Studies on the synthesis of 2-acyl-1*H*-indenes *via* one-pot palladium-catalysed tandem Heck–aldol reaction

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2-Acyl-1*H*-indenes were synthesised efficiently by the reaction of *o*-halogenatedbenzaldehydes (or aryl ketones) with prop-2-en-1-ols *via* one-pot palladium-catalysed tandem Heck–aldol reaction in moderate to good yields. The optimal reaction conditions have been investigated and it was found that sodium acetate was the most effective base and in addition tetrabutylammonium chloride and LiCl was crucial for this process. Moreover, it was found that *o*-halogenatedbenzaldehydes react with various substituted prop-2-en-1-ols smoothly to produce the title compounds while 2-bromoacetophenone only reacted with 2-propen-1-ol to give the desired product.

Keywords: 2-acyl-1*H*-indenes, one-pot, palladium-catalysed, tandem Heck–aldol reaction

2-Acylindenes **3** present potential applications in the synthesis of pharmaceutical and bioactive materials.[1,2] This type of compound has been synthesised first by the reaction of 1*H*-indene-2-acyl chloride with $LiCu(CH_3)_2$ at –60 °C.[3] Other reported methods normally used highly functionalised materials or suffered a multistep reaction.[4–7] In 1996, Dyker and Grundt reported briefly that 2-acylindenes could be prepared by palladium-catalysed domino-Heck–aldol-condensation.[8] We considered the synthesis of 2-acetylindenes which were used as key intermediates in our research.[9,10] This process appears promising for the preparation of a wide variety of 2-acylindenes.

This process was shown in Scheme 1. In order to optimise the reaction conditions and find the scope and limitations of this process, various factors which might influence this reaction were investigated. At the same time, various *o*-halogenatedbenzaldehydes (or ketones) and prop-2-en-1-ols were examined. According to our survey, some new conclusions which differed from the reported literature[8] were found and might provide useful information for the synthesis of 2-acylindenes.

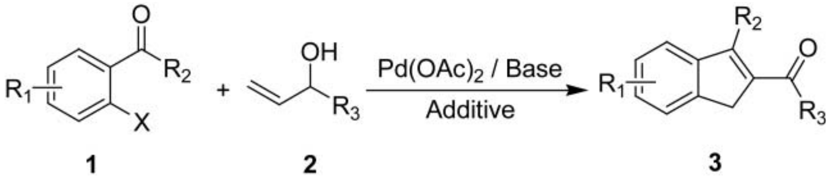
Our initial studies focused on the development of optimal reaction conditions for this process. We used 2-bromobenzaldehyde **1a** to react with but-3-en-2-ol **2a** for this purpose

First, the influence of base, temperature and reaction time to the reaction were investigated (Table 1). When **1a** reacted with **2a** at 110 °C using $NaHCO_3$ as base and PPh_3 as additive (the synthetic process reported in literature[8]), **3a** was not obtained (Table 1, entry 1). It was also found that when using tetrabutylammonium chloride (TBAC) and LiCl as additive, $NaHCO_3$ or Et_3N were not efficient enough to produce **3a** while the Heck-type products **4a** were obtained in moderate yields (Table 1, entries 2–4). However, when using NaOAc as base, **1a** reacted with **2a** to produce the desired product **3a** in 67% (Table 1, entry 5). When **1a** reacted with **2a** at 90 °C, **3a** was not produced while the Heck-type product **4a** was obtained in the yield of 74% (Table 1, entry 6). It was also found that the yield of **3a** was decreased when **1a** reacted with **2a** in a longer reaction time (Table 1, entries 7 and 8 compared with entry 5). One of the reasons might be was that some other reaction, such as the intermolecular aldol reaction, would occur under these reaction conditions. However, if the reaction time was too short, the yield of **3a** was also low because the Heck-type intermediate **4a** could not be transferred to the target compounds completely (Table 1, entry 9).

It is well known that quaternary ammonium salt (QX) and lithium chloride are important additives in an Heck-type reaction.[11] So their influence was also investigated (Table 2). Surprisingly, it was found that the **3a** was not produced when 2-bromobenzaldehyde **1a** reacted with prop-2-en-1-ol **2a** in the absence of quaternary ammonium salt while the target product **3a** was given in 62% yield using 2 equiv. of tetrabutylammonium bromide (TBAB) as an additive (Table 2, entries 1 and 2). It was also found when using tetrabutylammonium chloride (TBAC) instead of TBAB, the yield of product **3a** increased from 62 to 67% (Table 2, entry 3 compared with entry 2).

There is a possible mechanism that would explain the role of quaternary ammonium salt (QX) (Fig. 1).[11] Quaternary ammonium salt would involve an exchange process with the base NaOAc to generate the base [n-Bu_4NOAc] which is more efficient to regenerate the Pd(0) catalyst by deprotonation of hydridopalladium halide in the organic phase. The higher promoting efficiency of n-Bu_4NCl (compared to n-Bu_4NBr) can be explained if its chloride anion acts as a stabilising agent when there is no phosphine ligand in the reaction mixture.[11,12]

It was found that the yield of **3a** decreased when **1a** reacted with **2a** using TBAB as additive without LiCl (Table 2, entry 4 compared with entry 2). However, when **1a** reacted with **2a** using TBAC as additive, addition of LiCl had little effect to the yield of the product (Table 2, entry 5 compared with entry 3). It was also found that addition of LiCl had little effect to the yield of product when the more active aryl halide 2-iodobenzaldehyde **1b** reacted with **2a** using TBAB as additive



Scheme 1

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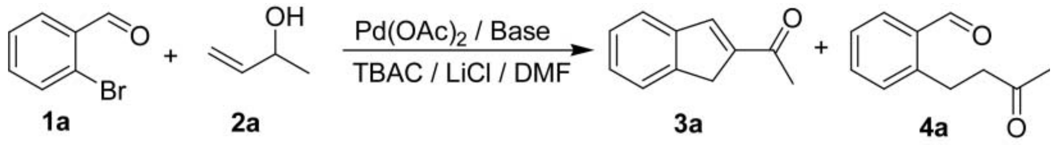
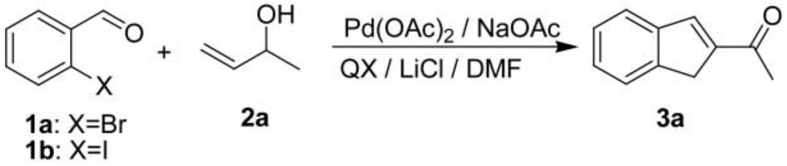
Table 1 The influence of base, temparature and reaction time to the reaction[a]



Entry	Base	Time/h	Temp./°C	Yield/%[b]	
				3a	**4a**
1	$NaHCO_3$[c]	24	110	0[d]	0
2	$NaHCO_3$	4	110	Trace	62
3	Et_3N[e]	4	110	Trace	56
4	Et_3N[e]	10	80	Trace	45
5	NaOAc	4	110	67	0
6	NaOAc	4	90	Trace	74
7	NaOAc	24	110	0[d]	0
8	NaOAc	6.5	110	32[d]	0
9	NaOAc	2	110	28	63

[a] General reaction conditions: 2-bromobenzaldehyde **1a** (0.5 mmol), prop-2-en-1-ol **2a** (0.6 mmol), DMF 5 mL, $Pd(OAc)_2$ (0.025 mmol), base (1.25 mmol), tetrabutylammonium chloride (TBAC, 1.0 mmol), LiCl (1.0 mmol).
[b] Isolated yields.
[c] 10 mol% PPh_3 and 0.6 mmol $NaHCO_3$ were used without other additives.
[d] Indeterminate complex compound was produced.
[e] 4.0 mmol Et_3N was used.

Table 2 The influence of quaternary ammonium salt (QX) and LiCl to the reaction[a]



Entry	1	QX[b]/equiv.	LiCl[b]/equiv.	**3a** Yield/%[c]
1	**1a**	none	2.0	0
2	**1a**	TBAB 2.0	2.0	62
3	**1a**	TBAC 2.0	2.0	67
4	**1a**	TBAB 2.0	None	29
5	**1a**	TBAC 2.0	None	64
6	**1b**	TBAB 2.0	None	66
7	**1b**	TBAB 2.0	2.0	67
8	**1a**	TBAC 1.0	2.0	47
9	**1a**	TBAC 1.5	2.0	60
10	**1a**	TBAC 3.0	2.0	67

[a] General reaction conditions: *o*-halogenatedbenzaldehydes **1** (0.5 mmol), prop-2-en-1-ol **2a** (0.6 mmol), DMF 5 mL, $Pd(OAc)_2$ (0.025 mmol), NaOAc (1.25 mmol), quaternary ammonium salt (QX), LiCl, 110 °C, 4 hours.
[b] The dosage of quaternary ammonium salt (QX) and LiCl based on the aryl halides.
[c] Isolated yields.

(Table 2, entry 6 compared with entry 7). The role of LiCl can also be explained by its involving an exchange process with n-Bu_4NBr to generate n-Bu_4NCl, which is more efficient for regenerating the Pd(0) catalyst as mentioned above.[11]

In order to avoid the intermolecular aldol reaction and other side reactions, the concentration of the reactants was reduced by using excessive solvent. So it was believed that the dosage of additives would influence the reaction when other reaction conditions had not changed. It was found when **1a** reacted with **2a** using the same dosage of LiCl as additive, the yield of product **3a** was decreased with reducing the dosage of TBAC (Table 2, entries 8 and 9 compared with entry 3). But further increasing the dosage of TBAC had little effect on the yield of product **3a** (Table 2, entry 10).

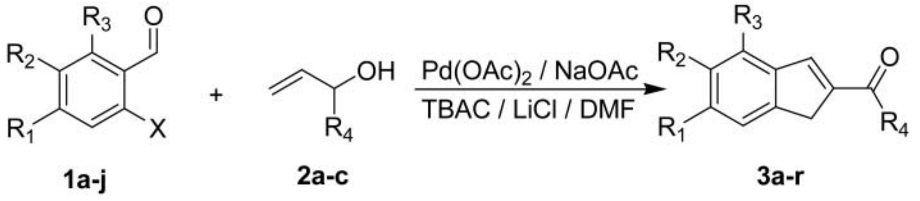
According to the above investigations, the optimum reaction conditions for the synthesis of 2-acylindenes by the reaction of *o*-halogenatedbenzaldehydes with prop-2-en-1-ols *via* a palladium-catalysed tandem Heck–aldol reaction should be as follows: *o*-halogenatedbenzaldehydes **1** reacted with prop-2-en-1-ols **2** using $Pd(OAc)_2$ (5 mol%) as the catalyst and NaOAc (2.5 equiv.) as the base; using tetrabutylammonium chloride (TBAC 2.0 equiv.) and LiCl (2.0 equiv.) as the additives. The

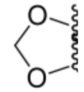
$$\text{n-Bu}_4\text{NX} + \text{NaOAc} \longrightarrow \left[\text{n-Bu}_4\text{NOAc}\right] + \text{NaX}$$

$$\left[\text{n-Bu}_4\text{NOAc}\right] + \left[\text{H-Pd-X'}\right] \longrightarrow \left[\text{Pd}^0\right] + \text{n-Bu}_4\text{NX'} + \text{HOAc}$$

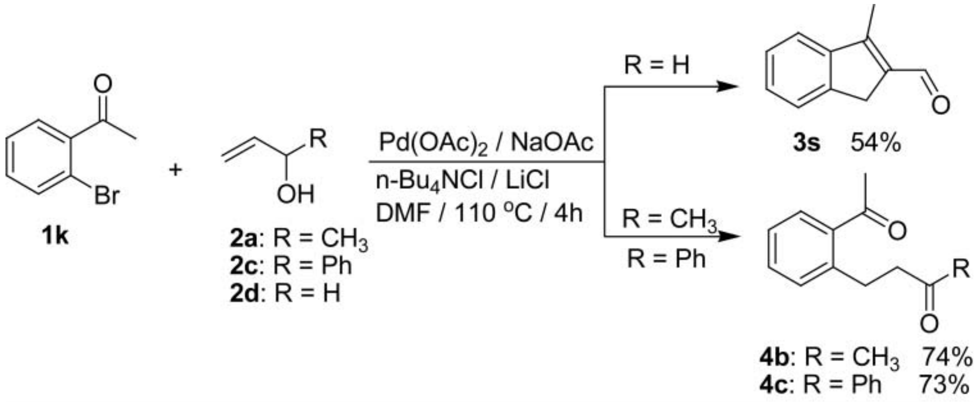
Fig. 1

Table 3 Synthesis of 2-acyl-1*H*-indenes by palladium-catalysed tandem Heck–aldol reaction[a]



Entry	1					2		Time /h[b]	Product **3**	Yield /%[c]
	No.	R[1]	R[2]	R[3]	X	No.	R[4]			
1	**1a**	H	H	H	Br	**2a**	Me	4	**3a**	67
2	**1a**	H	H	H	Br	**2b**	Isopropyl	4	**3b**	48
3	**1a**	H	H	H	Br	**2c**	Ph	4	**3c**	64
4	**1c**	Cl	H	H	Br	**2a**	Me	2.5	**3d**	64
5	**1c**	Cl	H	H	Br	**2c**	Ph	2.5	**3e**	66
6	**1d**	F	H	H	I	**2a**	Me	2	**3f**	58
7	**1d**	F	H	H	I	**2c**	Ph	2	**3g**	62
8	**1e**	H	Cl	H	Br	**2a**	Me	3	**3h**	63
9	**1e**	H	Cl	H	Br	**2c**	Ph	3	**3i**	66
10	**1f**	H	F	H	Br	**2a**	Me	1.5	**3j**	61
11	**1f**	H	F	H	Br	**2c**	Ph	1.5	**3k**	58
12	**1g**	H	H	Cl	I	**2a**	Me	4	**3l**	52
13	**1g**	H	H	Cl	I	**2c**	Ph	4	3m	54
14	**1h**	CH_3	H	H	Br	**2a**	Me	2	3n	64
15	**1h**	CH_3	H	H	Br	**2c**	Ph	2	3o	67
16	**1i**			H	Br	**2a**	Me	2	3p	63
17	**1i**			H	Br	**2b**	Isopropyl	2	3q	43
18	**1i**			H	Br	**2c**	Ph	2	3r	63
19	**1j**	NO_2	H	H	Br	**2a**	Me	4	–[d]	0

[a] General reaction conditions: *o*-halogenatedbenzaldehydes **1** (1.0 mmol), prop-2-en-1-ols **2** (1.2 mmol), DMF 10 mL, $Pd(OAc)_2$ (0.05 mmol), NaOAc (2.5 mmol), tetrabutylammonium chloride (TBAC, 2.0 mmol), LiCl (2.0 mmol), 110 °C.
[b] Reaction time was determined by tracing the starting material *o*-halogenatedbenzaldehydes with TLC analysis.
[c] Isolated yields.
[d] Indeterminate complex compound was produced.



Scheme 2

reaction temperature should be 110 °C and the reaction time should be around 4 hours.

Under the optimal conditions, various *o*-halogenatedbenzaldehydes **1** and prop-2-en-1-ols **2** were tested and 2-acylindenes **3** were produced in moderate to good yields. The results were summarised in Table 3.

Initially, 2-bromobenzaldehyde **1a** was reacted with prop-2-en-1-ols **2a**, **2b** and **2c** to give the corresponding 2-acylindenes **3a**, **3b** and **3c** in 67, 48 and 64% yields respectively (Table 3, entries 1–3). At the same time, it was found that the products **3d–k** were efficiently prepared in a short time in moderate to good yields when halogen substituted *o*-halogenatedbenzaldehydes **1c–f** reacted with representative prop-2-en-1-ols **2a** and **2c** respectively (Table 3, entries 4–11). However, when 2-iodo-6-chlorobenzaldehyde **1g** was tested, 2-acylindenes **3l** and **3m** were only obtained in 52 and 54% yields (Table 3, entries 12 and 13). But the reaction of 2-bromo-4-methylbenzaldehyde **1h** with prop-2-en-1-ols **2a** and **2c** also gave 2-acyl-indenes **3n** and **3o** in good yields efficiently (Table 3, entries 14 and 15). When the substrate **1i** which bearing a strong electron donating group reacted with prop-2-en-1-ols **2a–c**, the title products **3p**, **3q** and **3r** were also obtained in 63, 43 and 63% yields respectively(Table 3, entries 16–18). However, when 2-bromo-4-nitrobenzaldehyde **1j** was reacted with prop-2-en-1-ol **2a**, the desired product could not be obtained using the same reaction conditions (Table 3, entry 19).

Next, 2-bromoacetophenone **1k** was tested to broaden the scope of this process (Scheme 2). Surprisingly, under identical conditions, only prop-2-en-1-ol **2d** reacted with 2-bromoacetophenone **1k** to produce **3s** in 54% yield. However, when

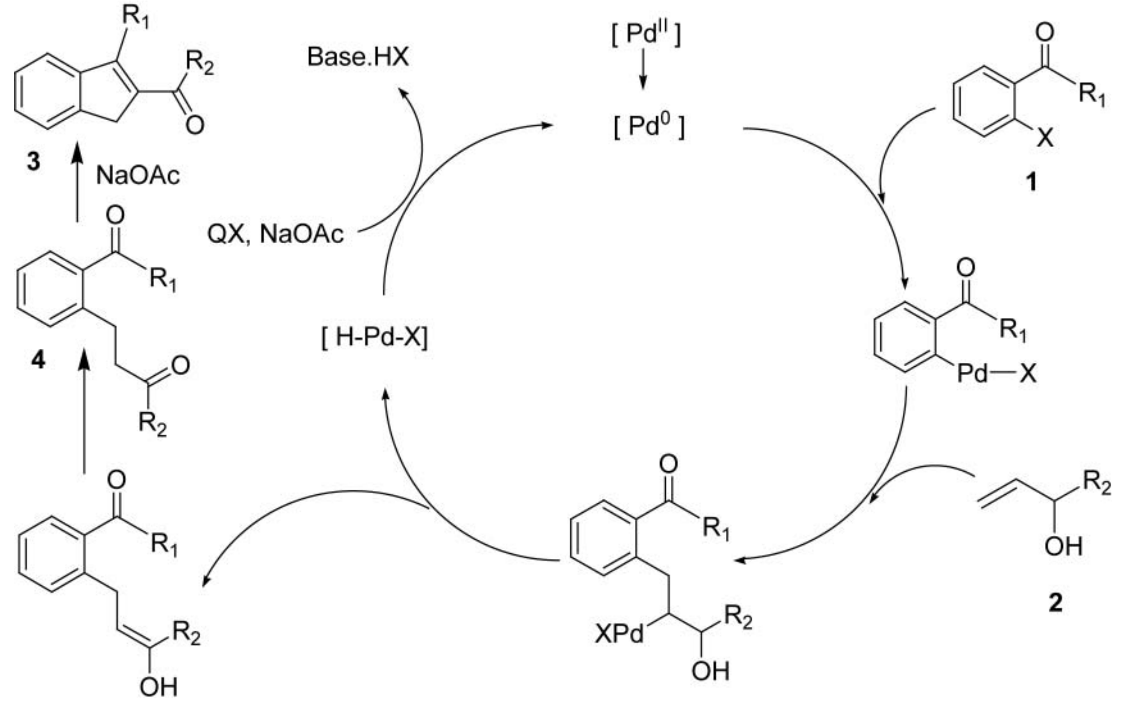


Fig. 2

other substituted prop-2-en-1-ols **2a** and **2c** reacted with 2-bromoacetophenone **1k**, only the Heck-type products **4b** and **4c** were produced in 74 and 73% yields respectively. Under similar reaction conditions, prolonging the reaction time to 24 hours did not afford the title products. This result also differed from those reported.[8] The in-depth investigation of reaction of *o*-halogenated aryl ketones with substituted prop-2-en-1-ols is now in progress.

A possible mechanism for this one-pot palladium-catalysed reaction is shown in Fig. 2. First, *o*-halogenatedbenzaldehydes (or ketones) **1** react with prop-2-en-1-ols **2** to form the *o*-acyl substituted aryl ketones (or aldehydes) **4** by Heck-type reaction with elimination of palladium hydride towards the hydroxy side and undergoing tautomerisation to the keto forms (or aldehyde forms).[13–15] Then an intramolecular aldol condensation occurs in the presence of NaOAc and produces 2-acylindenes **3**. The possible mechanism of regeneration of Pd(0) catalyst by deprotonation of hydridopalladium halide ([H–Pd–X]) in the presence of NaOAc and quaternary ammonium salt (QX) is shown in Fig. 1.

We have developed an efficient and convenient process to synthesise 2-acylindenes *via* one-pot palladium-catalysed reaction. It is found that NaOAc is the most effective base and addition tetrabutylammonium chloride (TBAC) and LiCl is crucial for this process. Further applications of this methodology for the synthesis of bioactive products are also being investigated in our laboratories.

Experimental

Starting materials *o*-halogenatedbenzaldehydes **1b, 1c, 1e, 1g** and **1j** were synthesised according to our previous reports.[10] Prop-2-en-1-ols **2b** and **2c** were synthesised according to the reported literature.[16] Other reagents were purchased from Aldrich and used as received. DMF and Et_3N was distilled and dried over 4Å molecular sieves. Other solvents were obtained from commercial sources and used without further purification. Silica gel (100–140 mesh) was used for column chromatography. Melting points were determined on a Buchi melting point apparatus and are uncorrected. The spectra of ^{1}H NMR were recorded in $CDCl_3$ solution on a Varian Mercury V×300 NMR spectrophotometer with TMS as the internal standard. A Perkin-Elmer 983 was used to determine the IR spectra. Elementary analyses were performed on a Vario EL III elementary analysis instrument and the results were within 0.3% of the calculated value.

Synthesis of 2-acylindenes **3a–s;** *general procedure*

The *o*-halogenatedbenzaldehydes (or 2-bromoacetophenone) **1** (1.0 mmol), prop-2-en-1-ols **2** (1.2 mmol), $Pd(OAc)_2$ (5 mol%), tetrabutylammonium chloride (TBAC) (2.0 mmol), NaOAc (2.5 mmol) and LiCl (2.0 mmol) were added to a sealed flask. DMF (10 mL) was added to the flask after the flask was charged with nitrogen. Then the flask was placed into a 110 °C oil bath and stirring was continued for 1.5–4 hours (as shown in Table 3). The reaction mixture was extracted with EtOAc (3 × 20 mL) and washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography (hexane/EtOAc=5/1) to afford products 2-acyl-1*H*-indenes **3**. The physical and spectra data of the compounds **2k–o** are as follows.

1-(1H-Inden-2-yl)ethanone (**3a**): Yield 67%; yellowish solid; m.p. 57.3–59.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.48 (s, 3H), 3.65 (s, 2H), 7.32–7.37 (m, 2H), 7.48–7.55 (m, 2H), 7.62 (s, 1H); IR (KBr) ν: 1650, 1555, 1460, 1370, 1335, 1190, 880, 760, 720 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.36; H, 6.26%.

1-(1H-Inden-2-yl)-2-methylpropan-1-one (**3b**): Yield 48%; white solid; m.p. 53.2–55.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.19 (d, J = 6.3 Hz, 6H), 3.38–3.68 (m, 1H), 3.69 (s, 2H), 7.35–7.38 (m, 2H), 7.51–7.57 (m, 2H), 7.66 (s, 1H); IR (KBr) ν: 1710, 1660, 1465, 1380, 1025, 755 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C 83.95; H, 7.39.

(1H-Inden-2-yl)(phenyl)methanone (**3c**): Yield 64%; yellowish crystal; m.p. 68.4–69.3 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.88 (s, 2H), 7.34–7.40 (m, 2H), 7.46–7.58 (m, 6H), 7.82–7.85 (m, 2H); IR (KBr) ν: 1635, 1560, 1345, 1255, 1205, 1115, 760, 710 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.03; H, 5.60%.

1-(6-Chloro-1H-inden-2-yl)ethanone (**3d**): Yield 64%; yellowish solid; m.p. 71.8–73.6 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.50 (s, 3H), 3.66 (s, 2H), 7.27–7.28 (m, 1H), 7.32 (dd, J = 8.1 Hz, 2.1 Hz, 1H), 7.48–7.50 (m, 1H, ArH), 7.59 (s, 1H); IR (KBr) ν: 1660, 1550, 1365, 1190, 880, 850 cm^{-1}. Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.71. Found: C, 68.72; H, 4.87%.

(6-Chloro-1H-inden-2-yl)(phenyl)methanone (**3e**): Yield 66%; yellowish solid; m.p. 82.1–83.8 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.84 (s, 2H), 7.36–7.41 (m, 2H), 7.49–7.63 (m, 5H), 7.83–7.85 (m, 2H); IR (KBr) ν: 1640, 1565, 1345, 1250, 1215, 1120, 760 cm^{-1}. Anal. Calcd for $C_{16}H_{11}ClO$: C, 75.45; H, 4.35. Found: C, 75.62; H, 4.21%.

1-(6-Fluoro-1H-inden-2-yl)ethanone (**3f**): Yield 58%; yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.50 (s, 3H), 3.65 (s, 2H), 7.05-7.11

(m, 1H), 7.20–7.24 (m, 1H), 7.47–7.52 (m, 1H), 7.60 (s, 1H); IR (KBr) ν: 1645, 1560, 1345, 1250, 1220, 1115, 760 cm^{-1}. Anal. Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15. Found: C, 75.13; H, 5.02%.

(6-Fluoro-1H-inden-2-yl)(phenyl)methanone (**3g**): Yield 62%; yellowish solid; m.p. 71.1–72.6 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.85 (s, 2H), 7.36–7.45 (m, 2H), 7.50–7.66 (m, 5H), 7.87–7.91 (m, 2H); IR (KBr) ν: 1640, 1560, 1350, 1240, 1215, 1115, 765 cm^{-1}. Anal. Calcd for $C_{16}H_{11}FO$: C, 80.66; H, 4.65. Found: C, 80.51; H, 4.78%.

1-(5-Chloro-1H-inden-2-yl)ethanone (**3h**): Yield 63%; yellowish solid; m.p. 67.2–68.9 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.50 (s, 3H), 3.65 (s, 2H), 7.30–7.34 (m, 1H), 7.41–7.45 (m, 1H), 7.47–7.58 (m, 2H); IR (KBr) ν: 1660, 1560, 1370, 1220, 1100, 885 cm^{-1}. Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.71. Found: C, 68.69; H, 4.62%.

(5-Chloro-1H-inden-2-yl)(phenyl)methanone (**3i**): Yield 66%; yellowish solid; m.p. 78.5–80.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.86 (s, 2H), 7.32–7.36 (m, 1H), 7.40–7.43 (m, 1H), 7.48–7.66 (m, 5H), 7.87–7.91 (m, 2H); IR (KBr) ν: 1640, 1555, 1360, 1225, 710 cm^{-1}. Anal. Calcd for $C_{16}H_{11}ClO$: C, 75.45; H, 4.35. Found: C, 75.59; H, 4.18%.

1-(5-Fluoro-1H-inden-2-yl)ethanone (**3j**): Yield 61%; white solid; m.p. 54.3–55.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.49 (s, 3H), 3.63 (s, 2H,), 7.02–7.08 (m, 1H), 7.46 (m, 1H), 7.17–7.27 (m, 1H), 7.57–7.59 (m, 1H); IR (KBr) ν: 1660, 1560, 1375, 1220, 1095, 885 cm^{-1}. Anal. Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15. Found: C, 73.97; H, 5.12%.

(5-Fluoro-1H-inden-2-yl)(phenyl)methanone (**3k**): Yield 58%; white solid;, m.p. 69.8–70.7 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.88 (s, 2H), 7.04–7.11 (m, 1H), 7.20–7.30 (m, 1H), 7.44–7.59 (m, 5H), 7.84–7.88 (m, 2H); IR (KBr) ν: 1635, 1560, 1350, 1230, 705 cm^{-1}. Anal. Calcd for $C_{16}H_{11}FO$: C, 80.66; H, 4.65. Found: C, 80.63; H, 4.76%.

1-(4-Chloro-1H-inden-2-yl)ethanone (**3l**): Yield 52%; yellowish solid; m.p. 63.5–64.8 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.44 (s, 3H), 3.61 (s, 2H), 7.21–7.27 (m, 2H), 7.41–7.45 (m, 1H), 7.58 (s, 1H); IR (KBr) ν: 1645, 1560, 1460, 1360, 1200, 880, 760, 710 cm^{-1}. Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.71. Found: C, 68.47; H, 4.85%.

(4-Chloro-1H-inden-2-yl)(phenyl)methanone (**3m**): Yield 54%; yellowish solid; m.p. 74.2–76.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.88 (s, 2H), 7.24–7.30 (m, 2H), 7.46–7.58 (m, 5H), 7.81–7.84 (m, 2H); IR (KBr) ν: 1640, 1560, 1350, 1255, 1205, 1120, 760, 710 cm^{-1}. Anal. Calcd for $C_{16}H_{11}ClO$: C, 75.45; H, 4.35. Found: C, 75.62; H, 4.15%.

1-(6-Methyl-1H-inden-2-yl)ethanone (**3n**): Yield 64%; yellowish solid; m.p. 71.3–72.6 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.42 (s, 3H), 2.48 (s, 3H, $COCH_3$), 3.63 (s, 2H), 7.14–7.18 (m, 1H), 7.33–7.45 (m, 2H), 7.58–7.61 (m, 1H); IR (KBr) ν: 1660, 1555, 1370, 1210, 805 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.50; H, 7.21%.

(6-Methyl-1H-inden-2-yl)(phenyl)methanone (**3o**): Yield 67%; yellow solid; m.p. 92.4–93.6 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.43 (s, 3H), 3.63 (s, 2H), 7.15–7.21 (m, 1H), 7.35–7.58 (m, 6H), 7.80–7.84 (m, 2H); IR (KBr) ν: 1635, 1550, 1345, 1220, 1115, 705 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.32; H, 5.91%.

1-(5H-Indeno[5,6-d][1,3]dioxol-6-yl)ethanone (**3p**): Yield 63%, white solid; m.p. 149.1–150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.45 (s, 3H), 3.58 (s, 2H), 6.01 (s, 2H), 6.98 (s, 2H), 7.55 (s, 1H); IR (KBr) ν: 1650, 1560, 1470, 1220 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.28; H, 4.96%.

1-(5H-indeno[5,6-d][1,3]dioxol-6-yl)-2-methylpropan-1-one (**3q**): Yield 43%; yellow solid; m.p. 87.8–89.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.19 (d, *J* = 6.9 Hz, 6H), 3.36–3.66 (m, 1H), 3.59 (s, 2H), 6.01 (s, 2H), 6.98 (s, 1H), 6.99 (s, 1H), 7.56 (s, 1H); IR (KBr) ν: 1645, 1550, 1465, 1330, 1200, 1160, 1040, 950 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.21; H, 6.01%.

(5H-Indeno[5,6-d][1,3]dioxol-6-yl)(phenyl)methanone (**3r**): Yield 63%; yellowish solid; m.p. 144.8–145.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.80 (s, 2H,), 6.02 (s, 2H), 6.97 (s, 1H), 7.05 (s, 1H, ArH), 7.38–7.57 (m, 4H), 7.79–7.81 (m, 2H); IR (KBr) ν: 1625, 1600, 1545, 1470, 1325, 1230, 940, 715 cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.16; H, 4.58%.

3-Methyl-1H-indene-2-carbaldehyde (**3s**): Yield 54%; yellow solid; m.p. 74.0–75.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.57 (s, 3H), 3.64 (s, 2H,), 7.40–7.45 (m, 2H), 7.52–7.60 (m, 2H), 10.24 (s, 1H); IR (KBr) ν: 1645, 1355, 760 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.54; H, 6.37%.

Synthesis of Heck-type products **4b** *and* **4c;** *general procedure*

The procedure for the synthesis of Heck-type products **4b** and **4c** was similar with the procedure for the synthesis of 2-acylindenes **3a–s**.

4-(2-Acetylphenyl)butan-2-one (**4b**): Yield 74%; Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.15 (s, 3H), 2.77 (t, 2H, *J* = 7.8 Hz), 3.28 (t, 2H, *J* = 7.8 Hz), 7.31–7.39 (m, 1H), 7.41–7.44 (m, 1H), 7.49–7.54 (m, 1H), 7.80 (dd, 1H, *J* = 7.8 Hz, 1.5 Hz), 10.19 (s, 1H); IR (KBr) ν: 3020, 1725, 1690, 1610, 1580, 1490, 1450, 810 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.62; H, 7.63%.

3-(2-acetylphenyl)-1-phenylpropan-1-one (**4c**): Yield 73%; brownish-yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.16 (s, 3H), 2.60 (s, 3H), 2.78 (t, 2H, *J* = 7.8 Hz), 3.08 (t, 2H, *J* = 7.8 Hz), 7.27–7.39 (m, 2H), 7.41–7.44 (m, 1H), 7.70–7.73 (m, 1H); IR (KBr) ν: 3020, 1720, 1640, 1610, 1580, 1480, 800, 760, 710 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.79; H, 6.58%.

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