

Electronic Supplementary Information

Synthesis of Energetic Polynorbornene with Pendant Bis-Azidoacetoxyethyl Groups (PNBAA)

Kun Jiang,^[a] Han-Lin Deng,^[a] Qi Zhang,^[b] Shuifeng Wang,^[c] Hao Wu,^[a] Yan Liu,^[a] Chunpeng Chai^[a] and Mu-Hua Huang*^[a]

^a. School of Materials Science and Engineering, Beijing Institute of Technology
No. 5, Zhongguancun South Street, Beijing 100081, China
E-mail: mhuang@bit.edu.cn

^b. Institute of Chemical Materials, China Academy of Engineering Physics, Manyang 621900,
Sichuan, China

^c. Analytical and Testing Center, Beijing Normal University, Beijing Normal
University, Beijing 100875, China

Table of Contents

Table S1 : The optimization on solvent-free Diels-Alder reaction.....	1
Table S2 The comparison of ¹ H-NMR between 3 and reported data	1
Table S3 The comparison of ¹³ C-NMR between 3 and reported data	1
Table S4 Elemental analysis on NBCA, PNBCA and PNBAA	1
Table S5 ICP-Ms analysis on PNBCA for Ru content	1
Figure S1 : The ¹ H-NMR spectrum of norbornene-dimethanol (3) in CDCl ₃	2
Figure S2 : The ¹³ C-NMR spectrum of norbornene-dimethanol (3) in CDCl ₃	3
Figure S3 : The gCOSY-NMR spectrum of norbornene-dimethanol (3) in CDCl ₃	4
Figure S4 : The gHSQC-NMR spectrum of norbornene-dimethanol (3) in CDCl ₃	5
Figure S7 The ¹ H-NMR spectrum of NBCA (4) in CDCl ₃	8
Figure S8 : The ¹³ C-NMR spectrum of NBCA (4)in CDCl ₃	9
Figure S10 : The gHSQC-NMR spectrum of NBCA (4)in CDCl ₃	11
Figure S11 : TheFT-IR spectrum of NBCA (4).....	12
Figure S12 : The HR-MS spectrum of NBCA(4).....	13
Figure S13:The DSCgraph of NBCA (4)	14
Figure S14: The TGAgraph of NBCA (4)	14
Figure S15 : The ¹ H-NMR spectrum of PNBCA (5) in CDCl ₃	15
Figure S16:The ¹³ C-NMR spectrum of PNBCA (5) in CDCl ₃	16
Figure S17:The array ¹ H-NMR on ROMP reaction in CDCl ₃ (Entry 1, Table 2).....	17
Figure S18: The array ¹ H-NMR on ROMP reaction in CDCl ₃ (Entry 2, Table 2)	18
Figure S19: The array ¹ H-NMR on ROMP reaction in CDCl ₃ (Entry 4, Table 2)	19
Figure S20 Photograph on solvent-free ROMP reaction on NBCA (4)	20
Figure S21: Photograph ofROMP adduct before (top) and after (bottom) removal of Ru comtaminant	21

Figure S22 : The FT-IR spectrumof PNBCA (5)	22
Figure S23 : The ¹ H-NMR spectrum of PNBAA (6) in CDCl ₃	23
Figure S24 : The FT-IR spectrumof PNBAA (6)	24
Figure S29 :The DTG graph of PNBCA(5) and PNBAA (6).....	29
Figure S30 : The DSC graph of PNBCA(5) and PNBAA (6) from 80 °C to 600 °C.....	30

Table S1 : The optimization on solvent-free Diels-Alder reaction

Entry	n_{CPD}:n_{diol}	Temperature(°C)	Time(h)	Yield (%)
1	1:1	100	5	<10
2	1:1	150	5	<10
3	1:1	170	5	<20
4	1:1	190	5	45
5	1:1	200	5	60
6	1:1	250	5	55
7	1.05:1	200	5	55
8	1.2: 1	200	5	40
9	2.5: 1	200	5	41
10	1: 1.2	200	5	50
11	1:1	200	1	<10
12	1:1	200	2	<10
13	1:1	200	3	30
14	1:1	200	4	50

Table S2 The comparison of 1H-NMR between 3 and reported data

norbornene diol reported by Paul R. Hanson (in CDCl ₃)	Norbornene-dimethanol (3)(in CDCl ₃)	△δ
6.02(H-1)	6.00(H-1)	0.02
4.07 (H-6)	4.33 (H-6)	0.26
3.61 (H-4)	3.59-3.56 (H-4)	0.02
3.39-3.30(H-5)	3.33 (H-5)	0.00
2.78 (H-2)	2.76 (H-2)	0.02
2.55-2.47(H-3)	2.50(H-3)	0.00
1.42-1.35(H-7)	1.34-1.40(H-7)	0.02
Ref: <i>J. Org. Chem.</i> 2007 , 72, 3194-3198.		

Table S3 The comparison of ^{13}C -NMR between 3 and reported data

norbornene diol reported by Paul R. Hanson (in CDCl_3)	Diels-Alder-norbornene diol(in CDCl_3)	$\Delta\delta$
45.0 (C-c)	45.2 (C-c)	0.2
46.5 (C-b)	46.6 (C-b)	0.1
49.9 (C-e)	49.9 (C-e)	0.0
63.4 (C-d)	63.6 (C-d)	0.1
134.7 (C-a)	134.8 (C-a)	0.1

Ref: *J. Org. Chem.* **2007**, 72, 3194-3198.

Table S4 Elemental analysis on NBCA, PNBCA and PNBA

Sample	Mass Percentage (%)					
	Found			Theoretical ^a		
	N	C	H	N	C	H
NBCA	0	51.04	5.49	0	50.83	5.25
PNBCA	0	50.14	5.30	0	50.83	5.25
PNBA	24.10	48.90	5.27	26.24	48.75	5.04

[a] Theoretical values were calculated assuming an ideal structure of PNBCA for the elemental analysis.

Table S5 ICP-Ms analysis on PNBCA for Ru content

PNBCA ^[a]	Ru Content (ppm)
First -precipitating ^[b]	966
Second -precipitating ^[b]	823
Third -precipitating ^[b]	790

[a] PNBCA was synthesis through solvent free way with 1 mol% of Grubbs' I catalyst. [b] 500 mg PNBCA was dissolve in 5 ml 3-pentone and added 5 ml methanol to precipitate.

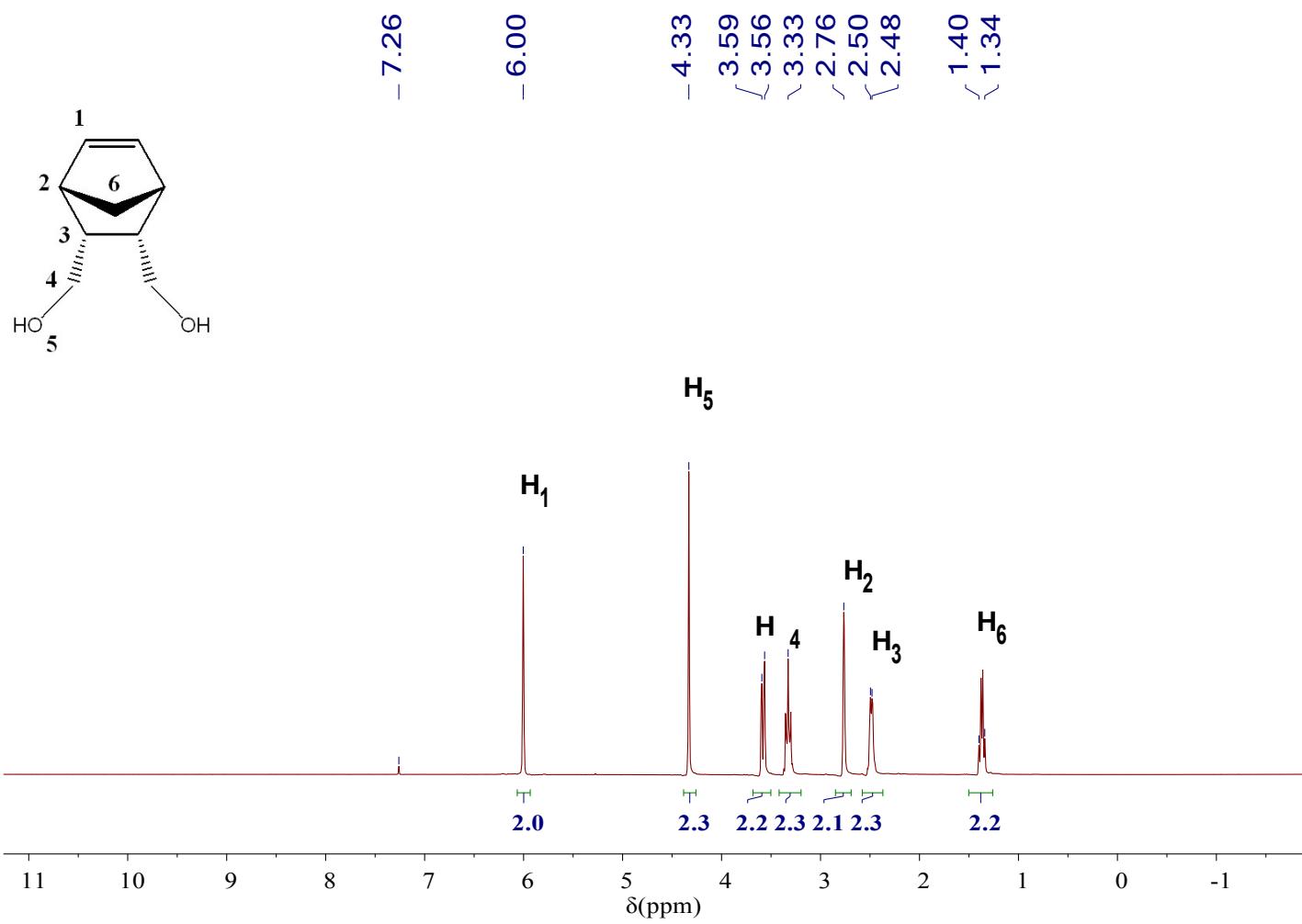


Figure S1 : The ¹H-NMR spectrum of norbornene-dimethanol (3) in CDCl₃

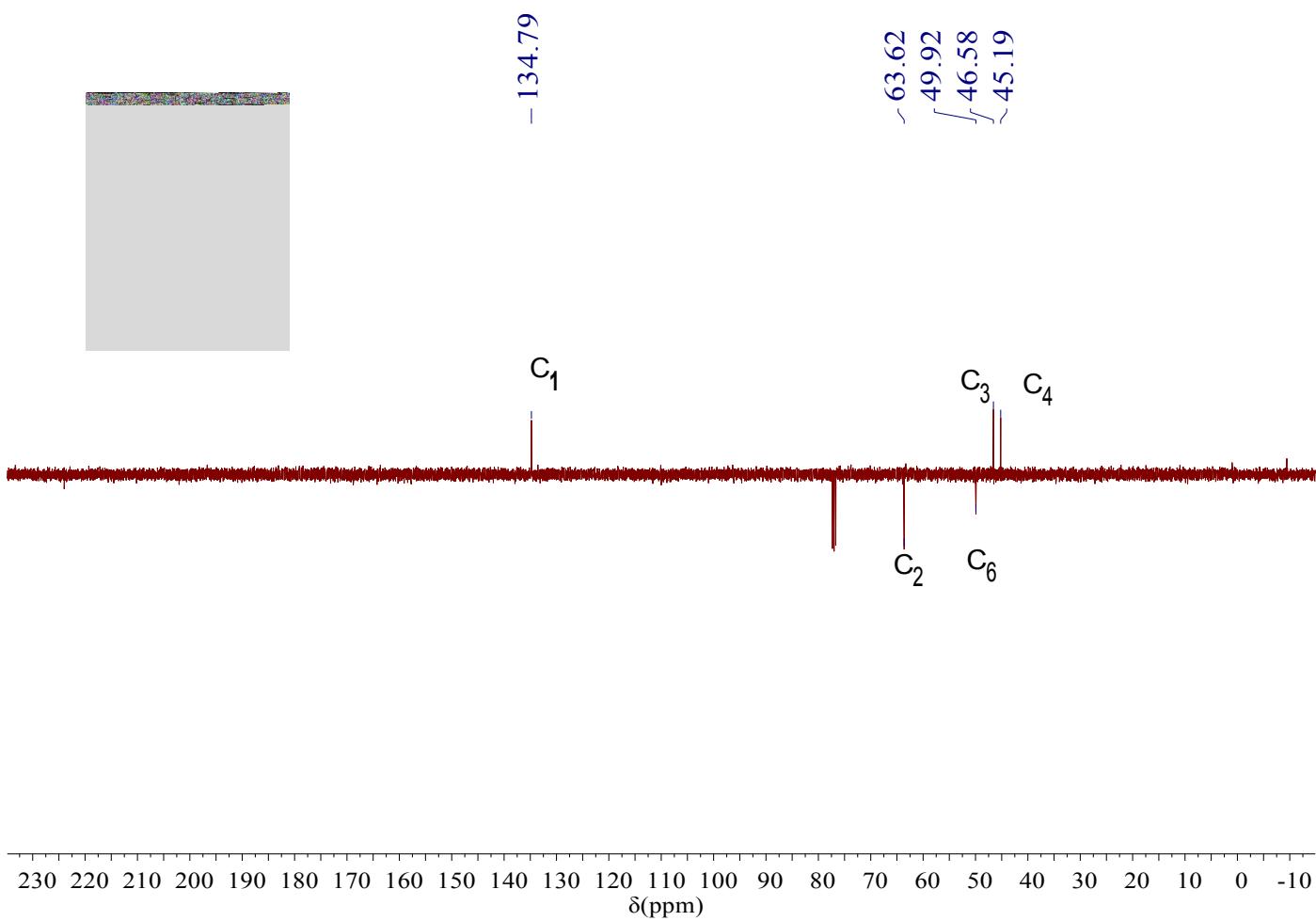


Figure S2 : The ^{13}C -NMR spectrum of norbornene-dimethanol (3) in CDCl_3

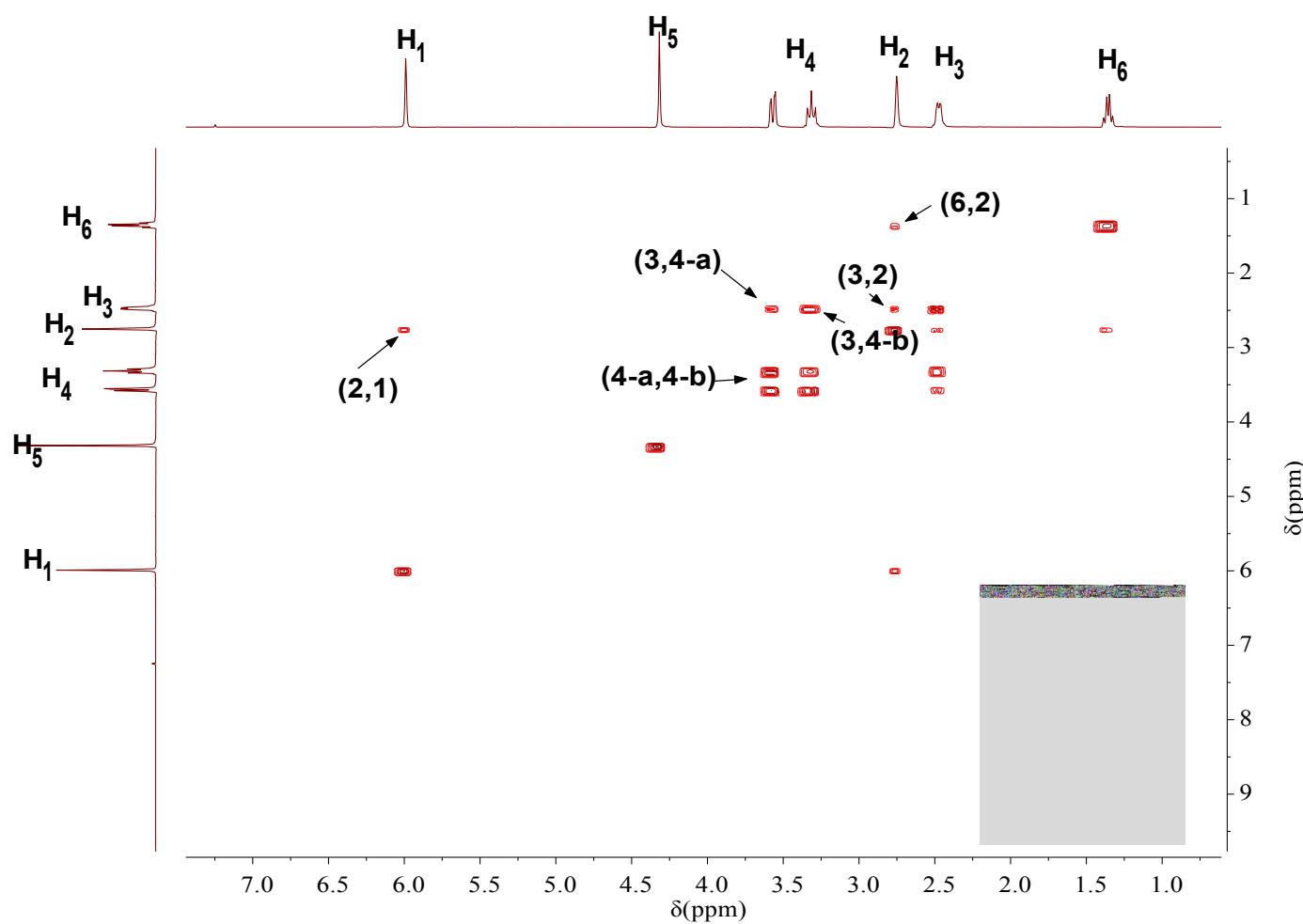


Figure S3 : The gCOSY-NMR spectrum of norbornene-dimethanol (3) in CDCl_3

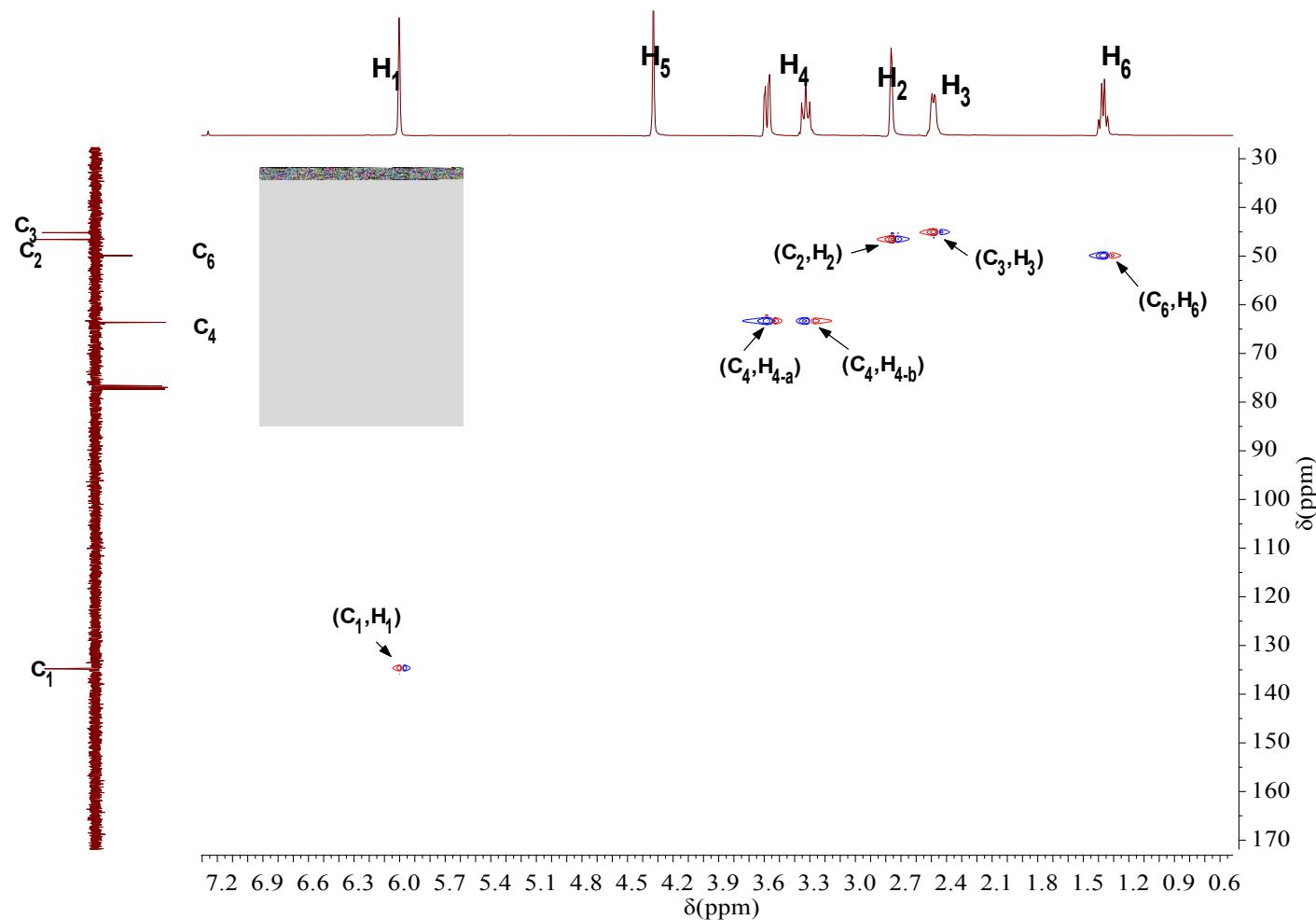


Figure S4 : The gHSQC-NMR spectrum of norbornene-dimethanol (3) in CDCl_3

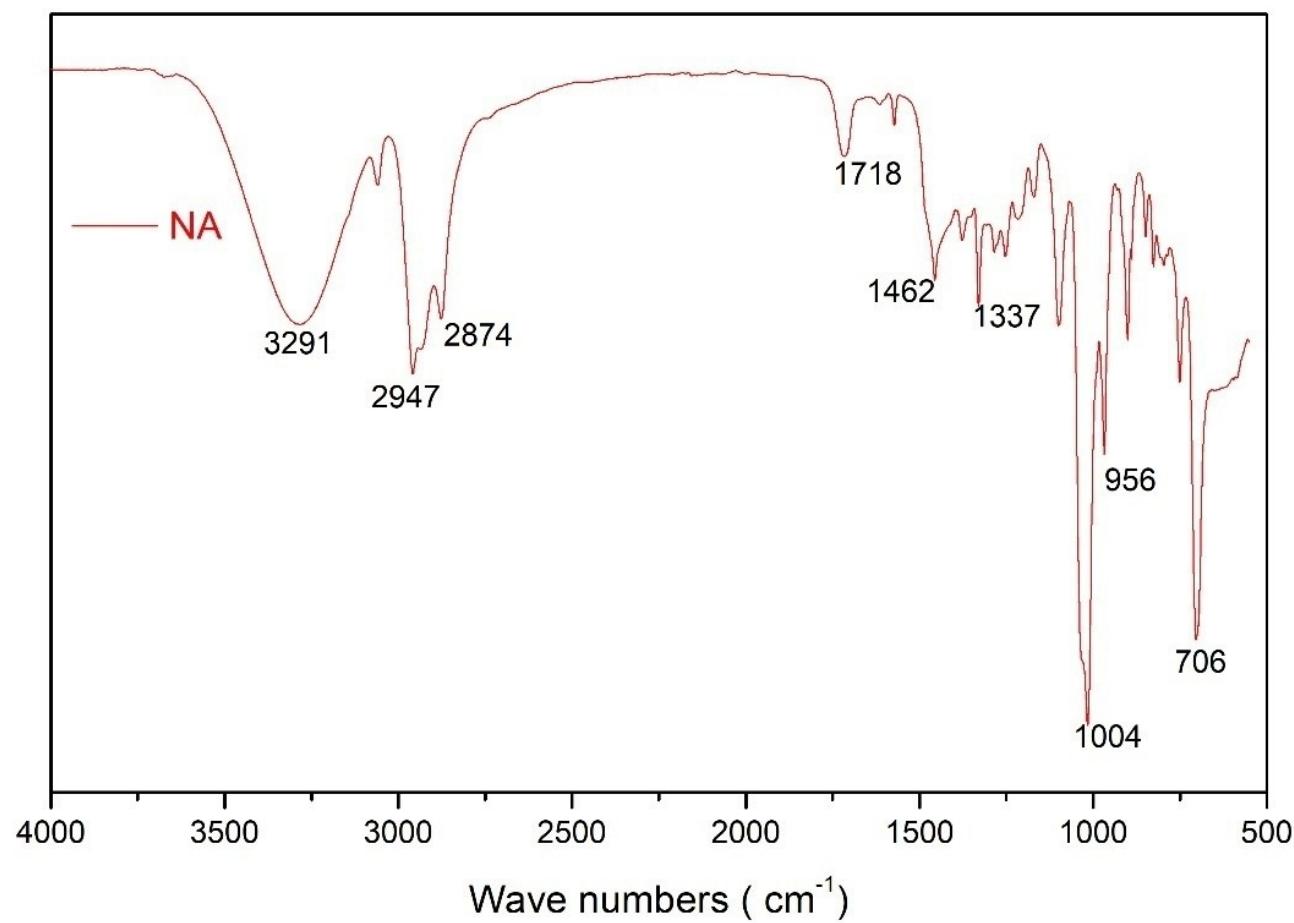


Figure S5 : The FT-IR spectrum of norbornene-dimethanol (3)

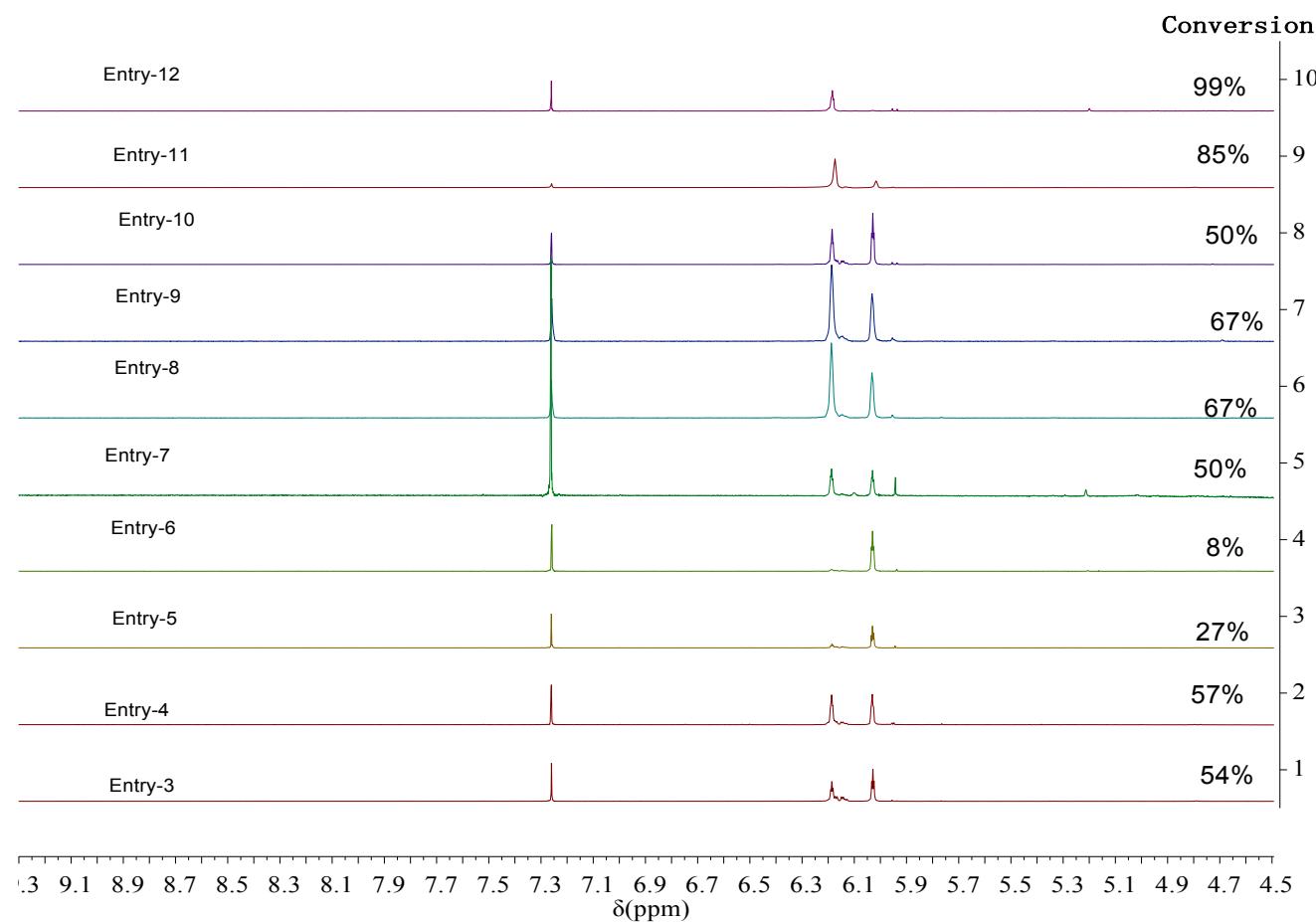


Figure S6 Array NMR study on the optimization on chloroacetylation on diol 3

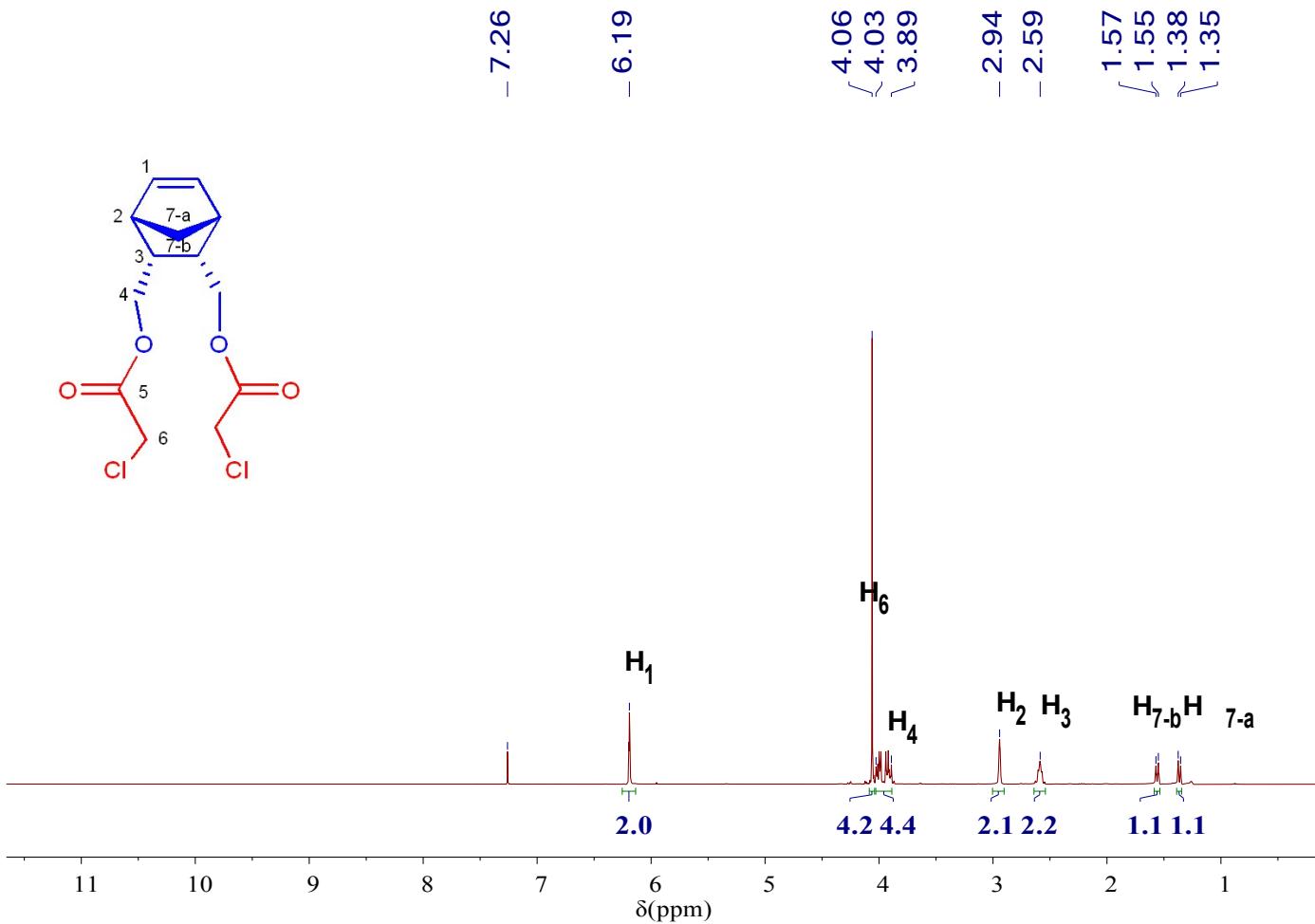


Figure S7 The ^1H -NMR spectrum of NBCA (4) in CDCl_3

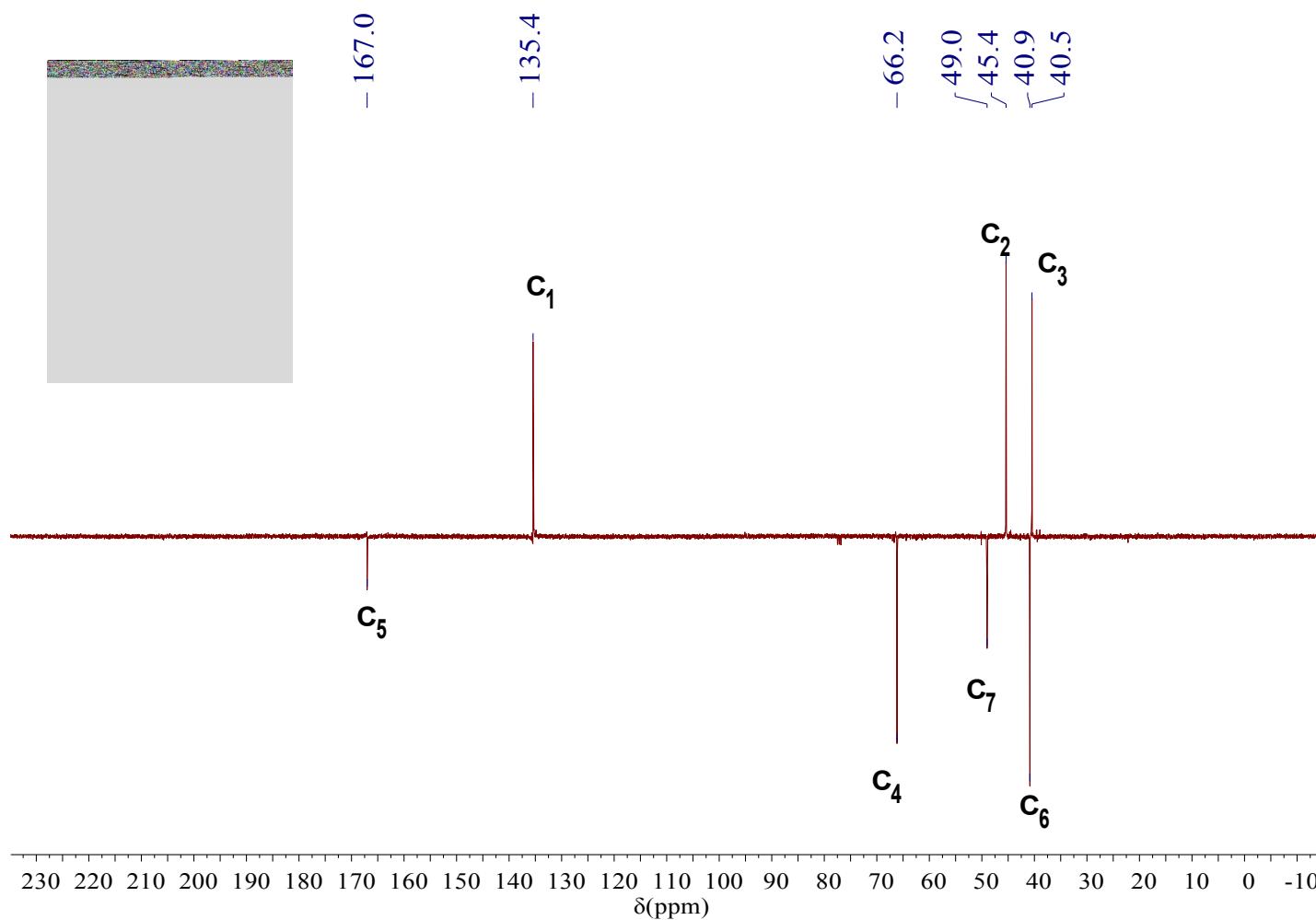


Figure S8 : The ^{13}C -NMR spectrum of NBCA (4)in CDCl_3

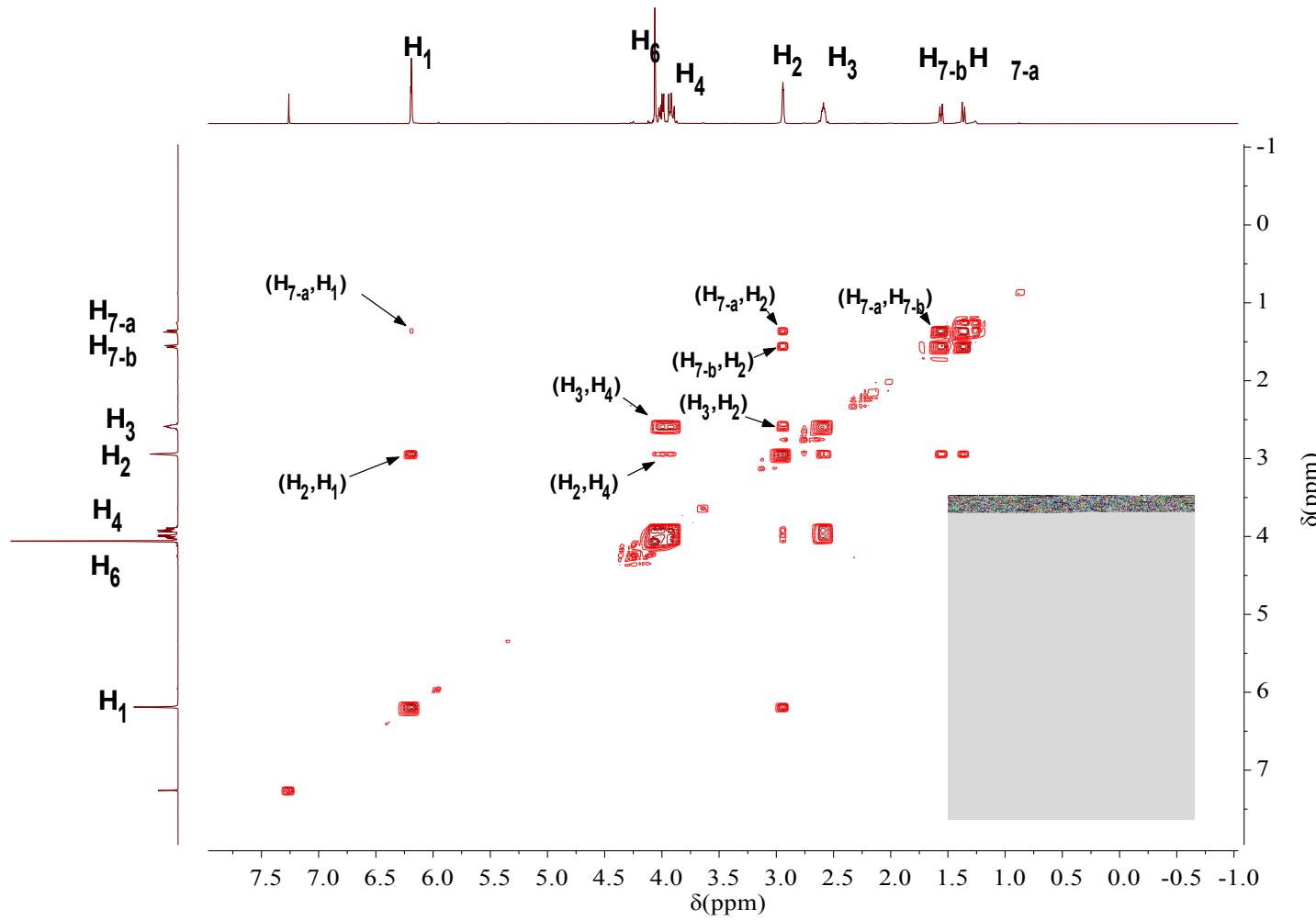


Figure S9 :The gCOSY-NMR spectrum of NBCA (4)in CDCl_3

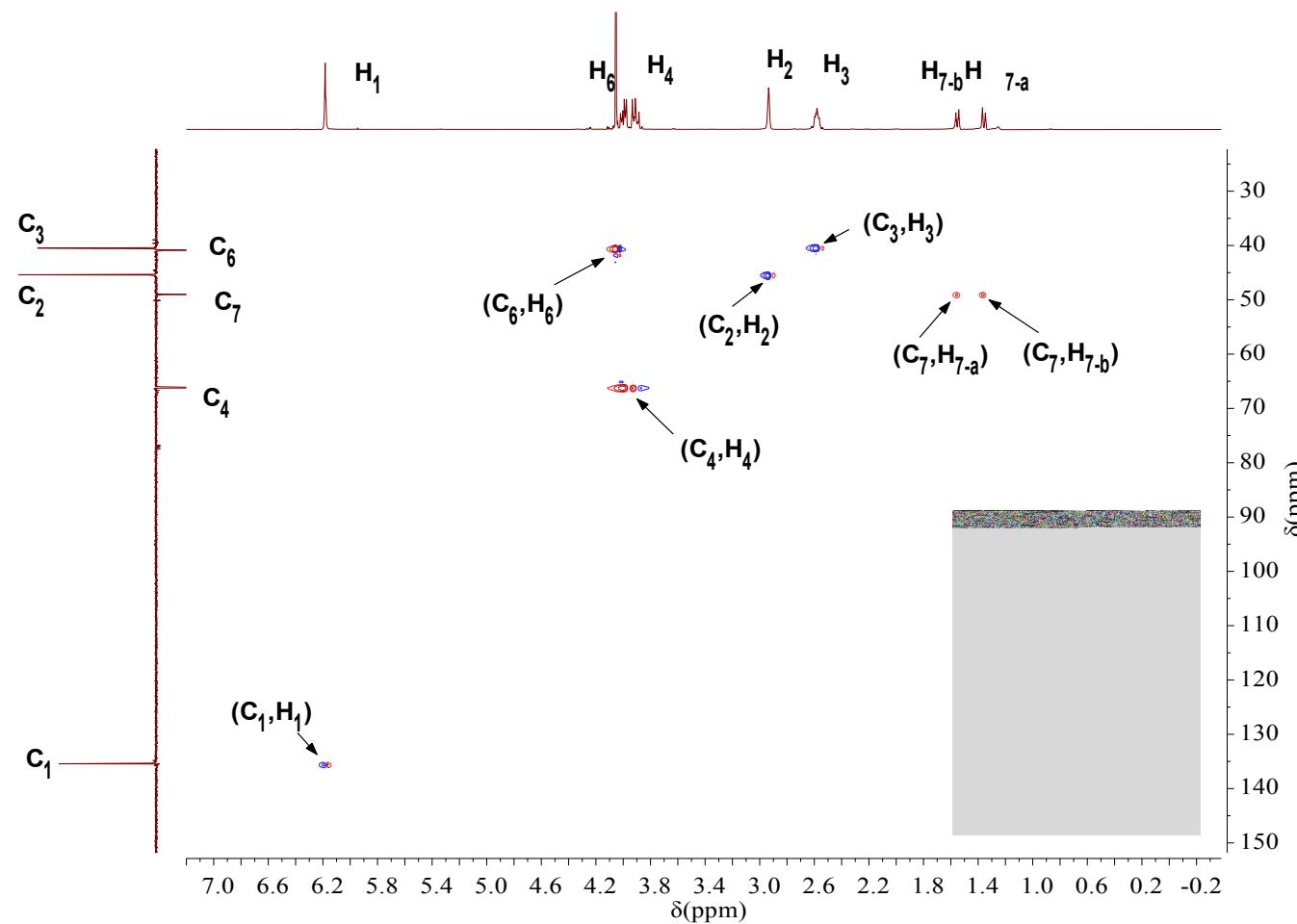


Figure S10 : The gHSQC-NMR spectrum of NBCA (4)in CDCl_3

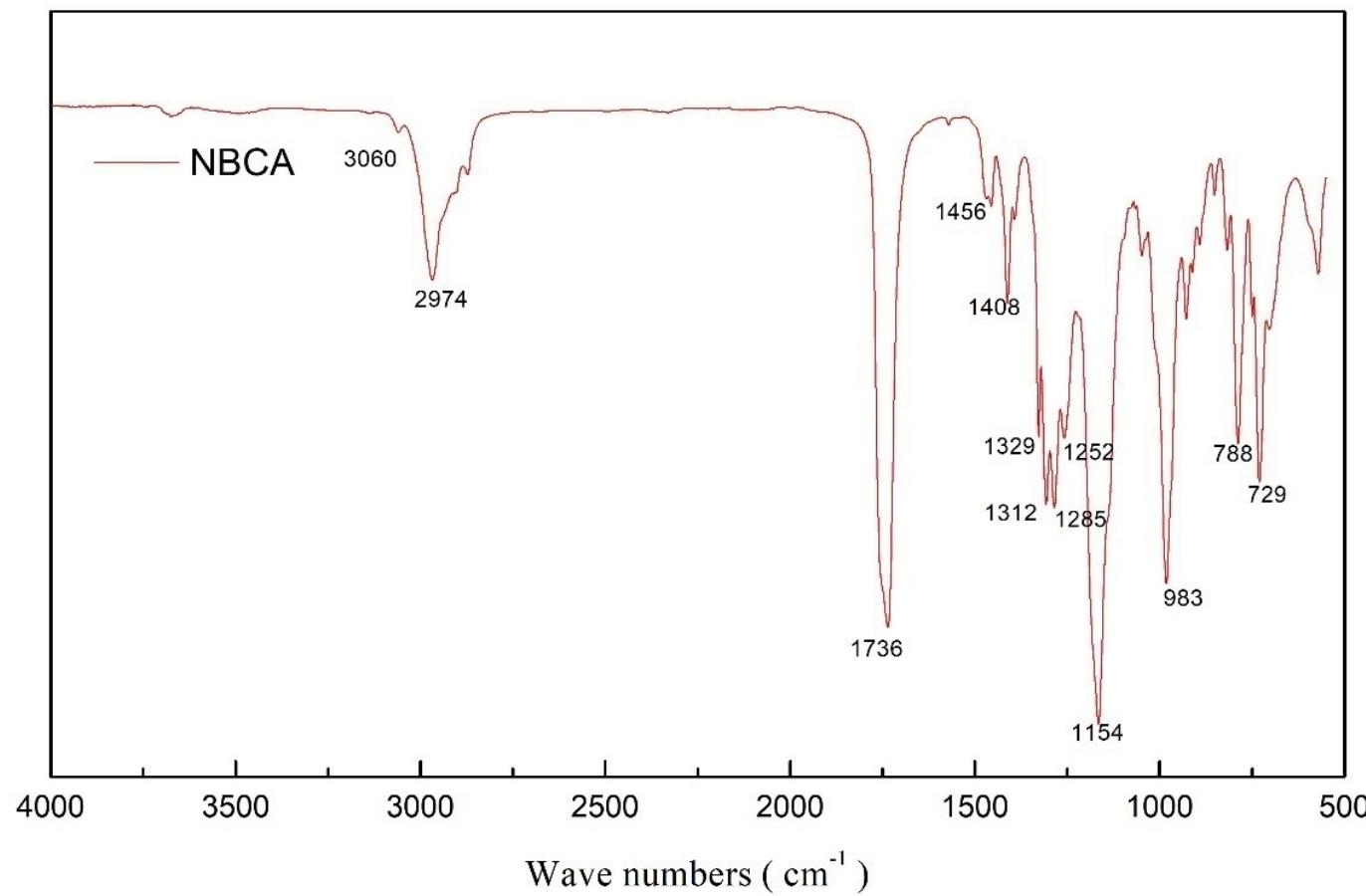


Figure S11 : TheFT-IR spectrum of NBCA (4)

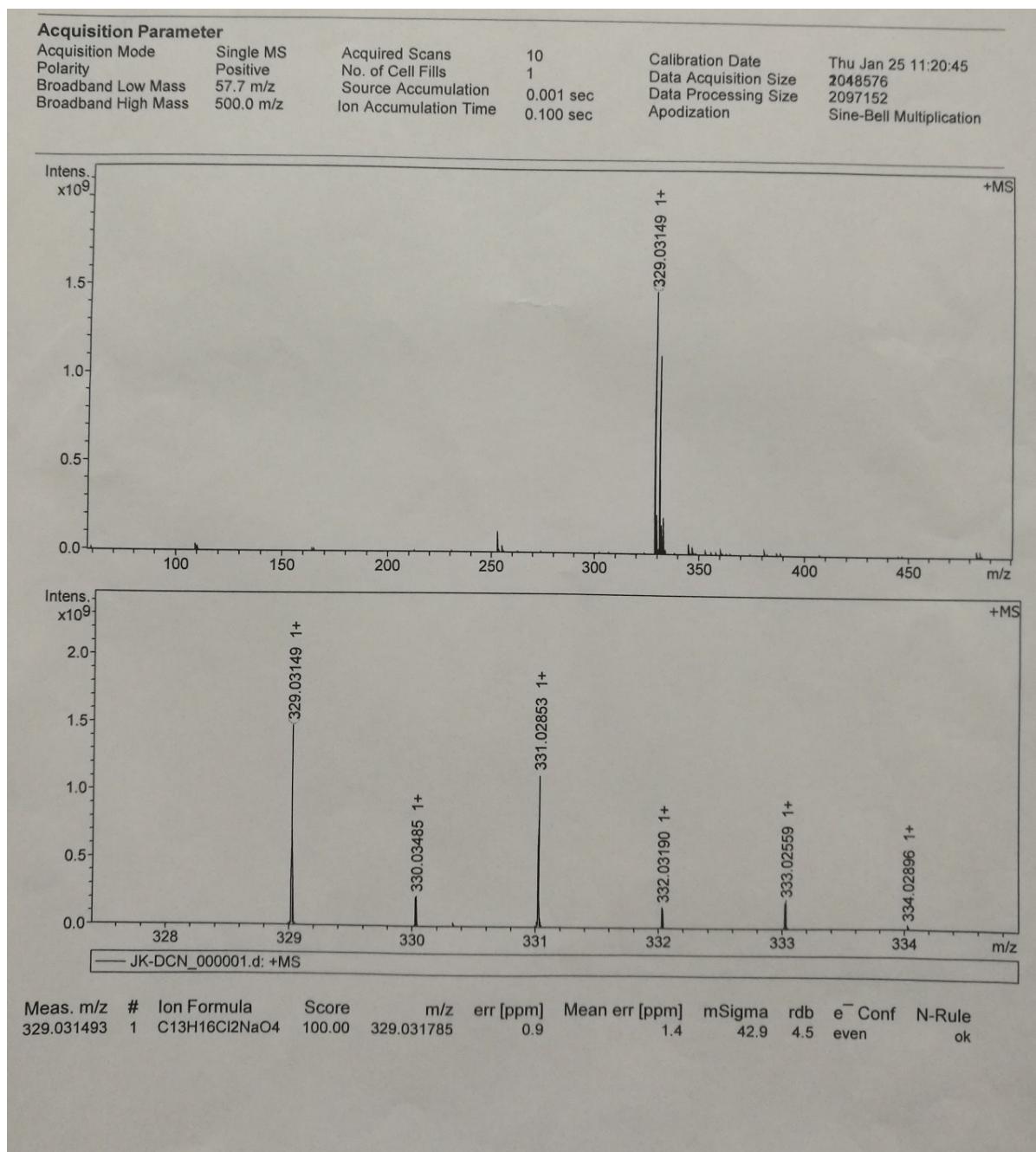


Figure S12 : The HR-MS spectrum of NBCA(4)

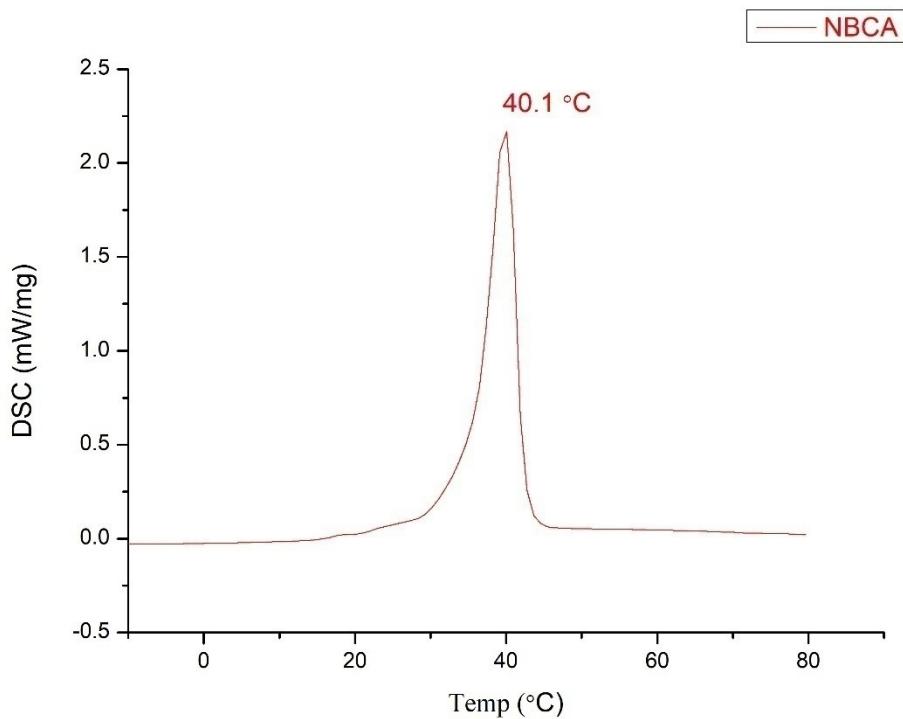


Figure S13: The DSCgraph of NBCA (4)

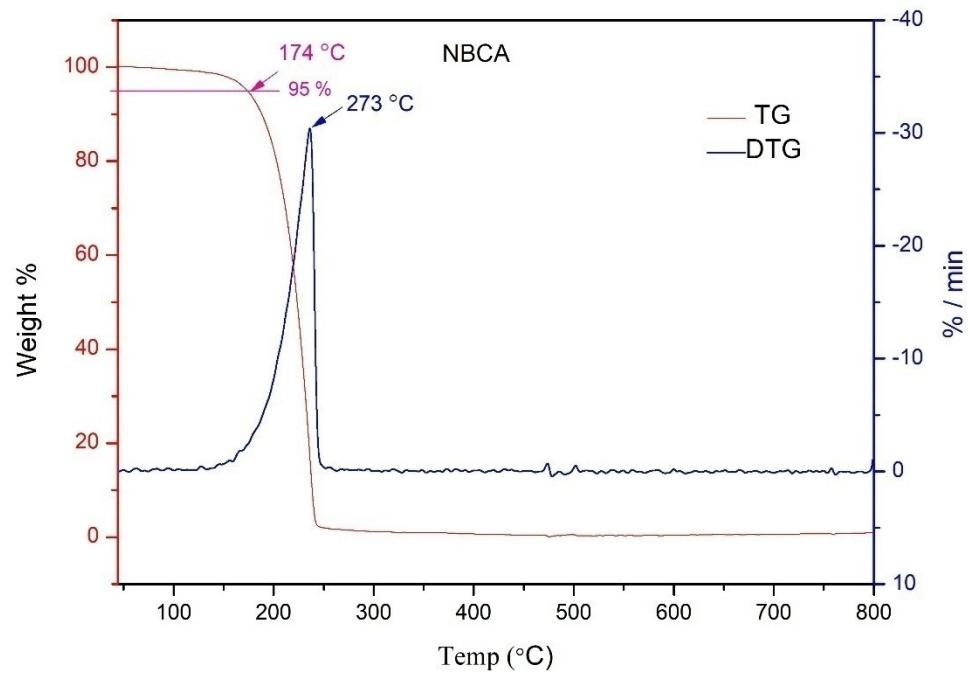


Figure S14: The TGAggraph of NBCA (4)

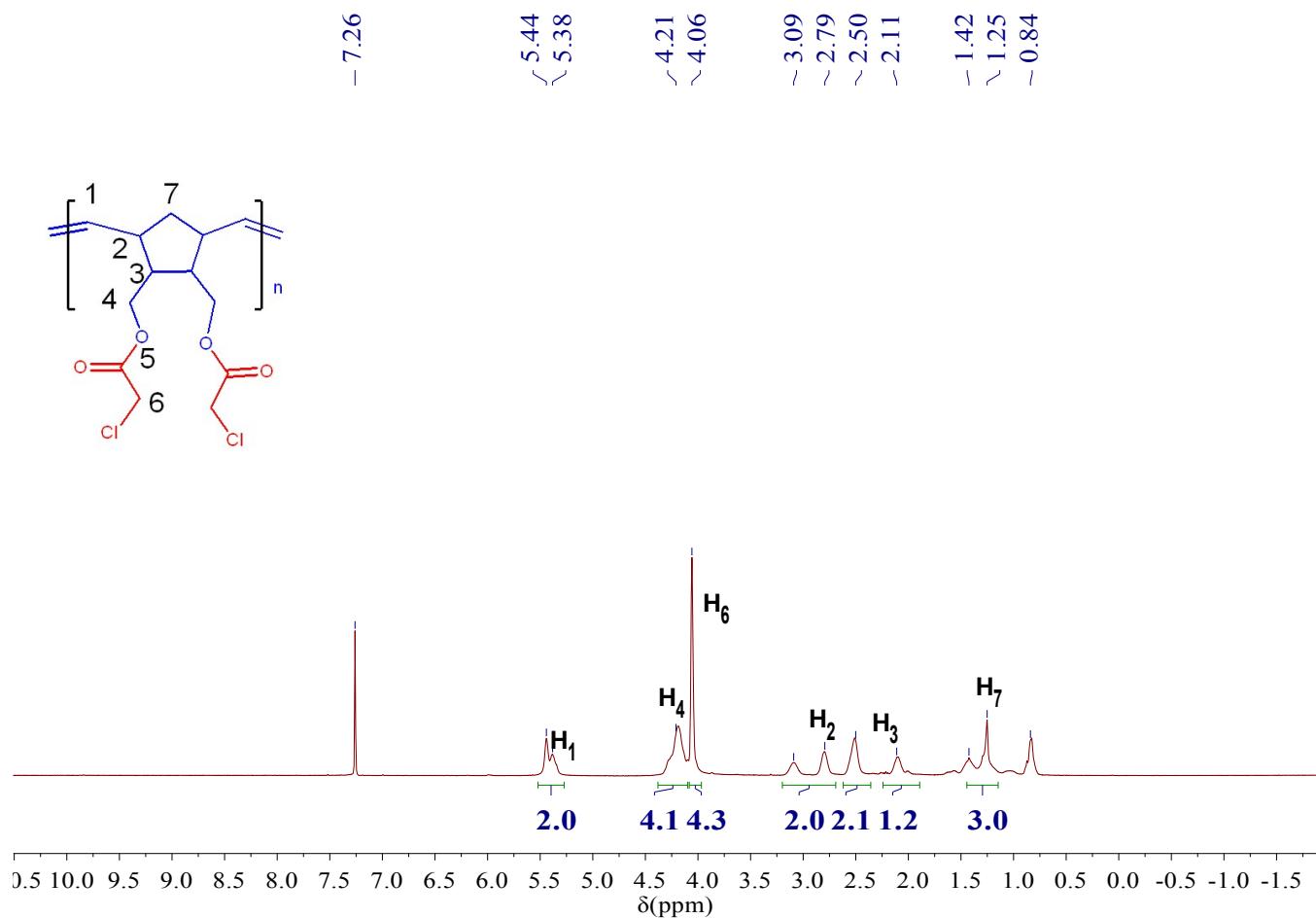


Figure S15 : The ^1H -NMR spectrum of PNBCA (5) in CDCl_3

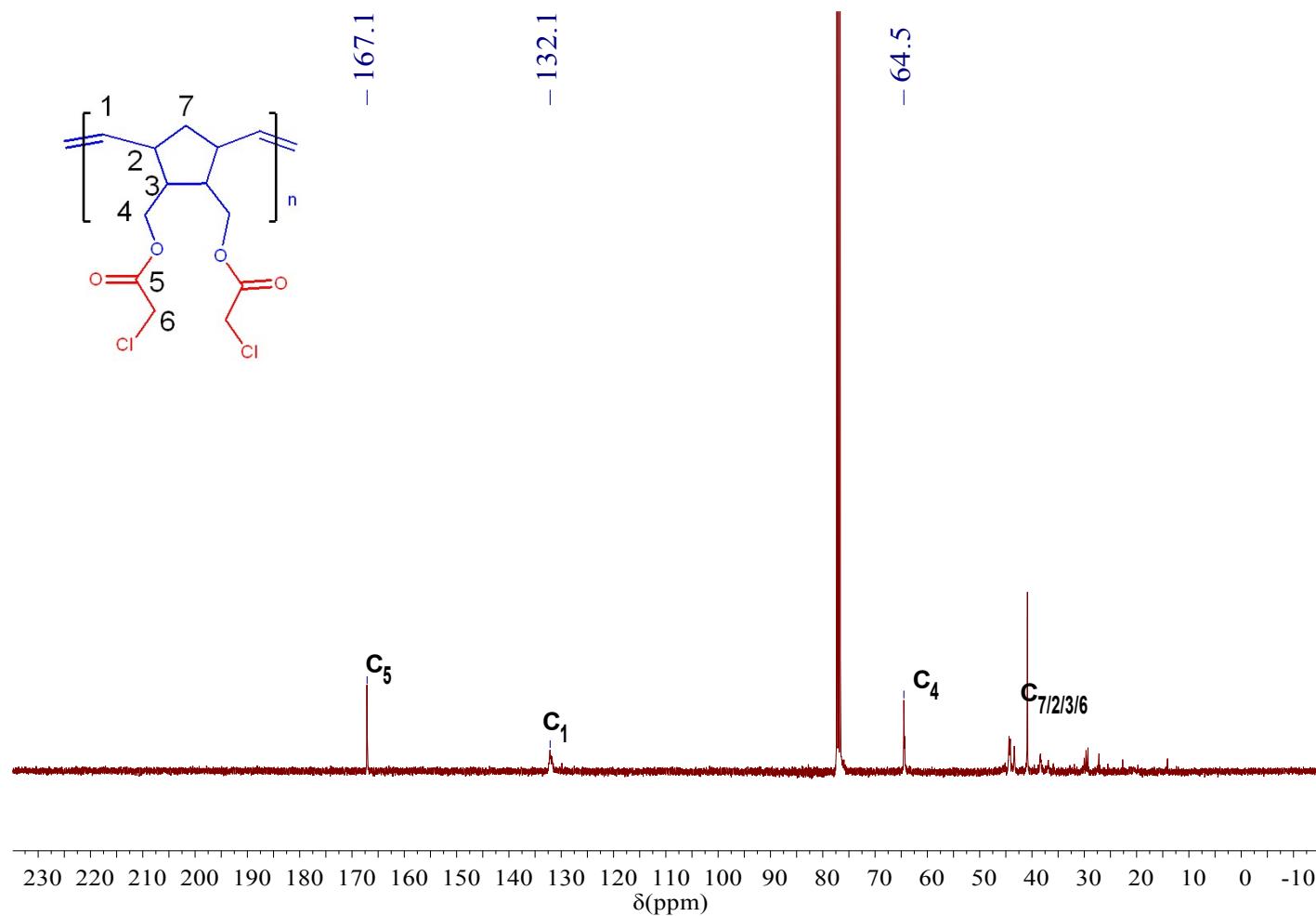


Figure S16: The ^{13}C -NMR spectrum of PNBCA (5) in CDCl_3

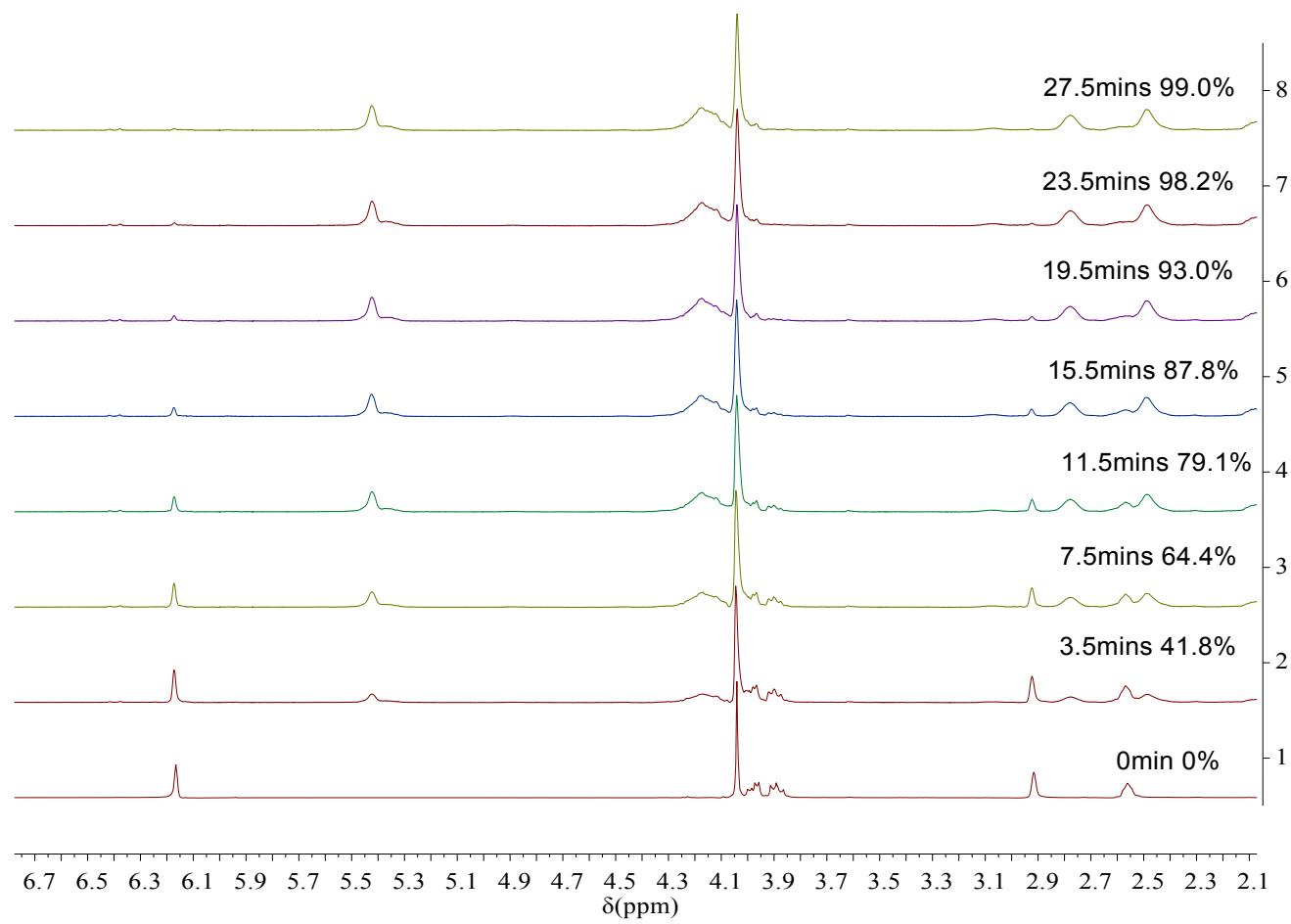


Figure S17: The array ^1H -NMR on ROMP reaction in CDCl_3 (Entry 1, Table 2)

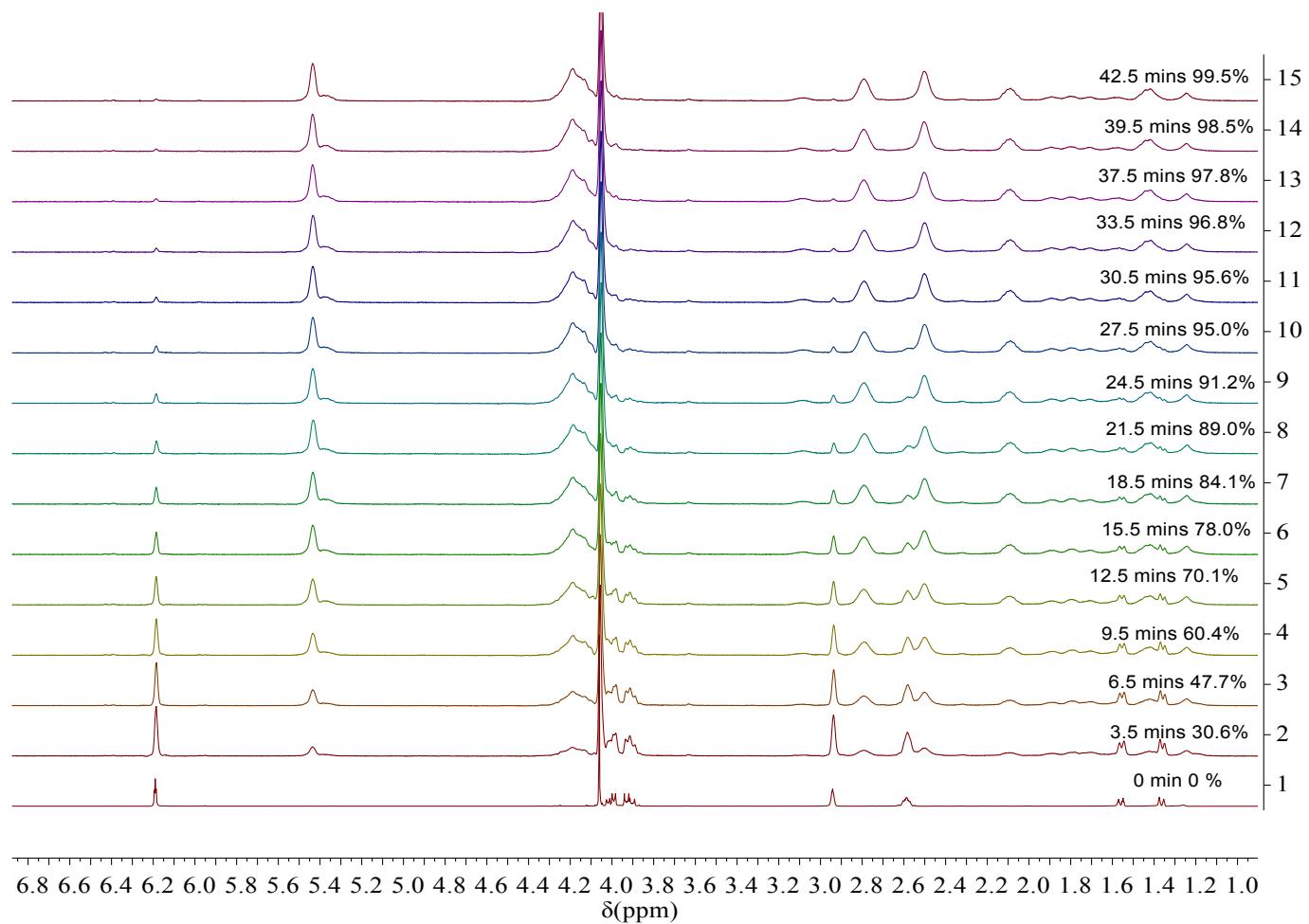


Figure S18: The array ^1H -NMR on ROMP reaction in CDCl_3 (Entry 2, Table 2)

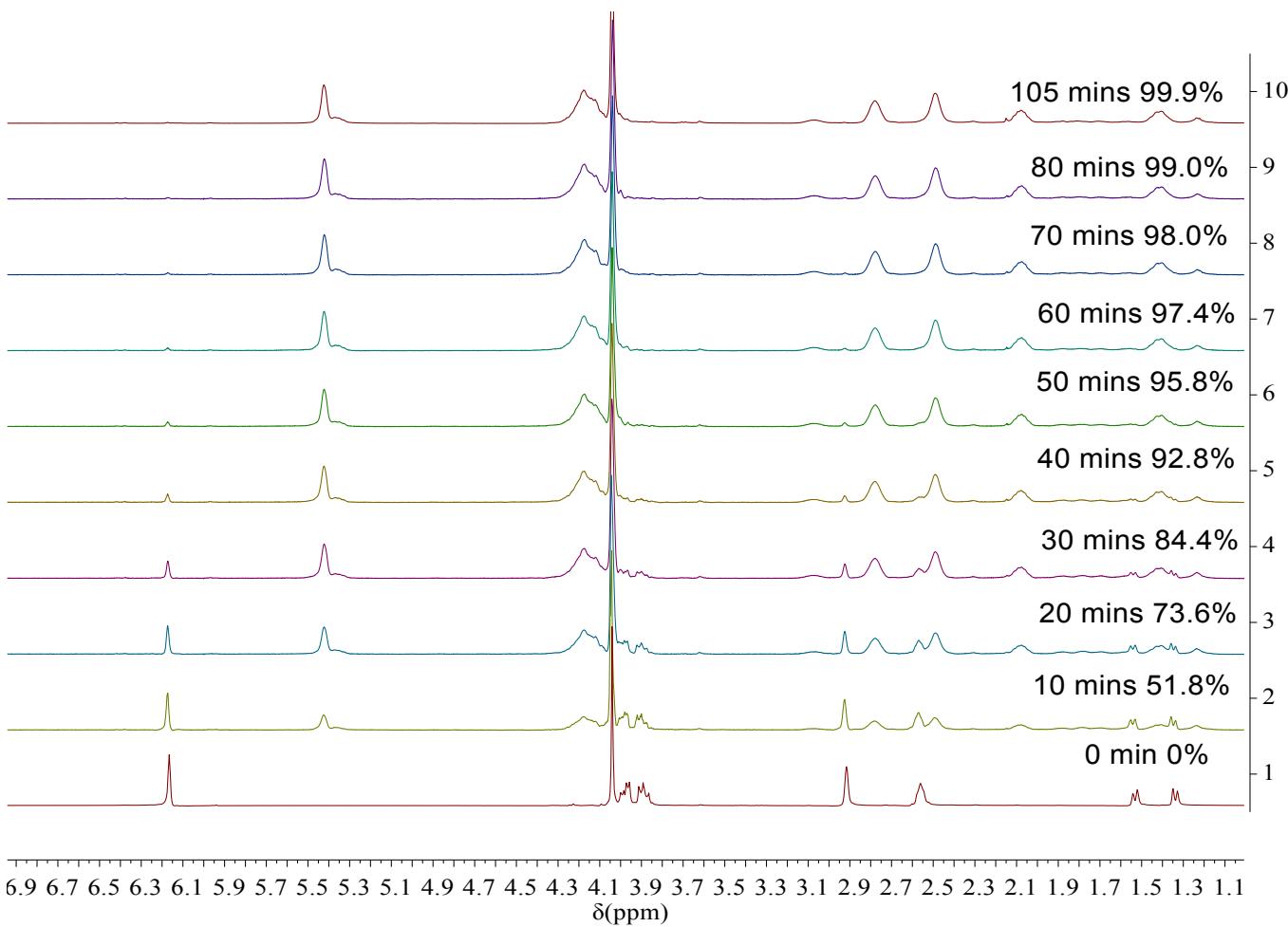


Figure S19: The array ^1H -NMR on ROMP reaction in CDCl_3 (Entry 4, Table 2)



Figure S20 Photograph on solvent-free ROMP reaction on NBCA (4)

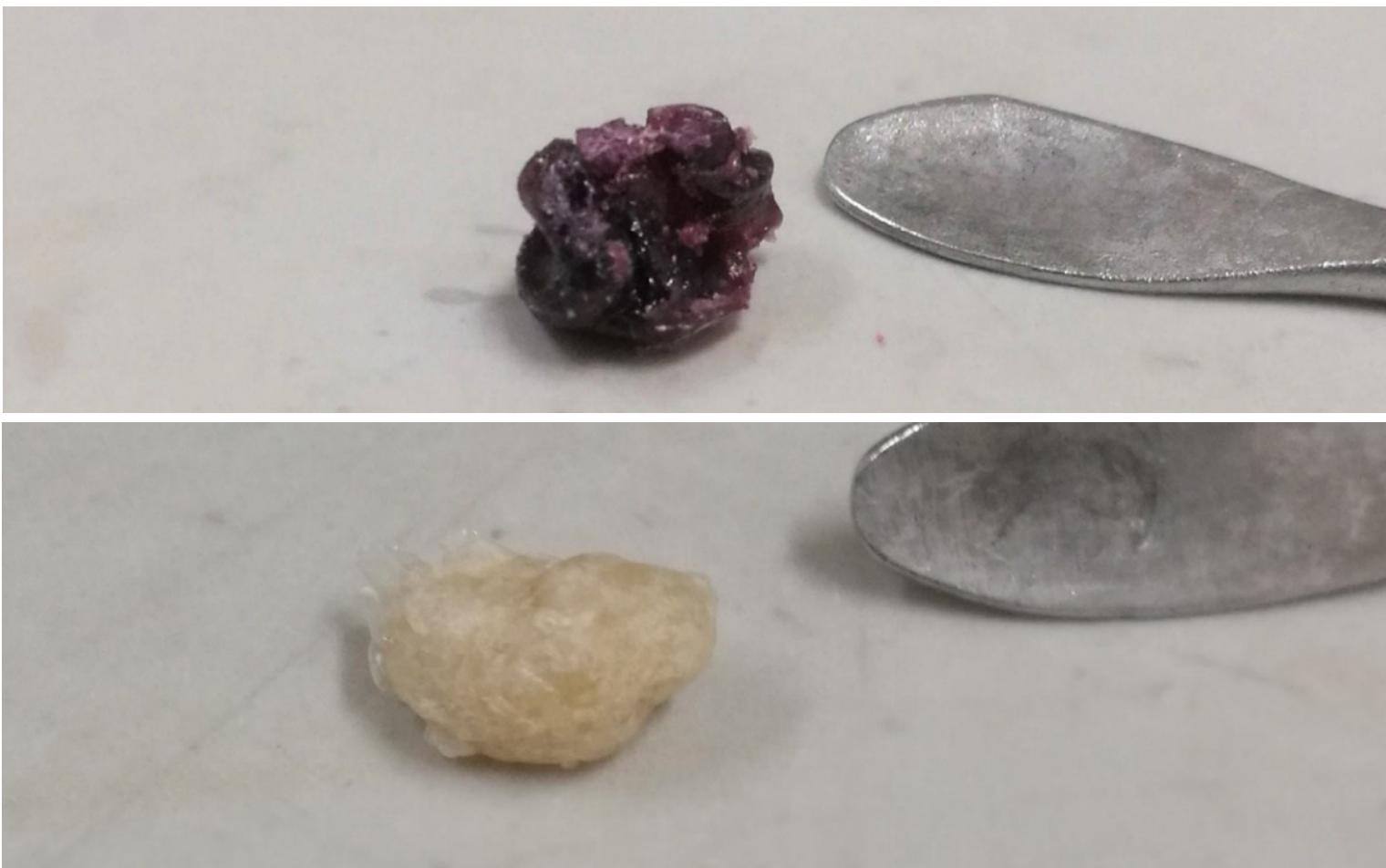


Figure S21: Photograph ofROMP adduct before (top) and after (bottom) removal of Ru comtaminant

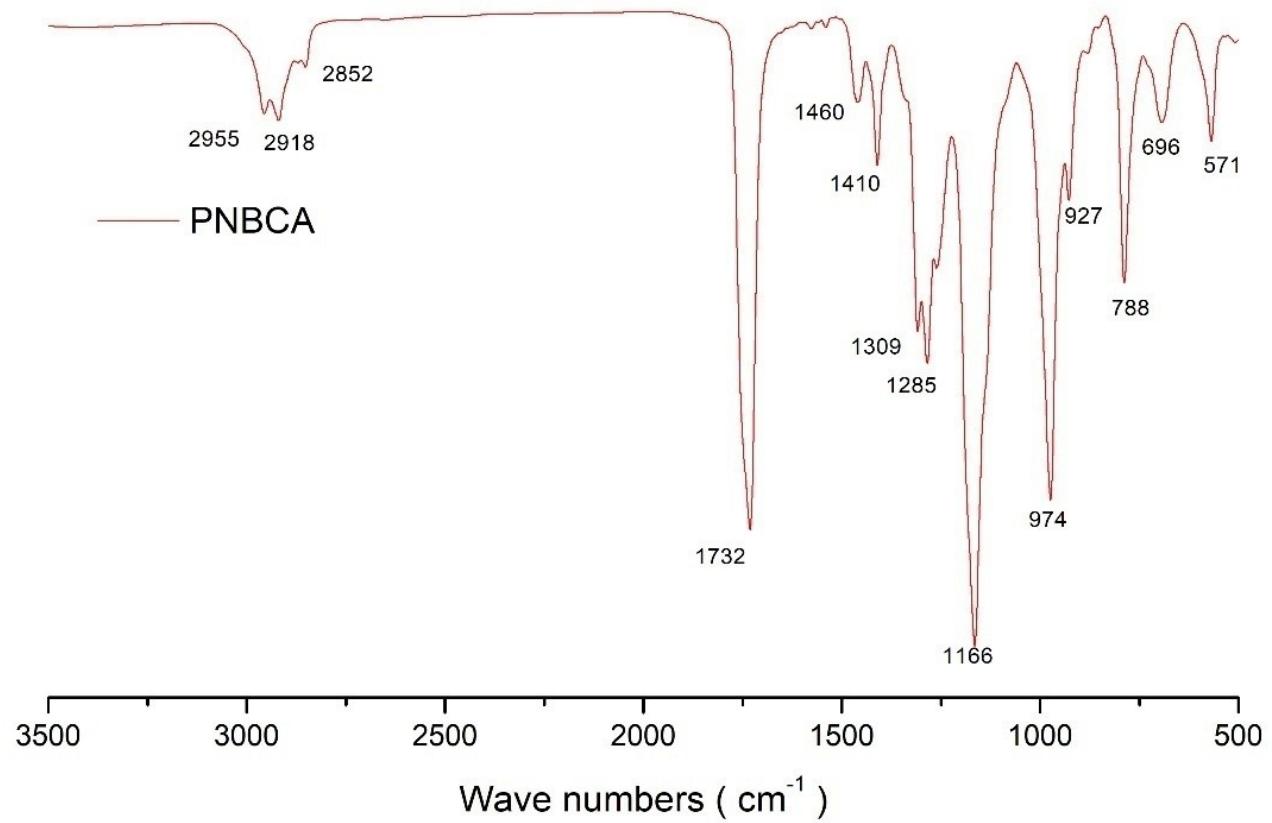


Figure S22 : The FT-IR spectrum of PNBCA (5)

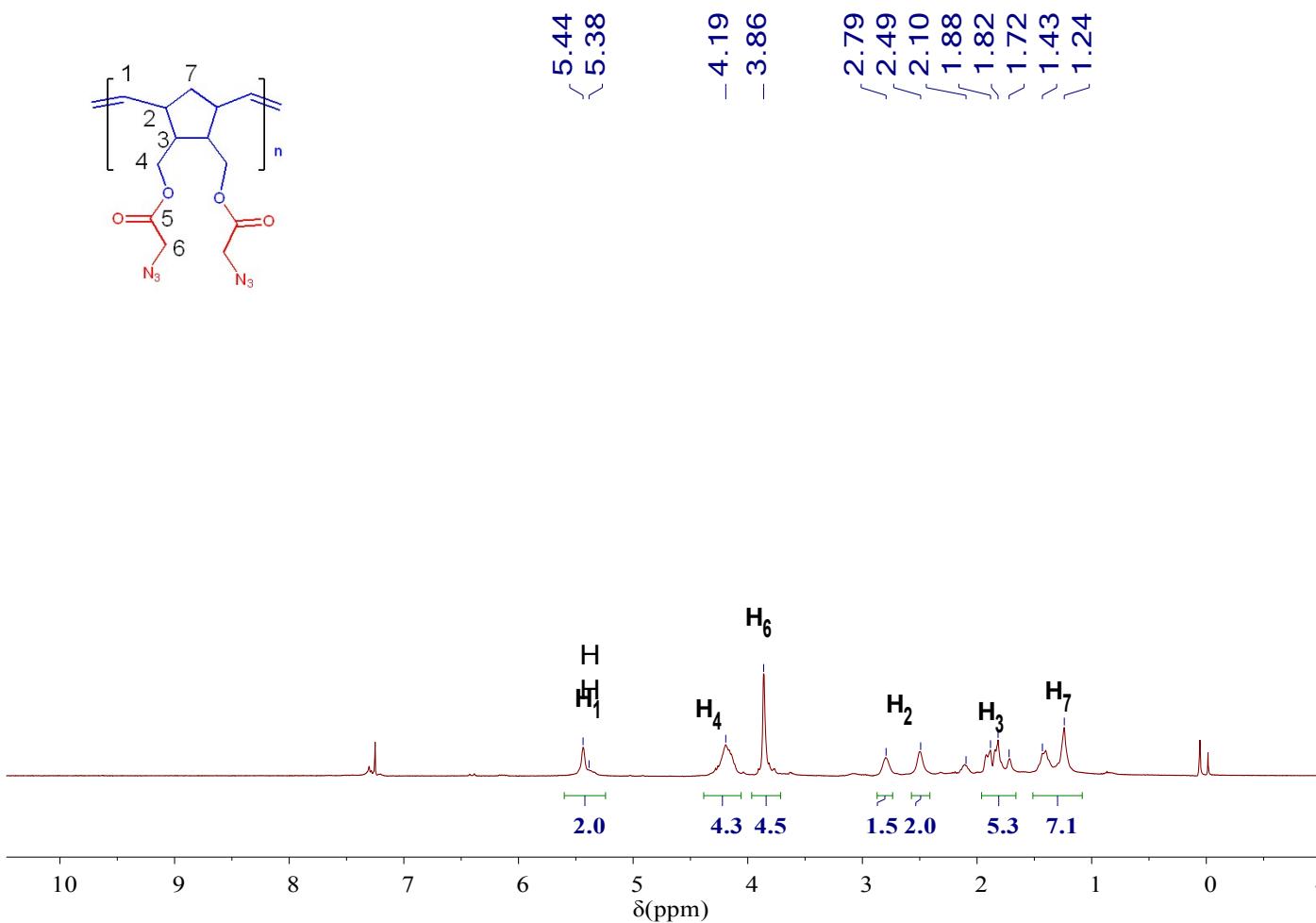


Figure S23 : The ^1H -NMR spectrum of PNBAA (6) in CDCl_3

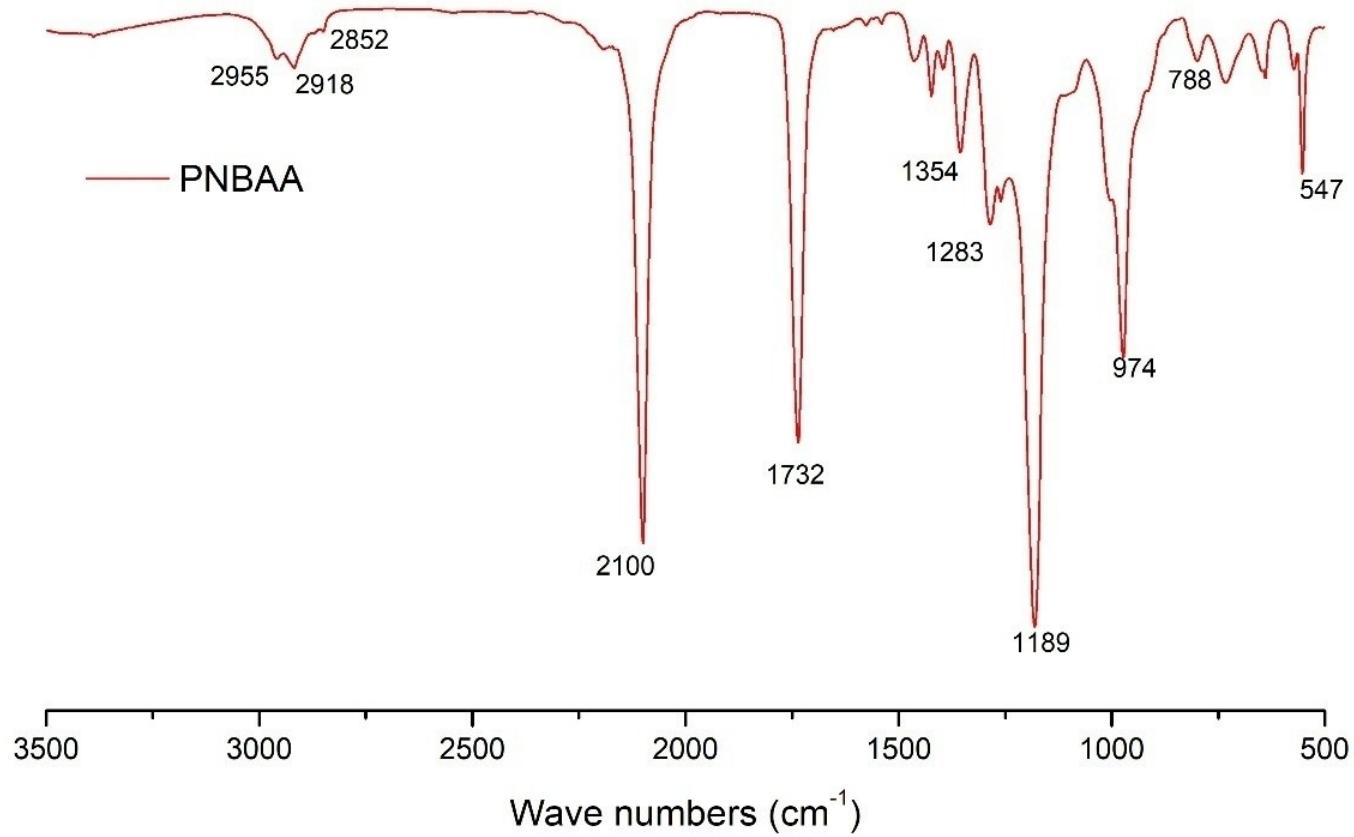


Figure S24 : The FT-IR spectrum of PNBA (6)

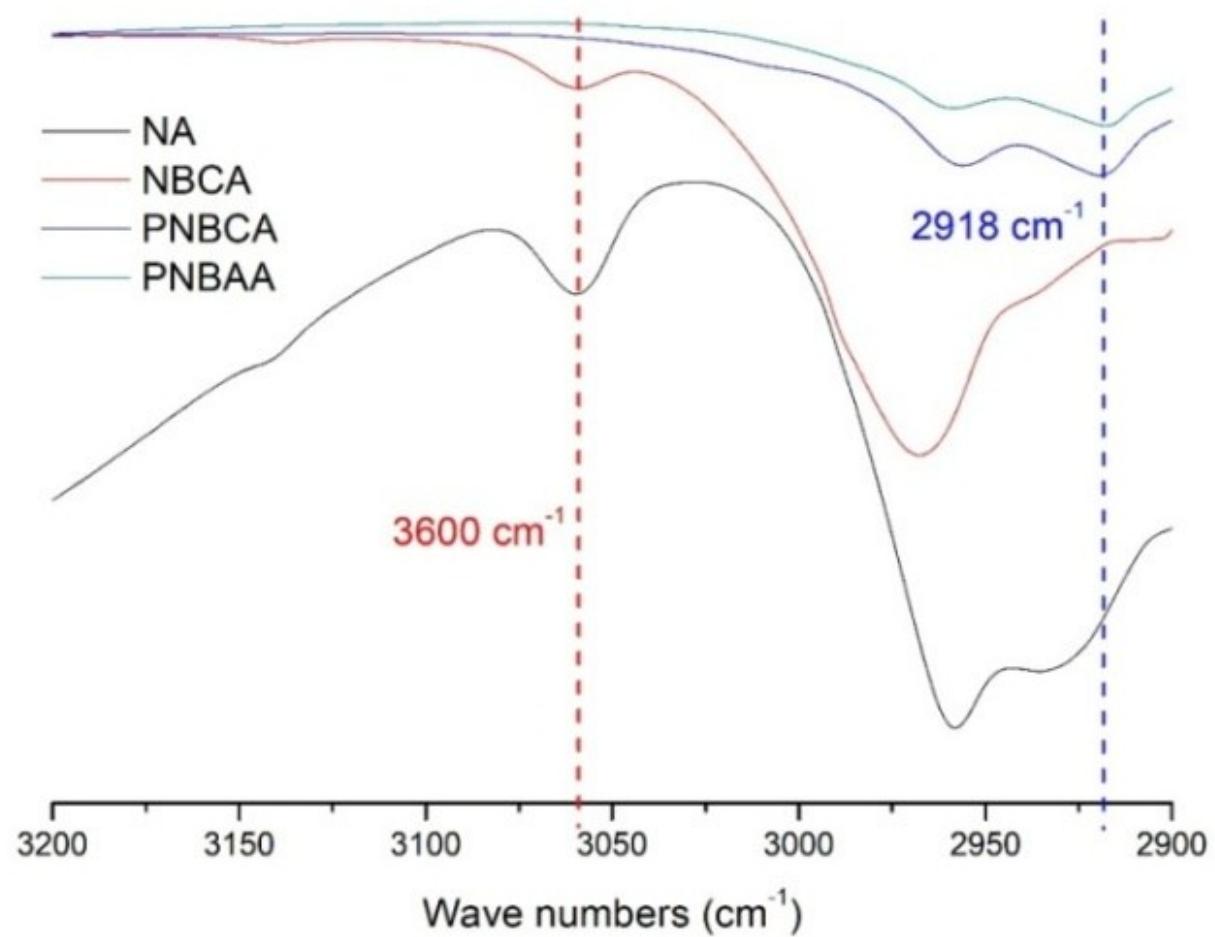


Figure S25 The comparison among the FT-IR spectra of monomers and polymers

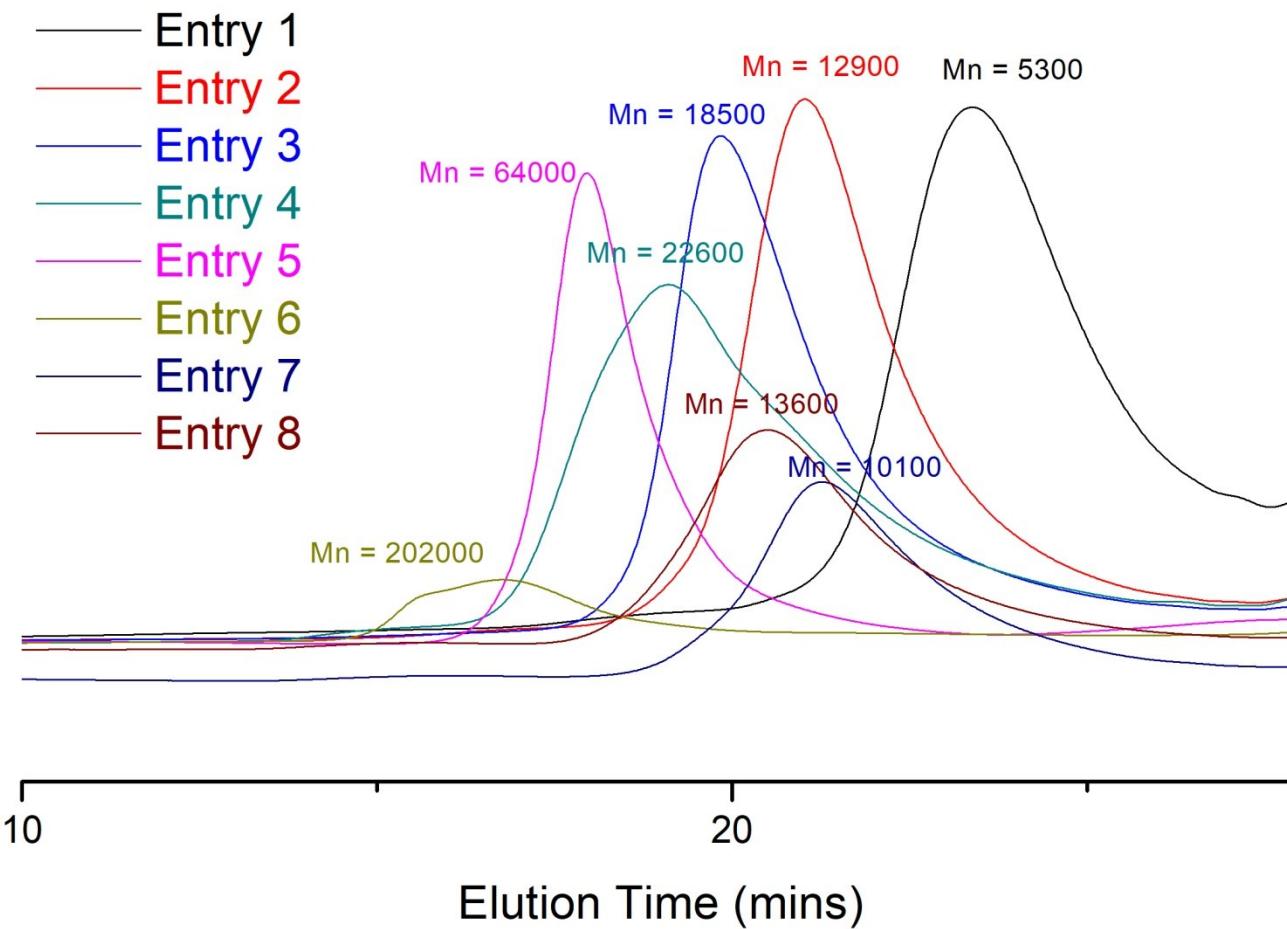


Figure S26 The GPC graph of PNBCA with different Mn

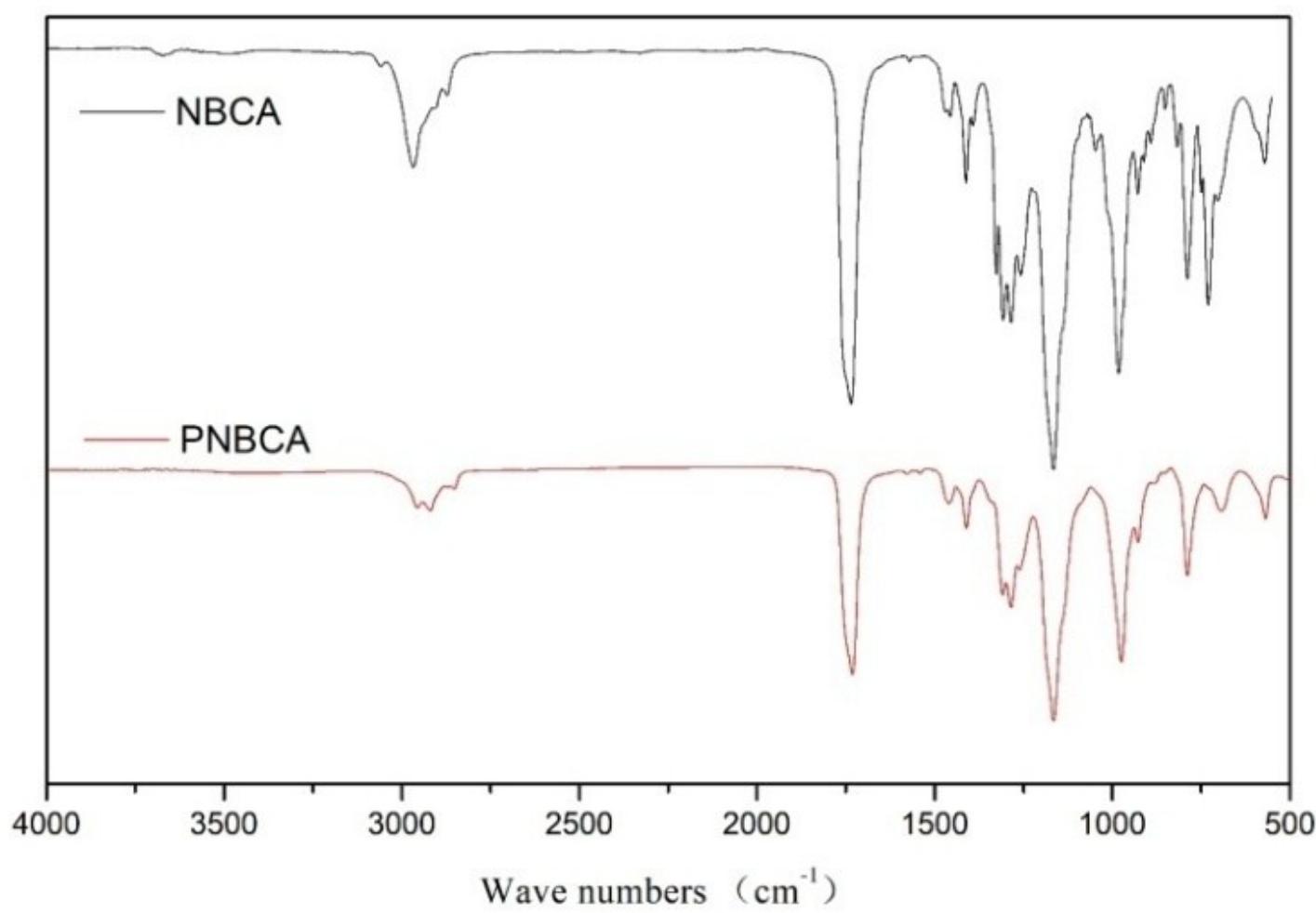


Figure S27 The comparison of FT-IR spectra between NBCA and PNBCA

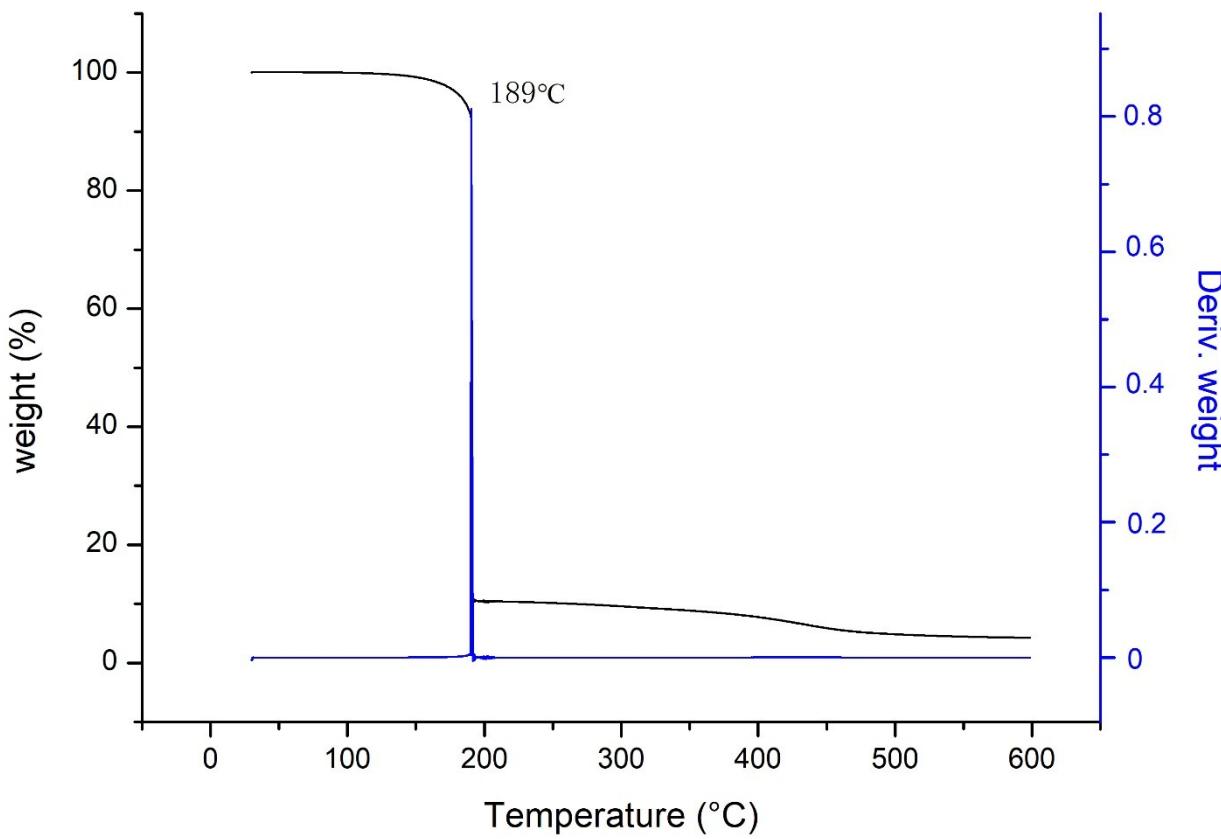


Figure S28: The TG and DTG graph of PNBAA (6)

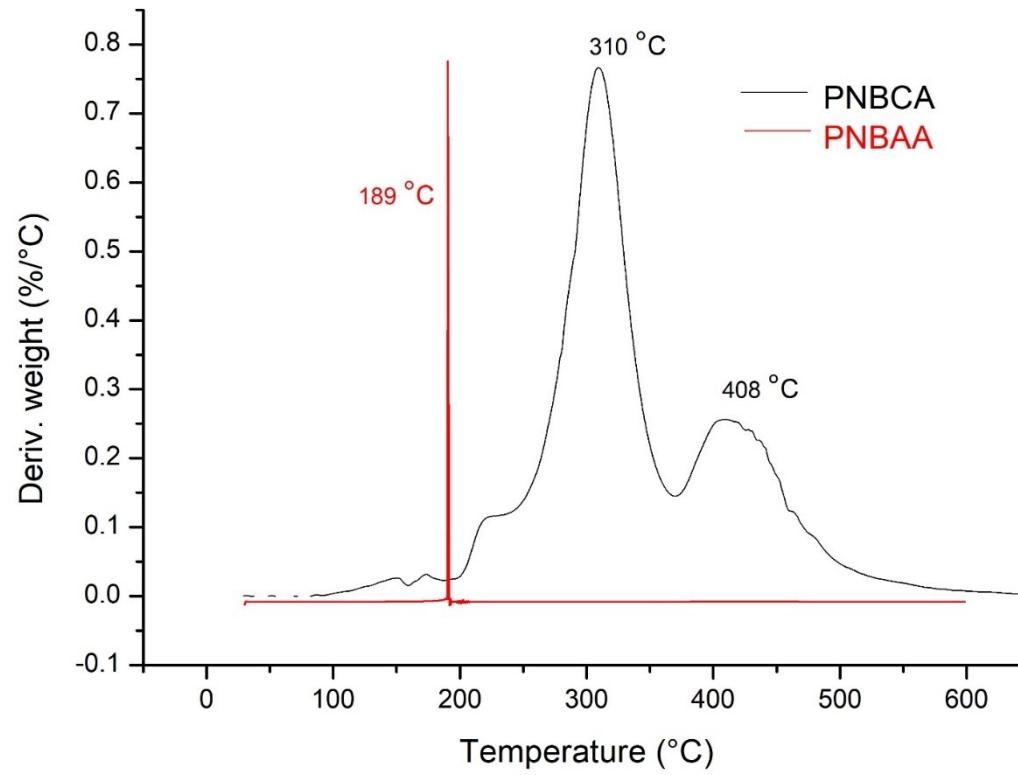


Figure S29 :The DTG graph of PNBCA(5) and PNBAA (6)

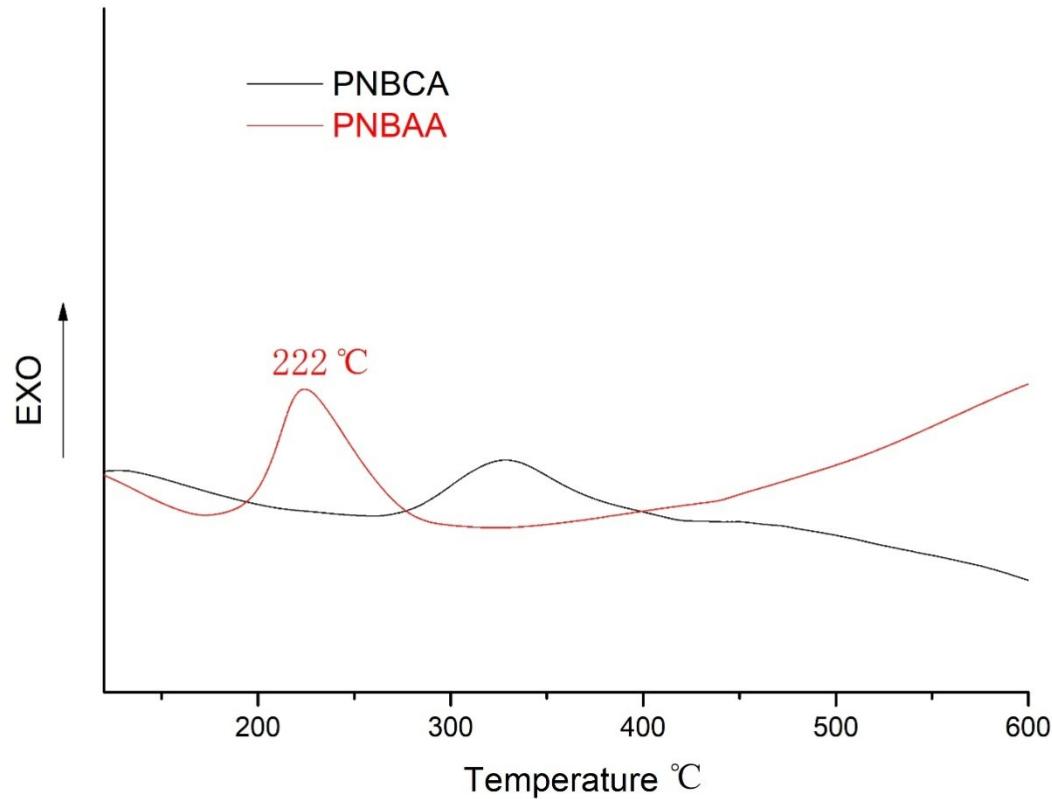


Figure S30 : The DSC graph of PNBCA(5) and PNBAA (6) from 80 °C to 600 °C