Electronic Supplementary Material (ESI) for Materials Advances.

Rapid synthesis of diol homologs-based thermosets with tunable properties *via* ring-opening metathesis polymerization

Liuyang Zhang, Fei Huangfu, Wanrong Li and Po Yang*

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, Sichuan 610065, China

Corresponding Author

E-mail: yangpo@scu.edu.cn (P. yang)

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Synthesis of diols-based Monomers

All the monomers in this article were synthesized through two steps, converting 5-norbornene-2-carboxylic acid (NBE-COOH, the mixture of endo- and exo-) to acyl chloride, and then adding the diol. Under ice-water bath and nitrogen, slowly adding oxalyl chloride (60 g, 1.6 equiv) dropwise to the NBE-COOH (the mixture of endo and exo, 41.45 g, 1.0 equiv) in dichloromethane (DCM, 300 mL) solution. After that, introducing two drops of DMF, and then stirring at room temperature for 8 hours. The resulting mixture was subsequently removed excess oxalyl chloride by rotary evaporator. Under the ice water bath and nitrogen, DCM (150 mL) was added to the resulting product, and a solution of diol (0.525 equiv) with triethylamine (120 mL) was slowly dropped into it. The reaction was stirred at room temperature for 12 hours, and then quenched with deionized water. The crude product was purified by flash chromatography to give the target compounds.

Ratio of endo-/exo-

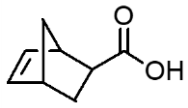
The ratio of endo/exo compounds are determined by ^{1}H NMR using equations S-1 and S-2. The equations are expressed as:

$$\text{endo}\% = \frac{A_{endo}}{A_{endo}+A_{exo}} \times 100\% \quad \text{S-1}$$

$$\text{exo}\% = \frac{A_{exo}}{A_{endo}+A_{exo}} \times 100\% \quad \text{S-2}$$

Where A_{endo} and A_{exo} are the areas corresponding to endo- and exo- carbon-carbon double bonds which respectively located at 6.21/6.00 ppm and 6.15/6.12 ppm.

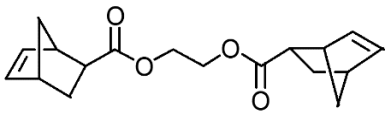
NBE-COOH



The ratio of endo-/exo- is 75/25.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.21 (dd, J= 5.6Hz and 2.8Hz, 3H), 6.15 (dd, J= 5.6Hz and 3.2Hz, 1H), 6.12 (dd, J= 5.2Hz and 2.8Hz, 1H), 6.00 (dd, J= 5.6Hz and 2.8Hz, 3H), 3.24 (s, 3H), 3.1 (s, 1H), 3.02-2.98 (m, 3H), 2.92 (s, 4H), 2.27-2.24 (m, 1H), 1.95-1.89 (m, 4H), 1.53 (d, J=8.4Hz, 1H), 1.46-1.37 (m, 8H), 1.29 (d, J=8.4Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 175.95, 174.46, 138.10, 127.83, 135.67, 132.29, 62.21, 62.02, 49.61, 46.63, 46.34, 45.70, 43.24, 43.07, 42.53, 41.64, 30.33, 29.24.

NB2

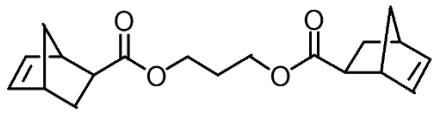


Yellow transparent liquid, yield 61%. The ratio of endo-/exo- is 67/33.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.20 (dd, J=6Hz and 3.2Hz, 4H), 6.15 (dd, J=5.6Hz and 2.8Hz, 2H), 6.11 (dd, J=5.6Hz and 2.8Hz, 2H), 5.94 (dd, J=5.6Hz and 2.8Hz, 4H), 4.31-4.19 (m, 12H), 3.22 (s, 4H), 3.05 (s, 2H), 2.99-2.92 (m, 12H), 2.25 (dd, J=9.2Hz and 4.4Hz, 2H), 1.95-1.89 (m, 6H), 1.52 (d, J=8.4Hz, 2H), 1.45-1.37 (m, 10H), 1.28 (J=8.4Hz, 4H); ^{13}C

NMR ($CDCl_3$): δ 175.95, 174.46, 138.10, 137.83, 135.67, 132.29, 62.21, 62.02, 49.61, 46.63, 46.34, 45.70, 43.24, 43.07, 42.53, 41.64, 30.33, 29.24; FTIR (cm^{-1}): 1736, 1632, 1570.

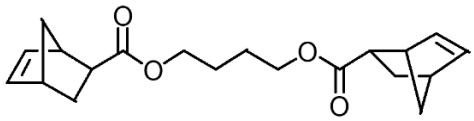
NB3



Yellow transparent liquid, yield 54%. The ratio of endo-/exo- is 77/23.

^1H NMR ($CDCl_3$, 400 MHz) δ 6.20 (dd, J=5.6Hz and 2.8Hz, 7H), 6.14 (dd, J=5.6Hz and 2.8Hz, 2H), 6.11 (dd, J=5.2Hz and 2.8Hz, 2H), 5.92 (dd, J=5.6Hz and 2.8Hz, 7H), 4.20-4.15 (m, 4H), 4.13-4.06(m, 14H), 3.21(s, 7H), 3.03 (s, 2H), 2.97-2.91 (m, 16H), 2.23 (dd, J=10Hz and 4.4Hz, 2H), 2.00-1.87 (m, 18H), 1.51 (d, J=8Hz, 2H), 1.44-1.37 (m, 18H), 1.28 (d, J=8.4Hz, 7H); ^{13}C NMR ($CDCl_3$): δ 176.17, 174.66, 138.07, 137.84, 135.71, 132.27, 61.02, 60.73, 49.66, 46.63, 45.75, 43.31, 43.12, 42.53, 41.64, 30.35, 29.21, 28.09; FTIR (cm^{-1}): 1727, 1621, 1570.

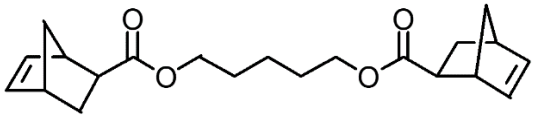
NB4



Yellow transparent liquid, yield 53%. The ratio of endo-/exo- is 75/25.

^1H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J=6Hz and 3.2Hz, 8H), 6.13 (dd, J=5.6Hz and 3.2Hz, 2H), 6.10 (dd, J=5.2Hz and 2.8Hz, 2H), 5.91 (dd, J=5.6Hz and 2.8Hz, 8H), 4.12-4.08 (m, 4H), 4.06-4.03 (m, 16H), 3.20 (s, 8H), 3.02 (s, 2H), 2.96-2.90 (m, 18H), 2.22 (dd, J=10Hz and 4.4Hz, 2H), 1.93-1.86 (m, 10H), 1.70-1.66 (m, 20H), 1.51 (d, J=8.4Hz, 2H), 1.43-1.37 (m, 20H), 1.27 (d, J=8.4Hz, 8H); ^{13}C NMR (CDCl3): δ 176.23. 174.72, 138.05, 137.81, 135.73, 132.30, 63.93, 63.70, 49.65, 46.36, 45.73, 43.35, 43.17, 42.53, 30.34, 29.20, 25.45; FTIR (cm^{-1}): 1723, 1621, 1570.

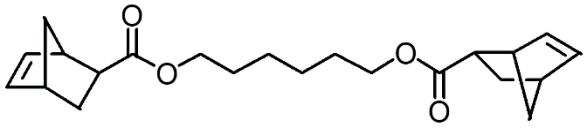
NB5



Yellow transparent liquid, yield 45.4%. The ratio of endo-/exo- is 75/25.

^1H NMR ($CDCl_3$, 400 MHz) δ 6.19 (dd, J=5.6Hz and 2.8Hz, 6H), 6.14 (dd, J=5.6Hz and 2.8Hz2H), 6.10 (dd, J=5.6Hz and 2.8Hz, 2H), 5.92 (dd, J=5.6Hz and 2.8Hz, 6H), 4.11-4.07 (m, 4H), 4.06-3.97 (m, 12H), 3.20 (s, 6H), 3.03 (s, 2H), 2.96-2.90 (m, 12H), 2.22 (dd, J=8.8Hz and 3.2Hz, 2H), 1.93-1.86 (m, 8H), 1.69-1.60 (m, 18H), 1.51 (d, J=8.4Hz, 2H), 1.43-1.33 (m, 24H), 1.27 (d, J=8Hz, 6H); ^{13}C NMR (CDCl3, 400 MHz) δ 176.28, 174.78, 138.04, 137.77, 135.74, 132.32, 64.21, 63.98, 49.63, 46.62, 46.37, 45.72, 43.36, 43.20, 42.53, 41.63, 30.33, 29.19, 28.32, 22.56; FTIR (cm-1): 1727, 1620, 1570.

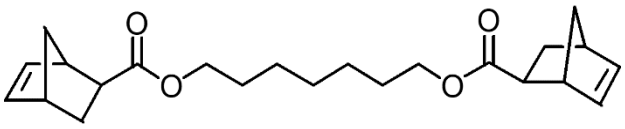
NB6



Yellow transparent liquid, yield 57%. The ratio of endo-/exo- is 76/24.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.19 (dd, J=5.2Hz and 2.8Hz, 6H), 6.14 (dd, J=5.2Hz and 2.4Hz, 2H), 6.10 (dd, J=5.2Hz and 2.4Hz, 2H), 5.92 (dd, J=5.2Hz and 2.4Hz, 6H), 4.11-4.05 (m, 4H), 4.04-3.98 (m, 12H), 3.20 (s, 6H), 3.03 (s, 2H), 2.96-2.90 (m, 10H), .2.22 (dd, J=88.Hz and 2.8Hz, 2H), 1.94-1.86 (m, 8H). 1.67-1.60 (m, 20H), 1.52 (d, J=8.4Hz, 2H), 1.44-1.36 (m, 32H), 1.27 (d, J=8.4Hz, 6H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 176.31, 174.81, 138.03, 137.76, 135.76, 132.33, 64.36, 64.12, 49.63, 46.62, 46.36, 45.72, 43.37, 43.20, 42.54, 41.64, 30.33, 29.20, 28.60, 25.65; FTIR (cm^{-1}): 1727, 1620, 1570.

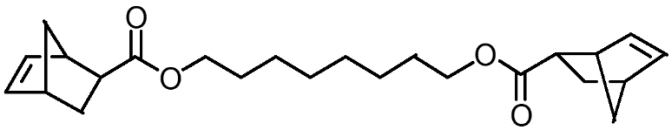
NB7



Yellow transparent liquid, yield 62%. The ratio of endo-/exo- is 71/29.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J= 5.6Hz and 3.2Hz, 5H), 6.13 (dd, J=5.6Hz and 3.2Hz, 2H), 6.10 (dd, J=5.2Hz and 2.8Hz, 2H), 5.91 (dd, J=5.6Hz and 2.8Hz, 5H), 4.11-4.06 (m, 4H), 4.04-3.97 (m, 10H), 3.20 (s, 5H), 3.03 (s, 2H), 2.96-2.90 (m, 13H), 2.23-2.19 (m, 2H), 1.94-1.87 (m, 6H), 1.63-1.58 (m, 16H), 1.52 (d, J=8,4Hz, 2H), 1.43-1.40 (m, 10H), 1.35 (s, 22H), 1.27 (d, J=8Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 176.21, 175.82, 138.03, 137.74, 135.76, 132.34, 64.45, 64.21, 49.63, 46.62, 46.36, 45.72, 43.37, 43.21, 42.54, 41.63, 30.32, 29.19, 28.84, 28.60, 25.87; FTIR (cm^{-1}): 1732, 1628, 1570.

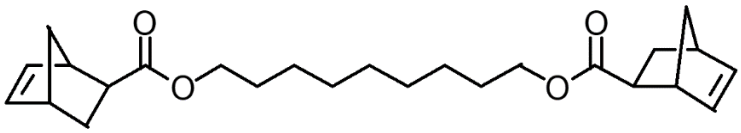
NB8



Yellow transparent liquid, yield 75%. The ratio of endo-/exo- is 67/33.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J=5.6Hz and 2.8Hz, 4H), 6.13 (dd, J=5.6Hz and 3.2Hz, 2H), 6.10 (dd, J=5.2Hz and 2.8Hz), 5.91 (dd, J=5.6Hz and 2.8Hz, 4H), 4.11-4.04 (m, 4H), 4.03-3.97 (m, 8H), 3.20 (s, 4H), 3.03 (s, 2H), 2.96-2.90 (m, 10H), 2.21 (dd, J=10Hz and 4.4Hz, 2H), 1.94-1.86 (m, 6H), 1.63-1.56 (m, 16H), 1.52 (d, J=8.4Hz, 2H), 1.43-1.39 (m, 8H), 1.33 (s, 22H), 1.27 (d, J=8.4Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 176.33, 174.84, 138.02, 137.73, 135.77, 132.35, 64.52, 64.27, 49.62, 46.62, 46.36, 45.72, 43.37, 43.22, 42.54, 41.64, 30.32, 29.19, 28.65, 25.88; FTIR (cm^{-1}): 1723, 1621, 1570.

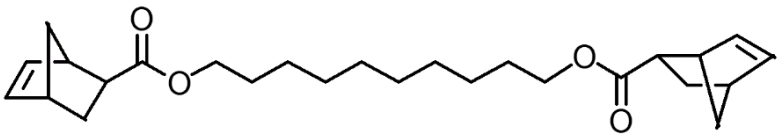
NB9



Yellow transparent liquid, yield 80%. The ratio of endo-/exo- is 67/33.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J=5.6Hz and 2.8Hz, 4H), 6.13 (dd, J=5.6Hz and 2.8Hz, 2H), 6.10 (dd, J=5.6Hz and 2.8Hz, 2H), 5.91 (dd, J=5.6Hz and 2.8Hz, 4H), 4.10-4.04 (m, 4H), 4.03-3.95 (m, 8H), 3.20 (s, 4H), 3.03 (s, 2H), 2.96-2.88 (m, 10H), 2.21 (dd, J=9.6Hz and 4.4Hz, 2H), 1.94-1.86 (m, 6H), 1.66-1.57 (m, 16H), 1.52 (d, J=8.4Hz, 2H), 1.44-1.40 (m, 8H), 1.31 (s, 26H), 1.27 (d, J=8.4Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 176.32, 174.83, 138.02, 137.72, 135.77, 132.36, 64.55, 64.30, 49.62, 46.62, 46.36, 45.72, 43.37, 43.22, 42.54, 41.64, 30.32, 29.39, 29.19, 28.67, 25.93; FTIR (cm^{-1}): 1732, 1620, 1571.

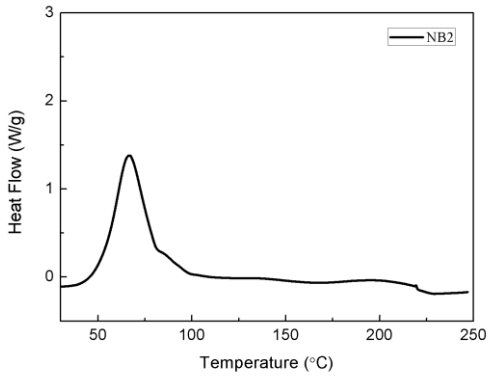
NB10

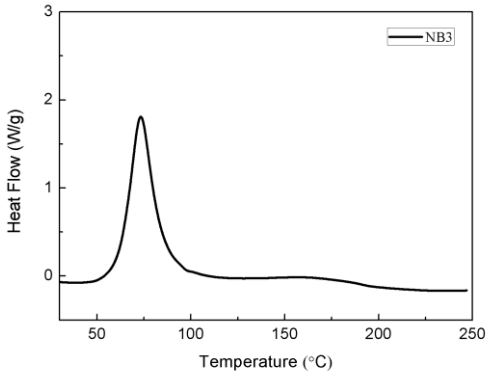


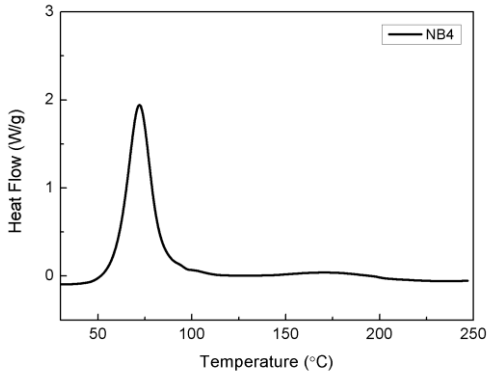
Yellow transparent liquid, yield 69%. The ratio of endo-/exo- is 75/25.

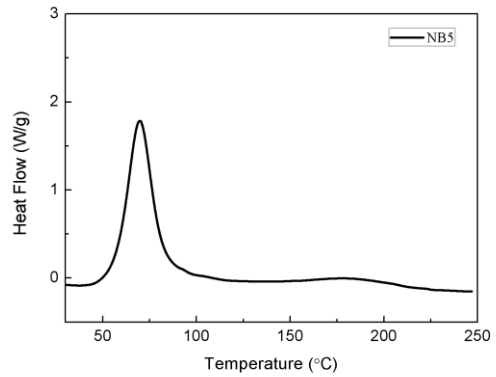
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J=5.6Hz and 3.2Hz, 6H), 6.13 (dd, J=5.6Hz and 3.2Hz, 2H), 6.10 (dd, J=5.2Hz and 2.8Hz, 2H), 5.91 (dd, J=5.6Hz and 2.8Hz, 6H), 4.11-4.05 (m, 4H), 4.04-3.97 (m, 12H), 3.20 (s, 6H), 3.03 (s, 2H), 2.96-2.88 (m, 14H), 2.21 (dd, J=10Hz and 4.4Hz, 2H), 1.94-1.86 (m, 8H), 1.66-1.55 (m, 20H), 1.52 (d, J=8.4Hz, 2H), 1.43-1.38 (m, 16H), 1.33-1.25 (m, 50H); ^{13}C NMR ($CDCl_3$): δ 176.32, 174.83, 138.02, 137.71, 135.77, 132.36, 64.57, 64.32, 49.62, 46.36, 45.72, 43.37, 43.23, 42.54, 41.64, 30.31, 29.43, 29.20, 28.68, 25.94; FTIR (cm^{-1}): 1727, 1618, 1570.

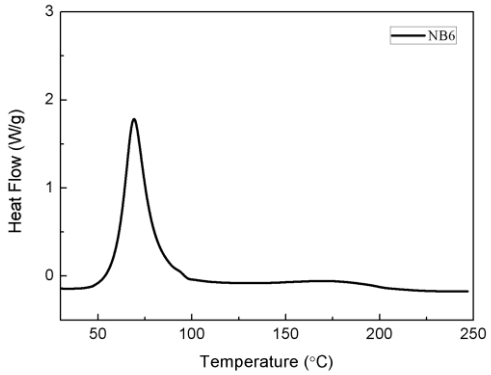
DSC curves of diols-based monomers

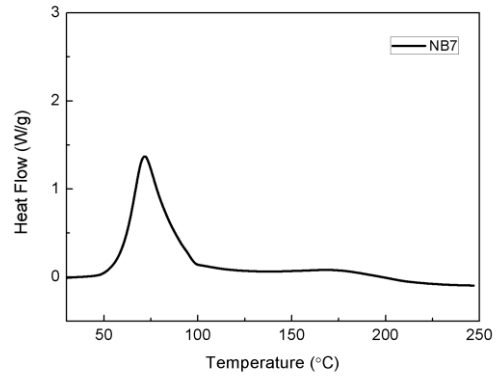


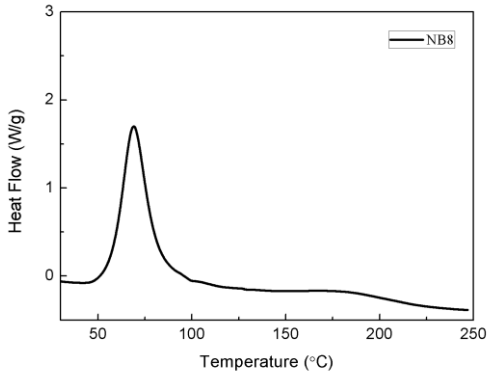


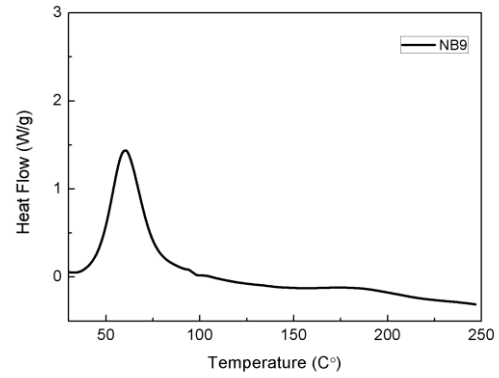












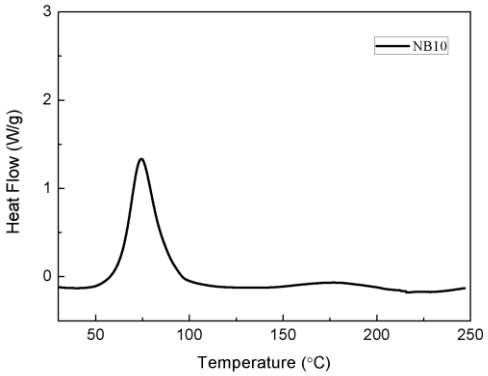
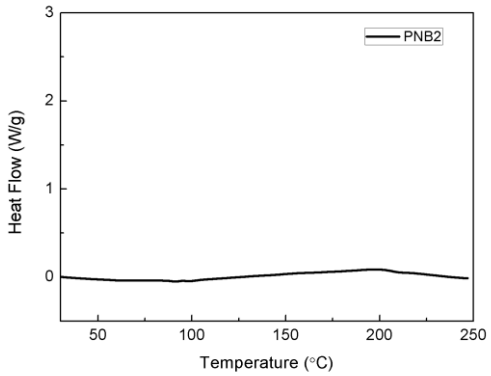
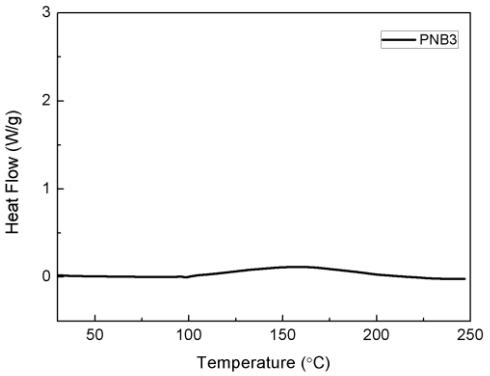
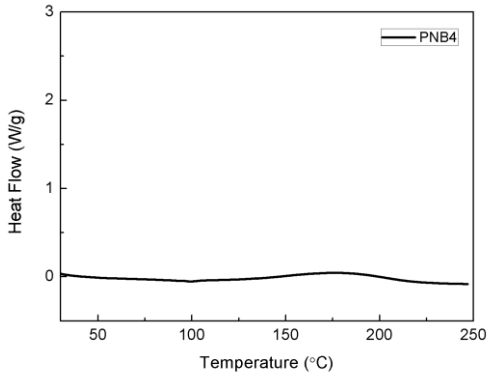


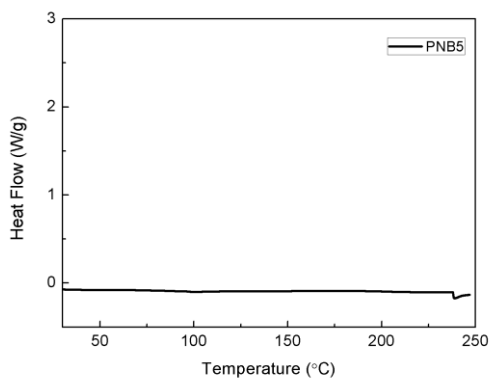
Fig. S1 DSC traces of diols-based monomers with GC2.

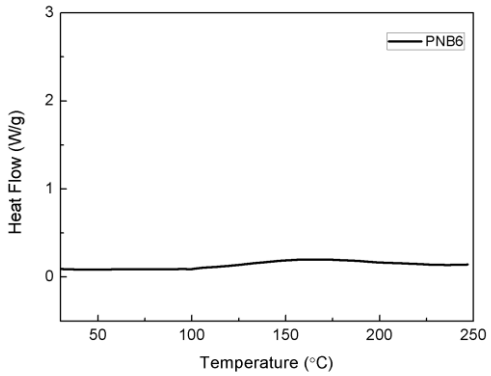
DSC curves of diols-based thermosets

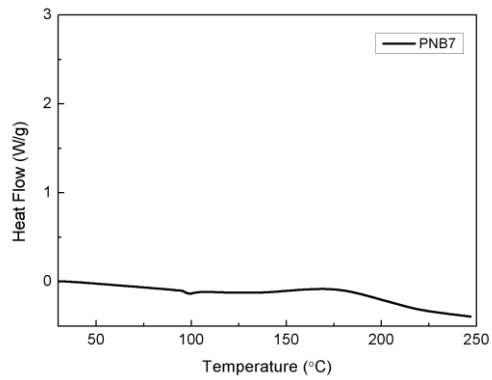


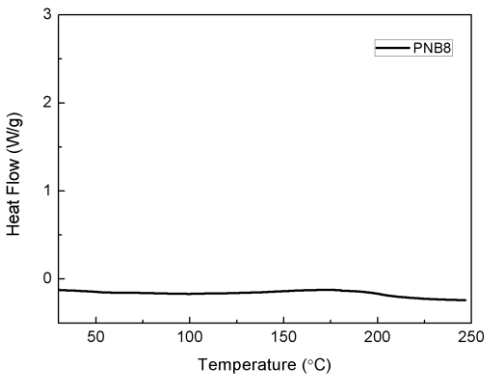


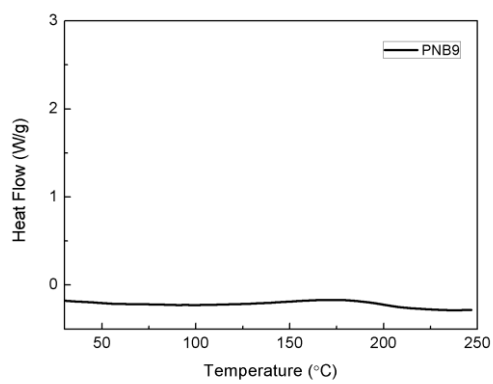












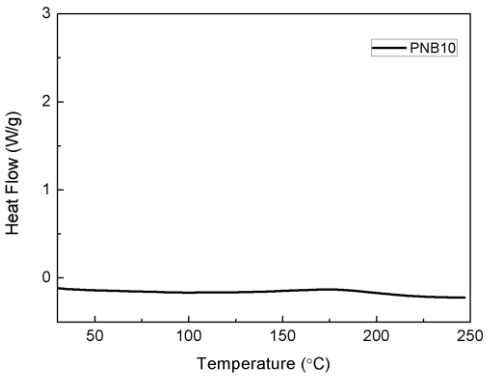


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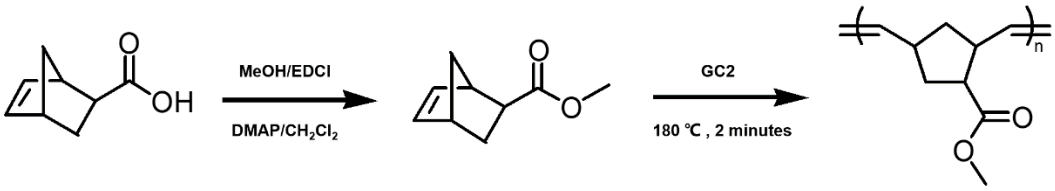
Fig. S2 DSC traces of diols-based thermosets

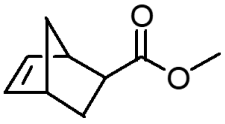
Synthesis and characterization of methyl 5-norbornene-2-carboxylate (NB-Me)



Scheme S1. Synthesis of methyl 5-norbornene-2-carboxylate and its polymer.

To a solution of DCM (150 mL) and NBE-COOH (13.92 g, 0.1 mol, 1.0 equiv), adding 4-dimethylaminopyridine (DMAP, 6.1 g, 0.05 mol, 0.5 equiv) and N-(3-dimethylamino-propyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 23.05 g, 0.12 mol, 1.2 equiv), then dropwise adding methanol (32 g, 1 mol, 10 equiv). The mixture was stirred at room temperature for 12 hours. The solution was washed with 1 M HCl aqueous three times. Then washed with saturated $NaHCO_3$ aqueous solution and deionized water three times. Adding anhydrous magnesium sulfate to dry, then filtering. The crude product was purified by flash chromatography to give the target compound as a yellow transparent liquid.

NB-Me



Yellow transparent liquid, yield 58.2%. The ratio of endo-/exo- is 85/15.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.18 (dd, J=5.6Hz and 3.2Hz, 6H), 6.13 (dd, J=5.6Hz and 2.8Hz, 1H), 6.09 (dd, J=5.6Hz and 3.2Hz, 1H), 5.92 (dd, J=5.6Hz and 2.8Hz, 6H), 3.68 (s, 3H), 3.62 (s, 18H), 3.19 (s, 6H), 3.03 (s, 1H), 2.96-2.90 (m, 7H), 2.22 (dd, J=10Hz and 4.4Hz, 1H), 1.93-1.87 (m, 7H), 1.52 (d, J=8.4Hz, 1H), 1.43-1.36 (m, 14H), 1.27 (d, J=8.4Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 176.73, 175.25, 138.05, 137.74, 135.74, 132.37, 51.71, 51.47, 49.63, 46.58, 46.37, 45.67, 43.18, 42.99, 42.53, 41.63, 30.35, 29.17; FTIR (cm^{-1}): 1740, 1625, 1571.

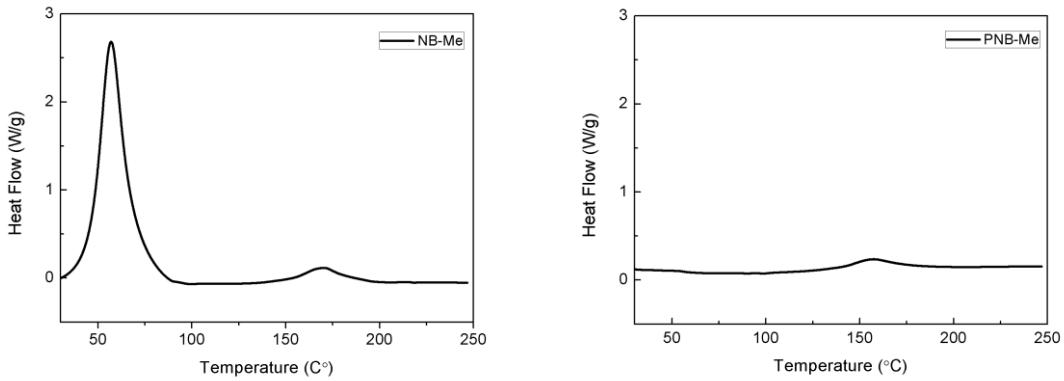


Fig. S3 DSC traces of NB-Me and PNB-Me.

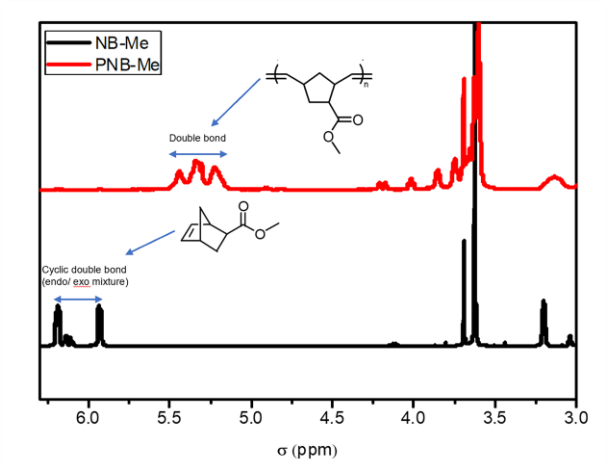


Fig. S4 ^{1}H NMR spectra of NB-Me and PNB-Me.

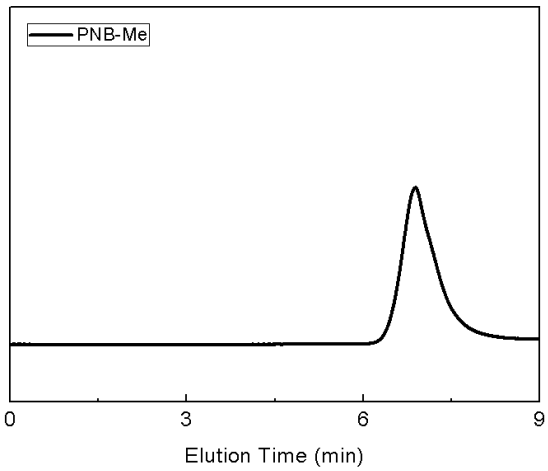


Fig. S5 GPC trace of PNB-Me. (M_n= 58 KD, M_w= 86 KD, $Đ$ =1.4)

FTIR spectral analysis

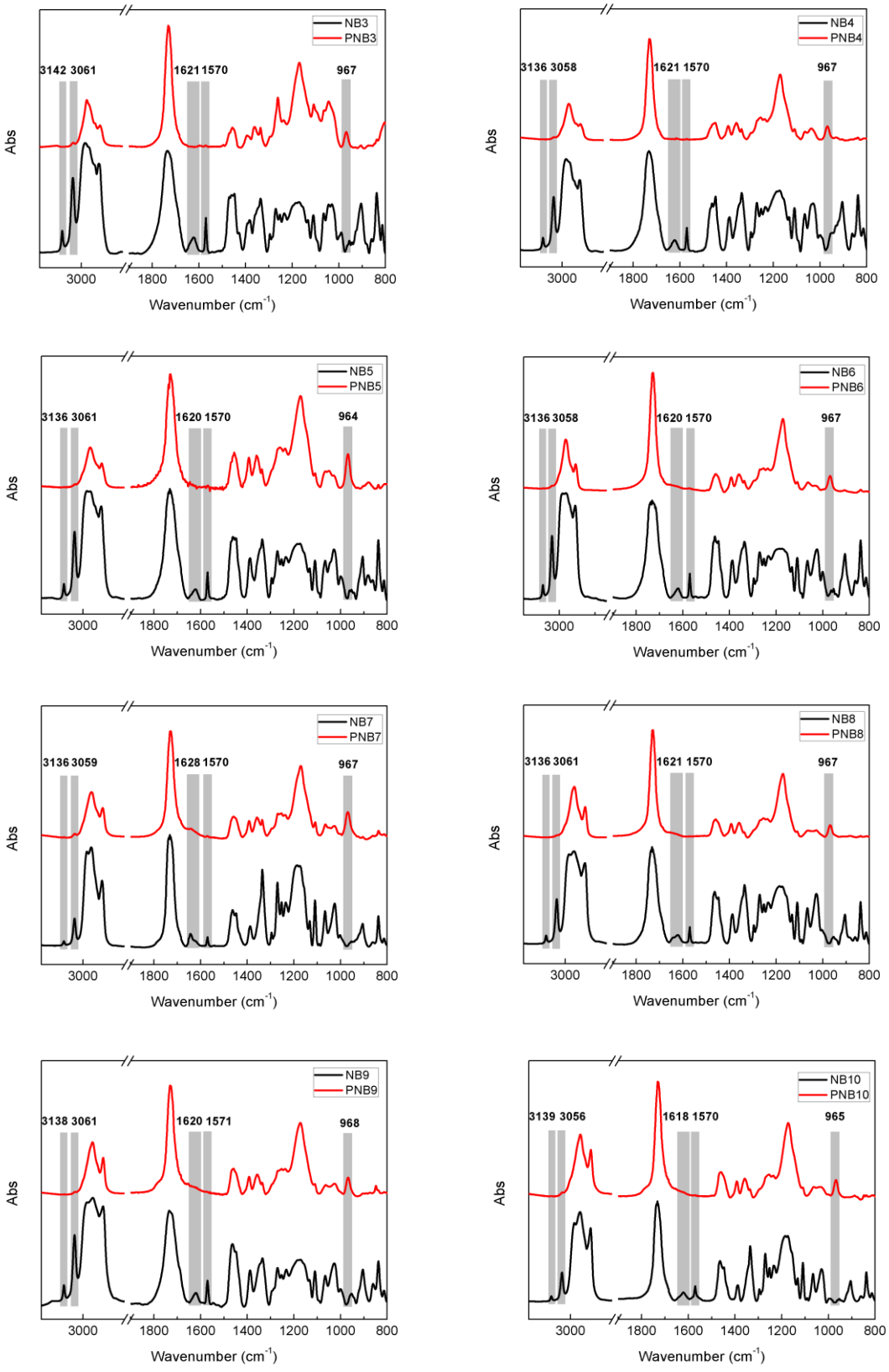
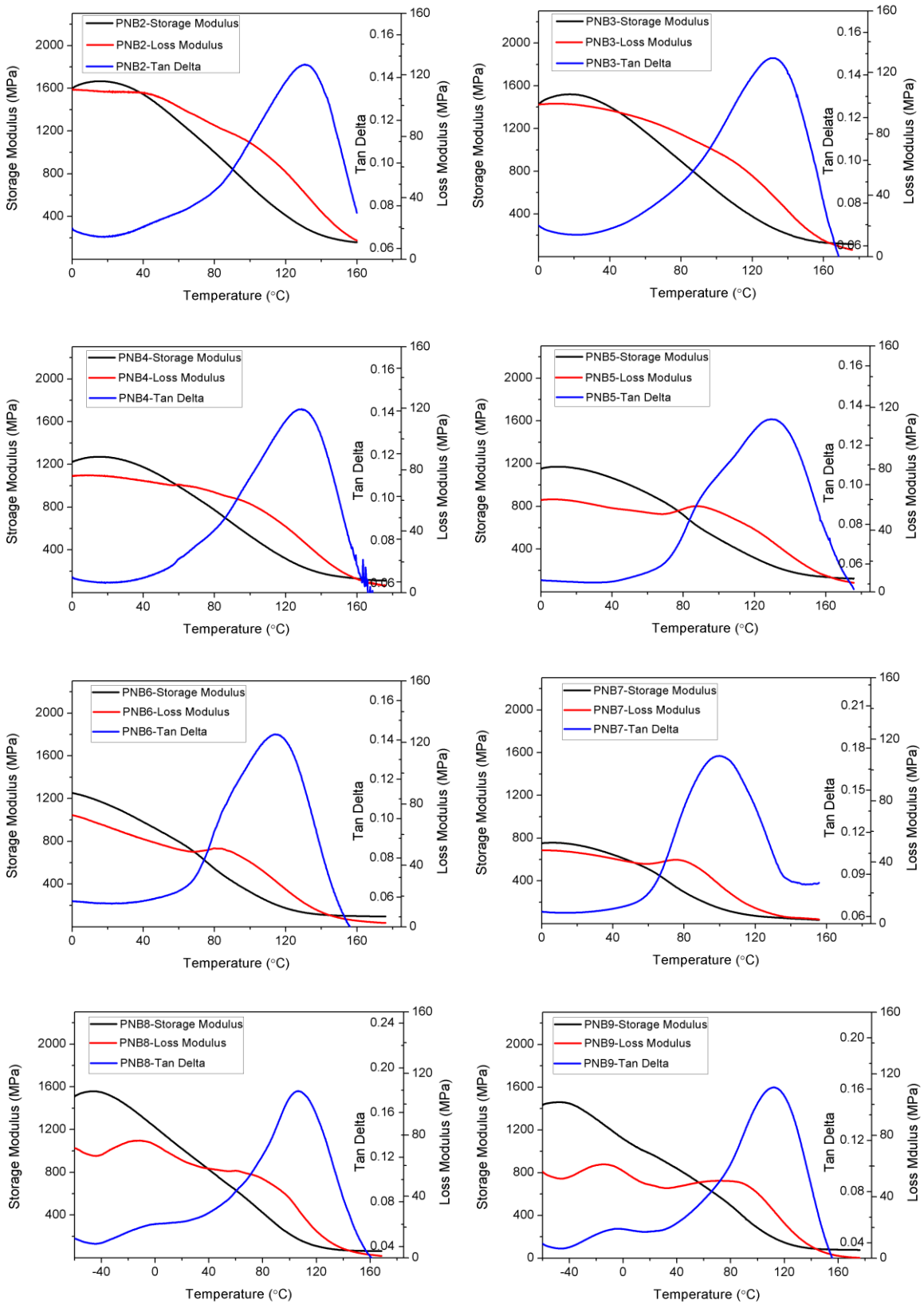


Fig. S6 FTIR spectra of diols-based monomers and thermosets.

Dynamic mechanical analysis



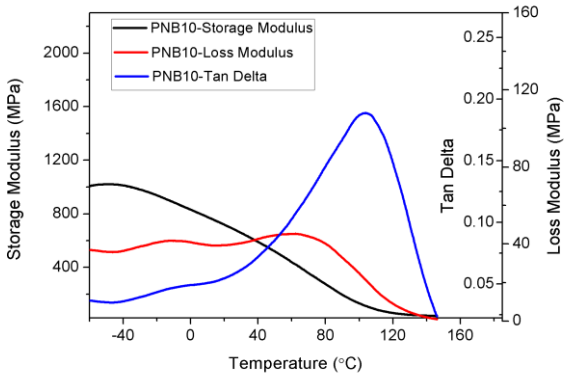
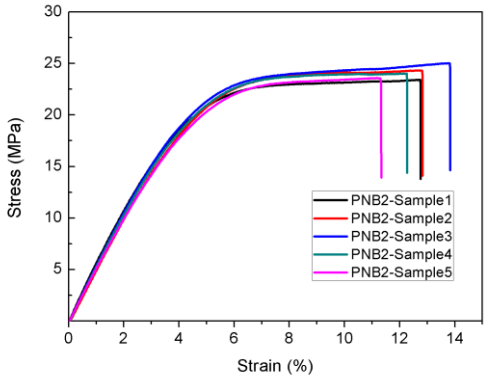
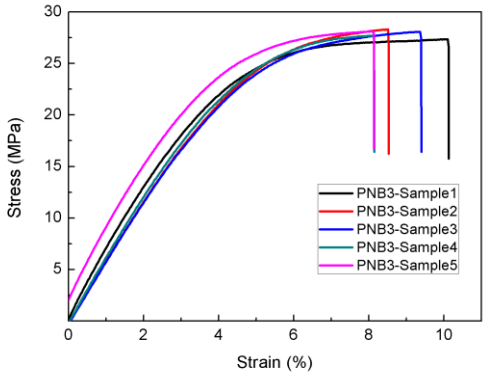
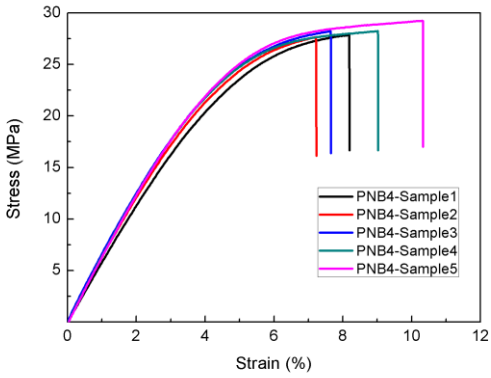


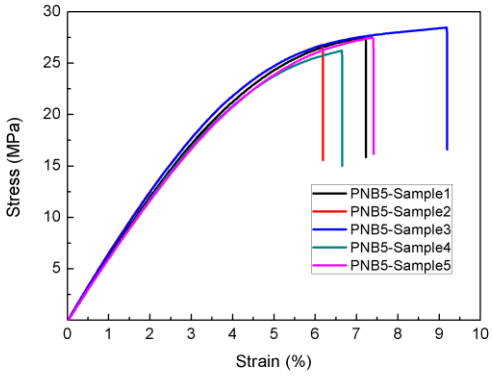
Fig. S7 Storage modulus, loss modulus and tan delta of diols-based thermosets.

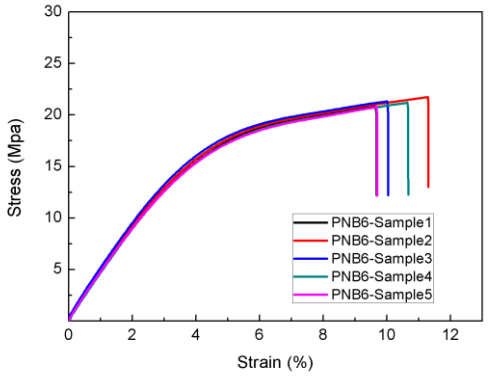
Tensile properties testing

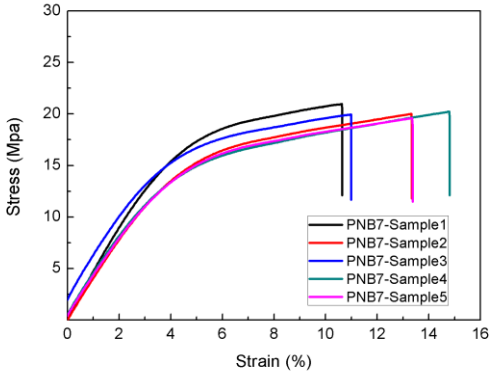


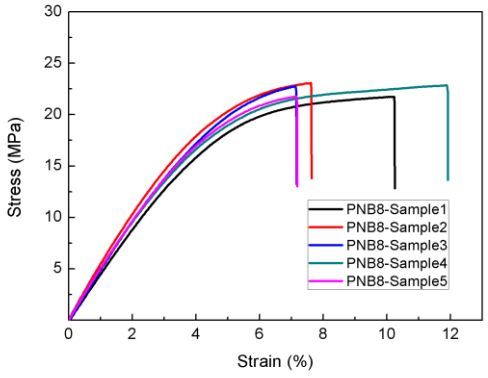


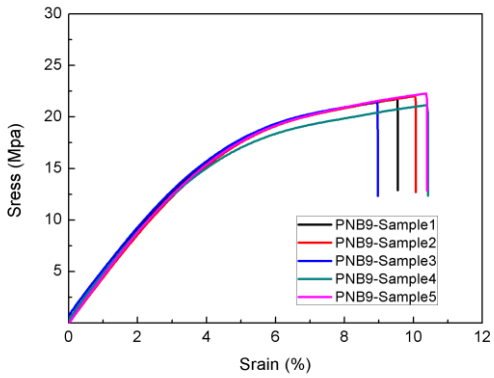












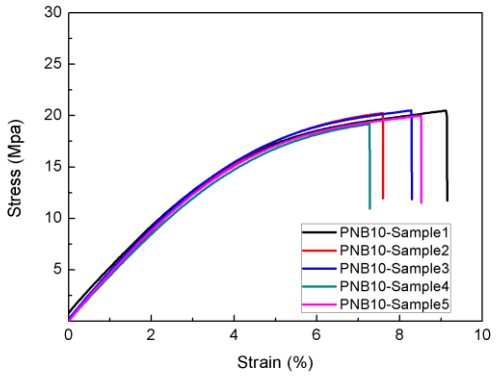


Fig. S8 Stress-strain curves of diols-based thermosets.

Thermal stability analysis

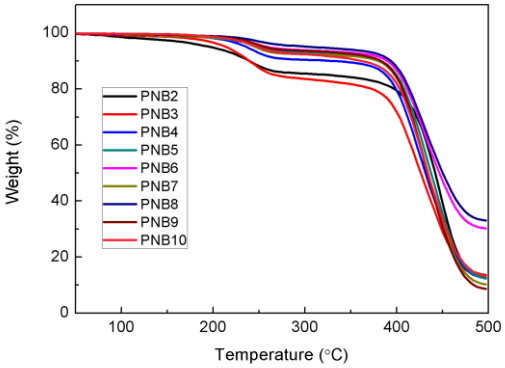


Fig. S9 TGA curves of diols-based thermosets.

Preparation and characterization of woven flax fibers composites

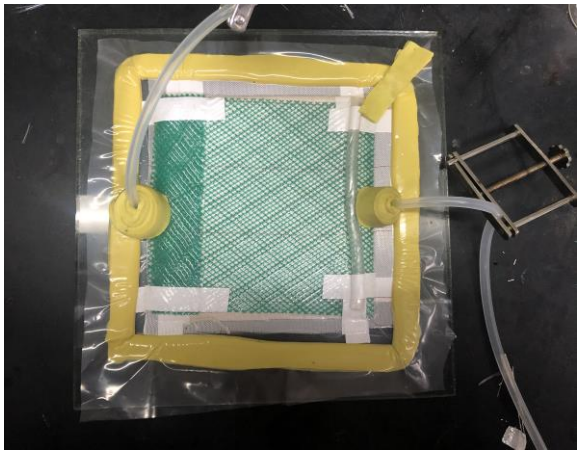


Fig. S10 The vacuum assistant resin transfer molding (VARTM).

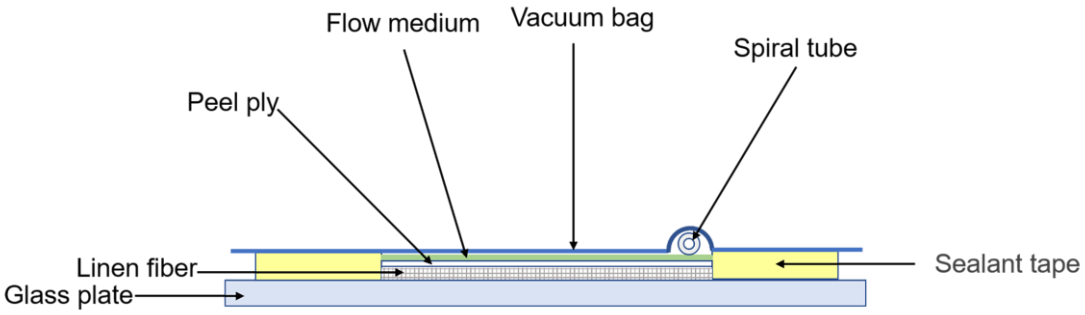


Fig. S11 The cross section of VARTM.

Resin contents of woven flax fibers composites were calculated by equation S-3.

$$Resin\ contents = \frac{m_c - m_f}{m_c} \times 100\% \quad \text{S-3}$$

Where m_c and m_f are respectively the mass of composites and woven flax fibers. Because the relationship between mass and density, equation S-3 became

$$Resin\ contents = \frac{\rho_c - \rho_f}{\rho_c} \times 100\% \quad \text{S-4}$$

where ρ_c is the areal density of composites, ρ_f is the areal density of woven flax fibers. After getting the mass of composites and woven flax fiber per unit area, the resin contents of PNB5C and PNB10C are respectively 67.0% and 65.6%, calculating by equation S-4.

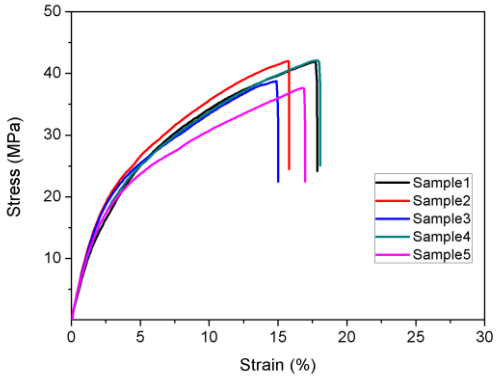


Fig. S12 Stress-strain curves of PNB5C.

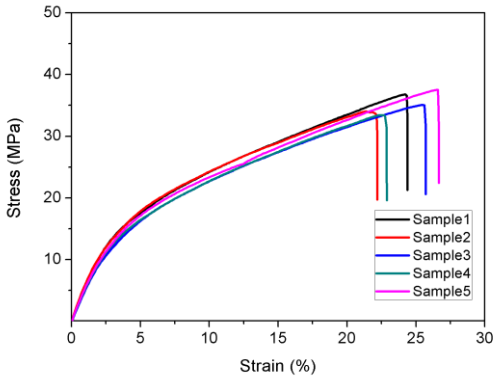


Fig. S13 Stress-strain curves of PNB10C.

Study on the thermo-trigged reactions of diols-derived monomers

To determine whether thermo trigged the reactions of diols-derived monomers, NB5 was applied as a control and kept at 180°C for 2 minutes in the absence of GC2, Fig. S14. No obvious change was observed, probably suggesting that there was no thermo-trigged the crosslinking.

^{1}H NMR (Fig. S15) was used to further study the thermo-trigged reactions. As can been seen from Fig. S15, there was almost no change before or after keeping NB5 at 180°C for 2 minutes. These prove that little reactions occurred and no cyclopentadiene formed under this works' process.

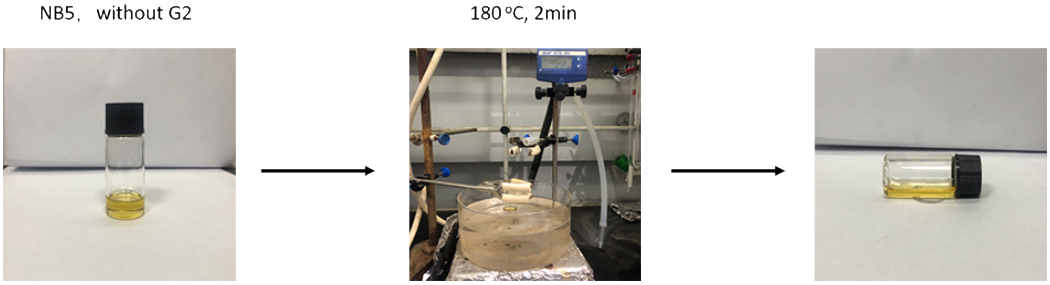


Fig. S14 NB5 was kept at 180°C for 2 minutes

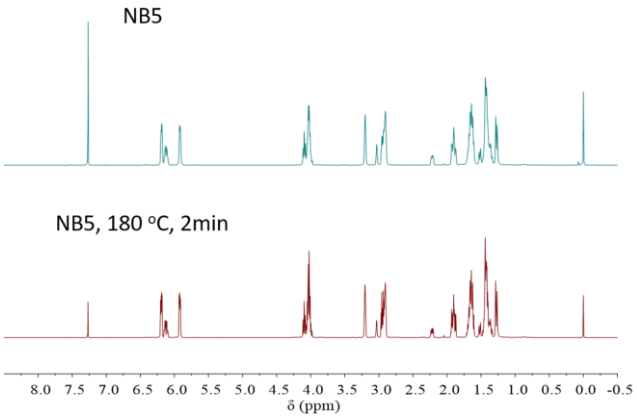
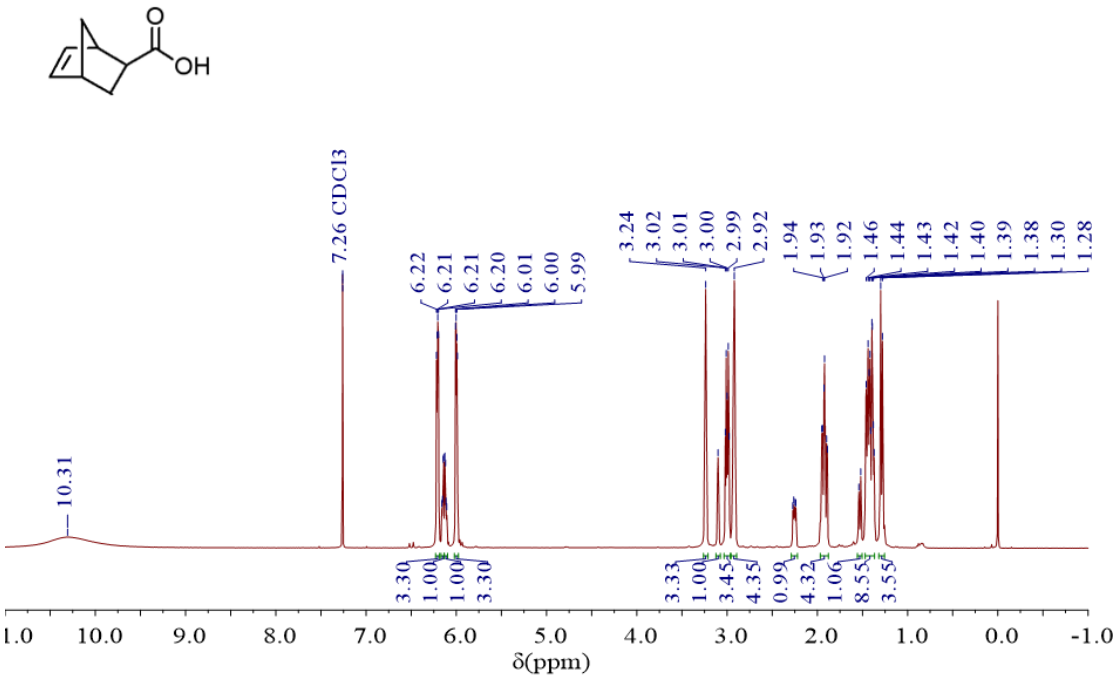
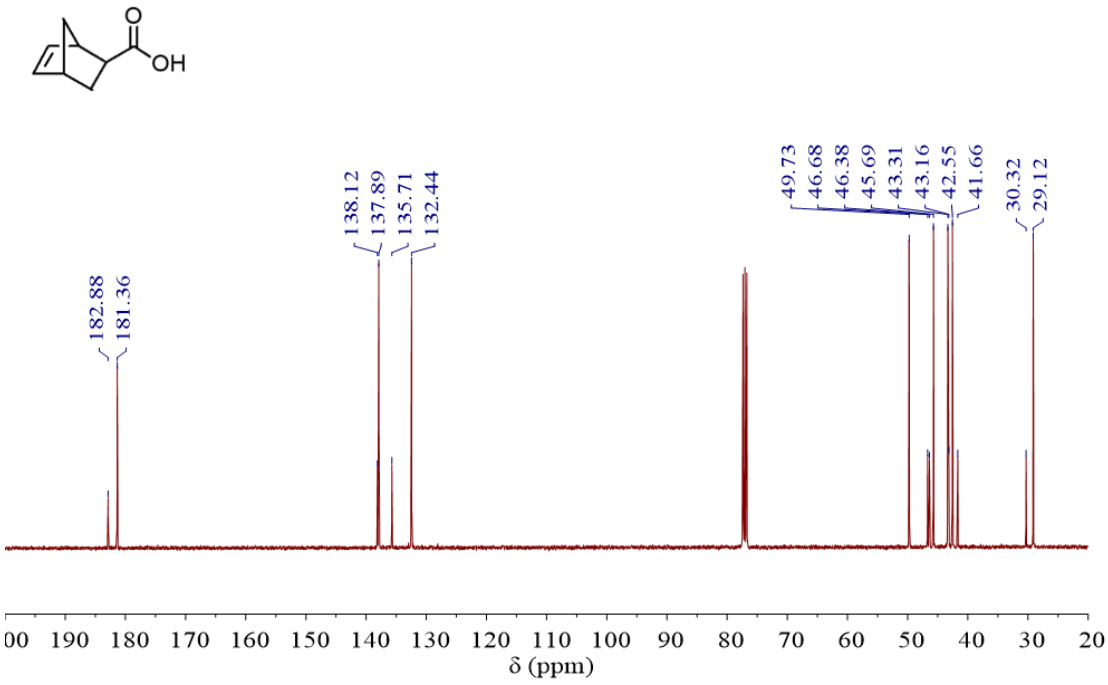


Fig. S15 ^{1}H NMR spectra of NB5, and NB5 at 180°C for 2 minutes

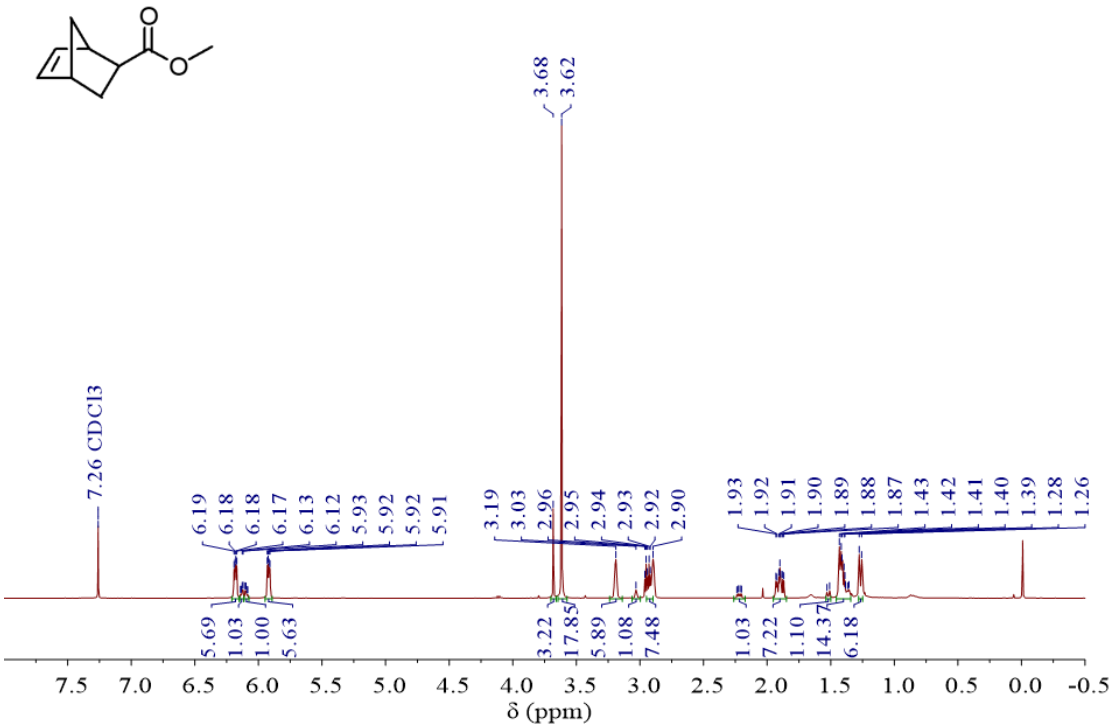
^{1}H and ^{13}C NMR Spectra

NBE-COOH





NB-Me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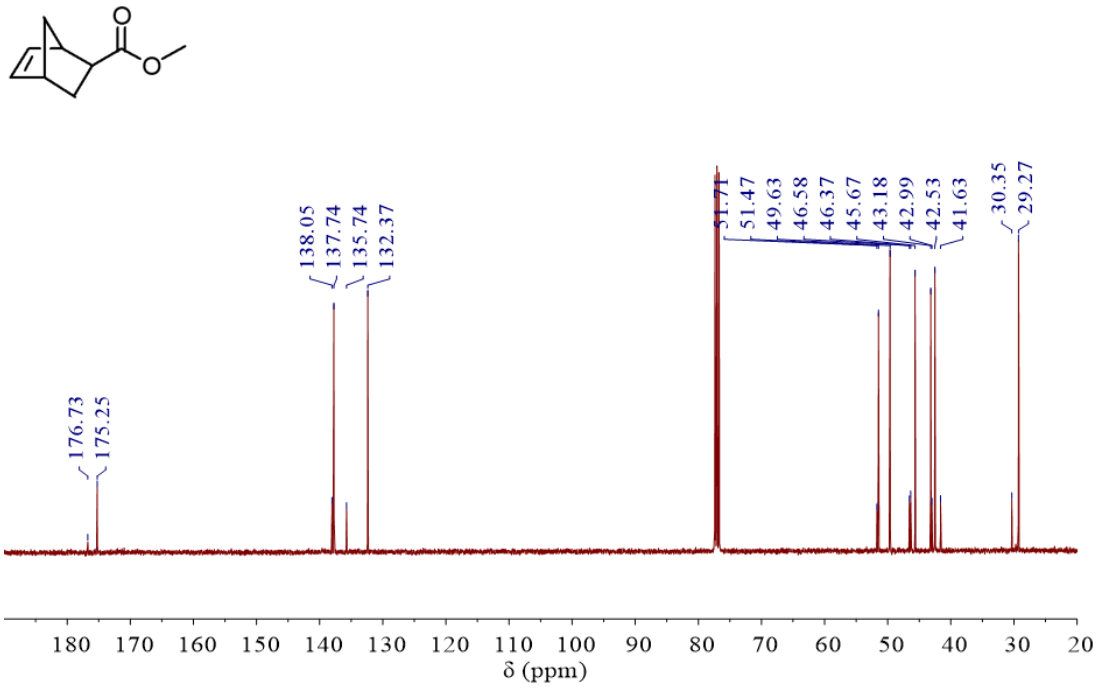
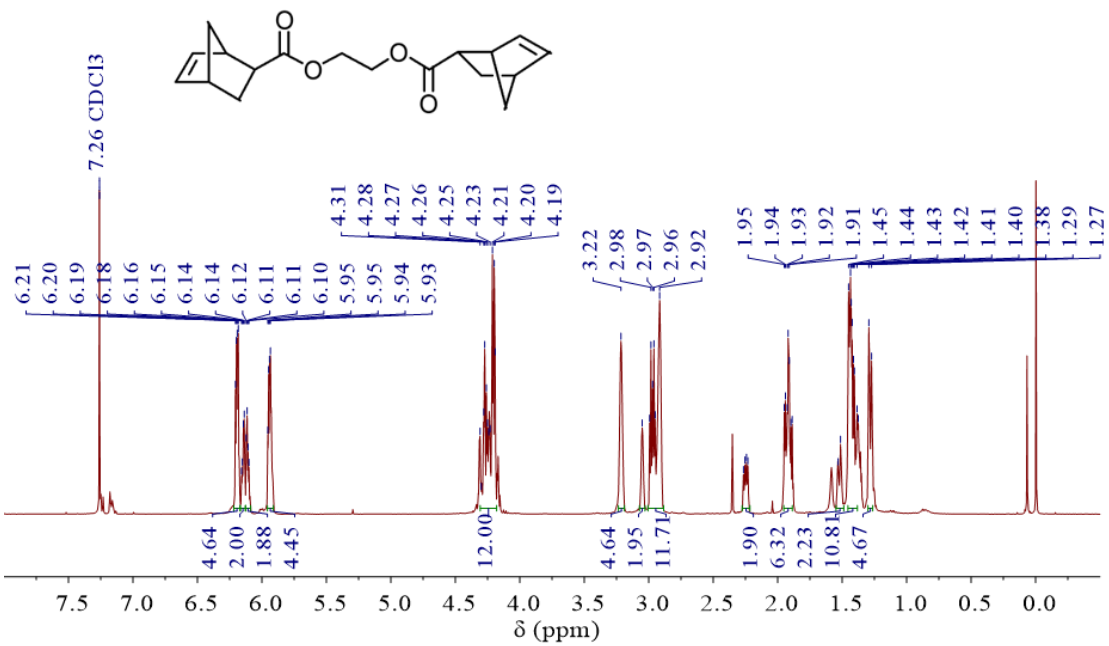
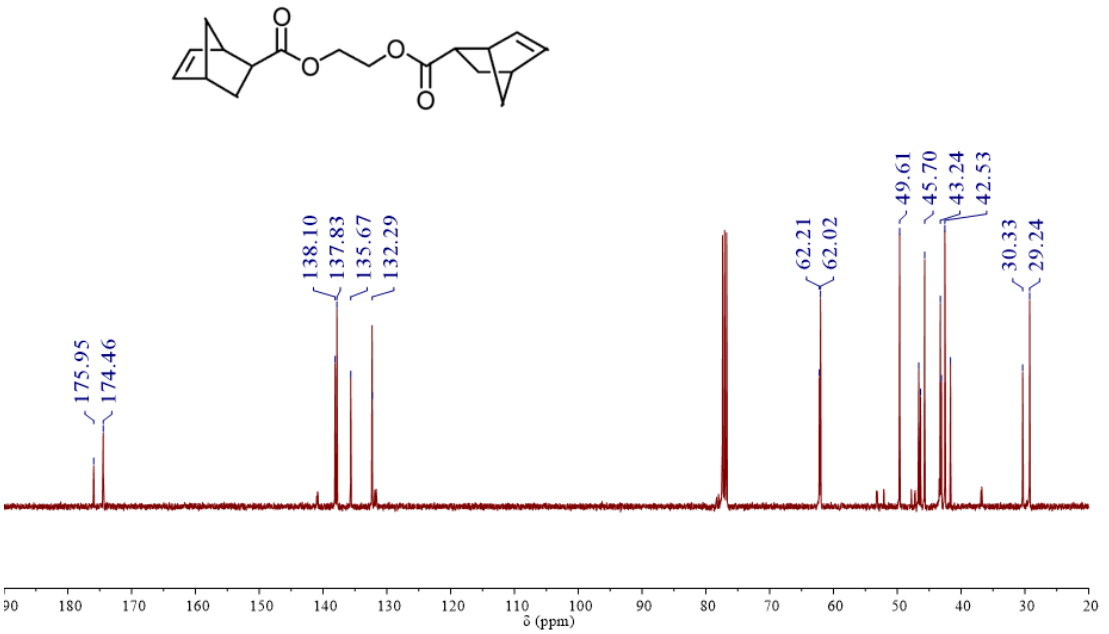
3.68
3.62
δ (ppm)

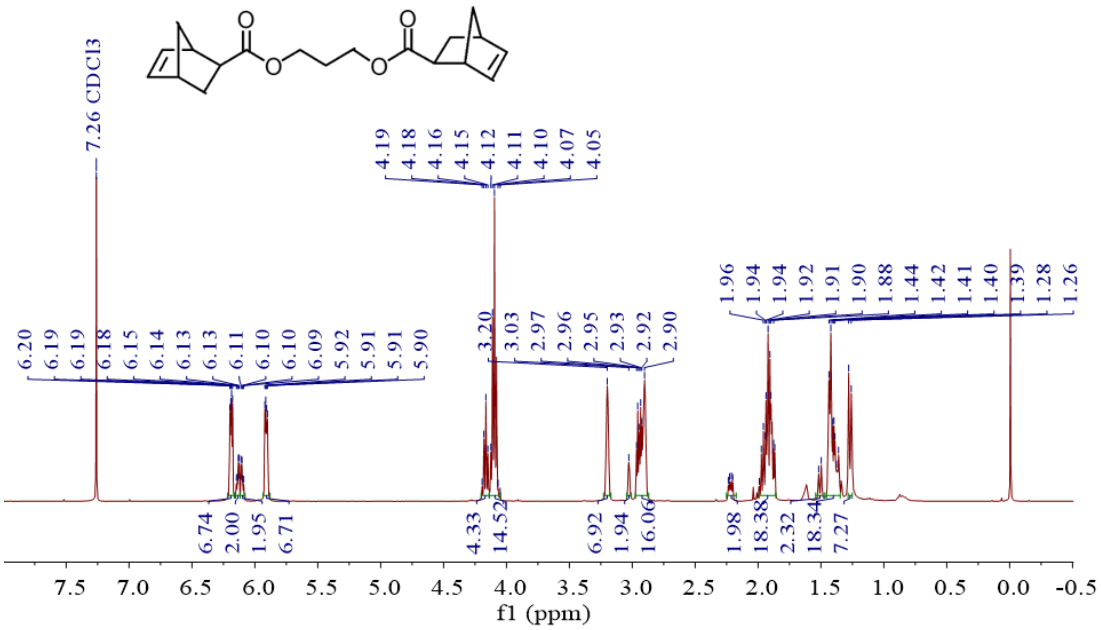

176.73
175.25
138.05
137.74
135.74
132.37
51.71
51.47
49.63
46.58
46.37
45.67
43.18
42.99
42.53
41.63
30.35
29.27
δ (ppm)

NB2


7.26 CDCl3
6.21 6.20 6.19 6.18 6.16 6.15 6.14 6.14 6.12 6.11 6.11 6.10 5.95 5.95 5.94 5.93
4.31 4.28 4.27 4.26 4.25 4.23 4.21 4.20 4.19
3.22 2.98 2.97 2.96 2.92
1.95 1.94 1.93 1.92 1.91 1.45 1.44 1.43 1.42 1.41 1.40 1.38 1.29 1.27
4.64 2.00 1.88 4.45
12.00
4.64 1.95 11.71
1.90 6.32 2.23 10.81 4.67
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


175.95
174.46
138.10
137.83
135.67
132.29
62.21
62.02
49.61
45.70
43.24
42.53
30.33
29.24
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
δ (ppm)

NB3


7.26 CDCl3
4.19 4.18 4.16 4.15 4.12 4.11 4.10 4.07 4.05
6.20 6.19 6.19 6.18 6.15 6.14 6.13 6.13 6.11 6.10 6.10 6.09 5.92 5.91 5.91 5.90
3.20 3.03 2.97 2.96 2.95 2.93 2.92 2.90
1.96 1.94 1.94 1.92 1.91 1.90 1.88 1.44 1.42 1.41 1.40 1.39 1.28 1.26
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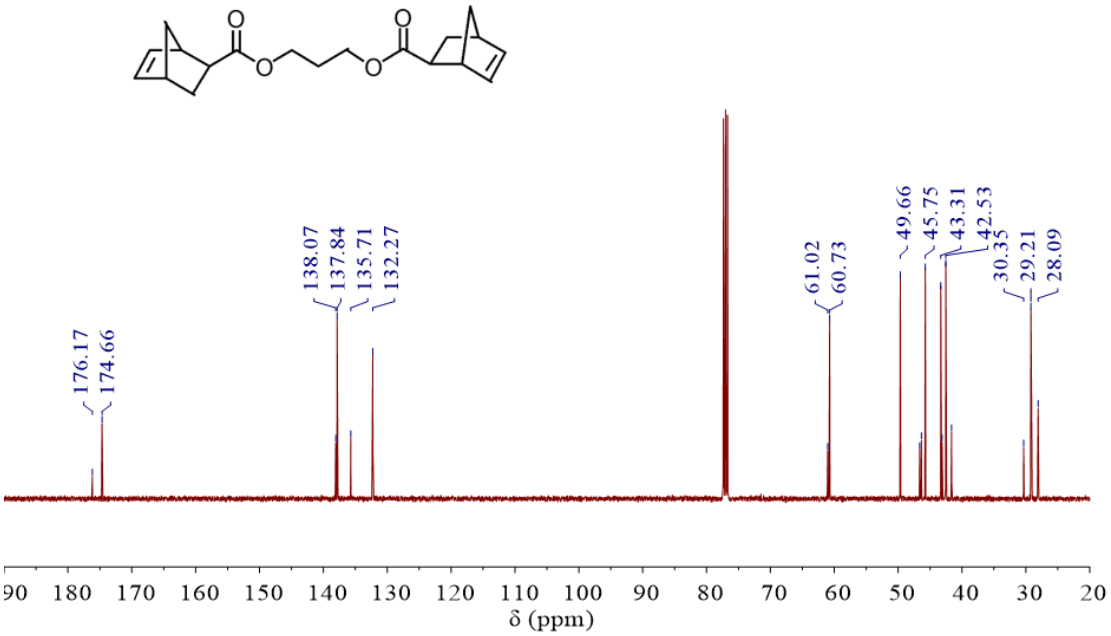
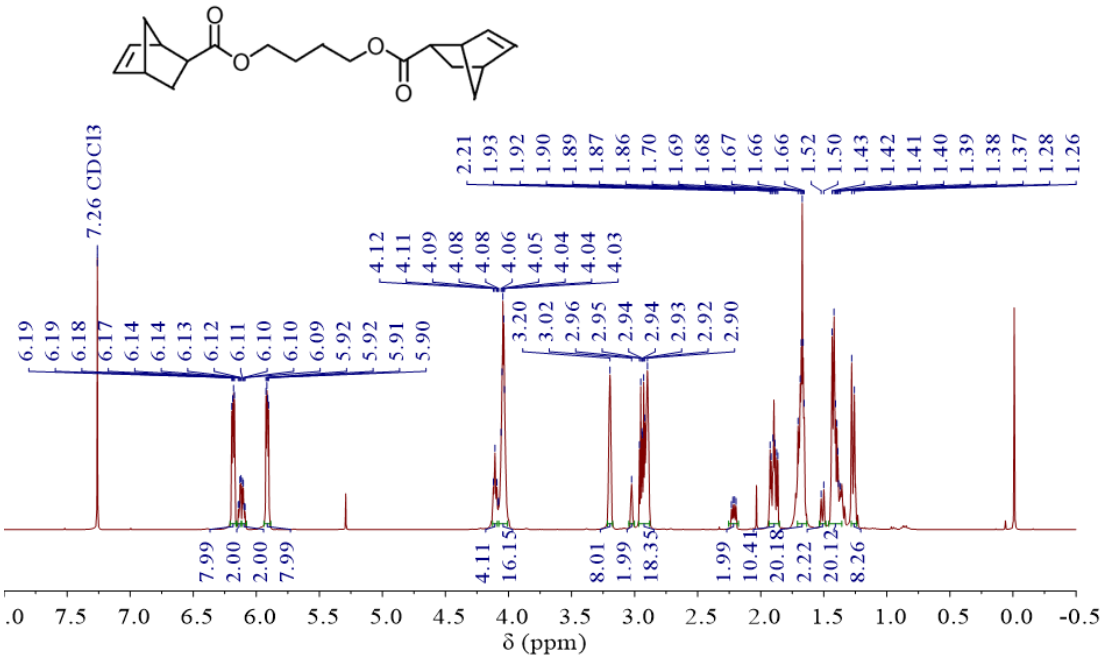
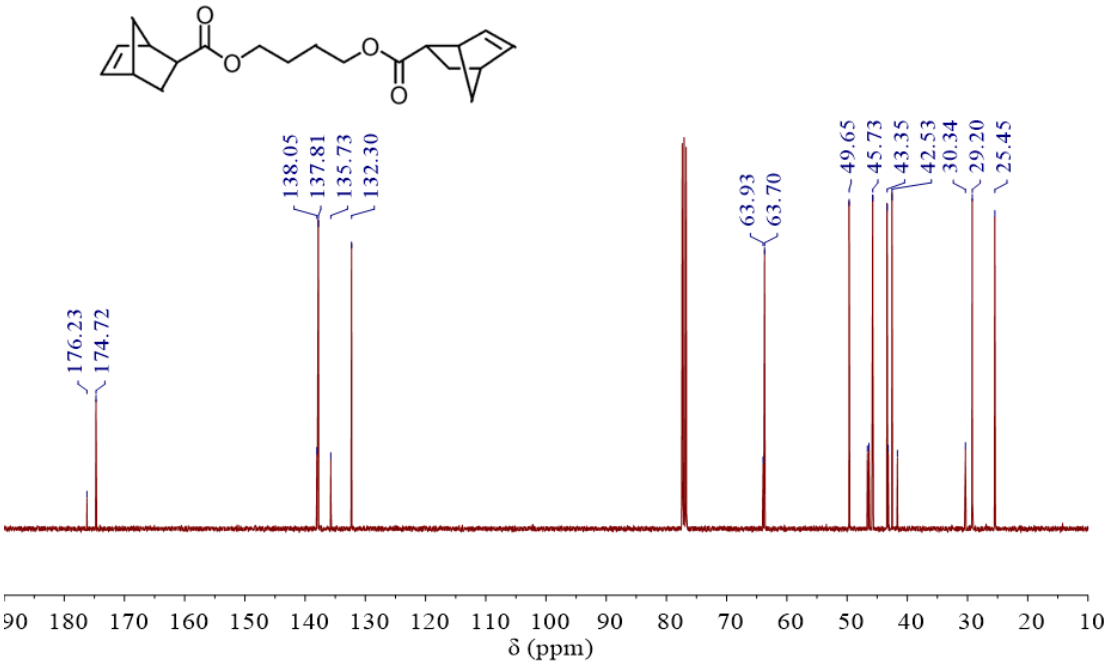
1.98 18.38 2.32 18.34 7.27
f1 (ppm)

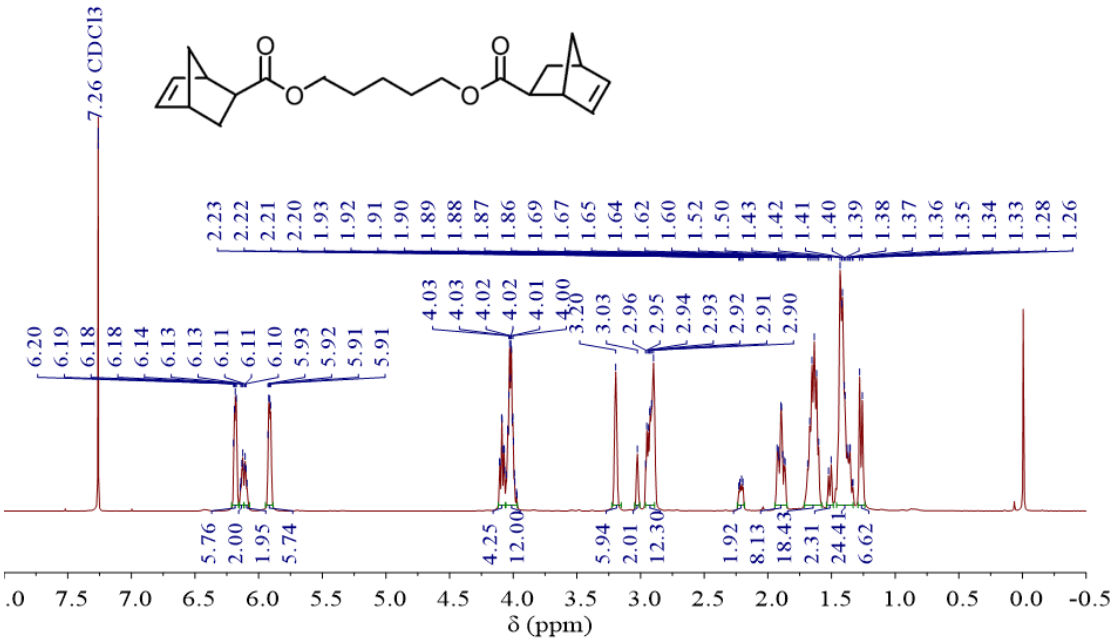

176.17 174.66
138.07 137.84 135.71 132.27
61.02 60.73
49.66 45.75 43.31 42.53 30.35 29.21 28.09
δ (ppm)

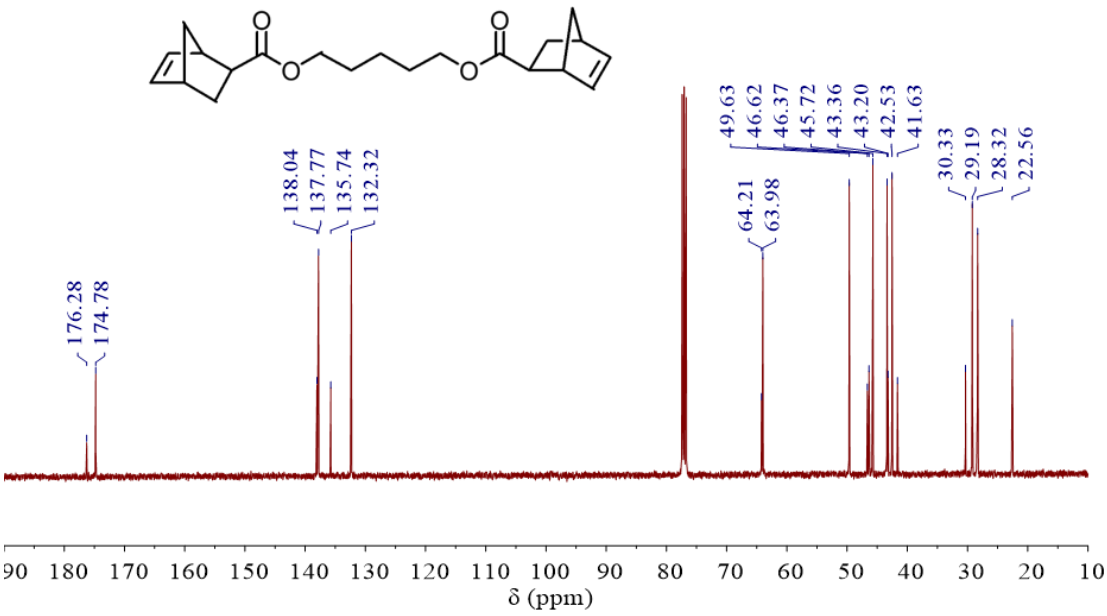
NB4



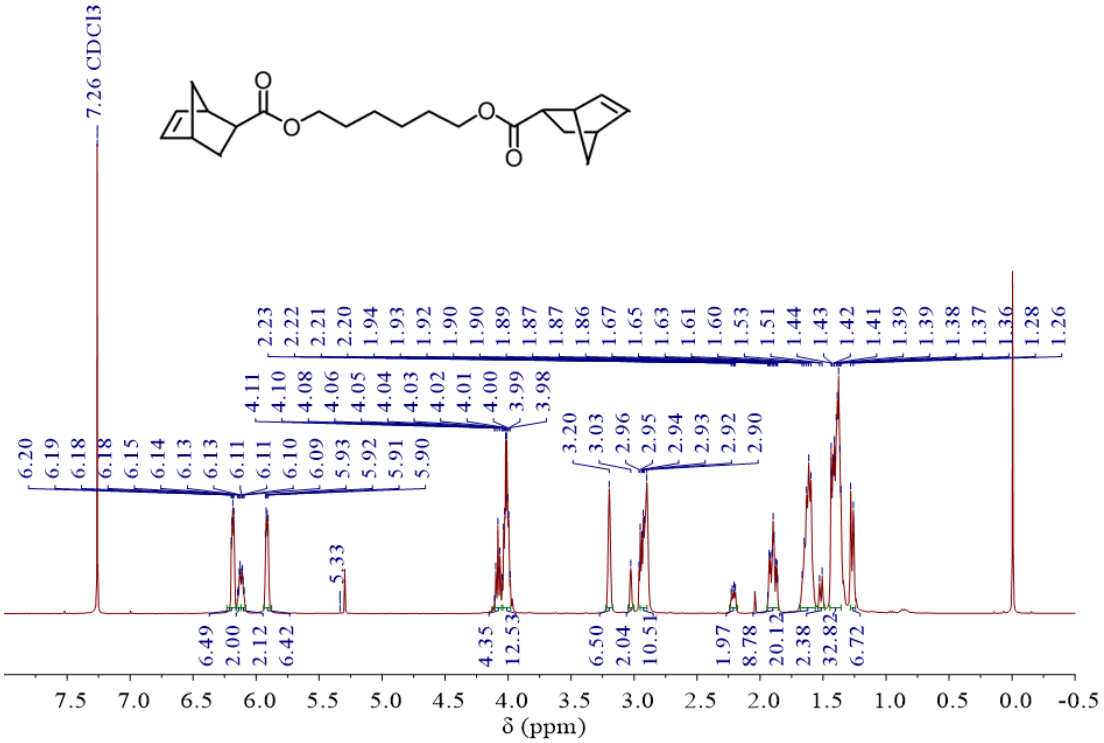


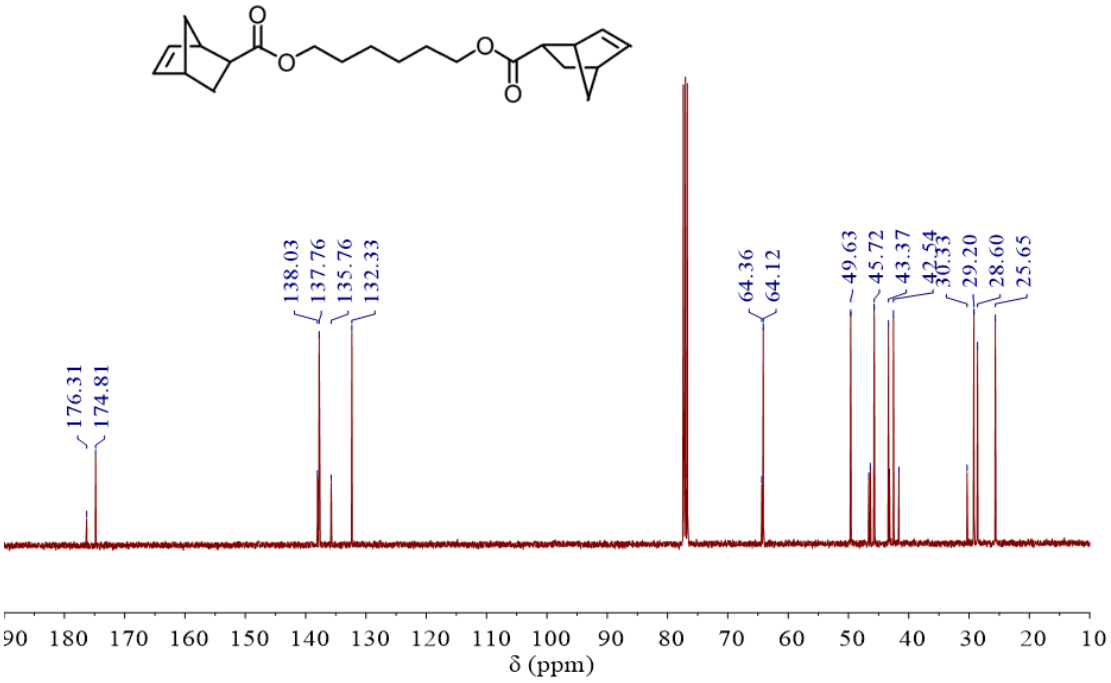
NB5



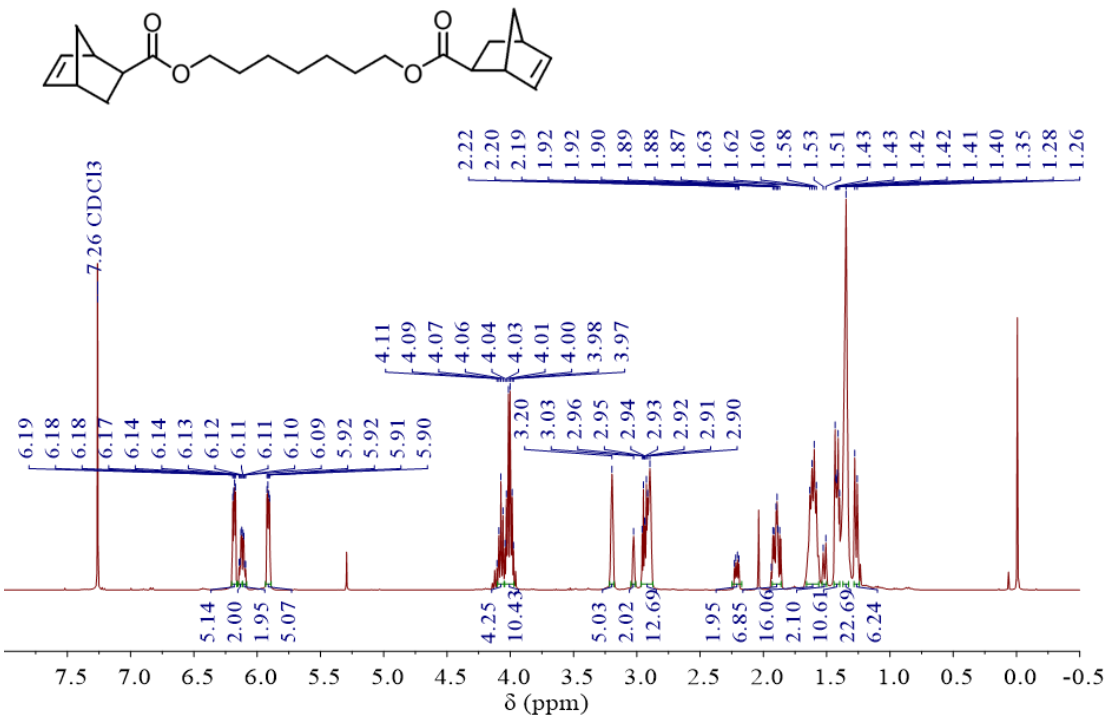


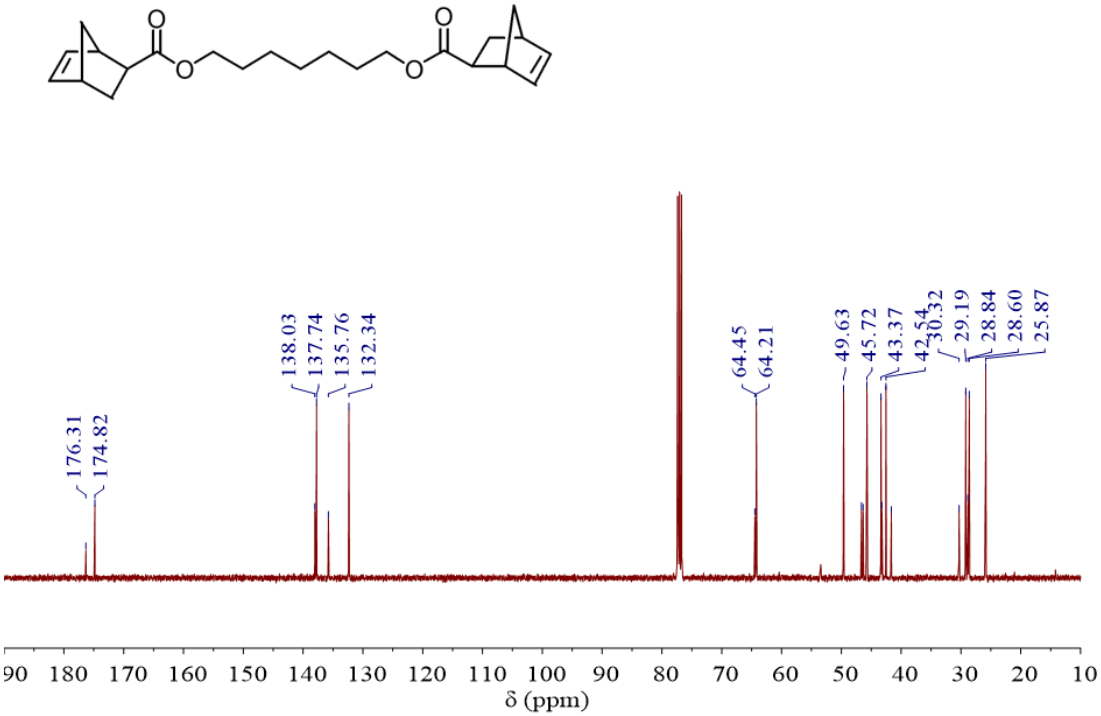
NB6



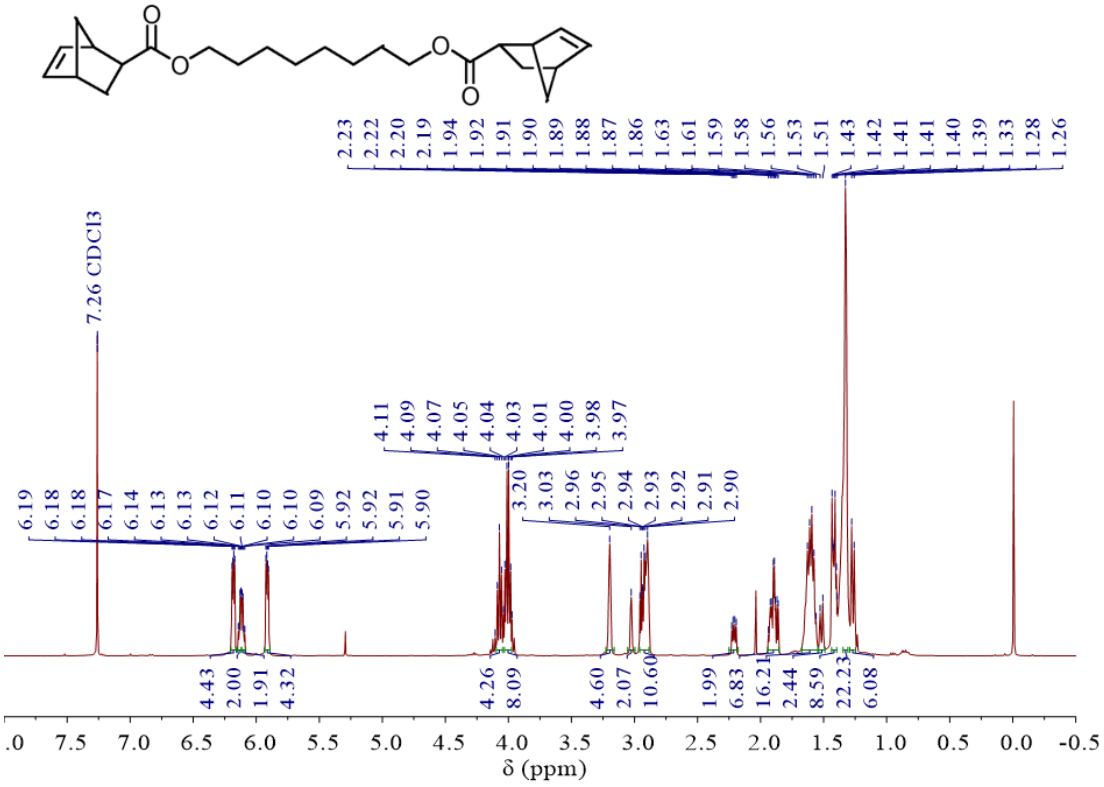


NB7





NB8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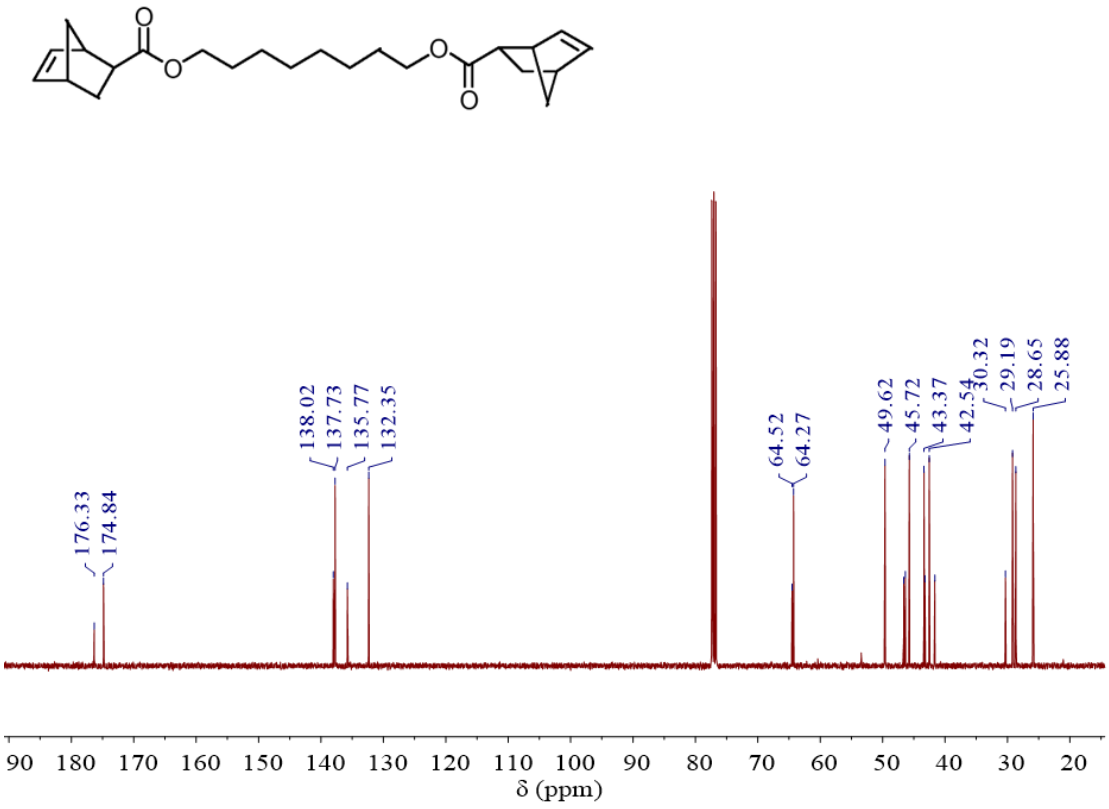
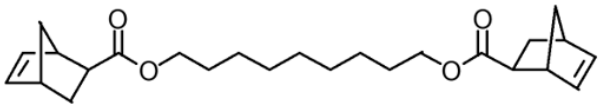
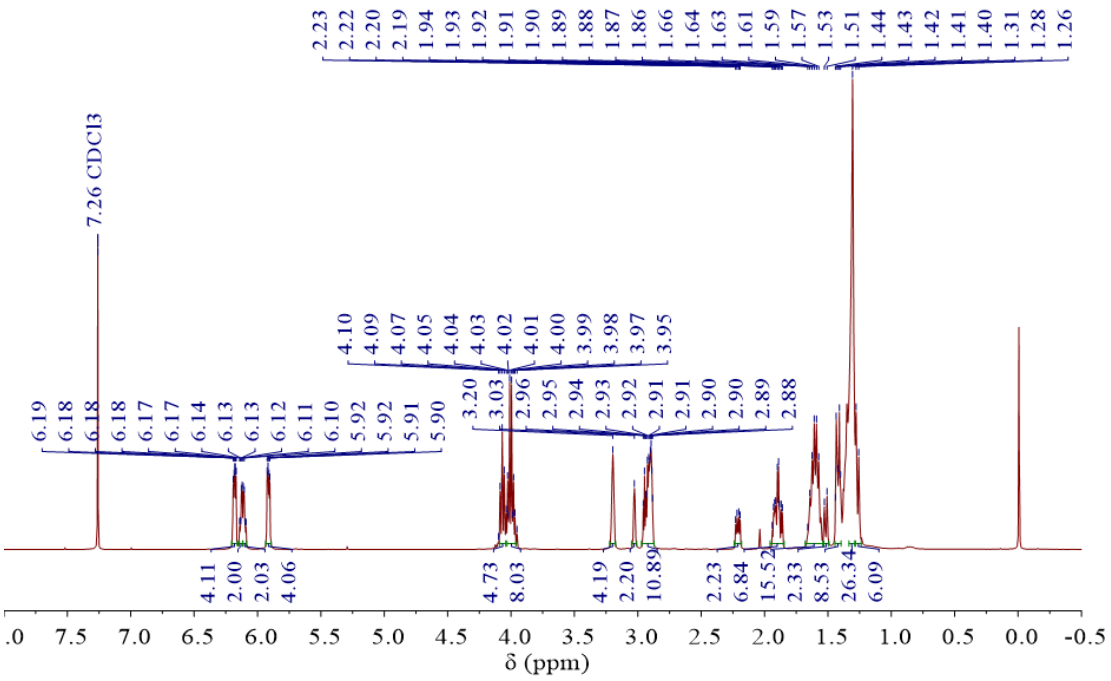
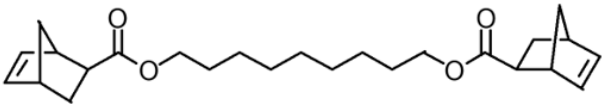
7.26 CDCl3
4.11 4.09 4.07 4.05 4.04 4.03 4.01 4.00 3.98 3.97
3.20 3.03 2.96 2.95 2.94 2.93 2.92 2.91 2.90
6.19 6.18 6.18 6.17 6.14 6.13 6.13 6.12 6.11 6.10 6.10 6.09 5.92 5.92 5.91 5.90
4.43 2.00 1.91 4.32 4.26 8.09 4.60 2.07 10.60 1.99 6.83 16.21 2.44 8.59 22.23 6.08
δ (ppm)

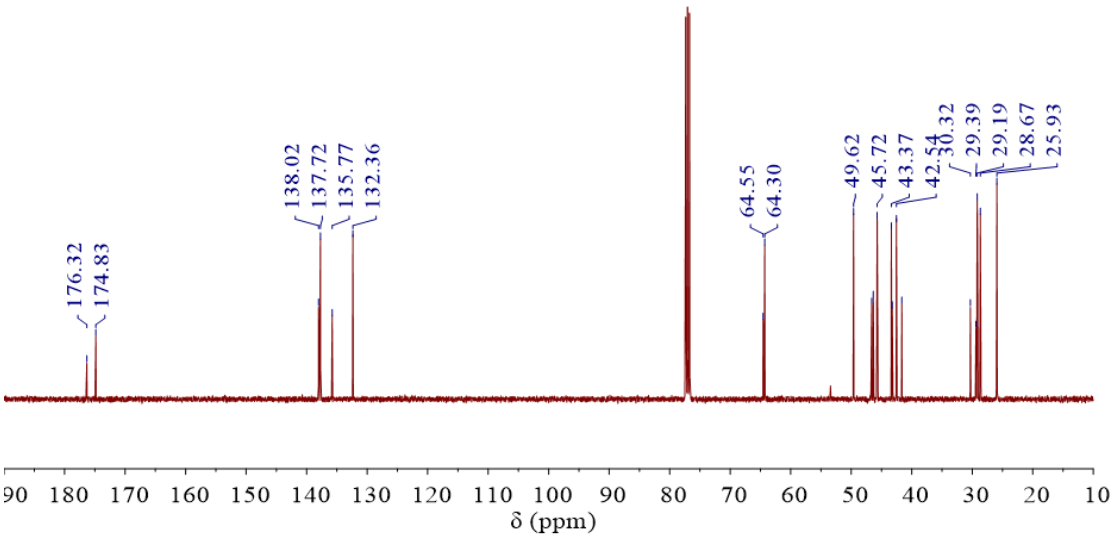

176.33
174.84
138.02
137.73
135.77
132.35
64.52
64.27
49.62
45.72
43.37
42.54
30.32
29.19
28.65
25.88
δ (ppm)

NB9

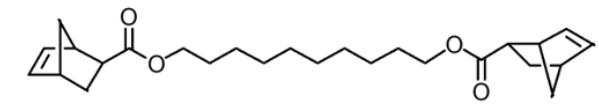




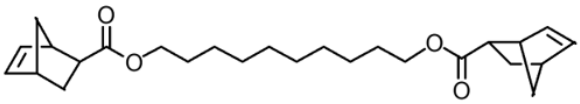


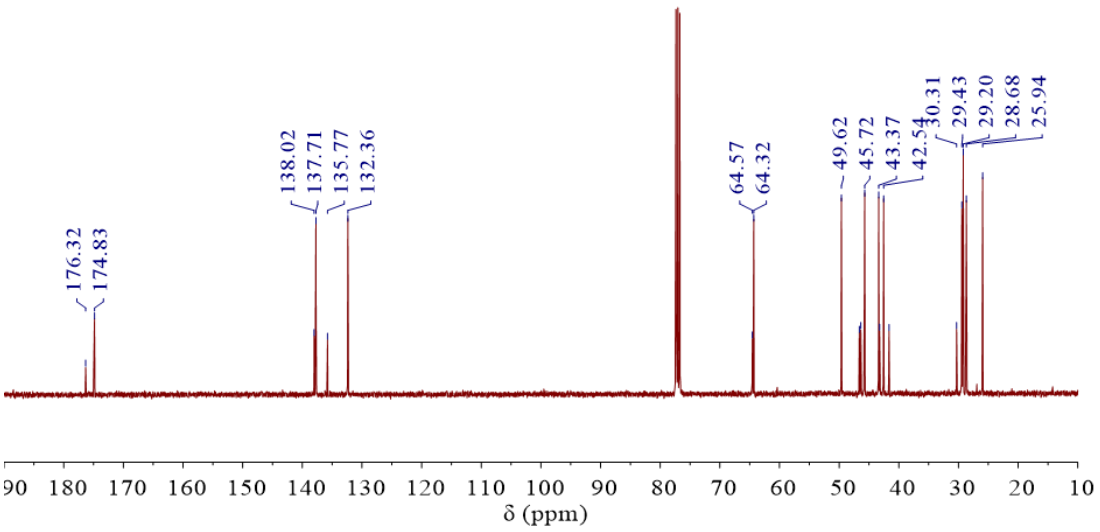


NB10



2.23 2.22 2.20 2.19 1.94 1.93 1.92 1.91 1.90 1.89 1.88 1.87 1.86 1.66 1.64 1.62 1.61 1.59 1.57 1.55 1.53 1.51 1.43 1.42 1.41 1.40 1.39 1.38 1.33 1.30 1.29 1.28 1.26 1.25
7.26 CDCl3
4.11 4.09 4.07 4.05 4.04 4.03 4.02 4.01 4.00 3.99 3.98 3.97
6.19 6.18 6.18 6.17 6.14 6.13 6.13 6.12 6.11 6.10 6.10 6.09 5.92 5.92 5.91 5.90
3.20 3.03 2.96 2.95 2.94 2.93 2.92 2.91 2.90 2.90 2.89 2.88
6.16 2.00 1.99 6.16 4.73 12.75 6.36 2.09 14.33 2.05 8.79 20.02 2.52 16.47 50.33
δ (ppm)




176.32 174.83
138.02 137.71 135.77 132.36
64.57 64.32
49.62 45.72 43.37 42.54 30.31 29.43 29.20 28.68 25.94
δ (ppm)