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*Supporting information*

# Neutral lutetium complex/polyamine mediated immortal ring-opening polymerization of *rac*-lactide: facile synthesis of well-defined hydroxyl-end and amide-core stereoregular star polylactide†

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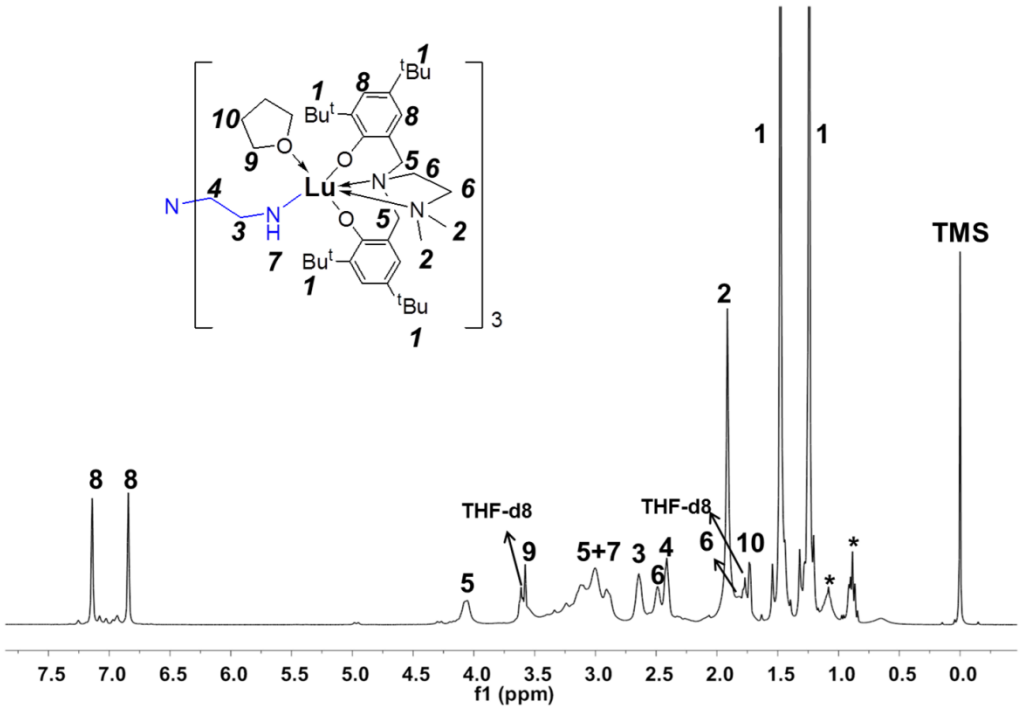


**Figure S1.** $^{1}$H NMR spectrum of complex **2** (600 MHz, THF-d8, 25°C).

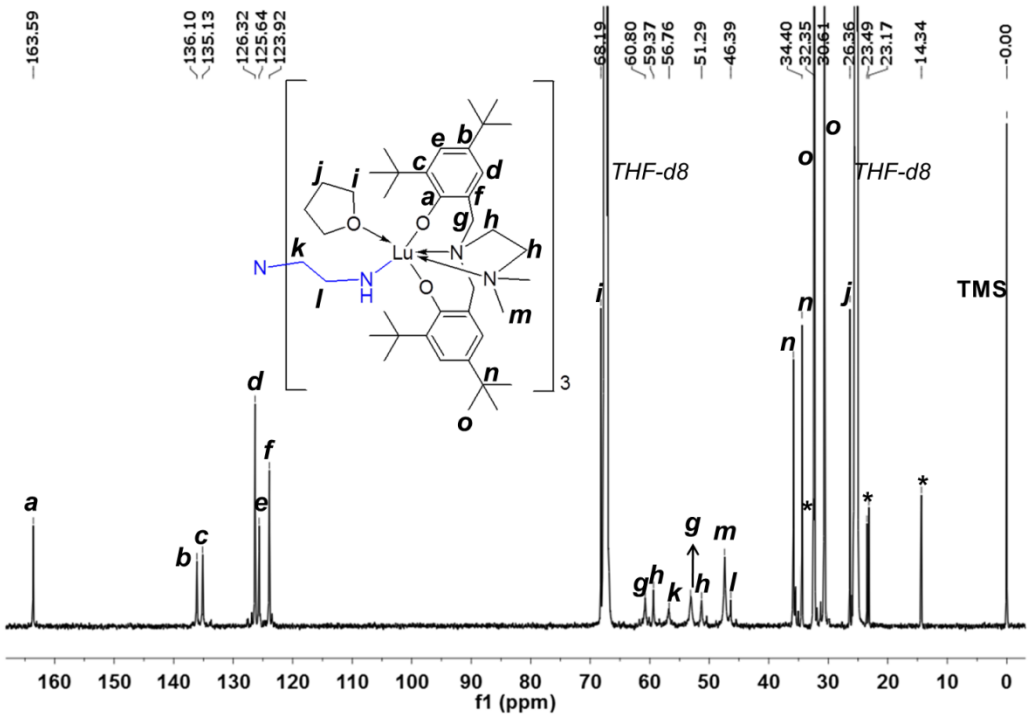


**Figure S2.** $^{13}C$ NMR spectrum of complex **2** (150 MHz, THF-d8, 25°C, * residual hexane).

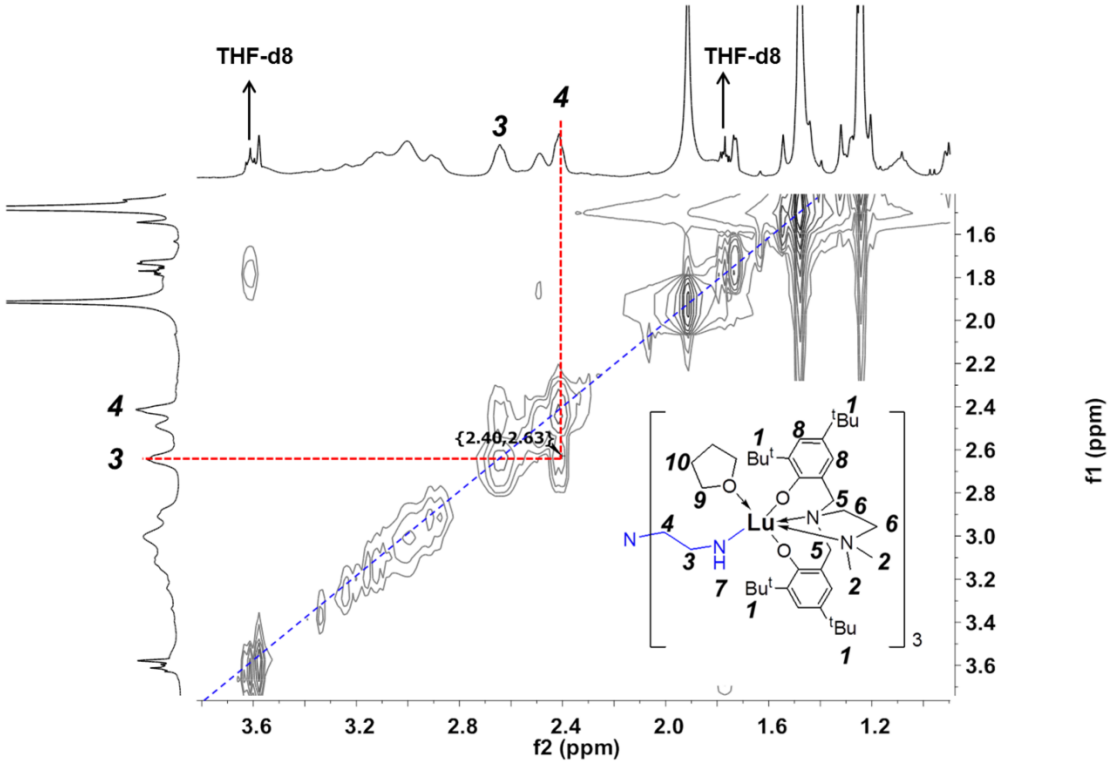


**Figure S3.** Expanded $^{1}H$-$^{1}H$ COSY NMR spectrum of complex **2** (600 MHz, THF-d8, 25°C).

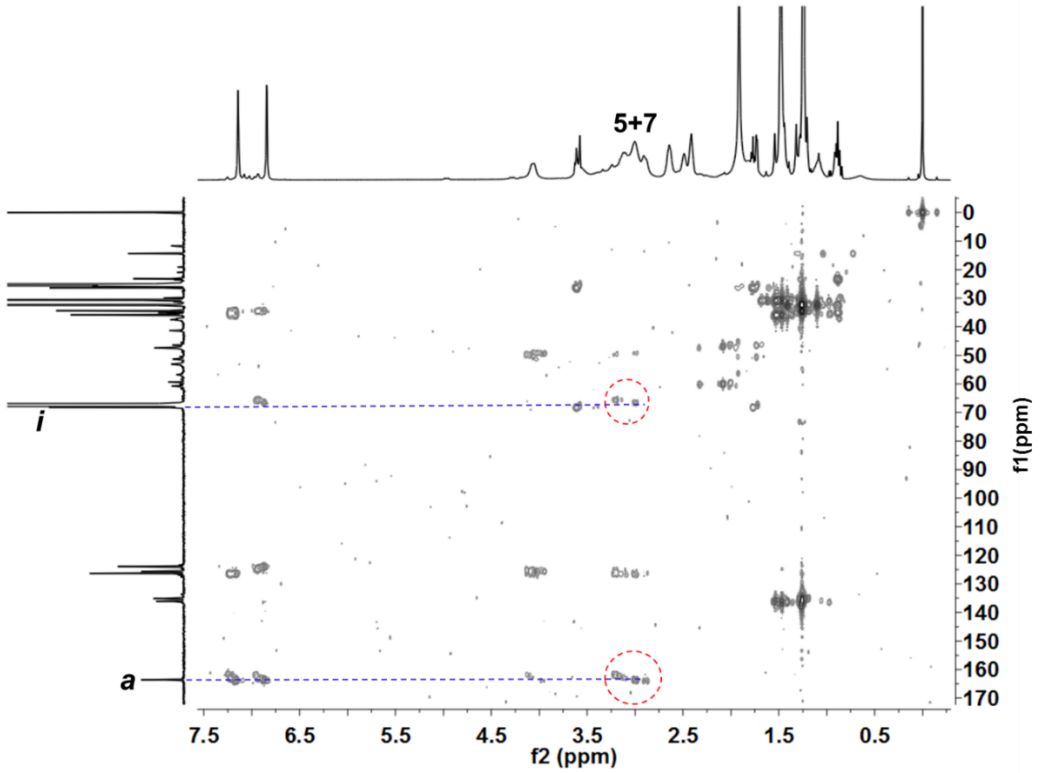


**Figure S4.** $^{1}H$-$^{13}C$ HMBC spectrum of complex **2** (600 MHz, THF-$d_8$, 25°C).

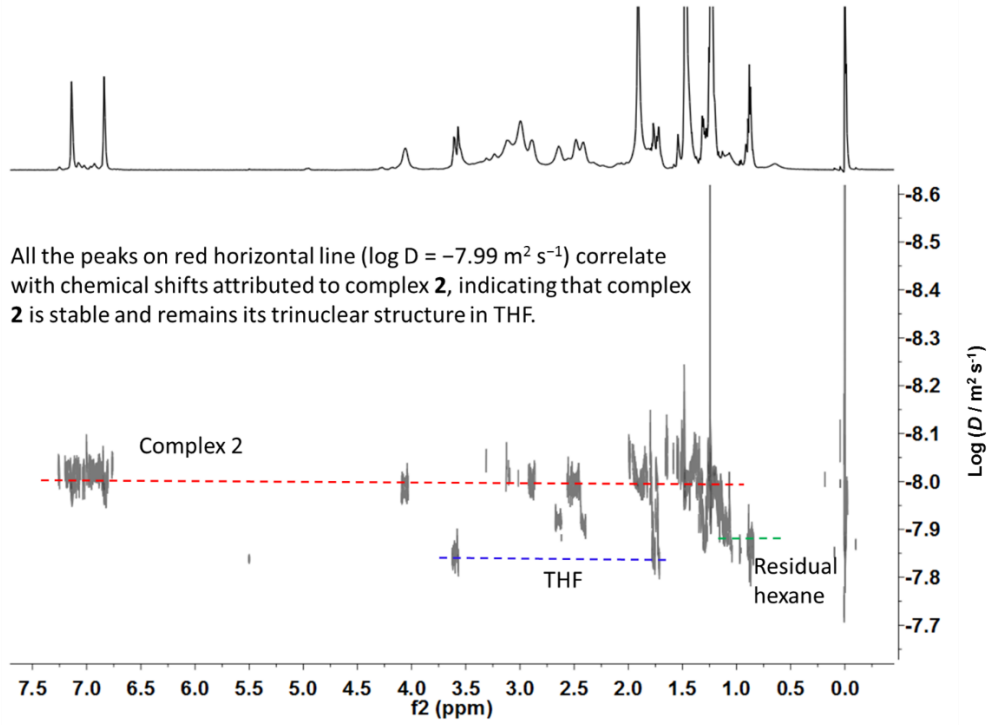


**Figure S5**. 2D DOSY spectrum of complex **2** in (600 MHz, THF-$d_8$, 25 °C). Note: the peaks on three horizontal lines correlate with the chemical shifts of complex **2**, tetrahydrofuran, and hexane (impurity), respectively. The chemical shifts from complex **2** correlate with the log D = −7.99 $m^2$ $s^{-1}$ line, indicating that complex **2** is stable and remains its trinuclear structure in solution state.

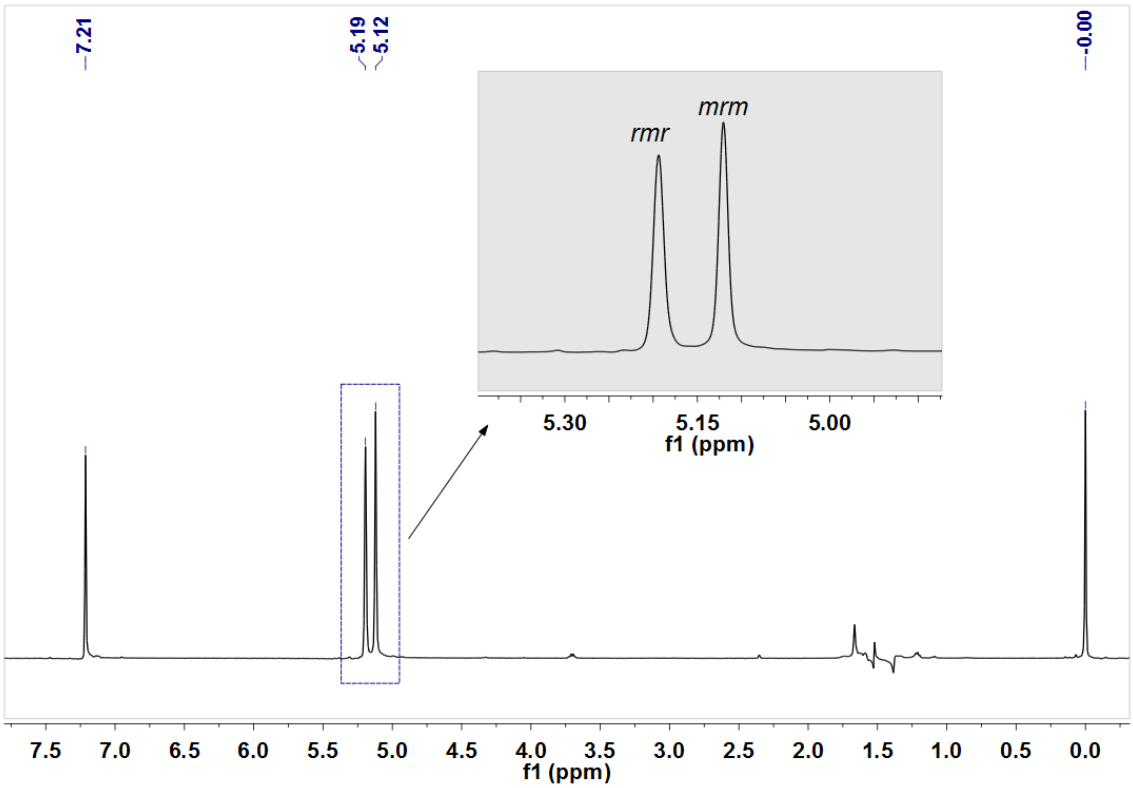


**Figure S6.** Homonuclear decoupled $^{1}H$ NMR spectra of the methine region of PLA (Table 1. Entry 1) (400 MHz, $CDCl_3$, 25°C)

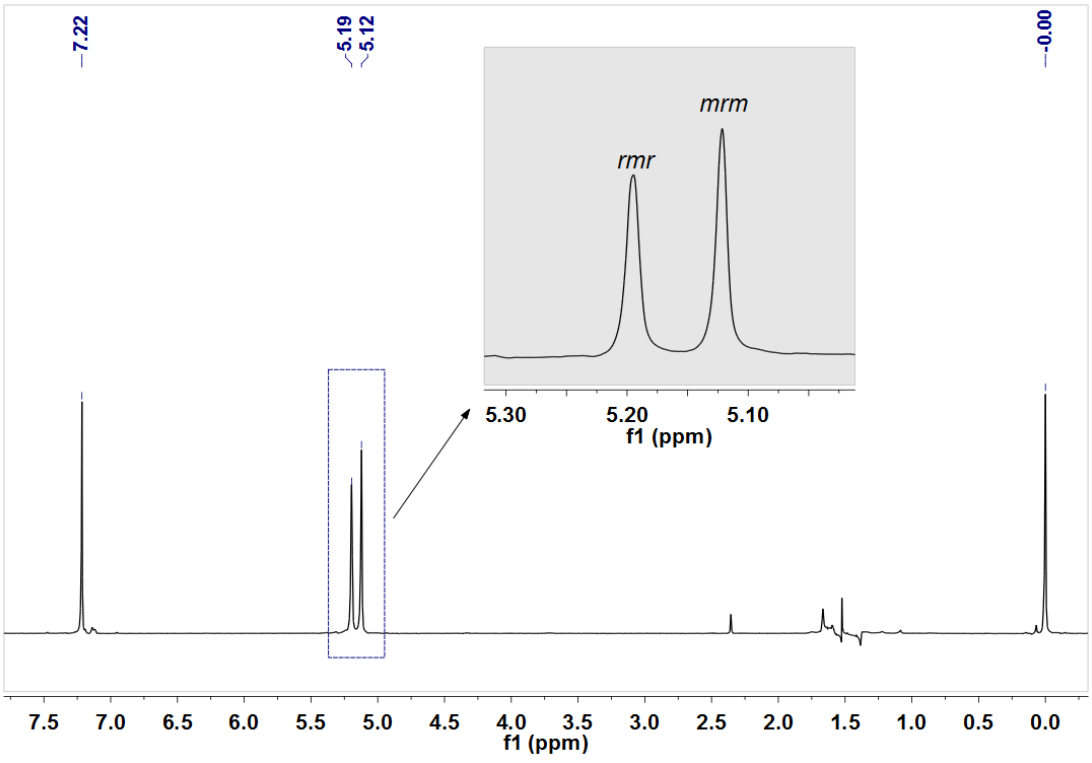

**Figure S7.** Homonuclear decoupled $^{1}H$ NMR spectra of the methine region of PLA (Table 1. Entry 4) (400 MHz, $CDCl_3$, 25°C)

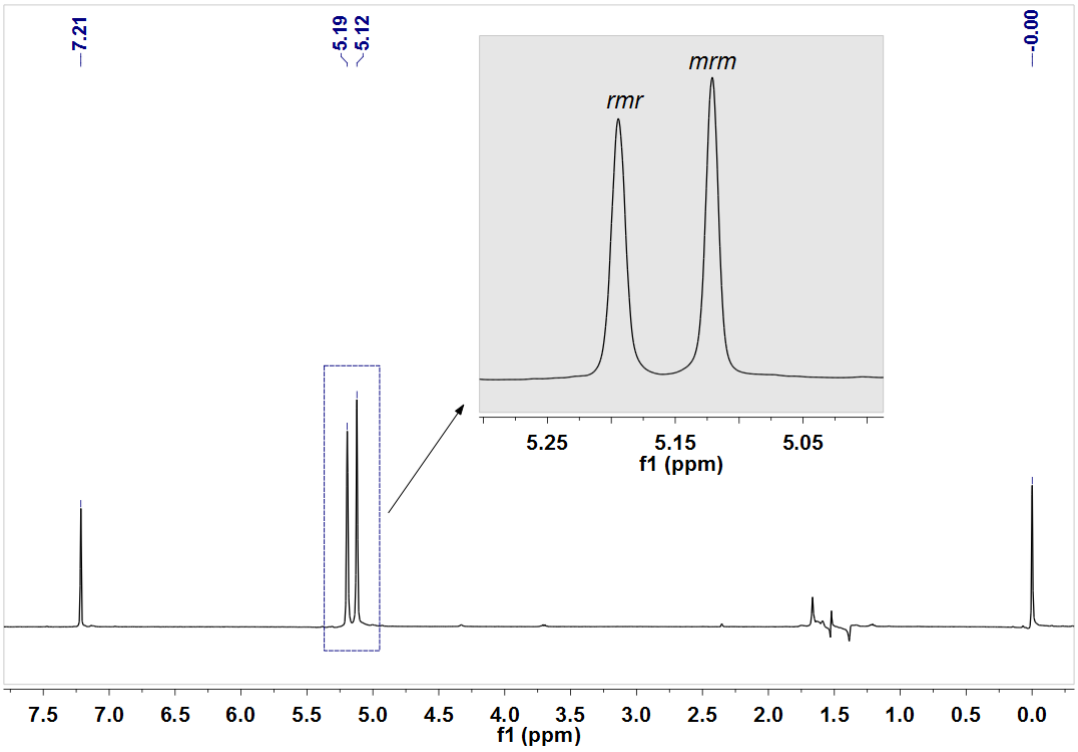


**Figure S8.** Homonuclear decoupled $^{1}H$ NMR spectra of the methine region of PLA (Table 1. Entry 6) (400 MHz, $CDCl_3$, 25°C)

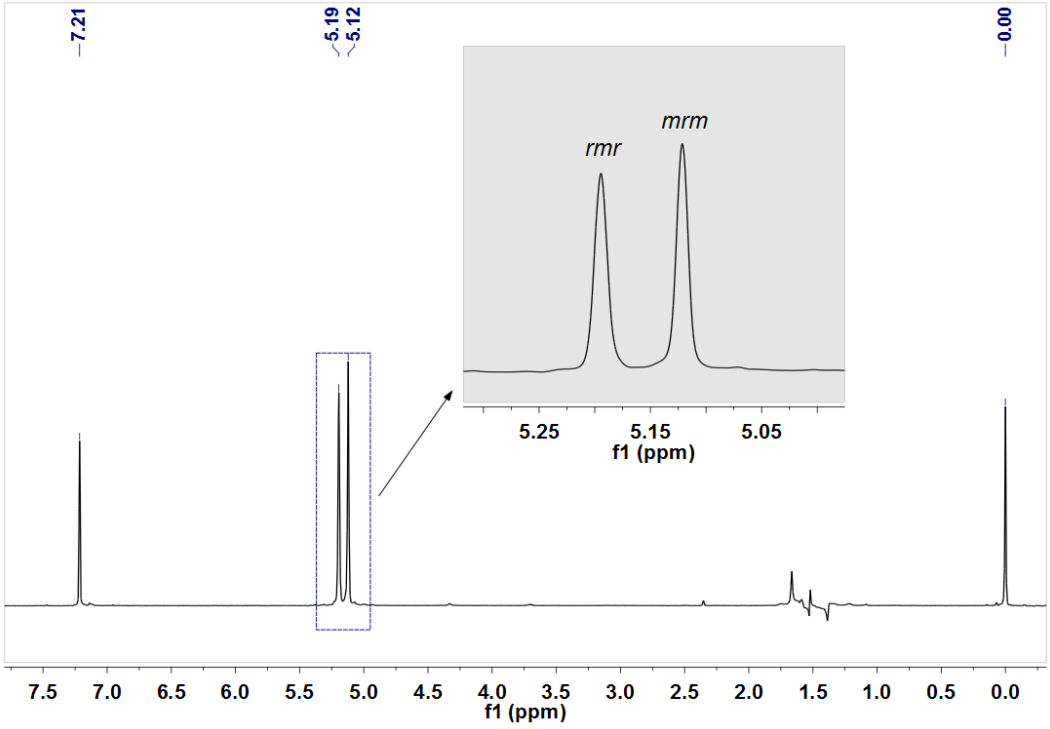

**Figure S9.** Homonuclear decoupled $^{1}H$ NMR spectra of the methine region of PLA (Table 1. Entry 9) (400 MHz, $CDCl_3$, 25°C)

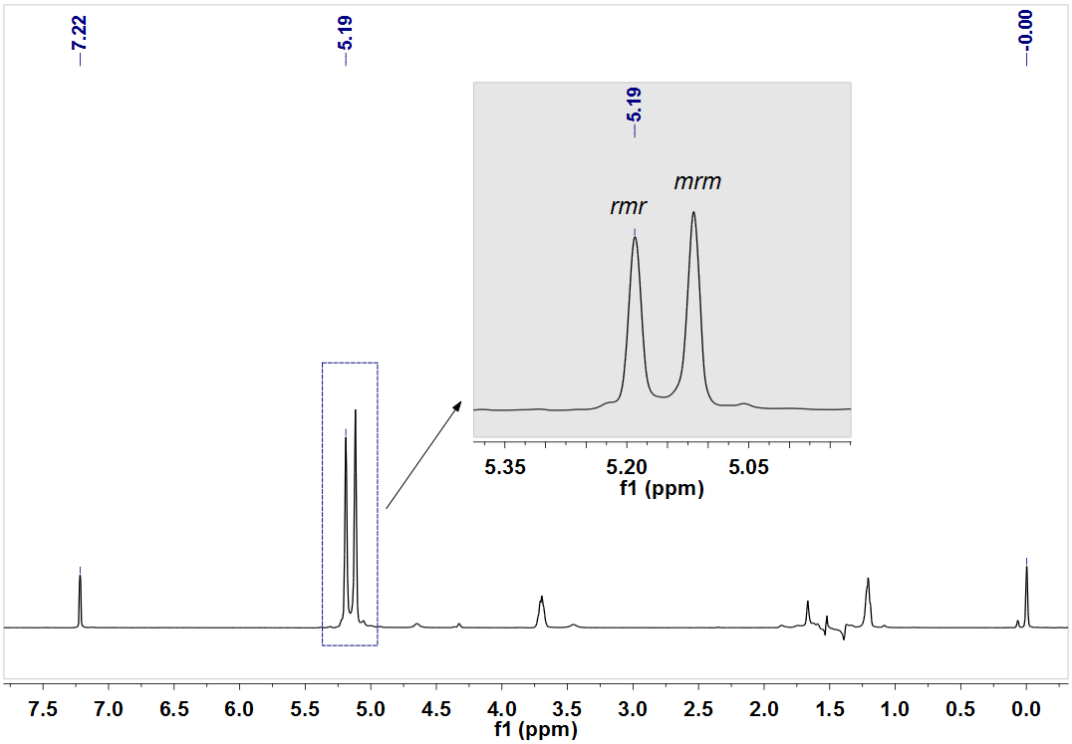


**Figure S10.** Homonuclear decoupled $^{1}H$ NMR spectra of the methine region of PLA (Table 1. Entry 10) (400 MHz, $CDCl_3$, 25°C)

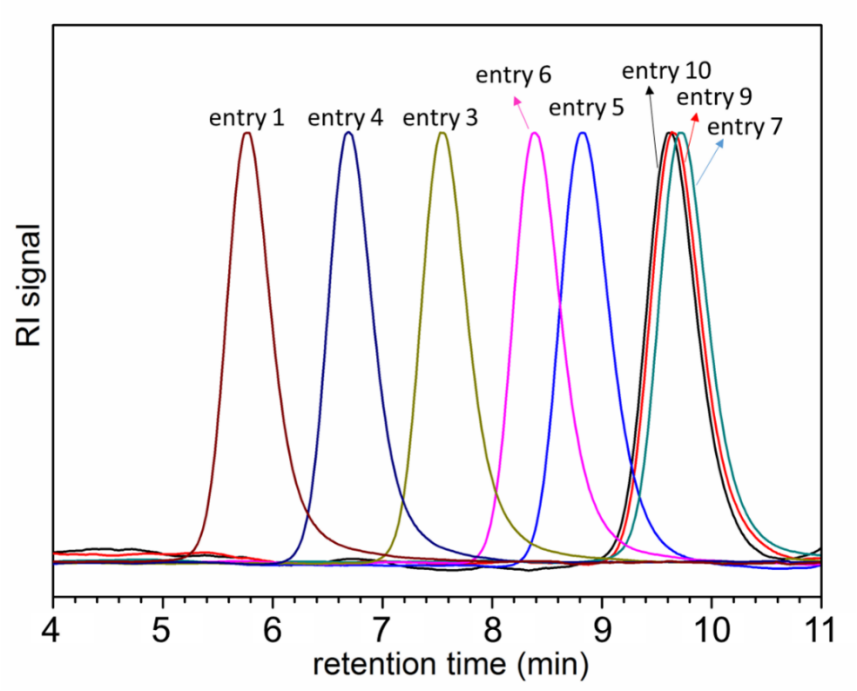


**Figure S11.** Representative GPC traces of obtained polylactides in Table 1.