Manuscript Title : Suzuki- Miyaura Coupling of Alkynylboronic Esters Generated *in situ* from Acetylenic Derivatives.

GENERAL EXPERIMENTAL PROCEDURE FOR THE COUPLING REACTIONS

Suzuki cross coupling reaction of 1-octyne and *p*-bromotoluene :

A solution of n-BuLi (1.2 ml, 1.6 M in hexane, 1.92 mmol) was slowly added to a cooled solution (-78°C) of 1-octyne (0.27 ml, 1.83 mmol) in dimethoxyethane, DME (10 ml, freshly distilled and degazed) under argon. After 1h at –78°C triisopropylborate (freshly distilled) (0.42 ml, 1.82 mmol) was slowly added. After stirring for 2h at –78°C the temperature was raised to 20°C during 30 min. At the same time palladiumtetrakistriphenylphosphine $Pd(PPh_3)_4$ (15.1 mg, 0.013 mmol) and *p*-bromotoluene (229mg, 1.34 mmol) were dissolved in DME (10 ml) and stirred 10 min at room temperature. To the lithiated borate THF (3 ml) was added before adding the solution of $Pd(PPh_3)_4$ and p-bromotoluene *via canula*. 2X5ml of DME were then added to the mixture for rinsing the *canula* and the flask.

After 5h refluxing at 80°C, the reaction mixture was cooled at room temperature and quenched with 50 ml of water. The aqueous layer was extracted with AcOEt (3X100ml), the organic phases were collected, dried over $MgSO_4$ and the solvents were removed under reduced pressure. Flash column chromatography (hexane 100%) of the crude product gave 92% yield of the *p*-octynyltoluene. ^{1}H NMR (200MHz, $CDCl_3$) δ 0.9 (t, 3H, J=6.45Hz, CH_3), 1.2-1.64 (m, 8H, $4CH_2$), 2.32 (s, 3H, CH_3(Tol)), 2.39 (t, 2H, J=6.9Hz, acetylenic CH2), 7.18 (AB, 4H, JAB=8.6Hz, pTol) ^{13}C NMR (50MHz, $CDCl_3$) δ 137.45, 131.48, 129.01, 121.11, 89.71, 80.65, 31.48, 28.89, 28.71, 22.67, 21.46, 19.52, 14.15.