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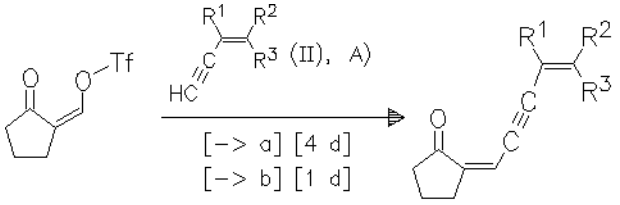
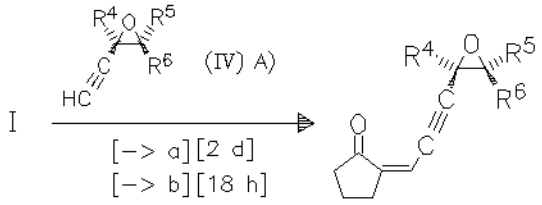
Synthesis of Enynes Related to Neocarzinostatine Using the New Pd/Ag Catalyzed Coupling Reaction. — 2-Triflyloxymethylene cyclopentanone (I) can be readily converted to 2-(alkynyl)methylene cyclopentanones (III) or the corresponding epoxides (V) via a stereoselective sp-sp^2 coupling using a Pd/Ag couple catalyst. The products are versatile intermediates in the preparation of neocarzinostatin chromophore analogues. — (BERTUS, P.; PALE, P.; Tetrahedron Lett. 38 (1997) 47, 8193-8196; Lab. React. Sel. Appl., CNRS, Univ. Reims-Champagne-Ancienne, F-51687 Reims, Fr.; EN)



I III

a R^1: —Me ; R^2: —H ; R^3: —CH_2—O—$SiPh_2$—tBu 96%
b R^1: —H ; R^2: —O—$SiPh_2$—tBu ; R^3: —C≡C—Tbs 46%

A): iPr_2N—Et, $Pd(PPh_3)_4$/AgI (1:2) (cat.), DMF



V

a R^4: —Me ; R^5: —H ; R^6: —CH_2—O—$SiPh_2$—tBu 52%
b R^4: —H ; R^5: —Me ; R^6: —$SiMe_2$—tBu 56%