

*Supplementary Information for:*

**A Ru-Isocyanate Initiator for Fast, Living Ring-Opening Metathesis Polymerization at Ambient Temperatures**

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## 1. Experimental Details

Reactions were carried out under N<sub>2</sub> using standard Schlenk and glove-box techniques. Dry, oxygen-free solvents were obtained using a Glass Contour solvent purification system, with the exception of acetone (distilled from CaSO<sub>4</sub>). CDCl<sub>3</sub> was distilled from CaH<sub>2</sub>, and degassed by consecutive freeze/pump/thaw cycles. CD<sub>2</sub>Cl<sub>2</sub> (1-g ampoules under N<sub>2</sub>; Cambridge Isotopes) was used as received. Solvents were stored under N<sub>2</sub> over Linde 4Å molecular sieves, with the exception of hexanes (3Å sieves). NMR spectra were recorded on a Bruker Avance 300 or 500 MHz spectrometer at 298 K, and referenced to the residual signal of the deuterated solvent. Signals are reported in ppm relative to TMS (<sup>1</sup>H, <sup>13</sup>C) at 0 ppm. GPC data were measured using CH<sub>2</sub>Cl<sub>2</sub> as eluent (flow rate 1.0 mL/min; sample 1 mg/mL) on a Wyatt Technology DAWN light-scattering GPC instrument equipped with an Optilab DSP refractometer, an HPLC system with a Waters model 515 HPLC pump, Rheodyne model 7725i injector with 200 µL injection loop, and Waters Styragel HR3 and HR4 columns in series. IR spectra were recorded on a Bomem MB100 spectrometer. The succinimide-functionalized monomer **M1**,<sup>1</sup> galactose-functionalized monomer **M2**,<sup>2</sup> RuCl<sub>2</sub>(H<sub>2</sub>IMes)(3-bromopyridine)<sub>2</sub>(=CHPh) **2a**,<sup>3</sup> and RuCl<sub>2</sub>(IMes)(py)<sub>2</sub>(=CHPh) **3**<sup>4</sup> were prepared by literature methods. Silver isocyanate (Aldrich) was used without purification. Ethyl vinyl ether (Aldrich) was degassed by three freeze/pump/thaw cycles.

**Synthesis of Ru(NCO)<sub>2</sub>(IMes)(py)<sub>2</sub>(=CHPh) 5.** To a stirred green solution of RuCl<sub>2</sub>(IMes)(py)<sub>2</sub>(=CHPh) **3** (302 mg, 0.42 mmol) in 10 mL benzene in the glovebox was added solid Ag(NCO) (139 mg, 0.93 mmol, 2.2 equiv). The solution underwent a color change to emerald green within minutes, and a gray-brown precipitate deposited. The suspension was stirred for 45 min, at which time an aliquot showed complete conversion to **5** (<sup>1</sup>H NMR analysis). The solution was filtered through Celite to remove the silver salts, and the filtrate was stripped to a green residue. A minor contaminant in the crude product (<5%) was identified as [Ag(IMes)<sub>2</sub>][NCO]; see below. This was removed by reprecipitation from THF-hexanes. Yield of emerald-green **5** after filtering off and drying under vacuum: 282 mg (92%). Note: A/B subscripts in the NMR data indicate nuclei on the two distinct pyridine ligands. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ 18.72 (s, 1H, Ru=CH), 8.58 (br s, 2H, py<sub>B</sub> *o*-CH), 7.82 (br s, 2H, py<sub>A</sub> *o*-CH), 7.65 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, Ph *o*-CH), 7.48 (m, 1H, py<sub>B</sub> *p*-CH), 7.42 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 1H, Ph *p*-CH), 7.29 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 1H, py<sub>A</sub> *p*-CH), 7.07 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, Ph *m*-CH), 7.03 (s, 2H, IMes =CH), 7.00 (m, 2H, py<sub>B</sub> *m*-CH), 6.78 (m, 2H, py<sub>A</sub> *m*-CH), 6.70 (s, 4H, Mes CH), 2.17 (s, 6H, Mes *p*-CCH<sub>3</sub>), 2.17 (s, 12H, Mes *o*-CCH<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta$  318.6 (Ru=CH), 183.7 (IMes NCN), 156.4 (Mes *i*-C), 152.3 (Ph *i*-C), 151.5 ( $\text{py}_\text{A}$  *o*-C), 150.2 ( $\text{py}_\text{B}$  *o*-C), 139.4 (Mes *p*-C), 137.0 (Mes *o*-C), 136.6 (overlapping NCO,  $\text{py}_\text{A}$  *p*-C), 135.3 ( $\text{py}_\text{B}$  *p*-C), 130.1 (overlapping Ph *o*-C, *p*-C), 129.3 (Mes *m*-CH), 128.4 (Ph *m*-CH), 124.9 (IMes =CHN), 123.85 (overlapping  $\text{py}_\text{B}$  *m*-CH;  $\text{py}_\text{A}$  *m*-CH), 21.1 (Mes *p*-CH<sub>3</sub>), 18.0 (Mes *o*-CH<sub>3</sub>). IR (Nujol,  $\text{cm}^{-1}$ ): 2230 (m, NCO). Anal. calcd. for  $\text{C}_{40}\text{H}_{40}\text{N}_6\text{O}_2\text{Ru}$ : C, 65.11; H, 5.46; N, 11.39 %. Found: C, 64.95; H, 5.69; N, 11.19 %. X-ray quality crystals were grown from a saturated THF solution by vapour diffusion of hexanes at  $-35^\circ\text{C}$ . For crystallographic data, see Section 2 below.

**Synthesis of  $[\text{Ag}(\text{IMes})_2][\text{NCO}]$ .** Solid IMes (871 mg, 2.9 mmol, 2.1 equiv) was added to a stirred suspension of Ag(NCO) (213 mg, 1.4 mmol) in acetone (1 mL) at RT. Reaction was complete after 1.5 h (NMR). The red solution was filtered through Celite, stripped to an oily red residue, and treated with diethyl ether to precipitate a cream-coloured solid, leaving a red supernatant. The precipitate was filtered off and reprecipitated ( $\text{CH}_2\text{Cl}_2$ -hexanes) to afford a white powder. Yield: 674 mg (63%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.15 (d,  $^4J_{\text{HAg}} = 1.5$  Hz, 4H, IMes =CH), 6.90 (s, 8H, Mes CH), 2.43 (s, 12H, Mes *p*-CH<sub>3</sub>), 1.72 (s, 24H, Mes *o*-CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  182.0 (overlapping doublets,  $^1J(\text{C}-^{107}\text{Ag}) = 180$  Hz;  $^1J(\text{C}-^{109}\text{Ag}) = 208$  Hz, NCN), 139.8 (Mes *i*-C), 135.1 (NCO), 134.5 (Mes *p*-CCH<sub>3</sub>), 129.6 (Mes CH), 122.8 (IMes =CH), 122.7 (Mes *o*-CCH<sub>3</sub>), 21.1 (Mes *p*-CH<sub>3</sub>), 17.6 (Mes *o*-CH<sub>3</sub>). IR (Nujol,  $\text{cm}^{-1}$ ): 2205 (m,  $\nu(\text{NCO})$ ). MALDI-MS, *m/z*: positive ion mode: Calcd. for  $[\text{Ag}(\text{IMes})_2]^+$ : 715.3; Found, 715.1.  $^1\text{H}$  NMR chemical shifts agree with data reported<sup>5-8</sup> for  $[\text{Ag}(\text{IMes})_2]^+$ . The 1.5 Hz splitting of the IMes NCH protons is very close to the 2.0 Hz value reported,<sup>8,9</sup> while  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts and coupling constants for the carbene carbon agree precisely with those for  $[\text{Ag}(\text{IMes})_2]\text{X}$  ( $\text{X} = \text{PF}_6^-$  and  $[\text{Ag}(\textit{closo}\text{-CB}_{11}\text{H}_{12})_2]^-$ ).<sup>6,8</sup>

**Representative procedure for ROMP at RT.** In the glovebox, a solution of **M2** (104 mg, 0.442 mmol) in THF (3 mL) was rapidly added to a green solution of **5** (32.5 mg, 0.044  $\mu\text{mol}$ , 10 mol%) in THF (3 mL). The solution was stirred vigorously until ROMP was complete, as indicated by  $^1\text{H}$  NMR analysis. The metal end-group was cleaved by stirring with excess ethyl vinyl ether (0.5 mL) for 0.5 h, after which the solution was stripped of solvent to yield a gummy brown-yellow residue. This was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  (ca. 1 mL), and the polymer was precipitated by addition of ice-cold methanol. The powder was collected by centrifugation, dried under vacuum, weighed, and analyzed by light-scattering GPC. Copolymerizations were carried out similarly, with sequential addition of **M1** and **M2**.

## 2. Crystallographic details for Ru(NCO)<sub>2</sub>(IMes)(py)<sub>2</sub>(=CHPh) **5** (CCDC number 791246)

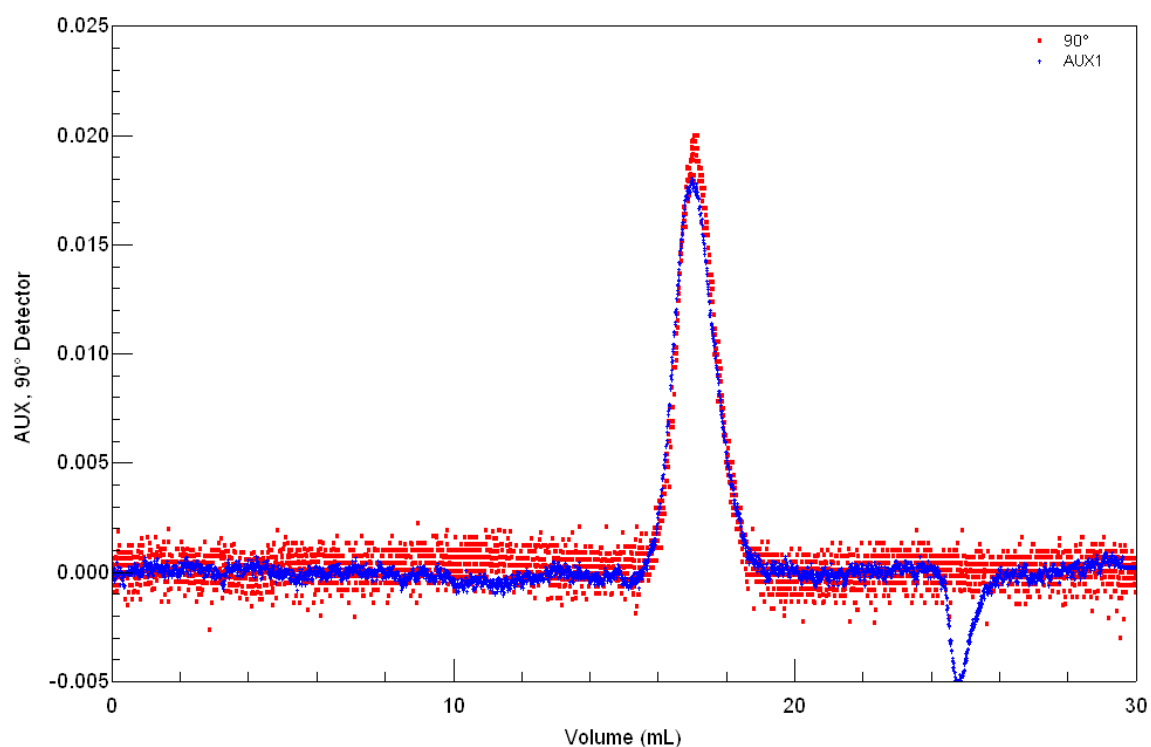
formula	C <sub>40</sub> H <sub>40</sub> N <sub>6</sub> O <sub>2</sub> Ru
formula weight	737.85
crystal dimensions (mm)	0.30 × 0.29 × 0.23
crystal system	tetragonal
space group	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2 (No. 92)
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	9.5752 (8)
<i>c</i> (Å)	39.106 (3)
<i>V</i> (Å <sup>3</sup> )	3585.4 (5)
<i>Z</i>	4
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.367
μ (mm <sup>-1</sup> )	0.481
diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	-100
scan type	ω scans (0.3°) (25 s exposures)
data collection 2θ limit (deg)	51.00
total data collected	26313 (-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -47 ≤ <i>l</i> ≤ 47)
independent reflections	3346 ( <i>R</i> <sub>int</sub> = 0.0464)
number of observed reflections ( <i>NO</i> )	3159 [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]
structure solution method	direct methods ( <i>SHELXS-97</i> <sup>c</sup> )
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup> ( <i>SHELXL-97</i> <sup>c</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8959–0.8708
data/restraints/parameters	3346 / 12 <sup>d</sup> / 288
Flack absolute structure parameter <sup>e</sup>	0.01(7)
goodness-of-fit ( <i>S</i> ) <sup>f</sup> (all data)	1.185
final <i>R</i> indices <sup>g</sup>	
<i>R</i> <sub>1</sub> [ <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	0.0452
<i>wR</i> <sub>2</sub> (all data)	0.1097
largest difference peak and hole	0.917 and -0.507 e Å <sup>-3</sup>

<sup>a</sup>Obtained from least-squares refinement of 7640 reflections with 4.74° < 2θ < 40.96°. <sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. <sup>c</sup>Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122. <sup>d</sup>C–C distances within the disordered phenyl ring were constrained to be equal (within 0.01 Å) during refinement (d(C5–C6) = d(C5–C10) = d(C6–C7) = d(C7–C8) = d(C8–C9) = d(C9–C10)), as were N–C (d(N40–C41) = d(N40–C45)) and C–C (d(C(41)–C(42) = d(C(42)–C(43) = d(C(43)–C(44) = d(C(44)–C(45)) distances within the disordered pyridine ligand. <sup>e</sup>Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

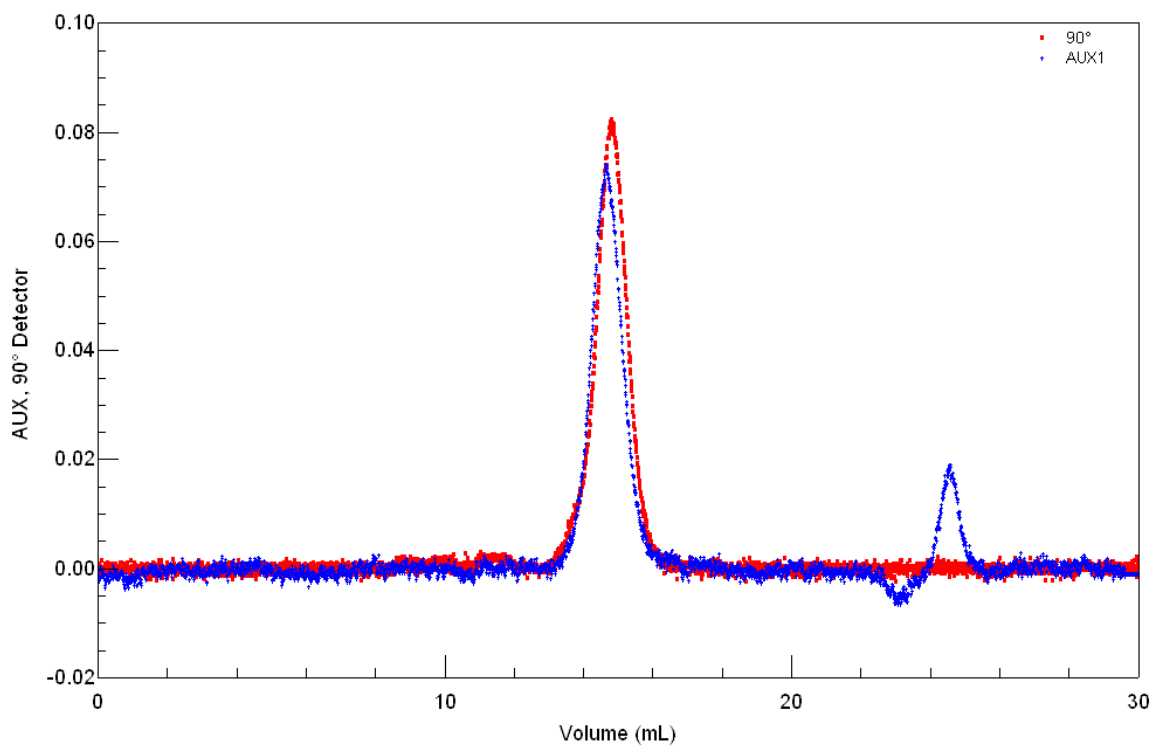
$fS = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  (*n* = number of data; *p* = number of parameters varied;  $w = [\sigma^2(F_o^2) + (0.0331P)^2 + 4.0037P]^{-1}$  where  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ ).

$gR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$ .

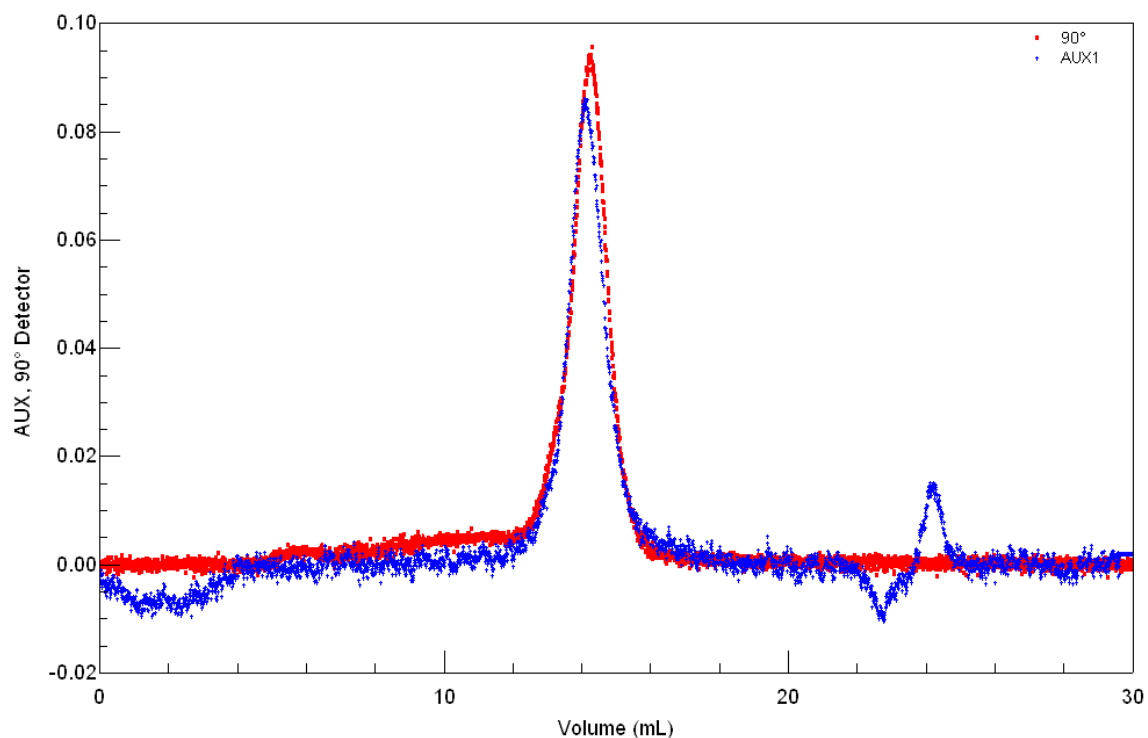
### 3. Representative GPC Traces for Polymers Prepared via Ru-NCO Initiator 5



**Figure S1.** GPC trace for [M1]<sub>10</sub> (red trace: light-scattering; blue: RI; PDI 1.03). The signal at ca. 25 min is due to the solvent front.

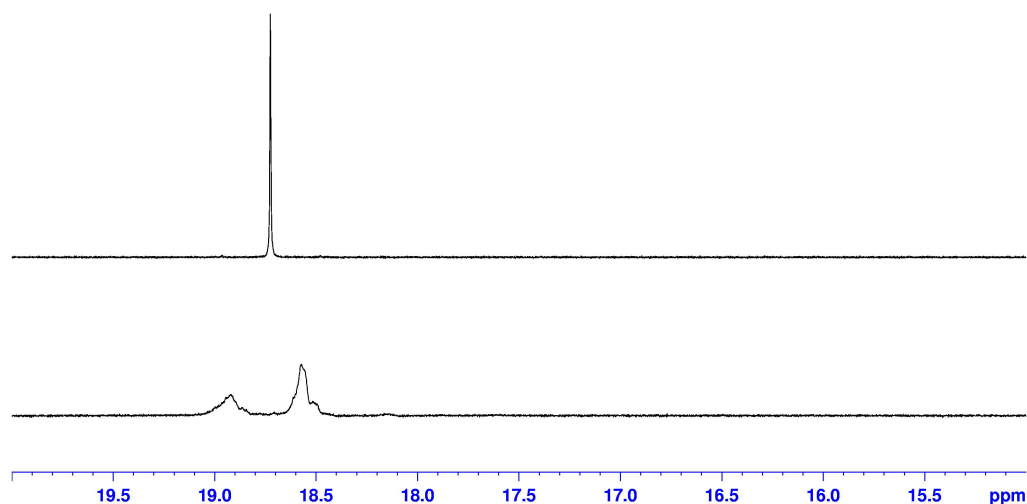


**Figure S2.** GPC trace for [M1]<sub>50</sub> (red trace: light-scattering; blue: RI; PDI 1.02). The signal at ca. 25 min is due to the solvent front.



**Figure S3.** GPC trace for  $[M1]_{25}[M2]_{25}$  (red trace: light-scattering; blue: RI; PDI 1.05). The signal at ca. 25 min is due to the solvent front.

#### 4. $^1H$ NMR Spectrum of Propagating Alkylidene from $Ru(NCO)_2(IMes)(py)_2(=CHPh)$ **5**



**Figure S4.**  $^1H$  NMR spectra (300 MHz,  $CD_2Cl_2$ ) showing the alkydene region for: (top)  $Ru(NCO)_2(IMes)(py)_2(=CHPh)$  **5**; (bottom) after adding **M1** (40 equiv). The signals for the propagating species reflect the presence of *cis/trans*, *endo/exo*, and head-to-head, head-to-tail, and tail-to-tail repeat units. These signals remain apparent after 24 h in solution under  $N_2$ .

## 5. References

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