



Au(I) as a π -Lewis Base Catalyst: Controlled Synthesis of Sterically Congested Bis(triflyl)enals from α -Allenols

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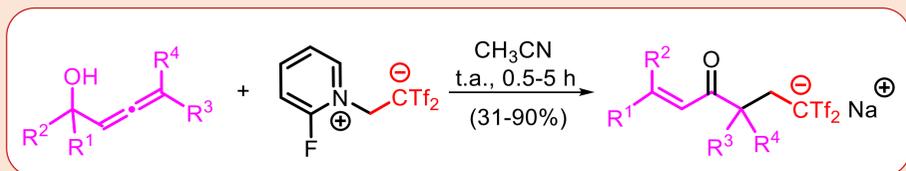
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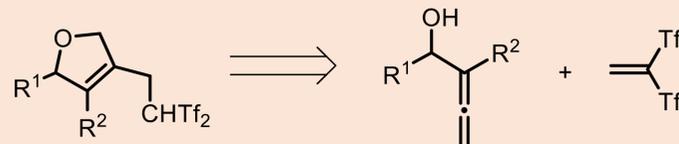
INTRODUCTION

In the last decades, allenes have experienced great growth in the field of organic synthesis due to their interesting reactivity that allows a great variety of possible transformations.

Recently, our research group has described that the reaction of metal-free allenols with the Yanai reagent selectively produces bis(triflyl)enones through the electrophilic attack of $\text{Tf}_2\text{C}=\text{CH}_2$ on the terminal sp^2 -hybridized C4 atom of the allene rest [1].

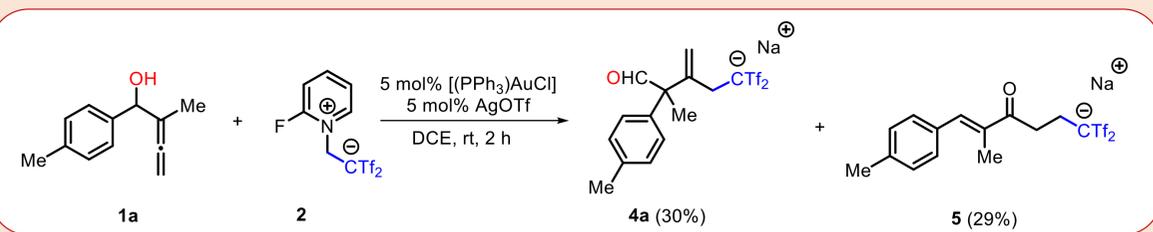


OBJECTIVE



Due to the interest of our working group in the study of allenes and the Yanai reagent, which serves as a source of highly electrophilic $\text{Tf}_2\text{C}=\text{CH}_2$, we propose as the main objective of the work the study of the reactivity of α -allenols against Yanai salt, in the presence of a gold catalyst with the assumption of a cycloetherification [2].

RESULTS

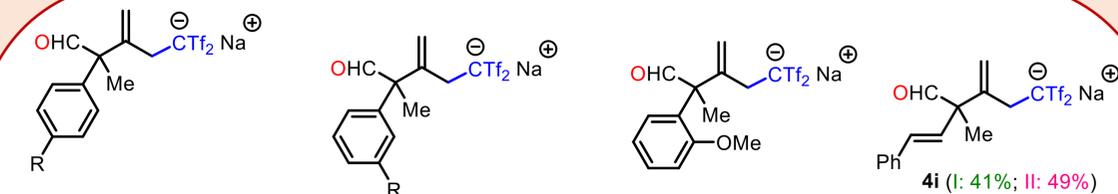


By using $[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$ as a catalyst and carried out the reaction at room temperature, a separable mixture of the aldehyde **4a** together with the ketone **5** was obtained.

Optimization of reaction conditions

Entry 1	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, DCE, rt, 2 h	4a (30%)
Entry 2	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, MS 3 Å, DCE, rt, 2 h	4a (41%)
Entry 3	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, DCE, 130 °C, 30 min	4a (61%)
Entry 4	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, C_6H_{12} , 130 °C, 30 min	4a (6%)
Entry 5	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, HFIP, 130 °C, 30 min	4a (0%)
Entry 6	1a	2 (2.0 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgOTf}$, DCE, 130 °C, 30 min	4a (60%)
Entry 7	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)_3\text{AuCl}]/\text{AgSbF}_6$, DCE, 130 °C, 30 min	4a (55%)
Entry 8	1a	2 (1.1 equiv.)	A/AgOTf, DCE, 130 °C, 30 min	4a (68%)
Entry 9	1a	2 (1.1 equiv.)	A/AgSbF ₆ , DCE, 130 °C, 30 min	4a (74%)
Entry 10	1a	2 (1.1 equiv.)	B/AgOTf, DCE, 130 °C, 30 min	4a (56%)
Entry 11	1a	2 (1.1 equiv.)	B/AgSbF ₆ , DCE, 130 °C, 30 min	4a (62%)
Entry 12	1a	2 (1.1 equiv.)	C/AgOTf, DCE, 130 °C, 30 min	4a (45%)
Entry 13	1a	2 (1.1 equiv.)	C/AgSbF ₆ , DCE, 130 °C, 30 min	4a (40%)

Study of the scope of the methodology

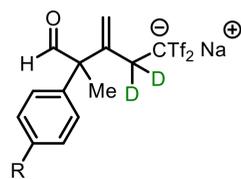


4a R = Me (I: 61%; II: 74%)
4b R = H (I: 57%; II: 64%)
4c R = Cl (I: 54%; II: 61%)
4d R = MeO (I: 74%; II: 85%)
4e R = Br (I: 50%; II: 58%)

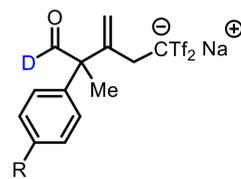
4f R = Me (I: 52%; II: 60%)
4g R = MeO (I: 45%; II: 52%)

4h (I: 32%; II: 41%)

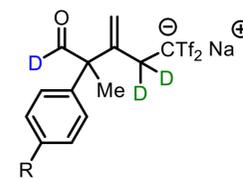
4i (I: 41%; II: 49%)



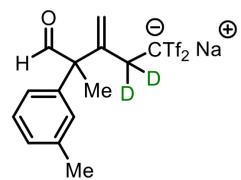
[D₂]-4a R = Me (I: 53%)
[D₂]-4d R = MeO (I: 73%)



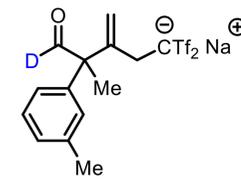
[D₁]-4b R = H (I: 60%)
[D₁]-4d R = MeO (I: 49%)



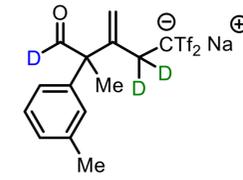
[D₃]-4b R = H (I: 46%)
[D₃]-4d R = MeO (I: 49%)



[D₂]-4f (I: 48%)



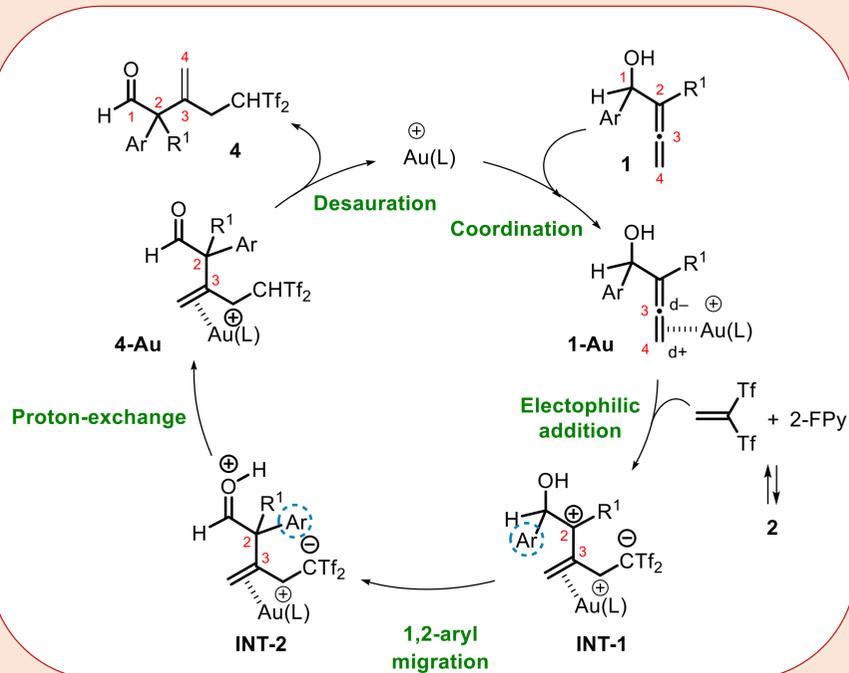
[D₁]-4f (I: 48%)



[D₃]-4f (I: 48%)

Method I: [Au] = $[(\text{PPh}_3)_3\text{AuCl}]$, [Ag] = AgOTf; Method II: [Au] = $[\text{AuClIPr}]$, [Ag] = AgSbF₆

Catalytic Cycle for the formation of 4



CONCLUSIONS

The reactivity of α -allenols against the highly polarized molecule $\text{Tf}_2\text{C}=\text{CH}_2$, generated in situ from a Koshar-type zwitterion, has been studied. The novel transformation was carried out through a basic π -type catalysis based on a cationic gold complex, which led to the synthesis of different bis(triflyl)enals [3].

REFERENCES

[1] C. Lázaro-Milla, J. Macicior, H. Yanai, P. Almendros, *Chem. Eur. J.* **2020**, *26*, 8983.

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[3] Toledano-Pinedo, M.; Martínez del Campo, T.; Yanai, H.; Almendros, P. *ACS Catal.* **2022**, *12*, 11675.