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Materials

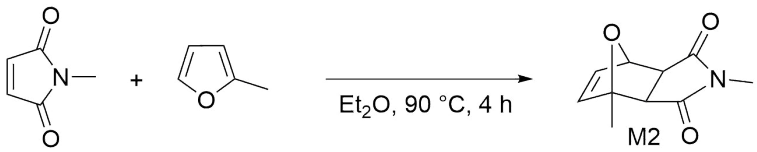
Grubbs' catalysts G1 and G3, 3,4-dihydro-2H-pyran (C1), ethyl vinyl ether and all other starting materials were purchased from Sigma-Aldrich unless stated otherwise and used without further purification. *N*-methyl-*exo*-norbornene carboximide (M1)[1], *N*-methyl-1-ethyl-7-oxa-*exo*-norbornene carboximide (M3)[2], *N*-methyl-7-oxa-*exo*-norbornene carboximide (M4)[3] and *N*-ferrocenylcarbonyloxyethyl-*exo*-norbornene carboximide (M6)[2] were synthesized as reported previously. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc. Deuterated dichloromethane was degassed by 3 successive freeze-vacuum-thaw cycles immediately before use.

Instrumentation

Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with an Agilent Technologies 1260 Infinity II GPC system (pump, autosampler, RI detector), two MZ-Gel SDplus linear columns (5 µm, 300×8.0 mm) and an MZ-Gel SDplus linear precolumn (5 µm, 50×8.0 mm) at a flow rate of 1 mL/min using $CHCl_3$ as an eluent. Calibrations were carried out using polystyrene standards in a range from 10^3 to 3×10^6 Da. NMR spectra were recorded on a Bruker Avance III 300/400 MHz NMR spectrometer (^{1}H NMR: 300/400 MHz; ^{13}C NMR: 75/101 MHz). NMR signals were referenced internally to residual solvent signals. High-resolution mass spectra (HR-MS) were obtained by electrospray ionization (ESI) on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Surface morphology was determined using FEI Tecnai F20 transmission electron microscope operated at an acceleration voltage of 200 kV. Bright field (BF) technique was used for measurements. MATLAB has been used to do the fittings in order to obtain the reactivity ratios.

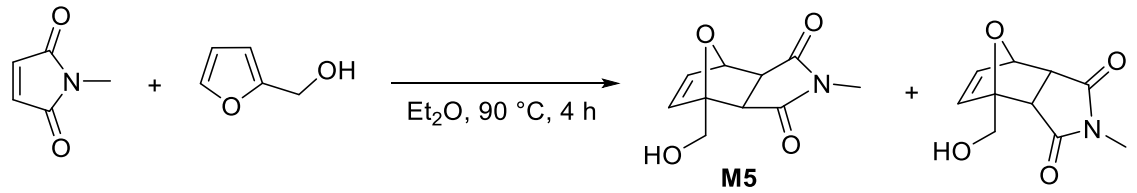
Synthesis

Synthesis of *N*-methyl-1-methyl-7-oxa-*exo*-norbornene carboximide (M2):



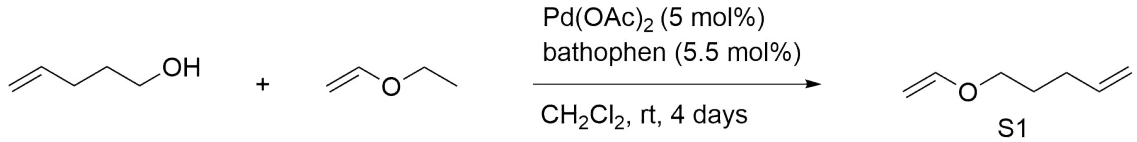
N-Methylmaleimide (0.8 g, 7.2 mmol, 1 eq) and 2-methylfuran (1.18 g, 1.28 mL, 14.4 mmol, 2 eq) were transferred in a heavy walled flask under argon. Then 4 mL of dry diethyl ether were added to this flask and the flask was sealed. This reaction mixture was heated at 90 °C for 4 hours. Upon cooling, white crystals were formed. The crystals were washed 3-4 times with diethyl ether to give M2 (0.92 g, 66% yield). ^{1}H NMR (DICHLOROMETHANE-d_2, 300MHz): δ 6.49 (dd, J=5.6, 1.6 Hz, 1 H), 6.31 (d, J=5.7 Hz, 1 H), 5.11 (d, J=1.7 Hz, 1 H), 2.95 (d, J=6.4 Hz, 1 H), 2.91 (s, 3 H), 2.70 (d, J=6.3 Hz, 1 H), 1.67 ppm (s, 3 H). ^{13}C NMR (DICHLOROMETHANE-d_2, 75MHz): δ 176.8, 175.5, 141.0, 137.4, 88.5, 81.1, 51.3, 50.0, 25.1, 16.0 ppm. ESI-HRMS m/z $[M+H]^+$: calculated 194.0817, found 194.0807.

Synthesis of *N*-methyl-1-hydroxymethyl-7-oxa-*exo*-norbornene carboximide (M5):



N-Methylmaleimide (2 g, 18.0 mmol, 1 eq) and 2-(hydroxymethyl)furan (3.53 g, 3.12 mL, 36.0 mmol, 2 eq) were transferred in a heavy walled flask under argon. Then 10 mL of dry diethyl ether were added to this flask and the flask was sealed. This reaction mixture was heated at 90 °C for 4 hours. The reaction mixture was concentrated *in vacuo* and purified by column chromatography using ethyl acetate as eluent to give the product (*exo*:*endo* isomers=79:21) as a viscous liquid (1.6 g, 43% yield). ^{1}H NMR (DICHLOROMETHANE-d_2, 300MHz) (*exo* isomer): δ 6.55 - 6.60 (m, 1 H), 6.51 - 6.55 (m, 1 H), 5.20 (d, J=1.7 Hz, 1 H), 4.05 (s, 2 H), 2.98 (q, J=6.6 Hz, 2 H), 2.94 (s, 3 H), 2.40 ppm (br. s., 1 H). ^{13}C NMR (DICHLOROMETHANE-d_2 ,75MHz) (*exo* isomer): δ 176.7, 176.6, 138.7, 137.5, 91.9, 81.4, 61.3, 50.6, 48.7, 25.3 ppm. ESI-HRMS m/z $[M+Na]^+$: calculated 232.0586, found 232.0589.

Synthesis of 5-(vinyloxy)pent-1-ene (S1):



A solution of 4-penten-1-ol (0.5 g, 5.8 mmol) in ethyl vinyl ether (0.3 M) was prepared in a flask. Then a solution of palladium(II) acetate (5 mol%) and bathophenanthroline (5.5 mol%) in 1.5 mL of dichloromethane was added to this flask. The reaction mixture was stirred for 4 days at room temperature, filtered over celite and carefully concentrated by rotary evaporation. The crude product was purified over a short silica column using pentane as an eluent to give S1 (0.3 g, 46% yield). ^{1}H NMR (CHLOROFORM-d, 300MHz): δ 6.47 (dd, J=14.4, 6.8 Hz, 1 H), 5.73 - 5.92 (m, 1 H), 4.94 - 5.11 (m, 2 H), 4.18 (dd, J=14.4, 1.9 Hz, 1 H), 3.99 (dd, J=6.8, 1.9 Hz, 1 H), 3.70 (t, J=6.5 Hz, 2 H), 2.10 - 2.22 (m, 2 H), 1.70 - 1.83 (m, 2 H) ppm. ^{13}C NMR (CHLOROFORM-d, 75MHz): δ 151.9, 137.8, 115.1, 86.3, 67.3, 30.1, 28.2 ppm. This is a known compound.[4]

Procedure for one-step block copolymer synthesis from M1 and M2 using G1:

A stock solution of monomers M1 (3x15 eq) and M2 (3x15 eq), and 1,3,5-trimethoxybenzene (3x10 mg) (NMR standard) was prepared in dry, degassed CD_2Cl_2 (3x0.4 mL) under argon. A portion of this stock solution was transferred to an NMR tube under argon and ^{1}H NMR spectrum was recorded. Then 0.4 mL of the stock solution containing monomers and NMR standard were injected to a vial containing the solution of G1 (9 mg, 0.0109 mmol, 1 eq) in CD_2Cl_2 (0.2 mL) under argon. This whole solution was transferred to another NMR tube under argon and ^{1}H NMR spectra were recorded at different time intervals. When both the monomers were almost consumed, the reaction was terminated with 0.1 mL of ethyl vinyl ether and the polymer P1-G1 (M_n, found (GPC, $CHCl_3$)=6.5 kDa, Đ=1.12, M_n, theo=5.6 kDa) was precipitated in methanol (94% yield). The same reaction was repeated and followed by ^{1}H NMR spectroscopy.

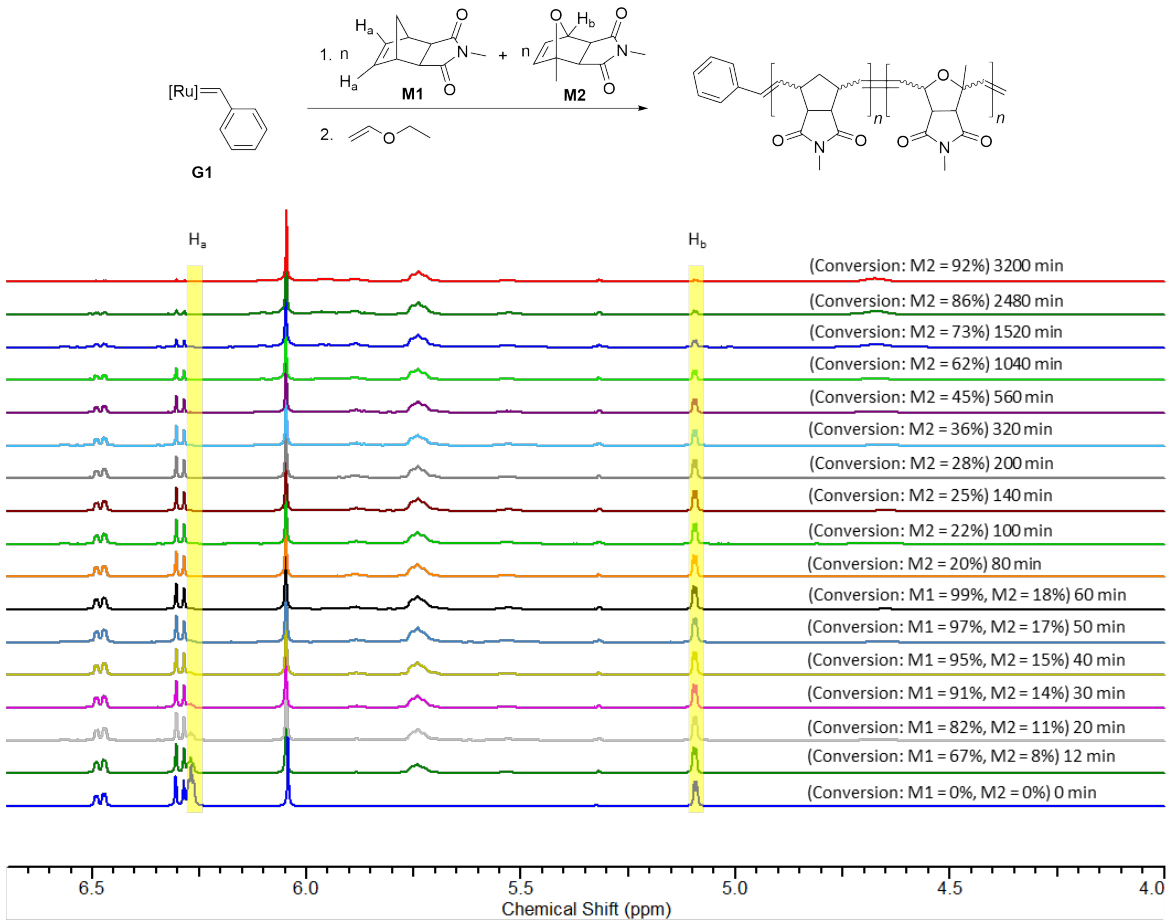


Figure S1: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G1 (9 mg, 0.0109 mmol, 1 eq) with M1 (15 eq) and M2 (15 eq) in CD_2Cl_2 at room temperature. As the peak of H_a (M1) in these spectra is overlapping with one olefinic proton of M2, the integral over both olefinic peaks was recorded and the value of the integral of H_b (5.1 ppm) subtracted. This resulted in a value for H_a.

When this reaction was repeated a similar rate for the consumption of monomers was observed.

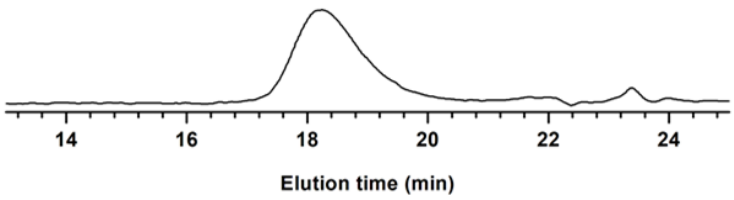


Figure S2: GPC ($CHCl_3$) trace of polymer P1-G1.

Procedure for one-step block copolymer synthesis from M1 and M2 using G3:

A stock solution of monomers M1 (8x15 eq) and M2 (8x15 eq), and 1,3,5-trimethoxybenzene (8x10 mg) (NMR standard) was prepared in dry, degassed CD_2Cl_2 (8x0.4 mL) under argon. A portion of this stock solution was transferred to an NMR tube under argon and a ^{1}H NMR spectrum was recorded. Separately, a stock solution of G3 (8x9 mg, 8x0.0102 mmol, 8x1 eq) was prepared in dry, degassed CD_2Cl_2 (8x0.2 mL) under argon. Then 0.4 mL of the stock solution containing monomers and NMR standard were injected to a vial containing 0.2 mL of the stock solution of G3 under argon and the reaction was quenched after 10 s with 0.1 mL of ethyl vinyl ether. This whole solution was transferred to another NMR tube and a ^{1}H NMR spectrum was recorded. The same procedure was repeated two more times and one reaction was quenched with 0.1 mL of ethyl vinyl ether after 20 s while the other after 30 s to be analyzed by ^{1}H NMR spectroscopy (M1 was almost consumed). Subsequently, 0.4 mL

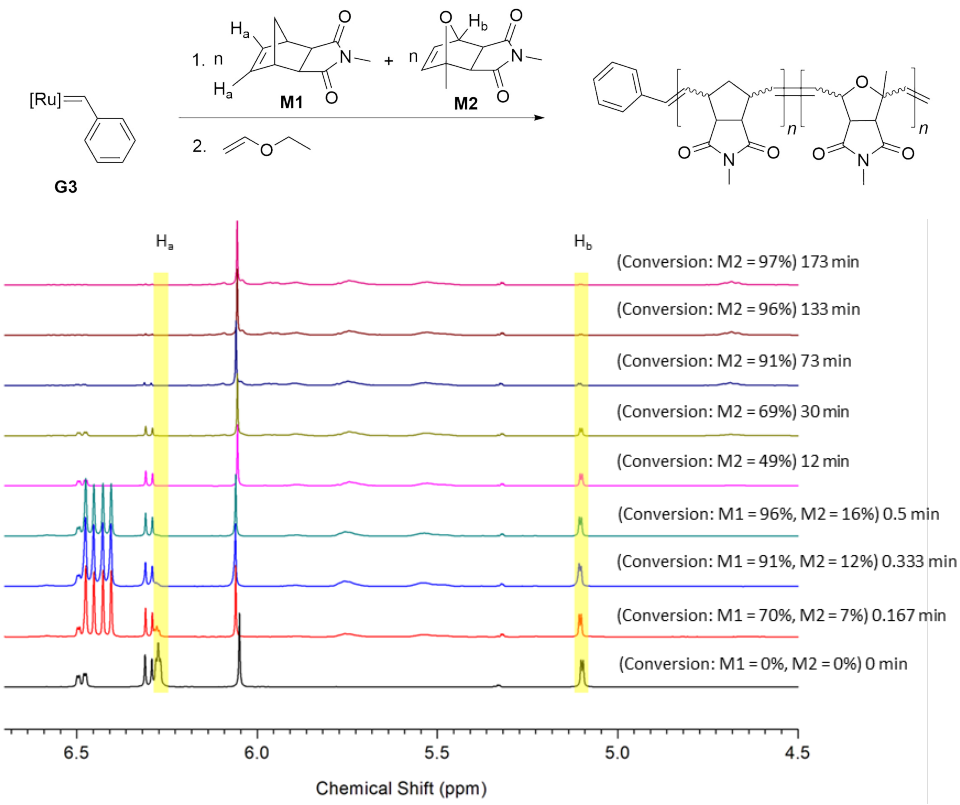
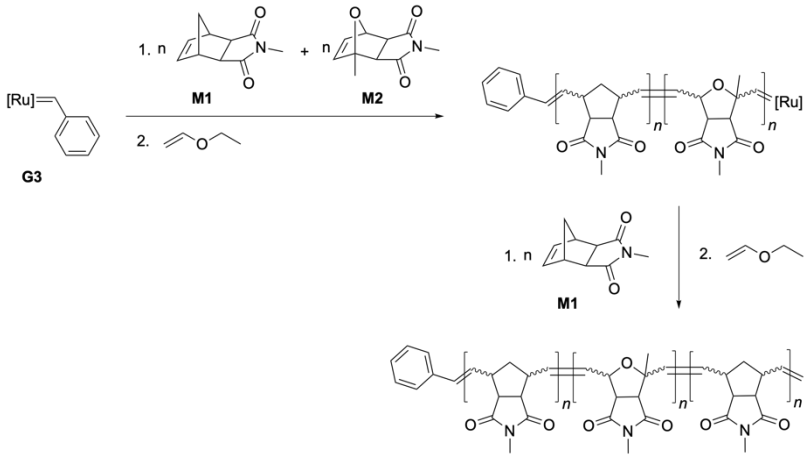


Figure S3: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G3 (9 mg, 0.0102 mmol, 1 eq) with M1 (15 eq) and M2 (15 eq) in CD_2Cl_2 at room temperature. The intensities of spectra are adjusted due to the dilution caused by the addition of excess ethyl vinyl ether.

of the stock solution containing monomers and NMR standard were injected into a vial containing 0.2 mL of the stock solution of G3 under argon. This whole solution was transferred to another NMR tube and a ^{1}H NMR spectrum was recorded at different time intervals until both M1 and M2 got consumed. The reaction was terminated with 0.1 mL of diethyl ether and the polymer P1-G3 (M_n, found (GPC, $CHCl_3$)=5.4 kDa, Đ=1.12, M_n, theo=5.6 kDa) was precipitated in methanol (95% yield).

A solution of monomers M1 (30 eq) and M2 (30 eq) was prepared in dry, degassed CH_2Cl_2 (0.8 mL) under argon. Separately, a solution of G3 (9 mg, 0.0102 mmol, 1 eq) was prepared in dry, degassed CH_2Cl_2 (0.4 mL) under argon. Then solution of monomers was injected to a vial containing the solution of G3 under argon and the reaction was terminated after 360 min (6 h) with 0.1 mL of ethyl vinyl ether and the polymer P2-G3 (M_n, found (GPC, $CHCl_3$)=12.9 kDa, Đ=1.09, M_n, theo=11.1 kDa) was precipitated in methanol (93% yield). The same procedure was repeated with different amounts of reactants i.e.

M1 (60 eq) and M2 (60 eq) in 1.6 mL of dry, degassed CH_2Cl_2, and G3 (9 mg, 0.0102 mmol, 1 eq) in 0.8 mL of dry, degassed CH_2Cl_2. This reaction was terminated after 720 min (12 h) with 0.1 mL of ethyl vinyl ether and the polymer P3-G3 (M_n, found (GPC, $CHCl_3$)=24.7 kDa, Đ=1.08, M_n, theo=22.2 kDa) was precipitated in methanol (86% yield).



A solution of monomers M1 (15 eq) and M2 (15 eq) was prepared in dry, degassed CH_2Cl_2 (0.4 mL) under argon. Separately, a solution of G3 (9 mg, 0.0102 mmol, 1 eq) was prepared in dry, degassed CH_2Cl_2 (0.2 mL) under argon. Then solution of monomers was injected to a vial containing the solution of G3 under argon and the reaction was continued for 180 min (3 h). Subsequently, a solution of M1 (15 eq) in dry, degassed CH_2Cl_2 (0.2 mL) was added to this reaction mixture. The reaction was continued for next 10 min and then terminated with 0.1 mL of ethyl vinyl ether and the polymer P4-G3 (M_n, found (GPC, $CHCl_3$)=10.1 kDa, Đ=1.11, M_n, theo=8.2 kDa) was precipitated in methanol (87% yield).

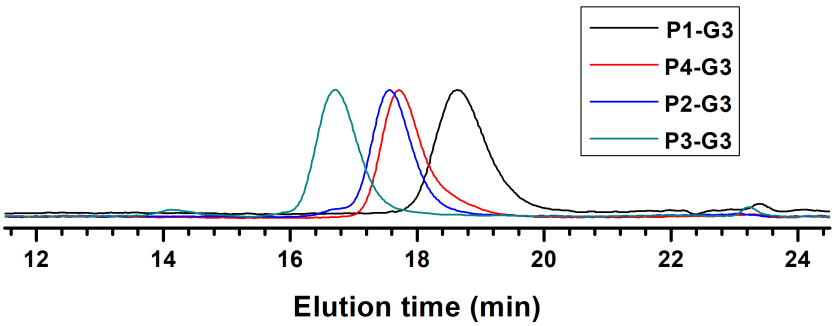


Figure S4: GPC ($CHCl_3$) trace of polymer P1-G3, P2-G3, P3-G3 and P4-G3.

Reaction of catalyst G1/G3 with compound S1/C1:

A solution of the catalyst# and 1,3,5-trimethoxybenzene (10 mg) (NMR standard) in dry, degassed CD_2Cl_2 (0.6 mL) was transferred to the NMR tube under argon. ^{1}HNMR spectra were recorded before and at various time intervals after the addition of a solution of compound# in dry, degassed CD_2Cl_2 (0.3 mL).

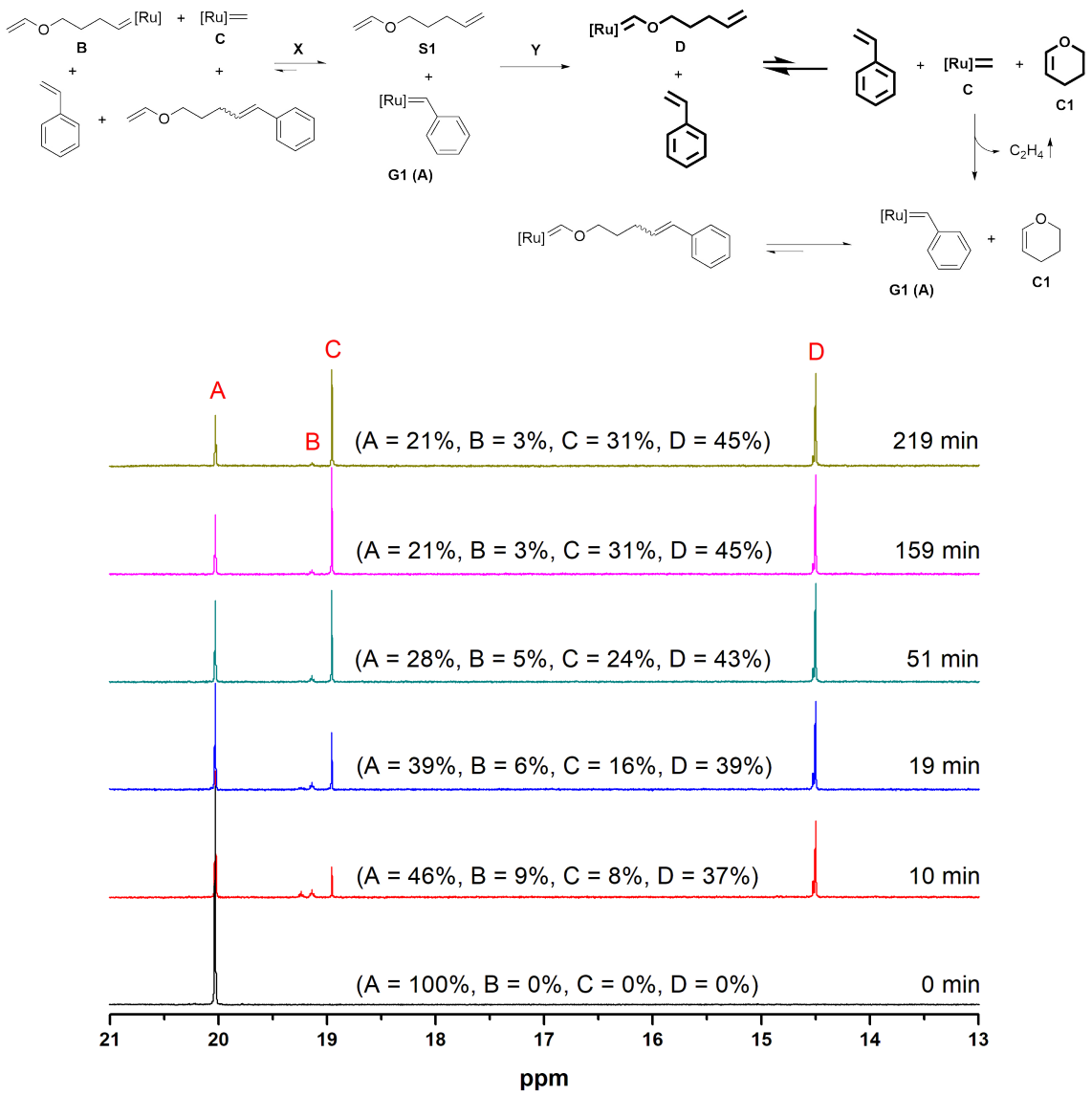


Figure S5: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G1 (9 mg, 1 eq) with S1 (1 eq) in CD_2Cl_2 at room temperature to show the conversion of G1 Fischer-carbene to G1 methylidene. The decomposition of carbenes is ignored.

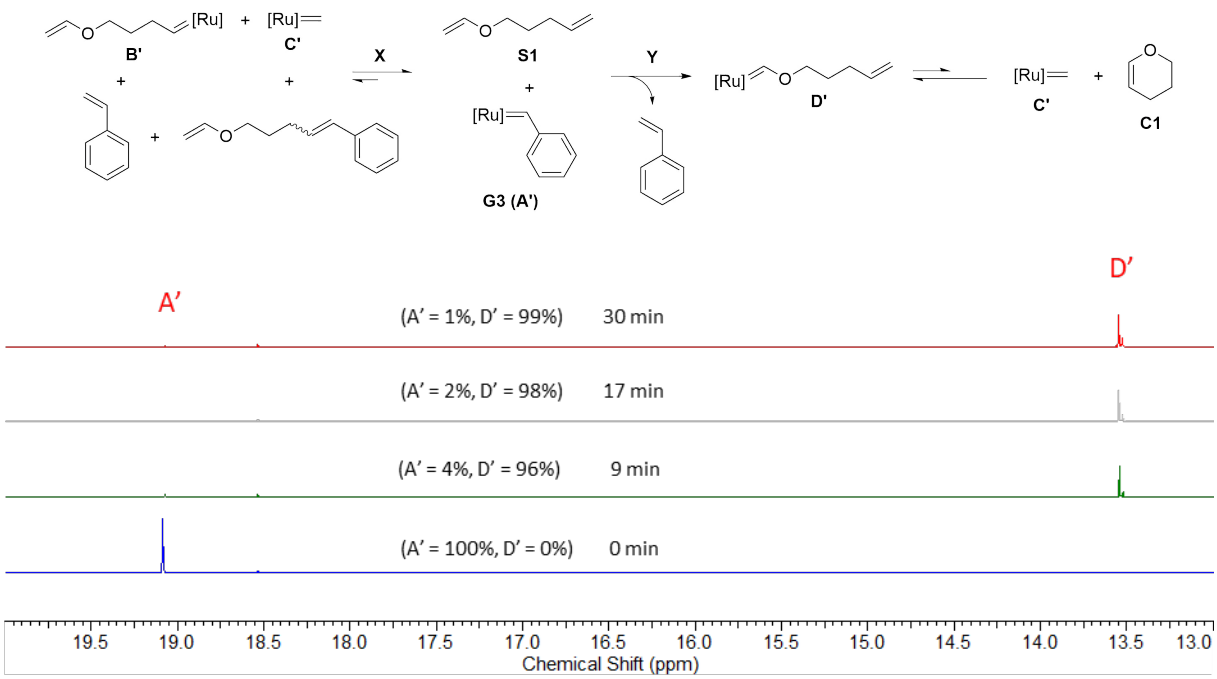


Figure S6: Time resolved ^{1}H NMR (400 MHz) spectra of the reaction of G3 (19.07 ppm) (9 mg, 0.0102 mmol, 1 eq) with S1 (1 eq) yielding D' (13.54 ppm) in CD_2Cl_2 at room temperature. A small singlet at 13.52 ppm could be due to the intramolecular coordination of terminal olefin bond to the 16 e$^-$ ruthenium center. The decomposition of carbenes is ignored.

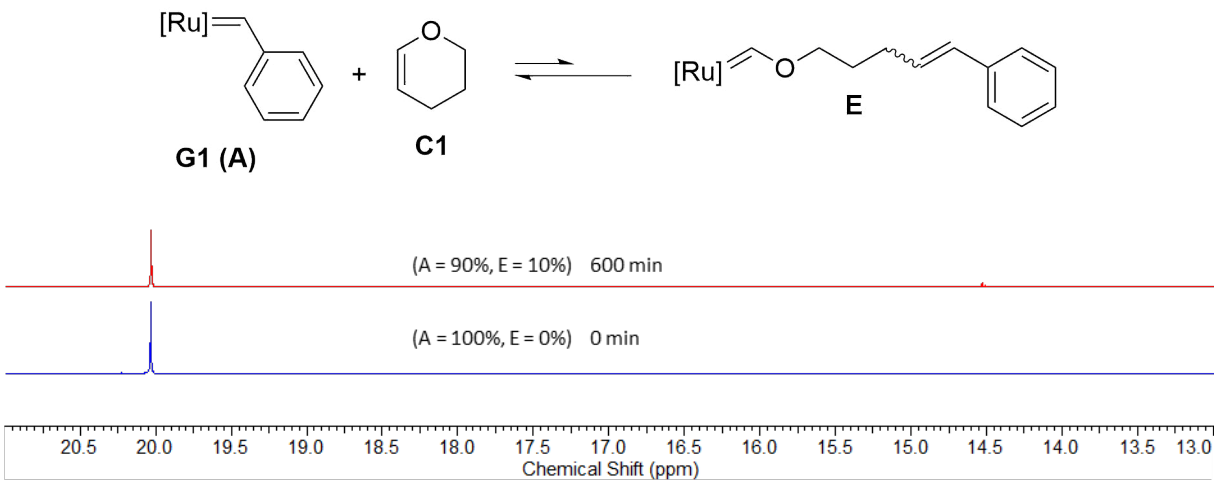


Figure S7: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G1 (20.03 ppm) (9 mg, 0.0109 mmol, 1 eq) with C1 (1 eq) yielding E (14.53 ppm) in CD_2Cl_2 at room temperature. A small singlet at 14.50 ppm could be due to the intramolecular coordination of styrenic double bond to the 16 e$^-$ ruthenium center. The decomposition of carbenes is ignored.

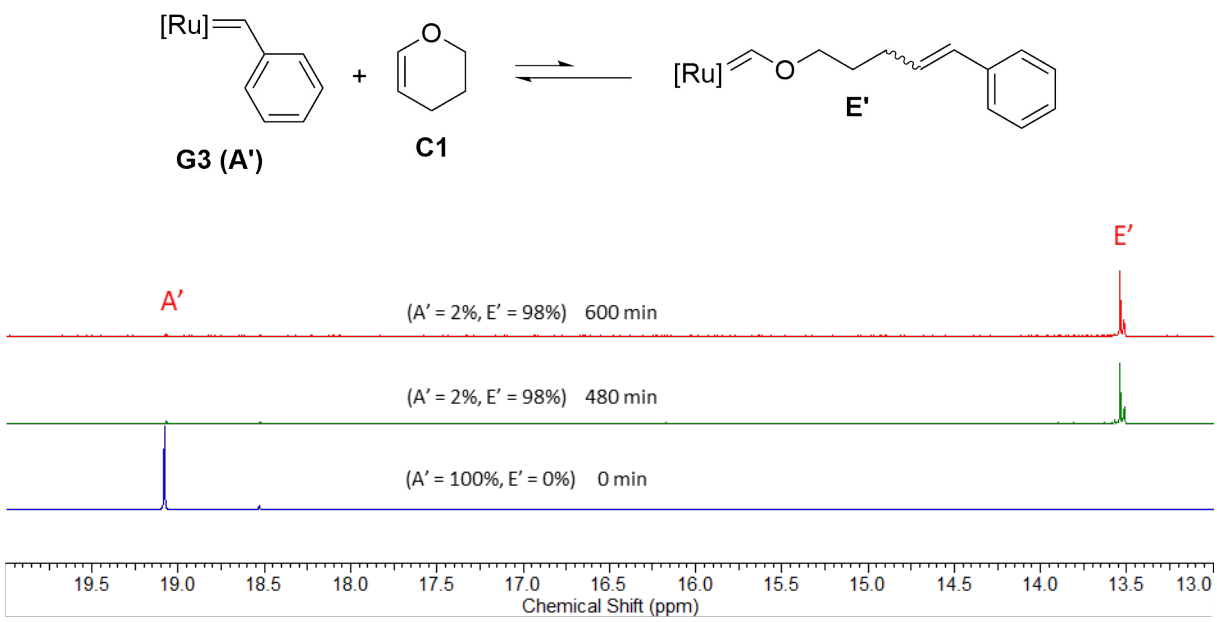


Figure S8: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G3 (19.07 ppm) (9 mg, 0.0102 mmol, 1 eq) with C1 (1 eq) yielding E' (13.54 ppm) in CD_2Cl_2 at room temperature. The two small singlets at 13.51 ppm and 13.57 ppm could be due to the intramolecular coordination of styrenic double bond to the 16 e- and 18 e- ruthenium centers, respectively. The decomposition of carbenes is ignored.

The reaction of G1 with S1 can proceed via two pathways, X and Y (Figure S5). In reversible path X, G1 alkylidenes (B and C) will form. Irreversible path Y, being regioselective, will yield a G1 Fischer carbene (D). As the path X is reversible, it will ultimately lead to irreversible path Y by going through starting materials with the progress of time. It actually happens as the intensity of G1 alkylidene B (19.14 ppm) decreases while intensity of G1 Fischer carbene D (14.50 ppm) increases with time. Surprisingly, the intensity of G1 methylidene C (18.95 ppm) increases instead of decreasing with the progress of time. This unusual increment in the intensity of G1 methylidene is attributed to the intramolecular nature of the reversible reaction between G1 Fischer carbene and right terminal double bond to yield 6 membered ring, pyran (C1). Thus, it can be concluded that the conversion of G1 Fischer carbene D to G1 methylidene C is occurring via this intramolecular reaction (shown in bold, Figure S5). This newly formed G1 methylidene C (18.95 ppm) can react irreversibly with styrene, one of the reaction products, to form the G1 benzylidene (A) (20.03 ppm) and ethylene gas. This reaction system achieved equilibrium after 159 min.

When the same compound S1 was reacted with G3 under the same conditions as in the case of G1, we only observed the formation of G3 Fischer carbene D' (13.54 ppm) (Figure S6). We assume that the formation of G3 methylidene C' and conversion of G3 Fischer carbene to G3 methylidene are still occurring. Since G3 is considerably more reactive than G1, the equilibrium is significantly shifted towards the Fischer carbene in the case of G3. This reactivity difference of C1 with G1 and G3 was proved by the separate ^{1}H NMR spectroscopy experiments. When G1 (1 eq) was reacted with commercially available C1 (1eq), a 8.66:1 (G1 benzylidene (20.03 ppm):G1 Fischer carbene (14.53 ppm)) ratio was observed after 600 min (10 h) (Figure S7) while with G3 a 1:44 (G3 benzylidene (19.07 ppm):G3 Fischer carbene (13.54 ppm)) ratio was observed after same time interval (Figure S8).

Reaction of M1 and M2 with the mixture of G3 and C1:

A stock solution of monomers M1 (3x15 eq) and M2 (3x15 eq), and 1,3,5-trimethoxybenzene (3x10 mg) (NMR standard) was prepared in dry, degassed CD_2Cl_2 (3x0.4 mL) under argon. A portion of this stock solution was transferred to an NMR tube under argon and a ^1H NMR spectrum was recorded. Separately, a solution of G3 (9 mg, 0.0102 mmol, 1 eq) in dry, degassed CD_2Cl_2 (0.3 mL) was transferred to the NMR tube under argon. ^1H NMR spectra were recorded at various time intervals after the addition of a solution of C1 (2 eq) in dry, degassed CD_2Cl_2 (0.3 mL) to this NMR tube. Then 0.4 mL of the stock solution containing monomers and NMR standard were injected to the NMR tube containing the solution of G3 and C1 in CD_2Cl_2 and ^1H NMR spectra were recorded at different time intervals.

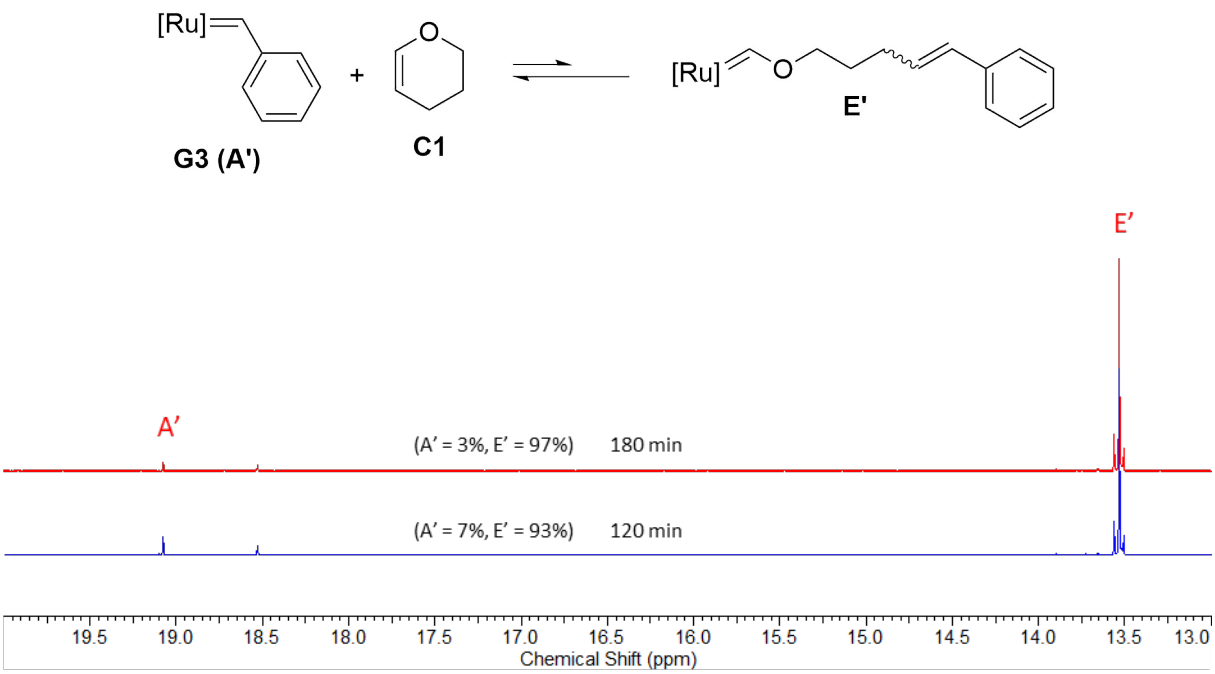


Figure S9: Time resolved ^1H NMR (400 MHz) spectra of the reaction of G3 (9 mg, 0.0102 mmol, 1 eq) with C1 (2 eq) in CD_2Cl_2 at room temperature. The decomposition of carbenes is ignored.

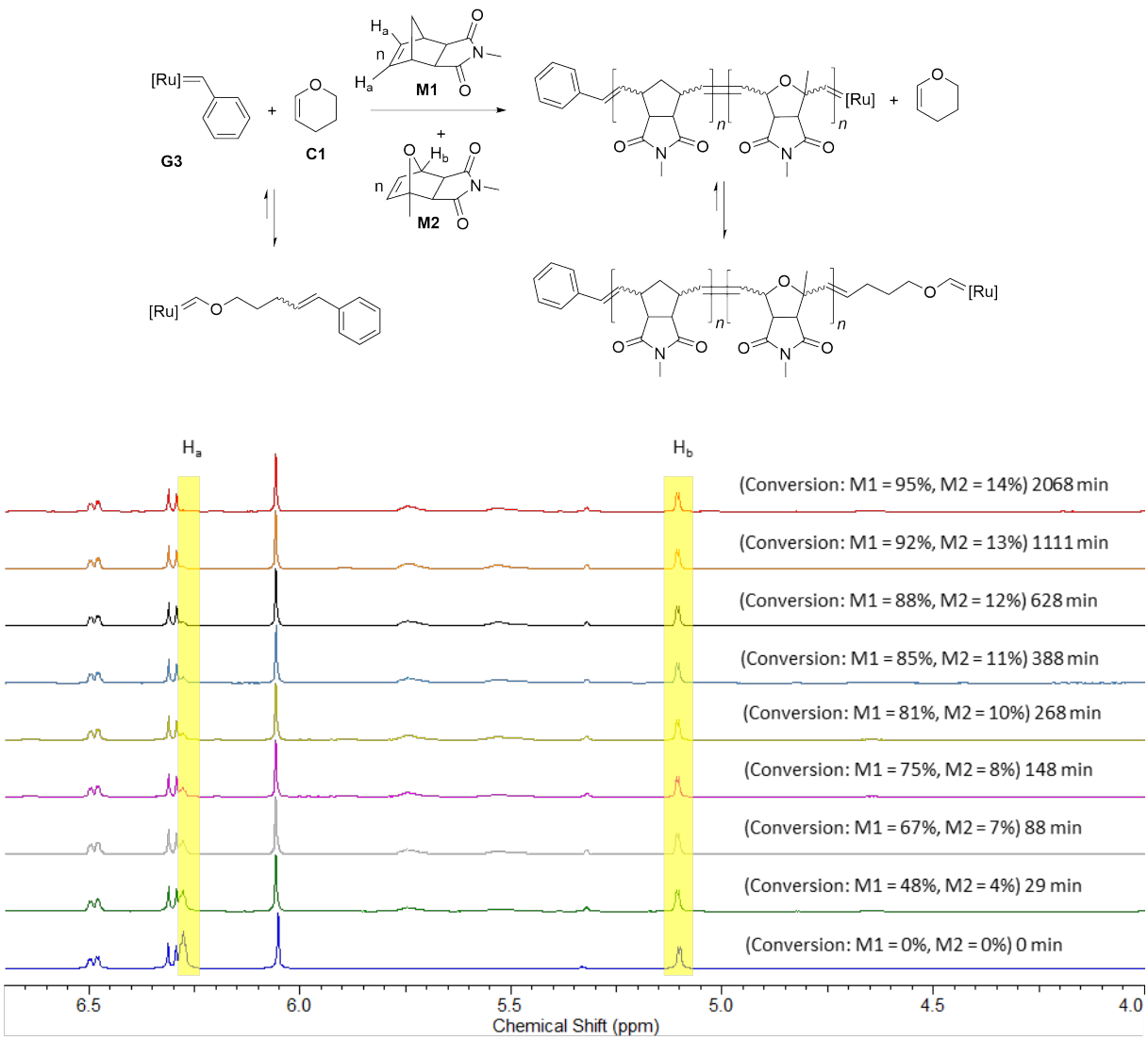
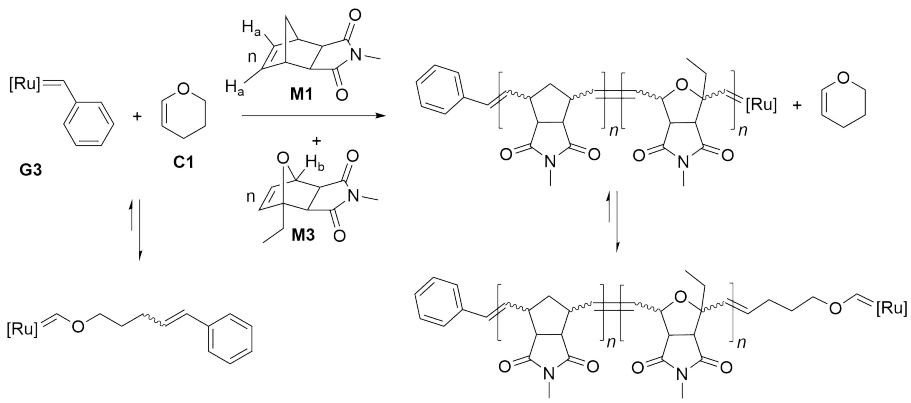


Figure S10: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of the mixture of G3 (9 mg, 0.0102 mmol, 1 eq) and C1 (2 eq) with M1 (15 eq) and M2 (15 eq) in CD_2Cl_2 at room temperature.

Procedure for one-step block copolymer synthesis from M1 and M3 using G3:

A stock solution of monomers M1 (3x15 eq) and M3 (3x15 eq), and 1,3,5-trimethoxybenzene (3x10 mg) (NMR standard) was prepared in dry, degassed CD_2Cl_2 (3x0.4 mL) under argon. A portion of this stock solution was transferred to an NMR tube under argon and a ^{1}H NMR spectrum was recorded. Separately, a solution of C1 (2 eq) in dry, degassed CD_2Cl_2 (0.3 mL) was added to a vial containing the solution of G3 (9 mg, 0.0102 mmol, 1 eq) in dry, degassed CD_2Cl_2 (0.3 mL) under argon. After 3 h, 0.4 mL of the stock solution containing monomers and NMR standard were injected to this vial. This whole solution was transferred to an NMR tube and ^{1}H NMR spectra were recorded at different time intervals.



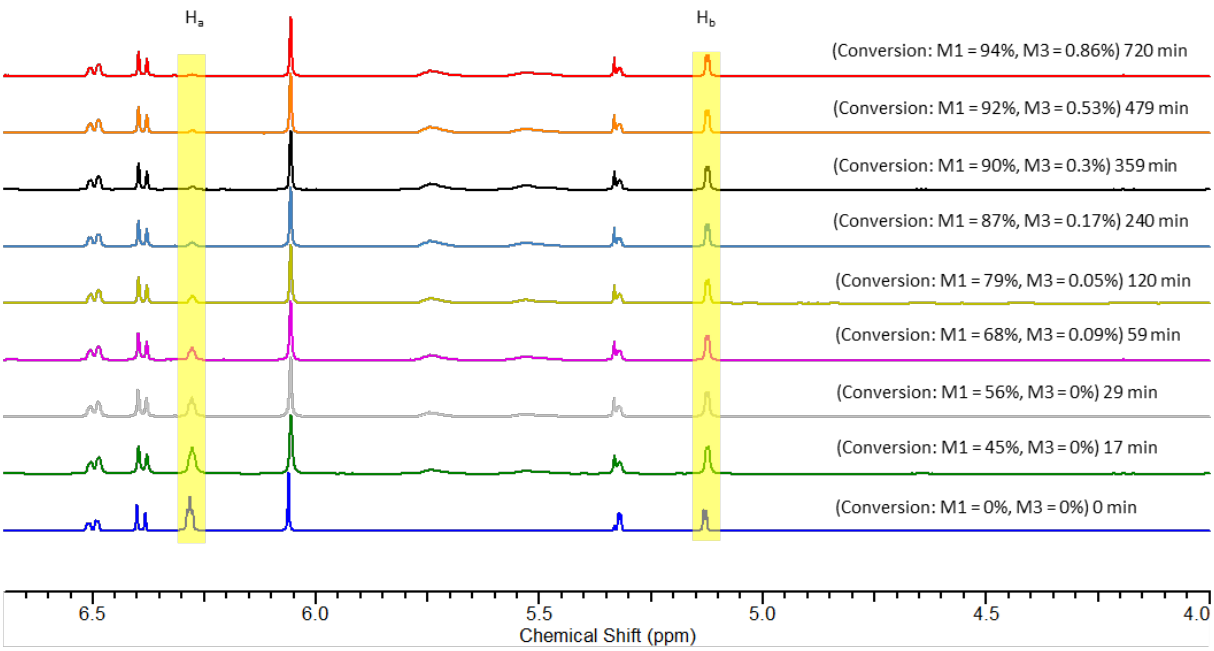


Figure S11: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of the mixture of G3 (9 mg, 0.0102 mmol, 1 eq) and C1 (2 eq) with M1 (15 eq) and M3 (15 eq) in CD_2Cl_2 at room temperature.

Separately, a solution of G3 (9 mg, 0.0102 mmol, 1 eq) was prepared in dry, degassed CD_2Cl_2 (0.2 mL) under argon. Then 0.4 mL of the stock solution containing monomers and NMR standard were injected to a vial containing 0.2 mL of the solution of G3 under argon. This whole solution was transferred to another NMR tube and a ^{1}H NMR spectrum was recorded at different time intervals until 88% consumption of M3 (within 420 min (7 h)). 100% consumption of M1 is already observed in the first ^{1}H NMR spectrum recorded after 30 min. The reaction was quenched with 0.1 mL of diethyl ether and the polymer P5-G3 (M_n, found (GPC, $CHCl_3$)=7.1 kDa, Đ=1.12, M_n, theo=5.8 kDa) was precipitated in methanol (90% yield).

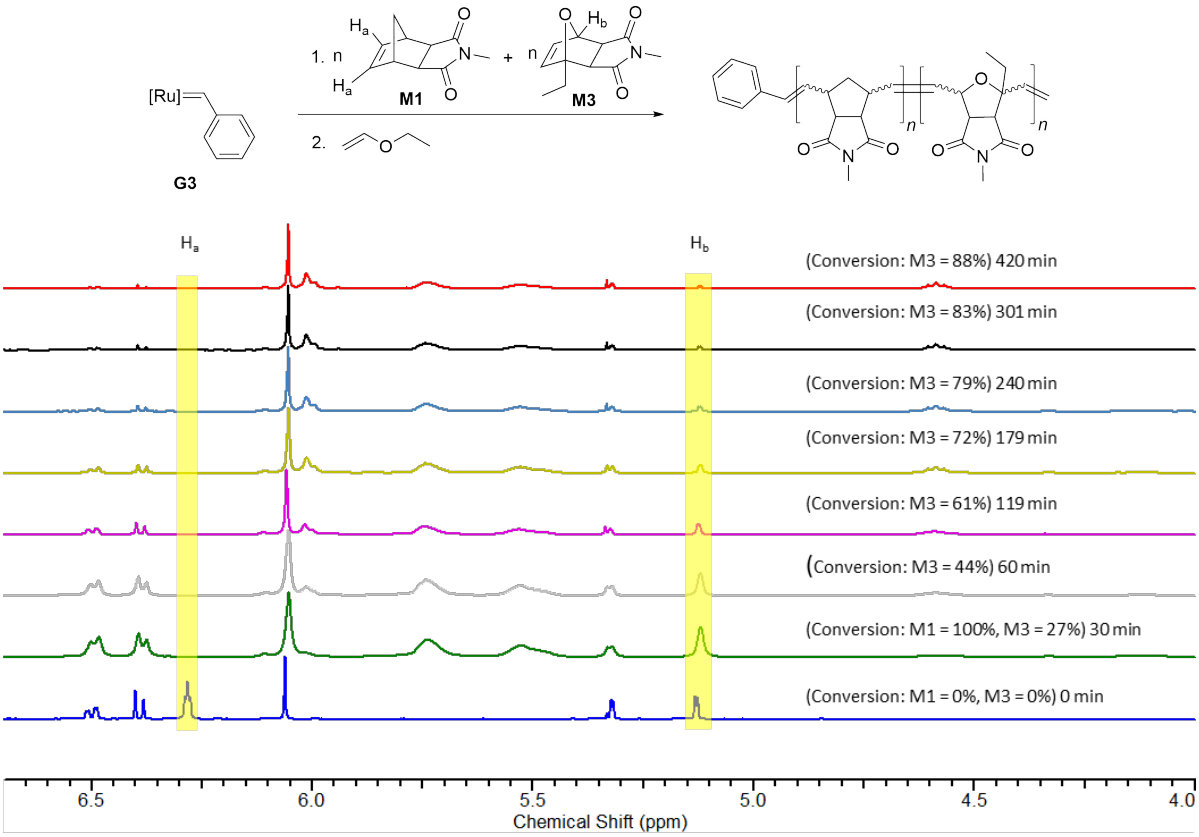


Figure S12: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G3 (9 mg, 0.0109 mmol, 1 eq) with M1 (15 eq) and M3 (15 eq) in CD_2Cl_2 at room temperature.

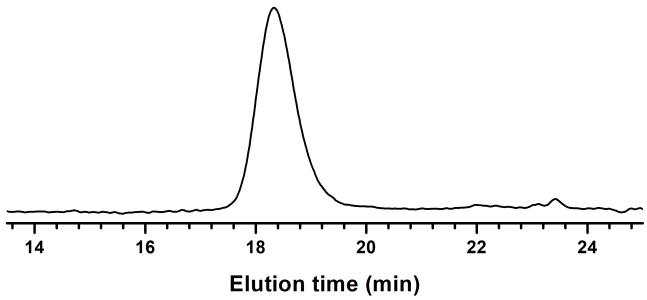


Figure S13: GPC ($CHCl_3$) trace of polymer P5-G3.

Procedure for one-step block copolymer synthesis from M4 and M5 using G3:

A stock solution of monomers M4 (3x15 eq) and M5 (3x15 eq), and 1,3,5-trimethoxybenzene (3x10 mg) (NMR standard) was prepared in dry, degassed CD_2Cl_2 (3x0.4 mL) under argon. A portion of this stock solution was transferred to an NMR tube under argon and ^{1}H NMR spectrum was recorded. Then 0.4 mL of the stock solution containing monomers and NMR standard were injected to a vial containing the solution of G3 (9 mg, 0.0109 mmol, 1 eq) in CD_2Cl_2 (0.2 mL) under argon. This whole solution was transferred to another NMR tube under argon and ^{1}H NMR spectra were recorded at different time intervals. The reaction was terminated with 0.1 mL of ethyl vinyl ether after 1922 min (32 h) and the polymer P6-G3 (M_n, found (GPC, $CHCl_3$)=1.6 kDa, Đ=1.88, M_n, theo=4.3 kDa) was precipitated in methanol (74% yield). The experimental M_n is lower than theoretical M_n probably due to the coiling of polymer chains caused by intramolecular hydrogen bonding. The reaction was not followed till the complete consumption of monomer M5 due to the decomposition of propagating metathesis catalyst during the course of polymerization caused by -OH group of monomer M5 (a known reaction).[5]

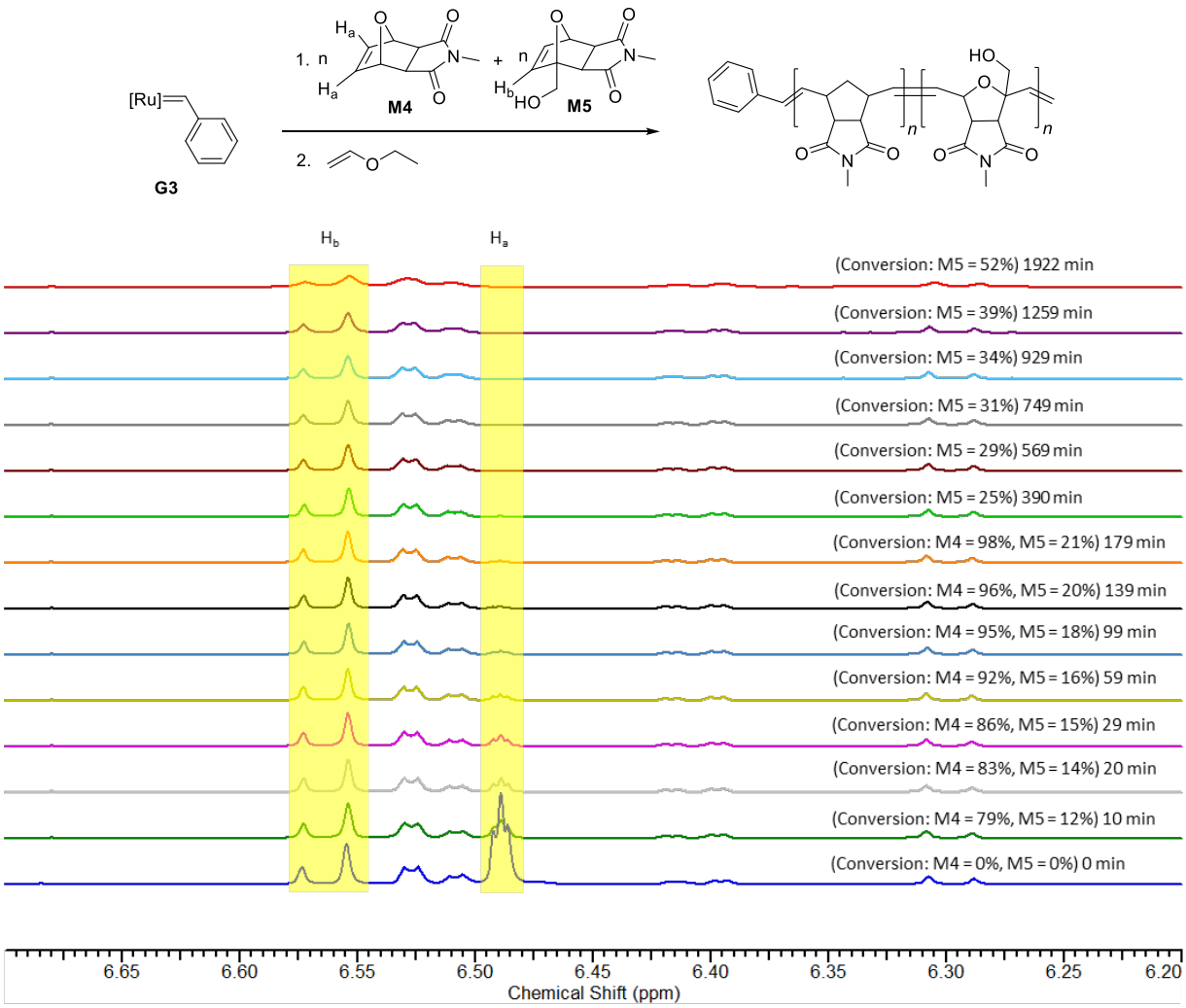


Figure S14: Time resolved ^{1}H NMR (300 MHz) spectra of the reaction of G3 (9 mg, 0.0109 mmol, 1 eq) with M4 (15 eq) and M5 (15 eq) in CD_2Cl_2 at room temperature. The *endo* isomer does not get consumed during the course of reaction.

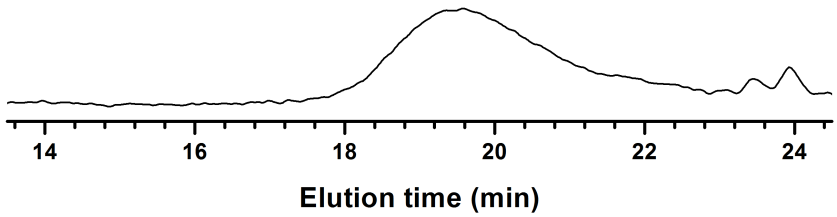
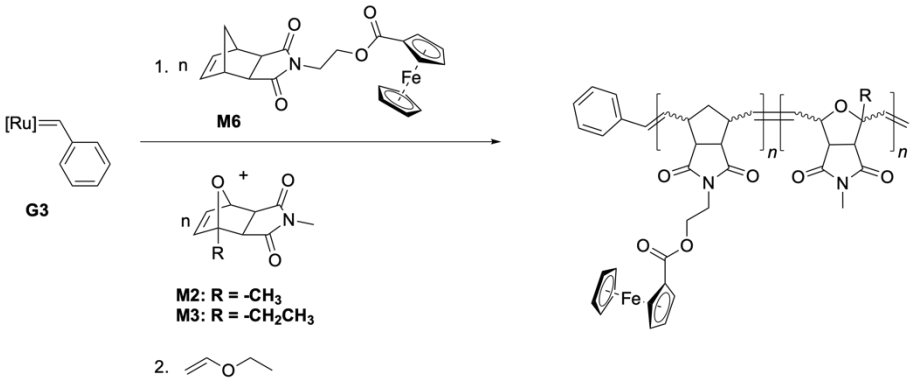


Figure S15: GPC ($CHCl_3$) trace of polymer P6-G3.

Synthesis of block copolymers for TEM imaging:



A solution of monomers M6 (30 eq) and M2 (30 eq) or M3 (30 eq) was prepared in dry, degassed CH_2Cl_2 (0.8 mL) under argon. Separately, a solution of G3 (9 mg, 0.0102 mmol, 1 eq) was prepared in dry, degassed CH_2Cl_2 (0.4 mL) under argon. Then solution of monomers was injected to a vial containing the solution of G3 under argon and the reaction was terminated after 360 min (6 h) or 840 min (14 h) with 0.1 mL of ethyl vinyl ether and the polymer P7-G3 (M_n, found (GPC, $CHCl_3$)=16.4 kDa, Đ=1.10, M_n, theo=18.4 kDa) (90% yield) or P8-G3 (M_n, found (GPC, $CHCl_3$)=16 kDa, Đ=1.11, M_n, theo=18.8 kDa) was precipitated in methanol (88% yield).

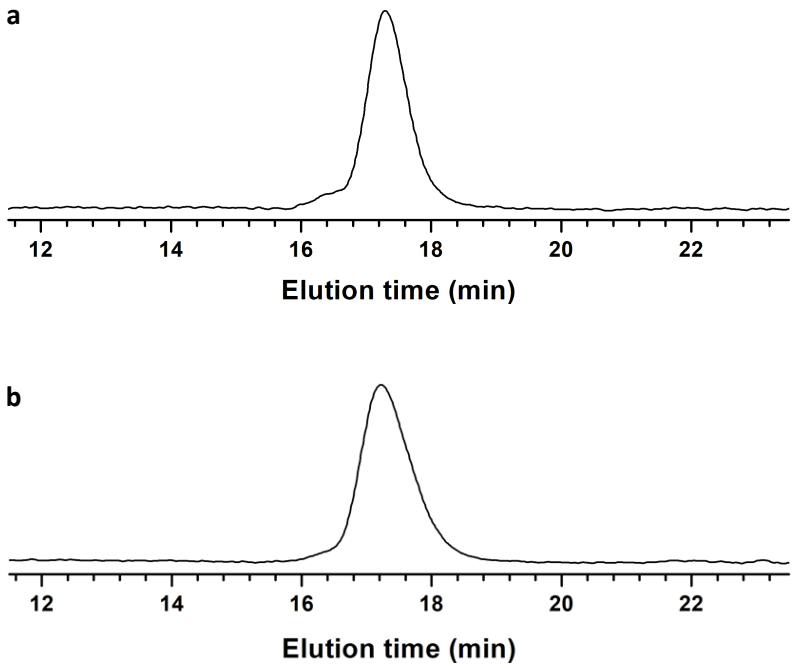


Figure S16: GPC ($CHCl_3$) traces of polymer (a) P7-G3 and (b) P8-G3.

Sample preparation for TEM images

For TEM examination the melt crystallized bulk samples were prepared using ultramicrotomy. The samples were embedded in epoxy resin and subsequently sectioned at room temperature using a Leica ultracut UCT. To decrease the compression of the sample, a 35° DiATOME ultrasonic oscillating diamond knife was used for sectioning. The thin sections were collected on the copper grids and subsequently RuO_4 stained for 2 h.

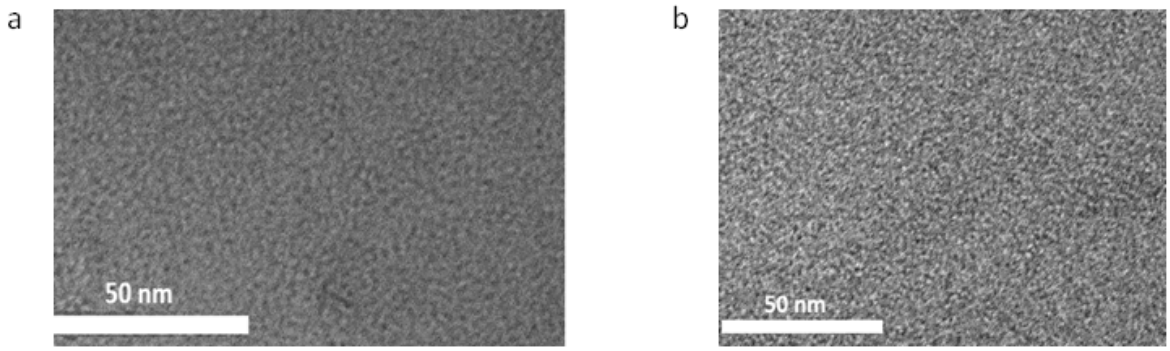


Figure S17: TEM images of polymer (a) P7-G3 and (b) P8-G3.

Reactivity ratio evaluation

(A) Lynd method: Lynd et al. proposed a method for the estimation of reactivity ratios based on the nonterminal model.[6] Lynd equation for the evaluation of reactivity ratios is given below.

$$X = 1 - f_{1,0}\left[1 - \left(1 - \frac{M_1}{M_{1,0}}\right)\right] - \left(1 - f_{1,0}\right)\left[1 - \left(1 - \frac{M_1}{M_{1,0}}\right)\right]^{r_2}$$

$$X = 1 - f_{1,0}\left[1 - \left(1 - \frac{M_x}{M_{x,0}}\right)\right]^{r_1} - \left(1 - f_{1,0}\right)\left[1 - \left(1 - \frac{M_x}{M_{x,0}}\right)\right]$$

Where,

r_1 and r_2 are the reactivity ratios for monomers M1/M4 and M2/M3/M5, respectively.

M_1 and M_X are the concentrations of monomers M1/M4 and M2/M3/M5 at a given time, respectively.

$M_{1,0}$ and $M_{X,0}$ are the initial concentrations of monomers M1/M4 and M2/M3/M5, respectively.

$f_{1,0}$ is the initial mole fraction of the monomer M1/M4.

X is the total conversion.

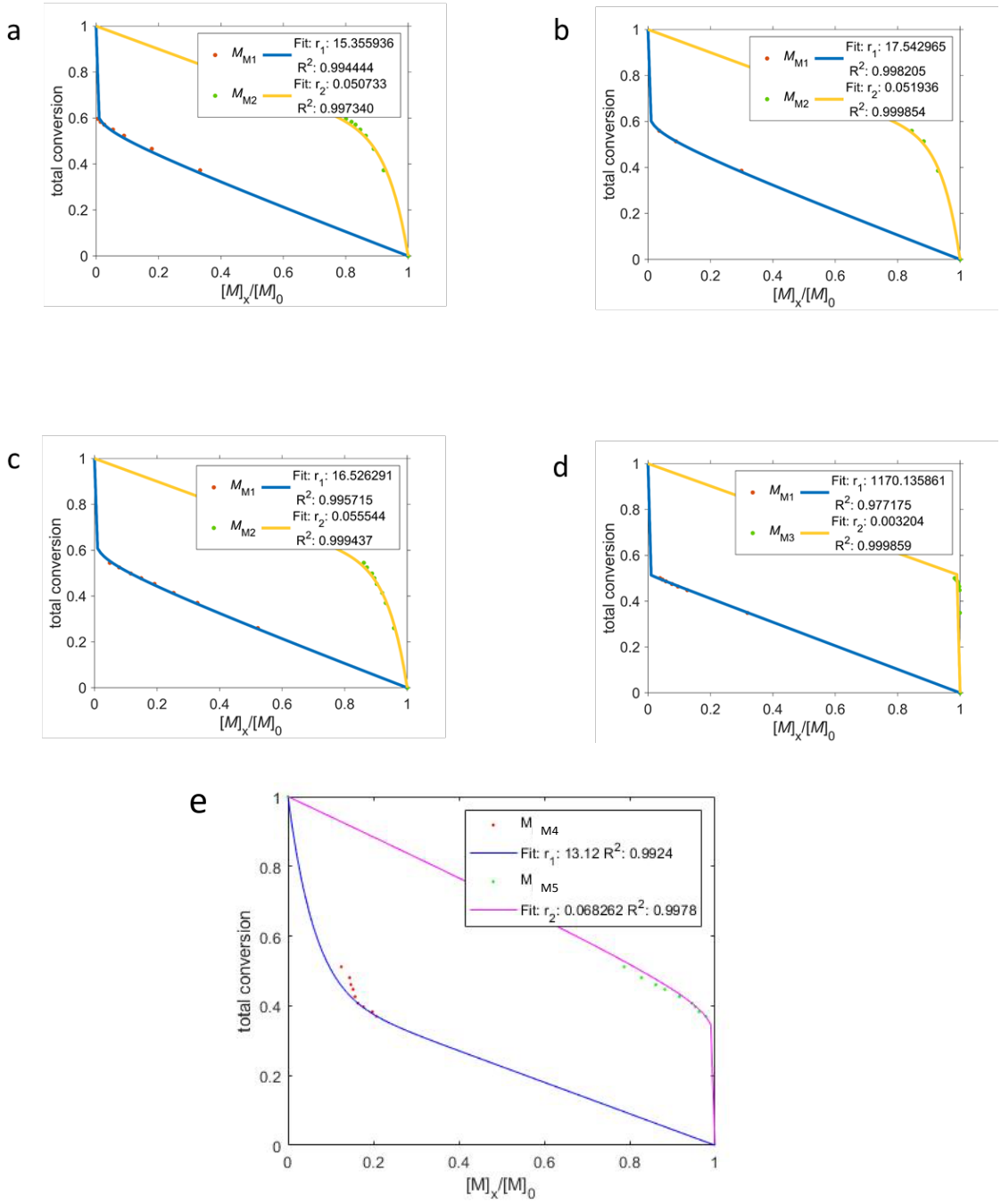


Figure S18: (a) Lynd fit from the ^{1}H NMR data of the reaction of M1 and M2 with G1, taken from the Figure S1, (b) Lynd fit from the ^{1}H NMR data of the reaction of M1 and M2 with G3, taken from the Figure S3, (c) Lynd fit from the ^{1}H NMR data of the reaction of M1 and M2 with the mixture of G3 and C1, taken from the Figure S10, (d) Lynd fit from the ^{1}H NMR data of the reaction of M1 and M3 with the mixture of G3 and C1, taken from the Figure S11 and (e) Lynd fit from the ^{1}H NMR data of the reaction of M4 and M5 with G3, taken from the Figure S14.

(B) Ideal integrated equation: A new copolymerization equation for the nonterminal model was recently proposed by Frey et al.[7] The ideal integrated equation for the evaluation of reactivity ratios is given below.

$$X = 1 - \left(\frac{f_1}{f_{1,0}}\right)^{\frac{1}{r_1 - 1}} \left(\frac{1 - f_1}{1 - f_{1,0}}\right)^{\frac{r_1}{1 - r_1}}$$

$$r_2 = 1 / r_1$$

Where,

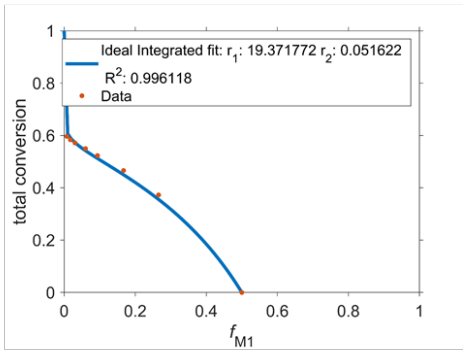
r_1 and r_2 are the reactivity ratios for monomers M1/M4 and M2/M3/M5, respectively.

$f_{1,0}$ is the initial mole fraction of the monomer M1/M4.

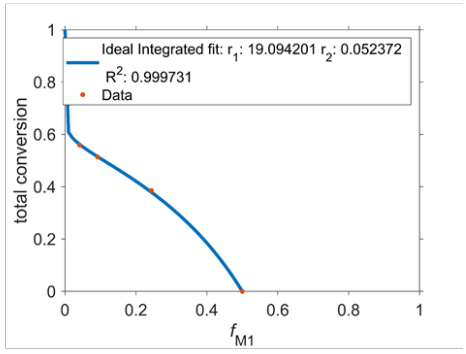
f_1 is the mole fraction of the monomer M1/M4 at a given time.

X is the total conversion.

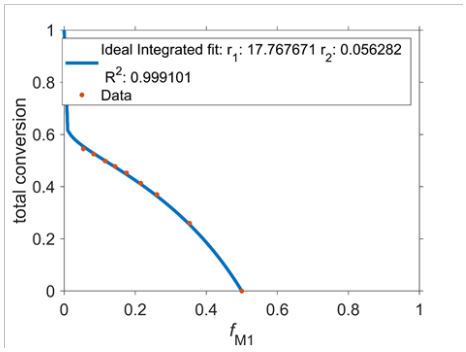
a



b



c



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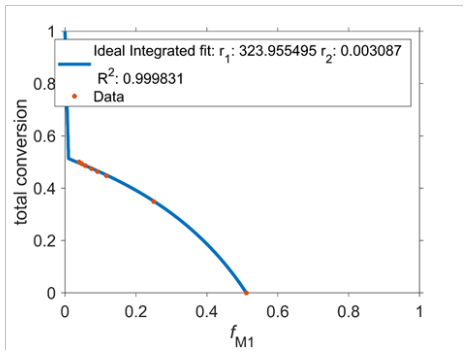

e

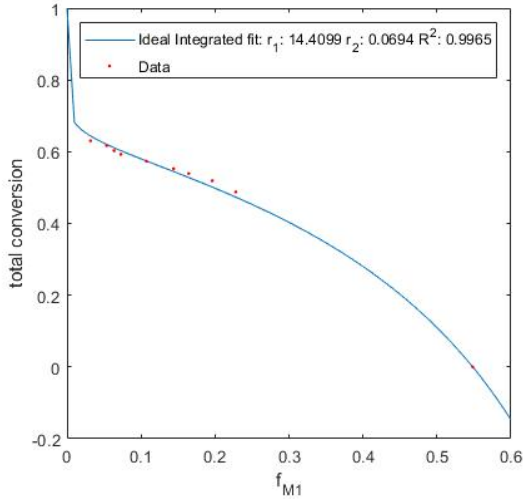

Figure S19: (a) Ideal integrated fit from the ^{1}H NMR data of the reaction of M1 and M2 with G1, taken from the Figure S1, (b) ideal integrated fit from the ^{1}H NMR data of the reaction of M1 and M2 with G3, taken from the Figure S3, (c) ideal integrated fit from the ^{1}H NMR data of the reaction of M1 and M2 with the mixture of G3 and C1, taken from the Figure S10, (d) ideal integrated fit from the ^{1}H NMR data of the reaction of M1 and M3 with the mixture of G3 and C1, taken from Figure S11 and (e) ideal integrated fit from the ^{1}H NMR data of the reaction of M4 and M5 with G3, taken from Figure S14.

Table S1: Overview of the evaluated reactivity ratios for M1/M2, M1/M3 and M4/M5 under different reaction conditions. The values of r_1 are rounded to the nearest integer while the values of r_2 are rounded to nearest 1/1000 decimal place. The standard errors of the mean r_1 and r_2 values for M1/M2 with G1 were obtained from duplicate ^{1}H NMR spectroscopy measurements.

Fit	M1/M2									M1/M3*			M4/M5		
	G1			G3			G3 and C1			G3 and C1			G3		
	r_1	r_2	$r_1.r_2$	r_1	r_2	$r_1.r_2$	r_1	r_2	$r_1.r_2$	r_1	r_2	$r_1.r_2$	r_1	r_2	$r_1.r_2$
Lynd	15±0.4	0.051±0.004	0.76	18	0.052	0.94	17	0.056	0.95	1170	0.003	3.5	13	0.068	0.88
Ideal integrated	19±0.8	0.052±0.003	0.99	19	0.052	0.99	18	0.056	1	324	0.003	0.97	14	0.069	0.97

*The disagreement between the reactivity ratios calculated from Lynd and ideal integrated fit could be due to the fact that M3 reacts negligibly while M1 gets consumed completely. Ideal integrated fit is less sensitive to the errors.

Calculation of the copolymer microstructure

The copolymer microstructure can be calculated by the previously obtained r parameters. Therefore, the instantaneous copolymer composition F_1 is plotted against the total conversion X.[8]

Equations used for the calculation of the copolymer microstructure are given below.

$$X = 1 - \frac{M_1 + M_x}{M_{1,0} + M_{x,0}}$$

$$t = \frac{M_1}{M_x}$$

$$\varepsilon = \frac{1 + r_1 t}{1 + r_2 t^{-1}}$$

$$F_1 = \frac{\varepsilon}{1 + \varepsilon}$$

Where,

F_1 is the instantaneous copolymer composition.

M_1 and M_x are the concentrations of monomers M1 and M2/M3 at a given time, respectively.

$M_{1,0}$ and $M_{X,0}$ are the initial concentrations of monomers M1 and M2/M3, respectively.

X is the total conversion.

^{1}H NMR and ^{13}C NMR data

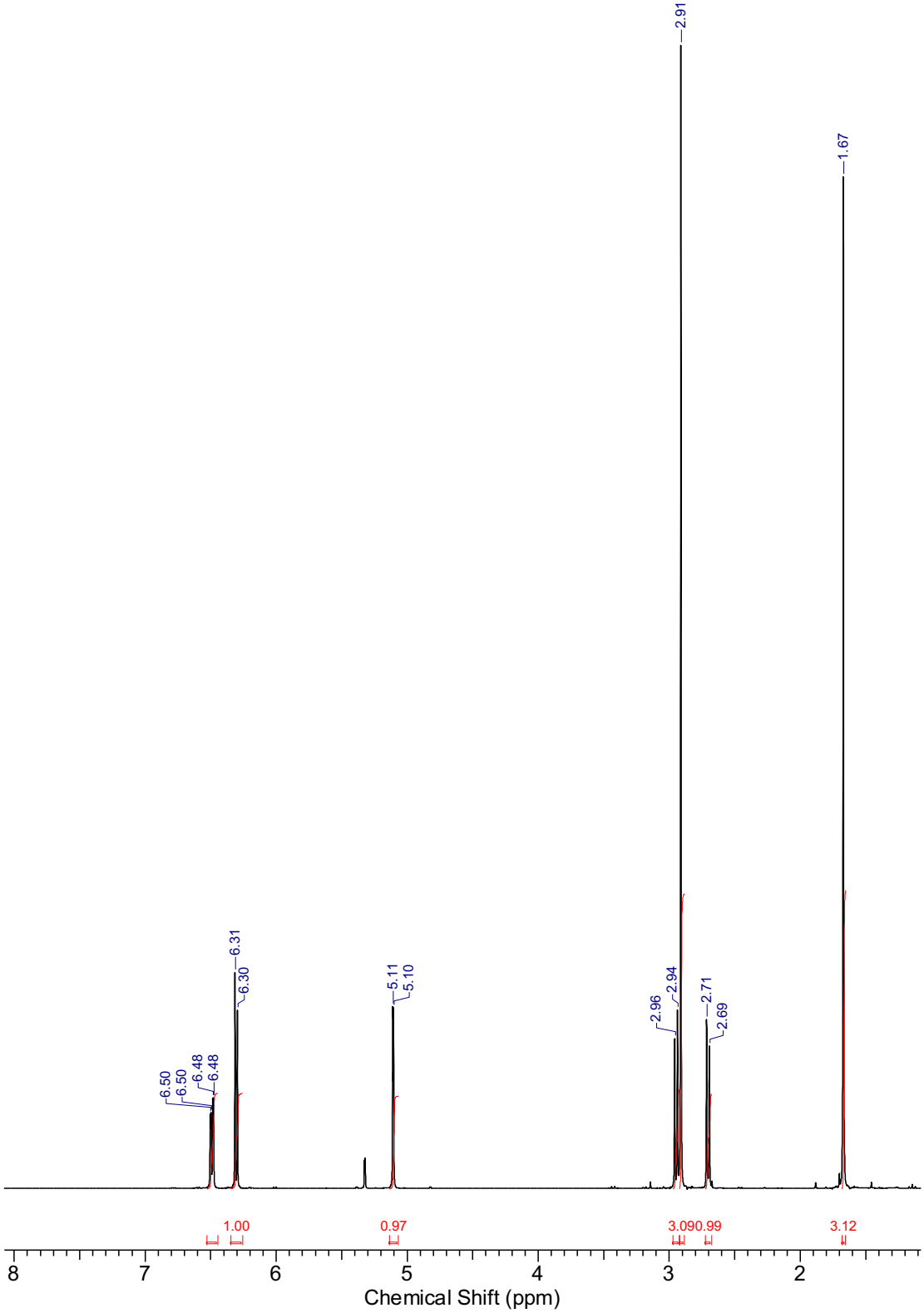

Figure S20: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of M2.

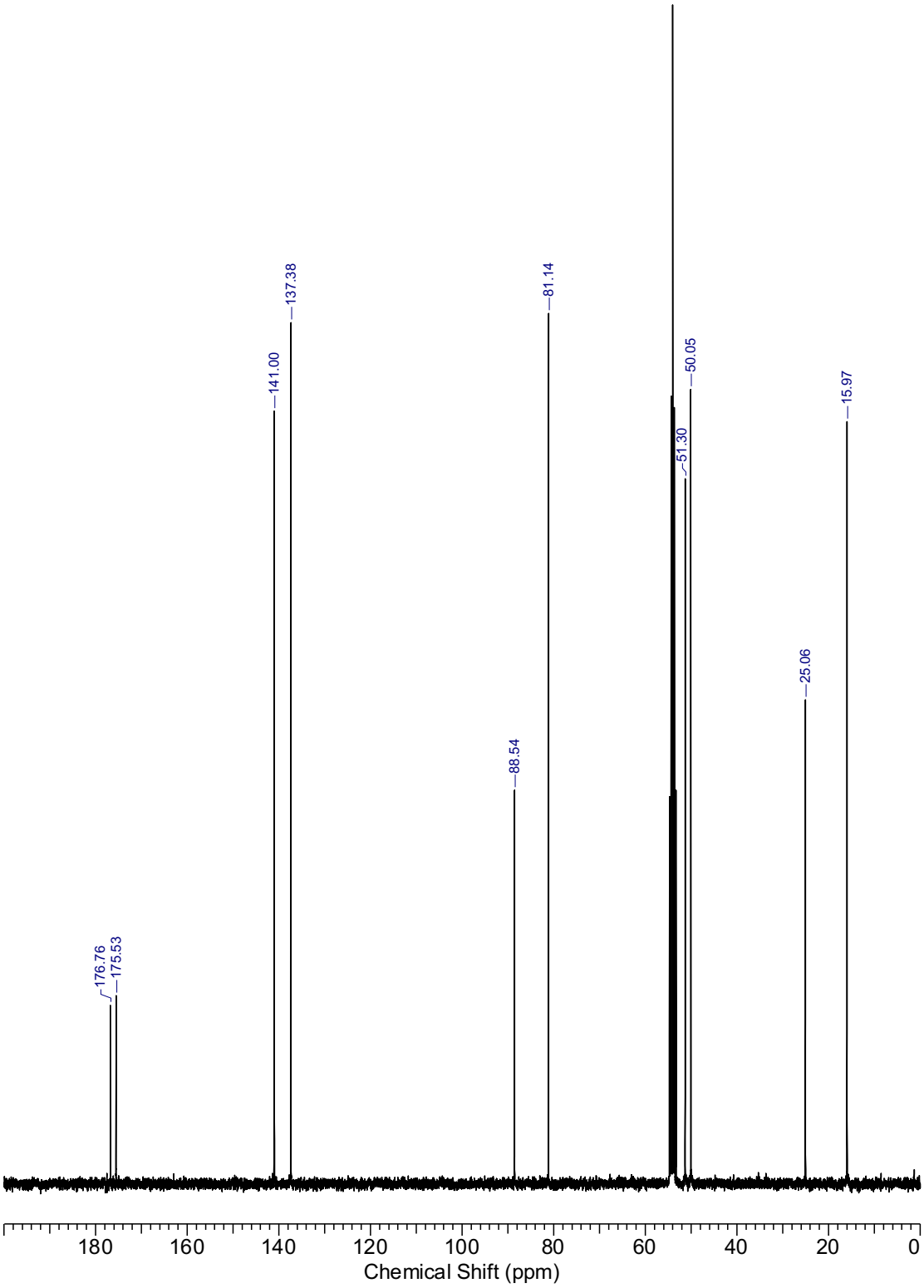

Figure S21: ^{13}C NMR (dichloromethane-d_2, 75 MHz) spectrum of M2.

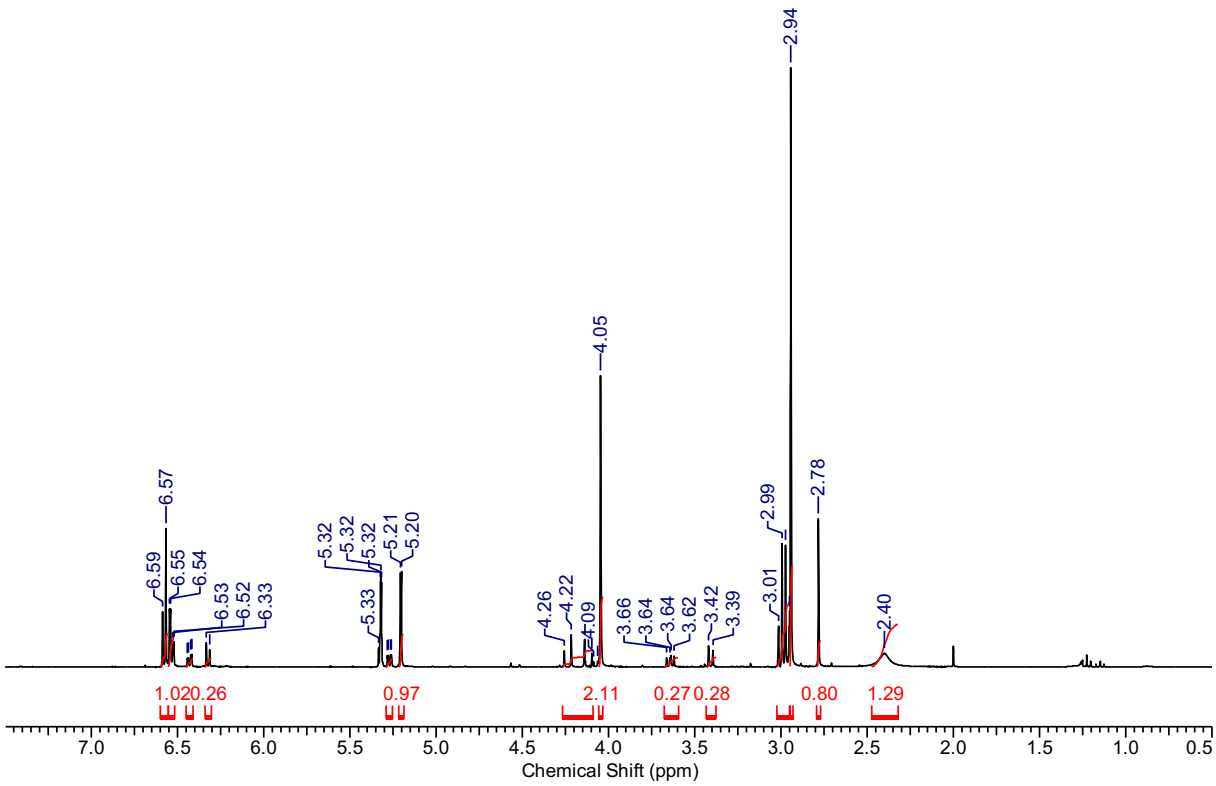

Figure S22: ^{1}H NMR (dichloromethane-d$_2$, 300 MHz) spectrum of M4.

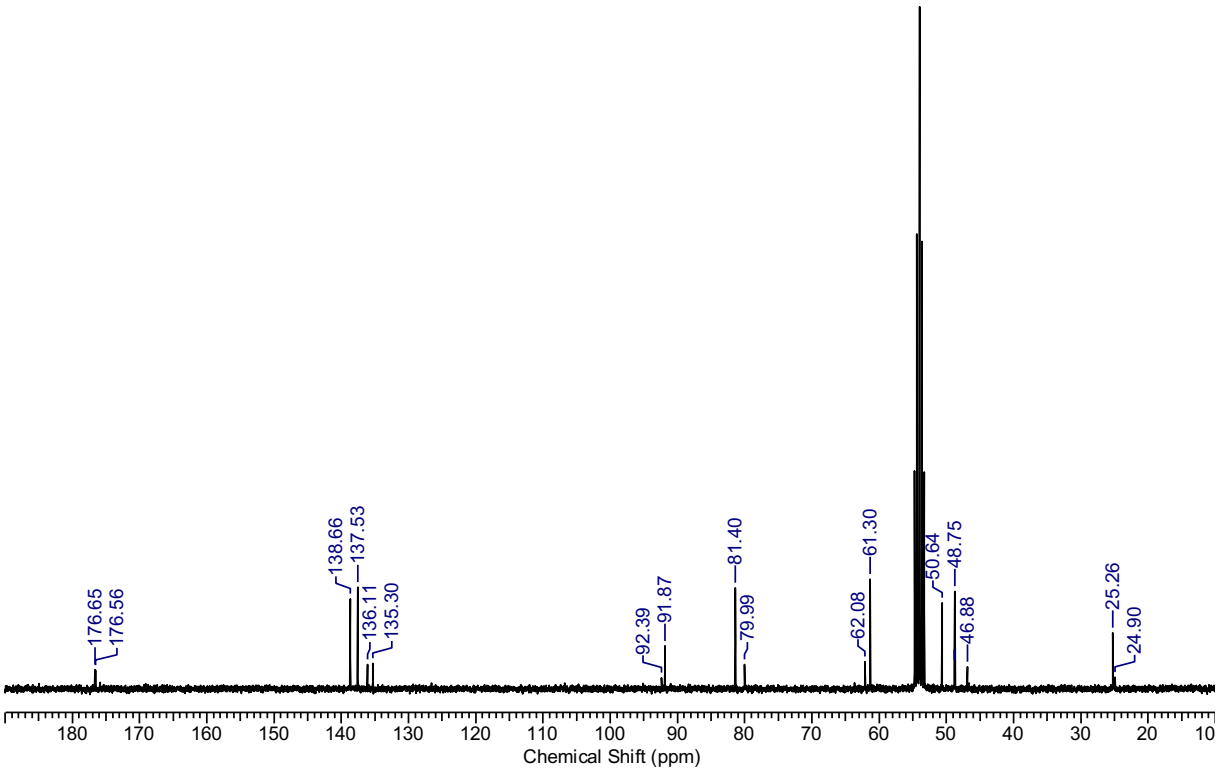

Figure S23: ^{13}C NMR (dichloromethane-d$_2$, 75 MHz) spectrum of M4.

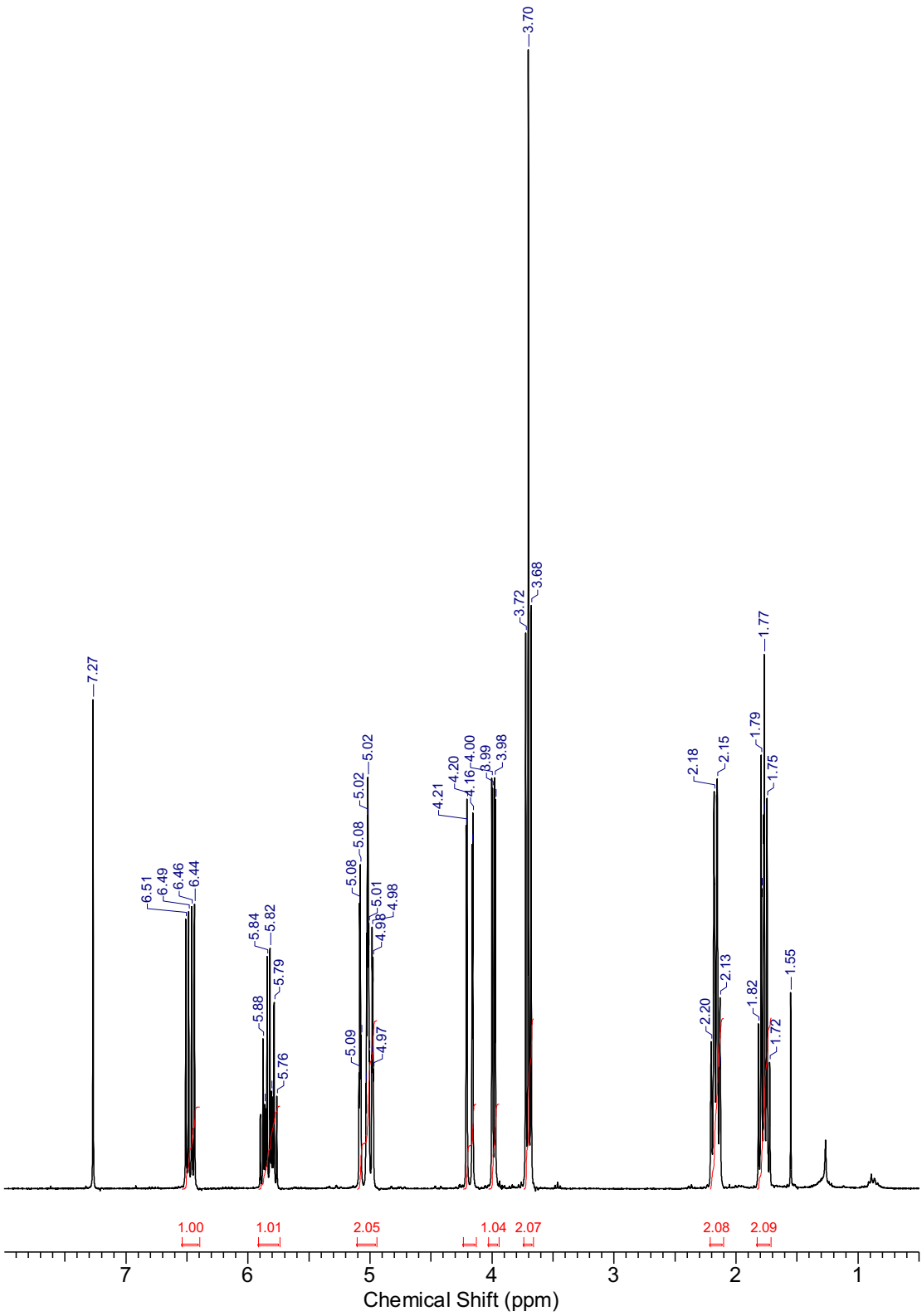

Figure S24: ^{1}H NMR (chloroform-d, 300 MHz) spectrum of S1.

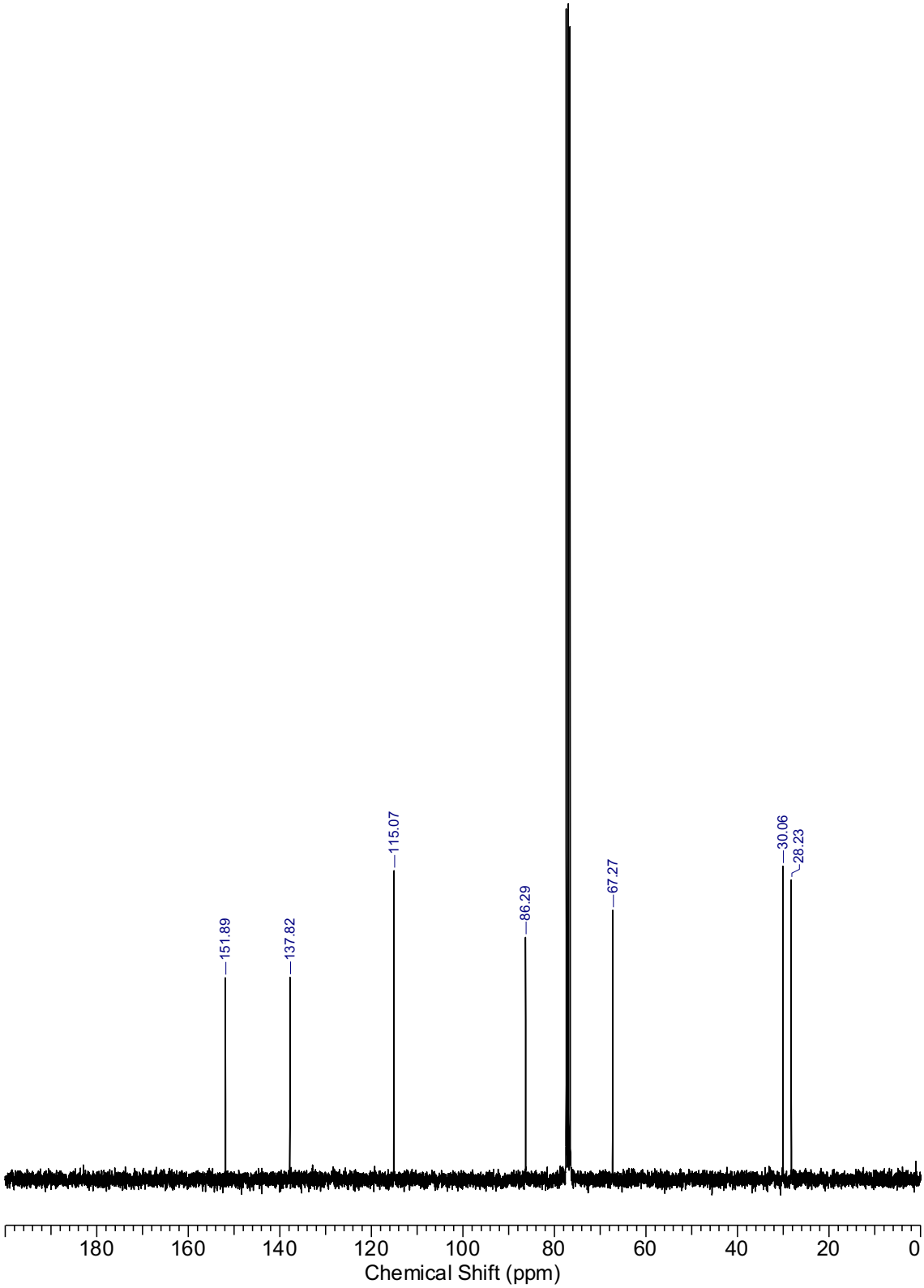

Figure S25: ^{13}C NMR (chloroform-d, 75 MHz) spectrum of S1.

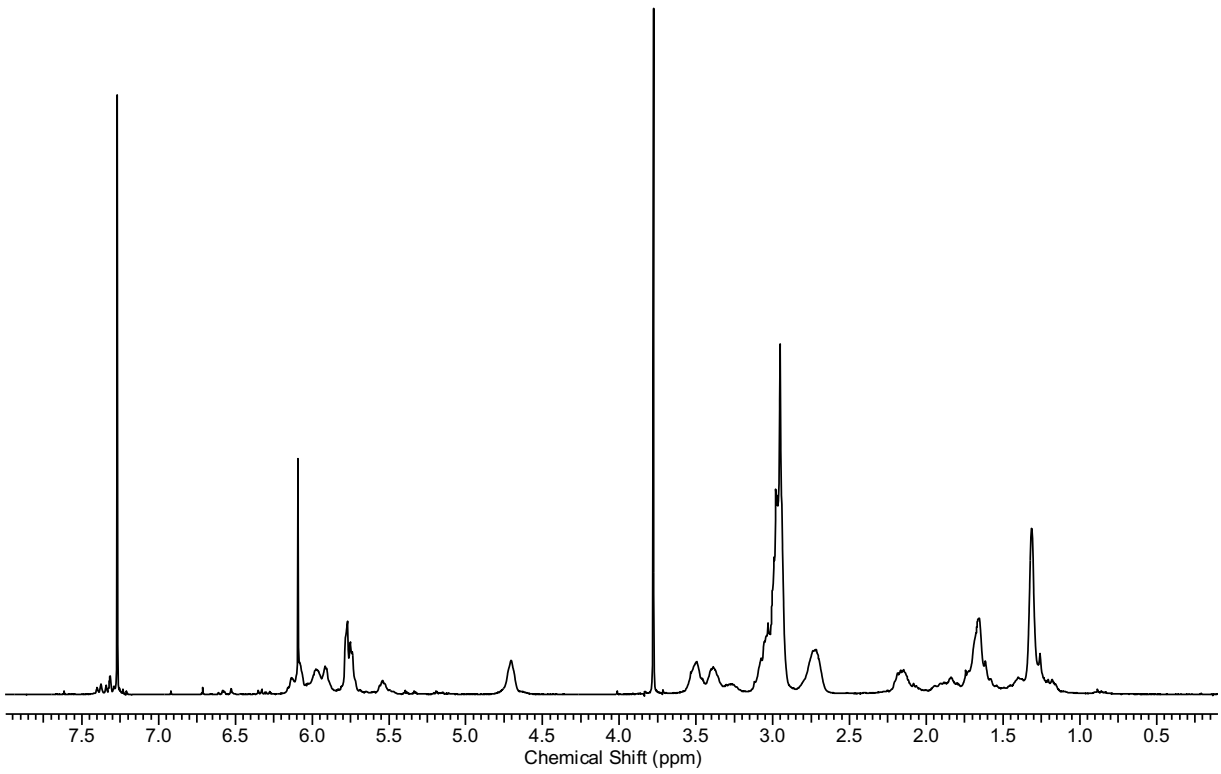

Figure S26: ^{1}H NMR (chloroform-d, 300 MHz) spectrum of P1-G1.

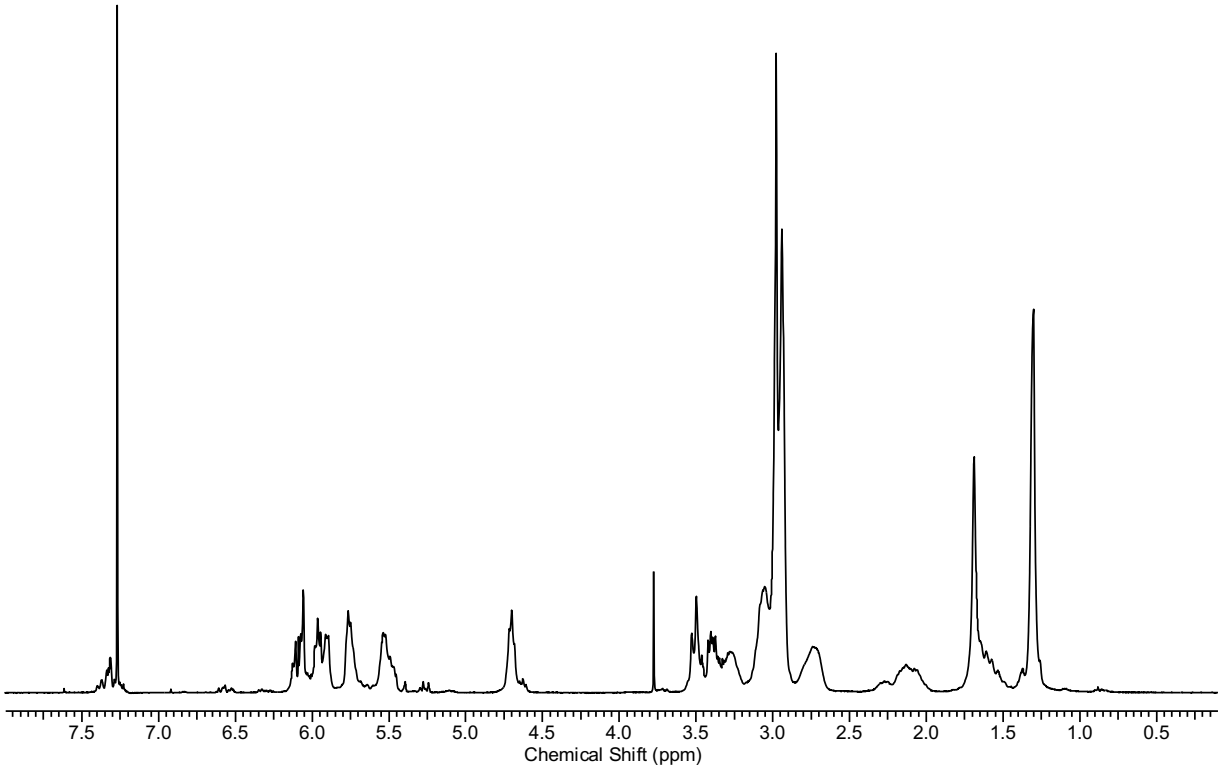

Figure S27: ^{1}H NMR (chloroform-d, 300 MHz) spectrum of P1-G3.

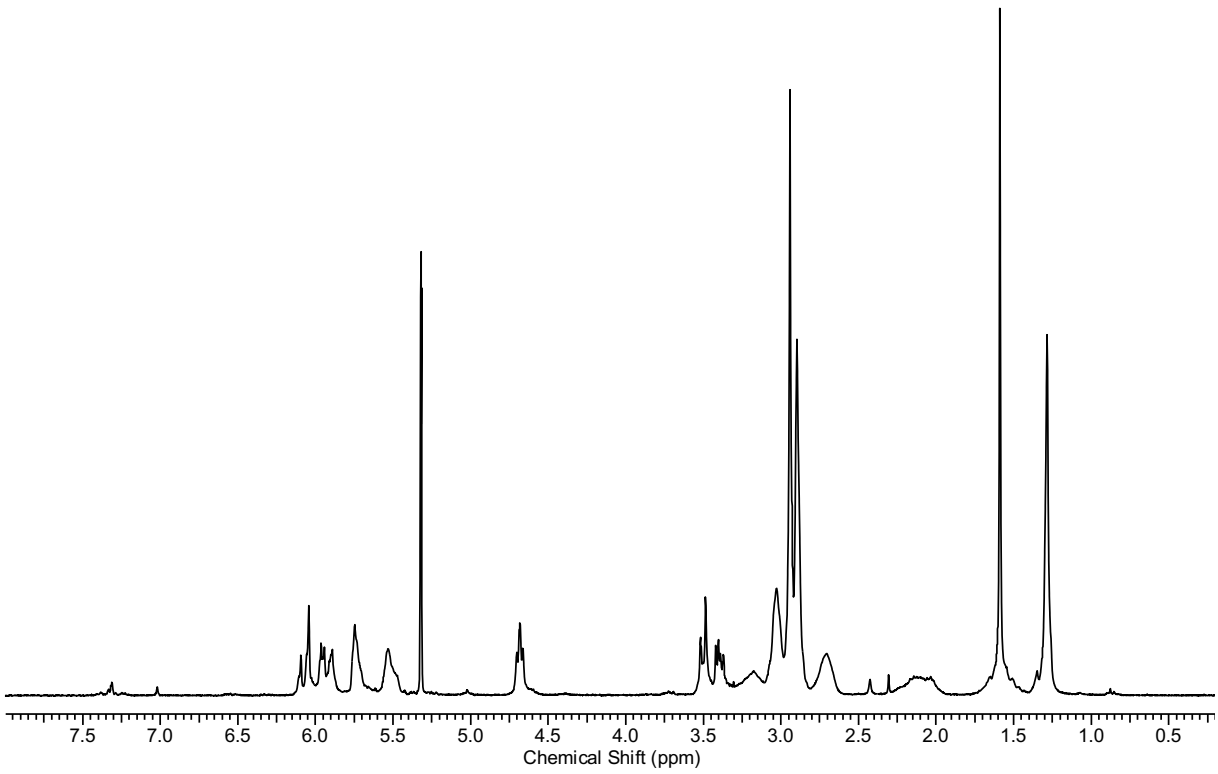

Figure S28: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P2-G3.

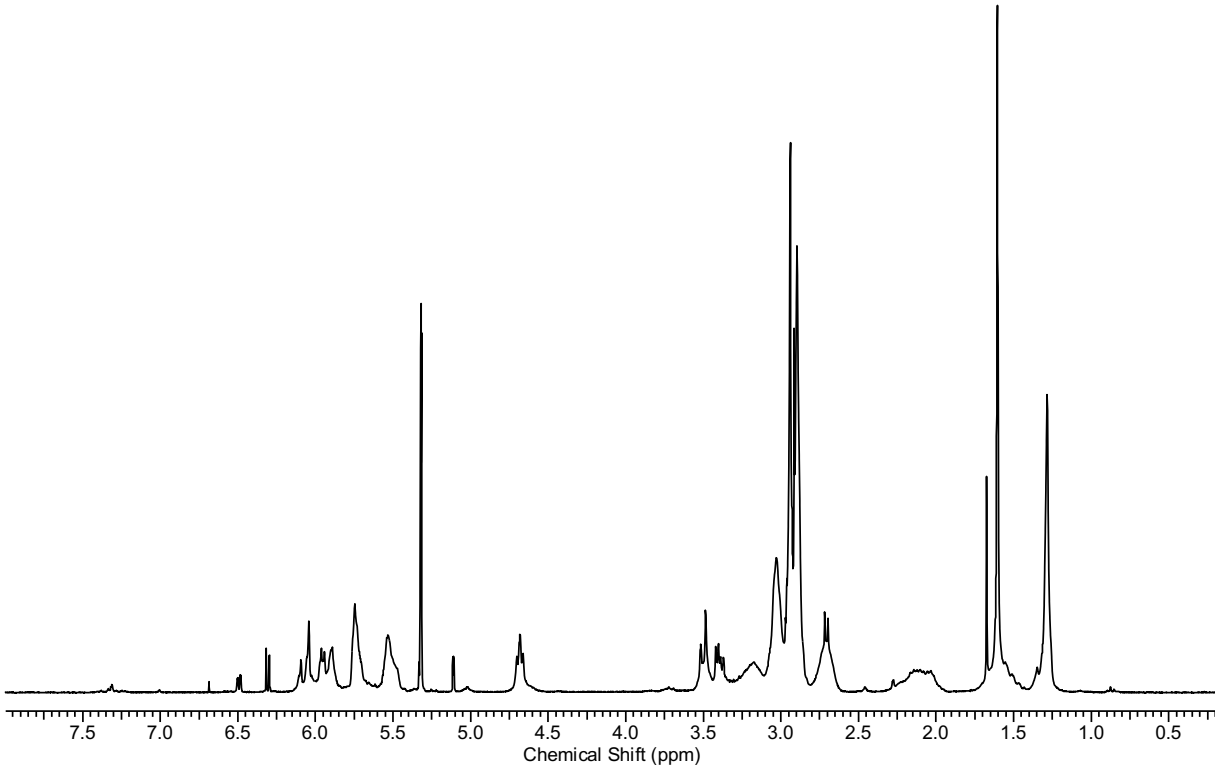

Figure S29: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P3-G3.

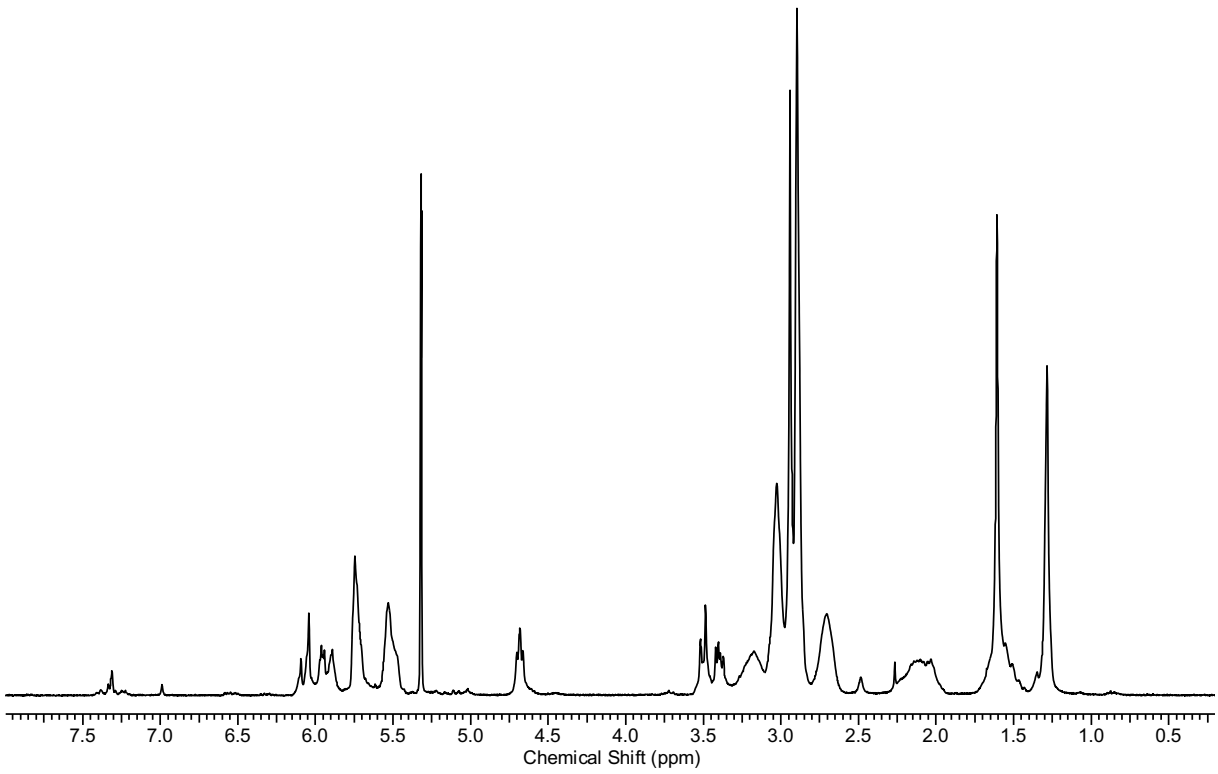

Figure S30: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P4-G3.

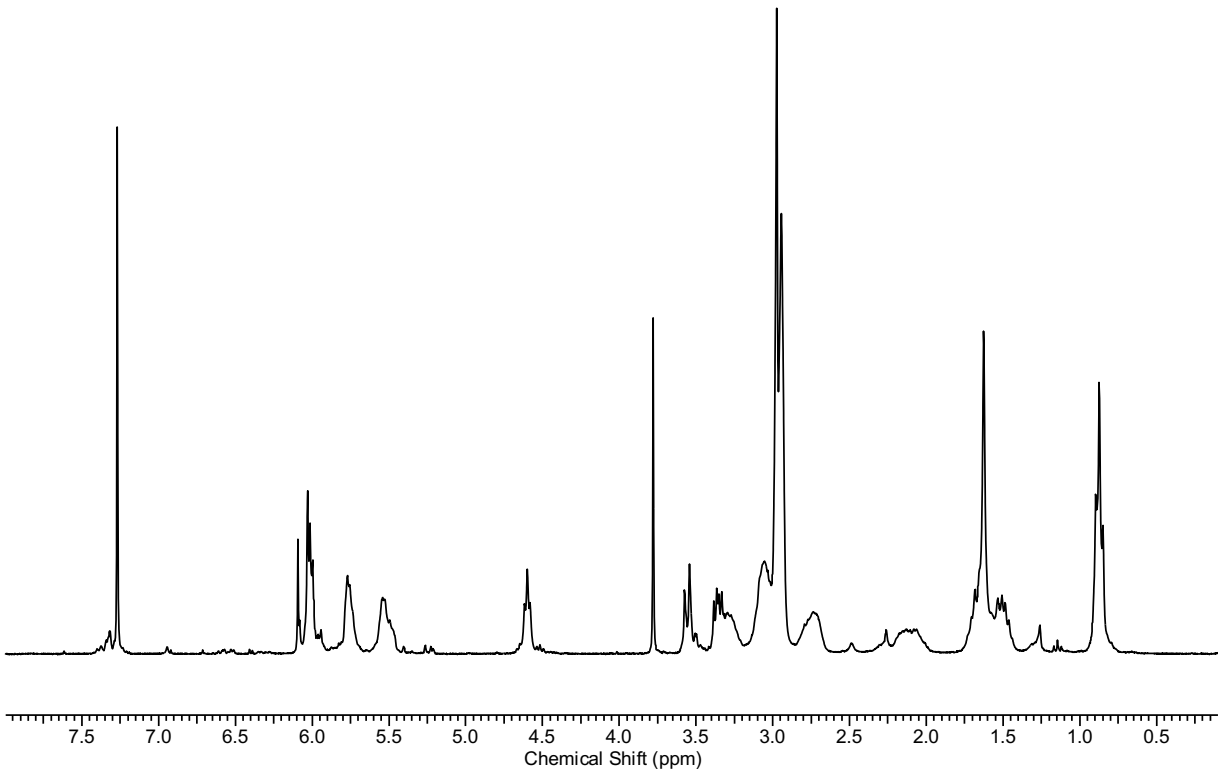

Figure S31: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P5-G3.

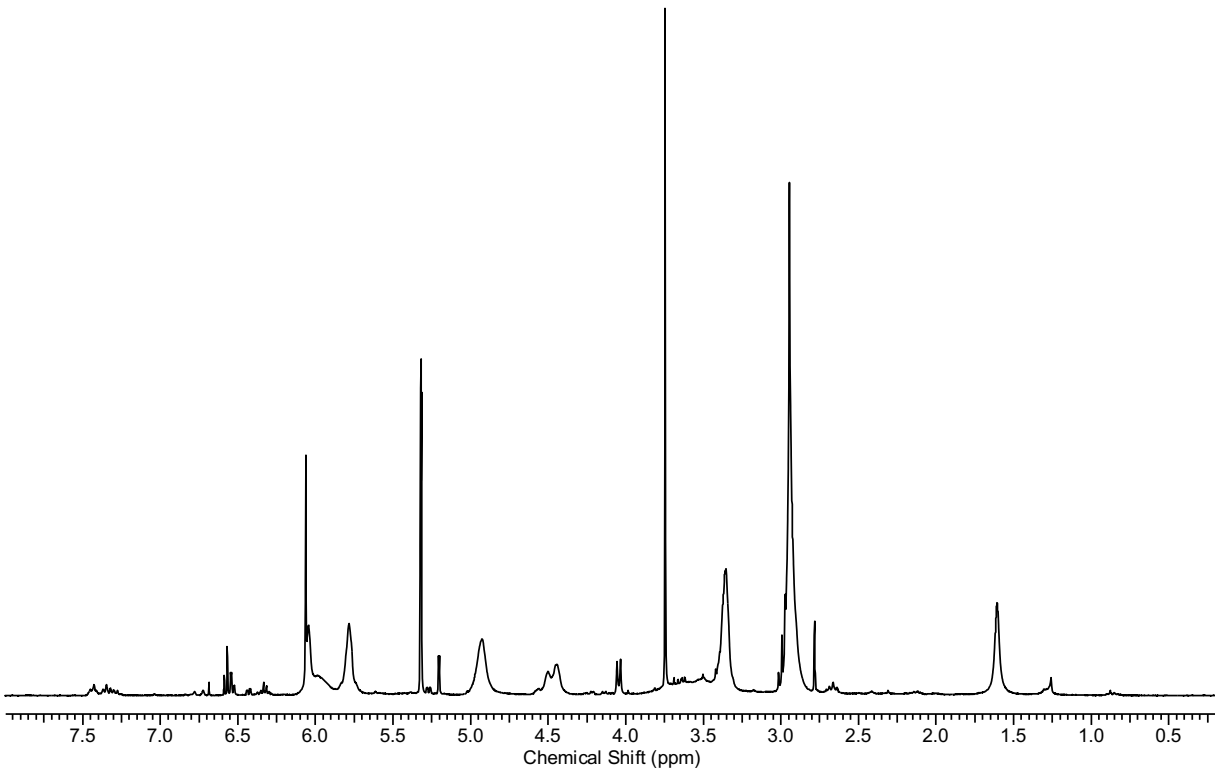

Figure S32: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P6-G3.

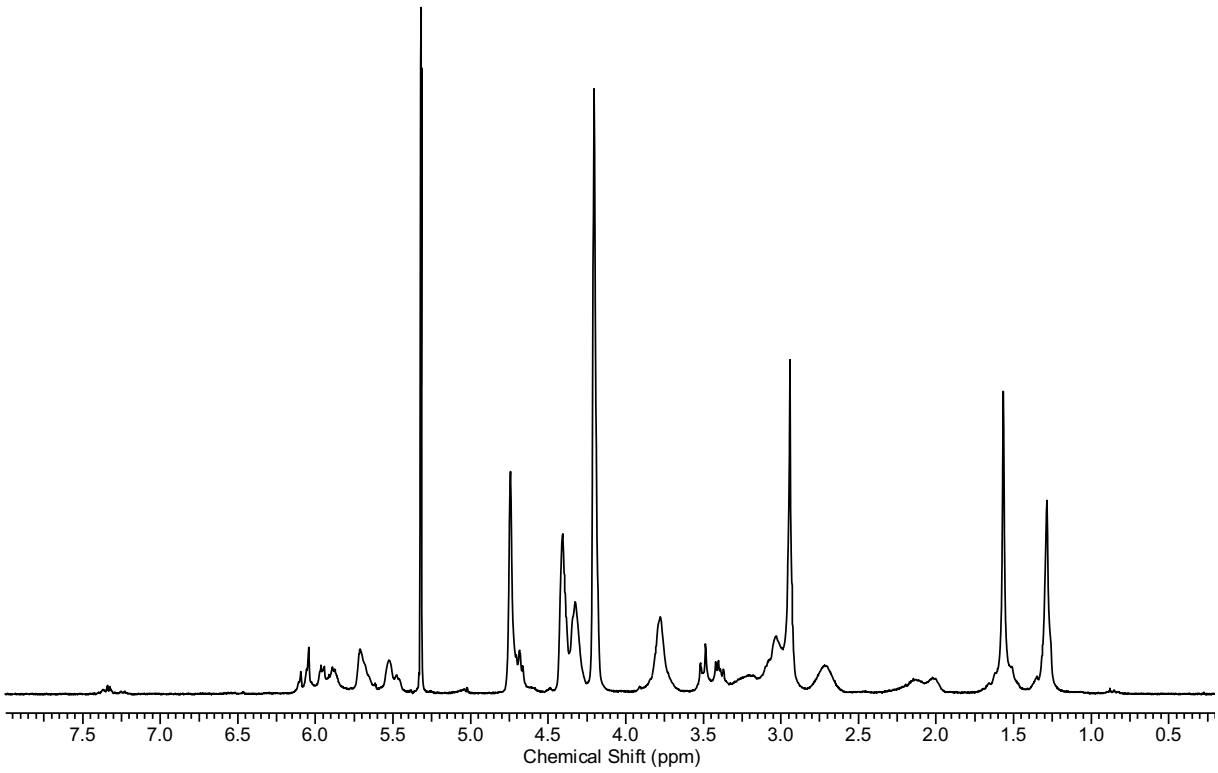

Figure S33: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P7-G3.

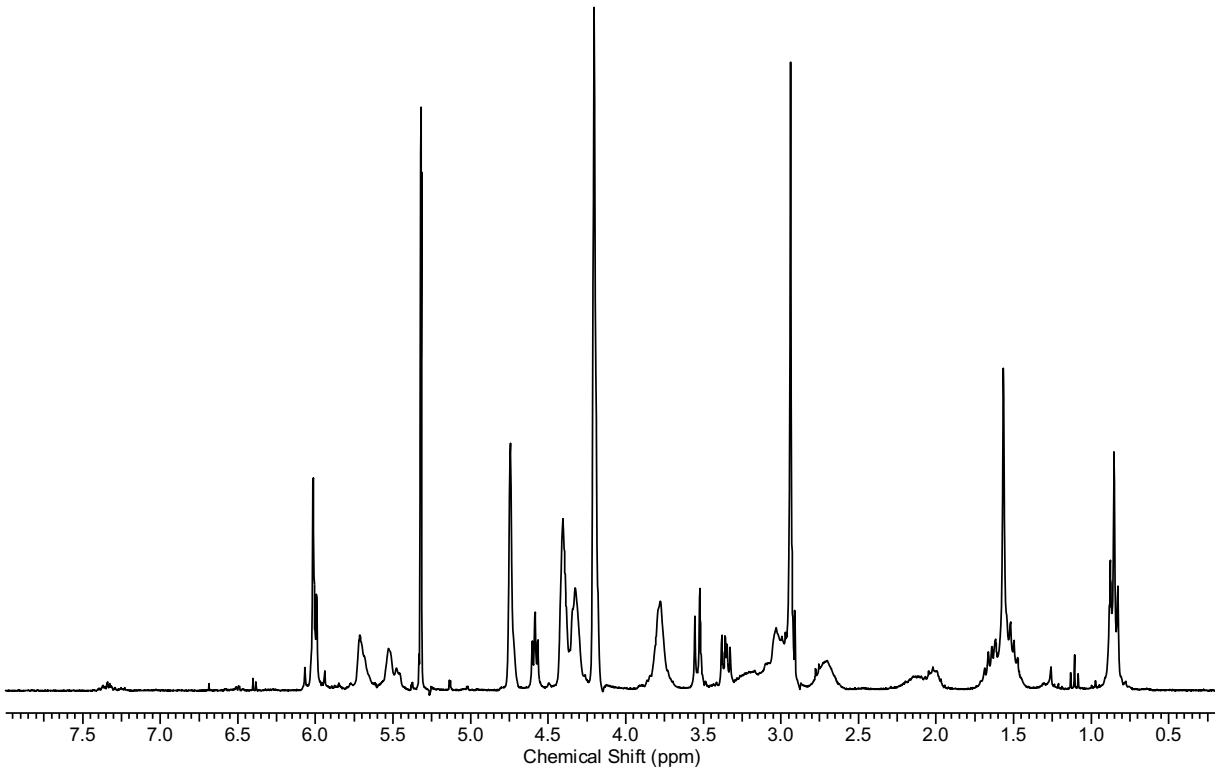

Figure S34: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of P8-G3.

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