Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Ring Opening Metathesis Polymerization of Cyclopentene Using a Ruthenium Catalyst Confined by a Branched Polymer Architecture

Clément Mugemana,[†‡] Konstantin V. Bukhryakov,[†‡] Olivier Bertrand,[#] Khanh B. Vu,[†] Jean-François Gohy,[#] Nikos Hadjichristidis,[†] and Valentin O. Rodionov[†*]

† KAUST Catalysis Center and Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Kingdom of Saudi Arabia.

Université Catholique de Louvain, Institute of Condensed Matter and Nanosciences (IMCN), Bio and soft matter (BSMA) Place Louis Pasteur 1bte L4.01.01- 1348 Louvain-la-Neuve Belgium.

E-mail: valentin.rodionov@kaust.edu.sa
Tel: +966 (12) 8084592

Table of Contents

1. Nomenclature and Abbreviations

Table S1. Nomenclature and Abbreviations

Abbreviation	Description
AFM	Atomic Force Microscopy
CuAAC	Copper-Catalyzed Azide-Alkyne Cycloaddition
CMS	4-chloromethyl styrene
DCM	Dichloromethane
DLS	Dynamic Light Scattering
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DVB	Divinylbenzene
EDTA	Ethylenediaminetetraacetic acid
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Performance Liquid Chromatography
HR-MS	High resolution mass spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LCMS	Liquid Chromatography Coupled With Mass Spectrometry
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NHC	N-Heterocyclic Carbenes
NMP	Nitroxide Mediated Polymerization
NMR	Nuclear Magnetic Resonance Spectroscopy
PDI	Polydispersity Index
PS	Polystyrene
PS22K	22K Polystyrene - linear polymer
RID	Refractive Index Detector
SEC	Size Exclusion Chromatography
SLS	Static Light Scattering
S10K-NHC	S10K star polymer core-functionalized with the NHC precursor
S10K-NHC-Ru	S10K star polymer core-functionalized with NHC-Ru complexes
S22K-Cl	S22K star polymer core-functionalized with chlorides
S22K-N_3	S22K star polymer core-functionalized with azides
S22K-NHC	S22K star polymer core-functionalized with the NHC precursor
S22K-NHC-Ru	S22K star polymer core-functionalized with NHC-Ru complexes

TBAF	Tetrabutylammonium Fluoride
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
TMS	Trimethylsilane
***wt* %**	Weight Percent
UV-Vis	Ultraviolet-Visible

2. Materials and Methods

Materials and Synthetic Techniques

All reagents and solvents were provided by commercial suppliers (Sigma-Aldrich, Fisher Scientific and VWR) and used without further purification unless otherwise noted. Reactions requiring anhydrous conditions were performed under positive argon or nitrogen pressure using standard Schlenk line techniques. THF used for preparative CuAAC reactions was freshly distilled in the presence of sodium/benzophenone. Water was purified on a Barnstead Nanopure system (Thermo Fisher Scientific, USA) to a final conductivity of 17 megohms or better. Styrene, divinylbenzene and 4-chloromethyl styrene monomers were purified over Al_2O_3 (basic) before use. Cyclopentene was purified by distillation over CaH at 70 °C. The purified monomer was then stored at -19 °C in a glove box freezer. The details of the synthesis and the characterization of 1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1H-imidazol-3-ium chloride and the star polymers S10K-Cl and S10K-N_3 have been described previously.[1]

Liquid Chromatography – Mass Spectrometry (LCMS):

LCMS analyses were performed on an Agilent 1260 HPLC equipped with an Agilent 6130 quadrupole mass selective detector. Chromatographic separation was achieved on an Epic C18 column, 1.8µ 120 Å 3 cm X 3.0 mm (ES Industries, West Berlin, NJ; Cat.# 583A91-EC18). Analyses were performed in an isocratic mode (50% MeCN: 50% H_2O, 0.05% TFA *v/v*) with a solvent flow of 0.4 mL/min at 25 °C. The MSD drying gas flow was 12.0 l/min, the nebulizer pressure was 11 psig and the drying gas temperature was 350 °C.

Nuclear Magnetic Resonance Spectroscopy (NMR):

Data for routine characterization of small molecules and polymers were recorded at room temperature on a Bruker Avance-III 400 MHz (^1H) NMR spectrometer equipped with a Z-axis gradient BBO probe. NMR chemical shifts are reported in ppm and are calibrated against residual solvent signals of $CDCl_3$ (^1H δ 7.26, ^{13}C δ 77.16).

Infrared spectroscopy (ATR-FTIR):

Data were collected on a Thermo Scientific Nicolet 6700 instrument equipped with a nitrogen purge line and aligned for signal clarity. The instrument was calibrated against a newly cleaned (acetone) and dried crystal surface before sampling. Solid polymer samples were placed directly on the crystal and secured with a needle press. Scans (32) from 4000 to 550 cm^{-1} were recorded.

Size Exclusion Chromatography (SEC):

SEC analysis was performed on an Agilent 1260 liquid chromatography system fitted with refractive index (RID) and UV-Vis detectors was used. The first instrument was equipped with two identical PLgel columns (5 µm, MIXED-C) connected in series with THF as the mobile phase (1 mL/min). The column and flow path were temperature controlled at 40 °C. The second instrument was equipped with two identical PLgel columns (10 µm, MIXED-B) connected in series with $CHCl_3$ as the mobile phase (1 mL/min). The column and flow path were temperature controlled at 35 °C. Data analysis was performed using GPC Add-on for ChemStation software from Agilent.

High Resolution Mass Spectrometry (HR-MS):

Measurements were performed on an Orbitrap mass analyzer at the KAUST Analytical Core Labs (4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia). The sample was ionized using an ESI ion source operating in positive mode.

Refractive Index and dn/dC

Refractive index n and refractive index increment dn/dC were determined with a Mettler Toledo RE40D Refractometer.

Dynamic Light Scattering (DLS):

DLS measurements were performed using a Malvern Zetasizer Nano ZS instrument equipped with a 632.8 nm He-Ne laser. The measurement angle was 173°. The cells were temperature-controlled at 25 ± 0.1 °C.

Static Light Scattering (SLS):

SLS measurements were performed on a Malvern CGS-3 instrument equipped with a 632.8 nm He-Ne laser. The cells were temperature controlled at 25 ± 0.1 °C. Measurements were performed in toluene. The scattering intensity was measured at angles from 30 to 150°.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):

The ruthenium content of polymers was determined using a Varian 720-ES instrument. Each polymer sample (~ 10 mg) was digested with concentrated HNO_3 (3 mL) in a Teflon vessel. The Teflon vessel containing the sample and concentrated nitric acid was heated at 200 °C for 10 min in a microwave digestion system. After cooling down to room temperature, the digested samples were diluted with an HNO_3 solution (2 % *v/v* in deionized water) to 25 mL. The diluted samples were introduced into the ICP-OES instrument for the measurement of Ru content. The selected emission wavelengths for the Ru and background measurements were 240.272, 349.894, and 372.803 nm. The calibration curve was established for each round of measurement from 5 different standards (0, 0.1, 1, 10, and 100 mg/L). The validity of the calibration curve was confirmed using an independent Ru standard. The limit of detection of Ru is 0.05 mg/L (according to the specification of the instrument provided by Varian). Taking into account all of our dilution steps, this translates into ~0.0125 wt. % in any of our polymer samples.

Transmission Electron Microscopy (TEM):

Sample imaging was either performed on a Titan G2 80–300 kV TEM (FEI Company) equipped with a 4 k × 4 k CCD camera model US4000 and an energy filter model GIF Tridiem (Gatan, Inc.) or a Titan Krios equipped with a 2K _ 2K CCD placed at the end of Gatan energy filter and operated at 300 kV. Typically, electron doses of 100 electrons/ $Å^2$ were used. Samples were dissolved in toluene to reach 1 mg/mL and 5 mg/mL, and one drop of the solution was placed on a TEM grid for characterization.

Atomic Force Microscopy (AFM):

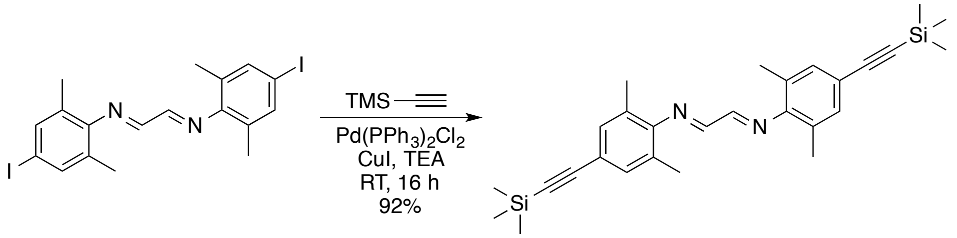
AFM images were obtained on an Agilent 5400 SPM instrument in tapping mode, using Pico View software. Silicon cantilevers were obtained from Bruker (k = 42 N/m; fo = 320 kHz; T: 4um; L: 125 um; W: 40 um). The samples were prepared by spin coating the polymer onto a silicon wafer at 4000 rpm for 30 seconds from a 1 mg/mL solution. Gwyddion 2.33 was used for data analysis and visualization of AFM images.

Elemental Analysis:

Elemental analysis of star polymers were performed at Mikroanalytisches Labor Pascher Germany.

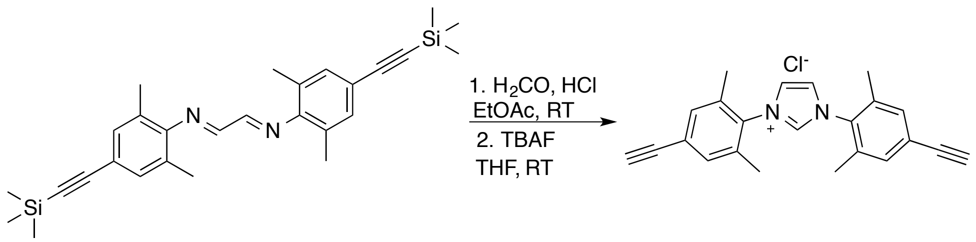
3. Synthesis of the *N*-Heterocyclic Carbene Precursor

(1E,2E)-N1,N2-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-diimine



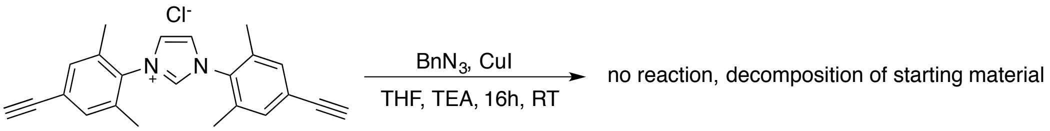
(1E,2E)-N^1,N^2-bis(4-iodo-2,6-dimethylphenyl)ethane-1,2-diimine[2] (21.20 g, 41.07 mmol, 1 eq.) was suspended in 200 mL of triethylamine. Ethynyltrimethylsilane (8.88 g, 90.36 mmol, 2.2 eq.), triphenylphosphine dichloropalladium (0.29 g, 0.41 mmol, 0.01 eq.) and copper iodide (0.08 g, 0.41 mmol, 0.01 eq.) were added and the reaction was stirred under Ar at room temperature overnight. The next day, triethylamine hydrogen iodide was filtered out and the solid was washed with ether. Filtrates were combined and the solvents were evaporated. Trituration in methanol followed by filtration provided pure product. After drying under vacuum, (1E,2E)-N1,N2-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-diimine was obtained as yellowish powder (17.3 g, 92 %). ^{1}H NMR (400 MHz; CDCl$_3$): δ 8.06 (s, 2H), 7.23 (s, 4H), 2.13 (s, 12H), 0.25 (s, 18H). ^{13}C NMR (101 MHz; CDCl$_3$): δ 163.4, 150.1, 132.0, 126.7, 119.6, 105.3, 93.5, 18.2, 0.2. HRMS (ESI+) calculated for [$C_{28}H_{37}N_2Si_2$]+: 457.24898, found: 457.24752.

1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1H-imidazol-3-ium chloride (NHC)

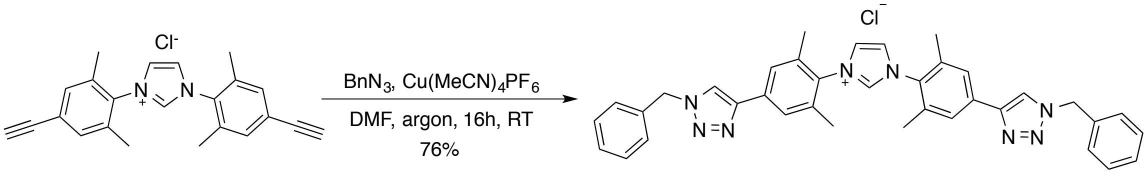


Paraformaldehyde (256 mg, 8.54 mmol, 1.3 eq.) was added to a solution of HCl in 1,4-dioxane (1.71 mL of 6.13 M solution, 10.51 mmol, 1.6 eq.). The solution was stirred for 20 min at room temperature and then added to a suspension of (1E,2E)-N^1,N^2-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-diimine (3.00 g, 6.57 mmol, 1 eq.) in 50 mL of ethyl acetate at –30 °C under Ar. The reaction mixture was stirred at room temperature overnight and then washed with NaCO$_3$ (10 % *wt.* in water). The organic layer was separated, dried under Na$_2$SO$_4$ and concentrated on a rotary evaporator. The product was purified by flash chromatography (ethyl acetate : methanol 0 %- > 20 %), concentrated in vacuum and used for next step without further purification. The crude material (2.40 g, 4.55 mmol) was dissolved in 24 mL of THF and a solution of TBAF (10 mL of 1M in THF, 10 mmol) was added. The reaction mixture was stirred at room temperature for 10 min. Then, the precipitate that formed during the reaction was filtered off and washed by diethyl ether, HCl (5% *wt.* in water) and water. After drying under a vacuum, the final product (0.8 g, 34 % after 2 step) was obtained as a white powder. ^{1}H NMR (400 MHz; DMSO-d$_6$): δ 9.74 (s, 1H), 8.35 (d, J = 1.5 Hz, 2H), 7.55 (s, 4H), 4.43 (s, 2H), 2.16 (s, 12H). ^{13}C NMR (101 MHz; DMSO-d$_6$): δ 138.5, 135.5, 133.7, 131.9, 124.6, 124.2, 82.7, 82.1, 16.8. HRMS (ESI+) calculated for [$C_{23}H_{21}N_2$]+: 325.16993, found: 325.16946.

CuAAC reaction



In order to establish optimal CuAAC reaction conditions, a reaction was performed with benzyl azide based on a previously reported procedure for a similar (albeit more sterically bulky) compound.[1] Neither product nor starting material were observed by LCMS after reacting overnight. This was probably due to the deprotonation of the NHC salt in the presence of triethylamine. Base-free conditions were developed and led to the product in good yield:

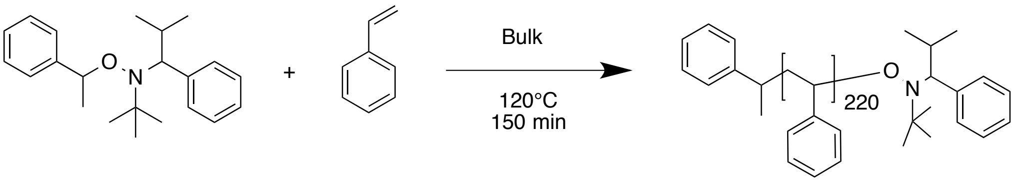


1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1H-imidazol-3-ium chloride (50 mg, 0.14 mmol, 1 eq.) and benzyl azide (40 mg, 0.30 mmol, 2.2 eq.) were dissolved in 3 mL of DMF and transferred into the glove box. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (3 mg, 0.007 mmol, 0.05 eq.) was added and the reaction mixture was stirred at room temperature overnight. The solution was then diluted with 30 mL of diethyl ether, resulting in the formation of a precipitate, which was filtered off, washed with diethyl ether, a saturated aqueous solution of EDTA and then water. The solid residue was dried under vacuum to give 1,3-bis(4-(1-benzyl-1H-1,2,3-triazol-4-yl)-2,6-dimethylphenyl)-1H-imidazol-3-ium chloride as a white powder (67 mg, 76%). ^{1}H NMR (400 MHz; DMSO-d$_6$): δ 9.73 (s, 1H), 8.75 (s, 2H), 8.36 (s, 2H), 7.90 (s, 4H), 7.42-7.37 (m, 10H), 5.68 (s, 4H), 2.22 (s, 12H). ^{13}C NMR (101 MHz; DMSO-d$_6$): δ 145.3, 138.6, 135.7, 135.4, 132.9, 132.6, 128.9, 128.33, 128.15, 125.3, 124.8, 122.5, 53.2, 17.1. HRMS (ESI+) calculated for [$C_{37}H_{35}N_8$]+: 591.29792, found: 591.29703.

4. Synthesis of Star Polymers

The details of the synthesis and the characterization of and the star polymers S10K-Cl and S10K-N$_3$ have been described previously.[1]

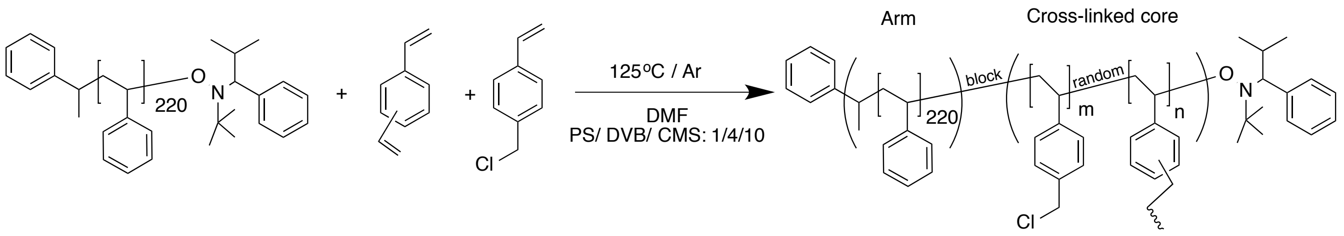
PS22K



Styrene (27.27 g, 0.26 mol, 950 eq.) was introduced into a Schlenk tube containing the NMP initiator (0.09 g, 2.7 mmol, 1 eq.). The mixture was stirred and the solution underwent 5 freeze-pump-thaw cycles to remove oxygen. The Schlenk tube was then filled with Ar and immersed in a 120 °C oil bath for 2.5 hours. After the reaction, the linear polymer was dissolved in dichloromethane and precipitated from cold methanol, then collected and dried for 24 hours under vacuum. SEC: M$_n$:

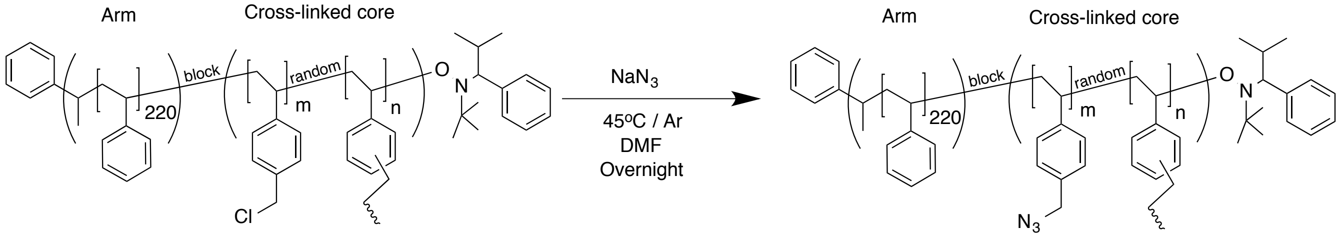
21,900 g/mol; M_w: 25,000 g/mol; (Calibration PS) PDI: 1.15 ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.4-6.4 ppm (m, 1100H); δ 2.2-1.2 ppm (m, 665H) δ 0.9 ppm (s, 3H); δ 0,91-0.85 ppm (m, 15H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 145.7, 128.4, 126.1, 40.8

S22K-Cl



PS22K (5.1 g, 2.3 mmol, 1 eq.) was introduced into a Schlenk tube and dissolved in 22.3 mL of DMF. DVB (0.117 g, 0.9 mmol, 4 eq.) and CMS (0.35 g, 2.3 mmol, 10 eq.) were introduced into the Schlenk tube and the solution mixture underwent 5 freeze-pump-thaw cycles to remove oxygen. The Schlenk tube was then filled with Ar and transferred to a 125 °C oil bath for 16 hours. The solution was then azeotropically concentrated on a rotary evaporator in presence of toluene. The resulting residue was dissolved in dichloromethane and precipitated from cold methanol, collected and dried under vacuum. The product was then purified of unreacted PS macroinitiator via fractionation in benzene and methanol:. A 2.5 *wt*% solution of the PS22K/S22K-Cl polymer blend was prepared in benzene by dissolving 4.5 g of the dry mixture in 200 mL of benzene in a 1 L three-neck round-bottom flask. The flask was then transferred into a water bath heated at 40 °C. Methanol was then introduced into a separate 0.5 L round-neck bottom flask and connected to the three-neck round bottom flask via cannula. A dropwise addition of methanol into the benzene solution was performed until the solution mixture became cloudy. The three-neck round-bottom flask was then removed from the water bath and allowed to stand overnight at room temperature until a phase separation occurred. The S22K-Cl star polymer was then extracted from the bottom of the flask via syringe, dried under vacuum and precipitated from cold methanol. This procedure was repeated until SEC analysis did not reveal any shoulder assigned to the PS22K macroinitiator. SLS analysis allowed us to determine the M_w and the number of arms of star polymers. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.4-6.4 ppm (m, 1100H); δ 4.51 ppm (m, 4H) δ 2.2-1.2 ppm (m, 665H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 145.7, 128.4, 126.1, 40.8; SLS: M_w: 270,000; N_{arms}: ≈10 arms. EA (unit: mass-%) C: 90.68; H: 7.66; Cl: 0.72. Yield: 1 g (20 %).

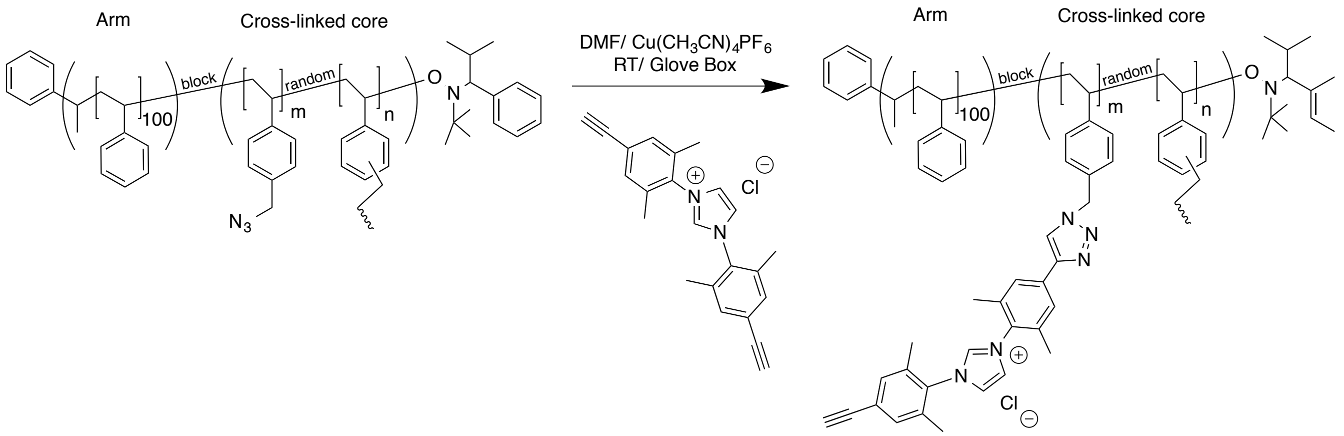
S22K-N_3



S22K-Cl (0.6 g, 0.198 mmol of Cl, 1 eq.) was dissolved in 5 mL of dry DMF and sodium azide (0.04 g, 0.6 mmol, 3 eq.) was added to the solution. The vial was filled with Ar and the mixture was stirred overnight at 45 °C. The excess of sodium azide was extracted in a DCM/H_2O mixture after the reaction. The organic phases were then collected and dried using anhydrous sodium sulfate. The solid residue was filtered off and the organic phase was concentrated on a rotary evaporator. The star polymer was then precipitated from cold methanol, collected and dried under vacuum. ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.4-6.4 ppm (m, 1100H); δ 4 ppm (broad, 4H); δ 2.2-1.2 ppm (m, 710H). ^{13}C NMR (101 MHz; CDCl$_3$): δ 145.3, 127.8, 125.7, 40.4. EA (unit: mass-%) C: 90.65; H: 7.67; N: 1.42. Yield 0.5 g (83 %).

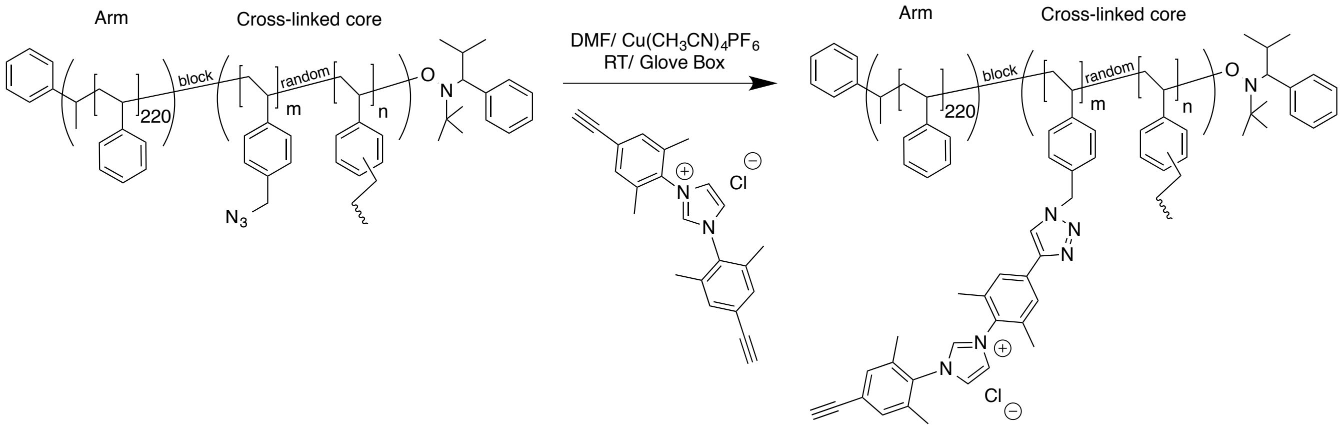
5. CuAAC with the Star Polymers

S10K-NHC



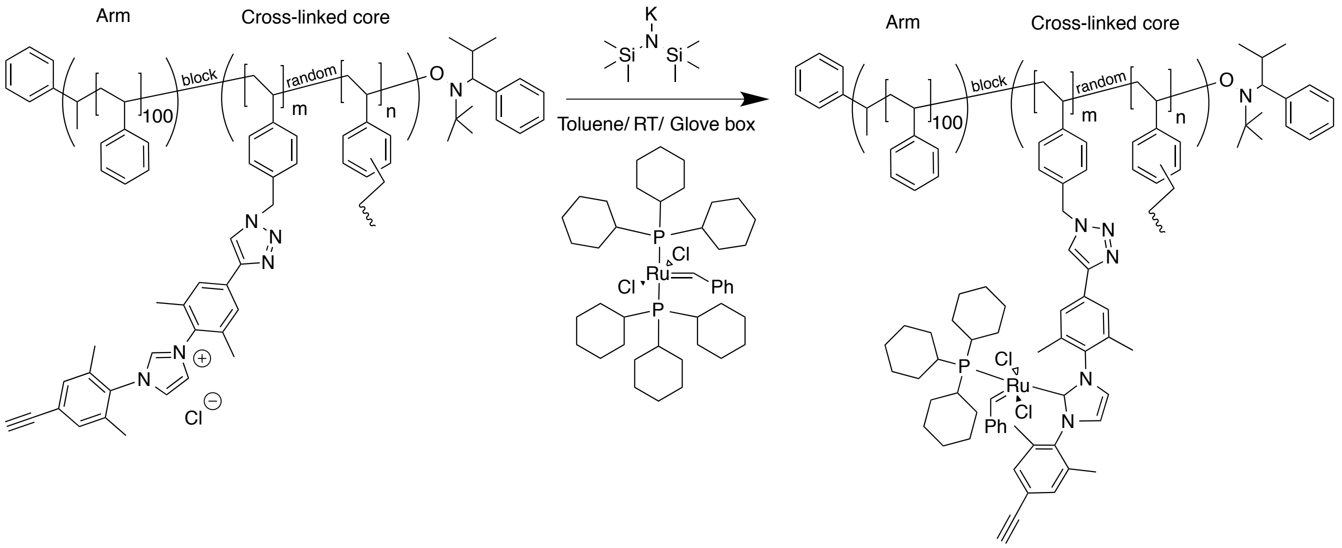
The 10K arm-star polymer[1] (0.500 g, 0.285 mmol of N$_3$, 1 eq.) was dissolved in 40 mL of dry DMF and the vial was placed in a glove box. **NHC** (0.123 g, 0.342 mmol, 1.2 eq.) and tetrakis(acetonitrile) copper(I) hexafluorophosphate (0.106 g, 0.285 mmol, 1 eq.) were added to the solution and the mixture was stirred overnight. The solution was then azeotropically concentrated on a rotary evaporator in the presence of toluene, diluted in DCM and extracted with 0.1N KCN to remove the copper salt then washed with water. The organic phase was dried using anhydrous sodium sulfate and concentrated on a rotary evaporator. The polymer was precipitated from cold methanol, filtered and dried under vacuum. FTIR analysis did not reveal any peak assigned to azide ≈ 2100 cm^{-1}. Yield 400 mg (80 %).

S22K-NHC



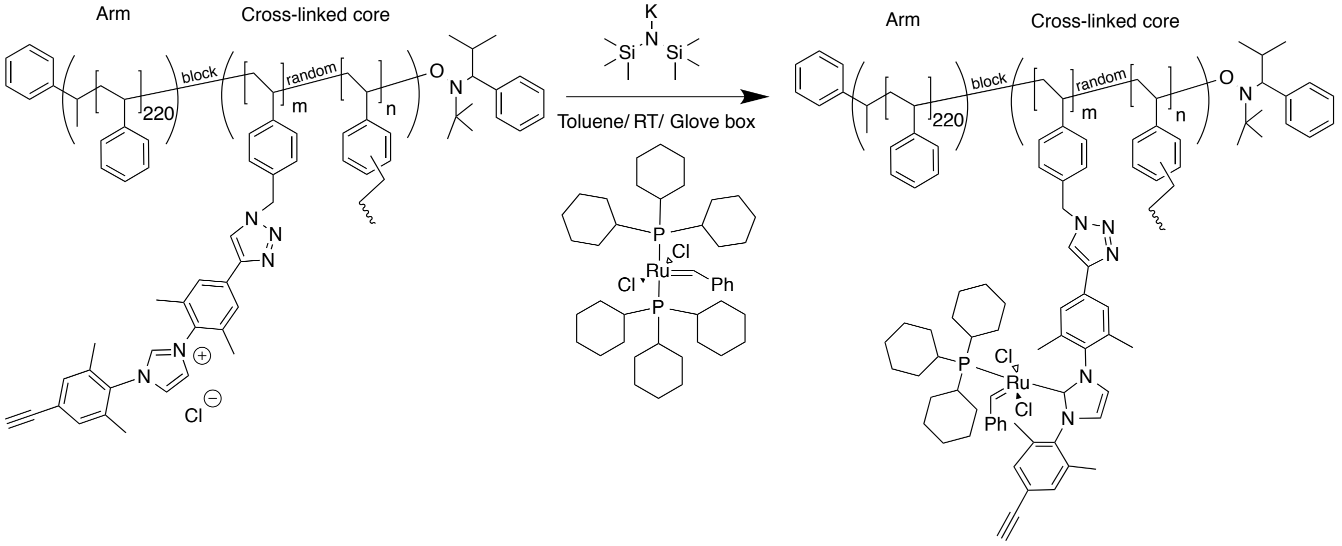
S22K-N$_3$ (0.100 g, 0.033 mmoles of N$_3$, 1 eq.) was dissolved in 5 mL of dry DMF and the vial was placed in a glove box. **NHC** (0.015 g, 0.04 mmol, 1.2 eq.) and tetrakis(acetonitrile) copper(I) hexafluorophosphate (0.02 g, 0.1 mmol, 3 eq.) were added to the solution and the mixture was stirred overnight. The solution was then azeotropically concentrated on a rotary evaporator in presence of toluene, diluted in DCM and extracted with 0.1N KCN to remove the copper salt, then washed with water. The organic phase was dried using anhydrous sodium sulfate and concentrated on a rotary evaporator. The polymer was precipitated from cold methanol, filtered and dried under vacuum. FTIR analysis did not reveal any peak assigned to azide ≈ 2100 cm^{-1}. Yield 82 mg (82 %).

S10K-NHC-Ru



S10K-NHC (0.120 g, 0.068 mmol of NHC, 1 eq.) was dissolved in 5 mL of toluene and the vial was placed in a glove box. Potassium bis(trimethylsilyl)amide (0.040 g, 0.204, 3 eq.) was then added and the solution was stirred for one hour. The color of the solution turned from yellowish to dark red. First genreation Grubbs catalyst (0.056 g, 0.068 mmol,1 eq.) was then added and the mixture was stirred overnight. The solution was concentrated on a rotary evaporator after the reaction and the polymer was precipitated from a MeOH:dioxane solution mixture (4:1), filtred and quickly placed in the glove box. ICP analysis of Ru: 1.8 *wt*%.

S22K-NHC-Ru



S22K-NHC (0.120 g, 0.040 mmol of NHC, 1 eq.) was dissolved in 5 mL of toluene and the vial was placed in a glove box.

Potassium bis(trimethylsilyl)amide (0.023 g, 0.11 mmol, 3 eq.) was then added and the solution was stirred for one hour. The color of the solution turned from yellowish to dark red. First generation Grubbs catalyst (0.033 g, 0.040 mmol, 1 eq.) was then added and the mixture was stirred overnight. The solution was concentrated on a rotary evaporator after the reaction and the polymer was precipitated from a MeOH:dioxane solution mixture (4:1), filtred and quickly placed in the glove box. ICP analysis of Ru:1.9 *wt*%.

6. Characterization Data

^{1}H NMR Spectra

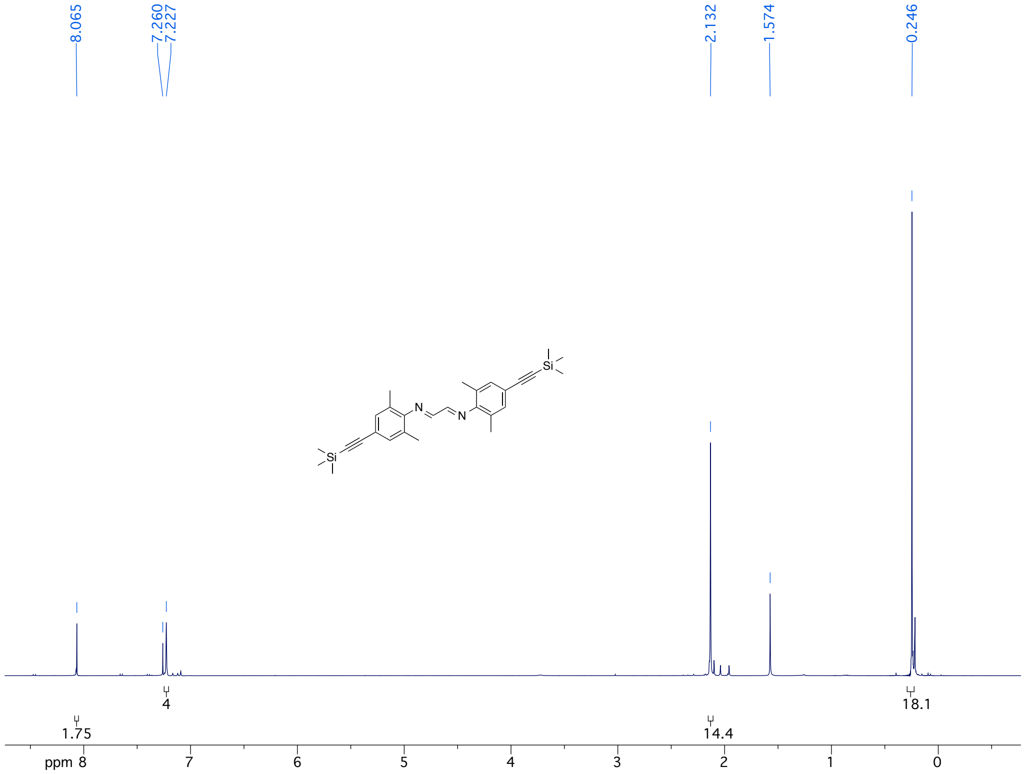


Figure S1. ^{1}H NMR spectrum of the (1*E*,2*E*)-*N*^{1},*N*^{2}-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-diimine (CDCl$_3$).

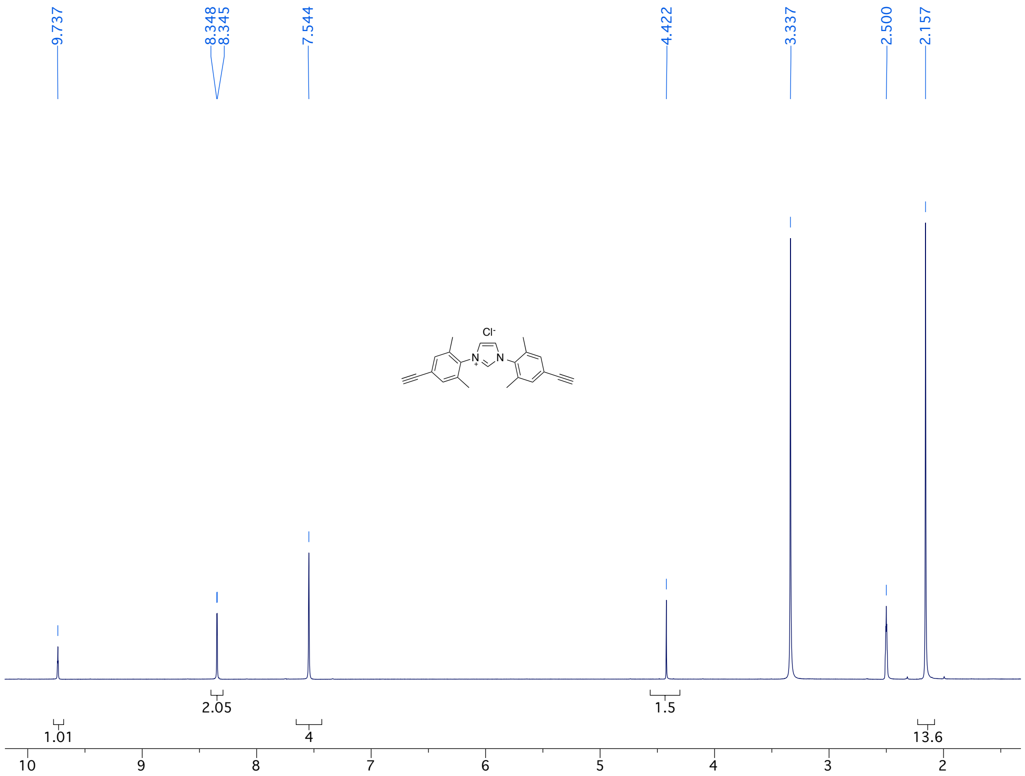


Figure S2. ^{1}H NMR spectrum of the 1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride ($CDCl_3$).

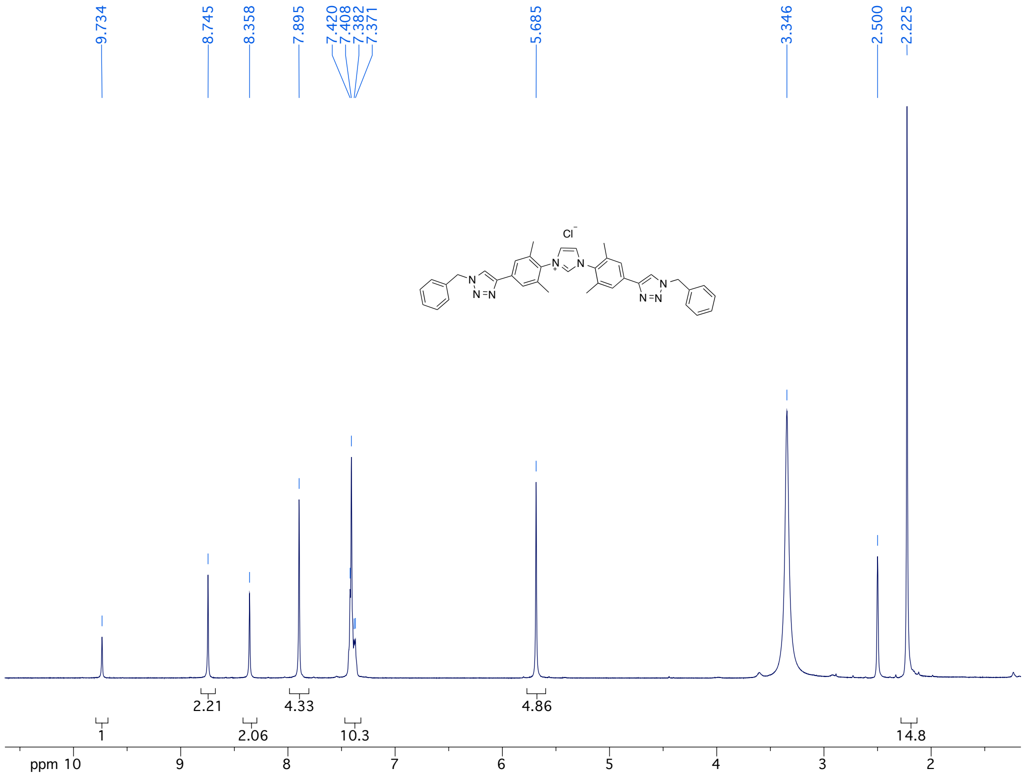


Figure S3. ^{1}H NMR spectrum of the 1,3-bis(4-(1-benzyl-1H-1,2,3-triazol-4-yl)-2,6-dimethylphenyl)-1H-imidazol-3-ium chloride ($CDCl_3$).

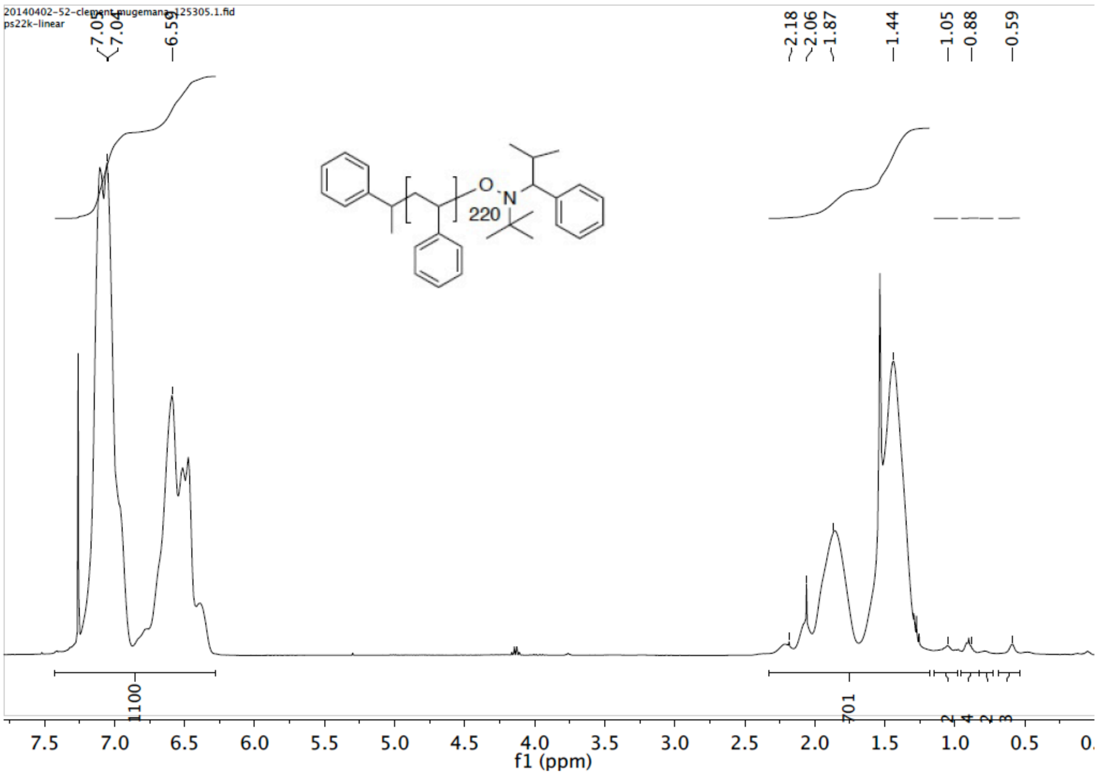


Figure S4. ^{1}**H NMR spectrum of PS22K (CDCl$_3$).**

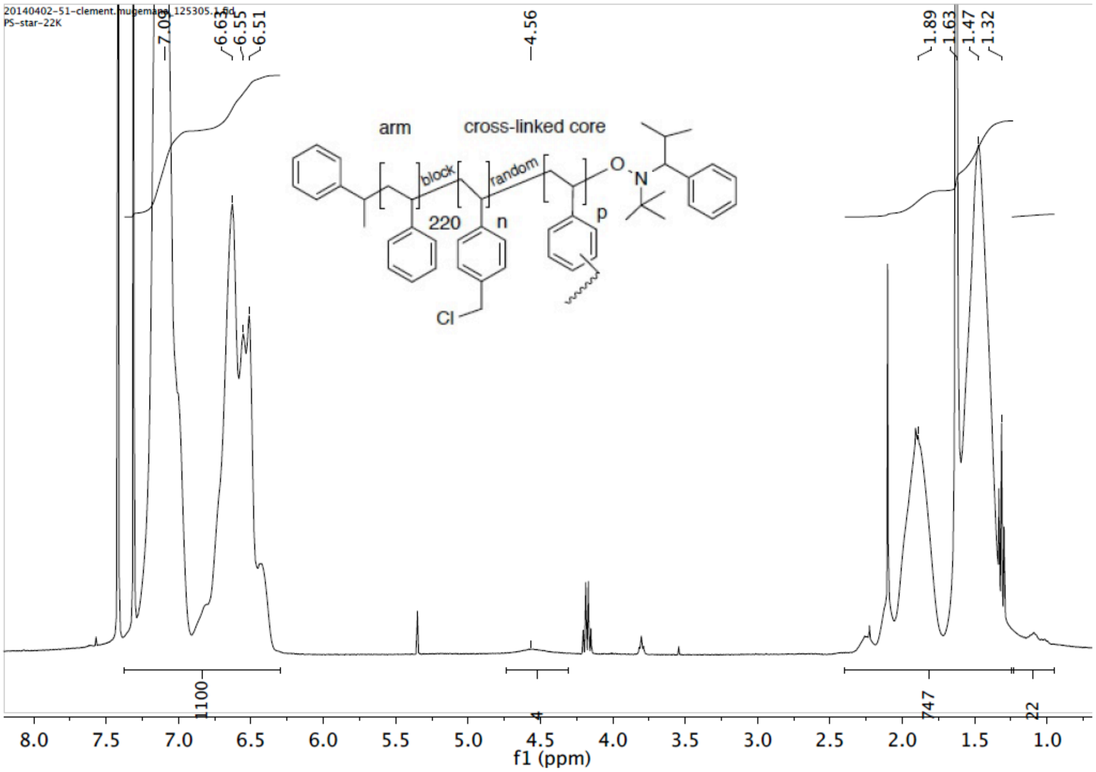


Figure S5. ^{1}**H NMR spectrum of S22K-Cl (CDCl$_3$).**

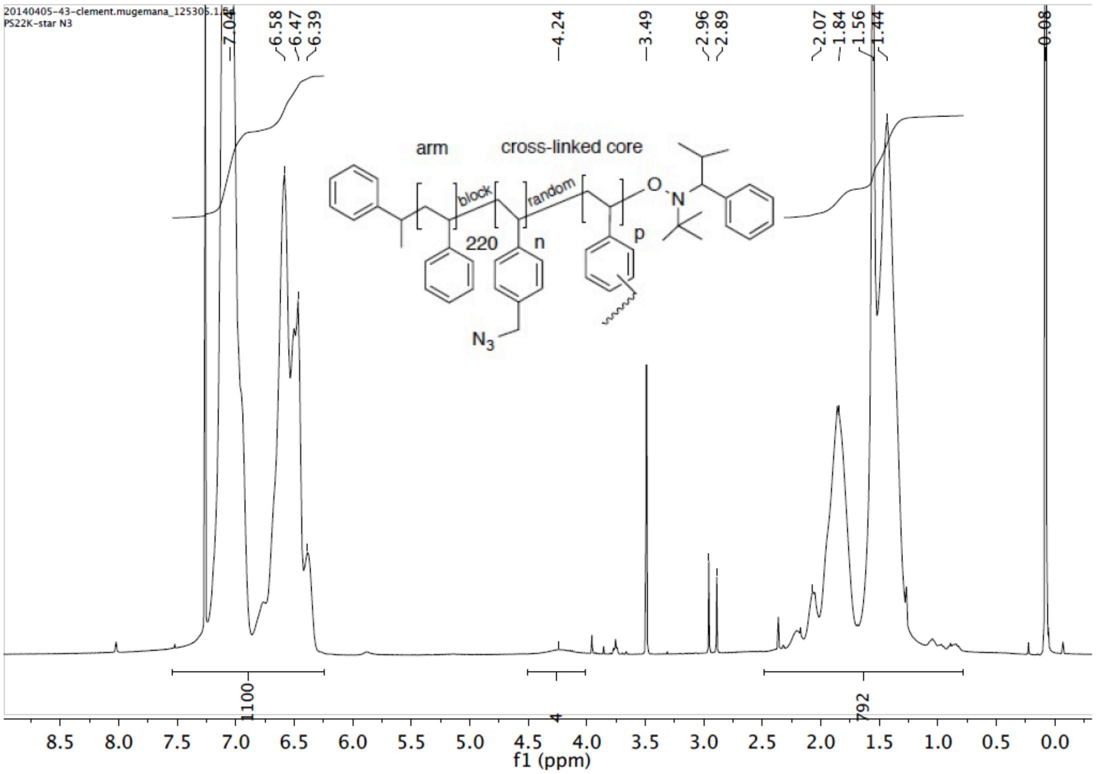


Figure S6. ^{1}H NMR spectrum of S22K-N_3 ($CDCl_3$).

^{13}C NMR spectra

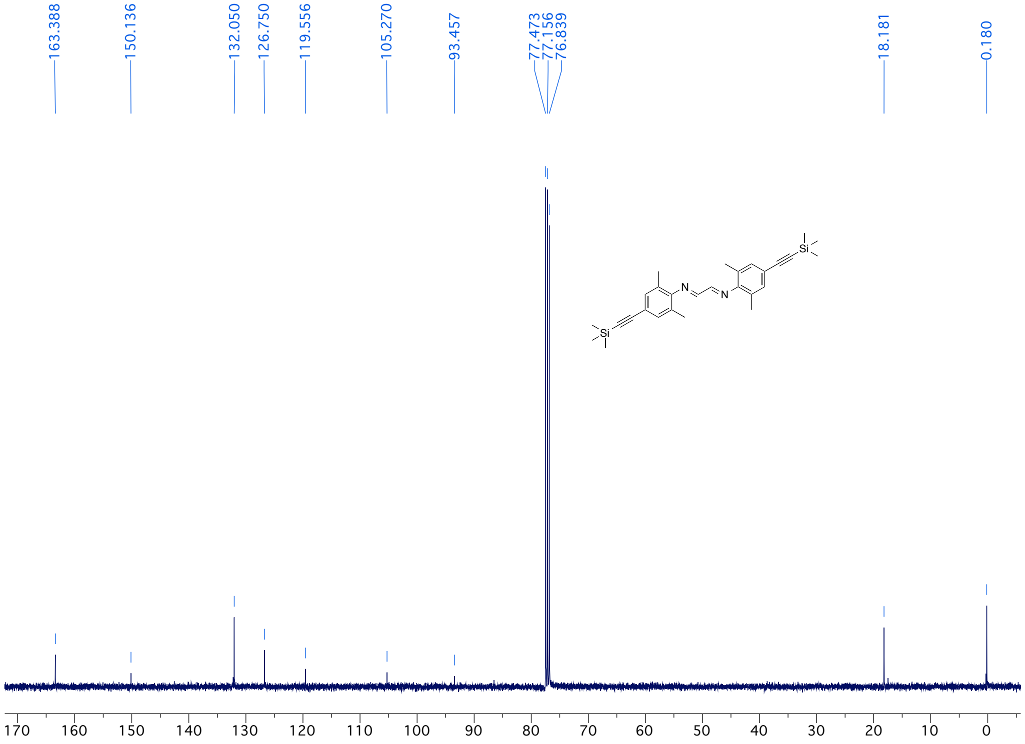


Figure S7. ^{13}C NMR spectrum of the (1*E*,2*E*)-N^1,N^2-bis(2,6-dimethyl-4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-diimine (CDCl$_3$).

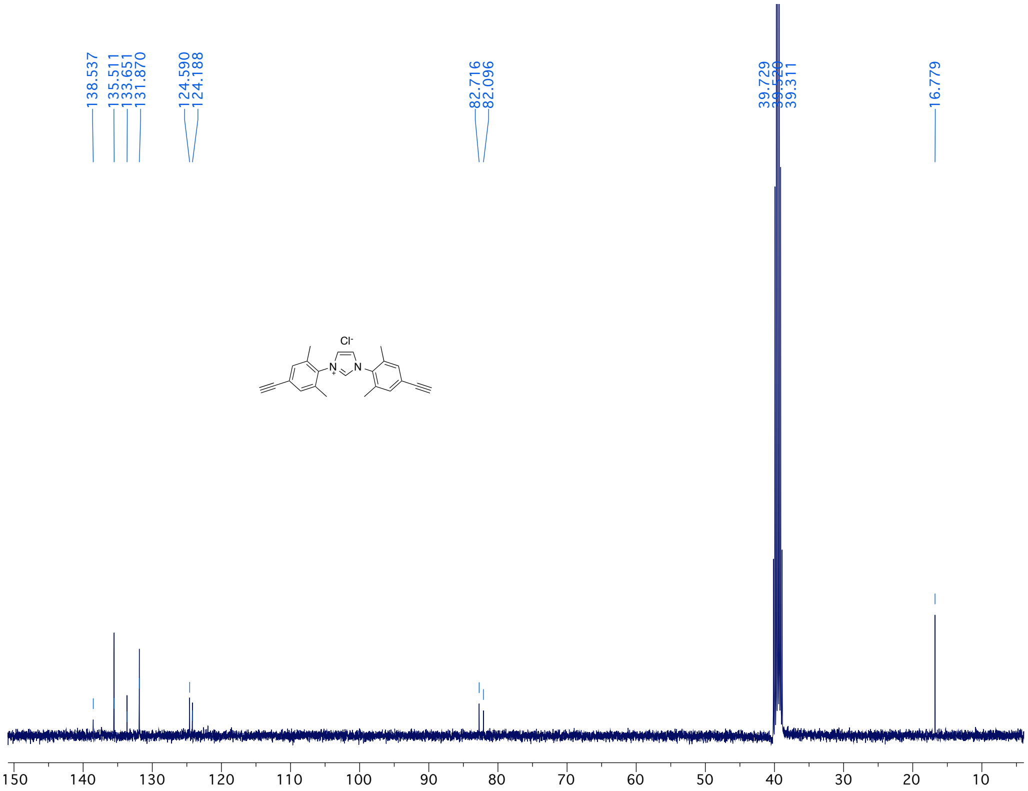


Figure S8. ^{13}C NMR spectrum of the 1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride (CDCl$_3$).

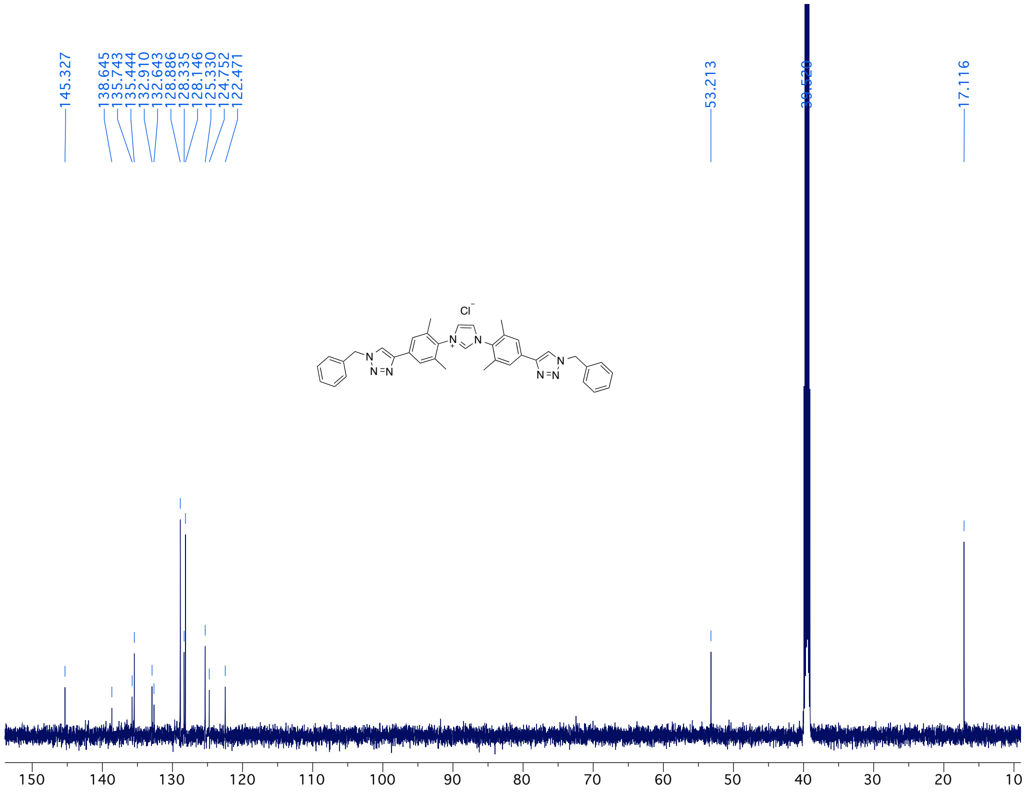


Figure S9. ^{13}C NMR spectrum of the 1,3-bis(4-ethynyl-2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride (CDCl$_3$).

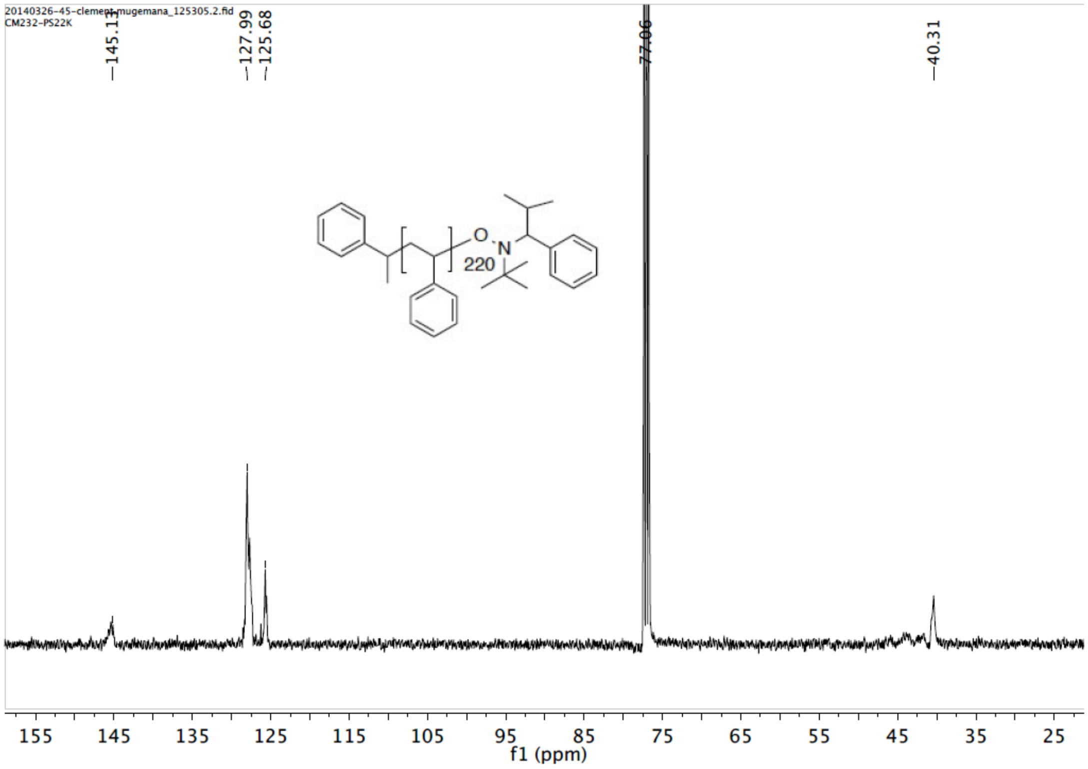


Figure S10. ^{13}C NMR spectrum of PS22K (CDCl$_3$).

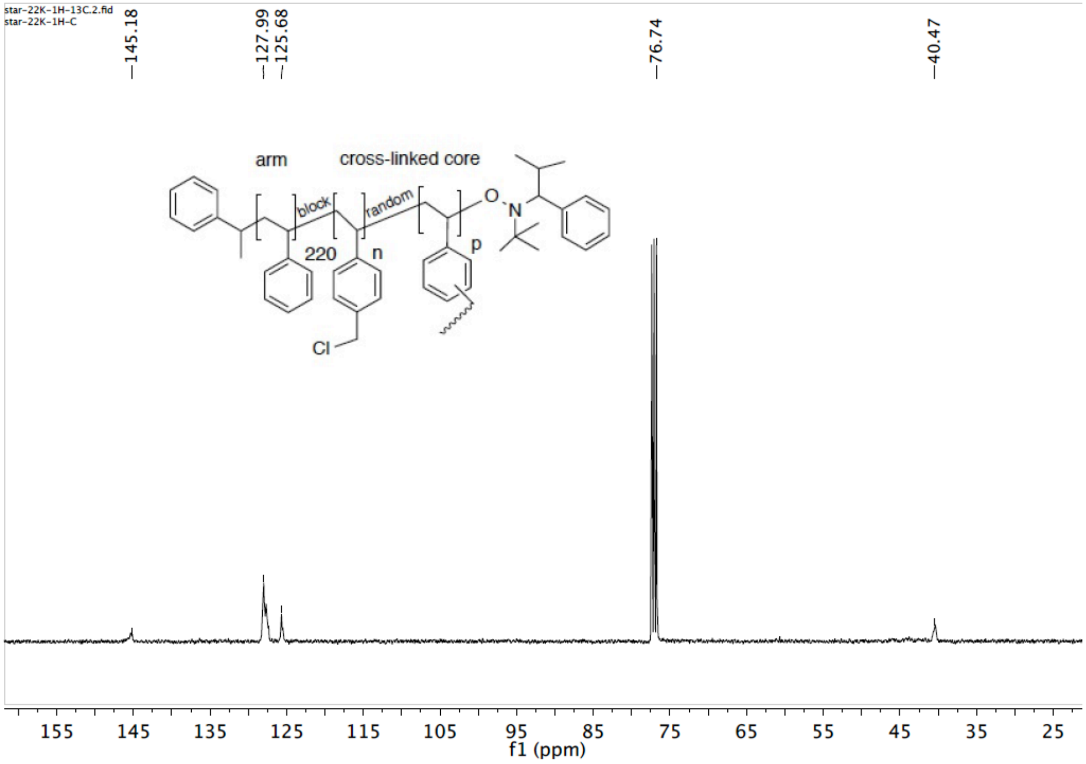


Figure S11. ^{13}C NMR spectrum of S22K-Cl ($CDCl_3$).

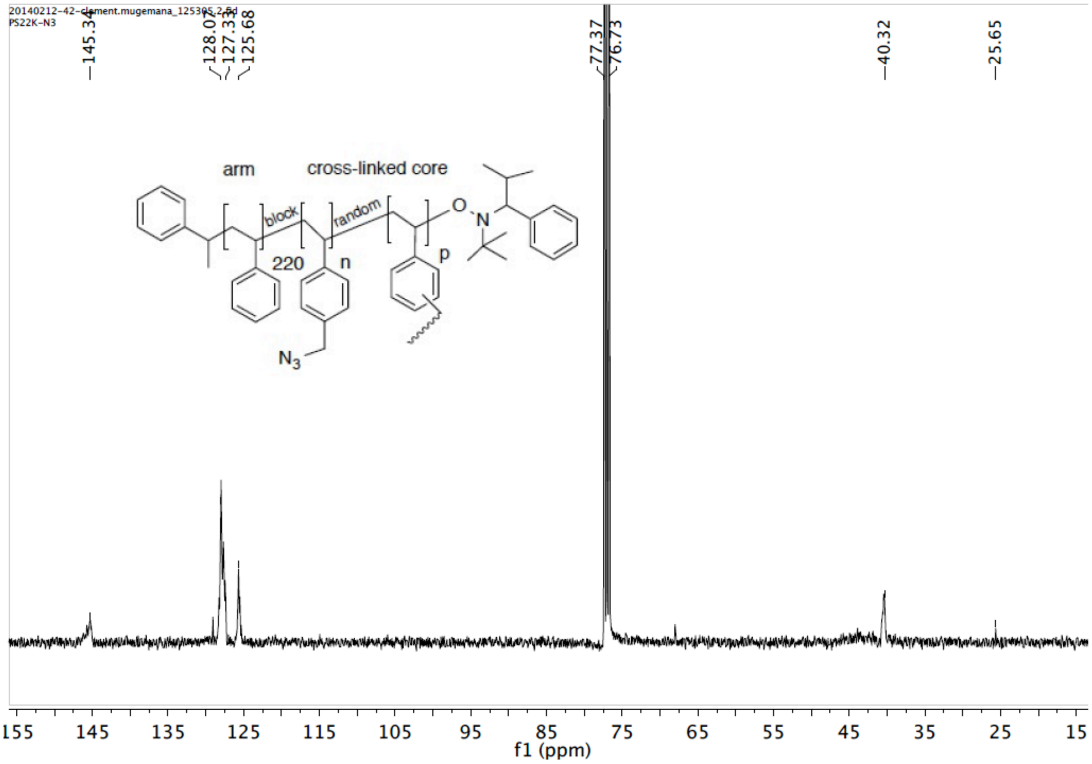


Figure S12. ^{13}C NMR spectrum of S22K-N_3 ($CDCl_3$).

FTIR analysis

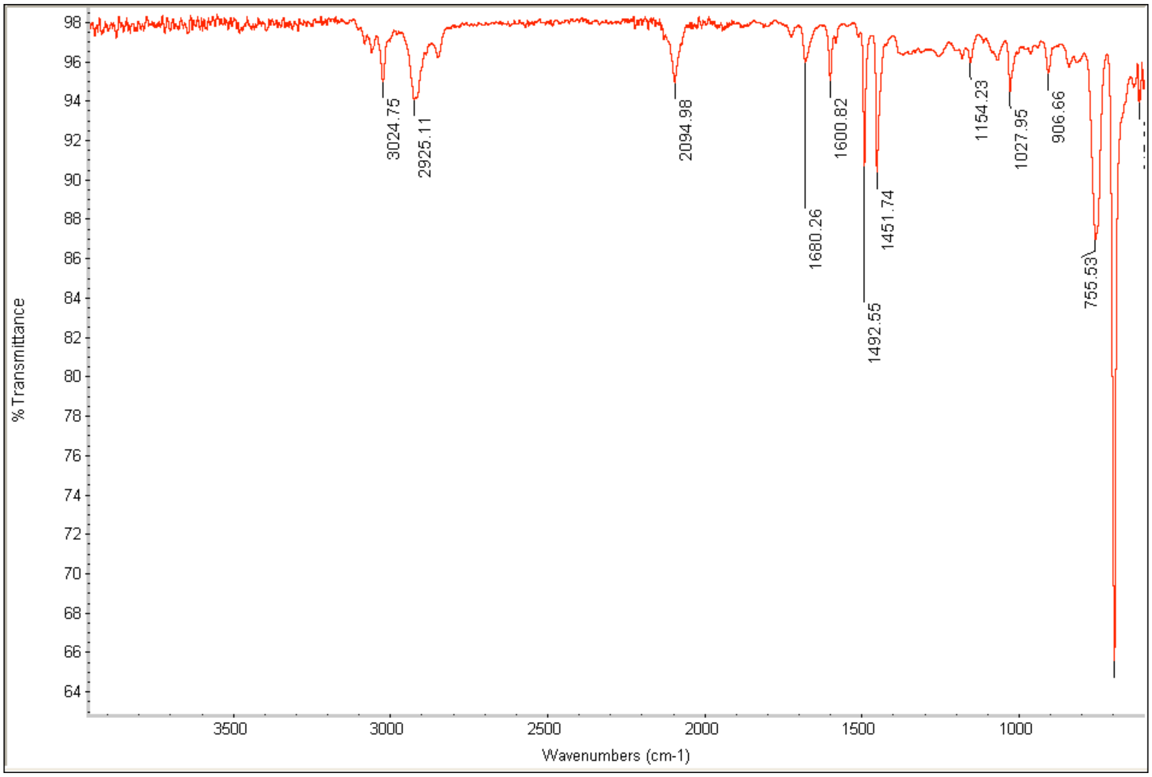


Figure S13. FTIR spectrum of S10K-N_3

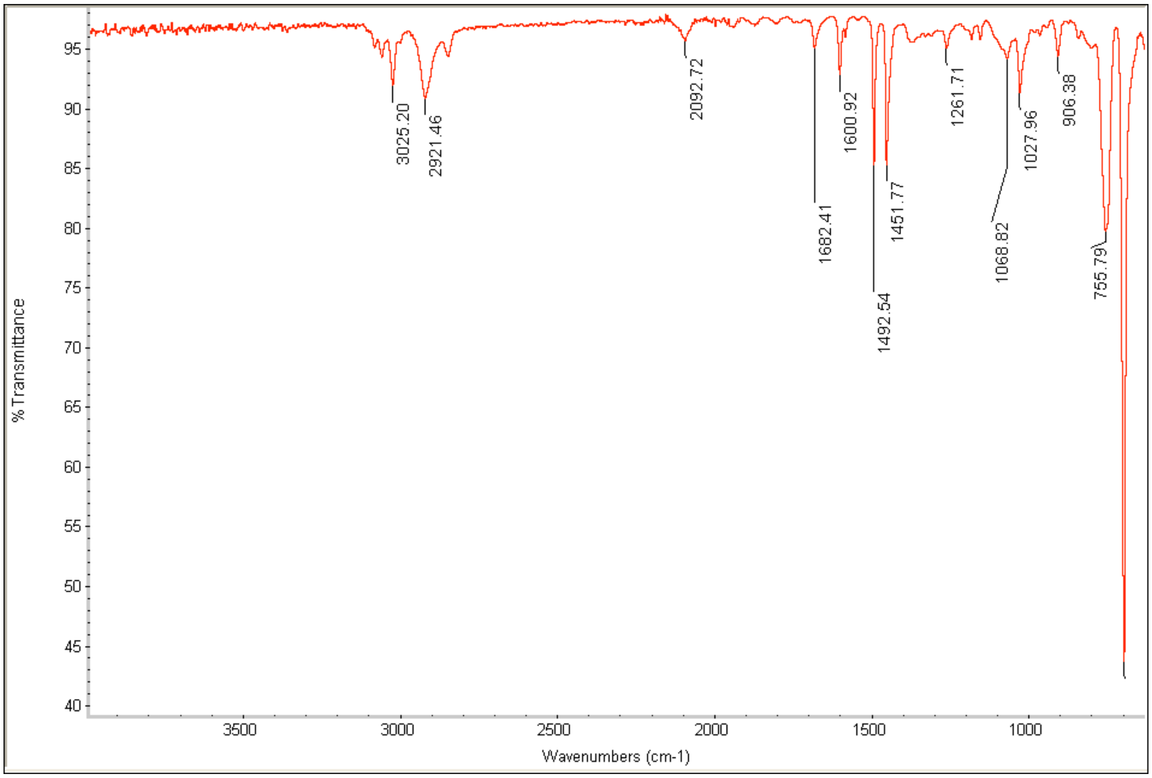


Figure S14. FTIR spectrum of S22K-N_3

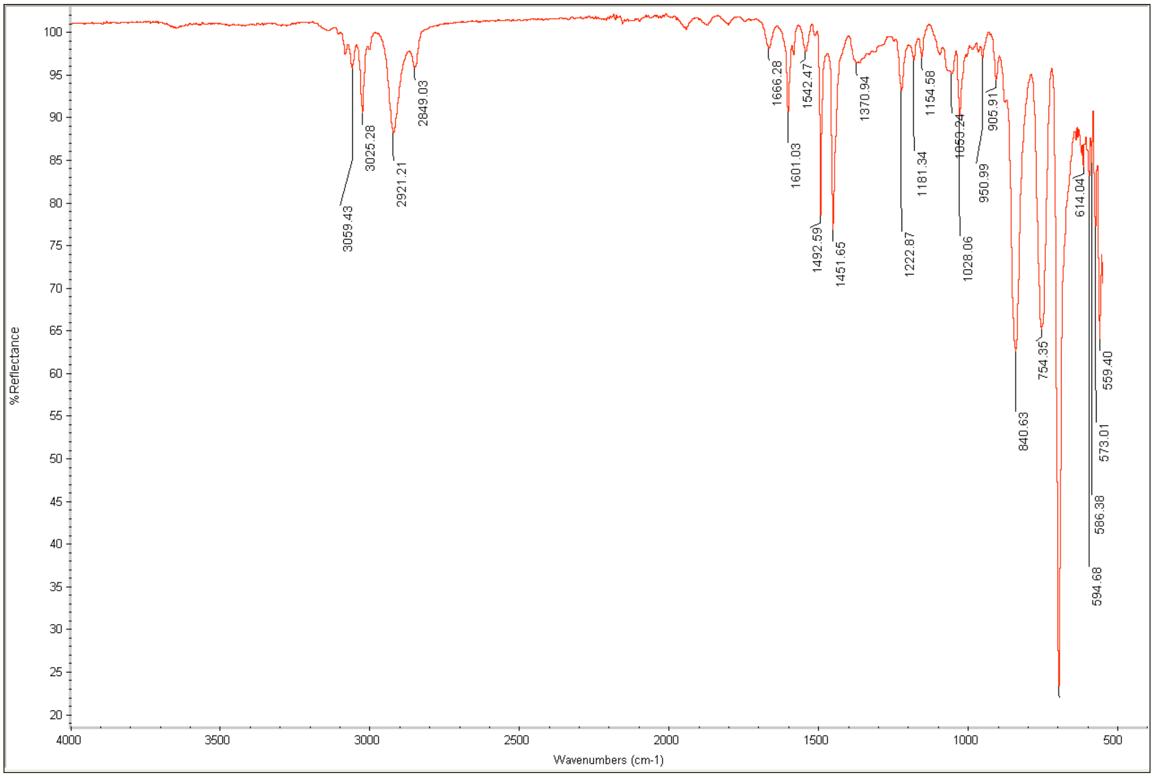


Figure S15. FTIR spectrum of S10K-NHC

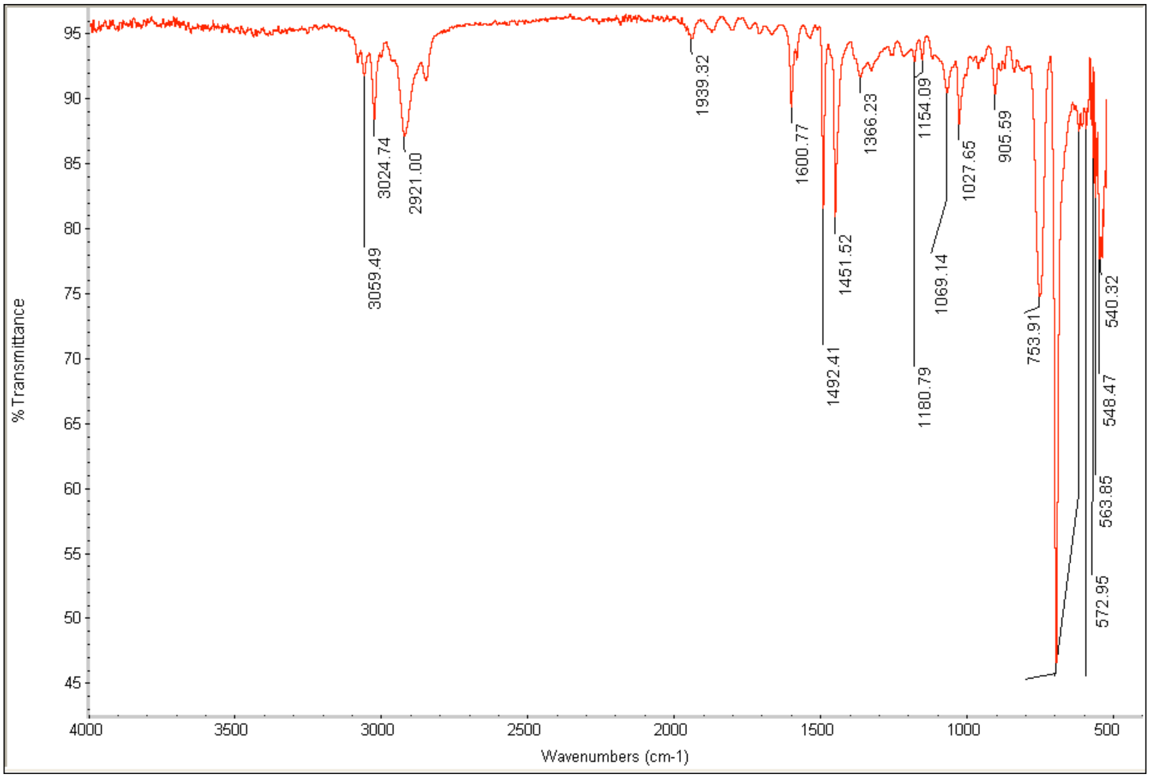


Figure S16. FTIR spectrum of S22K-NHC

SEC analysis

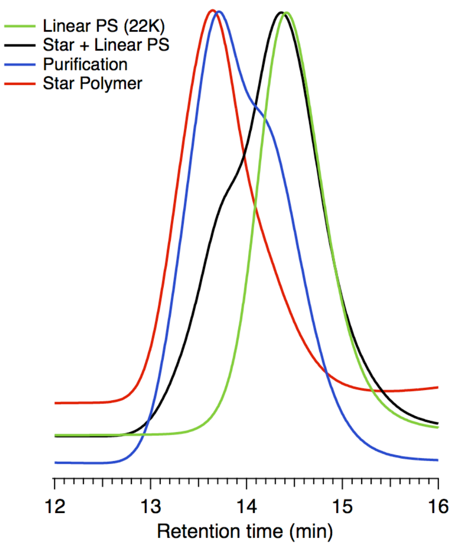


Figure S17. SEC chromatograms (eluent: THF) of PS 22K (green), after crosslinking (black) and purification S22K-Cl (1st (blue) and 2nd (red) fractionation).

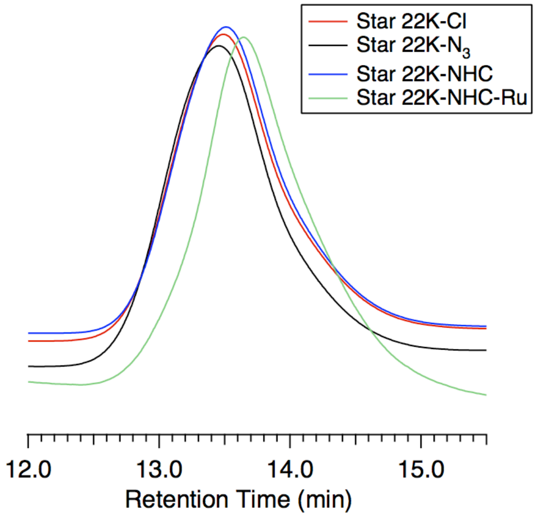


Figure S18. SEC chromatograms (eluent: THF) of S22K-Cl (red), S22K-N_3 (black), S22K-NHC (blue) and S22K-NHC-Ru (green).

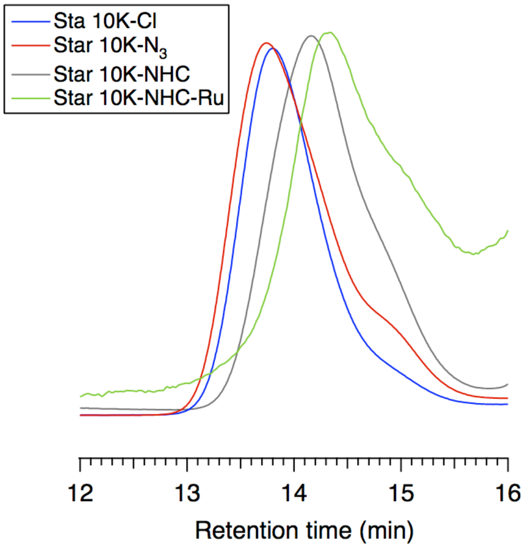


Figure S19. SEC chromatograms (eluent: THF) of S10K-Cl (blue), S10K-N_3 (red), S10K-NHC (black) and S10K-NHC-Ru (green).

DLS analysis

The star polymer samples were dissolved in toluene to reach a concentration of 1 g/L. The solutions were vigorously stirred at room temperature overnight and then filtered through a 450 μm PTFE filter before analysis.

Table S2. Characterization data for the S10K and S22K polymer families.

Entry	Polymer	M_n, kDa [a]	M_w, kDa [a]	PDI (SEC)	Diam., nm [b]	PDI (DLS)
1	S10K-Cl	34	40	1.19	18	0.10
2	S22K-Cl	57	64	1.12	20	0.14
3	S10K-N_3	35	42	1.20	23	0.12
4	S22K-N_3	63	70	1.10	20	0.16
5	S10K-NHC	23	28	1.17	105	0.16
6	S22K-NHC	66	76	1.14	25	0.50
7	S10K-NHC-Ru	41	51	1.24	178	0.16
8	S22K-NHC-Ru	40	49	1.21	67	0.11

[a] Determined by SEC in THF. The calibration was performed against linear polystyrene; however, all of the S10K and S22K polymers are globular. Thus, the values are not a direct measure of M_w/M_n, yet they are related to he hydrodynamic diameters of the polymers. [b] Hydrodynamic diameter determined by DLS in toluene at 1 g/L.

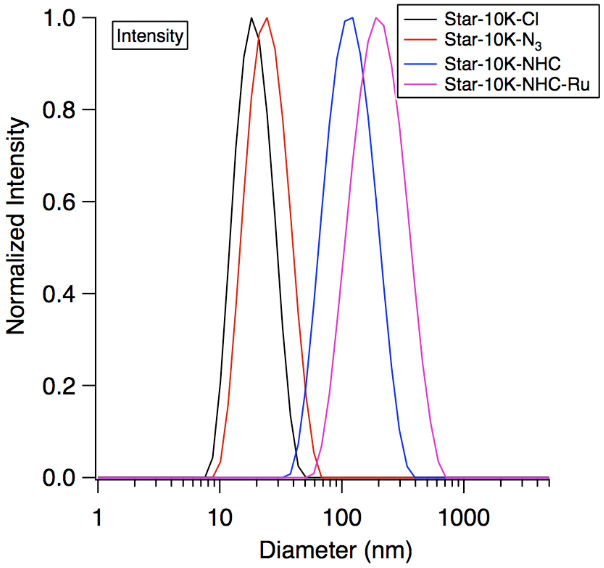


Figure S20. Size distribution by intensity of S10K-Cl (black), S10K-N_3 (red), S10K-NHC (blue) and S10K-NHC-Ru (pink).

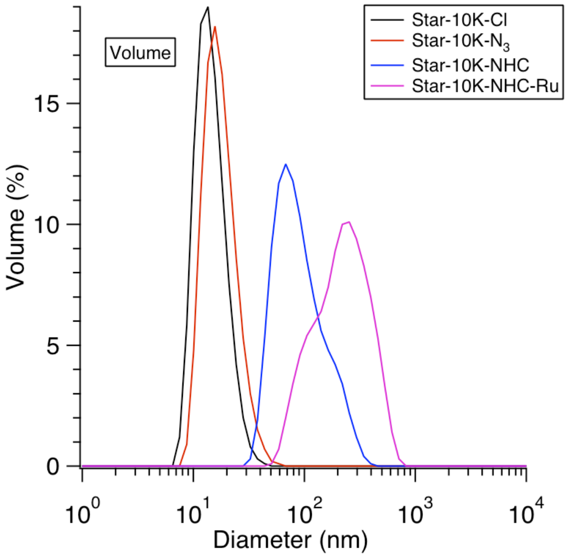


Figure S21. Size distribution by volume of S10K-Cl (black), S10K-N_3 (red), S10K-NHC (blue) and S10K-NHC-Ru (pink).

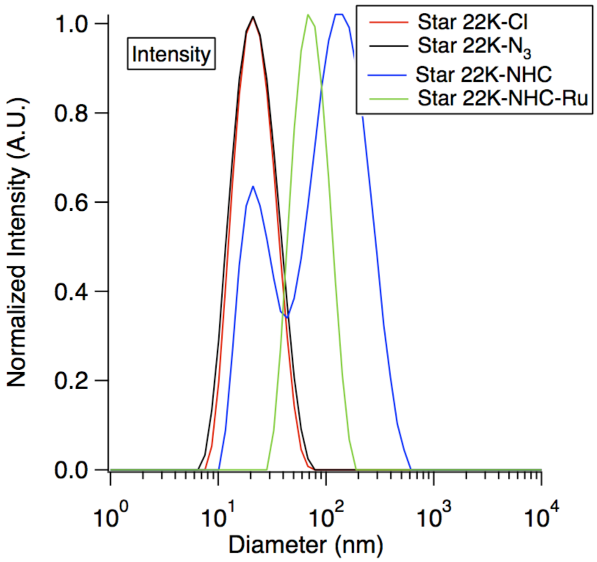


Figure S22. Size distribution by intensity of S22K-Cl (red), S22K-N_3 (black), S22K-NHC (blue) and S22K-NHC-Ru (green).

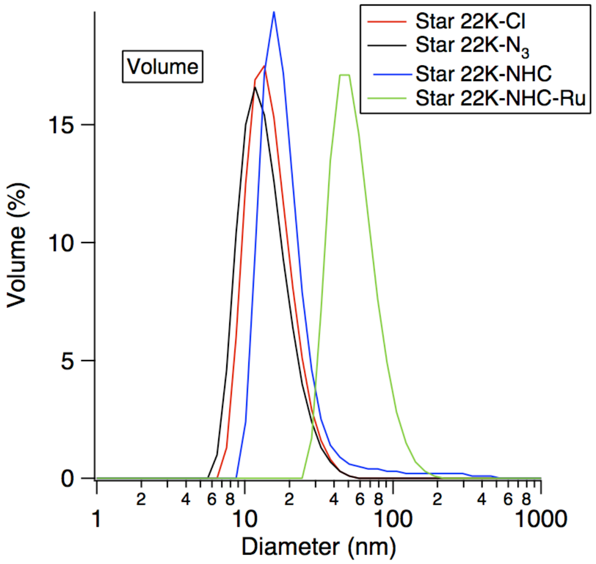


Figure S23. Size distribution by volume of S22K-Cl (red), S22K-N_3 (black), S22K-NHC (blue) and S22K-NHC-Ru (green).

SLS analysis

The S22K-Cl and S10K-Cl samples were dissolved in toluene to reach a concentration of 10 and 15 g/L, respectively. The solutions were then vigorously stirred for a week and sonicated for 10 min, diluted to reach 6, 4 and 1 g/L, and then filtered through a 0.2 µm PTFE filter before analysis. The samples were thermostatted at 25 °C for 5 minutes and the scattering intensity was recorded at angles varying from 30 to 150°.

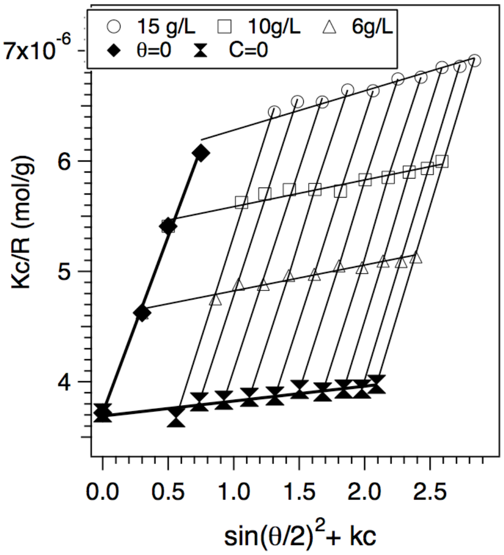


Figure S24. Zimm plot of S10K-Cl.

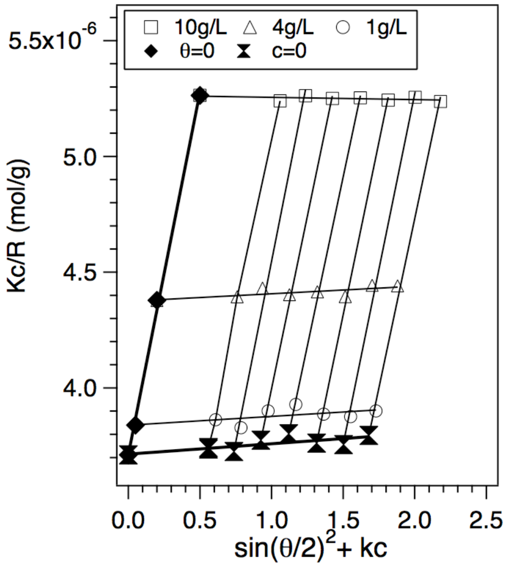


Figure S25. Zimm plot of S22K-Cl.

TEM analysis

S22K-NHC-Ru and S10K-NHC-Ru were dissolved in toluene to reach a concentration of 5 g/L. The solution was vigorously stirred overnight at room temperature and filtered through a 0.450 µm PTFE filtrer. The S10K-NHC-Ru sample was drop-cast on a TEM grid (lacy carbon, 300 mesh Cu), while Ultrathin Carbon Type A (3-4nm) with a removable Formvar 400 mesh was used for the S22K-NHC-Ru sample.

Table S3. Diameter of the star polymers determined by TEM analysis

Sample	Diameter
S10K-NHC-Ru	21.26 ± 2.24
S22K-NHC-Ru	32.52 ± 1.90

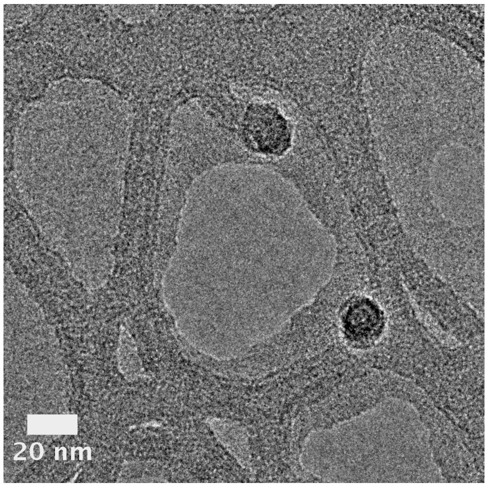


Figure S26. TEM image of S10K-NHC-Ru.

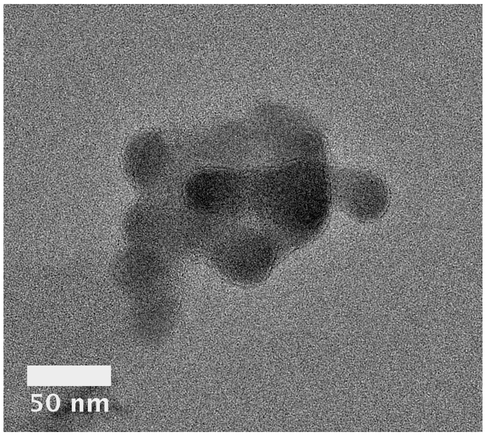


Figure S27. TEM image of S22K-NHC-Ru.

AFM analysis

Table S4. Diameter of the star polymers determined by TEM analysis

Sample	Height Image	Diameter (nm)/Height Image	Diameter (nm)/ Phase Image
S10K-Cl	12 ± 3	290 ± 20	175 ± 35
S22K-Cl	65± 40	200 ± 60	250 ± 60

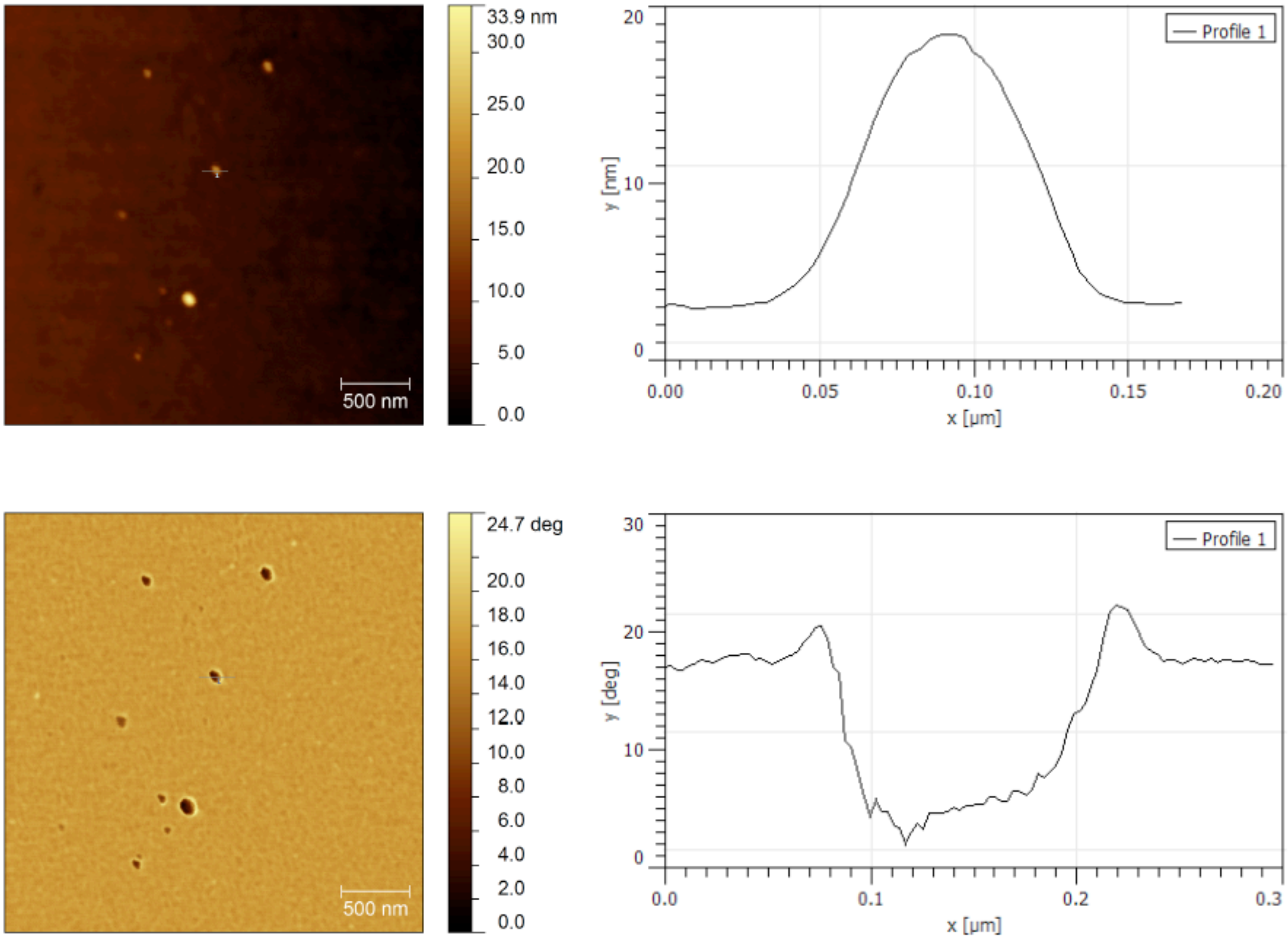


Figure S28. AFM height (top) and phase (down) images of S22K-Cl with the graphs showing the diameter and the height of the star polymers.

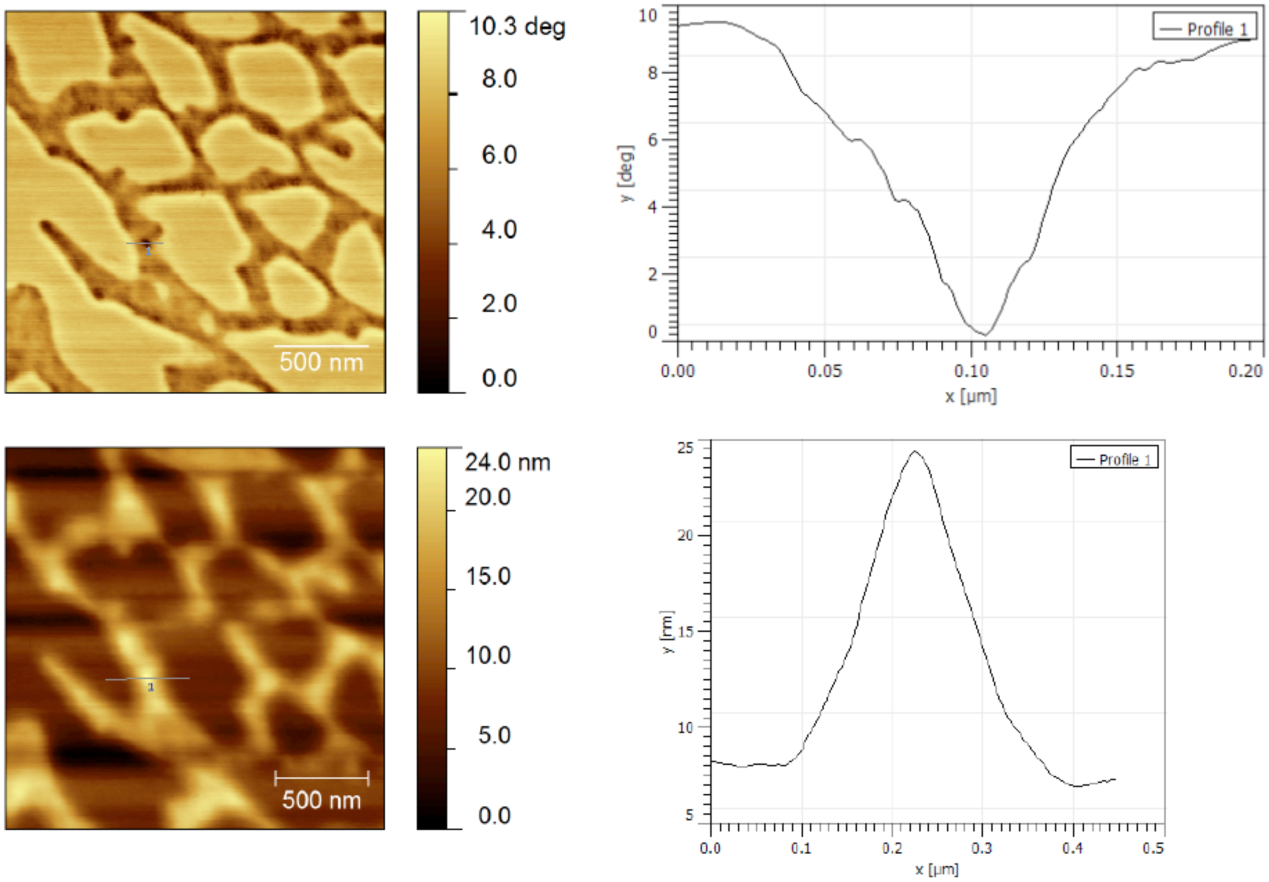
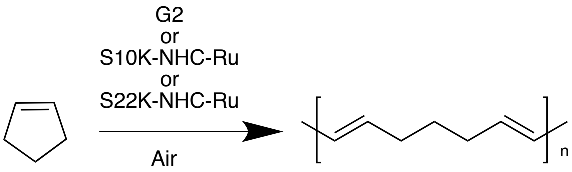


Figure S29. AFM phase (top) and height (down) images of S10K-Cl with the graph showing the diameter and the height of the star polymers.

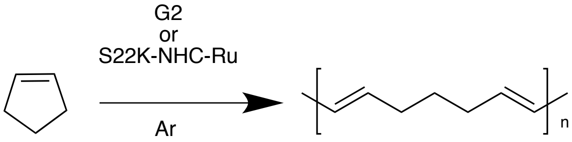
7. Catalysis

Polymerization of cyclopentene (ambient conditions)



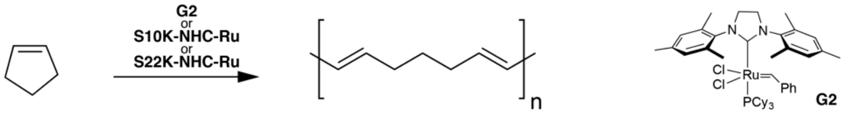
S22K-NHC-Ru (5 x 10^{-3} g, 1.65 µmol of Ru, 1 eq.), **S10K-NHC-Ru** (5 x 10^{-3} g, 1.56 µmol of Ru, 1 eq.) and the second generation Grubbs catalyst (1.4 x 10^{-3} g, 1.65 µmol, 1 eq.) were each massed into separate vials and dissolved in 1 mL of toluene. Cyclopentene (0.223 g, 3.27 mmol, 1980 eq.) was then added to each vial and the mixtures were stirred at room temperature for 24 hours. The reactions were monitored by ^{1}H-NMR analysis to determine the conversion: a 50 µL aliquot of each sample was transferred into a vial containing 20 µL of ethyl vinyl and 600 µL of $CDCl_3$ at different time slots. The molecular weight of each sample was determined by SEC analysis using $CHCl_3$ as eluent. For the second generation Grubbs catalyst no conversion of the monomer was observed. The solutions with the star polymers displayed an increase in viscosity over time. After the reaction, the solution mixture containing **S22K-NHC-Ru** was transferred in the fridge at -18 °C overnight. A phase separation was then observed allowing for easy separation of the polypentenamer from the catalyst. The supernatant containing the polypentenemer was precipitated from acetone, filtered and dried under vaccum. ICP: *no* Ru.

Polymerization of cyclopentene



S22K-NHC-Ru (5 10^{-3} g, 1.65 µmol of Ru, 1eq.) and the second generation Grubbs catalyst (1.4 x 10^{-3} g, 1.65 µmol, 1 eq.) were each massed into separate vials and dissolved in 1 mL of toluene. Cyclopentene (0.223 g, 3.27 mmol, 1980 eq.) was then added to each mixture and they were stirred at room temperature for 24 hours. The conversion of the polymerization reactions were determined by ^{1}H-NMR: a 50 µL aliquot of each sample was transferred in a vial containing 20 µL of ethyl vinyl and 600 µL of $CDCl_3$ at different time slots. The molecular weight of each sample was determined by SEC analysis using $CHCl_3$ as the eluent.

Table S5. ROMP reactions of cyclopentene with **G2**, **S10K-NHC-Ru** and **S22K-HNC-Ru** catalysts.



entry	catalyst [a]	time, h	conversion, % [b]	air/Ar	temp., °C	Mn, kDa [c]	Mw, kDa [c]	PDI
1	G2	0.5	78	Ar	20	33	48	1.48
2	G2	20	78	Ar	20	gel		
3	G2	0.5	0	air	20	-	-	-
4	G2	20	1	air	20	-	-	-
5	S22K-NHC-Ru	0.5	8	air	20	41	64	1.56
6	S22K-NHC-Ru	20	67	air	20	73	120	1.64
7	S22K-NHC-Ru	0.5	48	air	35	41	64	1.56
8	S22K-NHC-Ru	20	66	air	35	60	92	1.54
9	S22K-NHC-Ru	0.5	27	Ar	20	140	220	1.60
10	S22K-NHC-Ru	20	84	Ar	20	160	300	1.80
11	S10K-NHC-Ru	0.5	8	air	20	20	25	1.27
12	S10K-NHC-Ru	20	28	air	20	43	76	1.76
13	S10K-NHC-Ru	0.5	-	air	35	gel		

[a] Loading is 0.028 mol % for polymer catalysts, and 0.027 mol % for G2 based on Ru. [b] Determined by ^{1}H NMR. [c] Determined by SEC in CHCl$_3$ (calibration was performed against linear polystyrene).

Spontaneous Separation of Polypentenamer

The solution of **S22K-NHC-Ru** catalyst was brown, and the color persisted after the addition of cyclopentene (Figure S30-A). After the solution was kept overnight at -18°C, spontaneous phase separation occurred (Figure S30-B). The transparent supernatant containing the polypentenamer was precipitated in acetone, leading to white polypentenamer free from ruthenium (Figure S30-C). The solid polymer was then dried under vacuum to yield a transparent film as shown on Figure S30-D.

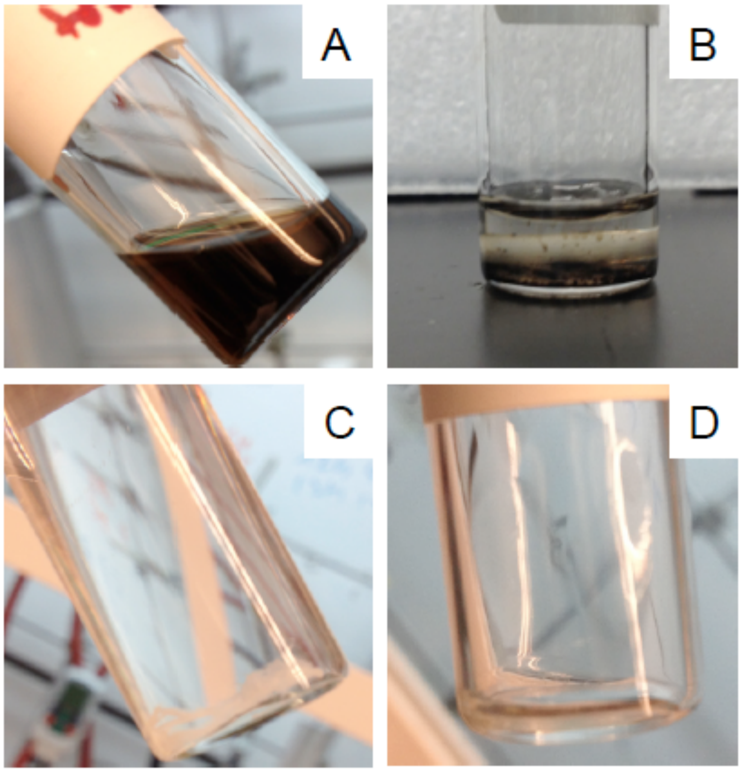


Figure S30. Purification steps of the polypentenamer from the star polymer catalyst.

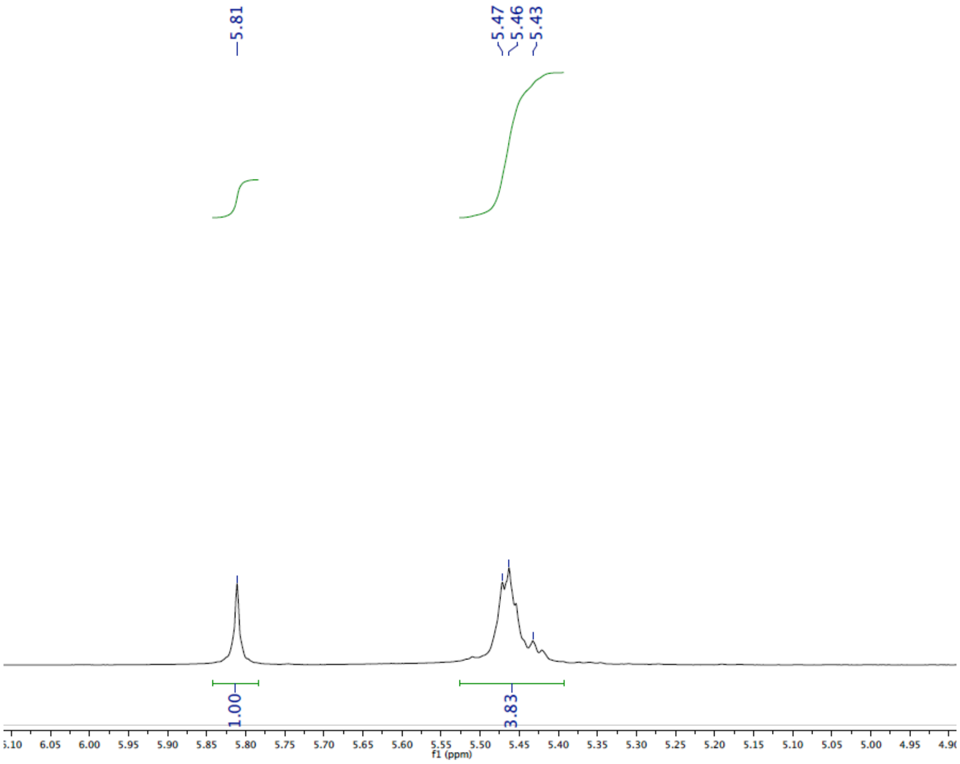


Figure S31. ^{1}H NMR spectrum showing the signal of the vinlylic protons of the monomer (5.85 ppm) and the polymer (5.51 ppm) using G2 catalyst (after 20 hours-Ar).

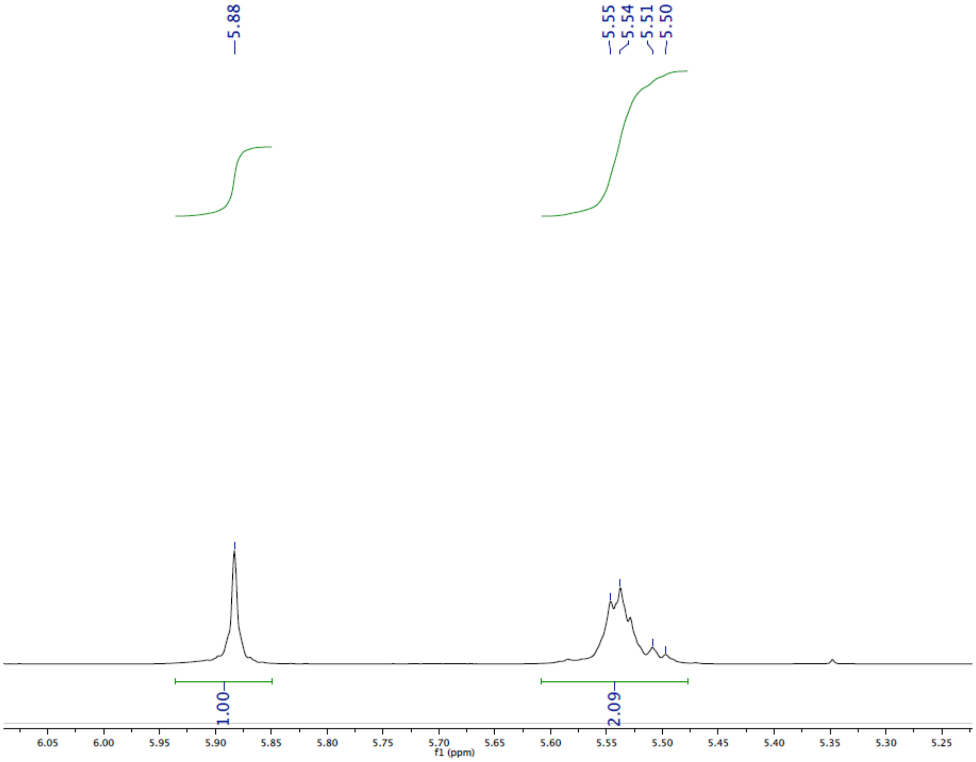


Figure S32. ^{1}H NMR spectrum showing the signal of the vinlylic protons of the monomer (5.88 ppm) and the polymer (5.51pm) using S22K-NHC-Ru catalyst (after 20 hours-air).

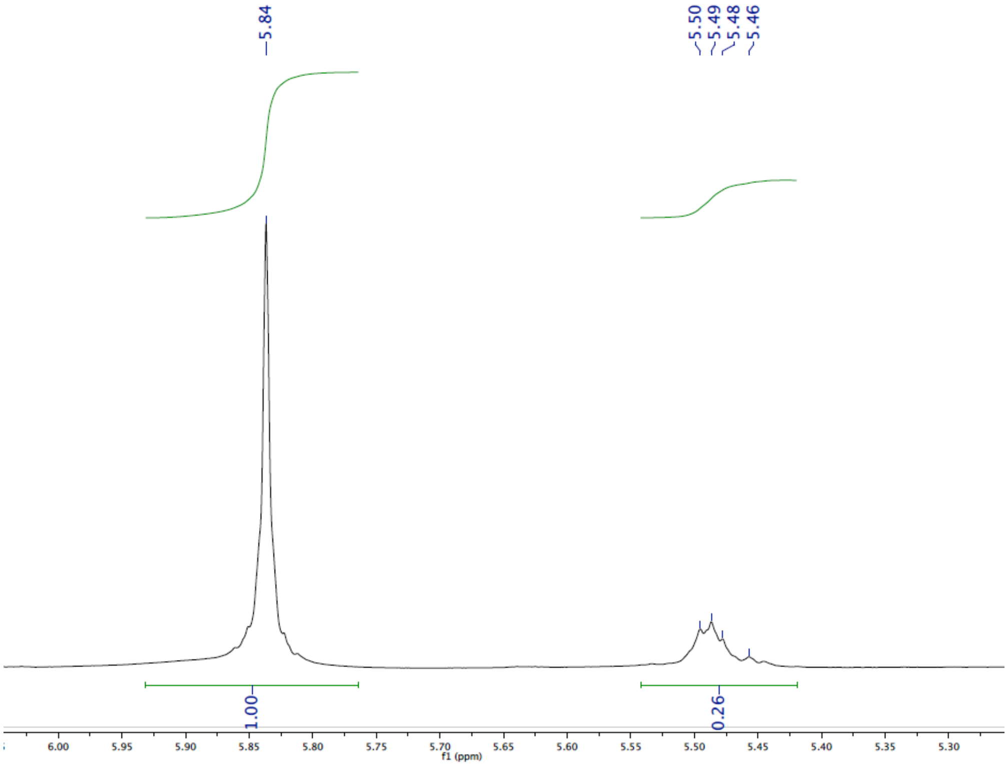


Figure S33. ^{1}H NMR spectrum showing the signal of the vinlylic protons of the monomer (5.84 ppm) and the polymer (5.49pm) using S10K-NHC-Ru catalyst (after 4 hours-air).

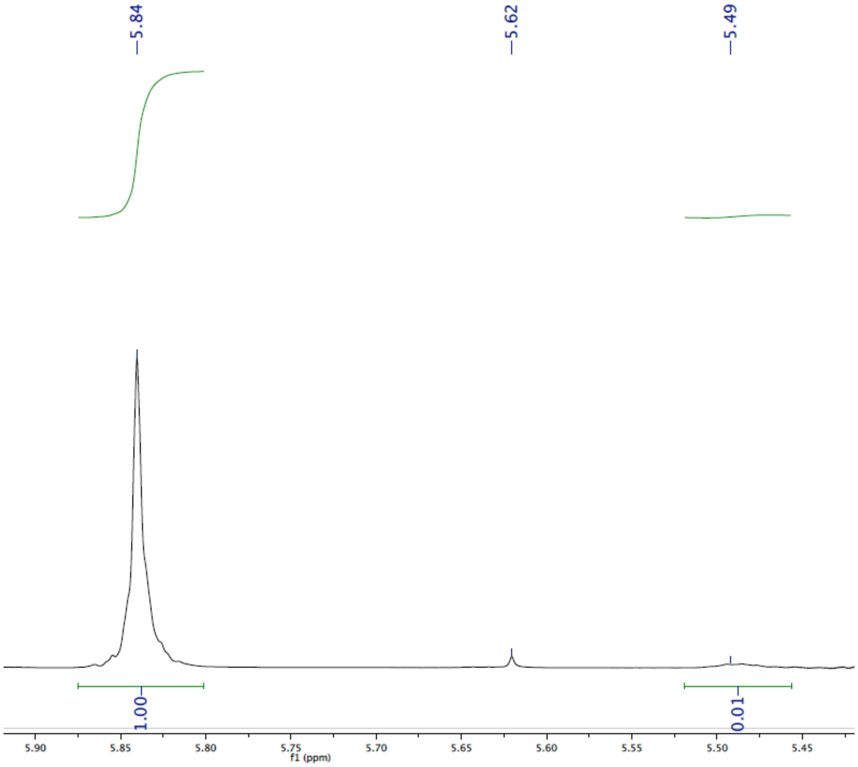


Figure S34. ^{1}H NMR spectrum showing the signal of the vinlylic protons of the monomer (5.84 ppm) and the polymer (5.49pm) using G2 catalyst (after 20 hrs-air).

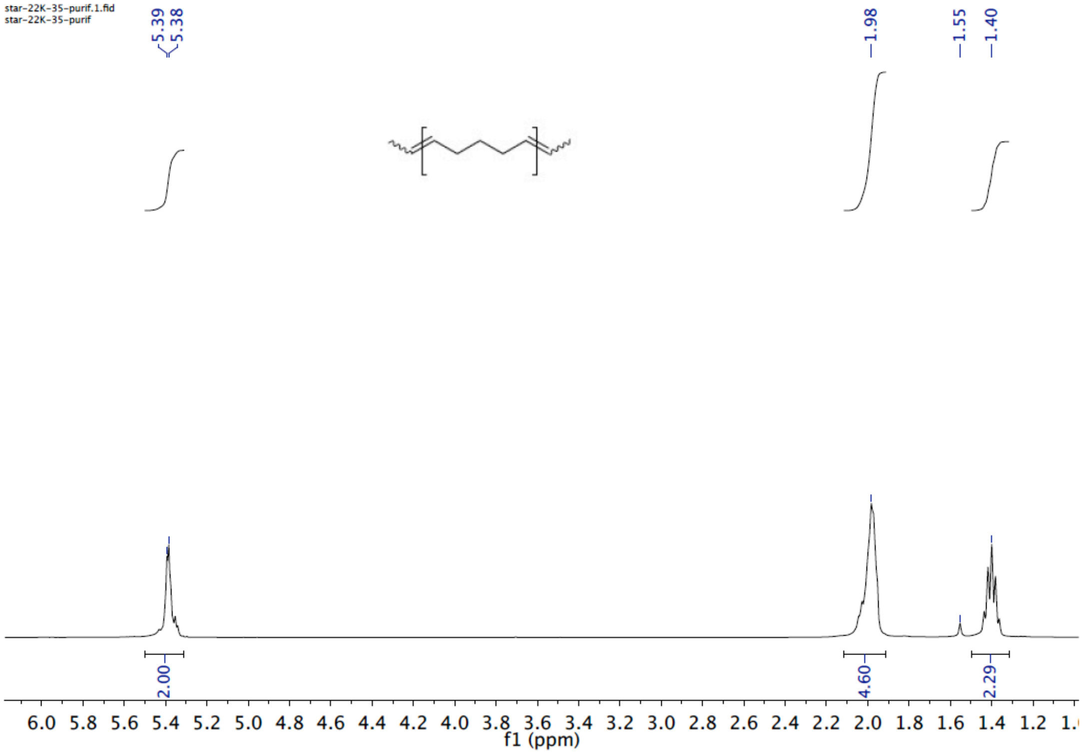


Figure S35. ^{1}H NMR spectrum of the pentenamer after purification from the S22K-NHC-Ru catalyst.

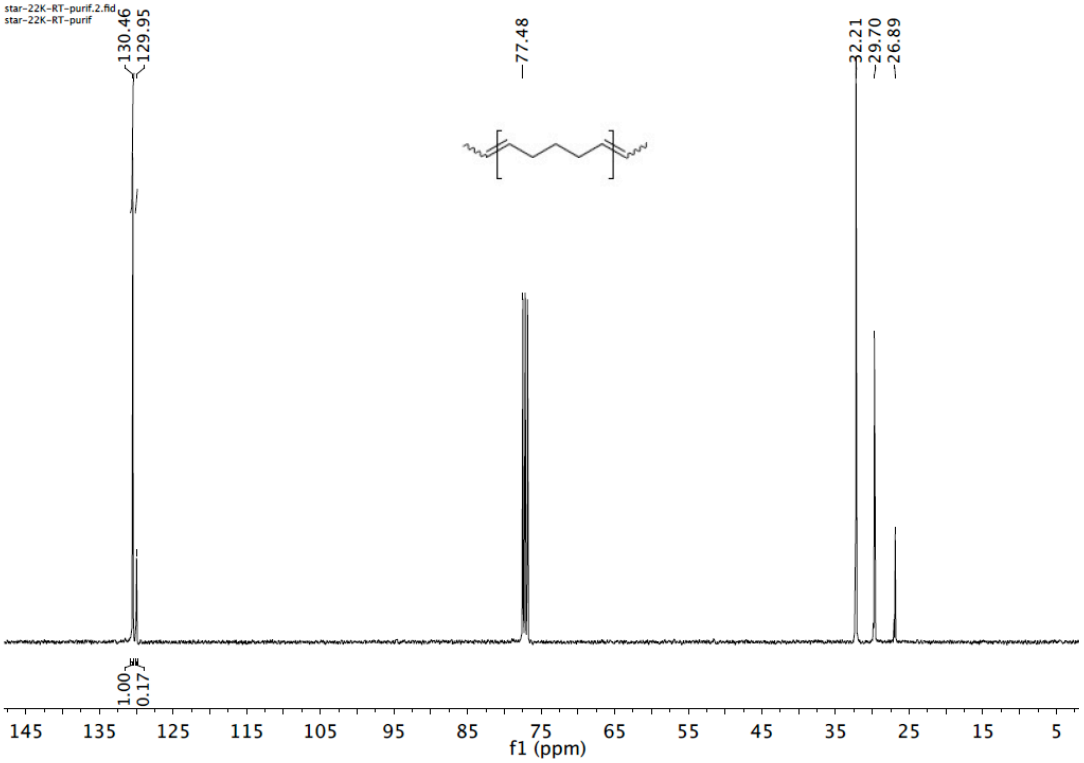


Figure S36. ^{13}C NMR spectrum of the pentenamer after purification from the S22K-NHC-Ru catalyst.

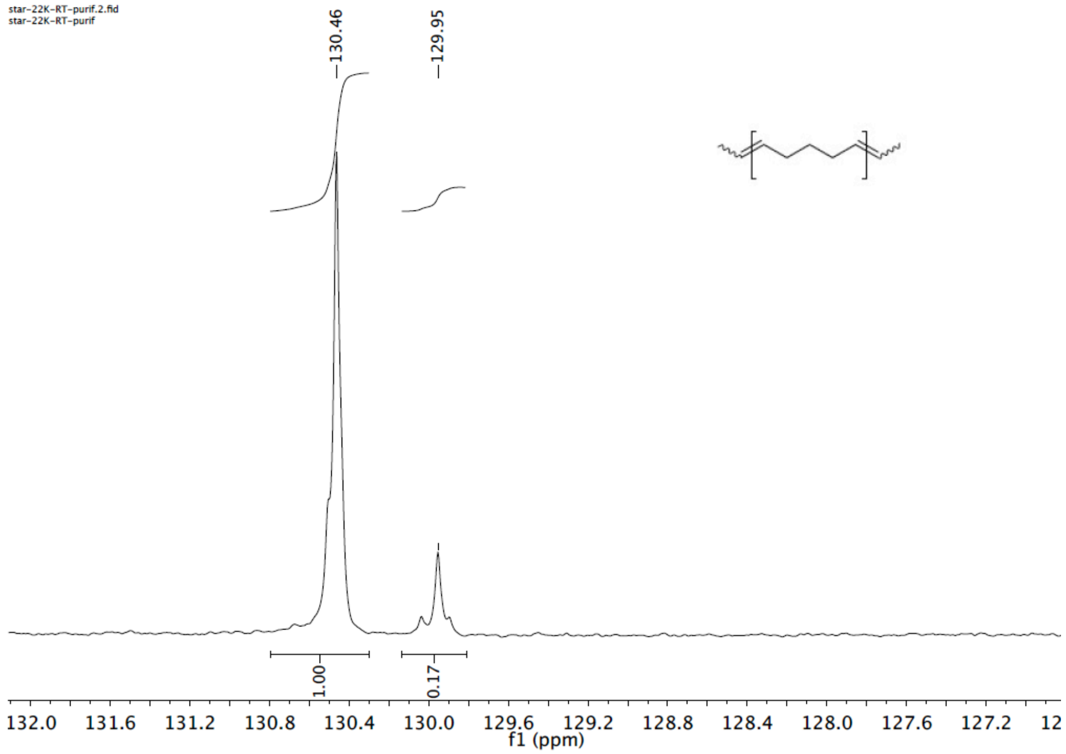


Figure S37. ^{13}C NMR spectrum of the pentenamer highlighting the distinct peaks of *trans* and *cis* polypentenamer.

8. References

1. Bukhryakov, K.V.; Mugemana, C.; Vu, K.B.; Rodionov, V. *Org. Lett.* **2015**, 17, 4826
2. Leuthausser, S.; Schmidts, V.; Thiele, C. M.; Plenio, H. *Chem. Eur. J.* **2008**, 14, 5465