Supporting Information

Oxanorbornenes: Promising New Single Addition Monomers for the Metathesis Polymerization.

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Materials

Grubbs' initiators G3, *N*-methylmaleimide, *N*-ethylmaleimide, 2-Methylfuran, 2-Pentylfuran, dimethyl acetylenedicarboxylate, Furfuryl alcohol, 3-Bromopyridine and 1,3,5-Trimethoxybenzene were purchased from Sigma-Aldrich and used without further purification. 2-Propylfuran and Triisopropylsilyl chloride was purchased from Alfa-Aesar and used without further purification. All other reagents and solvents were purchased from Acros organics or Sigma-Aldrich and used without further purification. Deuterated solvents (CD_2Cl_2 , $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc.

Characterization

All ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX (360 MHz) FT NMR spectrometer. Chemical shifts were given in ppm relative to the residual solvent peak (CDCl₃: 7.26 for ¹H; CDCl₃: 77.16 for ¹³C and CD₂Cl₂: 5.32 for ¹H; CD₂Cl₂: 53.88). HR MALDI FT-ICR mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II in positive mode using trans-2-[3-(tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix and silver trifluoroacetate (AgTFA), sodium trifluoroacetate (NaTFA) as counter ion source. HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with tetrahydrofuran as eluent with a flow rate of 1 mL/min at room temperature. The system was calibrated with polystyrene standards in a range from 10^3 to 3×10^6 Da. The instrument is an automated Viscotek GPCmax VE-2001 with a set of two Viscotek T6000M linear columns (300 x 8 mm, 5 µm particle size). Signal detection occurred by use of a Viscotek Smartline 2600 UV detector (set to 254 nm wavelength) and a Viscotek VE 3580 RI detector (refractive index). The Chloroform GPC is an automated PSS SECcurity System (Agilent Technologies 1260 infinity ll) with a set two MZ-Gel SDplus linear columns (300 x 8 mm, 5 µm particle size). The Chloroform GPC was calibrated with polystyrene standards in a range from 10^3 to 3×10^6 Da and the samples were run at 40 °C and a flow rate of 1.0 mL/min.

Synthesis of substrates *N*-methyl-7-oxanorborneneimide (1)



A mixture of *N*-methylmaleimide (10g, 90 mmol, 1eq) and furan (9.19g, 135 mmol, 1.5eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 0 C until complete disappearance of N-methylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 57:43 endo-, exo- mixture (15.78g, 98%). The mixture was used for metathesis without any further purifications. The mixture was also purified by column chromatography with hexane: ethyl acetate (75:25) to obtain pure **1-endo** (white solid) and **1-exo** (crystalline colorless solid). The endo isomer was stored at -20 0 C. Endo- isomer: ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 6.39 (t, *J*=0.86 Hz, 2 H), 5.32 (ddd, *J*=2.69, 1.71, 0.86 Hz, 2 H), 3.52 (dd, *J*=3.61, 1.65 Hz, 2 H), 2.81 (s, 3 H) ppm. Exo- isomer: ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 6.51 (t, *J*=0.86 Hz, 2 H), 2.97 (s, 3 H), 2.85 (s, 2 H) ppm. HR-MS (ESI) calcd. For C₉H₉NO₃H+ [M+H]+: 180.0661; Found: 180.0658.

4-Methyl-N-methyl-7-oxanorbornenecarboximide (2)



A mixture of N-methylmaleimide (10g, 90 mmol, 1eq) and 2-methylfuran (14.7g, 180 mmol, 2 eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 °C until complete disappearance of *N*-methylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 57:43 endo-, exo- mixture (17g, 98%). The mixture was used for metathesis without any further purifications. The mixture was also purified by column chromatography with hexane: ethyl acetate (80:20) to obtain pure **2-endo** (white solid) and **2-exo** (crystalline colorless solid). The endo isomer was stored at -20 °C. Endo- isomer: ¹H NMR (400 MHz, CHLOROFORM-d) δ 6.38 (dd, J=5.75, 1.47 Hz, 1 H), 6.21 (d, J=5.75 Hz, 1 H), 5.21 (dd, J=5.56, 1.65 Hz, 1 H), 3.64 (dd, J=7.52, 5.56 Hz, 1 H), 3.11 (d, J=7.58 Hz, 1 H), 2.81 (s, 3 H), 1.83 (s, 3 H) ppm. Exo- isomer: ¹H NMR (400 MHz, CHLOROFORM-d) & 6.49 (dd, J=5.62, 1.59 Hz, 1 H), 6.29 (d, J=5.62 Hz, 1 H), 5.16 (d, J=1.71 Hz, 1 H), 2.92 - 3.00 (m, 4 H), 2.70 (d, J=6.48 Hz, 1 H), 1.71 (s, 3 H)6.51 (dd, J=5.64, 1.51 Hz, 1 H), 6.31 (d, J=5.69 Hz, 1 H), 5.18 (d, J=1.74 Hz, 1 H), 2.93 - 3.01 (m, 4 H), 2.72 (d, J=6.51 Hz, 1 H), 1.73 (s, 3 H) ppm. Endo-isomer: ¹³C NMR (101 MHz, CHLOROFORM-*d*) δ 175.2, 175.1, 137.6, 134.9, 88.4, 79, 50.8, 48.8, 24.5, 18.4 ppm. Exo-mixture: ¹³C NMR (101 MHz, CHLOROFORM-d) δ 176.1, 174.9, 140.4, 136.8, 88, 80.5, 50.6, 49.4, 24.8, 15.6 ppm. MS (ESI) calcd. For C₁₀H₁₁NO₃Na+ [M+H]+: 216.0637; Found: 216.0295.

4-Propyl-N-methyl-7-oxanorbornenecarboximide (3)



A mixture of *N*-methylmaleimide (10g, 90 mmol, 1eq) and 2-propylfuran (19.8g, 180 mmol, 2 eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 0 C until complete disappearance of *N*-methylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 57:43 endo-, exo- mixture (19.5g, 98%). The mixture was used for metathesis without any further purifications. Endo- isomer: ¹H NMR (300 MHz, CHLOROFORM-*d*) δ 6.35 - 6.38 (m, 1 H), 6.25 (d, J=5.69 Hz, 1 H), 5.23 (dd, J=5.55, 1.60 Hz, 1 H), 3.61 (dd, J=7.52, 5.50 Hz, 1 H), 3.16 (d, J=7.61 Hz, 1 H), 2.81 (s, 3 H), 1.88 - 2.12 (m, 2 H), 1.42 - 1.73 (m, 2 H) 1.02 (m, 3 H) ppm. Exo- isomer: ¹H NMR (300 MHz, CHLOROFORM-*d*) δ 6.50 (dd, J=5.73, 1.60 Hz, 1 H), 6.38 (d, J=5.69 Hz, 1 H), 5.20 (d,

J=1.74 Hz, 1 H), 2.92 - 2.99 (m, 4 H), 2.76 (d, J=6.42 Hz, 1 H), 2.16 - 2.33 (m, 2 H), 1.42 - 1.73 (m, 2 H), 1.02 (td, J=7.36, 3.44 Hz, 3 H) ppm. Endo-, Exo-mixture: ¹³C NMR (75 MHz, CHLOROFORM-*d*) δ 176.3, 175.3, 175.2, 174.9, 138.9, 136.8, 136.7, 134.7, 91.9, 91.7, 80.4, 78.8, 50.5, 49.7, 49.1, 48.5, 34.4, 31.7, 24.8, 24.5, 18.7, 17.9, 14.5, 14.4 ppm. HR-MS (ESI) calcd. For C₁₂H₁₅NO₃Na+ [M+Na]+: 244.0950 ; Found: 244.0949.

4-Pentyl-N-methyl-7-oxanorbornenecarboximide (4)



A mixture of N-methylmaleimide (10g, 90 mmol, 1eq) and 2-pentylfuran (24.8g, 180 mmol, 2 eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 °C until complete disappearance of *N*-methylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 57:43 endo-, exo- mixture (21.9g, 98%). The mixture was used for metathesis without any further purifications. The mixture was also purified by column chromatography with hexane: ethyl acetate (90:10) to obtain pure 4-endo (vellow waxy solid) and 4-exo (crystalline colorless solid). The endo isomer was stored at -20 ⁰C. Endo- isomer: ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 6.35 (dd, J=5.75, 1.47 Hz, 1 H), 6.24 (d, J=5.75 Hz, 1 H), 5.22 (dd, J=5.56, 1.65 Hz, 1 H), 3.60 (dd, J=7.52, 5.56 Hz, 1 H), 3.15 (d, J=7.46 Hz, 1 H), 2.80 (s, 3 H), 2.19 - 2.33 (m, 1 H), 1.94 - 2.08 (m, 1 H), 1.44 -1.59 (m, 2 H), 1.28 - 1.42 (m, 4 H), 0.82 - 0.95 (m, 3 H) ppm. Exo- isomer: ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 6.49 (dd, J=5.69, 1.65 Hz, 1 H), 6.38 (d, J=5.75 Hz, 1 H), 5.19 (d, J=1.71 Hz, 1 H), 2.90 - 3.01 (m, 4 H), 2.75 (d, J=6.36 Hz, 1 H), 1.89 - 2.14 (m, 2 H), 1.54 - 1.67 (m, 1 H), 1.30 - 1.54 (m, 5 H), 0.86 - 0.95 (m, 3 H)ppm. Endo-mixture: ¹³C NMR (101 MHz, CHLOROFORM-d) δ 175.3, 175.1, 136.7, 134.7, 91.9, 78.8, 49.7, 48.5, 32.2, 31.9, 24.5, 24.2, 22.4, 13.9 ppm. Exo-mixture: ¹³C NMR (101 MHz, CHLOROFORM-d) & 176.2, 174.9, 138.9, 136.8, 91.8, 80.4, 50.5, 49, 32.1, 29.5, 24.9, 24.8, 22.5, 13.9 ppm. HR-MS (ESI) calcd. For C₁₄H₁₉NO₃Na+ [M+Na]+: 272.1263 ; Found: 272.1258.

4-Methoxytriisopropylsilane-N-methyl-7-oxanorbornenecarboximide (5)



A mixture of *N*-ethylmaleimide (5g, 40 mmol, 1eq) and furfuryl alcohol (7.8g, 80 mmol, 2 eq) was dissolved in 2 mL of tetrahydrofuran. The solution was heated to 40 $^{\circ}$ C until complete disappearance of *N*-ethylmaleimide was observed. The reaction was concentrated under vacuum to give a yellow liquid as 70:30 endo-, exo- mixture (8.8g, 99%). The mixture was used for next step without any further purifications.

A mixture of crude product (4g, 17.9 mmol, 1eq) and imidazole (3.6g, 53.8 mmol, 3eq) were dissolved in 30 mL dry dichloromethane and cooled to 0 $^{\circ}$ C. To the precooled solution triisopropylsilyl chloride (4.1g, 21.5 mmol, 1.2eq) was added dropwise and the mixture was allowed to warm to room temperature. The reaction mixture was stirred for a further 12 hours at room temperature. The reaction mixture was concentrated under reduced pressure and purified by column chromatography with hexane: ethyl acetate (95:5) to obtain **5** as endo/exo mixture (6.1g, 90%). Endo- isomer: ¹H NMR (300 MHz, CHLOROFORM-*d*) δ 6.40 (dd, J=5.78, 1.56 Hz, 1 H), 6.26 (d, J=5.78 Hz, 1 H), 5.29 (dd, J=5.23, 1.56 Hz, 1 H), 4.27 - 4.40 (m, 2 H), 3.47 - 3.64 (m, 2 H), 3.38 (q, J=7.15 Hz, 2 H), 0.96 - 1.23 (m, 24 H) ppm. Exo- isomer: ¹H NMR (300 MHz, CHLOROFORM-*d*) δ 6.59 (d, J=5.69 Hz, 1 H), 6.50 (dd, J=5.73, 1.60 Hz, 1 H), 5.24 (d, J=1.65 Hz, 1 H), 4.42 (d, J=7.61 Hz, 1 H), 4.08 (d, J=11.28 Hz, 1 H), 3.48 - 3.54 (m, 2 H), 2.94 (d, J=6.42 Hz, 1 H), 2.86 (d, J=6.42 Hz, 1 H), 0.96 - 1.23 (m, 24 H) ppm. Endo-, Exo-mixture: ¹³C NMR (75 MHz, CHLOROFORM-*d*) δ 176, 175.1, 175, 174.5, 138.4, 136.2, 134.9, 92.8, 91.8, 81, 79.5, 77.4, 76.6, 61.7, 61.1, 50.2, 47.8, 47.7, 44.8, 33.8, 33.3, 17.9, 12.9, 12.6, 11.9 ppm. MS (ESI) calcd. For C₂₀H₃₃NO₄SiNa+ [M+Na]+: 402.2077; Found: 402.0018.

Dimethyl-1-pentyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (6)



A mixture of dimethyl acetylenedicarboxylate (1g, 7 mmol, 1eq), 2-pentylfuran (1.2g, 8.4 mmol, 1.2 eq) and 3 mL of toluene was heated to 100 $^{\circ}$ C for 24h. The reaction was concentrated under reduced pressure and purified by column chromatography with hexane: ethyl acetate (90:10) to obtain monomer **5** as red liquid (1.8g, 94%). HR-MS (ESI) calcd. For C₁₅H₂₀O_{5Na}+ [M+Na]+: 303.1208 ; Found: 303.1198.

Control ¹H NMR initiation experiments



An equal mixture of endo- and exo- isomer of monomer (1-4) was dissolved in 0.5 mL of dry degassed dichloromethane-d2. The resulting solution was transferred to degassed NMR tube containing internal standard (1, 3, 5 trimethoxybenzene) and ¹H NMR spectra was measured. Separately, 0.4 eq of G3 was dissolved in dry degassed dichloromethane-d2 and quickly added to the NMR tubbe, ensuring efficient mixing. Then, ¹H NMR spectrum of the reaction mixture was recorded over time.

Polymerization with cyclohexene



The monomer (2-4) and 20eq. of cyclohexene were dissolved in dry degassed dichloromethane to obtain 0.3M monomer solution (with respect to 2-4). Separately, a stock solution of catalyst G3 was prepared. The required amount of G3 solution was quickly added to the monomer solution and ensuring efficient mixing. The reaction mixture was stirred for 12-18 hours (for monomer 2, 12 hours and monomer 3-4, 18 hours) at rt under argon atmosphere. The reactions were quenched with excess ethyl vinyl ether and precipitated into cold methanol to obtain alternating polymers.

Polymerization with cycloheptene and cyclopentene



An equimolar mixture of monomers (2-4) and cycloheptene/ cyclopentene were transfer into vials equipped with a stir bar under argon atmosphere. Separately, a stock solution of catalyst G3 was prepared. The required amount of G3 solution was quickly added to the monomer solution and ensuring efficient mixing. The reaction mixture was stirred for 12-18 hours (for monomer 2, 12 hours and monomer 3-4, 18 hours) at rt under argon atmosphere. The reactions were quenched with excess ethyl vinyl ether and precipitated into cold methanol to obtain alternating polymers.

End capping of ROMP polymer with monomer 6



Monomer MNI (0.5g, 2.8 mmol, 30 eq) was dissolved in 2.5 mL dry degassed dichloromethane. Separately, a stock solution of catalyst G3 was prepared. The required amount of G3 (83 mg, 0.09 mmol, 1eq) solution was quickly added to the monomer solution and ensuring efficient mixing. The reaction mixture was stirred for 10 min and an aliquot was collected for ¹H NMR measurement. A stock solution of monomer 6 was prepared and required amount of monomer 6 (76 mg, 0.27 mmol, 3eq) solution was quickly added to the polymerization mixture was continue stirring for 10 min. A sample was collected for ¹H NMR measurement. Then, the reaction was quenched with excess of ethyl vinyl ether. Finally, the reaction mixture was concentrated under reduced pressure and precipitated into cold methanol to obtain P18 (SEC, THF, Mn=6.1 kDa.; D=1.08).

End functionalization of P18



Polymer **P18** (40 mg, 1eq) was dissolved in 0.5 mL of dry THF. Separately, 10eq of thiol derivative was dissolved in 0.5 mL of dry DMF and 0.2eq of NaH (60% dispersed in mineral oil) was added. The resulting mixture was stirred for 20 min and quickly transfer into the polymer solution. The reaction mixture was heated at 40 $^{\circ}$ C for 12 h. Finally, the reaction mixture was concentrated under reduced pressure and precipitated into cold methanol to obtain polymer **P19** (ethanolthiol) or **P20** (pentanedithiol).

Polymer	Monomer (M)	Monomer to Initiator ratio (M/G3)	M _{n-theo} [kDa]	M _{n-GPC} [kDa]	Đ ^a	Time [Hour]	Yield [%]
P1	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 1 \text{eq.} 20 \text{eq.} \end{array} $	16	4.4	4.1	1.2	12	90
P2	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 1 \text{eq.} \\ 20 \text{eq.} \end{array} $	33	9	10.6	1.5	18	90
Р3	$ \begin{array}{c} $	16	4.6	4.2	1.2	12	94
P4	$ \begin{array}{c} 0 \\ -1 \\ -1 \\ 0 \\ 1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 $	33	9.5	10.9	1.6	18	94
P5	$ \begin{array}{c} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	16	4.2	3.9	1.2	12	92
P6	0 0 0 0 1eq. 20eq.	16	4.8	5.3	1.2	18	80

Table S1. Polymerization results and SEC data for different polymers

P7 ^b	0 1 eq. 20 eq.	60	18	13	1.3	40	70
P8	$ \begin{array}{c} 0\\ 0\\ 0\\ 1eq. \end{array} + \\ 1eq. $	16	4.6	3.7	1.2	18	85
Р9	$ \begin{array}{c} $	16	5.1	5	1.2	18	88
P10	$ \begin{array}{c} $	16	5.3	5.6	1.1	20	80
P11 ^b	$ \begin{array}{c} $	60	19.8	14.1	1.4	40	70
P12	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 1 \text{eq.} \end{array} + \begin{array}{c} 0 \\ 0 \\ 1 \text{eq.} \end{array} $	16	5.1	4.4	1.2	20	80
P13	$ \begin{array}{c} $	16	5.5	5	1.2	20	84
P14	0 	16	5.3	5.8	1.1	12	90

P15 ^b	16	7.3	10.6	1.3	35	70
P16 ^b	30	13.8	17.8	1.3	47	70
P17 ^b	60	27.6	24.9	1.3	67	70

a. All the copolymers were analysed by THF GPC except **b** which are measured in $CHCl_3$ GPC.

¹H NMR spectroscopic experiments



Fig S1. ¹H NMR (CD₂Cl₂, 400 MHz) analysis of the stability of 4-exo and 4-endo in solution. A biased concentration (85% **4-endo** and 15% **4-exo** in the presence of an internal standard 1, 3, 5 trimethoxybenzene) of *exo* and *endo* isomer was used to study dynamic behavior between two isomers. Over 16 hours in solution at rt no appreciable change was detected.



Fig S2. ¹H NMR spectra (CD_2Cl_2 , 400 MHz) of the reactions of 1:1 mixture of endo-, exo- N-methylnorborneneimide with 0.4 eq G3 in presence of internal standard 1, 3, 5 trimethoxybenzene and 30 eq. 3-bromopyridine.



Fig S3. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of endo-, exo- Nmethylnorborneneimide with 0.4 eq G3 in presence of internal standard 1, 3, 5 trimethoxy benzene and 30 eq. 3-bromopyridine.



Fig S4. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of endo-, exo- Nphenylnorborneneimide with 0.5 eq G3 in presence of internal standard 1, 3, 5 trimethoxy benzene and 30 eq. 3-bromopyridine.



Fig S5. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of **2-endo**, **2-exo** with 0.4 eq **G3** in presence of internal standard 1, 3, 5 trimethoxybenzene (Monomer double bond are focused).



Fig S6. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of **2-endo-**, **2-exo** with 0.4 eq **G3** in presence of internal standard 1, 3, 5 trimethoxybenzene (Metal carbene signal are focused).



Fig S7. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of **4-endo**, **4-exo** with 0.4 eq **G3** in presence of internal standard 1, 3, 5 trimethoxybenzene (Monomer double bond are focused).



Fig S8. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of 1:1 mixture of **4-endo-**, **4-exo** with 0.4 eq **G3** in presence of internal standard 1, 3, 5 trimethoxybenzene (Metal carbene signal are focused).





Fig S10. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of **4-exo** with 3 mol% **G3** in presence of internal standard 1, 3, 5 trimethoxy benzene.



Fig S11. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of **4-endo** with 10 mol% **G3** in presence of internal standard 1, 3, 5 trimethoxy benzene. 17% **4-exo** impurity was present (integration 1.04, δ 6.48 ppm).



Fig S12. ¹H NMR spectra (CD₂Cl₂, 400 MHz) of the reactions of **2-endo** with 10 mol% **G3** in presence of internal standard 1, 3, 5 trimethoxy benzene. 24% **4-exo** impurity was present (integration 2.40, δ 6.3 ppm).



Fig S13. ¹H NMR spectra (CD_2Cl_2 , 300MHz) of the homopolymerization of 2 (Endo-, Exo- mixture) with 6.6 mol% G3 in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



with 6.6 mol% G3 in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



Fig S15. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of **2** and cyclohexene with 6.6 mol% G3 in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



Fig S16. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of **2** and cycloheptene with 6.6 mol% **G3** in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



Fig S17. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of **2** and cyclopentene with 6.6 mol% **G3** in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



Fig S18. Plot of 5-*endo*, 5-*exo* (70:30, 16 eq) conversion vs time in the copolymerization with cyclohexene (320 eq) and 6.6 mol% G3 (1 eq).



Fig S19. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of **5** and cyclohexene with 6.6 mol% **G3** in the presence of the internal standard 1, 3, 5-trimethoxybenzene.



Fig S20. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of equivalent mixture of **exo-**N-**phenylnorborneneimide** and **4**-*endo* with 6.6 mol% **G3** in the presence of the internal standard 1, 3, 5-trimethoxybenzene. Complete consumption of **exo-**N-**phenylnorborneneimide** was observed within 5 min and **4**-*endo* remain unreacted.



Fig S21. ¹H NMR spectra (CD₂Cl₂, 300MHz) of the copolymerization of equivalent mixture of **endo**-*N*-**phenylnorborneneimide** and **4**-*endo* with 6.6 mol% **G3** in the presence of the internal standard 1, 3, 5-trimethoxybenzene. Complete consumption of **endo**- *N*-**phenylnorborneneimide** was observed within 60 min and **4**-*endo* remain unreacted.



Fig S22. ¹H NMR spectra (CD₂Cl₂, 300 MHz) of the reactions of 5 with 5 mol% G3 in presence of internal standard 1, 3, 5 trimethoxy benzene.



Fig S23. ¹H NMR spectra (CD_2Cl_2 , 300 MHz) of the reactions of MNI, G3 and **5**. (a) Pure G3 benzylidene. (b) Alkylidene after complete consumption of MNI. (c) MNI alkylidene after reacting with 3eq of monomer **5**. (d) Fischer carbene after reacting with ethyl vinyl ether.



Fig S24. ¹H NMR (chloroform-d, 300 MHz) spectra of *endo* (top) and *exo* (bottom) *N*-methyl-7-oxanorborneneimide.















Fig S34. ¹³C NMR (chloroform-d, 75 MHz) spectrum of compound 3.



Fig S36. ¹³C NMR (chloroform-d, 75 MHz) spectrum of compound 4.









GPC elugrams of polymers



Fig S46. GPC (THF) trace of the crude polymer P2.



Fig S50. GPC (THF) trace of the crude polymer P6.



Fig S52. GPC (THF) trace of the crude polymer P8.







Fig S56. GPC (THF) trace of the crude polymer P12.





Fig S59. GPC (CHCl₃) trace of the crude polymer P15.



Fig S60. GPC (CHCl₃) trace of the crude polymer P16.



Fig S61. GPC (CHCl₃) trace of the crude polymer P17.



Fig S62. GPC (CHCl₃) trace of the crude polymer P18.



Fig S63. GPC (CHCl₃) trace of the crude polymer P19.



Fig S64. GPC (CHCl₃) trace of the crude polymer **P20.** We believe formation of disulfide is the origin of bimodal distribution.

MALDI-ToF mass spectra of polymers



Fig S65. MALDI-ToF mass spectrum (DCTB) of polymer P14.



Fig S66. MALDI-ToF mass spectrum (DCTB, AgTFA) of polymer **P18**. The smaller distribution most likely generated under ionization conditions in the MALDI-ToF mass spectrometer.



Fig S67. MALDI-ToF mass spectrum (DCTB, NaTFA) of polymer **P19**. The same smaller distribution appeared in both cases, most likely generated under ionization conditions in the MALDI-ToF mass spectrometer.



Fig S68. MALDI-ToF mass spectrum (DCTB, NaTFA) of polymer **P20**. The same smaller distribution appeared in both cases, most likely generated under ionization conditions in the MALDI-ToF mass spectrometer.

NMR spectra of polymers













Fig S78. ¹³C NMR (chloroform-d, 101 MHz) spectrum of Poly P7.



Fig S80. ¹³C NMR (chloroform-d, 101 MHz) spectrum of Poly P8.



Fig S81. ¹H NMR (chloroform-d, 400 MHz) spectrum of Poly P9.



Fig S82. ¹³C NMR (chloroform-d, 101 MHz) spectrum of Poly P9.







Fig S87. ¹H NMR (chloroform-d, 400 MHz) spectrum of Poly P12.



Fig S88. ¹³C NMR (chloroform-d, 101 MHz) spectrum of Poly P12.

























Fig S108. ¹³C NMR (DCM-d2, 101 MHz) spectrum of **P20**.

NMR spectra comparisons of homo and alternating copolymer



Fig S109. Stacking of ¹H NMR spectrum the alternating copolymer P1 (90% alternating diads) synthesized from endo/exo mixture (2 + cyclohexene) and homopolymer of 2-exo.



Fig S110. Stacking of ¹³C NMR spectrum of the alternating copolymer P1 synthesized from endo/exo mixture (2 + cyclohexene) and homopolymer of 2-exo.



Fig S111. Stacking of ¹H NMR spectrum the alternating copolymer P3 (92% alternating diads) synthesized from endo/exo mixture (2 + cycloheptene), homopolymer of 2-exo and homopolymer of cycloheptene.



Fig S112. Stacking of ¹H NMR spectrum the alternating copolymer **P5** (92% alternating diads) synthesized from endo/exo mixture ($\mathbf{2}$ + cyclopentene), homopolymer of $\mathbf{2}$ -exo and homopolymer of cyclopentene.



Fig S113. Stacking of ¹H NMR spectrum the alternating copolymer **P10** (96% alternating diads) synthesized from endo/exo mixture (4 + cyclohexene), homopolymer of **4-exo**.



Fig S114. Stacking of ¹³C NMR spectrum of the alternating copolymer P10 synthesized from endo/exo mixture (4 + cyclohexene) and homopolymer of 4-exo.



Fig S115. Stacking of ¹H NMR spectrum the alternating copolymer P12 (96% alternating diads) synthesized from endo/exo mixture (4 + cyclopentene), homopolymer of 4-exo and homopolymer of cyclopentene.



Fig S116. Stacking of ¹H NMR spectrum the alternating copolymer P13 (94% alternating diads) synthesized from endo/exo mixture (4 + cycloheptene), homopolymer of 4-exo and homopolymer of cycloheptene.



Fig S117. Stacking of ¹H NMR spectrum the alternating copolymer **P14** (strictly alternating) synthesized from pure (**4-endo** + cyclohexene), homopolymer of **4-exo**.



Fig S118. Stacking of ¹³C NMR spectrum the alternating copolymer **P14** (strictly alternating) synthesized from pure (**4-endo** + cyclohexene), homopolymer of **4-exo**.

High-resolution mass spectrometric data



Fig S119. HR-MS of monomer 1.







Fig S121. HR-MS of monomer 3.



Fig S122. HR-MS of monomer 4.



Fig S123. ESI-MS of monomer 5.



Fig S124. HR-MS of monomer 6.