Fig. S1. $^1$H (above), $^{13}$C NMR (middle) and IR spectra (down) of the material obtained from the reaction of opbaH$_2$Et$_2$ with MeNH$_2$ in MeOH, referred to as crude.
Fig. S2. $^1$H (above) and $^{13}$C NMR spectra (below) of the recrystallized crude from MeOH and MeOH:THF (1:1), respectively.
**Fig. S3.** IR spectrum of opbaH$_2$Me$_2$ (2).
Fig. S4. $^1$H (above) and $^{13}$C NMR spectra (below) of opbaH$_2$Me$_2$ (2).
Fig. S5. $^1$H (above) and $^{13}$C NMR spectra (below) of the residue B.
**Fig. S6.** IR spectrum of 1,4-dihydro-2,3-quinoxalinedione (3).
Fig. S7: $^1$H (above) and $^{13}$C NMR spectra (below) of 1,4-dihydro-2,3-quinoxalinedione (3).
**Fig. S8:** $^1$H (above) and $^{13}$C NMR spectra (below) of C.
Fig. S9. IR spectrum of opboH$_2$Me$_2$ (4).
Fig. S10: $^1$H (above) and $^{13}$C NMR spectra (below) of opboH$_4$Me$_2$ (4).
Fig. S11. The IR spectrum of opooH$_3$Me$_2$ (1).
Fig. S12: $^1$H (above) and $^{13}$C NMR spectra (below) of opooH$_3$Me$_2$ (1).
Fig. S13. The IR spectrum of opooH$_3$EtMe (9).
Fig. S14. $^1$H (above) and $^{13}$C NMR spectra (below) of opooH$_3$EtMe (9).
Fig. S15. $^1$H (above) and $^{13}$C NMR spectra (below) of the residue obtained from the filtrate of the reaction of opbaH$_2$Et$_2$ with 5/6 equivalent of MeNH$_2$ in EtOH.
Fig. S16. Optical photography of single crystals of 7@5 (the three crystals on the left side) and 8@6 (right). Crystals on the left side have even optically well recognizable crystals faces, their different colours are due to the use of an optical polarisation filter. Crystal faces of the crystal shown on the right side are less well formed.

Remark I: The identities of the single crystals shown here have been verified by unit cell measurements. It should be noted again, that the differently shaped crystals were collected from one and the same crystallization of 99% of the orange together with 1% of the purple coloured powder.

Remark II: It is mentioned within the manuscript that from the crystallization of the orange powder containing 5 and 6 or the crystallization of the purple powder containing 7 and 8 the crystals formed were optically distinguishable. Their respective different shapes refer approximately to the shapes shown here.
Obviously, the formation of compounds 1 and 2 is due to a transesterification reaction\textsuperscript{1-3} of opbaH\textsubscript{2}Et\textsubscript{2} with MeOH in the presence of MeNH\textsubscript{2} which, in addition to its role as nucleophile in the amide formation reaction, may further catalyze the transesterification reaction. Transesterification reactions are well known and have been studied by achieving the reaction using a variety of alcohols to react with different esters catalyzed by Lewis acids,\textsuperscript{4} bases,\textsuperscript{5,6} were performed under neutral conditions\textsuperscript{7-9} and by addition of other catalysts.\textsuperscript{10-17} Nevertheless, all the transesterification reactions carried out to-date were performed under reflux and call for somewhat long time. Interestingly, the reaction under study had gone to end at 60 °C in 30 min, which makes it a good candidate catalytic reaction for related transesterification reactions in future. For example, it seems to be interesting to study the use of tertiary amines as catalysts.


