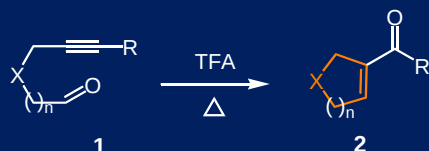


Carbocyclization of Alkynals Promoted by Brönsted Acids

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We recently described the carbocyclization of 5-, 6- and 7-alkynals **1** promoted by trifluoroacetic acid to exo cycloalkenones **2**.¹



X = C(CO₂Me)₂, CH₂
R = Alkyl, Ph
n = 1, 2, 3

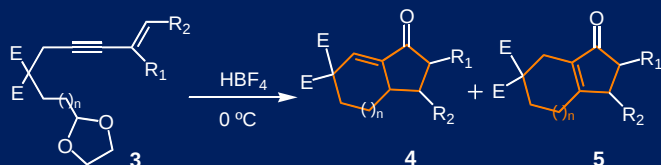
Table 1.- Carbocyclization of 5-, 6- and 7-alkynals **1** in TFA

Alkynals 1	Cycloalkenones 2	R	%
		Et C ₅ H ₁₁ Ph	60 60 83
		Me C ₅ H ₁₁	63 67
		Me	57
		a $\begin{cases} \text{Me} & 92 \\ \text{C}_5\text{H}_{11} & 74 \\ \text{Ph} & 56 \end{cases}$ b C ₅ H ₁₁	92 74 56 77

a X = C(CO₂Me)₂
b X = CH₂

Conditions: 0.5 mmol of alkynals **1** in 3 mL of TFA, 90 °C, 1-2 h.

Interestingly, when cyclization of enynals **3** was performed bicyclic enones **4** and **5** were obtained.



E = C(CO₂Me)₂
R₁ = alkyl, H
R₂ = alkyl, H
n = 1, 2

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Referencias: ¹ González-Rodríguez, C.; Escalante, L.; Varela, J.A.; Castedo, L.; Saá, C. *Org. Lett.*, 2009, 11, 1531.

Table 2.- Carbocyclization of conjugated enynals **3** in HBF₄

Enynal 3	Bicyclic enones 4, 5	% (4:5 ratio)
		46 (1:3)
		79 (1:4.5)
		89 (3:1)
		30 (3:1)
		66 (1:1.7)

Conditions: 0.5 mmol of enynals **3** in 3 mL of CH₂Cl₂ and 3 eq HBF₄, 0 °C, 10-40 min.

Mechanism

The bicyclic enones **4** and **5** could be derived from an acid-promoted carbocyclization followed by Nazarov cyclization.

