1, 119.0, 111.4, 106.7, 43.8, 16.7. EI-HRMS (*m/z*) calcd for $C_{14}H_{12}O$ (M^+) 196.0888, found 196.0897

Multi-gram scale synthesis of 10a₁₅ without fraction distillation or column chromatography

Into a 100 mL round-bottom flask, was filled with a mixture of 4-bromo-2-methyl 1-indanone **7** (4.50 g, 20 mmol), 3,5-ditrifluoromethyl phenylboronic acid **8a₁₅** (5.40 g, 21 mmol, 1.05 eq.), $Pd(OAc)_2$ (0.225 mg, 1.0 umol, 0.005 mol%), TBAB (7.16 g, 20 mmol, 1.0 eq.), K_2CO_3 (5.53g, 40 mmol, 2.0 eq.) and PEG400 50 g. The mixture was stirred at 110 °C till complition (TLC)**.** 50 mL of water was added and the contents were extracted with EtOAc (100 mL X 3). The organic phase was washed with brine (100 mL X 2), dried over Na_2SO_4 and concentrated to dryness. 20 mL of methanol was added and the suspension was stirred overnight. After filtration, the white solid was dissolved in 300 mL of THF/MeOH (2:1) and 1.14 g (30 mmol, 1.5 eq.) of $NaBH_4$ was added in portions at 0 °C. The reaction was stirred at rt till completion (TLC). After evaporation, the residue was partitioned between EtOAc and H_2O (200 mL, 1:1). The aqueous phase was extracted with EtOAc (100 mL × 2). The combined organic extracts were dried and evaporated to dryness. The crude product was taken up in 350 mL of toluene and mixed with 200 mg of TsOH monohydrate. The formed mixture was refluxed with Dean-Stark head for 5 h. Toluene was removed under reduce pressure and the residue was re-dissolved in EtOAc/MeOH (200 mL, 1:1). The aqueous phase was extracted with EtOAc (100 mL × 2). The combined organic extracts were washed subsequently with saturated $NaHCO_3$ (100 mL × 2), brine (100 mL × 2) and dried over Na_2SO_4. After evaporation, the residue was suspended in methanol (15 mL) and stirred overnight. The slurry was filtered to yield 2-methyl-7-(3,5-bistrifluoromethylphenyl)indene **10a₁₅** 5.9 g (17.2 mmol) in 85.8% yield.

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