Acetone: solvent or reagent depending on the order of addition in SET-LRP

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Experimental

Materials

Acetone (98%) grade synthesis was purchased from Scharlab and distilled over CaH_2. Cu(II)Br_2 (99% Aldrich), tris(2-aminoethyl)amine (TREN, 98%, Aldrich), hexamethylated tris(2-aminoethyl)amine (Me_6-TREN, 97%, Aldrich) and $CDCl_3$ (eurisotp, 99.9%) were used as received. Deuterated acetone (eurisotop, 99%) was freshly distilled over CaH_2 before use.

Techniques

400 Mhz ^{1}H-NMR and D-NMR were recoded in a Varian VNMRS400 instrument at 25 ºC. Samples were dissolved in 0.6 mL of $CDCl_3$ and $CHCl_3$ respectively, containing tetramethylsilane (TMS) as internal standard. For the Cu(II)Br_2-

mediated bromination quantification experiment, the delay time (D1) was set at 10 s and the number of scans (nt) was set a minimum of 150 scans.

Typical procedure for the Cu(II)Br_2-mediated bromination of acetone.

$CuBr_2$ (63.0 mg, 0.282 mmol) was placed in a dry vial (dried in an oven O.N.) containing a magnetic stir bar and deoxygenized by purging with N_2 for 10 min at 25 ºC. In another vial acetone (2 mL) was deoxygenized by bubbling with N_2 for 30 min at 0 ºC. Then, the deoxygenized acetone was transferred via a syringe and added to $CuBr_2$ (under N_2) and the reaction was stirred. Samples were withdrawn periodically from the reaction mixture, the excess of acetone was removed by evaporating with N_2 flow during 5 seconds. The obtained residue was dissolved in $CDCl_3$ and ^{1}H-NMR and were recorded immediately. The ratio of the products was determined using bromoacetone as a reference.

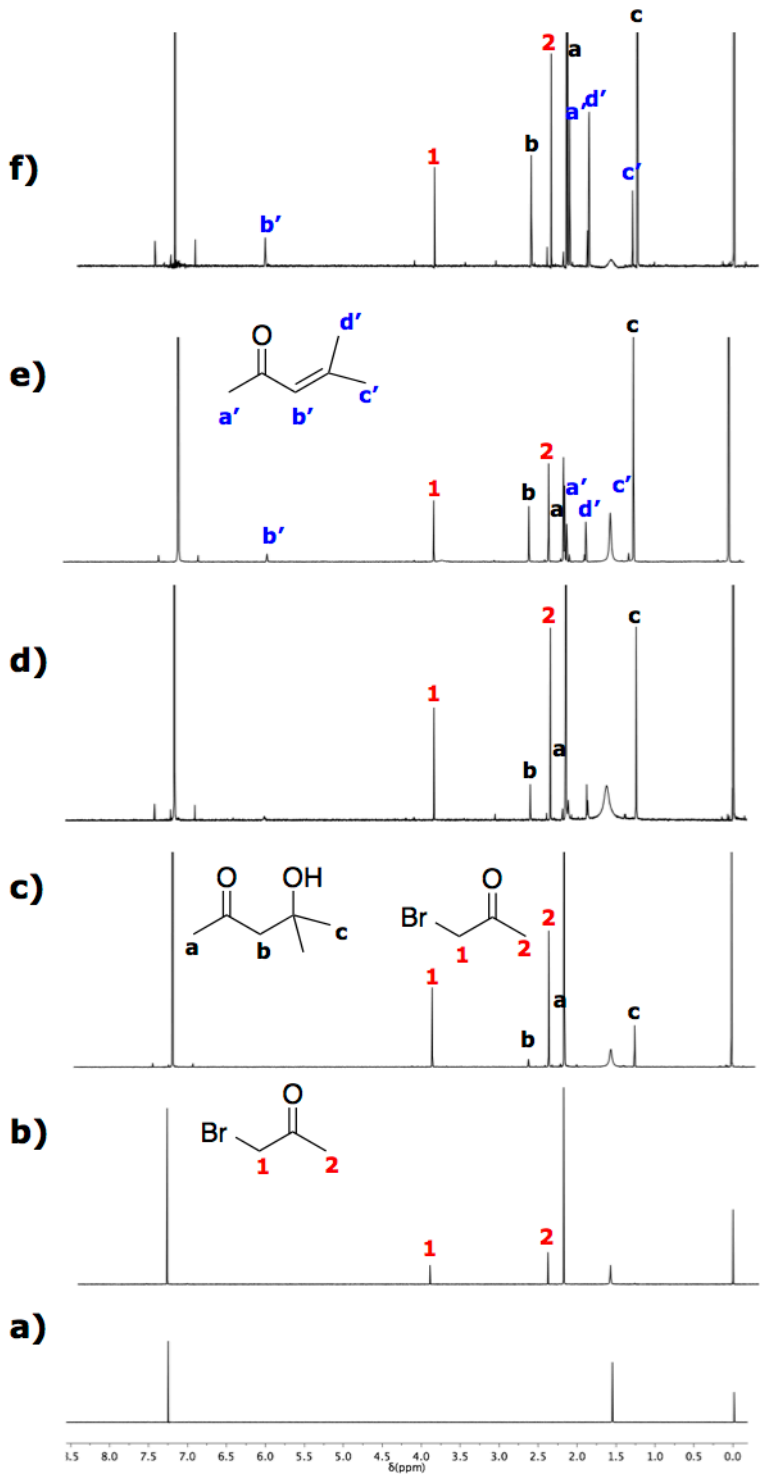

Figure S1. ^{1}H-NMR traces of Cu(II)Br_2-mediated bromination of freshly distilled acetone (**a**) after 5 mintues, (**b**) after 10 minutes, (**c**) after 15 minutes, (**d**) after 30 hours, (**e**) after 4h and (**f**) after 17h in $CDCl_3$.