Supporting Information

Functional Metathesis catalyst through Ring Closing Enyne Metathesis: One Pot Protocol for Living Hetero-telechelic Polymers.

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Materials

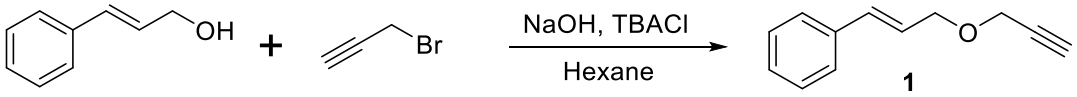
Grubbs initiators G1 and G3, cis-2-butene-1,4-diol (CTA 7), cis-1,4-dichloro-2-butene (CTA 8) ,3,4-dihydro-2-methoxy-2H- pyran (CTA 10) and 3-bromopyridine were purchased from Sigma-Aldrich and used without further purification. All other reagents and solvents were purchased from Acros organics or Sigma-Aldrich and used without further purification**.** Exo-N-methylnorbornene imide (MNI), Exo-N-ethylhexylnorbornene imide and di-tert-butyl but-2-ene-1,4-diyl(Z)-dicarbamate (CTA 9) were synthesized as reported previously**.**[1,2] Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc.

Characterization

All ^1H NMR (400 MHz) and ^{13}C 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 ($CDCl_3$: 7.26 for ^1H; $CDCl_3$: 77.16 for ^{13}C and CD_2Cl_2: 5.32 for ^1H; CD_2Cl_2: 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). UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 40 spectrometer. Fluorescence spectra were performed on an Edinburgh FS 5 fluorimeter. All spectroscopic measurements were performed in spectroscopic grade $CHCl_3$ (Sigma Aldrich). The labelled polymer was purified by JAI LC-9130 recycling GPC with $CHCl_3$ as eluent. The system consisting of two linear Jaigel-2H and Jaigel-1H columns. Signal detection was performed with UV 600 Next detector.

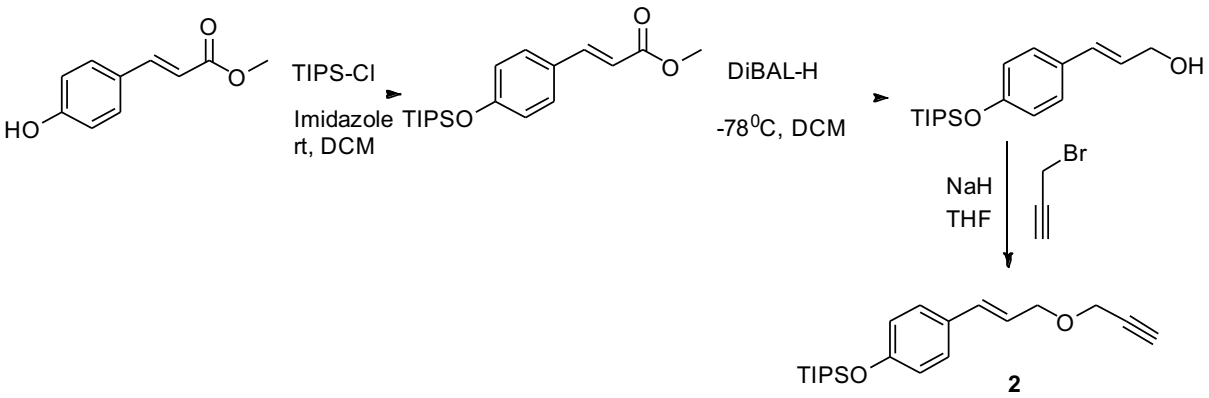
Synthesis of substrates

(E)-1-phenyl-4-oxa-1-hepten-6-yne (1):



Synthesized according to published protocol.[3] ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ 7.38 - 7.47 (m, 2 H), 7.31 - 7.38 (m, 2 H), 7.23 - 7.31 (m, 1 H), 6.67 (d, *J*=15.89 Hz, 1 H), 6.30 (dt, *J*=15.96, 6.14 Hz, 1 H), 4.26 (dd, *J*=6.17, 1.41 Hz, 2 H), 4.22 (d, *J*=2.45 Hz, 2 H), 2.48 (t, *J*=2.38 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ 136.5, 133.3, 128.5, 127.8, 126.5, 125, 79.7, 74.7, 70.2, 57, 57 ppm. GC-MS: calcd. for $C_{12}H_{12}O$ [M]+: 172.0888; Found: 171.1.

(E)-triisopropyl(4-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)phenoxy)silane (2):[1,4]

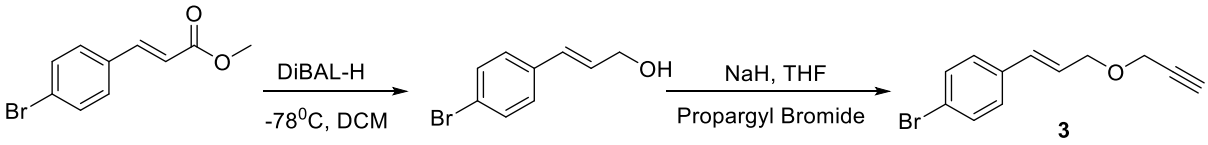


A mixture of 4-hydroxy methyl cinnamate (3g, 16.9 mmol, 1eq) and imidazole (2.3g, 33.7 mmol, 2 eq) was dissolved in 10 mL of dry dichloromethane. The solution was cooled to 0^{0}C. TIPS-Cl (3.5g, 18.5 mmol, 1.1 eq) was added dropwise. The mixture was stirred for 5 hours until complete disappearance of the starting material was observed. The reaction mixture was concentrated in vacuum and silica was added. This silica was loaded onto the column and eluted with hexane:EtOAc = 19:1 to give 5.4g (96 %) of a clear oil. This clear oil was used directly in the next step. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.65 (d, J=16.02 Hz, 1 H), 7.36 - 7.46 (m, 2 H), 6.82 - 6.93 (m, 2 H), 6.30 (d, J=15.89 Hz, 1 H), 3.80 (s, 3 H),1.22 - 1.33 (m, 3 H), 1.11 (d, J=7.21 Hz, 18 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 167.8, 158.3, 144.6, 129.7, 127.4, 120.3, 115.2, 51.5, 17.8, 12.7 ppm.

This clear oil (2g, 6 mmol, 1eq) was dissolved in 10 mL of dry dichloromethane. The resulting solution was cooled to -78^{0}C. To this solution, 8.3 mL of DiBAL-H (1.6M in hexane, 13.2 mmol, 2.2eq) was added dropwise over 30 min. The solution was stirred at -78^{0}C for 30 min and allowed to warm to room temperature. The mixture was stirred for a further 4 h at room temperature. The reaction was quenched by cooling the solution to -20^{o}C and 5mL water was added dropwise. The mixture was allowed to stir at room temperature for another 30 min. The resulting emulsion was filtered over Celite. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure giving a clear oil (1.65g,90%). This clear oil was used in the next step without any purification. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 7.24-7.27 (m, 2 H), 6.84 (d, J=8.68 Hz, 2 H), 6.52 (s, 1 H), 4.28 (d, J=5.87 Hz, 2 H), 1.81 (s, 1 H), 1.19 - 1.36 (m, 3 H), 1.10 (d, J = 7.3 Hz, 18 H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 155.9, 131.2, 129.6, 127.6, 126.2, 120.0, 63.9, 17.9, 12.7 ppm. The clear oil (1g, 3.3 mmol, 1eq) was dissolved in dry DMF (3 mL) and cooled to 0^0 C. NaH (60% dispersion, 143.8mg, 3.6 mmol, 1.1 equiv.) was added portion wise at 0^0 C. The solution was allowed to warm to room temperature and was stirred for

another 1 hour. Afterwards, the solution was cooled again to 0^0C and propargyl bromide(80 wt% in toluene, 0.98g, 6.6 mmol, 1.1 eq.)was added dropwise. The mixture was stirred overnight at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 times with EtOAc. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the material was chromatographed on neutral alumina (hexane:EtOAc = 99:1) to obtain product **2** (0.96 g, 85 %) as a yellow oil. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.24 - 7.32 (m, 2 H), 6.85 (d, J=8.68 Hz, 2 H), 6.60 (d, J=15.89 Hz, 1 H), 6.15 (dt, J=15.89, 6.42 Hz, 1 H), 4.24 (dd, J=6.42, 1.28 Hz, 2 H), 4.21 (d, J=2.32 Hz, 2 H), 2.47 (t, J=2.38 Hz, 1 H), 1.22 - 1.33 (m, 4 H), 1.12 (d, J=7.09 Hz, 19 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 156.0, 133.4, 129.5, 127.7, 122.6, 120.0, 79.8, 74.3, 70.4, 56.8, 17.9, 12.6 ppm. HR-MS (ESI) calcd. for $C_{21}H_{32}O_2SiNa$+ [M+Na]+: 367.2069; Found: 367.2063.

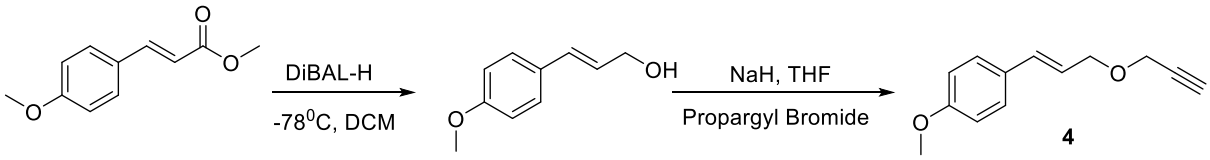
(E)-1-bromo-4-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (3):[1,4]



4-Bromo methyl cinnamate (2g, 8.3 mmol, 1 eq.) was dissolved in 10 mL of dry dichloromethane and cooled to -78^{0}C. To this cooled solution DiBAL-H (11.4 mL, 1.6M in hexane,18.3 mmol, 2.2eq.) wad added dropwise over 30 min. The mixture was stirred for 30 min at -78^{0}C and allowed to warm to room temperature. The mixture was stirred for a further 4h at room temperature. The reaction was quenched by cooling the solution to -20^{o}C and 5mL water was added dropwise. The mixture was allowed to stir at room temperature for another 30 min. The resulting emulsion was filtered through Celite. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure to give a yellowish solid (1.7g, 95%). This solid was used in the next step without further purification. ^{1}H NMR (400 MHz, CDCl3) δ 7.40-7.49 (m, 2 H), 7.19-7.30 (m, 2 H), 6.56 (d, J = 15.9 Hz, 1 H), 6.35 (dt, J = 15.9, 5.6 Hz, 1 H), 4.32 (d, J = 7.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 135.6, 131.7, 129.8, 129.3, 128.0, 121.5, 63.5 ppm.

The yellowish solid (1g, 4.7 mmol, 1eq.) was dissolved in dry DMF (3 mL) and cooled to 0^0 C. NaH (60% dispersion, 208.5mg, 5.2 mmol, 1.1 eq.) was added portion wise at 0^0C. The solution was allowed to warm to room temperature and was stirred for another 1 hour. Afterwards, the solution was cooled again to 0^0C and propargyl bromide (80 wt% in toluene, 0.77g, 5.2 mmol, 1.1 eq.)was added dropwise. The mixture was stirred overnight at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 times with EtOAc. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the material was chromatographed on silica (hexane:EtOAc = 98:2) to obtain product **3** (1.1 g, 90%) as a yellow solid. ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 7.41 - 7.51 (m, 2 H), 7.21 - 7.32 (m, 2 H), 6.60 (d, *J*=15.89 Hz, 1 H), 6.28 (dt, *J*=15.96, 6.08 Hz, 1 H), 4.24 (dd, *J*=6.05, 1.41 Hz, 2 H), 4.21 (d, *J*=2.32 Hz, 2 H), 2.47 (t, *J*=2.45 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 135.5, 131.9, 131.7, 128.0, 125.9, 121.6, 79.6, 74.6, 70.0, 57.2 ppm. GC-MS: calcd. for $C_{12}H_{11}BrO$ [M]+: 249.9993; Found: 250.1.

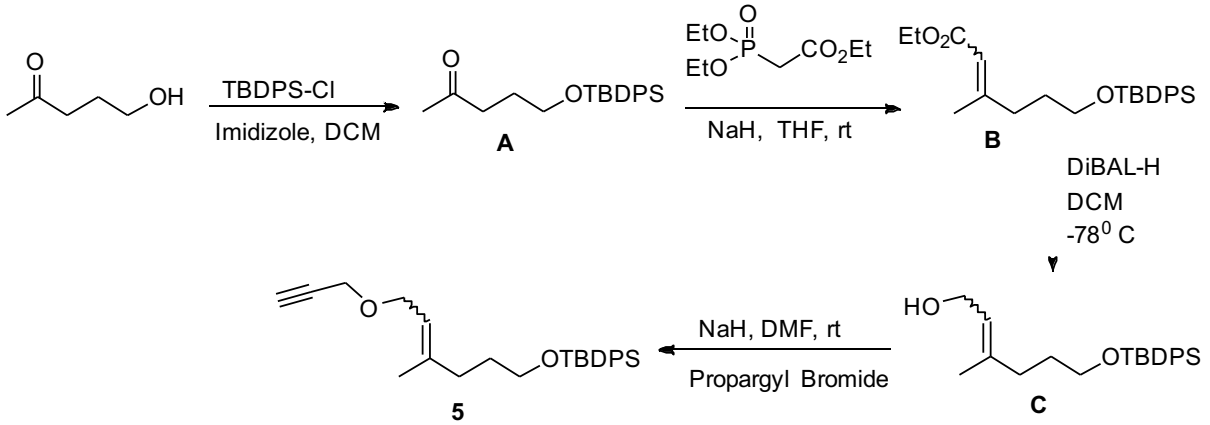
(E)-1-methoxy-4-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (4):[1,4]



4-Methoxy methyl cinnamate (2g, 10.4 mmol, 1 eq.) was dissolve in 10 mL of dry dichloromethane and cooled to -78^{0}C. To this cooled solution 14.3 mL DiBAL-H (1.6M in hexane,22.9 mmol, 2.2 eq.) wad added dropwise over 30 min. The mixture was stirred 30 min at -78^{0}C and allowed to warm to room temperature. The mixture was stirred for further 4h at room temperature. The reaction was quenched by cooling the solution to -20^{o}C and 5mL water was added dropwise. The mixture was allowed to stir at room temperature for another 30 min. The resulting emulsion was filtered through Celite. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure to give a yellowish liquid (1.6g, 92%). This liquid was used in the next step without further purification. ^{1}H NMR (400 MHz, CDCl3) δ 7.33 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.8 Hz, 2 H), 6.56 (d, J = 15.9 Hz, 1 H), 6.24 (d, J = 15.8 Hz, 1 H), 4.30 (t, J = 6.4 Hz, 2 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 159.3, 131.0, 129.4, 127.7, 126.3, 114.0, 64.0, 55.3 ppm.

The yellowish liquid (1g, 6.1 mmol, 1eq.) was dissolved in dry DMF (3 mL) and cooled to 0^0 C. NaH (60% dispersion, 268.3mg, 6.7 mmol 1.1 equiv.) was added portion wise at 0^0 C. The solution was allowed to warm to room temperature and was stirred for another 1 hour. Afterwards, the solution was cooled again to 0^{0}C and propargyl bromide (80 wt% in toluene, 1g, 6.7 mmol, 1.1 eq.)was added dropwise. The mixture was stirred for overnight at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 time with EtOAc. The combined organic layers were dried over MgSO4 and the solvent was removed under reduced pressure. Finally, the material was chromatographed on silica (hexane:EtOAc = 98:2) to obtainproduct 4 (1.1 g, 90 %) as yellow liquid. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.31 - 7.37 (m, 2 H), 6.82 - 6.91 (m, 2 H), 6.60 (d, J=15.89 Hz, 1 H), 6.15 (dt, J=15.86, 6.37 Hz, 1 H), 4.23 (dd, J=6.36, 1.35 Hz, 2 H), 4.20 (d, J=2.32 Hz, 2 H), 3.82 (s, 3 H), 2.46 (t, J=2.38 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 159.4, 133.2, 129.3, 127.8, 122.7, 114.0, 79.8, 74.4, 70.4, 56.9, 55.3 ppm. HR-MS (ESI) calcd. for $C_{13}H_{14}O_2Na$+ [M+Na]+: 225.0891; Found: 225.0886.

(E)-tert-butyl((4-methyl-6-(prop-2-yn-1-yloxy)hex-4-en-1-yl)oxy)diphenylsilane (5):[4]



A mixture of 5-hydroxy-2-pentanone (4g, 39 mmol, 1eq.) and imidazole (5.3g, 78 mmol, 2eq.) was dissolved in 20 mL of dry dichloromethane. The solution was cooled to 0^{0}C. TBDPS-Cl (11.8g, 43 mmol, 1.1eq.) was added dropwise. The mixture was stirred for 5 hours until complete disappearance of the starting material was observed. The reaction mixture was concentrated in vacuum and silica was added. This silica was loaded onto the column and eluted with hexane:EtOAc = 95:5 to give 11.27g

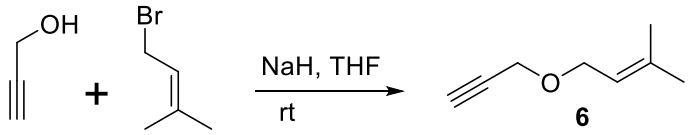
(85%) of a clear oil. This clear oil was used directly in the next step. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.64 - 7.72 (m, 4 H), 7.34 - 7.50 (m, 6 H), 3.70 (t, J=6.11 Hz, 2 H), 2.56 (t, J=7.27 Hz, 2 H), 2.14 (s, 3 H), 1.81 - 1.90 (m, 2 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 208.9, 135.5, 134.8, 129.6, 127.6, 63.0, 40.1, 29.9, 26.8, 19.2 ppm.

NaH (60% dispersion, 566.4mg, 14.2 mmol, 1.2 eq.) was dispersed in dry THF and cooled to 0^0 C. Triethyl phosphonoacetate (3.2g, 14.2 mmol, 1.2eq.) was added dropwise to the solution and stirred for another 1 hour at room temperature. To the solution 5-((tert-butyldiphenylsilyl)oxy)pentan-2-one (4g, 11.8 mmol, 1eq.) (**A**) in dry THF was added dropwise and stirred overnight at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 times with EtOAc. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the material was chromatographed on silica (hexane:EtOAc = 98:2) to obtain product **B** (4.3g, 90%)) as a yellow oil. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.63 - 7.70 (m, 4 H), 7.35 - 7.46 (m, 6 H), 5.66 - 5.71 (m, 1 H), 4.16 (q, J=7.09 Hz, 2 H), 3.68 (t, J=6.24 Hz, 2 H), 2.25 (t, J=7.27 Hz, 2 H), 2.15 (d, J=1.22 Hz, 3 H), 1.68 - 1.80 (m, 2 H), 1.29 (t, J=7.09 Hz, 3 H), 1.07 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 166.8, 159.7, 135.5, 133.8, 129.6, 127.6, 127.6, 115.7, 77.3, 76.7, 63.1, 59.4, 37.3, 30.4, 26.8, 19.2, 18.8, 14.3 ppm.

Ethyl (E)-6-((tert-butyldiphenylsilyl)oxy)-3-methylhex-2-enoate (**B**) (2g, 4.9 mmol, 1 eq.) was dissolved in 10 mL of dry dichloromethane and cooled to -78^{0}C. To this cooled solution DiBAL-H (6.8 mL , 1.6M in hexane, 10.8 mmol, 2.2 eq.) was added dropwise over 30 min. The mixture was stirred for 30 min at -78^0 C and allowed to warm to room temperature. The mixture was stirred for a further 4h at room temperature. The reaction was quenched by cooling the solution to -20^{o}C and 5mL water was added dropwise. The mixture was allowed to stir at room temperature for another 30 min. The resulting emulsion was filtered through Celite. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. Finally, the material was chromatographed on silica (hexane:EtOAc = 90:10) to obtain product **C** (1.5g, 85 % yield) as a yellow oil. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.63 - 7.75 (m, 4 H), 7.35 - 7.48 (m, 6 H), 5.40 (tdd, J=6.95, 6.95, 2.48, 1.22 Hz, 1 H), 4.14 (d, J=3.18 Hz, 2 H), 3.67 (t, J=6.36 Hz, 2 H), 2.09 - 2.15 (m, 2 H), 1.68 - 1.75 (m, 2 H), 1.66 (s, 3 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 139.5, 135.6, 134.0, 129.5, 127.6, 123.4, 63.4, 59.4, 35.7, 30.6, 26.9, 19.2, 16.2 ppm.

The yellow liquid (**C**) (1g, 2.7 mmol, 1eq.) was dissolved in dry DMF (3 mL) and cooled to 0^0C. NaH (60% dispersion, 118.8mg,3 mmol, 1.1 eq.) was added portion wise at 0^0C. The solution was allowed to warm to room temperature and was stired for another 1 hour. Afterwards, the solution was cooled again to 0^0C and propargyl bromide (80 wt% in toluene, 0.45g, 3 mmol, 1.1 eq.)was added dropwise. The mixture was stirred for overnight at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 times with EtOAc. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the material was chromatographed on silica (hexane:EtOAc = 99:1) to obtain product **5** (0.98g, 90 % yield) as a yellow liquid. ^{1}H NMR (400 MHz, DICHLOROMETHANE-d2) δ 7.68 (dd, J=7.82, 1.71 Hz, 4 H), 7.34 - 7.47 (m, 6 H), 5.28 - 5.36 (m, 1 H), 4.08 (d, J=2.32 Hz, 2 H), 4.04 (d, J=6.85 Hz, 2 H), 3.68 (t, J=6.42 Hz, 2 H), 2.45 (t, J=2.42 Hz 1 H), 2.10 - 2.18 (m, 2 H) 1.68 - 1.76 (m, 2 H) 1.67 (s, 3 H) 1.05 (s, 9 H) ppm. ^{13}C NMR (100 MHz, DICHLOROMETHANE-d2) δ 141.7, 136.1, 134.7, 130.1, 128.2, 120.8, 80.9, 74.3, 66.5, 64.1, 57.2, 36.3, 31.3, 27.2, 19.7, 16.7 ppm. HR-MS (ESI) calcd. for $C_{26}H_{34}O_2SiNa+$ [M+Na]+: 429.2226; Found: 429.2219.

3-methyl-1-(prop-2-yn-1-yloxy)but-2-ene (6):

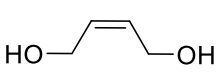


Propargyl alcohol (1g, 17.8 mmol, 1 eq.) was dissolved in dry THF (3 mL) and cooled to 0^0 C. NaH (60% dispersion,0 784mg,19.6 mmol, 1.1 equiv.) was added portion wise at 0^0 C. The solution was allowed to warm to room temperature and was stired for another 1 hour. Afterwards, the solution was cooled again to 0^0C and prenyl bromide (2.7g,17.8 mmol,1 eq.)was added dropwise. The mixture was stirred for 12h at room temperature. The reaction was quenched with aq. NH_4Cl and extracted 3 times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the material was chromatographed on silica (pentane:ether = 98:2) to obtain product 6 (1.9g, 90 % yield) as a yellow liquid. ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 5.34 (ddt, 1 H), 4.13 (d, J=2.45 Hz, 2 H), 4.07 (d, J=7.09 Hz, 2 H), 2.42 (t, J=2.38 Hz, 1 H), 1.74 - 1.82 (s, 3 H), 1.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 138.4, 120.2, 80.1, 74.1, 66.0, 56.8, 25.8, 18.0 ppm. GC-MS: calcd. for $C_8H_{12}O$ [M]+: 124.0888; Found: 122.8.

Syntheis of (Z) and (E)-3-styryl-2, 5-dihydrofuran (DHF)

(E)-1-phenyl-4-oxa-1-hepten-6-yne (0.5g, 2.9 mmol, 1eq.) was dissolved in dry degassed dichloromethane and cooled to -10^0C. Separately **G3** (10 mol%) was dissolved in dry degassed dichloromethane. The **G3** solution was quickly added to the substrate solution and was stired overnight at -10^0C. The reaction was quenched with excess ethyl vinyl ether and the solvent was removed under reduced pressure. The material was chromatographed on silica (hexane:EtOAc = 96:4) to obtain products in 1:6 ratio (Z)- and (E)- respectively (overall yield 95%). (Z)- isomer: ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.19 - 7.31 (m, 3 H), 7.10 - 7.19 (m, 2 H), 6.56 (d, J=11.98 Hz, 1 H), 6.26 (d, J=11.86 Hz, 1 H), 5.84 (br. s., 1 H), 4.44 - 4.66 (m, 2 H), 4.06 - 4.30 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 137.9, 137.4, 131.4, 128.5, 127.9, 127.3, 127.3, 123.1, 75.2, 74.7 ppm. GC-MS: calcd. for $C_{12}H_{12}O$ [M]+: 172.0888; Found: 171.1. (E)- isomer: ^{1}H NMR (400 MHz, CHLOROFORM-d) δ 7.24 - 7.35 (m, 2 H), 7.16 - 7.24 (m, 2 H), 7.06 - 7.16 (m, 1 H), 6.75 - 6.89 (m, 1 H), 6.17 (d, J=16.38 Hz, 1 H), 5.73 - 5.86 (m, 1 H), 4.69 - 4.83 (m, 2 H), 4.54 - 4.69 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CHLOROFORM-d) δ 138.1, 136.7, 130.7, 128.6, 127.8, 126.3, 125.2, 121.0, 76.0, 74.1 ppm. GC-MS: calcd. for $C_{12}H_{12}O$ [M]+: 172.0888; Found: 172.1.

Chain transfer agents used for termination



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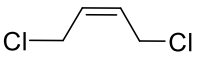

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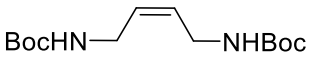
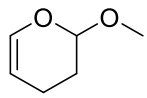


9



10

Procedure for Ring closing Enyne Metathesis (RCEYM)

Procedure for RCEYM with G1 at room temperature in an NMR tube:

The RCEYM substrates were dissolved in dry degassed dichloromethane-d_2. Separately **G1** was dissolved in dry degassed dichloromethane-d_2. The **G1** solution was quickly added to the substrate solution ensuring efficient mixing. The combined solution was transferred to an NMR tube to measure ^{1}H-NMR spectra until complete consumption of substrate was observed. For the reaction kinetics, the ^{1}H-NMR spectra were recorded every 20 min for 2 hours and then every 1 hour until complete conversion of substrate was detected.

Procedure for RCEYM with G3 at room temperature in an NMR tube:

The RCEYM substrates and 3-bromopyridine (30 eq. of catalyst) were dissolved in dry degassed dichloromethane-d_2. Separately **G3** was dissolved in dry degassed dichloromethane-d_2. The **G3** solution was quickly added to the substrate solution and ensuring efficient mixing. The combined solution was transferred to an NMR tube to measure ^{1}H-NMR spectra until complete consumption of substrate was observed. For the reaction kinetics, the ^{1}H-NMR spectra were recorded every 10 min for 30 min and then every 20 min until complete conversion of substrate was detected.

Procedure for RCEYM with G3 at -10^0 C in an NMR tube:

The RCEYM substrates were dissolved in dry degassed dichloromethane-d_2 and cooled to -10^0 C. Separately **G3** was dissolved in dry degassed dichloromethane-d_2. The **G3** solution was quickly added to substrates solution and ensuring efficient mixing. The combined solution was transferred to an NMR tube at -10^0 C to measure ^{1}H-NMR spectra at -10^0 C until complete consumption of substrate was observed . For the reaction kinetics, the ^{1}H-NMR spectra were recorded every 10 min for 30 min and then every 20 min until complete conversion of substrate was detected.

One-pot hetero-telechelic polymerization procedure:

Catalysts **G1** and **G3** were subjected to respective RCEYM and converted into the functional initiators as mentioned above. Separately, monomer MNI was dissolved in dry degassed dichloromethane. The monomer solution was quickly transferred to the initiator solution while ensuring efficient mixing. The mixture was stirred for 1.5 h (3 hour in case of T=-10^0 C) to ensure complete consumption of the monomer. The functional CTA (20 eq.) was also dissolved in dry degassed dichloromethane, quickly transferred to the polymer solution and further stirred for 2 h to ensure complete end capping. Then the solution was concentrated by a flow of argon (in case of T=-10^0 C, the resulting polymer solution was warmed to room temperature before concentration) and precipitated into cold methanol to yield the hetero-telechelic polymers.

^{1}H-NMR spectra - catalyst pre-functionalization

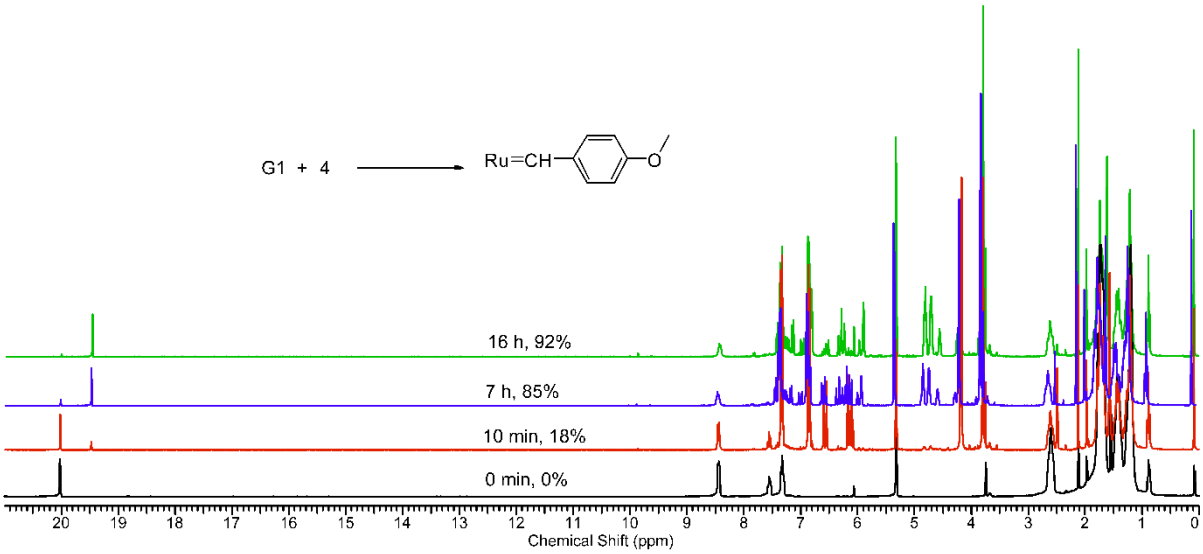


Figure S1: ^{1}H NMR spectra (CD_2Cl_2, 300MHz) of the reaction of **4** with **G1** give **G1-OMe** (19.48 ppm) in the presence of the internal standard 1, 3, 5-trimethoxybenzene.

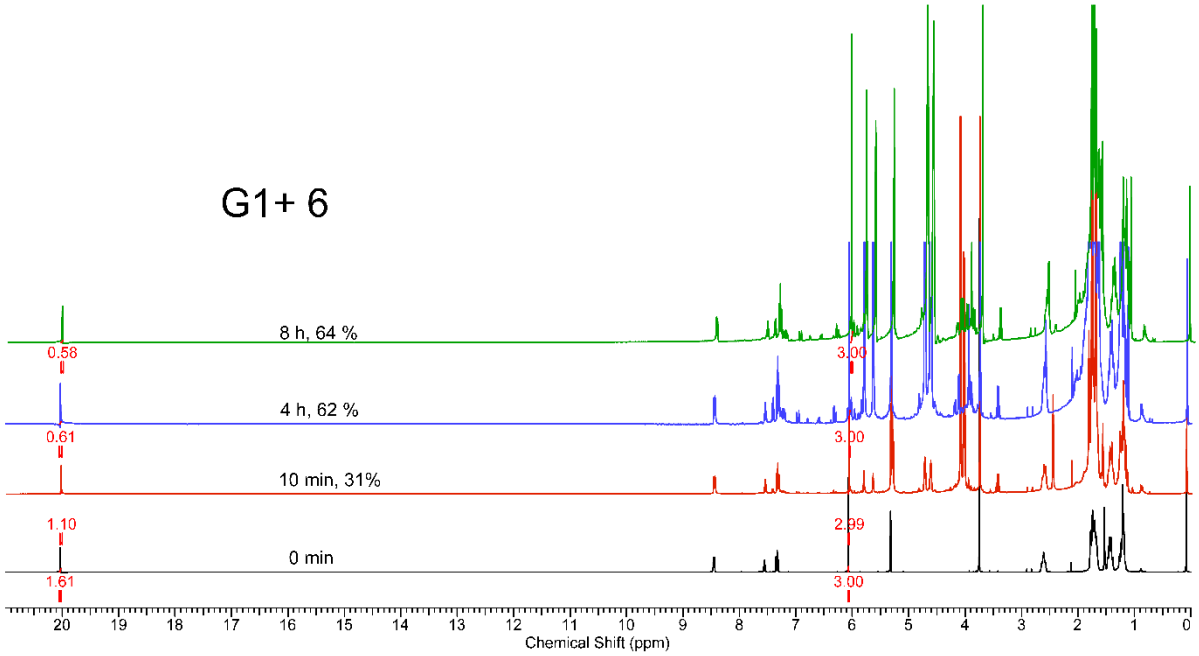


Figure S2: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of **6** with **G1** in the presence of the internal standard 1, 3, 5-trimethoxybenzene.

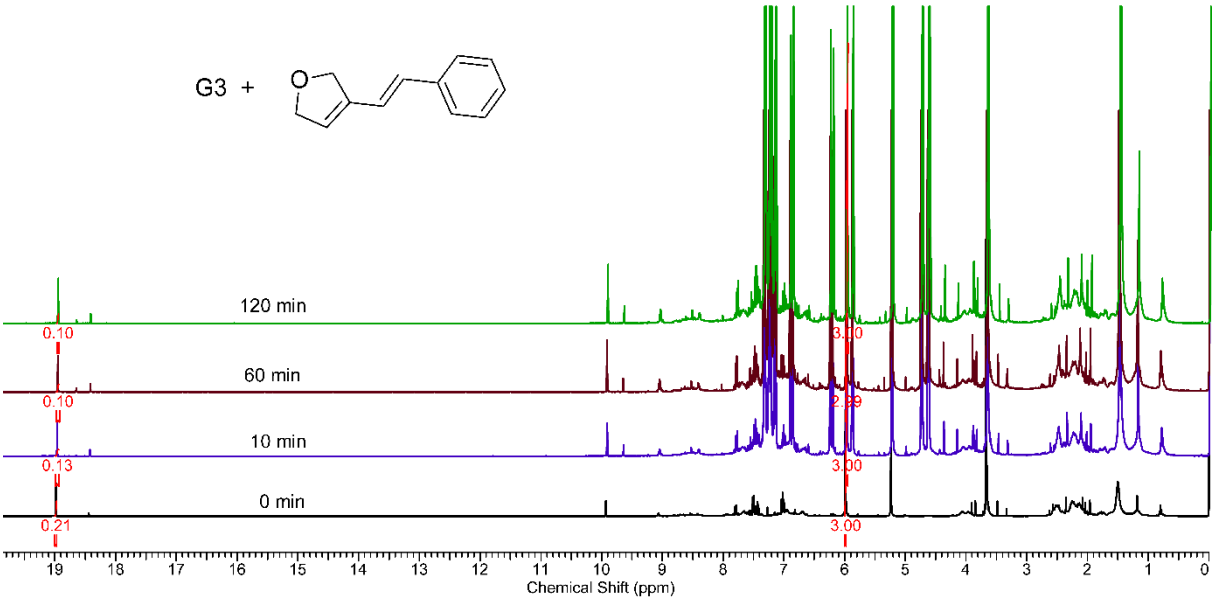


Figure S3: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of (E)-3-styryl-2, 5-dihydrofuran (**DHF**) with **G3** in the presence of 1, 3, 5-trimethoxybenzene as an internal standard.

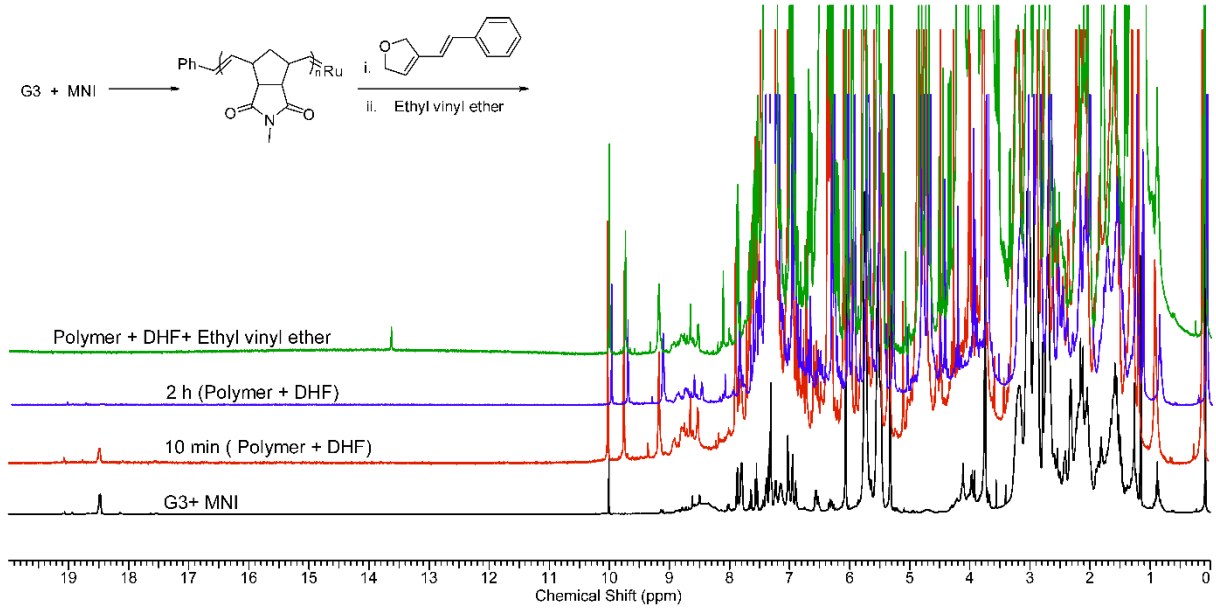


Figure S4: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of **G3**, **MNI** and (E)-3-styryl-2, 5-dihydrofuran (**DHF**).

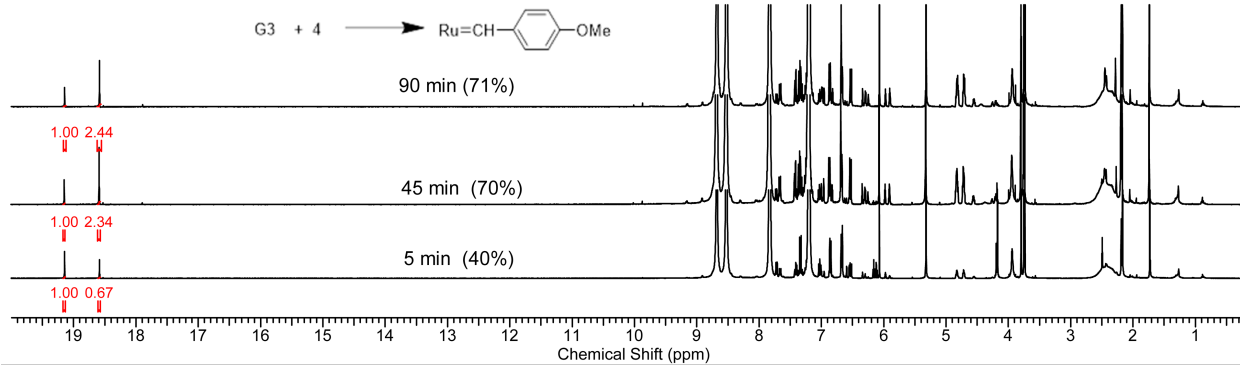


Figure S5: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of 1eq. **4** with **G3** in the presence of 30eq. 3-bromopyridine at 0.03M.

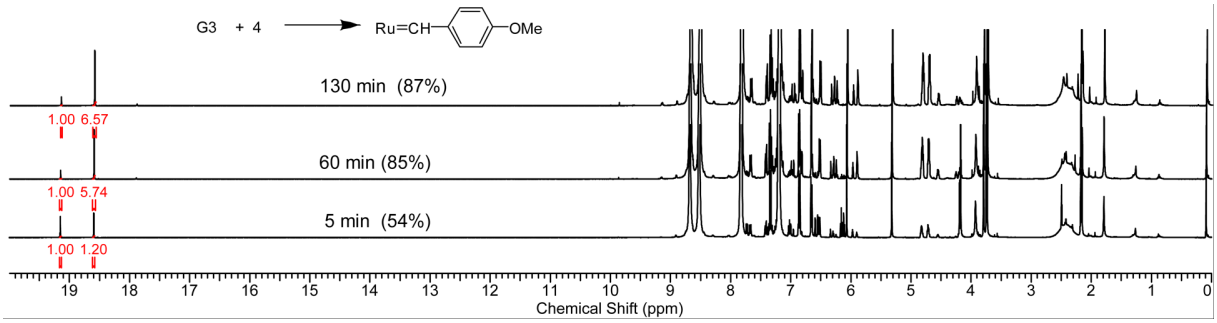


Figure S6: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of 2eq. **4** with **G3** in the presence of 30eq. 3-bromopyridine at 0.03M.

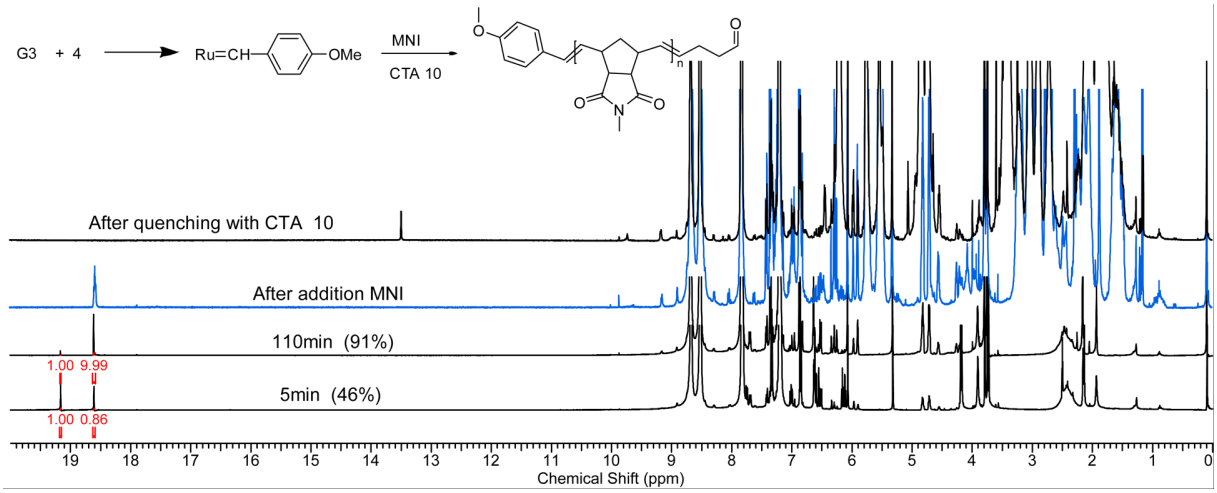
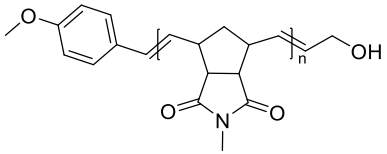
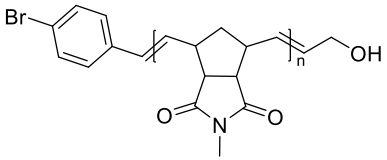
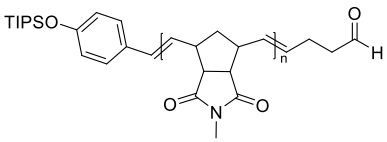
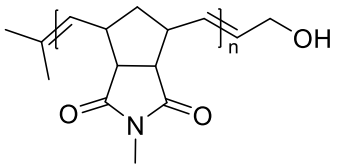
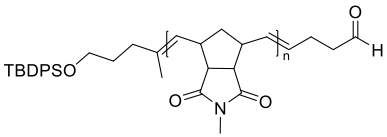


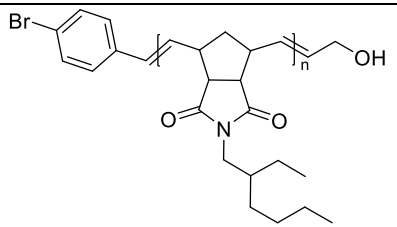
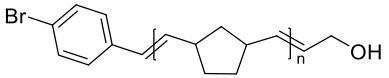
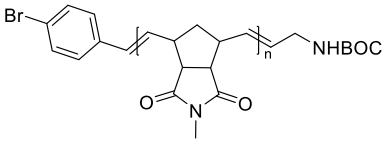
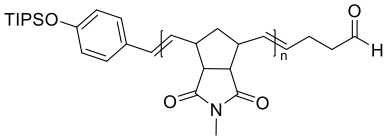
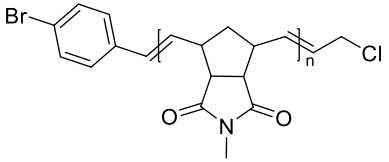
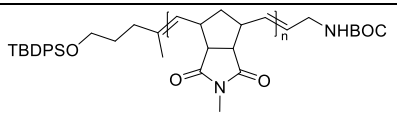
Figure S7: ^{1}H NMR spectra (CD_2Cl_2, 400MHz) of the reaction of 1.5eq. **4** with **G3** in the presence of 30eq. 3-bromopyridine at 0.06M.

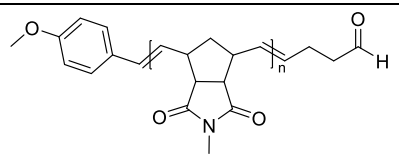
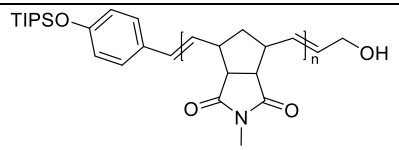
Table 1. Optimized conditions for RCEYM with G1 and G3 catalysts

Entry	Catalyst(I)	Substrates (S)	S/I (eq.)	Substrate conc. (mol.)	Yield(%)	Time	Temperature (^{0}C)	Additive
a	G1	2	3	0.05	88	16h	rt	
b	G1	3	3	0.05	92	9h	rt	
c	G1	4	3	0.05	92	16h	rt	
d	G3	2	3	0.03	90	90min	-10	
e	G3	3	3	0.03	92	90min	-10	
f	G3	4	3	0.03	96	90min	-10	
g	G3	5,6	5	0.03	Full conversion to alkylidene	5min	-10	
h	G3	2	3	0.03	92	3h	rt	3-bromopyridine
i	G3	3	3	0.03	97	3h	rt	3-bromopyridine
j	G3	4	3	0.03	94	3h	rt	3-bromopyridine
k	G3	5,6	10	0.03	Full conversion to alkylidene	5min	rt	3-bromopyridine
l	G3	4	1	0.03	71	90min	rt	3-bromopyridine
m	G3	4	2	0.03	87	130min	rt	3-bromopyridine
n	G3	4	1.5	0.06	91	110min	rt	3-bromopyridine

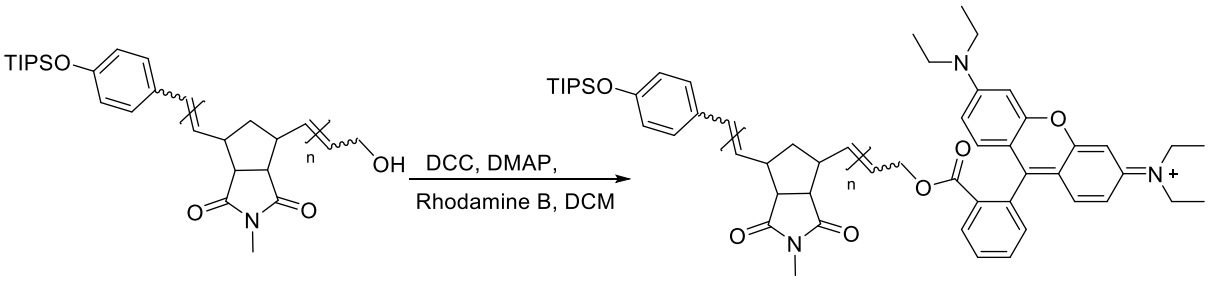
Table 2. Summary of all polymers

Entry	Initiator	Method	Monomer	CTA	Polymer structure	Mn (theo) kDa.	Mn (GPC)	PDI
Poly a	G3-OMe	-10 ^{0}C	MNI	7		5.3	6.1	1.07
Poly b	G3-Br	-10^{0}C	MNI	7		3.9	4.5	1.06
Poly c	G3-OTIPS	-10^{0}C	MNI	10		4.8	5.2	1.06
Poly d	G3-Isopropylidene	rt	MNI	7		10.6	11.3	1.06
Poly e	G3-5	-10^{0}C	MNI	10		6.4	7.3	1.06

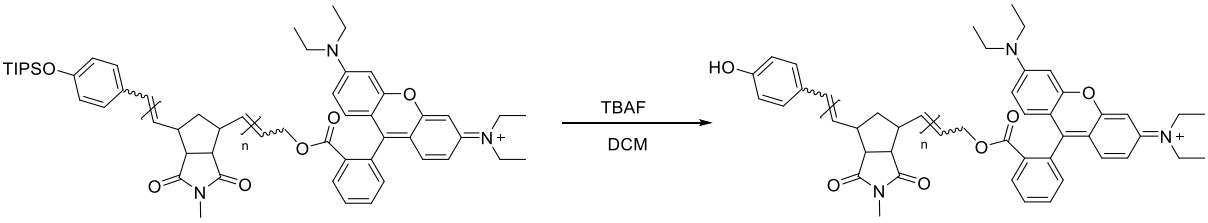
Poly f	G3-Br	rt	EHNI	7		4.7	5.3	1.06
Poly g	G3-Br	-10^{0}C	NBE	7		2.8	3.9	1.24
Poly h	G1-Br	rt	MNI	9		4.2	6.3	1.2
Poly i	G1-OTIPS	rt	MNI	10		3	5.1	1.2
Poly j	G3-Br	rt	MNI	8		3.5	4.2	1.07
Poly k	G3-5	rt	MNI	9		6.4	7.3	1.08

Poly l	G3-OMe	rt	MNI	10		3.5	4.2	1.08
Poly m	G3-OTIPS	-10^{0}C	MNI	7		1.6	2.2	1.05

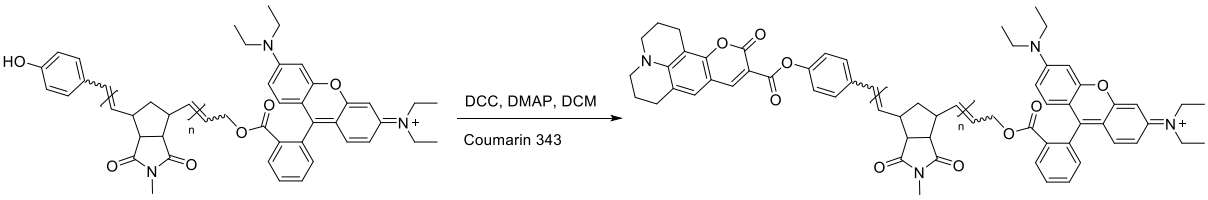
Labelling Experiments



Poly m (0.05mmol, 1eq.), Rhodamine B (0.5mmol, 10eq.) and DMAP (0.05mmol, 1eq.) were dissolved in 1.5ml dry dichloromethane and was cooled to 0^0C. DCC (0.5mmol, 10eq.) was dissolved separately in 0.5ml dry dichloromethane and added to the precool solution of polymer. The mixture was stirred for 12h at room temperature and concentrated under dry argon flow. The concentrated polymer solution was precipitated in cool methanol to get **Poly n** (yield 90%).



Poly n (0.05mmol, 1eq.) was dissolved in 1.5 ml of dry dichloromethane at room temperature. To this solution TBAF (1 M in THF, 0.4mmol, 8eq.) was added dropwise and was stirred for a further 12 h at room temperature. Resulting mixture was concentrated under dry argon flow and precipitated in cool methanol to get **Poly o** (yield 92%).



Poly o (0.05mmol, 1eq.), Coumarin 343 (0.5mmol, 10eq.) and DMAP (0.05mmol, 1eq.) were dissolved in 1.5ml dry dichloromethane and was cooled to 0^0C. DCC (0.5mmol, 10eq.) was dissolved separately in 0.5ml dry dichloromethane and added to the precool solution of polymer. The mixture was stirred for a further 12h at room temperature and concentrated under dry argon flow. The concentrated polymer solution was precipitated in cool methanol to get **Poly p** (yield 80%). The polymer was purified further by recycling GPC in $CHCl_3$.

NMR Spectra of substrates

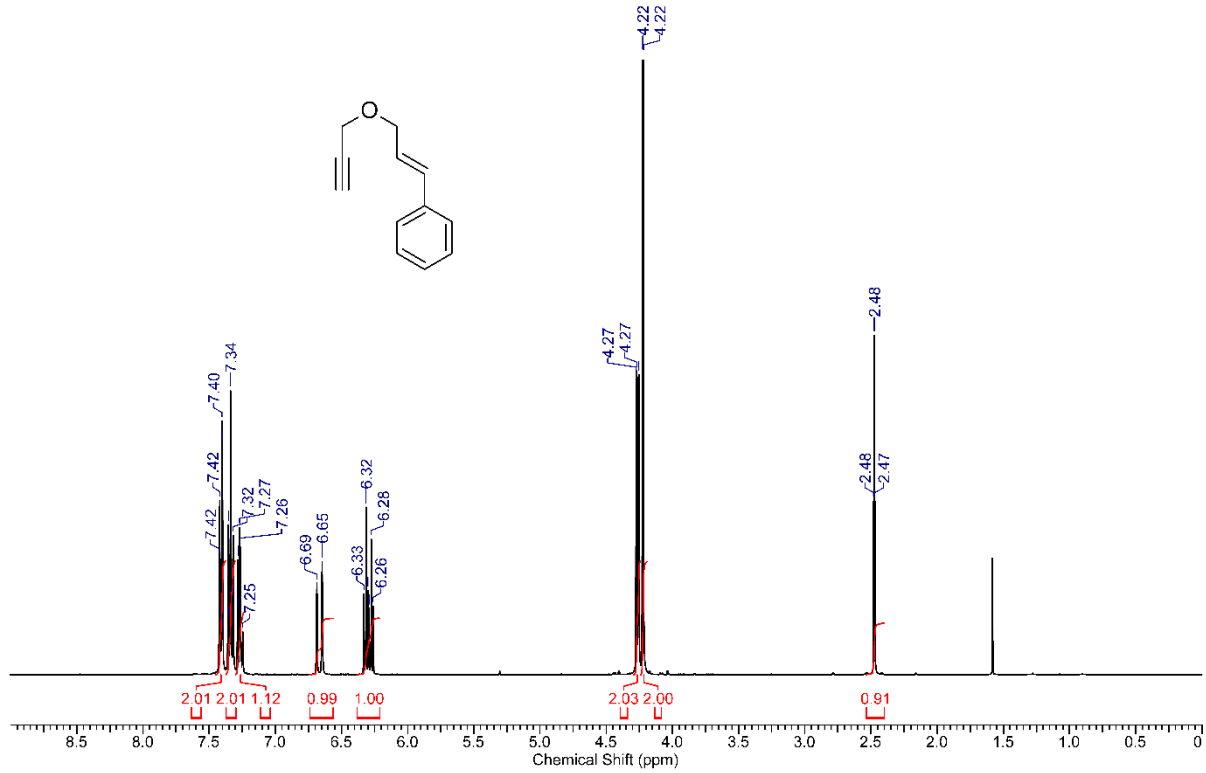


Figure S8: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **1**.

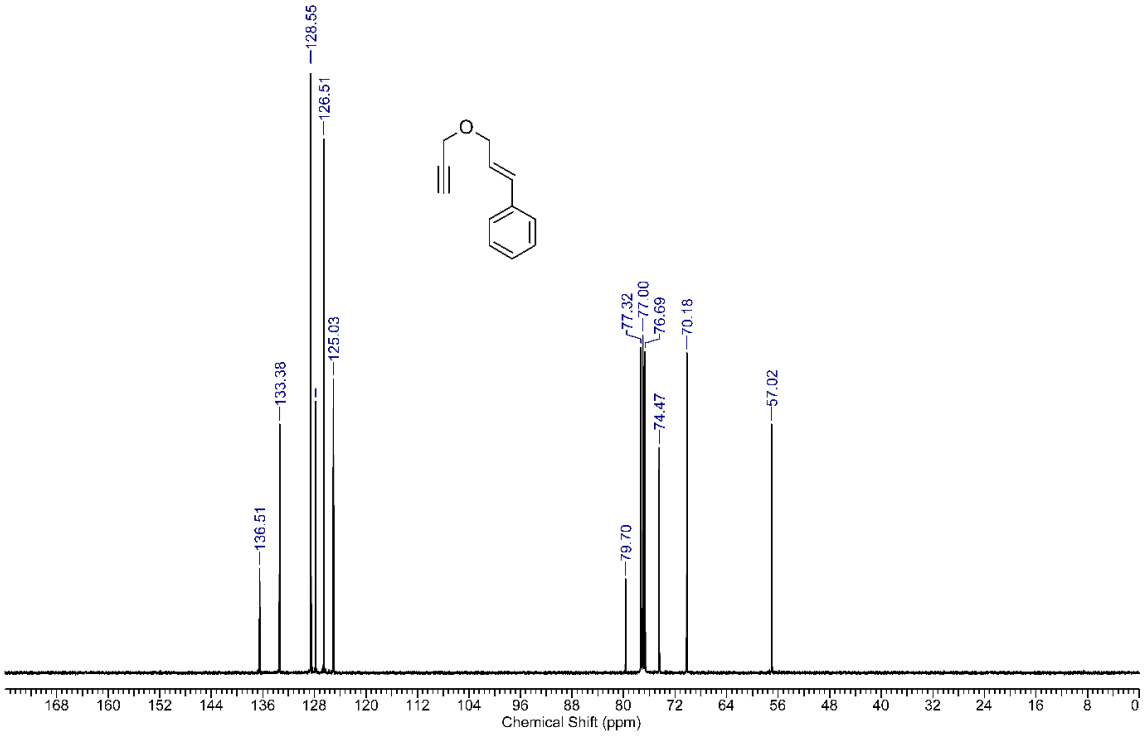


Figure S9: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **1**.

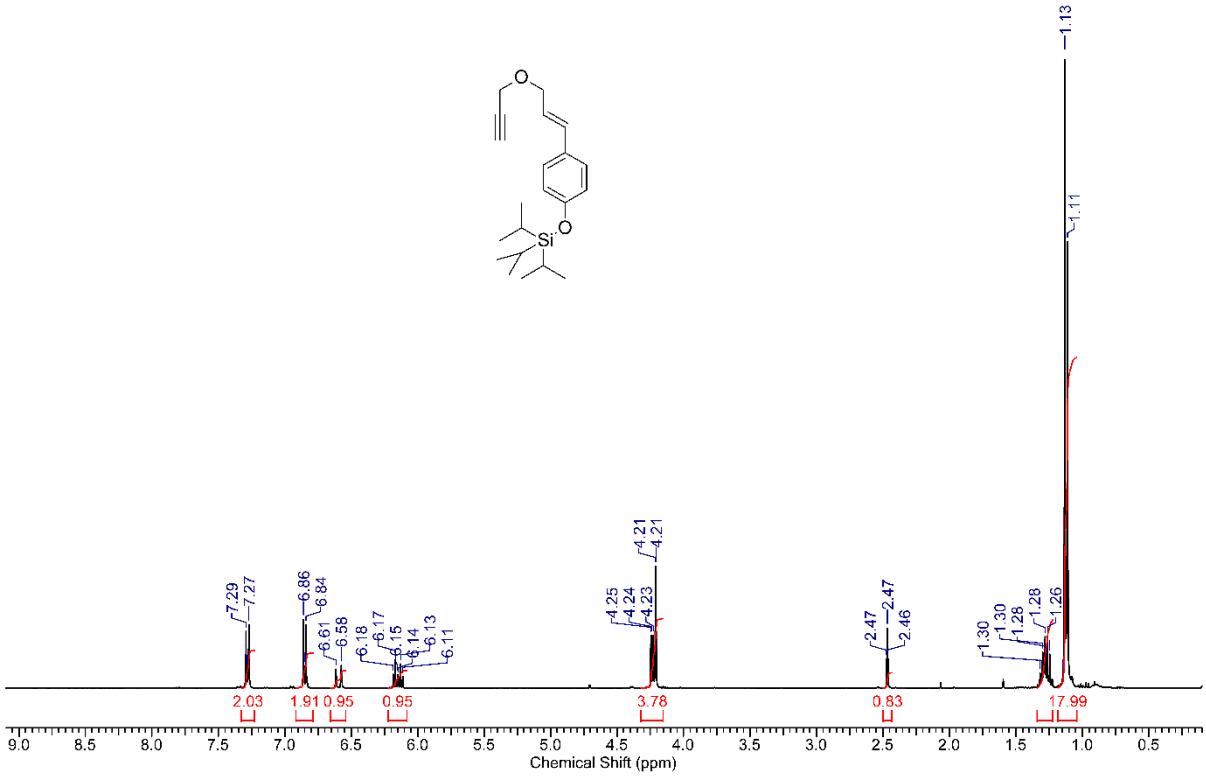


Figure S10: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **2**.

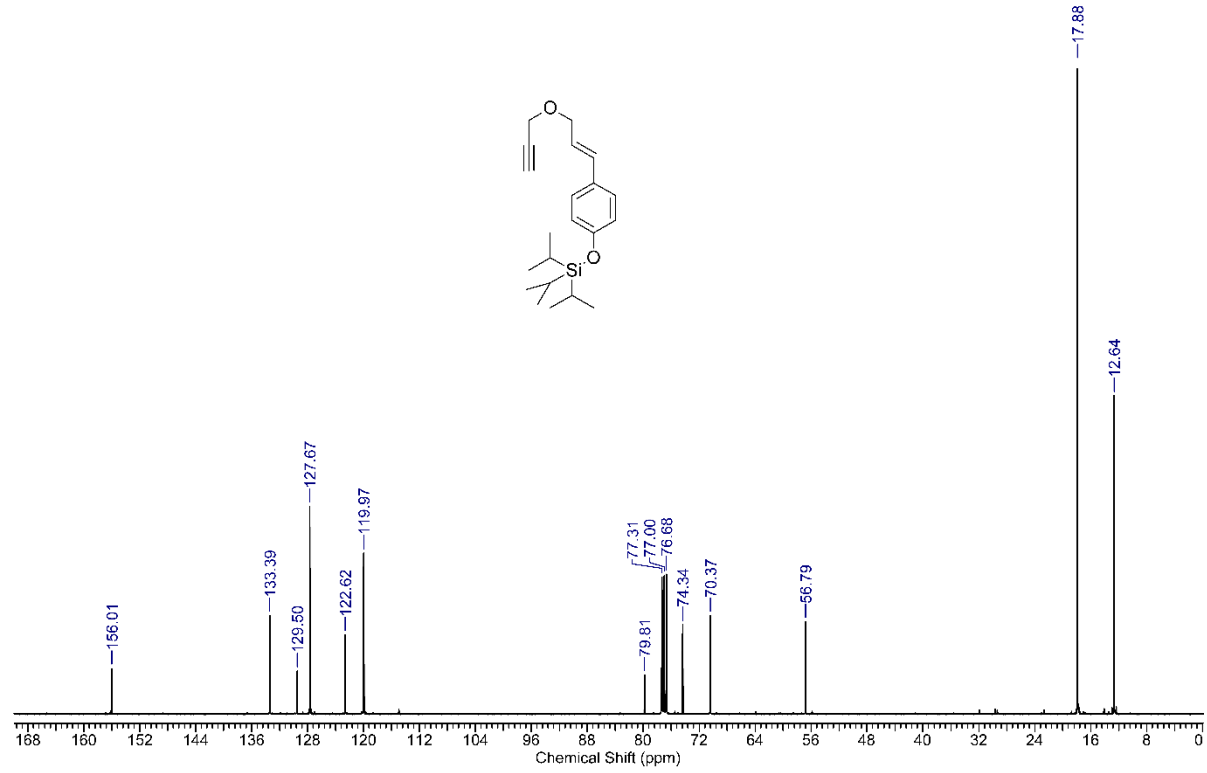


Figure S11: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **2**.

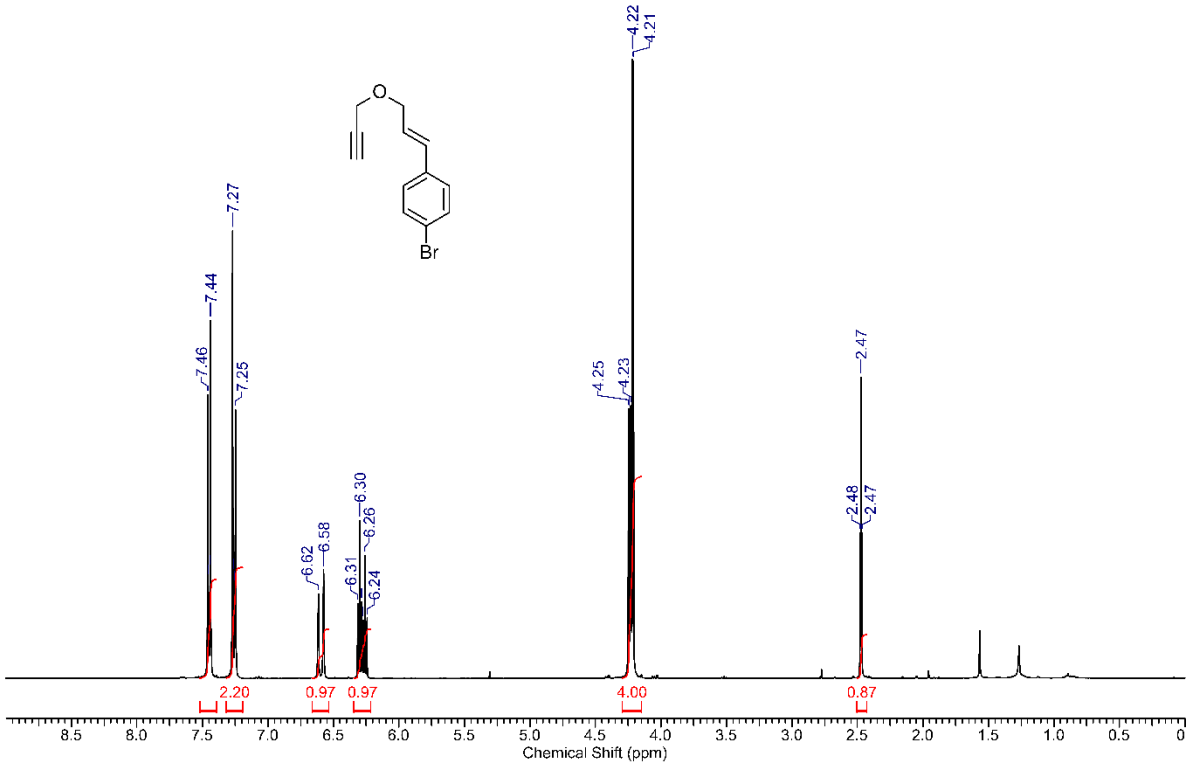


Figure S12: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **3**.

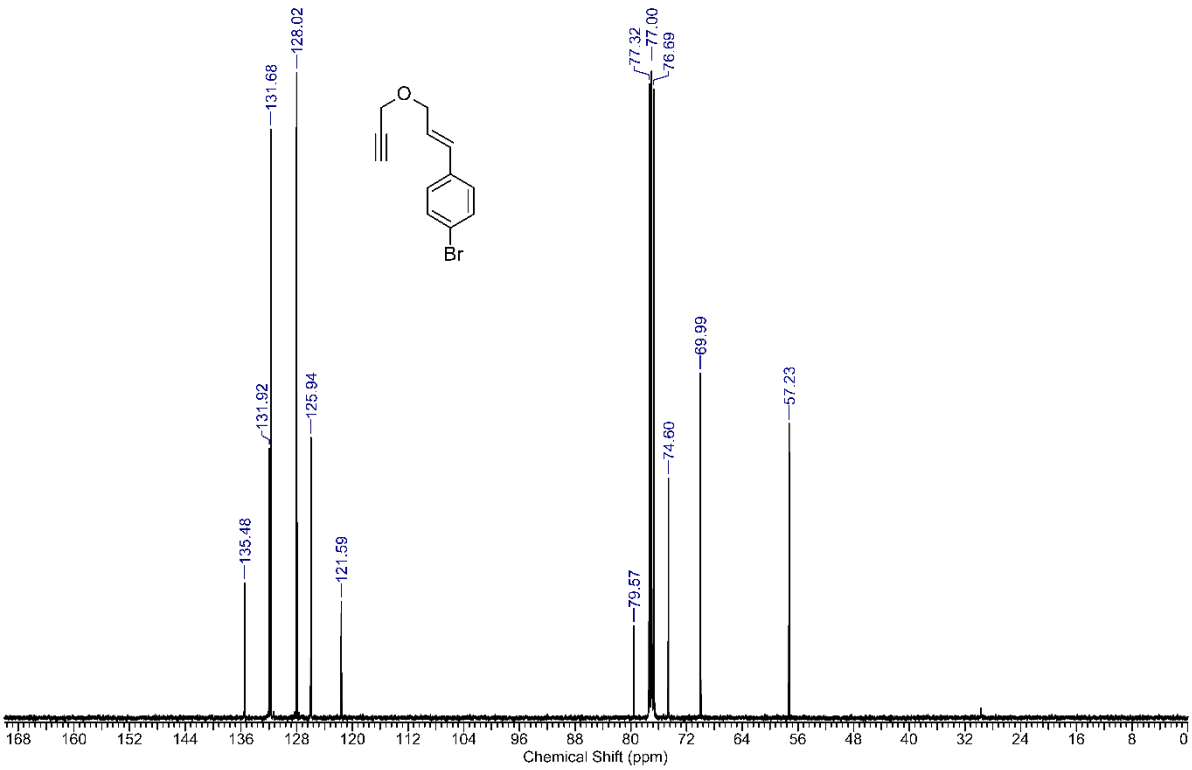


Figure S13: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **3**.

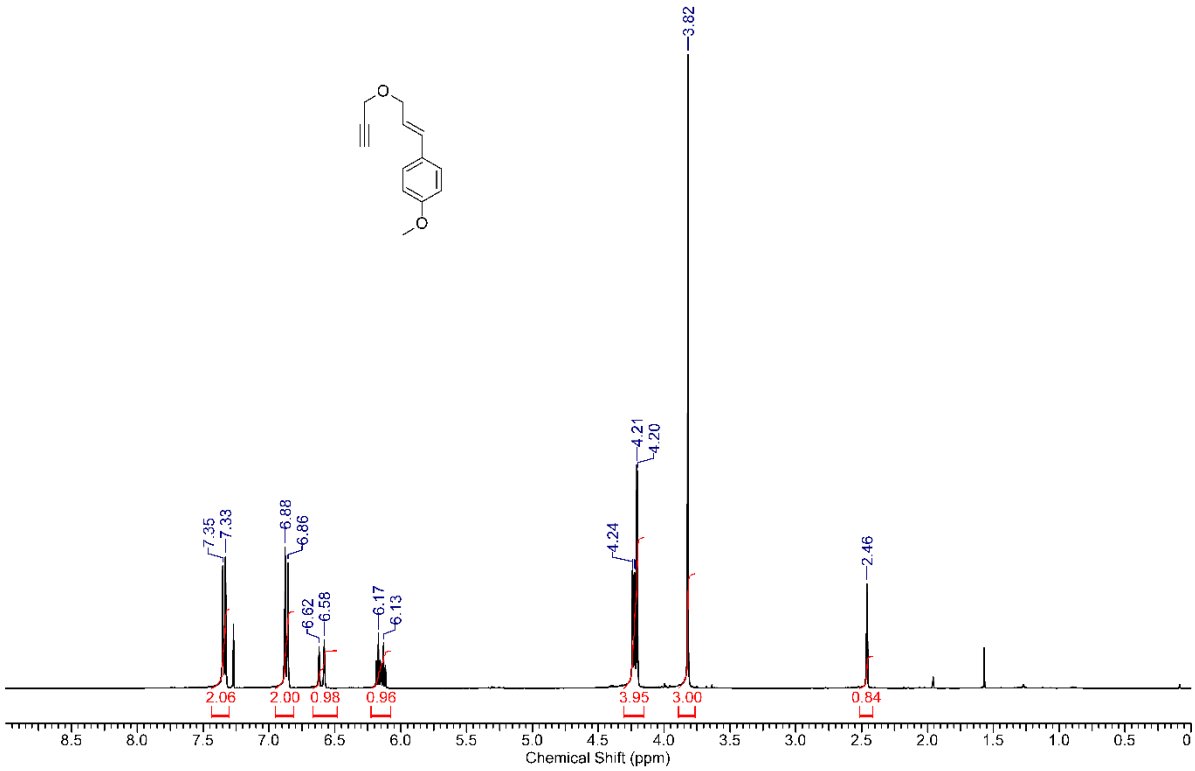


Figure S14: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **4**.

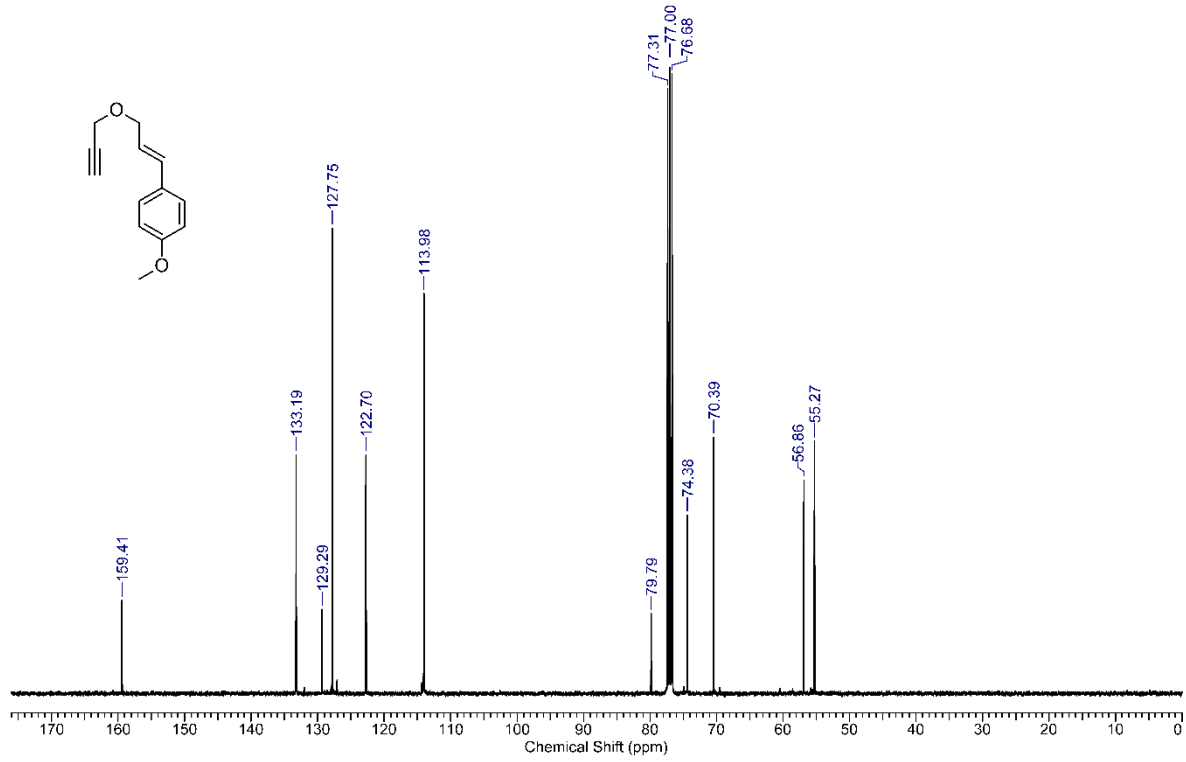


Figure S15: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **4**.

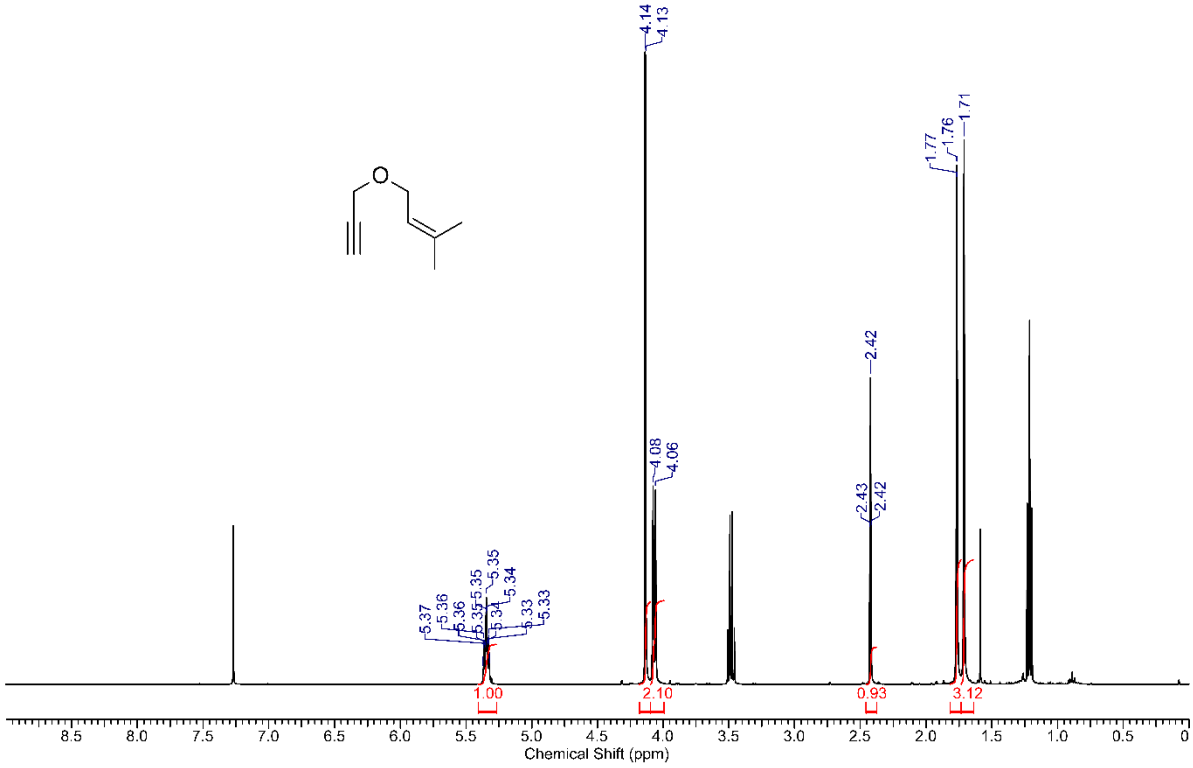


Figure S16: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **5**.

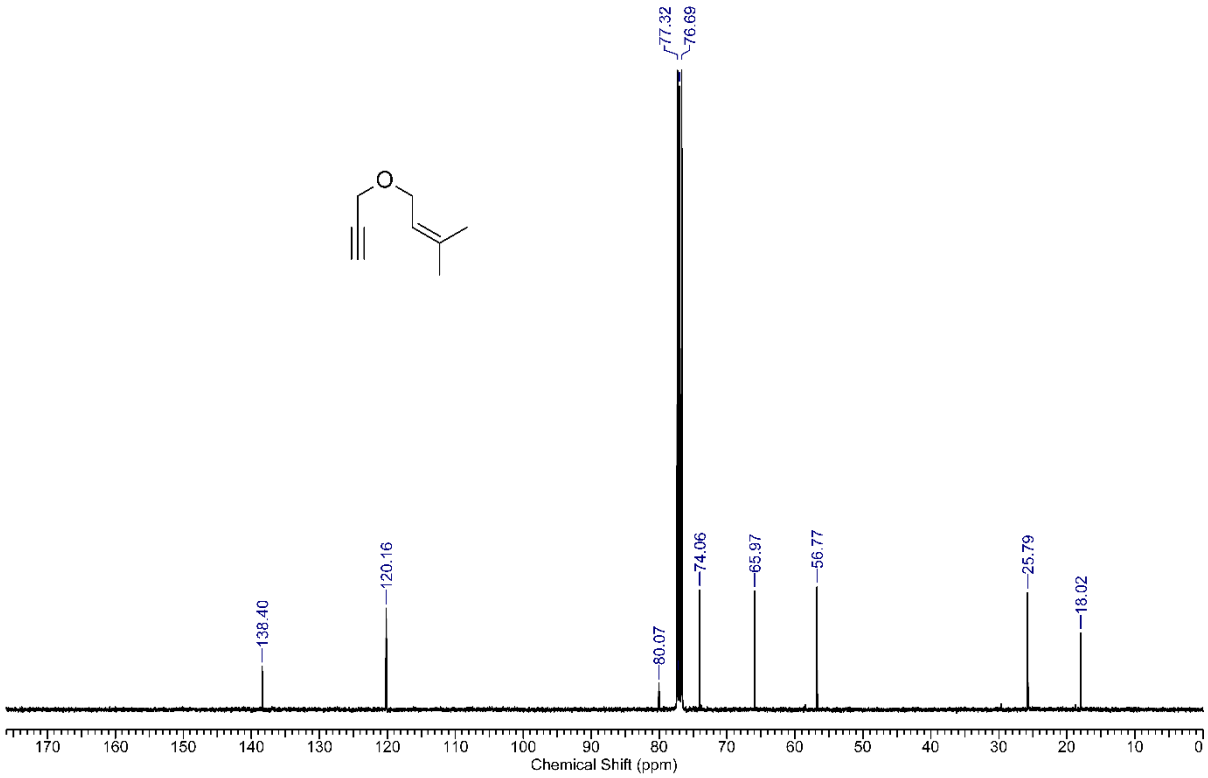


Figure S17: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **5**.

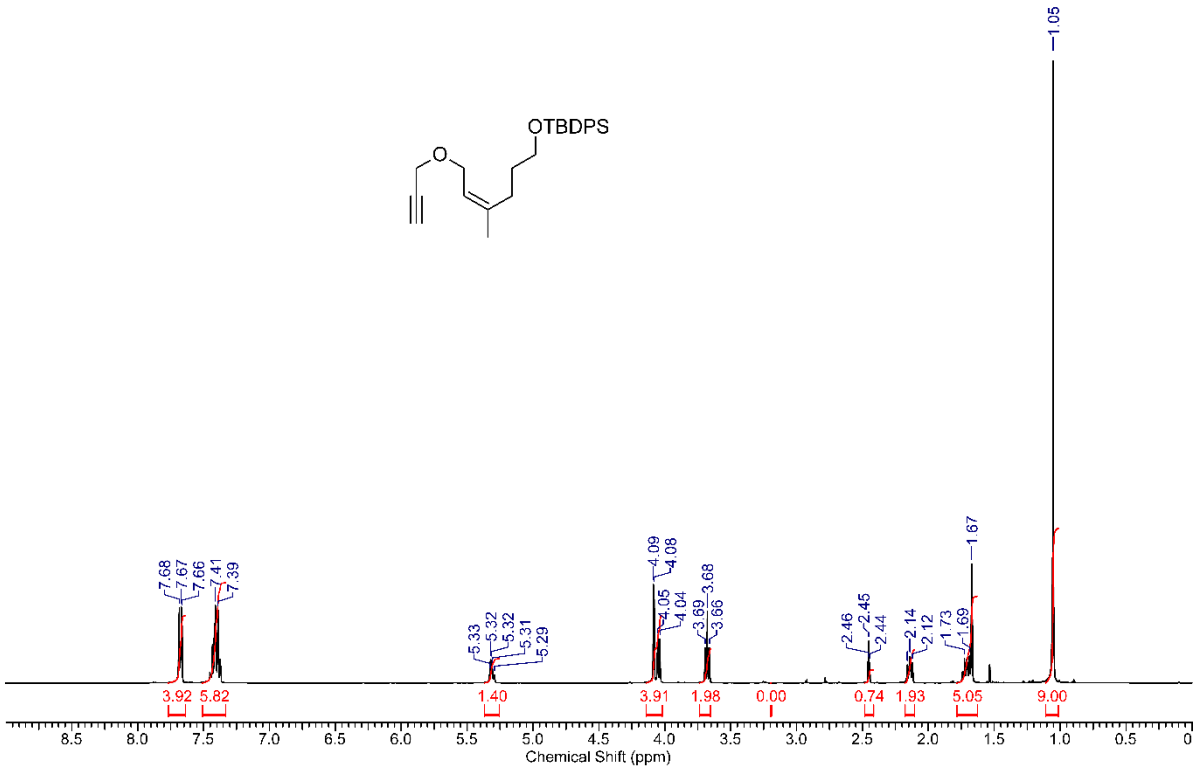


Figure S18: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of compound **6**.

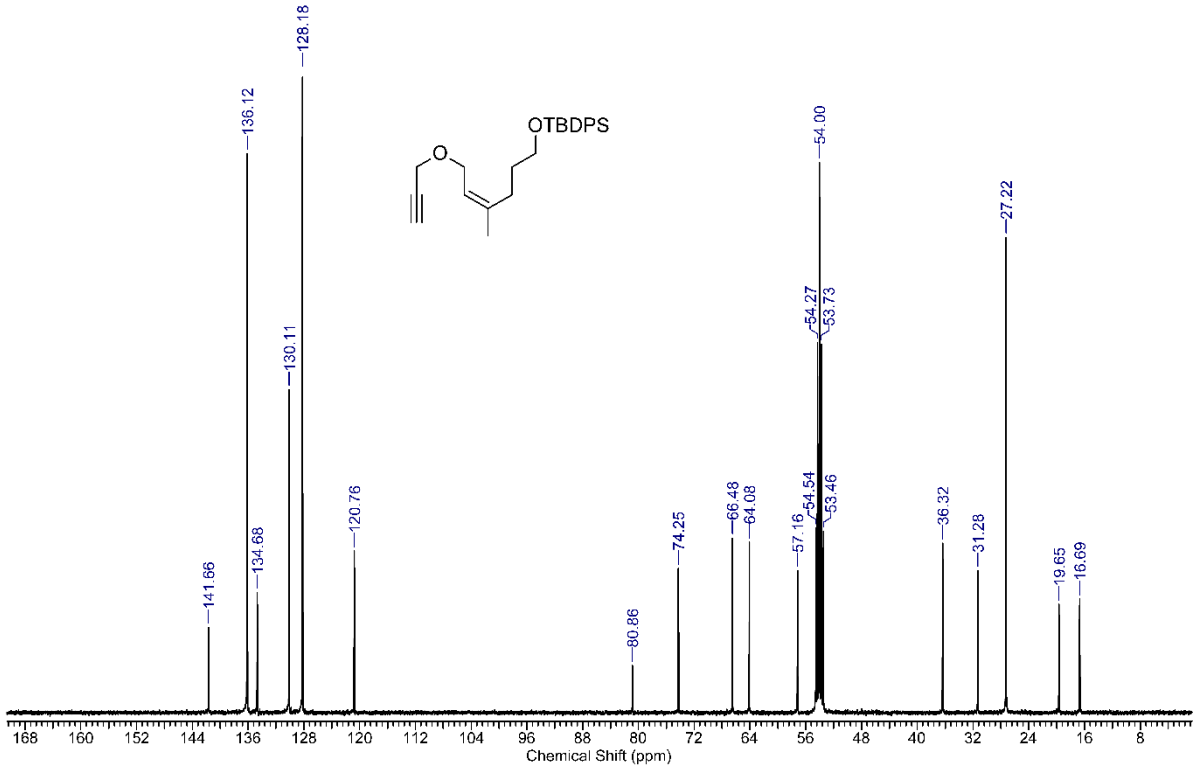


Figure S19: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of compound **6**.

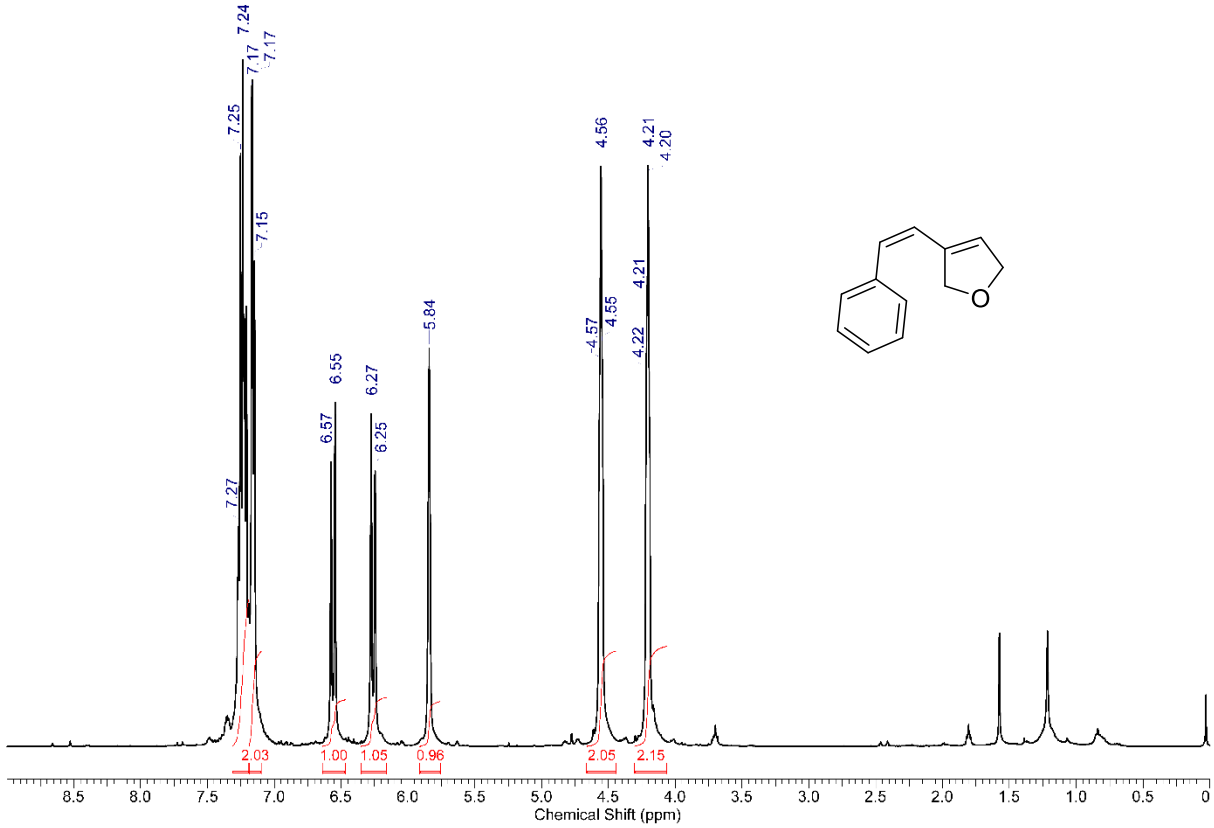


Figure S20: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran.

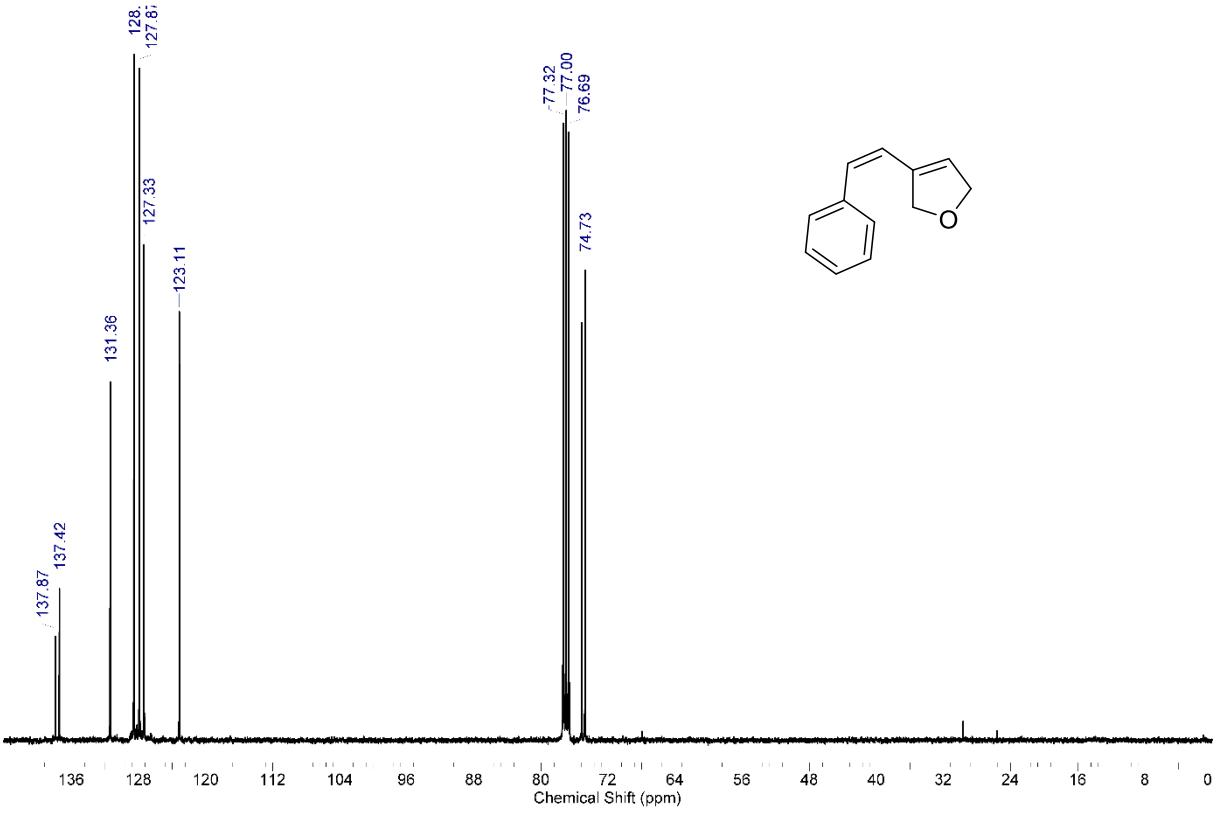


Figure S21: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran.

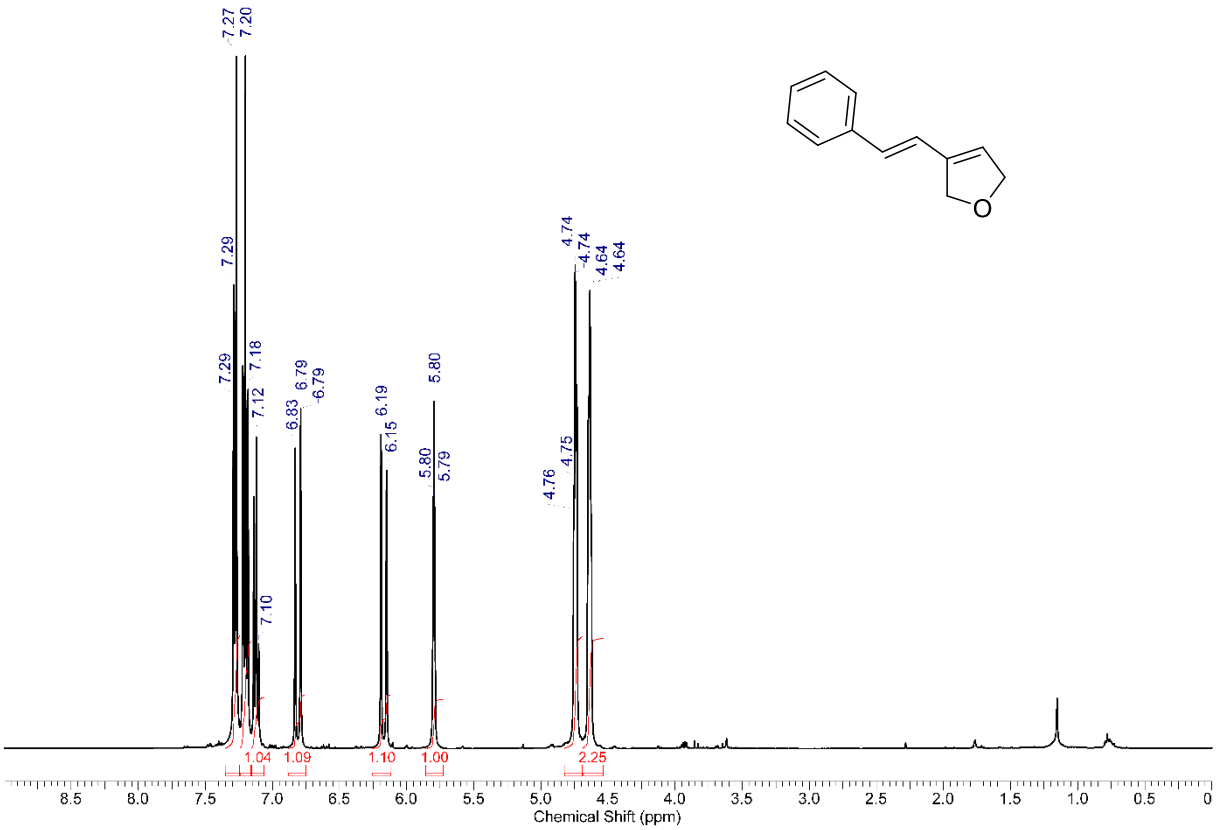


Figure S22: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran.

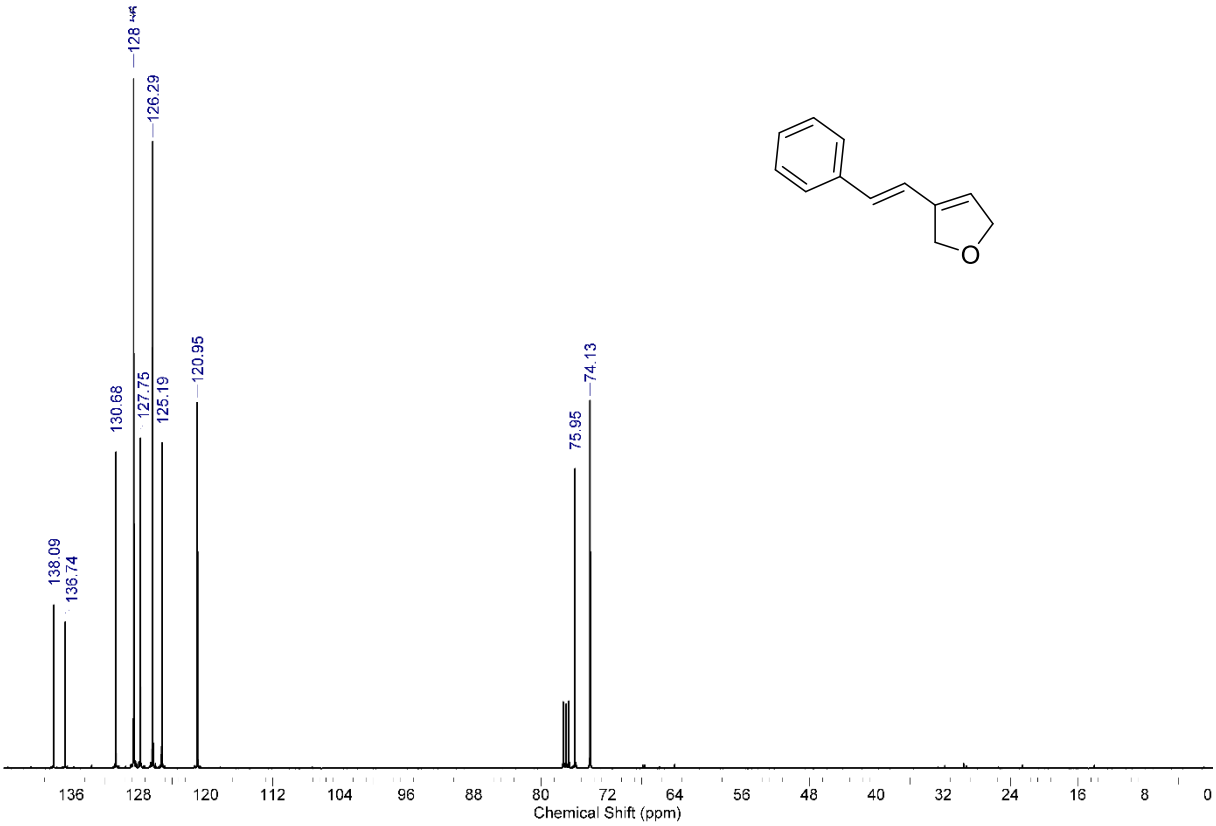


Figure S23: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran.

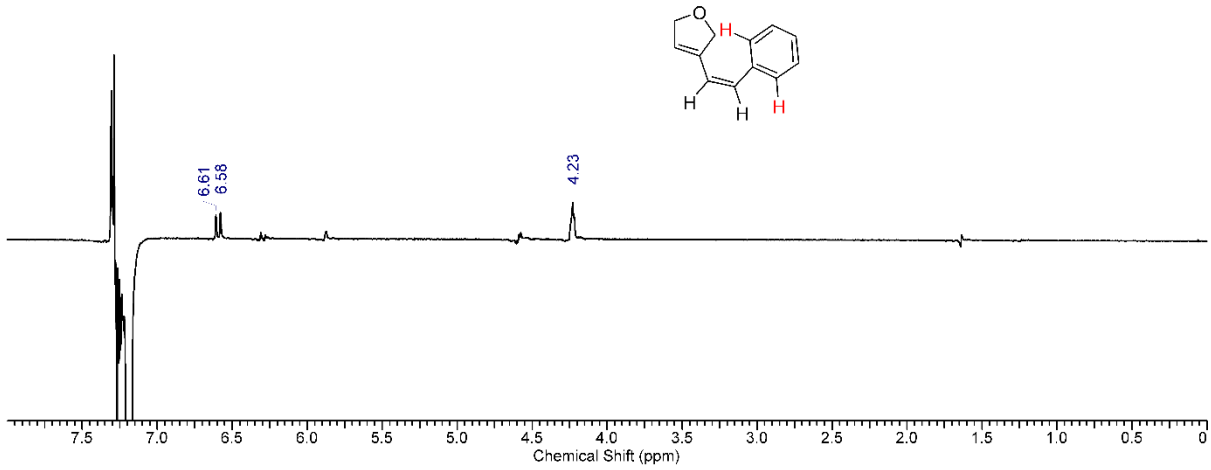


Figure S24: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

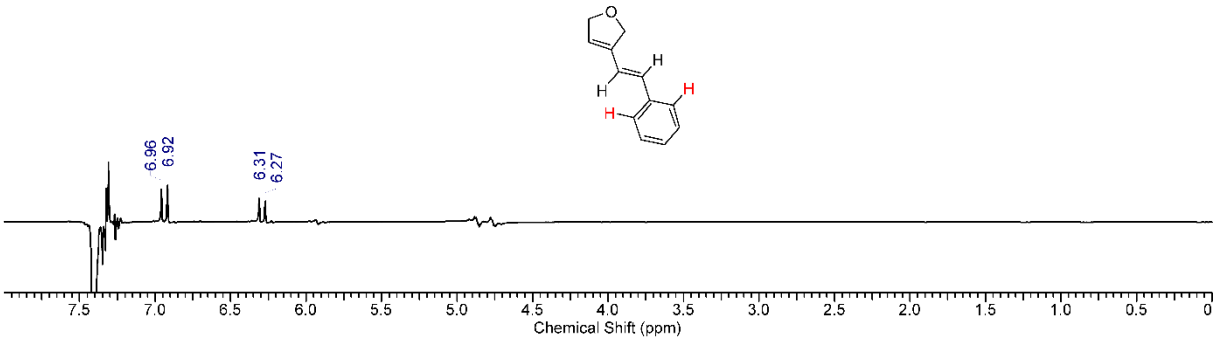


Figure S25: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

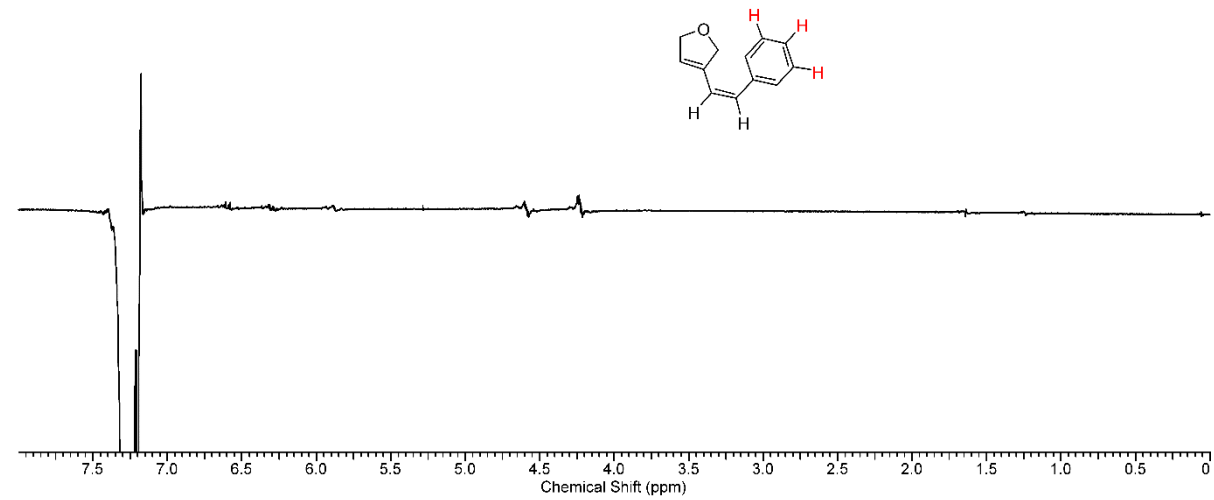


Figure S26: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

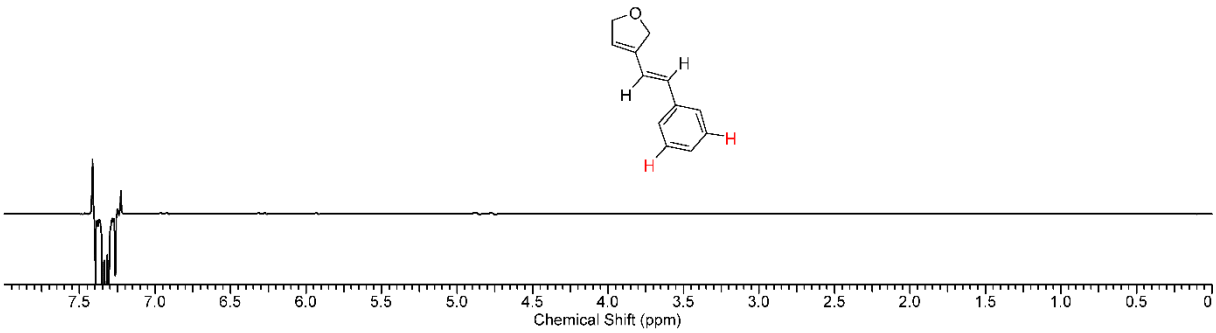


Figure S27: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

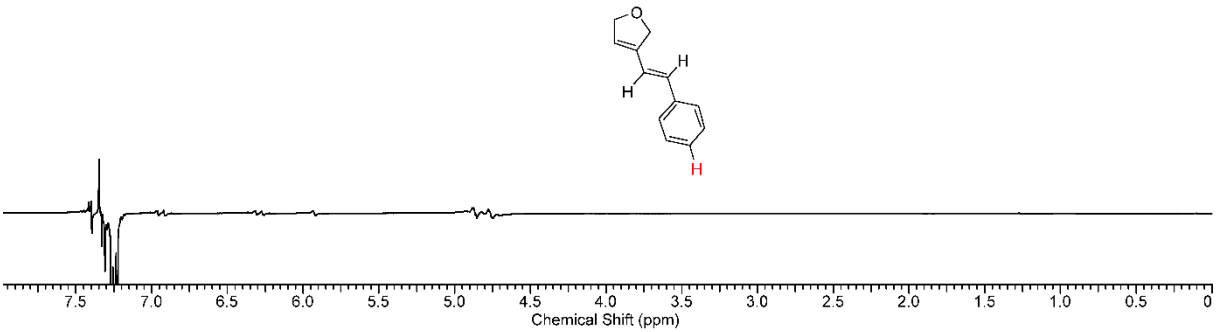


Figure S28: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

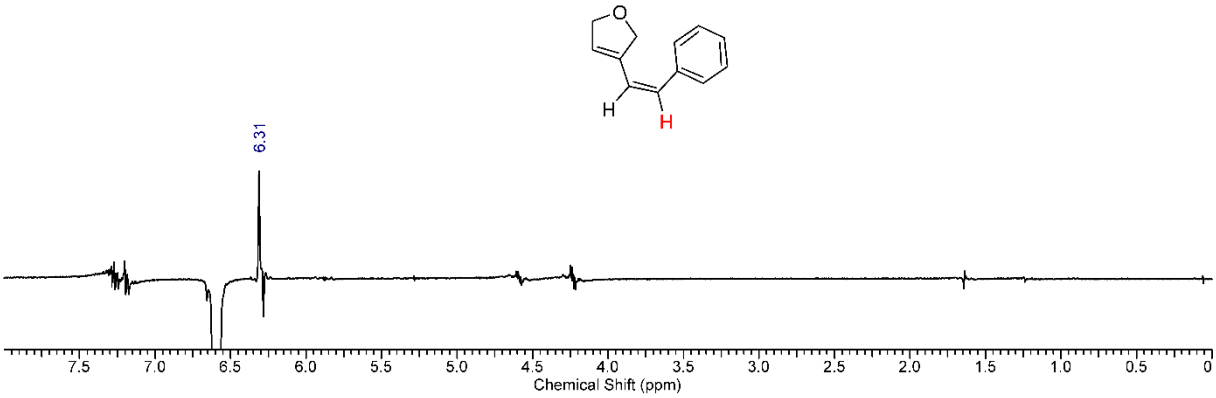


Figure S29: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

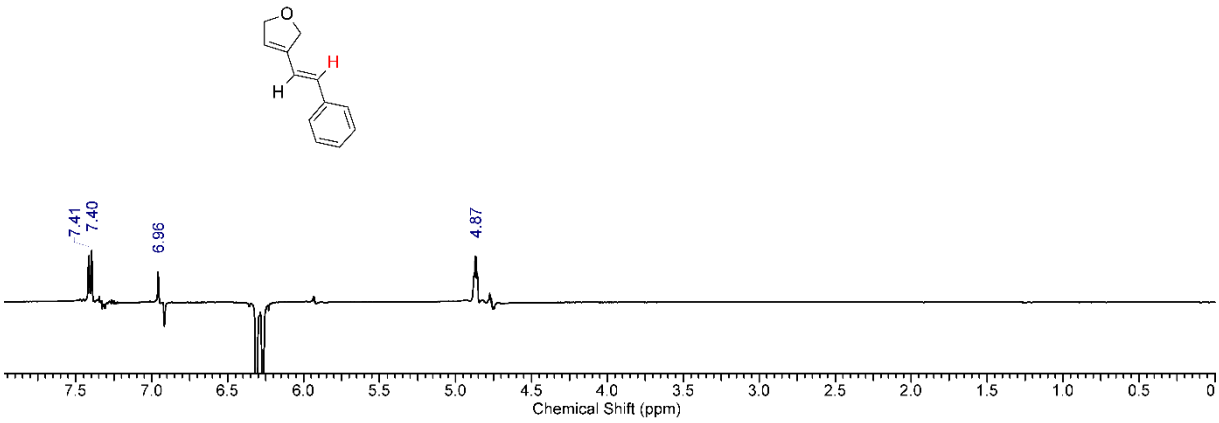


Figure S30: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

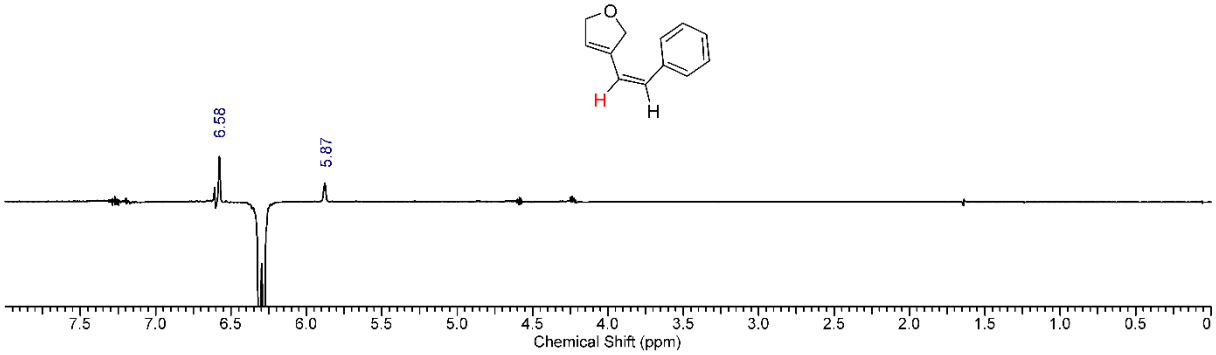


Figure S31: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

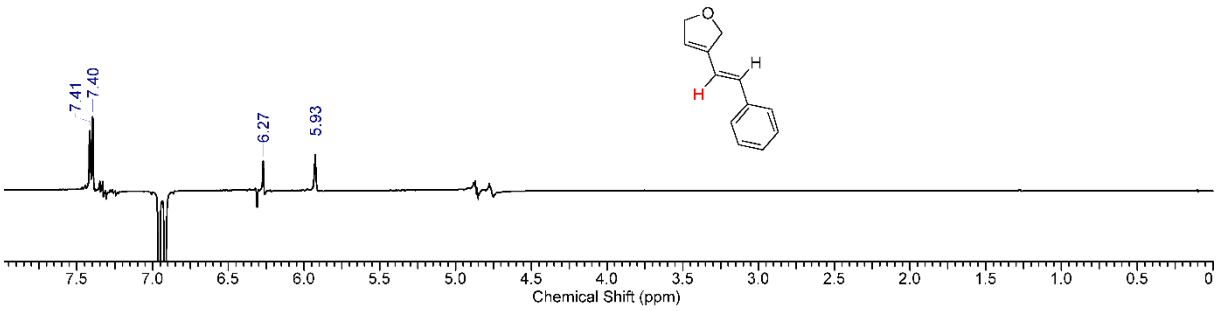


Figure S32: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

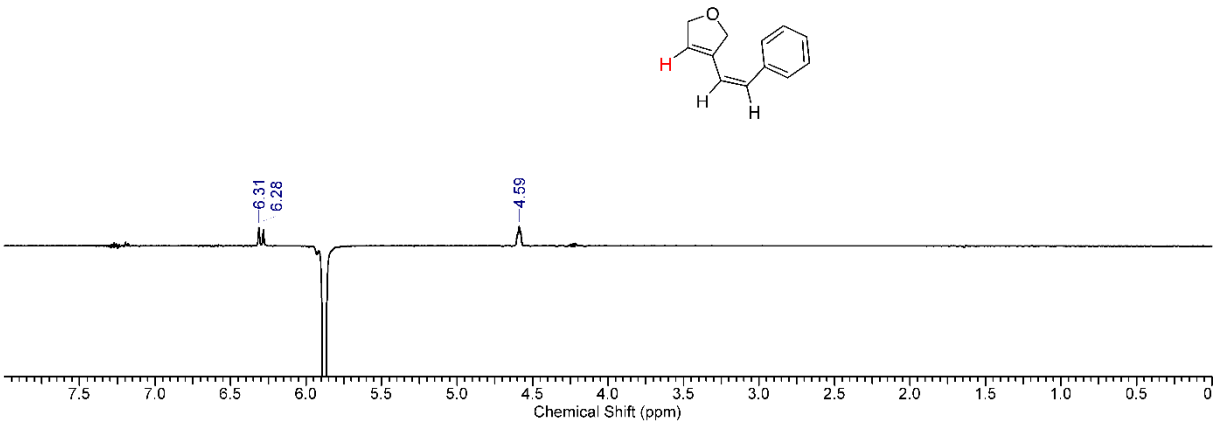


Figure S33: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

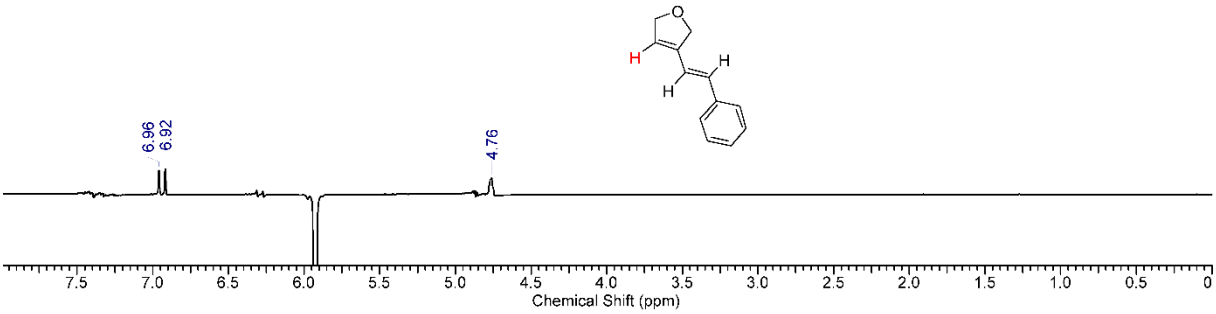


Figure S34: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

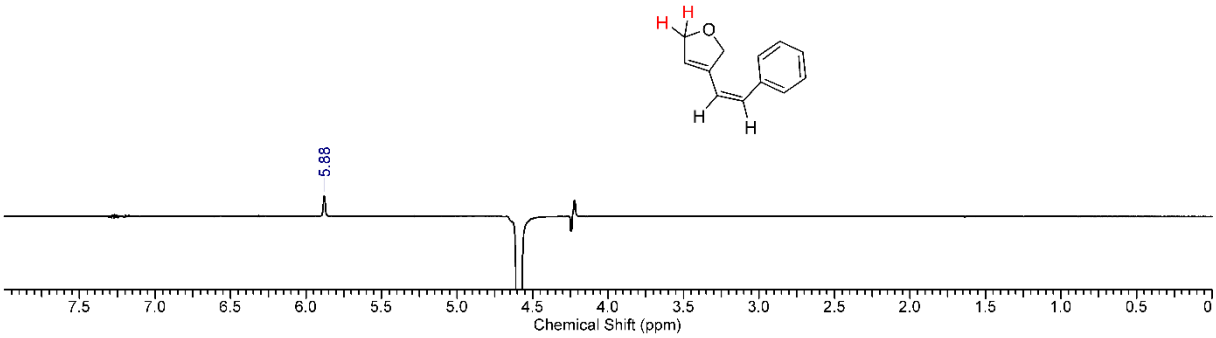


Figure S35: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

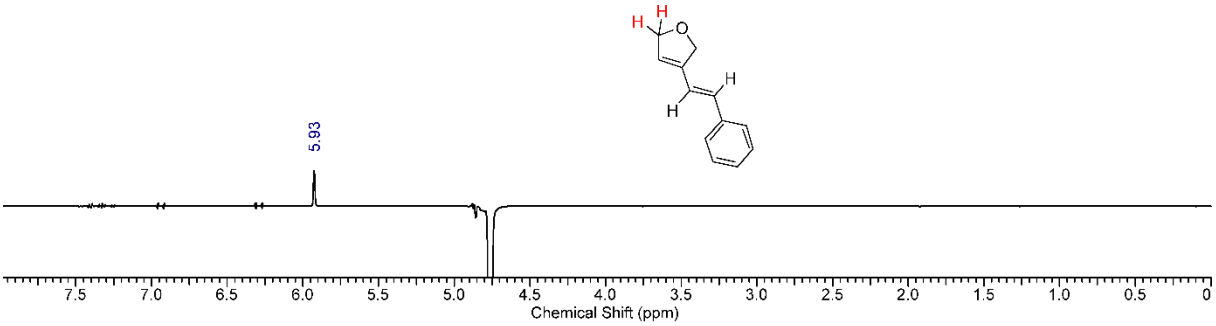


Figure S36: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

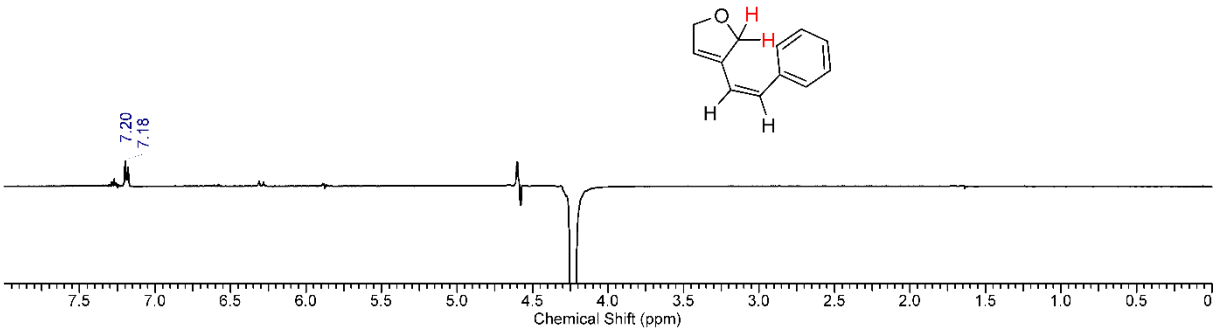


Figure S37: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (Z)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red .

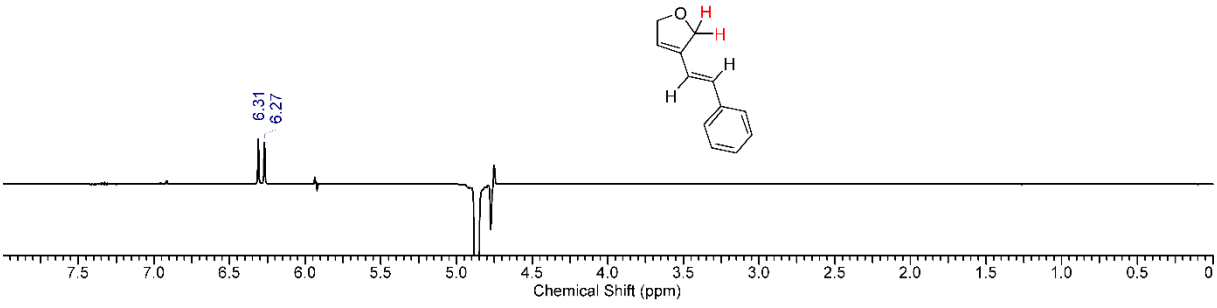


Figure S38: ^{1}H NOE NMR (chloroform-d, 400 MHz) spectrum of (E)-3-styryl-2, 5-dihydrofuran. Irradiated nuclei are presented in red.

GPC and MALDI-ToF mass spectrometric data of polymers

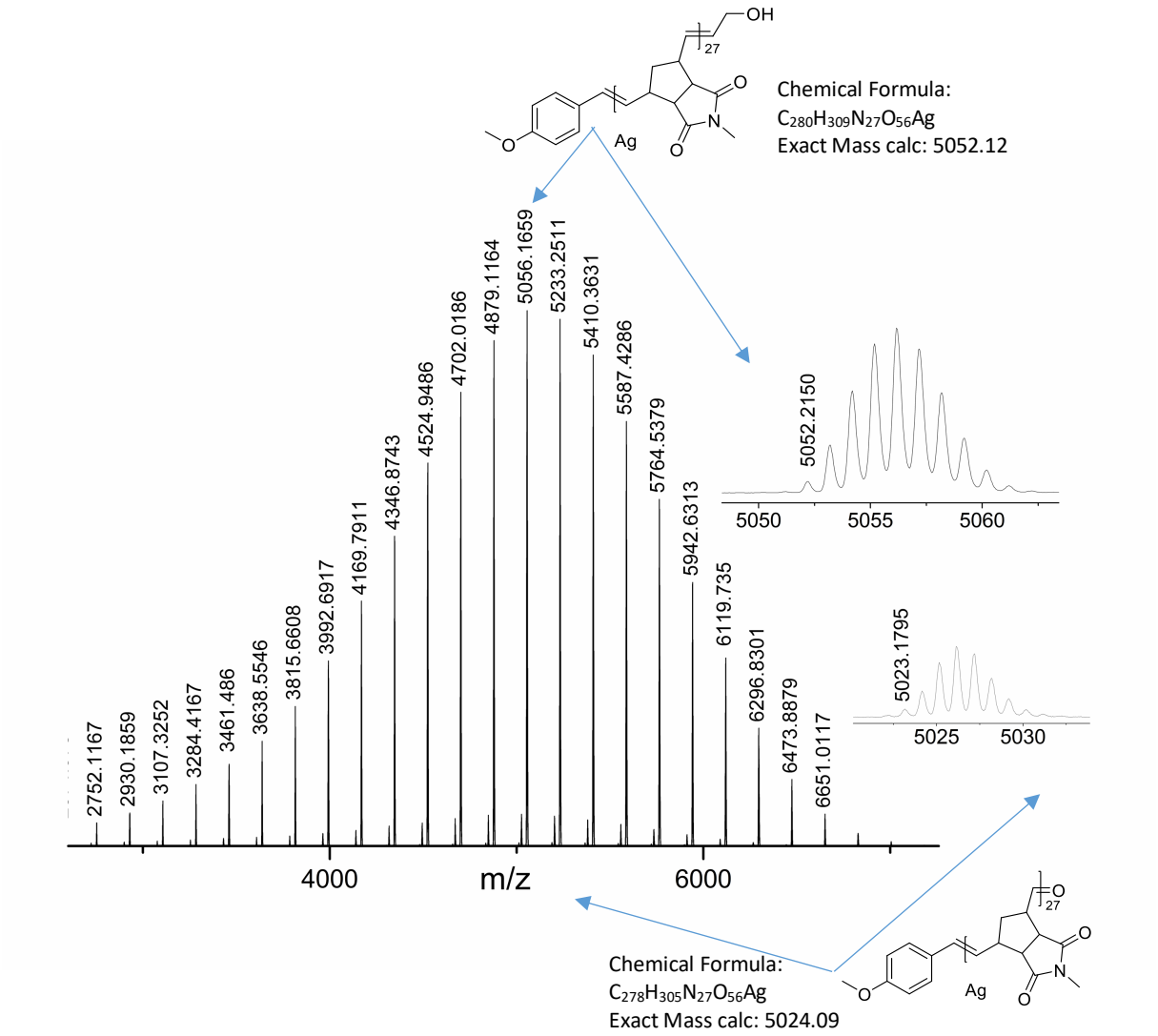


Figure S39: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly a**.

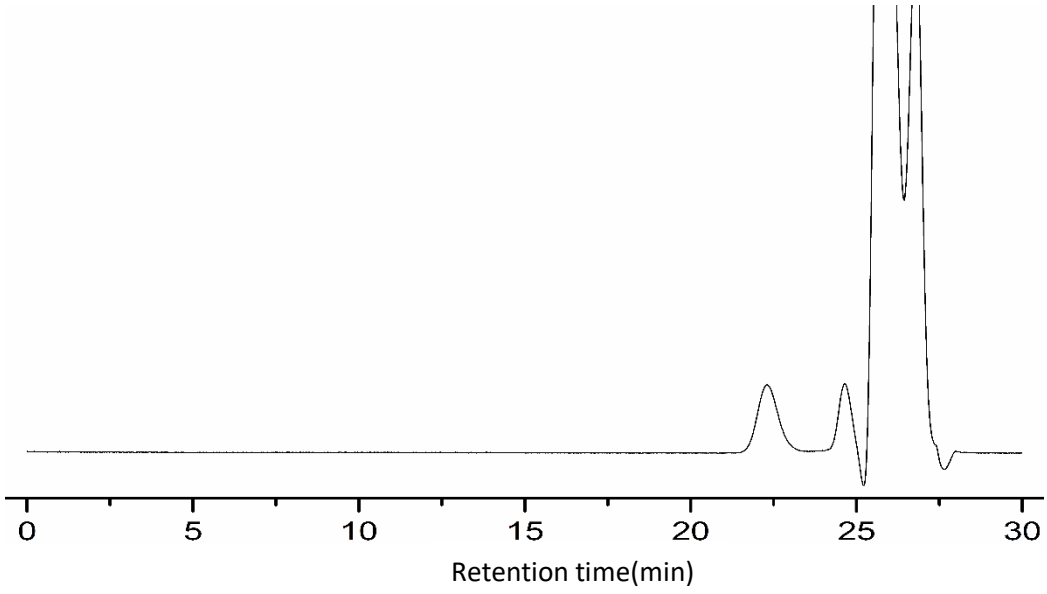


Figure S40: GPC (THF) trace of hetero-telechelic **poly a**.

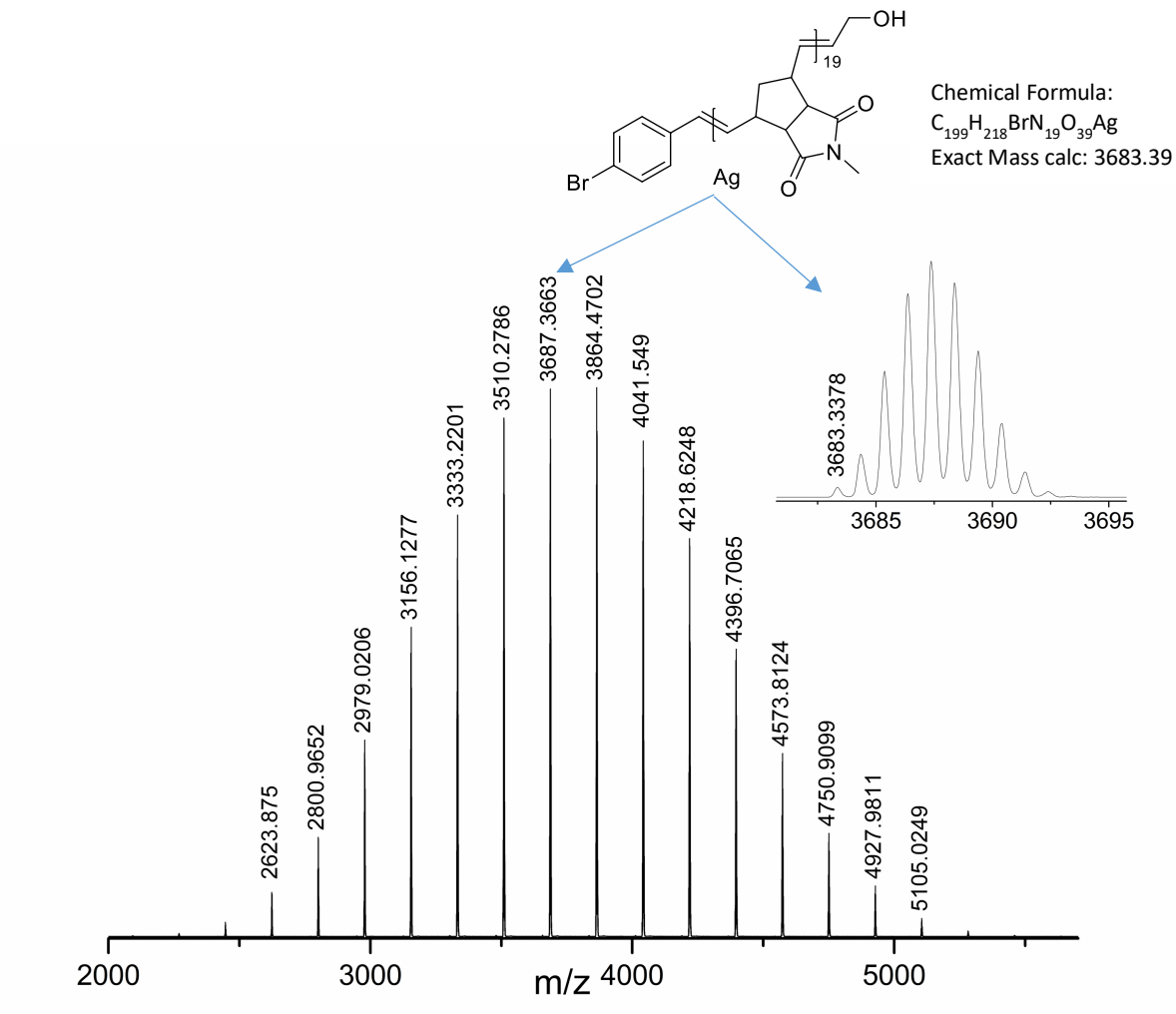


Figure S41: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly b**

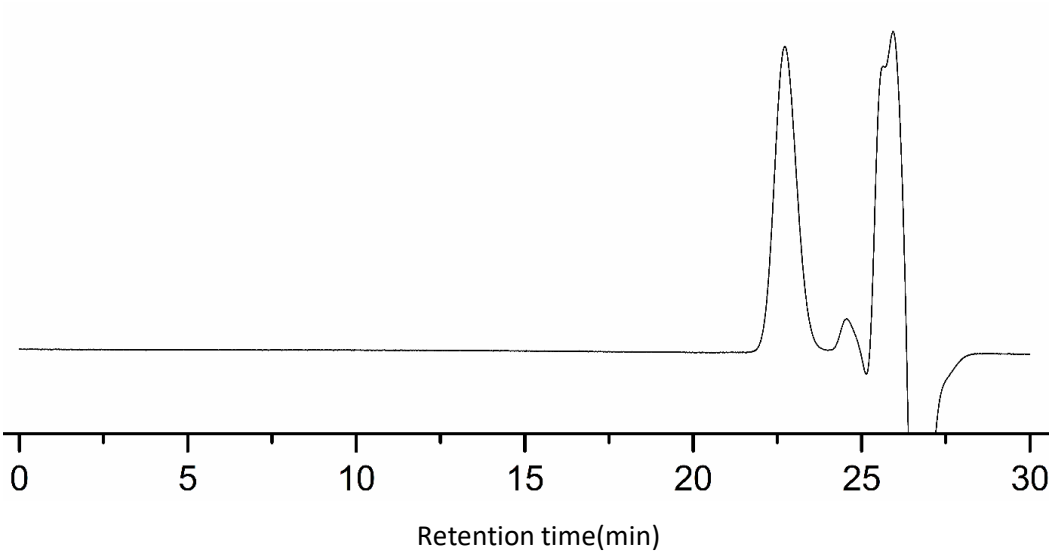


Figure S42: GPC (THF) trace of hetero-telechelic **poly b**.

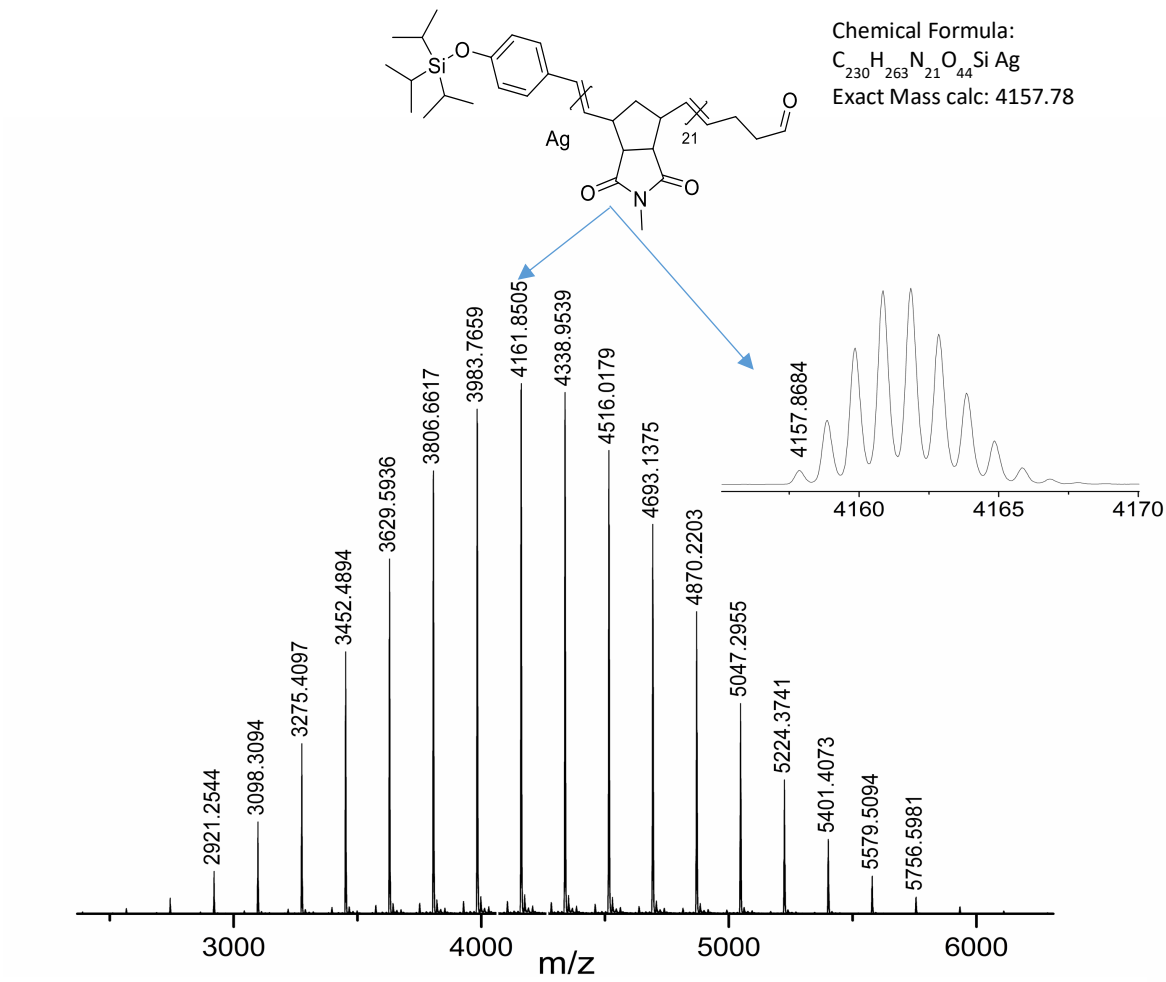


Figure S43: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly c**.

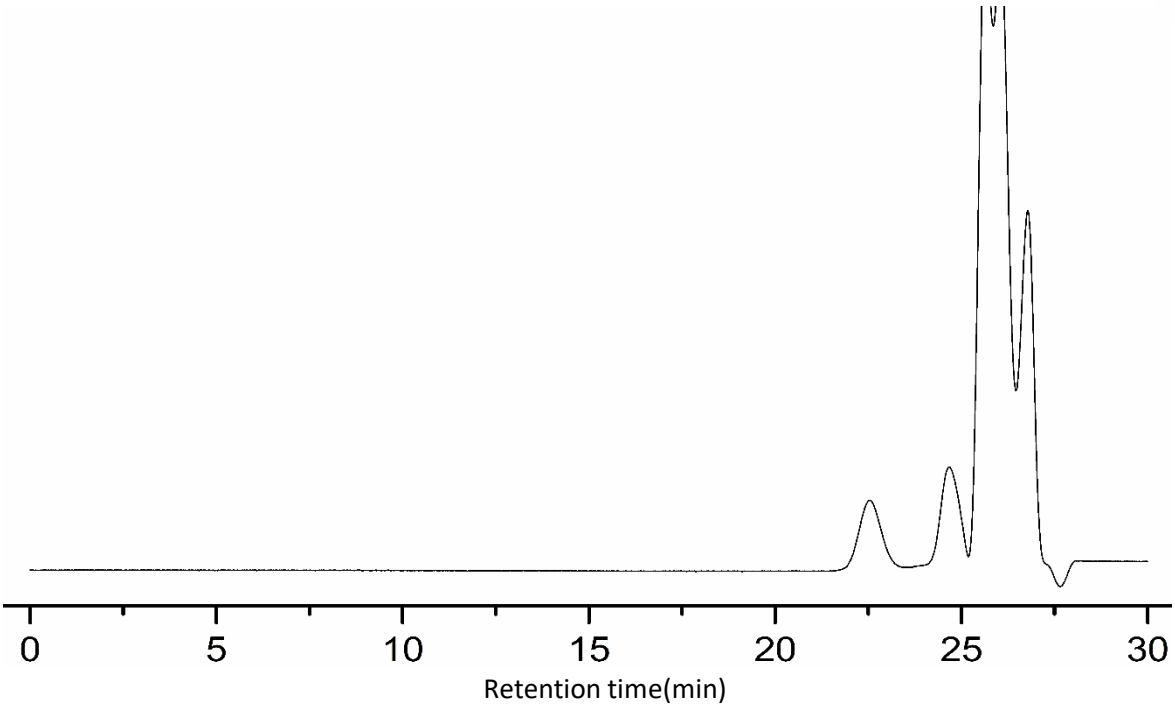


Figure S44: GPC (THF) trace of hetero-telechelic **poly c**.

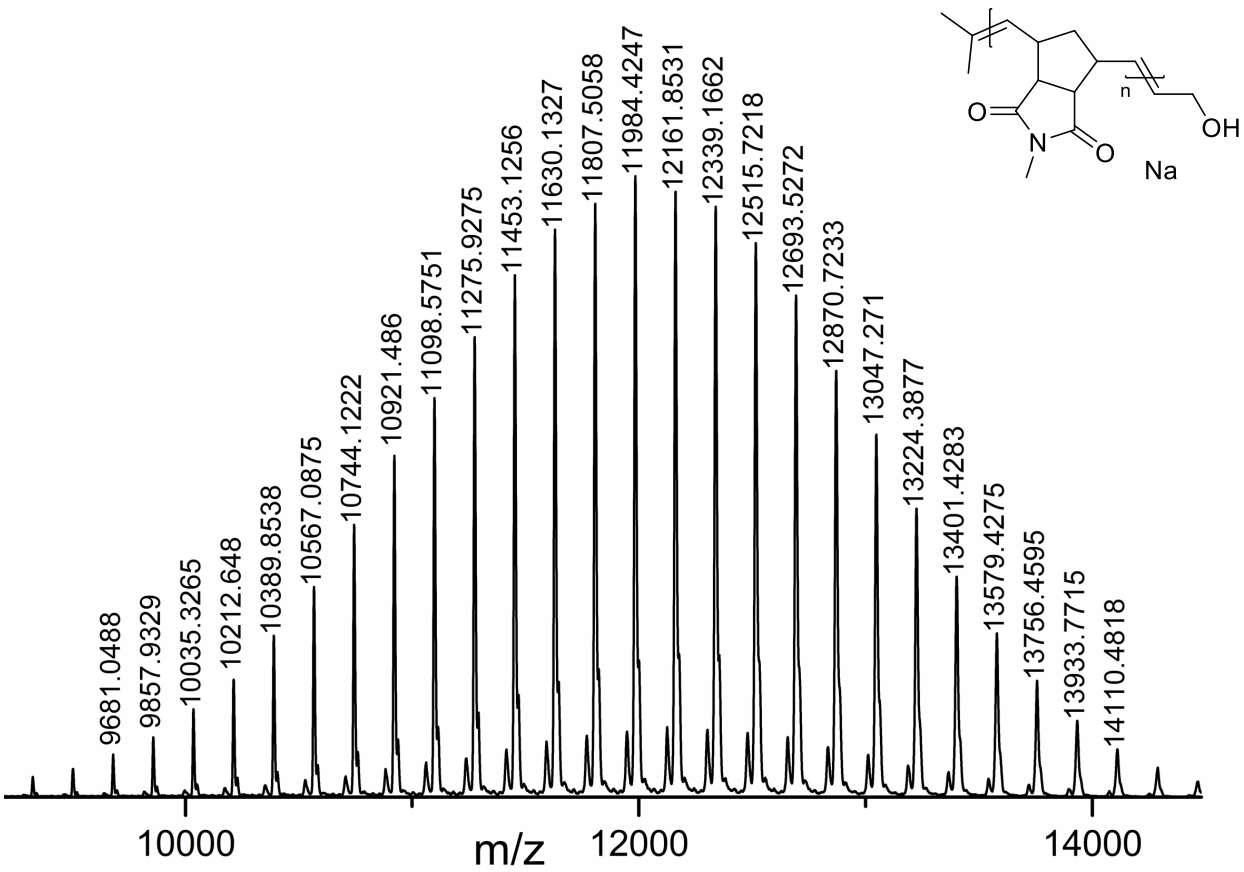


Figure S45: MALDI-ToF mass spectra (DCTB, NaTFA) of **poly d**. Isotopic resolution was not possible because of high molecular weight.

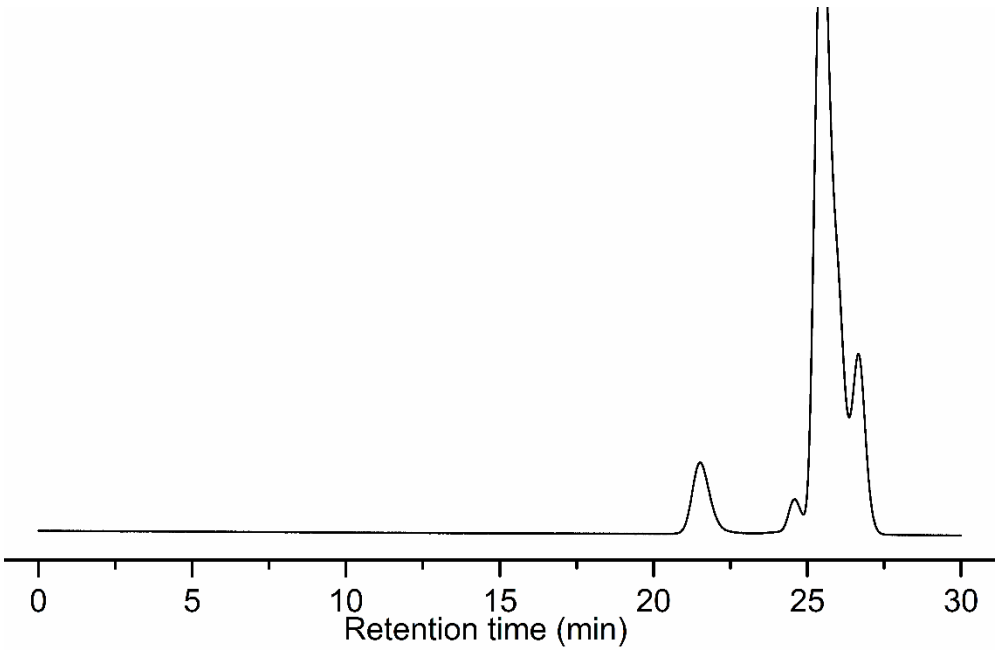


Figure S46: GPC (THF) trace of hetero-telechelic **poly d**.

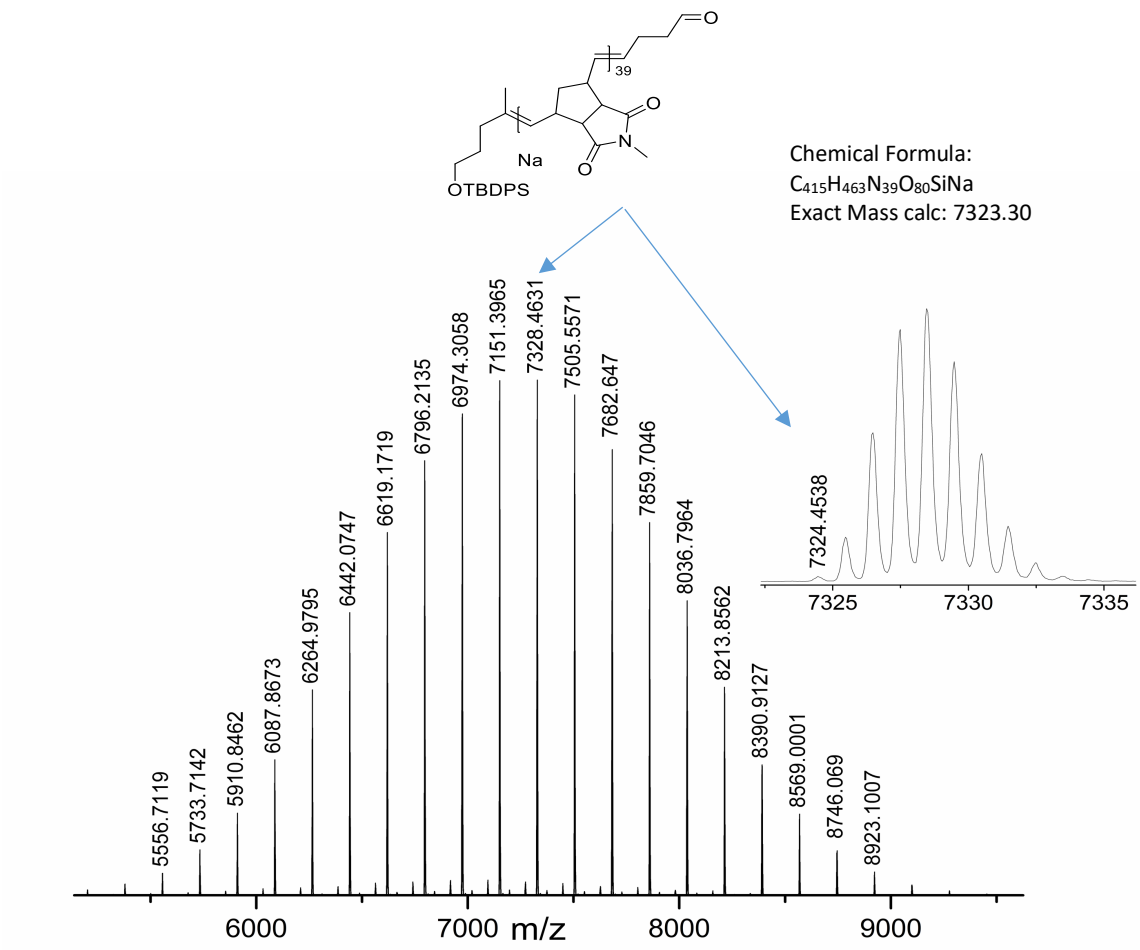


Figure S47: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly e.**

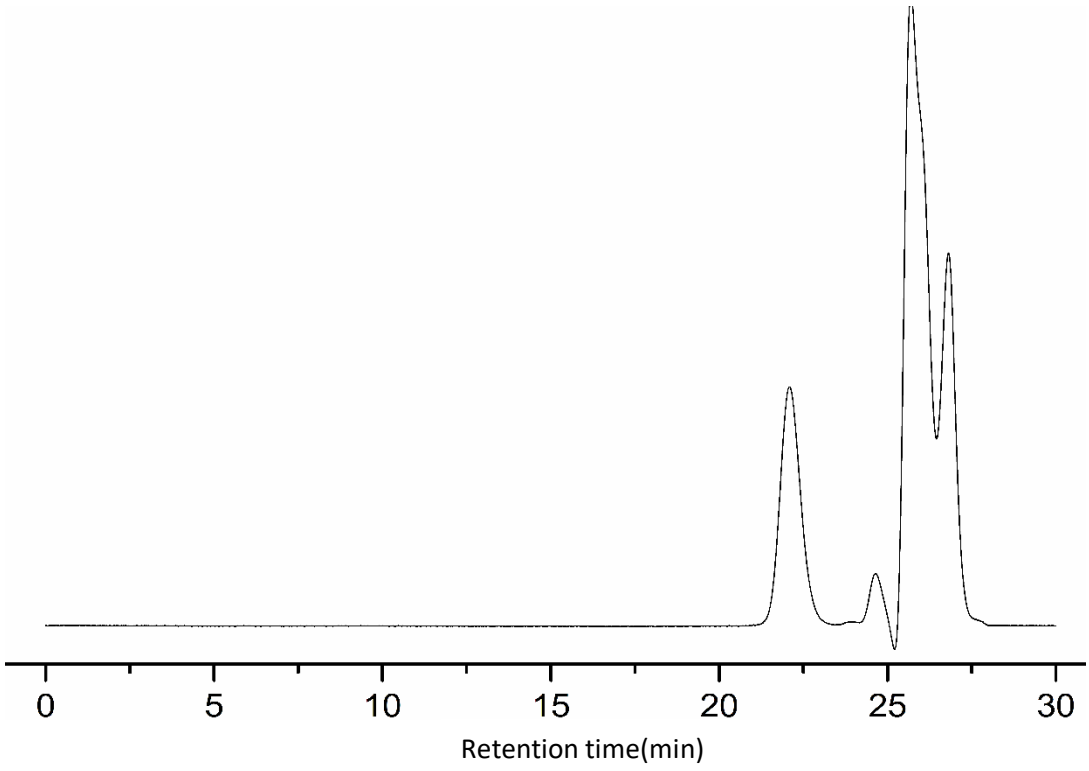


Figure S48: GPC (THF) trace of hetero-telechelic **poly e**.

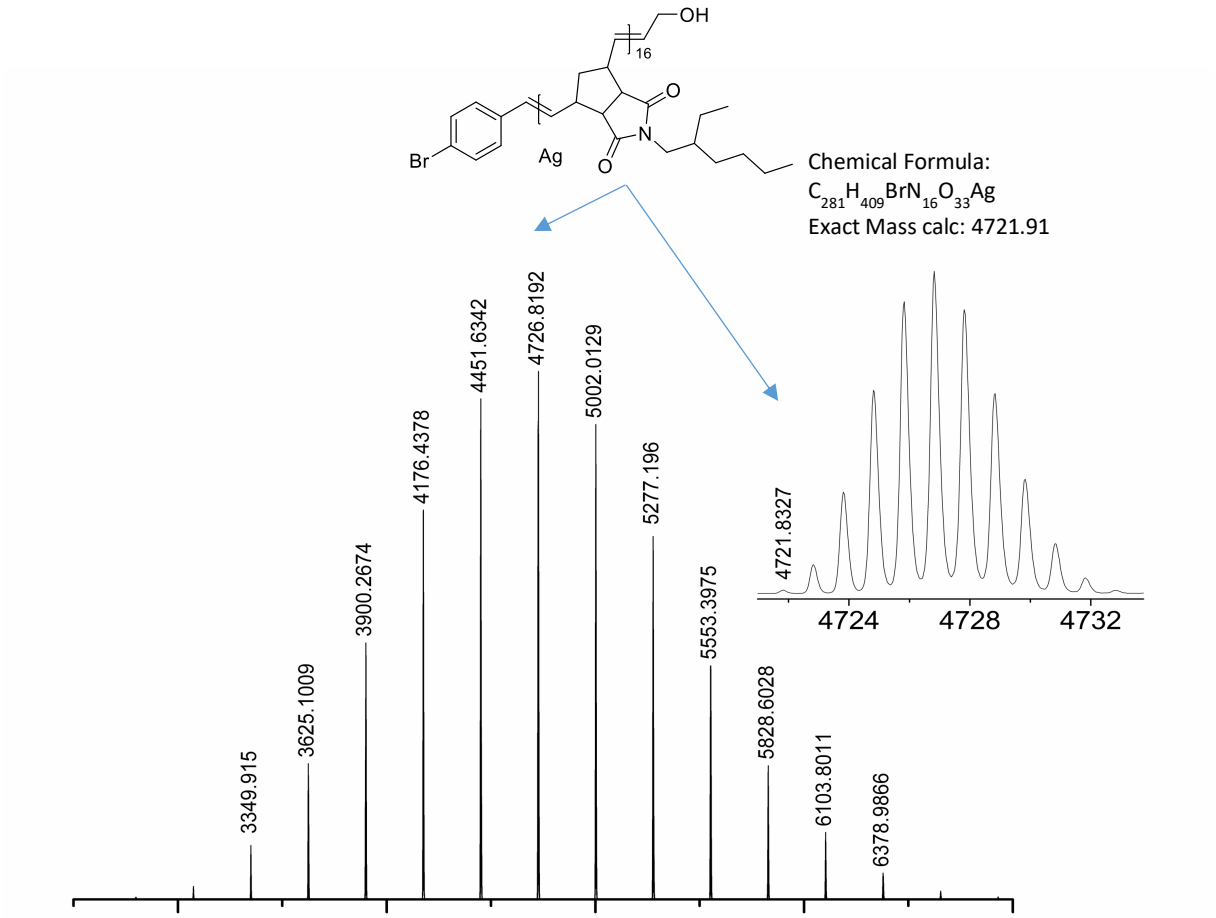


Figure S49: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly f**.

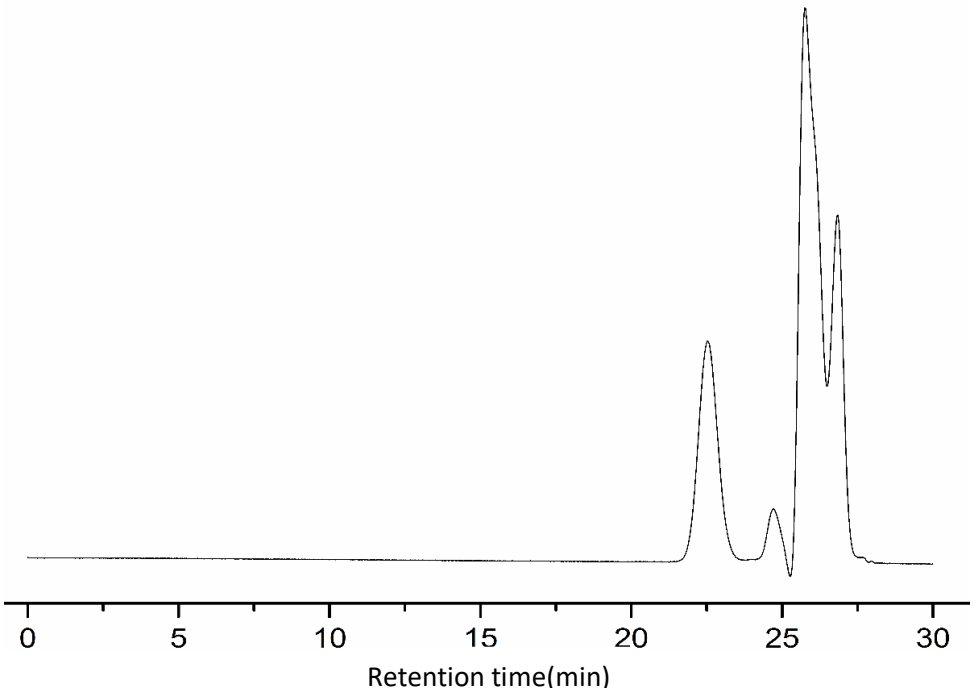


Figure S50: GPC (THF) trace of hetero-telechelic **poly f**.

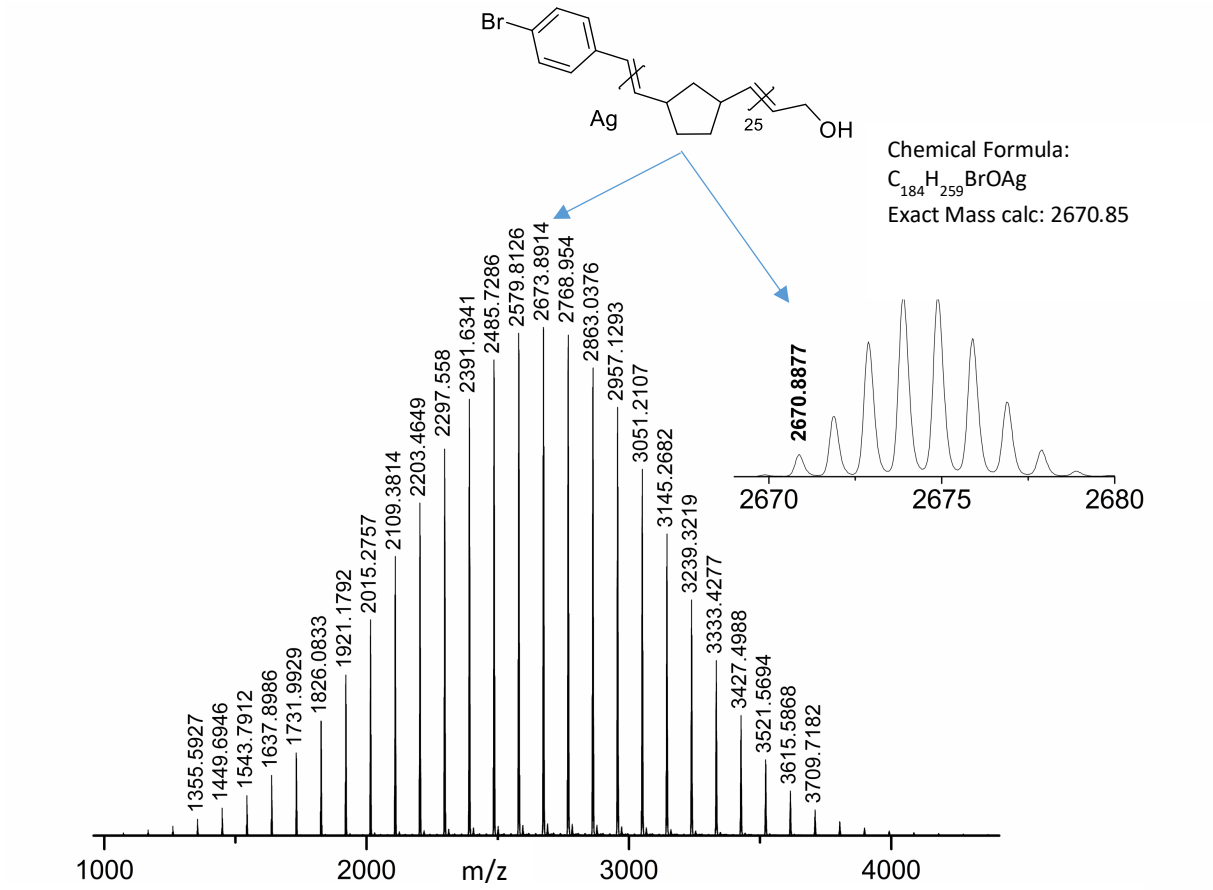


Figure S51: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly g**.

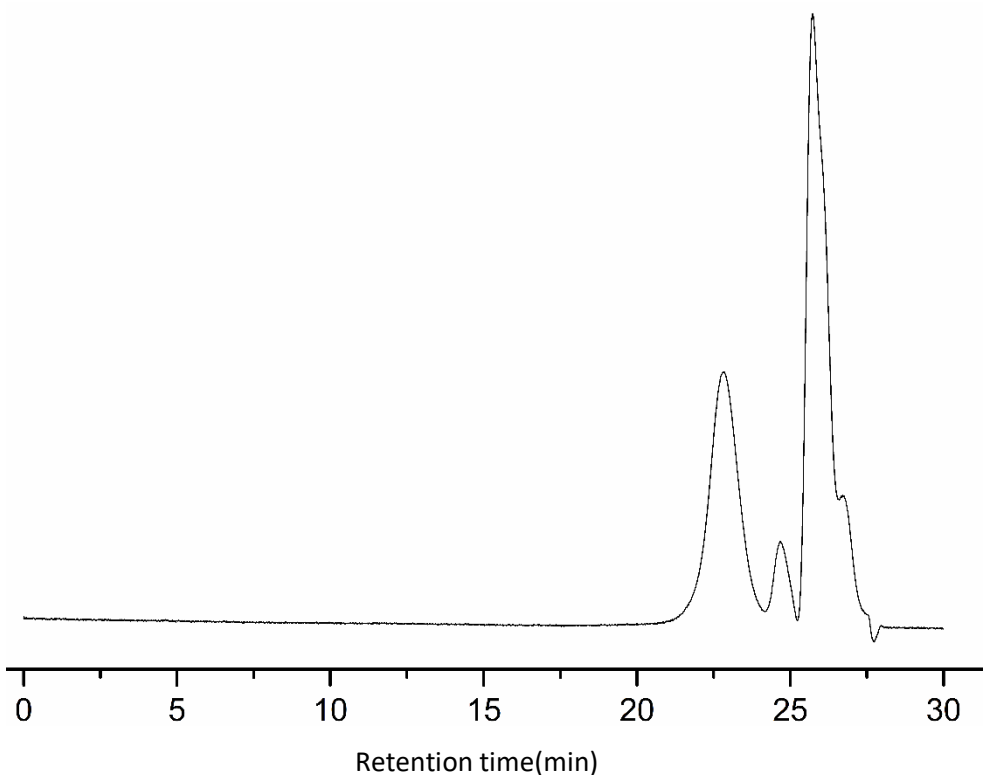


Figure S52: GPC (THF) trace of hetero-telechelic **poly g**.

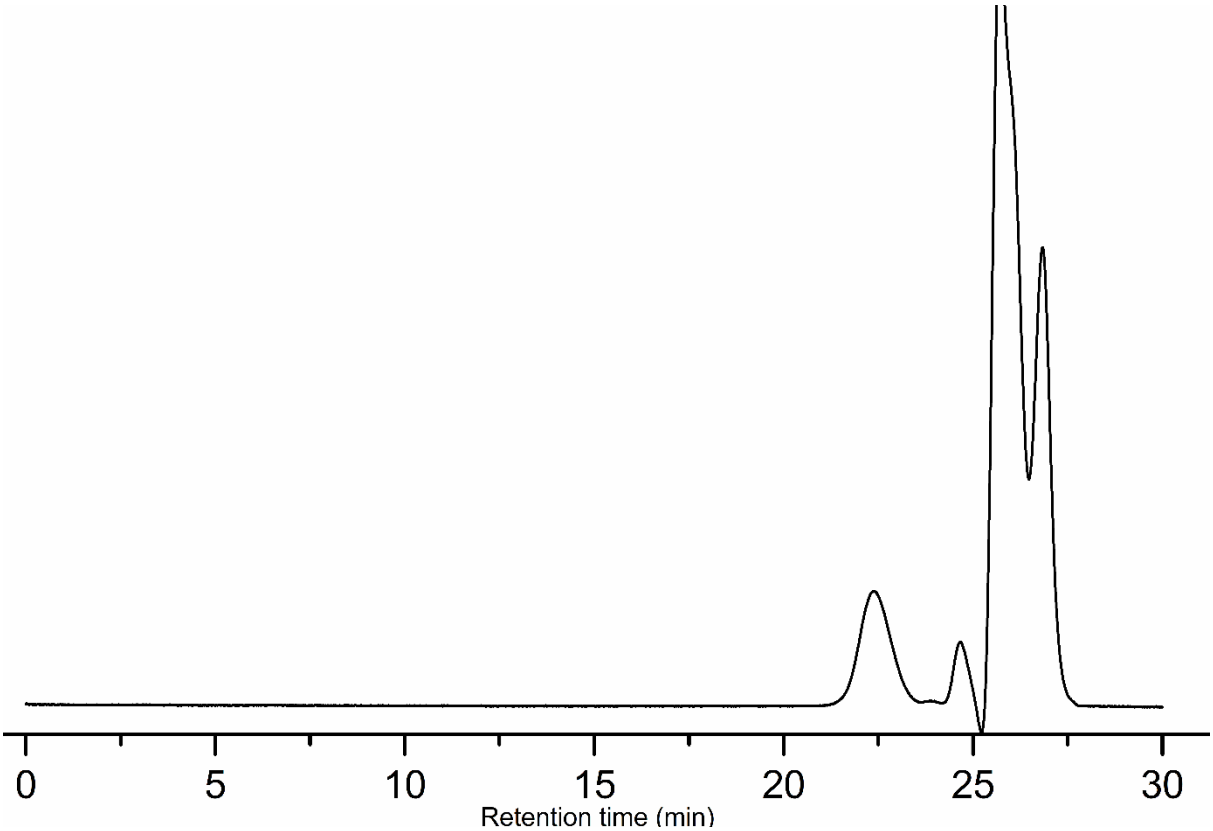


Figure S53: GPC (THF) trace of hetero-telechelic **poly h**.

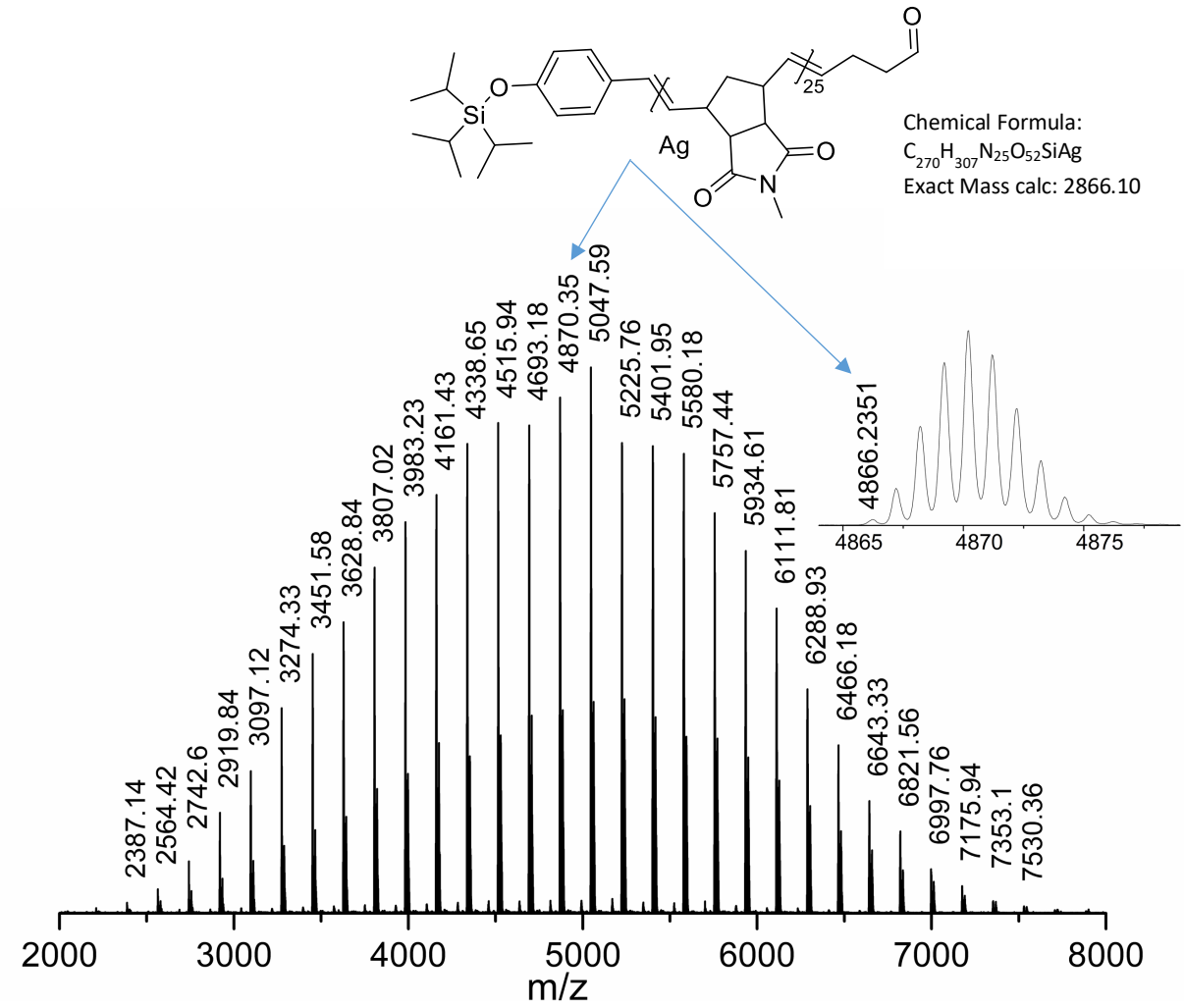


Figure S54: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly i**.

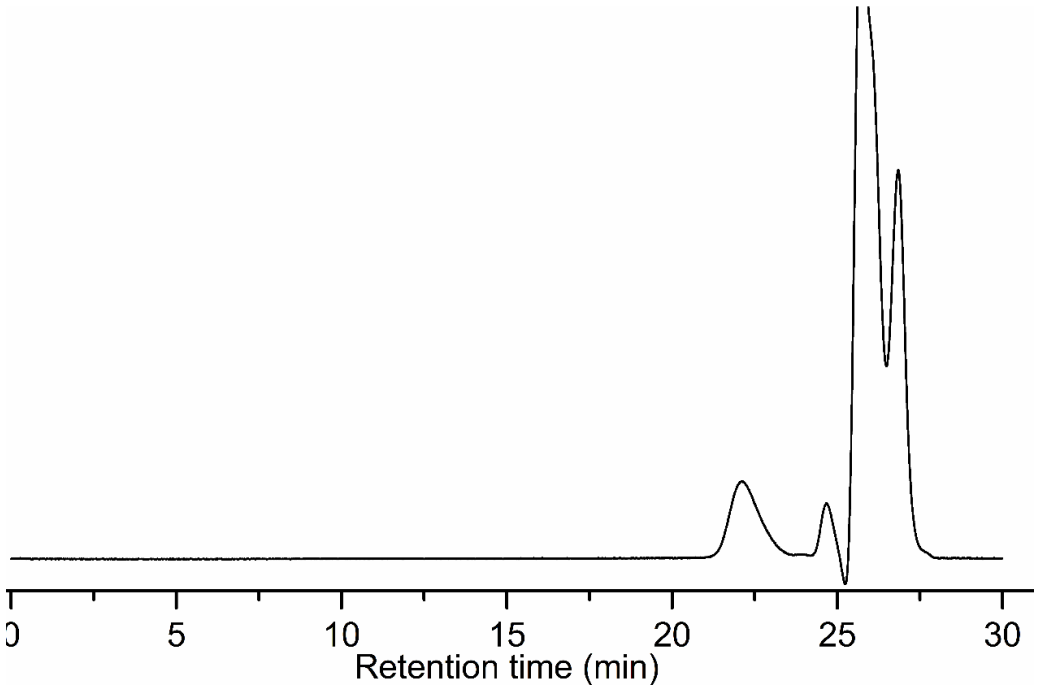


Figure S55: GPC (THF) trace of hetero-telechelic **poly i**.

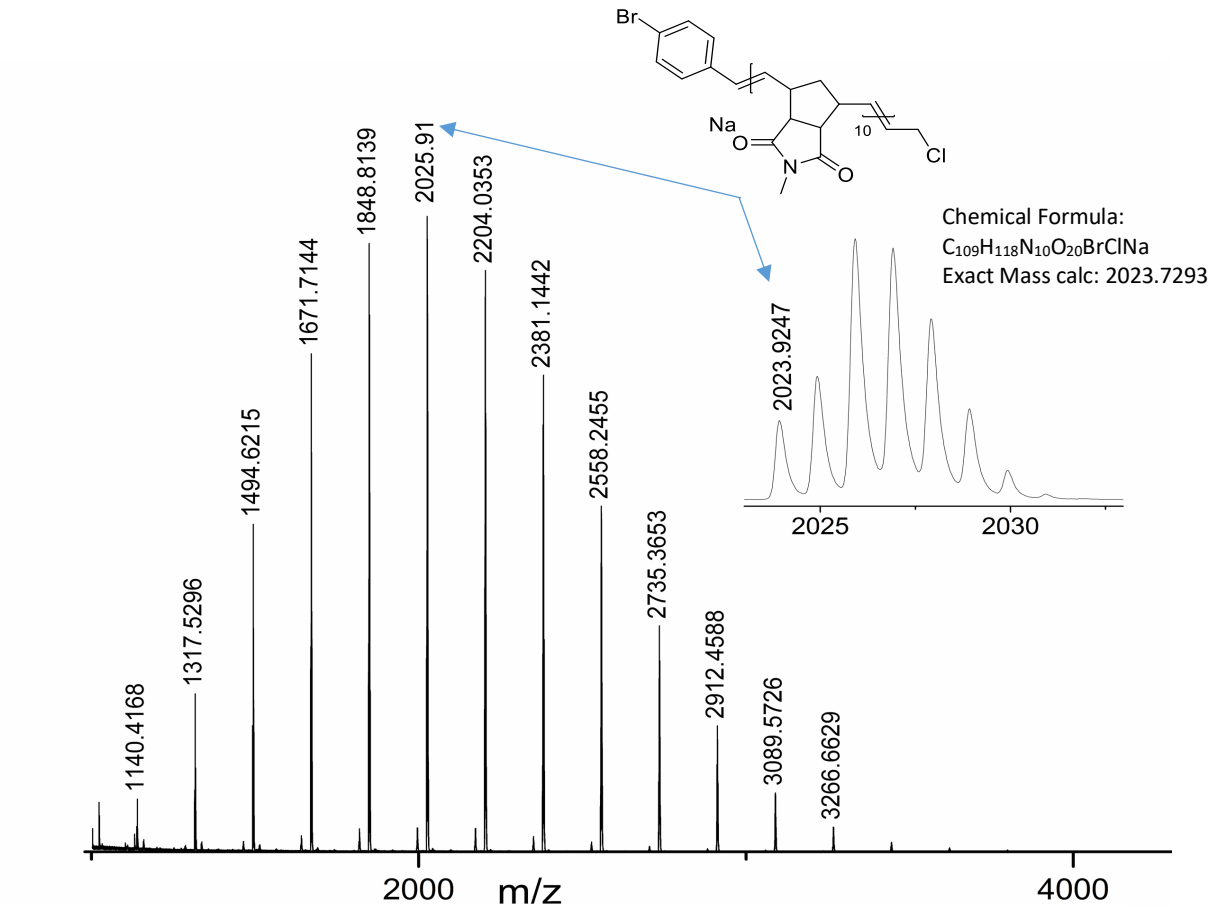


Figure S56: MALDI-ToF mass spectra (DCTB, NaTFA) of **poly j**.

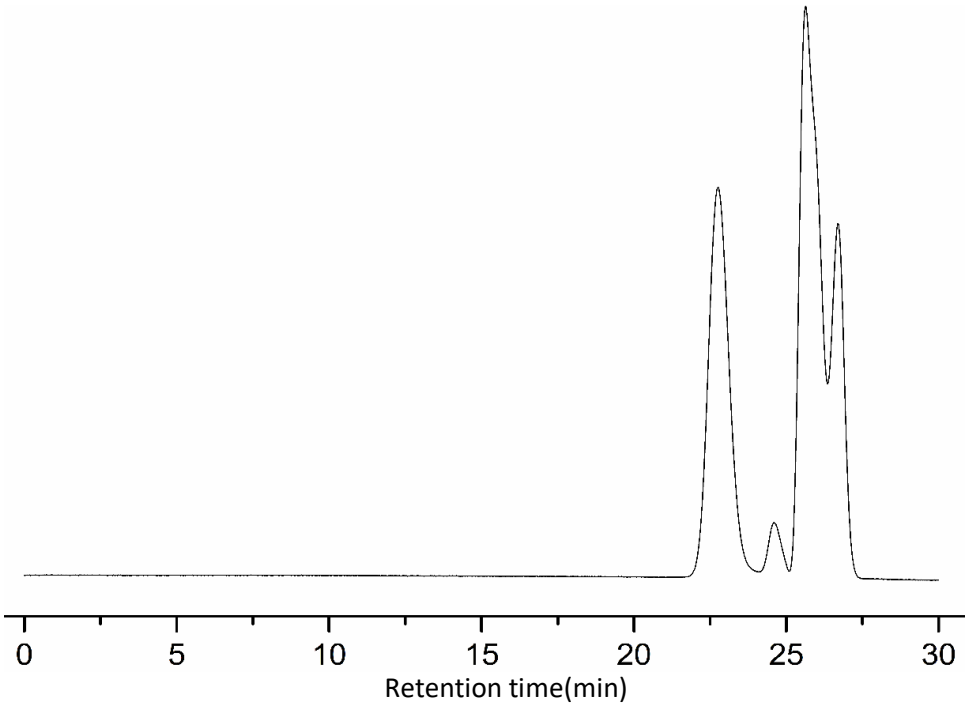


Figure S57: GPC (THF) trace of hetero-telechelic **poly j**.

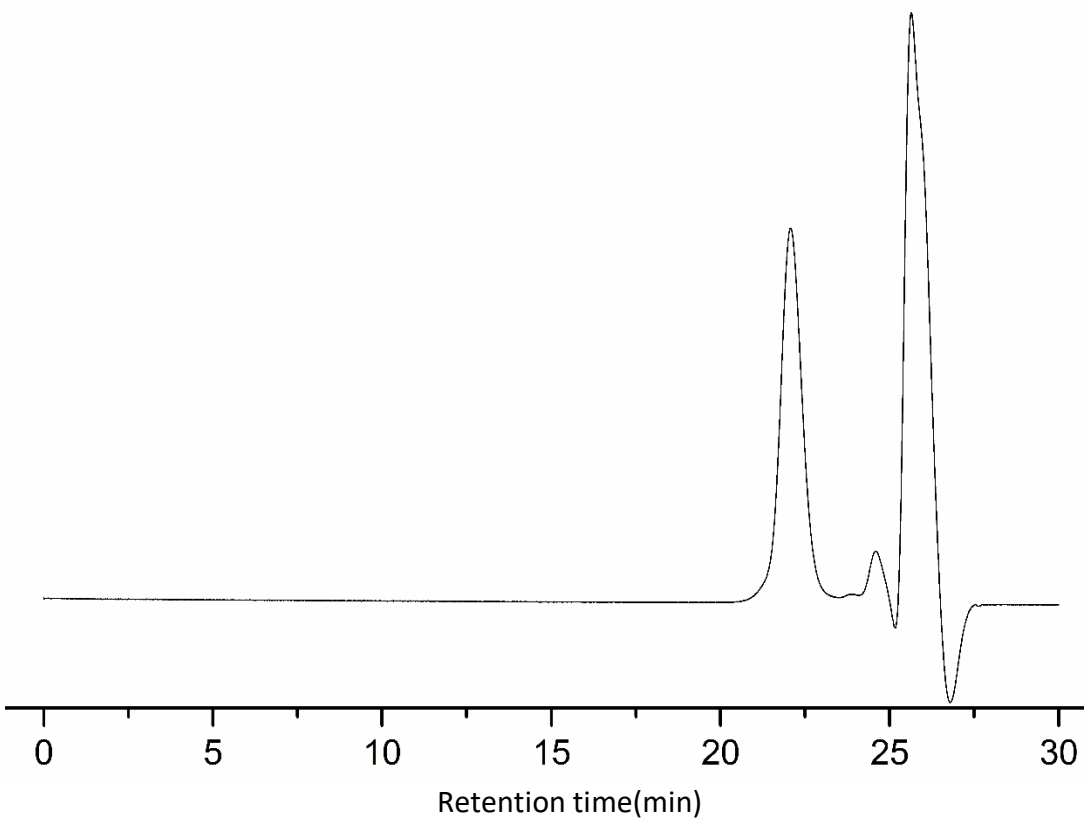


Figure S58: GPC (THF) trace of hetero-telechelic **poly k**.

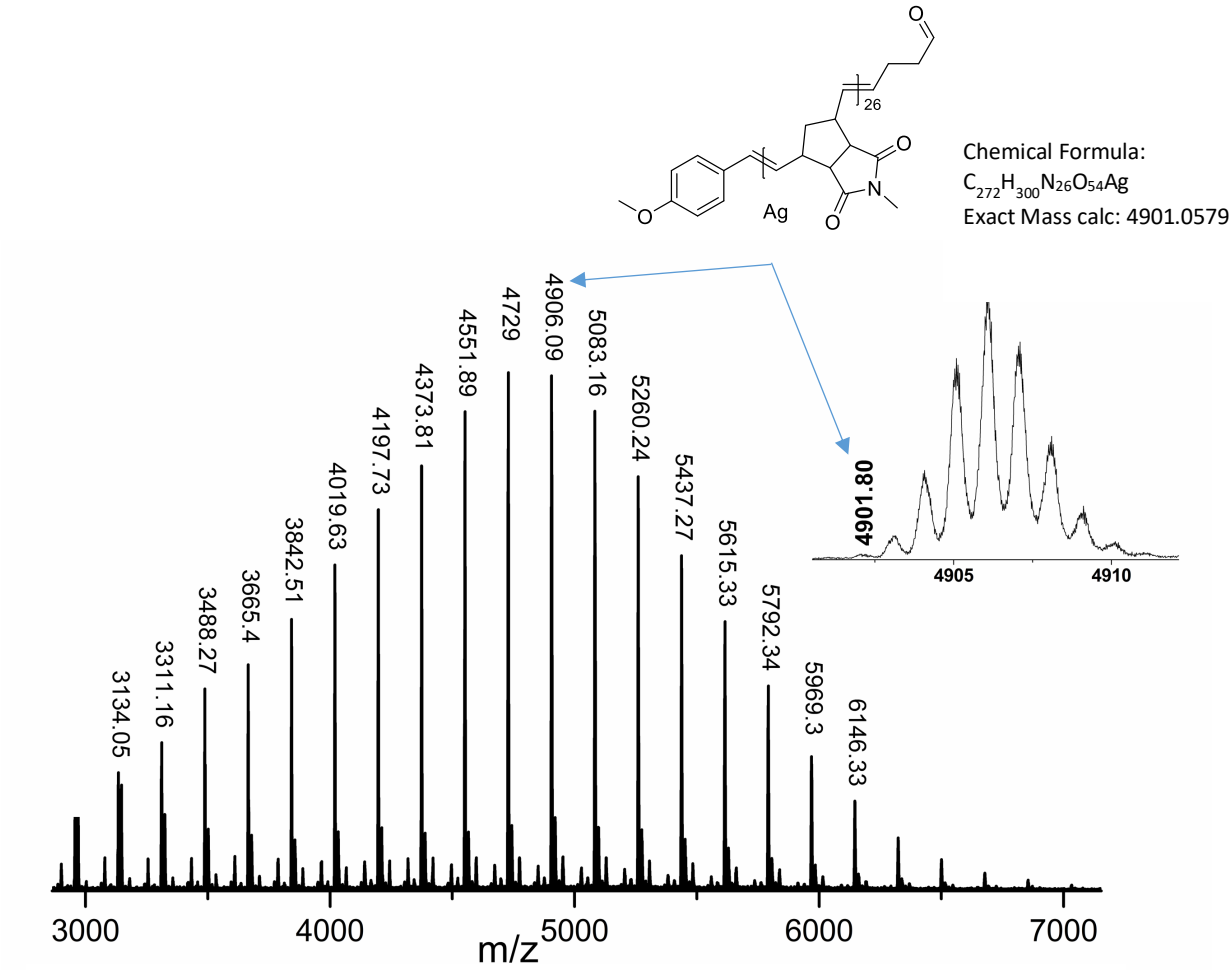


Figure S59: MALDI-ToF mass spectra (DCTB, AgTFA) of **poly l**.

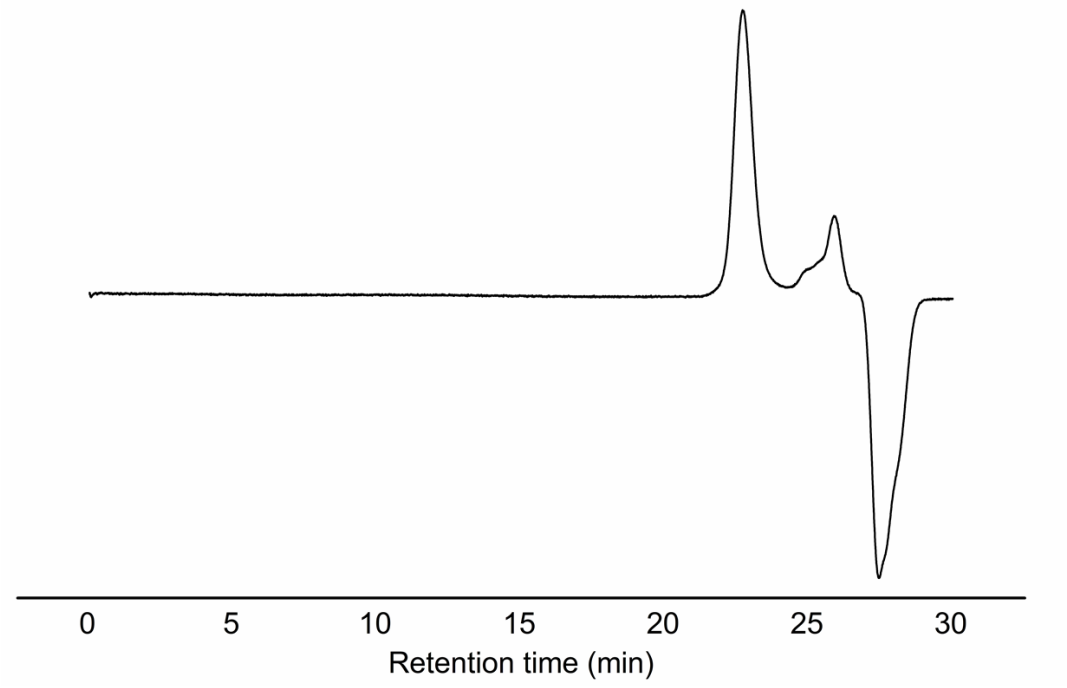


Figure S60: GPC (THF) trace of hetero-telechelic **poly l**.

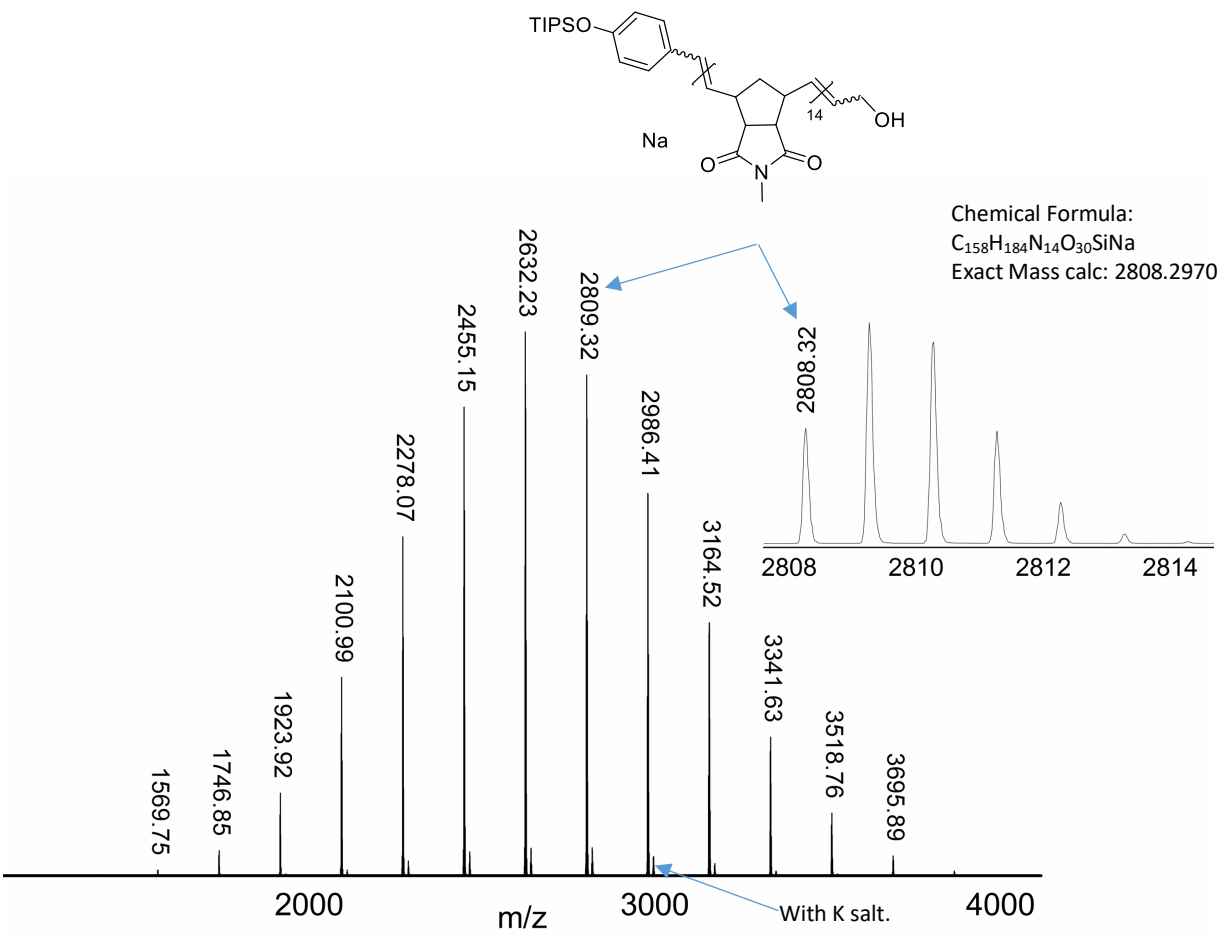


Figure S61: MALDI-ToF mass spectra (DCTB, NaTFA) of **poly m**.

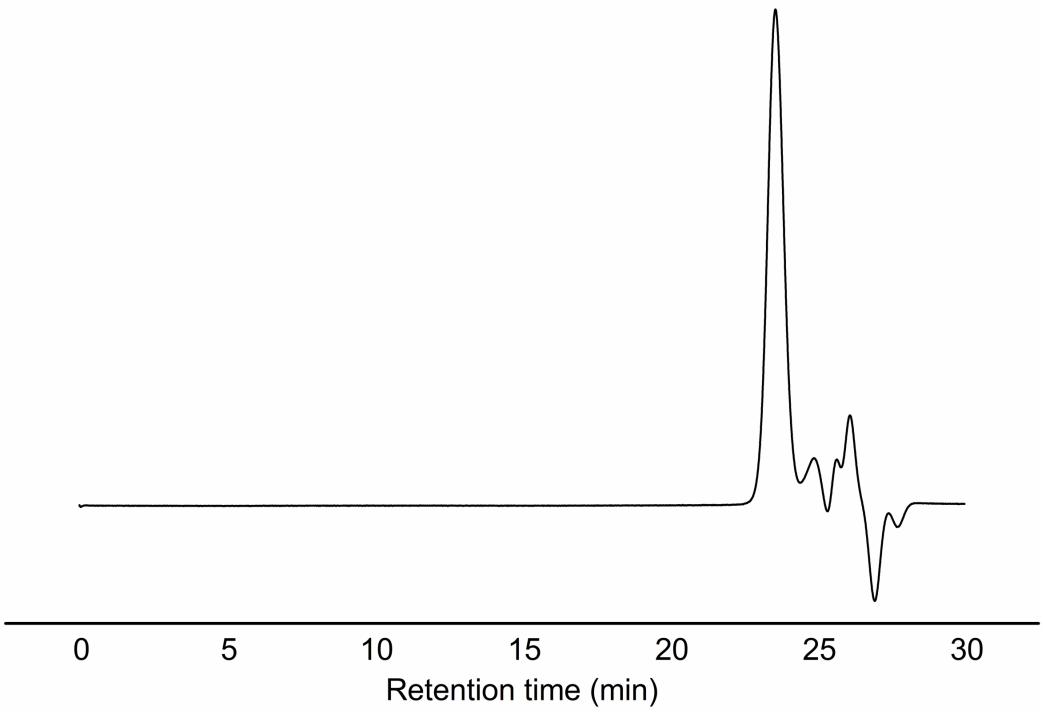


Figure S62: GPC (THF) trace of hetero-telechelic **poly m**.

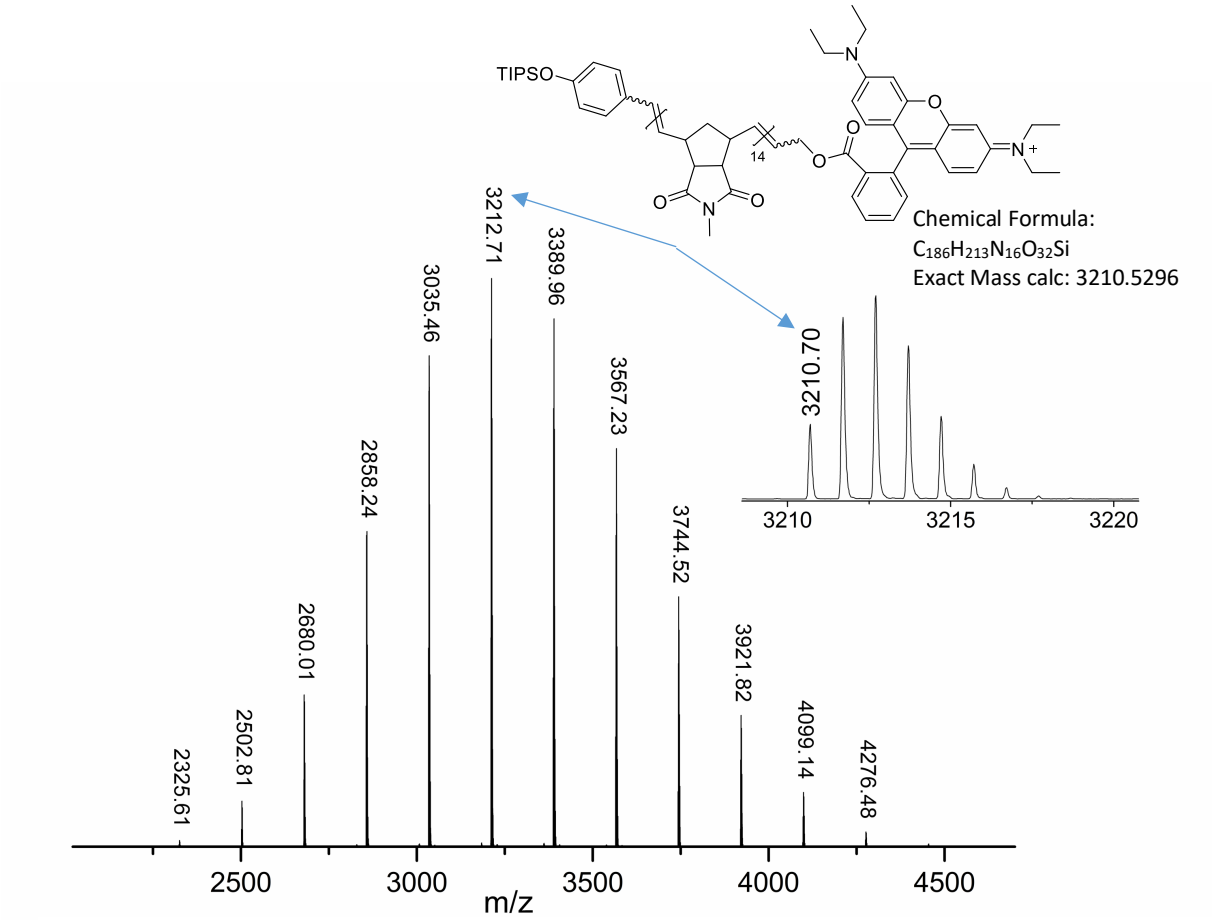


Figure S63: MALDI-ToF mass spectra (DCTB) of **poly n**.

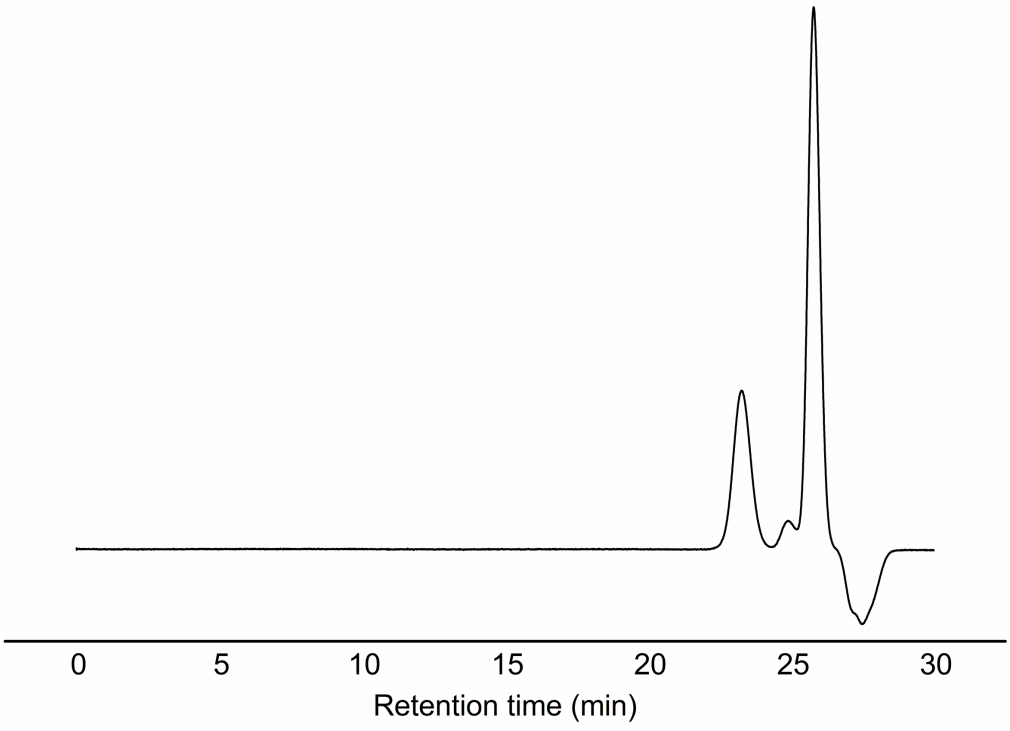


Figure S64: GPC (THF) trace of hetero-telechelic **poly n**.

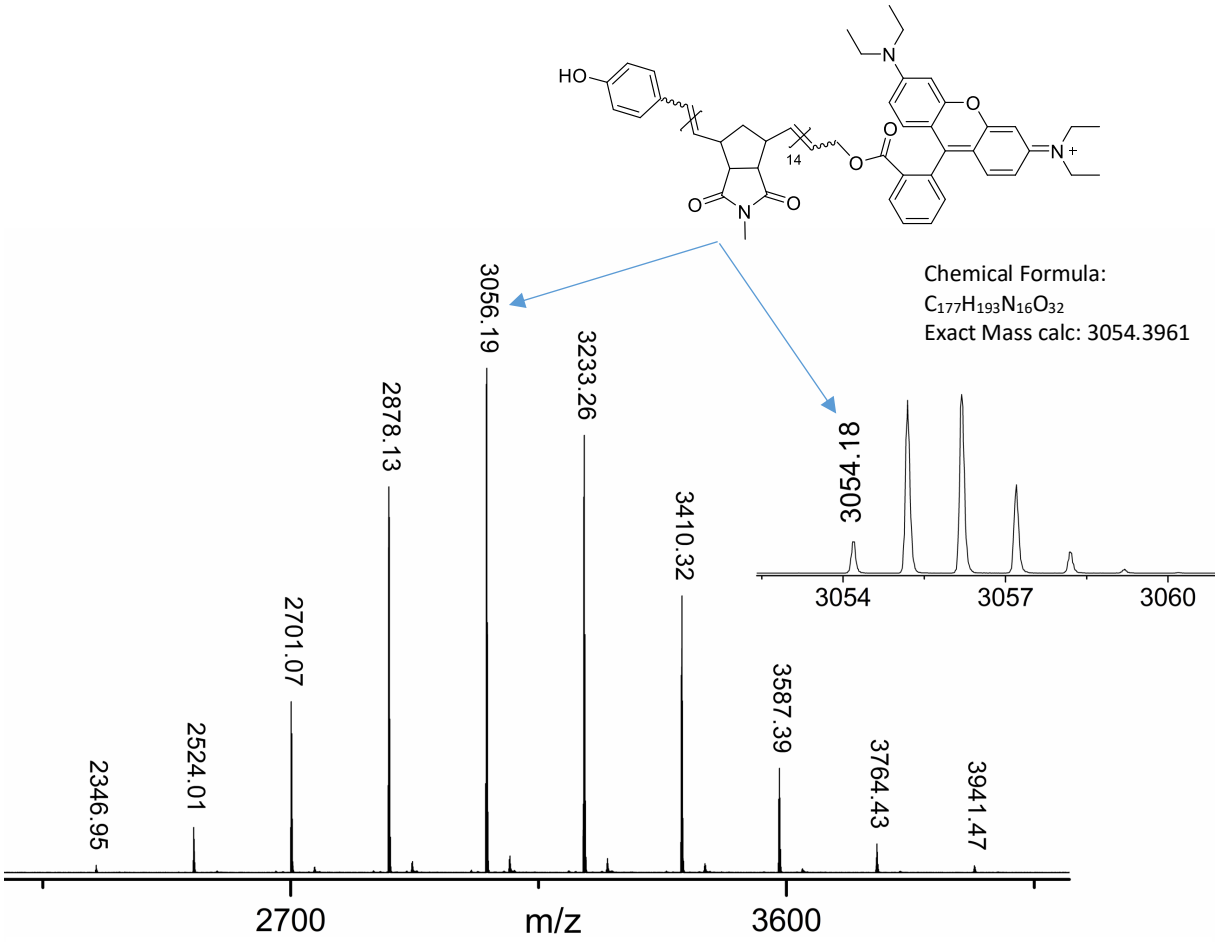


Figure S65: MALDI-ToF mass spectra (DCTB) of **poly 0**.

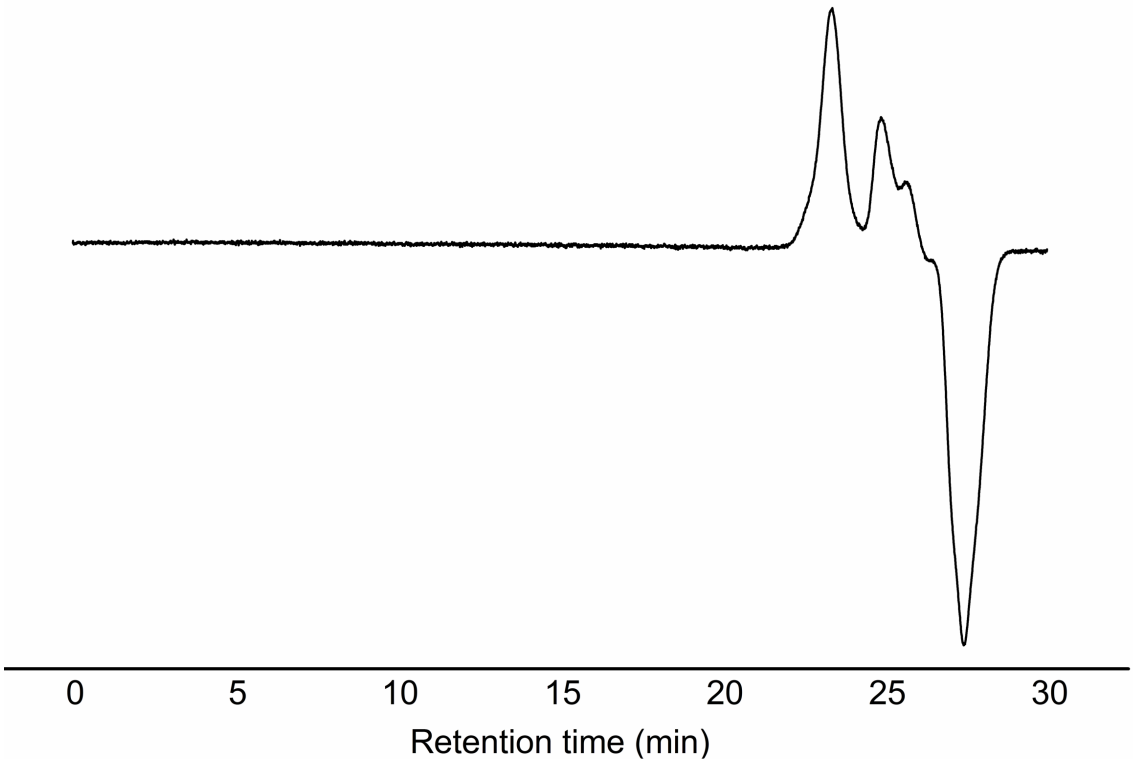


Figure S66: GPC (THF) trace of hetero-telechelic **poly o**.

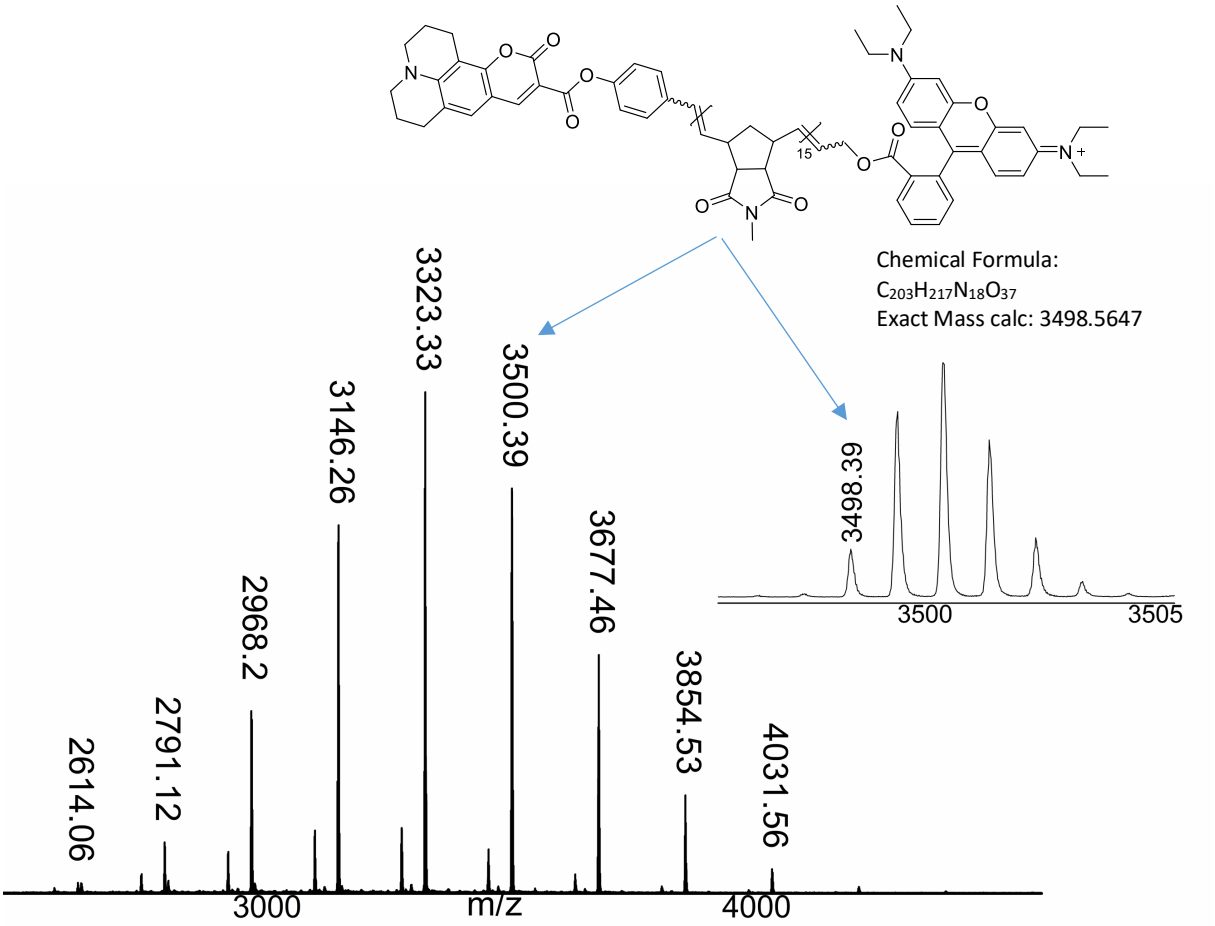


Figure S67: MALDI-ToF mass spectra (DCTB) of **poly p**.

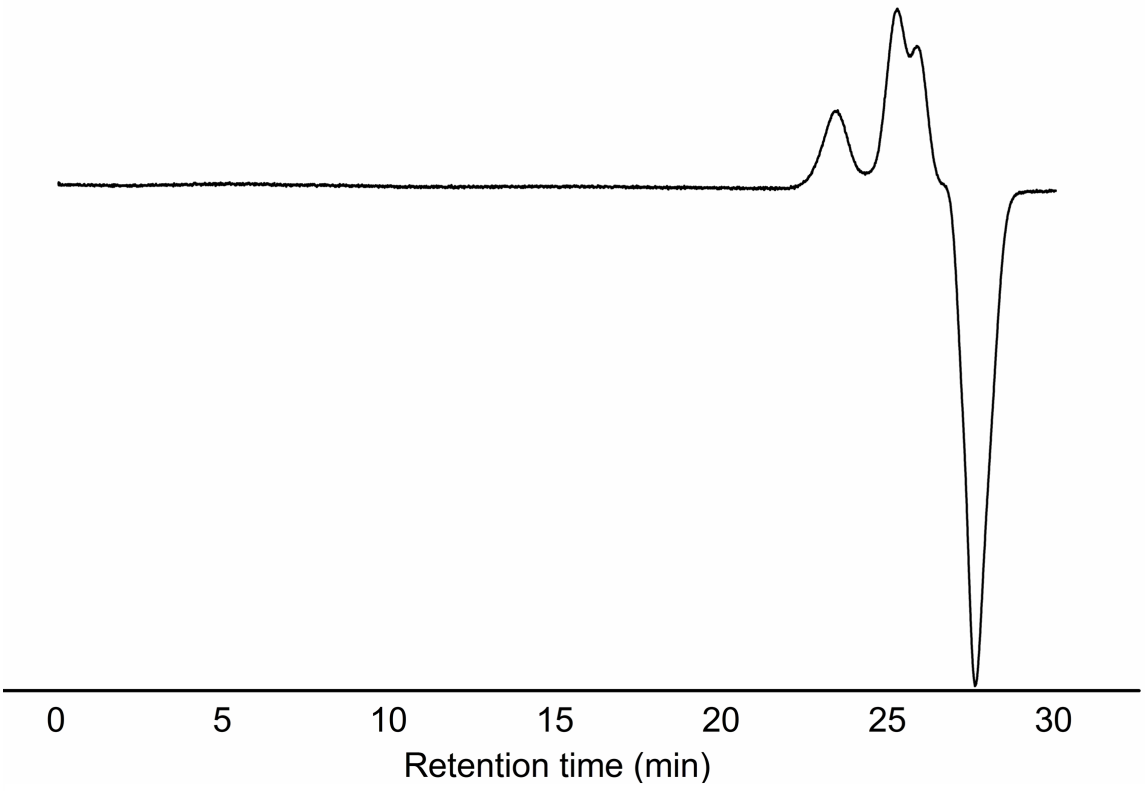


Figure S68: GPC (THF) trace of hetero-telechelic **poly p**.

NMR spectra of polymers

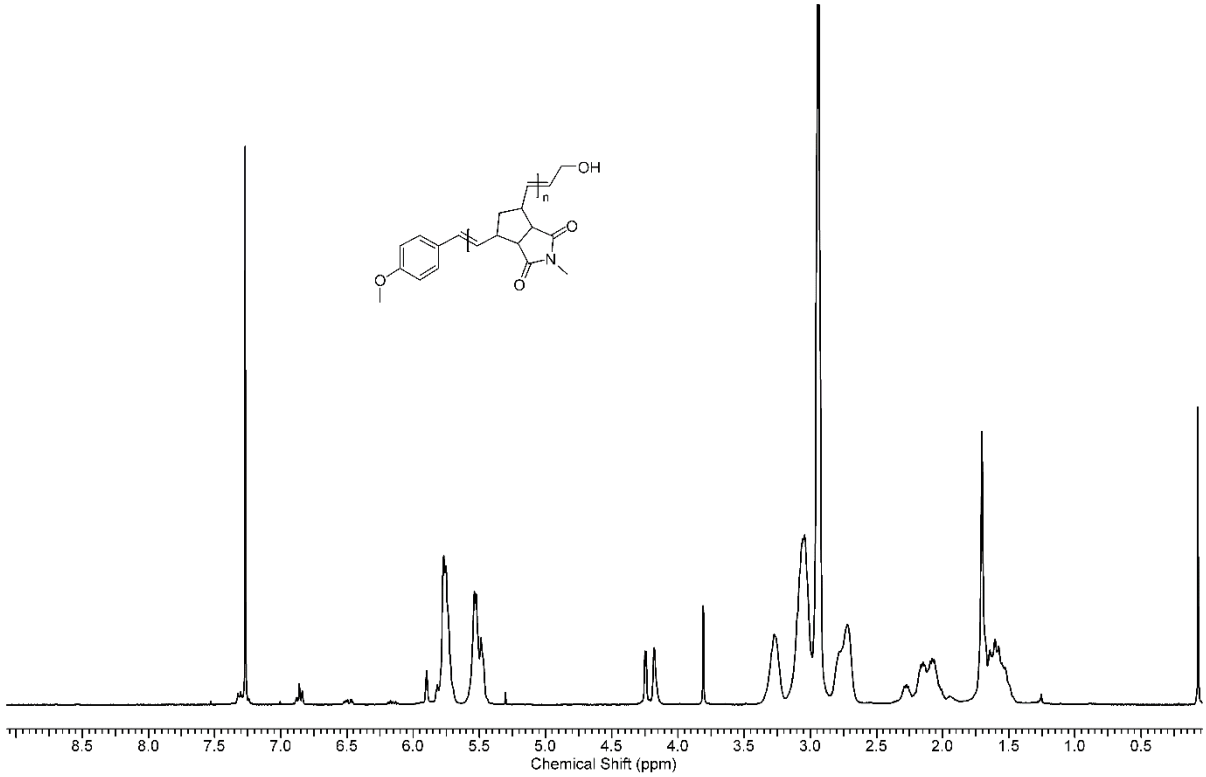


Figure S69: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly a**.

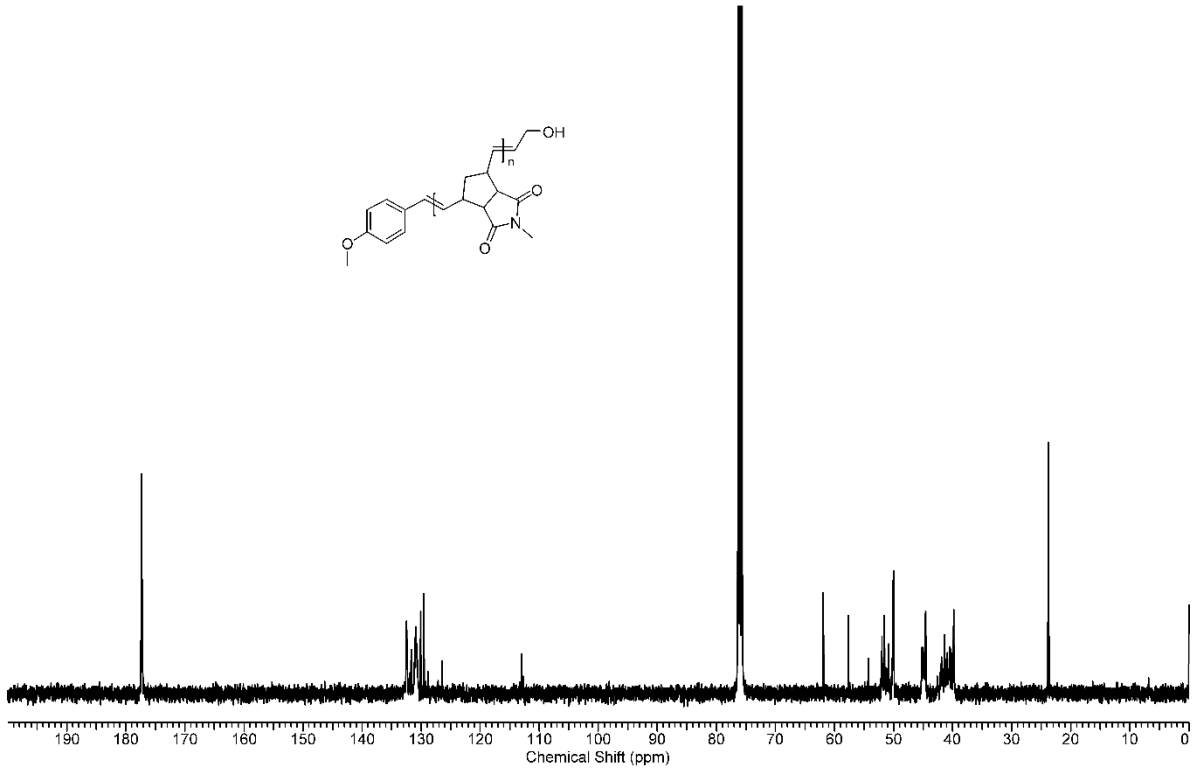


Figure S70: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly a.**

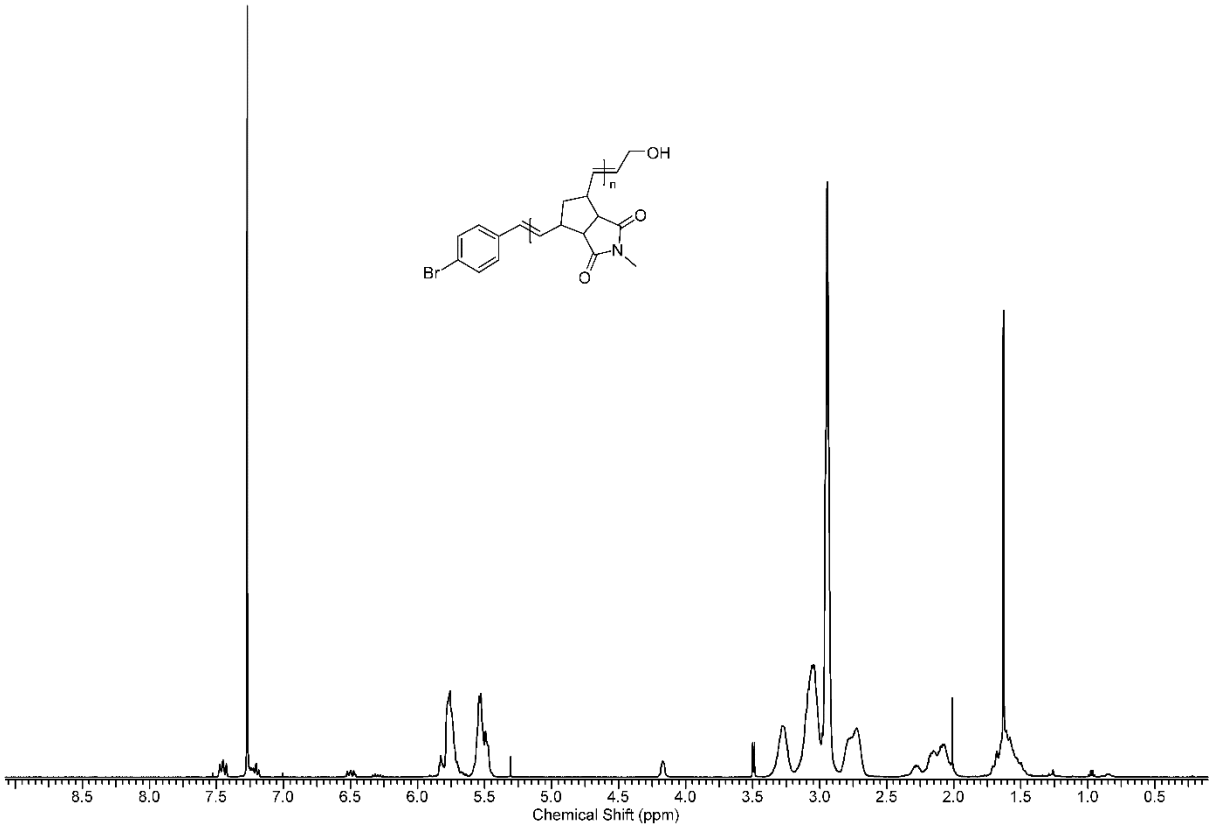


Figure S71: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly b**.

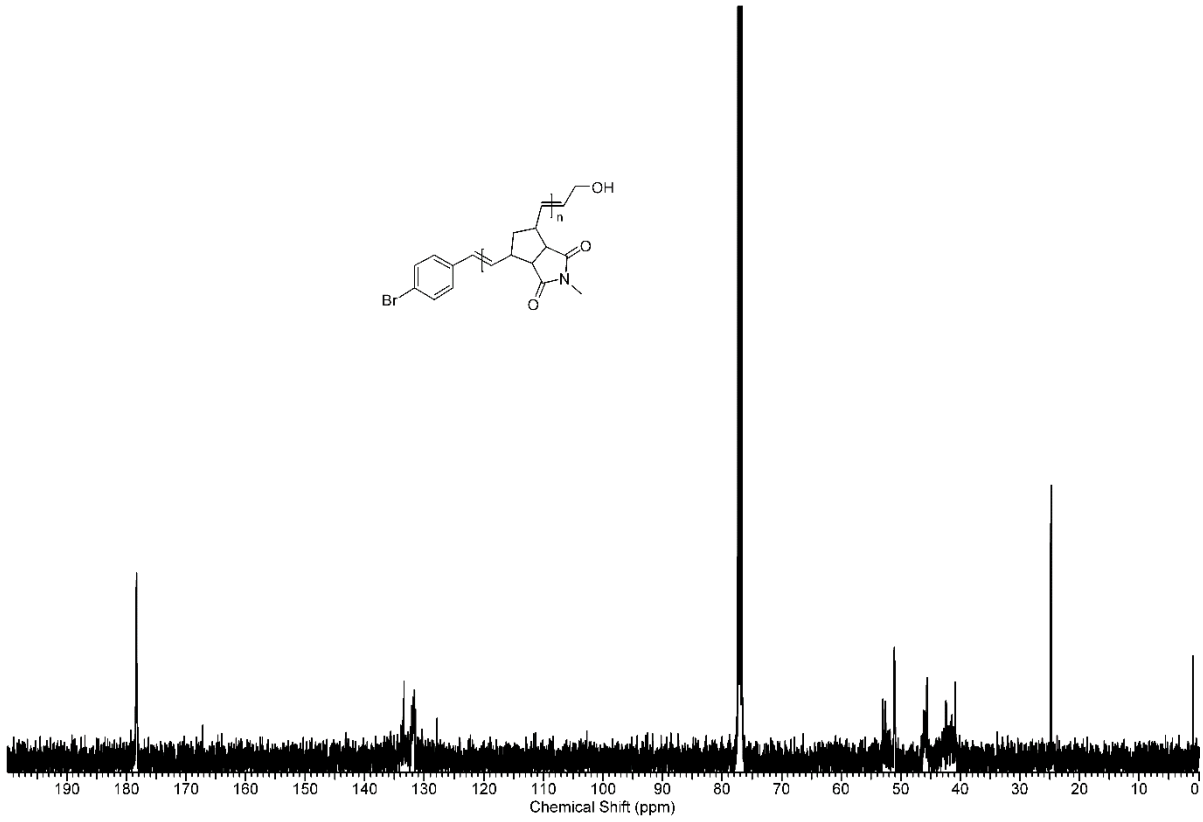


Figure S72: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly b**.

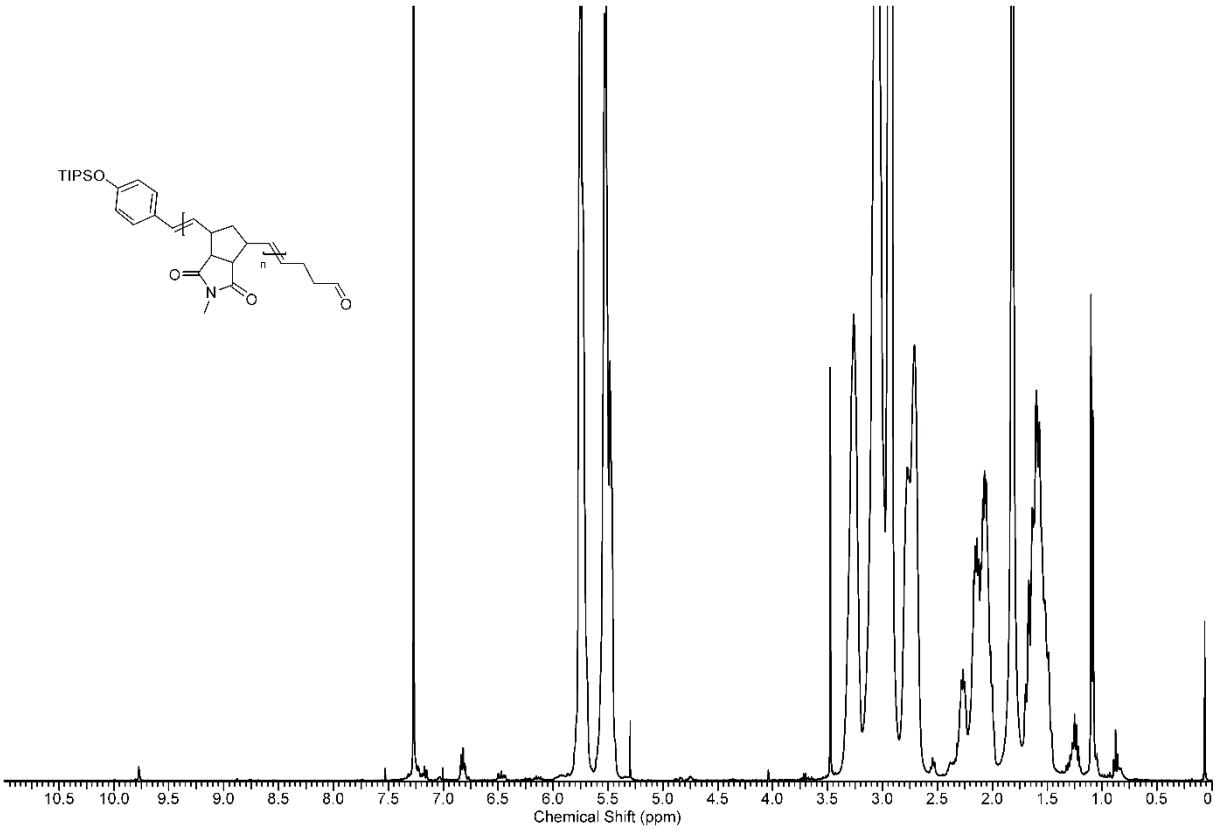


Figure S73: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly c**.

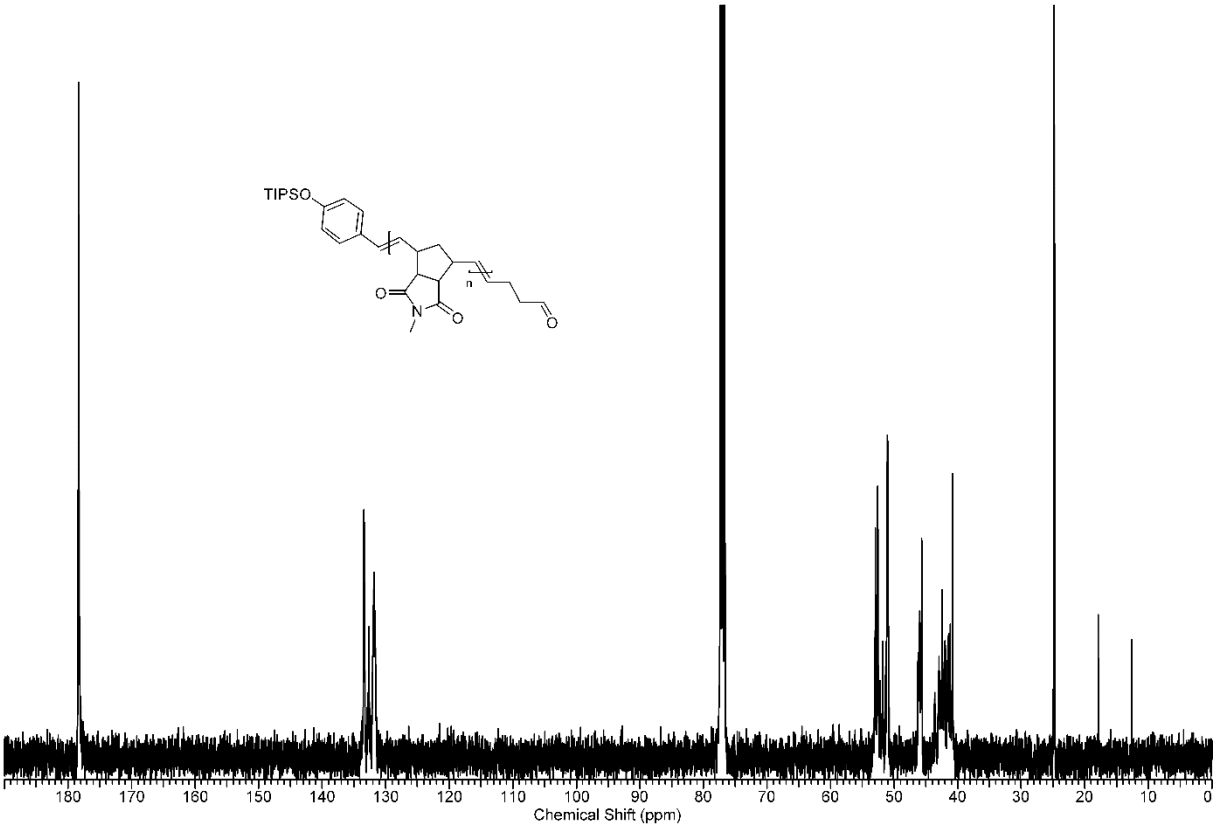


Figure S74: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly c**.

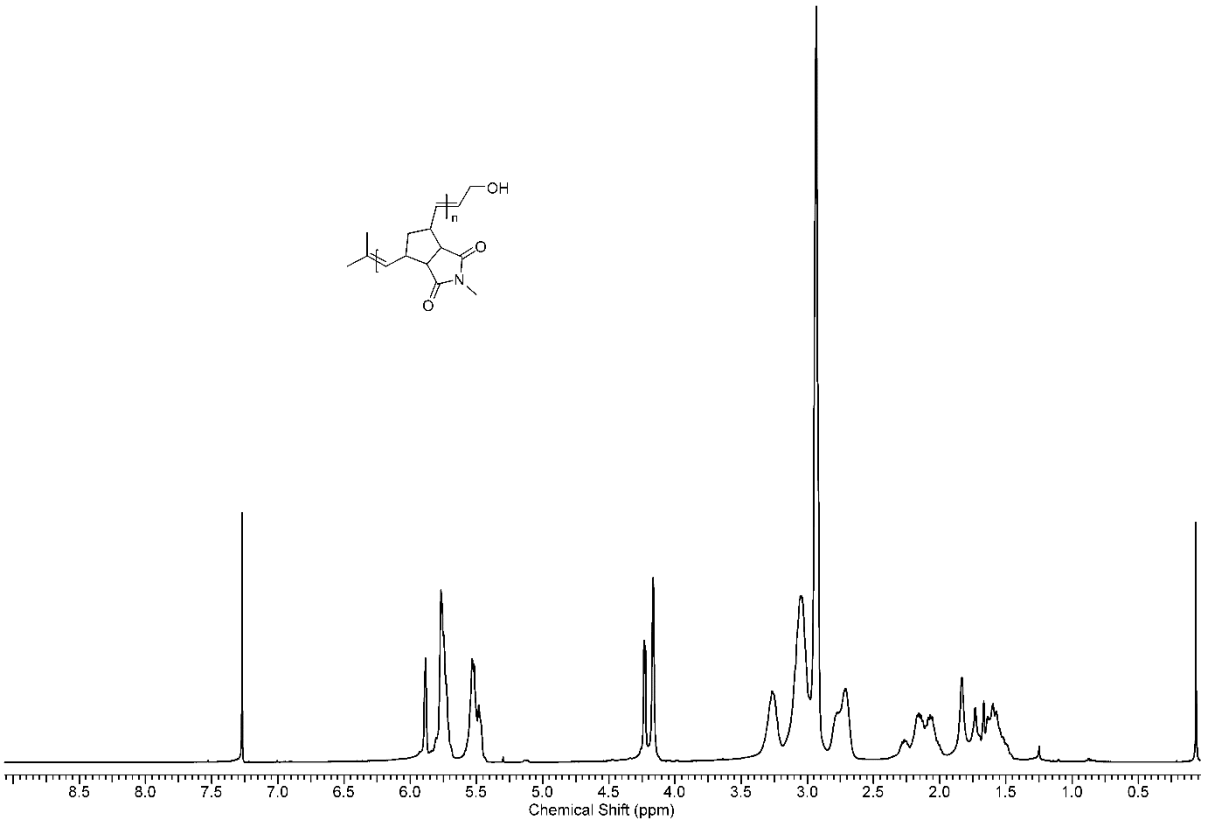


Figure S75: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly d**.

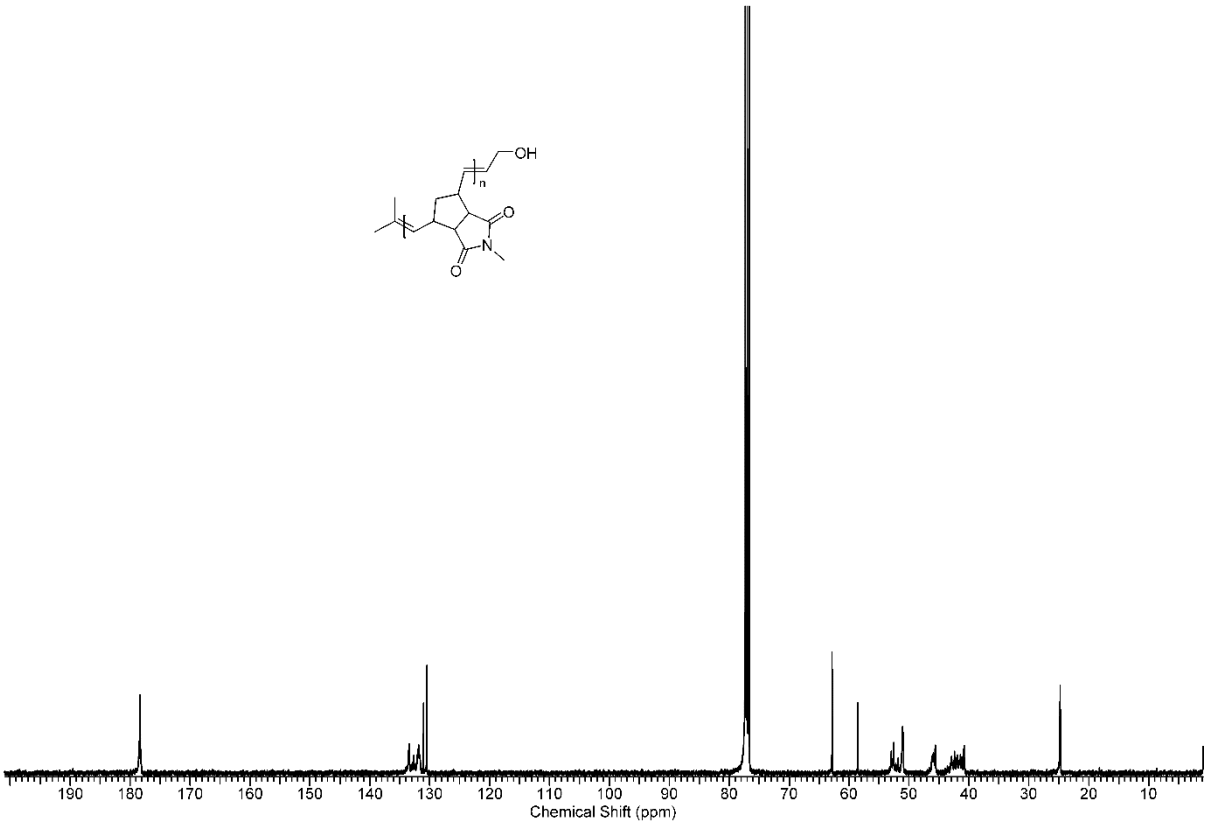


Figure S76: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly d**.

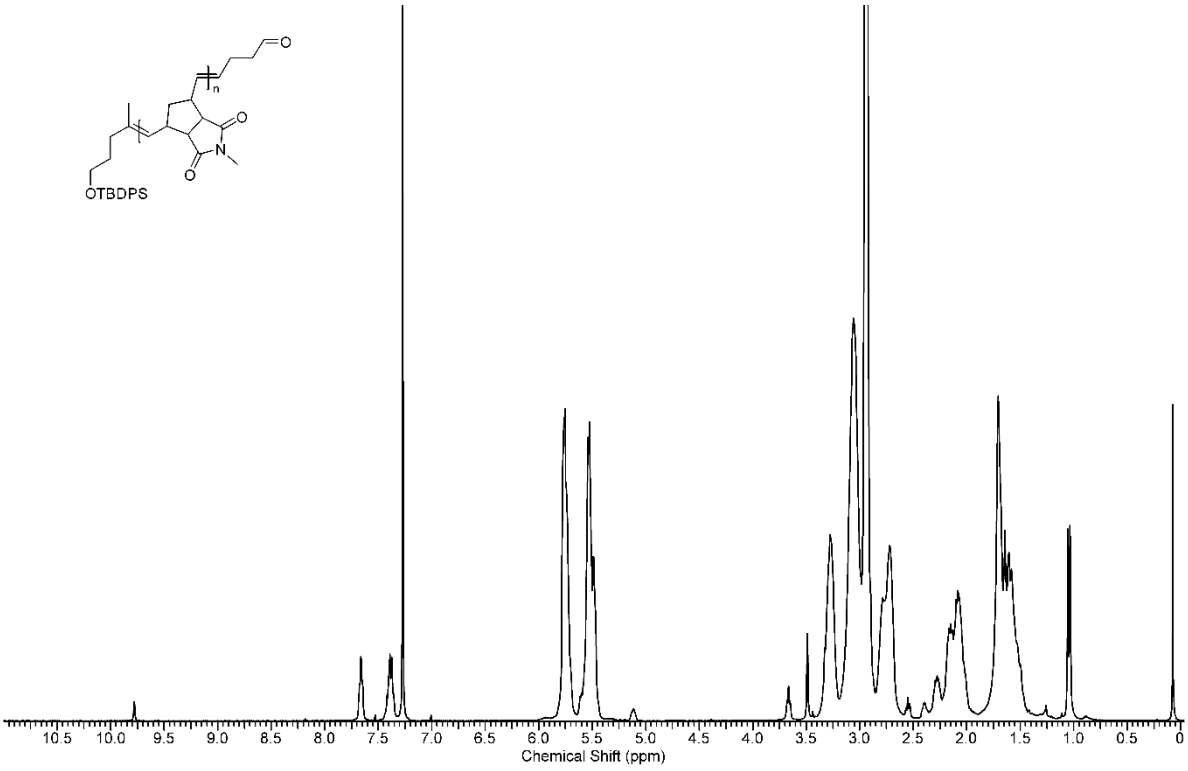


Figure S77: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly e**.

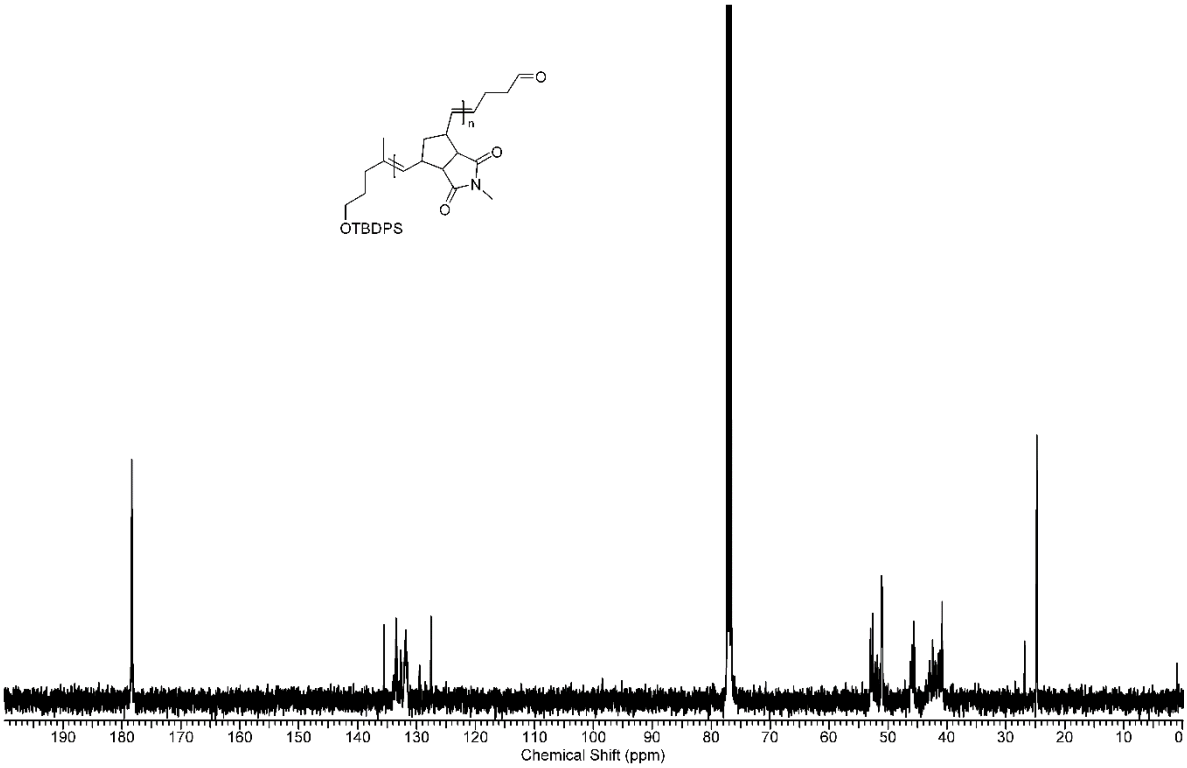


Figure S78: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly e**.

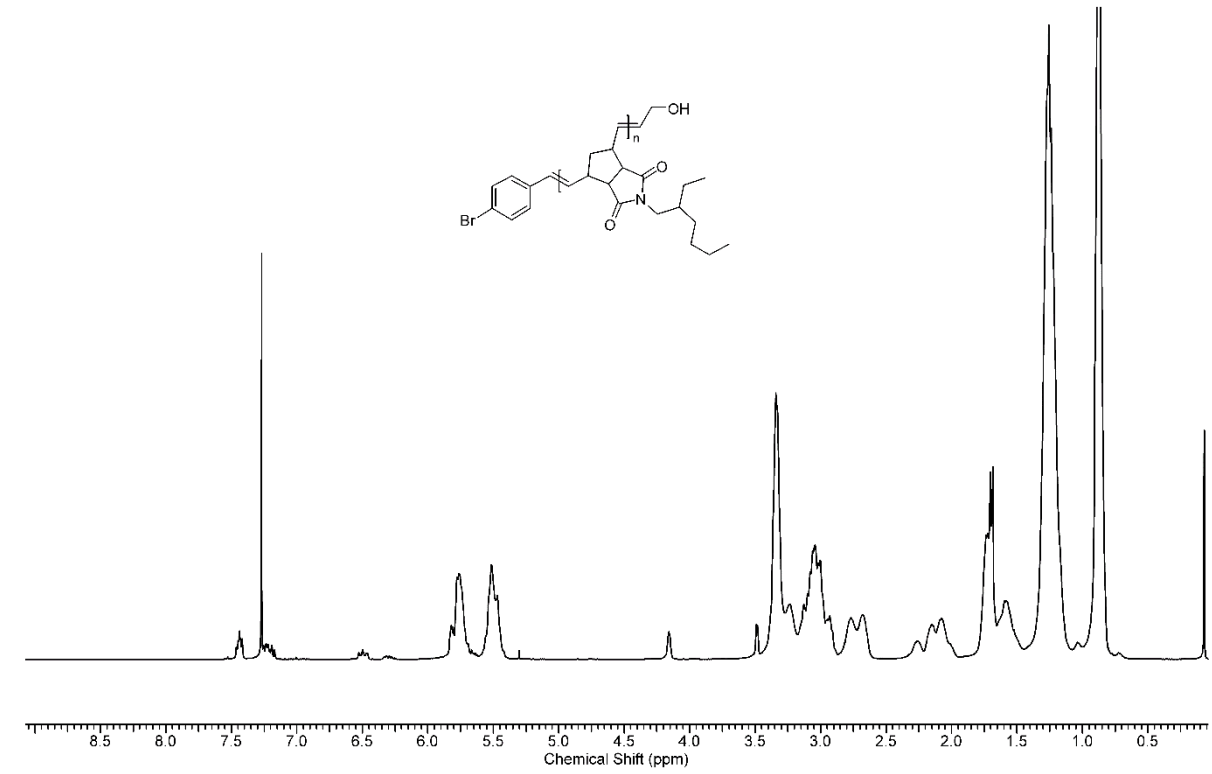


Figure S79: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly f**.

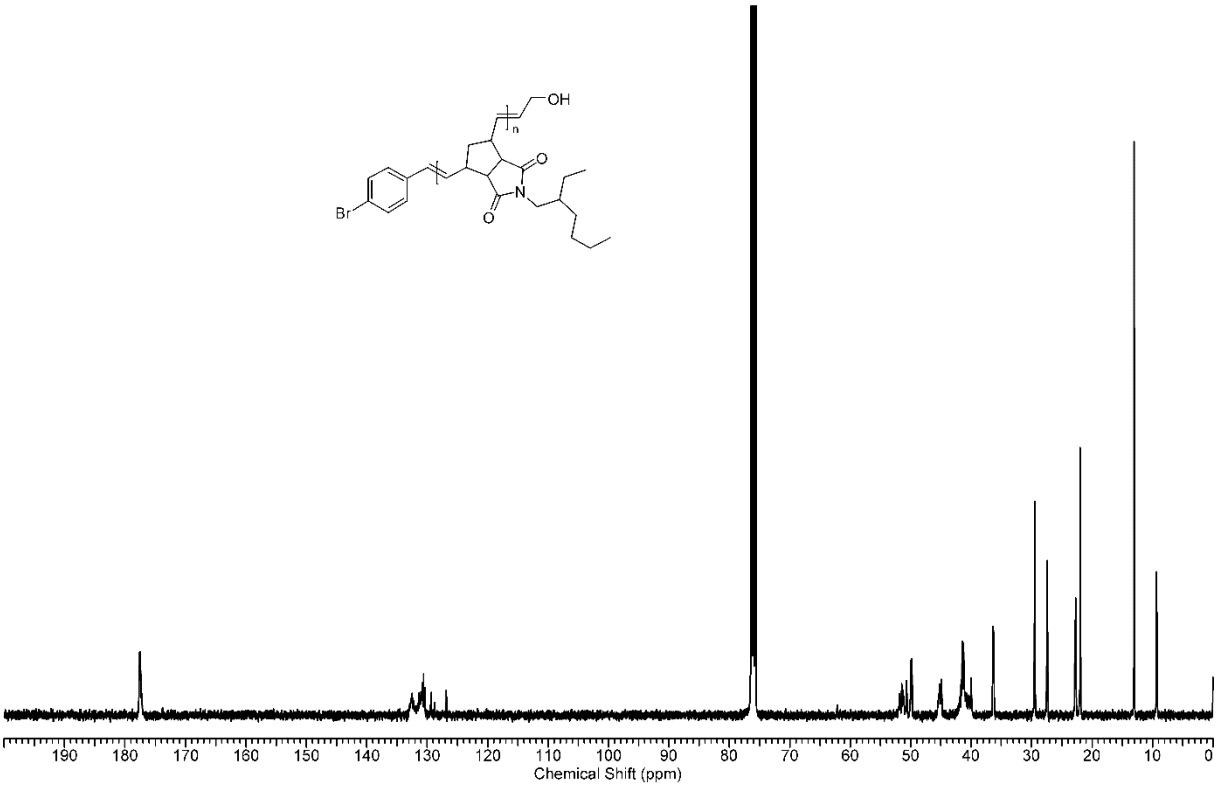


Figure S80: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly f**.

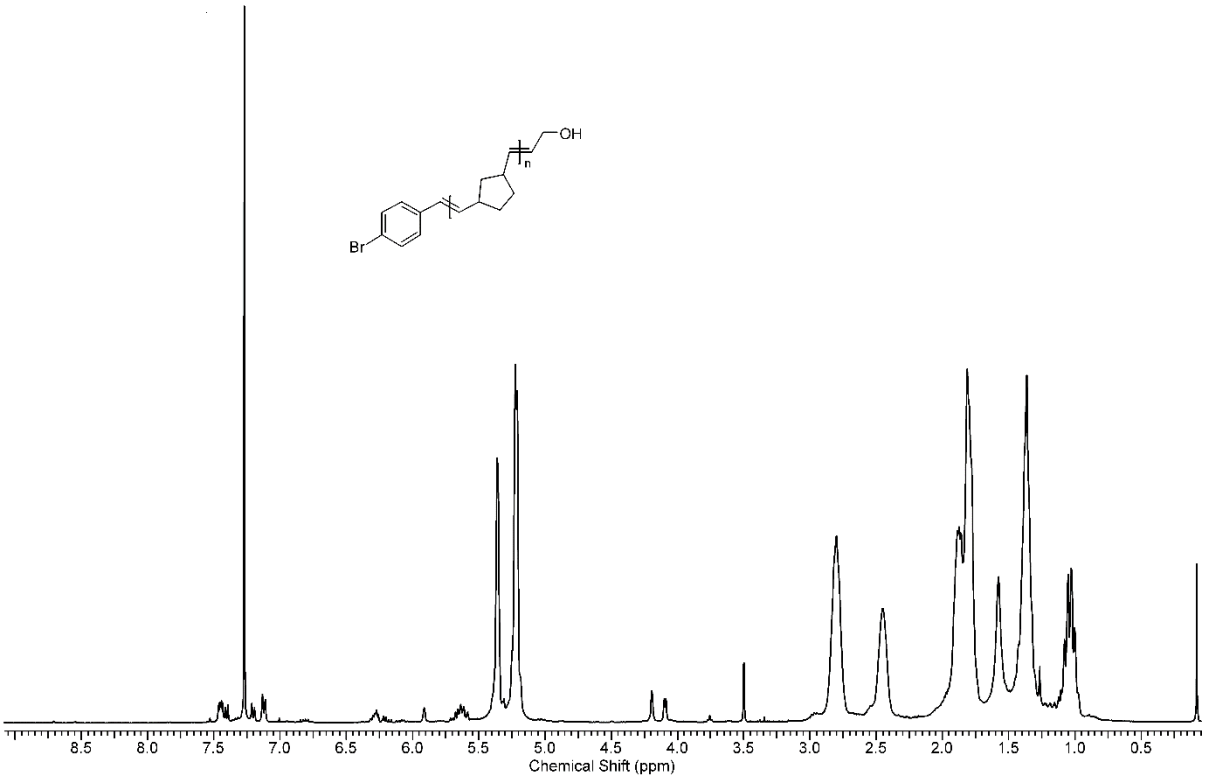


Figure S81: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly g**.

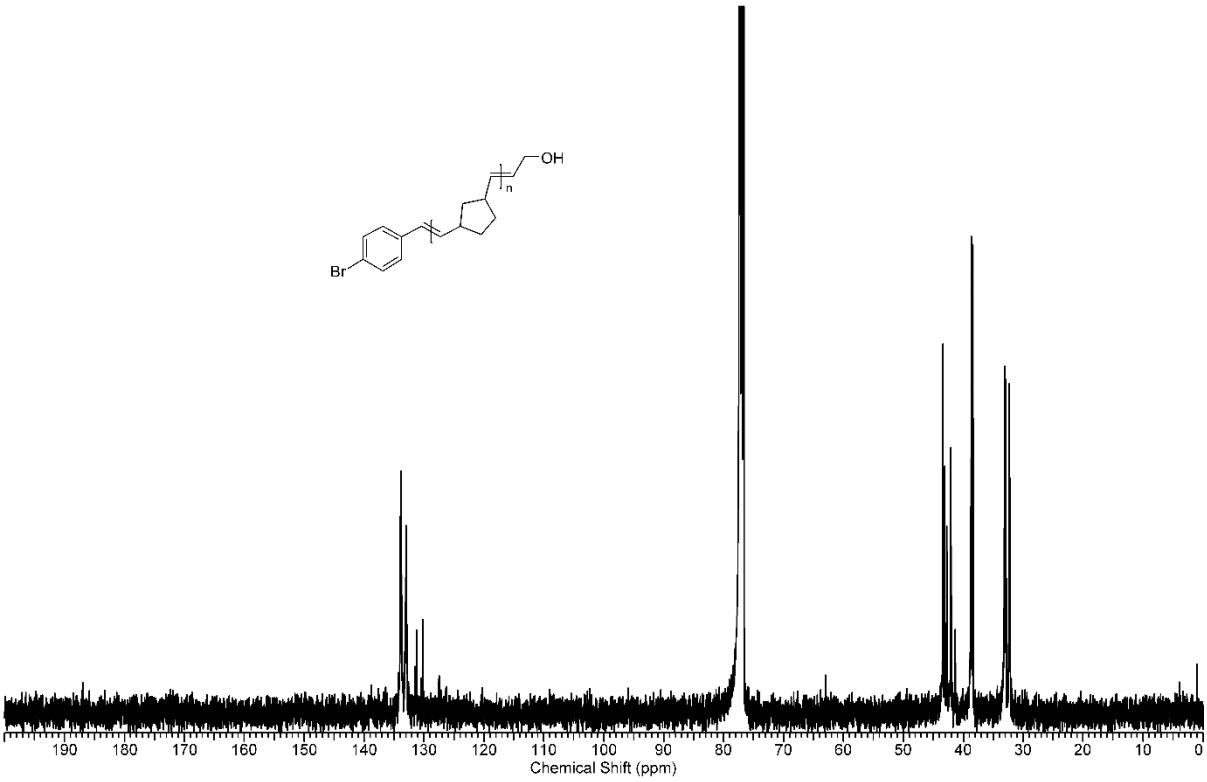


Figure S82: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly g**.

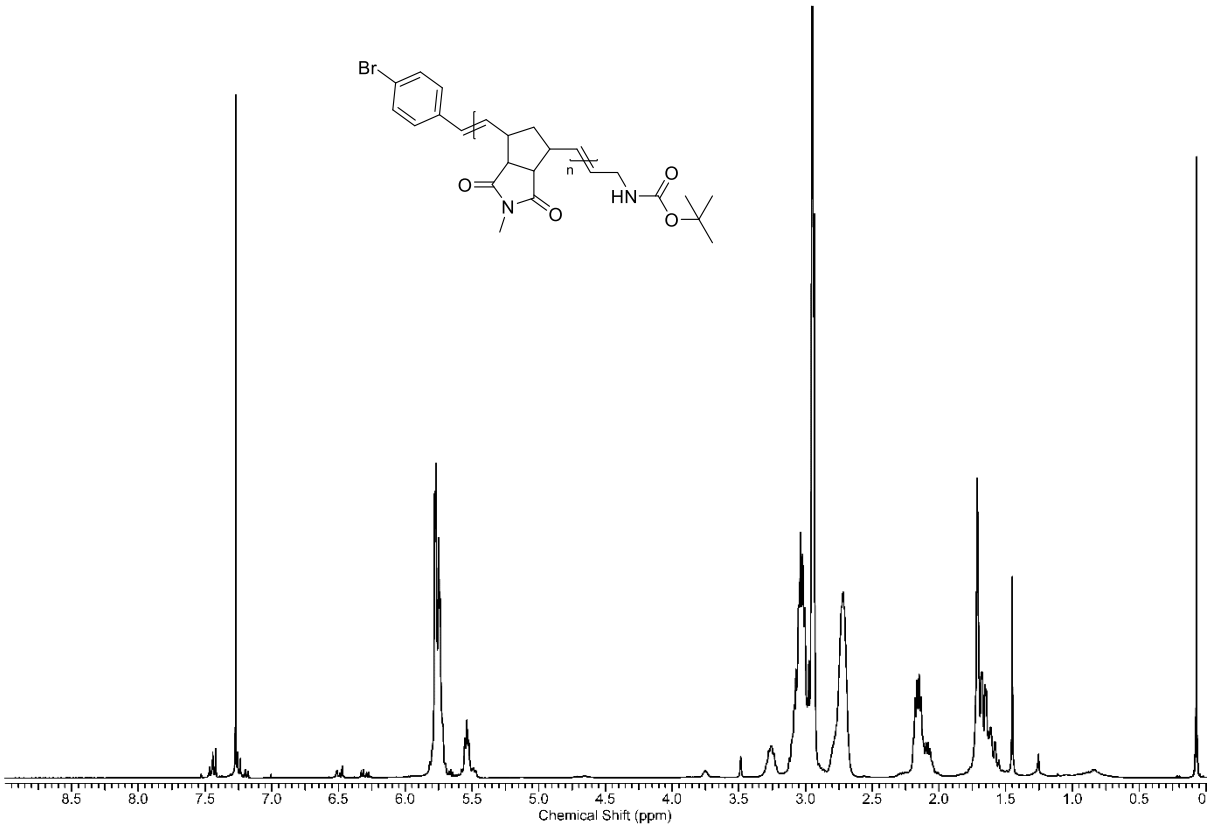


Figure S83: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly h**.

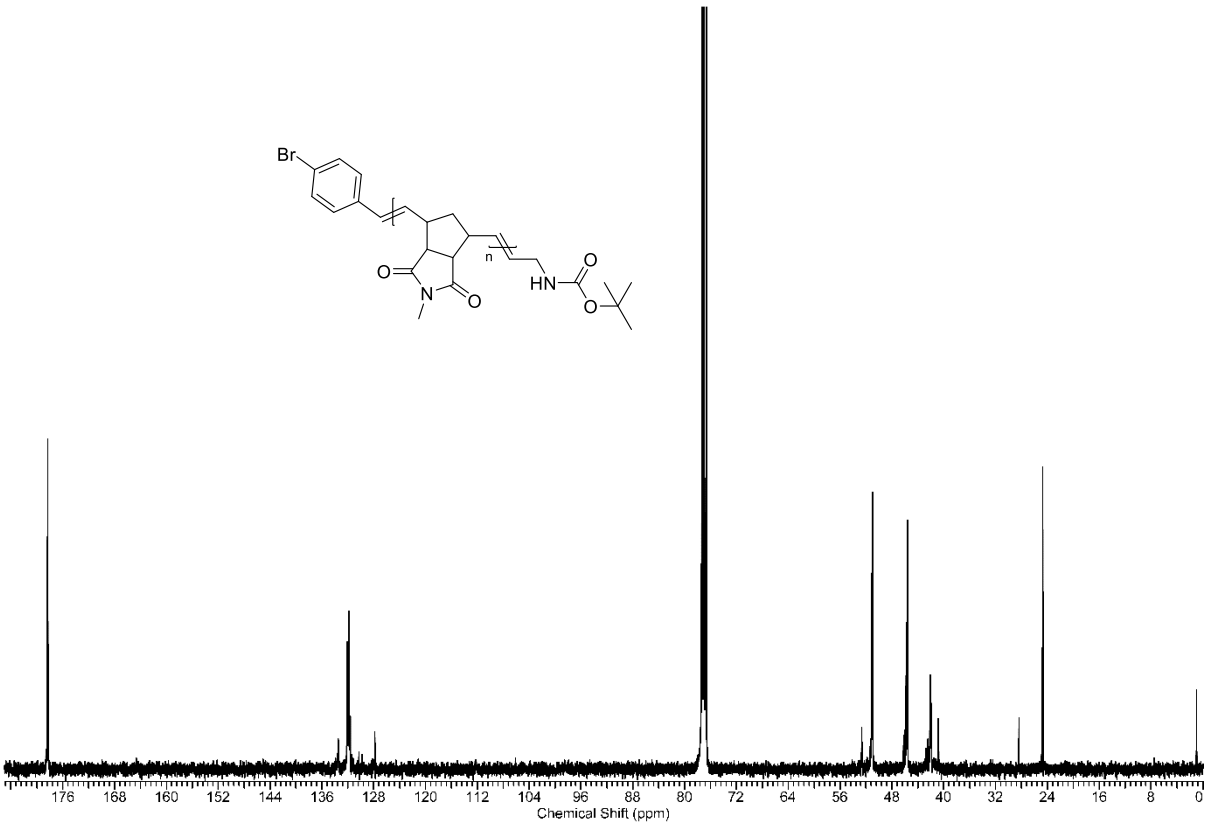


Figure S84: ^{13}C NMR (chloroform-d, 101 MHz) spectrum of **poly h**.

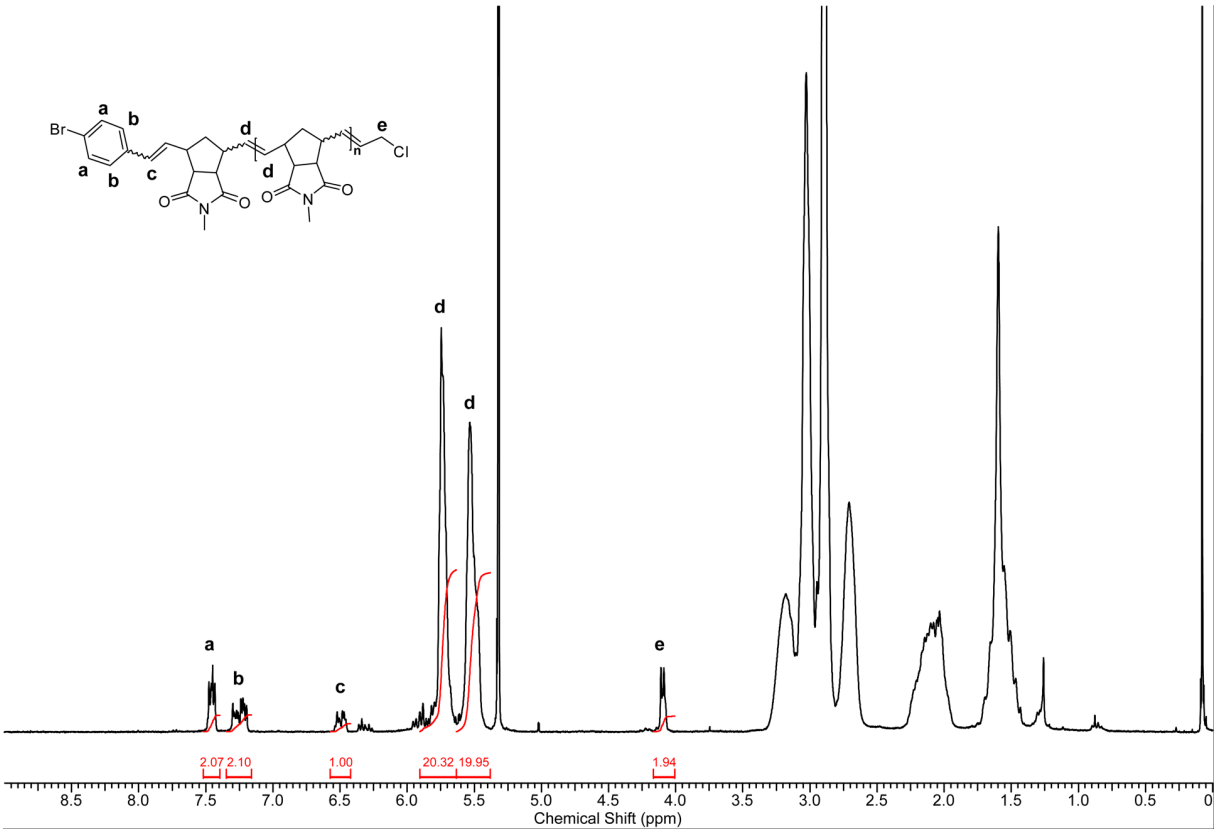


Figure S85: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of **poly j**.

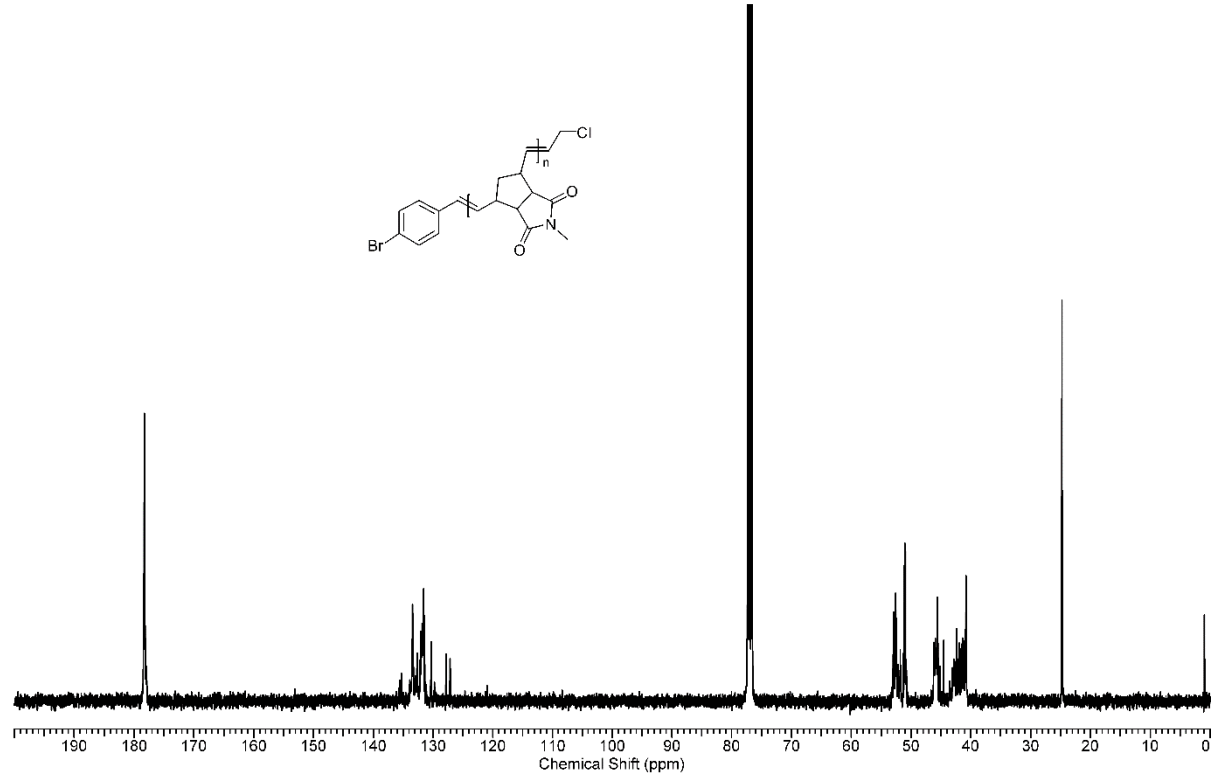


Figure S86: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly j**.

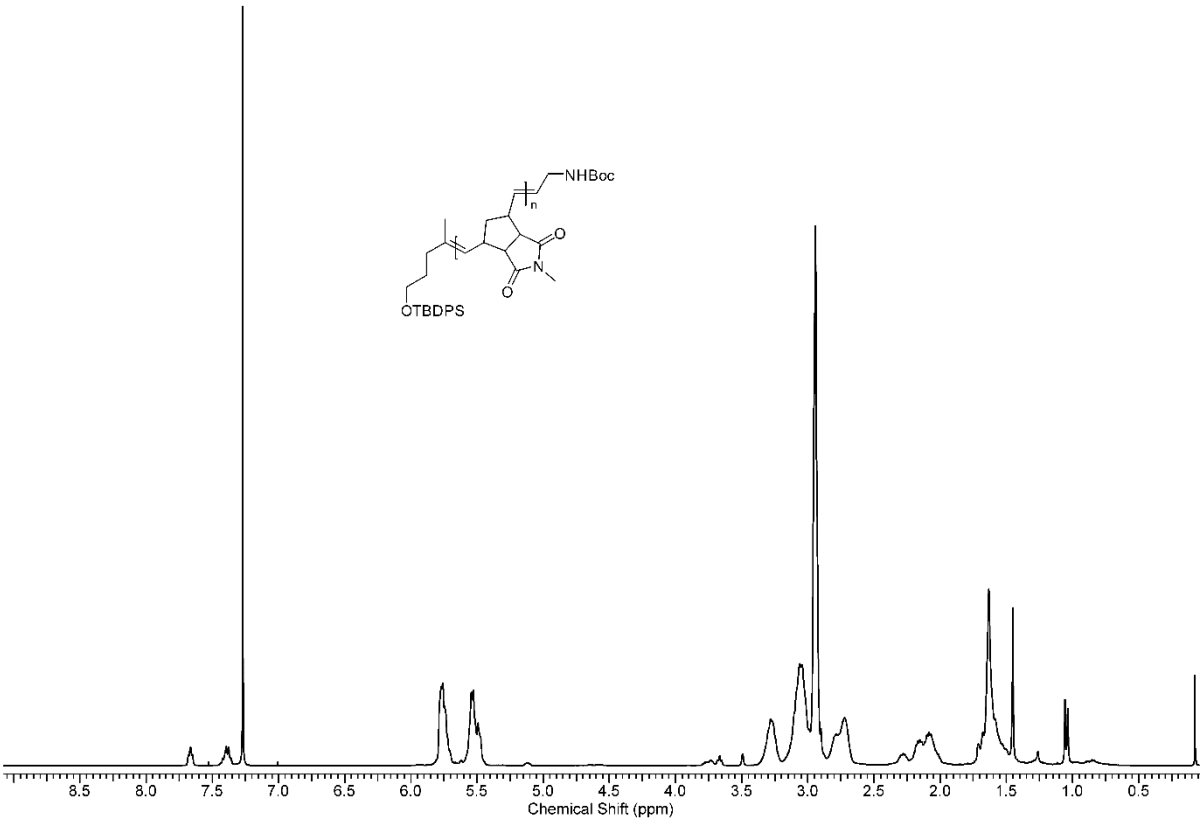


Figure S87: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly k**.

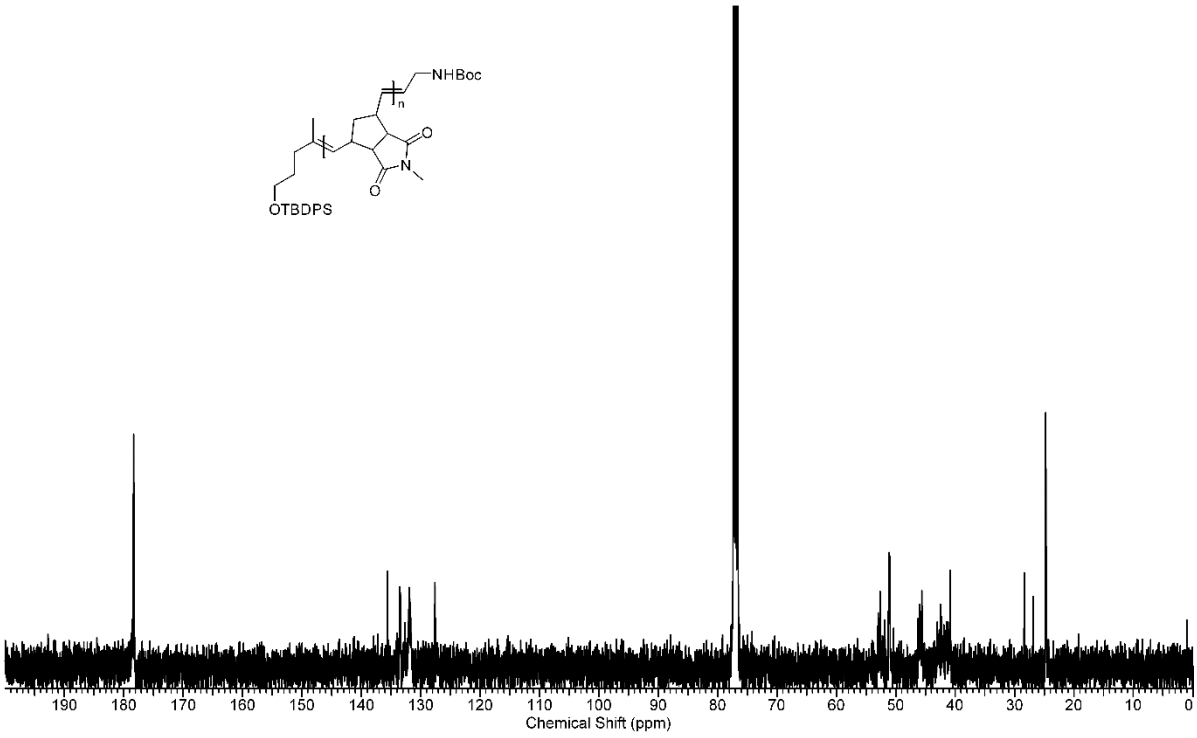


Figure S88: ^{13}C NMR (chloroform-d, 101 MHz) spectrum of **poly k**.

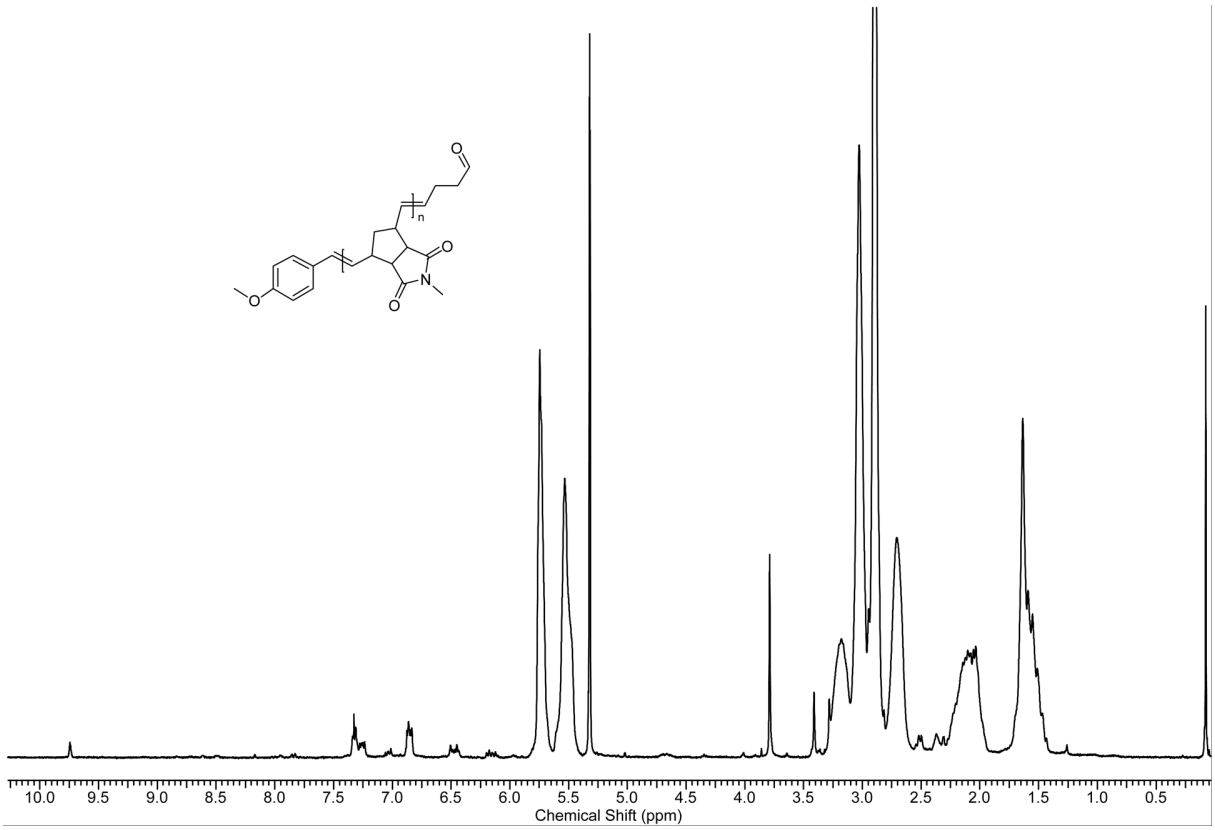


Figure S89: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of **poly l**.

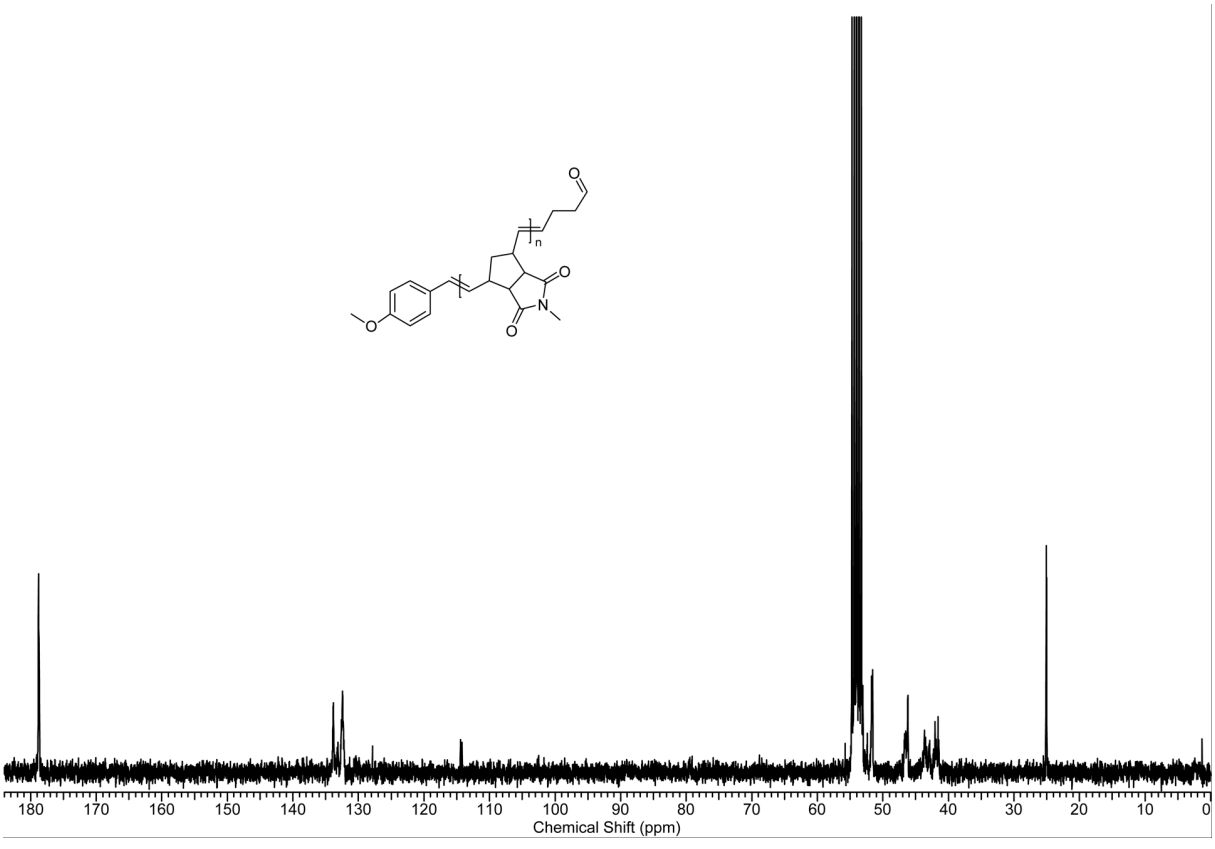


Figure S90: ^{13}C NMR (dichloromethane-d_2, 75 MHz) spectrum of **poly l**.

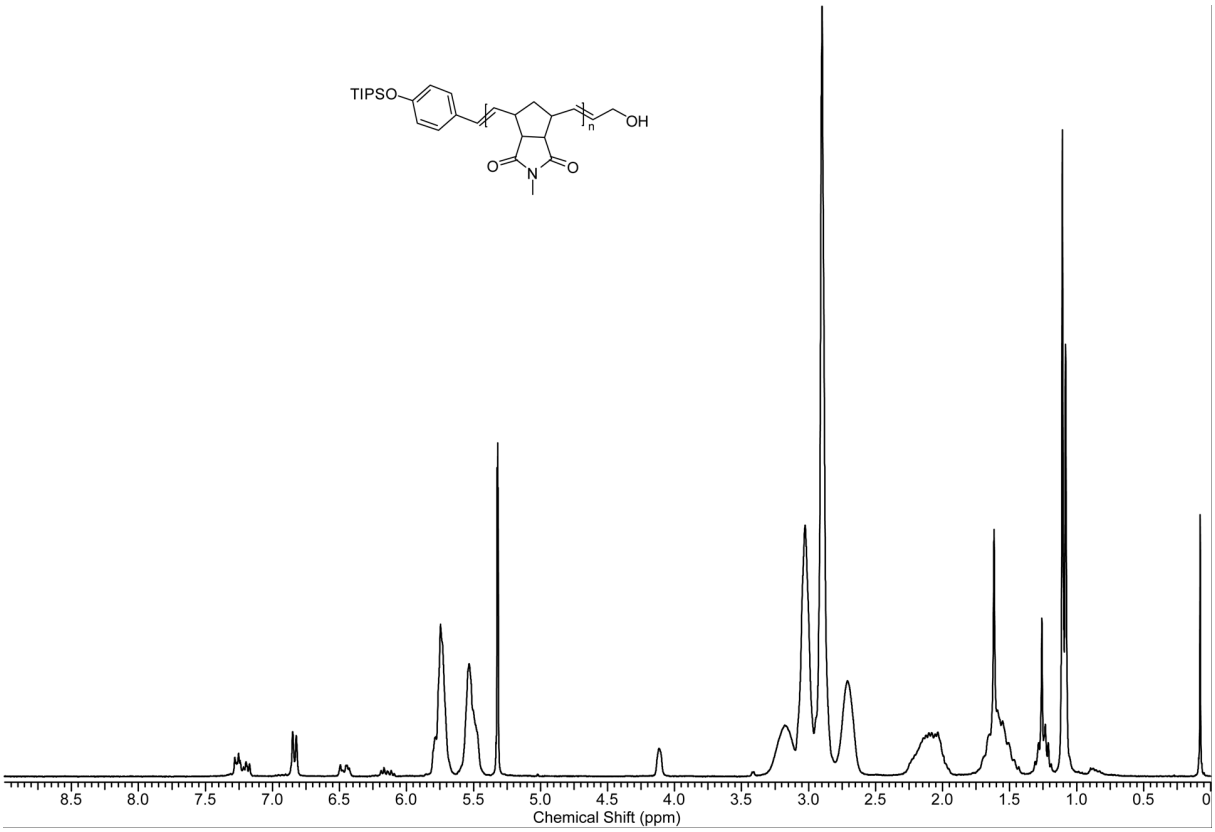


Figure S91: ^{1}H NMR (dichloromethane-d_2, 300 MHz) spectrum of **poly m**.

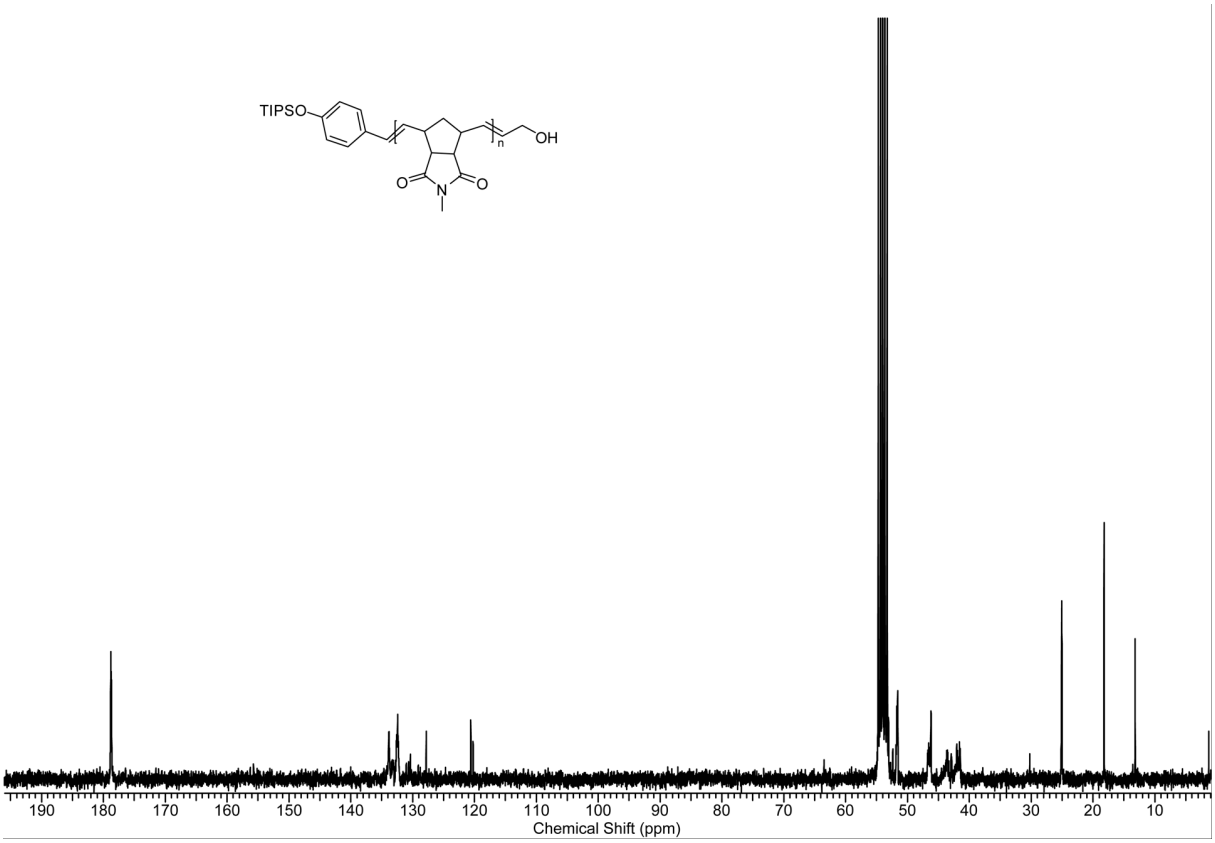


Figure S92: ^{13}C NMR (dichloromethane-d_2, 75 MHz) spectrum of **poly m**.

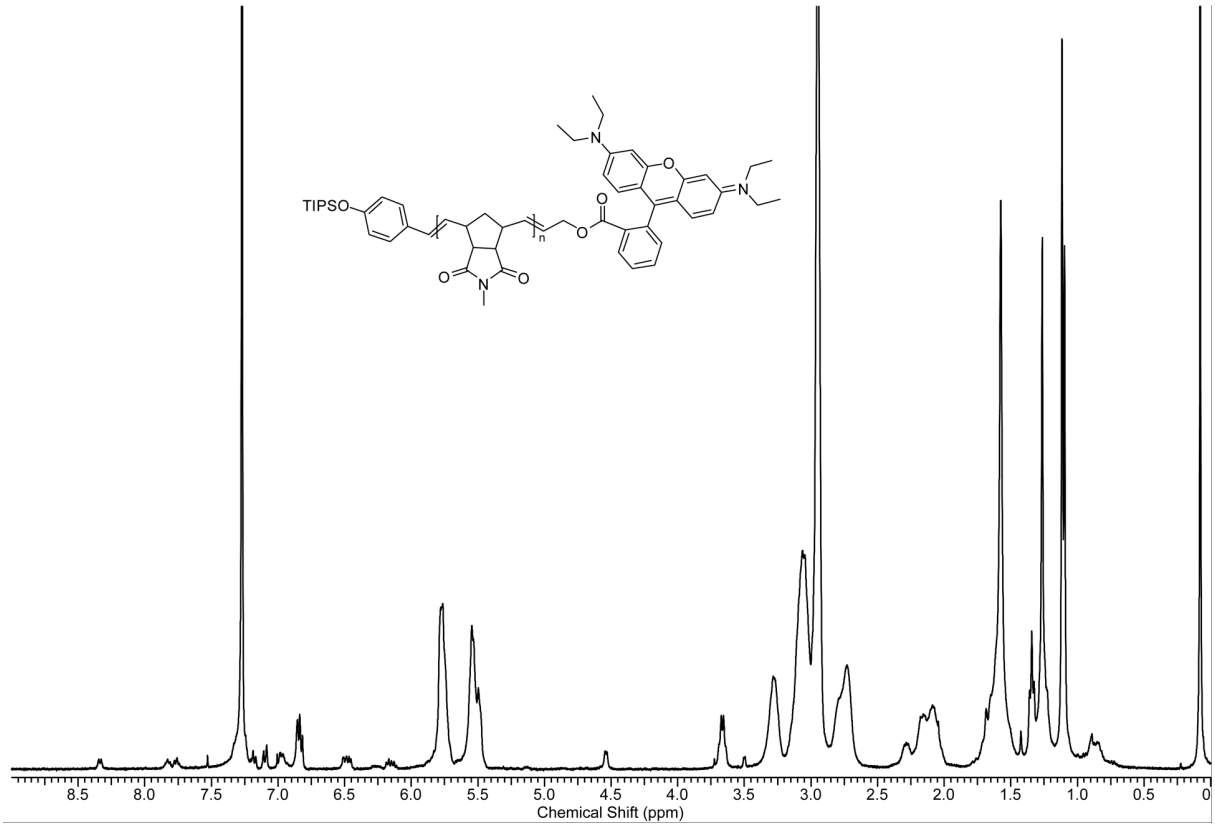


Figure S93: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly n**.

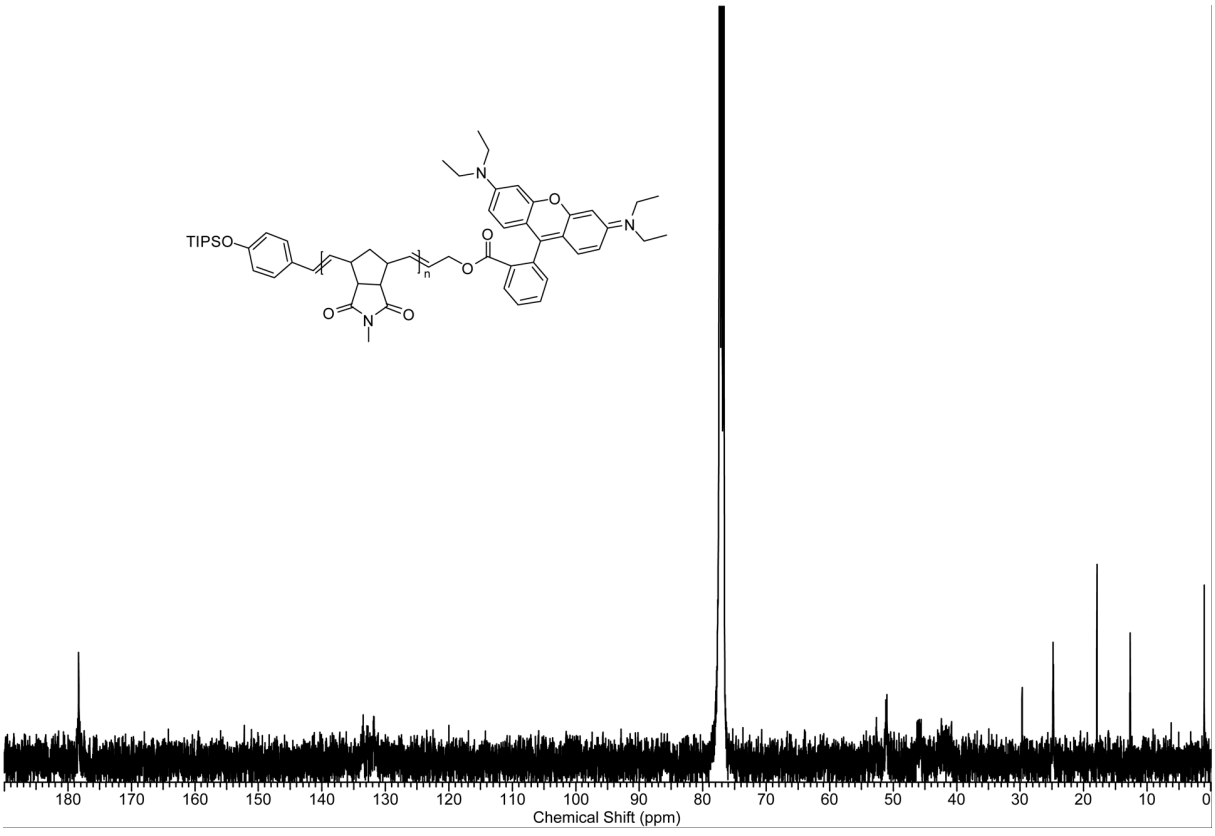


Figure S94: ^{13}C NMR (chloroform-d, 100 MHz) spectrum of **poly n**

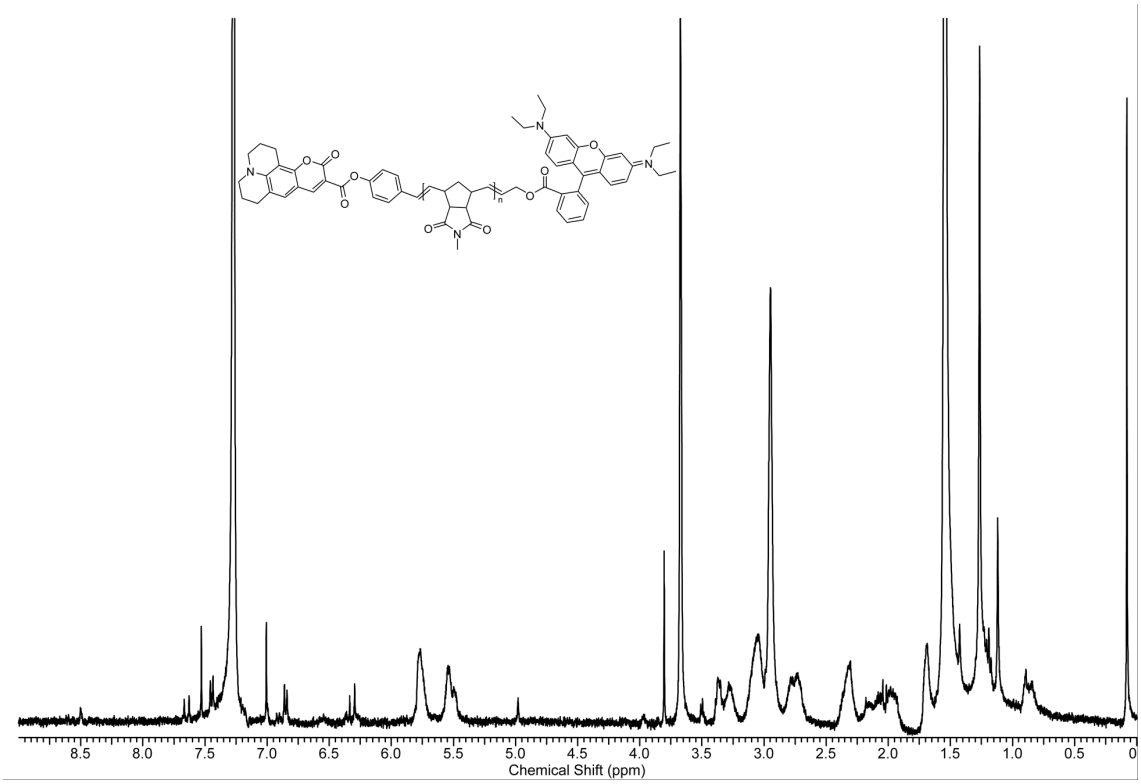


Figure S95: ^{1}H NMR (chloroform-d, 400 MHz) spectrum of **poly p**.

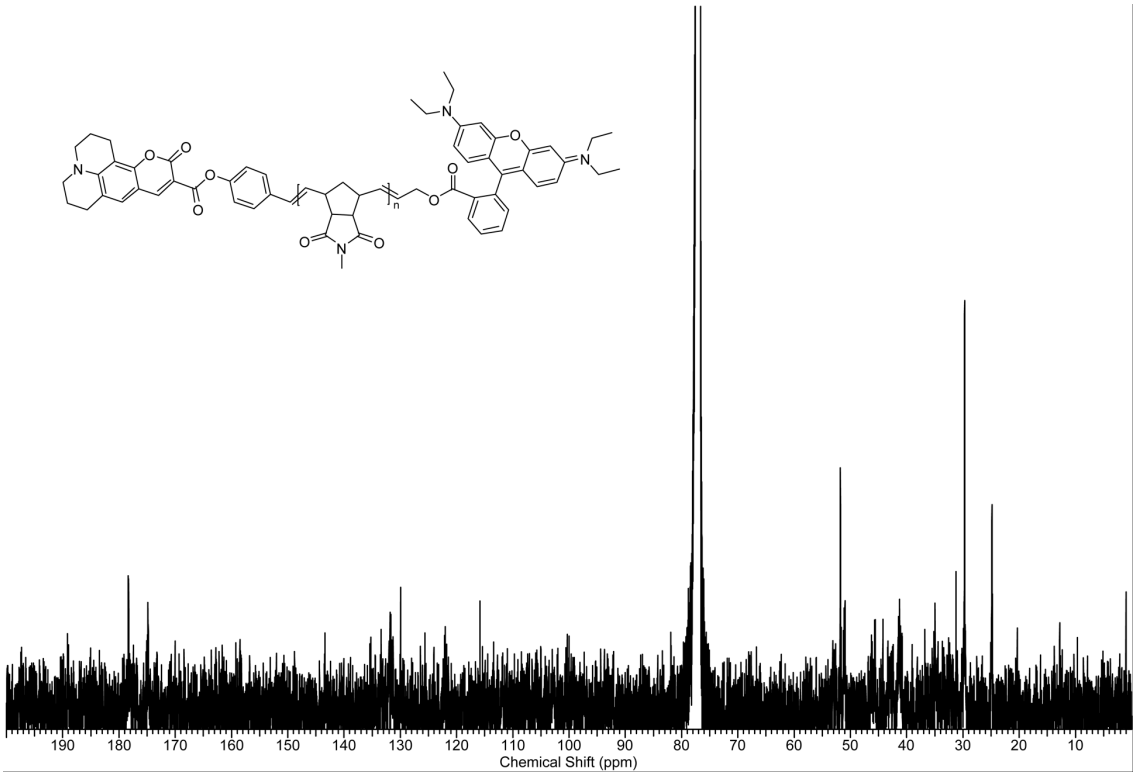


Figure S96: ^{13}C NMR (chloroform-d, 125 MHz) spectrum of **poly p.**

FRET Experiment

Förster resonance transfer (FRET) experiment was performed on polymer **p**, functionalized with Coumarin 343 and Rhodamine B fluorophores, which are supposed to behave respectively as donor and acceptor moieties. The sensitized emission of the acceptor was investigated comparing polymer **p** to polymer **n**, functionalized only with Rhodamine B. The absorption spectra of **p** and **n** were carried out in $CHCl_3$ (**Figure S97**) adjusting the concentrations in order to have the same absorption in the 500-600 nm region (belonging to Rhodamine).

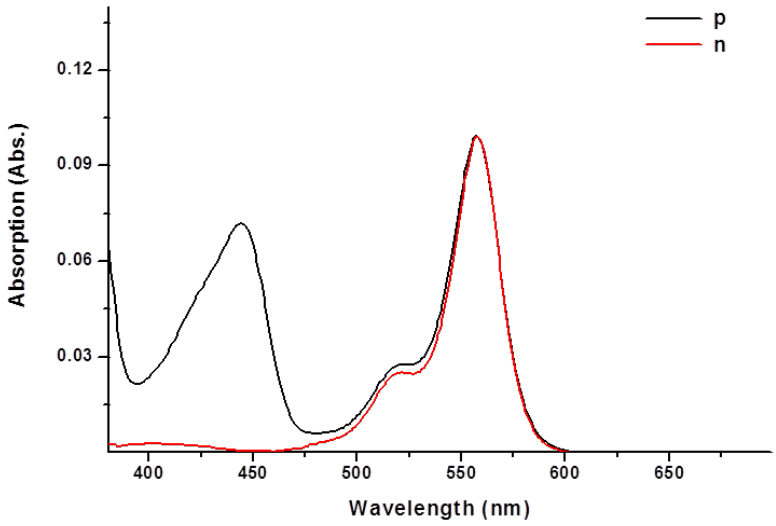


Figure S97: Absorption spectra of optically diluted solutions of **Poly p** (black) and **Poly n** (red) in $CHCl_3$.

Emission spectra were acquired exciting two optically diluted solutions of polymers at λ_{exc} = 435 nm. (**Figure S98**). Emission spectrum of poly n shows one peak belonging to Rhodamine (λ_{max} = 575 nm) while Poly p presents two emission peaks at 468 nm and 575 nm, respectively assigned to Coumarin and Rhodamine. The presence of FRET is evidenced by the almost 8-fold higher intensity of Rhodamine peak observed in p with respect to n.

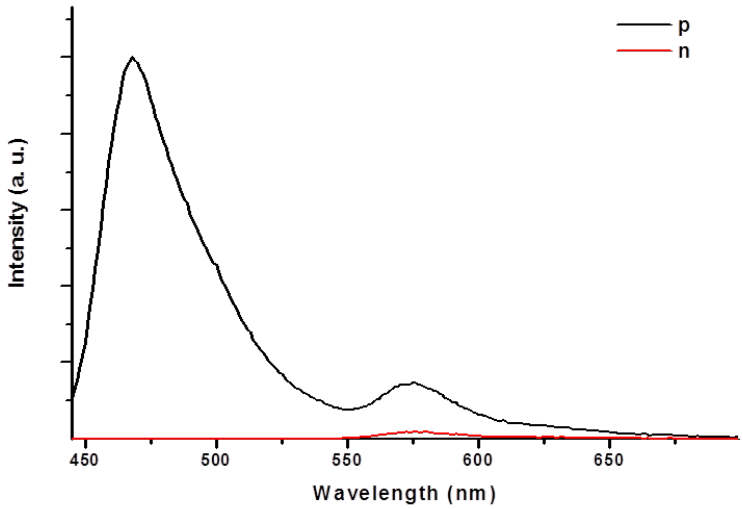


Figure S98: Emission spectra of **p** (black) **n** (red) in $CHCl_3$ at λ_{exc} = 435 nm.

A FRET efficiency of 12% was calculated according to equation (X) where φ_{Rhod} is the quantum yield of Rhodamine B, φ_{Coum} is the quantum yield of Coumarin 343, I_{DA} and I_{AD} are the emission intensities of Coumarin and Rhodamine in **p** and I_A is the emission intensity of Rhodamine in **n**.[5]

$$E = \left(1 + \frac{\varphi_{Rhod}}{\varphi_{Coum}} \frac{I_{DA}}{I_{AD} - I_A}\right)^{-1} \quad \text{(X)}$$

High resolution mass spectrometric data

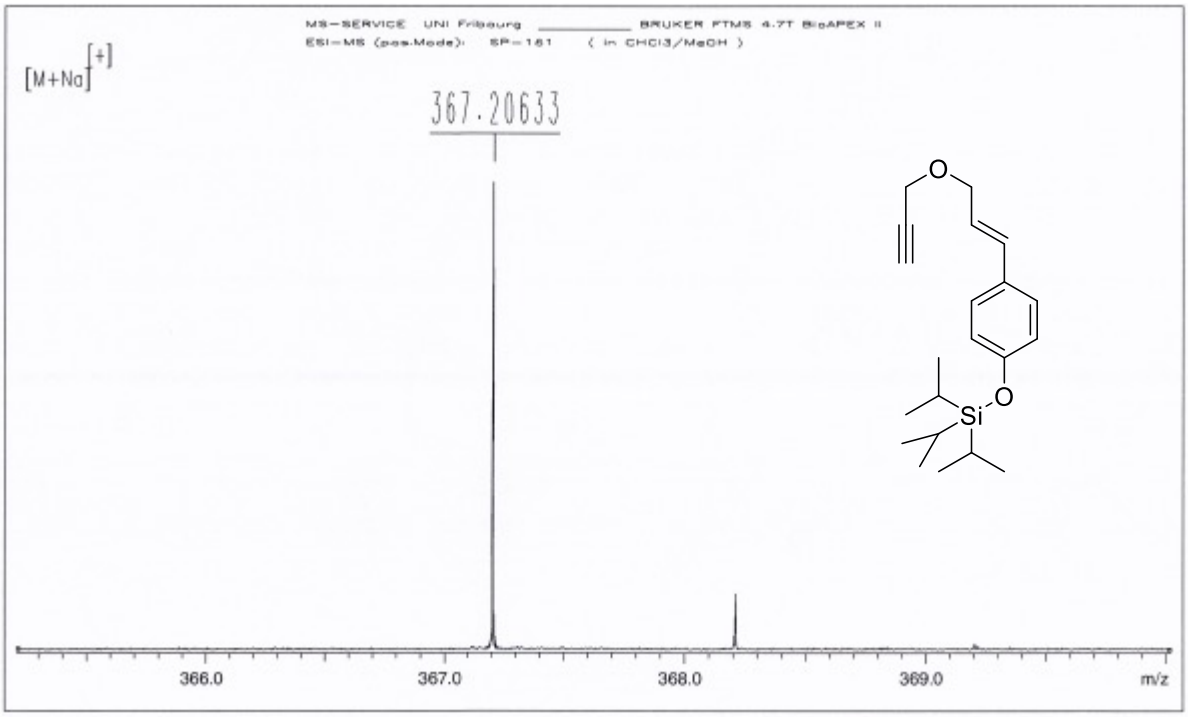


Figure S99: HR-MS spectrum of **2**.

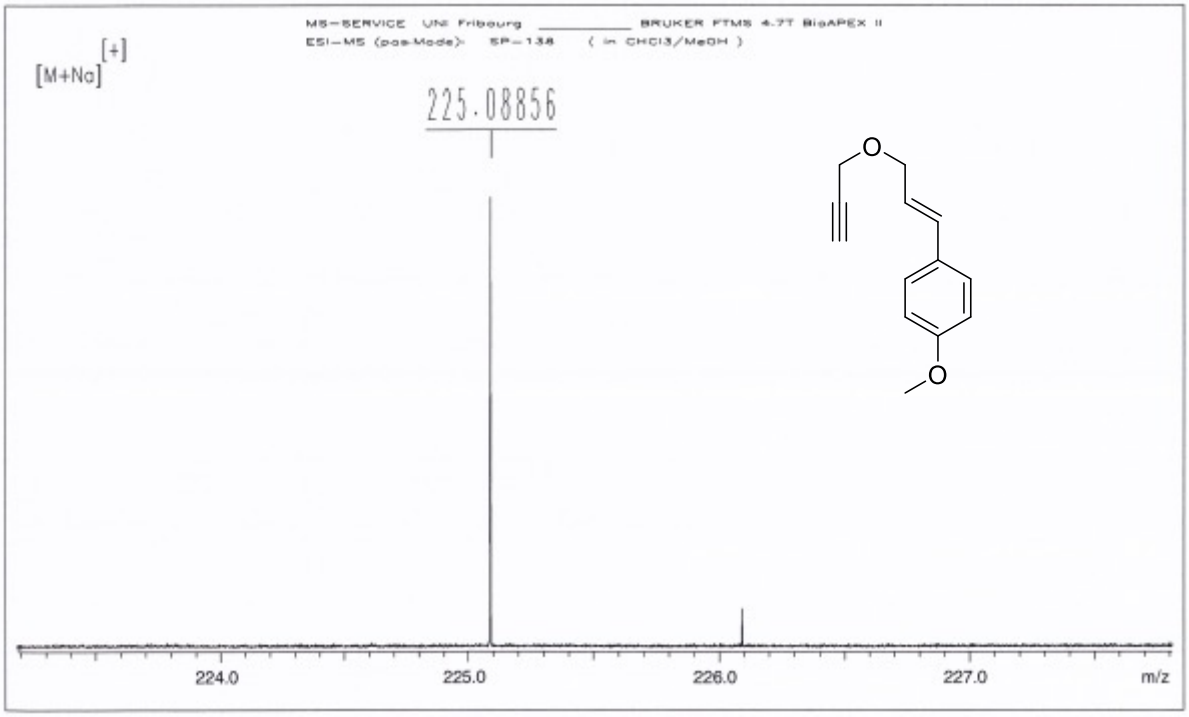


Figure S100: HR-MS spectrum of **4**.

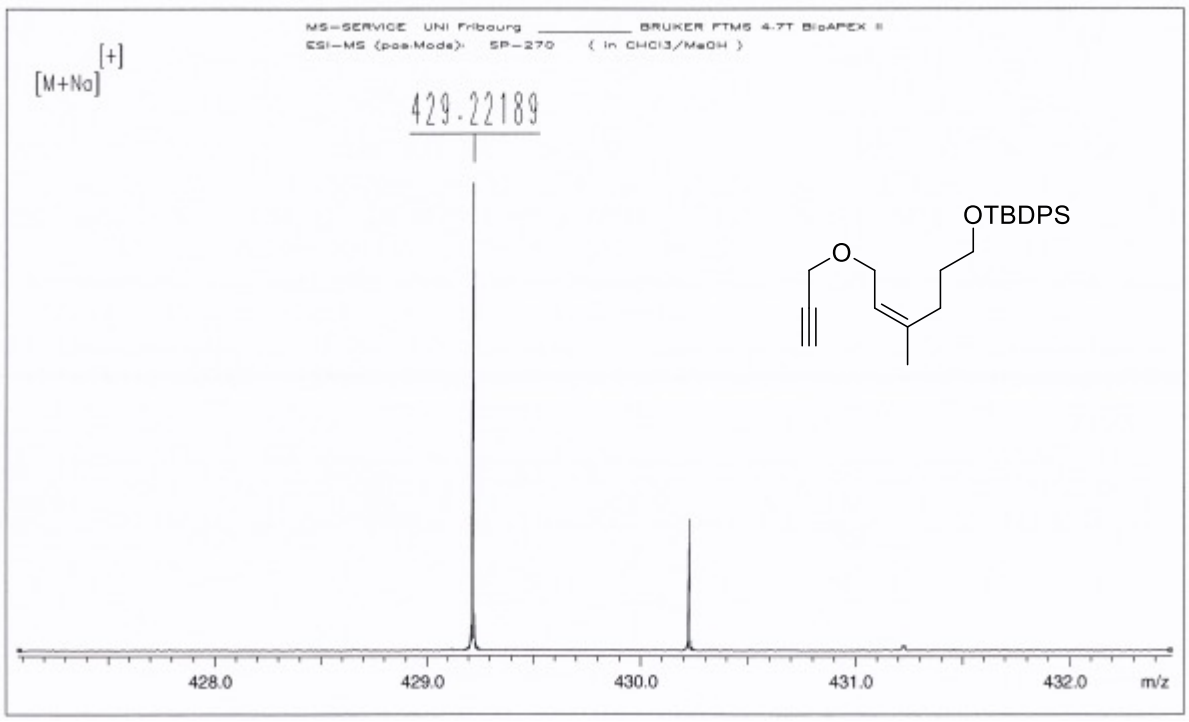


Figure S101: HR-MS spectrum of **5**.

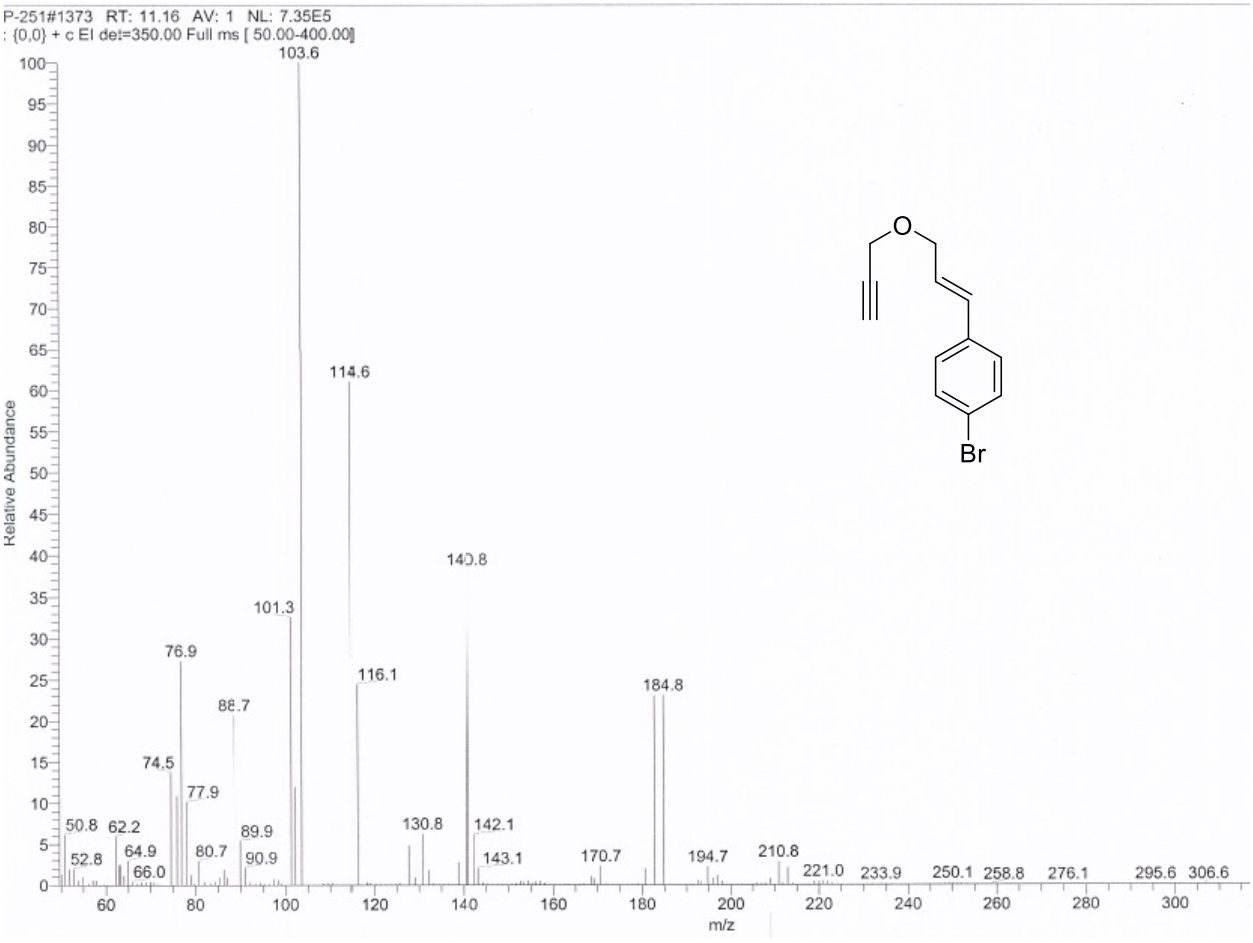


Figure S102: GC-MS spectrum of **3**.

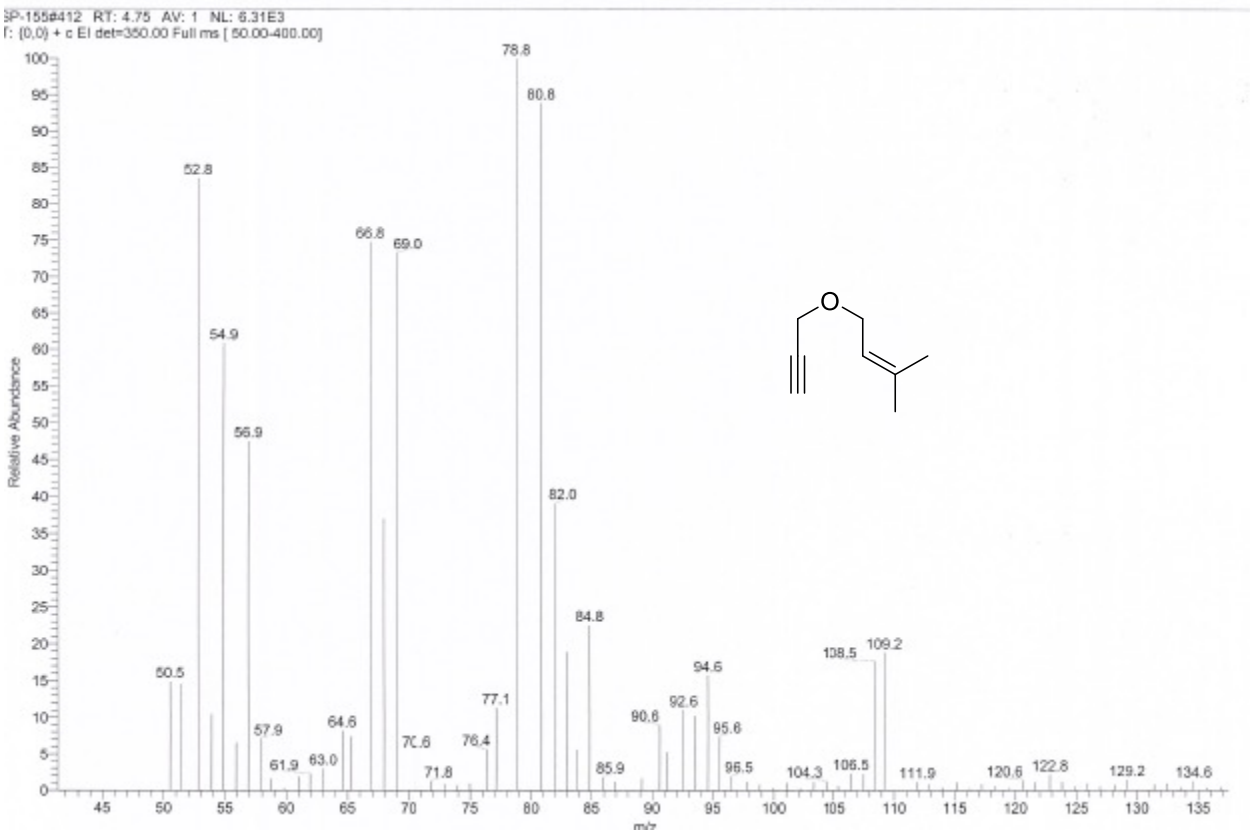


Figure S103: GC-MS spectrum of **6**.

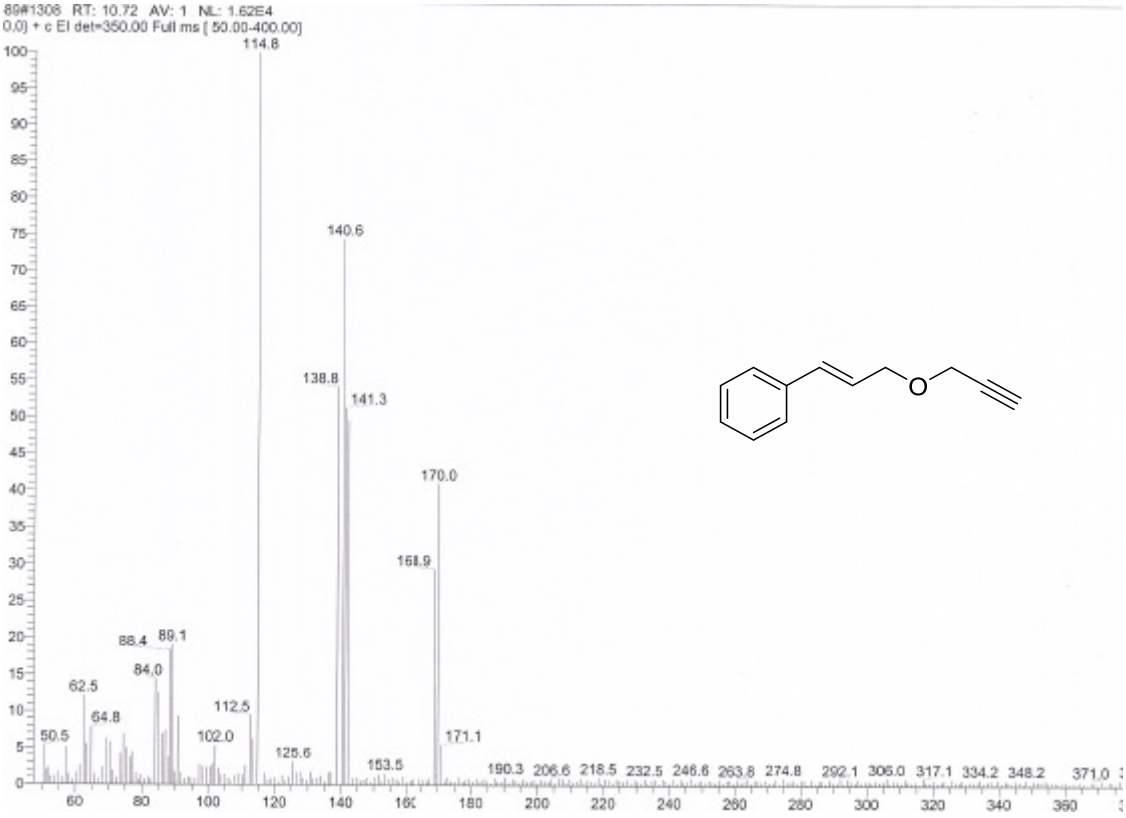


Figure S104: GC-MS spectrum of **1**.

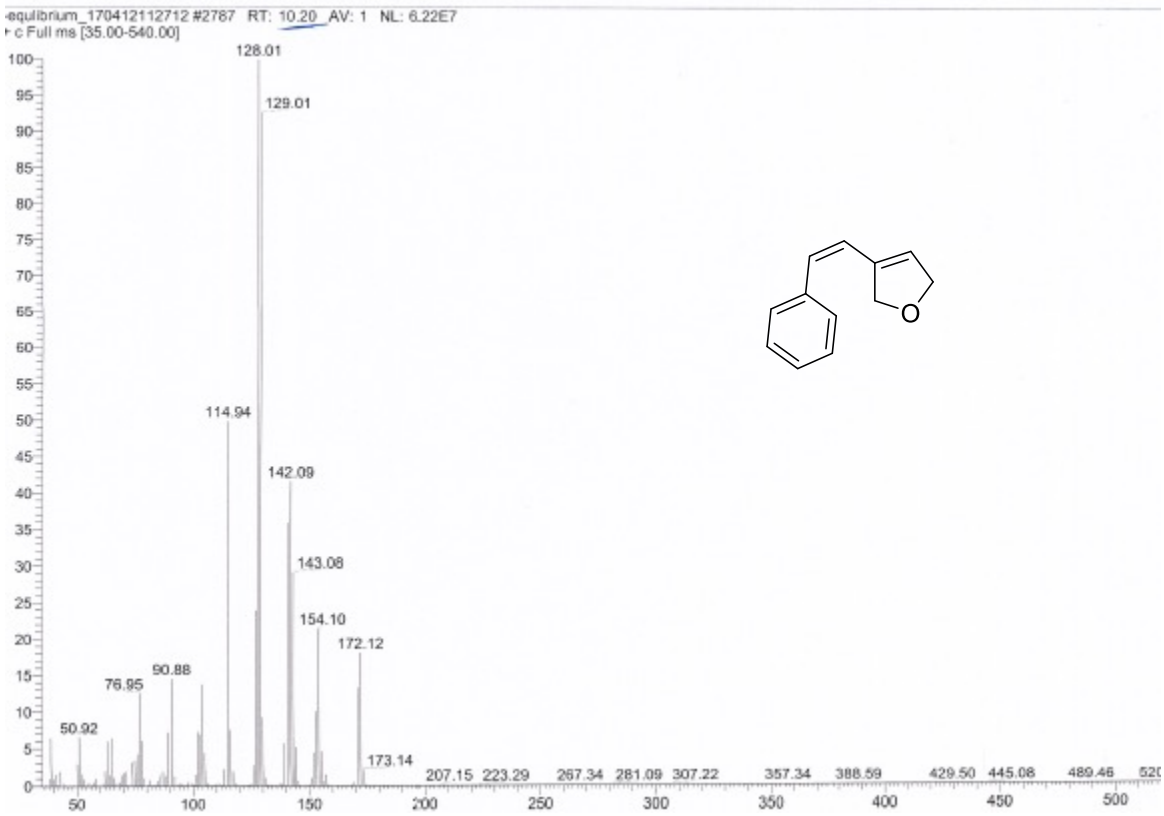


Figure S105: GC-MS spectrum of (Z)-3-styryl-2, 5-dihydrofuran (**DHF**).

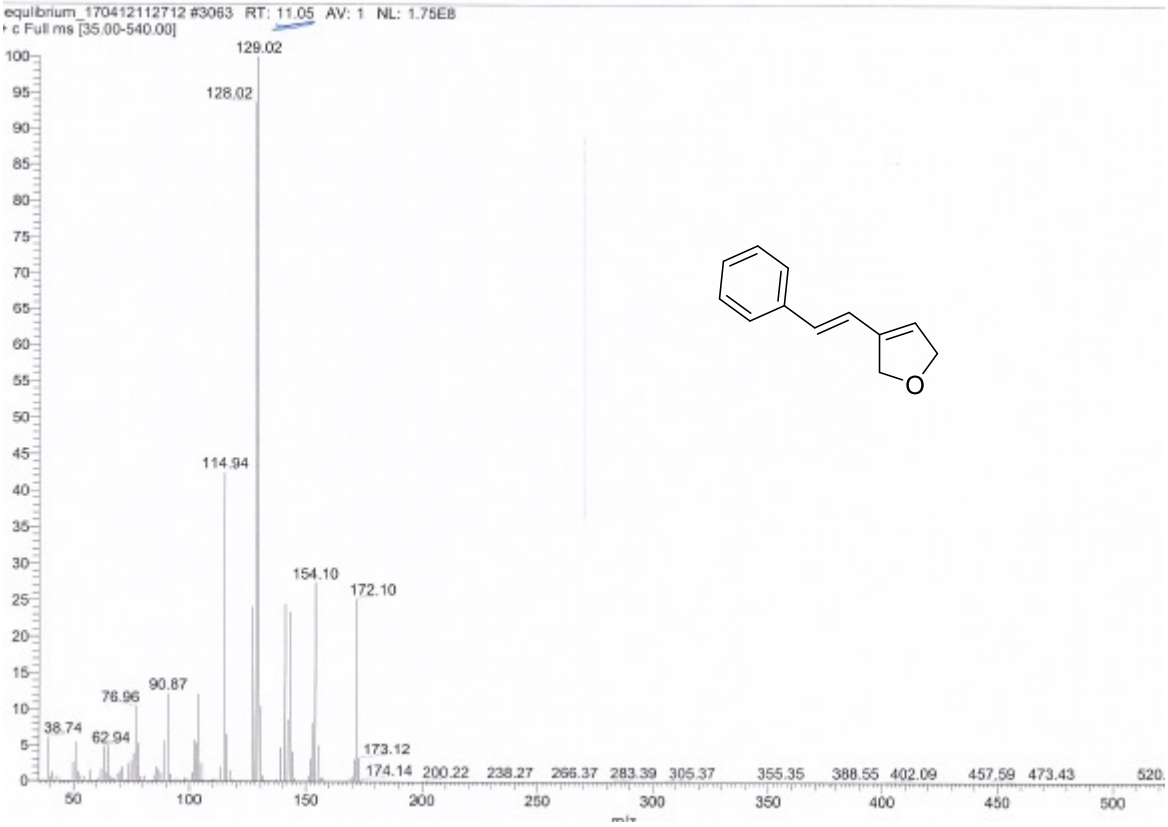


Figure S106: GC-MS spectrum of (E)-3-styryl-2, 5-dihydrofuran (**DHF**).

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2. Nagarkar, A.; Crochet. A.; Fromm, K.; Kilbinger, A.F.M. *Macromolecules* **2012***, 45,* 4447.
3. Trost, B. M., Edstrom, E. D., Carter-Petillo, M.B. *J. Org. Chem*. **1989**, *54*, 4489**.**
4. Huple, D.B.; Mokar, B. D.; Liu, R.S. *Angew. Chem. Int. Ed.* **2015**, *54*, 14924.
5. Hildebrandt, N. (2013) How to Apply FRET: From Experimental Design to Data Analysis, in FRET - Förster Resonance Energy Transfer: From Theory to Applications (eds I. Medintz and N. Hildebrandt), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.