

Supporting Information

to

Influence of Constraints within a Cyclic Polymer on Solution Properties

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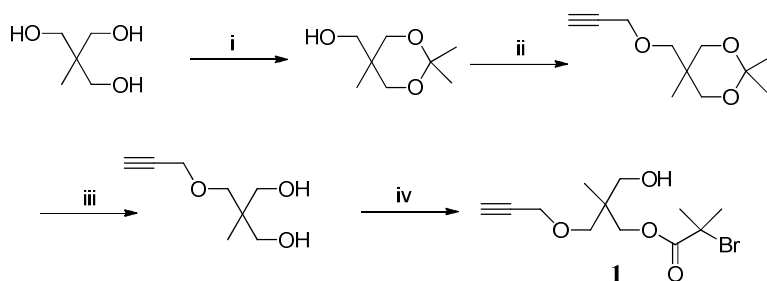
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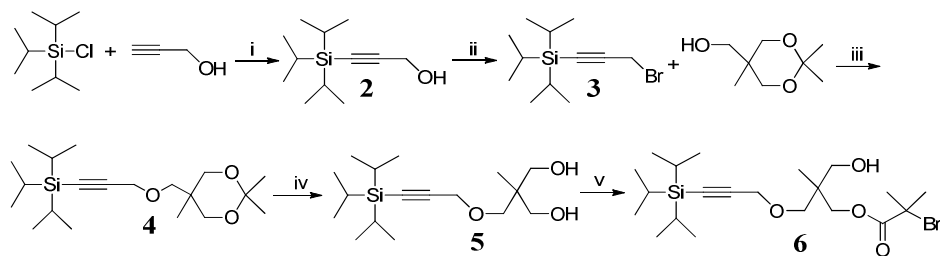
1. Characterization

Scheme S1: Synthesis of alkyne (hydroxyl) functional Initiator (1).



Reactants and conditions: i) Acetone, p-TsOH, RT, 16h; ii) THF, NaH, propargyl bromide, -78 °C, 16 h; iii) DOWEX, Methanol, R.T. 16 h; iv) THF, 2-bromoisobutyryl bromide, 0 °C - RT, 16 h.

Scheme S2: Synthetic scheme for protected alkyne (hydroxyl) functional initiator.



Reactants and conditions: (i) EtMgBr, THF, reflux at 76 °C, (ii) PBr₃, pyridine, diethyl ether 0~ 25 °C (iii) NaH/ THF, -78 °C - 25 °C (iv) DOWEX resin in MeOH at 40 °C (v) 2-bromoisobutyryl bromide, TEA in THF at 0 °C-25 °C for 24 h.

Table S1. Molecular weight data of starting polymers for complex topologies.

Polymer	Purity by LND (%)		Coupling efficiency (%) ^a	RI detection ^b			Triple detection ^c			M _n by NMR	Δ HDV ^d
	Crude	Prep		M _n	M _p	PDI	M _n	M _p	PDI		
7a				2150	21340	1.12					
8a				2261	2295	1.10					
9a				1780	1840	1.06					
11a				1940	1975	1.06					
7b				2890	2900	1.11				3120	
8b				2880	2900	1.11				2980	
9b	84.0	> 99.0		2140	2180	1.04	2780	2860	1.016	2980	0.76
10b				2350	2400	1.04				3110	
11b				2250	2300	1.04	2930	3090	1.018	3178	0.74
14b				2440	2470	1.04	3170	3320	1.021	3520	0.74
7c				6470	6450	1.08				6240	
8c				6390	6440	1.08				6310	
9c	84.8	> 99.0		4690	4900	1.04	6220	6390	1.005	6310	0.77
10c				4580	4670	1.04				6340	
11c				4750	4850	1.04	6420	6670	1.01	6200	0.73
14c				4930	5030	1.04	6520	6660	1.004	6650	0.75
15c				5020	5100	1.03	6500	6650	1.004	6860	0.77
7d				9130	9240	1.08				9580	
8d				9020	9130	1.08				9540	
9d	81.1	> 99.0		6890	7100	1.04	9190	9400	1.005	8910	0.76
10d				6670	6950	1.04				9150	
11d				6880	7100	1.04	8900	9100	1.006	9220	0.78
14d				7050	7280	1.04	9040	9240	1.007	9460	0.79
7e				17110	17730	1.09				17490	
16a				2250	2290	1.09					
17a				2320	2330	1.09					
18a				4580	4780	1.07					
19a				4490	4660	1.05					
25a				6850	7110	1.06					
26a				6840	7100	1.06					
27a				6550	6820	1.06					
30a				5430	5540	1.03					
16b				2870	3040	1.08				2960	
17b				2890	2910	1.06				3030	
18b	90.8		90.8	5510	5600	1.05				6350	
19b				5510	5550	1.06				6210	
20b		91.0		5350	5400	1.06				6420	
21b	82.1	> 99.0		4110	4170	1.03	5350	5500	1.020	6475	0.76
22b				4350	4370	1.03				6220	
23b				4470	4590	1.03	5850	5990	1.005	6250	0.77
24				4720	4830	1.04	6420	6520	1.001	6830	0.74
25b	82.0		82.0	8830	8990	1.06				9230	
26b				8750	8860	1.06				9400	
27b		86.0		8720	8880	1.05				9660	
28b	76.5	> 99.0		6600	6780	1.03	8830	8980	1.007	8930	0.75
29b				7210	7320	1.03				9230	
30b				7070	7220	1.03	9250	9390	1.004	8910	0.77
31				5750	5890	1.03					

^aCuAAC coupling efficiency was determined from the RI traces of SEC. Coupling efficiency calculated as follows: purity (LND)/max. purity by theory×100. ^bThe data was acquired using SEC (RI detector) and is based on PSTY calibration curve. ^cThe data was acquired using DMac Triple Detection SEC

with 0.03 wt% of LiCl as eluent. $^d\Delta\text{HDV}$ was calculated by dividing M_p of RI with M_p of triple detection.

Table S2. Click efficiency and molecular weight data of complex topologies.

Polymer	Purity by LND (%)		Coupling efficiency (%) ^a	RI detection ^b			Triple detection ^c			M _n by NMR	Δ HDV ^d
	Crude	Prep		M _n	M _p	PDI	M _n	M _p	PDI		
8e				17300	17970	1.06	18300	18660	1.004	17770	0.96
9e	79.8	> 99.0		13430	13760	1.04	18330	18580	1.003	17770	0.74
32	92.2	98.5	92.2	13320	13590	1.04	19140	19440	1.003	18580	0.70
33	91.4	99.0	91.4	12850	12940	1.04	19700	20400	1.017	19250	0.63
34	83.8	91.23	86.6	14050	14280	1.06	19080	19330	1.001	19030	0.74
35	77.75	97.02	80.9	12890	13130	1.04	18900	19400	1.005	18400	0.68
36	70.53	84.15	74.25	13920	13980	1.05	19680	19800	1.002	18450	0.71
37	40.0	75.3	42.0	14920	15020	1.13	19440	20244	1.05		0.74

^aCuAAC coupling efficiency was determined from the RI traces of SEC. Coupling efficiency calculated as follows: purity (LND)/max. purity by theory $\times$ 100. ^bThe data was acquired using SEC (RI detector) and is based on PSTY calibration curve. ^cThe data was acquired using DMAc Triple Detection SEC with 0.03 wt% of LiCl as eluent. ^d Δ HDV was calculated by dividing M_p of RI with M_p of triple detection.

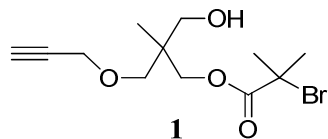
Table S3: LND simulation data for all the final products based on the weight distribution (w(M)).

Polymer	Type	Product purity w(M)	Unreacted reactants and by-products (%)					
$\equiv(\text{OH})\text{-PSTY}_{163}\text{-N}_3$, 8e		8e	8e*2	--	--	--	--	--
	Crude	88.1	11.9	--	--	--	--	--
	Prepped	91.7	8.3	--	--	--	--	--
c-PSTY ₁₆₃ -OH, 9e		9e	8e	High MW	--	--	--	--
	Crude	44.4	3.1	52.5	--	--	--	--
	Prepped	98	0.5	1.5	--	--	--	--
(c-PSTY ₈₄) ₂ 32		32	11d	14d	--	--	--	--
	Crude	92.2	4.3	3.5	--	--	--	--
	Prepped	98.5	--	1.5	--	--	--	--
st-(c-PSTY ₅₈) ₃ , 33		33	11c	15c	11c+15c	--	--	--
	Crude	91.4	4.0	2.6	2.0	--	--	--
	Prepped	98.57	--	--	1.43	--	--	--
sp-(c-PSTY) ₃ , 34		34	14c	23c	14c+23c	--	--	--
	Crude	83.8	1.2	3.0	12	--	--	--
	Prepped	94.0	--	--	6.0	--	--	--
G1-(c-PSTY) ₅ , 35		35	11b	24	11b+24	11b*2+24	11b*3+24	High MW
	Crude	77.75	2.69	0.45	0.9	8.09	--	10.11
	Prepped	97.02	--	--	--	1.98	--	1.0
G1-(c-PSTY) ₄ , 36		36	14b	30b	14b+30b	14b*2+30b	14b*2	High MW
	Crude	70.53	1.46	0.41	4.06	0.81	4.06	18.65
	Prepped	84.15	--	--	1.58	6.92	--	8.71
G1-(c-PSTY) ₇ , 37		37	11a	11a*2+31	11a*4+31	--	--	High MW
	Crude	40.0	0.6	0.8	0.4			57.4
	Prepped	75.0	1.13	1.5	0.8			22.75

Experimental Section

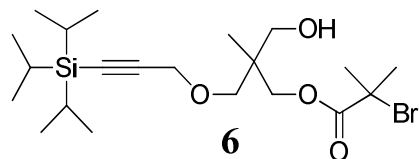
Synthesis of Alkyne (hydroxyl) Functional Initiator (1)

The alkyne (hydroxyl) functional initiator **1** was synthesized according to the literature procedure previously reported by our group.¹



Synthesis of Protected Alkyne (hydroxyl) Functional Initiator (6)

The protected alkyne (hydroxyl) functional initiator **6** was synthesized according to the literature procedure reported previously.²



Synthesis of $\equiv(HO)$ -PSTY₁₉-Br 7a by ATRP

Styrene (5.51 g, 52.9×10^{-3} mol), PMDETA (0.28 mL, 8.1×10^{-4} mol), CuBr₂/PMDETA (6.4×10^{-2} g, 4.05×10^{-4} mol) and initiator (0.5 g, 1.6277×10^{-3} mol) were added to a 100 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.12 g, 8.1×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 3 h an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (15 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in high vacuo* overnight at 25 °C, SEC (M_n = 2150, PDI = 1.12).

Synthesis of $\equiv(HO)$ -PSTY₁₉-N₃ 8a by Azidation with NaN₃

Polymer **7a** (0.7 g, 3.3×10^{-4} mol) was dissolved in 5 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (0.22 g, 3.3×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (15 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 2260, PDI = 1.1).

Synthesis of c-PSTY₁₉-OH, 9a

A solution of polymer **8a** (0.6 g, 2.7×10^{-4} mol) in 30.0 ml of dry toluene and 1.96 mL of PMDETA (9.38×10^{-3} mol) in 30 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 1.35 g of CuBr (9.38×10^{-3} mol) was taken in a 100 mL of dry schlenk flask and maintained argon flow in the flask at the same time. PMDETA solution was transferred to CuBr flask by applying argon pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, polymer solution was added via syringe pump using a syringe that is pre-filled with argon. The feed rate of argon was set at 1.24 mL/min. After the addition of polymer solutions, the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts were removed by passage through activated basic alumina column by adding few drops of glacial acetic acid. The polymer was recovered by precipitation into MeOH (15 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. (Purity by SEC > 95%). SEC (M_n =1780, PDI=1.04).

Synthesis of c-PSTY₁₉-Br, 10a

c-PSTY₁₉-OH, **9a** (0.29 g, 1.3×10^{-4} mol), TEA (0.18 mL, 1.3×10^{-3} mol) and 2.0 ml of dry THF were added under an argon blanket to a dry schlenk flask that has been flushed with argon. The reaction was then cooled on ice bath. To this stirred mixture, a solution of 2-bromopropionyl bromide (0.14 mL, 1.3×10^{-3} mol) in 0.5 mL of dry THF was added drop wise under argon via an air-tight syringe over 1 min. After stirring the reaction mixture for 48 h at room temperature, the crude polymer solution was added in 30 mL of acetone and filtered

to remove salt precipitate. Solvent was removed by rotavap and precipitated into MeOH, filtered and washed three times with MeOH. The polymer was dried for 24 h in high vacuum oven at 25 °C. The polymer was used in the next step without further characterization.

Synthesis of c-PSTY₁₉-N₃ 11a

Polymer c-PSTY₁₉-Br **10a** (0.26 g, 1.11×10^{-4} mol) was dissolved in 2 mL of DMF in a reaction vessel equipped with magnetic stirrer. To this solution, NaN₃ (0.07 g, 1.1×10^{-3} mol) was added and the mixture stirred for 24 h at room temperature. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (15 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was purified by preparative SEC and precipitated and filtered. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 1940, PDI = 1.06).

Synthesis of $\equiv$ (HO)-PSTY₂₅-Br 7b by ATRP

Styrene (8.11g, 77.86×10^{-3} mol), PMDETA (0.17 mL, 8.1×10^{-4} mol), CuBr₂/PMDETA (6.4×10^{-2} g, 4.05×10^{-4} mol) and initiator (0.5 g, 1.6277×10^{-3} mol) were added to a 100 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.12 g, 8.1×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 4 h an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in high vacuo* overnight at 25 °C, SEC (M_n = 2890, PDI = 1.11). Final conversion was calculated by gravimetry 53.3%. The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of $\equiv$ (HO)-PSTY₂₅-N₃ 8b by Azidation with NaN₃

Polymer **7b** (2.9 g, 1.0×10^{-3} mol) was dissolved in 20 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN_3 (0.65 g, 10.0×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 2880, PDI = 1.11). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of c-PSTY₂₅-OH, 9b

A solution of polymer **8b** (2.0 g, 6.667×10^{-4} mol) in 80.0 ml of dry toluene and 6.97 mL of PMDETA (33.35×10^{-3} mol) in 80 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 4.78 g of CuBr (33.35×10^{-3} mol) was taken in a 250 mL of dry schlenk flask and maintained argon flow in the flask at the same time. PMDETA solution was transferred to CuBr flask by applying argon pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, polymer solution was added via syringe pump using a syringe that is pre-filled with argon. The feed rate of argon was set at 1.24 mL/min. After the addition of polymer solutions (65 min), the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts were removed by passage through activated basic alumina column by adding few drops of glacial acetic acid. The polymer was recovered by precipitation into MeOH (20 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. (Purity by SEC=88.9%). A small fraction of crude product was purified by preparative SEC for characterization. SEC (M_n =2140, PDI=1.04), Triple Detection SEC (M_n = 2780, PDI=1.02). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of c-PSTY₂₅-Br, 10b

c-PSTY₂₅-OH, **9b** (1.6 g, 5.867×10^{-4} mol), TEA (1.63 mL, 11.73×10^{-3} mol) and 30.0 ml of dry THF were added under an argon blanket to a dry schlenk flask that has been flushed with argon. The reaction was then cooled on ice bath. To this stirred mixture, a solution of 2-bromopropionyl bromide (1.23 mL, 11.73×10^{-3} mol)

in 10 mL of dry THF was added drop wise under argon via an air-tight syringe over 10 min. After stirring the reaction mixture for 48 h at room temperature, the crude polymer solution was added in 300 mL of acetone and filtered to remove salt precipitate. Solvent was removed by rotavap and precipitated into MeOH, filtered and washed three times with MeOH. A fraction of crude product was purified by preparative SEC for characterization. The polymer was dried for 24 h in high vacuum oven at 25 °C. SEC (M_n =2350, PDI=1.04). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₂₅-N₃, 11b

Polymer c-PSTY₂₅-Br **10b** (1.5 g, 0.5×10^{-3} mol) was dissolved in 10 mL of DMF in a reaction vessel equipped with magnetic stirrer. To this solution, NaN₃ (0.65 g, 1.0×10^{-3} mol) was added and the mixture stirred for 24 h at room temperature. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. A fraction of the polymer was purified by preparative SEC and precipitated and filtered. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 2250, PDI = 1.04) and Triple Detection SEC (M_n = 2930, PDI=1.02). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₂₅-≡ 14b

Polymer c-PSTY₂₅-N₃ **11b** (0.4 g, 0.133×10^{-3} mol), PMDETA (27.87×10^{-3} mL, 0.133×10^{-3} mol) and methyl 3,5-bis (propargyloxyl) benzoate **12** (0.49 g, 1.99×10^{-3} mol) were dissolved in 3.0 mL toluene. CuBr (19.0×10^{-3} g, 1.33×10^{-4} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both reaction vessels were purged with argon for 20 min. The polymer solution was then transferred to CuBr flask by applying argon pressure using double tip needle. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and

filtration. The polymer was purified by preparative SEC to remove excess linker as well as high MW impurities. After precipitation and filtration, the polymer was dried *in vacuo* for 24 h at 25 °C. SEC ($M_n=2440$, PDI=1.04) and Triple Detection SEC ($M_n=3170$, PDI=1.02). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of $\equiv(HO)$ -PSTY₅₈-Br 7c by ATRP

Styrene (3.7 g, 35.53×10^{-3} mol), PMDETA (0.034 mL, 1.63×10^{-4} mol), CuBr₂/PMDETA (1.3×10^{-2} g, 0.32×10^{-4} mol) and initiator (0.1 g, 3.2×10^{-4} mol) were added to a 50 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.023 g, 1.63×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 4 h an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in high vacuo* overnight at 25 °C, SEC (M_n = 6470, PDI = 1.08). Final conversion was calculated by gravimetry 53.1%. The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of $\equiv(HO)$ -PSTY₅₈-N₃ 8c by Azidation with NaN₃

Polymer **7c** (1.0 g, 1.6×10^{-4} mol) was dissolved in 10 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (0.16 g, 2.4×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 6390, PDI = 1.08). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of c-PSTY₅₈-OH, 9c

A solution of polymer **8c** (0.75 g, 1.19×10^{-4} mol) in 37.5 ml of dry toluene and 1.24 mL of PMDETA (5.95×10^{-3} mol) in 37.5 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 0.854 g of CuBr (5.95×10^{-3} mol) was taken in a 100 mL of dry schlenk flask and maintained argon flow in the flask at the same time. PMDETA solution was transferred to CuBr flask by applying argon

pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, polymer solution was added via syringe pump using a syringe that is pre-filled with argon. The feed rate of argon was set at 0.5 mL/min. After the addition of polymer solutions (75 min), the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts were removed by passage through activated basic alumina column by adding few drops of glacial acetic acid. The polymer was recovered by precipitation into MeOH (20 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. (Purity by LND (based on number distribution) =80.0%). A small fraction of crude product was purified by preparative SEC for characterization. SEC (M_n =4690, PDI=1.04), Triple Detection SEC (M_n = 6220, PDI=1.005). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₅₈-Br, 10c

c-PSTY₅₈-OH, **9c** (0.15 g, 2.4×10^{-5} mol), TEA (0.066 mL, 4.8×10^{-4} mol) and 2.0 ml of dry THF were added under an argon blanket to a dry schlenk flask that has been flushed with argon. The reaction was then cooled on ice bath. To this stirred mixture, a solution of 2-bromopropionyl bromide (0.05 mL, 4.8×10^{-4} mol) in 1 mL of dry THF was added drop wise under argon via an air-tight syringe over 2 min. After stirring the reaction mixture for 48 h at room temperature, the crude polymer solution was precipitated into MeOH, filtered and washed three times with MeOH. The polymer was dried for 24 h in high vacuum oven at 25 °C. SEC (M_n =4580, PDI=1.04). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₅₈-N₃, 11c

Polymer c-PSTY₅₈-Br **10c** (0.134 g, 2.12×10^{-5} mol) was dissolved in 1.5 mL of DMF in a reaction vessel equipped with magnetic stirrer. To this solution, NaN₃ (0.028 g, 4.25×10^{-4} mol) was added and the mixture stirred for 24 h at room temperature. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 4750, PDI = 1.04)

and Triple Detection SEC (M_n = 6420, PDI=1.01). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₅₈-≡, 14c

Polymer c-PSTY₅₈-N₃ **11c** (0.1 g, 1.59×10^{-5} mol), PMDETA (3.32×10^{-3} mL, 1.59×10^{-5} mol) and methyl 3,5-bis(propargyloxy) benzoate **12** (0.039 g, 1.59×10^{-4} mol) were dissolved in toluene/DMSO (0.75 mL/0.05 mL) mixed solvent. CuBr (2.28×10^{-3} g, 1.59×10^{-5} mol) was added to a 10 mL schlenk tube equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 25 min. The polymer solution was then transferred to CuBr flask by applying argon pressure using double tip needle. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was purified by preparative SEC to remove excess linker as well as high MW impurities. After precipitation and filtration, the polymer was dried *in vacuo* for 24 h at 25 °C. SEC (M_n =4930, PDI=1.04) and Triple Detection SEC (M_n =6520, PDI=1.004). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₅₈-(≡)₂, 15c

Polymer c-PSTY₅₈-N₃, **11c** (0.09 g, 1.42×10^{-5} mol), PMDETA (2.98×10^{-3} mL, 1.42×10^{-5} mol) and 1,3,5-tris(prop-2-ynyloxy)benzene, **13** (0.034 g, 1.42×10^{-4} mol) were dissolved in 0.5 mL toluene. CuBr (2.0×10^{-3} g, 1.42×10^{-5} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 15 min. The polymer solution was then transferred to CuBr flask using double tipped needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution)

and filtration. The polymer was further purified by preparative SEC to remove residual linker as well as high MW impurities. After precipitation and filtration, the polymer was dried *in vacuo* for 24 h at 25 °C, SEC ($M_n=5020$, PDI=1.03) and Triple Detection SEC ($M_n=6500$, PDI=1.004). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of $\equiv(\text{HO})\text{-PSTY}_{84}\text{-Br}$, 7d by ATRP

Styrene (4.23 g, 40.7×10^{-3} mol), PMDETA (0.026 mL, 1.2×10^{-4} mol), $\text{CuBr}_2/\text{PMDETA}$ (9.68×10^{-3} g, 2.4×10^{-5} mol) and initiator (0.075 g, 2.4×10^{-4} mol) were added to a 50 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.018 g, 1.2×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 4 h an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in high vacuo* overnight at 25 °C, SEC ($M_n = 9130$, PDI = 1.08). Final conversion was calculated by gravimetry 46.0%. The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of $\equiv(\text{HO})\text{-PSTY}_{84}\text{-N}_3$, 8d by Azidation with NaN_3

Polymer **7d** (1.0 g, 1.1×10^{-4} mol) was dissolved in 10 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN_3 (0.14 g, 2.2×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/ H_2O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC ($M_n = 9020$, PDI = 1.08). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₈₄-OH, 9d

A solution of polymer **8d** (0.5 g, 5.5×10^{-5} mol) in 25 mL of dry toluene and 0.575 mL of PMDETA (2.75×10^{-3} mol) in 25 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 0.394 g of CuBr (2.75×10^{-3} mol) was taken in a 100 mL of dry schlenk flask and maintained argon flow in the flask at the same time. PMDETA solution was transferred to CuBr flask by applying argon pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, polymer solution was added via syringe pump using a syringe that is pre-filled with argon. The feed rate of argon was set at 0.5 mL/min. After the addition of polymer solutions (50 min), the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts were removed by passage through activated basic alumina column by adding few drops of glacial acetic acid. The polymer was recovered by precipitation into MeOH (20 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. (Purity by LND (based on number distribution) =74.5%). A small fraction of crude product was purified by preparative SEC for characterization. SEC (M_n =6890, PDI=1.04), Triple Detection SEC (M_n = 9190, PDI=1.005). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₈₄-Br, 10d

c-PSTY₈₄-OH, **9d** (0.2 g, 2.2×10^{-5} mol), TEA (0.092 mL, 1.1×10^{-3} mol) and 3.0 mL of dry THF were added under an argon blanket to a dry schlenk flask that has been flushed with argon. The reaction was then cooled on ice bath. To this stirred mixture, a solution of 2-bromopropionyl bromide (0.069 mL, 1.1×10^{-3} mol) in 1 mL of dry THF was added drop wise under argon via an air-tight syringe over 2 min. After stirring the reaction mixture for 48 h at room temperature, the crude polymer solution was precipitated into MeOH, filtered and washed three times with MeOH. The polymer was dried for 24 h in high vacuum oven at 25 °C. SEC (M_n =6670, PDI=1.04). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₈₄-N₃ 11d

Polymer c-PSTY₈₄-Br **10d** (0.195 g, 2.12×10^{-5} mol) was dissolved in 2.0 mL of DMF in a reaction vessel equipped with magnetic stirrer. To this solution, NaN₃ (0.041 g, 6.4×10^{-4} mol) was added and the mixture stirred for 24 h at room temperature. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC (M_n = 6880, PDI = 1.04) and Triple Detection SEC (M_n = 8900, PDI = 1.006). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of c-PSTY₈₄-≡, 14d

Polymer c-PSTY₈₄-N₃, **11d** (0.12 g, 1.3×10^{-5} mol), PMDETA (2.72×10^{-3} mL, 1.3×10^{-5} mol) and methyl 3,5-bis (propargyloxy) benzoate **12** (0.031 g, 1.3×10^{-4} mol) were dissolved in toluene/DMSO (0.75 mL/0.05 mL) mixed solvent. CuBr (1.86×10^{-3} g, 1.3×10^{-5} mol) was added to a 10 mL schlenk tube equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 25 min. The polymer solution was then transferred to CuBr flask by applying argon pressure using double tip needle. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was purified by preparative SEC to remove excess linker as well as high MW impurities. After precipitation and filtration, the polymer was dried *in vacuo* for 24 h at 25 °C. SEC (M_n = 7050, PDI = 1.04) and Triple Detection SEC (M_n = 9040, PDI = 1.007). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of ≡(HO)-PSTY₁₆₃-Br, 7e by ATRP

Styrene (5.76 g, 55.3×10^{-3} mol), PMDETA (0.018 mL, 8.5×10^{-5} mol), CuBr₂/PMDETA (6.78×10^{-3} g, 2.4×10^{-5} mol) and initiator (0.075 g, 2.4×10^{-4} mol) were added to a 50 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.018 g, 1.7×10^{-5} mol) was

then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 4 h an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in high vacuo* overnight at 25 °C, SEC ($M_n = 17110$, PDI = 1.09). Final conversion was calculated by gravimetry 33.3%. The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of $\equiv(\text{HO})\text{-PSTY}_{163}\text{-N}_3$, 8e by Azidation with NaN_3

Polymer **7e** (1.0 g, 5.6×10^{-5} mol) was dissolved in 10 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN_3 (0.11 g, 16.8×10^{-4} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/ H_2O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with MeOH. The polymer was dried *in vacuo* for 24 h at 25 °C, SEC ($M_n = 17300$, PDI = 1.06). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of c-PSTY₁₆₃-OH, 9e

A solution of polymer **8e** (0.1 g, 5.5×10^{-6} mol) in 10 mL of dry toluene and 0.116 mL of PMDETA (5.5×10^{-4} mol) in 25 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 0.08 g of CuBr (2.75×10^{-3} mol) was taken in a 50 mL of dry schlenk flask and maintained argon flow in the flask at the same time. PMDETA solution was transferred to CuBr flask by applying argon pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, polymer solution was added via syringe pump using a syringe that is pre-filled with argon. The feed rate of argon was set at 0.2 mL/min. After the addition of polymer solutions (50 min), the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts

were removed by passage through activated basic alumina column by adding few drops of glacial acetic acid. The polymer was recovered by precipitation into MeOH (20 fold excess to polymer solution) and then by filtration. The polymer was dried *in vacuo* for 24 h at 25 °C. (Purity by LND (based on number distribution) =73.4%). A small fraction of crude product was purified by preparative SEC for characterization. SEC (M_n =13430, PDI=1.04), Triple Detection SEC (M_n = 18330, PDI=1.003). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of Complex Topologies

Synthesis of spiro dicyclic, (c-PSTY₈₄)₂ 32

Polymer c-PSTY₈₄-N₃ **11d** (2.97×10^{-2} g, 3.2×10^{-6} mol), polymer c-PSTY₈₄-≡ **14d** (3.0×10^{-2} g, 3.2×10^{-6} mol) and PMDETA (6.7×10^{-4} mL, 3.2×10^{-6} mol) were dissolved in 0.5 mL of toluene. CuBr (4.6×10^{-4} g, 3.2×10^{-6} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 20 min. The polymer solution was then transferred to CuBr flask using double tip needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC (M_n =13320, PDI=1.04), Triple Detection SEC (M_n =19140, PDI=1.003). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of star tricyclic, (c-PSTY₅₈)₃, 33

Polymer c-PSTY₅₈-N₃ **11c** (4.9×10^{-2} g, 7.68×10^{-6} mol), polymer c-PSTY₅₈-(≡)₂, **15c** (2.5×10^{-2} g, 3.8×10^{-6} mol) and PMDETA (1.6×10^{-3} mL, 7.68×10^{-6} mol) were dissolved in 0.5 mL of toluene. CuBr (1.12×10^{-3} g, 7.68×10^{-6} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction

vessels were purged with argon for 20 min. The polymer solution was then transferred to CuBr flask using double tip needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC ($M_n=12850$, PDI=1.04), Triple Detection SEC ($M_n=19700$, PDI=1.017). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of spiro tricyclic, (c-PSTY)₃ 34

Polymer c-PSTY₅₀-(N₃)₂ **23b** (2.0×10^{-2} g, 3.2×10^{-6} mol), polymer c-PSTY₅₈-≡ **14c** (4.4×10^{-2} g, 6.77×10^{-6} mol) and PMDETA (1.35×10^{-3} mL, 3.2×10^{-6} mol) were dissolved in 0.5 mL of toluene. CuBr (9.25×10^{-4} g, 3.2×10^{-6} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 25 min. The polymer solution was then transferred to CuBr flask using double tip needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC ($M_n=14050$, PDI=1.06), Triple Detection SEC ($M_n=19080$, PDI=1.001). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of G1 Dendrimer Pentacyclic (c-PSTY)₅ 35

Polymer c-PSTY₅₀-(≡)₄ **24** (2.5×10^{-2} g, 3.8×10^{-6} mol), polymer c-PSTY₂₅-N₃, **11b** (4.8×10^{-2} mg, 1.6×10^{-5} mol) and PMDETA (3.16×10^{-3} mL, 1.5×10^{-5} mol) were dissolved in 0.5 mL of toluene. CuBr (2.2 mg, 0.015 mmol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 15 min. The polymer solution was then transferred to CuBr flask using double tip needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then further purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC ($M_n=12890$, PDI=1.04), Triple Detection SEC ($M_n=18900$, PDI=1.005). The polymer was further characterized by ¹H NMR and MALDI-ToF.

Synthesis of G1 Star Tetracyclic (c-PSTY)₄ 36

Polymer c-PSTY₇₅-(N₃)₃ **30b** (3.0×10^{-2} g, 3.2×10^{-6} mol), polymer c-PSTY₂₅-≡ **14b** (3.2×10^{-2} g, 1.0×10^{-5} mol) and PMDETA (2.0×10^{-3} mL, 9.5×10^{-6} mol) were dissolved in 0.6 mL of toluene. CuBr (1.4×10^{-3} g, 9.5×10^{-6} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 15 min. The polymer solution was then transferred to CuBr flask using double tipped needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then further purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC

(M_n =13920, PDI=1.05), Triple Detection SEC (M_n =19680, PDI=1.002). The polymer was further characterized by ^1H NMR and MALDI-ToF.

Synthesis of G1 Star Heptacyclic (c-PSTY)₇, 37

Polymer c-PSTY₅₄-($\equiv$)₆⁴ **31** (5.0×10^{-2} g, 7.0×10^{-6} mol), polymer c-PSTY₁₈-N₃, **11a** (10.1×10^{-2} mg, 4.4×10^{-5} mol) and PMDETA (8.8×10^{-3} mL, 4.2×10^{-5} mol) were dissolved in 1.5 mL of toluene. CuBr (6.0 mg, 4.2×10^{-5} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 15 min. The polymer solution was then transferred to CuBr flask using double tip needle by applying argon pressure. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was then further purified by preparatory SEC to remove undesired high molecular weight polymers and residual reactant polymers. The polymer was dried *in vacuo* for 24 h at 25 °C and characterized. SEC (M_n =14920, PDI=1.13), Triple Detection SEC (M_n =19440, PDI=1.05).

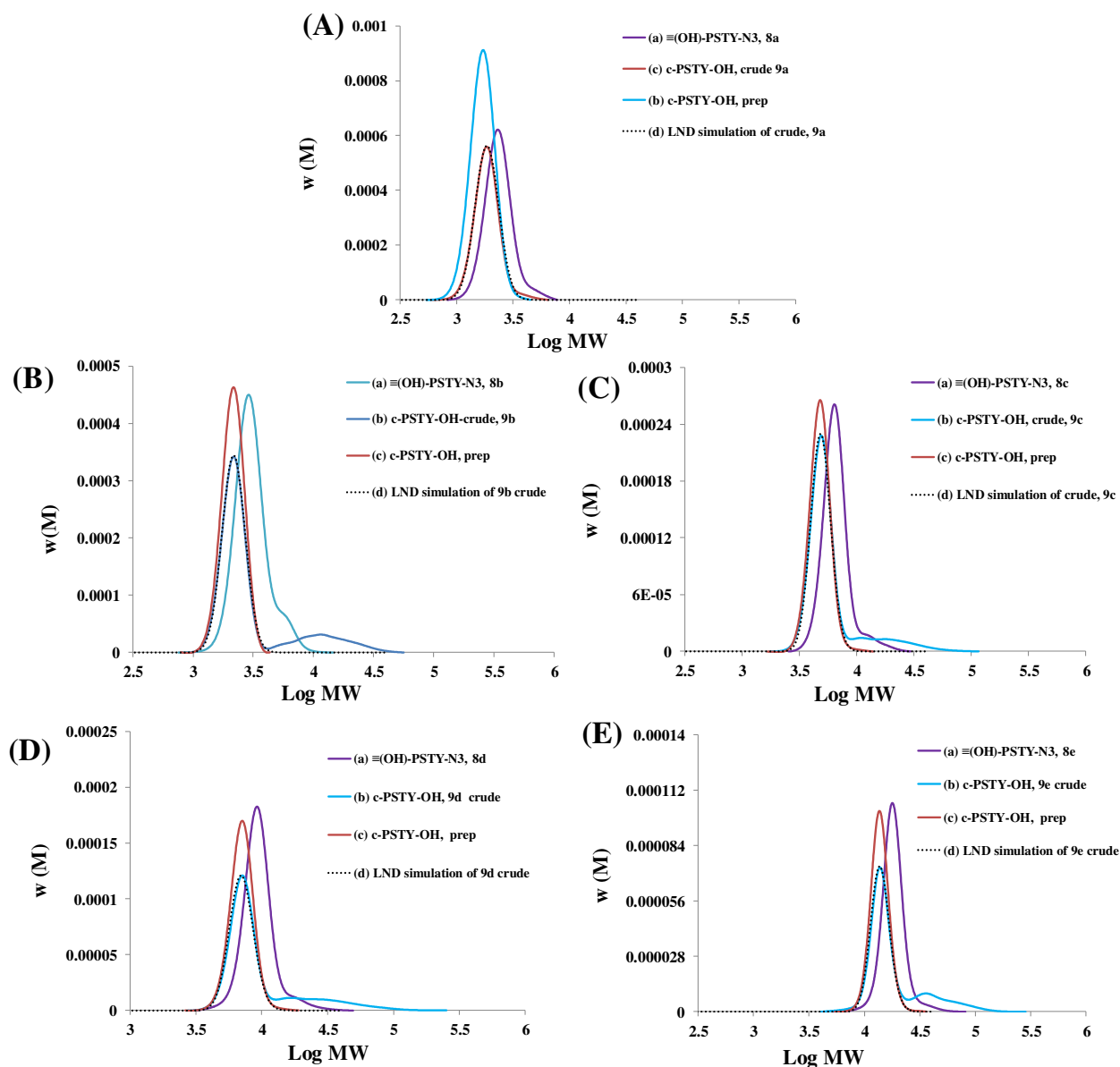


Figure S1. SEC chromatograms for cyclization: (A) (a) $\equiv(\text{OH})\text{-PSTY}_{18}\text{-N}_3$ **8a** (b) c-PSTY₁₈-OH crude, **9a** (c) c-PSTY₁₈-OH purified by prep and (d) LND simulation of **9a** crude with hydrodynamic volume change of 0.76; (B) (a) $\equiv(\text{OH})\text{-PSTY}_{25}\text{-N}_3$ **8b** (b) c-PSTY₂₅-OH crude, **9b** (c) c-PSTY₁₈-OH purified by prep and (d) LND simulation of **9b** crude with hydrodynamic volume change of 0.75 (C) (a) $\equiv(\text{OH})\text{-PSTY}_{58}\text{-N}_3$ **8c** (b) c-PSTY₅₈-OH crude, **9c** (c) c-PSTY₅₈-OH purified by prep and (d) LND simulation of **9c** crude with hydrodynamic volume change of 0.75; (D) (a) $\equiv(\text{OH})\text{-PSTY}_{84}\text{-N}_3$ **8d** (b) c-PSTY₈₄-OH crude, **9d** (c) c-PSTY₈₄-OH purified by prep and (d) LND simulation of **9d** crude with hydrodynamic volume change of 0.76; (E) (a) $\equiv(\text{OH})\text{-PSTY}_{163}\text{-N}_3$ **8e** (b) c-PSTY₁₆₃-OH crude, **9e** (c) c-PSTY₁₆₃-OH purified by prep and (d) LND simulation of **9e** crude with hydrodynamic volume change of 0.765; SEC analysis based on polystyrene calibration curve.

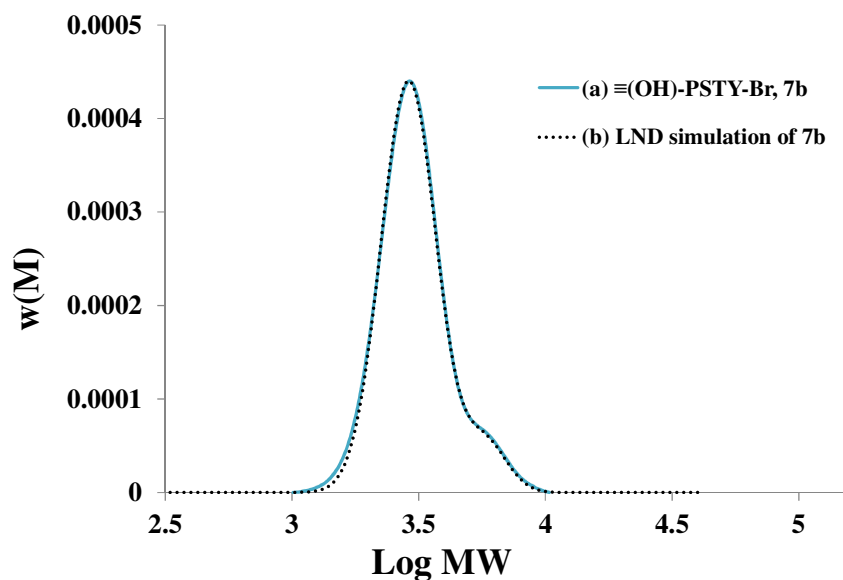


Figure S2: SEC trace of (a) $\equiv(\text{OH})\text{-PSTY}_{25}\text{-Br}$ **7b** and (b) LND simulation. SEC analysis based on polystyrene calibration curve.

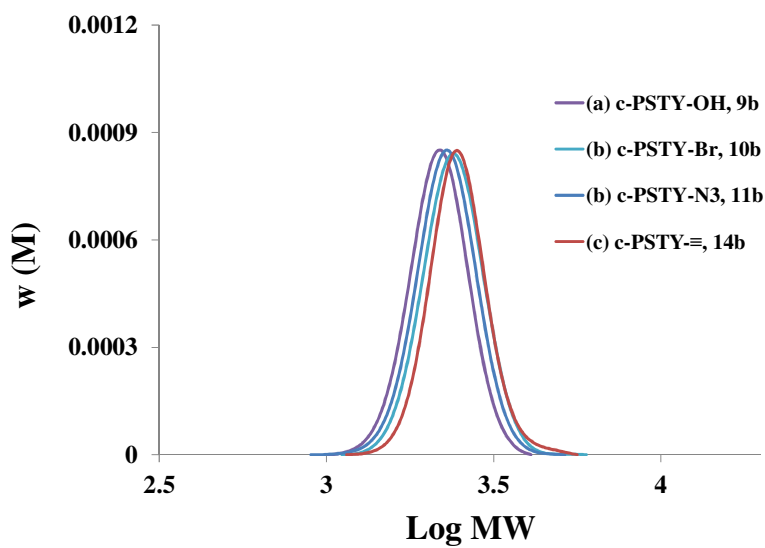


Figure S3: SEC trace of (a) $\text{c-PSTY}_{25}\text{-OH}$, **9b**, (b) $\text{c-PSTY}_{25}\text{-Br}$, **10b**, (c) $\text{c-PSTY}_{25}\text{-N}_3$, **11b** and (d) $\text{c-PSTY}_{25}\text{-}\equiv$, **14b**. SEC analysis based on polystyrene calibration curve.

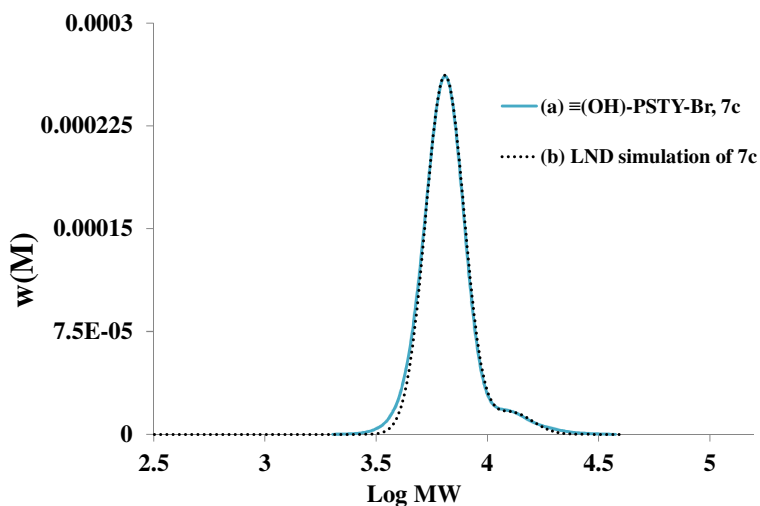


Figure S4: SEC trace of (a) $\equiv(\text{OH})\text{-PSTY}_{58}\text{-Br}$ **7c** and (b) LND simulation. SEC analysis based on polystyrene calibration curve.

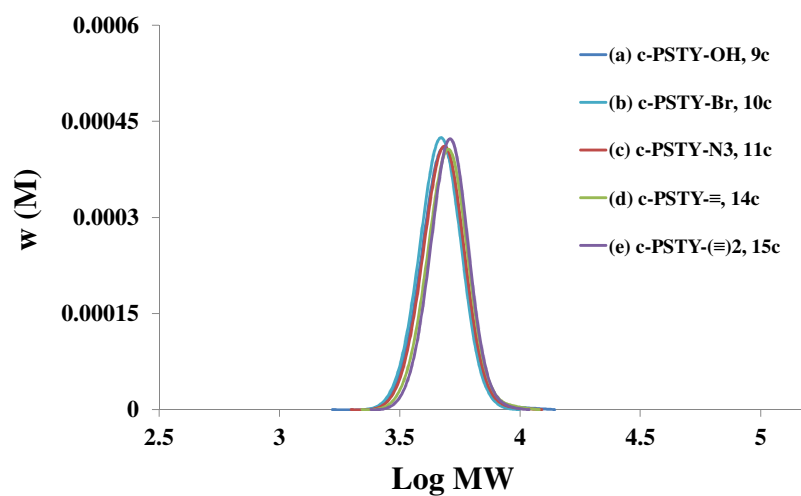


Figure S5: SEC trace of (a) $\text{c-PSTY}_{58}\text{-OH}$, **9c**, (b) $\text{c-PSTY}_{58}\text{-Br}$, **10c**, (c) $\text{c-PSTY}_{58}\text{-N}_3$, **11c**, (d) $\text{c-PSTY}_{58}\text{-}\equiv$, **14c** and (e) $\text{c-PSTY}_{58}\text{-(}\equiv\text{)}_2$, **15c**. SEC analysis based on polystyrene calibration curve.

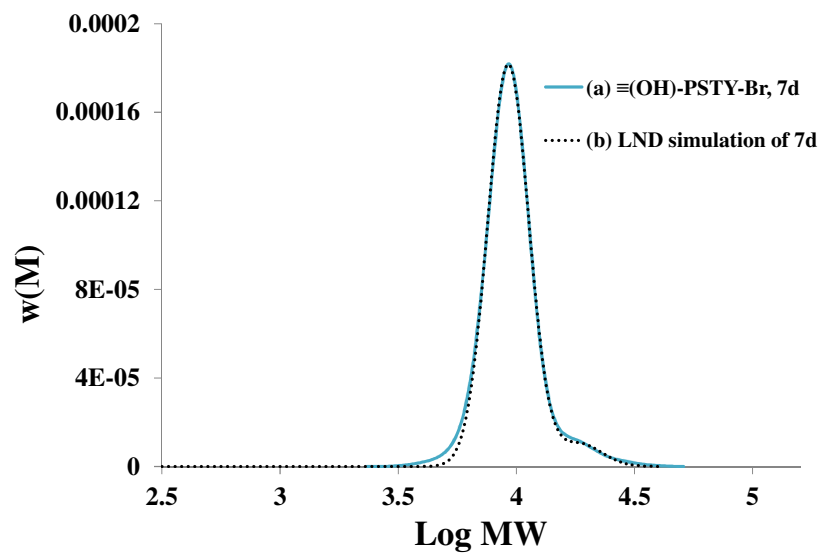


Figure S6: SEC trace of (a) $\equiv(\text{OH})\text{-PSTY}_{84}\text{-Br}$ 7d and (b) LND simulation. SEC analysis based on polystyrene calibration curve.

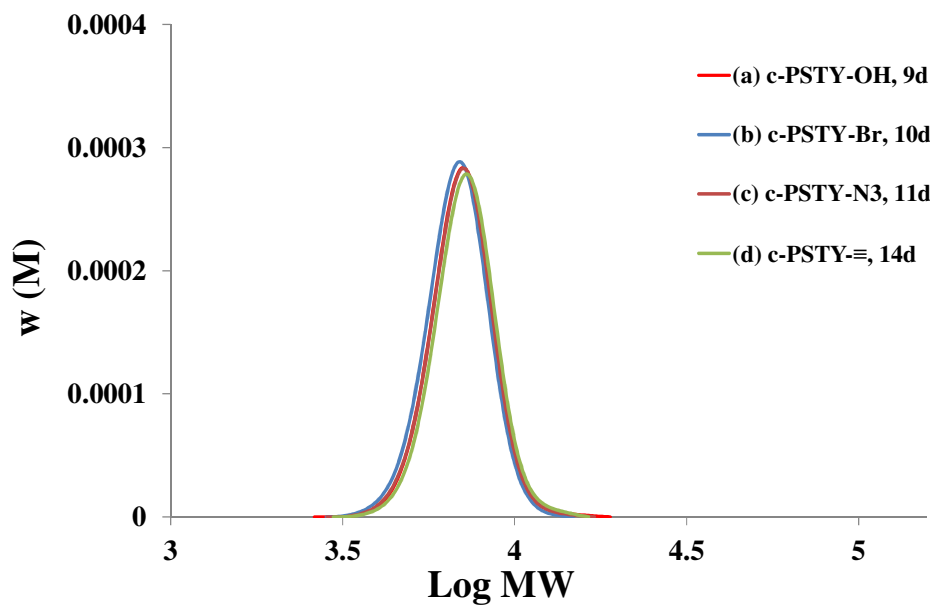


Figure S7: SEC trace of (a) c-PSTY₈₄-OH, **9d**, (b) c-PSTY₈₄-Br, **10d**, (c) c-PSTY₈₄-N₃, **11d** and (d) c-PSTY₈₄- $\equiv$, **14d**. SEC analysis based on polystyrene calibration curve.

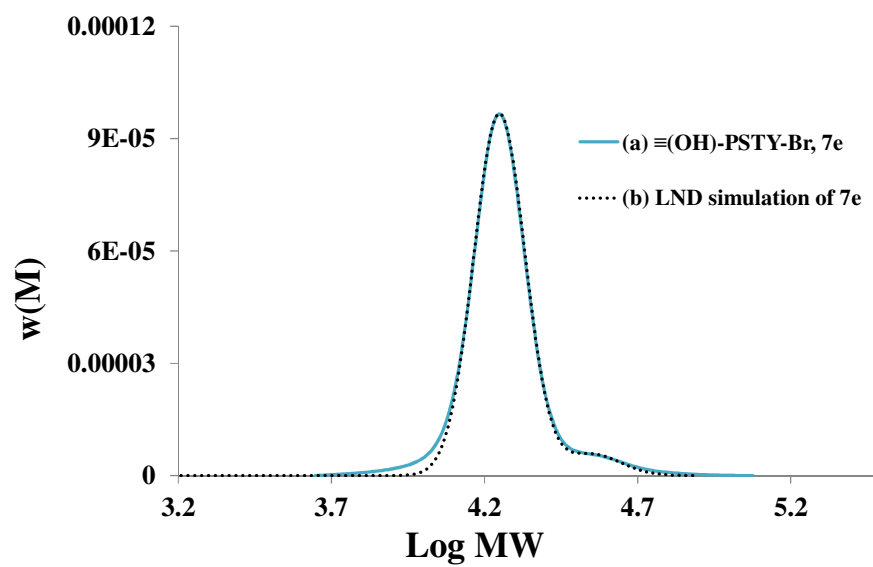


Figure S8: SEC trace of (a) $\equiv(\text{OH})\text{-PSTY}_{164}\text{-Br}$ 7e and (b) LND simulation. SEC analysis based on polystyrene calibration curve.

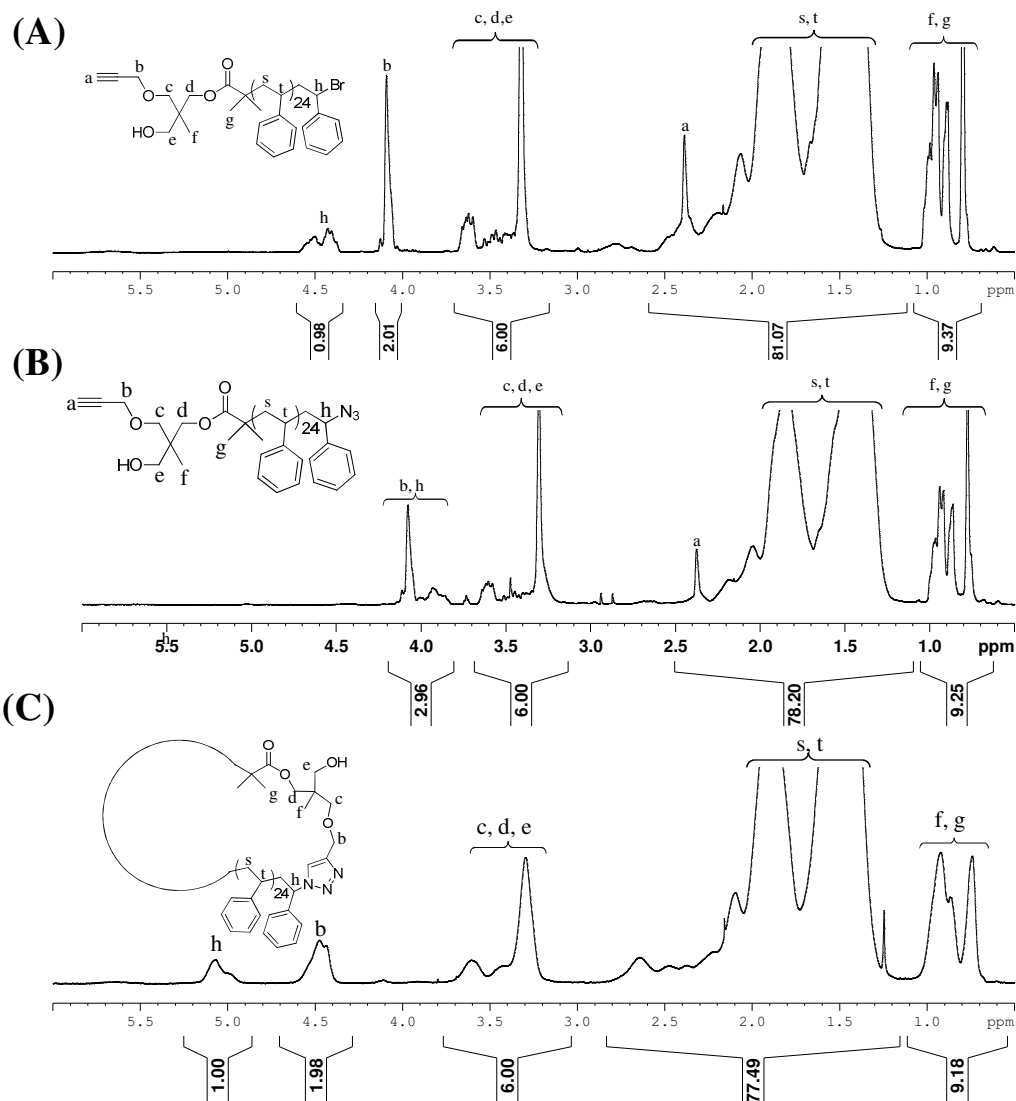


Figure S9. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) $\equiv(\text{OH})\text{-PSTY}_{25}\text{-Br}$ **7b**, (b) $\equiv(\text{OH})\text{-PSTY}_{25}\text{-N}_3$ **8b**, (c) $\text{c-PSTY}_{25}\text{-OH}$ **9b**.

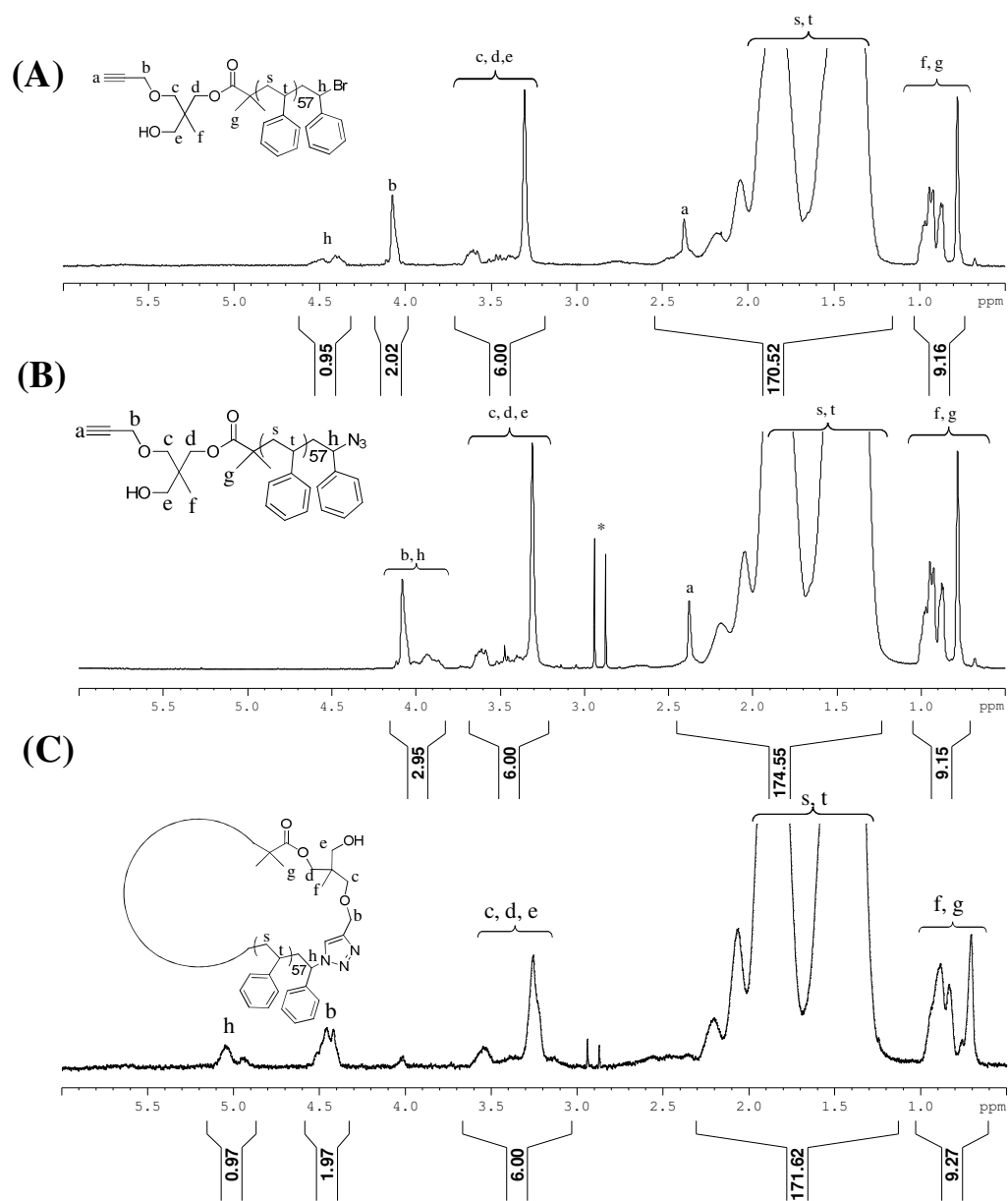


Figure S11. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) $\equiv(\text{OH})\text{-PSTY}_{58}\text{-Br}$ **7c**, (b) $\equiv(\text{OH})\text{-PSTY}_{58}\text{-N}_3$ **8c**, (c) $\text{c-PSTY}_{58}\text{-OH}$ **9c**.

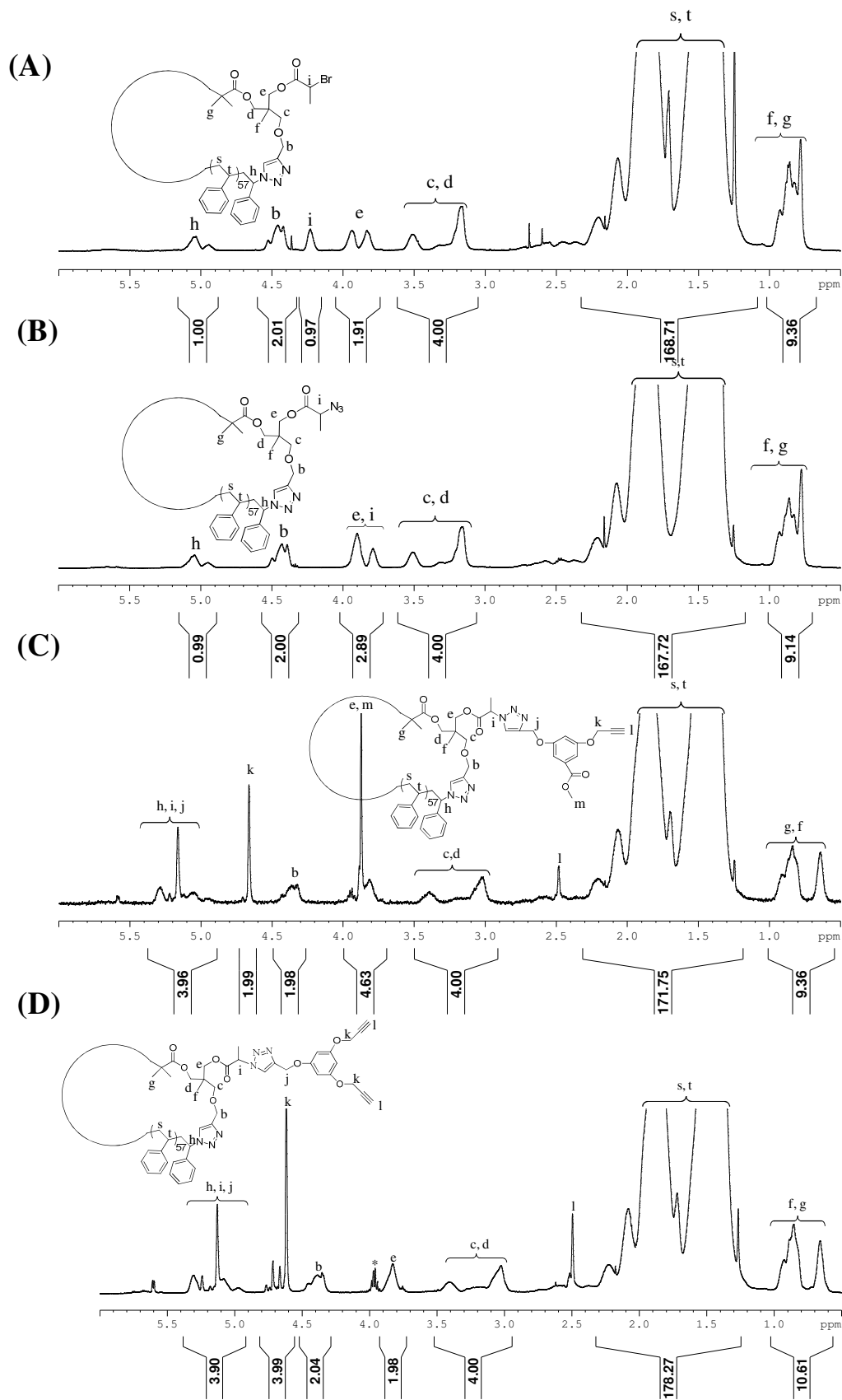


Figure S12. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) c-PSTY₅₈-Br **10c**, (B) c-PSTY₅₈-N₃ **11c**, (C) c-PSTY₅₈-≡ **14c** and (D) c-PSTY₅₈-(≡)₂ **15c**.

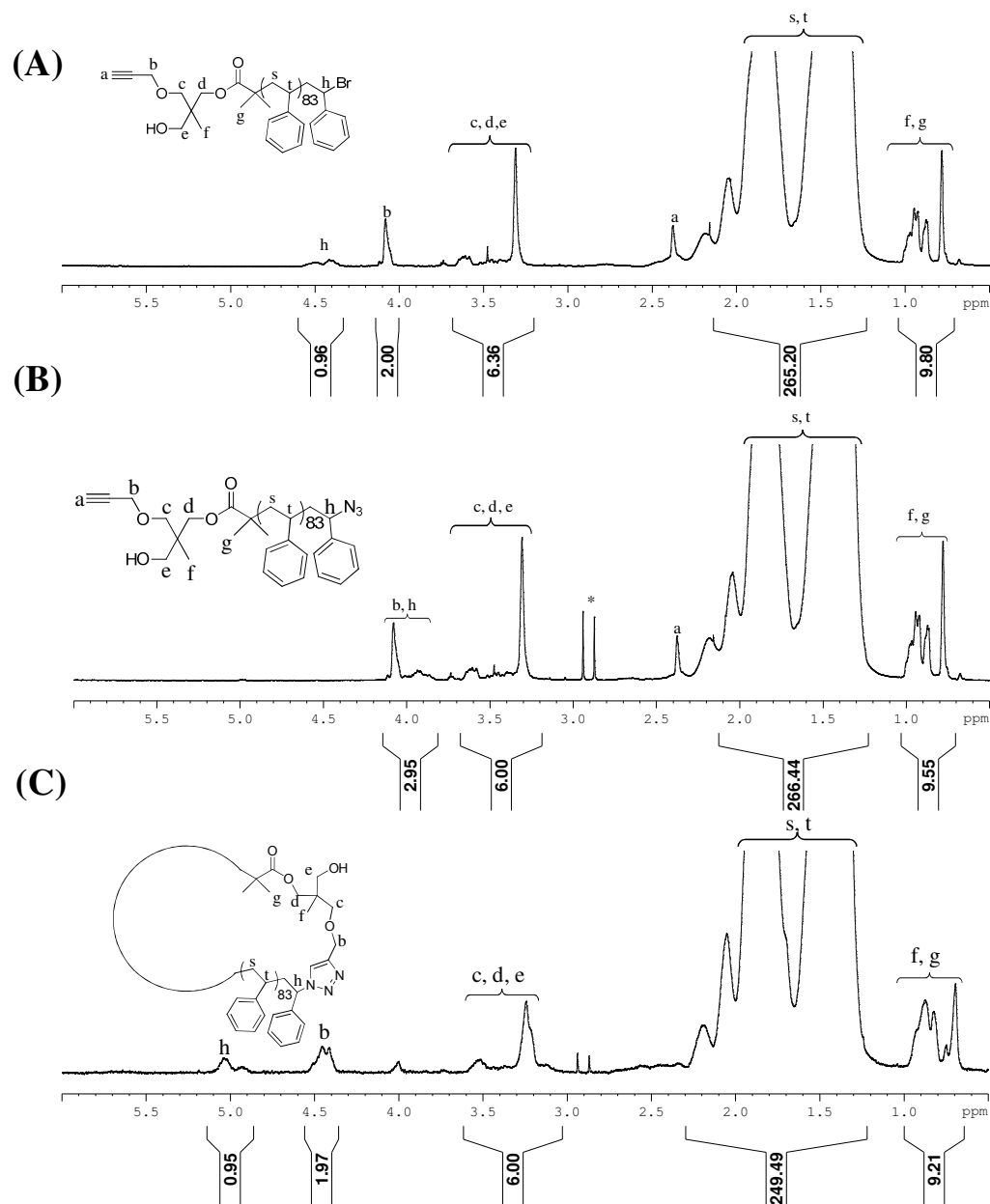


Figure S13. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) $\equiv(\text{OH})\text{-PSTY}_{84}\text{-Br}$ **7d**, (b) $\equiv(\text{OH})\text{-PSTY}_{84}\text{-N}_3$ **8d**, (c) $\text{c-PSTY}_{84}\text{-OH}$ **9d**.

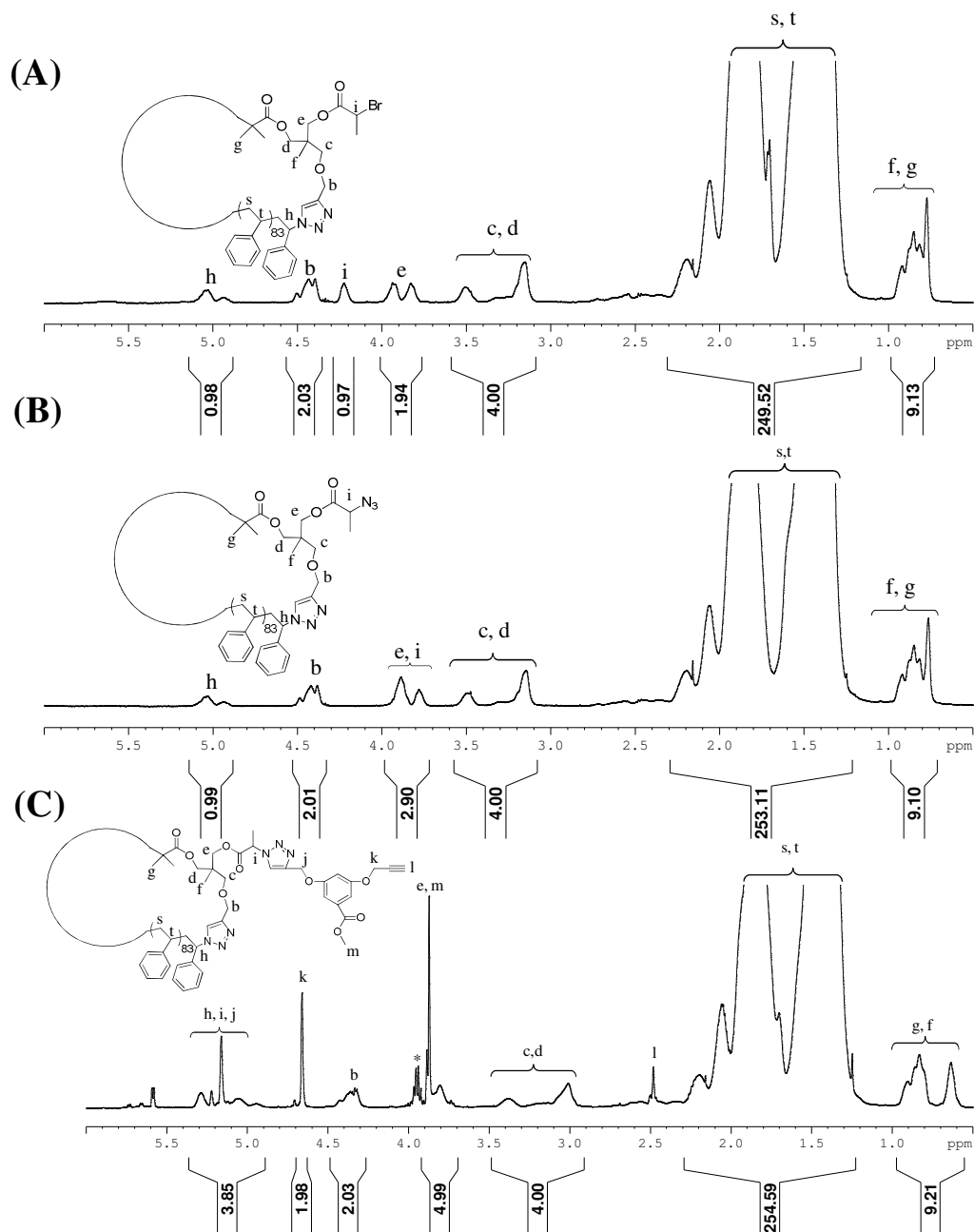


Figure S14. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) c-PSTY₈₄-Br **10d**, (B) c-PSTY₈₄-N₃ **11d** and (C) c-PSTY₈₄≡ **14d**.

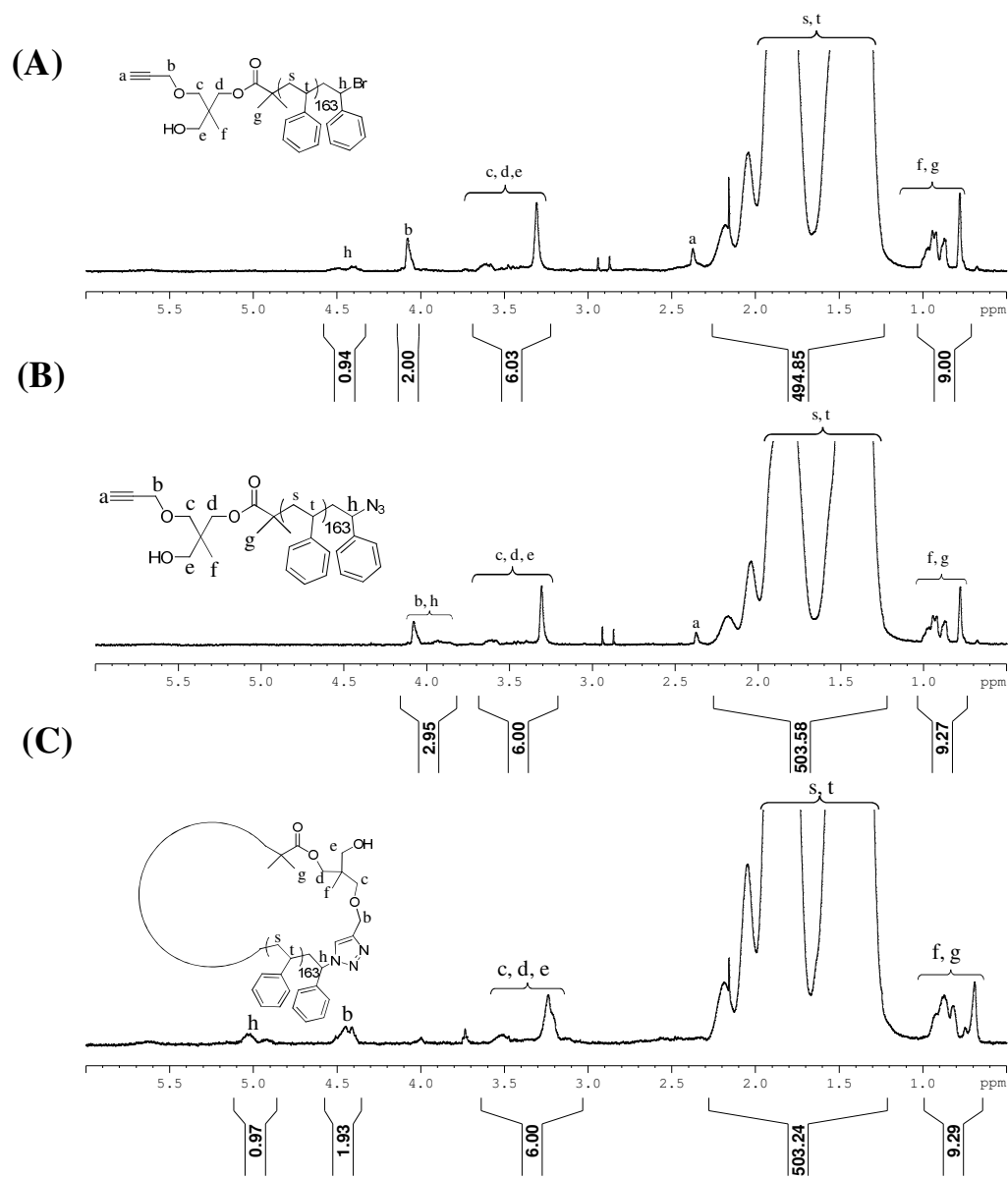


Figure S15. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of (a) $\equiv(\text{OH})\text{-PSTY}_{164}\text{-Br}$ **7e**, (b) $\equiv(\text{OH})\text{-PSTY}_{163}\text{-N}_3$ **8e**, (c) $\text{c-PSTY}_{164}\text{-OH}$ **9e**.

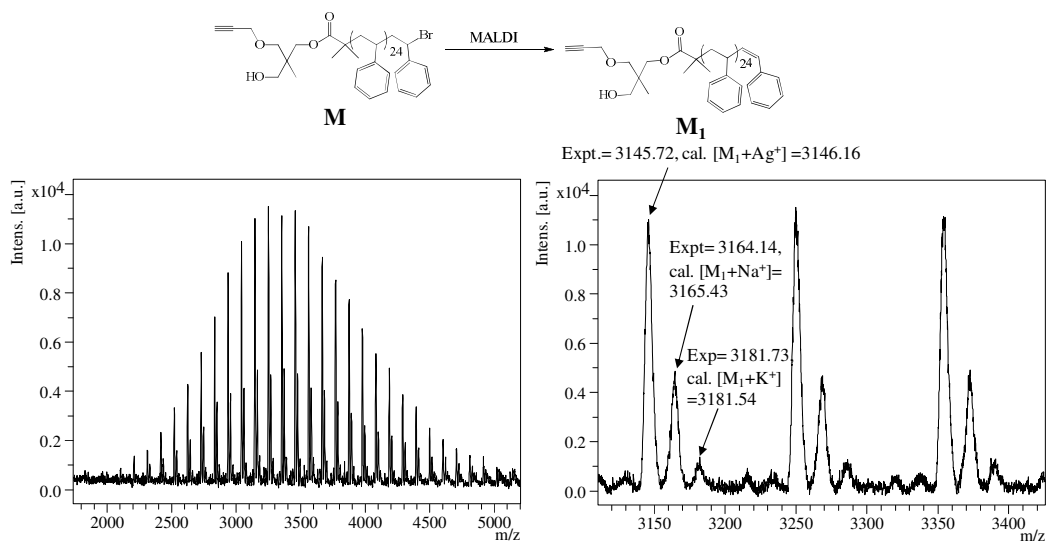


Figure S16: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{25}\text{-Br}$, **7b**.

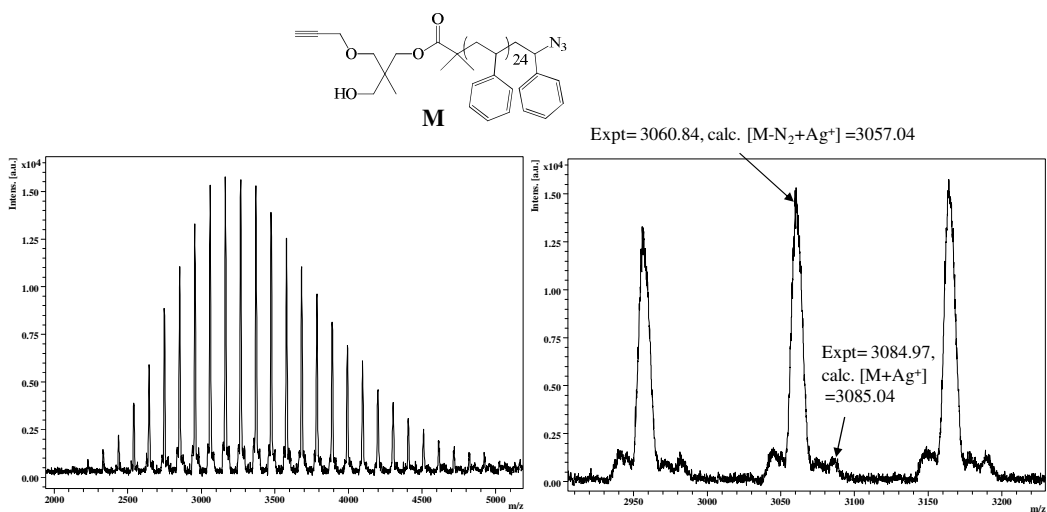


Figure S17 : MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{25}\text{-N}_3$, **8b**.

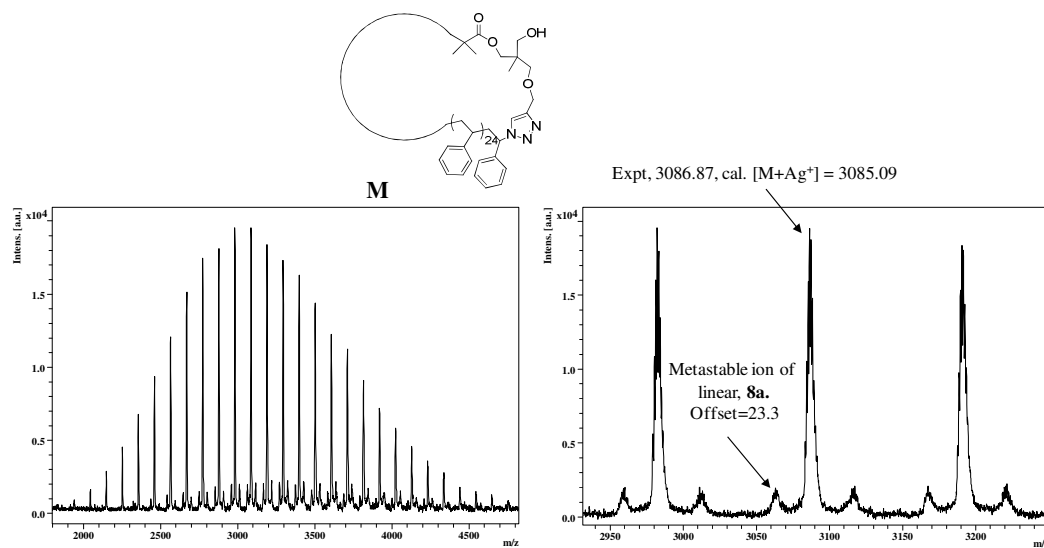


Figure S18 : MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₂₅-OH, **9b**.

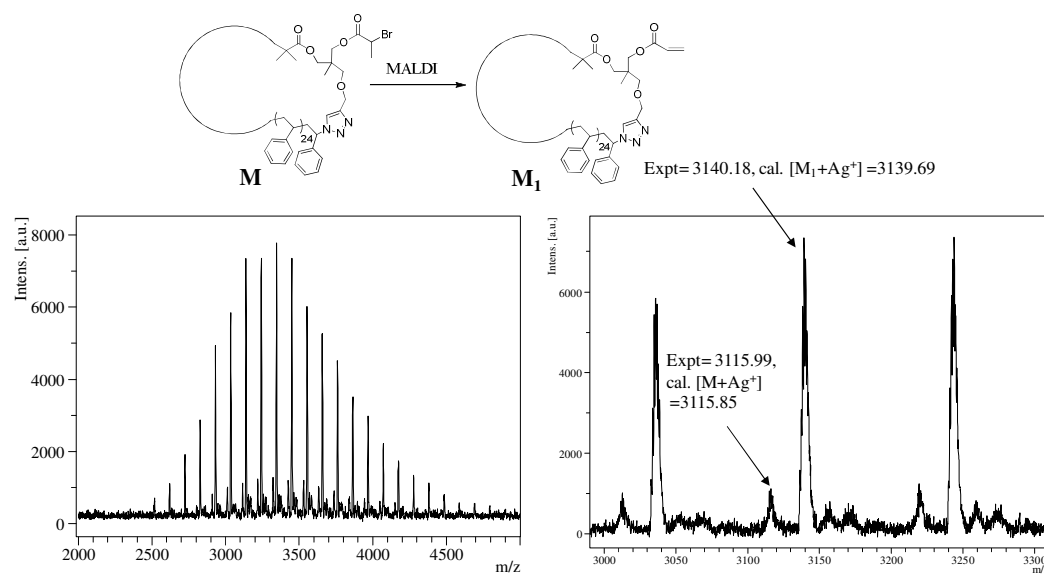


Figure S19: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₂₅-Br, **10b**.

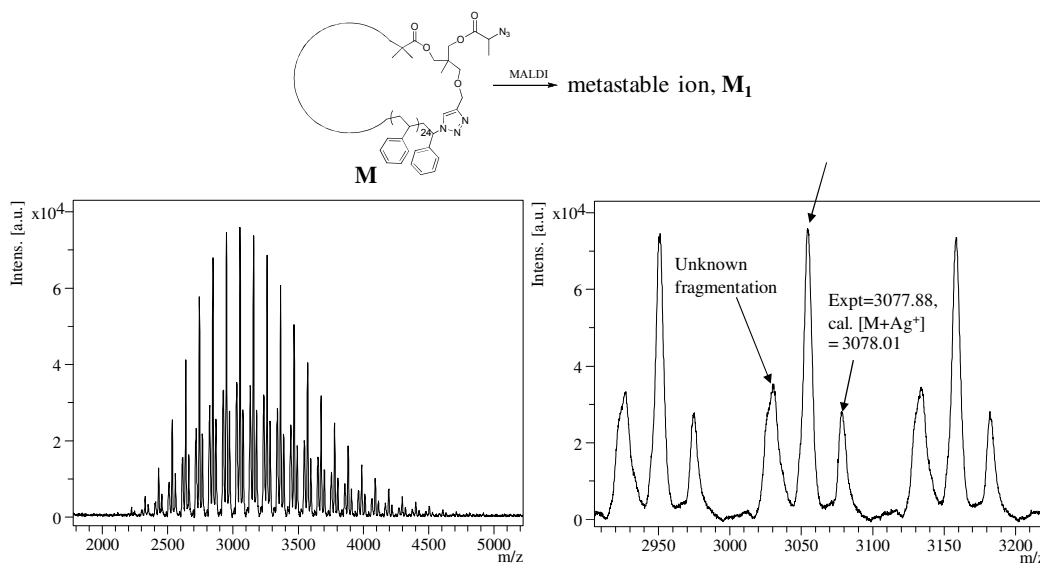


Figure S20: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₂₅-N₃, **11b**.

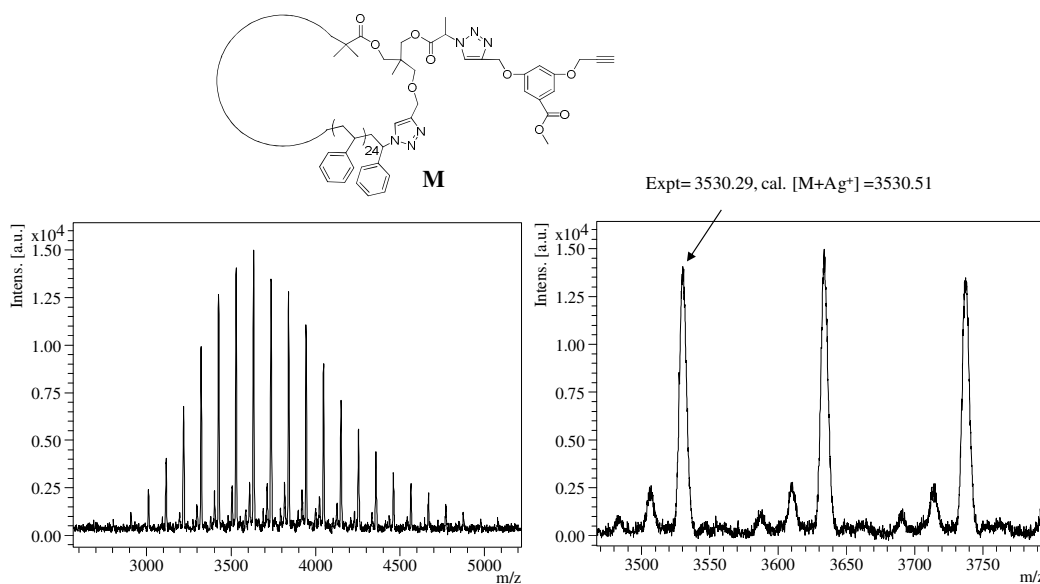


Figure S21: MALDI-ToF mass spectrum acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₂₅-≡, **14b**.

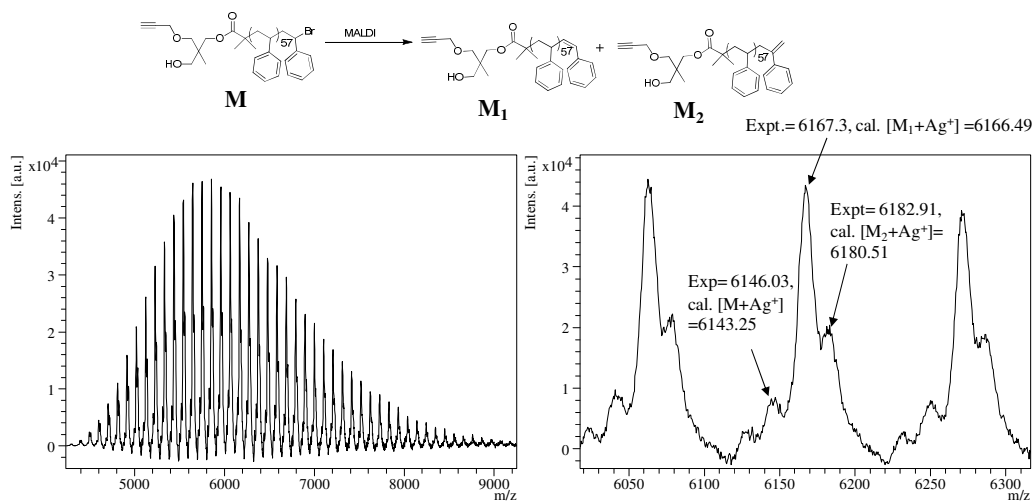


Figure S22: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{58}\text{-Br}$, **7c**.

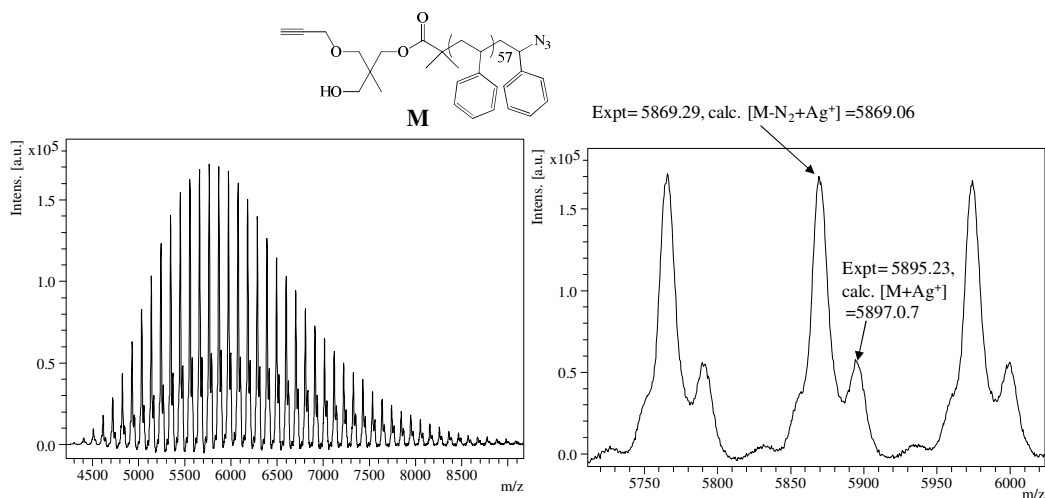


Figure S23: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{58}\text{-N}_3$, **8c**.

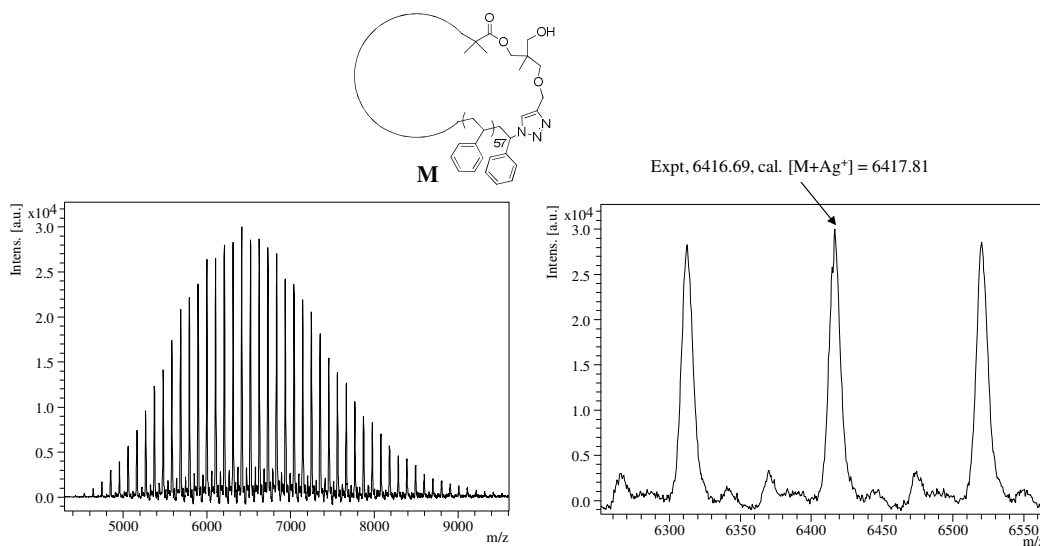


Figure S24: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₅₈-OH, **9c**.

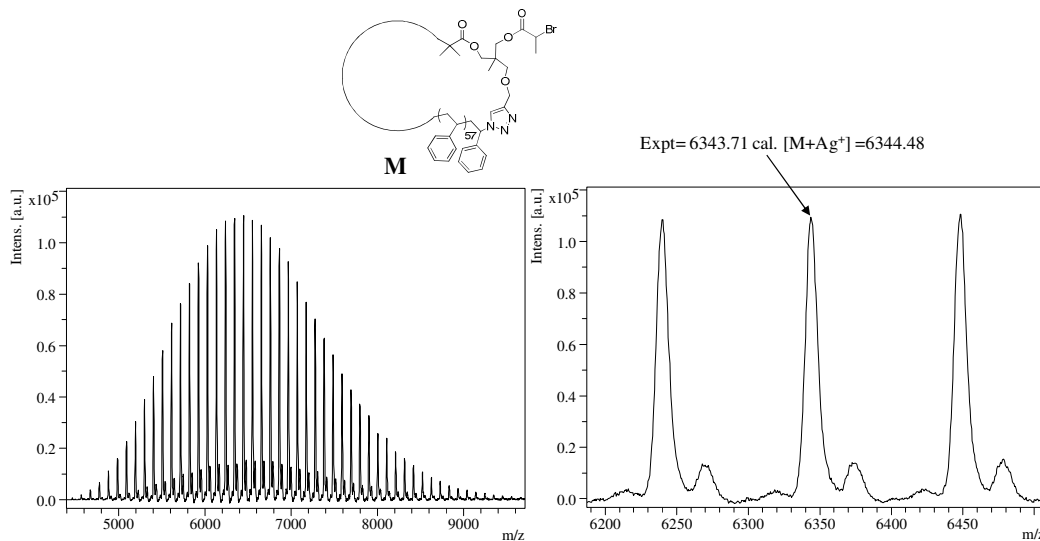


Figure S25: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₅₈-Br, **10c**.

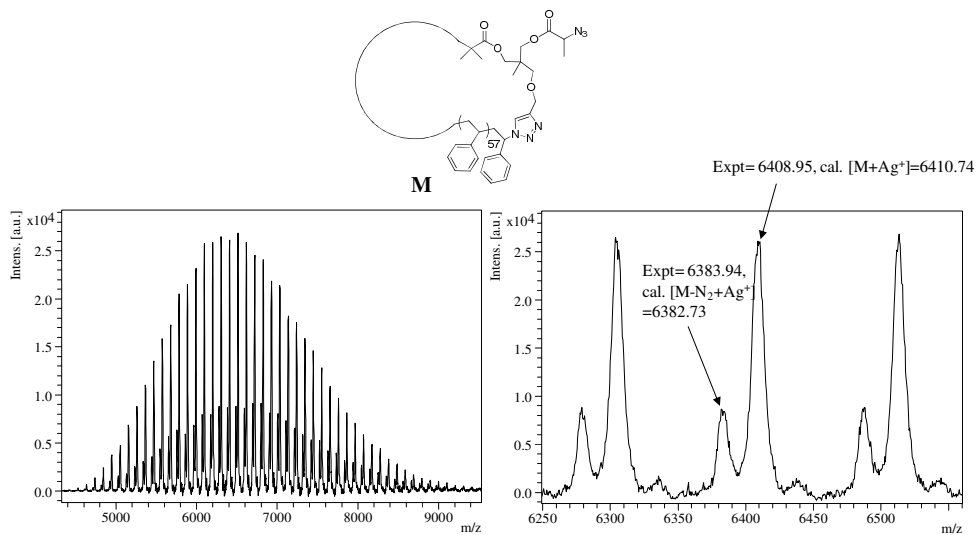


Figure S26: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₅₈-N₃, **11c**.

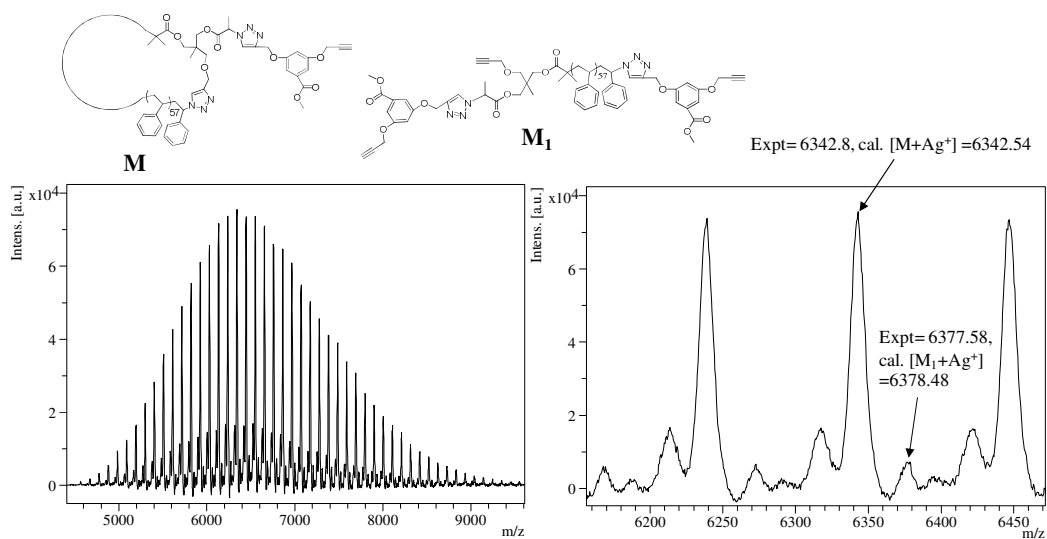


Figure S27: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₅₈-≡, **14c**.

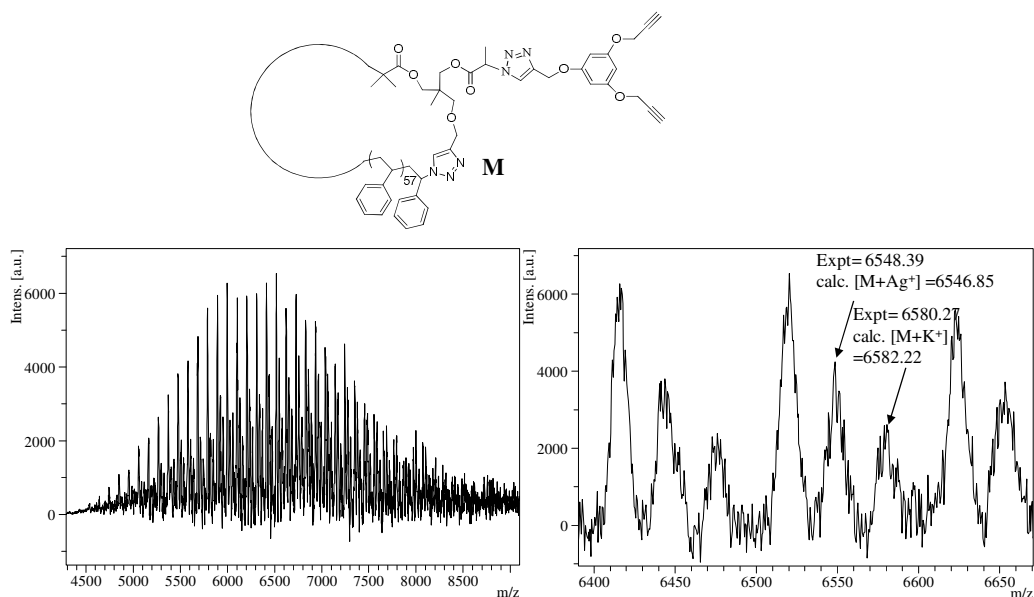


Figure S28: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to **c-PSTY₅₈-(≡)₂, 15c**.

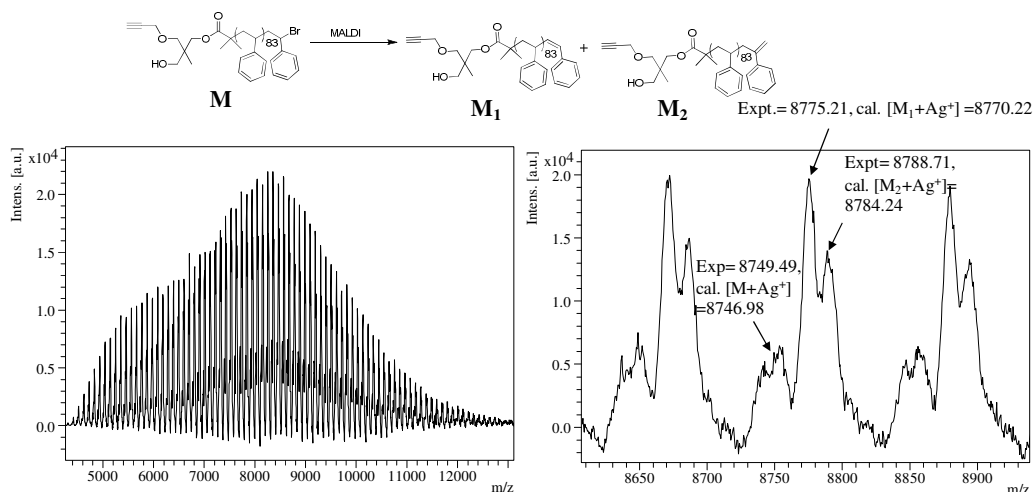


Figure S29: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to **≡(HO)-PSTY₈₄-Br, 7d**.

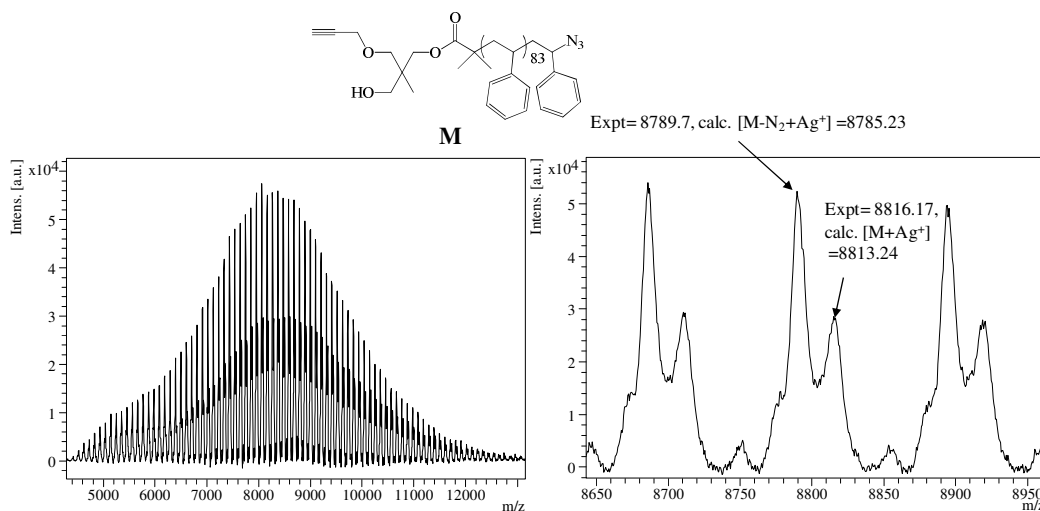


Figure S30: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{84}\text{-N}_3$, **8d**.

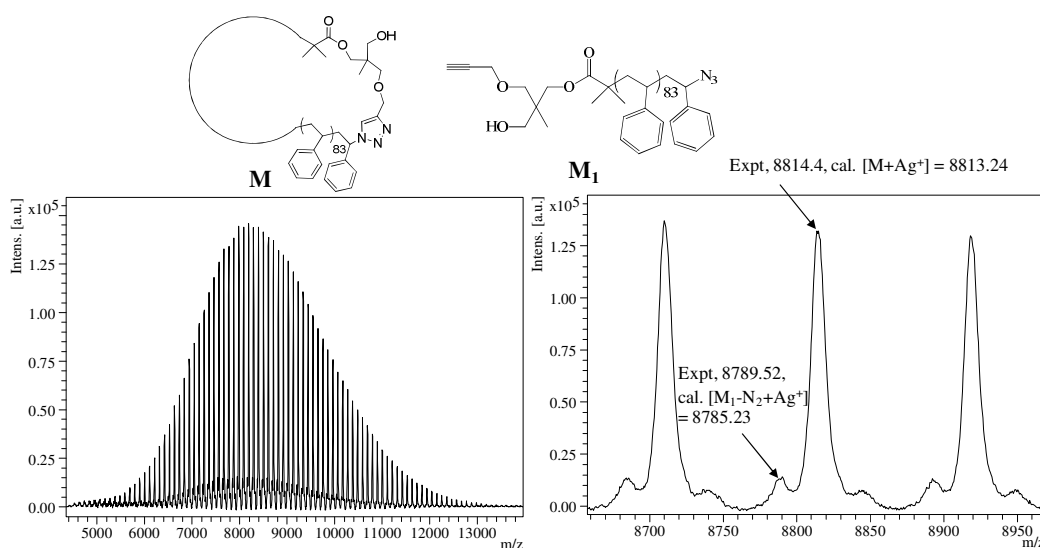


Figure S31: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\text{c-PSTY}_{84}\text{-OH}$, **9d**.

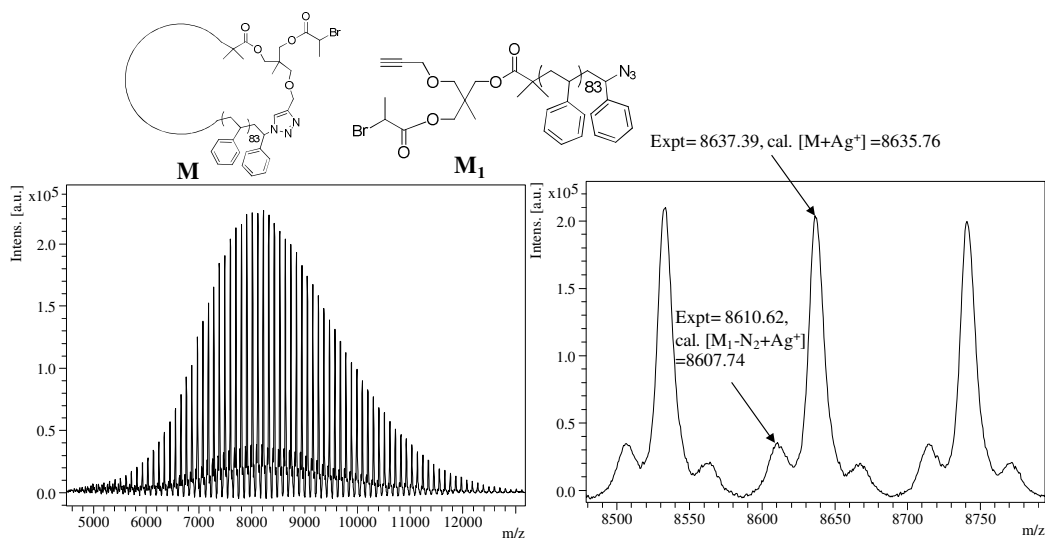


Figure S32: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₈₄-Br, **10d**.

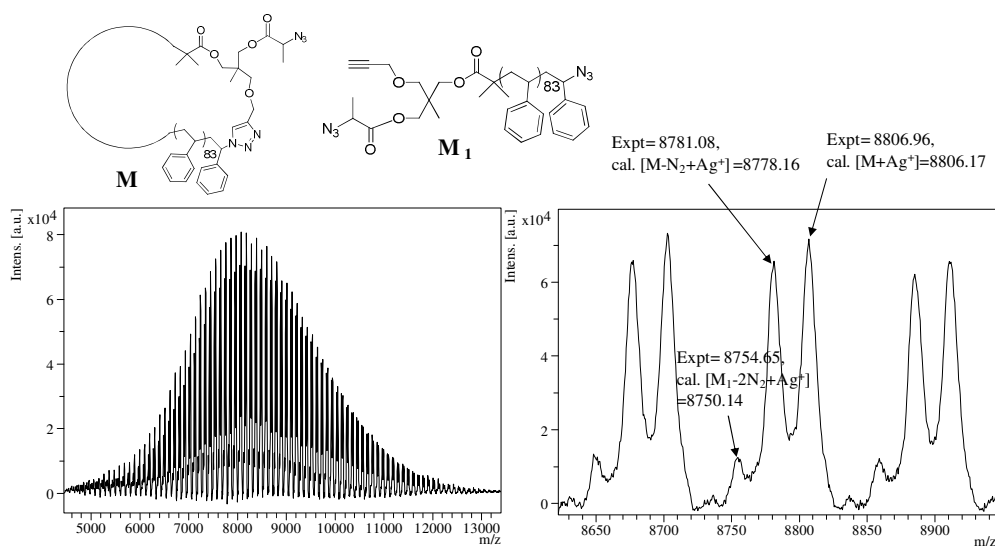


Figure S33: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₅₈-N₃, **11d**.

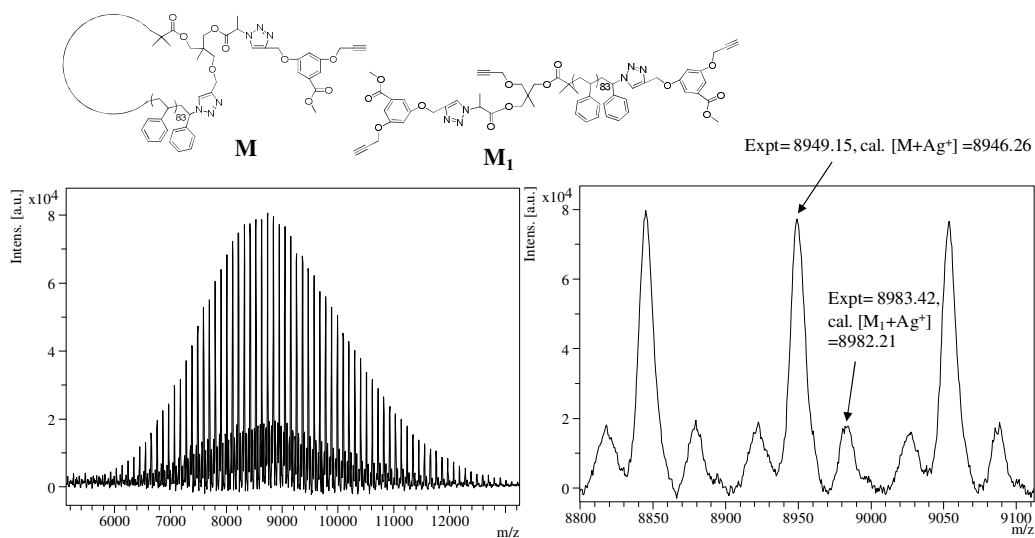


Figure S34: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to c-PSTY₈₄-≡, **14d**.

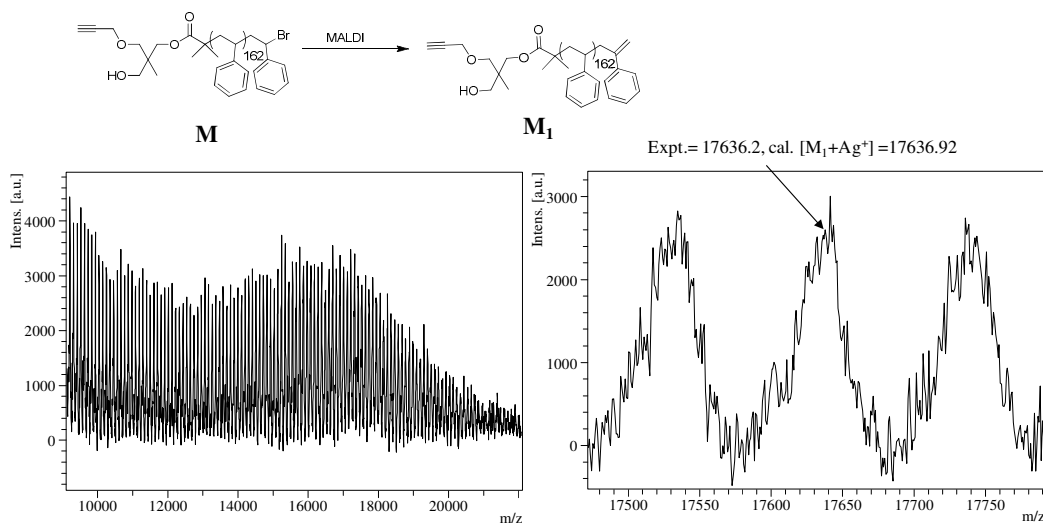


Figure S35: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to ≡(HO)-PSTY₁₆₃-Br, **7e**.

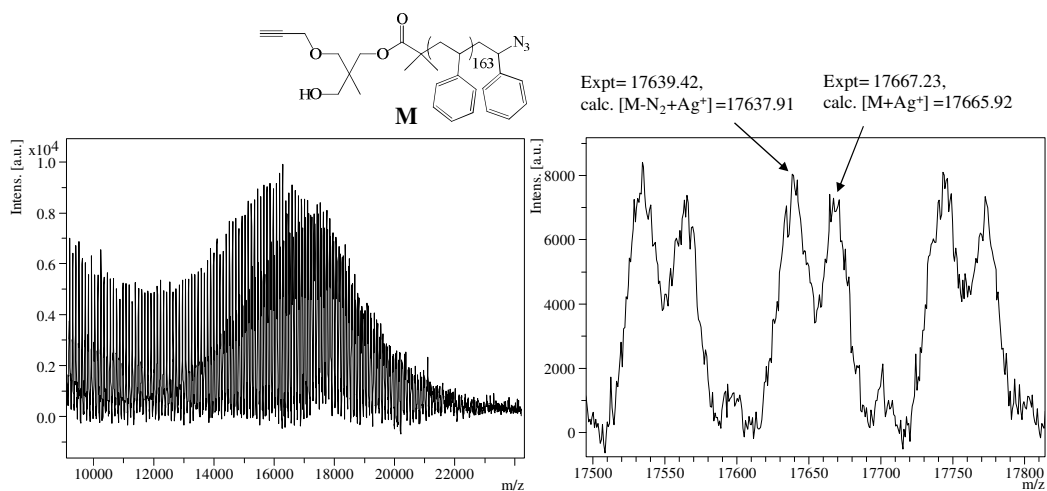


Figure S36: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\equiv(\text{HO})\text{-PSTY}_{163}\text{-N}_3$, **8e**.

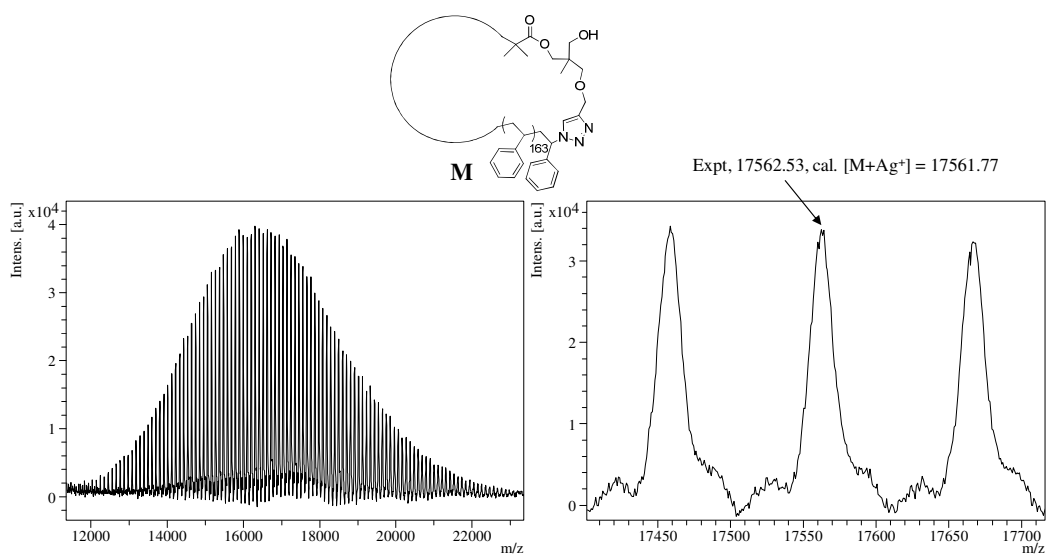


Figure S37: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to $\text{c-PSTY}_{163}\text{-OH}$, **9e**.

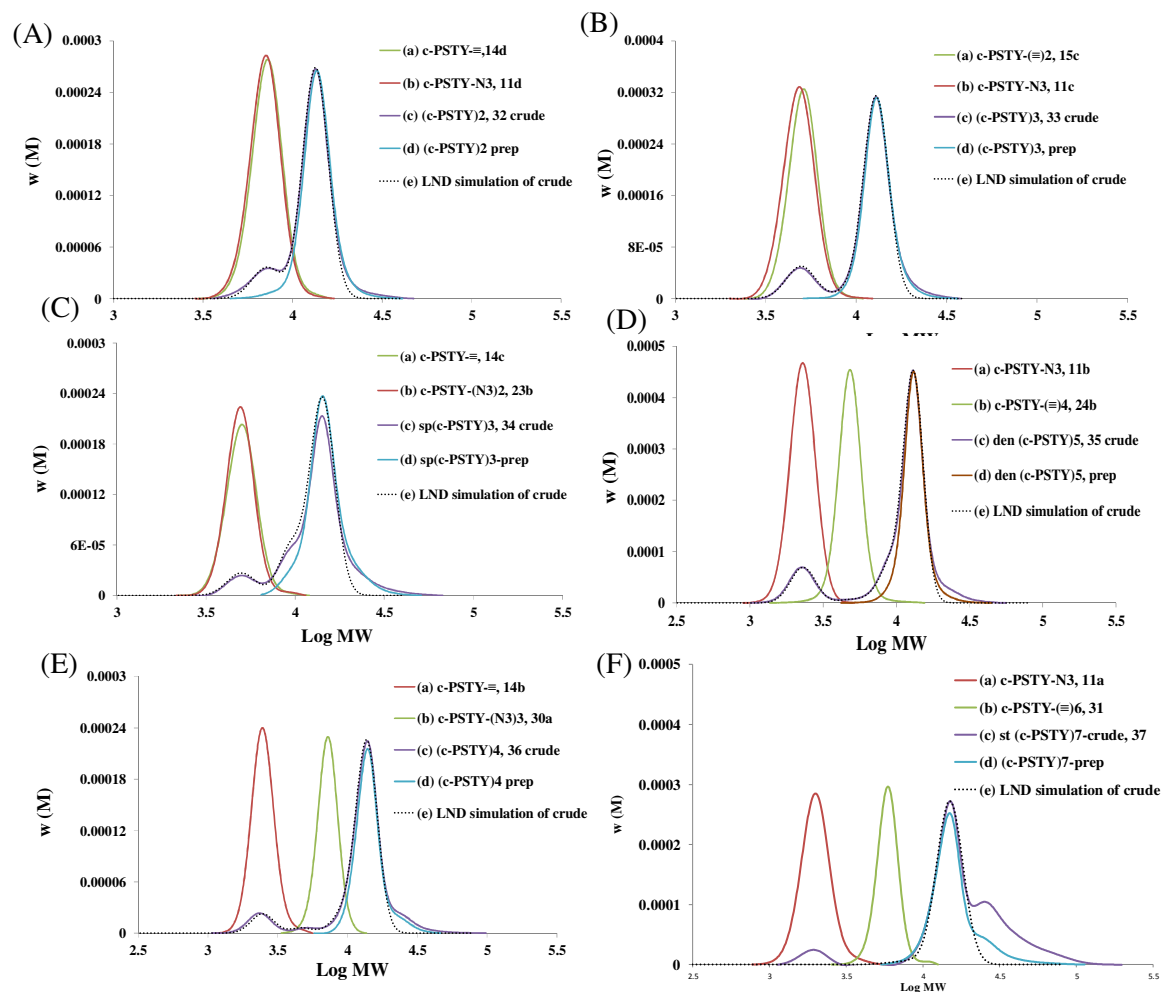


Figure S38: SEC of molecular weight distributions (MWDs) for the synthesis of (A) (c-PSTY)₂ **32** by CuAAC of (a) c-PSTY₈₄-≡, **14d**, and (b) c-PSTY₈₄-N₃, **11d**; (c) (c-PSTY)₂ **32**, crude, (d) (c-PSTY)₂ prepped and (e) LND simulation of crude, (B) (c-PSTY)₃, **33** by CuAAC of (a) c-PSTY₅₈-(≡)₂, **15c** and (b) c-PSTY₅₈-N₃, **11c**; (c) star (c-PSTY)₃, **32**, crude, (d) (c-PSTY)₃, prep and (e) LND simulation of crude, (C) spiro (c-PSTY)₃, **34** by CuAAC of (a) c-PSTY₅₈-≡, **14c** and (b) c-PSTY₅₀-(N₃)₂, **23b**; (c) spiro (c-PSTY)₃, **34** crude, (d) spiro (c-PSTY)₃, prep and (e) LND simulation of crude, (D) den (c-PSTY)₅, **35** by CuAAC of (a) c-PSTY₅₀-(≡)₄, **24b** and (b) c-PSTY₂₅-N₃, **11b**; (c) den (c-PSTY)₅, **35** crude, (d) den (c-PSTY)₅, prep and (e) LND simulation of crude, (E) G1 star (c-PSTY)₄, **36** by CuAAC of (a) c-PSTY₇₅-(N₃)₃, **30a** and (b) c-PSTY₂₅-≡, **14b**; (c) G1 star (c-PSTY)₄, **36** crude, (d) G1-star (c-PSTY)₄, prep and (e) LND simulation of crude and (F) G1 star (c-PSTY)₇, **37** by CuAAC of (a) c-PSTY₇₅-(≡)₆, **31** and (b) c-PSTY₂₅-N₃, **11a**; (c) G1 star (c-PSTY)₇, **37** crude, (d) G1-star (c-PSTY)₇, prep and (e) LND simulation of crude. SEC analysis

based on polystyrene calibration curve. Simulation was achieved by adding M_p s of reactants (RI SEC) to fit with the crude products (RI SEC).

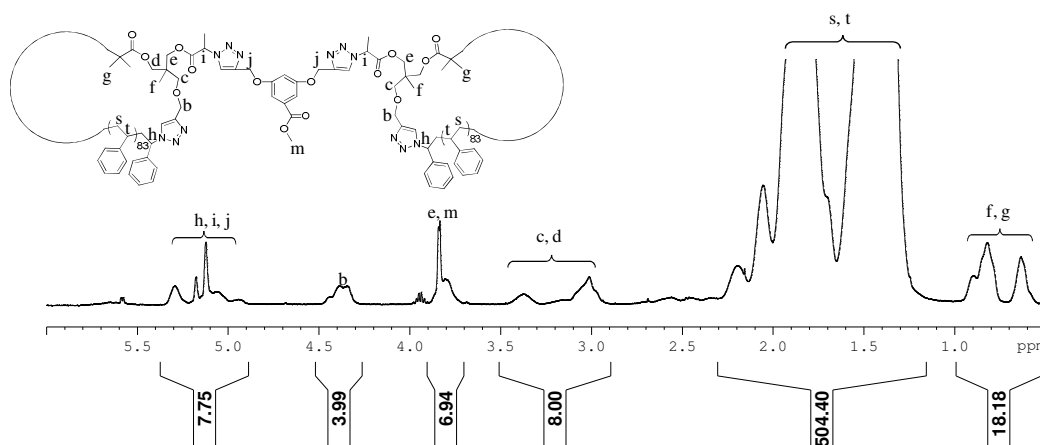


Figure S39. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of $(\text{c-PSTY}_{84})_2$, **32**.

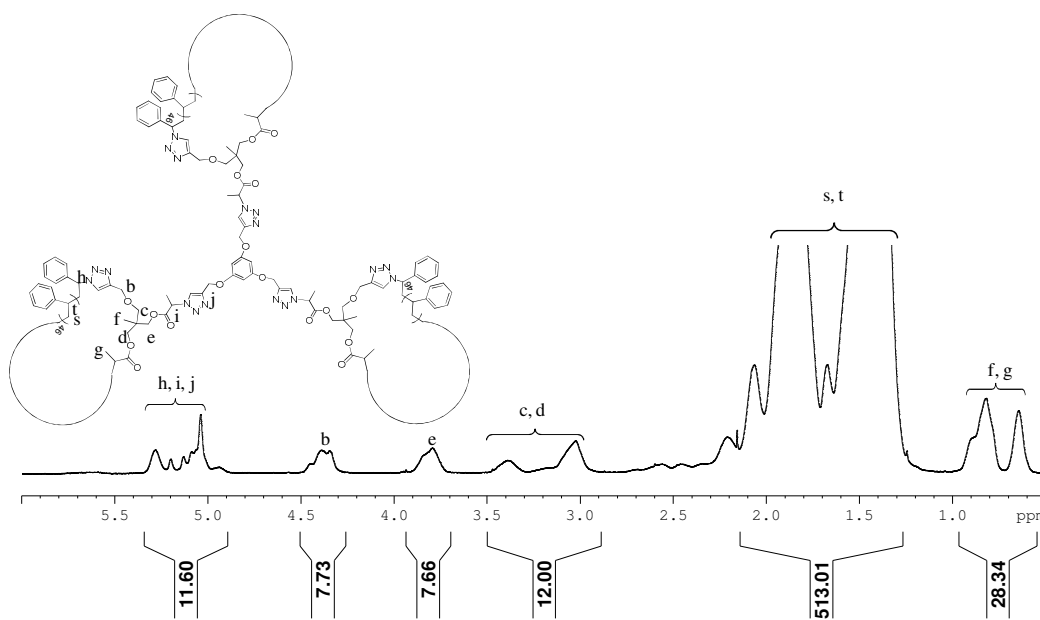


Figure S40. 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of $\text{st-(c-PSTY}_{58})_3$, **33**.

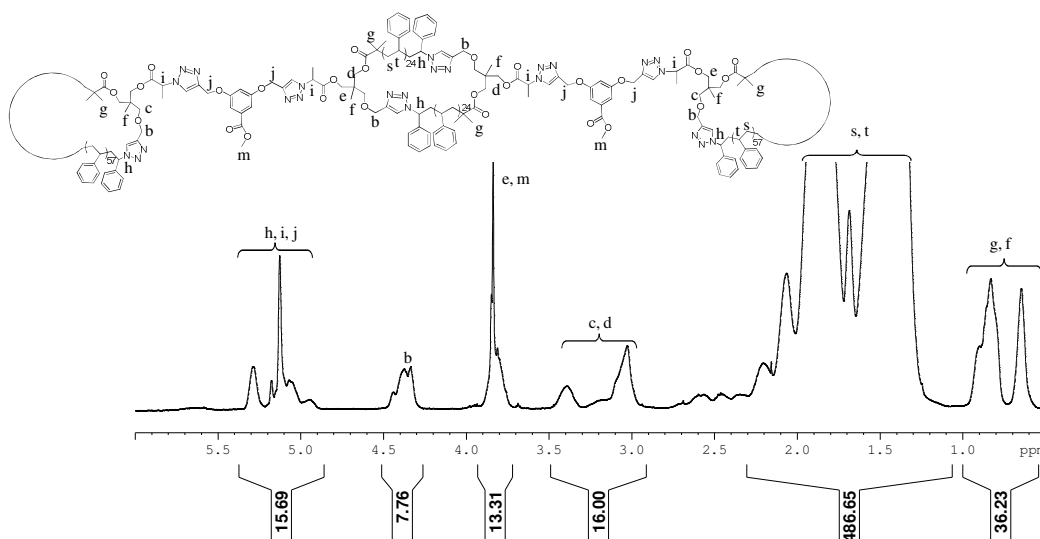


Figure S41: 500 MHz ¹H 1D DOSY NMR spectra in CDCl₃ of sp-(c-PSTY)₃, **34**.

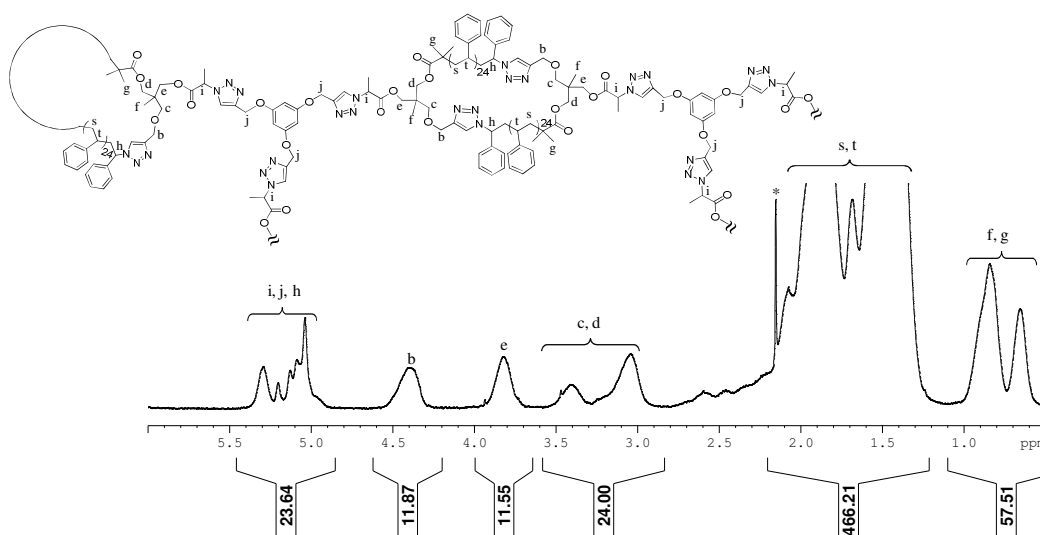


Figure S42: 500 MHz ¹H 1D DOSY NMR spectra in CDCl₃ of dendrimer (c-PSTY)₅, **35**. *Acetone peak.

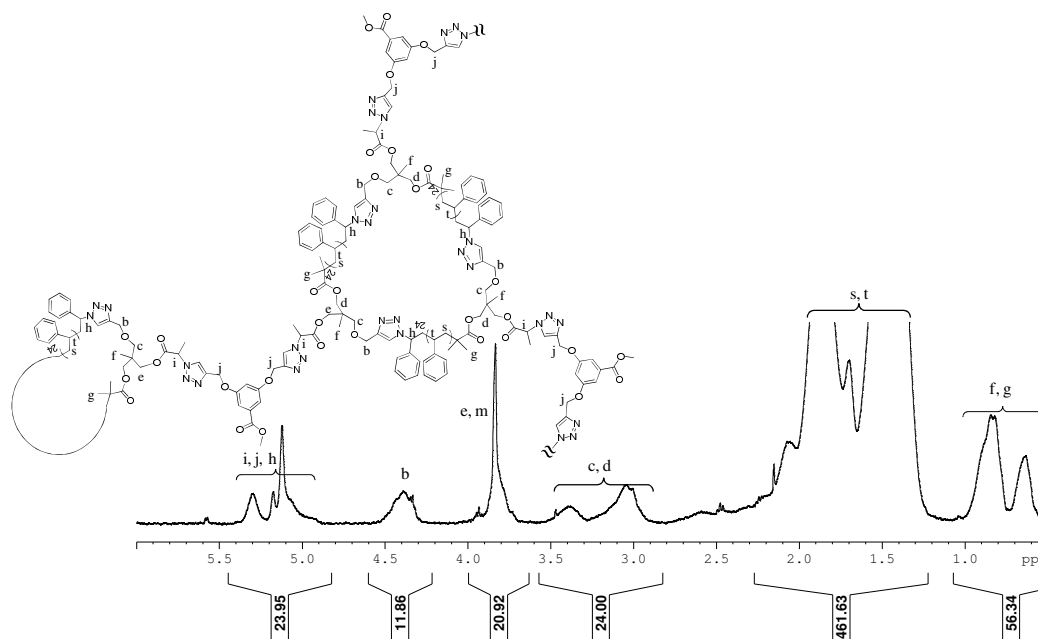


Figure S43: 500 MHz ^1H 1D DOSY NMR spectra in CDCl_3 of G1 (c-PSTY) $_4$, **36**.

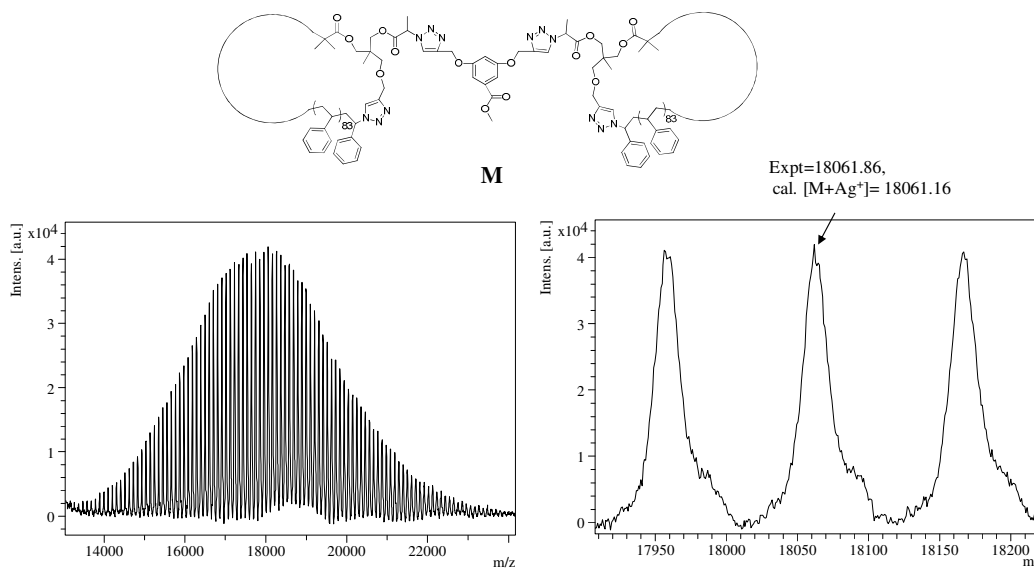


Figure S44: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to (c-PSTY $_{84}$) $_2$, **32**.

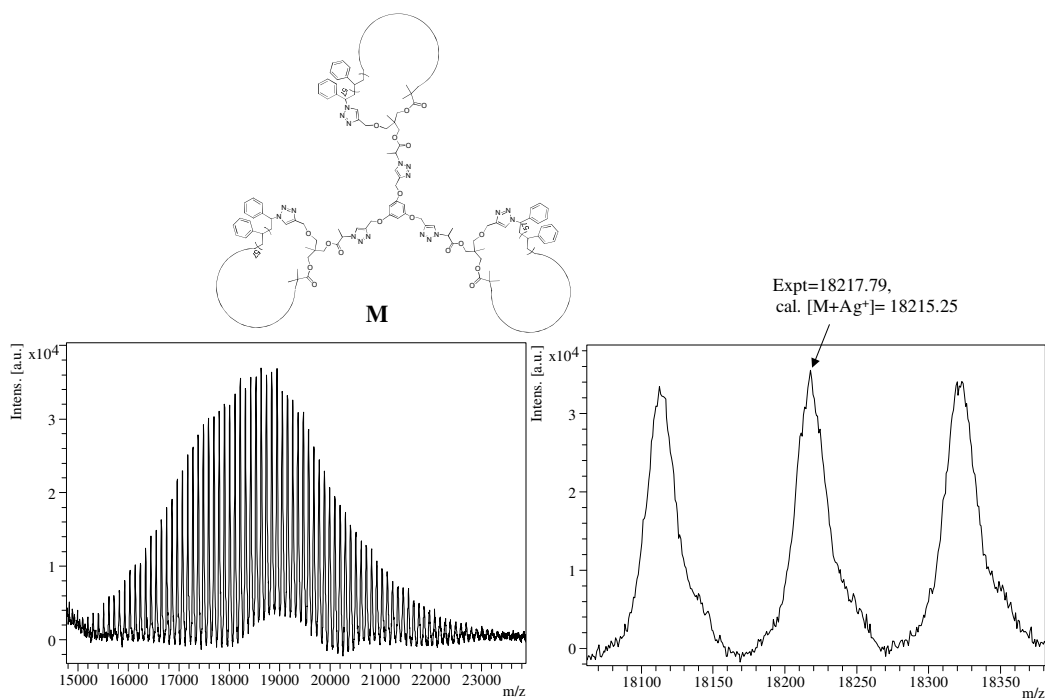


Figure S45: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond (c-PSTY)₅₈)₃, **33**.

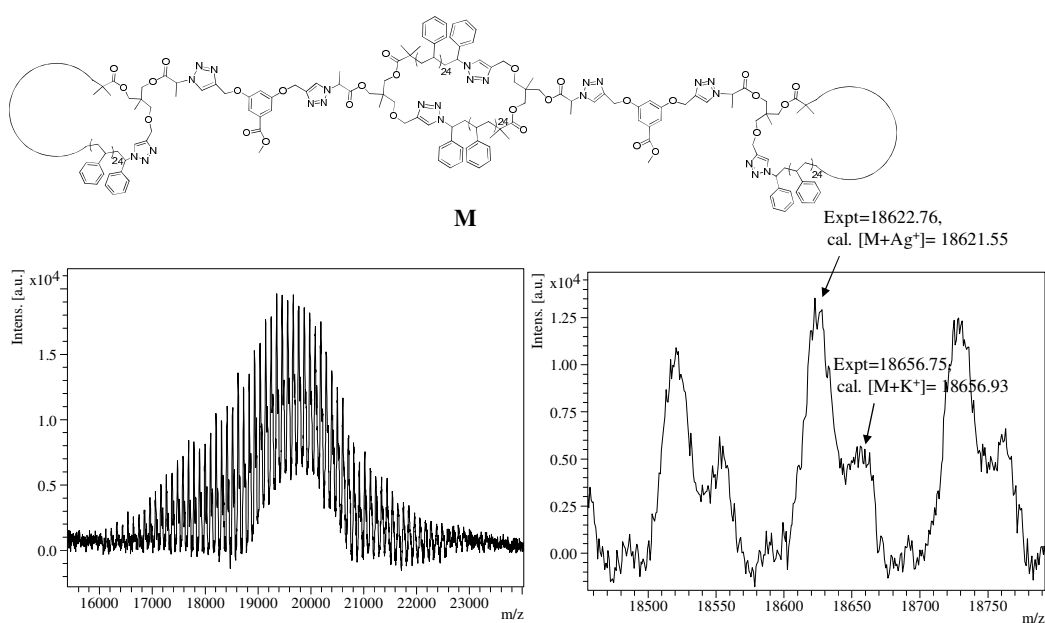


Figure S46: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to Spiro (c-PSTY)₃, **34**.

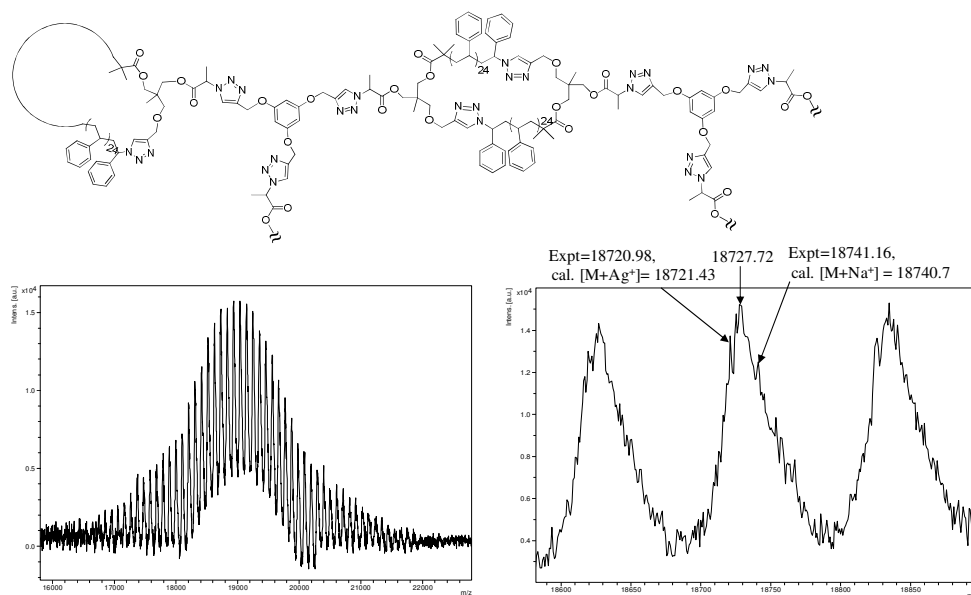


Figure S47: MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to G1-den-(c-PSTY)₅, **35**.

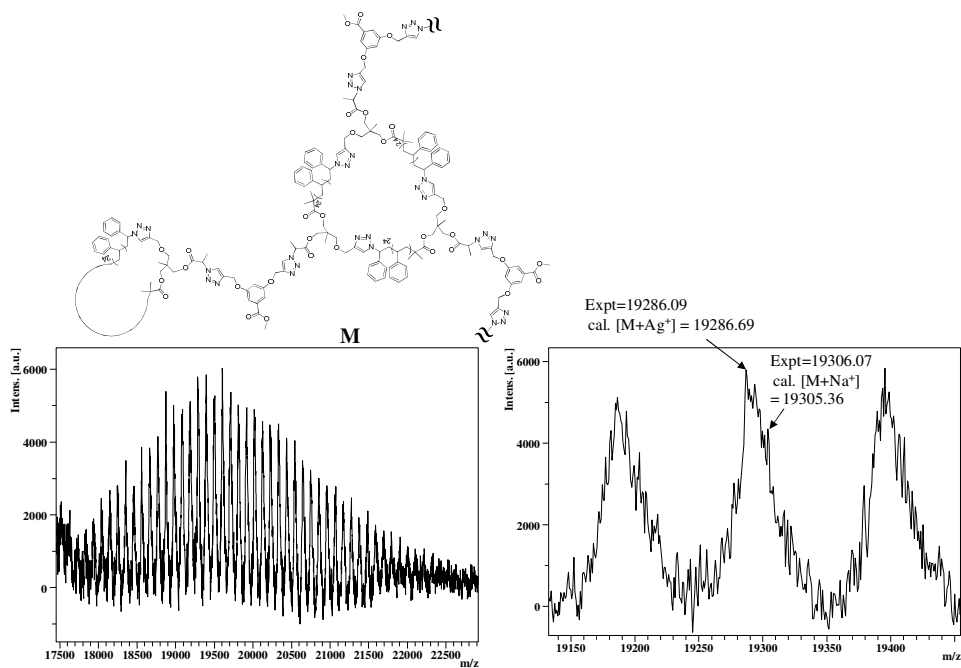


Figure S48 : MALDI-ToF mass spectrum acquired in linear mode with Ag salt as cationizing agent and DCTB matrix. The full and expanded spectra correspond to G1-st-(c-PSTY)₄, **36**.

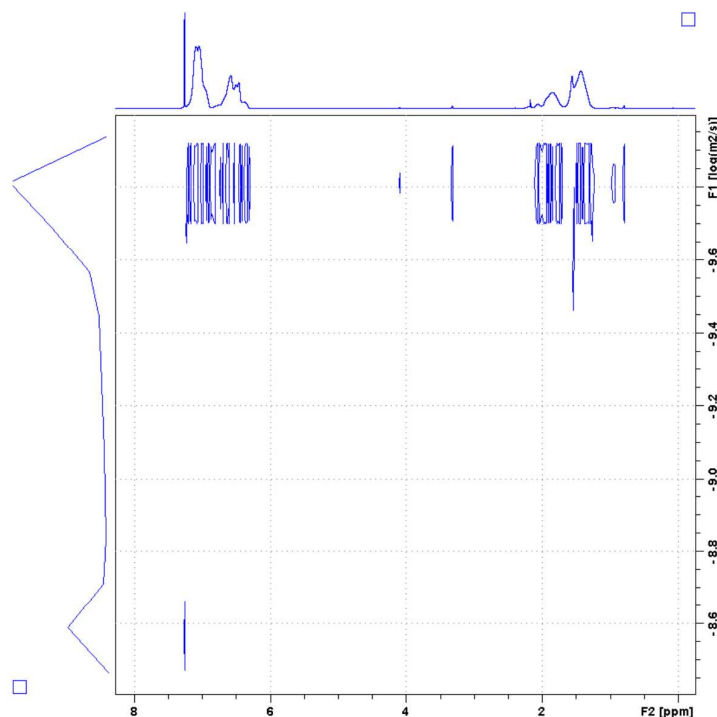


Figure S49: 2D DOSY NMR spectrum of **8e**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

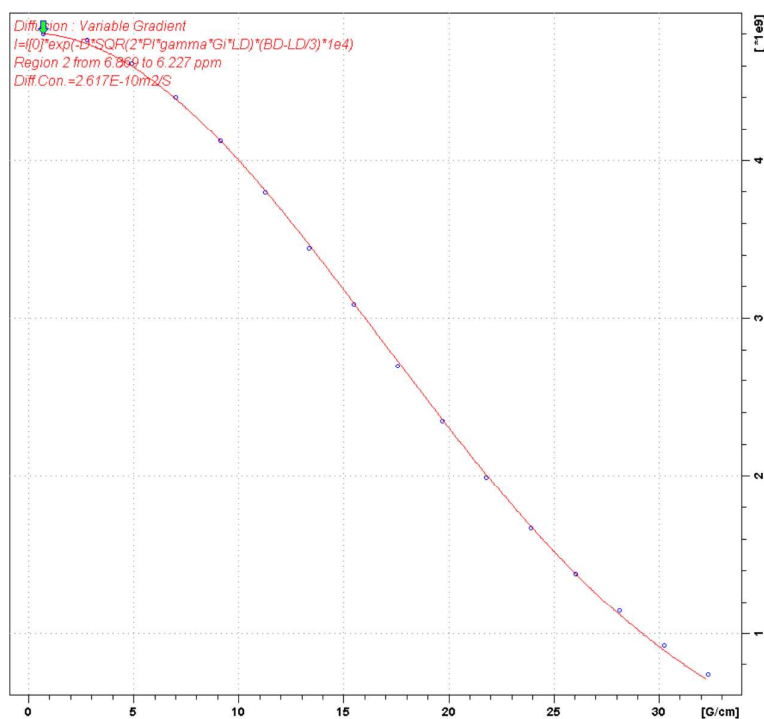


Figure S50: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **8e**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 1.28 \times 10^{-10} \text{ m}^2 \text{ S}^{-1}$.

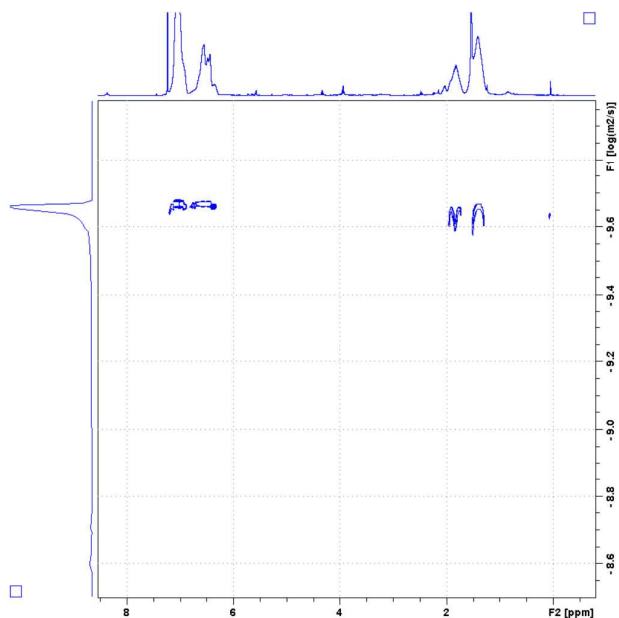


Figure S51: 2D DOSY NMR spectrum of **9e**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

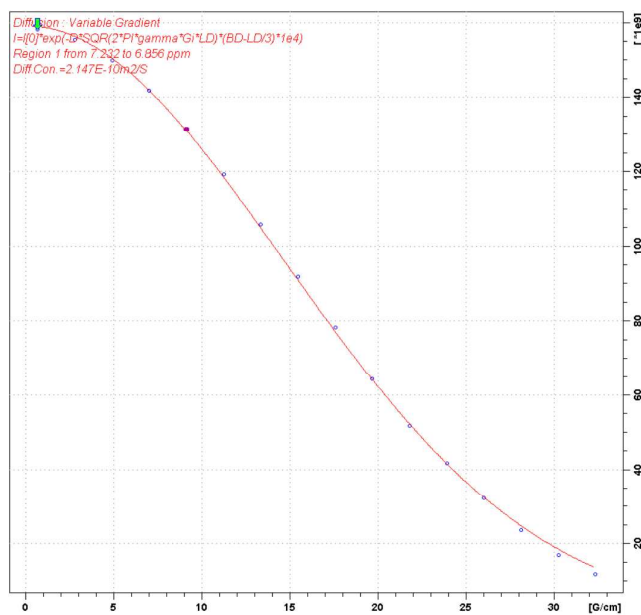


Figure S52: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **9e**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 2.14 \times 10^{-10} \text{ m}^2 \text{ S}^{-1}$.

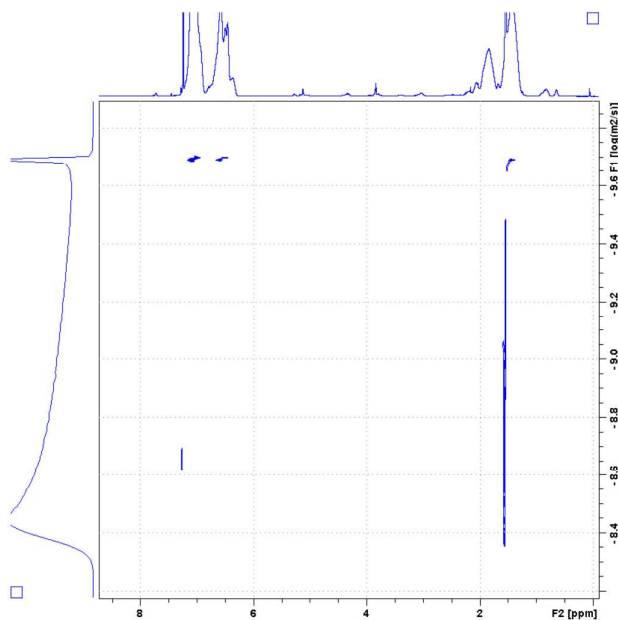


Figure S53: 2D DOSY NMR spectrum of **32**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

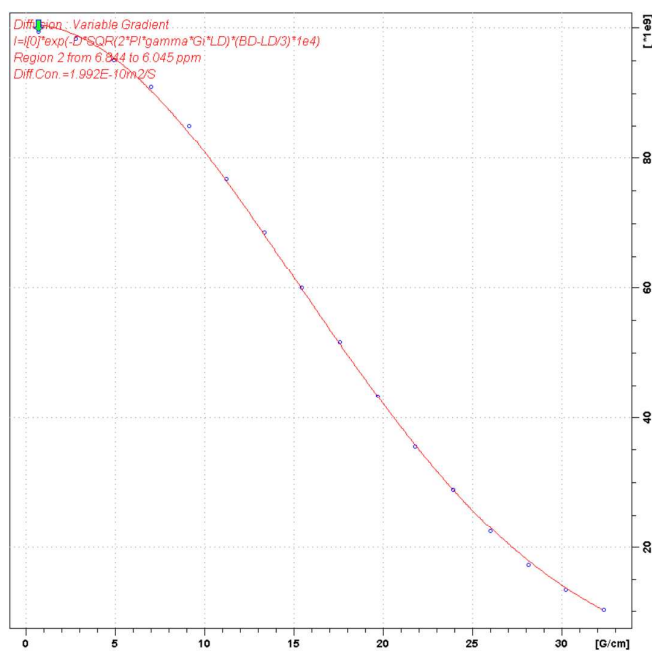


Figure S54: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **32**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 1.99 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

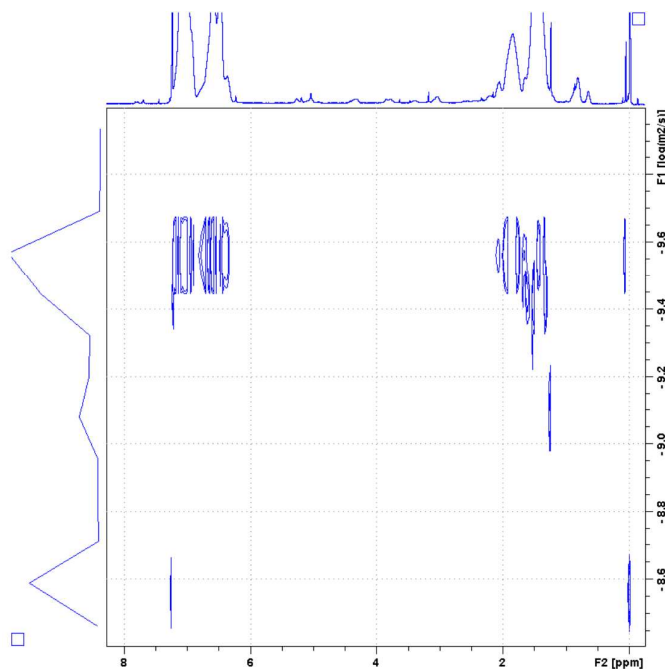


Figure S55: 2D DOSY NMR spectrum of **33**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

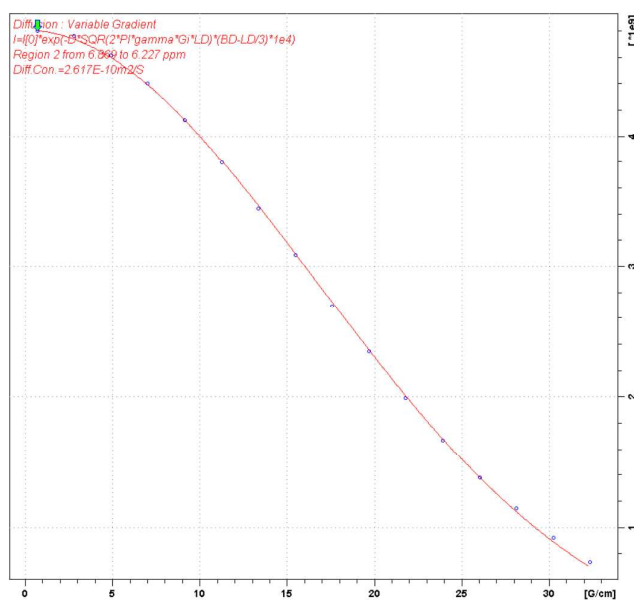


Figure S56: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **33**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion co-efficient $D = 2.60 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

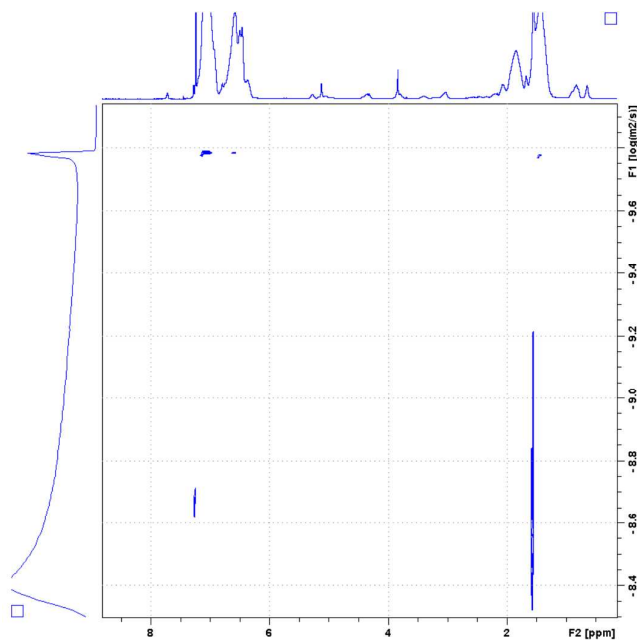


Figure S57: 2D DOSY NMR spectrum of **34**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

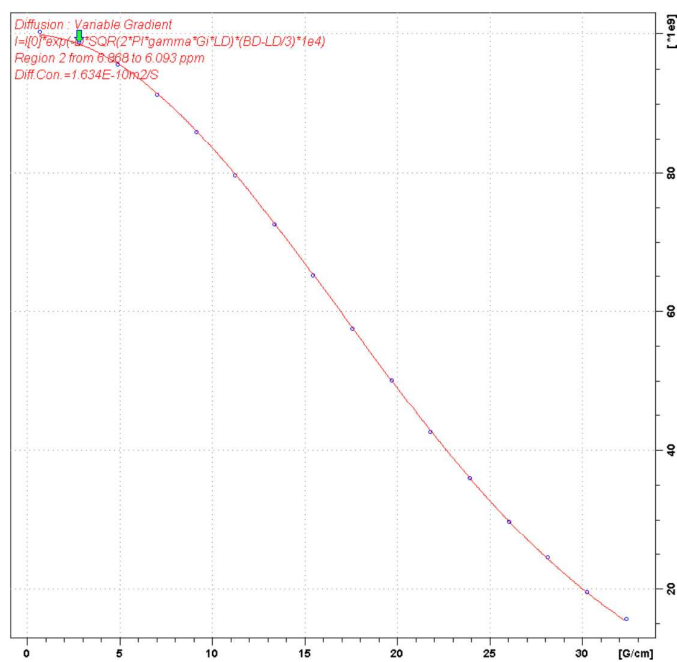


Figure S58: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **34**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 1.63 \times 10^{-10} \text{ m}^2 \text{ S}^{-1}$.

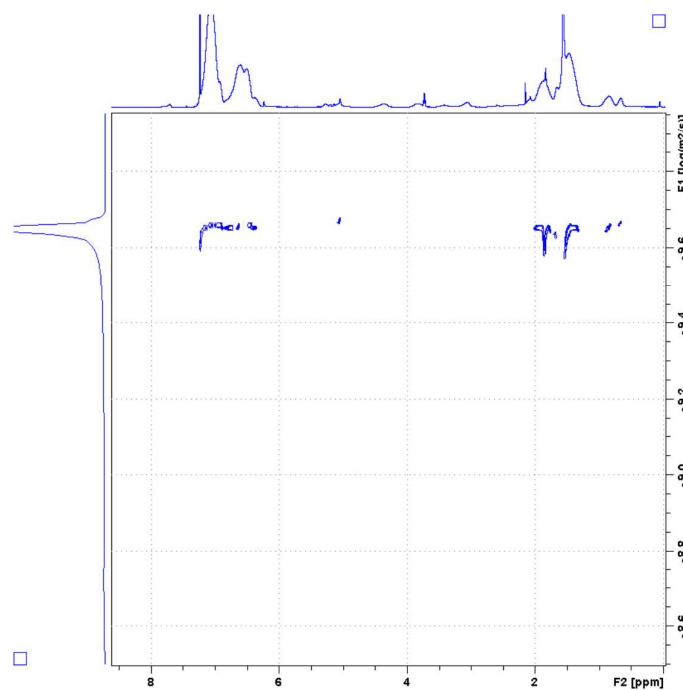


Figure S59: 2D DOSY NMR spectrum of **35**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

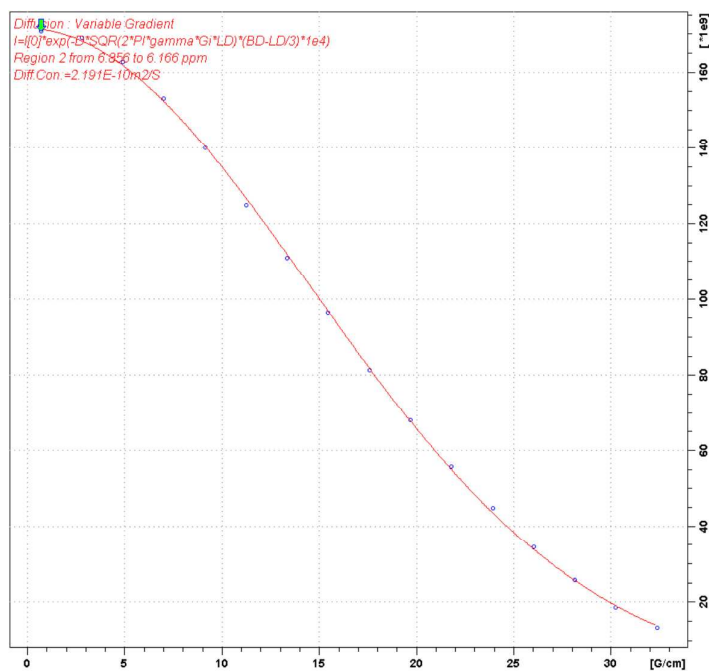


Figure S60: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **35**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 2.19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

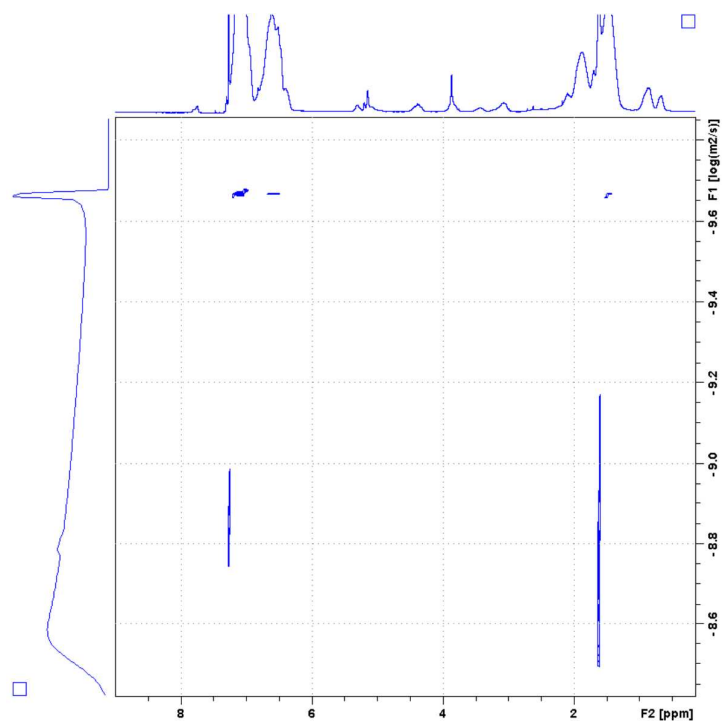


Figure S61: 2D DOSY NMR spectrum of **36**, recorded in CDCl₃, 298K, the parameters were used as following: diffusion delay (Δ , 150 ms) gradient pulse length (p30, 1.6 ms).

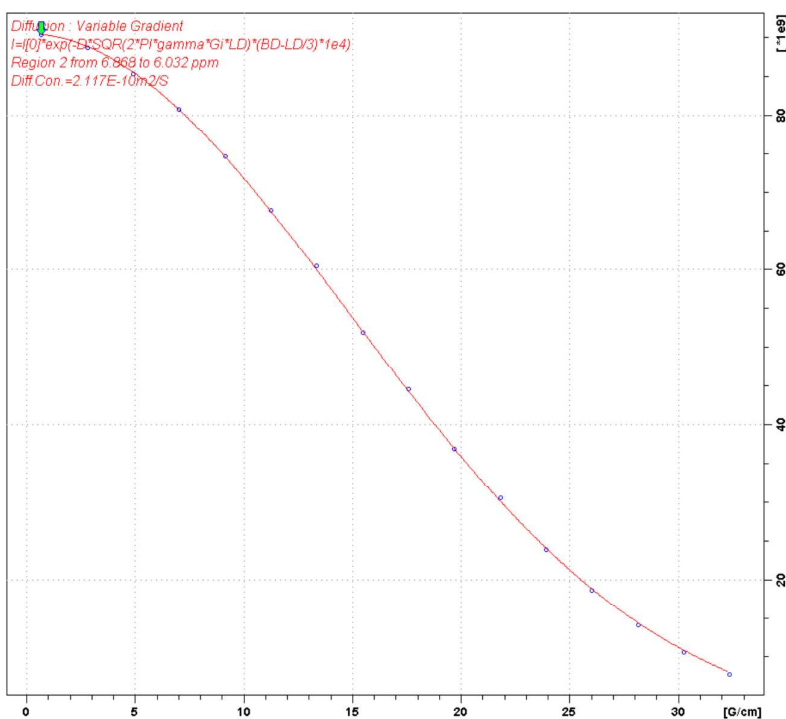


Figure S62: Exponential fit for NMR signal decay due to the gradients using equation (S1) for **36**. Processed with the Bruker XWIN NMR software using vargard fitting function giving diffusion coefficient $D = 2.11 \times 10^{-10} \text{ m}^2 \text{ S}^{-1}$.

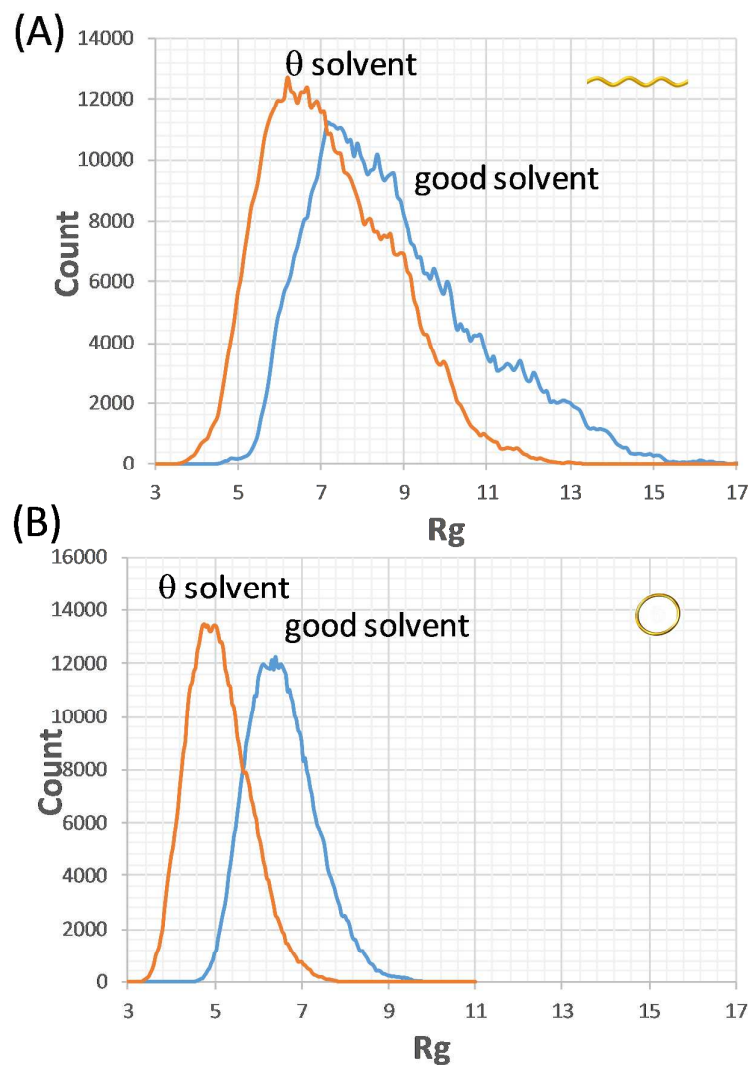


Figure S63: Molecular dynamic (MD) simulations of the radius of gyration (R_g) distributions for (A) linear polymer chain **8e**, and (B) monocyclic **9e** in a good and a theta solvent. R_g is given in reduced units. Total number of conformations was 600,000 (i.e. total counts).

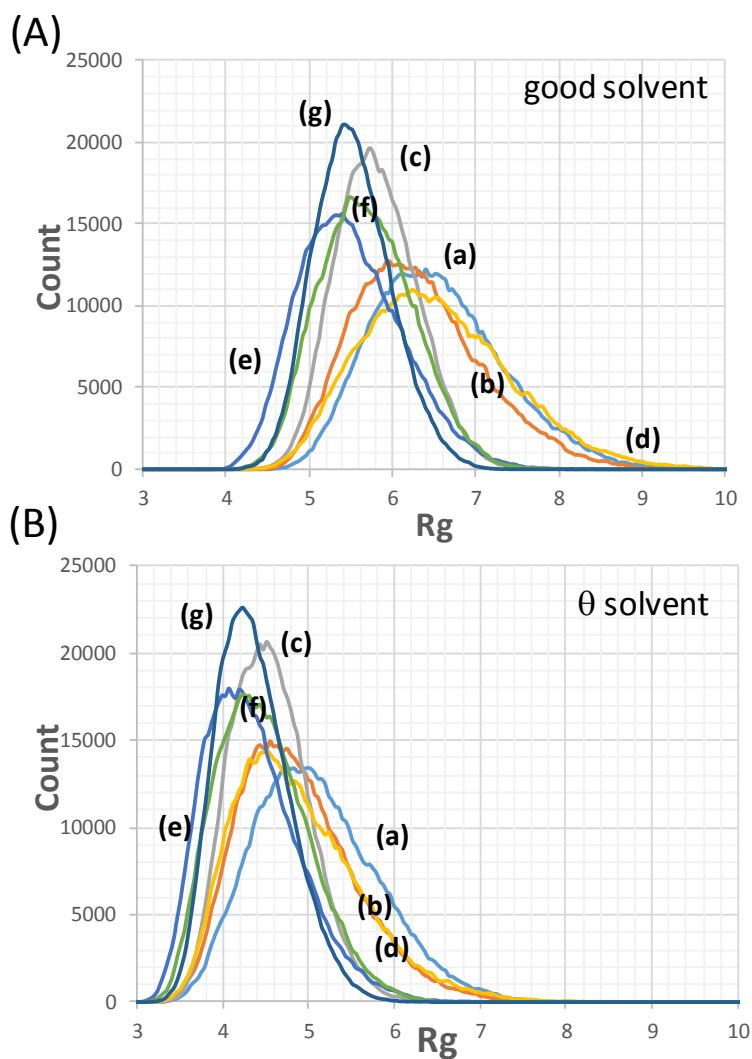


Figure S64: Molecular dynamic (MD) simulations of the radius of gyration (R_g) distribution for all cyclic structures in Scheme 1. (A) Cyclics in a good solvent, and (B) cyclics in a theta solvent. Curves (a) **9e**, (b) **32**, (c) **33**, (d) **34**, (e) **35**, (f) **36**, and (g) **37**. R_g is in reduced units. Total number of conformations was 600,000 (i.e. total counts).

References:

1. Zhongfan Jia, Daria E. Lonsdale, Jakov Kulis, and Michael J. Monteiro, ACS Macro Lett. 2012, 1, 780–783.
2. Md. D. Hossain, Zhongfan Jia, and Michael J. Monteiro, Macromolecules 2014, 47, 4955–4970.