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PII: S0040-4020(16)30117-X

DOI: 10.1016/j.tet.2016.02.055

Reference: TET 27525

To appear in: *Tetrahedron*

Received Date: 1 October 2015

Revised Date: 9 February 2016

Accepted Date: 25 February 2016

Please cite this article as: Rajasekaran T, Sridhar B, Subba Reddy BV, $Rh_2(OAc)_4$ catalyzed highly diastereoselective synthesis of 2,4,5-triaryl-1,3-oxazolidines and spirooxindolyl oxazolidines, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.02.055.

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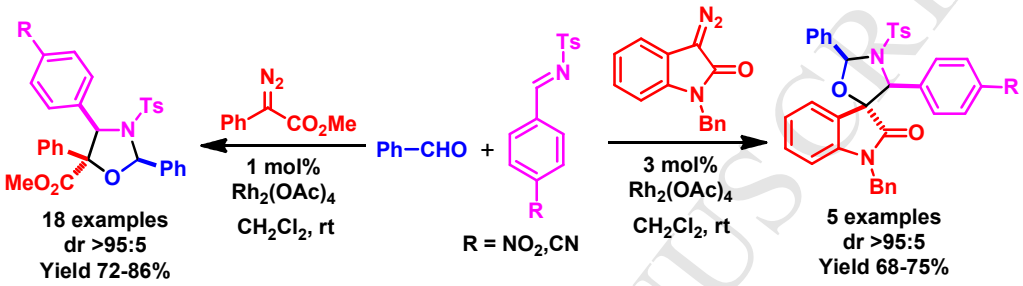
T. Rajasekaran,[a] B. Sridhar,[b] B. V. Subba Reddy*[a]



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$Rh_2(OAc)_4$ catalyzed highly diastereoselective synthesis of 2,4,5-triaryl-1,3-oxazolidines and spirooxindolyl oxazolidines

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Diazoester
Three component reaction
1,3-Oxazolidine
Spirooxazolidine
Rhodium(II) acetate

ABSTRACT

A three-component coupling (3CC) of aryl diazoacetate, aldehyde and *N*-tosylimine has been achieved using 1 mol% of $Rh_2(OAc)_4$ for the synthesis of highly substituted triaryl-1,3-oxazolidines in good yields with high diastereoselectivity. This protocol has been successfully extended to cyclic diazoamide, i.e. 3-diazooxindole for the synthesis of fully substituted spirooxindolyl oxazolidines using 3 mol% of $Rh_2(OAc)_4$ under similar reaction conditions.

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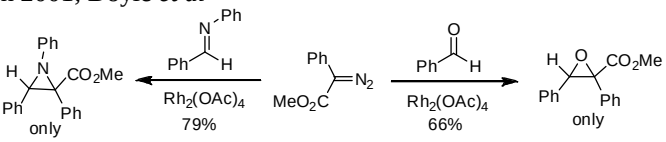
Introduction

Oxazolidines are common structural units in many biologically active natural products and designed molecules of pharmaceutical importance.[1] In particular, 1,3-oxazolidines act as pro-drugs for β-blockers, β_3-adrenoreceptor agonists and precursors for α-hydroxy-β-amino esters which are frequently found in a wide range of biologically active molecules and used as building blocks in natural product synthesis.[2,3] On the other hand, spirooxindoles are often found in medicinally important natural products and pharmaceutical agents. As a result, a myriad of catalytic methods have been developed for their synthesis.[4,] However, the development of a three component strategy to generate the novel series of oxazolidines and spirooxindoles is highly desirable as they offer rapid access to highly functionalized biologically relevant scaffolds with wide structural diversity and excellent bond forming efficiency in a single step process. Furthermore, transition metal catalyzed reactions of α-diazocarbonyl compounds have emerged as powerful synthetic tools in organic synthesis. They have been extensively used in the synthesis of highly functionalized five-membered heterocyclic compounds such as dihydrofurans, tetrahydrofurans,[5] pyrrolidines,[6] and dioxolanes.[7] In particular, the synthesis of 1,3-oxazolidines using diazo chemistry is one of the most useful protocols but less studied when compared to furans and dioxolanes due to the competitive side reactions such as epoxidation and dioxolane formation, which diminish the efficiency of three component reaction of diazo compounds, aldehydes and imines. In 2005, Somfai *et al*. reported the three component reaction of diazoester, aldehyde and aldimine for the synthesis of *syn*-α-hydroxy-β-amino esters.[8]

Recently, we developed a method for the synthesis of spirooxindolyl oxazolines using 1,3-dipolar cycloaddition of carbonyl ylides with ketimines derived from isatin, without the formation of side products.[9]

Following our interest on diazo chemistry,[10] we herein report the three component reaction of aryldiazoacetate, aldehyde and imine to produce the highly functionalized triaryl oxazolidines, which could easily be converted into α-hydroxy-β-amino esters with a quaternary carbon centre by hydrolysis. In general, the coupling of 2-diazo-2-arylacetate with aldehyde generates the epoxide exclusively, whereas imines furnish the aziridines (Scheme 1).[11] Hu *et al*. reported the chemoselective synthesis of 2,4,5-triaryl-1,3-dioxolane from 2-diazo-2-arylacetate and aryl aldehydes without the formation of epoxide.[12] To the best of our knowledge, there have been no reports on the synthesis of 2,4,5-triaryl-1,3-oxazolidines from 2-diazo-2-arylacetate and spirooxindolyl oxazolidines from 3-diazooxindole.

In 2001, Doyle *et al*



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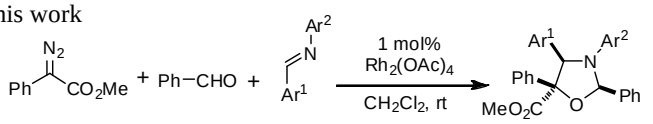

Ar^1 = *p*-NO_2-C_6H_4 or *p*-CN-C_6H_4

Ar^2 = *p*-CH_3-C_6H_4-SO_2

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Scheme 1. Rh(II) catalyzed reaction of aryl diazoacetate with aldehyde and imine.

Results and Discussion

To find an efficient imine as a dipolarophile, we initially performed the three component reaction (3CR) of methyl phenyldiazoacetate **1a**, benzaldehyde **2a** and aldimines **3a** and **3b** that are derived from benzyl amine and aniline (entries 1 and 2, Table 1) respectively.

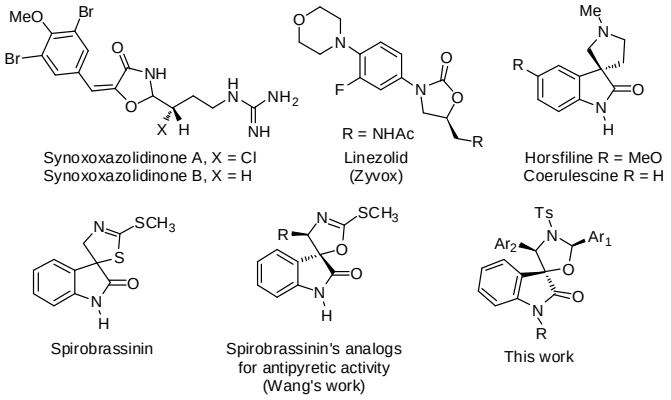
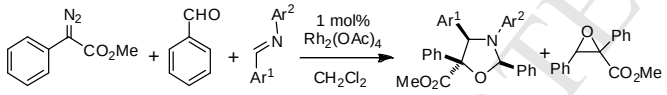


Figure 1. Biologically active oxazolidinone and spirooxindoles

To our surprise, no desired 1,3-oxazolidine was formed with these aldimines instead the formation of complex mixture was observed from ^{1}H NMR analysis of crude reaction mixture. Similar results were also observed with electron-deficient aldimine **3c** derived from tosylamine and ketimine **6** derived from aniline and *N*-methylisatin (entries 3 and 4, Table 1).

Table 1. Optimization of the reaction in the formation of **4/5**[a]



Entry	Ar^1	Ar^2	Imine	Solvent	Yield (%)[b] **4**	Yield (%)[c] **5**	dr[d]
1	Ph	Bn	3a	CH_2Cl_2	-	-	-
2	Ph	Ph	3b	CH_2Cl_2	-	-	-
3	Ph	Ts	3c	CH_2Cl_2	-	-	-
4	*N*-Methyl oxindole	Ph	6	CH_2Cl_2	-	60	-
5	*p*-NO_2Ph	Ts	3d	CH_2Cl_2	68	10	>95:5
6[e]	*p*-NO_2Ph	Ts	3d	CH_2Cl_2	81	-	>95:5

[a]All the reactions were performed using 1 mol% $Rh_2(OAc)_4$ with imine (1 equiv), aldehyde **2a** (1 equiv) and diazoester **1a** (1 equiv) in dry dichloromethane at 25 °C. [b]Yield refers to pure products after column chromatography. [c]Mixture of epoxide and imine (entries 1,2 and 3). [d]dr was determined by ^{1}H NMR analysis of crude reaction mixture. [e]Reaction was performed using 1 mol% $Rh_2(OAc)_4$ with imine (1 equiv), aldehyde **2a** (1.3 equiv) and diazoester **1a** (1.3 equiv) in dry dichloromethane at 25 °C.

Next we examined the electronic effect of substituents that are present on aromatic ring of the aldehyde part of the imine. Accordingly, we performed the 3CR reaction of methyl phenyldiazoacetate **1a**, benzaldehyde **2a** and electron-deficient aldimine **3d**. To our delight, the formation of desired 1,3-oxazolidinde **4a** was observed from ^{1}H NMR analysis of the crude reaction mixture, which was then purified by column chromatography to afford the pure 1,3-oxazolidinde **4a** in 68% yield along with epoxide **5a** in 10% yield (entry 5, Table 1). The results are summarized in Table 1.

With a suitable aldimine in hand, we were curious to further optimize the reaction conditions to improve the yield and diastereoselectivity. Interestingly, the yield was increased considerably to 81% when aldehyde and aryldiazoacetate were used in 1.3 equiv with slow addition of aryldiazoacetate. To optimize the catalyst loading, we further performed this 3CR reaction by varying the amount of catalyst from 1 mol% to 5 mol%. The reaction was quite successful even with 1 mol% of the catalyst affording the desired product in 81% yield with excellent diastereoselectivity (entry 6, Table 1). Further increase in catalyst loading did not improve the yield. The structure of **4f** was confirmed by NMR, IR and mass spectrometry. The relative configuration of **4f** was unambiguously confirmed by a single crystal X-ray diffraction studies.[13]

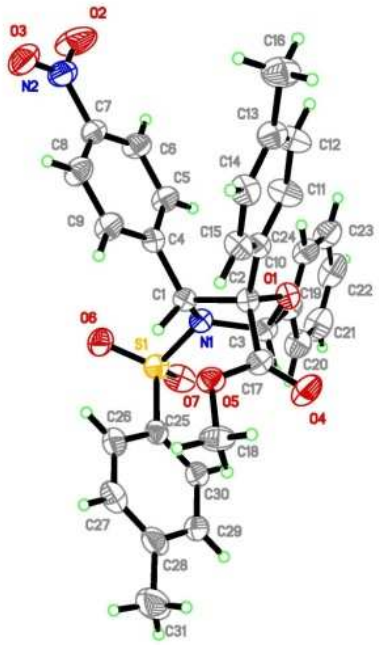


Figure 2. ORTEP structure of **4f**

With optimized reaction conditions in hand, we further studied the electronic effect of substituents on aromatic ring of the diazoacetate. In all cases, the reactions proceeded smoothly at room temperature under mild conditions and no significant change in yield or diastereoselectivity was observed with substituted aryldiazoacetates (entries 1-7, Table 2). Notably, halo substituted aryldiazoacetates such as bromo-, chloro- and fluoro- gave the products in good yields (entries 2, 3 and 4, Table 2). In deed, fluoro substituted aryldiazoacetate gave the product in higher yield than chloro substituted aryldiazoacetate (entry 4, Table 2). Furthermore, dichloro substitued aryldiazoacetate afforded the product in higher yield than mono-chloro derivative (entry 5, Table 2). We have also studied the effect of electron releasing groups such as methyl- and methoxy- on the aromatic ring of aryldiazoacetate. Interestingly, these substrates gave the expected products **4f** and **4g** in 82% and 85% yields respectively (entries 6 and 7, Table 2). However, nitro subtituted aryldiazoacetate failed to undergo three component

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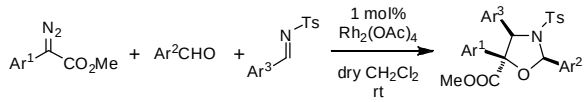
reaction under the identical reaction conditions (entry 8, Table 2). We further performed the 3CR reaction of aryldiazoacetate with aryl aldehyde bearing electron releasing and electron withdrawing groups.

Interestingly, aryl aldehydes with electron releasing groups such as *p*-methyl- and *p*-methoxy- on aromatic ring gave the product in 81% and 84% yields respectively without the loss of diastereoselectivity (entries 9 and 10, Table 2). It is worth mentioning that di- and tri-methoxybenzaldehydes also gave the products in 84% and 86% yields respectively with good diastereoselectivity (entries 11 and 12, Table 2). Although no product formation was observed with *ortho*-chlorobenzaldehyde (entry 13, Table 2), *para*-bromo, chloro and fluoro substituted aryl aldehydes participated well in the reaction (entries 14, 15 and 16, Table 2), In addition, β-naphthaldehyde was also effective for this conversion (entry 17, Table 2). It is noteworthy to mention that the reaction also proceeded effectively with heterocyclic aldehyde such as furan-2-carboxaldehyde (entry 18, Table 2).

Table 2. Three component reaction of aryldiazoacetate, aryl aldehyde and *N*-tosylimine[a]



1a-h **2a-j** **3d-f** **4a-t**

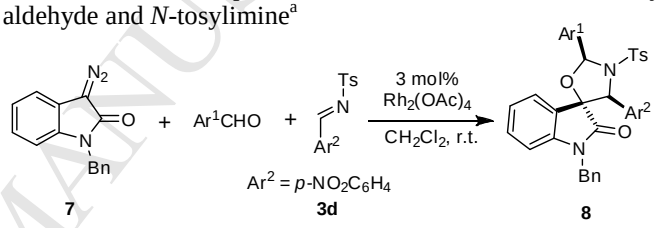
Entry	Ar^1	Ar^2	Ar^3	Yield (%)[b]	dr[c]
1	C_6H_5	C_6H_5	*p*-$NO_2C_6H_4$	81 (**4a**)	>95:5
2	*p*-BrC_6H_4	C_6H_5	*p*-$NO_2C_6H_4$	78 (**4b**)	>95:5
3	*p*-ClC_6H_4	C_6H_5	*p*-$NO_2C_6H_4$	80 (**4c**)	>95:5
4	*p*-FC_6H_4	C_6H_5	*p*-$NO_2C_6H_4$	86 (**4d**)	>95:5
5	*m,p*-$(Cl)_2C_6H_3$	C_6H_5	*p*-$NO_2C_6H_4$	84 (**4e**)	>95:5
6	*p*-MeC_6H_4	C_6H_5	*p*-$NO_2C_6H_4$	82 (**4f**)	>95:5
7	*p*-$MeOC_6H_4$	C_6H_5	*p*-$NO_2C_6H_4$	85 (**4g**)	>95:5
8[d]	*p*-$NO_2C_6H_4$	C_6H_5	*p*-$NO_2C_6H_4$	-(**4h**)	n.d
9	C_6H_5	*p*-MeC_6H_4	*p*-$NO_2C_6H_4$	81 (**4i**)	>95:5
10	C_6H_5	*p*-$MeOC_6H_4$	*p*-$NO_2C_6H_4$	84 (**4j**)	>95:5
11	C_6H_5	*m,p*-$(CH_3O)_2C_6H_3$	*p*-$NO_2C_6H_4$	84 (**4k**)	>95:5
12	C_6H_5	3,4,5-$(CH_3O)_3C_6H_2$	*p*-$NO_2C_6H_4$	86 (**4l**)	>95:5
13[d]	C_6H_5	*o*-ClC_6H_4	*p*-$NO_2C_6H_4$	-(**4m**)	n.d
14	C_6H_5	*p*-BrC_6H_4	*p*-$NO_2C_6H_4$	80 (**4n**)	>95:5
15	C_6H_5	*p*-ClC_6H_4	*p*-$NO_2C_6H_4$	81 (**4o**)	>95:5
16	C_6H_5	*p*-FC_6H_4	*p*-$NO_2C_6H_4$	80 (**4p**)	>95:5
17	C_6H_5	2-Napthyl	*p*-$NO_2C_6H_4$	82 (**4q**)	>95:5
18	C_6H_5	2-Furyl	*p*-$NO_2C_6H_4$	72 (**4r**)	>95:5
19	C_6H_5	C_6H_5	*p*-CNC_6H_4	76 (**4s**)	>95:5
20	*p*-FC_6H_4	C_6H_5	*p*-CNC_6H_4	75 (**4t**)	>95:5
21[d]	C_6H_5	C_6H_5	*p*-$CF_3C_6H_4$	-(**4u**)	n.d
22[d]	C_6H_5	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	-(**4v**)	n.d
23[d]	C_6H_5	*p*-CNC_6H_4	*p*-$NO_2C_6H_4$	-(**4w**)	n.d

[a]All the reactions were performed using 1 mol% $Rh_2(OAc)_4$ with imine (1 equiv), aldehyde (1.3 equiv) and diazoester (1.3 equiv) in dry dichloromethane at 25 °C. [b]Yield refers to pure products after column chromatography. [c]dr was determined by ^1H NMR analysis of crude reaction mixture. [d]no data.

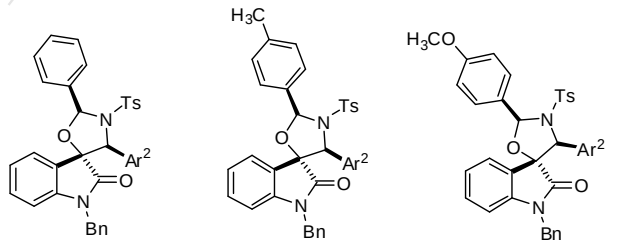
Furthermore, we examined the effect of *p*-cyano- and *p*-trifluoromethyl- groups that are present on aromatic ring of the aldehyde part of the imine. It is interesting to note that the cyano substituted aldimine underwent a smooth cycloaddition with carbonyl ylide (entries 19 and 20, Table 2) as efficient as nitro substituted aldimine (entries 1-7, 9-12, and 14-18, Table 2), but trifluoromethyl substituted aldimine afforded the product as a complex mixture (entry 21, Table 2). To our surprize, no product formation was observed with aryl aldehydes bearing electron-withdrawing groups such as *p*-nitro- and *p*-cyano- on the aromatic ring (entries 22 and 23, Table 2).

Due to the importance of spirooxindoles in drug discovery, we further extended this method to cyclic diazoamide (**7**) (Table 3). The reaction was successful only with electron-deficient aldimine 3d. Accordingly, the coupling of **7** with **3d** in the presence of 3 mol% $Rh_2(OAc)_4$ gave the expected spirocycle **8a** in 68% yield with >95:5 diastereoselectivity. The structure of the product was unambiguously confirmed by NMR, IR and mass spectrometry.

Table 3. Three-component reaction of diazooxindole, aryl aldehyde and *N*-tosylimine[a]



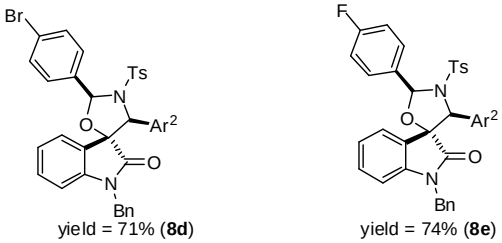
7 $Ar^2 = p\text{-}NO_2C_6H_4$ **3d** **8**



yield = 68% (**8a**) dr ratio = >95:5

yield = 74% (**8b**) dr ratio = >95:5

yield = 75% (**8c**) dr ratio = >95:5



yield = 71% (**8d**) dr ratio = >95:5

yield = 74% (**8e**) dr ratio = >95:5

[a]All the reactions were performed using 3 mol% $Rh_2(OAc)_4$ with imine **3d** (1 equiv), aldehyde (1.1 equiv) and diazoamide **7** (1.1 equiv) in dry dichloromethane at 25 °C. [b]Yield refers to pure products after column chromatography. [c]dr was determined by ^1H NMR analysis of crude reaction mixture.

Similar yield and selectivity were achieved even with 3 mol% of the catalyst. But further decrease in catalyst loading drastically reduces the yield to 40%. This 3CR was further extended to various aryl aldehydes bearing electron releasing and electron withdrawing groups on aromatic ring. It was observed that the aldehydes with electron releasing groups such as *p*-methyl- and *p*-methoxy- afforded the desired

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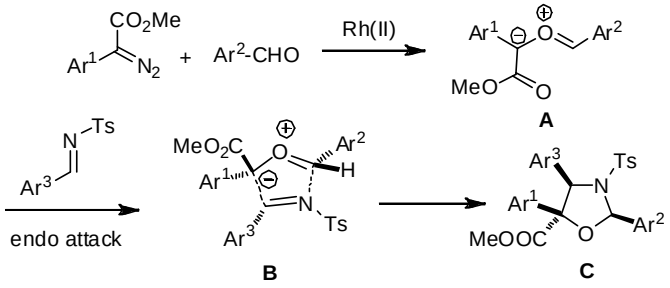
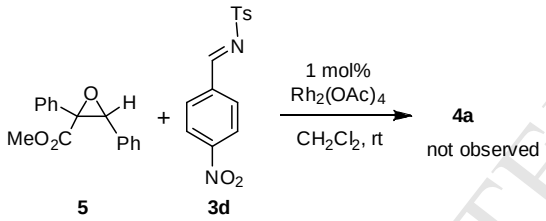
spirooxazolidines **8b** and **8c** in 74% and 75% yields respectively with excellent diastereoselectivity. However, the aldehydes with electron withdrawing groups such as *p*-nitro- and *p*-cyano- failed to give the desired product. It is worth mentioning that halo substituted aryl aldehydes such as *p*-bromo- and *p*-fluoro- gave the products **8d** and **8e** in 71% and 74% yields respectively without any significant change in the diastereoselectivity.

Mechanistically, the reaction was assumed to proceed *via* the Huisgen's cycloaddition of tosylimine with carbonyl ylide (**A**) formed *in situ* from aryldiazoacetate and aromatic aldehyde.

As shown in scheme 3, the carbonyl ylide (**A**) can undergo [3+2] cycloaddition with tosylimine (*via* endo attack as shown in concerted transition state **B**) to give the expected oxazolidine (**C**). The presence of π-π interaction between aryl group of diazoester (Ar^1) and aryl group of imine (Ar^3) attributes to the exclusive formation of *trans*-4,5-oxazolidine (**C**).

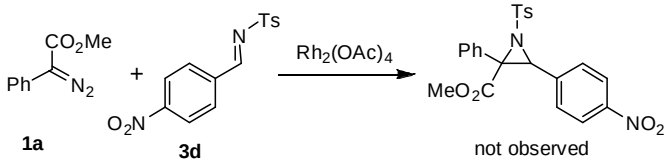


Scheme 3. A plausible reaction mechanism



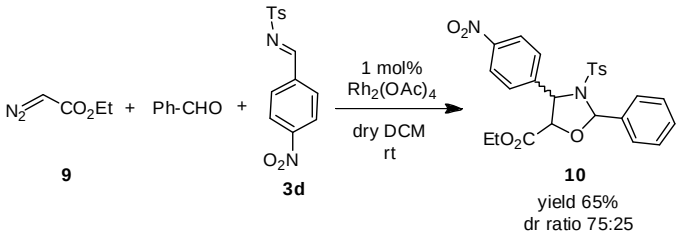
Scheme 4. Reaction of epoxide **5** with imine **3d**

To know the actual reaction pathway, a controlled experiment was performed between epoxide **5** and imine **3d** using 1 mol% of $Rh_2(OAc)_4$ (Scheme 4). The reaction is expected to proceed through the cycloaddition of epoxide with imine.[14] However, in the present case, no oxazolidine (**4a**) formation was observed by cycloaddition of epoxide with imine and therefore unreacted starting materials were recovered. Alternatively, the reaction of methyl phenyldiazoacetate **1a** with imine **3d** did not afford the aziridine (Scheme 5). Thus we have excluded the formation of oxazolidine *via* the epoxide or aziridine.[15]



Scheme 5. Reaction of diazoester **1a** with imine **3d**

To study the diastereoselectivity of this reaction, we have carried out three component coupling of ethyl diazoacetate, benzaldehyde and imine **3d (**Scheme 6).



Scheme 6. 3CC of ethyl diazoacetate **9**, benzaldehyde and imine **3d**

In the above reaction, the desired oxazolidine was obtained in 65% yield with moderate dr ratio 75:25. It shows that the presence of aryl ring in the diazoester enhances the diastereoselectivity via π-π interaction. Further, the reaction of diazo compound **1a** with benzaldehyde and imine **3d** was carried out using 1 mol% of the catalyst with bulky ligands such as $Rh_2(cap)_4$, and $Rh_2(esp)_2$ to address if ylide **A** is metal associated. Preliminary result supports metal-free ylide intermediate. Product **4a** was obtained in similar yield and dr ratio with both catalysts. In addition, no enantioselectivity was observed with the chiral catalyst Rh_2(*S*-DOSP)$_4$ or Rh_2(*S*-TCPTTL)$_4$.

Conclusion

In summary, we have developed a highly efficient protocol for the synthesis of a novel class of highly substituted 1,3-oxazolidines *via* a 1,3-dipolar cycloaddition of carbonyl ylides with *N*-tosylimines. This protocol was also extended to cyclic diazoamide for the synthesis of spirooxindolyl oxazolidines. Due to a broad range of biological activities of both oxazolidines and spirooxindolyl oxazolidines, this method will find significant application in medicinal chemistry.

Experimental

Procedure for Synthesis of 4(a-u)

To a suspension of *N*-tosylimine **3a** (200 mg, 0.66 mmol), benzaldehyde **2a** (90 mg, 0.86 mmol) and $Rh_2(OAc)_4$ (3.8 mg, 0.0085 mmol) in dry DCM (10 mL) under argon atmosphere at room temperature was added slowly a solution of methyl 2-diazo-2-phenylacetate **1a** (150 mg, 0.86 mmol) in dry DCM (5 mL) through a syringe pump for a period of 3 h. After complete addition, the mixture was stirred for another 30 min. After complete consumption of the diazo compound as monitored by TLC, the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (4:1 hexane/EtOAc) afforded the oxazolidine **4a** (298 mg, 81%) as a colourless solid. The above procedure was followed for the synthesis of remaining products (**4b-u**).

Procedure for Synthesis of 8a-e

To a suspension of *N*-tosylimine **3a** (200 mg, 0.66 mmol), benzaldehyde **2a** (90 mg, 0.86 mmol) and $Rh_2(OAc)_4$ (9 mg, 0.02 mmol) in dry DCM (10 mL) under argon atmosphere at room temperature was added slowly a solution of *N*-benzyl-3-diazooxindole **7** (180 mg, 0.72 mmol) in dry DCM (5 mL) through a syringe pump for a period of 4 h. After complete addition, the mixture was stirred for another 30 min. After

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complete consumption of the diazo compound as monitored by TLC, the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (4:1 hexane/EtOAc) afforded the product **8a** (282 mg, 68%) as a colourless solid. The above procedure was followed for the synthesis of compounds 8b-e

Methyl 4-(4-nitrophenyl)-2,5-diphenyl-3-tosyloxazolidine-5-carboxylate (**4a**): Colorless solid. mp: 168–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.37 (m, 5H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.13 (m, 4H), 7.10 – 7.02 (m, 3H), 6.20 (s, 1H), 6.06 (s, 1H), 3.61 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 146.9, 144.7, 144.3, 135.5, 134.3, 133.5, 129.8, 129.7, 129.4, 128.4, 128.3, 128.1, 128.0, 127.8, 125.7, 122.8, 91.6, 89.7, 67.1, 53.4, 21.3. IR (neat) ν_{max} 2925, 2856, 1746, 1609, 1519, 1349, 1243, 1164, 728 cm^{-1}; ESI-MS *m/z* 559 $(M+H)^+$; HRMS (ESI) calcd for $C_{30}H_{27}N_2O_7S$, 559.15335 $(M+H)^+$; Found, 559.15328.

Methyl 5-(4-bromophenyl)-4-(4-nitrophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4b**): Colorless solid. mp: 166–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.63 - 7.55 (m, 2H), 7.49 – 7.37 (m, 5H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.15 (m, 4H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 6.02 (s, 1H), 3.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 147.2, 144.4, 135.4, 134.4, 132.8, 131.3, 129.9, 129.9, 129.5, 128.4, 128.1, 127.9, 127.6, 123.2, 122.8, 91.7, 89.4, 77.3, 67.1, 53.7, 21.5; IR (neat) ν_{max} 3073, 2954, 2841, 1744, 1610, 1517, 1355, 1345, 1293, 1252, 1092, 1025, 831, 816, 665 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{26}O_7N_2BrS$ 637.06386 $(M)^+$; Found, 637.06212.

Methyl 5-(4-chlorophenyl)-4-(4-nitrophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4c**): Colorless solid. mp: 176–177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.11 (m, 4H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 6.02 (s, 1H), 3.61 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 147.2, 144.4, 135.3, 134.4, 132.8, 131.3, 129.9, 129.9, 129.5, 128.4, 128.1, 127.9, 127.6, 123.1, 122.8, 91.7, 89.4, 77.2, 67.1, 53.7, 21.5; IR (neat) ν_{max} 2954, 2841, 1740, 1610, 1520, 1345, 1293, 1252, 1166, 1092, 1025, 816 cm^{-1}; ESI-MS *m/z* 593 $(M+H)^+$; HRMS (ESI) calcd for $C_{30}H_{26}ClN_2O_7S$, 593.1143 $(M+H)^+$; Found, 593.1123

Methyl 5-(4-fluorophenyl)-4-(4-nitrophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4d**): Colorless solid. mp: 169–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.48 – 7.40 (m, 5H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.15 (m, 4H), 6.76 (t, *J* = 8.6 Hz, 2H), 6.21 (s, 1H), 6.02 (s, 1H), 3.62 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 147.2, 144.6, 144.4, 135.5, 134.5, 129.9, 129.5, 128.5, 128.2, 127.9, 123.1, 115.4, 115.1, 91.7, 89.4, 67.3, 53.6, 21.5; IR (neat) ν_{max} 3073, 2954, 2841, 1740, 1610, 1517, 1350, 1292, 1250, 1166, 1092, 1025, 816, 665 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{26}O_7N_2FS$, 577.14393 $(M+H)^+$; Found, 577.14398.

Methyl 5-(3,4-dichlorophenyl)-4-(4-nitrophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4e**): Colorless solid. mp: 178–179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.62 - 7.56 (m, 2H), 7.48 – 7.31 (m, 8H), 7.22 – 7.10 (m, 3H), 7.04 – 6-98 (m, 1H), 6.22 (s, 1H), 5.99 (s, 1H), 3.62 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 147.4, 144.5, 144.2, 135.2, 134.4, 133.9, 132.9, 132.6, 130.1, 129.9, 129.9, 129.5, 128.5, 128.1, 128.0, 127.9, 125.4, 123.3, 91.9, 88.7, 67.2, 53.8, 21.5; IR (neat) ν_{max} 2954, 2941, 1736, 1517, 1350, 1342, 1252, 1160, 1092, 1025, 816, 665 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}N_2O_7Cl_2S$, 627.0754 $(M+H)^+$; Found, 627.0736.

Methyl 4-(4-nitrophenyl)-2-phenyl-5-(p-tolyl)-3-tosyloxazolidine-5-carboxylate (**4f**): Colorless solid. mp: 174–175 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.48 – 7.38 (m, 5H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.18 (s, 1H), 6.03 (s, 1H), 3.59 (s, 3H), 2.39 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 147.1, 144.9, 144.3, 138.4, 135.7, 134.8, 130.7, 130.0, 129.84, 129.5, 128.9, 128.4, 128.3, 127.9, 125.8, 122.9, 91.7, 89.9, 67.2, 53.5, 21.5, 21.0; IR (neat) ν_{max} 2854, 2840, 1735, 1615, 1510, 1348, 1293, 1160, 1092, 1025, 831, 670 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{29}O_7N_2S$ 573.1690 $(M+H)^+$; Found, 573.1691.

Methyl 5-(4-methoxyphenyl)-4-(4-nitrophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4g**): Colorless solid. mp: 174–175 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.24 – 7.15 (m, 5H), 7.12 – 7.03 (m, 4H), 7.00 – 6.94 (m, 1H), 6.18 (s, 1H), 6.07 (s, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, CDCl3) δ 170.7, 159.5, 147.1, 144.8, 144.3, 137.0, 134.7, 133.6, 130.0, 129.4, 128.5, 128.1, 127.9, 125.9, 122.9, 120.5, 115.4, 113.7, 91.5, 89.9, 67.2, 55.2, 53.5, 21.4; IR (neat) ν_{max} 2858, 2842, 1734, 1618, 1515, 1354, 1342, 1290, 1252, 1092, 1021, 816, 665 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{29}N_2O_8S$, 589.16391 $(M+H)^+$; Found, 589.16391.

Methyl 4-(4-nitrophenyl)-5-phenyl-2-(p-tolyl)-3-tosyloxazolidine-5-carboxylate (**4i**): Colorless solid. mp: 158–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.55 – 7.43 (m, 4H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.14 (m, 6H), 7.12 – 6.99 (m, 3H), 6.15 (s, 1H), 6.02 (s, 1H), 3.58 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 147.1, 144.9, 144.3, 139.9, 134.7, 133.7, 132.7, 129.9, 129.46, 129.1, 128.5, 128.2, 128.1, 127.9, 125.9, 122.91\, 91.7, 89.8, 67.3, 53.5, 21.5, 21.3; IR (neat) ν_{max} 3074, 2949, 2921, 1745, 1597, 1515, 1450, 1346, 1243, 1162, 1019, 1009, 734, 674 cm^{-1}; ESI-MS *m/z* 595 $(M+Na)^+$; HRMS (ESI) calcd for $C_{31}H_{28}N_2O_7SNa$, 595.1509 $(M+Na)^+$; Found, 595.1511.

Methyl 2-(4-methoxyphenyl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4j**): Colorless solid. mp: 165–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.23 – 7.16 (m, 4H), 7.10 – 7.02 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.13 (s, 1H), 6.04 (s, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 160.8, 147.0, 144.9, 144.2, 134.8, 133.7, 129.9, 129.7, 129.4, 128.5, 128.2, 127.9, 127.6, 125.9, 122.9, 113.8, 91.5, 89.7, 67.2, 55.3, 53.6, 21.5; IR (neat) ν_{max} 3073, 2954, 2841, 1757, 1744, 1610, 1517, 1355, 1345, 1293, 1252, 1166, 1092, 1025, 831, 816, 665 cm^{-1}; ESI-MS *m/z* 611 $(M+Na)^+$; HRMS (ESI) calcd for $C_{31}H_{28}N_2O_8SNa$, 611.14586 $(M+Na)^+$; Found, 611.14590.

Methyl 2-(3,4-dimethoxyphenyl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4k**): Colorless solid. mp: 180–181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 3H), 7.10 – 7.05 (m, 3H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.19 (s, 1H), 6.12 (s, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 3.65 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 150.1, 148.7, 147.0, 144.9, 144.2, 134.9, 133.7, 130.0, 129.3, 128.5, 128.1, 127.7, 125.8, 122.8, 121.2, 110.9, 110.6, 91.6, 89.7, 66.99, 55.9, 55.7, 53.5, 21.4; IR (neat) ν_{max} 3072, 2958, 2841, 1757,

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1744, 1610, 1517, 1345, 1293, 1252, 1167, 1092, 1025, 816, 665 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{30}N_2O_9NaS$, 641.1564 $(M+Na)^+$; Found, 641.1565.

Methyl 4-(4-nitrophenyl)-5-phenyl-3-tosyl-2-(3,4,5-trimethoxyphenyl)oxazolidine-5-carboxylate (**4l**): Colorless solid. mp: 188–189 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.25 – 7.21 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.04 (m, 3H), 6.71 (s, 2H), 6.20 (s, 1H), 6.17 (s, 1H), 3.88 (s, 3H), 3.75 (s, 6H), 3.68 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 153.0, 147.1, 144.8, 144.3, 139.0, 135.2, 133.7, 130.6, 130.2, 129.3, 128.5, 128.2, 127.7, 125.9, 122.8, 105.4, 91.7, 89.8, 66.9, 60.8, 55.9, 53.6, 21.4; IR (neat) ν_{max} 3073, 2954, 2841, 1757, 1744, 1610, 1517, 1355, 1345, 1293, 1252, 1166, 1092, 1025, 831, 665 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{32}N_2O_{10}NaS$, 671.1670 $(M+Na)^+$; Found, 671.1673.

Methyl 2-(4-bromophenyl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4n**): Colorless solid. mp: 185–186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 - 7.46 (m, 4H), 7.30 – 7.25 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.09 – 7.05 (m, 3H), 6.16 (s, 1H), 6.01 (s, 1H), 3.59 (s, 3H), 2.42 (s, 3H): ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 147.2, 144.6, 144.6, 134.8, 134.5, 133.5, 131.7, 129.9, 129.8, 129.6, 128.6, 128.2, 127.9, 125.9 124.1, 123.0, 91.0, 90.02, 67.3, 53.6, 21.5. IR (neat) ν_{max} 3070, 298, 1758, 1746, 1610, 1517, 1358, 1290, 1166, 758, 685 cm^{-1}.

Methyl 2-(4-chlorophenyl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4o**): Colorless solid. mp: 172–173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.13 (m, 7H), 7.11 – 7.02 (m, 3H), 6.18 (s, 1H), 6.01 (s, 1H), 3.59 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 147.2, 144.6, 144.6, 135.9, 134.5, 134.3, 133.5, 129.9, 129.6, 129.6, 128.7, 128.6, 128.2, 127.9, 125.9, 123.0, 90.9, 90.0, 67.3, 53.6, 21.5; HRMS (ESI) calcd for $C_{30}H_{25}O_7N_2ClS$, 593.1143 $(M+H)^+$; Found, 593.1127.

Methyl 2-(4-fluorophenyl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4p**): Colorless solid. mp: 161–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.61 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.25 - 7.15 (m, 4H), 7.15 – 7.03 (m, 5H), 6.17 (s, 1H), 6.03 (s, 1H), 3.60 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 164.5, 162.5, 147.1, 144.6, 144.5, 134.5, 133.5, 131.6, 130.2, 130.1, 129.9, 129.5, 128.6, 128.2, 127.9, 125.8, 122.9, 115.5, 115.4, 90.9, 89.9, 67.2, 53.6, 21.47. ESI-MS *m/z* 594 $(M+NH_4)^+$; HRMS (ESI) calcd for $C_{30}H_{25}FN_2O_7SNH_4$, 594.1705 $(M+NH_4)^+$; Found, 594.1705.

Methyl 2-(naphthalen-2-yl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4q**): Colorless solid. mp: 176–177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.97- 7.80 (m, 5H), 7.68 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.47 – 7.36 (m, 4H), 7.25 – 7.19 (m, 2H), 7.13 – 7.03 (m, 5H), 6.37 (s, 1H), 6.14 (s, 1H), 3.65 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 147.1, 144.8, 144.3, 134.5, 133.9, 133.7, 132.8, 132.6, 130.0, 129.4, 128.6, 128.5, 128.4, 128.1, 127.9, 127.6, 126.9, 126.4, 125.9, 124.6, 122.9, 91.9, 89.9, 77.3, 67.2, 53.5, 21.3; IR (neat) ν_{max} 3057, 2950, 1743, 1599, 1523, 1347, 1242, 1167, 1133, 1011, 733, 674 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{28}N_2O_7NaS$, 631.1512 $(M+Na)^+$; Found, 631.1509.

Methyl 2-(furan-2-yl)-4-(4-nitrophenyl)-5-phenyl-3-tosyloxazolidine-5-carboxylate (**4r**): Colorless solid. mp: 137–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.32 – 7.19 (m, 5H), 7.14 – 7.04 (m, 5H), 6.7 (d, *J* = 3.2 Hz, 1H), 6.45 – 6.41 (m, 1H), 6.23 (s, 1H), 6.07 (s, 1H), 3.72 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 147.9, 147.2, 144.7, 144.1, 144.0, 135.4, 133.3, 129.9, 129.3, 128.6, 128.2, 127.5, 125.8, 122.8, 113.3, 110.6, 90.3, 84.4, 66.8, 53.7, 21.5; IR (neat) ν_{max} 2954, 2841, 1757, 1742, 1518, 1345, 1290, 1160, 1092, 836, 670 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{24}N_2O_8NaS$, 571.1145 $(M+Na)^+$; Found, 571.1140.

Methyl 4-(4-cyanophenyl)-2,5-diphenyl-3-tosyloxazolidine-5-carboxylate (**4s**): Colorless solid. mp: 172–173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.59 (m, 2H), 7.42 (d, *J* = 8.1 Hz. 4H), 7.37-7.31 (m, 2H), 7.28-7.24 (m, 2H), 7.21-7.15 (m, 4H), 7.09-7.04 (m, 2H), 6.18 (s, 1H), 5.99 (s, 1H), 3.60 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 144.2, 142.7, 135.6, 134.5, 133.6, 131.4, 129.7, 129.6, 129.4, 128.4, 128.3, 128.2, 128.0, 127.8, 125.8, 118.4, 111.3, 91.5, 89.8, 67.5, 53.4, 21.4; IR (neat) ν_{max} 3005, 2974, 2231, 1746, 1609, 1509, 1355, 1251, 1163, 1012, 754, 669 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{26}N_2O_5NaS$, 561.1454 $(M+Na)^+$; Found, 561.1449.

Methyl 4-(4-cyanophenyl)-5-(4-fluorophenyl)-2-phenyl-3-tosyloxazolidine-5-carboxylate (**4t**): Colorless solid. mp: 158–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.39 (m, 2H), 7.29 – 7.03 (m, 11H), 6.18 (s, 1H), 5.98 (s, 1H), 3.59 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 165.1, 161.8, 144.4, 142.6, 134.4, 133.6, 131.6, 131.6, 131.5, 130.2, 130.1, 129.6, 129.5, 128.9, 128.5, 128.1, 127.8, 125.8, 118.4, 115.5, 115.2, 111.5, 90.9, 89.8,67.5, 53.5, 21.4. IR (neat) ν_{max} 3010, 2974, 2230, 1746, 1610, 1509, 1355, 1251, 1163, 1012, 836, 754, 669 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}O_5N_2FNaS$, 579.1360 $(M+Na)^+$; Found, 579.1359.

1-Benzyl-4'-(4-nitrophenyl)-2'-phenyl-3'-tosylspiro[indoline-3,5'-oxazolidin]-2-one (**8a**): Colorless solid. mp: 188–189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.78 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.58 – 7.01 (m, 15H), 6.89 (s, 1H), 6.70 – 6.51 (m, 2H), 6.13 (d, *J* = 7.4 Hz, 1H), 5.50 (s, 1H), 4.87 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 147.4, 144.9, 144.4, 143.1, 136.3, 134.9, 134.6, 130.9, 130.0, 129.5, 128.9, 128.5, 128.4, 127.9, 127.2, 126.9, 123.2, 122.6, 122.5, 109.5, 92.0, 84.7, 66.8, 43.7, 21.6. IR (neat) ν_{max} 3062, 2917, 1725, 1609, 1524, 1470, 1358, 1170, 1029, 744, 668 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{29}O_6N_3NaS$ = 654.1669 $(M+Na)^+$; Found, 654.1660.

1-Benzyl-4'-(4-nitrophenyl)-2'-(p-tolyl)-3'-tosylspiro[indoline-3,5'-oxazolidin]-2-one (**8b**): Colorless solid. mp: 182–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.10 (m, 10H), 7.01 – 6.90 (m, 2H), 6.74 (s, 1H), 6.58 – 6.44 (m, 2H), 6.12 – 5.98 (m, 1H), 5.37 (s, 1H), 4.82 – 4.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 147.4, 145.1, 144.3, 143.1, 140.0, 135.0, 134.5, 133.3, 130.8, 129.4, 129.2, 128.9, 128.5, 128.2, 128.0, 127.9, 127.2, 126.9, 123.2, 122.6, 122.6, 109.4, 92.0, 84.5, 66.8, 43.6, 21.6, 21.4. . IR (neat) ν_{max} 3061, 2920, 1716, 1613, 1523, 1368, 1171, 1104, 1034. 668 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{31}O_6N_3NaS$ = 668.1825 $(M+Na)^+$; Found, 668.1820.

1-Benzyl-2'-(4-methoxyphenyl)-4'-(4-nitrophenyl)-3'-tosylspiro[indoline-3,5'-oxazolidin]-2-one (**8c**): Colorless solid. mp: 201–202 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.42 – 6.83 (m, 14H), 6.74 (s,

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1H), 6.52 (dd, *J* = 15.8, 7.9 Hz, 2H), 6.06 (d, *J* = 6.9 Hz, 1H), 5.39 (s, 1H), 4.77 (d, *J* = 1.5 Hz, 2H), 3.81 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 160.9, 147.4, 145.1, 144.3, 143.1, 134.9, 134.6, 130.8, 129.7, 129.4, 128.9, 128.5, 128.1, 127.9, 127.9, 127.2, 126.9, 123.2, 122.6, 122.6, 113.9, 109.5, 91.8, 84.3, 66.6, 55.4, 43.6, 21.6. IR (neat) ν_{max} 3059, 2900, 1719, 1611, 1515, 1347, 1251, 1170, 1101, 1023, 669 cm^{-1}; HRMS (ESI) $C_{37}H_{31}O_7N_3NaS$ Found, 684.1758 $(M+Na)^+$

1-Benzyl-2'-(4-bromophenyl)-4'-(4-nitrophenyl)-3'-tosylspiro[indoline-3,5'-oxazolidin]-2-one (**8d**): Colorless solid. mp: 196–197 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.62 – 7.46 (m, 4H), 7.43 – 6.91 (m, 13H), 6.74 (s, 1H), 6.59 – 6.43 (m, 2H), 6.03 (d, *J* = 7.6 Hz, 1H), 5.36 (s, 1H), 4.75 (d, *J* = 3.4 Hz, 2H), 2.34 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 147.4, 144.7, 143.1, 135.4, 134.9, 134.2, 131.7, 130.9, 129.9, 129.6, 128.9, 128.4, 128.0, 127.2, 126.8, 124.2, 123.2, 122.7, 122.2, 109.6, 91.3, 84.7, 66.7, 43.7, 21.6. IR (neat) ν_{max} 2927, 1724, 1523, 1346, 1162, 1103, 673 cm^{-1}; HRMS (ESI) $C_{36}H_{28}O_6N_3BrS$ Found, 734.0735 $(M+2+Na)^+$

1-Benzyl-2'-(4-fluorophenyl)-4'-(4-nitrophenyl)-3'-tosylspiro[indoline-3,5'-oxazolidin]-2-one (**8e**): Colorless solid. mp: 178–179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.74 – 7.61 (m, 2H), 7.42 – 6.93 (m, 15H), 6.78 (s, 1H), 6.63 – 6.45 (m, 2H), 6.04 (d, *J* = 6.9 Hz, 1H), 5.39 (s, 1H), 4.77 (s, 2H), 2.35 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 165.3, 161.9, 147., 144.8, 144.6, 143.2, 134.9, 134.4, 132.3, 132.2, 130.9, 130.4, 130.2, 129.5, 128.9, 128.4, 127.9, 127.2, 126.8, 123.2, 122.7, 122.3, 115.7, 115.4, 109.6, 91.2, 84.6, 66.7, 43.7, 21.6. IR (neat) ν_{max} 2927, 1725, 1610, 1519, 1347, 1162, 1036, 674 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{28}O_6N_3FNaS$ = 672.1575 $(M+Na)^+$; Found, 672.1568.

Acknowledgments

TRS thanks UGC, New Delhi for the award of fellowship

Supplementary data

Supplementary data (Copies of ^{1}H and ^{13}C NMR spectra of products) related to this article can be found at

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