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Article

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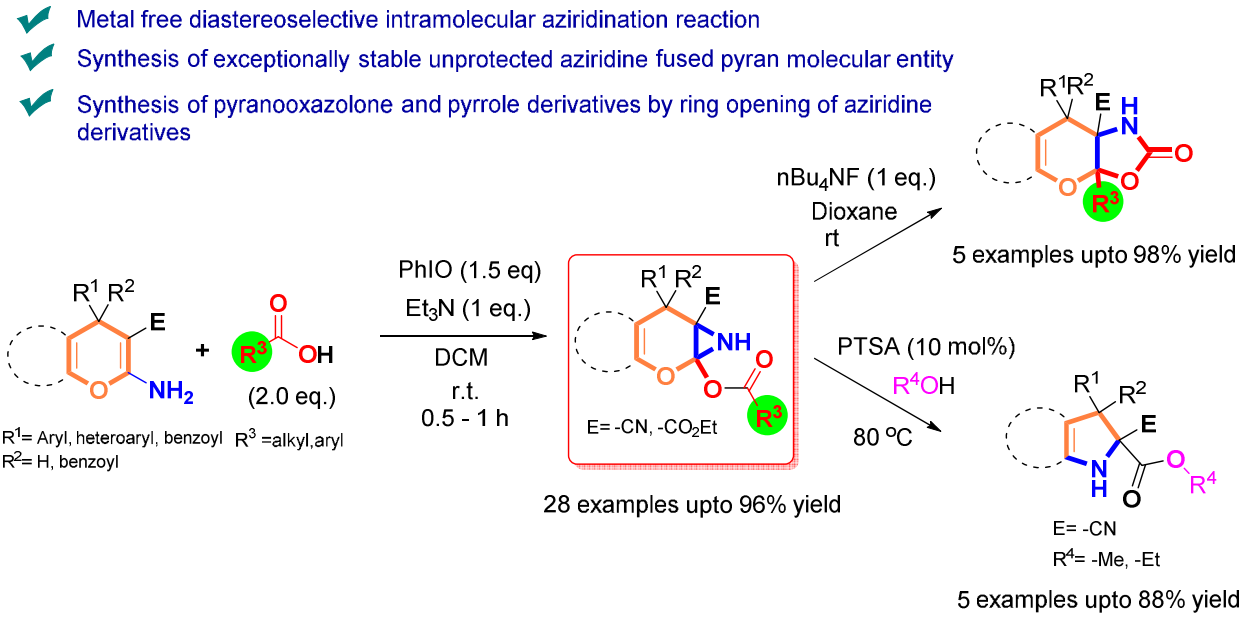


ABSTRACT

An advanced protocol for the diastereoselective intramolecular aziridination reaction has been developed to synthesize 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylate from their corresponding 4-H-pyrans and spiropyrans analogues employing iodosylbenznene as the exclusive oxidant in presence of carboxylic acid and triethylamine. High structural and stereochemical diversity of these pyran fused NH-azridine scaffolds make them useful in evaluating their biological and pharmacological activities by SAR studies. Additionally their potential synthetic application has been uncovered by efficient transformation into biologically relevant novel pyranooxazolone and pyrrole derivatives.

INTRODUCTION

Fused heterocyclic moiety is one of the fundamental structural requirements for numerous natural products and synthetic compounds to exhibit their extensive variety of biological activities.[1] Fused heterocycles, being essentially the hybrid of two or more bioactive heterocyclic fragments, possess versatile biological and pharmacological activities originated due to the presence of multiple pharmacophores in a single molecular entity. Further, carefully designed synthetic hybrid molecules, possessing high skeletal and stereochemical diversity, with bioactivity can be used as protein function modulator and key leads in drug development of medicinal field.[2] Thus development of efficient and direct synthetic route to synthesize fused heterocyclic compounds bearing multiple chiral centers has taken a great deal of attention over the past decades.[3]

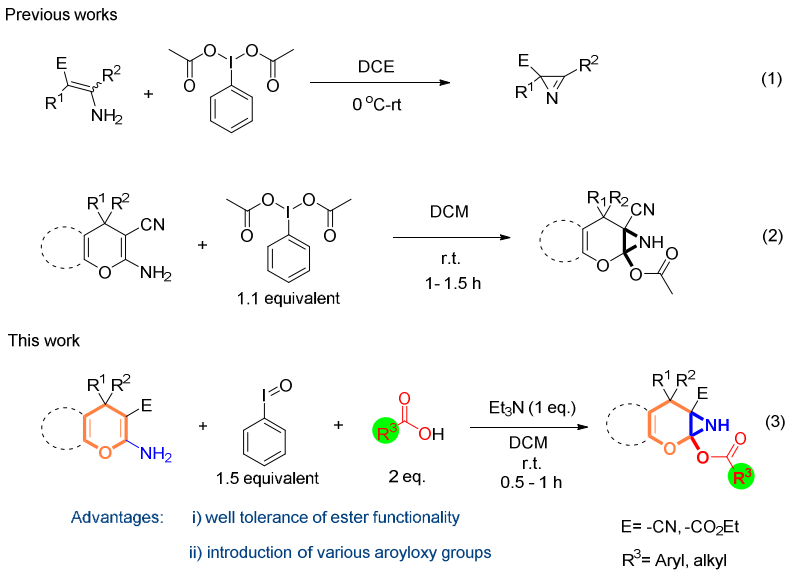
Pyran framework is a privileged pharmacophore embedded as the structural core in numerous biologically relevant natural products and synthetic compounds.[4] On the other hand aziridine is

the key constituent of several bioactive natural products[5] regardless of its high affinity towards countless ring opening reactions due to the ring strain.[6] Although various literature reports concerning bioactivities of pyran and aziridine derivatives intensely justify the construction of hybrid molecular entities having aziridine fused pyran scaffold as the structural motif, but much less effort has been specified to develop the synthetic methodologies to achieve them.[7] Availability of a handful literature data regarding the synthesis of pyran fused aziridine molecular entities may be due to their inherent instability which prevents their isolation as stable molecular entity. In this context, it is noteworthy to mention some previous reports enlighten the in situ synthesis of pyran fused aziridine molecular scaffolds which then induced immediate chemical transformations without isolating them as stable compounds.[8] Consequently, their preparation and isolation are still remaining challenging as well as important synthetic targets to the organic chemists.

Plentiful synthetic methods have been developed over the past decades to synthesize aziridine derivatives in their protected and unprotected form.[9] Most of them consist of intramolecular substitution reaction within the amine derivatives, reaction of carbenes with imines and reaction of nitrenes with olefins. Recently Zhao et al. have established a synthetic route to construct 2H-azirines from several enamine derivatives using iodobenzene diacetate (scheme 1, entry 1).[10] In our previous work, [7d] we have demonstrated an intramolecular aziridination reaction to construct pyran fused 2-acetoxy-NH-aziridine molecular scaffold by exploiting the enamine fragment of 2-amino-4H-pyrans and 2-amino-spiropyrans employing iodobenzene diacetate (scheme 1, entry 2). It was indeed the first report of the synthesis and isolation of highly stable pyran fused 2-acetoxy-NH-aziridines. The use of hypervalent iodine as the sole reagent for aziridination is beneficial since it offers a metal free mild reaction condition. In addition, hypervalent iodine

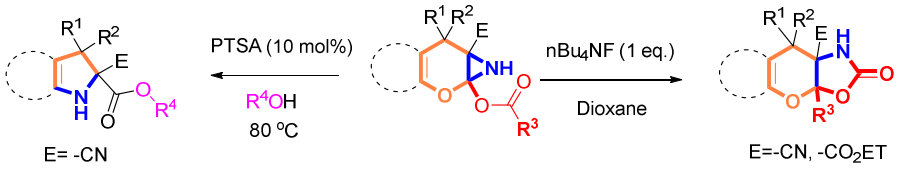
reagents are easily available, less toxic and easy to handle. Despite of the success, our previous protocol suffers from generalized functionalization of the target molecule, since only acetoxy group can be introduced in the angular position of the 2-oxa-7-azabicyclo[4.1.0]hept-3-ene framework. Also the protocol has the limitation to be unproductive when -CN group is replaced by -CO_2Et group in the starting pyran derivatives. Thus development of a comprehensive methodology with broader substrate scope and higher functional group tolerance, and suitable for introducing higher degree of diversity in the resulting pyran fused NH-aziridines is still challenging and of course in demand.

Concentrating to the efforts in the development of innovative and efficient methodologies towards the synthesis of biologically relevant compounds,[11] herein we wish to reveal a simple and robust diastereoselective protocol to construct a stable, highly functionalized and stereochemically diversified pyran fused NH-aziridine scaffold by reacting 2-amino-4H-pyran and 2-aminospiropyran derivatives with iodosylbenzene as the exclusive oxidant in presence of triethylamine and carboxylic acids (1:2) at room temperature avoiding metal catalysts (Scheme 1, entry 3).



Scheme 1. Synthesis of 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates by intramolecular aziridination

Additionally, synthetic applications of these synthesized NH- aziridine derivatives was also explored by carrying out their ring opening transformations under different reaction conditions. Interestingly, they have found to be the key precursor in synthesizing densely functionalized novel pyranooxazolone molecular scaffolds when treated with tetrabutylammoniumfluoride. In addition, acid catalyzed ring opening of these NH- aziridines leads to the formation of biologically privileged highly functionalized pyrrole derivatives (scheme 2). To the best of our knowledge, this is the first report revealing the synthesis of these particular functionalized pyranooxazolone and pyrrole molecular scaffolds originating from pyran fused aziridine derivatives upon simple and efficient ring transformation conditions.



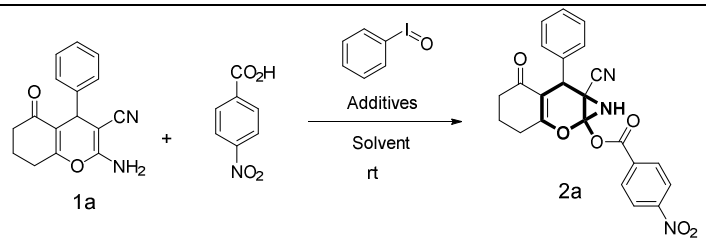
Scheme 2. Acid and fluoride ion catalyzed ring opening of 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates

RESULTS AND DISCUSSION

To investigate the feasibility of this strategic approach for intramolecular aziridination reaction, 2-amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **1a** was synthesized using a known method[12a] and employed as a model substrate in this reaction. When **1a** was treated with iodosylbenzene (1 mmol) in presence of 4-nitrobenzoic acid (1 mmol) in DCM (5 mL) at room temperature, after 60 min **2a** was obtained in very low yield (Table 1, entry 1).

Interestingly, use of triethylamine (1 mmol) as an additive increased the product yield to 40% in comparatively shorter reaction time (Table 1, entry 2). Use of higher amount of oxidant found to be effective for improving the product yield within shorter reaction time (Table 1, entry 3and 4). However further enhancement of product yield was not observed when more than 1.5 mmol of iodosylbenzene was used (Table 1, entry 5). When carboxylic acid loading was increased, the yield of **2a** was greatly elevated and isolated yield was 92% (applying 2mmol of carboxylic acid) (Table 1, entry 6-8). Further increase of carboxylic acid amount did not afford any better result (Table 1, entry 9). Furthermore, to improve the reaction time and product yield, the reaction was performed in presence of different additives and different

Table 1. Optimization of reaction conditions [a]



Entry	PhIO (mmol)	Carboxylic acid (mmol)	Additive (1 mmol)	Solvent	Time (min)	Yield[b](%)
1	1.0	1	_	DCM	60	10
2	1.0	1	Et_3N	DCM	40	40
3	1.2	1	Et_3N	DCM	35	45
4	1.5	1	Et_3N	DCM	30	55
5	1.6	1	Et_3N	DCM	30	50
6	1.5	1.5	Et_3N	DCM	30	70

7	1.5	1.8	Et_3N	DCM	30	90
8	**1.5**	**2.0**	**Et_3N**	**DCM**	**30**	**92**
9	1.5	2.1	Et_3N	DCM	30	91
10	1.5	2.0	Cs_2CO_3	DCM	45	15
11	1.5	2.0	NaOAc	DCM	55	12
12	1.5	2.0	Et_3N	DCE	50	74
13	1.5	2.0	Et_3N	EtOAc	50	62
14	1.5	2.0	Et_3N	Toluene	45	60
15	1.5	2.0	Et_3N	Dioxane	55	65
16	1.5	2.0	Et_3N	THF	52	70
17	1.5	2.0	Et_3N	Acetonitrile	55	72

[a] 1 mmol of 1a was taken in 5mL of solvent in all the cases. [b] Yield of the isolated product.

solvents. Bases like Cs_2CO_3 and NaOAc were found to be inefficient compared to triethylamine (Table 1, entry 10 and 11) and **2a** was isolated in low yield when solvents like dichloroethane, ethylacetate, toluene, dioxane, tetrahydrofuran and acetonitrile were used replacing DCM (Table 1, entry 12-17).

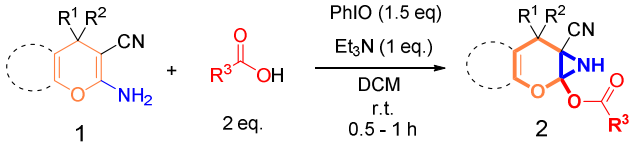
With this optimized reaction conditions (Table 1, entry 8), we then focused our attention to explore the feasibility of this intramolecular aziridination reaction. Several known 2-amino-3cyano-4H-pyran derivatives[12a-j] with high functionalization were synthesized via the above mentioned three component reaction[12a] in which a variety of aromatic and heteroaromatic aldehydes along with phenylglyoxal were reacted with malononitrile and ethylcyanoacetate in presence of various 1,3-dicarbonyls such as dimedone, cyclohexane-1,3-dione, 4-hydroxycoumarin and 2-hydroxy-1,4-naphthoquinone. These pyran derivatives were then treated

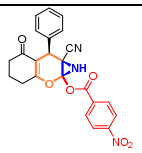
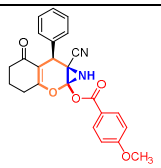
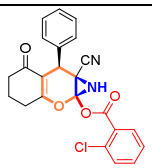
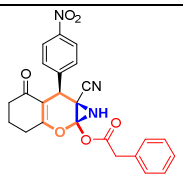
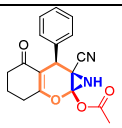
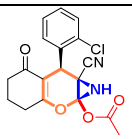
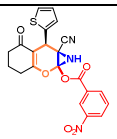
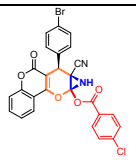
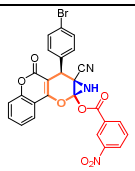
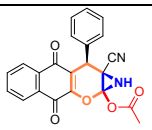
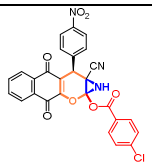
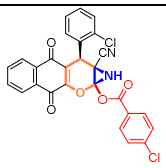
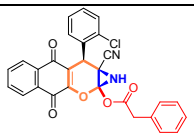
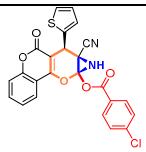
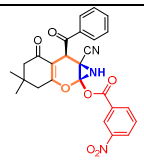
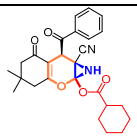
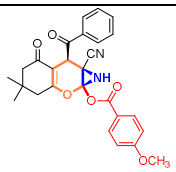
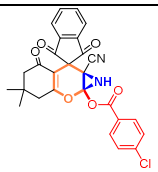
with iodosylbenzene (1.5 mmol) in presence of carboxylic acid (2 mmol) and triethylamine (1mmol) in 5 mL of DCM to synthesize 2-oxa-7-azabicyclo[4.1.0]hept-3-enes. In this purpose a large variety of aromatic as well as aliphatic carboxylic acids were employed to amplify this developed protocol. Astonishingly, this protocol was found to be really efficient in affording diversified 2-oxa-7-azabicyclo[4.1.0]hept-3-enes in good to excellent yields (Table 2 and 3). A wide range of aromatic carboxylic acids containing electron donating as well as electron withdrawing groups at different positions of the ring along with aliphatic acids such as acetic acid, phenylacetic acid and sterically bulky diphenyl acetic acid were successfully introduced at the angular position of the 2-oxa-7-azabicyclo[4.1.0]hept-3-ene framework. This protocol offers absolutely clean reaction as no other side products were obtained after completion of the reaction. It may be due to the high reactivity of the oxidant towards the enamine fragment of the starting material while alternative double bond of pyran ring and other functional groups during the reaction remained non reactive. Notably the reaction has found to proceed with the same efficiency in case of ethyl 2-amino-4H-pyran-3-carboxylate derivatives which broadens the scope of this protocol further (Table 3, entry 4a-4i). Compounds **4a-i** were obtained at slightly lower yield compared to **2a-s** which seem to be probably due to the greater electron withdrawing ability of nitrile than that of ethoxycarbonyl group. Apart from their role in protecting the enamine tautomeric form in starting materials, -CN and -CO_2Et groups also induce nucleophilic property of the carbon center to which they are stitched, since the pyran oxygen atom and amine group are in conjugation with them through the intervening double bond. To test the viability of the reaction in case of spiropyran system a known spiropyran derivative[12k] was synthesized using the same procedure which was used to synthesize 4H-pyrans.[12a] The reaction also found to be convenient in transforming the spiropyran into the corresponding pyran fused NH-aziridine with

excellent product yield (Table 2, entry 2r). The starting materials which possess coumarin or naphthoquinone fused pyran substructures were found to take longer reaction time for this transformation, however not affecting the yield of their corresponding products (Table 2, entry 2i-o and Table 3, entry 4d-i). The reaction proceeded with almost equal efficiency in presence of several aromatic and aliphatic acids (Table 2, entry 2a-r and Table 3, entry 4a-i). All the synthesized 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates are significantly stable and they remain unaffected during column chromatographic separation of the reaction mixture (silica gel mesh size 100-200). All products are well characterized through ^{1}H NMR, ^{13}C NMR, IR, HRMS and elemental analysis data and finally the structural motif of the synthesized compounds were established through X-ray crystallographic analysis of one representative compound **4g** (CCDC 1472710). The information about the relative stereochemistry obtained from the X-ray crystallographic analysis of compound **4g** (see supporting information) enables us to assign the relative configuration of C^2, C^3 and C^4 centers of the pyran ring as *R*, *R* and *S* respectively.

In this present endeavor we have also successfully evaluated the synthetic application of these synthesized 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates by converting them into highly functionalized pyranooxazolone and pyrrole derivatives by devising fluoride ion and acid catalyzed ring opening of aziridine moiety. For the fluoride ion catalyzed transformation, tetrabutylammonium fluoride was employed as suitable reagent owing to its solubility in organic solvents. Further strong hydrogen bonding affinity of fluoride ion and its speciality in providing clean reaction by maintaining neutral reaction environment make it a better choice of reagent for

Table 2. Substrate scope to synthesize 3-cyano-2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates[a]



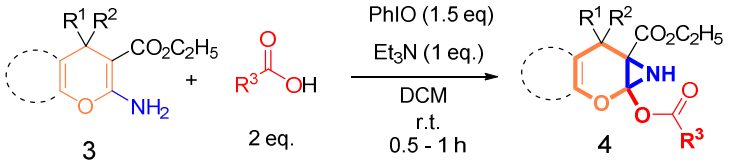
 2a, 92%, 30 min	 2b, 90%, 30 min	 2c, 93%, 30 min	 2d, 94%, 30 min
 2e, 96%, 30 min	 2f, 95%, 30 min	 2g, 89%, 30 min	 2h, 90%, 60 min
 2i, 88%, 60 min	 2j, 90%, 60 min	 2k, 88%, 60 min	 2l, 90%, 60 min
 2m, 92%, 60 min	 2n, 84%, 60 min	 2o, 90%, 30 min	 2p, 95%, 30 min
 2q, 94%, 30 min	 2r, 90%, 30 min		

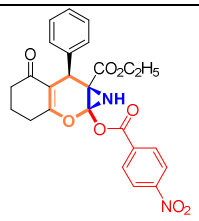
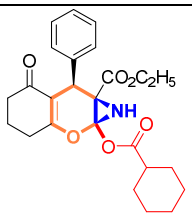
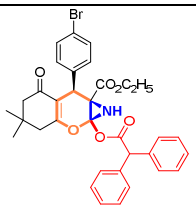
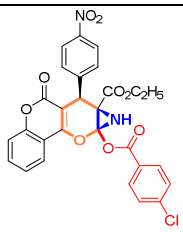
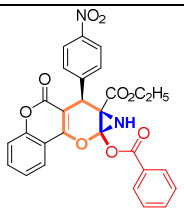
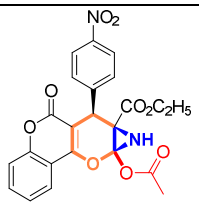
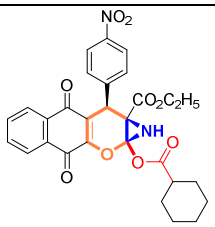
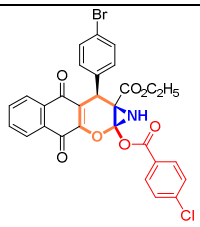
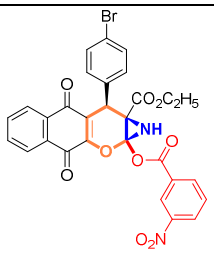
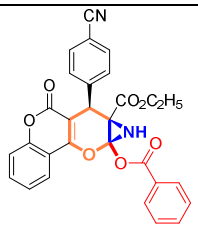
[a]Reaction conditions: 1 (1 mmol), PhIO (1.5 mmol), carboxylic acids (2 mmol), Et_3N (1 mmol) DCM (5 mL), r.t. [b] Isolated yield and reaction time.

this purpose. Some selective 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates were transformed into pyranooxazolones in presence of one equivalent of tetrabutylammonium fluoride in dioxane medium at room temperature. The transformation was very fast (~30 min) (when R^3 = methyl, benzyl) and almost quantitatively afforded a well decorated pyranooxazolone scaffold bearing angular functionality (Table 4, entry 5a-d). Applying this method **2e**, **2f**, **2d**, **4f** and **2a** were successfully transformed into **5a-e** respectively. The transformation is equally efficient for both the ester and nitrile derivative of 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates (Table 4, entry 5a-e). They were (5a-e) well characterized by ^{1}H NMR, ^{13}C NMR, IR, HRMS and elemental analysis data and their structural motif was fully confirmed through X-ray crystallographic analysis of a single crystal of compound **5c** (CCDC 1472711). One very interesting structural feature (see supporting information) of this pyranooxazolone molecular scaffold is that the p-nitrophenyl, nitrile and benzyl groups are in syn relationship to each other. Literature reviews suggest that both this type of pyranooxazolones and their synthetic route are new.

Furthermore, when some selective 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates were treated with p-toluenesulphonic acid (10 mol%) in refluxing methanol they were transformed into well functionalized pyrrole derivatives. In all cases the conversion took place in short reaction time (~2h) and the products are obtained in excellent yields (Table 5, 6a-d). **2a**, **2d**, **2f**, **2g** were converted to **6a-d** respectively by applying this protocol and when compound **2d** was subjected to same p-TsOH catalyzed reaction in ethanol medium , pyrrole **6e** was obtained in

Table 3. Substrate scope to synthesize ethyl 1-(carbethoxy)-2-oxa-7-azabicyclo[4.1.0]hept-3-ene-6-carboxylates[a]



 4a, 88%, 30 min	 4b, 90%, 30 min	 4c, 86%, 30 min	 4d, 82%, 60 min
 4e, 80%, 60 min	 4f, 90%, 60 min	 4g, 84%, 60 min	 4h, 82%, 60 min
 4i, 80, 60 min	 4j, 88%, 60 min		

[a]Reaction conditions: 3 (1 mmol), PhIO (1.5 mmol), carboxylic acids (2 mmol), Et_3N (1 mmol) DCM (5 mL), r.t. [b] Isolated yield and reaction time.

good yield. However this conversion is very efficient only for cyano derivatives of 2-oxa-7-

azabicyclo[4.1.0]hept-3-enyl carboxylates which possess cyclohexanone fragment fused with the pyran moiety.

Table 4. Synthesis of pyranooxazolones[a]

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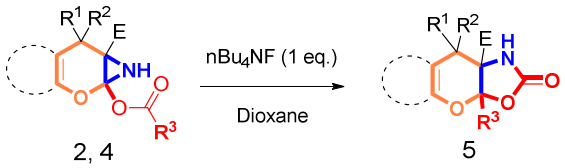
<tr><td colspan="4"> 
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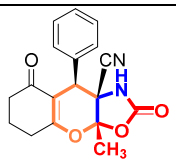
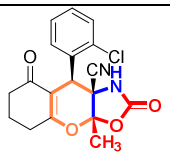
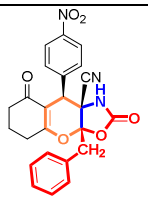
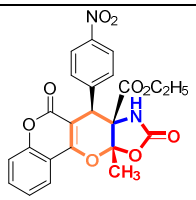
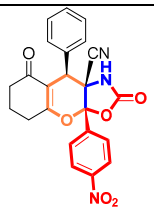
<tr><td> 

5a, 98%, 30 min</td><td> 

5b, 96%, 30 min</td><td> 

5c, 92%, 30 min</td><td> 

5d, 96%, 30 min</td></tr>
<tr><td> 

5e[b], 50%, 30 min</td><td></td><td></td><td></td></tr>
</table>

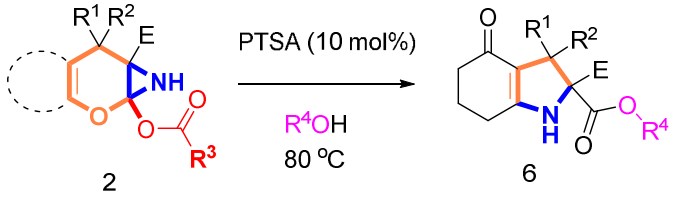
[a]Reaction conditions: 2 or 4 (1 mmol), nBu_4NF (1 mmol), Dioxane (2 mL), r.t. [b] heated at 60 ^oC.

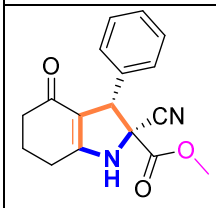
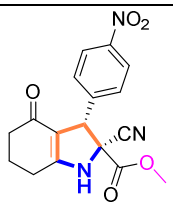
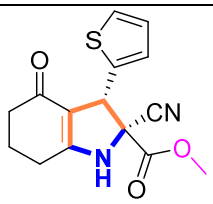
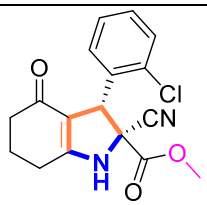
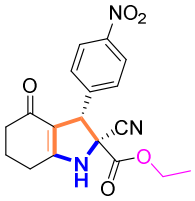
[b] Isolated yield and reaction time.

Compounds 6a-e are also fully characterized by ^1H NMR, ^{13}C NMR, IR, HRMS and elemental analysis data and confirmation of the structural motif was done by single crystal X-ray crystallographic analysis of compound **6a** (CCDC 1472712). Interestingly product pyrroles evolved via acid catalyzed transformation, features a quaternary carbon atom, attached with both a nitrile and a methoxy carbonyl group at the same time and the –CN group is in syn relationship with the aryl group of the C^3 atom. In case of compound 6a the relative configuration of C^2 and

C^3 center of the pyrrole ring can be assigned as R and S respectively from the X-ray crystal structure of it (see supporting information).

Table 5. Synthesis of pyrroles[a]

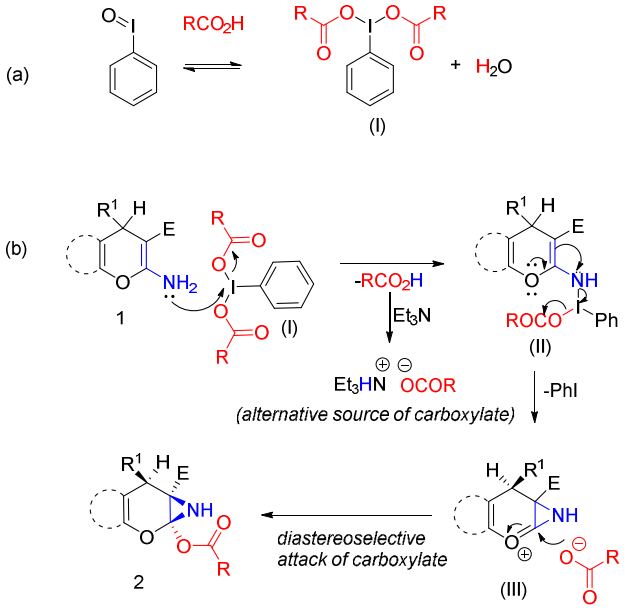


 6a, 90%, 2h	 6b, 88%, 2h	 6c, 87%, 2h	 6d, 90%, 2h
 6e, 74%, 2h			

[a] Reaction conditions: **2** (1 mmol), PTSA (10 mol%), alcohol (3 mL), 80 °C. [b] Isolated yield and reaction time.

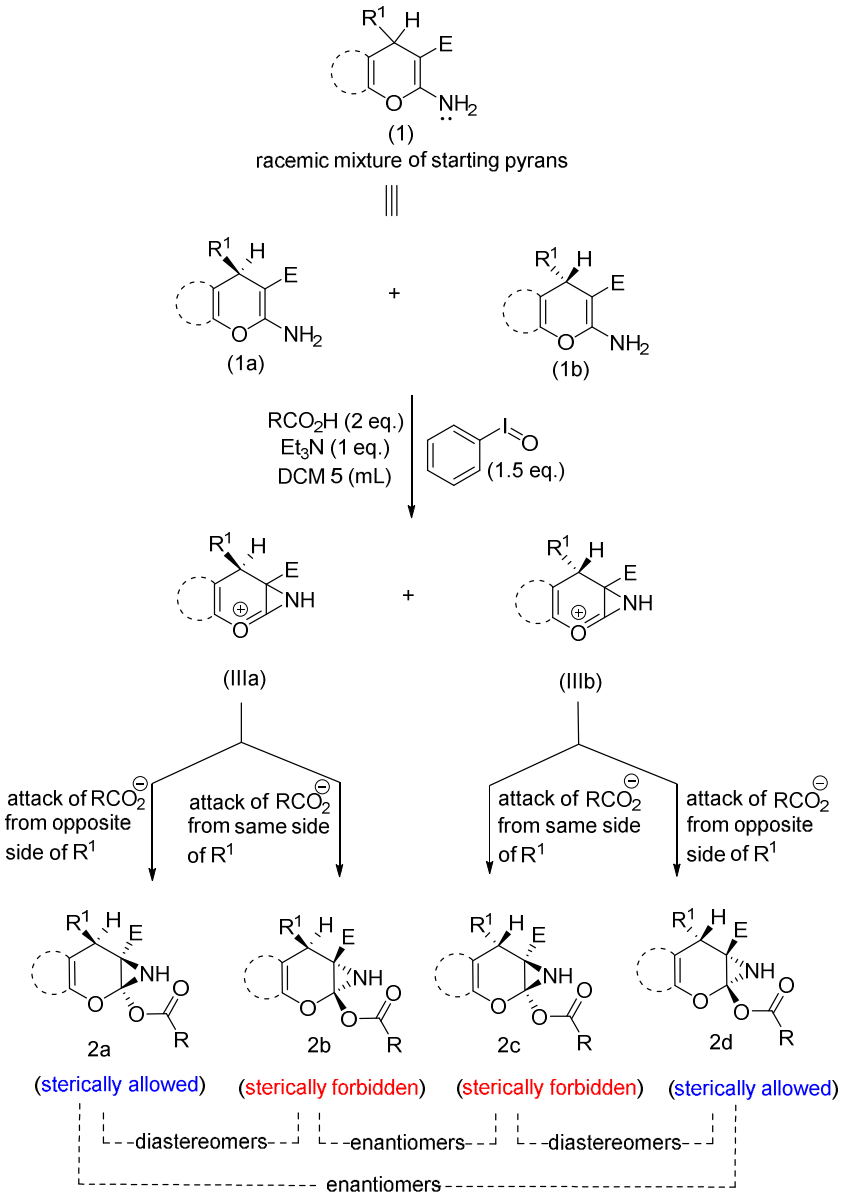
A mechanism for the formation of 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates is depicted in scheme 3. Based on the fact that iodobenzene diacetate undergoes ligand exchange in presence of carboxylic acids,[13] we tentatively assume that the initial reaction between iodosyl benzene and carboxylic acid have produced the species $PhI(OCOR)_2$ (I) which then acted as the actual reagent in this reaction. Initially **I** attacks the amino group of the starting material (**1**) leading to the formation of N-iodo intermediate **II**. The carboxylic acid released in this step is consumed by

triethylamine to produce an ion pair which could serve as a source of carboxylate ion. Attack by the double bond, assisted by the pyran oxygen atom, to the electrophilic nitrogen center



Scheme 3. Mechanism for the synthesis of 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates

generates the intermediate **III** by releasing iodobenzene and carboxylate ion. The attachment of the pyran oxygen atom with the enamine moiety is crucial for the formation of 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates since it assists in the formation and stabilization of the intermediate **III.** Subsequently, attack by the carboxylate ion to the C^2 center of the pyran ring of **III** takes place which ultimately generates 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylate **2**. The X-ray crystal structure of compound 4g (see supporting information) explains the relative stereochemistry in the pyran fused NH-aziridine scaffold and clearly displays the syn relationship between the aziridine ring and 4-nitrophenyl substituent of C^4 center of pyran ring. This syn orientation in the product aziridine molecules undoubtedly indicates that the attacking



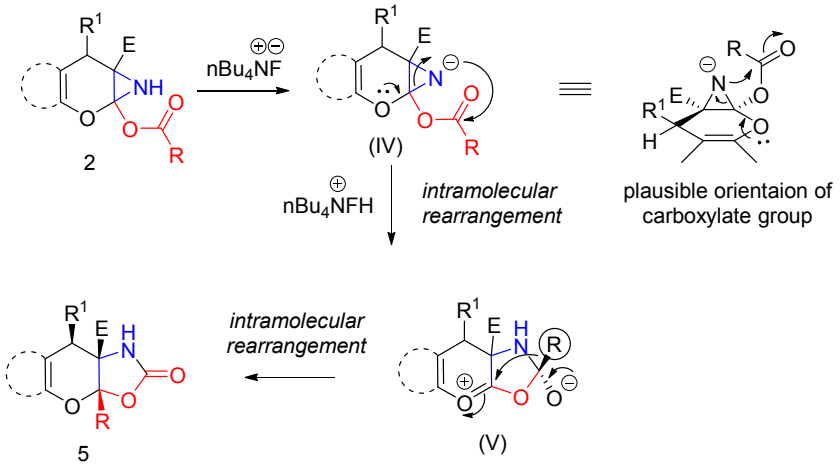
Scheme 4. Stereochemical course of the aziridination reaction

carboxylate ion has approached from the opposite side of 4-nitrophenyl group. This in turn establishes the diastereoselective nature of this particular reaction. During the nucleophilic attack (carboxylate ion), the large group (R^1) of the C^4 carbon atom controls the facial selectivity. Carboxylate ion prefers α-attack, i.e., the attack from the opposite side of R^1, hence leads to the

formation of **2** as the exclusive diastereomer. The β attack which is sterically hindered does not take place at all under the imposed experimental condition.

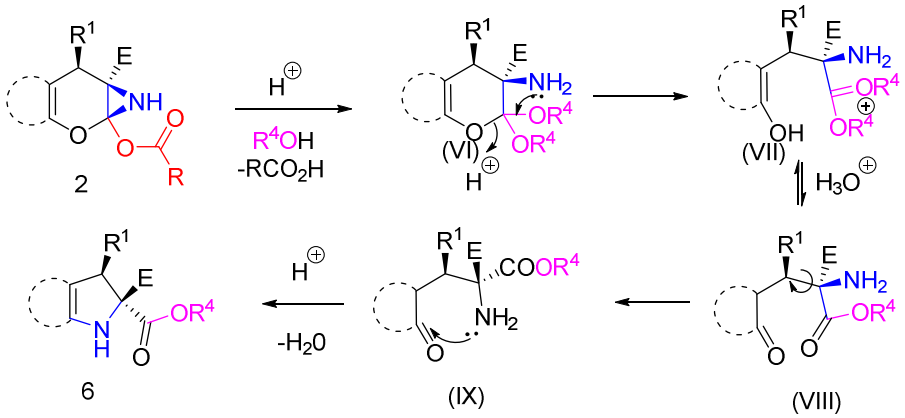
The stereochemical course of this aziridination reaction is described in scheme 4. The starting pyran compounds are racemates since they have synthesized applying achiral methodology. When a starting pyran derivative **1** is treated with 1.5 eq. of iodosylbenzene in presence of 2 eq. of a carboxylic acid and 1 eq. of triethylamine, it's corresponding enantiomers **1a** and **1b** results in the formation of the intermediates **IIIa** and **IIIb** following the same mechanistic pathway as proposed in scheme 3**.** In the next step, subsequent attack by the carboxylate ion to the C^2 center of the pyran ring of both IIIa and IIIb takes place to generate the final aziridine product. Now, during the neucleophilic attack of carboxylate ion, the preferred approach is controlled by steric factor and takes place from the opposite side of the R^1 group. Consequently the intermediate IIIa and IIIb rapidly transformed into the product 2a and 2d respectively. The formation of 2b and 2c is sterically forbidden and they have not formed at all during the course of reaction. Now, 2a and 2d possess enantiomeric relationship to each other. On the other hand, 2a and 2d possess diastereomeric relationship with 2b and 2c respectively. Thus the reaction follows the diastereoselective pathway and eventually transforms the racemic pyran compound to the corresponding pyran fused NH-aziridine racemate in diastereoselective manner.

Plausible mechanisms for the fluoride ion and acid catalyzed transformations of the 2-oxa-7-azabicyclo[4.1.0]hept-3-enyl carboxylates are also depicted in scheme 5 and 6 respectively. Acidic nature of the H of the aziridine ring in **2** facilitates its abstraction by the fluoride ion to



Scheme 5. Mechanism for the synthesis of pyranooxazole

generate intermediate **IV**. This negatively charged species **IV** then immediately undergo intramolecular rearrangement with concomitant proton abstraction to generate **V.** During this step the plausible orientation of the carboxylate group in intermediate **IV** is depicted in scheme 3. **V** then follows second intramolecular rearrangement pathway in which migration of the R group takes place to the α-position of the positively charged oxygen atom, which ultimately afford the compound 5.



Scheme 6. Mechanism for the synthesis of pyrroles

In case of acid catalyzed ring opening reaction (scheme 6), the aziridine ring of 2 is first opened up in presence of H^+ ion resulting in the formation of intermediate V**I** which then undergoes acid catalyzed ring opening and generates V**II**. V**II** on tautomerization changes into its keto form V**III** which then transformed into **IX** in presence of acid. Finally **IX** undergoes acid catalyzed cyclization to assume the product **6** i.e. fused pyrrole derivative.

CONCLUSION

In conclusion, an advanced protocol of intramolecular aziridination reaction has been developed to synthesize 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylate from their corresponding 4-H-pyrans and spiropyrans using iodosylbenznene as the exclusive oxidant in presence of various aromatic as well as aliphatic carboxylic acids and triethylamine. Regardless of its broader substrate scope this methodology offers a very simple, robust and diastereoselective route to construct pyran fused NH-aziridine molecular scaffolds. Well functional group tolerance of the oxidant makes this protocol suitable to introduce high skeletal and stereochemical diversity in the product NH-azridines. Their potent synthetic efficacy has been discovered by efficiently transforming them into biologically relevant novel pyranooxazolone and pyrrole derivatives under mild reaction conditions.

EXPERIMENTAL SECTION

General procedure for the synthesis of 4-H-pyrans[12a]

Triethylamine (1 drop) was added to a solution of aromatic aldehydes (2 mmol), malononitrile (or ethyl 2-cyanoacetate) (2 mmol), and 1,3-diketones (2 mmol) in EtOH (5ml) and the reaction mixture was refuxed for 15 min. The precipitate thus appeared was filtered off, washed with water (5×10 ml) and EtOH (3×5 ml), and finally recrystallized from EtOH. The crystallized pure

compounds[12a-j] were then subjected for the synthesis of 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates.

General procedure for the synthesis of spiropyran[12a]

Triethylamine (1 drop) was added to a solution of ninhydrin (2 mmol), malononitrile (2 mmol), and dimedone (2 mmol) in EtOH (5ml) and the reaction mixture was refuxed for 15 min. The precipitate thus formed was filtered off, washed with water (5×10 ml) and EtOH (3×5 ml), and finally recrystallized from EtOH. The crystallized pure compound [12k]was then subjected for the synthesis of 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates.

General procedure for the synthesis of 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylate 2a-r and 4a-j

To a stirring suspension of iodosylbenzene (1.5 mmol) in 5mL DCM was added carboxylic acid (2 mmol) and stirred for 5 min at rt followed by addition of triethylamine (1 mmol) and stirred for another 2 min. Finally 2-amino-4-H-pyrans (1 mmol) were added in the reaction mixture and stirred for the stipulated time (Table 2 and 3) until the total consumption of the starting material (monitored by TLC) was observed. After completion of the reaction, the mixture was diluted with DCM(10mL) and washed with saturated sodium bicarbonate solution (10mL×3 times). The combined organic layers were dried over sodium sulphate and subjected to column chromatographic separation (20- 50% ethylacetate in petroleum ether) to get the pure products. The same procedure was applied in case of 2-amino spiropyran. All the synthesized compounds were characterized by spectral (^{1}H NMR, ^{13}C NMR, IR, HRMS and elemental analysis) data, and X-ray crystallographic analysis (4g).

7a-cyano-6-oxo-7-phenyl-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 4-nitrobenzoate 2a

Yield: 396 mg, 92%; white solid; Mp: 208-210^{o}C; IR (KBr): 3214, 2956, 2832, 2245, 1750, 1710, 1680, 1632, 1530, 1350, 1091, 987 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 2.07 (d, *J*=4.8 Hz, 2H), 2.30-2.41 (m, 3H), 2.60 (d, *J*=4.8 Hz, 2H), 4.61 (s, 1H), 7.21-7.25 (m, 2H), 7.30-7.36 (m, 3H), 8.26-8.35 (m, 4H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.2, 27.9, 36.8, 36.9, 38.9, 88.8, 110.2, 116.0, 123.9, 127.4, 128.1, 129.0, 131.6, 132.5, 136.3, 151.5, 161.6, 165.4, 195.7; HRMS (ESI-TOF) m/z Calcd for $[C_{23}H_{17}N_3O_6+H]^+$: 432.1190, found: 432.1215 and $[C_{23}H_{17}N_3O_6+Na]^+$: 454.1010, found: 454.1016.

7a-cyano-6-oxo-7-phenyl-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 4-methoxybenzoate 2b

Yield: 374 mg, 90%; white solid; Mp: 190-200 ^{o}C; IR (KBr): 3254, 2938, 2844, 2243, 1726, 1675, 1630, 1605, 1166, 1100, 937, 606 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.91 (s, 2H), 2.26 (d, *J*=3.9 Hz, 2H), 2.53 (s, 2H), 3.85 (s, 3H), 4.33 (s, 1H), 5.84 (s, 1H), 7.13 (d, *J*=8.7 Hz, 2H), 7.20-7.32 (m, 5H), 8.02 (d, *J*=8.7 Hz, 2H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 24.9, 32.6, 40.7, 41.7, 60.8, 84.2, 93.4, 114.5, 118.8, 119.7, 121.4, 123.9, 132.1, 132.8, 133.2, 133.4, 133.9, 136.4, 137.3, 143.1, 167.4, 169.6, 170.7, 200.6; Anal. Calcd for $C_{24}H_{20}N_2O_5$: C, 69.22; H, 4.84; N, 6.73%. Found: C 69.20; H 4.86; N 6.70%.

7a-cyano-6-oxo-7-phenyl-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 2-chlorobenzoate 2c

Yield: 391 mg, 93%; white solid; Mp: 182-184^{o}C; IR (KBr): 3277, 2922, 2890, 2243, 1751, 1672, 1632, 1369, 1188, 1099, 1088, 1025, 918, 743 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.91-2.07 (m, 2H), 2.19-2.36 (m, 2H), 2.40 (s, 1H), 2.45-2.60 (m, 2H), 4.50 (s, 1H), 7.14-7.33

(m, 6H), 7.45-7.46 (d, *J*=3.6 Hz, 2H), 7.92-7.95 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (75 MHz; CDCl3; Me_4Si): δ 19.8, 27.7, 36.6, 38.7, 88.3, 109.8, 115.8, 126.0, 126.7, 127.1, 127.14, 127.2, 127.6, 128.6, 131.4, 132.1, 134.2, 135.1, 136.3, 161.2, 165.3, 195.6; HRMS (ESI-TOF) m/z Calcd for $[C_{23}H_{17}ClN_2O_4+H]^+$: 421.0950, found: 421.0931 and $[C_{23}H_{17}ClN_2O_4+Na]^+$: 443.0769, found: 443.0748.

7a-cyano-7-(4-nitrophenyl)-6-oxo-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 2-phenylacetate 2d [7d]

Yield: 419 mg, 94%; white solid; Mp: 204-206 ^{o}C; IR (KBr): 3114, 2956, 2826, 2243, 1788, 1653, 1632, 1515, 1347, 1236, 1091, 995 cm^{-1}; ^{1}H NMR (300 MHz; DMSO-d_6; Me_4Si): δ 2.02 (s, 2H), 2.27-2.55 (m, 5H), 3.83 (s, 2H), 4.41 (s, 1H), 7.30-7.39 (m, 7H), 8.16-8.18 (d, *J*=8.7 Hz, 2H); ^{13}C NMR (75 MHz; DMSO-d_6; Me_4Si): δ 15.3, 23.2, 31.5, 32.0, 34.5, 35.6, 83.3, 104.8, 110.6, 119.1, 123.1, 124.05, 124.1, 124.6, 126.6, 139.5, 142.7, 161.4, 163.4, 191.0; Anal. Calcd for $C_{24}H_{19}N_3O_6$: C 64.72; H 4.30; N 9.43%. Found: C 64.74; H 4.32; N 9.40%.

7a-cyano-6-oxo-7-phenyl-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl acetate 2e[7d]

Yield: 311 mg, 96%; off-white solid; Mp: 132-134 ^{o}C; IR (KBr): 3175, 2963, 2238, 1791, 1631, 1238, 1229, 1152, 1100, 1063, 936 cm^{-1}; ^{1}H NMR (300 MHz; DMSO-d_6; Me_4Si): δ 1.90 (s, 2H), 2.24 (s, 5H), 2.50 (s, 2H), 4.26 (s, 1H), 5.67 (s, 1H), 7.17-7.33 (m, 5H); ^{13}C NMR (75 MHz; DMSO-d_6; Me_4Si): δ 20.3, 20.7, 28.0, 36.0, 37.1, 88.5, 109.8, 116.8, 127.5, 128.2, 128.6, 138.5, 166.0, 168.1, 196.0; HRMS (ESI-TOF) m/z Calcd for $[C_{18}H_{16}N_2O_4+H]^+$: 325.1183, found: 325.1188.

7-(2-chlorophenyl)-7a-cyano-6-oxo-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl acetate 2f[7d]

Yield: 341 mg, 95%; white solid; Mp 142-144 ^{o}C; IR (KBr):cm^{-1}; 3217, 2956, 2937, 2244, 1788, 1668, 1626, 1234, 1175, 1102, 1064, 768 cm^{-1}; ^{1}H NMR (300 MHz; CDCl3; Me_4Si): δ 1.90-1.98 (m, 2H), 2.18 (s, 3H), 2.22-2.26 (t, *J*=6.2 Hz, 2H), 2.36 (s, 1H), 2.48-2.51 (t, *J*=5.3 Hz, 2H), 5.06 (s, 1H), 6.85-6.88 (d, *J*=7.5 Hz, 1H), 7.04-7.16 (m, 2H), 7.36-7.39 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (75 MHz; CDCl3; Me_4Si): δ 19.8, 20.1, 27.5, 34.4, 35.2, 36.5, 87.8, 110.6, 115.6, 126.2, 128.5, 128.8, 129.4, 133.7, 134.3, 165.5, 166.9, 195.1; HRMS (ESITOF) m/z Calcd for $[C_{18}H_{15}ClN_2O_4+H]+$: 359.0793, found: 359.0799.

7a-cyano-6-oxo-7-(thiophen-2-yl)-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 3-nitrobenzoate 2g

Yield: 389 mg, 89%; pale yellow solid; Mp: 180-182 ^{o}C; IR (KBr):cm^{-1}; 3188, 2954, 2840, 2246, 1786, 1688, 1632, 1528, 1352, 1234, 1091, 930 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.80 (s, 2H), 2.19 (s, 2H), 2.43 (s, 2H), 4.65 (s, 1H), 6.20 (s, 1H), 6.91 (s, 2H), 7.30 (s, 1H), 7.83 (s, 1H), 8.37 (d, *J*=6 Hz, 1H), 8.52 (d, *J*=6 Hz, 1H), 8.64 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 19.8, 27.6, 35.0, 35.2, 36.7, 88.9, 110.0, 116.0, 124.4, 125.2, 126.0, 126.6, 128.5, 129.6, 131.4, 135.9, 140.4, 148.2, 161.4, 164.7, 195.5; Anal. Calcd for $C_{21}H_{15}N_3O_6S$: C 57.66; H 3.46; N 9.61%. Found: C 57.64; H 3.44; N 9.64%.

7-(4-bromophenyl)-7a-cyano-6-oxo-7a,8-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirin-8a(7H)-yl 4-chlorobenzoate 2h

Yield: 495 mg, 90%; off-white solid; Mp: 220-222 ^{o}C; IR (KBr): 3310, 2241, 1768, 1712, 1645, 1489, 1384, 1241, 1108, 701, 564 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 4.76 (s, 1H), 6.43 (s, 1H), 7.23 (d, *J*=8.4 Hz, 2H), 7.29-7.38 (m, 2H), 7.49 (d, *J*=8.1 Hz, 2H), 7.60-7.68 (m, 3H), 7.78 (d, *J*=6.9 Hz, 1H), 8.04 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 35.9, 90.0, 100.4, 113.7, 115.9, 116.9, 121.5, 123.3, 125.2, 126.1, 130.1, 130.8, 131.8, 132.3,

133.6, 136.9, 140.8, 152.4, 155.2, 159.9, 162.6; Anal. Calcd for $C_{26}H_{14}BrClN_2O_5$: C 56.80; H 2.57; N, 5.10%. Found: C 56.78; H 2.59; N, 5.12%.

7-(4-bromophenyl)-7a-cyano-6-oxo-7a,8-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirin-8a(7H)-yl 3-nitrobenzoate 2i

Yield: 493 mg, 88%; pale yellow solid; Mp: 230-232 ^oC; IR (KBr): 3320, 2241, 1768, 1720, 1645, 1530, 1489, 1384, 1330, 1241, 762 cm^{-1}; ^1H NMR (300 MHz; DMSO d_6; Me_4Si): δ 4.87 (s, 1H), 6.60 (s, 1H), 7.32 (d, *J*=8.1 Hz, 2H), 7.39-7.52 (m, 2H), 7.58 (d, *J*=8.4 Hz, 2H), 7.72 (t, *J*=7.8 Hz, 1H), 7.89 (d, *J*=8.1 Hz, 1H), 7.97 (t, *J*=8.1 Hz, 1H), 8.52 (d, *J*=7.8 Hz, 1H), 8.66 (d, *J*=8.4 Hz, 1H), 8.80 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 35.9, 90.1, 100.5, 115.9, 116.9, 121.5, 123.3, 124.9, 125.2, 128.9, 130.1, 130.8, 131.8, 133.7, 136.4, 136.8, 148.6, 152.4, 155.1, 161.8; HRMS (ESI-TOF) m/z Calcd for $[C_{26}H_{14}BrN_3O_7+H]^+$: 560.0088, found: 560.0113.

7a-cyano-7-(4-nitrophenyl)-6-oxo-7a,8-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirin-8a(7H)-yl 4-chlorobenzoate 2j

Yield: 348 mg, 90%; off-white solid; Mp: 216-218 ^oC; IR (KBr): 3291, 2244, 1752, 1720, 1678, 1661, 1636, 1239, 1118, 949 cm^{-1}; ^1H NMR (300 MHz; DMSO d_6; Me_4Si): δ 2.24 (s, 3H), 4.77 (s, 1H), 6.01 (s, 1H), 7.25 (s, 5H), 7.75 (d, *J*=7.2 Hz, 3H), 7.94-7.97 (m, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 20.7, 35.8, 89.3, 116.3, 119.6, 126.3, 126.5, 128.0, 128.7, 128.9, 130.8, 131.7, 134.5 135.2, 137.8, 150.2, 168.1, 177.6, 182.7; Anal. Calcd for $C_{22}H_{14}N_2O_5$: C 68.39; H 3.65; N 7.25%. Found: C 68.37; H 3.63; N 7.28%.

9a-cyano-9-(4-nitrophenyl)-3,8-dioxo-3,8,9,9a-tetrahydrobenzo[6,7]chromeno[2,3-b]azirin-1a(1H)-yl 4-chlorobenzoate 2k

Yield: 465 mg, 88%; yellow solid; Mp: 222-224 ^oC; IR (KBr): 3298, 2246, 1756, 1722, 1678, 1661, 1636, 1534, 1350, 1295, 1101, 701 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$ and DMSO d_6;

Me$_4$Si): δ 4.80 (s, 1H), 5.26 (s, 1H), 7.42 (d, *J*=8.4 Hz, 2H), 7.51 (d, *J*=8.1 Hz, 2H), 7.66-7.68 (m, 2H), 7.82 (d, *J*= 2.4 Hz,1H), 7.99-8.05 (m, 3H), 8.16 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (75 MHz; DMSO d$_6$; Me$_4$Si): δ 35.1, 89.8, 115.7, 118.8, 124.0, 126.0, 126.4, 126.6, 130.2, 130.9, 131.5, 132.3, 134.7, 135.2, 140.9, 145.3, 147.5, 150.5, 162.4, 177.4, 182.7; HRMS (ESI-TOF) m/z Calcd for $[C_{27}H_{14}ClN_3O_7+Na]^+$: 550.0412, found: 550.0428.

9-(2-chlorophenyl)-9a-cyano-3,8-dioxo-3,8,9,9a-tetrahydrobenzo[6,7]chromeno[2,3-b]azirin-1a(1H)-yl 4-chlorobenzoate 2l

Yield: 466 mg, 90%; yellow solid; Mp: 212-214 ^{o}C; IR (KBr): 3291, 2242, 1752, 1720, 1678, 1661, 1636, 1239, 1094, 714 cm^{-1}; ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ 2.87 (s, 1H), 5.62 (s, 1H), 7.10 (s, 1H), 7.19 (d, *J*=7.2 Hz, 1H), 7.28 (d, *J*=3Hz, 1H), 7.48-7.57 (m, 3H), 7.73 (d, *J*=3.3 Hz, 2H), 7.94 (d, *J*=3.9 Hz, 1H), 8.04-8.08 (m, 2H), 8.13 (d, *J*=2.7 Hz, 1H); ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si): δ 35.8, 36.0, 89.2, 115.3, 120.0, 125.3, 126.7, 127.0, 129.3, 129.5, 129.9, 130.1, 130.4, 131.5, 131.9, 133.8, 134.0, 134.8, 141.8, 150.1, 162.3, 182.2; Anal. Calcd for $C_{27}H_{14}Cl_2N_2O_5$: C 62.69; H 2.73; N, 5.42%. Found: C 62.66; H 2.75; N, 5.40%.

9-(2-chlorophenyl)-9a-cyano-3,8-dioxo-3,8,9,9a-tetrahydrobenzo[6,7]chromeno[2,3-b]azirin-1a(1H)-yl 2-phenylacetate 2m

Yield: 457 mg, 92%; yellow solid; Mp: 208-210 ^{o}C; IR (KBr): 3180, 2244, 1754, 1735, 1670, 1661, 1636, 1350, 1295, 1239, 1094, 949, 701 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d$_6$; Me$_4$Si): δ 3.97-4.13 (m, 2H), 5.29 (s, 1H), 6.45 (s, 1H), 7.23 (s, 2H), 7.36 (s, 6H), 7.59 (d, *J*=7.2 Hz, 1H), 7.82 (s, 3H), 8.03 (d, *J*=5.7 Hz, 1H); ^{13}C NMR (75 MHz; DMSO d$_6$; Me$_4$Si): δ 34.2, 36.5, 89.4, 119.6, 126.3, 126.5, 127.7, 127.8, 128.7, 129.0, 129.7, 130.0, 130.8, 131.3, 131.5, 132.9, 134.6, 135.2, 150.5, 169.2, 177.4, 182.6; Anal. Calcd for $C_{28}H_{17}ClN_2O_5$: C 67.68; H 3.45; N 5.64%. Found: C 67.66; H 3.48; N 5.62%.

7a-cyano-6-oxo-7-(thiophen-2-yl)-7a,8-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirin-8a(7H)-yl 4-chlorobenzoate 2n

Yield: 401 mg, 84%; off-white solid; Mp: 214-216 ^{o}C; IR (KBr): 3235, 2254, 1755, 1729, 1638, 1379, 1228, 1090, 755, 708 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 2.86 (s, 1H), 5.04 (s, 1H), 6.96 (t, *J*=4.4 Hz, 1H), 7.09 (d, *J*=3.3 Hz, 1H), 7.17-7.26 (m, 3H), 7.43 (d, *J*=8.1 Hz, 2H), 7.51 (t, J=7.8 Hz, 1H), 7.73 (d, *J*=7.5 Hz, 1H), 8.00 (d, *J*=8.1 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 36.5, 37.1, 89.4, 100.4, 113.4, 115.2, 116.8, 123.1, 124.5, 125.2, 125.9, 127.1, 127.2, 129.4, 131.9, 133.1, 137.5, 141.9, 152.6, 159.9, 162.2; Anal. Calcd for $C_{24}H_{13}ClN_2O_5S$: C 60.45; H 2.75; N, 5.87%. Found: C 60.43; H 2.77; N, 5.85%.

7-benzoyl-7a-cyano-4,4-dimethyl-6-oxo-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 3-nitrobenzoate 2o

Yield: 439 mg, 90%; white solid; Mp: 188-190 ^{o}C; IR (KBr): 3240, 2959, 2840, 2244, 1743, 1660, 1605, 1533, 1350, 1260, 1200, 1168, 1094, 934 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.05 (s, 6H), 2.22 (s, 2H), 2.29-2.47 (m, 2H), 3.20 (s, 1H), 5.19 (s, 1H), 7.49 (t, *J*=7.4 Hz, 2H), 7.58-7.68 (m, 2H), 8.09 (d, *J*=7.5 Hz, 2H), 8.35 (d, *J*=7.5 Hz, 1H), 8.44 (d, *J*=8.1 Hz, 1H), 8.86 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 27.8, 28.4, 32.6, 34.1, 38.1, 41.2, 50.0, 88.1, 108.3, 115.2, 125.4, 129.0, 129.1, 129.2, 130.2, 134.6, 135.3, 135.8, 148.5, 161.6, 164.4, 196.0, 196.1; HRMS (ESI-TOF) m/z Calcd for $[C_{26}H_{21}N_3O_7+Na]^+$: 510.1272, found: 510.1251.

7-benzoyl-7a-cyano-4,4-dimethyl-6-oxo-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl cyclohexanecarboxylate 2p

Yield: 426 mg, 95%; white solid; Mp: 136-138 ^{o}C; IR (KBr): 3272, 2966, 2928, 2840, 2242, 1740, 1668, 1605, 1250, 1208, 1168, 1094, 934 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.11 (s, 6H), 1.24-1.32 (m, 3H), 1.52 (d, *J*=10.8 Hz, 2H), 1.77 (s, 2H), 1.99 (d, *J*=12.6 Hz, 2H),

2.25 (s, 2H), 2.32-2.52 (m, 3H), 2.97 (s, 1H), 5.16 (s, 1H), 7.55 (t, *J*=7.7 Hz, 2H), 7.66 (d, *J*=7.5 Hz, 1H), 8.15 (d, *J*=7.8 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 25.1, 25.5, 27.7, 28.3, 28.5, 32.5, 34.1, 38.3, 41.2, 42.4, 50.0, 87.1, 108.0, 115.5, 129.1, 134.4, 135.4, 164.6, 172.9, 195.9, 196.2; HRMS (ESI-TOF) m/z Calcd for $[C_{26}H_{28}N_2O_5+H]^+$: 449.2071, found: 449.2068, and $[C_{26}H_{28}N_2O_5+Na]^+$: 471.1890, found: 471.1869.

7-benzoyl-7a-cyano-4,4-dimethyl-6-oxo-3,4,5,6,7,7a-hexahydrochromeno[2,3-b]azirin-1a(1H)-yl 4-methoxybenzoate 2q

Yield: 444 mg, 94%; white solid; Mp: 184-186 ^{o}C; IR (KBr): 3272, 2959, 2932, 2864, 2244, 1743, 1660, 1605, 1373, 1260, 1200, 1168, 1094, 934, 767, 612 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.03 (s, 6H), 2.20 (s, 2H), 2.26-2.46 (m, 2H), 3.02 (s, 1H), 3.79 (s, 3H), 5.16 (s, 1H), 6.87 (d, *J*=9.0 Hz, 2H), 7.48 (t, *J*=7.7 Hz, 2H), 7.58 (t, *J*=7.4 Hz, 1H), 7.98 (d, *J*=9.0 Hz, 2H), 8.09 (d, *J*=7.8 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 27.7, 28.5, 32.5, 34.2, 38.4, 41.2, 50.0, 55.6, 87.7, 108.1, 114.2, 115.5, 119.4, 129.1, 129.1, 132.7, 134.4, 135.5, 163.0, 164.7, 164.8, 196.0, 196.2; HRMS (ESI-TOF) m/z Calcd for $[C_{27}H_{24}N_2O_6+Na]^+$: 495.1527, found: 495.1529.

7a-cyano-4,4-dimethyl-1',3',6-trioxo-1,1',3,3',4,5,6,7a-octahydro-1aH-spiro[chromeno[2,3-b]azirine-7,2'-inden]-1a-yl 4-chlorobenzoate 2r

Yield: 453 mg, 90%; off-white solid; Mp: 220-222 ^{o}C; IR (KBr): 3247, 2967, 2939, 2833, 2249, 1790, 1752, 1713, 1665, 1644, 1369, 1249, 1214, 942, 720 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me4Si): δ 0.98 (d, *J*=5.4 Hz, 3H), 1.04 (s, 3H), 1.98-2.50 (m, 3H), 2.58-2.74 (m, 1H), 6.86 (d, *J*=6.0 Hz, 1H), 7.69-7.74 (m, 2H), 8.05-8.10 (m, 6H); ^{13}C NMR (75 MHz; DMSO d_6; Me4Si): δ 26.4, 28.8, 32.8, 35.6, 49.4, 54.8, 87.9, 109.3, 113.8, 124.2, 125.9, 130.1, 132.3, 137.3, 137.8,

140.8, 141.1, 161.9, 169.0, 193.9, 196.6, 196.8; HRMS (ESI-TOF) m/z Calcd for $[C_{27}H_{19}ClN_2O_6+H]^+$: 503.1004, found: 503.1033.

ethyl 1a-((4-nitrobenzoyl)oxy)-6-oxo-7-phenyl-1,1a,3,5,6,7-hexahydrochromeno[2,3-b]azirine-7a(4H)-carboxylate 4a

Yield: 421 mg, 88%; off-white solid; Mp: 202-204 ^oC; IR (KBr): 3290, 2967, 2833, 1740, 1713, 1642, 1611, 1530, 1350, 1200, 1093, 941 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.27 (t, *J*=7.1 Hz, 3H), 2.05 (s, 2H), 2.34-2.46 (m, 2H), 2.58 (d, *J*=4.2 Hz, 2H), 4.21-4.26 (m, 2H), 5.07 (s, 1H), 7.25 (s, 5H), 8.23 (d, *J*=7.8 Hz, 2H), 8.33 (d, *J*=6.6 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.1, 20.3, 28.1, 35.9, 37.2, 48.4, 63.4, 90.0, 112.1, 123.9, 127.0, 128.1, 128.2, 131.4, 133.0, 138.8, 151.3, 161.9, 165.2, 167.2, 196.5; HRMS (ESI-TOF) m/z Calcd for $[C_{25}H_{22}N_2O_8+H]^+$: 479.1449, found: 479.1441 and $[C_{25}H_{22}N_2O_8+Na]^+$: 501.1268, found: 501.1255.

ethyl 1a-((cyclohexanecarbonyl)oxy)-6-oxo-7-phenyl-1,1a,3,5,6,7-hexahydrochromeno[2,3-b]azirine-7a(4H)-carboxylate 4b

Yield: 396 mg, 90%; white solid; Mp: 120-122 ^oC; IR (KBr): 3280, 2980, 2940, 2826, 1740, 1715, 1642, 1611, 1200, 1093, 950 cm^{-1}; ^1H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.20-1.34 (m, 8H), 1.57 (s, 1H), 1.64 (s, 2H), 1.78 (s, 2H), 1.90 (t, *J*=5.9 Hz, 2H), 2.24 (s, 2H), 2.39 (s, 1H), 4.10 (s, 1H), 4.13-4.21 (m, 2H), 4.73 (s, 1H), 7.07 (d, *J*=7.5 Hz, 2H), 7.12-7.24 (m, 3H); ^{13}C NMR (75 MHz; DMSO d_6; Me4Si): δ 19.0, 25.0, 29.4, 30.1, 32.6, 33.0, 33.1, 41.0, 41.7, 46.4, 52.5, 67.5, 93.9, 115.6, 131.4, 132.8, 132.9, 144.6, 170.6, 171.7, 177.2, 201.0; Anal. Calcd for $C_{25}H_{29}NO_6$: C 68.32; H 6.65; N 3.19%. Found: C 68.30; H 6.63; N 3.21%.

ethyl 7-(4-bromophenyl)-1a-(2,2-diphenylacetoxy)-4,4-dimethyl-6-oxo-1,1a,3,5,6,7-hexahydrochromeno[2,3-b]azirine-7a(4H)-carboxylate 4c

Yield: 542 mg, 86%; off-white solid; Mp: 140-142 ^{o}C; IR (KBr): 3330, 2967, 2939, 2833, 1735, 1720, 1642, 1243, 1093, 1051, 1029, 950, 744, 668 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ .99-1.06 (m, 9H), 2.11 (s, 2H), 2.30 (s, 2H), 2.64 (s, 1H), 3.85-3.92 (m, 2H), 4.77 (s, 1H), 4.96 (s, 1H), 7.00 (d, *J*=7.8 Hz, 2H), 7.16-7.29 (m, 12H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 13.9, 28.0, 28.4, 31.7, 35.6, 41.6, 48.2, 50.9, 56.0, 63.1, 89.5, 110.4, 120.8, 127.6, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.9, 131.1, 136.9, 137.1, 138.0, 163.8, 166.6, 169.6, 196.4; Anal. Calcd for $C_{34}H_{32}BrNO_6$: C 64.77; H 5.12; N 2.22%. Found: C 64.75; H 5.10; N 2.25%.

ethyl 8a-((4-chlorobenzoyl)oxy)-7-(4-nitrophenyl)-6-oxo-8,8a-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirine-7a(7H)-carboxylate 4d

Yield: 462 mg, 82%; off-white solid; Mp: 180-182 ^{o}C; IR (KBr): 3315, 1740, 1642, 1529, 1349, 1200, 1093, 1051, 1029, 941, 746 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.29 (t, *J*=7.1 Hz, 3H), 3.12 (s, 1H), 4.19-4.36 (m, 2H), 5.36 (s, 1H), 7.27-7.33 (m, 2H), 7.45-7.60 (m, 4H), 7.69-7.75(m, 1H), 7.87 (d, *J*=7.8 Hz, 1H), 8.02 (d, *J*=8.4 Hz, 2H), 8.13 (d, *J*=8.4 Hz, 1H), 8.25 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.1, 37.5, 48.4, 63.9, 90.4, 101.0, 113.9, 116.7, 122.7, 123.1, 123.7, 124.4, 125.6, 129.2, 129.4, 131.7, 132.7, 135.0, 140.0, 141.5, 148.3, 152.6, 155.8, 160.8, 162.6, 166.1; Anal. Calcd for $C_{28}H_{19}ClN_2O_9$: C 59.74; H 3.40; N 4.98%. Found: C 59.72; H 3.42; N 4.96%.

ethyl 8a-(benzoyloxy)-7-(4-nitrophenyl)-6-oxo-8,8a-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirine-7a(7H)-carboxylate 4e

Yield: 423 mg, 80%; off-white solid; Mp: 170-172 ^{o}C; IR (KBr): 3350, 1745, 1640, 1540, 1350, 1190, 1093, 1050, 1029, 941, 745 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.25-1.33 (m, 3H), 3.00 (d, *J*=9.3 Hz, 1H), 4.18-4.30 (m, 2H), 5.30 (d, *J*=9.6Hz, 1H), 7.17-7.65 (m, 8H), 7.82 (t, *J*=8.4 Hz, 1H), 7.93 (t, *J*=8.4 Hz, 1H), 8.07 (t, *J*=8.4 Hz, 1H), 8.18 (d, *J*=10.5 Hz, 1H); ^{13}C

NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.1, 37.4, 48.4, 64.1, 90.3, 101.0, 113.9, 116.7, 122.7, 123.1, 123.7, 124.4, 126.3, 127.0, 129.2, 131.7, 132.3, 132.7, 134.5, 134.9, 135.3, 139.9, 148.3, 152.6, 155.8, 160.8, 161.6, 166.3; Anal. Calcd for $C_{28}H_{20}N_2O_9$: C 63.64; H 3.81; N 5.30%. Found: C 63.66; H 3.83; N 5.28%.

ethyl 8a-acetoxy-7-(4-nitrophenyl)-6-oxo-8,8a-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirine-7a(7H)-carboxylate 4f

Yield: 420 mg, 90%; off-white solid; Mp: 196-198 ^oC; IR (KBr): 3328, 1750, 1638, 1535, 1350, 1190, 1093, 1050, 1025, 941, 740 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.26 (t, *J*=6.3 Hz, 3H), 2.08 (s, 3H), 2.79 (s, 1H), 4.21 (t, *J*=7.2 Hz, 2H), 5.14 (s, 1H), 7.21 (t, *J*=8.0 Hz, 2H), 7.37 (d, *J*=7.5 Hz, 2H), 7.46 (t, *J*=7.8 Hz, 1H), 7.75 (d, *J*=7.8 Hz, 1H), 8.03 (d, *J*=7.2 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.2, 20.3, 37.5, 48.0, 63.8, 89.7, 101.0, 113.9, 116.7, 123.0, 123.6, 124.4, 129.5, 132.7, 145.3, 147.4, 152.6, 155.6, 160.8, 166.2, 167.5; Anal. Calcd for $C_{23}H_{18}N_2O_9$: C 59.23; H 3.89; N 6.01%. Found: C 59.21; H 3.87; N 6.04%.

ethyl 1a-((cyclohexanecarbonyl)oxy)-9-(4-nitrophenyl)-3,8-dioxo-1,1a,3,9-tetrahydrobenzo[6,7]chromeno[2,3-b]azirine-9a(8H)-carboxylate 4g

Yield: 459 mg, 84%; yellow solid; Mp: 180-182 ^oC; IR (KBr): 3291, 3103, 2967, 2833, 1752, 1720, 1678, 1661, 1636, 1530, 1350, 1295, 1239, 1216, 1200, 1118, 1101, 1054, 949 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.12-1.39 (m, 8H), 1.59 (s, 2H), 1.68 (s, 2H), 1.84 (s, 1H), 2.35 (t, *J*=10.8 Hz, 1H), 2.79 (s, 1H), 4.18-4.29 (m, 2H), 5.30 (s, 1H), 7.43 (d, *J*= 7.8 Hz, 2H), 7.59-7.67 (m, 2H), 7.79-7.82 (m, 1H), 8.04-8.10 (m, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.2, 25.0, 25.1, 25.5, 28.3, 28.6, 37.5, 42.3, 48.0, 63.7, 89.5, 120.1, 123.6, 126.4, 126.6, 129.4, 129.6, 130.6, 130.7, 131.6, 133.8, 134.5, 145.4, 147.3, 150.5, 166.1, 172.8, 177.5, 183.1; HRMS (ESI-TOF) m/z Calcd for $[C_{29}H_{26}N_2O_9+Na]^+$: 569.1531, found: 569.1530.

ethyl 9-(4-bromophenyl)-1a-((4-chlorobenzoyl)oxy)-3,8-dioxo-1,1a,3,9-tetrahydrobenzo[6,7]chromeno[2,3-b]azirine-9a(8H)-carboxylate 4h

Yield: 499 mg, 82%; yellow solid; Mp: 172-174 ^{o}C; IR (KBr): 3300, 3113, 1750, 1722, 1675, 1668, 1632, 1294, 1236, 1216, 1200, 1120, 1106, 1055, 945, 724, 663 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.14 (t, *J*=7.2 Hz, 3H), 2.96 (s, 1H), 4.08-4.20 (m, 2H), 5.28 (s, 1H), 7.15-7.19 (m, 2H), 7.37 (t, *J*=8.4 Hz, 4H), 7.61-7.7.73 (m, 2H), 7.83-7.86 (m, 1H), 7.91 (d, *J*=8.4 Hz, 2H), 8.02-8.05 (m, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.1, 37.1, 48.3, 63.6, 90.3, 120.9, 121.6, 125.8, 126.5, 127.0, 129.2, 130.4, 131.0, 131.6, 131.7, 133.7, 134.5, 137.0, 141.3, 150.2, 162.7, 166.3, 177.8, 183.1; Anal. Calcd for $C_{29}H_{19}BrClNO_7$: C 57.21; H 3.15; N 2.30%. Found: C 57.23; H 3.12; N 2.28%.

ethyl 9-(4-bromophenyl)-1a-((3-nitrobenzoyl)oxy)-3,8-dioxo-1,1a,3,9-tetrahydrobenzo[6,7]chromeno[2,3-b]azirine-9a(8H)-carboxylate 4i

Yield: 496 mg, 80%; yellow solid; Mp: 184-186 ^{o}C; IR (KBr): 3291, 3103, 1752, 1720, 1678, 1661, 1536, 1350, 1239, 1216, 1200, 1118, 1054, 949, 714 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.19 (t, *J*=7.1 Hz, 3H), 3.03 (s, 1H), 4.17 (t, *J*=7.8 Hz, 2H), 5.29 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J*=8.1 Hz, 2H), 7.66 (d, *J*=7.8 Hz, 3H), 7.86 (s, 1H), 8.05 (s, 1H), 8.31 (d, *J*=7.2 Hz, 1H), 8.44 (d, *J*=8.1 Hz, 1H), 8.80 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 14.2, 37.2, 48.2, 63.9, 90.6, 121.1, 121.8, 125.4, 126.7, 129.0, 129.3, 130.3, 130.5, 130.6, 131.7, 131.9, 133.8, 134.7, 135.9, 136.9, 148.5, 150.2, 161.7, 166.4, 177.8, 183.2; Anal. Calcd for $C_{29}H_{19}BrN_2O_9$: C 56.24; H 3.09; N 4.52%. Found: C 56.22; H 3.07; N 4.54%.

ethyl (7R,7aR)-8a-(benzoyloxy)-7-(4-cyanophenyl)-6-oxo-8,8a-dihydro-6H-chromeno[3',4':5,6]pyrano[2,3-b]azirine-7a(7H)-carboxylate 4j

Yield: 447 mg, 88%; white solid; Mp: 170-172 ^{o}C; IR (KBr): 3350, 2244, 1745, 1640, 1615, 1385, 1295, 1243, 1190, 1093, 1050, 1029, 941, 745 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.14-1.21 (m, 3H), 3.02 (s, 1H), 4.13-4.23 (m, 2H), 5.25 (s, 1H), 7.19-7.55 (m, 8H), 7.61 (t, *J*=8.1 Hz, 2H), 7.70 (d, *J*=7.8 Hz, 1H), 7.79 (d, *J*=7.8 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 13.7, 37.4, 48.0, 63.4, 89.9, 100.7, 111.1, 113.6, 116.4, 117.1, 118.5, 122.8, 124.0, 126.8, 127.8, 128.6, 129.1, 130.0, 131.9, 132.3, 133.0, 133.8, 134.5, 143.0, 152.3, 155.4, 160.5, 163.0, 165.8; HRMS (ESI-TOF) m/z Calcd for $[C_{29}H_{20}N_2O_7+Na]^+$: 531.1163, found: 531.1153.

General procedure for the synthesis of pyranooxazolones (5a-e)

In a dry 25 mL r.b.flask having a calcium chloride guard tube , 1 mmol 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates and 3 mL of dry dioxane were taken. Then to it 1 mmol of tetrabutylammonium fluoride was added and the reaction mixture was stirred at rt for the stipulated time. After completion of the reaction (monitored by TLC), dioxane was removed under reduced pressure and the resulting mass was then immediately subjected for column chromatographic separation (30-50% ethyl acetate in petroleum ether) to get the pure products. Same procedure was applied to get **5e** except the reaction mixture was stirred at 60 ^{o}C. All the synthesized compounds were characterized through analysis of spectral (^{1}H NMR, ^{13}C NMR, IR, HRMS and elemental analysis) data, and X-ray crystallography(5c).

3a-methyl-2,8-dioxo-9-phenyl-1,2,5,7,8,9-hexahydro-6H-chromeno[3,2-d]oxazole-9a(3aH)-carbonitrile 5a

Yield: 318 mg, 98%; white solid; Mp: 200-202 ^{o}C; IR (KBr): 3317, 2962, 2925, 2853, 1790, 1646, 1379, 1070, 961, 917, 719 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 1.75 (s, 3H), 1.92-2.10 (m, 2H), 2.37-2.46 (m, 2H), 2.62 (t, *J*=5.6 Hz, 2H), 4.50 (s, 1H), 7.16-7.19 (m, 2H), 7.26-

7.31 (m, 3H), 7.49 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.1, 24.7, 28.3, 36.3, 41.3, 64.6, 104.2, 113.2, 115.6, 129.1, 129.2, 129.3, 134.1, 153.8, 170.9, 197.1; HRMS (ESI-TOF) m/z Calcd for $[C_{18}H_{16}N_2O_4+H]^+$: 325.1183, found: 325.1191.

9-(2-chlorophenyl)-3a-methyl-2,8-dioxo-1,2,5,7,8,9-hexahydro-6H-chromeno[3,2-d]oxazole-9a(3aH)-carbonitrile 5b

Yield: 344 mg, 96%; off-white solid; Mp: 268-270 ^{o}C; IR (KBr): 3330, 2962, 2935, 2846, 1790, 1646, 1314, 1281, 1070, 945 729 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.76 (s, 3H), 1.94 (s, 2H), 2.28-2.33 (m, 2H), 2.65 (s, 2H), 4.95 (s, 1H), 7.18 (d, *J*=7.5 Hz, 1H), 7.35 (t, *J*=6.6 Hz, 2H), 7.56 (d, *J*=7.2 Hz, 1H), 9.96 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$ and DMSO d_6; Me_4Si): δ 20.0, 24.6, 28.0, 36.1, 37.0, 63.0, 103.3, 112.7, 115.4, 126.9, 128.4, 129.8, 130.4, 132.9, 135.9, 153.9, 169.5, 194.9; Anal. Calcd for $C_{18}H_{15}ClN_2O_4$: C 60.26; H 4.21; N 7.81%. Found: C 60.24; H 4.19; N 7.84%.

3a-benzyl-9-(4-nitrophenyl)-2,8-dioxo-1,2,5,7,8,9-hexahydro-6H-chromeno[3,2-d]oxazole-9a(3aH)-carbonitrile 5c

Yield: 410 mg, 92%; pale yello solid; Mp: 236-238 ^{o}C; IR (KBr): 3349, 2924, 2852, 1796, 1637, 1526, 1384, 1120, 938, 698 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.88 (t, *J*=5.4 Hz, 2H), 2.24-2.31 (m, 2H), 2.46 (s, 2H), 2.94 (d, *J*=14.4 Hz, 1H), 3.35 (s, 1H), 4.45 (s, 1H), 7.23-7.29 (m, 5H), 7.57 (d, *J*=8.4 Hz, 2H), 8.16 (d, *J*=8.1 Hz, 2H), 9.64 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 19.9, 27.8, 36.0, 40.9, 42.5, 64.0, 102.6, 110.8, 116.0, 124.1, 127.6, 128.1, 131.0, 131.4, 132.1, 142.8, 147.7, 153.3, 170.1, 195.5; Anal. Calcd for $C_{24}H_{19}N_3O_6$: C 64.72; H 4.30; N 9.43%. Found: C 64.70; H 4.32; N 9.41%.

ethyl 10a-methyl-7-(4-nitrophenyl)-6,9-dioxo-8,9-dihydro-6H,7H-chromeno[3',4':5,6]pyrano[3,2-d]oxazole-7a(10aH)-carboxylate 5d

Yield: 448 mg, 96%; white solid; Mp: 210-212 ^{o}C IR (KBr): 3317, 1790, 1750, 1646, 1530, 1412, 1379, 1350, 1314, 961, 719 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.21 (t, *J*=7.1 Hz, 3H), 1.70 (s, 3H), 4.21-4.33 (m, 2H), 5.09 (s, 1H), 7.31-7.39 (m, 4H), 7.63 (t, *J*=7.2 Hz, 1H), 7.79 (d, *J*=7.2 Hz, 1H), 8.05 (d, *J*=8.7 Hz, 2H), 8.17 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 14.2, 19.8, 64.2, 70.1, 101.1, 105.3, 114.5, 116.8, 123.1, 124.2, 125.0, 130.4, 133.3, 144.8, 147.4, 152.7, 156.5, 157.0, 160.1, 169.3; HRMS (ESI-TOF) m/z Calcd for $[C_{23}H_{18}N_2O_9+H]^+$: 467.1085, found: 467.1077.

3a-(4-nitrophenyl)-2,8-dioxo-9-phenyl-1,2,5,7,8,9-hexahydro-6H-chromeno[3,2-d]oxazole-9a(3aH)-carbonitrile 5e

Yield: 216 mg, 50%; pale yellow solid; Mp: 152-154 ^{o}C; IR (KBr): 3400, 2925, 2852, 1810, 1644, 1527, 1384, 1354, 1089, 994, 854 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me4Si): δ 2.12 (d, *J*=15 Hz, 2H), 2.52 (s, 2H), 2.77 (s, 2H), 3.63 (bs, 1H), 4.68 (s, 1H), 7.18-7.29 (m, 5H), 7.50 (d, *J*=7.8 Hz, 2H), 8.08 (d, *J*=7.5 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.1, 28.5, 36.4, 42.7, 67.8, 105.3, 114.9, 116.1, 123.7, 128.0, 129.1, 129.4, 129.5, 132.5, 140.3, 149.1, 153.1, 171.5, 197.0; Anal. Calcd for $C_{23}H_{17}N_3O_6$: C 64.04; H 3.97; N 9.74%. Found: C 64.06; H 3.99; N 9.76%.

General procedure for the synthesis of pyrroles (6a-e)

1 mmol of 2-oxa-7-azabicyclo[4.1.0]hept-3-en-1-yl carboxylates was taken in 3 mL of alcohol and then to it 10 mol% of PTSA (.019 g) was added and the reaction mixture was heated at 80 ^{o}C for the stipulated time. After completion of the reaction (monitored by TLC), alcohol was removed and the mixture was immediately subjected for column chromatographic separation (50-70% ethyl acetate in petroleum ether) to get the pure products. All the synthesized

compounds were characterized through spectral (^{1}H NMR, ^{13}C NMR, IR, HRMS and elemental analysis) data, and X-ray crystallographic analysis (6a).

methyl (3R)-2-cyano-4-oxo-3-phenyl-2,3,4,5,6,7-hexahydro-1H-indole-2-carboxylate 6a

Yield: 267 mg, 90%; white solid; Mp: 180-182 ^{o}C; IR (KBr): 3433, 3197, 2950, 2861, 1770, 1740, 1579, 1495, 1231, 1181, 700 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): δ 2.02 (t, *J*=6 Hz, 2H), 2.30 (d, *J*=5.4 Hz, 4H), 3.89 (d, *J*=1.5 Hz, 3H), 4.71 (s, 1H), 6.52 (s, 1H), 7.23-7.42 (m, 5H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 21.9, 23.1, 36.1, 54.4, 54.9, 68.1, 111.1, 114.4, 127.9, 128.2, 128.5, 136.6, 167.0, 167.5, 192.2; HRMS (ESI-TOF) m/z Calcd for $[C_{17}H_{16}N_2O_3+H]^+$: 297.1234, found: 297.1232.

methyl (3R)-2-cyano-3-(4-nitrophenyl)-4-oxo-2,3,4,5,6,7-hexahydro-1H-indole-2-carboxylate 6b

Yield: 300 mg, 88%; pale yellow solid; Mp: 200-202 ^{o}C; IR (KBr): 3132, 2957, 2854, 1758, 1597, 1516, 1473, 1349, 1231, 703 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me_4Si): δ 1.85-1.91 (m, 2H), 2.03 (s, 2H), 2.36-2.53 (m, 2H), 3.76 (s, 3H), 4.76 (s, 1H), 7.37 (d, *J*=7.8 Hz, 2H), 8.09 (d, *J*=7.5 Hz, 2H), 8.64 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 22.4, 23.4, 36.6, 54.6, 55.1, 68.3, 109.0, 123.9, 130.4, 146.2, 190.6; Anal. Calcd for $C_{17}H_{15}N_3O_5$: C 59.82; H 4.43; N 12.31%. Found: C 59.84; H 4.44; N 12.28%.

methyl (3R)-2-cyano-4-oxo-3-(thiophen-2-yl)-2,3,4,5,6,7-hexahydro-1H-indole-2-carboxylate 6c

Yield: 263 mg, 87%; off-white solid; Mp: 160-162 ^{o}C; IR (KBr): 3125, 2949, 2861, 2767, 1766, 1582, 1496, 1182, 1140, 1140, 701 cm^{-1}; ^{1}H NMR (300 MHz; DMSO d_6; Me4Si): δ 6.53 (t, *J*=6.53 Hz, 2H), 2.10 (t, *J*=6.3 Hz, 2H), 2.38-2.56 (m, 2H), 3.82 (s, 3H), 4.89 (s, 1H), 6.95 (d, *J*=3.6 Hz, 2H), 7.38 (t, *J*=3.3 Hz, 1H), 8.66 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ

21.9, 22.9, 36.2, 49.8, 54.5, 68.5, 109.7, 114.9, 125.8, 126.5, 127.0, 141.9, 166.5, 167.6, 189.9; HRMS (ESI-TOF) m/z Calcd for $[C_{15}H_{14}N_2O_3S+H]^+$: 303.0798, found: 303.0790.

methyl (3S)-3-(2-chlorophenyl)-2-cyano-4-oxo-2,3,4,5,6,7-hexahydro-1H-indole-2-carboxylate 6d

Yield: 298 mg, 90%; off-white solid; Mp: 170-172 ^oC; IR (KBr): 3123, 2951, 2857, 1754, 1602, 1585, 1476, 1447, 1277, 1243, 1189, 1120, 923, 742, 673 cm^{-1}; ^1H NMR (300 MHz; DMSO d_6; Me4Si): δ 1.98-2.10 (m, 2H), 2.18 (d, *J*=4.2 Hz, 2H), 2.49 (s, 1H), 2.59 (s, 1H), 3.88 (s, 1H), 5.04 (s, 1H), 7.13-7.16 (m, 1H), 7.31-7.34 (m, 2H), 7.503 (t, *J*=4.4 Hz, 1H), 8.76 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 22.4, 23.5, 36.6, 51.9, 55.0, 68.2, 108.7, 115.3, 127.9, 129.8, 130.2, 130.3, 133.9, 135.5, 167.2, 168.9, 190.7; Anal. Calcd for $C_{17}H_{15}ClN_2O_3$: C 61.73; H 4.57; N 8.47%. Found: C 61.71; H 4.55; N 8.50%.

ethyl (3R)-2-cyano-3-(4-nitrophenyl)-4-oxo-2,3,4,5,6,7-hexahydro-1H-indole-2-carboxylate 6e

Yield: 263 mg, 74%; off-white solid; Mp: 128-130 ^oC; IR (KBr): 3213, 2946, 2862, 1759, 1607, 1579, 1521, 1493, 1349, 1238, 1111, 962, 700 cm^{-1}; ^1H NMR (300 MHz; DMSO d_6; Me4Si): δ 1.31 (d, *J*=6.6 Hz, 3H), 1.98 (d, *J*=5.1 Hz, 2H), 2.16 (s, 2H), 2.50 (s, 2H), 4.36 (s, 2H), 4.83 (s, 1H), 7.51 (s, 2H), 8.22 (d, *J*=6.3 Hz, 2H), 8.78 (s, 1H); ^{13}C NMR (75 MHz; DMSO d_6; Me_4Si): δ 14.2, 22.3, 23.4, 36.5, 54.7, 63.5, 64.3, 68.4, 108.9, 123.9, 130.3, 146.1, 147.6, 166.2, 169.0, 190.6; HRMS (ESI-TOF) m/z Calcd for $[C_{18}H_{17}N_3O_5+H]^+$: 356.1241, found: 356.1247.

SUPPORTING INFORMATION

Supporting Information Available: Materials and method, ORTEP diagrams of compounds 4g, 5c and 6a, X-ray crystallography data of compounds 4g, 5c and 6a and ^{1}H and ^{13}C NMR spectra of all compounds (file type pdf) and X-ray data of compound 4g, 5c and 6a (file type cif) This material is available free of charge via the Internet at http://pubs.acs.org.

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