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Reactive Organoallyl Species Generated from Aryl halides and Allene: Allylation of α,β-Unsaturated Aldehydes and Cyclic Ketones Employing Pd/In Transmetallation Processes

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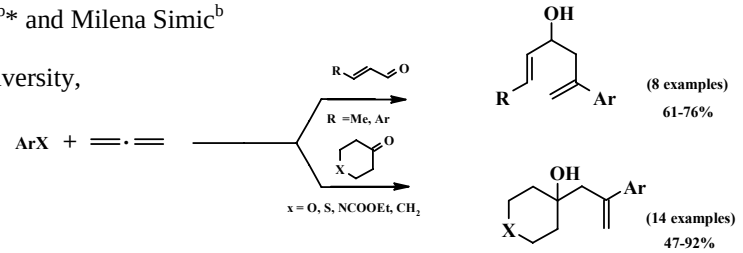

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Reactive Organoallyl Species Generated from Aryl halides and Allene: Allylation of α,β-Unsaturated Aldehydes and Cyclic Ketones Employing Pd/In Transmetallation Processes

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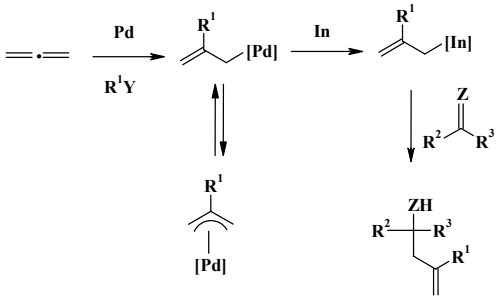
Abstract - Allylation of α,β–unsaturated aldehydes and cyclic ketones promoted by Pd/In transmetallation processes have been studied. The unsaturated aldehydes underwent regioselective 1,2-addition to afford secondary homoally alcohols. The reactions have been performed using $Pd(OAc)_2/PPh_3$ as catalytic system and metallic indium affording the products in good yields. The same transformation with unsaturated ketones proved to be less efficient, while saturated cyclic ketones delivered generally excellent yields in the presence of CuI. In these latter processes the presence of a distal heteroatom influences the reaction rate.

1. Introduction

Synthetic methodologies based on palladium have become indispensable for the preparation of a wide range of organic compounds.[1] The electrophilicity of π–allylpalladium species and the ability to finely tune their reactivity has led to the development of a plethora of very efficient synthetic procedures.[2] Occasional reports of π–allylpalladium(II) species displaying nucleophilic properties have appeared which invariably involve intramolecular processes and which merit further study.[3] In recent years, transmetallation processes of Pd-intermediates have been intensively studied.[4] Generally, these transformations provide an access to nucleophilic organometallic species generated from electrophilic organopalladium intermediates. Various procedures have been developed employing a range of metals/metal salts such as: Zn, Et_2Zn, Et_3B, SnX_2, $Et_2AlSnBu_3$, SmI_2, In, InX_n.[4] Particularly appealing is the use of indium in these processes[5] as the metal has a low oxidation potential, is not affected by water or alkali, does not form oxides when exposed to air and is non - toxic.[6] Consequently, it is being increasingly used in transmetallation processes involving Pd.

π–Allylpalladium(II) intermediates can be generated in different ways, most frequently from dienes, allenes and allyl acetates or related compounds. The advantage of the former two protocols is that they permit concomitant regioselective addition of further functionality as illustrated by **Scheme 1** for allene.



Scheme 1

The π–allylpalladium(II) intermediates undergo a reductive transmetallation in presence of indium, creating an allylindium and regenerating the Pd(0)-catalyst.

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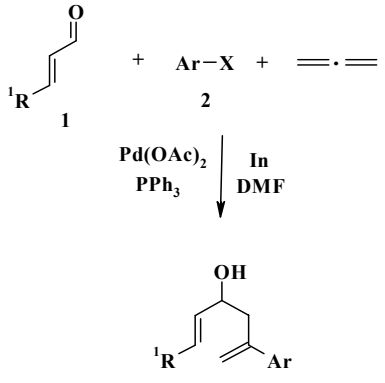
The *in situ* formed organoindium intermediate reacts with an electrophilic multiple bond to afford the final product. The process outlined in **Scheme 1** has proved to be very efficient and has been applied in stereoselective synthesis of amines[7] and both α– and β–aminoacids[8]. Recently we have shown that additives, such as secondary amines, CuI or ascorbic acid have a beneficial effect on cascades involving allene/ArX as allyl precursors by shortening the reaction time for some less reactive electrophilic multiple bonds and increasing the yields.[9]

In this paper we discuss further extensions of this methodology.

2. Results and discussion

1,2-Allylation of α,β–unsaturated aldehydes is synthetically useful transformation, which generates unsaturated secondary alcohols, **Scheme 2**. It suffers, in particular, from a lack of readily available allylating reagents with C(2) substituents. The allene/aryl or vinyl halide strategy overcomes this difficulty. The 1,5-diene products **3** potentially may undergo 3,3-sigmatropic rearrangement to afford δ–unsaturated aldehydes, providing further diversity and synthetic oportunities.[10]



Scheme 2

The allylation processes, outlined in **Scheme 2**, were studied under our typical conditions employing $Pd(OAc)_2/PPh_3$ as a catalytic system and 1.5 mol equivalents of In. Current evidence supports the involvement of In(I) allyl species[11] which requires two equivalents of In(0) for the reduction of Pd(II) to Pd(0) and the detail of this process is unclear.[12] All reactions were carried out in a Schlenk flask, using DMF as a solvent, at 85°C. After work-up the products were isolated by flash chromatography on silica gel.

The initial π–allyl palladium intermediate is formed *via* the oxidative addition of Pd(0) to the aryl halide followed by regioselective reaction with allene. The following step, the reductive transmetallation involving indium, generates the allylindium species and concomitantly regenerates Pd(0). The nucleophilic allylindium reacts by 1,2-addition to the α,β-unsaturated aldehyde to afford **3** in 61-76% yield (**Table 1**). The observed regioselectivity is in accordance with the general reactivity of allylindium intermediates, which favour 1,2- over 1,4- addition. The latter pathway has been observed in the case of highly activated double bonds[13a] or when tetraorganoindium ate complexes are employed as reactants.[13b] In addition, formal 1,4-addition was observed when Me_2S and TBSOTf were used as coreactants.[13c] The reaction cascade depicted by **Scheme 2** and **Table 1** does not seem to be significantly affected by the electronic properties of the reactants. Thus, both, β–alkyl and β–aryl enones react while electron rich and electron deficient aryl halides afford products in comparable yields. The potential dehydratation of diene to the conjugated triene did not significantly interfere with the reaction.

Table 1. Allylation of α,β–unsaturated aldehydes[a]

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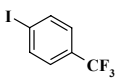
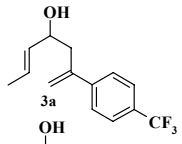
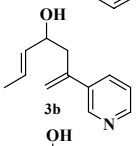
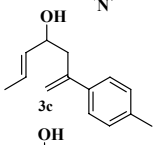
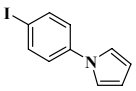
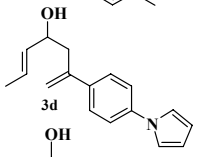
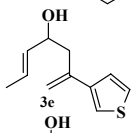
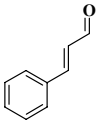
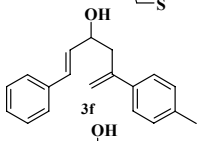
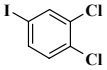
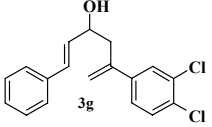
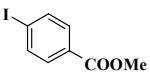
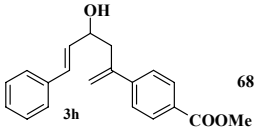
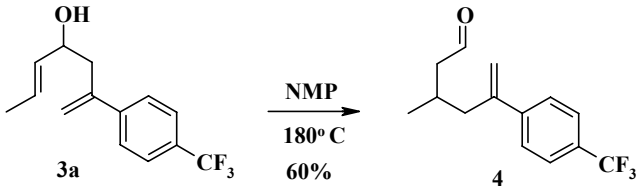
a				72
b				63
c				76
d				75
e				65
f				74
g				61
h				68

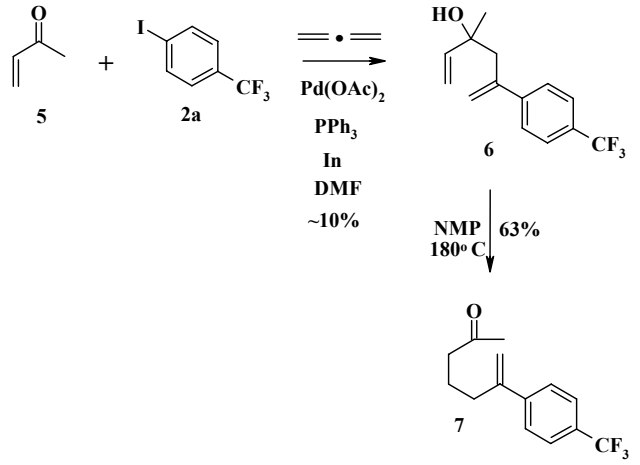
[a] reaction conditions: aldehyde 1mol equiv., aryl iodide 1mol equiv., $Pd(OAc)_2$ 10mol%, PPh_3 20 mol%, In 1.5 mol equiv., DMF, allene (Schlenk flask, 85°C, 12 h); [b] isolated yield

The potential for **3** to undergo 3,3-sigmatropic rearrangement was demonstrated using compound **3a,** which upon heating in *N*-methylpyrrolidinone (NMP) afforded unsaturated aldehyde **4** in 60% yield (**Scheme 3**).



Scheme 3

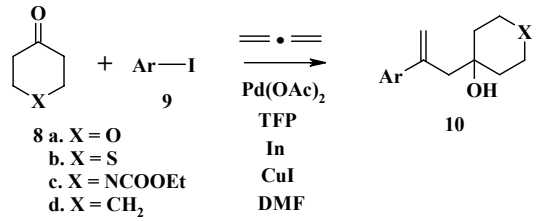
We have also attempted to use α,β-unsaturated ketones in place of aldehydes. Ketones have been used before in allylation procedures employing indium, but generally the scope of Pd/In transmetalation methodology in these processes was not fully investigated. In our hands, the use of methyl vinylketone resulted in very low conversion, (**Scheme 4**) in the absence of additives.



Scheme 4

Longer reaction time did not affect the yield significantly, neither did a range of different additives such as piperidine and CuI. However, diene **6** was shown to be more reactive in 3,3-sigmatropic rearrangement than **3a.** While yields for both reactions are comparable, under the same conditions, the reaction time is shorter for diene **6** (3 h vs 6 h, the reactions were monitored by t.l.c.). This is likely to be the result of the Thorpe-Ingold effect caused by the additional methyl substituent.[14]

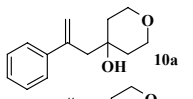
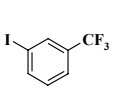
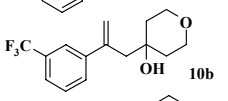
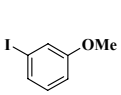
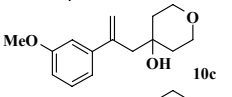
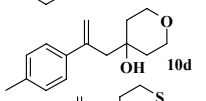
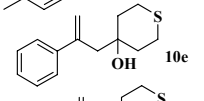
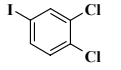
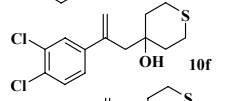
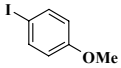
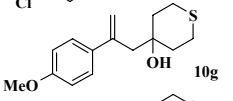
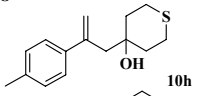
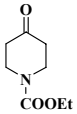
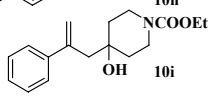
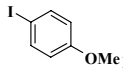
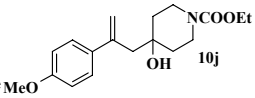
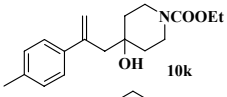
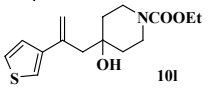
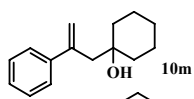
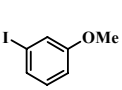
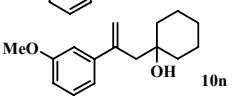
We have also investigated the reactivity of a group of 6-membered cyclic ketones to the Pd/In allylation cascade. Generally, ketones have been used in related processes but the reactivity of 2-arylallyl indium species has been little studied.



Scheme 5

A series of cyclic ketones **8** was successfully integrated into the Pd/In cascade reaction affording tertiary alcohols in moderate to good yields, **Scheme 5**, **Table 2**. Under optimized conditions, the reaction employed $Pd(OAc)_2$/TFP (trifurylphosphine) catalytic system and CuI as an additive, which is essential to obtain the products in good yields.

Table 2. Allylation of cyclic ketones[a]

Entry	Ketone **8**	Aryl halide **9**	Product	Yield(%)[b]
a				81
b				64
c				63
d				58
e				65
f				84
g				92
h				47
i				77[c]
j				61[c]
k				58[c]
l				72[c]
m				94[d]
n				88[d]

[a] Reaction conditions: aryl iodide 1.5 mol equiv., ketone 1 mol equiv., $Pd(OAc)_2$ 10 mol%, TFP 20 mol%, CuI 40 mol%, In 1.5 mol equiv., DMF, allene (Schlenk flask, 85° C, 3 h); [b] isolated yield; [c] 24 h at 85° C; [d] 19 h at 85° C

Cyclic ketones, such as cyclohexanone or heteroatom substituted cyclohexanones, afforded the products in the reaction with various aryl iodides in comparable yields.

The pyran **8a** and thiopyran **8b** reacted much faster (3 h) than cyclohexanone (19 h) or the *N*-substituted piperidone **8c** (24 h). This trend did not correlate with the IR stretching frequency or the ^{13}C chemical shift of the C=O moiety of the ketone. It is not clear which step, Pd or In promoted, is influenced by the heteroatom. If it is the latter one, the transition state may involve chelation of allyl-In by the heteroatom *via* the boat or the twisted boat conformation of the six membered ring (**Fig. 1**). This would increase the polarization of the carbonyl group making it more reactive as well as providing a lower energy, structured, transition state. Some ketones additionally activated by electron withdrawing substituents are known to be reactive in related proceses.[9] In case of the piperidone derivative this transition state would involve the carbamate oxygen rather then N-atom, creating the 8-membered chelate. Although known for many metals, these chelates are generally considered less favored than their 5- or 6-membered equivalents.[15] The coordinating ability of DMF, used as a solvent, may suppress formation of the 8-membered cyclic transition state. In addition, inspection of molecular models suggested that the keto and the carbamate oxygen are not ideally positioned to allow formation of the chelate. Alternatively, the heteroatom may help solubilising indium. This would suggest that additives other than those already studied [9] may be beneficial.[16] The observed effect remains to be studied in more detail.

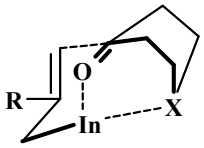


Figure 1

In conclusion, it has been shown that α,β-unsaturated aldehydes efficiently participate in the Pd/In promoted allylation processes affording exclusively products of 1,2-addition. Related unsaturated ketones are less reactive and afford the product but with a poor conversion. On the other hand cyclic saturated ketones under optimized conditions, in the presence of CuI, proved to be a good substrates for these transformations yielding the products in good yields.

3. Acknowledgement

We thank Leeds University and the Serbian Ministry of Science (grant no. 142071 and 142072) for support.

4. Experimental

General

Nuclear magnetic resonance spectra were recorded using Bruker DPX300 and DRX500 MHz spectrometers. Chemical shifts are reported in parts per million (δ) relative to the internal reference tetramethylsilane. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ at room temperature. Mass spectra were recorded using a micromass ZMD 2000 using electrospray ionisation. Infrared spectra were recorded using a Perkin-Elmer FTIR spectrometer. Microanalysis was performed using a Carlo-Erba 1108 elemental analyser. Chromatography columns were prepared using Fisher Chemicals 60A 35-70μm silica gel. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification.

General procedure for Pd/In mediated allylation of unsaturated aldehydes

Aryl iodide (1.4 mmol), aldehyde (1.4 mmol), indium powder (100 mesh, 1.5 eq.), $Pd(OAc)_2$ (0.14 mmol), PPh_3 (0.28 mmol), and DMF (10 mL) were added sequentially to a Schlenk tube which was then sealed, subjected to two freeze/pump/thaw cycles followed by the addition of allene gas (~ 1 bar). The tube was allowed to warm to rt then heated at 85 ^oC for 12 h before cooling to room temperature and venting. Et_2O (40 mL) and H_2O (10 mL) were added and the mixture was stirred for 20 min, the aqueous layer separated and extracted with Et_2O (3 x 15 mL). The combined Et_2O extracts were washed with H_2O (4 x 20 mL), the organic phase dried over $MgSO_4$, filtered and the filtrate evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO_2, petrol ether:Et_2O) to afford the product.

(E)-2-[4-(Trifluoromethyl)phenyl]hepta-1,5-dien-4-ol (3a)

Isolated as a pale yellow oil (72%).
δ_H(500 MHz): 7.59 (d, 2H, ArH), 7.52 (d, 2H, ArH), 5.62 (m, 1H, vinyl-H), 5.50 (m, 1H, vinyl-H), 5.44 (s, 1H, $=CH_2$), 5.27 (s, 1H, $=CH_2$), 4.10 (m, 1H, H-COH), 2.75 (m, 2H, CH_2 allyl), 1.56 (m, 3H, vinyl-CH_3) **δ_C(75 MHz)**: 144.50, 144.13, 133.16, 127.41, 126.63, 125.44, 125.34, 125.29, 117.24 (ArC, C=, CH_2=, CF_3), 70.88 (COH), 43.51 (CH_2), 34.39 (CH_2 allyl), 17.24 (vinyl-CH_3)**. HRMS (CI) m/z** calcd for $C_{14}H_{15}F_3O$ + Na 279.0967, found 279.096

(E)-2-(Pyridin-3-yl)hepta-1,5-dien-4-ol (3b)

Isolated as a pale yellow oil (63%).
δ_H(500 MHz): 8.65 (s, 1H, ArH), 8.52 (d, 1H, ArH), 7.70 (d, 1H, ArH), 7.27 (t, 1H, ArH), 5.63 (m, 1H, vinyl-H), 5.50 (m, 1H, vinyl-H), 5.43 (s, 1H, $=CH_2$), 5.27 (s, 1H, $=CH_2$), 4.11 (m, 1H, CH), 2.73 (m, 2H, CH_2 allyl), 1.66 (m, 3H, vinyl-CH_3) **δ_C(75 MHz)**: 149.08, 148.10, 142.63, 136.80, 133.88, 133.57, 127.77, 123.56, 117.24 (ArC, C=, CH_2=), 71.24 (COH), 43.56 (CH_2 allyl), 18.00 (vinyl-CH_3). **ν_{max} (film)/cm^{-1}**: 3348 (OH), 1673, 1628, 1415, 1026, 720. **HRMS (CI) m/z** calcd for $C_{12}H_{16}NO$ 190.1226, found 190.1231

(E)-2-*p*-Tolylhepta-1,5-dien-4-ol (3c)

Isolated as a pale yellow oil (76%).
δ_H(500 MHz): 7.29 (d, 2H, ArH), 7.15 (d, 2H, ArH), 5.61 (m, 1H, vinyl-H), 5.52 (m, 1H, vinyl-H), 5.38 (s, 1H, $=CH_2$), 5.13 (s, 1H, $=CH_2$), 4.10 (m, 1H, CH), 2.76 (m, 1H, CH_2 allyl), 2.65 (m, 1H, CH_2 allyl), 2.35 (s, 3H, CH_3Ar), 1.56 (s, 3H, vinyl-CH_3) **δ_C(75 MHz)**: 145.20,

137.99, 137.87, 133.68, 129.51, 127.30, 126.47 (ArC, C=), 115.05 (CH_2=), 70.99 (COH), 44.29 (CH_2 allyl), 21.49 (CH_3Ar), 18.05 (vinyl-CH_3). **ν_{max} (film)/cm^{-1}**: 3368 (OH), 3083 (ArH), 1625, 1513, 1447, 1030, 825**. HRMS (CI) m/z** calcd for $C_{14}H_{18}O$ + Na 225.1250, found 225.1252

(E)-2-[4-(1*H*-Pyrrol-1-yl)phenyl]hepta-1,5-dien-4-ol (3d)
Isolated as a pale yellow oil (75%) which solidified upon standing, m.p.81-82°C.
δ_H(500 MHz): 7.47 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.10 (s, 2H, ArH), 6.35 (s, 2H, ArH), 5.50 (m, 1H, vinyl-H), 5.45 (m, 1H, vinyl-H), 5.42 (s, 1H, =CH_2), 5.19 (s, 1H, =CH_2), 4.10 (m, 1H, CH), 2.76 (m, 2H, CH_2 allyl), 2.69 (m, 2H, CH_2 allyl), 1.56 (s, 3H, vinyl-CH_3) **δ_C(75 MHz)**: 144.04, 140.09, 137.93, 133.24, 127.41, 127.16, 120.27, 119.21, 115.36, 110.53 (ArC, C=C, CH_2=), 70.79 (COH), 43.70(CH_2 allyl), 17.65 (vinyl-CH_3). **HRMS (CI) m/z** calcd for $C_{17}H_{20}NO$ 254.1539, found 254.1539

(E)-2-(Thiophen-3-yl)hepta-1,5-dien-4-ol (3e)
Isolated as a pale yellow oil (65%).
δ_H(500 MHz): 7.28 (m, 3H, ArH), 5.69 (m, 1H, vinyl-H), 5.55 (m, 1H, vinyl-H), 5.48 (s, 1H, =CH_2), 5.12 (s, 1H, =CH_2), 4.24 (m, 1H, CH), 2.73 (m, 1H, CH_2 allyl), 2.59 (dd, 1H, CH_2 allyl, *J* 14.1 and 8.6 Hz), 1.56 (s, 3H, vinyl-CH_3) **δ_C(75 MHz)**: 141.95, 139.33, 133.29, 127.07, 126.62, 125.82, 120.78, 114.00, (ArC, C=C, CH_2=), 70.84 (COH), 44.07 (CH_2 allyl), 17.67 (vinyl-CH_3)**. ν_{max} (film)/cm^{-1}**: 3390 (OH), 3103, 1625, 1446, 1028, 996. **HRMS (CI) m/z** calcd for $C_{11}H_{14}OS$ + Na 217.0658, found 217.0667

(E)-1-Phenyl-5-*p*-tolylhexa-1,5-dien-3-ol (3f)
Isolated as a pale yellow oil (74%).
δ_H(500 MHz): 7.34-7.25 (m, 9H, ArH), 6.54 (d, 1H, vinyl-H, *J* 15.9 Hz), 6.21 (dd, 1H, vinyl-H, *J* 15.9 and 6.4 Hz), 5.40 (s, 1H, =CH_2), 5.17 (s, 1H, =CH_2), 4.36 (m, 1H, CH), 2.90 (m, 1H, CH_2 allyl), 2.78 (m, 1H, CH_2 allyl), 2.35 (s, 3H, CH_3Ar) **δ_C(75 MHz)**: 144.56, 137.61, 137.53, 136.78, 131.61, 130.20, 129.21, 128.53, 127.59, 126.48 126.21 (ArC, C=), 115.06 (CH_2=), 70.66 (COH), 44.00 (CH_2 allyl), 21.11 (CH_3Ar) **ν_{max} (film)/cm^{-1}**: 3368 (OH), 3082 (ArH), 3025, 1513, 1448, 966, 825. **HRMS (CI) m/z** calcd for $C_{19}H_{20}O$ + Na 287.1406, found 287.1400

(E)-5-(3,4-Dichlorophenyl)-1-phenylhexa-1,5-dien-3-ol (3g)
Isolated as a pale yellow oil (61%).
δ_H(500 MHz): 7.50 (s, 1H, ArH), 7.40 (d, 1H, ArH), 7.32 (m, 5H, ArH), 7.23 (d, 1H, ArH), 6.52 (d, 1H, vinyl-H, *J* 15.9 Hz), 6.18 (dd, 1H, vinyl-H, *J* 15.9 and 6.6 Hz), 5.41 (s, 1H, =CH_2), 5.26 (s, 1H, =CH_2), 4.34 (m, 1H, CH), 2.78 (m, 2H, CH_2 allyl) **δ_C(75 MHz)**: 142.83, 140.89, 136.45, 132.64, 131.64, 131.21, 130.75, 130.37, 128.61, 128.35, 127.82, 126.49, 125.68 (ArC, C=), 117.18 (CH_2=), 70.91 (COH), 43.47 (CH_2 allyl), 21.11 (CH_3Ar). **ν_{max} (film)/cm^{-1}**: 3368 (OH), 3083 (ArH), 1473, 1028, 966. **HRMS (CI) m/z** calcd for $C_{18}H_{16}{}^{35}Cl_2O$ + Na 341.0470, found 341.0465

(E)-Methyl 4-(4-hydroxy-6-phenylhexa-1,5-dien-2-yl)benzoate (3h)
Isolated as a pale yellow oil (68%).
δ_H(500 MHz): 8.01 (d, 2H, ArH), 7.50 (d, 2H, ArH), 7.30 (m, 5H, ArH), 6.52 (d, 1H, vinyl-H, *J* 15.9 Hz), 6.19 (dd, 1H, vinyl-H, *J* 15.9 and 6.6 Hz), 5.50 (s, 1H, =CH_2), 5.31 (s, 1H, =CH_2), 4.34 (m, 1H, CH), 3.92 (s, 3H, CH_3), 2.87 (m, 2H, CH_2 allyl) **δ_C(75 MHz)**: 166.84 (C=O ester), 145.26, 144.09, 136,55, 131.32, 130.62, 129.33, 128.57, 127.74, 126.48, 126.33, (ArC, C=), 117.53 (CH_2=), 70.90 (COH), 52.12 (CH_3-O), 43.61 (CH_2 allyl). **ν_{max} (film)/cm^{-1}**: 3424 (OH), 1720 (C=O ester), 1607, 1435, 1281, 1118, 966. **HRMS (CI) m/z** calcd for $C_{20}H_{20}O_3$ + Na 331.1305, found 331.1303

3-Methyl-5-[4-(trifluoromethyl)phenyl]hexa-1,5-dien-3-ol (6)
Isolated as a pale yellow oil (10%).
δ_H(500 MHz): 7.56 (d, 2H, ArH), 7.47 (d, 2H, ArH), 5.78 (dd, 1H, vinyl-H, *J* 17.2 and 10 Hz), 5.43 (s, 1H, =CH_2), 5.25 (s, 1H, =CH_2), 5.12 (d, 1H, =CH_2, *J* 17.2 Hz), 4.89 (d, 1H, =CH_2, *J* 10 Hz), 2.81 (q, 2H, CH_2), 1.22 (s, 3H, CH_3). **HRMS (CI) m/z** calcd for $C_{14}H_{15}F_3O$ + Na 279.0967, found 279.0949

General procedure for 3,3-sigmatropic rearrangement
Unsaturated alcohol (0.18mmol) was dissolved in N-methyl pyrrolidinone (3mL) and the mixture heated at 180°C (oil bath temperature) under N_2 atmosphere. The reaction was monitored by t.l.c. and when completed the mixture was allowed to cool to room temperature. Et_2O (20mL) was then added and the mixture washed with H_2O (3 x 5mL). The ethereal layer was dried over $MgSO_4$, filtered and the filtrate evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO_2, petrol ether:Et_2O) to afford the product.

3-Methyl-5-phenylhex-5-enal (4)
Isolated as a pale yellow oil (60%).
δ_H(500 MHz): 9.70 (s, 1H, H-CO), 7.59 (d, 2H, ArH), 7.50 (d, 2H, ArH), 5.38 (s, 1H, =CH_2) 5.17 (s, 1H, =CH_2), 2.61 (m, 1H, CH), 2.43 (m, 2H, CH_2-CO), 2.27 (m, 1H, CH_2 allyl), 2.13 (m, 1H, CH_2 allyl), 0.94 (d, 3H, CH_3).**HRMS (CI) m/z** calcd for $C_{14}H_{15}F_3O$ + Na 279.0967, found 279.0977

6-Phenylhept-6-en-2-one (7)
Isolated as a pale yellow oil (63%).
δ_H(500 MHz): 7.58 (d, 2H, ArH), 7.49 (d, 2H, ArH), 5.36 (s, 1H, =CH_2) 5.16 (s, 1H, =CH_2), 2.52 (m, 2H, CH_2 CO), 2.45 (m, 1H, CH_2 allyl), 2.12 (s, 3H, CH_3), 1.58 (m, 2H, CH_2) **δ_C(75 MHz**): 208.43 (C=O), 146.78, 144.50, 126.43, 125.36, 125.30, 125.25, 114.74, (ArC, C=, CH_2=, CF_3), 42.71 (CH_2CO), 34.39 (CH_2 allyl), 29.99 (CH_3-CO), 22.04 (CH_2). **HRMS (CI) m/z** calcd for $C_{14}H_{15}F_3O$ + Na 279.0967, found 279.0969

General procedure for Pd/In mediated allylation of cyclic ketones

Aryl iodide (1.5 mol eq.), cyclic ketone (1 mol equiv.), indium powder (100 mesh, 1.5 mol equiv.), $Pd(OAc)_2$ (0.1 mol equiv.), TFP (0.2 mol equiv.), CuI (0.4 mol equiv.) and DMF (AR, 10 mL/mmol) were added sequentially to a Schlenk tube which was then sealed, subjected to two freeze/pump/thaw cycles followed by the addition of allene gas (~ 1 bar). The tube was allowed to warm to rt then heated at 85 ^oC for 3-24 h (see **Table 2**) before cooling to room temperature and venting. Ether (20 mL) and H_2O (10 mL) were then added and the mixture stirred for 20 min, the aqueous layer separated and extracted with ether (3 x 15 mL) and the combined ether extracts washed with H_2O (4 x 20 mL). The organic phase was dried over $MgSO_4$, filtered and the filtrate evaporated to dryness. The crude residue was purified by column chromatography to afford the alcohol.

4-(2-Phenylprop-2-en-1-yl)tetrahydro-2*H*-pyran-4-ol (10a)

Purified by column chromatography (EtOAc, SiO_2) to afford the product as a colourless oil (81 %).

$C_{14}H_{18}O_2$ Found: C, 77.05; H, 8.5 %, Required: C, 77.03; H, 8.3 %. **δ_H(500 MHz):** 7.42 (d, 2H, ArH, *J* 7.3 Hz), 7.34 (t, 2H, ArH, *J* 7.3 Hz), 7.29 (d, 1H, ArH, *J* 7.3 Hz), 5.42 (s, 1H, 1a-H), 5.17 (s, 1H, 1b-H), 3.68 (dd, 3H, 3,5 pyran-H, *J* 4.2 and 2.3 Hz), 3.66 (d, 1H, 5 pyran-H, *J* 2.3 Hz), 2.76 (s, 2H, 3-H), 1.61 (ddd, 2H, 2-pyran-H, *J* 14.0, 6.4 and 3.4 Hz), 1.42 (s, 1H, OH) and 1.36 (dd, 2H, 6-pyran-H, *J*, 14.0 and 2.3 Hz). **δ_C(75 MHz):** 144.81, 129.03, 128.21 and 126.84 (ArC), 118.20 (CH_2), 69.16, 64.20 (CH_2), 48.85 (CH_2) and 38.53 (CH_2). **ν_{max}(film)/cm^{-1}:** 3417 (OH), 3076 (ArH), 2951 and 2862 (CH), 1621 (Ar), 1599, 1572, 1492. **m/z (ES$^+$, %):** 242 ([M+Na], 93), 218 ([M+H], 8), 201 ([M-OH], 100).

4-[2-(3-Trifluoromethylphenyl)prop-2-en-1-yl] tetrahydro-2*H*-pyran-4-ol (10b)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as colourless prisms (64 %), mp 39–41 °C.

$C_{15}H_{16}F_3O_2$ Found: C, 62.65; H, 5.9 %, Required: C, 62.93; H, 5.9 %. **δ_H(500 MHz):** 7.66 (s, 1H, 2-ArH), 7.60 (d, 1H, 6-ArH, *J* 7.7 Hz), 7.54 (d, 1H, 4-ArH, *J* 7.7 Hz), 7.45 (t, 1H, 5-ArH, *J* 7.7 Hz), 5.49 (s, 1H, 1a-H), 5.27 (s, 1H, 1b-H), 3.67 (d, 4H, 3,5-pyran-H, *J* 7.7 Hz), 2.77 (s, 2H, 3-H), 1.64 (dt, 2H, 2,6-pyran-H, *J* 13.6 and 7.7 Hz), 1.38 (s, 1H, OH) and 1.35 (s, 2H, 2,6-pyran-H). **δ_C(75 MHz):** 143.59 and 143.46 (ArC), 119.82 (CH_2), 69.25, 64.06 (CH_2), 48.77 (CH_2), 38.44 (CH_2). **ν_{max}(film)/cm^{-1}:** 3427 (OH), 3082 (ArH), 2953 and 2869 (CH), 1626 (Ar), 1489. **m/z (ES$^+$, %):** 310 ([M+Na], 93), 269 ([M-OH], 100).

4-[2-(3-Methoxyphenyl)prop-2-en-1-yl]tetrahydro-2*H*-pyran-4-ol (10c)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as a colourless oil (63 %).

$C_{15}H_{20}O_3$ Found: C, 72.25; H, 8.05 %, Required: C, 72.55; H, 8.12 %. **δ_H(500 MHz);** 7.25 (t, 1H, 5-ArH, *J* 7.9 Hz), 6.99 (d, 1H, 6-ArH, *J* 7.9 Hz), 6.94 (s, 1H, 2-ArH), 6.82 (dd, 1H, *J* 4-ArH, *J* 7.9 and 2.2 Hz), 5.43 (s, 1H, 1a-H), 5.16 (s, 1H, 1b-H), 3.82 (s, 3H, OCH_3), 3.67 (s, 4H, 3,5-pyran-H), 2.73 (s, 2H, 3-H), 1.62 (dd, 1H, 2-pyran- H, *J* 10.2 and 3.4 Hz) 1.60 (dd, 1H, 6-pyran-H, *J* 6.6 and 3.4 Hz), 1.48 (s, 1H, OH) and 1.37 (d, 2H, 2,6-pyran-H, *J* 13.5 Hz). **δ_C(75 MHz);** 160.10, 144.69, 144.08, 130.03, 119.32, and 113.22 (ArC), 112.90 (CH_2), 69.16, 64.19 (CH_2), 55.65 (CH_3), 48.94 (CH_2) and 38.45 (CH_2). **ν_{max}(film)/cm^{-1}**; 3425 (OH), 3081 (ArH), 2951 and 2866 (CH), 1598, 1579, 1487, 1465, 1427. **m/z (ES$^+$, %);** 349 ([M+H], 10), 231 ([M-OH], 35).

4-[2-(4-Methylphenyl)prop-2-en-1-yl]tetrahydro-2*H*-pyran-4-ol (10d)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as a colourless oil (55 %).

$C_{15}H_{20}O_2$ Found: C, 77.55; H, 8.68 %, Required: C, 77.15; H, 8.60 %. **δ_H(500 MHz);** 7.23 (d, 2H, 2,6-ArH, *J* 7.9 Hz), 7.06 (d, 2H, 3,5-ArH, *J* 7.9 Hz), 5.32 (s, 1H, 1a-H), 5.04 (s, 1H, 1b-H), 3.60-3.58 (m, 4H, 3,5-pyran-H), 2.66 (s, 2H, 3-H), 2.27 (s, 3H, CH_3), 1.52 (ddd, 2H, 2,6-pyran-H, *J* 14.0, 10.3 and 6.5 Hz), 1.43 (s, 1H, OH) and 1.29 (d, 2H, 2,6-pyran-H, *J* 13.9 Hz). **δ_C(75 MHz);** 143.13, 138.12, 136.52, 128.24, 125.26, 115.96 (CH_2), 67.64, 62.72 (CH_2), 47.36 (CH_2), 37.01 (CH_2) and 20.06. **ν_{max}(film)/cm^{-1};** 3428 (OH), 3084 (ArH), 2952 and 2868 (CH), 1622 (Ar), 1512, 1467. **m/z (ES$^+$, %);** 218 ([M+(H-Me)], 86), 177 ([M-(Me+OH)], 100).

4-(2-Phenylprop-2-en-1-yl)tetrahydro-2*H*-thiopyran-4-ol (10e)

Purified by column chromatography (9:1 v/v hexane : EtOAc, SiO_2) to afford the product as a colourless oil (65%).

$C_{14}H_{18}OS$ Found: C, 72.00; H, 7.65; S, 13.75 %, Required: C, 71.75; H, 7.74; S, 13.68 %. **δ_H(500 MHz);** 7.39 (d, 2H, ArH, *J* 7.5 Hz), 7.33 (t, 2H, ArH, *J* 7.5 Hz), 7.28 (d, 1H, ArH, *J* 7.5 Hz), 5.41 (d, 1H, 1a-H, *J* 1.1 Hz), 5.14 (s, 1H, 1b-H), 2.93 (td, 2H, 3,5-thiopyran-H, J_{axax} 18.8, J_{gem} 13.7 and J_{axeq} 1.8 Hz), 2.70 (s, 2H, 3-H), 2.35 (d, 2H, 3,5-thiopyran-H, J_{gem} 13.7 Hz), 1.77 (d, 2H, 2,6- thiopyran-H, J_{gem} 14.0 Hz), 1.65 (td, 2H, 2,6- thiopyran-H, J_{gem} 14.0, J_{axax} 11.7 and J_{axeq} 3.4 Hz) and 1.32 (s, 1H, OH). **δ_C(75 MHz);** 143.18, 141.02, 127.76 and 125.36 (ArC), 117.02 (CH_2), 68.65, 47.68(CH_2), 37.62(CH_2) and 23.50(CH_2). **ν_{max}(film)/cm^{-1};** 3444 (OH), 3079 and 3049 (ArH), 3021, 2929 and 2851 (CH), 1709, 1602 (Ar), 1596, 1573, 1493. **m/z (EI, %);** 234 ([M], 100).

4-[2-(3,4-Dichlorophenyl)prop-2-en-1-yl]tetrahydro-2*H*-thiopyran-4-ol (10f)

Purified by column chromatography (1 : 1 v/v hexane : Et_2O , SiO_2) to afford the product as yellow prisms (84 %), mp 44-45 ^oC.

$C_{14}H_{16}Cl_2OS$ Found: C, 55.35; H, 5.15; S, 10.30 %, Required: C, 55.45; H, 5.32; S, 10.57 %. **δ_H(500 MHz);** 7.49 (d, 1H, 2-ArH, *J* 2.0 Hz), 7.40 (t, 1H, 5-ArH, *J* 8.3 Hz), 7.24 (dd, 1H, 6-ArH, *J* 8.3 and 2.0 Hz), 5.44 (d, 1H, 1a-H, *J* 1.1 Hz), 5.20 (s, 1H, 1b-H), 2.92 (td, 2H, 3,5-thiopyran-H, J_{gem} 13.9, J_{axax} 11.9 and J_{axeq} 2.4 Hz), 2.66 (s, 2H, 3-H), 2.33 (d, 2H, 3,5- thiopyran-H, J_{gem} 13.9 Hz), 1.76 (d, 2H, 2,6- thiopyran-H, J_{gem} 13.9 Hz), 1.64 (td, 2H, 2,6- thiopyran-H, J_{gem} 13.9, J_{axax} 11.8 and J_{axeq} 3.4 Hz) and 1.22 (s, 1H, OH). **δ_C(75 MHz);** 142.70, 142.59, 130.87, 128.67 and 126.08 (ArC), 119.89 (CH_2), 70.28 (CH_2), 49.07 (CH_2), 39.11 (CH_2) and 24.49. **ν_{max}(film)/cm^{-1};** 3429 (OH), 3082 (ArH), 2929 and 2846 (CH), 1648, 1618, 1602, 1547, 1474.**m/z (EI, %);** 306 ([(^{37}Cl)M], 14), 304 ([(^{35}Cl) + (^{37}Cl) M], 73), 302 ([(^{35}Cl)M], 100)

4-[2-(4-Methoxyphenyl)prop-2-en-1-yl]tetrahydro-2*H*-thiopyran-4-ol (10g)

Purified by column chromatography (1:1 v/v hexane : Et_2O, SiO_2) to afford the product as a yellow oil (92%). **$C_{15}H_{20}O_2S$** Found: C, 68.15; H, 7.70; S, 12.90 %, Required: C, 68.14; H, 7.62; S, 12.13 %. **δ_H(500 MHz);** 7.34 (d, 2H, 2,6-ArH, *J* 8.7 Hz), 6.86 (d, 2H, 3,5-ArH, *J* 8.7 Hz), 5.35 (d, 1H, 1a-H, *J* 1.1 Hz), 5.06 (s, 1H, 1b-H), 3.82 (s, 3H, OCH_3), 2.91 (td, 2H, 3,5-thiopyran-H, J_{gem} 13.7, J_{axax} 11.9 and J_{axeq} 2.1 Hz), 2.68 (s, 2H, 3-H), 2.32 (d, 2H, 3,5- thiopyran-H, J_{gem} 13.7 Hz), 1.78 (d, 2H, 2,6-thiopyran-H, J_{gem} 13.9 Hz), 1.63 (td, 2H, 2,6- thiopyran-H, J_{gem} 13.9, J_{axax} 11.8 and J_{axeq} 3.3 Hz) and 1.38 (s, 1H, OH). **δ_C(75 MHz);** 159.72, 143.93, 134.76 and 116.85 (ArC), 114.36 (CH_2), 70.09, 55.70 (CH_3), 49.12 (CH_2), 39.18 (CH_2) and 24.62(CH_2). **ν_{max}(film)/cm^{-1};** 3450 (OH), 3076 (ArH), 2932 and 2835 (CH), 1607 (Ar), 1572, 1511, 1441. **m/z (ES$^+$, %);** 265 ([M+H], 100), 249 ([M-OH], 43).

4-[2-(4-Methylphenyl)prop-2-en-1-yl]tetrahydro-2*H*-thiopyran-4-ol (10h)

Purified by column chromatography (1:1 v/v hexane : Et_2O, SiO_2) to afford the product as a yellow oil (47 %).
$C_{15}H_{20}OS$ Found: C, 72.5; H, 8.1; S, 12.75 %, Required: C, 72.5; H, 8.1; S, 12.91 %. **δ_H(500 MHz);** 7.29 (d, 2H, 2,6-ArH, *J* 8.0 Hz), 7.14 (d, 2H, 3,5-ArH, *J* 8.0 Hz), 5.38 (d, 1H, 1a-H, *J* 1.1 Hz), 5.09 (s, 1H, 1b-H), 2.90 (td, 3,5-thiopyran-H, J_{gem} 14.3, J_{axax} 11.4 and J_{axeq} 2.4 Hz), 2.69 (s, 2H, 3-H), 2.34 (s, 3H, CH_3), 2.30 (d, 2H, 3,5-H, J_{gem} 14.3 Hz), 1.77 (d, 2H, 2,6-H, J_{gem} 14.0 Hz), 1.63 (td, 2H, 2,6-H, J_{gem} 14.0, J_{axax} 11.7 and J_{axeq} 3.3 Hz) and 1.36 (s, 1H, OH). **δ_C(75 MHz);** 144.10, 139.14, 137,65, 129.33 and 126.29 (ArC), 117.18 (CH_2), 69.69, 48.71 (CH_3), 38,77 (CH_2), 24.26 (CH_2) and 21.06 (CH_2). **ν_{max}(film)/cm^{-1};** 3453 (OH), 3082 and 3021 (ArH), 2920 and 2851 (CH), 1709, 1651, 1620, 1563. **m/z (ES$^+$, %);** 249 ([M+H], 71).

Ethyl 4-hydroxy-4-(2-phenylprop-2-en-1-yl)piperidine-1-carboxylate (10i)

Purified by column chromatography (1:1 v/v hexane : Et_2O, SiO_2) to afford the product as a yellow oil (77 %).

$C_{17}H_{23}NO_3$ Found: C, 70.30; H, 7.90 ; N, 4.85 %, Required: C, 70.56; H, 8.01; N, 4.84 %. **δ_H(500 MHz);** 7.39 (d, 2H, 2,6-PhH, *J* 7.1 Hz), 7.33 (t, 2H, 3,5-PhH, *J* 7.1 Hz), 7.27 (t, 1H, 4-PhH, *J* 7.1Hz), 5.42 (d, 1H, 1a-H, *J* 1.5 Hz), 5.15 (s, 1H, 1b-H), 4.08 (q, 2H, C*H*$_2$CH$_3$, *J* 7.1 Hz), 3.77 (bs rotamer, 2H, 2-piperidine-H), 3.08 (bs rotamer, 2H, 6- piperidine-H), 2.73 (s, 2H, 3-H), 1.53 (s, 1H, OH), 1.43 (s, 4H, 3,5-piperidine-H) and 1.22 (t, 3H, CH$_2$C*H*$_3$, *J* 7.1 Hz). **δ_C(75 MHz);** 155.87 (C=O), 144.78, 142.48, 129.00, 128.15 and 126.79 (ArC), 118.25 (CH_2), 69.87, 48.59 (CH_2), 40.17 (CH_3), 37.46 (CH_2) and 15.10 (CH_2). **ν_{max}(film)/cm^{-1};** 3435 (OH), 3076 and 3054 (ArH), 2978, 2949, 2917 and 2873 (CH), 1674 (C=O), 1624, 1572, 1472. **m/z (ES$^+$, %);** 580 (dimer), 290 ([M-H], 76), 272 ([M-OH], 100).

Ethyl 4-hydroxy-4-[2-(4-methoxyphenyl)prop-2-en-1-yl)piperidine-1-carboxylate (10j)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as a yellow oil (61 %).
$C_{18}H_{25}NO_4$ Found: C, 67.55; H, 7.70 ; N, 4.50 %, Required: C, 67.69; H, 7.89; N, 4.39 %. **δ_H(500 MHz);** 7.39 (d, 2H, 2,6-ArH, *J* 7.1 Hz), 7.33 (t, 2H, 3,5-ArH, *J* 7.1 Hz), 5.42 (d, 1H, 1a-H, *J* 1.5 Hz), 5.15 (s, 1H, 1b-H), 4.09 (q, 2H, C*H*$_2$CH$_3$, *J* 7.1 Hz), 3.81 (s, 3H, OCH_3 and 2H, 2,6-piperidine-H), 3.08 (bs rotamer, 2H, 2,6-piperidine-H), 2.70 (s, 2H, 3-H), 1.50 (s, 1H, OH), 1.43 (s, 4H, 3,5-piperidine-H) and 1.22 (t, 3H, CH$_2$C*H*$_3$, *J* 7.1 Hz). **δ_C(75 MHz);** 159.71, 155.88 (C=O), 144.02, 134.68, 127.95 and 116.68 (ArC), 114.34 (CH_2), 69.83, 61.56 (CH_2), 55.67, 48.54 (CH_2), 43.42, 40.20, 37.56 (CH_2) and 15.10. **ν_{max}(film)/cm^{-1}**; 3443 (OH), 3082 (ArH), 2983, 2953 and 2838 (CH), 1678 (C=O), 1607 (Ar), 1573, 1467, 1440, 1352. **m/z (ES$^+$, %);** 320 ([M+H], 53), 302 ([M-OH], 54).

Ethyl 4-hydroxy-4-[2-(2-thienyl)prop-2-en-1-yl) piperidine-1-carboxylate (10l)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as a yellow oil (72 %).
$C_{15}H_{21}NO_4S$ Found: C, 61.2; H, 7.0; N, 4.6 %, Required: C, 61.0; H, 7.2; N, 4.7 %. **δ_H(500 MHz);** 7.18 (d, 1H, thienyl 5-H, *J* 5.1 Hz), 7.06 (d, 1H, thienyl 3-H, *J* 3.7 Hz), 6.96 (t, 1H, thienyl 4-H, *J* 5.1 and 3.7 Hz), 5.57 (s, 1H, 1a-H), 5.02 (s, 1H, 1b-H), 4.08 (q, 2H, C*H*$_2$CH$_3$, *J* 7.1 Hz), 3.86 (bs rotamer, 2H, 2-piperidine-H), 3.11 (bs rotamer, 2H, piperidine 6-H), 2.67 (s, 2H, 3-H), 1.66 (s, 1H, OH), 1.53 (s, 4H, 3,5-piperidine-H) and 1.24 (t, 3H, CH$_2$C*H*$_3$, *J* 7.1 Hz). **δ_C(75 MHz);** 155.90 (C=O), 146.20, 137.36, 127.96, 125.35 and 124.98, 116.20 (CH_2), 69.69 (CH_2), 61.62, 48.94 (CH_2), 43.41, 40.18, 37.38 (CH_2), 15.10. **ν_{max}(film)/cm^{-1};** 3433 (OH), 3104 and 3082 (ArH), 2978, 2923 and 2873 (CH), 2241, 1674 (C=O), 1613, 1472, 1385, 1352. **m/z (ES$^+$, %);** 296 ([M+H], 86), 278 ([M-OH], 46).

Ethyl 4-hydroxy-4-[2-(4-methylphenyl)prop-2-en-1-yl)piperidine-1-carboxylate (10k)

Purified by column chromatography (Et_2O, SiO_2) to afford the product as a yellow oil (58 %).

$C_{18}H_{25}NO_3$ Found: C, 71.1; H, 8.2; N, 4.45 %, Required: C, 71.2; H, 8.3; N, 4.62 %. **δ_H(500 MHz);** 7.22 (d, 2H, 2,6-ArH, *J* 8.0 Hz), 7.06 (d, 2H, 3,5-ArH, *J* 8.0 Hz), 5.31 (s, 1H, 1a-H), 5.03 (s, 1H, 1b-H), 4.01 (q, 2H, CH_2CH_3, *J* 7.1 Hz), 3.71 (bs rotamer, 2H, 2-piperidine-H), 3.00 (bs rotamer, 2H, 6-piperidine-H), 2.64 (s, 2H, 3-H), 2.27 (s, 3H, CH_3), 1.45 (s, 1H, OH), 1.36 (s, 4H, 3,5-piperidine-H) and 1.15 (t, 3H, CH_2CH_3, *J* 7.1 Hz). **δ_C(75 MHz);** 155.90 (C=O), 146.20, 137.36, 127.96, 125.35 and 124.98 (ArC), 116.20 (CH_2), 69.69, 61.62(CH_2), 48.94 (CH_2), 43.41, 40.18, 37.38 (CH_2) and 15.10. **ν_{max}(film)/cm^{-1};** 3433 (OH), 3104, 3082 (ArH), 2978, 2923 and 2873 (CH), 1674 (C=O), 1613, 1472, 1385. **m/z (ES, %);** 304 ([M+H], 33), 286 ([M-OH], 100).

1-(2-Phenylprop-2-en-1-yl)cyclohexanol (10m)
Purified by column chromatography (8:2 v/v hexane:EtOAc, SiO_2) to give the product as a yellow oil (88 %).
$C_{15}H_{20}O$ Found: C, 83.05; H, 9.6 %, Required: C, 83.29; H, 9.3 %. **δ_H(300 MHz);** 7.43 -7.27 (m, 5H, PhH), 5.38 (d, 1H, 1a-H, *J* 1.8 Hz), 5.14 (d, 1H, 1b-H, *J* 0.8 Hz), 2.73 (s, 2H, 3-H) and 1.58-1.13 (m, 11H, cyclohexane-H and OH). **δ_C(75 MHz);** 145.74, 143.03, 128.83, 127.89 and 126.91, 117.76 (CH_2), 71.76 (CH), 48.13 (CH_2), 38.26 (CH_2), 26.12 (CH_2), 22.55 (CH_2). **ν_{max}(film)/cm^{-1}**; 3434 (OH), 2931 and 2857 (CH) , 1623, 1598 and 1576 (ArC), 1429, 1446. **m/z (ES$^+$, %);** 199 ([M-OH], 56 %).

1-(2-(3-Methoxyphenyl)-prop-2-en-1-yl)cyclohexanol (10n)
Purified by column chromatography (9:1 v/v hexane:EtOAc, SiO_2) to give the product as a yellow oil (216 mg, 94 %).
$C_{16}H_{22}O_2$ Found: C, 77.8; H, 9.0 %, Required: C, 78.0; H, 9.0 %. **δ_H(500 MHz);** 7.24 (t, 1H, 5-ArH, *J* 7.9 Hz), 7.00 (d, 1H, 6-ArH, *J* 7.9 Hz), 6.95 (t, 1H, 2-ArH, *J* 2.2 Hz), 6.81 (dd, 1H, 4-ArH, *J* 7.9 and 2.2 Hz), 5.38 (d, 1H, 1a-H, *J* 1.7 Hz), 5.14 (s, 1H, 1b-H), 3.81 (s, 3H, CH_3), 2.70 (s, 2H, 3-H), 1.54-1.33 (m, 9H, cyclohexane-H), 1.39 (s, 1H, OH) and 1.28 (d, 1H, cyclohexanol-H, *J* 10.3 Hz). **δ_C(75 MHz);** 159.98, 145.62, 144.61 and 129.81 (ArC), 119.44 (CH_2), 117.88, 113.00 and 112.92 (ArC), 71.75 (CH), 55.64 (CH_3), 48.24 (CH_2), 38.21 (CH_2), 26.12 (CH_2) and 22.56 (CH_2). **ν_{max}(film)/cm^{-1};** 3435 (OH), 2935 and 2858 (CH), 1598, 1576, 1489, 1449, 1238. **m/z (ES$^+$, %);** 230 ([M –OH]$^+$, 22), 278 ([M-OH], 97).

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