



The literature report

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Trifluoromethylation

**Copper-Catalyzed Tandem Trifluoromethylation/Semipinacol
Rearrangement of Allylic Alcohols****

Zhi-Min Chen, Wei Bai, Shao-Hua Wang, Bin-Miao Yang, Yong-Qiang Tu, and Fu-Min Zhang*



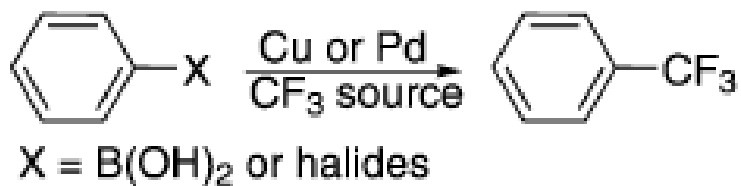
Yong-Qiang Tu

The academician of Chinese
Academy of Sciences

Lanzhou University

Previous metal-catalyzed trifluoromethylation reactions

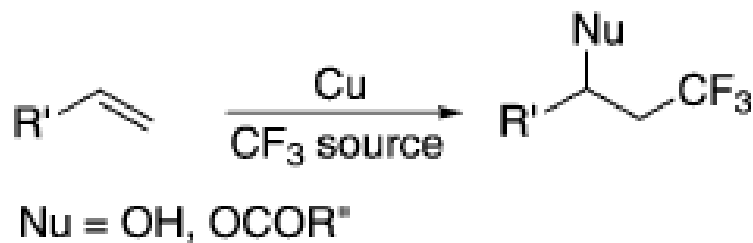
a)



b)



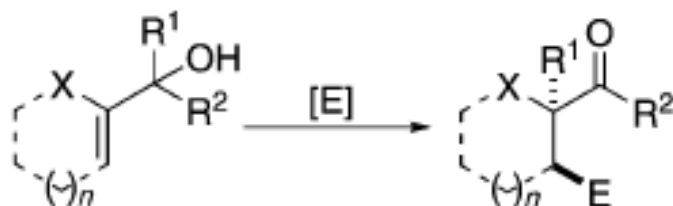
c)



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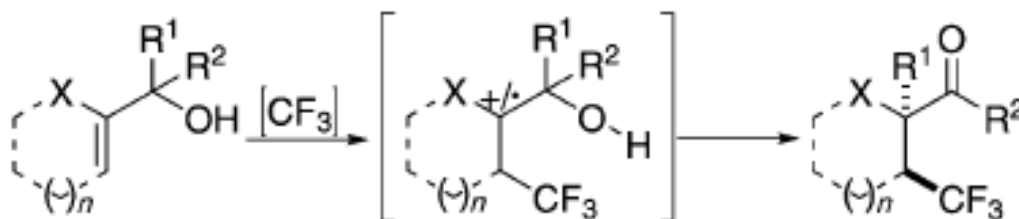
Design of the trifluoromethylation/semipinacol rearrangement reaction.

a) non-carbon electrophiles initiate semipinacol reaction (previous work)



E = H⁺, Halonium ion, RSe⁺ X = CH₂, O, NR

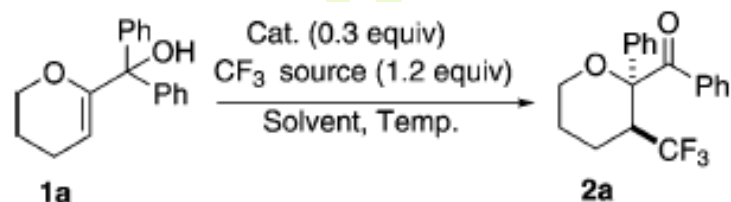
b) trifluoromethylation/semipinacol rearrangement reaction (this work)



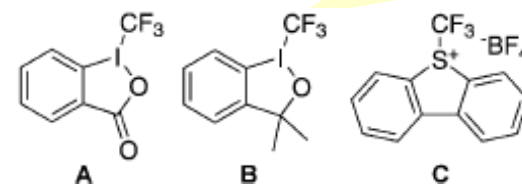
X = CH₂, O

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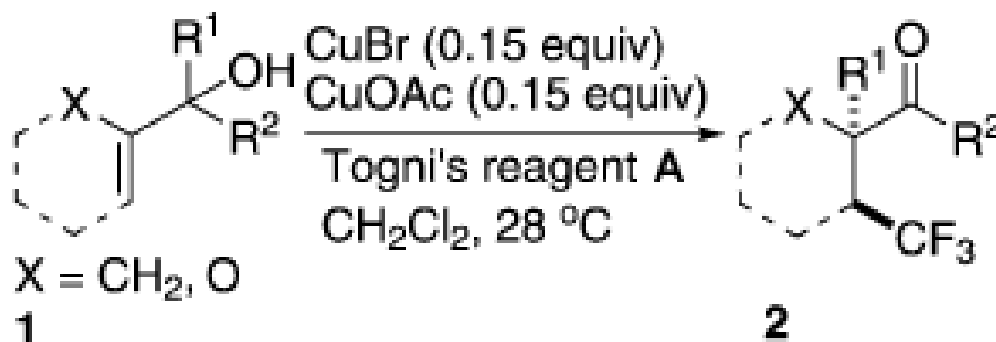
Optimization of Trifluoromethylation/Semipinacol Rearrangement Reaction



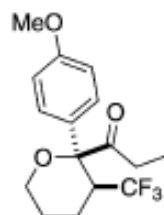
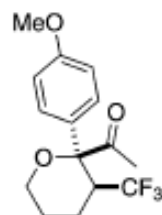
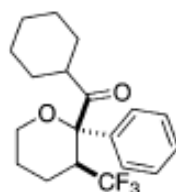
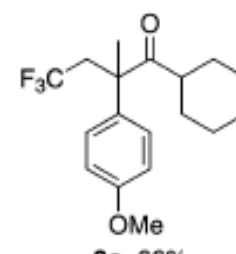
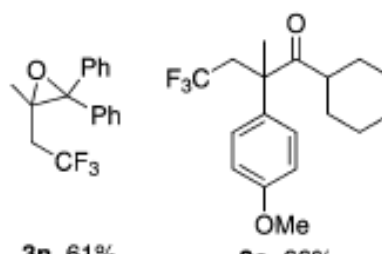
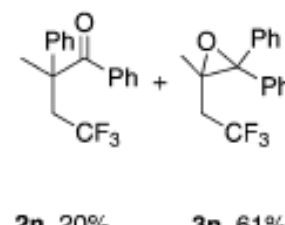
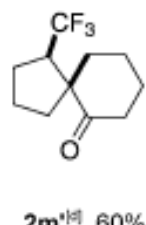
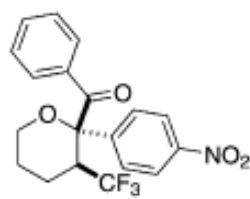
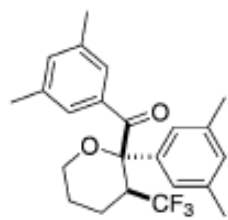
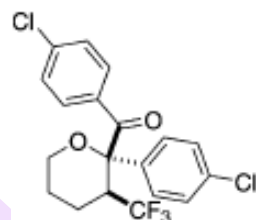
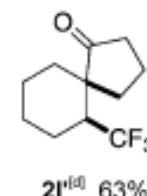
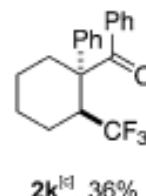
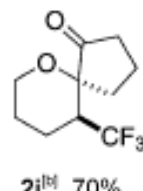
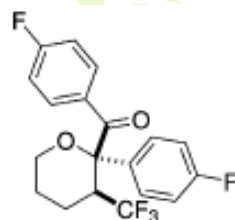
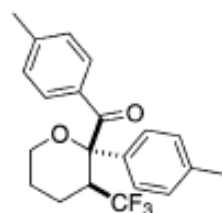
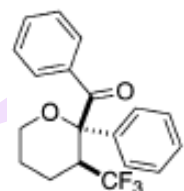
Entry	Catalyst	CF_3 source	Solvent	Yield [%] ^[b]
1	$\text{CuOTf} \cdot 0.5 \text{C}_6\text{H}_6$	A	CH_2Cl_2	12
2	$[(\text{MeCN})_4\text{Cu}]\text{PF}_6$	A	CH_2Cl_2	15
3	CuCl	A	CH_2Cl_2	34
4	CuBr	A	CH_2Cl_2	40
5	CuOAc	A	CH_2Cl_2	47
6	CuOAc	B	CH_2Cl_2	trace
7	CuOAc	C	CH_2Cl_2	–
8	CuOAc	A	CH_3CN	–
9	CuOAc	A	CH_3OH	–
10	CuOAc	A	DCE	45
11	CuOAc	A	toluene	n.r.
12 ^[c]	$\text{CuBr}, \text{CuOAc}$	A	CH_2Cl_2	54
13 ^[c,d]	$\text{CuBr}, \text{CuOAc}$	A	CH_2Cl_2	64
14 ^[c,d,e]	$\text{CuBr}, \text{CuOAc}$	A	CH_2Cl_2	n.r.
15 ^[c,d,f]	$\text{CuBr}, \text{CuOAc}$	A	CH_2Cl_2	41



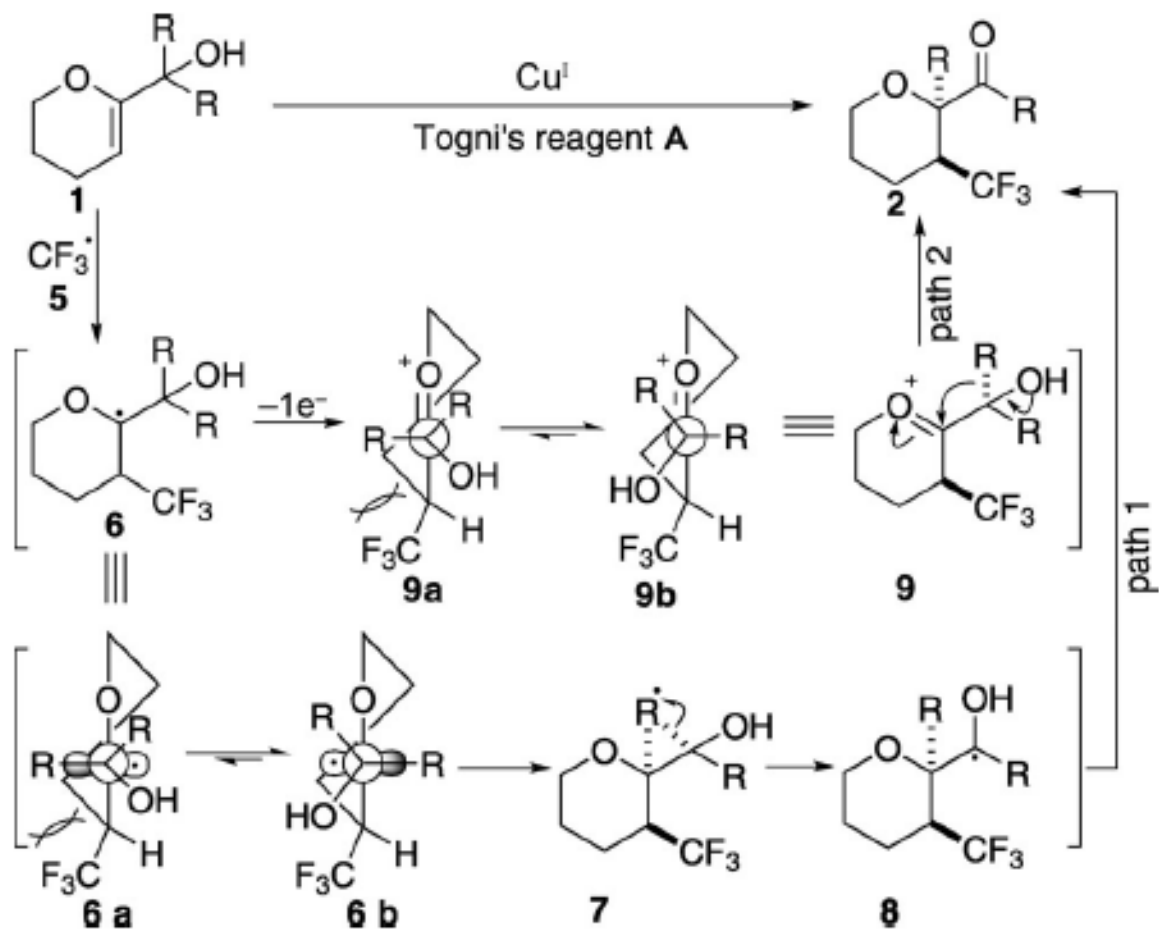
Scope of the trifluoromethylation/semipinacol rearrangement



Scope of the trifluoromethylation/semipinacol rearrangement



Proposed reaction mechanism



The background features several large, stylized, overlapping swirls in shades of green, purple, and light blue. Scattered throughout are numerous small, yellow, triangular shapes that resemble confetti or starbursts.

Thank you for your listening