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COMMUNICATION

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Spirocyclic Amide Acetal Synthesis by [CpRu]-Catalyzed Condensations of α-Diazo-β-Ketoesters with γ-Lactams

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Dedicated to Prof. *Peter Kündig* on the occasion of his 75th birthday

The synthesis of spirocyclic amide acetals (33–93%) has been achieved through Ru(II)-catalyzed condensations of *N*-carbamate protected pyrrolidinones with metal carbenes derived from α-diazo-β-ketoesters. Thanks to the mildness of the diazo decomposition conditions induced by a 1:1 combination of [CpRu(MeCN)$_3$][BAr$_F$] and 1,10-phenanthroline, the formation of the sensitive products is possible. Full characterization of this carbonyl-ylide mediated process is provided by DFT calculations.

Keywords: amide acetals, carbonyl ylides, [CpRu] catalysis, diazo decomposition, spiro compounds, ylides.

Introduction

Decomposition of diazo derivatives in the presence of *Lewis* bases is a recognized strategy to generate ylides efficiently.[1–9] With aldehydes and ketones, but also esters and amides, carbonyl ylides are formed, usually under light irradiation or metal-catalyzed conditions (*Scheme 1*, *A*).[8,10–25] These reactive intermediates condense to form epoxides (*A*, *path a*), act as 1,3-dipoles in intra- and intermolecular cycloadditions (*A*, *path b*) or form enol ethers (*A*, *path c*).[26–30] Using α-diazo-β-ketoesters as reagents, carbonyl ylides evolve toward the formation of dioxolene adducts instead that are formed by intramolecular condensation (*A*, *path d*).[31–38] While such a process occurs quite readily with aldehydes and ketones, but also with esters (lactones) and cyclic carbonates,[32] examples of dioxolene formation with amide functional groups are rare. In fact, the only reported examples of corresponding amide acetals have been reported by *Heimgartner*, *Nikolaev* and collaborators using succinimide derivatives as substrates (*Scheme 1*, *B*).[39–41] Herein, in a new development, reactions of *N*-protected γ-lactams **1** with α-diazo-β-ketoesters **2** are reported (*Scheme 1*, *C*). Thanks to the combined use of [CpRu(CH$_3$CN)$_3$][BAr$_F$] (Cp = C$_5$H$_5$, BAr$_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) and 1,10-phenanthroline **phen** as diazo decomposition catalyst,[42] spiro amide acetals **3** are afforded (33–93%). The reaction is compatible with traditional carbamate protecting groups and a variety of α-diazo-β-ketoester reagents were used successfully.

Results and Discussion

Previously, under copper-catalysis exclusively, our group has shown that *N*-aryl γ-lactams react intermolecularly with acceptor-acceptor diazo reagents, usually dicarbonyl compounds, to yield functionalized pyrrolidines carrying α-*pseudo* quaternary centers.[43] Wondering whether this reactivity could be extended

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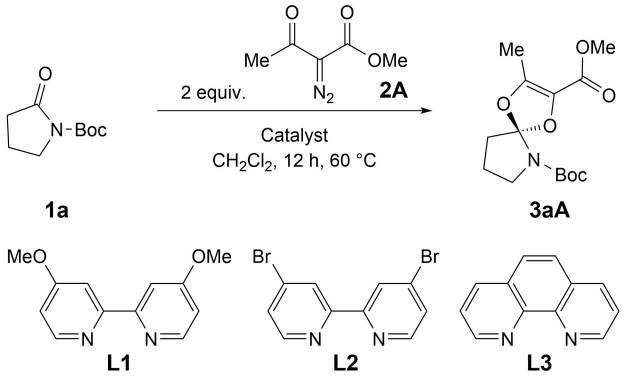
to other classes of pyrrolidinone derivatives, care was taken to study the reactivity of γ-lactams **1** substituted on the nitrogen atom by classical carbamate protecting groups, and with α-diazo-β-ketoester reagents **2** in particular.[44]

To set up reaction conditions, easily available Boc pyrrolidinone **1a** was selected as model substrate. Initial experiments were performed by mixing **1a** (1.0 equiv.), methyl 2-diazo-3-oxobutanoate (**2A**; 2.0 equiv.), and CuI or CuTC (10 mol-%) in CH_2Cl_2 (0.5 M); the reaction medium being heated at 100 °C during 12 h to ensure effective diazo decomposition (*Table 1*, *entries 1* and *2*). ^{1}H-NMR spectroscopic analysis of the crude mixtures revealed full conversion of pyrrolidinone carbonate **1a** and the presence spiro amide acetal **3aA** as a product in both CuI and CuTC mediated reactions, in 31 % and 58 % NMR yields respectively.[1]

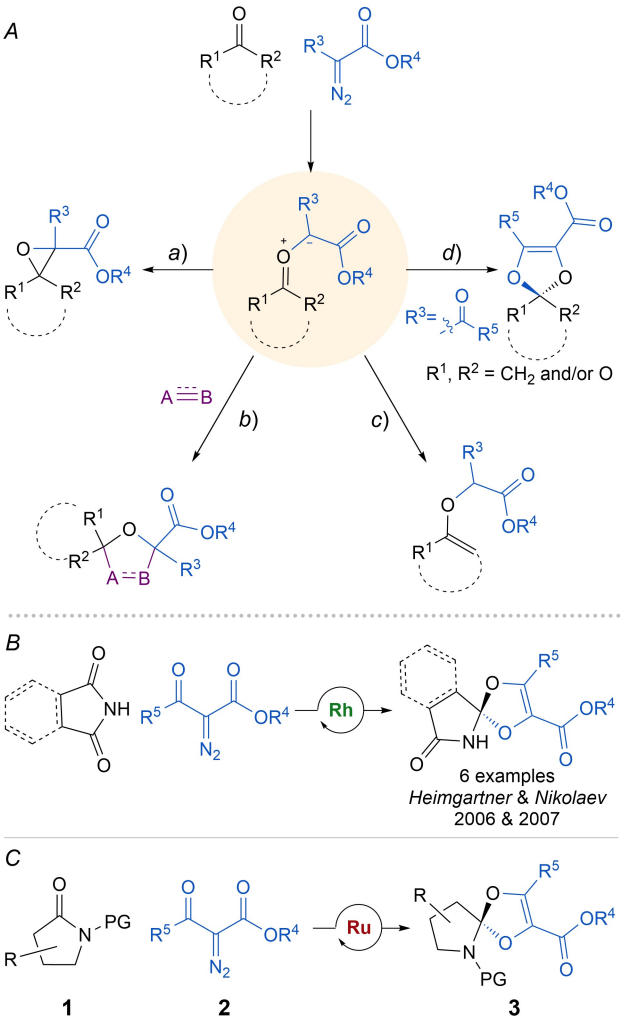
Table 1. Optimization of the spiro amide acetal formation.



Entry	Catalyst (*x* mol-%)	Yield[a] [%] **3aA**
1	CuI (10)[b]	(31)
2	CuTC (10)[b][c]	(58)
3	$Rh_2(OAc)_4$ (1.0)	(37)
4	$[CpRu(MeCN)_3][PF_6]$ (2.5)	(80)
5	$[CpRu(MeCN)_3][BAr_F]$ (2.5)	(90)
6	$[CpRu(MeCN)_3][BAr_F]$/**L1** (2.5)	(92)
7	$[CpRu(MeCN)_3][BAr_F]$/**L2** (2.5)	(93)
8	$[CpRu(MeCN)_3][BAr_F]$/**L3** (2.5)	84[d] (95)
9	–	0

[a] NMR yields in parenthesis calculated by integration of ^{1}H-NMR signals of product **3aA** relative to trimethoxybenzene used as an internal standard in the crude reaction mixtures. [b] Reaction carried out at 100 °C. [c] TC = thiophene-2-carboxylate. [d] Yield of isolated product.

With this result in hand, optimization studies were conducted further. First, the nature of the metal catalyst was investigated,[2] switching from copper to dirhodium and cyclopentadienyl ruthenium complexes (*entries 3* and *4*) while decreasing the temperature to 60 °C with these more reactive decomposition catalysts. Using $Rh_2(OAc)_4$ (1 mol-%),[45] a yield of 37 % was obtained, while decomposition with $[CpRu(MeCN)]_3PF_6$ (2.5 mol-%)[46,47] led to a drastic improvement and a corresponding yield of 80 %. Selecting the [CpRu]



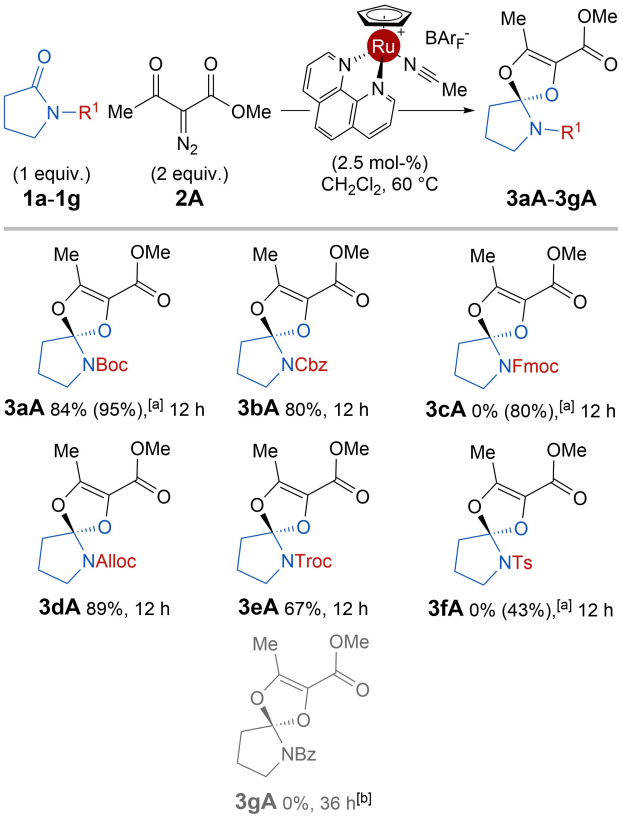
Scheme 1. *A*: Carbene-mediated synthesis and reactivity of carbonyl-ylide intermediates. *B*: Previous studies with succinimides as substrates (*Heimgartner*, *Nikolaev et al.*). *C*, **this work**: One-step synthesis of spirocyclic amide acetals derived from *N*-protected γ-lactams.

[1] For Boc derivative **3aA**, due to well-defined spectra at 20 °C, ^{1}H- and ^{13}C-NMR spectroscopic analyses could be performed under standard conditions.

[2] Experimental and theoretical studies in our group indicate that dirhodium carbenes are more electrophilic than CpRu analogues leading often to over-reactivity of the substrates. See references [26] and [45] for reactivity insights through DFT calculations.

complex for further experiments, the influence of the negative counterion was investigated, switching from PF_6^- to the large, lipophilic and less coordinating BAr_F^- anion.[42] To our satisfaction, the NMR yield improved to 90% (*entry 5*) validating the use of the bench-stable [BAr_F] complex over its [PF_6] analogue. To further enhance the efficiency of the reaction, several bipyridine-type ligands were screened (*entries 6* to *8*), in 1:1 combinations with the [CpRu$(MeCN)_3$][BAr_F] complex. The electron rich (*entry 6*, **L1**) and moderately electron poor (*entry 7*, **L2**) bipyridine ligands gave similar yields (92 and 93%, resp.), whereas 1,10-phenanthroline (*entry 8*, **L3**) improved the NMR yield further to 95% and afforded the cleanest crude of all. In fact, under conditions of *entry 8*, synthesis of **3aA** could be performed on preparative scale (84% isolated yield); the purification being rendered facile by the lower amounts of side products coming from the degradation of methyl 2-diazo-3-oxobutanoate (**2A**) in excess. Finally, as it could be expected, the reaction did not occur in the absence of catalyst (*entry 9*).

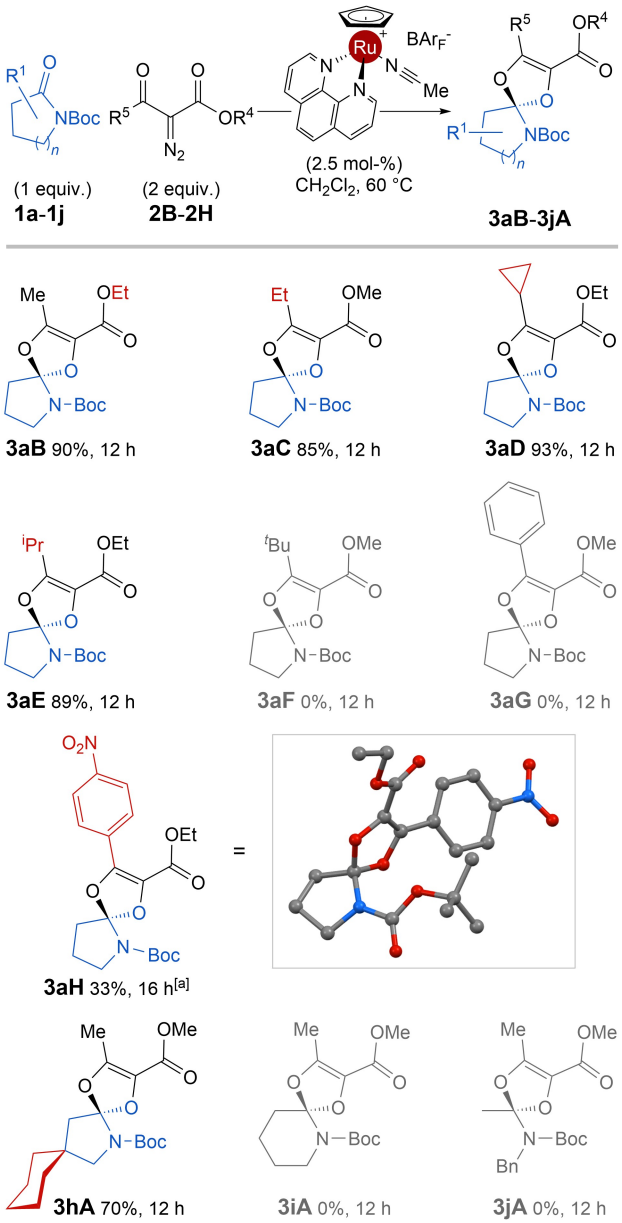
With the optimal conditions in hand, the present transformation was extended using a variety of *N*-protected lactams and α-diazo-β-ketoesters. Different carbonate protecting groups were first examined (products **3bA** to **3eA**) using **2A** as diazo reagent (*Scheme 2*). Switching from the lactam protected with Boc **3aA** to Cbz **3bA** or Fmoc **3cA** led to slight decrease of either isolated or NMR yields. In the particular case of Fmoc **3cA**, while the product could be clearly identified in the crude ^{1}H-NMR spectrum as well as in mass spectrometry, its separation from the diazo decomposition side product could never be achieved. The pyrrolidinones protected with Alloc **1d** and Troc **1e** were also tested. Satisfactorily, Alloc **1d** was fully compatible with the reaction leading to the formation of **3dA** in high isolated yield (89%), due the complete absence of cyclopropanation of the allyl functional group. The Troc protective group was also suitable and led to the formation of the amide acetal **3eA** with a yield of 67%. Of note, Troc **3eA** could be stored without any precaution for several weeks. As such, it is quite more stable than Boc **3aA**, and even more than Cbz **3bA** and Alloc **3dA** derivatives that are readily prone to hydrolysis. This stability increase of **3eA** might be due to the electron-poor nature of the Troc protecting group that stabilizes the electron-rich amide acetal structure. For this project, the Troc group seems to constitute a good balance between reactivity and stability. Then, other classical lactam protecting groups were considered, sulfonamide and ester. Reactions were thus performed with substrates **1f** (R^1 = Ts) and **1g** (R^1 = Bz). Only the tosylpyrrolidinone led to the formation of the corresponding spirocycle **3fA** (43% NMR yield). Unfortunately, product **3fA** is quite unstable and degrades within an hour after purification (chromatography over a short plug of silica gel) to form starting γ-lactam **1f**. As a consequence, product **3fA** was characterized by high resolution mass spectrometry and ^{1}H-NMR spectroscopy only.[3] Finally, benzoyl ester **1g** was evaluated and, in this case and somewhat surprisingly, conversion of the starting pyrrolidinone could not be observed.



Scheme 2. [CpRu]-catalyzed synthesis of spirocyclic amide acetals. [a] NMR yield. [b] Reactions carried out at 60 °C and 90 °C without success.

Next, using Boc pyrrolidinone **1a** as substrate, diazo reagents **2B** to **2H** were investigated (*Scheme 3*). For the formation of **3aB** and **3aC**, little or no change were observed upon modifications of methyl to ethyl

[3] The instability of sulfonylated amide acetal **3fA** might be due to the hybridization of the nitrogen atom that is closer to sp^3 than sp^2; the nitrogen lone pair might then be available and help the spirocycle hydrolysis.



Scheme 3. [CpRu]-catalyzed synthesis of spirocyclic amide acetals. [a] Reaction carried out at 90 °C.

groups (90 and 85% yields, resp.). Satisfactorily, more elaborated cyclopropyl or sterically-demanding isopropyl side chains were found to be compatible when introduced α to the diazo carbonyl group. Such substituents do not perturb the reaction as compounds **3aD** and **3aE** were formed in excellent isolated yields (93% and 89%, resp.). However, as already emphasized, some of derivatives **3** are unstable and hydrolyze rapidly upon standing. It was particularly true for ^{i}Pr derivative **3aE**, which had to be stored under strict anhydrous conditions at −20 °C. When steric hindrance was increased further (reagent **2F**, ^{t}Bu) or upon introduction of a phenyl substituent α-to the carbonyl group (reagent **2G**), reactivity was strongly impacted and none of the desired products were obtained; only unproductive decompositions of the diazo derivatives were noticed. Interestingly, in relation to the latter experiment, reaction of diazo **2H** bearing an electron-poor *p*-nitrobenzene substituent led to the formation of the corresponding amide acetal **3aH** albeit under more strenuous conditions (reaction temperature 90 °C). Moreover, **3aH** furnished crystals suitable for X-ray diffraction analysis, confirming the spirocyclic nature of the product (*Scheme 3*). With this structure in hand, a comparison was attempted with previously-obtained clichés from oxolene acetals derived from lactones and cyclic carbonates;[32] this survey did not reveal any particular structural features for the amide acetal.

Structural variations were also considered for the lactam moiety, *i.e.*, with substrates **1h** to **1j** (*Scheme 3*). First, using the spirocyclic cyclohexyl-γ-lactam **1h**, the formation of the derived bis(spiro) amide acetal **3hA** was achieved in 70% yield. Interestingly, in comparison with other Boc derivatives, this compound was found to be particularly unaffected by hydrolysis; the reasons for this increased stability remain so far unclear. Two other substrates were tested, namely piperidinone **1i** as well as acyclic amide **1j**. While a full conversion of δ-lactam **1i** could be monitored, the corresponding spiro amide acetal **3iA** could not be observed due to an over-reactivity.[4] In sharp contrast, acyclic amide **1j** was found to be unreactive.

Finally, a larger scale synthesis of spiro amide acetal **3aA** was performed starting from 3.7 mmol of **1a**. In this attempt, care was taken to decrease the loading of the catalyst, from 2.5 to 0.3 mol-%; full conversion being reached after 72 h to afford **3aA** in 62% yield. Further reduction of the catalyst loading to 0.1 mol-% was however detrimental leading to slow reaction kinetics and only 4% of substrate conversion after 24 h.

To rationalize the mechanism, DFT calculations were performed using the reaction of diazo **2A** and lactam **1a** as a model.[5] To save computational time, the *tert*-butyl substituent of **1a** was replaced by a methyl group. The reaction starts with the substitution

[4] MS Monitoring of the reaction reveals polyadditions on the starting material of carbenes derived from diazo **2A**.
[5] Computational details are given in the *Supporting Information*.

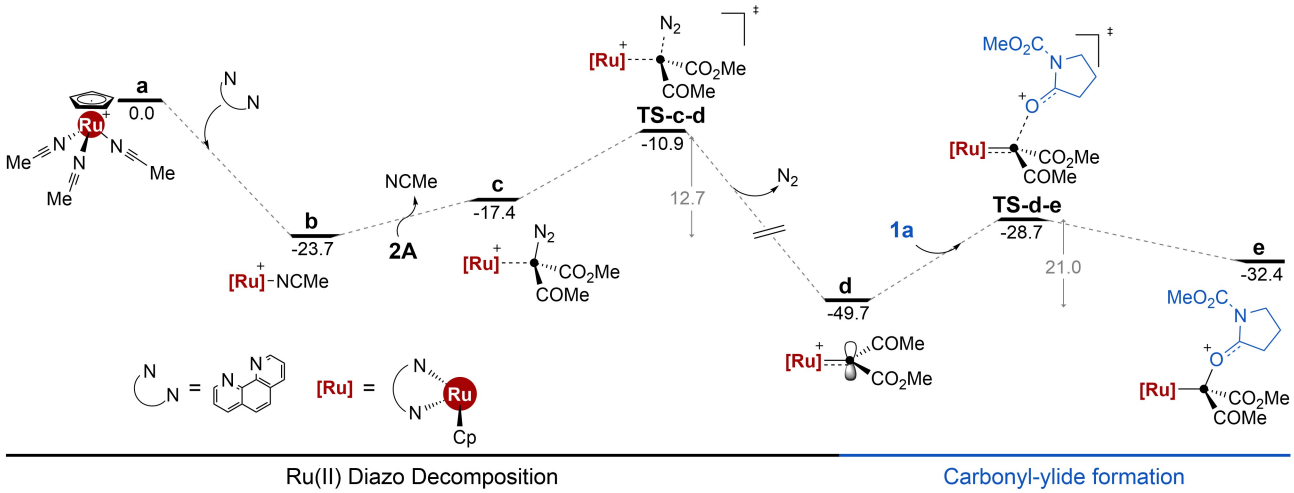


Figure 1. *Gibbs* energy profile for the formation of the metal-ylide **e** from the initial reactants. Energies in kcal·mol^{-1}.

of two coordinated acetonitrile molecules by a bidentate phenanthroline ligand yielding intermediate **b**; the chelation stabilizing the system by 23.7 kcal·mol^{-1}; this and following steps are depicted in *Figures 1* and *2*. At this point, reaction proceeds by substitution of the remaining acetonitrile by diazo molecule **2A**. This endergonic step, by 6.3 kcal·mol^{-1}, does not however prevent the following diazo decomposition that occurs *via* transition state **TS-c–d** found with an activation barrier of 12.7 kcal·mol^{-1}. Consequently, a very stable carbene intermediate **d** is formed, lying at −49.7 kcal·mol^{-1} from the initial reactants. This metal-carbene then traps the lactam substrate *via* **TS-d–e**, with an activation barrier of 21.0 kcal·mol^{-1}, yielding the metal-ylide **e**. This rate-determining step is also endergonic by 17.3 kcal·mol^{-1} (*Figure 1*). Fortunately, thanks to the high concentration of **2A** in the medium, the process moves forward, liberates ylide **f** and initiates a new catalytic cycle that will provoke *in fine* the favorable formation of carbene **d** (*Figures 1* and *2*). Free ylide **f** then evolves into final spiro product **g** with a relatively small barrier of 2.9 kcal·mol^{-1} (**TS-f–g**, *Figure 2*).

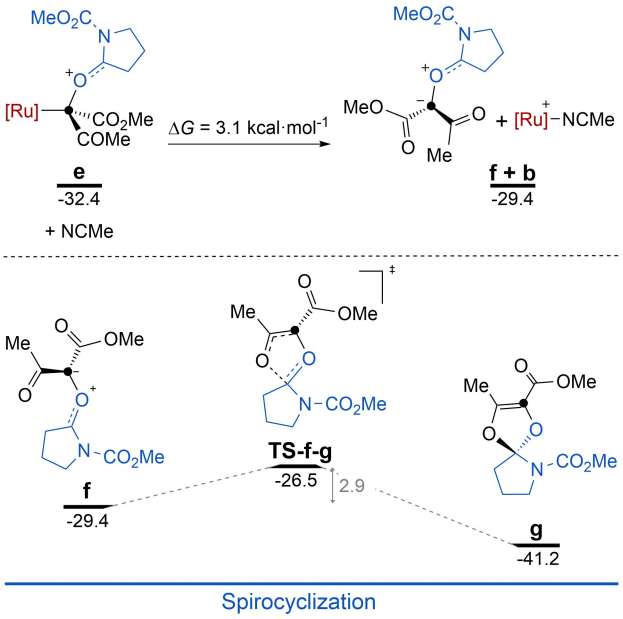


Figure 2. *Gibbs* energy profile for the formation of spirocyclic amide acetal **g** from **f**. Energies in kcal·mol^{-1}.

Conclusion

Herein, an effective formation of spirocyclic amide acetals **3** by [CpRu]-catalyzed decomposition of α-diazo-β-ketoesters in the presence of *N*-carbamate protected γ-lactams is reported. These spirocyclic amide acetals are obtained in yields up to 93%, and their mechanism of formation was elucidated based on DFT calculations. In that regard, the stability of the metal carbene intermediate (**d**, *Figure 1*) and the excess of diazo reagent **2** in the medium are key for the catalytic cycle.

Further studies to harness the reactivity and properties of the products are ongoing in the laboratory. We hope that this access to compounds **3** might draw the attention of other chemical communities since amide acetals can exhibit biological activities as acetylcholine esterase inhibitors[48] or anti-

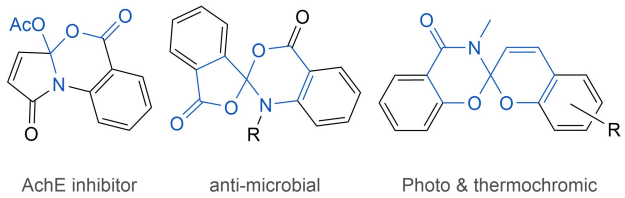


Figure 3. Selection of synthetic amide acetals with biological and physical properties.

microbials (*Figure 3*).[49] Amide acetals have also been prepared for their photo and thermochromic abilities.[50,51]

Experimental Section

Synthetic protocols, experimental conditions, full characterizations of new compounds, computational details are reported in the electronic *Supporting Information*.

Supplementary Material

CCDC-2095270 contains the supplementary crystallographic data for (**3aH**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk. Supporting information for this article is available on the WWW under https://doi.org/10.1002/hlca.202100122. In addition, the dataset for this article can be found at the following DOI: 10.26037/yareta:d32fvfoqfrglbi5e62or73tzeu. It will be preserved for 10 years.

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Author Contribution Statement

R. P. and *E. B.* carried out the experiments and characterizations of all materials. *A. A.* performed the computational study under the supervision of *A. I. P.-B.* X-ray diffraction studies were performed by *L. G. J. L.* devised the project and supervised the work. *R. P.* and *A. A.* co-wrote the draft of the manuscript which was finalized by *R. P.* and *J. L.* All authors commented on the manuscript.

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