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Graphical Abstract

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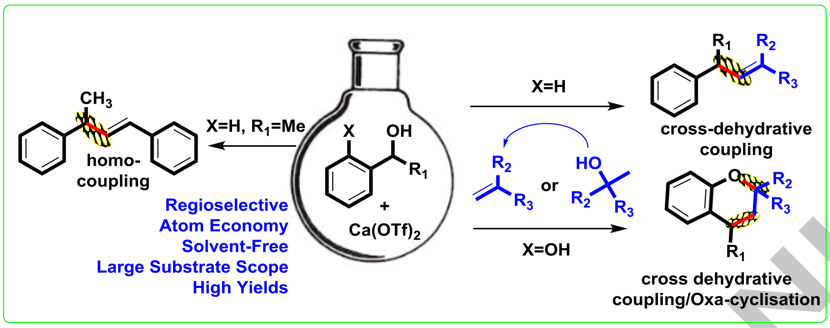

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Calcium(II) Catalyzed Regioselective Dehydrative Cross-Coupling Reactions: Practical Synthesis of internal alkenes and benzopyrans

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ABSTRACT

A simple and operationally easy protocol for the regioselective synthesis of internal alkenes through a dehydrative cross-coupling and direct coupling procedure has been described using the environmentally benign Ca(II) catalyst. Several alkenes and alcohols underwent the coupling reaction under solvent-free conditions in a short time to produce the desired alkenes. This method is further extended to show the application in the synthesis of novel benzopyran molecules through a cascade strategy.

Carbon-carbon bond formation by direct coupling of alkenes with other partners (alcohols/alkenes) is attracting many of the synthetic chemists owing to the atom efficiency and environmentally benign as water is the only byproduct.[1] However, the major challenge in this method is to activate the hydroxyl group which is not known to be a good leaving group.[2] One of the oldest direct cross coupling methods between 9-fluorenol and 9-alkylidene fluorenes has been reported 65 years ago.[3] Since then many transition metals catalyzed reactions have been developed.[4-6.] For example recently, Yamamoto *et al.*[5a] reported a Pd(II) catalyzed cross coupling of alkenes with alcohols and Ji *et al.*[5b] reported an efficient reaction with TfOH but the solvent was 1,2-dibromoethane. Liu *et al.*[5c] reported another interesting reaction of alcohols with alkenes in dichloromethane using $FeCl_3$ and stoichiometric amount of TsOH. Similarly many reports are available for the transition metal catalyzed dimerization of alkenes, such as Co(II)/Zn,[6a] $Pd(OAc)_2$/diazonium salt/$BmimPF_6$,[6b] $Pd(OAc)_2$-HFIP,[6c] $Pd(OAc)_2$/TFA[6d] and many others.[7] Nevertheless, most of these direct cross-coupling/homo-coupling methods are inevitably associated with some of the problems such as the use of expensive and readily-non available catalysts, use of stoichiometric amounts of catalysts, halogenated solvents etc. Hence there is still a high demand for the development of user-friendly and environmentally friendly methods to make sp^3-sp^2 C-C bonds (Figure 1) from sp^3-sp^3 or sp^3-sp^2 or sp^2-sp^2 C-C bond forming reactions. In this context herein, we report a user-friendly and a solvent free method for the formation of new C-C bonds (sp^3-sp^2) starting from easily available alcohols and alkenes using environmentally benign and highly abundant calcium salt as the green catalyst.

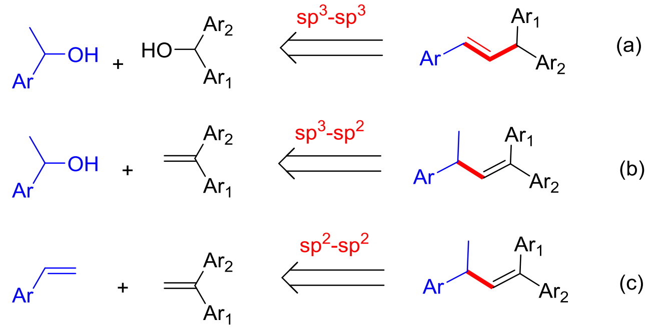

Figure 1. Possible direct/dehydrative cross-coupling reactions.

As described in the Figure 1 (equation b), we commenced the synthesis of but-2-ene-1,1,3-triyltribenzene (**3a**) from benzhydrol (**1a**) and α -methylstyrene (**2a**) through a dehydrative coupling reaction. 1.0 mmol of **1a** and 1.0 mmol of **2a** were stirred in 1, 2-dichloroethane at rt for 8 h using 5 mol% of $Ca(OTf)_2/Bu_4NPF_6$[8] and isolated the product **3a** but only in 28% yield. However encouraged by this result we investigated several other conditions for the better synthesis of **3a** (Table 1). When the above reaction was performed under reflux conditions (90 °C), the reaction yielded **3a** in 65% after 6 h (entry 2, Table 1). Increasing the catalyst loading from 5 to 10 mol% influenced the

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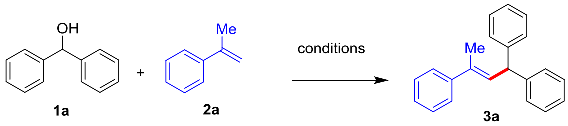
yield (76%) but not to a great extent (entry 3, Table 1). When **1a** and **2a** were heated at 90 °C with 10 mo% of catalyst and additive under neat conditions, the reaction gave the encouraging yield of 86% in 1.5 h (entry 4, Table 1). Further neither the raise in temperature (110 °C) nor the lowering in temperature (70 °C) could change the chemical yield of **3a** (entries 5, 6, Table 1). However the yield of **3a** was decreased to 60% at 50 °C (entry 7). These observations suggested us that 70 °C could be the ideal temperature for the synthesis of **3a** under neat conditions. To confirm the role of catalyst, the reaction was performed in the absence of catalyst (entry 8) and found that no reaction was initiated. Neither the $Ca(OTf)_2$ (catalyst) nor the Bu_4NPF_6 (additive) alone could furnish the better yield of **3a** (entries 9, 10) as it was well observed by us and others that Bu_4NPF_6 will help in solubilizing the Ca(II) salts for the enhanced reactivity.[9] $Ca(ClO_4)_2$ and $Mg(OTf)_2$ proved to be less efficient catalysts (entries 11, 12) in furnishing the **3a**. The reaction with 10 mol% of $FeCl_3$ gave a reasonable yield of 75% in 2 h. Among the thirteen different conditions tried (Table 1), entry 6 was found to be the better condition for the dehydrative cross coupling of **1a** and **2a** (Scheme 1).

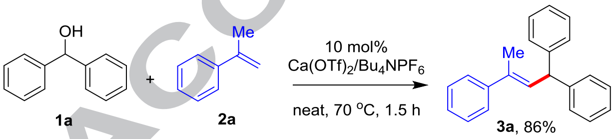
Table 1. Optimization study for the dehydrative coupling reaction between benzhydrol **1a** and 1-methyl styrene **2a**[a]



1a **2a** **3a**

Entry	Catalyst (mol%)	Solvent, Temperature[b], Time	Yield (%)[c]
1	$Ca(OTf)_2/Bu_4NPF_6$ (5)	DCE, rt, 8 h	28
2	$Ca(OTf)_2$ /Bu_4NPF_6 (5)	DCE, 90 °C, 6 h	65
3	$Ca(OTf)_2$ /Bu_4NPF_6 (10)	DCE, 90 °C, 6 h	76
4	$Ca(OTf)_2/Bu_4NPF_6$ (10)	neat, 90 °C, 1.5 h,	86
5	$Ca(OTf)_2/Bu_4NPF_6$ (10)	neat, 110 °C, 1.5 h	86
6[d]	$Ca(OTf)_2/Bu_4NPF_6$ (10)	neat, 70 °C, 1.5 h	86
7	$Ca(OTf)_2/Bu_4NPF_6$ (10)	neat, 50 °C, 6 h	60
8	--------	neat, 70 °C, 12 h	nr
9	$Ca(OTf)_2$ (10)	neat, 70 °C, 8 h	30
10	Bu_4NPF_6 (10)	neat, 70 °C, 8 h	45
11	$Ca(ClO_4)_2/Bu_4NPF_6$ (10)	neat, 70 °C, 6 h	55
12	$Mg(OTf)_2/Bu_4NPF_6$ (10)	neat, 70 °C, 5 h	74
13	$FeCl_3$ (10)	neat, 70 °C, 2 h	75

[a]Stoichiometric amounts of **1a** and **2a** were used. [b]Oil bath temperature. [c]Isolated yields. [d]Optimum conditions. nr=no reaction. rt=room temperature. DCE=1,2-dichloroethane

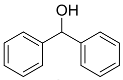
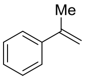
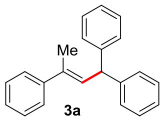
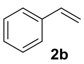
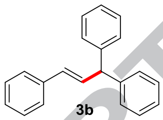
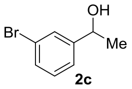
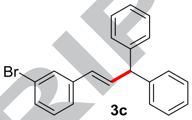
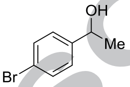
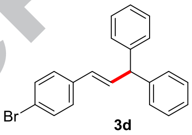
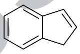
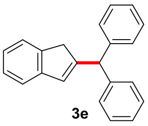
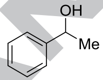
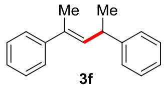
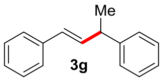
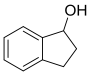
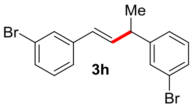
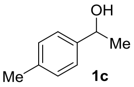
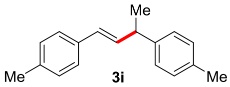
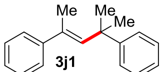
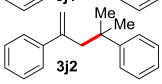
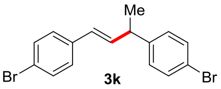
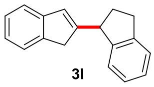
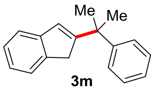


1a **2a** **3a**, 86%

Scheme 1. Ca(II)- catalyzed Cross- Dehydrative coupling reaction of benzhydrol (**1a**) and 1-methylystyrene (**2a**)

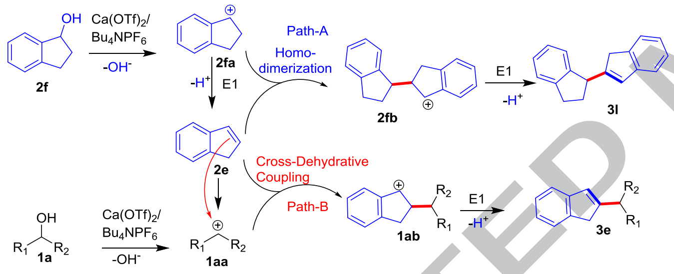
Having the optimum conditions in hand, we aimed to see the substrate scope of the method with various alcohol and alkene partners in the coupling reaction (Table 2). Under the standard conditions (entry 6 Table 1), styrene derivative **3b** was synthesized from styrene (**2b**) and benzhydrol (**1a**) (Table 2, entry 2) in 82% yield after 1 h. Cyclic alkene, indene (**2e**) gave 2-benzyhydryl-indene **3e** in 91% yield in 30 minutes. Similarly benzylic alcohol **1b** reacted with alkene **2a** and **2b** to furnish the alkenes **3f** and **3g** in 73%, 82% yields respectively (entries 6, 8).

Table 2. Substrate scope in the Ca(II) catalysed coupling reactions to yield internal alkenes.[a]

Entry	Coupling Partner **1**	Coupling Partner **2**	Cross-Coupled Product **3**	Yield (%)[b]	Time (h)
1	 **1a**	 **2a**	 **3a**	86	1.5
2	**1a**	 **2b**	 **3b**	82	1
3	**1a**	 **2c**	 **3c**	76	3
4	**1a**	 **2d**	 **3d**	82	2.5
5	**1a**	 **2e**	 **3e**	91	0.5
6	 **1b**	**2a**	 **3f**	73	3
7	**1a**	**1b**	**3b**	70	2
8	**1b**	**2b**	 **3g**	91	0.5
9	**1a**	 **2f**	**3e**	82	1
10	**1b**	**1b**	**3g**	91	0.5
11	**2c**	**2c**	 **3h**	84	1
12	 **1c**	**1c**	 **3i**	92	0.75
13	**2a**	**2a**	 **3j1**  **3j2**	95 (4:5)	0.5
14	**2d**	**2d**	 **3k**	88	1
15	**2f**	**2f**	 **3l**	93	0.6
16	**2b**	**2b**	**3g**	91	0.5
17	**2e**	**2e**	**3l**	80	1
18	**2e**	**2a**	 **3m**	74	2

[a]A mixture of 1eq. of 1 and 1 eq. of 2, 10 mol% $Ca(OTf)_2$/ Bu_4NPF_6 were heated at 70 °C.
[b]Isolated yields after Coloumn chromatography

Driven by the Ca(II) catalyzed dehydrative cross coupling of alkenes with alcohols, we extended the scope with two different alcohols to take part in the reaction to furnish alkene derivatives as shown in the Figure 1, equation-**a**. However there could be a self-dimerization possible in these reactions and hence to avoid this, we chose benzhydrol (**1a**) as one of the alcohol partner. **1a** was treated with other π-activated alcohols such as **2c**, **2d** and **1b** and furnished the respective alkenes **3c**, **3d** and **3b** in good yields. The homo dimerization of alcohols and alkenes (Table 2) was also investigated. Alcohol **1b** underwent a dimerization to form the alkene **3g** in in 91% yield after 30 min. Similarly benzylic alcohols **2c**, **2d**, **2f**, and **1c** took part in the dimerization to yield the corresponding alkenes in good yields (entries 11, 14, 15 and 12, Table 2). Alkene homo-coupling was also observed when α-methylstyrene (**2a**) alone was subjected under standard conditions. The reaction gave a mixture of **3j1** and **3j2**[10] in 95% yield. Other alkenes **2b** and **2e** gave the respective alkene derivatives **3g** and **3l** in good yields. The other possible combination to make the internal alkenes is the direct cross coupling between two different alkenes (Figure 1, equation –**c**), which was also pursued by treating the indene (**2e**) with α -methylstyrene (**2a**)[13] and isolated 2-(2-phenylpropan-2-yl)-1H-indene **3m** in 74% yield after 2 h (entry 18). All these experimemts proved Ca(OTf)$_2$ as an alternative and a green catalyst for the dehydrative cross coupling of alcohols-alkenes, alcohols-alcohols and direct coupling of alkenes to furnish the alkenes readily.

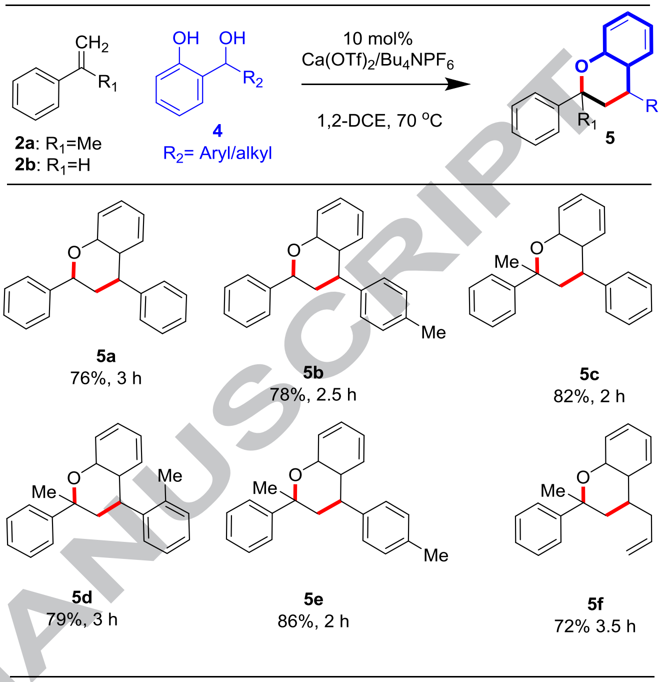


Scheme 2. Plausible mechanism for the Ca(II) catalyzed Cross-Dehydrative coupling reaction(path b) and Homo-dimerization(path a)

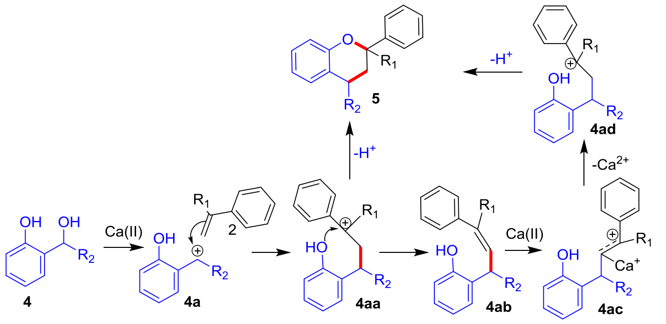
The plausible mechanism for the Ca(OTf)$_2$ catalyzed dehydrative coupling of alcohols and alkenes is described in the Scheme 2. Initially Ca(II) promotes the formation of benzylic cation **2fa** from 1-indanol (**2f**). This benzylic cation **2fa** would undergo elimination (E1) to produce the indene **2e**. In the absence of foreign body, a homo-coupling will take place between **2fa** and **2e** to produce **2fb** (path A), which would further experience elimination to yield a stable alkene **3l**. Alternatively, in presence of another reactive partner (**1a**), **2e** would participate in a dehydrative coupling reaction (path B) to form the cation **1ab**, which yields a stable alkene **3e** after elimination.

After a successful demonstration of Ca(II) catalyzed green approach (Table 2) for the coupling reaction of alcohols-alkenes (entries 1, 2, 5, 6 and 8), alcohols-alcohols (entries 3, 4, 7 and 9), alkenes-alkenes (entry 18) and homo-coupling of alcohols (entries 10, 11, 12, 14 and 15) and alkenes (entries 13, 16 and 17) to form a new C-C bonds (sp^3-sp^2), we were interested to extend this method towards the synthesis of novel benzopyran derivatives[12] using a cascade C-C bond formation followed by C-O bond formation in one pot (Scheme 3).[11] As proposed styrene **2b** reacted with 2-(hydroxy(phenyl)methyl)phenol (**4a**) in presence of 10 mol% Ca(OTf)$_2$/Bu$_4$NPF$_6$ in DCE at 70 °C and furnished the benzopyrans **5a** in 76% after 3 h (Table 3). **2b** also reacted with 2-(hydroxy(p-tolyl)methyl)phenol (**4b**) to yield the benzopyrans **5b** in 78% after 2.5 h. Similarly, α-methylstyrene (**2a**) furnished the 2-quaternary centered benzopyrans **5c**, **5d**, **5e** and **5f** in good yields (Table 3).

Table 3. Substrate scope of Ca(II) catalyzed one-pot dehydrative cross coupling and cyclisation towards benzopyrans



A plausible mechanism for this cascade synthesis of benzopyrans is described in the Scheme 3. Benzylic cation **4a** reacts with the alkene and furnish the intermediate **4aa**, which further undergo a cascade oxa-cyclisation to yield the desired product **5**. Parallelly, **4ab** could be formed by the dehydrative cross coupling of **4** with alkene, which will undergo a hydroalkoxylation reaction which was known before by Niggemann *et al.*[11] to furnish the compound **5** via the formation of **4ab**, **4ac** and **4ad**.



Scheme 3 Plausible mechanism for the Ca(II) catalyzed one pot cascade synthesis of benzopyrans through cross dehydrative coupling reaction of alcohols with alkenes

All compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, Mass and IR.[13]

In summary, we have developed a simple and user-friendly green synthetic procedure for the synthesis of various internal alkenes through a dehydrative cross coupling/homo-dimerization of alcohols and alkenes. The reaction also showed its utility to furnish the benzopyrans molecules through a dehydrative cross-coupling/oxa-cyclisation strategy. Solvent free condition, broad substrate scope, regioselective alkene formation and atom-economy are some of the highlights of this methodology.

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10. The ratio of 3j1/3j2 (4/5) is determined by ^{1}H NMR. Probably these two are thermodynamic/kinetic products.
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13. **General Experimental Procedure (3a - 3m):** A mixture of alcohol **1a** (100 mg, 0.54 mmol), alkene **2a** (43 mg, 0.54 mmol), Ca(OTf)$_2$ (18.3 mg, 0.05 mmol), Bu$_4$NPF$_6$ (21 mg, 0.05 mmol) was heated under solvent free condition at 70 ^{o}C for 1.5 h until complete consumption of the starting material as monitored by TLC. After the completion of the reaction the mixture was purified by flash column chromatography (petroleum ether) to afford the desired product **3a**. **Typical procedure for the construction of benzopyran** (5a – 5f)**:** A mixture of 2-hydroxy alcohol **4** (1 equiv.), alkene **2a** or **2b** (1.2 equiv.) and Ca(OTf)$_2$ (0.1 equiv.), Bu$_4$NPF$_6$ (0.1 equiv.) was stirred in 1,2-dichloroethane at 70 ^{o}C for 1.5 h until complete consumption of the starting material as monitored by TLC. After completion, the reaction mixture was diluted with water and extracted into dichloromethane. Combined organic layers were washed with brine solution, dried over anhydrous Na$_2$SO$_4$, evaporated under reduced pressure and the crude product was purified by column chromatography to obtain desired product **5. (**Please refer the supporting information for the spectral data and copies of the spectra.)

Highlights of the Work:

- ✓ Highly Versatile and Regioselective method for the synthesis of internal alkenes
- ✓ Unique method for dehydrative cross-coupling/homo-dimerization/direct cross couplings
- ✓ Successfully extended to the synthesis of novel Benzopyrans
- ✓ Solvent-Free; Step, Atom Economy and environmentally benign catalyst
- ✓ Large Substrate Scope, High Yields; User-Friendly Protocol