Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Mechanistic Investigation of the Ring Opening Metathesis Polymerisation of Alkoxy and Alkyl Substituted Paracyclophanedienes

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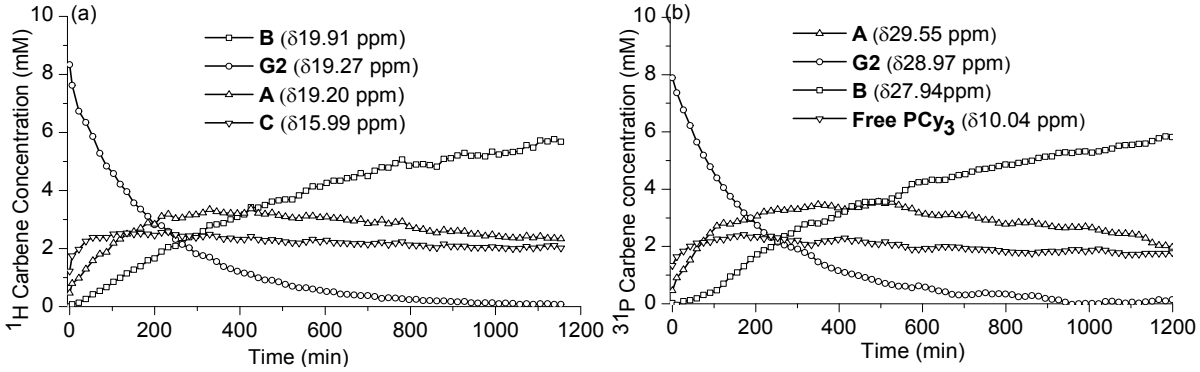

Figure S1. (a) Change of carbene concentration, H_a, H_b, H_c and **G2**, as observed by ^{1}H NMR spectroscopy, (b) change of carbene concentration and free PCy_3, as observed by ^{31}P NMR spectroscopy during ROMP initiation of **G2** with **M1** at 25 °C.

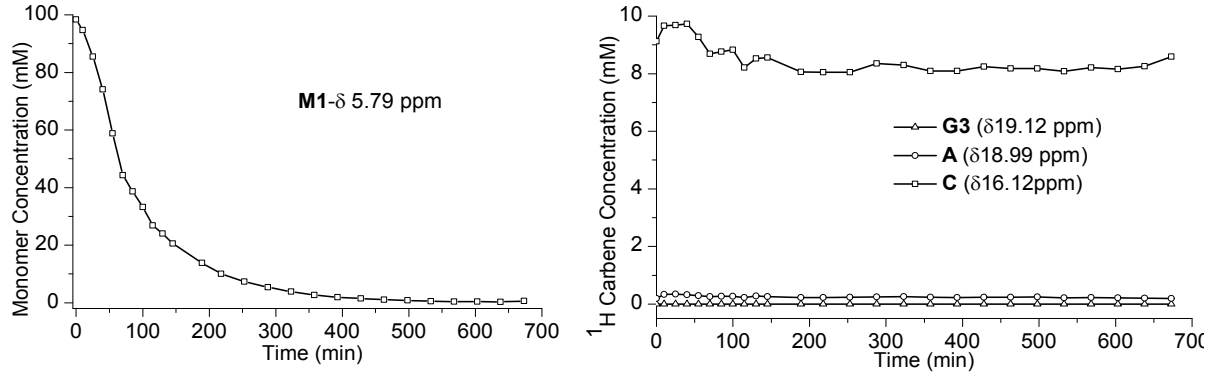

Figure S2. (a) Conversion of **M1** during ROMP with **G3** at 40 °C, (b) change of carbene concentration H_a, H_c and **G3**, as observed by ^{1}H NMR spectroscopy.

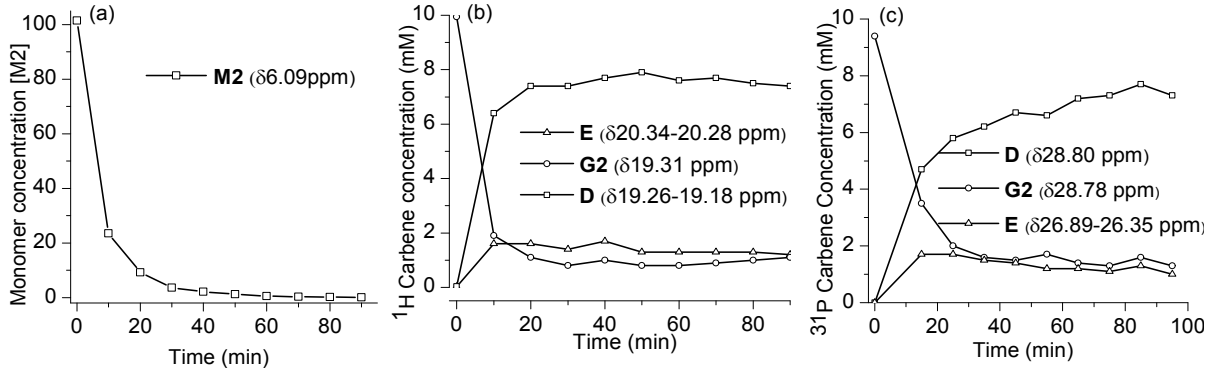

Figure S3.(a) Conversion of **M2** during ROMP with **G2** at 40 °C, (b) change of carbene concentrations, H_d, H_e and **G2**, as observed by ^{1}H NMR spectroscopy, (c) change of carbene concentrations, as observed by ^{31}P NMR spectroscopy.

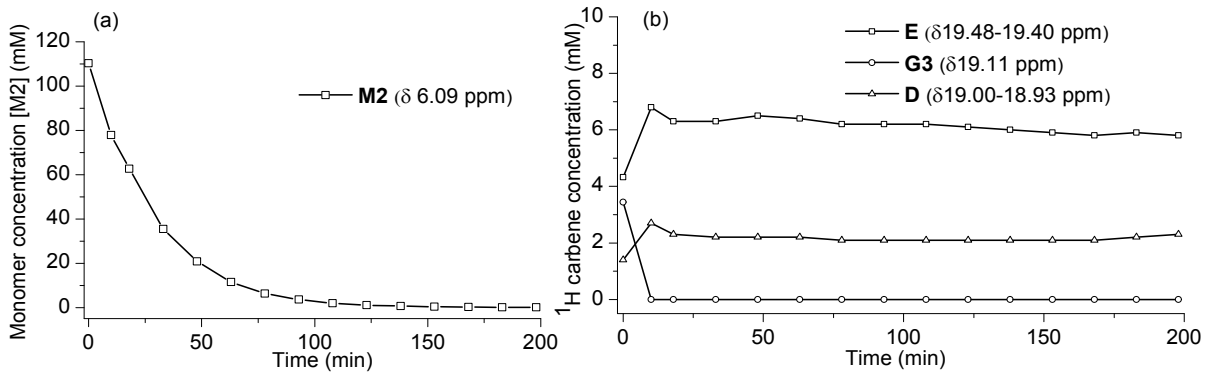

Figure S4. (a) Conversion of **M2** during ROMP with **G3** at 40 °C, (b) change of carbene concentration, H_d, H_e and **G3**, as observed by ^{1}H NMR spectroscopy.

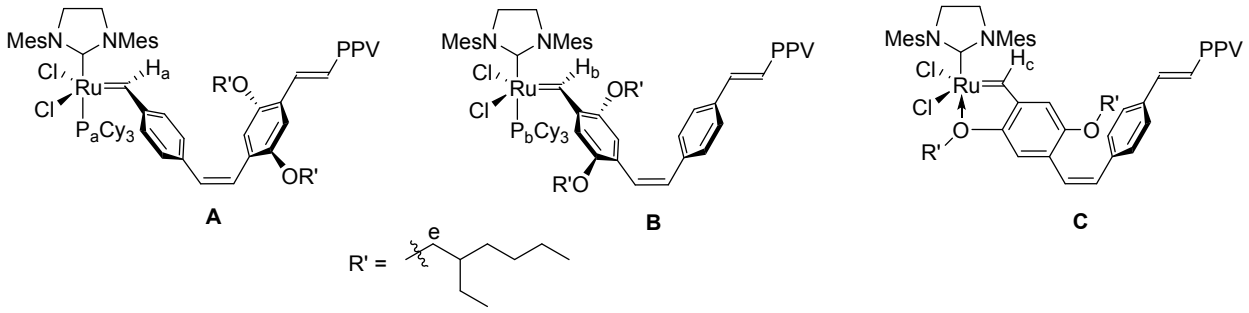

Figure S5. Resulting ruthenium carbene polymer chain ends (**A**, **B**, and **C**) during ROMP of **M1** with **G2.**

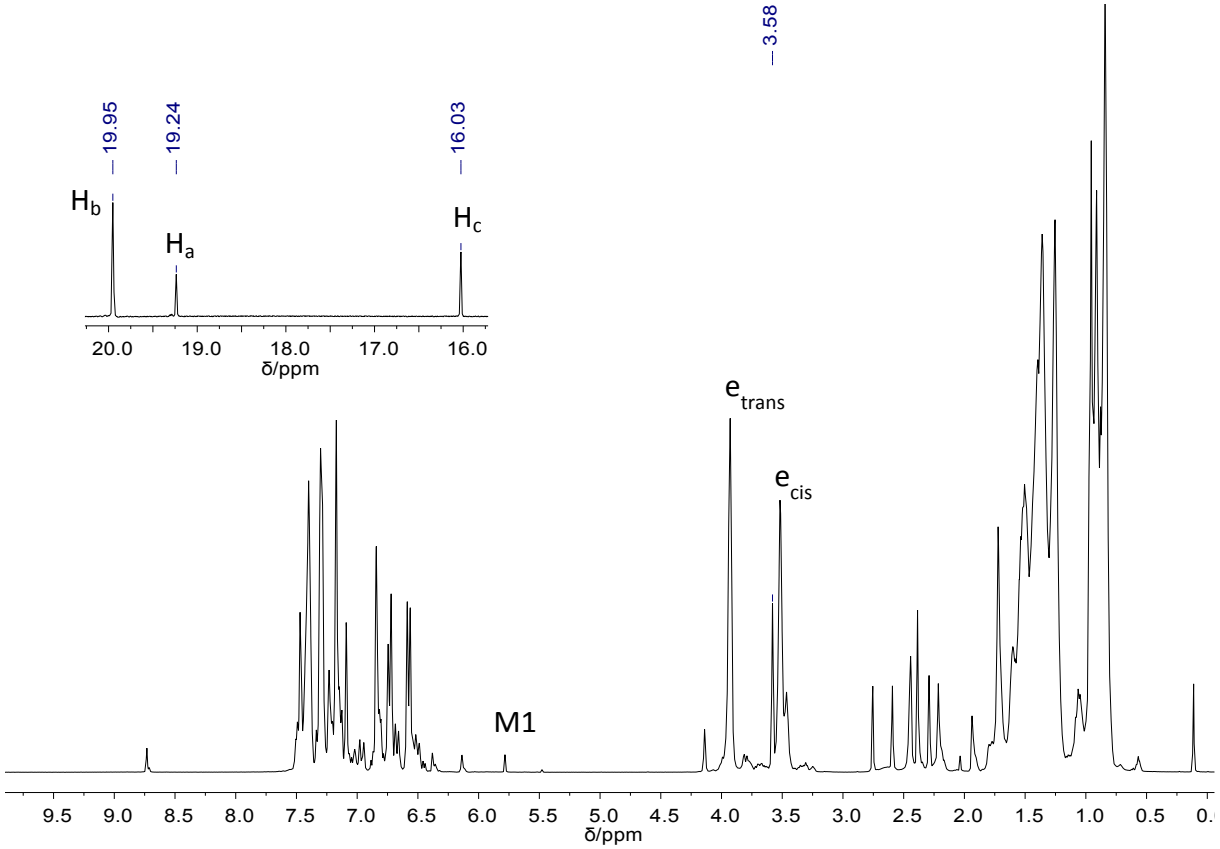

Figure S6. In-situ ROMP ^{1}H NMR (thf- d_8, 500 MHz) spectra of **M1** initiated with **G2** at 40 °C (1425 min).

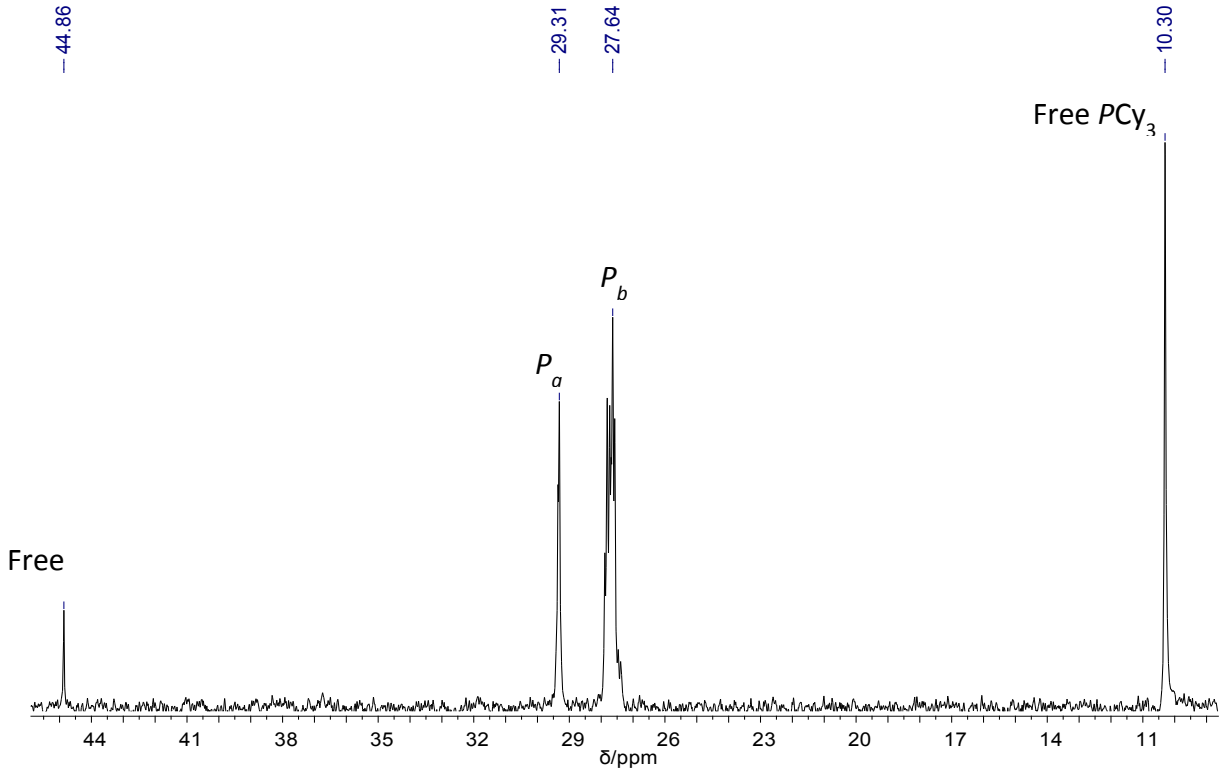

Figure S7. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) spectra of **M1** initiated with **G2** at 40 °C (1420 min).

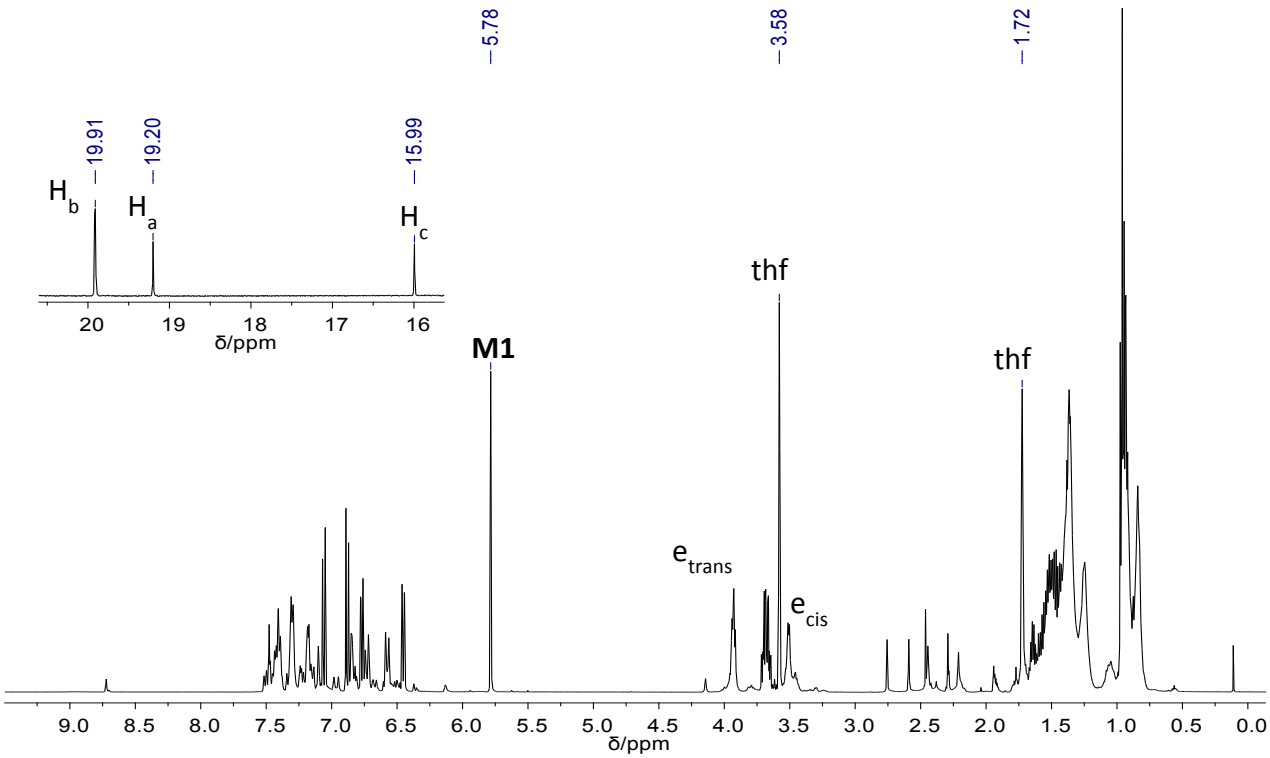

Figure S8. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M1** with **G2** at 25 °C (1000 min).

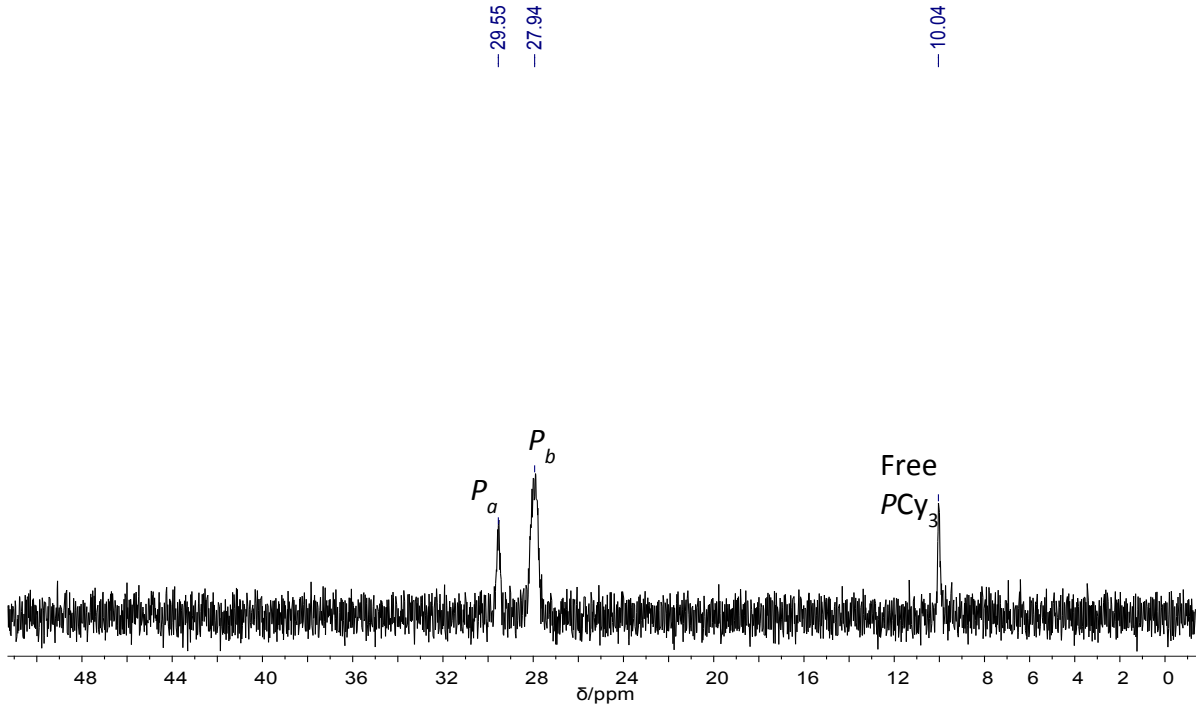

Figure S9. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) spectra of **M1** with **G2** at 25 °C (1005 min).

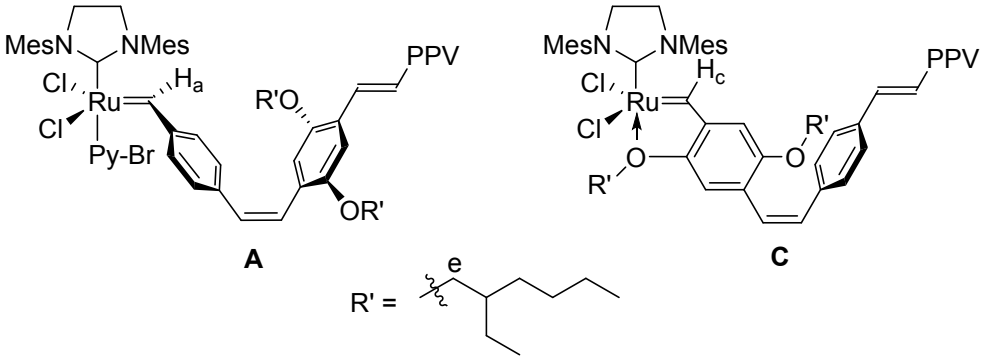

Figure S10. Resulting ruthenium carbene polymer chain ends (**A** and **C**) during ROMP of **M1** with **G3.**

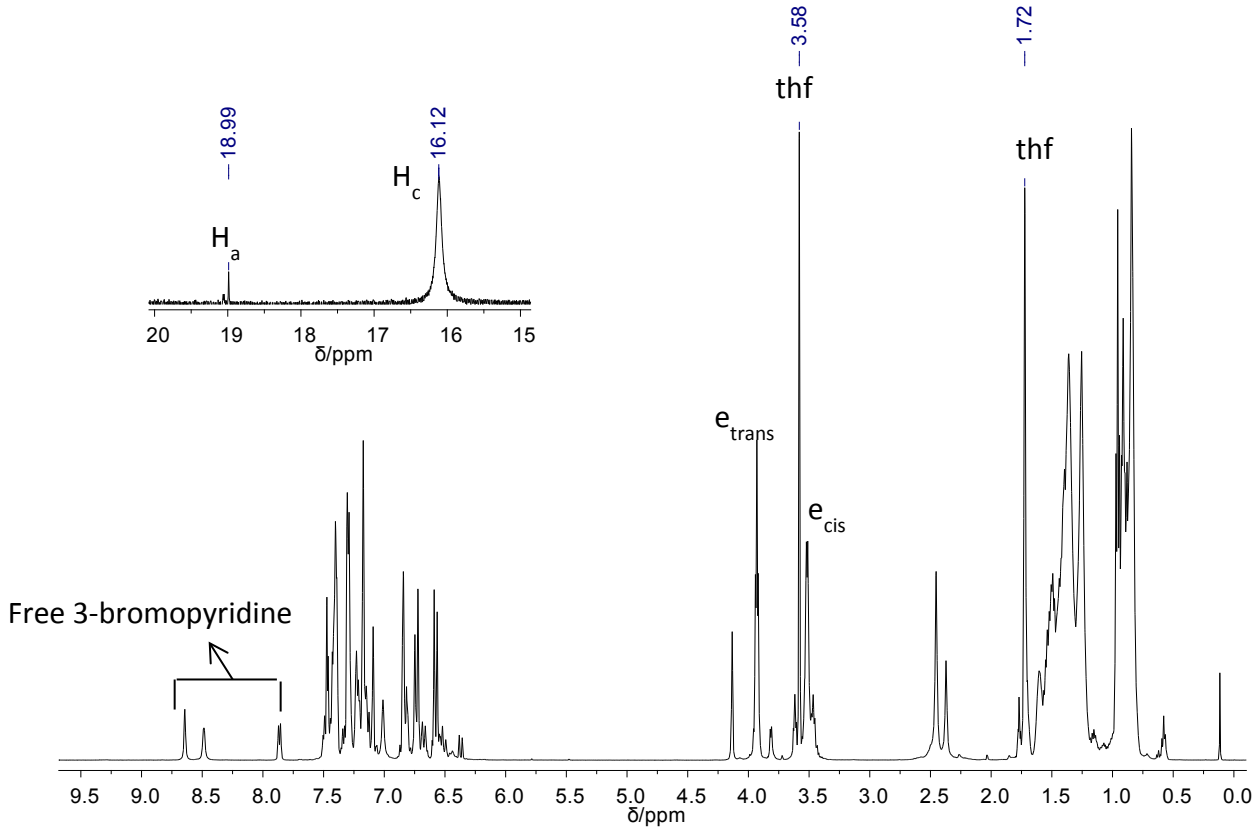

Figure S11. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M1** with **G3** at 40 °C (650 min).

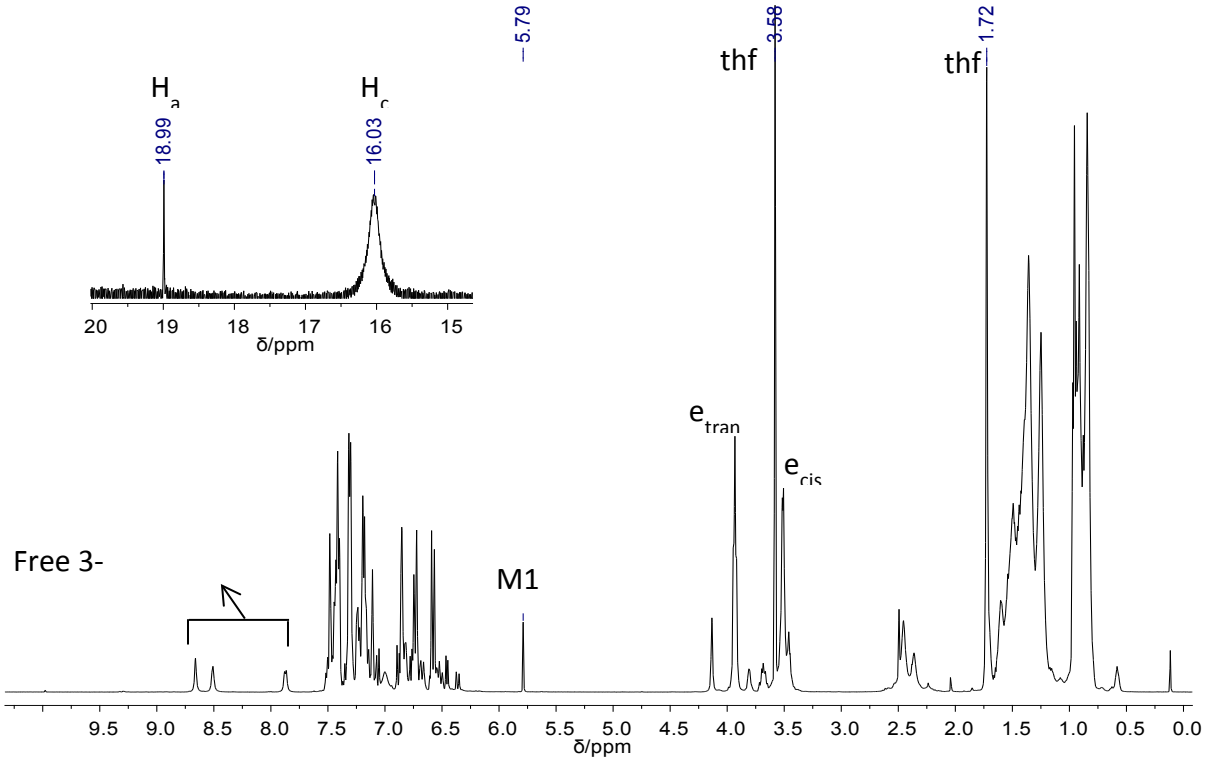

Figure S12. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M1** with **G3** at 25 °C (4000 min).

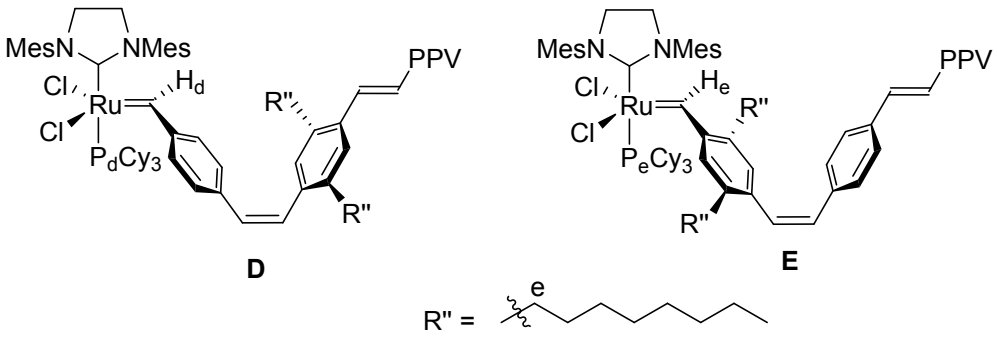

Figure S13. Resulting ruthenium carbene polymer chain ends (**D** and **E**) during ROMP of **M2** with **G2.**

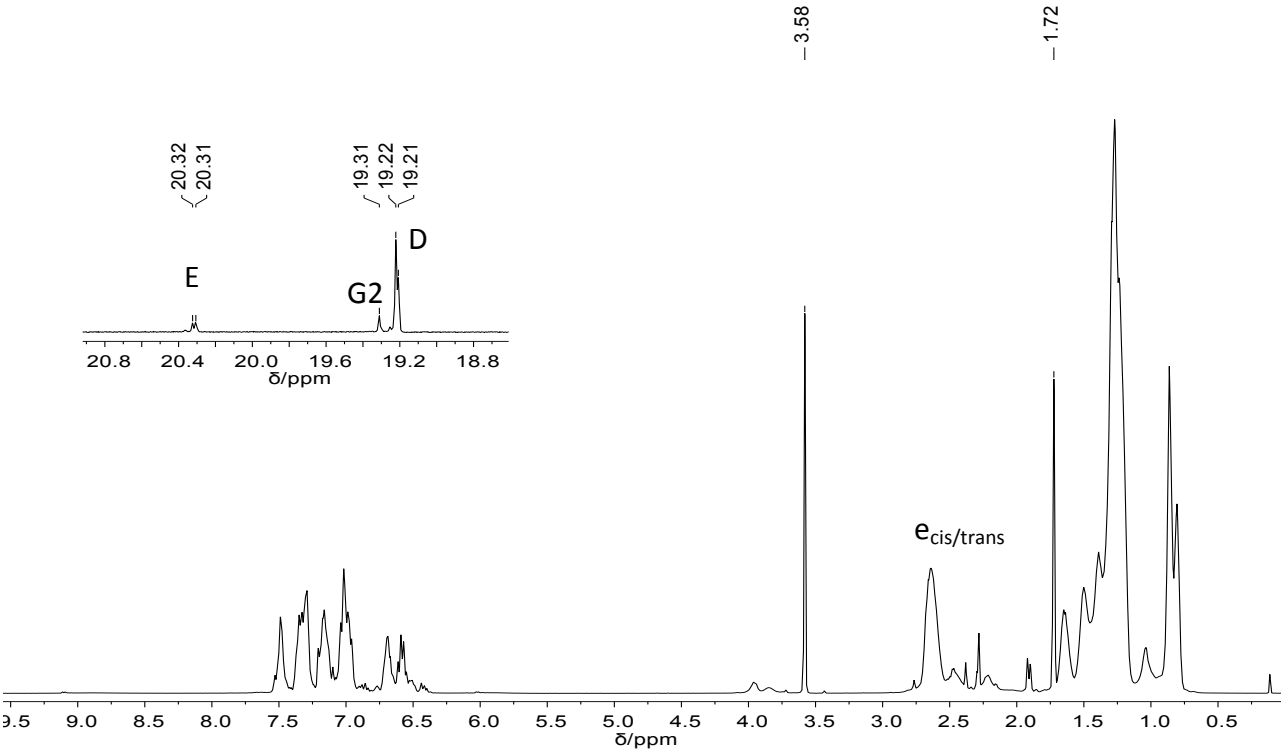

Figure S14. In-situ ROMP ^{1}H NMR (thf-d8, 500 MHz) spectra of **M2** with **G2** at 40 °C (90 min).

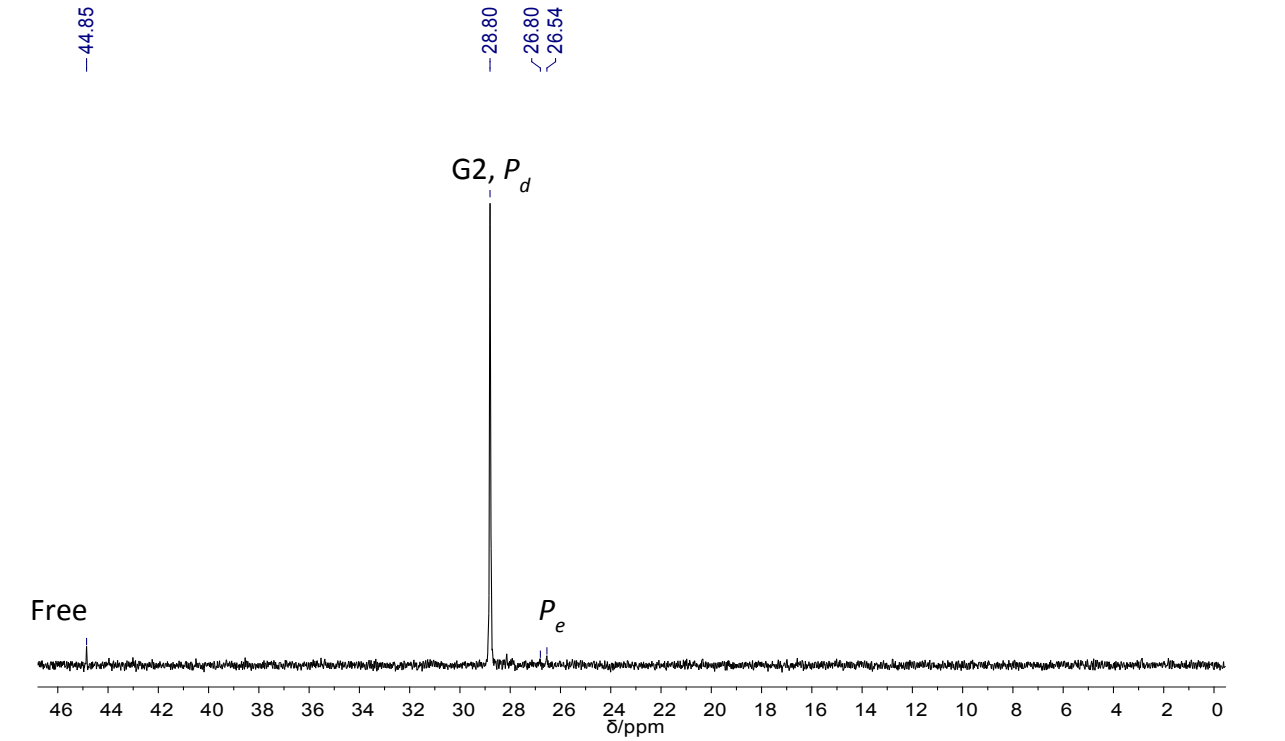

Figure S15. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) spectra **M2** with **G2** at 40 °C (95 min).

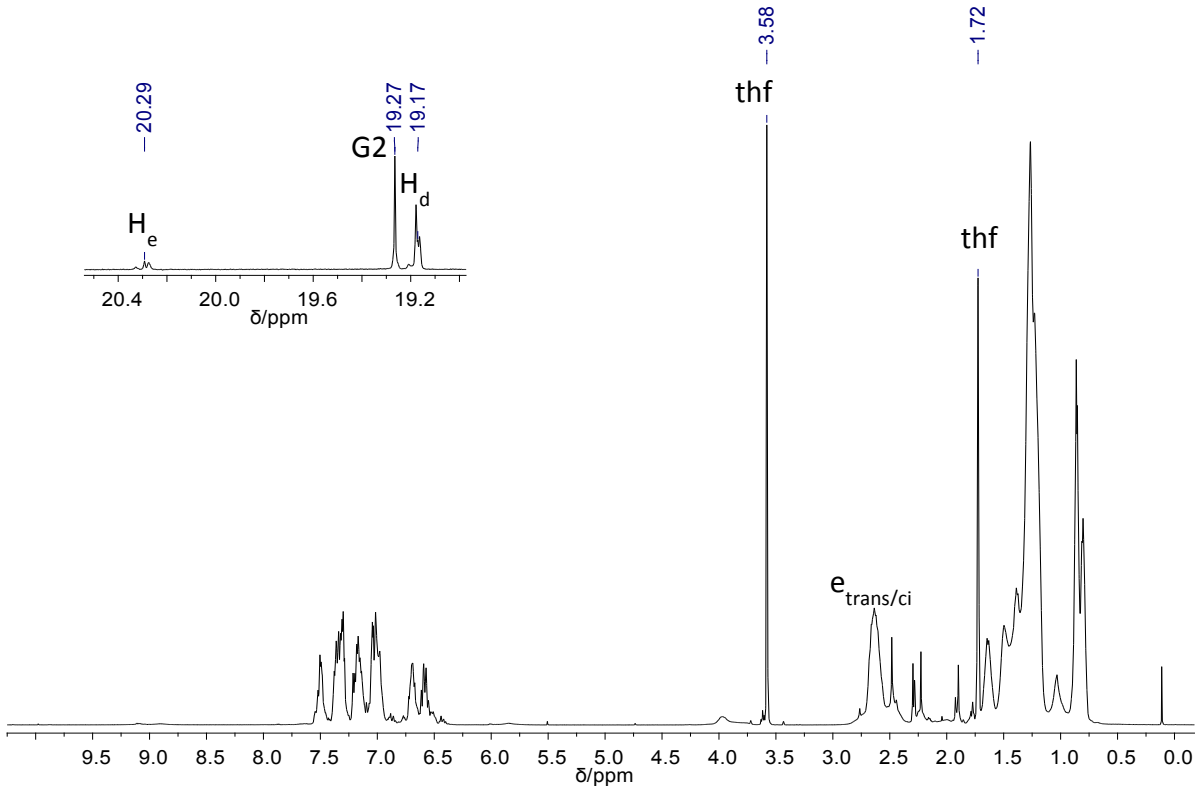

Figure S16. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M2** with **G2** at 25 °C (210 min).

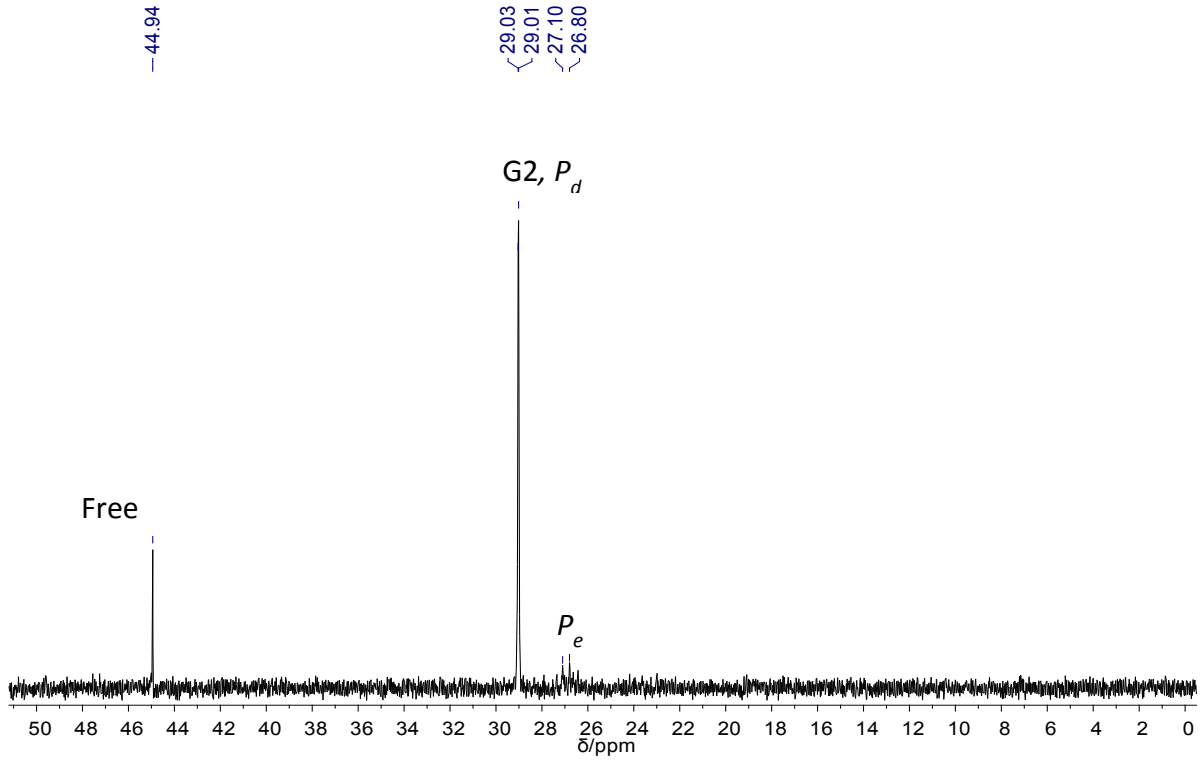

Figure S17. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) spectra **M2** with **G2** at 25 °C (215 min).

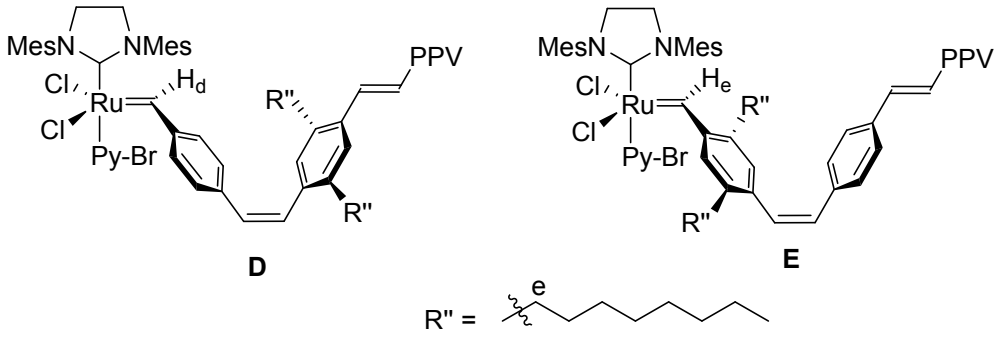

Figure S18. Resulting ruthenium carbene polymer chain ends (**D** and **E**) during ROMP of **M2** with **G3.**

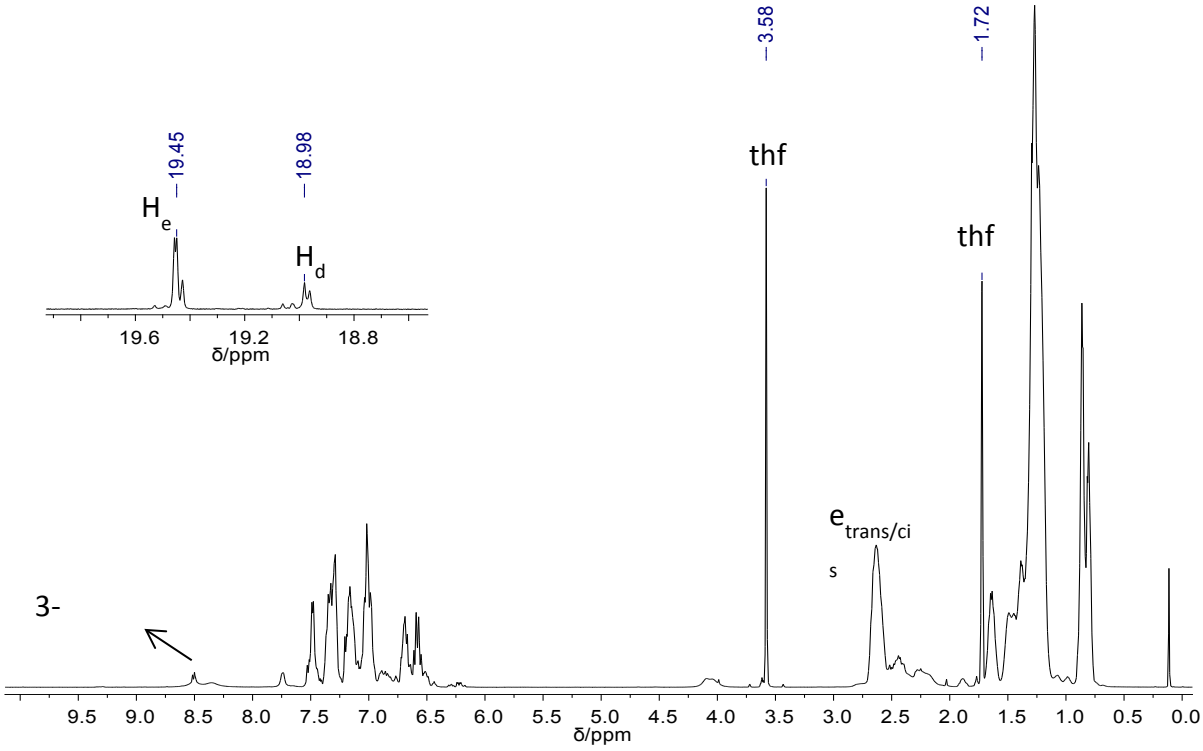

Figure S19. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M2** with **G3** at 40 °C (200 min).

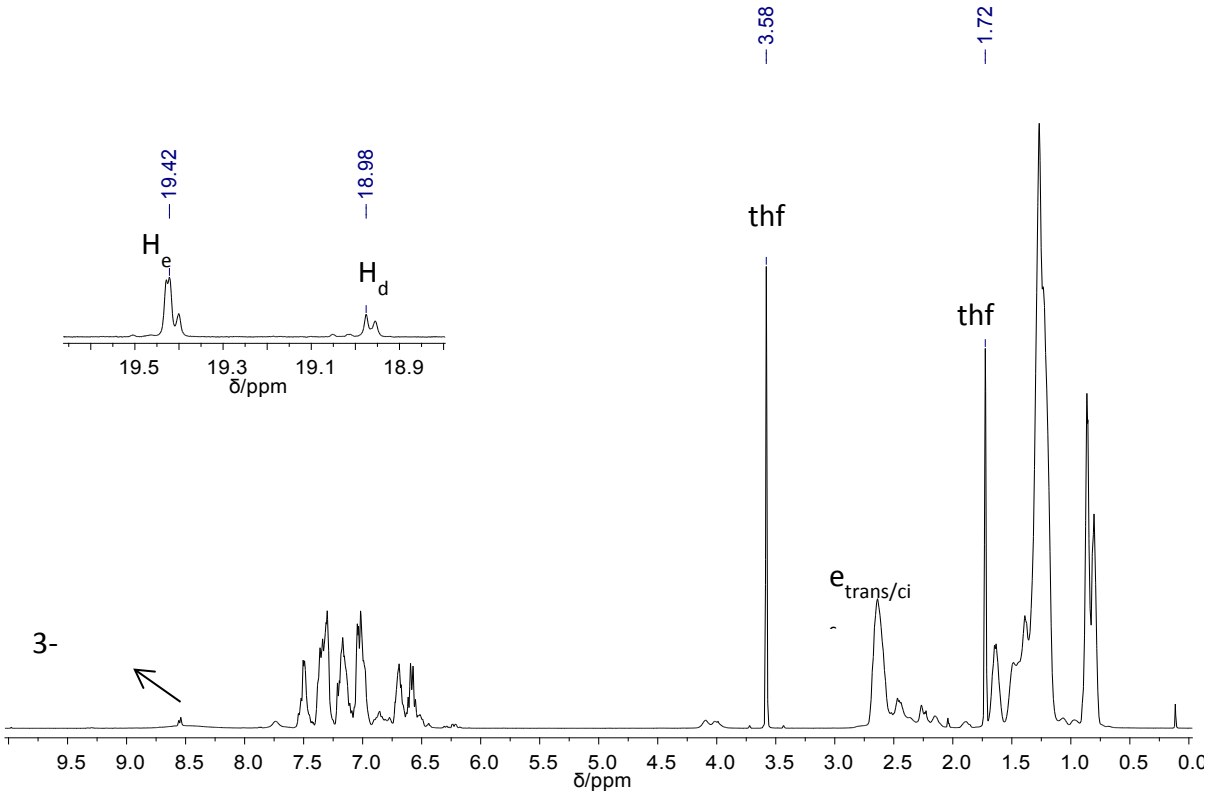

Figure S20. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) spectra of **M2** with **G3** at 25 °C (1000 min).

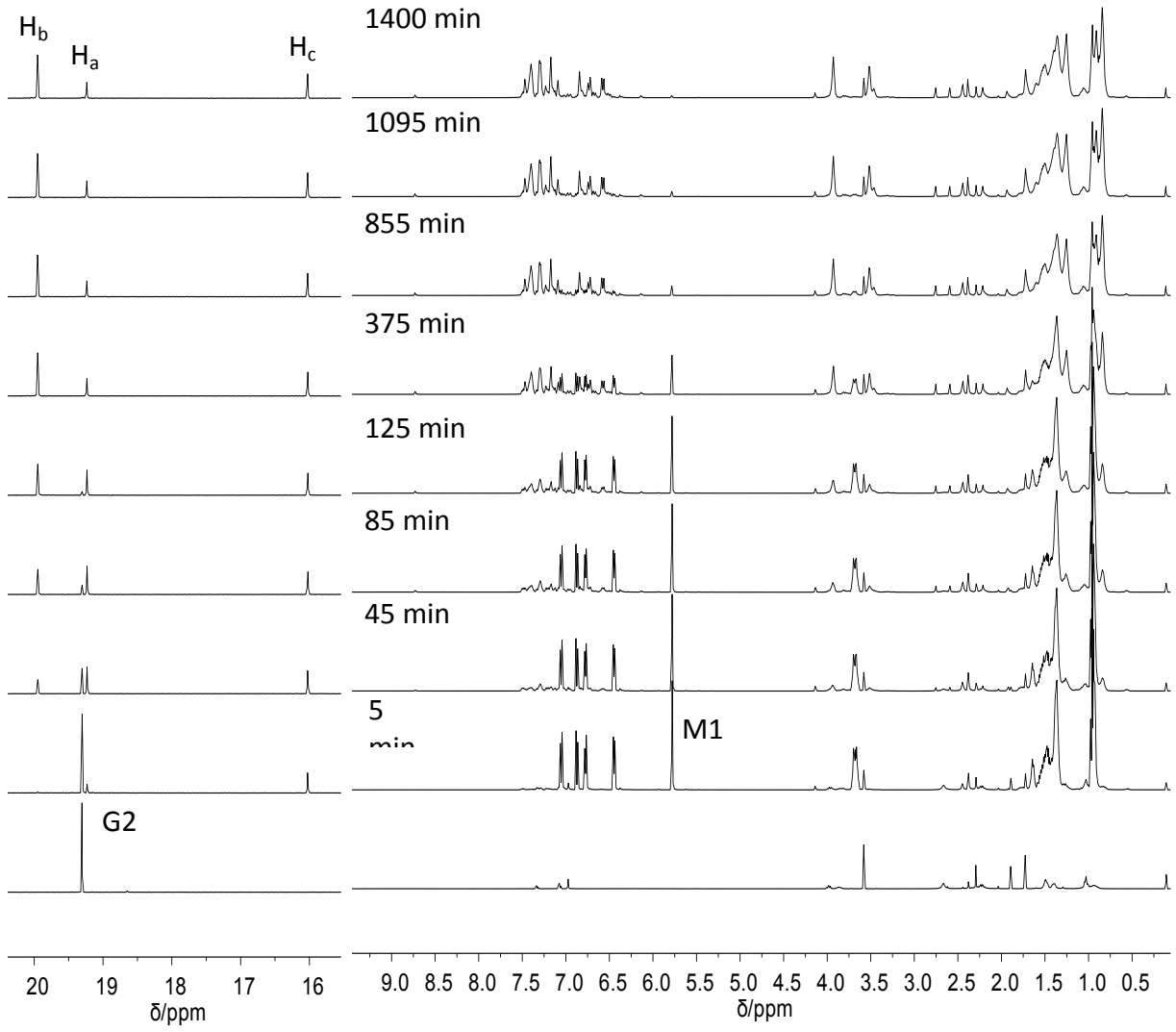

Figure S21. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M1** initiated by **G2** at 40 °C.

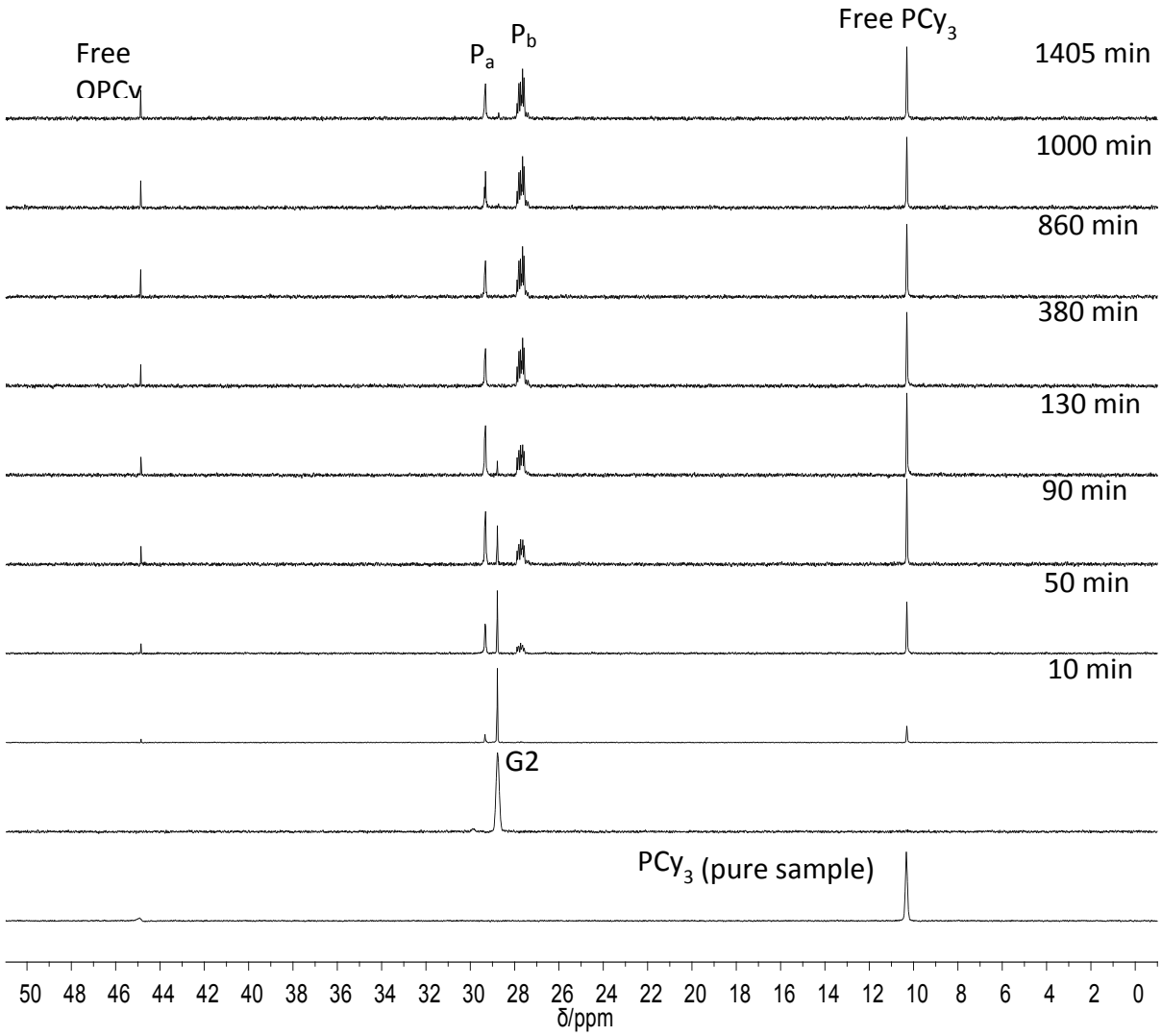

Figure S22. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) stack plot of **M1** initiated by **G2** at 40 °C.

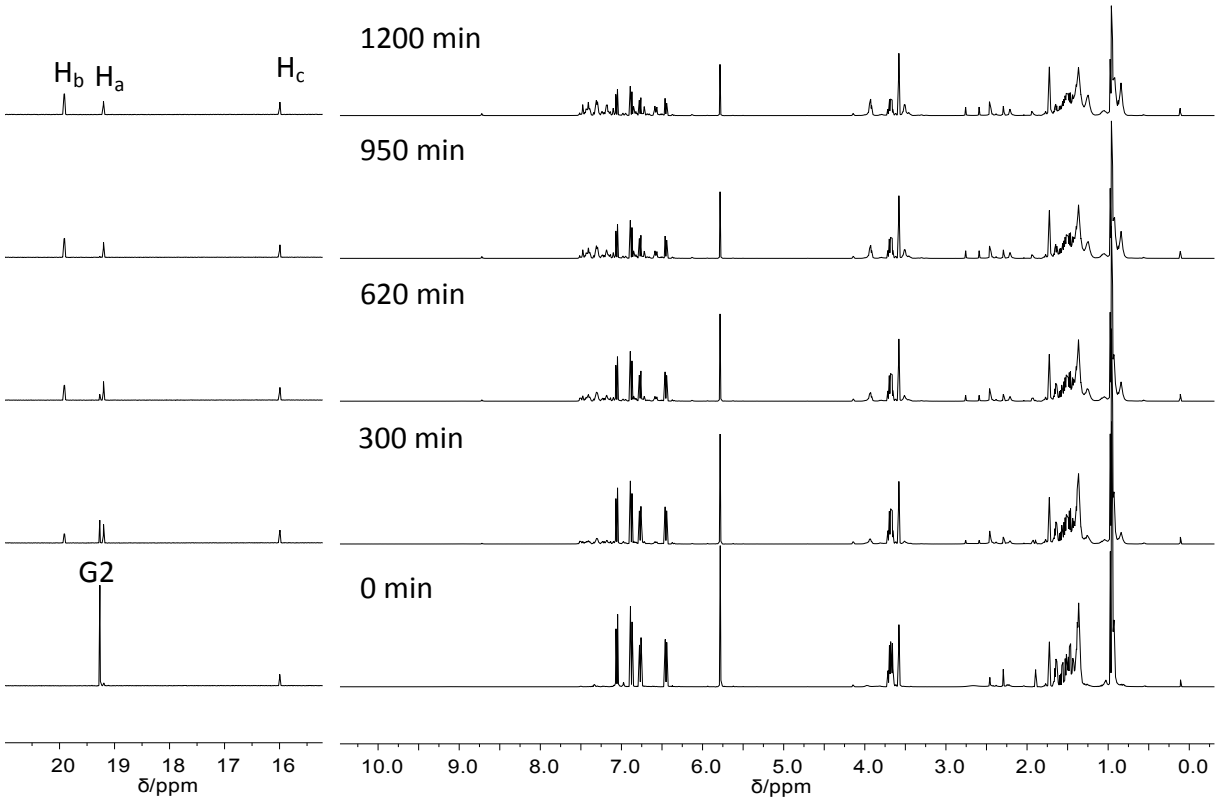

Figure S23. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M1** initiated by **G2** at 25 °C.

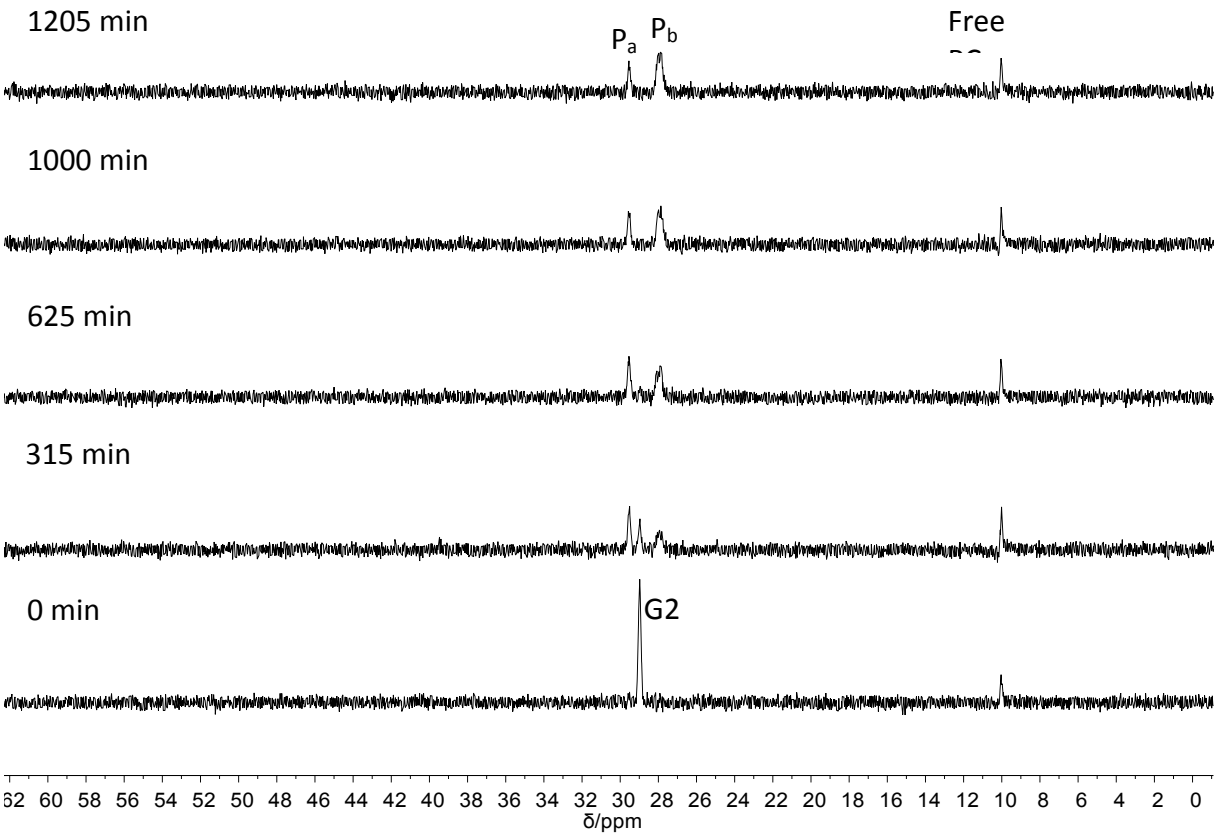

Figure S24. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) stack plot of **M1** initiated by **G2** at 25 °C.

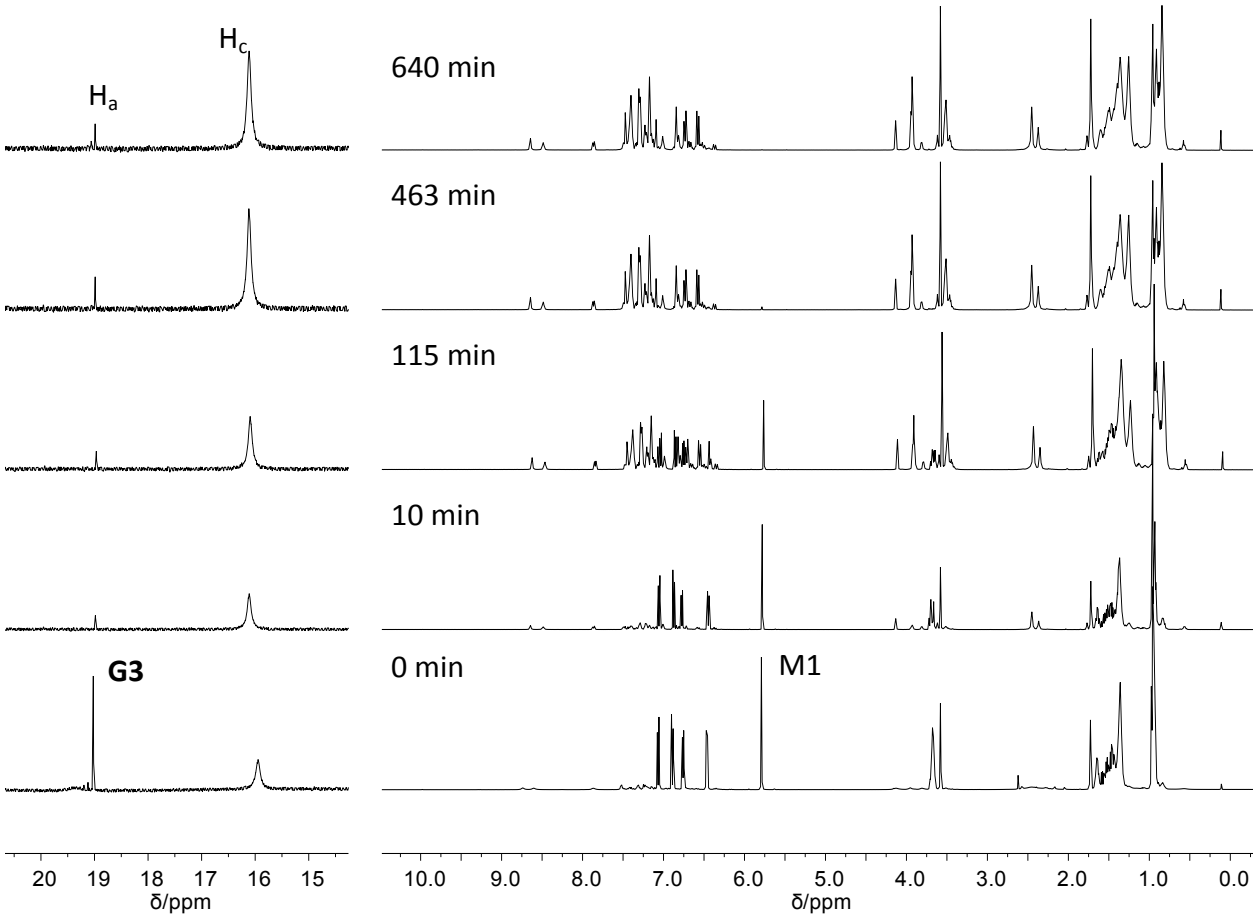

Figure S25. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M1** initiated by **G3** at 40 °C.

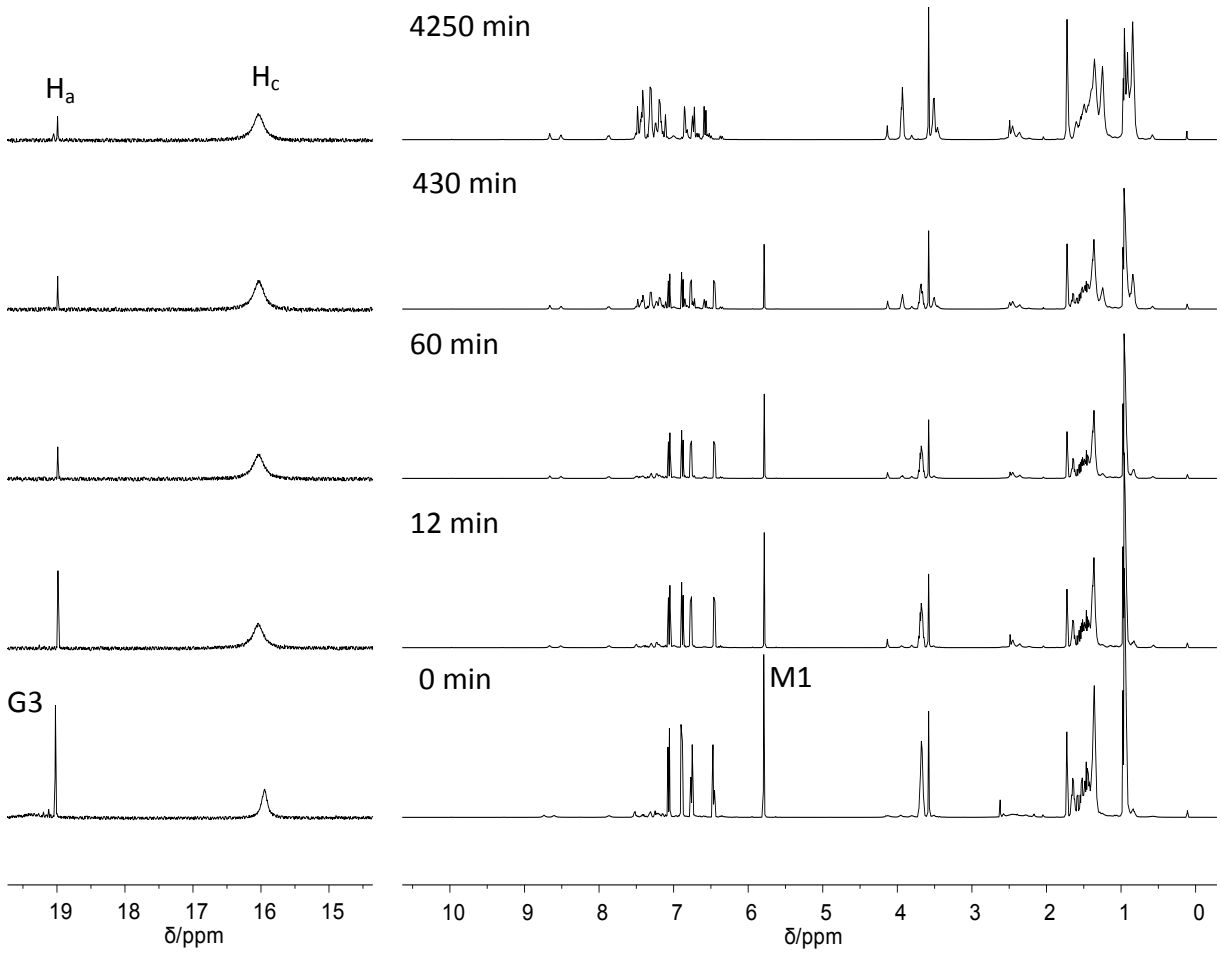

Figure S26. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot **M1** initiated by **G3** at 25 °C.

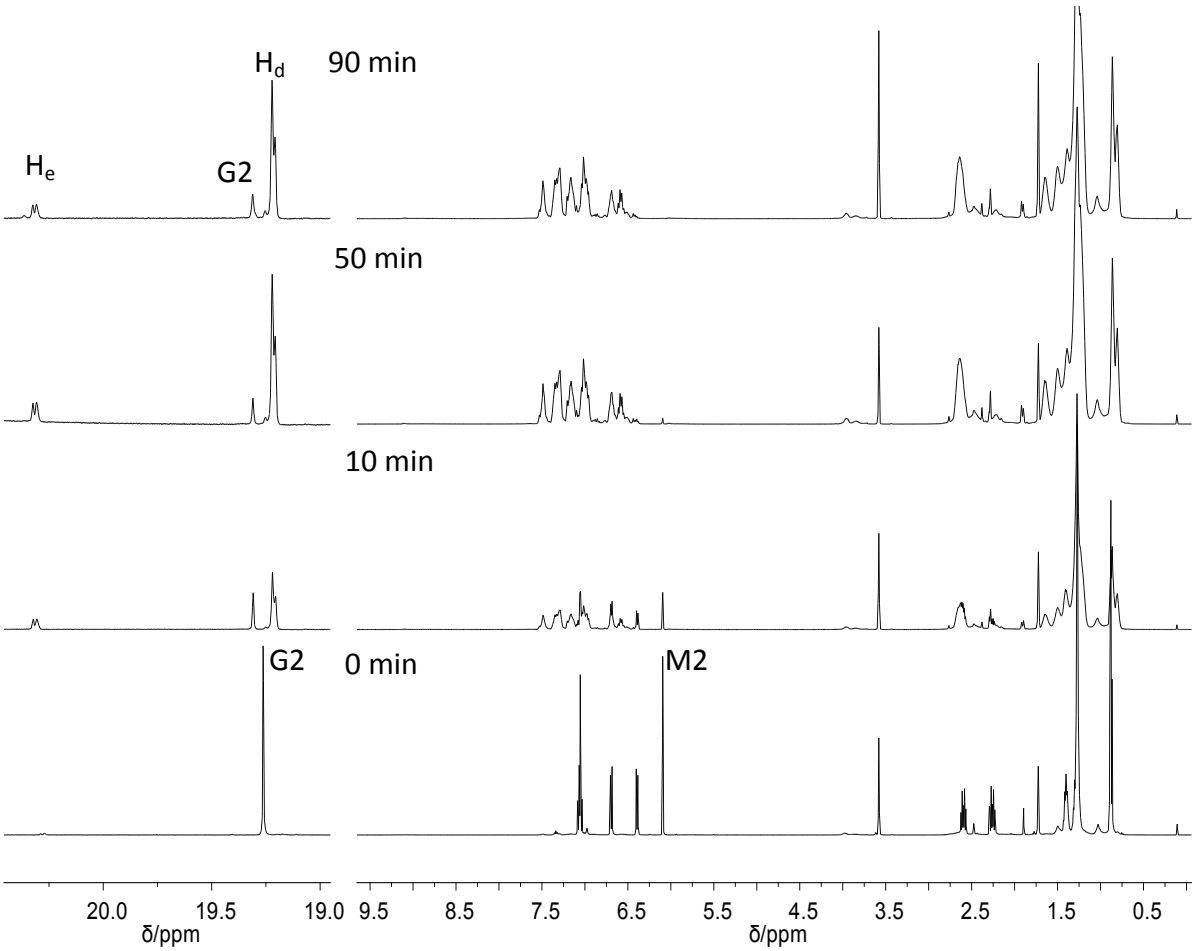

Figure S27. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M2** initiated by **G2** at 40 °C.

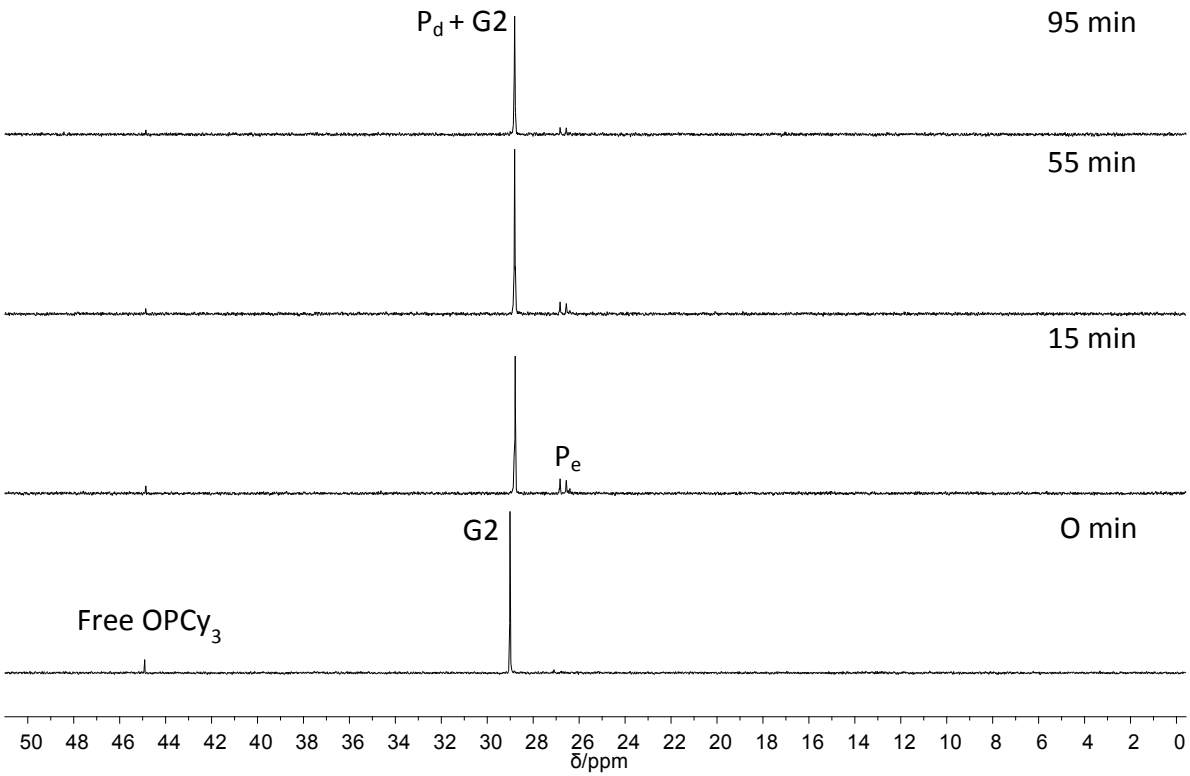

Figure S28. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) stack plot of **M2** initiated by **G2** at 40 °C.

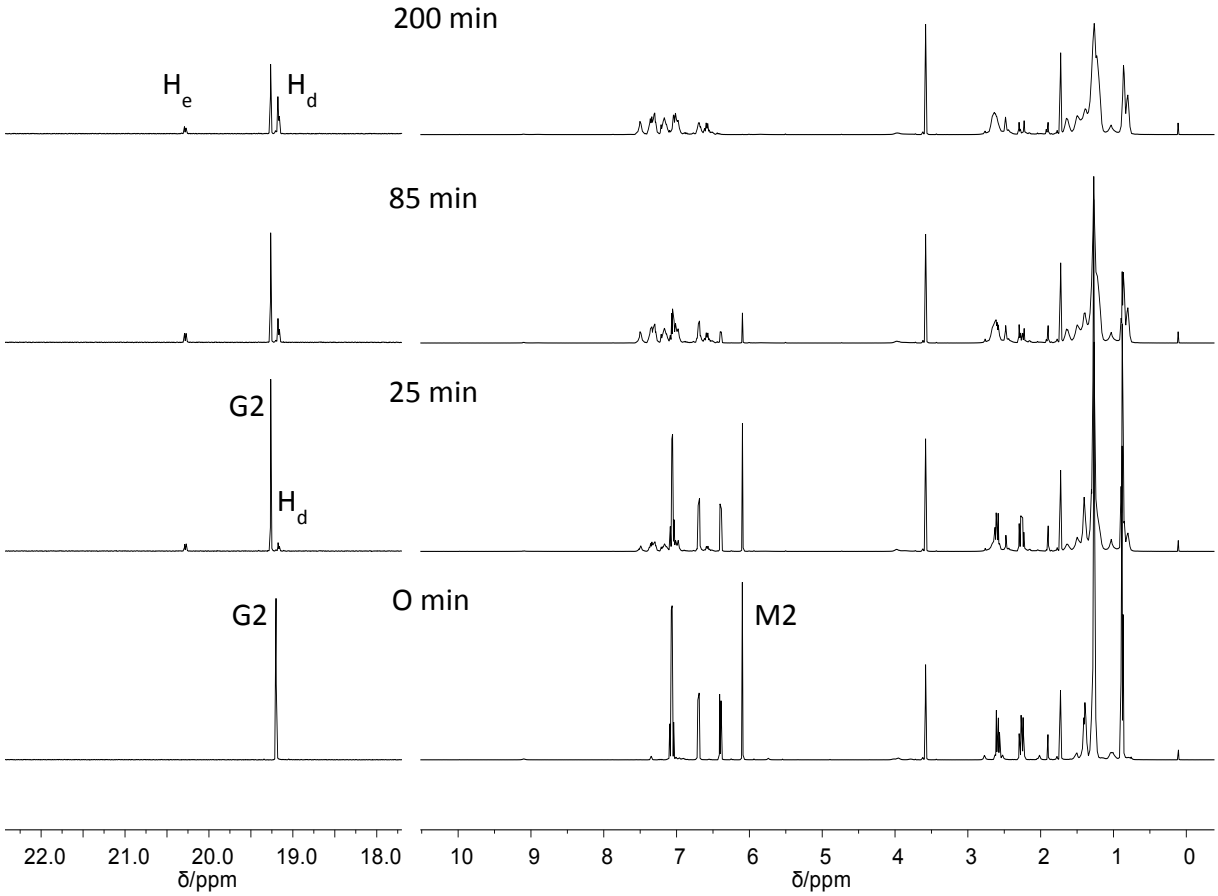

Figure S29. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M2** initiated by **G2** at 25 °C.

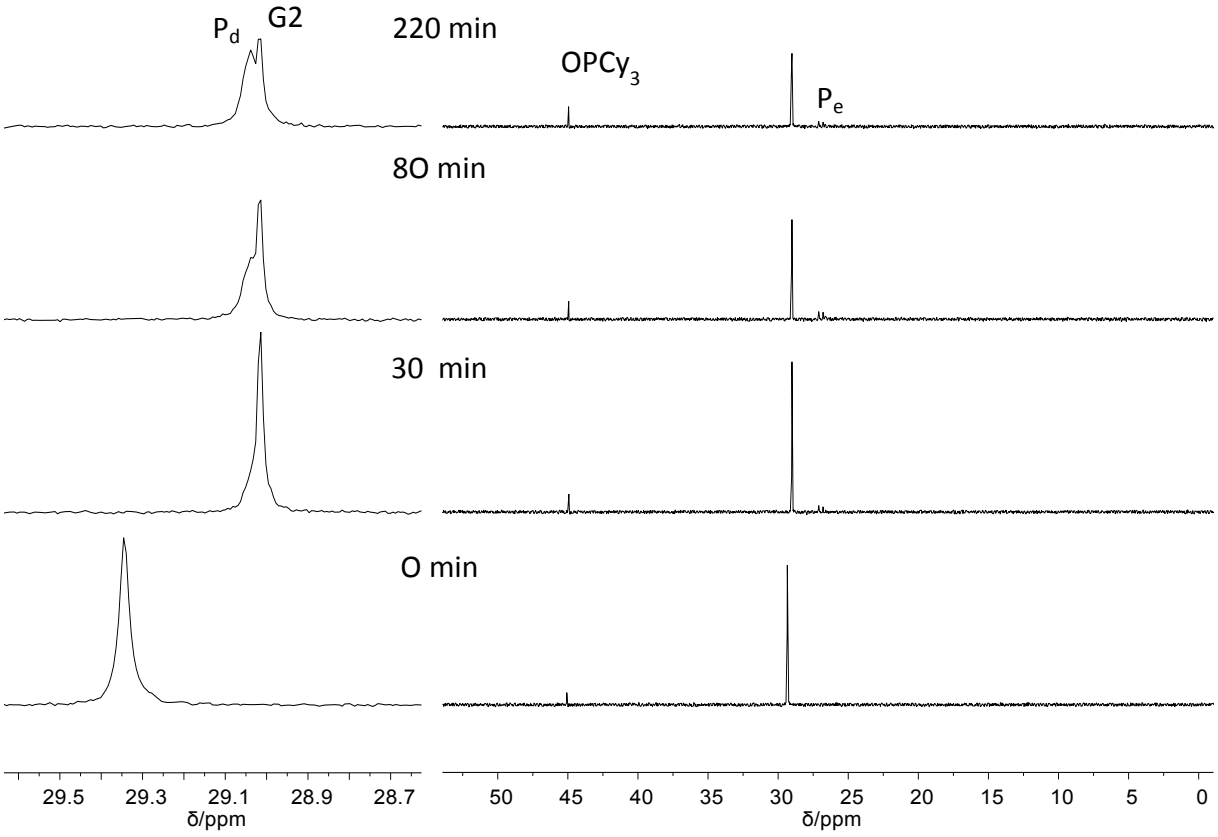

Figure S30. *In-situ* ROMP ^{31}P NMR (thf- d_8, 202 MHz) stack plot of **M2** initiated by **G2** at 25 °C.

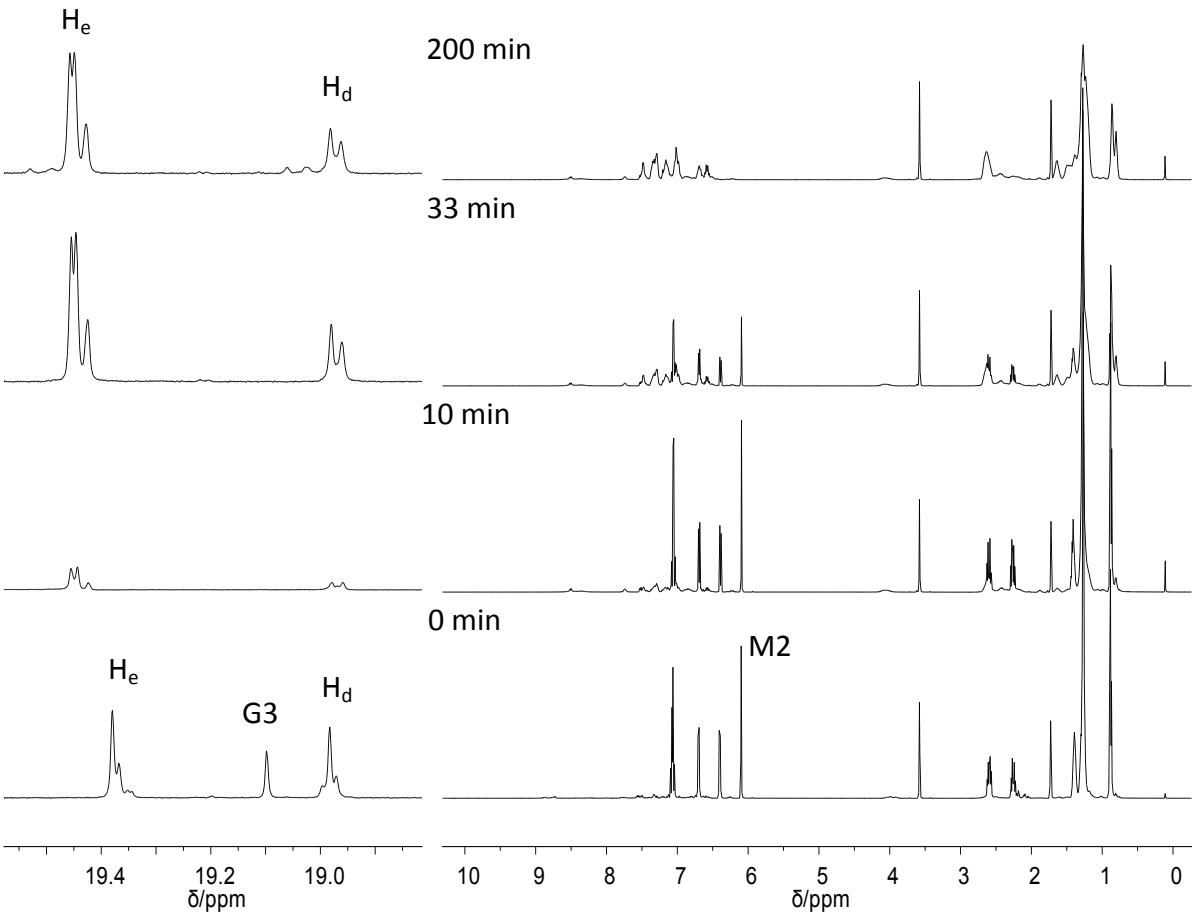

Figure S31. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M2** initiated by **G3** at 40 °C.

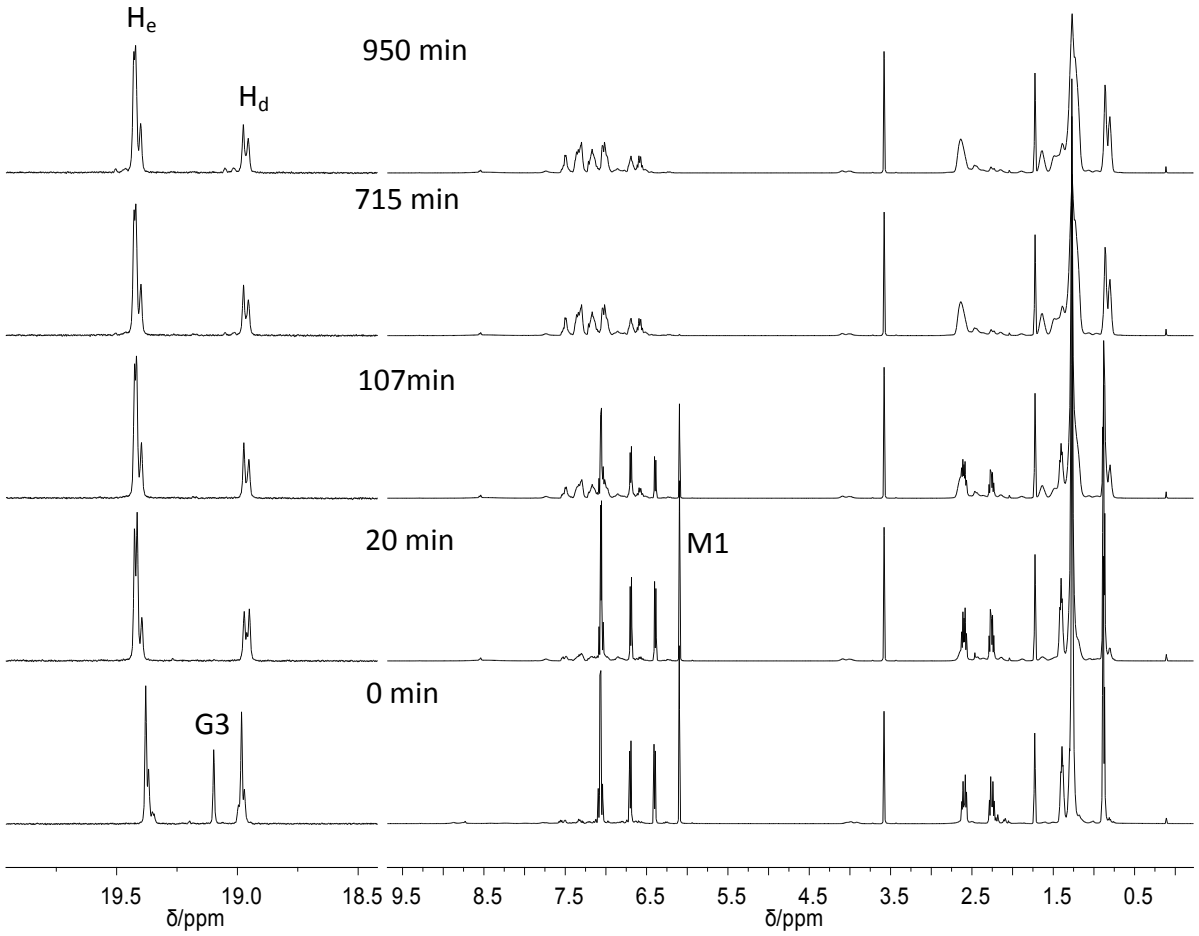

Figure S32. *In-situ* ROMP ^{1}H NMR (thf-d_8, 500 MHz) stack plot of **M2** initiated by **G3** at 25 **°**C.

Table S1. Reaction details, apparent rate constants and molecular weight data for PPV prepared by the ROMP of **M1** and **M2** initiated by **G2** and **G3** at 25 and 40 °C.

Entry	M	G	Temp (°C)	[M]/[G]	Complete Initiation of G (min)	Half Complete conversion of M (min)	Complete conversion of M (min)	k_i^{app}	k_p^{app}	k_i^{app}/k_p^{app}	M_n [a]	$Đ_m$ [a]
1	M1	G2	40	10	200	200	1425	0.0268	0.00264	10.2	4.90	1.58
2	M1	G2	25	10	1000	1000	~8500	0.0043	0.00035	12.14	4.46	1.58
3	M1	G3	40	10	< 5	60	640	-	0.00958	-	5.23	1.39
4	M1	G3	25	10	60	430	4250	0.0763	0.0014	54.52	6.09	1.38
5	M2	G2	40	10	Never complete	≤ 10	90	0.165	0.611	0.27	3.86	1.74
6	M2	G2	25	10	Never complete	44	210	0.0079	0.0226	0.34	7.38	1.77
7	M2	G3	40	10	< 5	25	200	-	0.0386	-	4.39	1.59
8	M2	G3	25	10	40	110	950	0.0984	0.0061	16.05	5.25	1.43

[a] determined by GPC with RI detection (calibrated against narrow $Đ_m$ polystyrene standards).