Supporting Information for:

Prop-2-yn-1-yl 2-bromo-2-methylpropanoate: Identification and Suppression of Side Reactions of a Commonly Used Terminal Alkyne-Functional ATRP Initiator

by

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Synthesis of Propargyl Acetate. Triethylamine (3.85 g, 38.0 mmol), DMAP (0.33 g, 2.7 mmol), propargyl alcohol (1.51 g, 26.9 mmol) and dry CH_2Cl_2 (30 mL) were placed in a 100 mL round bottom flask equipped with a stir bar, addition funnel, and nitrogen inlet, and cooled in an ice bath. Acetyl chloride (8.31g, 106 mmol) in dry CH_2Cl_2 (10 mL) was added by addition funnel over 30 min. After complete addition the reaction was warmed to room temperature and stirred for 12 h. The reaction was filtered to remove triethylammonium chloride and the filtrate washed with 5% aq. HCl (40 mL x 3) and water (40 mL x 3), dried over $MgSO_4$, filtered to remove the drying agent, and the filtrate concentrated using rotary-evaporation. The crude product was distilled under nitrogen and the product collected at 150 °C as 1.1g (57%) colorless liquid. ^{1}H-NMR (500 MHz): δ 2.11 (s, C*H*3), 2.48 (t, *H*CC, ^4J = 2.5 Hz), 4.67 (d, CH_2, ^4J = 2.5 Hz), ^{13}C-NMR (126 MHz): δ 20.7 (*C*H_3), 52.0 (*C*H_2), 74.9 (H*C*C), 77.8 (HC*C*), 170.2 (*C*=O).

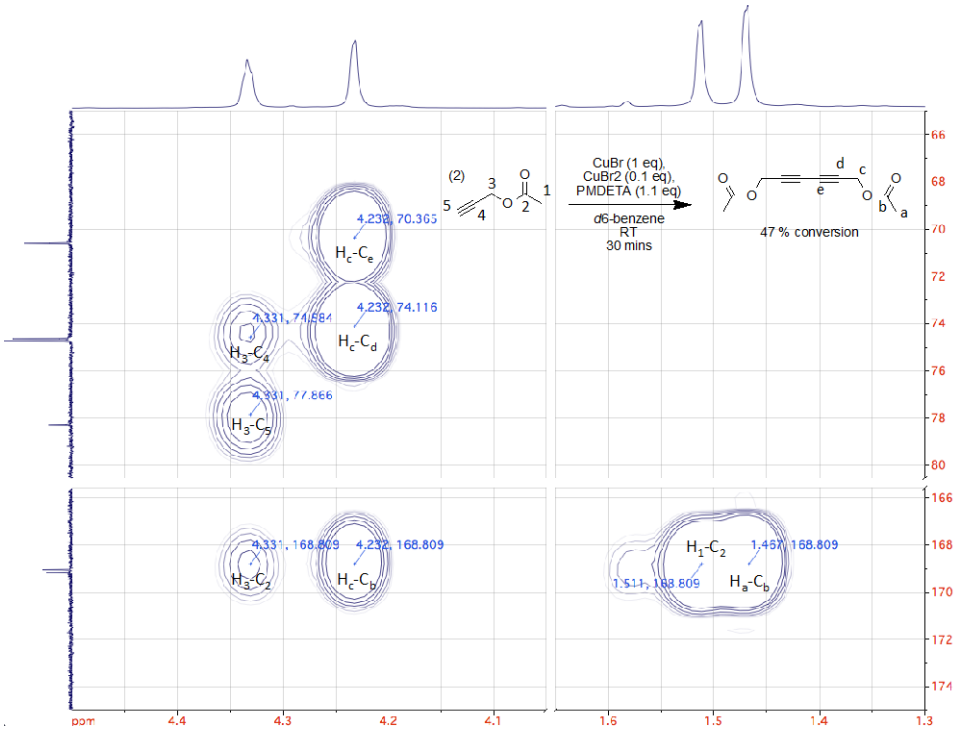

Figure S1. 2D ^{1}H-^{13}C gHMBC NMR (500 MHz) spectrum of an aliquot taken at 30 min from propargyl acetate in benzene-d_6 at 25 °C in the presence of CuBr, $CuBr_2$ and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) showing the connectivity of the oxidatively coupled alkyne-alkyne dimer; [propargyl acetate] : [CuBr] : [$CuBr_2$] : [PMDETA] = 1 : 1 : 0.1 : 1.1.