

Supplementary Information

Electronic vs. Steric Hindrance Effects in Amine Ligands to Ru-Based Initiators for ROMP

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Table S1. Dependence of yield, M_w and PDI on reaction time, temperature and [NBE]/[Ru] molar ratio for ROMP with **1**

time / min	Temperature / °C	[NBE]/[Ru]	Yield / %	$M_w / (10^3 \text{ g mol}^{-1})$	PDI	TON
5	25	1000	29	4	1.71	290
		3000	31	50	2.12	930
		5000	42	44	2.08	2100
		10000	18	40	1.92	1800
5	50	1000	39	230	2.08	390
		3000	49	36	1.90	1470
		5000	61	170	2.87	3050
		10000	67	340	1.90	6700
30	50	1000	85	52	3.13	850
		3000	96	64	3.50	2880
		5000	99	92	1.87	4950
		10000	97	880	1.73	9700

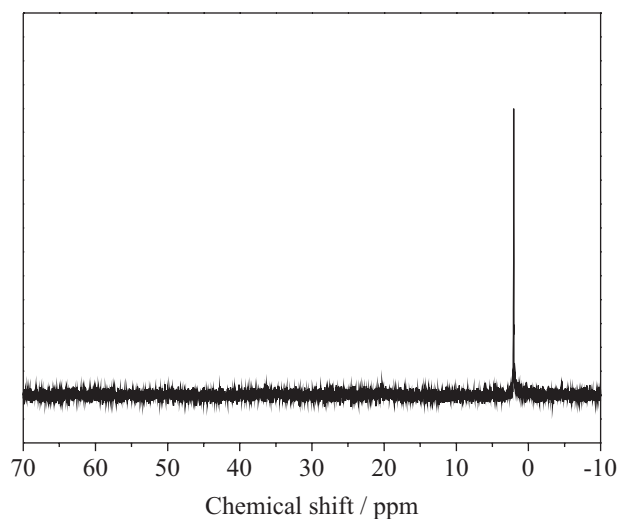
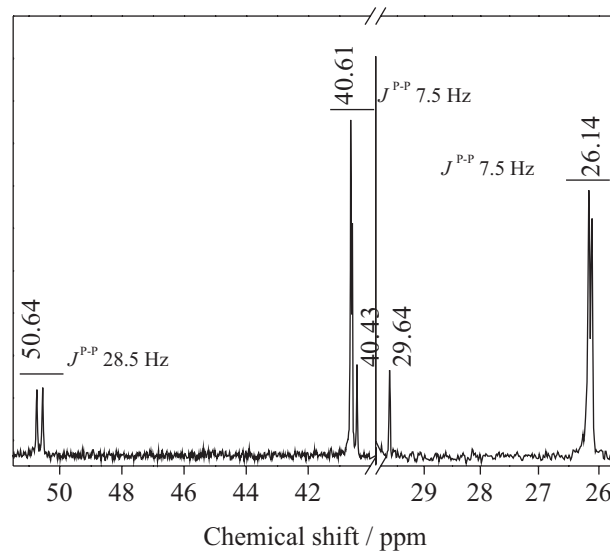
Table S2. Dependence of yield on the reaction time and temperature for ROMP of NBD with **1** and **2**; [NBD]/[Ru] = 5000

time / min	Temperature / °C	Yield / %	
		Complex 1	Complex 2
5	25	–	5
30		–	6
120		–	3
240		–	5
5	50	7	26
30		13	25
120		11	22
240		13	29

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Table S3. Data from a typical ^{13}C NMR spectrum of polyNBE obtained with **1**, **2** or **3**. $[\text{NBE}]/[\text{Ru}] = 5000$ at $25\text{ }^\circ\text{C}$ for 5 min

Chemical shift / ppm	Assignments	Relative peak areas / %		
		Complex 1	Complex 2	Complex 3
32.20	$\text{C}^{5,6} - tt$	7.68	6.26	6.57
32.35	$\text{C}^{5,6} - tc$	9.06	11.74	8.34
32.91	$\text{C}^{5,6} - ct$	8.16	7.06	7.64
33.09	$\text{C}^{5,6} - cc$	8.23	5.11	7.27
38.41	$\text{C}^{1,4} - cc$	7.45	4.95	6.79
38.65	$\text{C}^{1,4} - ct$	7.80	6.05	7.38
43.12	$\text{C}^{1,4} - tt$	8.35	10.69	7.34
43.42	$\text{C}^{1,4} - tc$	6.54	5.74	6.24
41.36	$\text{C}^7 - tt$	3.94	5.27	3.67
42.09	$\text{C}^7 - ct:tc$	6.7	5.69	6.79
42.74	$\text{C}^7 - cc$	3.94	2.37	3.82
133.02	$\text{C}^{2,3} - t$	11.43	13.7	10.14
133.92	$\text{C}^{2,3} - c$	11.19	9.85	11.20
	$\text{C}^{1,4}$	0.50	0.40	0.51
Fractions of the <i>cis</i> structures (σ_c) from the peak areas	$\text{C}^{2,3}$	0.49	0.41	0.52
	$\text{C}^{5,6}$	0.49	0.40	0.50
	C^7	0.50	0.42	0.50

**Figure S1.** ^{31}P NMR (162 MHz, CDCl_3) spectra of **1**.**Figure S2.** ^{31}P NMR (162 MHz, CDCl_3) spectra of **2**.

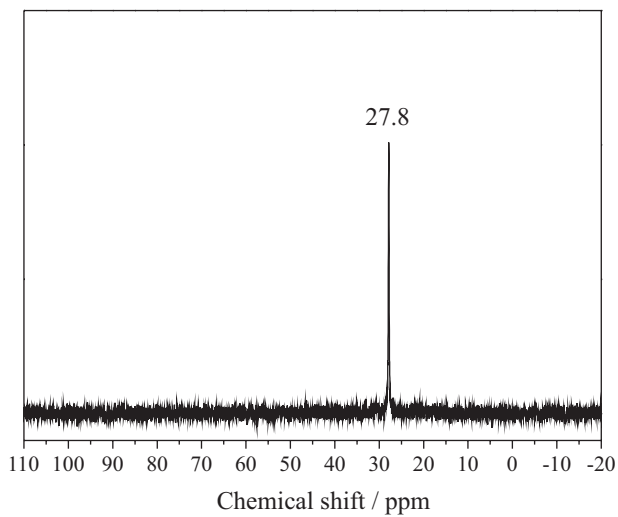


Figure S3. ^{31}P NMR (162 MHz, CDCl_3) spectra of **3**.

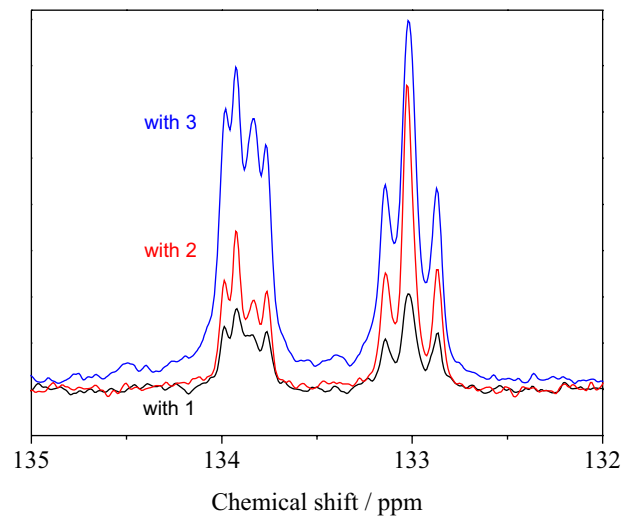


Figure S4. ^{13}C NMR (100 MHz, CDCl_3) spectra in the olefin range of polyNBE obtained with **1** (black), **2** (red) and **3** (blue line); $[\text{NBE}]/[\text{Ru}] = 5000$ at 25 °C for 5 min.