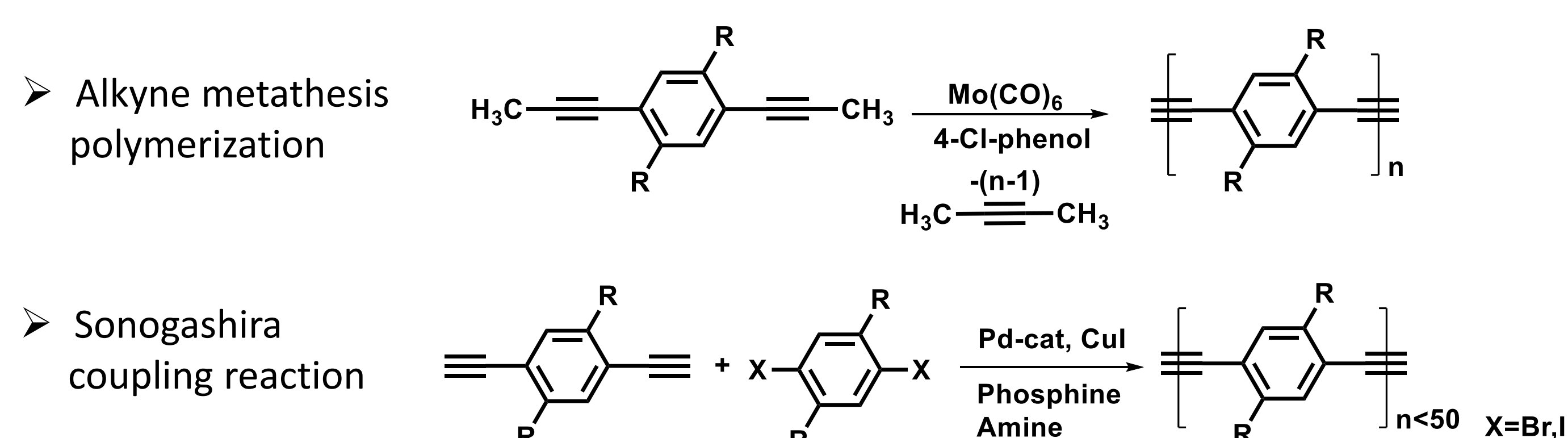


Abstract

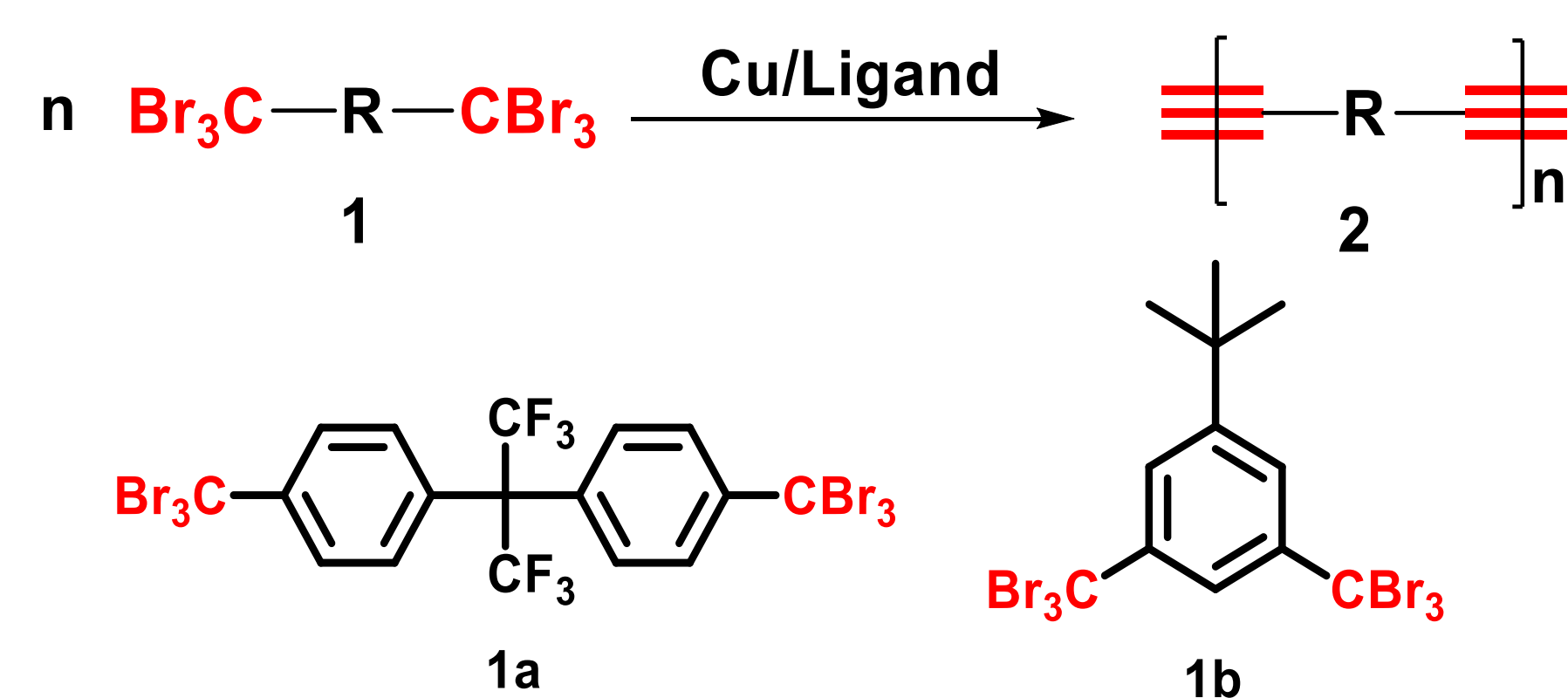
Ethynylene-bridged polymer is currently synthesized by alkyne metathesis polymerization or Pd-catalyzed coupling between diethynylarene and dihaloarene. We report the formation of C≡C linkages by reductive coupling polymerization of bis(benzylic *gem*-tribromide)s treated with Cu/polyamine under mild conditions using monomer without alkynyl groups. The polymer backbone was constructed through cascade formation of (Br)C=C(Br) bonds and C≡C bonds. This protocol provides a new method for synthesis of ethynylene-bridged polymers.

Introduction

Currently synthetic methods of ethynylene-bridged polymer



Proposed new method



Scheme 1. Ethynylene-bridged polymers prepared by polymerization of bis(benzylic *gem*-tribromide)s promoted by Cu/ligand.

Advantages:

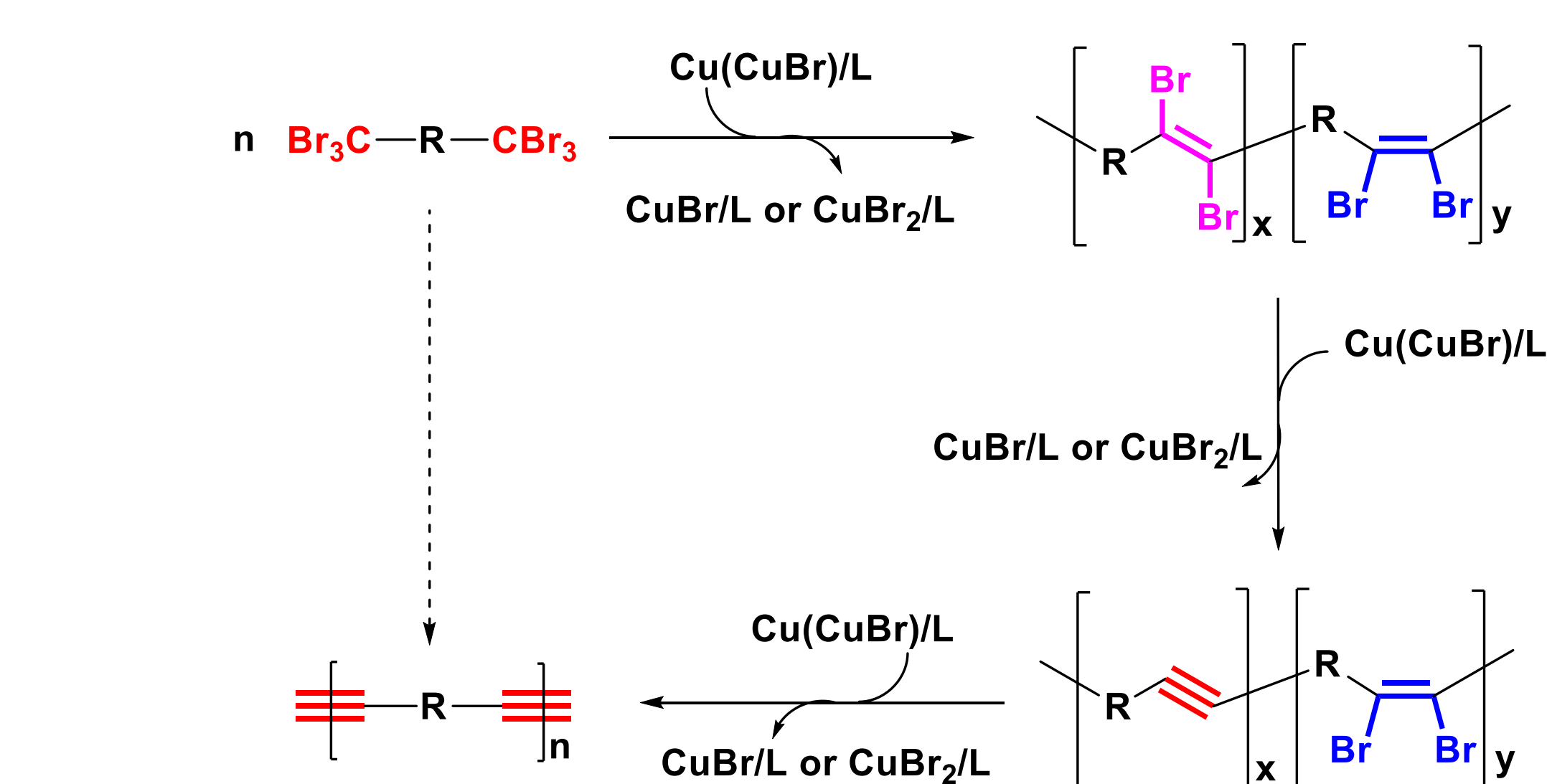
- Mild conditions 60 °C, 5h
- Defect-free ethynylene-bridged polymers
- Simple and cheap catalyst
- Construction of polymer through C≡C bonds formation

Results and discussion

Table. 1 Polymerization results of 2,2-bis(4-tribromomethyl phenyl)hexafluoropropane (**1a**) in the presence of Cu/ligands under different conditions

Run	Polymerization conditions	M _n /Đ ^[a]	Composition of linkage ^[b] [C≡C]/[Z-C=C]/[E-C=C] (mol%)	Yield (%) ^[c]
1	Ligand=Me ₆ TREN	23/2.1	100/0/0	98
2	Ligand=TPMA	24/3.4	60/40/0	-
3	Ligand=PMDETA	12/2.6	47/53/0	-
4	0.5 h@30 °C	17/2.5	0/61/39	-
5	0.5 h@30 °C+1.5 h@40 °C	20/2.2	55/45/0	-
6	0.5 h@30 °C+1.5 h@40 °C+3 h@60 °C	26/2.1	100/0/0	-
7	[1a]=0.01 M	23/2.0	78/22/0	-
8	[1a]=0.04 M	22/1.9	100/0/0	98
9	[1a]:[Cu]:[Me ₆ TREN]=1:4:4	22/2.1	94/6/0	-
10	[1a]:[Cu]:[Me ₆ TREN]=1:7:7	22/2.2	100/0/0	102
11	1 h@30 °C + 4 h@60 °C	25/2.4	100/0/0	-
12	1 h@40 °C + 4 h@60 °C	25/2.4	100/0/0	92
13	5 h@60 °C	23/2.1	100/0/0	98
14	[1a]:[CuBr]:[Me ₆ TREN]=1:6:6	8.4/3.8	88/12/0	-

[a] The number-average molecular weight (M_n in KDa) and dispersity (Đ) of polymer were measured by GPC with polystyrene as standard. [b] Measured by ¹H-NMR. [c] Polymer yield was calculated by assumption on formation of carbon-carbon triple bond. [d] [**1a**]:[Cu]:[Ligand]=1:5:5, [**1a**]=0.025 M, THF, 60 °C, 5 h. [e] [**1a**]:[Cu]:[Me₆TREN]=1:5:5, [**1a**]=0.025 M. [f] [**1a**]:[Cu]:[Me₆TREN]=1:5:5, 60 °C, 5 h. [g] [**1a**]=0.025M, 60 °C, 5 h. [h] [**1a**]=0.025 M, 60 °C, 5 h.



Scheme 2. Evolution of linkages during the polymerization of bis(benzylic *gem*-tribromide)s.

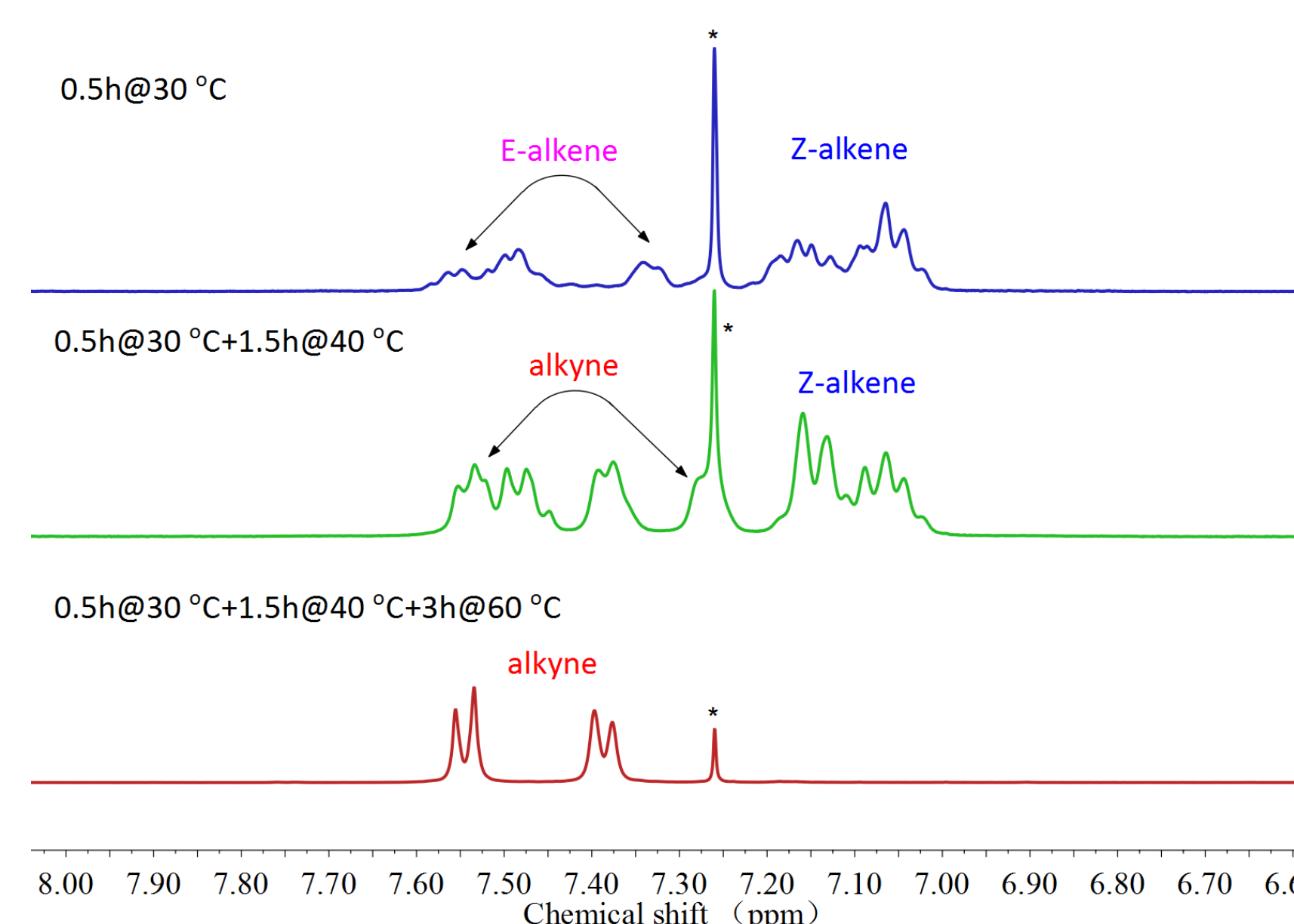


Fig. 1. ¹H-NMR spectra of polymers (Run 4-6 in Table 1) prepared from 2,2-bis(4-tribromomethyl phenyl)hexafluoropropane (**1a**) at different temperatures. (* CDCl₃)

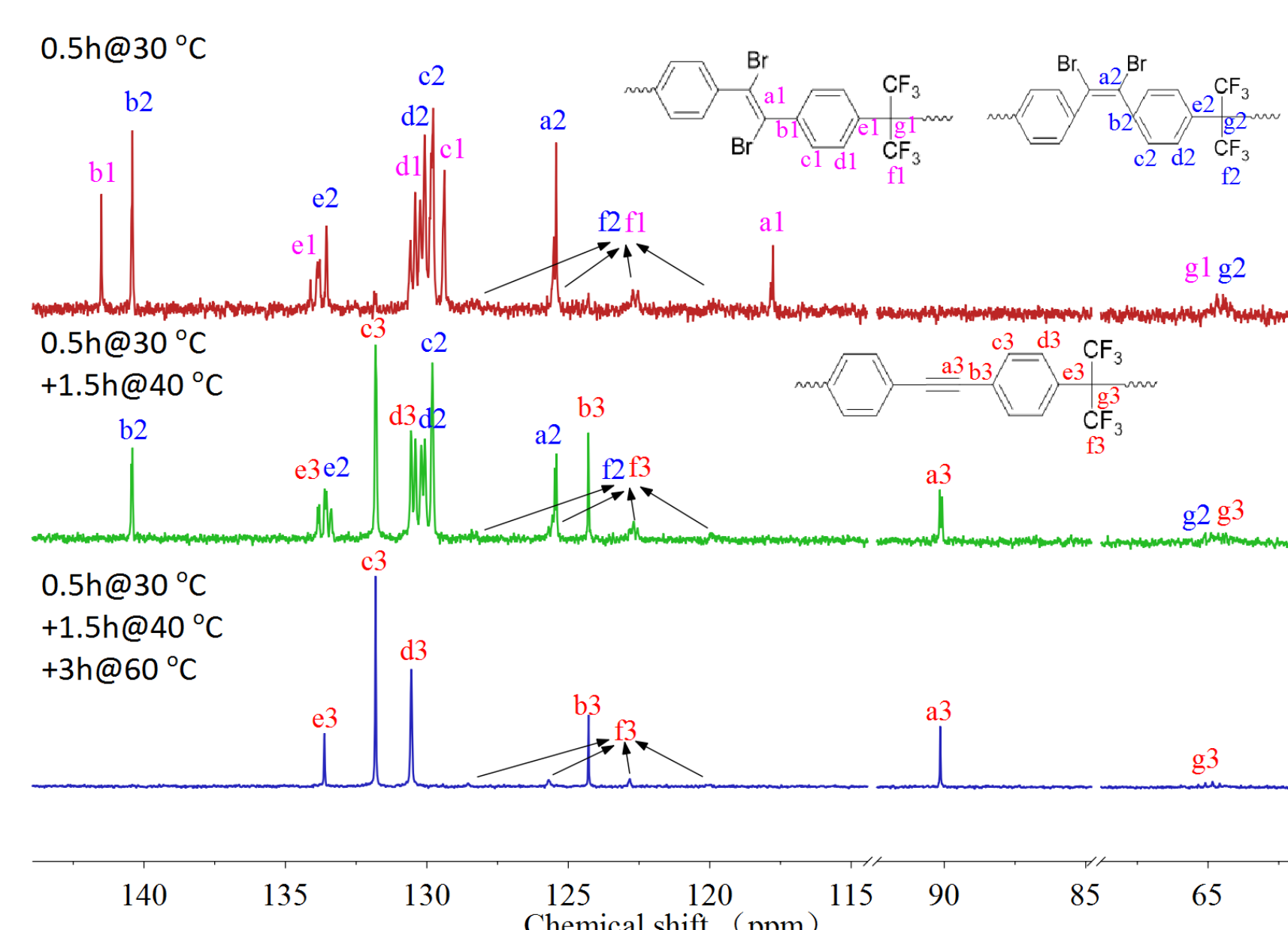


Fig. 2. ¹³C-NMR spectra of polymers (Run 4-6 in Table 1) prepared from 2,2-bis(4-tribromomethyl phenyl)hexafluoropropane (**1a**) at different temperatures.

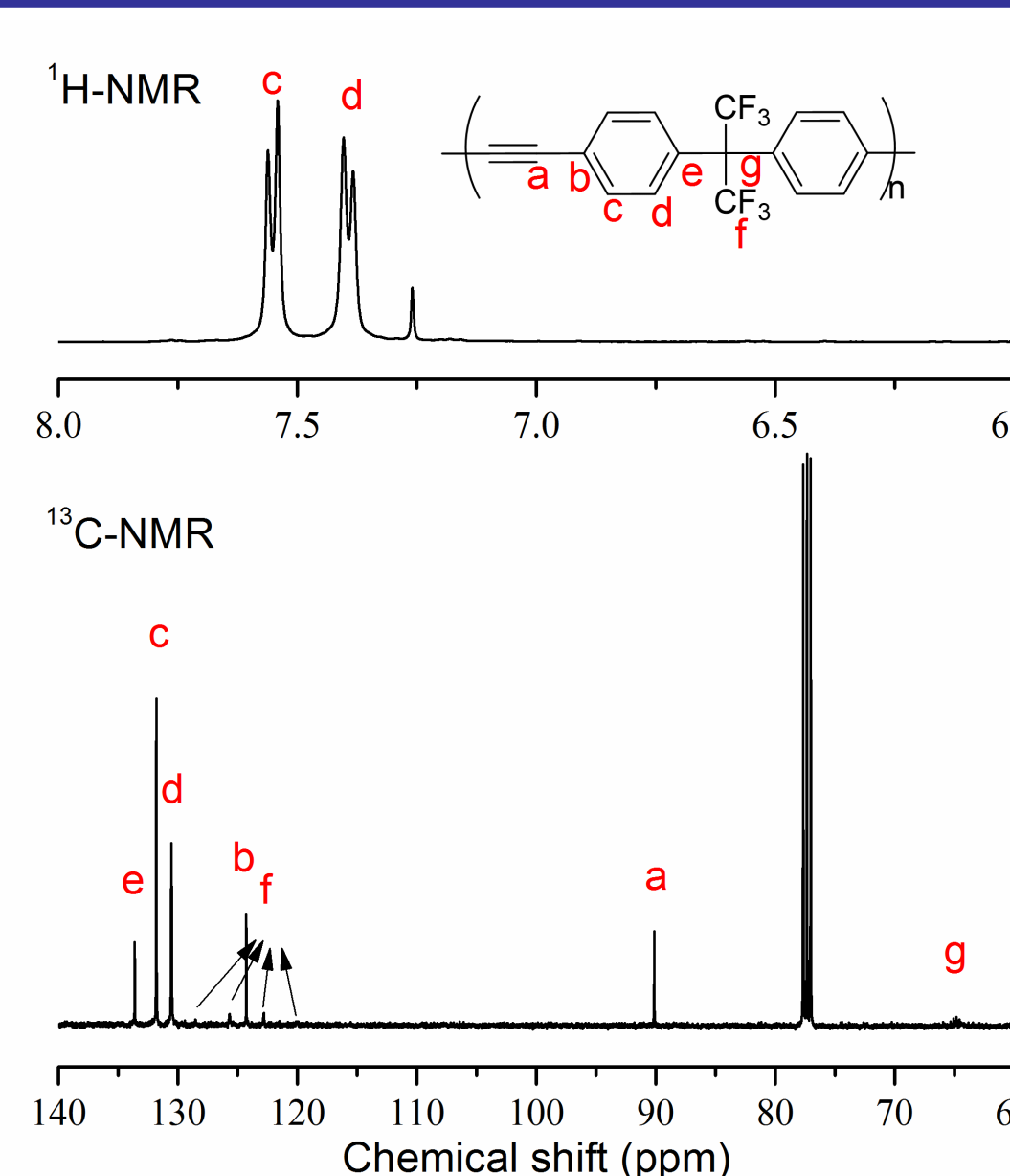


Fig. 3. NMR spectra of polymer **2a** prepared from 2,2-bis(4-tribromomethyl phenyl)hexafluoropropane (**1a**) promoted by Cu/Me₆TREN.

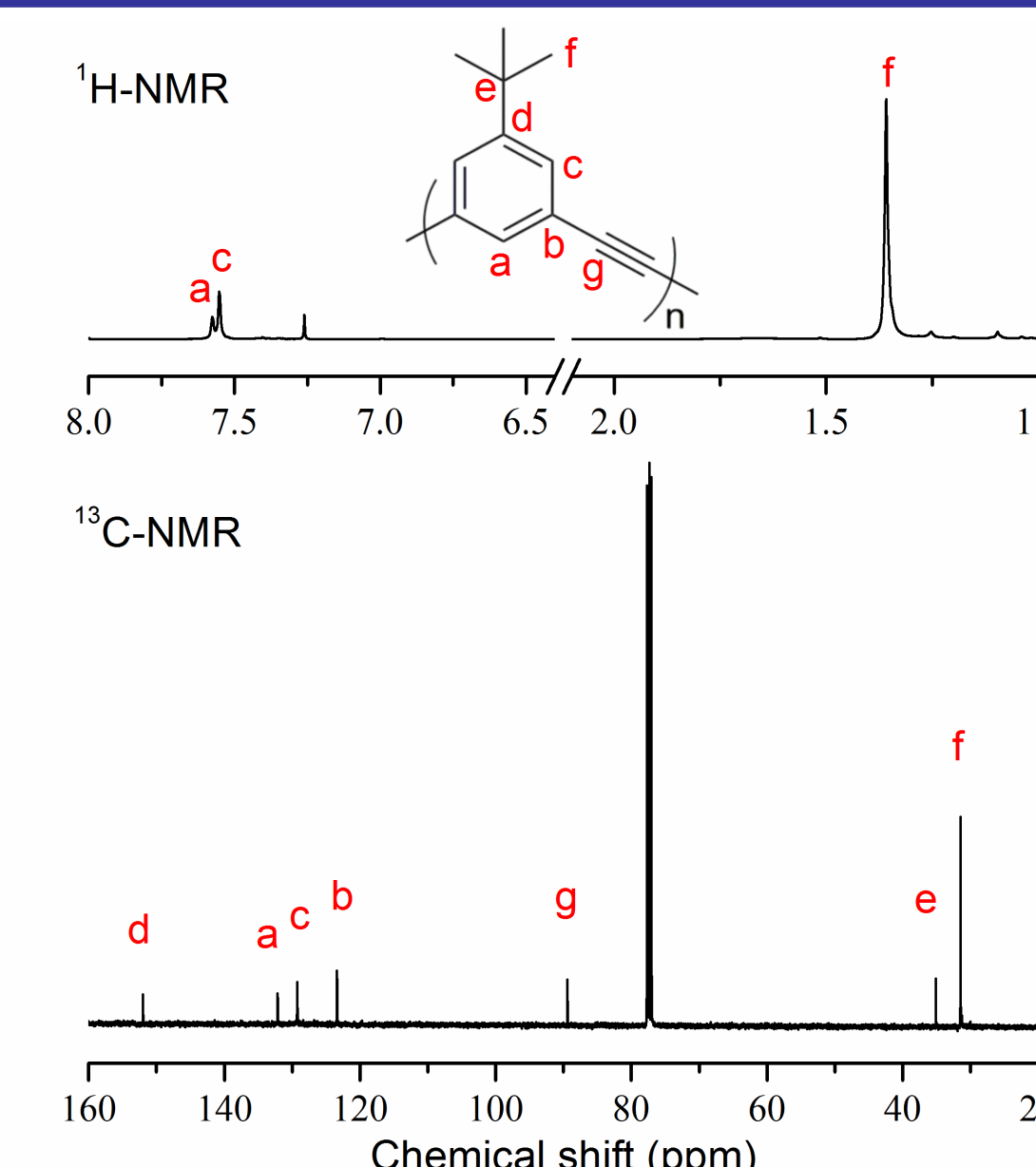


Fig. 4. NMR spectra of polymer **2b** prepared from 1,3-bis(tribromomethyl)-5-tert-butylbenzene (**1b**) promoted by Cu/Me₆TREN.

Conclusions

We present the first successful example of construction of C≡C linkages in polymer by reductive coupling polymerization of bis(benzylic *gem*-tribromide)s under mild conditions. The linkage is constructed by cascade formation of (Br)C=C(Br) and C≡C bonds, which can be manipulated by reaction temperature. The current method will find widespread application in the synthesis of attractive ethynylene-bridged polymers using easily available substrates without alkynyl groups.

Acknowledgement

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References

- (1) Z. Liu and Q. Wang, *RSC Adv.*, 2016, **6**, 39568–39572.
- (2) H. Cao, Z. Liu and Q. Wang, *Polym. Chem.*, 2017, **8**, 3810–3814.