

## ***Supporting information***

# **Regulation of tectonic sequence in chain-folding-directed monodisperse isomeric oligomers precisely tailored by Ugi-hydrosilylation orthogonal cycles**

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## 1. Experimental section

**Synthesis of discrete oligomers with well-defined linkage sequence:** The isomeric 3-(dimethylsilyl)aniline (3DA) and 4-(dimethylsilyl)aniline (4DA) units were synthesized according to the previous report. The linkage sequence defined discrete oligomers were fabricated using Ugi-4CRs and hydrosilylation orthogonal cycles via a stepwise iterative growth strategy, on varying meta- and para- linker in each hydrosilylation step, the linkage units were insert into chains in predesigned order. The detailed procedure of Ugi-4CRs and hydrosilylation reactions can be seen in the previous study. <sup>[1]</sup>

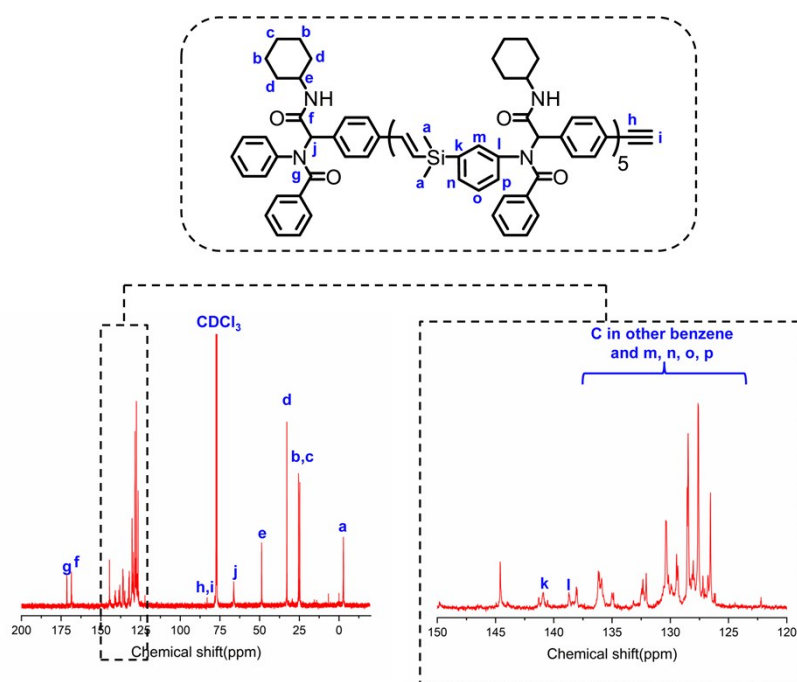
**Measurements:** <sup>1</sup>H NMR (5wt%, CDCl<sub>3</sub>) spectra were recorded on a Bruker Avance II 400MHz NMR spectrometer with (CH<sub>3</sub>)<sub>4</sub>Si (tetramethylsilane, TMS) as an internal standard. MALDI-TOF-MS analysis was performed on a Waters MALDI micro MX mass spectrometer (Waters, Milford, CT, USA) with 2-[(2E)-3-(4-tert-butylphenyl)-2-methyprop-2-enylidene] malonitrile (DCTB) and sodium trifluoroacetate as dopants and details of the sample preparation are provided in a previous study.<sup>[2]</sup> DSC was performed on TA Q20 at a heating rate of 10 °C /min under a nitrogen atmosphere. SEC results were tested on Viscotek TDA305 SEC with refractive index, light scattering and viscosity detectors. The solvent was THF with a flow rate of 1.0 ml/min at 35 °C.

**Computational methods:** The model was built in Material Studio software, molecular dynamic simulation (MD) was obtained using Forcite module Compass force field. After geometry optimization, molecular dynamic was performed in NVT

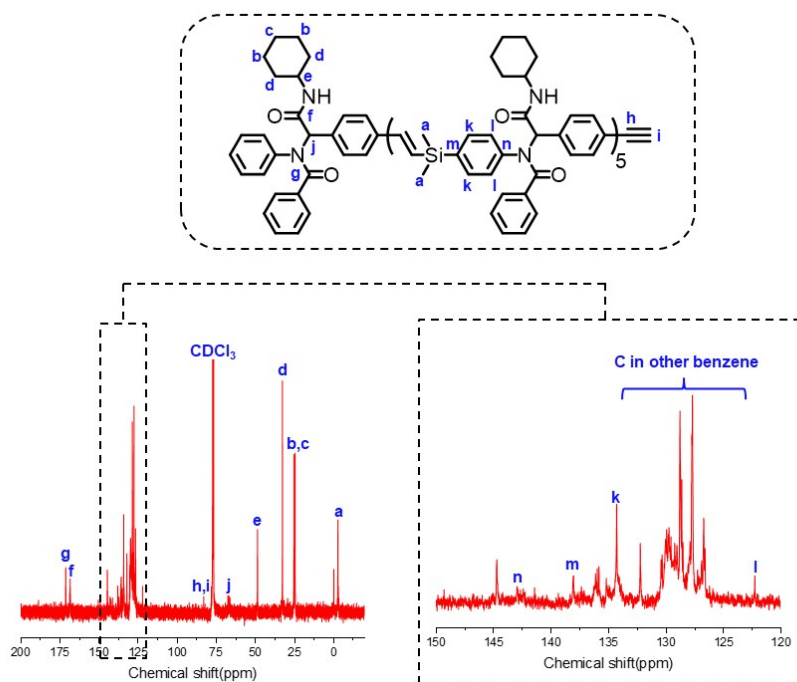
mode in 298K for a simulation time of 500 ns and time step of 2 fs. The radius gyration  $R_g$  was analyzed within the Forcite Module.

## 2. $^{13}\text{C}$ NMR spectra of discrete oligomers

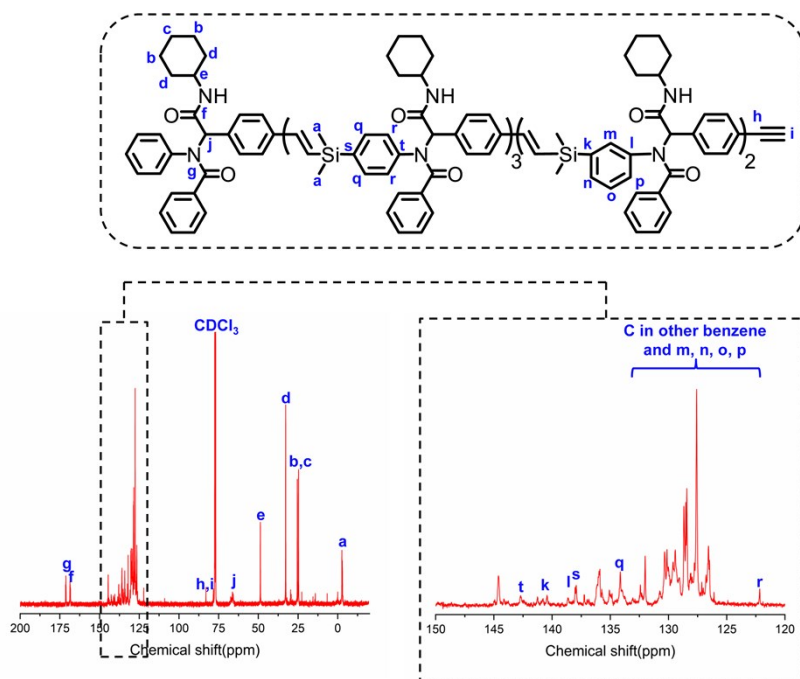
The  $^{13}\text{C}$  NMR of six oligomers were shown in Figure S1-S6 (except run 2). In the case of run 2 (ppppm), the scale of the product is not enough for the test of  $^{13}\text{C}$  NMR with clear carbon signals, but it shows the similar spectra with the other oligomers (run 3, run 4, run 5, run 6), which indicates that the oligomers with both meta- and para- linkers exhibit similar carbon signals.



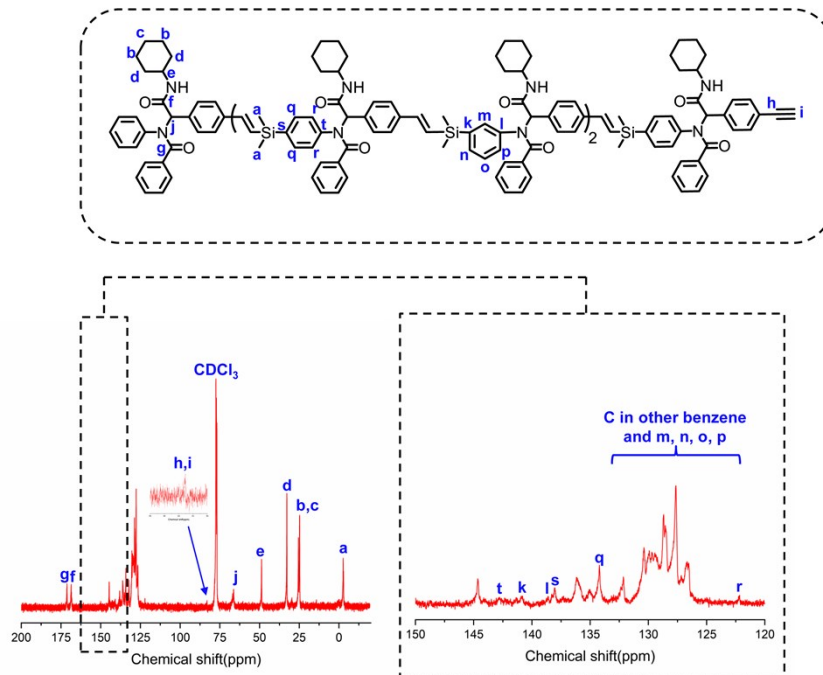
**Figure S1.**  $^{13}\text{C}$  NMR spectrum of run 7 (mmmmm)



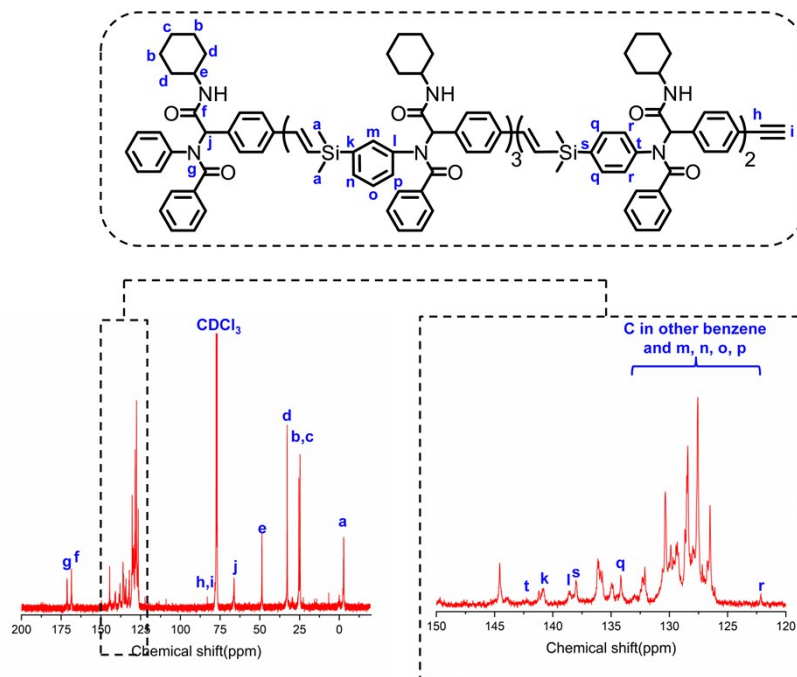
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of run 1 (ppppp)



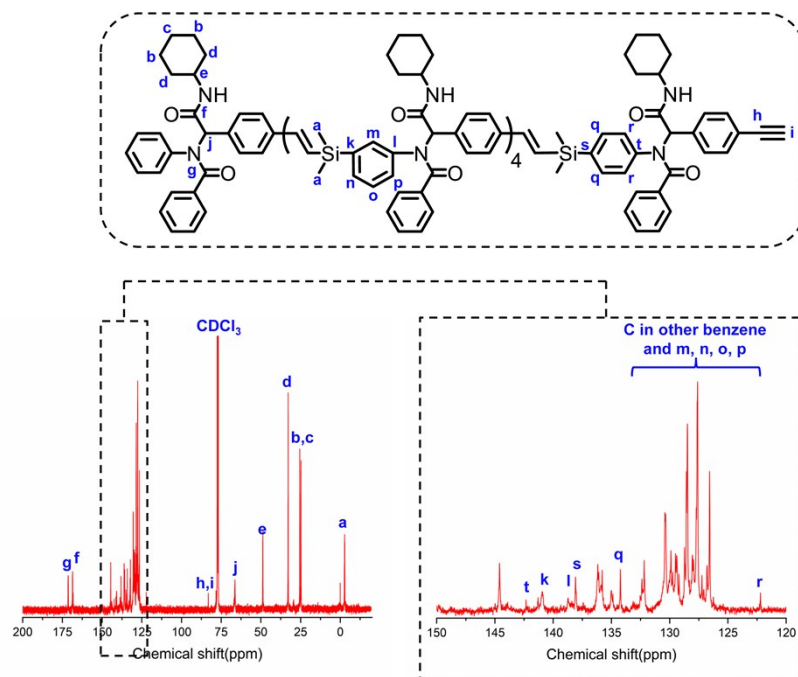
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of run 3 (pppmm)



**Figure S4.**  $^{13}\text{C}$  NMR spectrum of run 4 (pmpmp)



**Figure S5.**  $^{13}\text{C}$  NMR spectrum of run 5 (mmmp)

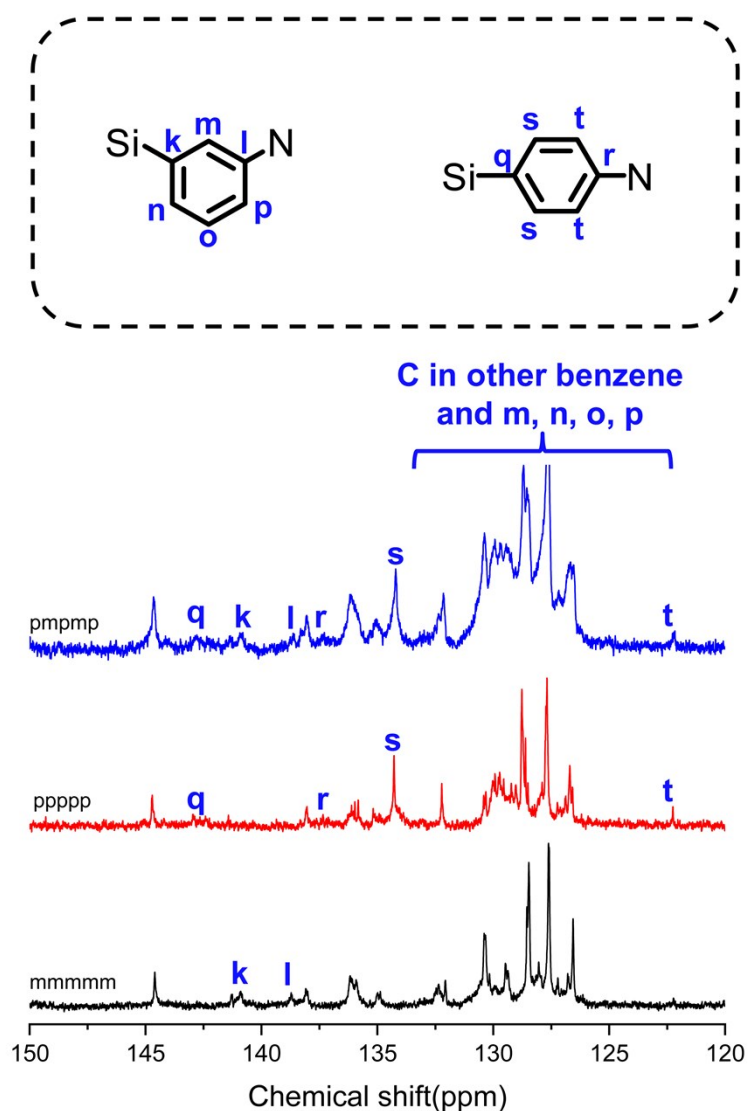


**Figure S6.**  $^{13}\text{C}$  NMR spectrum of run 6 (mmmp)

The representative  $^{13}\text{C}$  NMR spectra of homogeneous run1(pppp) and run7(mmmmm) are shown in **Figure S1** and **S2**, where the left part of the Figures are complete spectra while the right parts are enlarged area of 120-150 ppm. As shown in **Figure S1** and **S2**, the characteristic carbons were marked, while the common carbons of the benzene around 125-135 ppm were not marked. The well-designed discrete oligomers were confirmed by the  $^{13}\text{C}$  NMR. In addition, as the other oligomers show similar spectra compared to run 4 (pmpmp), seen in **Figure S3-S6**.

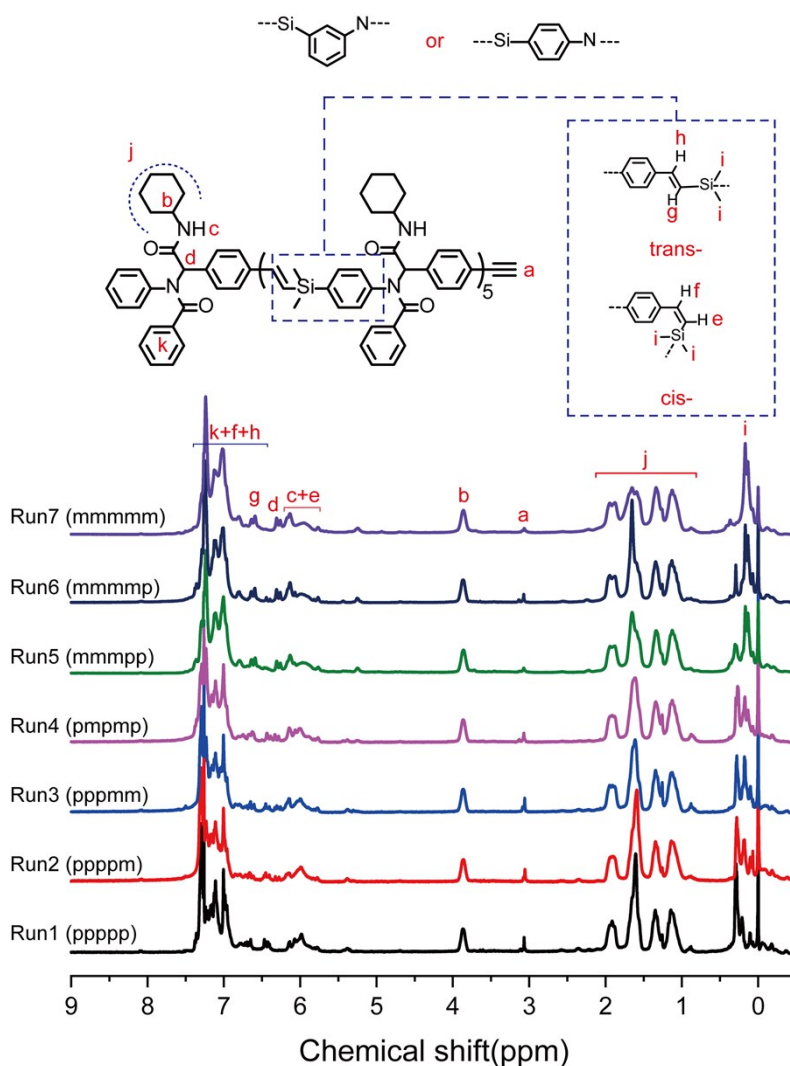
The partially enlarged  $^{13}\text{C}$  NMR of run 4 (pmpmp) as a heterogeneous example is taken to compare with those of homogeneous run1(pppp) and run7(mmmmm), seeing **Figure S7**, as the other area shows same peaks. As we can see the enlarged  $^{13}\text{C}$  NMR of run1(pppp) and run7(mmmmm), the main difference belongs to the marked

carbons of isomeric unit's benzene ring, in which the para (ppppp) linker exhibits four kinds of carbons (q,r,s,t) while meta (mmmmm) linker shows six kinds of carbons (k,l,m,n,o,p), while both carbons of para linker (q,r,s,t) and meta linker (k,l) can be seen in the enlarged  $^{13}\text{C}$  NMR of run 4 (pmpmp), indicating the existence of both para and meta linkers.



**Figure S7.** The partially enlarged  $^{13}\text{C}$  NMR spectrum of run 1 (ppppp), run 4 (pmpmp) and run 7 (mmmmm)

### 3. $^1\text{H}$ NMR spectra of discrete oligomers



**Figure S8.**  $^1\text{H}$  NMR spectra of seven discrete oligomers with tectonic sequence

Seen in **Figure S8**,  $^1\text{H}$  NMR was conducted to confirm the seven discrete oligomers with tectonic sequence, where seven oligomers show similar peaks in the spectra and the characteristic protons were assigned and marked. Proton **a** belongs to alkyne group, **b,c,d** can be regarded as Ugi-4CR structure in the repeating units, **f,g,h,i,j** are regarded as hydrosilylation structure in repeating units. In addition, according to the calculation method in our previous study, seeing Table S1, as the



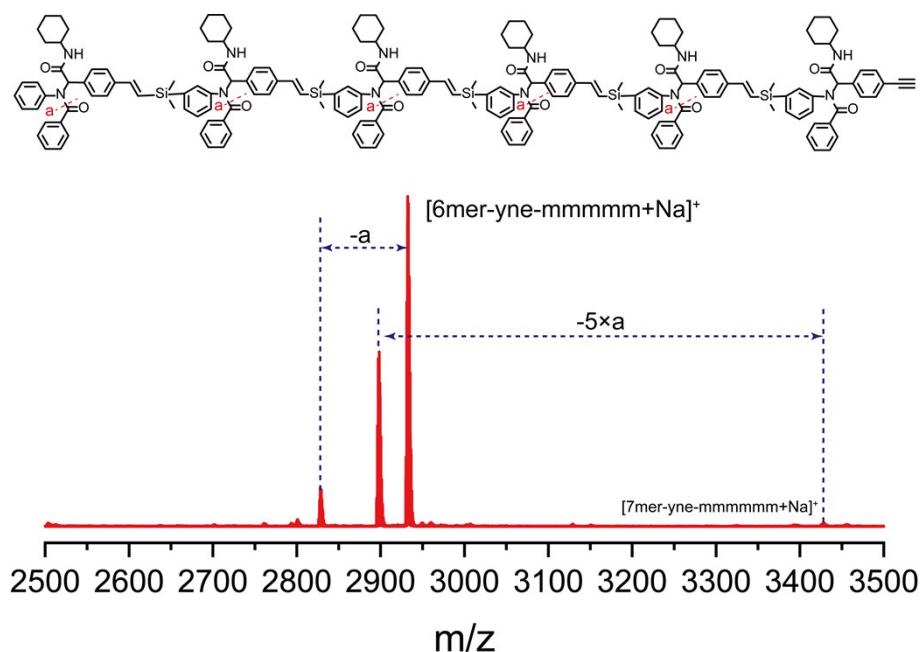
proportion of cis- and trans- linkage shows no obvious difference (*Polym. Chem.*, **2019**, *10*, 2758-2763), cis- and trans- linkages are not mainly discussed in this work.

#### 4. Overall yield and purity of discrete oligomers

**Table S1.** Overall yield and purity of seven oligomers

Run	6mer-yne-	MW(Da)	Purity	Scale(g)	Overall yield	Trans-
1	ppppp	2907.29	>90%	0.183	10.3%	74.2%
2	ppppm	2907.29	>90%	0.173	9.2%	76.9%
3	pppmm	2907.23	>90%	0.439	15.8%	64.8%
4	pmpmp	2907.16	>90%	0.333	11.2%	68.5%
5	mmmpp	2907.23	>90%	0.500	20.1%	69.0%
6	mmmp	2907.37	>90%	0.250	12.3%	67.7%
7	mmmmm	2907.22	>90%	0.340	16.9%	71.4%

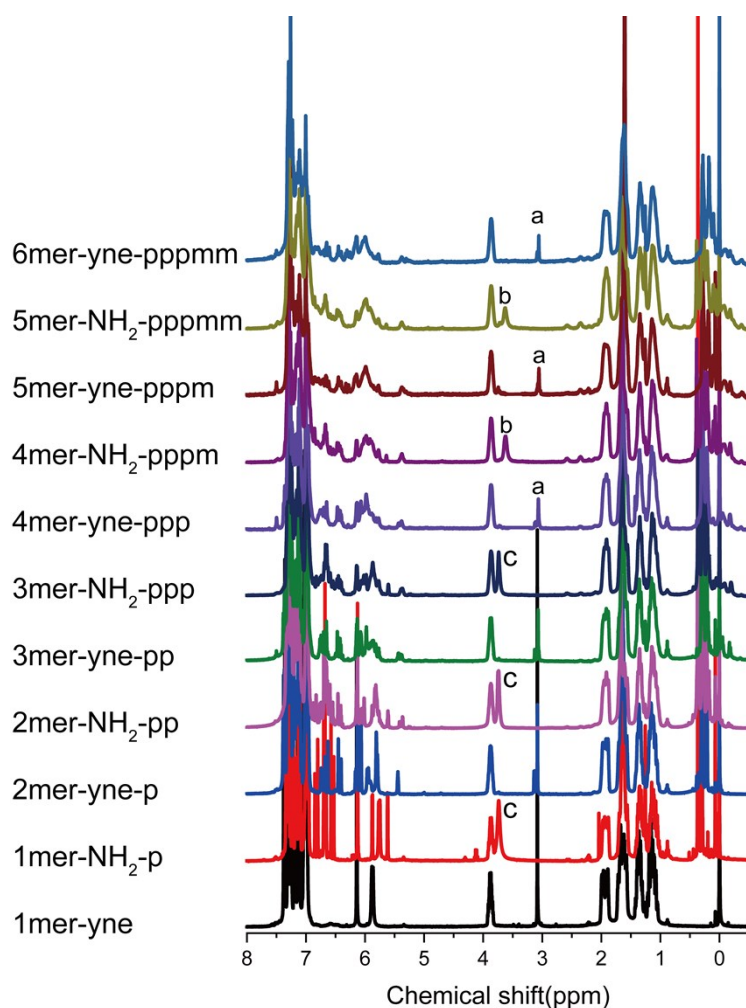
#### 5. Explanation of extra peaks in MALDI-TOF-MS



**Figure S9.** MALDI-TOF-MS spectrum of 6mer-yne-mmmmm

6mer-yne-mmmmm (run 7) was used as an example to explain extra peak in MADLI-TOF-MS of discrete oligomers. The peak 2825.1 was assigned to that the bond at a was broken during the measurement and cut cleavage a down. The peak 2895.3 was referred to that a small amount 7mer-yne-mmmmm cut 5 cleavage a down during the measurement. The extra peak in other oligomers exhibits similar feature.

### 6. $^1\text{H}$ NMR spectra of run 3 in each step



**Figure S10.**  $^1\text{H}$  NMR spectra of run 3 (pppmm) in the synthetic process

### References

[1] Li, C.; Han, L.; Ma, H. W.; Shen, H. Y.; Yang, L. C.; Liu, P. B.; Hao, X. Y.; Li, Y., Synthesis of monodisperse isomeric oligomers based on meta-/para- and linear/star-monomer precursors with Ugi-hydrosilylation orthogonal cycles. *Polym. Chem.* **2019**, *10*, 2758-2763.

[2] Sang, W.; Ma, H.; Wang, Q.; Hao, X.; Zheng, Y.; Wang, Y.; Li, Y., Monomer sequence determination in the living anionic copolymerization of styrene and asymmetric bi-functionalized 1,1-diphenylethylene derivatives. *Polym. Chem.* **2016**, *7*, 219-234