Supporting Information

Faster cyclopolymerisation of 4,4-disubstituted 1,7-octadiynes through enhanced Thorpe-Ingold effect

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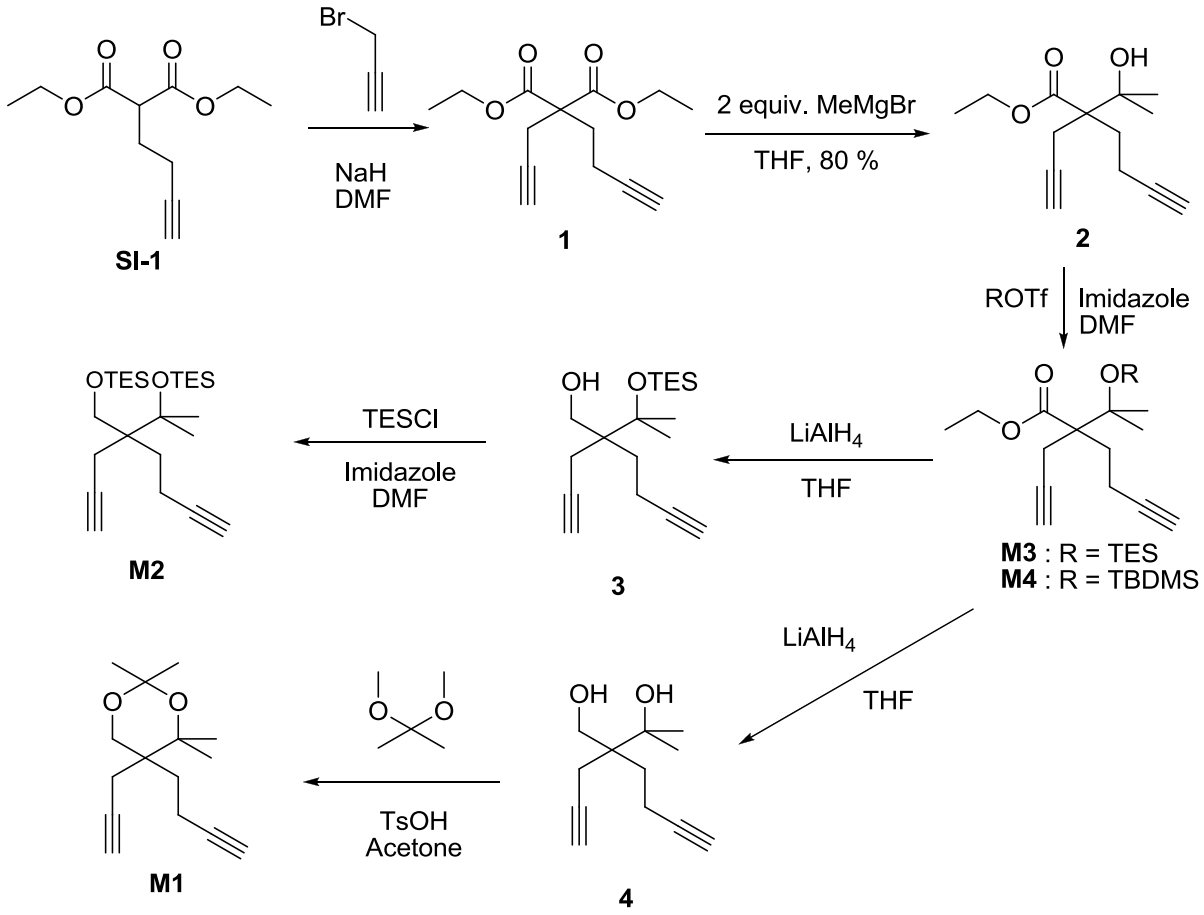
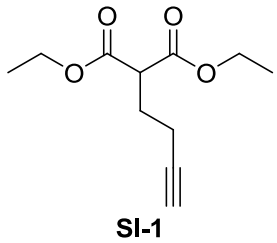
General experimental

All reagents which are commercially available were used without further purification. For polymerisation, THF was distilled from sodium and benzophenone. THF was degassed by Ar bubbling for 10 minutes before using on polymerisation. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm). ^{1}H-NMR and ^{13}C-NMR were recorded by Varian/Oxford As-500 (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR) and Bruker (75 MHz for ^{13}C-NMR) spectrometers. UV-Vis spectroscopy was measured by Jasco Inc. UV/Vis-Spectrometer V-550. THF SEC (size exclusion chromatography) was carried out at 1.0 mL/min. SEC for polymer analysis was carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column on samples diluted in 0.001-0.003 wt% THF (HPLC grade, Honeywell Burdick & Jackson®) and filtered with a 0.2-μm PTFE filter. The columns were thermostatted at 35 °C. High resolution mass spectroscopy (HRMS) analyses were performed at National Center for Inter-University Facility. Low resolution mass spectroscopy (LRMS) analyses were performed by Agilent 5973N GC-MS spectrometer. Infrared spectroscopy (IR) analyses were performed by JASCO FT/IR-660 plus spectrometer.

Preparation of monomers



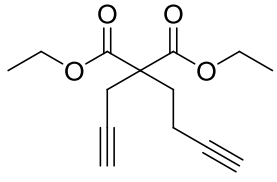
SI-1



SI-1

This molecule was prepared by method from the previous literature (J. E. H. Day, C. J. Moody, S. Y. Sharp, M. G. Rowlands, W. Aherne and P. Workman, *Chem. Eur. J.*, **2010**, *16*, 2758.).^{1}H-NMR, ^{13}C-NMR and MS analysis data are also available in the same literature.

1



1

SI-1 (1 mmol, 228 mg) was added to Ar-purged flask and dessolved in DMF(6 ml). Solution was cooled to

0 °C and sodium hydride (2 mmol, 80 mg) was added. Reaction mixture was stirred for 30 minutes at room temperature, followed by addition of propargyl bromide in toluene solution (1.2 mmol, 0.097 ml). After 2 hour, mixture was quenched by aqueous ammonium chloride solution. Product was extracted with ethyl acetate and organic layer was washed with brine and dried with $MgSO_4$. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10, R_f = 0.25) to yield **1** with 70 %.

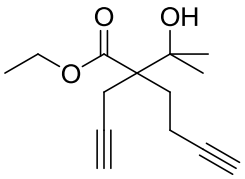
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 4.167 (4H, d, *J* = 8.5 Hz), 2.795 (2H, s), 2.287 (2H, t, *J* = 6.5 Hz), 2.167 (2H, t, *J* = 7.5 Hz), 2.132 (2H, s), 2.004 (1H, s), 1.935 (1H, s), 1.216 (6H, tt, *J* = 1, 9 Hz)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 169.54, 82.83, 78.41, 71.66, 68.89, 61.69, 6.06, 30.90, 22.85, 13.92, 13.79

HRMS (FAB+) calcd. for $C_{14}H_{19}O_4$, 251.1283, found, 251.1287.

IR (film): 3289, 2981, 2120, 1727, 1185 cm^{-1}

2



2

1 (1 mmol, 228 mg) was added to Ar-purged flask and dessolved in THF (6 ml). Solution was cooled to 0 °C and methyl magnesiumbromide solution (2 mmol, 0.67 ml, 3.0 M in diethyl ether) was added. Reaction mixture was stirred for 1 hour and quenched by aqueous ammonium chloride solution. Product was extracted with ethyl acetate and organic layer was washed with brine and dried with $MgSO_4$. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10, R_f = 0.2) to yield **2** with 80 %.

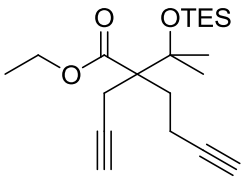
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 4.223 (2H, q, *J* = 7 Hz), 3.150 (1H, s), 2.734 (1H, d, *J* = 17.5 Hz), 2.629 (1H, d, *J* = 17.5 Hz), 2.369 (2H, m), 2.220 (1H, t, *J* = 13 Hz), 2.010 (1H, t, *J* = 11.5 Hz), 2.073 (1H, s), 1.983 (1H, s), 1.334 (3H, s), 1.306 (3H, s), 1.272 (3H, s)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 171.15, 83.82, 81.51, 74.25, 71.47, 68.67, 61.17, 55.52, 30.67, 26.33, 26.17, 20.65, 14.82, 14.00

HRMS (EI+) calcd. for $C_{14}H_{20}O_3$, 236.1412, found, 236.1416.

IR (film): 3532, 3294, 2981, 2940, 2861, 2117, 1717, 1196 cm^{-1}

M3



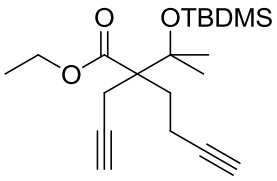
M3

2 (1 mmol, 236 mg) and imidazole (3 mmol, 198 mg) was added to Ar-purged flask and dessolved in DMF (6 ml). Reflux condenser was set and solution was heated to 90 °C. Triethylsilane trifluoromethylsulfonate (3 mmol, 0.678 ml) was added and the mixture was refluxed for 12 hours. After that, reaction mixture was cooled to room temperature and quenched by aqueous ammonium chloride solution. Product was extracted with diethyl ether and organic layer was washed with brine and dried with $MgSO_4$. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10, R_f = 0.2) to yield **M3** with 80 %.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 4.101 (2H, m), 3.468 (2H, d, *J* = 6 Hz), 2.698 (2H, s), 2.453 (1H, m), 2.209 (1H, m), 2.094 (2 H, m), 1.959 (1H, s), 1.953 (1H, s), 1.352 (3H, s), 1.295 (3H, s), 1.253 (3H, t, *J* = 6.5 Hz), 0.923 (9H, m), 0.559 (6H, m)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 173.25, 84.54, 84.51, 82.37, 77.40, 70.33, 68.04, 60.66, 57.03, 31.15, 27.46, 27.27, 20.30, 14.93, 14.01, 6.97, 6.70, 6.64
HRMS (CI+) calcd. for $C_{20}H_{35}O_3Si_2$, 351.2355, found, 351.2358.
IR (film): 3310, 2955, 2910, 2877, 2359, 2339, 2118, 1723, 1023 cm^{-1}

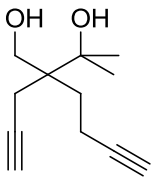
M4



M4

2 (1 mmol, 236 mg) and imidazole (3 mmol, 198 mg) were added to Ar-purged flask and dissolved in DMF (6 ml). Reflux condenser was set and solution was heated to 120 °C. *tert*-Butyldimethylsilane trifluoromethylsulfonate (3 mmol, 0.689 ml) was added and the mixture was refluxed for 12 hours. After that, reaction mixture was cooled to room temperature and quenched in aqueous ammonium chloride solution. Product was extracted with diethyl ether and organic layer was washed with brine and dried with $MgSO_4$. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10, R_f = 0.2) to yield **M4** with 80 %.
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 4.159 (1H, m), 4.100 (1H, m), 2.732 (2H, t, *J* = 3 Hz), 2.460 (1H, t, *J* = 17.5 Hz), 2.219 (1H, t, *J* = 17.5 Hz), 2.078 (2 H, m), 1.981 (1H, t, *J* = 3 Hz), 1.959 (1H, t, *J* = 2.5 Hz), 1.381 (3H, s), 1.350 (3H, s), 1.277 (3H, t, *J* = 6.5 Hz), 0.855 (6H, s), 0.113 (3H, s), 0.075 (3H, s)
^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 171.10, 84.41, 82.56, 77.83, 70.52, 68.12, 60.71, 57.13, 31.33, 27.34, 27.08, 25.74, 20.63, 18.17, 15.01, 14.04, -2.13, -2.17
HRMS (FAB+) calcd. for $C_{20}H_{35}O_3Si_2$, 351.2355, found, 351.2350.
IR (film): 3311, 2954, 2930, 2856, 2119, 1723, 1029, 834 cm^{-1}

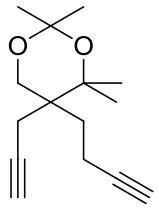
4



4

M3 (1 mmol, 350 mg) was added to Ar-purged flask and dessolved in THF (6 ml). Solution was cooled to 0 °C and lithium aluminum hydride (4 mmol, 160 mg) was added slowly. Reaction mixture was stirred for 2 hour until all silyl ether groups were deprotected. Resulting mixture was quenched by successive addition of 0.16 ml of water in ice bath, 0.32 ml of 10 % NaOH solution, and 0.48 ml of water. Resulting mixture was filtered through celite pad and evaporated under reduced pressure. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/3, R_f = 0.3) to yield **4** with 70 %.
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 3.898 (1H, dd, *J* = 3.5, 11.5 Hz), 3.797 (1H, dd, *J* = 3.5, 11.5 Hz), 3.197 (1H, s), 2.970 (1H, s), 2.477 (1H, d, *J* = 16.5 Hz), 2.420 (2 H, m), 2.323 (1H, d, *J* = 16.5 Hz), 2.079 (1H, s), 2.003 (1H, s), 1.836 (2H, m), 1.321 (3H, s),1.291 (3H, s)
^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 84.96, 82.09, 71.54, 68.40, 66.08, 45.02, 31.27, 26.36, 26.14, 20.95, 14.13
HRMS (CI+) calcd. for $C_{12}H_{19}O_2$, 195.2780, found, 195.2789.
IR (film): 3291, 2977, 2942, 2833, 1641, 1026 cm^{-1}

M1



M1

To the solution of **4** (194 mg, 1 mmol) in acetone (6 ml), *p*-toluenesulfonic acid monohydrate (0.1 mmol, 19 mg) was added, followed by addition of 2,2-dimethoxypropane (2 mmol, 0.246 ml). Reaction mixture was stirred for 3 hours and solvent was evaporated under reduced pressure. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/20, R_f = 0.2) to yield **M1** with 90 %.

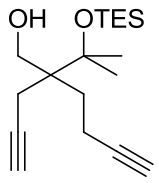
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 3.740 (2H, dd, *J* = 12, 40 Hz), 2.430 (2H, ddd, *J* = 2.5, 16.5, 40 Hz), 2.291 (2H, m), 2.043 (1H, s), 1.971 (1H, s), 1.756 (2 H, t, *J* = 8.5 Hz), 1.467 (3H, s), 1.397 (3H, s), 1.372 (3H, s), 1.213 (3H, s)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 98.04, 84.52, 81.68, 76.96, 71.34, 68.41, 63.01, 39.42, 30.79, 29.01, 26.53, 26.07, 21.14, 13.83

HRMS (CI+) calcd. for $C_{15}H_{23}O_2$, 235.3410, found, 235.3402.

IR (film): 3294, 2987, 2117, 1737, 1372, 1242 cm^{-1}

3



3

M3 (1 mmol, 350 mg) was added to Ar-purged flask and dessolved in THF (6 ml). Solution was cooled to 0 °C and lithium aluminum hydride (1 mmol, 38 mg) was added slowly. Reaction mixture was stirred for 1 hour. Resulting mixture was quenched by successive addition of 0.04 ml of water in ice bath, 0.08 ml of 10 % NaOH solution, and 0.12 ml of water. Resulting mixture was filtered through celite pad and evaporated under reduced pressure. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/10, R_f = 0.25) to yield **M3** with 90 %.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 3.691 (2H, ddt, *J* = 1, 11.5, 22 Hz), 3.495 (1H, t, *J* = 6 Hz), 2.358 (4H, m), 2.050 (1H, s), 1.977 (1H, s), 1.828 (2H, t, *J* = 6.5 Hz), 1.377 (3H, s), 1.361 (3H, s), 0.995 (9H, t, *J* = 8 Hz), 0.658 (6H, q, *J* = 8 Hz)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 85.01, 82.21, 81.16, 71.18, 68.08, 66.00, 46.03, 31.00, 26.54, 20.95, 14.16, 6.92, 6.68

HRMS (CI+) calcd. for $C_{18}H_{33}O_2Si$, 309.5389, found, 309.5395.

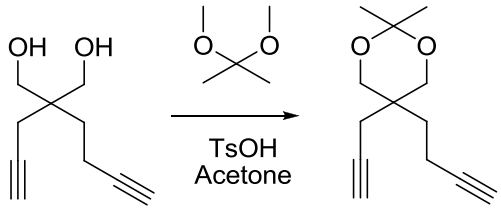
IR (film): 3463, 3309, 2956, 2911, 2877, 2116, 1739, 1006 cm^{-1}

M2

M2

M2 (1 mmol, 228 mg) and imidazole (3 mmol, 198 mg) were added to Ar-purged reaction flask and dessolved in DMF (5 ml). Solution was cooled to 0 °C and chlorotriethylsilane (1 mmol, 0.168 ml) was added. Reaction mixture was stirred for 1 hour and quenched by aqueous ammonium chloride solution. Product was extracted with diethyl ether and organic layer was washed with brine and dried with $MgSO_4$. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/50, R_f = 0.5) to yield **M2** with 90 %.
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 3.651 (2H, dd, *J* = 3, 28.5 Hz), 2.437 (2H, m), 2.394 (2H, s), 1.961 (1H, s), 1.939 (1H, s), 1.903 (1H, m), 1.809 (1H, m), 1.346 (3H, s), 1.290 (3H, s), 0.968 (18H, dt, J = 1.5, 7.5 Hz), 0.608 (12H, m)
^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 86.07, 83.25, 78.27, 70.26, 67.30, 65.49, 47.27, 32.11, 27.62, 27.28, 20.14, 14.64, 7.12, 6.82, 6.75, 6.42, 4.28
HRMS (CI+) calcd. for $C_{24}H_{47}O_2Si_2$, 423.3115, found, 423.3109.
IR (film): 3311, 2994, 2910, 2877, 2117, 1007 cm^{-1}

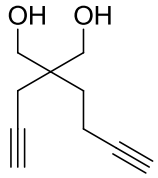
M1-1



SI-2 **M1-1**

To the solution of **SI-2** (166 mg, 1 mmol) in acetone (6 ml), *p*-toluenesulfonic acid monohydrate (0.1 mmol, 19 mg) was added, followed by addition of 2,2-dimethoxypropane (2 mmol, 0.246 ml). Reaction mixture was stirred for 3 hours and solvent was evaporated under reduced pressure. Product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/20, R_f = 0.2) to yield **M1-1** with 90 %.
^{1}H NMR (500 MHz, $CDCl_3$, ppm) : δ 3.664 (3.5H, s), 3.571 (0.5H, s), 2.430 (2H, s), 2.208 (2H, t, *J* = 6.5 Hz), 2.015 (1H, s), 1.957 (1H, s), 1.647 (2H, t, *J* = 8 Hz), 1.389 (3H, s), 1.373 (3H, s)
^{13}C NMR (125 MHz, $CDCl_3$, ppm) : δ 98.19, 84.11, 80.32, 71.14, 68.77, 68.63, 67.26, 66.70, 35.18, 31.70, 31.03, 26.11, 23.70, 22.03, 21.31, 12.81, 12.76
HRMS (CI+) calcd. for $C_{13}H_{19}O_2$, 207.1385, found, 207.1387.
IR (film):3306, 2972, 2865, 2118, 1622 cm^{-1}

SI-2



SI-2

This molecule was prepared by method from the previous literature (I. S. Lee, E. -H. Kang, H. Park and T. -L. Choi, *Chem. Sci.*, **2012**, *3*, 761.).^{1}H-NMR, ^{13}C-NMR and HRMS analysis data are also available in the same

literature.
IR (film): 3289, 2931, 2115, 1639, 1429, 1041 cm^{-1}

Polymerisation kinetics study procedures

Polymerisation kinetics study of M1 and M1-1 (Scheme 3)

Monomer (0.1 mmol) was put into a NMR tube with septum and purged with Ar-gas. 0.1 mL of degassed deuterated THF was added to the vial. Solution of 3rd generation Grubbs catalyst in deuterated THF was prepared in another Ar-purged vial with septum, and 0.05 mL of solution was added by microsyringe rapidly due to rapid initiation. Conversion was checked with 500 MHz ^{1}H-NMR during reaction.

Polymerisation kinetics study of M2 (Scheme 4)

M2 (0.1 mmol, 42.3 mg) and 4,4'-dimethylbiphenyl (0.01 mmol, 1.8 mg) as a standard was put into a 5-mL sized vial with septum and purged with Ar-gas. 0.2 mL of degassed THF was added to the vial and stirred. Before catalyst injection, a small amount of mixture was sampled and checked with ^{1}H-NMR for reference. Solution of 3rd generation Grubbs catalyst in THF was prepared in another Ar-purged vial with septum, and 0.05 mL of solution was added by microsyringe rapidly due to rapid initiation. After 1-30 minutes, reaction was quenched by ethyl vinyl ether. Conversion was checked with crude ^{1}H-NMR, by checking the intensity decrease of terminal alkyne signal of **M2**, based on 4,4'-dimethylbiphenyl standard.

UV-Vis spectra of conjugated polymers

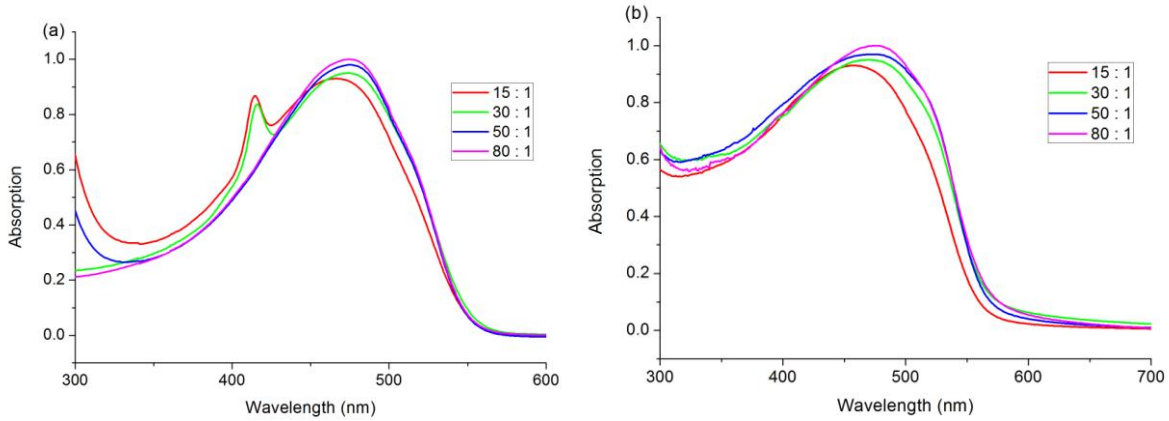


Figure S1. UV-Vis spectra of **P2** (a) in THF solution and (b) in thin film with different DPs (n = 15-80)

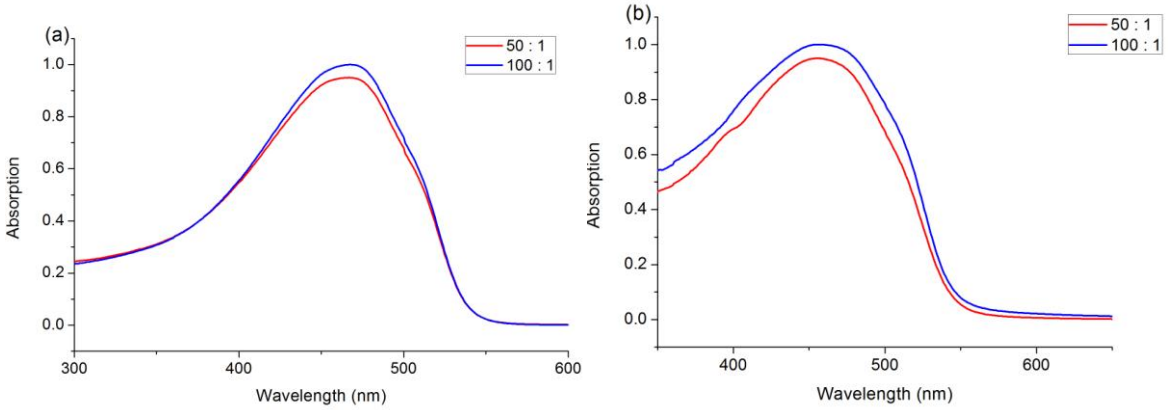


Figure S2. UV-Vis spectra of **P3** (a) in THF solution and (b) in thin film with different DPs (n = 50 and 100)

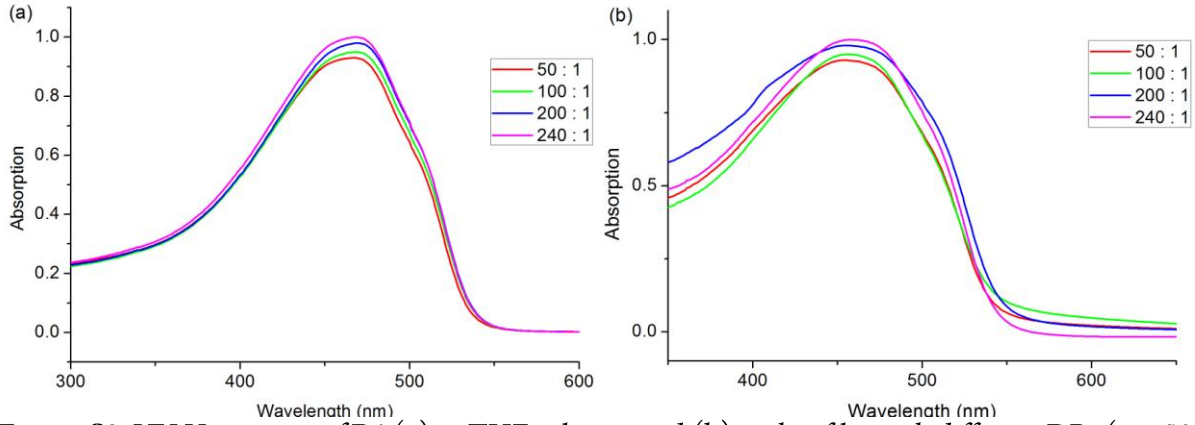
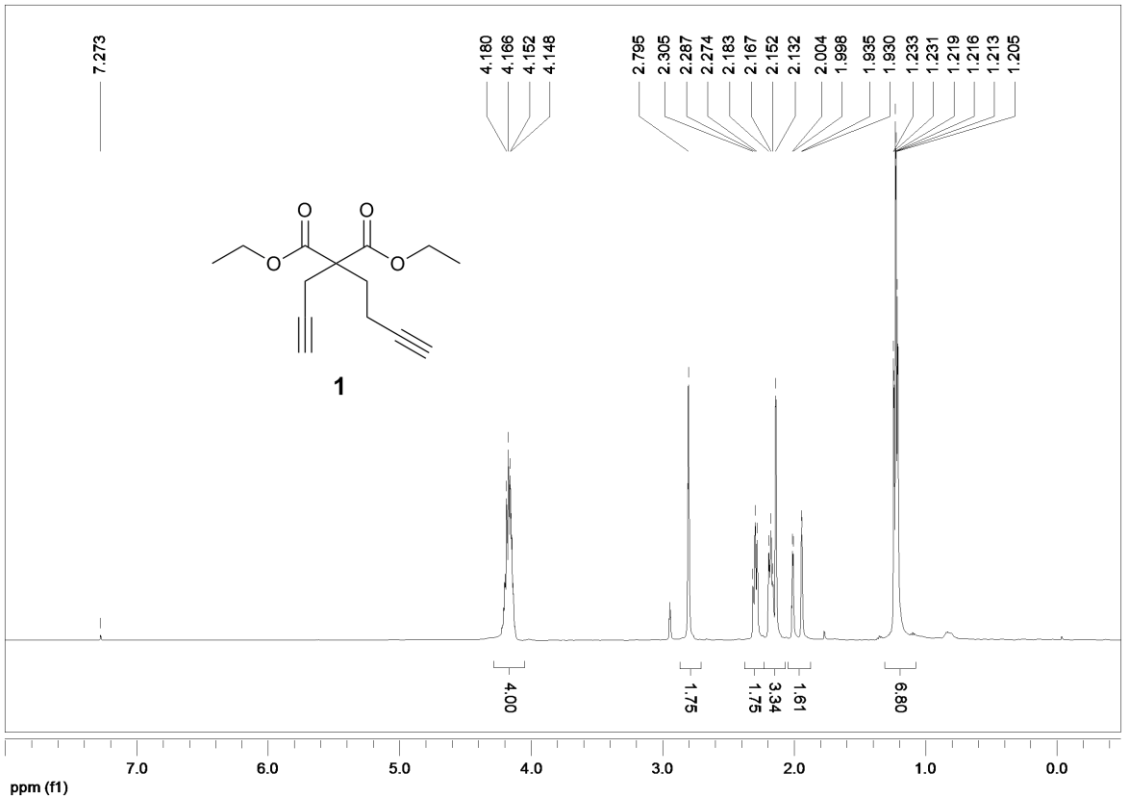


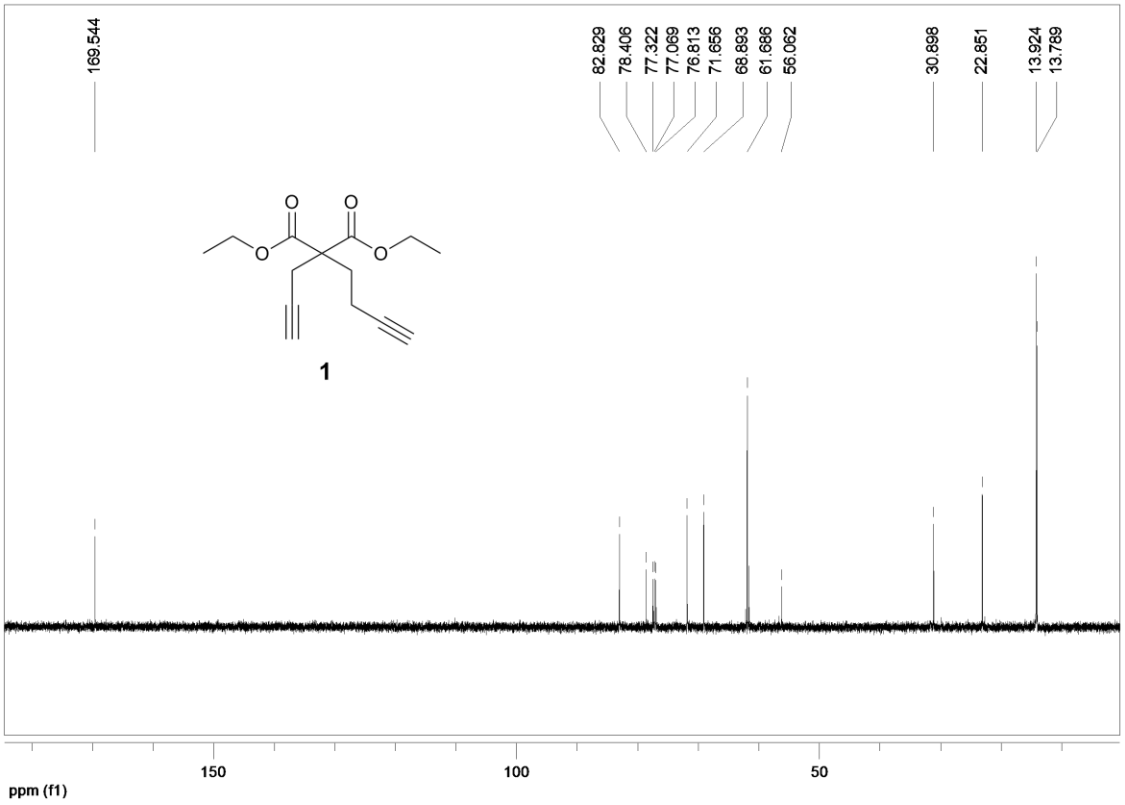
Figure S3. UV-Vis spectra of **P4** (a) in THF solution and (b) in thin film with different DPs (n = 50-240)

^{1}H-NMR and ^{13}C-NMR spectra of monomers and polymers

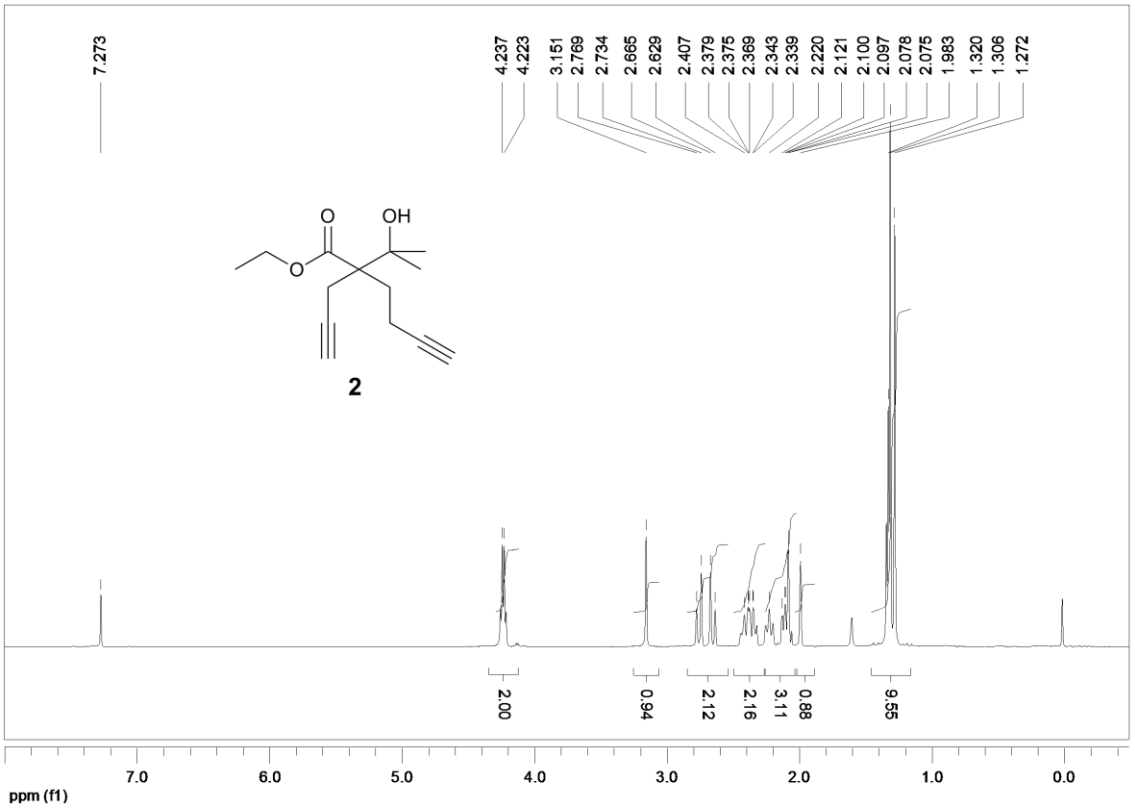
1 (^{1}H, $CDCl_3$, 500 MHz)



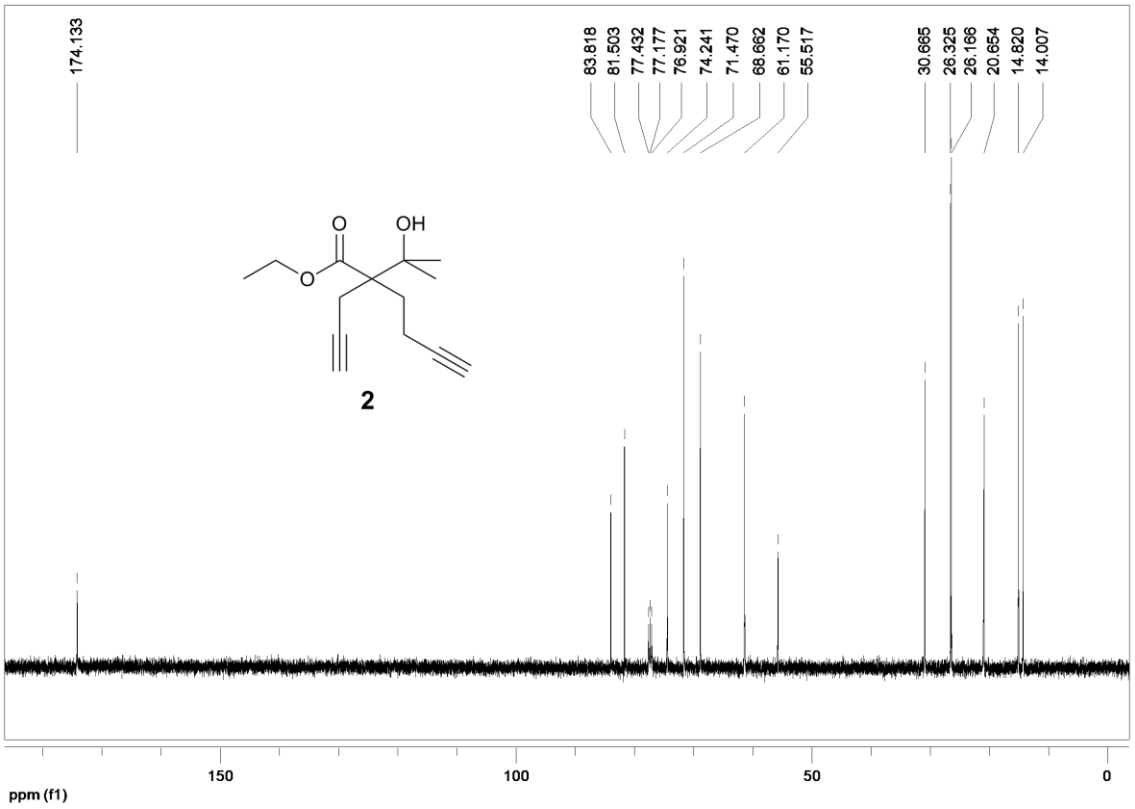
1 (^{13}C, $CDCl_3$, 125 MHz)



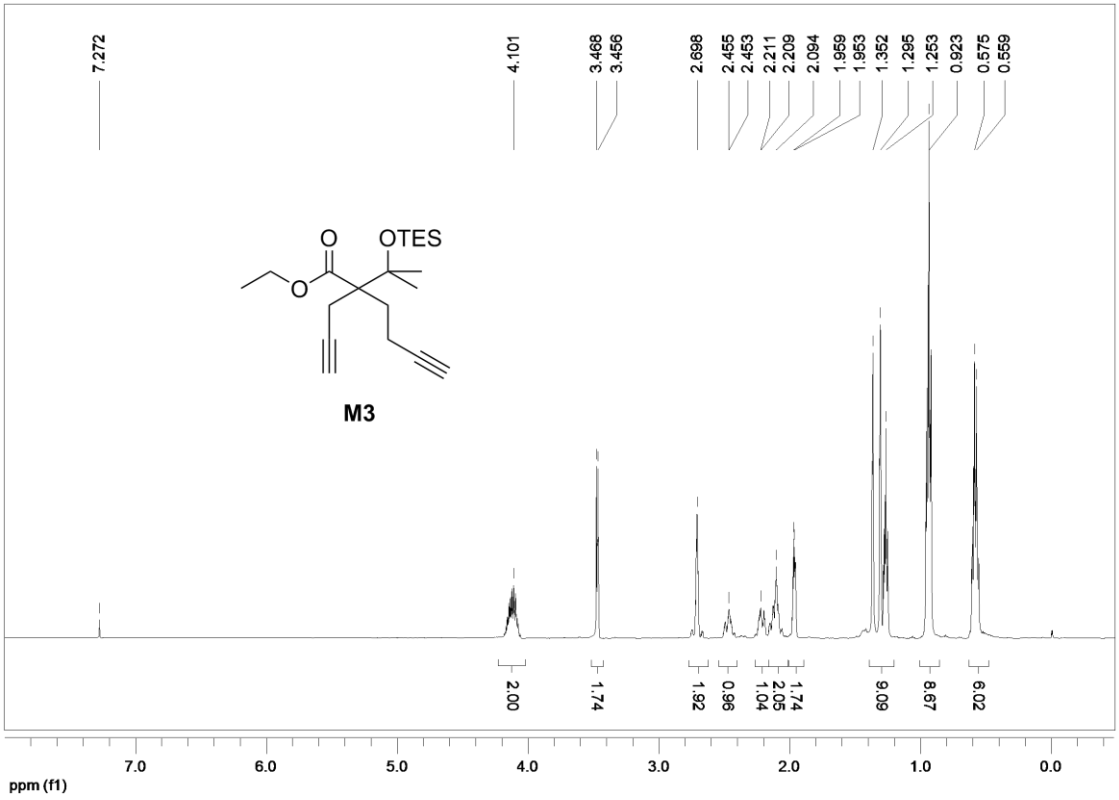
2 (^{1}H, $CDCl_3$, 500 MHz)



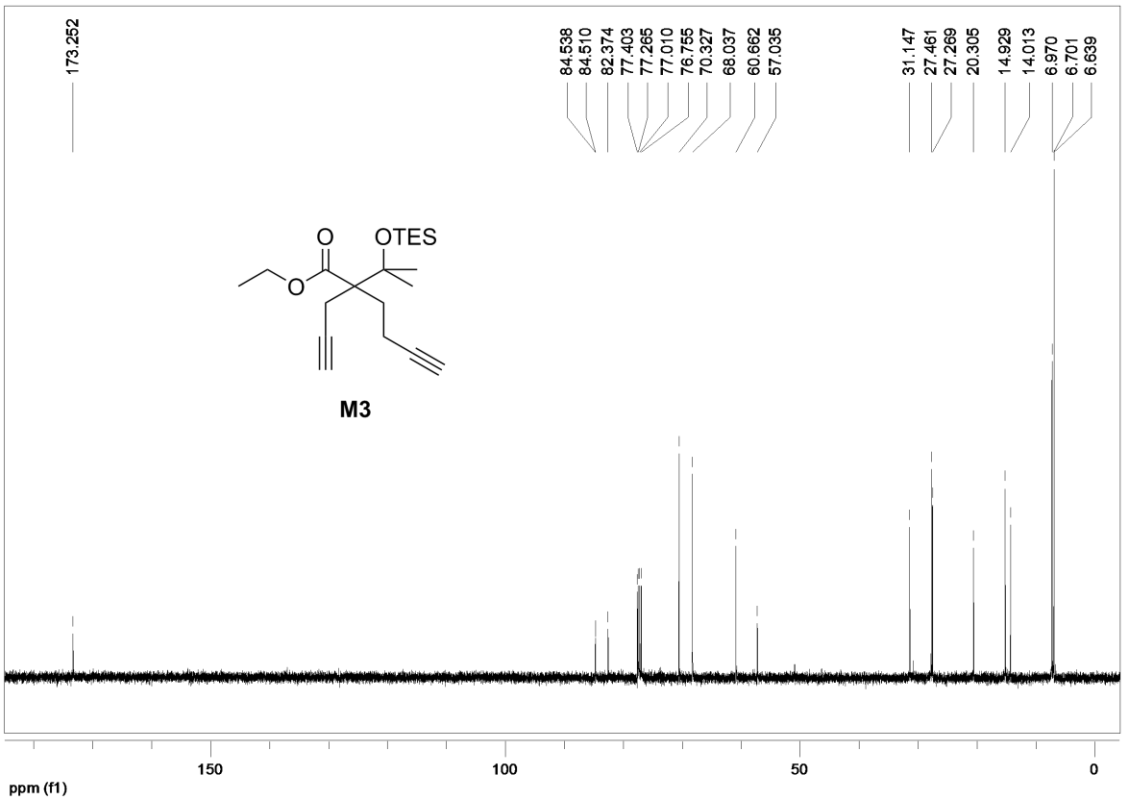
2 (^{13}C, $CDCl_3$, 125 MHz)



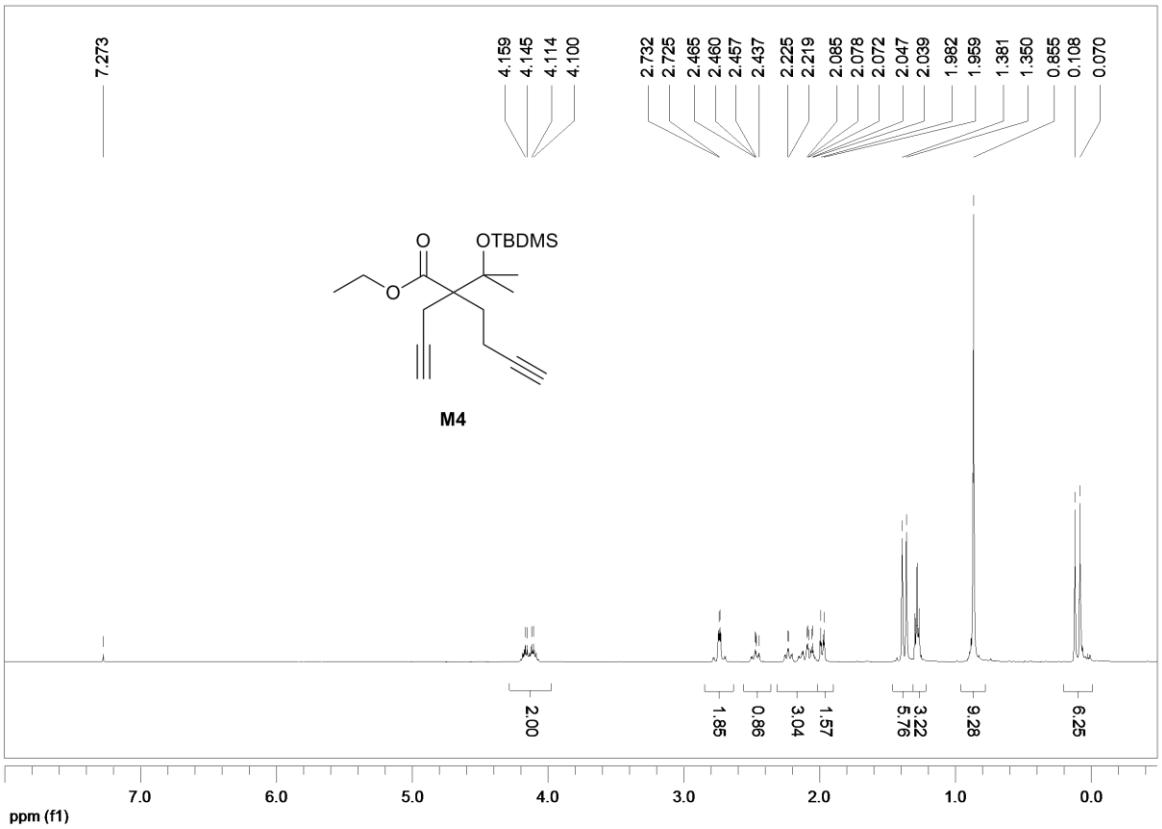
M3 (^{1}H, $CDCl_3$, 500 MHz)



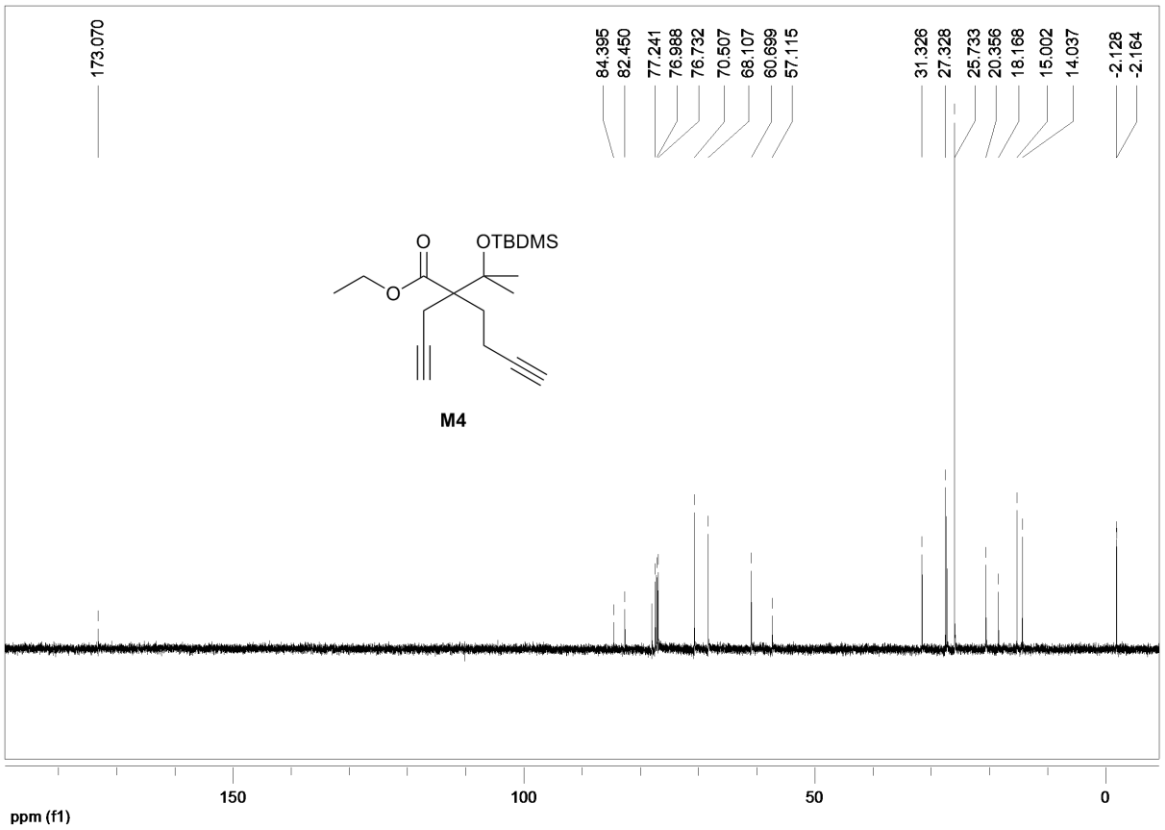
M3 (^{13}C, $CDCl_3$, 125 MHz)



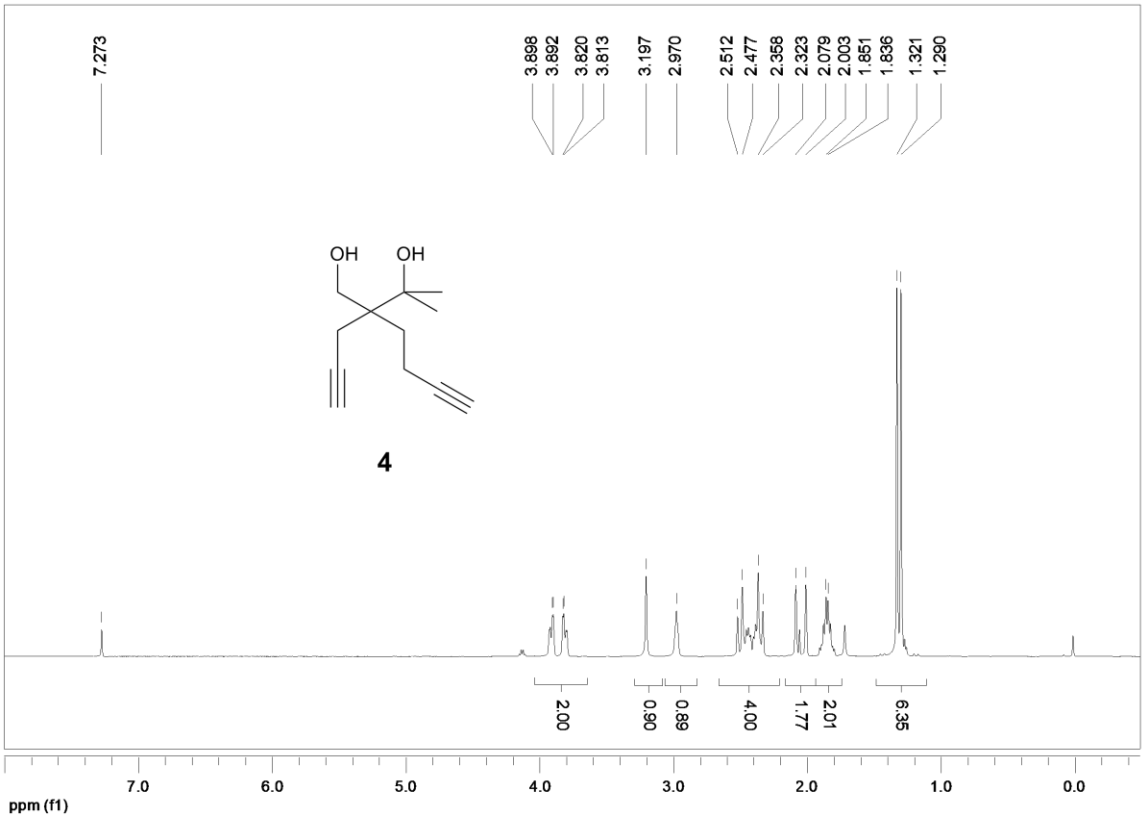
M4 (^{1}H, $CDCl_3$, 500 MHz)



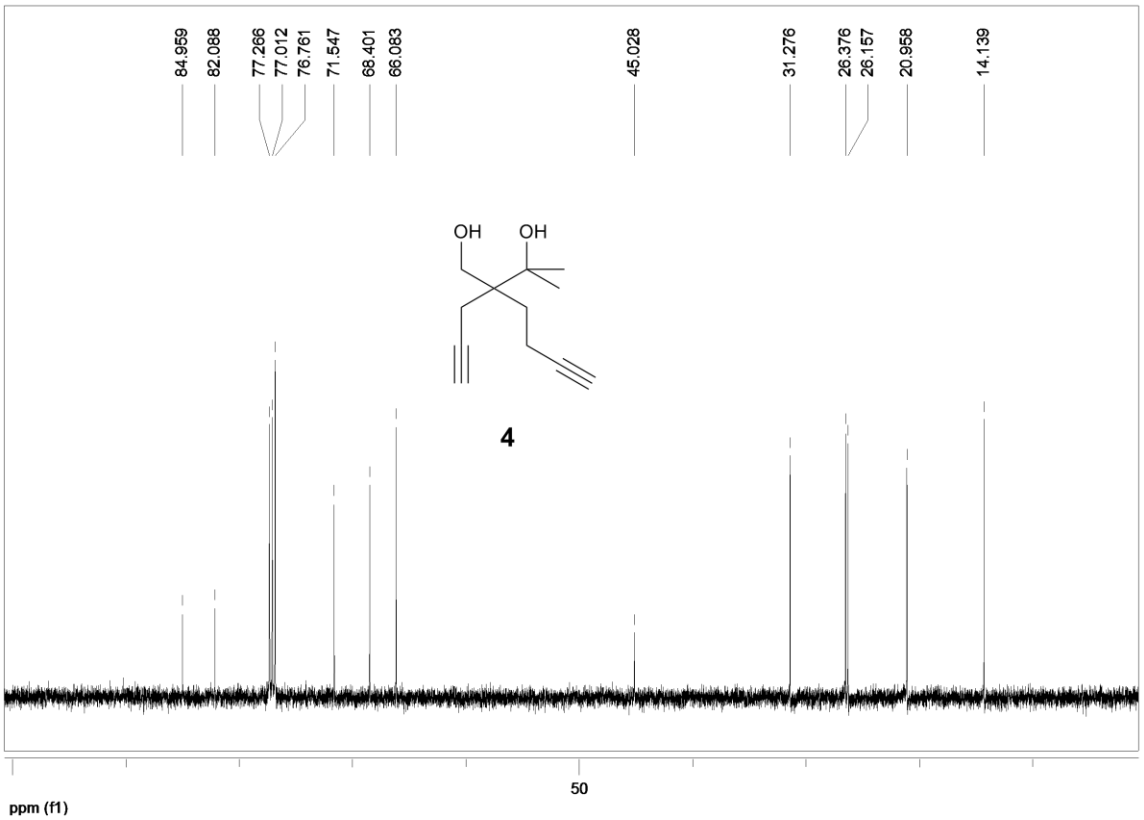
M4 (^{13}C, $CDCl_3$, 125 MHz)



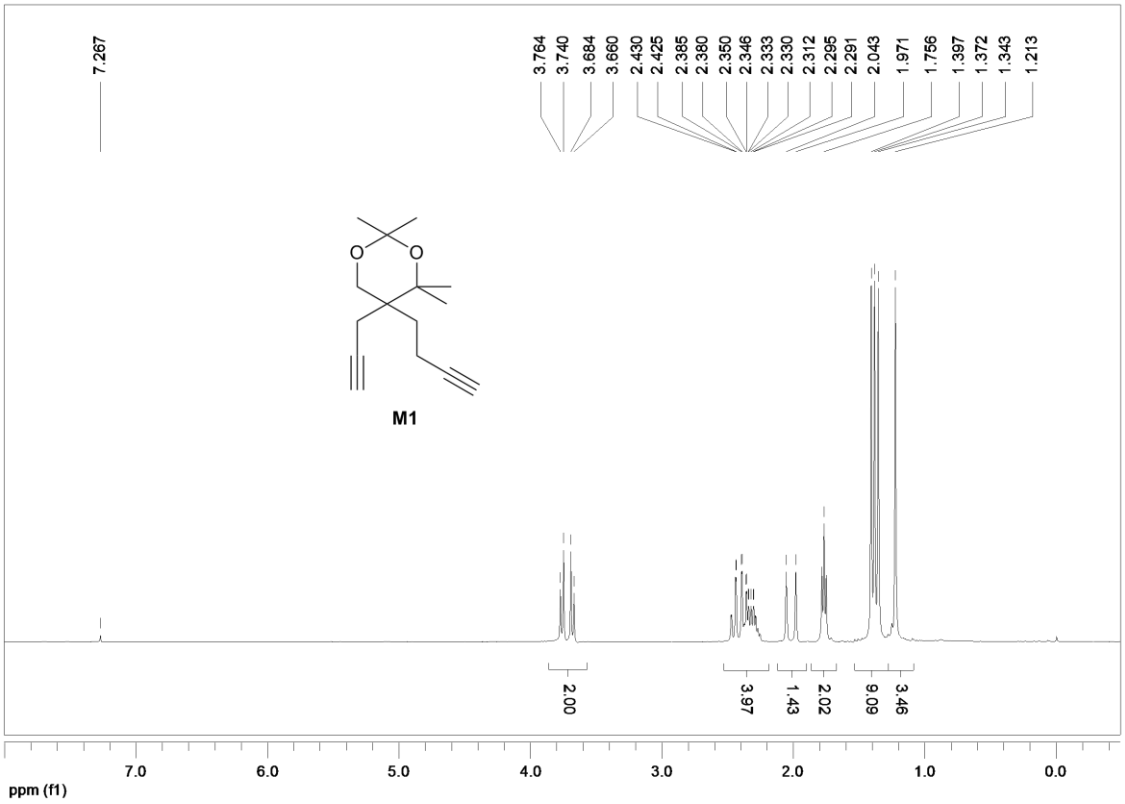
4 (^{1}H, $CDCl_3$, 500 MHz)



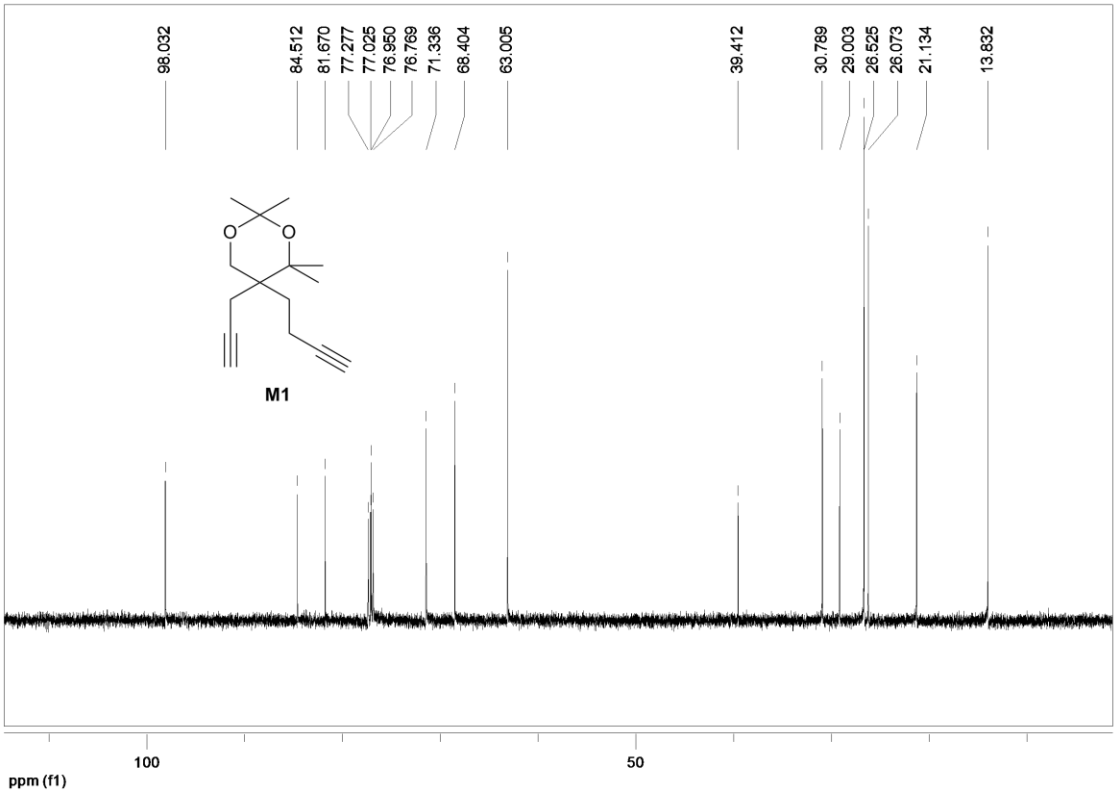
4 (^{13}C, $CDCl_3$, 125 MHz)



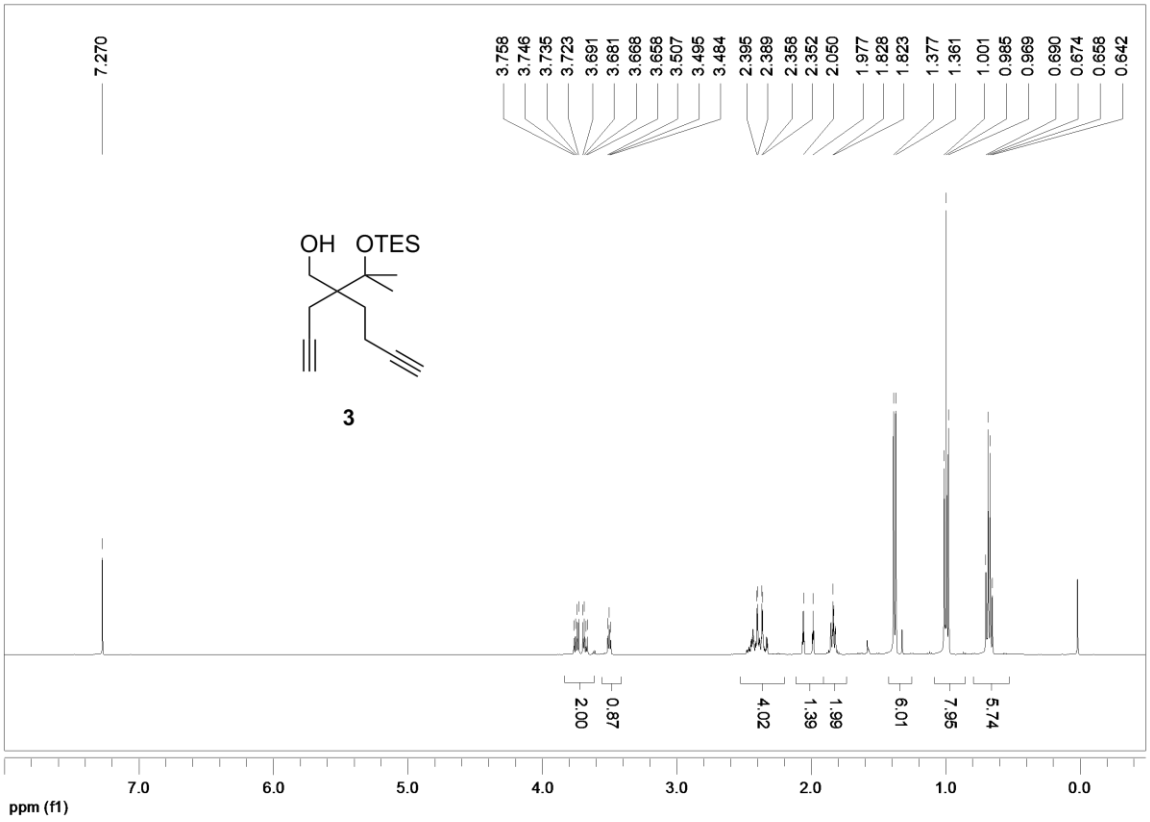
M1 (^{1}H, $CDCl_3$, 500 MHz)



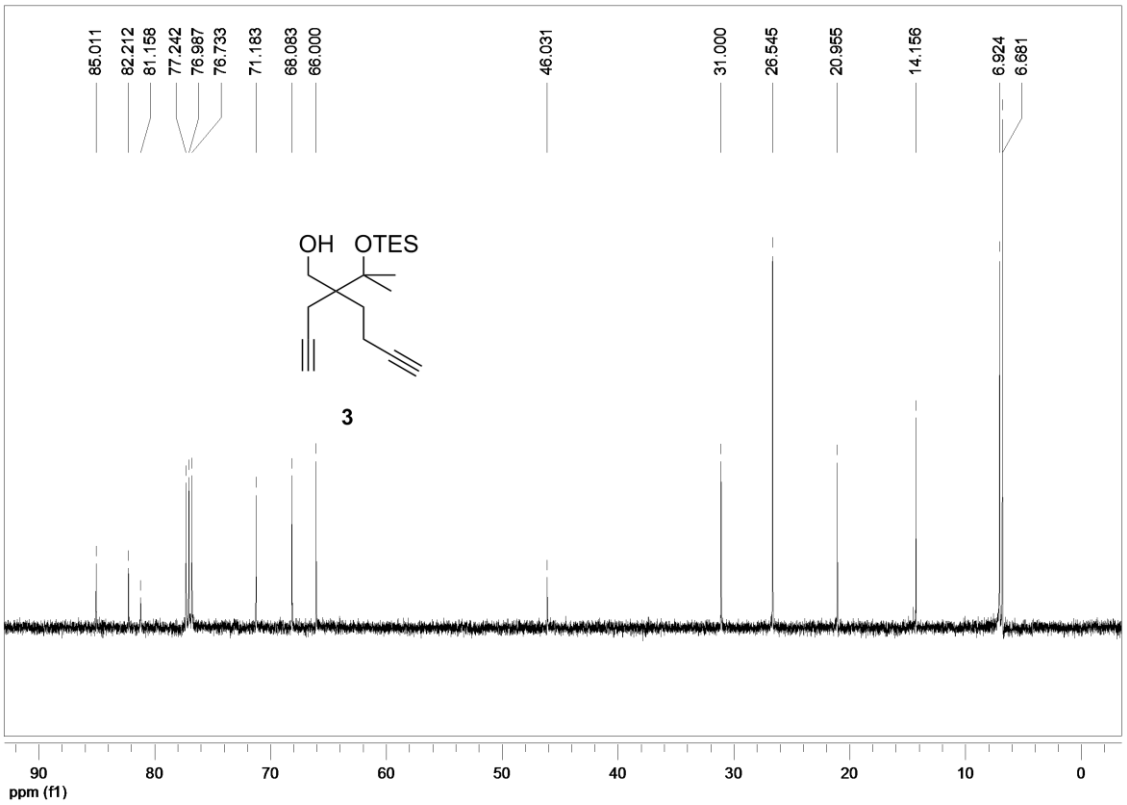
M1 (^{13}C, $CDCl_3$, 125 MHz)



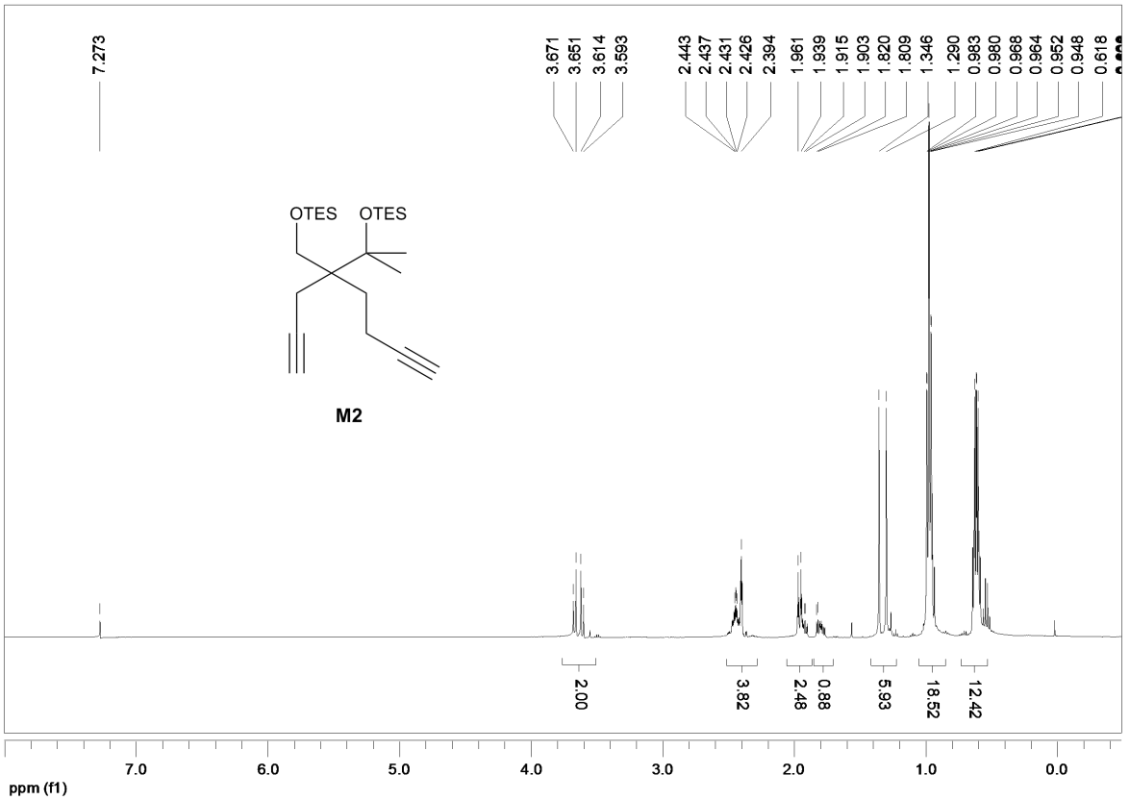
3 (^{1}H, $CDCl_3$, 500 MHz)



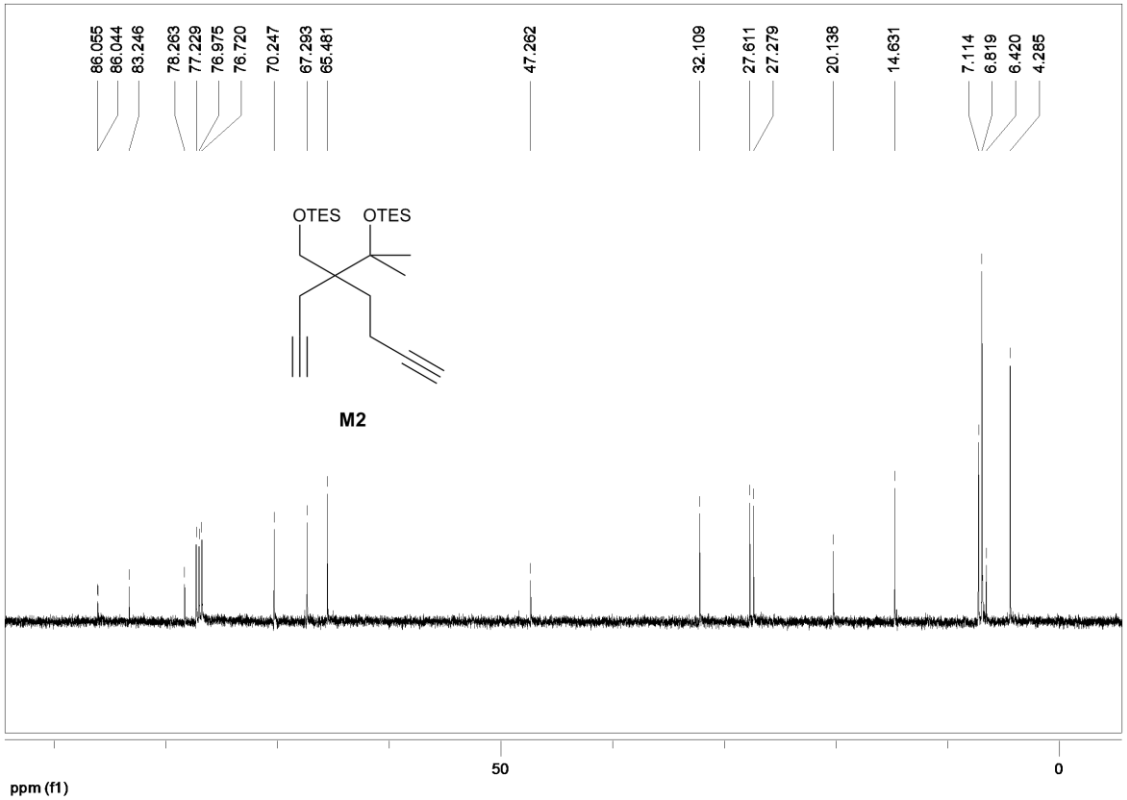
3 (^{13}C, $CDCl_3$, 125 MHz)



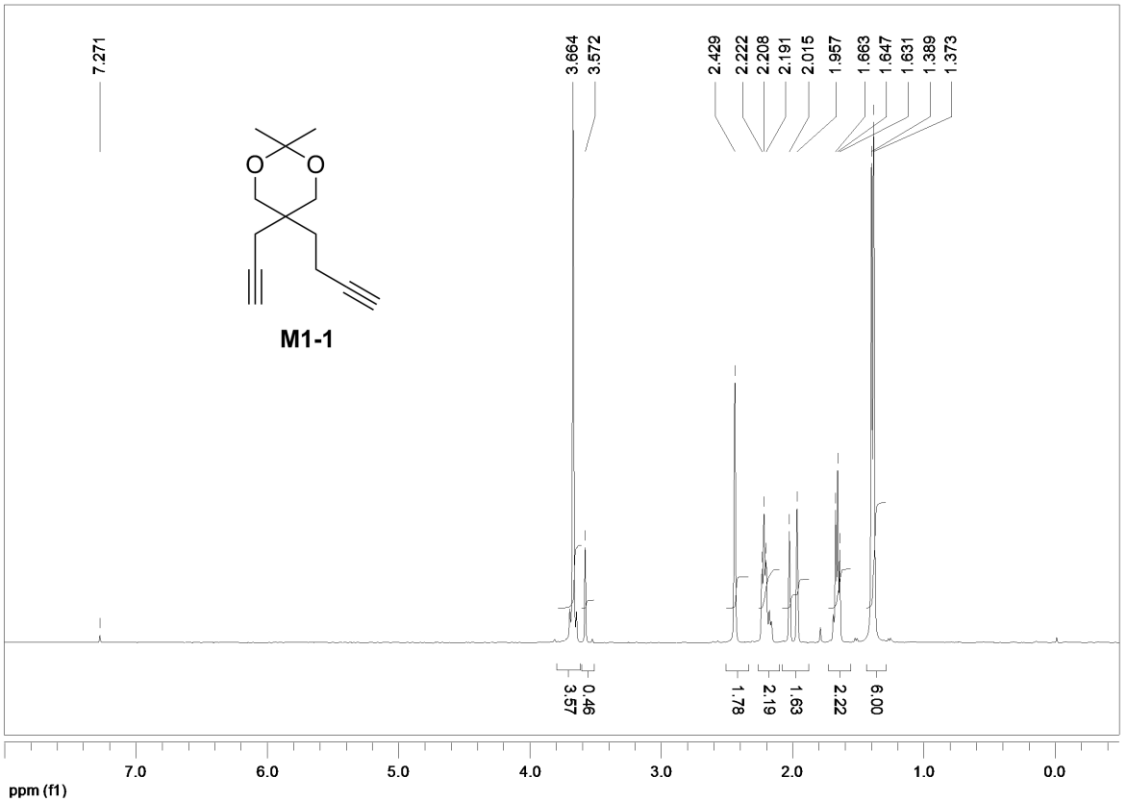
M2 (^{1}H, $CDCl_3$, 500 MHz)



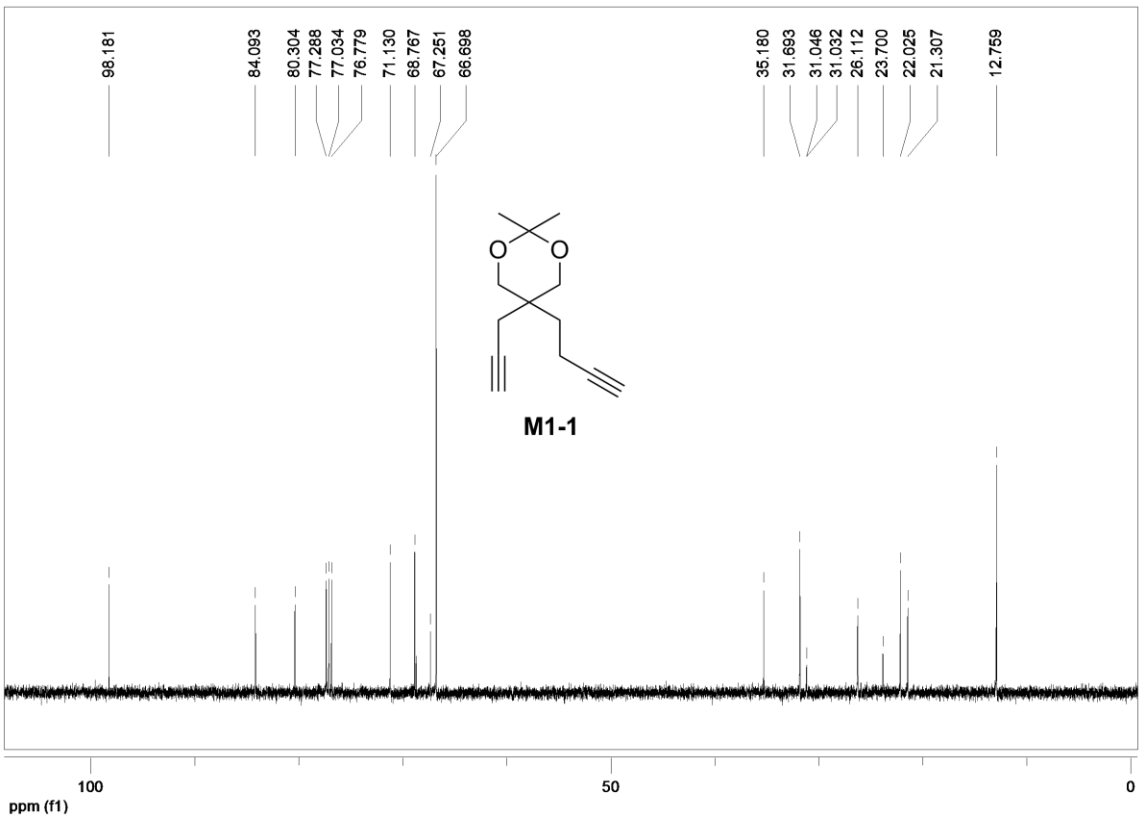
M2 (^{13}C, $CDCl_3$, 125 MHz)



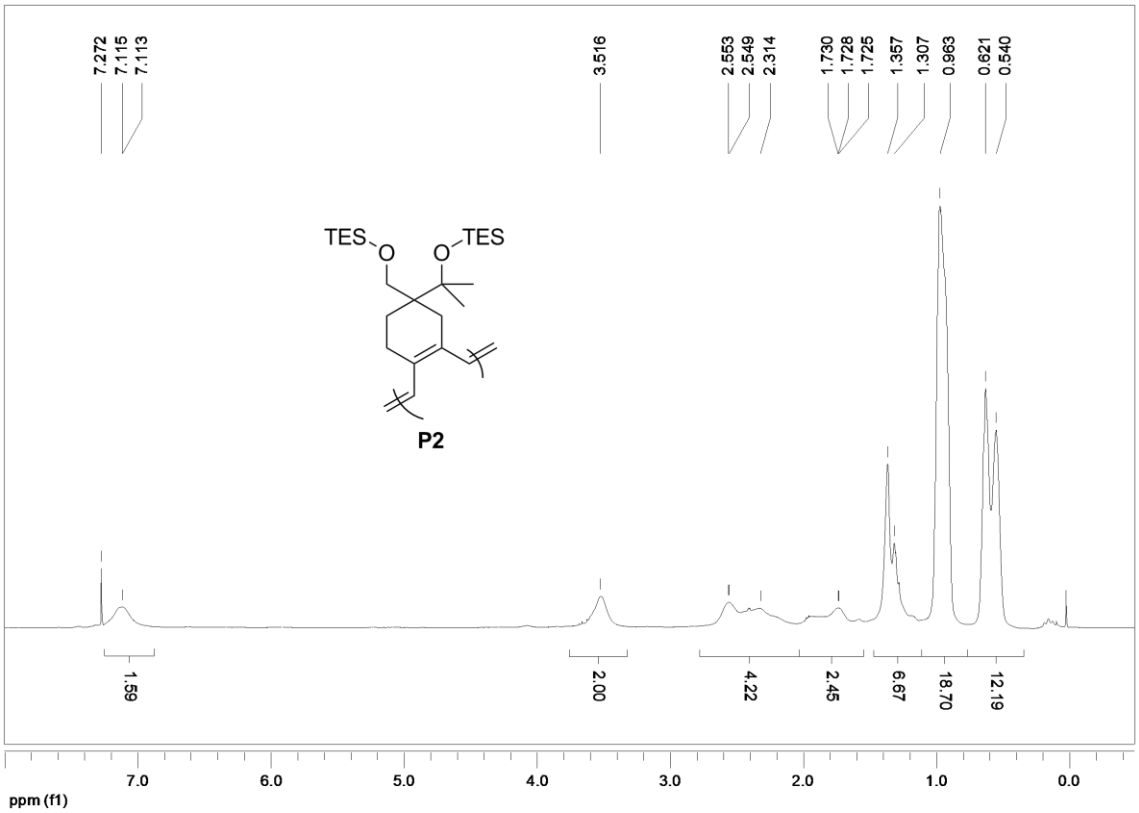
M1-1 (^{1}H, $CDCl_3$, 500 MHz)



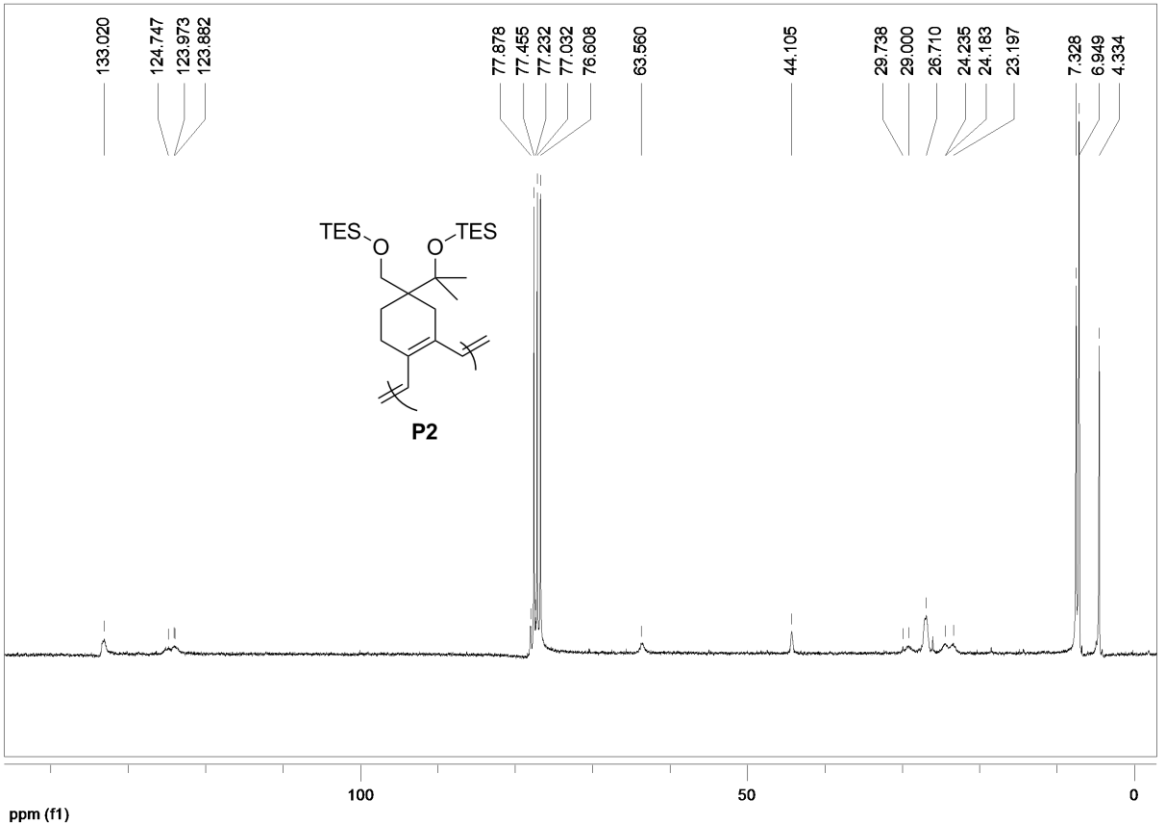
M1-1 (^{13}C, $CDCl_3$, 125 MHz)



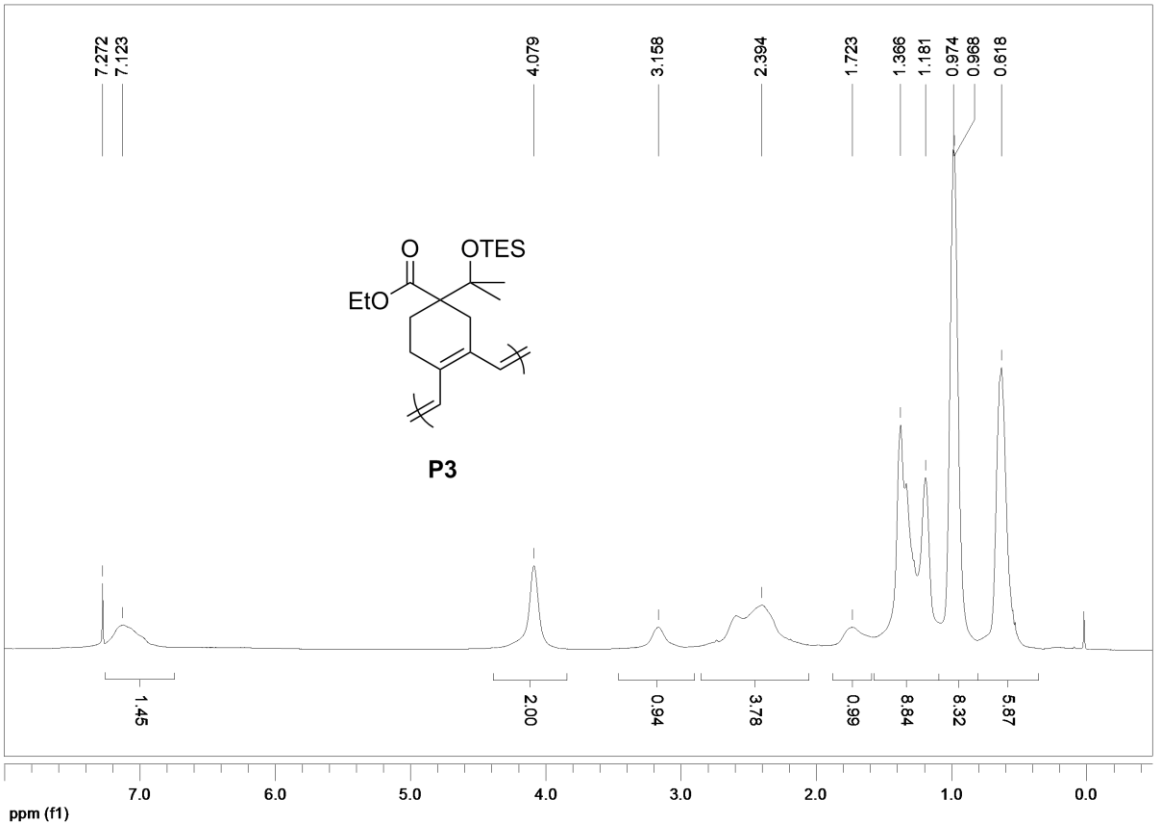
P2 (^{1}H, $CDCl_3$, 500 MHz)



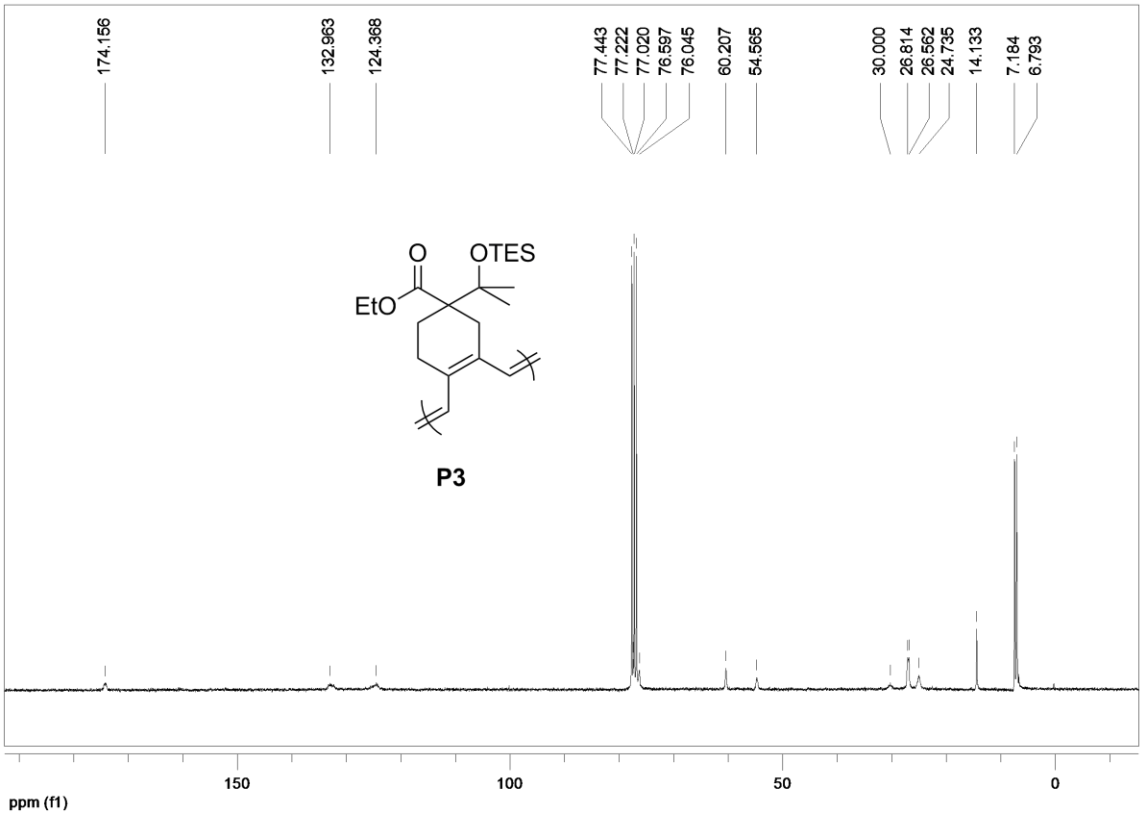
P2 (^{13}C, $CDCl_3$, 75 MHz)



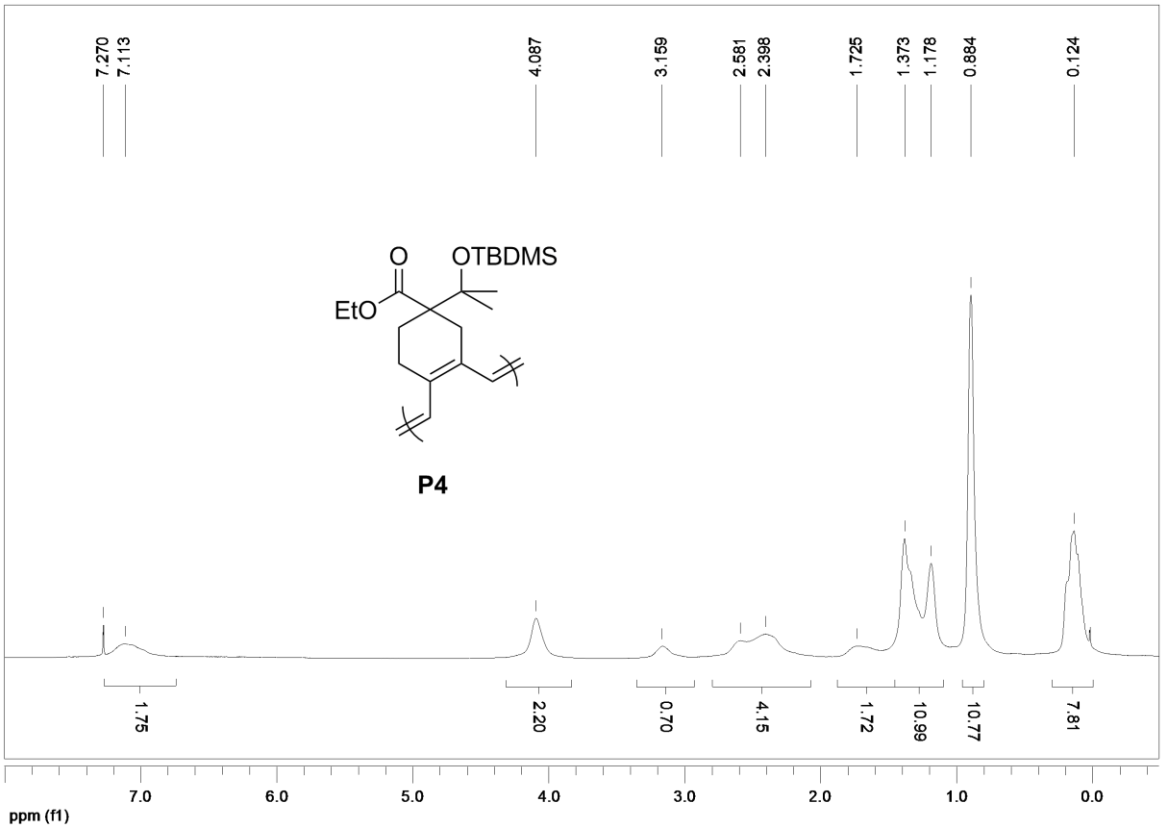
P3 (^{1}H, $CDCl_3$, 500 MHz)



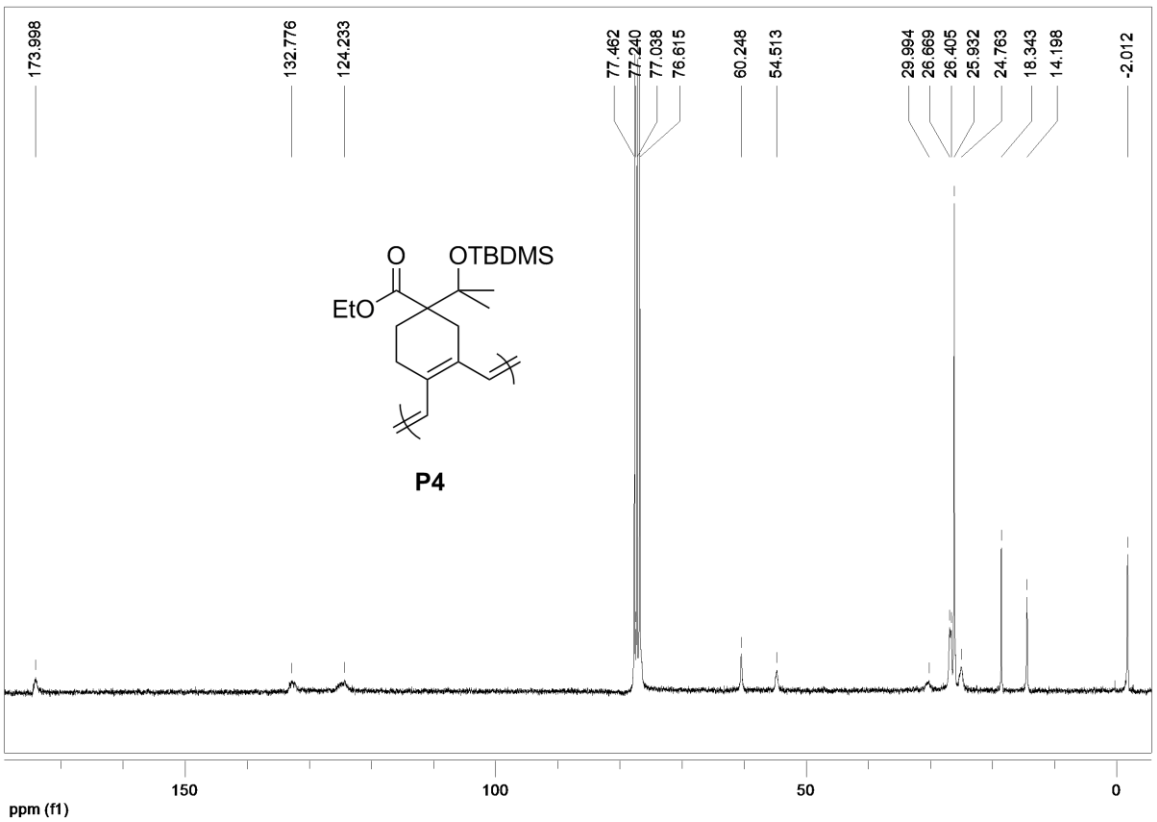
P3 (^{13}C, $CDCl_3$, 75 MHz)



P4 (^{1}H, $CDCl_3$, 500 MHz)



P4 (^{13}C, $CDCl_3$, 75 MHz)



P5-*b*-P2 (^{1}H, $CDCl_3$, 500 MHz)