Nickel–Copper-Catalyzed C(sp 2) À N Cross-Coupling of Cyclic and Bridged Amides: An Access to Cyclic Enamides and Alkenyl Vince Lactams

ARTICLE *in* ADVANCED SYNTHESIS & CATALYSIS · OCTOBER 2015

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Nickel–Copper-Catalyzed C(sp^2)–N Cross-Coupling of Cyclic and Bridged Amides: An Access to Cyclic Enamides and Alkenyl Vince Lactams

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Received: May 8, 2015; Revised: August 5, 2015; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500457.

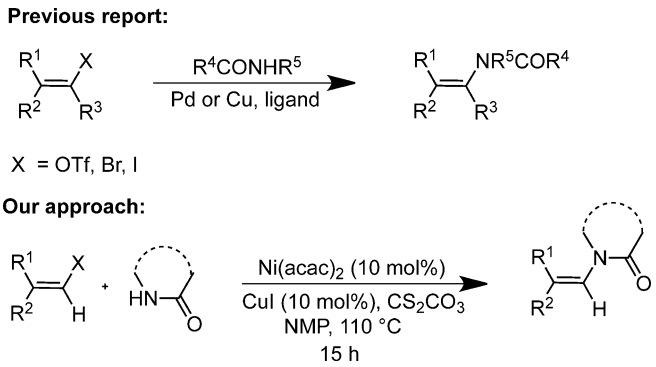
Abstract: An efficient C(sp^2)–N cross-coupling of styrenyl and vinyl halides with cyclic and bridged amides catalyzed by nickel acetonylacetonate [Ni(acac)$_2$] and copper(I) iodide (CuI) in the absence of any ligand has been developed. The reaction conditions are optimized to give the maximum yield of products using cesium carbonate (Cs_2CO_3) (2.0 equiv.) in *N*-methyl-2-pyrrolidinone (NMP) at 110 °C under argon in the presence of Ni(acac)$_2$/CuI (10 mol% each). A series of alkenyl derivatives of Vince lactams (bridged amides) and cyclic amides are obtained by this procedure. Halogen-containing styrenyl bromides also underwent coupling with amides to provide the products. The coupling is highly chemoselective as during the reactions the halogens (Br, Cl, F) on the aromatic ring remained intact and these can be used for further functionalization to make these enamides more useful. Although the (*E*)-styrenyl halides produced the corresponding (*E*)-styrenyl enamides, reactions with (*Z*)-styrenyl halides produced 1,3-di-ynes instead of (*Z*)-styrenyl enamides. This may be explained by the possibility of E_2 type elimination of (*Z*)-styrenyl halides in the presence of a strong base like cesium carbonate followed by homocoupling. This catalyst system works efficiently for the N-arylation too along with N-styrenylation and vinylation. The bridged as well as cyclic amides successfully coupled with substituted aryl halides to provide the corresponding products. In general, the reactions are clean and high yielding. The operations are very simple and the products are obtained pure by standard column chromatography. The reaction is compatible with variety of amides and alkenyl bromides. The roles of nickel acetonylacetonate and copper(I) iodide in this reaction have been established and a possible reaction pathway has been outlined. The significant feature of this protocol is the alkenylation of Vince lactams *via* C(sp^2)–N cross-coupling, which has not been reported so far and these products may have much potential in the pharmaceutical industry.

Keywords: copper; cross-coupling; nickel; Vince lactams; vinyl halides

Introduction

Enamides are of much importance as they constitute the key structural motifs in many natural products[1] and are used as versatile synthetic intermediates.[2] The cyclic, particularly the bicyclic (bridged) enamide, Vince lactam, has received considerable current attention because of its presence as an active scaffold in many life-saving drugs and its use as building block[3] for the synthesis of several therapeutic agents.[4] Thus an easy access to diverse derivatives of Vince lactam is of much importance for screening of these pharmaceutically useful compounds. Surprisingly, the synthesis of substituted, particularly *N*-vinyl/alkenyl Vince lactams is not adequately addressed and this prompted us to start work in this area.

The transition metal-catalyzed cross-coupling reaction is a powerful tool for C–C and C–heteroatom bond formation.[5] The coupling with a C(sp^2) center is usually more challenging than with a C(sp^3) one. The C(sp^2)–N coupling is an important reaction as it leads to many pharmaceutically active molecules.[6] Among various N-nucleophiles such as N-heterocycles, amines, anilines and amides the coupling with amides is a difficult one due to the their less reactivity for conjugation of the lone pair of electrons of the N-center with the adjacent carbonyl moiety. Although C(sp^2)–N coupling with amides was achieved by Pd



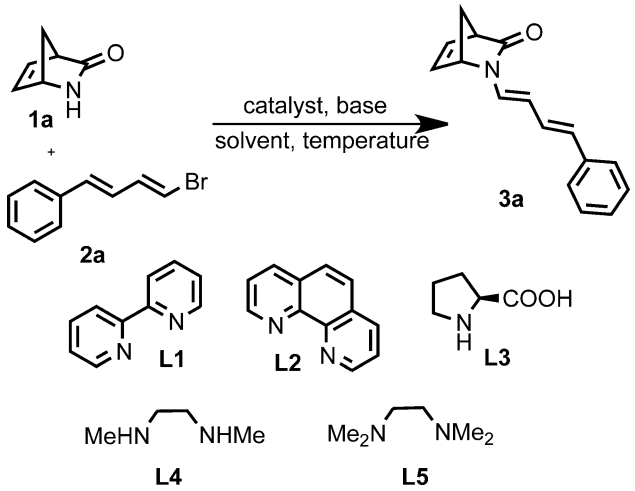
Scheme 1. Nickel-catalyzed *N*-vinylation of amides *via* C(sp^2)–N cross-coupling.

catalysis,[7] this reaction is associated with disadvantages of high cost of catalyst, and tedious separation of Pd catalysts from polar reaction medium, especially in the later stages of the reaction. Ullman's[8] Cu-catalyzed N-arylation of amines and Goldberg's[9] Cu-catalyzed N-arylations of amides have been widely used since the last decades. However, these procedures often require high temperature (nearly 200 °C), expensive and toxic dinitrogen ligands. Later Chan[10] reported an alternative for the arylation of amides with triarylbismuth in the presence of cupric acetate at room temperature using a stoichiometric amount of Cu catalyst. A couple of reports on the Cu-catalyzed cross-coupling of amides with potassium alkenyltrifluoroborate salts,[11] vinyl halides[12] and arylboronic acids[13] in the presence of ligand are also available. Recently, Teo et al.[14] reported a cobalt-catalyzed protocol for the N-arylation of benzamides with aryl iodide in the presence of a dinitrogen ligand whereas Singh et al.[15] demonstrated a Ni-catalyzed one using arylboronic acids. However, to the best of our knowledge, a metal-catalyzed alkenylation of bridged amide by coupling reaction has not been reported so far. Considering the importance of enamides and functionalized Vince lactams,[16] we sought to develop a more convenient protocol for the alkenylation of bridged amides using a less expensive metal and avoiding a ligand. Being motivated with our recent works on carbon-carbon[17a] and carbon-heteroatom bond formation[17b] using an Ni/Cu system we report here a Ni-catalyzed C(sp^2)–N cross-coupling of styrenyl/vinyl halides with bridged and cyclic amides in the presence of CuI (Scheme 1).

Results and Discussion

To standardize the reaction conditions, a series of experiments was carried out with variation of reaction parameters such as catalyst, base, solvent, temperature and time for a representative reaction of 2-azabicyclo[2.2.1]hept-5-en-3-one (**1a**) and 4-phenyl-(*E,E*)-1,3-dienyl bromide (**2a**). The results are summarized in Table 1. The reaction using $Ni(acac)_2$ or nickel chloride ($NiCl_2$) in the presence of a reducing agent, zinc (Zn), did not lead to any product (Table 1, entries 1 and 2). Use of several N-base ligands (**L1**, **L2**, **L3**, **L4** and **L5**) together with $NiCl_2$ provided marginal yields of product (Table 1, entries 3–7). Interestingly, addition of CuI (10 mol%) along with $NiCl_2{\cdot}6H_2O$ in the presence of a reducing agent, Zn, slightly improved the yield (Table 1, entry 8). However, use of

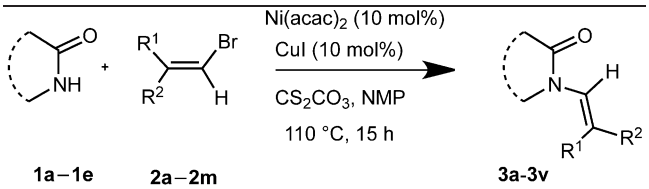
Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Base	Time [h]	Yield[b]
1	$Ni(acac)_2$	NMP	Cs_2CO_3	24	–
2[c]	$NiCl_2{\cdot}6H_2O$	NMP	Cs_2CO_3	24	trace
3	$NiCl_2{\cdot}6H_2O$/**L1**	NMP	Cs_2CO_3	24	trace
4	$NiCl_2{\cdot}6H_2O$/**L2**	NMP	Cs_2CO_3	24	10 %
5	$NiCl_2{\cdot}6H_2O$/**L3**	NMP	Cs_2CO_3	24	15 %
6	$NiCl_2{\cdot}6H_2O$/**L4**	NMP	Cs_2CO_3	24	11 %
7	$NiCl_2{\cdot}6H_2O$/**L5**	NMP	Cs_2CO_3	24	16 %
8	$NiCl_2{\cdot}6H_2O$/ CuI	NMP	Cs_2CO_3	24	20 %
9	$Ni(acac)_2$/CuI	NMP	Cs_2CO_3	15	75 %
10	$Ni(acac)_2$/CuCl	NMP	Cs_2CO_3	15	40 %
11	$Ni(acac)_2$/CuI	NMP	K_2CO_3	20	trace
12	$Ni(acac)_2$/CuI	NMP	K_3PO_4	20	20 %
13	$Ni(acac)_2$/CuI	toluene	Cs_2CO_3	15	trace
14	$Ni(acac)_2$/CuI	DMF	Cs_2CO_3	15	10 %
15	$Ni(acac)_2$/CuI	DMSO	Cs_2CO_3	15	trace
16[d]	$Ni(acac)_2$/CuI	NMP	Cs_2CO_3	15	45
17[e]	$Ni(acac)_2$/CuI	NMP	Cs_2CO_3	15	–
18	CuI	NMP	Cs_2CO_3	20	trace

[a] *Reaction conditions*: A mixture of **1a** (1.0 mmol), **2a** (1.0 mmol), 10 mol% Ni catalyst and Cs_2CO_3 (2.0 mmol) was heated at 110 °C under an argon atmosphere.
[b] Yield of isolated pure products.
[c] 1.5 equiv. Zn were used.
[d] 5 mol% each of $Ni(acac)_2$/CuI were used.
[e] The reaction was performed at room temperature (30 °C).

Table 2. Ni/Cu co-catalyzed coupling of amides and vinyl halides.[a]



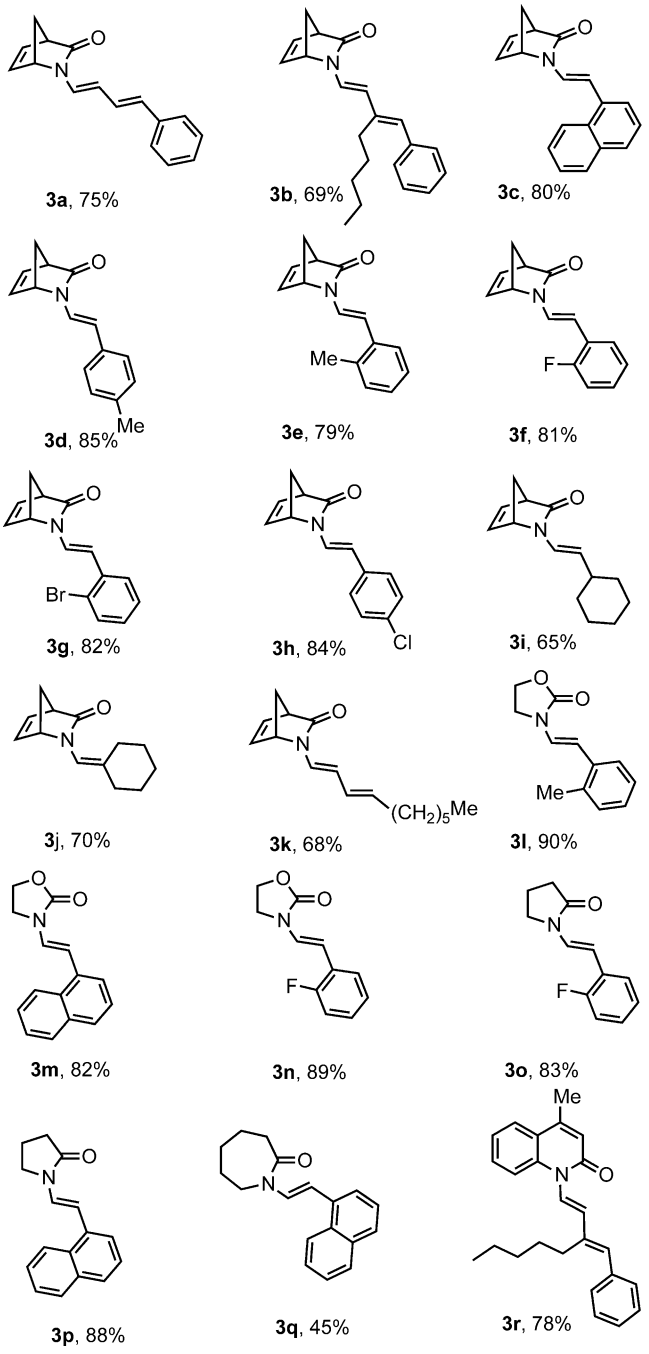
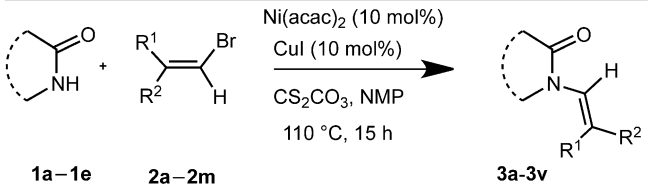
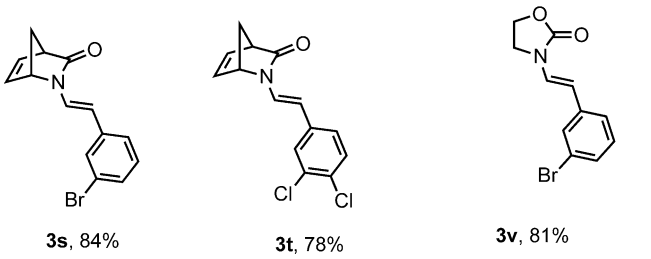


Table 2. (Continued)





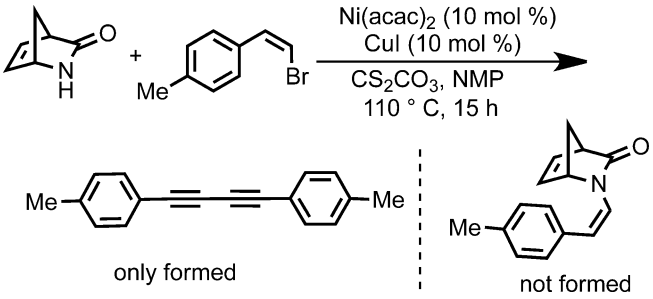
[a] *Reaction conditions*: cyclic amide (2.0 mmol), vinyl bromide (1.0 mmol), Ni(acac)$_2$ (10 mol%), CuI (10 mol%), Cs_2CO_3 (2.0 equiv.), NMP (3 mL), 110 °C, 15 h, under argon atmosphere.

[b] Yield of isolated pure products.

Ni(acac)$_2$/CuI (10 mol% each), CS_2CO_3 as a base and NMP (*N*-methyl-2-pyrrolidinone) as a solvent in the absence of a ligand and reducing agent produced the best result (Table 1, entry 9). Use of copper chloride (CuCl) instead of CuI reduced the yield (Table 1, entry 10). The reaction did not proceed using a weaker base such as K_2CO_3 and K_3PO_4 in place of CS_2CO_3 (Table 1, entries 11 and 12). Use of toluene or dimethyl sulfoxide (DMSO) failed to initiate the reaction; however in *N*,*N*-dimethylformamide (DMF) the reaction progressed marginally (10%) (Table 1, entries 13–15). To check the catalyst loading, use of 5 mol% of Ni(acac)$_2$/CuI instead of 10 mol% decreased the yield of product (Table 1, 16). The reaction did not occur at room temperature (Table 1, entry 17). Use of CuI (10 mol%) without Ni catalyst led to only a trace amount of product (Table 1, entry 18). Thus, in a typical experimental procedure, a mixture of bridged/cyclic amide (2.0 mmol), vinyl halide (1.0 mmol) and CS_2CO_3 (2.0 equiv.) in NMP was heated at 110 °C under argon in the presence of Ni(acac)$_2$/CuI (10 mol% each) for a certain period of time (monitored by TLC). Standard work-up and column chromatography provided the pure products.

A series of diversely substituted styrenyl and vinyl halides underwent C(sp^2)–N coupling with a variety of bridged and cyclic amides under the standardized conditions to afford the corresponding enamides. All the products are summarized in Table 2.

4-Phenyl-(*E*,*E*)-1,3-dienyl bromide and 4-phenyl-3-pentyl-(*E*,*E*)-1,3-dienyl bromides underwent efficient coupling with 2-azabicyclo[2.2.1]hept-5-en-3-one to give the corresponding bridged enamides (**3a**, **3b**).



Scheme 2. Reaction between *cis*-vinyl bromide and amide.

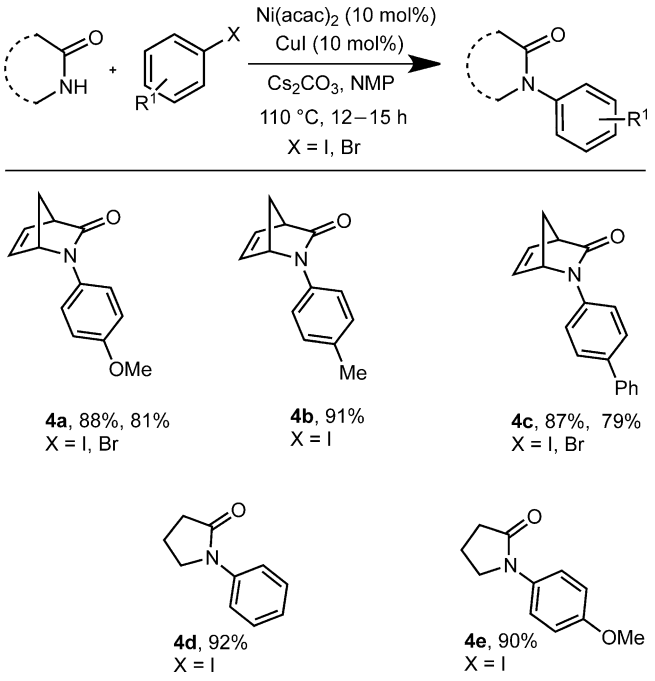
Styrenyl bromides containing naphthyl and Me moieties in the aromatic ring coupled with 2-azabicyclo[2.2.1]hept-5-en-3-one, oxazolidinone, pyrolidinone and azepan-2-one to produce the corresponding enamides without any difficulty (**3c**, **3d**, **3e**, **3l**, **3m**, **3p** and **3q**). In general, styrenyl bromides containing halogen substituents at *o*-, *m*-, and *p*-positions underwent coupling with amides to provide the products (**3f**, **3g**, **3h**, **3n**, **3o**, **3s**, **3t** and **3v**). The coupling is highly chemoselective as during the reactions the halogens (Br, Cl, F) on the aromatic ring remained intact and these can be used for further functionalization to make these enamides more useful. Bromomethylenecyclohexene and [(*E*)-2-bromovinyl]cyclohexane were compatible in this C(sp^2)–N coupling to produce the corresponding enamides (**3i** and **3j**). 4- Phenyl-3-pentyl-(*E,E*)-1,3-dienyl bromide coupled with 4-methylquinolin-2(1*H*)-one to provide the compound, **3r** which may be of potential for nucleic acid detection.[18] (1*E*,3*E*)-1-Bromodeca-1,3-diene also underwent successful coupling with 2-azabicyclo[2.2.1]hept-5-en-3-one to afford the product (**3k**). The electron-donating (Me) and mildly electron-withdrawing (F, Cl, Br) group-substituted styrenyl bromides underwent reactions cleanly (**3d**, **3e**, **3l**, **3f**, **3g**, **3h**, **3n**, **3o**, **3s**, **3t** and **3v**). However, reactions with strong electron-withdrawing groups (CO_2Me and NO_2)-substituted styrenyl bromides are not successful.

Although the (*E*)-styrenyl halides produced the corresponding (*E*)-styrenyl enamides (Scheme 2), reaction with (*Z*)-styrenyl halides produced 1,3-di-ynes instead of (*Z*)-styrenyl enamides. This may be explained by the possibility of E_2 type elimination of (*Z*)-styrenyl halides in the presence of a strong base like Cs_2CO_3[19] followed by homocoupling.

This catalyst system works efficiently for the *N*-arylation too along with *N*-styrenylation and *N*-vinylation. The bridged as well as cyclic amides successfully coupled with substituted aryl halides to provide the corresponding products (Table 3, **4a**, **4b**, **4c**, **4d** and **4e**).

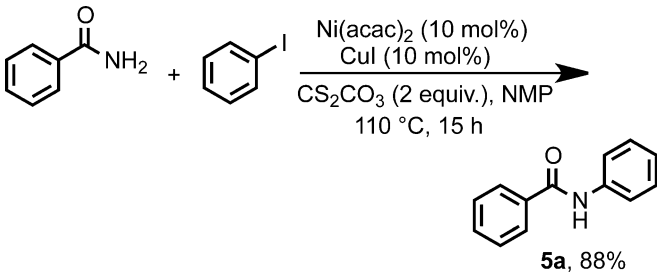
The standardized conditions are also applicable for the coupling of acyclic amides and aryl halides

Table 3. Ni/Cu co-catalyzed coupling of amides and aryl halides.[a]



[a] *Reaction conditions*: cyclic amide (2.0 mmol), vinyl bromide (1.0 mmol), Ni(acac)$_2$ (10 mol%), CuI (10 mol%), Cs_2CO_3 (2.0 equiv.), NMP (3 mL), 110 °C, 15 h, under argon atmosphere.

[b] Yield of isolated pure products.



Scheme 3. *N*-Arylation of benzamide.

(Scheme 3) although the reaction with a primary aliphatic amide (butyl amide) did not succeed.

In general, the reactions are clean and high yielding. The operations are very simple and the products are obtained pure by standard column chromatography. The reaction is compatible with a variety of amides and alkenyl bromides. To compare our procedure with a reported one,[12d] when we performed a reaction of Vince lactam (bridged amide) and 1-[(*E*)-2-bromovinyl]-4-methylbenzene under the reported conditions using CuI (10 mol%), *N,N*-dimethylglycine (20 mol%), Cs_2CO_3 (2 mmol) and dioxane at 80 °C for 12 h the coupled product was obtained in only 30% yield. This demonstrates the superior efficacy of our procedure in the alkenylation of bridged amides.

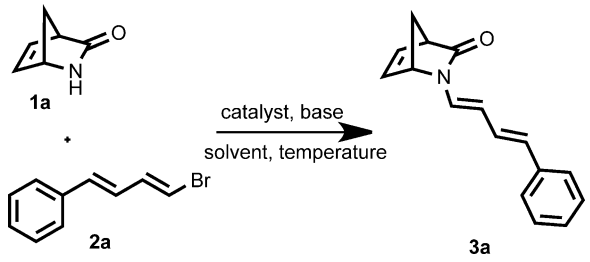
We then turned our attention to deduce the mechanism for this Ni/Cu-mediated coupling. To check the involvement of a radical process, the coupling of **1a** and **2a** was performed in the presence of TEMPO (radical quencher), THF (electron receptor), nitroarene (electron acceptor) separately. Notably, the reactions remained unaffected. The high stereoselectivity in coupling also does not suggest the presence of a radical intermediate due to the inherent nature of vinyl radicals to undergo rapid inversion of conversion.[20] So the possibility of radical pathway is unlikely for this reaction. Increase of steric hindrance of the reactant decreases the rate of the reaction and this indicates that the reaction is more likely to follow an oxidative addition and reductive elimination pathway.

During optimization we have observed that the reaction did not proceed in the presence of $Ni(acac)_2$ or CuI alone. It clearly indicates the involvement of a co-operative Ni/Cu catalytic system for the reaction. In principle, there are two possibilities involving either copper or nickel in the catalytic cycle. If we consider the reaction to be catalyzed by copper, it may proceed through the Cu(I)/Cu(III) oxidative addition. But it appears very unlikely due to the high redox potential of the Cu(I)-Cu(III) system in ligand-free conditions.[21]

We then considered catalysis by nickel compounds. The nickel(II) catalysts are well explored to perform cross-coupling reactions at C($sp2$) centres through Ni(0)-Ni(II) oxidative addition-reductive elimination pathway where an initial reduction of Ni(II) occurs by a reducing agent such as Zn, Grignard reagents, etc. So, to find out a possible reducing agent for the initial reduction of Ni(II) to Ni(0) in our system, several control experiments were performed (Table 4, expts. 1–5). It has been observed that in the presence of $NiCl_2$ and CuI only a trace amount of product was obtained (expt. no. 1). However, addition of either Zn or PPh_3 (20 mol%) along with $NiCl_2$/CuI triggered the reaction leading to 20% yield (expt. no. 2). This experiment indicates that a reduction of Ni(II) to Ni(0) is one of the vital parameters for this reaction. The reaction was not successful using $NiCl_2$ (10 mol%)/Zn (20 mol%) (expt. no. 3) and CuI (10 mol%)/Zn (20 mol%) (expt. no. 4) catalytic systems separately. Interestingly, the reaction with the combined $NiCl_2$/CuI system in presence of 20 mol% acetylacetone leads to the desired product in 60% yield (expt. no. 5).

Based on these results it may be concluded that the acetylacetone moiety in $Ni(acac)_2$ is responsible for the reduction of Ni(II) to Ni(0) which subsequently takes part in oxidative addition.[17] We then concentrated our attention to investigate the precise function of Ni and Cu in this reaction. As stated earlier, O-ligands also facilitate Cu(I)-Cu(III) oxidative addition,

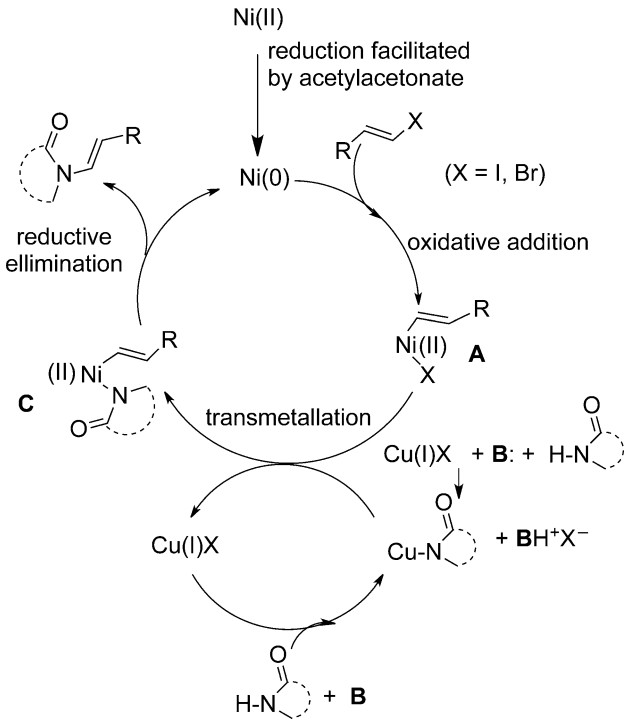
Table 4. Control experiments to explore the role of acetylacetone and Ni-Cu catalyst.



Expt. no.	Catalytic conditions	Product, yield
1	$NiCl_2$ (10 mol%), CuI (10 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, trace
2	$NiCl_2$ (10 mol%), CuI (10 mol%), Zn/PPh_3 (20 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, 20%
3	$NiCl_2$ (10 mol%), Zn (20 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, trace
4	CuI (10 mol%), Zn (20 mol%),Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, trace
5	$NiCl_2$ (10 mol%), CuI (10 mol%), acetylacetone (20 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, 60%
6	CuI (10 mol%), acetylacetone (20 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, trace
7	$Cu(acac)_2$ (10 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, not formed
8	$NiBr_2$ (10 mol%), $Cu(acac)_2$ (10 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, not formed
9	$Ni(acac)_2$ (10 mol%), $Cu(acac)_2$ (10 mol%), Cs_2CO_3, 110 °C, NMP, 15 h	**3a**, not formed

so the possibility of catalysis by CuI in the presence of acetylacetone (present in the reaction medium) without any involvement of nickel may be considered. Thus to check the involvement of Cu catalysis, further experiments were performed (Table 4, expt. 6–9). The reactions using CuI and acetylacetone (expt. 6) and $Cu(acac)_2$ (expt. 7) in the absence of Ni did not produce any product. We also performed the coupling reaction with $Cu(acac)_2$ and $NiBr_2$ (expt. 8) and $Cu(acac)_2$ and $Ni(acac)_2$ (expt. 9) and both these experiments did not lead to a successful result. Thus it is quite logical to conclude that in the absence of either Cu(I) or $Ni(acac)_2$ the reaction is not initiated. The essential parameter is the combined co-operative effect of $Ni(acac)_2$ and CuI which only leads to reaction. Hence the involvement of $Cu(acac)_2$ in this reaction is ruled out.

Thus, we propose a mechanism for this Ni–Cu-catalyzed C–N cross-coupling reaction as outlined in Scheme 4. The reaction is initiated by acetylacetonate-facilitated *in situ* reduction of Ni(II) to Ni(0) which then undergoes oxidative addition with vinyl halide to form intermediate **A**. In another cycle Cu(I)



Scheme 4. Possible mechanistic pathway.

interacts with amide in the presence of a base leading to the formation of amide-Cu(I) intermediate **B** through the chelation by nitrogen. Then transfer of amide species occurs from Cu(I) centre to Ni(II) centre *via* transmetallation between **A** and **B** leading to the formation of intermediate **C**. Finally reductive elimination from intermediate **C** leads to the product with regeneration of active catalytic species Ni(0) which takes part in the next cycle.

Conclusions

In conclusion, we have demonstrated an efficient C(sp^2)–N cross-coupling of styrenyl/vinyl halides with bridged (Vince lactam) and cyclic amides catalyzed by $Ni(acac)_2$ in association with CuI in the absence of a ligand. A series of alkenyl derivatives of bridged and cyclic lactams were obtained by this procedure. This procedure is also successful for coupling with acyclic amides and aryl halides. The significant feature of this protocol is alkenylation of Vince lactam *via* C(sp^2)–N cross coupling, which has not been reported so far and these products may possess much potential in the pharmaceutical industry. The other advantages are use of less expensive Ni/Cu catalyst, no use of ligand and relatively good yield of products. We believe, this reaction will find useful applications in academia and industry.

Experimental Section

General Methods

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids. NMR spectra were recorded at 300, 400 and 500 MHz for ^{1}H spectra and at 75, 100 and 125 MHz for ^{13}C spectra in $CDCl_3$ solutions. $Ni(acac)_2$ and CuI were purchased from Sigma–Aldrich chemicals. Vinyl halides were purchased from Aldrich Chemicals and all styrenyl halides were prepared using previously reported protocols.[17c]

Elemental analyses were done at our Institute with an autoanalyzer. HR-MS analysis was performed in a Qtof mass analyzer using ESI ionization method

Representative Experimental Procedure for the Coupling of (*1S,4R*)-2-Azabicyclo[2.2.1]hept-5-en-3-one and 1-[(1*E*,3*E*)-4-Bromobuta-1,3-dienyl]benzene

A mixture of 2-azabicyclo[2.2.1]hept-5-en-3-one (218 mg, 2.0 mmol), 1-[(1*E*,3*E*)-4-bromobuta-1,3-dienyl]benzene (209 mg, 1.0 mmol), Cs_2CO_3 (650 mg, 2 mmol), $Ni(acac)_2$ (26 mg, 10 mol%), CuI (20 mg, 10 mol%) and NMP (3 mL) was heated at 110 °C under an argon atmosphere for 15 h (TLC). Then the reaction mixture was allowed to cool and extracted with ethyl acetate (3×25 mL). Then the extract was washed with water (2×10 mL) and the organic phase was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give the crude product which was purified by column chromatography over silica gel (hexane/ethyl acetate 85:15) to provide the pure product as yellowish gummy liquid; yield: 177 mg (75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.27$ (d, $J = 8.1$ Hz, 1H), 2.34–2.38 (m, 1H), 3.44–3.46 (m, 1H), 4.70–4.72 (m, 1H), 5.84 (dd, $J_1 = 14.1$ Hz, $J_2 = 10.5$ Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 6.66–6.94 (m, 5H), 7.18–7.20 (m, 1H), 7.21–7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 53.5$, 57.0, 61.4, 110.2, 126.0 (2C), 127.0, 127.2, 127.3, 128.7 (2C), 129.1, 137.8, 139.0, 139.2, 176.3; IR (neat): $\nu = 2923$, 2852, 1701, 1683, 1650, 1541 cm^{-1}; anal. calcd. for $C_{16}H_{15}NO$: C 80.98, H 6.37, N 5.90; found: C 80.94, H 6.41, N 5.96%.

This procedure was followed for all the reactions listed in Table 2, Table 3 and Scheme 3. All these compounds except six (**4a–4e** and **5a**) are new and have been characterized by their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR), HR-MS and elemental analysis.

(*1S,4R*)-2-[(*1E,3E*)-3-Benzylideneoct-1-enyl]-2-azabicyclo[2.2.1]hept-5-en-3-one (3b): Yield: 211 mg (69%); yellowish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.87$–0.91 (m, 3H), 1.32–1.37 (m, 4H), 1.54–1.59 (m, 2H), 2.25–2.45 (m, 4H), 3.46 (s, 1H), 4.75 (d, $J = 1.5$ Hz, 1H), 5.72 (d, $J = 14.7$ Hz, 1H), 6.39 (s, 1H), 6.66–6.69 (m, 1H), 6.88 (d, $J = 14.7$ Hz, 1H), 6.93–6.96 (m, 1H), 7.17–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$, 22.5, 27.7, 29.1, 32.2, 53.6, 57.0, 61.2, 113.8, 123.2, 126.3, 128.0, 128.2 (2C), 128.3 (2C), 128.7, 138.1, 138.9, 19.2, 139.7, 176.6; IR (neat): $\nu =$ 3018, 2958, 2931, 1701, 1647, 1215 cm^{-1}; anal. calcd. for $C_{21}H_{25}NO$: C 82.04, H 8.20, N 4.56; found: C 82.10, H 8.15, N 4.60%.

(*1S,4R*)-2-[(*E*)-2-(Naphthalen-1-yl)vinyl]-2-azabicyclo[2.2.1]hept-5-en-3-one (3c): Yield: 209 mg (80%); brown

gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (d, J = 8.1 Hz, 1H), 2.42–2.46 (m, 1H), 3.49–3.51 (m, 1H), 4.88–4.90 (m, 1H), 6.65 (d, J = 14.4 Hz, 1H), 6.69–6.73 (m, 1H), 7.01–7.04 (m, 1H), 7.28 (d, J = 14.4 Hz, 1H), 7.39–7.56 (m, 4H), 7.72 (d, J = 8.1 Hz, 1H), 7.83–7.86 (m, 1H), 8.07–8.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.6, 57.0, 61.5, 105.9, 123.0, 123.7, 125.8, 125.9 (2C), 126.1, 127.1, 128.7, 131.2, 133.7, 133.8, 139.0, 139.1, 176.7; IR (neat): ν = 3058, 3012, 2923, 1716, 1635, 1365 cm^{-1}; HR-MS: m/z = 284.0635, calcd. for $C_{18}H_{15}NO$ $[M+Na]^+$: 284.1046.

(*1S,4R*)-2-(4-Methylstyryl)-2-azabicyclo[2.2.1]hept-5-en-3-one (3d): Yield: 191 mg (85%); colorless gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (d, J = 8.1 Hz, 1H), 2.38 (s, 3H), 2.43–2.47 (m, 1H), 3.52–3.54 (m, 1H), 4.83–4.85 (m, 1H), 5.96 (d, J = 15.0 Hz, 1H), 6.72–6.76 (m, 1H), 7.00–7.03 (m, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.26–7.33 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 53.6, 57.0, 61.2, 109.2, 123.3, 125.4 (2C), 129.5 (2C), 133.6. 136.1, 148.9, 139.2, 176.6; IR (neat): ν = 3014, 2950, 1712, 1647, 1382 cm^{-1}; HR-MS: m/z = 248.1046, calcd. for $C_{15}H_{15}NO$ $[M+Na]^+$: 248.0211.

(*1S,4R*)-2-(2-Methylstyryl)-2-azabicyclo[2.2.1]hept-5-en-3-one (3e): Yield: 178 mg (79%); brownish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (d, J = 8.1 Hz, 1H), 2.34 (s, 3H), 2.37–2.41 (m, 1H), 3.46–3.48 (m, 1H), 4.79 (d, J = 1.8 Hz, 1H), 6.07 (d, J = 14.7 Hz, 1H), 6.67–6.69 (m, 1H), 6.95–6.98 (m, 1H), 7.10–7.17 (m, 4H), 7.36–7.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0, 53.5, 56.8, 61.3, 106.8, 124.7, 124.8, 126.2, 126.4, 130.3, 134.6, 135.2, 138.9, 139.0, 176.5; IR (neat): ν = 3016, 2952, 1712, 1639, 1380 cm^{-1}; HR-MS: m/z = 248.1050, calcd. for $C_{15}H_{15}NO$ $[M+Na]^+$: 248.1046.

***(1S,4R*)-2-(2-Fluorostyryl)-2-azabicyclo[2.2.1]hept-5-en-3-one (3f):** Yield: 185 mg (81%); brownish solid; mp 66–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (d, J = 8.1 Hz, 1H), 2.36–2.40 (m, 1H), 3.46–3.48 (m, 1H), 4.81–4.82 (m, 1H), 6.02 (d, J = 14.7 Hz, 1H), 6.65–6.69 (m, 1H), 6.95–7.14 (m, 4H), 7.32 (d, J = 14.7 Hz, 1H), 7.36–7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.5, 56.9, 61.1, 101.2 (d, $J_{C,F}$ = 4.5 Hz), 115.6 (d, $J_{C,F}$ = 22.5 Hz), 124.3 (d, $J_{C,F}$ = 3.0 Hz), 124.5, 125.6 (d, $J_{C,F}$ = 4.5 Hz), 126.0 (d, $J_{C,F}$ = 3.7 Hz), 127.4 (d, $J_{C,F}$ = 8.2 Hz), 139.0 (d, $J_{C,F}$ = 15.7 Hz), 159.7 (d, $J_{C,F}$ = 236 Hz), 176.7; IR (neat): ν = 3020, 1712, 1643, 1382 cm^{-1}; HR-MS: m/z = 252.0795, calcd. for $C_{14}H_{12}FNO$ $[M+Na]^+$: 252.0801.

(*1S,4R*)-2-(2-Bromostyryl)-2-azabicyclo[2.2.1]hept-5-en-3-one (3g): Yield: 238 mg (82%); brownish solid; mp 102–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 = (d, J = 8.4 Hz, 1H), 2.39–2.42 (m, 1H), 3.48–3.49 (m, 1H), 4.85 (d, J = 1.6 Hz, 1H), 6.22 (d, J = 14.4 Hz, 1H), 6.67–6.69 (m, 1H), 6.98–7.03 (m, 2H), 7.20–7.26 (m, 2H), 7.45–7.50 (m, 1H), 7.50–7.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.4, 56.8, 61.3, 107.8, 123.2, 126.8, 126.0, 127.7, 133.0, 138.9, 139.2, 176.7; IR (neat): ν = 3064, 3018, 2995, 1716, 1635, 1375 cm^{-1}; HR-MS: m/z = 312.0002, calcd. for $C_{14}H_{12}BrNO$ $[M+Na]^+$: 311.9994.

(*1S,4R*)-2-(4-Chlorostyryl)-2-azabicyclo[2.2.1]hept-5-en-3-one (3h): Yield: 206 mg (84%); yellowish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (d, J = 8.1 Hz, 1H), 2.40–2.44 (m, 1H), 3.51–3.52 (m, 1H), 4.80 (d, J = 1.8 Hz, 1H), 5.89 (d, J = 14.7 Hz, 1H), 6.69–6.73 (m, 1H), 6.97–6.99 (m, 1H), 7.23–7.29 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.5, 57.0, 61.3, 107.9, 124.5, 126.7 (2C), 128.9 (2C), 131.8, 135.2, 139.1, 139.2, 176.7; IR (neat): ν = 3018, 2925, 1708, 1645, 1382 cm^{-1}; HR-MS: m/z = 268.0505, calcd. for $C_{14}H_{12}ClNO$ $[M+Na]^+$: 268.0500.

(*1S,4R*)-2-[(*E*)-2-Cyclohexylvinyl]-2-azabicyclo[2.2.1]-hept-5-en-3-one (3i): Yield: 141 mg (65%); brownish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01–1.33 (m, 6H), 1.63–1.72 (m, 4H), 1.93–1.98 (m, 1H), 2.18 (d, J = 7.8 Hz, 1H), 2.29–2.32 (m, 1H), 3.38–3.40 (m, 1H), 4.56–4.57 (m, 1H), 4.91 (dd, J_1 = 14.4 Hz, J_2 = 7.2 Hz, 1H), 6.47 (d, J = 14.4 Hz, 1H), 6.61–6.64 (m, 1H), 6.87–6.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2 (2C), 33.8, 33.9 (2C), 38.7 (2C), 53.7, 57.3, 61.1, 115.8, 122.3, 138.7, 139.0, 176.5; IR (neat): ν = 2923, 2850, 1712, 1658, 1388 cm^{-1}; anal. calcd. for $C_{14}H_{19}NO$: C 77.38, H 8.81, N 6.45; found: C 77.33, H 8.75, N 6.50%.

(*1S,4R*)-2-(Cyclohexylidenemethyl)-2-azabicyclo[2.2.1]-hept-5-en-3-one (3j): Yield: 142 mg (70%); yellowish viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (s, 6H), 2.07–2.18 (m, 5H), 2.42 (d, J = 7.8 Hz, 1H), 3.35 (s, 1H), 4.31 (d, J = 1.8 Hz, 1H), 5.54 (s, 1H), 6.67–6.69 (m, 1H), 6.85–6.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5, 27.3, 28.1, 28.9, 33.4, 53.6, 58.1, 66.5, 117.4, 136.9, 138.7, 139.7, 180.3; IR (neat): ν = 3029, 2955, 1712, 1650, 1480,1335 cm^{-1}; anal. calcd. for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.89; found: C 76.75, H 8.50, N 6.93%.

(*1S,4R*)-2-[(*1E,3Z*)-Deca-1,3-dienyl]-2-azabicyclo[2.2.1]-hept-5-en-3-one (3k): Yield: 167 mg (68%); yellowish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87–0.89 (m, 3H), 1.22–1.27 (m, 8H), 2.02–2.13 (m, 2H), 2.20–2.25 (m, 1H), 2.30–2.34 (m, 1H), 3.40–3.42 (m, 1H), 4.62 (d, J = 1.8 Hz. 1H), 5.54–5.66 (m, 2H), 5.92–6.01 (m, 1H), 6.60–6.65 (m, 2H), 6.87–6.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 22.8, 28.9, 29.6, 31.9, 32.9, 53.6, 57.1, 61.3, 110.3, 124.7, 127.8, 132.0, 138.9, 139.2, 176.5; IR (neat): ν = 3016, 2956, 2930, 1701, 1622, 1386 cm^{-1}; anal. calcd. for $C_{16}H_{23}NO$: C 78.32, H 9.45, N 5.71; found: C 78.30, H 9.48, N 5.65%.

(*E*)-3-(2-Methylstyryl)oxazolidin-2-one (3l): Yield: 183 mg (90%); white solid; mp 112–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.87–3.90 (m, 2H), 4.53 (t, J = 8.0 Hz, 2H), 5.91 (d, J = 14.5 Hz, 1H), 7.14–7.18 (m, 3H), 7.29 (d, J = 14.0 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 42.7, 62.4, 108.9, 124.9, 125.1, 126.5, 126.9, 130.4, 134.8, 134.9, 155.6; IR (neat): ν = 3018, 2950, 1751, 1649, 1413 cm^{-1}; HR-MS: m/z = 226.0588, calcd. for $C_{12}H_{13}NO_2$ $[M+Na]^+$: 226.0838.

(*E*)-3-[2-(Naphthalen-1-yl)vinyl]oxazolidin-2-one (3m): Yield: 196 mg (82%); brownish gummy liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.94–3.99 (m, 2H), 4.51–4.57 (m, 2H), 6.45 (d, J = 14.4 Hz, 1H), 7.38–7.58 (m, 4H), 7.76 (d, J = 7.1 Hz, 1H), 7.83–7.88 (m, 1H), 8.03–8.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.8, 62.4, 108.1, 123.4, 123.6, 125.9 (2C), 126.2, 127.5, 128.8, 131.2, 133.2, 133.9, 155.6; IR (neat): ν = 3049, 2922, 2852, 1759, 1645, 1418, 1393 cm^{-1}; HR-MS: m/z = 262.1020, calcd. for $C_{15}H_{13}NO_2$ $[M+Na]^+$: 262.0838.

(*E*)-3-(2-Fluorostyryl)oxazolidin-2-one (3n): Yield: 184 mg (89%); brownish solid; mp 135–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82–3.87 (m, 2H), 4.47–4.52 (m, 2H), 5.85 (d, J = 14.7 Hz, 1H), 6.98–7.18 (m, 3H), 7.37–7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.5, 62.5, 103.5

(d, $J_{C,F}$ = 3.7 Hz), 115.6 (d, $J_{C,F}$ = 21.7 Hz), 123.7 (d, $J_{C,F}$ = 12.7 Hz), 124.3 (d, $J_{C,F}$ = 3.0 Hz), 125.8 (d, $J_{C,F}$ = 5.2 Hz), 126.3 (d, $J_{C,F}$ = 3.7 Hz), 127.9 (d, $J_{C,F}$ = 8.2 Hz), 155.5, 159.7 (d, $J_{C,F}$ = 246.7 Hz); IR (neat): ν = 3020, 2906, 1751, 1650, 1492 cm^{-1}; HR-MS: m/z = 230.0673, calcd. for $C_{11}H_{10}FNO_2$ $[M+Na]^+$: 230.0588.

(*E*)-1-(2-Fluorostyryl)pyrrolidin-2-one (3o): Yield: 170 mg (83%); brownish solid; mp 85–89 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14–2.23 (m, 2H), 2.57 (t, J = 8.4 Hz, 2H), 3.69 (t, J = 7.2 Hz, 2H), 6.02 (d, J = 15.2 Hz, 1H), 7.01–7.17 (m, 3H), 7.46–7.50 (m, 1H), 7.69 (d, J = 15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5, 31.3, 45.3, 104.1 (d, $J_{C,F}$ = 3.7 Hz), 115.6 (d, $J_{C,F}$ = 12.5 Hz), 124.2 (d, $J_{C,F}$ = 3.7 Hz), 124.3, 125.3 (d, $J_{C,F}$ = 5.0 Hz), 126.2, 127.7 (d, $J_{C,F}$ = 7.5 Hz), 159.8 (d, $J_{C,F}$ = 246.2 Hz), 173.7; IR (neat): ν = 3012, 2962, 2926, 1689, 1641, 1489, 1402 cm^{-1}; HR-MS: m/z = 228.0780, calcd. for $C_{12}H_{12}FNO$ $[M+Na]^+$: 228.0795.

(*E*)-1-[2-(Naphthalen-1-yl)vinyl]pyrrolidin-2-one (3p): Yield: 208 mg (88%); brownish solid; mp 120–125 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.17–2.27 (m, 2H), 2.56–2.62 (m, 2H), 3.77–3.82 (m, 2H), 6.58 (d, J = 14.7 Hz, 1H), 7.41–7.54 (m, 3H), 7.60–7.67 (m, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.82–7.87 (m, 1H), 8.05–8.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 31.4, 45.6, 108.7, 123.3, 123.7, 125.7, 125.8, 125.9, 126.0, 127.4, 128.8, 131.3, 133.7, 133.9, 173.6; IR (neat): ν = 3014, 2927, 1697, 1639, 1411, 1388 cm^{-1}; HR-MS: m/z = 260.1077, calcd. for $C_{16}H_{15}NO$ $[M+Na]^+$: 260.1046.

(*E*)-1-[2-(Naphthalen-1-yl)vinyl]azepan-2-one (3q): Yield: 120 mg (45%); yellowish gummy liquid; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 2H), 1.84 (s, 4H), 2.72 (d, J = 8.8 Hz, 2H), 3.86 (s, 2H), 6.70 (d, J = 14.8 Hz, 1H), 7.43–7.52 (m, 2H), 7.60 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 14.8 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.3, 29.6, 29.7, 30.7, 43.2, 48.5, 107.6, 123.5, 123.7, 125.8, 126.9, 127.2, 128.5, 128.8, 129.0, 134.1, 199.7; IR (neat): ν = 3346, 2926, 2854, 1724, 1692, 1627, 1445 cm^{-1}; anal. calcd. for $C_{18}H_{19}NO$: C 81.47, H 7.22, N 5.28; found: C 81.45, H 7.20, N 5.34%.

1-[(*1E,3E*)-3-Benzylideneoct-1-enyl]-4-methylquinolin-2(1*H*)-one (3r): Yield: 279 mg (78%); yellowish viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.95 (m, 3H), 1.37–1.46 (m, 4H), 1.76–1.81 (m, 2H), 2.49 (s, 3H), 2.60–2.65 (m, 2H), 6.53–6.74 (m, 4H), 7.24–7.40 (m, 6H), 7.49–7.58 (m, 2H), 7.70–7.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 19.2, 22.6, 27.8, 29.0, 32.3, 116.1, 121.4, 121.6, 122.4, 122.9, 125.3, 127.2, 128.4 (2C), 128.9 (2C), 130.3, 133.4, 137.3, 137.8, 138.3, 139.9, 147.1, 162.1; IR (neat): ν = 3058, 2955, 2928, 2868, 1662, 1595, 1450 cm^{-1}; HR-MS: m/z = 358.2168, calcd. for $C_{25}H_{27}NO$ $[M+H]^+$: 358.2165.

(*1S,4R*)-2-[(*E*)-3-Bromostyryl]-2-azabicyclo[2.2.1]hept-5-en-3-one (3s): Yield: 234 mg (84%); white solid; mp 135–138 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.28 (d, J = 8.1 Hz, 1H), 2.35–2.39 (m, 1H), 3.45–3.47 (m, 1H), 4.74–4.76 (m, 1H), 5.82 (d, J = 14.7 Hz, 1H), 6.65–6.68 (m, 1H), 6.91–6.94 (m, 1H), 7.08–7.13 (m, 1H), 7.18–7.26 (m, 3H), 7.43 (t, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 53.4, 56.9, 61.2, 107.5, 122.9, 123.9, 125.1, 128.3, 129.1, 130.2, 138.9, 139.0, 139.1, 176.6; IR (neat): ν = 3058, 2948, 1720, 1643, 1589, 1377 cm^{-1}; HR-MS: m/z = 311.9994, calcd. for $C_{14}H_{12}BrNO$ $[M+Na]^+$: 312.0001.

(*1S,4R*)-2-[(*E*)-3,4-Dichlorostyryl]-2-azabicyclo[2.2.1]-hept-5-en-3-one (3t): Yield: 218 mg (78%); brownish solid; mp 150–153 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.29 (d, J = 8.1 Hz, 1H), 2.36–2.39 (m, 1H), 3.46–3.48 (m, 1H), 4.74–4.75 (m, 1H), 5.79 (d, J = 14.7 Hz, 1H), 6.65–6.68 (m, 1H), 6.91–6.94 (m, 1H), 7.08–7.12 (m, 1H), 7.19–7.35 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 53.4, 56.9, 61.3, 106.6, 124.5, 125.5, 127.1, 129.6, 130.6, 132.7, 137.0, 139.1, 176.6; IR (neat): ν = 3064, 2954, 1708, 1639, 1402 cm^{-1}; HR-MS: m/z = 302.0110, calcd. for $C_{14}H_{11}Cl_2NO$ $[M+Na]^+$: 302.0114.

(*E*)-3-(3-Bromostyryl)oxazolidin-2-one (3v): Yield: 216 mg (81%); brownish gummy liquid; ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.80–3.85 (m, 2H), 4.47–4.53 (m, 2H), 5.67 (d, J = 14.7 Hz, 1H), 7.12–7.17 (m, 1H), 7.21–7.46 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 42.5, 62.4, 109.6, 122.9, 124.0, 125.2, 128.6, 129.6, 130.3, 138.2, 155.6; IR (neat): ν = 3018, 2852, 1760, 1652, 1409 cm^{-1}; HR-MS: m/z = 289.9787, calcd. for $C_{11}H_{10}BrNO_2$ $[M+Na]^+$: 289.9791.

(*1S,4R*)-2-(4-Methoxyphenyl)-2-azabicyclo[2.2.1]hept-5-en-3-one (4a):[13e] Yield (X = I, Br): 189 mg (88%), 174 mg (81%); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24–2.27 (m, 1H), 2.49 (d, J = 8.1 Hz, 1H), 3.48–3.49 (m, 1H), 3.78 (s, 3H), 4.67 (d, J = 2.1 Hz, 1H), 6.72 (s, 1H), 6.86–6.89 (m, 2H), 6.99–7.01 (m, 1H), 7.24–7.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8, 54.7, 55.6, 57.8, 65.5, 114.4 (2C), 120.9 (2C), 133.0, 138.6, 139.3, 156.5, 177.7.

(*1S,4R*)-2-*p*-Tolyl-2-azabicyclo[2.2.1]hept-5-en-3-one (4b):[10b] Yield: 181 mg (91%); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.21–2.25 (m, 1H), 2.29 (s, 3H), 2.43–2.46 (m. 1H), 3.46–3.47 (m, 1H), 4.70 (q, J = 1.8 Hz, 1H), 6.67–6.70 (m, 1H), 6.98–7.00 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.23–7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 54.7, 57.4, 64.8, 118.8 (2C), 129.4 (2C), 133.5, 137.1, 138.4, 139.2, 177.4.

(*1S,4R*)-2-(Biphenyl-4-yl)-2-azabicyclo[2.2.1]hept-5-en-3-one (4c):[13e] Yield (X = I, Br): 230 mg (87%), 206 mg (70%); brownish solid; mp 140–145 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.29 (d, J = 7.5 Hz, 1H), 2.50 (d, J = 8.0 Hz, 1H), 3.53 (s, 1H), 4.81 (d, J = 1.5 Hz, 1H), 6.73 (s, 1H), 7.05 (d, J = 4.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.55–7.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.8, 57.3, 64.7, 118.9 (2C), 126.9 (2C), 127.2, 127.7 (2C), 128.9 (2C), 136.8, 138.7, 138.9, 139.1, 140.6, 177.4.

1-Phenylpyrrolidin-2-one (4d):[9h] Yield: 147 mg (91%); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.07–2.17 (m, 2H), 2.55–2.60 (m, 2H), 3.80–3.85 (m, 2H), 7.09–7.15 (m, 1H), 7.31–7.37 (m, 2H), 7.57–7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 32.8, 48.8, 120.1 (2C), 124.5, 128.9 (2C), 139.5, 174.4.

1-(4-Methoxyphenyl)pyrrolidin-2-one (4e):[9h] Yield: 172 mg (90%); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.10–2.16 (m, 2H), 2.53–2.58 (m, 2H), 3.78 (s, 3H), 3.80 (d, J = 6.9 Hz, 1H), 6.86–6.89 (m, 2H), 7.45–7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 32.6, 49.3, 55.6, 114.2 (2C), 121.9 (2C), 132.8, 156.7, 174.0.

***N*-Phenylbenzamide (5a):**[15] Yield: 173 mg (88%); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.14 (t, J = 7.5 Hz, 1H), 7.32–7.38 (m, 2H), 7.42–7.55 (m, 3H), 7.64 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 7.2 Hz, 2H), 8.01 (s, 1H); ^{13}C NMR

(75 MHz, $CDCl_3$): $\delta = 120.4$ (2C), 124.7, 127.2 (2C), 128.9 (2C), 129.2 (2C), 131.9, 135.1, 138.1, 166.0.

Acknowledgements

We gratefully acknowledge financial support from DST, Govt. of India, New Delhi with an award of the J. C Bose fellowship to B.C.R. (Grant no. SR/S2/JCB-11/2008) and Indian National Science Academy, New Delhi for an offer of INSA Sr. Scientist position to B.C.R. Finally, P.M. and D.K. thank CSIR, New Delhi for their Fellowships

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Adv. Synth. Catal. **2015**, *357*, 1 – 11

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