

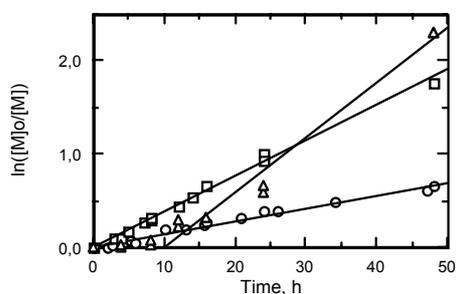
## Tuning of ruthenium *N*-heterocyclic carbene catalysts for ATRP

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### Electronic supplementary information

#### Polymerisation of methyl methacrylate catalysed by complexes 1, 2, and 3.

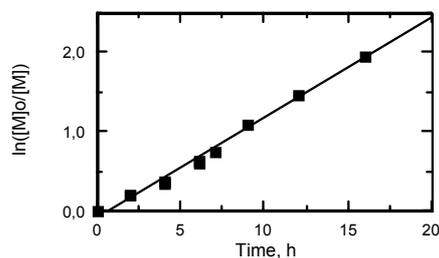
Semilogarithmic plot of  $\ln([M]_0/[M])$  vs. time:



**Fig. S1** Time dependence of  $\ln([M]_0/[M])$  at 85 °C where  $[M]_0$  and  $[M]$  are the MMA concentrations at times 0 and  $t$  (see Table 1 for reaction conditions): complex **1** ( $\Delta$ ),  $y = -0.60040 + 5.9069 \cdot 10^{-2} x$  for reaction times ranging from 10 to 50 h;  $r^2 = 0.974$ ; complex **2** ( $\square$ ),  $y = -4.6911 \cdot 10^{-4} + 3.8214 \cdot 10^{-2} x$ ;  $r^2 = 0.994$ ; complex **3** ( $\circ$ ),  $y = 1.1678 \cdot 10^{-2} + 1.3854 \cdot 10^{-2} x$ ;  $r^2 = 0.979$ .

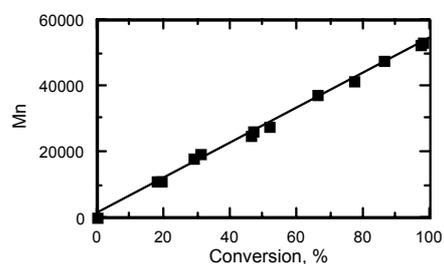
#### Polymerisation of styrene catalysed by complex 5.

Semilogarithmic plot of  $\ln([M]_0/[M])$  vs. time:



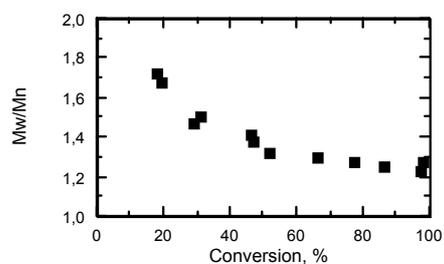
**Fig. S2** Time dependence of  $\ln([M]_0/[M])$  at 110 °C where  $[M]_0$  and  $[M]$  are the styrene concentrations at times 0 and  $t$  (see Table 1 for reaction conditions): complex **5** ( $y = -0.088024 + 0.12633 x$ ;  $r^2 = 0.991$ )

Plot of  $M_n$  vs. conversion:



**Fig. S3** Dependence of the polystyrene molecular weight  $M_n$  on monomer conversion (complex **5**,  $y = 1304 + 529.73 x$ ;  $r^2 = 0.997$ ).

Plot of  $M_w/M_n$  vs. conversion:



**Fig. S4** Dependence of the molecular weight distributions,  $M_w/M_n$ , on styrene conversion (complex **5**).