



# Au(I) as a $\pi$ -Lewis Base Catalyst: Controlled Synthesis of Sterically Congested Bis(triflyl)enals from $\alpha$ -Allenols

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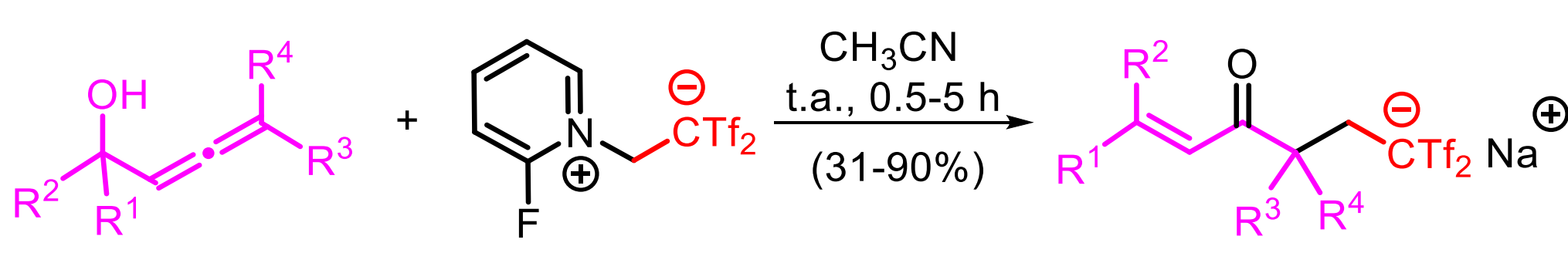
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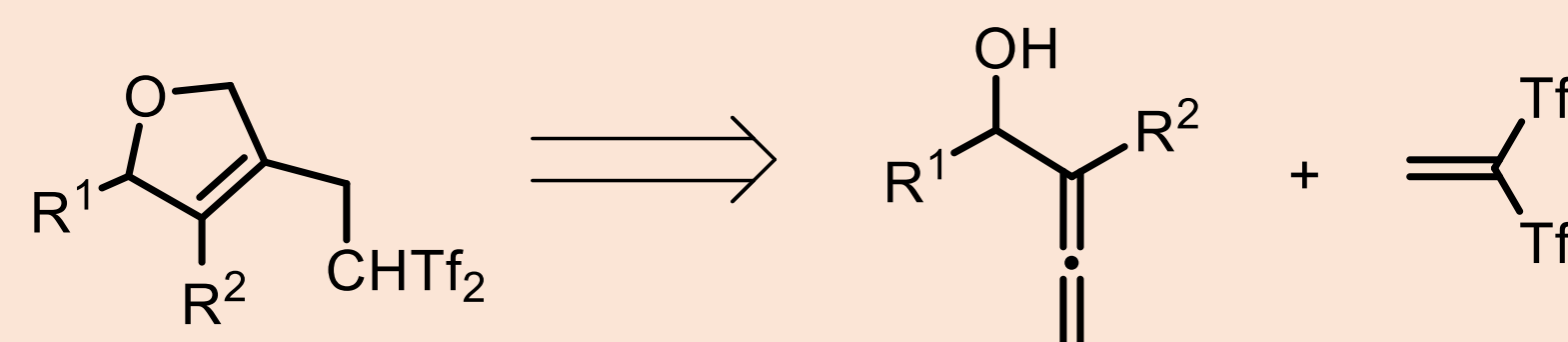
## INTRODUCTION

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  $\text{sp}^2$ -hybridized C4 atom of the allene rest [1].

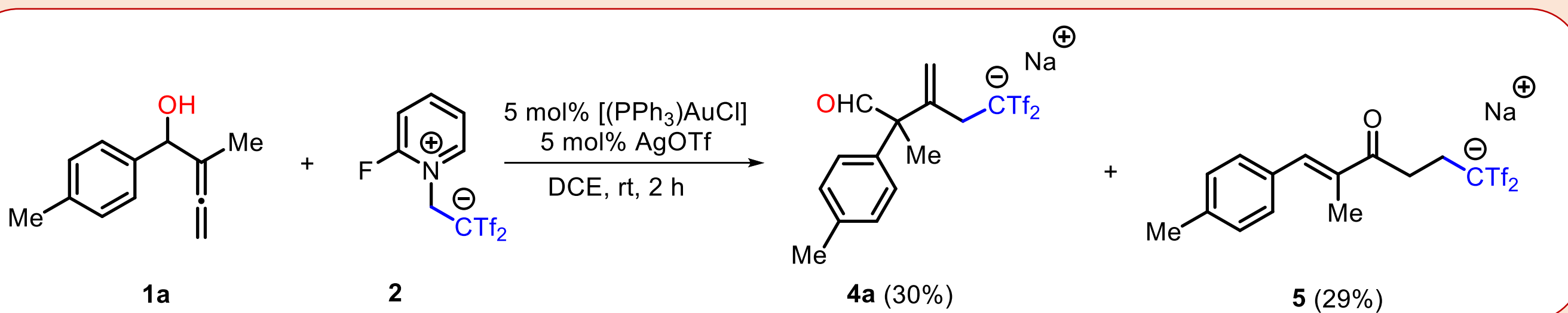


## OBJECTIVE



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  $\alpha$ -allenols against Yanai salt, in the presence of a gold catalyst with the assumption of a cycloetherification [2].

## RESULTS

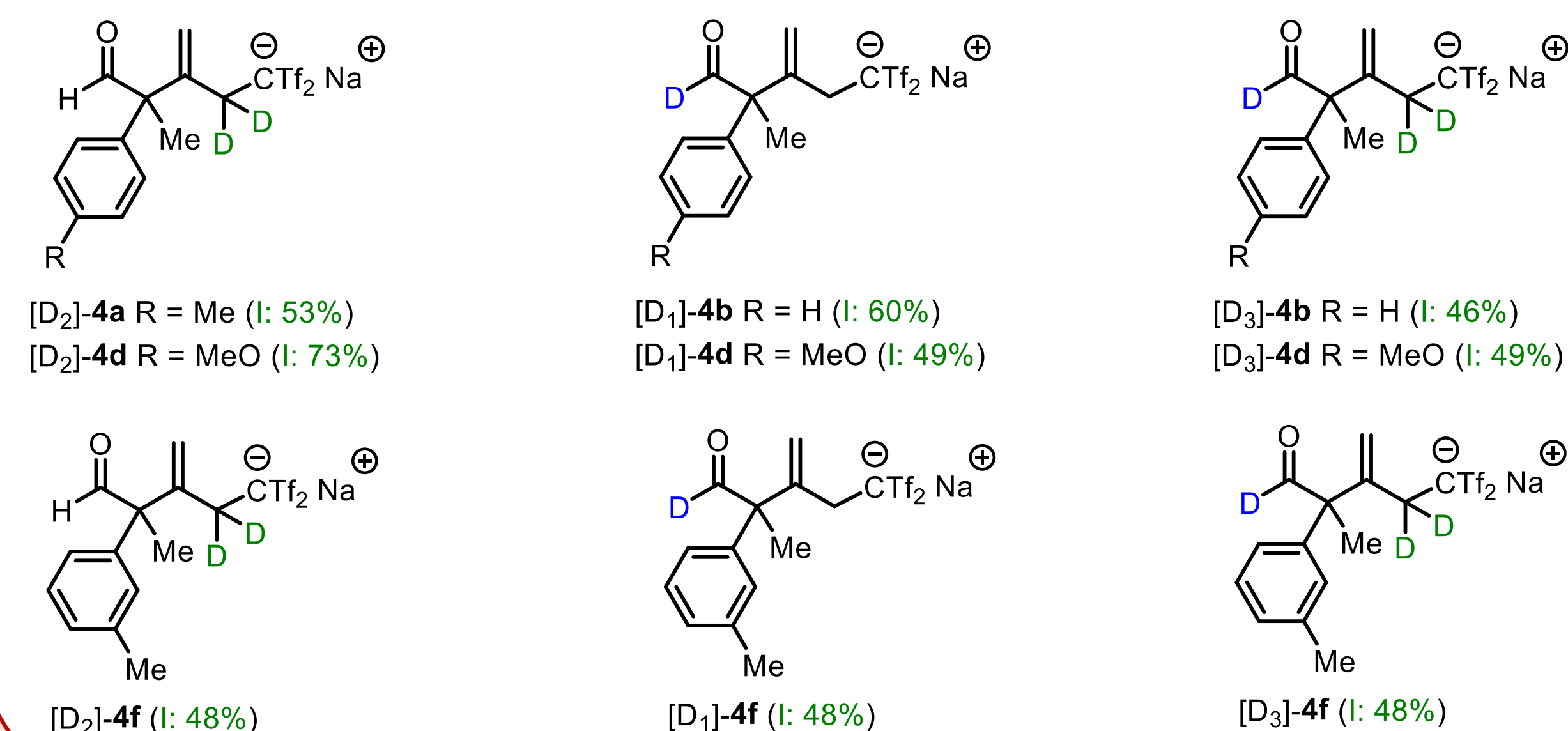
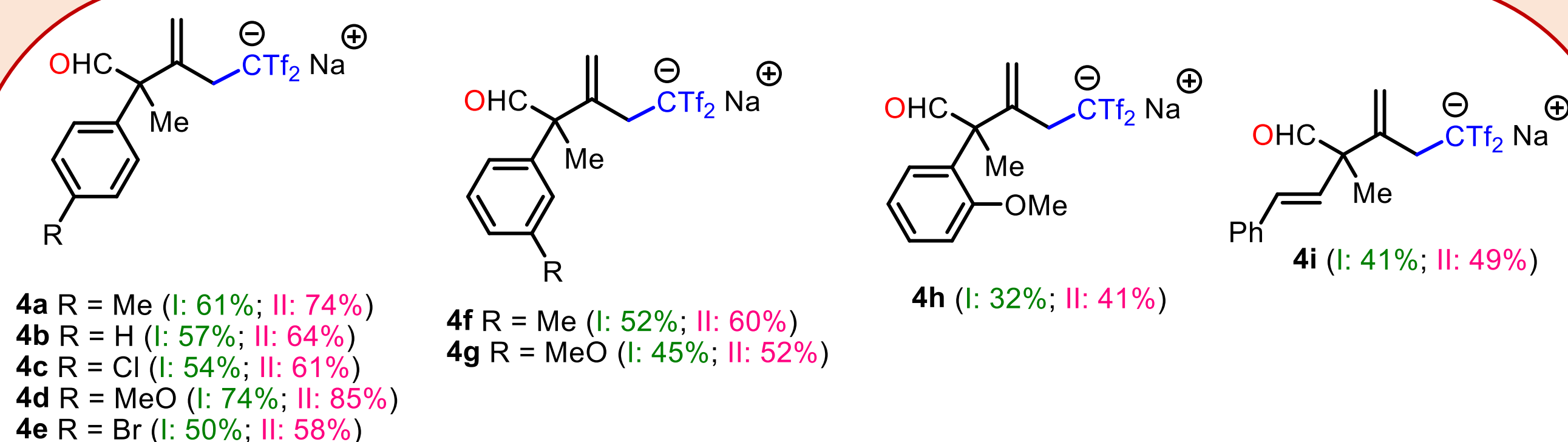


By using  $[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$  as a catalyst and carried out the reaction at room temperature, a separable mixture of the aldehyde **4a** together with the ketone **5** was obtained.

### Optimization of reaction conditions

Entry 1	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , DCE, rt, 2 h	4a (30%)
Entry 2	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , MS 3 Å, DCE, rt, 2 h	4a (41%)
Entry 3	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , DCE, 130 °C, 30 min	4a (61%)
Entry 4	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , $\text{C}_6\text{H}_{12}$ , 130 °C, 30 min	4a (6%)
Entry 5	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , HFIP, 130 °C, 30 min	4a (0%)
Entry 6	1a	2 (2.0 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ , DCE, 130 °C, 30 min	4a (60%)
Entry 7	1a	2 (1.1 equiv.)	$[(\text{PPh}_3)\text{AuCl}]/\text{AgSbF}_6$ , 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 <sub>6</sub> , 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 <sub>6</sub> , 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 <sub>6</sub> , DCE, 130 °C, 30 min	4a (40%)

### Study of the scope of the methodology

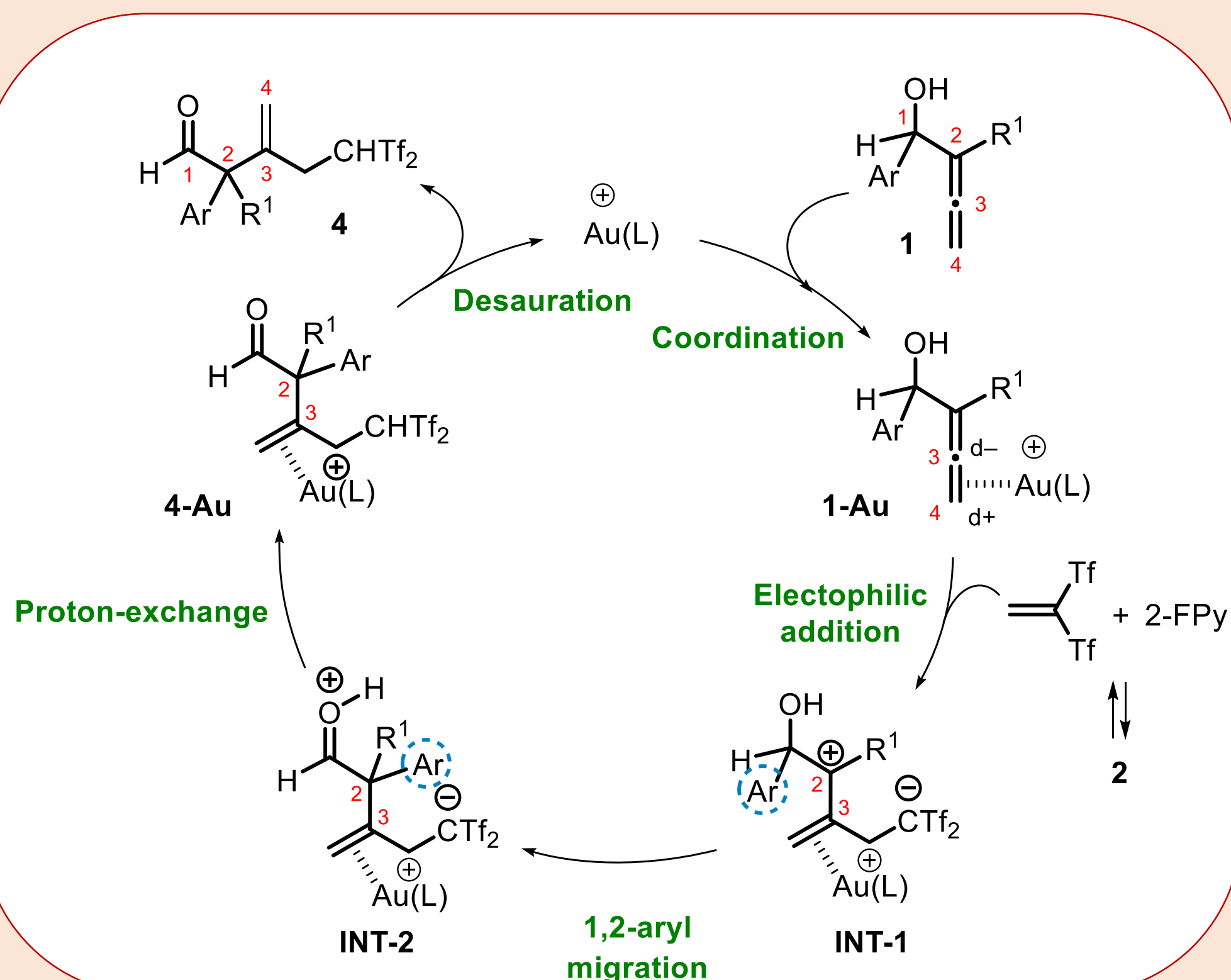


Method I:  $[\text{Au}] = [(\text{PPh}_3)\text{AuCl}]$ ,  $[\text{Ag}] = \text{AgOTf}$ ; Method II:  $[\text{Au}] = [\text{AuClIPr}]$ ,  $[\text{Ag}] = \text{AgSbF}_6$

## CONCLUSIONS

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

### Catalytic Cycle for the formation of 4



## REFERENCES

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

[2] a) Alcaide, B.; Almendros, P.; Martínez del Campo, T.; Fernández, I. *Chem. Commun.* **2011**, *47*, 9054. b) Alcaide, B.; Almendros, P.; Aparicio, B.; Lázaro-Milla, C.; Luna, A.; Faza, O. N. *Adv. Synth. Catal.* **2017**, *359*, 2789.

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