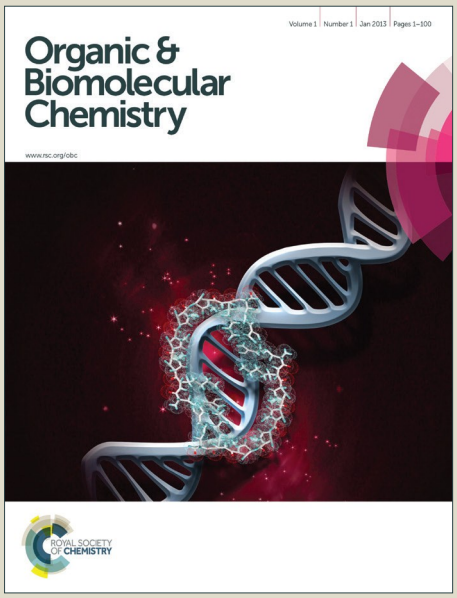
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Manikandan and M. Jeganmohan, *Org. Biomol. Chem.*, 2016, DOI: 10.1039/C6OB01498D.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

View Article Online
DOI: 10.1039/C6OB01498D

Journal Name

ARTICLE

Temperature-Controlled Redox-Neutral Ruthenium(II)-Catalyzed Regioselective Allylation of Benzamides with Allylic Acetates

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Rajendran Manikandan [a] and Masilamani Jeganmohan [*a]

Substituted aromatic amides reacted efficiently with allylic acetates in the presence of a cationic ruthenium complex in $ClCH_2CH_2Cl$ at room temperature providing *ortho* allylated benzamides in a highly regioselective manner without any oxidant and base. The whole catalytic has occurred in a Ru(II) oxidation state and thus oxidation step is avoided. By tuning the reaction temperature, *ortho* allyl and vinyl benzamides were prepared exclusively. Later, *ortho* allyl and vinylated benzamides were converted into biologically useful six- and five-membered containing benzolactones in the presence of HCl.

Introduction

The transition metal-catalyzed allylation at the C-H bond of substituted aromatics with allylic electrophiles is one of the effective methods for synthesizing allylaromatics in a highly regioselective manner.[1] Allylarenes are widely used as key intermediates for synthesizing various natural products and medicinally relevant molecules.[2] Traditionally, allylarenes are prepared via a Lewis acid-mediated Friedel-Crafts type allylation of electron rich aromatics with allylic electrophiles.[3] Meanwhile, allylarenes are prepared via a metal-catalyzed cross-coupling of aromatic electrophiles with allylating reagents.[4] However, a preactivated halogen or metal species is needed on the aromatic moiety of this transformation. Recently, allylarenes are efficiently prepared in a highly step- and atom-economical manner via C-H bond activation reaction.[5-7] However, in most of the reported reactions, mixtures of allyl as well as vinyl arenes were observed. Internal olefins are thermodynamically more stable than the terminal olefins. Thus, after allylation, the double bond migration takes place towards thermodynamically more stable internal olefins in the presence of a metal catalyst. Meanwhile, the mechanism of this type of allylation reaction as well as the mechanism and driving force for the double bond migration of allylarenes is not clearly studied.

In the reported allylation reaction via C-H bond activation, a stoichiometric amount of oxidant or acetate base or acid is needed. The oxidation step such as a metal with lower oxidation state into the higher oxidation state [Pd(0) to Pd(II), Co(I) to Co(III), Rh(I) to Rh(III) and Ru(0) to Ru(II)] is required for this type of transformation. Usually, this source is used for the regeneration of active catalyst. However, a stoichiometric amount of oxidant waste is produced. In addition, the elevated reaction temperature is required for the reaction.

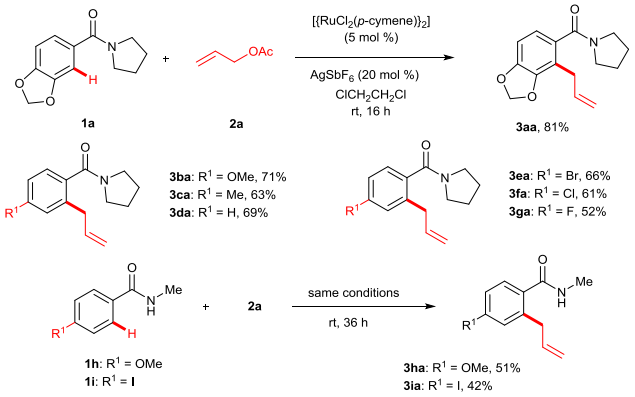
Herein, we report a redox-free ruthenium-catalyzed allylation of benzamides with allylic acetates without any oxidant or base at room temperature. The whole catalytic reaction has occurred in a Ru(II) oxidation state. In the reaction, acetate moiety of allylic acetate acts as a base to deprotonate the C-H bond. The acetate moiety of allylic acetate intramolecularly transferred into a ruthenium species via β-acetate elimination and maintain the Ru(II) oxidation state. It is important to note that the same reaction provided vinylarenes at a higher temperature. It is important to note that the C-H bond activation as well as allylation reaction takes place at room temperature. But, a higher reaction temperature is needed for the double bond migration. The reaction temperature decides the outcome of regioselectivity of the product. A possible reaction mechanism for allylation reaction was proposed. The alkene migration mechanism was supported by a deuterium labelling experiment. *ortho* Allyl and vinylated benzamides were converted into biologically useful six- and five-membered benzolactones in the presence of HCl.

Results and Discussion

When benzamide **1a** was treated with allyl acetate (**2a**) in the presence of $[\{RuCl_2(p\text{-cymene})\}_2]$ (5.0 mol %) and $AgSbF_6$ (20 mol %) in 1,2-dichloroethane (DCE) at room temperature for 16 h, *ortho* allylated benzamide **3aa** was observed in 81% yield

[a] *Department of Chemistry*
Indian Institution of Science Education and Research
Pune 411021, Maharashtra, India
Fax: (+)91-20-25865315
E-mail: mjeganmohan@iiserpune.ac.in dress here.
Electronic Supplementary Information (ESI) available: []. See DOI: 10.1039/x0xx00000x

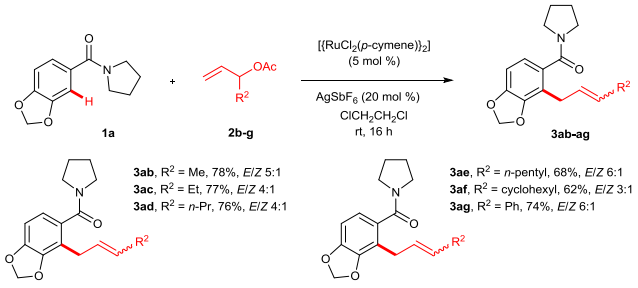
View Article Online
DOI: 10.1039/C6OB01498D



Scheme 1 Scope of substituted benzamides

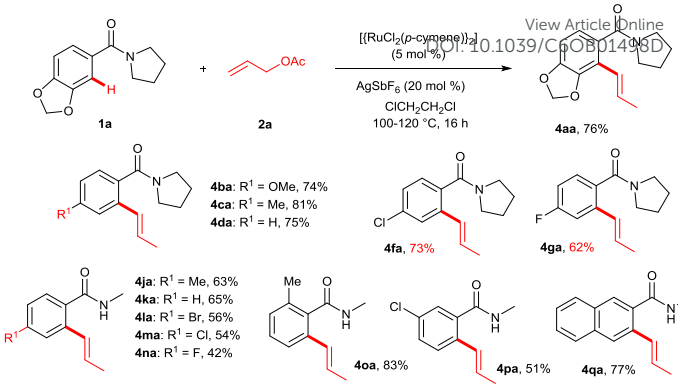
(Scheme 1). In the reaction, no double bond isomerization product of 3aa was observed and the C-H bond activation regioselectively takes place at the C2-H position. Initially, the allylation reaction was screened with various additives, solvents and allyl sources. The complete information is given in Table S1 in supporting information.

The scope of the allylation reaction was examined with various *N*-*N*-disubstituted aromatic amides **1b-g** (Scheme 1). The allylation reaction was compatible with sensitive functional group such as F, Cl, Br and I substituted benzamides. In all these reactions, the expected allylation products **3ba-ga** were observed in good to excellent yields. An electron-releasing substituent on the benzamides was very effective for the reaction as compared with electron-withdrawing substituent. *N*-Monosubstituted benzamides **1h-i** were also involved in the reaction, affording *ortho* allylated *N*-methyl benzamides **3ha-3ia** in moderate yields and the remaining unreacted *N*-monosubstituted benzamides starting materials were recovered (Scheme 1).



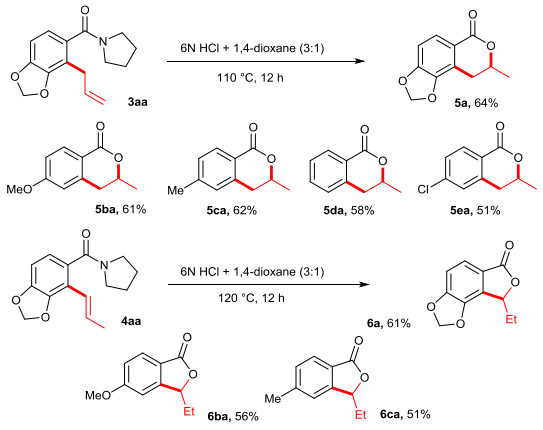
Scheme 2 Scope of allylic acetates

The scope of allylation reaction was further examined with substituted allylic acetates **2b-g** (Scheme 2). γ-Alkyl group such as methyl (**2b**), ethyl (**2c**), *n*-propyl (**2d**) and *n*-pentyl (**2e**) substituted allylic acetates reacted efficiently with **1a**, giving the corresponding allylated products **3ab-ae** in excellent yields in 3:1 to 6:1 *E*:*Z* stereoisomeric ratios. The allylation reaction was also compatible with hindered γ- cyclohexyl (**2f**) and phenyl (**2g**) substituted allylic acetates. In the reaction, the expected allylation products **3af** and **3ag** were observed in excellent yields in a 3:1 and 6:1 *E*:*Z* stereoisomeric ratios. However, the present allylation reaction was not compatible with α- as well as β-substituted allylic acetates.



Scheme 3 *ortho* Vinylation of substituted benzamides

When the allylation reaction of **1a** with **2a** was tried under the optimized reaction conditions at 100 °C, *ortho* vinylated benzamide **4aa** was product in 76% yield (Scheme 3). *N*-*N*-Disubstituted benzamides **1b-g** as well as *N*-methyl benzamides **1j-q** were equally reactive with **2a**, providing *ortho* vinylated benzamides **4ba-qa** in good to excellent yields in a highly *E* stereoselectivity. Generally, *N*-substituted benzamides were not suitable substrates for allylation as well as vinylation reaction. It is important to mention that the electron-withdrawing substituted benzamides **1f-g**, **1l-n** and **1p** need 120 °C to provide *ortho* vinylated benzamides exclusively. At 100 °C, mixtures of internal as well as terminal olefins were observed. This result clearly indicates that the double bond isomerization is most favorable for electron rich benzamides as compared with electron-deficient benzamides. In products **4pa** and **4qa**, vinylation was observed selectively at the less hindered C-6 or C-3 position. Meanwhile, γ-substituted allylic acetates were not selective for the reaction which providing regio- and stereoisomeric mixtures of internal as well as terminal olefins even at 120 °C.

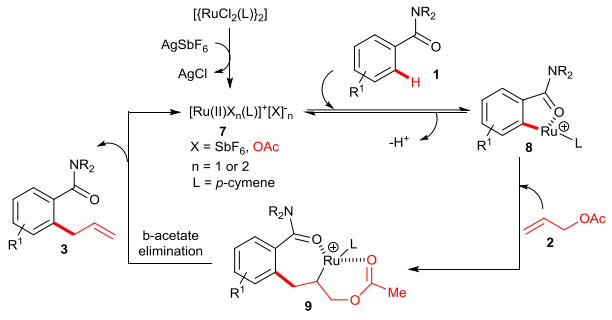


Scheme 4. Acid-Mediated Lactonization

Substituted *ortho* allylated benzamides **3aa-da** and **3fa** were efficiently converted into a six-membered benzolactones **5a-e** in good yields in the presence of a 3:1 mixture of 6 N HCl and 1,4-dioxane at 110 °C for 12 h (Scheme 4). Under similar reaction conditions, *ortho* vinylated benzamides **4aa-ca** provided a five-membered benzolactones **6a-c** in good yields.

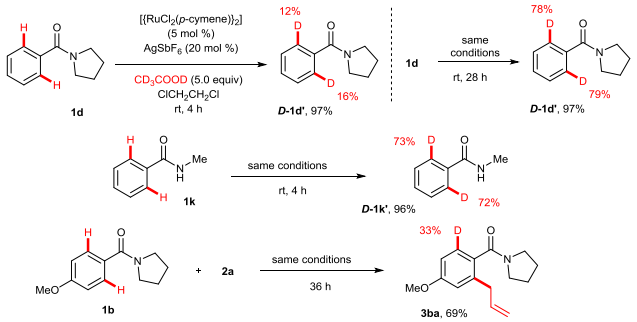
View Article Online
DOI: 10.1039/C6OB01403D

It is important to note that these structural units are present in various natural products and biologically active molecules.



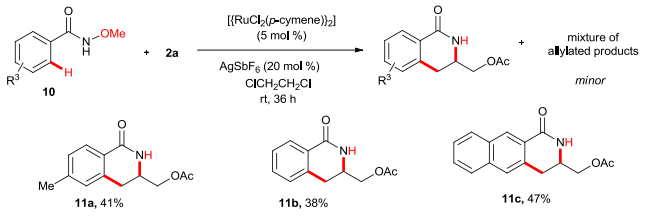
Scheme 5 Proposed mechanism

A possible reaction mechanism for *ortho* allylation of benzamides with allylic acetates is proposed in Scheme 5. $AgSbF_6$ likely removes Cl^- ligand from [{$RuCl_2$(*p*-cymene)}$_2$] complex, giving a cationic ruthenium complexes **7**. Later, the oxygen atom of amide **1** coordinates with a ruthenium species **7** followed by *ortho*-metalation providing a five-membered ruthenacycle intermediate **8**. Coordinative regioselective insertion of allyl acetate **2a** into the Ru–carbon bond of intermediate **8** gives intermediate **9**. β-Acetate elimination of intermediate **9** affords *ortho* allyl benzamide **3** and regenerates catalyst **7** for the next catalytic cycle. It is important to note that the acetate group of **2a** would be transferred into the ruthenium species **7** intramolecularly and the corresponding acetate species deprotonates the C-H bond. The whole catalytic reaction has occurred in a Ru(II) oxidation state without changing the oxidation state of ruthenium and thus oxidant is not required for the present allylation reaction.



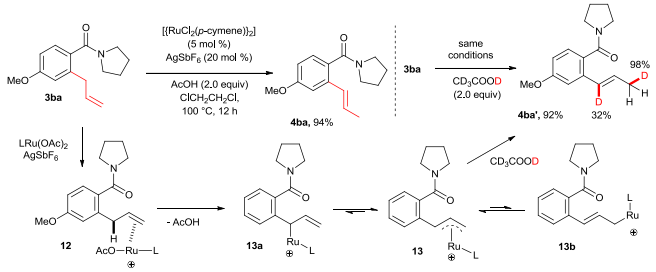
Scheme 6 Deuterium labelling experiment

The reactivity of benzamides varies based on the substituent on the nitrogen atom. To know more about the reactivity, the rate of the C-H bond activation of benzamides was studied via deuterium labelling experiment. *N*, *N*-Disubstituted benzamide **1d** was treated with CD_3COOD at room temperature for 4 h, yielding product ***D*-1d'** in 97% yield with 12% and 16% of deuterium incorporation at the both *ortho* carbons. But, the same reaction provided product ***D*-1d'** in the maximum deuterium incorporation at the both *ortho* carbons in 78% and 79% at room temperature for 28 h. Further, *N*-methyl benzamide (**1k**) was treated with CD_3COOD at room temperature for 4 h, yielding product **D-1k'** in 96% yield with 72% and 73% of deuterium incorporation at the both *ortho* carbons. Based on these deuterium studies, we concluded that the C-H bond of *N*-methyl benzamides can be activated at room temperature for 4 h, but the allylation step needs a longer reaction time. But, in the case of *N*,*N*-disubstituted benzamide, the C-H bond activation can be activated at room temperature, but the process is slow and needs a longer reaction time. Further, to prove the formation of intermediate **8** is a reversible process, **1b** was treated with **2a** and CD_3COOD in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] and $AgSbF_6$ in DCE at room temperature for 36 h. In the reaction, product **3ba** was observed in 69% yield with 33% deuterium incorporation at the *ortho* carbon (Scheme 6).



Scheme 7 Synthesis of 3,4-dihydroisoquinolin-1(2*H*)-ones

Subsequently, the formation of a seven-membered ruthenacycle intermediate **9** was supported by the reaction of *N*-methoxy benzamides **10** with allyl acetate (**2a**) under the optimized reaction conditions. In the reaction, cyclic 3,4-dihydroisoquinolin-1(2*H*)-ones **11a-c** were observed in moderate yields along with the formation of a minor amount of allylated products (Scheme 7). It is very interesting to note that in the metal-catalyzed allylation reaction, allylic acetates mostly act as an allylating agent with a leaving of acetate group. Surprisingly, in the reaction, an acetate group was not cleaved and stayed as such. In the particular reaction, a ruthenium species can eliminate from intermediate **9** by two ways; a) β-acetate elimination along with the formation of allylated product as suggested in Scheme 5; b) coupling of C-Ru with the free NH group of intermediate **9** via reductive elimination forming a cyclic product followed by cleavage of *N*-methoxy group of cyclic product **11**. In the reaction, both products such as a major amount of cyclic products along with a minor amount of allylated products were observed. This result provides indirect evidence that the allylation reaction occurred via a seven membered metalacycle intermediate **9** as well as the β-acetate elimination.



Scheme 8 Mechanism for isomerization reaction

To know more about the insight of isomerization mechanism, *ortho* allylated benzamide **3ba** was treated with [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) in DCE at 100 °C. In the reaction, no double bond isomerization product **4ba** was observed. Later, the same reaction was examined in the presence of NaOAc. In the reaction, a mixture of **3ba** and **4ba** was observed in an 1:1 ratio. Interestingly, in the presence of 2.0 equiv of AcOH, the same reaction provided exclusively internal alkene **4ba** in 94% yield (Scheme 8). This result clearly reveals that the AcOH is crucial for the isomerization reaction along with a catalyst. In the present allylation reaction, a stoichiometric amount of AcOH is formed at the C-H bond activation step (Scheme 5). It has been used for the isomerization reaction. To find out the exact role of AcOH, the same reaction was done by using CD_3COOD. Interestingly, in the reaction, product **4ba** was observed in 92% yield with 98% deuterium incorporation at the CH_3 group of alkene and 32% at the benzylic CH_2. This study reveals that the isomerization reaction proceeds via π-allyl ruthenium intermediate 13 and not in a typical oxidative addition pathway. In most of the reported allylation reaction, it has been proposed that the reaction proceeds via an oxidative addition pathway. The present reaction proceeds via coordination of double bond of alkene with a cationic ruthenium species followed by OAc mediated deprotonation at the benzylic CH_2 provides π-allyl ruthenium intermediate **13**. Protonation at the C-Ru bond of intermediate **13** by acetic acid affords isomerization product **4ba**' and regenerates the active catalyst.

Meanwhile, the reaction temperature is also crucial for the isomerization reaction. The isomerization reaction of **3ad** into **4ad** was carried out at different temperature such as 50 °C, 60 °C, 70 °C, 80 °C, 90 °C and 100 °C. The result shows that the reaction temperature up to 50 °C does not play any role for the isomerization reaction. At 60 °C to 90 °C, a mixture of terminal and internal olefins was observed in a higher ratio towards internal olefin. At 100 °C, terminal olefin was completely converted into internal olefin (see SI). To know further about the isomerization reaction, the energy of molecules **3ad** and **4ad** were calculated based on the DFT calculation. Based on the energy calculation, compound **4da** is stabilized by 19.2 kJ/mol than compound **3da** (see SI).

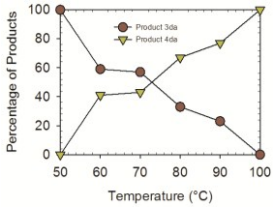


Chart 1

Conclusions

In conclusion, we have described a ruthenium-catalyzed highly regioselective *ortho* allylation of aromatic amides with allylic acetates at room temperature without any oxidant. In the reaction, two different regioisomeric alkene derivatives were observed exclusively by tuning the reaction temperature. Later, biologically active six- and five-membered containing benzolactones were prepared by HCl hydrolysis. The detailed mechanistic investigation for the allylation and isomerization reactions was carried out.

Experimental Section

General Information: All reactions were carried out under the nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents were used for the reaction. Column chromatographical purifications were performed using SiO_2 (120-200 mesh ASTM) from Merck if not indicated otherwise. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Starting Materials: Commercial available starting materials, metal complexes and metal salts were purchased from commercial sources and used without further purification.

A. General Procedure for the Allylation of Aromatic amides with Allylic Acetates Catalyzed by a Ruthenium Complex:

A 15-mL pressure tube with septum containing amide **1** (100 mg), [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, was then added 1,2-dichloroethane (1.0 mL) via syringe. After that, allylic acetate **2** (2.0-2.5 equiv) and 1,2-dichloroethane (2.0 mL) were added via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at rt for 16-36 h. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate (for some compounds CH_2Cl_2 and MeOH combination were used. It has been mentioned in the substrates below) as eluent to give pure **3**.

Note: Liquid amide reactants are added after adding 1.0 mL of solvent. For product **3aa,** 2.0 equiv of allyl acetate (**2a**) was used.

Spectral Data of Compounds

(4-Allylbenzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3aa): Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2a** (2.0 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 96 mg and yield is 81%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3011, 2931, 2817, 1651, 1425, 1317, 1049, 918, 871, 668. ^{1}H NMR (CDCl3, 400 MHz): δ 6.66 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 5.91 (s, 2H), 5.89 – 5.77 (m, 1H), 4.98 (dq, J = 16.0, 4.0 Hz, 1H), 4.93 (dt, J = 12.0, 4.0 Hz, 1H), 3.53 (t, J= 8.0 Hz, 2H), 3.36 (d, J = 8.0 Hz, 2H), 3.12 (t, J = 8.0 Hz, 2H), 1.87 (p, J = 8.0 Hz, 2H), 1.75 (p, J = 8.0 Hz, 2H).^{13}C NMR (CDCl3, 100 MHz): δ 168.9, 147.3, 146.2, 135.2, 131.8, 119.7, 118.6, 115.5, 106.3, 100.9, 48.9, 45.4, 30.9, 25.9, 24.5. HRMS (ESI):

calc. for [(C15H17NO3)H] (M+H) 260.1287, measured 260.1289

(2-Allyl-4-methoxyphenyl)(pyrrolidin-1-yl)methanone (3ba):

Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1b** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 85 mg and yield is 71%. IR (ATR)$\tilde{\nu}$ (cm-1): 2978, 2901, 1614, 1579, 1468, 1219, 1031, 858, 744, 598. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (d, J = 8.0Hz, 1H),6.74 (d, J = 4.0Hz, 1H),6.71 (dd, J = 8.0, 4.0 Hz, 1H),5.90 - 5.80 (m, 1H), 5.06 – 4.97 (m, 2H), 3.76 (s, 3H), 3.57 (t, J = 8.0Hz,2H), 3.34 (d, J = 8.0Hz, 2H), 3.11 (d, J = 8.0Hz, 2H), 1.88 (p, J = 4.0Hz, 2H), 1.79 (p, J = 4.0Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 159.8, 138.3, 136.5, 130.2, 127.4, 115.9, 115.3, 111.3, 55.2, 48.8, 45.4, 37.5, 25.9, 24.5. HRMS (ESI): calc. for [(C15H19NO2)H] (M+H) 246.1494, measured 246.1502.

(2-Allyl-4-methylphenyl)(pyrrolidin-1-yl)methanone (3ca).

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1c** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 76 mg and yield is 63%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.02 (dq, *J* = 16.0, 4.0 Hz, 1H), 4.98 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.58 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 138.7, 136.9, 136.1, 134.8, 130.4, 126.8, 125.9, 115.7, 48.7, 45.3, 37.3, 25.9, 24.5, 21.2.
HRMS (ESI): calc. for [($C_{15}H_{19}NO$)H] (M+H) 230.1545, measured 230.1553.

(2-Allylphenyl)(pyrrolidin-1-yl)methanone (3da):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1d** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 85 mg and yield is 69%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2979, 1614, 1570, 1413, 1261, 1048, 879, 717, 628.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (td, *J* = 8.0, 4.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 8.0, 4.0 Hz, 2H),5.94 -5.86 (m, 1H), 5.09 – 5.01 (m, 2H), 3.63 (t, *J* = 8.0Hz,2H), 3.44 (d, *J* = 8.0Hz,2H), 3.14 (t, *J* = 8.0Hz,2H), 1.94 (p, *J* = 4.0Hz,2H), 1.84 (p, *J* = 4.0Hz,2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.6, 138.7, 136.4, 135.7, 132.8, 129.4, 127.5, 122.9, 116.7,48.7, 45.5, 37.1, 25.9, 24.5. HRMS (ESI): calc. for [($C_{14}H_{17}NO$)H] (M+H) 216.1388, measured 216.1395.

(2-Allyl-4-bromophenyl)(pyrrolidin-1-yl)methanone (3ea):

Colorless solid; eluent (24% ethylacetate in hexane); The representative general procedure was followed using **1e** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 77 mg and yield is 66%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3078, 2931, 1634, 1589, 1463, 1259, 1041, 874, 747, 668. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, *J* = 4.0Hz,1H), 7.34 (dd, *J* = 8.0, 4.0 Hz,1H),7.05 (d, *J* = 8.0Hz,1H), 5.88 -5.78 (m, 1H), 5.08 – 5.02 (m, 2H), 3.58 (t, *J* = 8.0Hz,2H), 3.37 (d, *J* = 8.0Hz,2H), 3.09 (t, *J* = 8.0Hz,2H), 1.90 (p, *J* = 4.0Hz,2H), 1.81 (p, *J* = 4.0Hz,2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 137.5, 136.7, 136.1, 129.8, 128.9, 126.2, 125.9, 115.8, 48.7, 45.3, 37.4, 25.9, 24.5. HRMS (ESI): calc. for [($C_{14}H_{16}BrNO$)H] (M+H) 294.0494, measured 294.0495.

(2-Allyl-4-chlorophenyl)(pyrrolidin-1-yl)methanone (3fa):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1f** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 73 mg and yield is 61%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, *J* = 4.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.05 (dq, *J* = 12.0, 4.0 Hz, 1H), 5.02 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.37 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.08 (t, *J* = 8.0 Hz, 2H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 138.5, 135.9, 135.7, 134.6, 129.8, 127.3, 126.4, 116.7, 48.6, 45.4, 37.1, 25.9, 24.5. HRMS (ESI): calc. for [($C_{14}H_{16}ClNO$)H] (M+H) 250.0999, measured 250.1003.

(2-Allyl-4-Fluorophenyl)(pyrrolidin-1-yl)methanone (3ga):

Colorless solid; eluent (25% ethylacetate in hexane); The representative general procedure was followed using **1g** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 62 mg and yield is 52%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.89 (td, *J* = 8.0, 4.0 Hz, 1H), 5.88 – 5.79 (m, 1H), 5.06 (dq, *J* = 8.0, 4.0 Hz, 1H), 5.03 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.59 (t, *J* = 8.0 Hz, 2H), 3.39 (d, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.81 (p, *J* = 8.0 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 163.9, 161.5, 139.4 and 139.3 (F-coupling), 135.8, 133.6, 127.8 and 127.7 (F-coupling), 116.7 and 116.5(F-coupling), 113.3 and 113.1 (F-coupling), 48.7, 45.5, 37.2, 25.9, 24.4. HRMS (ESI): calc. for [($C_{14}H_{16}FNO$)H] (M+H) 234.1294, measured 234.1299.

2-Allyl-4-methoxy-*N*-methylbenzamide (3ha):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1h** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 63 mg and yield is 51%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3289, 2922, 1630, 1536, 1403, 1157, 1041, 999.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33(d, *J* = 8.0Hz, 1H), 6.73 – 6.69 (m, 2H), 6.02 – 5.92 (m, 1H), 5.87 (s, 1H), 5.05 (dq, *J* = 8.0, 4.0 Hz, 1H), 5.0 (dq, *J* = 12.0, 4.0 Hz, 1H), 3.78 (s, 3H), 3.53 (d, *J* = 8.0 Hz, 2H), 2.91 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 160.7, 139.9, 137.5, 129.0, 128.9, 116.0, 115.9, 111.3, 55.2, 37.8, 26.6. HRMS (ESI): calc. for [($C_{12}H_{15}NO_2$)H] (M+H) 206.1181, measured 206.1187.

2-Allyl-4-iodo-*N*-methylbenzamide (3ia):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1i** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 49 mg and yield is 42%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3289, 2922, 1630, 1536, 1403, 1157, 1041, 999.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33(d, *J* = 8.0Hz, 1H), 6.73 – 6.69 (m, 2H), 6.02 – 5.92 (m, 1H), 5.87 (s, 1H), 5.05 (dq, *J* = 8.0, 4.0 Hz, 1H), 5.0 (dq, *J* = 12.0, 4.0 Hz, 1H), 3.78 (s, 3H), 3.53 (d, *J* = 8.0 Hz, 2H), 2.91 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 160.7, 139.9, 137.5, 129.0, 128.9, 116.0, 115.9, 111.3,

55.2, 37.8, 26.6. HRMS (ESI): calc. for $[(C_{12}H_{15}NO_2)H]$ (M+H) 206.1181, measured 206.1187.

(4-(But-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ab):

Colorless solid; eluent (27% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2b** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 98 mg and yield is 78%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2989, 2717, 1637, 1485, 1212, 1041, 908, 875, 652. ^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.51 – 5.34 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J*= 8.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 1.64 (d, *J* = 8.0 Hz, 3H). **Z isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.51 – 5.34 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.29 (d, *J* = 4.0 Hz, 1H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 1.58 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.2, 147.3, 146.1, 131.7, 127.7, 127.1, 126.3, 124.8, 106.2, 100.9, 48.9, 45.4, 29.8, 25.9, 24.6, 12.8. **Z isomer:** δ 169.1, 147.3, 146.1, 131.7, 127.7, 126.3, 119.8, 119.7, 106.2, 100.9, 48.9, 45.4, 29.6, 25.9, 24.6, 17.8. HRMS (ESI): calc. for $[(C_{16}H_{19}NO_3)H]$ (M+H) 274.1443, measured 274.1446.

(4-(Pent-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ac):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2c** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 101 mg and yield is 77%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2948, 2811, 1616, 1435, 1212, 1021, 905, 875, 669.^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H),6.63 (d, *J* = 8.0 Hz, 1H),5.93 (s, 2H), 5.38 – 5.32 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.37 (d, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.08 (p, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H).**Z isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H),6.63 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.48 – 5.43 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.08 (p, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.78 (p, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.1, 147.3, 146.1, 133.4, 132.6, 131.7, 125.5, 119.9, 106.1, 100.9, 48.9, 45.4, 25.9, 24.8, 24.6, 20.5, 14.1. **Z isomer:** δ 170.7, 147.3, 146.1, 130.5, 125.4, 125.3, 119.7, 119.6, 106.1, 100.9, 48.9, 45.4, 39.0, 34.7, 29.8, 25.9, 25.4, 24.9, 24.8, 24.6, 20.5, 14.1, 13.5. HRMS (ESI): calc. for $[(C_{17}H_{21}NO_3)H]$ (M+H) 288.1600, measured 288.1610.

(4-(Hex-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ad):

Colorless solid; eluent (26% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2d** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 103 mg and yield is 76%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2967, 2819, 1614, 1435, 1312, 1041, 908, 818, 695. ^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.38 – 5.33 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.36 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.05 (q, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J* = 8.0 Hz, 2H), 5.38 – 5.33 (m, 2H), 0.87 (t, *J* = 8.0 Hz, 3H). **Z isomer:** δ 6.66 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.47 – 5.41 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.31 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.05 (q, *J* = 8.0 Hz, 2H), 1.89 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J* = 8.0 Hz, 2H), 5.38 – 5.33 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 170.7, 147.2, 146.0, 131.7, 130.8, 126.2, 126.0, 119.7, 106.2, 100.9, 48.8, 45.4, 29.2, 25.8, 24.9, 24.5, 22.7, 13.7. **Z isomer:** δ 169.1, 147.2, 146.0, 130.4, 126.5, 120.1, 119.9, 119.7, 106.2, 100.9, 48.8, 39.0, 34.7, 34.5, 29.9, 25.0, 22.4, 13.6. HRMS (ESI): calc. for $[(C_{18}H_{23}NO_3)H]$ (M+H) 302.1756, measured 302.1762.

(4-(Oct-2-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ae):

Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2e** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 102 mg and yield is 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.37 – 5.35 (m, 2H), 3.54 (t, *J* = 8.0 Hz, 2H), 3.35 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.06 (q, *J* = 8.0 Hz, 2H), 1.88 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J*= 8.0 Hz, 2H), 1.36 – 1.16 (m, 6H), 0.84 (t, *J* = 8.0 Hz, 3H). **Z isomer:** δ 6.65 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.43 – 5.40 (m, 1H), 3.54 (t, *J* = 8.0 Hz, 2H), 3.29 (d, *J* = 4.0 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.06 (q, *J* = 8.0 Hz, 2H), 1.88 (p, *J* = 8.0 Hz, 2H), 1.77 (p, *J*= 8.0 Hz, 2H), 1.36 – 1.16 (m, 6H), 0.84 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.1, 147.2, 146.1, 131.7, 131.1, 125.9, 119.9, 119.7, 106.1, 100.9, 48.8, 45.4, 31.4, 29.2, 27.1, 25.9, 24.9, 24.5, 22.5, 13.9. **Z isomer:** δ 169.1, 147.2, 146.1, 131.9, 131.1, 126.2, 119.9, 119.7, 106.1, 100.9, 48.8, 36.5, 34.7, 32.4, 31.3, 29.9, 29.6, 28.9, 22.4, 13.9. HRMS (ESI): calc. for $[(C_{20}H_{27}NO_3)H]$ (M+H) 330.2069, measured 330.2077.

(4-(3-Cyclohexylallyl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3af):

Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2f** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 96 mg and yield is 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.31 – 5.18 (m, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.38 (d, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 2H), 2.39 – 2.32 (m, 1H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.68 – 1.56 (m, 6H), 1.35 – 1.19 (m, 2H), 1.19 – 1.07 (m, 2H), 1.07 – 0.93 (m, 2H). **Z isomer:** δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.41 – 5.38 (m, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.30 (d, *J* = 8.0 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 2H), 2.39 – 2.32 (m, 1H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.68 – 1.56 (m, 6H), 1.35 – 1.19 (m, 2H), 1.19 – 1.07 (m, 2H), 1.07 – 0.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 169.1, 147.3, 146.1, 137.1, 131.7, 124.3, 120.2, 119.8, 106.2, 100.9, 48.9, 45.5, 36.2, 33.1, 26.0, 25.9, 25.8, 25.1, 24.6. **Z isomer:** δ 169.1, 137.9, 137.8, 137.1, 130.5, 124.1, 123.9, 119.8, 106.2, 100.9, 48.9, 45.5, 40.5, 39.1, 34.8, 32.9, 30.2, 29.6, 26.1. HRMS (ESI): calc. for $[(C_{21}H_{27}NO_3)H]$ (M+H) 342.2069, measured 342.2073.

(4-(3-Phenylallyl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (3ag):

Colorless solid; eluent (27% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2g** (2.5 equiv) and the reaction was done at rt for 16 h. The desired product was isolated in 113 mg and yield is 74%. ^{1}H NMR ($CDCl_3$, 400 MHz): **E isomer:** δ 7.35 – 7.17 (m, 6H), 6.67 (s, 2H), 6.43 (dt, *J* = 12.0, 4.0 Hz, 1H), 5.94 (s, 2H), 5.74 (dt, *J* = 12.0, 8.0 Hz, 1H), 3.68 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.62 (m, 4H). **Z isomer:** δ 7.35 – 7.17 (m, 6H), 6.67 (s, 2H), 6.43 (dt, *J* = 12.0, 4.0 Hz, 1H), 5.94 (s, 2H), 5.74 (dt, *J* = 12.0, 8.0 Hz, 1H), 3.56 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.52 (t, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.62 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): **E isomer:** δ 168.7, 147.3, 145.9, 136.8, 131.9, 129.4, 128.7, 128.1, 126.7, 119.6, 119.1, 106.6, 101.0, 48.6, 45.5, 26.5, 25.7, 24.3.
Z isomer: δ 168.9, 146.1, 137.1, 131.7, 131.1, 128.4, 127.1, 126.6, 125.9, 119.9, 118.8, 106.2, 101.0, 49.0, 45.1, 29.9, 29.6, 25.6. HRMS (ESI): calc. for $[(C_{21}H_{21}NO_3)H]$ (M+H) 336.1600, measured 336.1607.

B. General Procedure for the Alkenylation of Aromatic amides with Allylic Acetates catalyzed by Ruthenium Complex:

A 15-mL pressure tube with septum containing amide **1** (100 mg), $[\{RuCl_2(p\text{-cymene})\}_2]$ (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, was then added 1,2-dichloroethane (1.0 mL) via syringe. After that, allylacetate **2a** (1.2-2.0 equiv) and 1,2-dichloroethane (2.0 mL) were added via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 100-120 °C for 12-20 h. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent (for some compounds CH_2Cl_2 and MeOH combination were used. It has been mentioned in the substrates below) to give pure **4**.
Note: For products **4ba-4ga,** 1.2 equiv of allylacetate (**2a**) and products **4ja-4qa,** 2.0 equiv of allylacetate (**2a**) was used. Reaction temperature is 120 °C for products **4fa, 4ga, 4la, 4ma, 4na** and **4pa**.

Spectral Data of Compounds

(*E*)-(4-(Prop-1-en-1-yl)benzo[*d*][1,3]dioxol-5-yl)(pyrrolidin-1-yl)methanone (4aa):
Colorless solid; eluent (30% ethylacetate in hexane); The representative general procedure was followed using **1a** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 89 mg and yield is 76%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2881, 2797, 1647, 1435, 1312, 1041, 918, 874, 680. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.71 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.55 (dq, *J* = 16.0, 8.0 Hz, 1H), 6.22(dq, *J* = 16.0, 4.0 Hz, 1H), 5.98 (s, 2H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.84 (dd, *J* = 8.0, 4.0 Hz, 3H), 1.84 – 1.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 147.6, 144.8, 132.6, 130.7, 122.9, 119.9, 117.5, 106.6, 100.9, 48.4, 45.5, 25.9, 24.6, 19.4.
HRMS (ESI): calc. for $[(C_{15}H_{17}NO_3)H]$ (M+H) 260.1287, measured 260.1289.

(*E*)-(4-Methoxy-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ba):
Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1b** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 88 mg and yield is 74%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.74 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.25 – 6.16 (m, 1H), 3.79 (s, 3H), 3.62 (t, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 1.91 (p, *J* = 8.0 Hz, 2H), 1.83 (dd, *J* = 8.0, 4.0 Hz, 2H), 1.82 – 1.77 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 159.8, 135.9, 129.1, 128.5, 127.8, 127.6, 112.6, 110.4, 55.2, 48.3, 45.5, 25.9, 24.6, 18.7. HRMS (ESI): calc. for $[(C_{15}H_{19}NO_2)H]$ (M+H) 246.1494, measured 246.1502.

(*E*)-(4-Methyl-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ca):
Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1c** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100°C for12 h. The desired product was isolated in 98 mg and yield is 81%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2942, 2617, 1647, 1415, 1317, 1047, 918, 875, 598. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.23- 6.15 (m, 1H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.90 (p, *J* = 8.0 Hz, 2H), 1.81 (dd, *J* = 8.0, 4.0 Hz, 3H), 1.81 – 1.75(m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 138.5, 133.9, 133.3, 127.9, 127.6, 127.5, 126.0, 125.9, 48.2, 45.4, 25.8, 24.5, 21.3, 18.7. HRMS (ESI): calc. for $[(C_{15}H_{19}NO)H]$ (M+H) 230.1545, measured 230.1553.

(*E*)-(2-(Prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4da):
Colorless solid; eluent (27% ethylacetate in hexane); The representative general procedure was followed using **1d** (100 mg), **2a** (1.2 equiv) and the reaction was done at 100 °C for 12 h. The desired product was isolated in 92 mg and yield is 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 8.0Hz,1H),7.24 -7.18 (m, 1H), 7.12 (t, *J* = 4.0Hz,2H),6.33 (d, *J* = 16.0Hz,1H),6.20 - 6.13(m, 1H), 3.57 (t, *J* = 8.0Hz,2 H), 3.00 (t, *J* = 8.0Hz,2 H), 1.85 (p, *J* = 4.0Hz, 2 H), 1.77(dt, *J* = 8.0, 4.0Hz,3 H), 1.76 – 1.72 (m, 2 H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 135.8, 133.8, 128.7, 128.2, 127.4, 126.7, 125.8, 125.2, 48.0, 45.2, 25.7, 24.4, 18.6.
HRMS (ESI): calc. for $[(C_{14}H_{17}NO)H]$ (M+H) 216.1388, measured 216.1395.

(*E*)-(4-Chloro-2-(prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4fa):
Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1f** (100 mg), **2a** (1.2 equiv) and the reaction was done at 120°C for12 h. The desired product was isolated in 86 mg and yield is 73% ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 4.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.21 (m, 1H), 3.63 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 1.93 (p, *J* = 6.5 Hz, 2H), 1.85 (dd, *J* = 8.0, 2.0 Hz, 3H),

View Article Online
DOI: 10.1039/C6OB01498D

1.84 – 1.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.7, 136.1, 134.8, 134.5, 129.3, 127.6, 126.9, 126.6, 125.5, 48.2, 45.5, 25.9, 24.6, 18.7. HRMS (ESI): calc. for [($C_{14}H_{16}ClNO$)H] (M+H) 250.0999, measured 250.1003.

(*E*)-(4-Fluoro-2-(Prop-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ga):

Colorless solid; eluent (28% ethylacetate in hexane); The representative general procedure was followed using **1g** (100 mg), **2a** (1.2 equiv) and the reaction was done at 120°C for12 h. The desired product was isolated in 75 mg and yield is 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (d, *J* = 8.0Hz,1H),7.13 (dd, *J* = 8.0, 4.0Hz,1H), 6.88 (dt, *J* = 8.0, 4.0 Hz,1H), 6.35 (d, *J* = 16.0Hz,1H),6.27 -6.18(m, 1H), 3.61 (t, *J* = 8.0Hz,2H), 3.06 (t, *J* = 8.0Hz,2H), 1.91 (p, *J* = 4.0Hz,2H), 1.83 (dd, *J* = 8.0, 4.0Hz,3H), 1.81 – 1.77(m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 164.1 and 161.6 (F-coupling), 136.8 and 136.7 (F-coupling), 132.1, 129.8, 128.1 and 127.9 (F-coupling), 126.7, 114.0 and 113.8 (F-coupling), 111.9 and 111.7 (F-coupling), 48.3, 45.5, 25.9, 24.5, 18.7. HRMS (ESI): calc. for [($C_{14}H_{16}FNO$)H] (M+H) 234.1294, measured 234.1299.

(*E*)-*N*,4-Dimethyl-2-(prop-1-en-1-yl)benzamide (4ja):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1j** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 79 mg and yield is 63%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3289, 2922, 1630, 1536, 1403, 1157, 1041, 999. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, J = 4.0Hz, 1H), 7.25 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 8.0Hz, 1H), 6.67 (dd, J = 16.0, 4.0 Hz, 1H), 6.20-6.11 (m, 1H), 5.81 (s, 1H), 2.95 (d, J = 4.0 Hz,3 H), 2.32 (s, 3 H), 1.86 (dd, J = 8.0, 4.0Hz, 3 H). 13C NMR (CDCl3, 100 MHz): δ 170.3, 139.9, 135.9, 132.0, 128.6, 128.4, 127.5, 127.4, 126.9, 26.7, 21.3, 18.7. HRMS (ESI): calc. for [(C12H15NO)H] (M+H) 190.1232, measured 190.1236.

(*E*)-*N*-Methyl-2-(prop-1-en-1-yl)benzamide (4ka):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1k** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 84 mg and yield is 65%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3294, 2935, 1635, 1546, 1444, 1319, 1005, 954, 687. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, *J* = 4.0Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H),7.16 (t, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 12.0Hz, 1H), 6.20-6.11 (m, 1H), 5.92 (s, 1 H), 2.93(d, *J* = 4.0 Hz, 3 H), 1.85 (dd, *J* = 8.0, 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 135.8, 134.8, 129.8, 128.6, 128.3, 127.3, 126.6, 126.1, 26.6, 18.6. HRMS (ESI): calc. for [($C_{11}H_{13}NO$)H] (M+H) 176.1075, measured 176.1073.

(*E*)-4-Bromo-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4la):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1l** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 66 mg and yield is 56%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3282, 2945, 2817, 1635, 1547, 1441, 1312, 1041, 935, 875, 661. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 4.0Hz, 1 H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 6.60 (dd, *J* = 16.0, 4.0 Hz, 1 H), 6.23-6.14 (m, 1 H), 5.83 (s, 1 H), 2.96(d, *J* = 4.0 Hz,3 H), 1.87 (dd, *J* = 8.0, 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 137.9, 133.5, 130.3, 129.6, 129.2, 128.9, 127.2, 124.3, 26.7, 18.7. HRMS (ESI): calc. for [($C_{11}H_{12}BrNO$)H] (M+H) 254.0181, measured 254.0188.

(*E*)-4-Chloro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4ma):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1m** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120 °C for 20 h. The desired product was isolated in 66 mg and yield is 54%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3078, 2931, 1634, 1589, 1463, 1259, 1041, 874, 747, 668. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, *J* = 4.0Hz, 1 H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.14 (dt, *J* = 8.0, 4.0 Hz, 1 H), 6.60 (d, *J* = 16.0Hz, 1 H), 6.23-6.14 (m, 1 H), 5.89 (s, 1 H), 2.94 (dd, *J* =8.0, 4.0 Hz,3 H), 1.87 (d, *J* = 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 137.8, 135.9, 133.1, 130.2, 128.8, 127.3, 126.7, 126.2, 26.7, 18.7. HRMS (ESI): calc. for [($C_{11}H_{12}ClNO$)H] (M+H) 210.0686, measured 210.0691.

(*E*)-4-Fluoro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4na):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1n** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 47 mg and yield is 42%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.88 (td, *J* = 8.0, 4.0 Hz, 1H), 6.67 (dt, *J* = 16.0, 4.0 Hz, 1H), 6.20 (dq, *J* = 12.0, 4.0 Hz, 1H), 5.78(s, 1H), 2.97 (d, *J* = 4.0Hz, 3H), 1.88(dd, *J* = 8.0, 4.0 Hz,3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 164.8, 162.3, 138.7 and 138.6 (F-coupling), 130.9, 130.1, 129.6 and 129.5 (F-coupling), 127.5, 113.8 and 113.6 (F-coupling), 112.8 and 112.6 (F-coupling), 26.8, 18.7. HRMS (ESI): calc. for [($C_{11}H_{12}FNO$)H] (M+H) 194.0981, measured 194.0988.

(*E*)-*N*,2-Dimethyl-6-(prop-1-en-1-yl)benzamide (4oa):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1o** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16 h. The desired product was isolated in 104 mg and yield is 83%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (d, *J* = 8.0Hz, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 4.0 Hz, 1 H), 6.36 (d, *J* = 16.0,Hz, 1 H), 6.19-6.13 (m, 1 H), 5.75 (s, 1 H), 2.95 (d, *J* = 8.0 Hz,3 H), 2.25 (s, 3 H), 1.82 (dd, *J* = 8.0, 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 135.7, 134.7, 134.5, 128.7, 128.4, 128.2, 127.8, 122.5, 26.4, 19.1, 18.7. HRMS (ESI): calc. for [($C_{12}H_{15}NO$)H] (M+H) 190.1232, measured 190.1236.

(*E*)-5-Chloro-*N*-methyl-2-(prop-1-en-1-yl)benzamide (4pa):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1p** (100 mg), **2a** (2.0 equiv) and the reaction was done at 120°C for 20 h. The desired product was isolated in 64 mg and yield is 51%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* = 8.0Hz, 1 H), 7.35 (d, *J* = 4.0 Hz, 1 H), 7.27 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.59 (d, *J* = 16.0Hz, 1 H), 6.21-6.12 (m, 1 H), 5.86 (s, 1 H), 2.96 (d, *J* = 8.0 Hz, 3 H), 1.86 (dd, *J* = 8.0, 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 136.0, 134.4, 132.4, 130.0, 129.5, 127.6, 127.4, 127.3, 26.7, 18.7. HRMS (ESI): calc. for [($C_{11}H_{12}ClNO$)H] (M+H) 210.0686, measured 210.0685.

(*E*)-*N*-Methyl-3-(prop-1-en-1-yl)-2-naphthamide (4qa):

White Colour solid; eluent (0.3% methanol in DCM); The representative general procedure was followed using **1q** (100 mg), **2a** (2.0 equiv) and the reaction was done at 100°C for 16

h. The desired product was isolated in 93 mg and yield is 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1 H), 7.86 (s, 1 H), 7.76 (t, *J* = 8.0 Hz,2 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 16.0Hz, 1 H), 6.31-6.22 (m, 1 H), 5.99 (s, 1 H), 3.01 (d, *J* = 8.0 Hz,3 H), 1.91 (dd, *J* = 8.0, 4.0Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 133.9, 133.5, 133.5, 131.6, 128.8, 128.6, 127.9, 127.6, 127.3, 127.2, 126.1, 125.2, 26.8, 18.8. HRMS (ESI): calc. for [($C_{15}H_{15}NO$)H] (M+H) 226.1232, measured 226.1236.

C. General Procedure for the Synthesis of Isochromanone Derivatives.

ortho Allylated aromatic amides (3) (50 mg) was taken in a 10-mL sealed tube and dissolved with 0.5 mL of 1,4 dioxane and 2.0 mL of 6N HCl. Then, the reaction mixture heated at 110°C for 12 h. After cooling to ambient temperature, water was poured into the reaction mixture and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over Na_2SO_4. The solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure 5.

Spectral Data of Compounds

8-Methyl-8,9-dihydro-6*H*-[1,3]dioxolo[4,5-*f*]isochromen-6-one (5a):

Colorless solid; eluent (11% ethylacetate in hexanes); The representative general procedure was followed using **3aa** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 25 mg and yield is 64%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2927, 2854, 1707, 1589, 1232, 1116, 1041, 908, 845, 664. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J*= 4.0 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 5.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.88 – 1.78 (m, 1H), 0.99 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.1, 151.6, 143.8, 126.3, 119.8, 118.8, 107.6, 102.3, 74.6, 28.6, 20.9. HRMS (ESI): calc. for [($C_{11}H_{10}O_4$)H] (M+H) 207.0657, measured 207.0659.

6-Methoxy-3-methylisochroman-1-one (5b):

Colorless solid; eluent (10% ethyl acetate in hexanes); The representative general procedure was followed using **3ba** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 27 mg and yield is 61%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2980, 2935, 1713, 1607, 1458, 1117, 1041, 908, 741, 691 ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 4.0 Hz, 1H),6.67 (d, *J* = 4.0 Hz, 1H), 4.67 – 4.59 (m, 1H), 3.84 (s, 3H), 2.92 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.84 (dd, *J* = 16.0, 4.0 Hz, 1H),1.48 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.5, 163.7, 141.4, 132.6, 117.5, 113.4, 112.1, 74.7, 55.5, 35.2, 20.9. HRMS (ESI): calc. for [($C_{11}H_{12}O_3$)H] (M+H) 193.0865, measured 193.0874.

3,6-Dimethylisochroman-1-one (5c).

Colorless solid; eluent (10% ethyl acetate in hexanes); The representative general procedure was followed using **3ca** (50 mg) and the reaction was done at 110°C for12 h. The desired product was isolated in 24 mg and yield is 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 4.67 -4.58 (m, 1 H), 2.90 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.83 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.37 (s, 3H), 1.48 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 144.6, 139.1, 130.3, 128.5, 127.8, 122.3, 74.9, 34.9, 21.7, 20.9. HRMS (ESI): calc. for [($C_{11}H_{12}O_2$)H] (M+H) 177.0916, measured 177.0923.

3-Methylisochroman-1-one (5d).

Colorless solid; eluent (10% ethyl acetate in hexanes); The representative general procedure was followed using **3da** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 22 mg and yield is 58%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.51 (td, *J* = 8.0, 4.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.69 - 4.64(m, 1 H), 2.96 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.90 (dd, *J* = 16.0, 4.0 Hz, 1H),1.50 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 139.1, 133.6, 130.2, 127.6, 127.2, 124.9, 75.1, 34.9, 20.9. HRMS (ESI): calc. for [($C_{10}H_{10}O_2$)H] (M+H) 163.0759, measured 163.0770.

6-Chloro-3-methylisochroman-1-one (5e):.

Colorless solid; eluent (10% ethyl acetate in hexanes); The representative general procedure was followed using **3fa** (50 mg) and the reaction was done at 110°C for 12 h. The desired product was isolated in 20 mg and yield is 51%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 4.69 -4.61 (m, 1 H), 2.94 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.87 (dd, *J* = 16.0, 4.0 Hz, 1H),), 1.49 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.7, 140.7, 139.9, 131.8, 128.1, 127.4, 123.4, 74.9, 34.6, 20.8.

D. General Procedure for the Synthesis of Isobenzofuranone Derivatives.

ortho Vinylated aromatic amides (**4**) (50 mg) was taken in a 10-mL sealed tube and dissolved with 0.5 mL of 1,4-dioxane and 2.0 mL of 6N HCl. Then the reaction mixture heated at 120°C for 12 h. After cooling to ambient temperature, water was poured in to the reaction mixture and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over Na_2SO_4. The solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure **6**.

Spectral Data of Compounds

8-Ethyl-[1,3]dioxolo[4,5-*e*]isobenzofuran-6(8*H*)-one (6a):

Colorless solid; eluent (10% ethyl acetate in hexanes); The representative general procedure was followed using **4aa** (50 mg) and the reaction was done at 120 °C for 12 h. The desired product was isolated in 25 mg and yield is 61%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 4.0 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 5.42 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.16 -2.08(m, 1 H), 1.83 (dq, *J* = 12.0, 4.0 Hz, 1H), 0.99 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 152.4, 141.1, 129.2, 121.3, 120.8, 109.9, 102.6, 79.6, 26.7, 8.8. HRMS (ESI): calc. for [($C_{11}H_{10}O_4$)H] (M+H) 207.0657, measured 207.0666.

3-Ethyl-5-methoxyisobenzofuran-1(3*H*)-one (6b):

Colorless solid; eluent (12% ethyl acetate in hexanes); The representative general procedure was followed using **4ba** (50 mg) and the reaction was done at 120 °C for 12 h. The desired

product was isolated in 22 mg and yield is 56%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 2972, 2933, 1702, 1604, 1495, 1255, 1083, 1019, 689. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.35 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.88 (s, 3H), 2.15 – 2.04 (m, 1H),1.84 – 1.73 (m, 1H), 0.98 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 164.6, 152.5, 127.2, 118.7, 116.1, 105.8, 81.5, 55.8, 27.6, 8.7. HRMS (ESI): calc. for [($C_{11}H_{12}O_3$)H] (M+H) 193.0865, measured 193.0874.

3-Ethyl-5-methylisobenzofuran-1(3*H*)-one (6c):

Colorless solid; eluent (12% ethyl acetate in hexanes); The representative general procedure was followed using **4ca** (50 mg) and the reaction was done at 120 ^{o}C for 12 h. The desired product was isolated in 19 mg and yield is 51%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 5.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.46 (s, 3H), 2.13 – 2.02 (m, 1H), 1.81 – 1.74 (m, 1H), 0.96 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 150.3, 145.1, 130.2, 125.4, 123.7, 122.0, 82.0, 27.7, 22.1, 8.8. HRMS (ESI): calc. for [($C_{11}H_{12}O_2$)H] (M+H) 177.0916, measured 177.0923

6-Methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl acetate (11a):

Colorless solid; eluent (32% ethyl acetate in hexanes); The representative general procedure A was followed using **10a** (100 mg), **2a** (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 58 mg and yield is 41%. IR (ATR)$\tilde{\nu}$ (cm^{-1}): 3300 (broad), 2926, 2315, 1649, 1615, 1454, 1337, 1080, 657. ^{1}H NMR (DMSO d_6, 400 MHz): δ 7.96 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 4.08 (dd, *J*= 12.0, 4.0 Hz, 1H), 3.92 (dd, *J*= 12.0, 4.0 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.02 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.81 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.33 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (DMSO d_6, 100 MHz): δ 170.3, 164.3, 142.0, 137.2, 128.3, 127.5, 127.0, 126.1, 65.1, 48.7, 29.5, 21.1, 20.6. HRMS (ESI): calc. for [($C_{13}H_{15}NO_3$)H] (M+H) 234.1130, measured 234.1141.

(1-Oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl acetate (11b):

Colorless solid; eluent (32% ethyl acetate in hexanes); The representative general procedure A was followed using 10b (100 mg), 2a (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 55 mg and yield is 38%. IR (ATR)$\tilde{\nu}$ (cm-1): 2931, 2817, 1727, 1637, 1435, 1312, 1041, 908, 875, 661. 1H NMR (CDCl3, 400 MHz): δ 8.04 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 6.42 (s, 1H), 4.24 (dd, J = 12.0, 4.0 Hz, 1H), 4.05 (dd, J = 12.0, 8.0 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.02 (dd, J = 16.0, 4.0 Hz, 1H), 2.89 (dd, J = 16.0, 8.0 Hz, 1H), 2.06 (s, 3H).

(1-Oxo-1,2,3,4-tetrahydrobenzo[g]isoquinolin-3-yl)methyl acetate (11c):

Colorless solid; eluent (32% ethyl acetate in hexanes); The representative general procedure A was followed using 10c (100 mg), 2a (2.5 equiv) and the reaction was done at rt for 36 h. The desired product was isolated in 63 mg and yield is 47%. IR (ATR)$\tilde{\nu}$ (cm-1): 3267 (broad), 1734, 1727, 1656, 1413, 1229, 1042, 730. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.53 (d, J = 8.20 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 6.47 (s, 1H), 4.27 (dd, J = 12.0, 4.0 Hz, 1H), 4.07 (dd, J = 12.0, 4.0 Hz, 1H), 4.02 – 3.98 (m, 1H), 3.20 (dd, J = 16.0, 4.0 Hz, 1H), 3.04 (dd, J = 16.0, 4.0 Hz, 1H), 2.06 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ 170.7, 166.3, 135.4, 132.3, 132.1, 129.6, 129.4, 128.7, 128.5, 127.1, 126.3, 126.2, 65.9, 50.2, 30.6, 20.7. HRMS (ESI): calc. for [($C_{16}H_{16}NO_3$)H] (M+H) 270.1130, measured 270.1140.

Acknowledgements

We thank the DST-SERB (EMR/2014/000978), India for the support of this research. R. M thank the CSIR for a fellowship.

Notes and References

1 1. Recent reviews: *(a)* P. B. Arokiam, C. Bruneau and P. H. Dixneuf, *Chem. Rev*. 2012, **112**, 5879; *(b)* L. Ackermann, *Chem. Rev*., 2011, **111***,* 1315; *(c)* J. Li and L.Ackermann, *Nat. Chem*. 2015, **7***,* 686; *(d)* J. Wencel-Delord, T. Droge, F. Liu and F. Glorius, *Chem. Soc. Rev*. 2011, **40***,* 4740; *(e)* N. Kuhl, N. Schroder and F. Glorius, *Adv. Synth. Catal.* 2014, **356***,* 1443; *(f)* M. T. Lyons and M. S. Sanford, *Chem. Rev*., 2010, **110***,* 1147; *(g)* D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev*. 2010, **110**, 624; *(h)* K. M. Engle, T.-S. Mei, M. Wasa, and J.-Q. Yu, *Acc. Chem. Res*. **2012**, *45*, 788.

2 2. *(a)* S. R. Chemler and P. H. Fuller, *Chem. Soc. Rev.* 2007, **36**, 1153; *(b)* G. Ni, Q. J. Zhang, Z.-F. Zheng, R.-Y. Chen and D.-Q. Yu, *J. Nat. Prod.,* **2009***, 72*, 966. *(c)* J. A. Marshall, *Chem. Rev.,* 2000**, 100**, 3163; *(d)* B. M. Trost, O. R. Thiel and H.-C. Tsui, *J. Am. Chem. Soc.,* 2002, **124**, 11616. *(e)* R. M. Magid, *Tetrahedron* 1980, **36**, 1901; *(f)* H. Ohmiya, Y. Makida, T. Tanaka and M. Sawamura, *J. Am. Chem. Soc.* 2008, **130**, 17276; *(g)* D. Li, T. Tanaka, H. Ohmiya and M. Sawamura, *Org. Lett.* 2010**, 12**, 2438.

3 3 *(a)* J. Min, J. Lee, J. Yang and S. Koo, *J. Org. Chem.* 2003, **68**, 7925; *(b)* M. Niggemann and M. J. Meel, *Angew. Chem., Int. Ed*. 2010, **49**, 3684. *(c)* M. Kodomari, S. Nawa and T. Miyoshi, *Chem. Commun.* 1995, 1895. *(d)* T. B. Poulsen and K. A. Jorgensen, *Chem. Rev.* 2008, **108**, 2903.

4 4. *(a)*. M. D. Levin and F. D. Toste, *Angew. Chem. Int. Ed.* 2014, **53***,* 6211. *(b)* T. J. Tsuji, *Acc. Chem. Res.* 1969, **2**, 144. *(c)* B. M. Trost and D. L. Van Vranken, *Chem. Rev.* 1996, **96**, 395. *(d)* Y. Hatanaka, Y. Ebina and T. Hiyama, *J. Am. Chem. Soc*. 1991, **113**, 7076. *(e)* A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc*. 1987, **109**, 5478; *(f)* V. Farina and B. Krishnan, *J. Am. Chem. Soc.* 1991, **113**, 9585; *(g)* N. H. Frost, H. Leuser, M. I. Calaza, F. F. Kneisel and P.Knochel, *Org. Lett.,* 2003, **5**, 2111.

5 5 *(a)* C. Feng, D. Feng and T.-P. Loh, *Org. Lett.,* 2013, **15**, 3670; *(b)* S. A. Tsai, M. Brasse, G. R. Bergman and J. A. Ellman, *Org. Lett.,* 2011, **13**, 540; *(c)* R. Zeng, C. Fu and S. Ma, *J. Am. Chem. Soc.* 2012, **134**, 9597; *(d)* B. Ye and N. Cramer, *J. Am. Chem. Soc*. 2013, **135**, 636; *(e)* H. Wang, N. Schroder and F. Glorius, *Angew. Chem., Int. Ed*. 2013, **52**, 5386; *(f)* C. Feng, D. Feng and T.-P. Loh, *Chem. Commun*. 2015**, 51**, 342; *(g)* H. Dai, C. Yu, C. Lu and H. Yan, *Eur. J. Org. Chem.* 2016, 1255.

6 6. *(a)* S. Oi, Y. Tanaka and Y. Inoue, *Organometallics* 2006, **25**, 4773; *(b)* Y. Goriya and C. V. Ramana, *Chem. Eur. J.,* 2012**, 18**, 13288; *(c)* M. Kim, S. Sharma, N. K. Mishra, S. Han, J. Park, M. Kim, Y. Shin, J. H. Kwak, S. H. Han and I. S. Kim, *Chem. Commun*. 2014, **50**, 11303; *(d)* R. Manikandan, P. Madasamy and M. Jeganmohan, *Chem. Eur. J*. 2015, **21**, 13934; *(e)* G. S. Kumar and M. Kapur, *Org. Lett.* 2016, **18**, 1112; *(e)*L. V. Graux, M. Giorgi, G. Buono and H. Clavier, *Dalton Trans*., 2016, **45**, 6491; *(f)* E. F. Flegeau, C. Bruneau, P.

View Article Online
DOI: 10.1039/C6OB01498D

H. Dixneuf and A. Jutand, *J. Am. Chem. Soc.,* 2011, **133**, 10161; *(g)* G. Onodera , H. Imajima , M. Yamanashi , Y. Nishibayashi , M. Hidai and S. Uemura, *Organometallics*, 2004, **23**, 5841.

7 7. *(a)* S. Asako, L. Ilies and E. Nakamura, *J. Am. Chem. Soc.* 2013, **135**, 17755; *(b)* S. Asako, J. Norinder, L. Ilies, N. Yoshikai and E. Nakamura, *Adv. Synth. Catal.* 2014, **356**, 1481; *(c)* D.-G. Yu, T. Gensch, F. de Azambuja, S. Va´squez-Ce´spedes and F. Glorius, *J. Am. Chem. Soc.* 2014, **136***,* 17722; *(d)* T. Gensch, S. Va´squez-Ce´spedes, D.-G. Yu and F. Glorius, *Org. Lett.* 2015, **17***,* 3714; *(e)* M. Moselage, N. Sauermann, J. Koeller, W. Liu, D. Gelman and L. Ackermann, *Synlett* 2015, **26***,* 1596; *(f)* Y. Suzuki, B. Sun, K. Sakata, T. Yoshino, S. Matsunaga and M. Kanai, *Angew. Chem., Int. Ed*. 2015, **54***,* 9944; *(g)* G. Cera, T. Haven and L. Ackermann, *Angew. Chem. Int. Ed.* 2016, **55***,* 1484; *(h)* N. Barsu, D. Kalsi and B. Sundararaju, *Chem. Eur. J.* 2015, **21**, 9364; *(i)* W. Liu, S. C. Richter, Y. Zhang and L. Ackermann, *Angew. Chem. Int. Ed.* 2016, **55***,* 7747; (j) Y. Bunno, N. Murakami, Y. Suzuki, M. Kanai, T. Yoshino and S. Matsunaga, *Org. Lett.* 2016**, 18,** 2216.

8 8. Selected ruthenium papers: *(a)* I. Fabre, N.-V. Wolff, G.-L. Duc, E.-F. Flegeau, C. Bruneau, P. H. Dixneuf and A. Jutand, *Chem. Eur. J.* 2013, **19**, 7604; *(b)* P. B. Arockiam, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *Green Chem.* 2011, **13**, 3075; *(c)* F. Yang, K. Rauch, K. Kettelhoit and L. Ackermann, *Angew. Chem. Int. Ed*. 2014, **53**, 11285; *(d)* C. Suzuki, K. Hirano, T. F. Satoh and M. Miura, *Org. Lett.* 2013, **15**, 3990; *(e)* K. Parthasarathy, N. Senthilkumar, J. Jayakumar and C.-H. Cheng, *Org. Lett*. 2012, **14**, 3478; *(f)* K. Muralirajan, K. Parthasarathy and C.-H. Cheng, *Org. Lett*. 2012, **14**, 4262; *(g)* V. P. Mehta, J-A-G. Lopez and M. F. Greaney, *Angew. Chem. Int. Ed*. 2014, **53**, 1529; *(h)* C. J. Teskey, A-Y-W. Lui and M. F. Greaney, *Angew.Chem. Int. Ed.* 2015, **54**, 11677; *(i)* R. Manikandan, P. Madasamy and M. Jeganmohan, *ACS Catal*. **2016**, *6*, 230; *(j)* Y. Kommagala, V. B. Mullapudi, F. Francis and C. V. Ramana, *Catal. Sci. Technol*. 2015, **5**, 114; *(k)* M. R. Yadav, R. K. Rit, M. Shankar and A. K. Sahoo, *J. Org. Chem*. 2014, **79**, 6123; *(l)* M. Bhanuchandra, M. Ramu Yadav, R. K. Rit, M. Rao Kuram and A. K. Sahoo, *Chem. Commun.*, 2013, **49**, 5225