A quantitative on-line NIR (Near-Infrared) method for the monitoring of the formation of a Grignard reagent was developed on laboratory scale using chemometrics and tested in a 630 L pilot plant reactor. A good accuracy of the model was obtained and the feasibility of the on-line measurement was demonstrated. The concentrations of the added reagent (and thus its degree of accumulation) and of the formed Grignard reagent (indication of the reaction initiation) can be determined in real time. Therefore, the safety of the highly exothermic process and its robustness are significantly improved. Furthermore, the method is applicable to monitor the concentrations during the following cross-coupling reaction so that it can be used to determine in real time the reaction yield. By using on-line spectroscopy, the product quality and performance can be guaranteed on an industrial scale. Moreover, the cycle times are reduced due to the elimination of waiting times caused by traditional analysis.