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\textsubscript{2}. Cu(II)Br\textsubscript{2} (99\% Aldrich), tris(2-aminoethyl)amine (TREN, 98\%, Aldrich), hexamethylated tris(2-aminoethyl)amine (Me\textsubscript{6}-TREN, 97\%, Aldrich) and CDCl\textsubscript{3} (eurisotop, 99.9\%) were used as received. Deuterated acetone (eurisotop, 99\%) was freshly distilled over CaH\textsubscript{2} before use.

Techniques

400 MHz \textsuperscript{1}H-NMR and D-NMR were recoded in a Varian VNMRS400 instrument at 25 °C. Samples were dissolved in 0.6 mL of CDCl\textsubscript{3} and CHCl\textsubscript{3} respectively, containing tetramethylsilane (TMS) as internal standard. For the Cu(II)Br\textsubscript{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 °C. In another vial acetone (2 mL) was deoxygenized by bubbling with N$_2$ for 30 min at 0 °C. 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 Samples were withdrawn periodically from the reaction mixture, the excess of acetone was removed by evaporating with N$_2$ flow during 5 seconds.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 minutes, (b) after 10 minutes, (c) after 15 minutes, (d) after 30 hours, (e) after 4h and (f) after 17h in CDCl$_3$. 