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Enal-azomethine ylides: application in the synthesis of functionalized pyrroles†‡
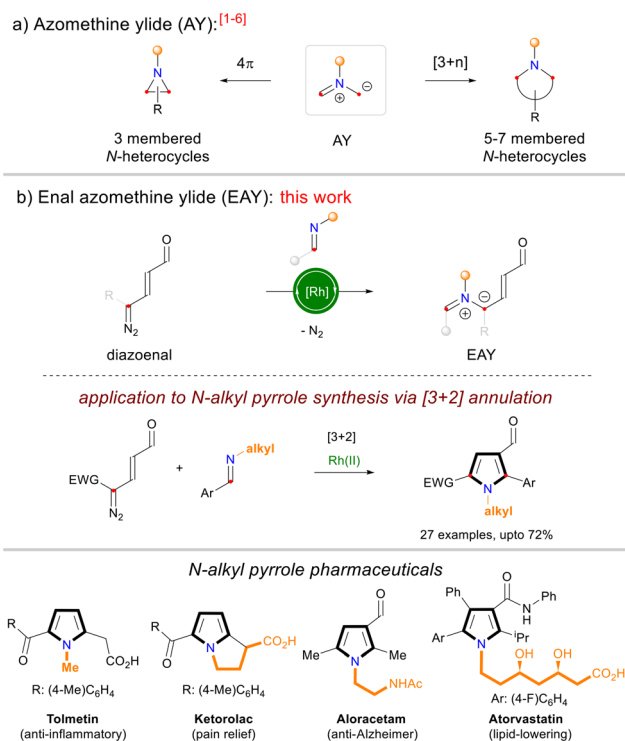
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Rhodium-catalyzed [3 + 2] annulation of diazoenals and *N*-alkyl imines resulted in *N*-alkyl-pyrrole-3-carbaldehyde derivatives. The reaction involves thermal 6π-electrocyclization and aromatization of a new class of enal-azomethine ylides (EAYs). The EAYs derived from dihydroisoquinoline and 2*H*-azirine gave fused-pyrrole and pyridine derivatives, respectively. The synthetic importance of pyrrole products has been demonstrated by one-step synthesis of the biologically relevant pyrrolo[3,2-*c*]quinoline scaffold as well as pyrrolo[2,1-*a*]isoquinoline which is a core structure of lamellarin alkaloids.

The azomethine ylide (AY), originally introduced by Huisgen, is a fundamentally important 1,3-dipole that finds broad applications in the construction of N-heterocycles (Scheme 1a).[1–6] AYs have been used as three-atom 4π-synthons in electrocyclizations and [3 + n] cycloadditions leading to the construction of valuable 3-membered and 5–7-membered monocyclic, fused, and bridged nitrogen heterocycles.[1–6] Inspired by the synthetic potential of azomethine ylides, herein we report the design of a conceptually new class of enal-functionalized azomethine ylides (Scheme 1b). The synthetic utility of enal-azomethine ylides (EAYs) has been demonstrated in the Rh-catalyzed [3 + 2] annulation of diazoenals and *N*-alkyl aldimines resulting in one-step synthesis of tetrasubstituted *N*-alkyl-3-formylpyrroles.[7,8] The *N*-alkyl pyrroles are core structures of many natural products and pharmaceuticals.[9]

Recently, we have introduced a new class of bench-stable enal-functionalized diazo compounds (diazoenals) which serve as precursors to the highly electrophilic Rh-enalcarbenoids.[10a] Our studies showed that Rh-enalcarbenoids react with a variety of carbon and heteroatom nucleophiles resulting in valuable functionalized enals which are used in the subsequent cycliza-

tion reactions to access diverse carbo/heterocycles.[10b–h] Continuing our studies, we have investigated the reactivity of Rh-enalcarbenoids with *N*-alkyl imines. Preliminary experiments showed that the reaction of diazoenal **1a** with imine **2a** in the presence of 3 mol% Rh₂(OAc)₄ in toluene solvent at 40 °C gives an unstable enal-azomethine ylide (EAY).[11] Gratifyingly, at an elevated temperature (110 °C), the reaction gave *N*-allyl-3-formylpyrrole **3a** in 57% yield (Table 1, entry 1) *via* an overall [3 + 2]-annulation involving 6π-electrocyclization of the EAY and the subsequent *in situ* oxidation. It is worth mentioning that this is the first report on enal-functionalized
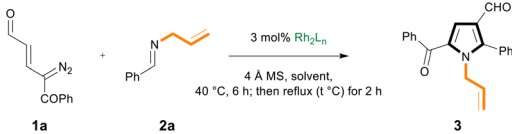

Scheme 1 Construction of N-heterocycles by azomethine ylide cyclizations.

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† Dedicated to Professor Sukh Dev on the occasion of his 100th birthday.
‡ Electronic supplementary information (ESI) available. CCDC 2213403. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4ob00859f

Table 1 Optimization of the [3 + 2] annulation[a]

Entry	Rh$_2$L$_n$	Solvent	t (°C)	Yield[b] (%)
1	Rh$_2$(OAc)$_4$	Toluene	110	57
2	**Rh$_2$(oct)$_4$**	**Toluene**	**110**	**72**
3	Rh$_2$(esp)$_2$	Toluene	110	54
4	Rh$_2$(S-DOSP)$_4$	Toluene	110	<10
5	Rh$_2$(TFA)$_4$	Toluene	110	12
6	Rh$_2$(oct)$_4$	Trifluorotoluene	102	59
7	Rh$_2$(oct)$_4$	Xylene	138	53
8	Rh$_2$(oct)$_4$	Benzene	80	34
9	Rh$_2$(OAc)$_4$	Dichloromethane	40	0
10	Rh$_2$(OAc)$_4$	Dichloroethane	84	<5

[a] **1a**/**2a** = 0.2 : 0.13 mmol. [b] Yield was calculated after excluding the recovered benzaldehyde.
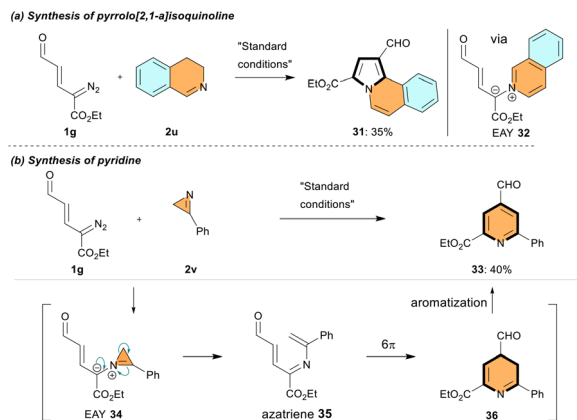
Table 2 Substrate scope of the [3 + 2] annulation[a,b]

[a] Reaction was performed using the optimized conditions in Table 1. [b] Isolated yield. [c] Yield was calculated after excluding the recovered aldehyde. [d] Reaction time.

azomethine ylides and their application in densely functionalized N-alkyl pyrrole synthesis.

Inspired by the preliminary studies, we further optimized the [3 + 2] annulation. Although, other Rh(II)-catalysts such as Rh$_2$(oct)$_4$, Rh$_2$(esp)$_2$, Rh$_2$(TFA)$_4$, and Rh$_2$(S-DOSP)$_4$ are also effective, Rh$_2$(oct)$_4$, gave the highest yield of 72% (entries 2–5). Rapid decomposition of diazoenal was observed with the highly electrophilic Rh$_2$(TFA)$_4$ leading to a low yield of pyrrole (entry 5). At elevated temperatures, the imine was slowly dissociated to the aldehyde and amine, leading to a reduced yield of pyrrole (entry 7). On the other hand, the yield was diminished upon reducing the temperature due to sluggish reactivity (entries 6 and 8). The reaction was compatible with aromatic solvents whereas non-aromatic solvents are not suitable (entries 9 and 10).

With the optimized conditions (Table 1, entry 2), the scope of the [3 + 2] annulation was studied by varying the imines and diazoenals (Table 2). The reaction was compatible with diverse N-alkyl imines resulting in the corresponding N-substituted pyrroles **4**–**9** in 49–68% yields. The sterically hindered N-^{t}Bu and N-cyclohexyl imines were also tolerated in the reaction (**6**, **7**). Notably, N-Boc-protected 1,2-ethylenediamine derived aldimine successfully delivered pyrrole **9**, an analogue of the drug aloracetam in 49% yield, despite the competing NH-insertion reaction of the side chain. N-Benzyl imine gave pyrrole **10** in 65% yield. Gratifyingly, N-propargyl imine furnished the desired pyrrole **11** in 68% yield despite potential cyclopropanation. Interestingly, N-aryl aldimines gave poor yields of annulation products **12**–**14** (11–36%) presumably due to the sluggish reactivity and competing NH-insertion of the dissociated arylamines at elevated temperatures. Subsequently, aldimines derived from electronically and sterically distinct aryl aldehydes were investigated. The reaction tolerated alkyl, trifluoroalkyl, and halo substituents on the aryl-ring and delivered the C-aryl pyrroles **15**–**25** in 53–69% yields. Aldimines

with electron-rich and electron-deficient aryl groups also smoothly participated in the reaction and gave good yields of pyrroles **26**–**28**. The reaction was not hampered by sterically hindered aryl groups (**23**–**24**, **26** and **28**). Aldimines derived from naphthaldehyde and pyrenecarboxaldehyde gave π-extended pyrrole products **29** and **30**, respectively, in decent yields. With respect to the diazoenals, both keto and ester diazoenals reacted smoothly to give the desired pyrrole products in good yields (*e.g.* **4**–**7**, **10**, **17**–**22**).

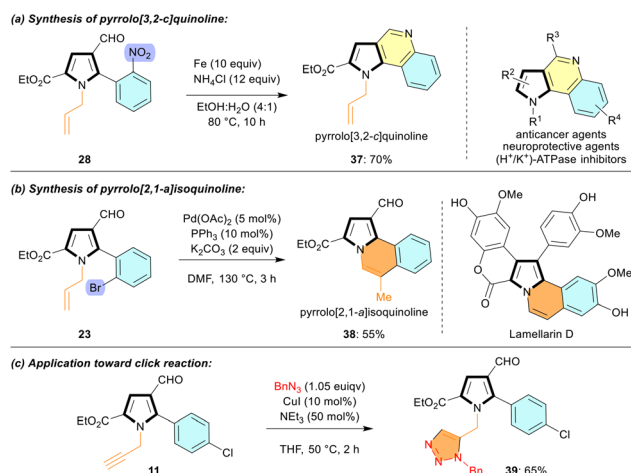Next, the synthetic utility of enal-azomethine ylides derived from the cyclic imines was investigated (Scheme 2a and b). A Rh-catalyzed reaction of 3,4-dihydroisoquinoline **2u** and diazoenal **1g** under standard conditions gave pyrroloisoquinoline **31** in 35% yield *via* EAY **32** (Scheme 2a). However, 3-phenyl-2*H*-
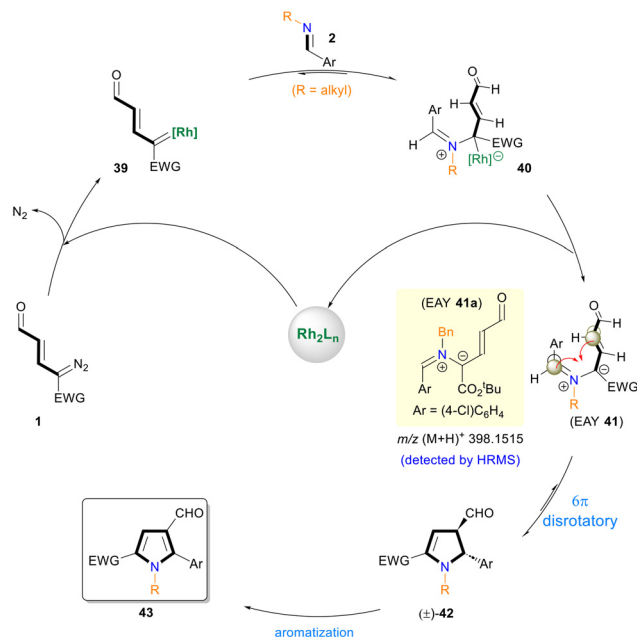
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Org. Biomol. Chem., 2024, **22**, 5734–5738 | **5735**

Scheme 2 Reaction with cyclic imines.

Scheme 4 Plausible mechanism of [3 + 2]-annulation.

azirine **2v** under the same reaction conditions produced 4-formyl pyridine **33** in 40% yield *via* an overall [3 + 3] annulation. The reaction is proposed to involve strain-induced ring opening of azirine derived EAY **34**, 6π-electrocyclization of the resulting azatriene **35** and the subsequent aromatization of dihydropyridine **36** (Scheme 2b).[12]

The tetrasubstituted *N*-allyl-3-formyl-pyrroles obtained from [3 + 2] annulation are valuable substrates for structural diversification (Scheme 3a and b). The ethyl 1-allyl-4-formyl-5-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate **28** was converted to pyrrolo[3,2-*c*]quinoline **37** in 70% yield *via* reductive cyclization (Scheme 3a).[13] The pyrrolo[3,2-*c*]quinoline derivatives are known to possess diverse biological properties, including anticancer and anti-Alzheimer activities.[14] Next, an intramolecular Heck reaction of ethyl 1-allyl-5-(2-bromophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate **23** gave pyrrolo[2,1-*a*]isoquinoline **38** in good yield (55%). Compound **38** has the core structure of the lamellarin D alkaloid (Scheme 3b).[15] The *N*-propargyl pyrrole **11** smoothly participated in the click reaction with benzyl

azide to give triazole-tethered pyrrole **39** in 65% yield (Scheme 3c).

A plausible mechanism for the [3 + 2] annulation reaction is proposed in Scheme 4. The transient Rh-enalcarbenoid **39** generated from diazoenal **1** reacts with *N*-alkyl aldimine **2** to give metal-bound EAY **40**. The release of the Rh-catalyst leads to metal-free EAY **41**. The formation of *N*-benzyl imine derived EAY **41a** was detected using the HRMS data. The subsequent 6π-electrocyclization and spontaneous dehydrogenative aromatization[7i,16] of dihydropyrrole (±)-**42** furnish the *N*-alkyl-pyrrole-3-carbaldehyde **43**.[17]

Scheme 3 Synthetic applications.

Conclusions

In conclusion, we have reported a new class of enal-functionalized azomethine ylides (EAYs). The synthetic utility of EAYs has been demonstrated by the Rh-catalyzed [3 + 2] annulation of *N*-alkyl imines and diazoenals resulting in the tetrasubstituted *N*-alkyl pyrrole-3-carbaldehyde derivatives. The EAYs derived from cyclic imines dihydroisoquinoline and 2*H*-azirine gave valuable fused pyrrole and pyridine derivatives. The synthetic utility of *N*-alkyl pyrrole products was demonstrated by the short synthesis of pyrrolo[3,2-*c*]quinoline and pyrrolo[2,1-*a*]isoquinoline scaffolds which are core structures of many biologically important compounds and natural products.

Data availability

The data supporting this article have been included as part of the ESI.‡

5736 | *Org. Biomol. Chem.*, 2024, **22**, 5734–5738

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Crystallographic data for compound **19** have been deposited at the CCDC under accession number 2213403.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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5738 | *Org. Biomol. Chem.*, 2024, **22**, 5734–5738

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