

Electronic Supplementary Information

A Novel Post-Polymerization Modification Route to Functional Poly(disubstituted acetylenes) Through Phenol-Yne Click Reaction

Wenjie Wang,^a Yang Shi,^a Xiao Wang,^a Anjun Qin,^b Jing Zhi Sun^{*a} and Ben Zhong Tang^{*abc}

^a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

E-mail: sunjz@zju.edu.cn; Fax: +86-571-87953734; Tel: +86-571-87953734.

^b Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.

^c Department of Chemistry, Jockey Club Institute for Advanced Study, Institute of Molecular Functional Materials, State Key Laboratory of Molecular Neuroscience, Division of Biomedical Engineering, and Hong Kong Branch of Chinese National Engineering Research Centre for Tissue Restoration and Reconstruction (CNERC-HK Branch). The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.
E-mail: tangbenz@ust.hk; Fax: +852-2358-7375; Tel: +852-2358-1594.

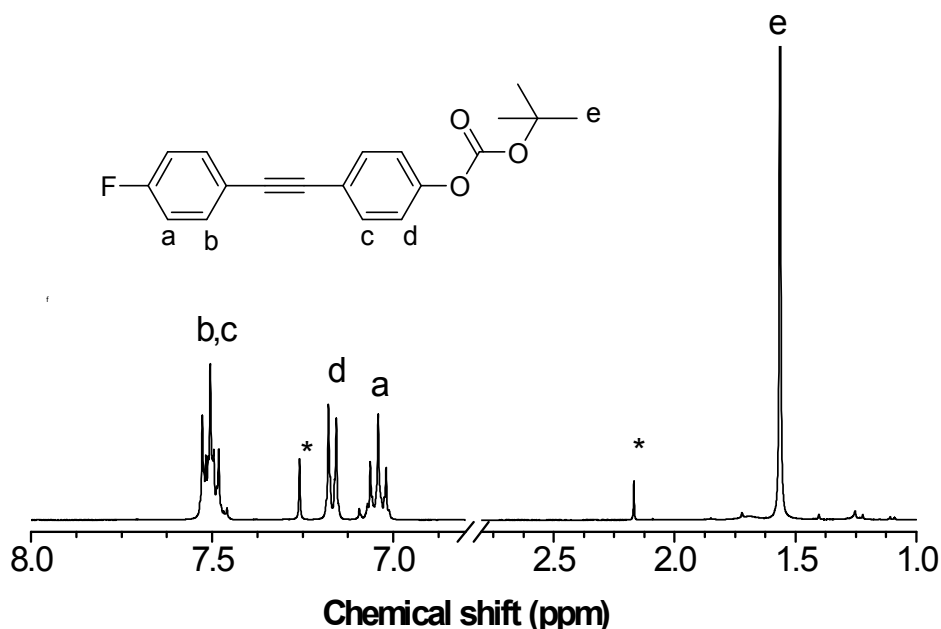


Figure S1. ¹H NMR spectra of M2 in chloroform-*d*. The solvent peak is are marked with asterisks.

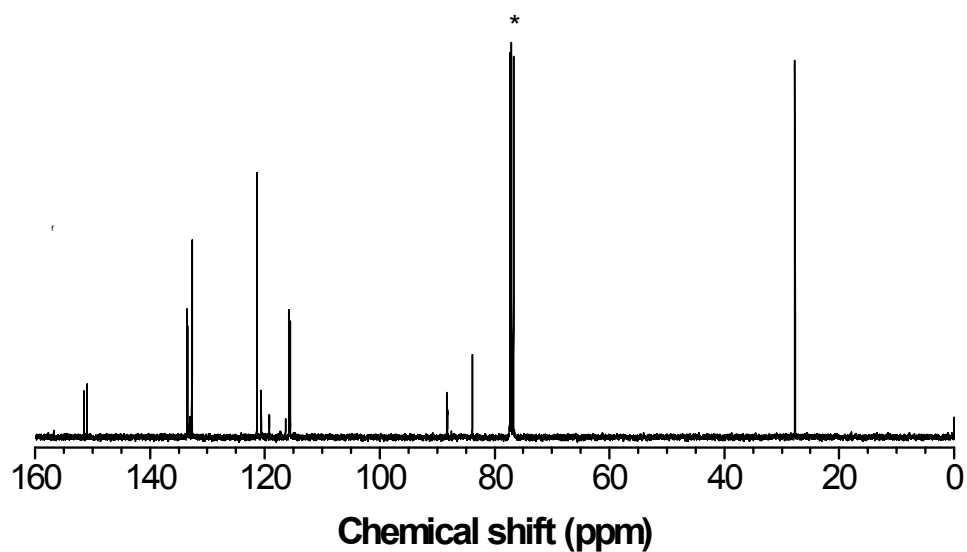


Figure S2. ^{13}C NMR spectra of M2 in chloroform-*d*. The solvent peak is marked with an asterisk.

Table S1 Polymerization of M2 in the presence of transition catalysts^a

entry	Catalyst	temp. (°C)	yield (%)	M_w^b	M_w/M_n^b
1	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	90	< 10	920	1.18
2	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	80	< 10	1180	1.26
3	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	60	trace		
4	$\text{WCl}_6\text{-Ph}_4\text{Sn}$	Rt	trace		
5	$\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$	80	0		
6	$\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$	80	0		

^a Polymerization were carried in toluene the N_2 for 24 h. $[\text{M}_2]_0 = 0.2$ M. $[\text{cat}] = [\text{co-cat}] = 0.02$ M.

Catalysts were aged for 10 minutes before initiating the polymerization. ^b Determined by GPC in THF on the basis of a polystyrene calibration at 40 °C.

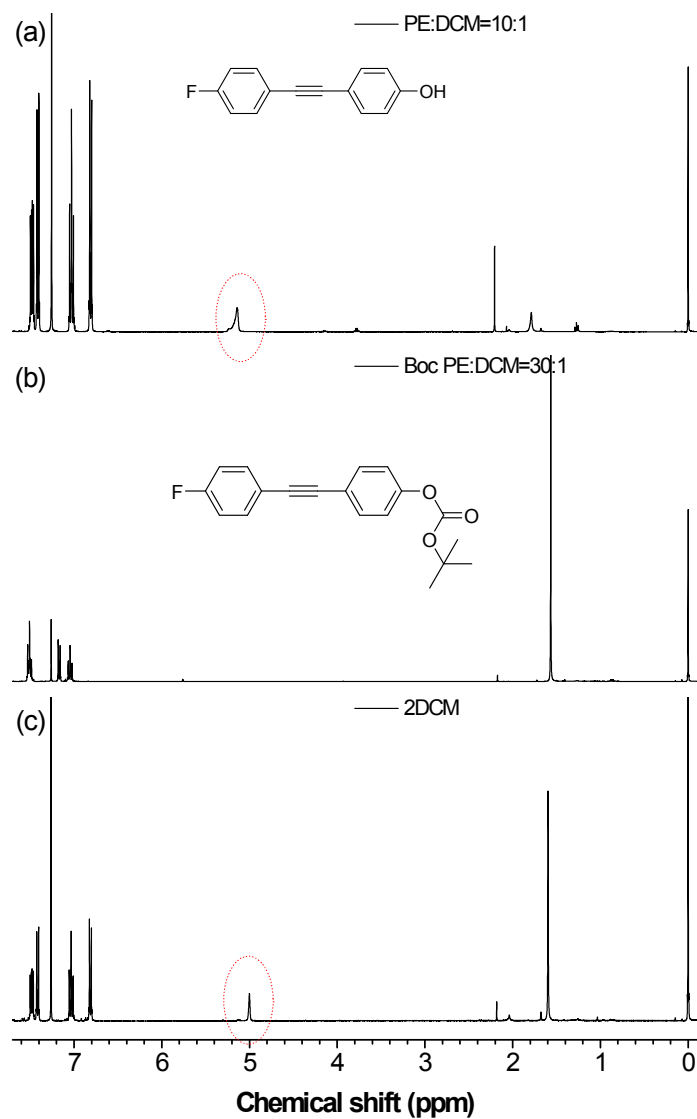


Figure S3. ^1H NMR M2 in different solvents. The solvent peaks are marked with circles.

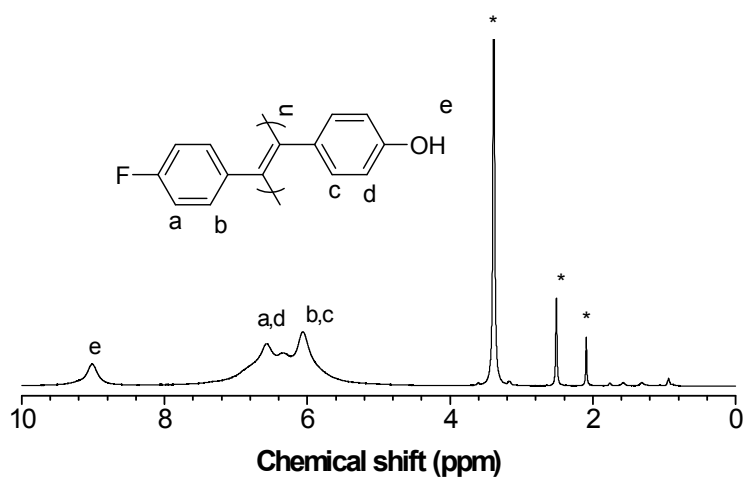


Figure S4. ^1H NMR spectra of precursor polymer P1 in DMSO-d_6 . The solvent peaks are marked with asterisks.

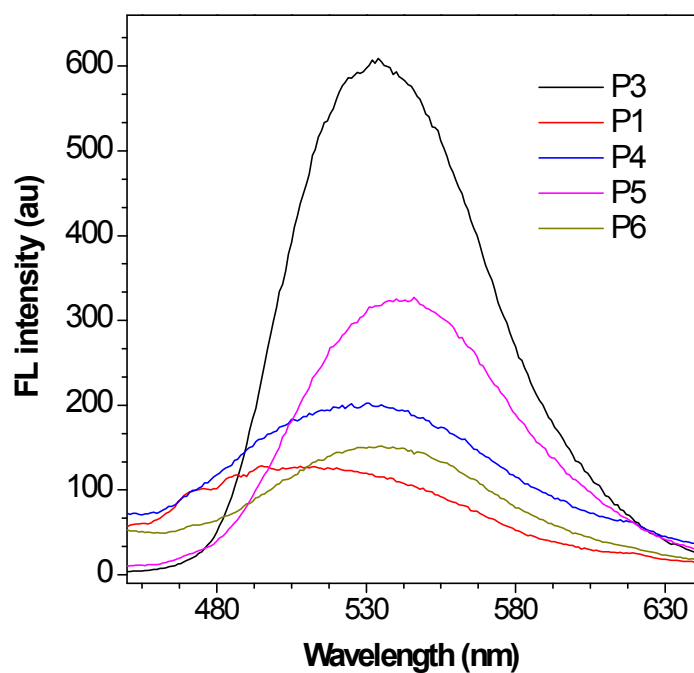


Figure S5. Fluorescence (FL) spectra of solid films (P1, P3~ P6) casted on glass substrates. Excitation at 410 nm.

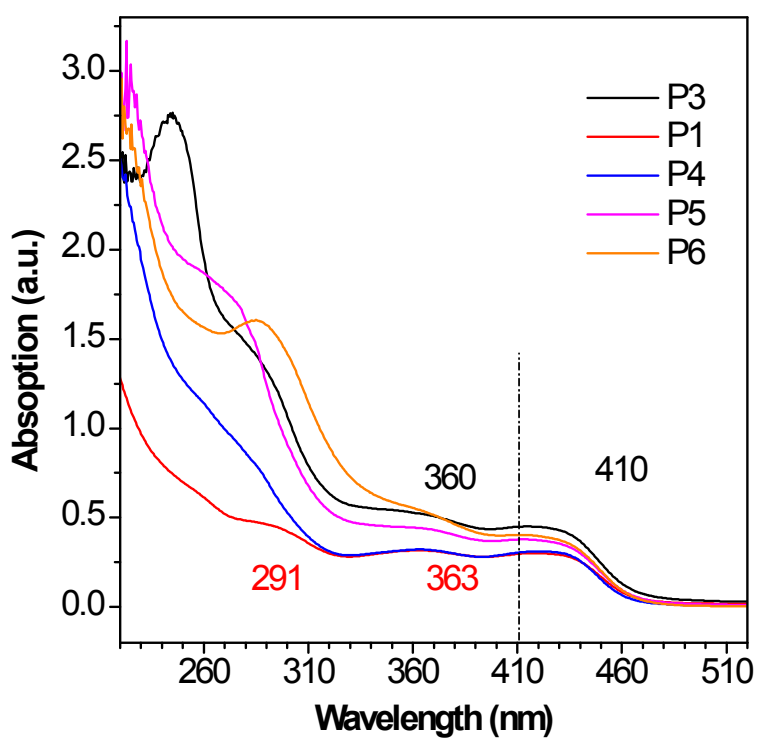


Figure S6. UV-visible absorption spectra of the polymers in the THF solution (100 μ M).

Elemental Composition Report

Page 1

Tolerance = 0.9 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 51 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

Elements Used:

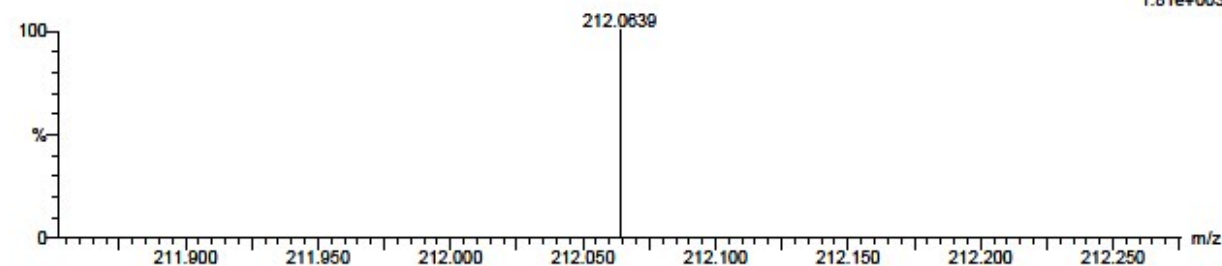
C: 0-50 H: 0-100 O: 0-6 F: 1-3

GCT Premier ZJU
 TOF MS EI+

26-Nov-2015

wwj-fep 334 (2.177)

1.81e+003



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
212.0639	212.0637	0.2	0.9	10.0	5546903.0	C14 H9 O F

Figure S7. Mass spectrum for M1.

Elemental Composition Report

Page 1

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 27 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)

Elements Used:

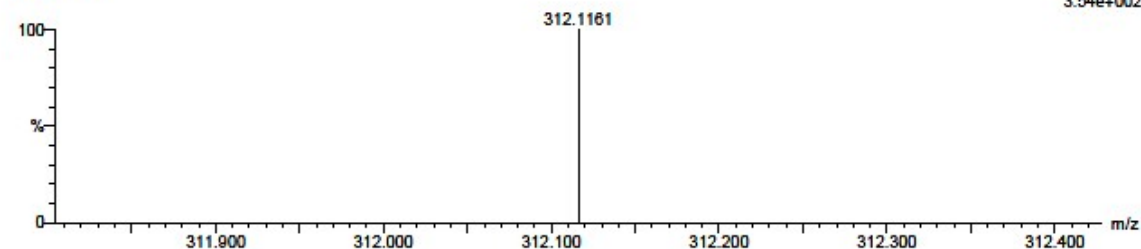
C: 0-80 H: 0-100 O: 0-6 F: 1-1

GCT Premier ZJU
 TOF MS EI+

18-Jul-2016

wwj-fep-boc 334 (2.177)

3.54e+002



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
312.1161	312.1162	-0.1	-0.3	11.0	5546187.5	C19 H17 O3 F

Figure S8. Mass spectrum for M2.

Tolerance = 0.9 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

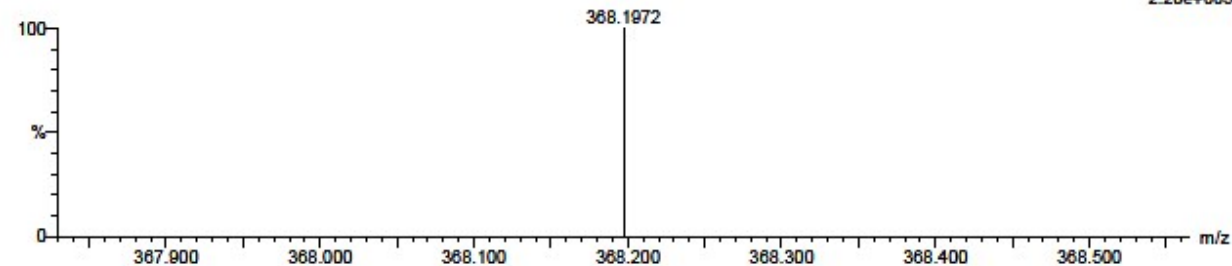
Monoisotopic Mass, Odd and Even Electron Ions
185 formula(e) evaluated with 1 results within limits (up to 70 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 O: 0-6 F: 1-3 Si: 1-2

GCT Premier ZJU
TOF MS EI+

26-Nov-2015

wvj-fep-si 561 (3.010)

2.20e+003



Minimum:				-1.5		
Maximum:	0.9	10.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
368.1972	368.1972	0.0	0.0	10.0	5547117.0	C23 H29 O F Si

Figure S9. Mass spectrum for M3.

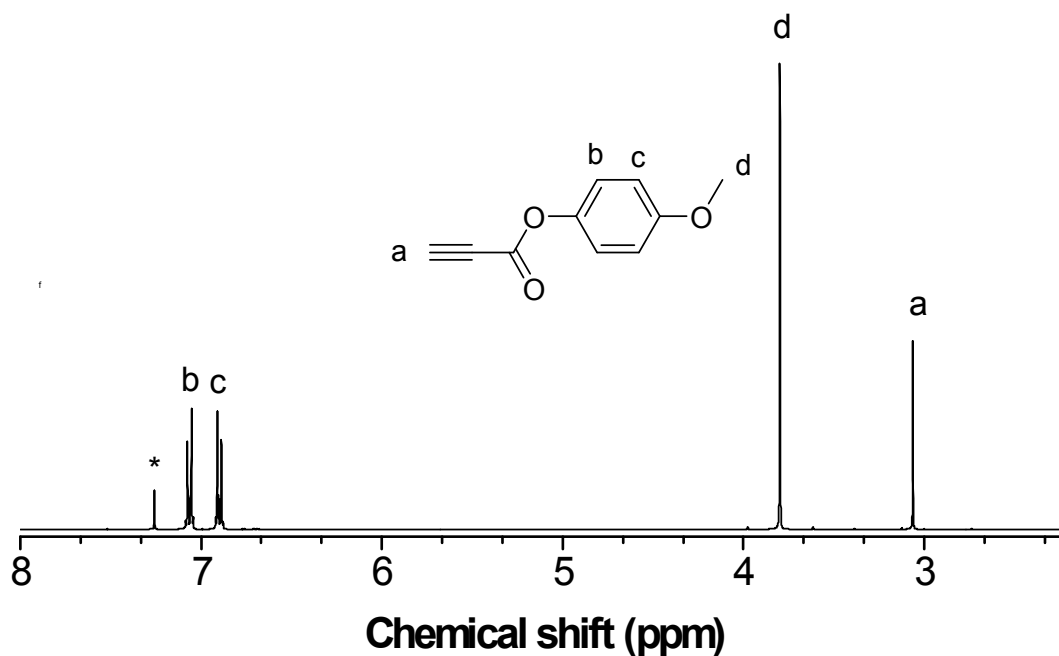


Figure S10. ¹H NMR of the modifier para-methoxyphenol propiolate in CDCl₃. The solvent peak is marked with an asterisk.

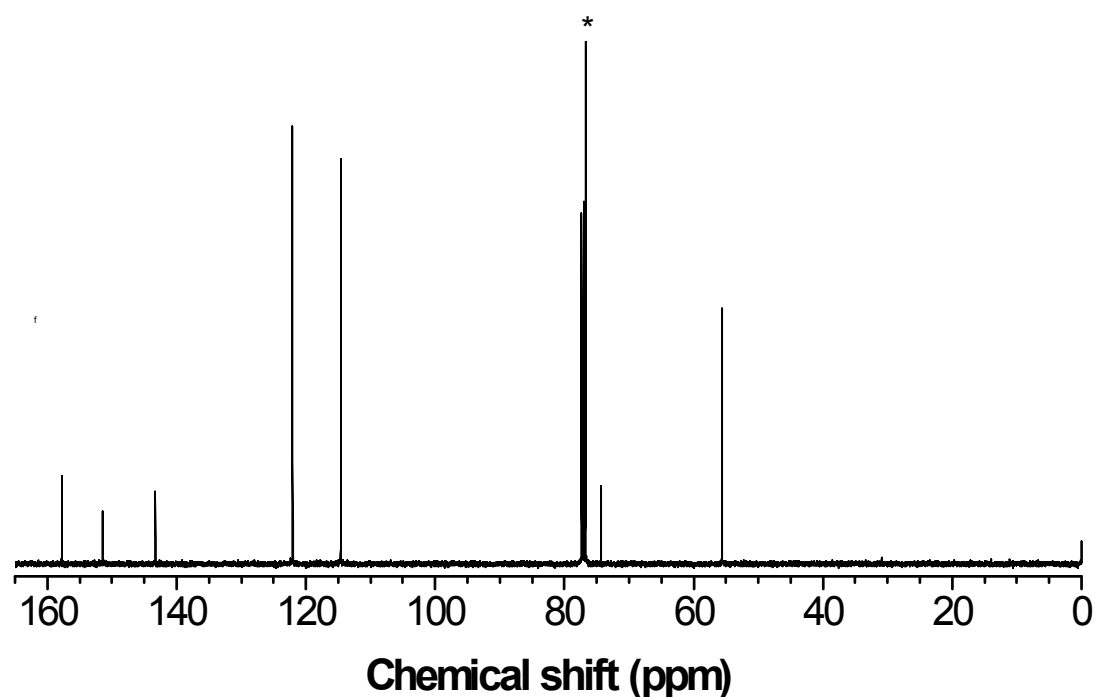


Figure S11. ^{13}C NMR spectrum of the modifier *para*-methoxyphenyl propiolate in CDCl_3 . The solvent peak is marked with an asterisk.

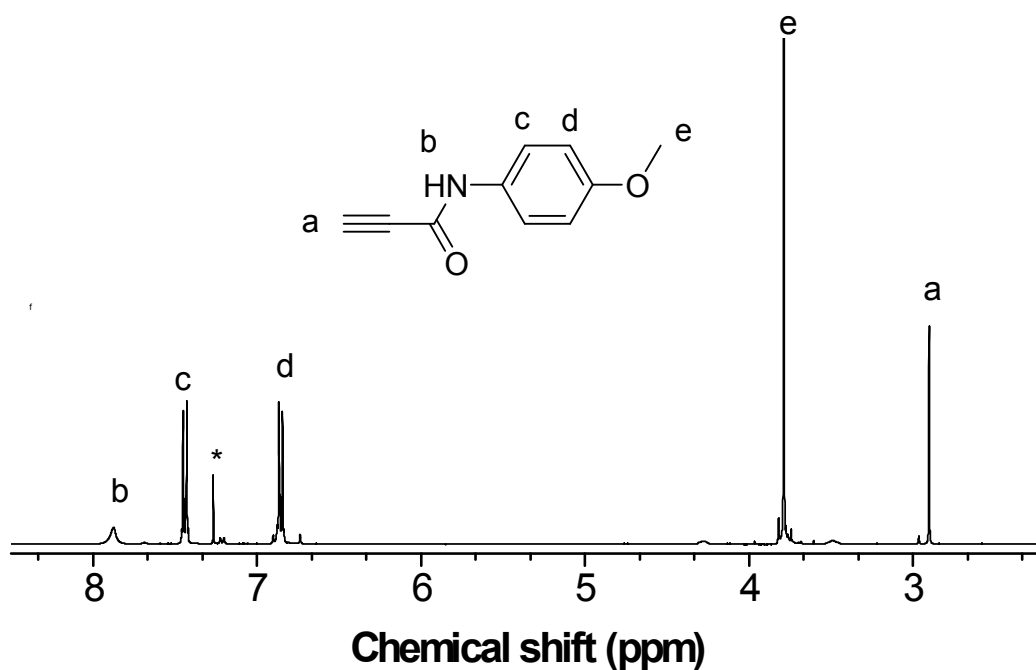


Figure S12. ^1H NMR spectrum for the modifier of *para*-methoxyphenyl propiolamide in CDCl_3 . The solvent peak is marked with an asterisk.

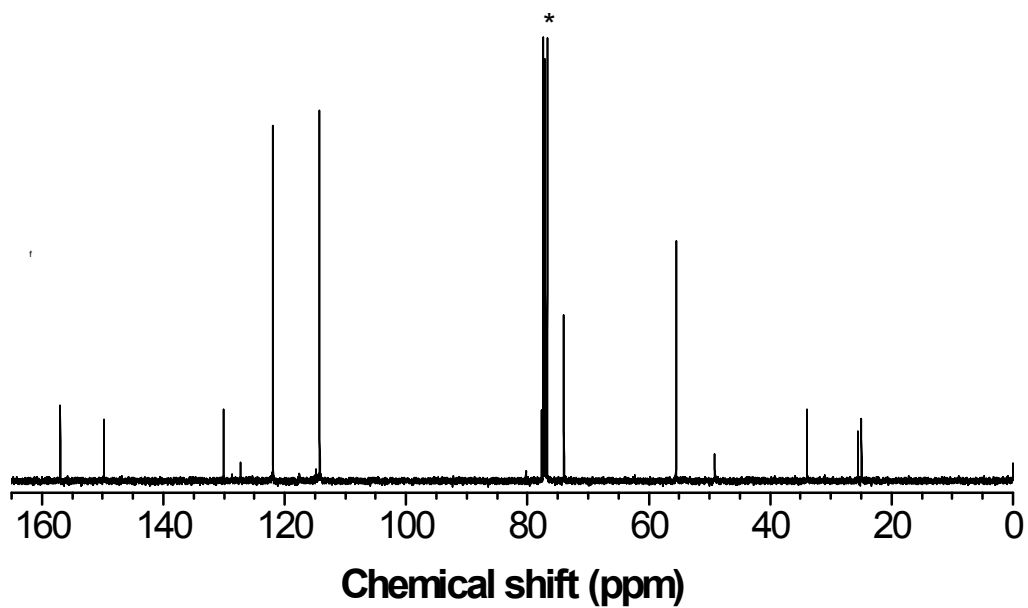


Figure S13. ¹³C NMR spectrum for the modifier of *para*-methoxyl phenyl propiolamide in CDCl₃. The solvent peak is marked with an asterisk.