† Electronic Supporting information

to

Combining a Ligand Photogenerator and a Ru Precatalyst: A Photoinduced Approach to Cross-linked ROMP Polymer Films

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I. Additional Experiments

Preparation of the active metathesis catalyst (p-cymene)$RuCl_2$(IMes) (Ru-1-IMes).

Noels' complex starting from Ru-1 and IMes was synthesized based on a protocol developed by Nolan *et al.*[1] ^{1}H NMR (400 MHz, THF-d_8. Chemical shift: 1.08 (d, J = 7 Hz, 6H, $CH(CH_3)_2$), 1.75 (s, 3H, CH_3), 2.22 (s, 12H, Mes-2,6-CH_3), 2.31 (s, 6H, Mes-4-CH_3), 2.46 (m, 1H, $CH(CH_3)_2$), 4.55 (d, J = 6 Hz, 2H, C_6H_4), 5.00 (d, J = 5.8 Hz, 2H, C_6H_4), 6.90 (m, 4H, Mes-3,5-H), 7.05 (s, 2H, NCHCHN).

II. Additional Figures

1. NHC photogeneration and structure of the active ROMP catalyst

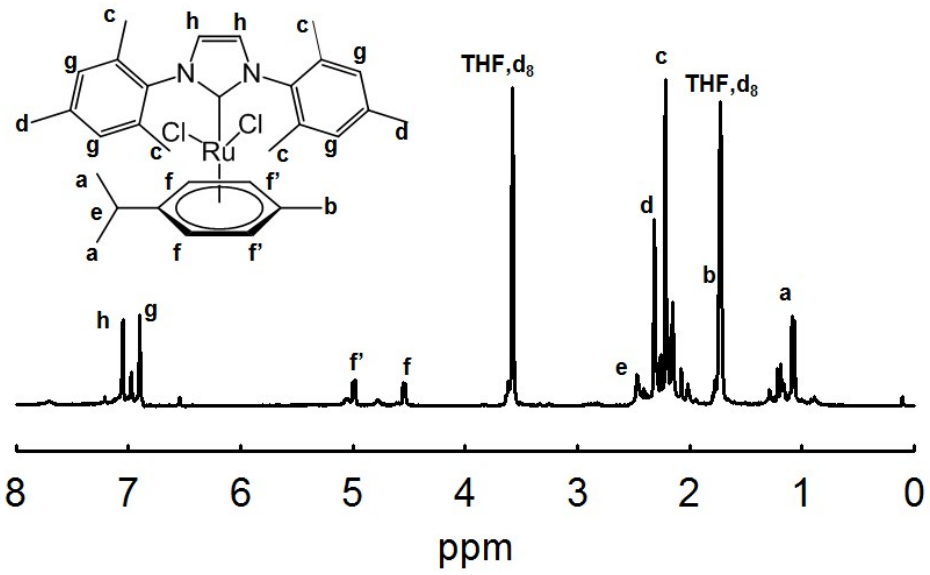

Figure S1. ^{1}H NMR spectrum of the reaction medium after reaction of [(*p-cymene*)$RuCl_2$]$_2$ (**Ru-1**, 1 equiv.) with **IMes** (2.02 equiv.) in THF-d_8 ([**Ru-1**] = 0.05 M).

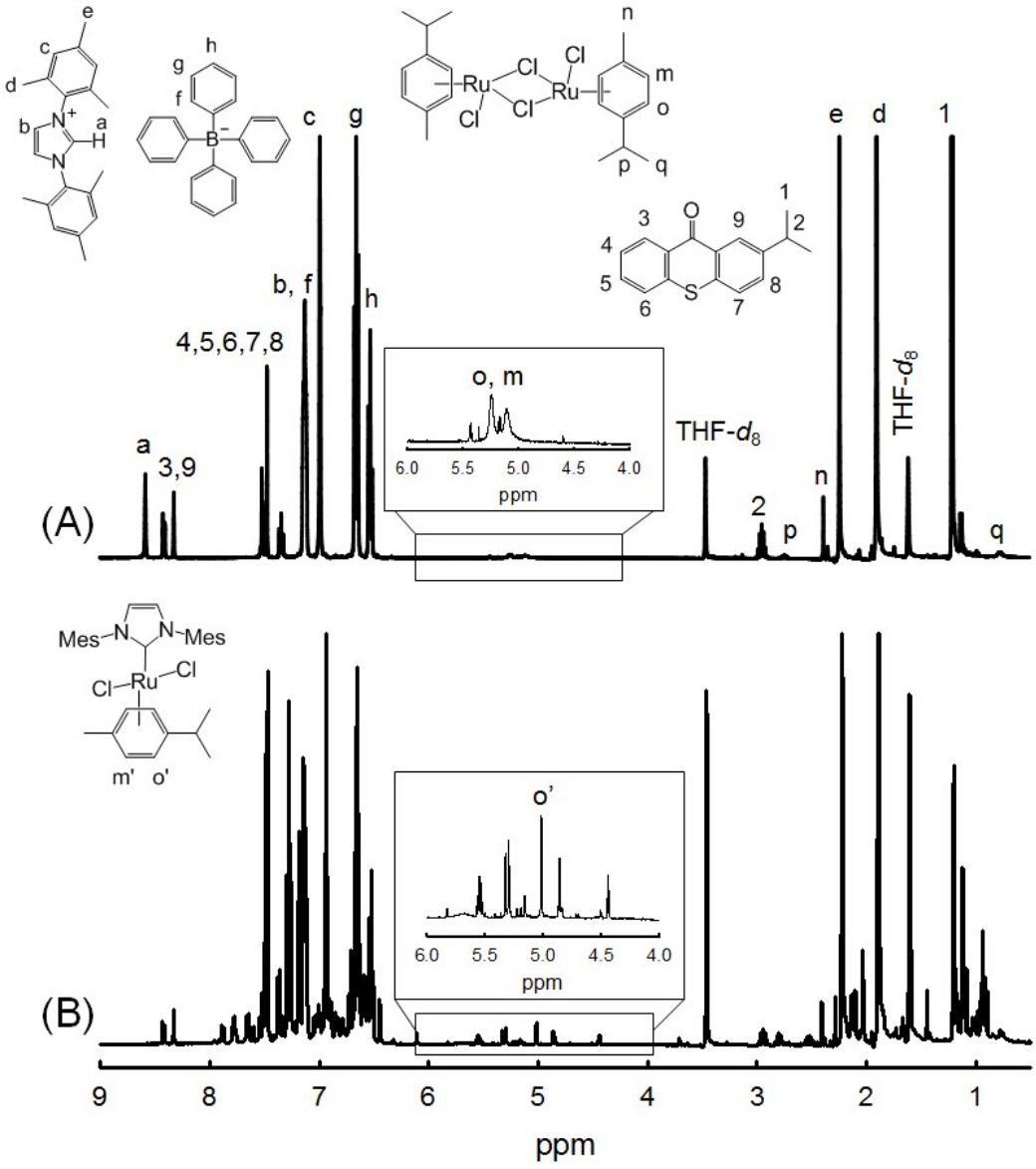

Figure S2. ^{1}H NMR of **1**/ **Ru-1**/ ITX in THF-d_8: (a) Prior to exposure to light and (b) After 30 min of irradiation (Conditions: see experimental section).

2. Photoactivated ROMP in solution

The reaction process was performed under similar conditions to those described for NB, except for irradiation time that was extended to 10 min. Indeed, we expect that a functional NB derivative such as ENB would be less reactive due to a greater steric crowding. Accordingly, only 64 % conversion was achieved after 10 min irradiation at 365 nm and lower M_n values were obtained (*entry a*)(Table S1). The influence of sensitizer concentration (*entry b*), excitation wavelength (*entry c*) and precatalyst nature (*entries d-e*) are consistent with the previous observations.

Table S1. Photopolymerization results of ENB using Ru dimer/**IMesH$^+$BPh$_4^-$**/ITX photoinitiating system in CD_2Cl_2 ([ENB] = 1 M, 510 equiv.). Irradiation conditions: 365 nm, 6.5 mW·cm^{-2}, 10 min

Entry	Precatalyst	Precatalyst/**1**/ITX (equiv.)	Conv.[a] (%)	$M_{n\text{-}th}$[c] (kg·mol^{-1})	$M_{n\text{-}SEC}$[d] (kg·mol^{-1})	$Đ$[d]
a	**Ru-1**	1/5/2.5	64	20	37.9	5.6
b	**Ru-1**	1/5/5	84	26	40.7	6.0
c[e]	**Ru-1**	1/5/2.5	11	3	28.1	4.6
d	**Ru-2**	1/5/2.5	71	22	55.6	2.7
e	**Ru-3**	1/5/2.5	78	24	31.6	4.7

[a] Determined by ^{1}H-NMR. [b] Calculated from ^{1}H-NMR spectrum, [c] Theoretical number average molar mass $M_{n\text{-}th} = Conv. \times \frac{[NB] \times M_{NB}}{2 \times [Ru-1]}$, [d] Experimental number average molar mass $M_{n\text{-}th}$ obtained by SEC, [e] Irradiation at 405 nm, 4.7 mW cm^{-2}, 10 min.

III. References

1 L. Jafarpour, J. Huang, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 3760–3763.