Photoinduced Decarbonylative rearrangement of Bicyclo[2.2.2]octenone

Synthesis of the Marasmane skeleton

Wang, C-C.; Ku, Y-C.; Chuang, G-J. *J. Org. Chem.* 2015
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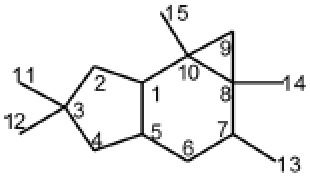
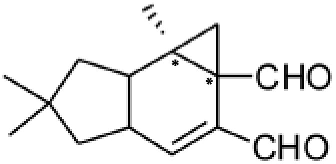
Background

- Marasmane is a sesquiterpenoid skeleton: fused-5,6,3-tricyclic ring
- Many bioactive properties: antibacterial



marasmane



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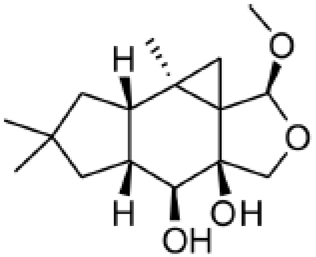
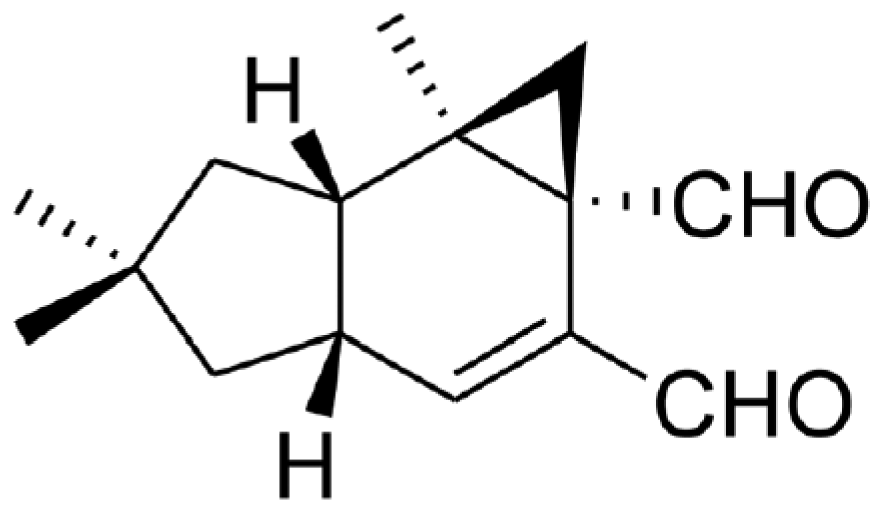


lactapiperanol A

Synthetic challenge



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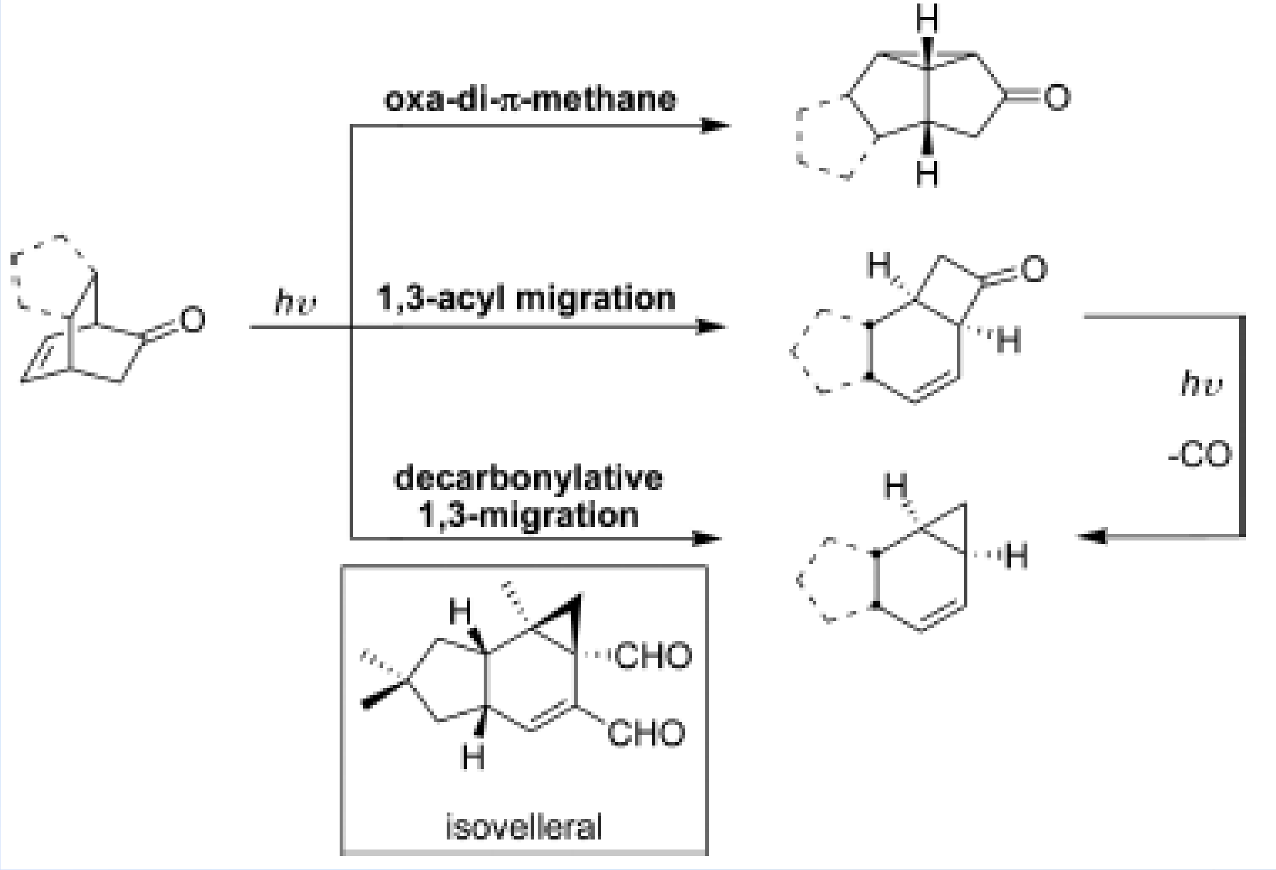
Price : 164 800 € / 1 g (sigma-aldrich)

Photochemical rearrangement

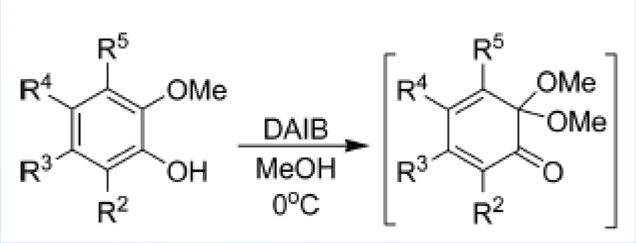
bicyclo[2.2.2]octenones



a) Liao, C.-C. *Chem. Eur. J*, **2010**, 16, *3121*. b) Yamauchi, M. *J. Chem. Soc. Perkin Trans*, **1997**, *561* ….

Scope of our bicyclooctenone derivate

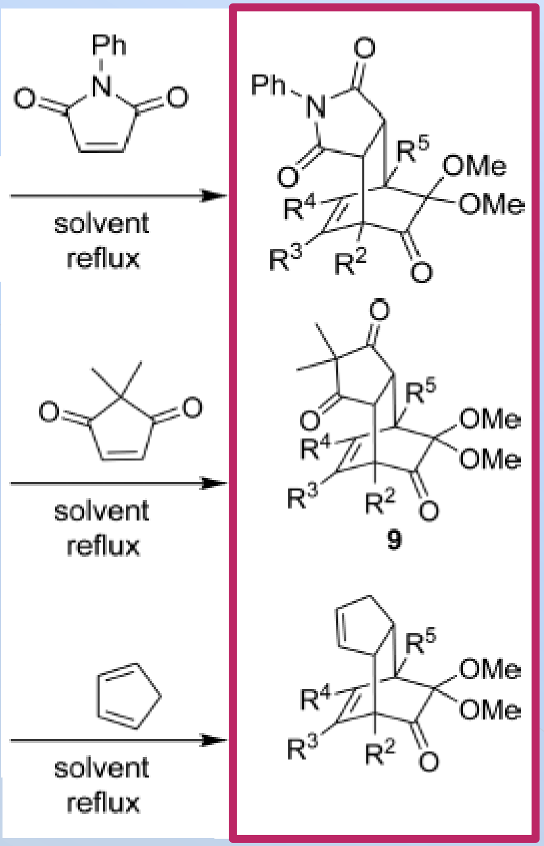
Synthesis of **MOB**: masked-o-benzoquinone



MOB

R2 = H, alkyl, acetal, OMe
R3 = H, alkyl, acetal, ester
R4 = H, alkyl, vinyl, TMS, EWG
R5 = H, OMe

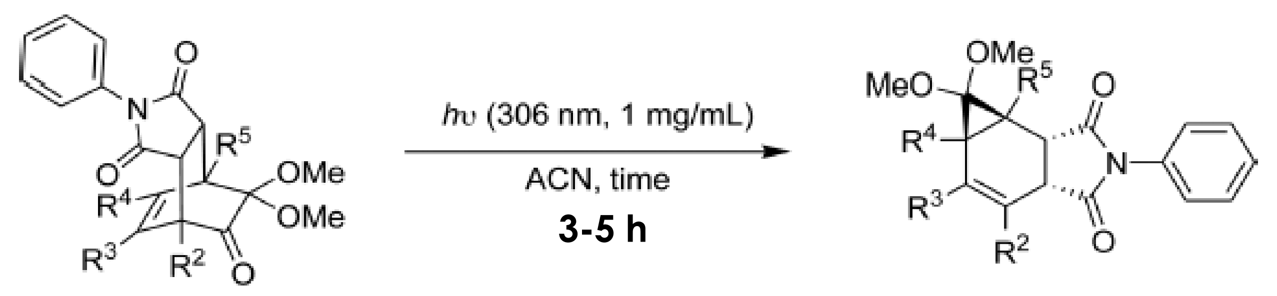
Diels-Alder



25-92 %
over two steps
25 examples

a) Liao, C.-C. Acc, Chem, Res, **2002**, 35, *856*. b) Quideau, S., *Org, Prep, Proced, Int*, **1999**, 31, *617*

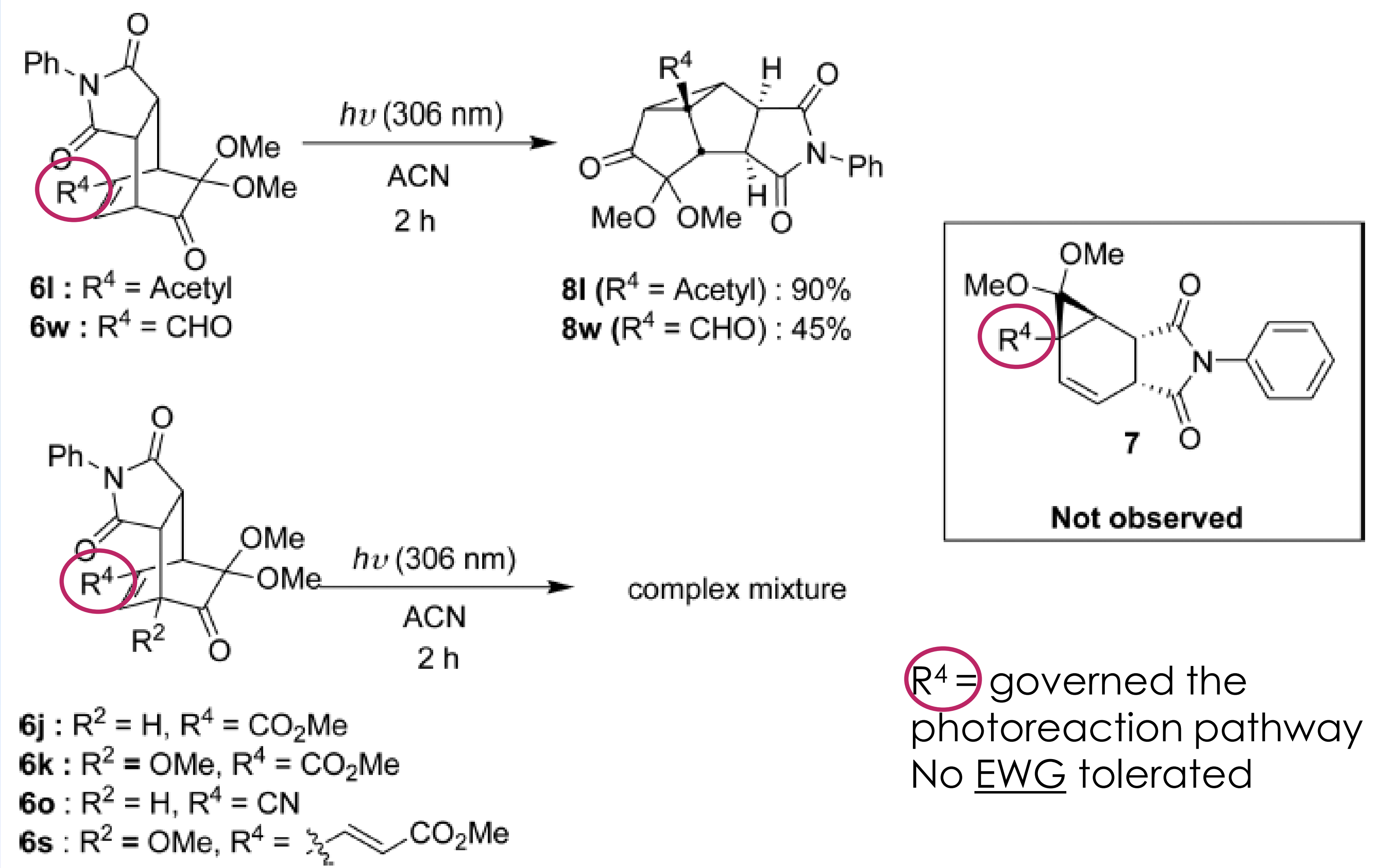
Scope of the reaction



33 – 99 %
18 examples

R^2 = H, Me, acetal,
R^3 = H, Me, acetal, EWG
R^4 = H, alkyl, vinyl, TMS,
R^5 = H, OMe

Limits of the reaction



6l : R^4 = Acetyl
6w : R^4 = CHO

8l (R^4 = Acetyl) : 90%
8w (R^4 = CHO) : 45%

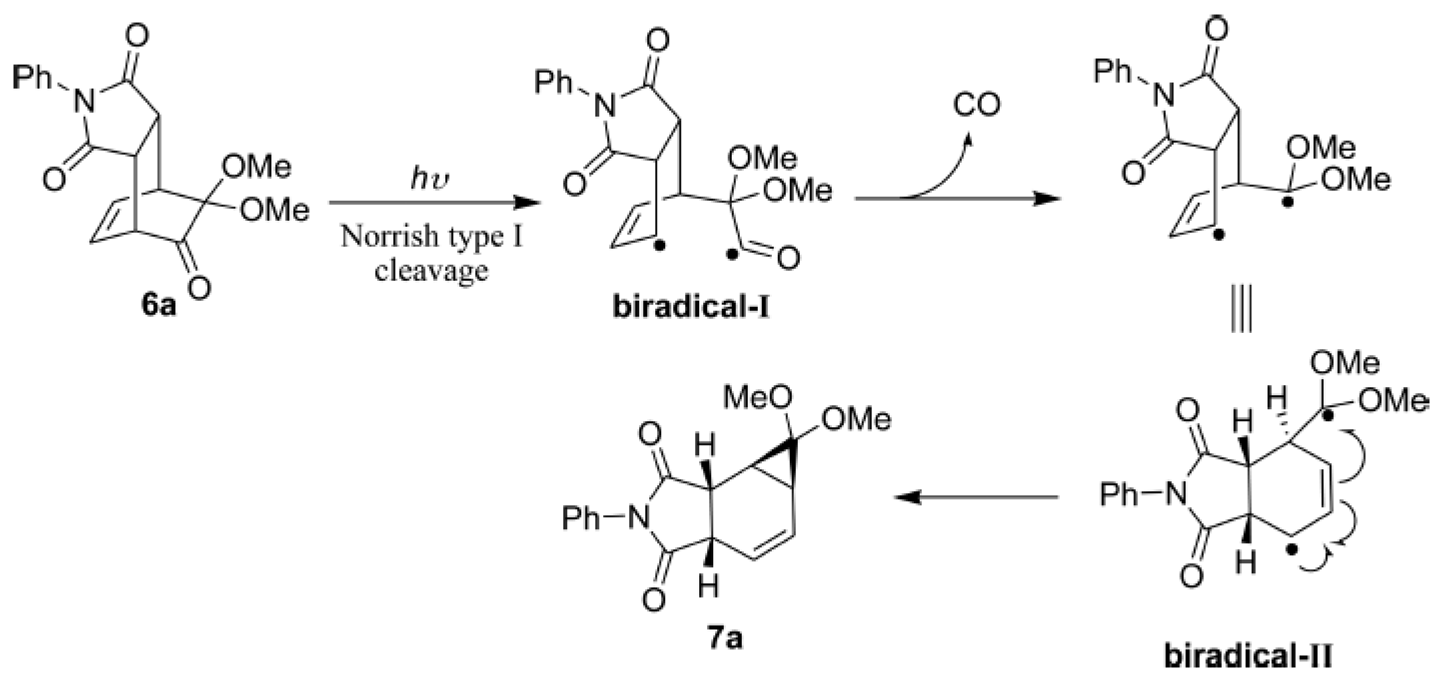
7

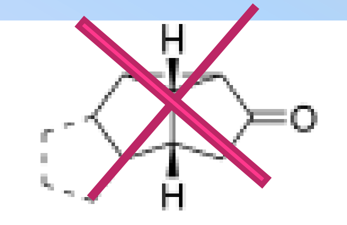
Not observed

6j : R^2 = H, R^4 = CO_2Me
6k : R^2 = OMe, R^4 = CO_2Me
6o : R^2 = H, R^4 = CN
6s : R^2 = OMe, R^4 = $CH{=}CHCO_2Me$

R^4 = governed the photoreaction pathway
No <u>EWG</u> tolerated

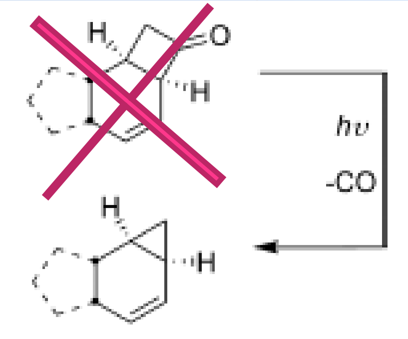
Proposed reaction pathway for the decarbonylative 1,3 migration





Oxa-di-π-methane

1,3-acyl migration



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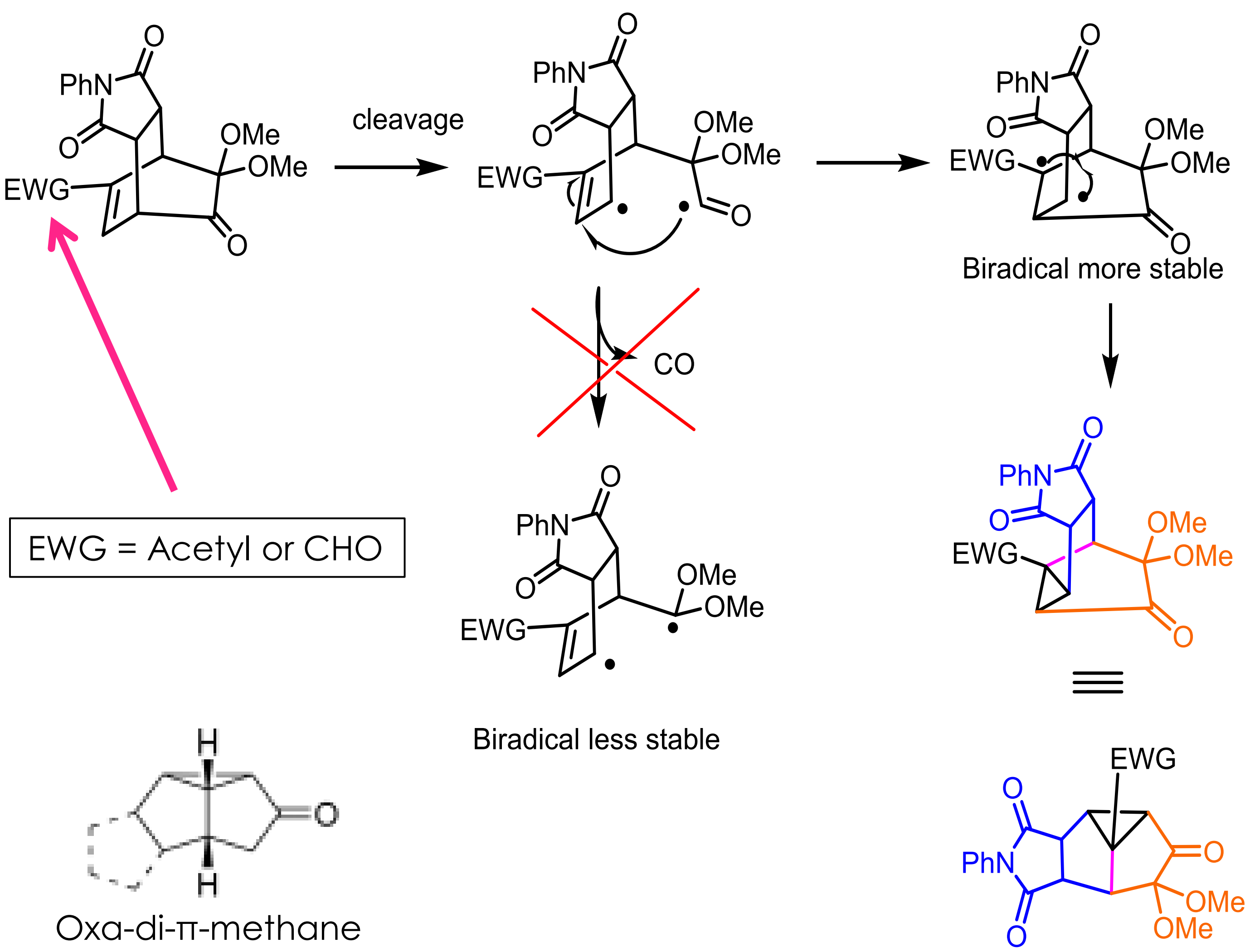
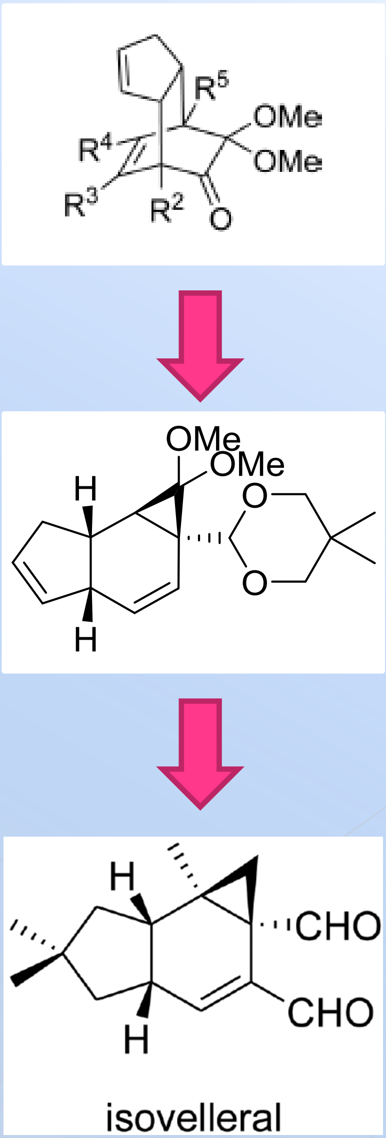


a) Liao, C.-C. *Chem. Eur. J.*, **2010**, *16*, *3121*

Results

- Disclosed a construction of Marasmane skeleton thank to a photochemical rearrangement of bicyclo[2.2.2]octenones
- Easily available precursors
- Many functional groups are compatibles
- This new photoreaction may be useful in synthesis of analogues of the Isovelleral skeleton



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