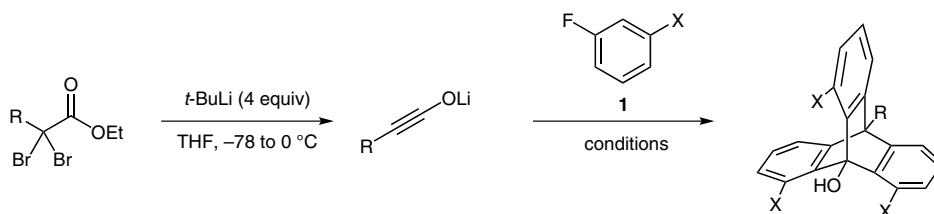


S. UMEZU, G. DOS PASSOS GOMES, T. YOSHINAGA, M. SAKAE, K. MATSUMOTO, T. IWATA, I. ALABUGIN, M. SHINDO* (FLORIDA STATE UNIVERSITY, USA AND KYUSHU UNIVERSITY, KASUGA, JAPAN)

Regioselective One-Pot Synthesis of Triptycenes via Triple-Cycloadditions of Arynes to Ynolates
Angew. Chem. Int. Ed. **2017**, *56*, 1298–1302.

Three Benzynes and the Ynolate



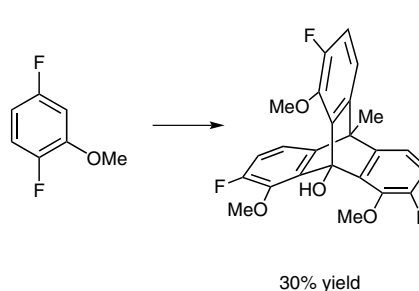
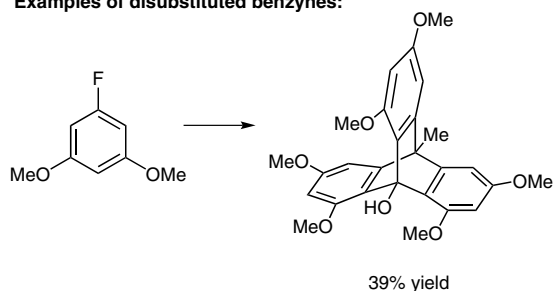
Substrate scope:

Entry	R	X	Conditions	Yield (%)
1	Me	H	A	42
2	<i>i</i> -Pr	H	A	35
3	<i>n</i> -Bu	H	A	52
4	<i>t</i> -Bu	H	A	39
5	Ph	H	A	27
6	Me	OMe	B	69
7	<i>i</i> -Pr	H	A	39
8	<i>n</i> -Bu	OMe	B	48
9	Hex	OMe	B	37
10	Ph	H	A	37

Conditions

A: **1** (6 equiv), then *n*-BuLi (4 equiv) addition over 1 h
B: **1** (4 equiv), then *n*-BuLi (4 equiv) addition over 5 min, -20 °C

Examples of disubstituted benzynes:



Significance: The triptycene structure is a remarkable scaffold that is frequently employed in functional materials as a result of its three dimensional, noncompliant structures and the interstitial space around the molecule. Most syntheses are based on a Diels–Alder cycloaddition between anthracene and an aryne. The authors describe a one-pot synthesis of triptycenes that proceeds through three cycloadditions of arynes to ynolates.

Comment: The approach of formally inserting three arynes into an alkyne is a new and powerful way to obtain both simple and substituted triptycenes. Calculations provide an insight into the mechanism and explain the high regioselectivity (head-to-head-to-head).

SYNFACTS Contributors: Timothy M. Swager, Constantin-Christian A. Voll
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Category

Synthesis of
Materials and
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Key words

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